Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Iridium-catalysed thioether-directed regioselective cycloaddition of internal alkynes with azides

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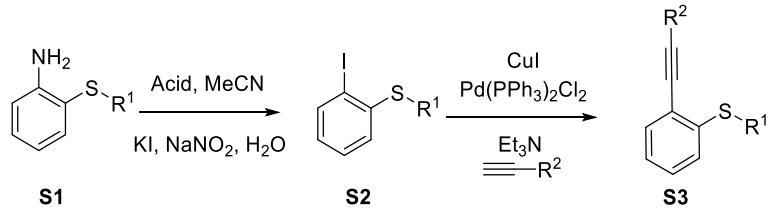
I. General

Unless otherwise stated, all experiments were carried out under air atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III HD 400 in $CDCl_3$ using TMS as an internal standard, operating at 400 MHz and 101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; $CHCl_3$ δ (7.28 ppm) and $CDCl_3$ δC (77.03 ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra (HRMS (ESI-TOF)) were obtained on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

II. Preparation of starting materials

S1 were purchased from commercial suppliers and used without further purification. **S2** were prepared according to the literature procedure[1]. **S3** were prepared according to the literature procedure[2]. Azides were prepared following the procedure [3]. These compounds ***S2, S3,*** and *azides* were known.



Synthesis of S2

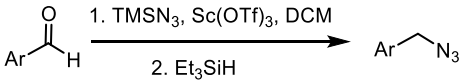
S1 (24.8 mmol, 1.0 equiv) and $TsOH{\cdot}H_2O$ (14.2 g, 74.7 mmol, 3.0 equiv) were suspended in 160 mL MeCN, KI (8.25 g, 47.7 mmol, 2.0 equiv) and $NaNO_2$ (4.28 g,

62.1 mmol, 2.5 equiv) were dissolved in 90 mL H_2O and added dropwise. After stirring at room temperature for 3h, 100 mL of a saturated $NaHCO_3$ solution were added followed by 100 ml of a saturated $Na_2S_2O_3$ solution. It was extracted three times with 100 mL DCM. The collected organic phases were dried over $MgSO_4$. After solvent evaporation in vacuo, the crude product was purified via silica column chromatography (eluent: pentane) giving the product in form of an oil, which is solidified by storing it in a freezer.

Synthesis of S3

To a solution of **S2** (5 mmol), CuI (2 mol%), and $Pd(Ph_3P)_2Cl_2$ (2 mol%) in triethylamine (15 mL) was added dropwise an alkyne (6 mmol) under N_2. The reaction mixture was stirred for 5-10 h at 25 ℃. Upon completion, the mixture was diluted with DCM and then washed with water and brine successively. The organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified through silica gel flash chromatography to give the desired product in mostly > 90% yield.

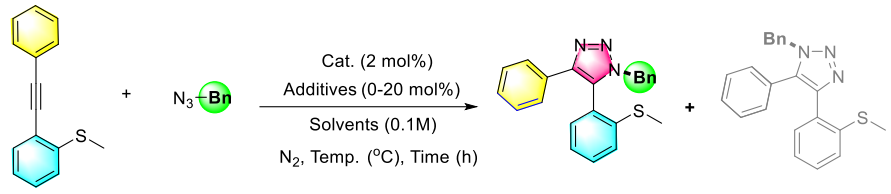
Synthesis of *azides*



To a stirred solution of aldehyde (1.0 mmol) in dichloromethane (3.0 mL) at room temperature, azidotrimethylsilane (2.8 equiv, 2.8 mmol) was added followed by the addition of $Sc(OTf)_3$ (0.05 equiv, 5 mol %). The reaction mixture was stirred at 0℃ (or refluxed). Then triethylsilane (2.0 equiv., 2.0 mmol) was added dropwise at the same temperature. After the completion, the reaction mixture was extracted with CH_2Cl_2 (20 mL × 3) and brine (8 mL). The organic portions were collected and dried over $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash column chromatography (EtOAc/Hexane) on silica gel.

III. Optimisation of reaction conditions

Table S1. Optimization of reaction conditions [a]



1 2a 3a 3a'

Entry	Solvent	Cat. (2 mol%)	Add. (20 mol%)	T. (□)	Time	Yield (%)[b]
1	DCM	$[Ir(cod)Cl]_2$	-	RT	12h	20
2	Toluene	$[Ir(cod)Cl]_2$	-	RT	12h	10
3	EtOH	$[Ir(cod)Cl]_2$	-	RT	12h	20
4	MeCN	$[Ir(cod)Cl]_2$	-	RT	12h	21
5	THF	$[Ir(cod)Cl]_2$	-	RT	12h	15
6	DCM	$[Ir(cod)Cl]_2$	-	30	12h	30
7	H_2O[d]	$[Ir(cod)Cl]_2$	-	RT	12h	10
8	DCM[d]	$[Ir(cod)Cl]_2$	-	RT	12h	12
9	DCM	$[Ir(cod)Cl]_2$	-	40	12h	33
10	H_2O	$[Ir(cod)Cl]_2$	-	40	12h	42
11	MeCN	$[Ir(cod)Cl]_2$	-	40	12h	18
12	H_2O	$[Ir(cod)Cl]_2$	-	80	12h	30
13	MeCN	$[Ir(cod)Cl]_2$	-	80	12h	23
14	DCE	$[Ir(cod)Cl]_2$	-	RT	12h	15
15	Et_2O	$[Ir(cod)Cl]_2$	-	RT	12h	8
16	Chlorobenzene	$[Ir(cod)Cl]_2$	-	RT	12h	5
17	DMF	$[Ir(cod)Cl]_2$	-	RT	12h	n.r.
18	DCM	$[Ir(cod)Cl]_2$	-	RT	48h	25
19	$CHCl_3$	$[Ir(cod)Cl]_2$	-	RT	12h	15
20	DMSO	$[Ir(cod)Cl]_2$	-	RT	12h	n.r.
21	1,4-Dioxane	$[Ir(cod)Cl]_2$	-	RT	12h	n.r.
22	n-Hexane	$[Ir(cod)Cl]_2$	-	RT	12h	15
23	Acetone	$[Ir(cod)Cl]_2$	-	RT	12h	18
24	-	$[Ir(cod)Cl]_2$	-	RT	12h	12
25	CH_3COOH	$[Ir(cod)Cl]_2$	-	RT	12h	n.r.
26	DCM	CuI	-	RT	12h	n.r.
27	DCM	$[Cp^*Ru(PPh_3)_2Cl]$	-	RT	12h	n.r.
28	DCM	$[(Cp^*RhCl_2)_2]$	-	RT	12h	n.r.
29	DCM	$[Ir(cod)Cl]_2$	$AgSbF_6$	RT	12h	42
30	DCM	$[Ir(cod)Cl]_2$	CH_3COOAg	RT	12h	25
31	DCM	$[Ir(cod)Cl]_2$	Ag_3PO_4	RT	12h	40
32	DCM	$[Ir(cod)Cl]_2$	AgOTf	RT	12h	80
33	DCM	$[Ir(cod)Cl]_2$	$AgNO_3$	RT	12h	n.r.
34	DCM	$[Ir(cod)Cl]_2$	$AgBF_4$	RT	12h	50

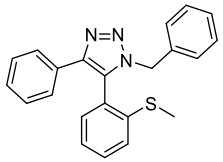
35	DCM	$[Ir(cod)Cl]_2$	$AgNTf_2$	RT	12h	83
36	DCM	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	12h	99
37	DCM	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	99(95[c])
38	DCM	-	$NaBAr^F{}_4$	RT	1h	n.r.
39	MeCN	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	57
40	H_2O	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	45
41	Et_2O	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	49
42	DMF	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	18
43	THF	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	46
44	EtOH	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	26
45	DCM[d]	$[Ir(cod)Cl]_2$	$NaBAr^F{}_4$	RT	1h	55

[a] Reaction conditions: **1** (0.1 mmol), **2** (1.5 equiv), Catalyst (2 mol%), Additives (0-20 mol%), solvents (1.0 mL), N_2, r.t.- 40 °C, 1-12h ; [b]GC-MS yield, **3a**:**3a'** > 20:1 in all cases; [c]Isolated yield; [d]Under air atomsphere, 1h. Bn = Benzyl; cod = Cycloocta-1,5-diene, DCM = Dichloromethane, THF = Tetrahydrofuran.

IV. General procedures for the cycloaddition of alkynes with azides

A mixture of **S3** (0.4 mmol, 1.0 equiv), azide (0.75mmol 1.5 equiv), $[Ir(cod)Cl]_2$ (2 mol%), $NaBAr^F{}_4$ (20 mol%) in a 10 mL Schlenk tube was added the DCM (3.0 mL) under N_2. Then the tube was sealed with a Teflon-lined screw cap and heated at RT for 1h to 12h. After the reaction was completed, quenched with water (2 mL) and extracted with dichloromethane (1 mL × 2). The combined organic layers were washed with water (5 mL) and dried over Na_2SO_4. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 2:1) to afford the desired compound **3a-3ad**.

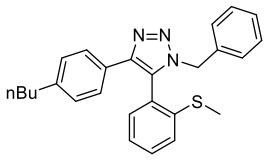
Characterization of products 3a-3ad.



3a

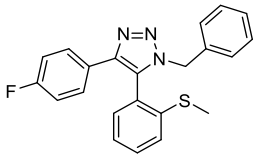
1-benzyl-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.34 - 7.18 (m, 7H), 7.13 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 5.54 (d, *J* = 14.9 Hz, 1H), 5.19 (d, *J* = 14.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.09,

140.55, 134.95, 131.62, 131.34, 131.02, 130.55, 128.44 (2C), 128.43 (2C), 128.04 (3C), 127.69, 126.16 (2C), 125.35, 125.00, 52.49, 15.16. HRMS (ESI, m/z): calcd. for $C_{22}H_{20}N_3S^+$ $[M+H]^+$: 358.1372, found: 358.1373.



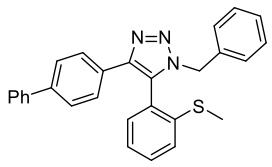
3b

1-benzyl-4-(4-butylphenyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.43 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.16 (m, 3H), 7.16 – 7.06 (m, 3H), 7.00 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.89 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.53 (d, *J* = 15.0 Hz, 1H), 5.19 (d, *J* = 15.0 Hz, 1H), 2.57 (t, 2H), 2.29 (s, 3H), 1.62 – 1.52 (m, 2H), 1.39-1.29 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.16, 142.44, 140.58, 135.05, 131.37, 131.27, 130.53, 128.53 (2C), 128.44 (2C), 128.41, 128.03 (3C), 126.26, 126.01 (2C), 125.31, 124.99, 52.46, 35.37, 33.39, 22.32, 15.16, 13.94. HRMS (ESI, m/z): cacld. for $C_{26}H_{28}N_3S^+$ $[M+H]^+$: 414.1998, found: 414.1999.



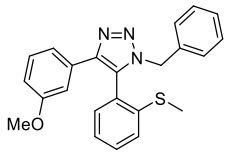
3c

1-benzyl-4-(4-fluorophenyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.49 (td, *J* = 7.8, 1.5 Hz, 1H), 7.33 - 7.28 (m, 1H), 7.26 - 7.17 (m, 3H), 7.15 - 7.10 (m, 1H), 7.05 - 6.98 (m, 2H), 6.98 - 6.86 (m, 3H), 5.51 (d, *J* = 14.9 Hz, 1H), 5.19 (d, *J* = 14.9 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.40 (d, *J* = 246.9 Hz), 144.33, 140.59, 134.86, 131.43, 131.25, 130.73, 128.48 (2C), 128.11, 128.06 (2C), 127.90 (d, *J* = 8.0 Hz), 127.28 (d, *J* = 3.2 Hz), 125.70, 125.22, 125.02, 115.42 (d, *J* = 21.5 Hz), 52.53, 15.05. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.06. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}N_3SF^+$ $[M+H]^+$: 376.1278, found: 376.1279.



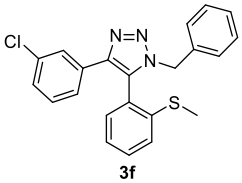
3d

4-([1,1'-biphenyl]-4-yl)-1-benzyl-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.62 (m, 2H), 7.57 - 7.45 (m, 5H), 7.42 - 7.36 (m, 2H), 7.34 - 7.28 (m, 2H), 7.23 - 7.15 (m, 3H), 7.15 - 7.11 (m, 1H), 7.01 - 6.88 (m, 3H), 5.53 (d, *J* = 15.0 Hz, 1H), 5.19 (d, *J* = 15.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.69, 140.61, 140.31, 134.94, 131.36, 130.62, 130.03, 128.71 (2C), 128.47 (2C), 128.07 (2C), 127.28, 127.24, 127.17, 127.14 (2C), 126.90 (2C), 126.44 (2C), 126.11, 125.30, 125.08, 125.03, 52.53, 15.16. HRMS (ESI, m/z): cacld. for $C_{28}H_{24}N_3S^+$ $[M+H]^+$: 434.1685, found: 434.1690.



3e

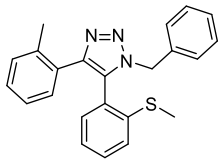
1-benzyl-4-(3-methoxyphenyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.45 (m, 1H), 7.32 (d, *J* = 8.1, 1.4 Hz, 1H), 7.27 - 7.18 (m, 4H), 7.16 - 7.10 (m, 3H), 7.02 - 6.99 (m, 2H), 6.90 (dt, *J* = 7.6, 1.5 Hz, 1H), 6.81 - 6.77 (m, 1H), 5.53 (d, *J* = 14.9 Hz, 1H), 5.19 (d, *J* = 14.9 Hz, 1H), 3.68 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.62, 144.92, 140.59, 134.93, 132.28, 131.77, 131.34, 130.60, 129.46, 128.46 (2C), 128.07, 128.05 (2C), 126.15, 125.35, 125.02, 118.50, 114.32, 110.84, 55.04, 52.49, 15.18. HRMS (ESI, m/z): cacld. for $C_{23}H_{22}N_3OS^+$ $[M+H]^+$: 388.1478, found: 388.1477.



3f

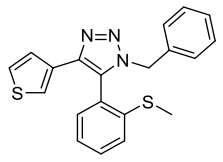
1-benzyl-4-(3-chlorophenyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.68 (t, *J* = 1.8 Hz, 1H), 7.50 (td, *J* = 7.8, 1.5 Hz, 1H), 7.38-7.31 (m, 2H), 7.25-7.13 (m, 6H), 7.01 (dd, *J* = 7.6, 2.0 Hz, 2H), 6.89 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.47 (d, *J* = 15.0 Hz, 1H), 5.20 (d, *J* = 15.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 143.78, 140.51, 134.76, 134.43, 132.87, 132.13, 131.17, 130.85, 129.69, 128.51 (2C), 128.15, 128.05 (2C), 127.71, 126.28, 125.50, 125.38, 125.09, 124.07, 52.55, 15.13. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}N_3ClS^+$ $[M+H]^+$: 392.0983, found: 392.0985.



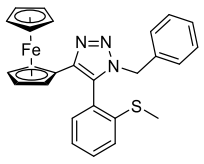
3g

1-benzyl-5-(2-(methylthio)phenyl)-4-(o-tolyl)-1H-1,2,3-triazole, ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 1H), 7.23-7.10 (m, 7H), 7.05-6.95 (m, 4H), 6.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.56 (d, *J* = 14.9 Hz, 1H), 5.26 (d, *J* = 14.9 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.56, 140.26, 137.64, 135.10, 133.16, 131.46, 130.37, 130.26, 130.19, 128.49 (3C), 128.09, 128.03 (3C), 125.78, 125.34, 125.27, 124.69, 52.71, 20.65, 15.36. HRMS (ESI, m/z): cacld. for $C_{23}H_{22}N_3S^+$ $[M+H]^+$: 372.1529, found: 372.1532.



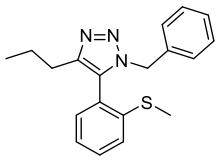
3h

1-benzyl-5-(2-(methylthio)phenyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole, ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (td, *J* = 7.7, 1.5 Hz, 2H), 7.35-7.19 (m, 7H), 7.16-7.12 (m, 1H), 7.03-6.99 (m, 2H), 6.91 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.54 (d, *J* = 15.0 Hz, 1H), 5.19 (d, *J* = 15.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.11, 140.66, 134.93, 131.97, 131.38, 131.09, 130.69, 128.46 (2C), 128.07 (2C), 128.02, 125.92, 125.87, 125.48, 125.44, 125.04, 121.12, 52.52, 15.21. HRMS (ESI, m/z): cacld. for $C_{20}H_{18}N_3S_2^+$ $[M+H]^+$: 364.0937, found: 364.0937.



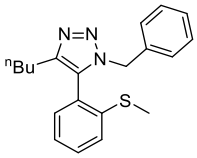
3i

1-benzyl-4-(ferrocenyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.7, 1.5 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.22– 7.10 (m, 4H), 6.93 (dd, *J* = 7.6, 2.0 Hz, 2H), 6.82 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.51 (d, *J* = 15.0 Hz, 1H), 5.10 (d, *J* = 15.0 Hz, 1H), 4.58 (s, 1H), 4.41 (s, 1H), 4.22 (d, *J* = 10.5 Hz, 2H), 4.11 (s, 5H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.83, 140.50, 135.15, 131.55, 130.53, 130.17, 128.42 (2C), 127.98, 127.88 (2C), 125.91, 124.83, 124.68, 69.96 (2C), 68.81, 68.78, 66.81, 66.59, 52.44, 15.05. HRMS (ESI, m/z): cacld. for $C_{26}H_{24}FeN_3S^+$ $[M+H]^+$: 466.1082, found:466.1078.



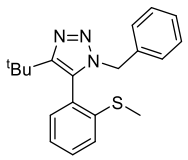
3j

1-benzyl-5-(2-(methylthio)phenyl)-4-propyl-1H-1,2,3-triazole, ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.43-7.4 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25-7.15 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.0 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 5.45 (d, *J* = 15.0 Hz, 1H), 5.16 (d, *J* = 15.0 Hz, 1H), 2.58-2.53 (m, 1H), 2.49-2.44 (m, 1H), 2.32 (s, 3H), 1.64-1.58 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.76, 140.50, 135.04, 132.38, 131.29, 130.30, 128.41 (2C), 127.99 (2C), 127.97, 125.40, 124.73, 124.51, 52.60, 27.22, 22.43, 15.08, 13.94. HRMS (ESI, m/z): cacld. for $C_{19}H_{22}N_3S^+$ $[M+H]^+$: 324.1529, found: 324.1531.



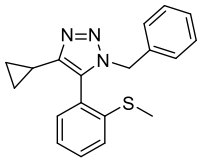
3k

1-benzyl-4-butyl-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 1H), 7.24-7.08 (m, 5H), 6.94-6.91 (m, 2H), 6.81 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.45 (d, *J* = 15.0 Hz, 1H), 5.16 (d, *J* = 15.0 Hz, 1H), 2.61- 2.44 (m, 2H), 2.32 (s, 3H), 1.61-1.53 (m, 2H), 1.27 (q, *J* = 7.4 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01, 140.49, 135.19, 132.20, 131.28, 130.20, 128.37 (2C), 127.95 (2C), 127.89, 125.70, 124.84, 124.51, 52.50, 31.20, 24.95, 22.36, 15.11, 13.73. HRMS (ESI, m/z): cacld. for $C_{20}H_{24}N_3S^+$ $[M+H]^+$: 338.1685, found: 338.1687.



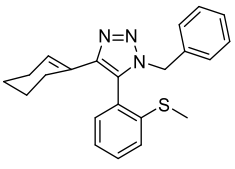
3l

1-benzyl-4-(tert-butyl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.7, 1.5 Hz, 1H), 7.21-7.16 (m, 4H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.92-6.90 (m, 2H), 6.75 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.40 (d, *J* = 14.9 Hz, 1H), 4.92 (d, *J* = 14.9 Hz, 1H), 2.35 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.85, 140.74, 135.22, 132.08, 130.42, 130.08, 128.30 (2C), 128.08 (2C), 127.84, 127.01, 123.95 (2C), 52.17, 31.95, 30.31 (3C), 14.75. HRMS (ESI, m/z): cacld. for $C_{20}H_{24}N_3S^+$ $[M+H]^+$: 338.1685, found: 338.1686.



3m

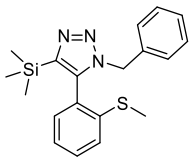
1-benzyl-4-cyclopropyl-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (td, *J* = 7.7, 1.5 Hz, 1H), 7.28(d, *J* = 8.0, 1.2 Hz, 1H), 7.20-7.07 (m, 4H), 6.92 (m, 3H), 5.44 (d, *J* = 14.9 Hz, 1H), 5.16 (d, *J* = 14.9 Hz, 1H), 2.32 (s, 3H), 1.66-1.61 (m, 1H), 0.98-0.92 (m, 2H), 0.82-0.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.88, 140.56, 135.15, 132.14, 131.45, 130.26, 128.37 (2C), 127.95 (2C), 127.90, 125.75, 125.19, 124.63, 52.44, 15.28, 7.14, 7.05, 6.42. HRMS (ESI, m/z): cacld. for $C_{19}H_{20}N_3S^+$ $[M+H]^+$: 322.1372, found: 322.1376.



3n

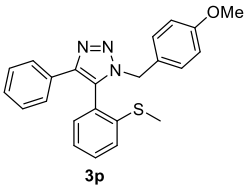
1-benzyl-4-(cyclohex-1-en-1-yl)-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 1H), 7.27 (t, *J* = 6.9 Hz, 1H), 7.22-7.15 (m, 3H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1H), 6.95-6.91 (m, 2H), 6.83 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.04-6.00 (m, 1H), 5.45 (d, *J* = 14.9 Hz, 1H), 5.10 (d, *J* = 14.9 Hz, 1H), 2.32 (s, 3H), 2.31-2.26 (m, 2H), 2.06-2.00 (m, 2H), 1.67-1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ147.04, 140.40, 135.14, 131.32, 130.16, 128.35, 128.25 (2C), 127.95 (2C), 127.90, 126.00, 125.00, 124.63, 52.26, 26.30, 25.46, 22.62, 22.00, 15.16. HRMS (ESI, m/z): cacld. for $C_{20}H_{24}N_3S^+$ $[M+H]^+$: 362.1685, found: 362.1691.



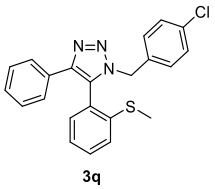
3o

1-benzyl-5-(2-(methylthio)phenyl)-4-(trimethylsilyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.28-7.16 (m, 4H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1H), 7.00-6.94 (m, 2H), 6.80 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.53 (d, *J* = 14.9 Hz, 1H), 5.11 (d, *J* = 14.9 Hz, 1H), 2.36 (s, 3H), 0.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.56, 141.04, 140.35, 135.22, 131.41, 130.22, 128.35 (2C), 128.10 (2C), 127.88, 126.70, 124.37, 124.12, 51.84, 14.97, -1.24 (3C). HRMS (ESI, m/z): cacld. for $C_{19}H_{24}N_3SiS^+$ $[M+H]^+$: 354.1455, found: 354.1458.



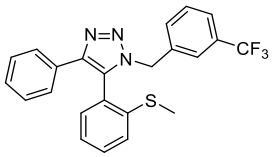
3p

1-(4-methoxybenzyl)-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.49 (td, *J* = 7.7, 1.5 Hz, 1H), 7.34-7.22 (m, 4H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1H), 6.95-6.91 (m, 3H), 6.75-6.72 (m, 2H), 5.46(d, *J* = 14.8 Hz, 1H), 5.13 (d, *J* = 14.8 Hz, 1H), 3.75 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.46, 145.03, 140.57, 131.48, 131.38, 131.10, 130.59, 129.57 (2C), 128.44 (2C), 127.66, 127.09, 126.20, 126.17 (2C), 125.33, 125.00, 113.84 (2C), 55.28, 52.03, 15.14. HRMS (ESI, m/z): cacld. for $C_{23}H_{22}N_3OS^+$ $[M+H]^+$: 388.1478, found: 388.1483.



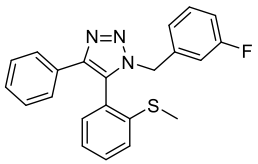
3q

1-(4-chlorobenzyl)-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.50 (td, *J* = 7.9, 1.4 Hz, 1H), 7.32-7.23 (m, 4H), 7.19-7.13 (m, 3H), 6.93-6.90 (m, 3H), 5.45 (d, *J* = 15.0 Hz, 1H), 5.19 (d, *J* = 15.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.23, 140.63, 134.11, 133.35, 131.54, 131.21, 130.86, 130.70, 129.52 (2C), 128.63 (2C), 128.47 (2C), 127.79, 126.15 (2C), 125.87, 125.26, 125.04, 51.78, 15.06. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}ClN_3S^+$ $[M+H]^+$: 392.0983, found: 392.0984.



3r

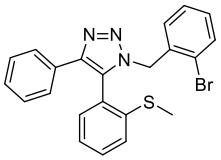
5-(2-(methylthio)phenyl)-4-phenyl-1-(3-(trifluoromethyl)benzyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.53-7.48 (m, 2H), 7.39-7.24 (m, 6H), 7.17-7.11 (m, 2H), 6.91 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.52 (d, *J* = 15.0 Hz, 1H), 5.32 (d, *J* = 15.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.32, 140.59, 135.68, 131.72, 131.57, 131.09, 130.95, 130.83, 130.78, 130.63, 129.12, 128.48 (2C), 127.85, 126.15 (2C), 125.63, 125.18, 125.15, 125.11, 125.03 (q, *J* = 3.4 Hz), 52.04, 14.89. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72. HRMS (ESI, m/z): cacld. for $C_{23}H_{19}F_3N_3S^+$ $[M+H]^+$: 426.1246, found: 426.1250.



3s

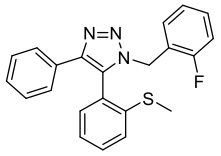
1-(3-fluorobenzyl)-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6-7.59 (m, 2H), 7.52-7.47 (m, 1H), 7.33-7.24 (m, 4H), 7.19 - 7.13(m,2H), 6.96-6.90 (m, 2H), 6.80 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.70 (dt, *J* = 9.4, 2.1 Hz, 1H), 5.49 (d, *J* = 15.1 Hz, 1H), 5.21 (d, *J* = 15.1 Hz, 1H), 2.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.65 (d, *J* = 246.7 Hz), 145.20, 140.57, 137.27 (d, *J* = 7.4 Hz), 131.69, 131.19, 130.91, 130.78, 130.08 (d, *J* = 8.2 Hz), 128.49 (2C), 127.81, 126.17 (2C), 125.77, 125.33, 125.07, 123.70 (d, *J* = 3.1 Hz), 115.19 (d, *J* = 2.5 Hz), 114.98 (d, *J* =

1.5 Hz), 51.86 (d, *J* = 2.0 Hz), 15.06. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.57. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}N_3SF^+$ $[M+H]^+$: 376.1278, found: 376.1278.



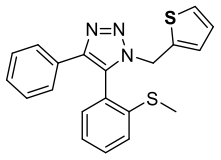
3t

1-(2-bromobenzyl)-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.48-7.32 (m, 2H), 7.33-7.19 m, 5H), 7.120 (t, *J* = 7.5 Hz, 2H), 7.01-6.98 (m, 1H), 6.91 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.63 (d, *J* = 15.8 Hz, 1H), 5.43 (d, *J* = 15.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.15, 140.54, 134.60, 132.55, 132.09, 131.03, 130.94, 130.66, 129.53, 129.43, 128.48 (2C), 127.78, 127.62, 126.18 (2C), 125.81, 125.63, 125.18, 122.81, 51.83, 15.28. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}BrN_3S^+$ $[M+H]^+$: 436.0478, found: 436.0481.



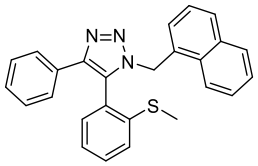
3u

1-(2-fluorobenzyl)-5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61– 7.59 (m, 2H), 7.48 (td, *J* = 7.8, 1.5 Hz, 1H), 7.33-7.20 (m, 5H), 7.15-7.00 (m, 3H), 6.95-6.89 (m, 2H), 5.50 (d, *J* = 15.3 Hz, 1H), 5.36 (d, *J* = 15.3 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.20 (d, *J* = 248.4 Hz), 145.05, 140.56, 131.85, 131.05, 130.98, 130.64, 130.18 (d, *J* = 3.3 Hz), 129.97 (d, *J* = 8.1 Hz), 128.46 (2C), 127.74, 126.19 (2C), 125.82, 125.39, 125.09, 124.24 (d, *J* = 3.9 Hz), 122.23 (d, *J* = 14.3 Hz), 115.20 (d, *J* = 21.4 Hz), 45.57 (d, *J* = 4.8 Hz), 15.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.26. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}N_3SF^+$ $[M+H]^+$: 376.1278, found: 376.1278.



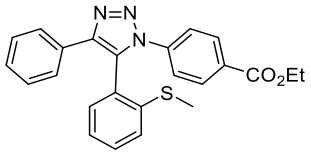
3v

5-(2-(methylthio)phenyl)-4-phenyl-1-(thiophen-2-ylmethyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.50 (m, 3H), 7.36 (d, *J* = 8.0, 1.2 Hz, 1H), 7.29-7.18 (m, 5H), 7.03 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.86-6.84 (m, 1H), 6.70 (dd, *J* = 3.5, 1.1 Hz, 1H), 5.68(d, *J* = 15.4 Hz, 1H), 5.38 (d, *J* = 15.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.02, 140.57, 136.79, 131.42, 131.34, 130.94, 130.72, 128.45 (2C), 127.74, 127.66, 126.75, 126.36, 126.23 (2C), 125.90, 125.37, 125.15, 46.87, 15.16. HRMS (ESI, m/z): cacld. for $C_{20}H_{18}N_3S_2^+$ $[M+H]^+$: 364.0937, found: 364.0941.



