The Salting-Out Effect Enables Electrochemical Selective 1,2-Diazidation of Conjugated and Simple Olefins by Aryl Iodine Catalysis

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Supporting Information

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General remarks

All the manipulations were performed in air, unless mentioned otherwise. MeCN, NaN_3 were purchased from J&K Chemicals and used without further purification. The following chemicals were purchased and used as received: 4-Iodobenzotrifluoride (98%, Aladdin), 4-iodoanisole (98%, Aladdin), K_3PO_4 (98%, Aladdin), $^nBu_4NBF_4$ (98%, Aladdin). All alkenes were prepared by literature report procedures.[1]

^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded using Agilent Technologies 600 MHz NMR spectrometer or Bruker 400 MHz NMR spectrometer. ^1H NMR and ^{13}C NMR spectra were referenced to resonances of the residual protons in the deuterated solvents. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, br = broad singlet and m = multiplet. HR-MS analyses were performed at a Thermo Scientific Exactive-TOF (ESI ionization source).

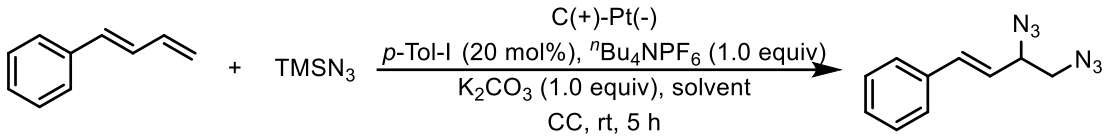
All electrolysis reactions were performed on HYELEC Instruments Power Supply (Model HY3001B) with oven-dried vial (10 mL) unless otherwise noted.

General procedure

In an undivided electrolysis cell, **1a** (39.2 mg, 0.3 mmol), Ar-I (0.06 mmol), NaN_3 (26 mg, 0.4 mmol), $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (63.6 mg, 0.3 mmol) and a magnetic stirring bar were added under air. Then MeCN (2.1 mL) and H_2O (0.9 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at rt for 15 min to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 10 mA until the complete consumption of the starting materials which was monitored by TLC. The solvent was removed in vacuo, and the crude residue was purified via column chromatography to afford the desired product.

Screening and optimization

Table S1 Screening of solvents and currents

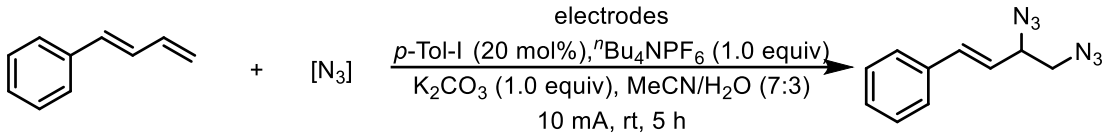


1a **2a**

entry	solvent	CC	yield of **2a** (%)
1	CH_3OH/H_2O (1:1)	3 mA	N.D.
2	$^{i}PrOH/H_2O$ (1:1)	3 mA	NR
3	$^{t}BuOH/H_2O$ (1:1)	3 mA	NR
4	$CHCl_3/H_2O$ (1:1)	3 mA	11
5	$DMSO/H_2O$ (1:1)	3 mA	trace
6	$MeCN/H_2O$ (1:1)	3 mA	13
7	$MeCN/H_2O$ (10:1)	3 mA	15
8	$MeCN/H_2O$ (7:3)	3 mA	19
9	$MeCN/H_2O$ (7:3)	5 mA	24
10	$MeCN/H_2O$ (7:3)	10 mA	35

Reaction conditions: undivided cell, graphite anode, Pt cathode, **1a** (0.3 mmol), $TMSN_3$ (1.8 mmol, 6.0 equiv), *p*-Tol-I (0.06 mmol, 20 mol%), $^{n}Bu_4NBF_4$ (0.1 M), K_2CO_3 (1.0 equiv), solvent (3 mL), CCE, rt, 5 h.

Table S2 Screening of azide sources and electrode materials



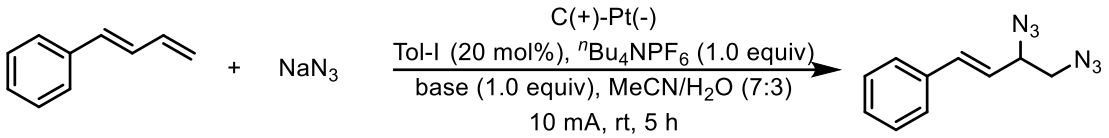
1a **2a**

entry	$[N_3]$	CC/CV	electrodes	yield of **2a** (%)
1	$TMSN_3$	10 mA	C/Pt	35
2	$TMSN_3$	10 mA	C/C	N.D.
3	$TMSN_3$	2.5 V	C/Pt	30
4	NaN_3	10 mA	C/Pt	44
5	NaN_3	10 mA	C/C	36

Reaction conditions: undivided cell, electrode, **1a** (0.3 mmol), $[N_3]$ (1.8 mmol, 6.0 equiv), *p*-Tol-I (0.06

mmol, 20 mol%), $^{n}Bu_4NBF_4$ (0.1 M), K_2CO_3 (1.0 equiv), MeCN/H_2O (7:3, 3 mL), CCE, rt, 5 h.

Table S3 Screening of base

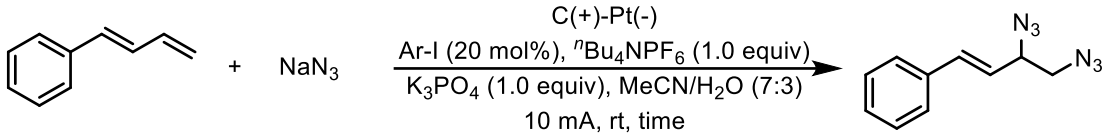


1a **2a**

entry	base	yield of **2a** (%)
1	K_2CO_3	44
2	K_3PO_4	65
3	NaH_2PO_4•$2H_2O$	25
4	Na_2SO_3	37
5	CH_3COOK	20

Reaction conditions: undivided cell, graphite anode, Pt cathode, **1a** (0.3 mmol), NaN_3 (1.8 mmol, 6.0 equiv), *p*-Tol-I (0.06 mmol, 20 mol%), $^{n}Bu_4NBF_4$ (0.1 M), base (1.0 equiv), MeCN/H_2O (7:3, 3 mL), 10 mA, rt, 5 h.

Table S4 Screening of aryl iodine and reaction time



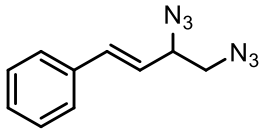
1a 6.0 equiv **2a**

entry	ArI	time	yield of **2a** (%)
1	Tol-I	5 h	65
2	4-Iodobenzotrifluoride	5 h	68
3	Iodobenzene	5 h	61
4	4-Iodobenzotrifluoride	4 h	71
5	4-Iodobenzotrifluoride	3 h	72
6	4-Iodobenzotrifluoride	2 h	52

Reaction conditions: undivided cell, graphite anode, Pt cathode, **1a** (0.3 mmol), NaN_3 (1.8 mmol, 6.0 equiv), Ar-I (0.06 mmol, 20 mol%), $^{n}Bu_4NBF_4$ (0.1 M), K_3PO_4 (1.0 equiv), MeCN/H_2O (7:3, 3 mL), 10 mA, rt, time.

Characterization data of diazide products

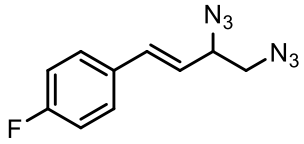
(*E*)-(3,4-diazidobut-1-en-1-yl) benzene (**1a**)



2a

The title compound was isolated (32.9 mg, 77%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.36 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.33 – 7.30 (m, 1H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.27 (td, *J* = 7.5, 4.9 Hz, 1H), 3.44 – 3.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 135.5, 128.9, 128.8, 127.0, 123.1, 64.1, 54.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}N_6^+$: 215.1040, found 215.1046.

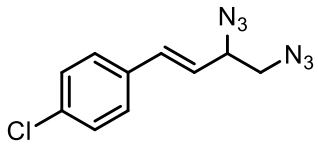
(*E*)-1-(3,4-diazidobut-1-en-1-yl)-4-fluorobenzene (**2b**)



2b

The title compound was isolated (30.2 mg, 65%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.09 – 7.00 (m, 2H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.43 – 3.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 248.5 Hz), 134.5, 131.7 (d, *J* = 3.4 Hz), 128.6 (d, *J* = 8.3 Hz), 122.9 (d, *J* = 2.4 Hz), 115.9 (d, *J* = 21.8 Hz), 64.0, 54.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.60. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}FN_6^+$:233.0945, found 233.0944.

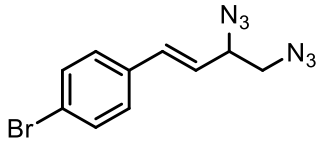
(*E*)-1-Chloro-4-(3,4-diazidobut-1-en-1-yl) benzene (2c)



2c

The title compound was isolated (30.3 mg, 61%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 4H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.25 (td, *J* = 7.4, 4.9 Hz, 1H), 3.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 134.3, 1344.0, 129.1, 128.1, 123.8, 63.9, 54.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}ClN_6^+$:249.0650, found 249.0650.

(*E*)-1-Bromo-4-(3,4-diazidobut-1-en-1-yl) benzene (**2d**)

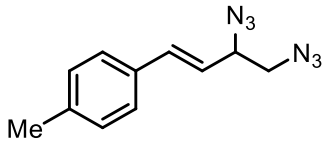


2d

The title compound was isolated (40.9 mg, 70%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* =

8.1 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.25 (td, *J* = 7.3, 4.9 Hz, 1H), 3.40 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 134.4, 132.0, 128.4, 124.0, 122.7, 63.9, 54.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}BrN_6^+$:293.0145, found 293.0148.

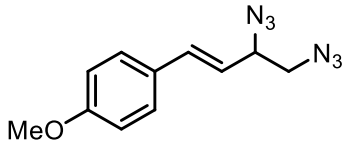
(*E*)-1-(3,4-Diazidobut-1-en-1-yl)-4-methylbenzene (2e)



2e

The title compound was isolated (30.1 mg, 66%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.25 (td, *J* = 7.5, 5.0 Hz, 1H), 3.43 – 3.35 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 135.7 132.7, 129.6, 126.9, 122.0, 64.2, 54.7, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}N_6^+$:229.1196, found 229.1192.

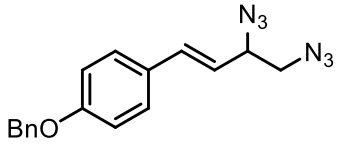
(*E*)-1-(3,4-Diazidobut-1-en-1-yl)-4-methoxybenzene (2f)



2f

The title compound was isolated (34.2 mg, 70%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 6.91 – 6.86 (m, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.24 (td, *J* = 7.4, 5.0 Hz, 1H), 3.82 (s, 3H), 3.43 – 3.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 135.3, 128.3, 128.2, 120.7, 114.3, 64.3, 55.5, 54.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}N_6O^+$:245.1145, found 245.1152.

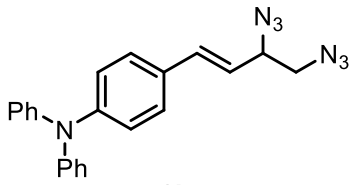
(*E*)-1-(Benzyloxy)-4-(3,4-diazidobut-1-en-1-yl) benzene (2g)



2g

The title compound was isolated (40.9 mg, 64%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 70:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.31 (m, 3H), 6.96 (dd, *J* = 8.6, 2.0 Hz, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 5.99 (m, 1H), 5.09 (s, 2H), 4.24 (dt, *J* = 7.9, 4.2 Hz, 1H), 3.44 – 3.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 136.8, 135.2, 128.8, 128.4, 128.3, 128.2, 127.6, 120.8, 115.2, 70.2, 64.3, 54.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}N_6O^+$:321,1458, found 321.1455.

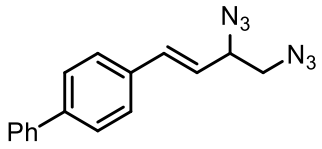
(*E*)-4-(3,4-Diazidobut-1-en-1-yl)-*N*,*N*-diphenylaniline (2h)



2h

The title compound was isolated (31.2 mg, 41%) as a brown solid after flash chromatography on silica gel (Hexane/EtOAc = 50:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 5H), 7.16 – 7.09 (m, 5H), 7.07 – 7.02 (m, 4H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.01 (m, 1H), 4.30 – 4.23 (m, 1H), 3.44 – 3.34 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 147.4, 135.3, 129.5, 129.2, 127.8, 124.8, 123.4, 123.2, 121.0, 64.3, 54.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_7^+$:382.1775, found 382.1784.

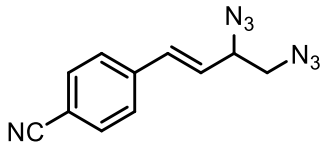
(*E*)-4-(3,4-Diazidobut-1-en-1-yl)-1,1'-biphenyl (**2i**)



2i

The title compound was isolated (26.1 mg, 45%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 8.3, 4.8 Hz, 4H), 7.52 – 7.40 (m, 5H), 7.35 (dd, *J* = 8.5, 6.0 Hz, 1H), 6.75 (dd, *J* = 15.8, 2.7 Hz, 1H), 6.15 (m, 1H), 4.33 – 4.21 (m, 1H), 3.47 – 3.32 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.5, 140.5, 135.2, 134.4, 129.0, 127.7, 127.5, 127.4, 127.1, 123.1, 64.1, 54.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}N_6^+$:293.1353, found 293.1350.

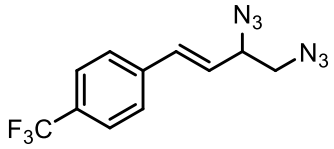
(*E*)-4-(3,4-Diazidobut-1-en-1-yl) benzonitrile (**2j**)



2j

The title compound was isolated (26.8 mg, 56%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 70:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.54 – 7.47 (m, 2H), 6.76 (dd, *J* = 15.9, 1.0 Hz, 1H), 6.26 (dd, *J* = 15.9, 7.6 Hz, 1H), 4.30 (m, 1H), 3.44 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 133.6, 132.7, 127.4, 127.2, 118.7, 112.0, 63.5, 54.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{10}N_7^+$:240.0992, found 240.0990.

(*E*)-1-(3,4-Diazidobut-1-en-1-yl)-4-(trifluoromethyl) benzene (2k)

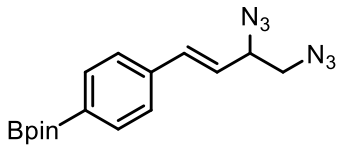


2k

The title compound was isolated (38.4 mg, 68%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.8, 7.7 Hz, 1H), 4.29 (td, *J* = 7.2, 4.8 Hz, 1H), 3.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.0, 134.1, 130.6 (d, *J* = 32.6 Hz),

127.2, 126.3 – 125.7 (m), 125.0, 123.2, 63.7, 54.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.64 HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{10}F_3N_6^+$:283.0914, found 283.0911.

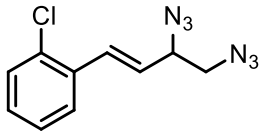
(*E*)-2-(4-(3,4-Diazidobut-1-en-1-yl) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**)



2l

The title compound was isolated (57.8 mg, 85%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.43 – 7.39 (m, 2H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.22 – 6.14 (m, 1H), 4.30 – 4.22 (m, 1H), 3.44 – 3.35 (m, 2H), 1.36 – 1.33 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.1, 135.6, 135.3, 126.21, 124.11, 84.04, 64.04, 54.65, 24.99. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}BN_6O_2^+$:381.1192, found 381.1192..

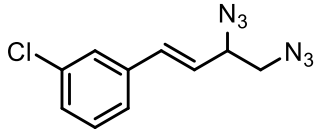
(*E*)-1-Chloro-2-(3,4-diazidobut-1-en-1-yl) benzene (**2m**)



2m

The title compound was isolated (24.3 mg, 49%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.38 (dd, *J* = 6.7, 2.5 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.12 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.31 (td, *J* = 7.4, 4.8 Hz, 1H), 3.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.8, 133.6, 131.9, 130.0, 129.8, 127.24, 127.15, 126.0, 63.9, 54.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}ClN_6^+$:249.0650, found 249.0651.

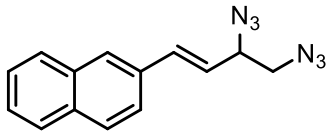
(*E*)-1-Chloro-3-(3,4-diazidobut-1-en-1-yl) benzene (**2n**)



2n

The title compound was isolated (30.3 mg, 61%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 1.5 Hz, 3H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 7.8 Hz, 1H), 4.32 – 4.20 (m, 1H), 3.40 (h, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 134.9, 134.2, 130.1, 128.7, 126.9, 125.2, 124.8, 63.8, 54.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}ClN_6^+$:249.0650, found 249.0652.

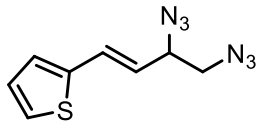
(*E*)-2-(3,4-Diazidobut-1-en-1-yl) naphthalene (**2o**)



2o

The title compound was isolated (39.1 mg, 74%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.61 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 6.90 (d, *J* = 15.8 Hz, 1H), 6.25 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.32 (td, *J* = 7.5, 4.9 Hz, 1H), 3.44 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.8, 133.6, 132.9, 128.6, 128.3, 127.9, 127.5, 126.7, 126.6, 123.5, 123.4, 64.2, 54.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{13}N_6^+$:287.1016, found 287.1018.

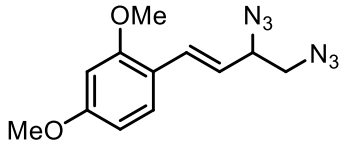
(*E*)-2-(3,4-Diazidobut-1-en-1-yl) thiophene (2p)



2p

The title compound was isolated (28.2 mg, 64%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.05 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 5.94 (dd, *J* = 15.6, 7.9 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.38 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 128.5, 127.7, 127.5, 125.8, 122.4, 63.9, 54.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_8H_9N_6S^+$:221.0604, found 221.0605.

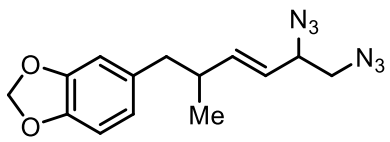
(*E*)-1-(3,4-Diazidobut-1-en-1-yl)-2,4-dimethoxybenzene (2q)



2q

The title compound was isolated (28.2 mg, 64%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.95 (m, 2H), 6.82 (d, *J* = 2.1 Hz, 2H), 6.14 (m, 1H), 4.26 (q, *J* = 6.9 Hz, 1H), 3.81 (d, *J* = 1.9 Hz, 3H), 3.79 (d, *J* = 1.9 Hz, 3H), 3.45 – 3.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 151.6, 130.6, 125.1, 123.7, 114.9, 112.6, 112.4, 64.5, 56.2, 55.8, 54.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{15}N_6O_2^+$:275.1251, found 275.1251.

(*E*)-5-(5,6-Diazido-2-methylhex-3-en-1-yl) benzo[*d*] [1,3] dioxole (2r)

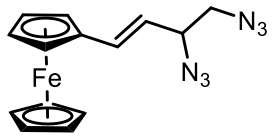


2r

The title compound was isolated (21.0 mg, 35%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 6.6, 2.5 Hz, 1H), 7.43 – 7.29 (m, 1H), 6.96 (dd, *J* = 10.0, 8.7 Hz, 1H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 7.8 Hz, 1H), 4.27 (td, *J* = 7.3, 4.8 Hz, 1H), 3.41 (m, 2H), 3.25 – 3.13 (m, 2H),

1.65 – 1.62 (m, 1H), 1.42 (p, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 158.7, 132.8, 132.7, 130.6, 130.6, 127.4, 127.3, 126.8, 126.7, 125.5, 125.4, 118.0, 117.8, 117.1, 117.0, 63.9, 58.8, 54.5, 24.0, 19.8, 13.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}N_6O_2^+$:301.1408, found 301.1400.

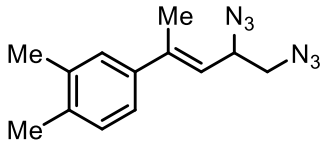
(*E*)-(3,4-Diazidobut-1-en-1-yl) ferrocene (2s)



2s

The title compound was isolated (30.3 mg, 47%) as a red solid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.55 – 6.45 (m, 1H), 5.69 (m, 1H), 4.41 (dt, *J* = 4.0, 1.9 Hz, 1H), 4.36 – 4.32 (m, 1H), 4.31 – 4.25 (m, 2H), 4.15 (dt, *J* = 6.4, 2.8 Hz, 1H), 4.13 – 4.07 (m, 4H), 3.34 – 3.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 119.3, 80.9, 69.7, 69.6, 69.5, 67.9, 66.8, 64.4, 54.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}F_eN_6^+$:323.0696, found 323.0696.

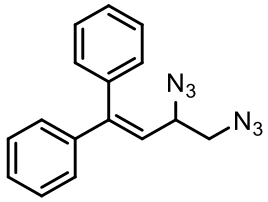
(*E*)-4-(4,5-Diazidopent-2-en-2-yl)-1,2-dimethylbenzene (**2t**)



2t

The title compound was isolated (33.3 mg, 65%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (s, 2H), 6.96 (s, 1H), 5.69 – 5.66 (m, 1H), 4.52 (dt, *J* = 9.2, 6.0 Hz, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.33 (s, 6H), 2.16 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 142.2, 138.1, 129.9, 125.4, 124.0, 120.9, 59.9, 54.7, 21.5, 17.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}N_6^+$:257.1509, found 257.1509.

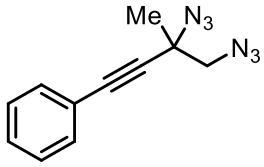
(3,4-Diazidobut-1-ene-1,1-diyl) dibenzene (2u)



2u

The title compound was isolated (23.8 mg, 41%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.31 (dt, *J* = 5.8, 2.4 Hz, 3H), 7.28 (dd, *J* = 6.9, 3.1 Hz, 2H), 7.22 – 7.17 (m, 2H), 6.06 (d, *J* = 9.9 Hz, 1H), 4.24 (dt, *J* = 9.9, 5.9 Hz, 1H), 3.35 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 140.6, 138.3, 129.6, 128.8, 128.6, 128.5, 128.2, 127.6, 121.9, 60.3, 54.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}N_6^+$:291.1353, found 291.1350.

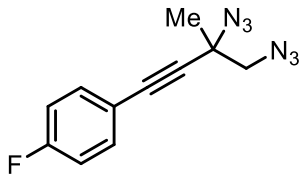
(3,4-Diazido-3-methylbut-1-yn-1-yl) benzene (2v)



2v

The title compound was isolated (31.7 mg, 70%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 3.50 – 3.35 (m, 2H), 1.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.2, 129.3, 128.5, 121.5, 88.0, 85.1, 60.5, 60.0, 25.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}N_6^+$:227.1040, found 227.1043.

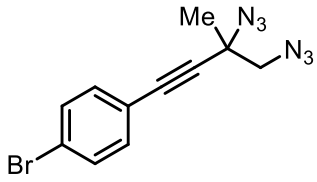
1-(3,4-Diazido-3-methylbut-1-yn-1-yl)-4-fluorobenzene (2w)



2w

The title compound was isolated (32.7 mg, 67%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.08 – 6.99 (m, 2H), 3.48 – 3.34 (m, 2H), 1.59 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, *J* = 250.4 Hz), 134.1 (d, *J* = 8.4 Hz), 117.5 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 22.5 Hz), 87.0, 84.8, 60.4, 59.9, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.47. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{10}FN_6^+$:245.0945, found 245.0944.

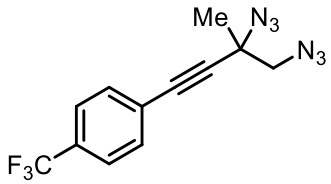
1-Bromo-4-(3,4-diazido-3-methylbut-1-yn-1-yl) benzene (2x)



2x

The title compound was isolated (43.3 mg, 71%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.38 – 7.31 (m, 2H), 3.52 – 3.31 (m, 2H), 1.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.6, 131.9, 123.7, 120.4, 86.9, 86.3, 60.4, 59.8, 25.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{10}BrN_6^+$:305.0145, found 305.0149.

1-(3,4-Diazido-3-methylbut-1-yn-1-yl)-4-(trifluoromethyl) benzene (2y)

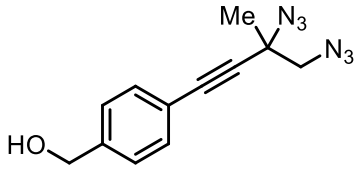


2y

The title compound was isolated (32.3 mg, 55%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (s,

4H), 3.50 – 3.35 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.2, 132.4, 131.2, 125.5 (d, *J* = 6.3 Hz), 87.5, 85.9, 60.3, 59.8, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.97. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{10}F_3N_6^+$:295.0914, found 295.0917.

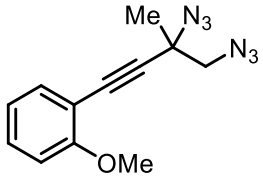
(4-(3,4-Diazido-3-methylbut-1-yn-1-yl) phenyl) methanol (2z)



2z

The title compound was isolated (22.5 mg, 44%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 60:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 4.70 (s, 2H), 3.51 – 3.33 (m, 2H), 1.90 (s, 1H), 1.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 132.3, 126.9, 120.6, 87.8, 85.1, 64.9, 60.5, 59.9, 25.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{13}N_6O^+$:257.1145, found 257.1146.

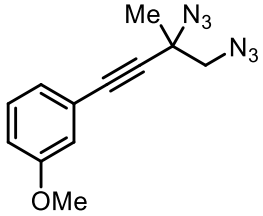
1-(3,4-Diazido-3-methylbut-1-yn-1-yl)-2-methoxybenzene (2aa)



2aa

The title compound was isolated (21.0 mg, 41%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 1H), 7.32 (td, *J* = 8.2, 1.8 Hz, 1H), 6.98 – 6.83 (m, 2H), 3.86 (s, 3H), 3.52 – 3.36 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 133.9, 130.7, 120.5, 110.9, 110.8, 89.1, 84.4, 60.6, 60.0, 55.8, 25.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{13}N_6O^+$:257.1145, found 257.1145.

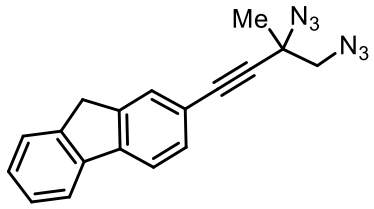
1-(3,4-Diazido-3-methylbut-1-yn-1-yl)-3-methoxybenzene (2ab)



2ab

The title compound was isolated (37.4 mg, 73%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 1H), 7.08 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.00 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.92 (m, 1H), 3.80 (s, 3H), 3.47 – 3.36 (m, 2H), 1.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 129.6, 124.7, 122.4, 116.9, 115.9, 87.9, 84.9, 60.4, 59.9, 55.5, 25.2. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{12}H_{13}N_6O^+$:279.0965, found 279.0966.

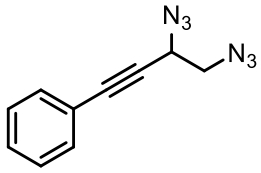
2-(3,4-Diazido-3-methylbut-1-yn-1-yl)-9H-fluorene (2ac)



2ac

The title compound was isolated (51.5 mg, 82%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.67 (s, 1H), 7.58 – 7.54 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.31 (m, 1H), 3.90 (s, 2H), 3.54 – 3.34 (m, 2H), 1.63 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 143.3, 142.8, 141.0, 131.0, 128.7, 127.6, 127.1, 125.3, 120.5, 119.9, 119.4, 88.8, 84.9, 60.6, 60.0, 36.8, 25.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{18}H_{15}N_6^+$:315.1353, found 315.1353.

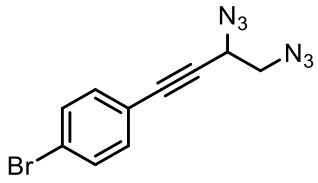
(3,4-Diazidobut-1-yn-1-yl) benzene (2ad)



2ad

The title compound was isolated (27.6 mg, 65%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.35 (m, 3H), 4.49 (t, *J* = 5.7 Hz, 1H), 3.53 – 3.50 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.2, 129.4, 128.6, 121.4, 89.2, 81.2, 54.7, 53.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_9N_6^+$:213.0883, found 213.0883.

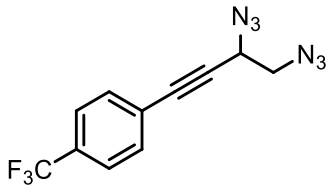
1-Bromo-4-(3,4-diazidobut-1-yn-1-yl) benzene (2ae)



2ae

The title compound was isolated (43.6 mg, 75%) as a yellow liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.47 (t, *J* = 5.7 Hz, 1H), 3.52 – 3.49 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.5, 131.9, 123.8, 120.2, 88.1, 82.4, 54.5, 53.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_8BrN_6^+$:290.9988, found 290.9994.

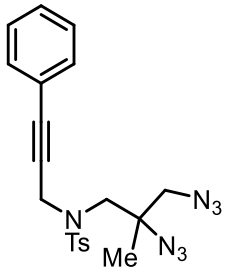
1-(3,4-Diazidobut-1-yn-1-yl)-4-(trifluoromethyl) benzene (2af)



2af

The title compound was isolated (29.1 mg, 52%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.3 Hz, 4H), 4.51 (t, *J* = 5.6 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.4, 126.3, 125.4 (d, *J* = 4.0 Hz), 125.1, 87.7, 83.7, 54.5, 53.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.00. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_8F_3N_6^+$:281.0757, found 281.0757.

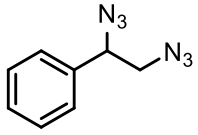
N-(2,3-Diazido-2-methylpropyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl) benzenesulfonamide (2ag)



2ag

The title compound was isolated (48.3 mg, 57%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 60:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.26 – 7.20 (m, 5H), 7.05 – 6.98 (m, 2H), 4.51 – 4.45 (m, 1H), 4.43 – 4.38 (m, 1H), 3.42 (d, *J* = 14.3 Hz, 1H), 3.40 – 3.34 (m, 1H), 2.83 (dd, *J* = 4.7, 2.1 Hz, 1H), 2.67 (dd, *J* = 4.7, 2.2 Hz, 1H), 2.33 (d, *J* = 2.2 Hz, 3H), 1.45 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 136.1, 131.6, 129.7, 128.5, 128.2, 127.9, 122.3, 86.0, 81.8, 55.8, 51.8, 51.2, 38.8, 21.6, 19.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{22}N_7O_2S^+$:424.1150, found 424.1153.

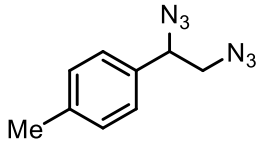
(1,2-Diazidoethyl) benzene (3a)



3a

The title compound was isolated (26.7 mg, 71%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 6.3 Hz, 2H), 7.41 – 7.38 (m, 1H), 7.37 – 7.33 (m, 2H), 4.68 (dd, *J* = 8.5, 4.8 Hz, 1H), 3.58 – 3.40 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.4, 129.1 (two peaks overlap), 127.0, 65.5, 56.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_8H_9N_6^+$:189.0883, found 189.0885.

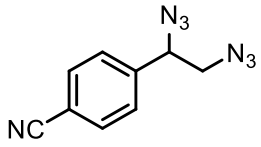
1-(1,2-Diazidoethyl)-4-methylbenzene (3b)



3b

The title compound was isolated (29.9 mg, 74%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.6 Hz, 4H), 4.65 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.55 – 3.40 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.0, 133.3, 129.8, 126.9, 65.4, 55.9, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{11}N_6^+$:203.1040, found 203.1042.

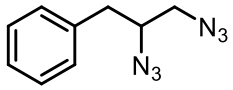
4-(1,2-Diazidoethyl) benzonitrile (3c)



3c

The title compound was isolated (26.8 mg, 63%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 80:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 4.73 (dd, *J* = 7.5, 5.2 Hz, 1H), 3.52 – 3.45 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.7, 132.9, 127.8, 118.2, 113.0, 64.8, 55.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_8N_7^+$:214.0836, found 214.0842.

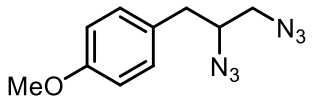
(2,3-Diazidopropyl) benzene (3d)



3d

The title compound was isolated (27.1 mg, 67%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.24 – 7.20 (m, 2H), 3.72 (dd, *J* = 7.0, 3.9, 1.0 Hz, 1H), 3.40 (dd, *J* = 12.8, 4.0, 1.0 Hz, 1H), 3.29 (dd, *J* = 12.7, 6.9, 1.1 Hz, 1H), 2.88 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5, 129.4, 129.0, 127.3, 63.0, 54.0, 38.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{11}N_6^+$:203.1040, found 203.1043.

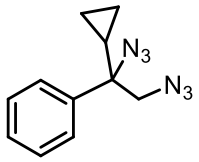
1-(2,3-Diazidopropyl)-4-methoxybenzene (3e)



3e

The title compound was isolated (32.5 mg, 70%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.67 (qd, *J* = 7.0, 3.9 Hz, 1H), 3.38 (dd, *J* = 12.7, 3.9 Hz, 1H), 3.27 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.82 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 130.4, 128.3, 114.3, 63.2, 55.4, 53.9, 37.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{13}N_6O^+$:233.1145, found 233.1142.

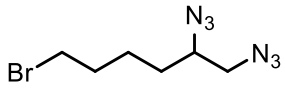
(1,2-Diazido-1-cyclopropylethyl) benzene (3f)



3f

The title compound was isolated (27.4 mg, 60%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 1H), 3.84 – 3.67 (m, 2H), 1.39 (m, 1H), 0.72 – 0.61 (m, 2H), 0.60 – 0.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 128.7, 128.4, 127.0, 68.9, 59.1, 18.1, 1.9, 1.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}N_6^+$:229.1196, found 229.1196.

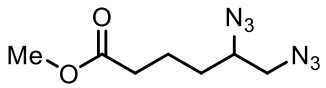
1,2-Diazido-6-bromohexane (3g)



3g

The title compound was isolated (32.0 mg, 65%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 150:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.50 – 3.45 (m, 1H), 3.45 – 3.39 (m, 3H), 3.34 (dd, *J* = 12.7, 7.2 Hz, 1H), 1.90 (m, 2H), 1.64 – 1.53 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 61.9, 54.9, 33.2, 32.3, 31.0, 24.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_6H_{12}BrN_6^+$:247.0301, found 247.0312.

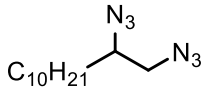
6,7-Diazido-1-methoxyheptan-2-one (3h)



3h

The title compound was isolated (33.9 mg, 75%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.50 – 3.44 (m, 1H), 3.41 (dd, *J* = 12.7, 4.1 Hz, 1H), 3.33 (dd, *J* = 12.6, 7.3 Hz, 1H), 2.36 (t, *J* = 7.3 Hz, 2H), 1.79 (m, 1H), 1.70 (m, 1H), 1.63 – 1.49 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 61.8, 54.9, 51.8, 33.5, 31.2, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_8H_{15}N_6O_2^+$:227.1251, found 227.1250.

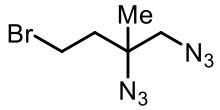
1,2-Diazidododecane (3i)



3i

The title compound was isolated (24.7 mg, 49%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 150:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.45 (dt, *J* = 12.6, 6.5 Hz, 1H), 3.38 (dd, *J* = 12.8, 4.1 Hz, 1H), 3.31 (dd, *J* = 12.8, 7.5 Hz, 1H), 1.60 – 1.50 (m, 2H), 1.44 (q, *J* = 7.0 Hz, 1H), 1.39 – 1.20 (m, 15H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 62.2, 55.0, 32.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 26.0, 22.8, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{25}N_6^+$:253.2135, found 253.2135.

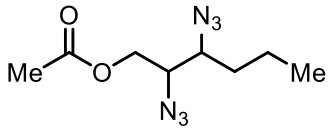
1,2-Diazido-4-bromo-2-methylbutane (3j)



3j

The title compound was isolated (37.1 mg, 80%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 150:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.47 – 3.36 (m, 2H), 3.34 (d, *J* = 2.9 Hz, 2H), 1.81 (m, 2H), 1.37 (d, *J* = 2.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 62.5, 59.2, 46.8, 36.2, 21.5. $[M + H]^+$ calcd for $C_5H_{10}BrN_6^+$:233.0145, found 233.0153.

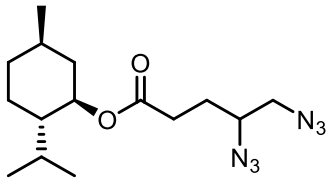
2,3-Diazidohexyl acetate (3k)



3k

The title compound was isolated (19.9 mg, 44%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 150:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.33 – 4.21 (m, 2H), 3.66 (dt, *J* = 8.2, 4.3 Hz, 1H), 3.34 (dt, *J* = 8.9, 4.6 Hz, 1H), 2.12 (s, 3H), 1.74 – 1.66 (m, 1H), 1.63 (m, 1H), 1.53 (m, 1H), 1.44 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 64.4, 63.2, 61.8, 33.1, 20.8, 19.5, 13.8. $[M + H]^+$ calcd for $C_8H_{15}N_6O_2^+$:227.1251, found 227.1251.

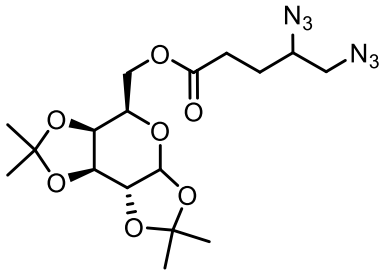
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4,5-diazidopentanoate (3l)



3l

The title compound was isolated (36.1 mg, 56%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.69 (m, 1H), 3.55 (m, 1H), 3.47 – 3.30 (m, 2H), 2.43 (m, 2H), 1.96 (m, 1H), 1.86 (m, 2H), 1.78 – 1.70 (m, 1H), 1.67 (m, 2H), 1.47 (m, 1H), 1.36 (m, 1H), 1.10 – 0.92 (m, 2H), 0.89 (dd, *J* = 6.8, 4.4 Hz, 6H), 0.87 – 0.82 (m, 1H), 0.75 (dd, *J* = 6.9, 2.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 74.7, 61.3, 55.0, 47.1, 41.0 (two peaks overlap), 34.3, 31.5, 30.7, 27.2, 26.4, 23.5, 22.1, 20.8, 16.4. $[M + H]^+$ calcd for $C_{15}H_{27}N_6O_2^+$:323.2190, found 323.2197.

((5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4,5-diazidopentanoate (3m)

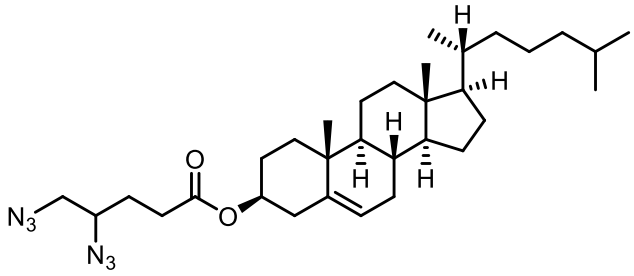


3m

The title compound was isolated (40.0 mg, 47%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ

5.52 (dd, *J* = 5.0, 1.9 Hz, 1H), 4.60 (dt, *J* = 7.9, 2.2 Hz, 1H), 4.31 (dt, *J* = 4.9, 2.2 Hz, 1H), 4.29 – 4.25 (m, 1H), 4.24 – 4.19 (m, 2H), 4.01 (m, 1H), 3.60 (m, 1H), 3.44 (m, 1H), 3.36 – 3.30 (m, 1H), 2.49 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.84 (m, 1H), 1.74 (m, *J* = 14.1, 9.1, 7.0, 2.1 Hz, 1H), 1.49 (d, *J* = 2.3 Hz, 3H), 1.43 (d, *J* = 1.7 Hz, 3H), 1.31 (dd, *J* = 4.0, 1.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 109.8, 108.8, 96.4, 71.1, 70.8, 70.4, 65.9, 63.8, 60.9, 54.9, 30.4, 27.2, 26.1, 26.0, 25.0, 24.5. $[M + H]^+$ calcd for $C_{17}H_{27}N_6O_7^+$:427.1936, found 427.1933.

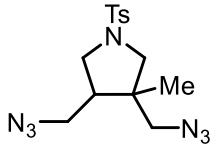
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4,5-diazidopentanoate (3n)



3n

The title compound was isolated (46.4 mg, 42%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 – 5.71 (m, 1H), 5.15 – 4.94 (m, 2H), 2.47 – 2.39 (m, 2H), 2.39 – 2.34 (m, 3H), 2.07 – 1.92 (m, 2H), 1.87 (dd, *J* = 15.3, 11.8, 7.5 Hz, 3H), 1.65 – 1.55 (m, 3H), 1.55 – 1.45 (m, 3H), 1.42 – 1.22 (m, 8H), 1.14 (dd, *J* = 32.2, 16.5, 7.4, 3.0 Hz, 8H), 1.07 – 0.96 (m, 5H), 0.90 (dd, *J* = 14.0, 6.4, 2.6 Hz, 4H), 0.86 (dd, *J* = 5.8, 2.9 Hz, 5H), 0.76 – 0.61 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 145.5, 136.8, 121.4, 119.3, 115.7, 73.8, 73.2, 64.1, 58.4, 56.1, 55.7, 50.6, 48.8, 43.4, 43.2, 42.4, 39.6, 36.9, 36.3, 35.9, 33.9, 29.1, 28.2, 24.0, 23.0, 22.7, 19.4, 18.9, 18.6, 12.1. $[M + H]^+$ calcd for $C_{32}H_{53}N_6O_2^+$:553.4225, found 553.4225.

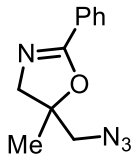
3,4-Bis(azidomethyl)-3-methyl-1-tosylpyrrolidine (4a')



4a'

The title compound was isolated as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 50:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 3.56 – 3.47 (m, 1H), 3.39 – 2.93 (m, 7H), 2.44 (d, *J* = 1.8 Hz, 3H), 2.13 – 1.99 (m, 1H), 1.05 (s, 1H), 0.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 133.5, 133.4, 129.9 (two peaks overlap), 127.6 (two peaks overlap), 58.5, 57.5, 57.0, 55.0, 50.6, 50.4, 50.3, 49.8, 46.6, 44.5, 44.4, 43.0, 22.4, 21.7, 17.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{20}N_7O_2^+$:350.1394, found 350.1394.

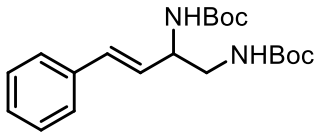
5-(Azidomethyl)-5-methyl-2-phenyl-4,5-dihydrooxazole (4b')



4b'

The title compound was isolated as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.52 – 3.40 (m, 2H), 2.46 (d, *J* = 35.4 Hz, 2H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 134.3, 132.9, 128.9, 128.7, 56.2, 43.8, 34.5, 18.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}N_4O^+$:217.1084, found 217.1082.

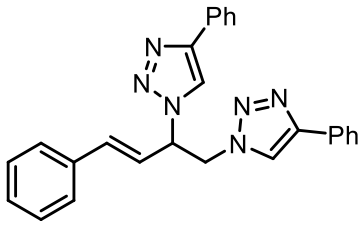
Di-tert-butyl (4-phenylbut-3-ene-1,2-diyl)(*E*)-dicarbamate (5)



5

The title compound was isolated (59.4 mg, 82%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 6.57 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.08 (dd, *J* = 16.0, 6.1 Hz, 1H), 5.01 (s, 1H), 4.86 (s, 1H), 4.37 (s, 1H), 3.34 (s, 2H), 1.45 (s, 9H), 1.44 (d, *J* = 3.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 136.6, 131.6, 128.7, 127.9, 127.5, 126.6, 79.8, 44.7, 28.5, 28.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{31}N_2O_4^+$:363.2278, found 363.2280.

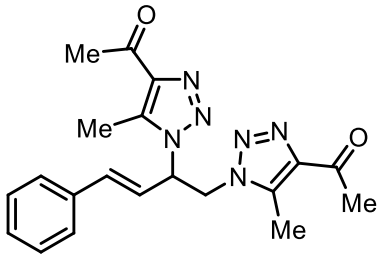
(*E*)-1,1'-(4-phenylbut-3-ene-1,2-diyl) bis(4-phenyl-1*H*-1,2,3-triazole) (6)



6

The title compound was isolated (75.2 mg, 90%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 5:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.80 (d, *J* = 1.8 Hz, 1H), 8.56 (d, *J* = 1.7 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.79 – 7.71 (m, 2H), 7.54 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 7.36 (td, *J* = 7.6, 5.9 Hz, 3H), 7.32 (dd, *J* = 8.9, 7.0, 1.9 Hz, 3H), 6.85 – 6.69 (m, 2H), 6.10 – 6.02 (m, 1H), 5.27 – 5.13 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.5, 146.3, 135.3, 134.8, 130.5 (two peaks overlap), 129.0, 128.9, 128.8, 128.6, 128.0, 126.8, 125.2, 125.1, 123.7, 122.0, 120.6, 62.2, 52.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}N_6^+$:419.1979, found 419.1983.

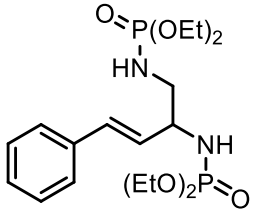
(*E*)-1,1'-((4-Phenylbut-3-ene-1,2-diyl) bis(5-methyl-1*H*-1,2,3-triazole-1,4-diyl))bis(ethan-1-one) (7)



7

The title compound was isolated (47.6 mg, 63%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 5H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.44 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.86 (td, *J* = 8.8, 5.0 Hz, 1H), 5.19 (dd, *J* = 14.0, 9.9 Hz, 1H), 4.85 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.65 (dd, *J* = 9.6, 1.0 Hz, 6H), 2.47 (dd, *J* = 2.8, 1.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.2, 194.1, 143.7, 143.4, 138.1, 137.6, 136.5, 134.6, 129.4, 129.0, 127.0, 121.9, 60.1, 49.9, 27.9 (two peaks overlap), 8.9, 8.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}N_6O_2^+$:379.1877, found 379.1875.

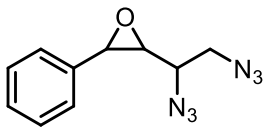
Tetraethyl (4-phenylbut-3-ene-1,2-diyl) (*E*)-bis(phosphoramidate) (8)



8

The title compound was isolated (73.8 mg, 85%) as a white solid after flash chromatography on silica gel (Hexane/EtOAc = 1:1). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.6 Hz, 1H), 5.06 (t, *J* = 10.6 Hz, 1H), 4.89 (dt, *J* = 11.7, 7.1 Hz, 1H), 3.89 (d, *J* = 22.0, 7.2 Hz, 8H), 3.68 (d, *J* = 7.7 Hz, 1H), 2.96 (m, 1H), 2.82 (m, 1H), 1.23 – 1.14 (m, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 136.8, 129.9, 128.6, 127.4, 126.2, 61.2 (two peaks overlap), 54.4, 16.0 (two peaks overlap). ^{31}P NMR (162 MHz, DMSO-d_6) δ 9.61, 8.45. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{33}N_2O_6P_2^+$:435.1808, found 435.1811.

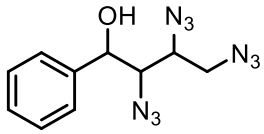
2-(1,2-Diazidoethyl)-3-phenyloxirane (9)



9

The title compound was isolated (41.9 mg, 91%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 100:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dq, *J* = 13.5, 7.1 Hz, 3H), 7.28 (dd, *J* = 7.6, 3.9 Hz, 2H), 3.98 (s, 1H), 3.68 (t, *J* = 5.6 Hz, 1H), 3.57 (td, *J* = 11.6, 9.9, 4.7 Hz, 1H), 3.52 (d, *J* = 6.1 Hz, 1H), 3.47 (dd, *J* = 12.9, 6.9 Hz, 1H), 3.15 (dd, *J* = 23.4, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 135.6, 128.9, 128.8 (two peaks overlap), 125.8, 125.7, 62.1, 62.0, 61.9, 60.8, 56.9, 56.5, 52.1, 51.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}N_6O^+$:231.0989, found 231.0989.

