Supporting information

Palladium-Catalyzed Oxidative C-H/C-H Cross-Coupling of 1-Substituted 1,2,3-Triazoles with Furans and Thiophenes

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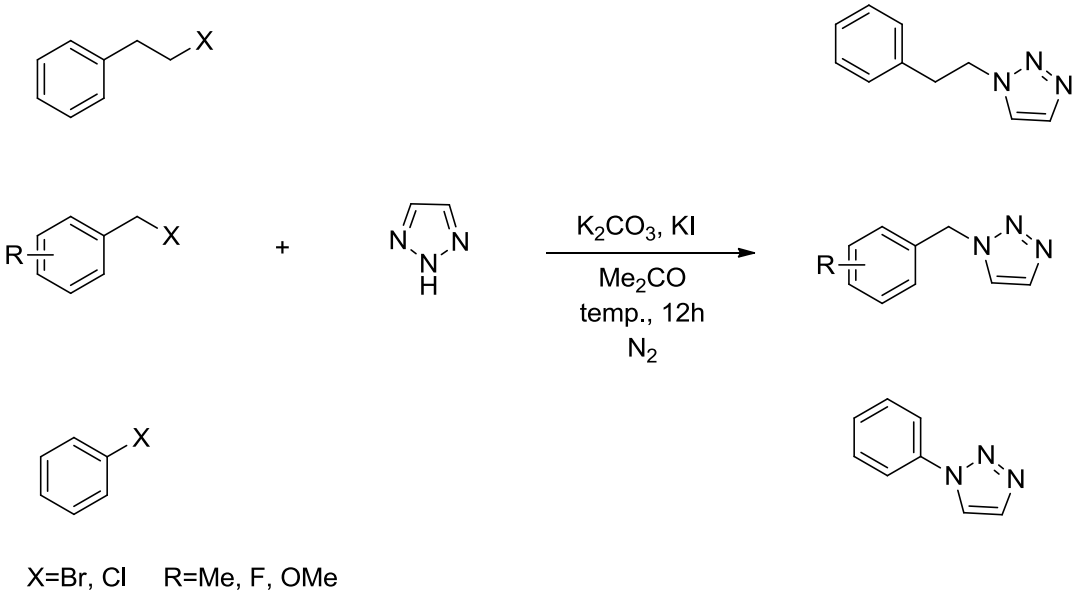
Table of Contents

1.
General Experimental

All commercially available reagents and solvent were obtained from the commercial providers and used without further purification. ^{1}H NMR spectra were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protic-solvent. ^{13}C NMR spectra were obtained at 101 MHz or 126MHz, and chemical shifts were record relative to the solvent resonance ($CDCl_3$, 77.0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). MS data were measured with a Varian-310 mass spectrometer. High resolution mass spectra were determined using a Finnigan-NAT GC/MS/DS 8430 spectrometer.IR spectra were obtained on a Nexus FT-IR spectrophotometer.

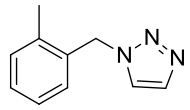
2.
The synthesis of 1-substituted-1, 2, 3-triazoles 1-Substituted-1,2,3-Triazoles were

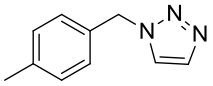
prepared according to known procedures (Scheme 1).[1]

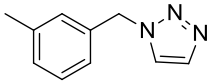


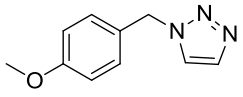
Scheme 1

Starting Material[2]


1-(2-methylbenzyl)-H-1,2,3-triazole
(1a)


1-(4-methylbenzyl)-H-1,2,3-triazole
(1b)


1-(3-methylbenzyl)-H-1,2,3-triazole (1c)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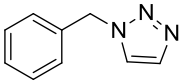
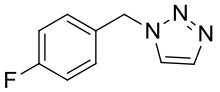
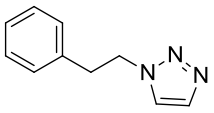
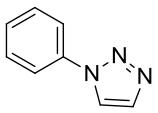
(1d)


1-benzyl-H-1,2,3-triazole
(1e)


1-(4-fluorobenzyl)-H-1,2,3-triazole
(1f)


1-phenethyl-H-1,2,3-triazole
(1aa)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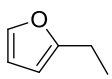
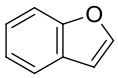
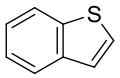

2-ethylfuran
(2a)


benzofuran
(2b)


2-methylfuran
(2c)


2-methylthiophene
(2d)

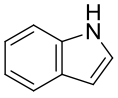

benzo[*b*]thiophene
(2e)

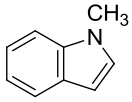

thiophene
(2f)


4,5-dimethylthiazole
(2g)


pyrrole
(2h)


1-methyl-pyrrole
(2i)


indole
(2j)

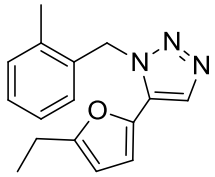

1-methyl-indole
(2k)

3.

General Procedure for Coupling of 1-benzyl-1,2,3-triazoles and thiophens or funans

Funans(Thiophens) **2** (115.4 mg, 1.2 mmol, 3 equiv) was added to an oven-dried, sealed tube charged with 1-substituted 1,2,3-triazoles **1** (69.2 mg, 0.4 mmol, 1 equiv), $Pd(OAc)_2$ (9 mg, 0.04 mmol, 10 mol%), Ag_2CO_3 (100 mg, 0.6 mmol, 1.5 equiv) and pyridine (0.1 mL, 1.2 mmol, 3 equiv) in toluene (2 mL). The reaction mixture was stirred at 90 ^oC for 18 h. After reaction was completed (as monitored by TLC), the mixture was cooled to room temperature. The solvent was then evaporated in vacuum. The resulting residue was purified by columnchromatography (silica gel, eluent: Petroleum ether/EtOAc=3:1) to afford product **3**.

Spectroscopic and Analytical Data of compound



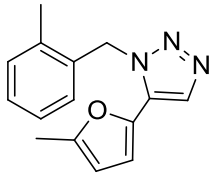
5-(5-ethylfuran-2-yl)-1-(2-methylbenzyl)-1H-1,2,3-triazole (3a, 70%), Brown Oil:

^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.21 (d, *J* = 6.7 Hz, 2H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 6.05 (d, *J* = 3.2 Hz, 1H), 5.75 (s, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.45 (s), 139.42 (s), 134.92 (s), 133.53 (s), 131.77 (s), 130.38 (s), 129.74 (s), 127.91 (s), 126.44 (s), 126.36 (s), 110.98 (s), 106.29 (s), 50.63 (s), 21.33 (s), 19.12 (s), 11.91 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{17}N_3O$ (M^+): 267.1372; found: 267.1366

IR:$_{max}$(thin film) (cm $^{-1}$) =2974, 1715, 1684, 1495, 1024, 742.



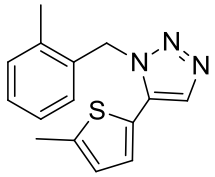
1-(2-methylbenzyl)-5-(5-methylfuran-2-yl)-1H-1,2,3-triazole (3b, 65%), Brown oil:

^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.21 (d, *J* = 6.2 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 5.75 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.82 (s), 139.54 (s), 134.99 (s), 133.48 (s), 131.80 (s), 130.40 (s), 129.65 (s), 127.95 (s), 126.46 (s), 111.15 (s), 107.84 (s), 50.59 (s), 19.14 (s), 13.50 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3O$ (M^+): 253.1215; found: 253.1207

IR:$_{max}$(thin film) (cm $^{-1}$) = 2921, 2851, 1646, 1582, 1450, 744, 977.



1-(2-methylbenzyl)-5-(5-methylthiophen-2-yl)-1H-1,2,3-triazole (3c, 56%), Yellow solid:

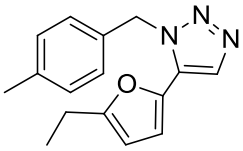
^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.12 (dt, *J* = 8.5, 4.3 Hz, 1H), 6.77 (d, *J* =

3.6 Hz, 1H), 6.72 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.64 (s, 2H), 2.50 (s, 3H), 2.35 (s, 3H). mp. 101.7 ^{o}C-102.3 ^{o}C

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00 (s), 134.88 (s), 133.74 (s), 133.35 (s), 132.40 (s), 130.45 (s), 128.21 (s), 128.01 (s), 126.53 (s), 126.33 (s), 126.22 (s), 124.11 (s), 49.86 (s), 19.16 (s), 15.23 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}N_{15}N_3S$ (M^+): 269.0987; found: 269.0981

IR:$_{max}$(thin film) (cm $^{-1}$) =3015, 2966, 1658, 1513, 1430, 951.



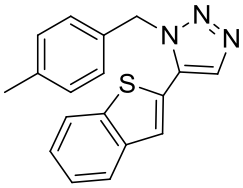
1-(4-methylbenzyl)-5-(5-methylfuran-2-yl)-1H-1,2,3-triazole (3d, 60%), Brown oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 3.1 Hz, 1H), 5.73 (s, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.38 (s), 139.51 (s), 137.87 (s), 132.28 (s), 131.70 (s), 129.45 (s), 128.14 (s), 127.02 (s), 111.05 (s), 106.28 (s), 52.55 (s), 21.38 (s), 21.06 (s), 12.04 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{17}N_3O$ (M^+): 267.1372; found: 267.1369

IR:$_{max}$(thin film) (cm $^{-1}$) =2358, 1665, 1580, 1409, 713.



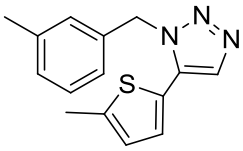
5-(benzothiophen-2-yl)-1-(4-methylbenzyl)-1H-1,2,3-triazole (3e, 59%), Brown solid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.89 – 7.83 (m, 1H), 7.79 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.42 (dd, *J* = 5.9, 3.2 Hz, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.73 (s, 2H), 2.35 (s, 3H). mp. 104.4-105.8 ^{o}C

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.24 (s), 139.38 (s), 138.13 (s), 134.34 (s), 132.16 (s), 129.61 (s), 126.98 (s), 125.52 (s), 125.15 (s), 125.02 (s), 124.17 (s), 123.72 (s), 122.19 (s), 121.41 (s), 52.09 (s), 21.10 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N_3S$ (M^+): 305.0987; found: 305.0979

IR:$_{max}$(thin film) (cm $^{-1}$) =3182, 2998, 1764, 1642, 1598.



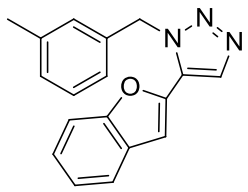
1-(3-methylbenzyl)-5-(5-methylthiophen-2-yl)-1H-1,2,3-triazole (3f, 63%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 5.63 (s, 2H), 2.52 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.91 (s), 138.67 (s), 135.31 (s), 133.47 (s), 128.88 (s), 128.72 (s), 128.45 (s), 127.58 (s), 126.15 (s), 124.17 (s), 123.97 (s), 51.86 (s), 21.35 (s), 15.20 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3S$ (M^+):269.0987; found: 269.0972.

IR:$_{max}$(thin film) (cm $^{-1}$) =3119, 3005, 2361, 1631, 1471, 1335, 789.



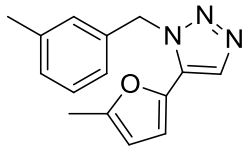
5-(benzofuran-2-yl)-1-(3-methylbenzyl)-1H-1,2,3-triazole (3g, 60%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.89 (s, 1H), 5.88 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.85 (s), 143.12 (s), 138.74 (s), 134.89 (s), 133.58 (s), 129.07 (s), 128.78 (s), 127.83 (s), 125.71 (s), 124.18 (s), 123.65 (s), 121.55 (s), 111.35 (s), 106.53 (s), 53.19 (s), 21.34 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N_3O$ (M^+): 289.1215; found: 289.1215; found: 289.1212

IR:$_{max}$(thin film) (cm $^{-1}$) =3012, 2501, 1789, 1560, 1485, 997, 765.



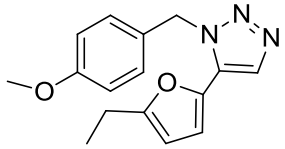
1-(3-methylbenzyl)-5-(5-methylfuran-2-yl)-1H-1,2,3-triazole (3h, 65%), Brown oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 9.6 Hz, 2H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 2.6 Hz, 1H), 5.73 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.74 (s), 139.62 (s), 138.58 (s), 135.18 (s), 131.72 (s), 129.31 (s), 128.86 (s), 128.65 (s), 127.77 (s), 124.14 (s), 111.23 (s), 107.83 (s), 52.72 (s), 21.34 (s), 13.56 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3O$ (M^+): 253.1215; found: 253.1208

IR:$_{max}$(thin film) (cm $^{-1}$) =2980, 2633, 1675, 1540, 1486, 1028, 798.



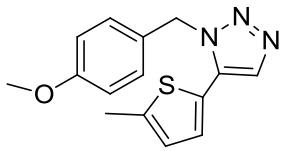
5-(5-ethylfuran-2-yl)-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4a, 79%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.44 (d, *J* = 3.3 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 5.71 (s, 2H), 3.79 (s, 3H), 2.73 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.43 (s), 159.39 (s), 139.53 (s), 131.81 (s), 129.78 (s), 128.56 (s), 127.37 (s), 114.17 (s), 111.09 (s), 106.30 (s), 55.25 (s), 52.30 (s), 21.41 (s), 12.07 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{17}N_3O_2$ (M^+): 283.1321; found: 283.1316

IR:$_{max}$(thin film) (cm $^{-1}$) =3021, 2918, 2848, 1658, 1547, 1467, 1024, 712.



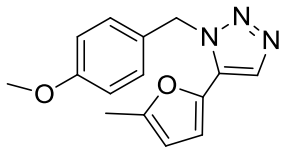
1-(4-methoxybenzyl)-5-(5-methylthiophen-2-yl)-1H-1,2,3-triazole (4b, 67%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.86 (dd, *J* = 6.3, 2.3 Hz, 3H), 6.77 – 6.74 (m, 1H), 5.59 (s, 2H), 3.80 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.47 (s), 142.92 (s), 133.53 (s), 131.89 (s), 128.51 (s), 128.48 (s), 127.42 (s), 126.13 (s), 124.17 (s), 114.23 (s), 55.27 (s), 51.45 (s), 15.22 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3OS$ (M^+): 285.0936; found: 285.0930

IR:$_{max}$(thin film) (cm $^{-1}$) =2979, 2847, 1701, 1532, 1310, 978.



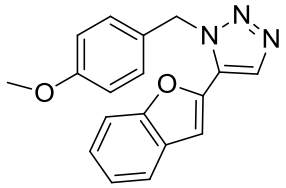
1-(4-methoxybenzyl)-5-(5-methylfuran-2-yl)-1H-1,2,3-triazole (4c, 76%), Brown oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 3.2 Hz, 1H), 6.08 (d, *J* = 2.9 Hz, 1H), 5.70 (s, 2H), 3.79 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.44 (s), 153.73 (s), 139.65 (s), 131.78 (s), 129.79 (s), 128.60 (s), 127.34 (s), 114.16 (s), 111.24 (s), 107.83 (s), 55.25 (s), 52.28 (s), 13.59 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3O_2$ (M^+): 269.1164; found: 269.1156

IR:$_{max}$(thin film) (cm $^{-1}$) =3024, 2878, 1726, 1691, 1564, 1153, 1076, 937.



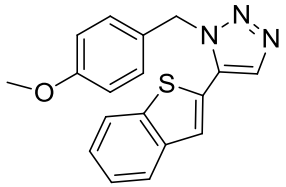
5-(benzofuran-2-yl)-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4d, 71%), Yellow solid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.91 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.86 (s, 2H), 3.77 (s, 3H). mp. 100.7-101.5 ^{o}C

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.58 (s), 154.88 (s), 143.19 (s), 133.63 (s), 129.82 (s), 128.71 (s), 127.82 (s), 127.06 (s), 125.69 (s), 123.68 (s), 121.55 (s), 114.29 (s), 111.35 (s), 106.54 (s), 55.25 (s), 52.77 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N_3O_2$ (M^+): 305.1164; found: 305.1161

IR:$_{max}$(thin film) (cm $^{-1}$) =3118, 3030, 1764, 1692, 1582, 1547, 1141, 975.



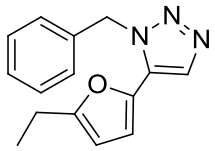
5-(benzo[b]thiophen-2-yl)-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4e, 70%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.90 – 7.84 (m, 1H), 7.83 – 7.75 (m, 1H), 7.46 – 7.38 (m, 2H), 7.29 (d, *J* = 3.1 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.70 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.57 (s), 140.27 (s), 139.35 (s), 128.54 (s), 127.12 (s), 126.92 (s), 125.53 (s), 125.27 (s), 125.02 (s), 124.17 (s), 122.19 (s), 114.30 (s), 55.26 (s), 51.96 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N_3OS$ (M^+): 321.0936; found: 321.0922.

IR:$_{max}$(thin film) (cm $^{-1}$) =3021, 2877, 2250, 1658, 1632, 1549, 1484, 1021, 949.



1-benzyl-5-(5-ethylfuran-2-yl)-1H-1,2,3-triazole (5a, 73%), Brown oil:

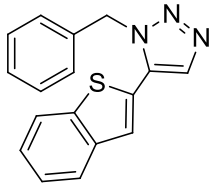
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.36 – 7.29 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 6.41 (d, *J* = 3.3 Hz,

1H), 6.07 (d, *J* = 3.3 Hz, 1H), 5.78 (s, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.44 (s), 139.43 (s), 135.32 (s), 131.71 (s), 129.41 (s), 128.79 (s), 128.08 (s), 126.99 (s), 111.09 (s), 106.30 (s), 52.75 (s), 21.37 (s), 12.02 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3O$ (M^+): 253.1215; found: 253.1200

IR:$_{max}$(thin film) (cm $^{-1}$) =3007, 2918, 2848, 1631, 1469, 1137, 717.



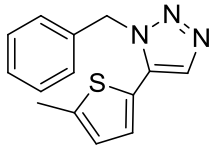
5-(benzo[b]thiophen-2-yl)-1-benzyl-1H-1,2,3-triazole (5b, 66%), Yellow solid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.88 – 7.83 (m, 1H), 7.78 (dd, *J* = 6.4, 2.7 Hz, 1H), 7.42 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.34 (d, *J* = 6.6 Hz, 3H), 7.28 (d, *J* = 6.3 Hz, 1H), 7.20 – 7.14 (m, 2H), 5.77 (s, 2H). mp. 100.9-101.6 ^{o}C

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.24 (s), 139.35 (s), 135.18 (s), 134.39 (s), 128.95 (s), 128.30 (s), 126.98 (s), 125.55 (s), 125.19 (s), 125.04 (s), 124.18 (s), 122.19 (s), 52.25 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{13}N_3S$ (M^+): 291.0830; found: 291.0825

IR:$_{max}$(thin film) (cm $^{-1}$) =3019, 2811, 1658, 1630, 1502, 1443, 990.



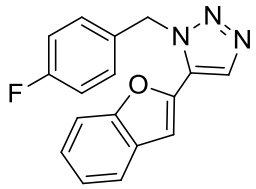
1-benzyl-5-(5-methylthiophen-2-yl)-1H-1,2,3-triazole (5c, 58%), Yellow solid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 3H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 3.5 Hz, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 5.67 (s, 2H), 2.52 (s, 3H). mp. 108.9-109.5 ^{o}C

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.96 (s), 135.40 (s), 133.50 (s), 128.87 (s), 128.46 (s), 128.13 (s), 126.93 (s), 126.16 (s), 124.08 (s), 51.88 (s), 15.21 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{13}N_3S$ (M^+): 255.0830; found: 255.0824.

IR:$_{max}$(thin film) (cm $^{-1}$) =3010, 1764, 1691, 1482, 1468, 1385, 975.



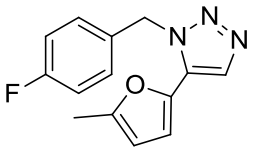
5-(benzofuran-2-yl)-1-(4-fluorobenzyl)-1H-1,2,3-triazole (6a, 55%), Yellow solid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.92 (s, 1H), 5.89 (s, 2H). mp. 101.3-102.5 ^{o}C

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.58 (d, *J* = 247.5 Hz), 154.88 (s), 142.94 (s), 133.65 (s), 130.83 (d, *J* = 2.7 Hz), 129.15 (d, *J* = 8.2 Hz), 127.70 (s), 125.80 (s), 123.77 (s), 121.59 (s), 115.87 (d, *J* = 21.8 Hz), 114.47 (s), 111.30 (s), 106.66 (s), 52.54 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{12}FN_3O$ (M^+): 293.0964; found: 293.0959

IR:$_{max}$(thin film) (cm $^{-1}$) =2880, 2792, 1819, 1744, 1428, 803.



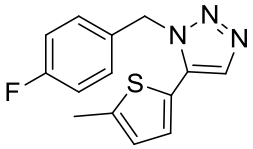
1-(4-fluorobenzyl)-5-(5-methylfuran-2-yl)-1H-1,2,3-triazole (6b, 60%), Brown oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.24 – 7.15 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H),6.42 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 2.4 Hz, 1H), 5.75 (s, 2H),2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.51 (d, *J* = 247.1 Hz), 153.88 (s), 139.45 (s), 131.82 (s), 131.09 (d, *J* = 2.7 Hz), 130.28 (s), 129.03 (d, *J* = 8.2 Hz), 115.75 (d, *J* = 21.7 Hz), 111.36 (s), 107.89 (s), 52.10 (s), 13.58 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{12}FN_3O$ (M^+): 257.0964; found: 257.0960

IR:$_{max}$(thin film) (cm $^{-1}$) =2918, 2848, 1735, 1631, 1597, 1021.



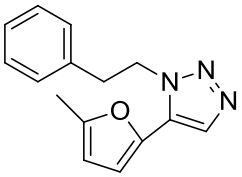
1-(4-fluorobenzyl)-5-(5-methylthiophen-2-yl)-1H-1,2,3-triazole (6c, 49%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.16 – 7.09 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.76 (d, *J* = 2.6 Hz, 1H), 5.63 (s, 2H), 2.53 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.53 (d, *J* = 247.2 Hz), 143.14 (s), 133.64 (s), 132.01 (s), 131.10 (d, *J* = 2.6 Hz), 128.92 (d, *J* = 8.2 Hz), 128.57 (s), 126.17 (s), 123.89 (s), 115.83 (d, *J* = 21.8 Hz), 51.23 (s), 15.22 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{12}FN_3S$ (M^+): 273.0736; found: 273.0729

IR:$_{max}$(thin film) (cm $^{-1}$) =3009, 2361, 1658, 1644, 1581, 1432, 1214, 1122, 990.



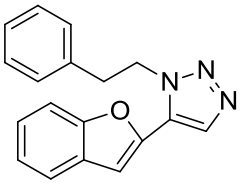
5-(5-methylfuran-2-yl)-1-phenethyl-1H-1,2,3-triazole (3ab, 51%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.34 – 7.29 (m, 2H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.47 (d, *J* = 3.3 Hz, 1H), 6.18 – 6.08 (m, 1H), 4.84 – 4.66 (m, 2H), 3.31 – 3.14 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 153.80 (s), 139.74 (s), 137.20 (s), 128.74 (s), 128.71 (s), 126.97 (s), 111.04 (s), 107.86 (s), 50.62 (s), 36.60 (s), 13.68 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{15}N_3O$ (M^+): 253.1215; found: 253.1204.