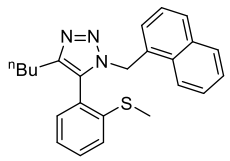
3w

5-(2-(methylthio)phenyl)-1-(naphthalen-1-ylmethyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (m, 1H), 7.84-7.80 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.59-7.56 (m, 2H), 7.51-7.40 (m, 3H), 7.29-7.17 (m, 5H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.81-6.76 (m, 2H), 6.06 (d, *J* = 15.2 Hz, 1H), 5.75 (d, *J* = 15.2 Hz, 1H), 2.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.11, 140.51, 133.59, 132.02, 131.22, 131.10, 131.02, 130.47, 130.20, 128.98, 128.57, 128.42 (2C), 127.67, 127.35, 126.71, 126.26, 126.17 (2C), 125.87, 125.26, 124.98, 124.91, 123.25, 50.91, 15.06. HRMS (ESI, m/z): cacld. for $C_{26}H_{22}N_3S^+$ $[M+H]^+$: 408.1529, found: 408.1528.



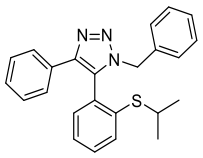
3x

Ethyl 4-(5-(2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazol-1-yl)benzoate, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.02 (m, 2H), 7.64-7.61 (m, 2H), 7.51-7.46 (m, 3H), 7.33-7.28 (m, 4H), 7.22-7.19 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.56, 145.64, 140.65, 140.14, 131.69, 131.27, 130.79, 130.62, 130.55, 130.42 (2C), 128.53 (2C), 128.05, 126.54 (2C), 126.34, 125.92, 125.42, 123.89 (2C), 61.33, 15.32, 14.27. HRMS (ESI, m/z): cacld. for $C_{24}H_{22}O_2N_3S^+$ $[M+H]^+$: 416.1427, found: 416.1430.



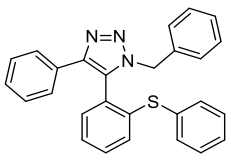
3y

4-butyl-5-(2-(methylthio)phenyl)-1-(naphthalen-1-ylmethyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, *J* = 7.2, 3.5 Hz, 1H), 7.83–7.78 (m, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.48-7.43 (m, *J* = 6.4, 3.5 Hz, 2H), 7.36 (td, *J* = 7.7, 1.5 Hz, 1H), 7.20-7.14 (m, 2H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 6.76-6.68 (m, 2H), 6.00 (d, *J* = 15.2 Hz, 1H), 5.73 (d, *J* = 15.2 Hz, 1H), 2.60-2.44 (m, 2H), 2.28 (s, 3H), 1.64-1.53 (m, 2H), 1.33-1.24 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.12, 140.44, 133.53, 131.17, 130.99, 130.45, 130.08, 128.78, 128.49, 127.13, 126.59, 125.79, 124.87, 124.71, 124.45, 123.22, 50.86, 31.19, 24.86, 22.34, 15.01, 13.73. HRMS (ESI, m/z): cacld. for $C_{24}H_{26}N_3S^+$ $[M+H]^+$: 388.1842, found: 388.1842.



3z

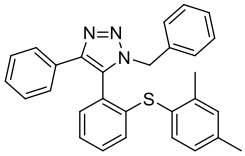
1-benzyl-5-(2-(isopropylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.52-7.43 (m, 2H), 7.28-7.18 (m, 6H), 7.12 (td, *J* = 7.4, 1.4 Hz, 1H), 7.02-7.00 (m, 2H), 6.87 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.62 (d, *J* = 15.0 Hz, 1H), 5.14 (d, *J* = 15.0 Hz, 1H), 3.36 (p, *J* = 6.7 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 138.44, 135.09, 132.26, 131.89, 131.17, 130.36, 129.44, 128.51 (2C), 128.39 (2C), 128.24, 128.07, 127.97 (2C), 127.60, 126.27 (2C), 125.98, 52.49, 36.54, 22.97, 22.60. HRMS (ESI, m/z): cacld. for $C_{24}H_{24}N_3S^+$ $[M+H]^+$: 386.1685, found: 386.1688.



3aa

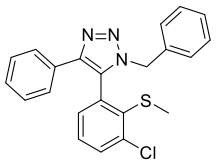
1-benzyl-4-phenyl-5-(2-(phenylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.38-7.15 (m, 14H), 7.06-7.02 (m, 2H), 6.94 (dd, *J* = 7.6,

1.1 Hz, 2H), 5.54 (d, *J* = 15.0 Hz, 1H), 5.18 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 139.67, 135.05, 133.65 (2C), 132.41, 131.81, 131.79, 131.06, 130.54, 129.95, 129.43 (2C), 128.59 (2C), 128.49, 128.38 (2C), 128.13, 127.93 (2C), 127.68, 126.57, 126.26 (2C), 52.41. HRMS (ESI, m/z): cacld. for $C_{27}H_{22}N_3S^+$ $[M+H]^+$: 420.1529, found: 420.1531.



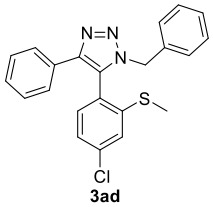
3ab

1-benzyl-5-(2-((2,4-dimethylphenyl)thio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.31-7.24 (m, 7H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.12-7.06 (m, 4H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.60 (d, *J* = 14.9 Hz, 1H), 5.25 (d, *J* = 14.9 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.96, 142.25, 140.43, 139.87, 136.17, 135.11, 131.83, 131.74, 131.68, 131.16, 130.47, 128.58 (2C), 128.34 (2C), 128.14, 128.03 (2C), 127.92, 127.66, 126.90, 126.44, 126.29 (2C), 125.72, 125.40, 52.43, 21.15, 20.43. HRMS (ESI, m/z): cacld. for $C_{29}H_{26}N_3S^+$ $[M+H]^+$: 448.1842, found: 448.1846.



3ac

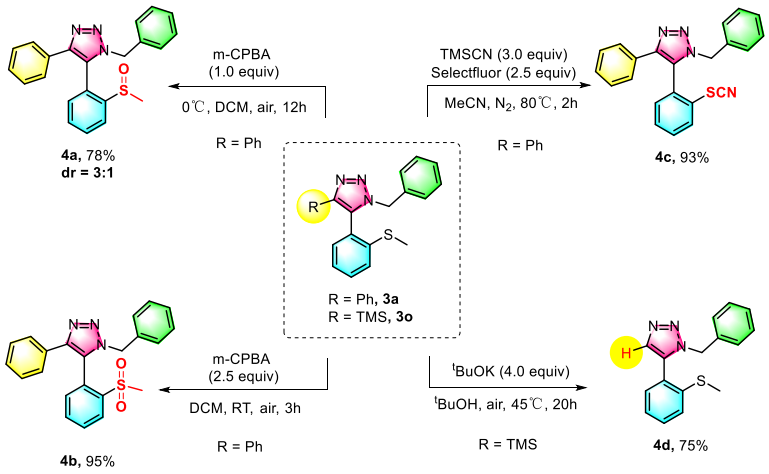
1-benzyl-5-(3-chloro-2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.30 – 7.19 (m, 7H), 6.98 – 6.95 (m, 3H), 5.52 (d, *J* = 15.0 Hz, 1H), 5.25 (d, *J* = 15.0 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.72, 140.88, 136.50, 134.75, 134.54, 132.76, 131.90, 130.91, 130.13, 129.62, 128.67 (2C), 128.58 (2C), 128.28, 127.92 (2C), 127.87, 126.33 (2C), 52.70, 17.89. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}ClN_3S^+$ $[M+H]^+$: 392.0983, found: 392.0988.



3ad

1-benzyl-5-(4-chloro-2-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazole ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.31-7.20 (m, 7H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.54 (d, *J* = 15.0 Hz, 1H), 5.18 (d, *J* = 15.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.40, 142.97, 136.93, 134.79, 132.35, 130.75, 130.39, 128.58 (3C), 128.23, 127.97 (2C), 127.94 (2C), 126.14 (2C), 125.00, 124.59, 124.03, 52.60, 15.01. HRMS (ESI, m/z): cacld. for $C_{22}H_{19}ClN_3S^+$ $[M+H]^+$: 392.0983, found: 392.0986.

V. Synthetic transformations



Scheme S1. Synthetic transformations of **3a** and **3o**

Procedure for preparation of ***4a-4d***

1) Synthesis of **4a**.

To an oven-dried 10 mL flask was added **3a** (0.4 mmol), m-CPBA (85% wt) (1.0 equiv), DCM (3.0 mL). The reaction was allowed to stir at 0 ℃ under air for 1h. Then the reaction was quenched by saturated $NaHCO_3$ solution (10 mL), extracted by DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated,

and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) to afford the product **4a**.

2) Synthesis of **4b**.

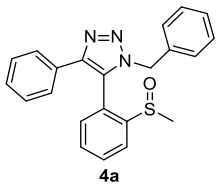
To an oven-dried 10 mL flask was added **3a** (0.4 mmol), m-CPBA (85% wt) (2.5 equiv), DCM (3.0 mL). The reaction was allowed to stir at RT under air for 2h. Then the reaction was quenched by saturated $NaHCO_3$ solution (20 mL), extracted by DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to afford the product **4b**.

3) Synthesis of **4c**.

To a reaction tube were sequentially added thioether **3a** (0.2 mmol), TMSCN (74.0 μL, 0.6 mmol, 3 equiv), Selectfluor reagent (177.0 mg, 0.5 mmol, 2.5 equiv). The tube was evacuated and backfilled with nitrogen for three times. Then, 1 mL of dry acetonitrile was added via a syringe, and the resulting solution was stirred in an 80 ℃ oil bath. When the reaction was completed (monitored by TLC), the solvent was removed by distillation under reduced pressure. The crude residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1) to afford the product **4c**.

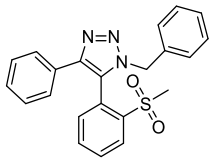
4) Synthesis of **4d**.

To a ^{t}BuOH (3.0 ml) solution of **3o** (0.5 mmol) was added ^{t}BuOK (4.0 equiv) and the mixture was stirred at 45 ℃ for 20 h, then the mixture was diluted water (10.0 ml) and extracted 3 times with ether. The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the product **4d**.



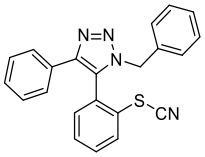
4a

1-benzyl-5-(2-(methylsulfinyl)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.78-7.73 (m, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.45-7.41 (m, 2H), 7.22-7.16 (m, 6H), 7.02 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.91 (m, 2H), 5.53 (d, *J* = 15.0 Hz, 1H), 5.17 (d, *J* = 15.0 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.59, 146.01, 134.15, 131.86, 131.79, 131.53, 130.24, 129.01, 128.86 (2C), 128.79 (2C), 128.50, 128.42, 127.84 (2C), 126.22 (2C), 124.96, 124.62, 52.94, 42.51. HRMS (ESI, m/z): cacld. for $C_{22}H_{20}N_3OS^+$ $[M+H]^+$: 374.1322, found: 374.1325.



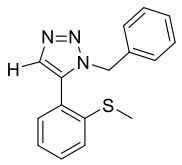
4b

1-benzyl-5-(2-(methylsulfonyl)phenyl)-4-phenyl-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.74 (td, *J* = 7.8, 1.3 Hz, 1H), 7.54 (td, *J* = 7.6, 1.4 Hz, 1H), 7.50-7.46 (m, 2H), 7.29– 7.18 (m, 6H), 6.99-6.93 (m, 3H), 5.78 (d, *J* = 15.3 Hz, 1H), 5.16 (d, *J* = 15.3 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52, 140.37, 134.91, 134.29, 133.70, 131.02, 130.53, 130.28, 129.61, 128.90 (2C), 128.64 (2C), 128.24, 128.22, 128.08 (2C), 127.54, 125.80 (2C), 53.35, 43.70. HRMS (ESI, m/z): cacld. for $C_{22}H_{20}N_3O_2S^+$ $[M+H]^+$: 390.1271, found: 390.1274.



4c

1-benzyl-4-phenyl-5-(2-thiocyanatophenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.64 (td, *J* = 7.8, 1.5 Hz, 1H), 7.53-7.46 (m, 3H), 7.33-7.22 (m, 7H), 6.97-6.95 (m, 2H), 5.45-5.36(m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.12, 134.05, 132.12, 131.95, 130.00 (2C), 129.83 (2C), 129.58, 129.23, 128.88, 128.82, 128.74, 128.47, 127.89 (3C), 127.70, 126.06 (2C), 108.98, 52.93. HRMS (ESI, m/z): cacld. for $C_{22}H_{17}N_4S^+$ $[M+H]^+$: 369.1168, found: 369.1178.



4d

1-benzyl-5-(2-(methylthio)phenyl)-1H-1,2,3-triazole, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 5.3 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 6.6 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 5.42 (s, 2H), 2.36 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.93, 135.48, 135.01, 134.43, 131.08, 130.44, 128.51 (2C), 128.08, 127.90 (2C), 125.30, 125.20, 124.63, 52.35, 15.38. HRMS (ESI, m/z): cacld. for $C_{16}H_{16}N_3S^+$ $[M+H]^+$: 282.1059, found: 282.1065.

VI. X-ray crystallographic data

Single crystal suitable for X-ray diffraction of compound **3y** was obtained from a solution of the compound **3y** in MeOH. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Center under reference number CCDC 2175071.

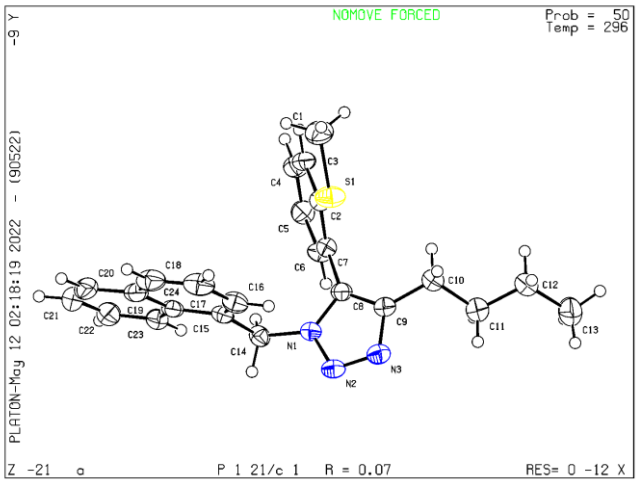


Figure S1. X-ray of **3y**

Table S2. Crystal data and structure refinement for **3y**.

Identification code	A
Empirical formula	$C_{24}H_{25}N_3S$
Formula weight	387.53

Temperature/K	296
Crystal system monoclinic	
Space group	P21/c
a/Å	10.5924(10)
b/Å	12.6329(11)
c/Å	15.3842(17)
α/°	90
β/°	92.600(4)
γ/°	90
Volume/Å3	2056.5(3)
Z	4
ρcalcg/cm3	1.252
μ/mm- 1	0.172
F(000)	824.0
Crystal size/mm3	0.12 × 0.11 × 0.1
Radiation MoKα (λ = 0.71073)	
2Θ range for data collection/°	4.174 to 61.798
Index ranges	$-13 \leq h \leq 15$, $-18 \leq k \leq 18$, $-22 \leq l \leq 18$
Reflections collected	23070
Independent reflections	6405 [Rint = 0.0729, Rsigma = 0.0684]
Data/restraints/parameters6405/0/255	
Goodness-of-fit on F2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0719, wR2 = 0.1808
Final R indexes [all data]	R1 = 0.1071, wR2 = 0.2034
Largest diff. peak/hole / e Å-3	0.46/-0.43

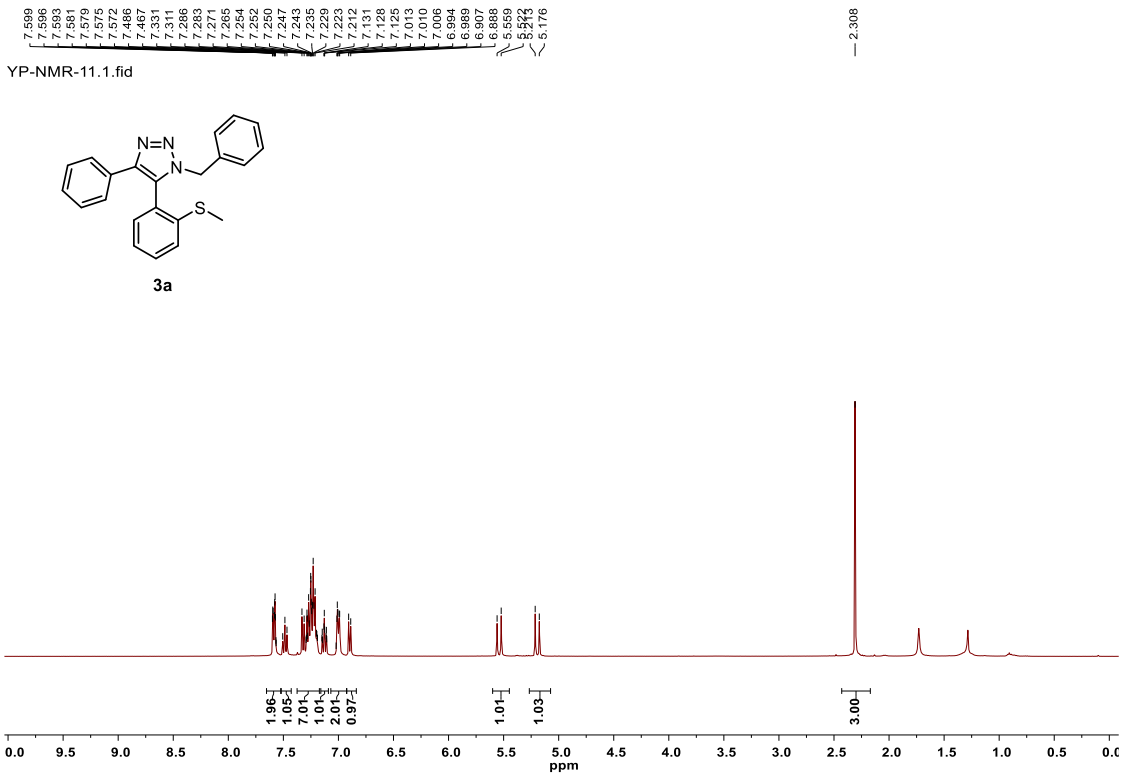
VII. References

[1] D. L. Reinhard, F. Heinen, J. Stoesser, E. Engelage and S. M. *Huber, Helv. Chim. Acta.*, 2021, **104**, e2000221.

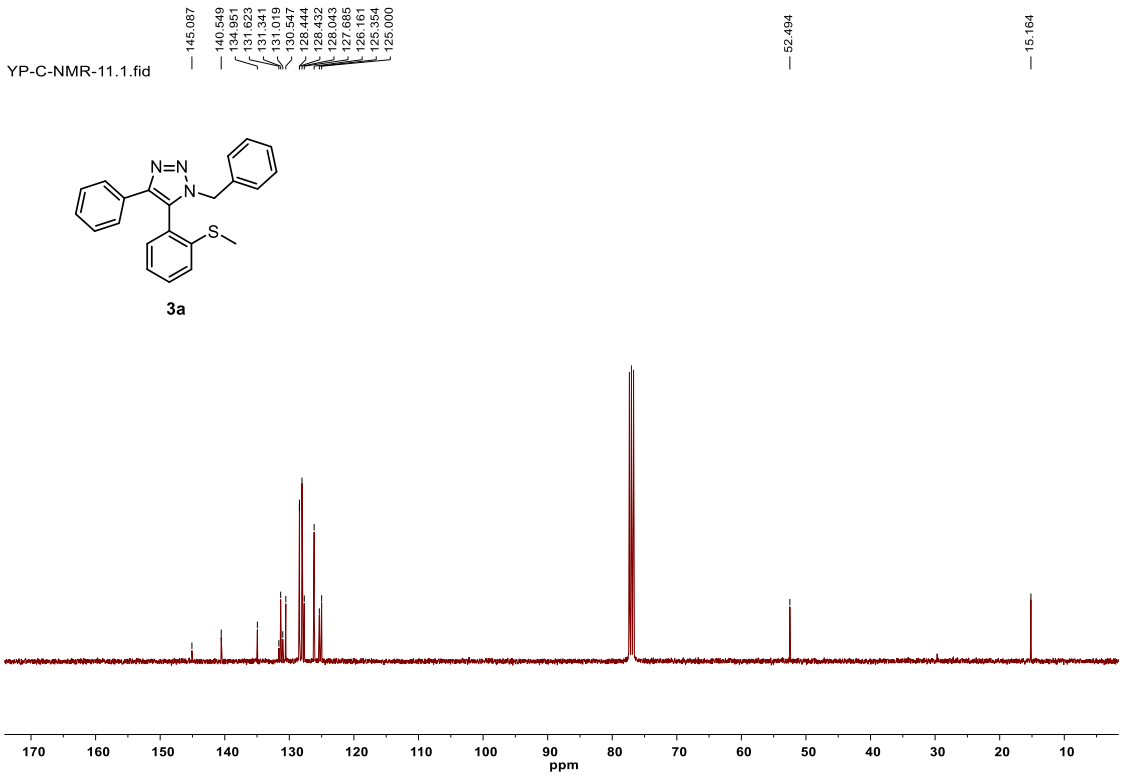
[2] T. Kesharwani, S. A. Worlikar and R. C. Larock, *J. Org. Chem.*, 2006, **71**, 2307.

[3] S. Pramanik and P. Ghorai. *Org. Lett.*, 2014, **16**, 2104.

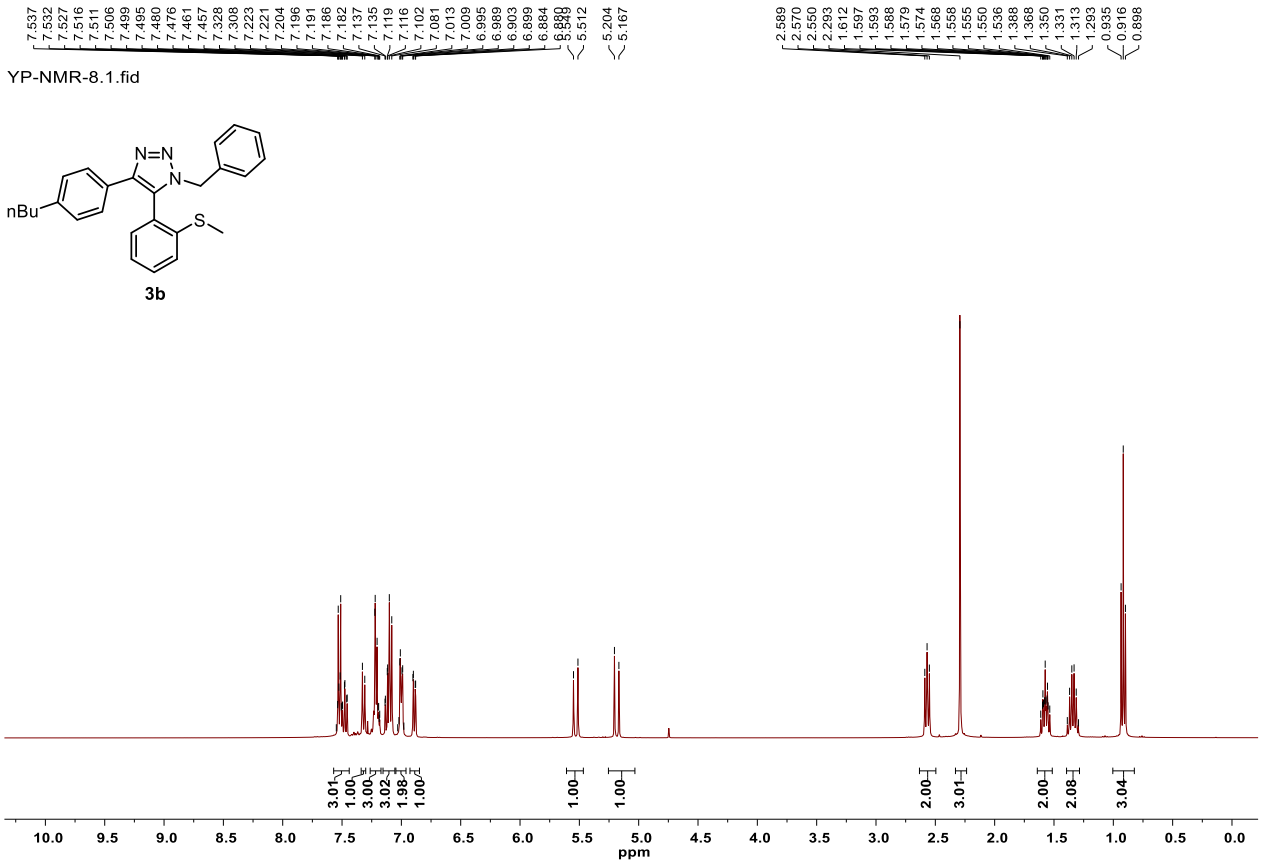
VIII. NMR spectra



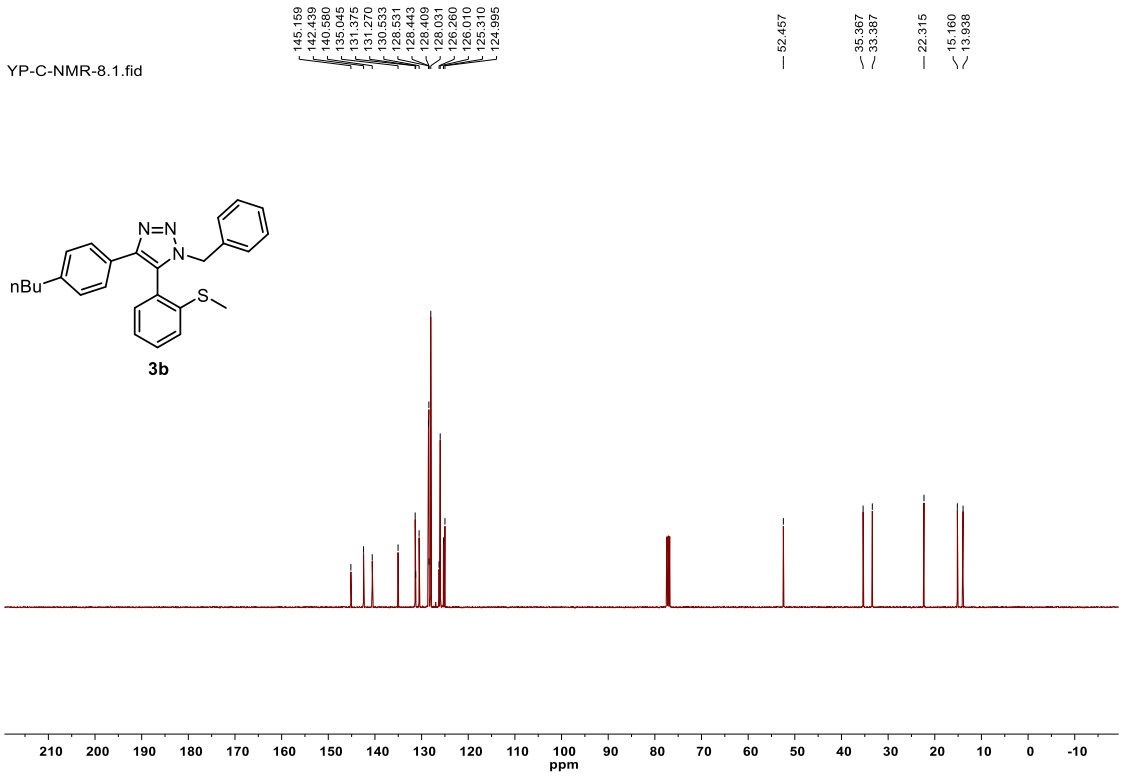
^{1}H NMR spectrum of 3a (400 MHz, $CDCl_3$)



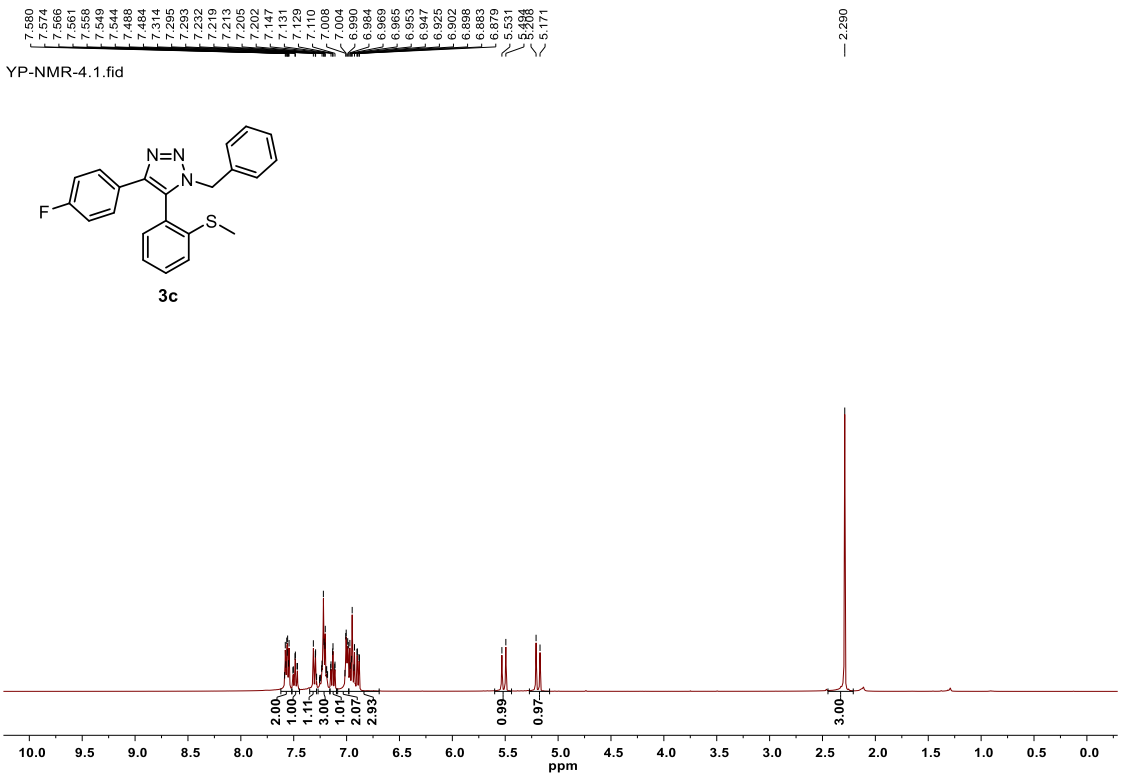
^{13}C NMR spectrum of 3a (101 MHz, $CDCl_3$)



