Design, Synthesis and Scope of Organocatalytic Azide-Carbonyl [3+2]-Cycloadditions

A
Thesis
Submitted for the Degree of

Doctor of Philosophy

By

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14CHPH19

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CERTIFICATE

Certified that the work contained in the thesis entitled "**Design, Synthesis and Scope of Organocatalytic Azide-Carbonyl [3+2]-Cycloadditions**" has been carried out by **Mr. Gundam Surendra Reddy** under my supervision and the same has not been submitted elsewhere for a degree.

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Parts of the thesis have been:

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3. **G. Surendra Reddy**, A. Suresh Kumar, D. B. Ramachary *Org. Biomol. Chem.* **2020**, *18*, 4470-4478.
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Design, Synthesis and Scope of Organocatalytic Azide-Carbonyl [3+2]-Cycloadditions

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Gundam Surendra Reddy.

PREFACE

Cycloadditions are one of the powerful reactions to generate multiple bonds in single step, among those 1,3–dipolar cycloadditions are considered as the "strongest pillar in the construction of complex molecular skeletons". More importantly, organocatalytic [3+2]-cycloadditions have become alternative to the metal mediated [3+2]-cycloadditions because of their simple operation technique, milder conditions, high efficiency, short reaction time, high regioselectivity, readily available precursors and potentially greener. The present thesis entitled ***"Design, Synthesis and Scope of Organocatalytic Azide-Carbonyl [3+2]-Cycloadditions"*** *describes the reactions involving catalytic enolate and push-pull dienolate intermediates in the synthesis of highly functionalized 1,2,3-triazoles molecules which have pharmaceutical and biological importance. In all these sections, a brief introduction is provided to keep the present work in proper perspective, the compounds are sequentially numbered (bold), and references are marked sequentially as superscript and listed at the end of the thesis. All the figures included in the thesis were obtained by DIRECT PHOTOCOPY OF THE ORIGINAL SPECTRA and in some of them uninformative areas have been cut to save the space.*

In the first chapter highly functionalized heterocycles such as N-vinyl 1,2,3-triazoles have found wide applications in medicinal, material and polymer chemistry. To synthesize these skeletons an efficient, green and sustainable protocol is required. Herein, we achieved those using simple starting materials such as aldehydes, ketones, and vinyl azides with a catalytic amount of tertiary amine. The organocatalytic enolate-mediated azide-carbonyl [3+2]-cycloaddition (OrgACC) reaction ensues in excellent yields with high regioselectivity and it constitutes an alternative to the previous synthetic methods.

In continuation to the development of dienolate-mediated synthesis of substituted C-vinyl 1,2,3-triazoles, second chapter demonstrates the organocatalytic azide-allyl ketone [3+2]-cycloaddition reaction to accomplish fully decorated C-vinyl 1,2,3-

triazoles in excellent yields with high regioselectivity. A variety of enolizable cyclic, acyclic, exo-cyclic allylic ketones and different azides are employed as starting materials under tertiary amine-catalysis. Furthermore, we demonstrated the applications of OrgACC strategy in metal-free synthesis of medicinally important and materially useful C-vinyl 1,2,3-triazoles.

In the third chapter, we demonstrated the metal-free regioselective synthesis of highly functionalized C/N-double vinyl 1,2,3-triazoles, N-aryl bicyclic 1,2,3-triazoles by treating highly functionalized unmodified cyclic and acyclic enones with vinyl and aryl azides through [3+2]-cycloaddition based on push-pull dienolate catalysis. The one-pot reaction resulted in good yields with high selectivity using DBU as the catalyst. Herein, we explore the utility of highly functionalized C/N-double vinyl-1,2,3-triazoles as starting materials for the synthesis of medicinally important N-vinyl-benzotriazoles through mild oxidative aromatization. Furthermore, we demonstrated the medicinal applications of N-vinyl benzotriazoles.

In continuation to the development of organocatalytic carbonyl-azide [3+2]-cycloaddition, fourth chapter illustrates the tertiary amine-catalyzed an organocatalytic selective enolization for the synthesis of functionally rich 1,4-diaryl-5-arylthiomethyl-1,2,3-triazoles from readily available non-symmetrical thioketones and different azides. Furthermore, we have demonstrated the medicinal applications of thiomethyl-1,2,3-triazoles.

LIST OF ABBREVIATIONS

Ac	acetyl
AcOH	acetic acid
Ac_2O	acetic anhydride
Anal.	analysis
aq.	aqueous
Ar	aryl
Bn	benzyl
Bp	boiling point
br	broad
Bu	butyl
*t*Bu or ^{t}Bu	*tertiar*y-butyl
n-BuLi	*n*-butyl lithium
calcd.	calculated
cat.	catalytic
cm	centimeter
CsF	Cesium fluoride
CuAAC	copper catalyzed azide-alkyne cycloaddition
DABCO	1,4-Diazabicyclo[2.2.2]octane
dABq	doublet of AB quartet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
dd	doublet of doublet
ddd	doublet of doublet of doublet
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
de	diastereomeric excess
DEPT	distortionless enhancement by polarization transfer
DFT	density functional theory
DMAP	dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DSSC	Dye sensitized solar cells
dr	diastereomeric ratio
dt	doublet of triplet
EDG	electron donating group
ee	enantiomeric excess
eq.	equation
equiv.	equivalent(s)
Et	ethyl
EtOH	ethyl alcohol
Et_2O	diethylether
EWG	electron withdrawing group
Fg	functional group
Fig.	figure
gm	gram (s)
h	hour (s)
Hz	hertz

Hex	hexyl
HIV	human immunodeficiency virus
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
^{i}Pr	isopropyln
IR	infrared
$LiAlH_4$	lithium aluminum hydride
lit.	literature
m	multiplet
m-CPBA	*m*-chloro perbenzoic acid
MeCN	Acetonitrile/ methane cynaide
M	molarity
Mp.	melting point
Me	methyl
mg	milligram (s)
mGluR1	metabotropic glutamate receptor 1
mL	milliliter
mmol	millimole
MsOH	Methanesulfonic acid
MW	microwave
NMR	nuclear magnetic resonance
NF-κB	nuclear factor kappa-light-chain-enhancer of activated B cells
OrgAAC	organocatalytic azide-aldehyde cycloaddition
OrgAKC	organocatalytic azide-ketone cycloaddition
OrgVACC	organocatalytic vinylazide-carbonyle cycloaddition
Ph	phenyl
ppm	parts per million
p-TSA	*p*-toluenesulfonic acid
pr	propyl
q	quartet
RT	room temperature
s	singlet
sec	secondary
t	triplet
TBD	Triazabicyclodecene
TMG	1,1,3,3-Tetramethylguanidine
*t*BuOK/KOtBu	Potassium tertiarybutoxide
*t*BuOK	Potassium tertiarybutanol
td	triplet of doublet
tert	tertiary
4-VTs	4-vinyl 1,2,3-triazoles
1-VTs	1-vinyl 1,2,3-triazoles
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Ts	toluenesulphonyl
TsOH	*p*-Toluenesulfonic acid

Design, Synthesis and Scope of Organocatalytic Azide-Carbonyl [3+2]-Cycloadditions

1.0 Abstract

For the first time, an enolate-mediated organocatalytic vinyl azide-carbonyl [3+2]-cycloaddition (OrgVACC) of various ketones/aldehydes with vinyl azides is reported. It is an efficient intermolecular reaction with excellent outcomes with reference to rate, yield, selectivity, operational simplicity, substrate scope, catalyst simplicity, and vast applications.

In the second chapter, for the first time, an enolate-mediated organocatalytic fluorogenic formal [3+2]-cycloaddition of (*E*)-1,4-diarylbut-3-en-1-ones and aryl azides is reported. The mild metal-free catalytic conditions of this reaction allowed us to synthesize a library of pure fluorescent coumarin-triazole dyes. It is an efficient formal [3+2]-cycloaddition for the synthesis of fully decorated *C*-vinyl-1,2,3-triazoles with excellent outcomes with reference to the rate, yield, selectivity, operation simplicity, substrate scope, and photophysical applications.

In the third chapter, we demonstrated the metal-free regioselective synthesis of highly functionalized *C/N*-double vinyl 1,2,3-triazoles, *N*-aryl bicyclic 1,2,3-triazoles by treating highly functionalized unmodified cyclic and acyclic enones with vinyl and aryl azides through [3+2]-cycloaddition based on push-pull dienolates. The one-pot reaction resulted in good yields with high selectivity using DBU as the catalyst. Herein, we explore the utility of highly functionalized *C/N*-double vinyl-1,2,3-triazoles as starting materials for the synthesis of medicinally important *N*-vinyl-benzotriazoles through mild oxidative aromatization.

In the fourth chapter, in continuation to the development of organocatalytic carbonyl-azide [3+2]-cycloadditions, the tertiary amine-catalyzed, an organocatalytic selective enolization for the synthesis of functionally rich 1,4-diaryl-5-arylthiomethyl-1,2,3-triazoles were developed from readily available non-symmetrical thioketones and different azides. Furthermore, we have demonstrated the medicinal applications of thiomethyl-1,2,3-triazoles.

2.0 Introduction:

Synthetic organic chemist always faces challenges from growing world due to constant need of drugs and functional materials with enhanced activity. The growth of material to medicinal sciences was interlinked with synthetic organic community to develop an efficient synthetic methodology for original building blocks (monomers) from readily available cheap starting materials without toxic by-products. Most of the traditional monomers were well studied in polymer chemistry. However, the vinyl 1,2,3-triazole was established as privileged monomer due to their multiple features of traditional monomers in a single unit such as stable aromaticity like styrene, availability of nitrogen atoms for hydrogen bond formation like vinyl pyridine and sustainable olefin functionality like acrylates (Figure 1).[1]

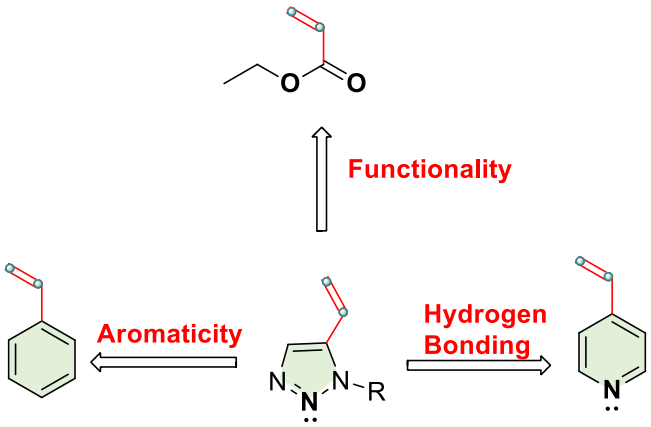


Figure 1: Structural similarities between vinyl-1,2,3-triazoles and traditional monomers.

Vinyl-1,2,3-triazoles also exhibit broad structural diversity and plays crucial role in bringing tenable properties to macromolecules. Based on corresponding position of the vinyl group, triazoles are majorly categorized into three regioisomers (Figure 2).[2a]

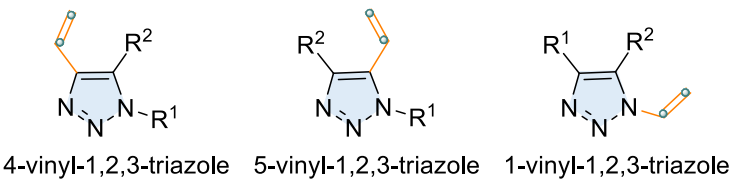


Figure 2: Different types of vinyl-1,2,3-triazole regioisomers.

The derivatives of the vinyl-1,2,3-triazole shows unique applications in both material and medicinal chemistry. Specially, *C*-vinyl-1,2,3-triazoles acts as a α-glucosidase inhibitor, anti-microbial agents and anti-mycobacterium tuberculosis. In addition, *N*-vinyl benzotriazoles acts as a tubulin inhibitor, anti-tubercular and anti-inflammatory agents (Figure 3).[3, 4]

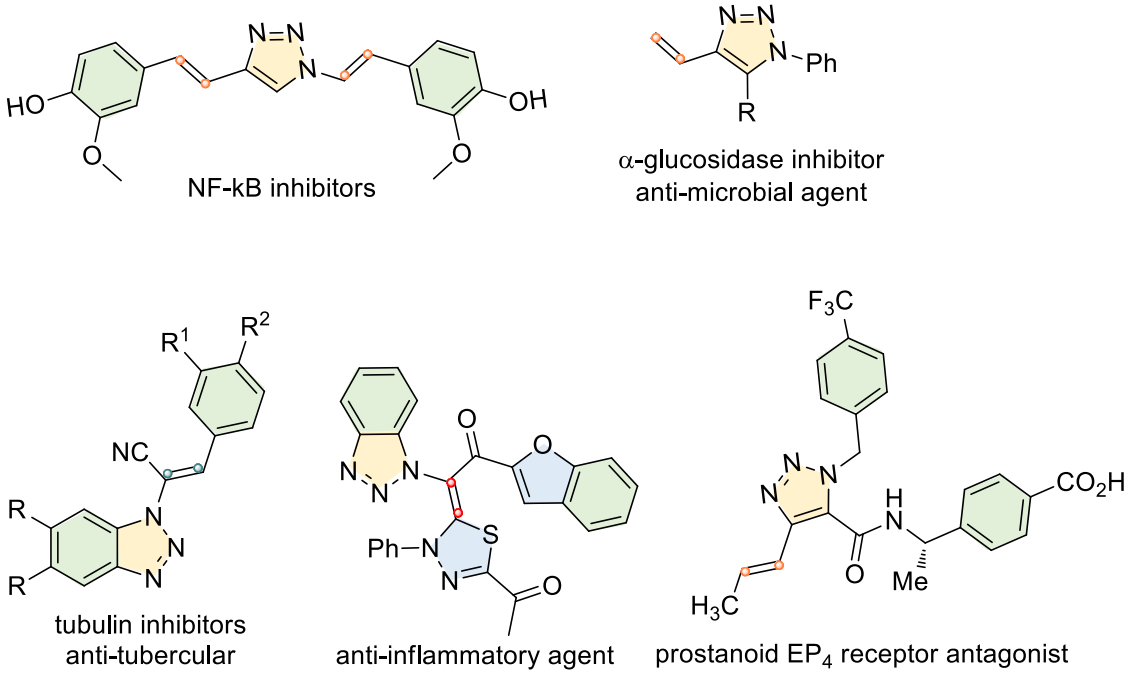


Figure 3: Few medicinally important *C*-vinyl- and *N*-vinyl-1,2,3-triazoles.

Mostly, the synthesis of vinyl-1,2,3-triazole was fulfilled by Huisgen or Copper(I)-catalysed alkyne-azide [3+2]-cycloaddition (CuAAC) followed by elimination or Wittig olefination. Each approach has its own drawbacks. Huisgen [3+2]-cycloaddition suffers from low yields and slow reaction rates whereas CuAAC click reactions suffers from substrate limitations.[5]

In the last decade, most of these problems faced by synthetic organic chemists had overcome by the introduction of organocatalytic azide-carbonyl [3+2]-cycloaddition (OrgACC). In OrgACC, small organic molecules can be used in sub-stoichiometric amount for the acceleration of [3+2]-cycloadditions. In a short span of time, OrgACC developed very rapidly due to its greener advantages over previous established [3+2]-cycloadditions. In these OrgACC reactions, various intermediates such as enamine, enolates, dienamine and dienolates can be generated *in situ* from

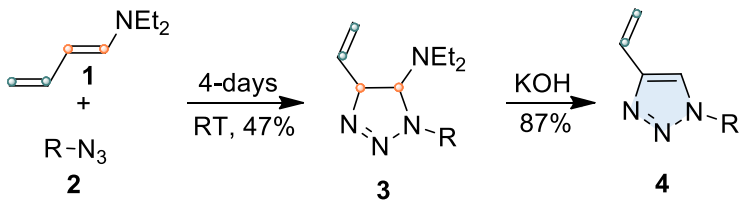
carbonyl compounds and amines under suitable conditions for the synthesis of various triazoles with high levels of regioselectivity in one-pot manner. These protocols require neither elimination nor Wittig olefination and most importantly these reactions can be performed under aerobic conditions without any dry solvents. Instead, the reaction rates can be accelerated often by the addition of water.[6, 7]

As we developed metal-free catalytic methods for the regioselective synthesis of vinyl 1,2,3-triazoles in this thesis, herein, we summarized the previous methods for the synthesis of different vinyl 1,2,3-triazoles.

2.1 Previous Synthetic Methods for *C*-Vinyl-1,2,3-Triazloes:

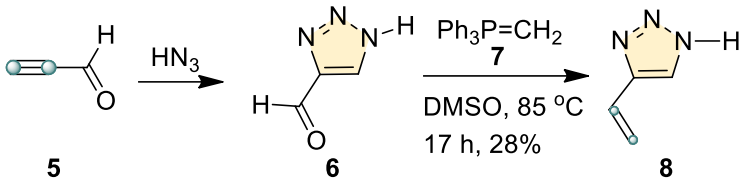
2.1.1 Historical Background:

In 1972, Labbe and co-workers initially attempted for the synthesis of *N*-substituted 4-vinyl triazole through Huisgen [3+2]-cycloaddition followed by elimination strategy. According to this protocol, the intermediate triazoline cycloadduct **3** was resulted from [3+2]-cycloaddition of *trans*-1-diethylamino-1,3-butadiene **1** with *p*-bromophenyl azide which was further treated with base to afford 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole **4** with the elimination of diethylamine (Scheme 1). Even though their initial attempt was successful, this protocol has limitations in the view of separation of by-products, longer reaction time and lower yields.[8a]



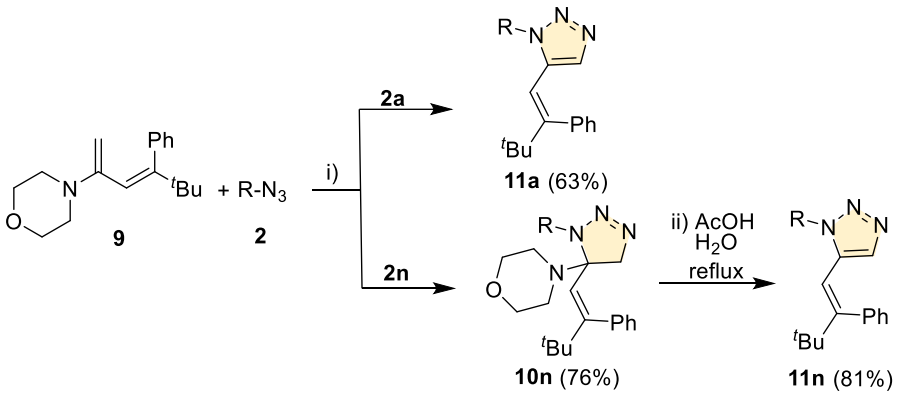
Scheme 1: Synthesis of 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole by Huisgen cycloaddition and elimination strategy.

In 1982, Smitt *et al.* developed a new protocol for 4(5)-vinyl-1,2,3-triazole based on [3+2]-cycloaddition followed by Wittig reaction and further applied radical co-polymerisation for macromolecule synthesis. In this protocol, 4-formyl *NH*-1,2,3-triazole **6** was resulted from the [3+2]-cycloaddition of propargyl aldehyde and hydrazoic acid. The formyl group of **6** was further converted into vinyl group through Wittig olefination resulting 4-vinyl *NH*-1,2,3-triazole **8** (Scheme 2). The major drawbacks of this method is handling of hazardous hydrazoic acid, lower yields and hydrogen tautomerism on nitrogen atoms of 1,2,3-triazole at room temperature.[8b]



Scheme 2: Synthesis of 4(5)-vinyl-1,2,3-triazole by [3+2]-cycloaddition followed by Wittig reaction.

2.1.2 Preformed Dienamines as Azidophiles in Huisgen Cycloaddition:



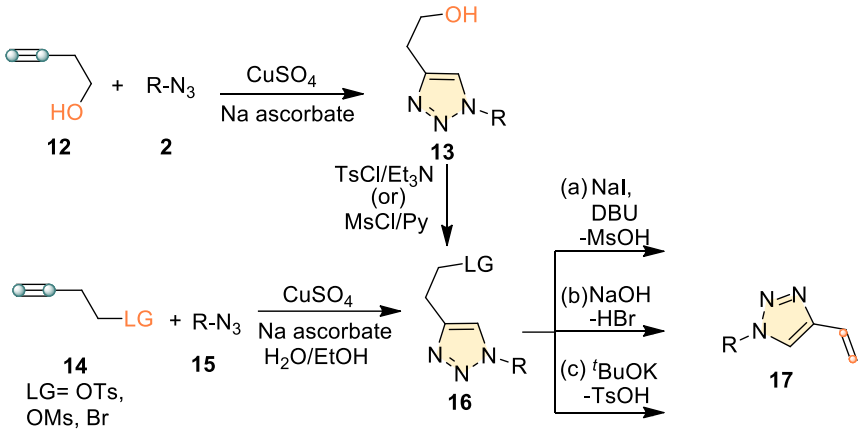
Scheme 3: Synthesis of substituted 5-vinyl-1,2,3-triazoles from [3+2]-cycloaddition followed by elimination.

In 2005, Gerhard Maas *et al.* demonstrated a protocol for *β, β'*-disubstituted 5-vinyl-1,2,3-triazole *via* Huisgen [3+2]-cycloaddition using preformed dienamines as azidophlies. According

to this methodology, the triazole **11a** was obtained from [3+2]-cycloaddition of 2-morpholinobuta-1,3-diene with phenyl azide **2a** at enamine double bond in a single step with 63% yield. In case of *para*-nitrophenyl azide **2n**, initially triazoline **10n** was isolated. Further elimination of morpholine from triazoline **10n** by acid treatment furnished desired product **11n** in 81% yield (Scheme 3).[8c]

2.1.3 CuAAC followed by Elimination Strategy:

In 2008, Hawker *et al.* demonstrated initial protocol for synthesis of 4-vinyl-1,2,3-triazoles (4-VTs) *via* CuAAC followed by elimination of MsOH in one-pot two-step manner. As per this protocol, *N*-substituted 2-(1*H*-1,2,3-triazol-4-yl)ethyl methanesulfonate derivatives resulted from direct CuAAC of organic azides with the but-3-yn-1-yl methanesulfonate or CuAAC of 3-butyn-1-ol with organic azides catalysed by $CuSO_4$ (5 mol%), sodium ascorbate (10 mol%) in *t*-BuOH:H_2O mixture followed by mesylation. Finally, the elimination of mesyl group in the presence of NaI and DBU in dimethoxyethane (glyme) at reflux temperature furnished the desired products **17** in 56-89 % overall yields (Scheme 4a).[8d]



Scheme 4: Synthesis of 4-vinyl-1,2,3-triazoles *via* [3+2]-cycloaddition followed by elimination.

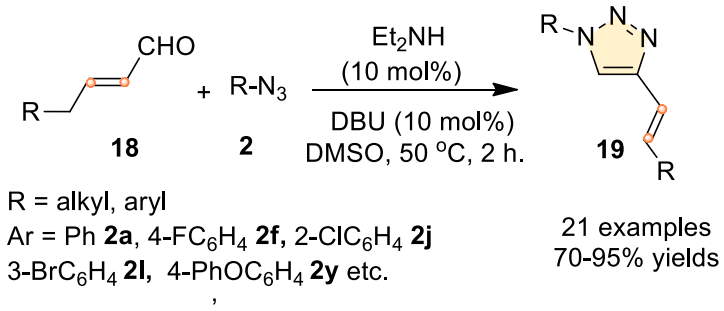
In 2013, Blache *et al.* demonstrated an efficient protocol for synthesis of 4-VTs through one-pot click followed by elimination. According to this protocol, *N*-substituted 4-(2-bromoethyl)-1*H*-

1,2,3-triazole derivatives resulted from CuAAC of 4-bromobutyne and preformed organic azides catalysed by $CuSO_4.5H_2O$ (2.5 mol%), sodium ascorbate (7.5 mol%) in $EtOH/H_2O$ mixture. Further, the elimination of HBr by NaOH treatment at 45 °C furnished the desired 4-VTs derivatives **17** in 82-88% yields (Scheme 4b).[8e]

In 2015, Giofre and co-workers synthesized 4-VTs *via* elimination of tosyl group from tosylted-1,2,3-triazoles. As per this protocol, the tosyl group was eliminated in the presence of *t*-BuOK in *t*-BuOH and resulted desired 4-VTs derivatives **17** in 78-90% yields (Scheme 4c).[8f]

2.1.4 In Situ Generated Dienamines as Azidophiles in [3+2]-Cycloaddition:

In 2013, Jain Wang *et al.* demonstrated an efficient organocatalytic protocol for the synthesis of 4-VTs through an inverse-electron-demand 1,3-dipolar cycloaddition. In this protocol, the *in situ* generated dienamine from *α, β*-unsaturated aldehyde **18** with catalytic amount of secondary amine undergo [3+2]-cycloaddition with organic azides in DMSO at 50 °C to furnish corresponding 4-VTs products **19** in 70-90% yields (Scheme 5).[8g]

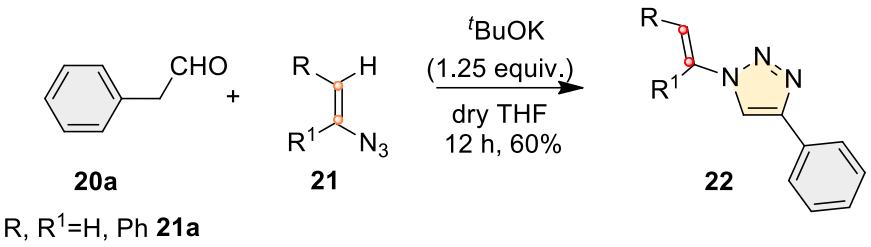


Scheme 5: One pot synthesis of *β*-substituted 4-vinyl-1,2,3-triazoles.

2.2 Previous Synthetic Methods for *N*-Vinyl-1,2,3-Triazloes:

2.2.1 In Situ Generated Enolates as Azidophiles in [3+2]-Cycloaddition:

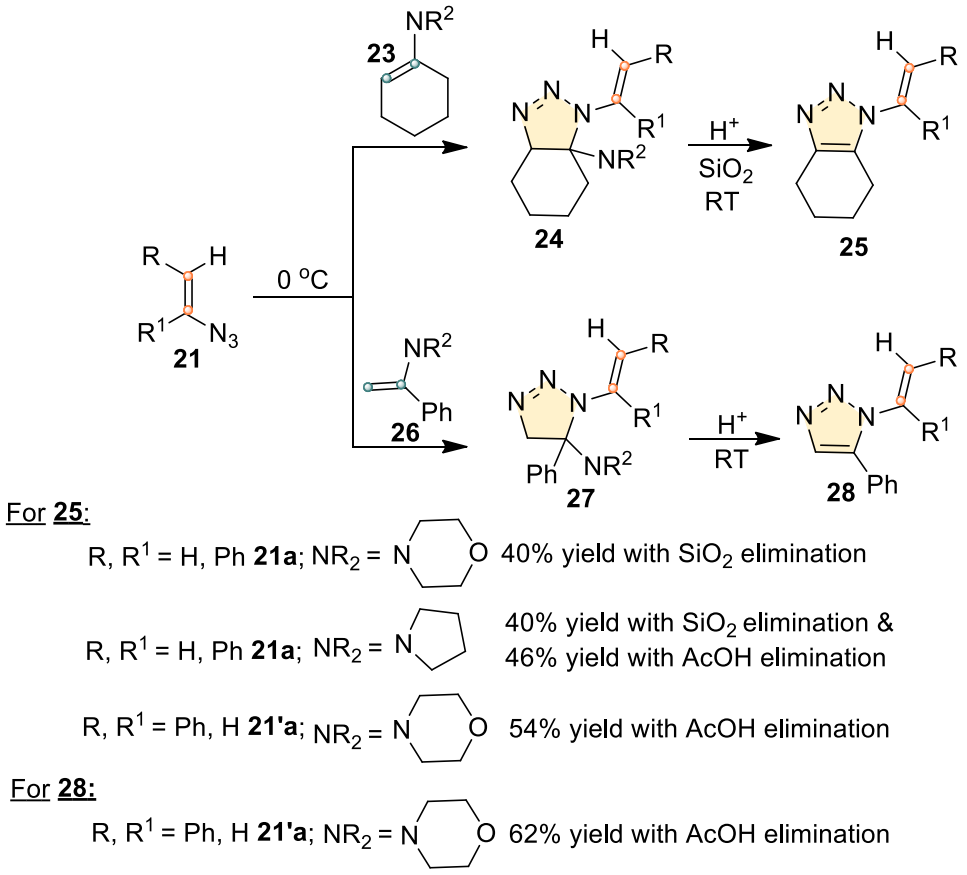
In 1971, Gilchrist *et al.* developed a protocol for the synthesis of *α*-substituted 1-vinyl-1,2,3-triazoles (1-VTs) *via* stoichiometric base mediated [3+2]-cycloaddition of aldehyde and vinyl azide. According to this protocol, the phenyl acetaldehyde **20a** underwent 1,3-dipolar cycloaddition with *α*-azidostyrene **21** in the presence of 1.25 equiv. of *t*-BuOK in dry THF at room temperature to furnish the desired 1-VTs product **22** in 60% yield (Scheme 6).[9a]



Scheme 6: Synthesis of 1-substituted vinyl-1,2,3-triazoles through base-mediated [3+2]-cycloaddition.

2.2.2 Preformed Enamines as Azidophiles in [3+2]-Cycloaddition:

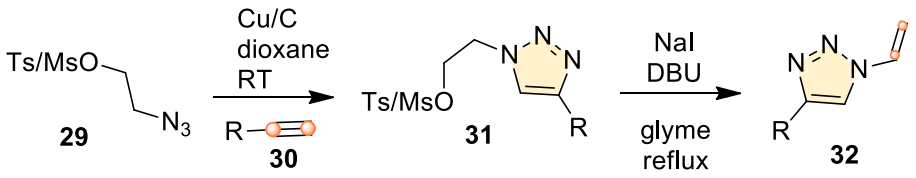
In 1981, Nomura *et al.* reported a protocol for the synthesis of α-substituted 1-vinyl-1,2,3-triazoles (1-VTs) from preformed enamines. As per this protocol, 4-aminovinyl triazoline intermediates were resulted from Huisgen [3+2]-cycloaddition of *α*-and *β*-azido styrenes with various preformed enamines in neat condition at 0 °C. Further, acidic treatment of triazoline intermediates furnished the desire 1-VTs products **25** and **28** in 40-60% yields (Scheme 7).[9b]



Scheme 7: Synthesis of 1-substituted vinyl-1,2,3-triazoles from the preformed enamines.

2.2.3 CuAAC followed by Elimination Strategy:

In 2008, Hawker *et al.* demonstrated initial protocol for the synthesis of 1-VTs through [3+2]-cycloaddition followed by elimination. As per this protocol, 4-substituted 2-(1*H*-1,2,3-triazol-1-yl)ethyl methanesulfonate derivatives or 4-substituted 2-(1*H*-1,2,3-triazol-1-yl)ethyl 4-methylbenzenesulfonate derivatives were resulted from CuAAC of different type of alkynes with 2-azidoethyl methanesulfonate or azidoethy methylbenzenesulfonate catalysed by Cu/C (10 mol%) in 1,4-dioxane at room temperature. Finally, the mesyl/tosyl group was eliminated in the presence of NaI (0.81 equiv.) and DBU (2.0 equiv.) in glyme at reflux temperature to furnish desired 1-VTs **32** derivatives in 50-70% overall yields (Scheme 8).[8d]



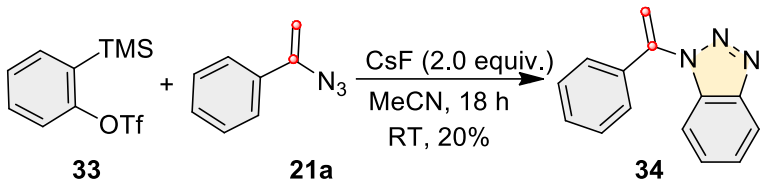
R= H, Ph, Bn, ^{n}Pr ,^{n}Oct, TMS, CH_2OTHP, CH_2NHBOC

8 examples, 50-70% overall yields

Scheme 8: Synthesis of 1-vinyl-1,2,3-triazoles from the cycloaddition followed by elimination.

2.2.4 In Situ Generated Benzynes as Azidophiles in [3+2]-Cycloaddition:

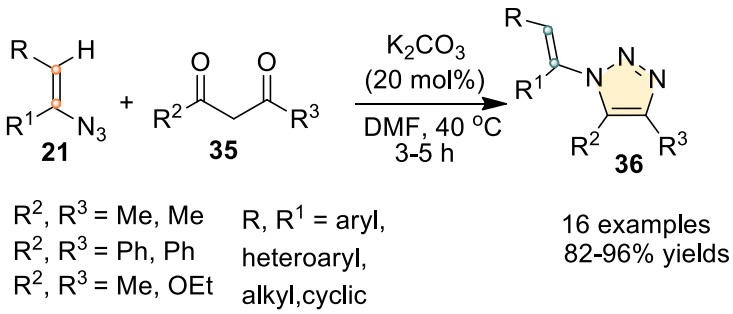
In 2010, Larock *et al.* demonstrated a protocol for synthesis of 1-styrenyl benzotriazoles *via* benzyne click reaction. According to this methodology, the highly reactive benzyne intermediate was generated *in situ* from *o*-(trimethylsilyl) phenyl triflate by treating with 2.0 equiv. of CsF in MeCN and concurrently undergoes [3+2]-cycloaddition with *α*-azidostyrene at room temperature to furnish the corresponding product **34** in 20% yield. The main drawback of this protocol is formation of unidentified by-products (Scheme 9).[9c]



Scheme 9: Synthesis of 1-substituted vinyl-1,2,3-triazoles from the benzyne precursor.

2.2.5 In Situ Generated Enolates as Azidophiles in [3+2]-Cycloaddition:

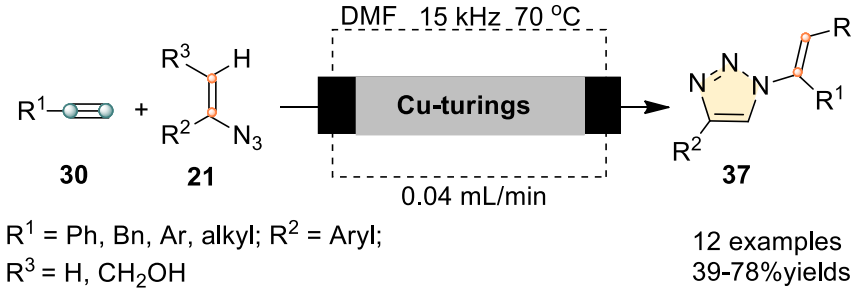
In 2011, Chiba *et al.* developed an efficient protocol for the synthesis of *α*-substituted 1-vinyl-1,2,3-triazoles *via* enolate-mediated [3+2]-cycloaddition of 1,3-dicarbonyl compounds with various *α*-azidostyrenes in the presence of K_2CO_3 (20 mol%) in DMF at 40 °C which furnished the desire products **36** in 82-96% yields (Scheme 10).[9d]



Scheme 10: Synthesis of 1-substituted vinyl-1,2,3-triazoles from 1,3-dicarbonyls catalysed by base.

2.2.6 Flow Mediated CuAAC for 1-Vinyl-1,2,3-Triazoles:

In 2011, Kirschning *et al.* developed a flow protocol for the synthesis of *α*-substituted 1-vinyl-1,2,3-triazoles *via* CuAAC. As per this protocol, different alkynes and vinyl azides were mixed in DMF solvent and passed through flow reactor which was packed inside with inductively heated copper turnings with 0.04 mL/min flow rate at 70 °C (copper turnings serves both as heating-coil as well as catalytically active for CuAAC) to furnish the desired products **37** in 39-78% yields (Scheme 11).[9e]



Scheme 11: Synthesis of 1-substituted vinyl-1,2,3-triazoles from the flow process.

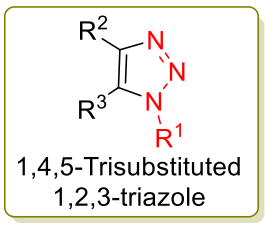
3.0 An Organocatalytic Vinyl Azide-Carbonyl [3 + 2]-Cycloaddition: High-yielding Synthesis of Fully Decorated *N*-Vinyl-1,2,3-Triazoles

3.1 Abstract:

For the first time, an enolate-mediated organocatalytic vinyl azide–carbonyl [3+2]-cycloaddition (OrgVACC) of various ketones/aldehydes with vinyl azides is reported. It is an efficient intermolecular reaction with excellent outcomes with reference to rate, yield, selectivity, operation simplicity, substrates scope, simple catalyst and vast applications.

3.2 Introduction:

Recently, functionalized 1,2,3-triazoles have become important molecules with many unique chemical/physical properties and are widely used as pharmaceuticals due to their bio-similarity with amide bonds.[1a-d] Fully decorated 1,2,3-triazoles have found vast applications in organic, bio-organic, polymer, medicinal, pharmaceutical and material chemistry.[10] Pharmacological outcome of 1,2,3-triazoles is completely based on their 1,4-, 1,5- or 1,4,5-substitutions and due to this reason, the design and development of more general green catalytic methods for their selective fully decorated synthesis are of significant interest (Scheme 1).[2, 5-7]



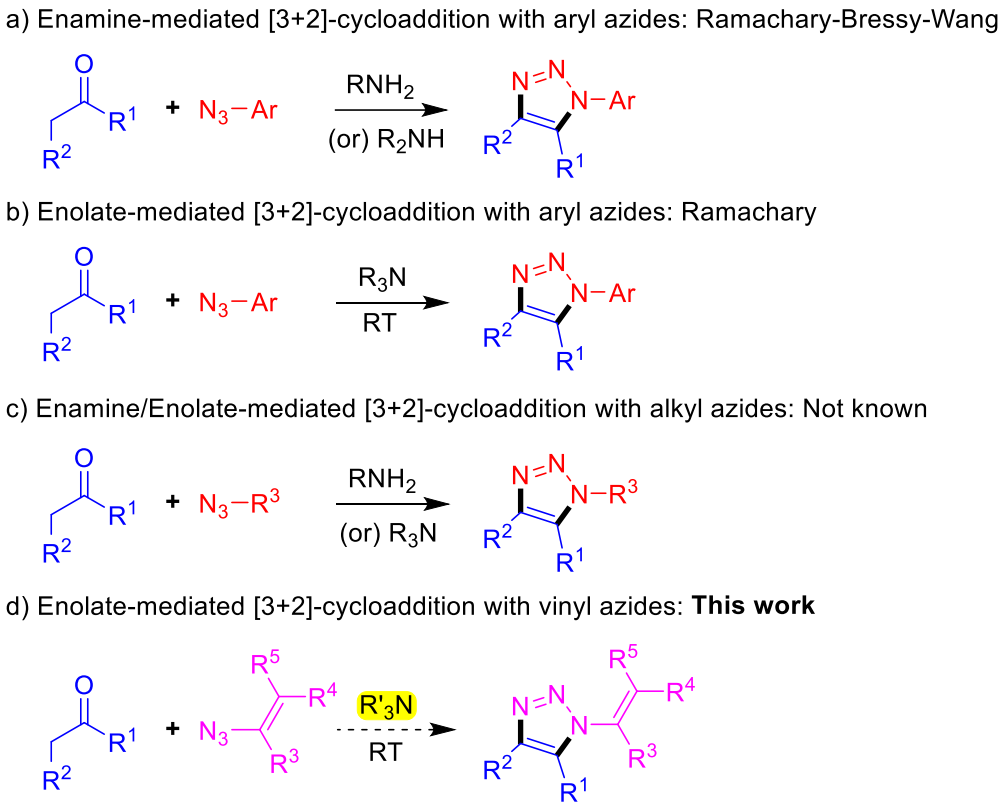
1,4,5-Trisubstituted 1,2,3-triazole

- HIV protease inhibitors
- Anticancer drugs
- Anti-tuberculosis drugs
- Antifungal agents
- Antibacterial drugs
- Histone deacetylase inhibitors
- Bioorthogonal probes

(1)

For example, 1,4- or 1,5-disubstituted 1,2,3-triazoles and 1,4,5-trisubstituted 1,2,3-triazoles have significant role in pharmaceutical chemistry [Eq. (1)] and as mentioned previously, their drug properties mainly depend on their aliphatic or aromatic substitutions.[10] Already four 1,2,3-triazole-based drugs [tazobactam, solithromycin, cefatrizine and rufinamide] are currently in use,[2g] which is inspiring us to develop novel functionalized 1,2,3-triazoles for more properties through organocatalysis.

Herein, we showed interest to develop a single-step general catalytic protocol for high-yielding regioselective synthesis of 1,4,5-trisubstituted *N*-vinyl-1,2,3-triazoles and 1,4- disubstituted *N*-vinyl-1,2,3-triazoles. Functionalized *N*-vinyl-1,2,3-triazoles are not only inspiring due to their novel functionality, but also can become suitable starting materials for *N*-alkyl-1,2,3-triazoles synthesis (eq. a-c, Scheme 1).



Scheme 1: Design for the enolate-mediated organocatalytic vinayl azide-ketone [3+2]-cycloaddition reaction.

Very little is known about the regioselective catalytic synthesis of functionalized *N*-vinyl-1,2,3-triazoles. In the previous synthetic methods, copper-catalyzed alkyne-vinylazide or alkyne-*β*-haloalkyl azide cycloaddition gave moderate to poor yields.[9e-k] gold-catalyzed 1,2,3-triazole addition to alkynes gave good yields at higher temperature,[9l-m] and pre-formed enamine/enolate cycloaddition with vinyl azide gave moderate to poor yields for longer reaction times.[9a-d, 9n] These drawbacks stimulated us to develop a general catalytic protocol for high-yielding regioselective synthesis of 1,4,5-/1,4-substituted *N*-vinyl-1,2,3-triazoles.[7] Herein, we revealed an operationally

simple, rapid, and general protocol "organocatalytic vinyl azide–carbonyl [3+2]-cycloaddition (OrgVACC)" for the selective synthesis of fully decorated *N*-vinyl-1,2,3-triazoles from the vinyl azides and simple deoxybenzoins, arylacetones or arylacetaldehydes utilizing organocatalyst (eq. d, Scheme 1).[7a-b]

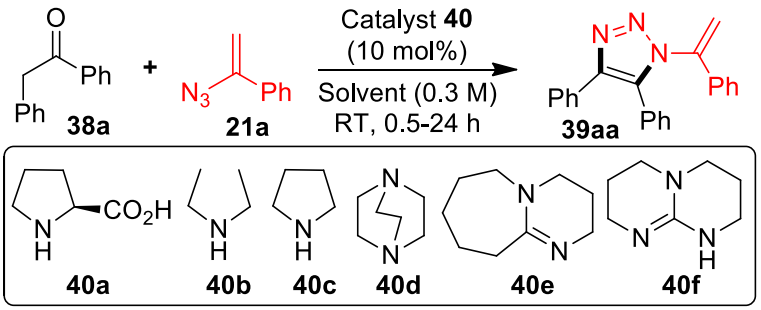
3.3 Results and Discussion:

We commenced the prior optimization of OrgVACC by screening the organocatalysts for the cycloaddition reaction of deoxybenzoin **38a** with 1.2 equiv. of *β*-azidostyrene **21a** (Table 1). [3+2]-Cycloaddition reaction of **38a** with **21a** in DMSO under 10-mol% of proline **40a**-catalysis at 25 °C for 17 h furnished the expected *N*-vinyl-1,2,3-triazole **39aa** as a single regioisomer in only 3% yield (Table 1, entry 1). The same reaction at 25 °C for 17 h under 10-mol% of diethyl amine **40b**, or pyrrolidine **40c**-catalysis furnished the *N*-vinyl-1,2,3-triazole **39aa** in 8%, and 45% yields, respectively (Table 1, entries 2-3). After obtaining poor results with secondary amine catalysts **40a-c** through enamine-formation, based on our previous experience,[7] we thought of exploring the same reaction through *in situ* enolate formation, using some *tert*-amines **40d-f** and non-amine bases **40g-h** as the catalysts for the OrgVACC reaction (Table 1). Under DABCO **40d**-catalysis, cycloaddition reaction of **38a** with **21a** in DMSO at 25 °C for 17 h furnished the expected product **39aa** in only 10% yield (Table 1, entry 4). Intriguingly, the [3+2]-cycloaddition reaction of **38a** with **21a** in DMSO under 10-mol% of DBU **40e**-catalysis at 25 °C in just 0.5 h furnished the *N*-vinyl-1,2,3-triazole **39aa** in 93% yield (Table 1, entry 5). The same OrgVACC reaction under the catalysis of DBU **40e** in other solvents like DMF, $CHCl_3$ and CH_3CN at 25 °C for 17 h furnished **39aa** in 90%, 5% and 22% yields, respectively (Table 1, entries 6, 7 and 8). Same OrgVACC reaction under the catalysis of triazabicyclodecene **40f** in DMSO at 25 °C for 8 h furnished **39aa** in 89% yield (Table 1, entry 9).

Interestingly, the reaction under 10-mol% of non-amine bases of K_2CO_3 **40g** and *t*BuOK **40h**-catalysis in DMSO furnished the *N*-vinyl-1,2,3-triazole **39aa** in good yields at 25 °C for 13 and 0.5 h, respectively (Table 1, entries 10-11). No cycloaddition reaction was observed under self- or autocatalytic conditions in DMSO even after 24 h at 25 °C (Table 1, entry 12). Finally, we envisioned the optimized condition to be 25 °C in DMSO under 10-mol% of DBU **40e**-catalysis,

DMSO under 10-mol% of DBU **40e**-catalysis, which furnished the single isomer of fully decorated *N*-vinyl-1,2,3-traizole **39aa** in 93% yield from **38a** and **21a** (Table 1, entry 5).

Table 1: Reaction optimization[a]



Entry	Catalyst **40**	Solvent	*t* [h]	Yield **39aa** [%][b]
1[c]	**40a**	DMSO	17	3
2[c]	**40b**	DMSO	17	8
3[c]	**40c**	DMSO	17	45
4[c]	**40d**	DMSO	17	10
5	**40e**	DMSO	0.5	93
6	**40e**	DMF	17	90
7[c]	**40e**	$CHCl_3$	17	5
8[c]	**40e**	CH_3CN	17	22
9	**40f**	DMSO	8.0	89
10	K_2CO_3 **40g**	DMSO	13	87
11	*t*BuOK **40h**	DMSO	0.5	88
12[c]	–	DMSO	24	–

[a] Reactions were carried out in solvent (0.3 M) with 1.2 equiv. of **21a** relative to the **38a** (0.3 mmol) in the presence of 10-mol% of catalyst **40**. *b* Yield refers to the column-purified product. [c] Ketone **38a** and azide **21a** was not consumed totally.

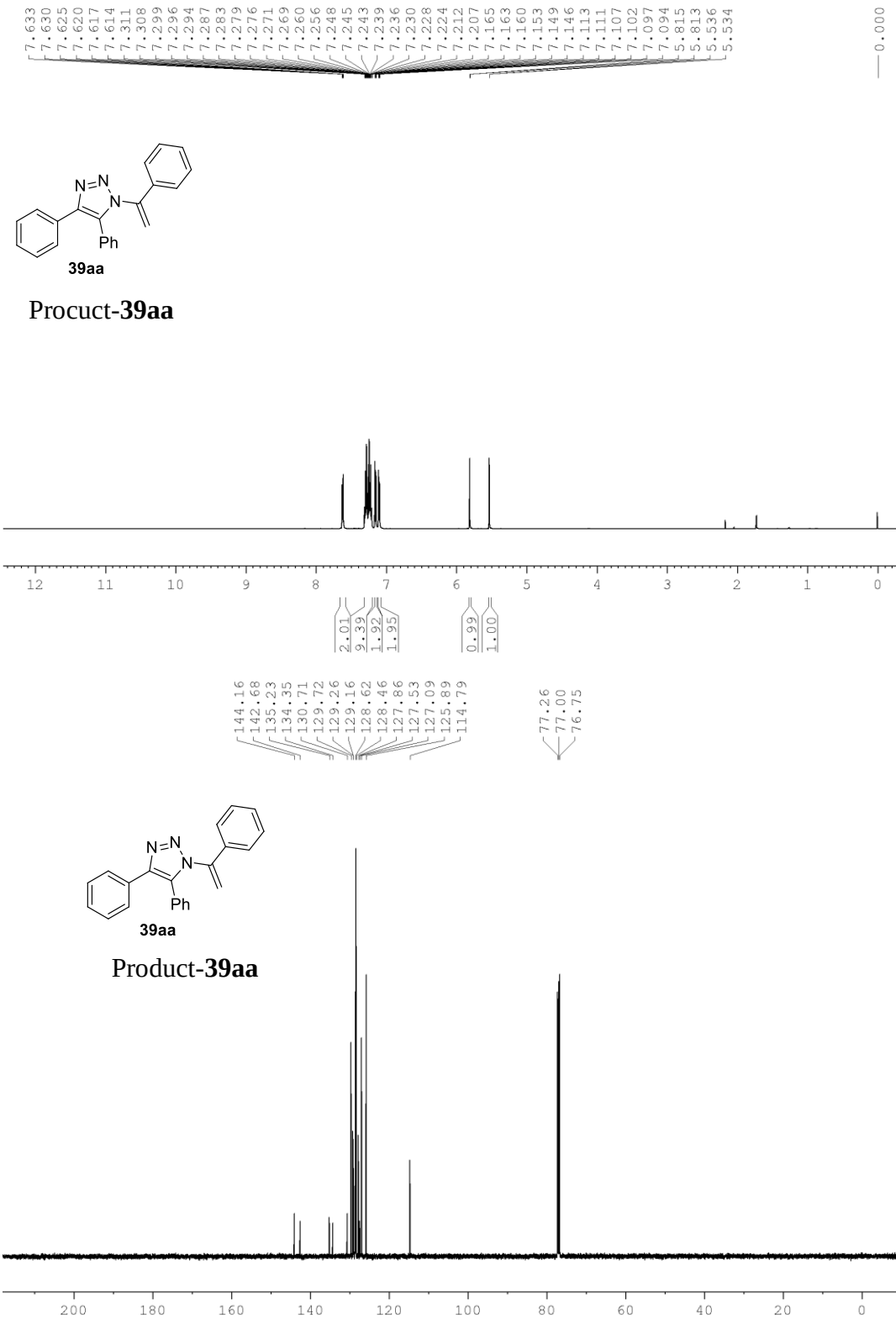
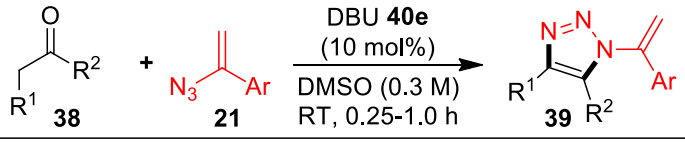
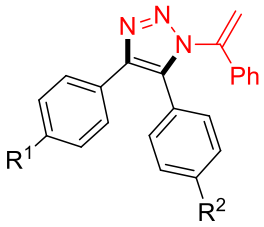


Figure 1: ^{1}H and ^{13}C spectra of the product **39aa**

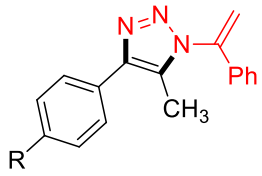
With the best catalytic conditions in hand, the scope and generality of the enolate-mediated OrgVACC reaction were investigated. Firstly, substituted deoxybenzoins **38b-d** were reacted with α-azidostyrene **21a** catalyzed by 10-mol% of DBU **40e** at 25 °C in DMSO for 0.5-0.75 h (Table 2, entries 1-3). Intriguingly, the deoxybenzoins containing different functional groups (H, alkyl, halogen and NO_2) **38b-d** furnished the expected fully substituted *N*-vinyl-1,2,3-traizoles **39ba-da** in excellent yields within 0.5-0.75 h (Table 2, entries 1-3). Further, DBU **40e**-catalyzed OrgVACC reaction of substituted arylacetones **38e-i** with α-azidostyrene **21a** at 25 °C in DMSO for 0.5-0.6 h furnished the fully substituted *N*-vinyl-1,2,3-traizoles **39ea-ia** in very good yields (Table 2, entries 4-8). In this reaction, we did not observe any substitution effect on the phenyl ring and OrgVACC reaction worked well for different substitutions (H, CH_3, OCH_3, Cl and NO_2) of phenylacetones **38e-i** (Table 2, entries 4-8). In a similar manner, functionalized arylketones, 1-(naphthalen-2-yl)propan-2-one **38j** and 1-phenylpentan-2-one 3**8k** with **21a** furnished the functionally rich *N*-vinyl-1,2,3-traizoles **39ja** and **39ka** in very good yields within 0.5 h (Table 2, entries 9-10). After comprehending the OrgVACC reaction by probing the electronic factors of deoxybenzoins or arylacetones **38a-k** with **21a**, we further showed interest to investigate the electronic factors of α-azidostyrenes **21b-j** with deoxybenzoin **38a** (Table 2, entries 11-18). Functionalized α-azidostyrenes **21b-h** were reacted with deoxybenzoin **38a** catalyzed by 10-mol% of DBU **40e** at 25 °C in DMSO for 0.25-1.0 h (Table 2, entries 11-16). Uneventfully, the α-azidostyrenes containing different functional groups on the aryl ring (4-F, 4-Cl, 4-Me, 2-Me, 4-OMe, and 2-naphthyl) **21b-h** furnished the expected fully substituted *N*-vinyl-1,2,3-triazoles **39ab-ah** in excellent to good yields (Table 2, entries 11-16). Though the *N*-vinyl-1,2,3-triazoles **39ab-ag** were obtained in good yields for all the different substituted α-azidostyrenes **21** reaction rate and yield were noticeably decreased with EDG substitution. Interestingly, the DBU **40e**-catalyzed OrgVACC reaction of **38a** with aliphatic vinyl azides 4-((2-azidoallyl)oxy)-1,1'-biphenyl **21i** and 1-((2-azidoallyl)oxy)-4-nitrobenzene **21j** furnished the expected *N*-vinyl-1,2,3-triazoles **39ai** in 75% and **39aj** in 80%, respectively under the optimized reaction conditions (Table 2, entries 17-18). This serves one of the important applications from OrgVACC, where we can generate a library of aliphatic substituted *N*-alkyl-1,2,3-triazoles from the corresponding *N*-vinyl-1,2,3-triazoles **39**. The structure and regiochemistry of the OrgVACC products **39** were established by NMR analysis and also finally confirmed by the X-ray structure analysis on **39ia** as shown in Figure 2. [11a]

Table 2: Substrate scope[a]

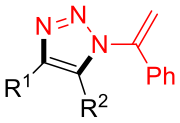




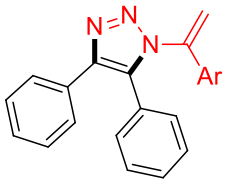
39ba: R^1 = Br, R^2 = Me (0.75 h; 92%)
39ca: R^1 = H, R^2 = Cl (0.5 h; 93%)
39da: R^1 = NO_2, R^2 = H (0.5 h; 90%)



39ea: R = H (0.5 h; 95%)
39fa: R = CH_3 (0.5 h; 90%)
39ga: R = OCH_3 (0.6 h; 90%)
39ha: R = Cl (0.6 h; 90%)
39ia: R = NO_2 (0.5 h; 92%)



39ja: R^1 = 2-naphthyl, R^2 = CH_3 (0.5 h; 90%)
39ka: R^1 = Ph, R^2 = $CH_2CH_2CH_3$ (0.5 h; 80%)



39ab: Ar = 4-FC_6H_4 (0.25 h; 85%)
39ac: Ar = 4-ClC_6H_4 (0.75 h; 80%)
39ad: Ar = 4-MeC_6H_4 (0.5 h; 85%)
39af: Ar = 2-MeC_6H_4 (0.6 h; 82%)
39ag: Ar = 4-$OMeC_6H_4$ (1.0 h; 55%)
39ah: Ar = 2-naphthyl (0.7 h; 86%)
39ai: Ar = 4-$PhC_6H_4OCH_2$ (0.75 h; 75%)
39aj: Ar = 4-$NO_2C_6H_4OCH_2$ (0.5 h; 80%)

[a] Reactions were carried out in DMSO (0.3 M) with 1.2 equiv. of **21** relative to the **38** (0.3 mmol) in the presence of 10-mol% of **40e** and yield refers to the column-purified product.

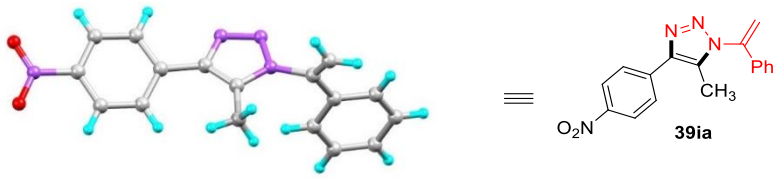


Figure 2: X-ray crystal structure of **39ia**.

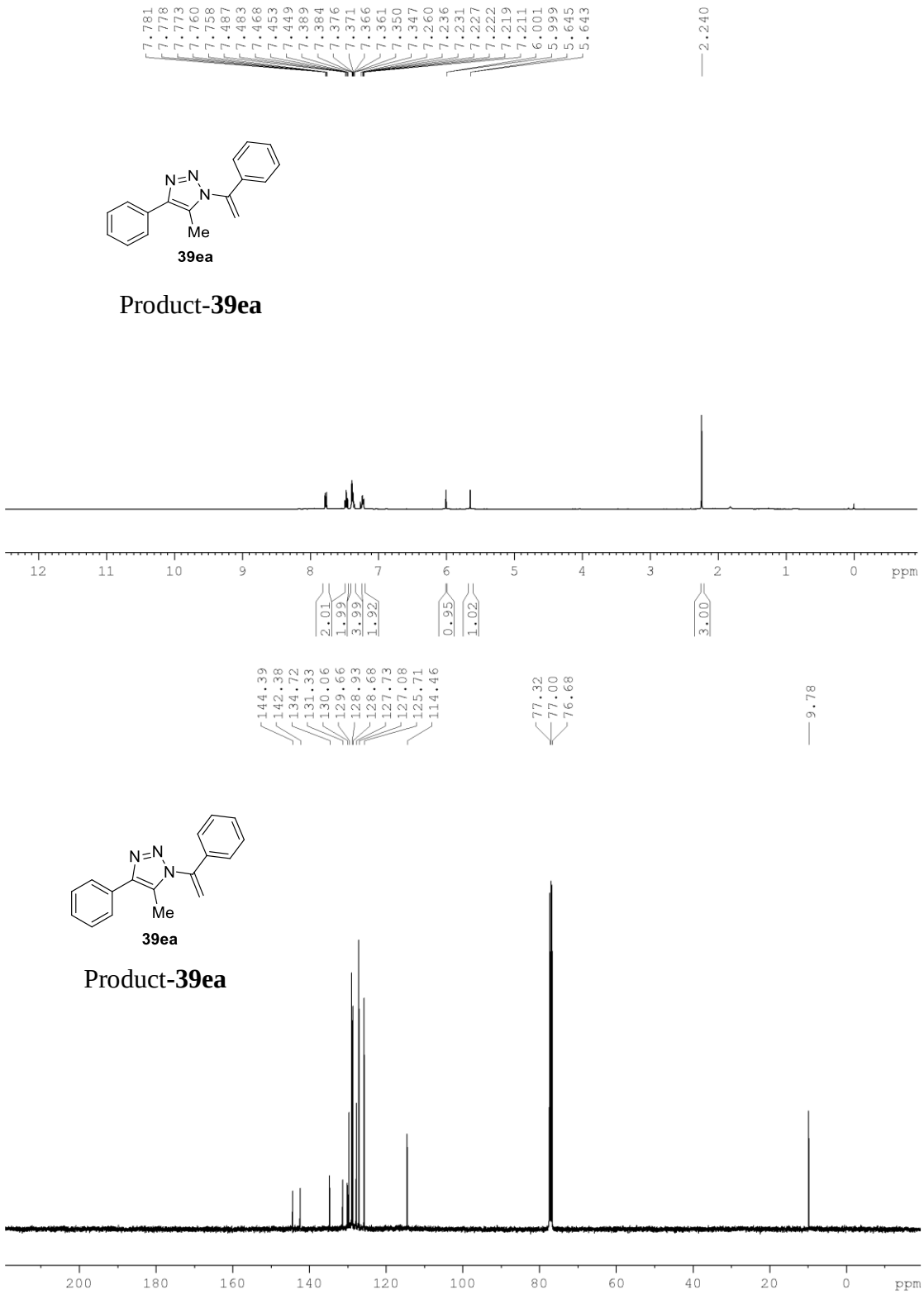


Figure 3: ^{1}H and ^{13}C spectra of the product **39ea**.

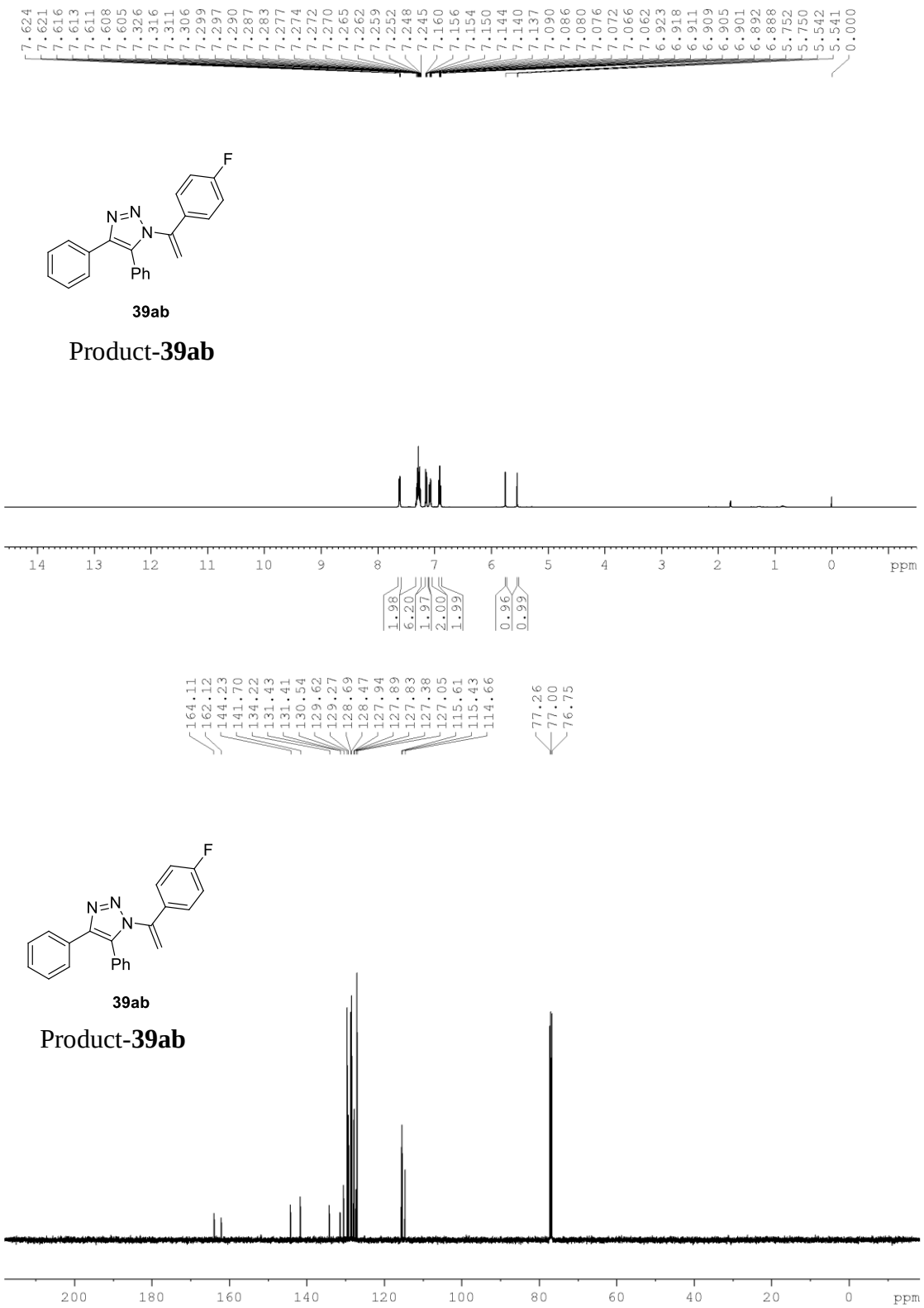


Figure 4: ^{1}H and ^{13}C spectra of the product **39ab**.

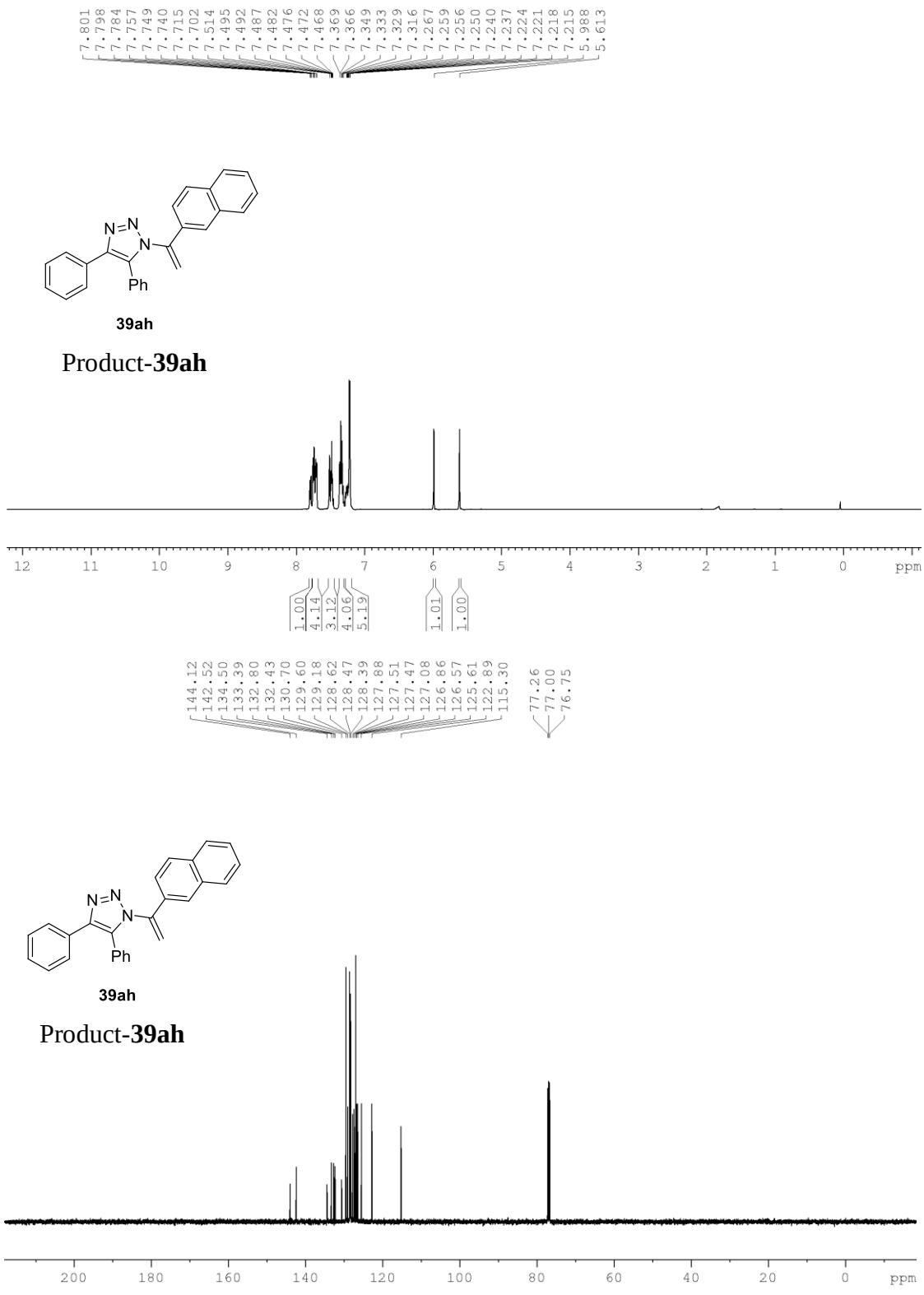


Figure 5: ^{1}H and ^{13}C spectra of the product **39ah**.

After investigation of the OrgVACC reaction by probing the electronic factors of alkyl or aryl ketones **38** with α-azidostyrenes **21** we further showed interest to investigate the electronic factors of aryl or alkyl acetaldehydes **20a-h** by reacting with α-azidostyrenes **21** in the OrgVACC reaction (Table 3). Fascinatingly, the reaction of aryl acetaldehydes **20a-g**, containing different functional groups of alkyl, halogen, EWG's, and EDG's on aryl ring with simple α-azidostyrene **21a** under 10-mol% of **40e**-catalysis furnished the single isomer of 1,4-disubstituted-*N*-vinyl-1,2,3-triazoles **41aa-ga** in excellent yields similar to the deoxybenzoin **38a**/phenylacetone **38e** (Table 3, entries 1-7). Although, the aliphatic aldehyde, 3-phenylpropanal **20h** didn't furnished the expected product under **40e**-catalysis, under the catalysis of *t*-BuOK **40h** at 25 °C for 6.0 h furnished the expected *N*-vinyl-1,2,3-triazole **41ha** in 85% yield (Table 3, entry 8). After these results, we further investigated the scope of this reaction by treating phenylacetaldehyde **20a** with functionalized α-azidostyrenes containing different functional groups on the aryl ring (4-F, 4-Cl, 4-Me, 2-Me, 4-OMe, and 2- naphthyl) **21b-h** to furnish the 1,4-disubstituted-*N*-vinyl-1,2,3-triazoles **41ab-ah** in excellent to good yields (Table 3, entries 9-14). The Table 3 results demonstrate the broad scope of this protocol covering a structurally diverse group of aryl acetaldehydes **20** and α-azidostyrenes **21** to furnish the 1,4-disubstituted-*N*-vinyl-1,2,3-triazoles **41**. In most of the cases, the product **41** yields obtained were excellent compared to the previously available multi-step methods.[12a-n] The structure and regiochemistry of the products **41** were established by NMR analysis and also finally confirmed by the X-ray structure analysis on **41ah** Figure 6.[11a]

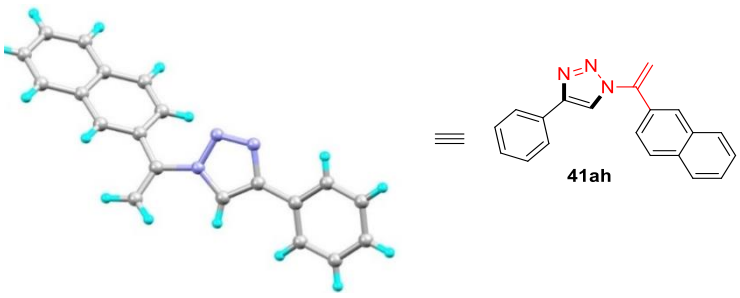
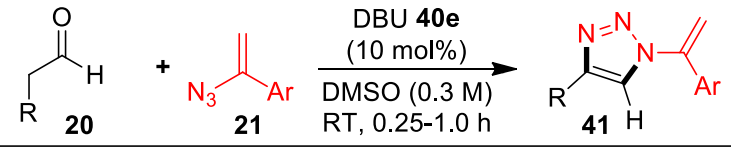
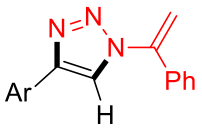


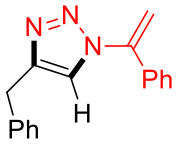
Figure 6: X-ray crystal structure of **41ah**

Table 3: Substrate scope[a]

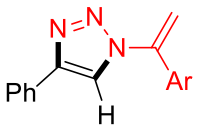




41aa: Ar = C_6H_5 (0.5 h; 90%)
41ba: Ar = 4-FC_6H_4 (0.25 h; 90%)
41ca: Ar = 4-BrC_6H_4 (0.75 h; 88%)
41da: Ar = 2-MeC_6H_4 (0.75 h; 85%)
41ea: Ar = 4-$OMeC_6H_4$ (0.75 h; 82%)
41fa: Ar = 2-$NO_2C_6H_4$ (0.5 h; 85%)
41ga: Ar = 2-naphthyl (0.75 h; 80%)



41ha: (6.0 h; 85%) @ KO^{t}Bu-catalysis



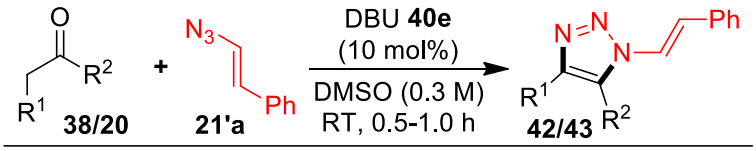
41ab: Ar = 4-FC_6H_4 (0.25 h; 85%)
41ac: Ar = 4-ClC_6H_4 (0.75 h; 80%)
41ad: Ar = 4-MeC_6H_4 (0.5 h; 87%)
41af: Ar = 2-MeC_6H_4 (0.5 h; 85%)
41ag: Ar = 4-$OMeC_6H_4$ (1.0 h; 50%)
41ah: Ar = 2-naphthyl (0.5 h; 88%)

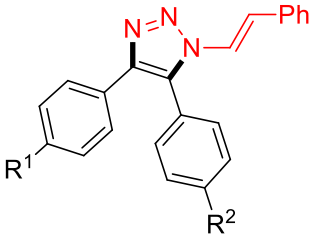
[a] Reactions were carried out in DMSO (0.3 M) with 1.2 equiv. of **21** relative to the **20** (0.3 mmol) in the presence of 10-mol% of **40e** and yield refers to the column-purified product.

To further develop the diverse library of fully decorated *N*-vinyl-1,2,3-triazoles **42/43** and also to understand the electronic factors of *β*-azidostyrenes in the OrgVACC reaction, we have chosen *β*-azidostyrene **21'a** which is more reactive towards carbonyls compared to α-azidostyrenes due to the linear conjugation (Table 4). The OrgVACC reaction of deoxybenzoin **38a** with *β*-azidostyrene **21'a** under the optimized conditions furnished the expected *N*-vinyl-1,2,3-triazole **42aa** in 85% yield (Table 4, entry 1). We have also tested two more examples of halogen-, and methyl-substituted deoxybenzoins **38b-c** for the OrgVACC reaction with **21'a**, which furnished the *N*-vinyl-1,2,3-triazoles **42ba-ca** in excellent yields (Table 4, entries 2-3). The OrgVACC reaction of hydrogen-, methyl-, methoxy-, chloro-, and nitro-substituted arylketones **38e-i** with **21'a** under the **40e**-catalysis furnished the fully decorated *N*-vinyl-1,2,3-triazoles **42ea-ia** in 70-92% yields

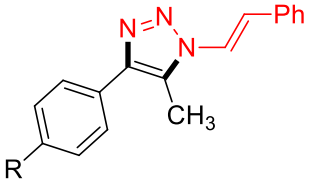
without showing much of electronic factors (Table 4, entries 4-8). Likewise, functionalized arylketones, 1-(naphthalen-2-yl)propan-2-one **38j** and 1-phenylpentan-2-one **38k** with **20a** furnished the 1,4,5-trisubstituted-*N*-vinyl-1,2,3-traizoles **42ja** and **42ka** in 90% yield, respectively (Table 4, entries 9-10). Reaction of phenylacetaldehyde **20a** with *β*-azidostyrene **21'a** under 10-mol% of **40e**-catalysis furnished the single isomer of 1,4-disubstituted-*N*-vinyl-1,2,3-triazole **43aa** in 90% yield (Table 4, entry 11).

Table 4: Azide scope[a]

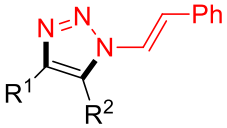




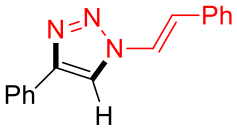
42aa: R^1 = H, R^2 = H (0.65 h; 85%)
42ba: R^1 = Br, R^2 = Me (1.0 h; 92%)
42ca: R^1 = H, R^2 = Cl (0.82 h; 95%)



42ea: R = H (0.75 h; 85%)
42fa: R = CH_3 (0.65 h; 90%)
42ga: R = OCH_3 (0.65 h; 85%)
42ha: R = Cl (0.75 h; 92%)
42ia: R = NO_2 (0.5 h; 70%)



42ja: R^1 = 2-naphthyl, R^2 = CH_3 (0.65 h; 90%)
42ka: R^1 = Ph, R^2 = $CH_2CH_2CH_3$ (0.5 h; 90%)



43aa: (0.5 h; 90%)

[a] Reactions were carried out in DMSO (0.3 M) with 1.2 equiv. of **21'a** relative to the **38/20** (0.3 mmol) in the presence of 10-mol% of **40e** and yield refers to the column-purified product.

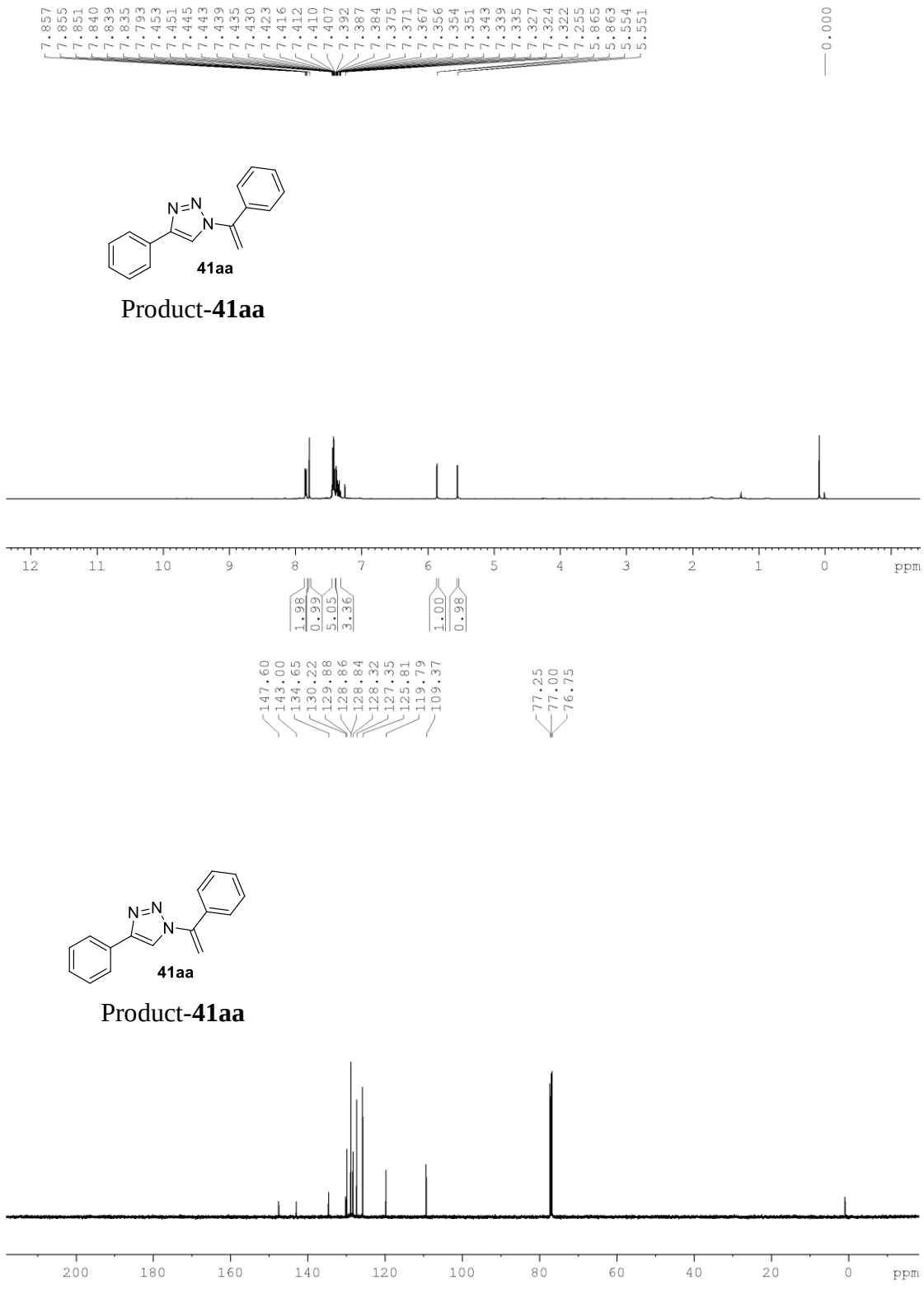


Figure 7: ^{1}H and ^{13}C spectra of the product **41aa**.

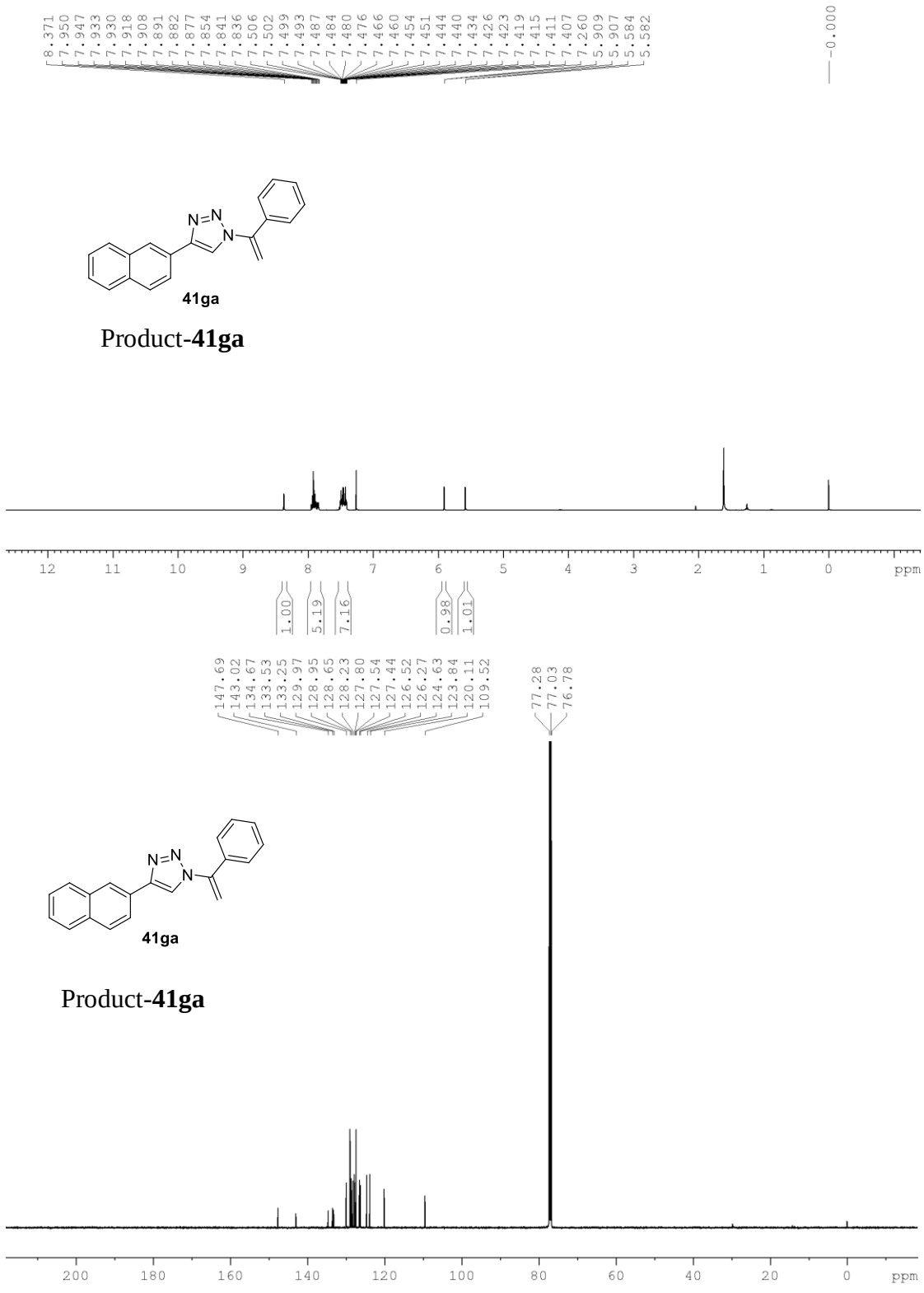


Figure 8: ^{1}H and ^{13}C spectra of the product **41ga.**

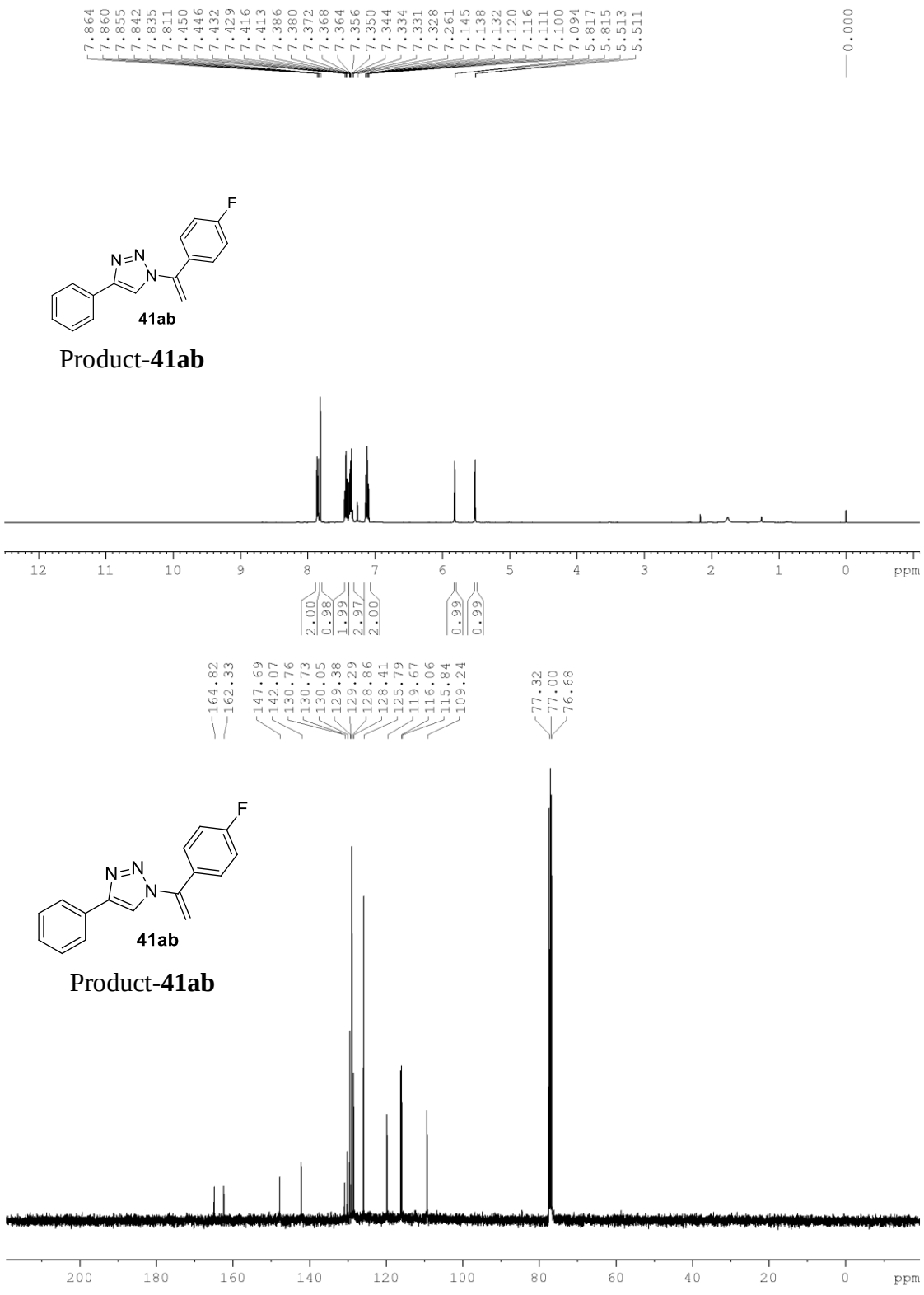


Figure 9: ^{1}H and ^{13}C spectra of the product **41ab**.