IR:$_{max}$(thin film) (cm $^{-1}$) =3119, 3020, 2880, 1659, 1573, 1484, 1441, 1110, 1052, 998.



5-(benzofuran-2-yl)-1-phenethyl-1H-1,2,3-triazole (3ac, 49%), Pink solid:

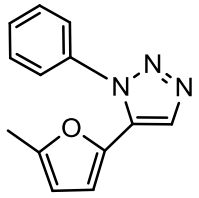
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.69 – 7.61 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 6.8 Hz, 2H), 6.92 (s, 1H), 4.98 – 4.87 (m, 2H), 3.34 – 3.24 (m, 2H). mp. 99.2-99.8 ^{o}C

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.95 (s), 143.22 (s), 137.00 (s), 133.31 (s), 128.75 (s), 127.80 (s), 127.04 (s),

125.70 (s), 123.75 (s), 121.54 (s), 111.36 (s), 106.43 (s), 51.11 (s), 36.74 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N_3O$ (M^+): 289.1215; found: 289.1206.

IR:$_{max}$(thin film) (cm $^{-1}$) =3195, 2847, 1764, 1646, 1631, 1469, 1422, 1029.



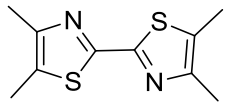
5-(5-methylfuran-2-yl)-1-phenyl-1H-1,2,3-triazole (3ad, 43%), Brown oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 3H), 6.22 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 2.5 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.64 (s), 140.15 (s), 138.55 (s), 133.27 (s), 132.24 (s), 126.02 (s), 117.64 (s), 113.64 (s), 112.35 (s), 107.96 (s), 13.54 (s).

HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{11}N_3O$ (M^+): 225.0902; found: 225.0898

IR:$_{max}$(thin film) (cm $^{-1}$) =3123, 2918, 1785, 1680, 1549, 1436, 1256. 1120, 993.



4,4',5,5'-tetramethyl-2,2'-bithiazole (3eg, 95%), Yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H), 2.40 (s, 6H).

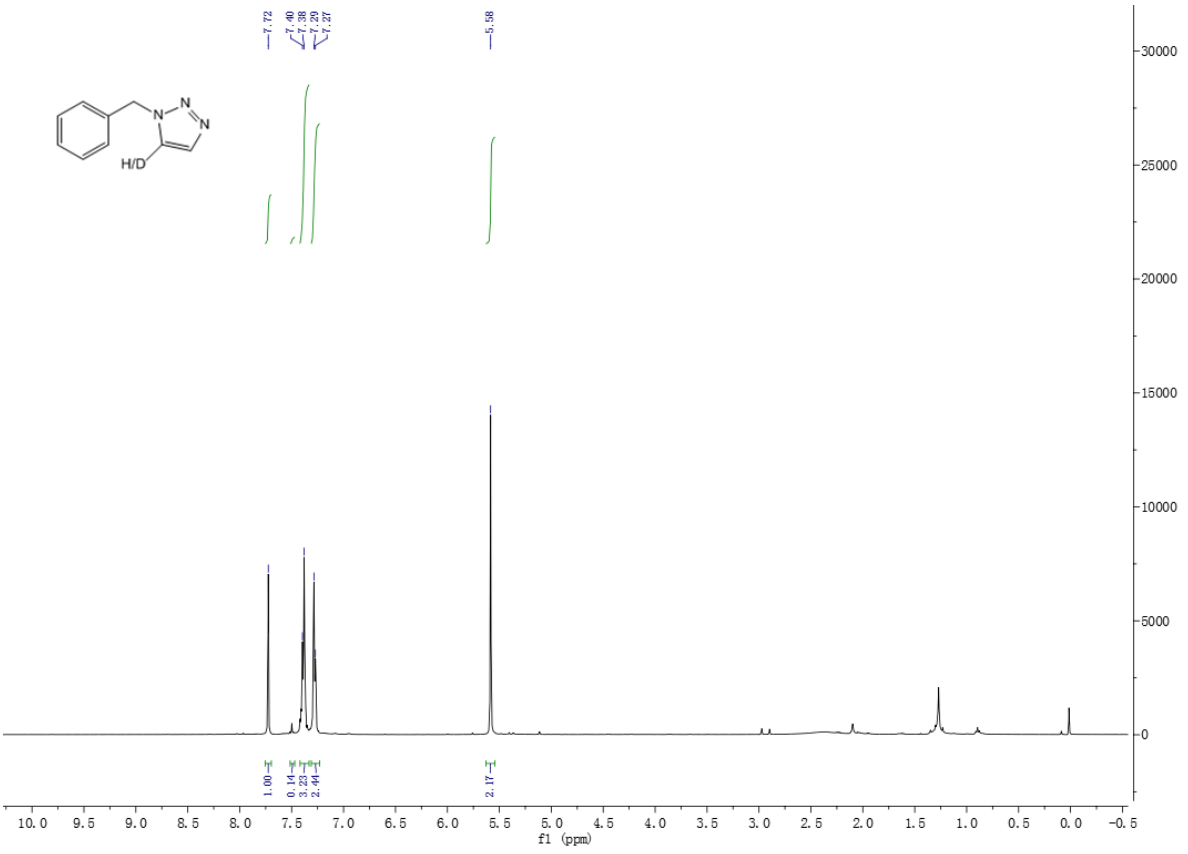
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.11 (s), 149.56 (s), 128.20 (s), 14.85 (s), 11.66 (s).

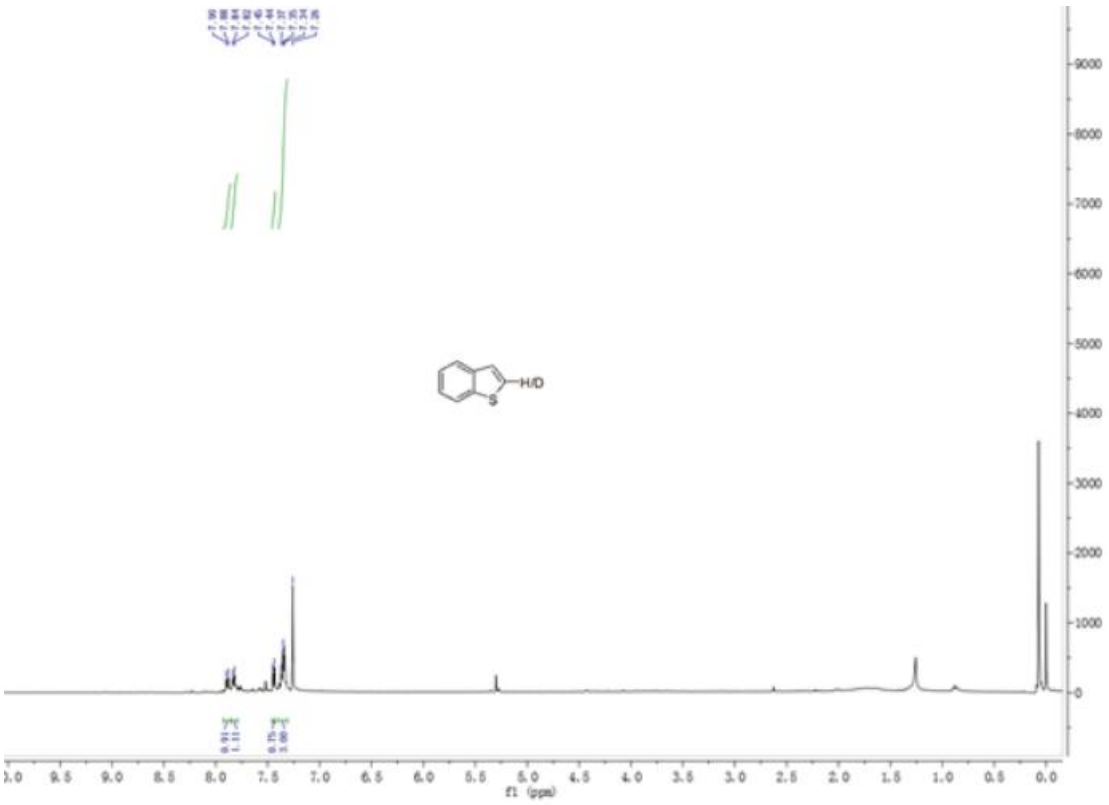
The spectral data obtained were in accordance with those described in the literature.[4]

4.

The H/D Exchange Control Experiments[3]

A mixture of 1-benzyl-1,2,3-triazole(1e) (0.4 mmol), $Pd(OAc)_2$ (0.04 mmol), Ag_2CO_3 (0.6 mmol) and D_2O (0.1 mL) in toluene (2 mL) as stirred at 100 ℃ for 18 h in sealed tube. After cooling, the reaction solution concentrated under vacuum to yield the crude product. The ratio of 1ee-H and 1ee-D was determined by ^{1}H NMR analysis of the crude product and found that the ratio of 1ee-H and 1ee-D was 1:7. The same operation of 2e. The ratio of 2ee-H and 2ee-D was 3:1.


7.72
7.40
7.38
7.29
7.27
5.58
H/D
1.00
0.14
3.23
2.44
2.17
f1 (ppm)


H/D
S
f1 (ppm)

5.

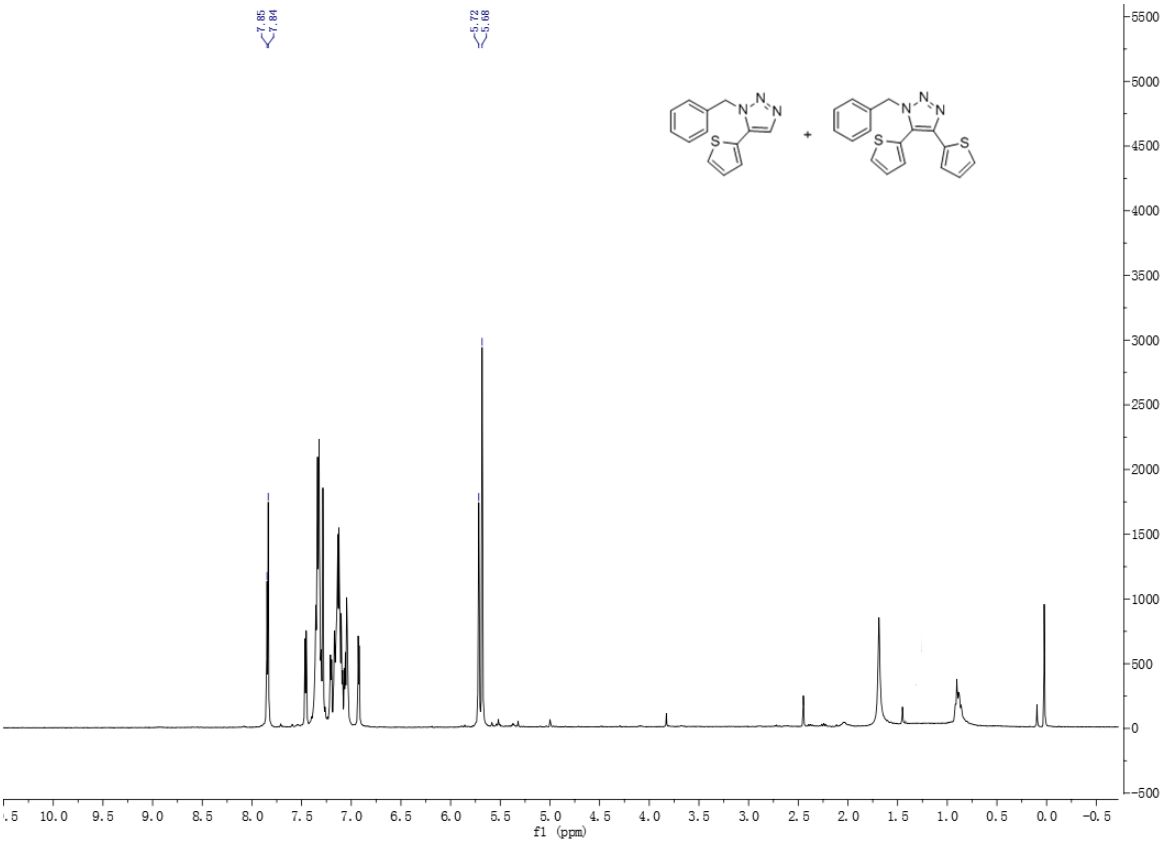
Coupling of 1-benzyl-H-1,2,3-triazole and thiophene

NMR Spectra of the 1-benzyl-H-1,2,3-triazole and thiophene coupling product.

we guessed that the products was mixture and later the data of GC-MS was affirmed this suspect

HRMS(ESI-TOF) m/z Calcd for $C_{13}H_{11}N_3S$ (M^+):241.0674; found: 241.0647.

HRMS(ESI-TOF) m/z Calcd for $C_{17}H_{13}N_3S_2$ (M^+):323.0551 found: 323.0519.



6.

Reference:

[1] M. Taillefer, N. Xia, A. Ouali, *Angew. Chem. Int. Ed* ., 2007, **46**, 934.

[2] J. Doiron, Al H. Soultan and M. Touaibia, *Eur. J. Med. Chem.*,2011, **46**, 4010.

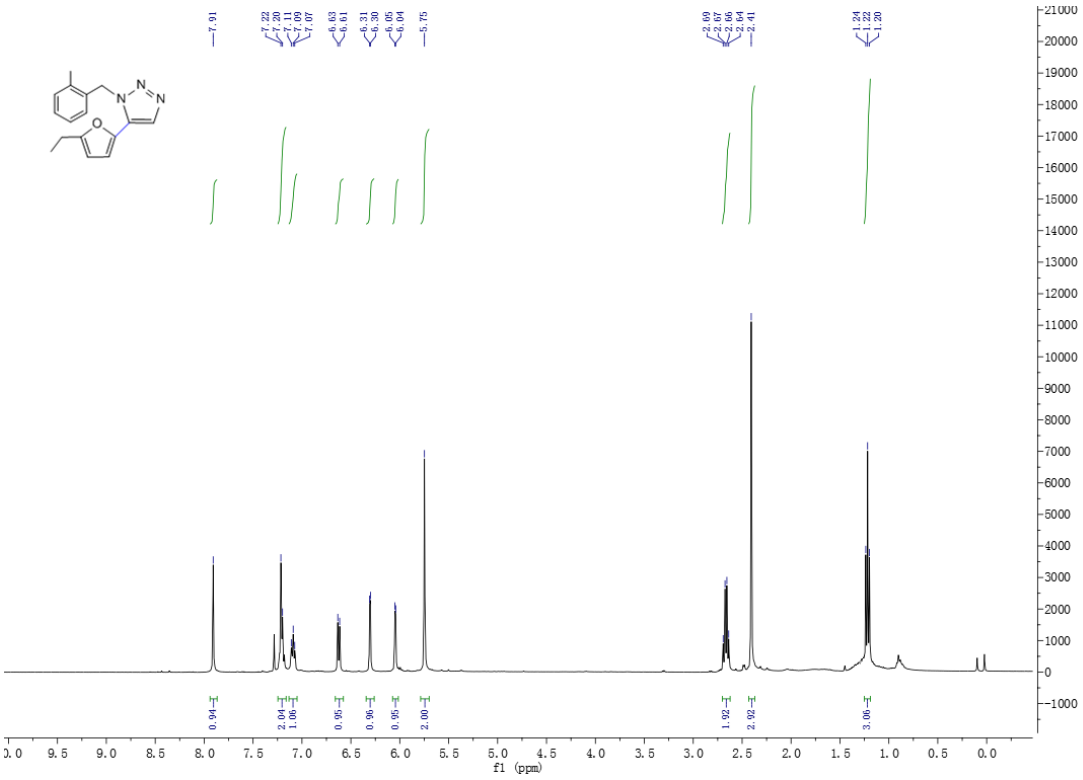
[3] W. Liu, X. Yu and C. X. Kuang, *Chem. Commun.*, 2014, **50**, 9291.

[4] M. W. Zhu, K. Fujita and R. Yamaguchi, *Chem. Commun.*, 2011, **47**, 12876.

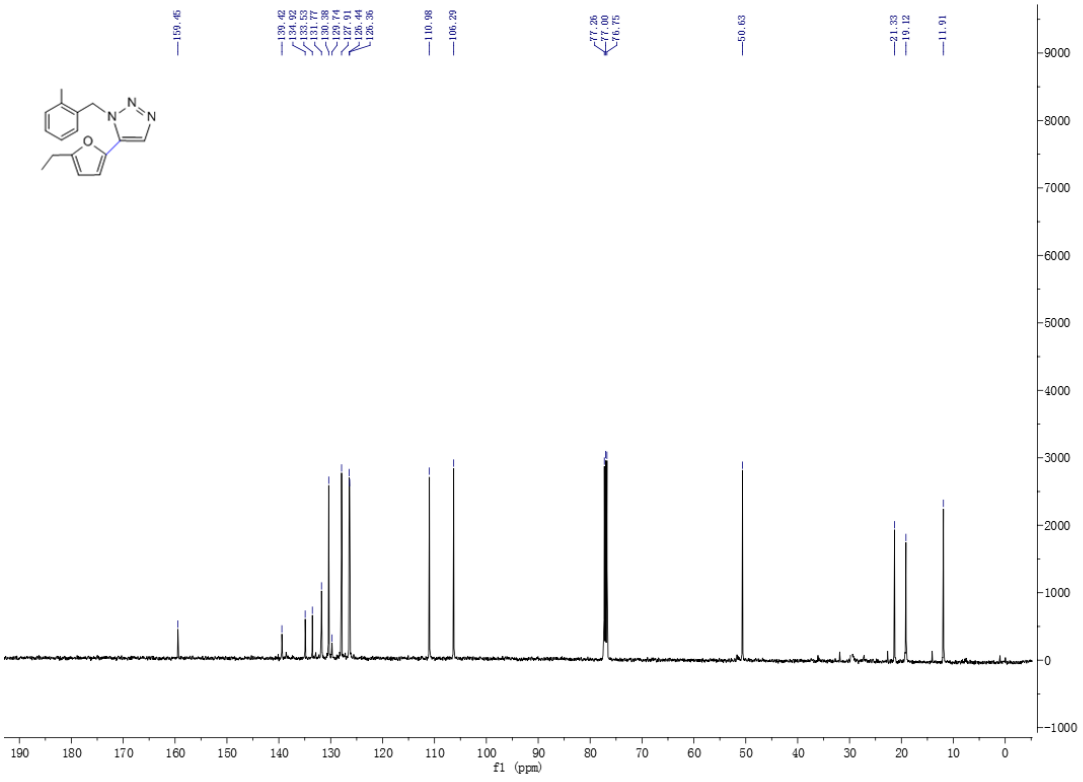
7.