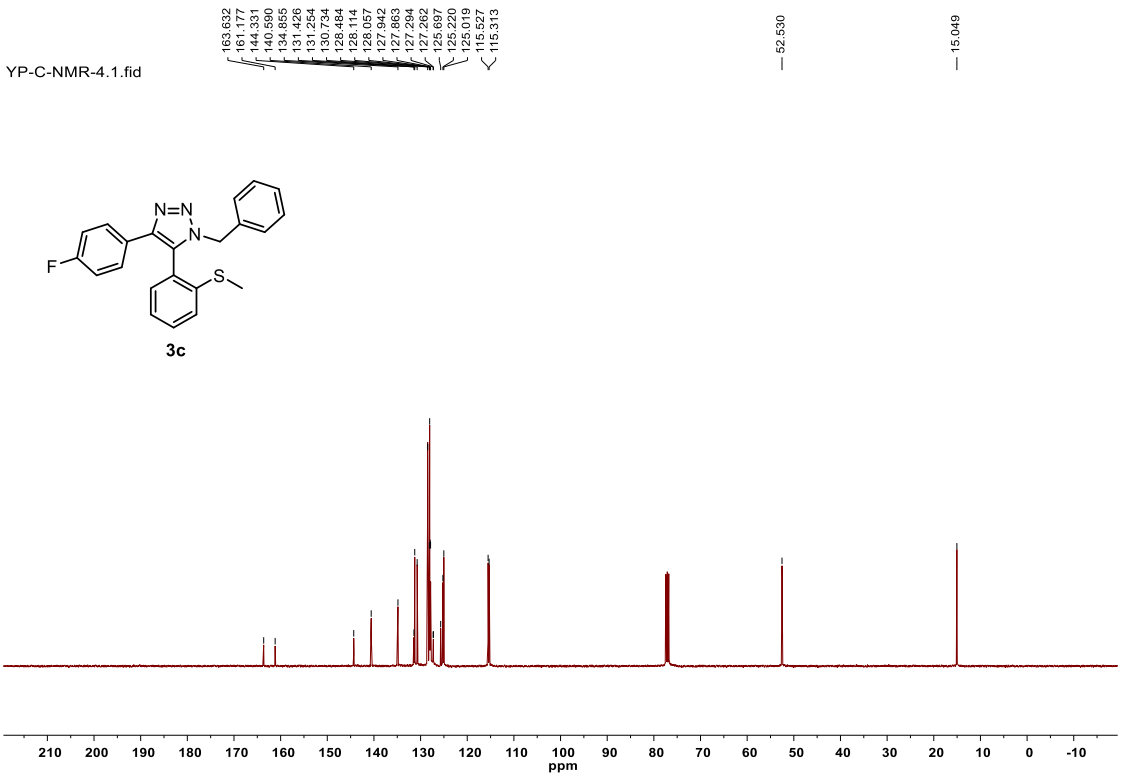
^{1}H NMR spectrum of 3b (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3b (101 MHz, $CDCl_3$)



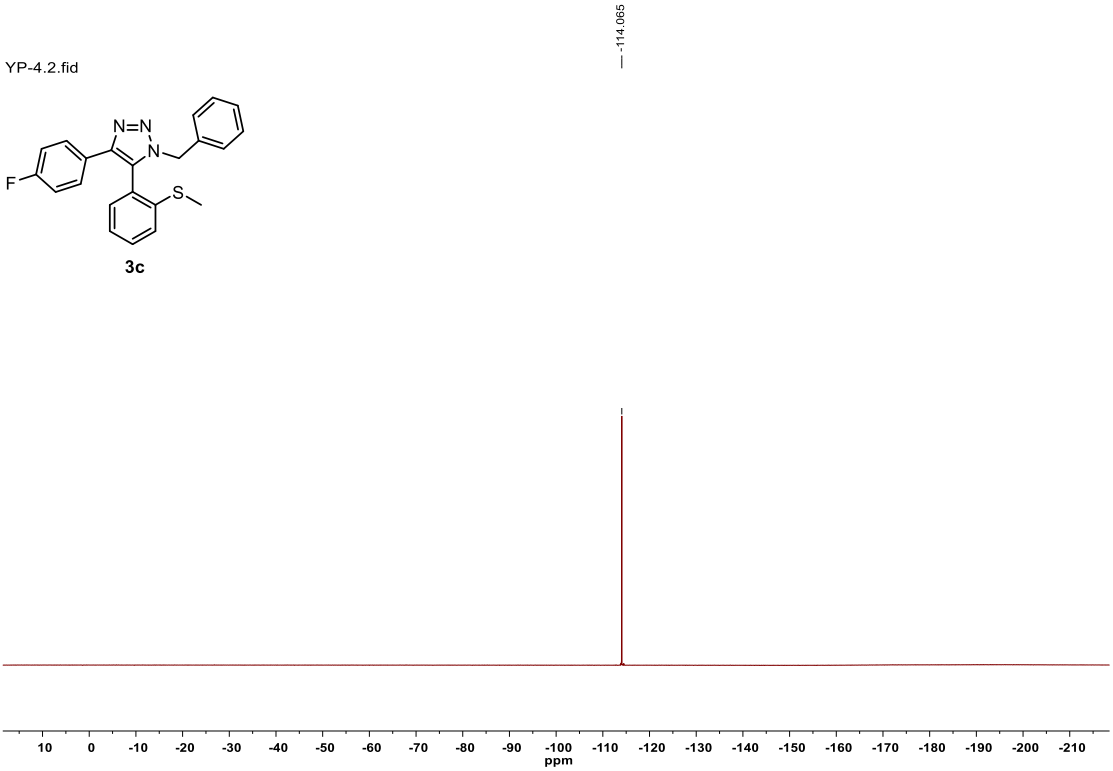
^{1}H NMR spectrum of 3c (400 MHz, $CDCl_3$)



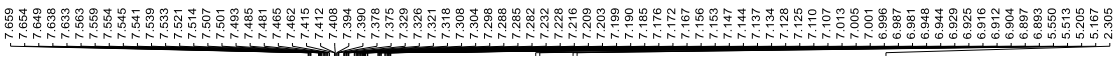
^{13}C NMR spectrum of 3c (101 MHz, $CDCl_3$)

YP-4.2.fid

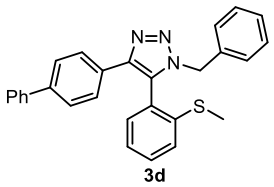
3c



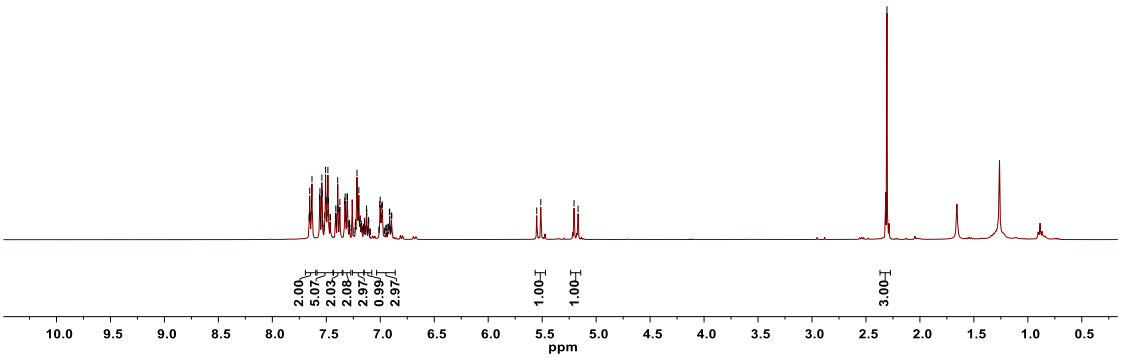
^{19}F NMR spectrum of 3c (376 MHz, $CDCl_3$)



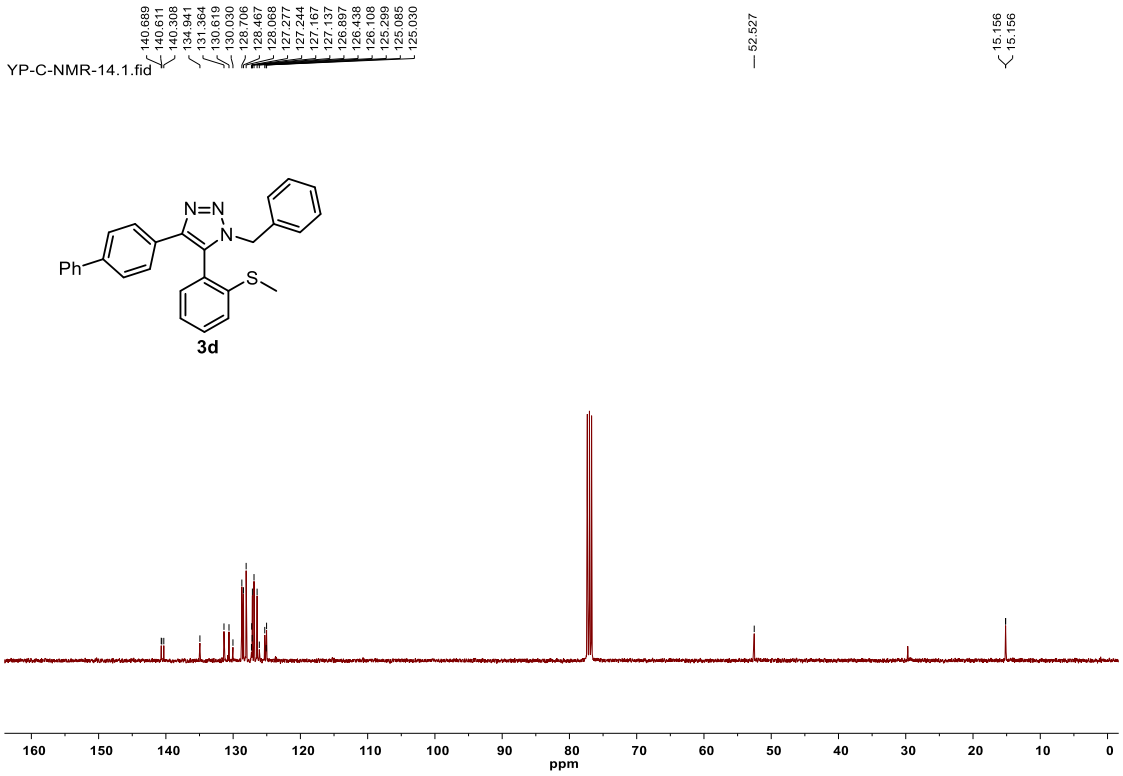
YP-NMR-14.1.fid



3d

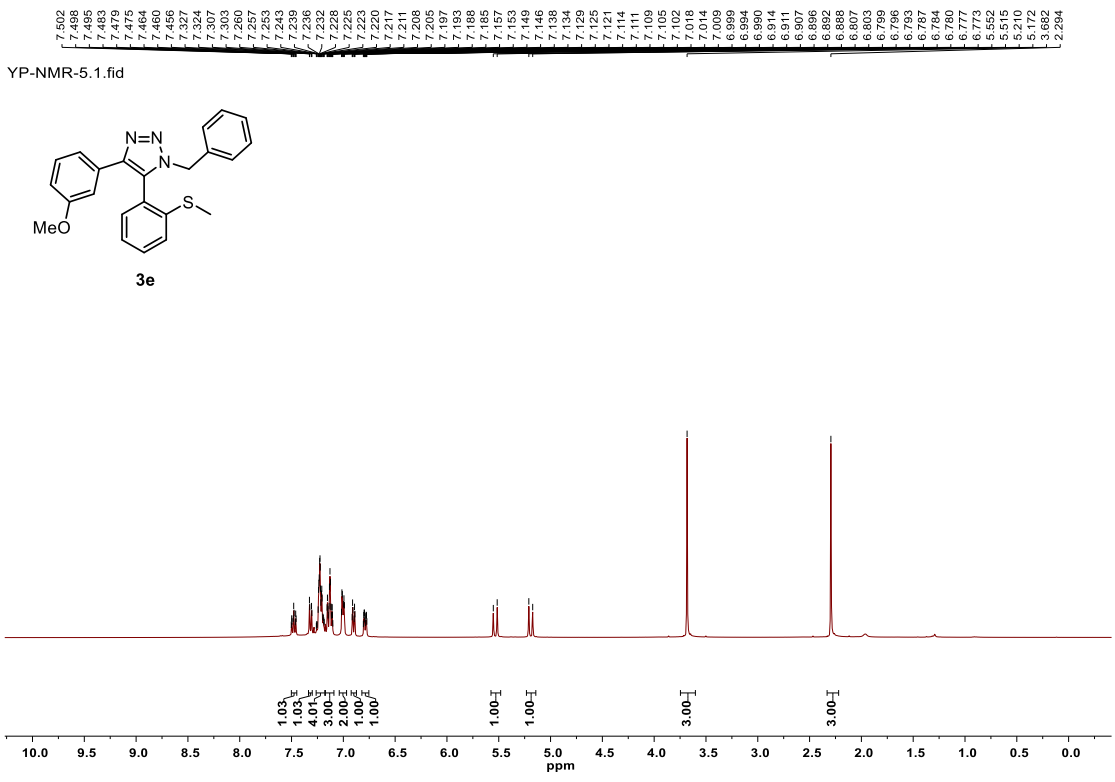


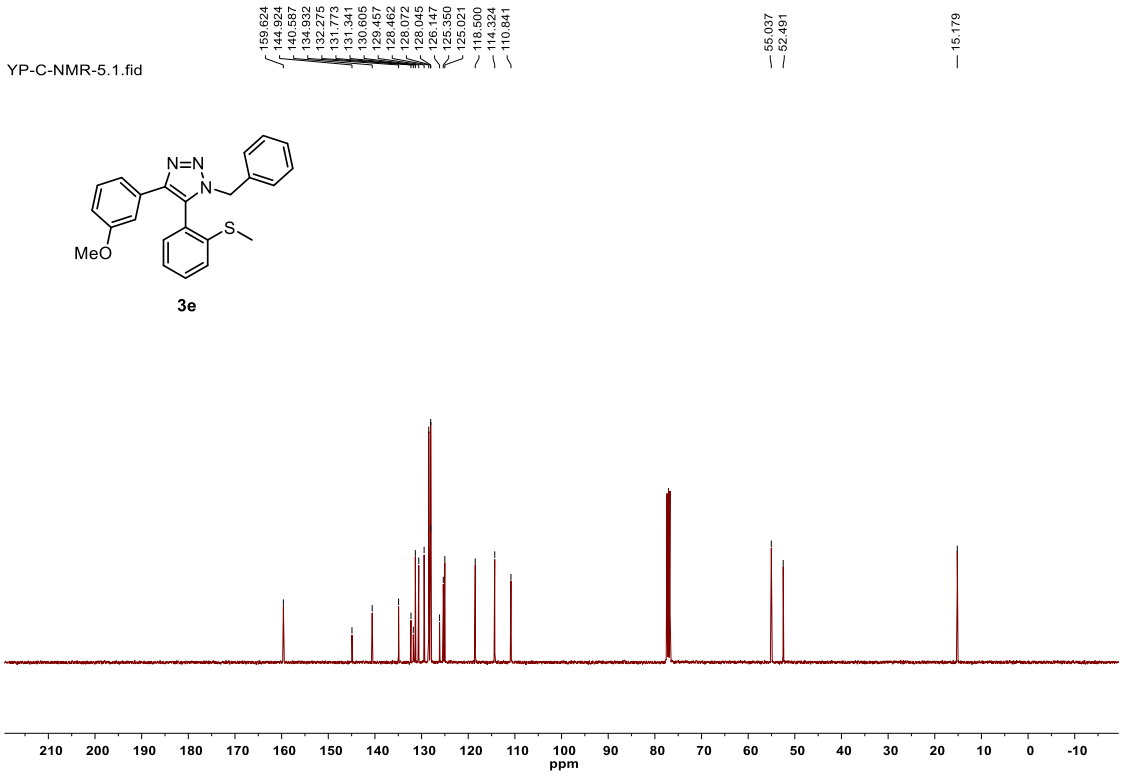
^{1}H NMR spectrum of 3d (400 MHz, $CDCl_3$)



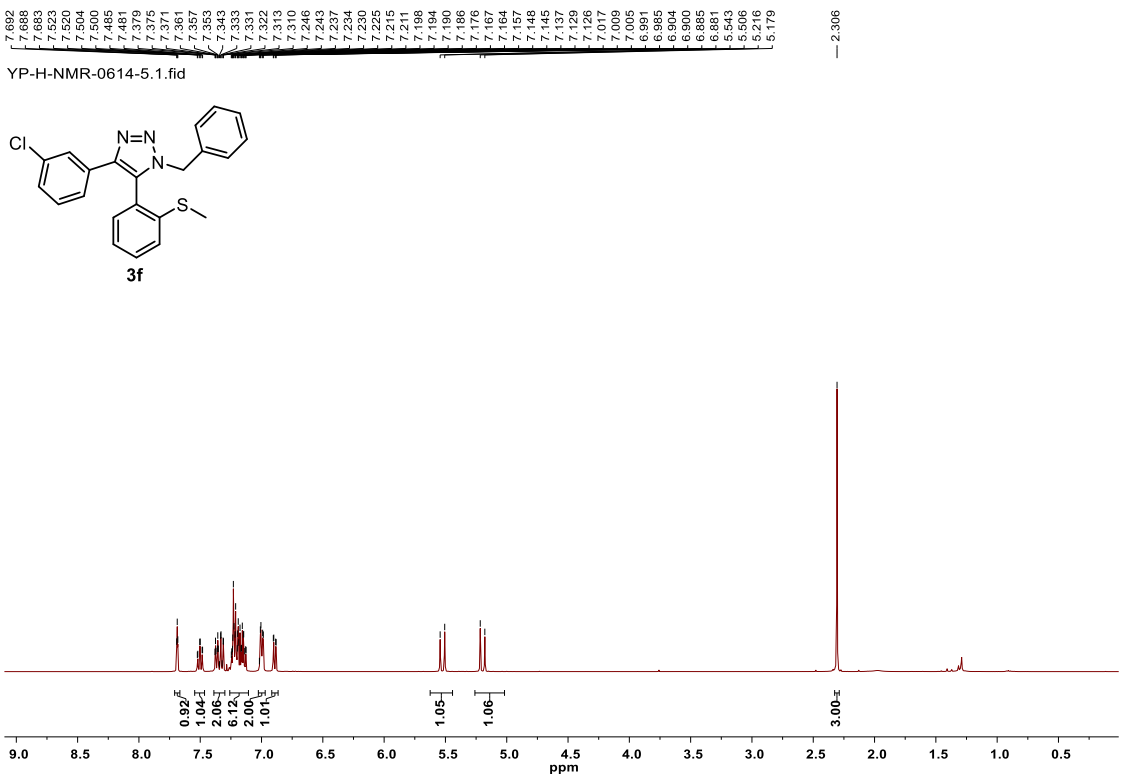
^{13}C NMR spectrum of 3d (101 MHz, $CDCl_3$)

^{1}H NMR spectrum of 3e (400 MHz, $CDCl_3$)

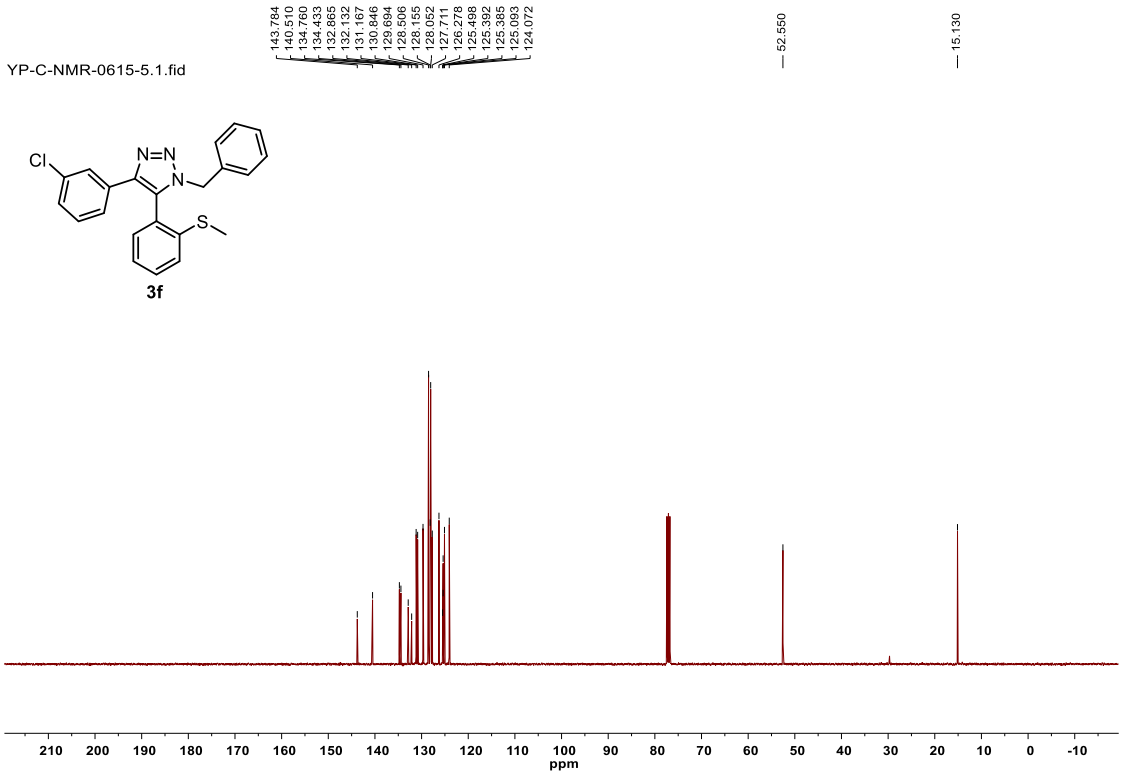




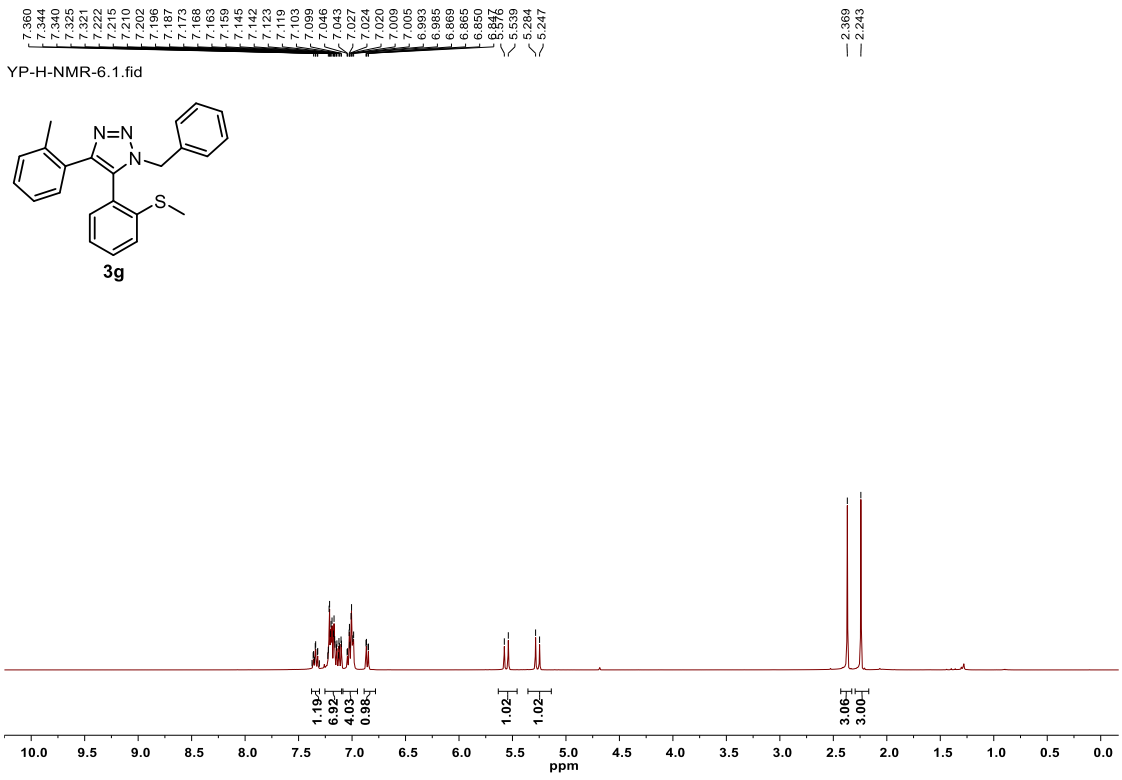
^{13}C NMR spectrum of 3e (101 MHz, $CDCl_3$)



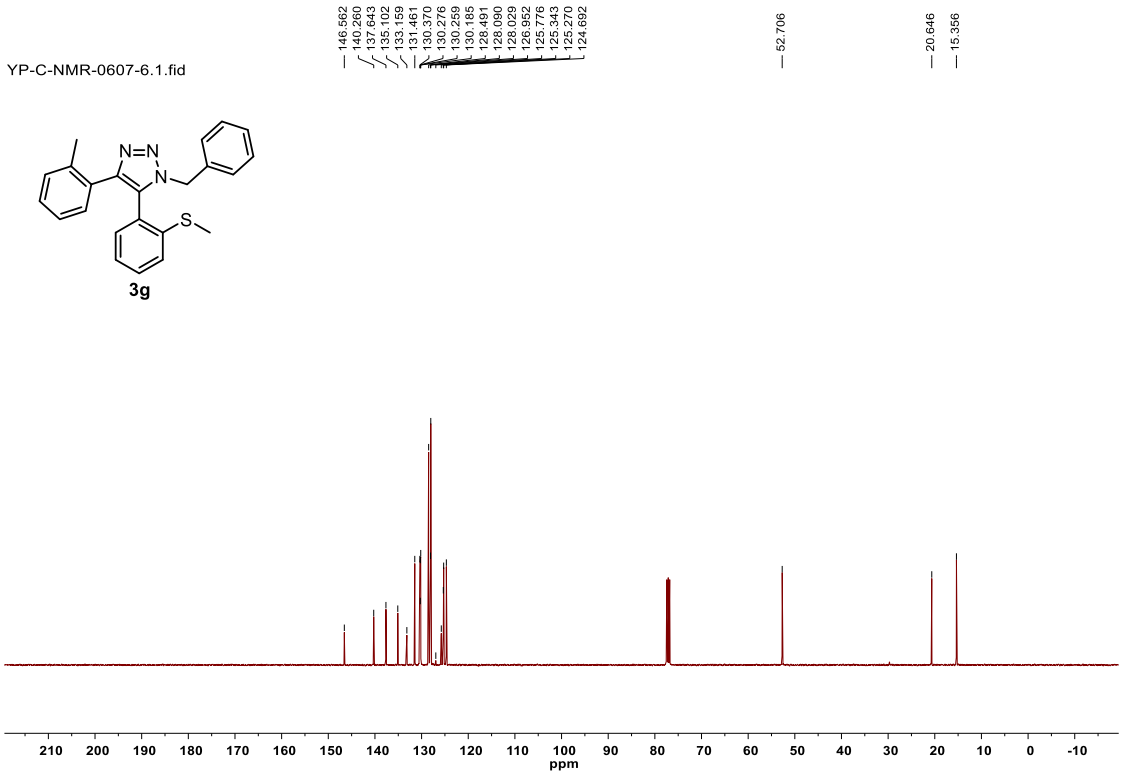
^{1}H NMR spectrum of 3f (400 MHz, $CDCl_3$)



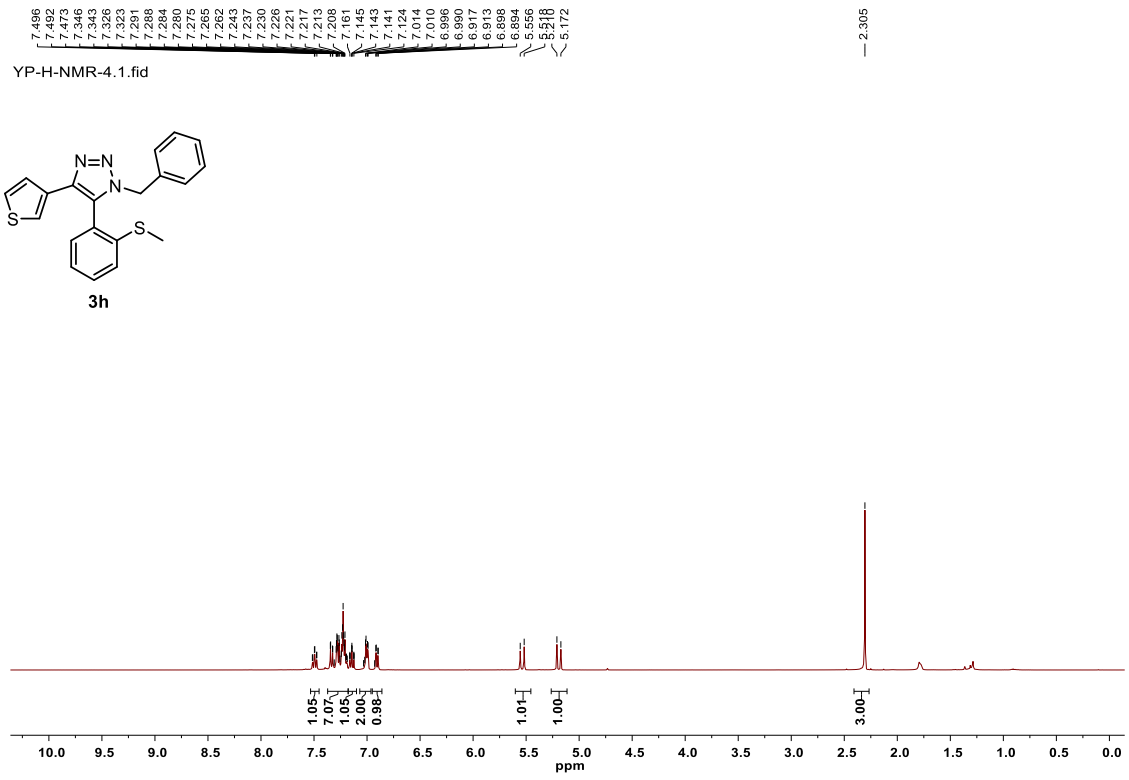
^{13}C NMR spectrum of 3f (101 MHz, $CDCl_3$)



