Supporting Information

Transition-metal-free azide insertion of *N*-triftosylhydrazones using non-metallic azide source

Xueyu Li,[a] Jin-Na Song*[b] Swastik Karmakar,[c] Ying Lu,[a] Ye Lv,[a] Peiqiu Liao*[a] and Zhaohong Liu*[a]

[a]Department of Chemistry, Northeast Normal University, Changchun 130024, China
[b]School of Life Science, Jilin University, Changchun 130012, China
[c]Basirhat College, A/w West Bengal State University, Basirhat-743412, West Bengal, India

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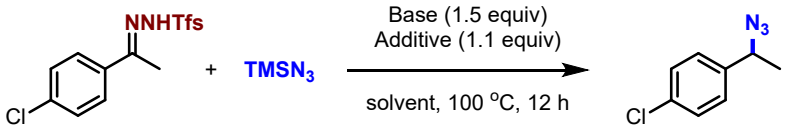
1. General Information

All manipulations were carried out by standard Schlenk techniques. The products were purified by column chromatography over silica gel (300-400 size). All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 565 MHz) and Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{19}F: 470 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, m = multiplet, br = broad. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm) and/or staining with aqueous $KMnO_4$ stain. High-resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method. All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Dry 1,4-dioxane (water < 0.005% (by K.F.), with molecular sieve) was purchased from J&K Scientific Ltd and was used without further purification.

2. Optimizations of the Reaction Conditions

Table S1. Optimizations of the Reaction Conditions



1a **2a**

Entry	PCT	Base	Solvent	H_2O	Yield (%)[a]
1	TBAB	^{t}BuOLi	1, 4-dioxane	0	45
2	TBAB	^{t}BuOLi	1, 4-dioxane	1	63
3	TBAB	^{t}BuOLi	1, 4-dioxane	2	85
4	TBAB	^{t}BuOLi	1, 4-dioxane	3	66
5	TBAB	^{t}BuOLi	1, 4-dioxane	2	42
6	TBAB	K_2CO_3	1, 4-dioxane	2	46
7	TBAB	Cs_2CO_3	1, 4-dioxane	2	52
8	TBAB	KOH	1, 4-dioxane	2	50
9	TBAB	^{t}BuOLi	THF	2	57
10	TBAB	^{t}BuOLi	CH_3CN	2	42
11	TBAB	^{t}BuOLi	$PhCF_3$	2	65
12	TEBAC	^{t}BuOLi	1, 4-dioxane	2	60
13	TBAC	^{t}BuOLi	1, 4-dioxane	2	70
14	TEAB	^{t}BuOLi	1, 4-dioxane	2	64
15	TEAC	^{t}BuOLi	1, 4-dioxane	2	56
16[b]	TBAB	^{t}BuOLi	1, 4-dioxane	2	72

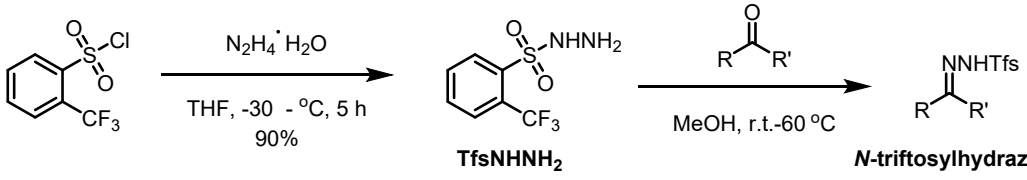
Reaction conditions: 1 (0.3 mmol), $TMSN_3$ (0.6 mmol), H_2O (0.6 mmol) TBAB (0.45 mmol), Base (0.33 mmol),

in Solvent (4.0 mL) at 100 °C for 12 h under argon atmosphere. [a]Isolated yields. [b]*N*-tosylhydrazone was used.

We reacted under anticipated conditions for azide insertion (Table S1). It was observed that the presence of water significantly affected the reaction yield, which indicated that the water was the proton source for the product (entries 1−4). The best result was obtained by using 2.0 equivalent of water to afford desired azide **2a** in 85% yield (entry 3). Other regular bases, such as ^{t}BuOK, K_2CO_3, Cs_2CO_3, and KOH, were then investigated but had no positive effect on the yield (entries 5-8). Although 1,4-dioxane was the best solvent, moderate yields were still obtained using other solvents such as CH3CN, THF, and PhCF3 (entries 3 & 9-11). Changing the phase transfer catalyst (PCT) from tetrabutylaminium bromide (TBAB) to benzyltriethylammonium chloride (TEBAC), tetrabutylammonium chloride (TBAC), tetraethylammonium bromide (TEAB), and tetraethylammonium chloride (TEAC) proved detrimental to the product formation (entries 3 & 12-15). Finally, compared to N-triftosylhydrazone 1a, the corresponding N-tosylhydrazone18 1a' gave a much lower yield under identical conditions (entry 16). Therefore, the optimum conditions were identified as 1,4-dioxane at 100 °C in the presence of 2.0 equivalent of water using ^{t}BuOLi as a base, and TBAB as the PCT (entry 3).

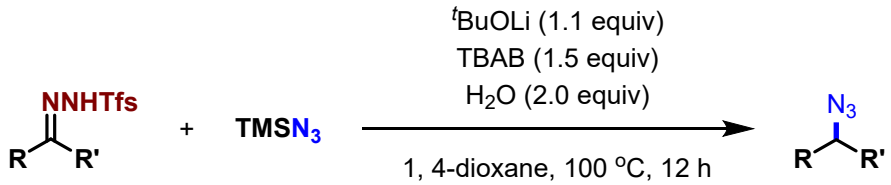
3. Experimental Procedure

2.1 Preparation of *N*-triftosylhydrazones.



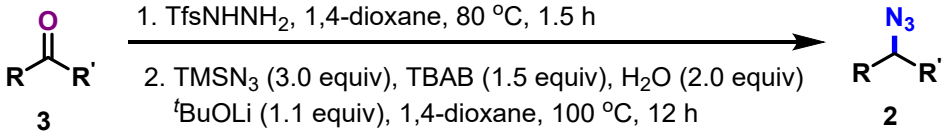
-Triftosylhydrazones were synthesized according to the literature *Org. Chem. Front.* 2019, **6**, 121-124 and *Chem Catalysis* 2022, **2**, 563-577.

2.2 Synthesis and Analytical Data of Benzyl Azides.



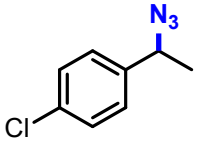
General Procedure A: *N*-Triftosylhydrazone (0.3 mmol), ^{t}BuOLi (62.0 mg, 0.33 mmol, 1.1 equiv) were added to an oven-dried sealed tube, which was evacuated and filled with Ar for three times, followed by addition of dry 1,4-dioxane (4 mL) via syringe. The resulting mixture was stirred at room temperature for 1 h. Then, tetrabutylammonium bromide (TBAB, 145.0 mg, 0.45 mmol), $TMSN_3$ (72.8 mg, 0.6 mmol, 2.0 equiv), and H_2O (11 μL, 2.0 equiv) were added under Ar atmosphere. The mixture was stirred at 100 °C for 12 h. After completion indicated by TLC, the resulting mixture was cooled to room temperature, and filtered through a short pad of silica gel with DCM as an eluent. The filtrate was evaporated

under reduced pressure a crude mixture, which was purified by column chromatography on silica gel to afford the desired benzyl azide.



General Procedure B: To a stirred solution of $TfsNHNH_2$ (0.3 mmol, 1.0 equiv) in 1,4-dioxane inside a glove box were added carbonyl compounds (0.3 mmol, 1.0equiv) and the mixture was stirred for 1.5 h at 80 °C. Then, the resulting mixture was cooled to room temperature, and was added ^{t}BuOLi (62.0 mg, 0.33 mmol, 1.1 equiv), TBAB (145.0 mg, 0.45 mmol), $TMSN_3$ (72.8 mg, 0.6 mmol, 2.0 equiv), and H_2O (11 μL, 2.0 equiv) under Ar atmosphere. The mixture was stirred at 100 °C for 12 h. After completion indicated by TLC, the resulting mixture was cooled to room temperature, and filtered through a short pad of silica gel with DCM as an eluent. The filtrate was evaporated under reduced pressure a crude mixture, which was purified by column chromatography on silica gel to afford the desired benzyl azide.

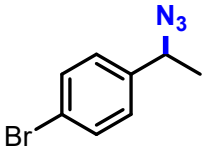
Note: Product can't be analyzed by HRMS, probably due to the decomposition.



2a

1-(1-Azidoethyl)-4-chlorobenzene (2a): According to **General Procedure A**, 1-(4-chlorophenyl)ethan-1-one derived *N*-triftosylhydrazone **1a** (113.0 mg, 0.3 mmol) afforded **2a** (46.3 mg, 85%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.60 (q, J = 6.6 Hz, 1H), 1.51 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.4, 133.9, 129.0, 127.8, 60.4, 21.6. **IR** (KBr): 3065, 2923, 2109, 1706, 1650, 1314, 1714, 912, 744 cm^{-1}.

Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.

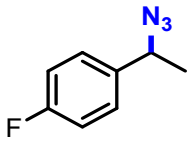


2b

1-(1-Azidoethyl)-4-bromobenzene (2b): According to **General Procedure A**, 1-(4-bromophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1b** (126.4 mg, 0.3 mmol) afforded **2b** (55.6 mg, 82%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 4.58 (q, J = 6.6 Hz, 1H), 1.50 (d, J = 7.2 Hz,

3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.9, 131.9, 128.0, 122.0, 60.4, 21.5. **IR** (KBr): 2980, 2104, 529 cm^{-1}.

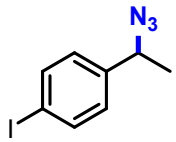
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2c

1-(1-Azidoethyl)-4-fluorobenzene (2c): According to **General Procedure A**, 1-(4-fluorophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1c** (108.1 mg, 0.3 mmol) afforded **2c** (28.7 mg, 58%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2H), 7.08-7.05 (m, 2H), 4.61 (q, *J* = 6.6 Hz, 1H), 1.52 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.1 Hz), 136.7 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.5 Hz), 60.4, 21.6. **IR** (KBr): 2101 cm^{-1}.

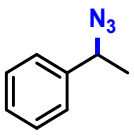
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2d

1-(1-Azidoethyl)-4-iodobenzene (2d): According to **General Procedure A**, 1-(4-iodophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1d** (140.5 mg, 0.3 mmol) afforded **2d** (51.6 mg, 63%) as a colorless oil. **(2d) ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.07(d, *J* = 8.4 Hz, 2H), 4.57 (q, *J* = 6.6 Hz, 1H), 1.50 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.6, 137.9, 128.3, 93.6, 60.5, 21.5. **IR** (KBr): 2976, 2098, 1481, 1405, 1237, 1061, 999, 913, 817, 745 cm^{-1}.

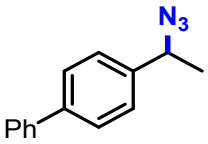
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2e

(1-Azidoethyl)benzene (2e): According to **General Procedure A**, acetophenone -derived *N*-triftosylhydrazone **1e** (102.7 mg, 0.3 mmol) afforded **2e** (30.5 mg, 69%) as a colorless oil. **(2e) ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.33-7.31 (m, 3H), 4.62 (q, *J* = 6.6 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.8, 128.8, 128.1, 126.4, 61.1, 21.6. **IR** (KBr): 2920, 2851, 2101, 1657, 1632, 1469, 1312, 1258, 913, 698 cm^{-1}.

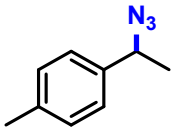
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2f

4-(1-Azidoethyl)-1,1'-biphenyl (2f): According to **General Procedure A**, 1-([1,1'-biphenyl]-4-yl)ethan-1-one-derived *N*-triftosylhydrazone **1f** (125.4 mg, 0.3 mmol) afforded **2f** (56.3 mg, 84%) as a colorless liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64-7.53 (t, *J* = 7.8 Hz, 4H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.65 (q, *J* = 6.6 Hz, 1H), 1.56 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.1, 140.6, 139.8, 128.8, 127.5, 127.4, 127.1, 126.8, 60.8, 21.5 cm^{-1}.

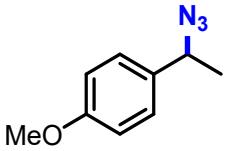
Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc.* 2020, **142**, 17693−17702.



2g

1-(1-Azidoethyl)-4-methylbenzene (2g): According to **General Procedure A**, 1-(p-tolyl)ethan-1-one-derived *N*-triftosylhydrazone **1g** (106.9 mg, 0.3 mmol) afforded **2g** (43.0 mg, 89%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.57 (q, *J* = 6.6 Hz, 1H), 2.35 (s, 3H), 1.51 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.9, 137.8, 129.4, 126.3, 60.9, 21.5, 21.1.

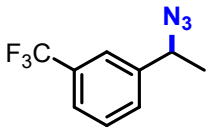
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2h

1-(1-Azidoethyl)-4-methoxybenzene (2h): According to **General Procedure A**, 1-(4-methoxyphenyl)ethan-1-one-derived *N*-triftosylhydrazone **1h** (111.7 mg, 0.3 mmol) afforded **2h** (51.0 mg, 96%) as a yellow oil; **(2h) ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.56 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.4, 132.8, 127.6, 114.1, 60.7, 55.3, 21.4. **IR** (KBr): 2978, 2934, 2837, 2102, 1611, 1513, 1248, 1178, 1034, 832 cm^{-1}.

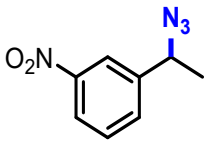
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2i

1-(1-Azidoethyl)-3-(trifluoromethyl)benzene (2i): According to **General Procedure A**, *N*-triftosylhydrazone **1i** (123.1 mg, 0.3 mmol) derived from 1-(3-(trifluoromethyl)phenyl)ethan-1-one afforded **2i** (47.1 mg, 73%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.53-7.49 (m, 2H), 4.70 (q, *J* = 6.6 Hz, 1H), 1.56 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.1, 131.2 (q, *J* = 32.3 Hz), 129.7, 129.3, 124.9 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.9 Hz), 123.2 (q, *J* = 3.8 Hz), 60.5, 21.7.

Spectroscopic data in agreement with those reported in *New J. Chem.,* 2016, **40**, 10240-10245.

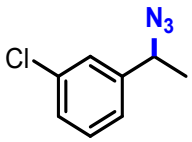


2j

1-(1-Azidoethyl)-3-nitrobenzene (2j): According to **General Procedure A**, 1-(3-nitrophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1j** (116.2 mg, 0.3 mmol)

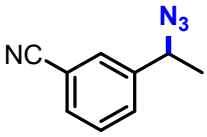
afforded **2j** (24.8 mg, 43%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21-8.18 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 8.4 Hz, 1H), 4.76 (q, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.5, 143.2, 132.4, 129.8, 123.1, 121.4, 60.0, 21.7. **IR** (KBr): 2981, 2920, 2850, 2109, 1530, 1351, 1247, 898, 807, 737, 687 cm^{-1}.

Spectroscopic data in agreement with those reported in *New J. Chem.* 2020, **40**, 10240-10245.



2k

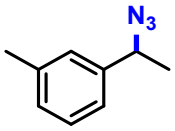
1-(1-Azidoethyl)-3-chlorobenzene (2k): According to **General Procedure A**, 1-(3-chlorophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1k** (113.0 mg, 0.3 mmol) afforded **2k** (41.3 mg, 76%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33-7.28 (m, 3H), 7.21 (dt, *J* = 6.6 Hz, *J* = 1.8 Hz, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 1.52 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 143.0, 134.6, 130.1, 128.3, 126.6, 124.5, 60.4, 21.6; **IR** (KBr): 2980, 2927, 2100, 1579, 1431, 1249, 1073, 998, 911, 788, 695 cm^{-1}.



2l

3-(1-Azidoethyl)benzonitrile (2l): According to **General Procedure A**, 3-acetylbenzonitrile-derived *N*-triftosylhydrazone **1l** (110.2 mg, 0.3 mmol) afforded **2l** (26.3mg 51%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 12.0 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 4.67 (q, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 142.6, 131.7, 130.7, 129.9, 129.6, 118.4, 113.0, 60.0, 21.6 cm^{-1}.

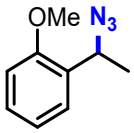
Spectroscopic data in agreement with those reported in *New J. Chem.* 2020, **44**, 21238-21242.



2m

1-(1-Azidoethyl)-3-methylbenzene (2m): According to **General Procedure A**, 1-(m-tolyl)ethan-1-one-derived *N*-triftosylhydrazone **1m** (106.9 mg, 0.3 mmol) afforded **2m** (39.7 mg, 82%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.8 Hz, 1H), 7.13-7.11 (m, 3H), 4.57 (q, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.8, 138.5, 128.9, 128.6, 127.1, 123.4, 61.1, 21.5, 21.4. **IR** (KBr): 3354, 3191, 2920, 2851, 2360, 2339, 2107, 1657, 1632, 1469, 1247, 912, 745 cm^{-1}.

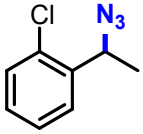
Spectroscopic data in agreement with those reported in *Adv. Synth. Catal.* 2014, **356**, 2769–2774.



2n

1-(1-Azidoethyl)-2-methoxybenzene (2n): According to **General Procedure A**, 1-(2-methoxyphenyl)ethan-1-one-derived *N*-triftosylhydrazone **1n** (111.7 mg, 0.3 mmol) afforded **2n** (48.4 mg, 91%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.06 (q, *J* = 6.6 Hz, 1H), 3.85 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 129.1, 129.0, 126.5, 120.7, 110.6, 55.4, 54.9, 20.1. **IR** (KBr): 2935, 2838, 2095, 1601, 1492, 1462, 1268, 1245, 1029, 910, 801, 753 cm^{-1}.

Spectroscopic data in agreement with those reported in *Synthesis* 2015, **47**, 323-329.

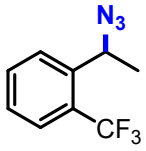


2o

1-(1-Azidoethyl)-2-chlorobenzene (2o): According to **General Procedure A**, 1-(2-chlorophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1o** (113.0 mg, 0.3 mmol) afforded **2o** (34.2 mg, 63%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 5.14 (q, *J* = 6.6 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.7, 132.5, 129.7, 129.0, 127.4, 127.2, 57.4, 20.7. **IR** (KBr): 3021, 2930, 2104,

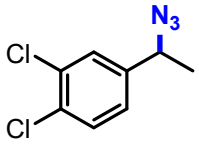
1475, 1394, 1318, 1250, 1131, 1031, 816.

Spectroscopic data in agreement with those reported in *J. C. Chem. Soc.* 2014, **61**, 737–742.



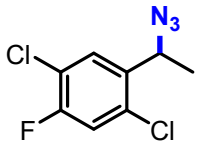
2p

1-(1-Azidoethyl)-2-(trifluoromethyl)benzene (2p): According to **General Procedure A**, 1-(3,4-dichlorophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1p** (123.4 mg, 0.3 mmol) afforded **2p** (29.7 mg, 46%) as a colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 5.11 (q, *J* = 6.5 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.5, 132.6, 128.0, 127.9, 127.4 (q, *J* =30.0 Hz), 125.6 (q, *J* = 5.8 Hz), 124.2 (q, *J* = 274.2 Hz), 56.6, 22.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -58.1 (s).



2q

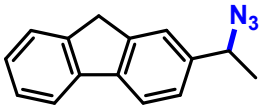
4-(1-Azidoethyl)-1,2-dichlorobenzene (2q): According to **General Procedure A**, 1-(2-(trifluoromethyl)phenyl)ethan-1-one-derived *N*-triftosylhydrazone **1q** (123.1 mg, 0.3 mmol) afforded **2q** (44.1 mg, 68%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 4.59 (q, *J* = 6.6 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.2, 132.9, 132.1, 130.7, 128.4, 125.7, 59.8, 21.6. **IR** (KBr): 2981, 2929, 2103, 1470, 1394, 1318, 1249, 1133, 1031, 821.



2r

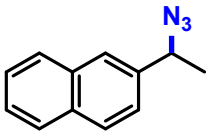
1-(1-Azidoethyl)-2,5-dichloro-4-fluorobenzene (2r): According to **General Procedure A**, 1-(2,5-dichloro-4-fluorophenyl)ethan-1-one-derived *N*-triftosylhydrazone **1r** (128.8 mg, 0.3 mmol) afforded **2r** (53.4 mg, 76%) as a colorless

oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.6 Hz, 1H), 7.28 (d, *J* = 9.6 Hz, 1H), 5.04 (q, *J* = 6.6 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2 (d, *J* = 249.2 Hz), 139.6 (d, *J* = 5.9 Hz), 131.1, 127.3 (d, *J* = 3.6 Hz), 121.1 (d, *J* = 19.5 Hz), 115.2 (d, *J* = 24.2 Hz), 57.0, 20.6. **IR** (KBr): 3357, 2983, 2921, 2851, 2094, 21 1473, 1386, 1262, 1089, 885, 727 cm^{-1}.



2s

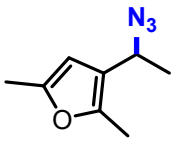
2-(1-Azidoethyl)-9H-fluorene (2s): According to **General Procedure A**, 1-(9H-fluoren-2-yl)ethan-1-one-derived *N*-triftosylhydrazone **1s** (129.1 mg, 0.3 mmol) afforded **2s** (56.5 mg, 80%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.50 (s, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.32-7.28 (m, 2H), 4.67 (q, *J* = 6.6 Hz, 1H), 3.88 (s, 2H), 1.57 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.8, 143.4, 141.8, 141.1, 139.4, 126.9, 126.8, 125.2, 125.0, 123.0, 120.0, 120.0, 61.4, 36.9, 21.7. **IR** (KBr): 2975, 2926, 2098, 1455, 1258, 1058, 913, 769, 737 cm^{-1}.



2t

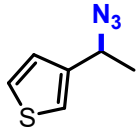
2-(1-Azidoethyl)naphthalene (2t): According to **General Procedure A**, 1-(naphthalen-2-yl)ethan-1-one-derived *N*-triftosylhydrazone **1t** (129.1 mg, 0.3 mmol) afforded **2t** (56.5 mg, 80%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87-7.83 (m, 3H), 7.76 (s, 1H), 7.51-7.48 (m, 2H), 7.45 (dd, *J* = 10.2 Hz, *J* = 2.4 Hz, 1H), 4.78 (q, *J* = 8.4 Hz, 1H), 1.61 (d, *J* = 8.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.2, 133.2, 133.1, 128.7, 128.0, 127.7, 126.4, 126.2, 125.3, 124.2, 61.3, 21.6.

Spectroscopic data in agreement with those reported in *New J. Chem.*, 2016, **40**, 10240-10245.



2u

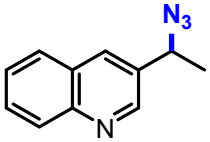
3-(1-Azidoethyl)-2,5-dimethylfuran (2u): According to **General Procedure A**, 1-(2,5-dimethylfuran-3-yl)ethan-1-one-derived *N*-triftosylhydrazone **1u** (108.1 mg, 0.3 mmol) afforded **2u** (41.6 mg, 84%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.92 (s, 1H), 4.48 (q, *J* = 6.6 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 1.41 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.3, 146.8, 119.4, 104.3, 53.2, 20.8, 13.4, 11.6. **IR** (KBr): 2960, 2923, 2852, 2105, 1586, 1454, 1260, 1229, 1062, 1016, 800 cm^{-1}.



2v

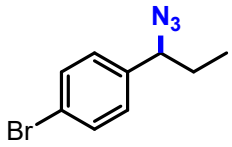
3-(1-Azidoethyl)thiophene (2v): According to **General Procedure A**, 1-(thiophen-3-yl)ethan-1-one-derived *N*-triftosylhydrazone **1v** (104.5 mg, 0.3 mmol) afforded **2v** (37.7 mg, 82%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35-7.34 (m, 1H), 7.22 (s, 1H), 7.08 (d, *J* = 4.8 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.8, 126.6, 125.8, 121.7, 56.6, 20.8. **IR** (KBr): 2920, 2850, 2361, 2339, 2105, 912, 669 cm^{-1}.

Spectroscopic data in agreement with those reported in *New J. Chem.*, 2016, **40**, 10240-10245.



2w

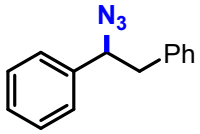
3-(1-Azidoethyl)quinoline (2w): According to **General Procedure A**, 1-(quinolin-3-yl)ethan-1-one-derived *N*-triftosylhydrazone **1w** (118.0 mg, 0.3 mmol) afforded **2w** (30.9 mg, 52%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 4.86 (q, *J* = 6.6 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.4, 147.9, 133.6, 133.0, 129.7, 129.3, 127.8, 127.6, 127.1, 58.8, 21.4. **IR** (KBr): 2977, 2929, 2102, 1571, 1495, 1259, 1062, 1017, 910, 788, 751 cm^{-1}.



2x

1-(1-Azidopropyl)-4-bromobenzene (2x): According to **General Procedure A**, 1-(4-bromophenyl)propan-1-one-derived *N*-triftosylhydrazone **1x** (130.6 mg, 0.3 mmol) afforded **2x** (61.2 mg, 85%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 7.2 Hz, 1H), 1.87-1.80 (m, 1H), 1.79-1.71 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.7, 131.9, 128.6, 122.0, 67.1, 29.3, 10.6. **IR** (KBr): 2969, 2929, 2096, 1485, 1242, 1075, 1009, 913, 818, 1009, 914, 817, 744, 523 cm^{-1}.

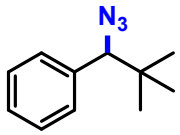
Spectroscopic data in agreement with those reported in *Angew. Chem. Int. Ed.* 2012, **51**, 5950-5952.



2y

(1-Azidoethane-1,2-diyl)dibenzene (2y): According to **General Procedure A**, 1,2-diphenylethan-1-one-derived *N*-triftosylhydrazone **1x** (125.5 mg, 0.3 mmol) afforded **2y** (54.3 mg, 81%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.33-7.31 (m, 1H), 7.29-7.26 (m, 4H), 7.25-7.22 (m,, 1H), 7.14 (d, *J* = 6.6 Hz, 2H), 4.66 (dd, *J* = 8.4 Hz, *J* = 6.6 Hz, 1H), 3.10-3.00 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.3, 137.4, 129.4, 128.7, 128.4, 128.3, 126.9, 126.9 67.7, 43.0. **IR** (KBr): 3028, 2921, 2097, 1489, 1449, 1234, 912, 745, 694 cm^{-1}.

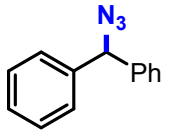
Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc.* 2020, 142, 11388-11393.



2z

(1-Azido-2,2-dimethylpropyl)benzene (2z): According to **General Procedure A**, 2,2-dimethyl-1-phenylpropan-1-one-derived *N*-triftosylhydrazone **1z** (115.3 mg, 0.3

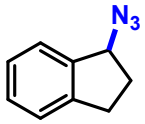
mmol) afforded **2z** (51.7 mg, 91%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.31-7.29 (m, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 4.27 (s, 1H), 0.91 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.6, 128.5, 127.9, 127.8, 76.6, 35.8, 26.4. **IR** (KBr): 2961, 2921, 2102, 1257, 911, 738, 702, 418 cm^{-1}.



2aa

(Azidomethylene)dibenzene (2aa): According to **General Procedure A**, benzophenone-derived *N*-triftosylhydrazone **1aa** (121.3 mg, 0.3 mmol) afforded **2aa** (58.4 mg, 93%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.31-7.30 (m, 6H), 5.71 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.6, 128.7, 128.0, 127.4, 68.5. **IR** (KBr): 3030, 2098, 1492, 1452, 1238, 742, 698, 640 cm^{-1}.

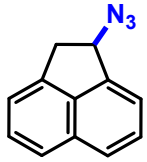
Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc.* 2020, **142**, 11388-11393.