2,3,4-Triazido-1-phenylbutan-1-ol (10)



10

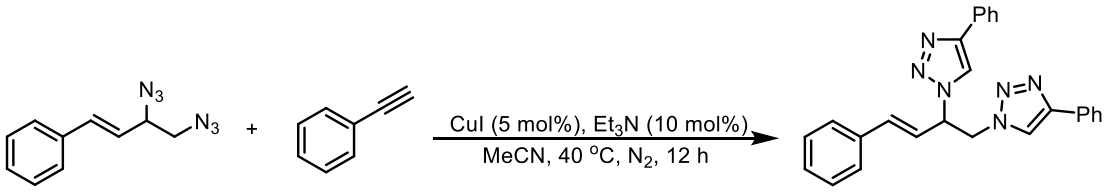
The title compound was isolated (32.2 mg, 59%) as a colorless liquid after flash chromatography on silica gel (Hexane/EtOAc = 50:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 21.8, 8.0 Hz, 5H), 4.76 (dd, *J* = 5.1, 1.8 Hz, 1H), 3.89 (td, *J* = 6.1, 5.1, 1.9 Hz, 1H), 3.68 (dt, *J* = 13.0, 2.7 Hz, 1H), 3.57 (m, 1H), 3.27 (td, *J* = 7.3, 3.8 Hz, 1H), 2.35 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4, 129.4, 129.2, 128.6, 73.0, 67.0, 62.2, 51.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{12}N_9O^+$:274.1159, found 274.1159.

The synthetic applications

3.0 mmol scale reaction

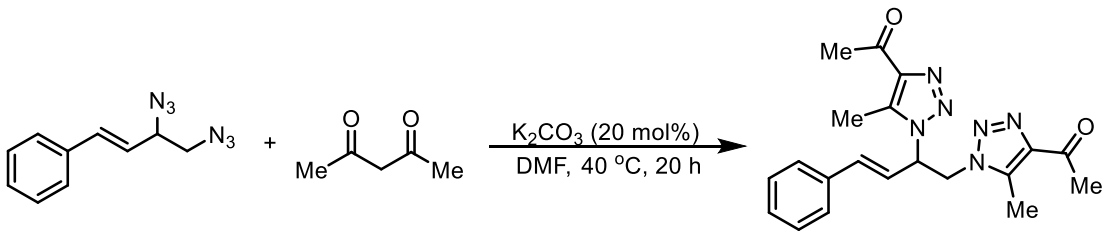
In a 20 mL undivided electrolysis cell, **1a** (392.1 mg, 3 mmol), 4-Iodobenzotrifluoride (163.1 mg, 0.6 mmol), NaN_3 (260.1 mg, 4 mmol), $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (636.8 mg, 0.3 mmol) and a magnetic stirring bar were added under air. Then MeCN (10 mL) and H_2O (5 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at room temperature for 15 minutes to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 15 mA for 7 h. The solvent was removed in vacuo, the crude product was purified by column chromatography on silica gel to give the product **2a** in 71% yield (0.61 g).

Transformation of products



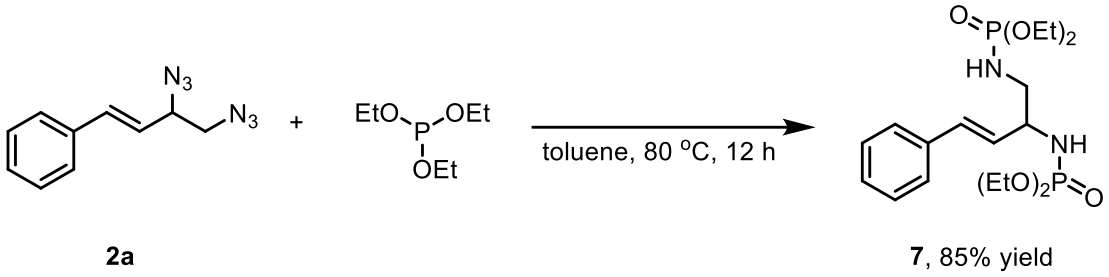
2a **5**, 90% yield

Prepared according to a previous reported method[2]. In a 10-mL schlenk tube, **2a** (42.8 mg, 0.2 mmol), phenylacetylene (51.0 mg, 0.5 mmol, 2.5 equiv), CuI (1.9 mg, 0.01 mmol, 5 mol%), Et_3N (2.1 mg, 0.02 mmol, 10 mol%), MeCN (2 mL) and a magnetic stirring bar were added under N_2. The schlenk tube was transferred to an oil bath at 40 °C. The reaction mixture was stirred at 40 °C for 12 h and the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (3:1) as eluent, obtained white solid product **5**.



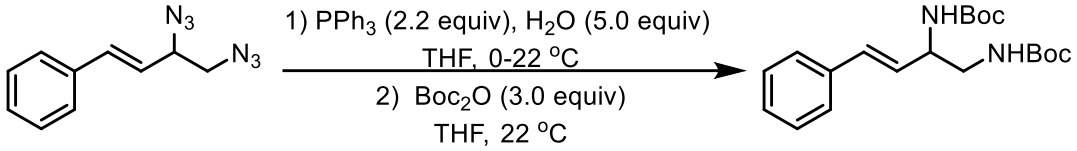
2a **6**, 63% yield

Prepared according to a previous reported method[3]. In a 10-mL schlenk tube, **2a** (42.8 mg, 0.2 mmol), acetylacetone (80.0 mg, 0.8 mmol, 4.0 equiv), K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol%), DMF (2 mL) and a magnetic stirring bar were added under N_2. The schlenk tube was transferred to an oil bath at 40 °C. The reaction mixture was stirred at 40 °C for 20 h and the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (1:1) as eluent, obtained white solid product **6**.



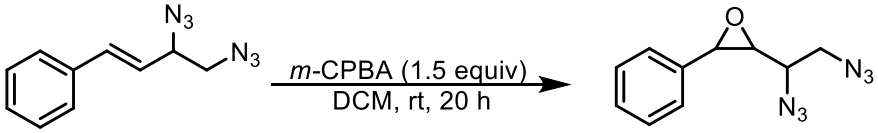
2a **7**, 85% yield

Prepared according to a previous reported method[3]. In a 10-mL schlenk tube, **2a** (42.8 mg, 0.2 mmol), $P(OEt)_3$ (99.6 mg, 0.6 mmol, 3.0 equiv), toluene (2 mL) and a magnetic stirring bar were added under air. The schlenk tube was transferred to an oil bath at 80 °C. The reaction mixture was stirred at 80 °C for 12 h and the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (1:1) as eluent, obtained yellow solid product **7**.



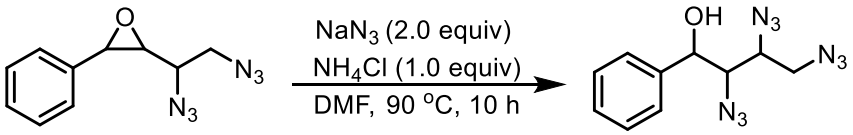
2a **8**, 82% yield

Prepared according to a previous reported method[4]. In a 10-mL schlenk tube, **2a** (42.8 mg, 0.2 mmol), PPh_3 (115.3 mg, 0.44 mmol, 2.2 equiv), H_2O (18 mg, 1.0 mmol, 5.0 equiv), THF (2 mL) and a magnetic stirring bar were added under air. The reaction mixture was stirred at room temperature for 5 h and added Boc_2O (130.8 mg, 0.6 mmol, 3.0 equiv) to the schlenk tube. Continue the reaction for 10 h, the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (5:1) as eluent, obtained yellow solid product **8**.



2a **9**, 91% yield, 1:1 d.r.

Prepared according to a previous reported method[5]. In a 10-mL schlenk tube, **2a** (42.8 mg, 0.2 mmol), *m*-CPBA (51.8 mg, 0.3 mmol, 1.5 equiv), DCM (2 mL) and a magnetic stirring bar were added under air. The reaction mixture was stirred at room temperature for 20 h and the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (50:1) as eluent, obtained colorless liquid product **9**.

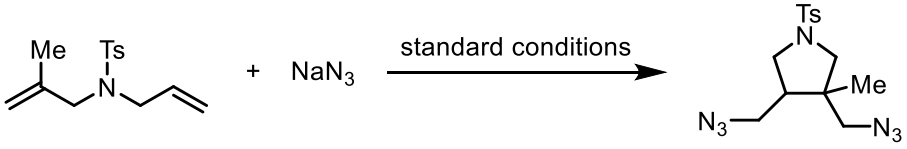


7 **10**, 59% yield, 3:1 d.r.

Prepared according to a previous reported method[6]. In a 10-mL schlenk tube, **7** (46.0 mg, 0.2 mmol), NaN_3 (26.0 mg, 0.4 mmol, 2.0 equiv), NH_4Cl (10.7 mg, 0.2 mmol, 1.0 equiv), DMF (2 mL) and a magnetic stirring bar were added under air. The schlenk tube was transferred to an oil bath at 90 °C. The reaction mixture was stirred at 90 °C for 10 h and the resulting solution was partitioned between EtOAc and H_2O, the aqueous layer was extracted with EtOAc and washed with H_2O. The organic layers were combined, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with a mixture of *n*-hexane and EtOAc (10:1) as eluent, obtained yellow liquid product **10**.

Mechanistic studies

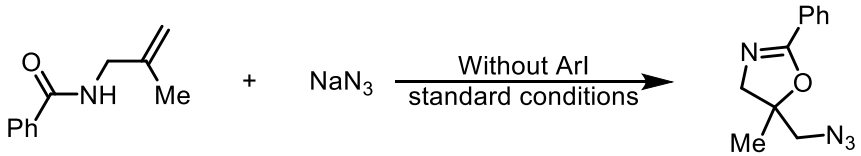
Radical clocks



4a **4a'**
47% yield, 2:1 *d.r.*

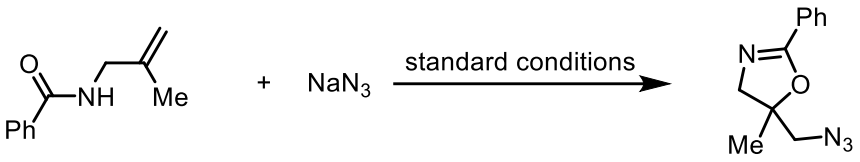
In an undivided electrolysis cell, **4a** (53.0 mg, 0.2 mmol), 4-iodobenzotrifluoride (10.9 mg, 0.04 mmol), NaN_3 (78.0 mg, 1.2 mmol) $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (42.4 mg, 0.2 mmol) and a magnetic stirring bar were added under air. Then MeCN (2.1 mL) and H_2O (0.9 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at rt for 15 min to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 10 mA until the complete consumption of the starting materials which was monitored by TLC. The solvent was removed in vacuo, and the crude residue was purified via column chromatography to afford the desired product **4a'** in 47% yield (32.8 mg) with 2:1 *dr*.

Carbocation trap



4b **4b'**, N.D.

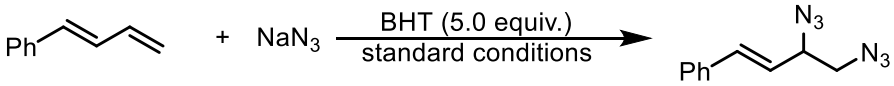
In an undivided electrolysis cell, **4b** (35.0 mg, 0.2 mmol), NaN_3 (78.0 mg, 1.2 mmol) $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (42.4 mg, 0.2 mmol) and a magnetic stirring bar were added under air. Then MeCN (2.1 mL) and H_2O (0.9 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at rt for 15 min to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 10 mA until the complete consumption of the starting materials which was monitored by TLC. Without any product **4b'** was detected.



4b **4b'**, 46% yield

In an undivided electrolysis cell, **4b** (35.0 mg, 0.2 mmol), 4-iodobenzotrifluoride (10.9 mg, 0.04 mmol), NaN_3 (78 mg, 1.2 mmol) $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (42.4 mg, 0.2 mmol) and a magnetic stirring bar were added under air. Then MeCN (2.1 mL) and H_2O (0.9 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at rt for 15 min to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 10 mA until the complete consumption of the starting materials which was monitored by TLC. The solvent was removed in vacuo, and the crude residue was purified via column chromatography to afford the desired product **4b'** in 46% yield (19.9 mg).

Radical trap



1a **2a**, 57% yield

In an undivided electrolysis cell, **1a** (39.2 mg, 0.3 mmol), BHT (330.5 mg, 1.5 mmol), 4-iodobenzotrifluoride (10.9 mg, 0.04 mmol), NaN_3 (117.0 mg, 1.8 mmol) $^nBu_4NBF_4$ (0.1 M), K_3PO_4 (63.7 mg, 0.3 mmol) and a magnetic stirring bar were added under air. Then MeCN (2.1 mL) and H_2O (0.9 mL) were added. The tube was installed by a graphite plate (20 × 10 × 0.1 mm^3) as anode and Pt plate (20 × 10 × 0.5 mm^3) as cathode. The distance of the electrodes is around 1 cm. The mixture was stirred at rt for 15 min to fully dissolve the supporting electrolyte and then electrolyzed under a constant current of 10 mA until the complete consumption of the starting materials which was monitored by TLC. The solvent was removed in vacuo, and the crude residue was purified via column chromatography to afford the desired product **2a** in 57% yield.

Cyclic voltammetry data

The CV studies showed that the oxidation potential of 4-iodobenzotrifluoride was lower than that of NaN_3 medium (Figure S1). Therefore, the oxidation of 4-iodobenzotrifluoride took place first.

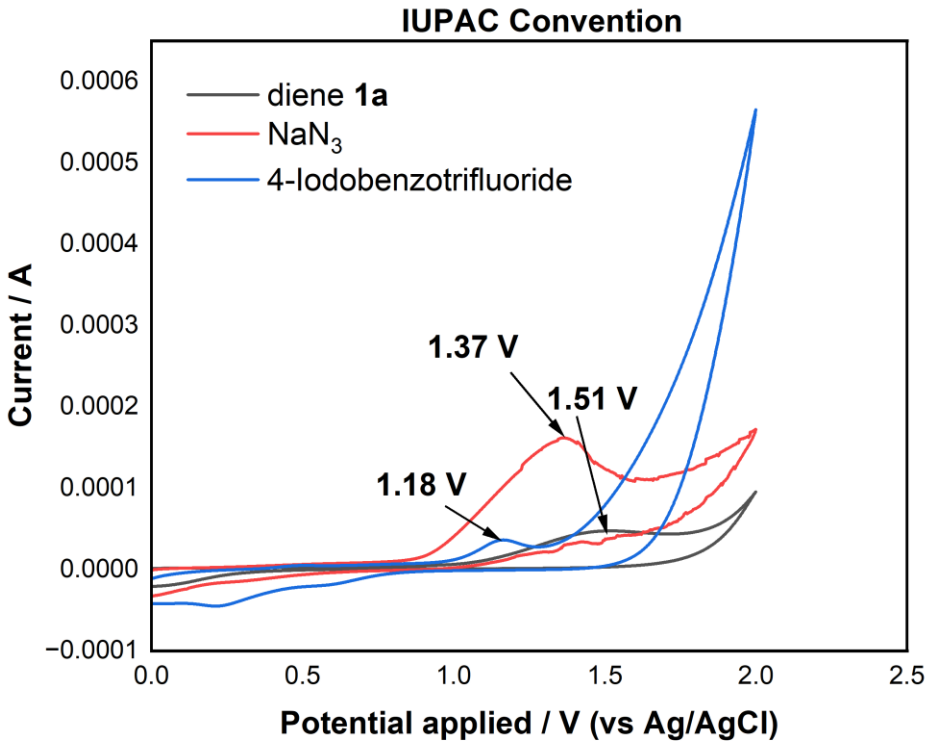


Figure S1: Cyclic voltammetry of diene **1a** (0.1 mmol, black line), NaN_3 (0.1 mmol, red line) and 4-iodobenzotrifluoride (0.1 mmol, blue line). CV conditions: MeCN/H_2O (7:3) as solvent, $^{n}Bu_4NBF_4$ (0.1 M) as electrolyte, platinum working electrode, platinum counter electrode, silver wire as reference electrode, 0.1 V/s.

The CV studies showed that the oxidation potential of 4-iodoanisole was lower than that of NaN_3 medium (Figure S2). Therefore, the oxidation of 4-Iodoanisole took place first.

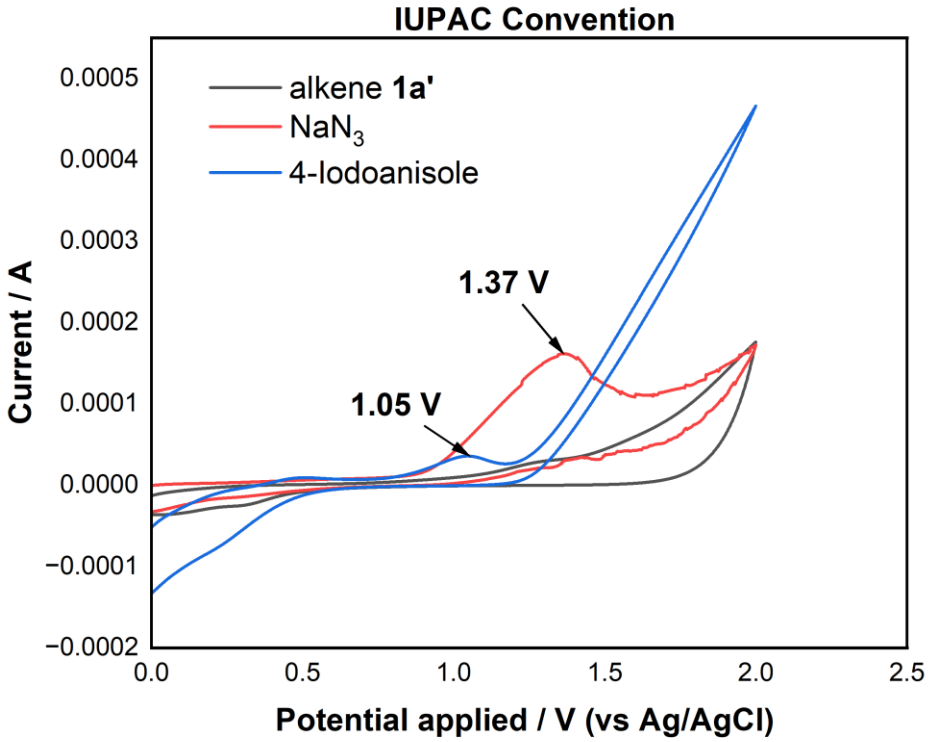


Figure S2: Cyclic voltammetry of alkene **1a'** (0.1 mmol, black line), NaN_3 (0.1 mmol, red line) and 4-iodoanisole (0.1 mmol, blue line). CV conditions: MeCN/H_2O (7:3) as solvent, $^nBu_4NBF_4$ (0.1 M) as electrolyte, platinum working electrode, platinum counter electrode, silver wire as reference electrode, 0.1 V/s.

References

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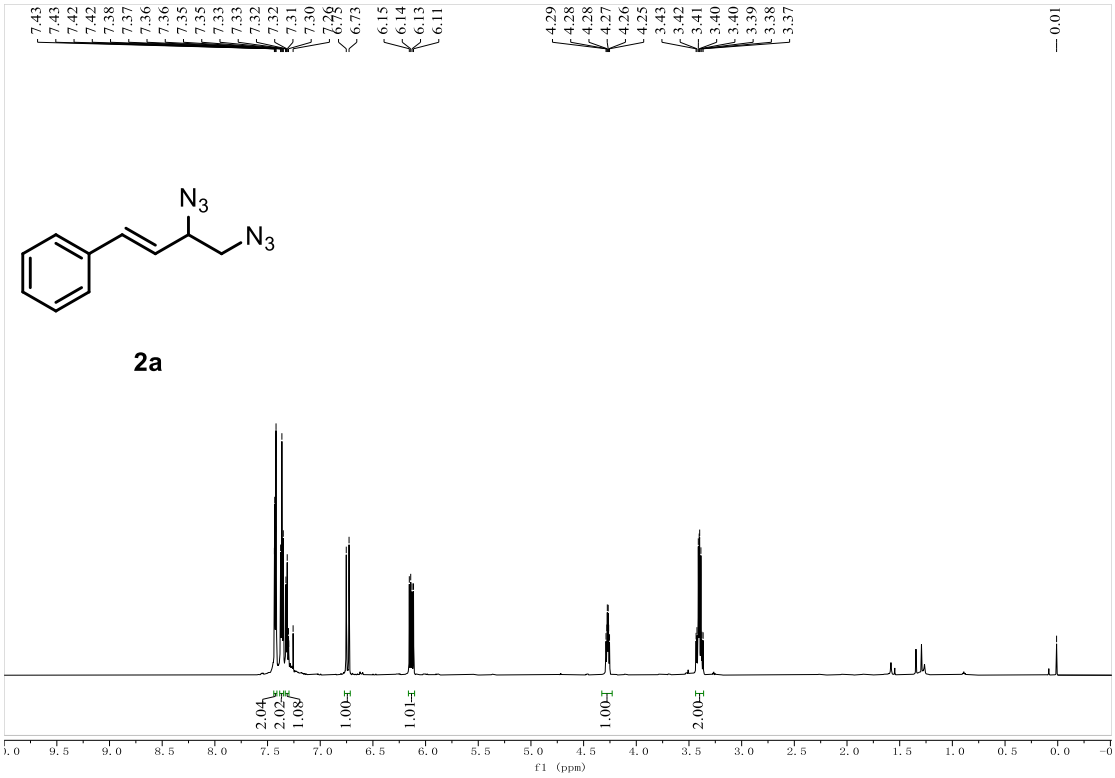
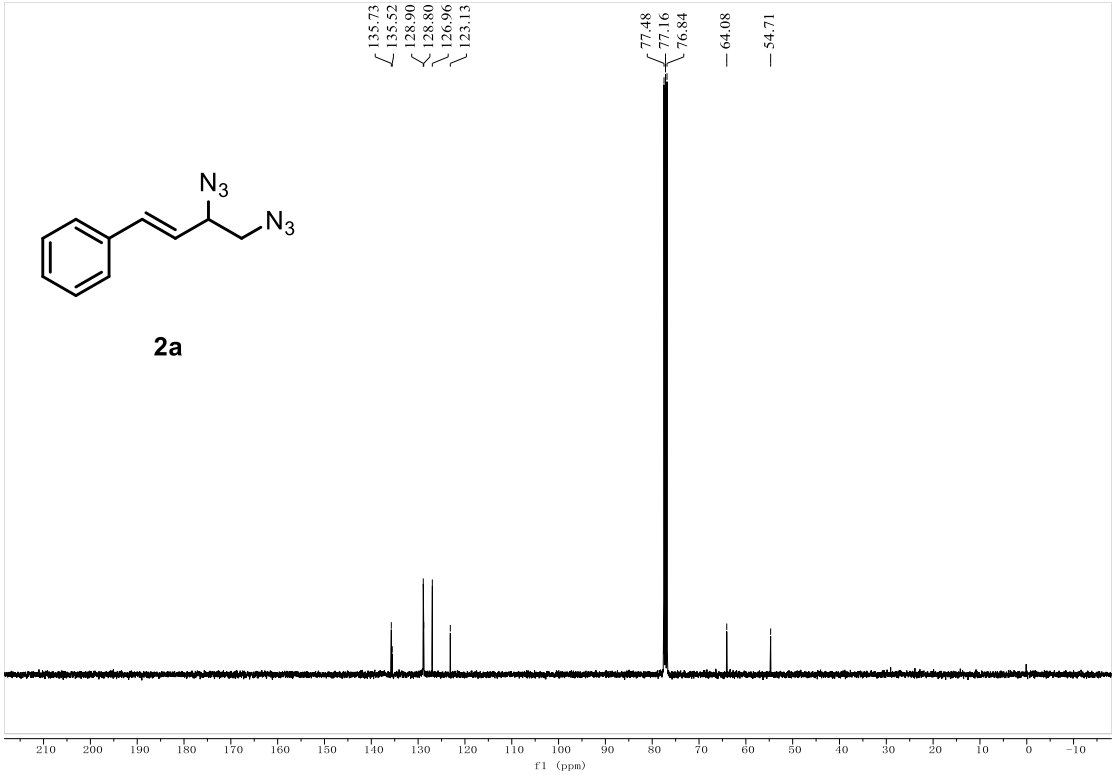
NMR spectra

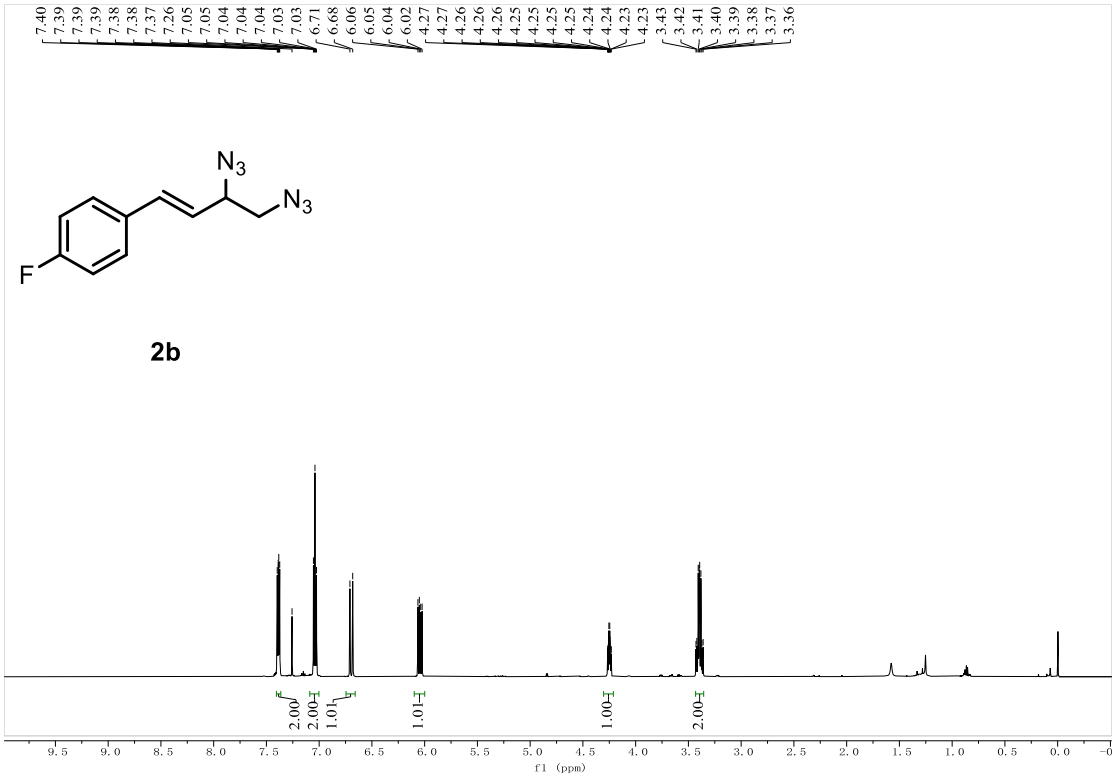
^{1}H NMR of **2a** (600 MHz, $CDCl_3$)



^{13}C NMR of **2a** (101 MHz, $CDCl_3$)



^{1}H NMR of **2b** (600 MHz, $CDCl_3$)



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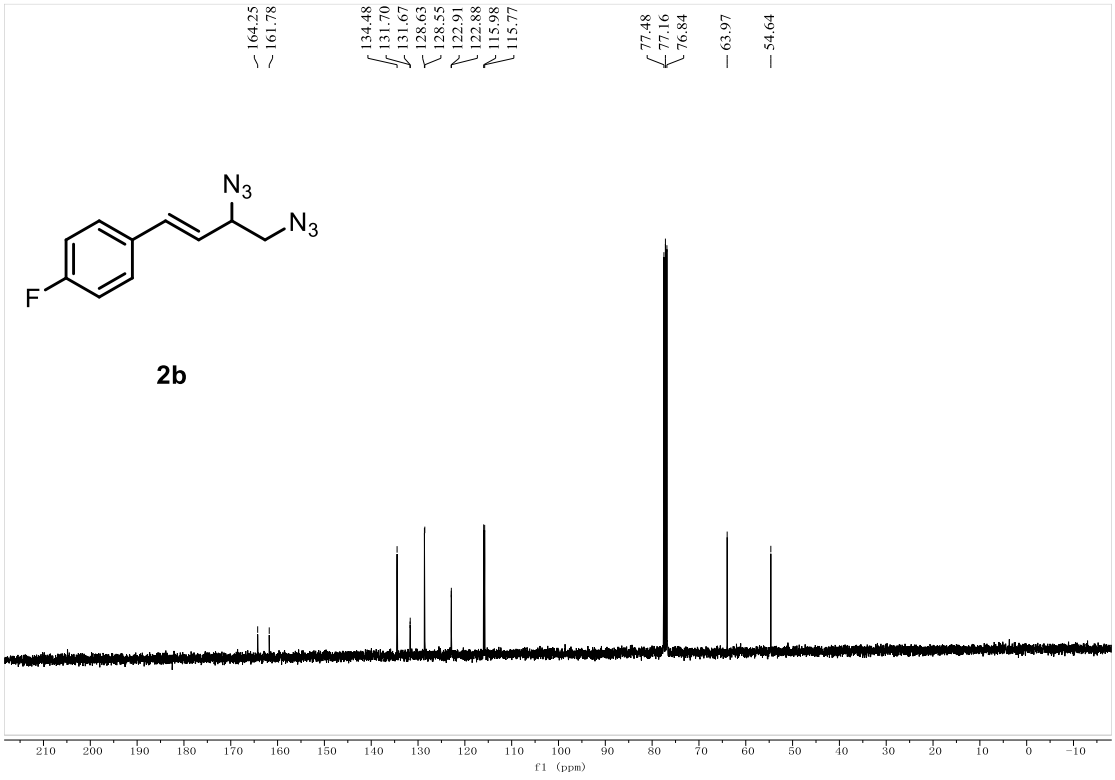
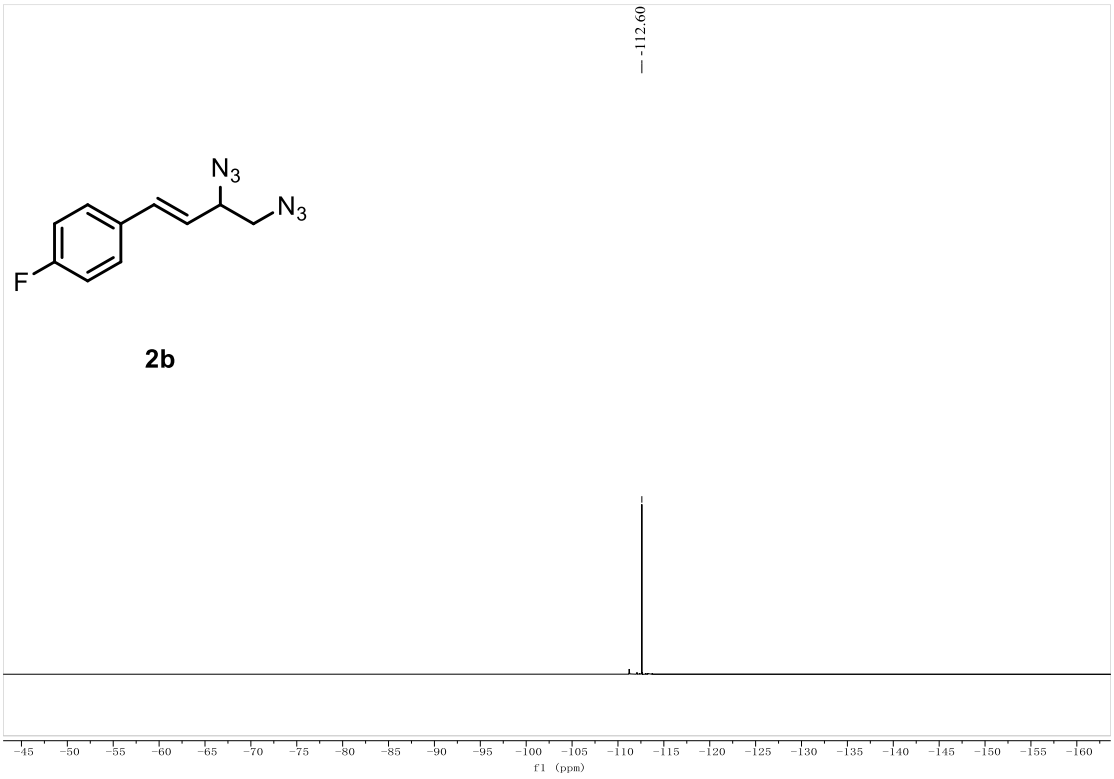
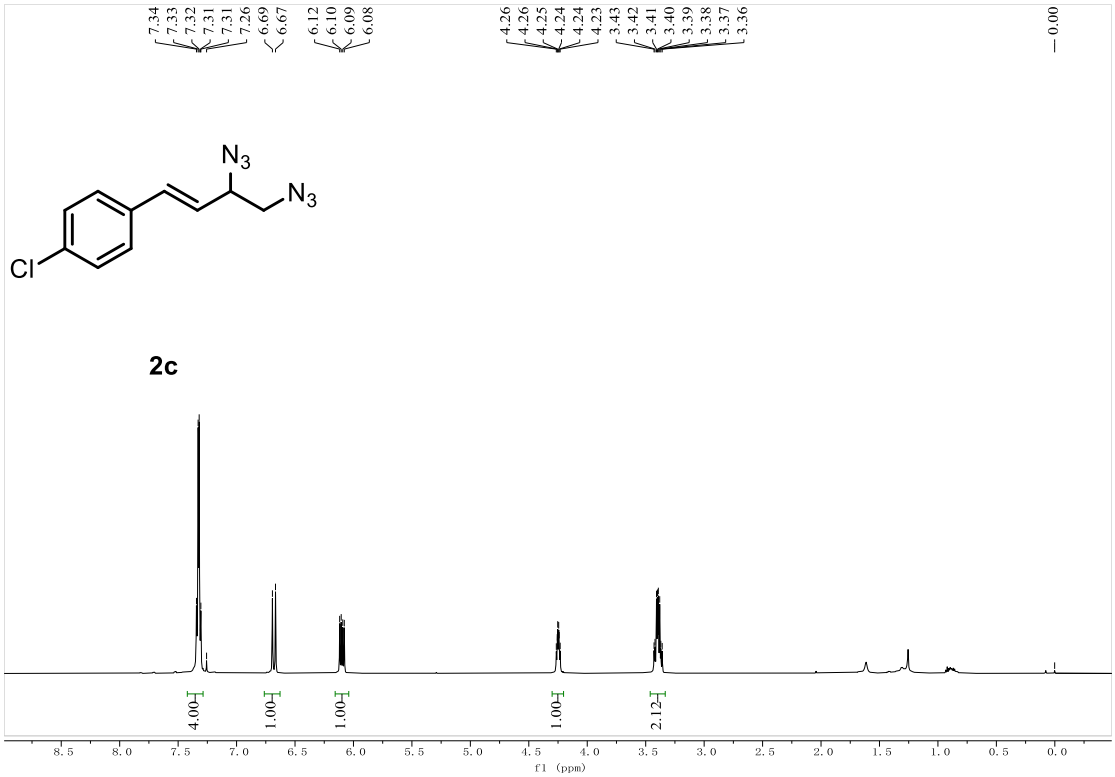


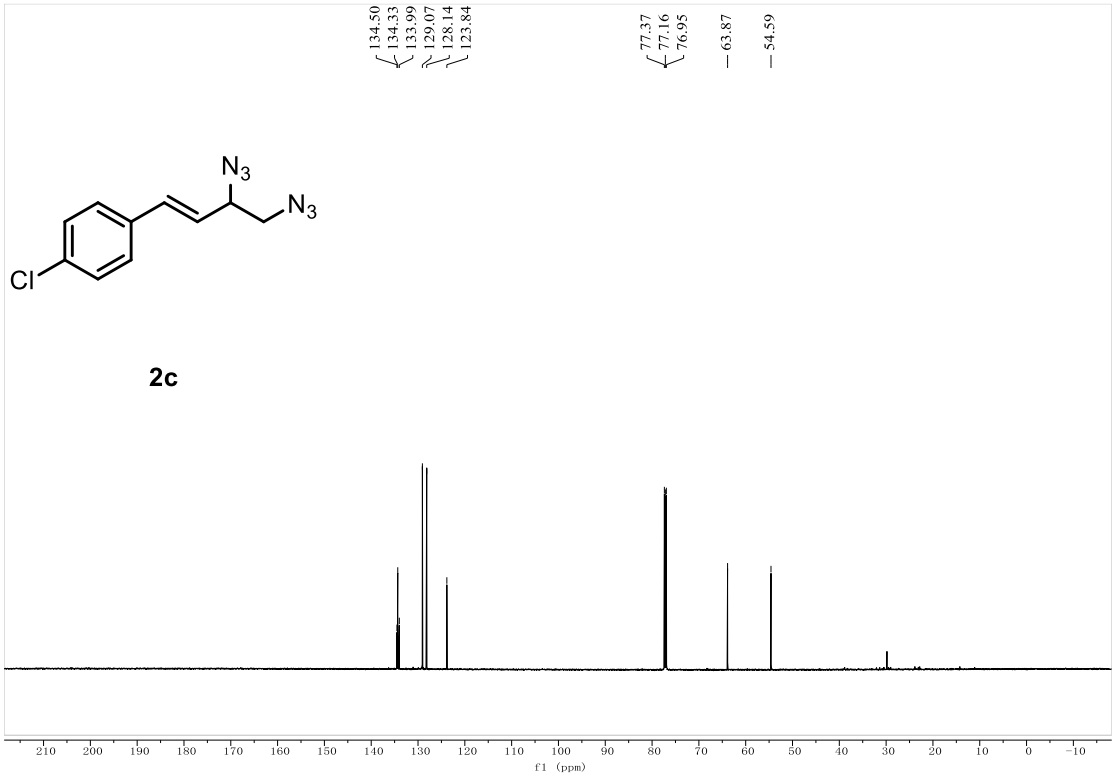
^{19}F NMR of **2b** (377 MHz, $CDCl_3$)



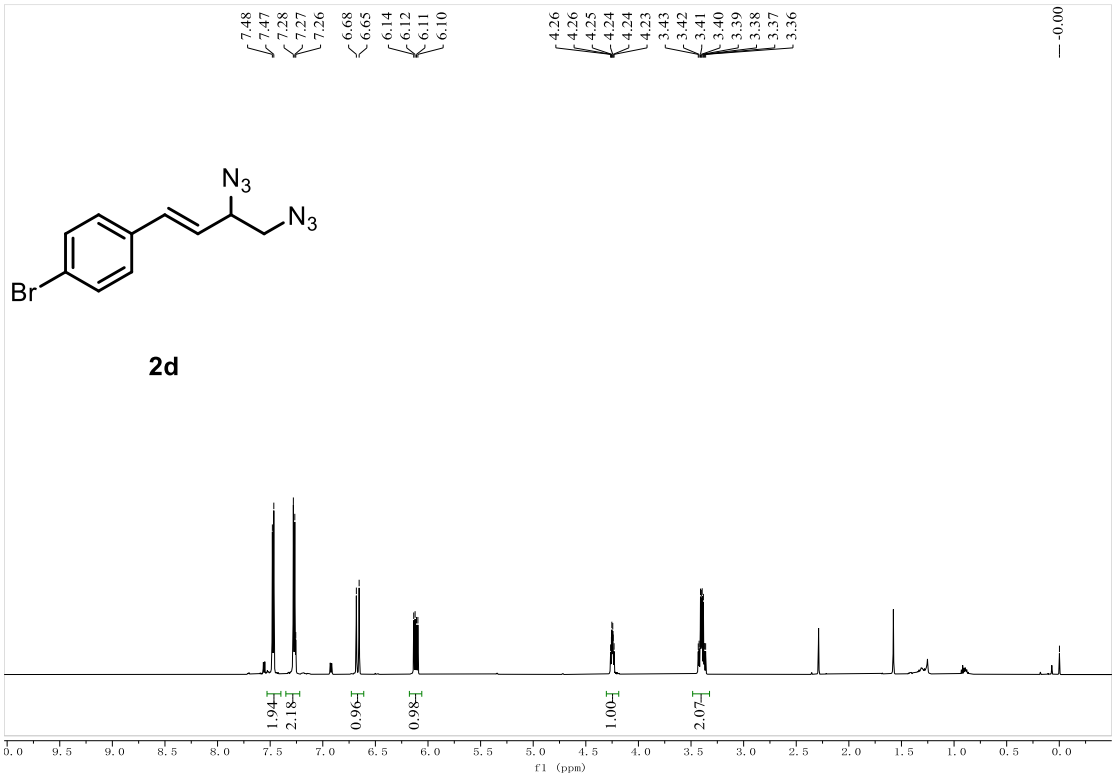
^{1}H NMR of **2c** (600 MHz, $CDCl_3$)



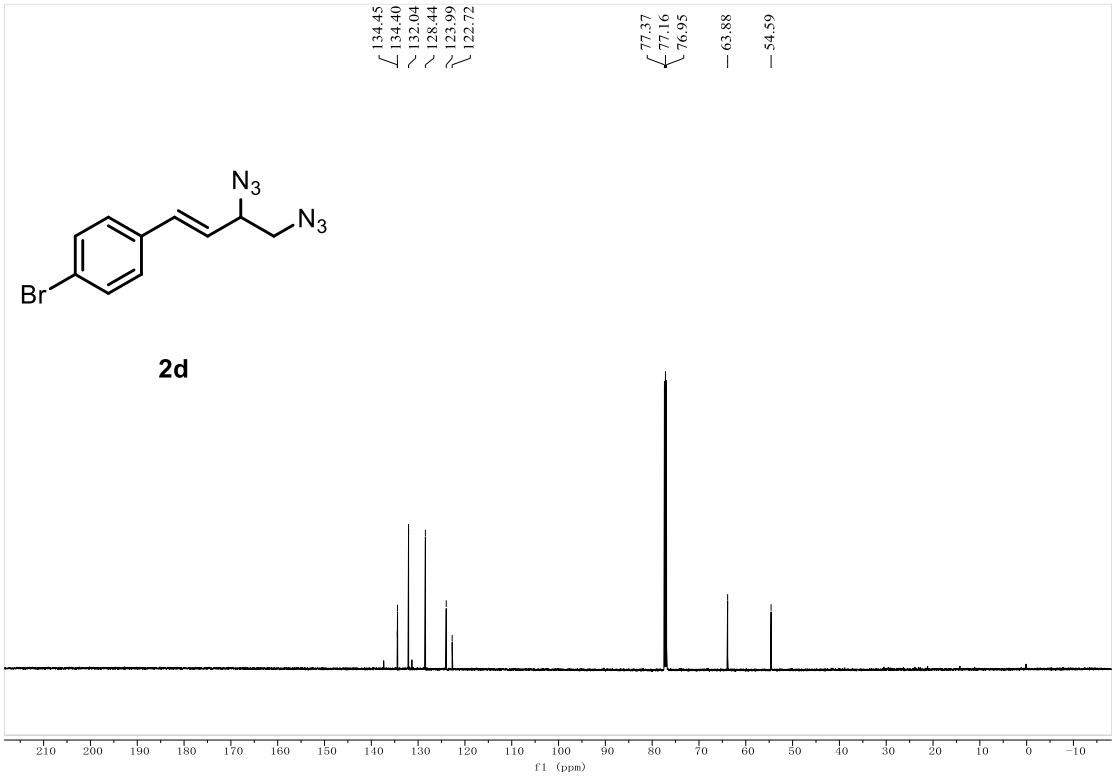
^{13}C NMR of **2c** (151 MHz, $CDCl_3$)



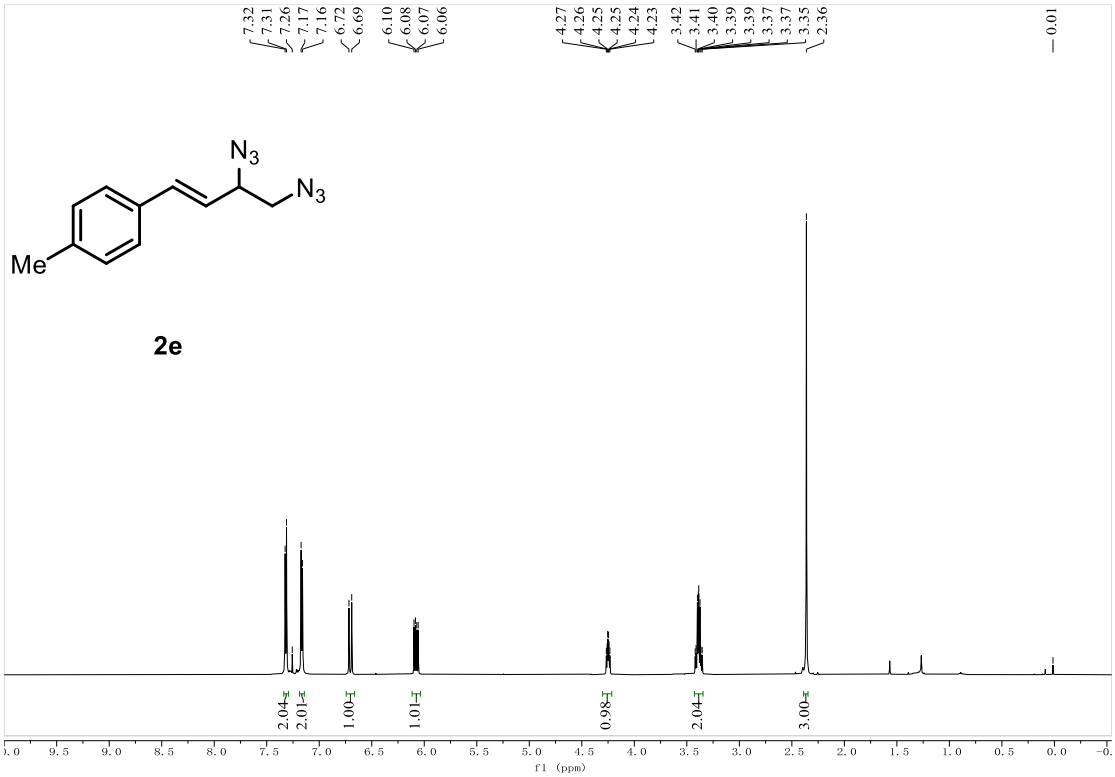
^{1}H NMR of **2d** (600 MHz, $CDCl_3$)