NMR Spectra of compounds

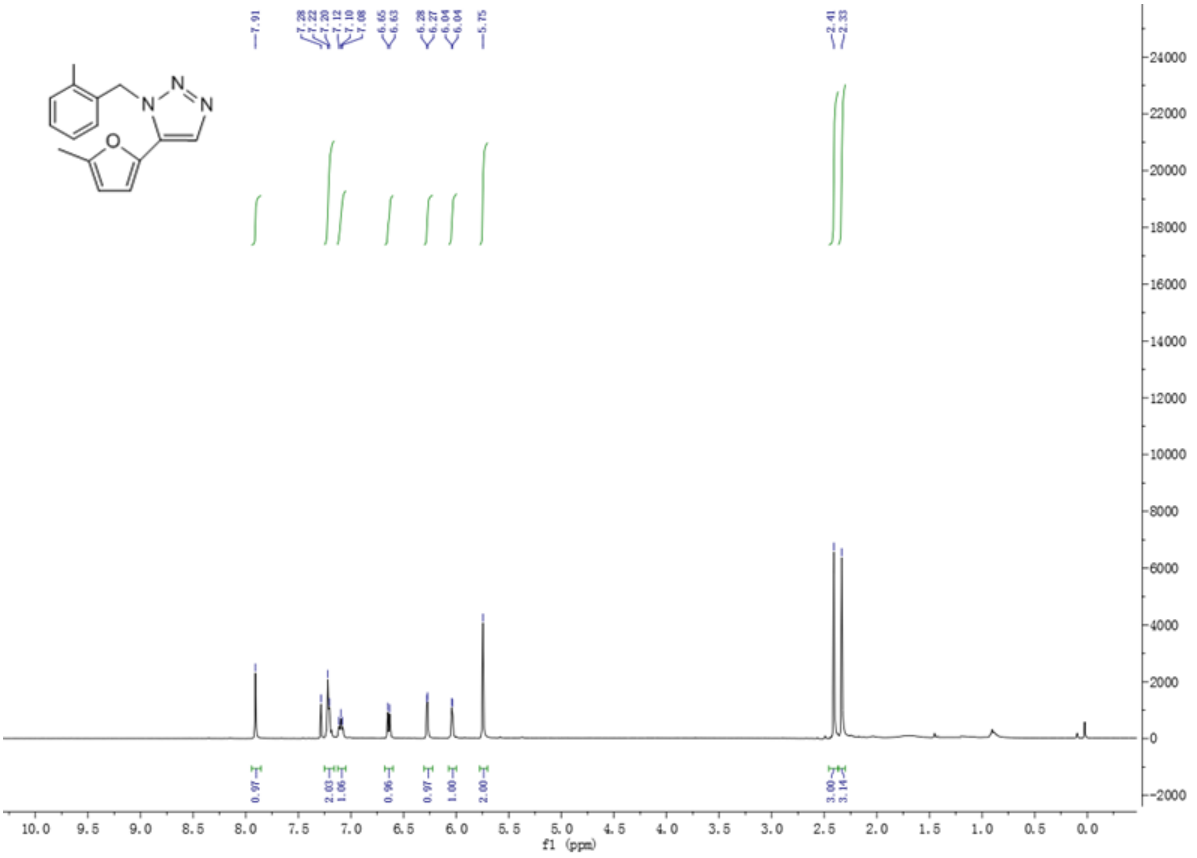
^{1}H NMR of 3a



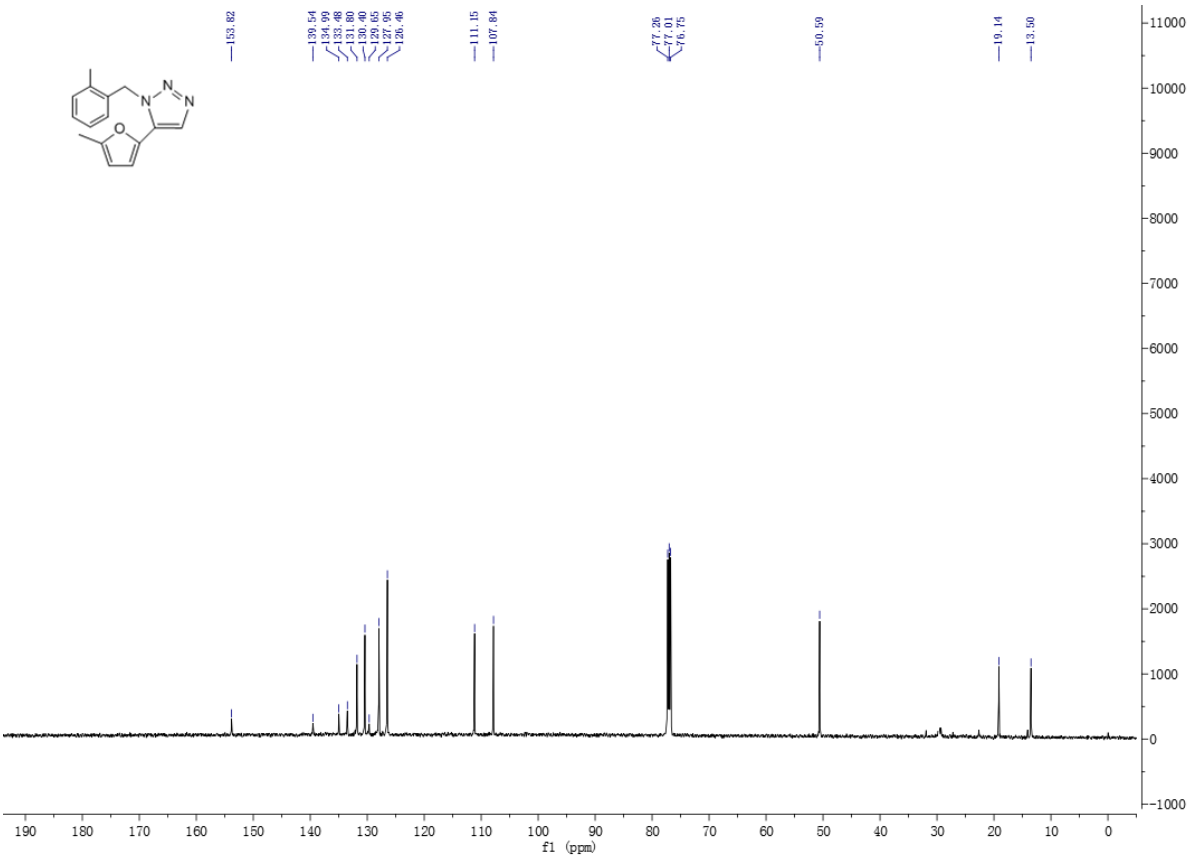
^{13}C NMR of 3a



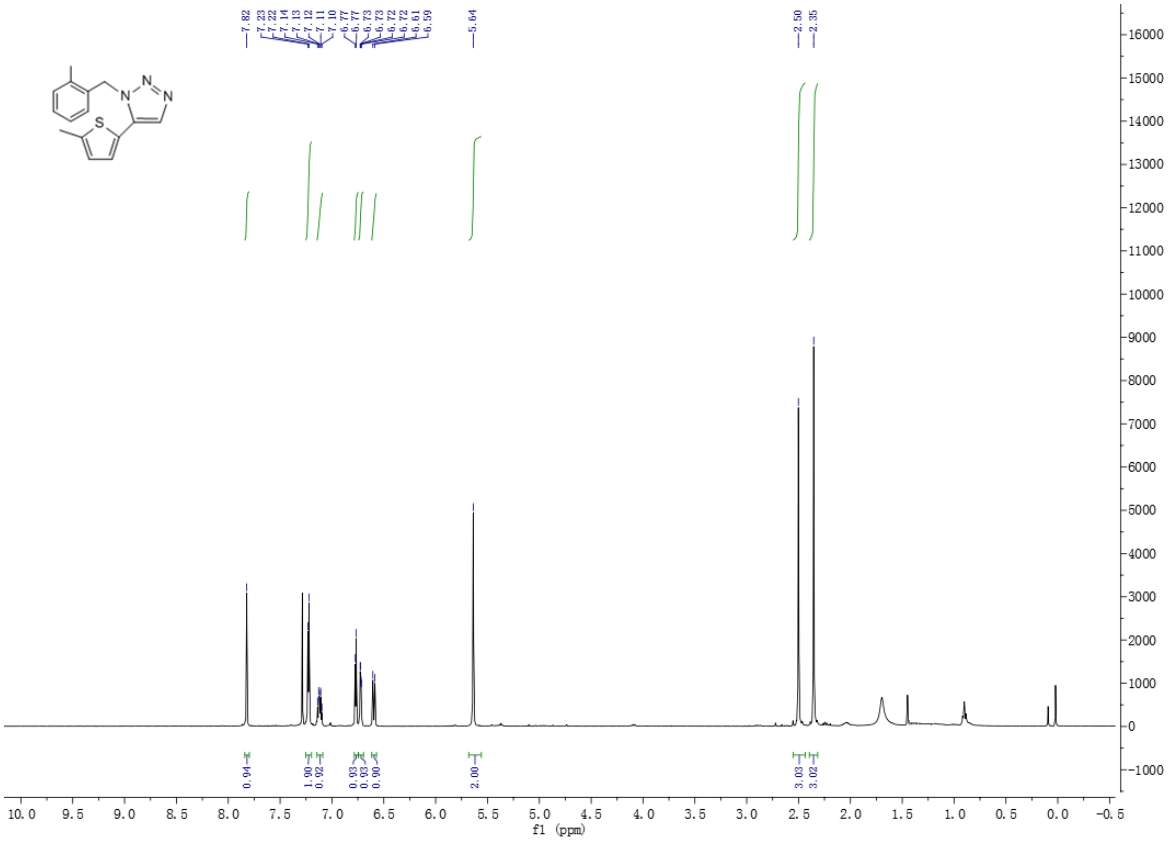
^{1}H NMR of 3b



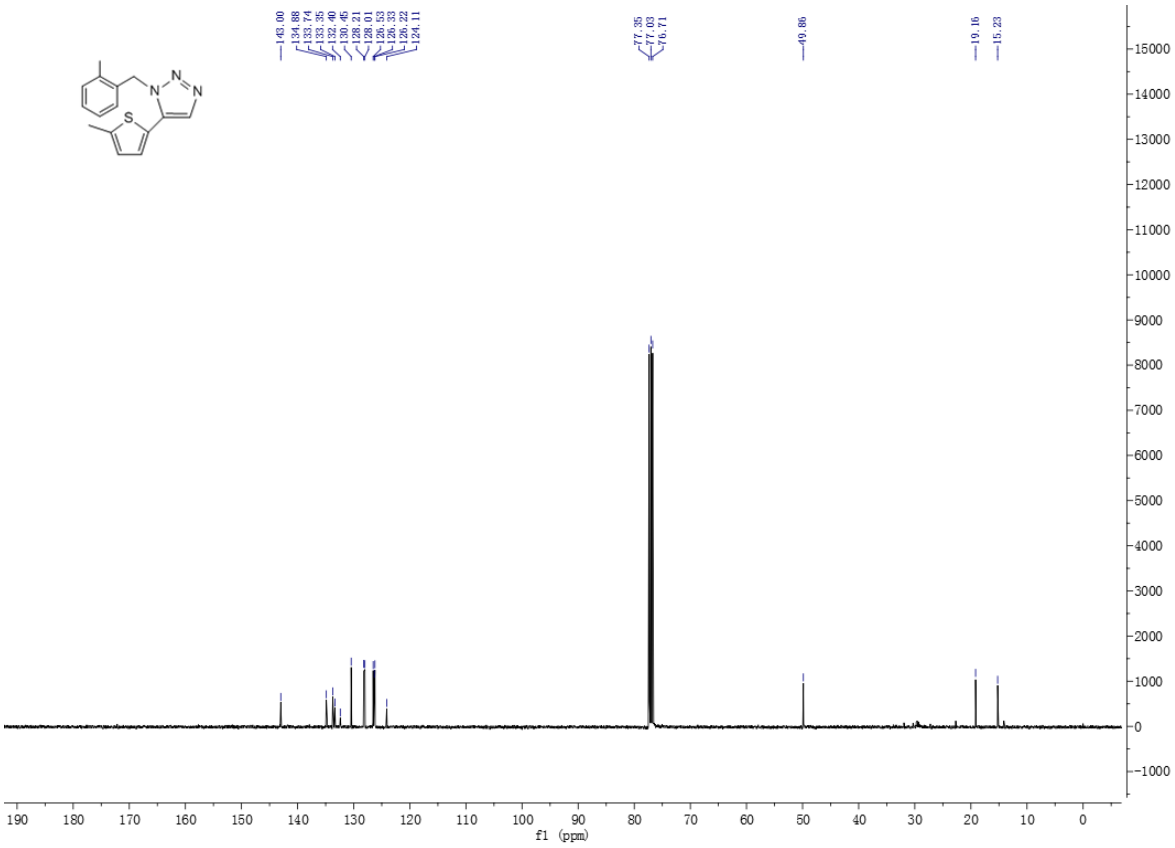
^{13}C NMR of 3b



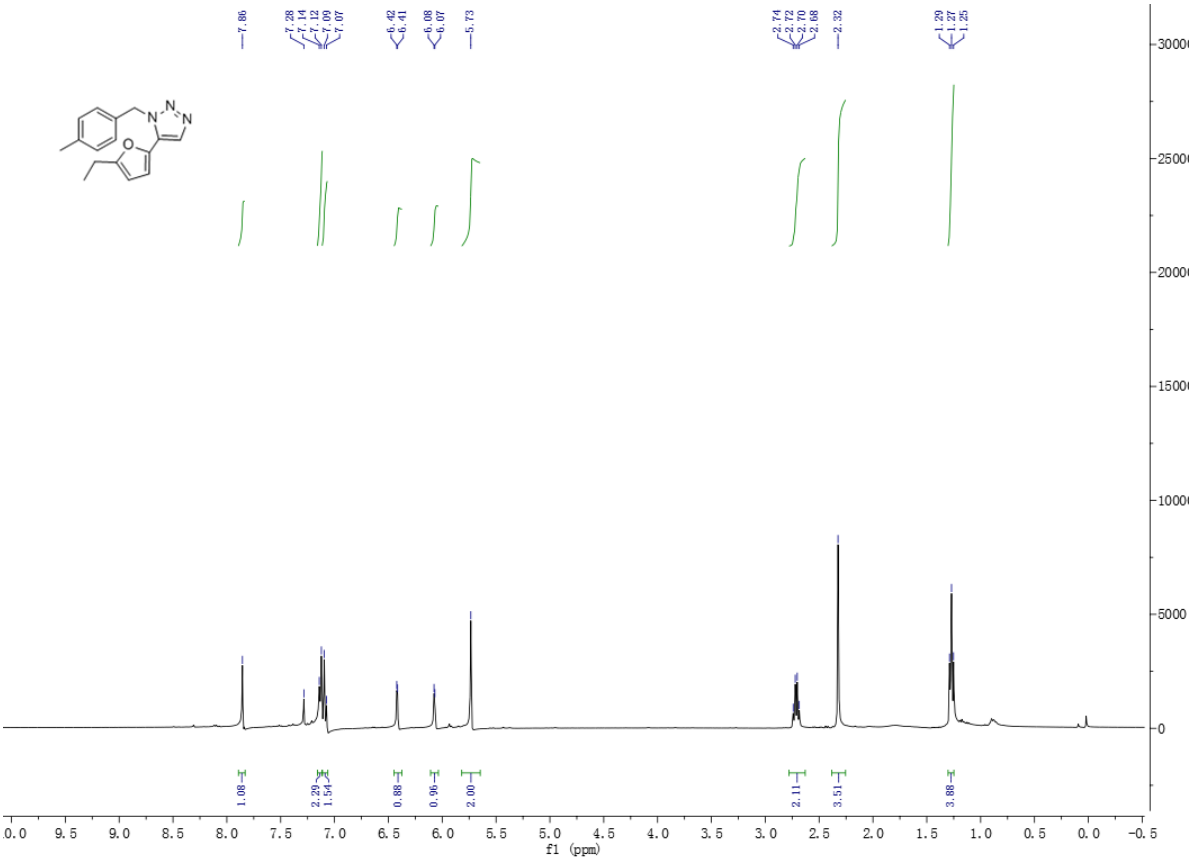
^{1}H NMR of 3c



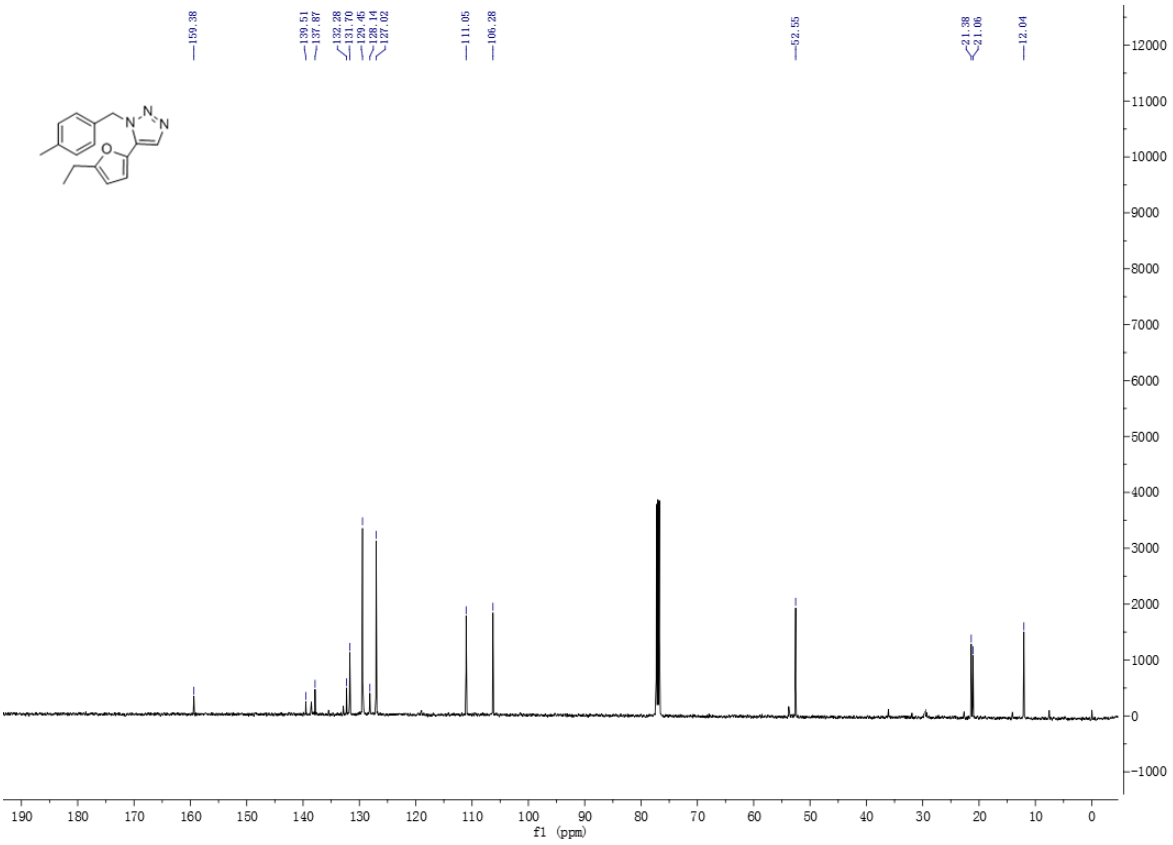
^{13}C NMR of 3c



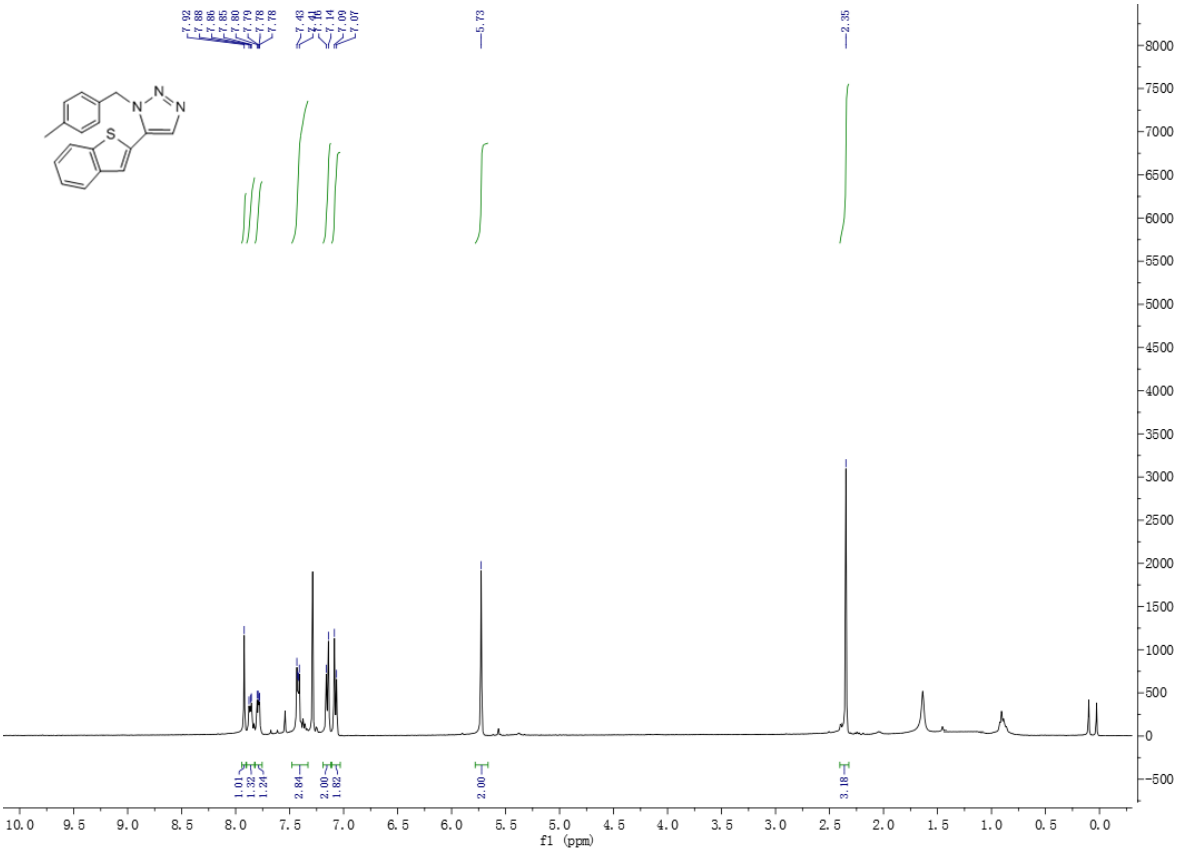
^{1}H NMR of 3d



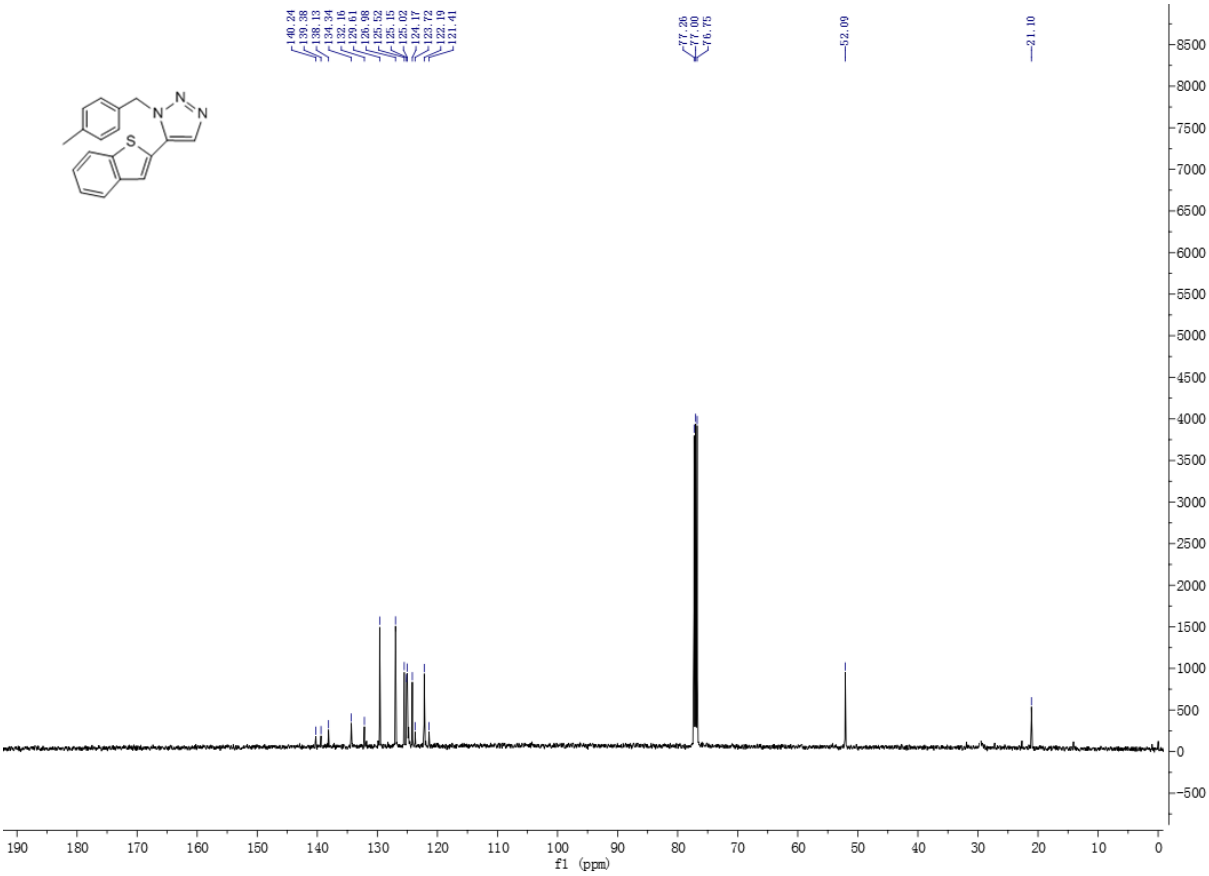
^{13}C NMR of 3d