2ab

1-Azido-2,3-dihydro-1H-indene (2ab): According to **General Procedure A**, 2,3-dihydro-1H-inden-1-one-derived *N*-triftosylhydrazone **1ab** (110.5 mg, 0.3 mmol) afforded **2ab** (59.6 mg, 83%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.30-7.25(m, 3H), 4.87-4.85 (m, 1H), 3.11-3.06 (m, 1H), 2.90-2.85 (m, 1H), 2.47-2.42 (m, 1H), 2.15-2.10 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.6, 140.6, 128.8, 126.8, 125.0, 124.5, 65.8, 32.5, 30.4. **IR** (KBr): 2922, 2851, 2093, 1475, 1458, 1322, 1257, 1089, 1019, 801, 752 cm^{-1}.

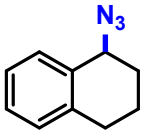
Spectroscopic data in agreement with those reported in *Synthesis* 2015, **47**, 323-329.



2ac

1-Azido-1,2-dihydroacenaphthylene (2ac): According to **General Procedure A**,

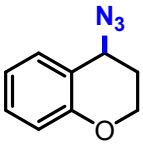
acenaphthylen-1(2H)-one-derived *N*-triftosylhydrazone **1ac** (121.3 mg, 0.3 mmol) afforded **2ac** (29.9 mg, 51%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.58-7.48 (m, 3H), 7.34 (d, *J* = 6.6 Hz, 1H), 5.37 (d, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 18.0 Hz, *J* = 7.8 Hz, 1H), 3.39 (d, *J* = 17.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.4, 141.1, 137.5, 131.4, 128.3, 127.9, 125.4, 123.0, 120.6, 119.9, 63.0, 38.6. **IR** (KBr): 3042, 2921, 2095, 1604, 1494, 1421, 1303, 1246, 971, 776, 556 cm^{-1}.



2ad

1-Azido-1,2,3,4-tetrahydronaphthalene (2ad): According to **General Procedure A**, 3,4-dihydronaphthalen-1(2H)-one-derived *N*-triftosylhydrazone **1ad** (114.7 mg, 0.3 mmol) afforded **2ad** (45.2 mg, 87%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.2 Hz, 1H), 7.24-7.20 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.57-4.56 (m, 1H), 2.87-2.83 (m, 1H), 2.77-2.73 (m, 1H), 2.04-1.95 (m, 3H), 1.84-1.80 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.3, 133.7, 129.4, 129.1, 128.1, 126.1, 56.5, 29.1, 28.7, 19.0. **IR** (KBr): 3021, 2937, 2095, 1490, 1453, 1232, 1059, 943, 765, 741 cm^{-1}.

Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc*. 2020, **142**, 11388-11393.

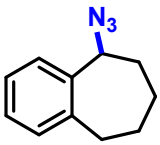


2ae

4-Azidochromane (2ad): According to **General Procedure A**, chroman-4-one-derived *N*-triftosylhydrazone **1ae** (115.3 mg, 0.3 mmol) afforded **2ae** (41.5 mg, 79%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26-7.23 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.61-4.59 (m, 1H), 4.30-4.26 (m, 1H), 4.24-4.20 (m, 1H), 2.20-2.14 (m, 1H), 2.05-2.01 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.6, 130.2, 129.9, 120.5, 119.1, 117.4, 62.0, 54.6, 28.1. **IR** (KBr): 2931, 2886, 2100, 1608, 1583, 1488, 1454, 1310, 1269, 1250, 1226, 1118, 1057, 1018, 755, 624 cm^{-1}.

Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc*. 2020, **142**,

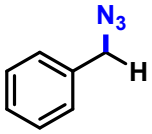
11388-11393.



2af

5-Azido-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (2ae): According to **General Procedure A**, benzaldehyde-derived *N*-triftosylhydrazone **1af** (102.7 mg, 0.3 mmol) afforded **2af** (47.7 mg, 85%) as a white solid; **^{1}H NMR** (600 MHz, CDCl3) δ 7.29 (dd, J = 6.6, 2.4 Hz, 1H), 7.22-7.16 (m, 2H), 7.16-7.14 (m, 1H), 4.79-4.77 (m, 1H), 3.03-2.96 (m, 2H), 2.75-2.71 (m, 1H), 2.13-2.07 (m, 1H), 1.95-1.88 (m, 2H), 1.84-1.81 (m, 1H), 1.74-1.69 (m, 1H), 1.62 (q, *J* = 11.4 H, 1H). ^{13}C NMR (150 MHz, CDCl3) δ 142.0, 139.3, 130.1, 128.0, 127.7, 126.1, 66.9, 35.7, 33.0, 27.6, 27.4. IR (KBr): 3450 ,3020, 2928, 2856, 2102,1450, 1258, 1055, 974, 750 cm^{-1};

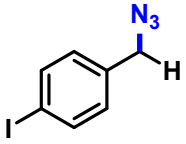
Spectroscopic data in agreement with those reported in *Bioorg. Med. Chem. Lett.* 2016, **26**, 4292–4295



2ag

(Azidomethyl)benzene (2ag): According to **General Procedure A**, benzaldehyde-derived *N*-triftosylhydrazone **1ag** (102.7 mg, 0.3 mmol) afforded **2ag** (26.0 mg, 65%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.26 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 135.4, 128.8, 128.3, 128.2, 54.8. IR (KBr): 2931, 2090 cm^{-1}.

Spectroscopic data in agreement with those reported in *Green Chem.* 2021, **23**, 7499–7505.

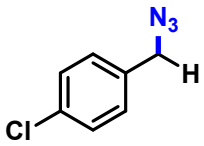


2ah

1-(Azidomethyl)-4-iodobenzene (2ah): According to **General Procedure A**, 4-iodobenzaldehyde-derived *N*-triftosylhydrazone **1ag** (140.5 mg, 0.3 mmol) afforded

2ah (63.7 mg, 82%) as a colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 4.27 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.8, 134.9, 129.9, 93.9, 54.0.

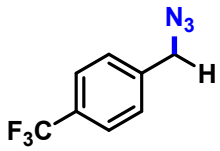
Spectroscopic data in agreement with those reported in *Org. Lett.* 2021, **23**, 118−123.



2ai

1-(Azidomethyl)-4-chlorobenzene (2ai): According to **General Procedure A**, 4-chlorobenzaldehyde-derived *N*-triftosylhydrazone **1ai** (113.0 mg, 0.3 mmol) afforded **2ai** (47.3 mg, 94%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 134.2, 133.9, 129.5, 129.0, 54.0.

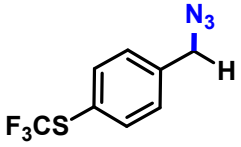
Spectroscopic data in agreement with those reported in *Org. Biomol. Chem.* **2013**, *11*,1463.



2aj

1-(Azidomethyl)-4-(trifluoromethyl)benzene (2aj): According to **General Procedure A**, 4-(trifluoromethyl)benzaldehyde-derived *N*-triftosylhydrazone **1aj** (123.1 mg, 0.3 mmol) afforded **2aj** (50.7mg, 84%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.4, 130.5 (q, *J* = 32.4 Hz), 128.2, 125.8 (q, *J* = 3.5 Hz), 124.0 (q, *J* = 270 Hz), 54.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.8 (s).

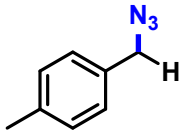
Spectroscopic data in agreement with those reported in *Org. Lett.* 2020, **22**, 5099−5013.



2ak

(4-(Azidomethyl)phenyl)(trifluoromethyl)sulfane (2ak): According to **General Procedure A**, 4-((trifluoromethyl)thio)benzaldehyde-derived *N*-triftosylhydrazone **1aj** (132.7 mg, 0.3 mmol) afforded **2ak** (41.3 mg, 59%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.6 Hz, 2H), 7.38 (d, *J* =9.6 Hz, 2H), 4.41 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.6, 136.7, 129.5 (q, *J* = 306.0 Hz), 128.9, 124.3 (d, *J* = 1.5 Hz), 54.1; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -42.6 (s).

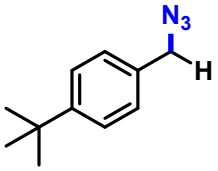
Spectroscopic data in agreement with those reported in *J. Am. Chem. Soc.* 2021, **143**, 16302–16310.



2al

1-(Azidomethyl)-4-methylbenzene (2al): According to **General Procedure A**, 4-methylbenzaldehyde-derived *N*-triftosylhydrazone **1al** (106.9 mg, 0.3 mmol) afforded **2al** (40.6 mg, 92%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21-7.18 (m, 4H), 4.38 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.1, 132.3, 129.5, 128.2, 54.6, 21.1.

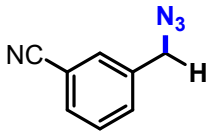
Spectroscopic data in agreement with those reported in *Org. Lett.* 2016, **18**, 1646−1649.



2am

1-(Azidomethyl)-4-(tert-butyl)benzene (2am): According to **General Procedure A**, 4-(tert-butyl)benzaldehyde-derived *N*-triftosylhydrazone **1am** (119.5 mg, 0.3 mmol) afforded **2am** (50.5 mg, 89%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.6 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 2H), 4.29 (s, 2H), 1.32 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.3, 132.4, 128.0, 125.7, 54.5, 34.6, 31.2.

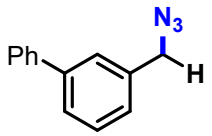
Spectroscopic data in agreement with those reported in *Angew. Chem. Int. Ed.* 2014, **53**, 6914 –6919.



2an

3-(Azidomethyl)benzonitrile (2an): According to **General Procedure A**, 3-formylbenzonitrile-derived *N*-triftosylhydrazone **1an** (110.2 mg, 0.3 mmol) afforded **2an** (28.5 mg, 60%) as a colorless oil; **^{1}H NMR** (600 MHz, CDCl3) δ 7.55-7.53 (m, 2H), 7.50-7.48 (m, 1H), 7.44-7.41 (m, 1H), 4.35 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.0, 132.1, 131.7, 131.2, 129.5, 118.2, 112.8, 53.5.

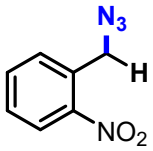
Spectroscopic data in agreement with those reported in *Green Chem.* 2018, **20**, 4418–4422.



2ao

3-(Azidomethyl)-1,1'-biphenyl (2ao): According to **General Procedure A**, [1,1'-biphenyl]-3-carbaldehyde-derived *N*-triftosylhydrazone **1ao** (125.5 mg, 0.3 mmol) afforded **2ao** (45.8mg, 73%) as a colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.6 Hz, 2H), 7.67-7.63 (m, 2H), 7.56 -7.52 (m, 3H), 7.48-7.45 (m, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 4.45 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.8, 140.5, 135.8, 129.2, 128.7, 127.5, 127.1, 127.0, 126.9, 126.8, 54.7.

Spectroscopic data in agreement with those reported in *Angew. Chem. Int. Ed.* 2010, **49**, 6817 –6820

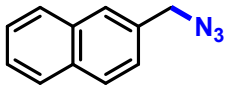


2ap

1-(Azidomethyl)-2-nitrobenzene (2ap): According to **General Procedure A**, 2-nitrobenzaldehyde-derived *N*-triftosylhydrazone **1ap** (116.2 mg, 0.3 mmol) afforded **2ap** (29.4 mg, 55%) as a colorless oil **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 10.2 Hz, 1H), 7.71-7.66 (m, 2H), 7.54 -7.50 (m, 1H), 4.85 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.7, 134.0, 131.6, 130.1, 129.0, 125.3, 52.0.

Spectroscopic data in agreement with those reported in *Green Chem.* 2021, **23**, 7499–

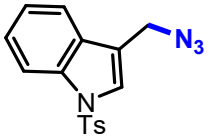
7505.



2aq

(Aidomethyl)benzene (2aq): According to **General Procedure A**, 2-naphthaldehyde-derived *N*-triftosylhydrazone **1aq** (117.7 mg, 0.3 mmol) afforded **2aq** (43.9 mg, 80%) as a white solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87-7.83 (m, 3H), 7.76 (s, 1H), 7.52-7.48 (m, 2H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.49 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 133.2, 133.1, 132.8, 128.8, 127.9, 127.7, 127.2, 126.5, 126.3, 125.8, 55.0.

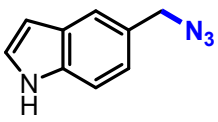
Spectroscopic data in agreement with those reported in *Green Chem.* 2021, **23**, 7499–7505.



2ar

3-(Aidomethyl)-1-tosyl-1H-indole (2ar): According to **General Procedure A**, 1-tosyl-1H-indole-3-carbaldehyde-derived *N*-triftosylhydrazone **1ar** (156.4 mg, 0.3 mmol) afforded **2ar** (90.0 mg, 92%) as a white solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.59 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.43 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.1, 135.3, 134.8, 129.9, 129.2, 126.7, 125.2, 125.0, 123.5, 119.5, 116.6, 113.7, 45.8, 21.4.

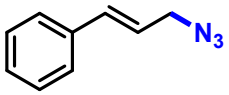
Spectroscopic data in agreement with those reported in *Eur. J. Med. Chem.* 2018, **143,** 1345-1360.



2as

5-(Azidomethyl)-1H-indole (2as): According to **General Procedure A**, 1*H*-indole-5-carbaldehyde-derived *N*-triftosylhydrazone **1as** (110.2 mg, 0.3 mmol) afforded **2as** (25.8 mg, 50%) as a white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.59 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 8.0 Hz, *J* = 2.0

Hz, 1H), 6.56 (t, J = 2.0 Hz, 1H), 4.41 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 135.6, 128.0, 126.7, 124.9, 122.7, 120.9, 111.4, 102.8, 55.6.

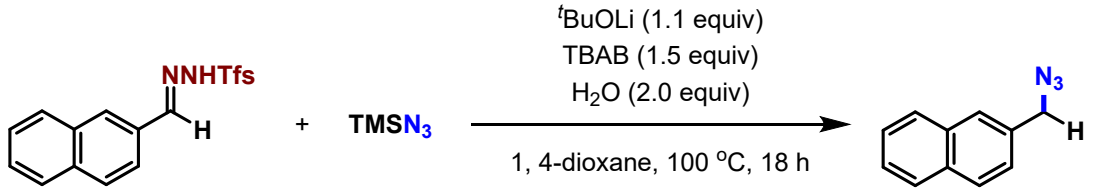


2at

(3-Azidoprop-1-en-1-yl)benzene (2at): According to **General Procedure A**, cinnamaldehyde-derived *N*-triftosylhydrazone **1at** (106.3 mg, 0.3 mmol) afforded **2at** (19.1 mg, 40%) as a yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, J = 9.0 Hz, 2H), 7.38 (t, J = 9.0 Hz, 2H), 7.33-7.30 (m, 1H), 6.68 (d, J = 19.2 Hz, 1H), 6.30-6.24 (m, 1H), 3.96 (d, J = 7.8 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 135.9, 134.4, 128.6, 128.1, 126.6, 122.3, 52.9.

Spectroscopic data in agreement with those reported in *Org. Lett.* 2020, **22**, 5099−5013.

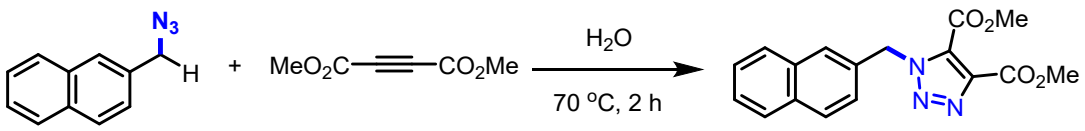
2.3 Gram-Scale Synthesis and Further Application



1aq, 5.68 g, 15 mmol

2aq, **2.19 g**, 80%

Following the general procedure **A**: *N*-triftosylhydrazone **1aq** (5.68 g, 15 mmol, 1.0 equiv), ^{t}BuOLi (1.32 g, 16.5 mmol, 1.1 equiv), TBAB (7.25 g, 22.5 mmol, 1.5 equiv), H_2O (0.54 g, 30 mmol, 2.0 equiv) and $TMSN_3$ (3.64 g, 30 mmol, 2.0 equiv) in 1.4-dioxane (120 mL) were used. The reaction mixture was stirred at 100 °C for 26 h. The crude material was purified by flash column chromatography (petroleum ether) to provide 3b as a colorless oil (2.19 g, 80%).

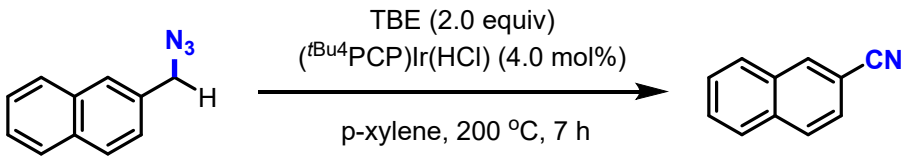


2aq **3a**

A screw capped reaction tube equipped with a magnetic bar was charged with **2aq**

(91.6 mg, 0.5 mmol), dimethyl acetylenedicarboxylate (0.6 mmol) in H_2O (8 mL) at 70 °C. After work-up, the crude residue was purified by flash column chromatography on silica gel to give **3a** (151.3 mg, 95%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81-7.78 (m, 3H), 7.70 (s, 1H), 7.50-7.47 (m, 2H), 7.36-7.34(m, 1H), 5.95 (s, 2H), 3.94 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ160.3, 158.8, 140.2, 133.1, 133.0, 131.2, 129.8, 128.9, 127.9, 127.7, 127.4, 126.7, 126.6, 125.0, 54.0, 53.2, 52.6.

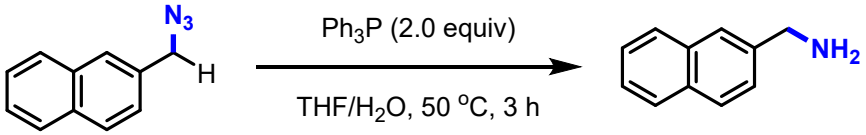
Spectroscopic data in agreement with those reported in *Angew. Chem. Int. Ed.,* 2006, **118**, 1463-1467.



2aq **3b**

In a glovebox, (^{tBu4}PCP)Ir(HCl) (12.4 mg, 4.0 mol%), sodium ^{t}BuOK (7.2 mg, 75 μmol, 15.0 mol%) and *p*-xylene (5.0 mL) were added to a 5 mL thick-wall Schlenk tube. The resulting mixture was added *tert*-butyl ethylene (TBE) (128 μL, 1.0 mmol) and azide **2aq** (91.6 mg, 0.5 mmol). The tube was sealed and heated in a preheated oil-bath at 200 °C for 7 h. After work-up, the crude residue was purified by flash column chromatography on silica gel to give **3b** (51.3 mg, 67%) as a yellow oil. **^{1}H NR** (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.89 (dd, J = 13.2, 8.4 Hz, 3H), 7.65 -7.62 (m, 1H), 7.61-7.58 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 134.6, 134.1, 132.2, 129.1, 129.0, 128.4, 128.0, 127.6, 126.3, 119.2, 109.3.

Spectroscopic data in agreement with those reported in *ChemCatChem*., 2020, *12*, 3661-3665.

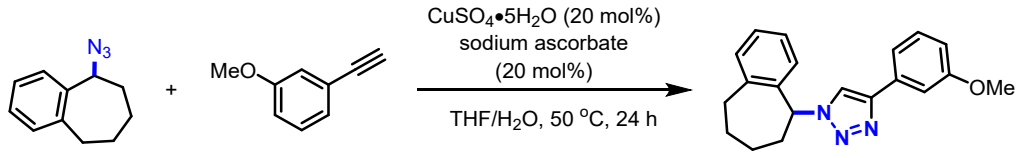


2aq **3c**

Azide **2aq** (91.6 mg, 0.5 mmol), PPh_3 (1.0 mmol), H_2O (200 μL) in THF (2.0 ml) at 50 °C for 3h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether) to give **3c** (68.4 mg, 87%) as a a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 3H), 7.75 (s, 1H), 7.49-

7.47 (m, 3H), 4.04 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.7, 133.5, 132.5, 128.2, 127.7, 127.6, 126.1, 46.6.

Spectroscopic data in agreement with those reported in *Synlett* 2006, **7**, 1047-1050.



2af **3d**

A 15 mL Schlenk tube was charged with **2af** (91.6 mg, 0.5 mmol), 1-ethynyl-3-methoxybenzene (79.3 mg, 1.2 equiv) and THF (1 mL). To the solution was added 20.0 mol% $CuSO_4{\cdot}5H_2O$ (25 mg, 20 mol%), sodium ascorbate (19.8 mg, 20 mol%) and H_2O (1 mL) sequentially at room temperature (25 °C). After vigorous stirring under nitrogen gas for 12 hours, 10 mL of water was added to the reaction mixture and organic layer was separated from extraction with ethyl acetate (20 mL) three times. The crude mixture was purified by flash column chromatography to afford **3d** (138.9 mg 87%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.23-7.19 (m, 2H), 7.12-7.09 (m, 1H), 6.90-6.88 (m, 1H), 6.43 (d, *J* = 6.6 Hz, 1H), 5.90 (d, *J* = 9.6 Hz, 1H), 3.88 (s, 3H), 2.92-2.79 (m, 2H), 2.57-2.39 (m, 2H), 2.10-1.89 (m, 3H), 1.61-1.56 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1, 147.4, 141.0, 139.7, 132.0, 130.2, 129.8, 128.2, 126.8, 125.8, 119.7, 118.1, 114.3, 110.7, 64.9, 55.4, 36.0, 33.7, 29.7, 28.6, 27.0.

Spectroscopic data in agreement with those reported in literature. *Bioorg. Med. Chem. Lett.* 2016, **26**, 4292-4295.

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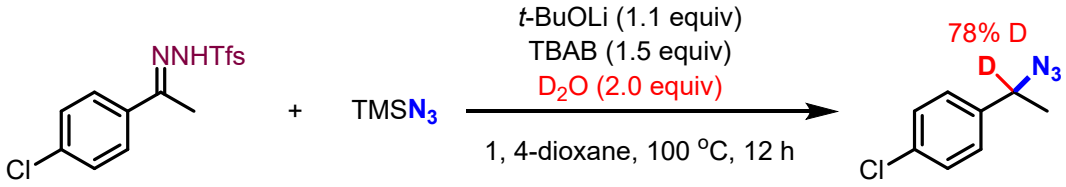
4. Mechanistic Studies

4.1 Deuterium Labelling Study



[D]-2a, 90%

Following the general procedure **A**: *N*-triftosylhydrazone **1a** (5.68 g, 0.3 mmol), ^{t}BuOLi (26.4 mg, 0.33 mmol, 1.1 equiv), TBAB (145.1 mg, 0.45 mmol, 1.5 equiv), D_2O (12 mg, 0.6 mmol, 2.0 equiv) and $TMSN_3$ (75.8 g, 0.6 mmol, 2.0 equiv) in 1.4-dioxane (4 mL) were used. The reaction mixture was stirred at 100 °C for 12 h. The crude material was purified by flash column chromatography (petroleum ether) to provide **[d]-2a** (49.3 mg, 90%).

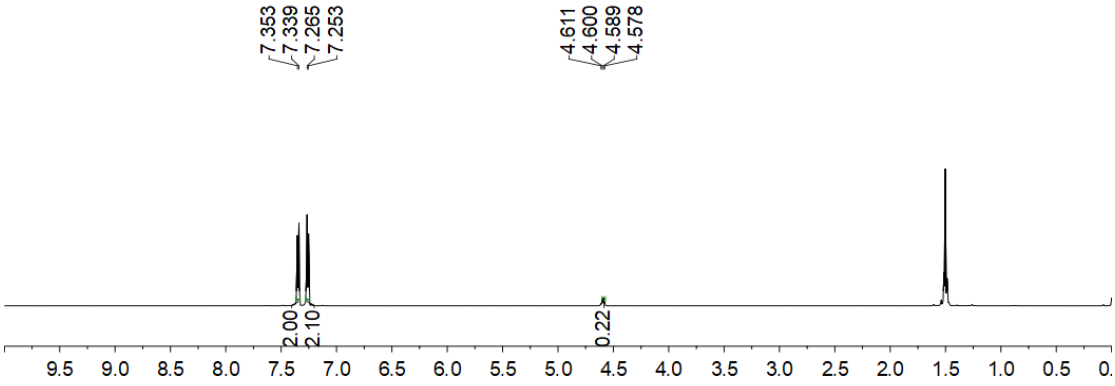


Fig. S1 Deuterium validation experiment.

4.2 Computational Method.

All calculations were performed using Gaussian 16 program package[1] using the B3LYP functional[2,3] and GD3BJ empirical dispersion[4] . All the other atoms C, H, O, N, S and Cl were described with 6-31G(d,p) basis set[5,6]. The nature of the extrema (minimum) was established with analytical frequencies calculations and geometry optimizations were computed without any symmetry constrained in solvent (1,4-dioxane) by using the SMD[7] solvation model. Intrinsic reaction coordinate (IRC)[8,9] calculations were carried out to ascertain the true nature of the transition states.

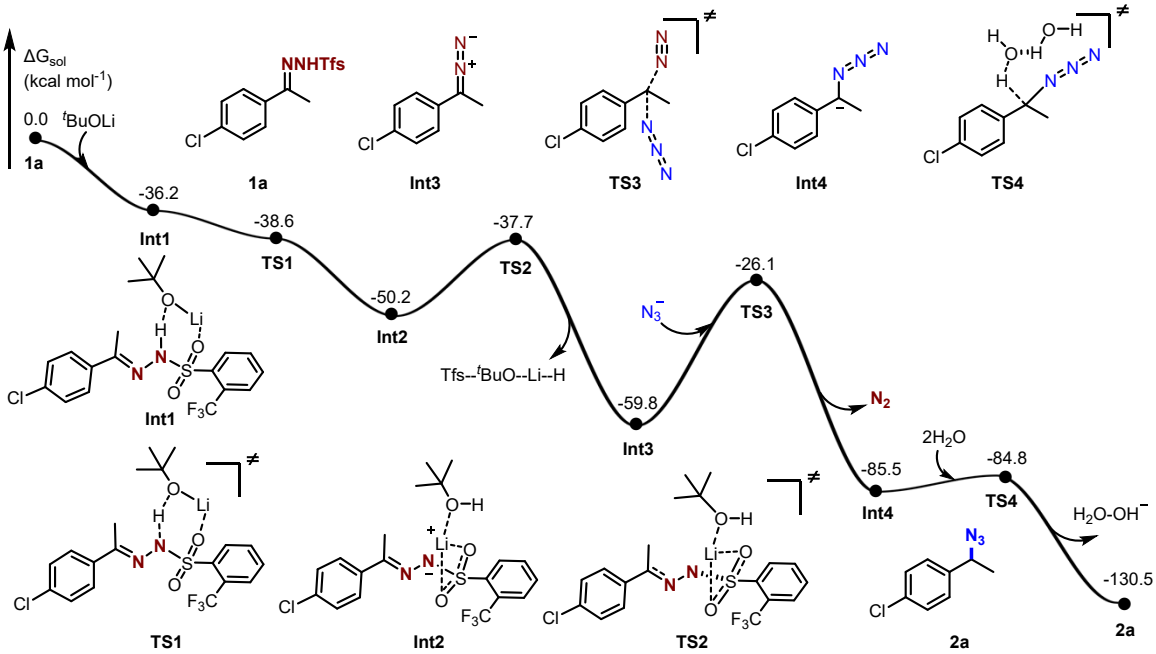


Fig. S2 Plausible mechanism based on DFT-computed free-energy profile at the SMD (1,4-dioxane)//B3LYP/6-31G(d,p) level of theory (ΔG, in kcal·mol $^{-1}$).