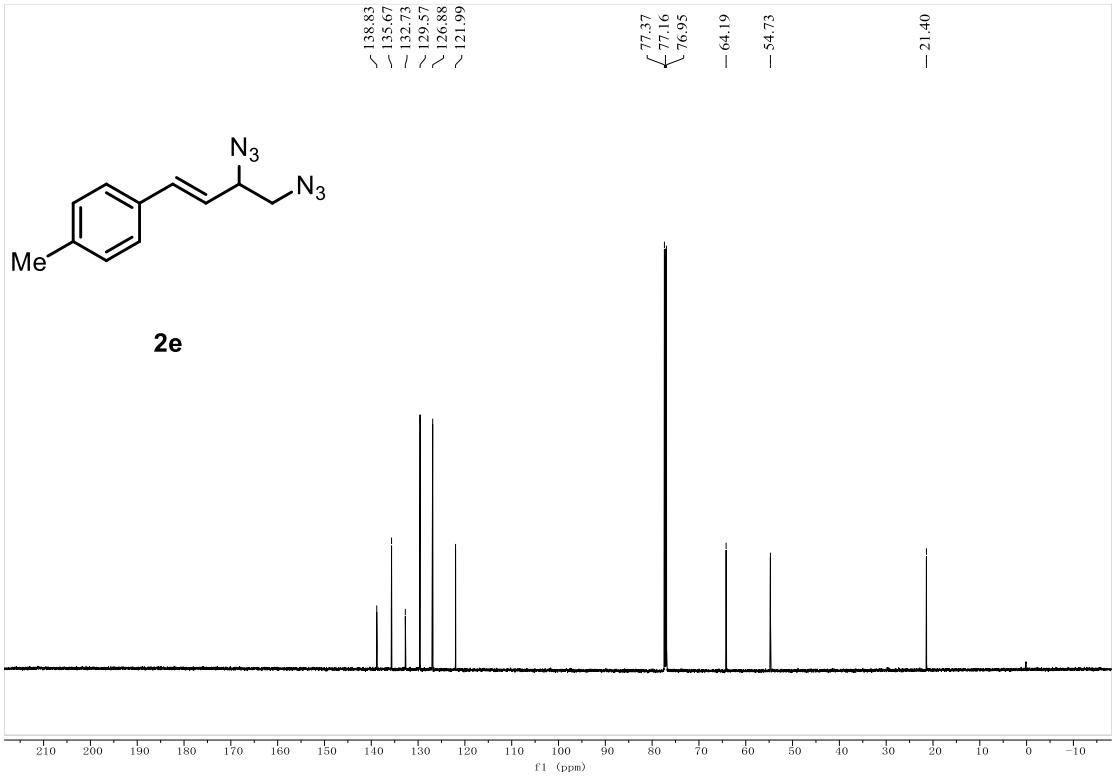
^{13}C NMR of **2d** (151 MHz, $CDCl_3$)



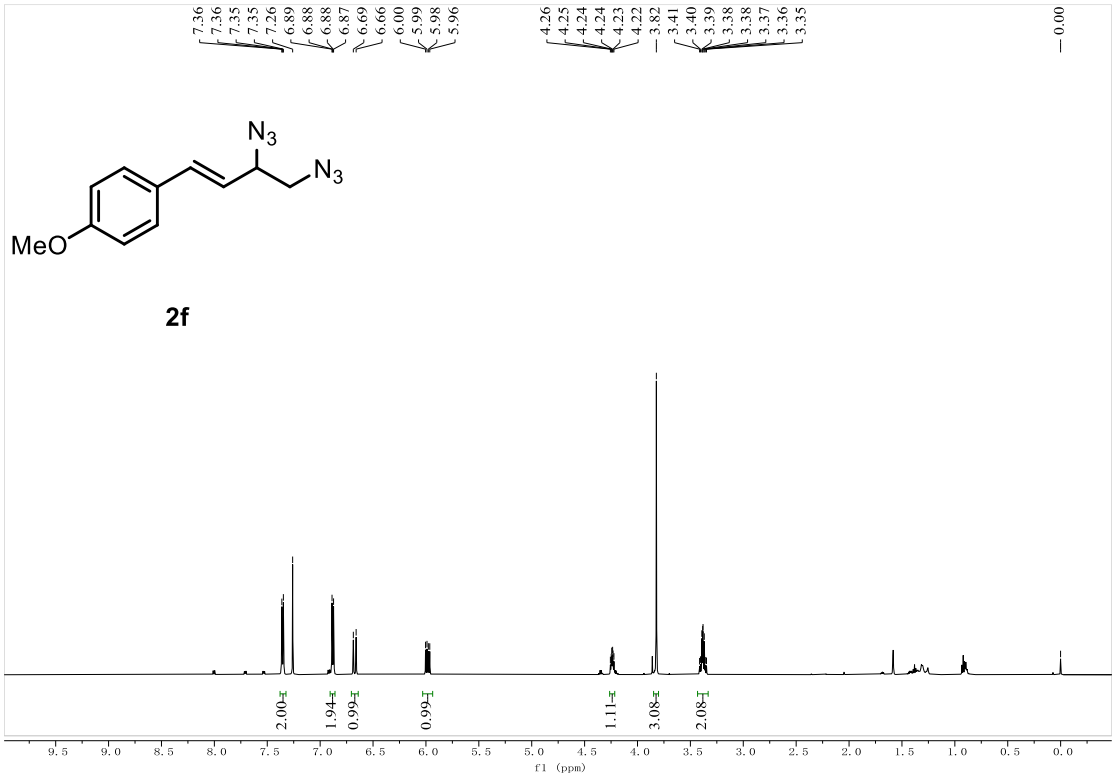
^{1}H NMR of **2e** (600 MHz, $CDCl_3$)



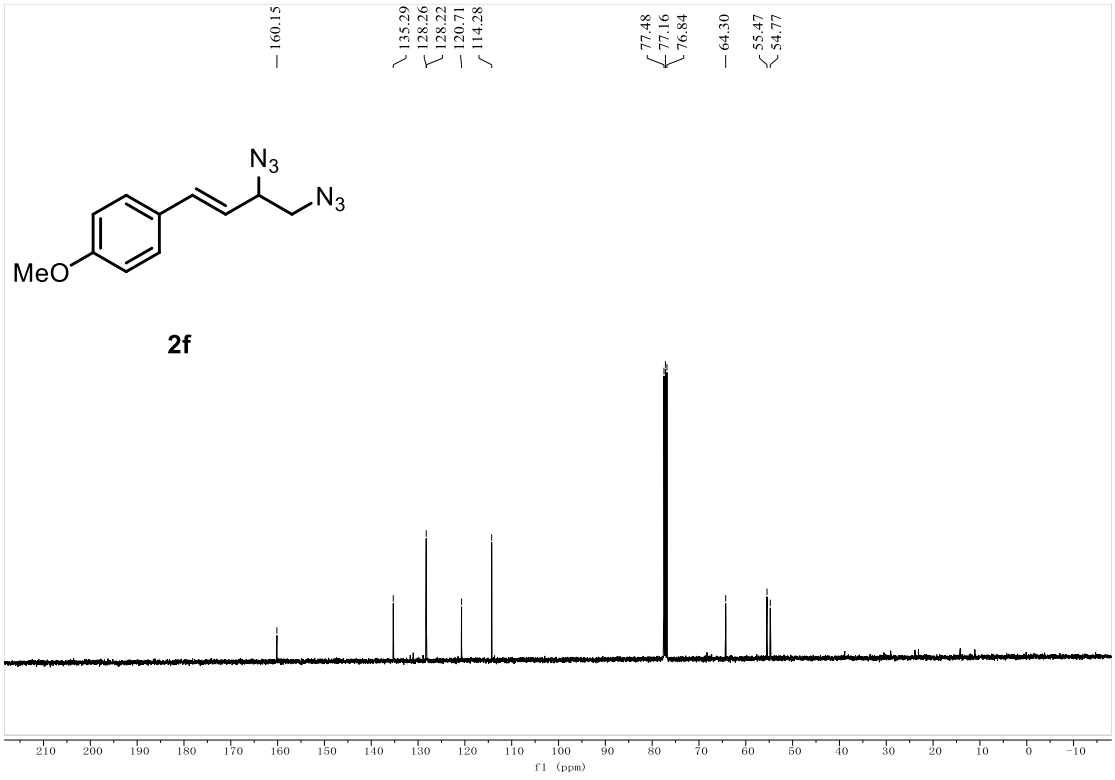
^{13}C NMR of **2e** (151 MHz, $CDCl_3$)



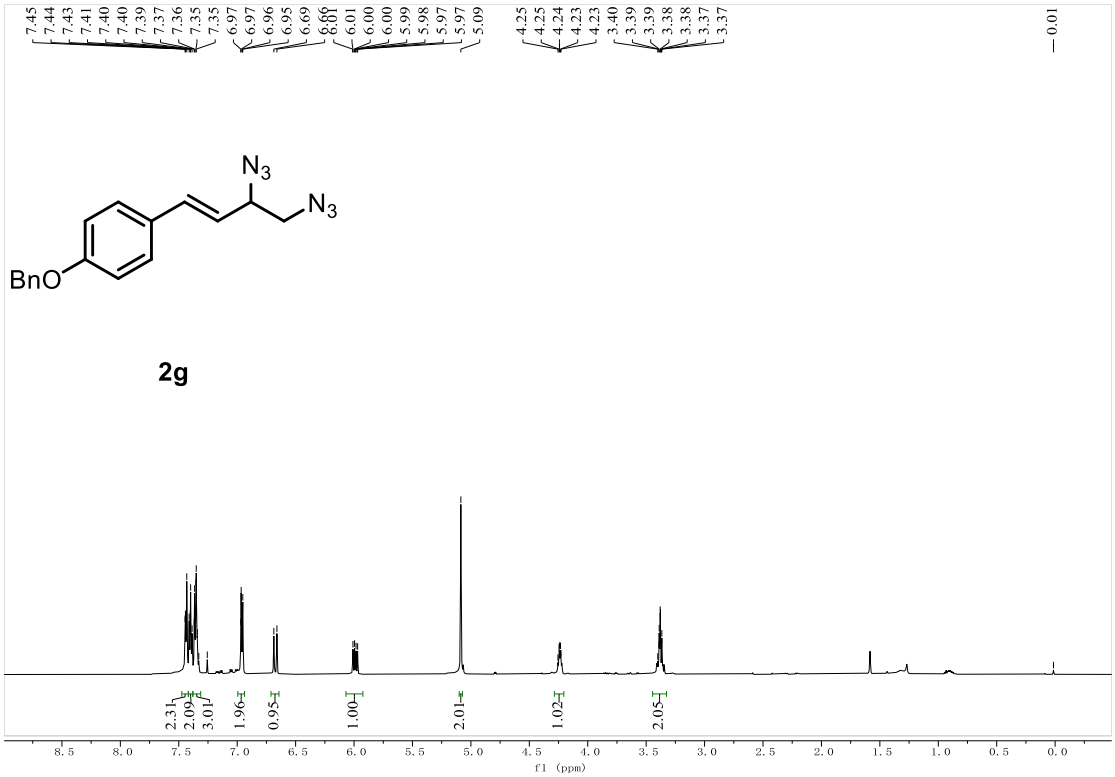
^{1}H NMR of **2f** (600 MHz, $CDCl_3$)



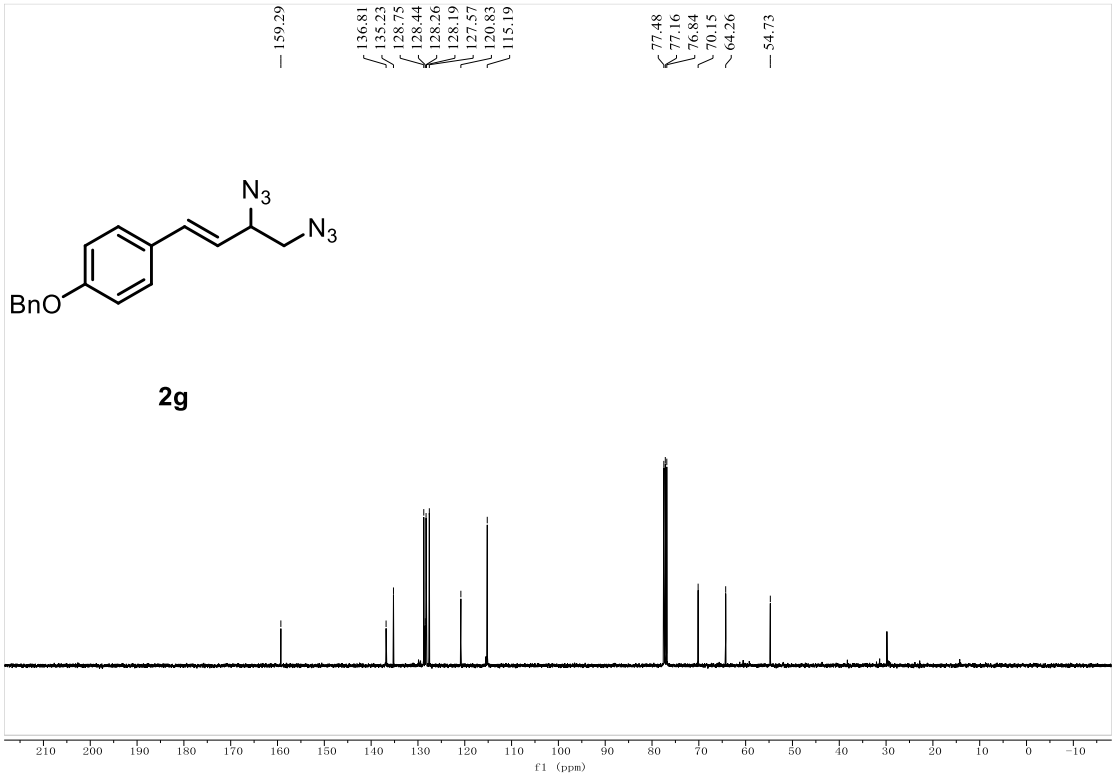
^{13}C NMR of **2f** (101 MHz, $CDCl_3$)



^{1}H NMR of **2g** (600 MHz, $CDCl_3$)



^{13}C NMR of **2g** (101 MHz, $CDCl_3$)



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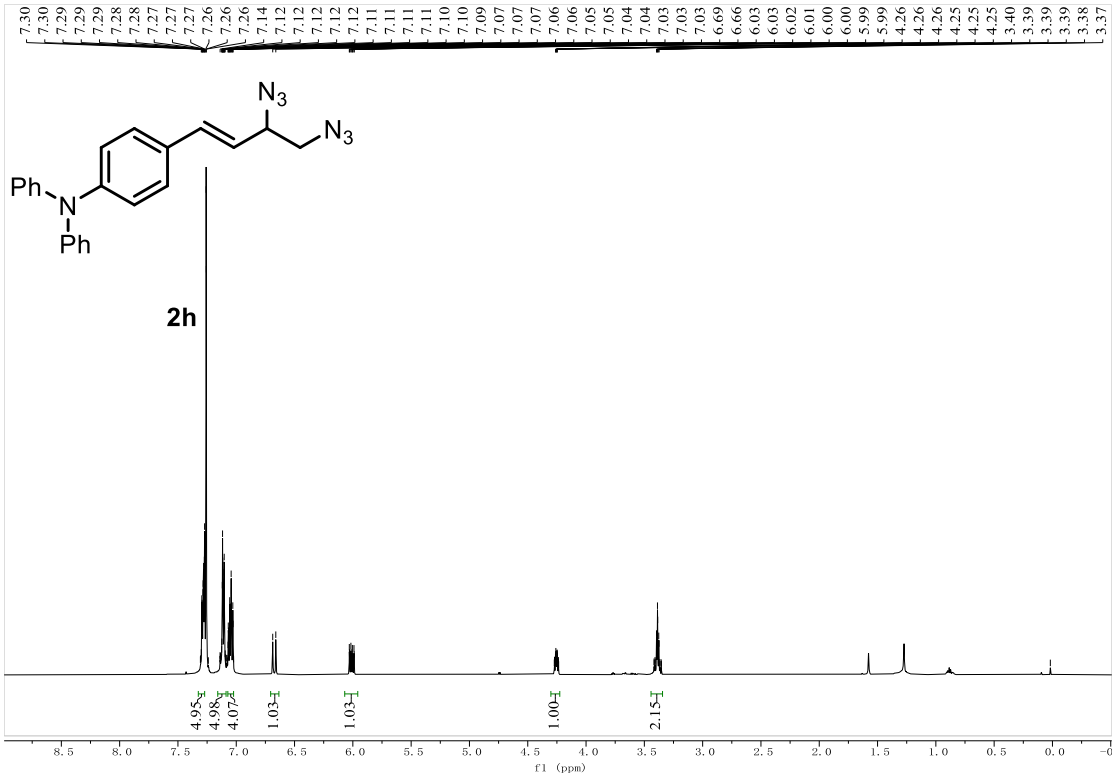
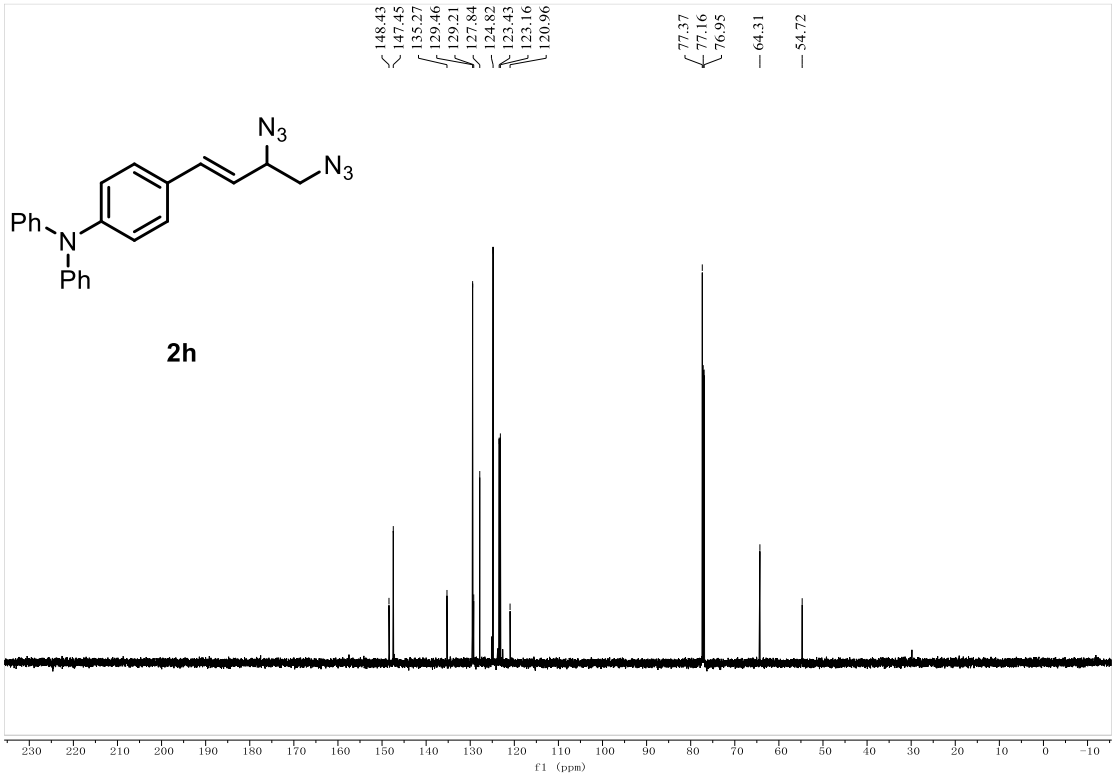
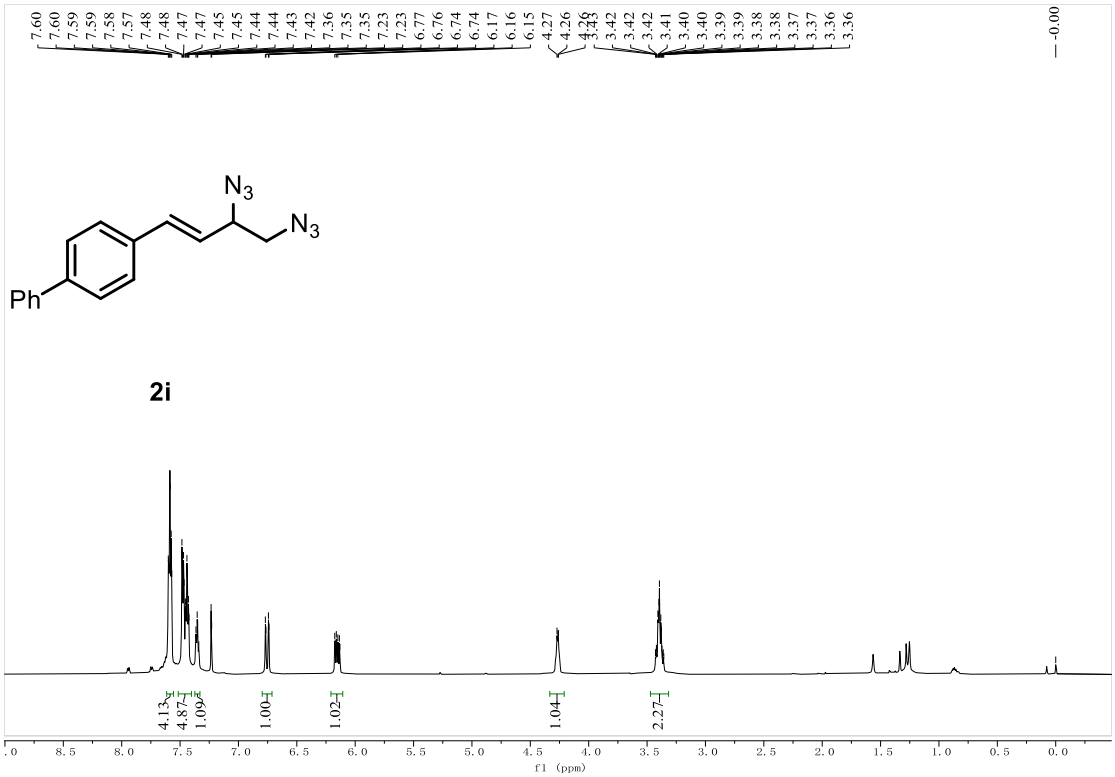


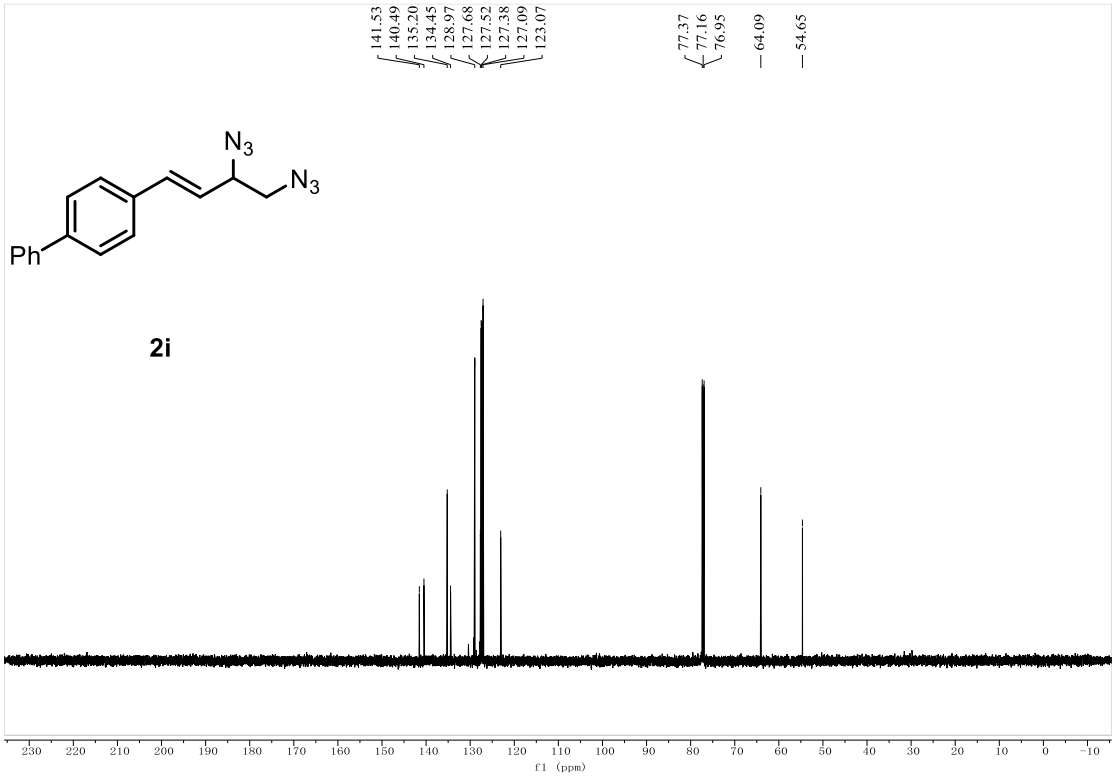
^{13}C NMR of **2h** (101 MHz, $CDCl_3$)



^{1}H NMR of **2i** (600 MHz, $CDCl_3$)



^{13}C NMR of **2i** (151 MHz, $CDCl_3$)



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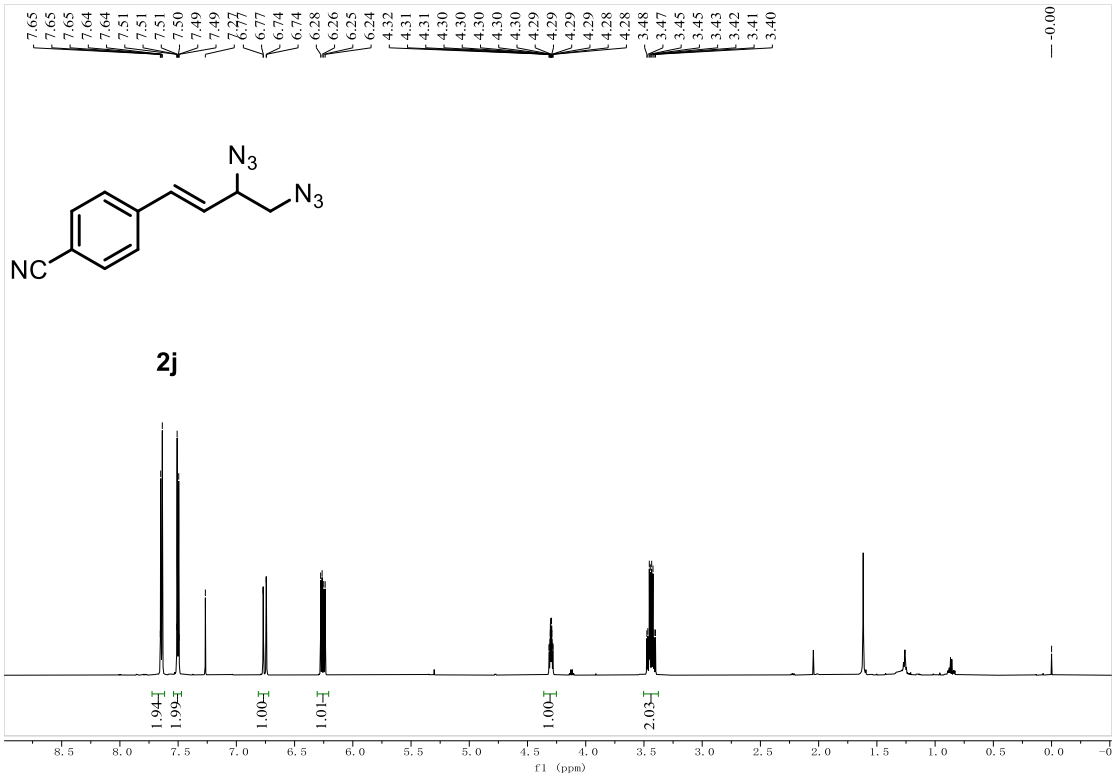

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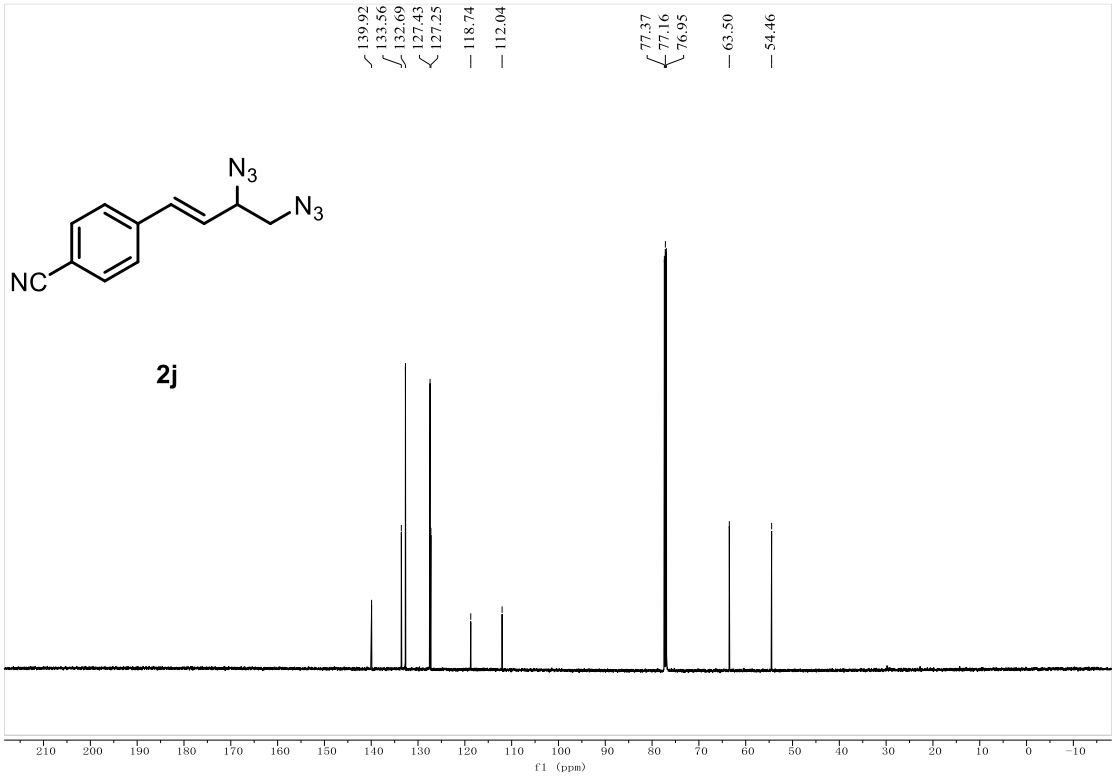

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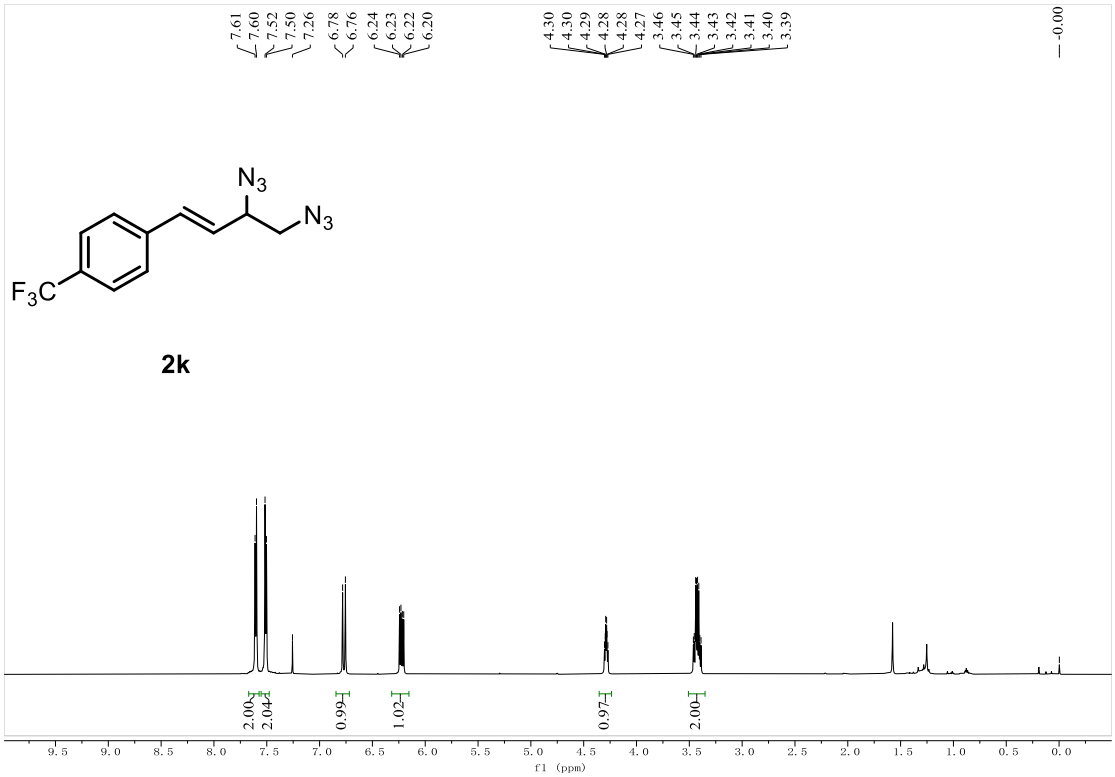
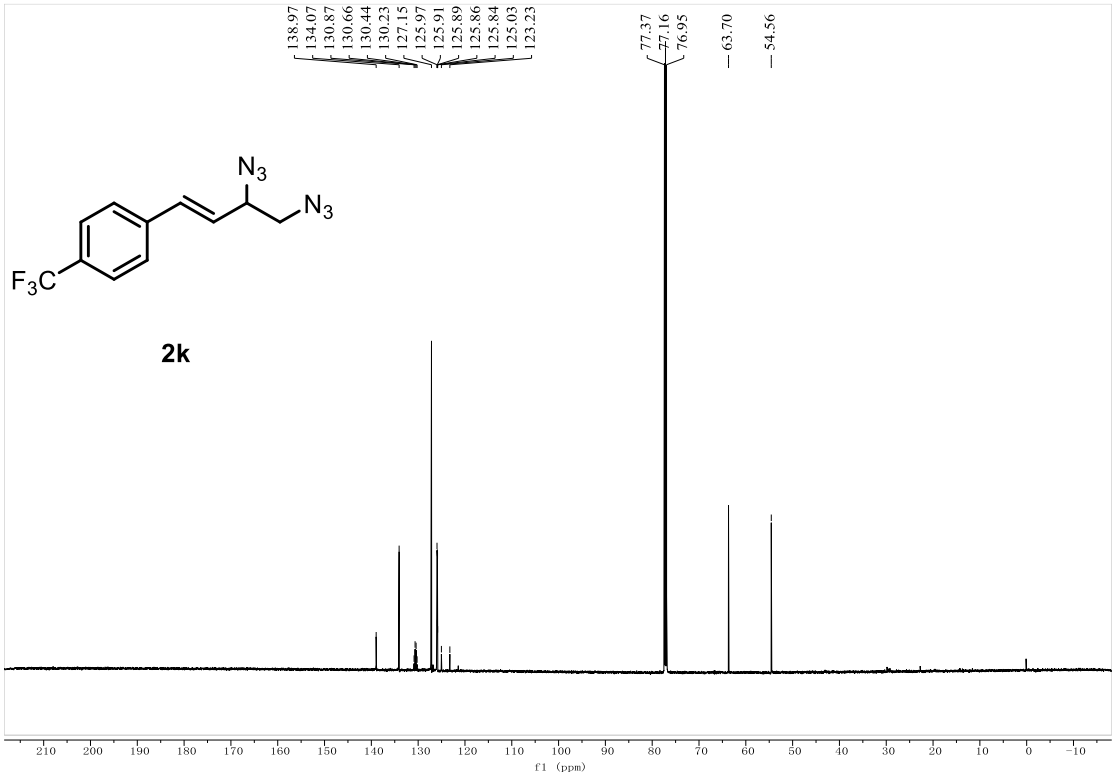
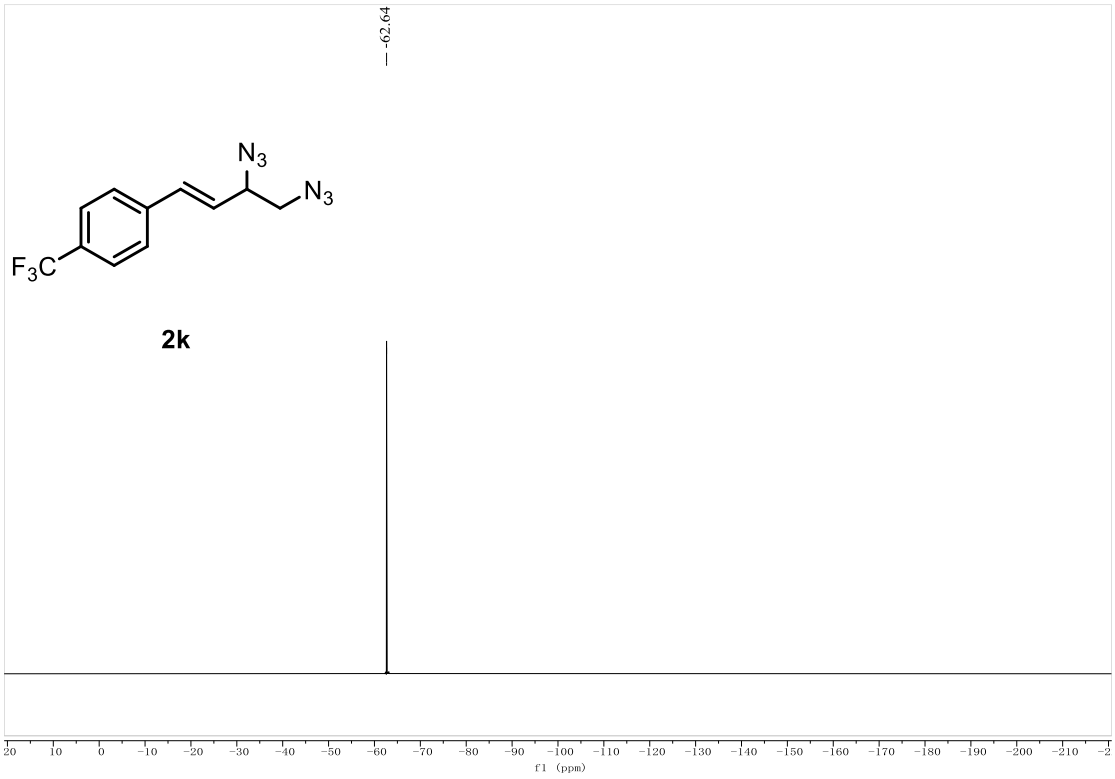


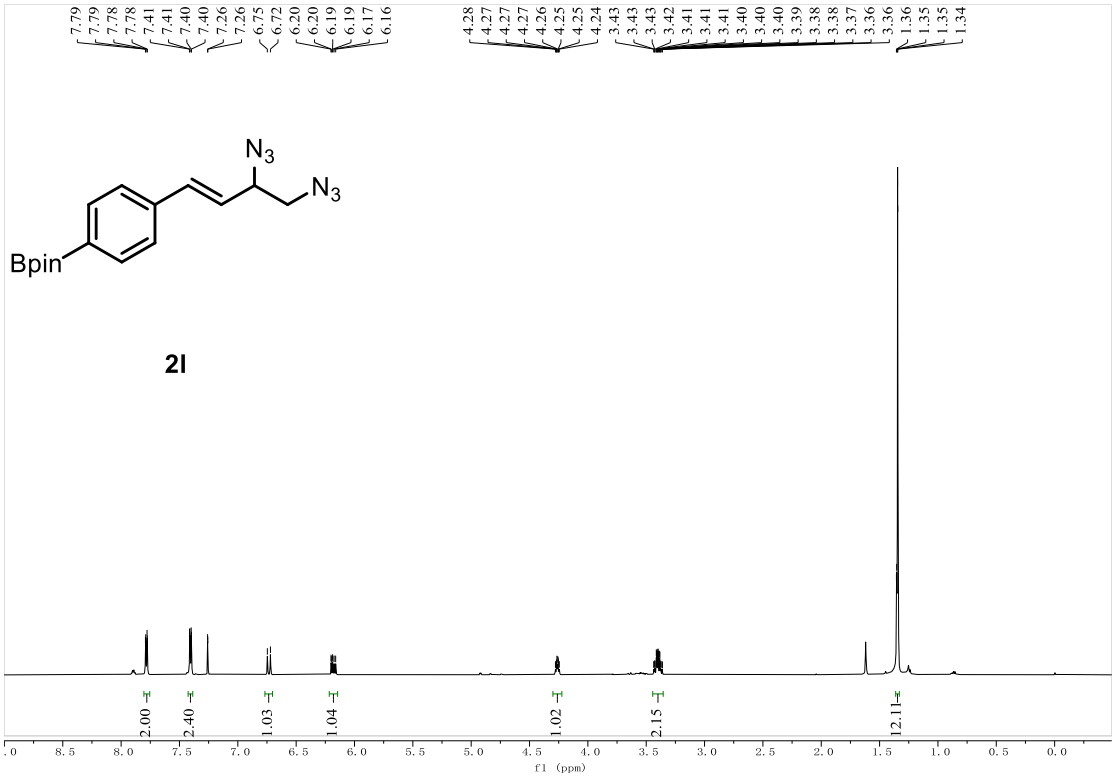
^{13}C NMR of **2k** (151 MHz, $CDCl_3$)



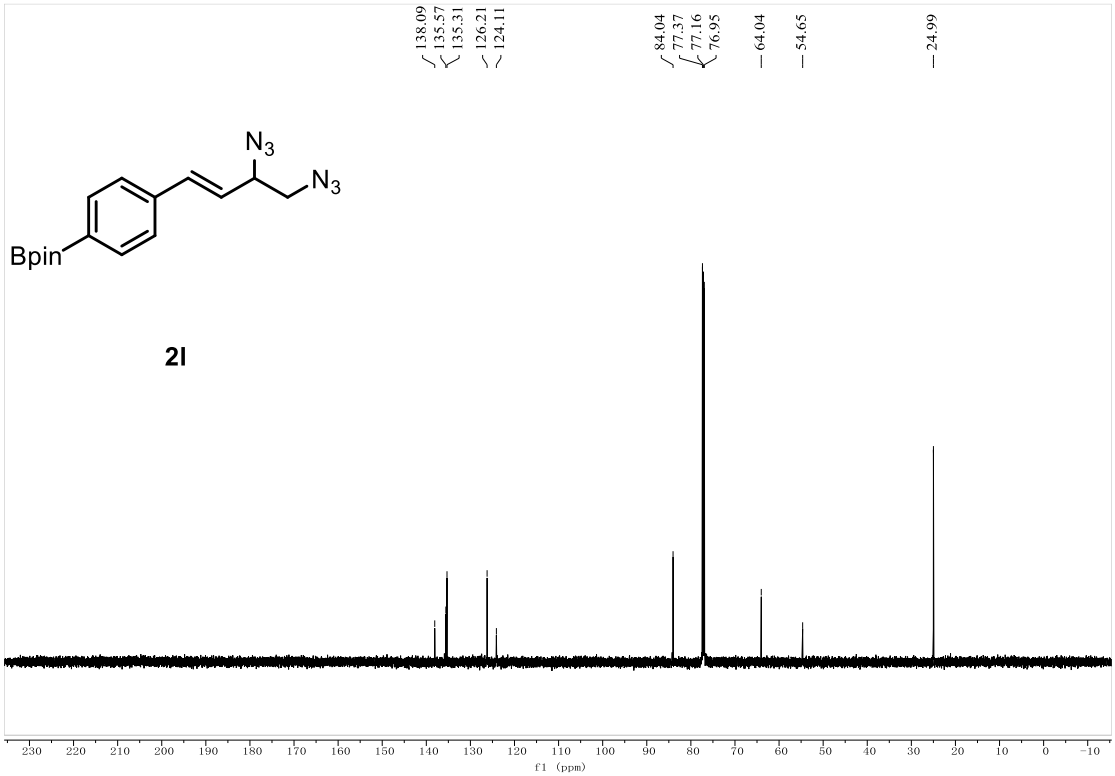
^{19}F NMR of **2k** (376 MHz, $CDCl_3$)



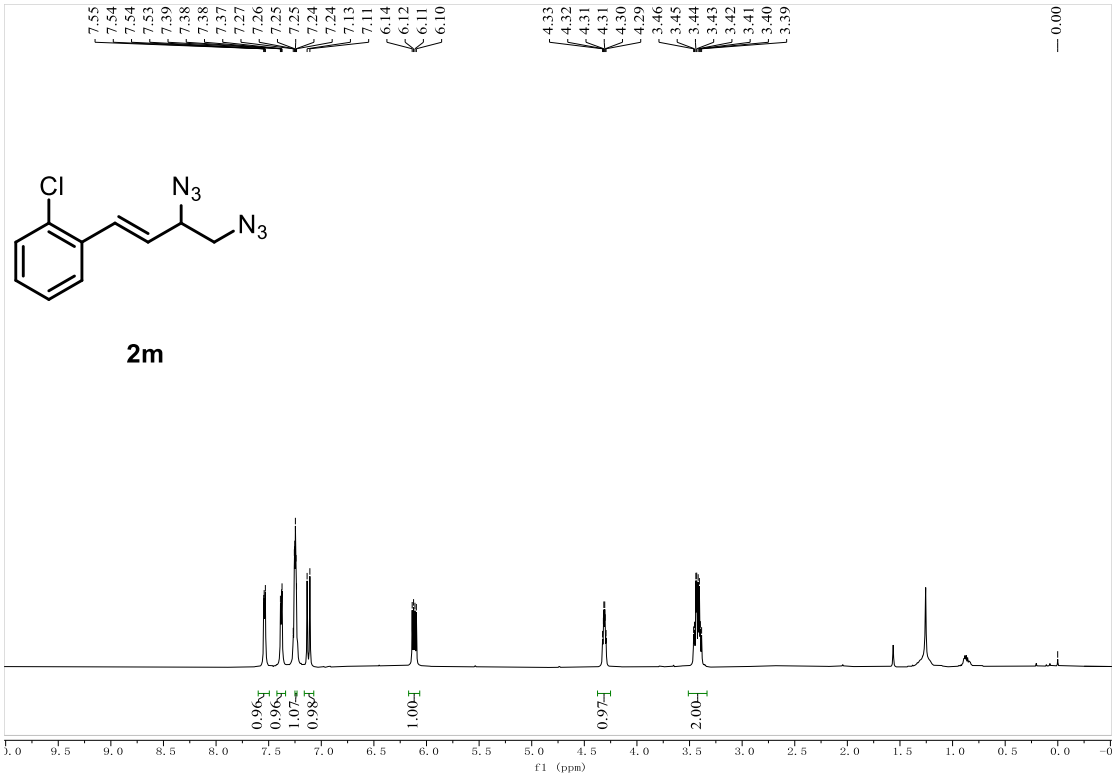
^{1}H NMR of **2l** (600 MHz, $CDCl_3$)



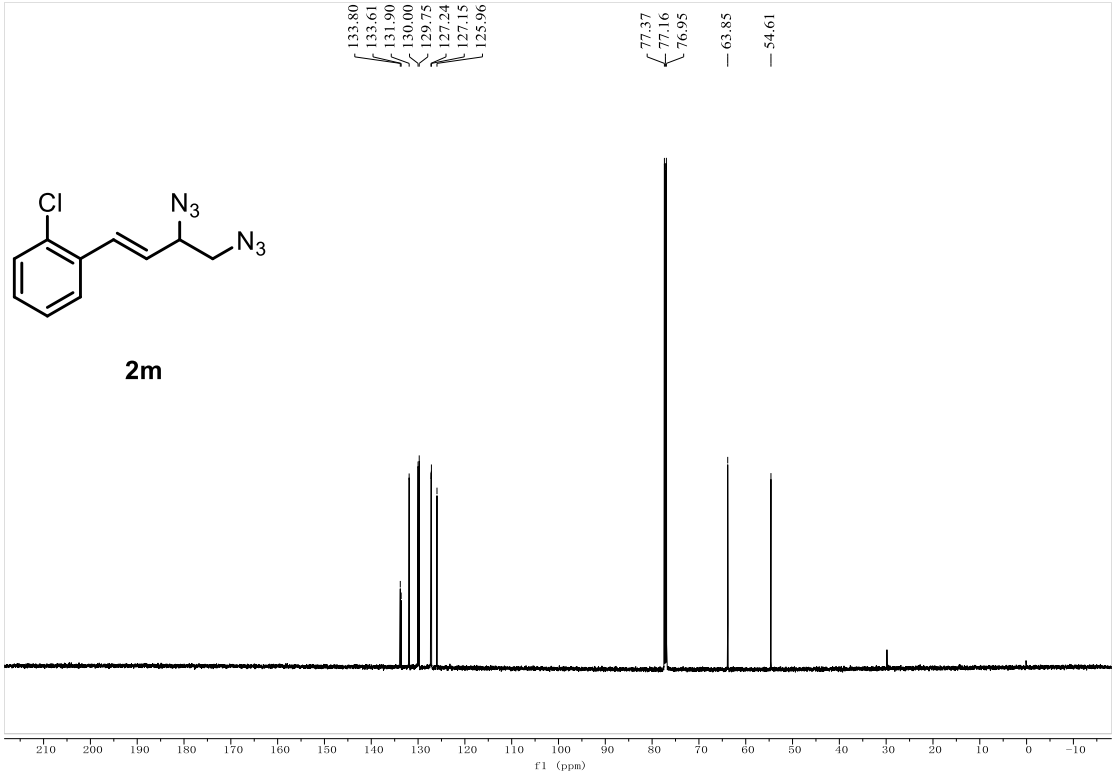
^{13}C NMR of **2l** (151 MHz, $CDCl_3$)