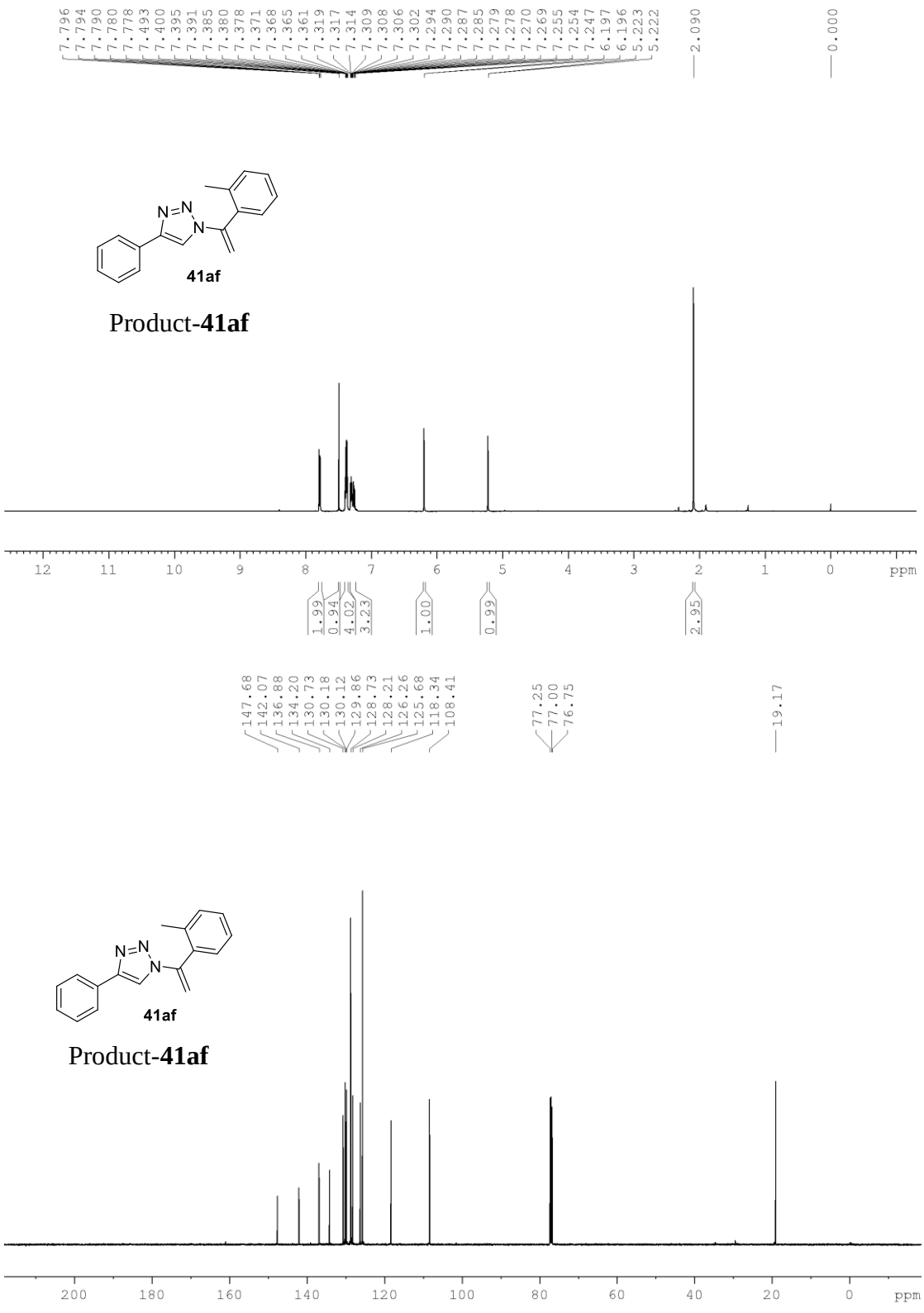


Figure 10: ^{1}H and ^{13}C spectra of the product **41af**.

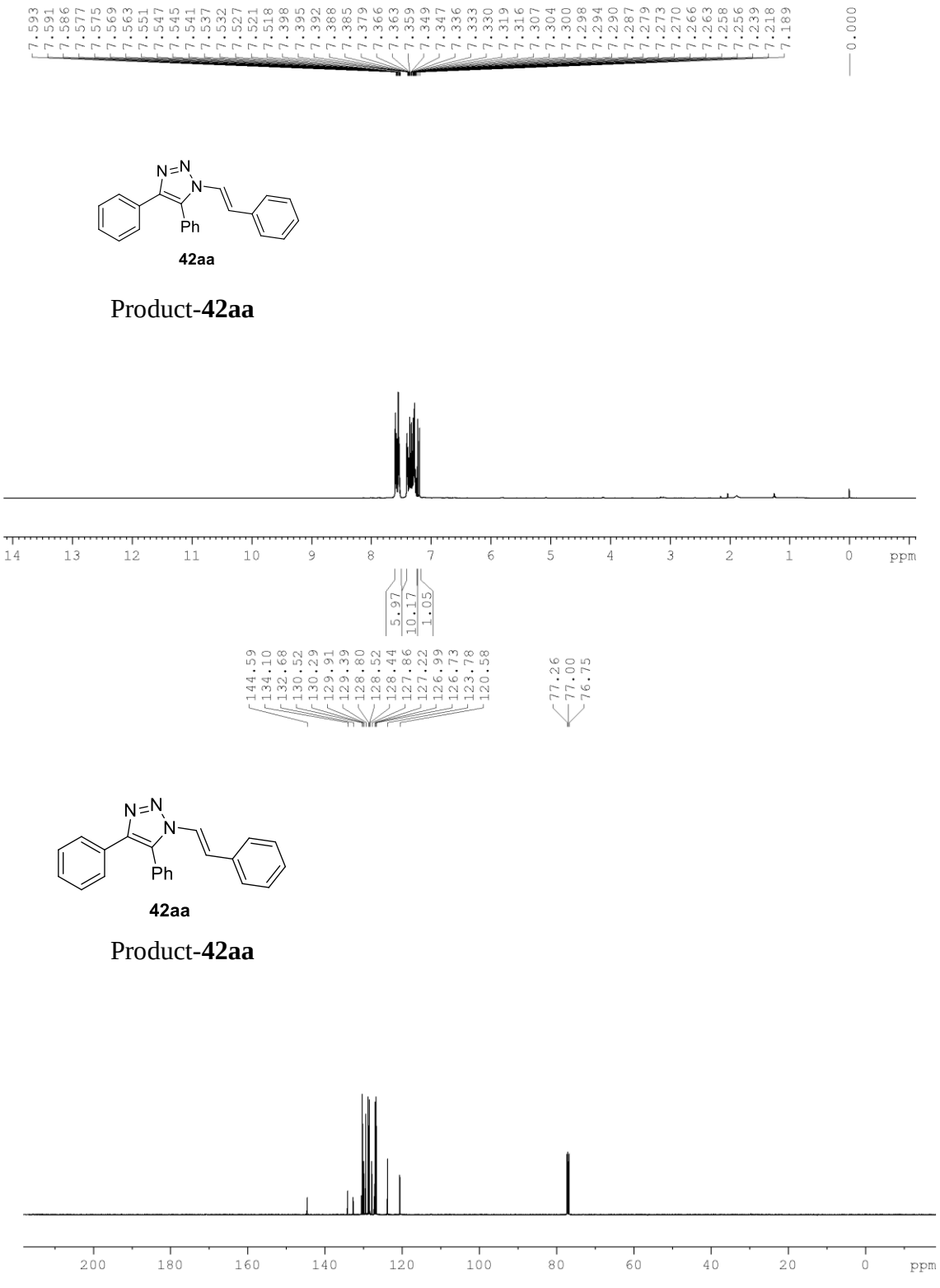


Figure 11: ^{1}H and ^{13}C spectra of the product **42aa**.

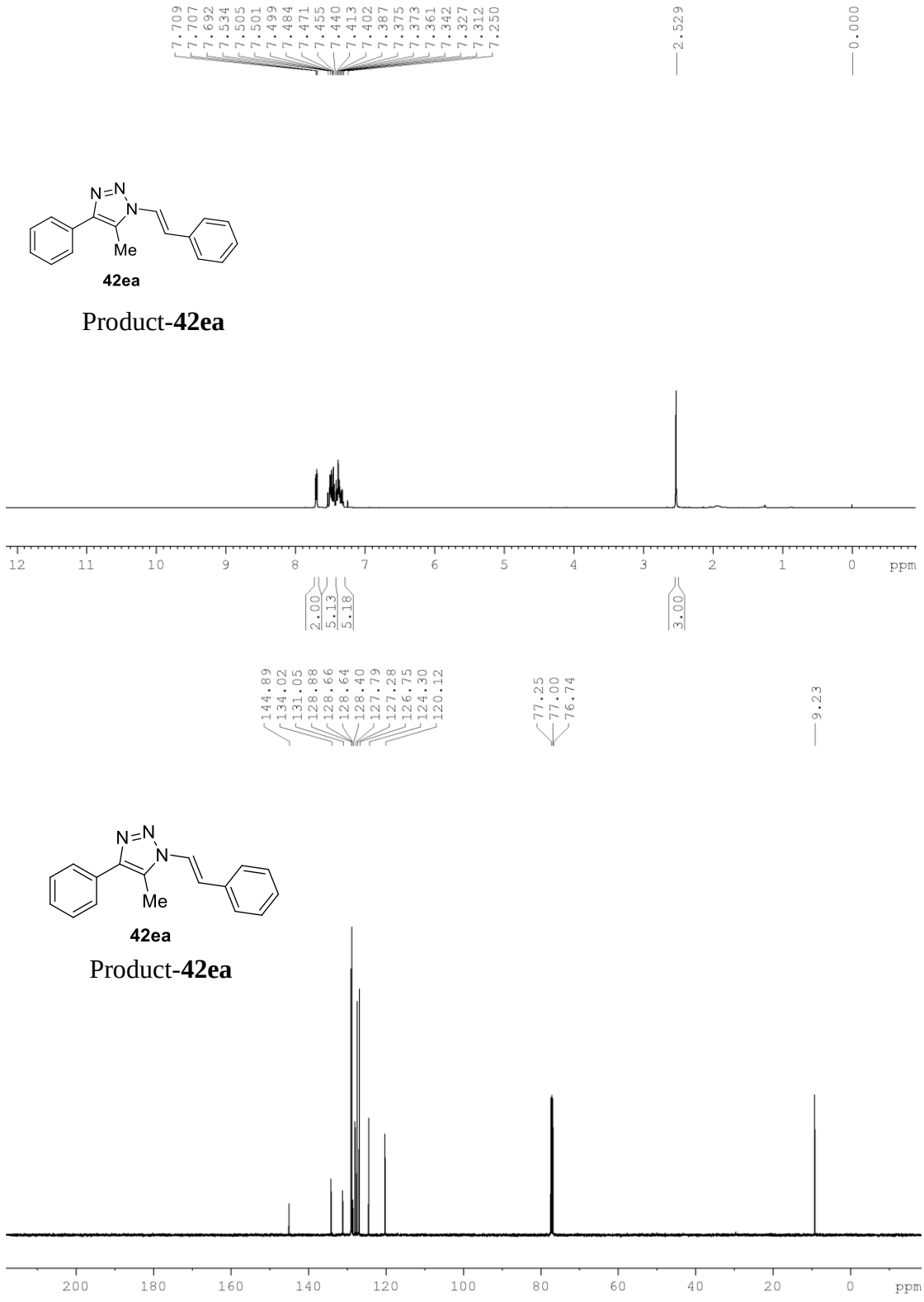


Figure 12: ^{1}H and ^{13}C spectra of the product **42ea**.

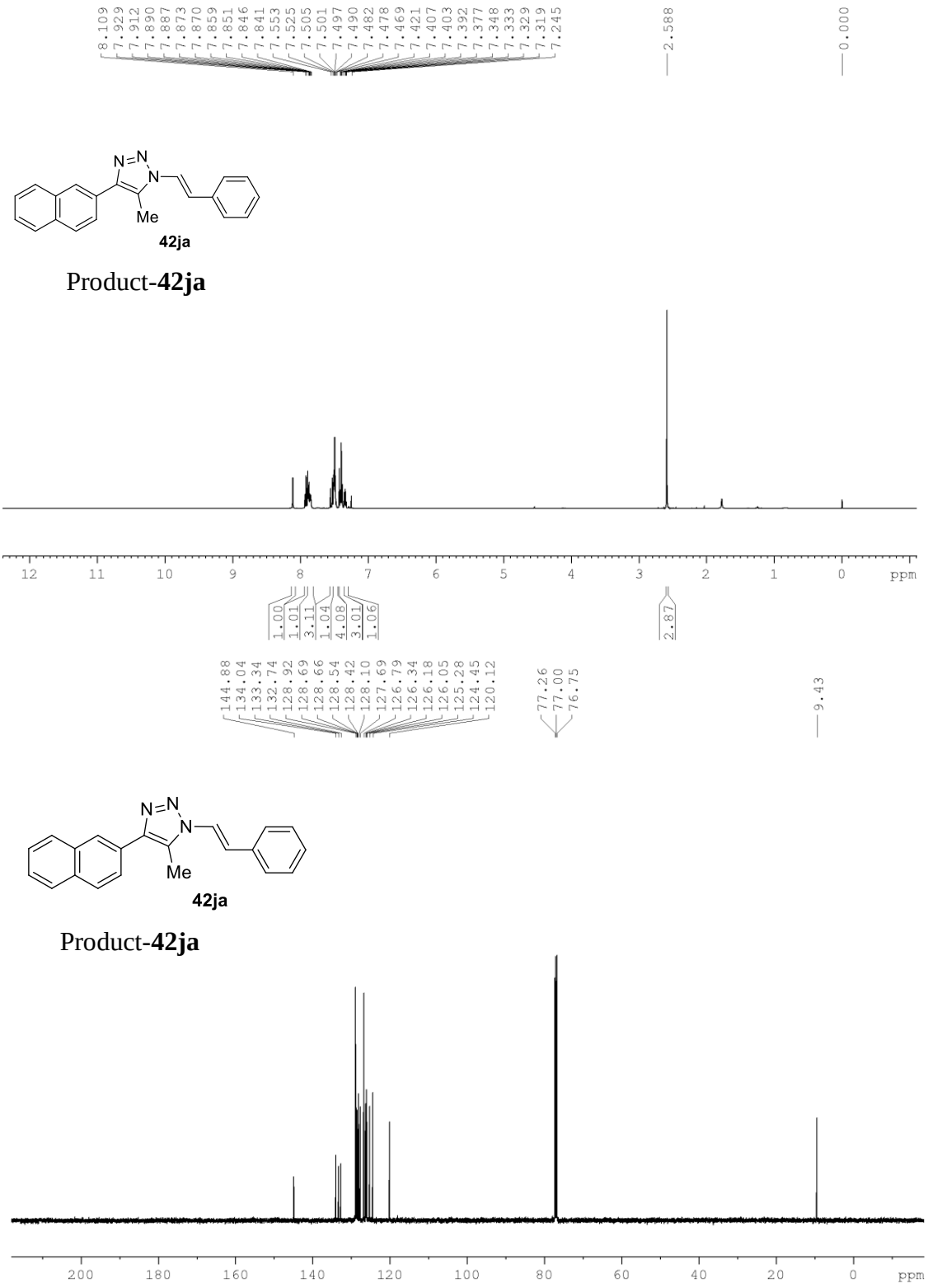
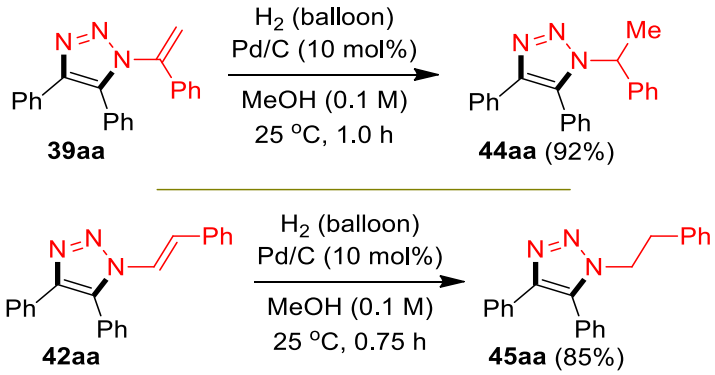


Figure 13: ^{1}H and ^{13}C spectra of the product **42ja**

3.4 Synthetic Applications:

The importance of OrgVACC reactions was further exemplified by synthesizing compounds **44aa** and **45aa** (Scheme 2).[10] Catalytic hydrogenation of 1,4,5-trisubstituted-*N*-vinyl-1,2,3-triazole **39aa** with hydrogen balloon under 10-mol% of Pd/C in methanol at 25 °C for 1.0 h furnished the functionalized *N*-alkyl-1,2,3-triazole **44aa** in 92% yield. Similarly, treatment of **42aa** with hydrogen balloon in the presence of Pd/C in methanol at 25 °C for 1.0 h furnished the functionalized *N*-alkyl-1,2,3-triazole **45aa** in 85% yield. On the contrary, the literature synthesis of this triazole **45aa** starting from the diphenylacetylene and (2-azidoethyl) benzene requires costly Ru-catalyst, high temperature and a long reaction time (Scheme 2).[5j-n] These results clearly demonstrate the exceptional advantages and more applications of OrgVACC protocol, which enables the simple high-yielding synthesis of fully substituted *N*-alkyl-1,2,3-triazoles, which are not easily accessible from other methods.



Scheme 2: Synthetic applications

3.5 Reaction mechanism:

The mechanism for the OrgVACC is illustrated in Scheme 3. Reaction of the deoxybenzoins/arylacetones/arylacetaldehydes **38/20** with catalyst DBU **40e** in DMSO generates the stable enolate **46,** which on in situ treatment with vinyl-azides **21** furnishes selectively the functionally-rich adduct 1,2,3-triazolines **47** by [3+2]-cycloaddition.[2c] The adduct **47** further transforms into the fully decorated *N*-vinyl-1,2,3-triazoles **39/41/42/43** through rapid elimination of water under ambient conditions.

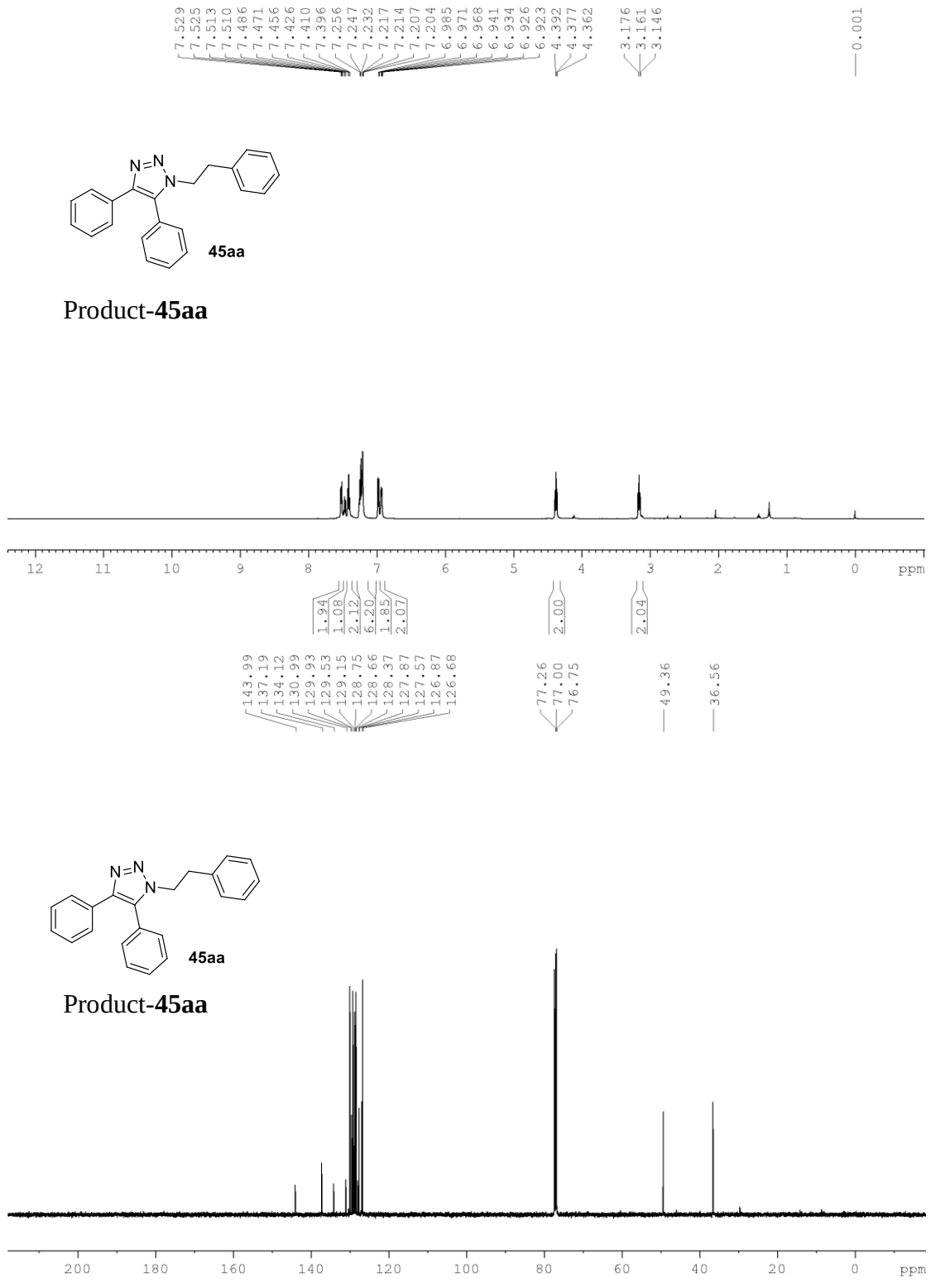
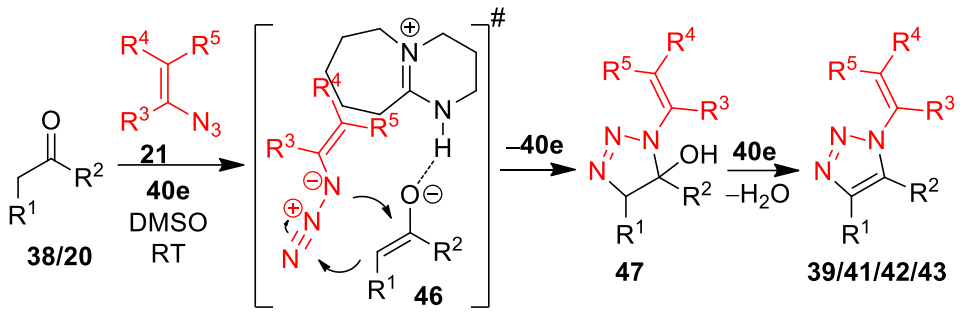


Figure 14: ^{1}H and ^{13}C spectra of the product **45aa**.



Scheme 3: Reaction mechanism

3.6 Conclusion:

In summary, we have developed a versatile organocatalytic enolate-mediated vinyl azide-carbonyl [3+2]-cycloaddition to furnish the functionally-rich 1,4,5-trisubstituted-*N*-vinyl-1,2,3-triazoles and 1,4-disubstituted-*N*-vinyl-1,2,3-triazoles with medicinally useful functional groups. Present method of OrgVACC highlights the metal-free conditions, high rate and selectivity, and easy access to the library of *N*-vinyl-1,2,3-triazoles. Moreover, many of the reported syntheses have the disadvantage of requiring multiple synthetic steps, harsh reaction conditions, heavy metals and less available unsymmetric internal alkynes; therefore, this OrgVACC protocol is very convenient to practice. Further work is in progress to utilize the enolate-mediated OrgVACC reactions in medicinal and material chemistry.

4.0 Reaction Engineering and Photophysical Studies of Fully Enriched *C*-Vinyl-1,2,3-Triazoles

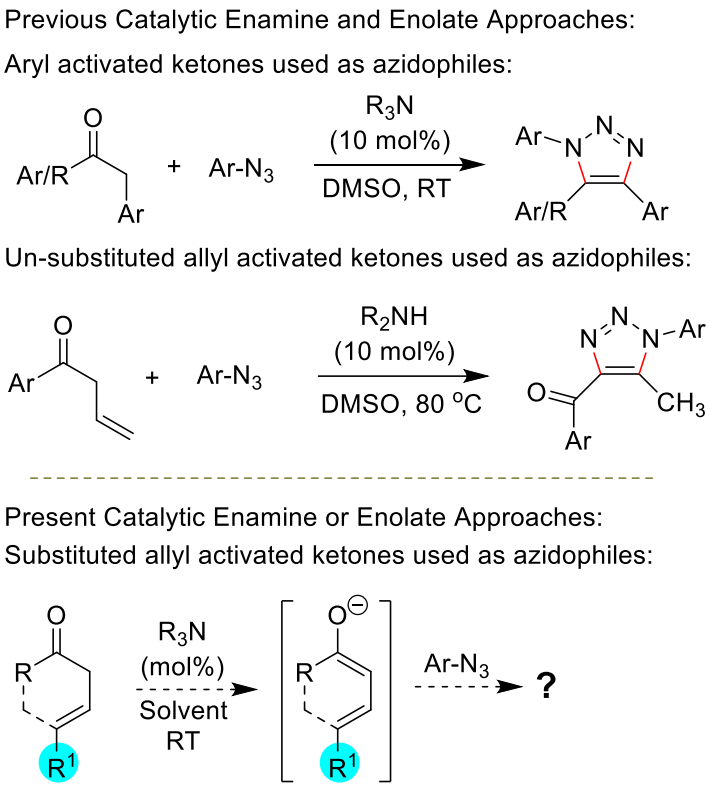
4.1 Abstract:

For the first time, an enolate-mediated organocatalytic fluorogenic formal [3+2]-cycloaddition of (*E*)-1,4-diarylbut-3-en-1-ones and aryl azides is reported. The mild metal-free catalytic conditions of this reaction allowed us to synthesize a library of pure fluorescent coumarin-triazole dyes. It is an efficient formal [3+2]-cycloaddition for the synthesis of fully decorated *C*-vinyl-1,2,3-triazoles with excellent outcomes with reference to rate, yield, selectivity, operation simplicity, substrates scope, and photophysical applications.

4.2 Introduction:

The simple and elegant 1,2,3-triazole scaffolds were found to be utilized in different spheres of science such as organic chemistry, life science, material science, drug discovery in medicinal chemistry on account of their vast biological activities, agrochemical industry, photophysical studies, semiconductors and DSSC's (dye sensitized solar cells).[10a-i] They also possess anti-cancer, anti-malarial, anti-viral, anti-inflammatory, anti-tubercular, anti-bacterial, and anti-microbial properties for pharmacology.[10j-o] These and much more wide interdisciplinary applications of 1,2,3-triazole scaffolds have incessantly created substantial amount of interest in the field of 1,2,3-triazole synthesis.

We were driven by the significance of click-chemistry as the building block for constructing functionally rich 1,2,3-triazoles,[5] so that the non-practitioners of organic chemistry, such as biologists, material chemists and pharmaceutical industry could be facilitated to construct these vital molecules easily and readily for studying their applications further. On account of our vested interest in click reaction chemistry and also based on the applications of 1,2,3-triazoles, since last one decade we have been studying both metal- free enamine- and enolate-mediated organocatalytic 1,2,3-triazole synthesis, starting from different type of carbonyls and azides.[6, 7]



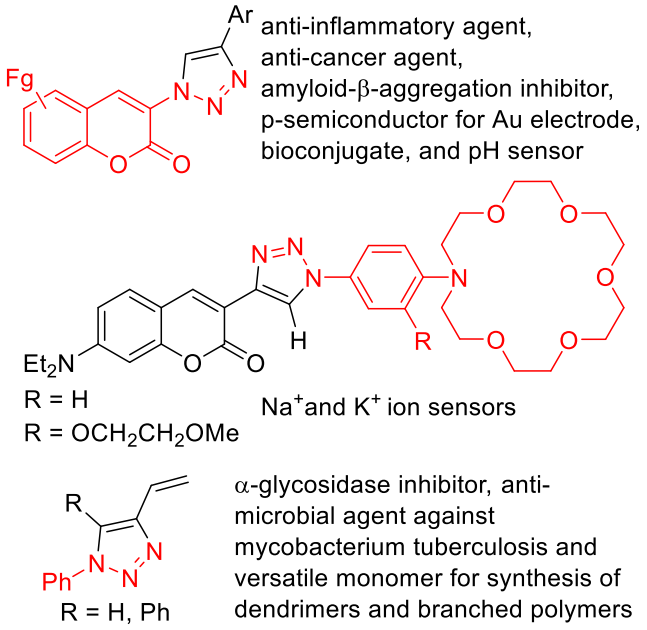
Scheme 1: Design for *C*-Vinylic 1,4,5-trisubstituted triazoles

Based on these prolific investigations from our lab, we have established enolate-based triazole synthesis to be far more efficient and faster than the enamine-based one. In this context, following our work, recently a paper by Wang's group appeared,[8h] which discussed an enamine-based approach for 1,2,3-triazole formation from un-substituted allyl group containing carbonyl compounds and aryl azides, wherein the reaction has progressed through isomerization followed by [3+2]-cycloaddition and air oxidation instead of direct [3+2]-cycloaddition (Scheme 1)[8h]

In continuation, our curiosity in enolate-based triazole synthesis kindled enthusiasm to study the reactivity of more functionalized allyl containing ketones as azidophiles towards 1,2,3-triazole formation. Thus prompted us to design the reaction based on the substituted allyl containing ketones with aryl azides, and to explore if the reaction will follow classical or isomerization mode during the product generation. The existent possibilities of formation of different products are discussed latter on in reaction mechanistic studies. These reactions are captivating not only from

the point of view of substrate reactivity pattern, but also from the essential pharmaceutical and photophysical applications of the products due to the phenyl/π-electrons conjugation with 1,2,3-triazole rings (Scheme 2).[1e, 3a-i]

Unambiguously, vinyl 1,2,3-triazoles were considered as privileged monomers for various type of polymer synthesis and dendrimers, in view of having the structural features (such as aromaticity, functionality and ability for hydrogen bonding) similar to the traditional monomers. Especially, coumarin-triazoles exhibit predominate utility in photophysical and medicinal community due to their flurogenic activity. They are used as pH sensors, metal ion (Na^+ and K^+) sensors, p-semiconductors with Au electrode, enzyme inhibitors, anti-inflammatory, anti-cancer and anti-microbial agents.[1e, 3a-i]



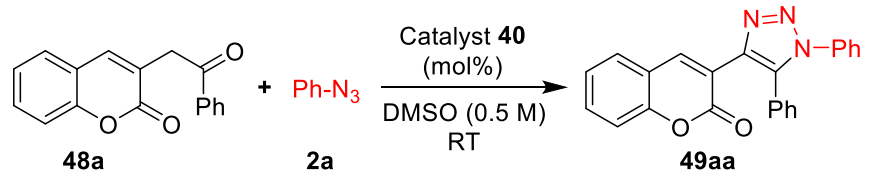
Scheme 2: Application of *C*-Vinylic- and *N*-vinyl triazoles in medicinal to material chemistry.

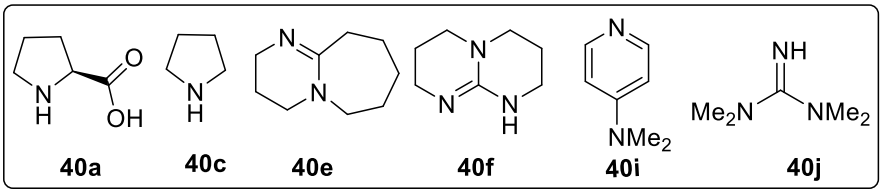
4.3 Results and Discussion:

4.3a Preliminary optimization for organocatalytic formal [3+2]-cycloaddition of coumarin 48a and phenyl azide 2a:

With reaction design in hand, optimization studies were initiated with the simple allyl containing ketone, 3-(2-oxo-2-phenylethyl)-coumarin **48a**, which on enamine-mediated click reaction with phenyl azide **2a** in the presence of 20 mol% of (*S*)-proline **40a** in DMSO at 25 °C to 60 °C did not produce any 1,2,3-triazole product even after 12 h (Table 1, entries 1-2). In the catalyst screening, the tertiary amine catalyst DMAP **40i** was unsuccessful in promoting the click reaction even at 60 °C (Table 1, entries 3-4). Though it was disappointing, shifting the catalyst to pyrrolidine **40c**, the enamine-mediated click reaction resulted in 20% yield of 3-(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)-coumarin **49aa** at 25 °C in 12 h, and same reaction at 60 °C furnished the click product **49aa** within 5 h in 68% yield, thereby giving hope (Table 1, entries 5-6). Fortunately, the enolate-mediated click reaction of 3-(2-oxo-2-phenylethyl)-coumarin **48a** with phenyl azide **2a** on treatment with 20 mol% of DBU **40e** in DMSO at 25 °C within 45 minutes, generated the coumarin-triazole **49aa** in 86% yield (Table 1, entry 7). Surprisingly, the catalysts TBD **40f** and TMG **40j** were realized to be no better than DBU **40e** and the coumarin-triazole **49aa** was formed in 60% and 72% yields after 3 and 1 h, respectively (Table 1, entries 8-9). Decreasing the catalyst loading of DBU **40e,** from 20 to 10 mol% resulted in reduced (73%) yield of the coumarin-triazole **49aa** for a little longer reaction time of 1 h (Table 1, entry 10). As part of solvent screening, reactions were performed in chloroform, DMF and acetonitrile solvents and found to be inferior to that in DMSO (Table 1, entries 11-13). While in chloroform and acetonitrile the click reaction produced no product, in DMF it generated 60% of the coumarin-triazole **49aa** (Table 1, entries 11-13). As a result of this optimization process, the reaction between the coumarin **48a** and phenyl azide **2a** was found to be optimal, when performed using 20 mol% of DBU **40e** in DMSO at 25 °C for 45 minutes (Table 1, entry 7).

Table 1. Reaction preliminary Optimization[a]





Entry	Catalyst	(mol%)	Solvent	*t* (h)	Yield[b] (%)
1[c]	**40a**	20	DMSO	12	-
2[c,d]	**40a**	20	DMSO	12	-
3[c]	**40i**	20	DMSO	12	-
4[c,d]	**40i**	20	DMSO	12	-
5[c]	**40c**	20	DMSO	12	20
6[d]	**40c**	20	DMSO	5	68
7	**40e**	20	DMSO	0.75	86
8	**40f**	20	DMSO	3	60
9	**40j**	20	DMSO	1	72
10	**40e**	10	DMSO	1	73
11[c]	**40e**	20	$CHCl_3$	12	-
12	**40e**	20	DMF	12	60
13[c]	**40e**	20	CH_3CN	12	-

[a] Reactions were performed in solvent (0.3 M) with 1.2 equiv. of **2a** relative to **48a** (0.3 mmol) in the presence of catalyst **40**. [b] Yield refers to the column-purified product. [c] Ketone **48a** and azide **2a** were not consumed totally. [d] Reactions were performed at 60 °C

4.3b Scope of the organocatalytic formal [3+2]-cycloaddition reaction with coumarins and aryl azides:

Most exciting and most awaited part of the investigative results regarding library synthesis of coumarin-triazoles **49** is epitomized in Table 2, articulating the versatility of the enolate-mediated organo-click reaction. Azidophiles, 3-(2-oxo-2-aryl/methylethyl)-coumarins **48a-f** encompassing diverse coumarin units, both plain as well as substituted with electron-donating groups such as

OCH_3 and NEt_2, participated in the enolate-mediated organocatalytic triazole formation. Initially we checked the reactivity of plain coumarin **48a** with electron rich **2b,** halogenated **2f** and **2h**, electron deficient **2q** & **2r** aryl azides under optimal condition resulted corresponding coumarin triazoles **49ab, 49af** & **49h** and **49aq** & **49ar** respectively up to 92% yields within 1.0 h at 25 °C. Then, keeping flouorogenic properities in mind we performed detailed investigation on electon rich coumarin **48b** with various azides. Aryl azides such as electron rich **2b,** halogenated **2f** & **2i** and electron deficient **2q** & **2r** aryl azides followed the above trend without showing electronic influence (Table 2). Interestingly, we observed *ortho*-substitution effect on the **40e**-catalyzed reaction of tolyl azides **2c-e** with coumarin **48b**. In regard to this, *o*-tolyl azide **2e** gave moderate yield of coumarin-triazole **49be** under relatively longer reaction time, may be due to the steric hindrance (Table 2). Treatment of coumarin **48b** with functionally rich sugar azide **2w** in the presence of 20 mol% **40e** in DMSO at 25 °C effortlessly generated coumarin-triazole **49bw** in excellent yields within 3 h (Table 2). Surprisingly, treatment of coumarin **48d** with phenylazide **2a** delivered highly fluorogenic coumarin triazole **49da** in 85% yield under optimal condition (Table 2). Even though the nature and position of the substituent on the coumarin unit appear to play only minimal effect on the reaction outcome with respect to rate, selectivity and yields (Table 2). Surprisingly, reaction of 3-(2-oxopropyl)-2*H*-chromen-2-one **48f** with PhN_3 **2a** in the presence of 20 mol% DBU **40e** in DMSO at 25 °C for 0.25 h furnished the coumarin-triazole **49fa** in 93% yield (Table 2). We didn't observed the coumarin-triazole **49bu** formation from the reaction of **48b** with aliphatic azide of $PhCH_2N_3$ **2u** under the **40e-**catalysis in DMSO at 25 °C for 3-24 h and within 3 h, coumarin **48b** was decomposed may be due to the low reactivity of **2u** (result not shown in Table 2). Same trend was observed under the KOtBu-catalysis. Exemplified in Table 2 are some of the analogous coumarin-triazoles **49**, whose applications are plentiful and make the exploration of this present organo-click reaction worthwhile as mentioned earlier (see Scheme 2).

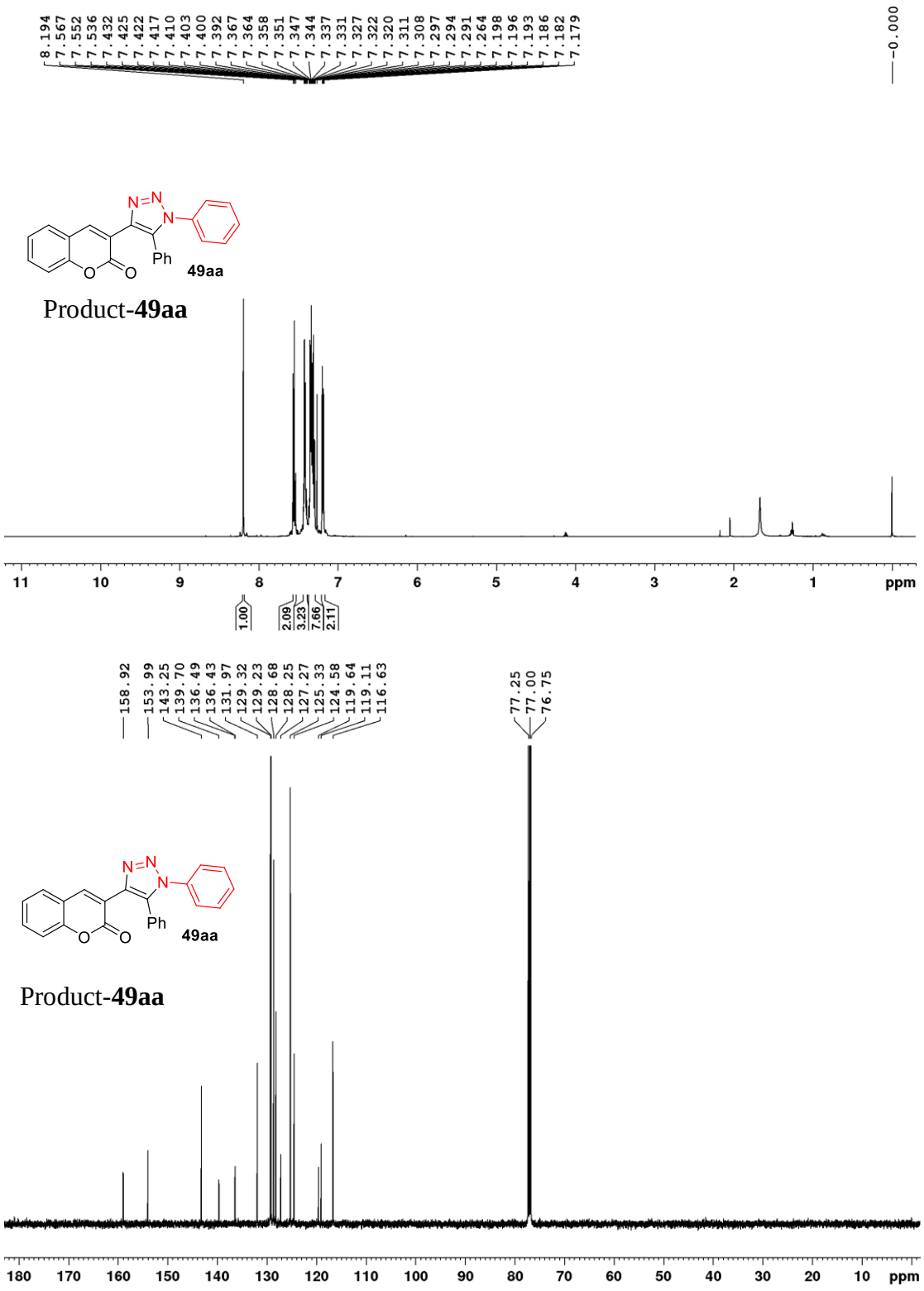
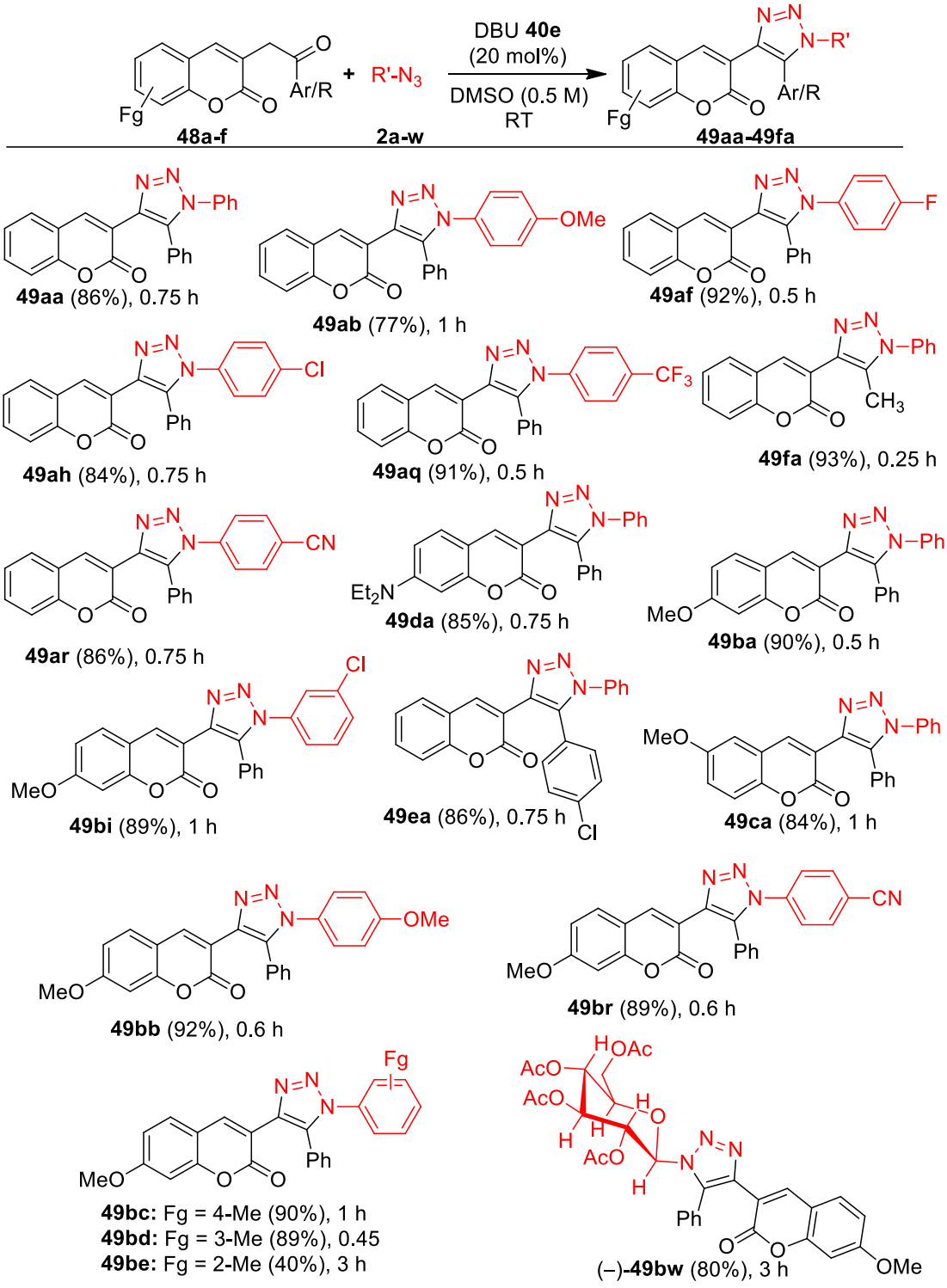


Figure 1: ^{1}H and ^{13}C spectra of the product **49aa**

Table 2: 3-(2-oxo-2-phenylethyl)-2*H*-chromen-2-one and azide scope. [a, b]



[a] Reactions were performed in DMSO (0.5M) with 1.5 equiv. of **2** relative to **48** (0.5 mmol) in the presence of 20 mol% of **40e**. [b] The yield refers to the column-purified product.

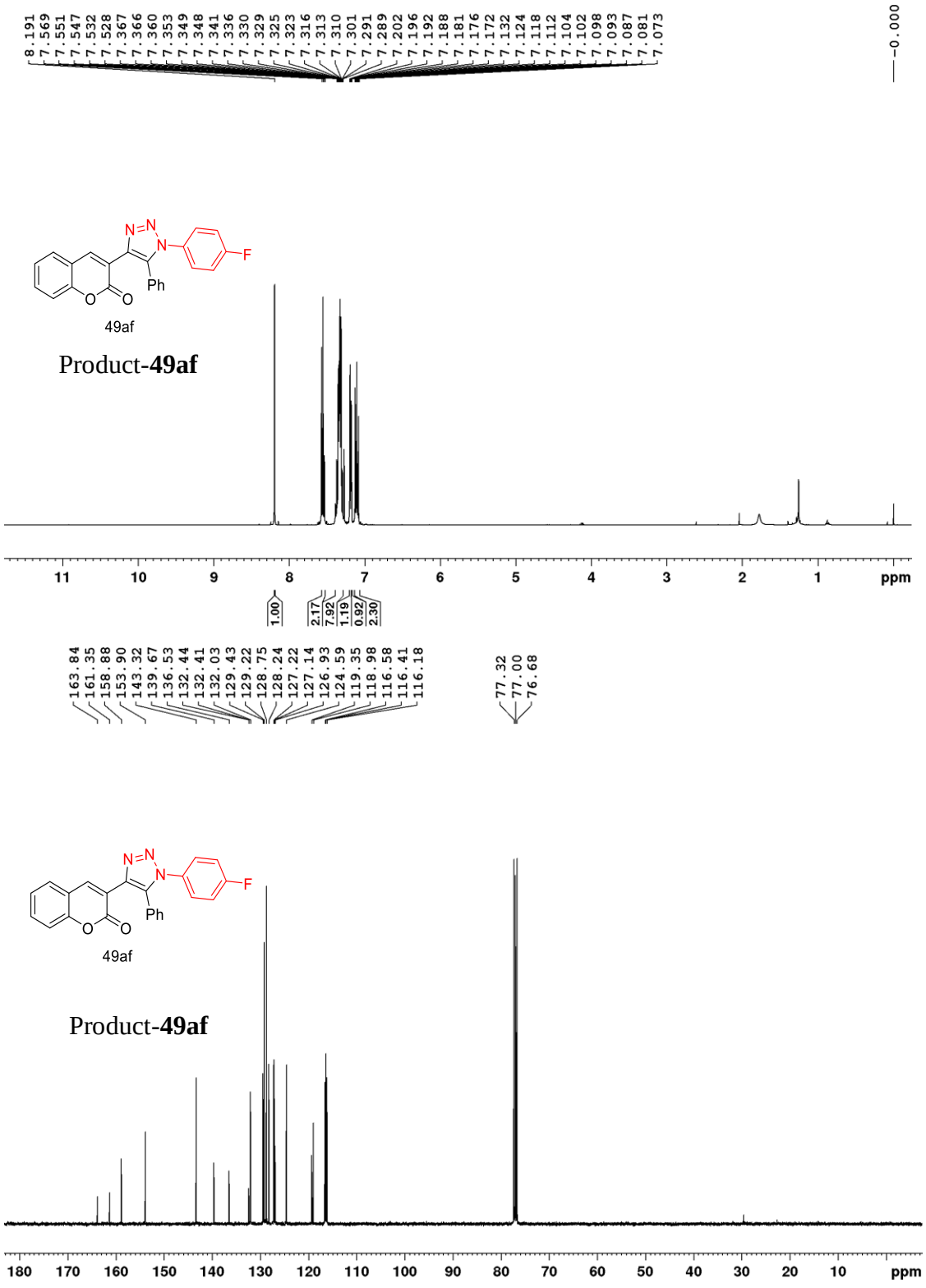


Figure 2: ^{1}H and ^{13}C spectra of the product **49af**.

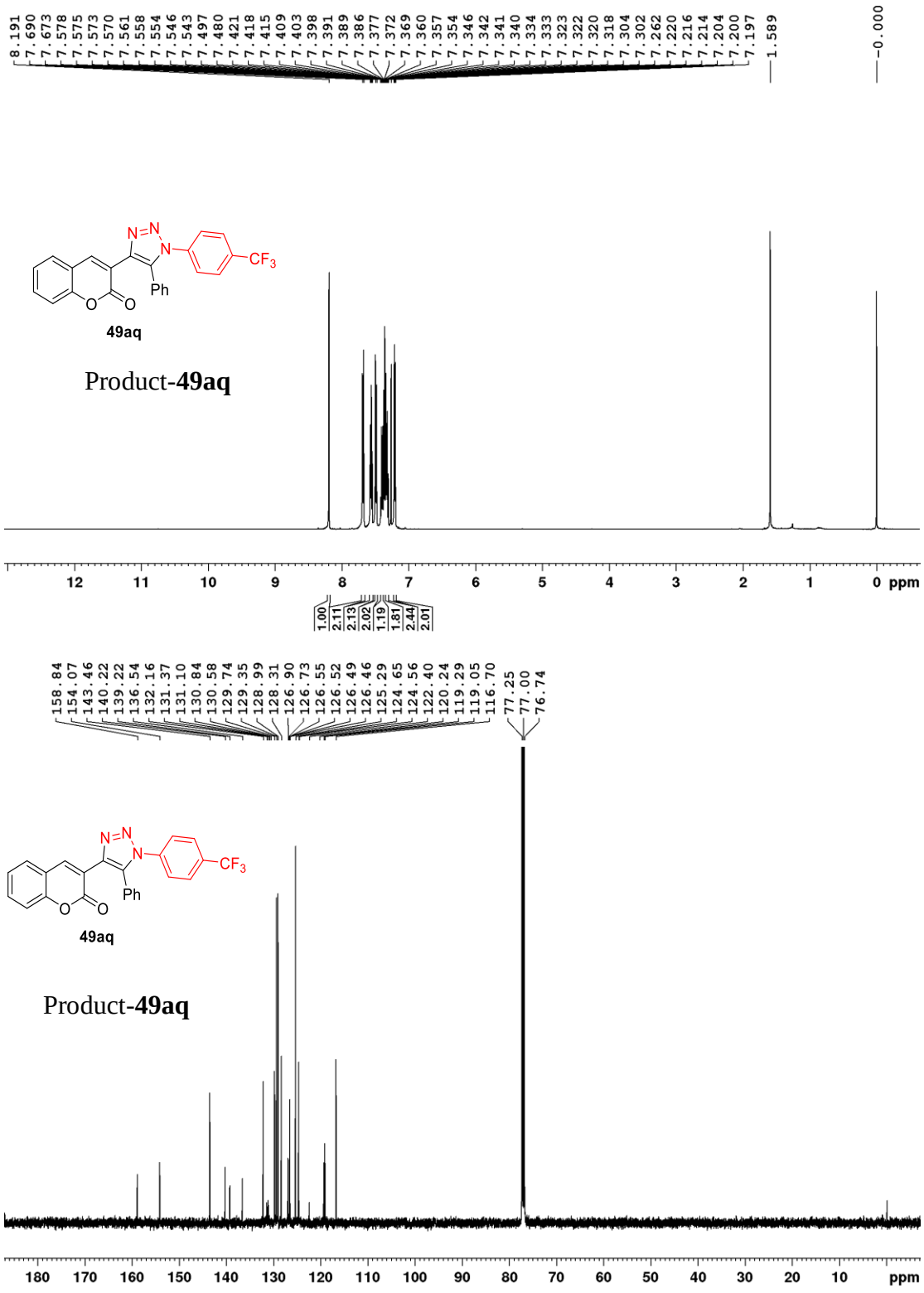


Figure 3: ^{1}H and ^{13}C spectra of the product **49aq**.

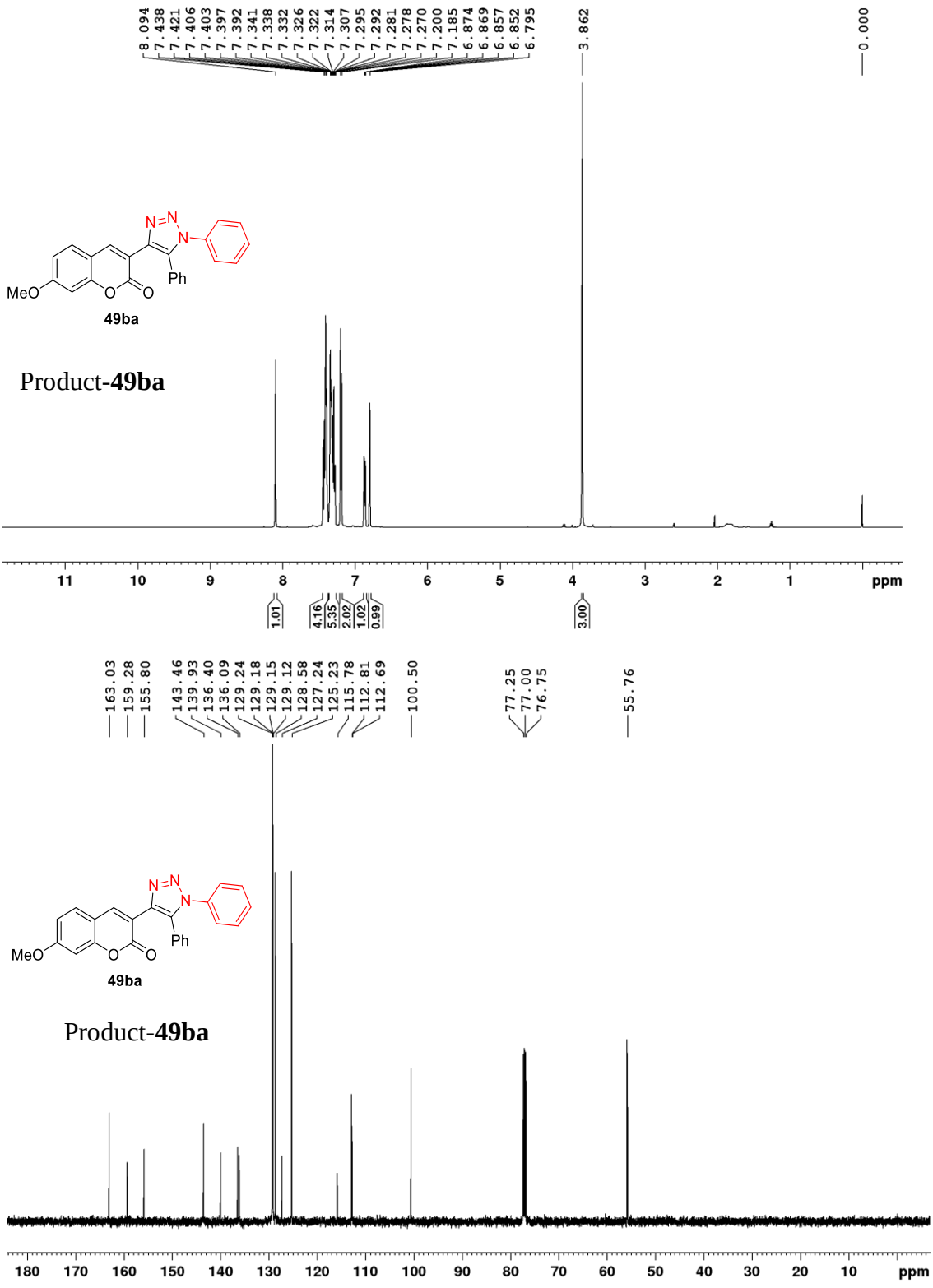


Figure 4: ^{1}H and ^{13}C spectra of the product **49ba.**

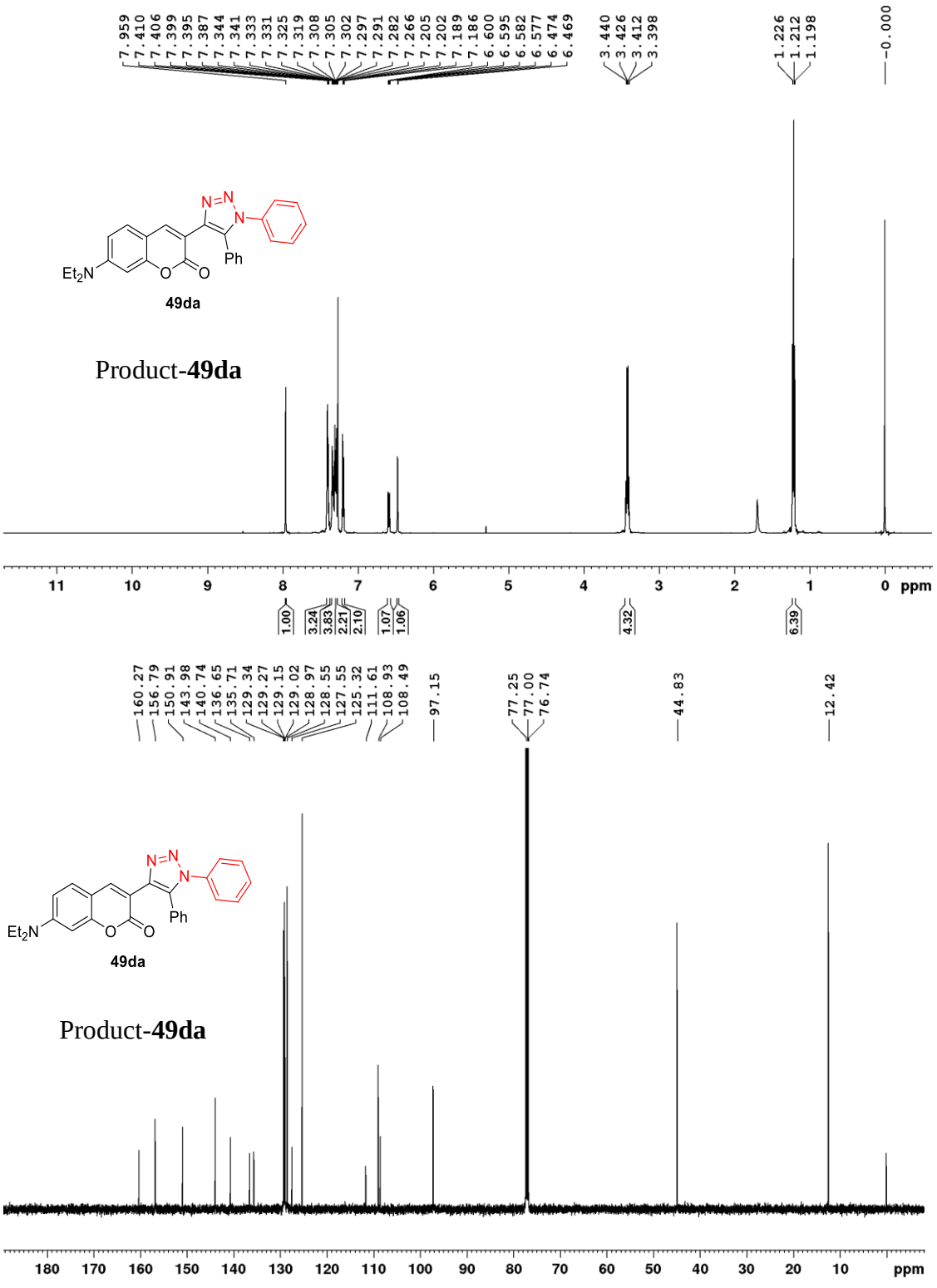


Figure 5: ^{1}H and ^{13}C spectra of the product **49da**.

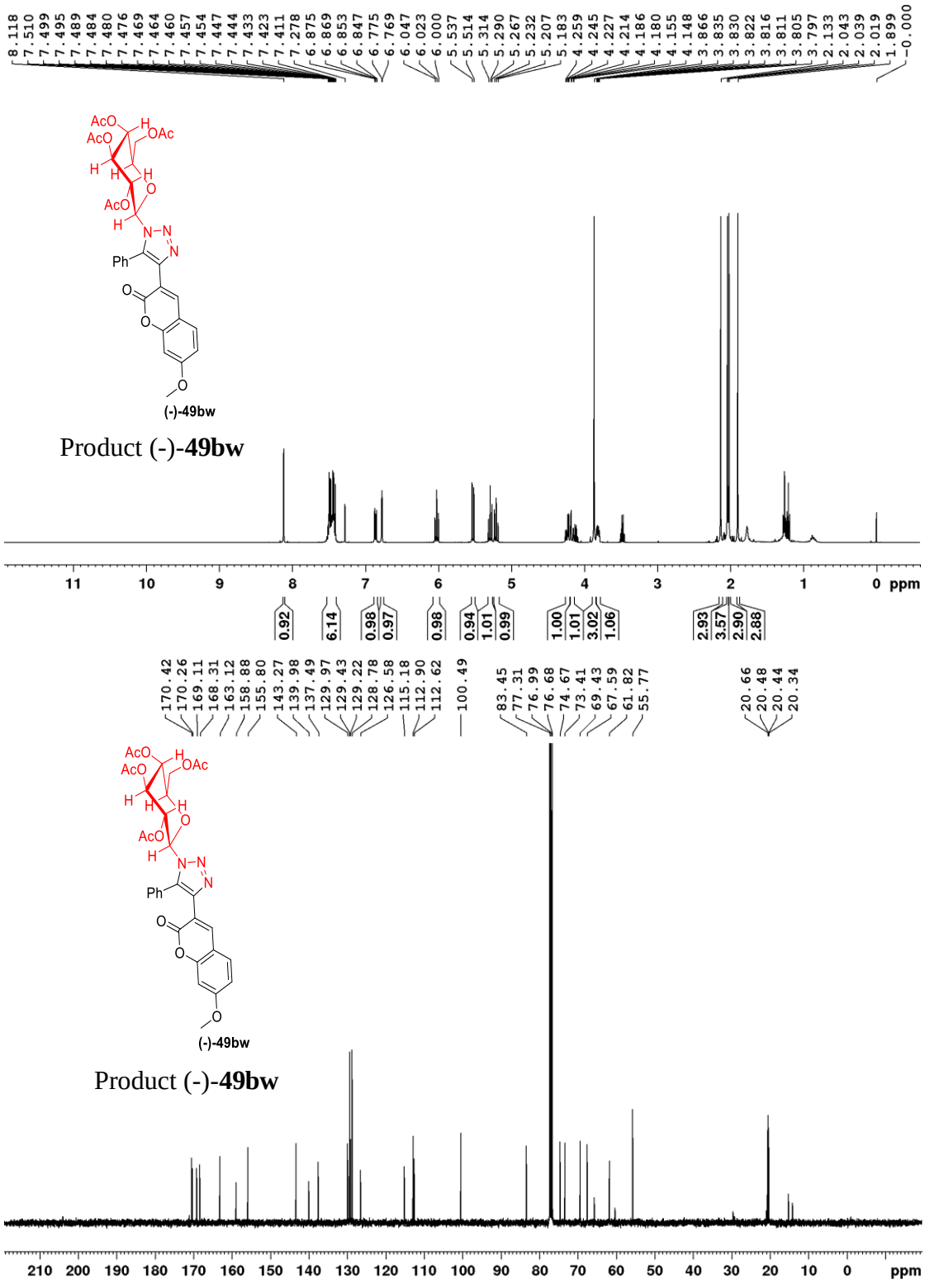
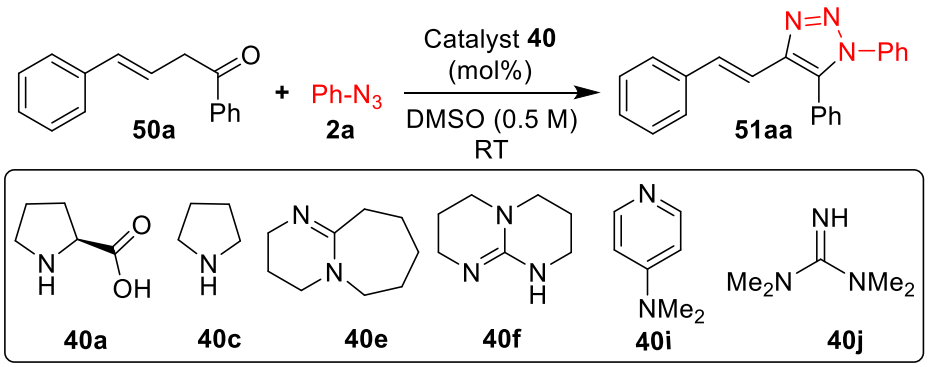


Figure 6: ^{1}H and ^{13}C spectra of the product (-)-**49bw**.

4.3c Optimization for organocatalytic formal [3+2]-cycloaddition of azidophile 50a and phenyl azide 2a: After understanding the enolate-mediated organocatalytic click reaction of aryl azides **2** with 3-(2-oxo-2-arylethyl)-coumarins **48a-f**, we further showed interest to investigate the click reaction with acyclic azidophiles, (*E*)-1,4-diphenylbut-3-en-1-one **50a** (Table 3).

Table 3. Reaction Optimization[a]



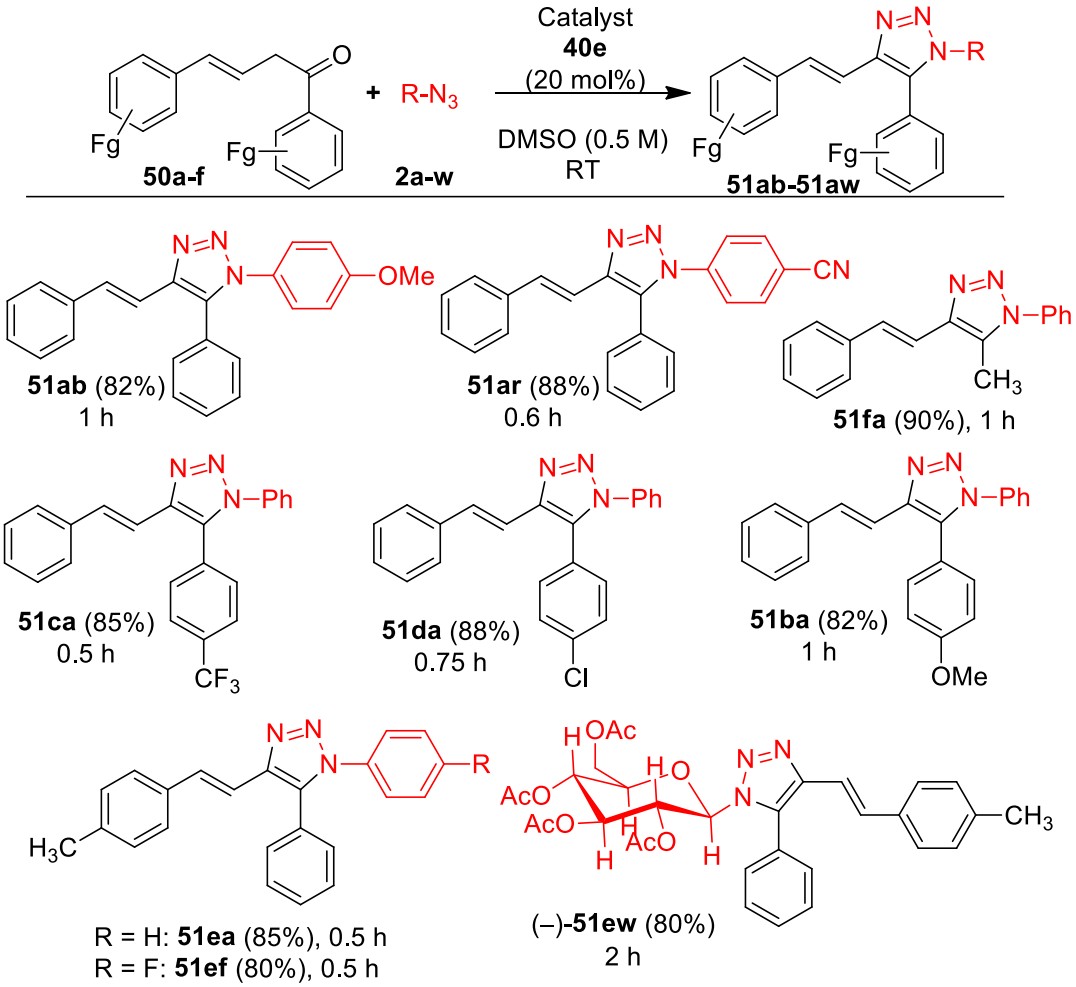
Entry	Catalyst	(mol%)	Solvent	*t* (h)	Yield[b] (%)
1[c]	**40a**	20	DMSO	12	-
2[c,d]	**40a**	20	DMSO	12	-
3[c]	**40i**	20	DMSO	12	-
4[c,d]	**40i**	20	DMSO	12	-
5[c]	**40c**	20	DMSO	12	20
6[d]	**40c**	20	DMSO	7	40
7	**40e**	20	DMSO	0.75	88
8	**40f**	20	DMSO	3	62
9	**40j**	20	DMSO	1	73
10	**40e**	10	DMSO	1	75
11[c]	**40e**	20	$CHCl_3$	12	-
12	**40e**	20	DMF	12	60
13[c]	**40e**	20	CH_3CN	12	-

[a] Reactions were performed in solvent (0.5 M) with 1.5 equiv. of **2a** relative to **50a** (0.5 mmol) in the presence of catalyst **40**. [b] Yield refers to the column-purified product. [c] Ketone **50a** and azide **2a** were not consumed totally. [d] Reactions were performed at 60 °C.

To find the best protocol of enamine- or enolate-mediated click strategy to make the functionalized 1,2,3-triazoles **51** from **50a** and **2a**, we have done quick optimization as shown in Table 3. Surprisingly, similar to the coumarins **48a-f**, acyclic (*E*)-1,4-diphenylbut-3-en-1-one **50a** with **2a** too has identical reactivity and selectivity pattern under the catalytic amount of **40a-j** in DMSO at 25-60 °C (Table 3, entries 1-13). As a result of this thorough optimization, we find 20 mol% of

DBU **40e** in DMSO at 25 °C for 45 minutes as the optimal condition for high yielding synthesis of (*E*)-1,5-diphenyl-4-styryl-1*H*-1,2,3-triazole **51aa** as a single product from the click reaction between the allyl ketone **50a** and phenyl azide **2a** (Table 3, entry 7).

Table 4: (E)-1,4-diphenylbut-3-en-1-one and azide scope. [a]



[a] Reactions were performed in DMSO (0.5 M) with 1.5 equiv. of **2** relative to **50** (0.5 mmol) in the presence of 20 mol% of **40e**. [b] The yield refers to the column-purified product.

4.3d Scope of the organocatalytic formal [3+2]-cycloaddition reaction with allyl ketones and aryl azides: Once optimization was complete, we focused our attention on crafting a library of several *C*-vinyl-1,2,3-triazoles, by studying the scope of different substituted (*E*)-1,4-diphenylbut-3-en-1-ones **50** and various aryl azides **2** (Table 4).Treatment of **50a** with aryl azides **2b** and **2r** possessing electron-donating and withdrawing substituents smoothly generated the corresponding

C-vinyl-1,2,3-triazoles **51ab** and **51ar** (82% & 88%) within 1.0 h (Table 4). and sugar azide (-)-**2w** were found to be equally acceptable, without much difference in the organo-click reaction rate and yield. Similarly, both electron-donating and withdrawing substituents were comfortably bearable on the different phenyl groups of (*E*)-1,4-diphenylbut-3-en-1-ones **50b-e** in the enolate-mediated click reaction to produce *C*-vinyl-1,2,3-triazoles in high yields (Table 4). Surprisingly, reaction of aliphatic group substituted (*E*)-5-phenylpent-4-en-2-one **50f** with PhN_3 **2a** in the presence of 20 mol% DBU **40e** in DMSO at 25 ^oC for within 1 h furnished the *C*-vinyl-1,2,3-triazole **51fa** in 90% yield without any difficulties (Table 4).

In order to extend the reactivity scope on the allyl ketones, the cyclic allyl ketones **52** were chosen. Various aryl azides containing electron-donating **2b,** alkyl **2c**, substituents were reacted efficiently with the cyclic allyl ketone **52a** to produce the *C*-vinyl 1,2,3-triazoles **53aa-53ac** in admirable yields (84-92%) within 30 minutes to 1 h (Table 5). halogen **2f, 2h** & **2i** and withdrawing **2q** substituted arylazides followed the same trend without electrionic influence on click reaction. Excitingly, the 2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosylazide (-)-**2w** also took part in the enolate-mediated triazole formation with the cyclic allyl ketone **52a,** uneventfully to generate the corresponding glucopyranosyl *C*-vinyl 1,2,3-triazole (-)-**53aw** in 81% yield within 1.5 h (Table 5, entry 9).

The flexibility of this enolate-mediated organocatalytic *C*-vinyl 1,2,3-triazole formation was tested further, by varying the substituents on the cyclic allyl group of the ketone **52**. Phenyl possessing electron-donating, alkyl and halogenated groups such as OCH_3, CH_3 and F; other aryl groups like 1-naphthyl and 9-phenanthrene groups were quite comfortably accepted as substituents on cyclohex-3-en-1-one **52b-f** for the click reaction with aryl azides **2a** and **2f** (Table 6). Following the same pattern here too, the click reaction yields were satisfyingly excellent (88-91%) and the reactions completed within 1 h (Table 6). From the results, it is obvious that the different substituents on the double bond in cyclohex-3-en-1-one **52a-f** did not seem to have much effect on the click reaction outcome with respect to rate, selectivity and yield.

Unfortunately, we didn't observed the *C*-vinyl-1,2,3-triazoles **53au/53av/53ay** formation from the reaction of **52a** with aliphatic azides of $PhCH_2N_3$ **2u**, $PhCH_2CH_2N_3$ **2v** and TsN_3 **2y** under the **40e**-catalysis in DMSO at 25 °C for 3-24 h and in this three reactions, within 3 h cyclic allyl ketone **51a** was decomposed may be due to the low or high reactivity of **2u-2v/2y,** respectively (results not shown in Table 6).

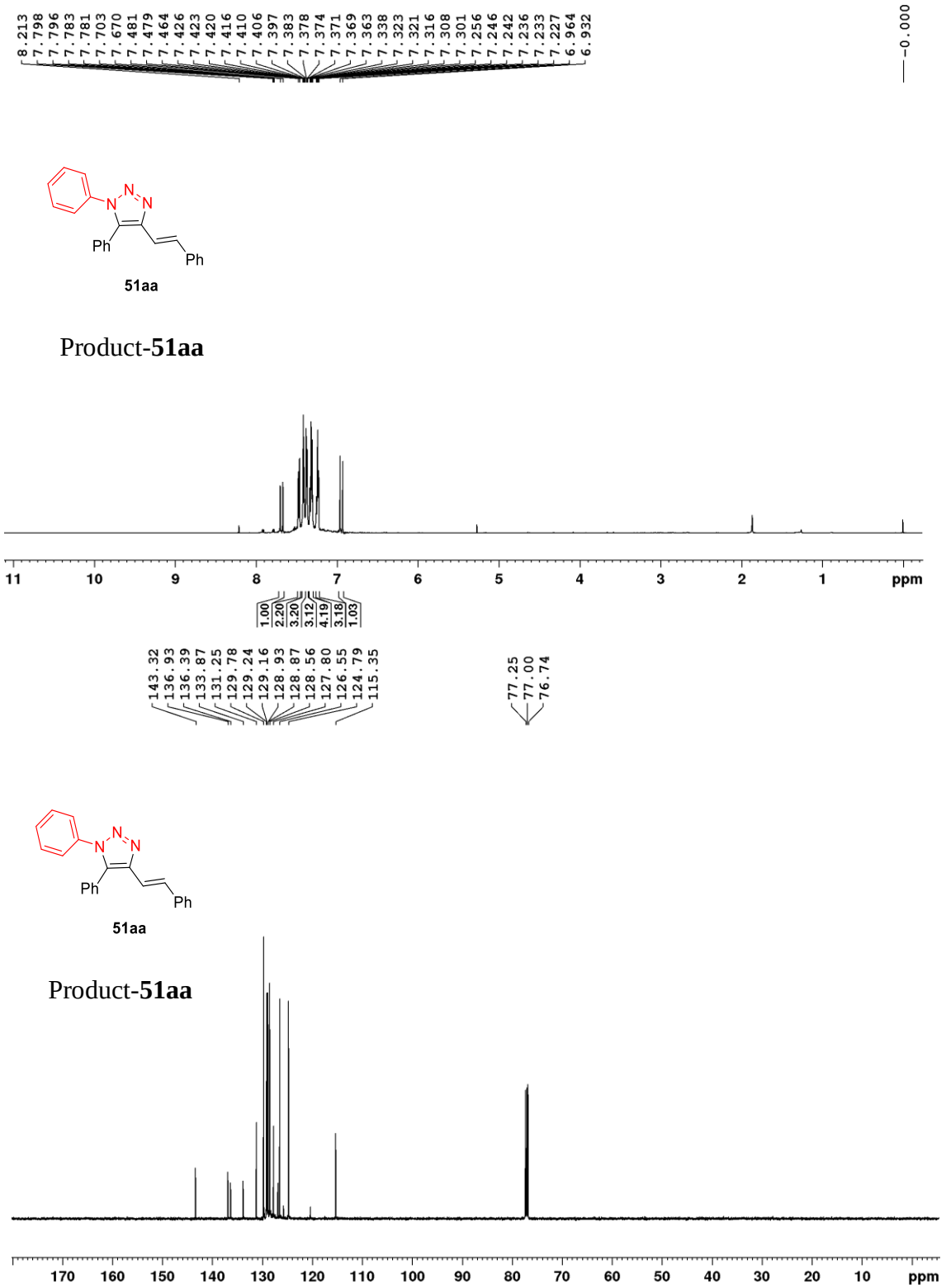


Figure 7: ^{1}H and ^{13}C spectra of the product **51aa.**

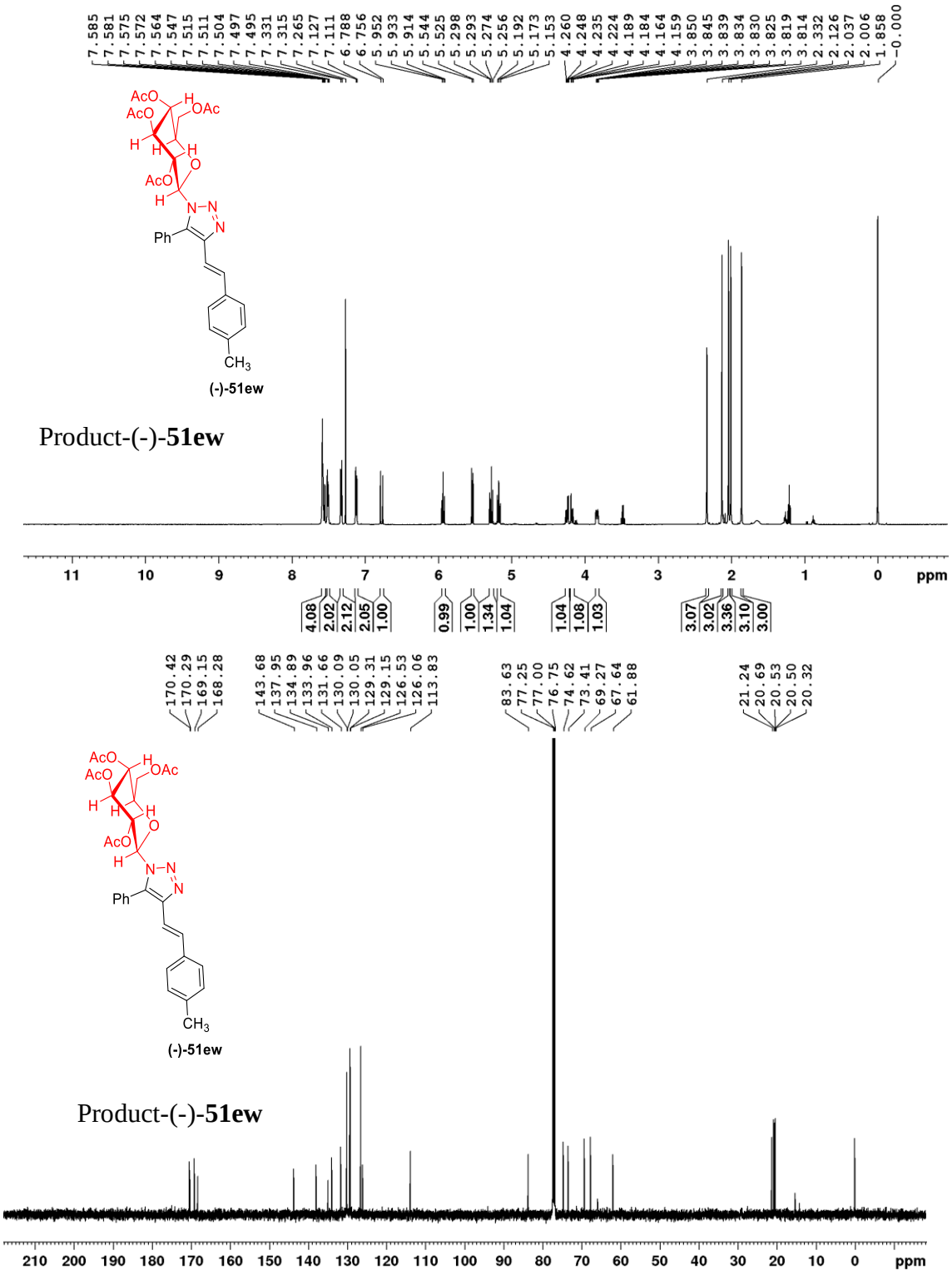


Figure 8: ^{1}H and ^{13}C spectra of the product (-)-**51ew**.