Int1

Zero-point correction=	0.377987 (Hartree/Particle)
Thermal correction to Energy=	0.407887
Thermal correction to Enthalpy=	0.408831
Thermal correction to Gibbs Free Energy=	0.313085
Sum of electronic and zero-point Energies=	-2237.105303
Sum of electronic and thermal Energies=	-2237.075403
Sum of electronic and thermal Enthalpies=	-2237.074459
Sum of electronic and thermal Free Energies=	-2237.170205

C	5.21150300	0.09286200	-0.21685500
C	3.84117600	0.30466000	-0.11997400
C	2.97986500	-0.71108000	0.33436200
C	3.53587400	-1.95364700	0.67385600
C	4.90875300	-2.18372100	0.57063300
C	5.73681800	-1.15491500	0.12987100
H	5.87068000	0.88373100	-0.55912000
H	3.41880500	1.26405000	-0.39631000
H	2.89978900	-2.76666300	1.00713800
H	5.32796400	-3.15072400	0.82739500
N	1.08613100	0.58951400	-0.15521000
N	-0.28031700	0.89896200	-0.09565600
C	-2.75140700	0.50439200	1.39479100
C	-3.69516400	0.33406800	2.40642400

C	-4.51306500	-0.79419800	2.40740400
C	-4.39747400	-1.73674100	1.38635500
C	-3.46637300	-1.57440100	0.35382600
C	-2.62611000	-0.44625000	0.37884600
H	-3.78036500	1.08050200	3.19038800
H	-5.24436000	-0.94419500	3.19577900
H	-5.04143000	-2.60785800	1.38120000
S	-1.38797200	-0.06344100	-0.89808600
O	-2.13425900	0.81303100	-1.85552600
O	-0.76812700	-1.28259400	-1.40233300
C	-3.41987200	-2.64270000	-0.72244400
F	-4.52231000	-3.43603000	-0.66970600
F	-3.38560400	-2.11816800	-1.96439300
F	-2.35517800	-3.46394300	-0.57965500
H	-2.09642900	1.36836500	1.39702500
Cl	7.46639600	-1.42865800	0.00453600
C	1.51707000	-0.47339800	0.43765500
C	0.67622600	-1.43180700	1.23805200
H	-0.23375700	-0.93387700	1.58010300
H	0.37939000	-2.30157000	0.64217900
H	1.22732100	-1.78144000	2.11563900
H	-0.45295700	1.94775500	-0.35829300
C	-0.34129700	4.39793800	-0.06922800
C	-0.58155300	4.21464800	1.44292100
H	-1.65914400	4.19033600	1.64840100
H	-0.14366000	3.26851800	1.78431800
H	-0.13589500	5.02687400	2.03097100
C	1.17238200	4.40330100	-0.35606100
H	1.61669000	3.44835600	-0.05248500
H	1.34718400	4.52891700	-1.43119400
H	1.68678000	5.21322800	0.17715000
C	-0.96459300	5.72543600	-0.53270000
H	-0.80667900	5.85667800	-1.61057800
H	-2.04494700	5.72098700	-0.34047500
H	-0.52662600	6.58857400	-0.01523800
O	-0.94420400	3.33797600	-0.76480700
Li	-1.92208100	2.65055100	-1.96231100

TS1

Zero-point correction=	0.375398 (Hartree/Particle)
Thermal correction to Energy=	0.405559
Thermal correction to Enthalpy=	0.406504
Thermal correction to Gibbs Free Energy=	0.310673

Sum of electronic and zero-point Energies= -2237.109340
Sum of electronic and thermal Energies= -2237.079179
Sum of electronic and thermal Enthalpies= -2237.078235
Sum of electronic and thermal Free Energies= -2237.174066

C	5.07639900	-0.33778500	0.05208400
C	3.72614900	-0.02244600	0.15259300
C	2.75279000	-1.02820500	0.29464600
C	3.17783300	-2.36508000	0.31961800
C	4.52930400	-2.69722300	0.20843400
C	5.46925500	-1.67844600	0.07974800
H	5.82132300	0.44481500	-0.04741300
H	3.40797500	1.01329300	0.12331200
H	2.45383800	-3.16841200	0.40662700
H	4.84597900	-3.73476100	0.21913800
N	1.00520200	0.51300300	0.02254600
N	-0.29852100	1.00143300	0.07262500
C	-2.66812300	0.43212500	1.73366200
C	-3.55182600	0.13592900	2.77039800
C	-4.50070100	-0.87080200	2.60289900
C	-4.57183200	-1.56354800	1.39472700
C	-3.70124600	-1.26873300	0.33882600
C	-2.73098600	-0.26762600	0.52698800
H	-3.48914900	0.68715800	3.70391700
H	-5.18847700	-1.11940500	3.40542700
H	-5.31605400	-2.33952600	1.26172300
S	-1.53594400	0.26441300	-0.74415700
O	-2.27792100	1.36911100	-1.44047500
O	-1.09499900	-0.88313900	-1.53270500
C	-3.85626100	-2.06972100	-0.94033200
F	-5.04630600	-2.72821800	-0.96109500
F	-3.83120000	-1.29307600	-2.04174100
F	-2.89870900	-3.01619000	-1.06727700
H	-1.90488100	1.19304600	1.85689600
Cl	7.17372400	-2.08235900	-0.05070700
C	1.31052600	-0.68165300	0.40106600
C	0.36268900	-1.70560100	0.96830300
H	-0.49327200	-1.21098400	1.43109700
H	-0.02002300	-2.37986000	0.19443000
H	0.86293200	-2.30174300	1.73663400
H	-0.29406700	2.17034300	-0.13066700
C	0.67678600	4.27883000	-0.08083200
C	1.05228000	4.00555200	1.38605600
H	0.19032100	4.19695400	2.03629400

H	1.35603200	2.96041600	1.51409200
H	1.88165200	4.64478700	1.71279500
C	1.87012900	3.95533200	-0.99654800
H	2.12479700	2.89330100	-0.91480300
H	1.61096400	4.16390800	-2.04195400
H	2.75380700	4.55198200	-0.73620100
C	0.25977700	5.74648500	-0.25036200
H	-0.02092000	5.94278600	-1.29333500
H	-0.60348300	5.97057700	0.38767100
H	1.07406100	6.43182000	0.01555600
O	-0.42149700	3.46082100	-0.44084000
Li	-1.71157600	3.11222000	-1.52251600

Int2

Zero-point correction=	0.379220 (Hartree/Particle)
Thermal correction to Energy=	0.410108
Thermal correction to Enthalpy=	0.411052
Thermal correction to Gibbs Free Energy=	0.314274
Sum of electronic and zero-point Energies=	-2237.127615
Sum of electronic and thermal Energies=	-2237.096728
Sum of electronic and thermal Enthalpies=	-2237.095783
Sum of electronic and thermal Free Energies=	-2237.192561

C	-4.81202400	-0.04029100	-0.84644600
C	-3.51246000	-0.51746100	-0.71607100
C	-3.21003400	-1.59390600	0.13945600
C	-4.26757500	-2.19066600	0.84574700
C	-5.57739700	-1.72152200	0.72621100
C	-5.83887600	-0.64589200	-0.11812400
H	-5.03487200	0.78614000	-1.51392500
H	-2.70650600	-0.06684300	-1.28348500
H	-4.07376700	-3.02368000	1.51402400
H	-6.38373400	-2.18522800	1.28498300
N	-0.88693000	-1.24700500	-0.06023400
N	0.41328600	-1.70341000	0.06089700
C	2.99749600	-2.72245600	-0.40405200
C	4.19137200	-3.44067700	-0.45204700
C	5.40546900	-2.77824000	-0.29308400
C	5.41825100	-1.39945400	-0.08885900
C	4.22957000	-0.65960400	-0.03604800
C	3.00142000	-1.34320900	-0.18482700
H	4.16462000	-4.51389100	-0.61611900
H	6.34370200	-3.32349400	-0.32912700

H	6.36508800	-0.88787700	0.03104900
S	1.40941800	-0.49311700	-0.21670000
O	1.30971700	0.23180500	-1.54254900
O	1.46041000	0.58912400	0.84014300
C	4.39092800	0.82383900	0.23993600
F	5.66271500	1.23228700	0.01769500
F	3.62639800	1.62778900	-0.58257900
F	4.09466100	1.16633300	1.50564000
H	2.04153300	-3.21566400	-0.52304300
Cl	-7.48580200	-0.04622200	-0.27984000
C	-1.81848200	-2.07391900	0.28832400
C	-1.55908900	-3.45239600	0.84286100
H	-0.54461900	-3.76999400	0.59654200
H	-1.64999200	-3.45943500	1.93803900
H	-2.27362200	-4.18071500	0.44440700
H	0.04267400	3.47231600	-1.70087100
C	-0.70783900	3.59591200	0.15541400
C	-1.31831600	4.96684500	-0.13232300
H	-0.56334600	5.75452900	-0.03936600
H	-1.74214600	5.00604300	-1.14443900
H	-2.12986500	5.17688800	0.57266500
C	-1.72205600	2.46716800	-0.02752900
H	-2.14284800	2.48343600	-1.04114000
H	-1.26648600	1.48698700	0.14056200
H	-2.55363400	2.58189300	0.67640300
C	-0.05507400	3.55025400	1.53418200
H	0.38733400	2.56851700	1.72884800
H	0.72059800	4.31934900	1.61911100
H	-0.81062800	3.73762600	2.30411900
O	0.40043400	3.39024900	-0.80135300
Li	1.53460800	1.90286200	-0.57081700

TS2

Zero-point correction=	0.376715 (Hartree/Particle)
Thermal correction to Energy=	0.407584
Thermal correction to Enthalpy=	0.408528
Thermal correction to Gibbs Free Energy=	0.310333
Sum of electronic and zero-point Energies=	-2237.106178
Sum of electronic and thermal Energies=	-2237.075309
Sum of electronic and thermal Enthalpies=	-2237.074365
Sum of electronic and thermal Free Energies=	-2237.172559

C	-5.37343000	-0.52029300	-0.84075800

C	-4.00314200	-0.57306500	-1.06606700
C	-3.11285300	-1.04835900	-0.08104200
C	-3.65966600	-1.46286700	1.14643300
C	-5.03447000	-1.41123200	1.38718900
C	-5.88367900	-0.94170600	0.39027900
H	-6.04576600	-0.15872600	-1.61224200
H	-3.60005300	-0.24559300	-2.01858500
H	-3.01173200	-1.81688900	1.94135800
H	-5.43804600	-1.73009000	2.34274800
N	-1.23078100	-0.48619300	-1.39165000
N	-0.11441500	-0.21173300	-1.94511400
C	2.43628600	-2.56379800	-1.40848700
C	3.28226100	-3.66858900	-1.29961200
C	4.31221500	-3.65608600	-0.36113500
C	4.50117800	-2.53805100	0.45294800
C	3.66463500	-1.41974000	0.34521300
C	2.61676800	-1.44800400	-0.59428500
H	3.13215800	-4.53136100	-1.94202900
H	4.97443200	-4.51032900	-0.25853300
H	5.30876700	-2.53261400	1.17590200
S	1.41047500	-0.07861200	-0.93553600
O	2.24294000	0.87158100	-1.76277800
O	1.12757000	0.56094100	0.41116200
C	3.93510400	-0.26721100	1.28711700
F	5.17169700	-0.34446800	1.82890500
F	3.90431400	0.96798300	0.66262600
F	3.06691500	-0.19992100	2.31302600
H	1.62327800	-2.55776800	-2.13069100
Cl	-7.61842700	-0.87326800	0.68125900
C	-1.65802100	-1.08777000	-0.32341500
C	-0.75208700	-1.84044700	0.61923500
H	0.14100500	-2.19188000	0.09546800
H	-0.41204000	-1.23000800	1.46414200
H	-1.26313200	-2.72708100	1.00796600
H	1.24111700	3.49617700	-1.65305300
C	0.14614900	4.06187900	-0.06616500
C	-0.07568900	5.52080300	-0.46500300
H	0.77716500	6.13730700	-0.16233900
H	-0.20221200	5.61322000	-1.55063800
H	-0.97978500	5.91564800	0.01169500
C	-1.00224200	3.16283700	-0.52683900
H	-1.12809900	3.20967700	-1.61571200
H	-0.82222200	2.12228300	-0.24854000
H	-1.94244500	3.48975500	-0.06892200

C	0.39678000	3.92092500	1.43356800
H	0.54459200	2.87007700	1.70645700
H	1.27530300	4.50248600	1.73604400
H	-0.46671500	4.29246000	1.99455100
O	1.39554300	3.60937600	-0.69910200
Li	2.27504400	2.03639500	-0.16028100

Int3

Zero-point correction=	0.144761 (Hartree/Particle)
Thermal correction to Energy=	0.158067
Thermal correction to Enthalpy=	0.159011
Thermal correction to Gibbs Free Energy=	0.102775
Sum of electronic and zero-point Energies=	-1042.944990
Sum of electronic and thermal Energies=	-1042.931684
Sum of electronic and thermal Enthalpies=	-1042.930740
Sum of electronic and thermal Free Energies=	-1042.986976

C	2.32142800	1.08952900	0.18984500
C	1.05074400	1.65728300	0.14209100
C	-0.09504800	0.86359400	-0.07470700
C	0.07073900	-0.52594900	-0.24252100
C	1.34232400	-1.09628100	-0.19412700
C	2.45624100	-0.28822200	0.02047700
H	3.19640800	1.70957900	0.35827500
H	0.95432600	2.73138600	0.27832900
H	-0.77735100	-1.18813900	-0.42854200
H	1.44972600	-2.16808800	-0.32622500
N	-1.55638100	2.72680700	-0.01810600
N	-1.64630300	3.87420600	0.08169700
Cl	4.07115300	-1.01117500	0.07960400
C	-1.44078300	1.43938400	-0.13254700
C	-2.70517000	0.62679800	-0.29007500
H	-3.57229100	1.28880400	-0.37331900
H	-2.65508000	-0.00414900	-1.18440800
H	-2.86660800	-0.04767700	0.56080200
N	-3.53001800	-2.37438400	1.10997700
N	-2.88612700	-2.57890800	0.13505400
N	-2.22997000	-2.75179900	-0.84416300

TS3

Zero-point correction=	0.142862 (Hartree/Particle)
Thermal correction to Energy=	0.155932

Thermal correction to Enthalpy= 0.156876
Thermal correction to Gibbs Free Energy= 0.101035
Sum of electronic and zero-point Energies= -1042.891456
Sum of electronic and thermal Energies= -1042.878386
Sum of electronic and thermal Enthalpies= -1042.877442
Sum of electronic and thermal Free Energies= -1042.933283

C	-1.97135700	-1.26993200	-0.17767700
C	-0.59468400	-1.43511700	-0.04372100
C	0.25150300	-0.34869200	0.25376900
C	-0.34549000	0.91916300	0.42261900
C	-1.72335700	1.09683300	0.29241800
C	-2.52743100	-0.00021400	-0.00276600
H	-2.60766300	-2.11779200	-0.41244800
H	-0.16010800	-2.42029500	-0.16777500
H	0.26691500	1.78786400	0.64102400
H	-2.16424100	2.08077600	0.42103500
N	2.13871500	-1.87986500	0.06762100
N	2.89298700	-2.32908900	-0.74538900
Cl	-4.28312800	0.21038400	-0.14098400
C	1.73848200	-0.48437800	0.28893900
C	2.42268200	0.01733600	1.55032100
H	3.51007700	-0.04436300	1.42384500
H	2.15167800	1.05734600	1.75954900
H	2.12454300	-0.59245100	2.40929600
N	2.36712300	0.51736700	-0.99715600
N	2.42704000	1.68785300	-0.68502300
N	2.48697500	2.81836000	-0.38022600

Int4

Zero-point correction= 0.184334 (Hartree/Particle)
Thermal correction to Energy= 0.200270
Thermal correction to Enthalpy= 0.201215
Thermal correction to Gibbs Free Energy= 0.140085
Sum of electronic and zero-point Energies= -1086.303619
Sum of electronic and thermal Energies= -1086.287682
Sum of electronic and thermal Enthalpies= -1086.286738
Sum of electronic and thermal Free Energies= -1086.347867

C	-2.31074100	-0.67391200	-1.03391100
C	-0.94725200	-0.76721600	-0.79316700
C	-0.33351100	-0.18073400	0.35669100
C	-1.22247600	0.47579400	1.26101500

C	-2.59009500	0.57626700	1.01714800
C	-3.13550500	0.00704000	-0.13232700
H	-2.73929100	-1.13062100	-1.92224600
H	-0.31840800	-1.29708300	-1.50121600
H	-0.83248000	0.91776200	2.17279300
H	-3.23303700	1.08715900	1.72926400
Cl	-4.88385900	0.12294100	-0.44014400
C	1.08048300	-0.20955900	0.57130300
C	1.66347300	0.06287500	1.93742300
H	1.38883400	-0.69611000	2.69803100
H	2.75873100	0.10818800	1.89908500
H	1.32966400	1.03434200	2.32203500
N	1.76284300	-1.20808800	-0.21829100
N	2.95678200	-1.41412400	-0.09811900
N	4.09149000	-1.67228300	-0.06296000
O	2.19191600	2.00391300	-0.85812800
H	1.68946100	1.25018700	-0.39324000
H	2.06151600	2.77162200	-0.28178000
O	4.94603600	1.28329000	-0.89739400
H	4.00138800	1.55765500	-0.93121000
H	4.91154900	0.32741500	-0.71435300

TS4

Zero-point correction=	0.180834 (Hartree/Particle)
Thermal correction to Energy=	0.196630
Thermal correction to Enthalpy=	0.197574
Thermal correction to Gibbs Free Energy=	0.136806
Sum of electronic and zero-point Energies=	-1086.302778
Sum of electronic and thermal Energies=	-1086.286982
Sum of electronic and thermal Enthalpies=	-1086.286038
Sum of electronic and thermal Free Energies=	-1086.346806

C	2.22018700	-0.95368500	-0.80849000
C	0.86389200	-0.63694800	-0.80130100
C	0.34100000	0.42873900	-0.02739400
C	1.27737900	1.16249100	0.74029300
C	2.63861000	0.85171500	0.74734600
C	3.10437200	-0.20700400	-0.02862200
H	2.58509800	-1.77688400	-1.41668700
H	0.18422500	-1.22583000	-1.40909600
H	0.94446200	1.99529300	1.35228600
H	3.32825100	1.43754100	1.34893100
Cl	4.83706400	-0.60015000	-0.03734700

C	-1.10473000	0.70253200	0.03834000
C	-1.52276800	2.13379300	0.36488300
H	-1.12473800	2.88328900	-0.34175500
H	-2.61692600	2.22292700	0.36809400
H	-1.19275300	2.41610100	1.37214600
N	-1.74616000	0.22714700	-1.21596100
N	-2.95895900	0.24983000	-1.32586400
N	-4.09303700	0.24456300	-1.55281400
O	-2.35568900	-0.79031600	1.81235400
H	-1.71281200	-0.11346300	1.04414200
H	-2.50713100	-0.23703100	2.59566900
O	-4.73639800	-1.78428500	0.89941600
H	-3.86766100	-1.45712600	1.26842000
H	-4.83396400	-1.28604500	0.07072900

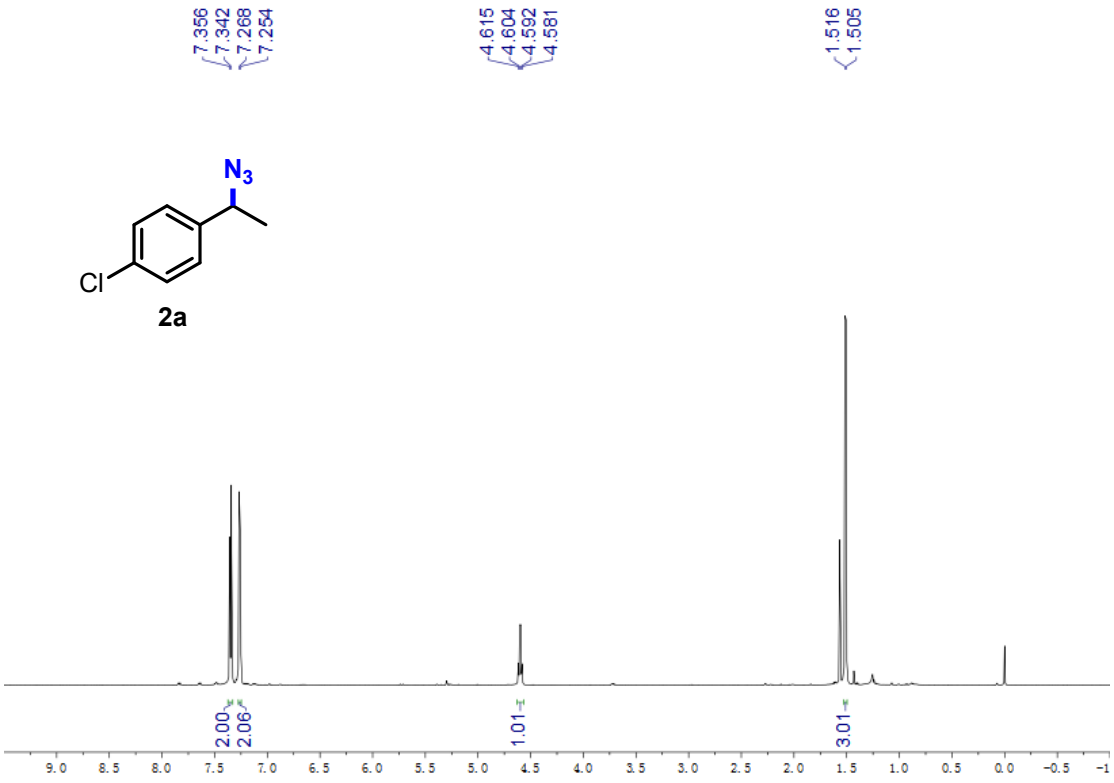
2a

Zero-point correction=	0.184283 (Hartree/Particle)
Thermal correction to Energy=	0.200390
Thermal correction to Enthalpy=	0.201334
Thermal correction to Gibbs Free Energy=	0.136106
Sum of electronic and zero-point Energies=	-1086.288238
Sum of electronic and thermal Energies=	-1086.272130
Sum of electronic and thermal Enthalpies=	-1086.271186
Sum of electronic and thermal Free Energies=	-1086.336415

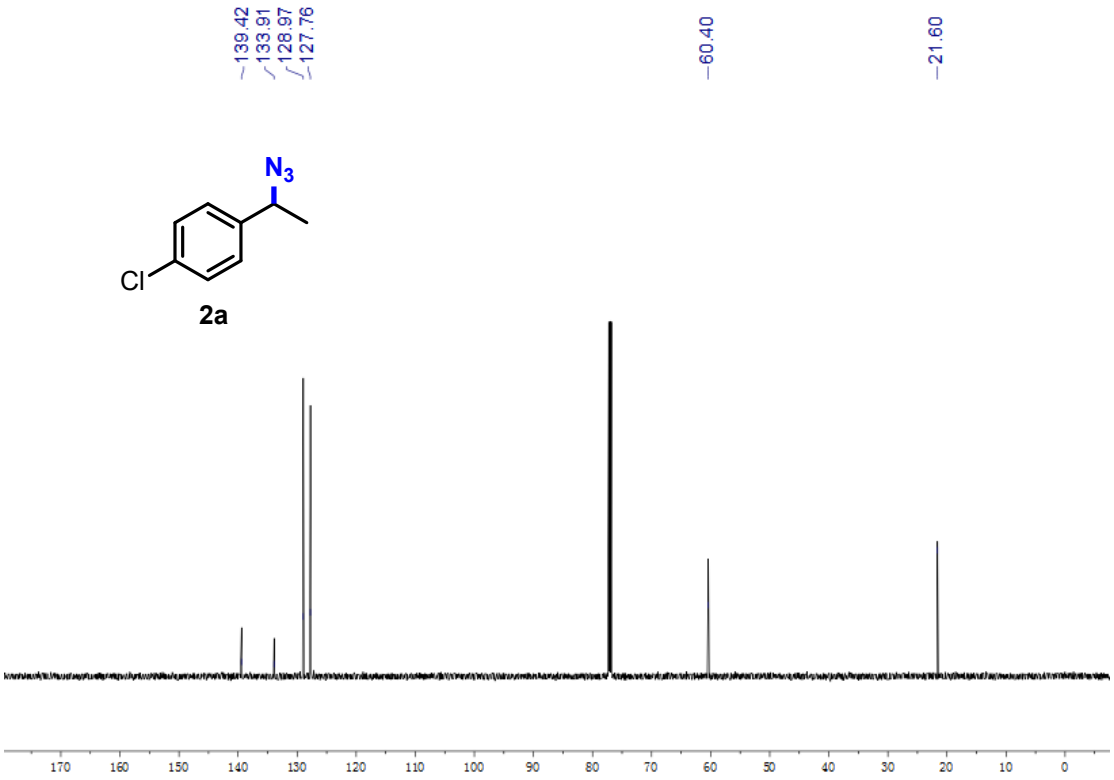
C	4.60011500	0.41085000	-0.17179500
C	3.78105800	-0.69740300	-0.39319700
C	2.38786300	-0.56279100	-0.46784100
C	1.80992500	0.70350300	-0.30010800
C	2.62020300	1.82214400	-0.07799600
C	4.00168500	1.66164000	-0.02100600
H	5.67936600	0.30868000	-0.11233300
H	4.23378900	-1.68086700	-0.49703600
H	0.71857700	0.78213300	-0.34329500
H	2.17626500	2.80272700	0.06219500
Cl	5.03519300	3.07719100	0.25742700
C	1.48435900	-1.75577600	-0.72089700
C	1.71985100	-2.39927600	-2.08298700
H	2.75151300	-2.75770700	-2.19470600
H	1.03931700	-3.24699400	-2.22197100
H	1.52024000	-1.66027100	-2.86603000
N	1.72621200	-2.83370200	0.30774900
N	1.42184100	-2.54140200	1.46244600

N	1.19214300	-2.37590100	2.57253900
O	-14.01891900	0.54368400	-1.33293900
H	0.43353300	-1.41069900	-0.64110700
H	-14.91197500	0.46419200	-1.70189200
O	-14.24683800	0.97719500	1.24831800
H	-14.19861300	0.83836200	0.22949500
H	-13.72595400	0.24083600	1.60321500

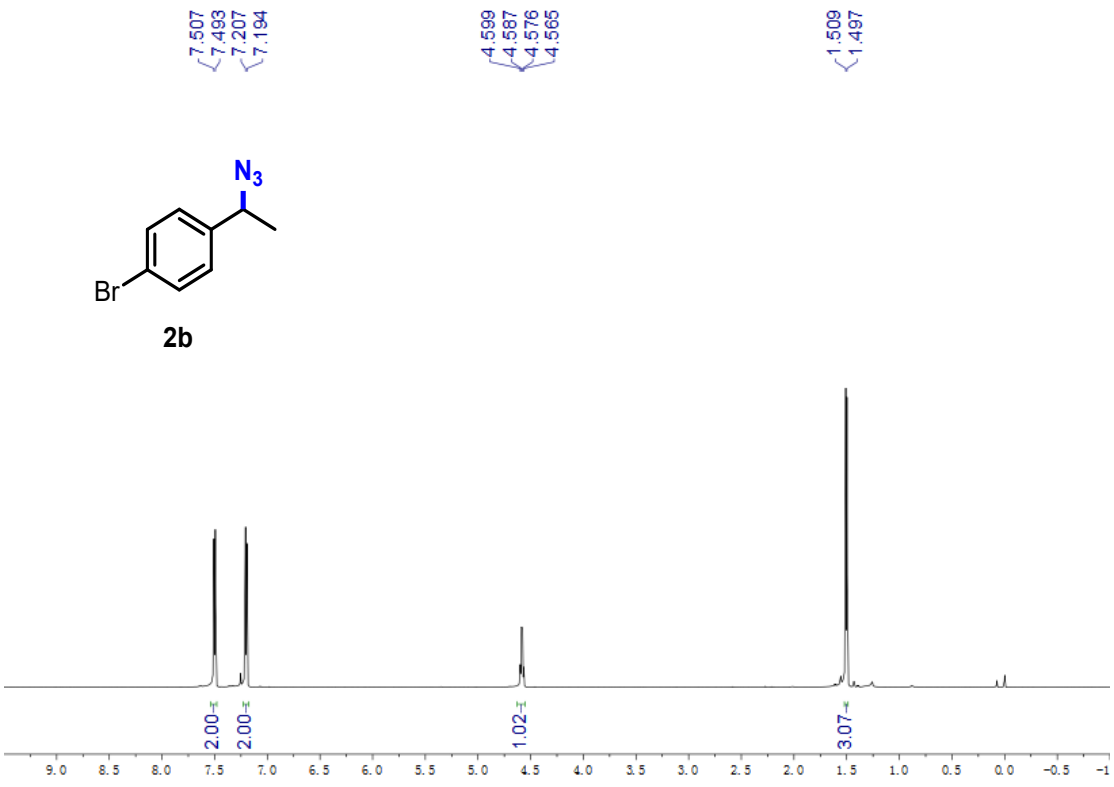
5. NMR Spectra Copies



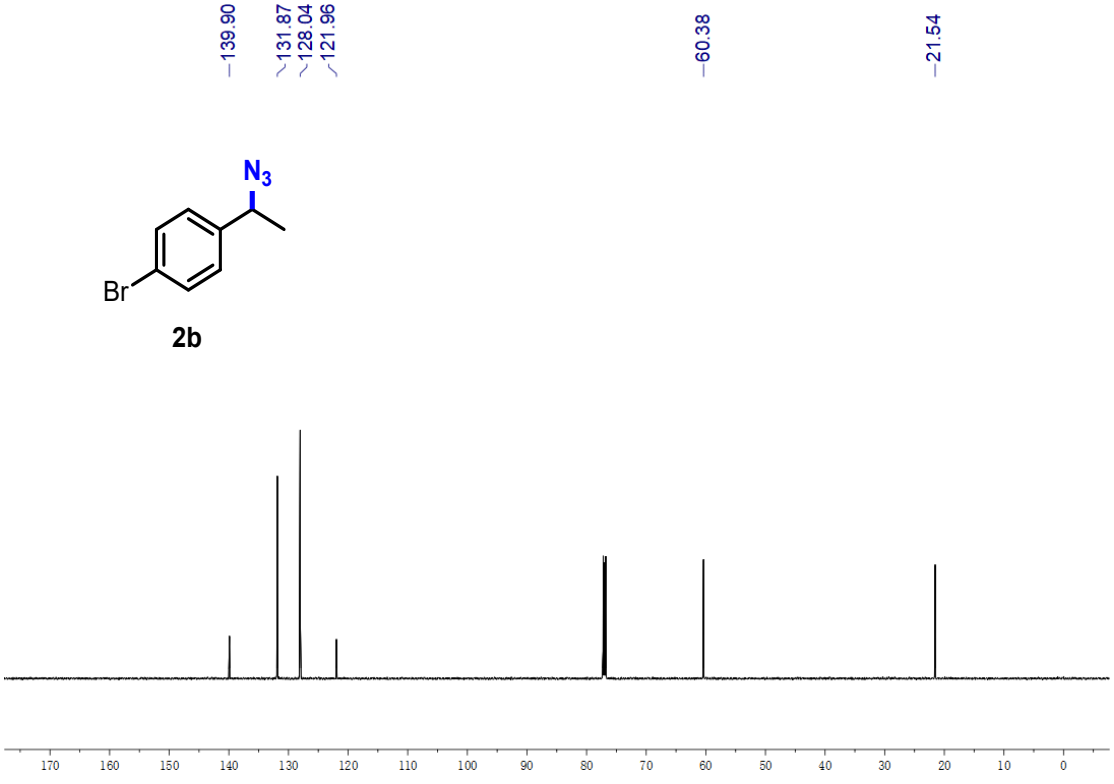
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a**.