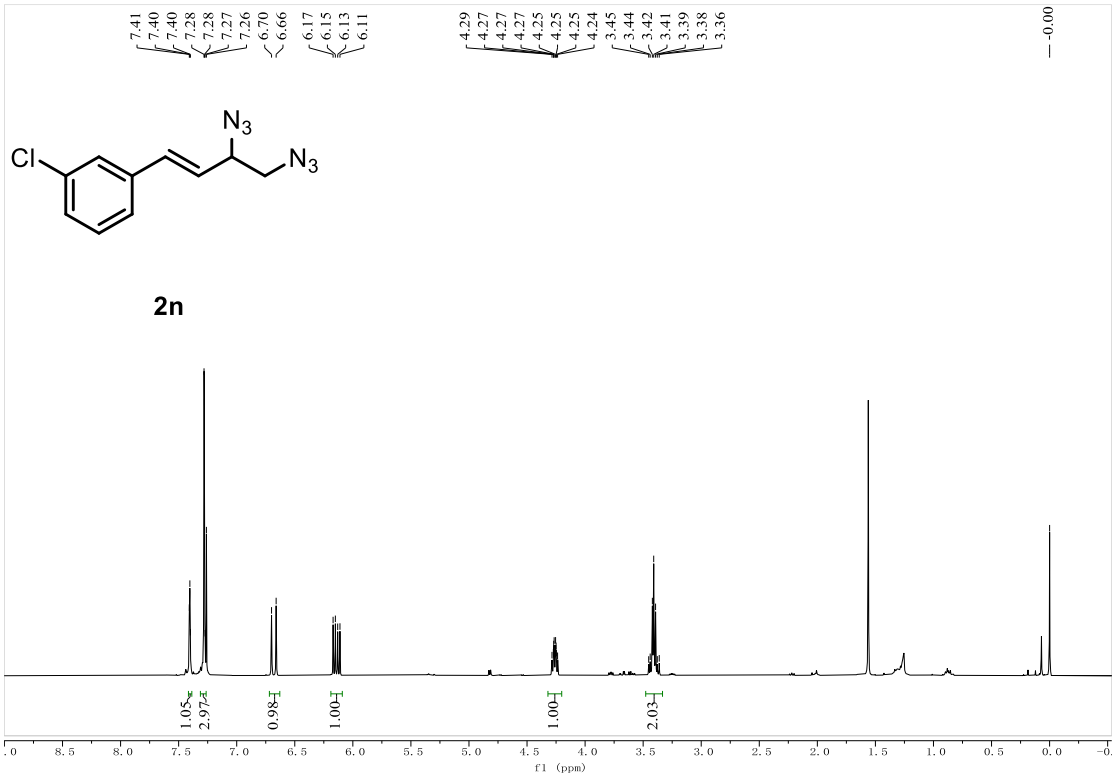
^{1}H NMR of **2m** (600 MHz, $CDCl_3$)



^{13}C NMR of **2m** (151 MHz, $CDCl_3$)



^{1}H NMR of **2n** (600 MHz, $CDCl_3$)



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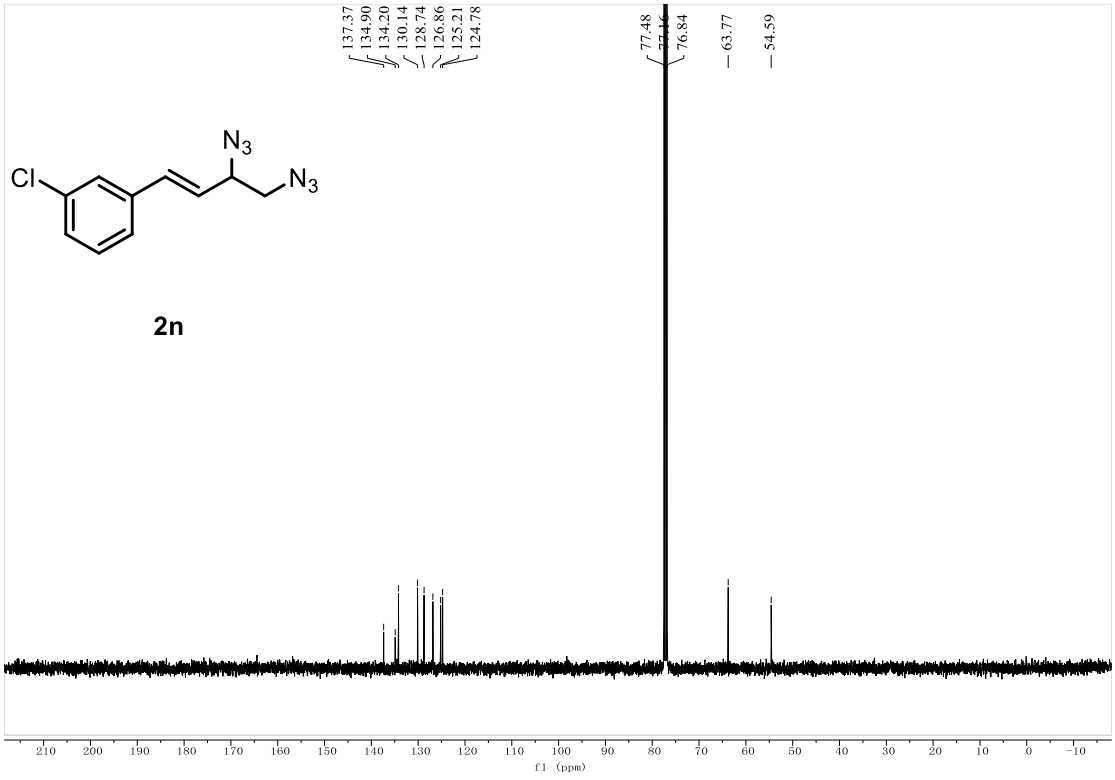

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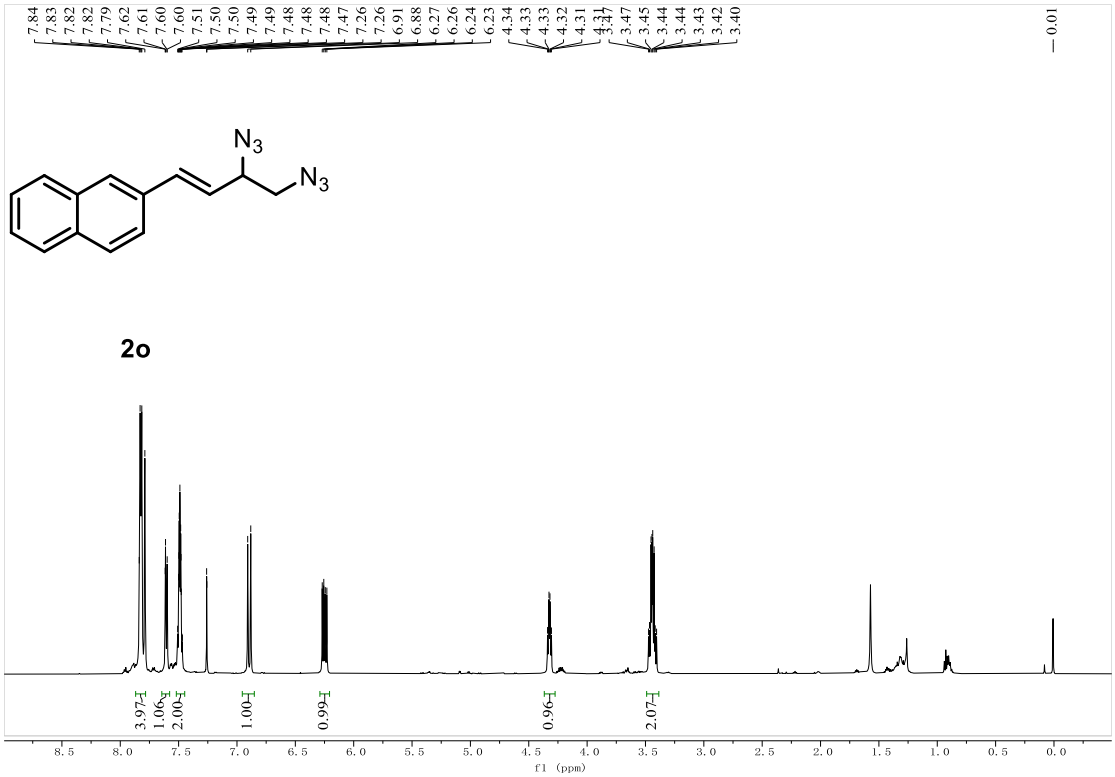
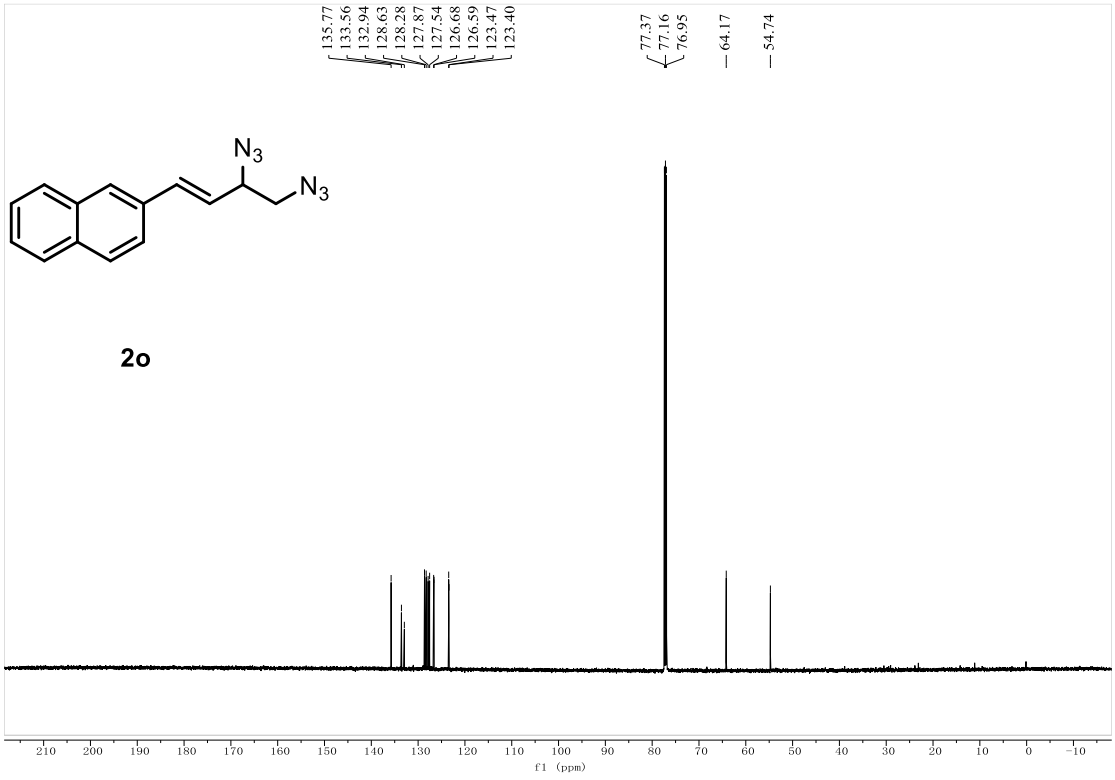
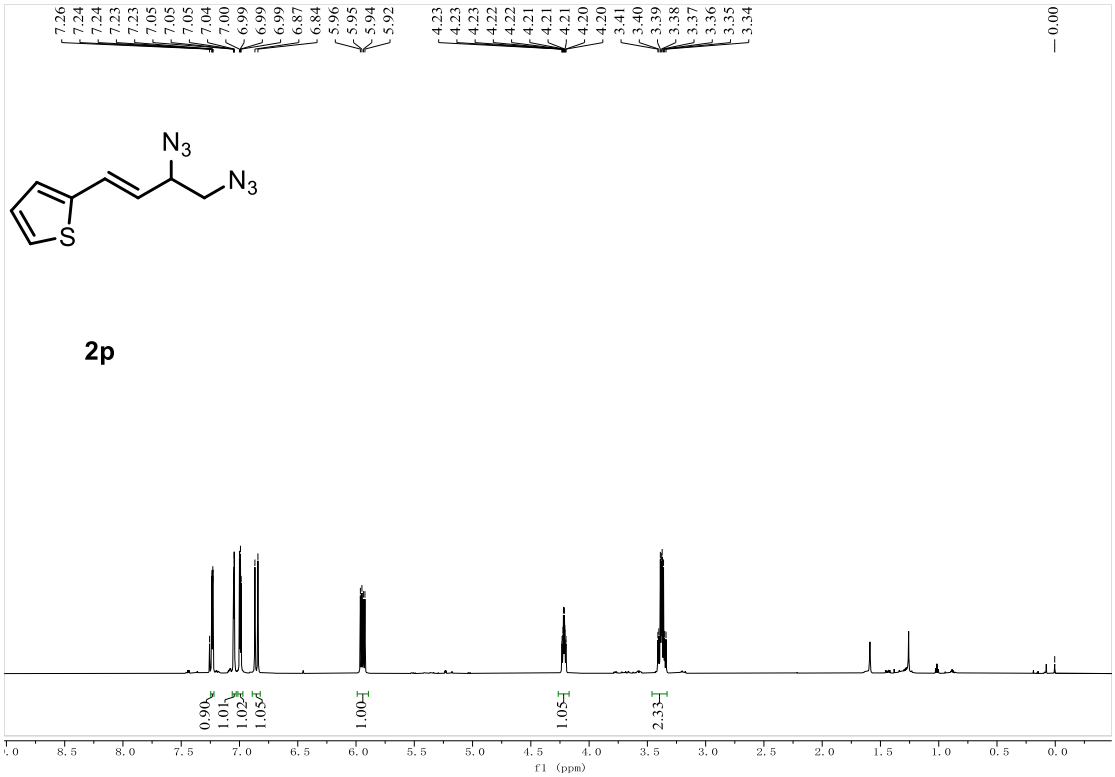


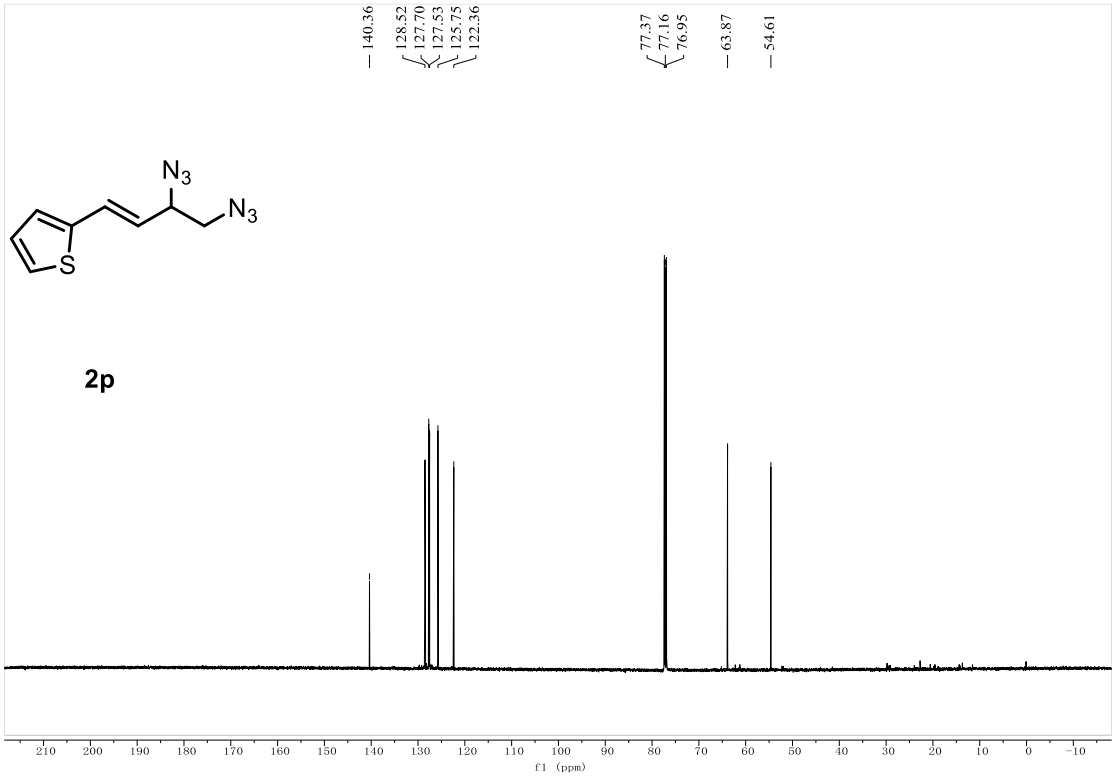
^{13}C NMR of **2o** (151 MHz, $CDCl_3$)



^{1}H NMR of **2p** (600 MHz, $CDCl_3$)



^{13}C NMR of **2p** (101 MHz, $CDCl_3$)



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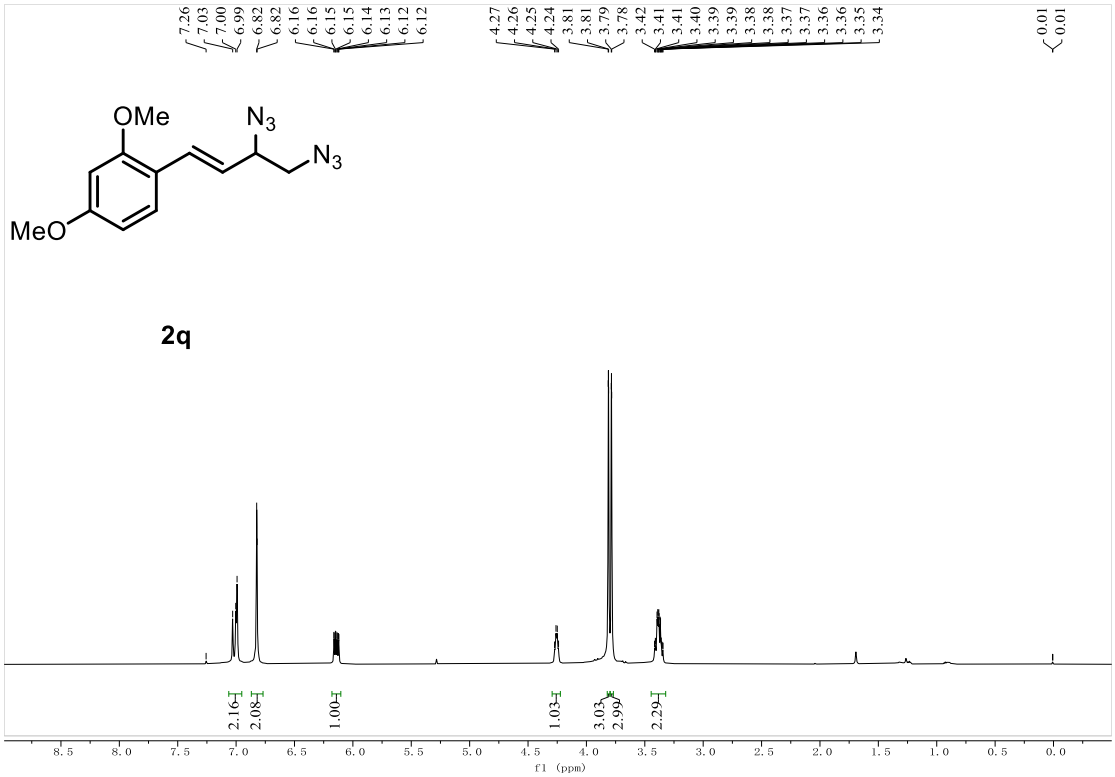
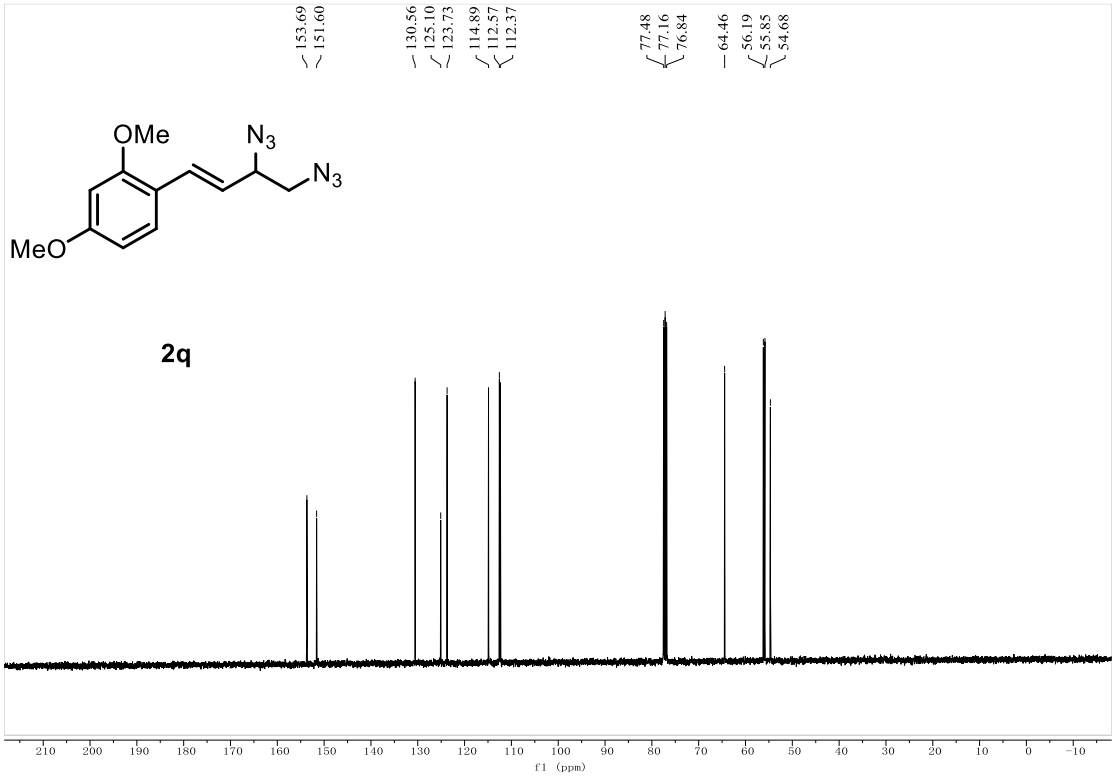
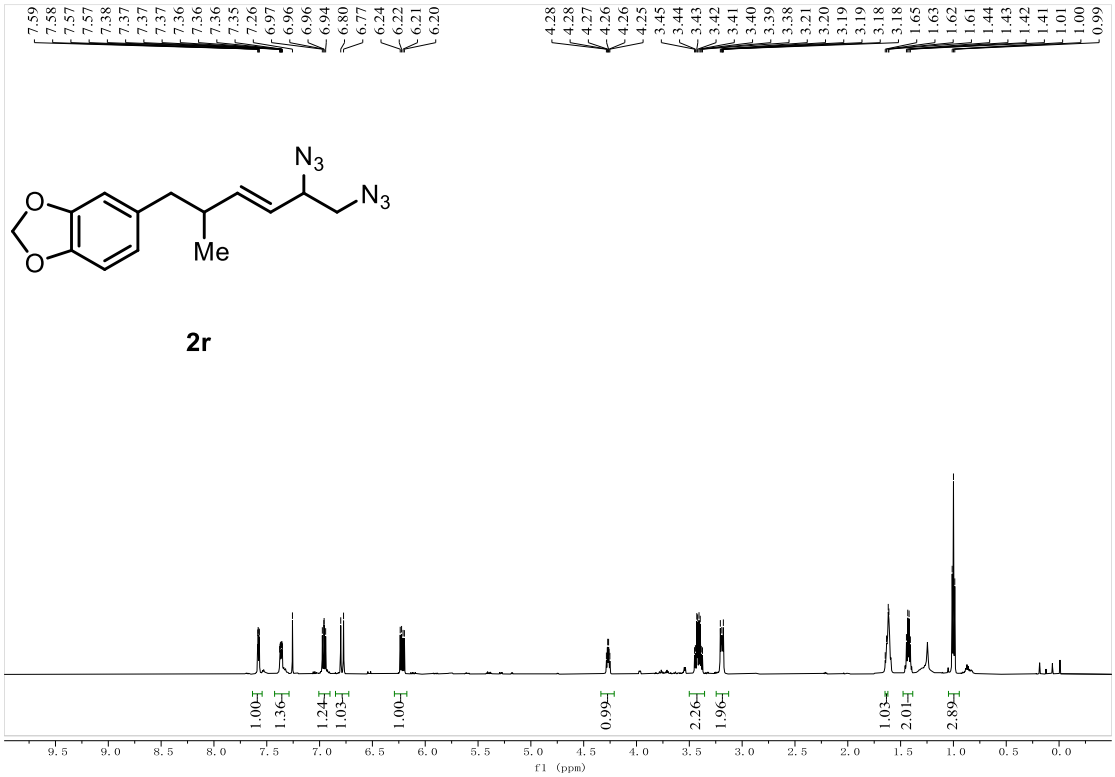


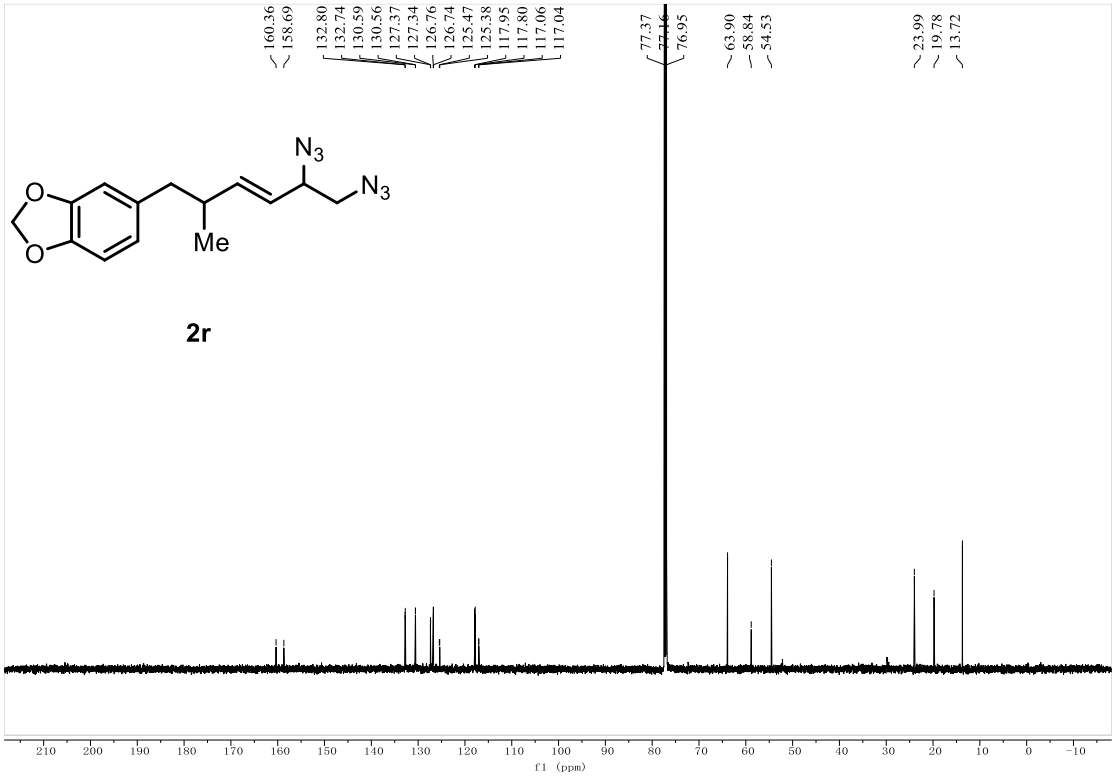
^{13}C NMR of **2q** (151 MHz, $CDCl_3$)



^{1}H NMR of **2r** (600 MHz, $CDCl_3$)



^{13}C NMR of **2r** (151 MHz, $CDCl_3$)



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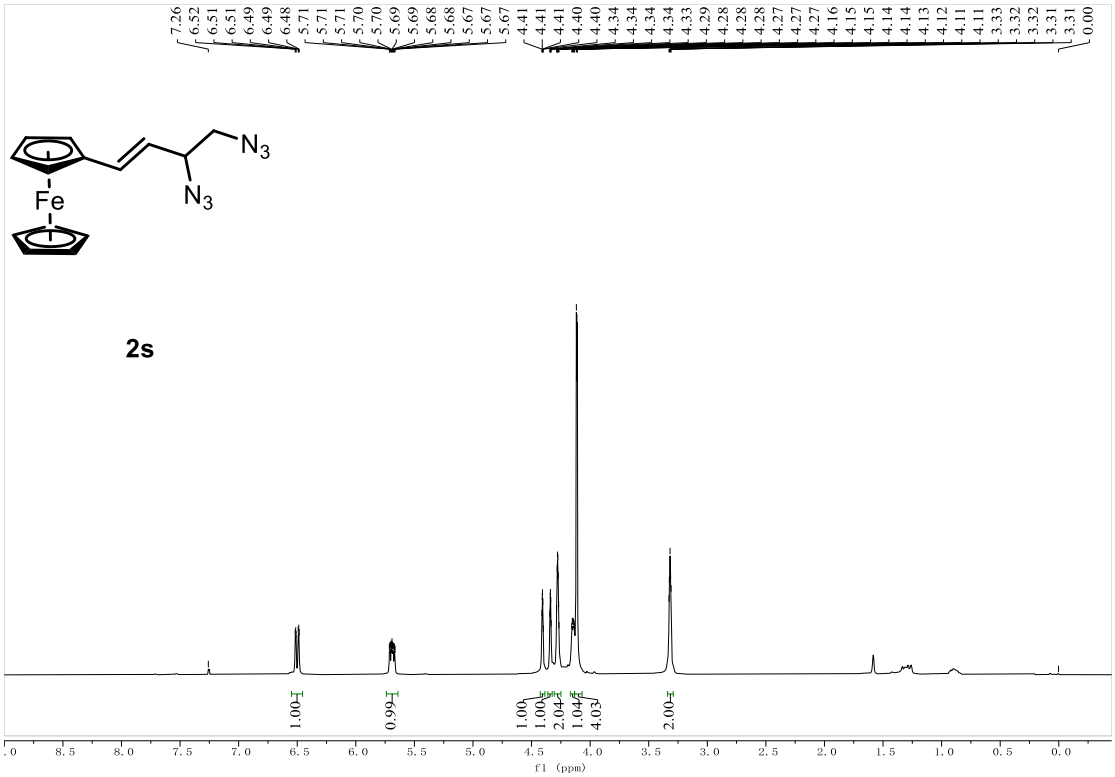
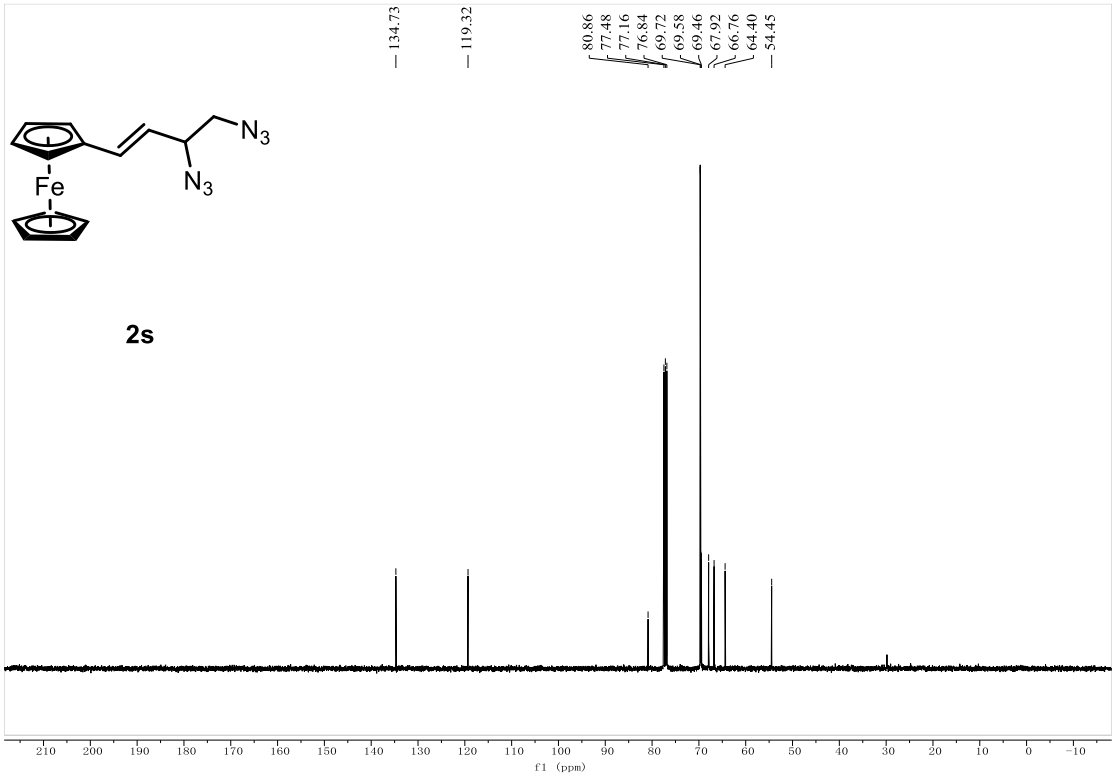
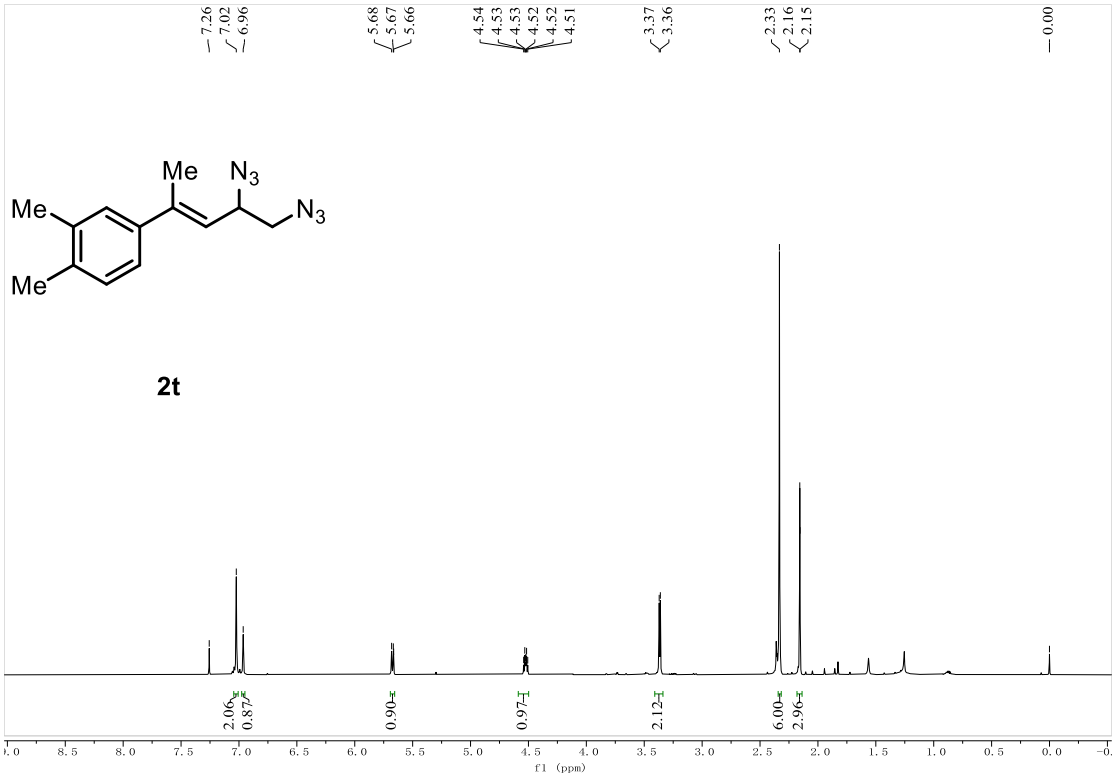


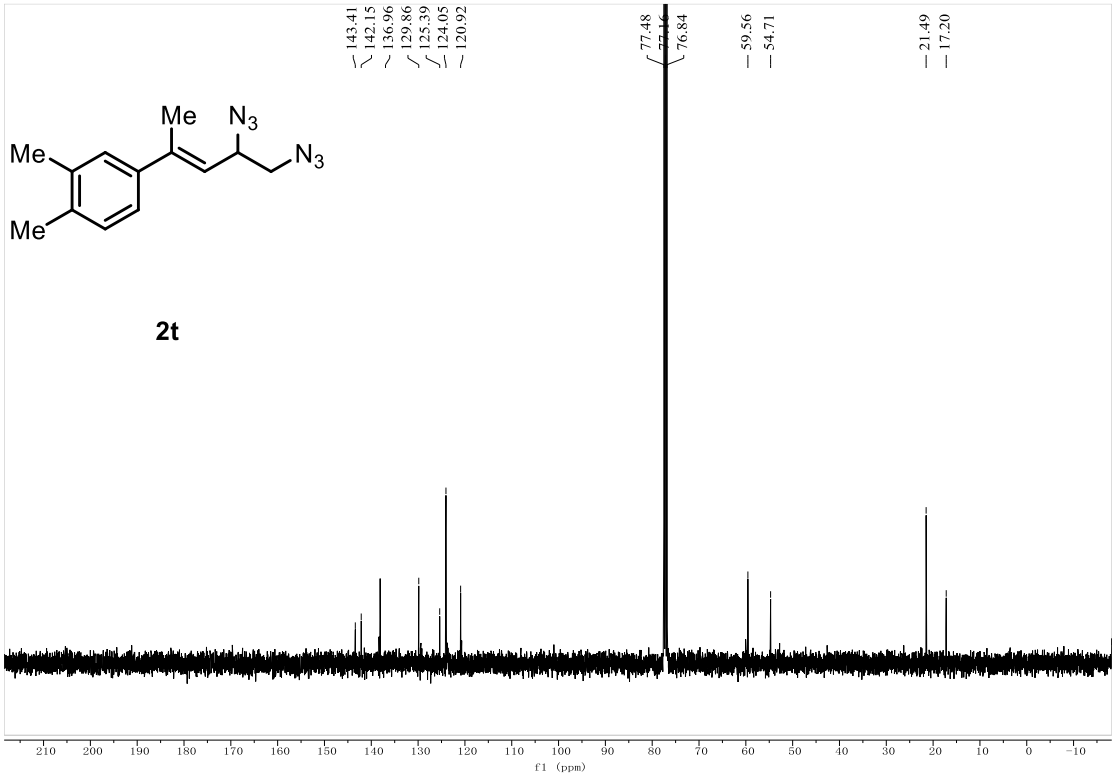
^{13}C NMR of **2s** (101 MHz, $CDCl_3$)



^{1}H NMR of **2t** (600 MHz, $CDCl_3$)



^{13}C NMR of **2t** (101 MHz, $CDCl_3$)



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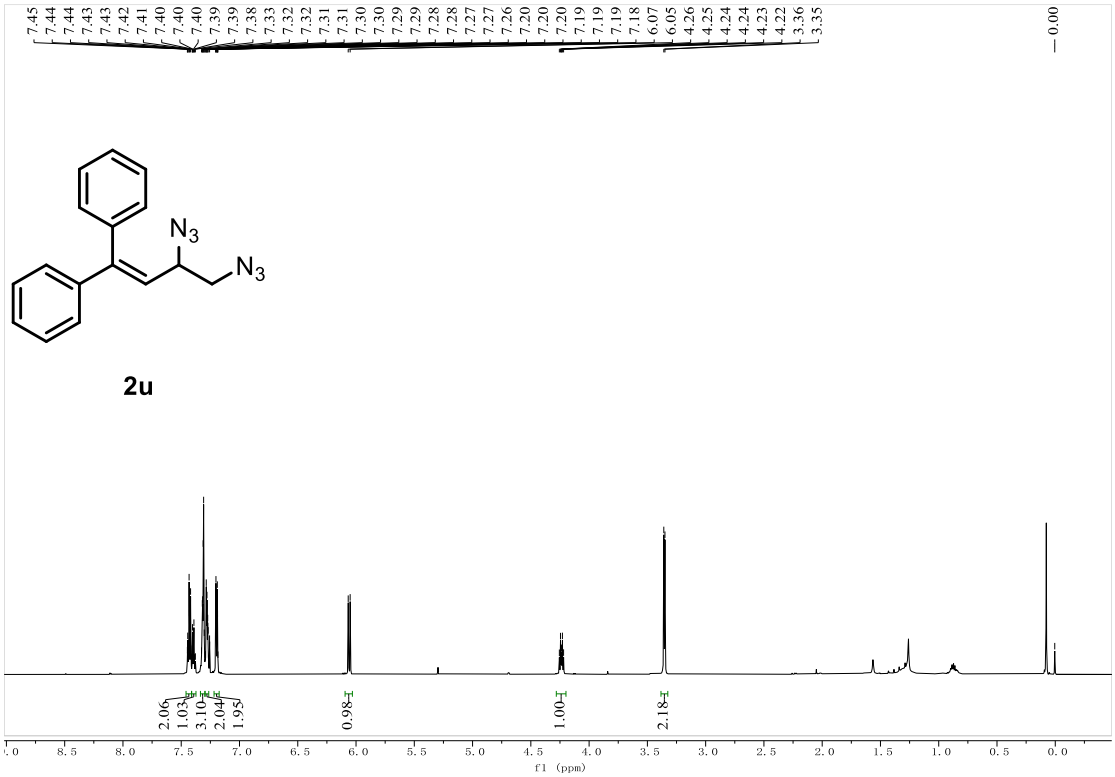

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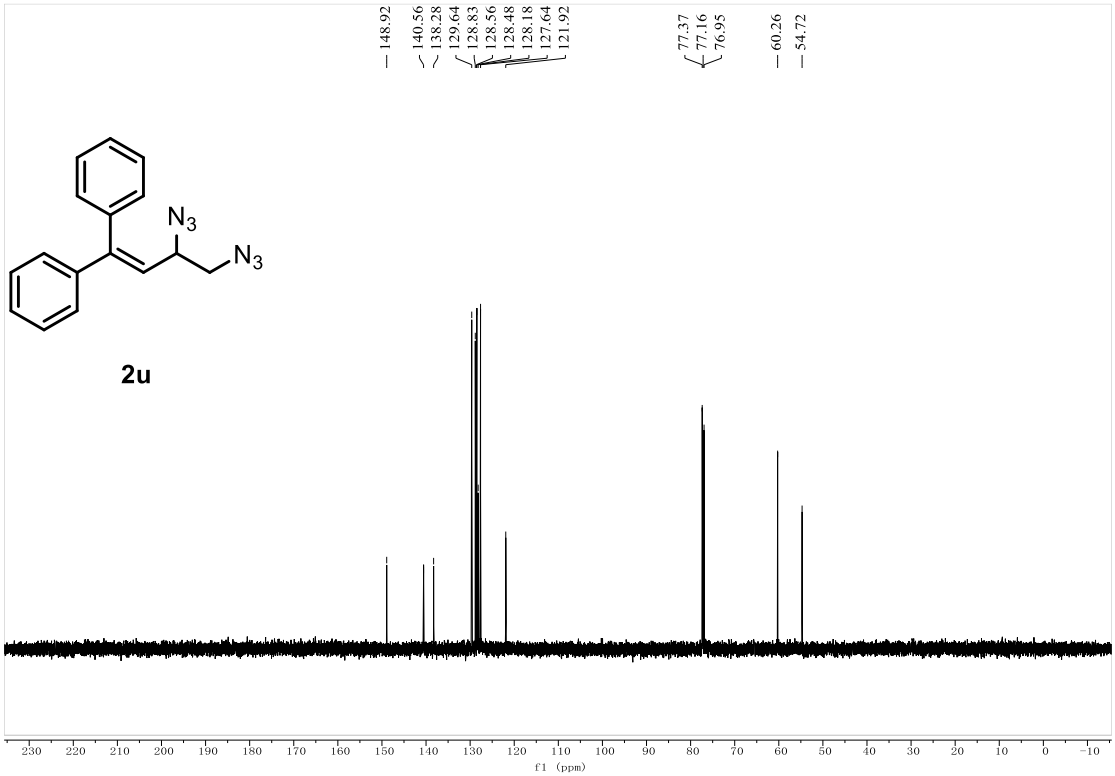
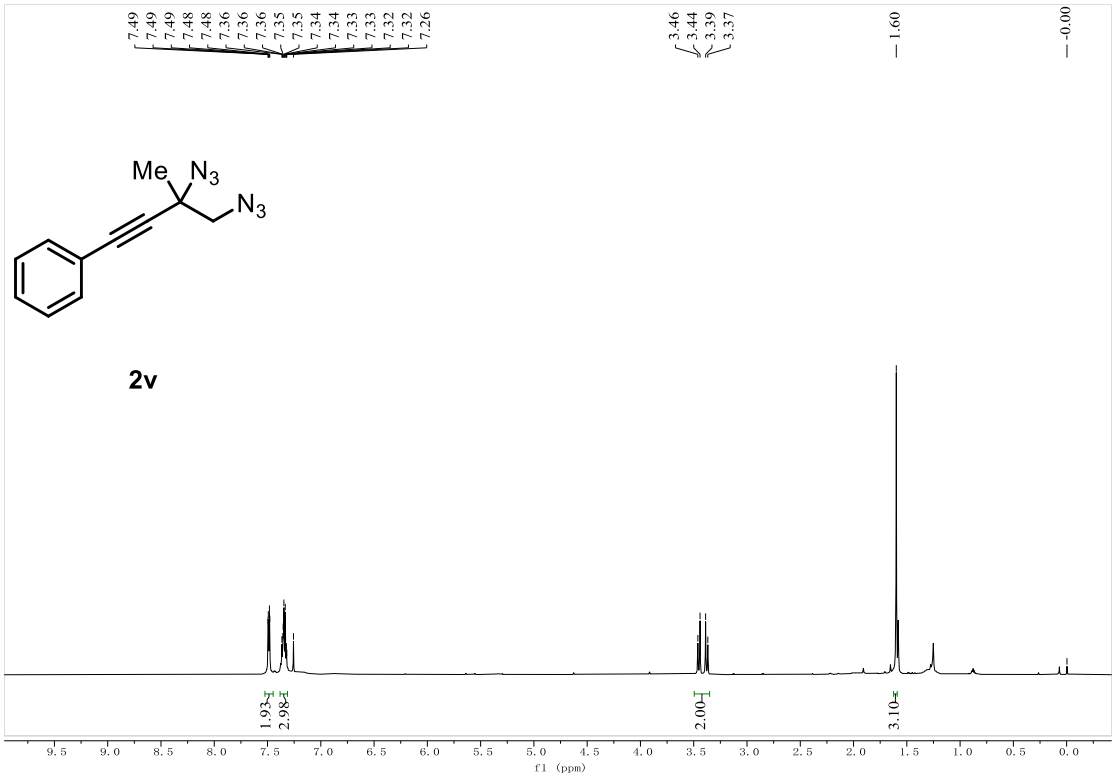


^{1}H NMR of **2v** (600 MHz, $CDCl_3$)