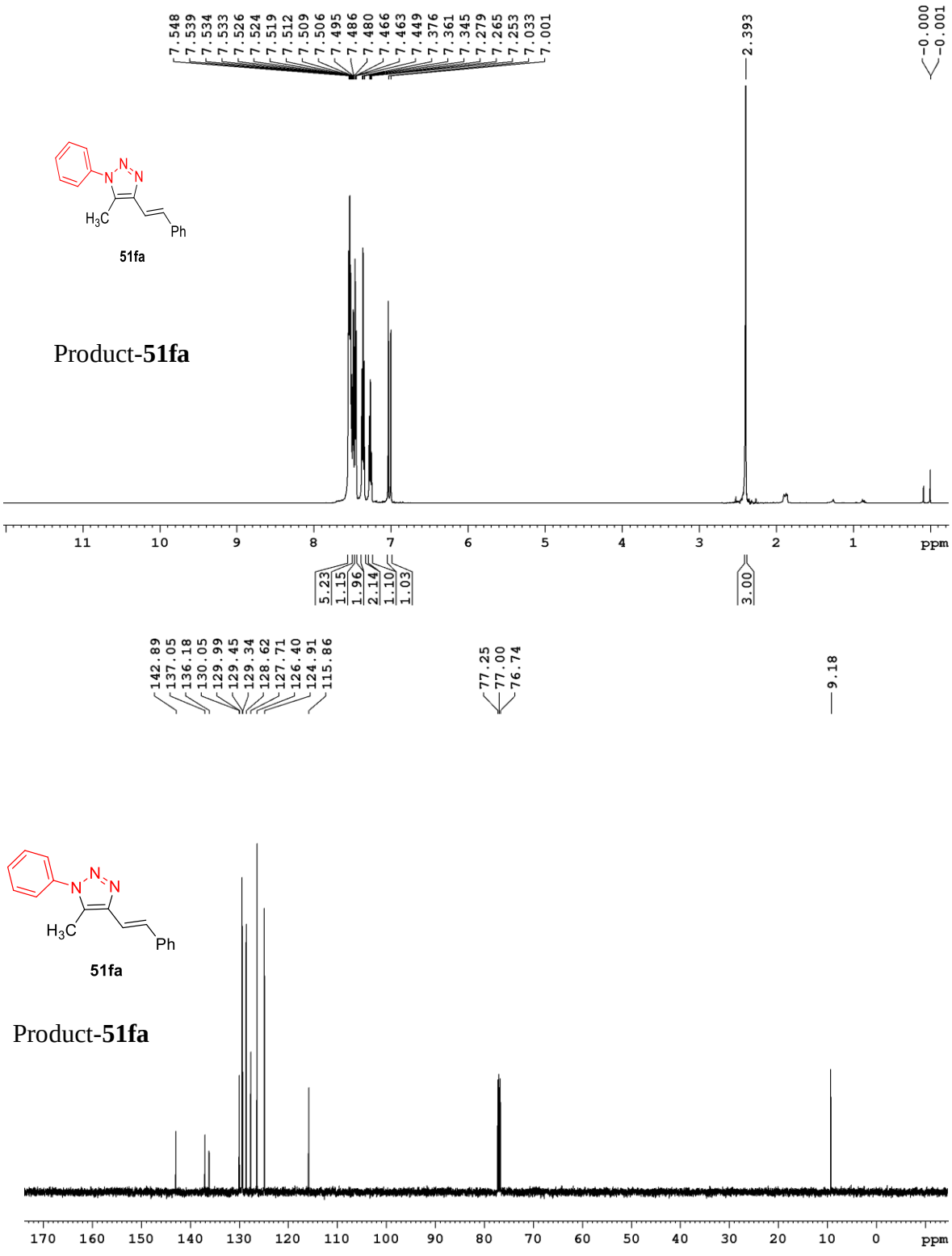
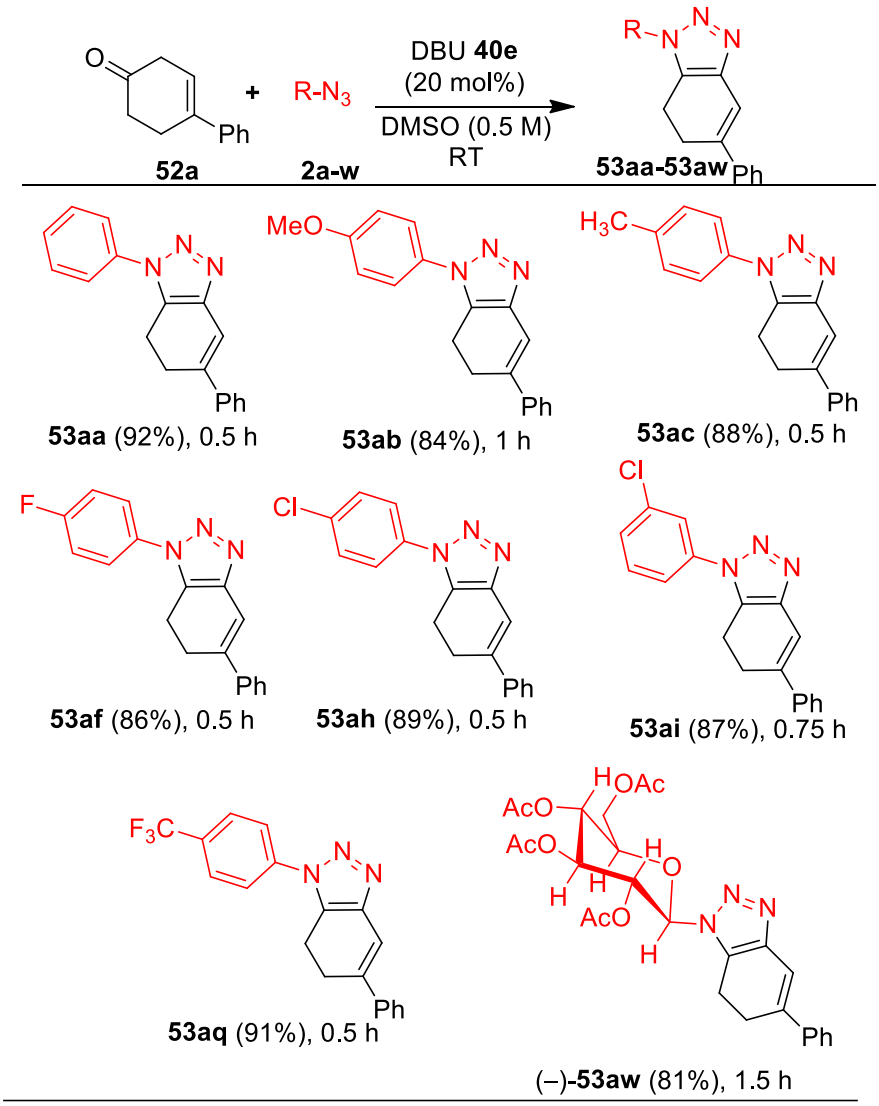


Figure 9: ^{1}H and ^{13}C spectra of the product **51fa**.

Table 5: Reaction scope of cyclic enones with azides [a]



[a] Reactions were performed in DMSO (0.5 M) with 1.5 equiv. of **2** relative to **52a** (0.5 mmol) in the presence of 20 mol% of **40e**.
[b] The yield refers to the column-purified product.

But enolate-mediated click reaction of cyclic allyl ketone **52d** with $PhCH_2N_3$ **2u** under the 20 mol% of KOtBu in DMSO at 25 ^oC for 1.0 h furnished the *C*-vinyl-1,2,3-triazole **53du** in 80% yield may be due to the matching of both the reactivities (Table 6). The structure and relative stereochemistry of the click products **49**, **51**, and **53** were established by IR, NMR, and mass analysis and also finally confirmed by correlation with the X-ray crystal structure of **49af**, **51ar**

and **53ah** (Figures 10-12).[11b] These functionally rich *C*-vinyl 1,2,3-triazoles will be highly useful intermediates for medicinal to material chemistry (see Scheme 2).

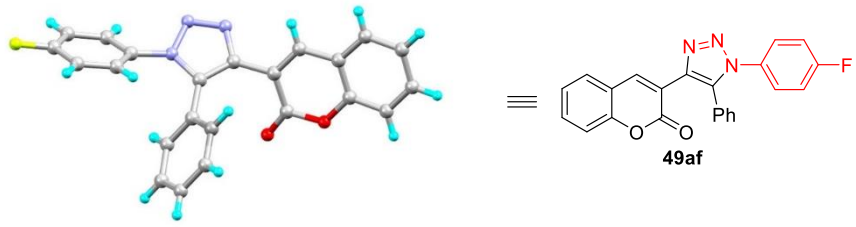


Figure 10: X-ray crystal structure of **49af**,

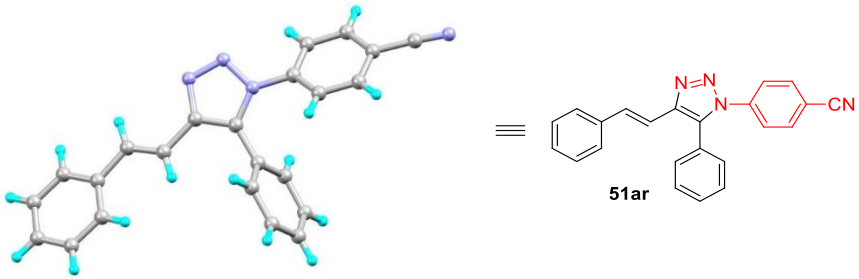


Figure 11: X-ray crystal structure of **51ar**

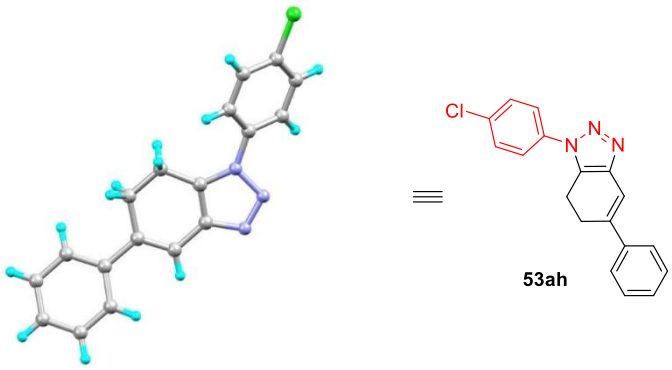
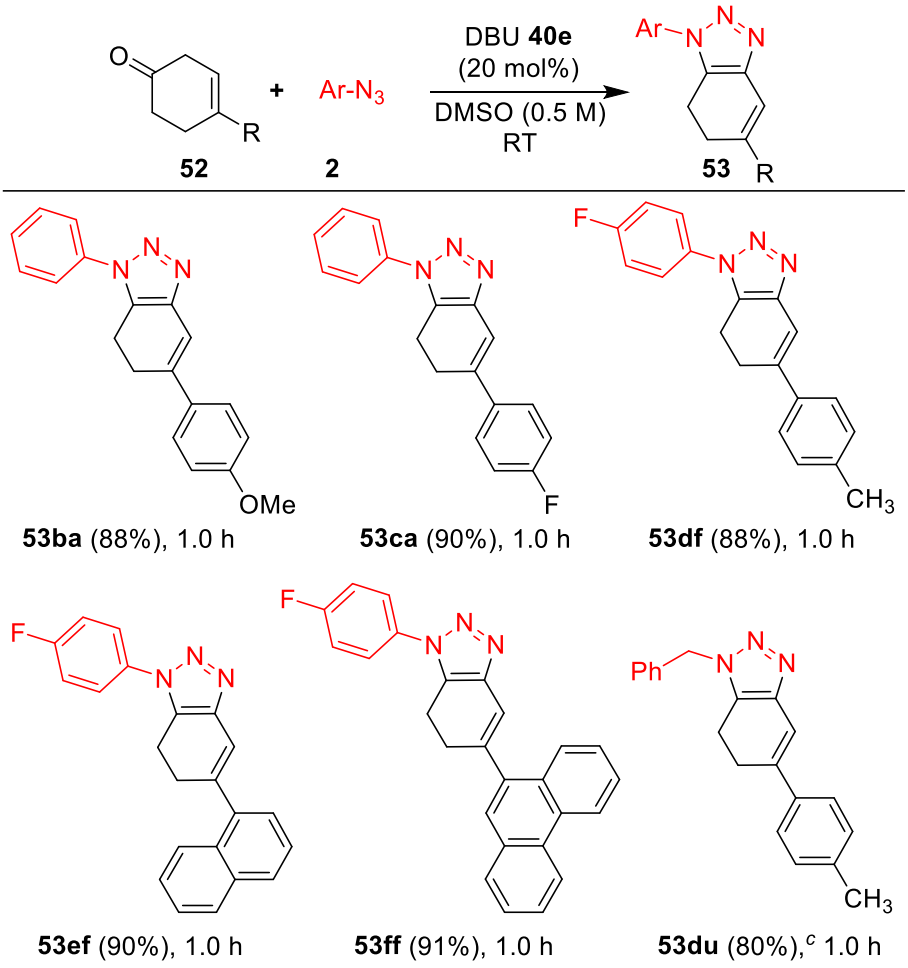


Figure 12: X-ray crystal structure of **53ah**

Table 6: Substituted cyclohex-3-en-1-one and aryl azide scope. [a, b]



[a] Reactions were performed in DMSO (0.5 M) with 1.5 equiv. of **2** relative to **52** (0.5 mmol) in the presence of 20 mol% of **40e.** [b] The yield refers to the column-purified product. [c] KO*t*Bu (20 mol%) used as catalyst at RT for 1 h.

4.4 Reaction mechanism:

A set of control experiments were carried out to prove that the enolate mechanism is prevailing in this amine-catalyzed formal [3+2]-cycloaddition reaction. The simple de-conjugated phenyl allyl ketone **54a** on treatment with 20 mol% Et_3N in the presence of phenyl azide **2a** in DMSO at 25 °C for 30 h resulted only in isomerization of the double bond to generate the corresponding enone **55a** in 57% yield, but not the 1,2,3-triazole (Scheme 3, eq. 1).

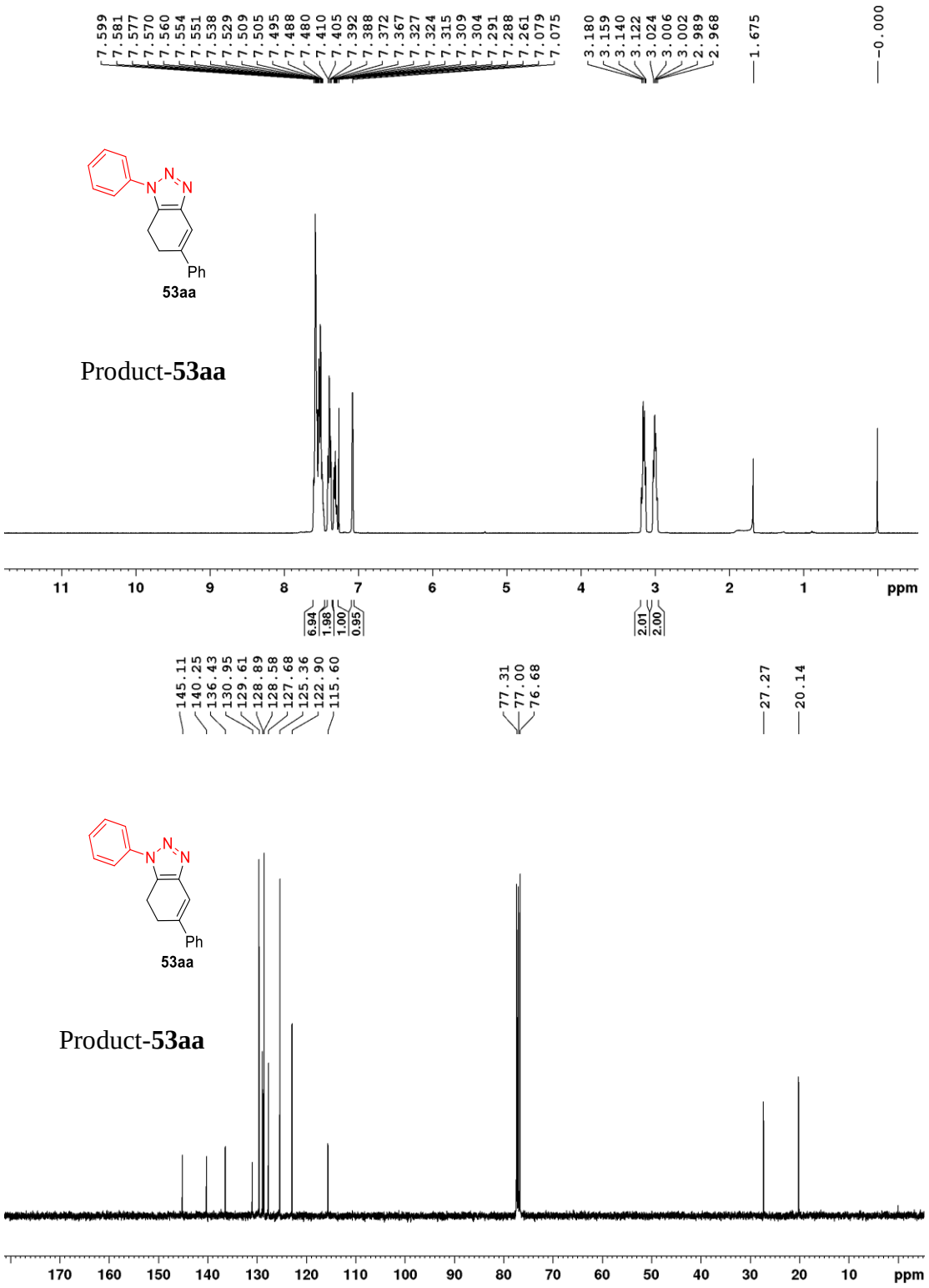


Figure 13: ^{1}H and ^{13}C spectra of the product **53aa**.

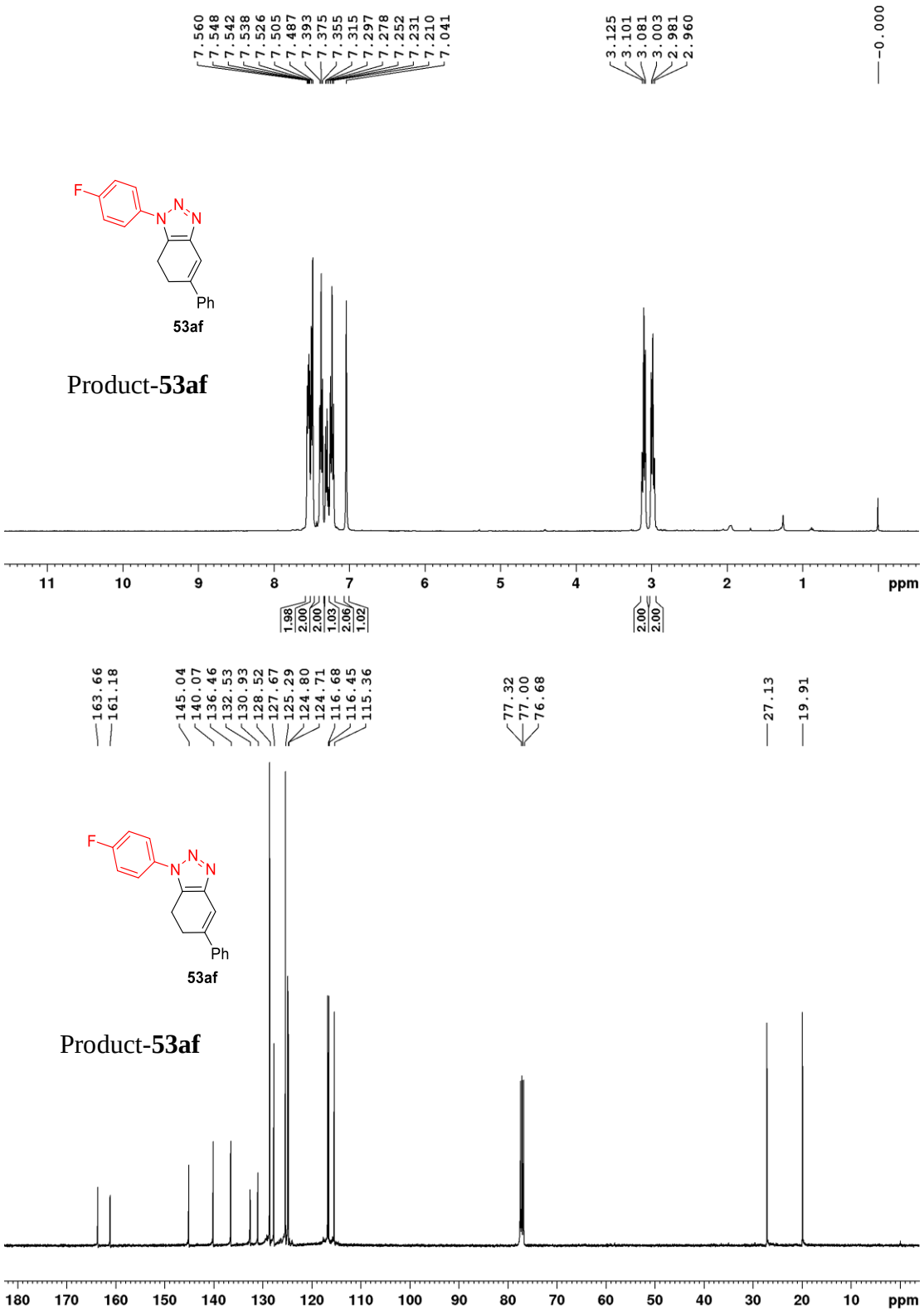


Figure 14: ^{1}H and ^{13}C spectra of the product **53af.**

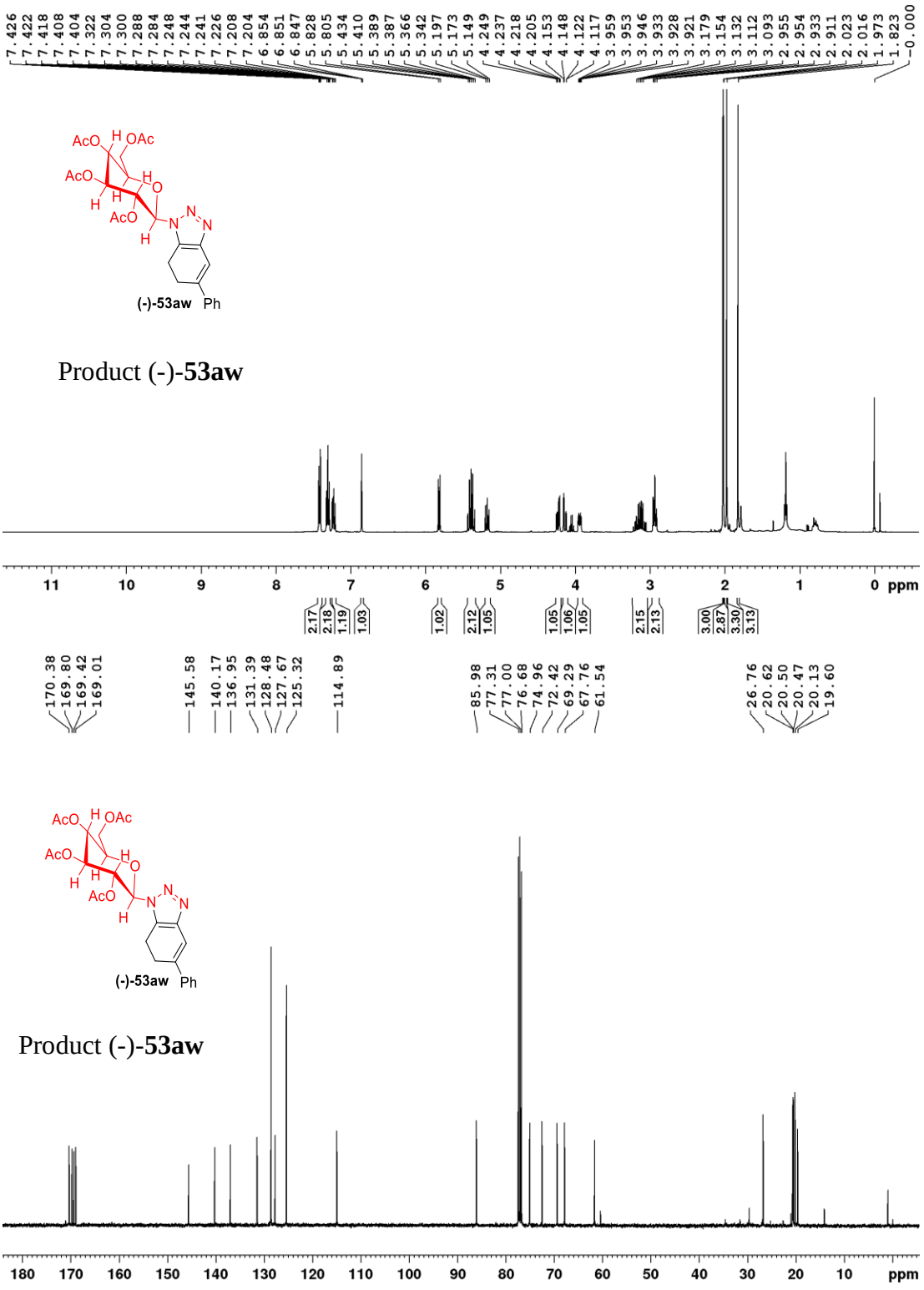


Figure 15: ^{1}H and ^{13}C spectra of the product (-)-**53aw**.

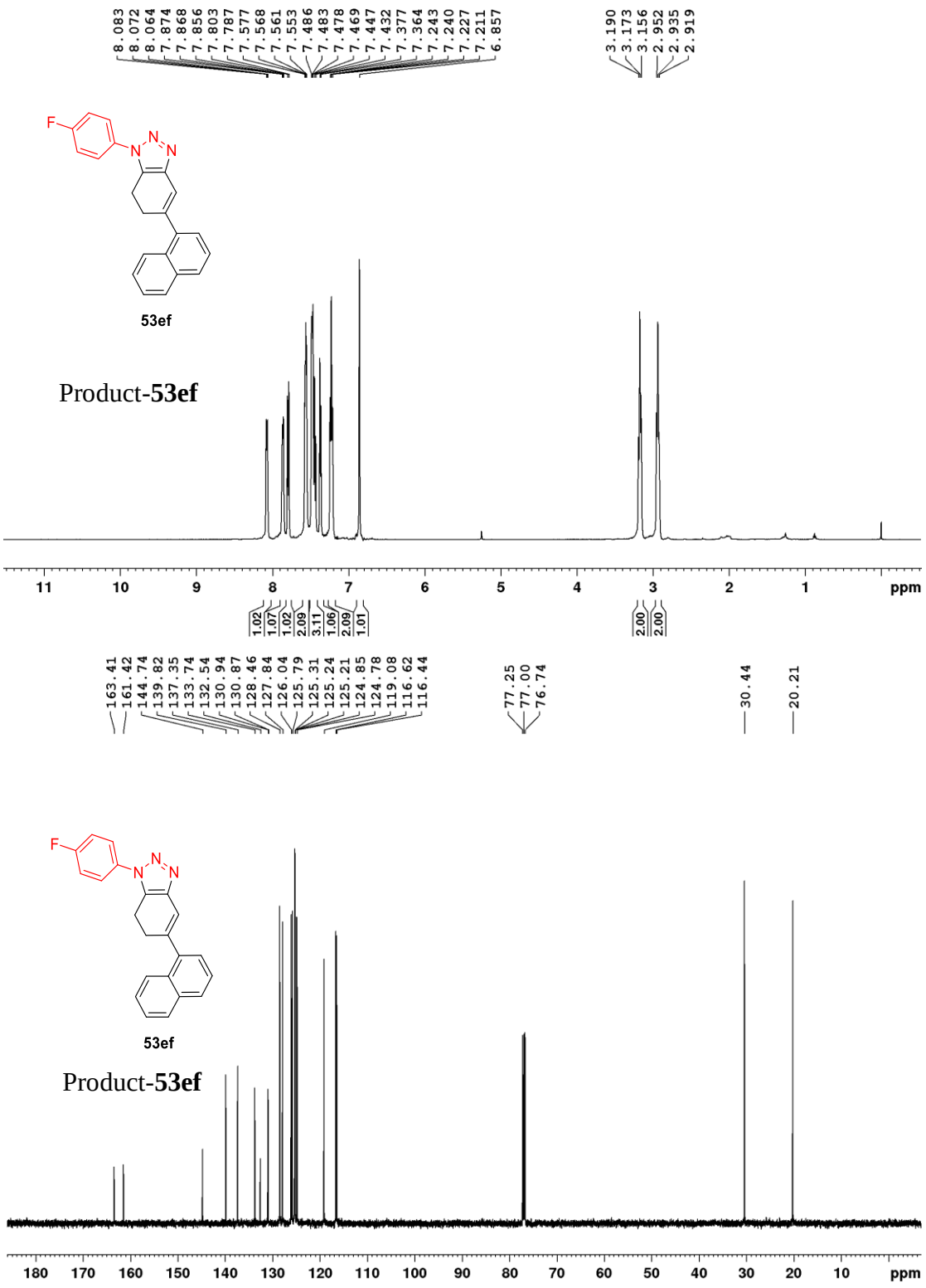
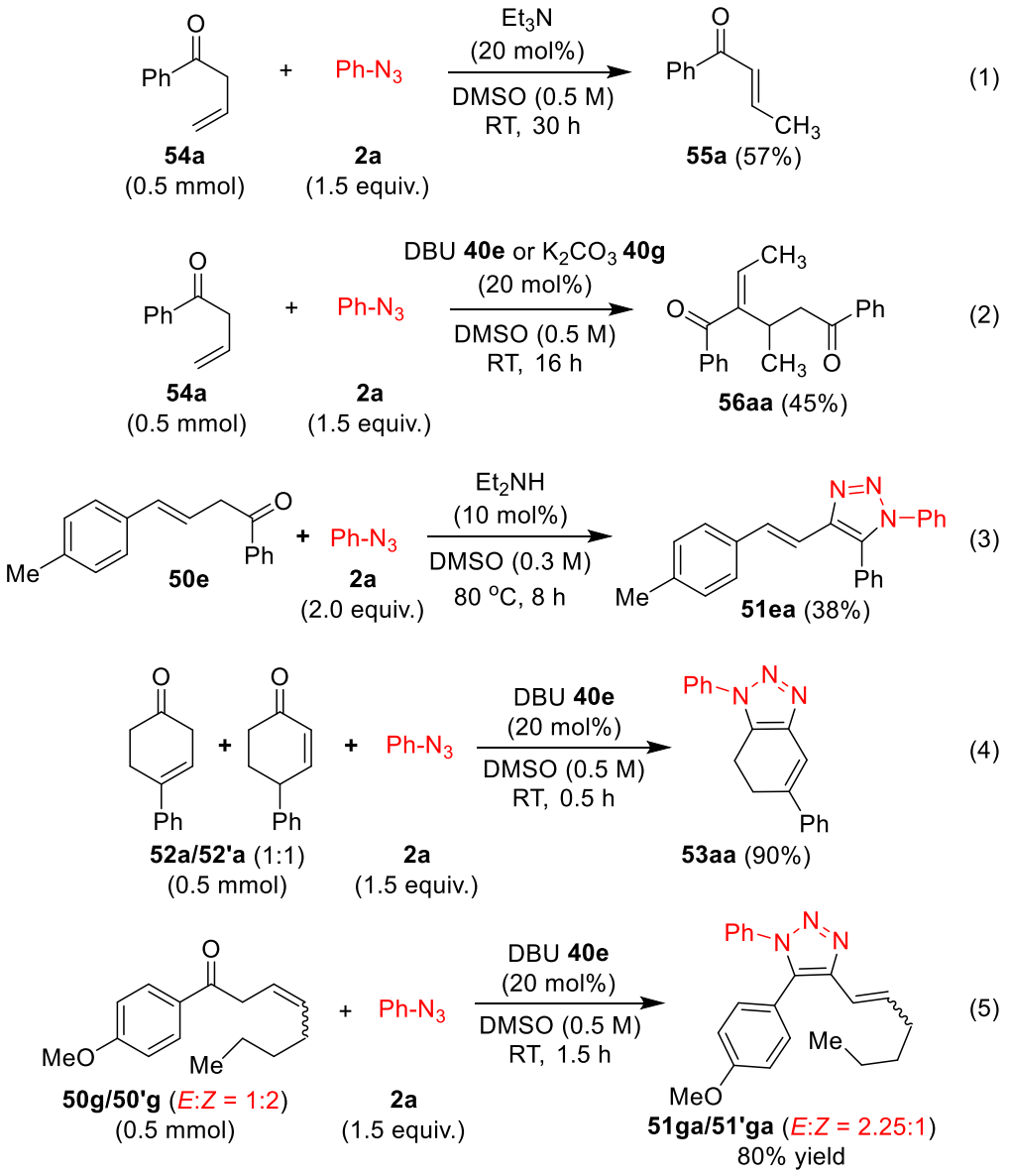


Figure 16: ^{1}H and ^{13}C spectra of the product **53ef**.

The same reaction when catalyzed with 20 mol% of DBU **40e** or K_2CO_3 **40g** underwent isomerization followed by Michael addition and further isomerization or Baylis-Hillman type reaction to give only a dimer **56aa** in 45% yield (Scheme 3, eq. 2). But the de-conjugated functionally rich phenyl allyl ketone with *p*-tolyl substituent **50e** underwent enamine-based formal [3+2]-cycloaddition with phenyl azide **2a**, catalyzed by 10 mol% Et_2NH in DMSO, at 80 °C in 8 h to furnish the respective *C*-vinyl 1,2,3-triazole **51ea** in 38% yield (Scheme 3, eq. 3), proving the fact that enamine-based reactions are slower and no Wang type isomerisation click product was observed (see Schemes 1 and 3). A 1:1 mixture of 4-pheylcyclohex-2-en-1-one **52á** and the corresponding de-conjugated isomer, 4-pheylcyclohex-3-en-1-one **52a** when subjected to reaction with phenyl azide **2a** in the presence of 20 mol% DBU **40e** in DMSO at 25 °C for 0.5 h, resulted singularly in the formation of a *C*-vinyl 1,2,3-triazole **53aa** in 90% yield (Scheme 3, eq. 4). This substantiates the fact that both the substrates **52a/52á** in the mixture transform into the same intermediate enolate, which was formed from delocalization of the double bond present.
In the next example, when a mixture of *E* and *Z* isomers of substituted aliphatic allyl ketone **50g/50'g** (*E*/*Z* = 1:2) was subjected to the click reaction with **2a** under the **40e**-catalysis in DMSO at 25 °C for 1.5 h, it resulted in a mixture of the *C*-vinyl 1,2,3-triazoles **51ga/51'ga** (*E*/*Z* = 2.25:1), but with a change in the ratio of the *E* and *Z* isomers (Scheme 3, eq. 5). The α-enolate **A** initially formed as mesomeric structure, delocalizing to the gamma carbon through two more mesomeric structures **B** and **C** is evident from the change in the ratio of the *E*/*Z* isomers (see Schemes 3 and 4).

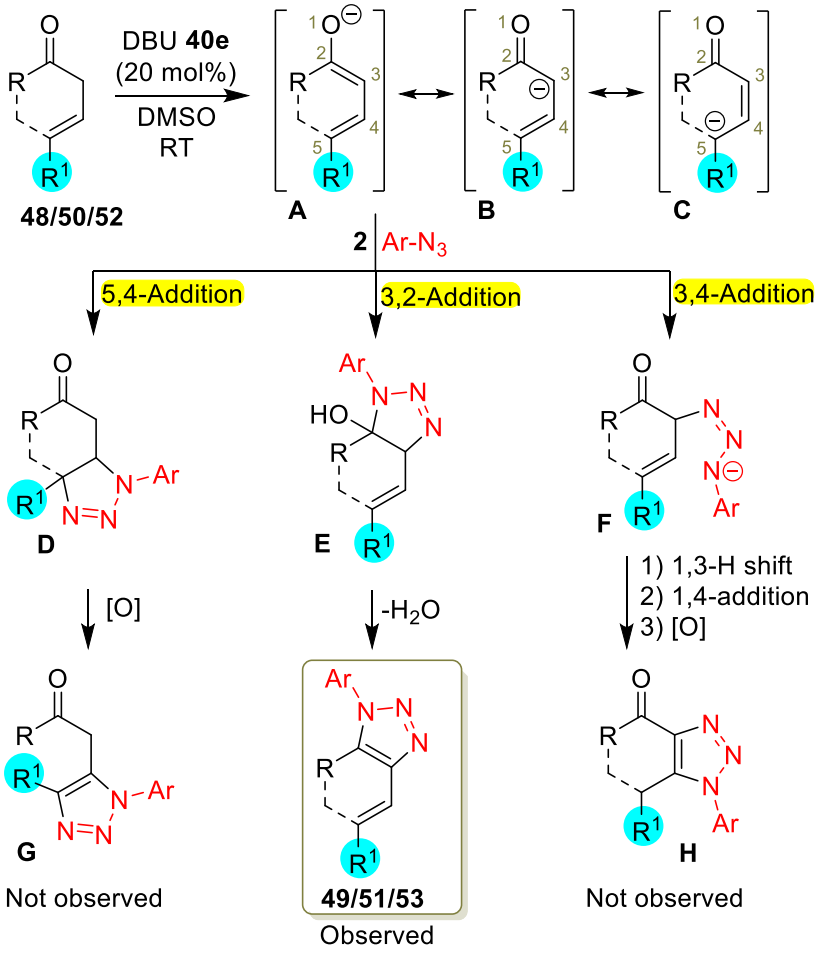
These control experiments collectively assisted in comprehending the mechanism of the [3+2]-cycloaddition reaction profoundly as shown in Scheme 4. Reaction of substituted acyclic and cyclic allyl ketones **48/50/52** with catalytic amount of DBU **40e** generates enolate, which on mesomerism or resonance and can be denoted as **A**, or **B** or **C** as shown in Scheme 4. The *in situ* generated mesomeric enolates **A/B/C** can partake in the formal [3+2]-cycloaddition with aryl azides **2** in three different ways, either through C3-C2 or C5-C4 or C3-C4 bond. Enchantingly, the *C*-vinyl 1,2,3-triazole **49/51/53** was formed as a sole product from the reaction between **48/50/52** and **2** under the **40e**-catalysis, even though theoretically there was opportunity for formation of two other products **G** and **H** from **D** and **F**, respectively as depicted in Scheme 4.



Sheme 3: Control experiments to prove enamine- vs. enolate-mediated organocatalytic formal [3+2]-cycloaddition.

From the generated products **49/51/53**, it is apparent that the probably major contributing mesomeric enolate **B** exclusively reacted at the C3-C2 bond with the aryl azides **2** to generate an intermediate **E** rapidly, which on elimination of water furnished the *C*-vinyl 1,2,3-triazoles **49/51/53**. This enolate-mediated reaction pathway is completely different with respect to rate and

product selectivity compared to enamine-mediated reactions of functionally rich allyl ketones **48/50/52** with aryl azides **2**.

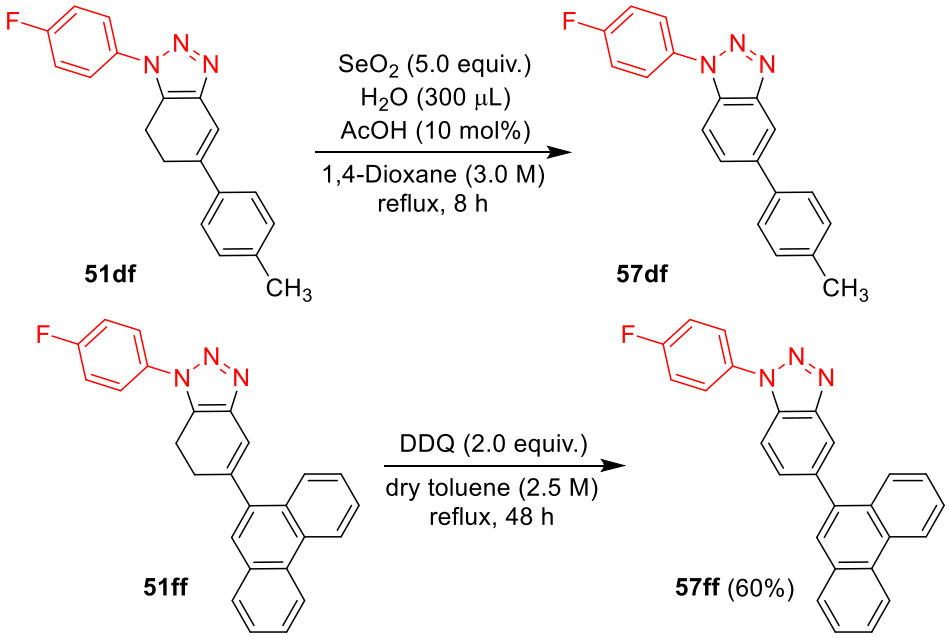


Scheme 4: Reaction mechanism

4.5 Synthetic Applications:

From the point of view of synthetic applications, two of the *C*-vinyl 1,2,3-triazoles **51df** and **51ff** were subjected to allylic oxidation and aromatization by using SeO_2 and DDQ respectively to furnish the corresponding hydroxylated and aromatized products (Scheme 5). But in the first case we observed only aromatized product **57df** in 70% yield instead of hydroxylated-*C*-vinyl 1,2,3-triazole may be due to the quick dehydration and in the second case we got the expected product

57ff in 60% yield (Scheme 5). This protocol will be highly useful for the high yielding synthesis of medicinally important functionally rich benzotriazoles.[6e, 12a.]



Scheme 5: Synthetic applications

4.6 Photophysical studies and applications of *C*-vinyl 1,2,3-triazoles:

Recently simple *N*-vinyl containing coumarin-triazoles are emerging as chromophores to utilize in photophysical and medicinal studies due to their flurogenic activity.[13a-c] Inspired by this work, herein we focused to investigate the photophysical properties of newly synthesized highly functionalized *C*-vinyl containing coumarin-triazoles **49aa-49ea** as chromophores in the dichloromethane (DCM) at 25 °C in 10^{-5} M concentration. The optical properties were tuned by **49aa-49ea** as chromophores in the dichloromethane (DCM) at 25 °C in 10^{-5} M concentration. The optical properties were tuned by substituting different functional groups such as OCH_3, NEt_2, CN, F and Cl on three different parts of functionalized coumarin- triazoles such as coumarin, and two aryl groups of 1,2,3-triazole. All the chromophores **49aa-49ea** exhibited the absorption spectrum in the range of 323-401 nm as shown in the Scheme 6, and the lowest energy band in the absorption spectra is due to an intramolecular π–π* excitations of the coumarin-triazoles.

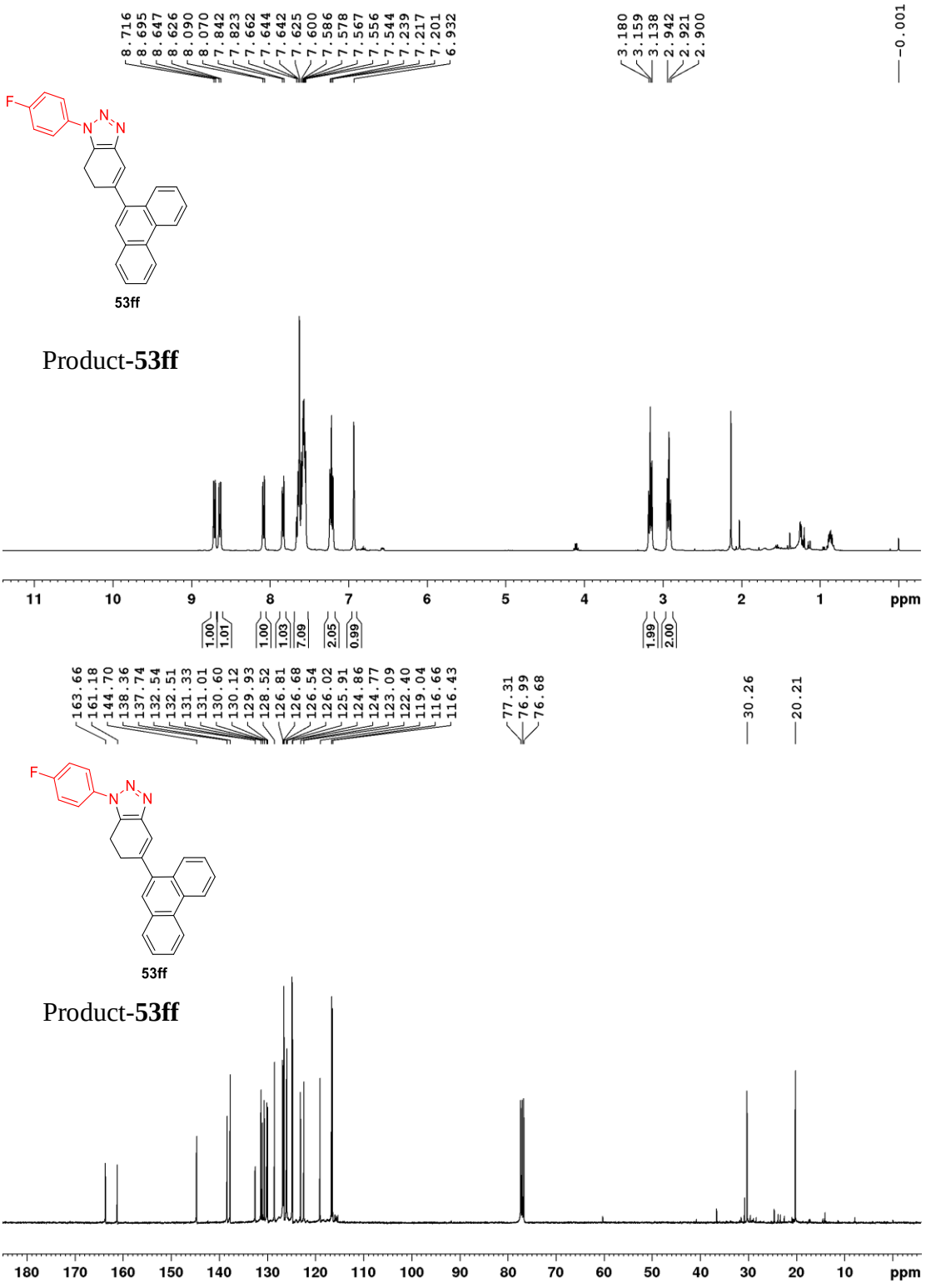
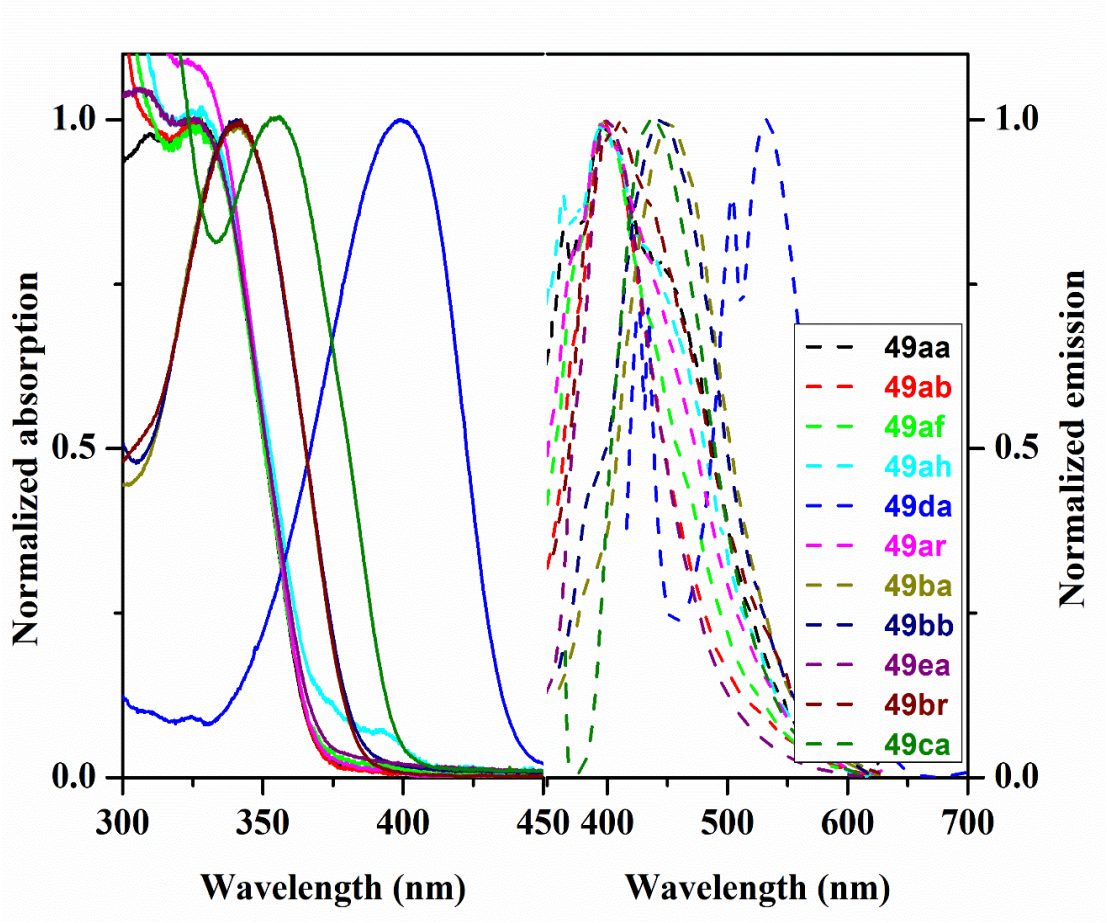


Figure 17: ^{1}H and ^{13}C spectra of the product **53ff**.



Scheme 6: Normalized UV/Vis Absorption (solid lines, *c*(**49**) = 10^{-5} M in CH_2Cl_2) and emission (dashed lines, *c*(**49**) = 10^{-5} M in CH_2Cl_2) profiles for newly synthesized 1,2,3-triazole-chromenones **49aa-49ea**. *T* = 298 K.

The photophysical properties of functionally rich *C*-vinyl coumarin-triazoles **49aa-ea** are summarized in Table 7. At the same concentration (10^{-5} M) the chromophore **49da** exhibits the high intense band and red shifted (401 nm) in absorption, compared to the other compounds **49**. It may be due to the conjugation of electron rich NEt_2 group present on the coumarin ring in the chromophore **49da,** which is giving the red shift absorption compared to OCH_3 group. The molar extinction coefficients were in the range of 9000 to 38000 $Lmol^{-1}cm^{-1}$ as show in Table 7. Upon excitation at the lowest energy absorption maxima, the coumarin-triazoles chromophores exhibit bright violet and blue emission except chromophore **49da**, with large stokes shift from the corresponding absorption maxima. The effect of OCH_3, and NEt_2 donors was found to be rather

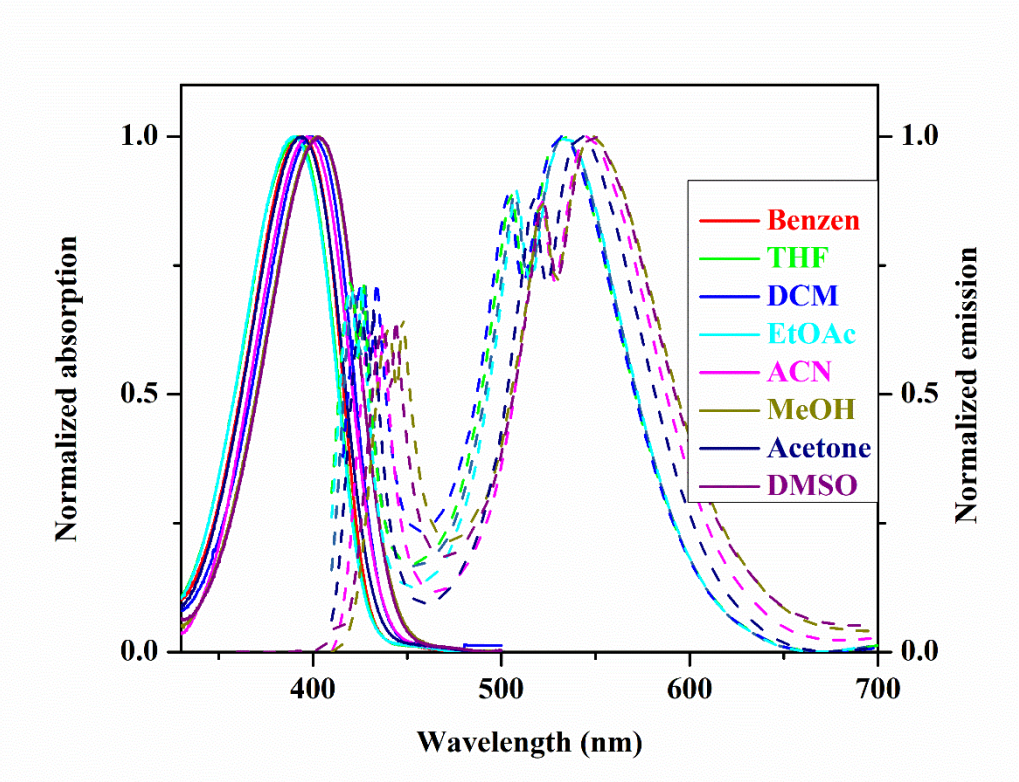
intense on the fluorescence behaviour of the relevant coumarin-triazoles chromophores. The NEt_2 donor possessing chromophore **49da** exhibits the green emission, whose maxima was at 533 nm. The impact of solvent polarity on the photoluminescence property of the current chromophores **49aa-49ea** was found to be noticeable as compared to the absorption spectra. To study the solvent effect on the chromophores, we have carried out the solvatochromic effect assets in different organic solvents based on the polarity.

Table 7: UV/Vis Absorption and emission data for newly synthesized 1,2,3-triazole-chromenones **49aa-49ea.**

Compound	λ_{abs} (nm)	λ_{em} (nm)	ε ($M^{-1}cm^{-1}$)	$\Delta\bar{\nu}$ (cm^{-1})
49aa	326	397	14000	5486
49ab	323	399	22000	5897
49ar	330	396	10000	5050
49af	324	397	14000	5675
49ah	323	395	15000	5643
49da	401	533	38000	6175
49ba	341	454	23000	7299
49bb	340	446	26000	6990
49br	340	410	17000	5021
49ca	356	439	11000	5310
49ea	331	400	19000	5211

[a] Recorded in CH_2Cl_2, $c(49) = 10^{-5}$ M at T = 298 K. [b] ε were measured in DCM solution; Stokes shift $\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_{em}$.

As shown in Scheme 7, by varying the polarity of solvent from low to high it doesn't exhibit a regular tend in the case of THF and ethyl acetate. Based on these preliminary results, *C*-vinyl 1,4,5-trisubstituted coumarin-triazole **49da** has red shift (533 nm) in photoluminescence compared to their corresponding *N*-vinyl 1,4-disubstituted coumarin-triazoles; and these compounds will have promising applications in many branches of chemistry and life sciences.



Scheme 7: Normalized UV/Vis Absorption (solid lines, *c*(**49da**) = 10^{-5} M) and emission (dashed lines, *c*(**49da**) = 10^{-5} M) profiles for 1,2,3-triazole-chromenone **49da** in different solvents. *T* = 298 K

4.7 Conclusion:

In summary, we have developed a general green process for the high-yielding synthesis of functionally rich *C*-vinyl 1,2,3-triazoles through an enolate-mediated organocatalytic formal [3+2]-cycloaddition between cyclic/acyclic allyl ketones and aryl azides. In this manuscript, we have shown the high-yielding synthesis of *C*-vinyl 1,4,5-trisubstituted coumarin-triazoles as privileged building blocks for photophysical studies and one of the coumarin-triazole **49da** has shown excellent fluorescent property (λem = 533 nm). Many of the *C*-vinyl 1,2,3-triazoles have been shown to be useful intermediates in the synthesis of pharmaceuticals and also directly applicable in material chemistry.

5.0 Organocatalytic Enolate-Mediated Enone-Azide [3+2]-Cycloaddition: High yielding Synthesis of Functionally Rich *C/N*-Double Vinyl 1,2,3-Triazoles

5.1 Abstract:

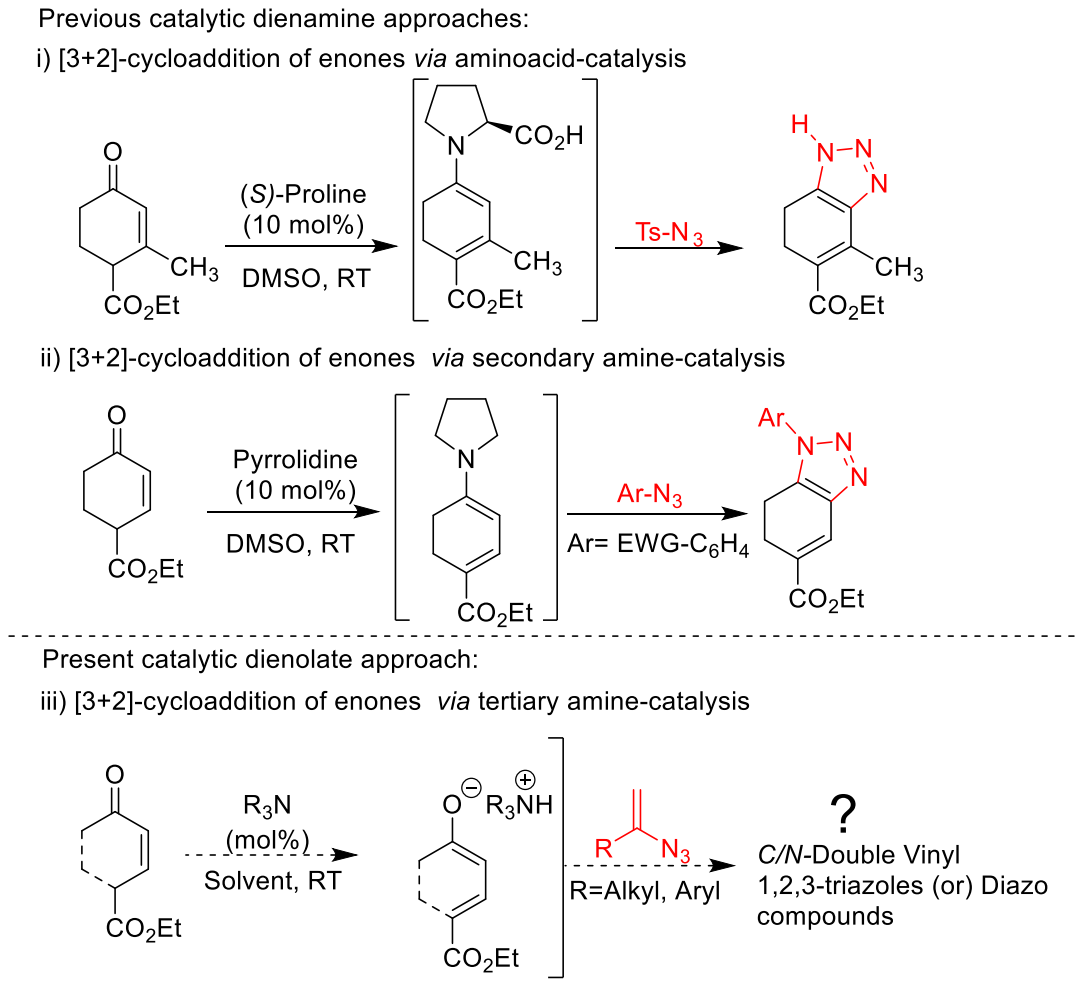
we demonstrated the metal-free regioselective synthesis of highly functionalized *C/N*-double vinyl 1,2,3-triazoles, *N*-aryl bicyclic 1,2,3-triazoles by treating highly functionalized unmodified cyclic and acyclic enones with vinyl and aryl azides through [3+2]-cycloaddition based on push-pull dienolates. The one-pot reaction resulted in good yields with high selectivity using DBU as the catalyst. Herein, we explore the utility of highly functionalized *C/N*-double vinyl-1,2,3-triazoles as starting materials for the synthesis of medicinally important *N*-vinyl-benzotriazoles through mild oxidative aromatization.

5.1 Introduction:

Small molecules are creating wonders in medicinal to material chemistry. Among those 1,2,3-triazole is one of the distinctive nucleuses. Since last few decades, 1,2,3-triazole synthesis has garnered special emphasis in various scientific fields (medicinal, material, agrochemical, and bioorganic) due to their elegant structural features along with interdisciplinary applications.[10a-o] Recent biological studies have revealed the bio-similarity of 1,2,3-triazole with amide linkage and their inertness towards enzymatic degradation, which made them as "amideisosteres".[1a-d] In that context, vinyl 1,2,3-triazoles are mimicked as traditional monomers, in the view of aromaticity, hydrogen bonding ability and functionality and further established as the "privileged monomers" in polymer synthesis.[1e] Analogously, triazole-curcuminoids in which a triazole nucleus is attached with doubly vinyl skeleton, were successfully tested for the curcumin bio-activities, especially to inhibit NF-kB without showing cytotoxicity.[1f]

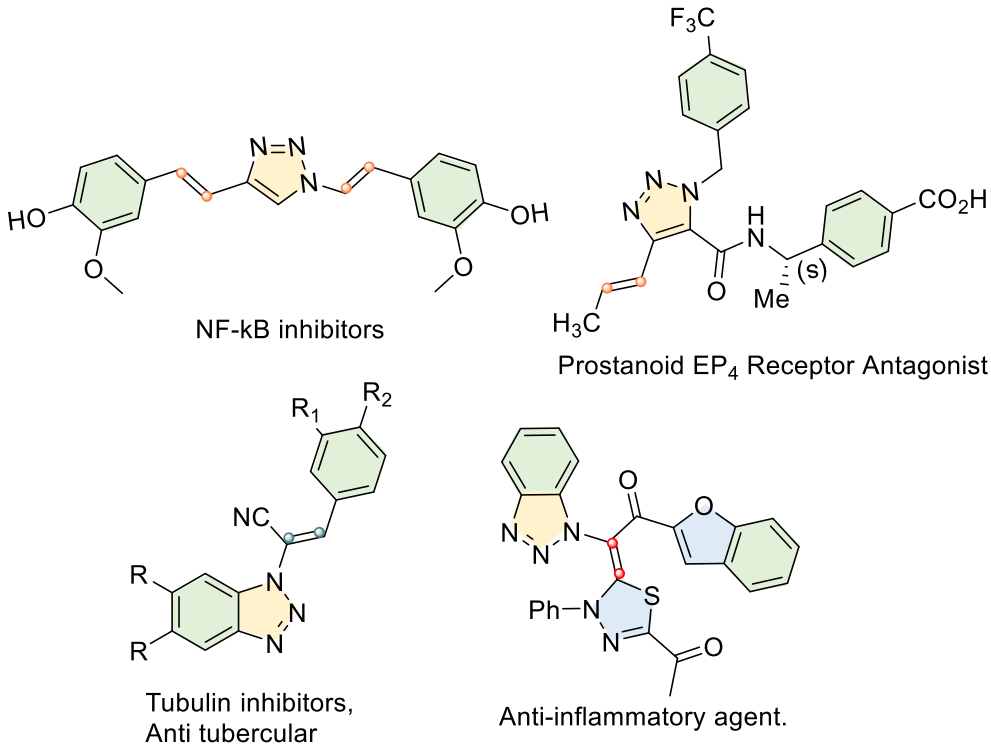
These factors prompted us to develop an efficient and simple protocol for the synthesis of *C/N*-double vinyl triazoles in eco-friendly and atom economic manner.

Sharpless-Meldal's splended work on 1,2,3-triazoles synthesis through Cu-mediated azide-alkyne [3+2]- cycloaddition[5] has been transmuted into a greener mode through an oraganocatalytic enamine- or enolate- mediated azide-carbonyl [3+2]-cycloaddition, which now flourishes as Ramachary-Bressy-Wang's [3+2]-cycloaddition.[6] As the active practitioners of organocatalysis, we have been developing efficient protocols through enamine or enolate mediated 1,2,3-triazole synthesis, considering the carbonyls as the equivalent of alkyne synthons.[7]



Scheme 1: Design for the organocatalytic synthesis of fully decorated *C/N* -double vinyl 1,2,3-triazoles.

Our recent studies have disclosed that tertiary amine catalysis is showing complete supremacy over primary or secondary amine catalysis in terms of reaction rate and outcome of 1,2,3-triazole library.[7] From 2008 to 2013, we demonstrated dienamine mediated [3+2]-cycloadditions of cyclic enones with activated azides under secondary amine catalysis. While, these strategies were highly facile with activated tosyl azides and with electron deficient aryl azides to generate *NH*- and *N*-aryl-1,2,3- triazoles, they were very sluggish with neutral and electron rich aryl azides.[6a, 6e] Later, we were emerged successful to apply enolate mediated [3+2]-cycloaddition on various unactivated/activated carbonyls with different azides under tertiary amine catalysis to achieve functionally rich 1,2,3-triazoles.[7]



Scheme 2: Applications of *C/N*-Double Vinyl, *C*-Vinyl and *N*-vinyl-1,2,3-triazoles in medicinal chemistry.

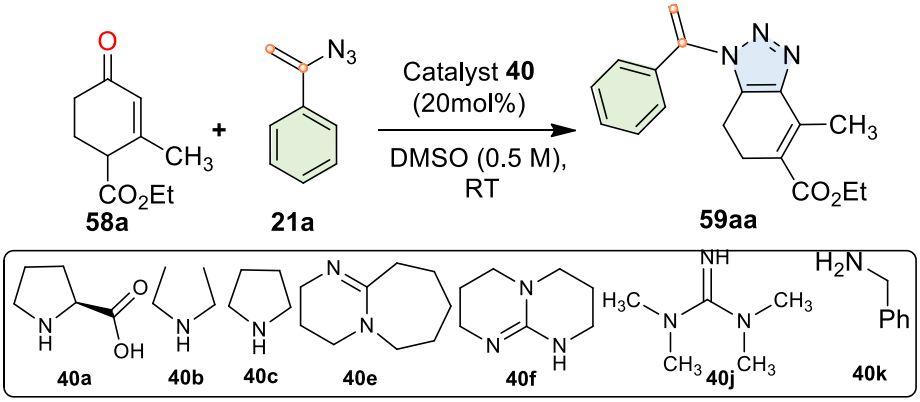
Herein, we were interested to investigate the reactivity of *in situ* generated push-pull dienolates with vinyl azides and other less reactive azides towards 1,2,3-triazole formation under tertiary amine catalysis. Interestingly, we found that *C*-vinyl 1,2,3-triazoles act as α-glycosidase inhibitors,

anti-microbial agents, anti-mycobacterium tuberculosis and prostanoid EP_4 receptor antagonist.[3, 4] In addition, *N*-vinyl benzotriazoles acts as tubulin inhibitors, anti-tubercular, anti-microbial and anti-inflammatory agents.[12] Finally, the interminable need of vinyl triazoles for drug development with improved activity and materials with enhanced features directed us to design new protocol for *C/N*-double vinyl 1,2,3-triazoles.

5.3 Results and Discussion:

With enthusiastic goal and previous experience, we switched our optimization studies step by step from primary amine catalysis to tertiary amine catalysis. We chose cyclic enone **58a** and 1.5 equiv. of α-azido styrene **21a** as the model substrates, 20 mol% of catalyst loading and DMSO as the solvent to optimize the reaction condition. We carried out initial studies with the primary amine, benzyl amine **40k** as catalyst, surprisingly we did not find triazole formation up to 24 h at 25 °C (Table 1, entry 1). Then, we moved to secondary amine and examined the catalysts, (*S)*-proline **40a**, diethylamine **40b** and pyrrolidine **40c**. Surprisingly, these experiments delivered no triazole formation even after 24 h at 25 °C (Tale 1, entries 2, 3 and 4). After these disappointing results, affixing hope on tertiary amine catalysis, we continued our investigation. We were pleased to find the formation of *C/N*-double vinyl 1,2,3-triazole **59aa** in 90% yield in presence of 20 mol% of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) **40e** within half an hour at 25 °C (Tale 1, entry 5). When we tested other tertiary amines like TBD **40f** and TMG **40j,** slightly reduced yields were obtained (Table 1 entries 6 and 7). To probe the catalyst loading on outcome of triazole formation, when we reduced the loading of catalyst from 20 mol% to 10 mol% of DBU **40e**, TBD **40f** and TMG **40j,** the corresponding experiments ended up with reduced yields (78%, 72% and 74% respectively) within half an hour at 25 °C (Table 1 entries 8-10). Further, the effect of the solvent medium was investigated considering DBU (20 mol %) as optimized catalyst. There is no triazole formation in solvents like $CHCl_3$, and CH_3CN even at longer reaction times and at higher temperatures (Table 1, entry 11-12). In DMF, the reaction was delivered the *C/N*- double vinyl 1,2,3-trazole **59aa** in 60% yield after long reaction time (6.0 h) at 25 °C (Table 1, entry13). Finally, we selected the reaction condition in entry 5 of Table 1 as the optimized condition for further studies.

Table 1: **Reaction optimization for Org-VACC** [a]



Entry	Catalyst	[mol%]	Solvent	t [h]	Yield[b] [%]
1[c]	**40k**	20	DMSO	24	-
2[c]	**40a**	20	DMSO	24	-
3[c]	**40b**	20	DMSO	24	-
4	**40c**	20	DMSO	24	-
5	**40e**	20	DMSO	0.5	90
6	**40f**	20	DMSO	0.6	80
7	**40j**	20	DMSO	0.6	87
8	**40e**	10	DMSO	0.5	78
9	**40f**	10	DMSO	0.5	72
10	**40j**	10	DMSO	0.5	74
11[c]	**40e**	20	$CHCl_3$	12	-
12[c]	**40e**	20	CH_3CN	12	-
13	**40e**	20	DMF	12	60

a] Reactions were performed in solvent (0.5 M) with 1.5 equivalents of **21a** relative to **58a** (0.5 mmol) in the presence of mol % of catalyst **40.** [b] Yield refers to the yield of the column-purified product. [c] Ketone**58a** and azide **21a** were not consumed totally.

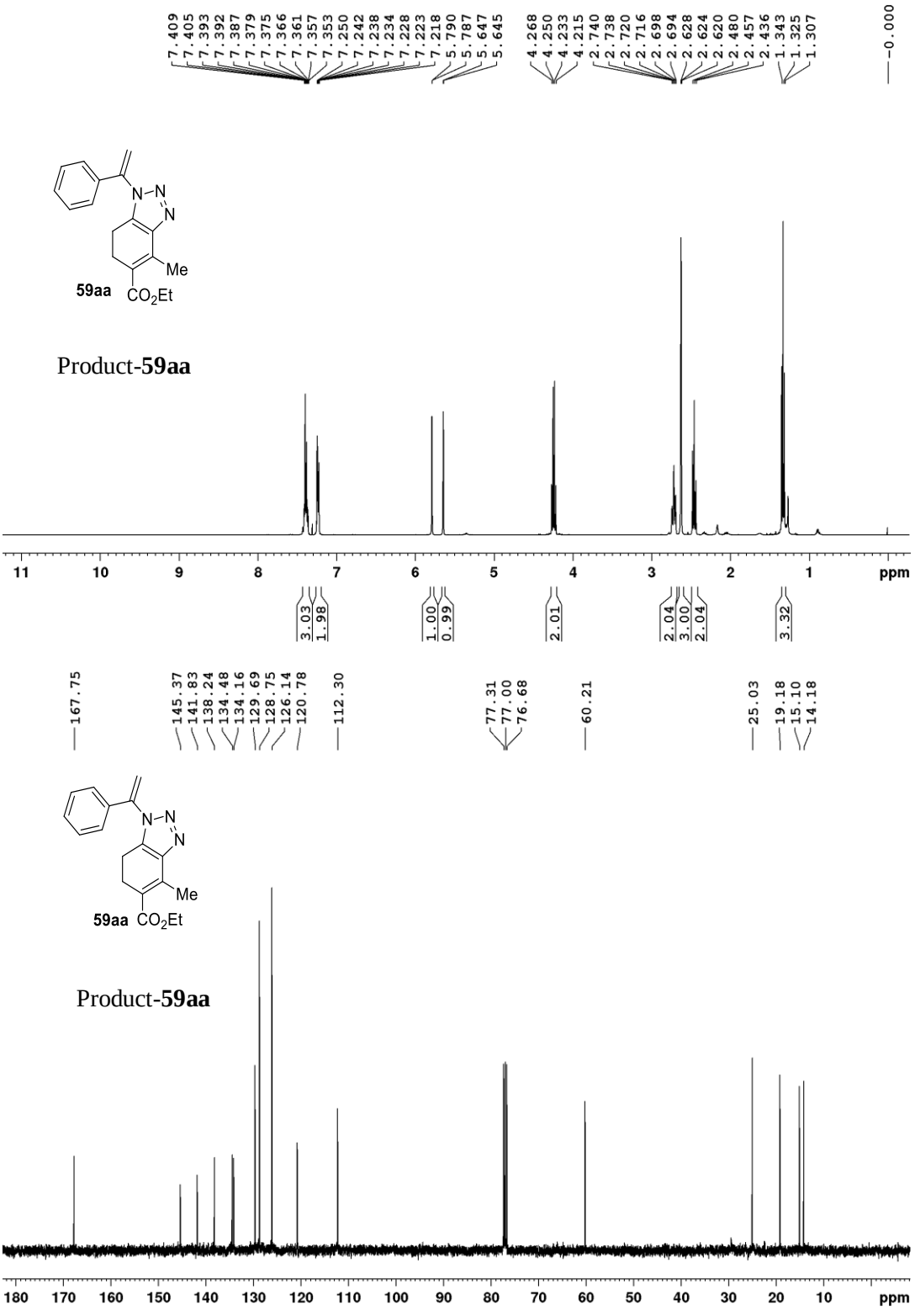
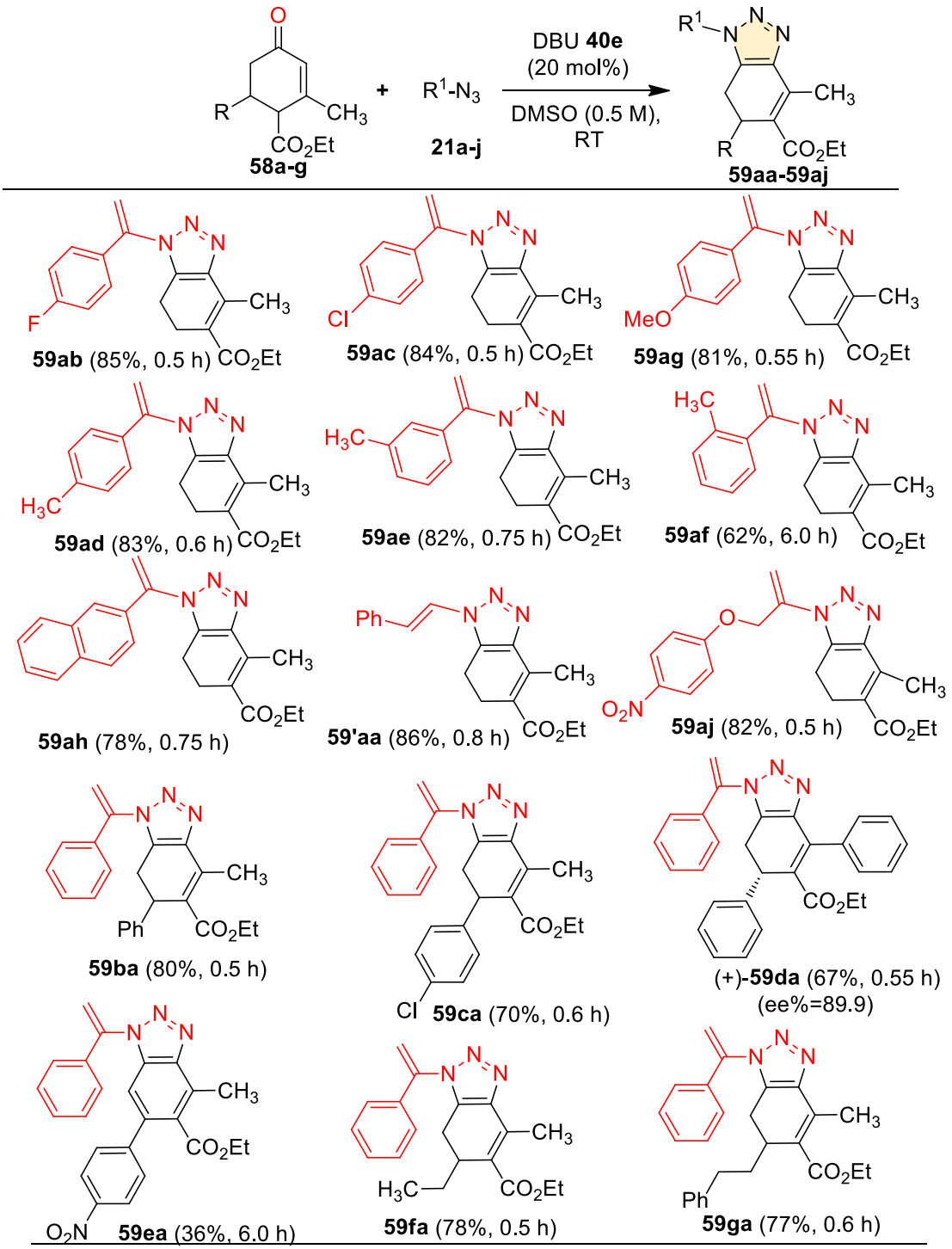


Figure 1: ^{1}H and ^{13}C spectra of the product **59aa**.

With optimization conditions in hand, we moved to investigate the scope and generality of DBU-promoted OrgACC reaction. A variety of substituted vinyl azides **21a-j** reacted with different types of cyclic enones **58a-g** catalysed by 20 mol% of DBU **40e** at 25 °C in DMSO solvent within 0.5-6.0 h (Table 2). Initially, the reactivity of various vinyl azides with cyclic enone **58a** was examined. The vinyl azides **21b**, **21c** and **21g** having substituents F, Cl and OMe on *para*-position of phenyl ring could deliver *C/N*-double vinyl 1,2,3-triazoles **59ab, 59ac** and **59ag** in 81-85% yields within half an hour (Table 2, entries 1-3). Surprisingly, we found *ortho*-substitution effect in case of tolyl vinyl azides **21d-f**. In this regard, *o*- tolyl vinyl azide **2f** furnished *C/N*-double vinyl 1,2,3-triazoles **59af** in 62% yield with a relatively longer reaction time (6.0 h) which may be due to steric influence of *ortho*-methyl group (Table 2, entries 4-6). Fascinatingly, the functionally rich azides like 2-napthyl, *β*-phenyl and benzyloxy vinyl azides **21h, 21j** & **21'a** were comfortably bearable in OrgVACC to produce *C/N*-double vinyl 1,2,3-triazoles **59ah-59'aa** in excellent yields within 1.0 h (Table 2 entries 7-9). Next, the reactivity of *α*-azido styrene **21a** with alkyl, aryl substituted unmodified cyclic enones was evaluated. The nature of substituents at 6^{th} position of the cyclic enones appeared to show slight variations in reaction rate and outcome of *C/N*-double vinyl 1,2,3-trazoles. Aryl substituted cyclic enones **58b** and **58c** resulted *CN*-double vinyl triazole**s 59ba** and **59ca** in 80 and 70% yields respectively, within 0.6 h (Table 2, entries 10-11). The chiral enone **58d (**92% ee & 27% de) with **21a** smoothly generated click product (+)-**59da'** in good yields (67%) without racemization at chiral center (89.9%) (Table 2, entry 12). Unexpectedly, the cyclic enone **58e** was furnished *N*-Vinyl benzotriazole **59ea** instead of *C/N*-double vinyl 1,2,3-triazole in 36% yield for stirring longer reaction time, may be due to the air oxidation followed by elimination facilitated by extended conjugation of NO_2-group on phenyl ring (Table 2, entry 13). In addition, alkyl substituted cyclic enones **58f** and **58g** were tolerated well in optimal condition and afforded *C/N*-double vinyl 1,2,3-trazoles **59fa** and **59ga** in 78 and 77% yields respectively, within 0.6 h without any electronic influence (Table 2, entries 14-15).

Table 2: Scope of different vinylazides and cyclic enones:



a] Reactions were performed in DMSO (0.5 M) with 1.5 equivalents of **21** relative to **58** (0.5 mmol) in the presence of 20 mol% of **40e**.The yield refers to the yield of the column-purified product.