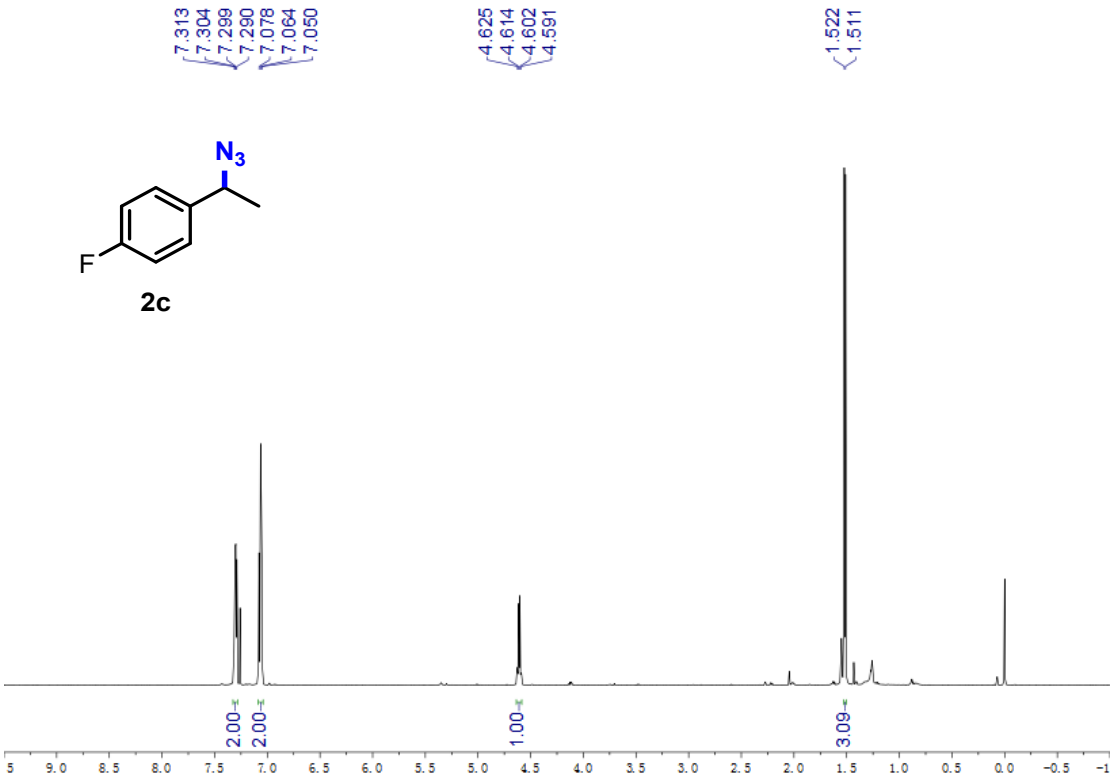
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2a**



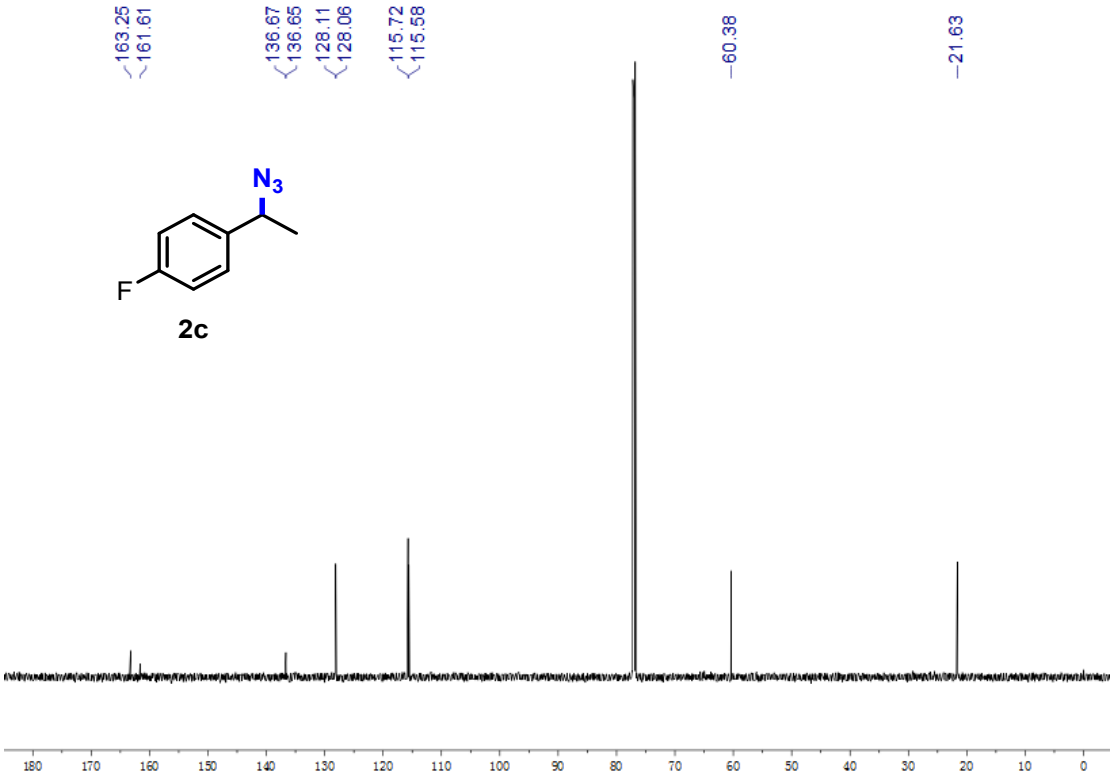
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b**.



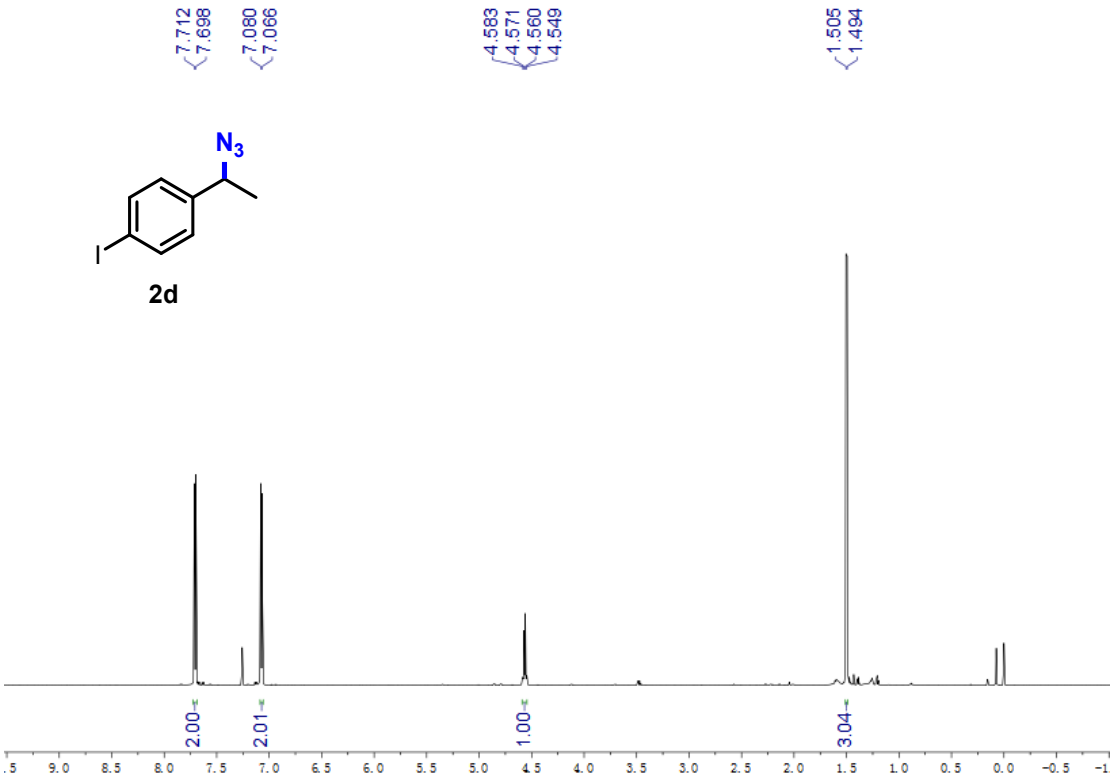
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2b**



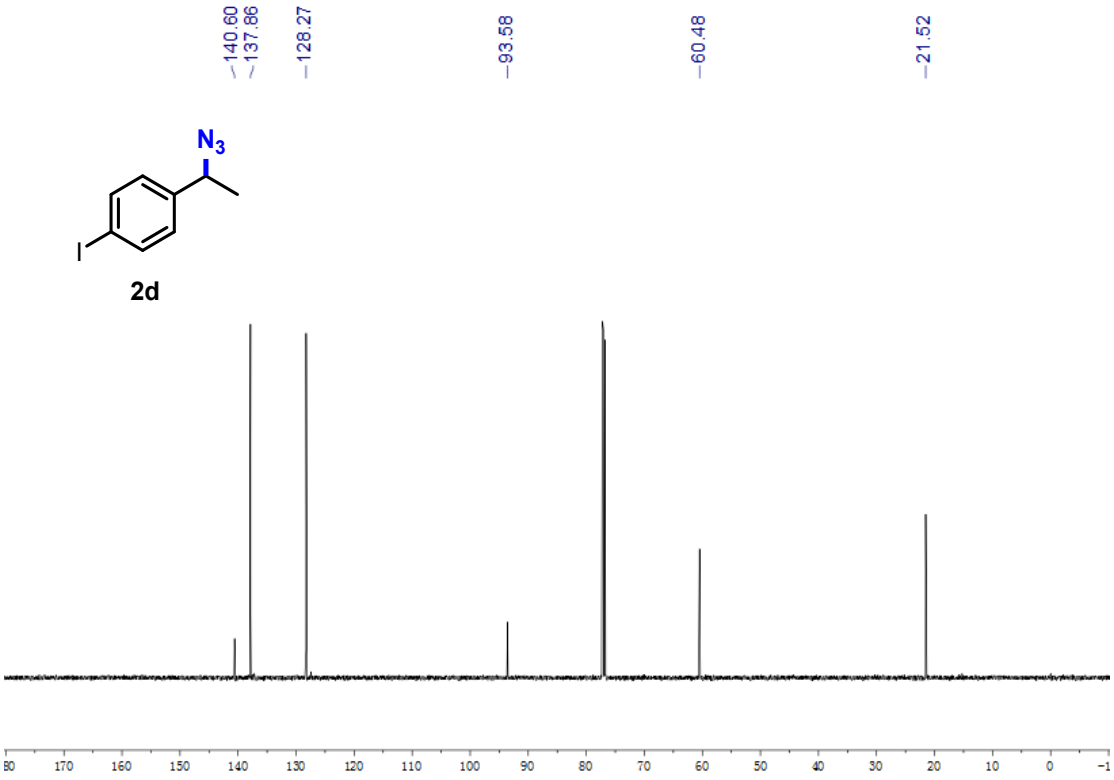
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c**.



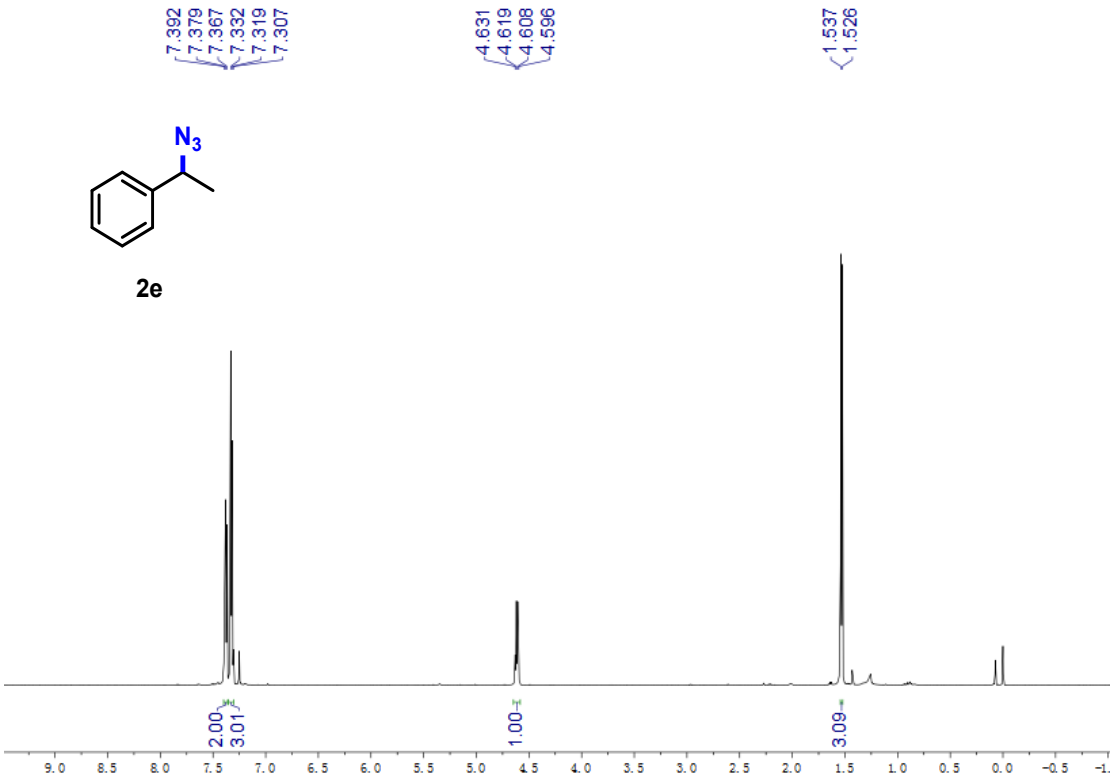
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2c**



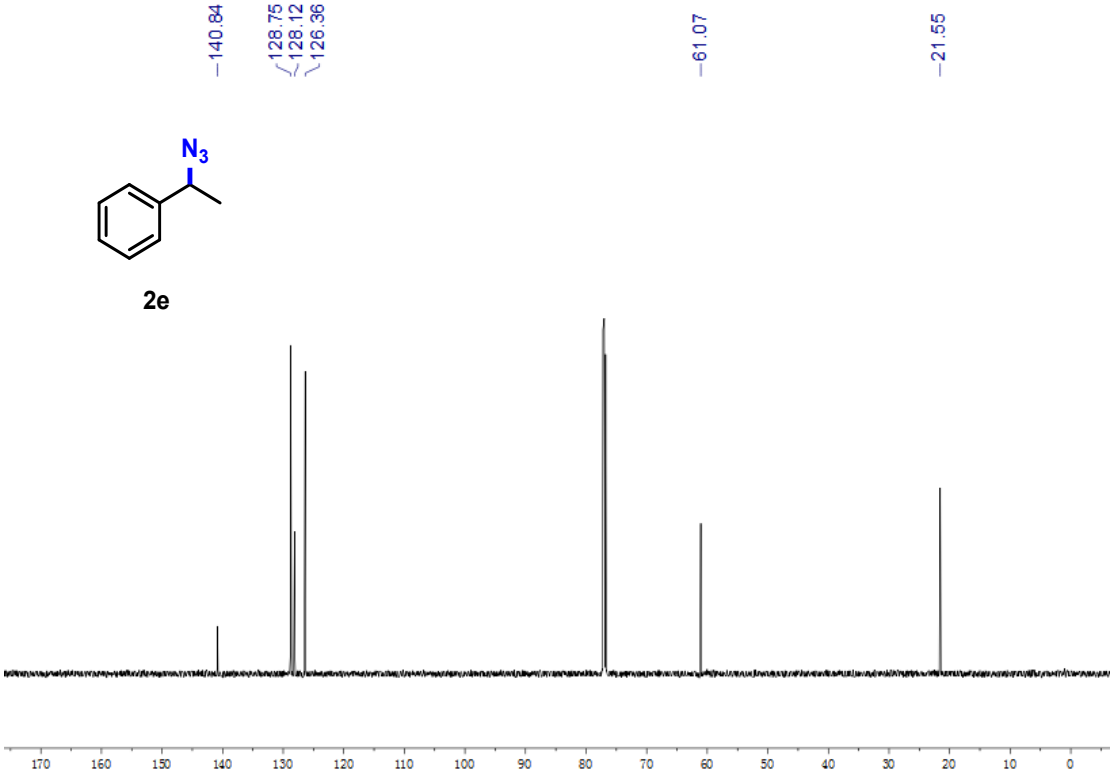
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2d**.



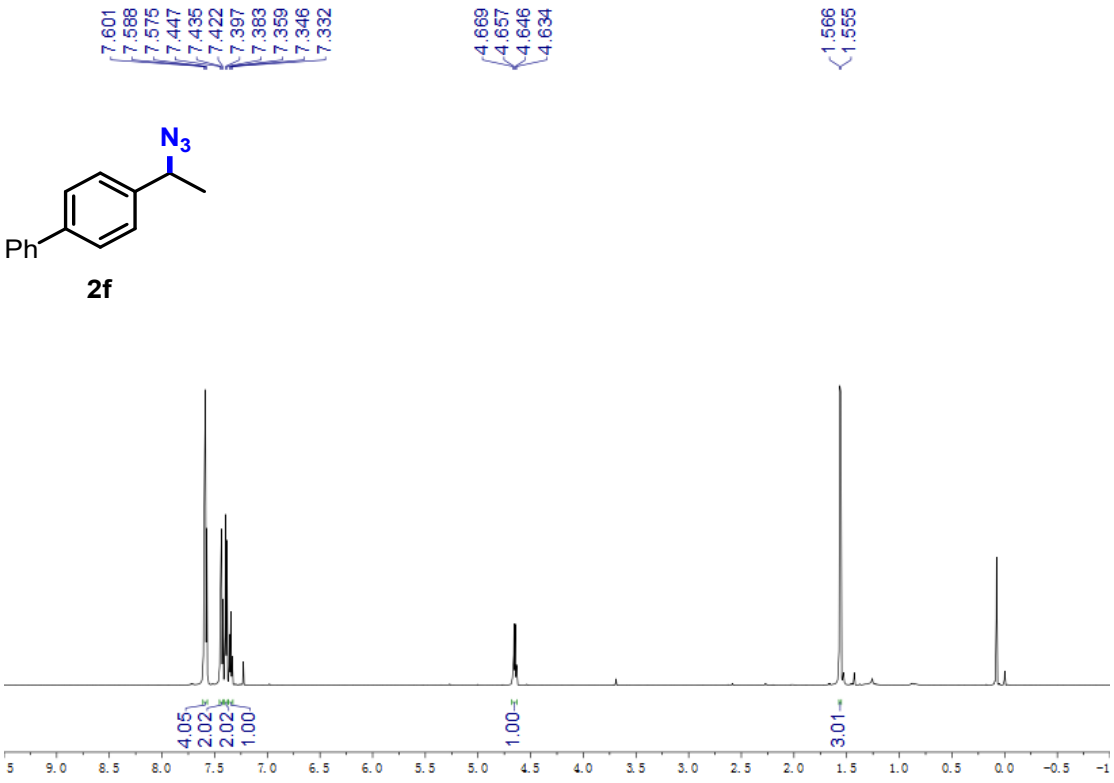
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2d**



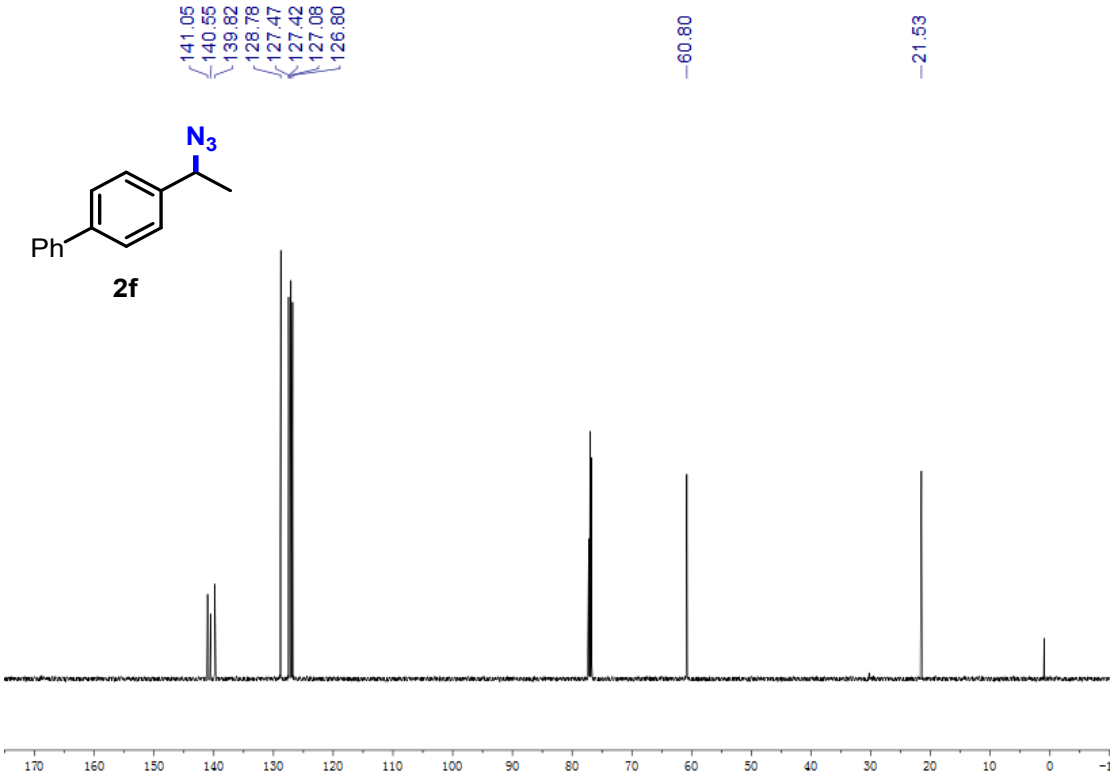
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2e**.



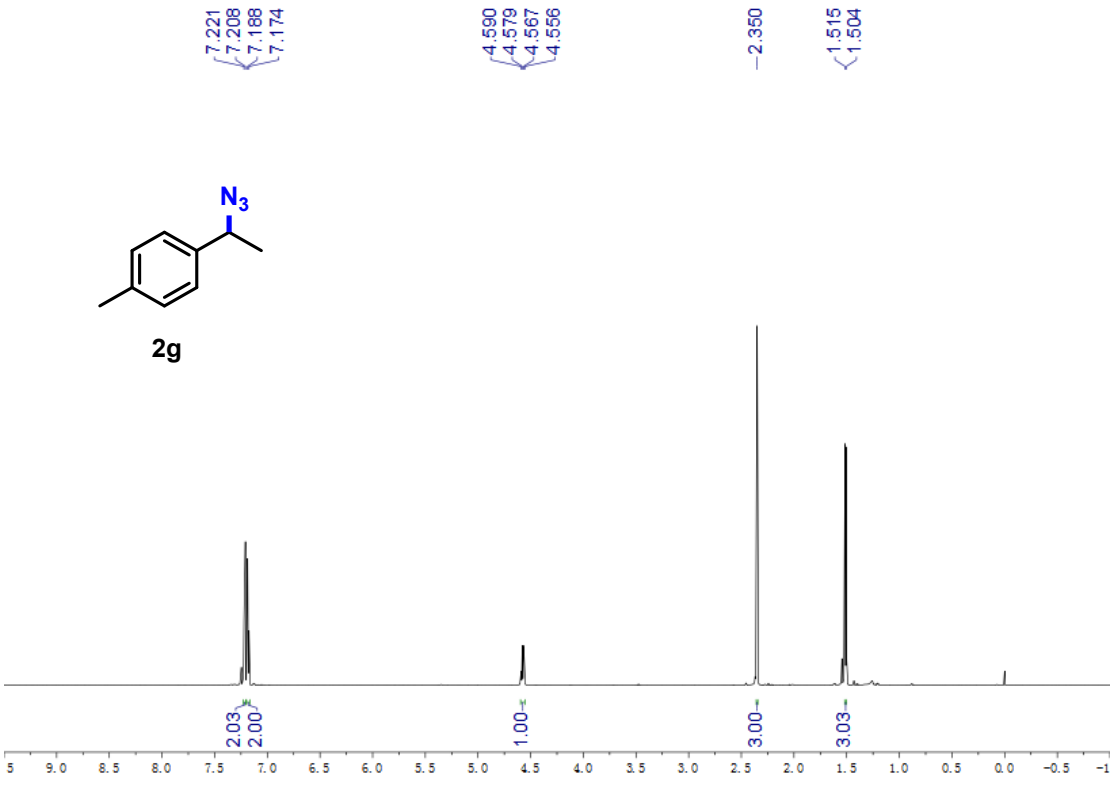
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2e**



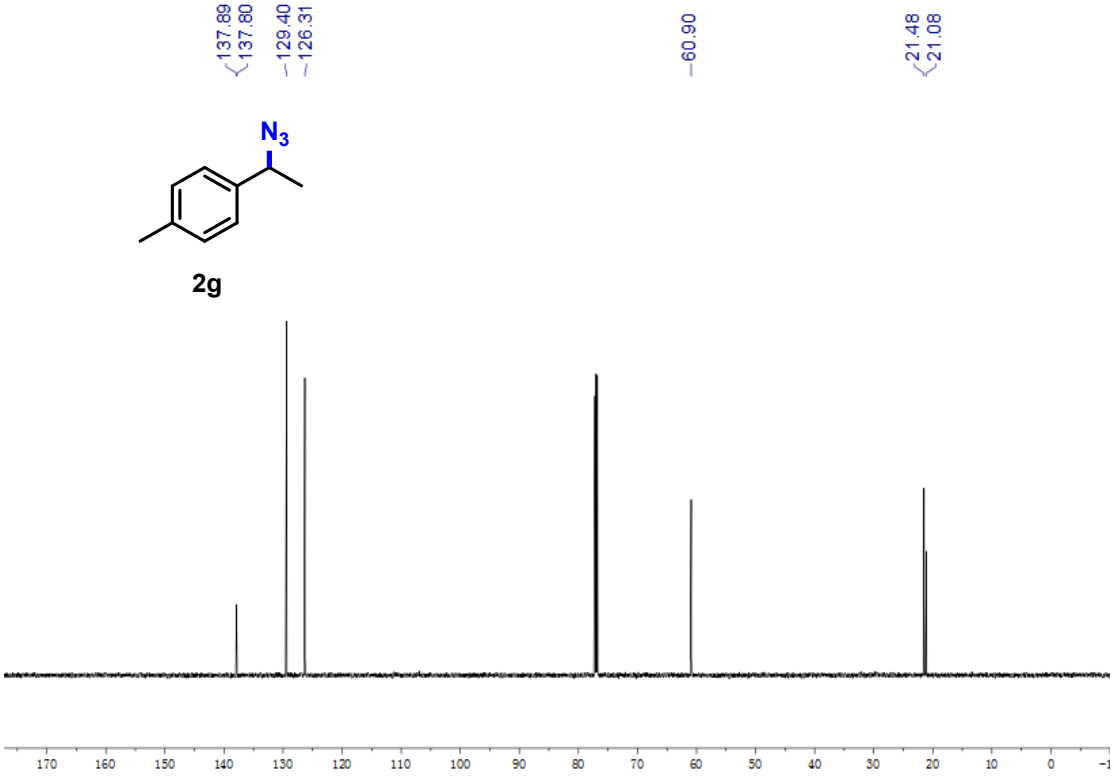
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2f**.