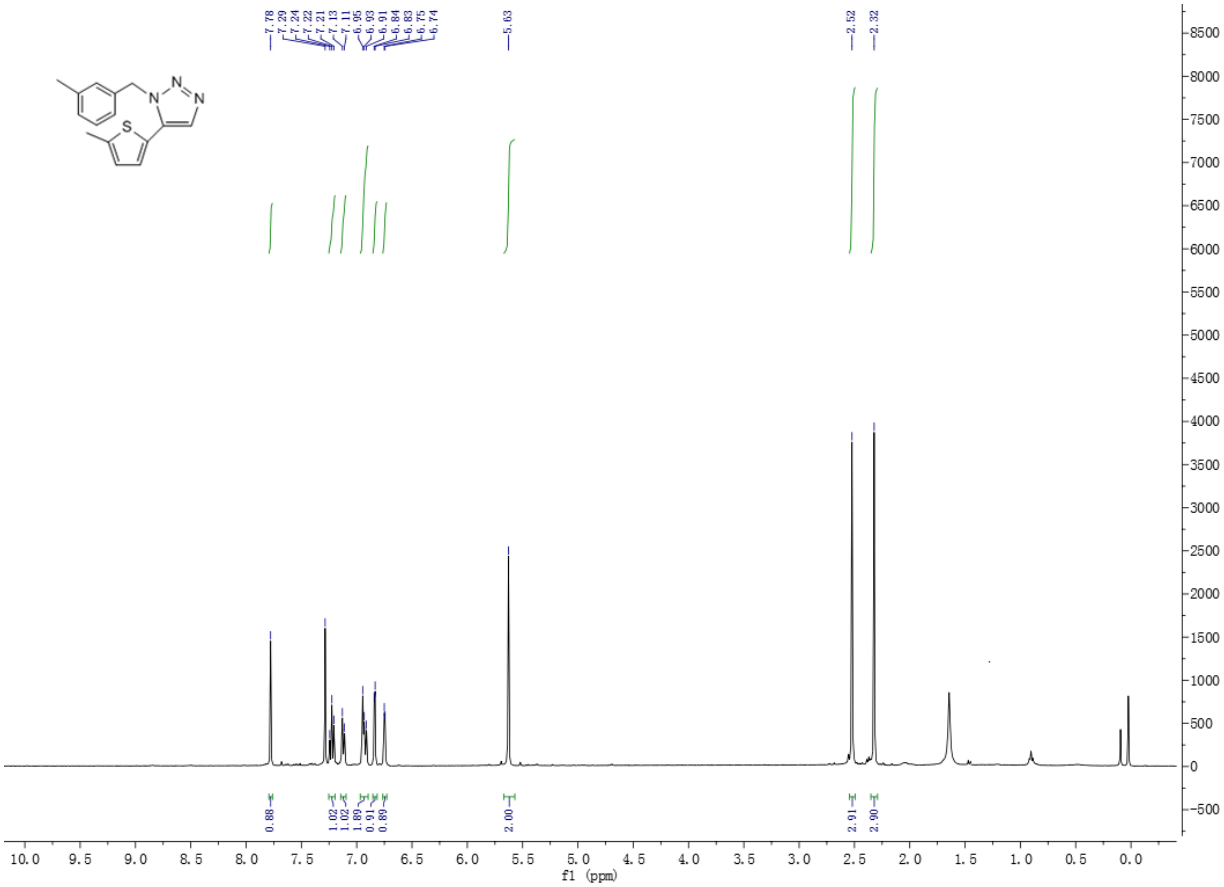
^{1}H NMR of 3e



^{13}C NMR of 3e



^{1}H NMR of 3f



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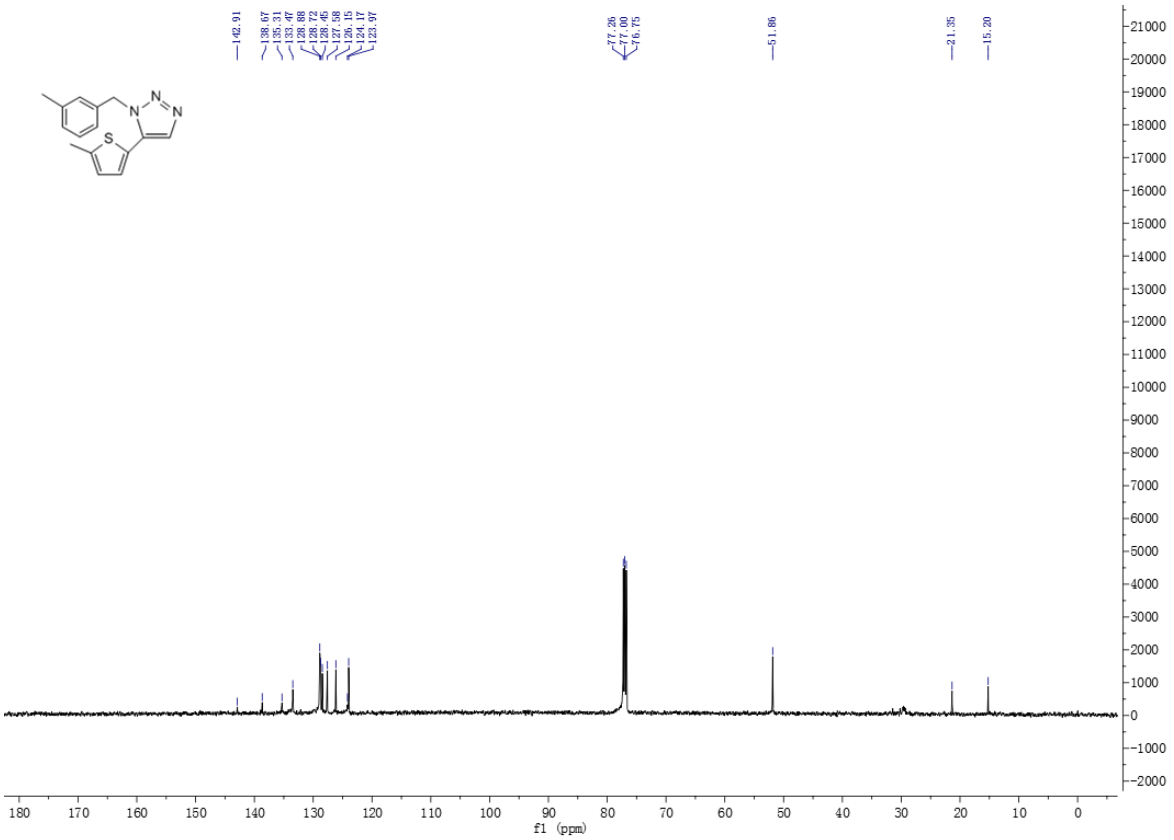
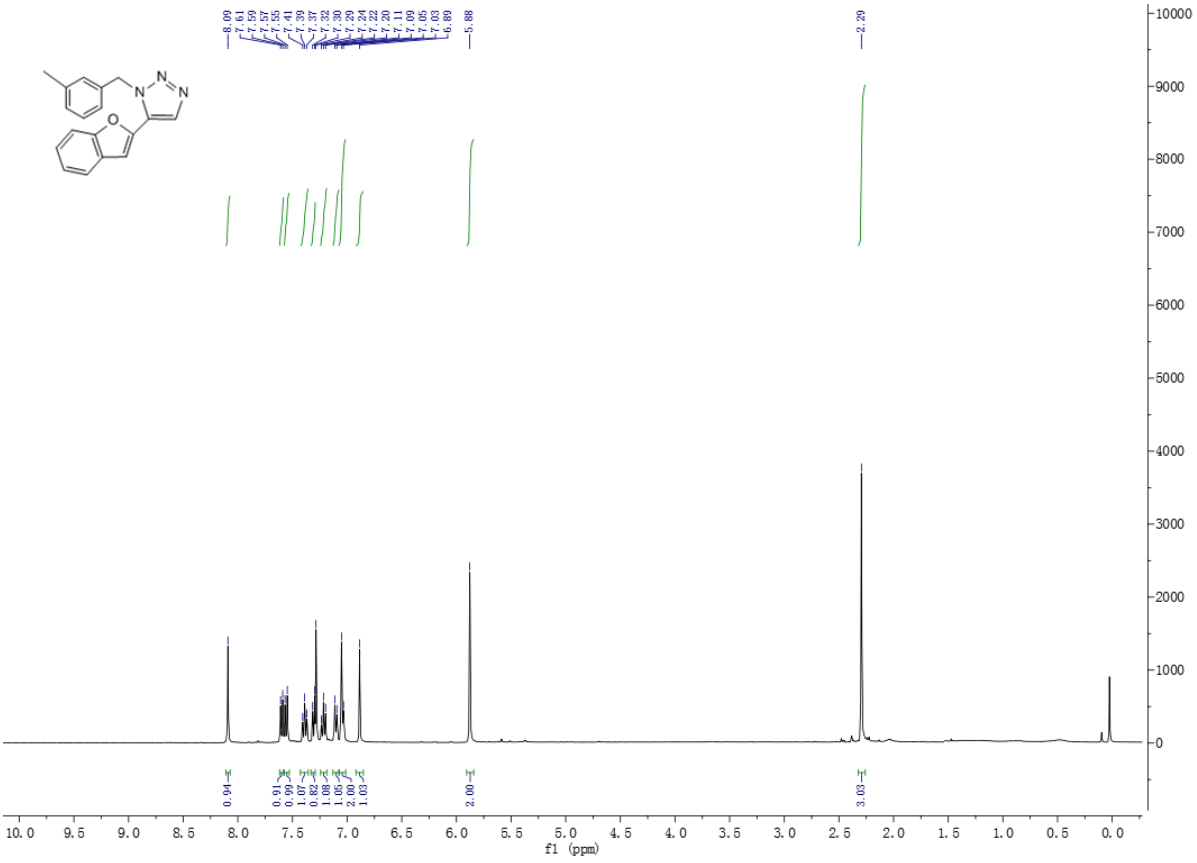
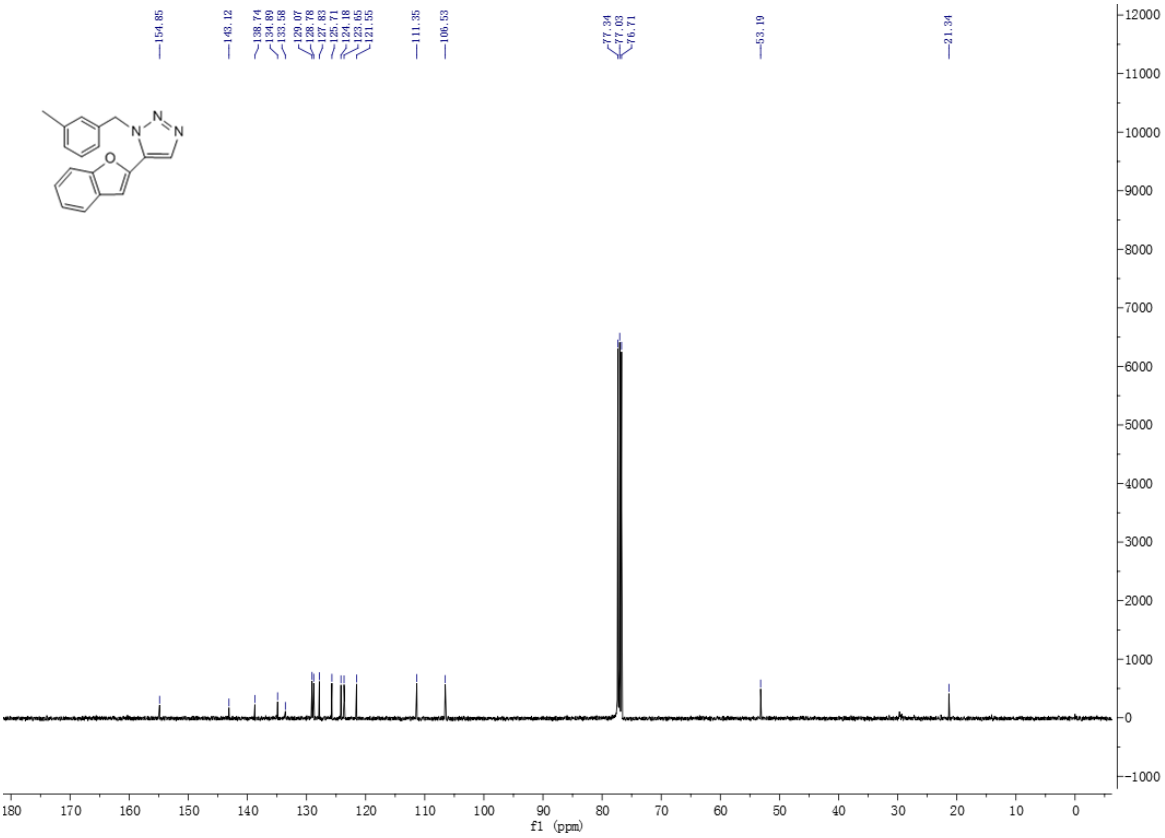


^{1}H NMR of 3g



^{13}C NMR of 3g



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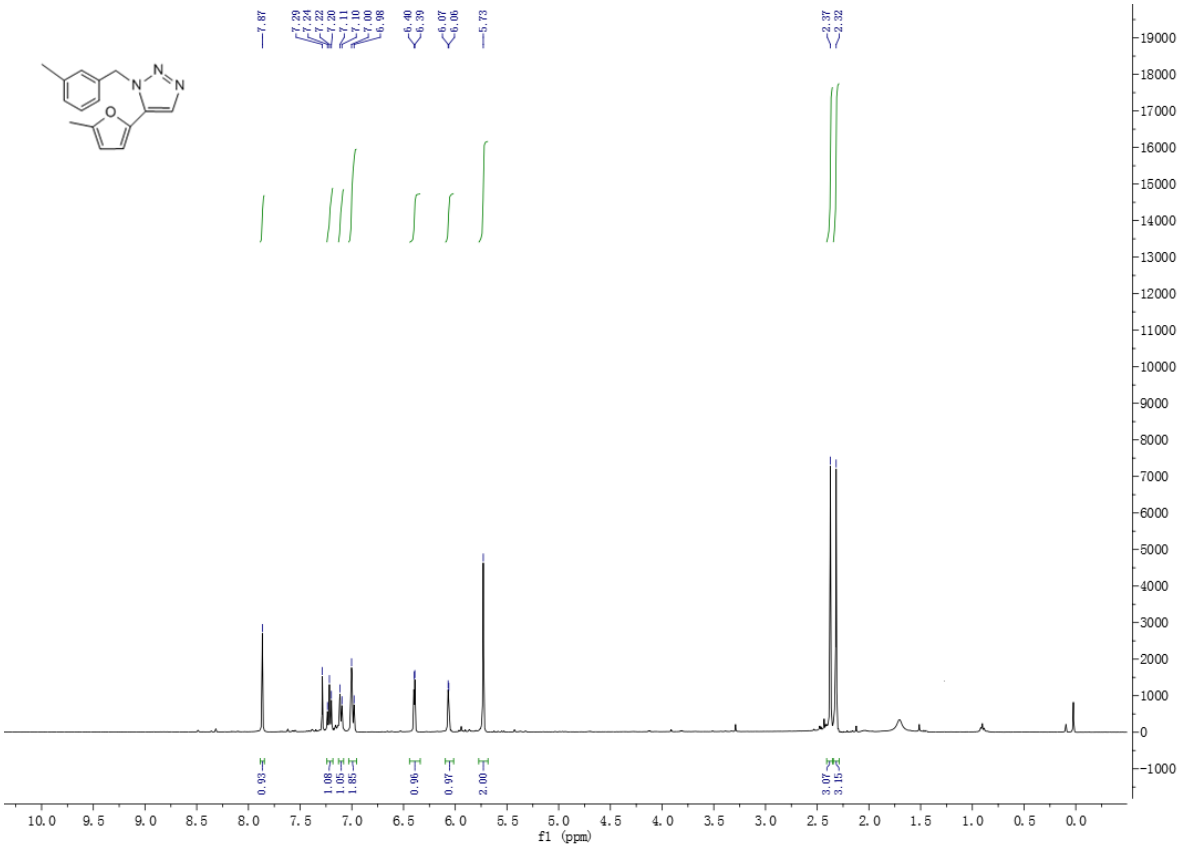
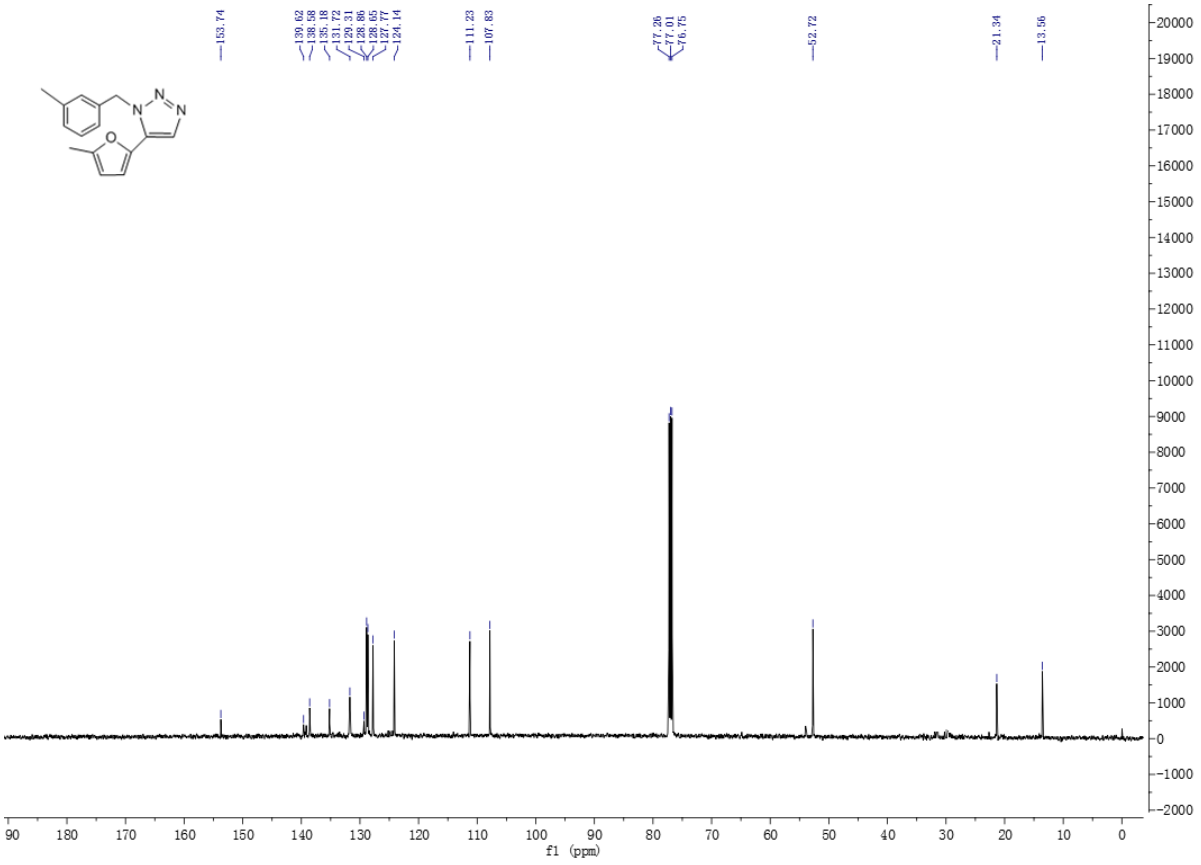
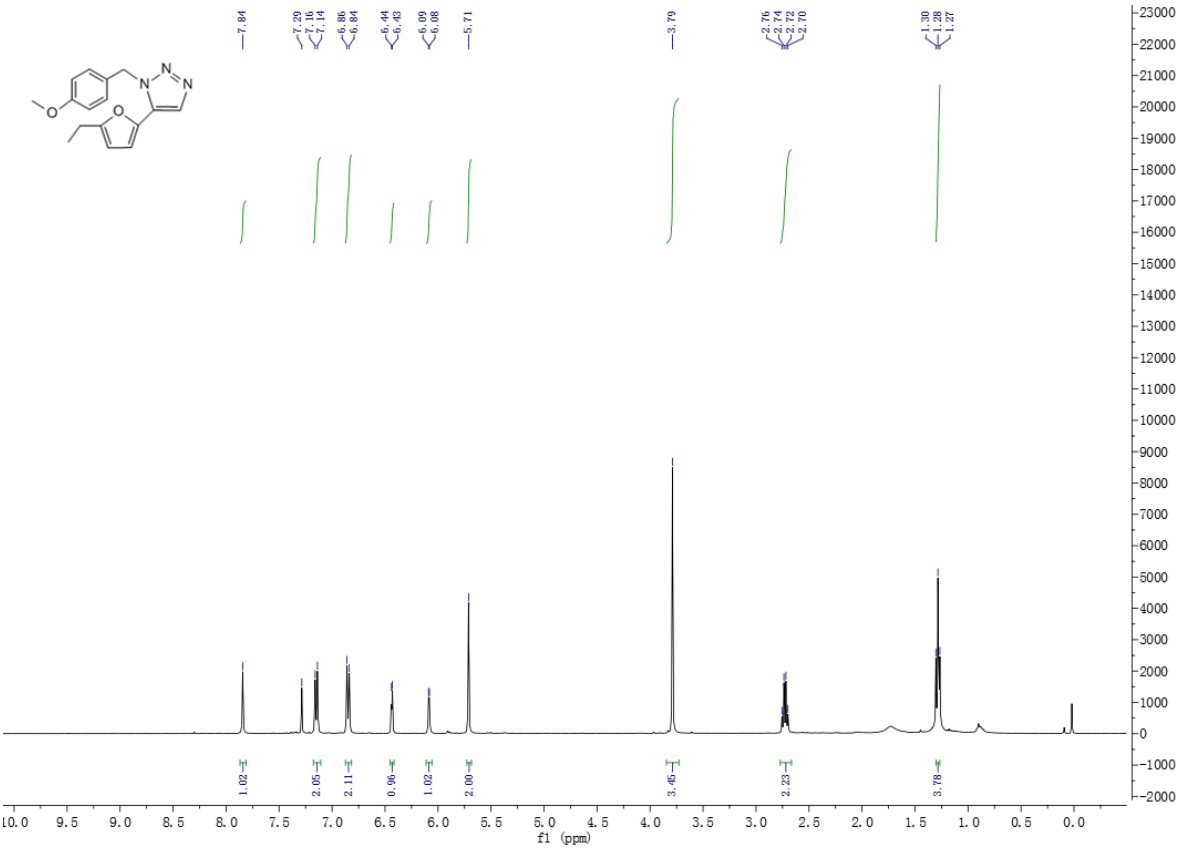