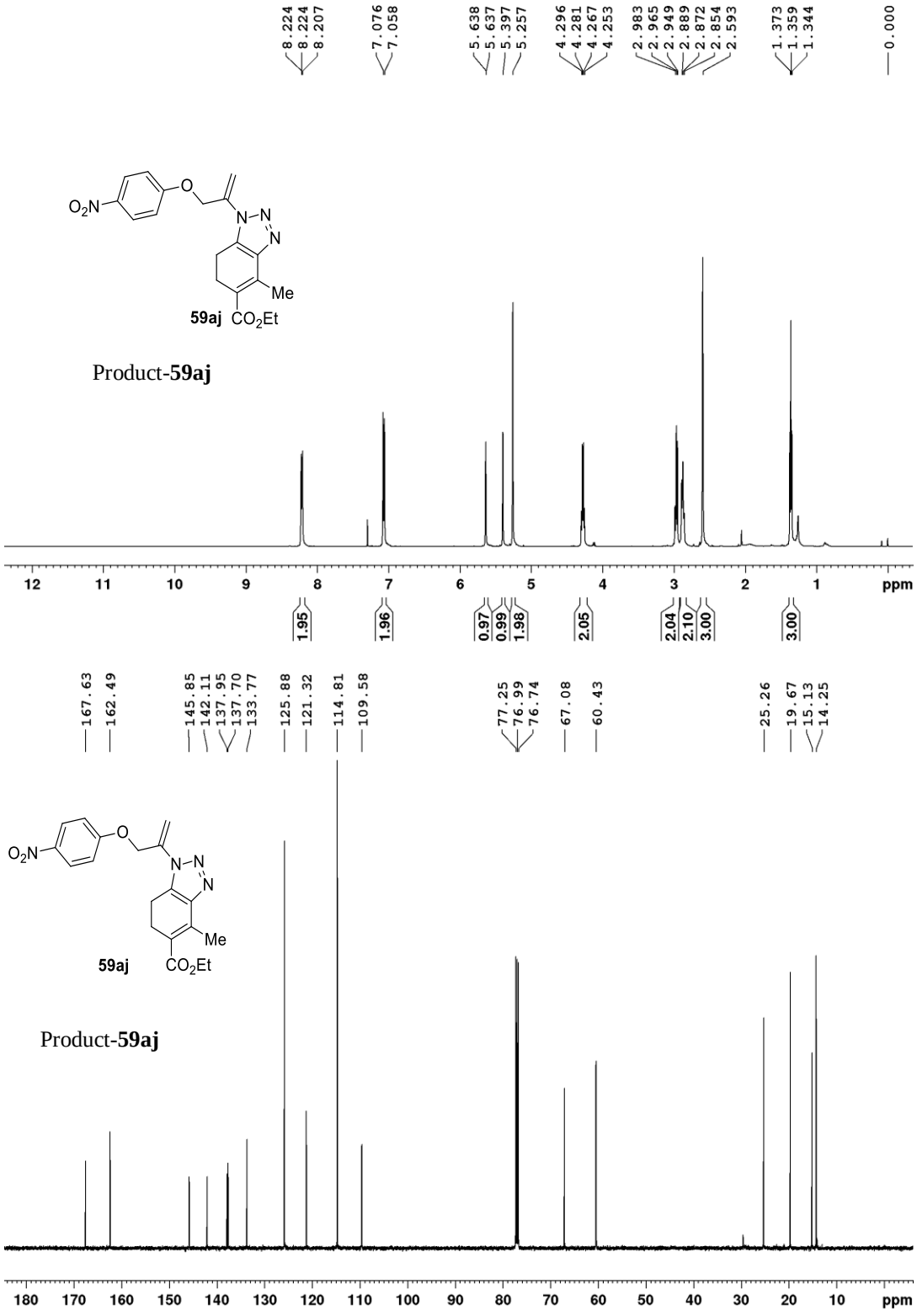


Figure 2: ^{1}H and ^{13}C spectra of the product **59aj**

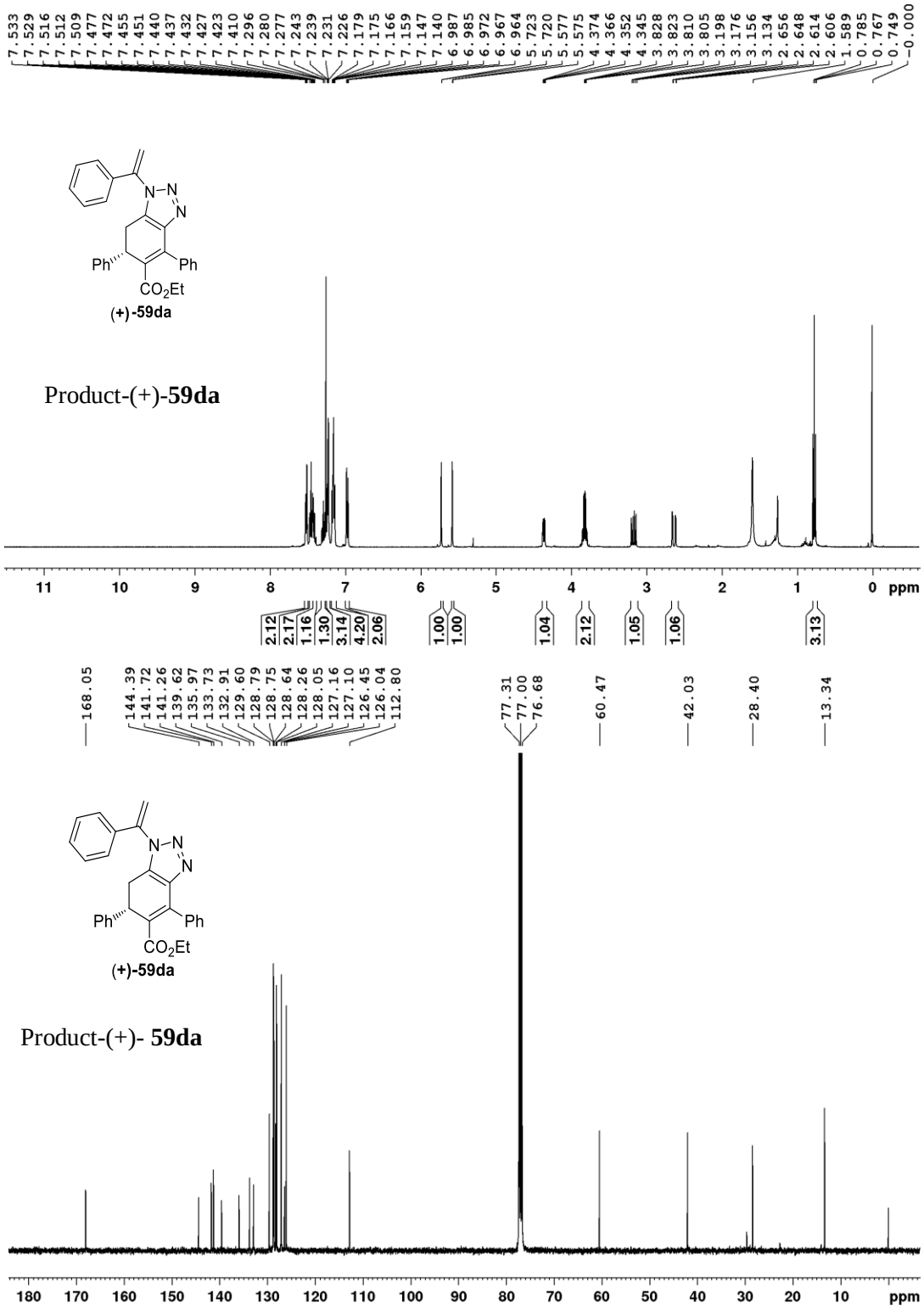
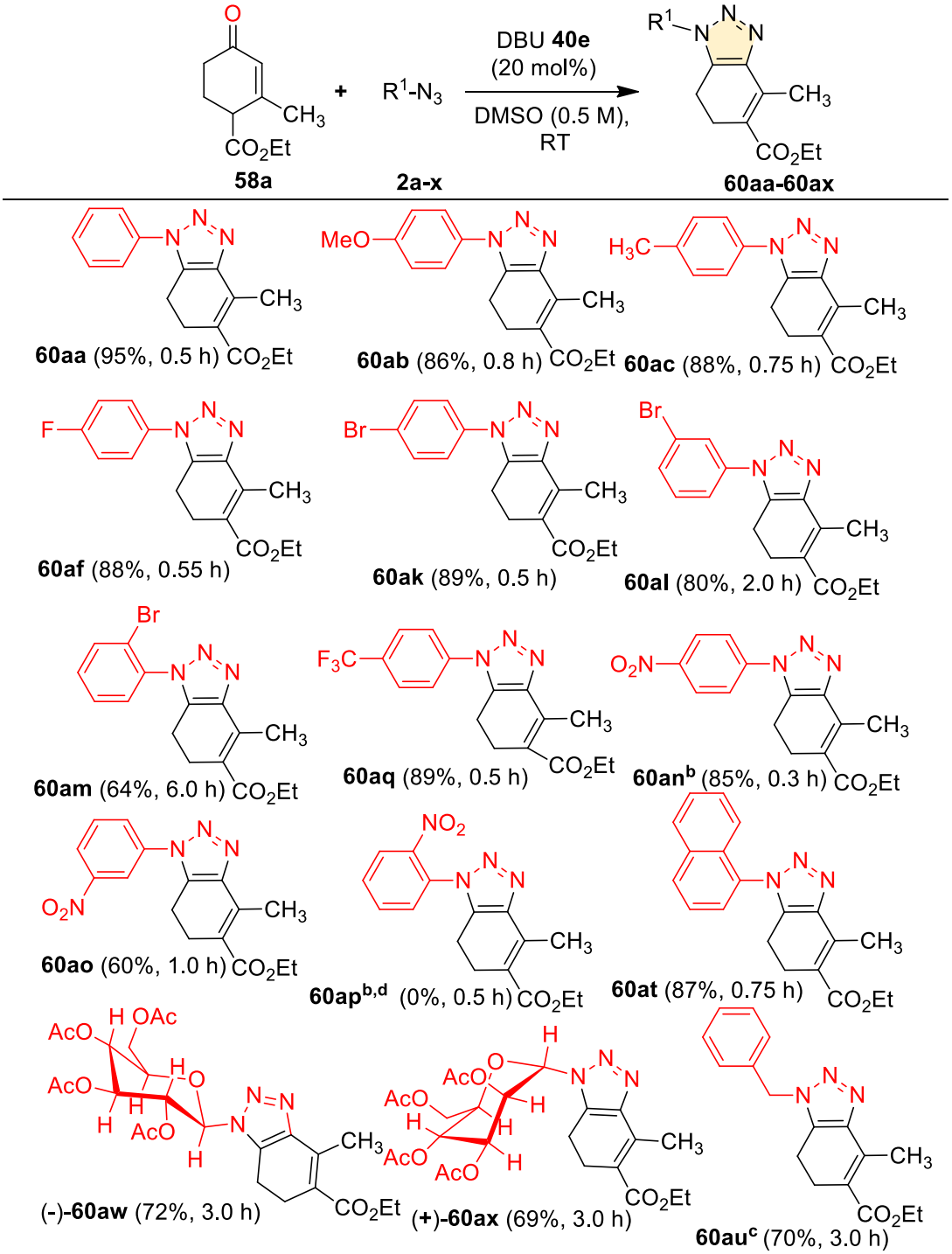


Figure 3: ^{1}H and ^{13}C spectra of the product (+)-**59da**

After comprehending the reaction rate, selectivity and yields of the OrgACC between vinyl azides with cyclic enones, we explored our protocol to different aryl azides **2** with various cyclic enones **58a-f**. At first, the reactivity of various aryl azides with cyclic enone **58a** was scrutinized. The aryl azides **2a-c** with substituents CH_3 and OCH_3 on the phenyl ring, smoothly participated in the OrgACC with the cyclic enone **58a** to generate bicyclic aryl 1,2,3-triazoles **60aa-ac** up to 95% yields, within 1.0 h (Table 3 entries 1-3). The fluorinated phenyl azide **2f** followed the trend without any electronic influence (Table 3, entry-4). Interestingly, we observed the *ortho*-substituent effect in the case of aryl azides also. For example, among the presence of bromo group at *para*-, *meta*-, and *ortho*-positions of aryl azides **2k-m**. **(**Table 3, entries 5-7), we found strong steric influence in the case of *ortho*-bromo phenyl azide **2m**, which resulted in the corresponding triazole **60am**, with reduced reaction rate and yield (6.0 h, 64%, Table 3, entry 7). The CF_3 containing aryl azide **2q** too easily partook in the OrgACC to produce the triazole **60aq** (Table 3, entry 8). Surprisingly, we received various outcome for the nitro substituted phenyl azides **2n-p**. (*para*- to *ortho*- positions). When the *m*-nitro phenyl azide **2o** cleanly furnished the bicyclic aryl 1,2,3-triazole **60ao** in yield 60% within half an hour (Table 3, entry 10), the *para*- and *ortho*-substituted nitro phenyl azides **2n** and **2p** were unable to deliver under optimal conditions. Further, we conjectured that the existed possibility of uncontrolled collisions of the highly activated azides **2n** and **2p** with the highly reactive dienolate of the cyclic enone or the self-destruction of the phenyl azides **2n** and **2p** due to strong negative mesomeric effect of the nitro group under DBU catalysis were the influencing factors for the negative results. Later, when we re-examined the azides **2n** and **2p**, by doubling the DMSO solvation at 25 °C, the *para*-nitro phenyl azide **2n** generated the bicyclic aryl 1,2,3-triazole **60an** in 85% yield within 0.3 h (Table 3, entry 9). But, the *ortho*-nitro phenyl azide **2p** was still unable to generate the bicyclic aryl 1,2,3-triazole, may be due to the additional *ortho*-substituent effect (Table 3, entry 11). In addition, functionally rich 1-napthyl **2t** and sugar azides **2w** and **2x** generated corresponding bicyclic 1,2,3-triazoles **60at**, (+)-**60aw** and (-)-**60ax** in 87%, 72% and 69% yields, respectively within 3.0 h (Table 3 entries 12-14). The aliphatic benzyl azide **2u** was unable to form bicyclic alkyl 1,2,3-triazole **60au** under the corresponding solvent medium but abled to furnish in solvent free condition at 25 °C in 70% yield within 3.0 h. (Table 3, entry 15).

Table 3: **Scope of arylazides**



a] Reactions were performed in DMSO (0.5 M) with 1.5 equivalents of **58** relative to **2** (0.5 mmol) in the presence of 20 mol% of **40e**.The yield refers to the yield of the column-purified product. b] 0.25 M of DMSO used c] Reaction performed in neat condition.d] both starting meterials consumed within 0.5 h,multiple spots are formed.

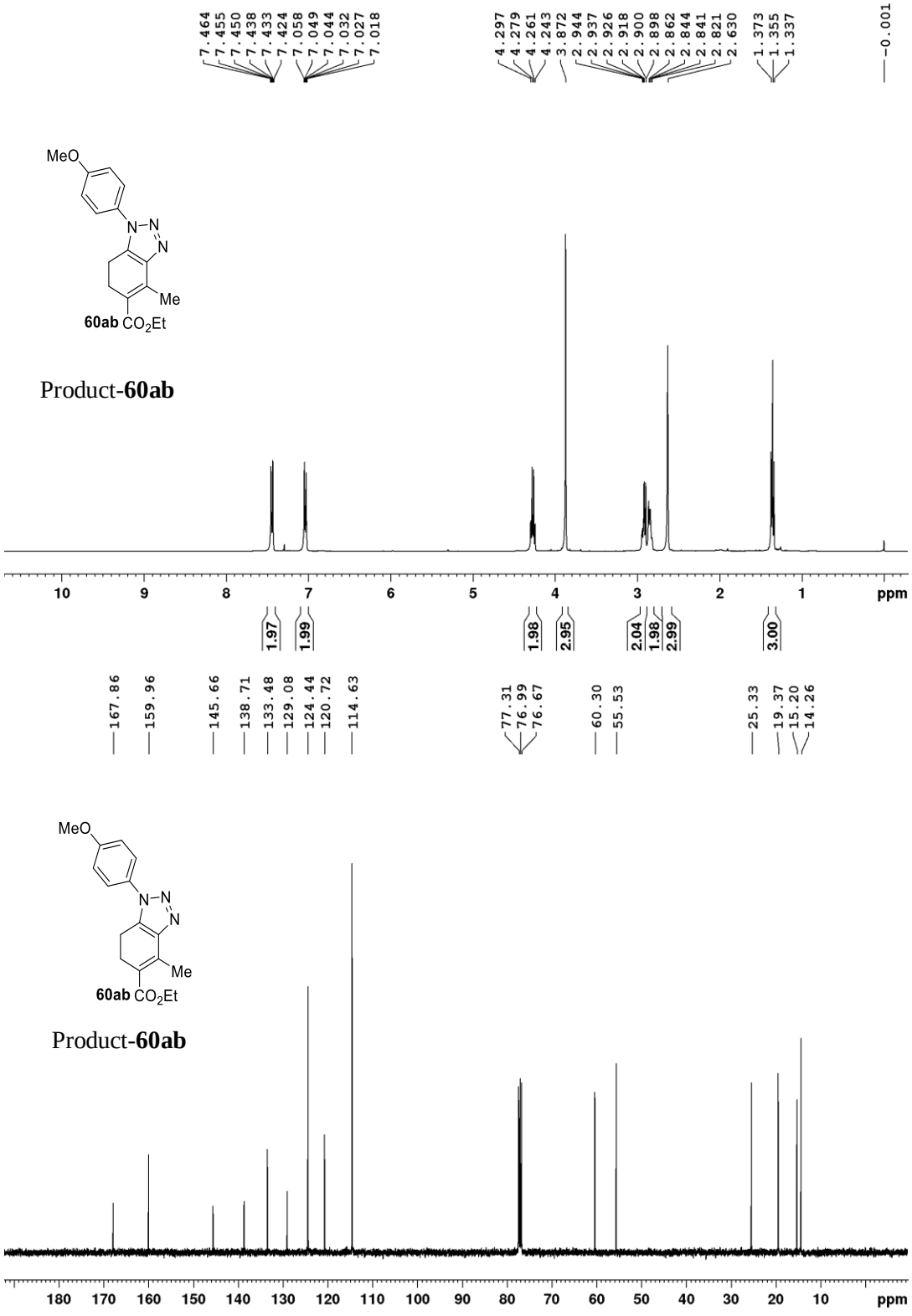


Figure 4: ^{1}H and ^{13}C spectra of the product **60ab**

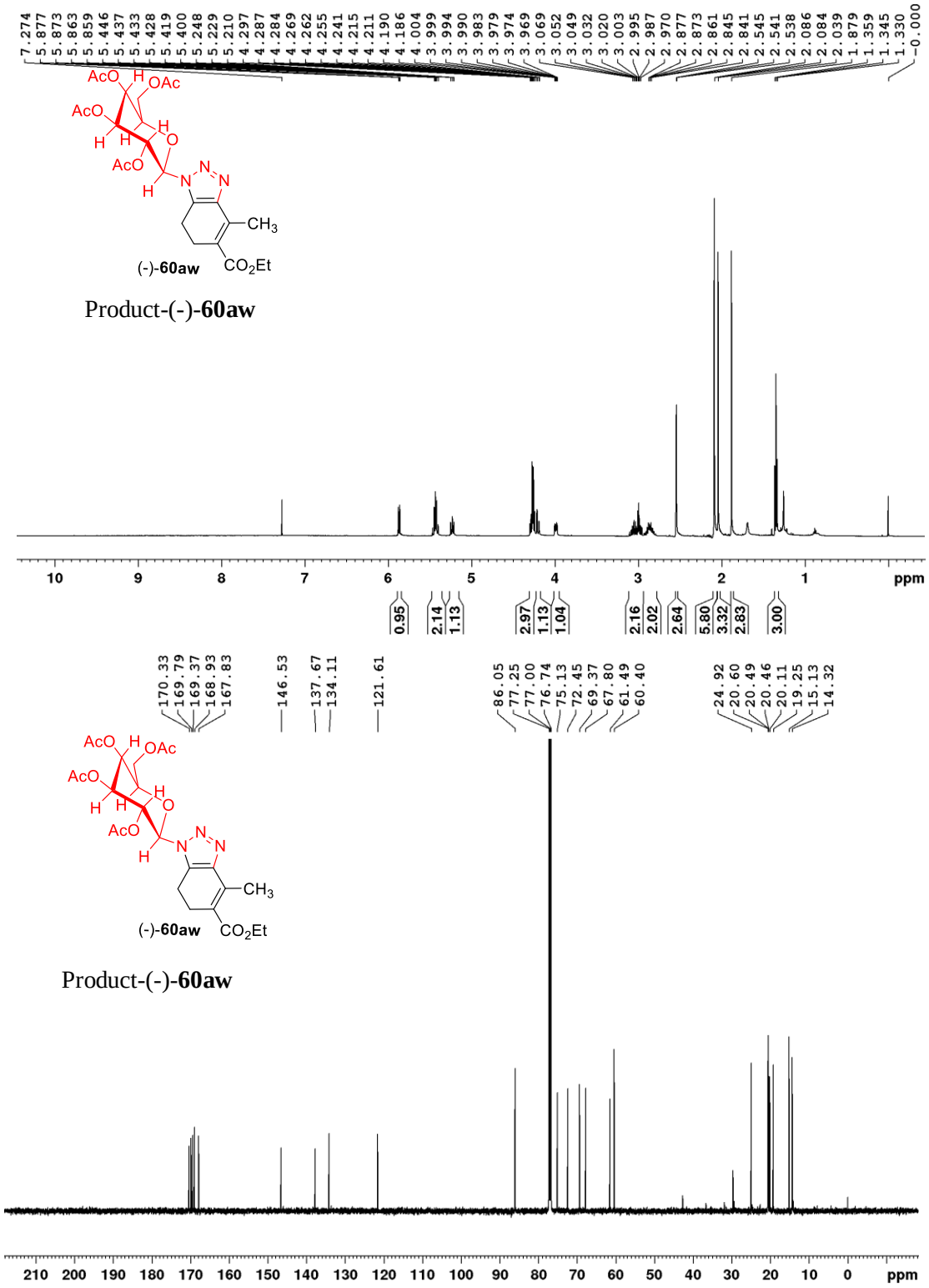


Figure 5: ^{1}H and ^{13}C spectra of the product (-)-**60aw**

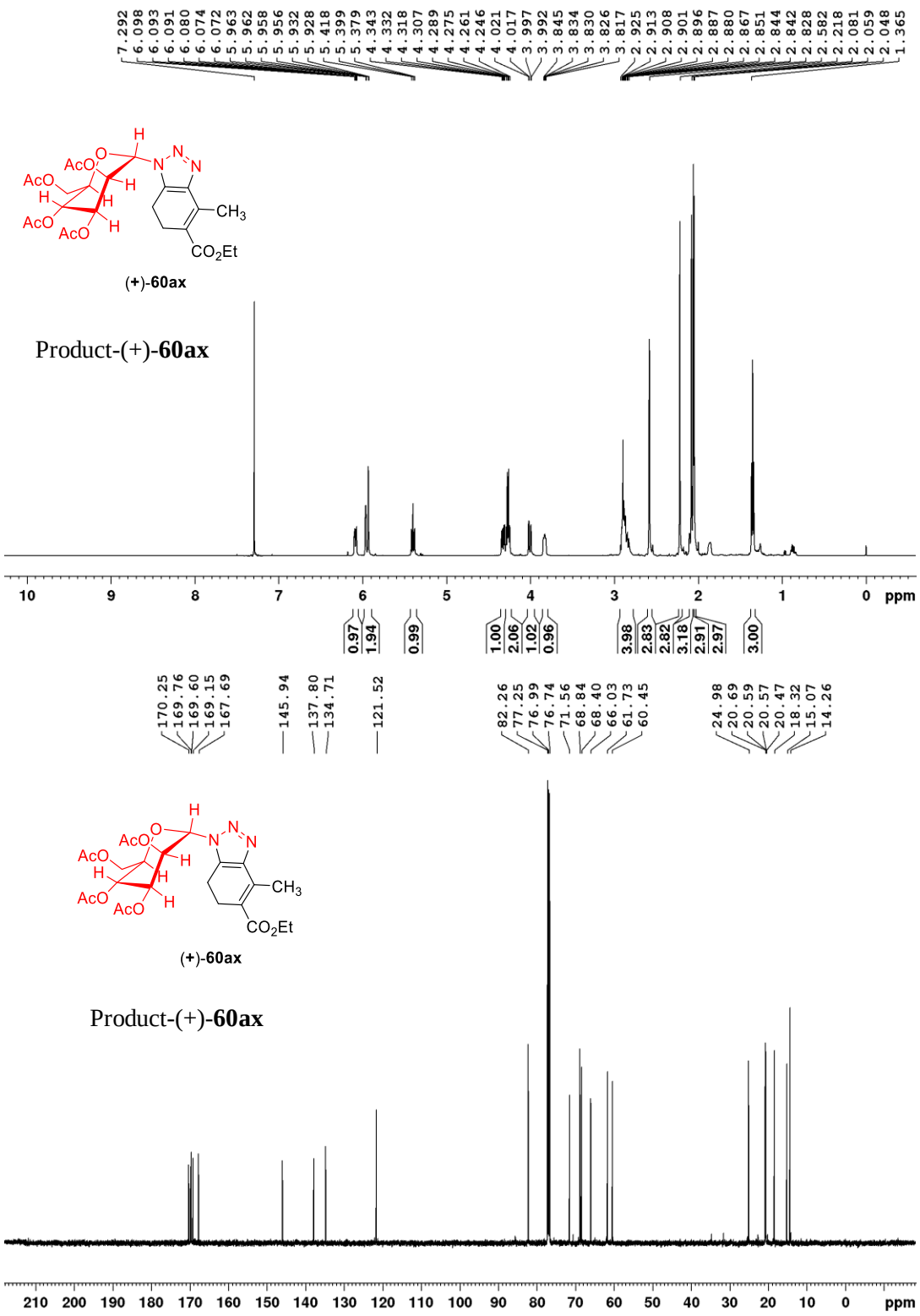
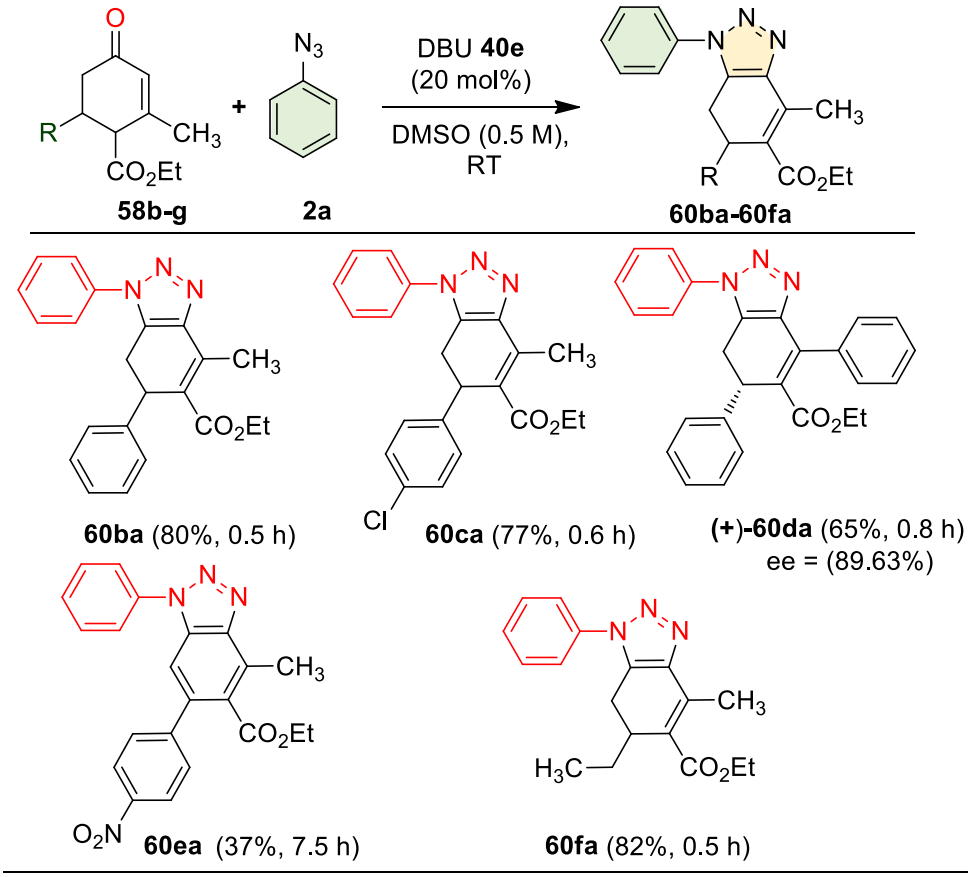


Figure 6: ^{1}H and ^{13}C spectra of the product (+)-**60ax.**

Further, the reactivity of phenyl azide **2a** with different alkyl and aryl substituted unmodified cyclic enones was investigated (Table 4). Eventually, we found that phenyl azide **2a** was equally tolerable with Aryl and alkyl substituted cyclic enones **58b-f** like α-azido styrene **21a** without showing much difference in the organo click reaction rate and yield (Table 4 entries 1-2 & 5). The OrgACC reaction performed with the chiral enone **58d (**92% *ee* & 27% *de*) gave the click product (+)-**60da** in good yields (65%) with 89.6% *ee* (Table 4, entry 3). The *para*-nitro phenyl substituted cyclic enone **58e** furnished the benzotriazole **60ea** instead of bicyclic aryl 1,2,3-triazole in reduced yield by stirring for longer reaction time, may be due to the air oxidation followed by elimination, because of extended conjugation with NO_2 group (Table 4, entry 4).

Table 4: scope of cyclic enones with phenyl azide



a] Reactions were performed in DMSO (0.5 M) with 1.5 equivalents of **2a** relative to **58** (0.5 mmol) in the presence of 20 mol% of **40e.**The yield refers to the yield of the column-purified product. .

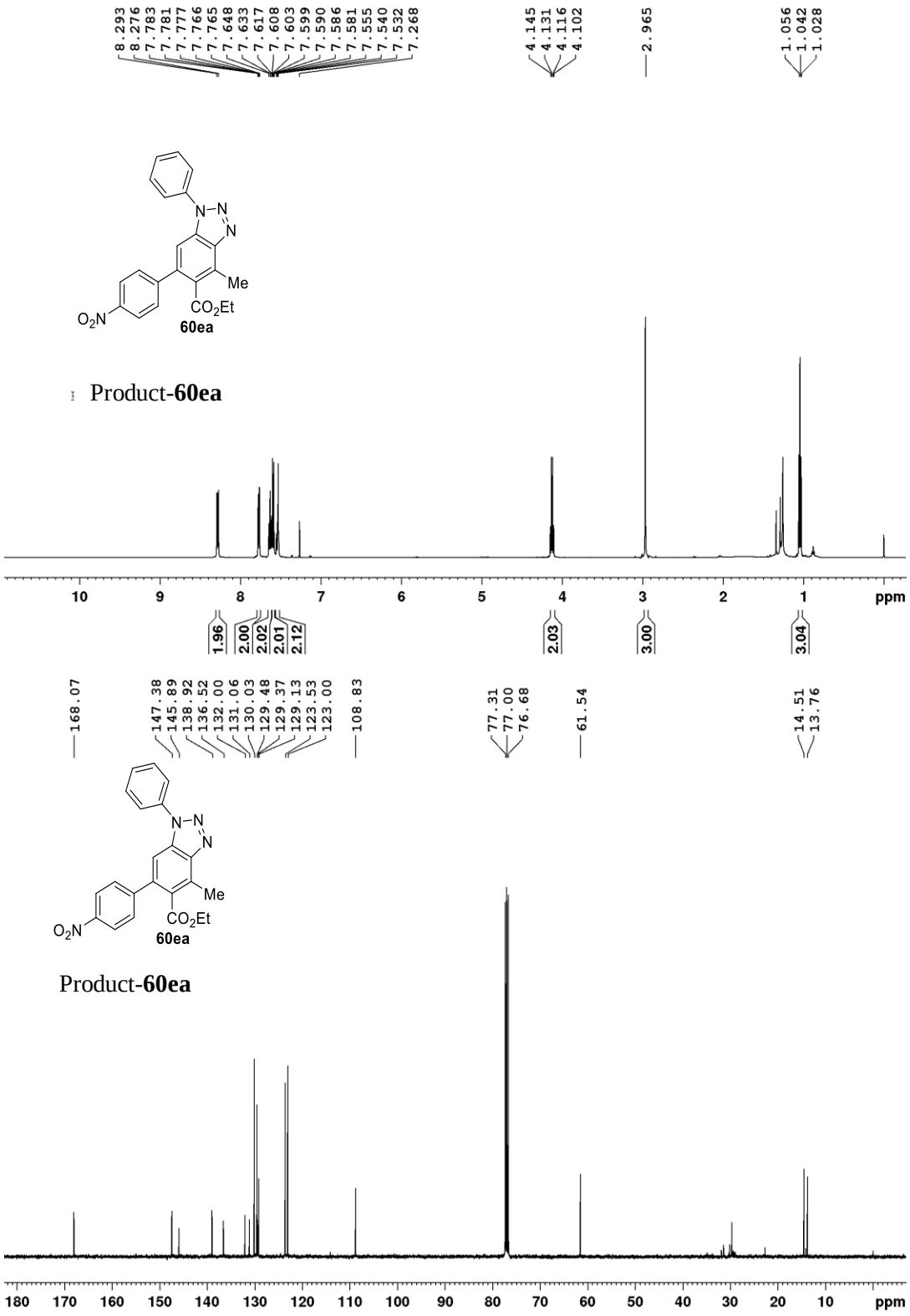
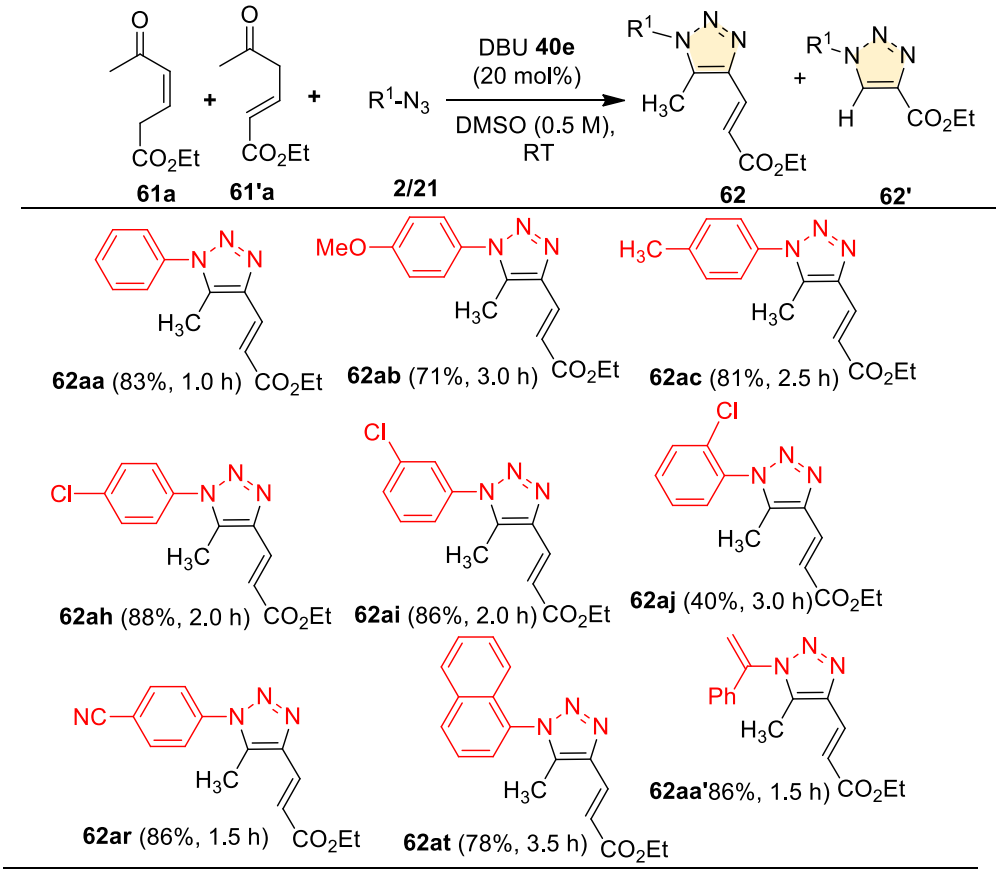


Figure 7: ^{1}H and ^{13}C spectra of the product **60ea**

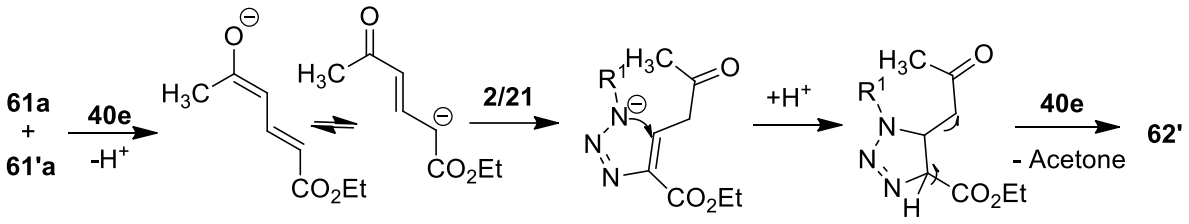
After concluding the investigation successfully on the cyclic enones, we applied DBU catalyzed [3+2]-cycloaddition on acyclic enone along with it's deconjugated isomer, for this we chose 1:1 mixture of ethyl (*Z*)-5-oxohex-2-enoate **61a** and ethyl (*E*)-5-oxohex-3-enoate **61'a** as model substrate and the reaction on examination with various aryl azides resulted the formation of *C*-vinyl-1,2,3-triazoles along with 1-5% of deacetonated product **62**'. The aryl azides **2a-c** with substituents like OCH_3 and CH_3 smoothly generated *C*-vinyl 1,2,3-triazoles **62aa-ac** up to 83%, yields within 3.0 h (Table 5 entries 1-3). We also observed *ortho*-substituent effect by substituting chloro group at *para*- to *ortho*- positions of aryl azide **2h-j**. In regard to this *o*-chloro phenyl azide **2j** furnished *C*- vinyl-1,2,3-triazole **62aj** in 40% yield due to steric influence of *ortho*- chloro group (Table 5, entry 6).

Table 5: **Scope of arylazides with acyclic azidophile**



a] Reactions were performed in DMSO (0.5 M) with 1.5 equivalents of **2/21** relative to **61/61'** (0.5 mmol) in the presence of 20 mol% of **40e**.The yield refers to the yield of the column-purified product.

In addition, *para*-cyano phenyl azide **2r** and 1-napthyl azide **2t** afforded corresponding *C*- vinyl-1,2,3-triazoles **62ar** and **62at** with 86% and 78/% yields within 3.5 h without showing any electronic influence (Table 5, entries 7-8). Further, the reactivity of α-azido styrene **21a** with 1:1 mixture of acyclic enone and it's deconjugated isomer **61a** and **61'a** was examined and resulted corresponding *C/N*-double vinyl 1,2,3-triazole **62aa'** with 86% yield within 1.5 h (Table 5, entry 9). This Table 5 gives insight into the fact that the reaction is impervious to the double bond position in the carbonyl reaction partner.



Scheme 3: Reaction mechanism of minor product **62'**

The structure and relative stereochemistry of the click products **59**, **60**, and **62** were established by IR, NMR, and mass analysis and also finally confirmed by correlation with the X-ray crystal structure of **59aj** and **62ah** (Figures 8-9).[11c]

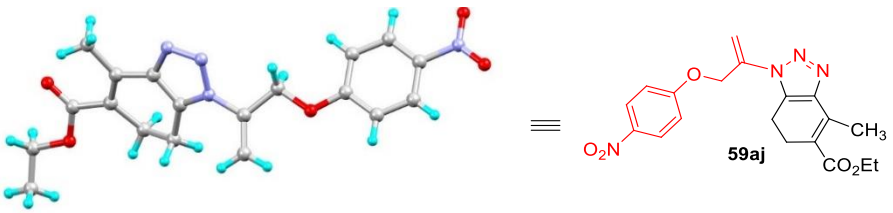


Figure 8: X-ray crystal structure of **59aj**

Figure 9: X-ray crystal structure of **62ah**

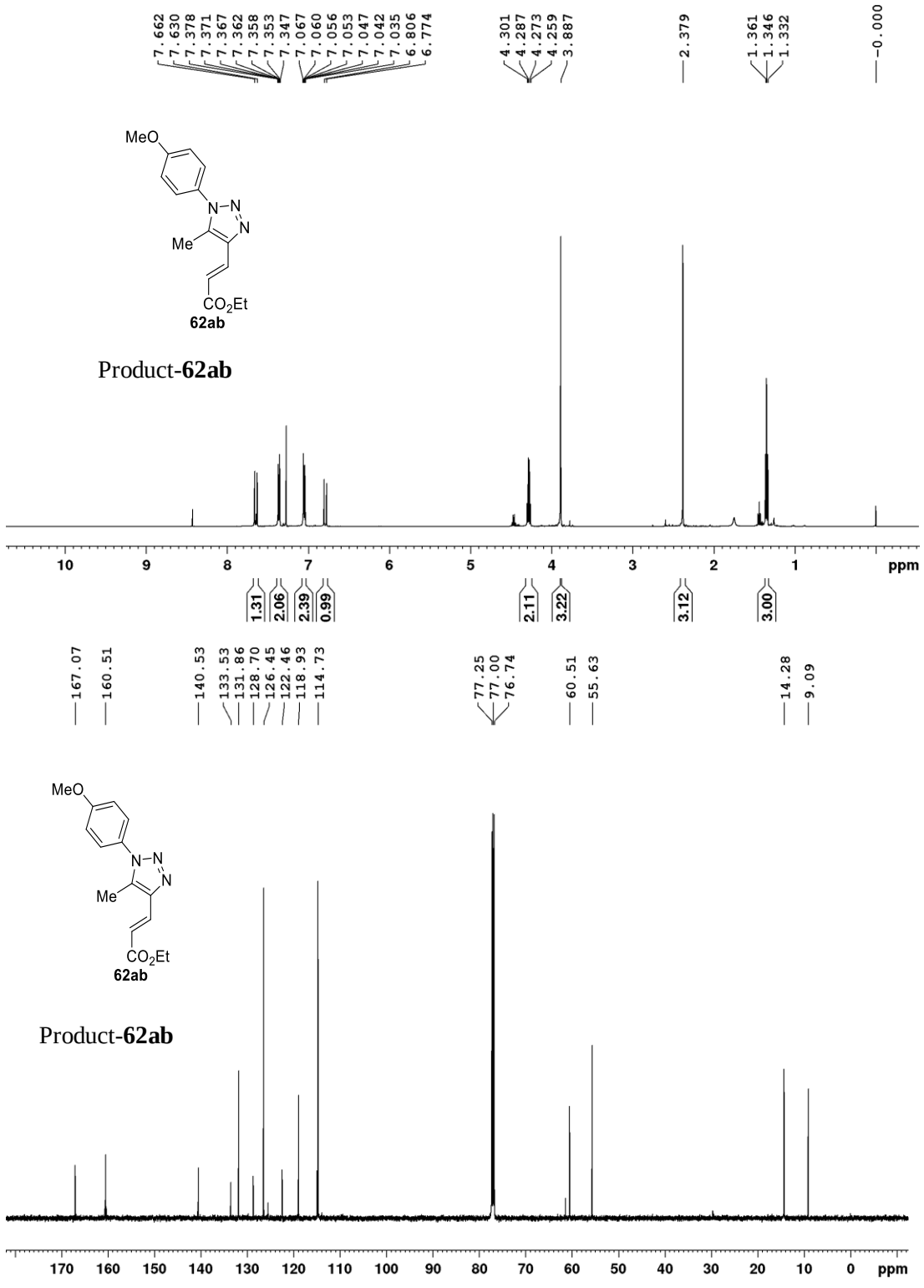


Figure 10: ^{1}H and ^{13}C spectra of the product **62ab**

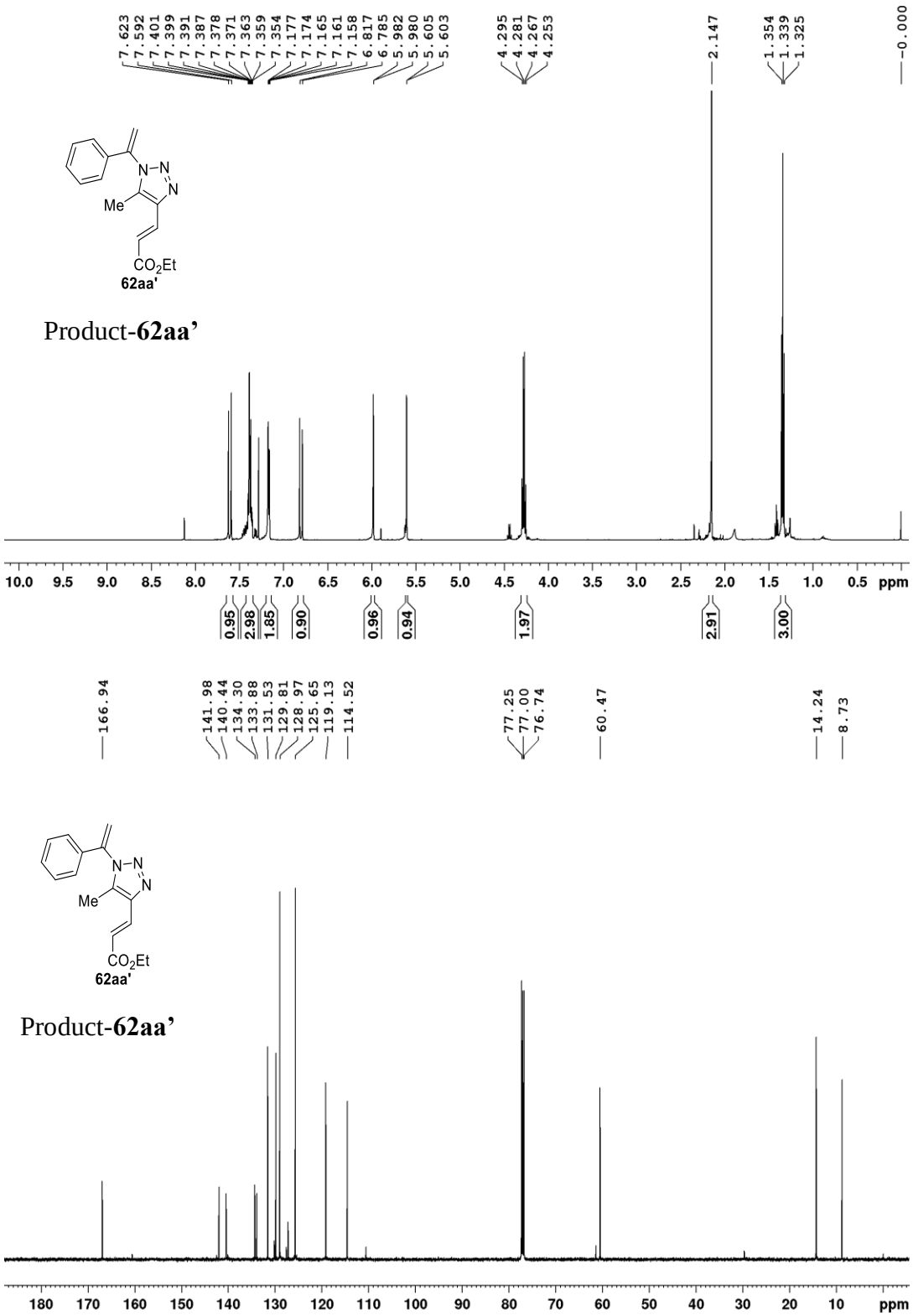
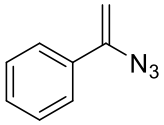
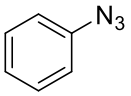
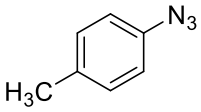
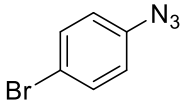
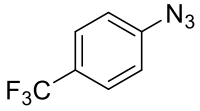
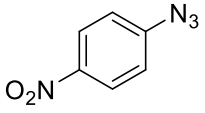
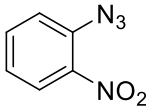


Figure 11: ^{1}H and ^{13}C spectra of the product **62aa'**

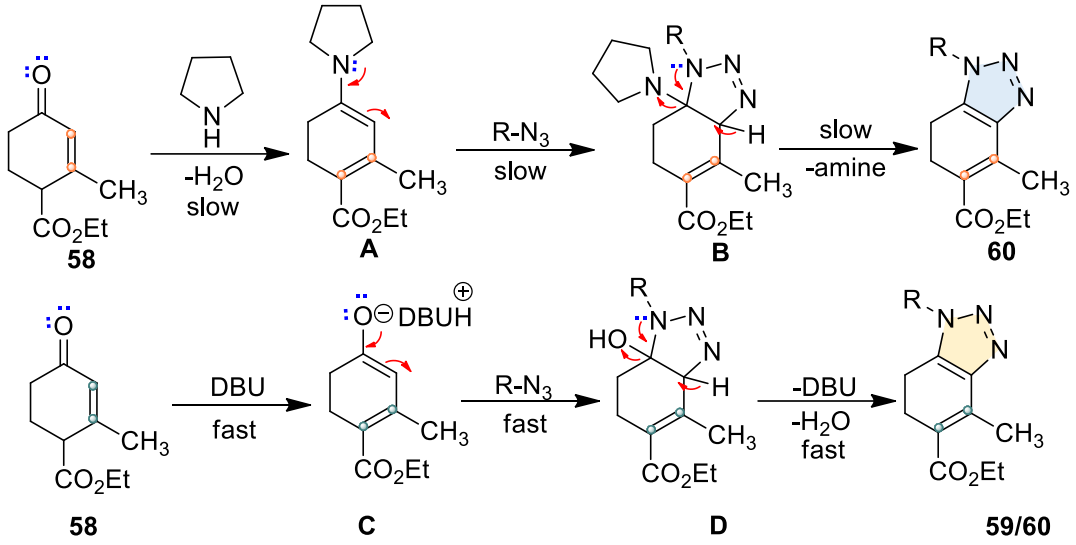
5.4 Reaction mechanism:

The reaction mechanism for high-yielding synthesis of *C/N*-double vinyl- and *C*-vinyl-1,2,3-triazoles were discussed by correlation between dienamine and dienolate reactivity (Scheme 3). As shown in Table 1 and Table 6, dienamine-mediated [3+2]-cycloaddition of enones **58** with less reactive vinyl azides **21** and aryl azides **2** under the primary and secondary amine-catalysis is very slow compared to the dienolate-mediated [3+2]-cycloaddition under the tertiary amine-catalysis (see Scheme 3).

Table 6: Correlation of reactivity of different azides with enone 58a under secondary amine catalysis and tertiary amine catalysis.

Entry	Azide	Pyrrolidine (10 mol%)		DBU (20 mol%)	
		Time (h)	yield %	Time (h)	yield %
1		24 h	No Reaction	0.5 h	90
2		66 h	50	0.5 h	95
3		40 h	50	0.5 h	90
4		24 h	75	0.5 h	89
5		1.0 h	93	0.5 h	89
6		1.0 h	95	0.3 h	85
7		1.0 h	95	0.5	Multiple spots

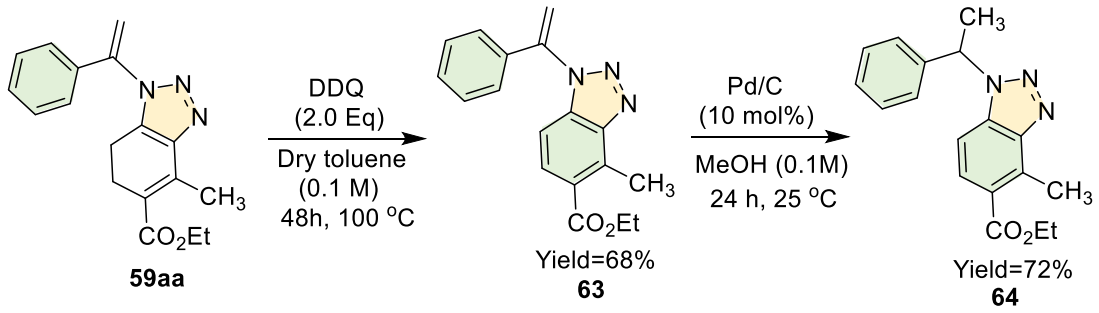
Rate of the ionic dienolate **C** formation from the deprotonation of enones **58** with DBU **40e** through acid-base reaction is faster compared to neutral dienamine A formation through bimolecular reaction of **58** with **40a-c.** In a similar manner, [3+2]-cycloaddition between neutral species of **A** with less reactive azides **2/21** is very slow compared to ionic species of **C** and same trend followed in the final elimination reaction to produce 1,2,3-triazoles. Correlation studies (Table 6) demonstrated that the enolate-mediated [3+2]-cycloaddition for 1,2,3-triazoles formation is more powerful than enamine-mediated clickreaction.



Scheme 4: Mechanistic engineering between secondary amine-catalysis and tertiary amine-catalysis.

5.5 Synthetic transformations:

Our concept was further progressed by conducting synthetic transformation on *C/N*-double vinyl 1,2,3-trazole **59aa.** Initially, we applied DDQ oxidation by using 2.0 equiv. of DDQ in 0.1 M Dry toluene under reflux temperature, after 48 h afforded *N*-vinyl benzotriazole **63** in 68% yield. At next, we performed heterogeneous hydrogenation on *N*-vinyl benzotriazole **63** by using 10 mol% of Pd/C in 0.1 M MeOH under H_2 balloon, after 24 h furnished *N*-alkyl benzotriazole **64** in 72% yield.



Scheme 5: Synthetic transformations

5.6 Conclusion:

we have developed a general and sustainable method for the high-yielding synthesis of *C/N*-double vinyl and *C*-vinyl-1,2,3-triazoles **59/60/62/62'**from the readily available cyclic and acyclic enones **58/61** and less reactive vinyl and aryl/alkyl azides **21/2** under the DBU-catalysis. In this manuscript, we have shown the synthesis of *C/N*-double vinyl 1,4,5-trisubstituted 1,2,3-triazoles as privileged building blocks for various applications. This work demonstrated the importance of enolate reactivity compared to the enamines for carbonyls mediated click reactions with less reactive azides at the ambient conditions. Further, we are working on to develop synthetic to medicinal applications of these functionally rich click compounds. Same time we are looking forward to see large library of various azides and azidophiles through sustainable enolate chemistry for synthesizing medicinally important 1,2,3-triazoles.

6.0 Engineering Organocatalytic Selective [3+2]-Cycloadditions: Synthesis of 1,4-Diaryl-5-Arylthiomethyl-1,2,3-Triazoles

6.1 Abstract:

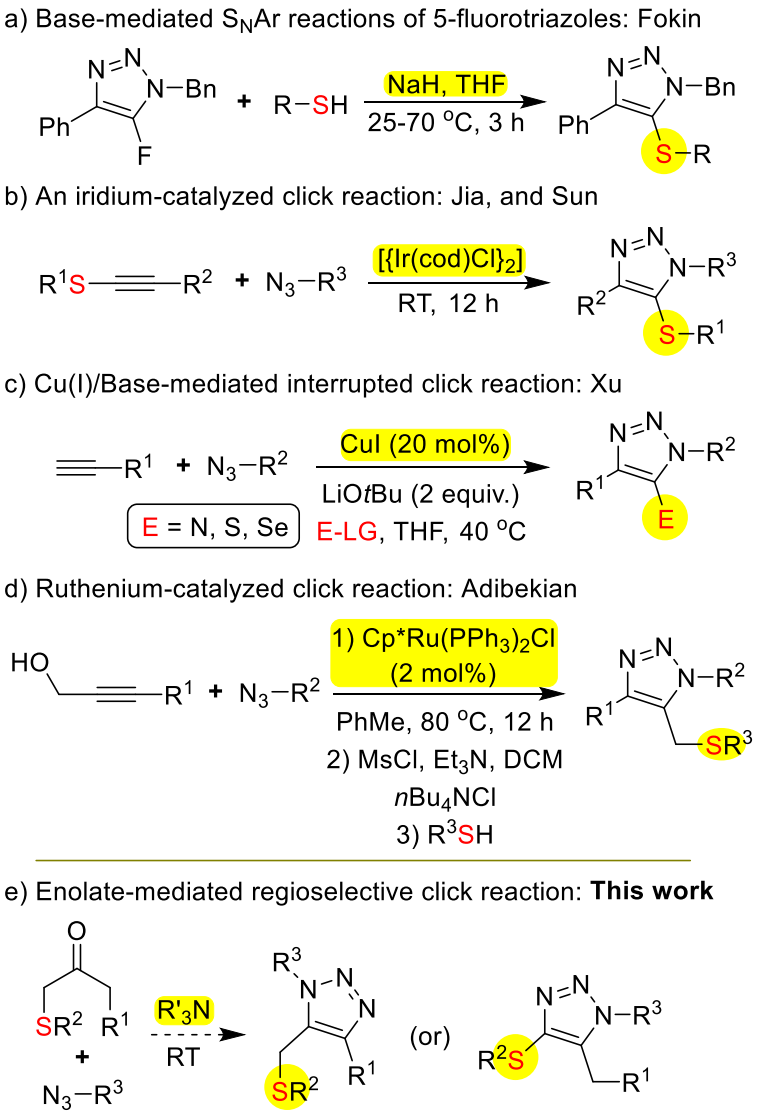
The tertiary amine-catalyzed an organocatalytic selective enolization for the synthesis of functionally rich 1,4-diaryl-5-arylthiomethyl-1,2,3-triazoles from readily available non-ssymmetrical thioketones and different azides reported. Furthermore, we have demonstrated the medicinal applications of thiomethyl-1,2,3-triazoles.

6.2 Introduction:

The revolutionary invention of copper(I)-catalyzed azide-alkyne cyloaddition reaction by Sharpless, for the construction of 1,4-disubstituted-1,2,3-triazoles in high yields, resulted in emergence of triazoles as very important molecules.[5a-i] This led to evolution of immense applicability of triazoles in biological studies, therapeutic drug discovery, material chemistry, agrochemical industry etc.[10] As the application of triazoles widened and gathered more attention, requirement for creation of new synthetic methods for diverse functionalized triazoles also escalated. As a result, more synthetic methods were invented to synthesize several differently functionalized triazoles. Synthetic methods such as ruthenium-catalyzed, iridium-catalyzed and strain-promoted triazole syntheses materialized.[5j-z]

It is obvious that introduction of functional groups at different positions in any back bone skeleton might result in difference in their material, biological and therapeutic properties. Besides, analogous compounds are usually expected to have similar properties varying only in the extent of their behavior. Understandably, a way of introducing extended possibilities was to incorporate some other functionality into the triazole system, which was done effectively in two ways, either in the starting material itself or later on in the product triazole through S_NAr reaction. A few existing synthetic strategies for achieving different functional groups in triazole are through S_NAr reaction on triazole products,[14a] iridium-catalyzed click reaction on special sulphur containing

substrate,[14b] interrupted click reaction[14c] and ruthenium-catalyzed click reaction of alkynols followed by nucleophilic substitution[14d] (Scheme 1).



Scheme 1: Different strategies for the preparation of thia-1,2,3-triazoles.

Of all the substitutions in triazole, sulphur is seemingly fascinating, as the element has much biological significance, being present in many bio-molecules. Sulphur group was introduced either in the product-triazole by nucleophilic substitution or by using specially designed substrates for triazole synthesis. As additional advantage, the Scheme 1 illustrates few sulphur functionalized triazoles and a chloride containing triazole, which possess essential qualities as listed. From our

group, we have reported two diverse enolate-mediated click reactions for the triazole synthesis, one on simple arylketones and the second on sulphur containing arylketones as substrates, both containing α-methylene group. A fantastic idea brewed in our mind that what if both type of methylenes are present in the same substrate as depicted in the present work (Scheme 1), how the reaction would be directed based on the α- and α'-methylene acidity and which of the two products would be formed. To uncover answers for our questions, we dived into investigating the reaction between the α-(arylthio)ketones with two different active methylenes and aryl azides, under enolate-mediated condition.

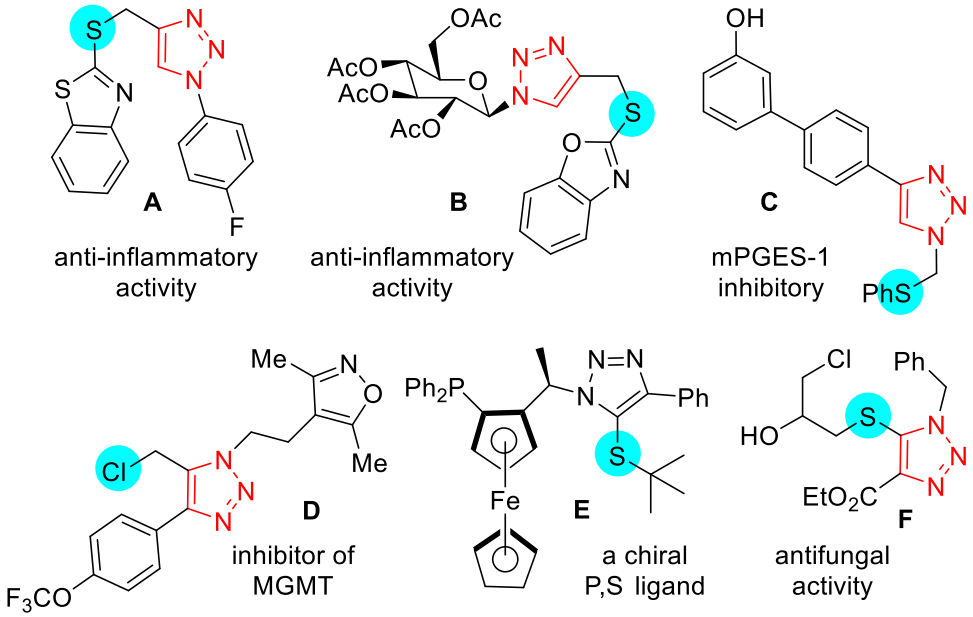


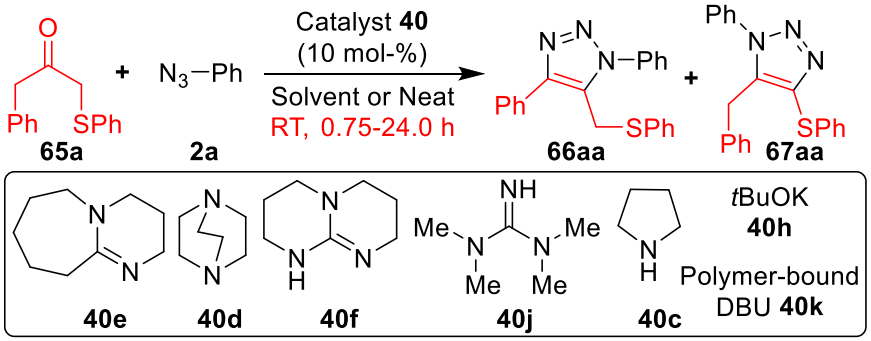
Figure 1: Few sulphur functionalized triazoles in medicinal chemistry.

6.3 Results and Discussion:

As planned, when the reaction was conducted between 1 equiv. of **65a** and 1.2 equiv. of **2a** in the presence of 10 mol% DBU **40e** in DMSO at room temperature for 1.5 hours, we were fortunate enough to obtain the triazole **66aa** in 70% yield with >99:1 regioselectivity (Table 1 entry 1). The same reaction when performed under identical conditions, using 1.5 equiv. of **2a**, for 1 equiv. of

65a, the reaction completed soon, within 0.75 hour and the triazole **66aa** was produced in improved yield (90%) with same >99:1 regioselectivity (Table 1 entry 2). When the reaction solvent was changed to DMF, the reaction took longer time (8 hours) for completion and the triazole **66aa** formed in 77% yield with >99:1 selectivity (Table 1 entry 3). Acetonitrile and chloroform were found to be unfavorable solvents (Table 1 entries 4-5).

Table 1: Reaction optimization[a]



Entry	Catalyst **40** [10 mol-%]	Solvent [0.5 M]	*t* [h]	Yield [%][b] **66aa**	Ratio[c] **66aa**:**67aa**
1[d]	**40e**	DMSO	1.5	70	>99:1
2	**40e**	DMSO	0.75	90	>99:1
3	**40e**	DMF	8.0	77	>99:1
4[e]	**40e**	CH_3CN	24.0	<10	–
5[e]	**40e**	$CHCl_3$	24.0	<3%	–
6	**40e**	Neat	1.0	80	>99:1
7[e]	**40d**	DMSO	24.0	<3%	–
8	**40f**	DMSO	1.0	82	>99:1
9	**40j**	DMSO	1.0	84	>99:1
10	**40c**	DMSO	24.0	40	>99:1
11	**40h**	DMSO	0.75	82	>99:1
12	**40k**	DMSO	10.0	70	>99:1

[a] Reactions were carried out in solvent (0.5 M) or neat with 1.5 equiv. of **2a** relative to the **65a** (0.5 mmol) in the presence of 10-mol% of catalyst **40**. [b] Yield refers to the column-purified product. [c] Ratio is based on ^{1}H NMR analysis of crude product. [d] 1.2 equiv. of **2a** was used. [e] Starting materials **65a**/**2a** was recovered.

To our surprise, the solvent-free (neat) reaction performed well, within 1 hour, to furnish the triazole **66aa** in 80% yield with >99:1 selectivity (Table 1 entry 6). Of the solvents screened, DMSO appears to be the solvent of choice. Catalyst DABCO, **40d** was inefficient in catalysing the reaction (Table 1 entry 7). The catalyst activity of TBD **40f** and 1,1,3,3-tetramethylguanidine **40j** in this reaction are alike and moreover quite comparable to that of DBU and both the reactions completed within 1 hour to furnish the triazole **66aa** in 82 and 84% yields with >99:1 selectivity (Table 1 entries 8-9). With pyrrolidine **40c** as catalyst, the reaction proceeded for 24 hours, but the triazole **66aa** formation was only in 40% yield (Table 1 entry 10). Potassium *tert*-butoxide **40k** catalyzed the reaction equivalent to TBD **40f** and 1,1,3,3-tetramethylguanidine **40j** and the triazole **66aa** was produced in 82% yield with >99:1 selectivity in a shorter reaction time of 0.75 hour (Table 1 entry 11). The reaction turned out to be lethargic and took 10 hours, when polymer-bound DBU **40k** was used as catalyst and the triazole **66aa** was generated in 70% yield with >99:1 selectivity (Table 1 entry 12). From this optimization, the most favourable protocol for the reaction was decided to be entry 2 enlisted in Table 1.

Now it was time to scrutinize the reaction for its efficacy on versatility. Firstly, we determined to work with several aryl as well as vinyl azides **2** and **21** in the reaction with the α-(phenylthio)ketone **65a**. All the aryl azides **2b-s** reacted exceptionally well with the α-(phenylthio)ketone **65a**, on treatment with DBU **40e** in DMSO within 0.5 to 0.7 hour to furnish the triazoles **66ab-as** in 88-92% yields. A variety of substituents such as nitro, CO_2Et, cyano, trifluoromethyl, halogen substituents, and methyl group on the phenyl ring of the aryl azide were well tolerated in the reaction and did not seem to have discernible influence on the reaction. With the electron donating methoxy group at the *para* position, the aryl azide **2b** reacted with **65a** though sluggishly in DMSO solvent and took long reaction time, the triazole **66ab** was created in reasonable 75% yield within 1 hour, under neat condition at room temperature (Table 2 entry 10). Diverse vinyl azides **21a**, **21b, 21h** and **21'a** too reacted with the α-(phenylthio)ketone **65a** amazingly and furnished the triazoles **68aa, 68ab, 68ah** and **68'aa** up to 88% yields, within 0.5 to 0.75 hour (Table 2 entries 11-14).

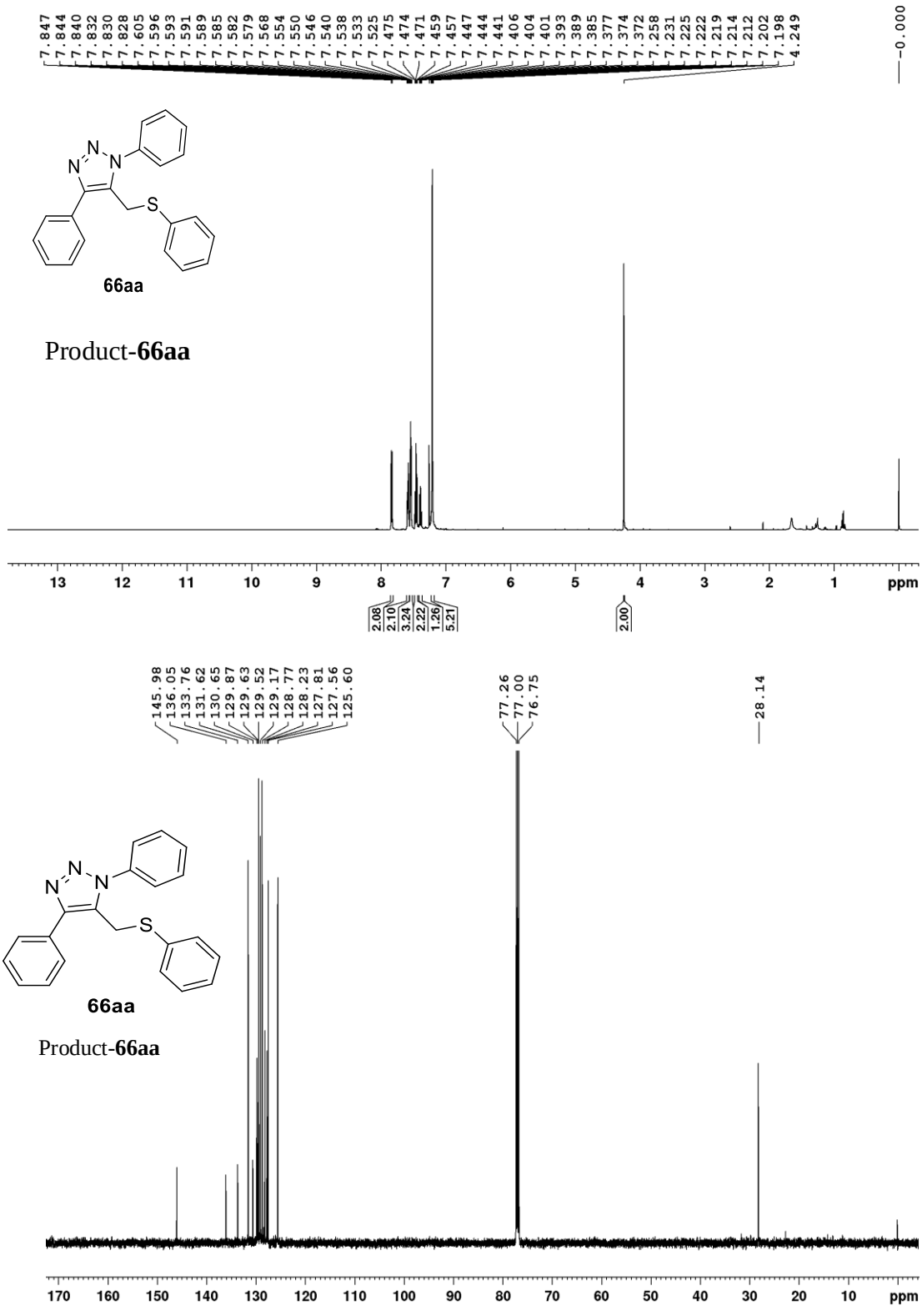
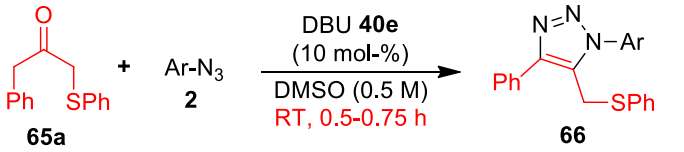
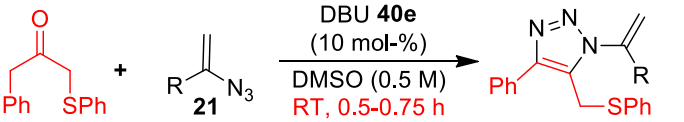


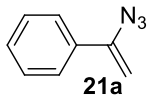
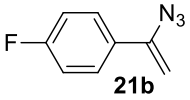
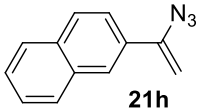
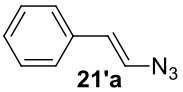
Figure 2: ^{1}H and ^{13}C spectra of the product **66aa**.

Table 2: Azide scope[a]



Entry	Ar-N_3 **2**	*t* [h]	Yield [%][b] **66**
1	**2n** (Fg = 4-NO_2)	0.5	**66an**: 90
2	**2s** (Fg = 4-CO_2Et)	0.66	**66as**: 90
3	**2r** (Fg = 4-CN)	0.6	**66ar**: 90
4	**2q** (Fg = 4-CF_3)	0.5	**66aq**: 92
5	**2f** (Fg = 4-F)	0.66	**66af**: 90
6	**2h** (Fg = 4-Cl)	0.66	**66ah**: 90
7	**2i** (Fg = 3-Cl)	0.7	**66ai**: 90
8	**2k** (Fg = 4-Br)	0.6	**66ak**: 88
9	**2c**(Fg = 4-Me)	0.5	**66ac**: 90
10[c]	**2b** (Fg = 4-OMe)	1.0	**66ab**: 75



11	 **21a**	0.5	**68aa**: 88
12	 **21b**	0.75	**68ab**: 85
13	 **21h**	0.75	**68ah**: 80
14	 **21'a**	0.66	**68'aa**: 85

[a] Reactions were carried out in DMSO (0.5 M) or neat with 1.5 equiv. of **2/21** relative to the **65a** (0.5 mmol) in the presence of 10-mol% of **40e**. [b] Yield refers to the column-purified product. [c] Reaction performed in neat at RT for 1.0 h.

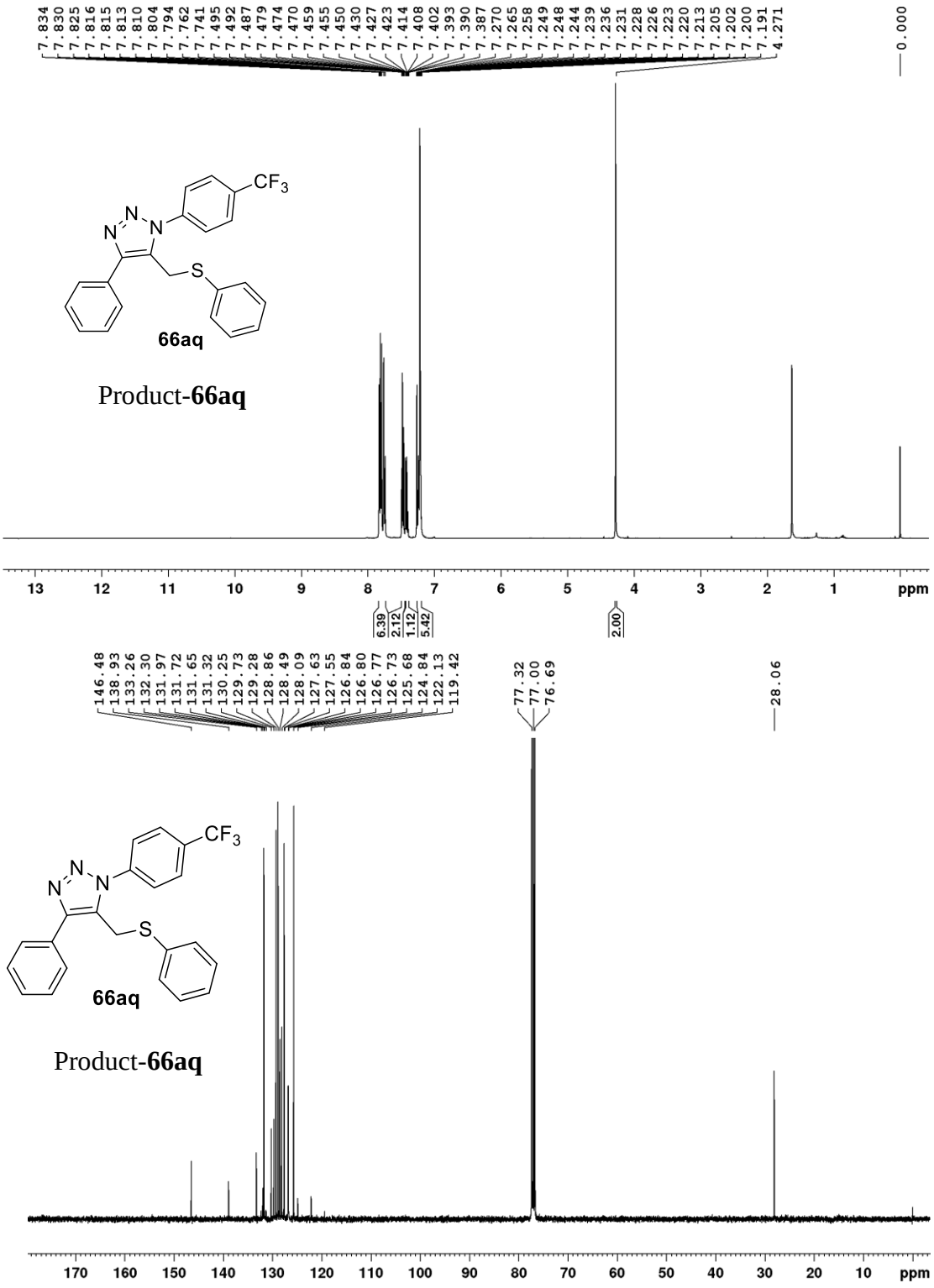


Figure 3: ^{1}H and ^{13}C spectra of the product **66aq**

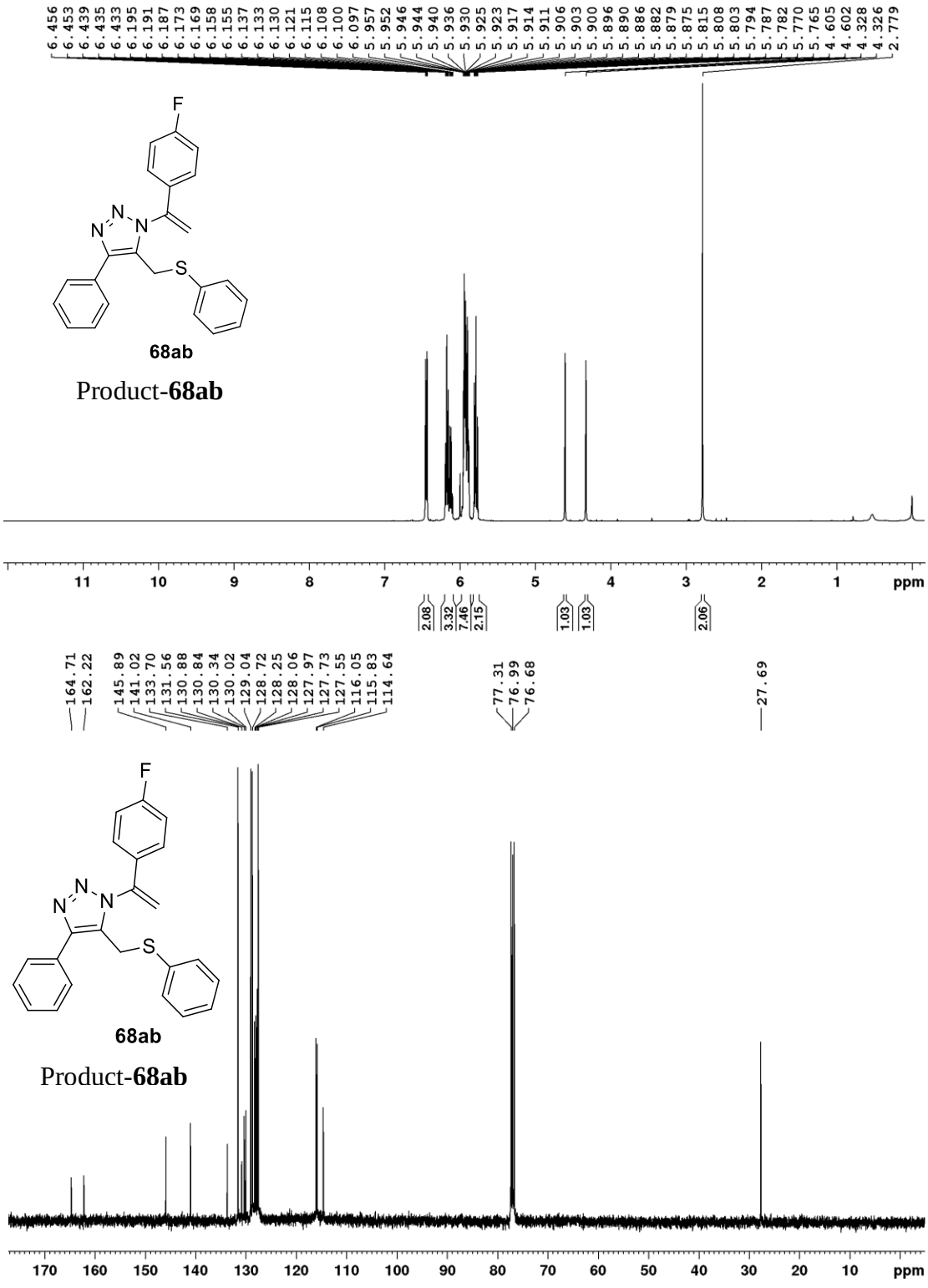


Figure 4: ^{1}H and ^{13}C spectra of the product **68ab**

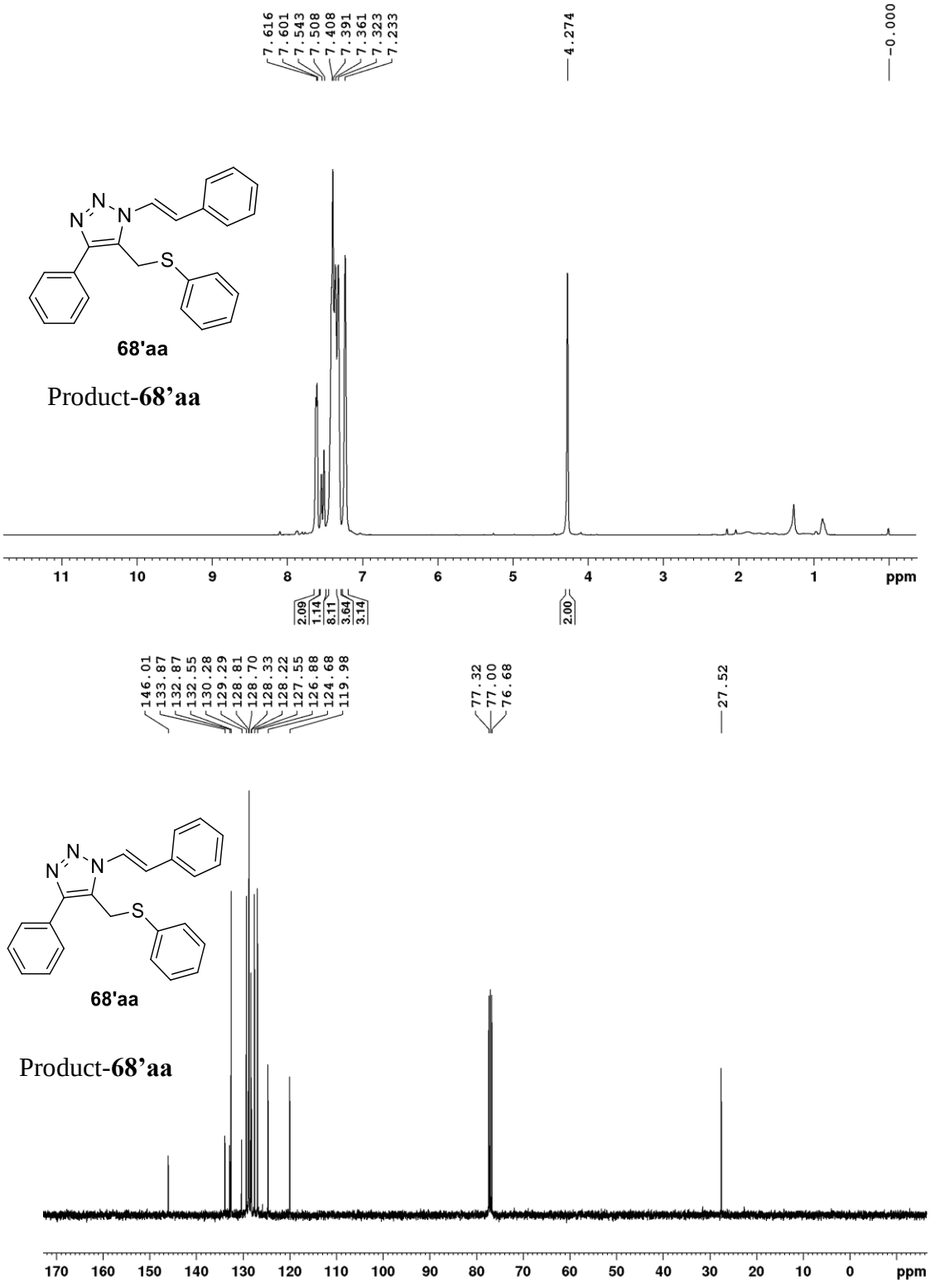
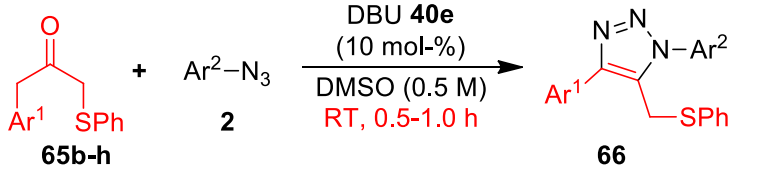


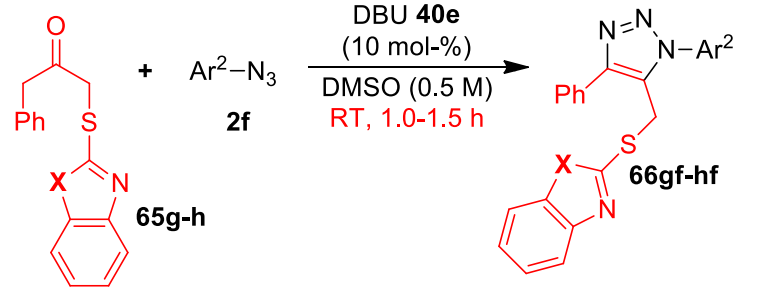
Figure 5: ^{1}H and ^{13}C spectra of the product **68'aa**

After witnessing the reactivity of several aryl and vinyl azides in the enolate-mediated triazole synthesis, it was the turn of the α-(phenylthio)ketones **65**. The selected α-(phenylthio)ketones, **65b-f** and α-(heteroarylthio)ketones, **65g-h** are showcased in Table 3. The α-(phenylthio)ketones, **65b-e** reacted with the aryl azide **2q** comfortably to furnish the triazoles **66bq-eq** in 50-85% yields in 0.5 to 1 hour (Table 3 entries 1-4).