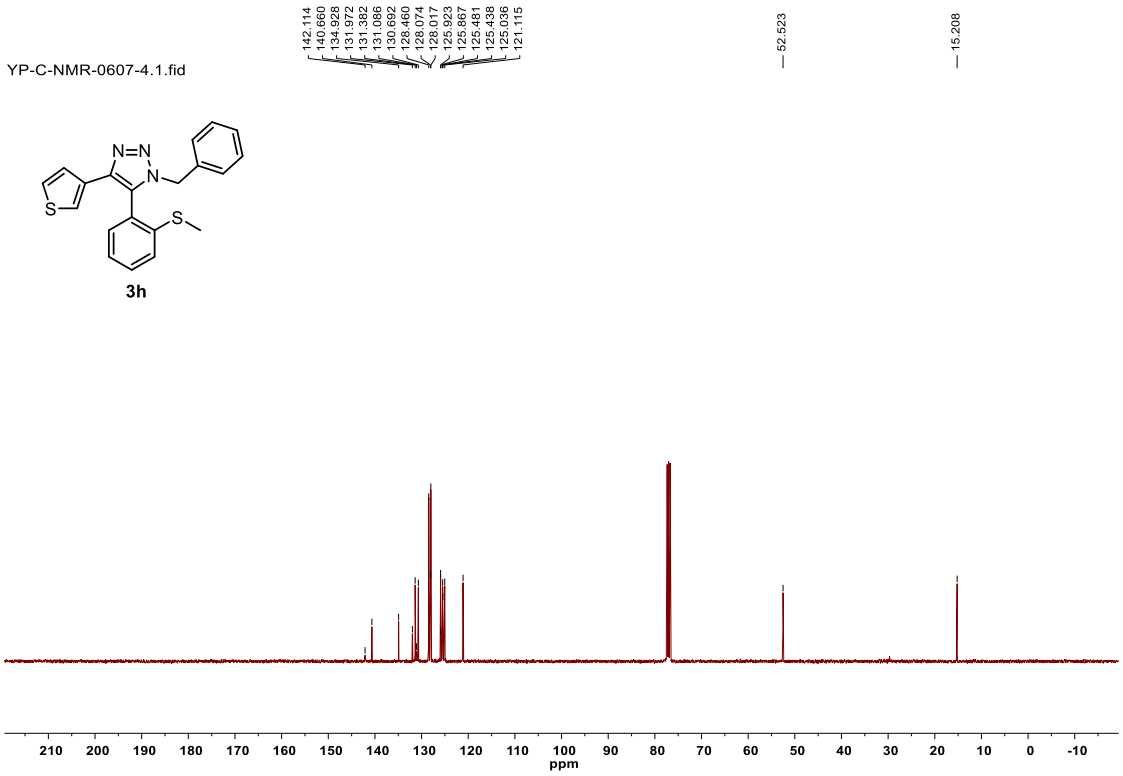
^{1}H NMR spectrum of 3g (400 MHz, $CDCl_3$)



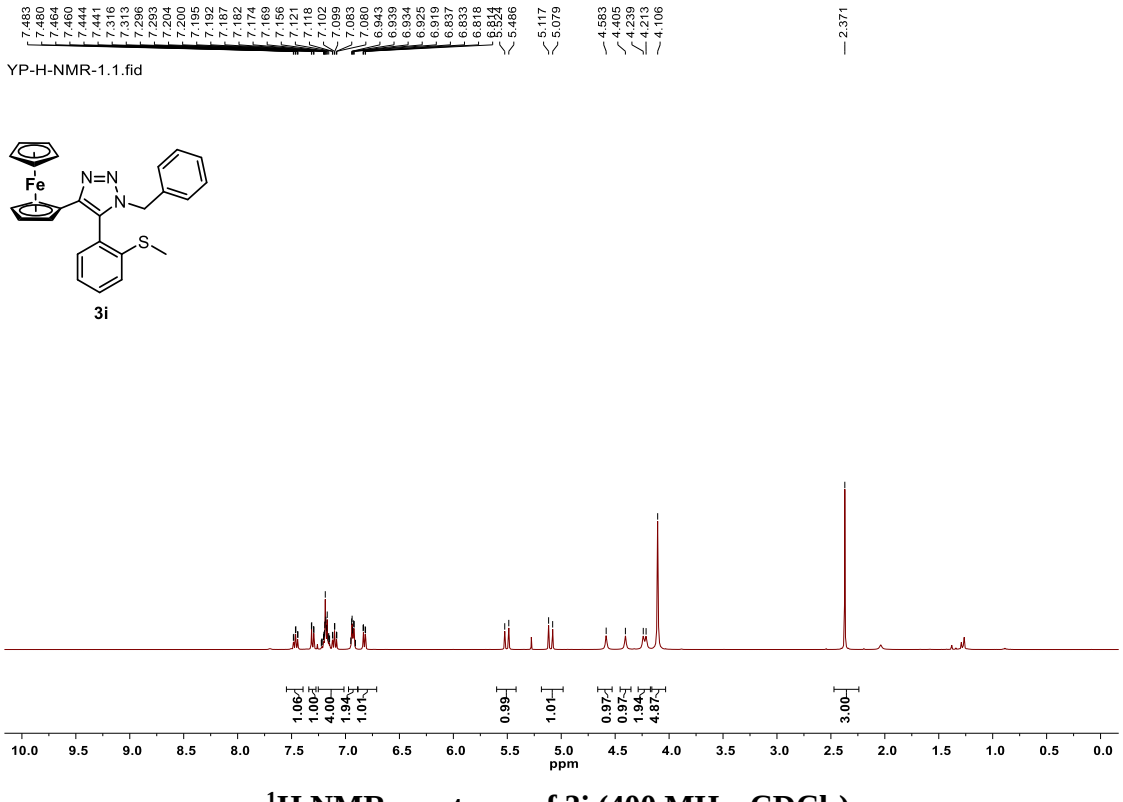
^{13}C NMR spectrum of 3g (101 MHz, $CDCl_3$)



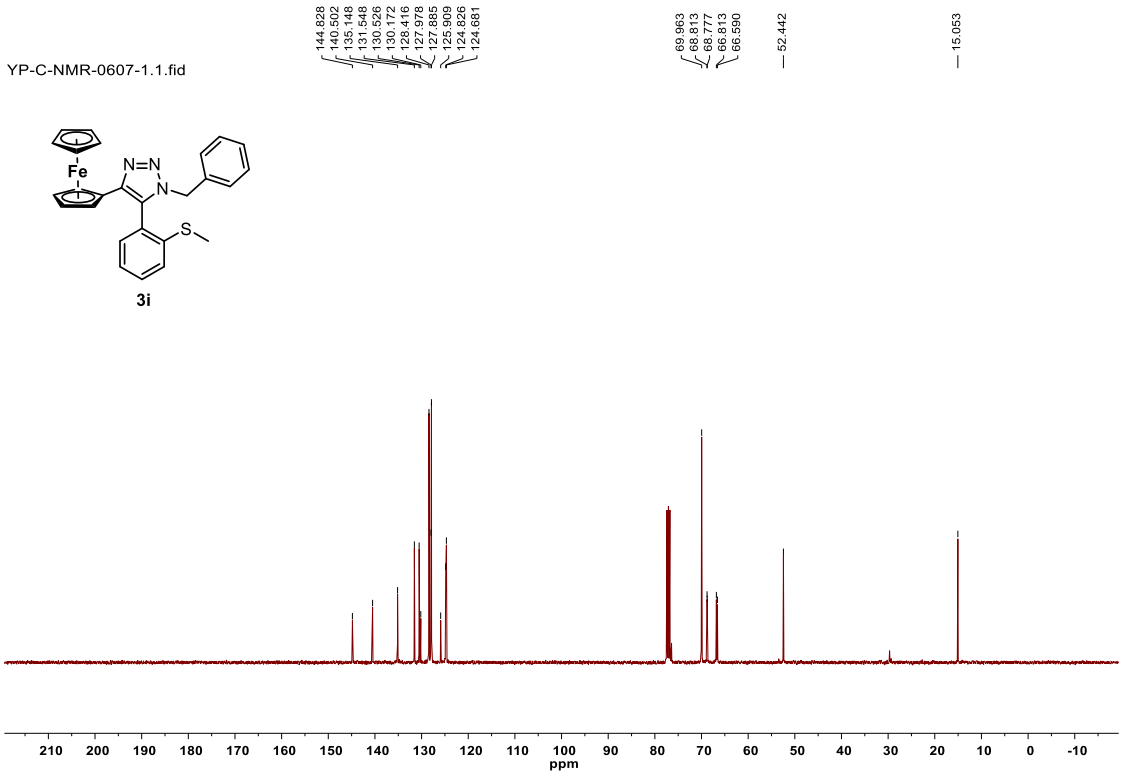
^{1}H NMR spectrum of 3h (400 MHz, $CDCl_3$)



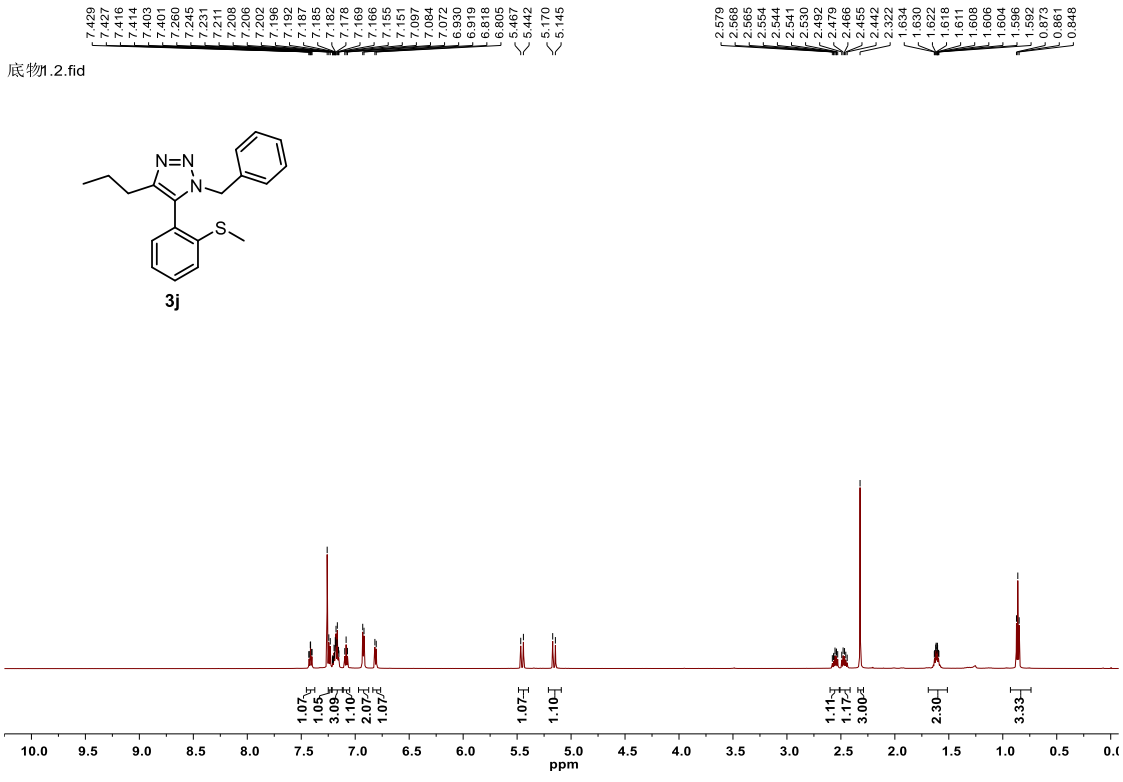
^{13}C NMR spectrum of 3h (101 MHz, $CDCl_3$)



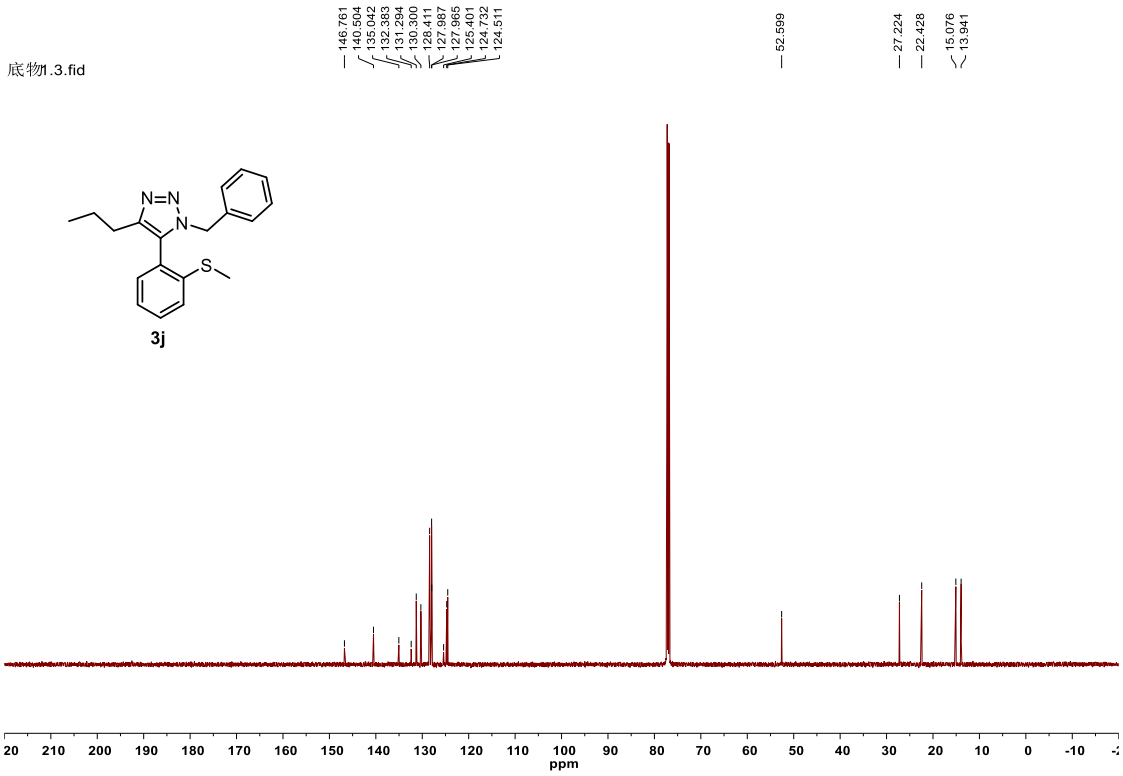
^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



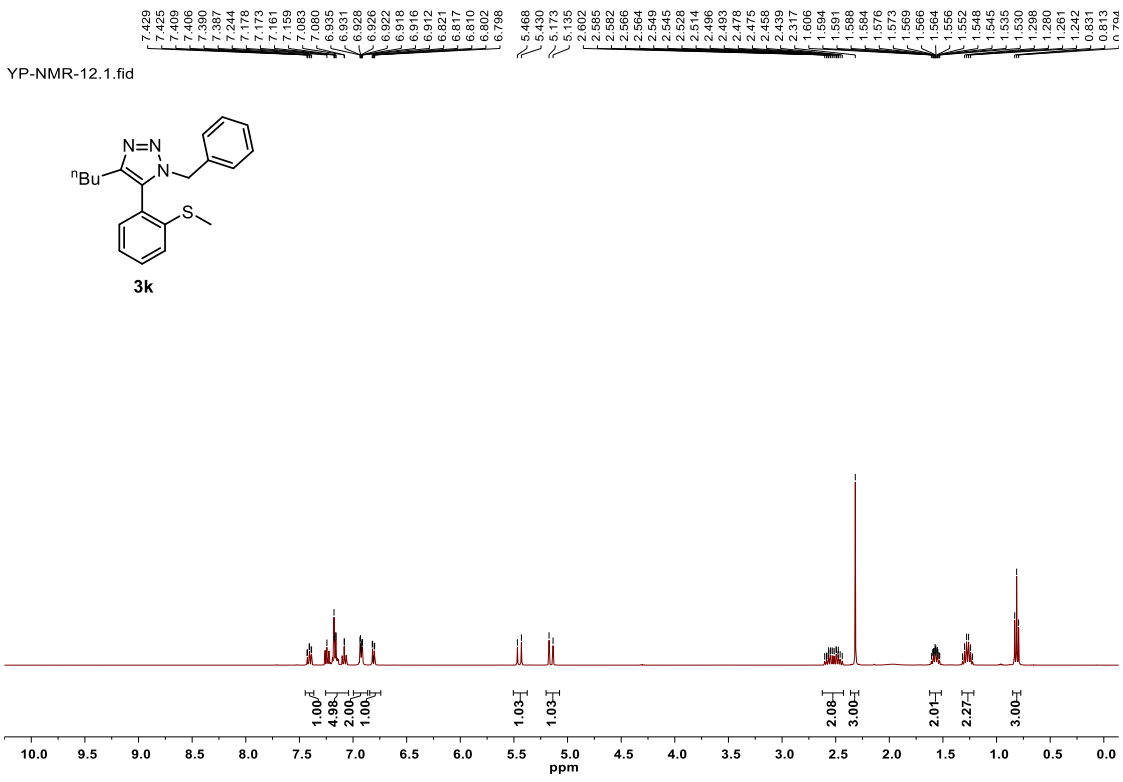
^{13}C NMR spectrum of 3i (101 MHz, $CDCl_3$)



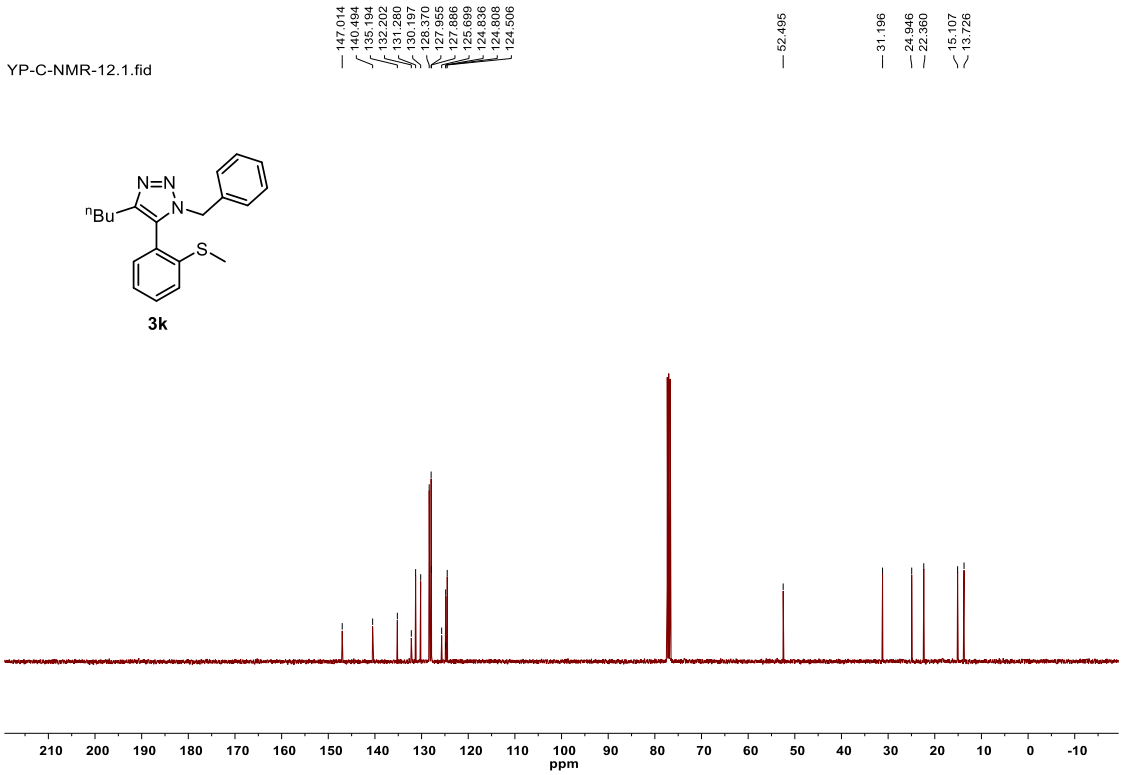
^{1}H NMR spectrum of 3j (600 MHz, $CDCl_3$)



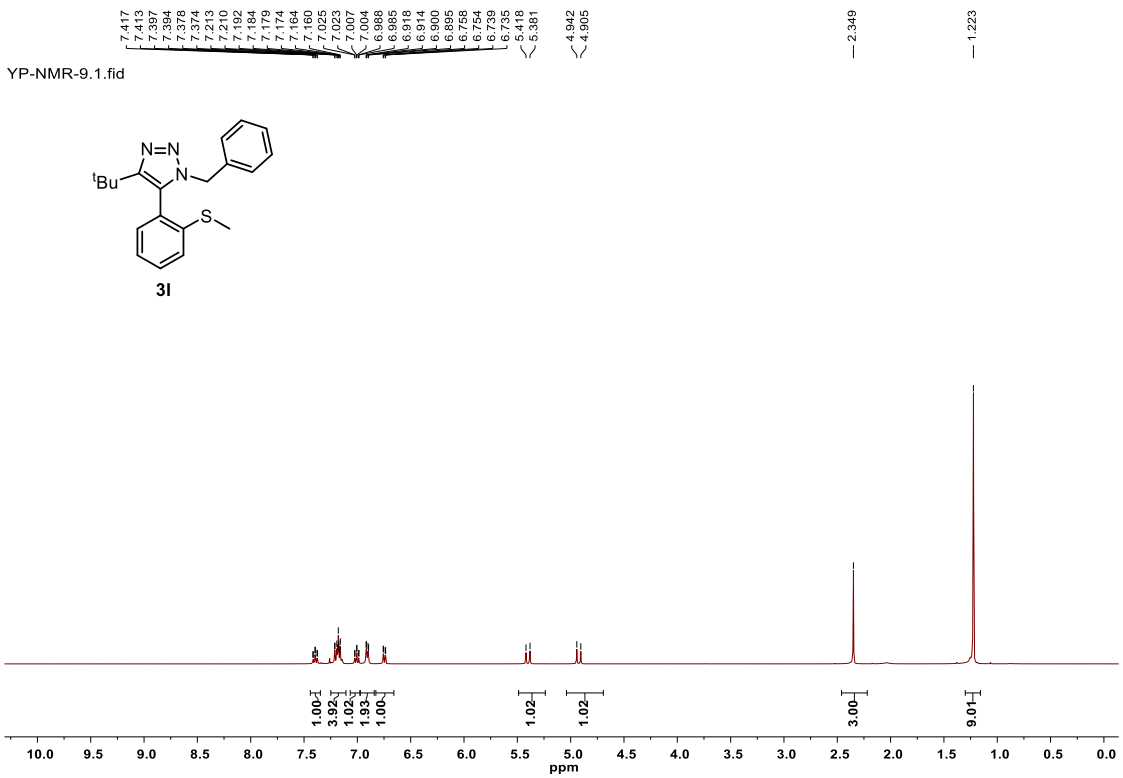
^{13}C NMR spectrum of 3j (125 MHz, $CDCl_3$)



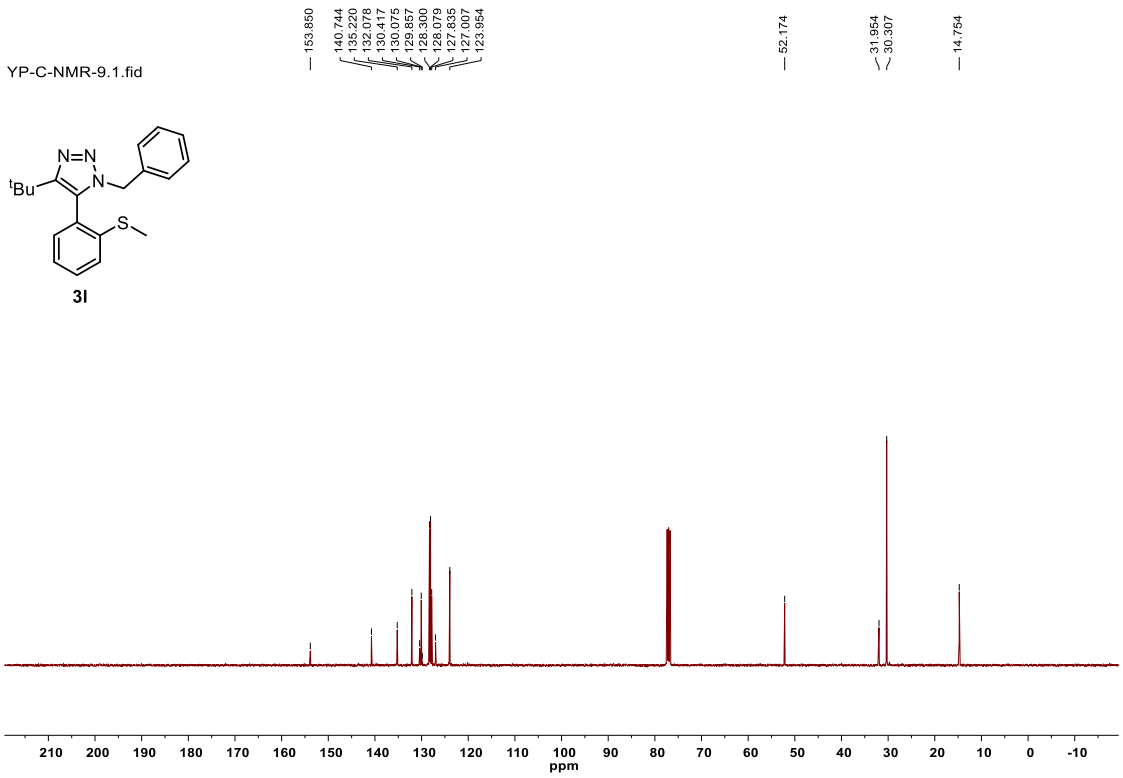
^{1}H NMR spectrum of 3k (400 MHz, $CDCl_3$)



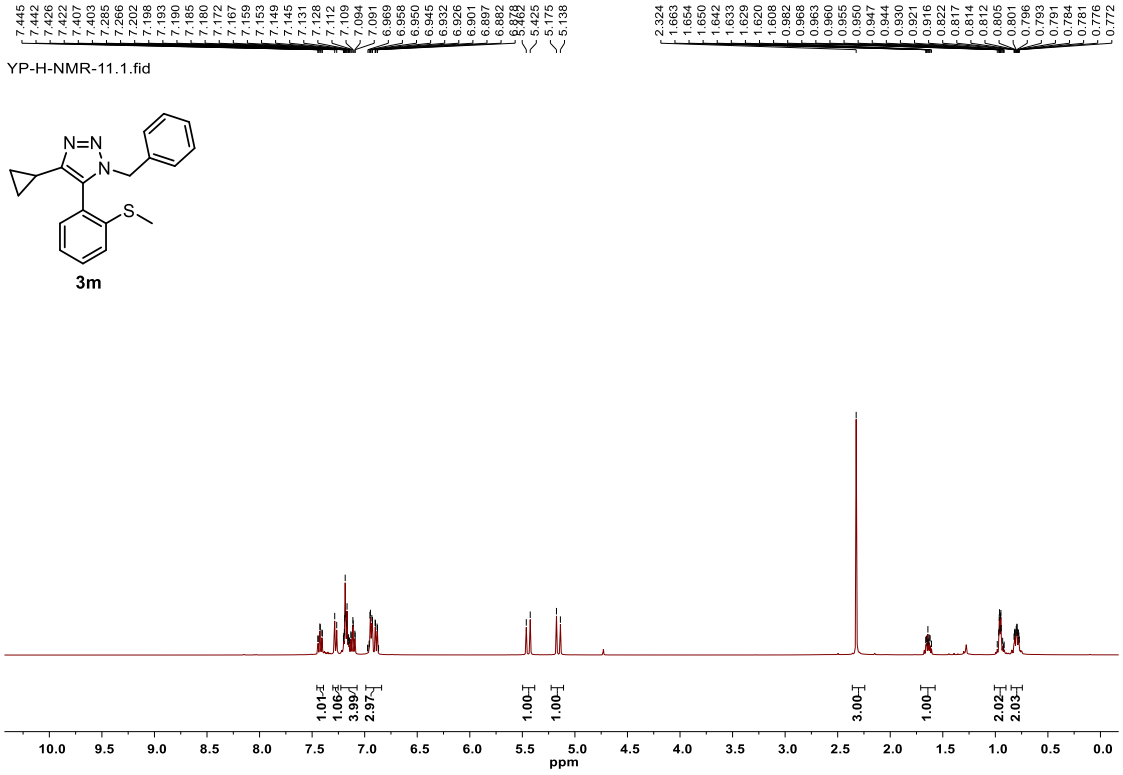
^{13}C NMR spectrum of 3k (101 MHz, $CDCl_3$)



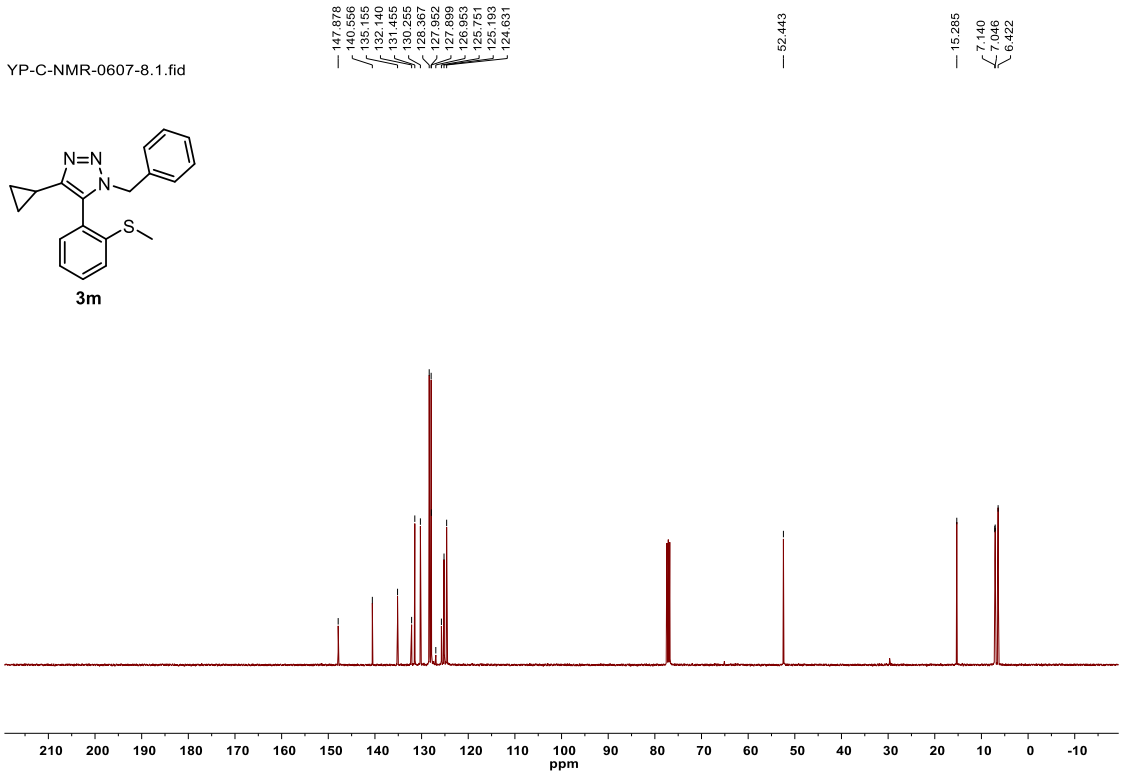
^{1}H NMR spectrum of 3l (400 MHz, $CDCl_3$)