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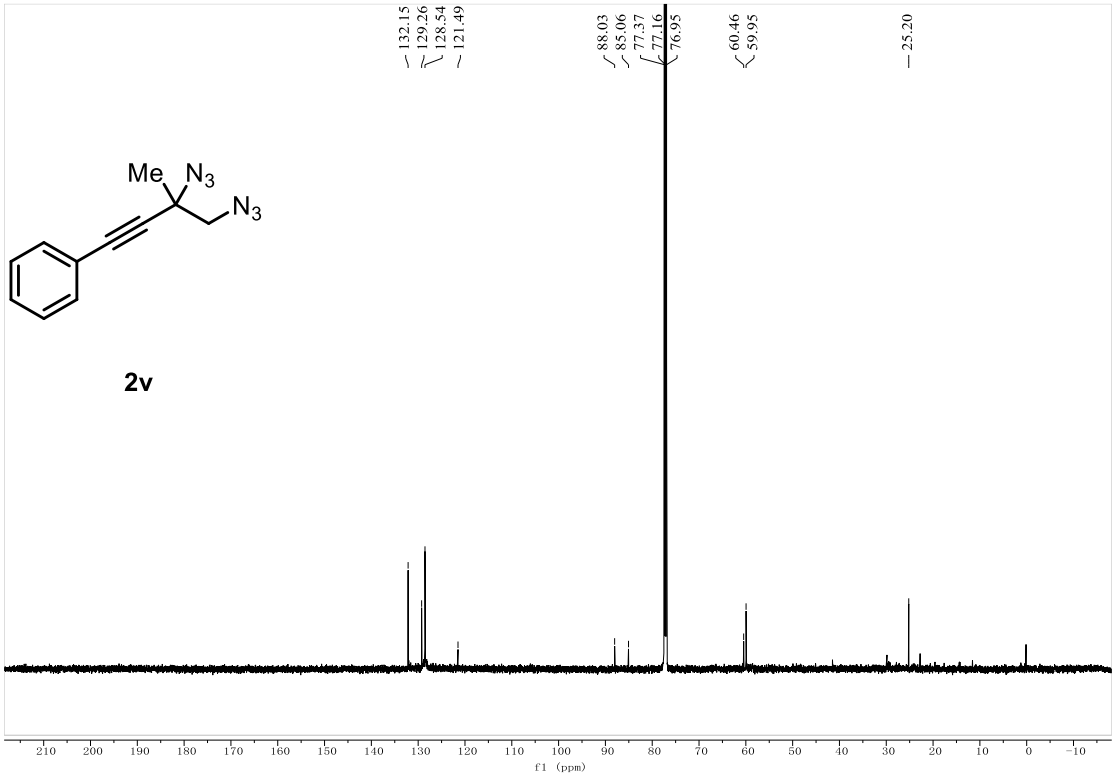
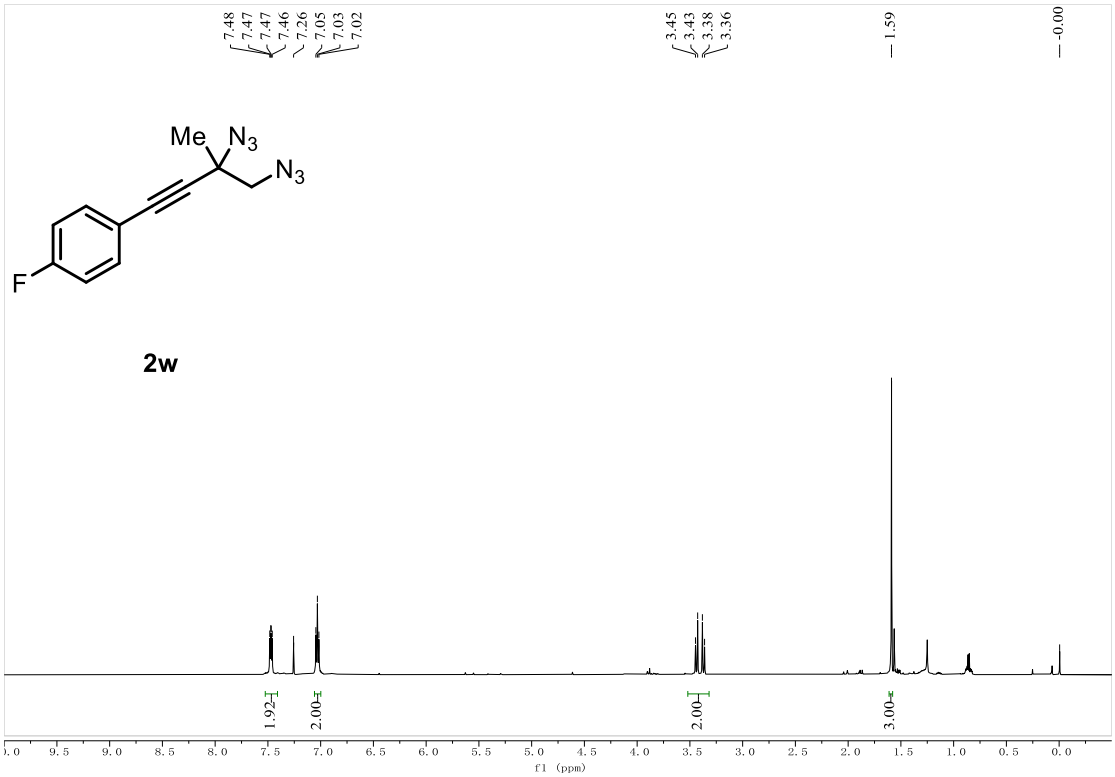
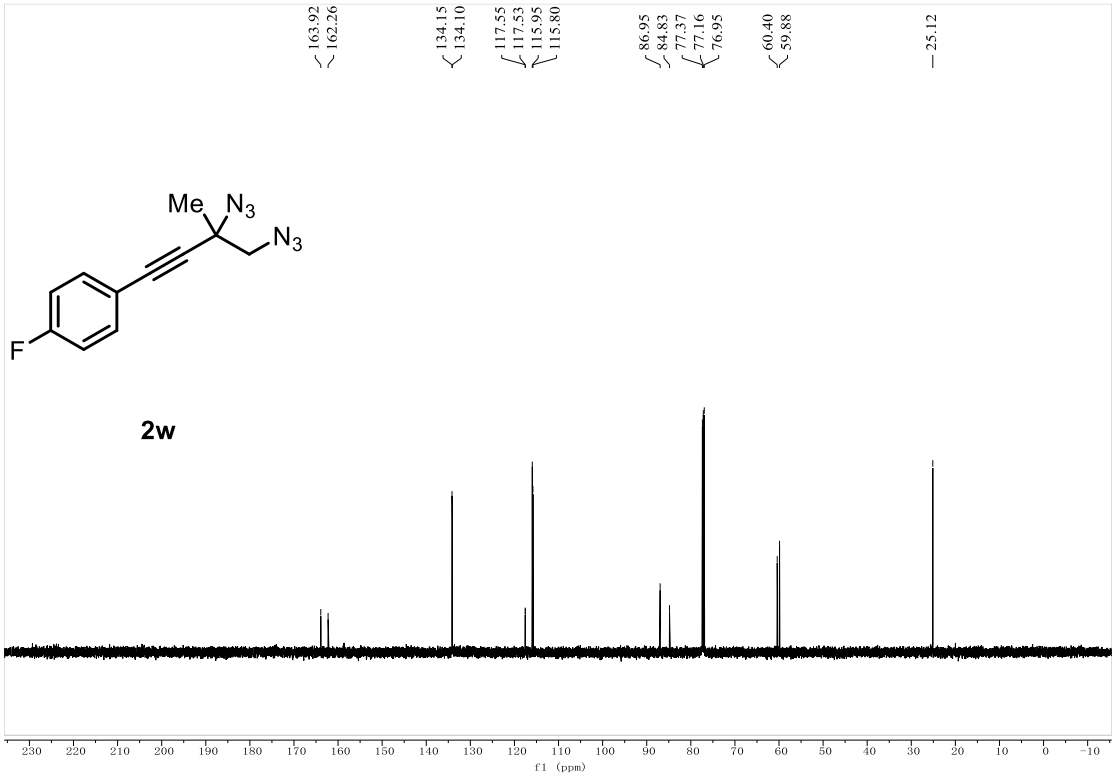


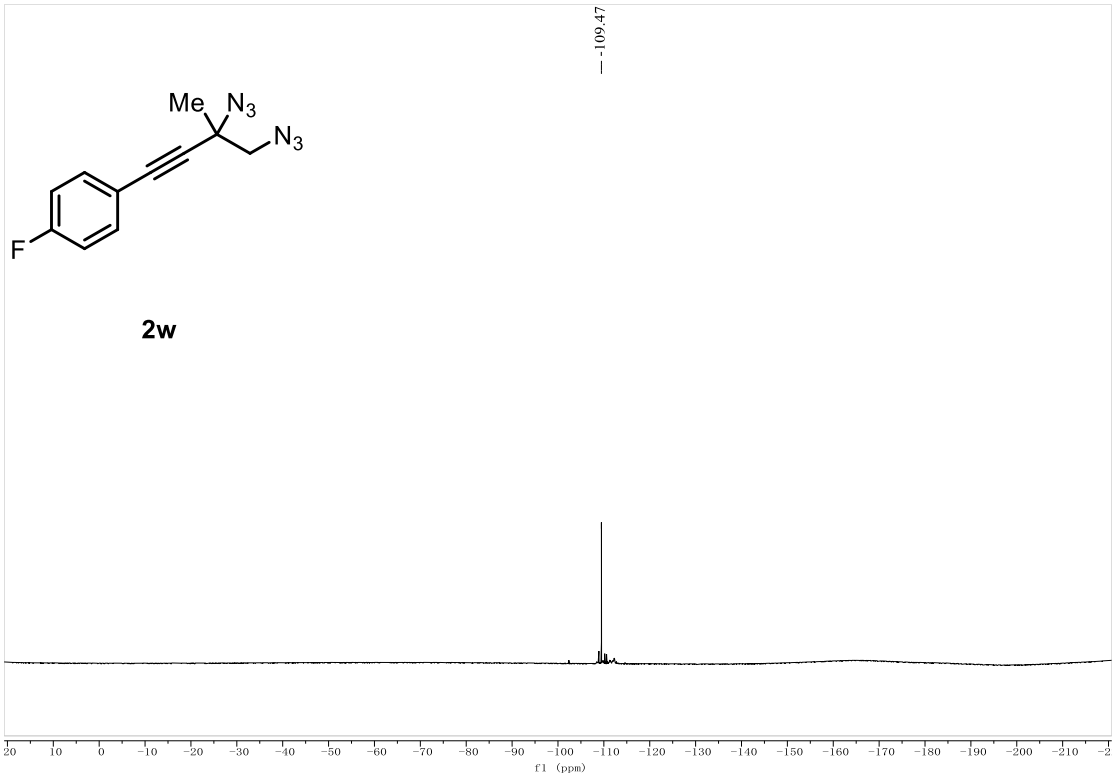
^{1}H NMR of **2w** (600 MHz, $CDCl_3$)



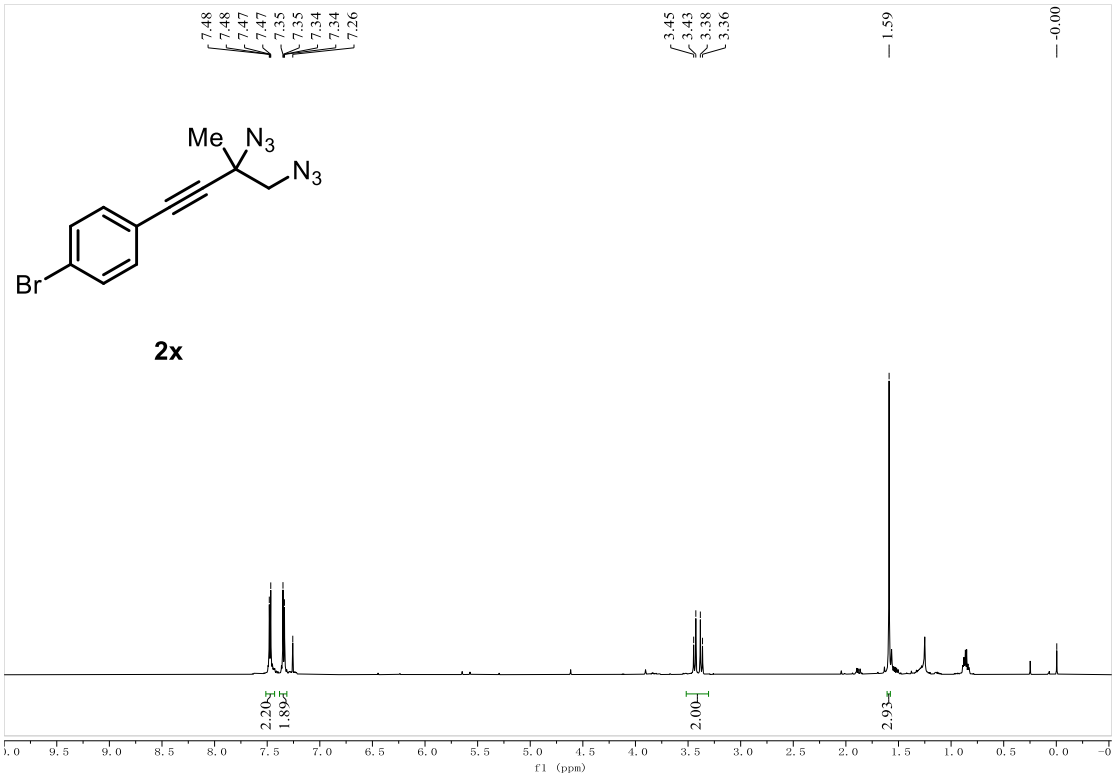
^{13}C NMR of **2w** (151 MHz, $CDCl_3$)



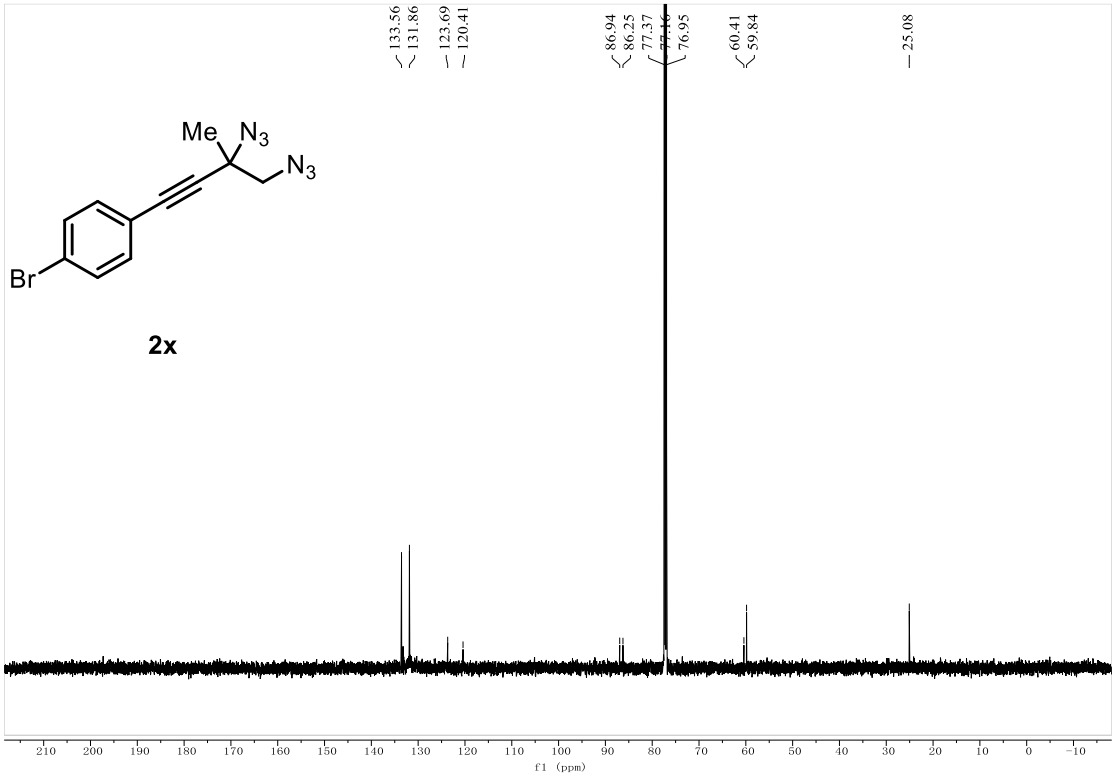
^{19}F NMR of **2w** ($CDCl_3$)



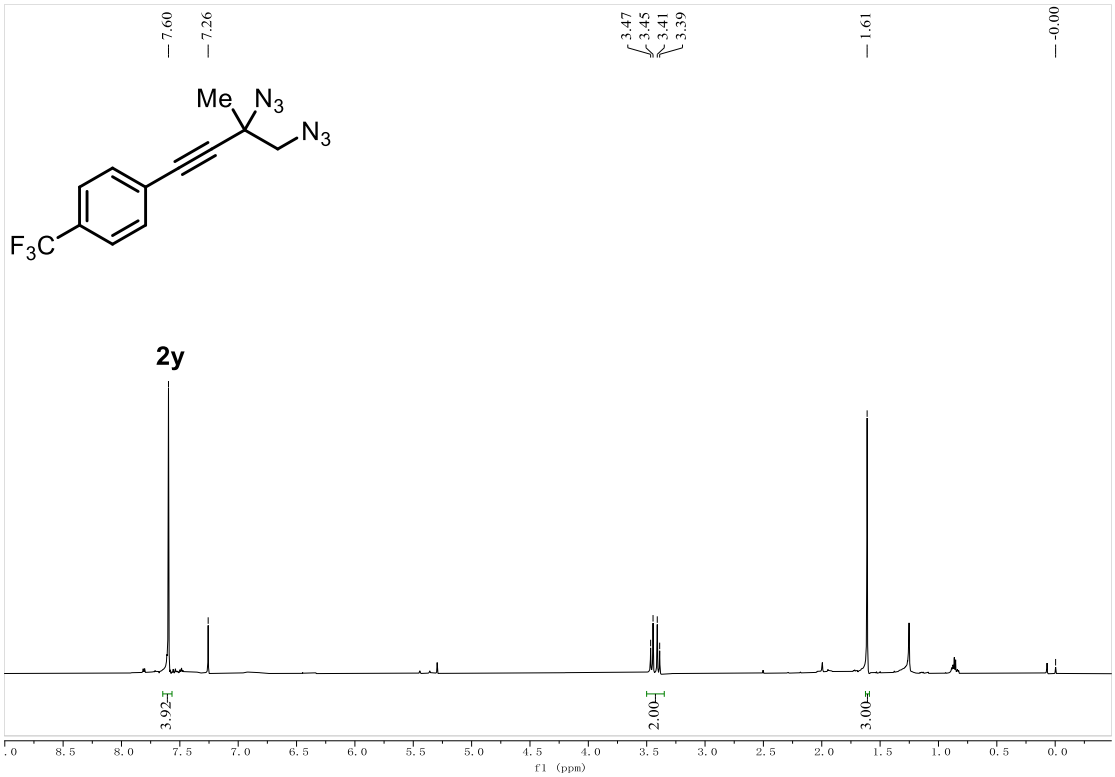
^{1}H NMR of **2x** (600 MHz, $CDCl_3$)



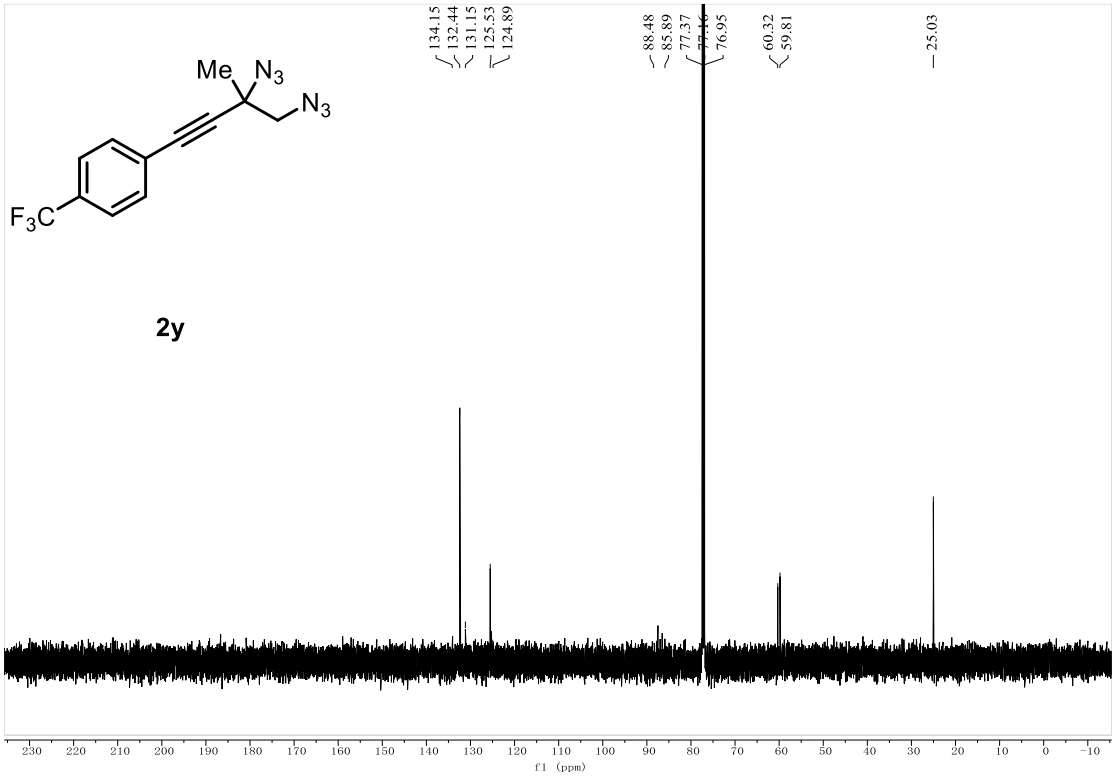
^{13}C NMR of **2x** (151 MHz, $CDCl_3$)



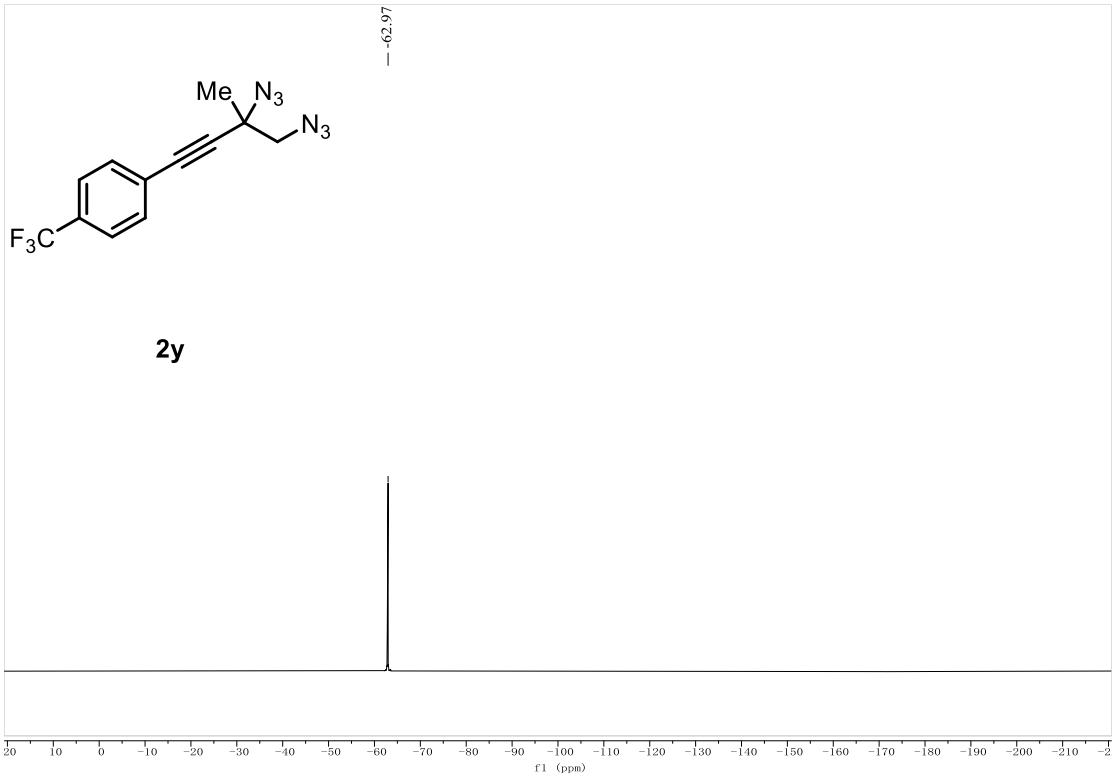
^{1}H NMR of **2y** (600 MHz, $CDCl_3$)



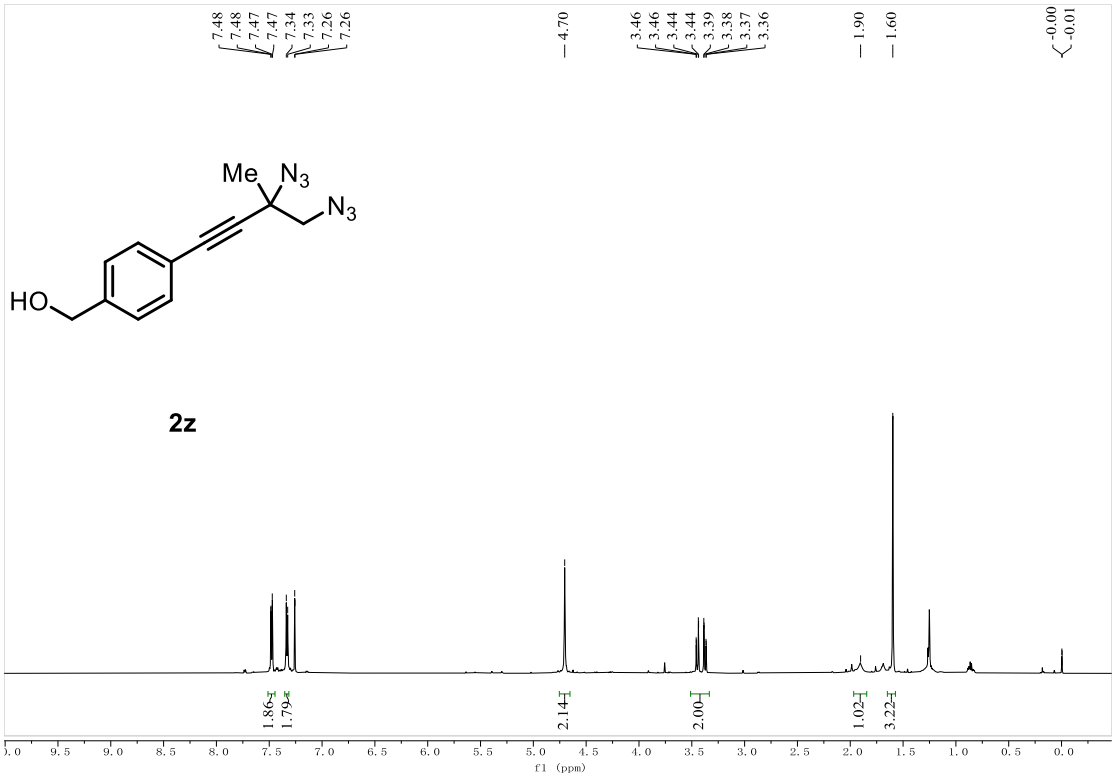
^{13}C NMR of **2y** (151 MHz, $CDCl_3$)



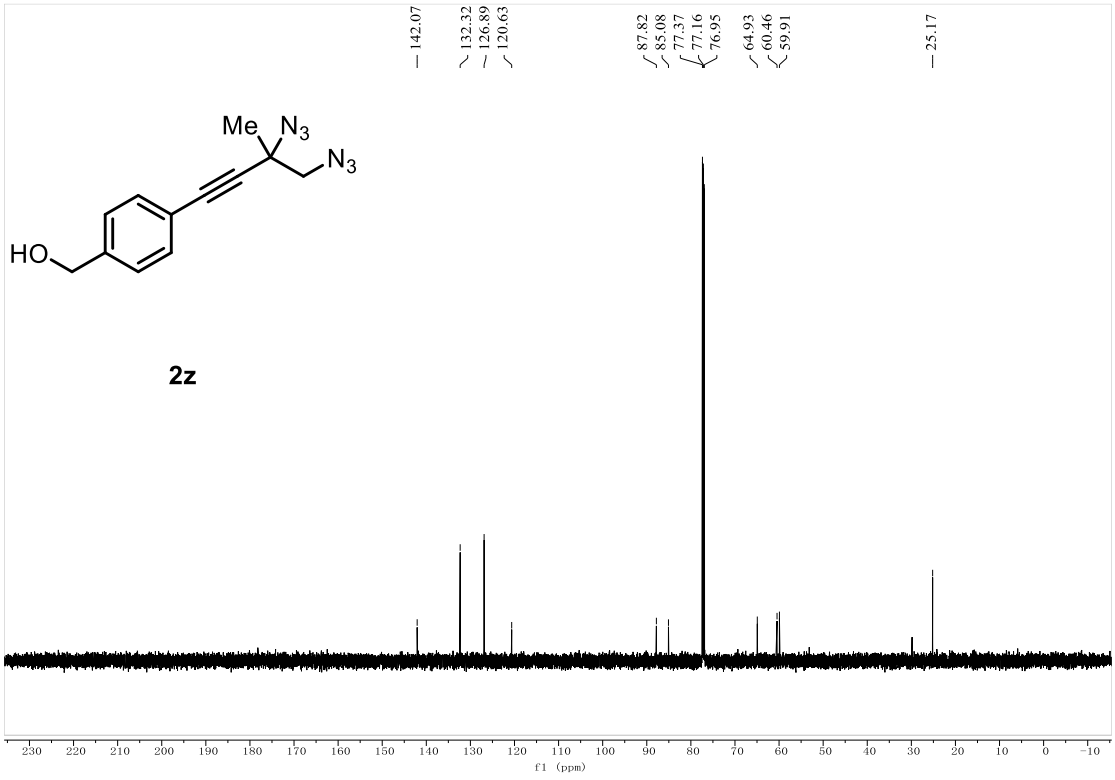
^{19}F NMR of **2y** (376 MHz, $CDCl_3$)



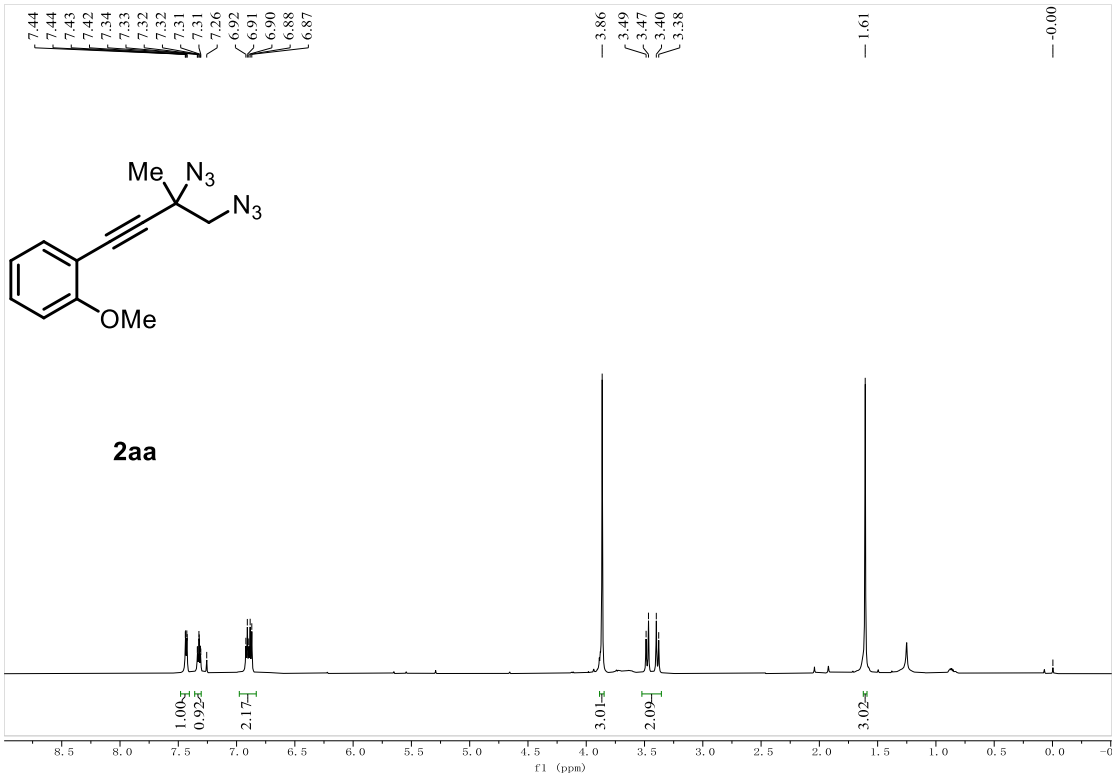
^{1}H NMR of **2z** (600 MHz, $CDCl_3$)



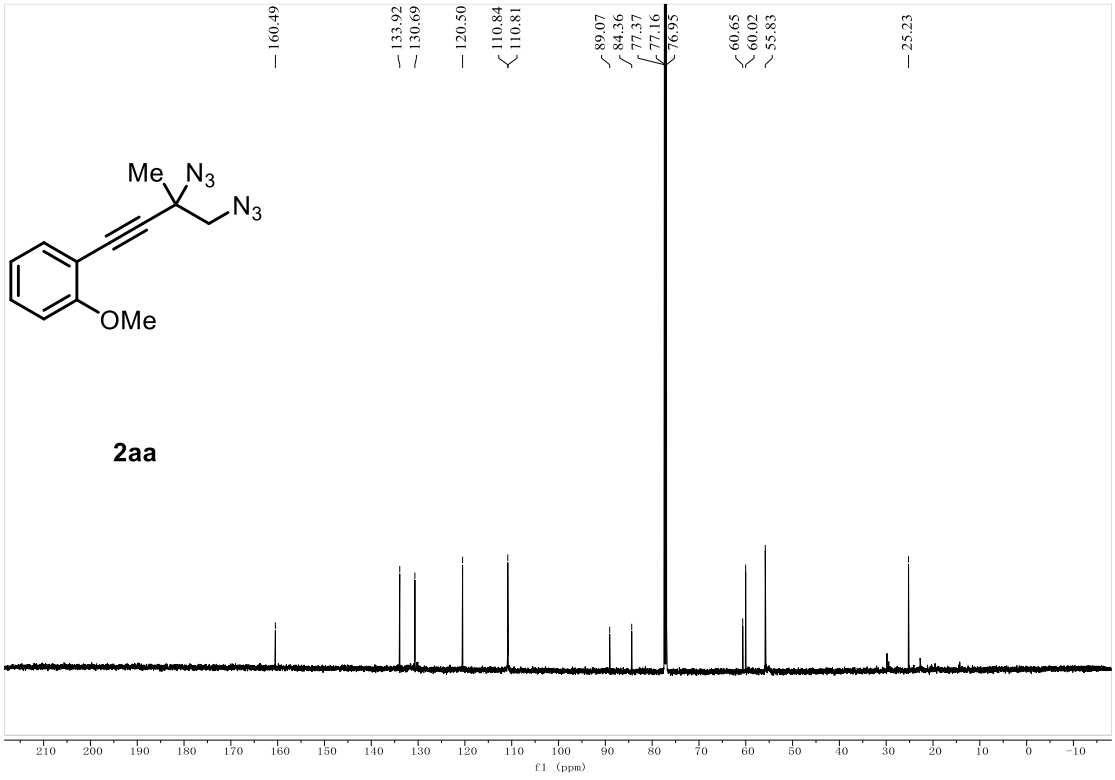
^{13}C NMR of **2z** (151 MHz, $CDCl_3$)



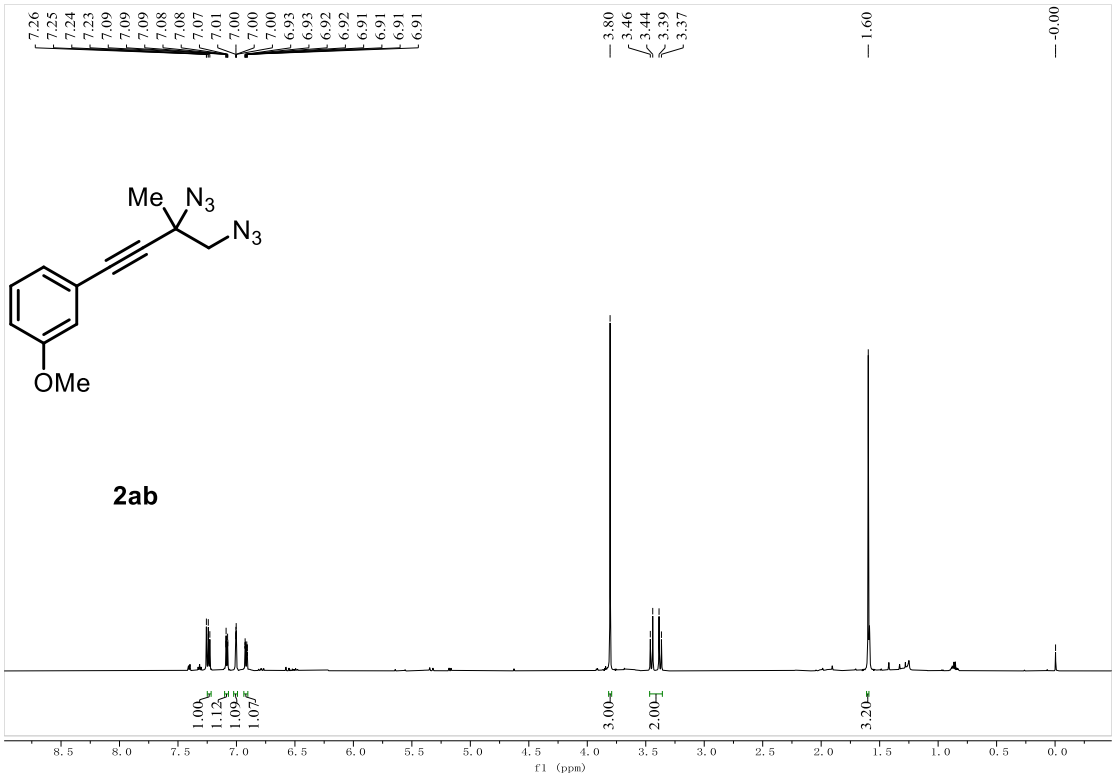
^{1}H NMR of **2aa** (600 MHz, $CDCl_3$)



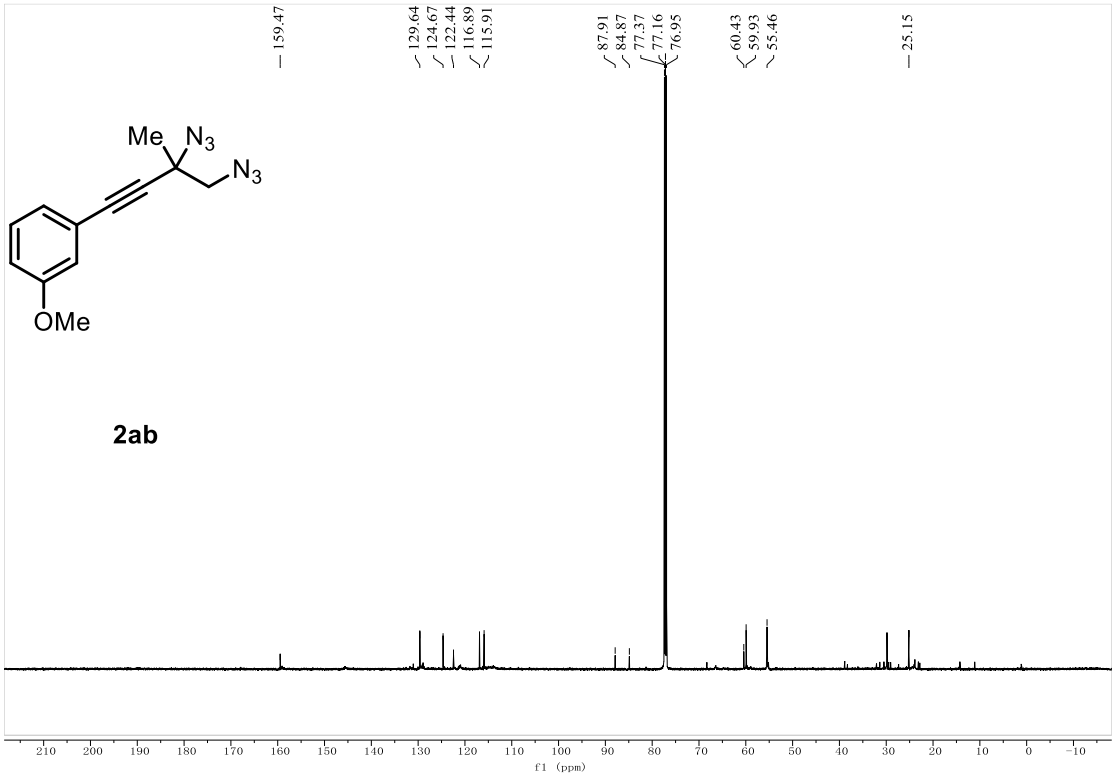
^{13}C NMR of **2aa** (151 MHz, $CDCl_3$)



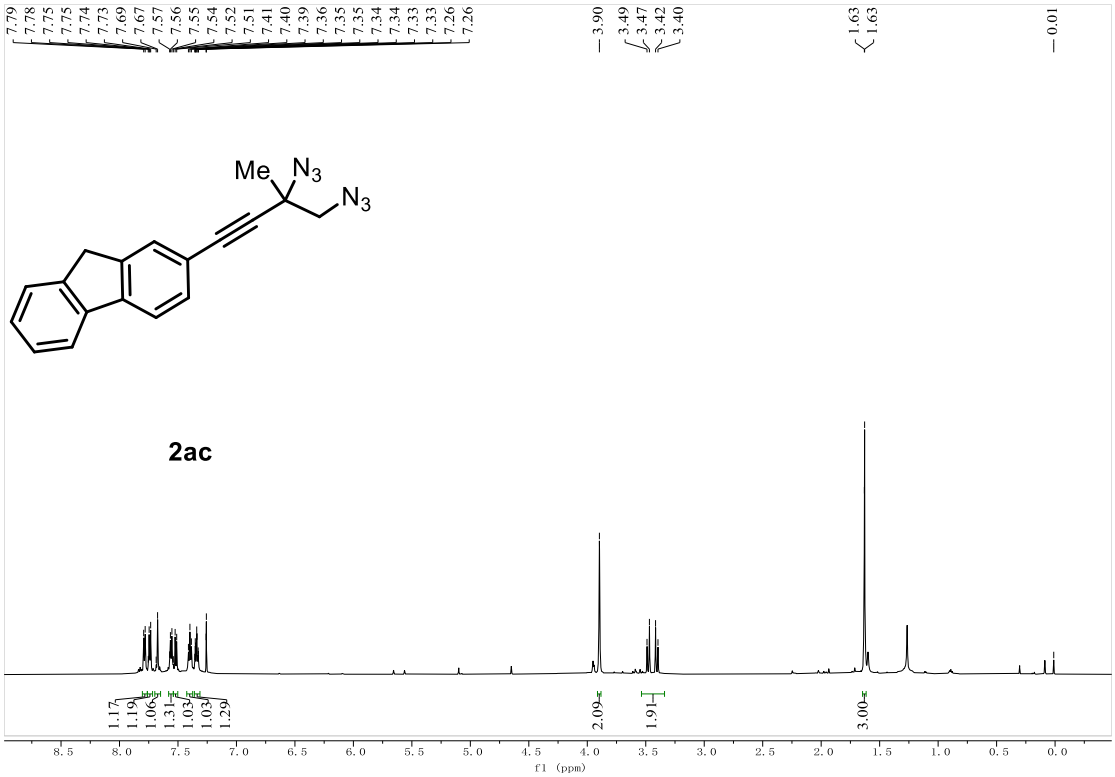
^{1}H NMR of **2ab** (600 MHz, $CDCl_3$)



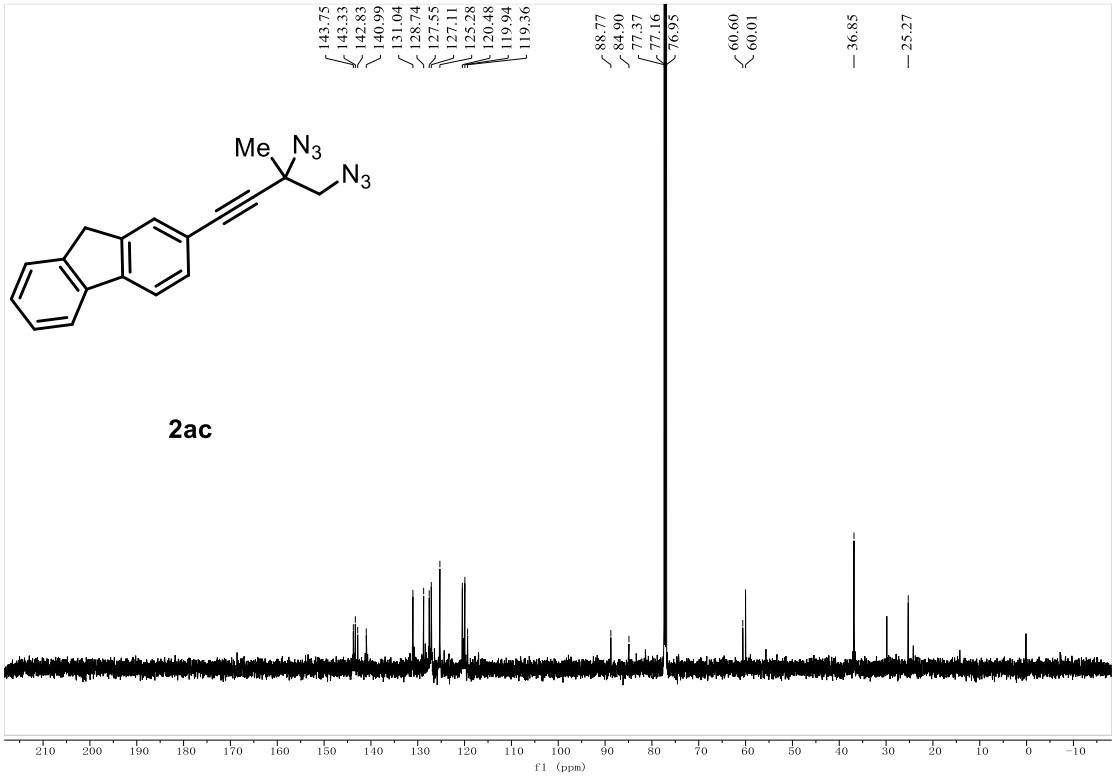
^{13}C NMR of **2ab** (151 MHz, $CDCl_3$)