Table 3: α-(Phenylthio)ketones scope[a]



Entry	Ar^1 **65**	Ar^2-N_3 **2**	*t* [h]	Yield [%][b] **66**
1	**65b** (Ar = 4-FC_6H_4)	**2q**	0.5	85 (**66bq**)
2	**65c** (Ar = 2-ClC_6H_4)	**2q**	1.0	81 (**66cq**)
3	**65d** (Ar = 2-BrC_6H_4)	**2q**	0.75	60 (**66dq**)
4	**65e** (Ar = 2-$CH_3C_6H_4$)	**2q**	1.0	50 (**66eq**)
5	**65f** (Ar = 4-$OMeC_6H_4$)	**2q**	1.0	90 (**66eq**)
6	**65f** (Ar = 4-$OMeC_6H_4$)	**2a**	1.0	80 (**66fa**)
7	**65f** (Ar = 4-$OMeC_6H_4$)	**2n**	0.5	85 (**66fn**)
8	**65f** (Ar = 4-$OMeC_6H_4$)	**2r**	0.55	88 (**66fr**)



9	**65g** (X = O)	**2f**	1.5	70 (**66gf**)
10[c]	**65h** (X = S)	**2f**	1.0	70 (**66hf**)

[a] Reactions were carried out in DMSO (0.5 M) with 1.5 equiv. of **2** relative to the **65** (0.5 mmol) in the presence of 10 mol-% of **40e**. [b] Yield refers to the column-purified product. [c] Reaction performed in neat at 50 °C for 1 h.

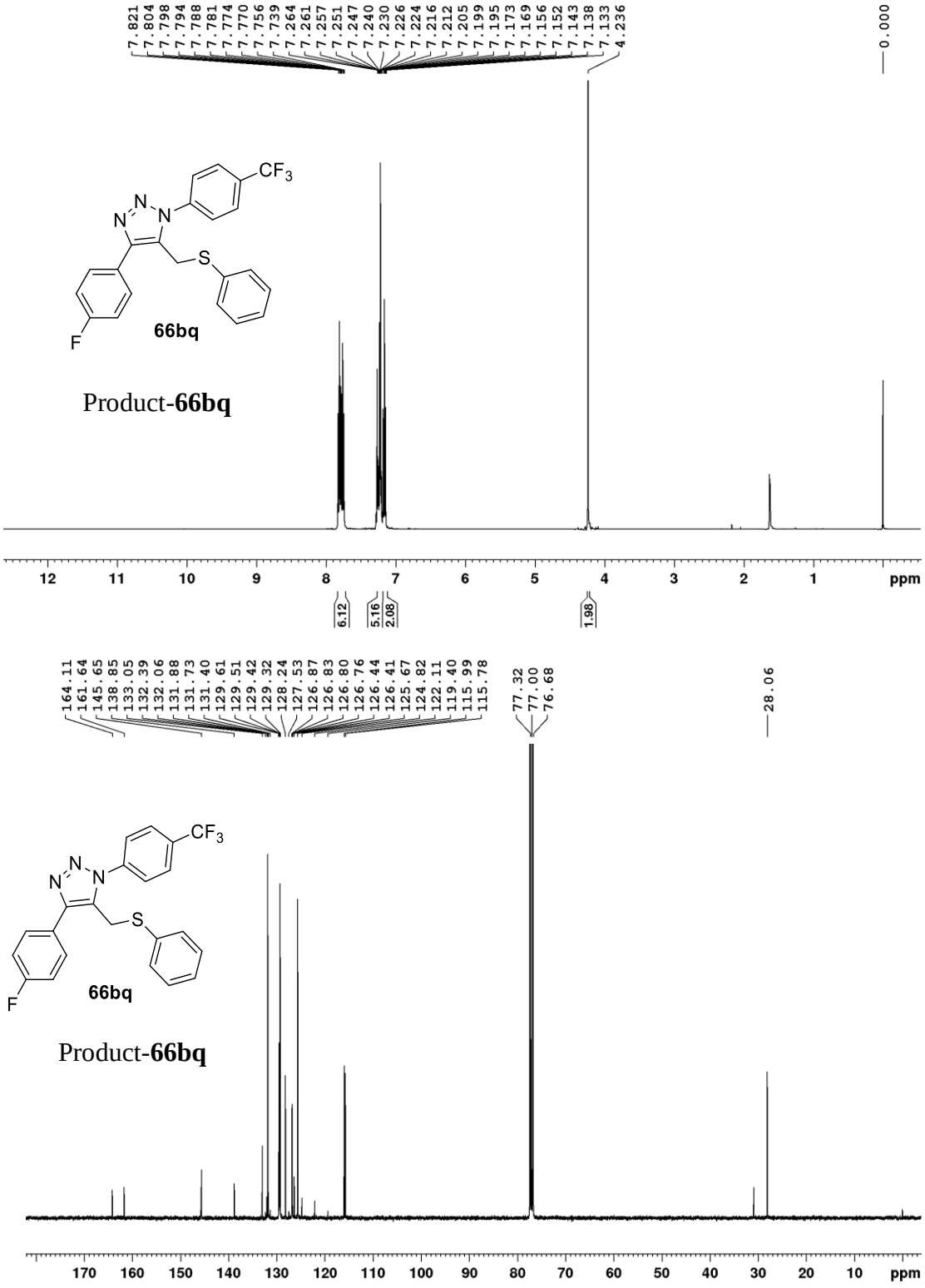


Figure 6: ^{1}H and ^{13}C spectra of the product **66bq.**

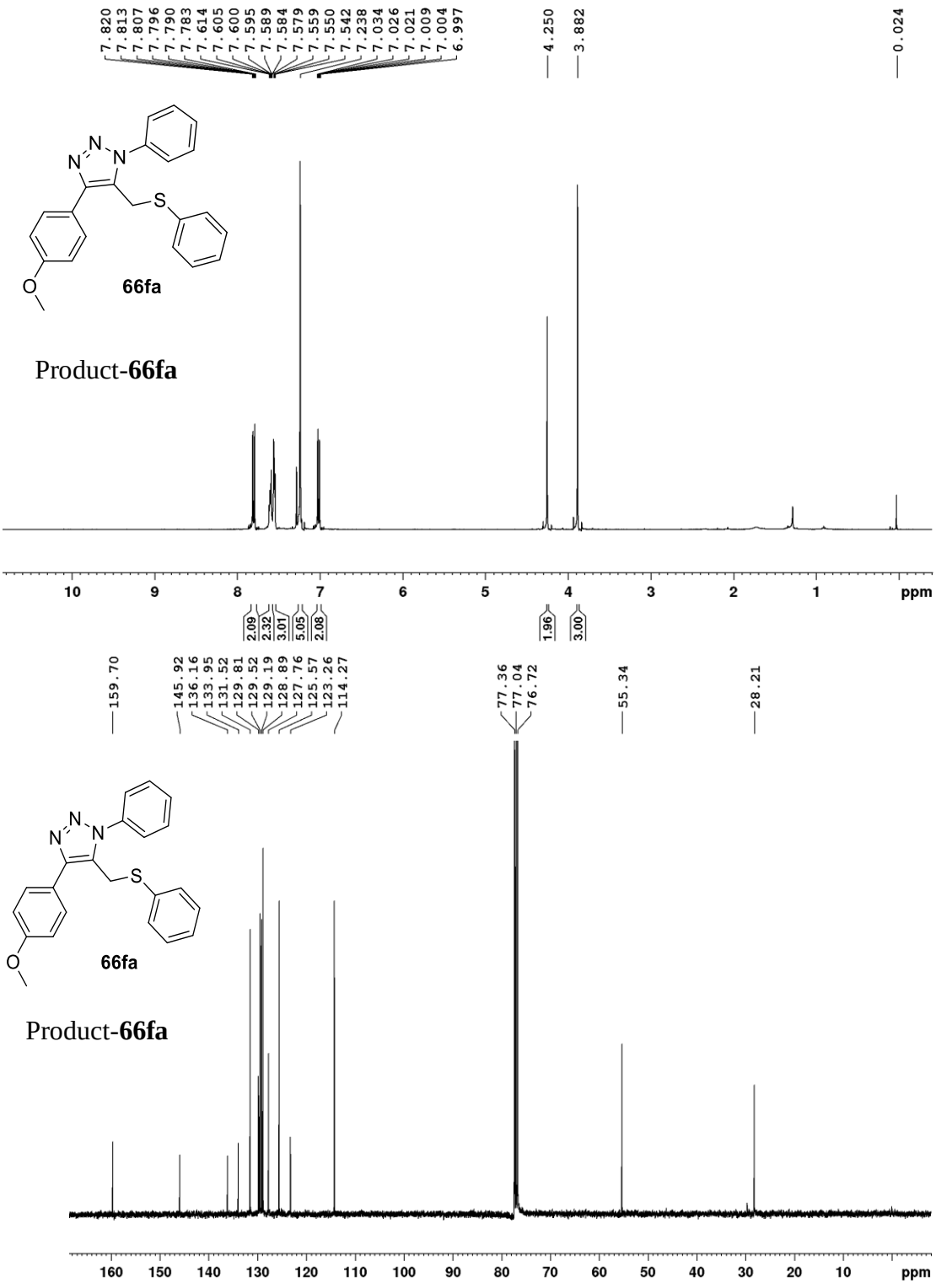
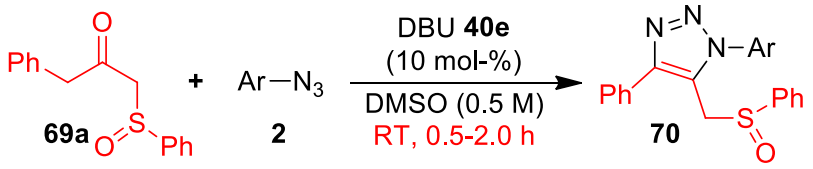


Figure 7: ^{1}H and ^{13}C spectra of the product **66fa**.

Likewise, the α-(phenylthio)ketone, **65f** reacted with the aryl azides **2q**, **2a**, **2n** and **2r** in an excellent fashion and gave the triazoles **66fq**, **66fa, 66fn** and **66fr** in 80-90% yields in 0.5 to 1 hour (Table 3 entries 5-8). As per these results, *para* substitution seems to be very favorable for the reaction in terms of yield. Correspondingly, the α-(heteroarylthio)ketones, **65g-h** also underwent the enolate-mediated triazole formation with the aryl azide **2f**, and resulted in the generation of the triazoles **66gf-hf** in 70% yield in 1.0 to 1.5 hour (Table 3 entries 9-10). Irrespective of the electronic nature of the substituents on the aryl group in the α-(phenylthio)ketones **66b-f**, the reaction was taking place only through the benzylic methylene group and not through the methylene α- to sulfur. Throughout the investigations so far, only one regioselective triazole product was generated under the reaction conditions and particularly, only the benzylic methylene was participating in the triazole formation.

Table 4: α-(Arylsulfinyl)ketones scope[a]



Entry	Ar-N_3 **2**	*t* [h]	Yield [%][b] **70**
1	**2a** (Ar = C_6H_5)	0.5	88 (**70aa**)
2	**2n** (Ar = 4-$NO_2C_6H_4$)	0.5	90 (**70an**)
3	**2r**(Ar = 4-CNC_6H_4)	0.5	88 (**70ar**)
4	**2q**(Ar = 4-$CF_3C_6H_4$)	0.66	85 (**70aq**)
5[c]	**2u**(Ar = $C_6H_5CH_2$)	1.3	65 (**70au**)
6[d]	**2v**(Ar = $C_6H_5CH_2CH_2$)	2.0	55 (**70av**)

[a] Reactions were carried out in DMSO (0.5 M) with 1.5 equiv. of **2** relative to the **69a** (0.5 mmol) in the presence of 10 mol-% of **40e**. [b] Yield refers to the column-purified product. [c] Reaction performed in neat at 25 °C. [d] Reaction performed in neat at 50 °C.

Constantly, a question was pestering in our mind which is, what would it take to direct the reactivity toward the methylene α- to sulfur instead of the benzylic methylene in the α-

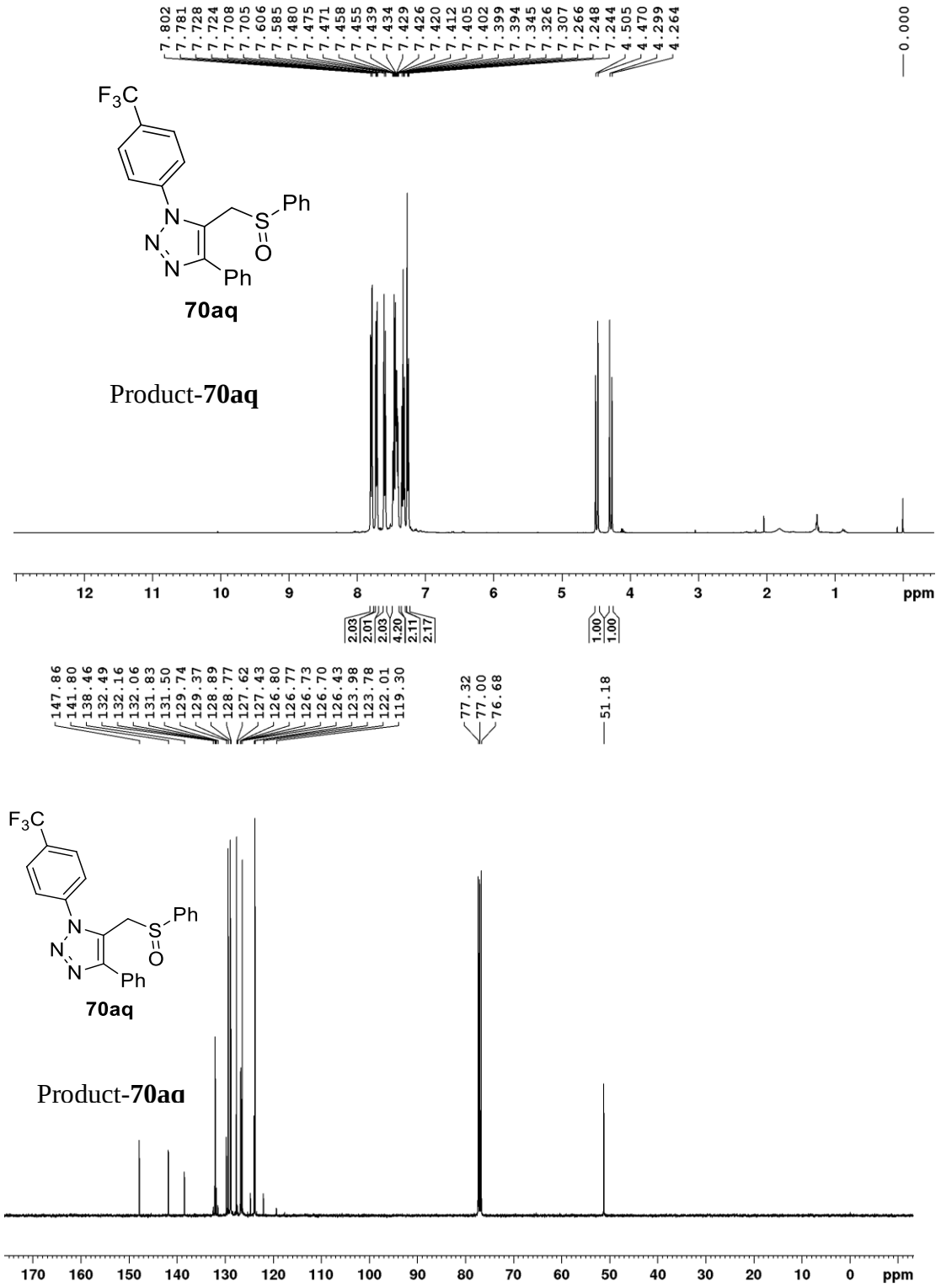


Figure 8: ^{1}H and ^{13}C spectra of the product **70aq**.

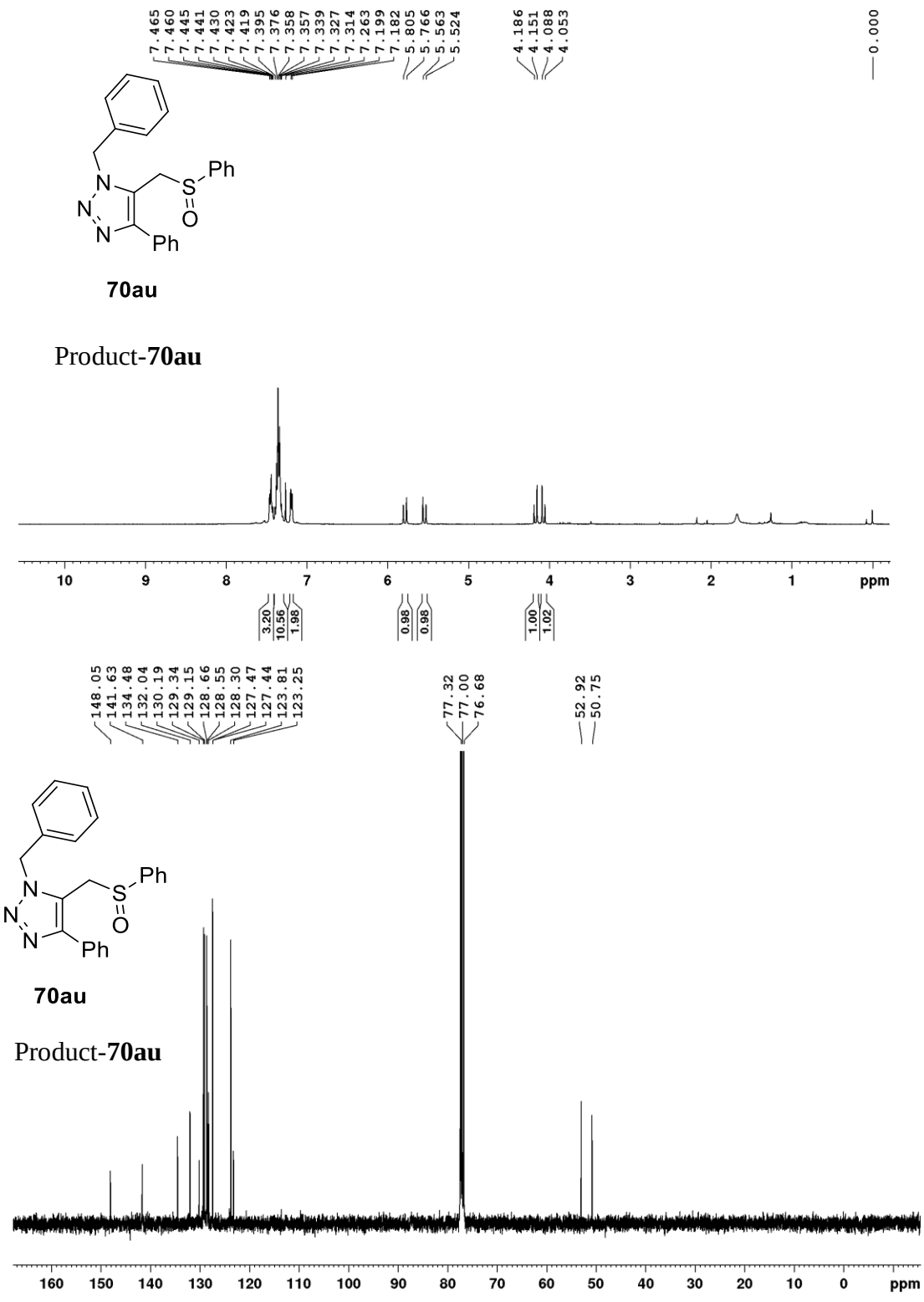
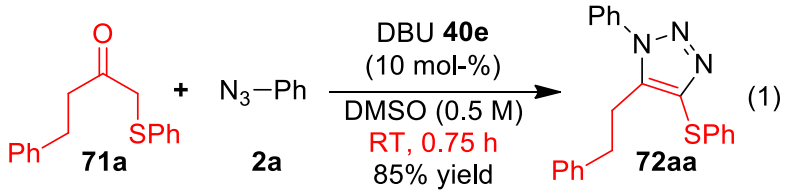


Figure 9: ^{1}H and ^{13}C spectra of the product **70au.**

(arylthio)ketone substrates. Our curiosity drove us to design the α-(arylsulfoxy)ketone substrate **69a** which has a sulfoxide group as a replacement for sulfur. Delightfully, the α-(arylsulfoxy)ketone **69a** reacted with the aryl azides **2a**, **2n,** **2r** and **2q** in a similar way and furnished the triazoles **70aa, 70an**, **70ar** and **70aq** respectively in 85-90% yields in 0.5 to 0.66 hour (Table 4 entries 1-4). The α-(arylsulfoxy)ketone **69a** reacted satisfactorily even with the alkyl azides namely benzyl azide **2u** and phenethyl azide **2v**, under neat condition, to generate the triazoles **70au-av** in 65 and 55% yields, in 1.3 and 2.0 hours respectively (Table 4 entries 5-6). It was intriguing that even the sulfoxide group was insufficient to drive the reaction to go the other way.

Finally, when the benzylic methylene was compromised by moving the phenyl group, one more carbon away from the keto group as in the substrate **71a**, the triazole formation was compelled to happen through the α-carbon as the acidity of α'-carbon dropped, and the triazole **72aa** formed under the optimized conditions in 85% yield. This tuning gave us huge insight into the mechanics of the reaction and facilitated us to pinpoint the force in action.



Equation 1: [3+2]-cycloaddition of 4-phenyl-1-(phenylthio)butan-2-one with arylazide

To understand even further, we designed the reaction substrates, **73a-c** in such a way that both the methylenes (α- and α'-) were benzylic, but differed slightly in their acidity, by controlling the phenyl substitution and executed few control experiments (Table 5). The results were astounding and in harmony with our expectation. For the ketones, **73a** and **73b** the enolate-mediated reaction with phenyl azide **2a** produced a mixture of the two triazoles **74aa** & **75aa**, and **74ba** & **75ba** in the ratio 1:1.56 and 1.14:1 correspondingly. The product ratio more or less reflects the enolate formation ratio in these two cases. When it came to the aryl ketone **73c**, the triazole **74ca** was the sole product formed in 75% yield with >99:1 selectivity. Clearly, the CF_3 group dictated the enolate formation very strongly and thereby directing exclusive formation of the triazole **74ca**

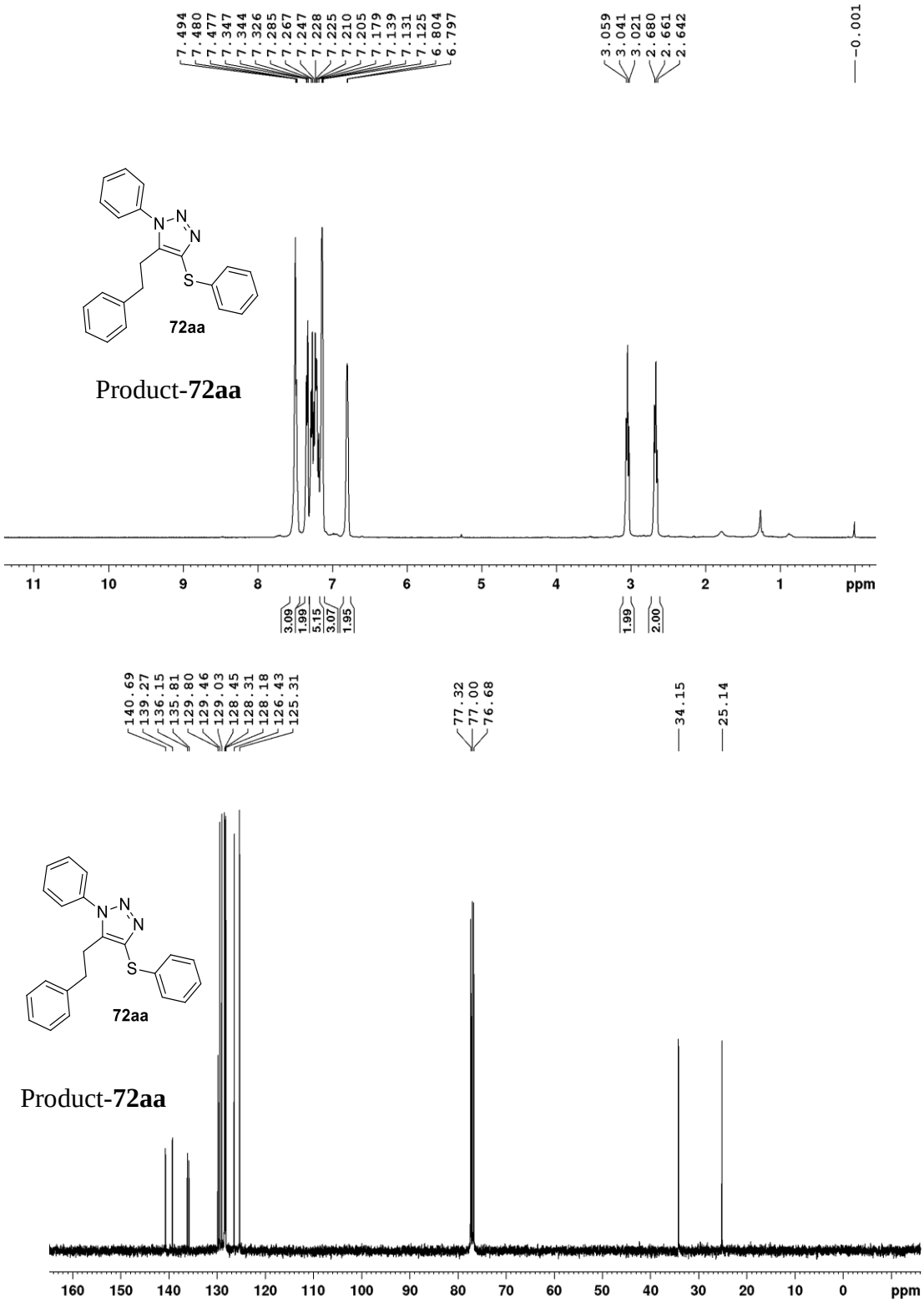


Figure 10: ^{1}H and ^{13}C spectra of the product **72aa**.

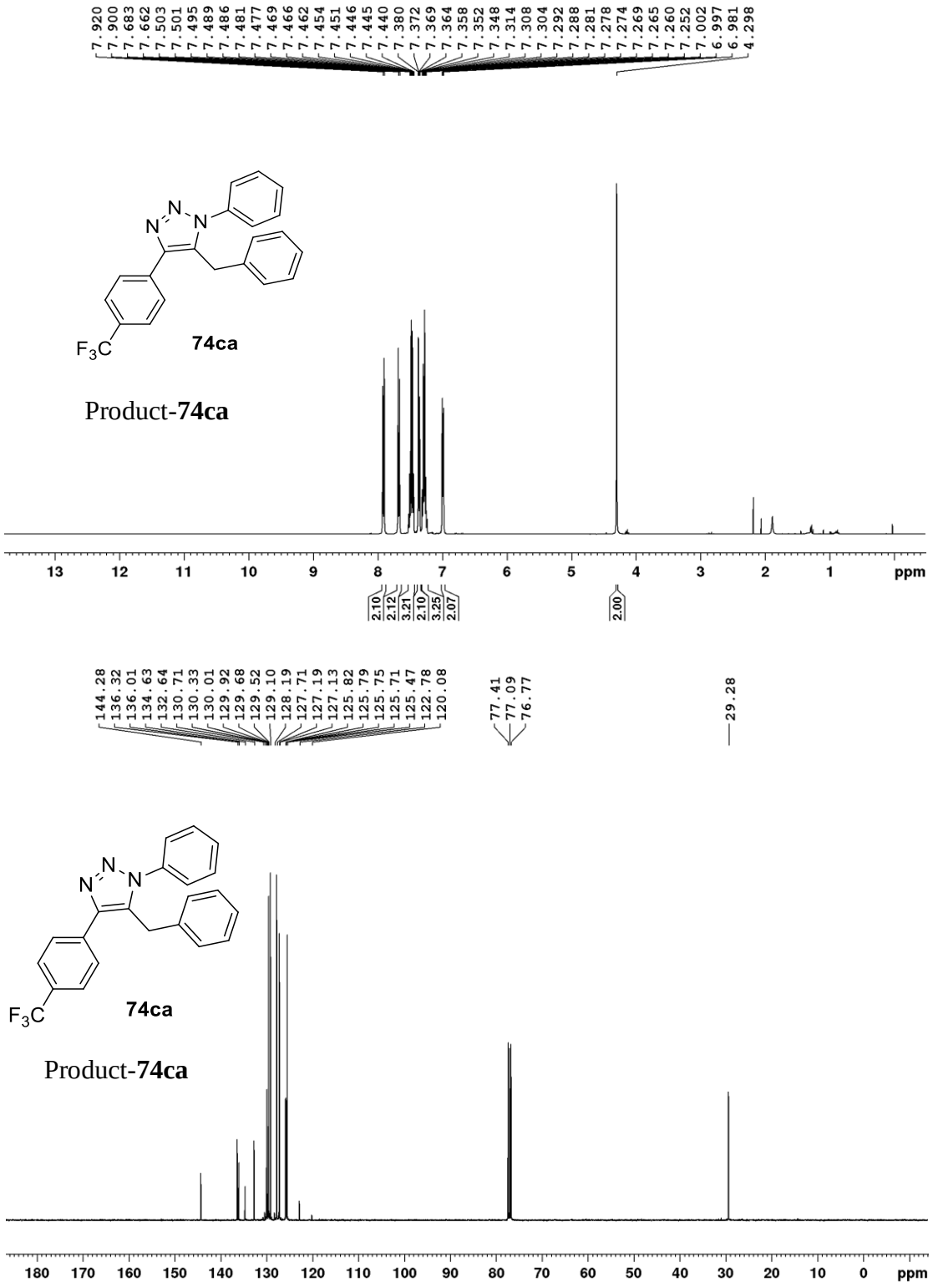
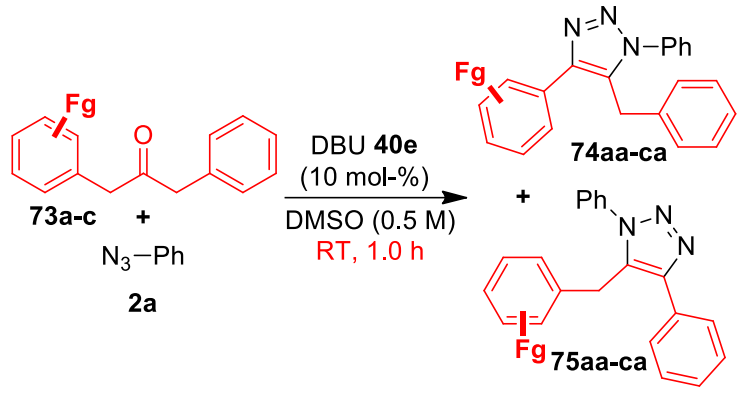


Figure 11: ^{1}H and ^{13}C spectra of the product **74ca.**

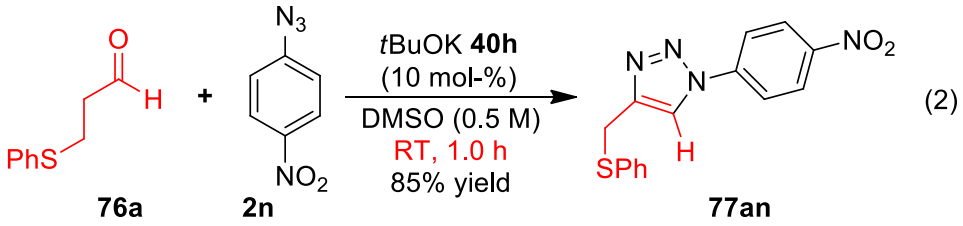
Table 5: Controlled experiments[a]



Entry	Fg **73**	Yield [%][b] **74**	Yield [%][b] **75**	Ratio[c] **74**:**75**
1	**72a**: Fg = 4-OMe	32 (**74aa**)	50 (**75aa**)	1:1.56
2	**72b**: Fg = 4-F	48 (**74ba**)	42 (**75ba**)	1.14:1
3	**72c**: Fg = 4-CF_3	75 (**74ca**)	<1 (**75ca**)	>99:1

[a] Reactions were carried out in solvent (0.5 M) with 1.5 equiv. of **2a** relative to the **73** (0.5 mmol) in the presence of 10-mol% of catalyst **40e**. [b] Yield refers to the column-purified product. [c] Ratio is based on ^{1}H NMR analysis of crude product.

When the competition came down to, between the methylenes adjacent to just sulfur and α- to an aldehyde, the winner was obviously the methylene α- to the aldehyde. Consequently, the β-(phenylthio)aldehyde **76a** reacted with *p*-nitrophenyl azide **2n** in the presence of 10 mol% of *t*BuOK in DMSO at room temperature to furnish the triazole **77an** in 1 hour, proving the fact that the methylene α- to aldehyde is more acidic.



(2)

Equation 2: [3+2]-cycloaddition of β-(phenylthio)aldehyde with arylazide

The (phenylthio)triazole product **66an**, which was obtained earlier (refer Table 2 entry 1), on oxidation with *m*CPBA in DCM at -78 ^{o}C for 0.5 hour, cleanly produced the (phenylsulfoxy)triazole **70an** in 80% yield. The (phenylsulfoxy)triazole **70an** was also generated previously through direct triazole formation (refer Table 4 entry 2). This cross correlation assisted in confirming the structure of both the triazole products **66an** and **70an** unambiguously. The structure and relative stereochemistry of the click products **66** and **70** were established by IR, NMR, and mass analysis and also finally confirmed by correlation with the X-ray crystal structure of **66ar** and **70an** (Figures 12-13)[11d]

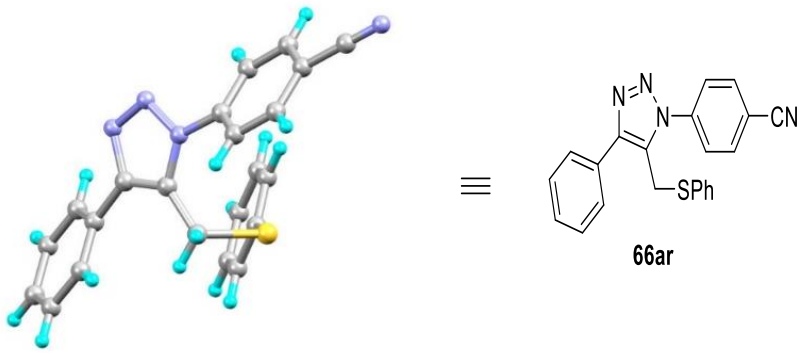


Figure 12: X-ray crystal structure of **66ar**

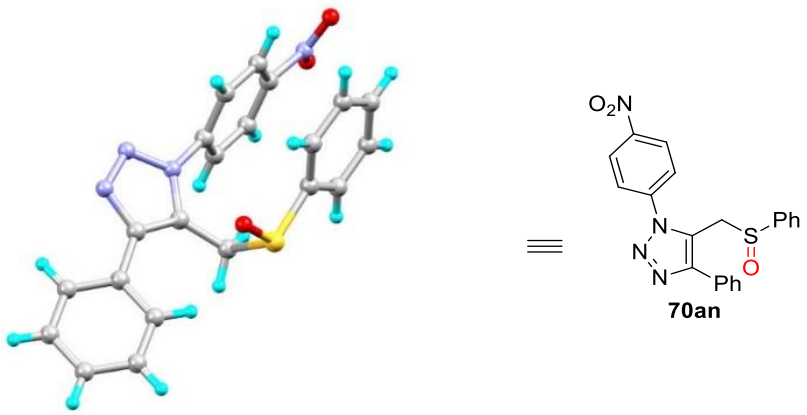
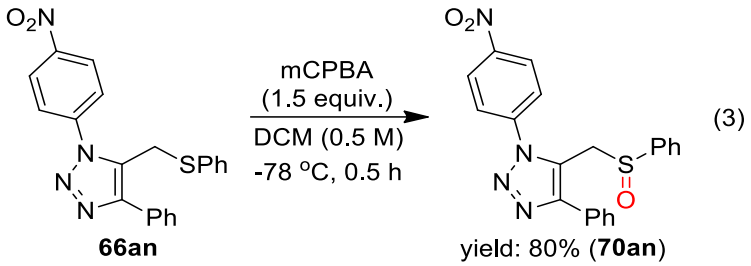


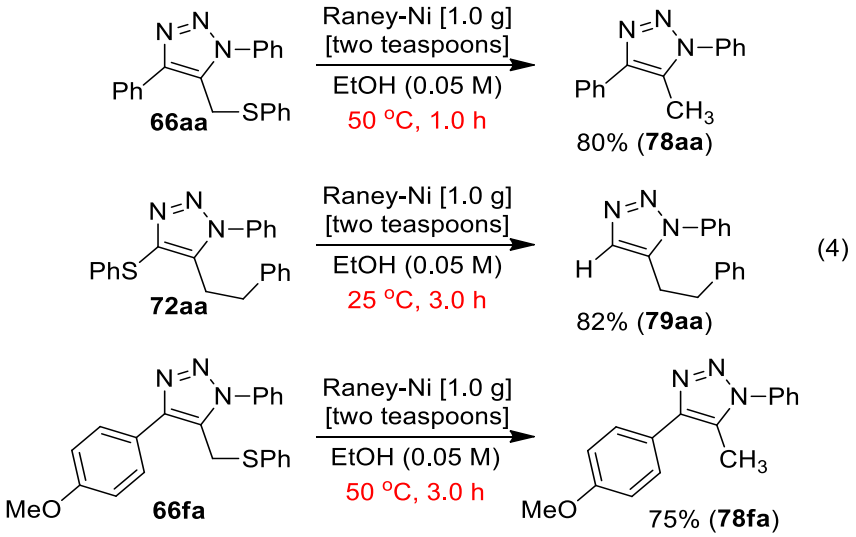
Figure 13: X-ray crystal structure of **70an**



Equation 3: mCPBA oxidation for conversion of Sulfur to sulphoxide

6.4 Synthetic Applications:

In view of applications, we also performed few more conversions (Equation 4). All the (phenylthio)triazoles **66aa**, **72aa** and **66fa** on desulfurization with Raney-Ni in ethanol gave the triazoles **78aa**, **79aa** and **78fa** in very good yields (75-82%). It is worth mentioning that this method would serve as a prominent protocol for arriving at the triazoles **78aa**, **79aa** and **78fa**, which might otherwise be difficult to accomplish.



Equation 4: desulfurization of phenylthiotriazoles with Raney-Ni

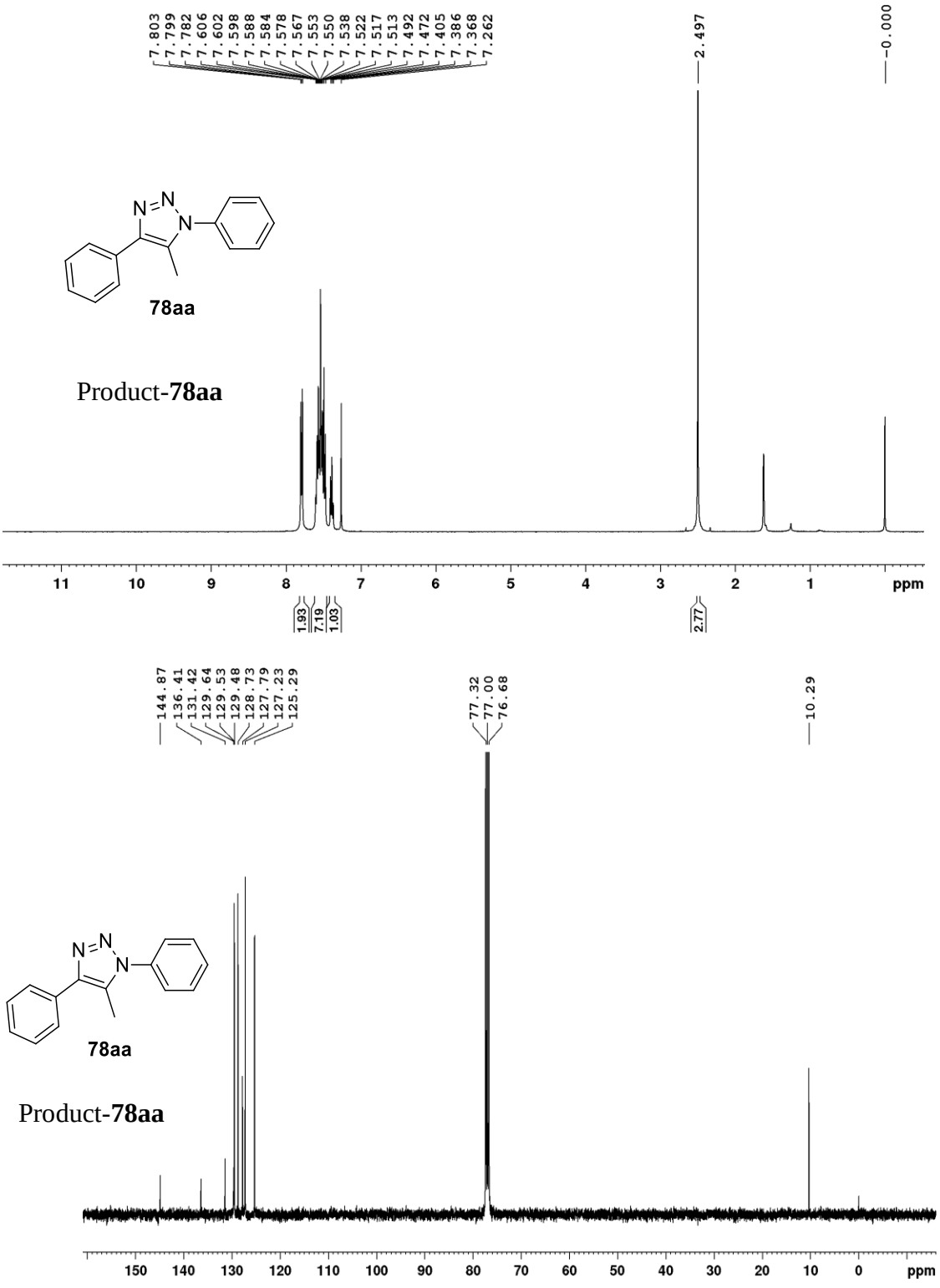
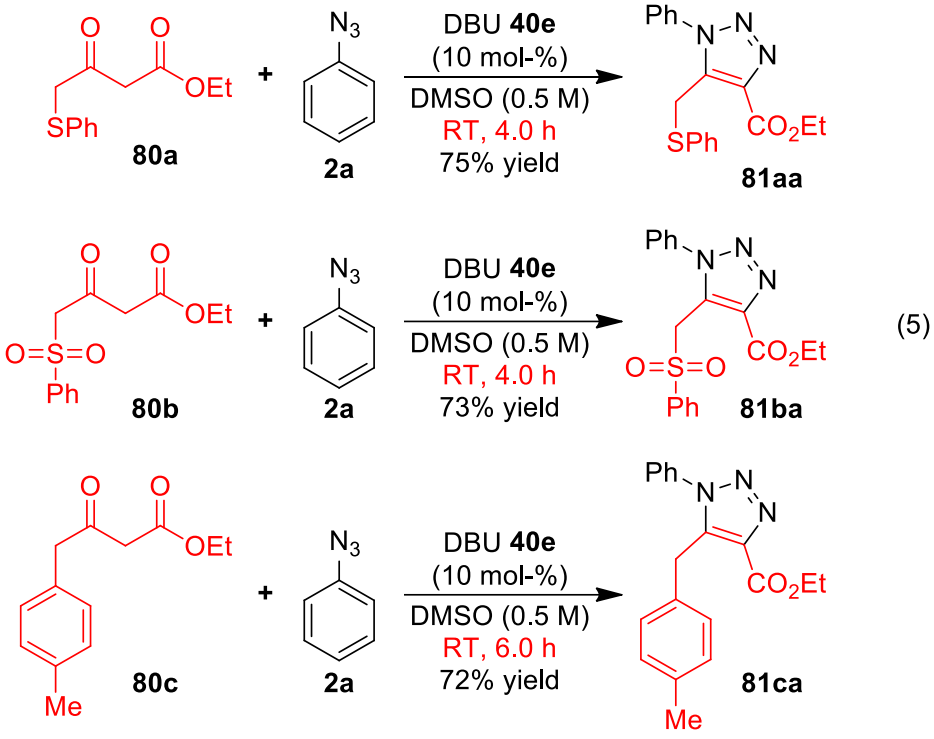


Figure 14: ^{1}H and ^{13}C spectra of the product **78aa**.

Before setting the platform for mechanistic discussion, we wanted to carry out some more reactions, to illuminate and establish the reactivity variance between the methylenes on a few more active methylene compounds, the β-ketoesters **80a-c** that are represented in Equation 5. It is well known that the α-methylene, flanked between the keto and the ester groups in β-ketoesters, are highly acidic Accordingly, in all the β-ketoesters **80a-c**, only the α-methylene predominantly took part in the reaction with phenyl azide **2a** and produced the triazoles **81aa-ca** in 75, 73 and 72% yields respectively. Even the presence of sulfonyl group in **80b** was insufficient in impacting the rise in acidity of the γ-methylene, significant enough, so as to make it participate in the reaction.



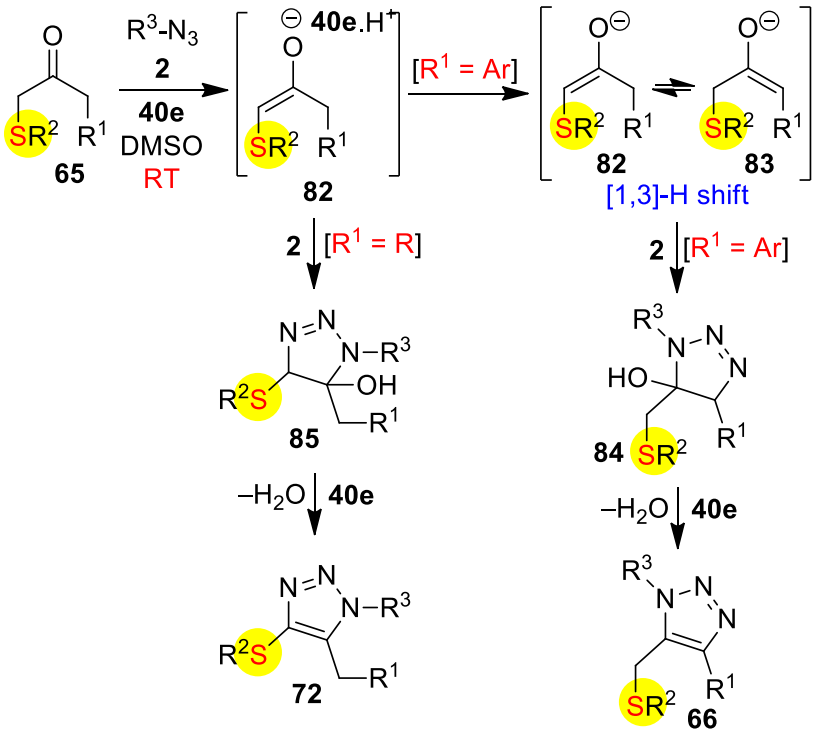
(5)

Equation 5: [3+2]-cycloaddition of β-ketoesters with arylazide

6.5 Reaction mechanism:

A conceivable mechanism proposed based on these present control experiment studies is presented in Scheme 2. Initially, the α-(arylthio)ketone **65** in the presence of DBU **40e**, forms the enolate **82** arising from the α-methylene group. Subsequently, if R^1 is aryl group, then a [1, 3]-hydride shift occurs to generate the enolate **83**, which is believed to exist in dynamic equilibrium with the

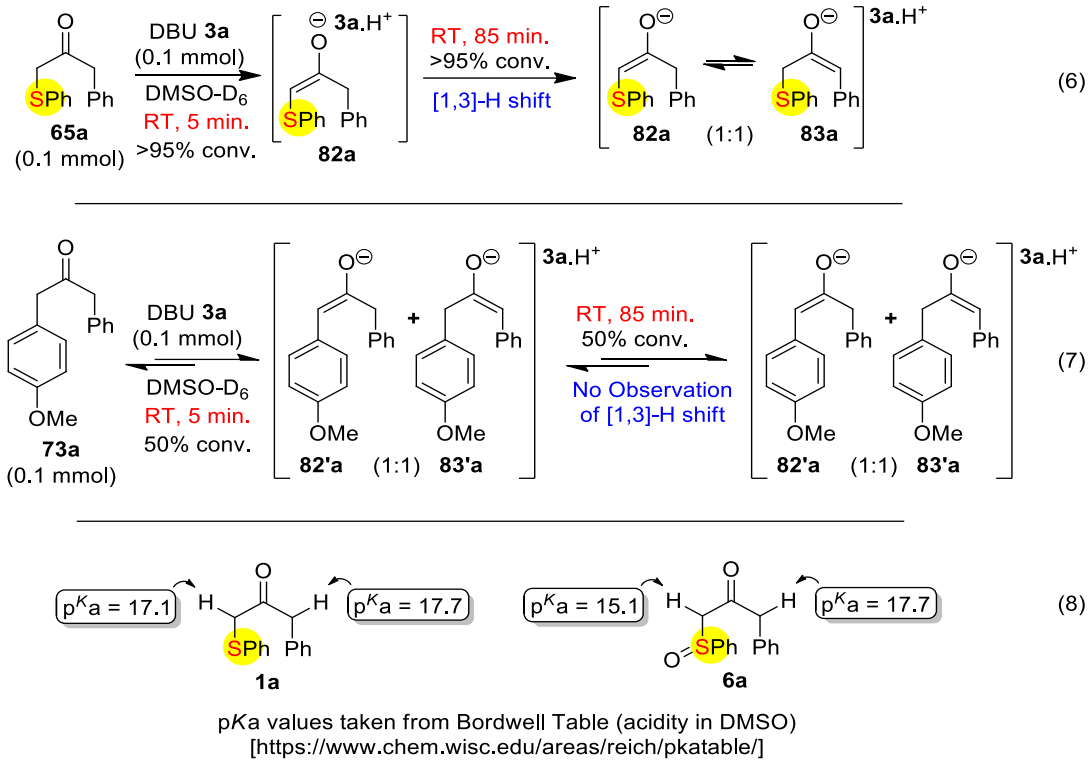
enolate **82**. With R^1 as aryl group, predominantly, the enolate **83** reacts with the aryl azide **2**, to form the intermediate **84**, which generates the triazole **66** after the elimination of water. And the equilibrium ought to have been shifting toward the right side gradually, as and when the enolate **83** reacts, as is evidenced from the >99:1 resioselectivity of the triazole formed. On the other hand, if R^1 is alkyl group, then the enolate **82** instantaneously adds to the aryl azide **2**, to generate the intermediate **85**, which after water elimination produces the triazole **72.**



Scheme 2: Reaction mechanism

Additional support for the mechanism was also obtained by conducting some NMR controlled experiments. When DBU **40e** was added to α-(phenylthio)ketone **65a** in DMSO-d_6, the α-methylene protons disappeared completely within 5 min, proving that the enolate **82a** is formed first (Equation 6). After 85 min, the NMR showed absence of α'-methylene protons too, which is evidence for the [1,3]-hydride shift and the existence of dynamic equilibrium. In the same way, on addition of DBU **40e** to the α-arylketone **73a** in DMSO-d_6, within 5 min, the NMR showed the presence of the enolates **82'a** and **83'a** in a 1:1 ratio with only 50% conversion (Equation 7). Even after 85 min, the NMR did not change and there was no observation of any [1,3]-hydride shift and

the same ratio of the enolates **82'a** and **83'a** maintained. The pKa values of the α- and α'-methylene protons of α-(phenylthio)ketone **65a** and α-(phenylsulfoxide)ketone **69a** are illustrated in Equation 8 and are in coherence with the observed reactivity pattern



Equation 6 to 8: NMR experiments for [1, 3]-hydride shift**.**

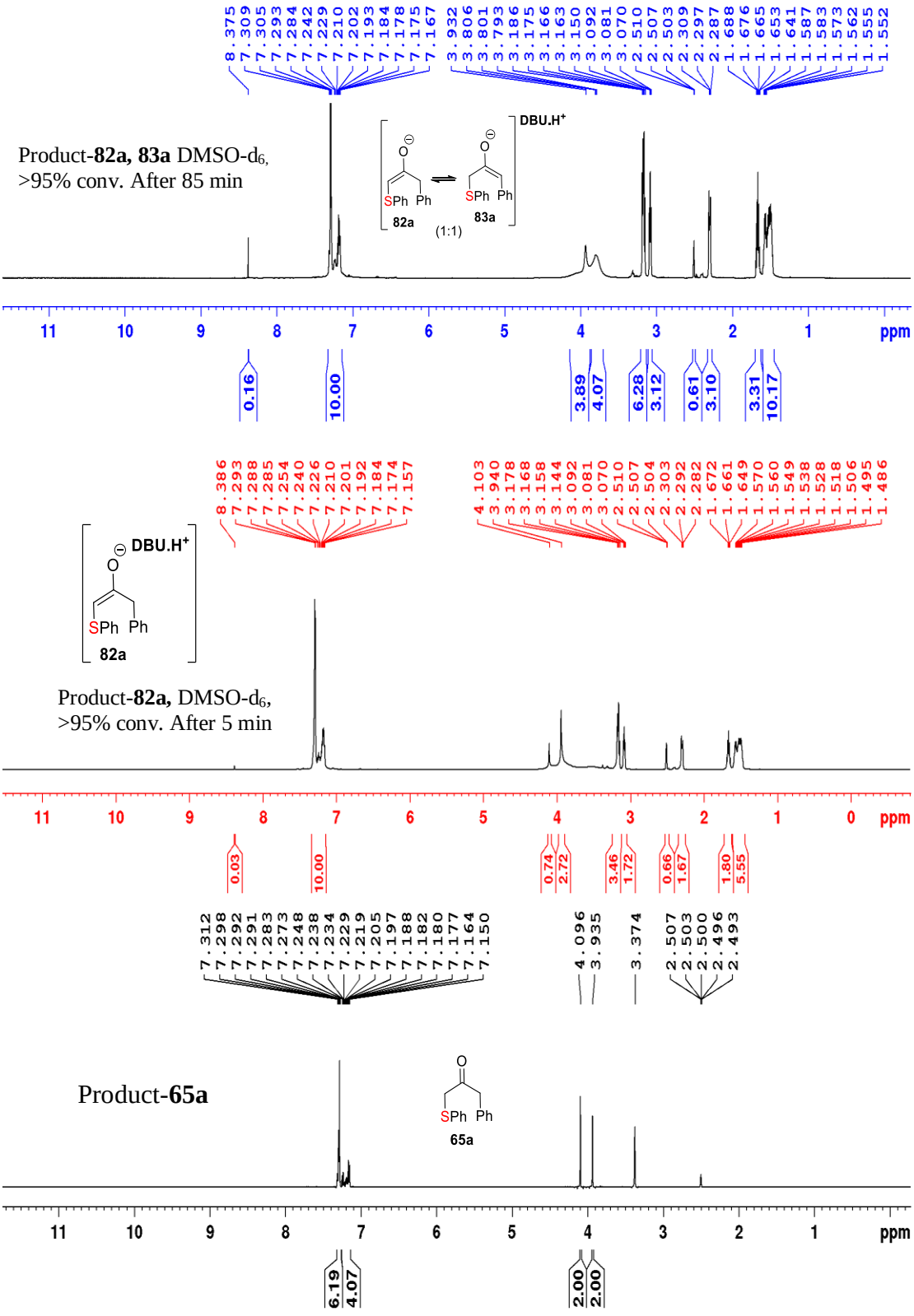


Figure 15: ^{1}H spectra of the product **65a** in presence of DBU

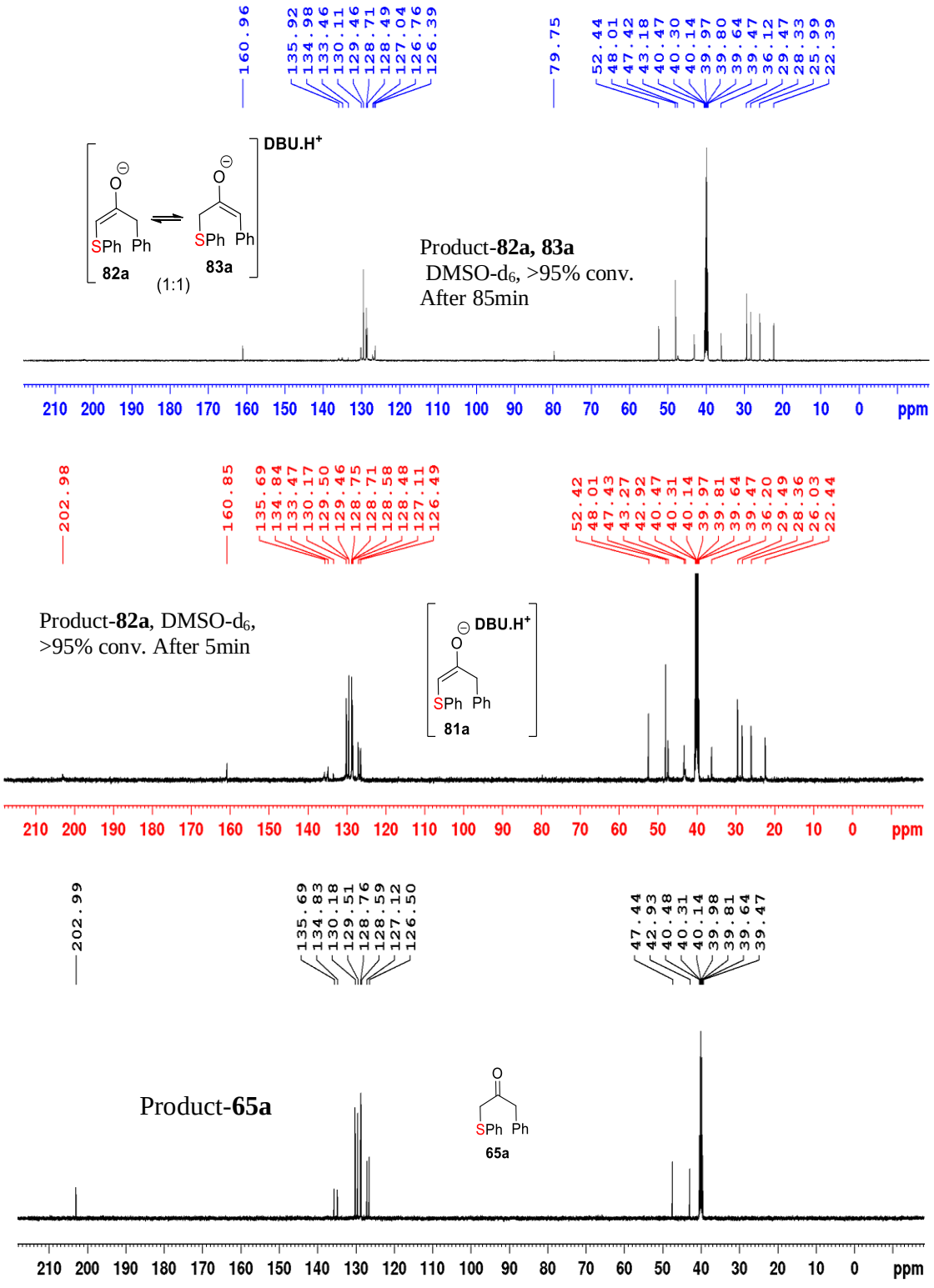


Figure 16: ^{13}C spectra of the product **65a** in presence of DBU

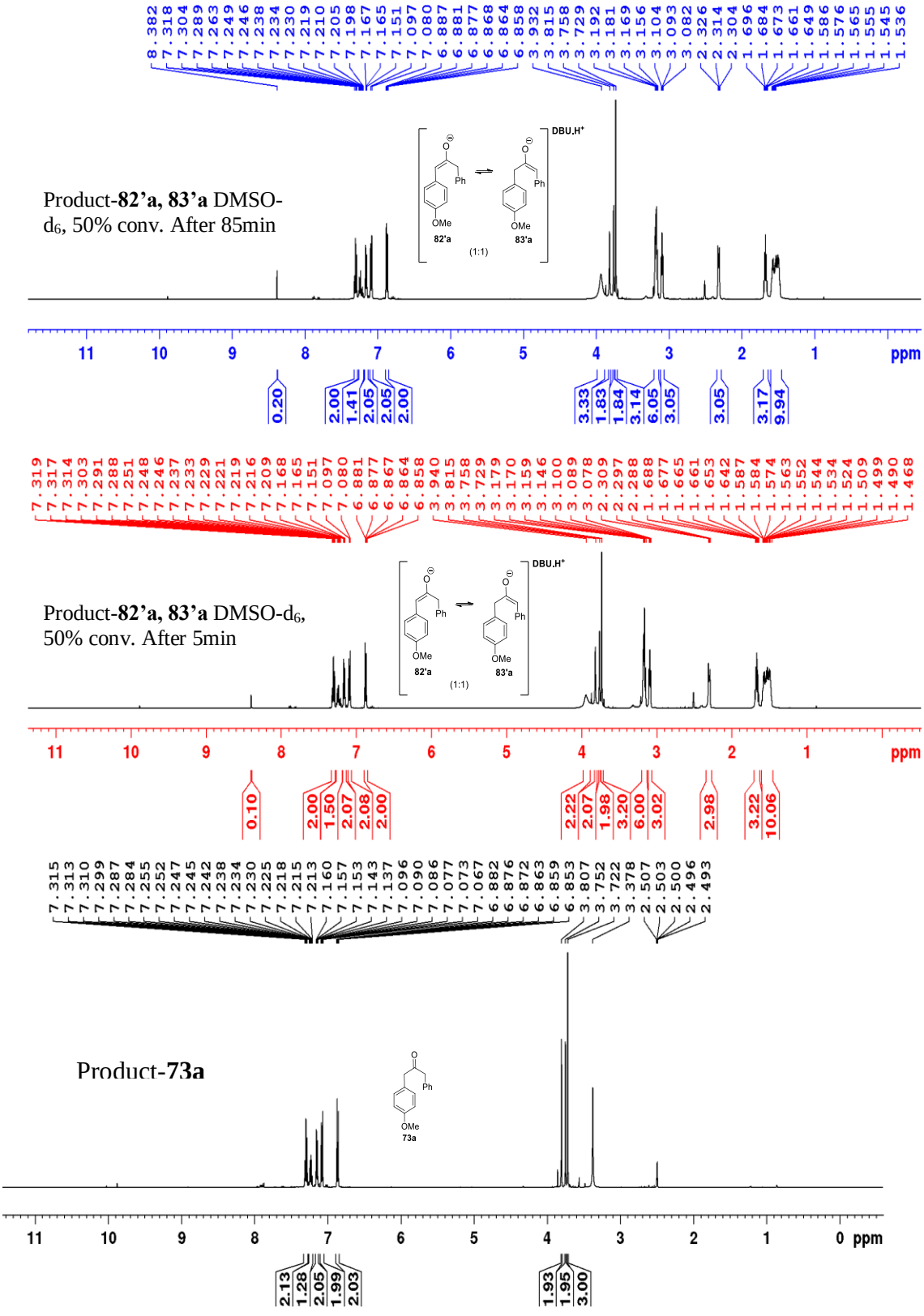


Figure 17: ^{1}H spectra of the product **73a** in presence of DBU

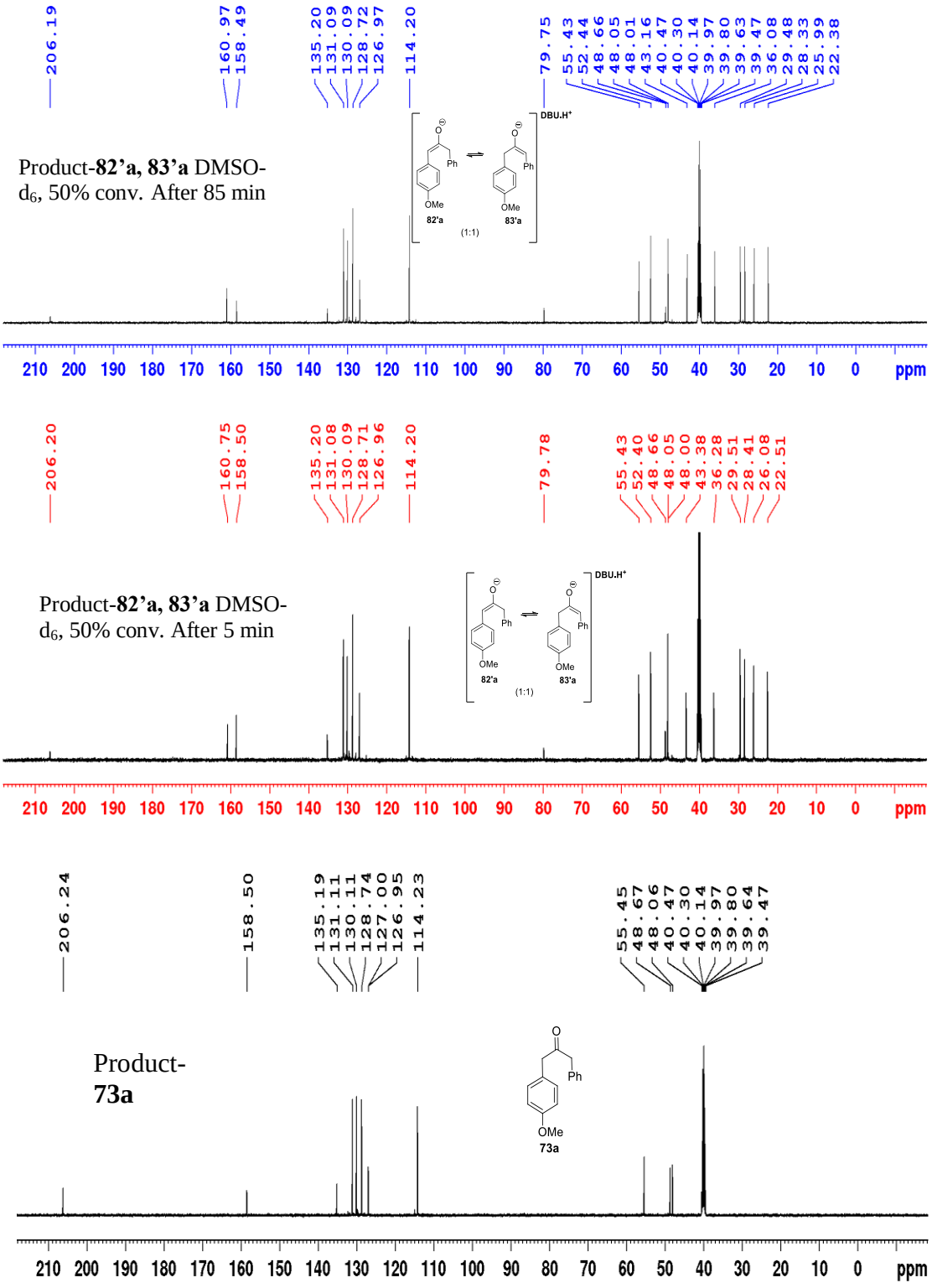


Figure 18: ^{13}C spectra of the product **73a** in presence of DBU

6.6 Conclusion:

We demonstrated the tertiary amine-catalyzed organocatalytic selective enolization for the synthesis of functionally rich 1,4-diaryl-5-arylthiomethyl-1,2,3-triazoles from readily available non-symmetrical thioketones and different azides. We have explained the high regioselectivity of click reaction through [1,3]-H shift during the enolization step and rate/regioselectivity of the click reaction is depending on the kinetic versus thermodynamic enolates generated in situ. Furthermore, we have demonstrated the medicinal applications of thiomethyl-1,2,3-triazoles.

7.0 Experimental Section:

General Methods:

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

7.1 General Experimental Procedure for An Organocatalytic Vinyl Azide-Carbonyl [3+2]-Cycloaddition: High-yielding Synthesis of Fully Decorated *N*-Vinyl-1,2,3-Triazoles.

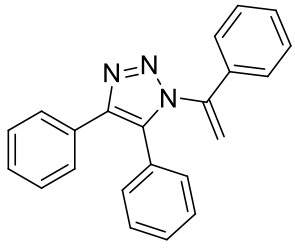
Procedure A: General Procedure for the DBU-catalyzed [3+2]-Cycloaddition Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.03 mmol of catalyst **40e** in DMSO (1.0 mL), was added 0.36 mmol of vinylazide **22** and 0.3 mmol of carbonyl compound **38/21** and the reaction mixture was stirred at 25 °C for 1-5 h. The crude reaction mixture was worked up with

aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure click products **39/41/42/43** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General Procedure for the *t*BuOK-catalyzed [3+2]-Cycloaddition Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.03 mmol of *t*BuOK in DMSO (1.0 mL), was added 0.36 mmol of vinyl azide **22** and 0.3 mmol of carbonyl compound **21h** and the reaction mixture was stirred at 25 °C for the time indicated in Tables 1-4. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure click product **41ha** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: Procedure for hydrogenation of [3+2]-cycloaddition products 39aa and 42aa: In a 10 mL round bottomed flask, a solution of 0.3 mmol of **39aa** or **42a**a in dry methanol (3 mL) was taken followed by addition of 30 mg of Pd/C (10 mol%). The reaction mixture was purged with nitrogen gas followed by hydrogen gas. The reaction mixture was allowed to stir at 25 °C under the pressure of a hydrogen gas filled balloon for 1 h. The crude reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The concentrate was subjected to column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain the pure compounds **44aa** and **46aa** respectively.

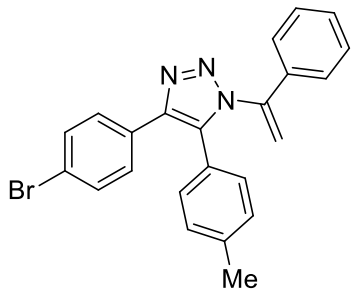
4,5-Diphenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 138-140 °C; IR (Neat): ν_{max} 3049, 2920, 2848, 1737, 1680, 1629, 1572, 1500, 1443, 1267, 1076, 1014, 983, 823, 766 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.62 (2H, m), 7.31-7.20 (9H, m), 7.16-7.14 (2H, m), 7.11-7.09 (2H, m), 5.81 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.35 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$,



39aa

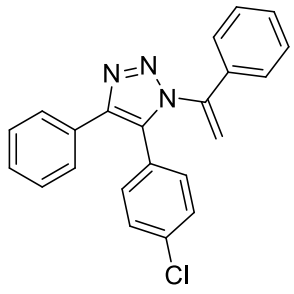
DEPT-135) δ 144.2 (C), 142.7 (C), 135.2 (C), 134.3 (C), 130.7 (C), 129.7 (2 x CH), 129.26 (CH), 129.16 (CH), 128.6 (2 x CH), 128.4 (4 x CH), 127.9 (CH), 127.5 (C), 127.1 (2 x CH), 125.9 (2 x CH), 114.8 (CH_2); HRMS m/z 324.1503 ($M + H^+$), calcd for $C_{22}H_{17}N_3H$ 324.1501.

4-(4-Bromophenyl)-1-(1-phenylvinyl)-5-(*p*-tolyl)-1*H*-1,2,3-triazole (39ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 99-101 °C; IR (Neat): ν_{max} 2920, 2854, 1638, 1484, 1369, 1260, 1073, 980, 904 and 739 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.50 (2H, td, *J* = 8.5, 1.0 Hz), 7.40 (2H, td, *J* = 8.5, 1.0 Hz), 7.27-7.21 (3H, m), 7.11-7.10 (2H, m), 7.06 (2H, d, *J* = 8.5 Hz), 7.03-7.01 (2H, m), 5.81 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.48 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 2.30 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 142.9 (C), 142.5 (C), 139.4 (C), 135.1 (C), 134.6 (C), 131.5 (2 x CH), 129.8 (C), 129.5 (2 x CH), 129.4 (2 x CH), 129.2 (CH), 128.5 (2 x CH), 128.4 (2 x CH), 125.8 (2 x CH), 124.0 (C), 121.8 (C), 114.8 (CH_2), 21.2 (CH_3); HRMS m/z 416.0766 ($M + H^+$), calcd for $C_{23}H_{18}BrN_3H$ 416.0762.



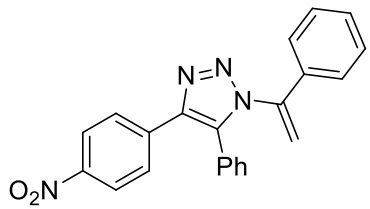
39ba

5-(4-Chlorophenyl)-4-phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 108-110 °C; IR (Neat): ν_{max} 3062, 2914, 1634, 1604, 1572, 1500, 1478, 1440, 1363, 1265, 1089, 908, 837, 777, and 591 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.60 (2H, br d, *J* = 7.0 Hz), 7.30 -7.27 (3H, m), 7.25 -7.20 (5H, m), 7.08 (4H, d, *J* = 8.5 Hz), 5.83 (1H, s, olefinic-*H*), 5.54 (1H, s, olefinic-*H*), ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.3 (C), 142.5 (C), 135.3 (C), 134.9 (C), 133.0 (C), 130.9 (2 x CH), 130.3 (C), 129.4 (CH), 128.9 (2 x CH) 128.49 (2 x CH), 128.50 (2 x CH), 128.0 (CH), 127.0 (2 x CH), 125.9 (C), 125.7 (2 x CH), 114.9 (CH_2); HRMS m/z 358.1111 ($M + H^+$), calcd for $C_{22}H_{16}ClN_3H$ 358.1111.



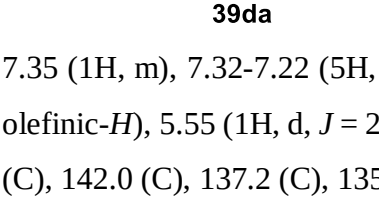
39ca

4-(4-Nitrophenyl)-5-phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 117-119 °C; IR (Neat): ν_{max} 2926, 2849, 1600, 1512, 1446, 1331, 1276, 1112, 1019, 980, 905, 854 and 772 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.15 (2H, td, *J* = 9.0, 2.0 Hz), 7.80 (2H, td, *J* = 9.5, 2.0 Hz), 7.39-7.35 (1H, m), 7.32-7.22 (5H, m), 7.17-7.14 (2H, m), 7.11-7.08 (2H, m), 5.85 (1H, d, *J* = 2.0 Hz, olefinic-*H*), 5.55 (1H, d, *J* = 2.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.1 (C), 142.4 (C), 142.0 (C), 137.2 (C), 135.9 (C), 134.9 (C), 129.8 (CH), 129.52 (2 x CH), 129.46 (CH), 129.0 (2 x CH), 128.5 (2 x CH), 127.3 (2 x CH), 126.7 (C), 125.8 (2 x CH), 123.8 (2 x CH); 115.2 (CH_2); HRMS m/z 369.1350 (M + H), calcd for $C_{22}H_{16}N_4O_2H$ 369.1352.



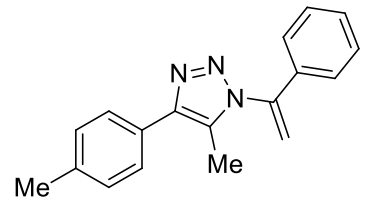
39da

5-Methyl-4-phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow liquid; IR (Neat): 3034, 2920, 2848, 1639, 1489, 1438, 1371, 1262, 1117, 1076, 1019, 973 and 689 cm; ^1H NMR ($CDCl_3$, 400 MHz)) δ 7.78-7.76 (2H, br d, *J* = 6.5 Hz), 7.49-7.45 (2H, br t, *J* = 6.5 Hz), 7.40-7.35 (4H, m), 7.24-7.21 (2H, m), 6.00 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 5.64 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.4 (C), 142.4 (C), 134.7 (C), 131.3 (C), 130.1 (C), 129.7 (CH), 128.9 (2 x CH), 128.7 (2 x CH), 127.7 (CH), 127.1 (2 x CH), 125.7 (CH), 114.5 (CH_2), 9.8 (CH_3); HRMS m/z 284.1164 (M + Na^+), calcd for $C_{17}H_{15}N_3Na$ 284.1164.



39ea

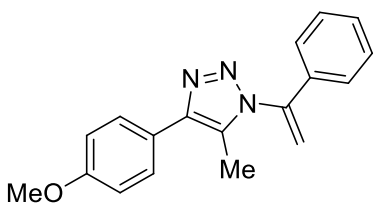
5-Methyl-1-(1-phenylvinyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (39fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a liquid; IR (Neat): ν_{max} 2920, 2859, 2355, 1637, 1577, 1500, 1451, 1396, 1363, 1259, 1111, 1007, 974, 815, 766, 689 and 609 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (2H, br d, *J* = 8.0 Hz), 7.38-7.36 (3H, m), 7.27 (2H, br d, *J* = 8.0 Hz), 7.23-7.21 (2H, m), 5.98 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.63 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 2.40 (3H, s, Ar-C*H*$_3$), 2.22 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.4 (C), 142.5 (C), 137.5 (C), 134.8 (C), 129.7 (C), 129.6 (CH),



39fa

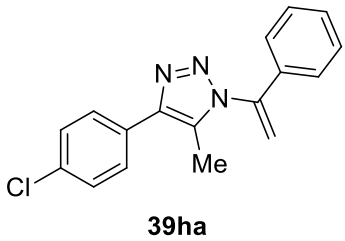
129.4 (2 x CH), 128.9 (2 x CH), 128.5 (C), 127.0 (2 x CH), 125.7 (2 x CH), 114.4 (CH_2), 21.2 (CH_3, Ar-*C*H_3), 9.8 (CH_3); HRMS m/z 276.1507 (M + H^+), calcd for $C_{18}H_{17}N_3H$ 276.1501.

4-(4-Methoxyphenyl)-5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid; IR (neat): ν_{max} 2930, 2832, 1696, 1613, 1510, 1365, 1247, 1107, 1024, 906, 771, 694 and 601 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (2H, td, *J* = 9.5, 2.0 Hz), 7.40-7.36 (3H, m), 7.23-7.21 (2H, m), 7.00 (2H, td, *J* = 9.5, 2.0 Hz), 5.98 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.63 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 3.85 (3H, s, Ar-OC*H*$_3$), 2.20 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.2 (C), 144.3 (C), 142.4 (C), 134.8 (C), 129.6 (CH), 129.3 (C), 128.9 (2 x CH), 128.4 (2 x CH), 125.7 (2 x CH), 123.9 (C), 114.3 (CH_2), 114.1 (2 x CH), 55.3 (CH_3, O*C*H_3), 9.7 (CH_3); HRMS m/z 292.1453 (M + H^+), calcd for $C_{18}H_{17}N_3OH$ 292.1450.



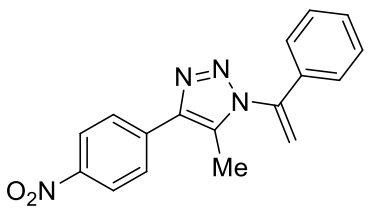
39ga

4-(4-Chlorophenyl)-5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ha): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 65-67 °C; IR (neat): ν_{max} 3057, 2920, 2849, 1649, 1490, 1446, 1364, 1254, 1090 , 1013, 975, 909, 838, and 778 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (2H, td, *J* = 8.5, 2.5 Hz), 7.43 (2H, td, *J* = 8.5, 2.5 Hz), 7.39-7.35 (3H, m), 7.22-7.20 (2H, m), 6.00 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.62 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 2.23 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.3 (C), 142.2 (C), 134.6 (C), 133.6 (C), 130.2 (C), 129.8 (C), 129.7 (CH), 128.9 (2 x CH), 128.8 (2 x CH), 128.2 (2 x CH), 125.6 (2 x CH), 114.6 (CH_2), 9.8 (CH_3); HRMS m/z 296.0954 (M + H^+), calcd for $C_{17}H_{14}ClN_3H$ 296.0955.



39ha

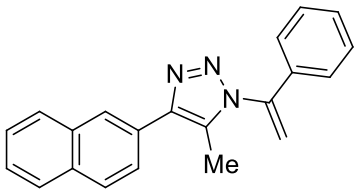
5-Methyl-4-(4-nitrophenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ia): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 119-121 °C; IR (Neat): ν_{max} 2910, 2843, 1634, 1605, 1506, 1336, 1265, 1101, 1019, 909, 849, and 712 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.33 (2H, br d, *J* = 9.0 Hz), 7.99 (2H, br d, *J* = 9.0 Hz), 7.44-7.38 (3H, m), 7.24-7.22 (2H, m), 6.06 (1H, d, *J* = 1.0, Hz, olefinic-*H*), 5.67 (1H, d, *J* = 1.0, Hz, olefinic-*H*), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.0 (C), 142.3 (C), 142.1 (C), 137.8 (C), 134.4



39ia

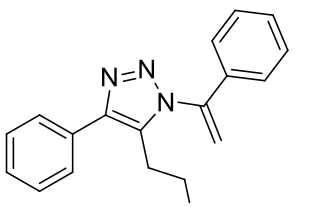
(C), 131.7 (C), 129.9 (CH), 129.1 (2 x CH), 127.2 (2 x CH), 125.6 (2 x CH), 124.1 (2 x CH), 115.0 (CH_2), 10.1 (CH_3); HRMS m/z 329.1015 (M + Na^+), calcd for $C_{17}H_{14}N_4O_2Na$ 329.1014.

5-Methyl-4-(naphthalen-2-yl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (39ja): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid; IR (Neat): ν_{max} 3049, 2920, 1639, 1603, 1577, 1494, 1443, 1427, 1262, 1185, 1112, 1024, 968, 906 and 854 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.18 (1H, s), 7.98-7.92 (2H, m), 7.88-7.84 (2H, m), 7.50-7.46 (2H, m), 7.37-7.36 (3H, m), 7.24-7.23 (2H, m), 5.99 (1H, s, olefinic-*H*), 5.64 (1H, s, olefinic-*H*), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.3 (C), 142.3 (C), 134.6 (C), 133.3 (C), 132.7 (C), 130.3 (C), 129.6 (CH), 128.9 (2 x CH), 128.8 (C), 128.3 (CH), 128.0 (CH), 127.6 (CH), 126.3 (CH), 126.1 (CH), 125.7 (CH), 125.7 (2 x CH), 125.1 (CH), 114.5 (CH_2), 9.9 (CH_3); HRMS m/z 312.1502 (M + H^+), calcd for $C_{21}H_{17}N_3H$ 312.1501.



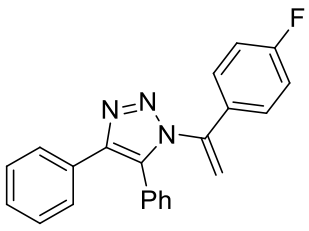
39ja

4-Phenyl-1-(1-phenylvinyl)-5-propyl-1*H*-1,2,3-triazole (39ka): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid; IR (Neat): ν_{max} 2961, 2920, 2868, 1639, 1494, 1448, 1371, 1252, 1123, 1071, 999, 916, 777 and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (2H, d, *J* = 7.2 Hz), 7.48 (2H, t, *J* = 7.2 Hz), 7.40-7.37 (4H, m), 7.26-7.23 (2H, m), 6.02 (1H, s, olefinic-*H*), 5.67 (1H, s, olefinic-*H*), 2.61 (2H, t, *J* = 7.2 Hz, Ar-C*H*$_2$CH$_2$CH$_3$), 1.47 (2H, sextet, *J* = 7.2 Hz, Ar-CH$_2$C*H*$_2$CH$_3$), 0.79 (3H, t, *J* = 7.2 Hz, Ar-CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.7 (C), 142.8 (C), 135.0 (C), 134.4 (C), 131.5 (C), 129.7 (CH), 128.9 (2 x CH), 128.7 (2 x CH), 127.8 (CH), 127.3 (2 x CH), 125.8 (2 x CH), 114.6 (CH_2), 25.4 (CH_2), 21.8 (CH_2), 13.8 (CH_3); HRMS m/z 290.1657 (M + H), calcd for $C_{19}H_{19}N_3H$ 290.1657.