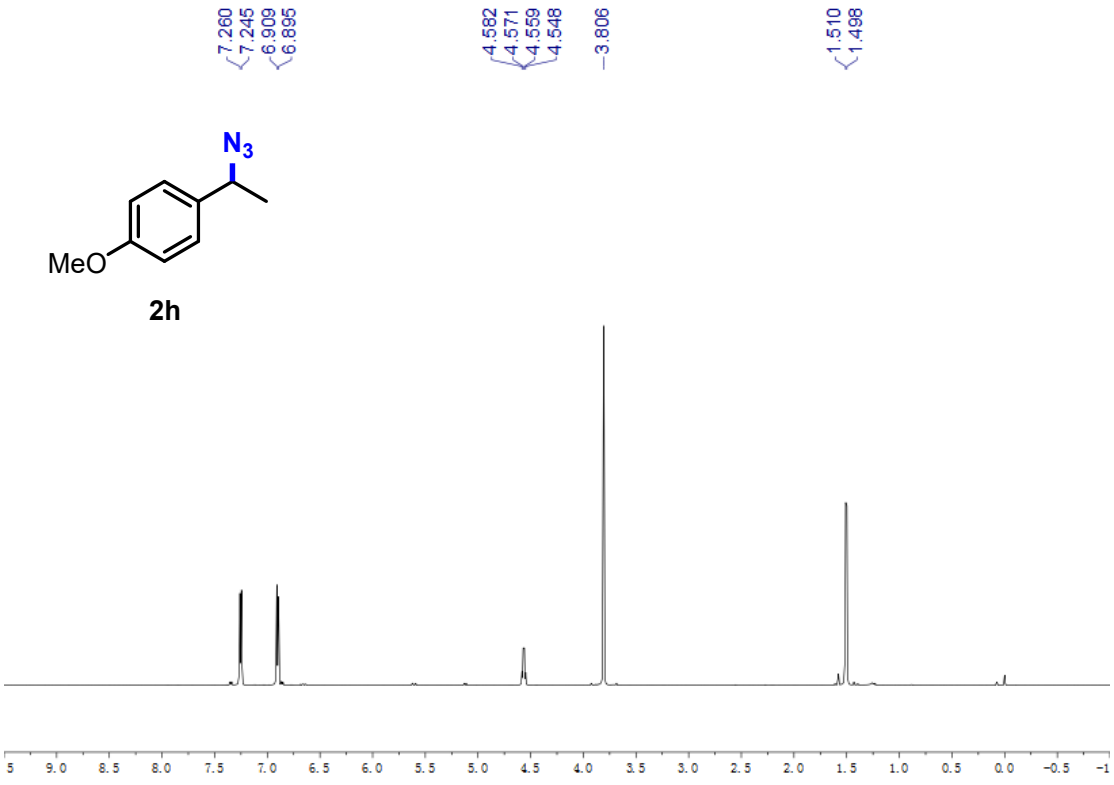
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2f**



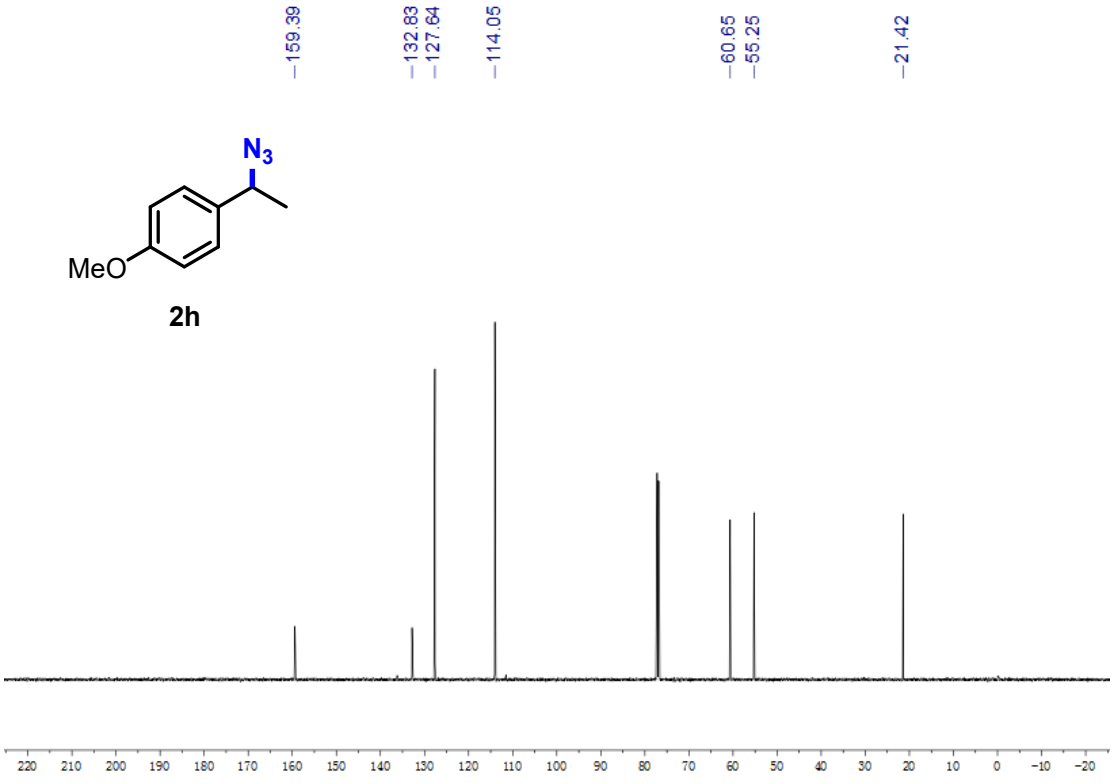
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2g**



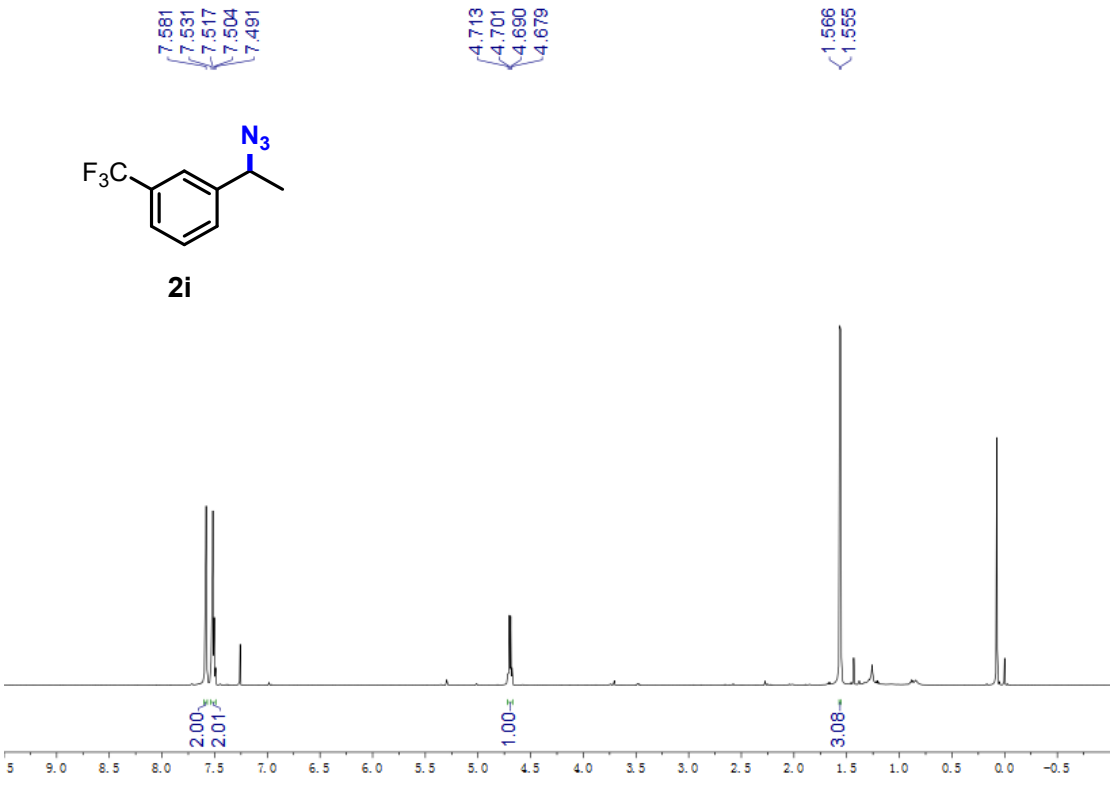
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2g**



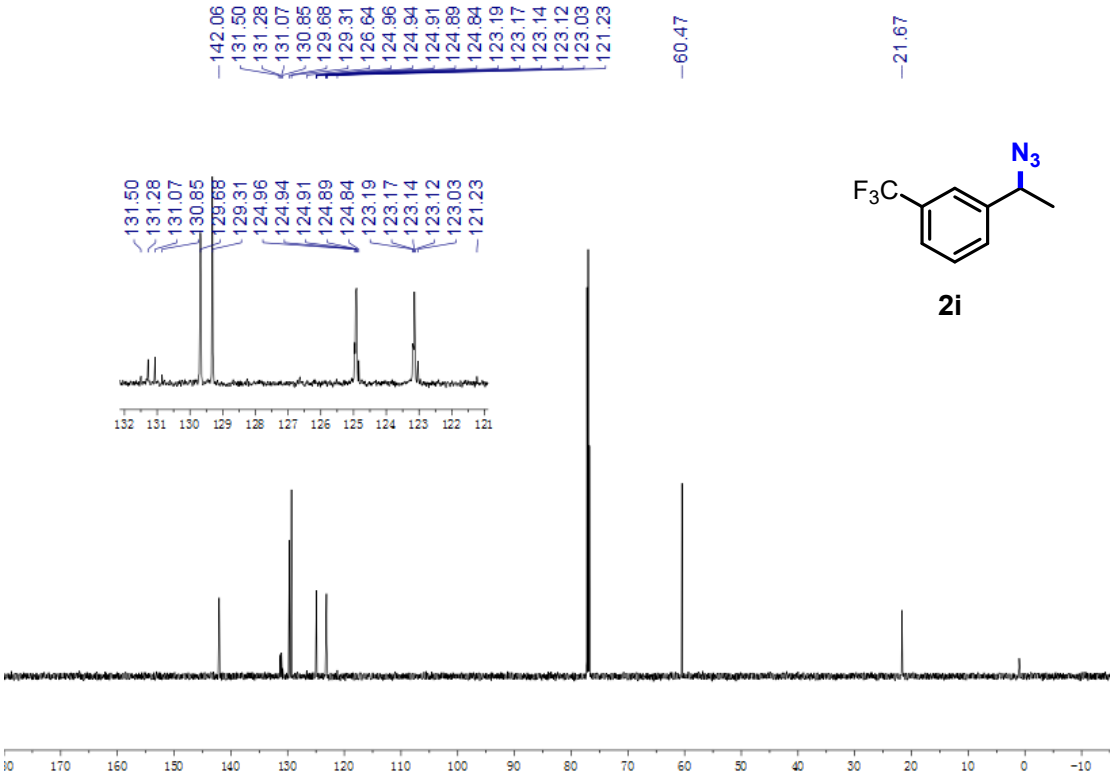
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2h**



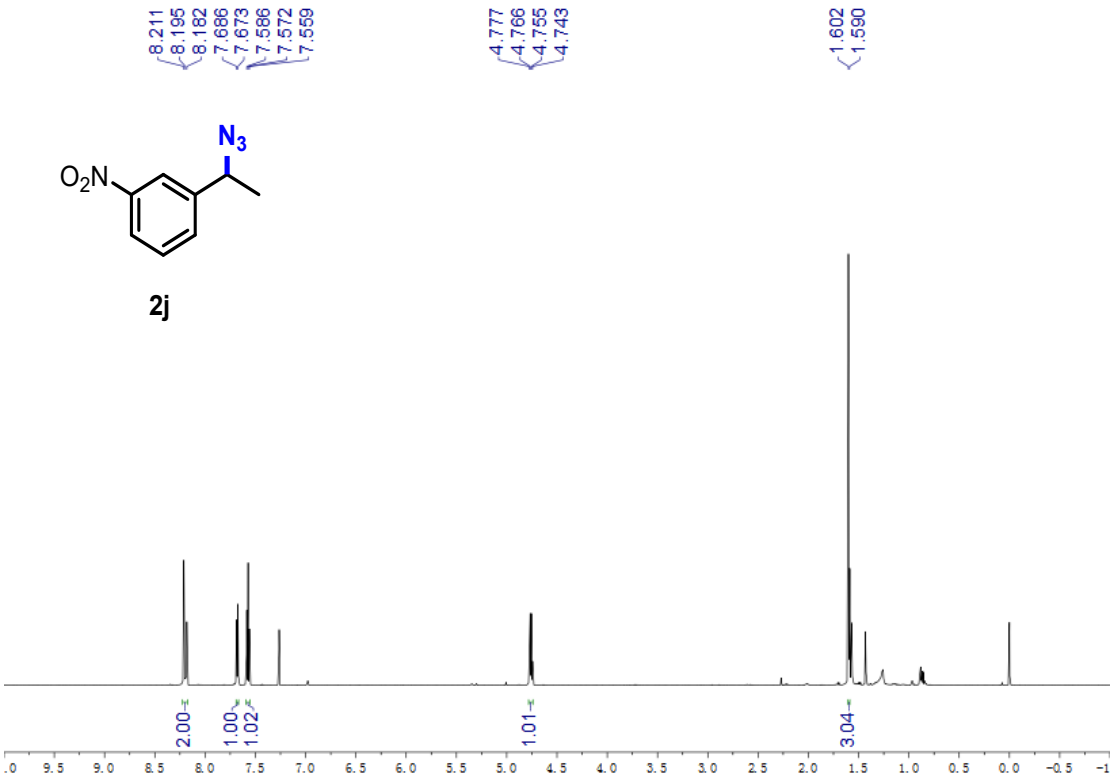
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2h**



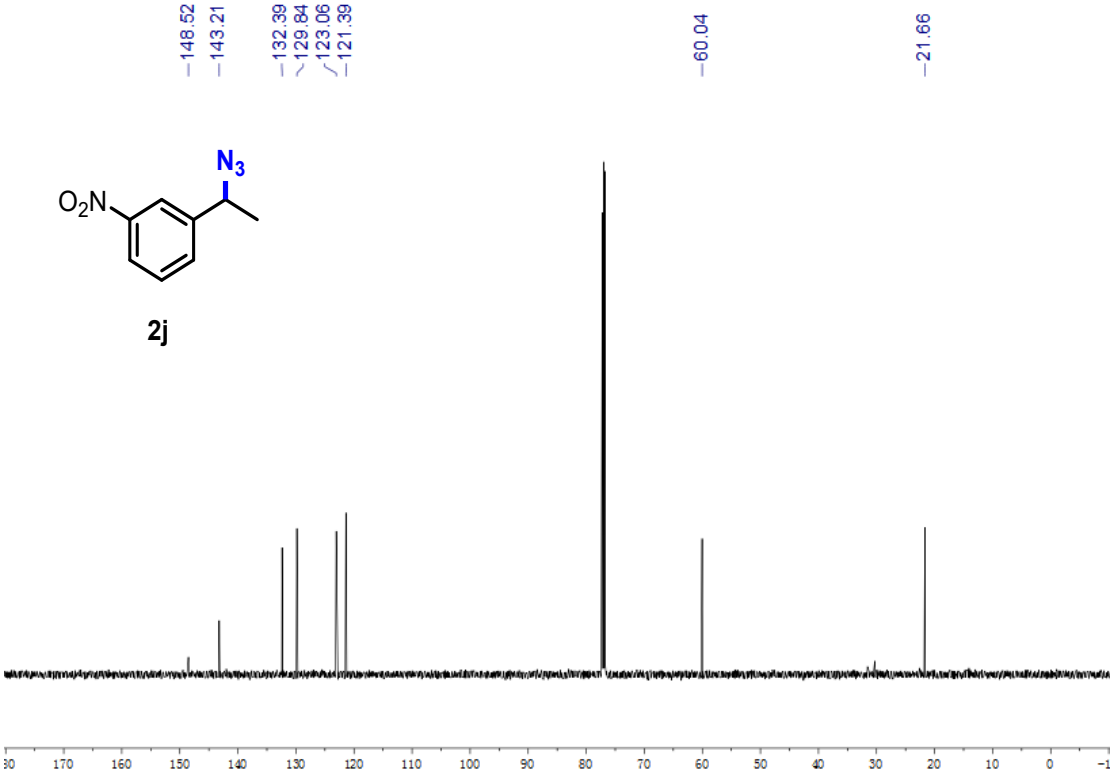
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2i**



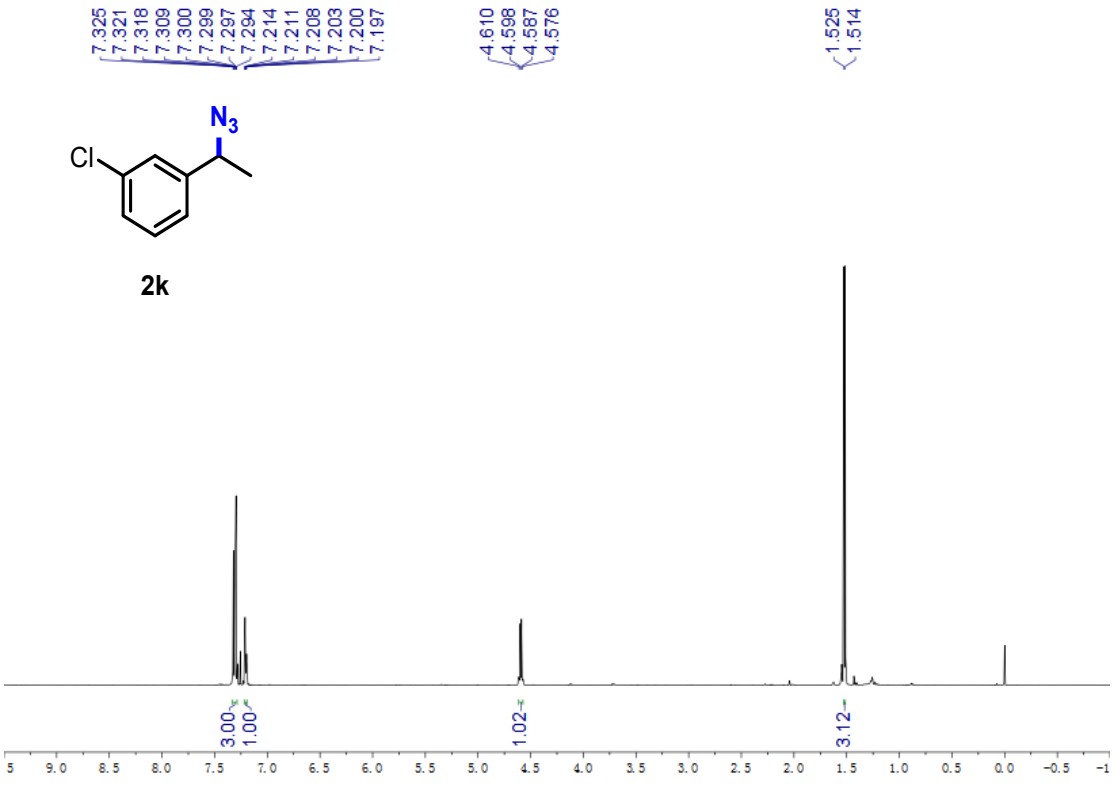
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2i**



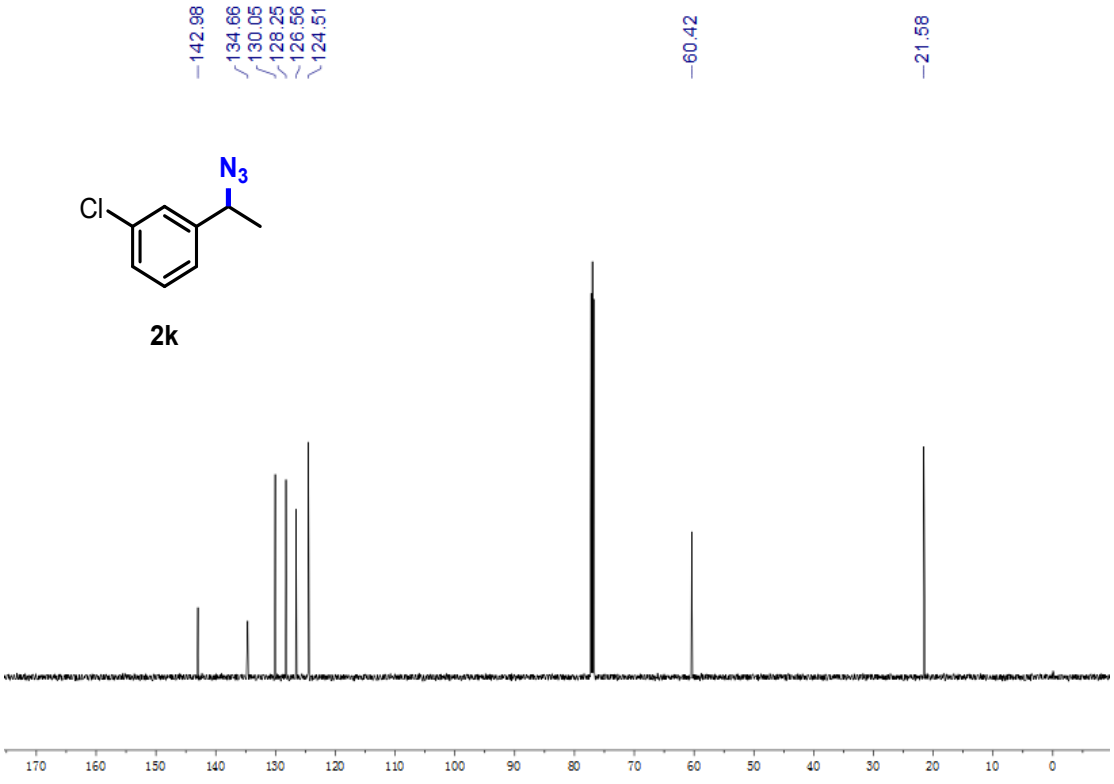
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2j**



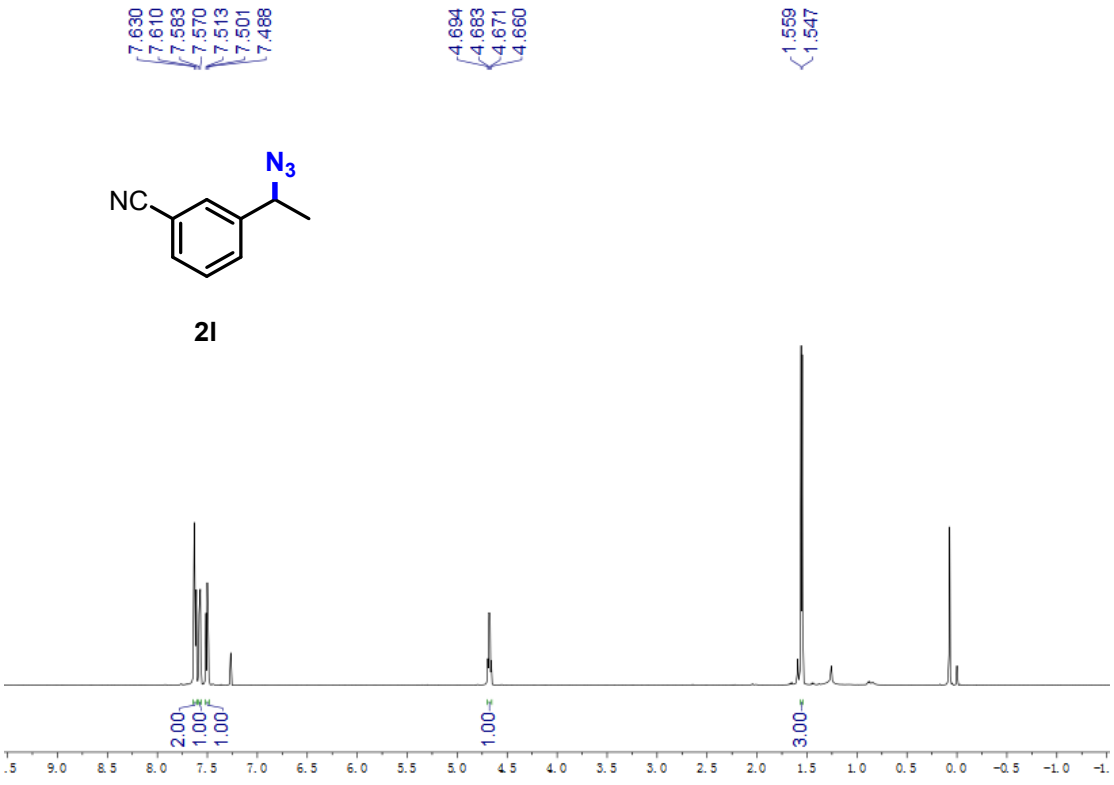
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2j**