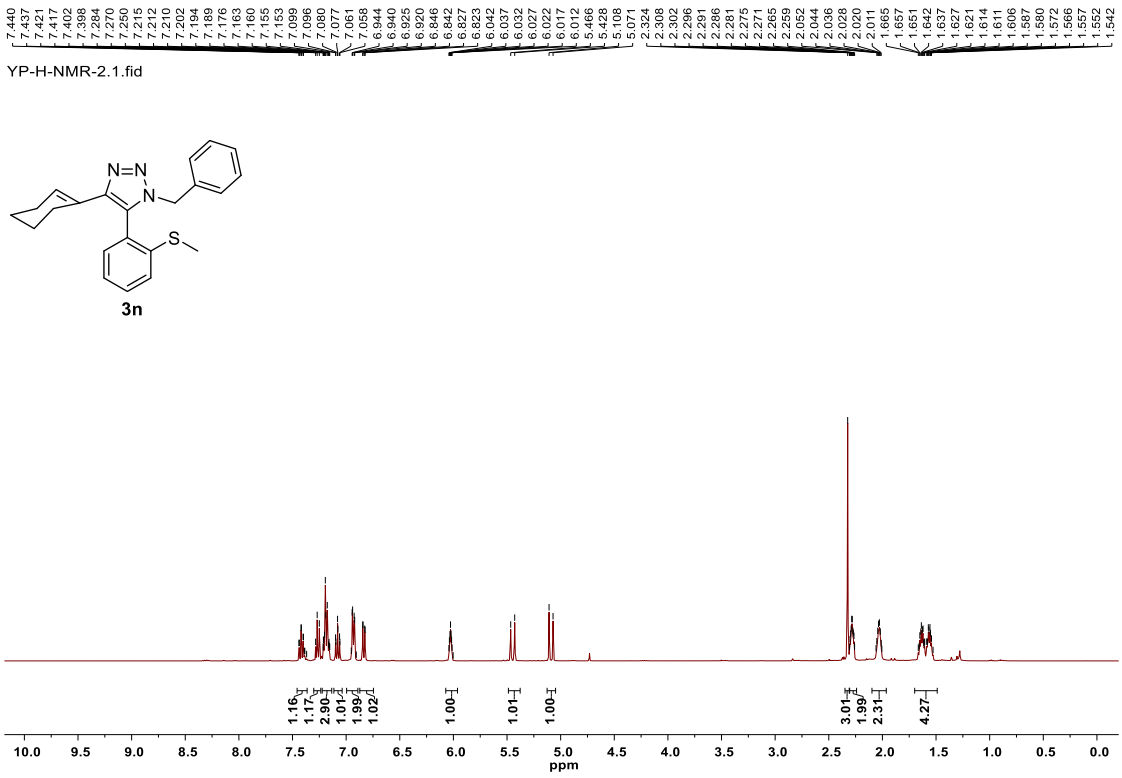
^{13}C NMR spectrum of 3l (101 MHz, $CDCl_3$)



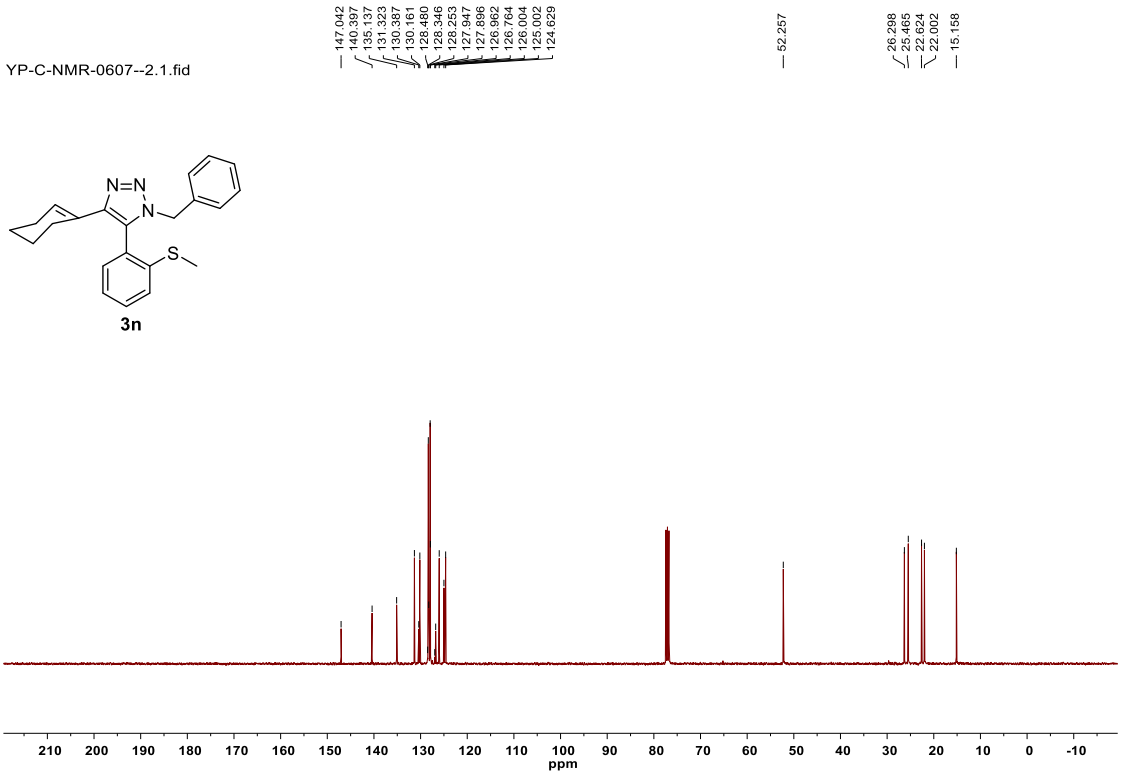
^{1}H NMR spectrum of 3m (400 MHz, $CDCl_3$)



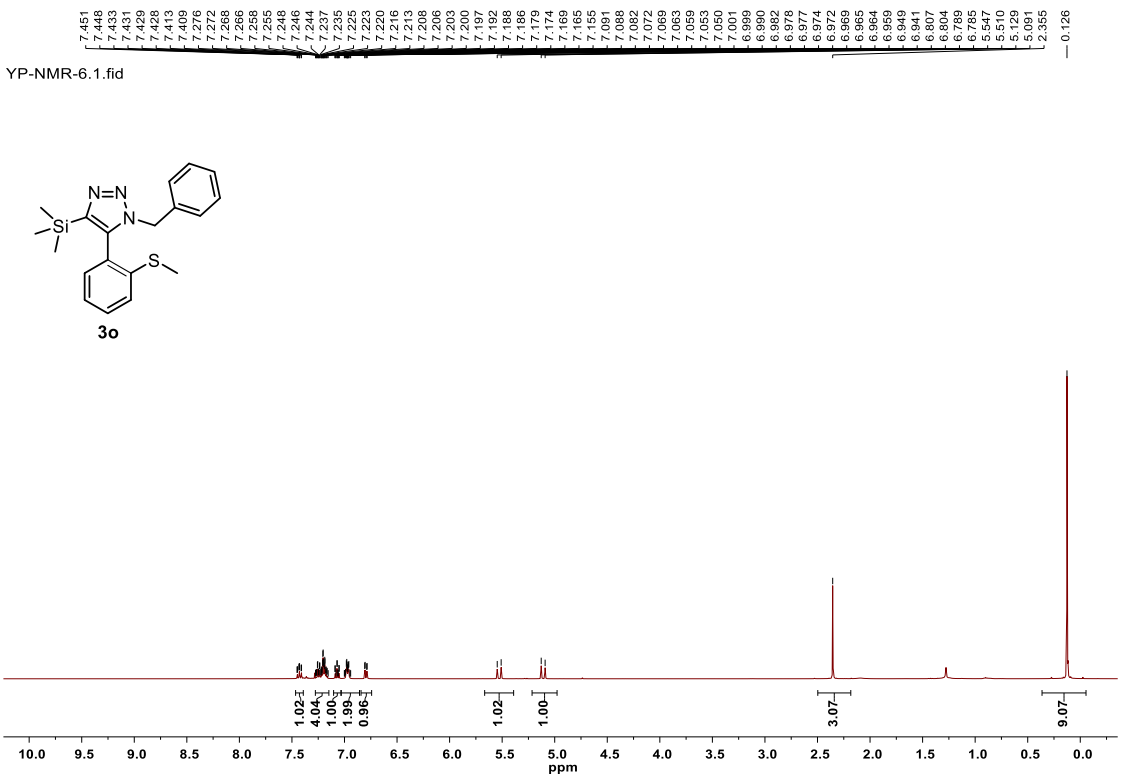
^{13}C NMR spectrum of 3m (101 MHz, $CDCl_3$)



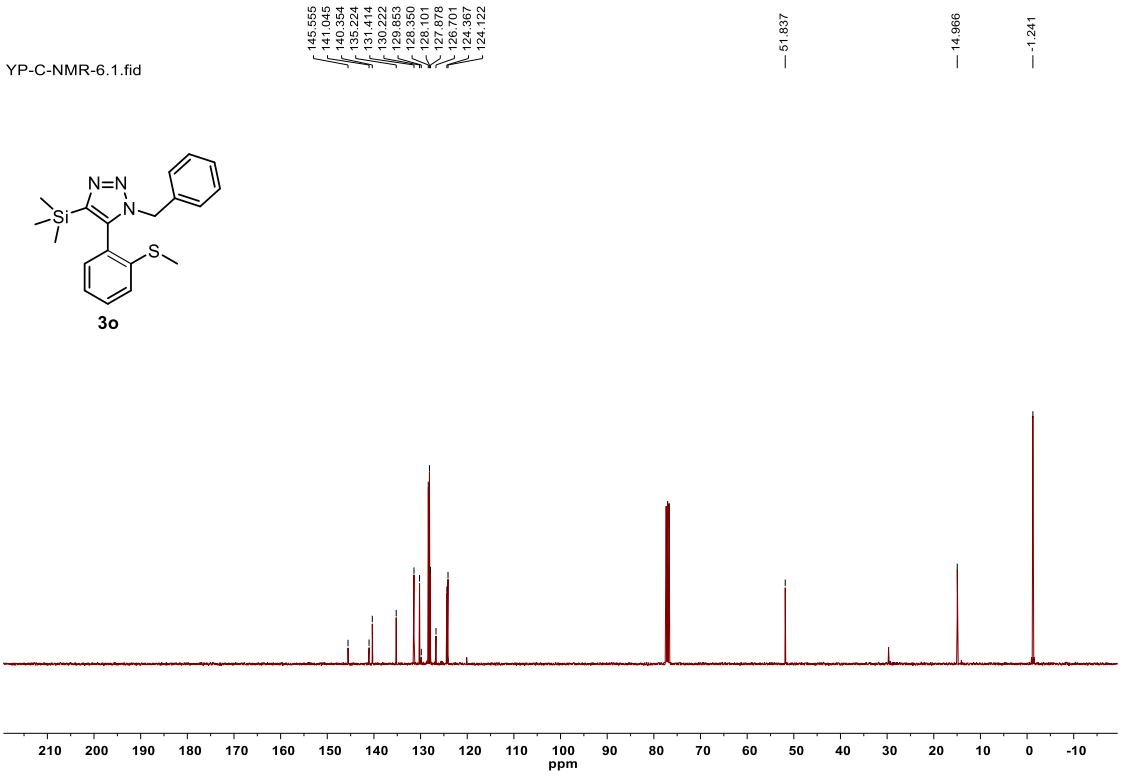
^{1}H NMR spectrum of 3n (400 MHz, $CDCl_3$)



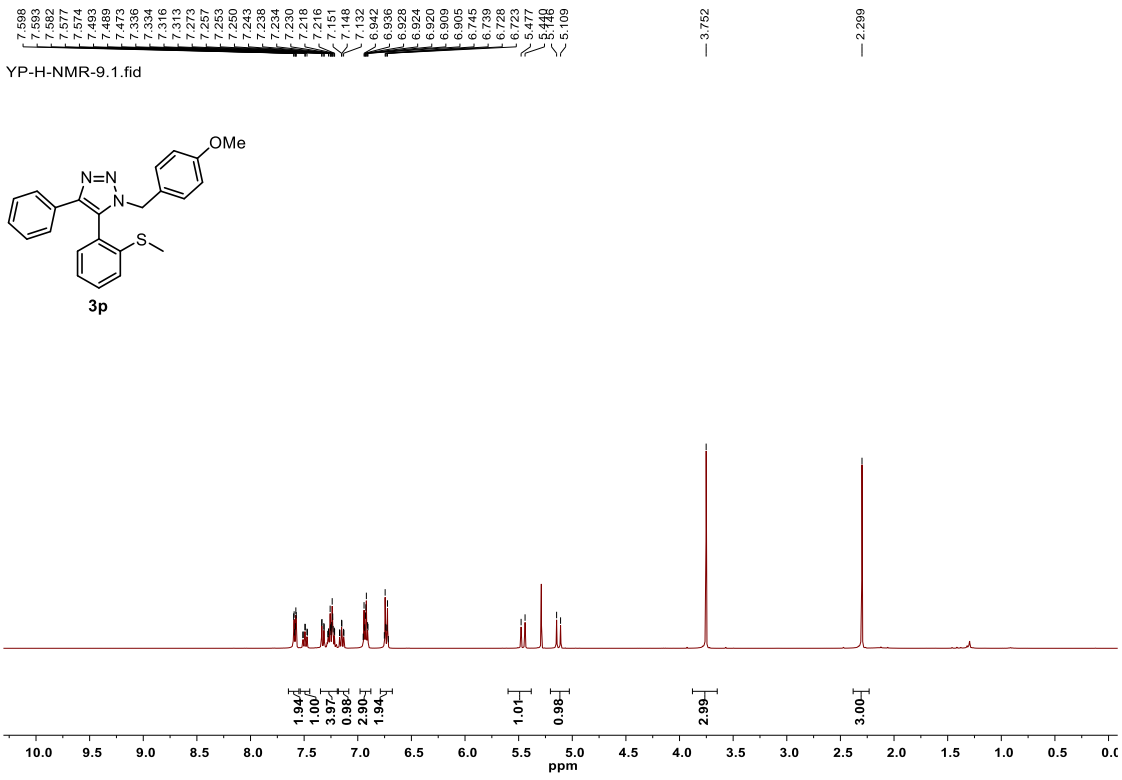
^{13}C NMR spectrum of 3n (101 MHz, $CDCl_3$)



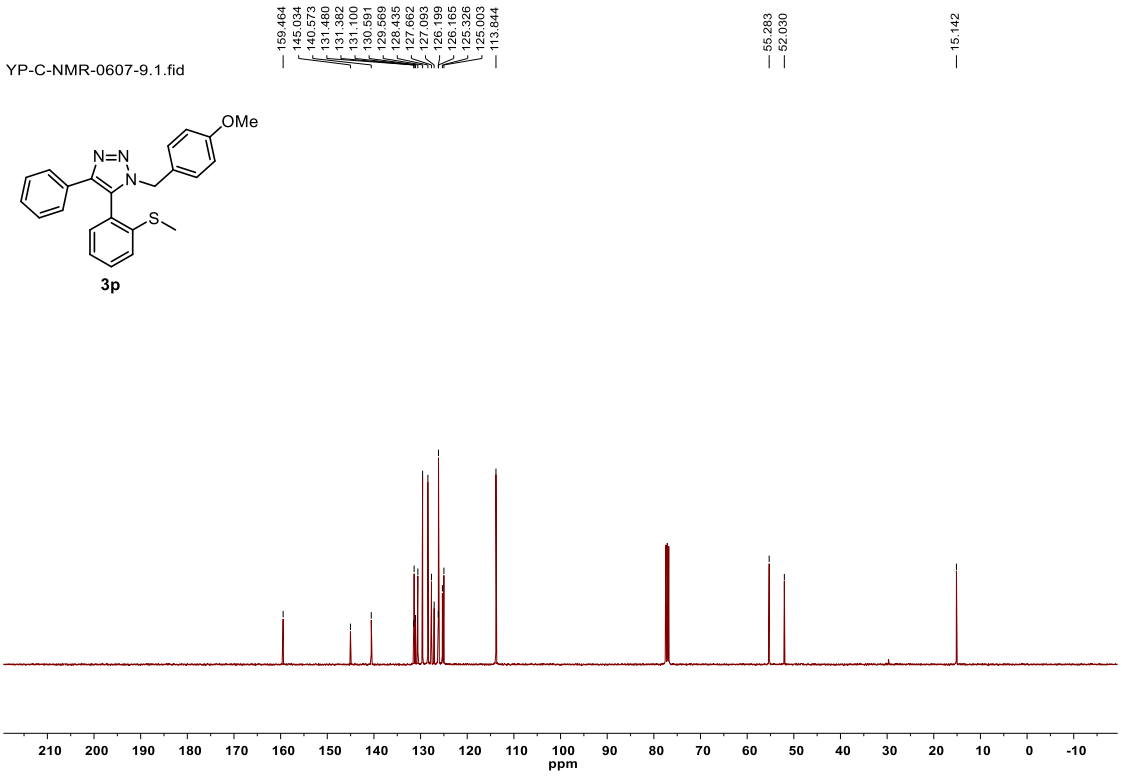
^{1}H NMR spectrum of 3o (400 MHz, $CDCl_3$)



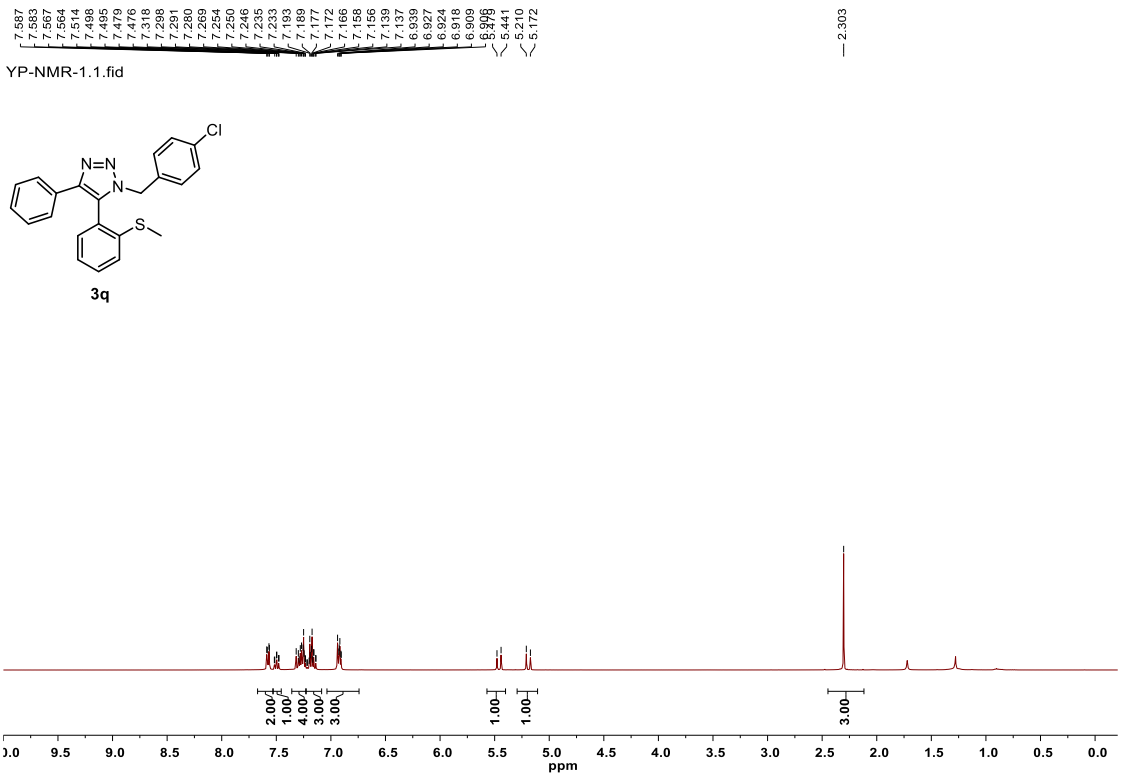
^{13}C NMR spectrum of 3o (101 MHz, $CDCl_3$)



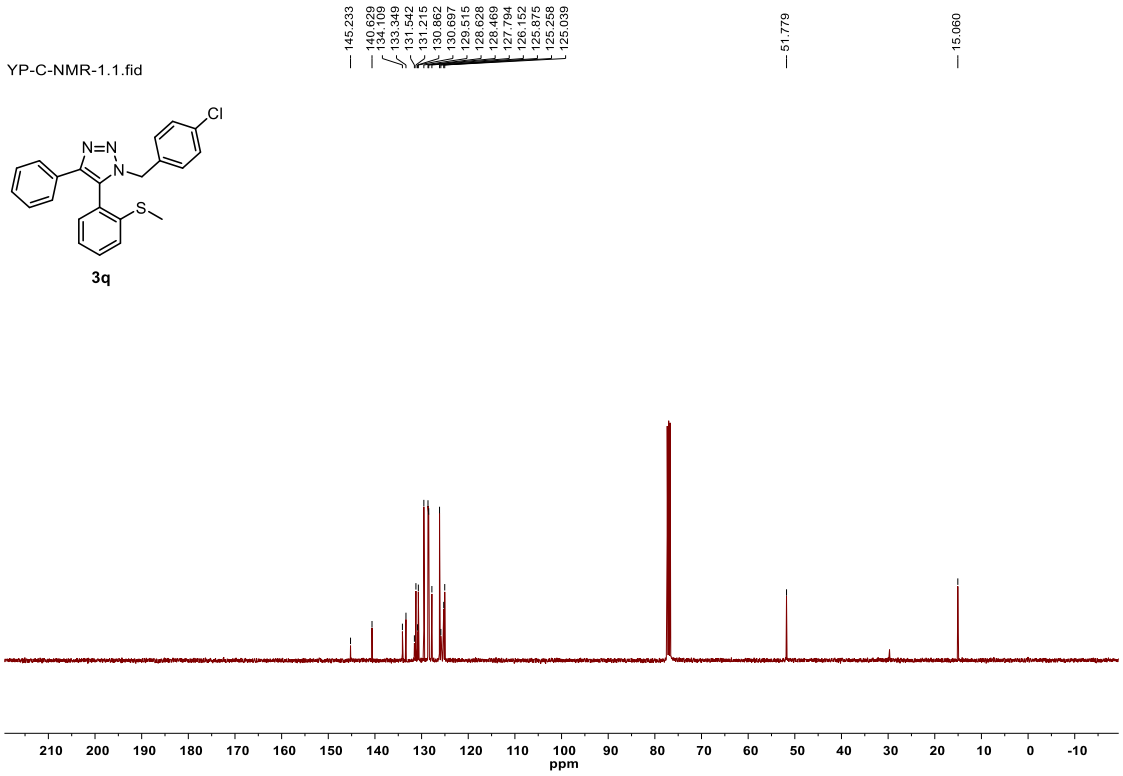
^{1}H NMR spectrum of 3p (400 MHz, $CDCl_3$)



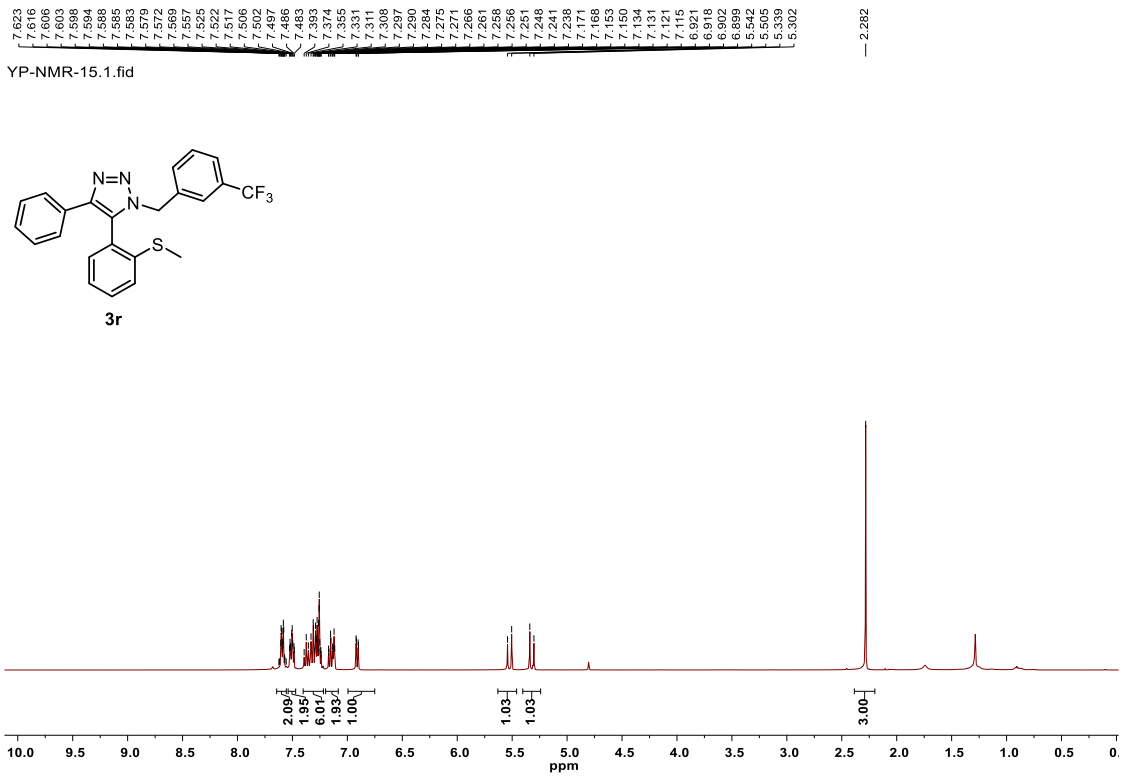
^{13}C NMR spectrum of 3p (101 MHz, $CDCl_3$)



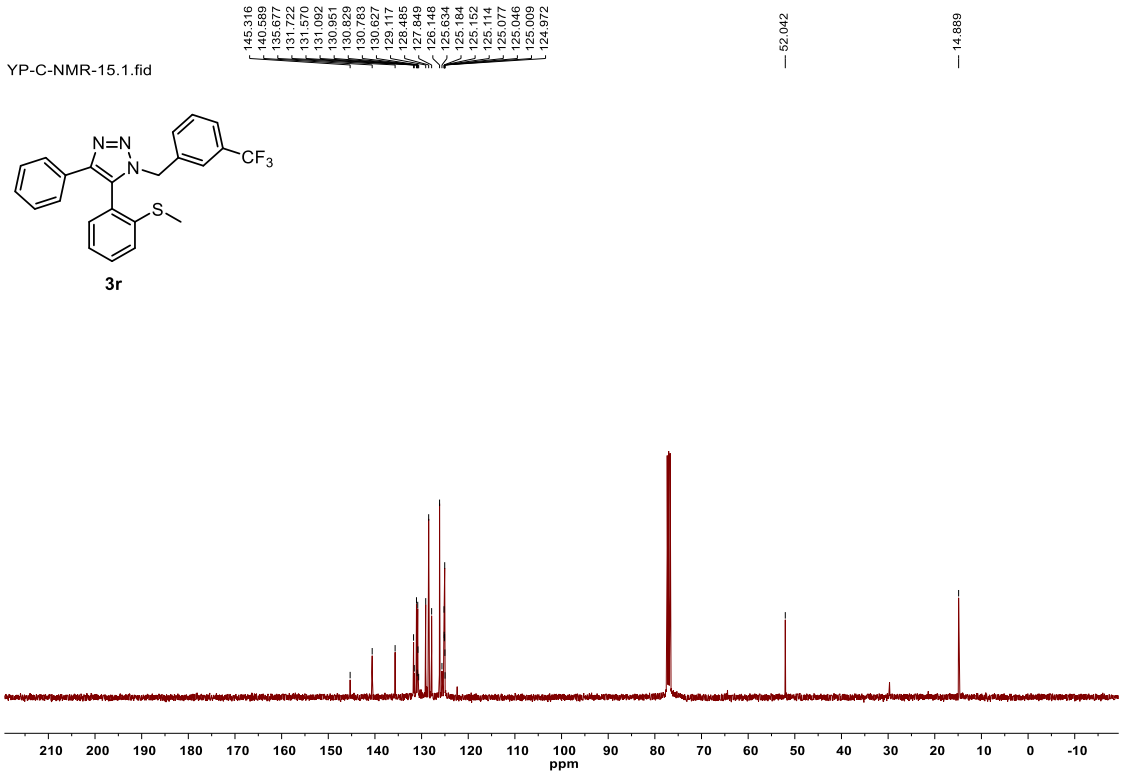
^{1}H NMR spectrum of 3q (400 MHz, $CDCl_3$)