39ka

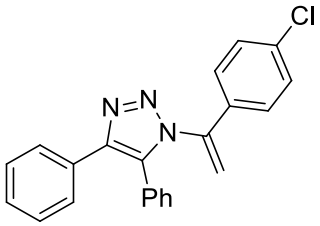
1-(1-(4-Fluorophenyl)vinyl)-4,5-diphenyl-1*H*-1,2,3-triazole (39ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 102-104 °C; IR (Neat): ν_{max} 3065, 1608, 1510, 1448, 1360, 1236, 1159, 1014, 839, and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.62-7.60 (2H, m), 7.33-7.24 (6H, m), 7.16-7.14 (2H, m), 7.09-7.06 (2H, m), 6.92-6.89 (2H, m), 5.75



39ab

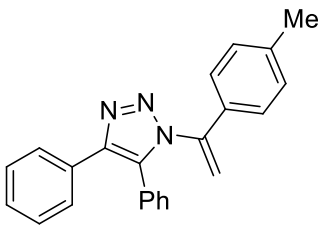
(1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.54 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.1 (C, d, *J* = 248.3 Hz, *C*-F), 144.2 (C), 141.7 (C), 134.2 (C), 131.4 (C, d, *J* = 3.0 Hz), 130.5 (C), 129.6 (2 x CH), 129.3 (CH), 128.7 (2 x CH), 128.5 (2 x CH), 127.9 (2 x CH, d, *J* = 25.0 Hz), 127.8 (CH), 127.4 (C), 127.1 (2 x CH), 115.5 (2 x CH, d, *J* = 90.0 Hz), 114.7 (CH_2); HRMS m/z 342.1408 (M + H^+), calcd for $C_{22}H_{16}FN_3H$ 342.1407.

1-(1-(4-Chlorophenyl)vinyl)-4,5-diphenyl-1*H*-1,2,3-triazole (39ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow semi solid; IR (Neat): 2920, 2848, 1637, 1599, 1369, 1084, 1007, 837, 700 and 558 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.63-7.61 (2H, m), 7.30-7.24 (6H, m), 7.18-7.14 (4H, m), 7.02 (2H, d, *J* = 8.5 Hz), 5.79 (1H, s, olefinic-*H*), 5.54 (1H, s, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.1 (C), 141.5 (C), 135.1 (C), 134.2 (C), 133.6 (C), 130.5 (C), 129.5 (2 x CH), 129.3 (CH), 128.7 (2 x CH), 128.6 (2 x CH), 128.4 (2 x CH), 127.9 (CH), 127.2 (C), 127.1 (2 x CH), 127.0 (2 x CH), 115.3 (CH_2); HRMS m/z 358.1113 (M + H^+), calcd for $C_{22}H_{16}ClN_3H$ 358.1111.



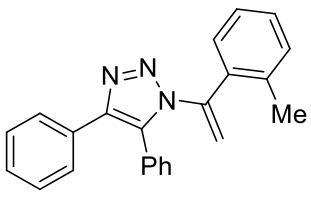
39ac

4,5-Diphenyl-1-(1-(*p*-tolyl)vinyl)-1*H*-1,2,3-triazole (39ad): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 110-112 °C; IR (neat): ν_{max} 3049, 3028, 2920, 1639, 1608, 1505, 1443, 1371, 1262, 1190,1076, 1009, 926, 818, 787, 689 and 554 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63-7.61 (2H, m), 7.32-7.24 (6H, m), 7.18-7.16 (2H, m), 7.05-7.00 (4H, m), 5.77 (1H, s, olefinic-*H*), 5.43 (1H, s, olefinic-*H*), 2.29 (3H, s, Ar-*C*H_3); ^{13}C NMR (500 MHz, $CDCl_3$) δ 144.1 (C), 142.6 (C), 139.4 (C), 134.4 (C), 132.5 (C), 130.8 (C), 129.7 (2 x CH), 129.2 (2 x CH), 129.1 (CH), 128.6 (2 x CH), 128.4 (2 x CH), 127.8 (CH), 127.6 (C), 127.1 (2 x CH), 125.8 (2 x CH), 113.9 (CH_2), 21.2 (CH_3); HRMS m/z 338.1656 (M + H^+), calcd for $C_{23}H_{19}N_3H$ 338.1657.



39ad

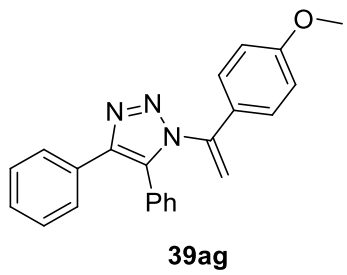
4,5-Diphenyl-1-(1-(*o*-tolyl)vinyl)-1*H*-1,2,3-triazole (39af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 105-107 °C; IR (Neat): ν_{max} 3116, 3059, 2956, 1649, 1603, 1577, 1489, 1365, 1262, 1205, 1143, 1071, 1019, 839, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.56 (2H, m), 7.27-7.21 (4H, m), 7.17 (2H, br t, *J* = 7.6 Hz), 7.06 (1H, dt, *J* = 7.6, 1.2



39af

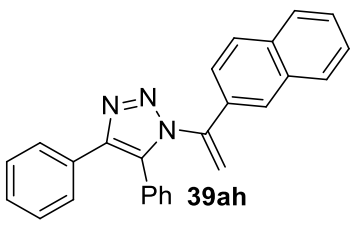
Hz), 6.99-6.97 (2H, m), 6.95-6.88 (2H, m), 6.82 (1H, dd, *J* = 7.6, 1.2 Hz), 5.92 (1H, s, olefinic-*H*), 5.43 (1H, s, olefinic-*H*), 1.95 (3H, s, Ar-*C*H_3); ^{13}C NMR (500 MHz, $CDCl_3$) δ 144.4 (C), 142.7 (C), 135.8 (C), 134.7 (C), 133.6 (C), 130.7 (C), 130.3 (CH), 129.6 (2 x CH), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.4 (2 x CH), 128.3 (2 x CH), 127.71 (CH), 127.71 (C), 126.7 (2 x CH), 125.6 (CH), 115.9 (CH_2), 19.3 (CH_3); HRMS m/z 338.1658 (M + H^+), calcd for $C_{23}H_{19}N_3H$ 338.1657.

1-(1-(4-Methoxyphenyl)vinyl)-4,5-diphenyl-1*H*-1,2,3-triazole (39ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid ; IR (neat): ν_{max} 2936, 2832, 2362, 1639, 1603, 1510, 1448, 1417, 1262, 1185, 1123, 1071, 1014, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.65-7.63 (2H, m), 7.34-7.27 (6H, m), 7.20-7.18 (2H, m), 7.06 (2H, td, *J* = 8.5, 1.0 Hz), 6.77 (2H, td, *J* = 8.5, 1.0 Hz), 5.73 (1H, d, *J* =1.0 Hz, olefinic-*H*), 5.41 (1H, d, *J* =1.0 Hz, olefinic-*H*), 3.78 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.4 (C), 144.1 (C), 142.2 (C), 134.4 (C), 130.8 (C), 129.7 (2 x CH), 129.2 (CH), 128.7 (2 x CH), 128.5 (2 x CH), 127.89 (CH), 127.89 (C), 127.6 (C), 127.3 (2 x CH), 127.2 (2 x CH), 113.9 (2 x CH), 112.9 (CH_2), 55.3 (CH_3, O*C*H_3); HRMS m/z 354.1606 (M + H^+), calcd for $C_{23}H_{19}N_3OH$ 354.1606.



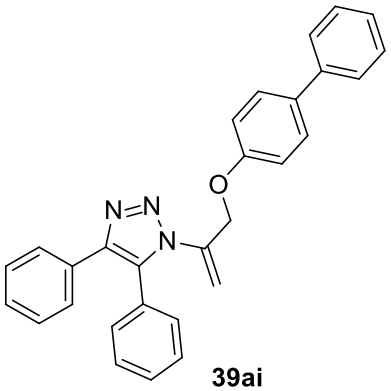
39ag

1-(1-(Naphthalen-2-yl)vinyl)-4,5-diphenyl-1*H*-1,2,3-triazole (39ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 142-144 °C; IR (neat): ν_{max} 3049, 1608, 1515, 1443, 1376, 1200, 1133, 1071, 1019, 983, 808, and 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80-7.78 (1H, m), 7.76-7.70 (4H, m), 7.51-7.47 (3H, m), 7.37-7.32 (4H, m), 7.27-7.21 (5H, m), 5.99 (1H, s, olefinic-*H*), 5.61 (1H, s, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.1 (C), 142.5 (C), 134.5 (C), 133.4 (C), 132.8 (C), 132.4 (C), 130.7 (C), 129.6 (2 x CH), 129.2 (CH), 128.6 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.9 (CH), 127.51 (CH), 127.47 (C), 127.1 (2 x CH), 126.9 (CH), 126.6 (CH), 125.6 (CH), 122.9 (CH), 115.3 (CH_2); HRMS m/z 374.1655 (M + H^+), calcd for $C_{26}H_{19}N_3H$ 374.1657.



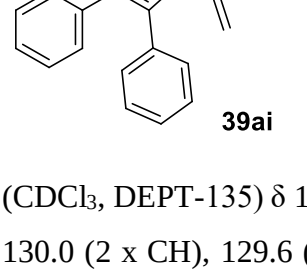
39ah

1-(3-([1,1'-Biphenyl]-4-yloxy)prop-1-en-2-yl)-4,5-diphenyl-1*H*-1,2,3-triazole (39ai): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a brown solid. Mp 138-139 °C; IR (Neat): ν_{max} 3059, 3023, 1660, 1603, 1515, 1484, 1350, 1241, 1174, 1117, 1040, 1019, 911, 833, 766, and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.56 (2H, m), 7.53-7.51 (2H, m), 7.49-7.38 (7H, m), 7.34-7.22 (6H, m), 6.90 (2H, td, *J* = 9.0, 2.0 Hz), 5.52 (1H, br d, *J* = 1.5 Hz, olefinic-*H*), 5.18 (1H, br d, *J* = 0.5 Hz, olefinic-*H*), 4.90 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 157.2 (C), 144.5 (C), 140.5 (C), 138.5 (C), 134.6 (C), 133.7 (C), 130.4 (C), 130.0 (2 x CH), 129.6 (CH), 129.2 (2 x CH), 128.7 (2 x CH), 128.4 (2 x CH), 128.1 (2 x CH), 127.9 (CH), 127.6 (C), 127.1 (2 x CH), 126.8 (CH), 126.7 (2 x CH), 115.1 (2 x CH), 114.5 (CH_2), 67.6 (CH_2); HRMS m/z 430.1919 ($M + H^+$), calcd for $C_{29}H_{23}N_3OH$ 430.1919.



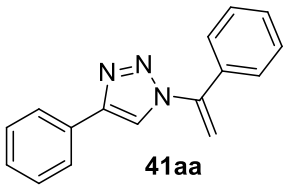
39ai

1-(3-(4-Nitrophenoxy)prop-1-en-2-yl)-4,5-diphenyl-1*H*-1,2,3-triazole (39aj): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid; IR (neat): ν_{max} 3059, 2357, 1665, 1587, 1515, 1494, 1443, 1334, 1262, 1169, 1107, 1019, 901, 844, 782, 751, and 715 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.16 (2H, td, *J* = 9.0, 1.5 Hz), 7.56-7.54 (2H, m), 7.49-7.47 (3H, m), 7.35-7.34 (2H, m), 7.29-7.27 (3H, m), 6.92 (2H, td, *J* = 9.0, 1.5 Hz), 5.51 (1H, br d, *J* = 1.5 Hz, olefinic-*H*), 5.23 (1H, br d, *J* = 1.5 Hz, olefinic-*H*), 4.99 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.5 (C), 144.6 (C), 142.0 (C), 137.3 (C), 133.7 (C), 130.2 (C), 129.9 (2 x CH), 129.8 (CH), 129.3 (2 x CH), 128.4 (2 x CH), 128.0 (CH), 127.4 (C), 127.0 (2 x CH), 125.8 (2 x CH), 115.1 (CH_2), 114.7 (2 x CH), 67.9 (CH_2); HRMS m/z 399.1457 ($M + H^+$), calcd for $C_{23}H_{18}N_4O_3H$ 399.1457.



39aj

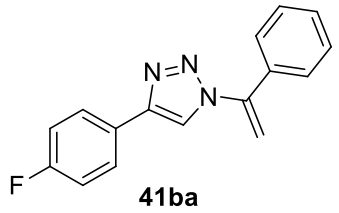
4-Phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp: 65-67°C; IR (Neat) ν_{max} 3137, 3059, 2925, 1701, 1598, 1448, 1262, 1226, 1076, 797 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86-7.83 (2H, m), 7.79 (1H, s), 7.45-7.41 (5H, m), 7.39-7.32 (3H, m), 5.86 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.55 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR



41aa

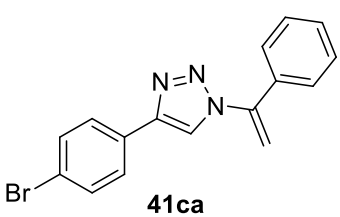
($CDCl_3$, DEPT-135) δ 147.6 (C), 143.0 (C), 134.6 (C), 130.2 (C), 129.9 (CH), 128.86 (2 x CH), 128.84 (2 x CH), 128.3 (CH), 127.3 (2 x CH), 125.8 (2 x CH), 119.8 (CH), 109.4 (CH_2); HRMS m/z 248.1189 ($M + H^+$), calcd for $C_{16}H_{13}N_3H$ 248.1188.

4-(4-Fluorophenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid. IR (Neat): ν_{max} 3132, 3060, 1701, 1598, 1510, 1407, 1231, 1154, 1081, 1019, 906, 839, and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84-7.80 (2H, m), 7.76 (1H, s), 7.47-7.40 (3H, m), 7.38-7.36 (2H, m), 7.13-7.09 (2H, m), 5.85 (1H, s, olefinic-*H*), 5.55 (1H, s, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.7 (C, d, *J* = 246.0 Hz, *C*-F), 146.7 (C), 142.9 (C), 134.5 (C), 129.9 (CH), 128.9 (2 x CH), 127.5 (2 x CH, d, *J* = 8.0 Hz), 127.3 (2 x CH), 126.4 (C, d, *J* = 4.0 Hz), 119.5 (CH), 115.8 (2 x CH, d, *J* = 22.0 Hz), 109.4 (CH_2); HRMS m/z 266.1092 ($M + H^+$), calcd for $C_{16}H_{12}FN_3H$ 266.1094.



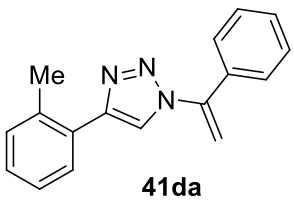
41ba

4-(4-Bromophenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp: 77-79 °C; IR (Neat): ν_{max} 3132, 1639, 1556, 1484, 1443, 1407, 1278, 1076, 1004, 962, 766 and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (1H, s), 7.69 (2H, br d, *J* = 8.8 Hz), 7.51 (2H, br d, *J* = 8.8 Hz), 7.45-7.38 (3H, m), 7.38-7.33 (2H, m), 5.82 (1H, s, olefinic-*H*), 5.53 (1H, s, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.4 (C), 142.8 (C), 134.3 (C), 131.9 (2 x CH), 129.8 (CH), 129.1 (C), 128.8 (2 x CH), 127.2 (4 x CH), 122.1 (C), 119.9 (CH), 109.4 (CH_2); HRMS m/z 326.0294 ($M + H^+$), calcd for $C_{16}H_{12}BrN_3H$ 326.0293.



41ca

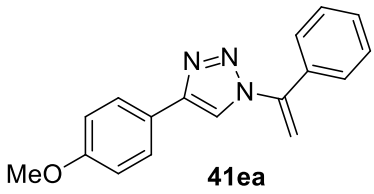
1-(1-Phenylvinyl)-4-(*o*-tolyl)-1*H*-1,2,3-triazole (41da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a semisolid. IR (Neat): ν_{max} 3023, 1701, 1644, 1603, 1494, 1381, 1329, 1262, 1221,1066 and 813 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.80-7.79 (1H, m), 7.68 (1H, s), 7.42-7.35 (5H, m), 7.27-7.23 (3H, m), 5.85 (1H, s, olefinic-*H*), 5.54 (1H, s, olefinic-*H*), 2.45 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.8 (C), 142.8 (C), 135.4 (C), 134.5 (C), 130.8 (CH), 129.8 (CH), 129.4 (C), 128.8 (CH), 128.7 (2 x



41da

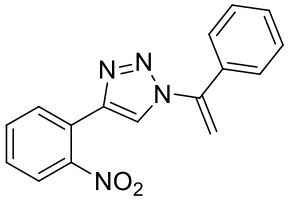
CH), 128.2 (CH), 127.2 (2 x CH), 126.0 (CH), 121.9 (CH), 109.2 (CH_2), 21.3 (CH_3); HRMS m/z 262.1345 ($M + H^+$), calcd for $C_{17}H_{15}N_3H$ 262.1344.

4-(4-Methoxyphenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semisolid ; IR (neat): ν_{max} 2997, 2930, 1624, 1494, 1417, 1257, 1117, 1024, 973 and 777 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.78-7.10 (3H, m), 7.44-7.39 (5H, m), 6.95 (2H, m), 5.84 (1H, s, olefinic-*H*), 5.53 (1H, s, olefinic-*H*), 3.84 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.7 (C), 147.4 (C), 143.0 (C), 134.7 (C), 129.8 (CH), 128.8 (2 x CH), 127.3 (2 x CH), 127.10 (2 x CH), 122.9 (C), 119.0 (CH), 114.2 (2 x CH), 109.2 (CH_2), 55.3 (CH_3, O*C*H$_3$); HRMS m/z 278.1294 ($M + H^+$), calcd for $C_{17}H_{15}N_3OH$ 278.1293.



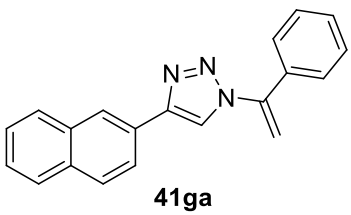
41ea

4-(2-Nitrophenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a red brown liquid; IR (Neat): ν_{max} 1598, 1510, 1443, 1340, 1340, 1267, 1107, 1019, 978, 921, 854, 782 and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.07 (1H, br d, *J* = 7.5 Hz), 7.85 (1H, s), 7.84 (1H, br d, *J* = 7.5 Hz), 7.68 (1H, dt, *J* = 7.5, 1.0 Hz), 7.52 (1H, dt, *J* = 8.0, 1.5 Hz), 7.47-7.41 (3H, m), 7.38-7.36 (2H, m), 5.87 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.60 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 148.2 (C), 142.8 (C), 141.9 (C), 134.2 (C), 132.6 (CH), 131.2 (CH), 130.0 (CH), 129.1 (CH), 128.9 (2 x CH), 127.2 (2 x CH), 124.4 (C), 124.1 (CH), 123.2 (CH), 109.9 (CH_2); HRMS m/z 293.1039 ($M + H^+$), calcd for $C_{16}H_{12}N_4O_2H$ 293.1039.



41fa

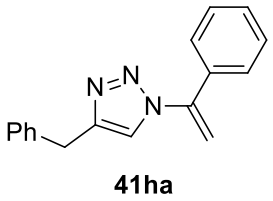
4-(Naphthalen-2-yl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid. IR (Neat): ν_{max} 2930, 2848, 1737, 1696, 1634, 1417, 1241, 1185, 1024, 931, 818 and 751 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz)) δ 8.37 (1H, s), 7.95-7.84 (5H, m), 7.51-7.41 (7H, m), 5.91 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.58 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.7 (C), 143.0 (C), 134.7 (C), 133.5 (C), 133.2 (C), 130.0 (CH), 128.9 (2 x CH), 128.6 (CH), 128.2 (CH), 127.8 (CH), 127.5 (C), 127.4



41ga

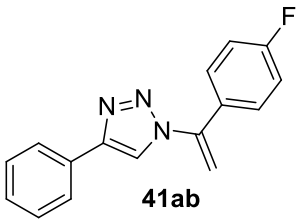
(2 x CH), 126.5 (CH), 126.3 (CH), 124.6 (CH), 123.8 (CH), 120.1 (CH), 109.5 (CH_2); HRMS m/z 298.1344 (M + H^+), calcd for $C_{20}H_{15}N_3H$ 298.1344.

4-Benzyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (41ha): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid; IR (neat): ν_{max} 3137, 3065, 3028, 2853, 1644, 1494, 1448, 1350, 1236, 1128, 1076, 1040, 895, 777 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.45-7.38 (3H, m), 7.34-7.28 (6H, m), 7.26-7.22 (2H, m), 5.75 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 5.49 (1H, d, *J* = 0.8 Hz, olefinic-*H*) 4.15 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.5 (C), 143.1 (C), 138.8 (C), 134.7 (C), 129.8 (CH), 128.8 (2 x CH), 128.72 (2 x CH), 128.67 (2 x CH), 127.3 (2 x CH), 126.6 (CH), 121.8 (CH), 109.2 (CH_2), 32.2 (CH_2); HRMS m/z 284.1164 (M + Na), calcd for $C_{17}H_{15}N_3Na$ 284.1164.



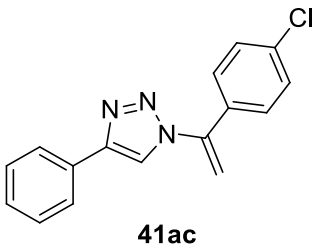
41ha

1-(1-(4-Fluorophenyl)vinyl)-4-phenyl-1*H*-1,2,3-triazole (41ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid; IR (Neat): ν_{max} 2915, 1686, 1644, 1608, 1489, 1443, 1231, 1081, 1019, 973, 849 and 777 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86-7.83 (2H, m), 7.81 (1H, s), 7.45-7.41 (2H, m), 7.39-7.33 (3H, m), 7.14-7.09 (2H, m), 5.81 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 5.54 (1H, d, *J* = 0.8 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.6 (C, d, *J* = 249.0 Hz, *C*-F), 147.7 (C), 142.1 (C), 130.7 (C, d, *J* = 3.0 Hz), 130.0 (C), 129.3 (2 x CH, d, *J* = 9.0 Hz), 128.9 (2 x CH), 128.4 (CH), 125.8 (2 x CH), 119.7 (CH), 116.0 (2 x CH, d, *J* = 22.0 Hz), 109.2 (CH_2); HRMS m/z 266.1095 (M + H^+), calcd for $C_{16}H_{12}FN_3H$ 266.1094.



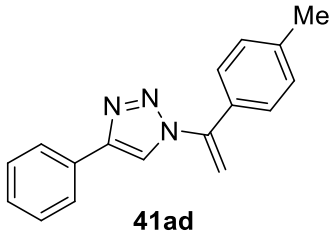
41ab

1-(1-(4-Chlorophenyl)vinyl)-4-phenyl-1*H*-1,2,3-triazole (41ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp: 108-110 °C; IR (Neat): ν_{max} 2926, 1643, 1594, 1484, 1397, 1265, 1227, 1101, 1013, 838, 767 and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.84 (2H, m), 7.82 (1H, s), 7.43-7.37 (4H, m), 7.35-7.29 (3H, m), 5.82 (1H, br s, olefinic-*H*), 5.54 (1H, br s, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.7 (C), 142.0 (C), 135.9 (C), 133.0 (C), 130.0 (C), 129.0 (2 x CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.4 (CH), 125.7 (2 x CH), 119.7 (CH), 109.7 (CH_2); HRMS m/z 282.0795 (M + H^+), calcd for $C_{16}H_{12}ClN_3H$ 282.0798.



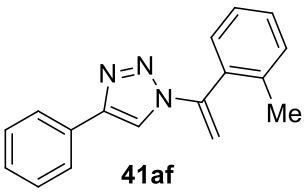
41ac

4-Phenyl-1-(1-(*p*-tolyl)vinyl)-1*H*-1,2,3-triazole (41ad): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a semi solid ; IR (Neat): ν_{max} 2925, 1626, 1610, 1445, 1429, 1018, 892, 815, 760 and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.85-7.83 (2H, m), 7.79 (1H, s), 7.43-7.40 (2H, m), 7.35-7.32 (1H, m), 7.27-7.25 (2H, m), 7.23-7.21 (2H, m), 5.80 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.50 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 2.40 (3H, s, Ar-*C*H_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.5 (C), 142.9 (C), 140.1 (C), 131.8 (C), 130.3 (C), 129.5 (2 x CH), 128.8 (2 x CH), 128.3 (CH), 127.2 (2 x CH), 125.8 (2 x CH), 119.8 (CH), 108.6 (CH_2), 21.3 (CH_3); HRMS m/z 262.1345 ($M + H^+$), calcd for $C_{17}H_{15}N_3H$ 262.1344.



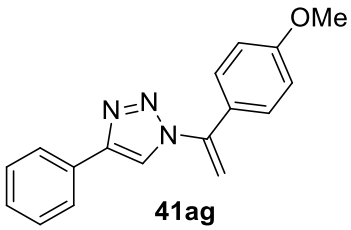
41ad

4-Phenyl-1-(1-(*o*-tolyl)vinyl)-1*H*-1,2,3-triazole (41af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow oily liquid; IR (Neat): ν_{max} 3137, 3059, 2915, 1639, 1608, 1484, 1427, 1376, 1345, 1267, 1076, 1014, 901 and 766 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.80-7.78 (2H, m), 7.49 (1H, s), 7.40-7.36 (4H, m), 7.32-7.26 (3H, m), 6.19 (1H, d, *J* = 0.5 Hz, olefinic-*H*), 5.22 (1H, d, *J* = 0.5 Hz, olefinic-*H*), 2.09 (3H, s, Ar-*C*H_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.7 (C), 142.1 (C), 136.9 (C), 134.2 (C), 130.7 (CH), 130.2 (CH), 130.1 (C), 129.9 (CH), 128.7 (2 x CH), 128.2 (CH), 126.3 (CH), 125.7 (2 x CH), 118.3 (CH), 108.4 (CH_2), 19.2 (CH_3); HRMS m/z 262.1346 ($M + H^+$), calcd for $C_{17}H_{15}N_3H$ 262.1344.



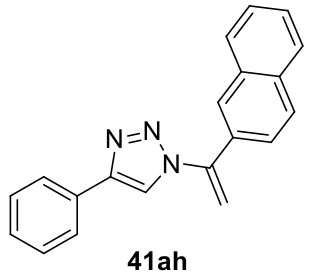
41af

1-(1-(4-Methoxyphenyl)vinyl)-4-phenyl-1*H*-1,2,3-triazole (41ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid; IR (Neat): ν_{max} 2967, 2837, 1686, 1608, 1510, 1453, 1309, 844, 771, and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86-7.84 (2H, m), 7.80 (1H, s), 7.44-7.41 (2H, m), 7.36-7.34 (1H, m), 7.31 (2H, m), 6.94 (2H, td, *J* = 9.0, 3.0 Hz), 5.75 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.46 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 3.85 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.9 (C), 147.5 (C), 142.7 (C), 130.3 (C), 128.85 (2 x CH), 128.77 (2 x CH), 128.3 (CH), 127.1 (C), 125.8 (2 x CH), 119.8 (CH), 114.2 (2 x CH), 107.8 (CH_2), 55.4 (CH_3, O*C*H_3); HRMS m/z 278.1295 ($M + H^+$), calcd for $C_{17}H_{15}N_3OH$ 278.1293.



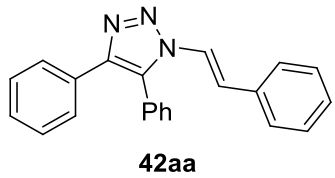
41ag

1-(1-(Naphthalen-2-yl)vinyl)-4-phenyl-1*H*-1,2,3-triazole (41ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp: 116-118 °C; IR (Neat): ν_{max} 3049, 1634, 1433, 1345, 1231, 1143, 1076, 1024, 968 and 901 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.92-7.86 (7H, m), 7.60-7.54 (2H, m), 7.49 (1H, dd, *J* = 8.5, 2.0 Hz), 7.47-7.44 (2H, m), 7.39-7.36 (1H, m), 5.96 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.71 (1H, d, *J* = 1.0 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.7 (C), 143.1 (C), 133.8 (C), 133.0 (C), 131.9 (C), 130.2 (C), 128.9 (2 x CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 125.8 (2 x CH), 124.3 (CH), 120.0 (CH), 110.0 (CH_2); HRMS m/z 298.1341 ($M + H^+$), calcd for $C_{20}H_{15}N_3H$ 298.1344.



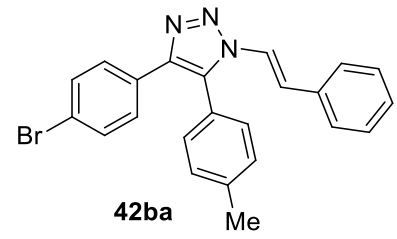
41ah

(*E*)-4,5-Diphenyl-1-styryl-1*H*-1,2,3-triazole (42aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 135-136 °C; IR (neat): 3075, 3049, 1665, 1598, 1541, 1365, 1257, 1205, 1019, 931, 808, 746, and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.52 (6H, m), 7.40-7.24 (10H, m), 7.20 (1H, d, *J* = 14.5 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.6 (C), 134.1 (C), 132.7 (C), 130.5 (C), 130.3 (2 x CH), 129.9 (CH), 129.4 (2 x CH), 128.8 (2 x CH), 128.5 (CH), 128.4 (2 x CH), 127.9 (CH), 127.2 (C), 127.0 (2 x CH), 126.7 (2 x CH), 123.8 (CH), 120.6 (CH); HRMS m/z 324.1500 ($M + H^+$), calcd for $C_{22}H_{17}N_3H$ 324.1501.



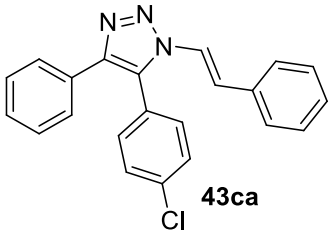
42aa

(*E*)-4-(4-Bromophenyl)-1-styryl-5-(*p*-tolyl)-1*H*-1,2,3-triazole (42ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid. IR (Neat): ν_{max} 3421, 2920, 1645, 1603, 1552, 1412, 1113, 715 and 627 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.59 (1H, d, *J* = 14.5 Hz, olefinic-*H*), 7.46 (2H, td, *J* = 9.0, 2.0 Hz), 7.42 (2H, td, *J* = 9.0, 2.0 Hz), 7.38-7.32 (6H, m), 7.31-7.29 (1H, m), 7.27-7.25 (2H, m), 7.19 (1H, d, *J* = 14.5 Hz, olefinic-*H*), 2.48 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.5 (C), 140.4 (C), 134.1 (C), 133.0 (C), 131.6 (2 x CH), 130.3 (2 x CH), 130.0 (2 x CH), 129.6 (C), 128.8 (2 x CH), 128.6 (CH), 128.4 (2 x CH), 126.8 (2 x CH), 123.8 (CH), 123.7 (C), 121.9 (C), 120.5 (CH), 21.5 (CH_3); HRMS m/z 416.0763 ($M + H^+$), calcd for $C_{23}H_{18}BrN_3H$ 416.0762.



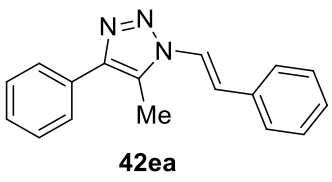
42ba

(*E*)-5-(4-Chlorophenyl)-4-phenyl-1-styryl-1*H*-1,2,3-triazole (42ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 141-143 °C; IR (neat): ν_{max} 3065, 3034, 1644, 1608, 1448, 1360, 1210, 1123, 1086, 1019, 839 and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (1H, d, *J* = 14.5 Hz, olefinic-*H*), 7.58-7.55 (2H, m), 7.52 (2H, td, *J* = 8.5, 2.0 Hz), 7.39-7.29 (10H, m), 7.17 (1H, d, *J* = 14.5 Hz, olefinic-*H*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.8 (C), 136.3 (C), 133.9 (C), 131.6 (2 x CH), 131.5 (C), 130.2 (C), 129.8 (2 x CH), 128.9 (2 x CH), 128.7 (CH), 128.6 (2 x CH), 128.1 (CH), 127.0 (2 x CH), 126.8 (2 x CH), 125.6 (C), 124.3 (CH), 120.2 (CH); HRMS m/z 358.1112 (M + H^+), calcd for $C_{22}H_{16}ClN_3H$ 358.1111.



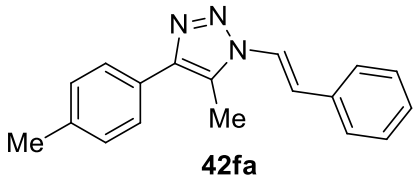
43ca

(*E*)-5-Methyl-4-phenyl-1-styryl-1*H*-1,2,3-triazole (42ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 118-120°C; IR (Neat): ν_{max} 3059, 3023, 1649, 1603, 1391, 1365, 1252, 1174, 1102, 947, 921, 746 and 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71-7.69 (2H, m), 7.53-7.44 (5H, m), 7.41-7.31 (5H, m), 2.53 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.9 (C), 134.0 (C), 131.0 (C), 128.9 (2 x CH), 128.7 (2 x CH), 128.6 (CH), 128.4 (C), 127.8 (CH), 127.3 (2 x CH), 126.7 (2 x CH), 124.3 (CH), 120.1 (CH), 9.2 (CH_3); HRMS m/z 262.1345 (M + H^+), calcd for $C_{17}H_{15}N_3H$ 262.1344.



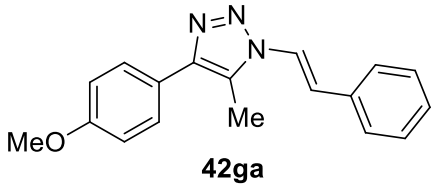
42ea

(*E*)-5-Methyl-1-styryl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (42fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 119-120 °C; IR (KBr): ν_{max} 3054, 2920, 2853, 1660, 1577, 1515, 1443, 1396, 1360, 1288, 1185, 1014, 952, 746 and 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (2H, br d, *J* = 8.0 Hz), 7.54-7.50 (3H, m), 7.43-7.38 (3H, m), 7.35-7.32 (1H, m), 7.28 (2H, br d, *J* = 8.0 Hz), 2.54 (3H, s), 2.40 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.0 (C), 137.7 (C), 134.1 (C), 129.4 (2 x CH), 128.9 (2 x CH), 128.6 (CH), 128.2 (C), 128.1 (C), 127.2 (2 x CH), 126.8 (2 x CH), 124.2 (CH), 120.2 (CH), 21.2 (CH_3), 9.3 (CH_3); HRMS m/z 276.1502 (M + H^+), calcd for $C_{18}H_{17}N_3H$ 276.1501.



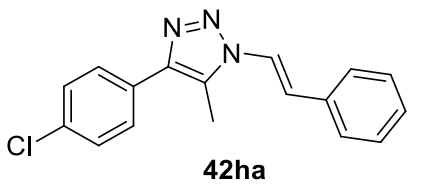
42fa

(*E*)-4-(4-Methoxyphenyl)-5-methyl-1-styryl-1*H*-1,2,3-triazole (42ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 124-126 °C; IR (Neat): ν_{max} 3028, 2951, 2920, 2853, 1608, 1567, 1453, 1365, 1309, 1247, 1179, 1102, 1045, 957, 849 and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62 (2H, br d, *J* = 8.8 Hz), 7.53-7.49 (3H, m), 7.42-7.38 (3H, m), 7.35-7.31 (1H, m), 6.99 (2H, br d, *J* = 8.8 Hz), 3.84 (3H, s, Ar-OC*H*$_3$), 2.52 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.3 (C), 144.8 (C), 134.1 (C), 128.9 (2 x CH), 128.58 (CH), 128.58 (2 x CH), 127.7 (C), 126.7 (2 x CH), 124.1 (CH), 123.6 (C), 120.2 (CH), 114.1 (2 x CH), 55.3 (CH_3, O*C*H$_3$), 9.2 (CH_3); HRMS m/z 292.1452 (M + H^+), calcd for $C_{18}H_{17}N_3OH$ 292.1450.



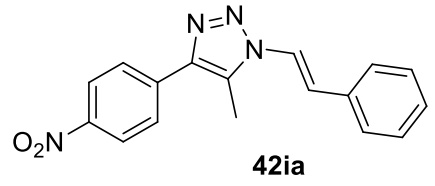
42ga

(*E*)-4-(4-Chlorophenyl)-5-methyl-1-styryl-1*H*-1,2,3-triazole (42ha): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 148-150 °C; IR (Neat): ν_{max} 3065, 3044, 2925, 2905, 1712, 1649, 1598, 1489, 1391, 1247, 1086, 828, 735, and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.64 (2H, td, *J* = 8.4, 2.4 Hz), 7.54-7.49 (3H, m), 7.44-7.32 (6H, m), 2.53 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.9 (C), 133.9 (C), 133.8 (C), 129.6 (C), 128.93 (2 x CH), 128.91 (2 x CH), 128.8 (CH), 128.47 (2 x CH), 128.47 (C), 126.8 (2 x CH), 124.7 (CH), 120.1 (CH), 9.8 (CH_3); HRMS m/z 296.0953 (M + H^+), calcd for $C_{17}H_{14}ClN_3H$ 296.0955.



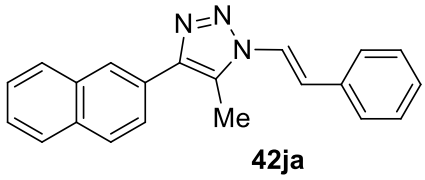
42ha

(*E*)-5-Methyl-4-(4-nitrophenyl)-1-styryl-1*H*-1,2,3-triazole (42ia): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 180-182 °C; IR (Neat): ν_{max} 1598, 1510, 1489, 1329, 1252, 1102, 1014, 942, 854, 756 and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.34 (2H, td, *J* = 9.0, 2.0 Hz), 7.94 (2H, td, *J* = 9.0, 2.0 Hz), 7.58 (1H, d, *J* = 14.5 Hz, olefinic-*H*), 7.54-7.53 (2H, m), 7.45-7.41 (3H, m), 7.39-7.36 (1H, m), 2.64 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.1 (C), 142.8 (C), 137.6 (C), 133.7 (C), 129.7 (C), 129.07 (CH), 129.05 (2 x CH), 127.5 (2 x CH), 126.9 (2 x CH), 125.7 (CH), 124.1 (2 x CH), 119.6 (CH), 9.6 (CH_3); HRMS m/z 307.1190 (M + H^+), calcd for $C_{17}H_{14}N_4O_2H$ 307.1195.



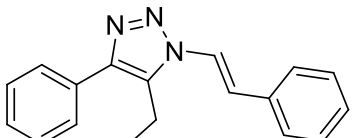
42ia

(*E*)-5-Methyl-4-(naphthalen-2-yl)-1-styryl-1*H*-1,2,3-triazole (42ja): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 154-156 °C; IR (Neat): ν_{max} 1598, 1500, 1448, 1386, 1329, 1247, 1200, 1086, 1030, 978, 937, 890, 854, 740and 684 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11 (1H, s), 7.92 (1H, d, *J* = 8.5 Hz), 7.89-7.84 (3H, m), 7.54 (1H, d, *J* = 14.0 Hz), 7.50-7.47 (4H, m), 7.42-7.38 (3H, m), 7.35-7.32 (1H, m), 2.59 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.9 (C), 134.0 (C), 133.3 (C), 132.7 (C), 128.9 (2 x CH), 128.69 (CH), 128.66 (C), 128.5 (C), 128.4 (CH), 128.1 (CH), 127.7 (CH), 126.8 (2 x CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 125.3 (CH), 124.4 (CH), 120.1 (CH), 9.4 (CH_3); HRMS m/z 312.1500 ($M + H^+$), calcd for $C_{21}H_{17}N_3H$ 312.1501.



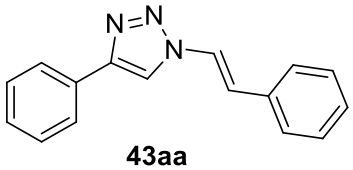
42ja

(*E*)-4-Phenyl-5-propyl-1-styryl-1*H*-1,2,3-triazole (42ka): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid. IR (neat): ν_{max} 3059, 3028, 2930, 2868, 1649, 1603, 1484, 1453, 1365, 1252, 1102, 1071, 993, 937, 746, and 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72-7.70 (2H, m), 7.61 (1H, d, *J* = 14.0 Hz), 7.51 (2H, br d, *J* = 7.0 Hz), 7.48-7.45 (2H, m), 7.43-7.33 (5H, m), 2.91 (2H, t, *J* = 7.5 Hz, Ar-C*H*$_2$CH$_2$CH$_3$), 1.71 (2H, sextet, *J* = 7.5 Hz, Ar-CH$_2$C*H*$_2$CH$_3$), 1.10 (3H, t, *J* = 7.5 Hz, Ar-CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.8 (C), 134.2 (C), 132.7 (C), 131.3 (C), 128.9 (2 x CH), 128.72 (2 x CH), 128.68 (CH), 127.9 (CH), 127.4 (2 x CH), 126.8 (2 x CH), 124.5 (CH), 120.0 (CH), 24.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3); HRMS m/z 290.1656 (M + H), calcd for $C_{19}H_{19}N_3H$ 290.1657.



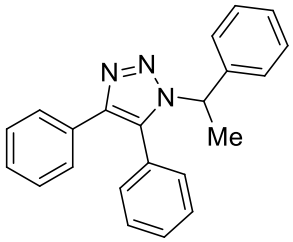
42ka

(*E*)-4-Phenyl-1-styryl-1*H*-1,2,3-triazole (43aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp: 166-168°C; IR (Neat): ν_{max} 2915, 1443, 1205, 1076, 1019, 942, 911, 828, 751, and 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (1H, br s), 7.89 (2H, br d, *J* = 7.2 Hz), 7.81 (1H, br d, *J* = 14.8 Hz, olefinic-*H*), 7.51-7.33 (8H, m), 7.19 (1H, br d, *J* = 14.8 Hz, olefinic-*H*), ^{13}C NMR ($CDCl_3$, DEPT-135) δ 148.0 (C), 133.6 (C), 130.0 (C), 129.0 (2 x CH), 128.9 (2 x CH), 128.8 (CH), 128.5 (CH), 126.7 (2 x CH), 125.9 (2 x CH), 123.1 (CH), 121.6 (CH), 116.5 (CH); HRMS m/z 248.1186 ($M + H^+$), calcd for $C_{16}H_{13}N_3H$ 248.1188.



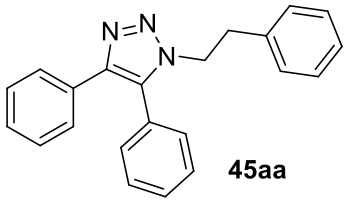
43aa

4,5-Diphenyl-1-(1-phenylethyl)-1*H*-1,2,3-triazole (44aa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 81-83°C; IR (Neat): ν_{max} 3065, 3028, 2982, 2925, 2848, 1603, 1494, 1443, 1340, 1257, 1164, 1071, 1019, 968 and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.57 (2H, m), 7.50 (1H, tt, *J* = 7.5, 2.5 Hz), 7.44(2H, br t, *J* = 7.5 Hz), 7.32-7.23 (6H, m), 7.17-7.15 (2H, m), 7.13-7.11 (2H, m), 5.40 (1H, q, *J* = 7.0 Hz), 2.05 (3H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.2 (C), 141.1 (C), 133.6 (C), 131.0 (C), 130.2 (2 x CH), 129.5 (CH), 129.0 (2 x CH), 128.6 (2 x CH), 128.3 (2 x CH), 128.1 (C), 127.8 (CH), 127.5 (CH), 126.6 (2 x CH), 126.2 (2 x CH), 58.5 (CH), 22.3 (CH_3); HRMS m/z 326.1657 ($M + H^+$), calcd for $C_{22}H_{19}N_3H$ 326.1657.



44aa

1-Phenethyl-4,5-diphenyl-1*H*-1,2,3-triazole (45aa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and was isolated as a colourless liquid. IR (neat): ν_{max} 3065, 3028, 2956, 2915, 1598, 1500, 1448, 1076, 983, 761 and 549 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.53-7.51 (2H, m), 7.49-7.46 (1H, m), 7.43-7.41 (2H, m), 7.26-7.20 (6H, m), 6.98-6.97 (1H, m), 6.94-6.92 (2H, m), 4.38 (2H, t, *J* = 7.5 Hz), 3.16 (2H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.1 (C), 137.2 (C), 134.1 (C), 131.1 (C), 129.9 (2 x CH), 129.5 (CH), 129. 1 (2 x CH), 128.75 (2 x CH), 128.66 (2 x CH), 128.4 (2 x CH), 127.9 (C), 127.6 (CH), 126.9 (CH), 126.7 (2 x CH), 49.4 (CH_2), 36.6 (CH_2); HRMS m/z 326.1660 ($M + H^+$), calcd for $C_{22}H_{19}N_3H$ 326.1657.



45aa

7.2 General Experimental Procedure for Reaction Engineering and Photophysical Studies of Fully Enriched *C*-Vinyl-1,2,3-Triazoles

Procedure A: General procedure for the DBU-catalyzed formal [3+2]-cycloaddition reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.10 mmol of DBU (**40e**) in DMSO (1.0 mL), was added 0.75 mmol of aryl azide **2** and 0.5 mmol of corresponding allylic ketones (**48**, **50** and **52)** and the reaction mixture was stirred at 25 °C. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and

concentrated. Pure click products were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General procedure for the SeO_2 oxidation: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.05 mmol of CH_3COOH and 300µL of H_2O in 1,4-dioxane (1.0 mL), was added 5 equivalents of SeO_2 and 0.5 mmol of compound **51df** and the reaction mixture was stirred at 100 °C for 8 h. The crude reaction mixture was worked up with water and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure oxidized product **57df** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: General procedure for the DDQ oxidation: In a 10 mL round bottom flask equipped with a magnetic stirring bar, to 0.5 mmol of compound **51ff** was added 5.0 mL of dry toluene as a solvent and then DDQ (2 equiv., 1.0 mmol) was added. The reaction mixture was refluxed for 48 h, the crude product was purified by column chromatography on silica gel (hexane/EtOAc) to afford the oxidized product **57ff**.

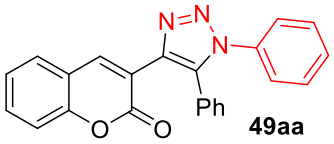
Procedure D: General procedure for the Et_2NH-catalyzed formal [3+2]-cycloaddition reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.01 mmol of Et_2NH in DMSO (0.3 mL), was added 0.2 mmol of aryl azide **2a** and 0.1 mmol of allylic ketone **50e** and the reaction mixture were stirred at 80 °C for 8 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: General procedure for the Et_3N-catalyzed isomerization of 1-phenylbut-3-en-1-one (54a): In an ordinary glass vial equipped with a magnetic stirring bar, to 0.10 mmol of Et_3N in DMSO (1.0 mL), was added 0.75 mmol of aryl azide **2a** and 0.5 mmol of 1-phenylbut-3-en-1-one **54a** and the reaction mixture were stirred at 25 °C for 30 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and

concentrated. Pure product was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

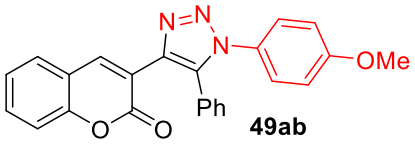
Procedure F: General procedure for the DBU- (or) K_2CO_3-catalyzed synthesis of 56aa: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.10 mmol of DBU or K_2CO_3 in DMSO (1.0 mL), was added 0.75 mmol of aryl azide **2a** and 0.5 mmol of 1-phenylbut-3-en-1-one **54a** and the reaction mixture was stirred at 25 °C for 16 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

3-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 86% (157.1 mg); Mp 252-254 °C; IR (Neat): ν_{max} 3063, 2923, 1724, 1608, 1497, 1450, 1276, 1251, 1132, 947, 761, 697, and 634 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, s), 7.55 (2H, t, *J* = 7.5 Hz), 7.43-7.39 (3H, m), 7.37-7.29 (7H, m), 7.19 (2H, td, *J* = 7.0, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.9 (C), 154.0 (C), 143.2 (CH), 139.7 (C), 136.5 (C), 136.4 (C), 132.0 (CH), 129.3 (3 x CH), 129.2 (3 x CH), 128.7 (2 x CH), 128.2 (CH), 127.3 (C), 125.3 (2 x CH), 124.6 (CH), 119.6 (C), 119.1 (C), 116.6 (CH); HRMS (ESI-TOF) m/z 388.1063 ($M + Na^+$), calcd for $C_{23}H_{15}N_3O_2Na$ 388.1062.



49aa

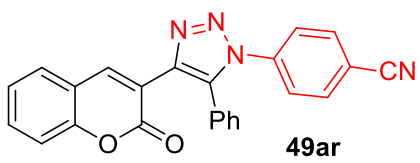
3-(1-(4-Methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 77% (152.1 mg); Mp 208-210 °C; IR (Neat): ν_{max} 2984, 1736, 1445, 1371, 1231, 1042, 937, 846, 633, and 607 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (1H, s), 7.56-7.53 (2H, m), 7.36-7.29 (5H, m), 7.25 (2H, td, *J* = 10.0, 2.0 Hz), 7.19 (2H, td, *J* = 8.0, 1.5 Hz), 6.90 (2H, td, *J* = 10.0, 2.0 Hz), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.0 (C), 158.9 (C), 153.9 (C), 143.2 (CH), 139.4 (C), 136.5 (C), 131.9 (CH), 129.33 (C), 129.26 (2 x CH), 129.2 (CH), 128.6 (2 x CH), 128.2 (CH), 127.3 (C), 126.7 (2



49ab

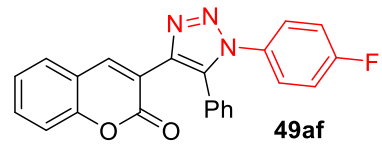
x CH), 124.6 (CH), 119.7 (C), 119.1 (C), 116.6 (CH), 114.3 (2 x CH), 55.5 (OCH_3); HRMS (ESI-TOF) m/z 418.1167 ($M + Na^+$), calcd for $C_{24}H_{17}N_3O_3Na$ 418.1168.

4-(4-(2-Oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-1,2,3-triazol-1-yl)benzonitrile (49ar): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 86% (168.0 mg); Mp 252-254 °C; IR (Neat): ν_{max} 2969, 2227, 1735, 1605, 1510, 1448, 1371, 1235, 1045, 735, and 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, s), 7.71 (2H, td, *J* = 9.0, 2.0 Hz), 7.59-7.55 (2H, m), 7.49 (2H, td, *J* = 9.0, 2.0 Hz), 7.42 (1H, tt, *J* = 9.0, 1.5 Hz), 7.37 (2H, tt, *J* = 8.0, 1.5 Hz), 7.33 (2H, br t, *J* = 8.0 Hz), 7.21 (1H, q, *J* = 2.0 Hz), 7.19 (1H, t, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.8 (C), 154.0 (C), 143.6 (CH), 140.3 (C), 139.6 (C), 136.4 (C), 133.3 (2 x CH), 132.3 (CH), 129.9 (CH), 129.2 (2 x CH), 129.1 (2 x CH), 128.3 (CH), 126.6 (C), 125.4 (2 x CH), 124.7 (CH), 118.92 (C), 118.90 (C), 117.6 (C), 116.7 (CH), 113.0 (C); HRMS (ESI-TOF) m/z 413.1015 ($M + Na^+$), calcd for $C_{24}H_{14}N_4O_2Na$ 413.1015.



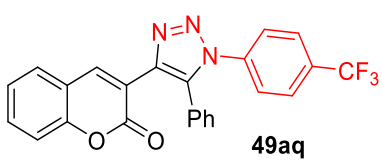
49ar

3-(1-(4-Fluorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 92% (176.3 mg); Mp 218-220 °C; IR (Neat): ν_{max} 2984, 1736, 1445, 1371, 1231, 1096, 1042, 937, 846, 633 and 607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, s), 7.57-7.53 (2H, m), 7.37-7.29 (7H, m), 7.19 (1H, q, *J* = 1.6 Hz), 7.18 (1H, t, *J* = 1.6 Hz), 7.13-7.07 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.6 (C, d, *J* = 249 Hz, *C*-F), 158.9 (C), 153.9 (C), 143.3 (CH), 139.7 (C), 136.5 (C), 132.4 (C, d, *J* = 3.0 Hz), 132.0 (CH), 129.4 (CH), 129.2 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 127.2 (2 x CH, d, *J* = 8.0 Hz), 126.9 (C), 124.6 (CH), 119.3 (C), 119.0 (C), 116.5 (2 x CH, d, *J* = 17.0 Hz), 116.2 (CH); HRMS (ESI-TOF) m/z 406.0968 ($M + Na^+$), calcd for $C_{23}H_{14}FN_3O_2Na$ 406.0968.



49af

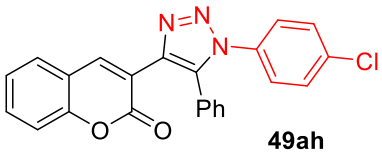
3-(5-Phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49aq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 91% (198 mg); Mp 196-198° C; IR (Neat): ν_{max} 2984, 1715, 1609, 1324, 1279, 1124, 1067, 992, 846, 749 and 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, s), 7.68 (2H, d, *J* = 8.5 Hz), 7.59-7.54 (2H, m),



49aq

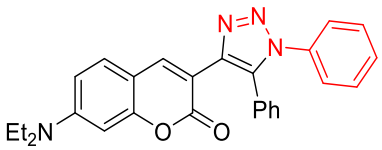
7.49 (2H, d, *J* = 8.5 Hz), 7.40 (1H, tt, *J* = 8.5, 1.5 Hz), 7.36 (2H, td, *J* = 7.5, 1.5 Hz), 7.35-7.30 (2H, m), 7.20 (2H, td, *J* = 8.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.8 (C), 154.1 (C), 143.5 (CH), 140.2 (C), 139.2 (C), 136.5 (C), 132.2 (CH), 131.0 (C, q, *J* = 32.5 Hz), 129.7 (CH), 129.3 (2 x CH), 129.0 (2 x CH), 128.3 (CH), 126.9 (C), 126.5 (2 x CH, q, *J* = 3.75 Hz), 125.3 (2 x CH), 124.6 (CH), 123.5 (C, q, *J* = 270.8 Hz, *C*F_3), 119.3 (C), 119.0 (C), 116.7 (CH); HRMS (ESI-TOF) m/z 434.1113 (M + H^+), calcd for $C_{24}H_{14}F_3N_3OH$ 434.1116.

3-(1-(4-Chlorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 84% (167.6 mg); Mp 220-222 °C; IR (Neat): ν_{max} 2968, 2923, 2853, 1715, 1607, 1495, 1366, 1228, 1216, 1092, 1019, 797, 760 and 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (1H, s), 7.55 (2H, dt, *J* = 7.5, 1.5 Hz), 7.38 (3H, m), 7.35-7.32 (3H, m), 7.29 (3H, m), 7.20 (1H, q, *J* = 1.5 Hz), 7.19 (1H, t, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.9 (C), 153.9 (C), 143.4 (CH), 139.8 (C), 136.4 (C), 135.2 (C), 134.8 (C), 132.1 (CH), 129.5 (CH), 129.4 (2 x CH), 129.2 (2 x CH), 128.8 (2 x CH), 128.2 (CH), 126.8 (C), 126.3 (2 x CH), 124.6 (CH), 119.2 (C), 118.9 (C), 116.6 (CH); HRMS (ESI-TOF) m/z 422.0672 (M + Na^+), calcd for $C_{23}H_{14}ClN_3O_2Na$ 422.0672.



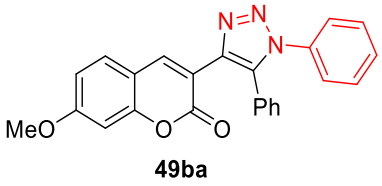
49ah

7-(Diethylamino)-3-(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and isolated as a yellow solid; Yield: 85% (186 mg); Mp 212-214 °C; IR (Neat): ν_{max} 2984, 1736, 1592, 1445, 1371, 1231, 1096, 1042, 937, 846, 633 and 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, s), 7.41-7.39 (3H, m), 7.34-7.30 (4H, m), 7.30-7.28 (2H, m), 7.20-7.19 (2H, m), 6.59 (1H, dd, *J* = 7.2, 2.0 Hz), 6.47 (1H, d, *J* = 2.5 Hz), 3.42 (4H, q, *J* = 5.6 Hz), 1.21 (6H, t, *J* = 5.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.3 (C), 156.8 (C), 150.9 (C), 144.0 (CH), 140.7 (C), 136.6 (C), 135.7 (C), 129.34 (2 x CH), 129.27 (CH), 129.1 (2 x CH), 129.02 (CH), 128.97 (CH), 128.5 (2 x CH), 127.5 (C), 125.3 (2 x CH), 111.6 (C), 108.9 (CH), 108.5 (C), 97.1 (CH), 44.8 (2 x CH_2), 12.4 (2 x CH_3); HRMS (ESI-TOF) m/z 459.1798 (M + Na^+), calcd for $C_{27}H_{24}N_4O_2Na$ 459.1797.



49da

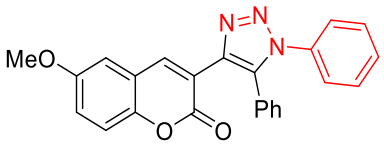
3-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)-7-methoxy-2*H*-chromen-2-one (49ba): Prepared



49ba

following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and isolated as a light orange solid; Yield: 90% (178 mg); Mp 210-212 °C; IR (Neat): ν_{max} 2983, 1728, 1602, 1446, 1372, 1232, 1097, 1042, 937, 846, 633 and 607 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.44-7.39 (4H, m), 7.34-7.27 (5H, m), 7.19 (2H, br d, *J* = 7.5 Hz), 6.86 (1H, br dd, *J* = 8.5, 2.5 Hz), 6.79 (1H, br s), 3.86 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.0 (C), 159.3 (C), 155.8 (C), 143.4 (CH), 139.9 (C), 136.4 (C), 136.1 (C), 129.24 (2 x CH), 129.18 (CH), 129.15 (3 x CH), 129.12 (CH), 128.6 (2 x CH), 127.2 (C), 125.2 (2 x CH), 115.8 (C), 112.8 (CH), 112.7 (C), 100.5 (CH), 55.8 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 396.1348 (M + H), calcd for $C_{24}H_{17}N_3O_3H$ 396.1348.

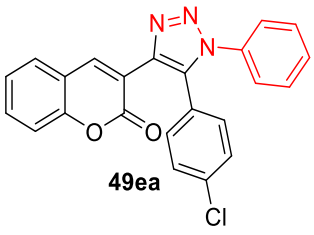
3-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)-6-methoxy-2*H*-chromen-2-one (49ca): Prepared



49ca

following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and isolated as a white solid; Yield: 84% (166 mg); Mp 238-240 °C; IR (Neat): ν_{max} 2984, 1736, 1446, 1372, 1233, 1043, 937, 846, 634 and 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (1H, s), 7.43-7.38 (3H, m), 7.34-7.28 (5H, m), 7.25 (1H, d, *J* = 8.0 Hz), 7.20 (1H, q, *J* = 2.0 Hz), 7.17 (1H, t, *J* = 2.0 Hz), 7.13 (1H, dd, *J* = 8.8, 2.8 Hz), 6.97 (1H, d, *J* = 2.8 Hz), 3.86 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.1 (C), 156.2 (C), 148.4 (C), 143.1 (CH), 139.7 (C), 136.5 (C), 136.4 (C), 129.3 (3 x CH), 129.2 (3 x CH), 128.7 (2 x CH), 127.2 (C), 125.3 (2 x CH), 119.9 (C), 119.8 (CH), 119.4 (C), 117.6 (CH), 110.1 (CH), 55.8 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 396.1347 (M + Na^+), calcd for $C_{24}H_{17}N_3O_3H$ 396.1348.

3-(5-(4-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one (49ea): Prepared

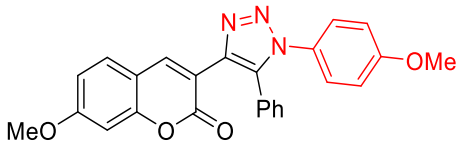


49ea

following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a yellow solid; Yield: 86% (173 mg); Mp 250-252 °C; IR (Neat): ν_{max}, 2983, 1722, 1607, 1446, 1372, 1232, 1097, 1042, 937, 846, 633 and 607 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (1H, s), 7.58-7.53 (2H, m), 7.45-7.41 (3H, m), 7.33-7.31 (4H, m), 7.27 (2H, td, *J* = 9.0, 2.0 Hz), 7.13 (2H, td, *J* = 9.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.8 (C), 153.8 (C), 143.4 (CH), 139.7 (C), 136.0 (C), 135.4 (C), 135.3 (C), 132.1 (CH), 130.5 (2 x CH), 129.4 (CH), 129.3 (2 x CH), 129.0 (2 x CH), 128.3 (CH), 125.7

(C), 125.2 (2 x CH), 124.6 (CH), 119.1 (C), 118.9 (C), 116.5 (CH); HRMS (ESI-TOF) m/z 400.0850 (M + H^+), calcd for $C_{23}H_{14}ClN_3O_2H$ 400.0853.

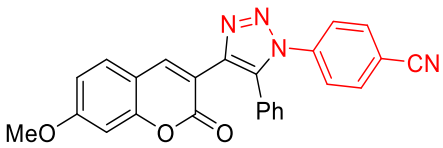
7-Methoxy-3-(1-(4-methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)-2*H*-chromen-2-one



49bb

(49bb): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and was isolated as a white solid; Yield: 92% (195 mg); Mp 162-164 °C; IR (Neat): ν_{max} 2984, 1737, 1614, 1514, 1442, 1353, 1228, 1015, 980, 937, 846, 835 and 727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.43 (1H, d, *J* = 8.5 Hz), 7.33-7.28 (3H, m), 7.25 (2H, td, *J* = 10.0, 2.0 Hz), 7.19 (1H, q, *J* = 1.5 Hz), 7.18 (1H, t, *J* = 1.5 Hz), 6.89 (2H, td, *J* = 10.0, 3.0 Hz), 6.86 (1H, dd, *J* = 7.2, 2.5 Hz), 6.79 (1H, d, *J* = 2.5 Hz), 3.87 (3H, s, OC*H*$_3$), 3.82 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.0 (C), 159.9 (C), 159.3 (C), 155.8 (C), 143.4 (CH), 139.7 (C), 136.1 (C), 129.4 (C), 129.25 (2 x CH), 129.17 (CH), 129.0 (CH), 128.5 (2 x CH), 127.4 (C), 126.6 (2 x CH), 115.9 (C), 114.3 (2 x CH), 112.8 (CH), 112.7 (C), 100.5 (CH), 55.8 (CH_3, O*C*H$_3$), 55.4 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 426.1454 (M + H), calcd for $C_{25}H_{19}N_3O_4H$ 426.1454.

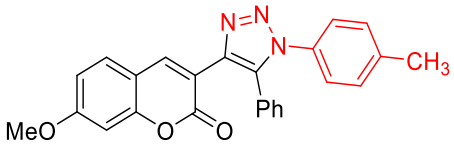
4-(4-(7-Methoxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-1,2,3-triazol-1-yl)benzonitrile



49br

(49br): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and isolated as a white solid; Yield: 89% (186 mg); Mp 194-196 °C; IR (Neat): ν_{max} 2921, 2851, 2228, 1753, 1609, 1581, 1445, 1312, 1233, 1097, 1043, 937, 840, 778, 647 and 597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (1H, br s), 7.71 (2H, br s), 7.48-7.37 (6H, m), 7.20 (2H, br s), 6.88 (1H, br s), 6.81 (1H, br s), 3.88 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.3 (C), 159.2 (C), 156.0 (C), 143.8 (CH), 140.7 (C), 139.7 (C), 136.1 (C), 133.2 (2 x CH), 129.8 (CH), 129.30 (CH), 129.26 (2 x CH), 129.0 (2 x CH), 126.7 (C), 125.4 (2 x CH), 117.6 (C), 115.2 (C), 113.1 (CH), 112.9 (C), 112.6 (C), 100.6 (CH), 55.8 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 421.1301 (M + H), calcd for $C_{25}H_{16}N_4O_3H$ 421.1301.

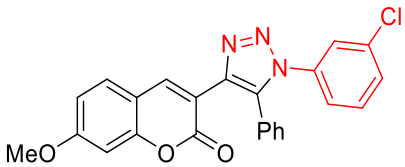
7-Methoxy-3-(5-phenyl-1-(*p*-tolyl)-*1H*-1,2,3-triazol-4-yl)-*2H*-chromen-2-one (49bc):



49bc

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and was isolated as a white solid; Yield: 90% (184 mg); Mp 200-202 °C; IR (Neat): ν_{max} 3040, 1716, 1610, 1510, 1231, 1159, 1135, 905, 777, 723, 696 and 646 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.43 (1H, d, *J* = 8.5 Hz), 7.36-7.28 (3H, m), 7.23-7.17 (6H, m), 6.87 (1H, dd, *J* = 8.5, 2.5 Hz), 6.80 (1H, d, *J* = 2.5 Hz), 3.87 (3H, s, OC*H*$_3$), 2.38 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.0 (C, O-*C*=O), 159.3 (C), 155.8 (C), 143.4 (CH), 139.8 (C), 139.3 (C), 136.1 (C), 133.9 (C), 129.7 (2 x CH), 129.25 (2 x CH), 129.18 (CH), 129.1 (CH), 128.6 (2 x CH), 127.4 (C), 125.0 (2 x CH), 115.9 (C), 112.8 (CH), 112.7 (C), 100.5 (CH), 55.8 (CH_3, O*C*H$_3$), 21.1 (CH_3, Ar-*C*H$_3$); HRMS (ESI-TOF) m/z 410.1505 ($M + H^+$), calcd for $C_{25}H_{19}N_3O_3H$ 410.1505.

3-(1-(3-Chlorophenyl)-5-phenyl-*1H*-1,2,3-triazol-4-yl)-7-methoxy-*2H*-chromen-2-one

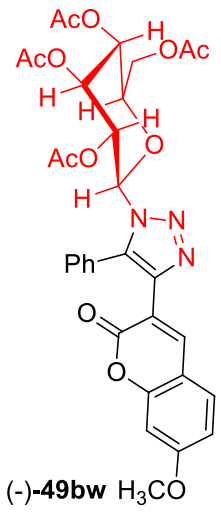


49bi

(49bi): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and was isolated as a white solid; Yield: 89% (214 mg); Mp 180-182 °C; IR (Neat): ν_{max} 3057, 1730, 1611, 1593, 1506, 1486, 1280, 1232, 1160, 1136, 1026, 873, 836, 731 and 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.44-7.43 (2H, m), 7.40-7.29 (5H, m), 7.20 (2H, d, *J* = 7.0 Hz), 7.16 (1H, d, *J* = 8.0 Hz), 6.87 (1H, br d, *J* = 9.0 Hz), 6.80 (1H, br s), 3.87 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.2 (C, O-*C*=O), 159.2 (C), 155.9 (C), 143.6 (CH), 140.2 (C), 137.4 (C), 136.2 (C), 134.9 (C), 130.1 (CH), 129.5 (CH), 129.33 (CH), 129.30 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 127.0 (C), 125.5 (CH), 123.3 (CH), 115.6 (C), 112.9 (CH), 112.7 (C), 100.6 (CH), 55.8 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 430.0959 ($M + H^+$), calcd for $C_{24}H_{16}ClN_3O_3H$ 430.0958.

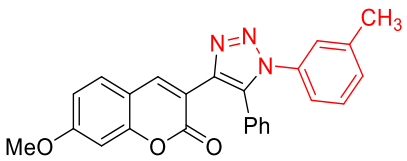
.

(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-(7-methoxy-2-oxo-*2H*-chromen-3-yl)-5-phenyl-*1H*-1,2,3-triazol-1-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate [(-)-49bw]: Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 6:4) and was isolated as a semi solid; Yield: 80% (261 mg); $[\alpha]_D^{25}$ = -67.62 (*C* = 0.084, $CHCl_3$); IR (Neat): ν_{max} 1719, 1614, 1366, 1229, 1203, 1139, 1094, 1031, 912, 840, 700 and 597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, s), 7.51-7.41 (6H, m), 6.86 (1H, dd, *J* = 8.8, 2.4 Hz), 6.77 (1H, d, *J* = 2.4 Hz), 6.02 (1H, t, *J* = 9.6 Hz), 5.52 (1H, d, *J* = 9.2 Hz), 5.29 (1H, t, *J* = 9.6 Hz), 5.21 (1H, t, *J* = 9.6 Hz), 4.24 (1H, dd, *J* = 12.8, 5.2 Hz), 4.17 (1H, dd, *J* = 12.8, 2.0 Hz), 3.87 (3H, s, OC*H*$_3$), 3.81 (1H, ddd, *J* = 10.0, 5.6, 2.4 Hz), 2.13 (3H, s, COC*H*$_3$), 2.04 (3H, s, COC*H*$_3$), 2.02 (3H, s, COC*H*$_3$), 1.90 (3H, s, COC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.4 (C, O-*C*=O), 170.3 (C, O-*C*=O), 169.1 (C, O-*C*=O), 168.3 (C, O-*C*=O), 163.1 (C, O-*C*=O), 158.9 (C), 155.8 (C), 143.3 (CH), 140.0 (C), 137.5 (C), 130.0 (CH), 129.4 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 126.6 (C), 115.2 (C), 112.9 (CH), 112.6 (C), 100.5 (CH), 83.4 (CH), 74.7 (CH), 73.4 (CH), 69.4 (CH), 67.6 (CH), 61.8 (CH_2), 55.8 (CH_3, O*C*H$_3$), 20.7 (CH_3, CO*C*H$_3$), 20.5 (CH_3, CO*C*H$_3$), 20.4 (CH_3, CO*C*H$_3$), 20.3 (CH_3, CO*C*H$_3$); HRMS (ESI-TOF) m/z 650.1986 (M + H^+), calcd for $C_{32}H_{31}N_3O_{12}H$ 650.1986.



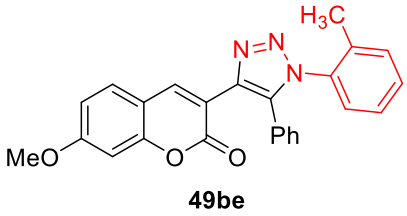
(-)-**49bw**

7-Methoxy-3-(5-phenyl-1-(*m*-tolyl)-*1H*-1,2,3-triazol-4-yl)-*2H*-chromen-2-one (49bd): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and was isolated as a white solid; Yield: 89% (182 mg); Mp 186-188 °C; IR (Neat): ν_{max} 2979, 1728, 1609, 1492, 1444, 1372, 1277, 1235, 1133, 1041, 980, 779, 732, 696 and 527 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, s), 7.43 (1H, d, *J* = 8.8 Hz), 7.34-7.27 (3H, m), 7.25-7.18 (5H, m), 7.02 (1H, tt, *J* = 6.8, 1.6 Hz), 6.87 (1H, dd, *J* = 8.4, 2.4 Hz), 6.80 (1H, d, *J* = 2.4 Hz), 3.87 (3H, s, OC*H*$_3$), 2.34 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.0 (C, O-*C*=O), 159.3 (C), 155.8 (C), 143.4 (CH), 139.8 (C), 139.4 (C), 136.3 (C), 136.1 (C), 129.9 (CH), 129.22 (2 x CH), 129.16 (CH), 129.1 (CH), 128.8 (CH), 128.5 (2 x CH), 127.3 (C), 125.9 (CH), 122.2 (CH), 115.8 (C), 112.8 (CH), 112.7 (C), 100.5 (CH), 55.7 (CH_3, O*C*H$_3$), 21.2 (CH_3, Ar-*C*H$_3$); HRMS (ESI-TOF) m/z 410.1501 (M + H^+), calcd for $C_{25}H_{19}N_3O_3H$ 410.1505.



49bd

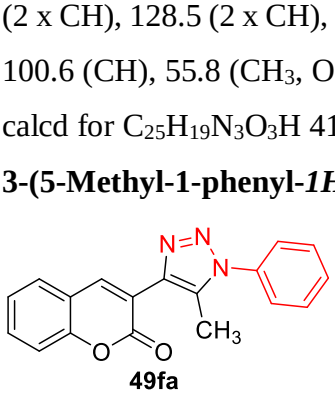
7-Methoxy-3-(5-phenyl-1-(o-tolyl)-*1H*-1,2,3-triazol-4-yl)-*2H*-chromen-2-one (49be):



49be

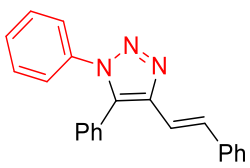
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 4:6) and was isolated as a semi solid; Yield: 40% (82 mg); IR (Neat): ν_{max} 3052, 2918, 1728, 1610, 1492, 1278, 1236, 1135, 733 and 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (1H, s), 7.47 (1H, d, *J* = 9.0 Hz), 7.39-7.36 (1H, m), 7.30-7.28 (4H, m), 7.23 (2H, tt, *J* = 8.5, 2.0 Hz), 7.12 (2H, td, *J* = 7.0, 2.0 Hz), 6.89 (1H, dd, *J* = 8.5, 2.5 Hz), 6.82 (1H, d, *J* = 2.5 Hz), 3.89 (3H, s, OC*H*$_3$), 2.00 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.1 (C, O-*C*=O), 159.1 (C), 155.9 (C), 143.2 (CH), 139.2 (C), 137.2 (C), 135.6 (C), 135.3 (C), 131.1 (CH), 130.1 (CH), 129.2 (CH), 129.0 (CH), 128.7 (2 x CH), 128.5 (2 x CH), 127.9 (CH), 127.3 (C), 126.7 (CH), 116.1 (C), 112.94 (CH), 112.89 (C), 100.6 (CH), 55.8 (CH_3, O*C*H$_3$), 17.6 (CH_3, Ar-*C*H$_3$); HRMS (ESI-TOF) m/z 410.1504 (M + H^+), calcd for $C_{25}H_{19}N_3O_3H$ 410.1505.

3-(5-Methyl-1-phenyl-*1H*-1,2,3-triazol-4-yl)-*2H*-chromen-2-one (49fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 3:7) and was isolated as a white solid; Yield: 93% (141 mg); Mp 158-160 °C; IR (Neat): ν_{max} 3057, 1718, 1679, 1608, 1502, 1453, 1421, 1384, 1252, 1186, 951, 920, 743, 702, 626 and 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (1H, s), 7.64-7.52 (7H, m), 7.41 (1H, t, *J* = 7.2 Hz), 7.35 (1H, t, *J* = 7.2 Hz), 2.47 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.6 (C, O-*C*=O), 153.8 (C), 142.3 (CH), 139.5 (C), 136.1 (C), 133.1 (C), 131.8 (CH), 129.6 (CH), 129.5 (2 x CH), 128.3 (CH), 125.3 (2 x CH), 124.7 (CH), 119.7 (C), 119.3 (C), 116.5 (CH), 10.8 (CH_3); HRMS (ESI-TOF) m/z 326.0903 (M + Na^+), calcd for $C_{18}H_{13}N_3O_2Na$ 326.0905.



49fa

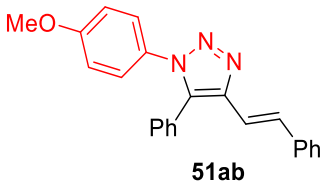
(*E*)-1,5-Diphenyl-4-styryl-1*H*-1,2,3-triazole (51aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and isolated as a white solid; Yield: 88% (142 mg); Mp 168-170 °C; IR (Neat): ν_{max} 3056, 1596, 1496, 1447, 1241, 1098, 1016, 759, 692 and 562 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.68 (1H, d, *J* = 16.5 Hz), 7.48-7.46 (2H, m), 7.43-7.40 (3H, m), 7.38-7.36 (3H, m), 7.34-7.30 (4H, m), 7.26-7.23 (3H, m), 6.95 (1H, d, *J* = 16.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.3 (C), 136.9 (C), 136.4 (C), 133.9 (C), 131.2 (CH), 129.8 (2 x CH), 129.24 (CH), 129.16 (2 x CH), 128.93 (2 x CH), 128.87 (CH), 128.6 (2 x



51aa

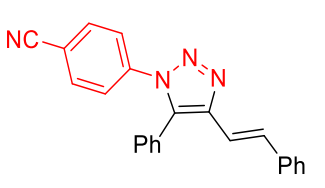
CH), 127.8 (CH), 126.9 (C), 126.5 (2 x CH), 124.8 (2 x CH), 115.3 (CH); HRMS (ESI-TOF) m/z 324.1501 ($M + H^+$), calcd for $C_{22}H_{17}N_3H$ 324.1501.

(*E*)-1-(4-Methoxyphenyl)-5-phenyl-4-styryl-1*H*-1,2,3-triazole (51ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a red solid; Yield: 82% (145 mg). Mp 172-174 °C; IR (Neat): ν_{max} 2983, 1596, 1513, 1446, 1372, 1232, 1042, 846, 692 and 587 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (1H, d, *J* = 16.0 Hz), 7.46 (2H, br d, *J* = 5.6 Hz), 7.42-7.40 (3H, m), 7.34-7.30 (2H, m), 7.25-7.21 (5H, m), 6.94 (1H, d, *J* = 16.0 Hz), 6.87 (2H, td, *J* = 10.0, 2.4 Hz), 3.78 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.7 (C), 143.1 (C), 136.9 (C), 134.0 (C), 131.0 (CH), 129.8 (2 x CH), 129.4 (C), 129.1 (CH), 128.9 (2 x CH), 128.5 (2 x CH), 127.7 (CH), 127.0 (C), 126.5 (2 x CH), 126.2 (2 x CH), 115.5 (CH), 114.3 (2 x CH), 55.4 (CH_3, O*C*H$_3$); HRMS (ESI-TOF) m/z 354.1605 ($M + H^+$), calcd for $C_{23}H_{19}N_3OH$ 354.1606.



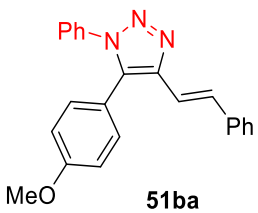
51ab

(*E*)-4-(5-Phenyl-4-styryl-1*H*-1,2,3-triazol-1-yl)benzonitrile (51ar): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and isolated as a white solid; Yield: 88% (153.1 mg); Mp 184-186 °C; IR (Neat): ν_{max} 3055, 2229, 1605, 1508, 1309, 1264, 1016, 990, 840, 733 and 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.68-7.65 (3H, m), 7.49-7.44 (7H, m), 7.32 (2H, t, *J* = 7.5 Hz), 7.26-7.24 (3H, m), 6.89 (1H, d, *J* = 16.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.0 (C), 139.6 (C), 136.6 (C), 133.5 (C), 133.2 (2 x CH), 132.0 (CH), 129.8 (CH), 129.7 (2 x CH), 129.3 (2 x CH), 128.6 (2 x CH), 128.0 (CH), 126.6 (2 x CH), 126.3 (C), 124.7 (2 x CH), 117.6 (C), 114.6 (CH), 112.5 (C); HRMS (ESI-TOF) m/z 371.1275 ($M + H^+$), calcd for $C_{23}H_{16}N_4Na$ 371.1273.



51ar

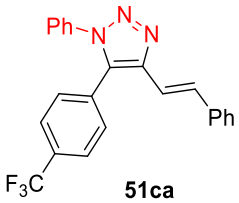
(*E*)-5-(4-Methoxyphenyl)-1-phenyl-4-styryl-1*H*-1,2,3-triazole (51ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a white solid; Yield: 82% (144.5 mg); Mp 172-174 °C; IR (Neat): ν_{max} 3054, 2926, 2857, 1610, 1597, 1500, 1252, 1177, 1033, 992, 967, 836, 760 and 562 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.66 (1H, d, *J* = 16.5 Hz), 7.48 (2H, d, *J* = 7.5 Hz), 7.38 (3H, br s), 7.33 (4H, m), 7.25-7.23 (1H, m), 7.16 (2H, br d, *J* = 8.5 Hz), 6.94 (3H, m), 3.84 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.2 (C), 143.1 (C), 137.0 (C), 136.5 (C), 133.9 (C), 131.1 (2 x CH),



51ba

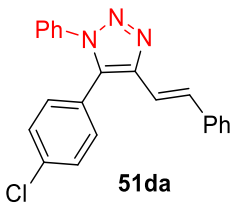
130.9 (CH), 129.2 (2 x CH), 128.8 (CH), 128.6 (2 x CH), 127.7 (CH), 126.5 (2 x CH), 124.8 (2 x CH), 118.9 (C), 115.6 (CH), 114.5 (2 x CH), 55.3 (CH_3, OCH_3); HRMS (ESI-TOF) m/z 354.1606 (M + H^+), calcd for $C_{23}H_{19}N_3OH$ 354.1606.

(*E*)-1-Phenyl-4-styryl-5-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (51ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a semi solid; Yield: 85% (166 mg); IR (Neat): ν_{max} 3059, 2923, 1595, 1494, 1372, 1232, 1042, 937 and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.71 (1H, d, *J* = 16.0 Hz), 7.67 (2H, d, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 7.5 Hz), 7.42-7.39 (3H, m), 7.37 (2H, br d, *J* = 8.5 Hz), 7.34-7.27 (4H, m), 7.25 (1H, tt, *J* = 7.0, 2.0 Hz), 6.89 (1H, d, *J* = 16.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.8 (C), 136.7 (C), 136.1 (C), 132.4 (C), 132.3 (CH), 131.22 (C, q, *J* = 32.5 Hz), 130.8 (C), 130.2 (2 x CH), 129.5 (2 x CH), 129.3 (CH), 128.7 (2 x CH), 128.1 (CH), 126.7 (2 x CH), 126.0 (2 x CH, q, *J* = 3.75 Hz), 124.7 (2 x CH), 123.7 (C, q, *J* = 271.25 Hz), 114.6 (CH); HRMS (ESI-TOF) m/z 392.1375 (M + H^+), calcd for $C_{23}H_{16}F_3N_3H$ 392.1375.



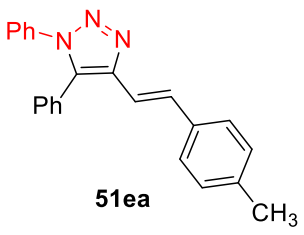
51ca

(*E*)-5-(4-Chlorophenyl)-1-phenyl-4-styryl-1*H*-1,2,3-triazole (51da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a white solid; Yield: 88% (156.6 mg); Mp 144-146 °C; IR (Neat): ν_{max} 3056, 1596, 1499, 1369, 1241, 1093, 1043, 917, 835 and 561 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (1H, d, *J* = 16.0 Hz), 7.48 (2H, d, *J* = 7.5 Hz), 7.42-7.39 (5H, m), 7.36-7.30 (4H, m), 7.28-7.25 (1H, m), 7.18 (2H, td, *J* = 9.0, 2.5 Hz), 6.90 (1H, d, *J* = 16.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.5 (C), 136.8 (C), 136.2 (C), 135.6 (C), 132.7 (C), 131.8 (CH), 131.1 (2 x CH), 129.4 (4 x CH), 129.1 (CH), 128.6 (2 x CH), 128.0 (CH), 126.6 (2 x CH), 125.4 (C), 124.9 (2 x CH), 114.9 (CH); HRMS (ESI-TOF) m/z 358.1111 (M + H^+), calcd for $C_{22}H_{16}N_3ClH$ 358.1111.



51da

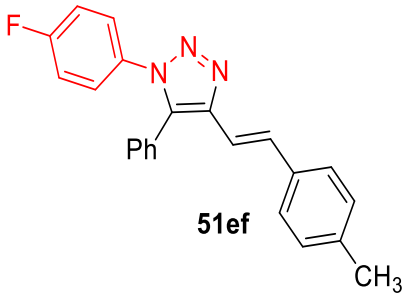
(*E*)-4-(4-Methylstyryl)-1,5-diphenyl-1*H*-1,2,3-triazole (51ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a white solid; Yield: 85% (144 mg); Mp 168-170 °C; IR (Neat) ν_{max} 3051, 2916, 1593, 1494, 1371, 1232, 1042, 847, 738, and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.65 (1H, d, *J* = 16.5 Hz), 7.43-7.40 (3H, m), 7.39-7.36 (5H, m), 7.32-7.30 (2H, m), 7.25-7.23 (2H, m), 7.14 (2H, d, *J* = 8.0 Hz), 6.90 (1H, d, *J* = 16.5 Hz), 2.34 (3H, s,



51ea

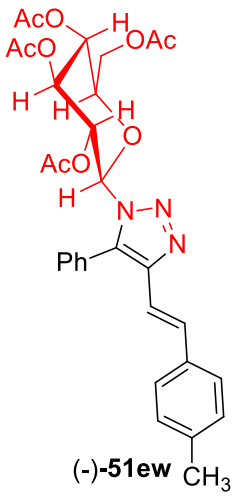
ArC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 143.5 (C), 137.8 (C), 136.5 (C), 134.2 (C), 133.7 (C), 131.3 (CH), 129.8 (2 x CH), 129.3 (2 x CH), 129.20 (CH), 129.18 (2 x CH), 128.94 (2 x CH), 128.87 (CH), 127.1 (C), 126.5 (2 x CH), 124.8 (2 x CH), 114.4 (CH), 21.2 (CH_3); HRMS (ESI-TOF) m/z 338.1658 ($M + H^+$), calcd for $C_{23}H_{19}N_3H$ 338.1658.