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

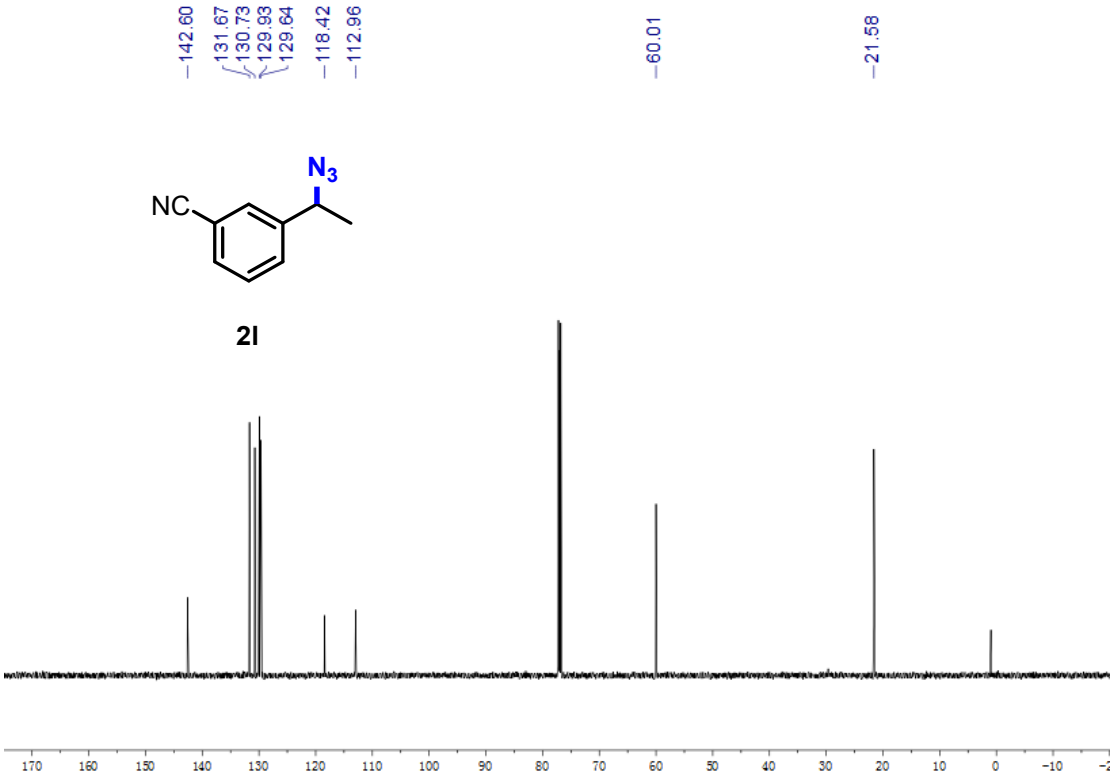


^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2k**



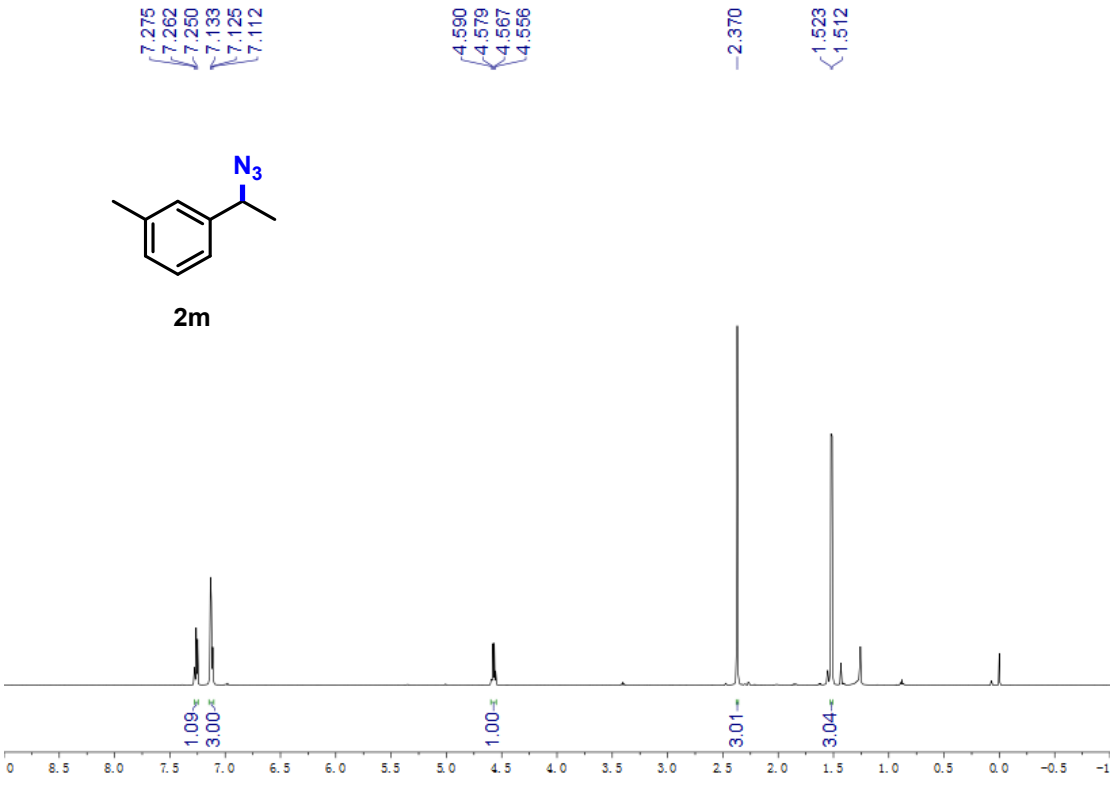
2l

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

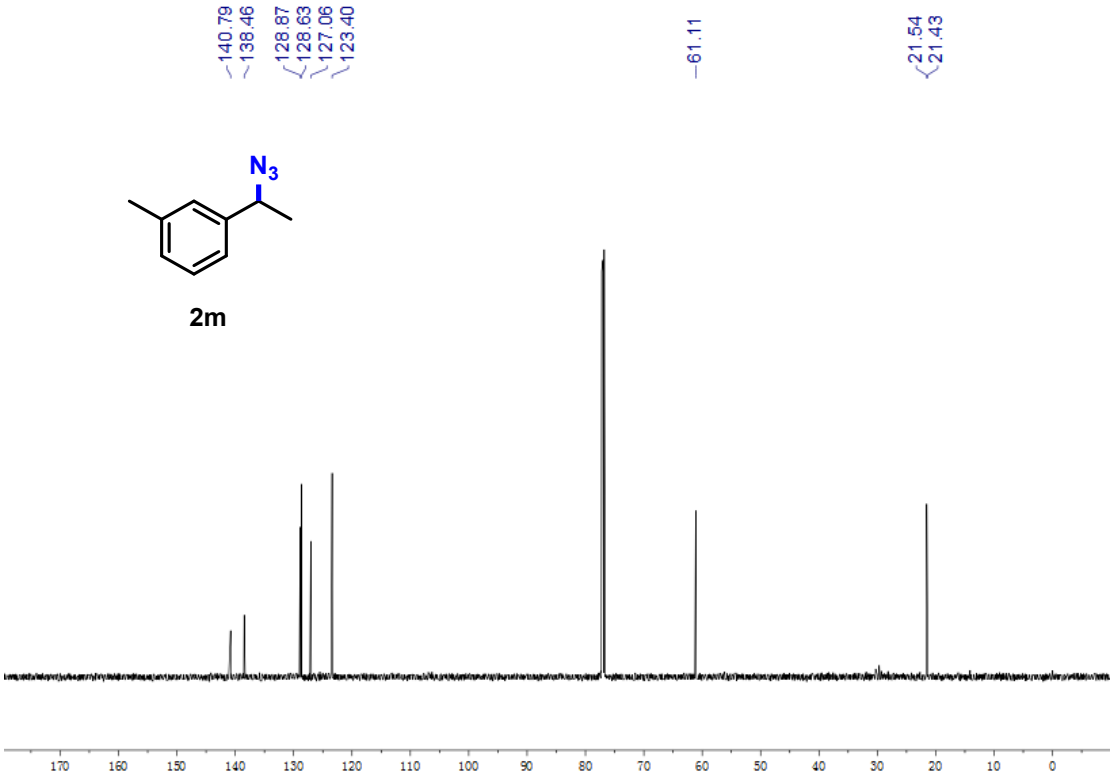


2l

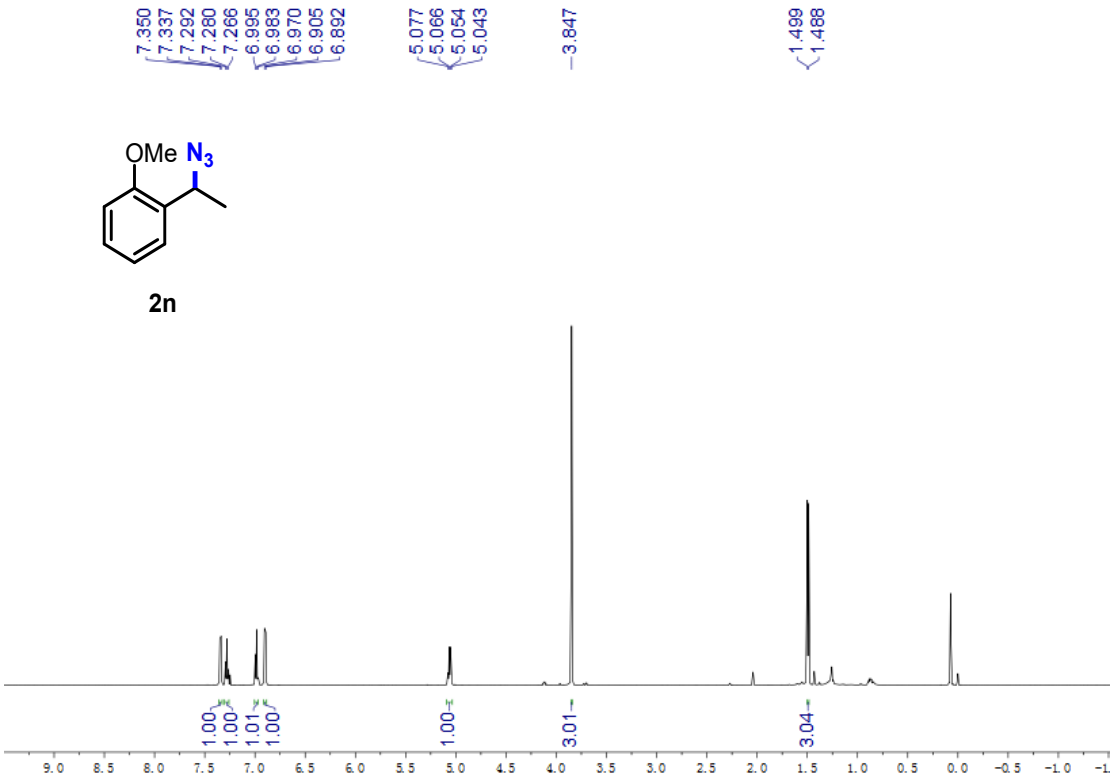
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2l**



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

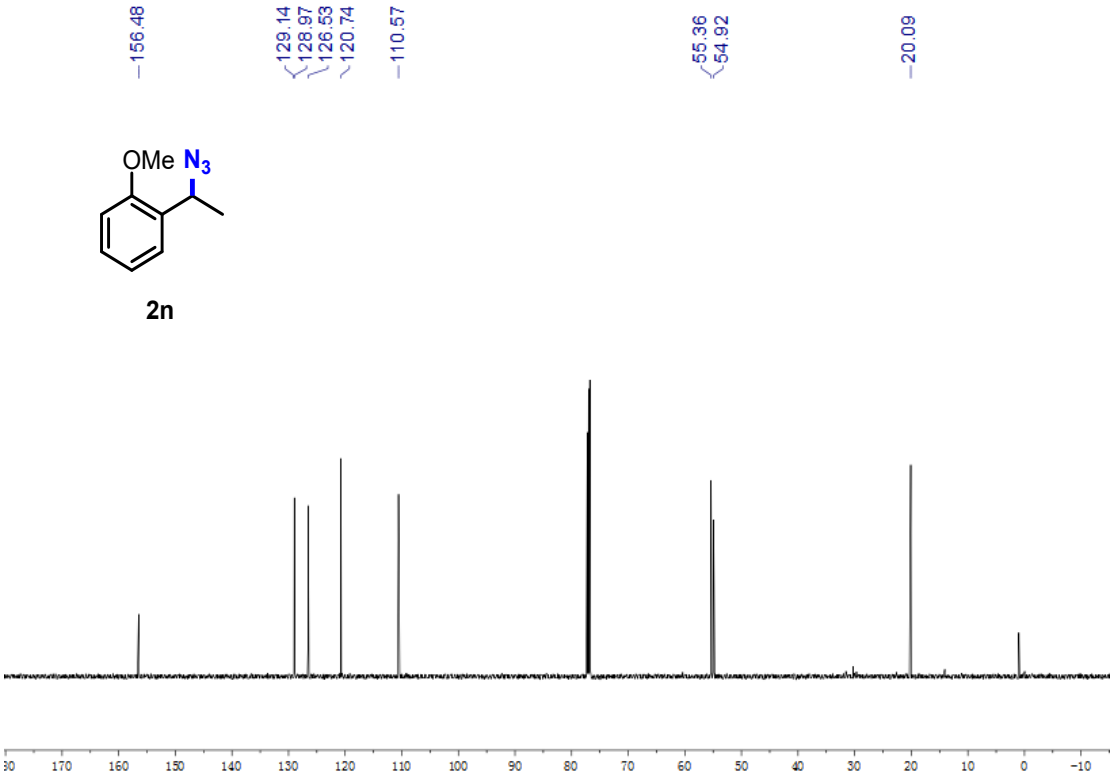


^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2m**



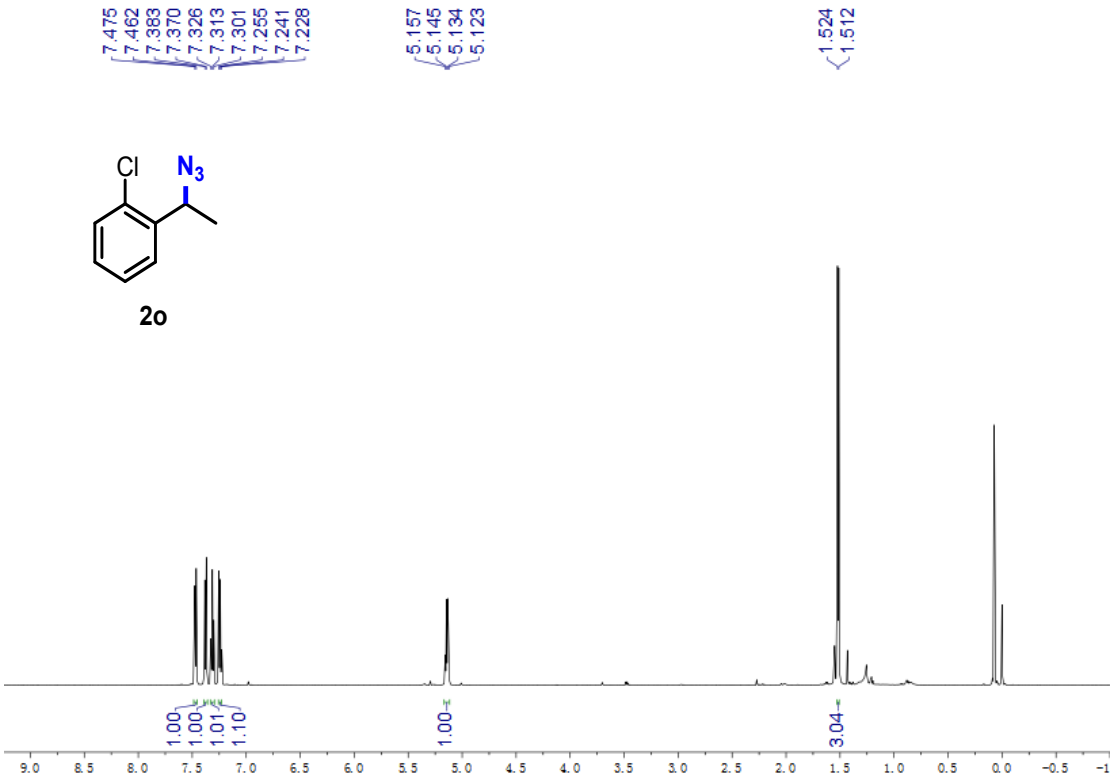
2n

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

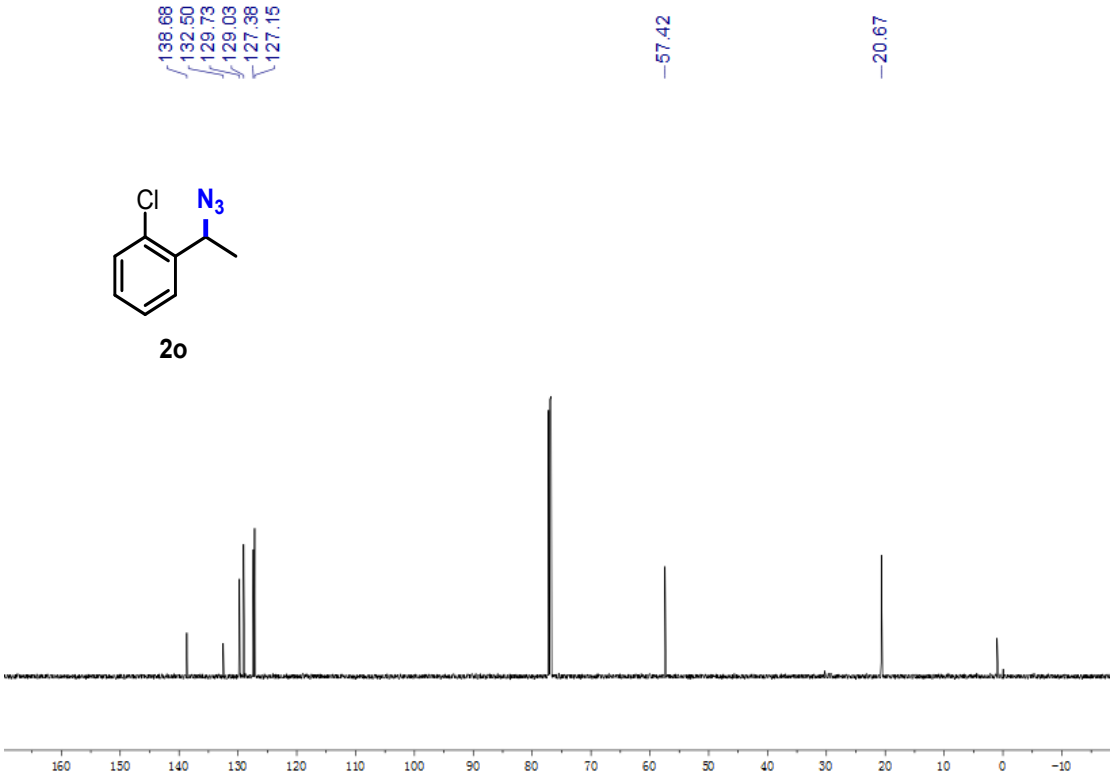


2n

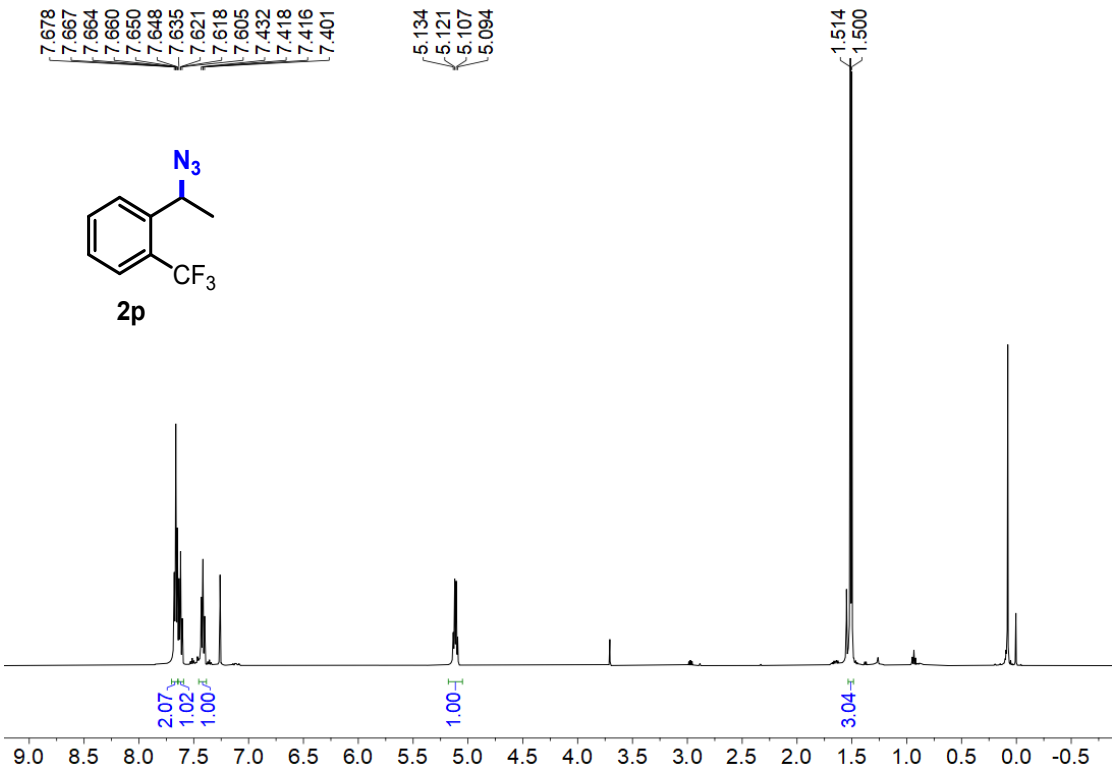
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2n**



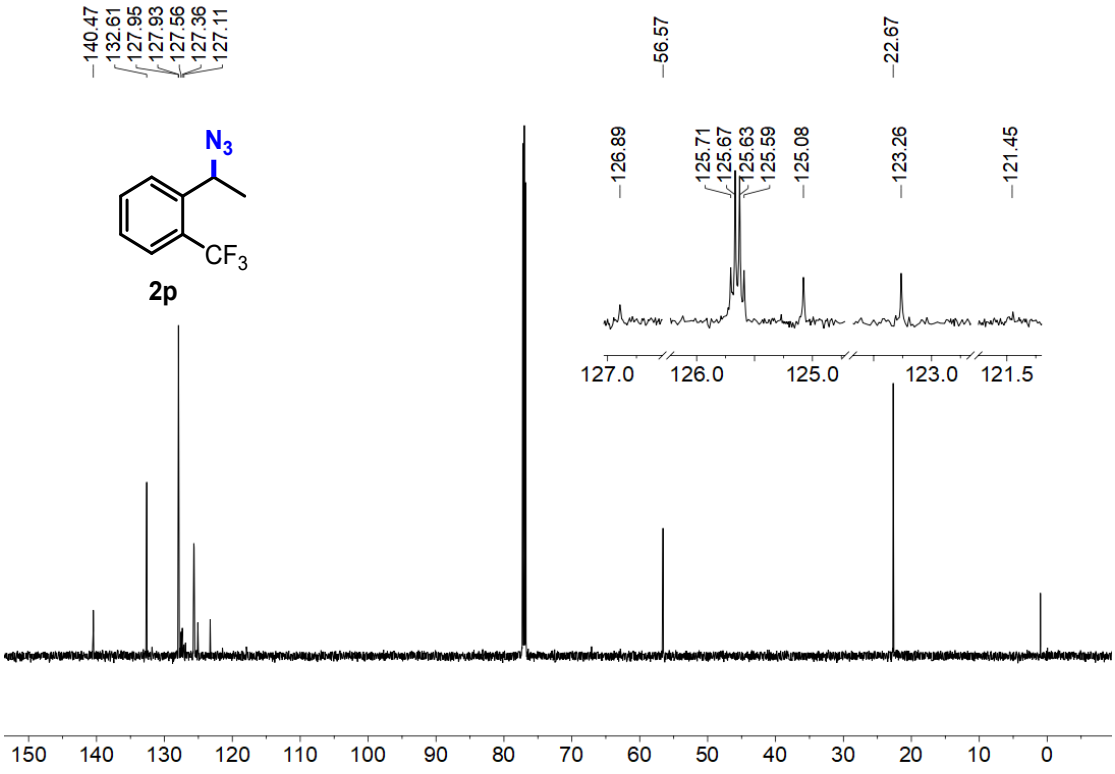
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2o**



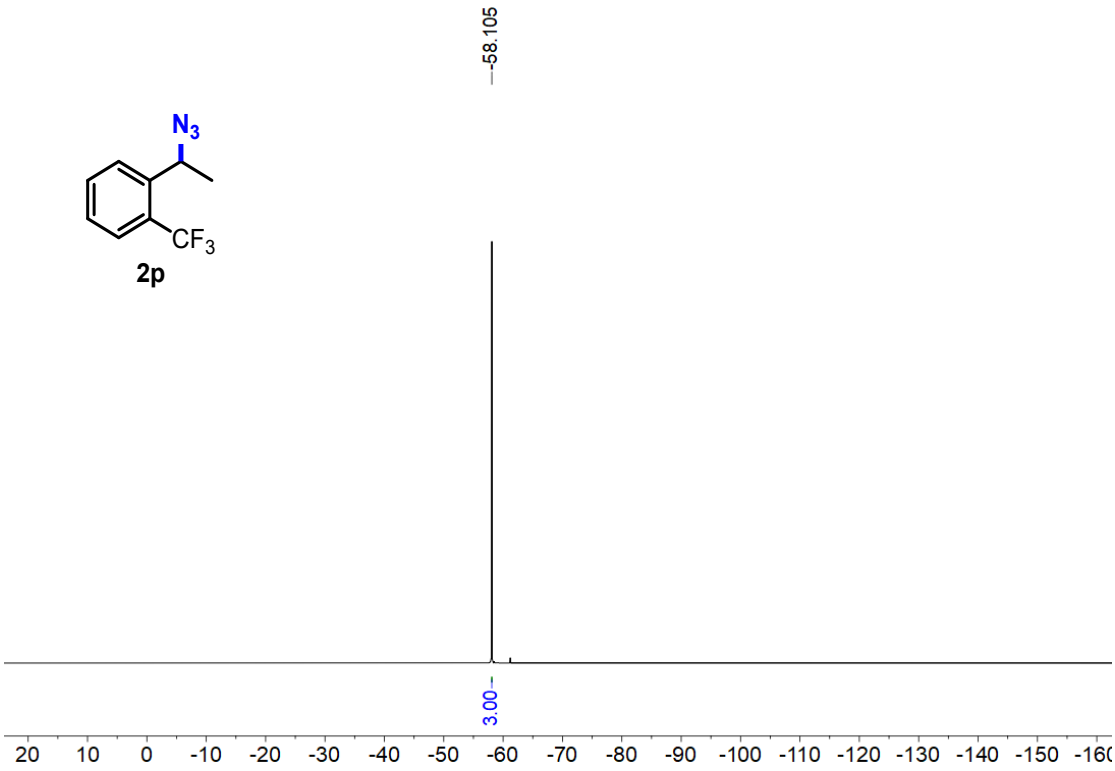
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2o**



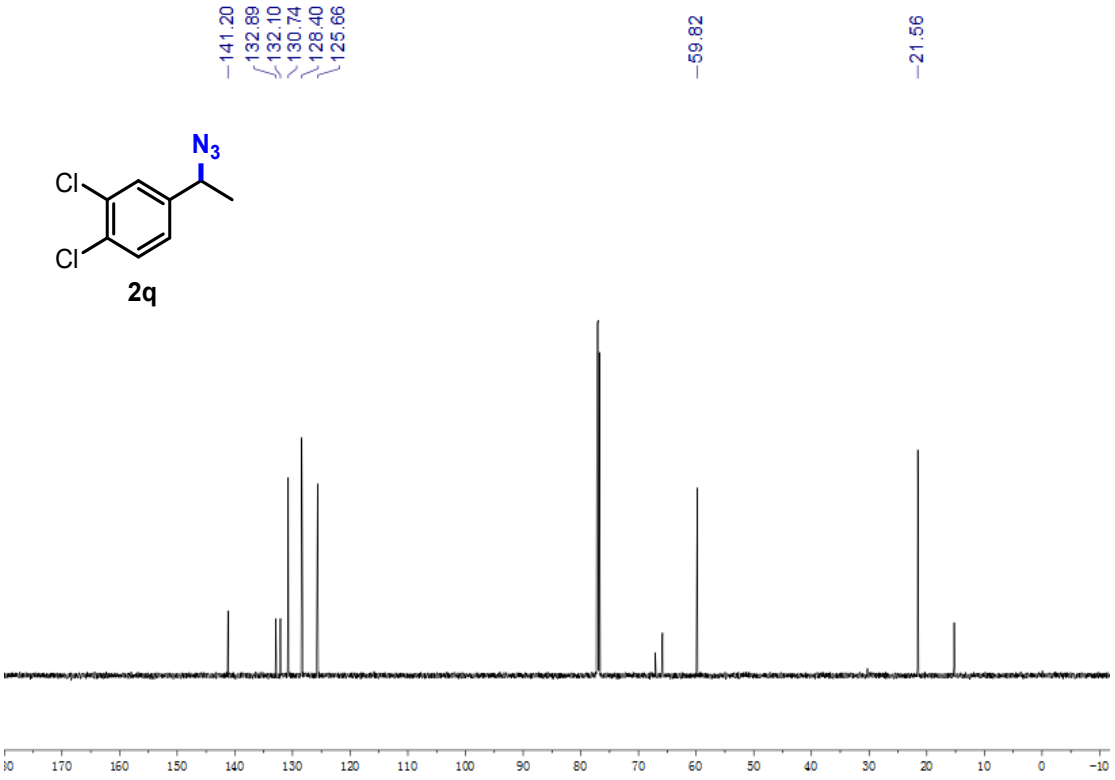
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2p**