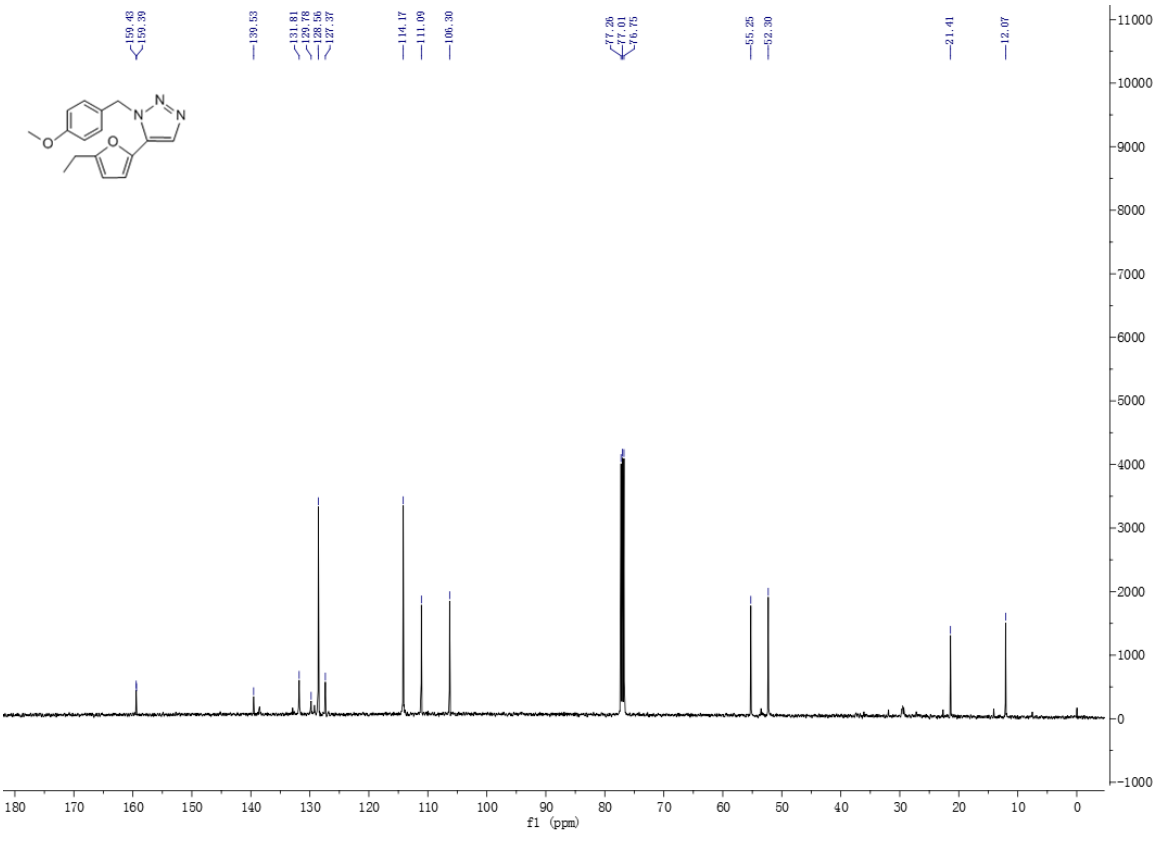
^{13}C NMR of 3h



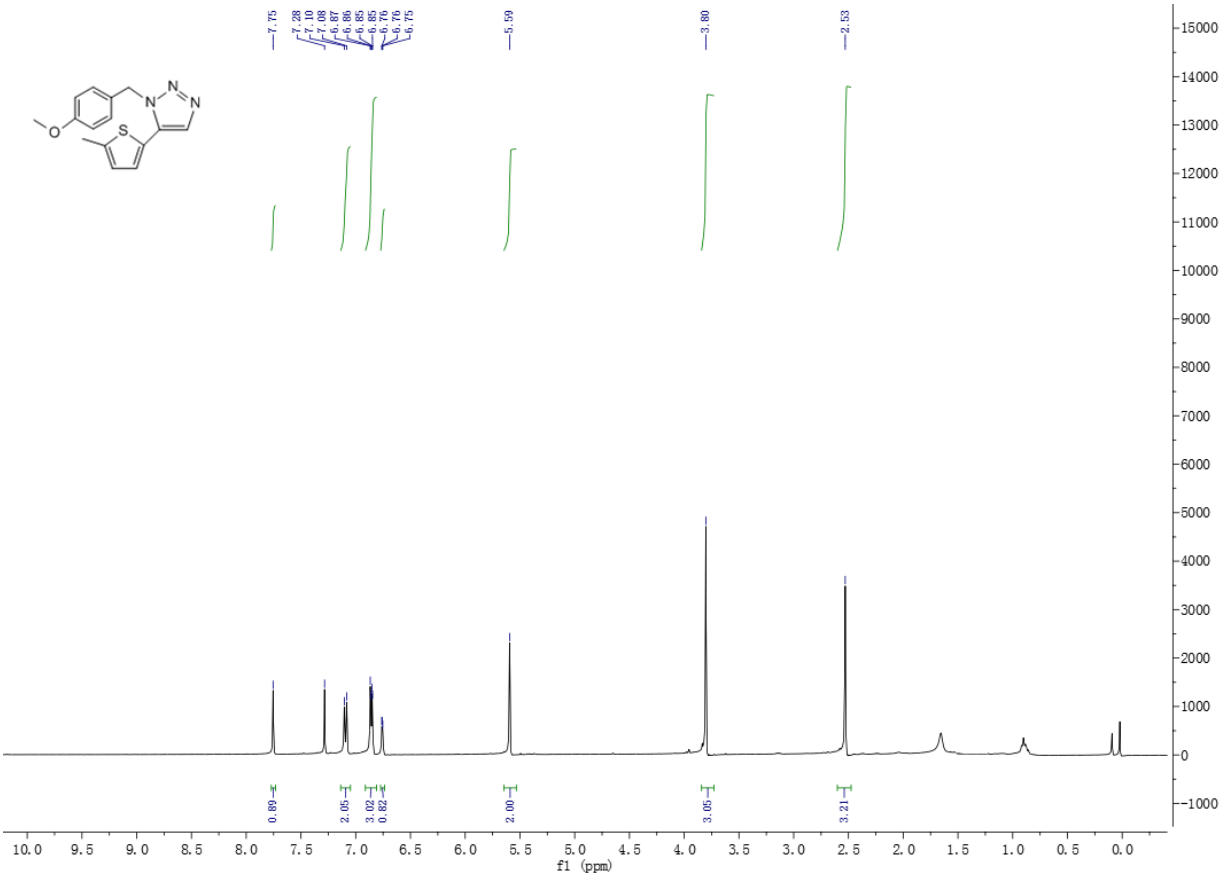
^{1}H NMR of 4a



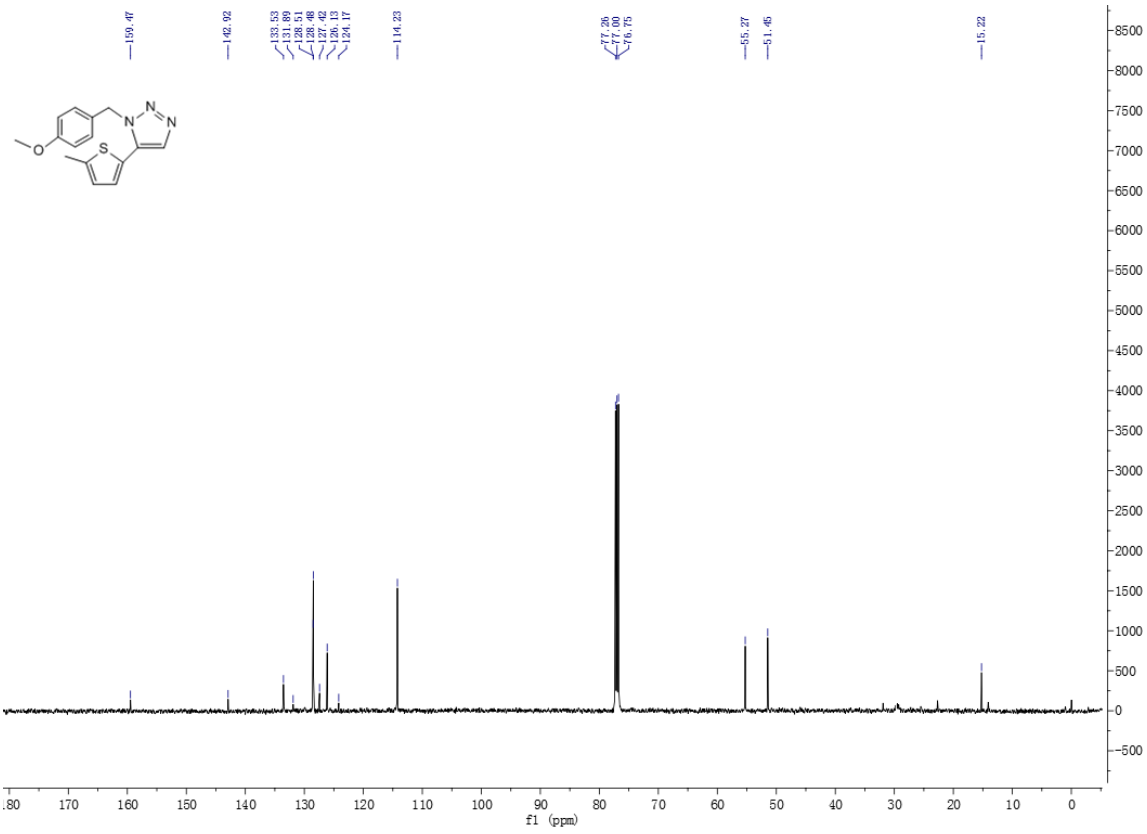
^{13}C NMR of 4a



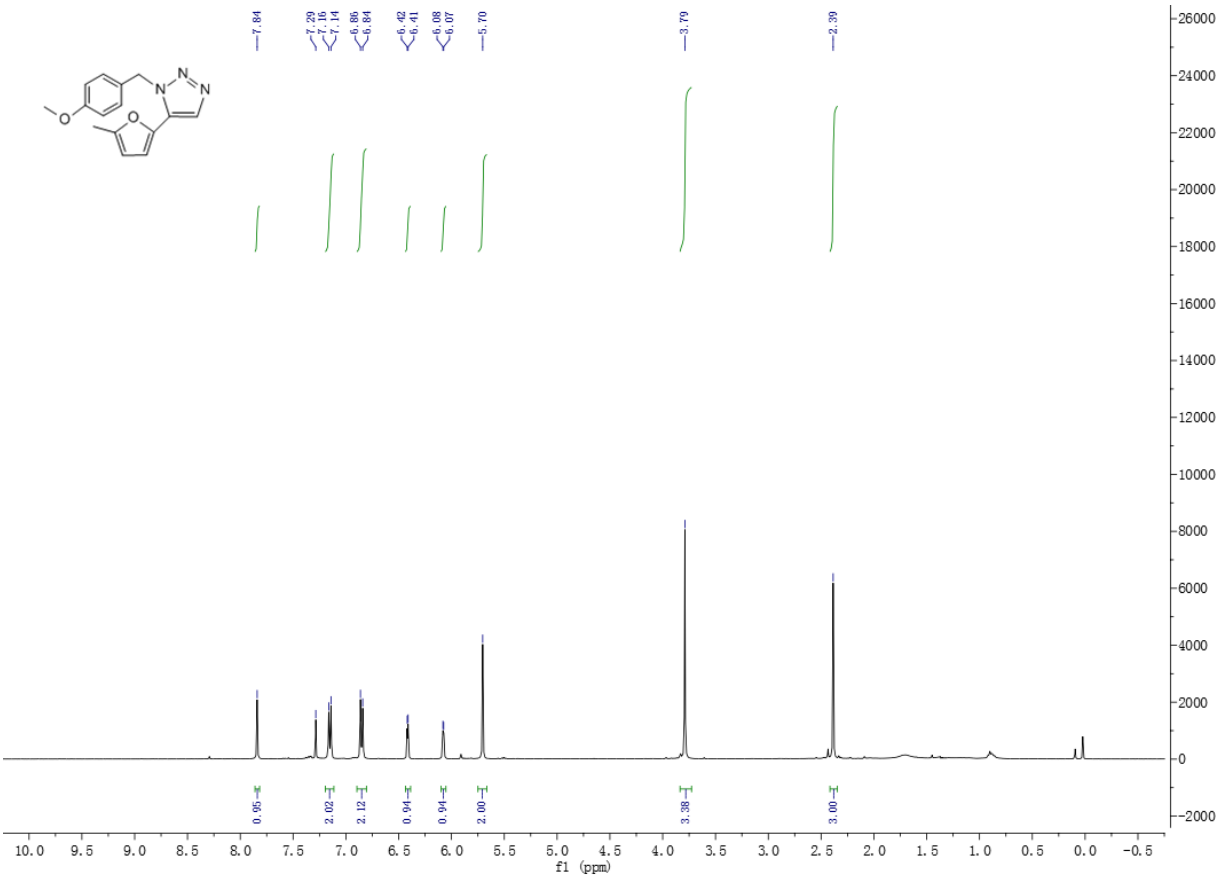
^{1}H NMR of 4b



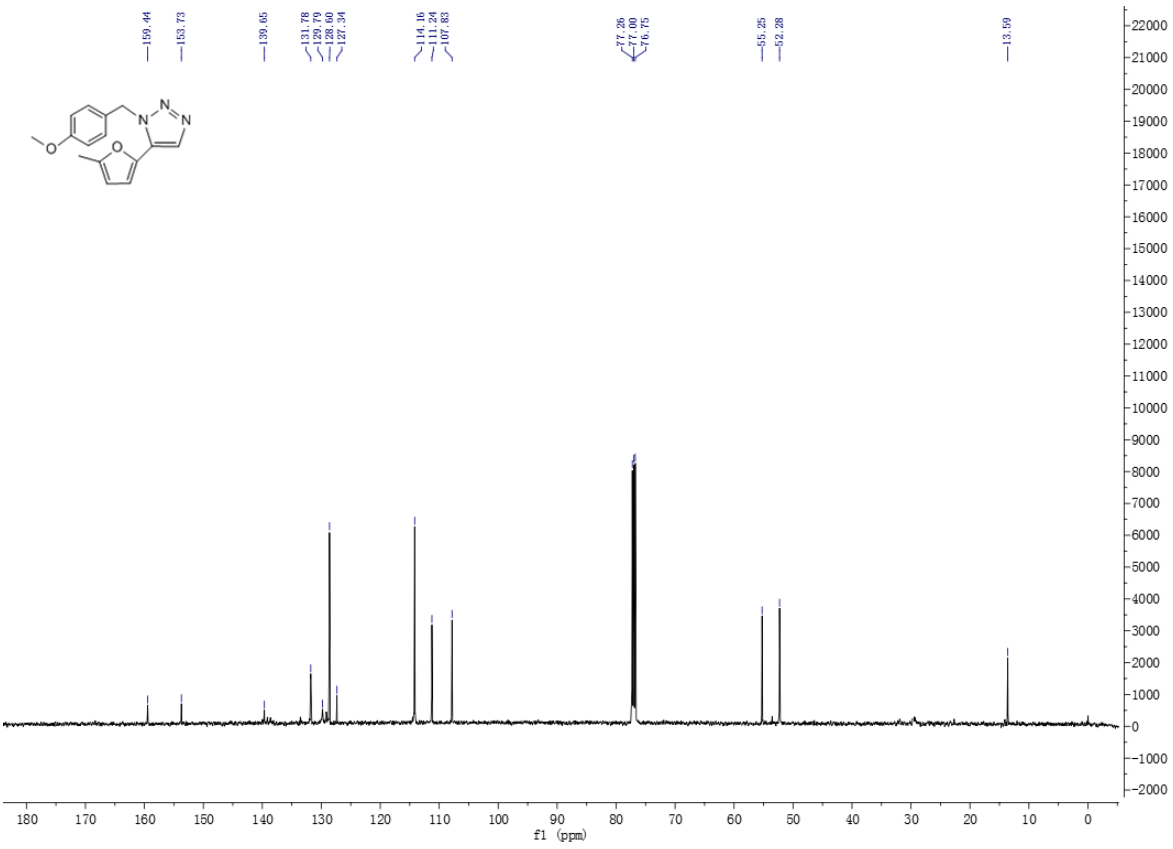
^{13}C NMR of 4b



^{1}H NMR of 4c



^{13}C NMR of 4c



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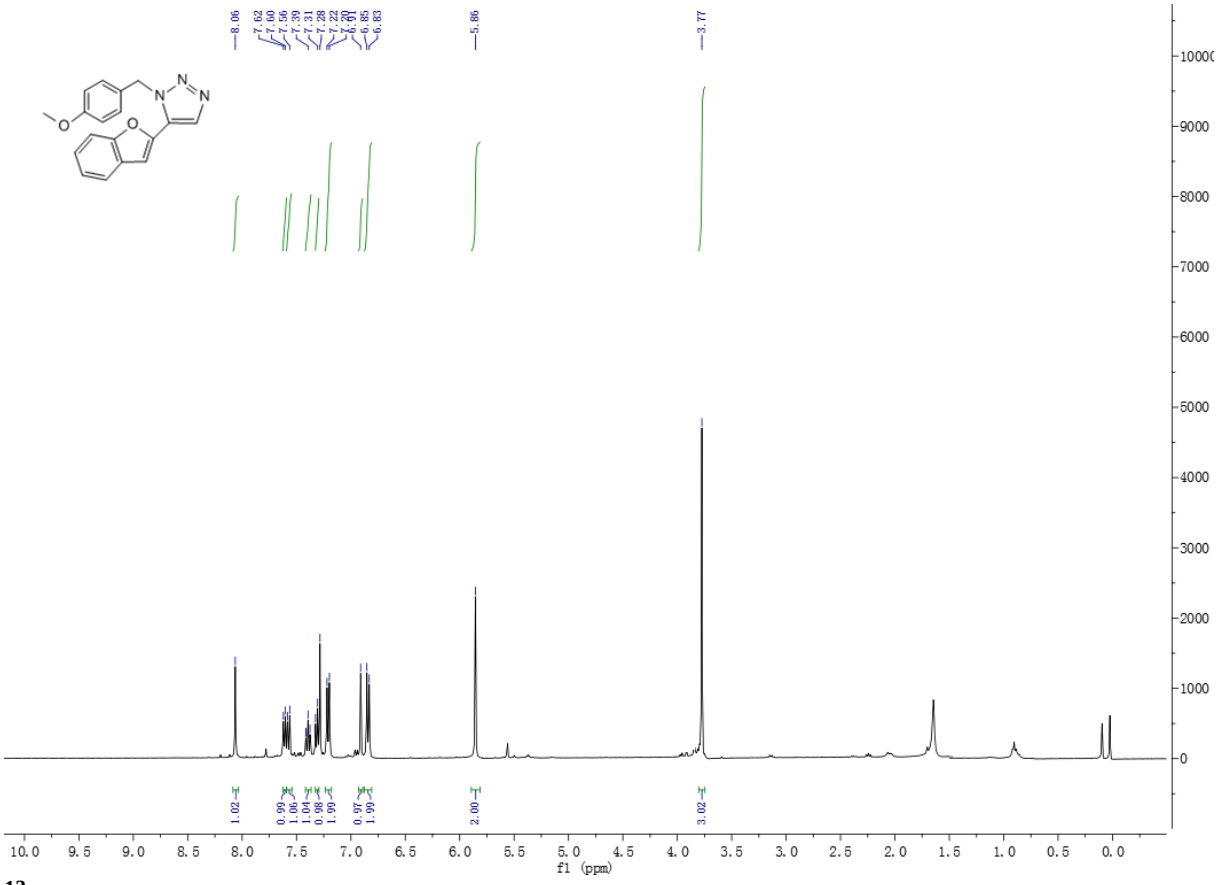

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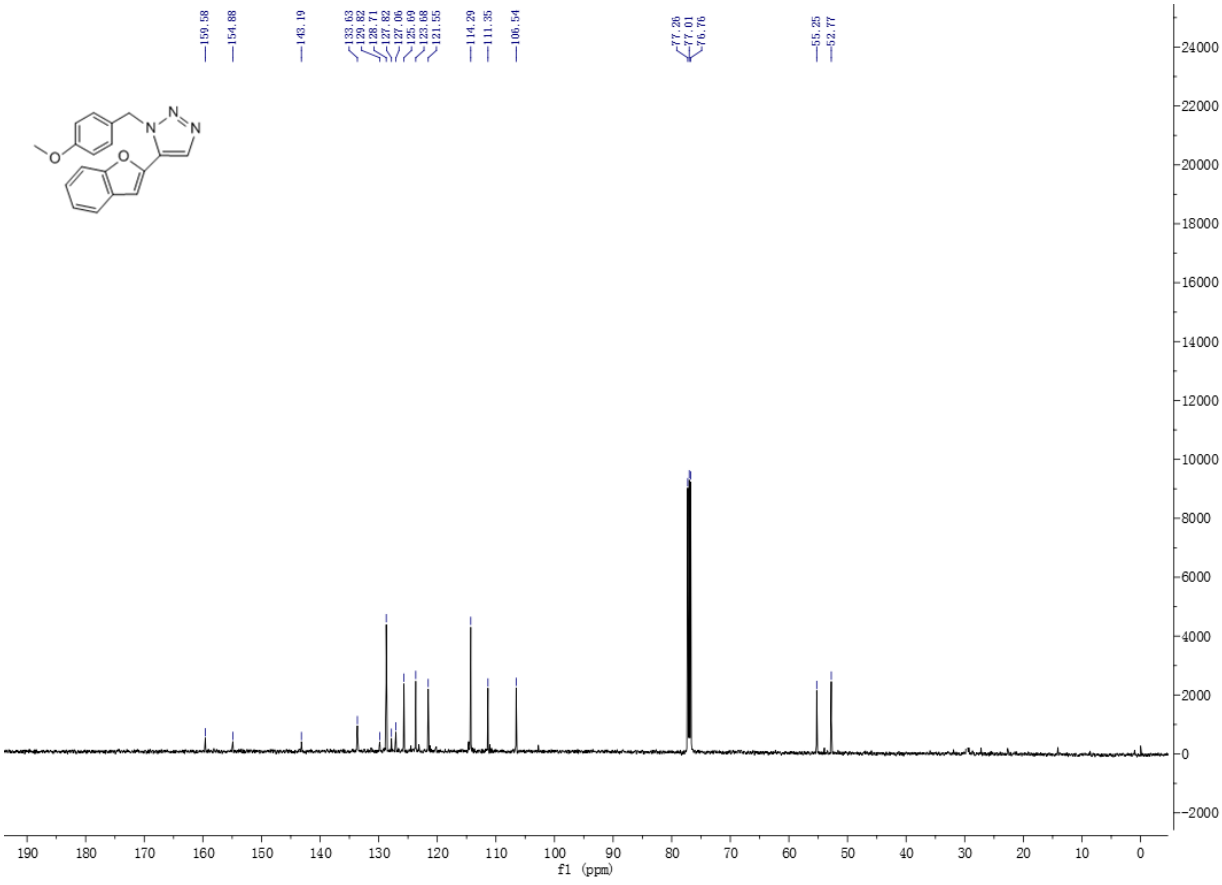
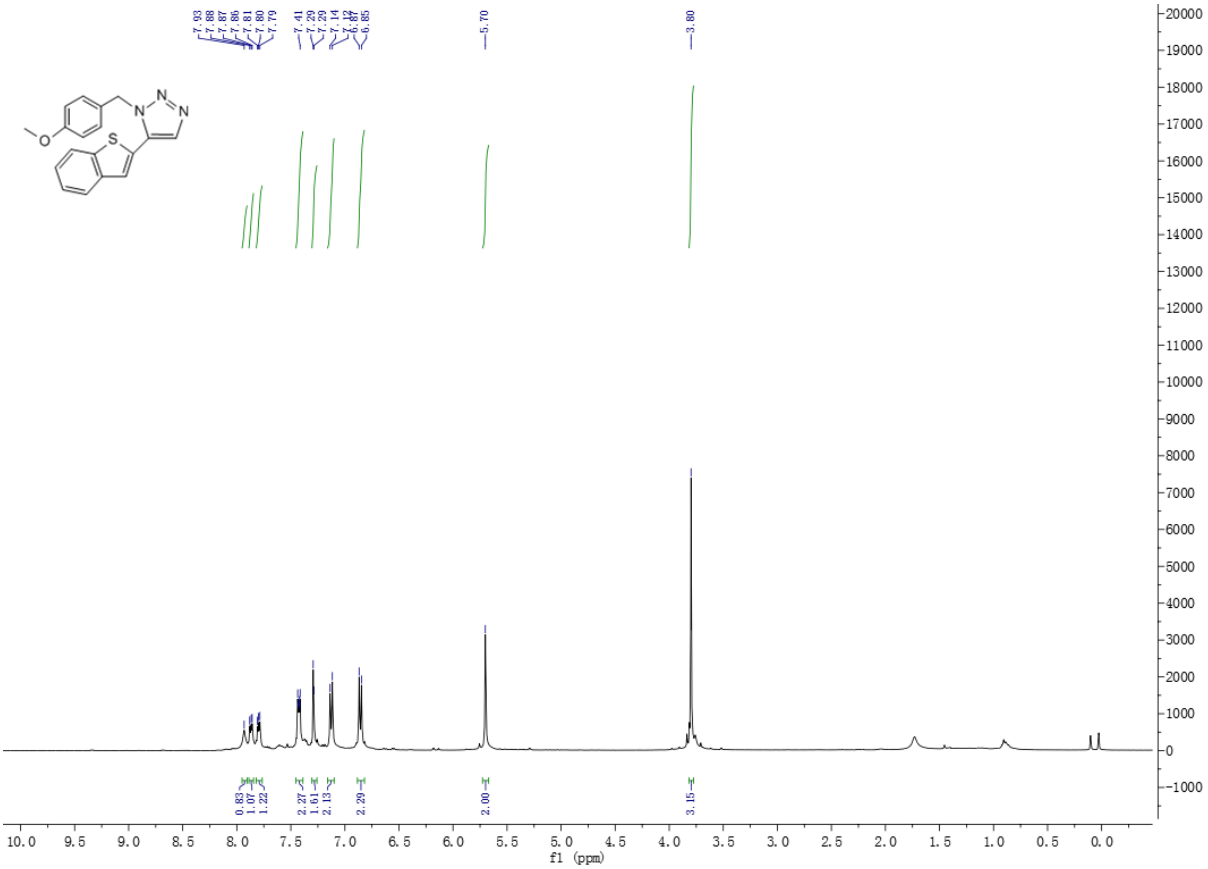