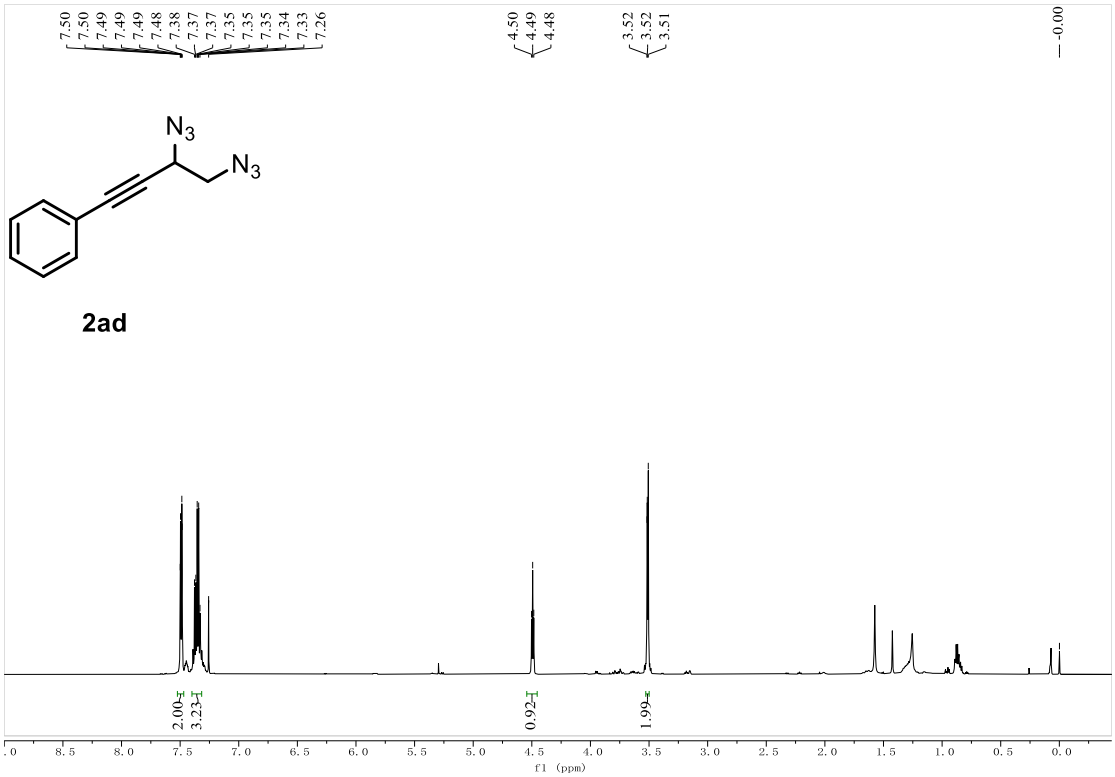
^{1}H NMR of **2ac** (600 MHz, $CDCl_3$)



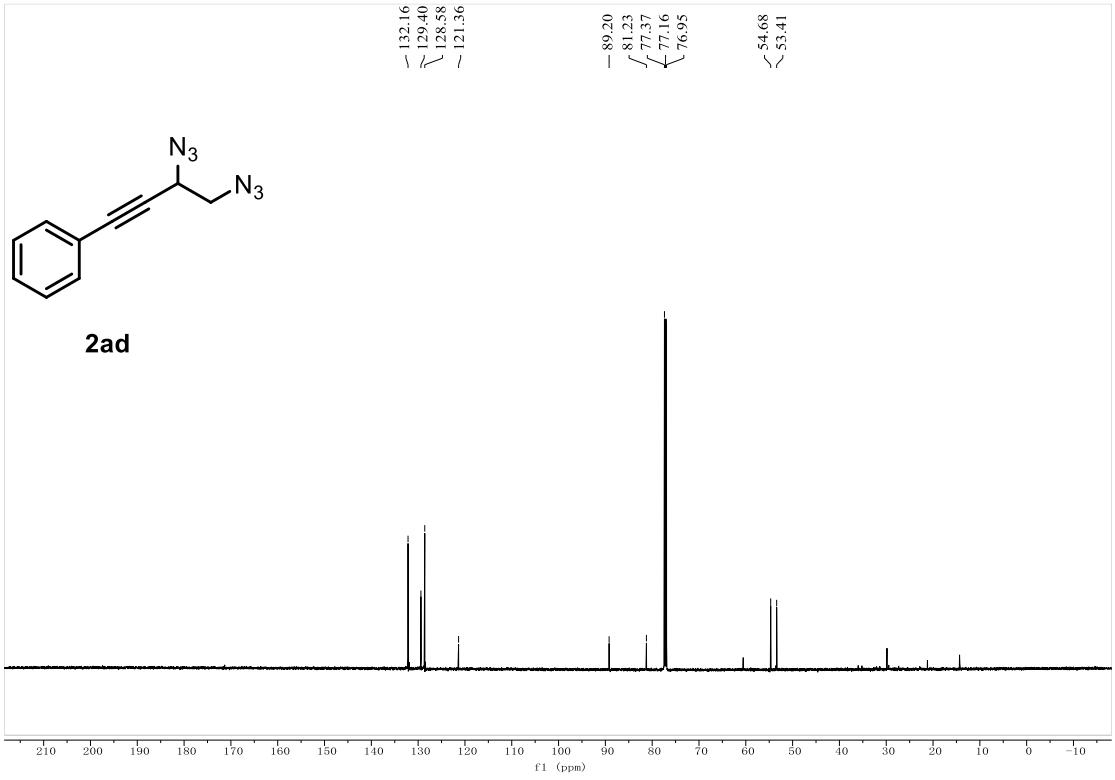
^{13}C NMR of **2ac** (151 MHz, $CDCl_3$)



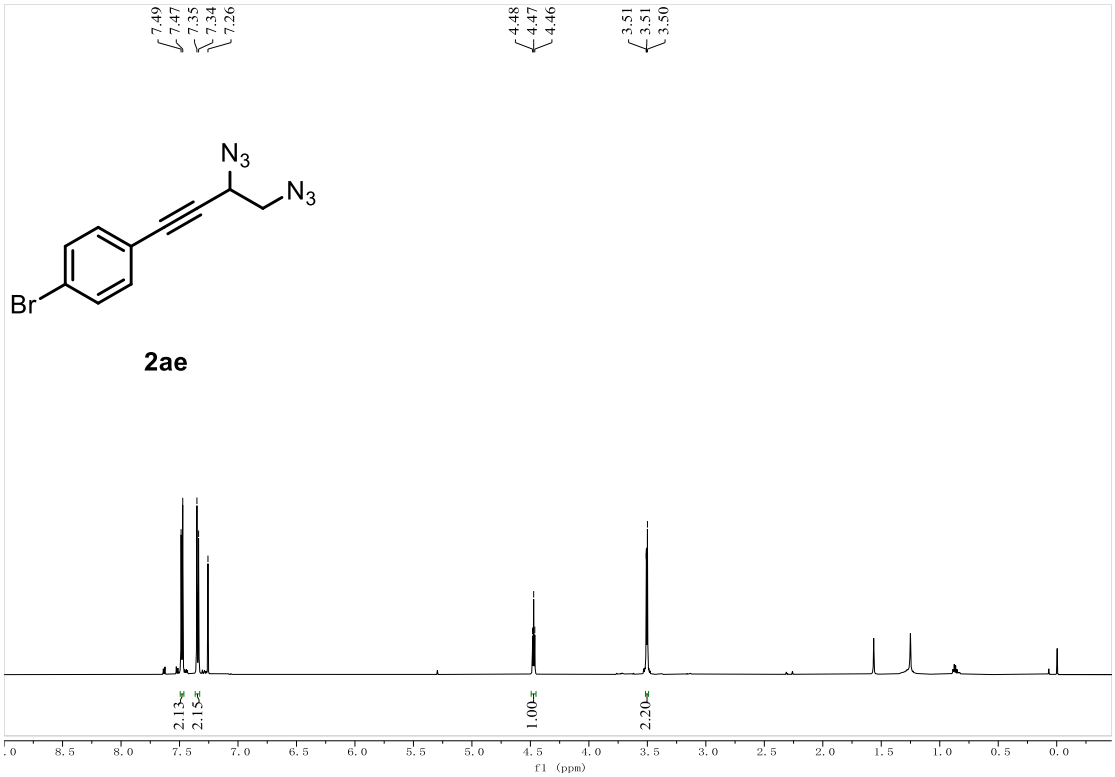
^{1}H NMR of **2ad** (600 MHz, $CDCl_3$)



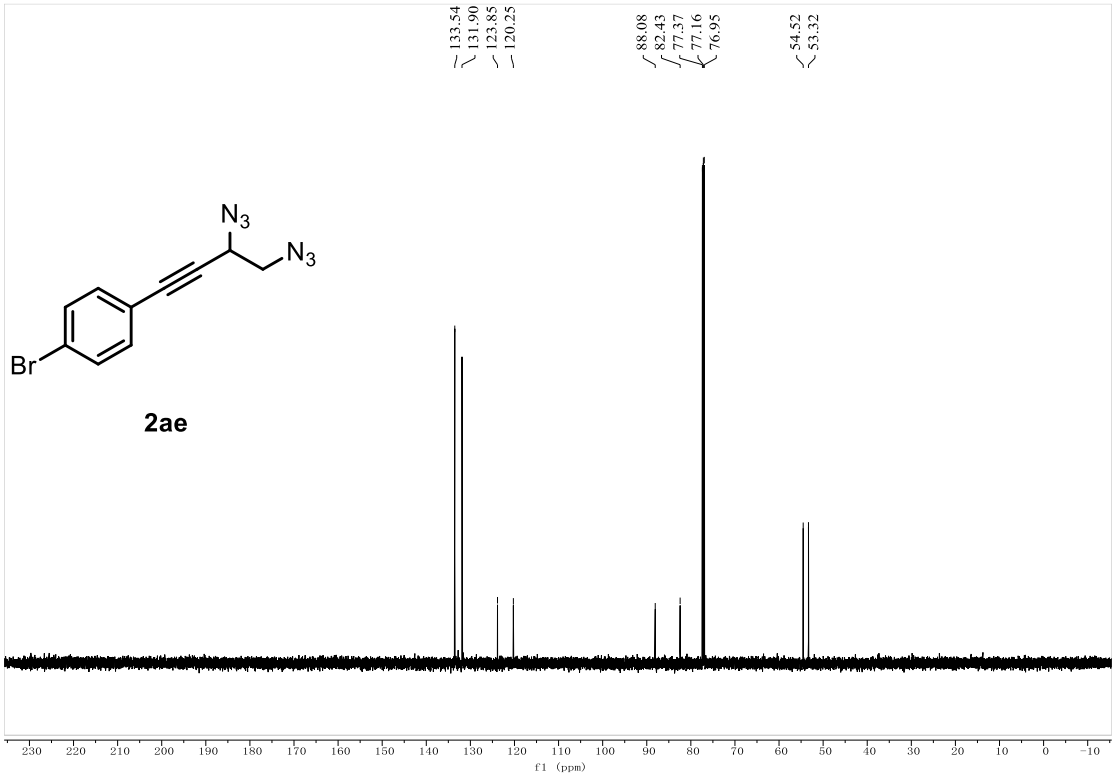
^{13}C NMR of **2ad** (151 MHz, $CDCl_3$)



^{1}H NMR of **2ae** (600 MHz, $CDCl_3$)

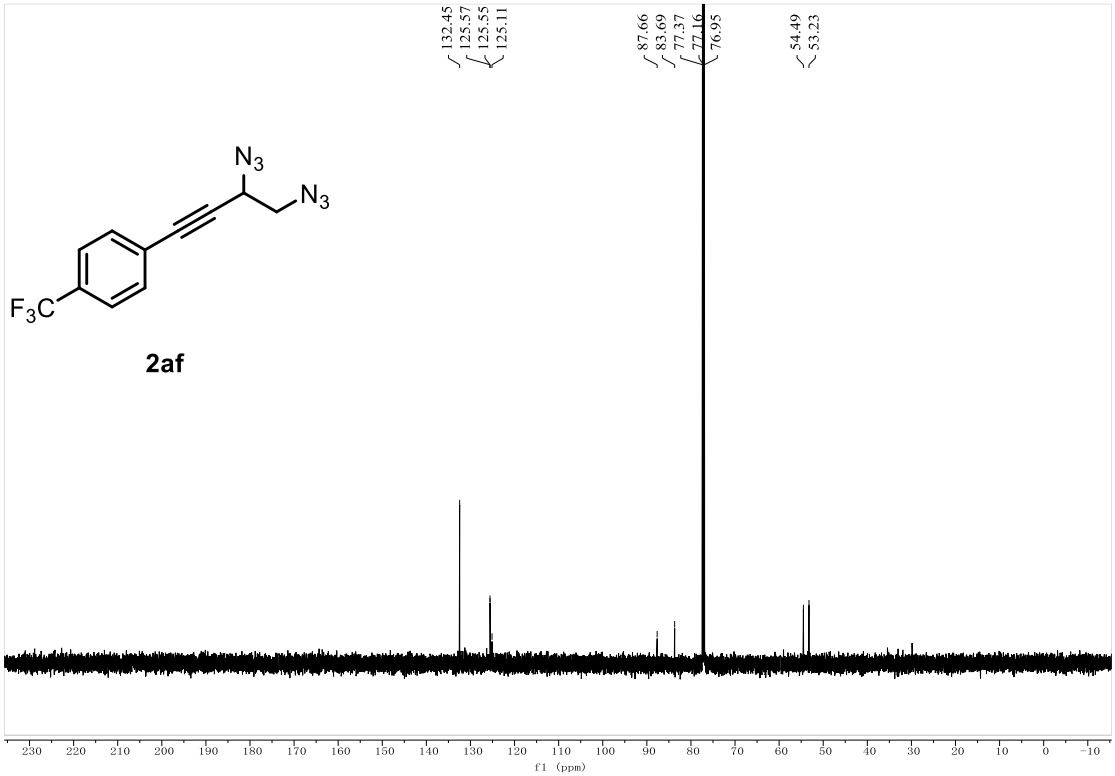


^{13}C NMR of **2ae** (151 MHz, $CDCl_3$)

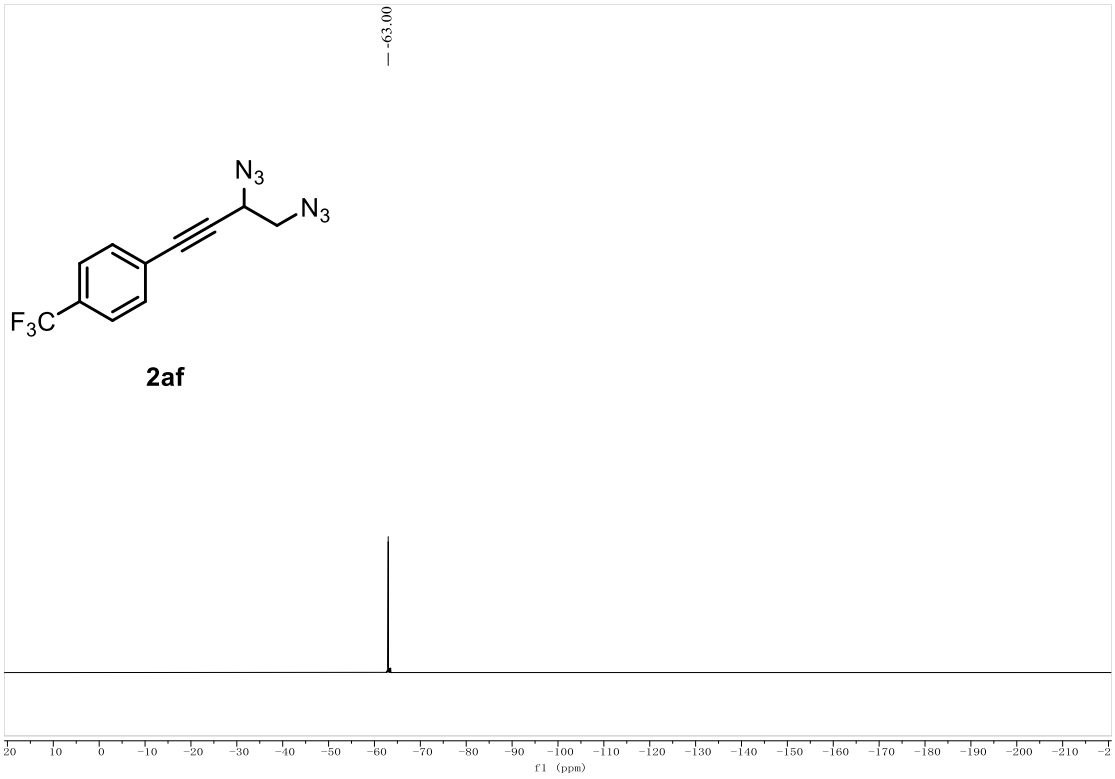


^{1}H NMR of **2af** (600 MHz, $CDCl_3$)

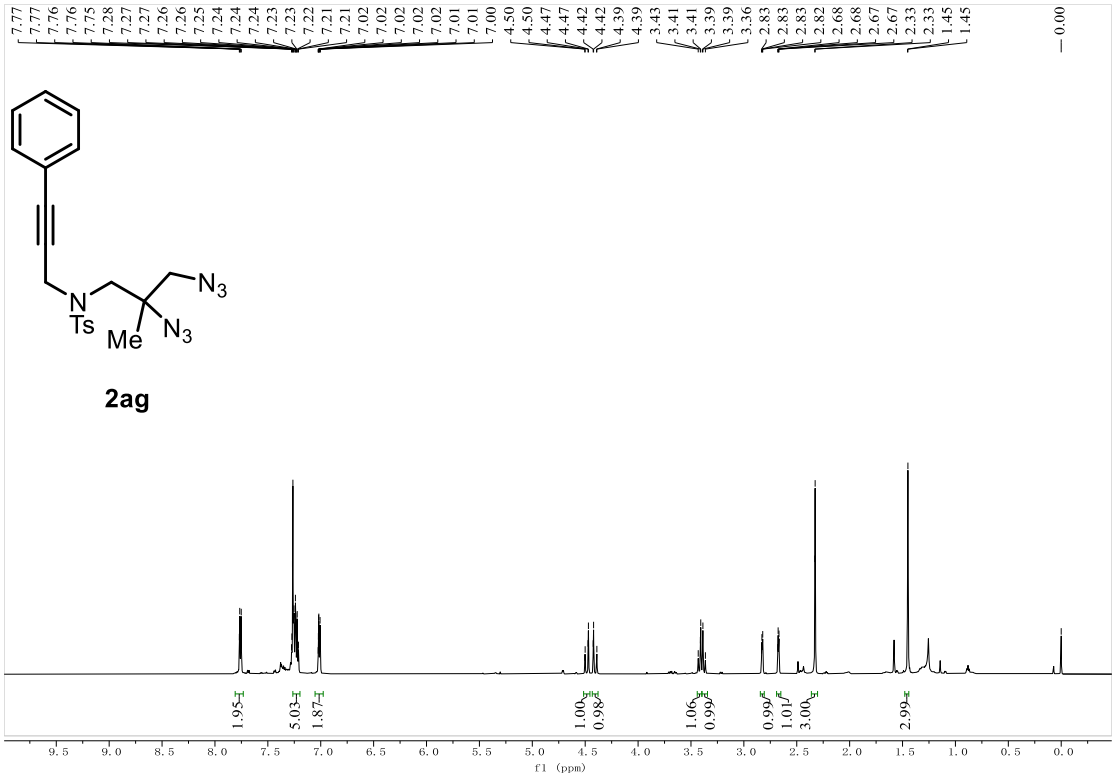
^{13}C NMR of **2af** (151 MHz, $CDCl_3$)



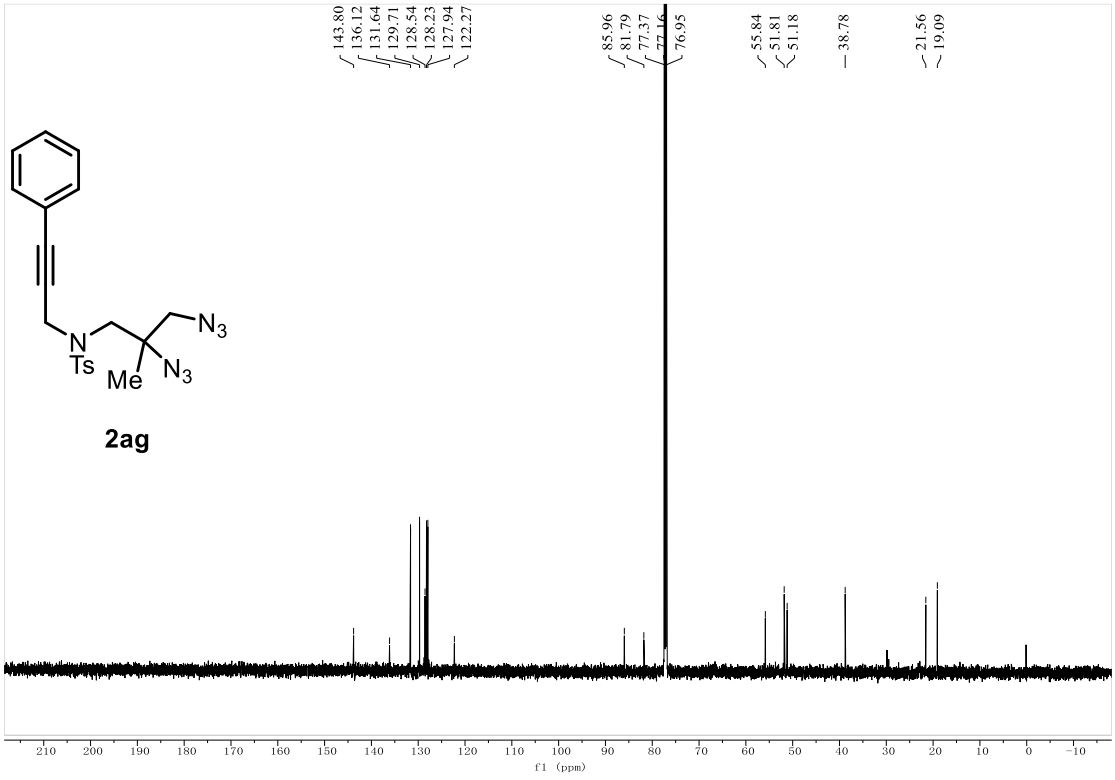
^{19}F NMR of **2af** (376 MHz, $CDCl_3$)



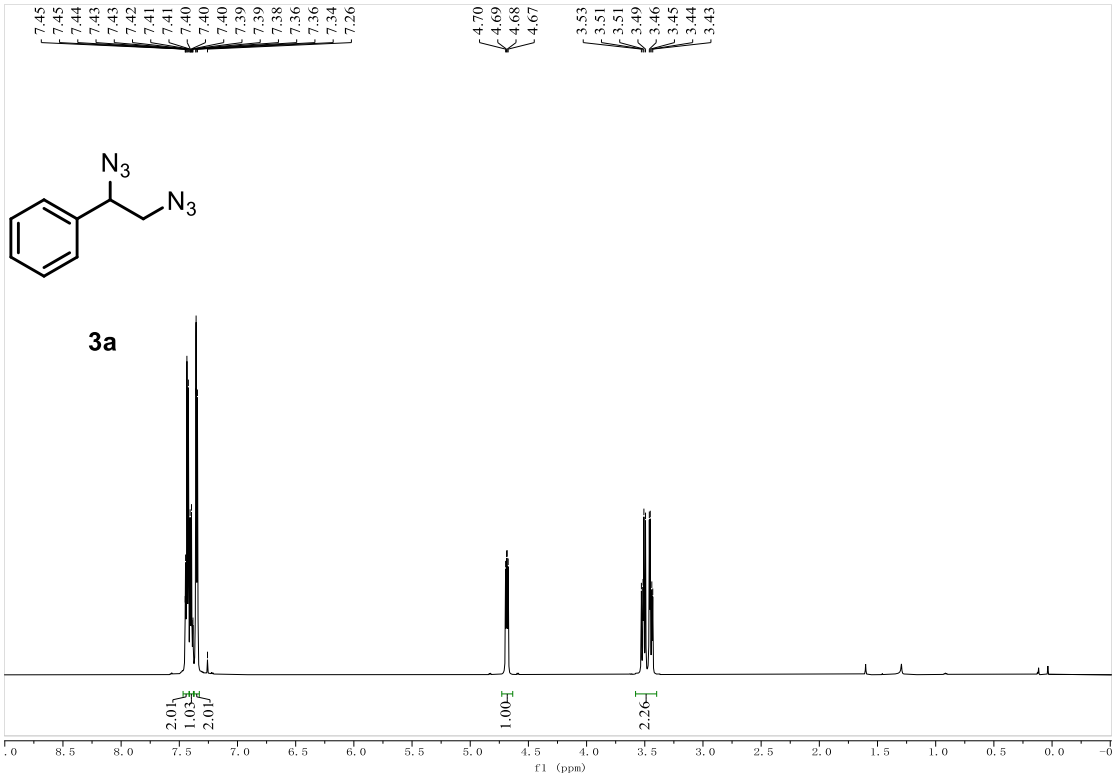
^{1}H NMR of **2ag** (600 MHz, $CDCl_3$)



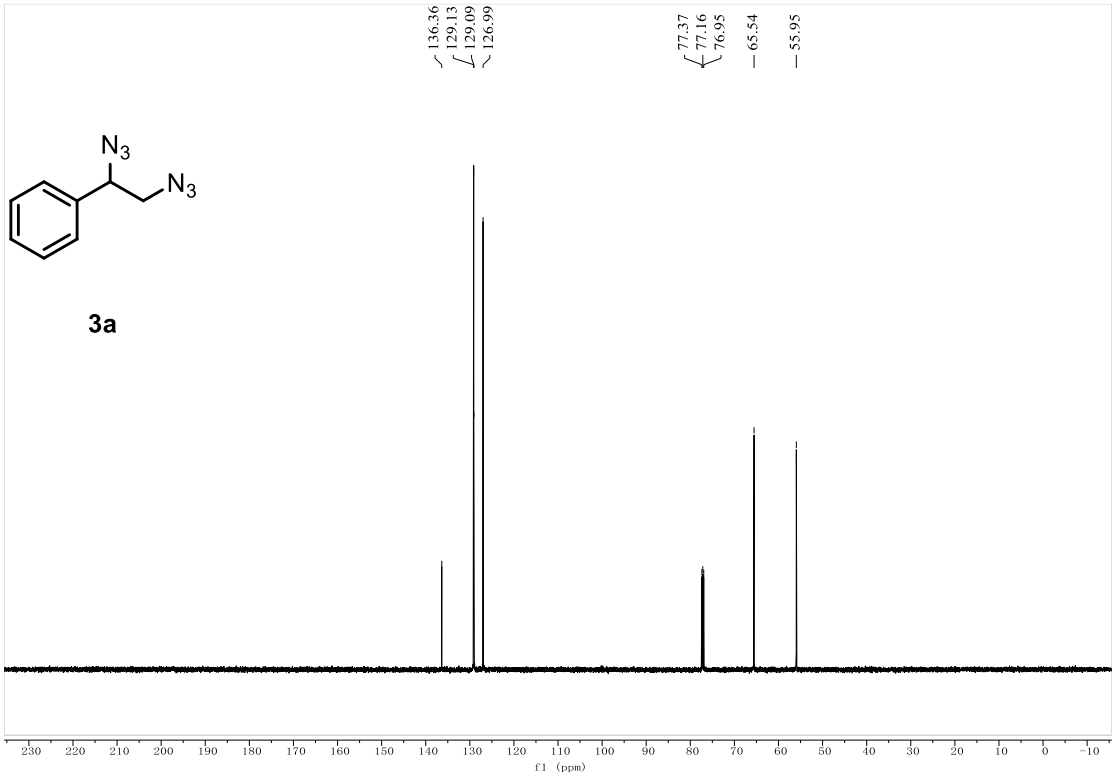
^{13}C NMR of **2ag** (151 MHz, $CDCl_3$)



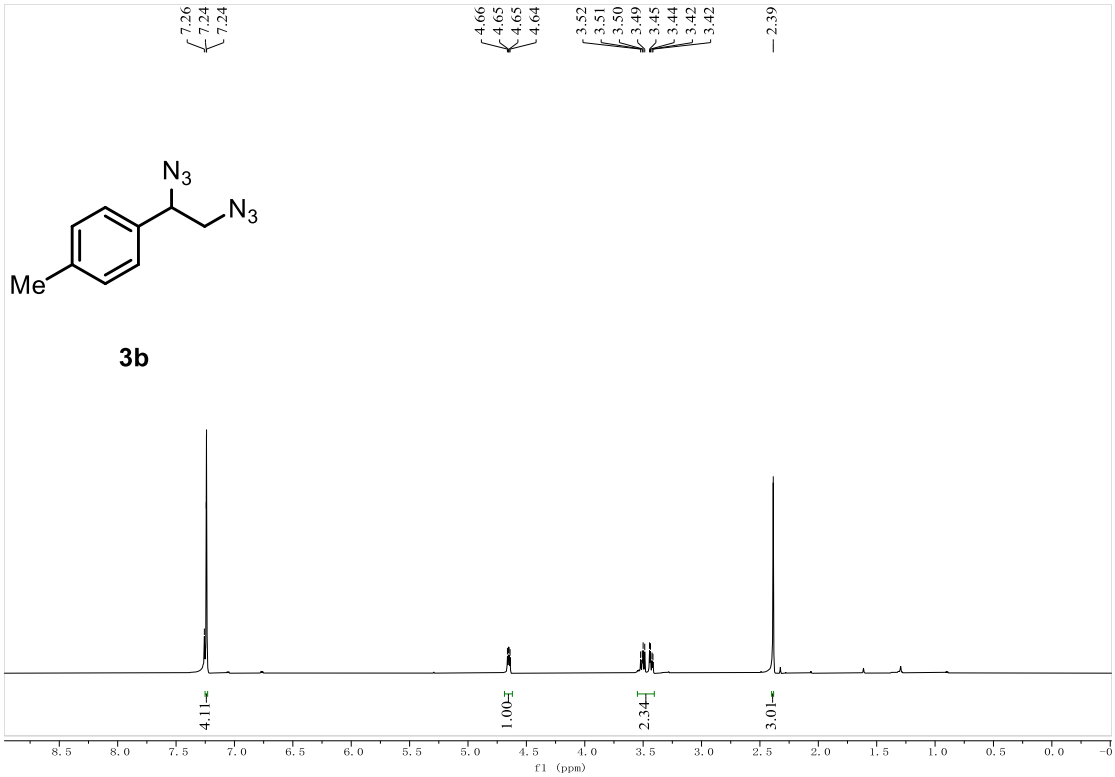
^{1}H NMR of **3a** (600 MHz, $CDCl_3$)



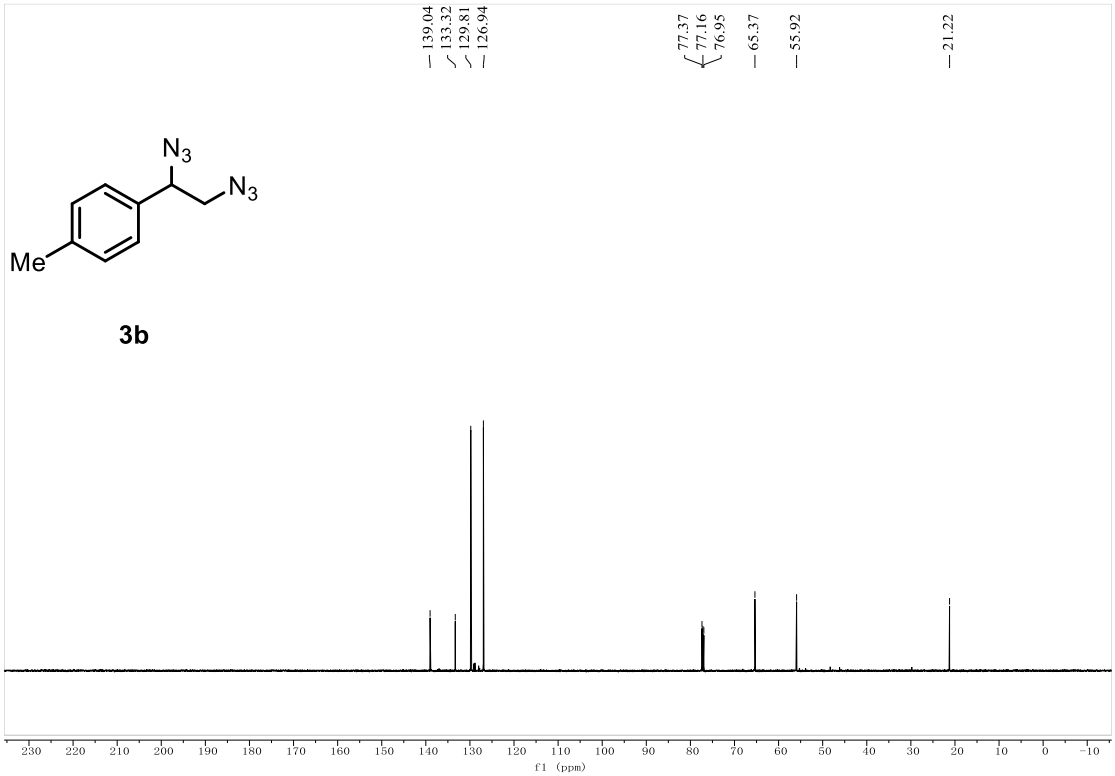
^{13}C NMR of **3a** (151 MHz, $CDCl_3$)



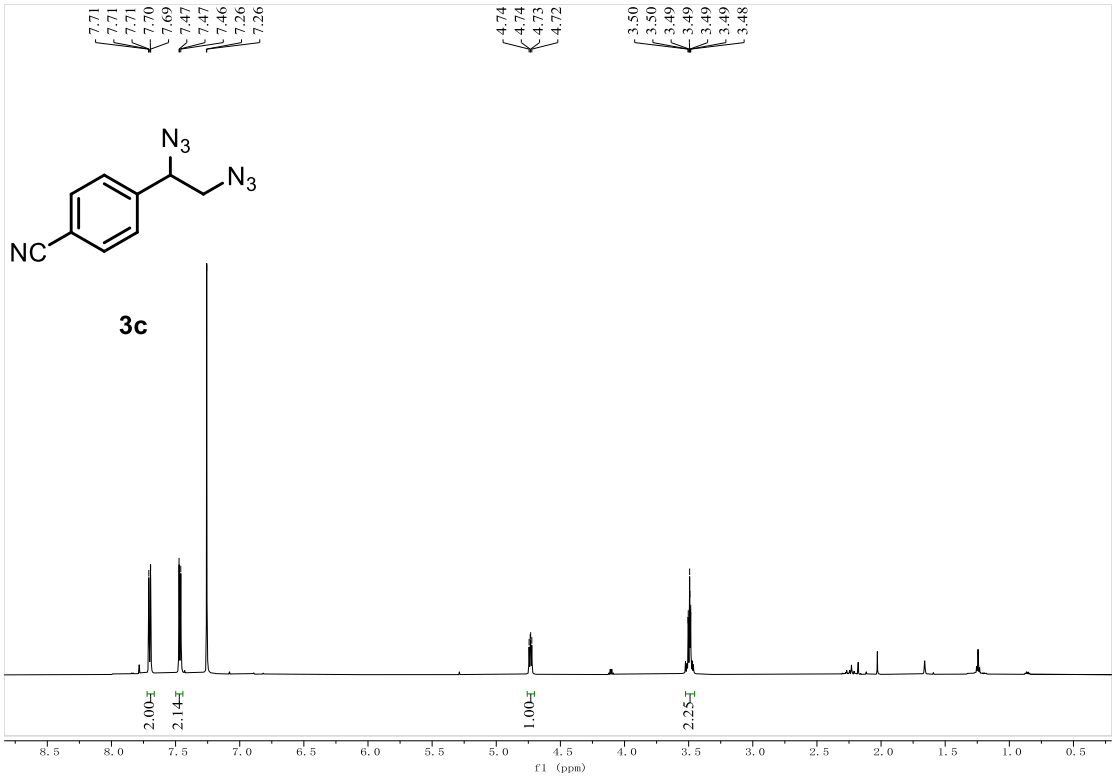
^{1}H NMR of **3b** (600 MHz, $CDCl_3$)



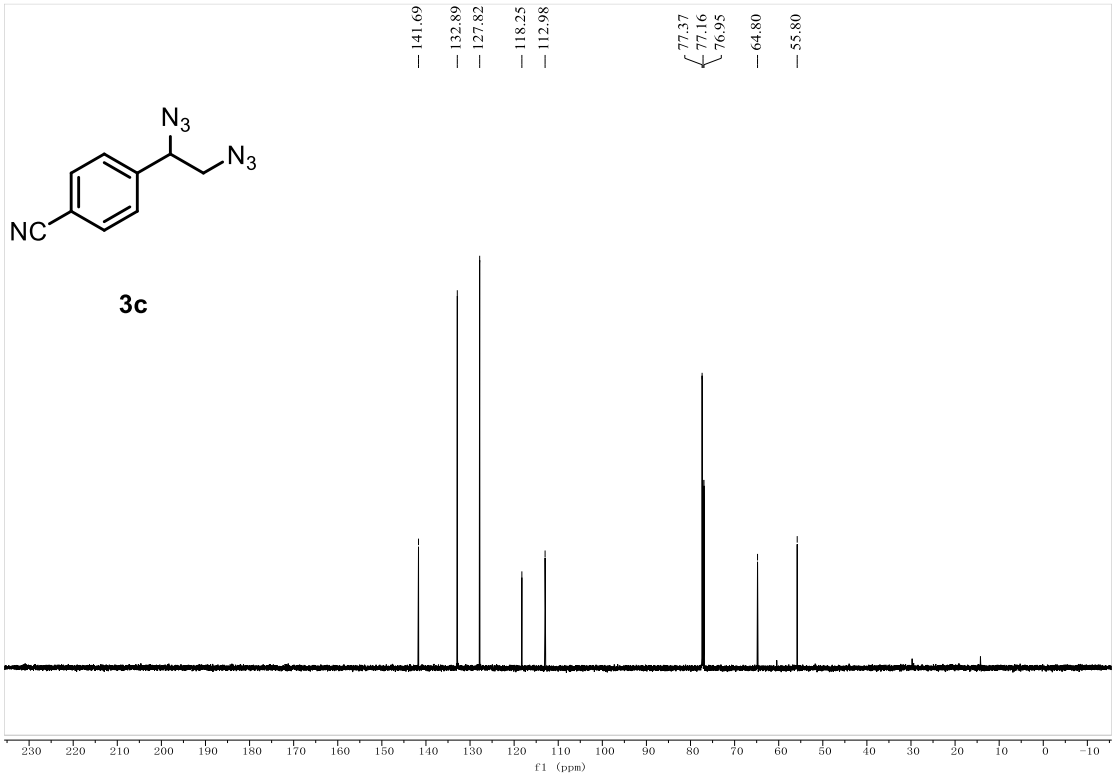
^{13}C NMR of **3b** (151 MHz, $CDCl_3$)



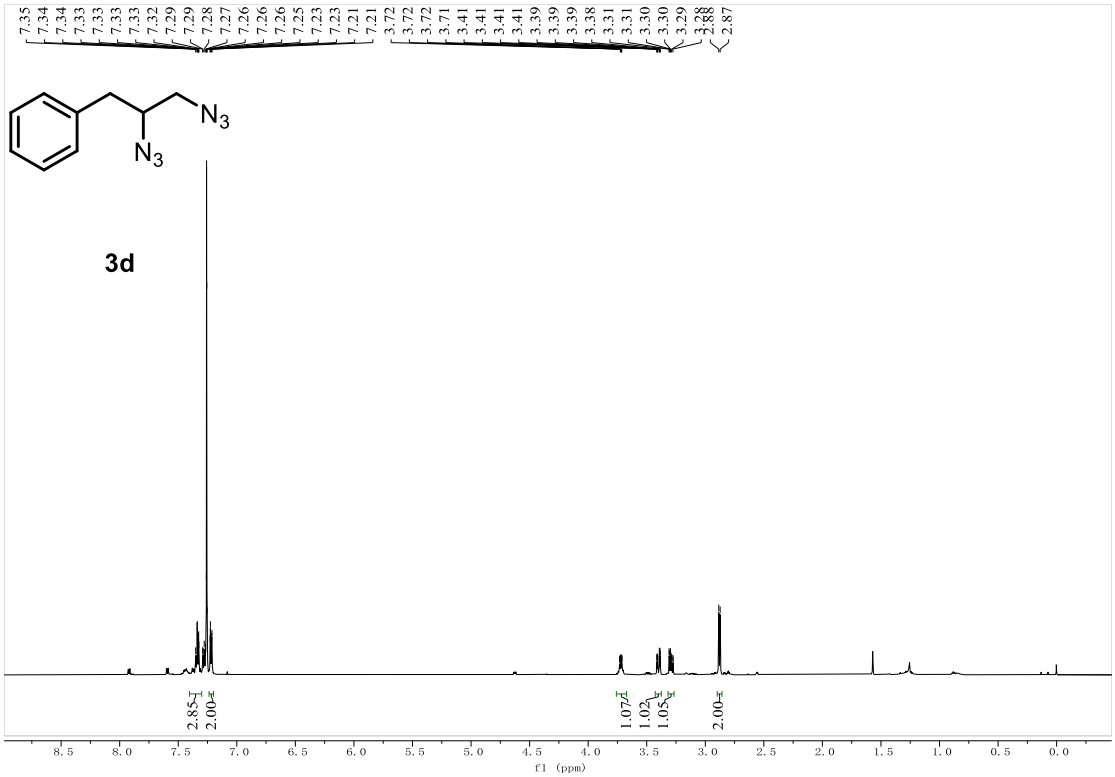
^{1}H NMR of **3c** (600 MHz, $CDCl_3$)



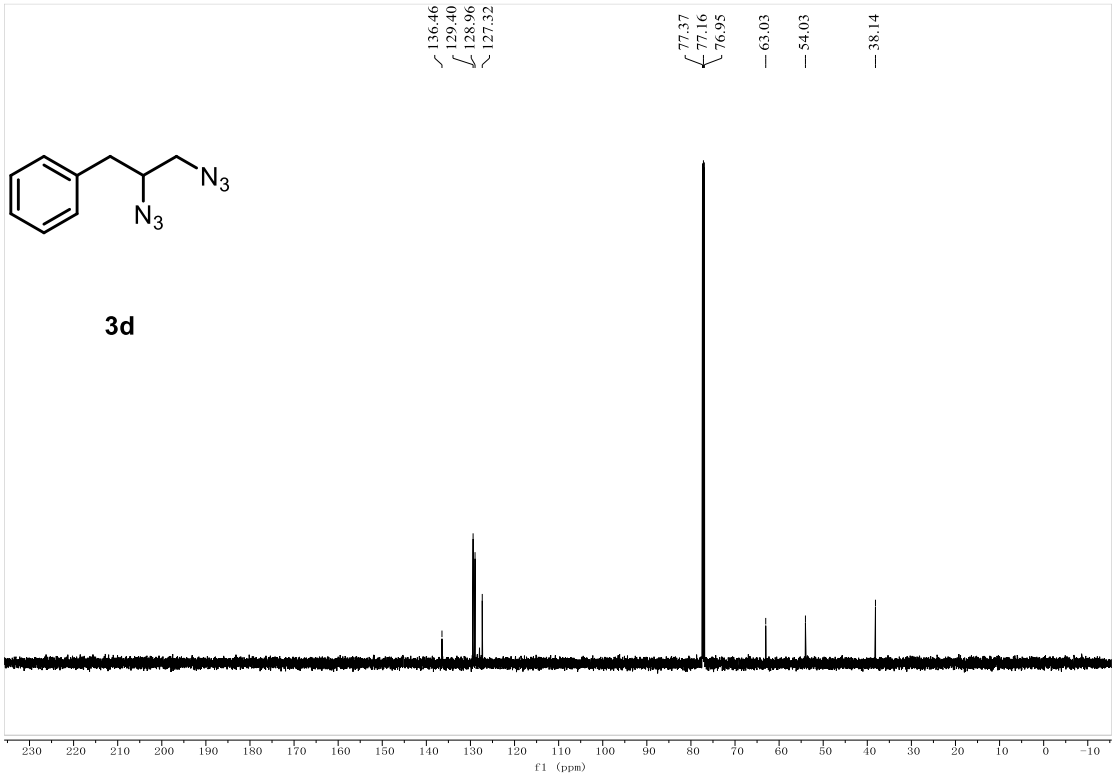
^{13}C NMR of **3c** (151 MHz, $CDCl_3$)



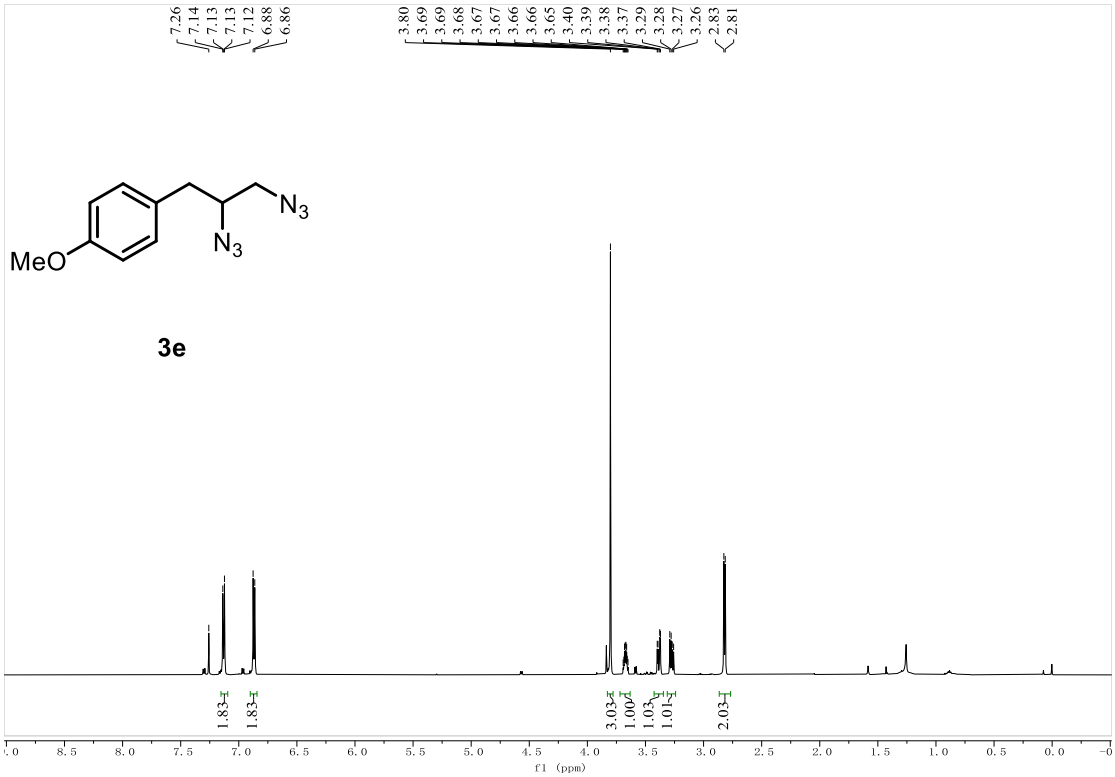
^{1}H NMR of **3d** (600 MHz, $CDCl_3$)



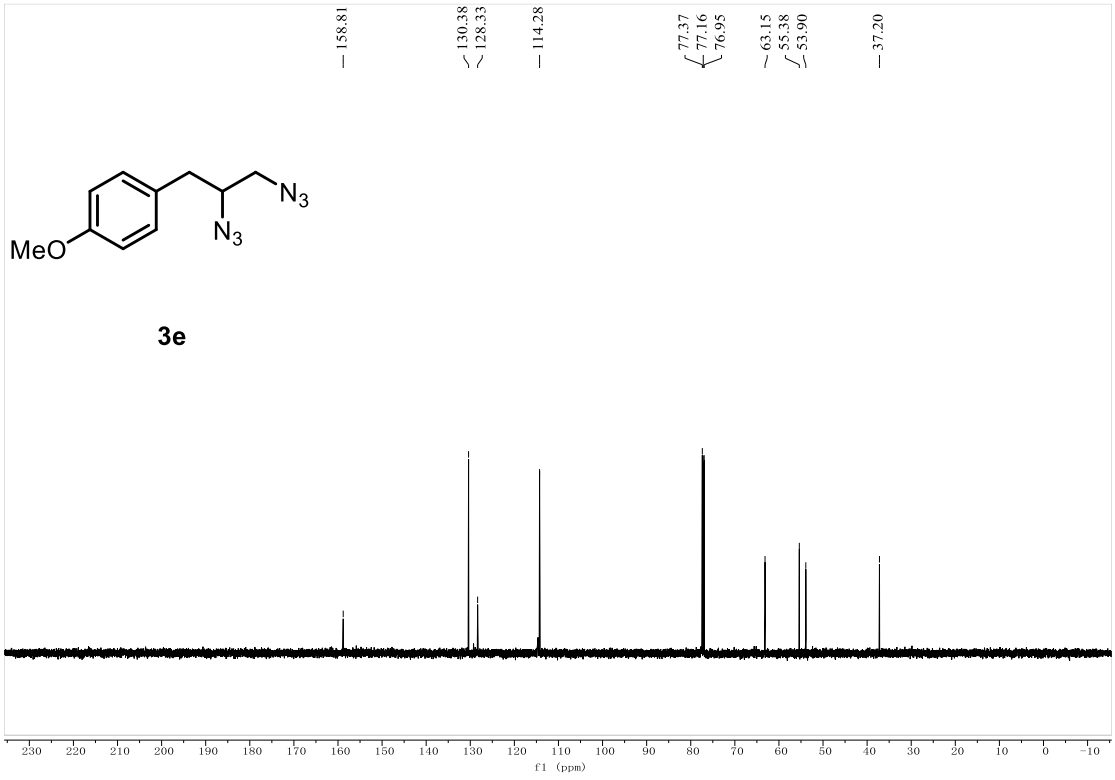
^{13}C NMR of **3d** (151 MHz, $CDCl_3$)