(*E*)-1-(4-Fluorophenyl)-4-(4-methylstyryl)-5-phenyl-1*H*-1,2,3-triazole (51ef): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a white solid; Yield: 80% (142 mg); Mp 150-152 °C; IR (Neat): ν_{max} 3018, 2914, 1511, 1362, 1218, 837 and 633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, d, *J* = 16.4 Hz), 7.45-7.41 (3H, m), 7.36 (2H, br d, *J* = 8.0 Hz), 7.33-7.27 (2H, m), 7.24-7.22 (2H, m), 7.13 (2H, br d, *J* = 8.0 Hz), 7.07 (2H, br tt, *J* = 8.0, 2.4 Hz), 6.88 (1H, d, *J* = 16.3 Hz), 2.34 (3H, s, ArC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.44 (C, d, *J* = 248 Hz, *C*-F), 143.6 (C), 137.9 (C), 134.1 (C), 133.7 (C), 132.6 (C, d, *J* = 3.0 Hz), 131.5 (CH), 129.8 (2 x CH), 129.4 (CH), 129.3 (2 x CH), 129.0 (2 x CH), 126.8 (C), 126.7 (2 x CH, d, *J* = 9.0 Hz), 126.5 (2 x CH), 116.23 (2 x CH, d, *J* = 23.0 Hz), 114.2 (CH), 21.2 (CH_3); HRMS (ESI-TOF) m/z 356.1561 ($M + H^+$), calcd for $C_{23}H_{18}FN_3H$ 356.1563.



51ef

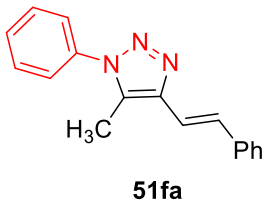
(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(4-(*E*)-4-methylstyryl)-5-phenyl-*1H*-1,2,3-triazol-1-yl)tetrahydro-*2H*-pyran-3,4,5-triyl triacetate (-)-**51ew:** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 6:4) and was isolated as a semi solid; Yield: 80% (237 mg); $[\alpha]_D^{25}$ = -54.86 (*C* = 0.140, $CHCl_3$); IR (Neat): ν_{max} 2946, 1748, 1730, 1366, 1235, 1211, 1079, 1066, 1033, 917, 773, 730, 707 and 521 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.55 (4H, m), 7.51-7.49 (2H, m), 7.32 (2H, d, *J* = 8.0 Hz), 7.12 (2H, d, *J* = 8.0 Hz), 6.77 (1H, d, *J* = 16 Hz), 5.93 (1H, t, *J* = 9.5 Hz), 5.53 (1H, d, *J* = 9.5 Hz), 5.27 (1H, t, *J* = 9.0 Hz), 5.17 (1H, t, *J* = 9.5 Hz), 4.24 (1H, dd, *J* = 12.0, 6.0 Hz), 4.17 (1H, dd, *J* = 12.5, 2.5 Hz), 3.83 (1H, ddd, *J* = 10.0, 5.6, 2.4 Hz), 2.33 (3H, s, Ar-C*H*$_3$), 2.13 (3H, s, COC*H*$_3$), 2.04 (3H, s, COC*H*$_3$), 2.01 (3H, s, COC*H*$_3$), 1.86 (3H, s, COC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.4 (C, O-*C*=O), 170.3 (C, O-*C*=O), 169.1 (C, O-*C*=O), 168.3 (C, O-*C*=O), 143.7 (C), 137.9 (C), 134.9 (C), 134.0 (C), 131.7 (CH), 130.1 (CH), 130.0 (2 x CH), 129.3 (2 x CH), 129.1 (2 x CH), 126.5 (2 x CH),



(-)-**51ew**

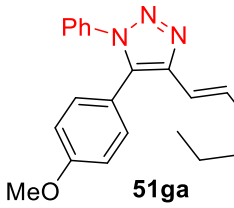
126.1 (C), 113.8 (CH), 83.6 (CH), 74.6 (CH), 73.4 (CH), 69.3 (CH), 67.6 (CH), 61.9 (CH_2), 21.2 (CH_3, Ar-*C*H_3), 20.7 (CH_3, CO*C*H_3), 20.53 (CH_3, CO*C*H_3), 20.50 (CH_3, CO*C*H_3), 20.3 (CH_3, CO*C*H_3); HRMS (ESI-TOF) m/z 592.2296 ($M + H^+$), calcd for $C_{31}H_{33}N_3O_9H$ 592.2295.

(*E*)-5-Methyl-1-phenyl-4-styryl-*1H*-1,2,3-triazole (51fa): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and isolated as a white solid; Yield: 90% (117 mg); Mp 108-110 °C; IR (Neat): ν_{max} 3062, 3039, 1596, 1502, 1430, 1366, 1260, 963, 800, 755, 692 and 556 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.55-7.51 (5H, m), 7.49-7.48 (1H, m), 7.47-7.45 (2H, m), 7.36 (2H, t, *J* = 8.0 Hz), 7.26 (1H, t, *J* = 7.0 Hz), 7.02 (1H, d, *J* = 16.0 Hz), 2.39 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 142.9 (C), 137.0 (C), 136.2 (C), 130.05 (CH), 129.99 (C), 129.4 (2 x CH), 129.3 (CH), 128.6 (2 x CH), 127.7 (CH), 126.4 (2 x CH), 124.9 (2 x CH), 115.9 (CH), 9.2 (CH_3); HRMS (ESI-TOF) m/z 262.1344 ($M + H^+$), calcd for $C_{17}H_{15}N_3H$ 262.1344.



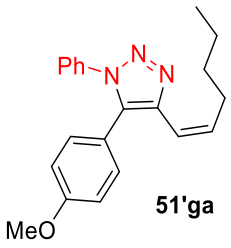
51fa

(*E*)-4-(Hex-1-en-1-yl)-5-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (51ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as a yellow solid; Yield: 56% (93.5 mg). Mp 130-132 °C; IR (Neat): ν_{max} 3027, 2957, 1611, 1498, 1366, 1228, 1216, and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.35 (3H, m), 7.30-7.28 (2H, m), 7.10 (2H, td, *J* = 9.5, 2.5 Hz), 6.90 (2H, td, *J* = 9.5, 2.0 Hz), 6.73 (1H, td, *J* = 15.5, 7.0 Hz), 6.25 (1H, td, *J* = 16.0, 1.5 Hz), 3.82 (3H, s), 2.20 (2H, dq, *J* = 7.0, 1.5 Hz), 1.48-1.42 (2H, m), 1.40-1.32 (2H, m), 0.91 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.0 (C), 143.3 (C), 136.7 (C), 134.2 (CH), 132.5 (C), 131.1 (2 x CH), 129.1 (2 x CH), 128.6 (CH), 124.8 (2 x CH), 119.2 (C), 117.0 (CH), 114.3 (2 x CH), 55.3 (CH_3), 32.9 (CH_2), 31.3 (CH_2), 22.3 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) m/z 334.1917 ($M + H^+$), calcd for $C_{21}H_{23}N_3OH$ 334.1919.



51ga

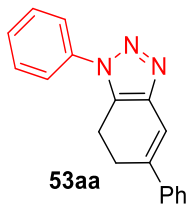
(*Z*)-4-(Hex-1-en-1-yl)-5-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (51'ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.3:9.7 to 1:9) and was isolated as an orange solid; Yield: 24% (40 mg); Mp 126-128 °C; IR (Neat): ν_{max} 2956, 2926, 2855, 1675, 1597, 1498, 1293, 1174, 834, 763 and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.36 (3H, m), 7.33-7.30 (2H, m), 7.10 (2H, td, *J* = 9.5, 2.5 Hz), 6.88 (2H, td, *J* = 9.5, 3.0 Hz), 6.13 (1H, td, *J* = 11.5, 1.5 Hz), 5.80 (1H, td, *J* = 11.5, 7.5 Hz), 3.81 (3H, s), 2.76 (2H,



51'ga

dq, *J* = 7.5, 1.5 Hz), 1.51-1.44 (2H, m), 1.43-1.38 (2H, m), 0.92 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.0 (C), 143.3 (C), 136.7 (C), 136.2 (CH), 134.2 (C), 131.2 (2 x CH), 129.1 (2 x CH), 128.6 (CH), 124.8 (2 x CH), 119.3 (C), 115.4 (CH), 114.2 (2 x CH), 55.2 (CH_3), 31.8 (CH_2), 29.3 (CH_2), 22.5 (CH_2), 14.0 (CH_3); HRMS (ESI-TOF) m/z 334.1921 (M + H^+), calcd for $C_{21}H_{23}N_3OH$ 334.1919.

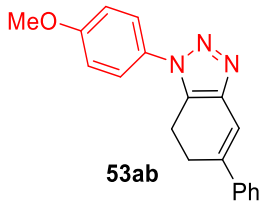
1,5-Diphenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53aa): Prepared following the procedure



53aa

A and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 92% (126 mg); Mp 152-154 °C ; IR (Neat): ν_{max} 3049, 2983, 1593, 1493, 1444, 1232, 1042, 937, 765, 746 and 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.48 (7H, m), 7.39 (2H, br dt, *J* = 7.2, 2.0 Hz), 7.31 (1H, br dt, *J* = 7.2, 2.0 Hz), 7.08 (1H, m), 3.15 (2H, m), 3.00 (2H, m); ^{13}C NMR ($CDCl_3$ DEPT-135) δ 145.1 (C), 140.2 (C), 136.4 (2 x C), 130.9 (C), 129.6 (2 x CH), 128.9 (CH), 128.6 (2 x CH), 127.7 (CH), 125.4 (2 x CH), 122.9 (2 x CH), 115.6 (CH), 27.3 (CH_2), 20.1 (CH_2); HRMS (ESI-TOF) m/z 274.1345 (M + H^+), calcd for $C_{18}H_{15}N_3H$ 274.1344.

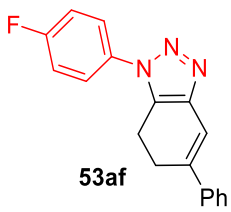
1-(4-Methoxyphenyl)-5-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ab): Prepared following the procedure



53ab

A and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colorless liquid; Yield: 84% (127 mg); IR (Neat): ν_{max} 3034, 2983, 1591, 1513, 1440, 1245, 1222, 1076, 937, 846, 786, 749 and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (2H, br d, *J* = 7.5 Hz), 7.47 (2H, br td, *J* = 9.0, 2.0 Hz), 7.38 (2H, br t, *J* = 7.5 Hz), 7.30 (1H, br tt, *J* = 7.5, 1.5 Hz), 7.06 (1H, br t, *J* = 2.0 Hz), 7.03 (2H, br td, *J* = 9.0, 2.0 Hz), 3.88 (3H, s, OC*H*$_3$), 3.09 (2H, br t, *J* = 9.5 Hz), 2.98 (2H, br t, *J* = 9.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.9 (C), 144.8 (C), 140.3 (C), 136.2 (C), 131.0 (C), 129.6 (C), 128.5 (2 x CH), 127.6 (CH), 125.3 (2 x CH), 124.4 (2 x CH), 115.7 (CH), 114.7 (2 x CH), 55.6 (CH_3, O*C*H$_3$), 27.3 (CH_2), 19.9 (CH_2); HRMS (ESI-TOF) m/z 304.1452 (M + H^+), calcd for $C_{19}H_{17}N_3H$ 304.1450.

1-(4-Fluorophenyl)-5-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53af): Prepared following the procedure

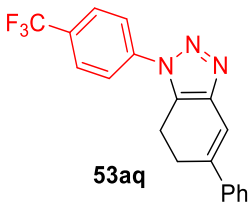


53af

A and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as an orange solid; Yield: 86% (124.5 mg); Mp 172-174 °C; IR (Neat): ν_{max} 3034, 2983, 1601, 1518, 1491, 1237, 1219, 1077, 1042, 937, 846, 694 and 632 cm^{-1}; ^{1}H NMR ($CDCl_3$,

400 MHz) δ 7.56-7.53 (2H, m), 7.50 (2H, br d, *J* = 7.2 Hz), 7.37 (2H, t, *J* = 7.2 Hz), 7.30 (1H, t, *J* = 7.2 Hz), 7.23 (2H, br t, *J* = 8.4 Hz), 7.04 (1H, br s), 3.10 (2H, br t, *J* = 8.0 Hz), 2.98 (2H, br t, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.4 (C, d, *J* = 248.0 Hz, *C*-F), 145.0 (C), 140.1 (C), 136.5 (C), 132.5 (C), 130.9 (C), 128.5 (2 x CH), 127.7 (CH), 125.3 (2 x CH), 124.7 (2 x CH, d, *J* = 9.0 Hz), 116.5 (2 x CH, d, *J* = 23.0 Hz), 115.4 (CH), 27.1 (CH_2), 19.9 (CH_2); HRMS (ESI-TOF) m/z 292.1253 (M + H^+), calcd for $C_{18}H_{14}FN_3H$ 292.1250.

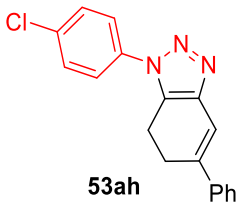
5-Phenyl-1-(4-(trifluoromethyl)phenyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53aq):



53aq

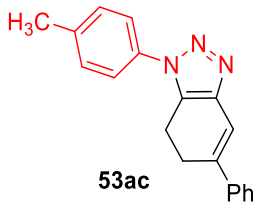
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 91% (155 mg); Mp 210-212 °C; IR (Neat): ν_{max} 3033, 2983, 1611, 1387, 1320, 1232, 1112, 1067, 842, 756, 694 and 598 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (2H, d, *J* = 8.5 Hz), 7.73 (2H, d, *J* = 8.5 Hz), 7.50 (2H, br d, *J* = 7.0 Hz), 7.38 (2H, br t, *J* = 8.0 Hz), 7.31 (1H, br t, *J* = 8.0 Hz), 7.03 (1H, br s), 3.18 (2H, br t, *J* = 8.5 Hz), 3.01 (2H, br t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.5 (C), 140.0 (C), 139.2 (C), 136.8 (C), 130.8 (C), 130.7 (C, q, *J* = 33.75 Hz), 128.6 (2 x CH), 127.8 (CH), 126.8 (2 x CH, q, *J* = 3.75 Hz), 125.3 (2 x CH), 123.5 (C, q, *J* = 270 Hz, *C*F_3), 122.7 (2 x CH), 115.1 (CH), 27.2 (CH_2), 20.2 (CH_2); HRMS (ESI-TOF) m/z 342.1220 (M + H^+), calcd for $C_{19}H_{14}F_3N_3H$ 342.1218.

1-(4-Chlorophenyl)-5-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 89% (137 mg); Mp 196-198 °C; IR (Neat): ν_{max} 3020, 2983, 1592, 1494, 1232, 1097, 1043, 1001, 827, 742 and 686 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53-7.50 (6H, m), 7.39 (2H, br t, *J* = 8.0 Hz), 7.31 (1H, br t, *J* = 8.0 Hz), 7.05 (1H, br s), 3.14 (2H, br t, *J* = 8.5 Hz), 3.00 (2H, br t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.3 (C), 140.1 (C), 136.6 (C), 135.0 (C), 134.8 (C), 130.8 (C), 129.8 (2 x CH), 128.6 (2 x CH), 127.8 (CH), 125.3 (2 x CH), 124.0 (2 x CH), 115.4 (CH), 27.2 (CH_2), 20.1 (CH_2); HRMS (ESI-TOF) m/z 308.0955 (M + H^+), calcd for $C_{18}H_{14}ClN_3H$ 308.0955.



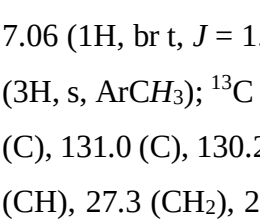
53ah

5-Phenyl-1-(*p*-tolyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (126 mg); Mp. 158-160 °C; IR (Neat): ν_{max} 3031, 2983, 1595, 1515, 1492, 1236, 1095, 1042, 817, 754 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50 (2H, td, *J* = 7.2, 2.0 Hz), 7.44 (2H, td, *J* = 8.8, 2.0 Hz), 7.39-7.32 (4H, m), 7.29 (1H, br tt, *J* = 8.4, 1.2 Hz), 7.06 (1H, br t, *J* = 1.2 Hz), 3.10 (2H, br dt, *J* = 8.8, 1.6 Hz), 2.97 (2H, br tt, *J* = 8.8, 1.6 Hz), 2.43 (3H, s, ArC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.0 (C), 140.3 (C), 139.1 (C), 136.3 (C), 134.1 (C), 131.0 (C), 130.2 (2 x CH), 128.6 (2 x CH), 127.7 (CH), 125.4 (2 x CH), 122.8 (2 x CH), 115.7 (CH), 27.3 (CH_2), 21.2 (CH_3), 20.1 (CH_2); HRMS (ESI-TOF) m/z 288.1501 (M + H^+), calcd for $C_{19}H_{17}N_3H$ 288.1501.



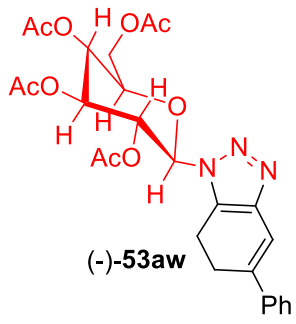
53ac

1-(3-Chlorophenyl)-5-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ai): Prepared following the procedure **A** and purified by chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 87% (134 mg); Mp 164-166 °C; IR (Neat): ν_{max} 3050, 2983, 1590, 1490, 1381, 1224, 1097, 1043, 916, 846, 751, 711 and 684 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.63 (1H, br s), 7.52-7.46 (5H, m), 7.39 (2H, br t, *J* = 7.5 Hz), 7.31 (1H, br t, *J* = 7.5 Hz), 7.06 (1H, br s), 3.17 (2H, br t, *J* = 8.5 Hz), 3.01 (2H, br t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.3 (C), 140.1 (C), 137.5 (C), 136.7 (C), 135.4 (C), 130.9 (C), 130.6 (CH), 129.0 (CH), 128.6 (2 x CH), 127.8 (CH), 125.4 (2 x CH), 123.1 (CH), 120.8 (CH), 115.4 (CH), 27.2 (CH_2), 20.2 (CH_2); HRMS (ESI-TOF) m/z 308.0956 (M + H^+), calcd for $C_{18}H_{14}ClN_3H$ 308.0955.



53ai

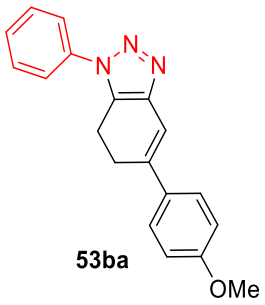
(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(5-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (-)-53aw: Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 5:5) and was isolated as a semi solid; Yield: 81% (214 mg); $[\alpha]_D^{25}$ = -32.67 (*C* = 0.06, $CHCl_3$); IR (Neat): ν_{max} 3058, 2983, 1724, 1607, 1489, 1372, 1232, 1097, 1042, 937, 846, 786, 759 and 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, td, *J* = 7.2, 1.6 Hz), 7.30 (2H, dt, *J* = 6.4, 1.6 Hz), 7.20 (1H, tt, *J* = 7.2, 1.6 Hz), 6.85 (1H, t, *J* = 1.6 Hz), 5.81 (1H, d, *J* = 9.2 Hz), 5.39 (2H, m), 5.17 (1H, t, *J* = 9.6 Hz), 4.23 (1H, dd, *J* = 12.4, 5.2 Hz), 4.13 (1H, dd, *J* = 12.4, 2.0 Hz), 3.94 (1H, ddd, *J* = 10.4, 5.2, 2.4 Hz), 3.22-3.05 (2H,



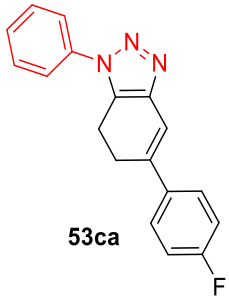
(-)-53aw

m), 2.93 (2H, br t, *J* = 8.8 Hz), 2.02 (3H, s), 2.01 (3H, s), 1.97 (3H, s), 1.82 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.4 (C), 169.8 (C), 169.4 (C), 169.0 (C), 145.6 (C), 140.2 (C), 136.9 (C), 131.4 (C), 128.5 (2 x CH), 127.7 (CH), 125.3 (2 x CH), 114.9 (CH), 86.0 (CH), 75.0 (CH), 72.4 (CH), 69.3 (CH), 67.8 (CH), 61.5 (CH_2), 26.8 (CH_2), 20.6 (CH_3), 20.5 (CH_3), 20.47 (CH_3), 20.1 (CH_3), 19.6 (CH_2); HRMS (ESI-TOF) m/z 528.1984 (M + H^+), calcd for $C_{26}H_{29}N_3O_9H$ 528.1984.

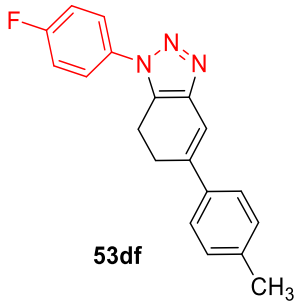
5-(4-Methoxyphenyl)-1-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a semi solid; Yield: 88% (133.5 mg); IR (Neat): ν_{max} 3053, 2984, 1592, 1493, 1372, 1264, 1097, 1045, 770, 742 and 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.53 (4H, m), 7.48 (1H, tt, *J* = 7.5, 2.0 Hz), 7.45 (2H, td, *J* = 9.0, 2.0 Hz), 6.99 (1H, t, *J* = 1.5 Hz), 6.92 (2H, td, *J* = 9.5, 2.0 Hz), 3.83 (3H, s, OC*H*$_3$), 3.13 (2H, t, *J* = 8.0 Hz), 2.96 (2H, t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.3 (C), 145.3 (C), 136.5 (C), 136.0 (C), 132.8 (C), 130.5 (C), 129.6 (2 x CH), 128.8 (CH), 126.6 (2 x CH), 122.9 (2 x CH), 114.0 (2 x CH), 113.9 (CH), 55.3 (CH_3, O*C*H$_3$), 27.3 (CH_2), 20.2 (CH_2); HRMS (ESI-TOF) m/z 304.1452 (M + H^+), calcd for $C_{19}H_{17}N_3OH$ 304.1450.



5-(4-Fluorophenyl)-1-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (131.5 mg); Mp 161-163 °C; IR (Neat): ν_{max} 2983, 1593, 1502, 1220, 1097, 1042, 937, 846, and 633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59-7.52 (4H, m), 7.49-7.45 (3H, m), 7.06 (2H, br tt, *J* = 8.5, 1.5 Hz), 6.99 (1H, br s), 3.14 (2H, br t, *J* = 8.5 Hz), 2.95 (2H, br t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.3 (C, d, *J* = 246.2 Hz, *C*-F), 144.9 (C), 136.43 (C), 136.36 (C, d, *J* = 3.75 Hz), 135.3 (C), 130.8 (C), 129.6 (2 x CH), 128.9 (CH), 127.0 (2 x CH, d, *J* = 7.5 Hz), 122.8 (2 x CH), 115.45 (CH), 115.41 (2 x CH, d, *J* = 21.25 Hz), 27.4 (CH_2), 20.1 (CH_2); HRMS (ESI-TOF) m/z 292.1253 (M + H^+), calcd for $C_{18}H_{14}FN_3H$ 292.1250.

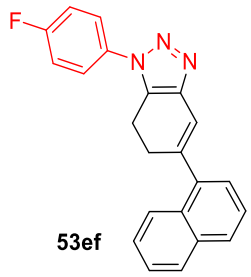


1-(4-Fluorophenyl)-5-(p-tolyl)-6,7-dihydro-1H-benzo[*d*][1,2,3]triazole (53df): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (134 mg); Mp 176-178 °C; IR (Neat): ν_{max} 2972, 2864, 1517, 1515, 1360, 1221, 1045, 838 and 813 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.54-7.52 (2H, m), 7.38 (2H, d, *J* = 6.4 Hz), 7.22 (2H, br t, *J* = 6.8 Hz), 7.17 (2H, br d, *J* = 6.4 Hz), 7.00 (1H, s), 3.07 (2H, br t, *J* = 6.8 Hz), 2.94 (2H, br t, *J* = 6.8 Hz), 2.35 (3H, s, ArCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.4 (C, d, *J* = 248.75 Hz, *C*-F), 145.1 (C), 137.5 (C), 137.1 (C), 136.4 (C), 132.5 (C), 130.7 (C), 129.2 (2 x CH), 125.1 (2 x CH), 124.7 (2 x CH, d, *J* = 8.75 Hz), 116.5 (2 x CH, d, *J* = 23.75 Hz), 114.4 (CH), 27.1 (CH_2), 21.0 (CH_2), 19.9 (CH_3); HRMS (ESI-TOF) m/z 306.1408 (M + H^+), calcd for $C_{19}H_{16}FN_3H$ 306.1407.



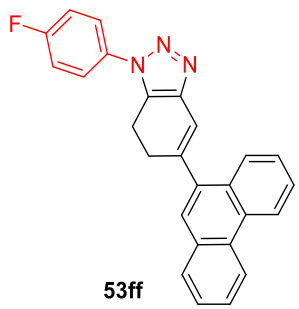
53df

1-(4-Fluorophenyl)-5-(naphthalen-1-yl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ef): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a semi solid; Yield: 90% (154 mg). IR (Neat): ν_{max} 3044, 2983, 1513, 1429, 1396, 1232, 1097, 1042, 937, 838, 771 and 630 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.08-8.06 (1H, m), 7.87-7.86 (1H, m), 7.79 (1H, d, *J* = 8.0 Hz), 7.58-7.55 (2H, m), 7.49-7.43 (3H, m), 7.37 (1H, d, *J* = 6.5 Hz), 7.24-7.21 (2H, m), 6.86 (1H, s), 3.17 (2H, br t, *J* = 8.5 Hz), 2.93 (2H, br t, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.4 (C, d, *J* = 248.75 Hz, *C*-F), 144.7 (C), 139.8 (C), 137.3 (C), 133.7 (C), 132.5 (C), 130.94 (C), 130.87 (C), 128.4 (CH), 127.8 (CH), 126.0 (CH), 125.8 (CH), 125.3 (CH), 125.24 (CH), 125.21 (CH), 124.8 (2 x CH, d, *J* = 8.75 Hz), 119.1 (CH), 116.53 (2 x CH, d, *J* = 22.5 Hz), 30.4 (CH_2), 20.2 (CH_2); HRMS (ESI-TOF) m/z 342.1408 (M + H^+), calcd for $C_{22}H_{16}FN_3H$ 342.1408.



53ef

1-(4-Fluorophenyl)-5-(phenanthren-9-yl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole (53ff):



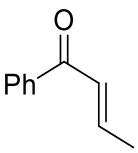
53ff

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as orange solid; Yield: 91% (180 mg); Mp 172-174 °C;.IR IR (Neat): ν_{max} 3061, 2983, 1514, 1447, 1213, 1097, 1042, 937, 846, 723 and 600 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.70 (1H, d, *J* = 8.4 Hz), 8.63 (1H, d, *J* = 8.4 Hz), 8.08 (1H, d, *J* = 8.0 Hz), 7.83 (1H, d, *J* = 7.6 Hz), 7.66-7.54 (7H, m), 7.21 (2H, t, *J* = 8.8 Hz), 6.93 (1H, s), 3.16 (2H, t, *J* = 8.4 Hz), 2.92 (2H, t, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.4 (C, d, *J* = 248 Hz, *C*-F), 144.7 (C), 138.4 (C), 137.7 (C), 132.5 (C, d, *J* = 3.0 Hz), 131.3 (C), 131.0 (C), 130.6 (C), 130.1 (C), 129.9 (C), 128.5 (CH), 126.8 (CH), 126.7 (CH), 126.5 (2 x CH), 126.0 (CH), 125.9 (CH), 124.8 (2 x CH, d, *J* = 9.0 Hz), 123.1 (CH), 122.4 (CH) 119.0 (CH), 116.5 (2 x CH, d, *J* = 28.75 Hz), 30.2 (CH_2), 20.2 (CH_2); HRMS (ESI-TOF) m/z 392.1564 ($M + H^+$), calcd for $C_{26}H_{18}FN_3H$ 392.1563.

1-Benzyl-5-(*p*-tolyl)-6,7-dihydro-*1H*-benzo[*d*][1,2,3]triazole (53du): Prepared following the procedure **A** (under the KO^{t}Bu-catalysis) and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a semi solid; Yield: 80% (120 mg); IR (Neat): ν_{max} 3028, 2919, 1513, 1497, 1454, 1197, 1019, 861, 831, 771, 723, 582, 522 and 473 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.31 (5H, m), 7.22 (2H, dd, *J* = 8.0, 1.2 Hz), 7.15 (2H, br d, *J* = 8.4 Hz), 6.94 (1H, t, *J* = 1.2 Hz), 5.48 (2H, s, NC*H*$_2$Ph), 2.85 (2H, tt, *J* = 8.0, 1.2 Hz), 2.77 (2H, dt, *J* = 8.0, 1.2 Hz), 2.34 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.0 (C), 137.5 (C), 137.4 (C), 135.8 (C), 134.6 (C), 131.1 (C), 129.2 (2 x CH), 129.0 (2 x CH), 128.4 (CH), 127.5 (2 x CH), 125.2 (2 x CH), 114.8 (CH), 52.1 (CH_2, N*C*H$_2$Ph), 26.8 (CH_2), 21.1 (CH_3, Ar-*C*H$_3$), 18.8 (CH_2); HRMS (ESI-TOF) m/z 302.1656 ($M + H^+$), calcd for $C_{20}H_{19}N_3H$ 302.1657.

53du

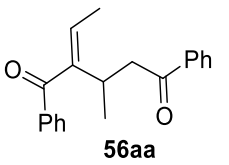
***(E)*-1-Phenylbut-2-en-1-one (55a):** Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 1:9) and was isolated as a colourless liquid; Yield: 57% (42 mg); IR (Neat): ν_{max} 3058, 2926, 1720, 1670, 1622, 1447, 1295, 759 and 668 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (2H, br td, *J* = 7.2, 1.6 Hz), 7.54 (1H, br tt, *J* = 6.4, 1.2 Hz), 7.46 (2H, br tt, *J* = 8.0, 1.6 Hz), 7.07 (1H, qd, *J* = 15.6, 6.8 Hz), 6.90 (1H, qd, *J* = 15.6, 1.6 Hz), 1.99 (3H, dd, *J* = 6.8, 1.6 Hz); ^{13}C NMR ($CDCl_3$,



55a

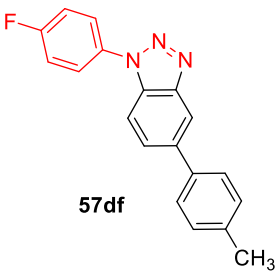
DEPT-135) δ 190.7 (C, *C*=O), 144.9 (CH), 137.9 (C), 132.5 (CH), 128.4 (4 x CH), 127.5 (CH), 18.5 (CH_3); HRMS (ESI-TOF) m/z 147.0807 ($M + H^+$), calcd for $C_{10}H_{10}OH$ 147.0810.

(*E*)-2-Ethylidene-3-methyl-1,5-diphenylpentane-1,5-dione (56aa): Prepared following the procedure **F** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 1:9) and was isolated colorless liquid; Yield: 45% (66 mg); IR (Neat): ν_{max} 3058, 2963, 1682, 1642, 1445, 1267, 728 and 691 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97 (2H, td, *J* = 8.0, 2.0 Hz), 7.63 (2H, td, *J* = 8.0, 2.0 Hz), 7.52 (1H, tt, *J* = 7.0, 1.5 Hz), 7.47 (1H, tt, *J* = 7.0, 1.5 Hz), 7.42 (2H, tt, *J* = 7.0, 1.5 Hz), 7.37 (2H, tt, *J* = 7.0, 1.5 Hz), 6.18 (1H, q, *J* = 7.0 Hz), 3.63-3.52 (2H, m), 3.34 (1H, dd, *J* = 16.5, 6.0 Hz), 1.94 (3H, d, *J* = 7.0 Hz, C*H*$_3$), 1.34 (3H, d, *J* = 7.0 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 200.0 (C), 199.4 (C), 144.5 (C), 139.8 (CH), 139.4 (C), 137.3 (C), 132.9 (CH), 131.6 (CH), 129.5 (2 x CH), 128.4 (2 x CH), 128.1 (2 x CH), 127.9 (2 x CH), 43.3 (CH_2), 29.2 (CH), 19.4 (CH_3), 14.0 (CH_3); HRMS (ESI-TOF) m/z 293.1541 ($M + H^+$), calcd for $C_{20}H_{20}O_2H$ 293.1542.



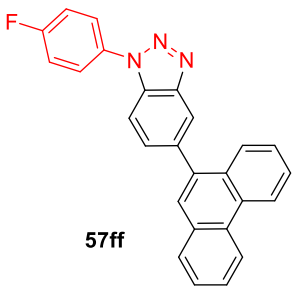
56aa

1-(4-Fluorophenyl)-5-(p-tolyl)-1*H*-benzo[*d*][1,2,3]triazole (57df): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 70% (106 mg); Mp 180-182 °C; IR (KBr): ν_{max} 2987, 2920, 1508, 1221, 1054, 837, 799 and 610 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.27 (1H, s), 7.79-7.75 (3H, m), 7.70 (1H, d, *J* = 8.8 Hz), 7.55 (2H, d, *J* = 8.0 Hz), 7.33-7.28 (4H, m), 2.42 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.3 (C, d, *J* = 247 Hz, *C*-F), 147.3 (C), 138.2 (C), 137.5 (C), 137.3 (C), 133.1 (C, d, *J* = 3.0 Hz), 131.6 (C), 129.7 (2 x CH), 128.4 (CH), 127.3 (2 x CH), 124.6 (2 x CH, d, *J* = 9.0 Hz), 117.7 (CH), 116.8 (2 x CH, d, *J* = 23.0 Hz), 110.1 (CH), 21.1 (CH_3); HRMS (ESI-TOF) m/z 304.1250 ($M + H^+$), calcd for $C_{19}H_{14}FN_3H$ 304.1250.



57df

1-(4-Fluorophenyl)-5-(phenanthren-9-yl)-1*H*-benzo[*d*][1,2,3]triazole (57ff): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a brown solid; Yield: 60% (116.8 mg); Mp 190-192 °C; IR (Neat): ν_{max} 2922, 2851, 1461, 1372, 1264, 739 and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.82 (1H, d, *J* = 8.0 Hz), 8.76 (1H, d, *J* = 8.0 Hz), 8.32 (1H, q, *J* = 0.8 Hz), 7.93 (1H, dd, *J* = 8.0, 0.8 Hz), 7.87-7.80 (4H, m), 7.77-7.76 (2H, m), 7.74-



57ff

7.68 (2H, m), 7.67-7.63 (1H, m), 7.56-7.52 (1H, m), 7.36 (2H, tt, *J* = 8.0, 3.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.4 (C, d, *J* = 248 Hz, *C*-F), 146.8 (C), 137.6 (C), 137.5 (C), 133.1 (C, d, *J* = 3.0 Hz), 131.8 (C), 131.3 (C), 131.2 (CH), 131.0 (C), 130.7 (C), 130.1 (C), 128.7 (CH), 128.2 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.69 (CH), 126.6 (CH), 124.4 (2 x CH, d, *J* = 8.0 Hz), 123.1 (CH), 122.6 (CH), 121.1 (CH), 116.9 (2 x CH, d, *J* = 23.0 Hz), 109.7 (CH); HRMS (ESI-TOF) m/z 390.1408 ($M + H^+$), calcd for $C_{26}H_{16}FN_3H$ 390.1407.

7.3 General Experimental Procedure for Organocatalytic Enolate-Mediated Enone-Azide [3+2]-Cycloaddition: High yielding Synthesis of Functionally Rich *C/N*-Double Vinyl 1,2,3-Triazoles.

Procedure A: General procedure for the DBU-catalyzed domino [3+2]-cycloaddition reactions in DMSO: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.10 mmol of DBU (**40e**) in DMSO (1.0 mL), was added 0.75 mmol of azides (**21** and **2)** and 0.5 mmol of corresponding enones (**58** and **61**) and the reaction mixture was stirred at 25 °C for 0.75-6.0 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure click products were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General procedure for the DDQ oxidation: In a 10 mL round bottom flask equipped with a magnetic stirring bar, to 0.5 mmol of compound **59aa** was added 5.0 mL of drytoluene as a solvent and then DDQ (2 equiv., 1.0 mmol) was added. The reaction mixture was refluxed for 48 h, the crude product was purified by column chromatography on silica gel (hexane/EtOAc) to afford the oxidized product **63**.

Procedure C: General procedure for the Hydrogenation**:** In a 10 mL round bottomed flask, a solution of 0.5 mmol of **63** in dry methanol (5 mL) was taken followed by addition of Pd/C (10 mol%). The reaction mixture was purged with nitrogen gas followed by hydrogen gas. The reaction mixture was allowed to stir at 25 ^{o}C under the pressure of a hydrogen gas filled balloon for 3 h. The crude reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The concentrate was subjected to column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain the pure compound **64** respectively.

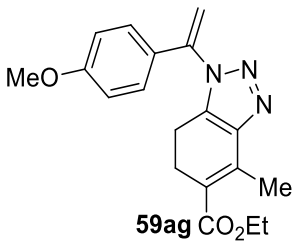
Ethyl 4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (139.5 mg); Mp 86-88 °C; IR (Neat): ν_{max} 2979, 2923, 1689, 1603, 1477, 1371, 1274, 1200, 1108, 905, 812, 774, 702, 613 and 524 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (3H, m), 7.25-7.22 (2H, m), 5.79 (1H, d, *J* = 1.2 Hz), 5.65 (1H, d, *J* = 0.8 Hz), 4.24 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.72 (2H, qt, *J* = 8.8, 5.6 Hz), 2.62 (3H, t, *J* = 1.6 Hz olefinic-C*H*$_3$), 2.46 (2H, t, *J* = 9.2 Hz), 1.32 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 145.4 (C), 141.8 (C), 138.2 (C), 134.5 (C), 134.2 (C), 129.7 (CH), 128.7 (2 x CH), 126.1 (2 x CH), 120.8 (C), 112.3 (CH_2), 60.2 (CH_2, O*C*H$_2$CH$_3$), 25.0 (CH_2), 19.2 (CH_2), 15.1 (CH_3), 14.2 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 310.1556 (M + H^+), calcd for $C_{18}H_{19}N_3O_2H$ 310.1556.

Ethyl 1-(1-(4-chlorophenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 84% (144.5 mg); Mp 92-94 °C; IR (Neat): ν_{max} 2982, 2925, 1696, 1603, 1562, 1484, 1443, 1278, 1200, 1097, 1055, 839, 782 and 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (2H, td, *J* = 8.4, 2.4 Hz), 7.18 (2H, td, *J* = 8.8, 2.0 Hz), 5.79 (1H, d, *J* = 0.8 Hz), 5.64 (1H, s), 4.25 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.74 (2H, qt, *J* = 8.8, 1.6 Hz), 2.62 (3H, t, *J* = 1.6 Hz olefinic-C*H*$_3$), 2.49 (2H, t, *J* = 8.4 Hz), 1.33 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.7 (C), 141.0 (C), 138.3 (C), 136.0 (C), 134.5 (C), 132.8 (C), 129.2 (2 x CH), 127.6 (2 x CH), 121.0 (C), 112.8 (CH_2), 60.4 (CH_2, O*C*H$_2$CH$_3$), 25.2 (CH_2), 19.4 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 344.1166 (M + H^+), calcd for $C_{18}H_{18}ClN_3O_2H$ 344.1166.

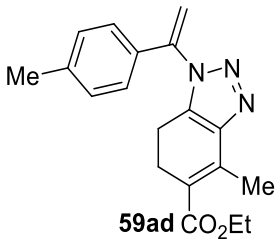
Ethyl 1-(1-(4-fluorophenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 85% (139.50 mg); Mp 103-105 °C; IR (Neat): ν_{max} 2977, 2920, 2843, 1696, 1603, 1510, 1371, 1205, 1164, 1050, 839, 782, 725 and 673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (2H,

tt, *J* = 8.5, 2.0 Hz), 7.08 (2H, tt, *J* = 8.5, 2.0 Hz), 5.74 (1H, d, *J* = 0.5 Hz), 5.61 (1H, s), 4.26 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.74 (2H, qt, *J* = 8.5, 1.5 Hz), 2.62 (3H, t, *J* = 1.5 Hz olefinic-C*H*$_3$), 2.49 (2H, t, *J* = 8.5 Hz), 1.34 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 163.5 (C, d, *J* = 248.7 Hz *C*-F), 145.6 (C), 141.1 (C), 138.3 (C), 134.5 (C), 130.6 (C, d, *J* = 3.75 Hz,), 128.3 (2 x CH, d, *J* = 8.75 Hz), 121.0 (C), 116.0 (2 x CH, d, *J* = 22.5 Hz), 112.2 (CH$_2$), 60.4 (CH$_2$, O*C*H$_2$CH$_3$), 25.2 (CH$_2$), 19.3 (CH$_2$), 15.2 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 328.1463 (M + H$^+$), calcd for $C_{18}H_{18}FN_3O_2H$ 328.1461.

Ethyl 1-(1-(4-methoxyphenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 81% (137.0 mg); IR (Neat): ν_{max} 2982, 2930, 1701, 1603, 1479, 1438, 1371, 1283, 1205, 1050, 895, 864 and 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (2H, td, *J* = 8.8, 2.4 Hz), 6.89 (2H, td, *J* = 8.8, 2.4 Hz), 5.67 (1H, s), 5.52 (1H, s), 4.25 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.83 (3H, s OC*H*$_3$), 2.71 (2H, t, *J* = 8.4 Hz), 2.62 (3H, s, olefinic-C*H*$_3$), 2.47 (2H, t, *J* = 8.8 Hz), 1.33 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 160.8 (C), 145.5 (C), 141.6 (C), 138.5 (C), 134.6 (C), 127.7 (2 x CH), 126.8 (C), 120.8 (C), 114.2 (2 x CH), 110.5 (CH$_2$), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 55.3 (CH$_3$, O*C*H$_3$), 25.2 (CH$_2$), 19.3 (CH$_2$), 15.2 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 340.1660 (M + H$^+$), calcd for $C_{19}H_{21}N_3O_3H$ 340.1661.

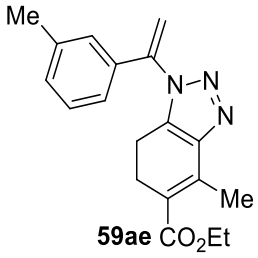


Ethyl 4-methyl-1-(1-(*p*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ad): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 83% (134.5 mg); Mp 100-102 °C; IR (Neat): ν_{max} 2982, 2920, 1686, 1629, 1603, 1567, 1515, 1365, 1283, 1200, 1159, 1055, 901, 828, 782 and 720 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (2H, d, *J* = 8.5 Hz), 7.11 (2H, d, *J* = 8.0 Hz), 5.73 (1H, s), 5.59 (1H, s), 4.24 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.70 (2H, qt, *J* = 9.0, 1.5 Hz), 2.62 (3H, t, *J* = 1.5 Hz olefinic-C*H*$_3$), 2.44 (2H, t, *J* = 9.0 Hz), 2.37 (3H, s Ar-C*H*$_3$), 1.33 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.5 (C), 142.0 (C), 140.0 (C), 138.5 (C), 134.6 (C), 131.5 (C), 129.6 (2 x CH), 126.2 (2 x CH), 120.8 (C), 111.5 (CH$_2$), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 25.2 (CH$_2$), 21.2 (CH$_2$), 19.4 (CH$_3$),

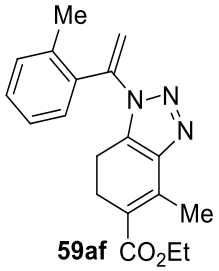


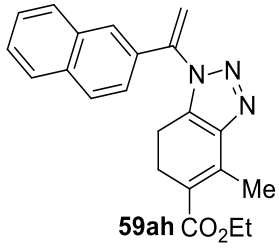
15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 324.1712 ($M + H^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

Ethyl 4-methyl-1-(1-(*m*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ae): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 82% (132.5 mg); IR (Neat): ν_{max} 2981, 2359, 1734, 1699, 1371, 1239, 1199, 1045, 893, 734, 701 and 608 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (1H, d, *J* = 7.5, Hz), 7.22 (1H, d, *J* = 7.5 Hz), 7.04-7.02 (2H, m), 5.76 (1H, s), 5.63 (1H, s), 4.25 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.68 (2H, qt, *J* = 8.5, 1.5 Hz), 2.63 (3H, t, *J* = 1.5 Hz olefinic-CH_3), 2.45 (2H, t, *J* = 8.5 Hz), 2.35 (3H, s Ar-CH_3), 1.33 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.4 (C), 142.0 (C), 138.6 (C), 138.4 (C), 134.6 (C), 134.2 (C), 130.6 (CH), 128.7 (CH), 126.8 (CH), 123.4 (CH), 120.8 (C), 112.2 (CH_2), 60.3 (CH_2, OCH_2CH_3), 25.1 (CH_2), 21.3 (CH_2), 19.3 (CH_3), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 324.1712 ($M + H^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

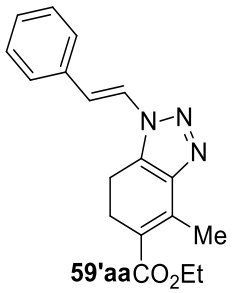


Ethyl 4-methyl-1-(1-(*o*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 62% (100.5 mg); IR (Neat): ν_{max} 2983, 1735, 1372, 1233, 1043, 917, 846, 733, 633, 607 and 461 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (2H, m), 7.26 (1H, dt, *J* = 8.0, 0.5 Hz), 7.20-7.19 (1H, m), 5.96 (1H, s), 5.41 (1H, s), 4.22 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.63 (2H, qt, *J* = 8.5, 2.0 Hz), 2.59 (3H, t, *J* = 2.0 Hz olefinic-CH_3), 2.20 (2H, t, *J* = 8.5 Hz), 1.97 (3H, s Ar-CH_3), 1.31 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 145.7 (C), 142.1 (C), 138.3 (C), 136.3 (C), 134.0 (C), 133.6 (C), 130.7 (CH), 129.74 (CH), 129.71 (CH), 126.2 (CH), 120.6 (C), 112.3 (CH_2), 60.2 (CH_2, OCH_2CH_3), 25.0 (CH_2), 19.2 (CH_2), 19.0 (CH_3), 15.1 (CH_3), 14.2 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 324.1714 ($M + H^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

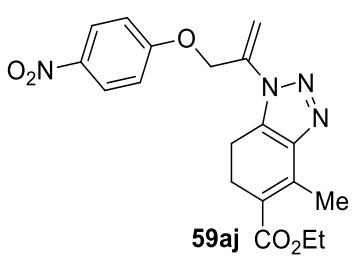


Ethyl 4-methyl-1-(1-(naphthalen-2-yl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ah): 

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 78% (140.5 mg); Mp 98-100 °C; IR (Neat): ν_{max} 2977, 2925, 2837, 1701, 1608, 1515, 1463, 1371, 1298, 1257, 1200, 1055, 1030, 833 and 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83-7.81 (2H, m), 7.77 (1H, d, *J* = 7.0 Hz), 7.61 (1H, s), 7.51-7.46 (2H, m), 7.36 (1H, d, *J* = 8.0 Hz), 5.90 (1H, s), 5.71 (1H, s), 4.23 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.70-2.67 (5H, m), 2.45 (2H, t, *J* = 8.0 Hz), 1.31 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 145.3 (C), 141.7 (C), 138.1 (C), 134.5 (C), 133.4 (C), 132.7 (C), 131.3 (C), 128.6 (CH), 128.2 (CH), 127.5 (CH), 127.0 (CH), 126.7 (CH), 125.8 (CH), 123.1 (CH), 120.8 (C), 112.7 (CH_2), 60.1 (CH_2, O*C*H$_2$CH$_3$), 25.0 (CH_2), 19.1 (CH_2), 15.1 (CH_3), 14.1 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 360.1713 (M + H^+), calcd for $C_{22}H_{21}N_3O_2H$ 360.1712.

Ethyl (*E*)-4-methyl-1-styryl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59'aa): 

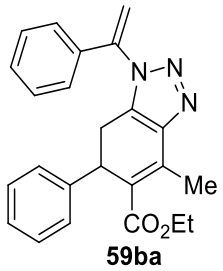
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (133.5 mg); Mp 140-142 °C; IR (Neat): ν_{max} 3049, 2977, 2924, 1679, 1612, 1477, 1448, 1226, 1212, 1024, 751 and 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (3H, m), 7.42-7.38 (2H, m), 7.36-7.27 (2H, m), 4.27 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.01 (2H, t, *J* = 7.6 Hz), 2.89 (2H, qt, *J* = 8.0, 1.2 Hz), 2.60 (3H, t, *J* = 1.2 Hz olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-*C*=O), 145.8 (C), 138.3 (C), 133.7 (C), 132.7 (C), 128.9 (2 x CH), 128.8 (CH), 126.7 (2 x CH), 123.6 (CH), 120.9 (CH), 120.8 (C), 60.4 (CH_2, O*C*H$_2$CH$_3$), 25.1 (CH_2), 18.9 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 310.1554 (M + H^+), calcd for $C_{18}H_{19}N_3O_2H$ 310.1556.

Ethyl 4-methyl-1-(3-(4-nitrophenoxy)prop-1-en-2-yl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59aj): 

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 82% (158.0 mg); Mp 138-140 °C; IR (Neat): ν_{max} 2923, 1749, 1597, 1525, 1506, 1341, 1242, 1042,

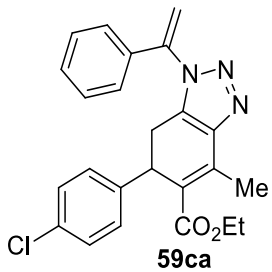
854, 748, 689 and 500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* = 8.5 Hz), 7.07 (2H, d, *J* = 9.0 Hz), 5.64 (1H, d, *J* = 0.5 Hz), 5.40 (1H, s), 5.26 (2H, s), 4.27 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.96 (2H, t, *J* = 9.0 Hz), 2.87 (2H, t, *J* = 8.5 Hz), 2.59 (3H, s olefinic-CH_3), 1.36 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 162.5 (C), 145.8 (C), 142.1 (C), 137.9 (C), 137.7 (C), 133.8 (C), 125.9 (2 x CH), 121.3 (C), 114.8 (2 x CH), 109.6 (CH_2), 67.1 (CH_2), 60.4 (CH_2, OCH_2CH_3), 25.3 (CH_2), 19.7 (CH_2), 15.1 (CH_3), 14.2 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 385.1512 ($M + H^+$), calcd for $C_{19}H_{20}N_4O_5H$ 385.1512.

Ethyl 4-methyl-6-phenyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (155.0 mg); Mp 80-82 °C; IR (Neat): ν_{max} 2918, 2849, 1699, 1602, 1491, 1447, 1263, 1209, 1501, 964, 908, 774 and 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.26 (1H, m), 7.19–7.17 (3H, m), 7.15–7.11 (2H, m), 7.01–6.98 (2H, m), 6.94 (2H, td, *J* = 8.0, 0.8 Hz), 5.70 (1H, d, *J* = 0.8 Hz), 5.55 (1H, d, *J* = 0.8 Hz), 4.32 (1H, br d, *J* = 8.0 Hz), 4.11 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.03 (1H, dd, *J* = 16.8, 8.8 Hz), 2.77 (3H, d, *J* = 0.8 Hz, olefinic-CH_3), 2.52 (1H, dd, *J* = 16.8, 2.0 Hz), 1.17 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-C=O), 145.6 (C), 142.0 (C), 141.7 (C), 139.2 (C), 133.7 (C), 132.8 (C), 129.5 (CH), 128.7 (2 x CH), 128.5 (2 x CH), 126.9 (2 x CH), 126.8 (CH), 126.0 (2 x CH), 124.1 (C), 112.5 (CH_2), 60.4 (CH_2, OCH_2CH_3), 41.0 (CH), 28.3 (CH_2), 15.5 (CH_3), 14.1 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 386.1869 ($M + H^+$), calcd for $C_{24}H_{23}N_3O_2H$ 386.1869.



59ba

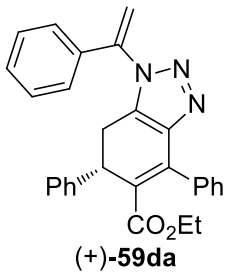
Ethyl 6-(4-chlorophenyl)-4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 70% (147.1 mg); Mp 96-98 °C; IR (Neat): ν_{max} 2979, 2919, 1699, 1638, 1603, 1488, 1367, 1260, 1208, 1051, 1014, 907, 733 and 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (1H, t, *J* = 7.5 Hz), 7.17–7.13 (4H, m), 6.93–6.91 (4H, m), 5.70 (1H, s), 5.57 (1H, s), 4.29 (1H, br d, *J* = 8.0 Hz), 4.12 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.02 (1H, dd, *J* = 17.0, 8.5 Hz), 2.78 (3H, s olefinic-CH_3), 2.44 (1H, dd, *J* = 16.5, 2.0 Hz), 1.19 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C,



59ca

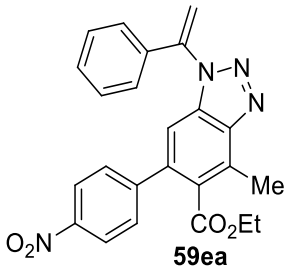
O-C=O), 145.5 (C), 141.7 (C), 140.5 (C), 139.7 (C), 133.8 (C), 132.6 (C), 132.5 (C), 129.7 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.4 (2 x CH), 126.0 (2 x CH), 123.6 (C), 112.7 (CH_2), 60.5 (CH_2, OCH_2CH_3), 40.5 (CH), 28.2 (CH_2), 15.5 (CH_3), 14.1 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 420.1479 ($M + H^+$), calcd for $C_{24}H_{22}ClN_3O_2H$ 420.1479.

Ethyl (*S*)-4,6-diphenyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate ((+)-59da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a semi solid; Yield: 67% (149.5 mg); $[\alpha]_D^{25}$ = 24.75 (*C* = 0.20, $CHCl_3$); IR (Neat): ν_{max} 2922, 2852, 1719, 1593, 1512, 1345, 1287, 1262, 1082, 1502, 854, 691 and 598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, td, *J* = 6.8, 1.6 Hz), 7.45 (2H, tt, *J* = 6.8, 2.0 Hz), 7.41 (1H, tt, *J* = 6.8, 1.6 Hz), 7.29 (1H, tt, *J* = 7.6, 1.6 Hz), 7.24–7.23 (3H, m), 7.18–7.14 (4H, m), 6.98 (2H, td, *J* = 8.0, 1.2 Hz), 5.72 (1H, d, *J* = 1.2 Hz), 5.57 (1H, d, *J* = 0.8 Hz), 4.36 (1H, dd, *J* = 8.8, 2.8 Hz), 3.85-3.79 (2H, m OCH_2CH_3), 3.17 (1H, dd, *J* = 16.8, 8.8 Hz), 2.63 (1H, dd, *J* = 16.8, 3.2 Hz), 0.77 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-C=O), 144.4 (C), 141.7 (C), 141.3 (C), 139.6 (C), 136.0 (C), 133.7 (C), 132.9 (C), 129.6 (CH), 128.8 (2 x CH), 128.7 (2 x CH), 128.6 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.2 (CH), 127.1 (2 x CH), 126.4 (C), 126.0 (2 x CH), 112.8 (CH_2), 60.5 (CH_2, OCH_2CH_3), 42.0 (CH), 28.4 (CH_2), 13.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 448.2024 ($M + H^+$), calcd for $C_{29}H_{25}N_3O_2H$ 448.2025.



(+)-59da

Ethyl 4-methyl-6-(4-nitrophenyl)-1-(1-phenylvinyl)-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 36% (78.0 mg); Mp 128-130 °C; IR (Neat): ν_{max} 3054, 2919, 2856, 1719, 1595, 1513, 1341, 1267, 1046, 778 and 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (2H, td, *J* = 8.8, 2.0 Hz), 7.46–7.42 (3H, m), 7.39 (2H, tt, *J* = 6.8, 2.8 Hz), 7.28 (2H, td, *J* = 6.8, 1.2 Hz), 6.83 (1H, s, Ar-*H*), 5.86 (1H, d, *J* = 1.2 Hz), 5.81 (1H, d, *J* = 1.2 Hz), 4.10 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.95 (3H, s, Ar-CH_3), 1.03 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.1 (C, O-*C*=O), 147.3 (C), 147.2 (C), 145.5 (C), 142.3 (C), 138.3 (C), 134.1 (C), 132.6 (C), 130.8 (C), 130.0 (CH), 129.3 (2 x CH), 129.2 (C), 128.9 (2 x CH), 126.7 (2 x CH),



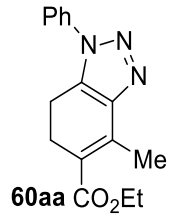
59ea

123.5 (2 x CH), 111.8 (CH_2), 109.6 (CH), 61.5 (CH_2, O*C*H_2CH_3), 14.4 (CH_3), 13.7 (CH_3); HRMS (ESI-TOF) m/z 429.1563 ($M + H^+$), calcd for $C_{24}H_{20}N_4O_4H$ 429.1563.

Ethyl 6-ethyl-4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellowish semi solid; Yield: 78% (132.0 mg); IR (Neat): ν_{max} 2961, 2926, 1695, 1601, 1296, 1207, 1051, 907, 773 and 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (3H, m), 7.23 (2H, dd, *J* = 8.0, 2.0 Hz), 5.79 (1H, d, *J* = 0.4 Hz), 5.65 (1H, s), 4.29-4.21 (2H, m, OC*H*$_2$CH$_3$), 2.97-2.91 (1H, m), 2.63-2.57 (4H, m), 2.41 (1H, dd, *J* = 17.2, 1.2 Hz), 1.47-1.38 (1H, m), 1.33 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 1.22–1.15 (1H, m), 0.67 (3H, t, *J* = 7.2 Hz, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.0 (C), 142.0 (C), 137.2 (C), 134.4 (C), 133.8 (C), 129.8 (CH), 128.9 (2 x CH), 126.3 (2 x CH), 126.2 (C), 112.6 (CH_2), 60.3 (CH_2, O*C*H$_2$CH$_3$), 36.9 (CH), 25.8 (CH_2), 22.9 (CH_2), 15.5 (CH_3), 14.3 (CH_3), 11.2 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 338.1868 ($M + H^+$), calcd for $C_{20}H_{23}N_3O_2H$ 338.1869

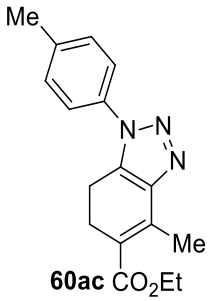
Ethyl 4-methyl-6-phenethyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (59ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 77% (160.1 mg); IR (Neat): ν_{max} 2924, 2853, 1699, 1602, 1451, 1367, 1258, 1207, 1051, 909, 749 and 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.33 (3H, m), 7.24-7.20 (5H, m), 7.00 (2H, d, *J* = 6.0 Hz), 5.78 (1H, s), 5.64 (1H, s), 4.23-4.19 (2H, m), 3.10-3.05 (1H, m), 2.64-2.58 (4H, m), 2.47-2.40 (2H, m), 2.33-2.27 (1H, m), 1.76-1.69 (1H, m), 1.55–1.47 (1H, m), 1.28 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 144.9 (C), 141.9 (C), 141.3 (C), 137.8 (C), 134.4 (C), 133.6 (C), 129.8 (CH), 128.9 (2 x CH), 128.2 (2 x CH), 128.1 (2 x CH), 126.3 (2 x CH), 125.9 (C), 125.8 (CH), 112.7 (CH_2), 60.3 (CH_2, O*C*H$_2$CH$_3$), 35.0 (CH), 34.1 (CH_2), 32.8 (CH_2), 23.2 (CH_2), 15.5 (CH_3), 14.2 (CH_3); HRMS (ESI-TOF) m/z 414.2182 ($M + H^+$), calcd for $C_{26}H_{27}N_3O_2H$ 414.2182.

Ethyl 4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



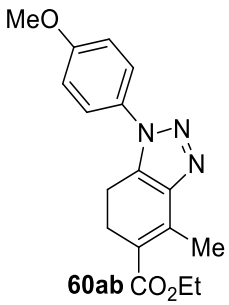
(60aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 95% (135 mg); Mp 96-98 °C; IR (Neat): ν_{max} 3066, 2988, 2930, 1699, 1605, 1508, 1449, 1285, 1201, 1054, 918, 761, 693 and 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (4H, s), 7.50 (1H, s), 4.28 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.97 (2H, t, *J* = 8.0 Hz), 2.85 (2H, t, *J* = 8.0 Hz), 2.64 (3H, s, olefinic-CH_3), 1.36 (3H, t, *J* = 6.8 Hz OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 146.0 (C), 138.7 (C), 136.1 (C), 133.5 (C), 129.6 (2 x CH), 129.1 (CH), 123.0 (2 x CH), 120.9 (C), 60.4 (CH_2 OCH_2CH_3), 25.4 (CH_2), 19.6 (CH_2), 15.3 (CH_3 OCH_2CH_3), 14.3 (CH_3); HRMS m/z 284.1402 ($M + H^+$), calcd for $C_{16}H_{17}N_3O_2H$ 284.1399;

Ethyl 4-methyl-1-(*p*-tolyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60ac):



Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (130.5 mg); Mp 100-102 °C; IR (Neat): ν_{max} 3039, 2982, 2928, 1693, 1520, 1441, 1284, 1202, 1116, 1046, 821 and 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (2H, d, *J* = 8.5 Hz), 7.34 (2H, d, *J* = 8.5 Hz), 4.27 (2H, q, *J* = 7.0 Hz OCH_2CH_3), 2.94 (2H, t, *J* = 8.0 Hz), 2.84 (2H, t, *J* = 8.0 Hz), 2.64 (3H, s, olefinic-CH_3), 2.44 (3H, s, Ar-CH_3), 1.36 (3H, t, *J* = 7.0 Hz OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.9 (C), 139.3 (C), 138.8 (C), 133.7 (C), 133.5 (C), 130.1 (2 x CH), 122.9 (2 x CH), 120.8 (C), 60.4 (CH_2, OCH_2CH_3), 25.4 (CH_2), 21.1 (CH_3), 19.6 (CH_2), 15.3 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 298.1559 ($M + H^+$), calcd for $C_{17}H_{19}N_3O_2H$ 298.1556.

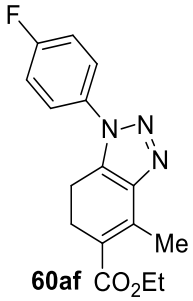
Ethyl 1-(4-methoxyphenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



(60ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (134.5 mg); Mp 120-122 °C; IR (Neat): ν_{max} 2992, 2951, 1768, 1696, 1605, 1518, 1285, 1248, 1205, 1114, 1035, 835 and 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, td, *J* = 8.8, 3.6 Hz), 7.04 (2H, td, *J* = 8.8, 3.6 Hz), 4.27 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.87 (3H, s OCH_3), 2.94-2.90 (2H, m), 2.86-2.82 (2H, m), 2.63 (3H, s, olefinic-CH_3), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3);

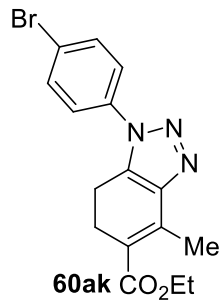
^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 160.0 (C), 145.7 (C), 138.7 (C), 133.5 (C), 129.1 (C), 124.4 (2 x CH), 120.7 (C), 114.6 (2 x CH), 60.3 (CH_2, O*C*H_2CH$_3$), 55.5 (CH_3, O*C*H_3), 25.3 (CH_2), 19.4 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH$_2$*C*H_3); HRMS (ESI-TOF) m/z 314.1505 (M + H^+), calcd for $C_{17}H_{19}N_3O_3H$ 314.1505.

Ethyl 1-(4-fluorophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



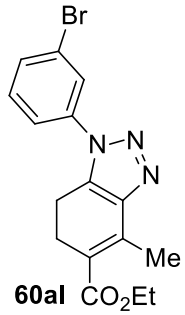
(6af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 88% (150.5 mg); IR (Neat): ν_{max} 3078, 2988, 2853, 1700, 1606, 1517, 1445, 1203, 1051, 842, 774, 703 and 603 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.53 (2H, m), 7.27-7.23 (2H, m), 4.27 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.95 (2H, t, *J* = 8.0 Hz), 2.86 (2H, t, *J* = 8.0 Hz), 2.62 (3H, s olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 162.6 (C, d, *J* = 248.7 Hz, *C*-F), 145.9 (C), 138.4 (C), 133.5 (C), 132.2 (C, d, *J* = 2.5 Hz,), 124.9 (2 x CH, d, *J* = 8.75 Hz), 121.0 (C), 116.6 (2 x CH, d, *J* = 23.7 Hz), 60.3 (CH_2, O*C*H_2CH$_3$), 25.3 (CH_2), 19.4 (CH_2), 15.2 (CH_3), 14.2 (CH_3, OCH$_2$*C*H_3); HRMS (ESI-TOF) m/z 302.1306 (M + H^+), calcd for $C_{16}H_{16}FN_3O_2H$ 302.1305.

Ethyl 1-(4-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate

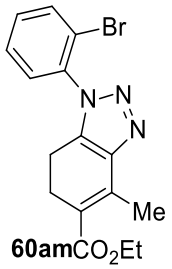


(60ak): Prepared following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 89% (160.4 mg); Mp 140-142 °C; IR (neat): ν_{max} 3400, 1698, 1608, 1494, 1458, 1283, 1202, 1107, 1040, 823 and 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (2H, td, *J* = 7.2, 1.6 Hz), 7.44 (2H, td, *J* = 7.2, 1.6 Hz), 4.27 (2H, q, *J* = 5.6 Hz), 2.98-2.95 (2H, m), 2.86 (2H, qt, *J* = 7.2, 1.2 Hz), 2.62 (3H, t, *J* = 1.2 Hz olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 5.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 146.2 (C), 138.4 (C), 135.1 (C), 133.3 (C), 132.8 (2 x CH), 124.3 (2 x CH), 122.9 (C), 121.1 (C), 60.4 (CH_2), 25.3 (CH_2), 19.6 (CH_2), 15.2 (CH_3), 14.3 (CH_3); HRMS (ESI-TOF) m/z 362.0504 (M + H^+), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.

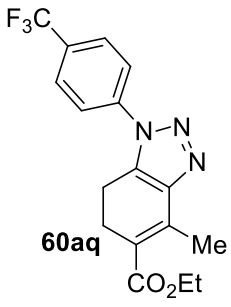
Ethyl 1-(3-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60al): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (144.4 mg); Mp 102-104 °C; IR (Neat): ν_{max} 2980, 1699, 1605, 1495, 1441, 1274, 1201, 1095, 1035, 995, 869, 783, 762 and 433 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (1H, t, *J* = 2.0 Hz), 7.63 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 7.49 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 7.43 (1H, t, *J* = 8.0 Hz), 4.28 (2H, q, *J* = 7.5 Hz, OCH_2CH_3), 2.98 (2H, t, *J* = 8.5 Hz), 2.87 (2H, qt, *J* = 8.0, 1.5 Hz), 2.63 (3H, t, *J* = 1.5 Hz olefinic-CH_3), 1.36 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-*C*=O), 146.2 (C), 138.4 (C), 137.2 (C), 133.4 (C), 132.1 (CH), 130.9 (CH), 126.1 (CH), 123.2 (C), 121.5 (CH), 121.2 (C), 60.4 (CH_2, OCH_2CH_3), 25.4 (CH_2), 19.7 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 362.0504 ($M + H^+$), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.



Ethyl 1-(2-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60am): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 64% (115.4 mg); Mp 252-254 °C; IR (Neat): ν_{max} 2979, 2925, 2853, 1700, 1608, 1507, 1442, 1369, 1285, 1202, 1052, 764 and 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (1H, m), 7.52-7.45 (3H, m), 4.27 (2H, q, *J* = 6.8 Hz, OCH_2CH_3), 2.85 (2H, t, *J* = 7.6 Hz), 2.76 (2H, t, *J* = 7.6 Hz), 2.65 (3H, s olefinic-CH_3), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.1 (C), 138.5 (C), 136.0 (C), 135.2 (C), 133.7 (CH), 131.8 (CH), 128.9 (CH), 128.5 (CH), 121.0 (C), 120.5 (C), 60.4 (CH_2, OCH_2CH_3), 25.2 (CH_2), 19.0 (CH_2), 15.3 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 362.0504 ($M + H^+$), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.

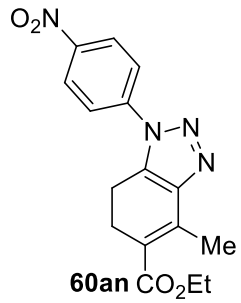


Ethyl 4-methyl-1-(4-(trifluoromethyl)phenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60aq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 89% (156.5 mg); Mp 143-145 °C; IR (Neat): ν_{max} 2989, 2894, 1688, 1614, 1525, 1442, 1417, 1373, 1324, 1261, 1205, 1166, 1118, 843, 777, 738 and 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (2H, d, *J* = 7.6 Hz), 7.72 (2H, d, *J* = 7.6 Hz), 4.28 (2H, q, *J* = 6.8 Hz, OCH_2CH_3), 3.02



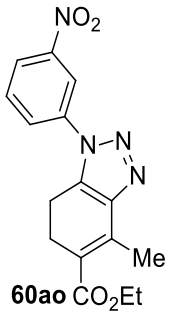
(2H, t, *J* = 8.0 Hz), 2.88 (2H, t, *J* = 8.0 Hz), 2.63 (3H, s, olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.7 (C, O-C=O), 146.5 (C), 138.9 (C), 138.3 (C), 133.5 (C), 131.1 (C, q, *J* = 26 Hz), 127.0 (2 x CH, q, *J* = 3.0 Hz), 123.5 (C, q, *J* = 217.0 Hz, *C*F$_3$), 123.0 (2 x CH), 121.4 (C), 60.5 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 19.8 (CH$_2$), 15.3 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 352.1274 (M + H$^+$), calcd for $C_{17}H_{16}FN_3O_2H$ 352.1273.

Ethyl 4-methyl-1-(4-nitrophenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



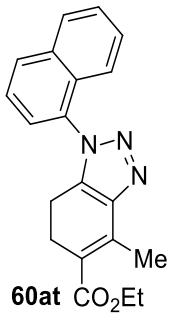
(60an): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 85% (140.0 mg); Mp 138-140 °C; IR (neat): ν_{max} 3096, 2976, 2926, 1699, 1598, 1527, 1444, 1347, 1297, 1203, 1114, 1054, 856, 749 and 686 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.45 (2H, td, *J* = 9.5, 1.5 Hz), 7.82 (2H, td, *J* = 9.0, 2.0 Hz), 4.29 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 3.07 (2H, t, *J* = 8.5 Hz), 2.91 (2H, t, *J* = 9.0 Hz), 2.63 (3H, s, olefinic-C*H*$_3$), 1.37 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 147.4 (C), 146.8 (C), 140.9 (C), 138.0 (C), 133.4 (C), 125.3 (2 x CH), 123.0 (2 x CH), 121.6 (C), 60.6 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 20.0 (CH$_2$), 15.2 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 329.1250 (M + H$^+$), calcd for $C_{16}H_{16}N_4O_4H$ 329.1250;

Ethyl 4-methyl-1-(3-nitrophenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



(60ao): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 60% (99 mg); Mp 108-110 °C; IR (Neat): ν_{max} 2982, 1735, 1702, 1537, 1371, 1239, 1201, 1045, 779, 756, 677 and 607 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.44 (1H, t, *J* = 2.0 Hz), 8.37 (1H, ddd, *J* = 8.5, 2.0, 1.0 Hz), 8.01 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 7.80 (1H, t, *J* = 8.5 Hz), 4.29 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 3.06 (2H, t, *J* = 9.0 Hz), 2.91 (2H, qt, *J* = 9.0, 1.5 Hz), 2.64 (3H, t, *J* = 2.0 Hz olefinic-C*H*$_3$), 1.37 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 148.8 (C), 146.6 (C), 138.0 (C), 137.1 (C), 133.5 (C), 130.9 (CH), 128.4 (CH), 123.6 (CH), 121.6 (C), 117.6 (CH), 60.5 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 19.8 (CH$_2$), 15.2 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 329.1251 (M + H$^+$), calcd for $C_{16}H_{16}N_4O_4H$ 329.1250;

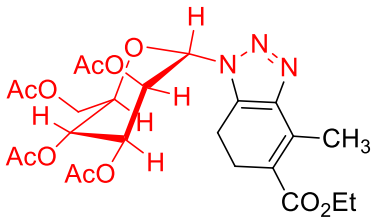
Ethyl 4-methyl-1-(naphthalen-1-yl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



60at

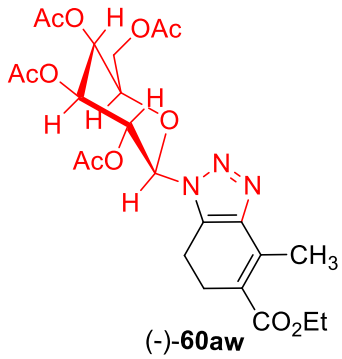
(60at): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semisolid; Yield: 87% (145.5 mg); IR (Neat): ν_{max} 2976, 1707, 1593, 1512, 1445, 1350, 1242, 1190, 1128, 824 and 534 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (1H, d, *J* = 8.0 Hz), 7.97 (1H, d, *J* = 8.0 Hz), 7.61-7.56 (2H, m), 7.54-7.50 (2H, m), 7.41 (1H, d, *J* = 8.5 Hz), 4.28 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.83 (2H, qt, *J* = 9.0, 1.5 Hz), 2.71 (3H, t, *J* = 1.5 Hz olefinic-C*H*$_3$), 2.66 (2H, t, *J* = 9.0 Hz), 1.35 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.1 (C), 138.5 (C), 136.2 (C), 134.1 (C), 131.9 (C), 130.6 (CH), 128.88 (C), 128.87 (CH), 127.8 (CH), 127.0 (CH), 124.9 (CH), 124.2 (CH), 122.2 (CH), 121.0 (C), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 25.2 (CH$_2$), 18.7 (CH$_2$), 15.3 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 334.1555 (M + H^+), calcd for $C_{20}H_{19}N_3O_2H$ 334.1556.

***(2R,3R,4S,5S,6S)*-2-(acetoxymethyl)-6-(5-(ethoxycarbonyl)-4-methyl-6,7-dihydro-1*H*benzo[d][1,2,3]triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate ((+)-60ax):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 5:5) and was isolated as a semi solid; Yield: 69% (186.5 mg); $[\alpha]_D^{25}$ = +7.63 (*C* = 0.059, $CHCl_3$); IR (Neat): ν_{max} 2981, 2359, 1745, 1367, 1209, 1048, 982, 903, 775, 599 and 504 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.10-6.07 (1H, m), 5.96-5.93 (2H, m), 5.40 (1H, t, *J* = 10.0 Hz), 4.32 (1H, dd, *J* = 12.5, 5.5 Hz), 4.27 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 4.00 (1H, dd, *J* =12.0, 2.0 Hz), 3.84-3.82 (1H, m), 2.92-2.83 (4H, m), 2.58 (3H, s olefinic-C*H*$_3$), 2.22 (3H, s COC*H*$_3$), 2.08 (3H, s COC*H*$_3$), 2.06 (3H, s COC*H*$_3$), 2.05 (3H, s COC*H*$_3$), 1.35 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.2 (C, O-*C*=O), 169.8 (C, O-*C*=O), 169.6 (C, O-*C*=O), 169.1 (C, O-*C*=O), 167.7 (C, O-*C*=O), 145.9 (C), 137.8 (C), 134.7 (C), 121.5 (C), 82.3 (CH), 71.6 (CH), 68.8 (CH), 68.4 (CH), 66.0 (CH), 61.7 (CH$_2$), 60.4 (CH$_2$, O*C*H$_2$CH$_3$), 25.0 (CH$_2$), 20.7 (CH$_3$ CO*C*H$_3$), 20.59 (CH$_3$ CO*C*H$_3$), 20.57 (CH$_3$ CO*C*H$_3$), 20.5 (CH$_3$ CO*C*H$_3$), 18.3 (CH$_2$), 15.1 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 538.2037 (M + H^+), calcd for $C_{24}H_{31}N_3O_{11}H$ 538.2037.

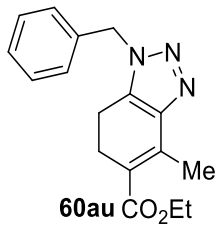


(+)-60ax

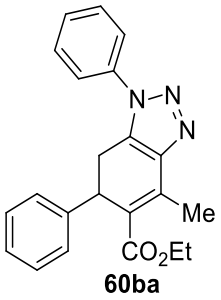
(*2R,3R,4S,5R,6R*)-2-(acetoxymethyl)-6-(5-(ethoxycarbonyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate ((-)-60aw): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 5:5) and was isolated as a semi solid; Yield: 72% (192.5 mg); $[\alpha]_D^{25}$ = -8.18 (*C* = 0.055, $CHCl_3$); IR (Neat): ν_{max} 2981, 1745, 1699, 1367, 1283, 1207, 1129, 1088, 1046, 982, 775 and 599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (1H, td, *J* = 7.0, 2.0 Hz), 5.46-5.40 (2H, m), 5.23 (1H, tt, *J* = 7.5, 2.0 Hz), 4.30-4.24 (3H, m), 4.20 (1H, dd, *J* = 12.5, 2.0 Hz), 3.99 (1H, ddd, *J* =10.5, 5.0, 2.5 Hz), 3.10-2.95 (2H, m), 2.86 (2H, qt, *J* = 8.5, 1.5 Hz), 2.54 (3H, t, *J* = 1.5 Hz olefinic-C*H*$_3$), 2.09-2.08 (6H, m 2 x COC*H*$_3$), 2.04 (3H, s COC*H*$_3$), 1.88 (3H, s COC*H*$_3$), 1.34 (3H, t, *J* = 7.5 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.3 (C, O-*C*=O), 169.8 (C, O-*C*=O), 169.4 (C, O-*C*=O), 168.9 (C, O-*C*=O), 167.8 (C, O-*C*=O), 146.5 (C), 137.7 (C), 134.1 (C), 121.6 (C), 86.0 (CH), 75.1 (CH), 72.4 (CH), 69.4 (CH), 67.8 (CH), 61.5 (CH_2), 60.4 (CH_2, O*C*H$_2$CH$_3$), 24.9 (CH_2), 20.6 (CH_3 CO*C*H$_3$), 20.49 (CH_3 CO*C*H$_3$), 20.46 (CH_3 CO*C*H$_3$), 20.1 (CH_3 CO*C*H$_3$), 19.2 (CH_2), 15.1 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 538.2037 ($M + H^+$), calcd for $C_{24}H_{31}N_3O_{11}H$ 538.2037.



Ethyl 1-benzyl-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60au): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 70% (104.5 mg); IR (Neat): ν_{max}, 2979, 2251, 1607, 1441, 1368, 1284, 1204, 1054, 906, 727 and 459 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (3H, m), 7.20-7.19 (2H, m), 5.49 (2H, s), 4.29 (2H, q, *J* = 7.0 Hz), 2.75 (2H, t, *J* = 8.5 Hz), 2.61 (2H, t, *J* = 8.5 Hz), 2.57 (3H, s olefinic-C*H*$_3$), 1.32 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 146.0 (C), 138.6 (C), 134.4 (C), 133.8 (C), 129.1 (2 x CH), 128.5 (CH), 127.5 (2 x CH), 120.5 (C), 60.3 (CH_2), 52.1 (CH_2), 25.1 (CH_2), 18.5 (CH_2), 15.1 (CH_3), 14.3 (CH_3); HRMS m/z 298.1557 ($M + H^+$), calcd for $C_{17}H_{19}N_3O_2H$ 298.1556;



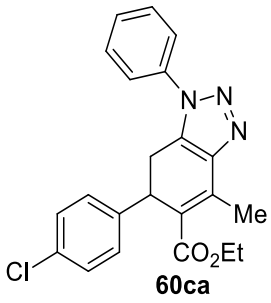
Ethyl 4-methyl-1,6-diphenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60ba):



60ba

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (133.5 mg); Mp 104-106 °C; IR (Neat): ν_{max} 2917, 2849, 1684, 1596, 1503, 1364, 1225, 1203, 1079, 1031, 752, 700 and 602 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (5H, m), 7.21-7.15 (3H, m), 7.11 (2H, td, *J* = 6.4, 2.0 Hz), 4.50 (1H, dd, *J* = 9.2, 1.2 Hz), 4.15-4.10 (2H, m OCH_2CH_3), 3.50 (1H, dd, *J* = 16.8, 8.8 Hz), 3.11 (1H, dd, *J* = 16.8, 2.8 Hz), 2.77 (3H, d, *J* = 0.8 Hz, olefinic-CH_3), 1.18 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.3 (C, O-C=O), 145.8 (C), 142.6 (C), 138.8 (C), 135.9 (C), 131.6 (C), 129.6 (2 x CH), 129.1 (CH), 128.6 (2 x CH), 126.95 (2 x CH), 126.91 (CH), 124.4 (C), 122.9 (2 x CH), 60.4 (CH_2, OCH_2CH_3), 41.4 (CH), 28.6 (CH_2), 15.5 (CH_3), 14.0 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 360.1712 ($M + H^+$), calcd for $C_{22}H_{21}N_3O_2H$ 360.1712.

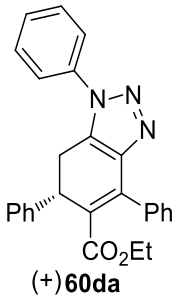
Ethyl 6-(4-chlorophenyl)-4-methyl-1-phenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60ca):



60ca

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 77% (151.1 mg); Mp 96-98 °C; IR (Neat): ν_{max} 2983, 2919, 2852, 1699, 1508, 1484, 1284, 1191, 1084, 1033, 1011, 961, 763 and 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.49 (2H, m), 7.48–7.44 (1H, m), 7.43–7.41 (2H, m), 7.15 (2H, td, *J* = 7.0, 2.5 Hz), 7.03 (2H, td, *J* = 8.5, 2.0 Hz), 4.48 (1H, br d, *J* = 8.0 Hz), 4.14 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.50 (1H, dd, *J* = 17.0, 9.0 Hz), 3.06 (1H, dd, *J* = 16.5, 2.5 Hz), 2.77 (3H, s olefinic-CH_3), 1.21 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O-C=O), 145.8 (C), 141.1 (C), 139.4 (C), 135.9 (C), 132.7 (C), 131.4 (C), 129.6 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 128.4 (2 x CH), 123.9 (C), 122.9 (2 x CH), 60.5 (CH_2, OCH_2CH_3), 40.8 (CH), 28.6 (CH_2), 15.5 (CH_3), 14.1 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 394.1323 ($M + H^+$), calcd for $C_{22}H_{20}ClN_3O_2H$ 394.1322.

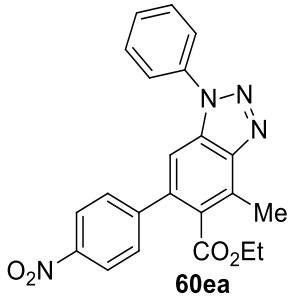
Ethyl (*R*)-1,4,6-triphenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60da):



(+)**60da**

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 65% (136.5 mg); $[\alpha]_D^{25}$ = 85.0 (*C* = 0.140, $CHCl_3$); IR (Neat): ν_{max} 3059, 2922, 2851, 1699, 1597, 1507, 1451, 1309, 1228, 1175, 1077, 762 and 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (3H, m), 7.48–7.39 (7H, m), 7.28–7.26 (4H, m), 7.24–7.19 (1H, m), 4.54 (1H, dd, *J* = 8.8, 4.0 Hz), 3.86-3.78 (2H, m OCH_2CH_3), 3.62 (1H, dd, *J* = 16.8, 8.8 Hz), 3.22 (1H, dd, *J* = 16.8, 4.0 Hz), 0.77 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-C=O), 144.7 (C), 141.8 (C), 139.2 (C), 135.95 (C), 135.91 (C), 131.8 (C), 129.6 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.2 (CH), 128.0 (2 x CH), 127.3 (CH), 127.1 (2 x CH), 126.8 (C), 123.1 (2 x CH), 60.5 (CH_2, OCH_2CH_3), 42.5 (CH), 28.8 (CH_2), 13.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 422.1869 ($M + H^+$), calcd for $C_{27}H_{23}N_3O_2H$ 422.1869.