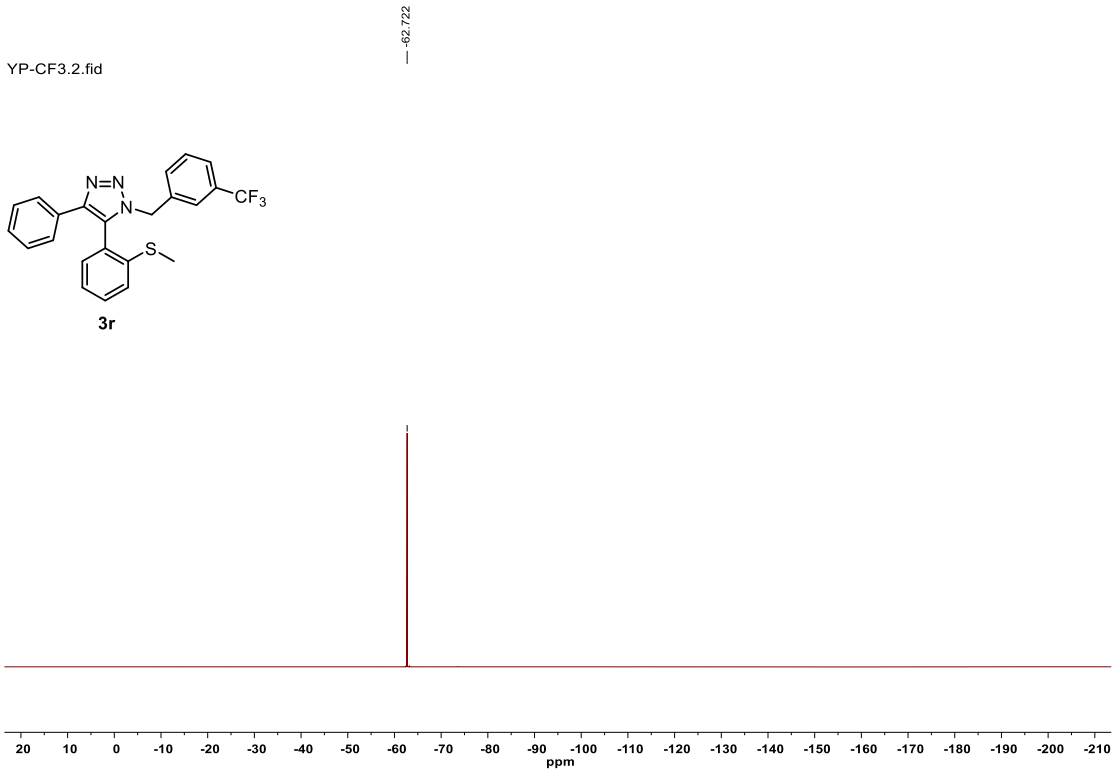
^{13}C NMR spectrum of 3q (101 MHz, $CDCl_3$)



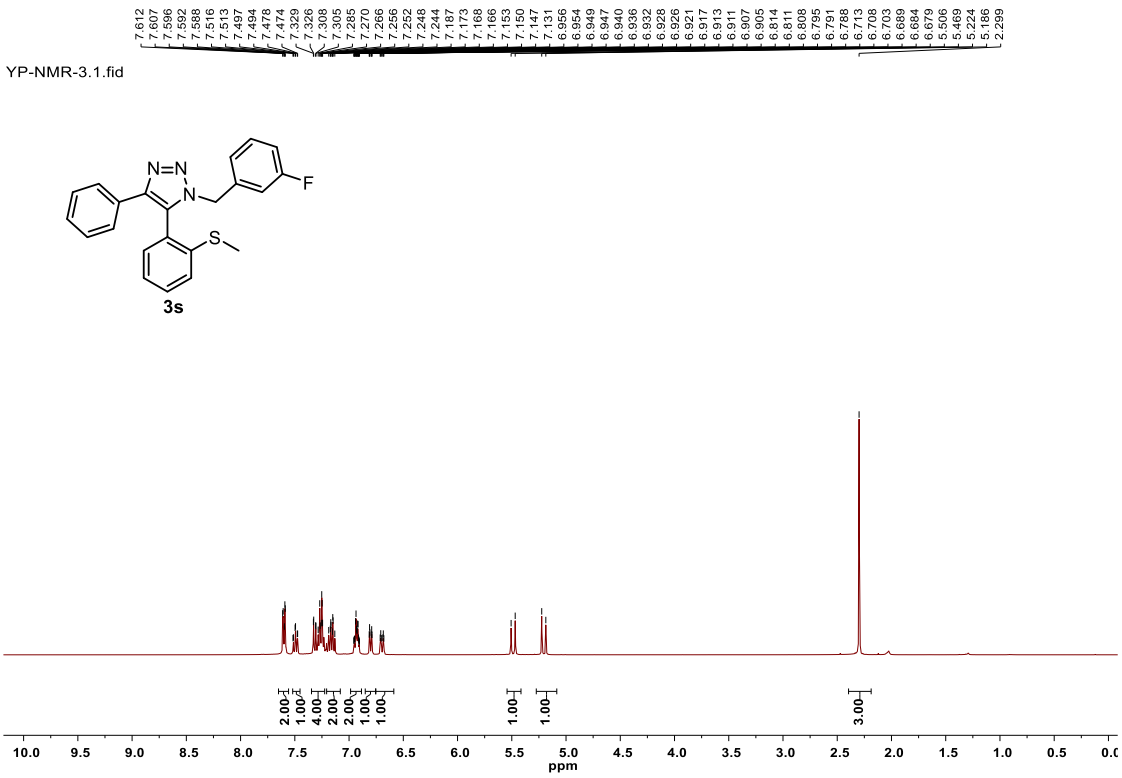
^{1}H NMR spectrum of 3r (400 MHz, $CDCl_3$)



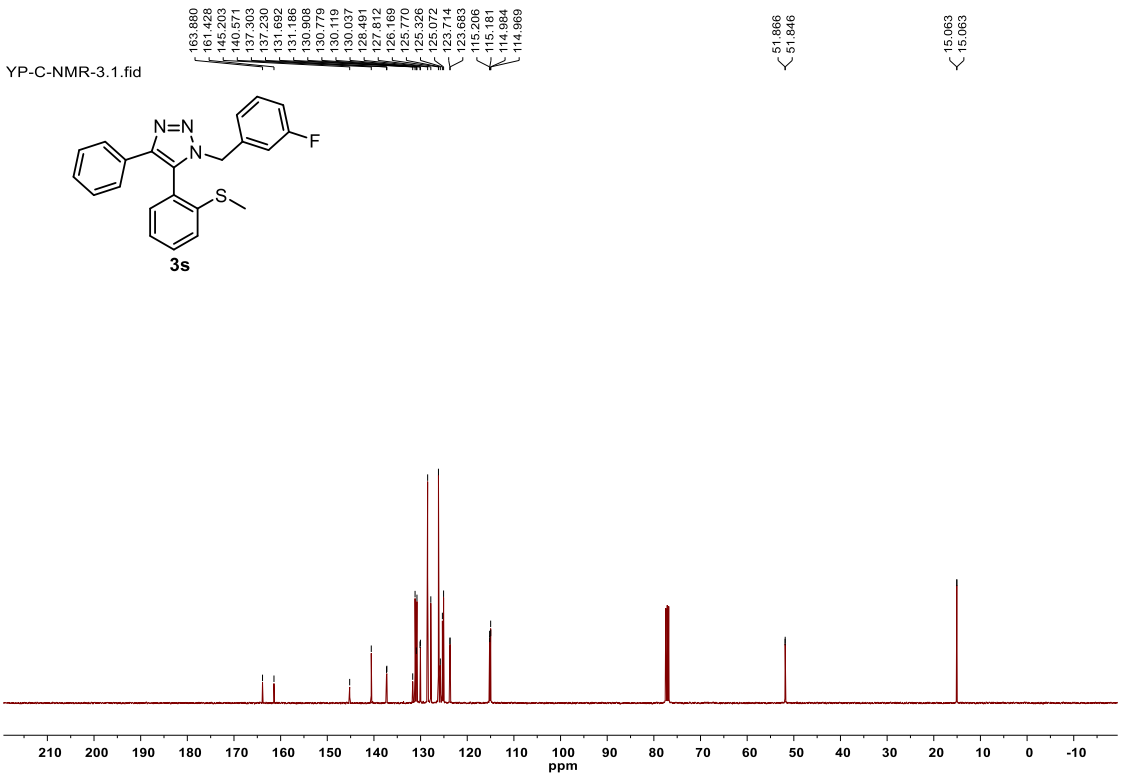
^{13}C NMR spectrum of 3r (101 MHz, $CDCl_3$)



^{19}F NMR spectrum of 3r (376 MHz, $CDCl_3$)

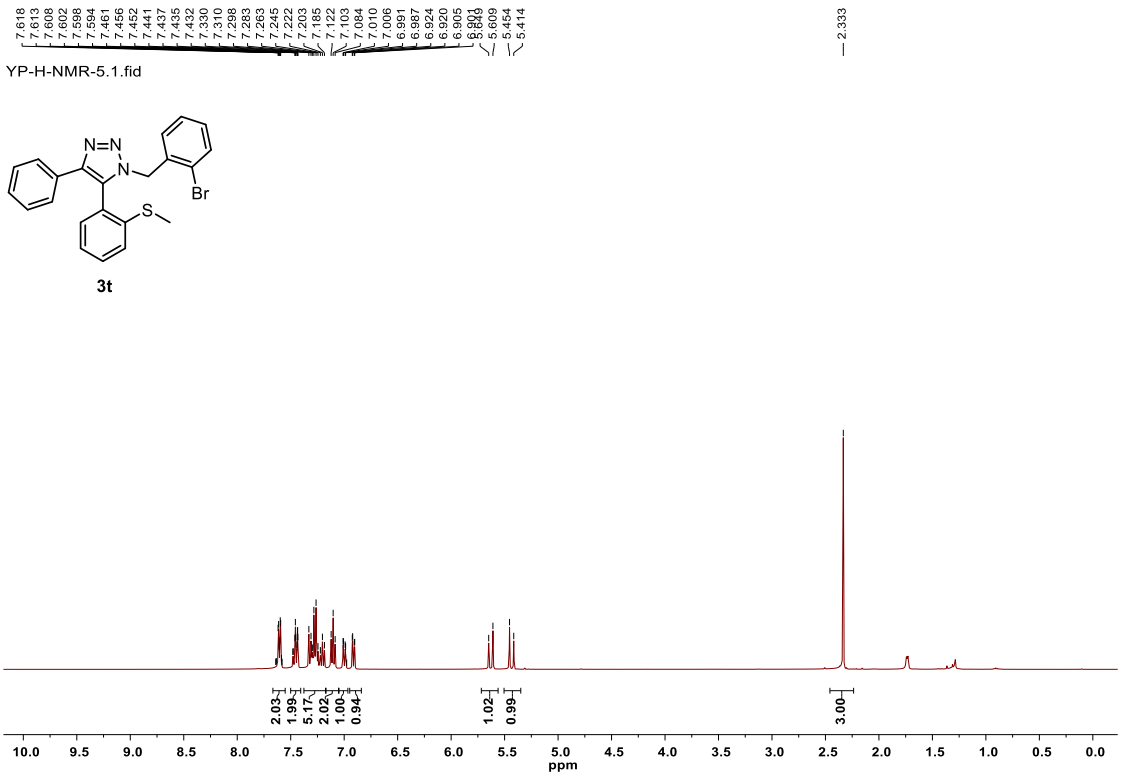


^{1}H NMR spectrum of 3s (400 MHz, $CDCl_3$)

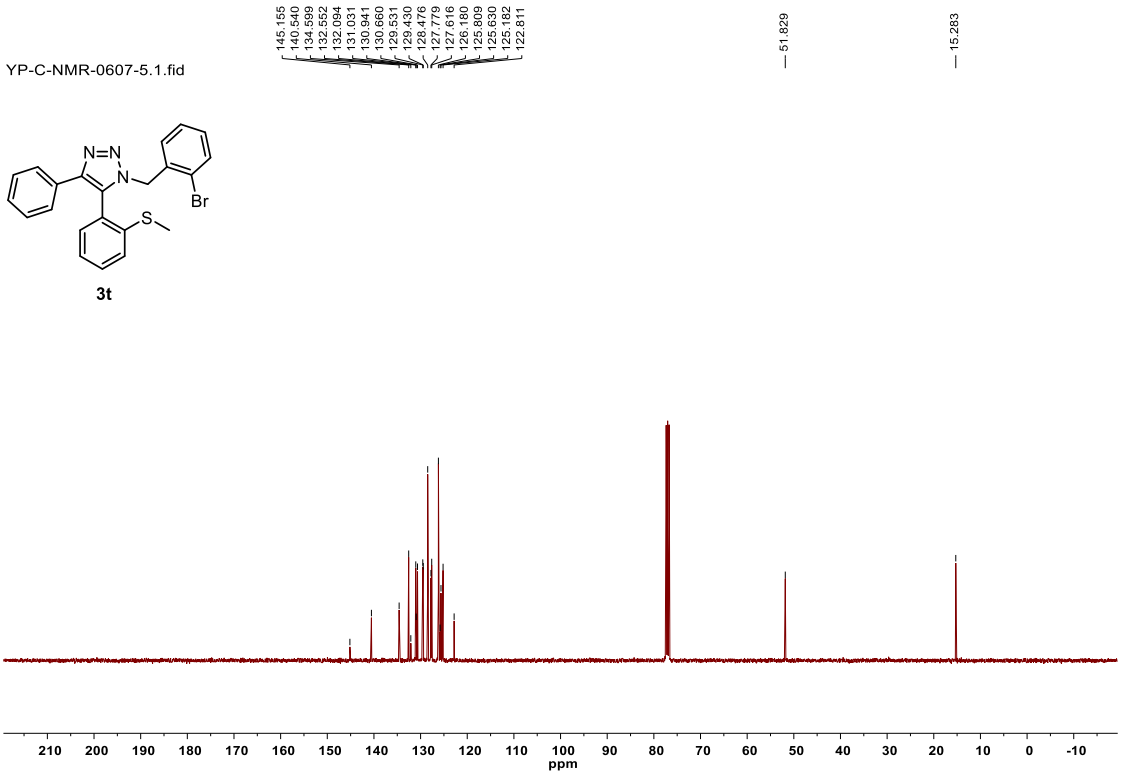


^{13}C NMR spectrum of 3s (101 MHz, $CDCl_3$)

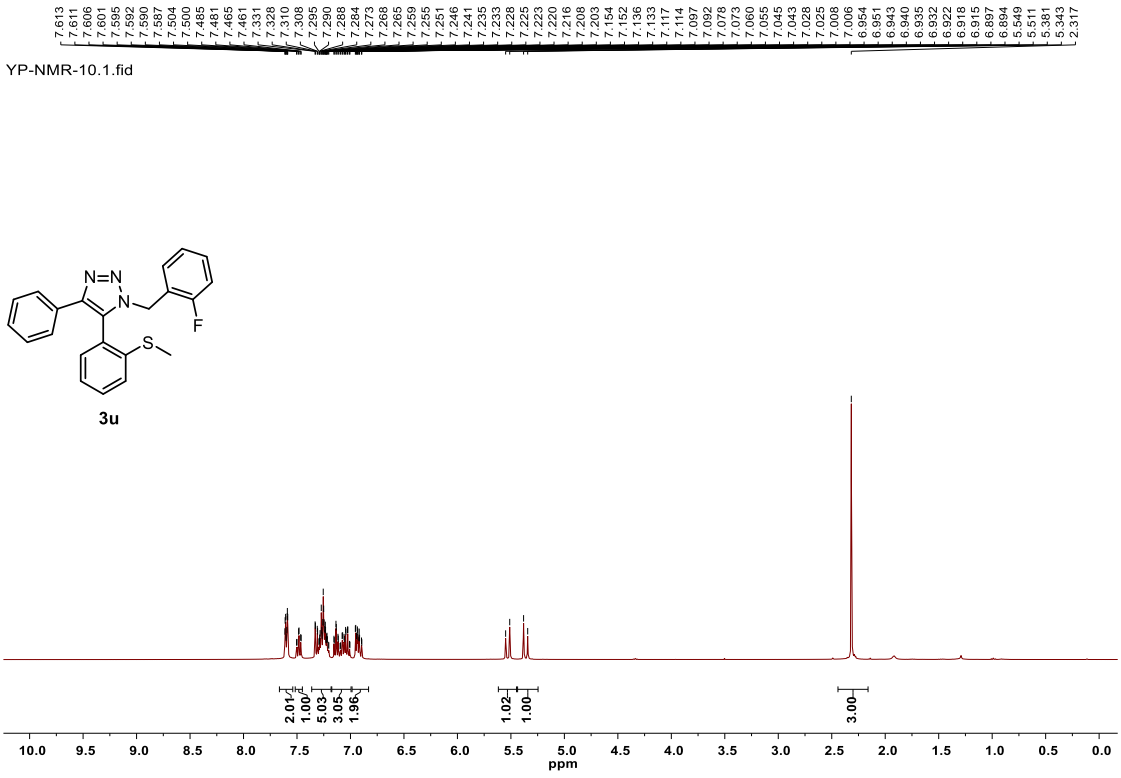
^{19}F NMR spectrum of 3s (376 MHz, $CDCl_3$)



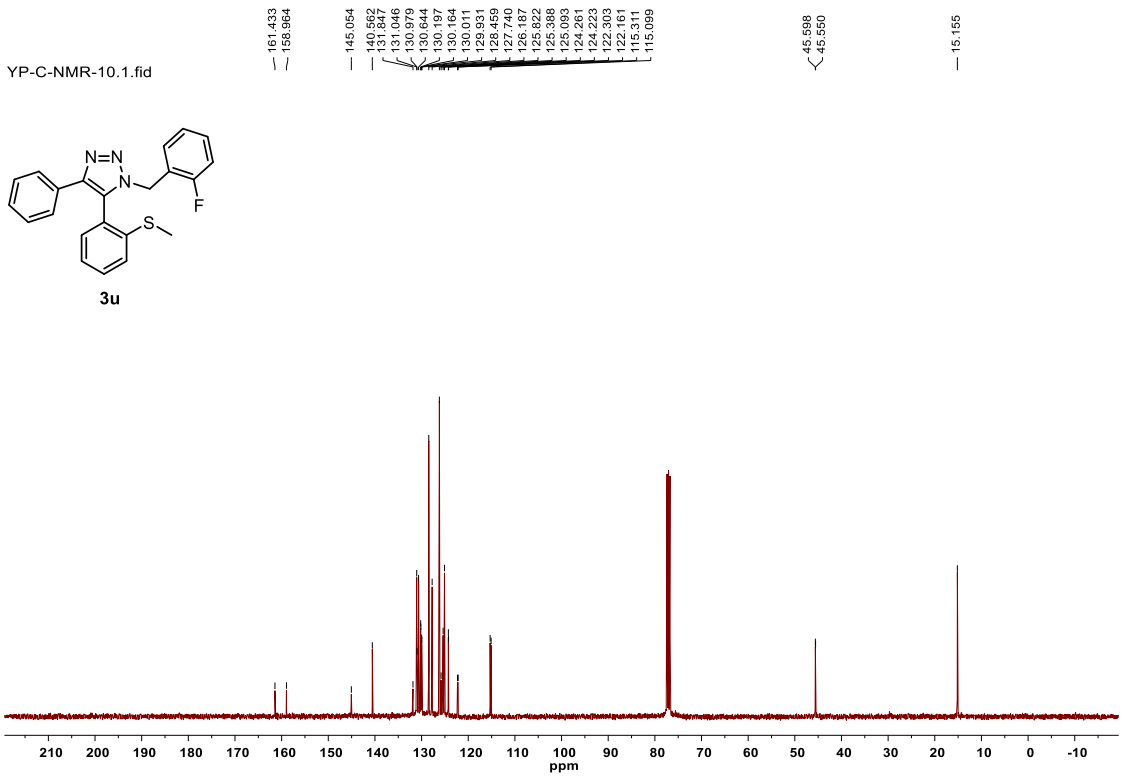
^{1}H NMR spectrum of 3t (400 MHz, $CDCl_3$)



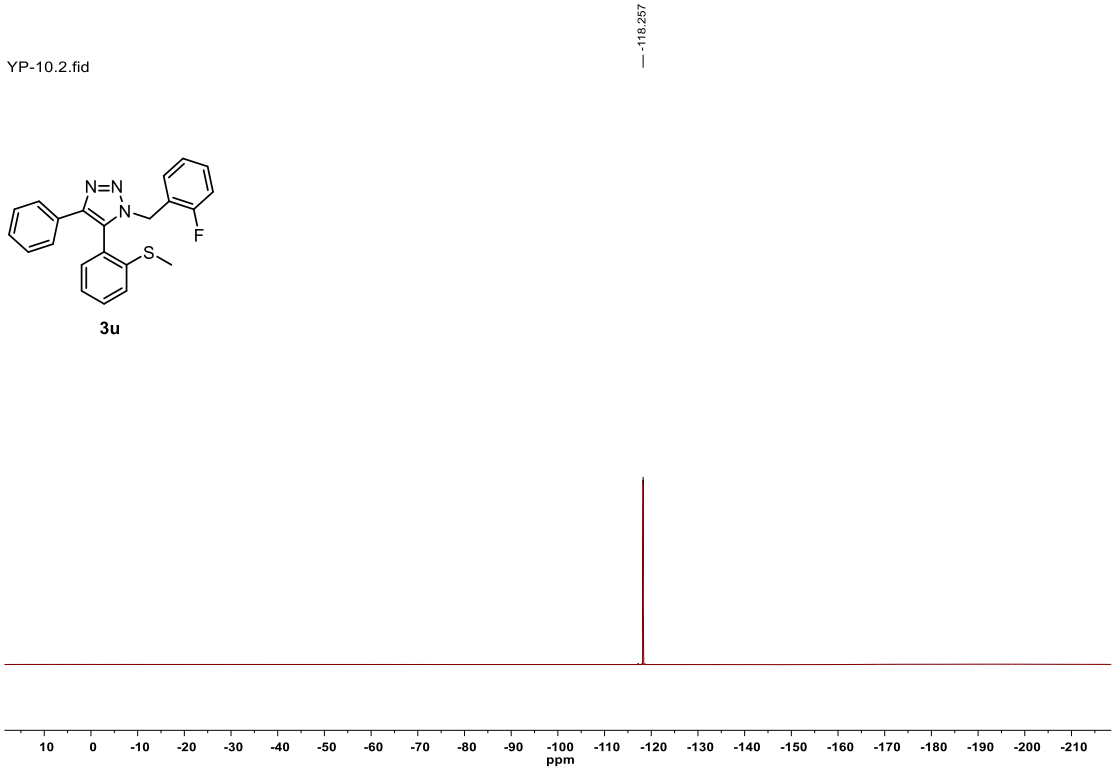
^{13}C NMR spectrum of 3t (101 MHz, $CDCl_3$)



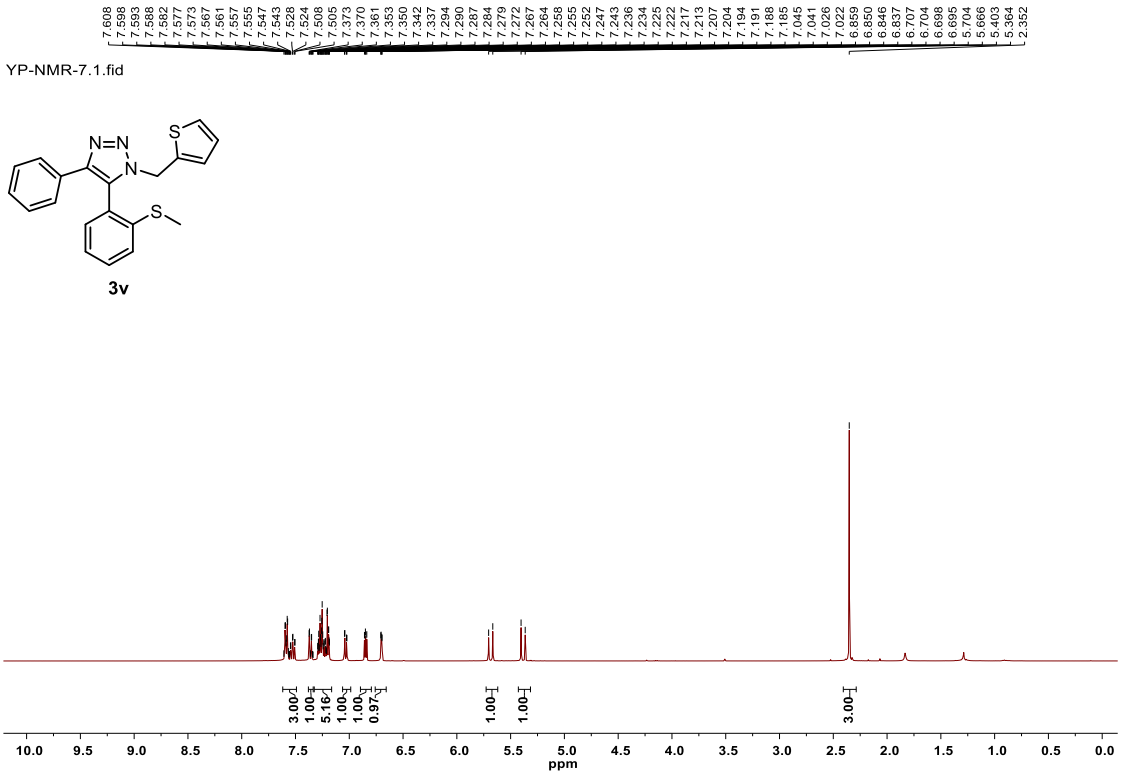
^{1}H NMR spectrum of 3u (400 MHz, $CDCl_3$)



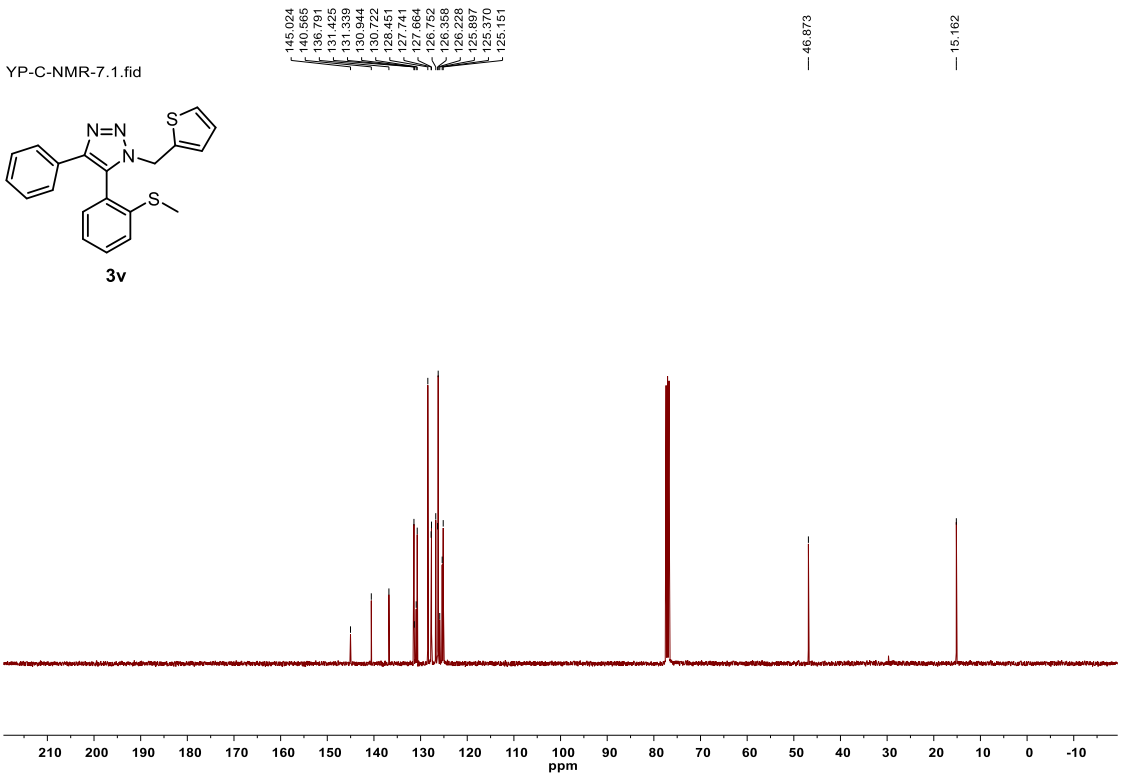
^{13}C NMR spectrum of 3u (101 MHz, $CDCl_3$)



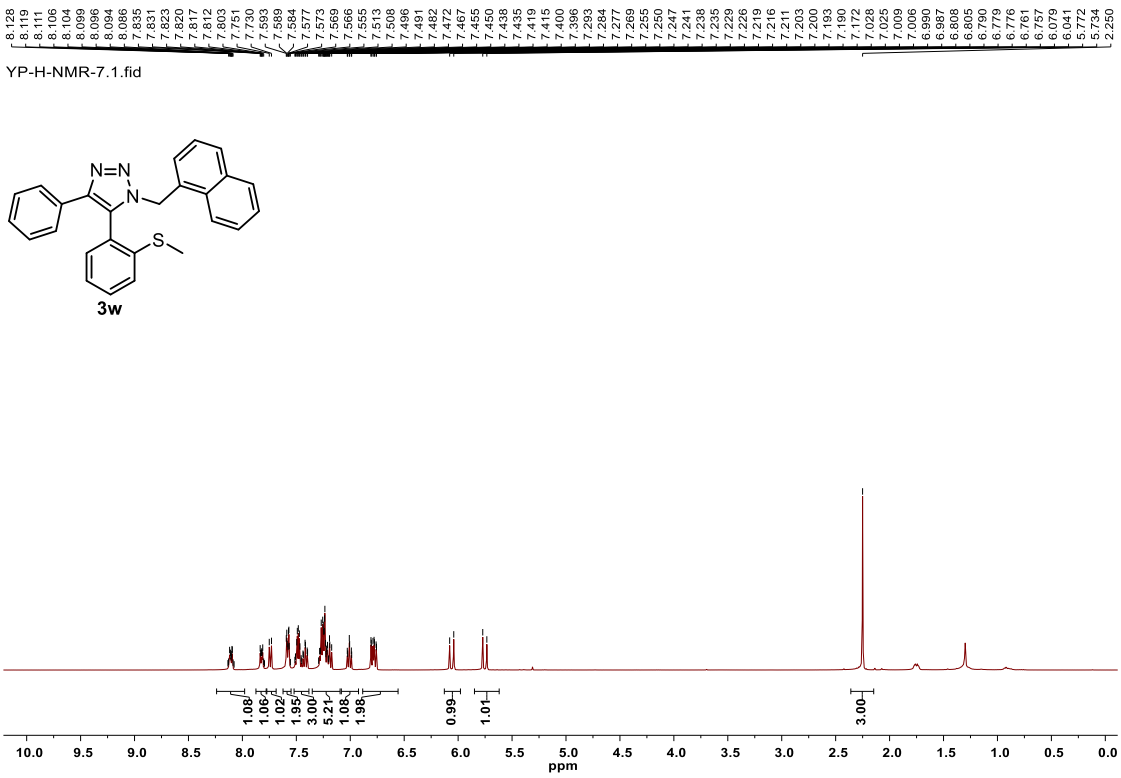
^{19}F NMR spectrum of 3u (376 MHz, $CDCl_3$)