^{1}H NMR of 4e



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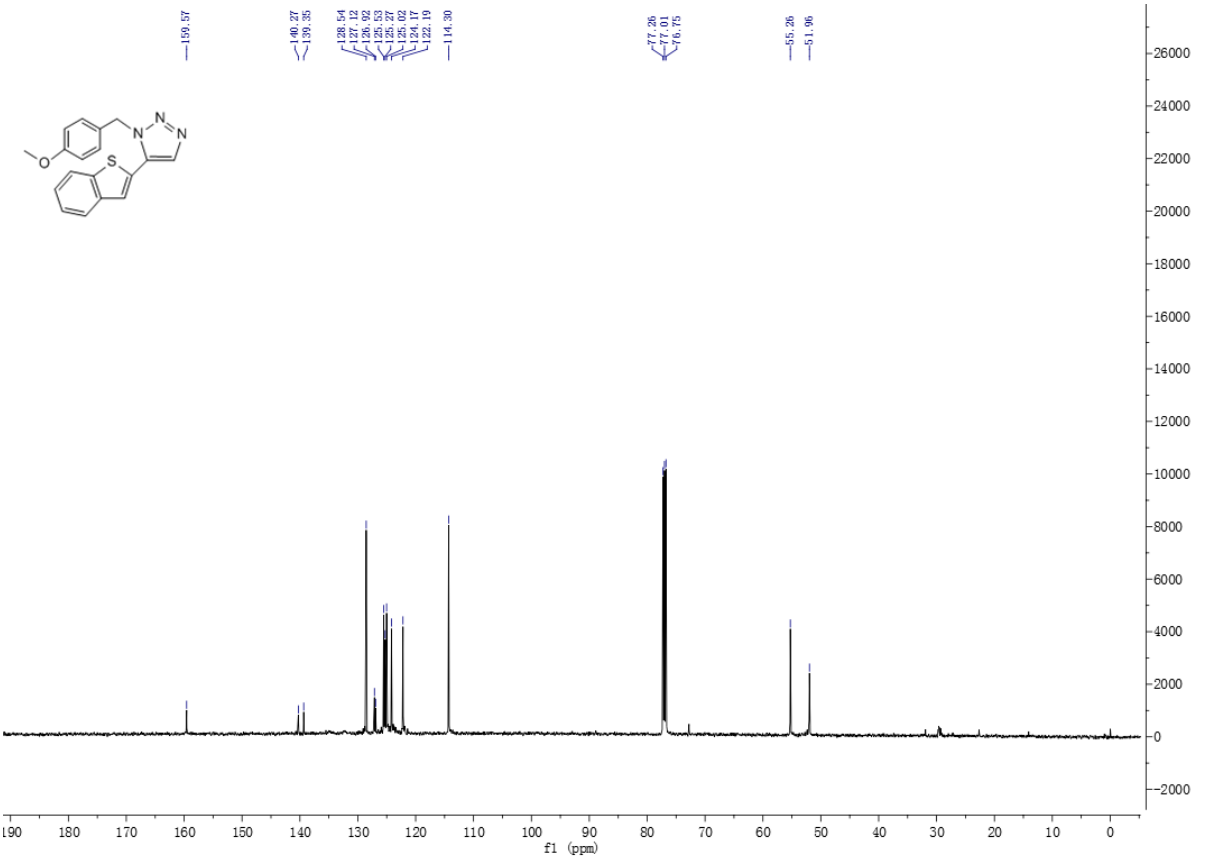
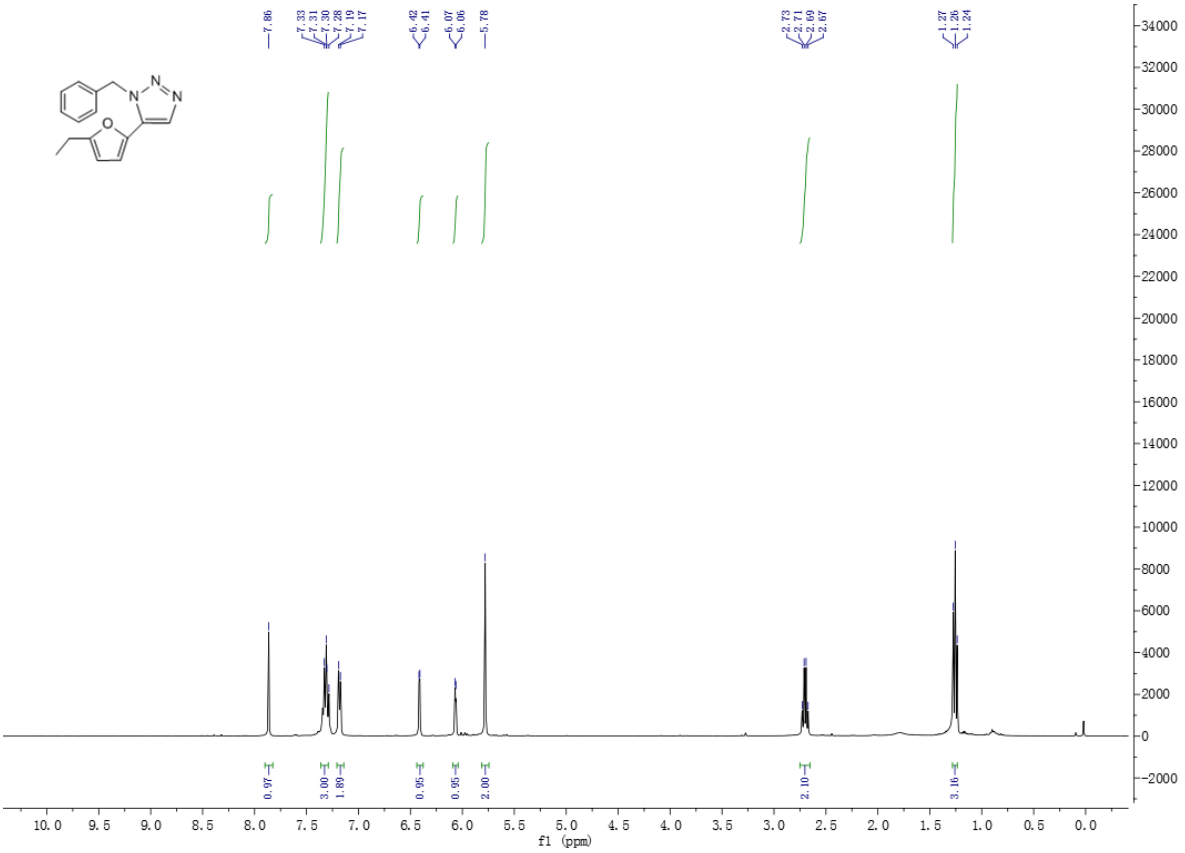
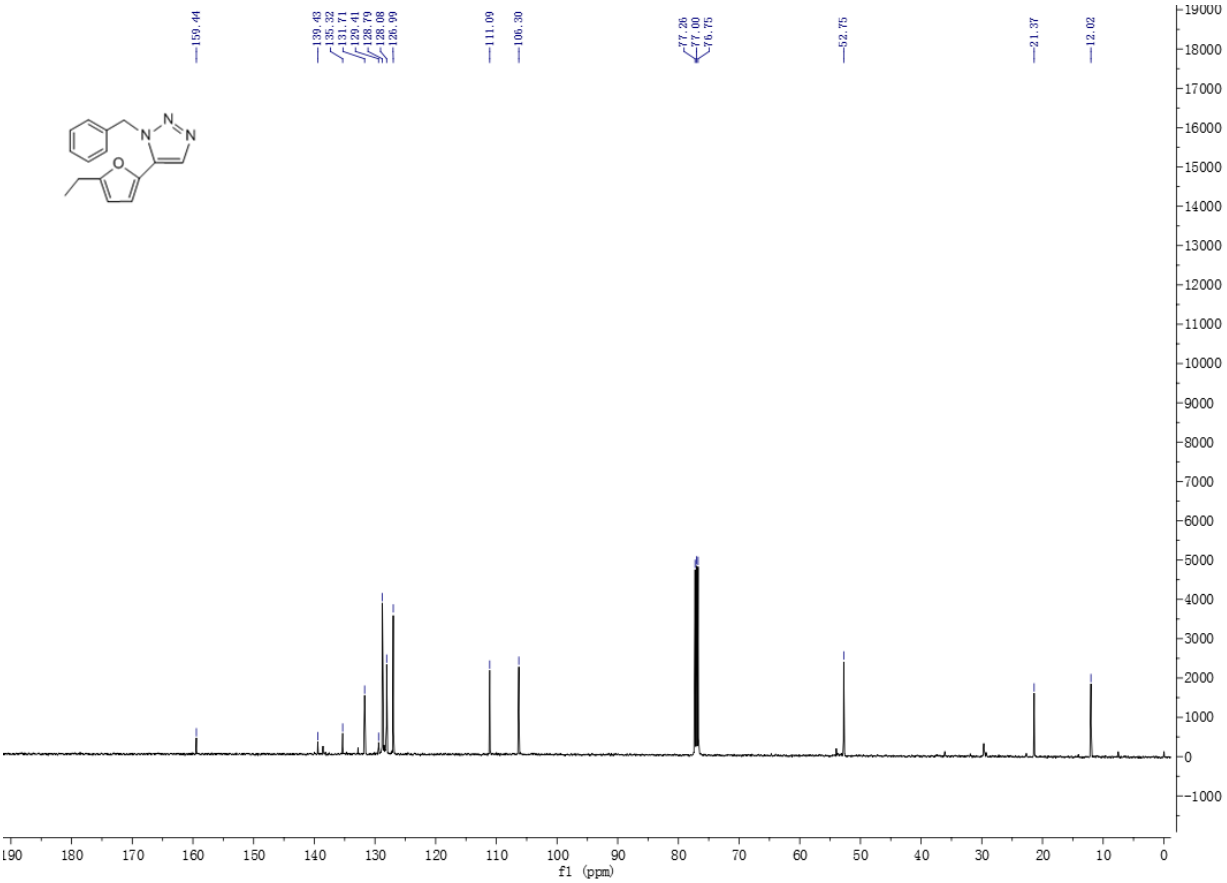


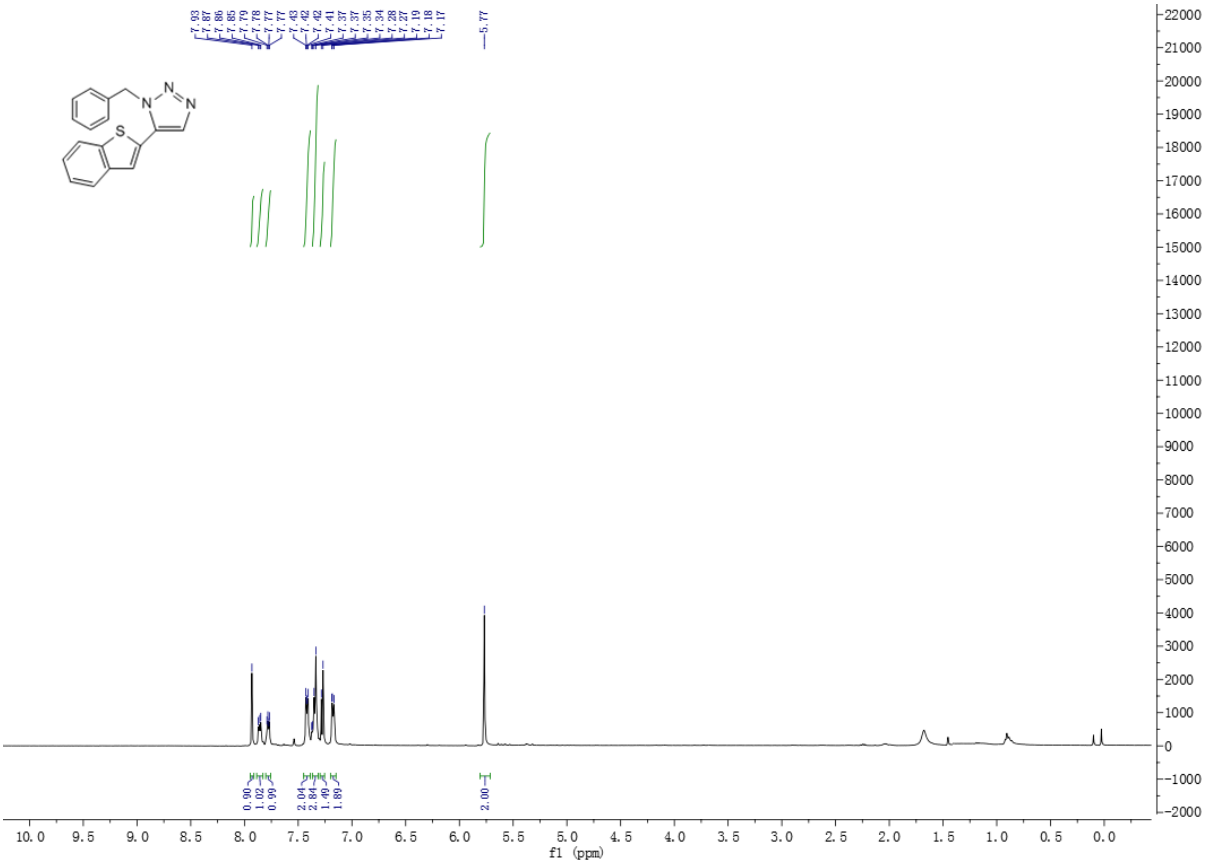
^{1}H NMR of 5a



^{13}C NMR of 5a



^{1}H NMR of 5b



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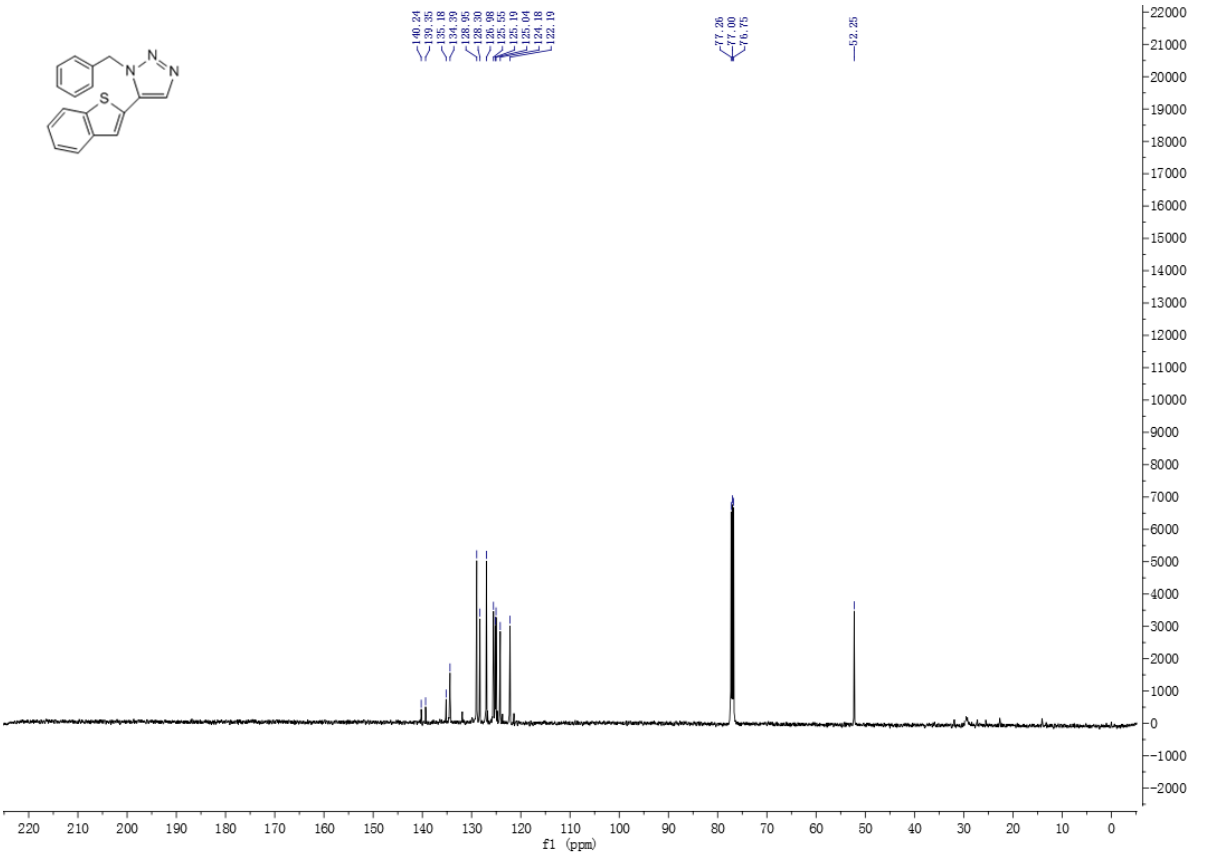

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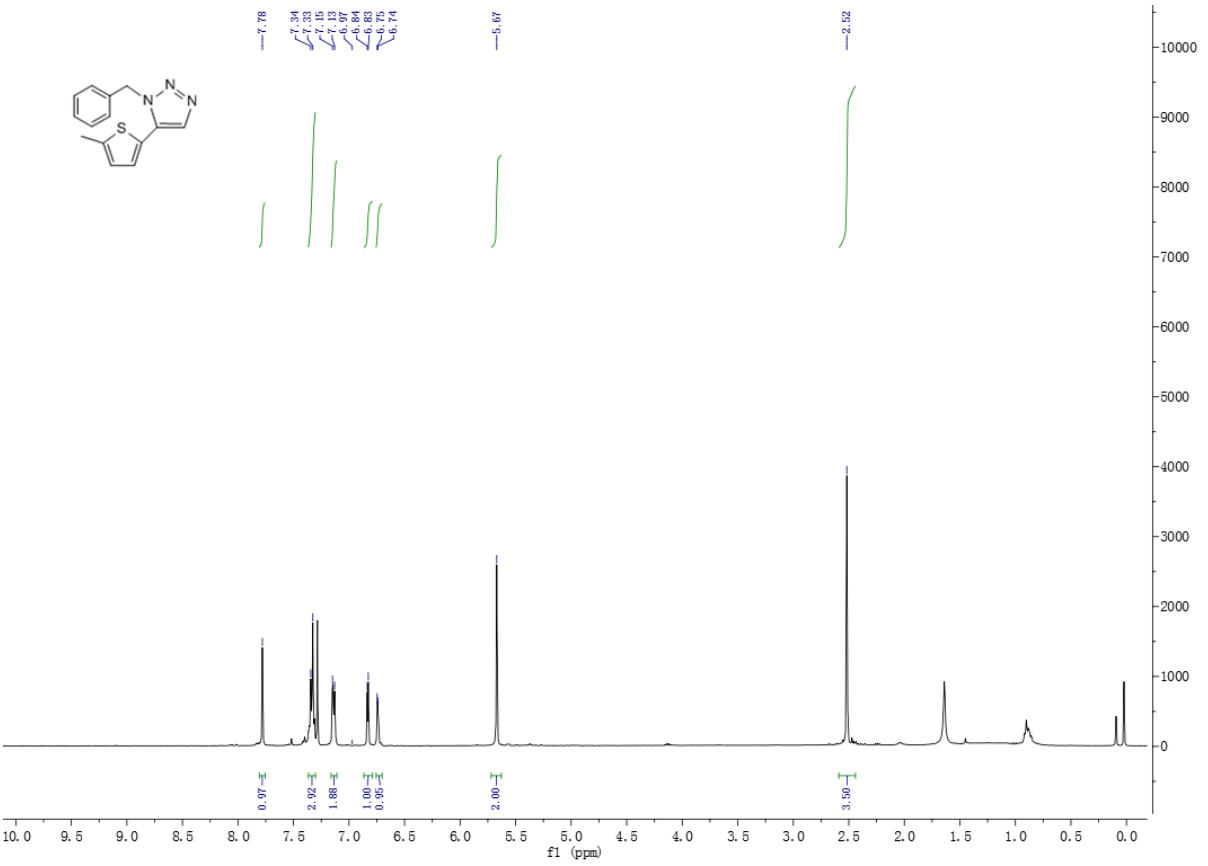

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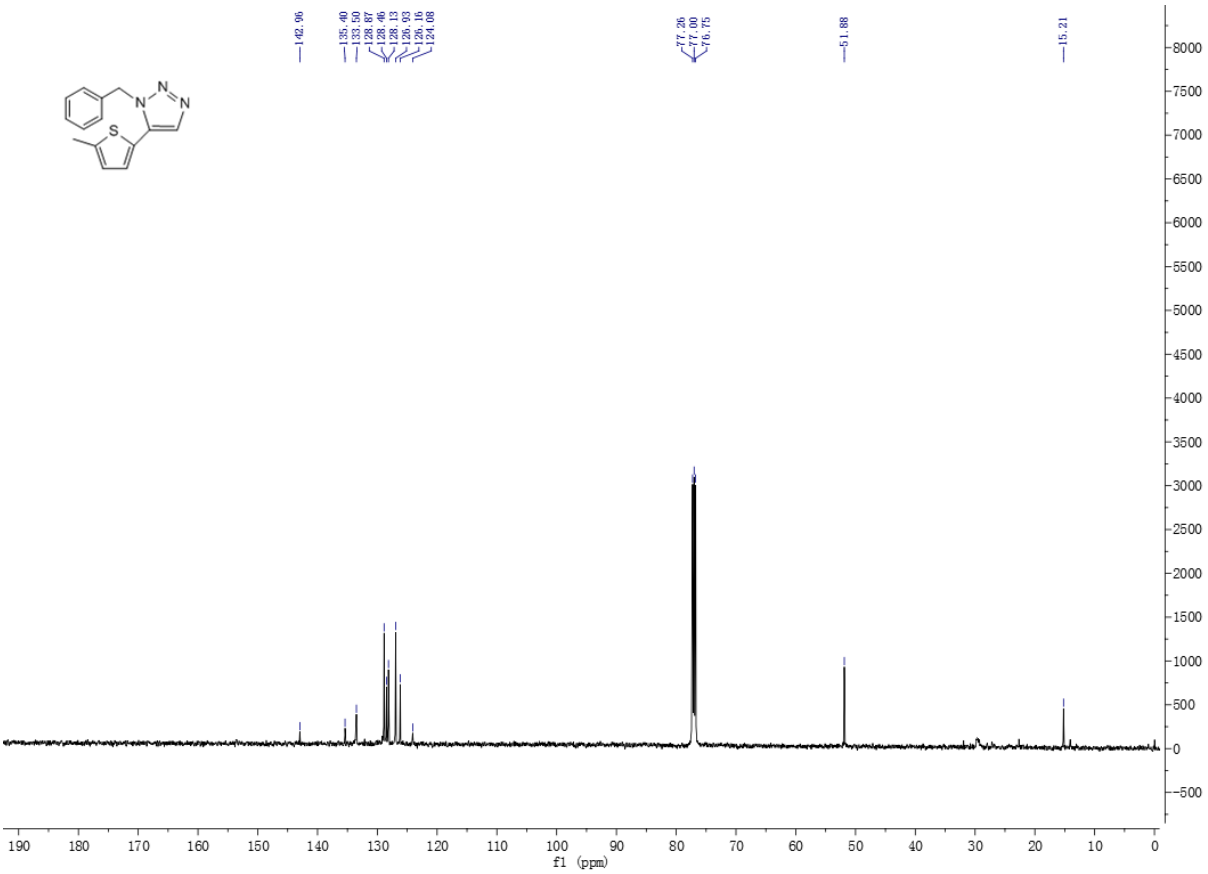