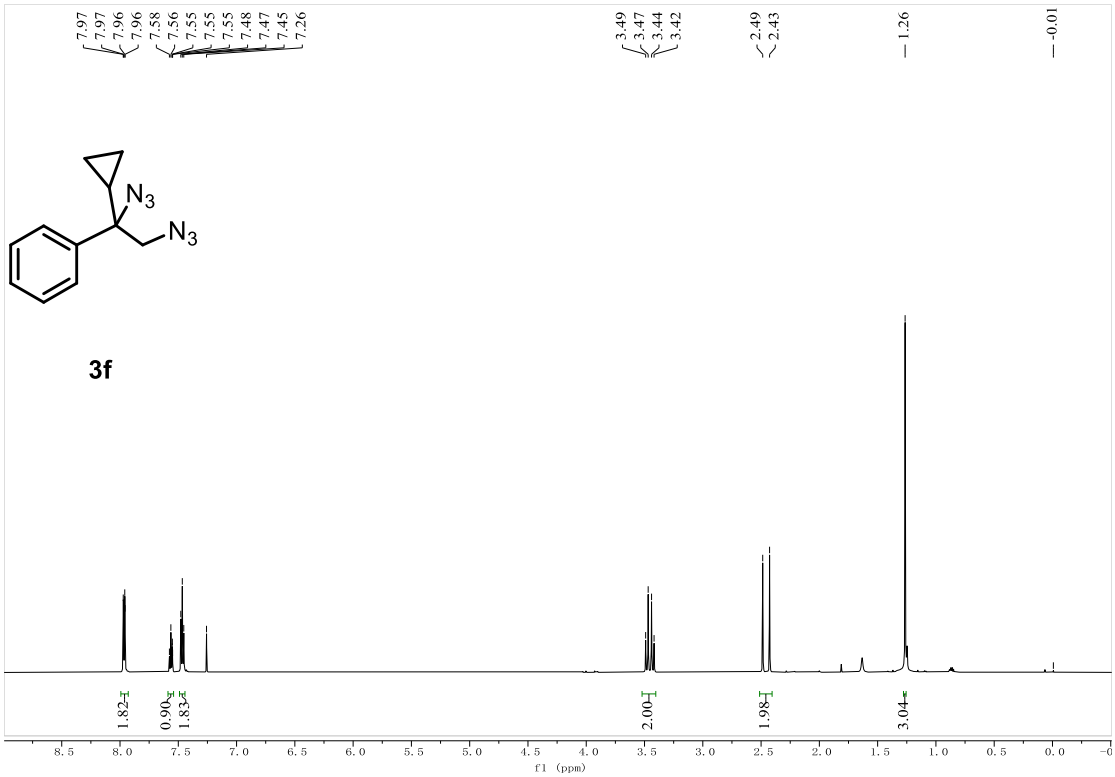
^{1}H NMR of **3e** (600 MHz, $CDCl_3$)



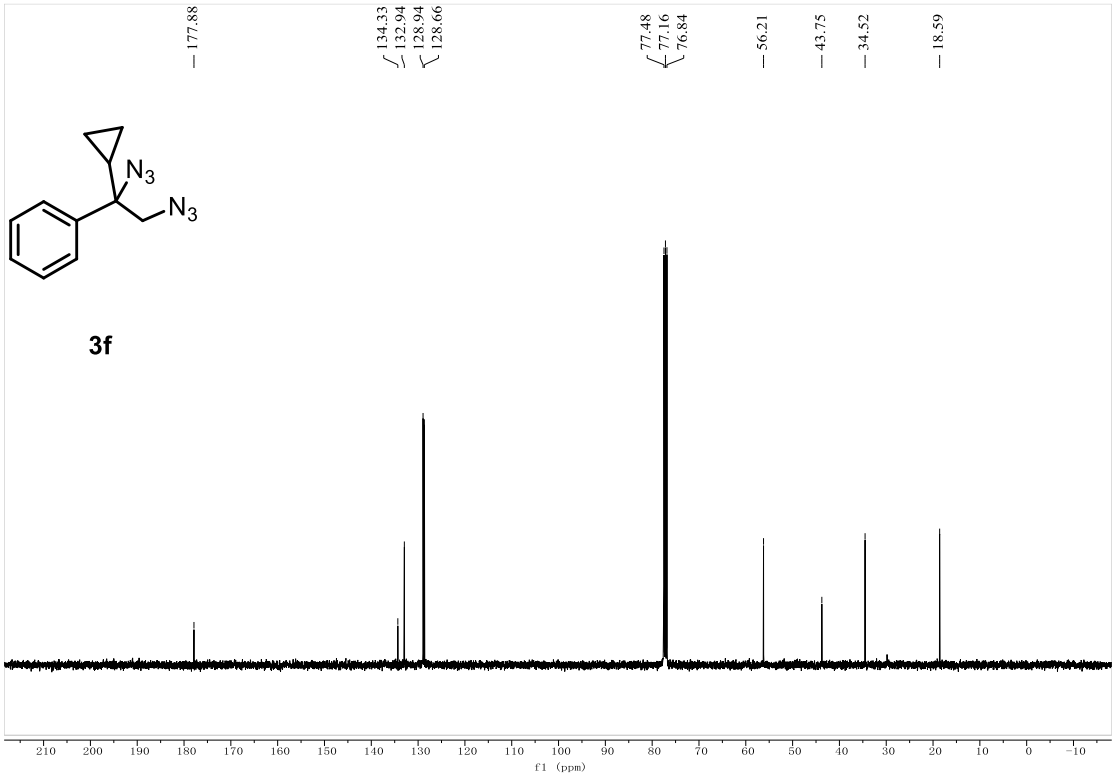
^{13}C NMR of **3e** (151 MHz, $CDCl_3$)



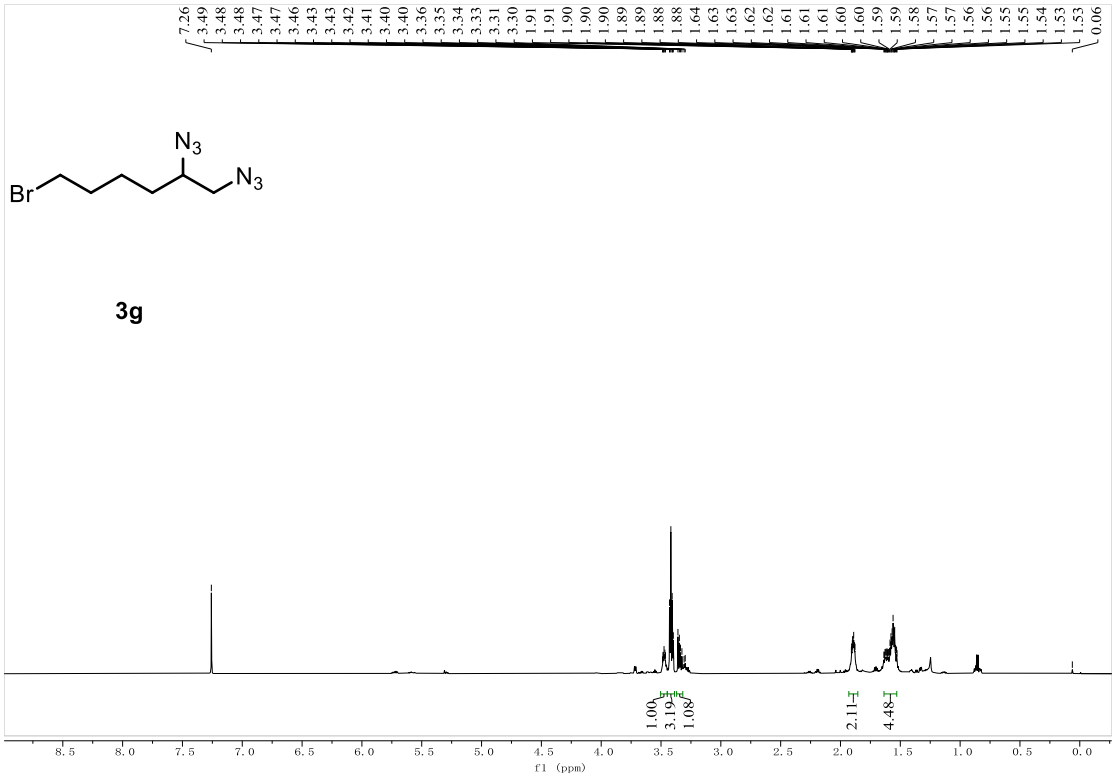
^{1}H NMR of **3f** (600 MHz, $CDCl_3$)



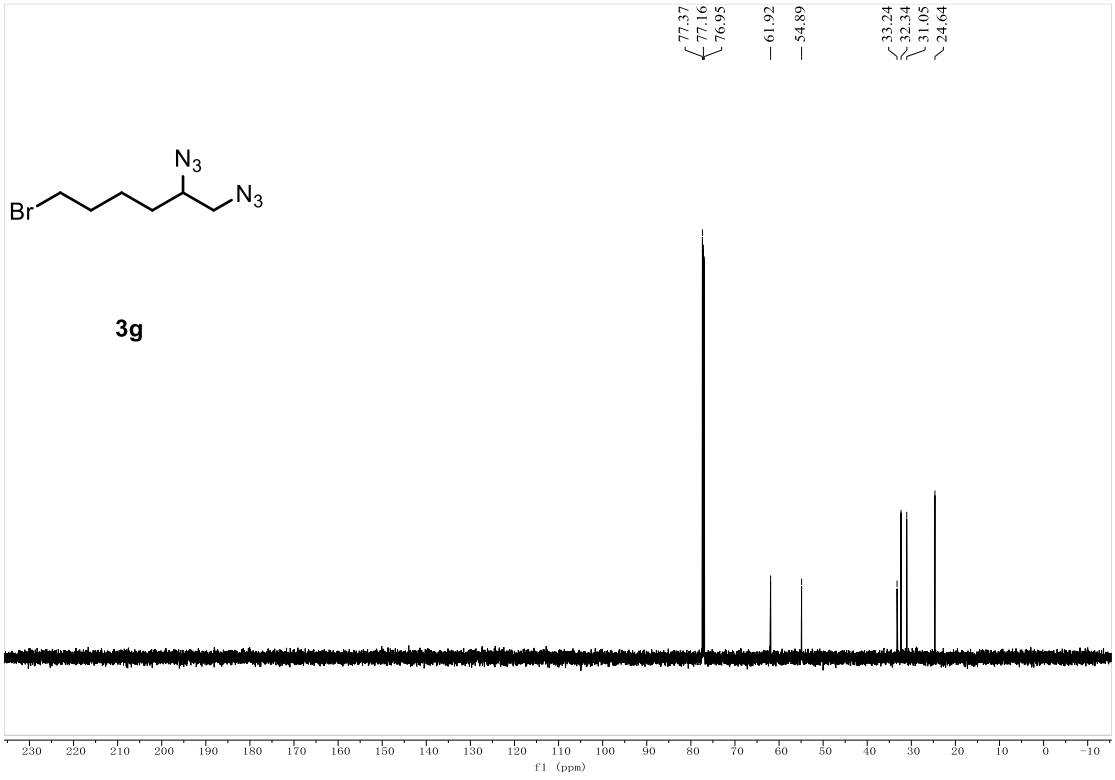
^{13}C NMR of **3f** (151 MHz, $CDCl_3$)



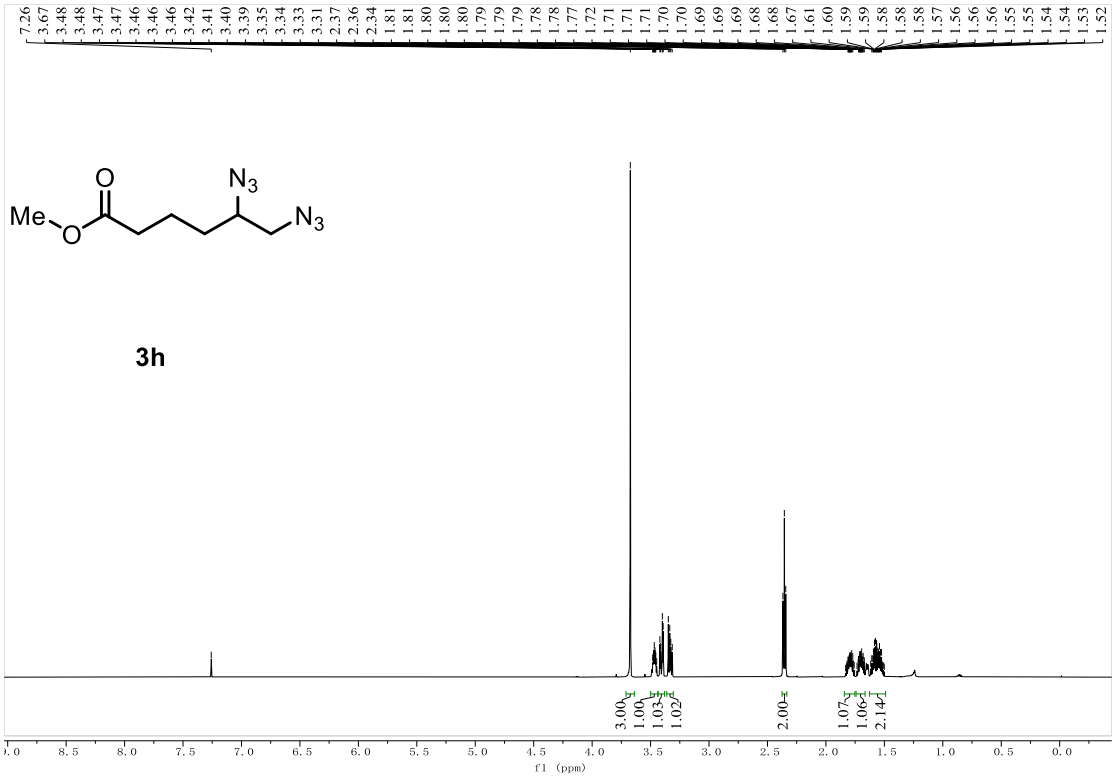
^{1}H NMR of **3g** (600 MHz, $CDCl_3$)



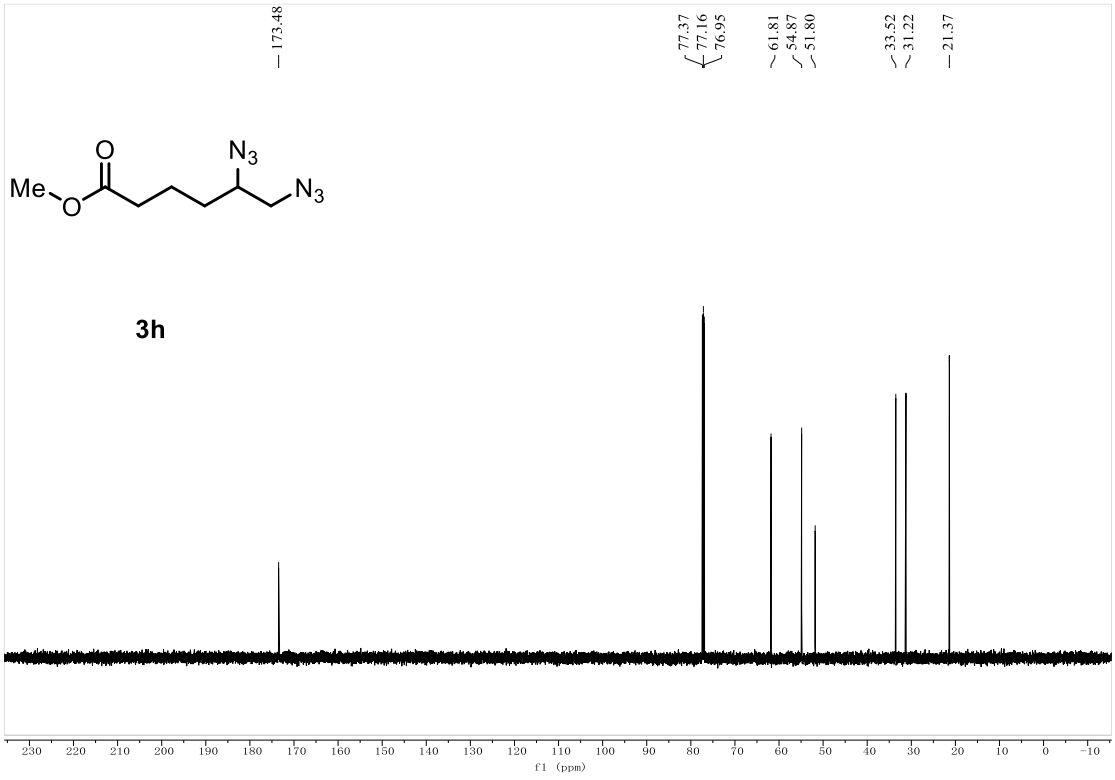
^{13}C NMR of **3g** (151 MHz, $CDCl_3$)



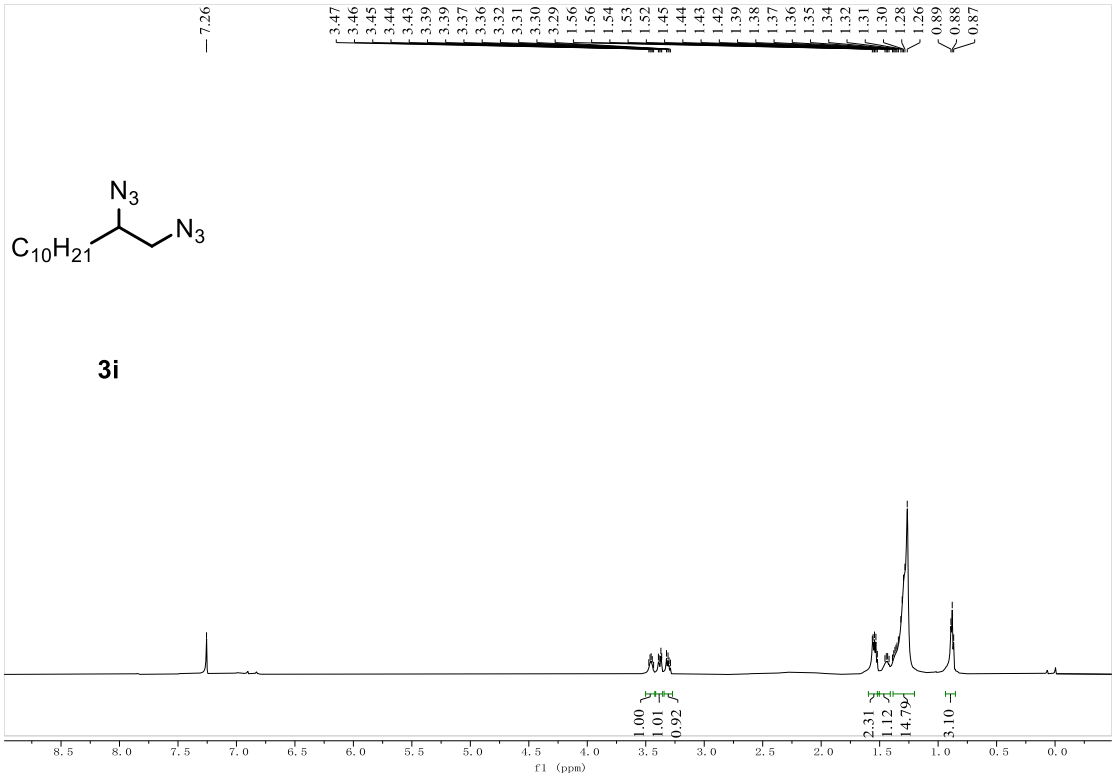
^{1}H NMR of **3h** (600 MHz, $CDCl_3$)



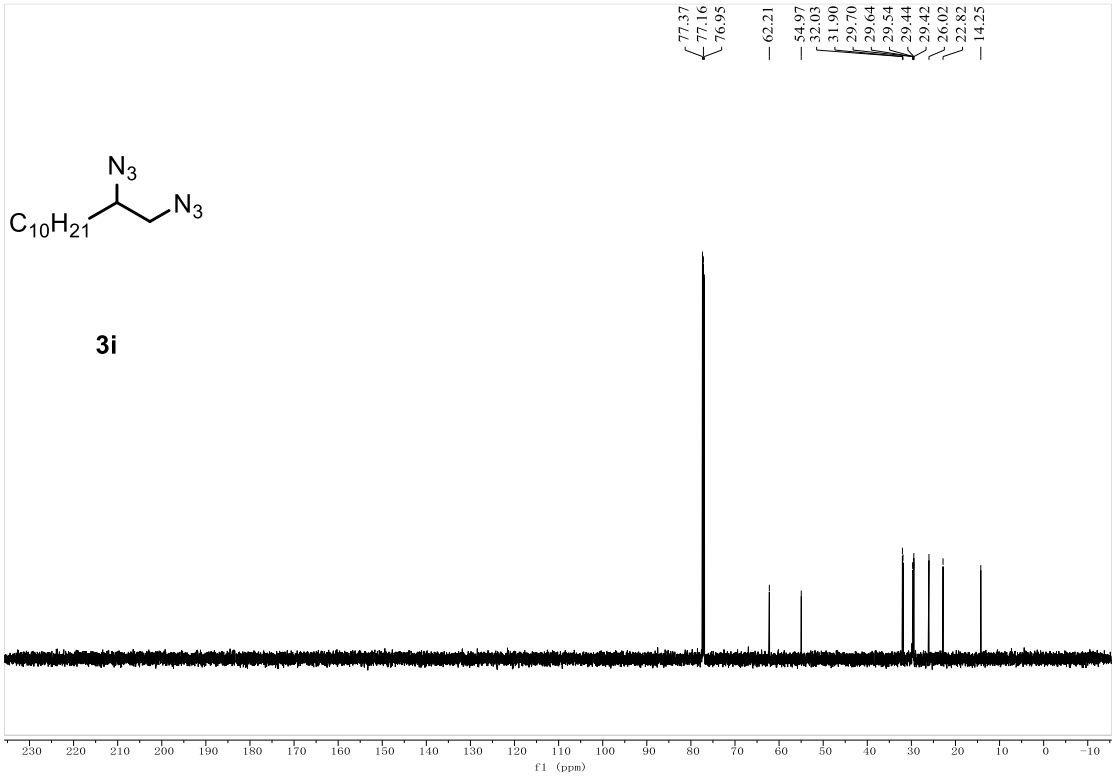
^{13}C NMR of **3h** (151 MHz, $CDCl_3$)



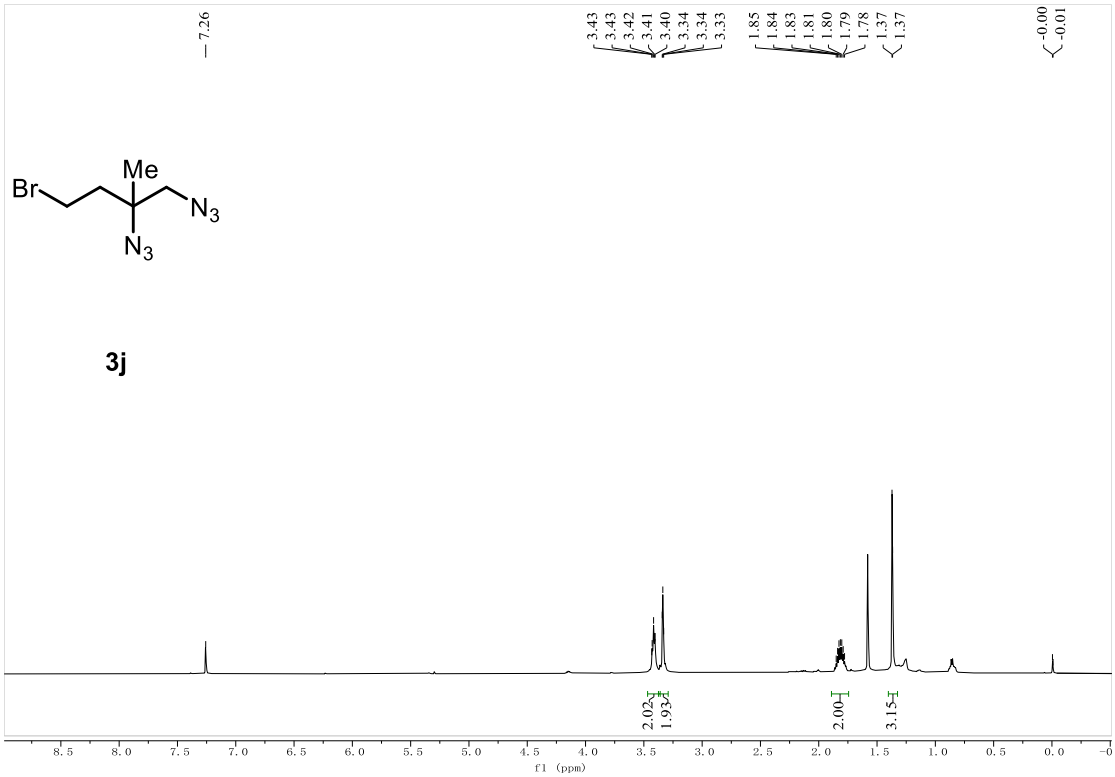
^{1}H NMR of **3i** (600 MHz, $CDCl_3$)



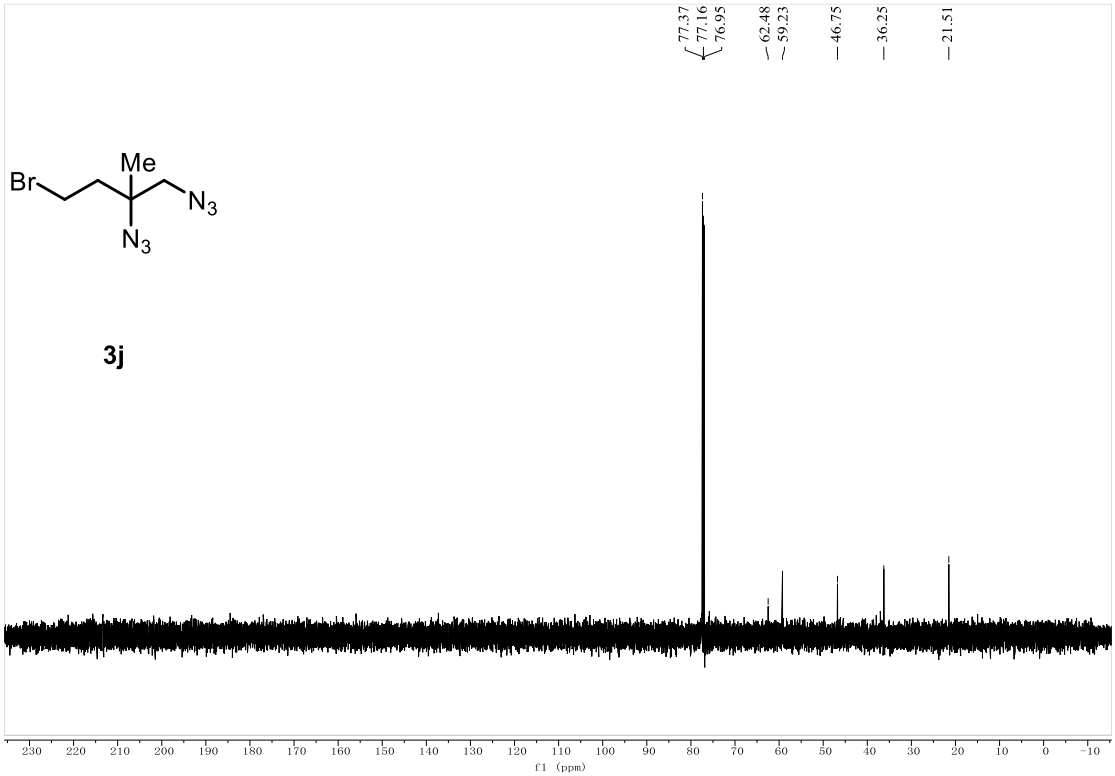
^{13}C NMR of **3i** (151 MHz, $CDCl_3$)



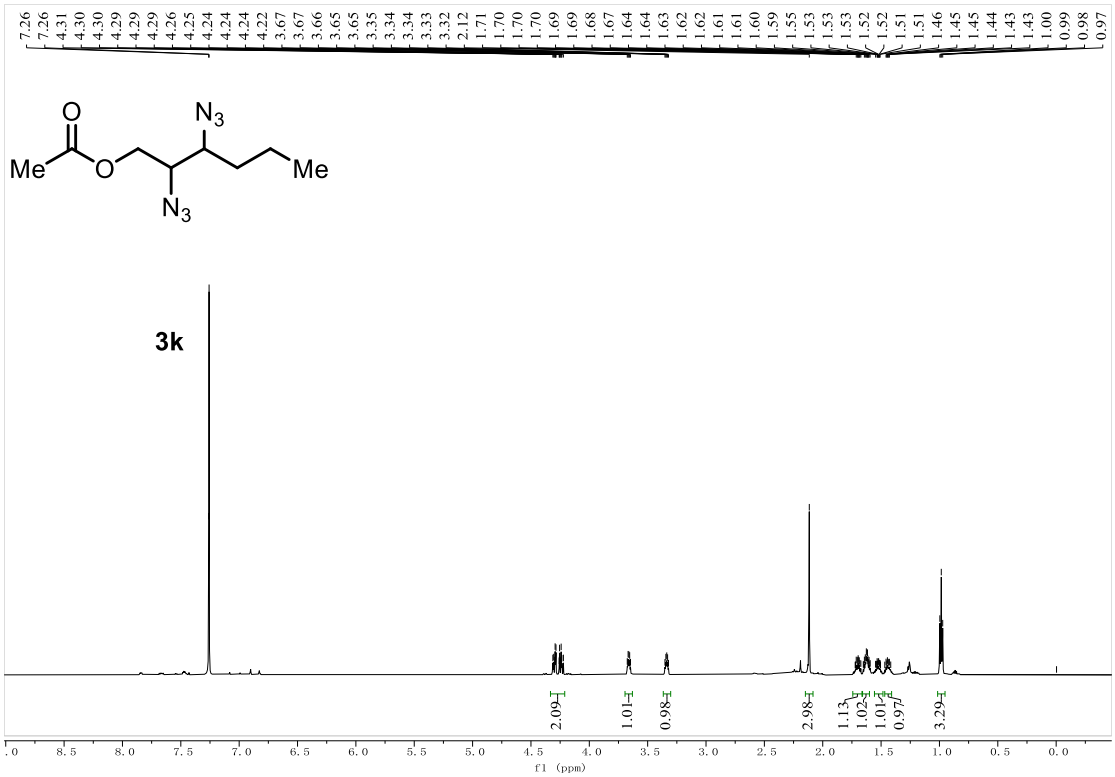
^{1}H NMR of **3j** (600 MHz, $CDCl_3$)



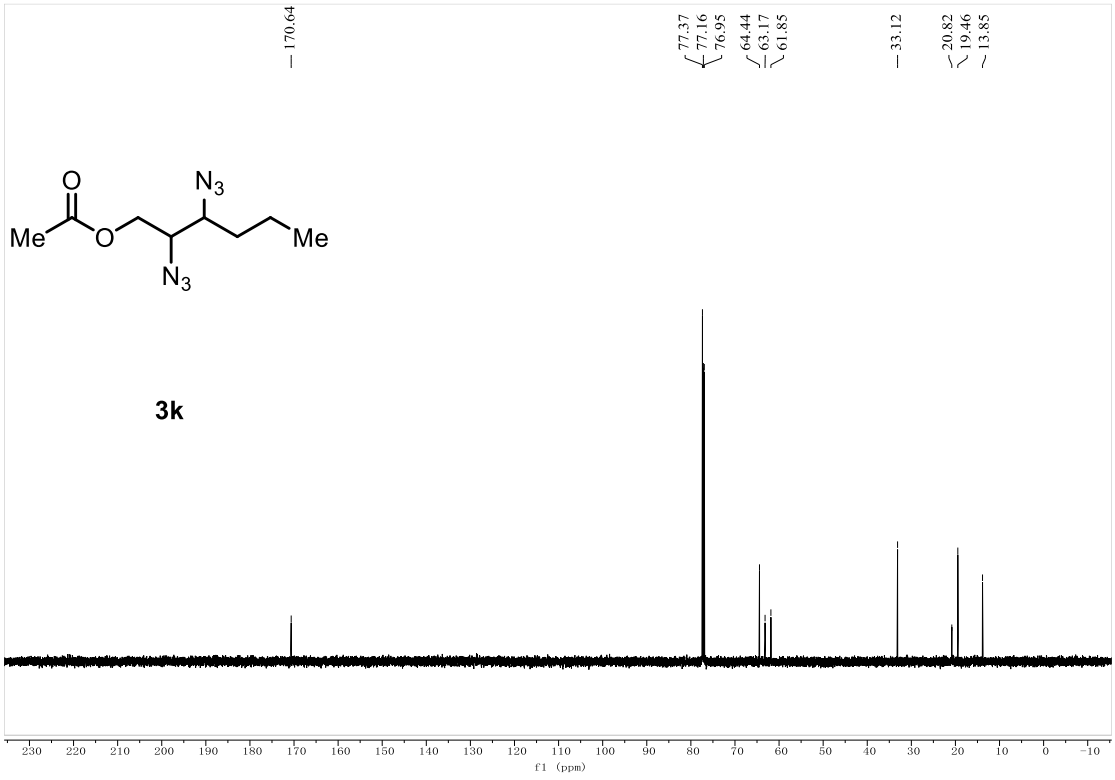
^{13}C NMR of **3j** (151 MHz, $CDCl_3$)



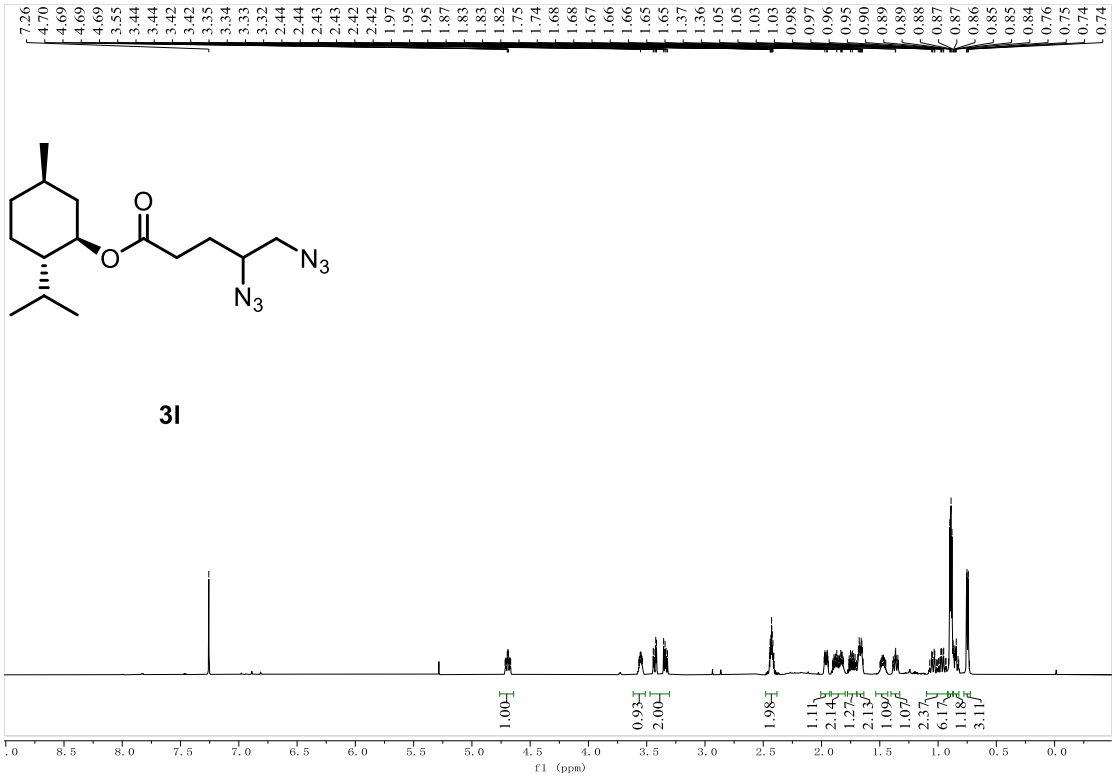
^{1}H NMR of **3k** (600 MHz, $CDCl_3$)



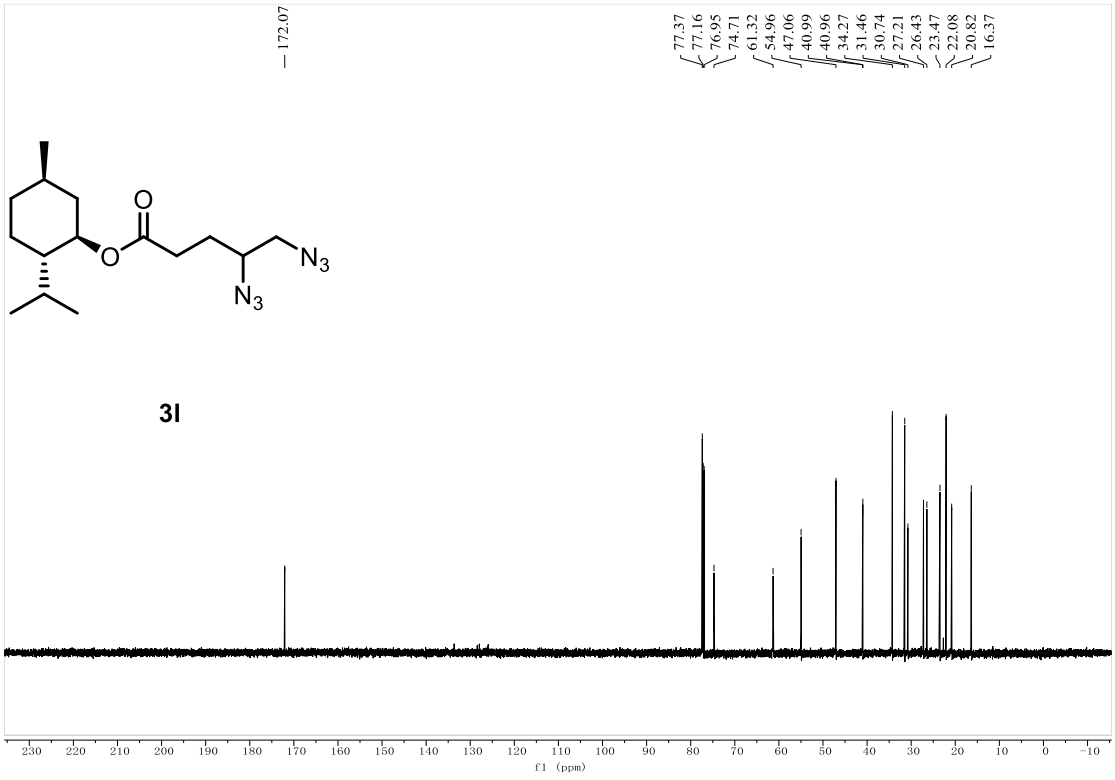
^{13}C NMR of **3k** (101 MHz, $CDCl_3$)



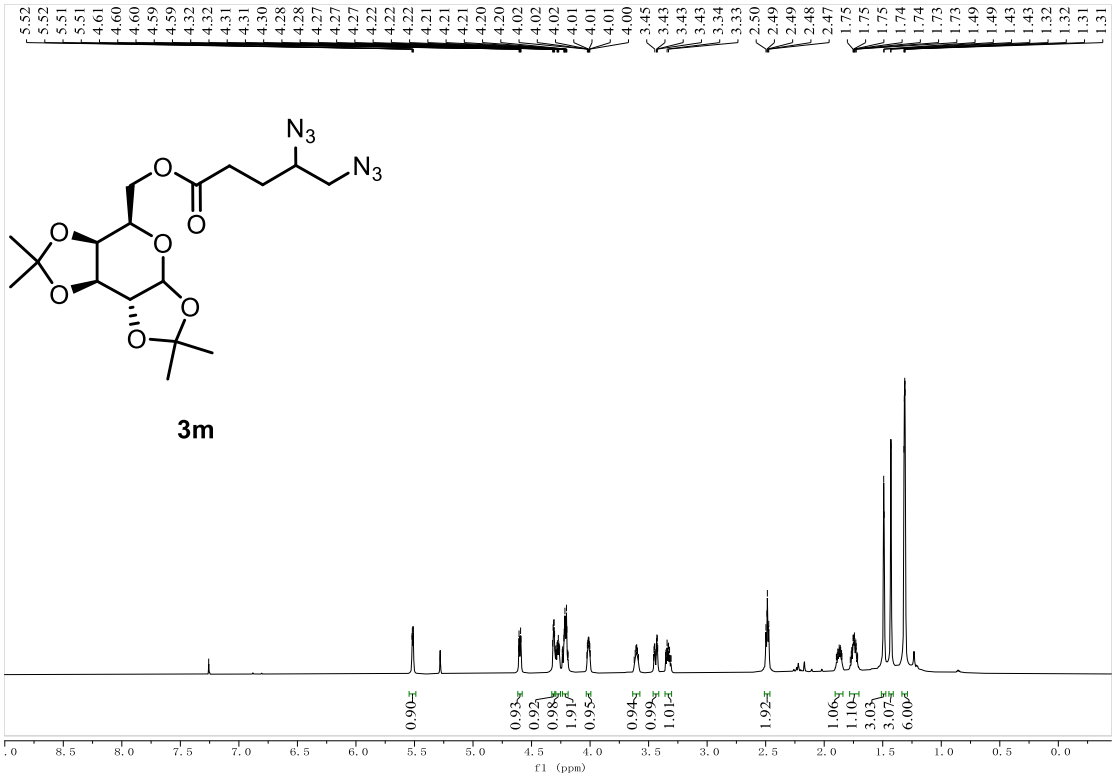
^{1}H NMR of **3l** (600 MHz, $CDCl_3$)



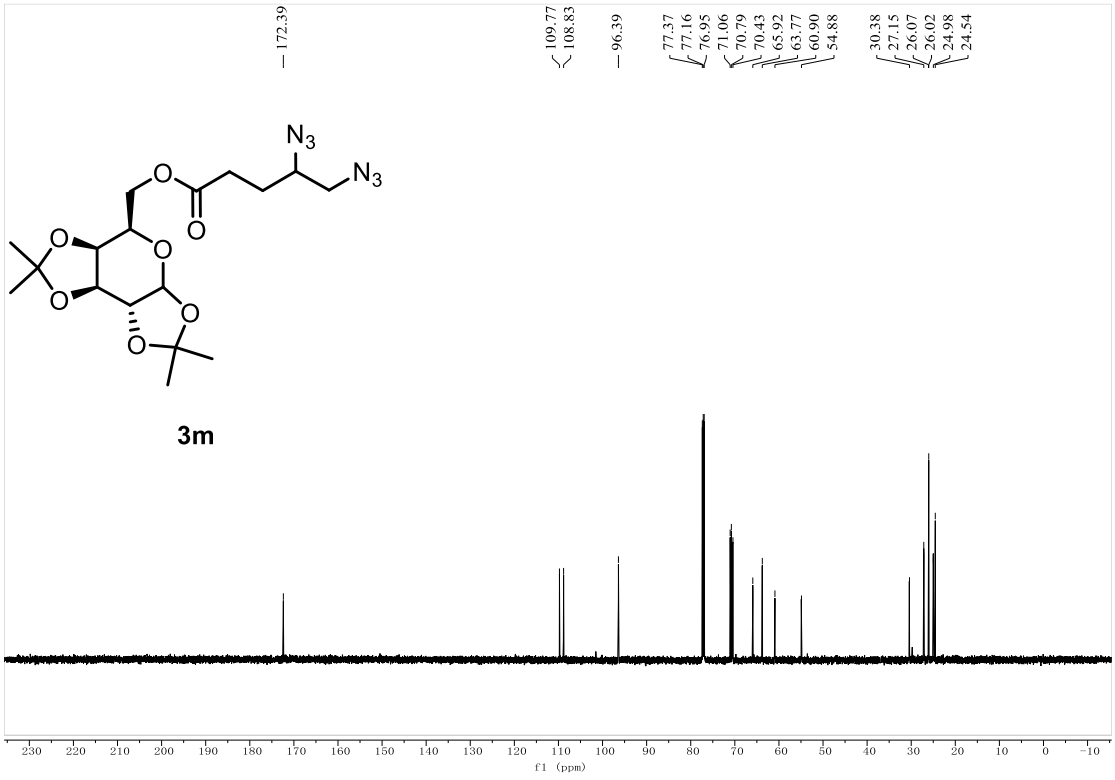
^{13}C NMR of **3l** (151 MHz, $CDCl_3$)



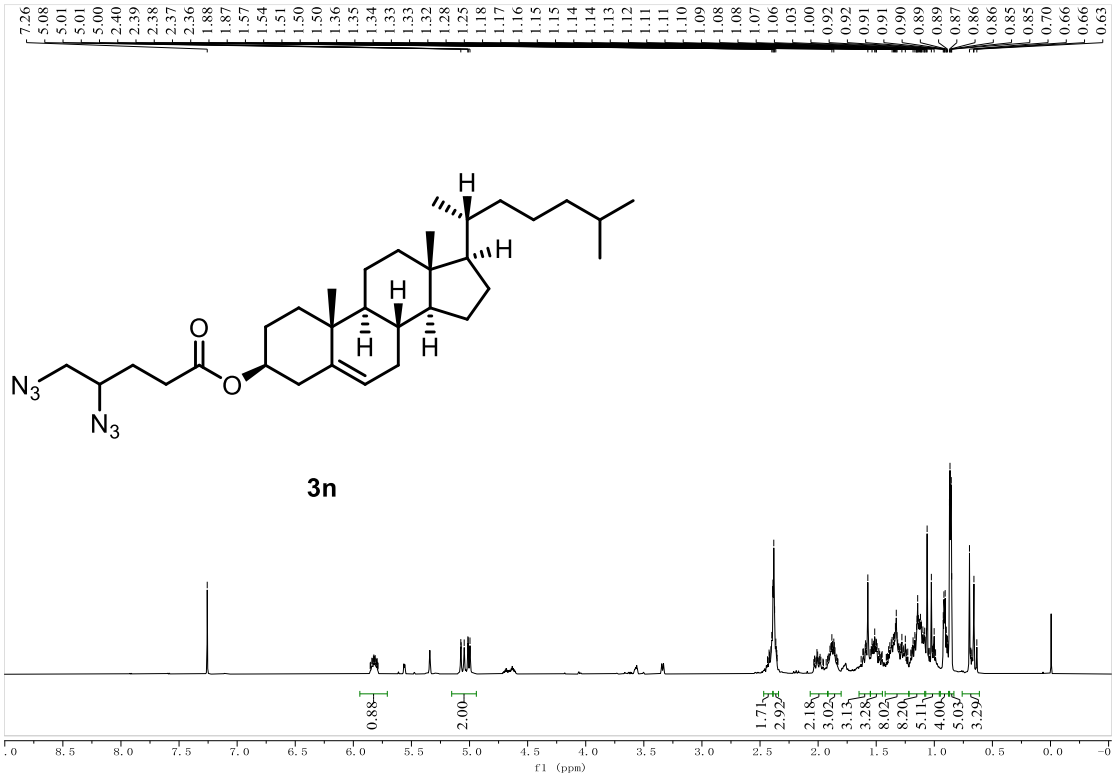
^{1}H NMR of **2m** (600 MHz, $CDCl_3$)