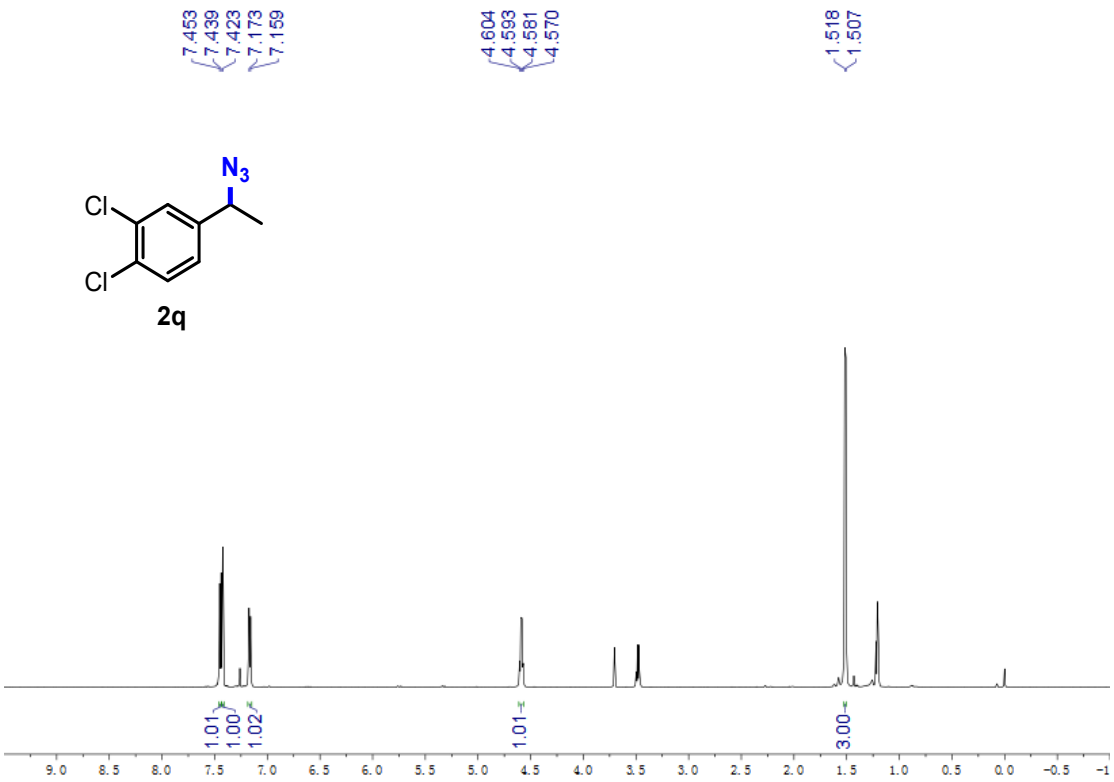
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2p**



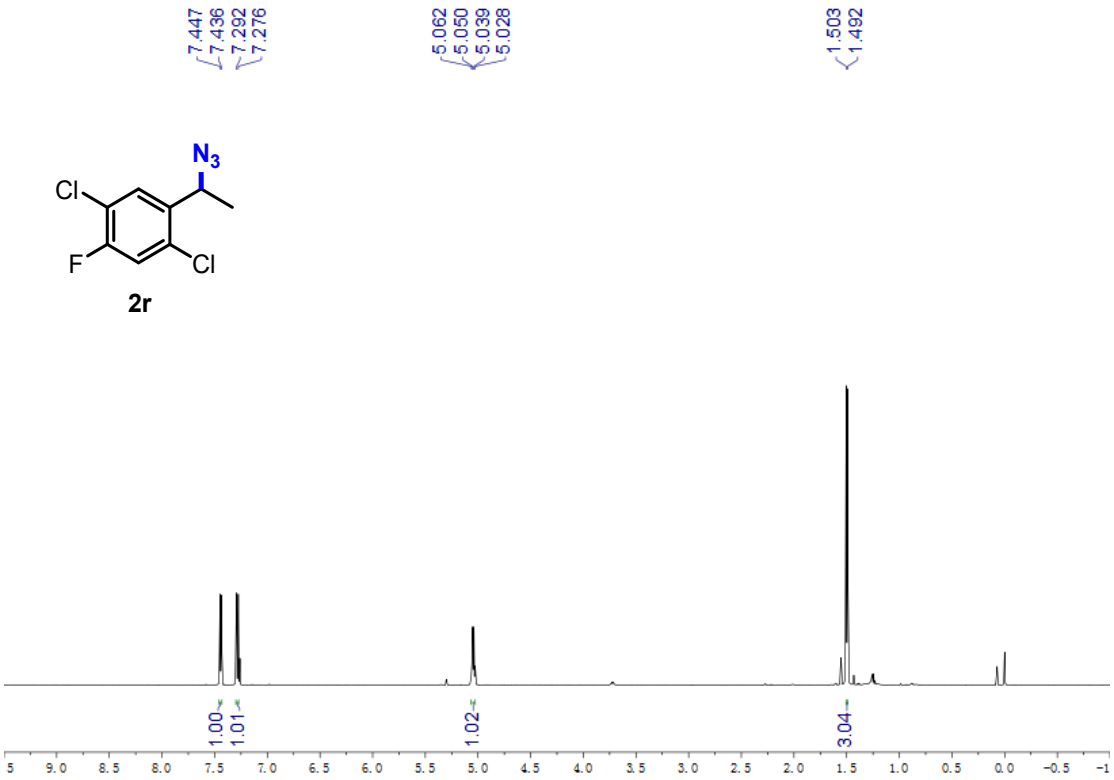
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2p**



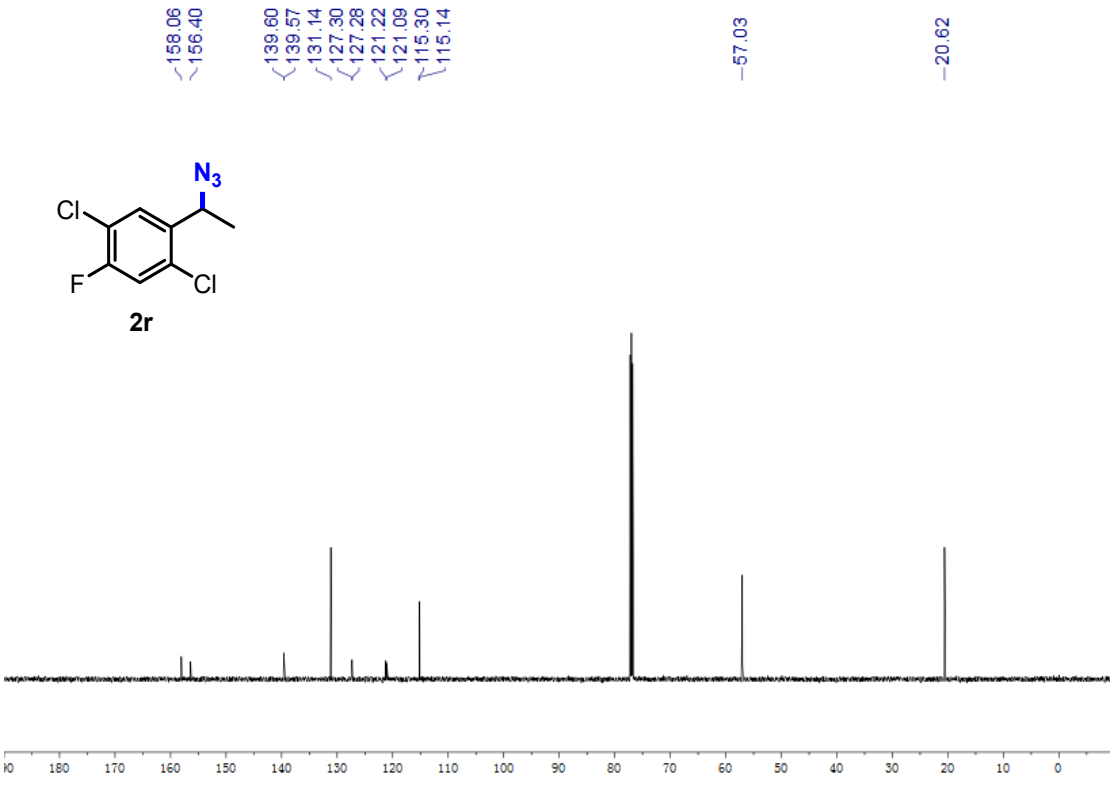
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2q**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2q**

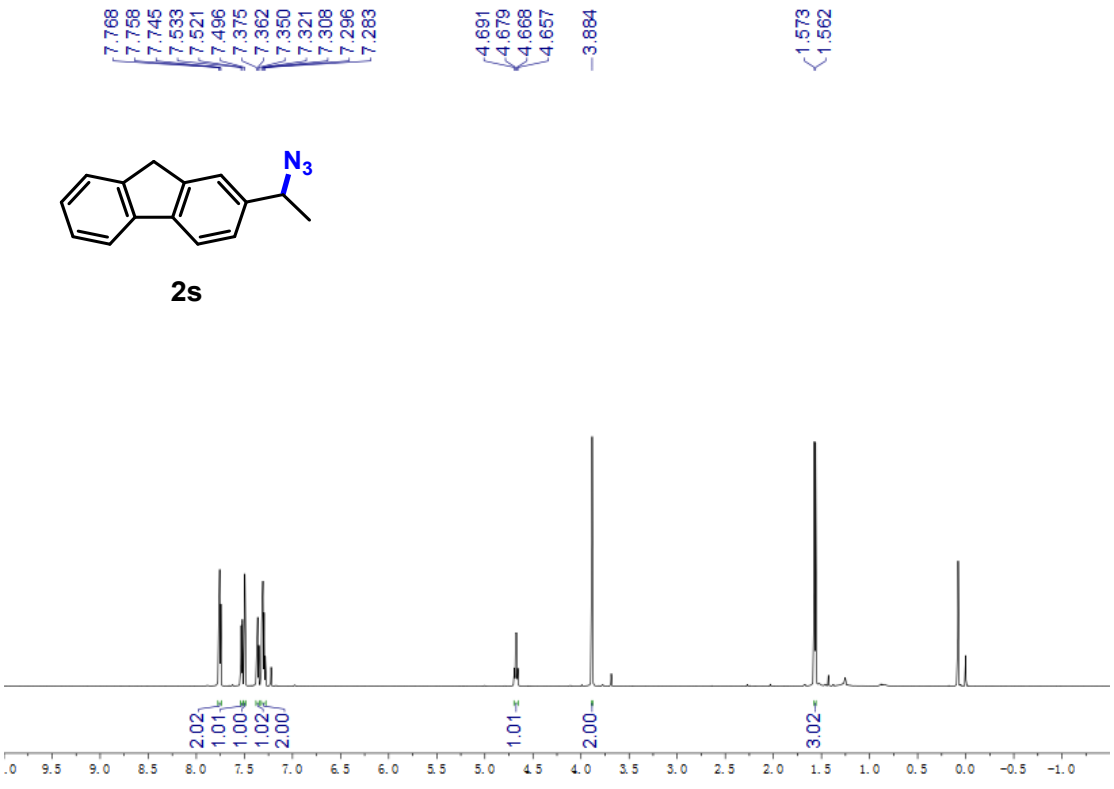


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2r**



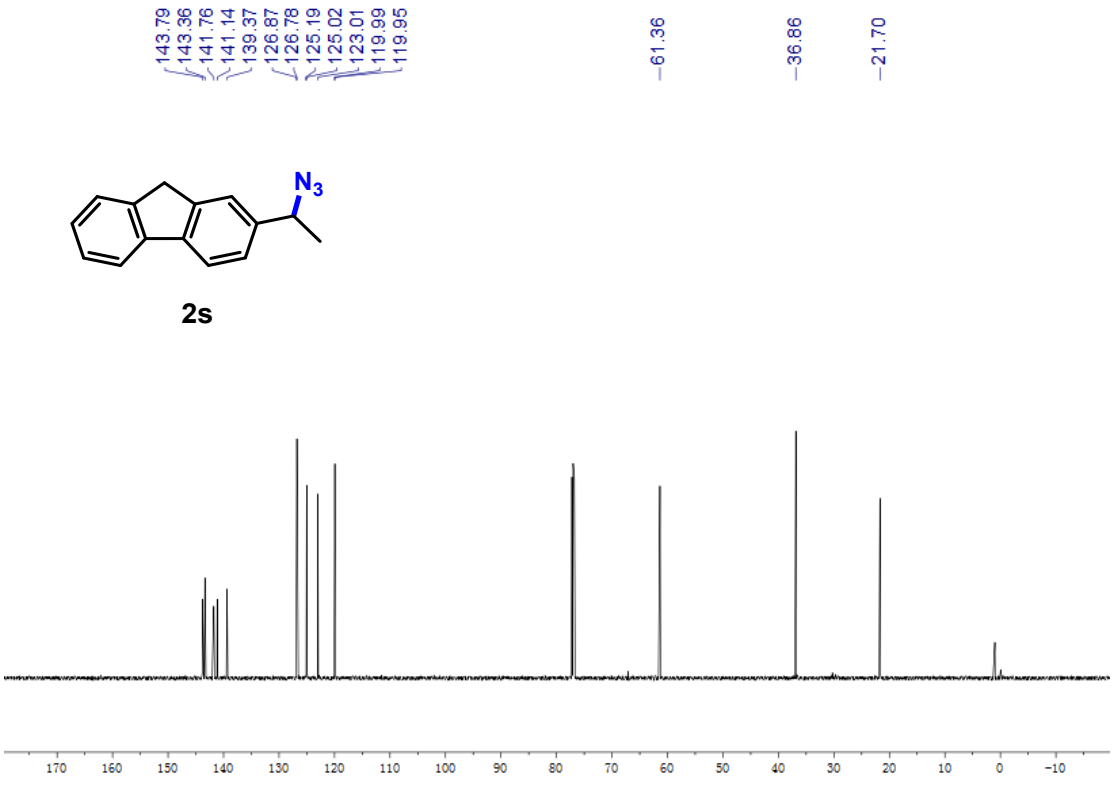
2r

^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2r**



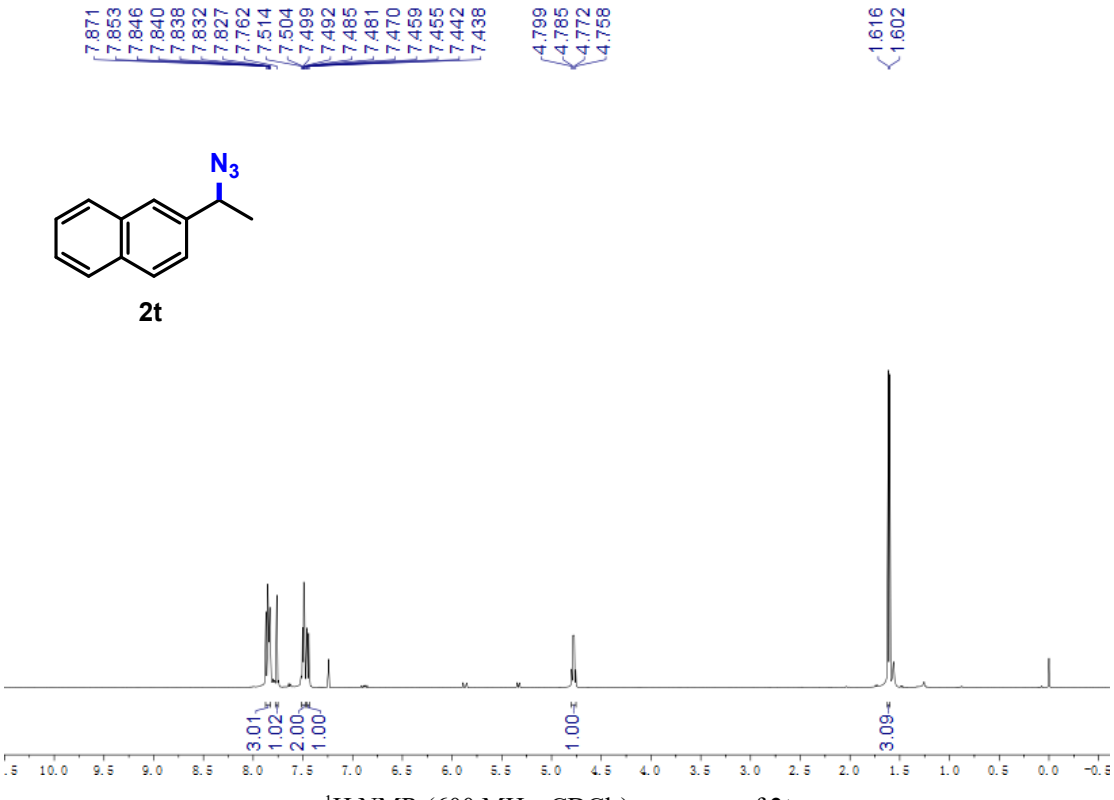
2s

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



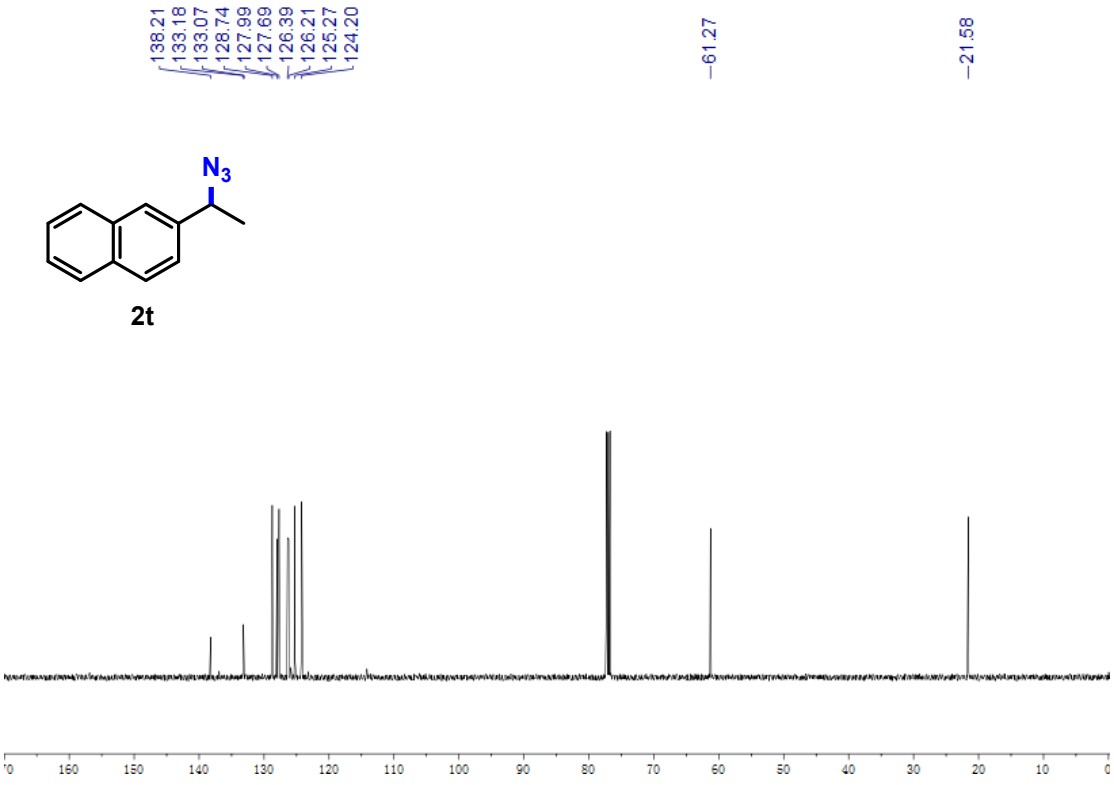
2s

^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2s**

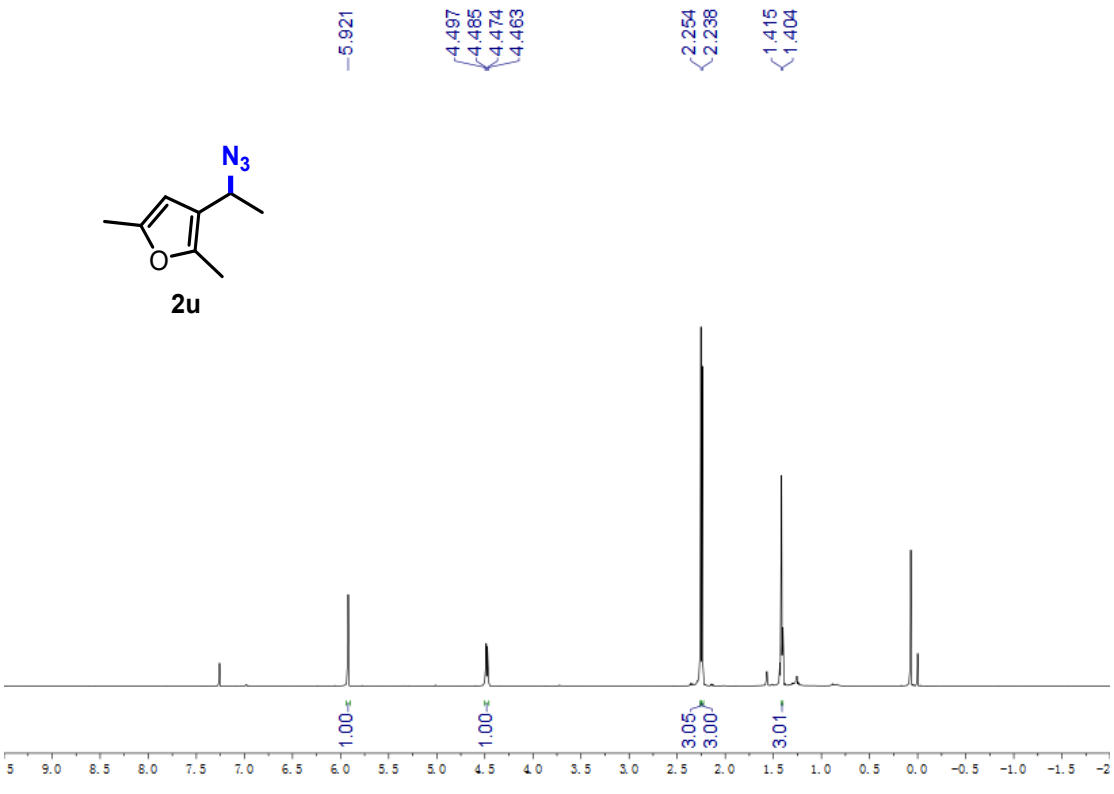


2t

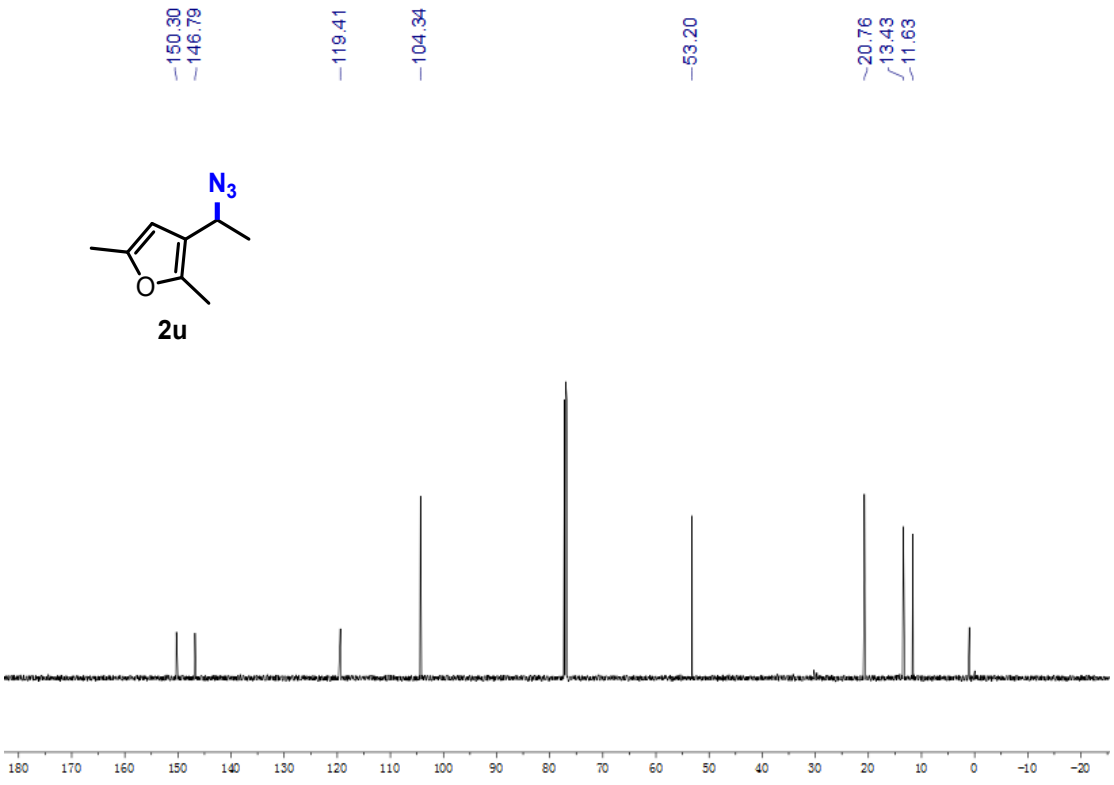
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2t**



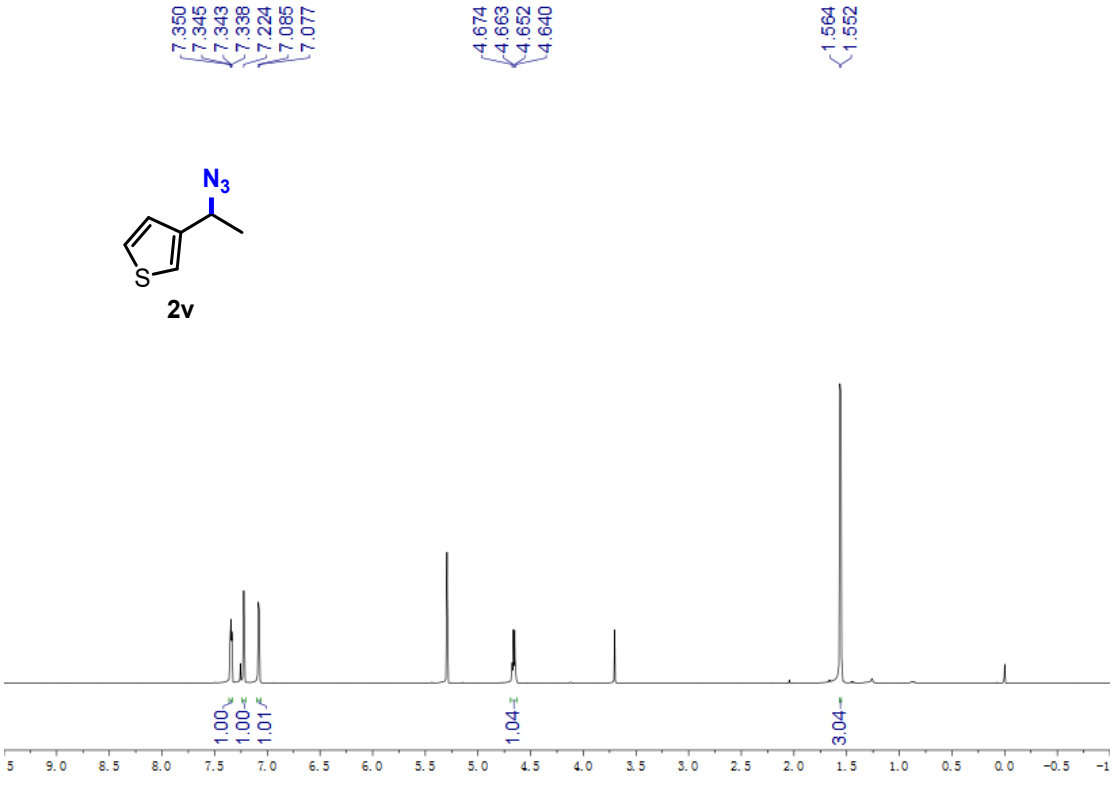
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2t**