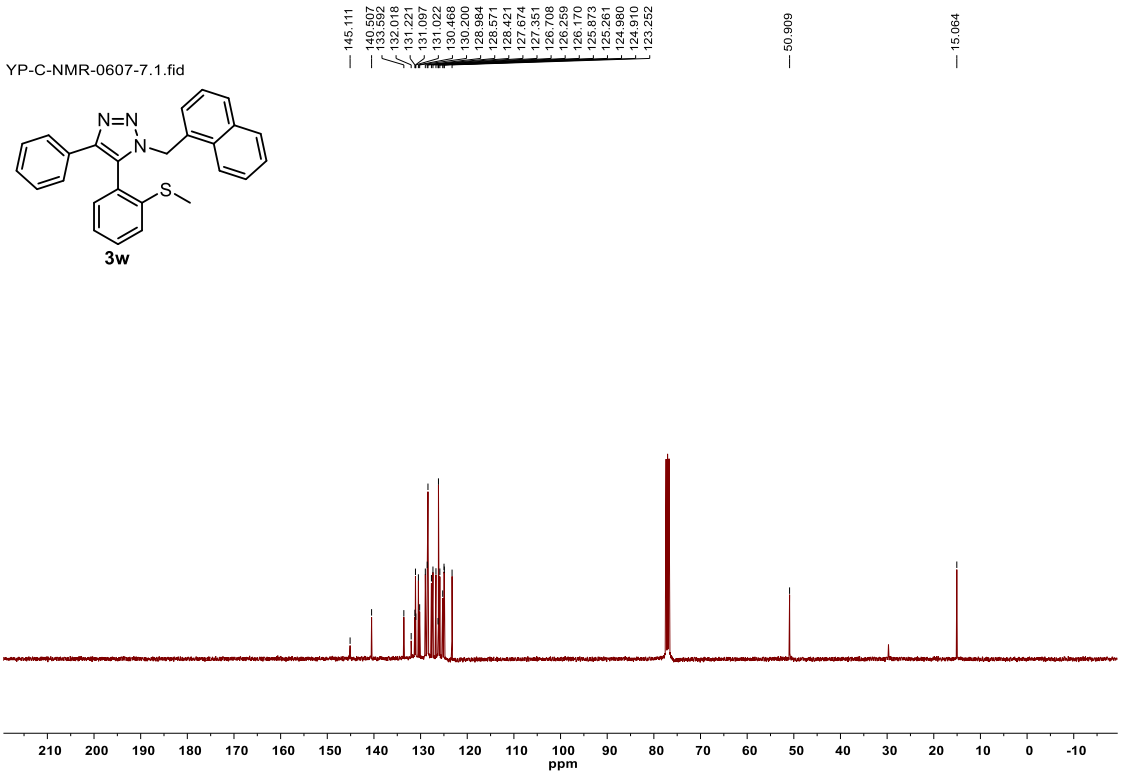
^{1}H NMR spectrum of 3v (400 MHz, $CDCl_3$)



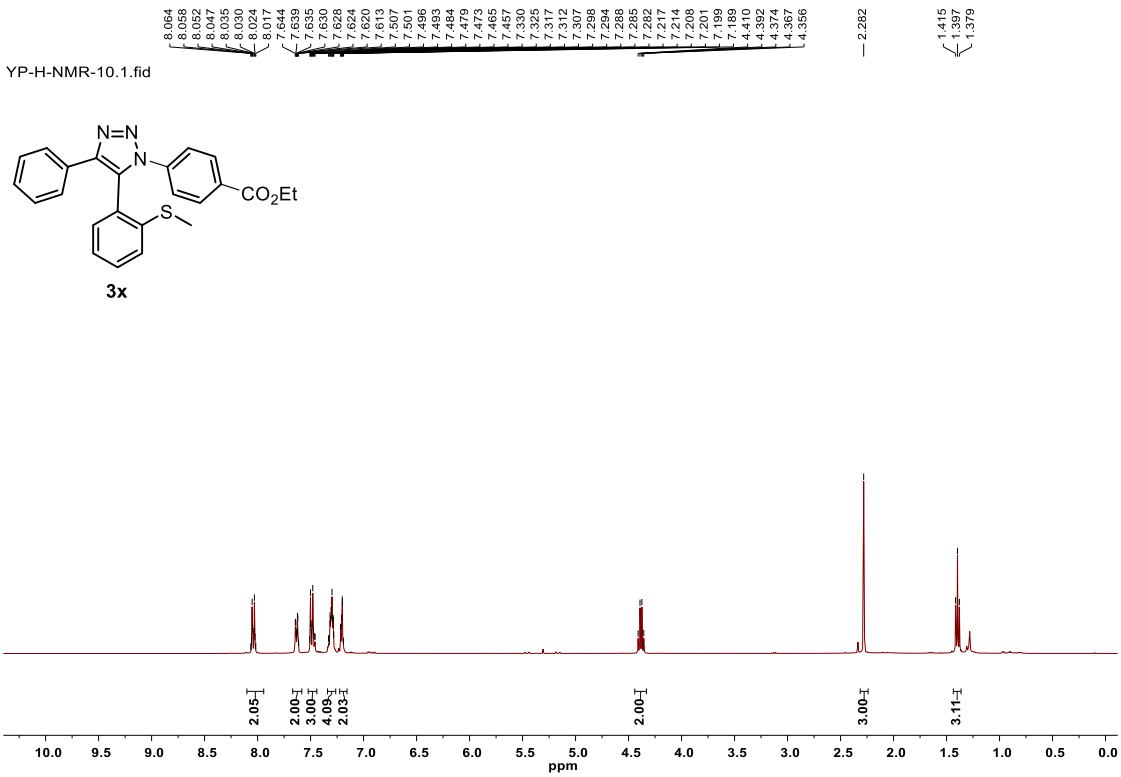
^{13}C NMR spectrum of 3v (101 MHz, $CDCl_3$)



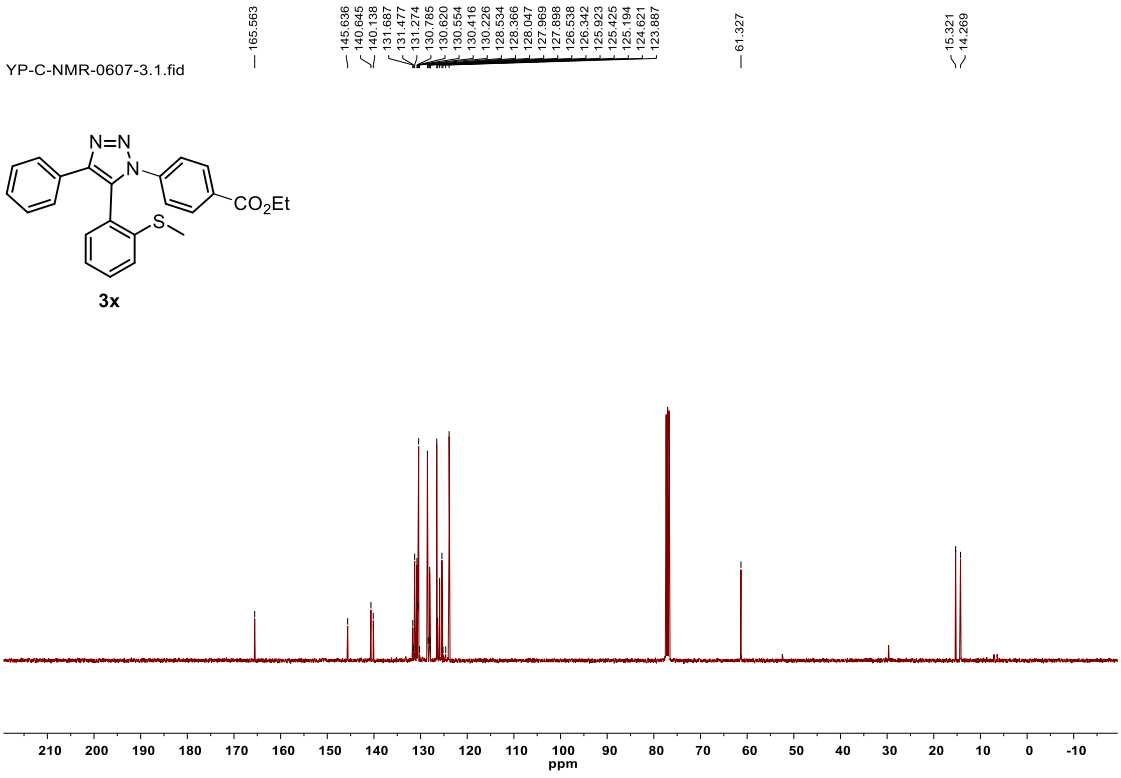
^{1}H NMR spectrum of 3w (400 MHz, $CDCl_3$)



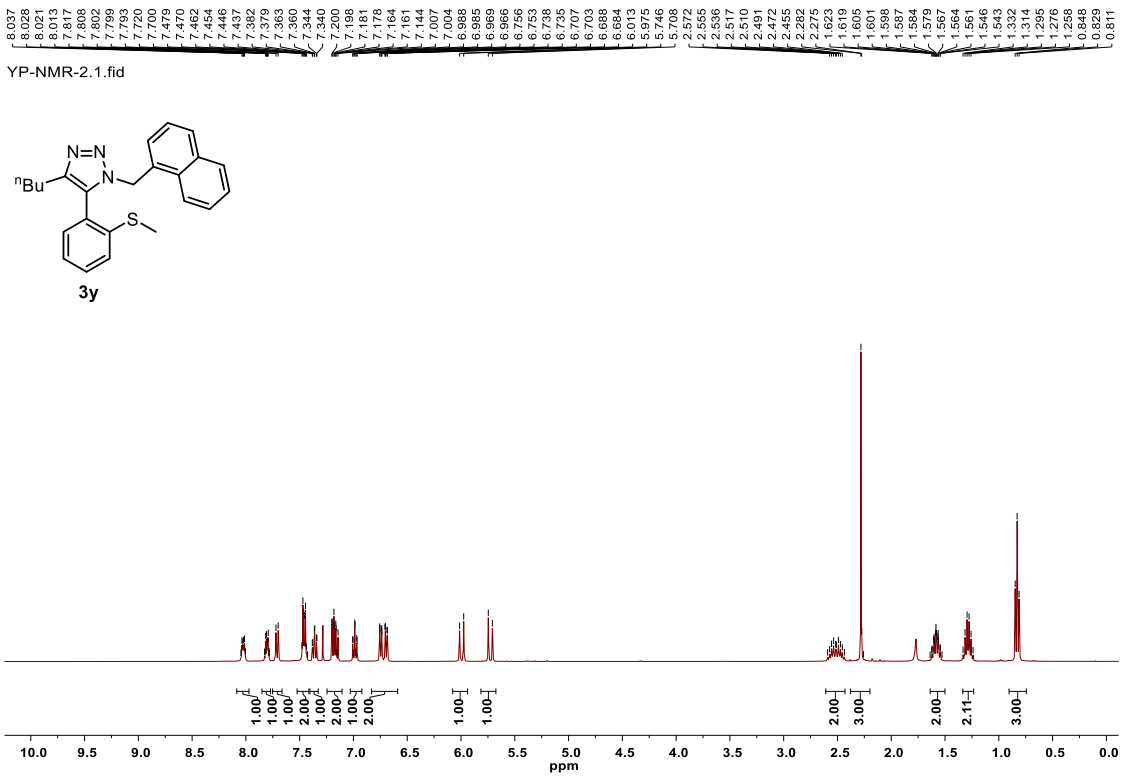
^{13}C NMR spectrum of 3w (101 MHz, $CDCl_3$)



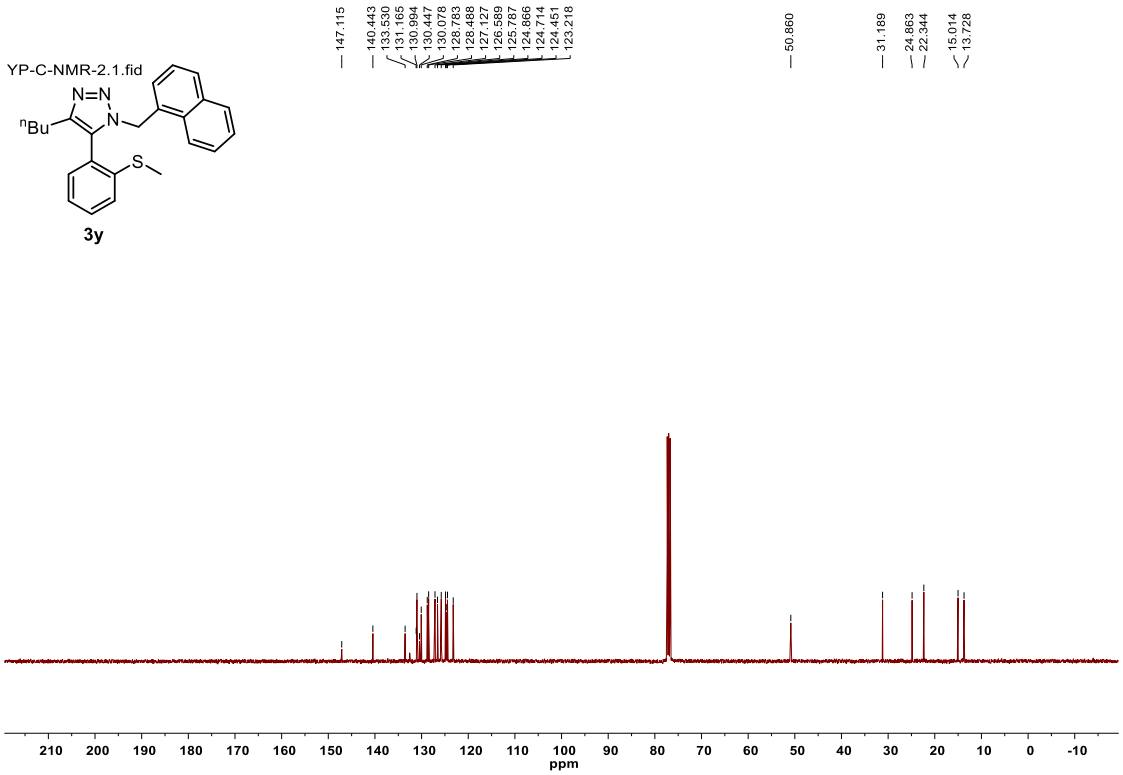
^{1}H NMR spectrum of 3x (400 MHz, $CDCl_3$)



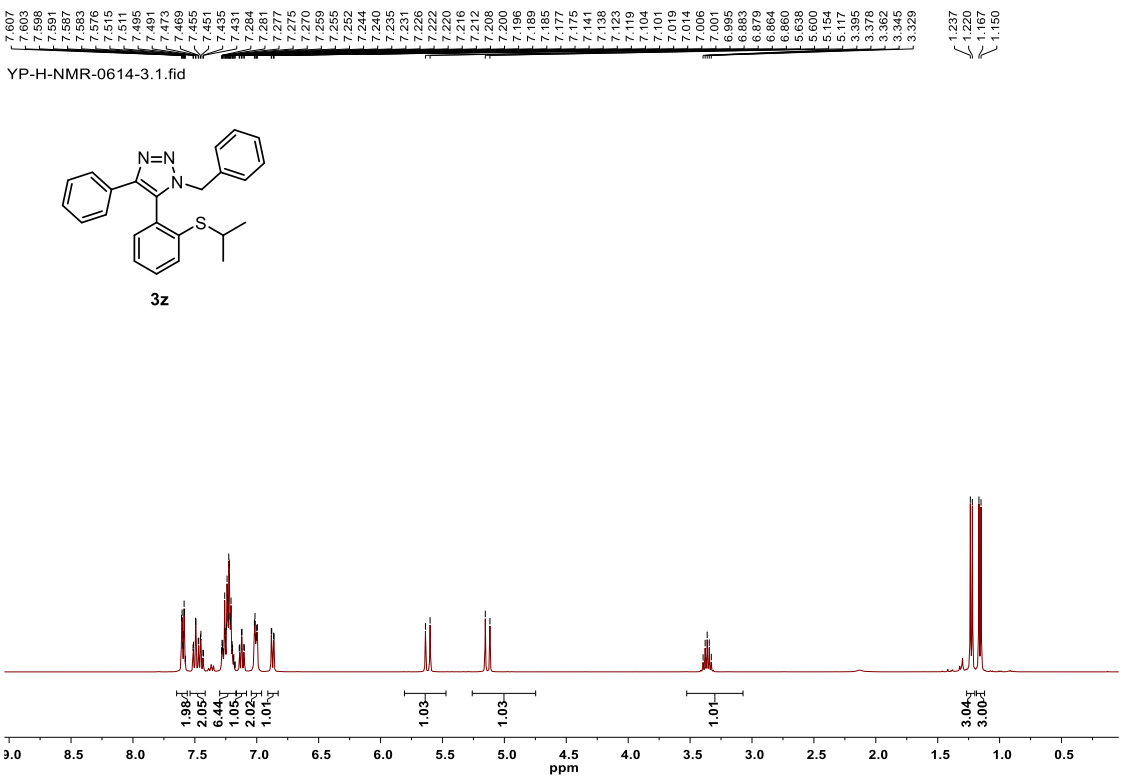
^{13}C NMR spectrum of 3x (101 MHz, $CDCl_3$)



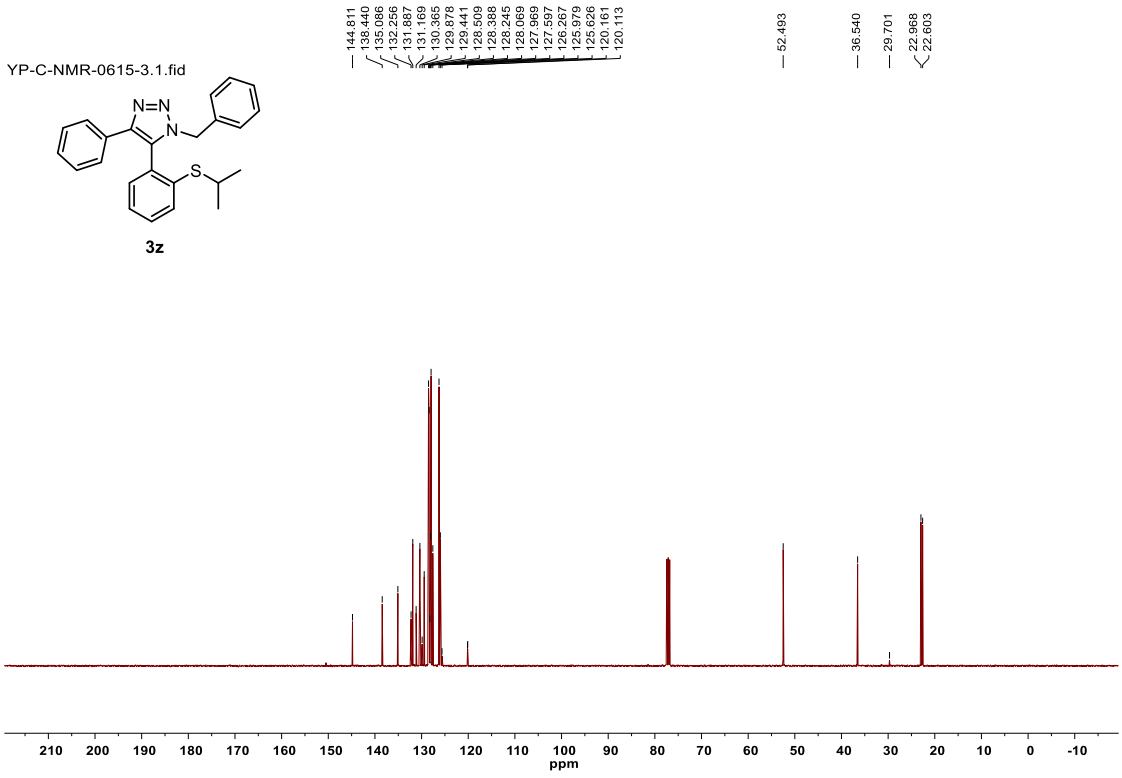
^{1}H NMR spectrum of 3y (400 MHz, $CDCl_3$)



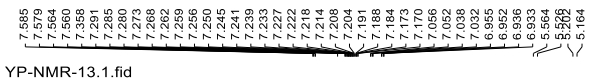
^{13}C NMR spectrum of 3y (101 MHz, $CDCl_3$)

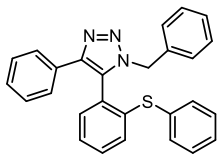


^{1}H NMR spectrum of 3z (400 MHz, $CDCl_3$)

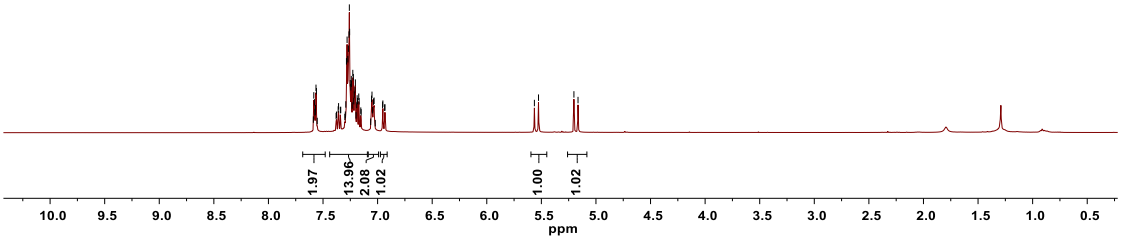


^{13}C NMR spectrum of 3z (101 MHz, $CDCl_3$)

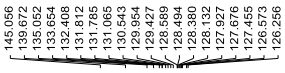


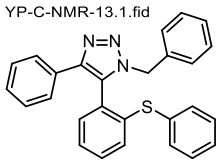


3aa

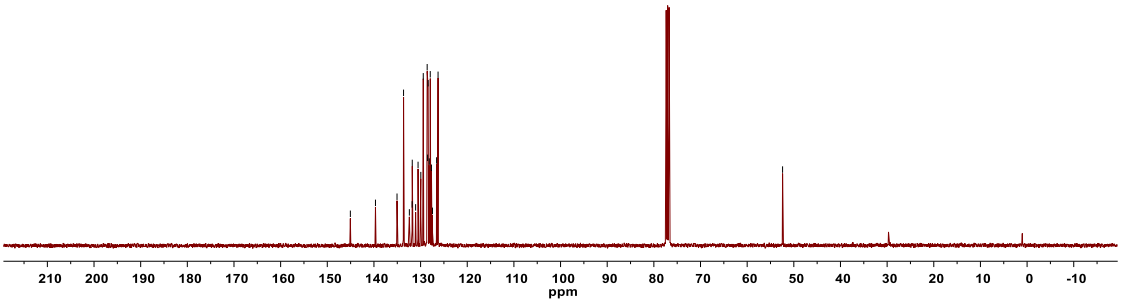


^{1}H NMR spectrum of 3aa (400 MHz, $CDCl_3$)

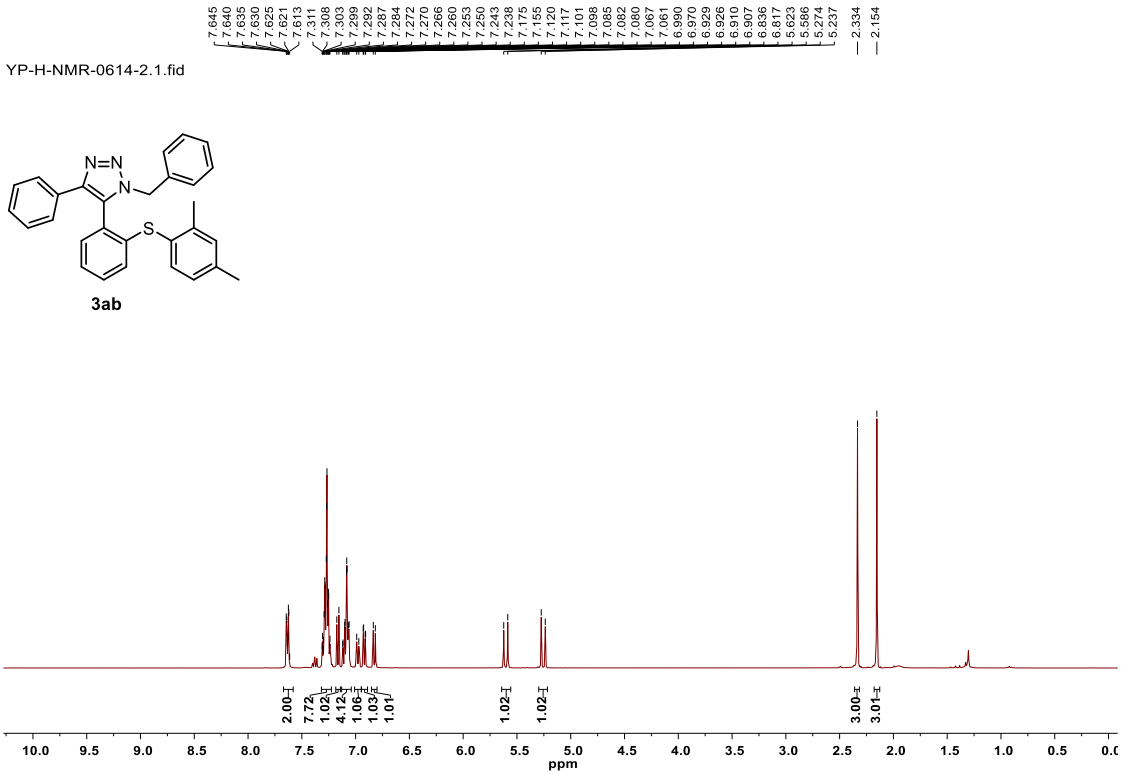




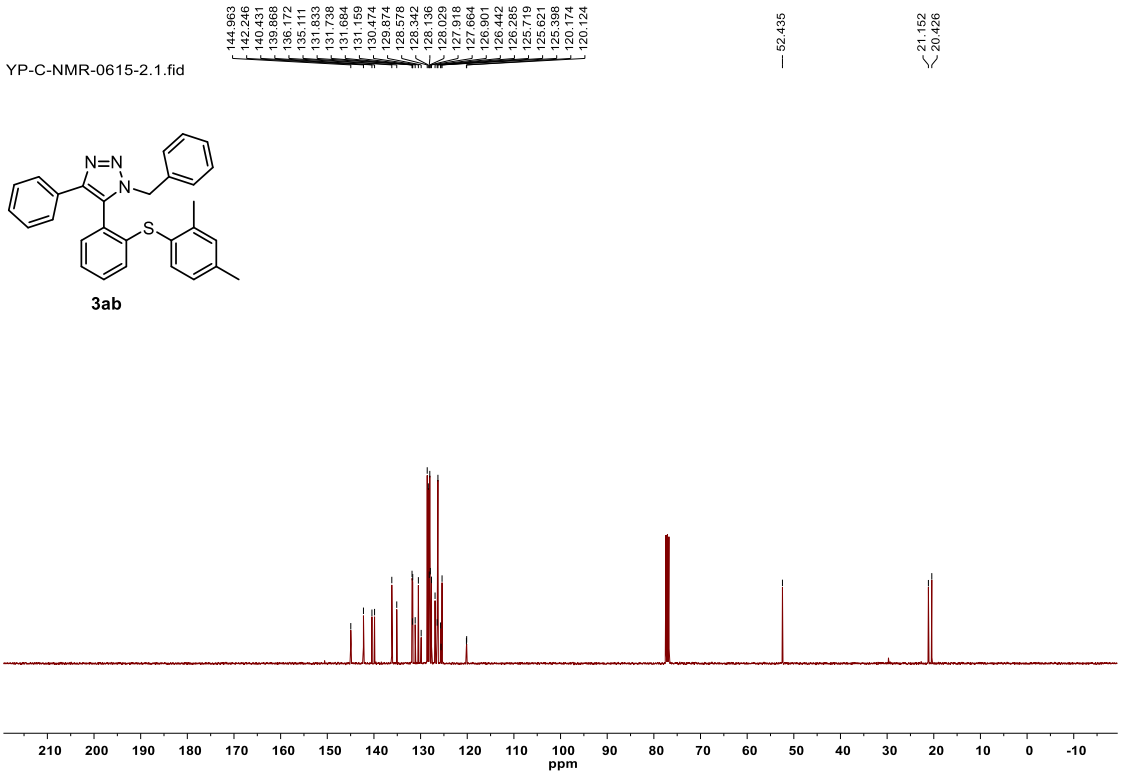
3aa



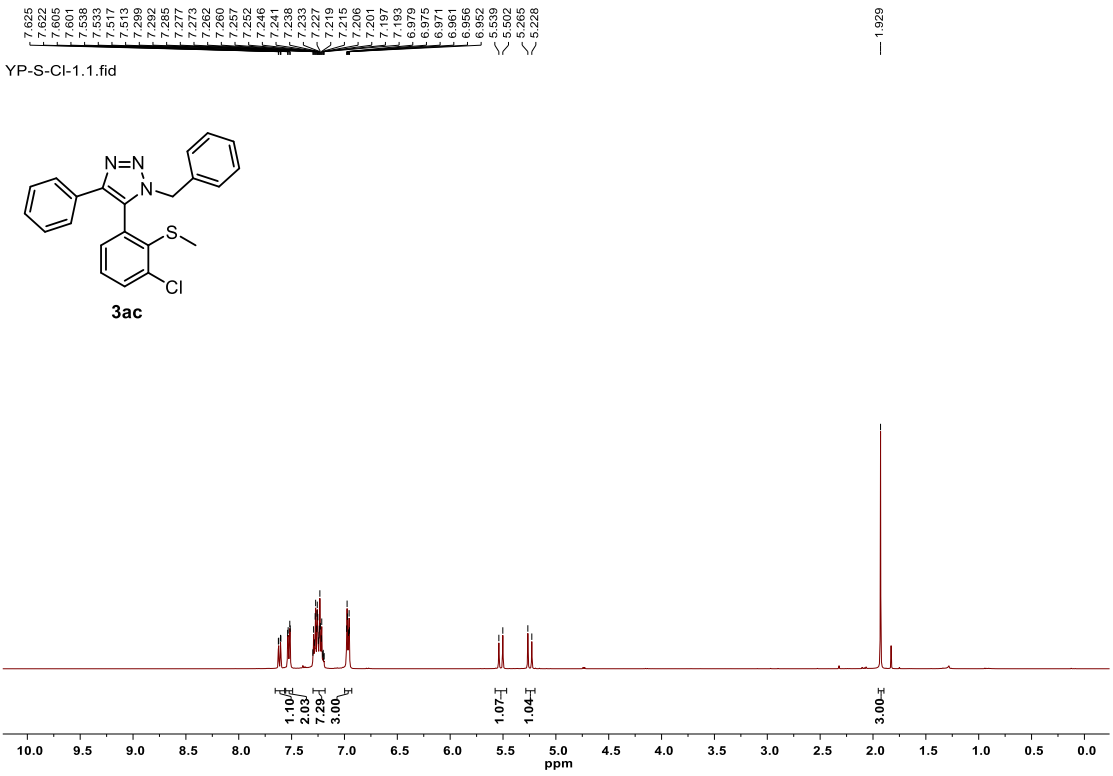
^{13}C NMR spectrum of 3aa (101 MHz, $CDCl_3$)