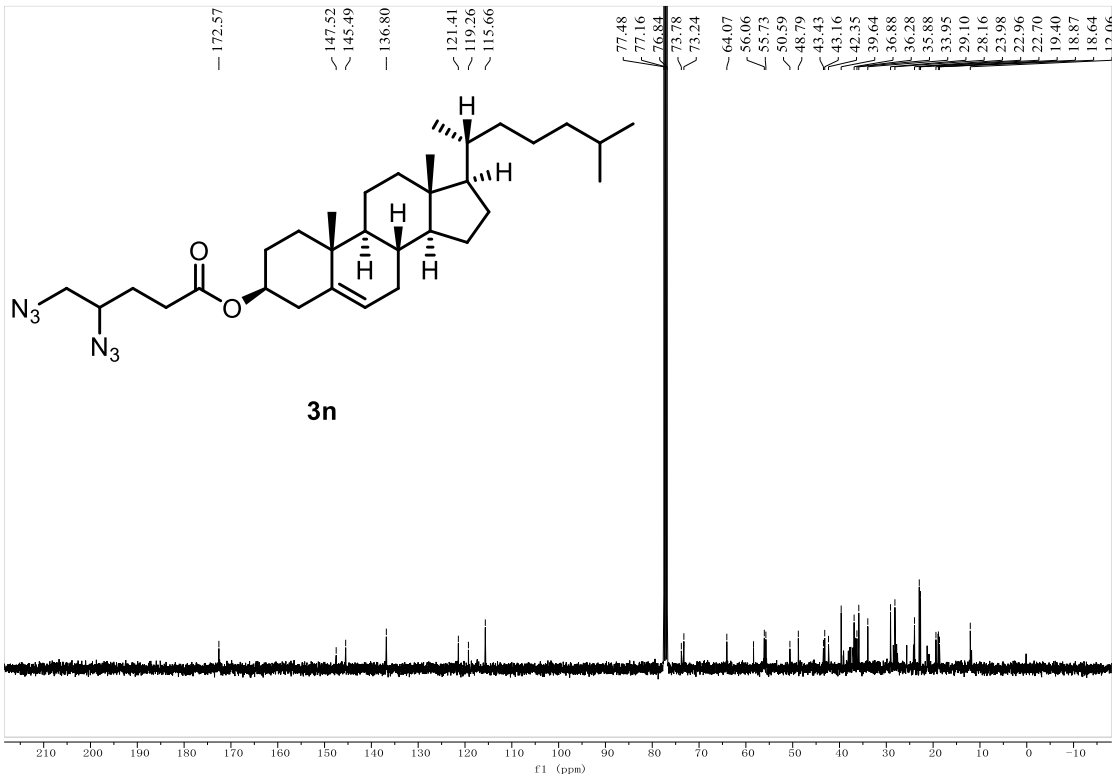
^{13}C NMR of **2m** (151 MHz, $CDCl_3$)



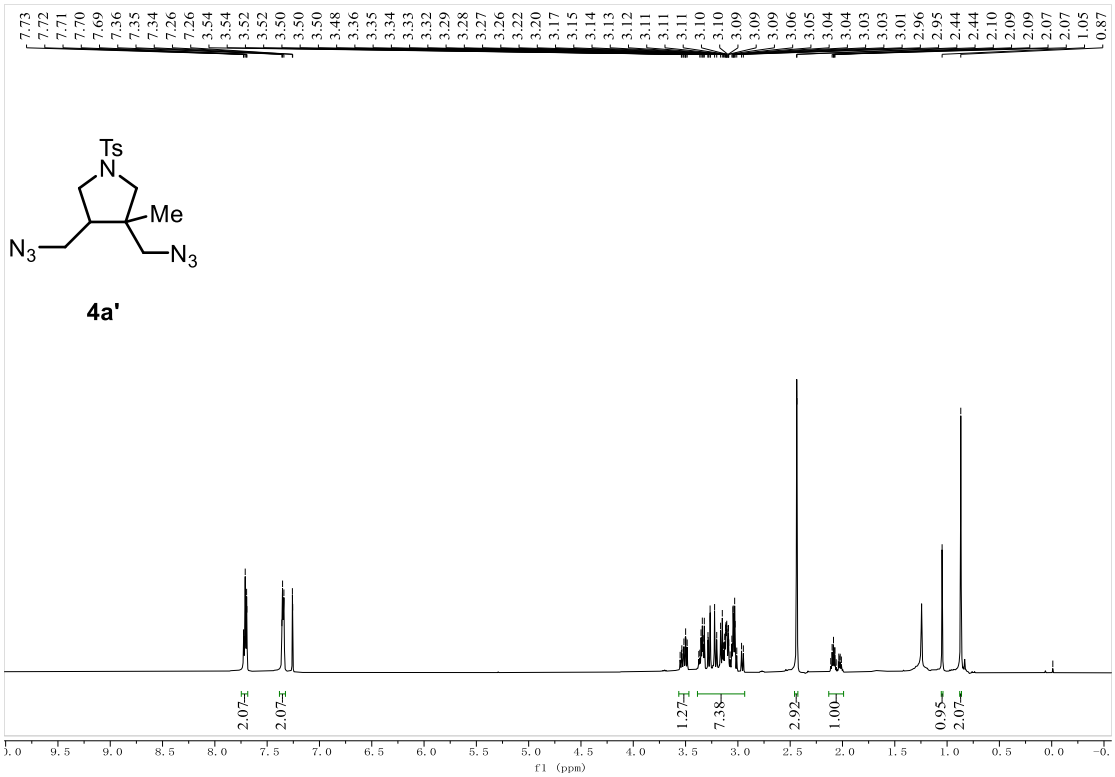
^{1}H NMR of **2n** (600 MHz, $CDCl_3$)



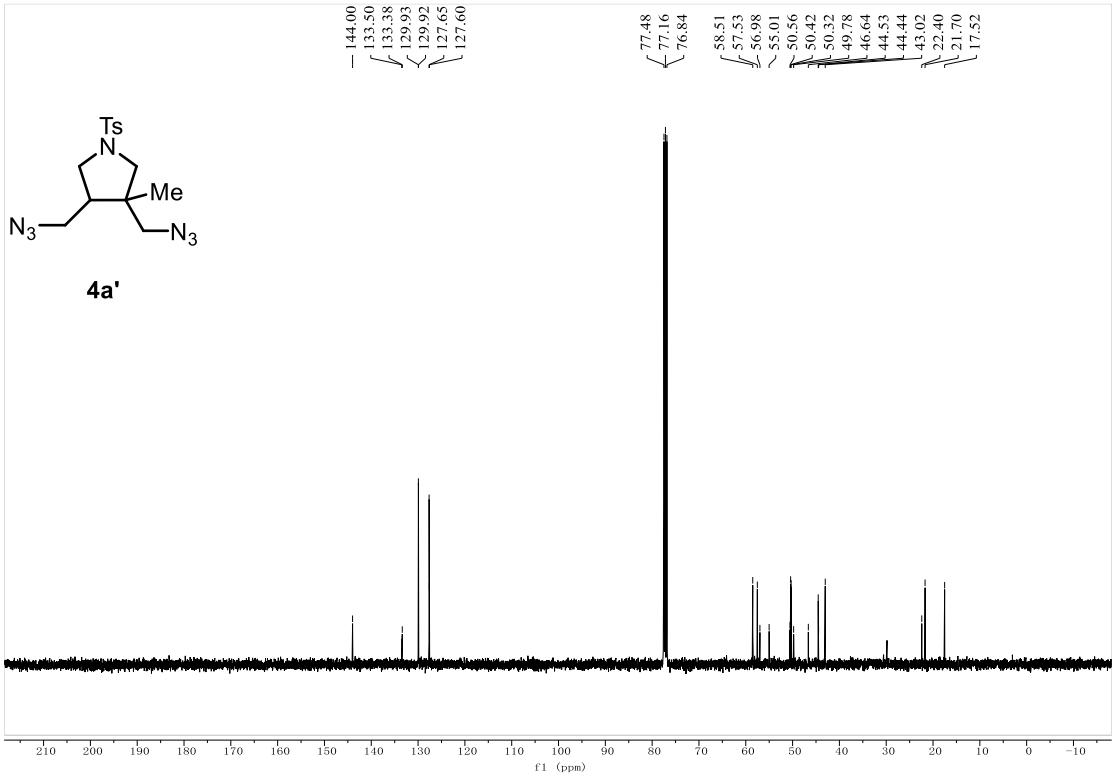
^{13}C NMR of **2n** (151 MHz, $CDCl_3$)



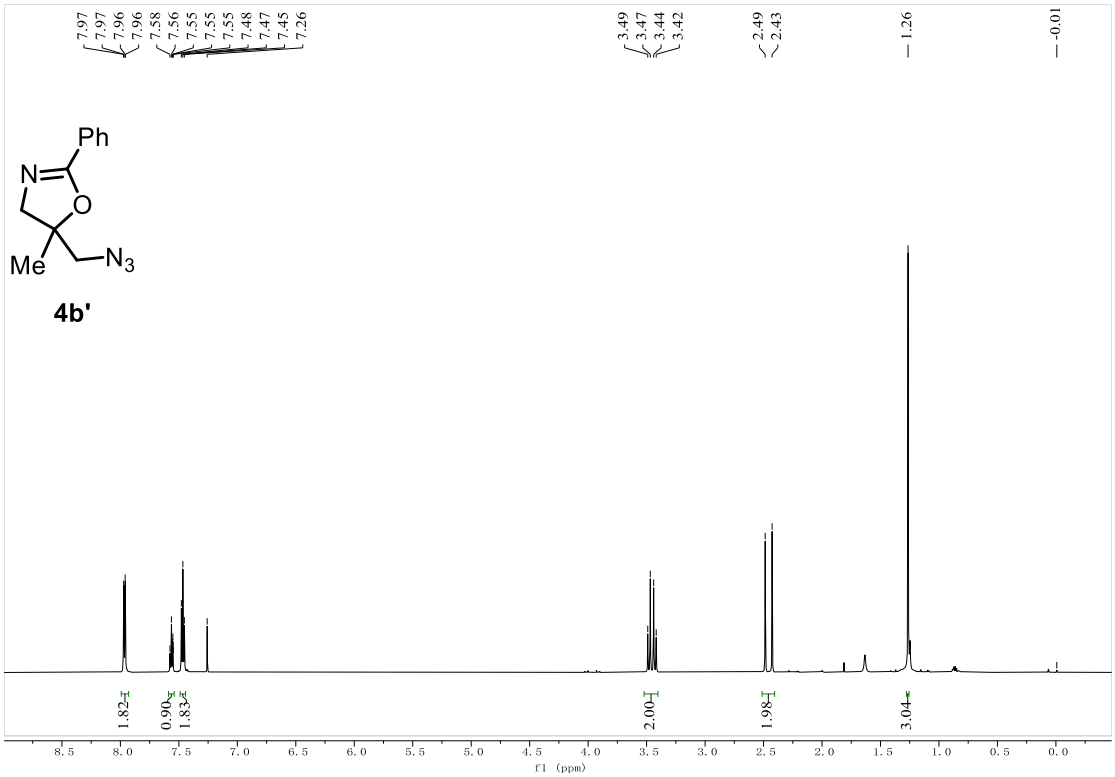
^{1}H NMR of **4a'** (600 MHz, $CDCl_3$)



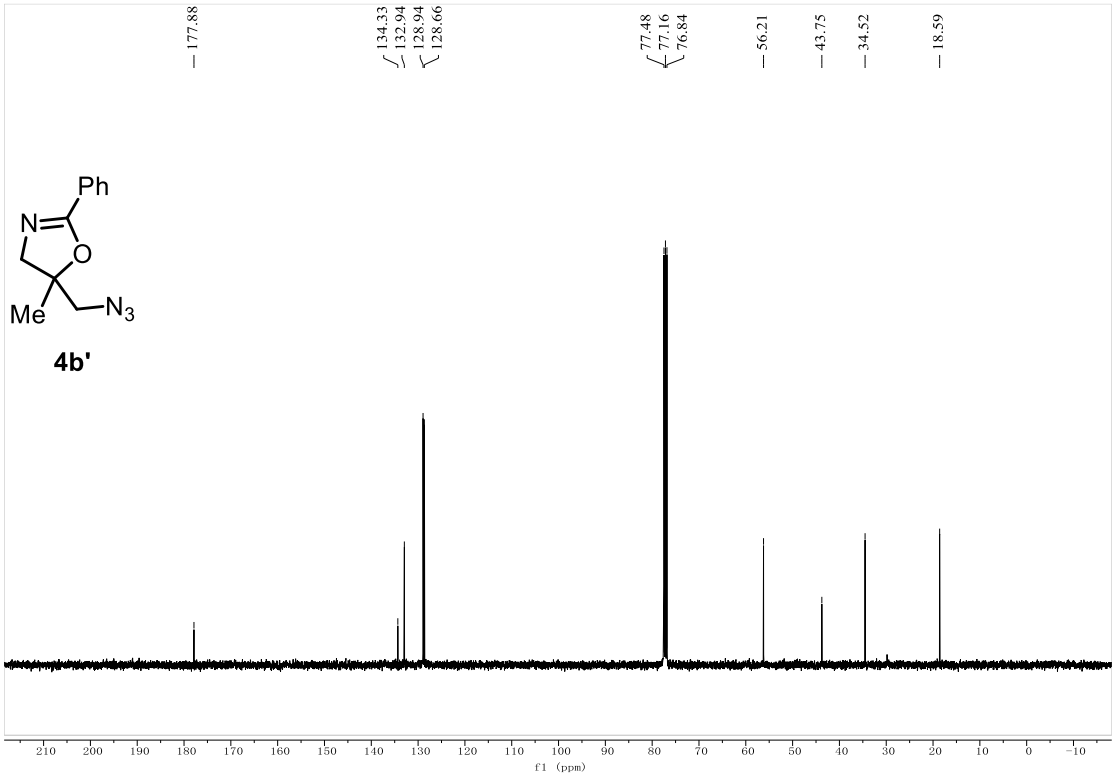
^{13}C NMR of **4a'** (101 MHz, $CDCl_3$)



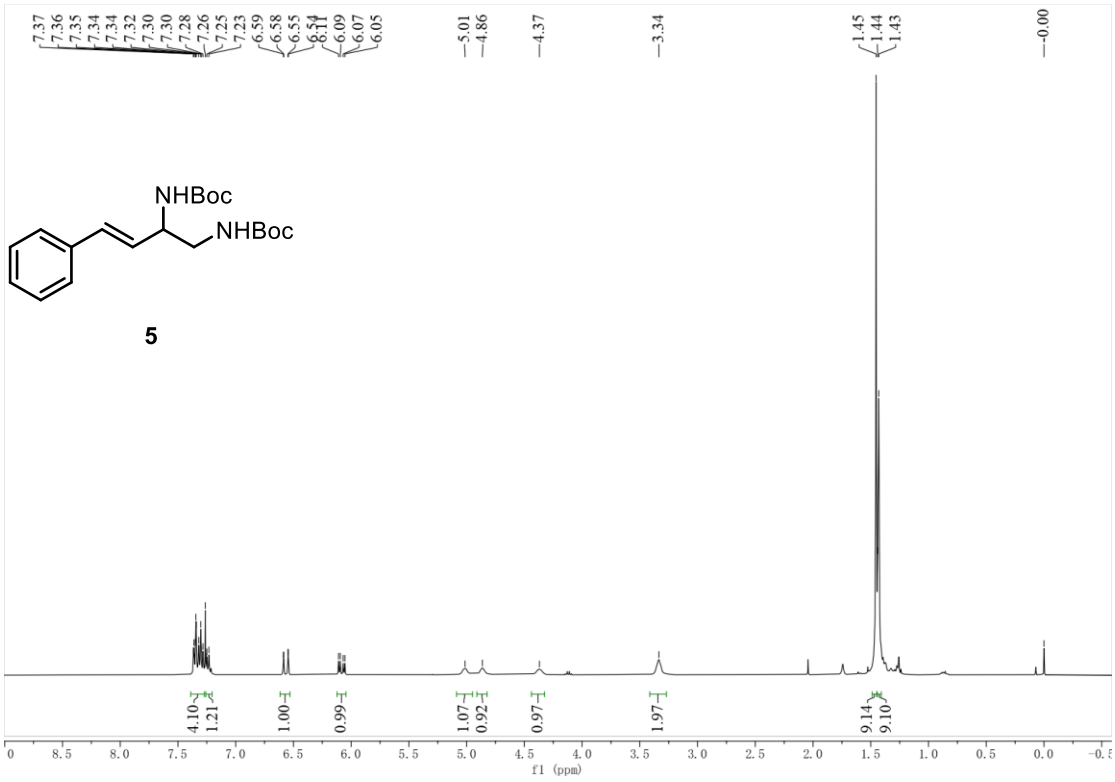
^{1}H NMR of **4b'** (600 MHz, $CDCl_3$)



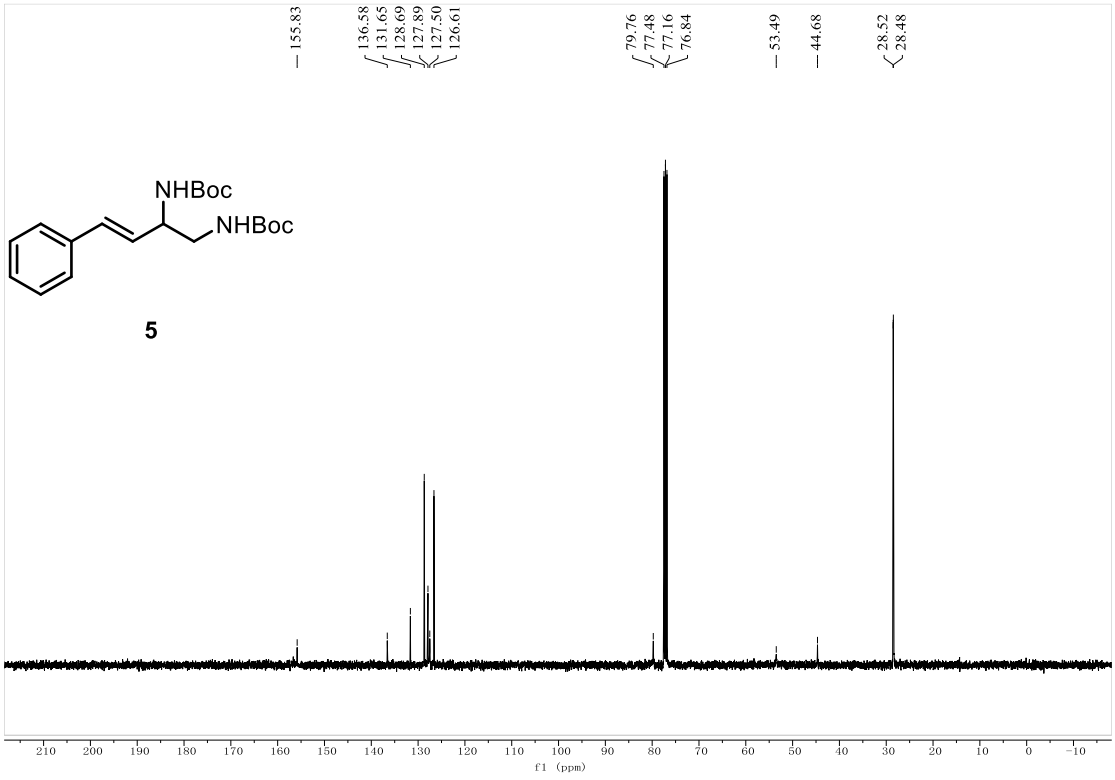
^{13}C NMR of **4b'** (101 MHz, $CDCl_3$)



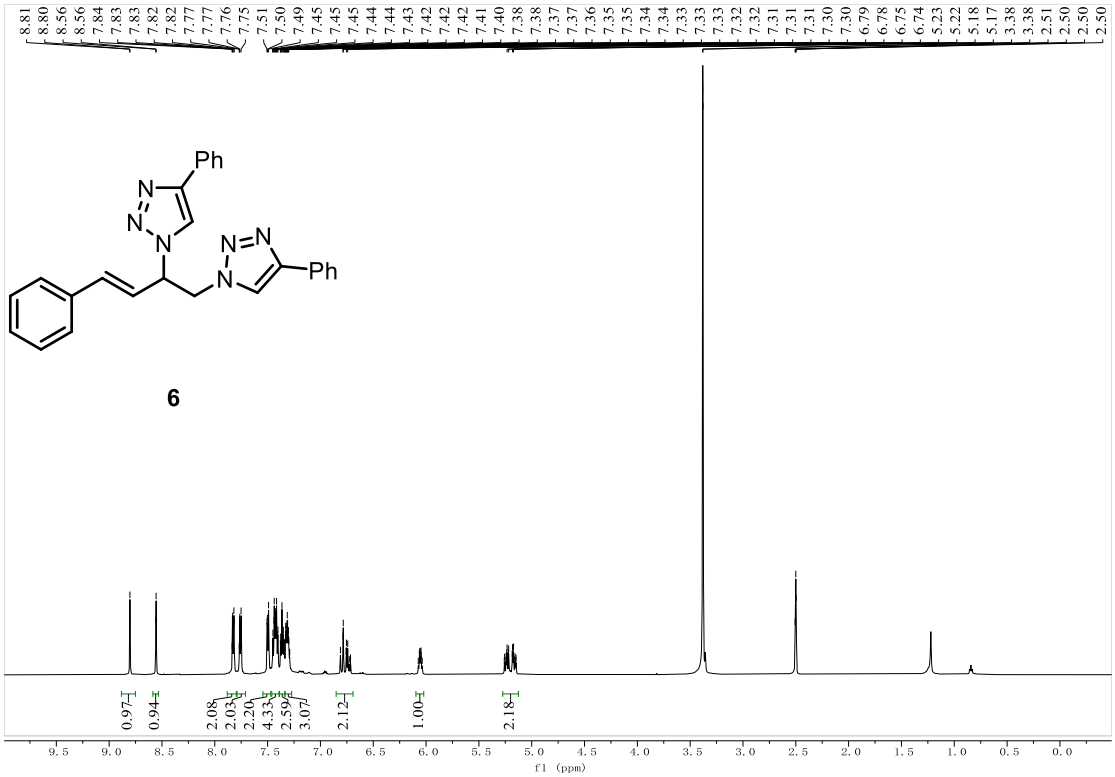
^{1}H NMR of **5** (600 MHz, $CDCl_3$)



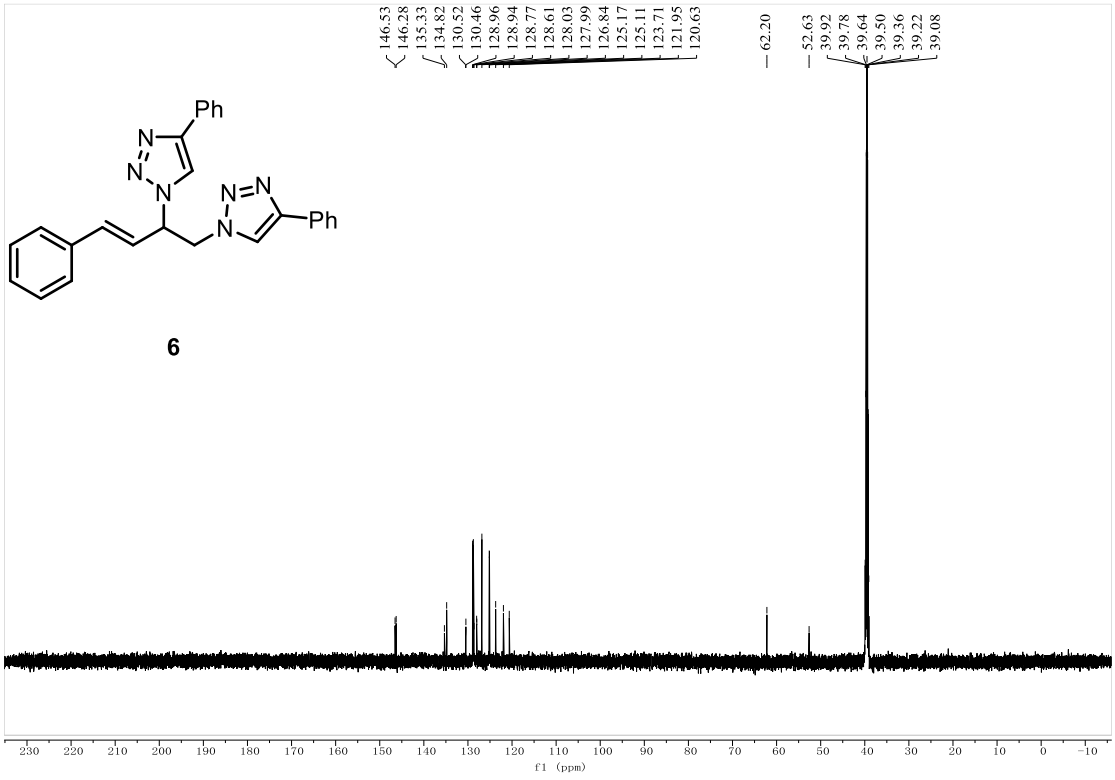
^{13}C NMR of **5** (101 MHz, $CDCl_3$)



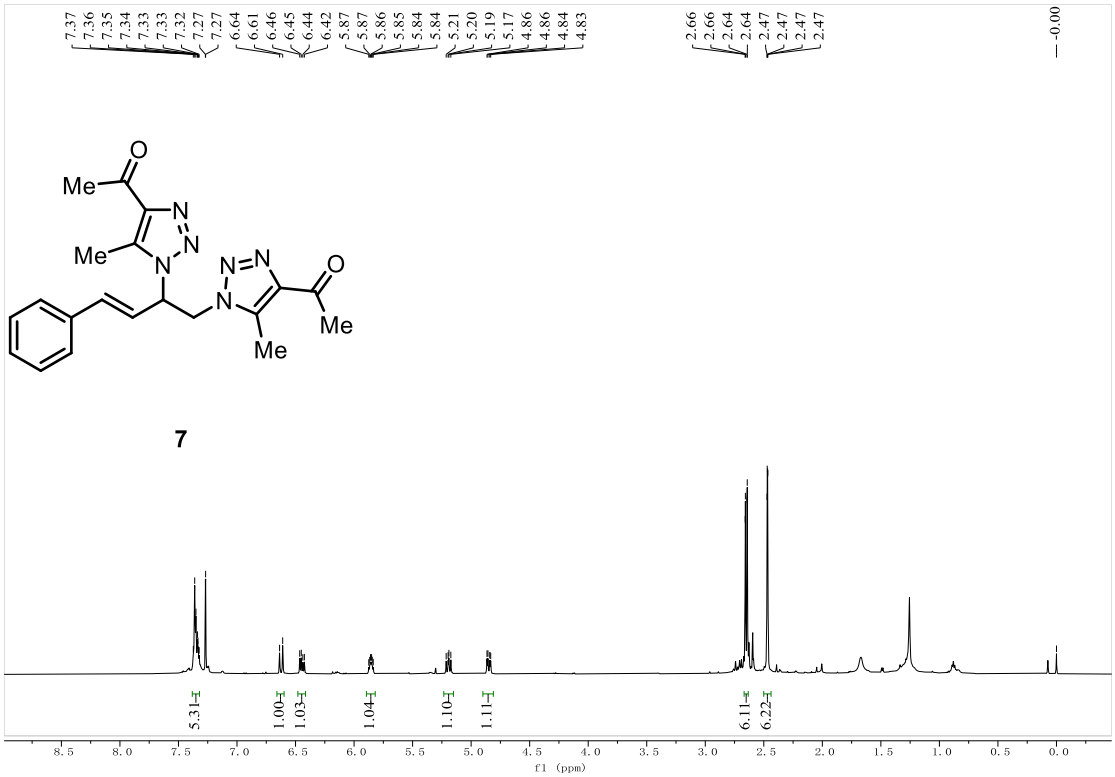
^{1}H NMR of **6** (600 MHz, DMSO-d_6)



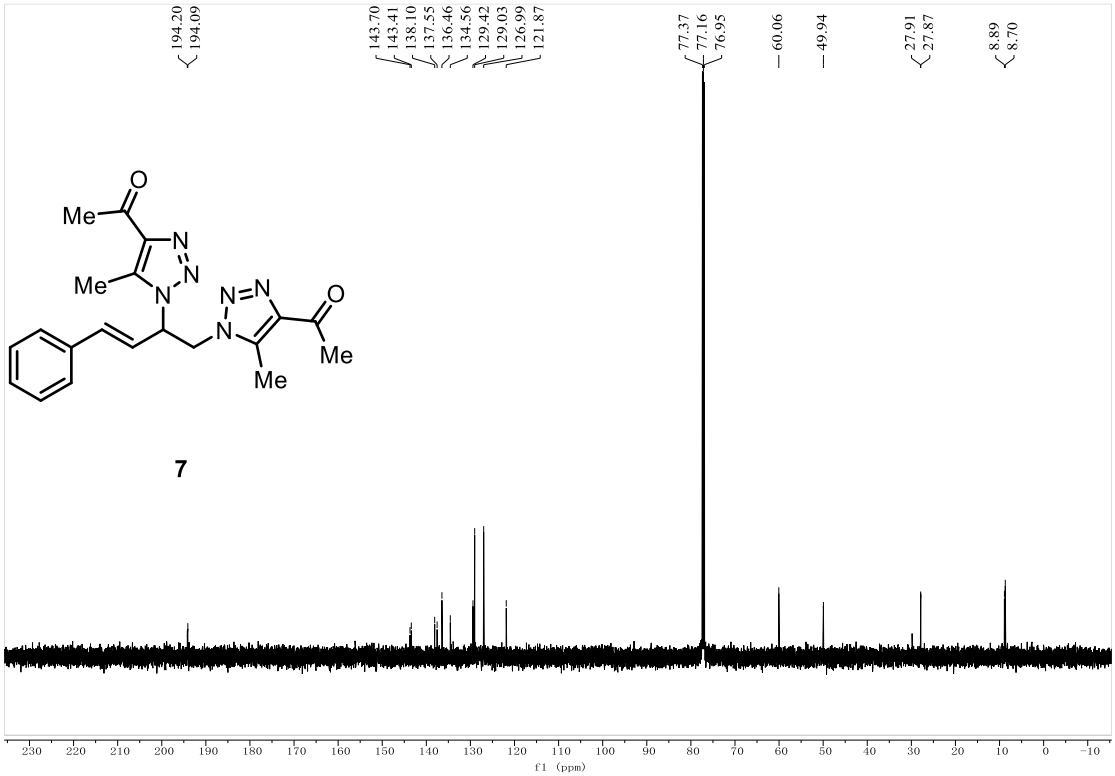
^{13}C NMR of **6** (151 MHz, DMSO-d_6)



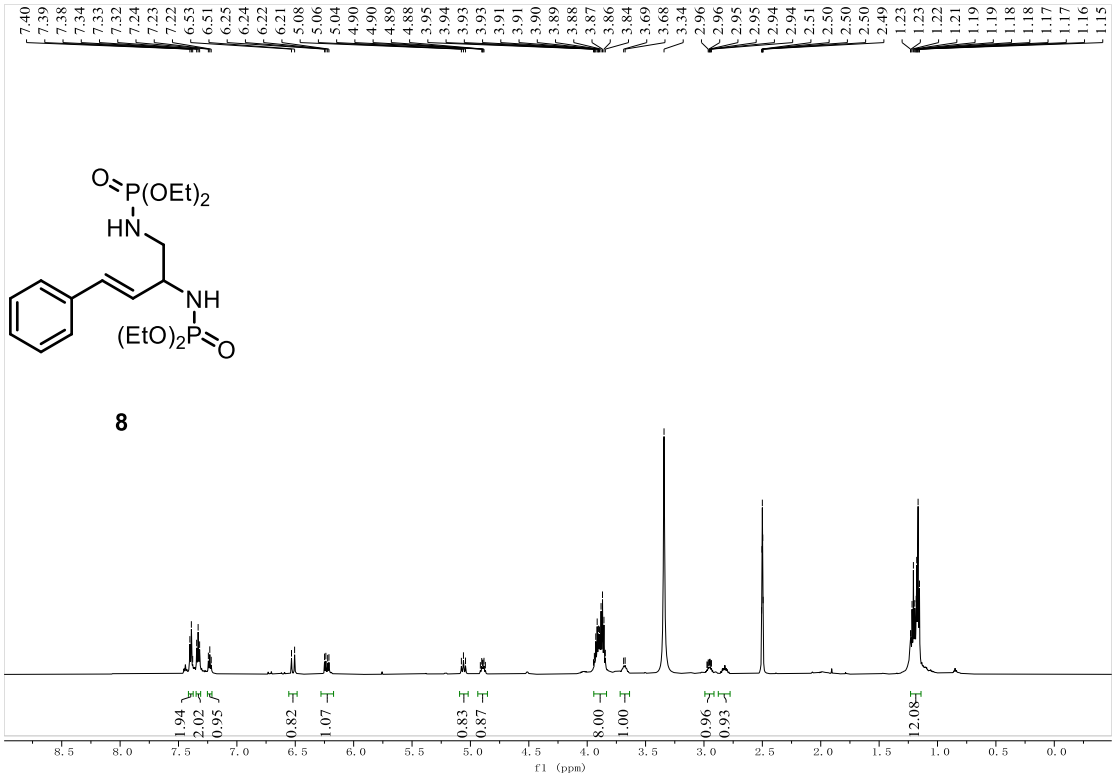
^{1}H NMR of **7** (600 MHz, $CDCl_3$)



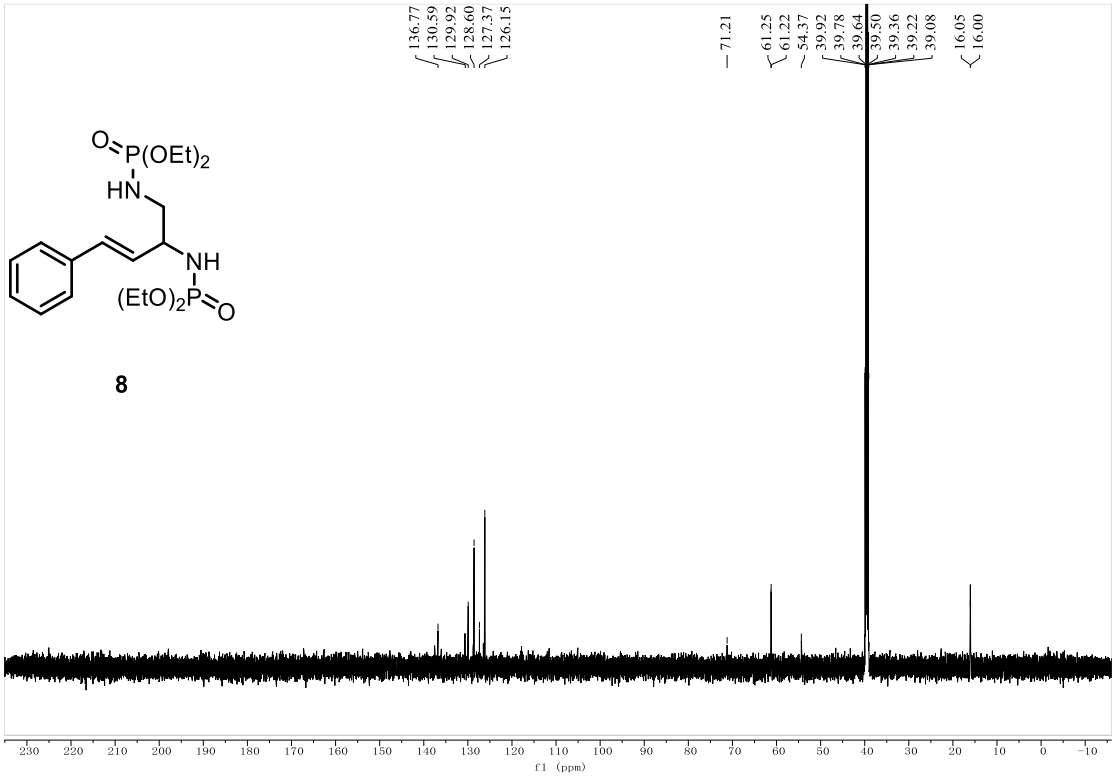
^{13}C NMR of **7** (101 MHz, $CDCl_3$)



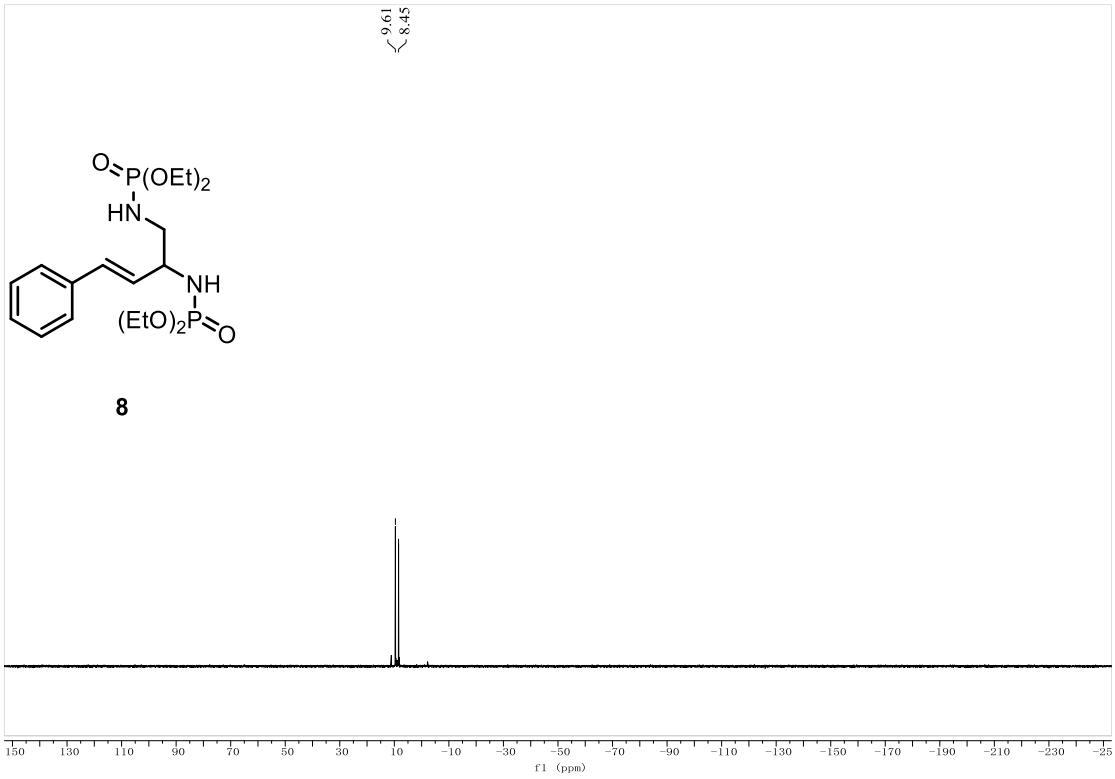
^{1}H NMR of **8** (600 MHz, DMSO-d_6)



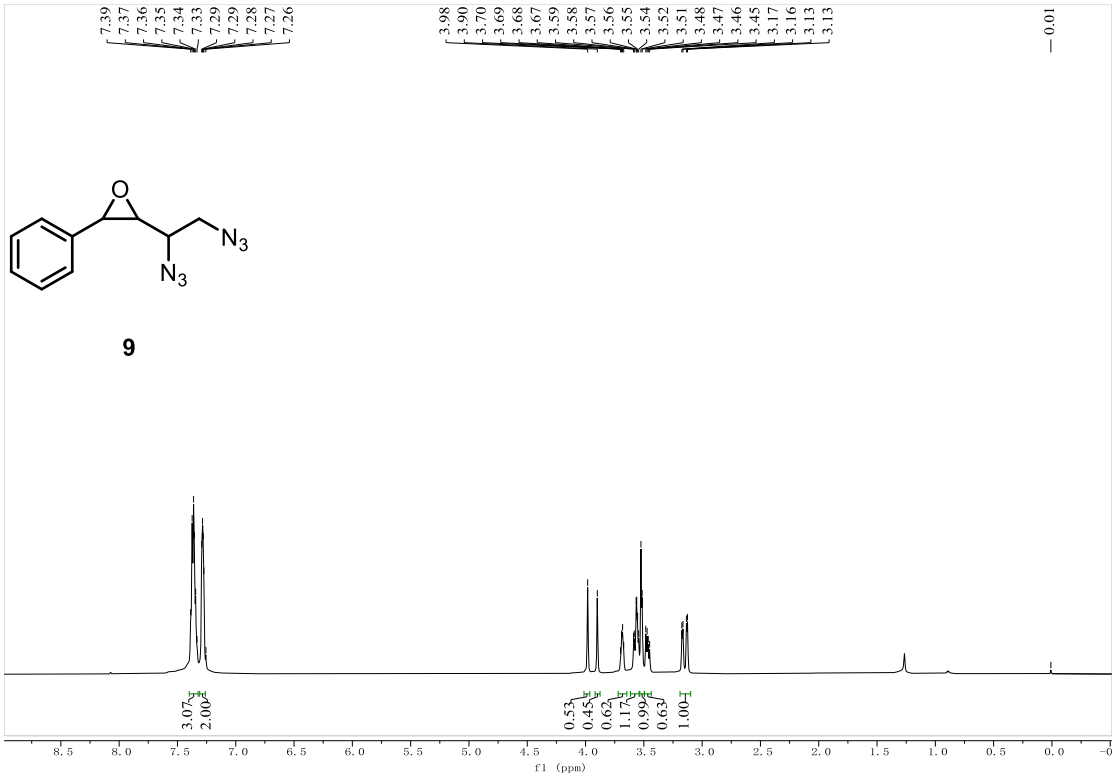
^{13}C NMR of **8** (151 MHz, DMSO-d_6)



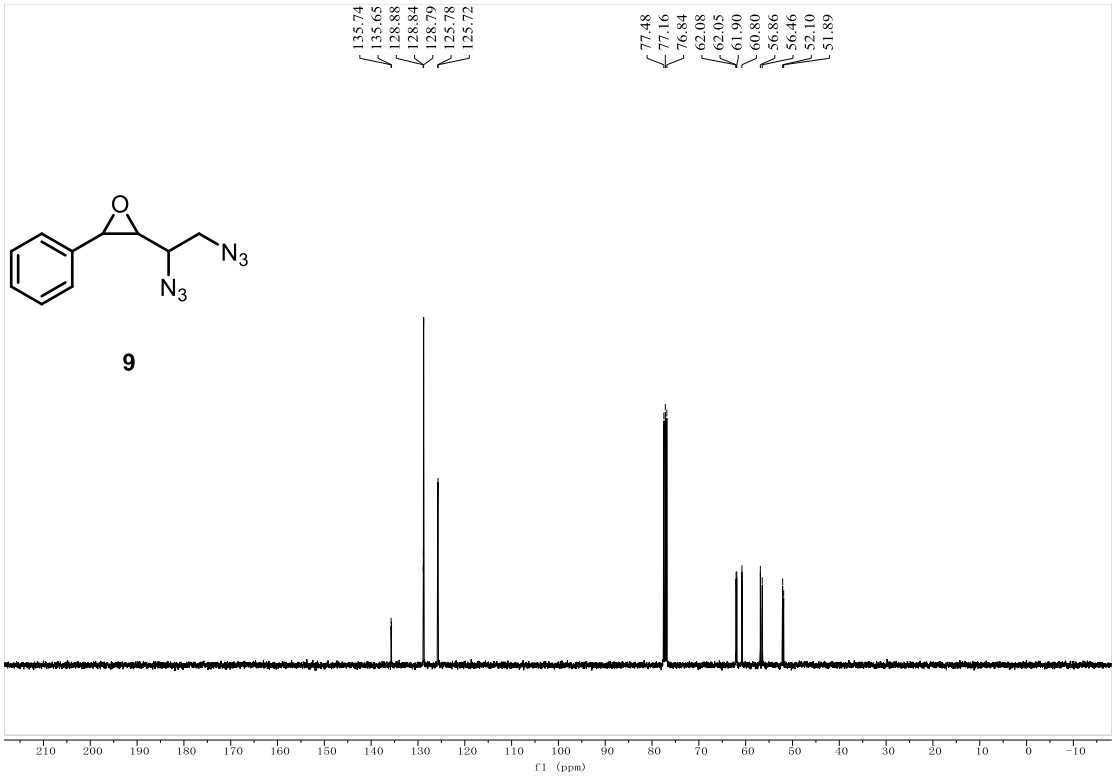
^{31}P NMR of **8** (162 MHz, DMSO-d_6)



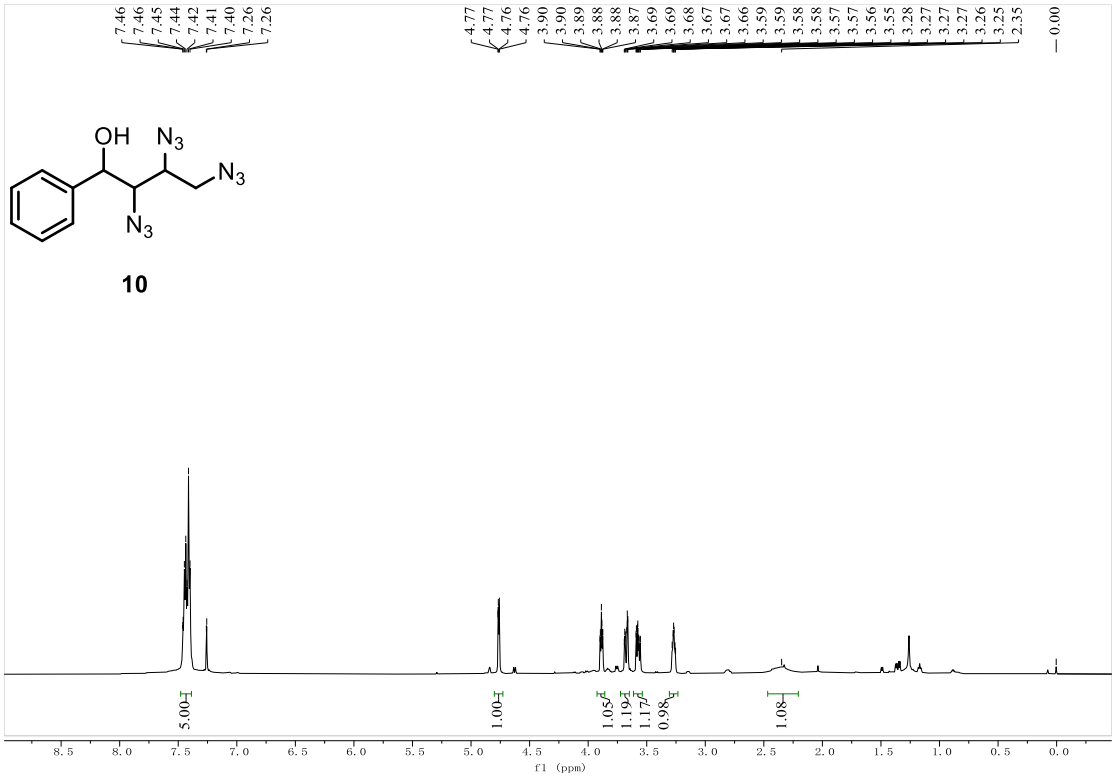
^{1}H NMR of **9** (600 MHz, $CDCl_3$)



^{13}C NMR of **9** (101 MHz, $CDCl_3$)



^{1}H NMR of **10** (600 MHz, $CDCl_3$)



^{13}C NMR of **10** (151 MHz, $CDCl_3$)