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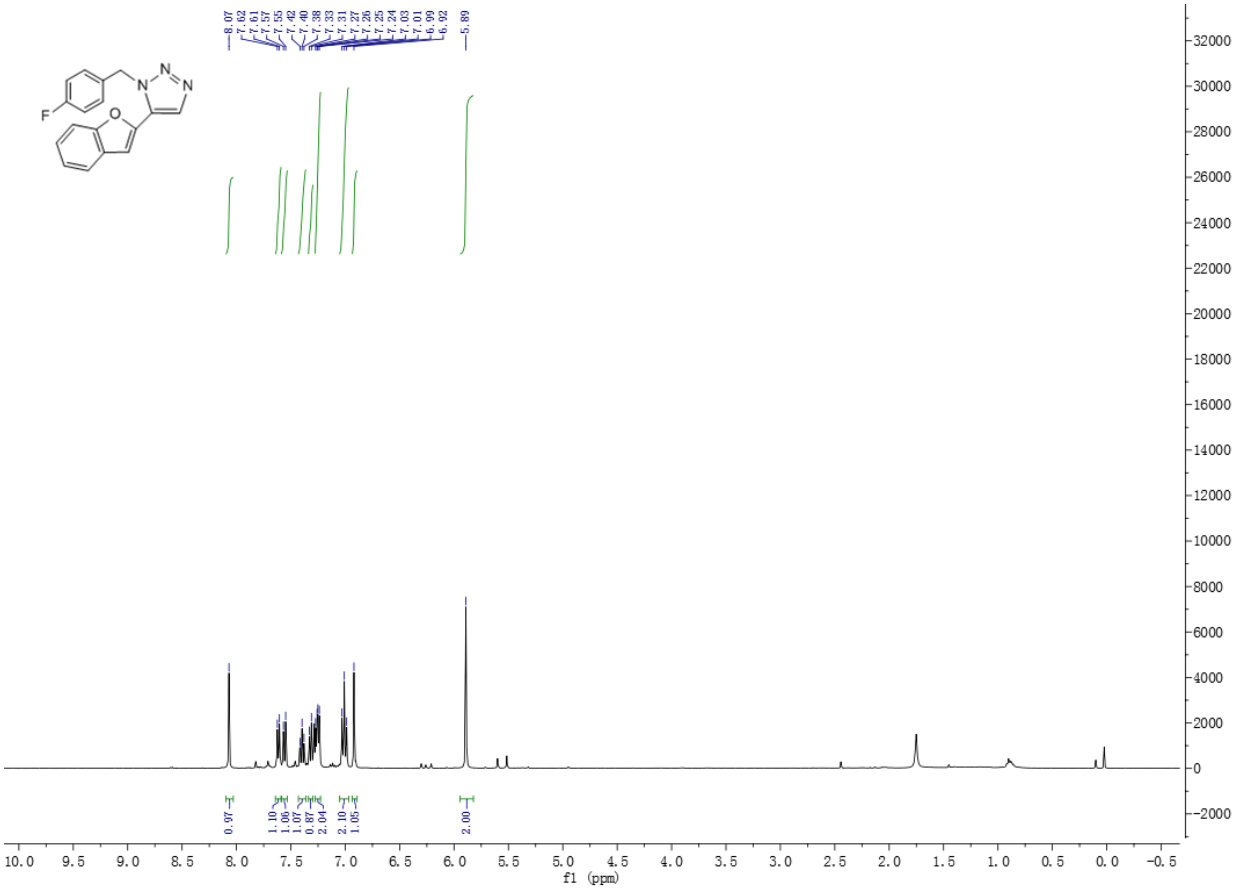

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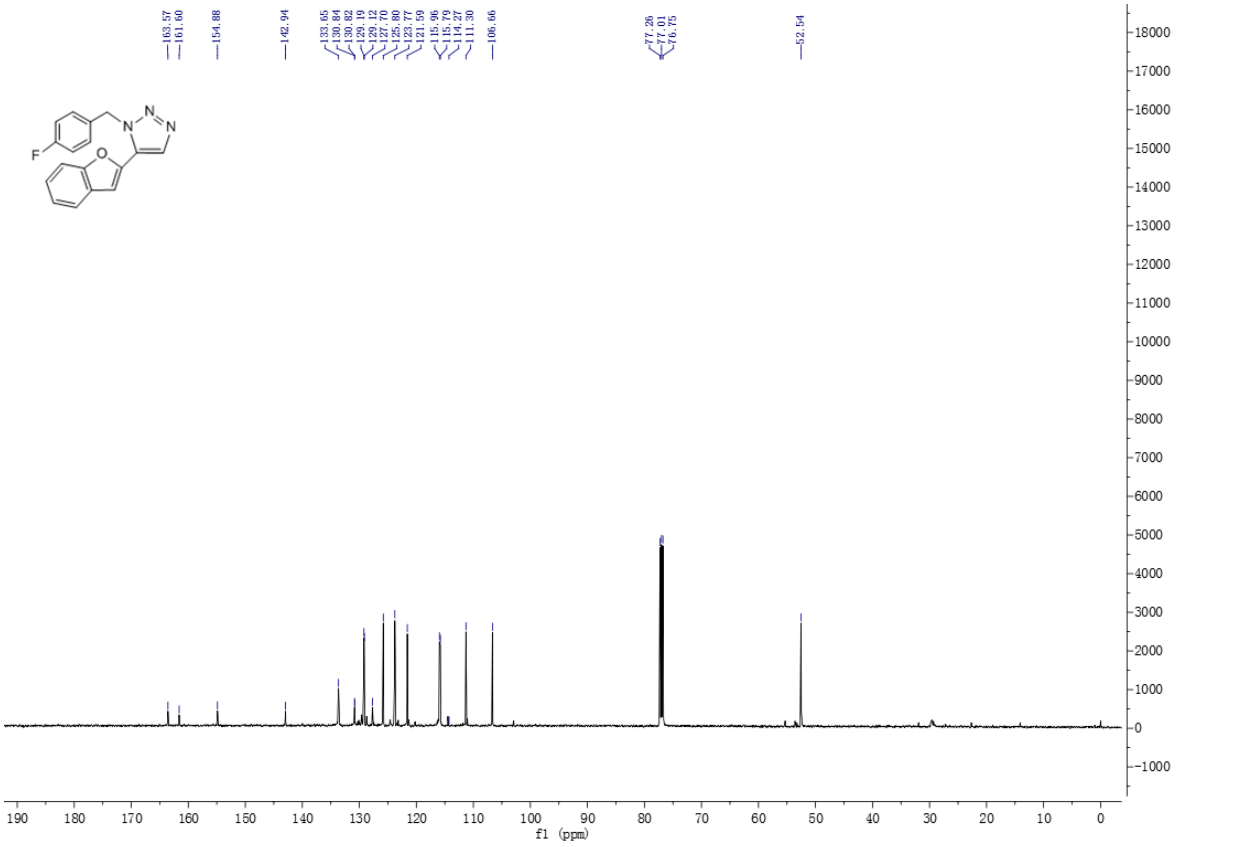

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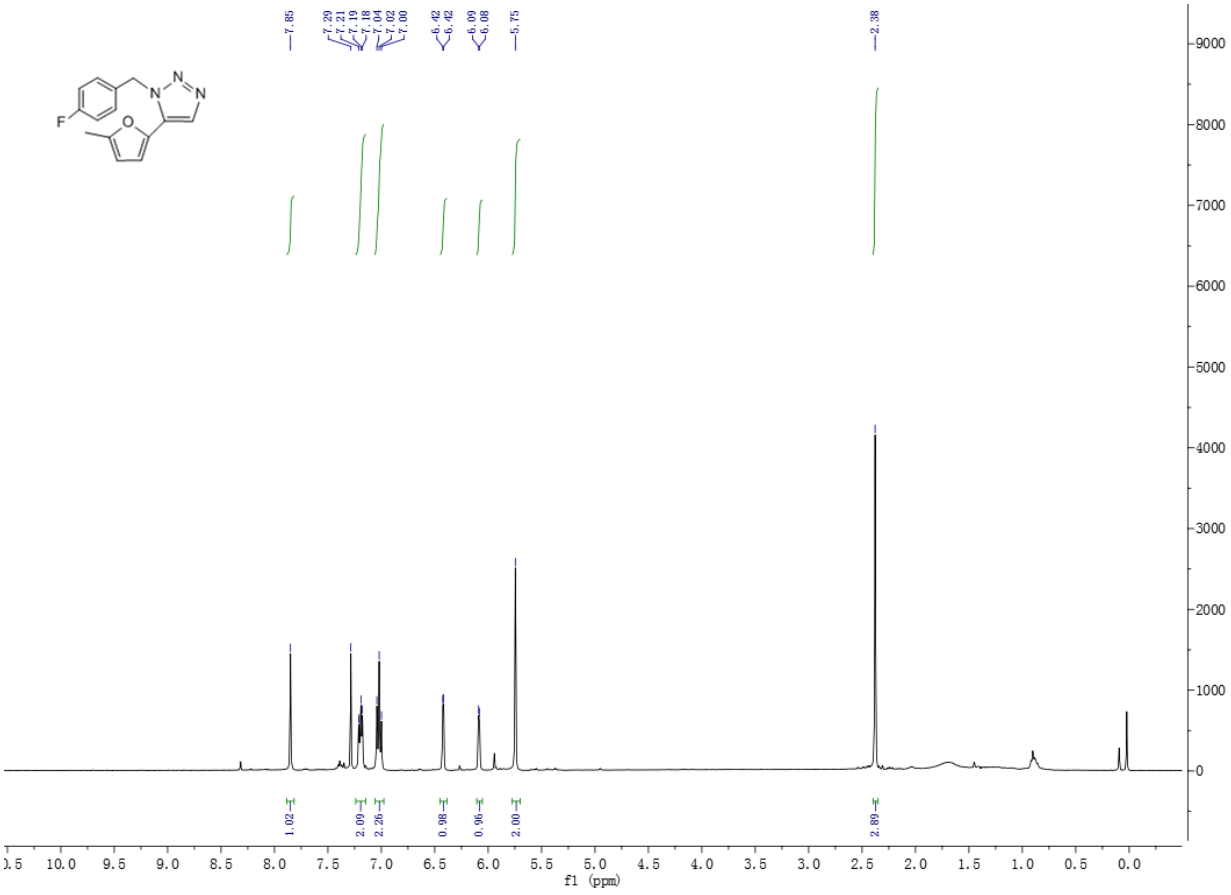

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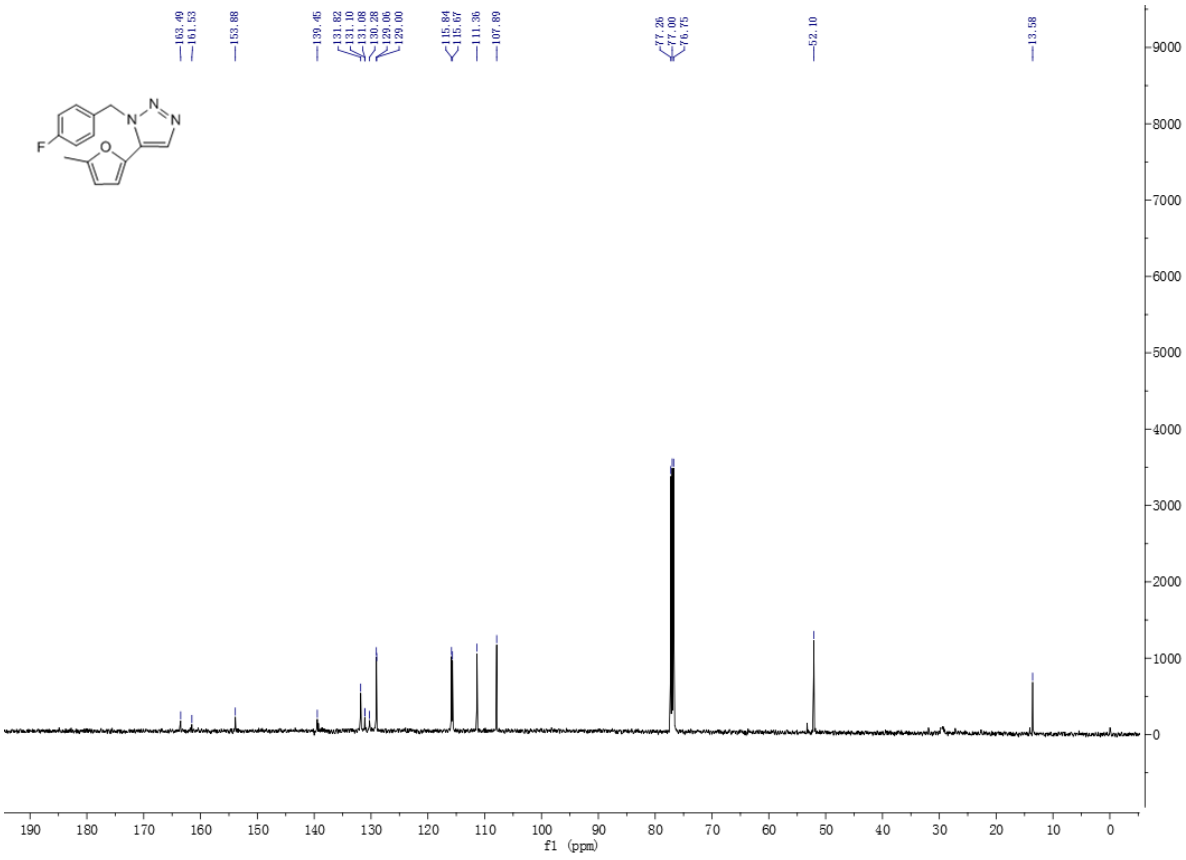

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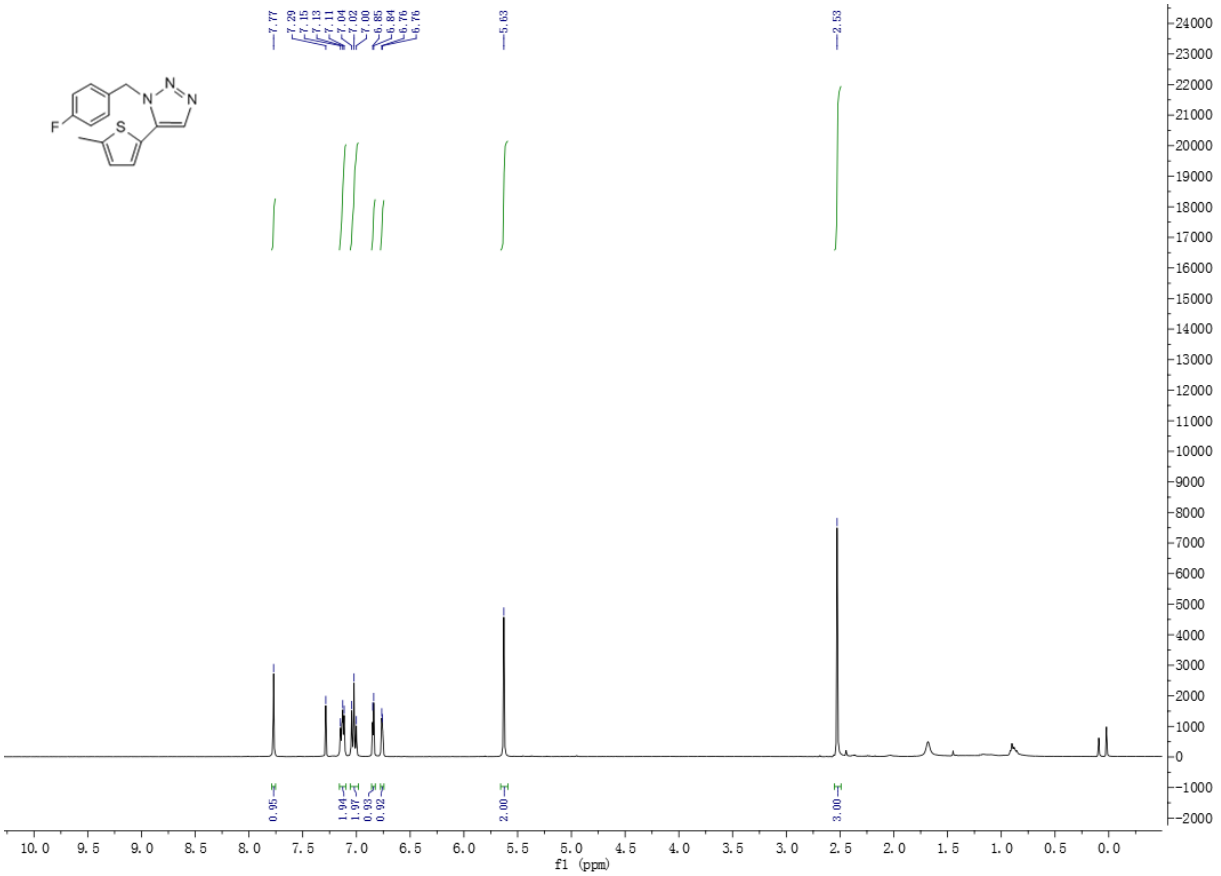

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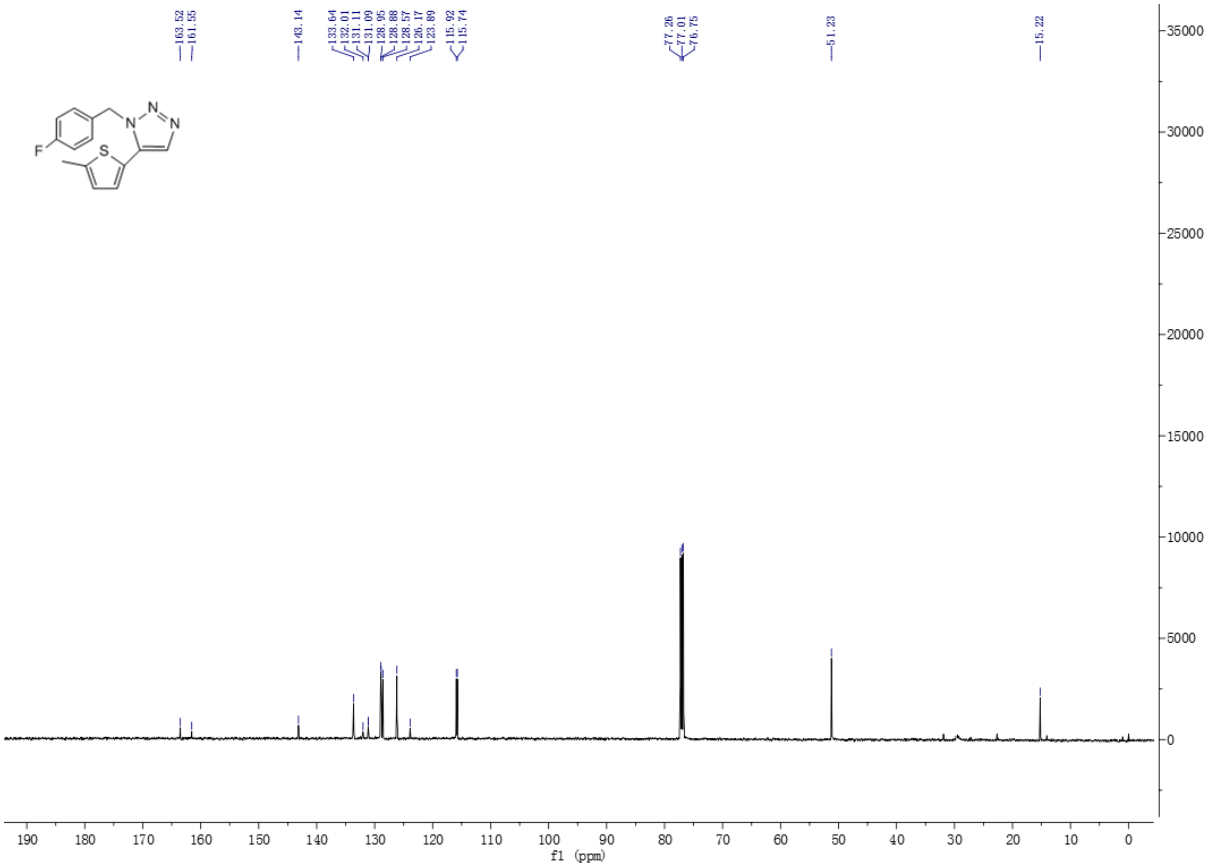
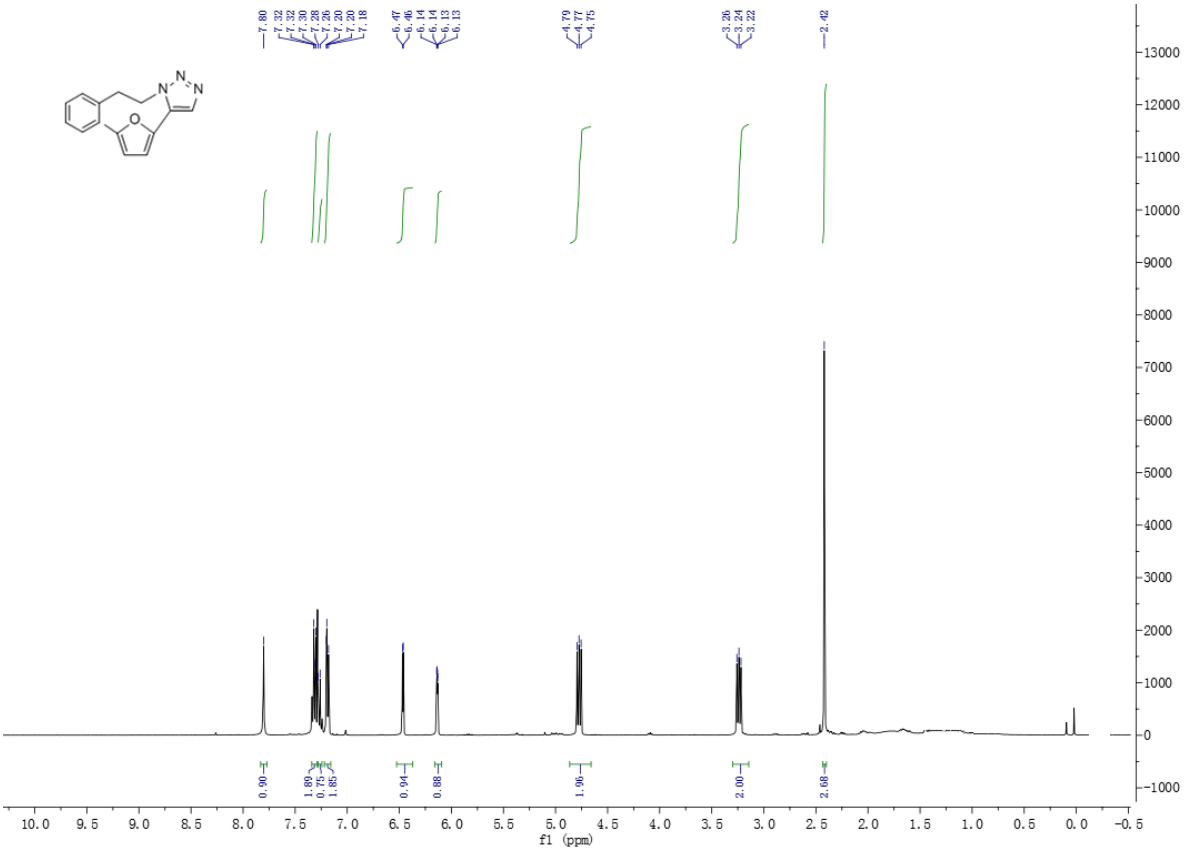