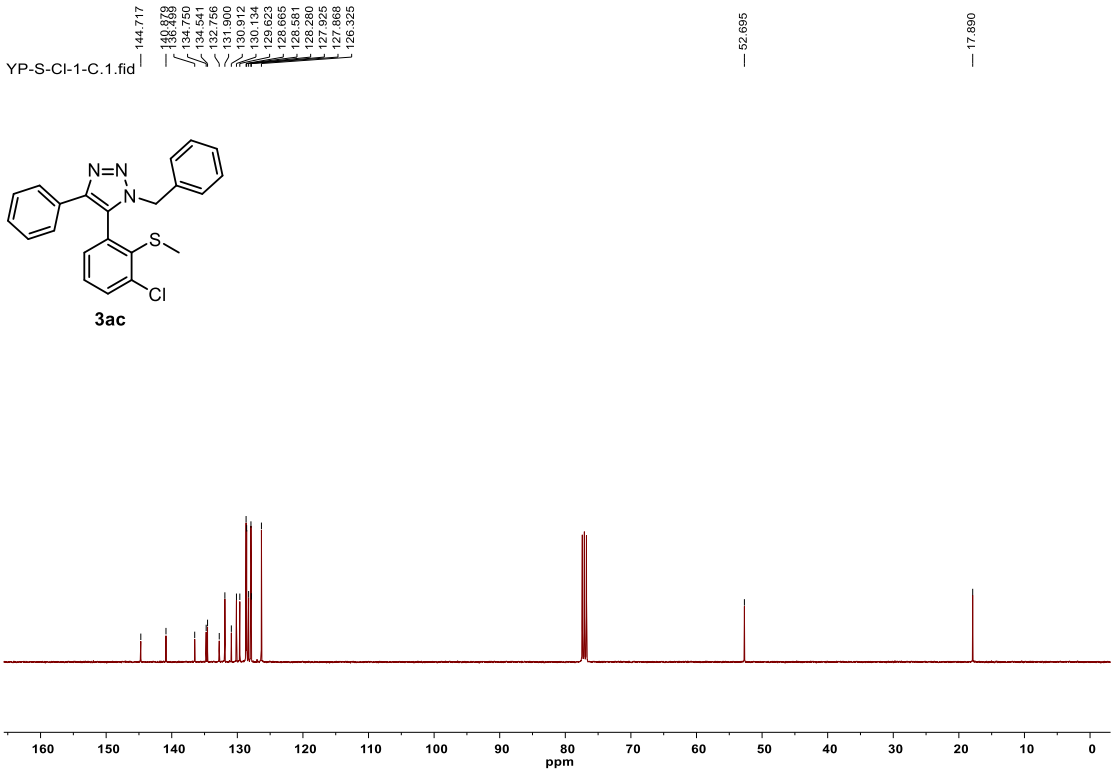
^{1}H NMR spectrum of 3ab (400 MHz, $CDCl_3$)



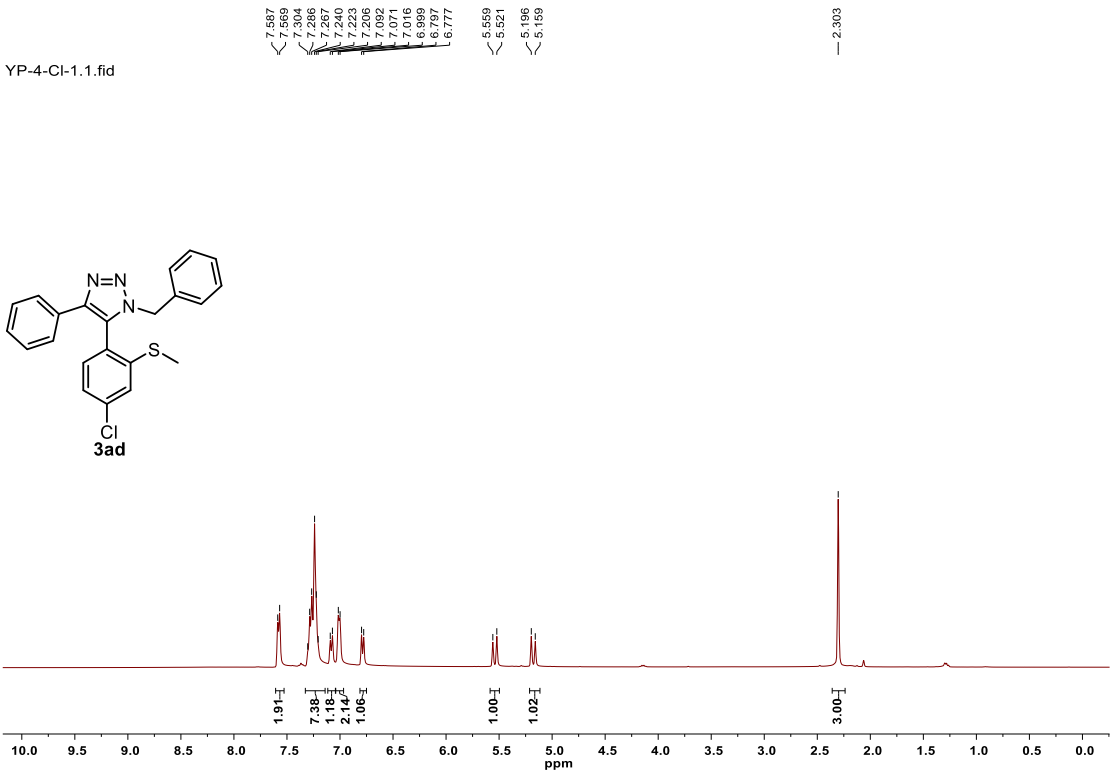
^{13}C NMR spectrum of 3ab (101 MHz, $CDCl_3$)



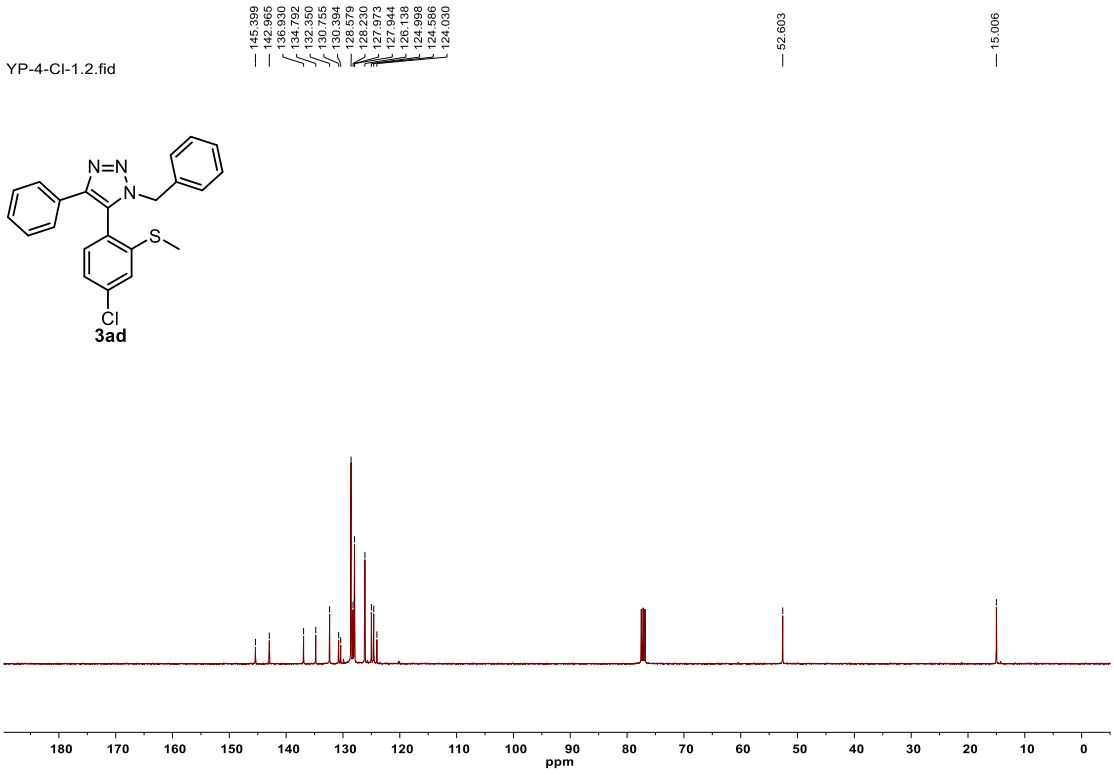
^{1}H NMR spectrum of 3ac (400 MHz, $CDCl_3$)



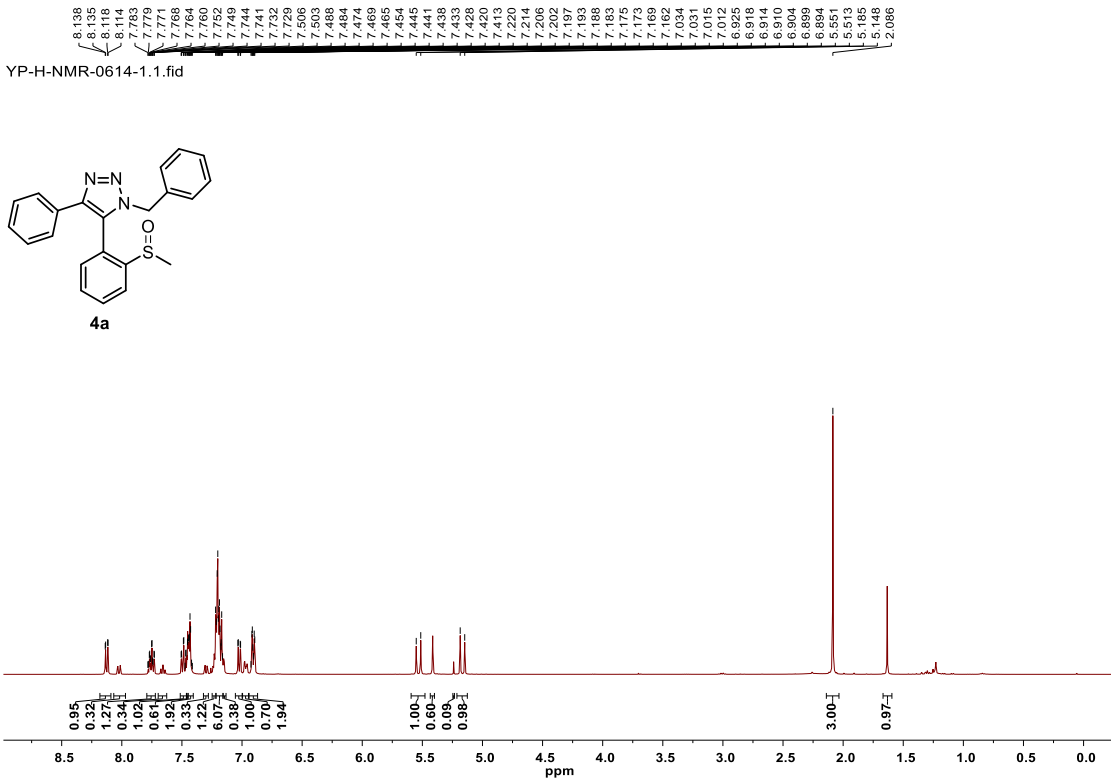
^{13}C NMR spectrum of 3ac (101 MHz, $CDCl_3$)



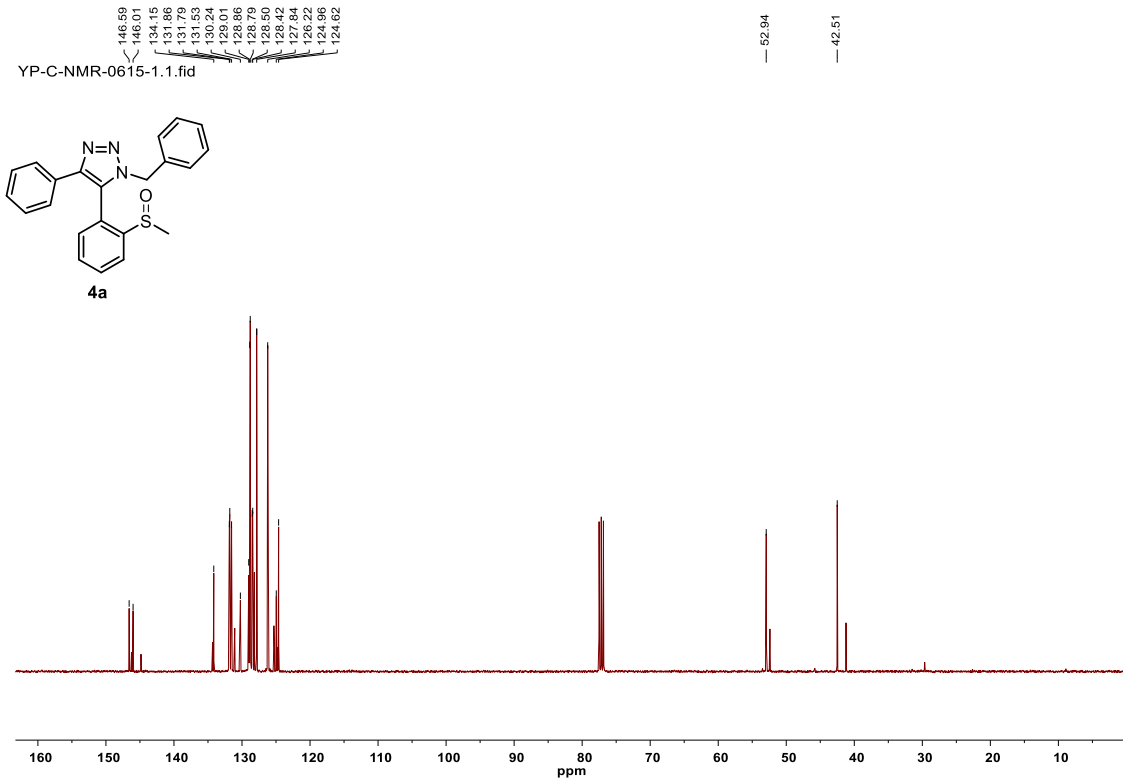
^{1}H NMR spectrum of 3ad (400 MHz, $CDCl_3$)



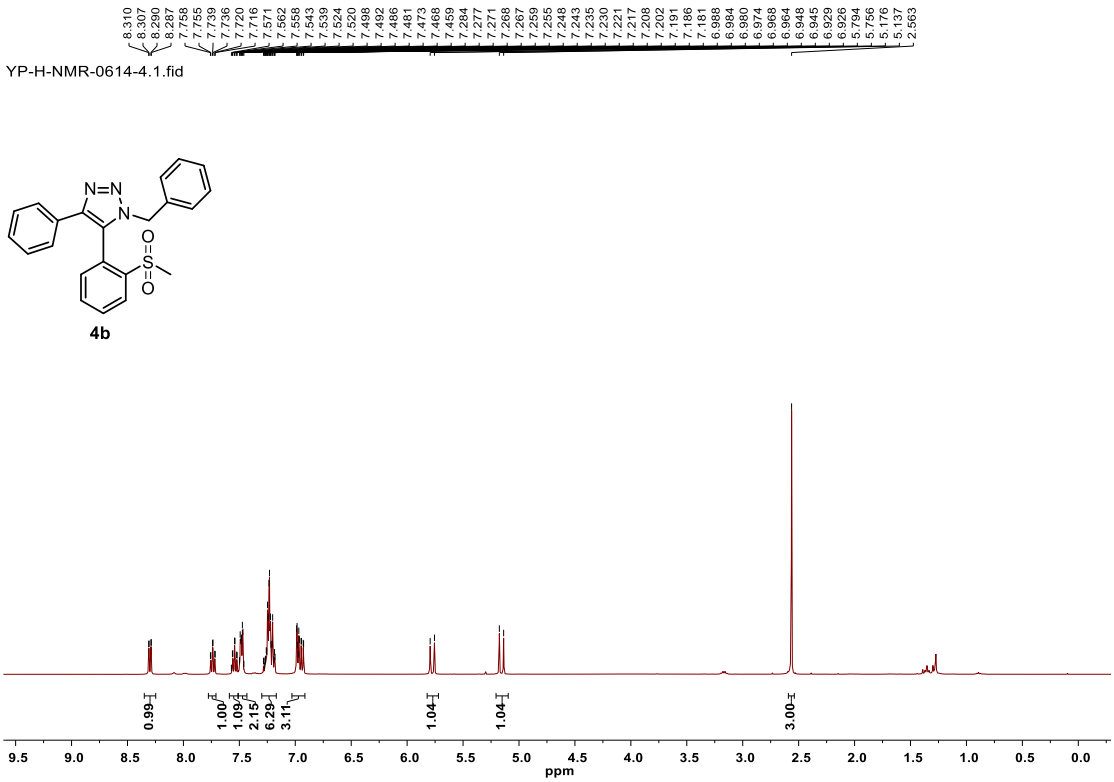
^{13}C NMR spectrum of 3ad (101 MHz, $CDCl_3$)



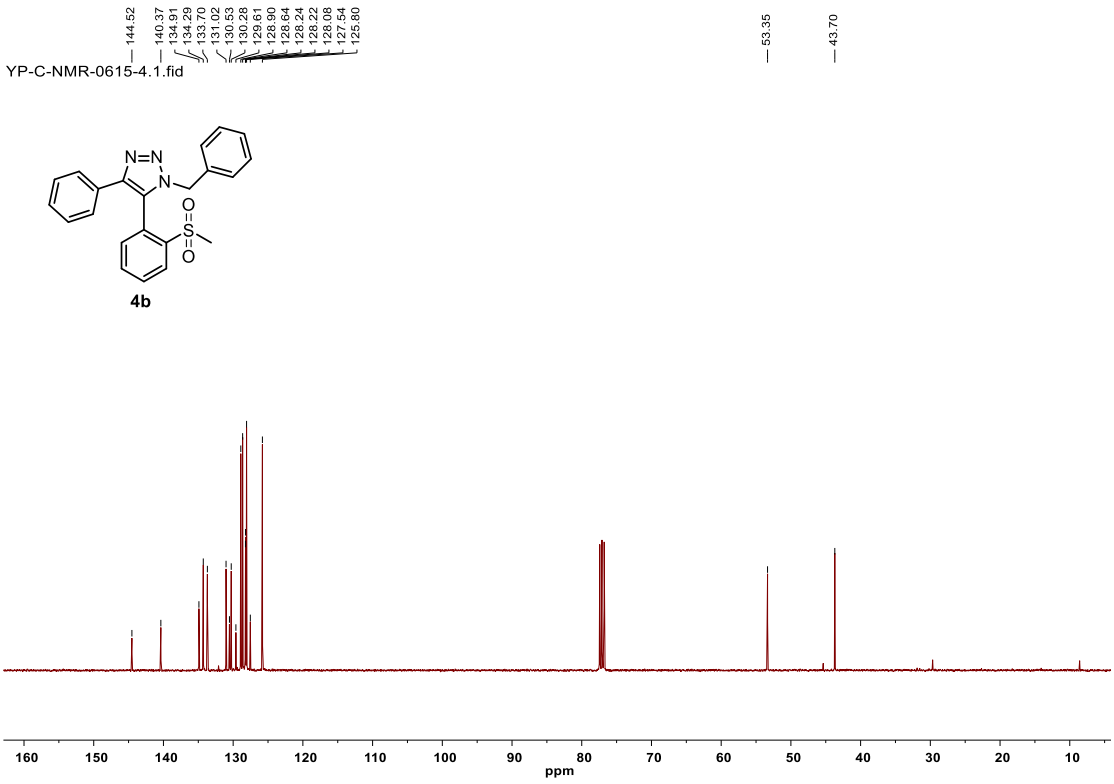
^{1}H NMR spectrum of 4a (400 MHz, $CDCl_3$)



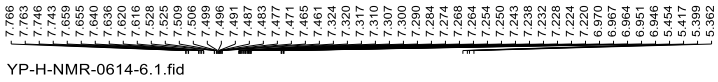
^{13}C NMR spectrum of 4a (101 MHz, $CDCl_3$)

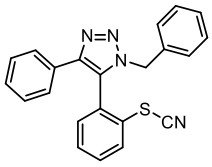


^{1}H NMR spectrum of 4b (400 MHz, $CDCl_3$)

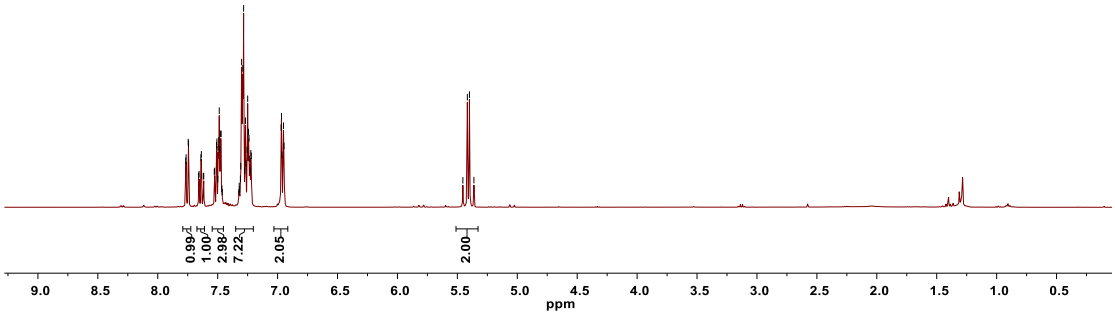


^{13}C NMR spectrum of 4b (101 MHz, $CDCl_3$)

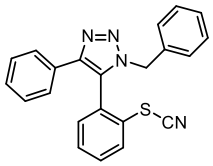




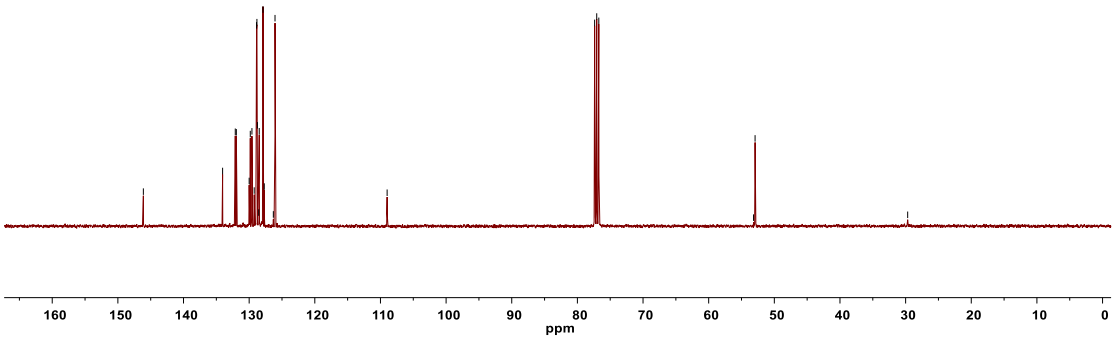
4c



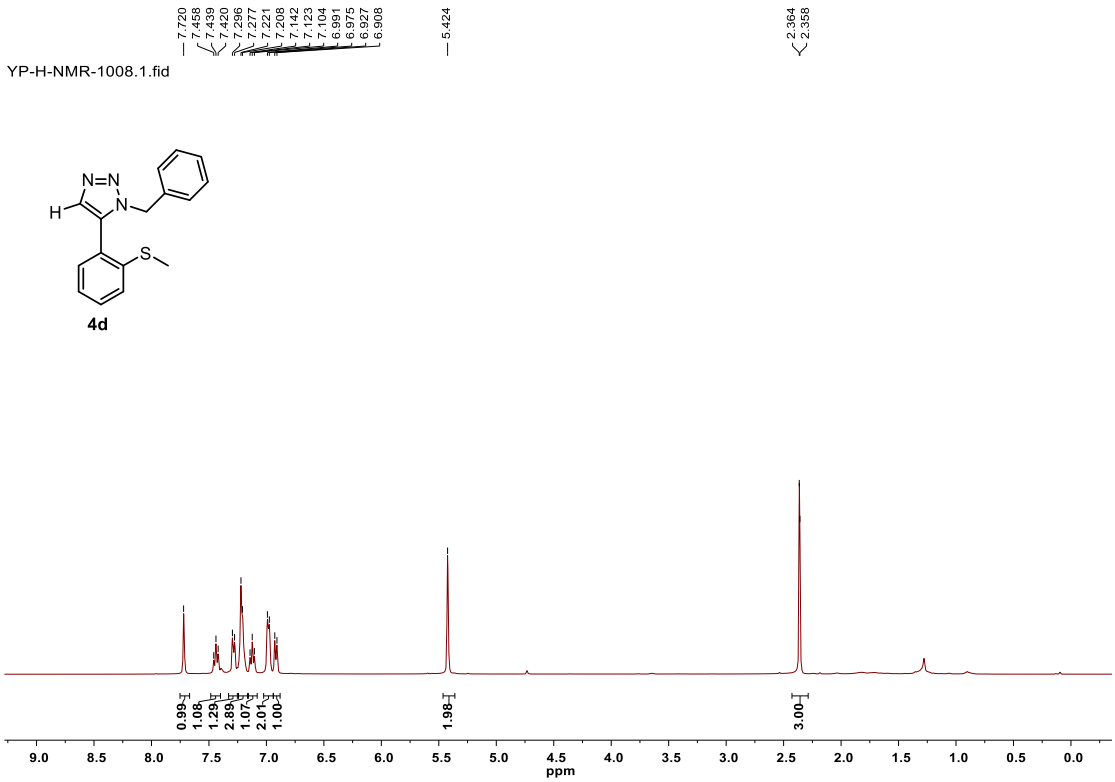
^{1}H NMR spectrum of 4c (400 MHz, $CDCl_3$)



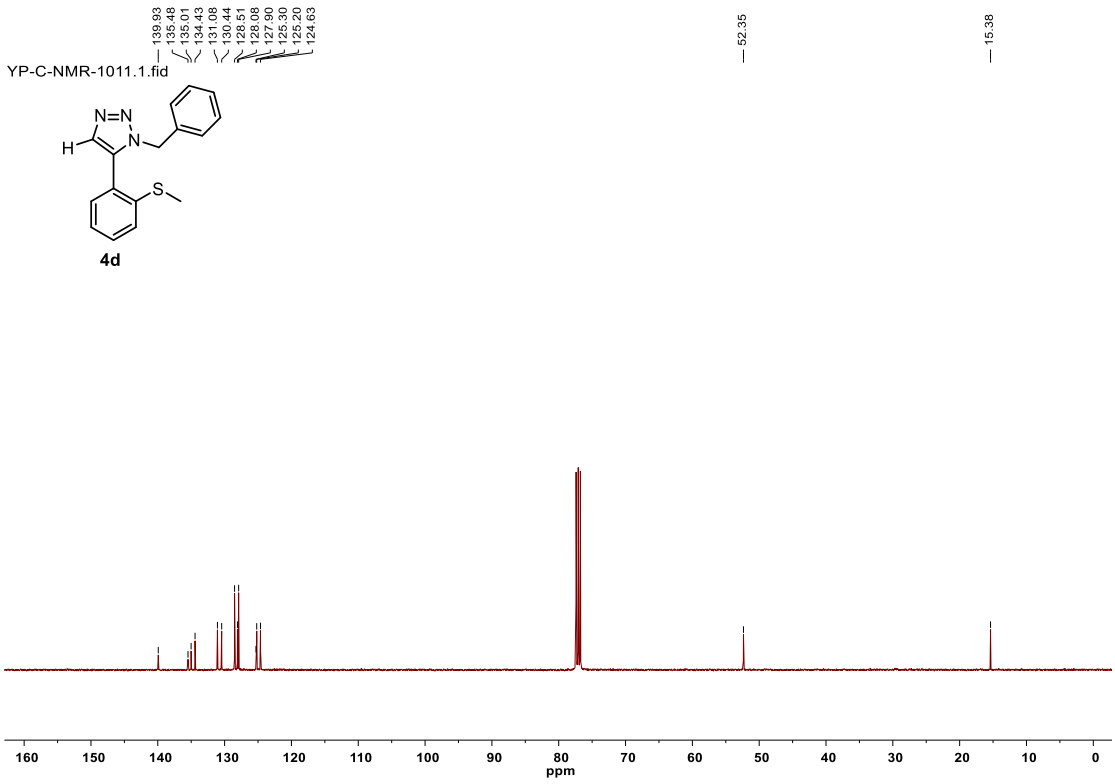
4c



^{13}C NMR spectrum of 4c (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of 4d (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4d (101 MHz, $CDCl_3$)