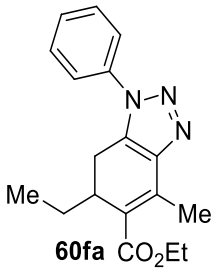
Ethyl 4-methyl-6-(4-nitrophenyl)-1-phenyl-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60ea):



60ea

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 37% (70 mg); Mp 118-120 °C; IR (Neat): ν_{max} 2922, 2360, 1950, 1720, 1513, 1435, 1302, 1083, 1053, 994 and 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (2H, d, *J* = 8.5 Hz), 7.77 (2H, td, *J* = 7.5, 1.5 Hz), 7.63 (2H, t, *J* =7.5Hz), 7.59 (2H, td, *J* = 8.5, 2.0 Hz), 7.55-7.53 (2H, m), 4.12 (2H, q, *J* = 7.5 Hz, OCH_2CH_3), 2.96 (3H, s, Ar-CH_3), 1.04 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.1 (C, O-*C*=O), 147.4 (2 x C), 145.9 (C), 138.9 (C), 136.5 (C), 132.0 (C), 131.1 (C), 130.0 (2 x CH), 129.5 (2 x CH), 129.4 (C), 129.1 (CH), 123.5 (2 x CH), 123.0 (2 x CH), 108.8 (CH), 61.5 (CH_2, OCH_2CH_3), 14.5 (CH_3), 13.8 (CH_3); HRMS (ESI-TOF) m/z 403.1406 ($M + H^+$), calcd for $C_{22}H_{18}N_4O_4H$ 403.1406

Ethyl 6-ethyl-4-methyl-1-phenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (60fa):

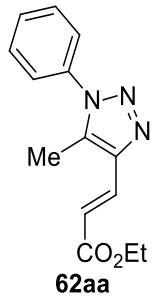


60fa

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 82% (128 mg); IR (Neat): ν_{max} 2961, 2926, 1693, 1599, 1508, 1454, 1367, 1249, 1191, 1131, 1050, 761 and 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (4H, m), 7.52-7.48 (1H, m), 4.32-4.24 (2H, m,

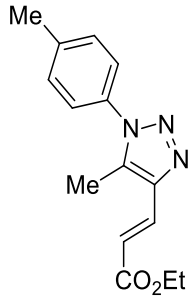
OC*H*$_2$CH$_3$), 3.17-3.05 (2H, m), 2.94 (1H, dd, *J* = 16.4, 1.2 Hz), 2.64 (3H, s, Ar-C*H*$_3$), 1.55-1.45 (1H, m), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 1.31–1.26 (1H, m), 0.80 (3H, t, *J* = 7.6 Hz, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.4 (C), 137.4 (C), 136.0 (C), 132.5 (C), 129.6 (2 x CH), 129.0 (CH), 126.2 (C), 122.9 (2 x CH), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 37.0 (CH), 26.1 (CH$_2$), 23.5 (CH$_2$), 15.5 (CH$_3$), 14.2 (CH$_3$), 11.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 312.1713 (M + H$^+$), calcd for C$_{18}$H$_{21}$N$_3$O$_2$H 312.1712.

Ethyl (*E*)-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)acrylate (62aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 83% (105 mg); Mp 108-110 °C; IR (Neat): ν$_{max}$ 2978, 2924, 1705, 1650, 1595, 1501, 1292, 1166, 1131, 1024, 979, 766, 722, 690 and 577 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (1H, d, *J* =16.0 Hz), 7.59-7.54 (3H, m), 7.47-7.45 (2H, m), 6.81 (1H, d, *J* =16.0 Hz), 4.28 (2H, q, *J* = 7.0 Hz OC*H*$_2$CH$_3$), 2.42 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 140.8 (C), 135.9 (C), 133.3 (C), 131.7 (CH), 129.7 (CH), 129.6 (2 x CH), 125.0 (2 x CH), 119.2 (CH), 60.5 (CH$_2$ O*C*H$_2$CH$_3$), 14.3 (CH$_3$), 9.2 (CH$_3$ OCH$_2$*C*H$_3$); HRMS m/z 258.1243 (M + H$^+$), calcd for C$_{14}$H$_{15}$N$_3$O$_2$H 258.1243;



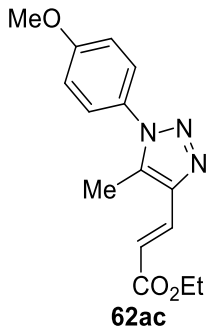
62aa

Ethyl (*E*)-3-(5-methyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)acrylate (62ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semi solid; Yield: 81% (110 mg); IR (Neat): ν$_{max}$ 2980, 2925, 1706, 1647, 1517, 1297, 1222, 1208, 1164, 1035, 1008, 870, 820, 733, 703, 564 and 509 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (1H, d, *J* =16.0 Hz), 7.36-7.32 (4H, m), 6.79 (1H, d, *J* =15.5 Hz), 4.28 (2H, q, *J* = 7.0 Hz OC*H*$_2$CH$_3$), 2.45 (3H, s Ar-C*H*$_3$), 2.40 (3H, s), 1.34 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 139.9 (C), 133.3 (C), 131.8 (CH), 130.3 (C), 130.1 (2 x CH), 124.8 (2 x CH), 120.6 (C), 118.9 (CH), 60.4 (CH$_2$ O*C*H$_2$CH$_3$), 21.1 (CH$_3$, Ar-*C*H$_3$), 14.2 (CH$_3$), 9.1 (CH$_3$ OCH$_2$*C*H$_3$); HRMS m/z 272.1399 (M + H$^+$), calcd for C$_{15}$H$_{17}$N$_3$O$_2$H 272.1399;



62ab

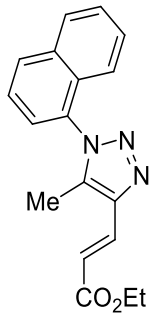
Ethyl (*E*)-3-(1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (62ac): Prepared



62ac

following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a orange solid; Yield: 71% (102); Mp 80-82 °C; IR (Neat): ν_{max} 2923, 2851, 1708, 1648, 1517, 1300, 1253, 1174, 1035, 977, 836 and 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (1H, d, *J* =16.0 Hz), 7.36 (2H, td, *J* = 9.0, 3.5 Hz), 7.05 (2H, td, *J* = 9.0, 3.5 Hz), 6.79 (1H, d, *J* =16.0 Hz), 4.28 (2H, q, *J* = 7.0 Hz OCH_2CH_3), 3.89 (3H, s OCH_3), 2.38 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.1 (C, O-*C*=O), 160.5 (C), 140.5 (C), 133.5 (C), 131.9 (CH), 128.7 (C), 126.4 (2 x CH), 118.9 (CH), 114.7 (2 x CH), 60.5 (CH_2 OCH_2CH_3), 55.6 (CH_3, OCH_3), 14.3 (CH_3), 9.1 (CH_3 OCH_2CH_3); HRMS m/z 288.1347 ($M + H^+$), calcd for $C_{15}H_{17}N_3O_3H$ 288.1348;

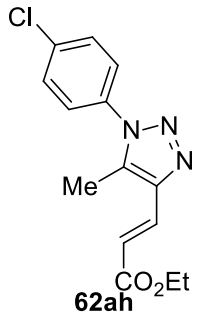
Ethyl (*E*)-3-(5-methyl-1-(naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)acrylate (62at): Prepared



62at

following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 78% (120 mg); IR (Neat): ν_{max} 3059, 2979, 2926, 1705, 1647, 1597, 1440, 1296, 1230, 1188, 1161, 1034, 975, 803 and 773 ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, d, *J* = 8.4 Hz), 7.98 (1H, d, *J* = 8.4 Hz), 7.73 (1H, d, *J* =16.0 Hz), 7.64-7.56 (2H, m), 7.51 (2H, t, *J* = 8.8 Hz), 7.19 (1H, d, *J* = 8.4 Hz), 6.87 (1H, d, *J* = 15.6 Hz), 4.50 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.22 (3H, s), 1.46 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 140.1 (C), 135.4 (C), 134.1 (C), 131.82 (C), 131.76 (CH), 130.9 (CH), 129.4 (C), 128.3 (CH), 128.0 (CH), 127.1 (CH), 125.05 (CH), 125.00 (CH), 121.9 (CH), 119.1 (CH), 60.5 (CH_2, OCH_2CH_3), 14.2 (CH_3), 8.5 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 308.1399 ($M + H^+$), calcd for $C_{18}H_{17}N_3O_2H$ 308.1399.

Ethyl (*E*)-3-(1-(4-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (62ah): Prepared

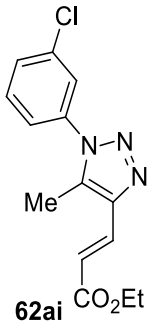


62ah

following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (128.5 mg); Mp 106-108 °C; IR (neat): ν_{max} 2993, 1717, 1651, 1497, 1300, 1169, 1109, 1005, 832, 748 and 518 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, d, *J* =15.6 Hz), 7.55 (2H, td, *J* = 8.8, 2.8 Hz), 7.42 (2H, td, *J* = 8.8, 2.0 Hz), 6.81 (1H, d, *J* =15.6 Hz), 4.28 (2H, q, *J* = 7.2 Hz OCH_2CH_3), 2.42 (3H, s), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 141.0 (C), 135.8 (C), 134.3 (C),

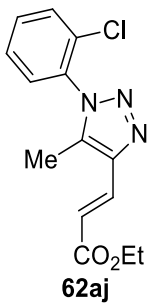
133.2 (C), 131.4 (CH), 129.9 (2 x CH), 126.2 (2 x CH), 119.5 (CH), 60.6 (CH_2 O*C*H_2CH_3), 14.3 (CH_3), 9.2 (CH_3 OCH_2*C*H_3); HRMS m/z 292.0853 ($M + H^+$), calcd for $C_{14}H_{14}ClN_3O_3H$ 292.0853;

Ethyl (*E*)-3-(1-(3-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (62ai): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (124.5 mg); Mp 90-92 °C; IR (Neat): ν_{max} 2980, 1706, 1648, 1549, 1298, 1252, 1221, 1172, 1034, 976, 835, 786 and 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (1H, d, *J* = 16.0 Hz), 7.53-7.51 (3H, m), 7.39-7.37 (1H, m), 6.80 (1H, d, *J* = 15.5 Hz), 4.28 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.44 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH_2C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 141.0 (C), 136.8 (C), 135.4 (C), 133.2 (C), 131.3 (CH), 131.0 (CH), 129.9 (CH), 125.2 (CH), 123.0 (CH), 119.5 (CH), 60.5 (CH_2, OCH_2CH_3), 14.2 (CH_3), 9.2 (CH_3, OCH_2*C*H_3); HRMS (ESI-TOF) m/z 292.0855 ($M + H^+$), calcd for $C_{14}H_{14}ClN_3O_2H$ 292.0853.



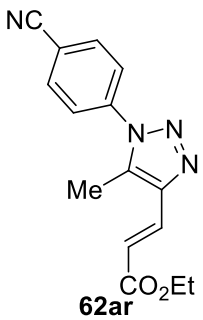
62ai

Ethyl (*E*)-3-(1-(2-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate 6aj): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 40% (58 mg); IR (Neat): ν_{max} 2925, 1709, 1650, 1497, 1301, 1264, 1177, 1034, 977 and 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* = 15.6 Hz), 7.63-7.60 (1H, m), 7.55 (1H, dt, *J* = 8.0, 2.0 Hz), 7.52-7.48 (1H, m), 7.45 (1H, dt, *J* = 8.0, 2.0 Hz), 6.81 (1H, d, *J* = 16.0 Hz), 4.29 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.29 (3H, s), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 140.2 (C), 135.2 (C), 133.5 (C), 131.9 (CH), 131.7 (C), 131.6 (CH), 130.6 (CH), 129.2 (CH), 128.0 (CH), 119.3 (CH), 60.6 (CH_2, O*C*H_2CH_3), 14.3 (CH_3), 8.5 (CH_3, OCH_2*C*H_3); HRMS (ESI-TOF) m/z 292.0856 ($M + H^+$), calcd for $C_{14}H_{14}ClN_3O_2H$ 292.0853.



62aj

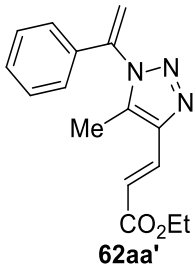
Ethyl (*E*)-3-(1-(4-cyanophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (62ar): Prepared following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (121.5 mg); Mp 158-160 °C; IR (neat): ν_{max} 2982, 2923, 2230, 1708, 1649, 1606, 1512, 1300, 1273, 1221, 1172, 1305, 977, 750 and 577 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (2H, dd, *J* = 8.5, 1.5 Hz), 7.70 (2H, d, *J* = 8.5 Hz), 7.61 (1H, d, *J* =16.0 Hz), 6.80 (1H, d, *J* =15.5 Hz), 4.28 (2H, q, *J* = 7.0 Hz OC*H*$_2$CH$_3$), 2.50 (3H, s),



62ar

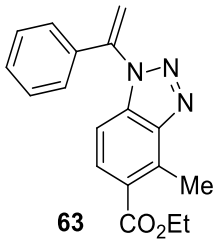
1.35 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.6 (C, O-*C*=O), 141.3 (C), 139.0 (C), 133.5 (2 x CH), 133.0 (C), 130.8 (CH), 125.0 (2 x CH), 119.7 (CH), 117.4 (C), 113.3 (C), 60.5 (CH_2 OCH_2CH_3), 14.1 (CH_3), 9.2 (CH_3 OCH_2CH_3); HRMS m/z 283.1191 ($M + H^+$), calcd for $C_{15}H_{14}N_4O_2H$ 283.1191;

Ethyl (*E*)-3-(5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)acrylate (62aa'): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 84% (118.5 mg); IR (Neat): ν_{max} 2980, 2359, 1709, 1646, 1370, 1298, 1261, 1184, 1094, 914, 755, 722, 697 and 524 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (1H, d, *J* =15.5 Hz), 7.40-7.35 (3H, m), 7.18-7.16 (2H, m), 6.80 (1H, d, *J* =16.0 Hz), 5.98 (1H, d, *J* = 1.0 Hz), 5.60 (1H, d, *J* = 1.0 Hz), 4.27 (2H, q, *J* = 7.0 Hz OCH_2CH_3), 2.15 (3H, s), 1.34 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 142.0 (C), 140.4 (C), 134.3 (C), 133.9 (C), 131.5 (CH), 129.8 (CH), 129.0 (2 x CH), 125.6 (2 x CH), 119.1 (CH), 114.5 (CH_2), 60.5 (CH_2 OCH_2CH_3), 14.2 (CH_3), 8.7 (CH_3 OCH_2CH_3); HRMS m/z 306.1218 ($M + H^+$), calcd for $C_{16}H_{16}N_3O_2Na$ 306.1218;



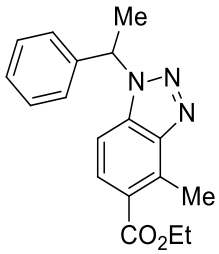
62aa'

Ethyl 4-methyl-1-(1-phenylvinyl)-1*H*-benzo[d][1,2,3]triazole-5-carboxylate-carboxylate (63): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 68% (104 mg); Mp 110-112 °C; IR (Neat): ν_{max} 2920, 2851, 1698, 1629, 1477, 1377, 1262, 1224, 1040, 899, 770, 594, 595, 696 and 595 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (1H, d, *J* = 9.0 Hz), 7.43 (1H, tt, *J* = 7.0, 2.0 Hz), 7.38 (2H, tt, *J* = 7.0, 2.0 Hz), 7.28 (2H, td, *J* = 7.0, 2.0 Hz), 6.85 (1H, dd, *J* = 9.0, 0.5 Hz), 5.83 (1H, d, *J* = 1.0 Hz), 5.80 (1H, d, *J* = 1.0 Hz), 4.41 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.16 (3H, s olefinic-CH_3), 1.42 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 147.0 (C), 142.4 (C), 135.6 (C), 134.3 (C), 134.0 (C), 129.9 (CH), 129.8 (CH), 128.8 (2 x CH), 126.8 (2 x CH), 125.0 (C), 111.4 (CH_2), 108.0 (CH), 61.0 (CH_2, OCH_2CH_3), 15.3 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 308.1396 ($M + H^+$), calcd for $C_{18}H_{17}N_3O_2H$ 308.1399.



63

Ethyl 4-methyl-1-(1-phenylethyl)-*1H*-benzo[d][1,2,3]triazole-5-carboxylate (64): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 72% (112 mg); IR (Neat): ν_{max} 2925, 1709, 1600, 1494, 1449, 1376, 1288 , 1264, 1233, 1185, 1130, 1051, 730, 699 and 532 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (1H, d, *J* = 8.5 Hz), 7.34-7.26 (5H, m), 7.05 (1H, d, *J* = 9.0 Hz), 6.04 (1H, q, *J* = 7.0 Hz), 4.38 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.11 (3H, s OCH_2CH_3), 2.17 (3H, d, *J* = 7.0 Hz); 1.40 (3H, t, *J* = 7.0 Hz, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O-*C*=O), 147.4 (C), 139.9 (C), 135.5 (C), 133.5 (C), 129.2 (CH), 128.9 (2 x CH), 128.3 (CH), 126.2 (2 x CH), 124.7 (C), 106.9 (CH), 60.9 (CH_2, OCH_2CH_3), 59.2 (CH), 21.0 (CH_3), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 332.1375 ($M + Na^+$), calcd for $C_{18}H_{19}N_3O_2Na$ 332.1375.



64

7.4 General Experimental Procedure for Engineering Organocatalytic Selective [3+2]-Cycloadditions: Synthesis of 1,4-Diaryl-5-Arylthiomethyl-1,2,3-Triazoles

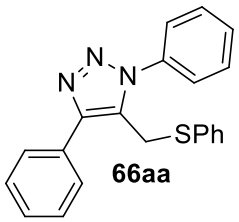
Procedure A: General procedure for the DBU-catalyzed domino [3+2]-cycloaddition reactions in DMSO: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.05 mmol of DBU (**40e**) in DMSO (1.0 mL), was added 0.75 mmol of azide **2/21** and 0.5 mmol of 1-aryl-2-(arylthio)ethanones or 1-alkyl-2-(alkylthio)ethanones and the reaction mixture was stirred at 25 °C for 0.75-6.0 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure domino products **66** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General procedure for the desulphurization of thia-1,2,3-triazoles with Raney-nickel: Two teaspoons of freshly prepared Raney-Nickel were added to a well stirred solution of thia-1,2,3-triazoles in ethanol (0.05 M) under argon atmosphere. The reaction mixture was allowed to stir for 1.0-3.0 h at 25 °C/50 °C. After completion, the reaction mixture was filtered through a tight packing of celite on a sintered glass funnel. The filter cake was rinsed thoroughly with ethanol then sucked damp-dry. The filtrate was evaporated under reduced pressure to obtain

crude reaction mixture. Desulphurized products were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate.

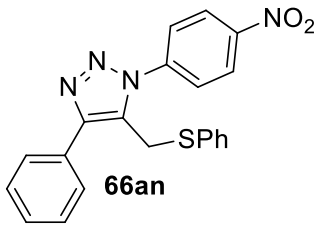
Procedure C: General Procedure for the Oxidation of 66an: In an oven dried round bottom flask, *m*-CPBA (1.5 equiv.) was added to a stirred solution of compound **66an** (1.0 equiv. in dry CH_2Cl_2 (0.5 M) at -78 °C After completion of reaction (as monitored by TLC), treated with 10% aqueous K_2CO_3solution and then the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Pure product **70an** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

1,4-Diphenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 90% (154 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 3342, 1665, 1605, 1534, 1386, 1304, 1210, 1019, 986 and 920 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.84 (2H, td, *J* = 7.5, 1.5 Hz), 7.60-7.57 (2H, m), 7.55-7.52 (3H, m), 7.46 (2H, tt, *J* = 7.5, 1.5 Hz), 7.39 (1H, tt, *J* = 7.5, 1.5 Hz), 7.23-7.20 (5H, m), 4.25 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.0 (C), 136.0 (C), 133.8 (C), 131.6 (2 x CH), 130.6 (C), 129.9 (CH), 129.6 (C), 129.5 (2 x CH), 129.2 (2 x CH), 128.8 (2 x CH), 128.2 (CH), 127.8 (CH), 127.6 (2 x CH), 125.6 (2 x CH), 28.1 (CH_2); HRMS (ESI-TOF) m/z 344.1221 ($M + H^+$), calcd for $C_{21}H_{17}N_3SH$ 344.1221.



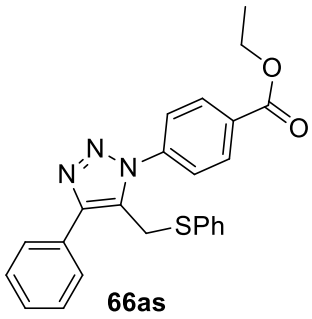
66aa

1-(4-Nitrophenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66an): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 90% (176 mg); Mp.: 25-127 °C; IR (Neat) ν_{max} 2925, 2854, 1665, 1594, 1495, 1435, 1391, 1315, 1074, 997, 854, 750 and 690 cm^{-1};^1H NMR ($CDCl_3$, 400 MHz) δ 8.39 (2H, td, *J* = 9.2, 2.0 Hz), 7.86 (2H, td, *J* = 8.8 , 2.0 Hz), 7.80 (2H, td, *J* = 7.2, 1.6 Hz), 7.47 (2H, tt, *J* = 7.6, 1.6 Hz), 7.42 (1H, tt, *J* = 7.2, 1.2 Hz), 7.26-7.21 (5H, m), 4.29 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT-135) δ 148.0 (C), 146.9 (C), 140.9 (C), 133.0 (C), 131.6 (2 x CH), 129.9 (C), 129.7 (C), 129.3 (2 x CH), 128.9 (2 x CH), 128.6 (CH), 128.2 (CH), 127.6 (2 x CH), 125.8 (2 x CH), 125.0 (2 x CH), 28.0 (CH_2); HRMS (ESI-TOF) m/z 389.1070 ($M + H^+$), calcd for $C_{21}H_{16}N_4O_2SH$ 389.1072.



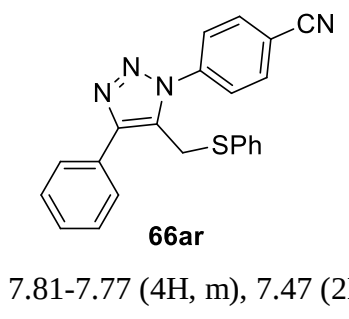
66an

Ethyl 4-(4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazol-1-yl)benzoate (66as): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 90% (186.6 mg); Mp.: 120-122 °C; IR (Neat): ν_{max} 2931, 1709, 1605, 1517, 1484, 1435, 1375, 1276, 1106, 1019, 986 , 854, 772 and 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (2H, td, *J* = 8.5, 2.0 Hz), 7.82 (2H, td, *J* = 7.0, 2.0 Hz), 7.71 (2H, td, *J* = 9.0, 2.0 Hz), 7.47 (2H, tt, *J* = 8.0, 2.0 Hz), 7.40 (1H, tt, *J* = 7.5, 2.0 Hz), 7.25-7.20 (5H, m), 4.44 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 4.27 (2H, s), 1.44 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 165.4 (C, O-*C*=O), 146.5 (C), 139.5 (C), 133.4 (C), 131.7 (2 x CH), 130.9 (2 x CH), 130.4 (C), 129.6 (2 x C), 129.2 (2 x CH), 128.8 (2 x CH), 128.4 (CH), 128.0 (CH), 127.6 (2 x CH), 125.1 (2 x CH), 61.5 (CH$_2$, O*C*H$_2$CH$_3$), 28.1 (CH$_2$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 416.1430 (M + H$^+$), calcd for $C_{24}H_{21}N_3O_2SH$ 416.1433.



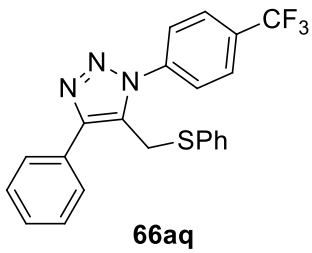
66as

4-(4-Phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazol-1-yl)benzonitrile (66ar): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (166 mg); Mp.: 140-142 °C; IR (Neat): ν_{max} 3057, 2931, 2848, 2330, 1610, 1582, 1517, 1484, 1440, 1095, 991, 739, and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.83 (2H, td, *J* = 8.8, 1.6 Hz), 7.81-7.77 (4H, m), 7.47 (2H, tt, *J* = 7.2, 1.6 Hz), 7.41 (1H, tt, *J* = 7.2, 1.6 Hz), 7.28-7.18 (5H, m), 4.27 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.7 (C), 139.5 (C), 133.5 (2 x CH), 133.0 (C), 131.6 (2 x CH), 130.0 (C), 129.6 (C), 129.3 (2 x CH), 128.9 (2 x CH), 128.6 (CH), 128.1 (CH), 127.6 (2 x CH), 125.7 (2 x CH), 117.6 (C), 113.6 (C), 28.0 (CH$_2$); HRMS (ESI-TOF) m/z 369.1173 (M + H$^+$), calcd for $C_{22}H_{16}N_4SH$ 369.1174.



66ar

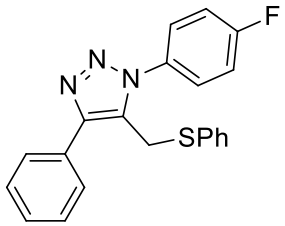
4-Phenyl-5-((phenylthio)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (66aq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 92% (190 mg); Mp.: 115-117 °C; IR (Neat): ν_{max} 2925, 2843, 1665, 1615, 1588, 1528, 1484, 1435, 1413, 1325, 1166, 1133, 1029, 908, 859, 739 and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.83-7.74 (6H, m), 7.47 (2H, tt, *J* = 7.6, 1.2 Hz), 7.41 (1H, tt, *J* = 7.6, 1.2 Hz), 7.27-7.19 (5H,



66aq

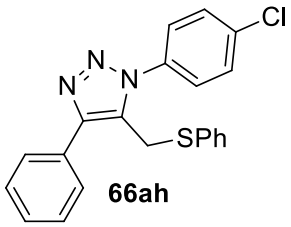
m), 4.27 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.5 (C), 138.9 (C), 133.3 (C), 131.8 (C, q, *J* = 33.0 Hz), 131.7 (2 x CH), 130.2 (C), 129.7 (C), 129.3 (2 x CH), 128.9 (2 x CH), 128.5 (CH), 128.1 (CH), 127.6 (2 x CH), 126.8 (2 x CH, q, *J* = 4.0 Hz), 125.7 (2 x CH), 123.5 (C, q, *J* = 271.0 Hz, *C*F_3), 28.1(CH_2); HRMS (ESI-TOF) m/z 412.1097 (M + H^+), calcd for $C_{22}H_{16}F_3N_3SH$ 412.1095.

1-(4-Fluorophenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (163 mg); Mp.: 111-113 °C; IR (Neat): ν_{max} 2958, 2931, 2860, 1638, 1572, 1512, 1238, 1150, 1084, 838, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (2H, td, *J* = 6.8, 2.0 Hz) 7.56 (2H, tt, *J* = 6.8, 2.0 Hz), 7.46 (2H, tt, *J* = 6.8, 1.6 Hz), 7.39 (1H, tt, *J* = 7.2, 1.6 Hz), 7.25-7.20 (7H, m), 4.22 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.2 (C, d, *J* = 249.0 Hz, *C*-F), 146.0 (C), 133.5 (C), 132.1 (C, d, *J* = 3.0 Hz), 131.6 (2 x CH), 130.5 (C), 129.8 (C), 129.2 (2 x CH), 128.8 (2 x CH), 128.3 (CH), 127.9 (CH), 127.7 (2 x CH, d, *J* =8.0 Hz), 127.5 (2 x CH,) 116.6 (2 x CH, d, *J* = 23.0 Hz), 28.0 (CH_2); HRMS (ESI-TOF) m/z 362.1125 (M + H^+), calcd for $C_{21}H_{16}FN_3SH$ 362.1127.



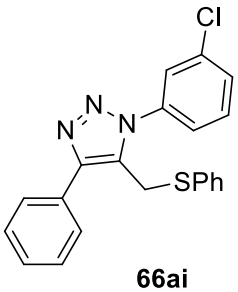
66af

1-(4-Chlorophenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (170 mg); Mp.: 104-106 °C; IR (Neat) ν_{max} 2915, 2849, 1583, 1501, 1435, 1271, 1090, 1024, 986, 915 and 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (2H, td, *J* = 8.5, 1.5 Hz), 7.52 (4H, tq, *J* = 8.5, 2.0 Hz), 7.46 (2H, tt, *J* = 8.5, 2.0 Hz), 7.40 (1H, tt, *J* = 7.5, 2.0 Hz), 7.25-7.21 (5H, m), 4.23 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.2 (C), 136.0 (C), 134.5 (C), 133.5 (C), 131.6 (2 x CH), 130.4 (C), 129.8 (2 x CH), 129.7 (C), 129.3 (2 x CH), 128.8 (2 x CH), 128.4 (CH), 128.0 (CH), 127.6 (2 x CH), 126.8 (2 x CH), 28.1 (CH_2); HRMS (ESI-TOF) m/z 378.0831 (M + H^+), calcd for $C_{21}H_{16}ClN_3SH$ 378.0832.



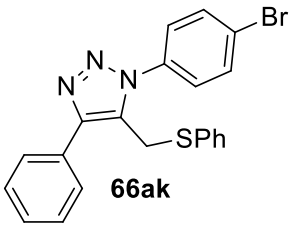
66ah

1-(3-Chlorophenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66ai): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 90% (171 mg); Mp.: 108-110 °C; IR (Neat): ν_{max} 2920, 2860, 1715, 1556, 1430, 1090, 986, and 909 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (2H, td, *J* = 7.0, 1.0 Hz), 7.60 (1H, t, *J* = 2.0 Hz), 7.52-7.494 (1H, m), 7.486-7.44 (4H, m), 7.40 (1H, tt, *J* = 7.5, 2.0 Hz), 7.26-7.20 (5H, m), 4.25 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.2 (C), 137.0 (C), 135.3 (C), 133.2 (C), 132.1 (2 x CH), 130.5 (CH), 130.4 (C), 130.0 (CH), 129.7 (C), 129.2 (2 x CH), 128.8 (2 x CH), 128.4 (CH), 128.2 (CH), 127.6 (2 x CH), 125.8 (CH), 123.6 (CH), 28.3 (CH_2); HRMS (ESI-TOF) m/z 378.0828 ($M + H^+$), calcd for $C_{21}H_{16}ClN_3SH$ 378.0832.



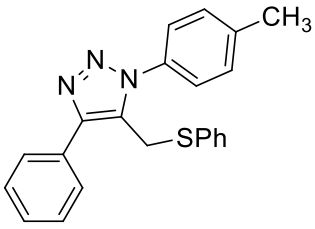
66ai

1-(4-Bromophenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66ak): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (185 mg); Mp.: 113-116 °C; IR (KBr): ν_{max} 2920, 2854, 2361, 2339, 1578, 1501, 1435, 1232, 1172, 986, 882, 734, and 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (2H, m), 7.66 (2H, td, *J* = 8.8, 2.4 Hz), 7.49-7.44 (4H, m), 7.40 (1H, tt, *J* = 7.6, 1.2 Hz), 7.25-7.20 (5H, m), 4.23 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.2 (C), 135.0 (C), 133.5 (C), 132.8 (2 x CH), 131.6 (2 x CH), 130.4 (C), 129.6 (C), 129.3 (2 x CH), 128.8 (2 x CH), 128.4 (CH), 128.0 (CH), 127.6 (2 x CH), 127.0 (2 x CH), 124.0 (C), 28.0 (CH_2); HRMS (ESI-TOF) m/z 422.0327 ($M + H^+$), calcd for $C_{21}H_{16}BrN_3SH$ 422.0327.



66ak

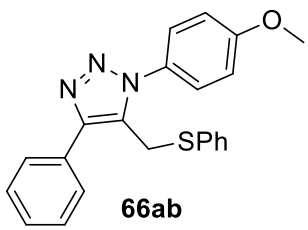
4-Phenyl-5-((phenylthio)methyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazole (66ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (162 mg); Mp.: 123-125 °C; IR (Neat): ν_{max} 3005, 1635, 1477, 1477, 1275l 1261, 1227, 1044, 895, 817, 749 and 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, td, *J* = 8.4, 1.6 Hz), 7.45 (4H, tt, *J* = 8.4, 1.6 Hz), 7.38 (1H, tt, *J* = 7.6, 1.6 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.21 (5H, s), 4.23 (2H, s), 2.46 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.8 (C), 140.1 (C), 133.9 (C), 133.5 (C), 131.5 (2 x CH), 130.7 (C), 130.1 (2 x CH), 129.6 (C), 129.1 (2 x CH), 128.7



66ac

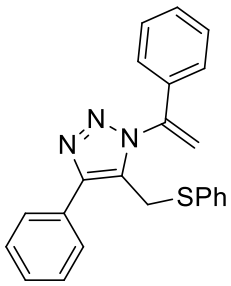
(2 x CH), 128.2 (CH), 127.7 (CH), 127.5 (2 x CH), 125.4 (2 x CH), 28.1 (CH_2) 21.3 (CH_3); HRMS (ESI-TOF) m/z 358.1378 ($M + H^+$), calcd for $C_{22}H_{19}N_3SH$ 358.1378.

1-(4-Methoxyphenyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a liquid; Yield: 75% (140 mg); IR (KBr): ν_{max} 2920, 2843, 1726, 1605, 1517, 1468, 1304, 1172, 1095, 1035, 991, 745 and 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (2H, td, *J* = 8.0, 1.5 Hz) 7.50-7.43 (4H, m), 7.38 (1H, tt, *J* = 7.5, 1.5 Hz), 7.22 (5H, s), 7.02 (2H, td, *J* = 9.0, 1.5 Hz), 4.22 (2H, s), 3.89 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$ DEPT-135) δ 160.6 (C), 145.7 (C), 134.0 (C), 131.5 (2 x CH), 130.8 (C), 129.8 (C), 129.2 (2 x CH), 128.9 (C), 128.8 (2 x CH), 128.2 (CH), 127.7 (CH), 127.5 (2 x CH), 127.1 (2 x CH), 114.6 (2 x CH), 55.6 (CH_3, O*C*H$_3$), 28.1 (CH_2) HRMS (ESI-TOF) m/z 374.1328 ($M + H^+$), calcd for $C_{22}H_{19}N_3OSH$ 374.1327.



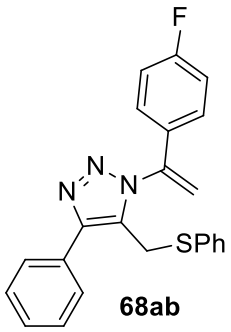
66ab

4-Phenyl-5-((phenylthio)methyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazole (68aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 88% (163 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 3058, 2926, 1968, 1887, 1807, 1676, 1641, 1578, 1490, 1443, 1336, 1264, 1232, 1132, 1088, 1025, 998, 915, 775, 742 and 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (2H, td, *J* = 8.0, 2.0 Hz), 7.42 (2H, tt, *J* = 7.5, 1.5 Hz), 7.38-7.34 (4H, m), 7.21-7.13 (7H, m), 5.90 (1H, d, *J* = 1.0 Hz), 5.60 (1H, d, *J* = 1.0 Hz), 4.00 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$, DEPT-135) δ 145.8 (C), 142.0 (C), 134.7 (C), 133.8 (C), 131.8 (2 x CH), 130.5 (C), 130.1 (C), 129.7 (CH), 129.0 (2 x CH), 128.9 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 127.7 (CH), 127.6 (2 x CH), 126.0 (2 x CH), 114.9 (CH_2), 27.8 (CH_2); HRMS (ESI-TOF) m/z 370.1380 ($M + H^+$), calcd for $C_{23}H_{19}N_3SH$ 370.1378.



68aa

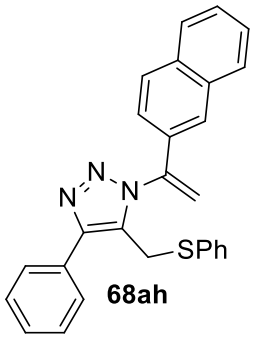
1-(1-(4-Fluorophenyl)vinyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (68ab):



68ab

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 85% (165 mg); Mp.: 111-113 °C; IR (KBr): ν_{max} 3060, 2925, 2853, 1639, 1602, 1508, 1438, 1235, 1161, 1086, 998, 915, 842, 741 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.44 (2H, td, *J* = 7.2, 1.2 Hz), 6.17 (2H, tt, *J* = 7.2, 1.2 Hz), 6.11 (1H, tt, *J* = 7.2, 1.2 Hz), 5.96-5.91 (5H, m), 5.90-5.87 (2H, m), 5.79 (2H, tt, *J* = 8.4, 2.8 Hz), 4.60 (1H, d, *J* = 1.2 Hz), 4.33 (1H, d, *J* = 1.2 Hz), 2.78 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.5 (C, d, *J* = 249.0 Hz, *C*-F), 145.9 (C), 141.0 (C), 133.7 (C), 131.6 (2 x CH), 130.9 (C, d, *J* = 4.0 Hz), 130.3 (C), 130.0 (C), 129.0 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 128.0 (2 x CH, d, *J* = 9.0 Hz), 127.7 (CH), 127.5 (2 x CH,) 115.9 (2 x CH, d, *J* = 22.0 Hz), 114.6 (CH_2), 27.7 (CH_2); HRMS (ESI-TOF) m/z 388.1284 (M + H^+), calcd for $C_{23}H_{18}FN_3SH$ 388.1284.

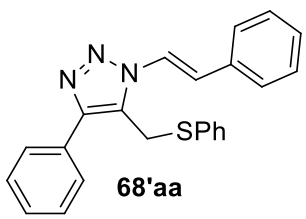
1-(1-(Naphthalen-2-yl)vinyl)-4-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (68ah):



68ah

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 80% (168 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 3050, 1626, 1582, 1478, 1438, 1367, 1269, 1088, 998, 914, 858, 818, 714 and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.83-7.81 (2H, m), 7.76-7.73 (3H, m), 7.51-7.47 (3H, m), 7.45-7.35 (4H, m), 7.17-7.08 (5H, m), 6.03 (1H, d, *J* = 0.8 Hz), 5.67 (1H, d, *J* = 0.8 Hz), 4.02 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$, DEPT-135) δ 145.8 (C), 141.9 (C), 133.7 (C), 133.6 (C), 132.9 (C), 131.8 (C), 131.6 (2 x CH), 130.5 (C), 130.2 (C), 128.9 (2 x CH), 128.8 (CH), 128.7 (2 x CH), 128.5 (CH), 128.2 (CH), 127.65 (CH), 127.62 (CH), 127.5 (2 x CH), 127.1 (CH), 126.8 (CH), 125.7 (CH), 122.9 (CH), 115.4 (CH_2), 27.8 (CH_2); HRMS (ESI-TOF) m/z 420.1535 (M + H^+), calcd for $C_{27}H_{21}N_3SH$ 420.1534.

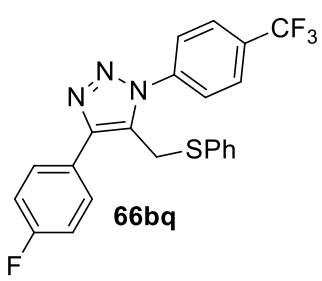
(*E*)-4-Phenyl-5-((phenylthio)methyl)-1-styryl-1*H*-1,2,3-triazole (68'aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 85% (158 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 3053, 2895, 1638, 1596, 1477, 1443, 1389, 1231, 1196, 1045, 947, 893, 739 and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 (2H, d, *J* = 6.0 Hz), 7.52 (1H, d, *J* =



68'aa

14.0 Hz), 7.41-7.36 (8H, m), 7.32 (3H, s) 7.23 (3H, s) 4.27 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.0 (C), 133.9 (C), 132.9 (C), 132.5 (2 x CH), 130.3 (C), 129.3 (2 x CH), 128.8 (2 x CH), 128.7 (3 x CH), 128.3 (CH), 128.3 (C), 128.2 (CH), 127.5 (2 x CH), 126.9 (2 x CH), 124.7 (CH), 120.0 (CH), 27.5 (CH_2); HRMS (ESI-TOF) m/z 370.1379 (M + H^+), calcd for $C_{23}H_{19}N_3SH$ 370.1378.

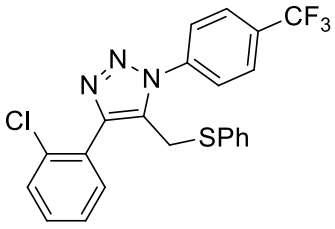
4-(4-Fluorophenyl)-5-((phenylthio)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole



66bq

(66bq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 85% (182 mg); Mp.: 112-114 °C; IR (KBr): ν_{max} 2350, 2334, 1616, 1501, 1413, 1369, 1320, 1232, 1178, 1145, 849, 810, and 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.74 (6H, m), 7.26-7.19 (5H, m), 7.15 (2H, tt, *J* = 7.2, 1.6 Hz), 4.24 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.9 (C, d, *J* = 247.0 Hz, *C*-F), 145.6 (C), 138.8 (C), 133.0 (C), 131.89 (C, q, *J* = 33.0 Hz), 131.88 (2 x CH), 129.6 (C), 129.5 (2 x CH, d, *J* = 9.0 Hz), 129.3 (2 x CH), 128.2 (CH), 126.8 (2 x CH, q, *J* = 4.0 Hz), 126.4 (C, d, *J* = 3.0 Hz), 125.7 (2 x CH), 123.5 (C, q, *J* = 271.0 Hz, *C*F_3), 115.9 (2 x CH, d, *J* = 21.0 Hz), 28.1 (CH_2); HRMS (ESI-TOF) m/z 430.1002 (M + H^+), calcd for $C_{22}H_{15}F_4N_3SH$ 430.1001.

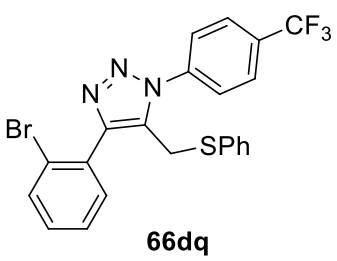
4-(2-Chlorophenyl)-5-((phenylthio)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole



66cq

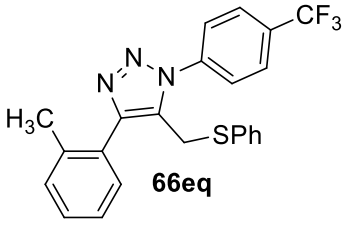
(66cq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless viscous liquid; Yield: 81% (188 mg); IR (KBr): ν_{max} 2926, 2019, 1753, 1665, 1610, 1473, 1375, 1331, 1254, 1134, and 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (2H, d, *J* = 6.8 Hz), 7.70 (2H, d, *J* = 7.2 Hz), 7.49-7.26 (4H, m), 7.18-7.00 (5H, m), 4.19 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.6 (C), 139.1 (C), 133.4 (C), 132.9 (C), 132.5 (C), 132.3 (CH), 132.1 (C, q, *J* = 33.0 Hz), 132.0 (2 x CH), 130.3 (CH), 129.8 (CH), 129.2 (C), 129.1 (2 x CH), 128.0 (CH), 127.0 (CH), 126.8 (2 x CH , q, *J* = 4.0 Hz), 125.7 (2 x CH), 125.5 (C, q, *J* = 270.0 Hz, *C*F_3), 28.0 (CH_2); HRMS (ESI-TOF) m/z 446.0707 (M + H^+), calcd for $C_{22}H_{15}ClF_3N_3SH$ 446.0706.

4-(2-Bromophenyl)-5-((phenylthio)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (66dq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow liquid; Yield: 60% (148 mg); IR (Neat): ν_{max} 2361, 1649, 1556, 1473, 1320, 1178, 1106, 1057, 1008 and 843 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (2H, br d, *J* = 8.4 Hz), 7.64 (2H, d, *J* = 8.4 Hz), 7.60 (1H, dd, *J* = 7.6, 1.2 Hz), 7.29-7.21 (2H, m), 7.20-7.16 (1H, m), 7.12 (1H, tt, *J* = 7.2, 1.2 Hz), 7.04 (2H, dt, *J* = 7.2, 1.6 Hz), 6.95 (2H, td, *J* = 8.0, 1.2 Hz), 4.10 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.1 (C), 139.1 (C), 133.05 (C), 132.97 (CH), 132.4 (CH), 132.2 (C), 132.00 (2 x CH), 131.98 (C, q, *J* = 33.0 Hz), 131.2 (C), 130.5 (CH), 129.1 (2 x CH), 128.0 (CH), 127.5 (CH), 126.8 (2 x CH, q, *J* = 3.0 Hz), 125.6 (2 x CH), 123.7 (C), 123.6 (C, q, *J* = 271.0 Hz, *C*F_3), 28.1 (CH_2); HRMS (ESI-TOF) m/z 490.0204 ($M + H^+$), calcd for $C_{22}H_{15}BrF_3N_3SH$ 490.0200.



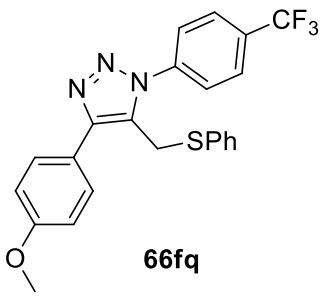
66dq

5-(Phenylthio)methyl)-4-(*o*-tolyl)-1-(4-(trifluoromethyl)phenyl)-*1H*-1,2,3-triazole (66eq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow liquid; Yield: 50% (108 mg); IR (KBr): ν_{max} 2915, 1736, 1660, 1621, 1441, 1408, 1326, 1172, 1079, 1019, 991, 810 and 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (2H, d, *J* = 8.4 Hz), 7.77 (2H, d, *J* = 8.4 Hz), 7.35-7.29 (2H, m), 7.26-7.17 (3H, m), 7.13 (2H, t, *J* = 7.6 Hz), 7.04 (2H, d, *J* = 7.6 Hz), 4.14 (2H, s), 2.28 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.0 (C), 139.3 (C), 138.1 (2 x C), 133.2 (C), 131.50 (C, q, *J* = 33.0 Hz), 131.47 (2 x CH), 131.2 (C), 130.7 (CH), 130.2 (CH), 129.1 (2 x CH), 129.0 (CH), 127.8 (CH), 126.8 (2 x CH, q, *J* = 3.0 Hz), 126.2 (C, q, *J* = 271.0 Hz, *C*F_3), 125.7 (CH), 125.5 (2 x CH), 27.3 (CH_2), 20.3 (CH_3); HRMS (ESI-TOF) m/z 426.1354 ($M + H^+$), calcd for $C_{23}H_{18}F_3N_3SH$ 426.1252.



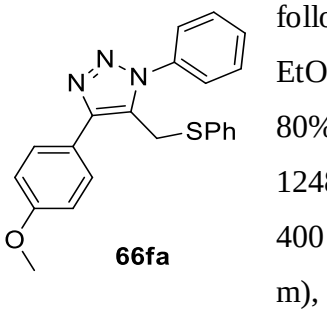
66eq

4-(4-Methoxyphenyl)-5-((phenylthio)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (66fq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (199 mg); Mp.: 112-114 °C; IR (KBr): ν_{max} 2964, 2838, 1616, 1572, 1495, 1419, 1369, 1326, 1167, 1073, 832, 745 and 701 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81-7.78 (3H, m), 7.76-7.74 (3H, m), 7.26-7.21 (5H, m), 7.01 (2H, td, *J* = 8.8, 2.8 Hz), 4.25 (2H s), 3.87 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.8 (C), 146.4 (C), 139.0 (C), 133.4 (C), 131.6 (2 x CH), 131.5 (C, q, *J* = 31.0 Hz), 129.3 (2 x CH), 128.95 (2 x CH), 128.90 (C), 128.0 (CH), 126.8 (2 x CH, q, *J* = 4.0 Hz), 126.2 (C, q, *J* = 271.0 Hz, *C*F_3), 125.6 (2 x CH), 122.8 (C), 114.3 (2 x CH), 55.3 (CH_3 O*C*H_3), 28.1(CH_2); HRMS (ESI-TOF) m/z 442.1205 ($M + H^+$), calcd for $C_{23}H_{18}F_3N_3OSH$ 442.1201.



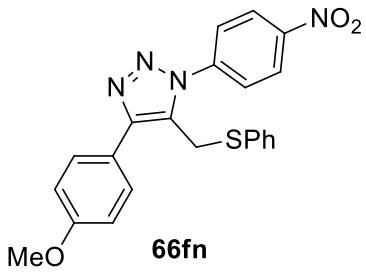
66fq

4-(4-methoxyphenyl)-1-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow liquid; Yield: 80% (150 mg); IR (KBr): ν_{max} 2924, 1614, 1502, 1460, 1438, 1365, 1296, 1248, 1176, 1028, 990, 835, 743, 764, 691and 531 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (2H, td, *J* = 9.2, 2.8 Hz), 7.61-7.58 (2H, m), 7.56-7.54 (3H, m), 7.24 (5H, s), 7.01 (2H, td, *J* = 8.8, 2.8 Hz), 4.25 (2H s), 3.88 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.7 (C), 145.9 (C), 136.2 (C), 133.9 (C), 131.5 (2 x CH), 129.8 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 128.9 (2 x CH), 128.9 (C), 127.8 (CH), 125.6 (2 x CH), 123.3 (C), 114.3 (2 x CH), 55.3 (CH_3 O*C*H_3), 28.2 (CH_2); HRMS (ESI-TOF) m/z 374.1327 ($M + H^+$), calcd for $C_{22}H_{19}N_3OSH$ 374.1327.



66fa

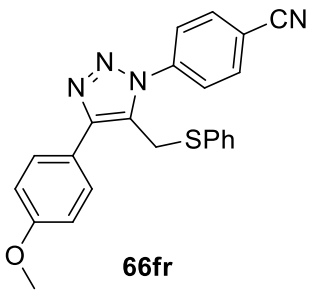
4-(4-Methoxyphenyl)-1-(4-nitrophenyl)-5-((phenylthio)methyl)-1*H*-1,2,3-triazole (66fn): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a Brown solid; Yield: 85% (179 mg); Mp.: 138-140 °C; IR (KBr): ν_{max} 2915, 2849, 1616, 1534, 1506, 1435, 1342, 1304, 1254, 1178, 1106, 1019, 991, 854, 756 and 684 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.40 (2H, td, *J* = 8.8, 2.0 Hz), 7.87 (2H, td, *J* = 8.8, 2.0 Hz), 7.76 (2H, td, *J* = 8.8, 2.0 Hz), 7.26-7.23 (5H, m), 7.02 (2H, td, *J* = 8.8, 2.0 Hz),



66fn

4.28 (2H, s), 3.88 (3H, s OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.0 (C), 148.0 (C), 146.9 (C), 141.1 (C), 133.2 (C), 131.6 (2 x CH), 129.4 (2 x CH), 129.0 (2 x CH), 128.8 (C), 128.2 (CH), 125.7 (2 x CH), 125.0 (2 x CH), 122.5 (C), 114.4 (2 x CH), 55.4 (CH_3 O*C*H_3), 28.2 (CH_2); HRMS (ESI-TOF) m/z 419.1184 (M + H^+), calcd for $C_{22}H_{18}N_4O_3SH$ 419.1184.

4-(4-(4-Methoxyphenyl)-5-((phenylthio)methyl)-*1H*-1,2,3-triazol-1-yl)benzonitrile (66fr):

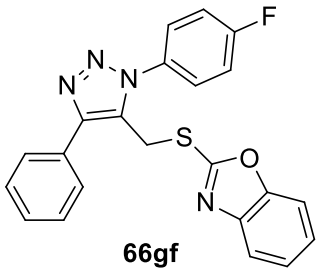


66fr

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (175 mg); Mp.: 120-122 °C; IR (KBr): ν_{max} 2920, 2854, 2224, 2213, 1605, 1517, 1249, 1178, 986, 832, and 739 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84-7.73 (6H, m), 7.27-7.20 (5H, m), 7.00 (2H, td, *J* = 8.8, 2.0 Hz), 4.25 (2H, s), 3.86 (3H, s OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.9 (C), 146.7 (C), 139.6 (C), 133.5 (2 x CH), 133.3 (C), 131.5 (2 x CH), 129.3 (2 x CH), 129.0 (2 x CH), 128.8 (C), 128.1 (CH), 125.6 (2 x CH), 122.5 (C), 117.6 (C), 114.3 (2 x CH), 113.5 (C), 55.3 (CH_3 O*C*H_3), 28.1 (CH_2); HRMS (ESI-TOF) m/z 399.1280 (M + H^+), calcd for $C_{23}H_{18}N_4OSH$ 399.1280.

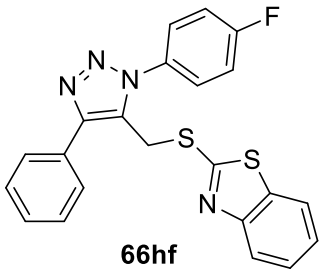
2-(1-(4-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-yl)methyl)thio)benzo[d]oxazole (66gf)

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white Semi solid; Yield: 70% (142 mg); IR (Neat): ν_{max} 2923, 1776, 1512, 1451, 1236, 1131, 1095, 991, 805 and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.89-7.86 (2H, m), 7.65-7.61 (2H, m), 7.55-7.50 (3H, m), 7.47-7.39 (2H, m), 7.34-7.22 (4H, m), 4.79 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.3 (C, d, *J* = 250.0 Hz, *C*-F), 161.9 (C), 151.8 (C), 146.7 (C), 141.4 (C), 131.7 (C, d, *J* = 3.0 Hz), 130.3 (C), 129.0 (2 x CH), 128.7 (CH), 128.0 (C), 127.7 (2 x CH, d, *J* = 9.0 Hz), 127.5 (2 x CH), 124.6 (CH), 124.5 (CH), 118.6 (CH), 116.8 (2 x CH, d, *J* =23.0 Hz), 110.1 (CH), 25.3 (CH_2); LCMS m/z 403.30 (M + H+), Calcd for $C_{22}H_{15}FN_4OSH$ 403.10. Anal. calcd for $C_{22}H_{15}FN_4OS$: C, 65.72; N, 13.85 H, 3.68. Found: C, 65.66; N, 13.92 H, 3.76.



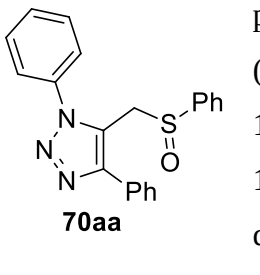
66gf

2-(1-(4-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-yl)methyl)thio)benzo[d]thiazole (66hf): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white Semi solid; Yield: 70% (147 mg); IR (Neat): ν_{max} 3062, 2921, 2850, 1602, 1514, 1460, 1237, 1155, 1076, 992, 840, 756, 727 and 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) 7.87 (2H, d, *J* = 7.5 Hz), 7.76 (2H, q, *J* = 8.5 Hz), 7.63-7.60 (2H, m), 7.50 (2H, t, *J* = 7.5 Hz), 7.44 (2H, q, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.21 (2H, t, *J* = 8.5 Hz), 4.87 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 163.3 (C, d, *J* = 250.0 Hz, *C*-F), 163.2 (C), 152.7 (C), 146.5 (C), 135.4 (C), 131.9 (C, d, *J* = 3.7 Hz), 130.3 (C), 128.9 (2 x CH), 128.7 (C), 128.6 (CH), 127.7 (2 x CH, d, *J* =8.7 Hz), 127.6 (2 x CH), 126.3 (CH), 124.8 (CH), 121.7 (CH), 121.1 (CH) 116.7 (2 x CH, d, *J* = 21.2 Hz); 26.0 (CH_2); LCMS m/z 419.15 (M + H+), Calcd for $C_{22}H_{15}FN_4S_2H$ 419.08. Anal. Calcd for $C_{22}H_{15}FN_4S_2$: C, 63.21; N, 13.45 H, 3.57. Found: C, 63.14; N, 13.39 H, 3.61.



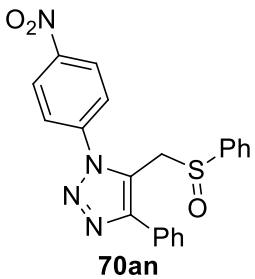
66hf

1,4-diphenyl-5-((phenylsulfinyl)methyl)-1*H*-1,2,3-triazole (70aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a white solid; Yield: 88% (159 mg); Mp.: 110-112 °C; IR (KBr): ν_{max} 3052, 2924, 2161, 2032, 1731, 1595, 1497, 1443, 1250 1079, 1044, 893, and 739 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.74 (2H, d, *J* = 7.5 Hz), 7.57-7.52 (3H, m), 7.45 (2H, t, *J* = 7.5 Hz), 7.40 (2H, t, *J* = 7.5, Hz), 7.36 (2H, d, *J* = 8.0, Hz), 7.32 (2H, t, *J* = 7.5, Hz), 7.24 (2H, t, *J* = 7.5, Hz), 4.53 ((1H, d, *J* = 14.0 Hz), 4.23 ((1H, d, *J* = 13.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.6 (C), 142.1 (C), 135.6 (C), 132.0 (CH), 130.2 (CH), 130.1 (C), 129.6 (2 x CH), 129.3 (2 x CH), 128.9 (2 x CH), 128.6 (CH), 127.6 (2 x CH), 126.2 (2 x CH), 124.1 (C), 123.9 (2 x CH), 51.9 (CH_2); HRMS m/z 360.1175 ($M + H^+$), calcd for $C_{21}H_{17}N_3OSH$ 360.1171.



70aa

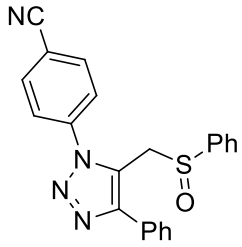
1-(4-Nitrophenyl)-4-phenyl-5-((phenylsulfinyl)methyl)-1*H*-1,2,3-triazole (70an): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a white solid; Yield: 90% (182 mg); Mp.: 140-142 °C; IR (KBr): ν_{max} 2925, 2887, 2361, 1731, 1594, 1528, 1347, 1249, 1090, 1041, 860, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.42 (2H, td, *J* = 7.0, 2.0 Hz), 7.77 (2H, td, *J* = 9.0, 2.0 Hz), 7.70 (2H, td, *J* = 8.0, 2.0 Hz), 7.50-7.42 (4H, m), 7.36 (2H, t, *J* = 7.5 Hz), 7.29



70an

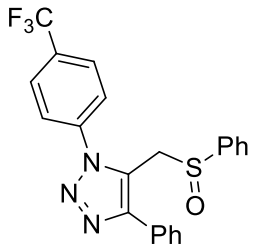
(2H, dd, *J* = 8.5, 1.0 Hz), 4.47 ((1H, d, *J* = 14.0 Hz), 4.31 (1H, d, *J* = 14.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 148.2 (2 x C), 141.9 (C), 140.7 (C), 132.2 (CH), 129.6 (C), 129.5 (2 x CH), 128.99 (2 x CH), 128.97 (CH), 127.7 (2 x CH), 126.9 (2 x CH), 125.0 (2 x CH), 124.1(C), 123.8 (2 x CH), 51.1 (CH_2); HRMS (ESI-TOF) m/z 405.1026 ($M + H^+$), calcd for $C_{21}H_{16}N_4O_3SH$ 405.1021.

4-(4-Phenyl-5-((phenylsulfinyl)methyl)-1*H*-1,2,3-triazol-1-yl)benzonitrile (70ar): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a white solid; Yield: 88% (170 mg); Mp.: 173-175 °C; IR (KBr): ν_{max} 2915, 2849, 2350, 2230, 1610, 1512, 1358, 1052 and 854 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (2H, td, *J* = 8.4, 2.0 Hz), 7.70-7.65 (4H, m), 7.48-7.40 (4H, m), 7.35 (2H, tt, *J* = 7.2, 1.2 Hz), 7.27 (2H, td, *J* = 7.2, 1.2 Hz), 4.45 ((1H, d, *J* = 14.0 Hz), 4.29 ((1H, d, *J* = 14.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 148.0 (C), 141.7 (C), 139.1 (C), 133.4 (2 x CH), 132.1 (CH), 129.6 (C), 129.4 (2 x CH), 128.9 (2 x CH), 128.8 (CH), 127.6 (2 x CH), 126.7 (2 x CH), 124.0 (C), 123.7 (2 x CH), 117.4 (C), 113.8 (C), 51.0 (CH_2); HRMS (ESI-TOF) m/z 385.1175 ($M + H^+$), calcd for $C_{22}H_{16}N_4OSH$ 385.1123.



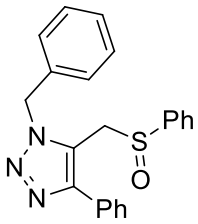
70ar

4-Phenyl-5-((phenylsulfinyl)methyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (70aq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a white solid; Yield: 85% (182 mg); Mp.: 146-148 °C; IR (KBr): ν_{max} 2915, 2367, 1616, 1523, 1446, 1419, 1369, 1167, 1063, 849, 739 and 608 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (2H, d, J = 8.4, 2.0 Hz), 7.73-7.70 (2H, m), 7.59 (2H, d, J = 8.4, 2.0 Hz), 7.48-7.39 (4H, m), 7.33 (2H, t, J = 7.6 Hz), 7.27-7.24 (2H, m), 4.45 ((1H, d, J = 14.0 Hz), 4.28 ((1H, d, J = 14.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.9 (C), 141.8 (C), 138.5 (C), 132.1 (CH), 132.0 (C, q, *J* = 33.0 Hz), 129.7 (C), 129.4 (2 x CH), 128.9 (2 x CH), 128.8 (CH), 127.6 (2 x CH), 126.7 (2 x CH, q, *J* = 3.0 Hz), 126.4 (2 x CH), 124.0 (C), 123.8 (2 x CH), 123.4 (C, q, *J* = 271.0 Hz, *C*F_3); 51.2 (CH_2); HRMS (ESI-TOF) m/z 428.1043 ($M + H^+$), calcd for $C_{22}H_{16}F_3N_3OSH$ 428.1044.



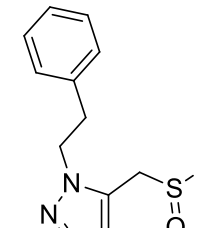
70aq

1-Benzyl-4-phenyl-5-((phenylsulfinyl)methyl)-*1H*-1,2,3-triazole (70au): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a colourless viscous liquid; Yield: 65% (122 mg); IR (KBr): ν_{max} 2969, 2942, 2082, 1944, 1884, 1736, 1561, 1446, 1369, 1238, 1095 and 942 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 (3H, dt, *J* = 7.6, 2.0 Hz), 7.39-7.31 (10H, m), 7.19 (2H, d, *J* = 6.8 Hz), 5.78 (1H, d, *J* = 15.6 Hz), 5.54 (1H, d, *J* = 15.6 Hz), 4.17 ((1H, d, *J* = 14.0 Hz), 4.07 ((1H, d, *J* = 14.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 148.0 (C), 141.6 (C), 134.5 (C), 132.0 (CH), 130.2 (C), 129.3 (2 x CH), 129.1 (2 x CH), 128.7 (2 x CH), 128.5 (CH), 128.3 (CH), 127.5 (2 x CH), 127.4 (2 x CH), 123.8 (2 x CH), 123.2 (C), 52.9 (CH_2), 50.7 (CH_2), HRMS (ESI-TOF) m/z 374.1330 ($M + H^+$), calcd for $C_{22}H_{19}N_3OSH$ 374.1327.



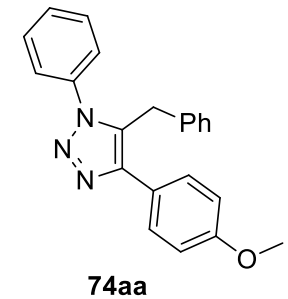
70au

1-Phenethyl-4-phenyl-5-((phenylsulfinyl)methyl)-1*H*-1,2,3-triazole (70av): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 3:7) and was isolated as a colourless viscous liquid; Yield: 55% (107 mg); IR (KBr): ν_{max} 3057, 2931, 2849, 1720, 1600, 1490, 1435, 1358, 1084, 1052, 745, 695 and 580 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (1H, tt, *J* = 7.6, 1.2 Hz), 7.33-7.27 (7H, m), 7.26-7.20 (5H, m), 7.05 (2H, dd, *J* = 7.6, 1.2 Hz), 4.63 (1H, quint, *J* = 7.2, Hz); 4.48 (1H, quint, *J* = 7.2, Hz), 3.78 (1H, d, *J* = 14.4 Hz), 3.67 (1H, d, *J* = 14.4 Hz); 3.29-3.17 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.9 (C), 141.5 (C), 137.5 (C), 131.9 (CH), 130.4 (C), 129.2 (2 x CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.2 (CH), 127.6 (2 x CH), 127.2 (CH), 123.8 (2 x CH), 123.7 (C), 50.6 (CH_2), 49.9 (CH_2), 36.9 (CH_2); HRMS m/z 388.1484 ($M + H^+$), calcd for $C_{23}H_{21}N_3OSH$ 388.1484.



70av

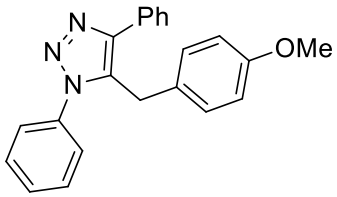
5-Benzyl-4-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (74aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white liquid; Yield: 32% (55 mg); IR (Neat): ν_{max} 2923, 2852, 1742, 1615, 1598, 1505, 1460, 1250, 1177, 1108, 1031, 993, 763, 731, 695 and 531 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.70 (2H, td, *J* = 8.8, 2.0 Hz), 7.48-7.42 (3H, m), 7.35-7.33 (2H, m), 7.29-7.23 (4H, m), 7.00-6.96 (3H, m), 4.24 (2H, s), 3.85 (3H, s O*CH*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.5 (C), 145.6 (C), 137.0 (C), 136.4 (C),



74aa

131.1 (C), 129.6 (CH), 129.4 (2 x CH), 128.9 (2 x CH), 128.4 (2 x CH), 127.8 (2 x CH), 126.9 (CH), 125.4 (2 x CH), 123.6 (C), 114.3 (2 x CH), 55.3 (CH_3, OCH_3), 29.7 (CH_2); HRMS (ESI-TOF) m/z 342.1624 ($M + H^+$), calcd for $C_{22}H_{19}N_3OH$ 342.1606

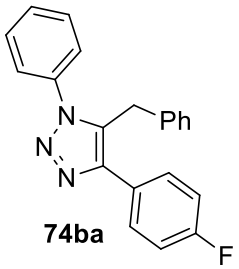
5-(4-Methoxybenzyl)-1,4-diphenyl-1*H*-1,2,3-triazole (75aa): Prepared following the procedure



75aa

A and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white liquid; Yield: 50% (86 mg); IR (Neat): ν_{max} 3061, 3000, 2954, 2932, 2835, 1598, 1583, 1509, 1248, 1177, 1032, 992, 818, 769, 692 and 516 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.75 (2H, m), 7.47-7.40 (5H, m), 7.37-7.31 (3H, m), 6.87 (2H, td, *J* = 8.8, 2.0 Hz), 6.78 (2H, td, *J* = 8.8, 2.0 Hz), 4.19 (2H, s), 3.77 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 158.4 (C), 145.5 (C), 136.3 (C), 132.1 (C), 131.1 (C), 129.6 (CH), 129.3 (2 x CH), 128.8 (4 x CH), 128.8 (C), 128.0 (CH), 127.1 (2 x CH), 125.4 (2 x CH), 114.3 (2 x CH), 55.2 (CH_3 OCH_3), 28.4 (CH_2); HRMS (ESI-TOF) m/z 364.1424 ($M + Na^+$), calcd for $C_{22}H_{19}N_3ONa$ 364.1424.

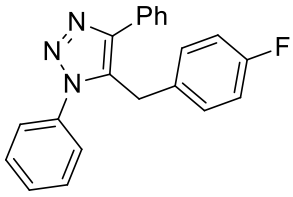
5-Benzyl-4-(4-fluorophenyl)-1-phenyl-1*H*-1,2,3-triazole (74ba) Prepared following the



74ba

procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semi solid; Yield: 48% (79 mg); IR (Neat): ν_{max} 3063, 3029, 1563, 1503, 1454, 1431, 1367, 1224, 1158, 1097, 994, 840, 817, 762, 735, 694, 608, 565 and 524 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.72 (2H, tt, *J* = 8.4, 2.8 Hz), 7.47-7.41 (3H, m), 7.34-7.31 (2H, m), 7.28-7.22 (3H, m), 7.09 (2H, tt, *J* = 8.8, 2.8 Hz), 6.96 - 6.94 (2H, m), 4.17 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 162.6 (C, d, *J* = 246.0 Hz), 144.9 (C), 136.7 (C), 136.2 (C), 131.6 (C), 129.7 (CH), 129.4 (2 x CH), 129.0 (2 x CH), 128.9 (2 x CH, d, *J* = 8.0 Hz), 127.8 (2 x CH), 127.2 (C, d, *J* = 3.0 Hz), 127.0 (CH), 125.5 (2 x CH), 115.8 (2 x CH, d, *J* = 22.0 Hz), 29.2 (CH_2); HRMS (ESI-TOF) m/z 330.1437 ($M + H^+$), calcd for $C_{21}H_{16}FN_3H$ 330.1438.

5-(4-Fluorobenzyl)-1,4-diphenyl-1*H*-1,2,3-triazole (75ba): Prepared following the procedure **A**

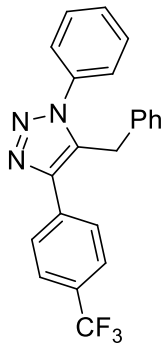


75ba

and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semi solid; Yield: 42% (70 mg); IR (Neat): ν_{max} 3066, 2924, 1599, 1507, 1430, 1367, 1255, 1224, 1158, 993, 820, 771, 695, and 507 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.74 (2H, td, *J* = 8.0, 1.5 Hz), 7.49-7.41 (5H, m), 7.37 (1H, tt, *J* = 7.5, 1.5 Hz), 7.30

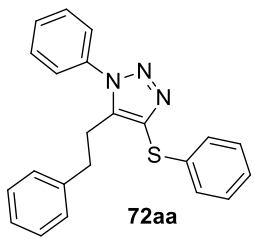
(2H, td, *J* = 6.5, 1.5 Hz), 6.93 (1H, td, *J* = 9.0, 1.2 Hz), 6.91-6.87 (3H, m), 4.22 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 161.7 (C, d, *J* = 243.7 Hz *C*-F), 145.7 (C), 136.3 (C), 132.4 (C, d, *J* = 2.5 Hz), 131.8 (C), 131.0 (C), 129.8 (CH), 129.4 (2 x CH), 129.3 (2 x CH, d, *J* = 7.5 Hz), 128.9 (2 x CH), 128.2 (CH), 127.2 (2 x CH), 125.5 (2 x CH), 115.8 (2 x CH, d, *J* = 21.2 Hz), 28.5 (CH_2); HRMS (ESI-TOF) m/z 352.1221 ($M + H^+$), calcd for $C_{21}H_{16}FN_3Na$ 352.1226.

5-Benzyl-1-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (74ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semi solid; Yield: 75% (142 mg); IR (Neat): ν_{max} 3064, 3011, 1621, 1598, 1502, 1454, 1433, 1323, 1257, 1165, 1108, 749, 691, 669 and 500 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (2H, d, *J* = 8.0 Hz), 7.67 (2H, d, *J* = 8.4 Hz), 7.50-7.44 (3H, m), 7.38-7.35 (2H, m), 7.31-7.25 (3H, m), 7.00-6.98 (2H, m), 4.30 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.3 (C), 136.3 (C), 136.0 (C), 134.6 (C), 132.6 (C), 129.9 (CH), 129.8 (C, q, *J* = 32.0 Hz), 129.5 (2 x CH), 129.1 (2 x CH), 127.7 (2 x CH), 127.2 (CH), 127.1 (2 x CH), 125.8 (2 x CH, q, *J* = 3.0 Hz), 125.5 (2 x CH), 124.1 (C, q, *J* = 270.0 Hz, *C*F_3); 29.3(CH_2); HRMS (ESI-TOF) m/z 420.1190 ($M + Na^+$), calcd for $C_{22}H_{16}F_3N_3Na$ 402.1194.



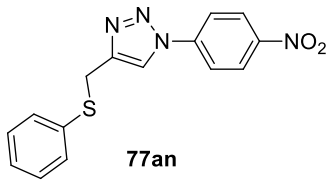
74ca

5-Phenethyl-1-phenyl-4-(phenylthio)-1*H*-1,2,3-triazole (72aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a white solid; Yield: 85% (152 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 3063, 2925, 1763, 1582, 1498, 1478, 1454, 1248, 1063, 1024, 1000, 743 and 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.48 (3H, m), 7.35-7.33 (2H, m), 7.28-7.18 (5H, m), 7.14-7.12 (3H, m), 6.804-6.797 (2H, m), 3.04 (2H, t, *J* = 7.2 Hz), 2.66 (2H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 140.7 (C), 139.3 (C), 136.1 (2 X C), 135.8 (C), 129.8 (CH), 129.5 (2 x CH), 129.0 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 128.2 (2 x CH), 126.4 (2 x CH), 125.3 (2 x CH), 34.1 (CH_2), 25.1 (CH_2); HRMS (ESI-TOF) m/z 358.1379 ($M + H^+$), calcd for $C_{22}H_{19}N_3SH$ 358.1378.



72aa

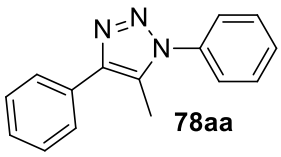
1-(4-Nitrophenyl)-4-((phenylthio)methyl)-1*H*-1,2,3-triazole (77an): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and isolated as a yellow oily solid; Yield: 85% (133 mg); IR (Neat): ν_{max} 2923, 2854, 1597, 1524, 1340, 1244, 1175, 1110, 1041, 1023, 986, 853, 749, 689 and 503 cm^{-1}; ^{1}H



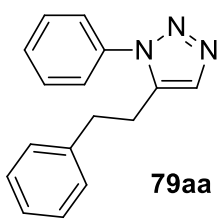
77an

NMR ($CDCl_3$, 500 MHz) δ 8.40-8.38 (2H, m), 7.91-7.86 (3H, m), 7.38-7.37 (2H, m), 7.31-7.28 (2H, m), 7.26-7.20 (1H, m), 4.32 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 147.3 (C), 147.0 (C), 141.1 (C), 135.1 (C), 129.8 (2 x CH), 129.1 (2 x CH), 126.8 (CH), 125.5 (2 x CH), 120.4 (2 x CH), 120.0 (CH), 28.8 (CH_2); HRMS (ESI-TOF) m/z 313.0754 ($M + H^+$), calcd for $C_{15}H_{12}N_4O_2SH$ 313.0759.

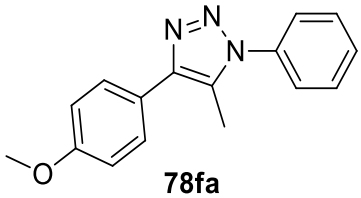
5-Methyl-1,4-diphenyl-1*H*-1,2,3-triazole (78aa): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (95 mg); Mp.: 404-406 °C; IR (KBr): 3063, 1501, 1473, 1260, 1068, 909, 761, 695, 597 and 465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* = 6.8 Hz), 7.61-7.47 (7H, m), 7.39 (1H, t, *J* = 7.2 Hz), 2.50 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 144.9 (C), 136.4 (C), 131.4 (C), 129.6 (C), 129.53 (2 x CH), 129.48 (CH), 128.7 (2 x CH), 127.8 (CH), 127.2 (2 x CH), 125.3 (2 x CH), 10.3 (CH_3); HRMS (ESI-TOF) m/z 236.1189 ($M + H^+$), calcd for $C_{15}H_{13}N_3H$ 236.1188.



5-Phenethyl-1-phenyl-1*H*-1,2,3-triazole (79aa): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 82% (102 mg); IR (Neat): 2916, 2848, 2359, 2339, 1705, 1598, 1500, 1454, 1263, 976, 738, 697 and 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.62 (1H, s), 7.55-7.52 (3H, m), 7.37-7.35 (2H, m), 7.28 (2H, tt, *J* = 6.8, 2.0 Hz), 7.22 (2H, tt, *J* = 6.8, 1.6 Hz), 7.09-7.07 (1H, m), 3.03-2.98 (2H, m), 2.94-2.89 (2H, m), ^{13}C NMR ($CDCl_3$, DEPT-135) δ 139.7 (C), 137.3 (C), 136.3 (C), 132.6 (CH), 129.54 (CH), 129.50 (2 x CH), 128.6 (2 x CH), 128.3 (2 x CH), 126.6 (CH), 125.4 (2 x CH), 34.6 (CH_2), 25.6 (CH_2); HRMS (ESI-TOF) m/z 272.1166 ($M + H^+$), calcd for $C_{16}H_{15}N_3Na$ 272.1164.

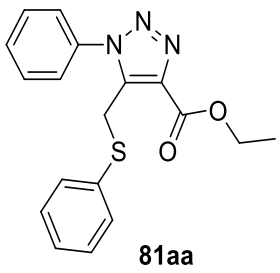


4-(4-Methoxyphenyl)-5-methyl-1-phenyl-1*H*-1,2,3-triazole (78fa): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 75% (100 mg); Mp.: 404-406 °C; IR Neat): 2923, 2851, 1709, 1669, 1603, 1499, 1459, 1245, 1178, 1034, 821, 595 and 524 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.73 (2H, td, *J* = 8.8, 2.0 Hz), 7.61-7.52 (5H, m), 7.04 (2H, td, *J* = 8.8, 2.8 Hz), 3.88 (3H, s), 2.48 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.4 (C), 144.8 (C), 136.5



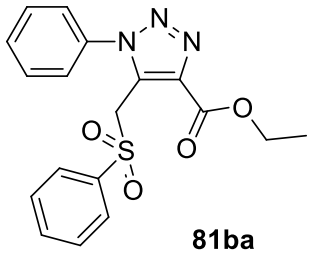
(C), 129.5 (2 x CH), 129.4 (CH), 128.9 (C), 128.6 (2 x CH), 125.2 (2 x CH), 124.1 (C), 114.2 (2 x CH), 55.3 (CH_3 -O*C*H3*)*, 10.2 (CH_3); HRMS (ESI-TOF) m/z 266.2263 ($M + H^+$), calcd for $C_{16}H_{15}N_3H$ 266.2293.

Ethyl 1-phenyl-5-((phenylthio)methyl)-1*H*-1,2,3-triazole-4-carboxylate (81aa);Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated yellow liquid; Yield: 75% (128 mg); IR (KBr): ν_{max} 3058, 2981, 2927, 2851, 1730, 1712, 1596, 1562, 1499, 1462, 1350, 1154, 1002, 794, 763 and 490 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.45 (3H, m), 7.355-7.348 (2H, m), 7.17 (5H, s), 4.362 (2H, s), 4.358-4.29 (2H, m $OC\mathit{H}_2CH_3$), 1.34-1.32 (3H, m, $OCH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 161.0 (C, O-*C*=O), 139.2 (C), 137.0 (C), 135.1 (C), 133.1 (2 x CH), 132.8 (C), 130.3 (CH), 129.6 (2 x CH), 129.1 (2 x CH), 128.3 (CH), 125.6 (2 x CH), 61.2 (CH_2, OCH_2CH_3), 27.4 (CH_2), 14.3 (CH_3, OCH_2CH_3) HRMS (ESI-TOF) m/z 340.1129. ($M + H^+$), calcd for $C_{18}H_{17}N_3O_2SH$ 340.1120.



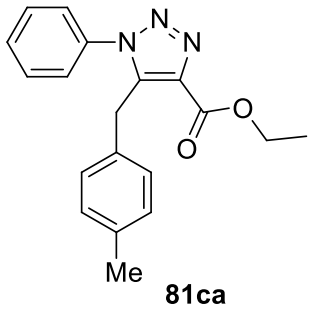
81aa

Ethyl 1-phenyl-5-((phenylsulfonyl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (81ba); Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a reddish liquid; Yield: 73% (135 mg); IR (KBr): ν_{max} 3064, 2981, 2958, 2852, 1730, 1717, 1499, 1462, 1447, 1326, 1248, 1215, 1139, 1081, 1001, 845, 800, 765, 745 and 552 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.66-7.60 (3H, m), 7.58-7.53 (3H, m), 7.49-7.46 (4H, m), 4.91 (2H, s), 4.16 (2H, q, *J* = 7.0 Hz $OC\mathit{H}_2CH_3$), 1.31 (3H, t, *J* = 7.0 Hz $OCH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.5 (C, O-*C*=O), 138.6 (C), 137.7 (C), 134.8 (C), 134.3 (CH), 130.7 (CH), 130.5 (C), 129.8 (2 x CH), 129.3 (2 x CH), 128.7 (2 x CH), 126.2 (2 x CH), 61.4 (CH_2 $OC\mathit{H}_2CH_3$) 50.4 (CH_2), 14.1 (CH_3 $OCH_2C\mathit{H}_3$)HRMS (ESI-TOF) m/z 372.1014. ($M + H^+$), calcd for $C_{18}H_{17}N_3O_4SH$ 372.1018.



81ba

Ethyl 5-(4-methylbenzyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate(81ca);Prepared following



81ca

the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a reddish liquid; Yield: 72% (116 mg); IR (Neat): ν_{max} 3056, 2981, 2924, 1732, 1712, 1597, 1561, 1513, 1502, 1444, 1376, 1351, 1212, 846, 792, 765 and 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.45 (3H, m), 7.28-7.25 (2H, m), 6.99 (2H, d, *J* = 7.6 Hz), 6.78 (2H, d, *J* = 8.0 Hz), 4.46 (2H, q, *J* = 7.2 Hz OCH_2CH_3), 4.35 (2H, s), 2.27 (3H, s Ar-CH_3), 1.41 (3H, t, *J* = 7.2 Hz OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 161.6 (C, O-*C*=O), 141.3 (C), 136.9 (C), 136.5 (C), 135.5 (C), 133.0 (C), 130.3 (CH), 129.5 (2 x CH), 129.3 (2 x CH), 128.0 (2 x CH), 125.9 (2 x CH), 61.2 (CH_2 OCH_2CH_3), 28.6 (CH_2), 21.0 (CH_3 Ar-CH_3), 14.3 (CH_3 OCH_2CH_3) ; HRMS (ESI-TOF) m/z 322.1557 ($M + H^+$), calcd for $C_{19}H_{19}N_3O_2H$ 322.1556.

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Publications:

1. Organocatalytic Vinyl Azide-Carbonyl [3+2] Cycloaddition: High-Yielding Synthesis of Fully Decorated *N*-Vinyl-1,2,3-Triazoles D. B. Ramachary, **G. Surendra Reddy**, Swamy Peraka, Jagjeet Gujral. *ChemCatChem.* **2017**, *9*, 263-267.
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6. Enantioselective synthesis of vicinal quaternary spirocyclohexene pyrazolones via bifunctional organocatalysis. A. Vamshi Krishna[+], **G. Surendra Reddy[+],** B. Gorachand and D. B. Ramachary. (*under revision*)

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Poster and Oral Presentations:

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2. **Oral presentation**: "*Organocatalytic Click Reaction and Design and Applications*" ***Chemfest-2019,*** 16th Annual In-House Symposium School of Chemistry, Hyderabad, University of Hyderabad, March 2019.

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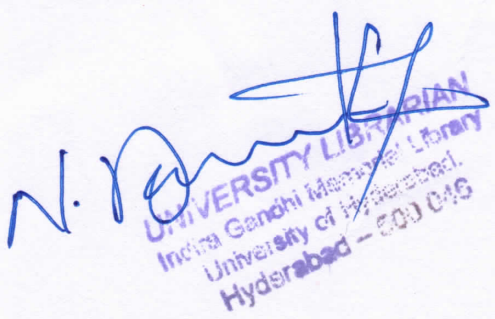

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