^{1}H NMR of 3ab



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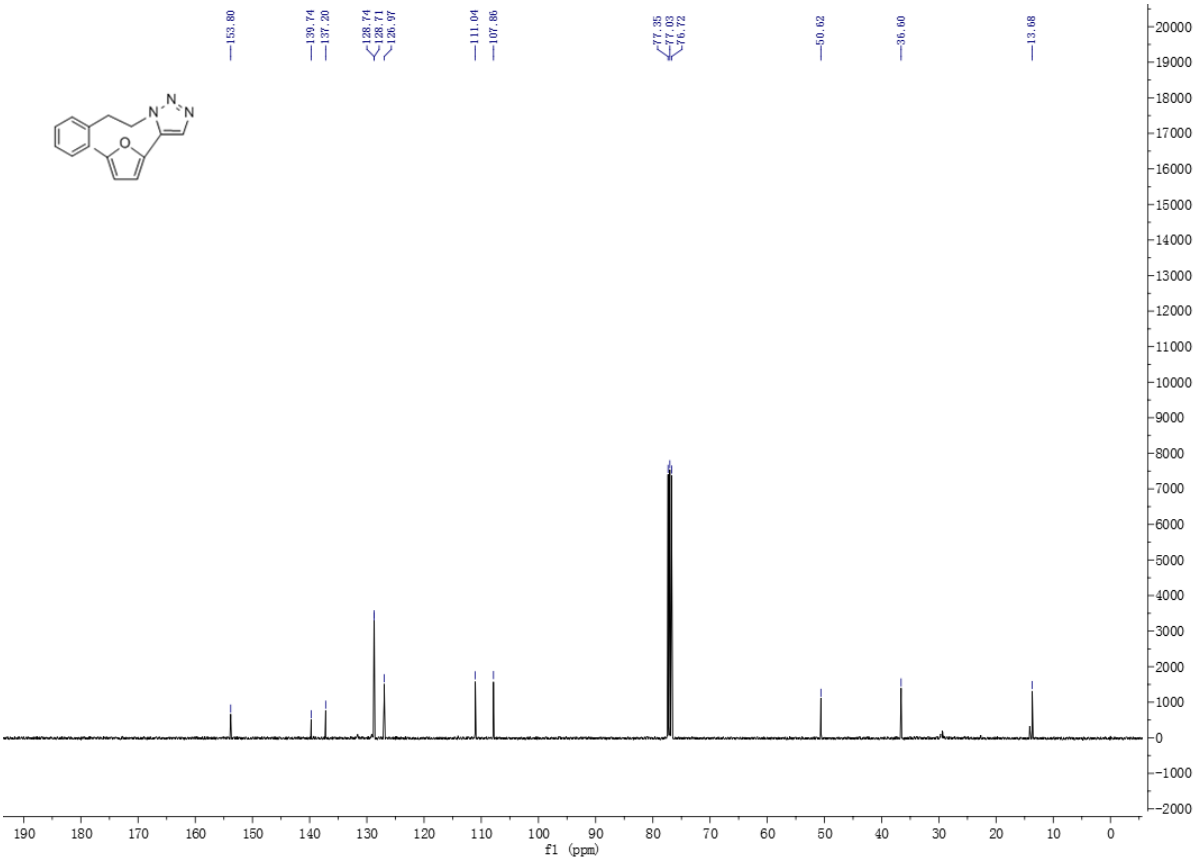
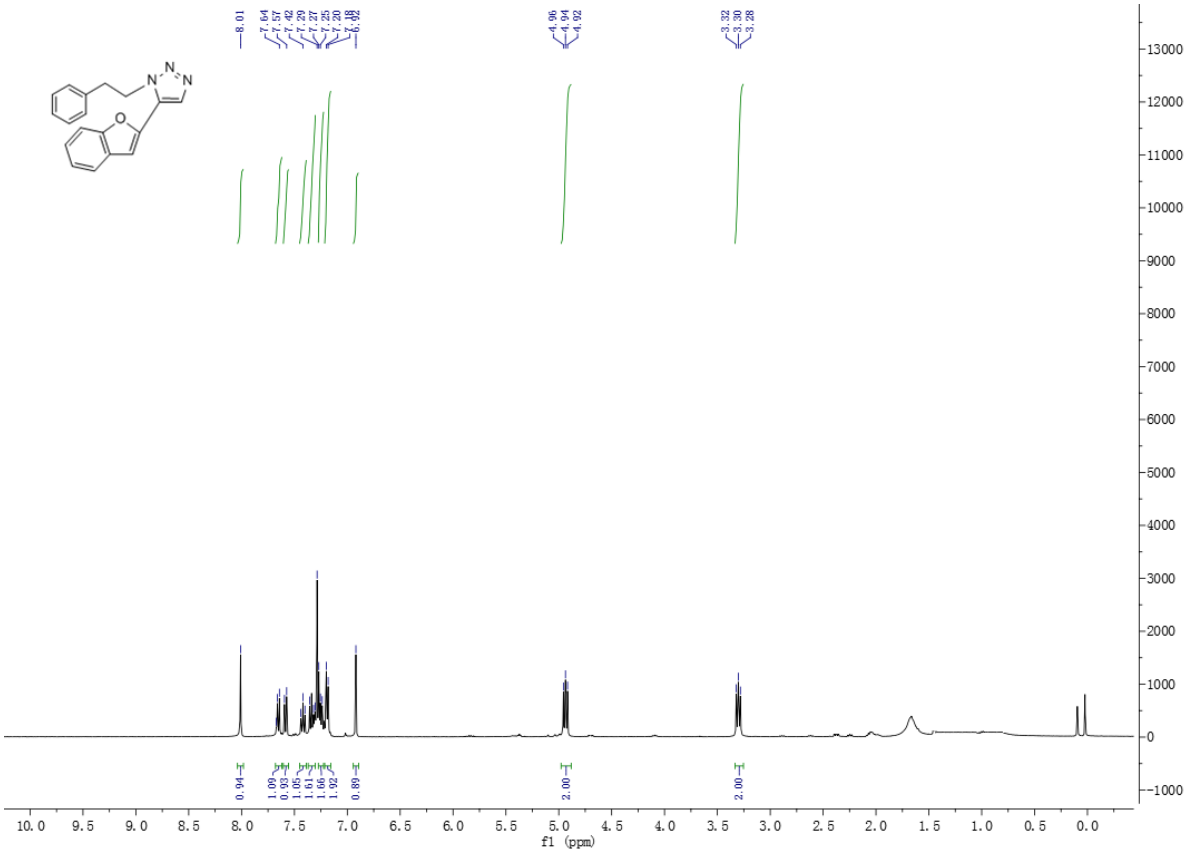


^{1}H NMR of 3ac



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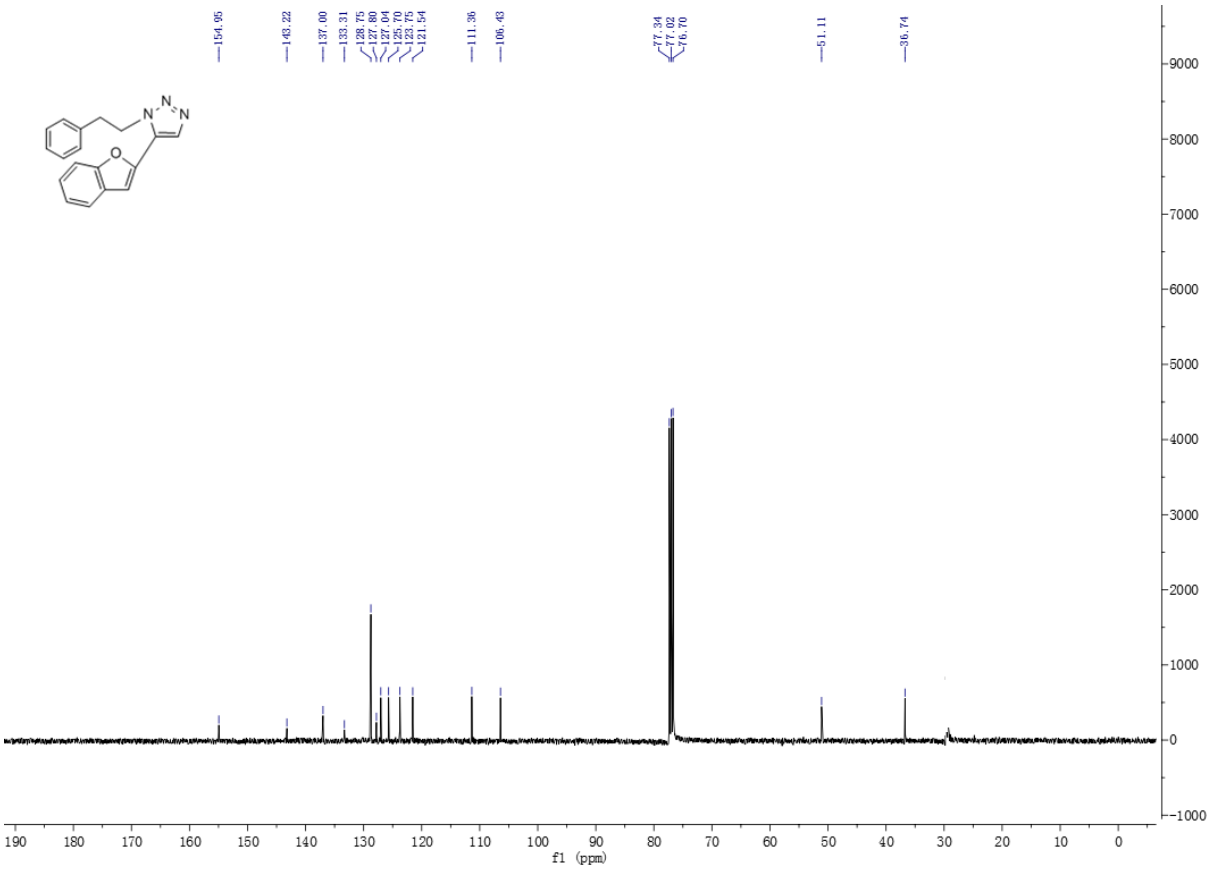
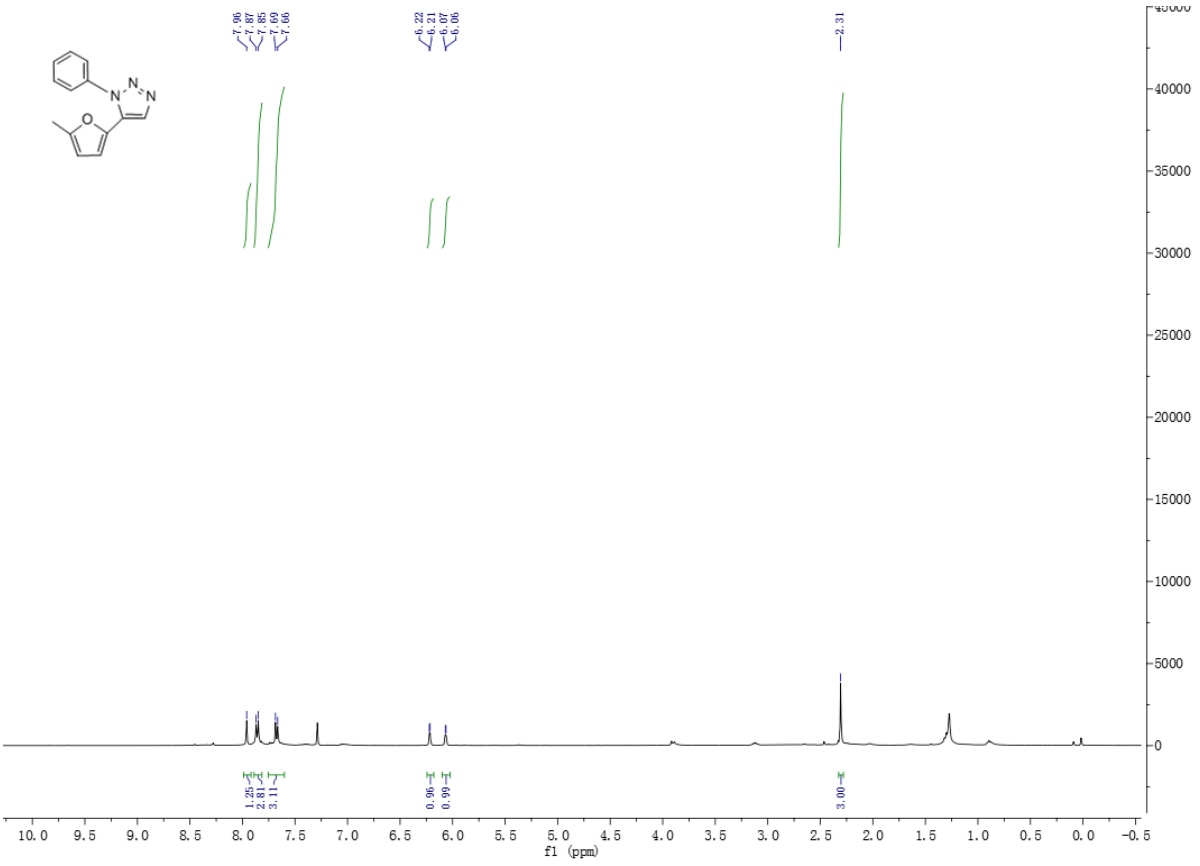


^{1}H NMR of 3ad



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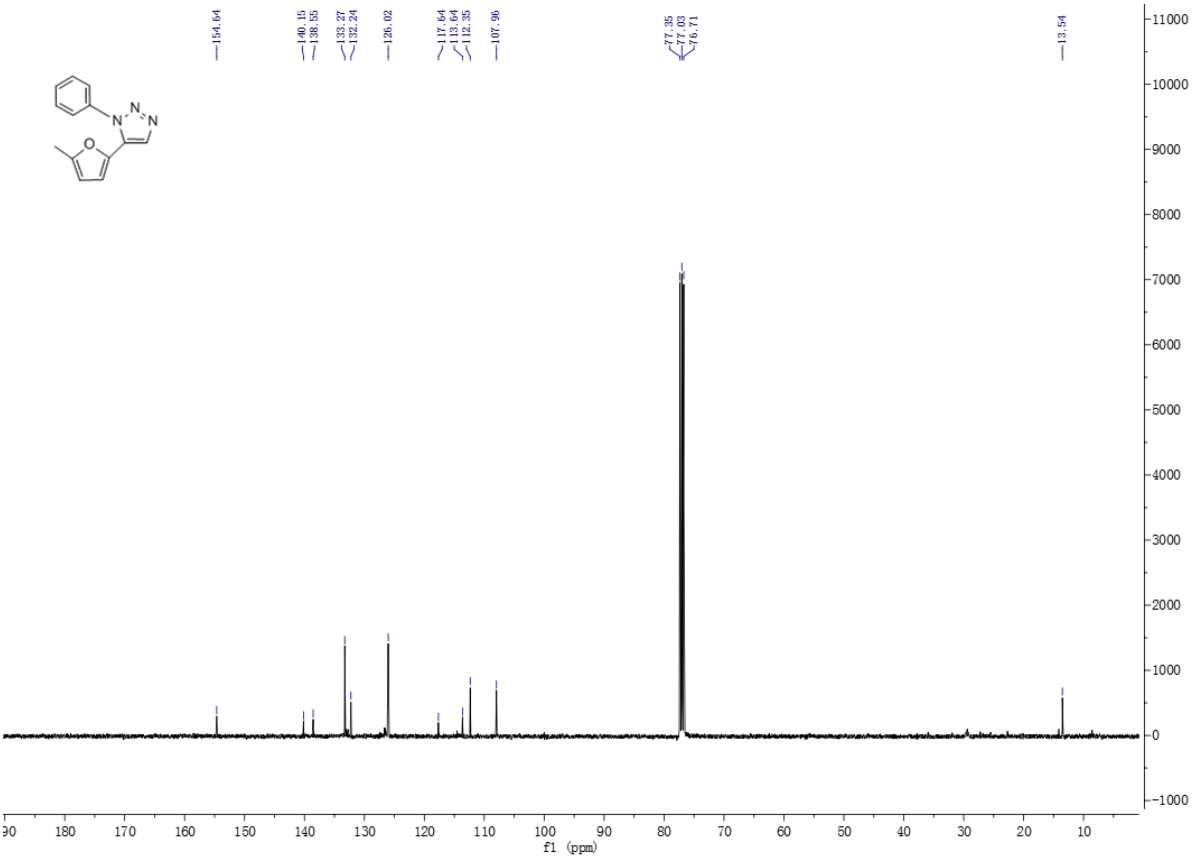

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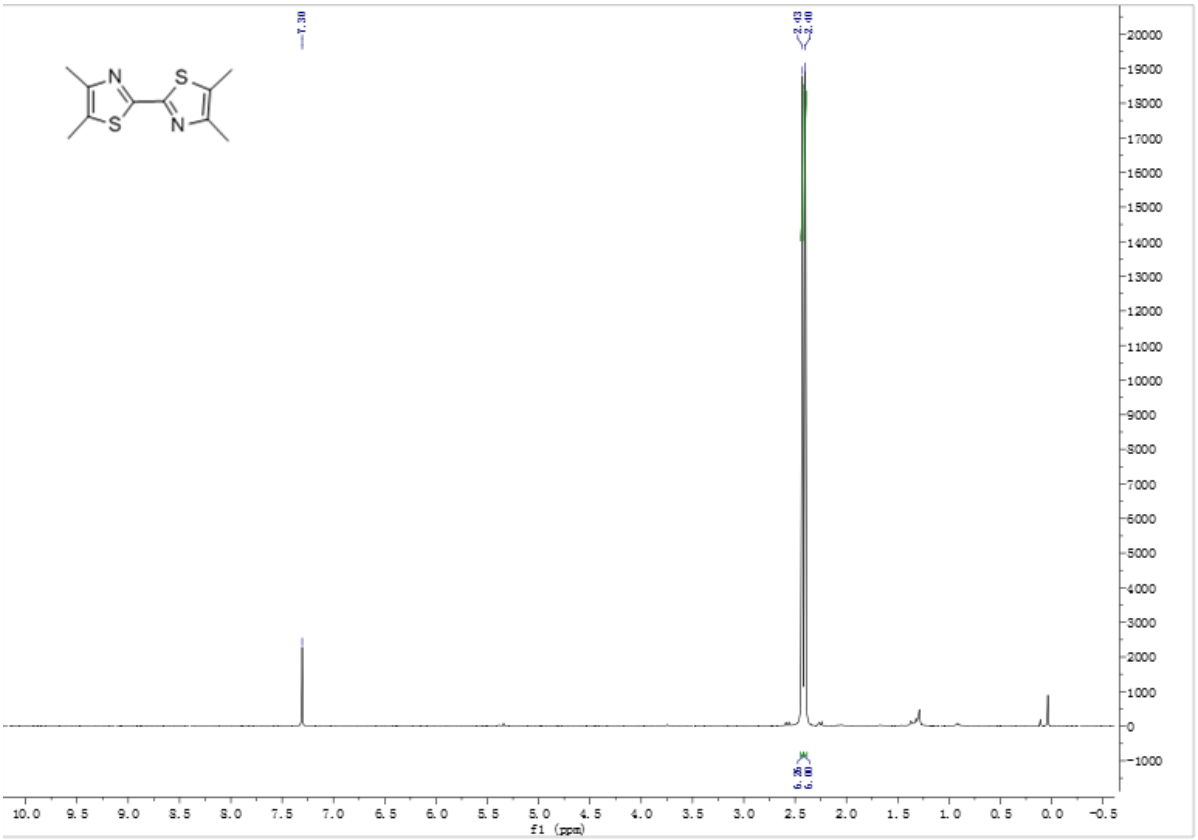
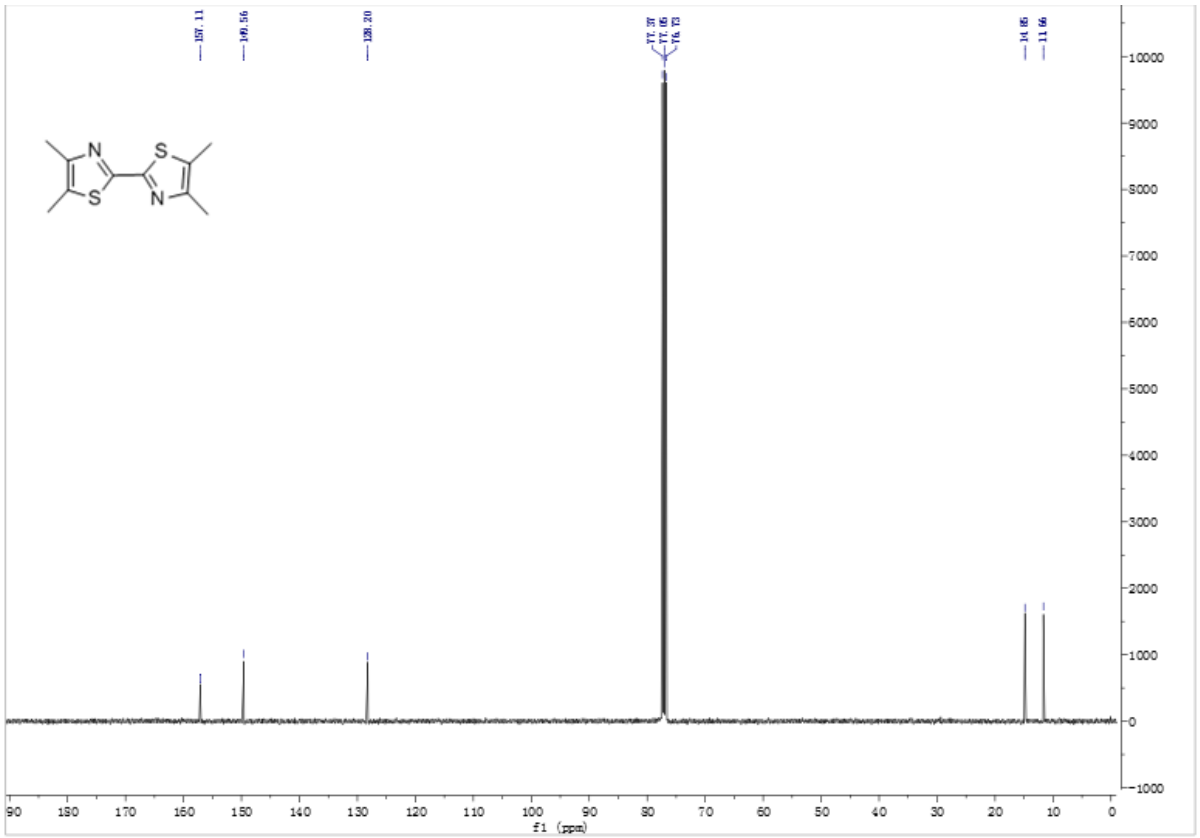

7.30
2.43
2.40
6.26
6.00
f1 (ppm)


157.11
149.56
128.20
77.37
77.05
76.73
14.85
11.66
f1 (ppm)