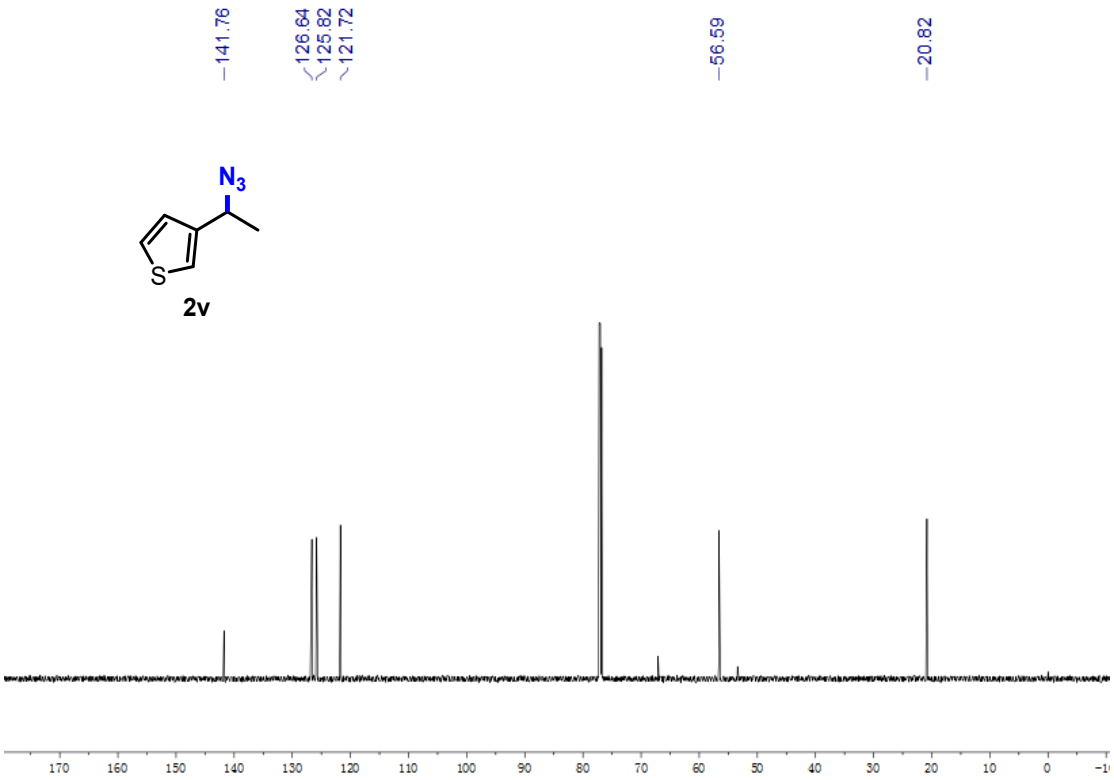
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2u**



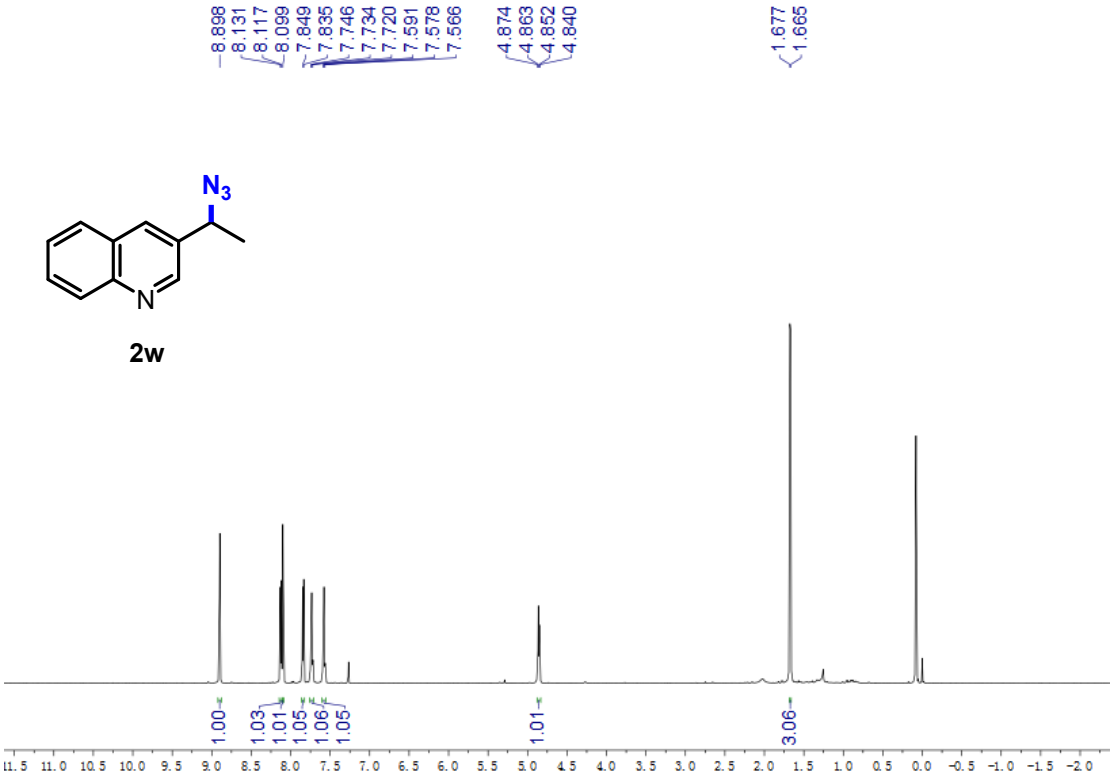
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2u**



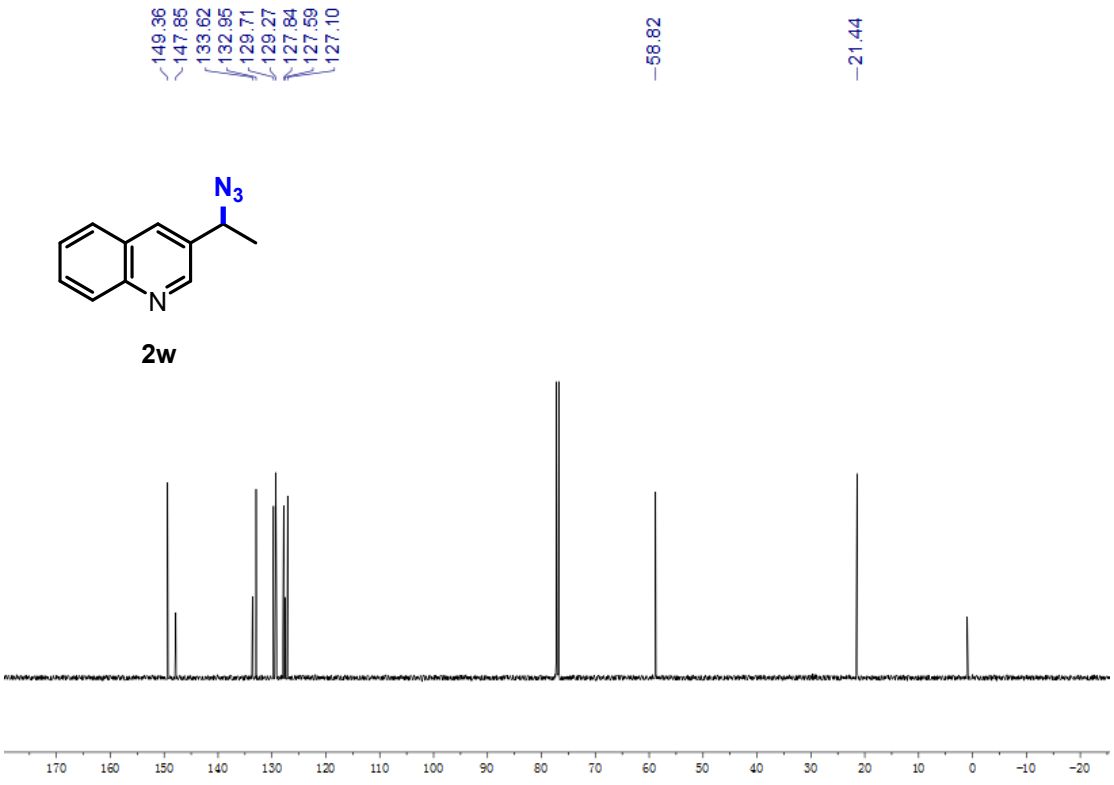
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2v**



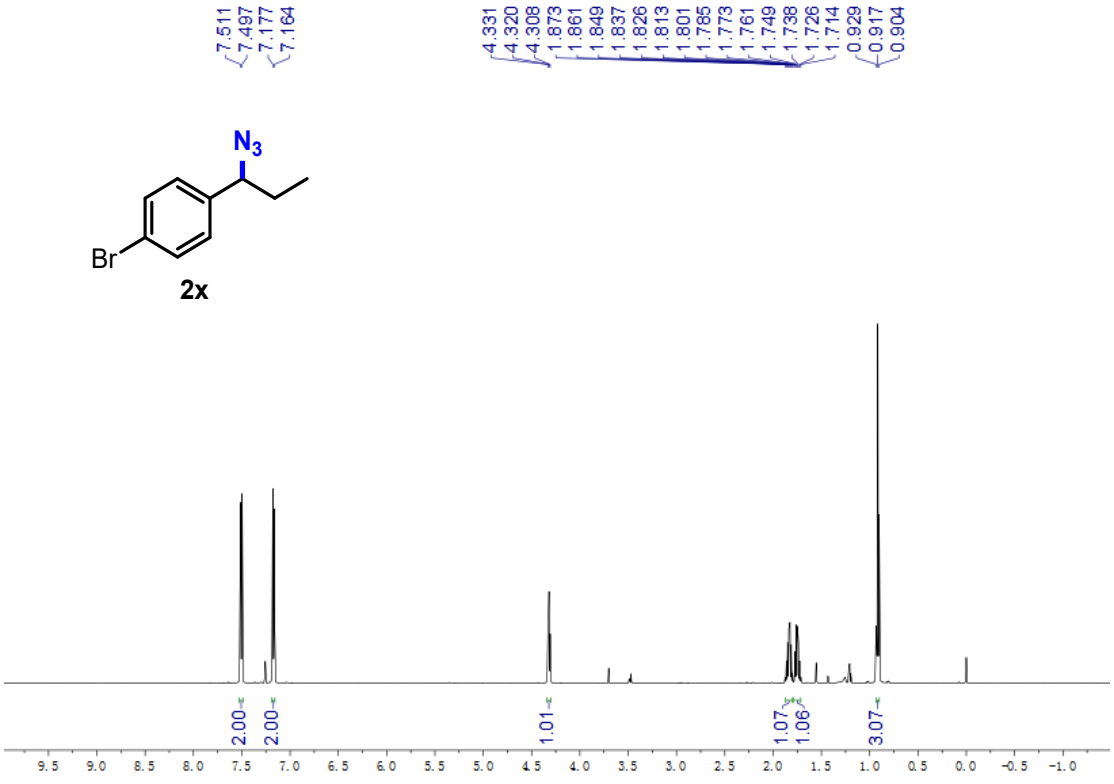
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2v**



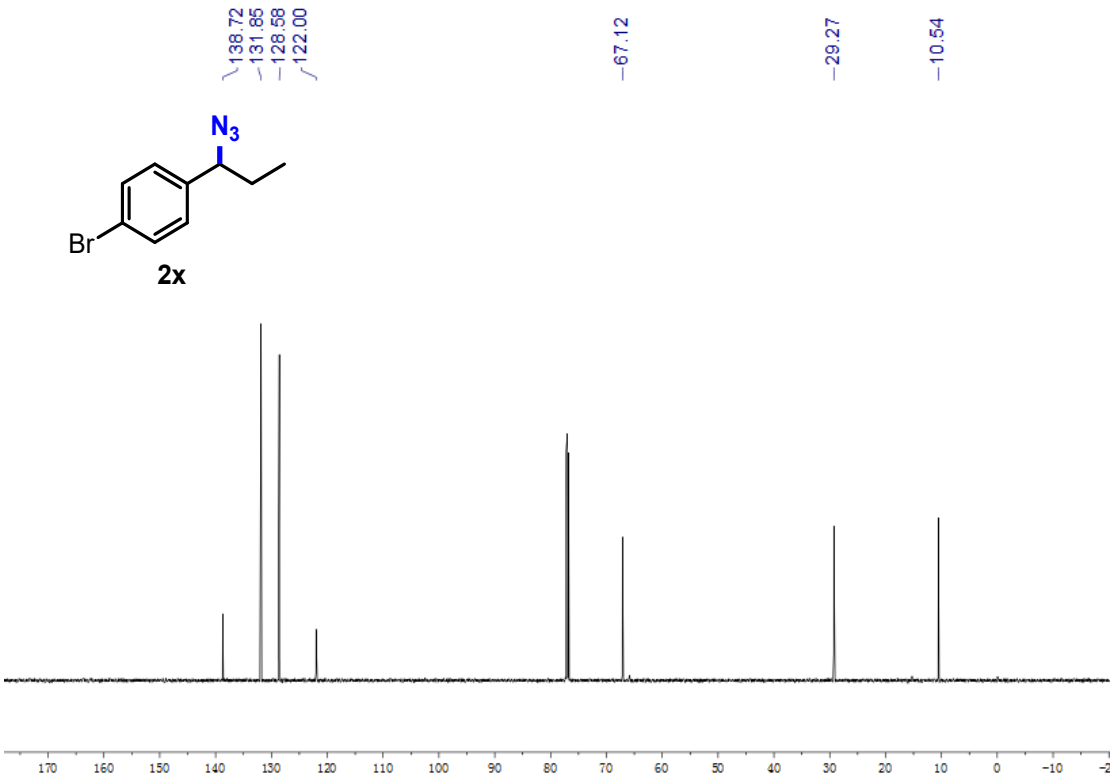
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2w**



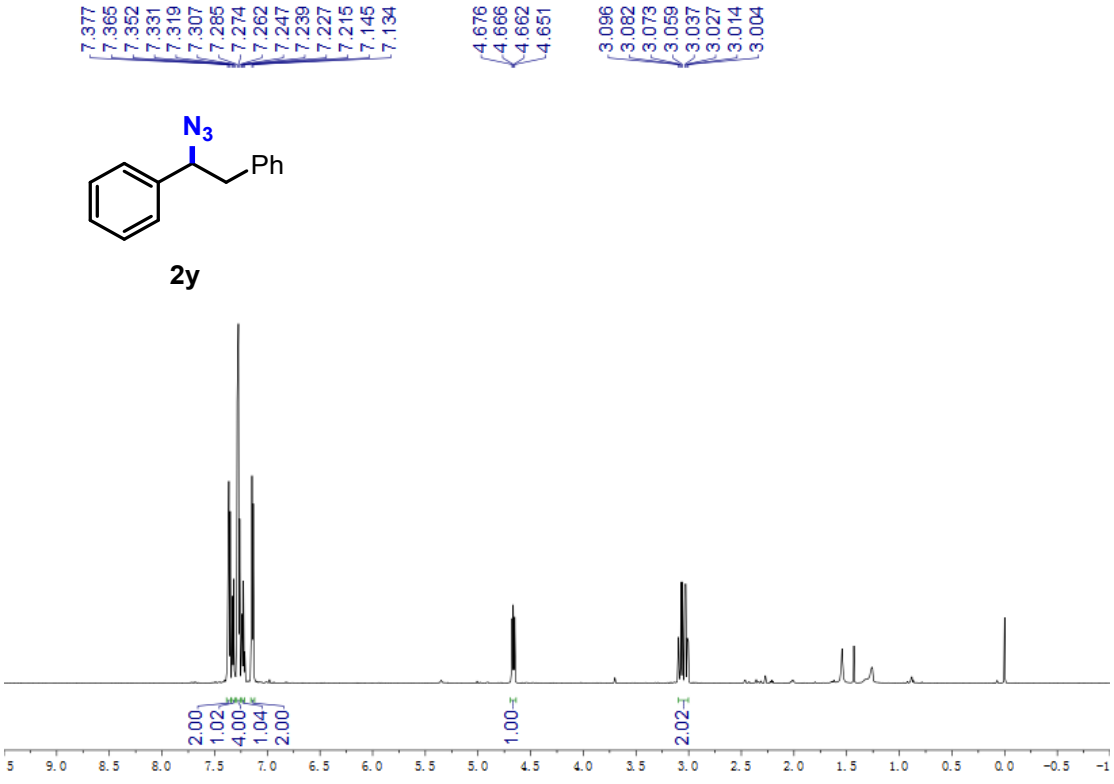
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2w**



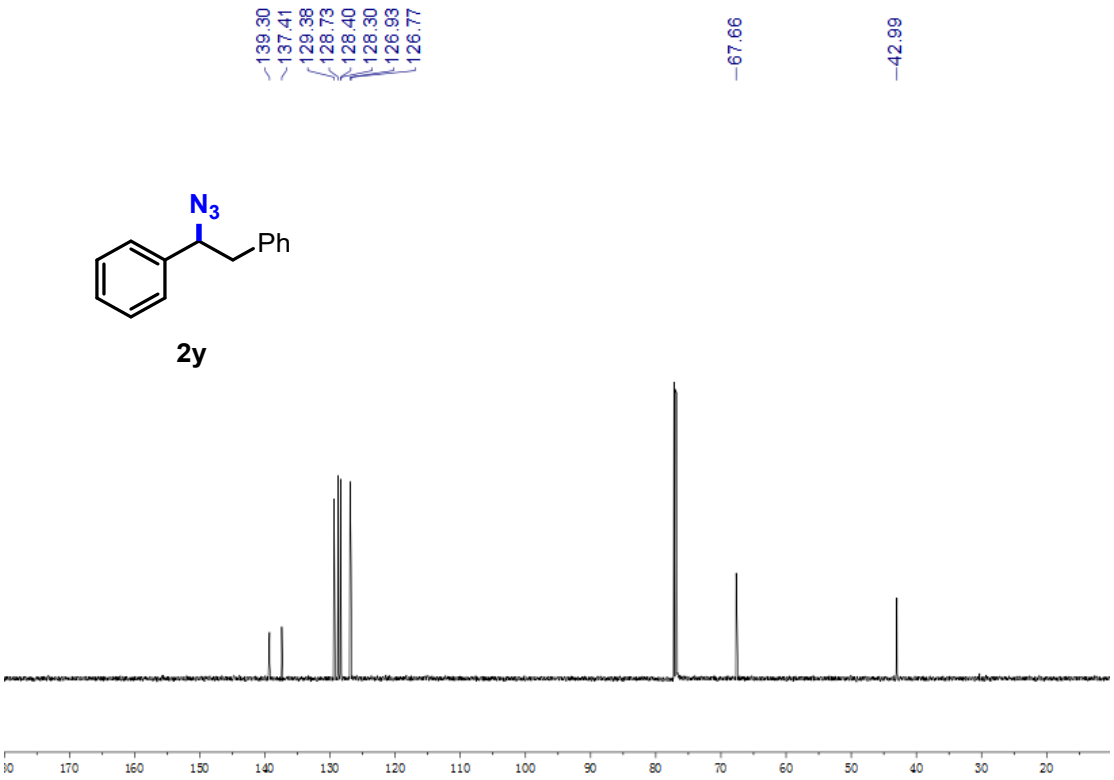
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2x**



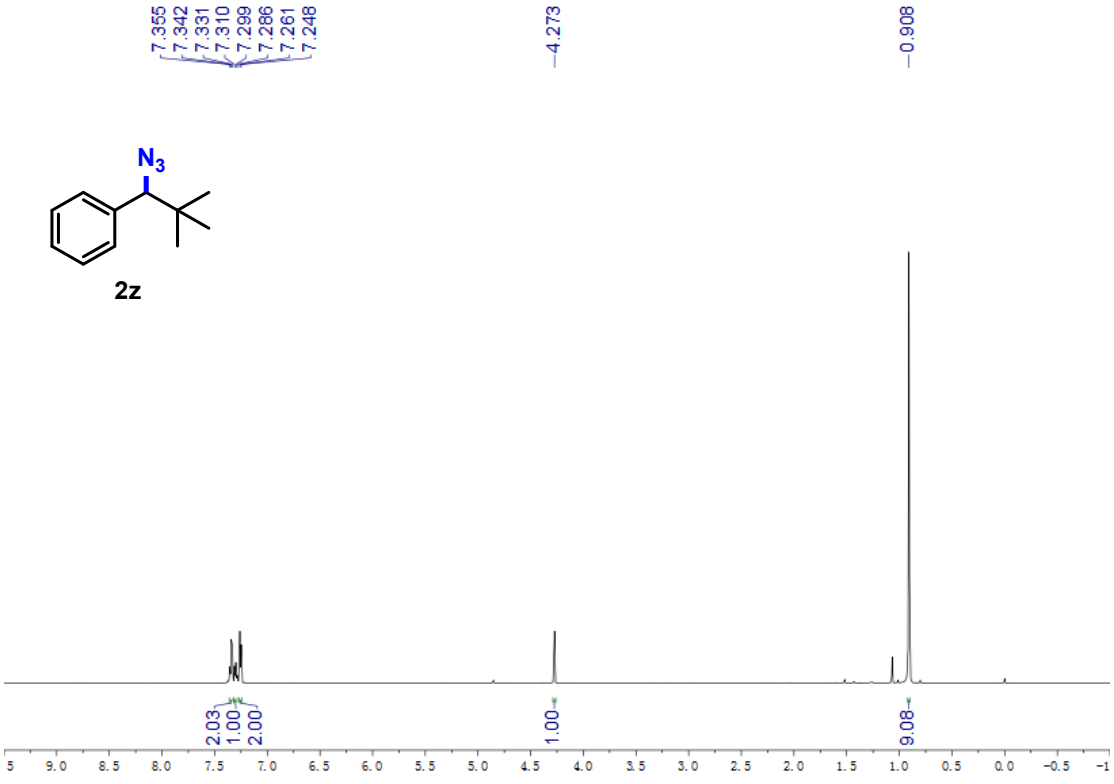
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2x**



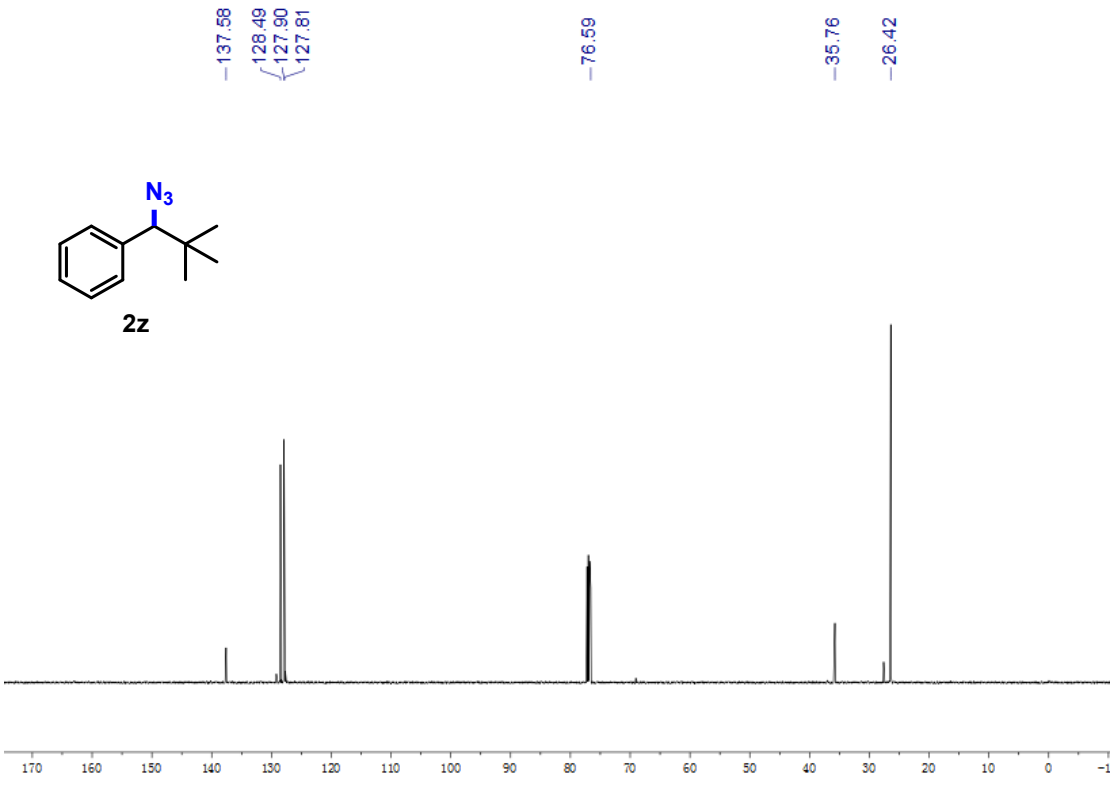
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2y**



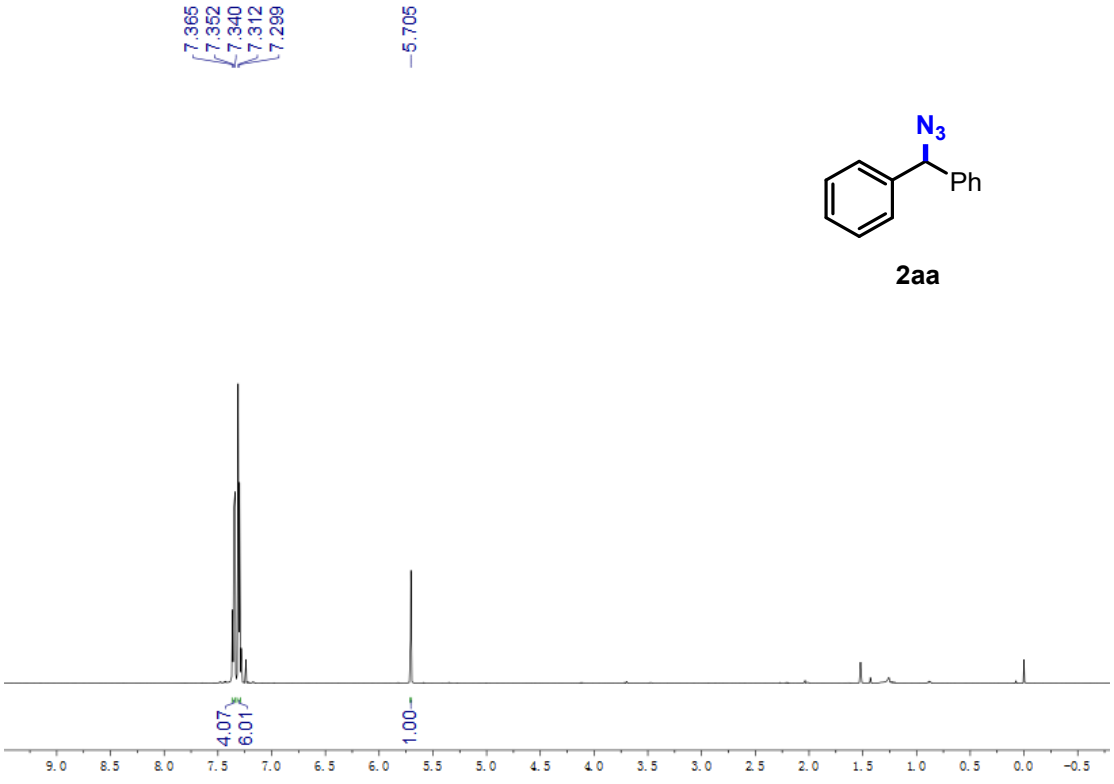
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2y**



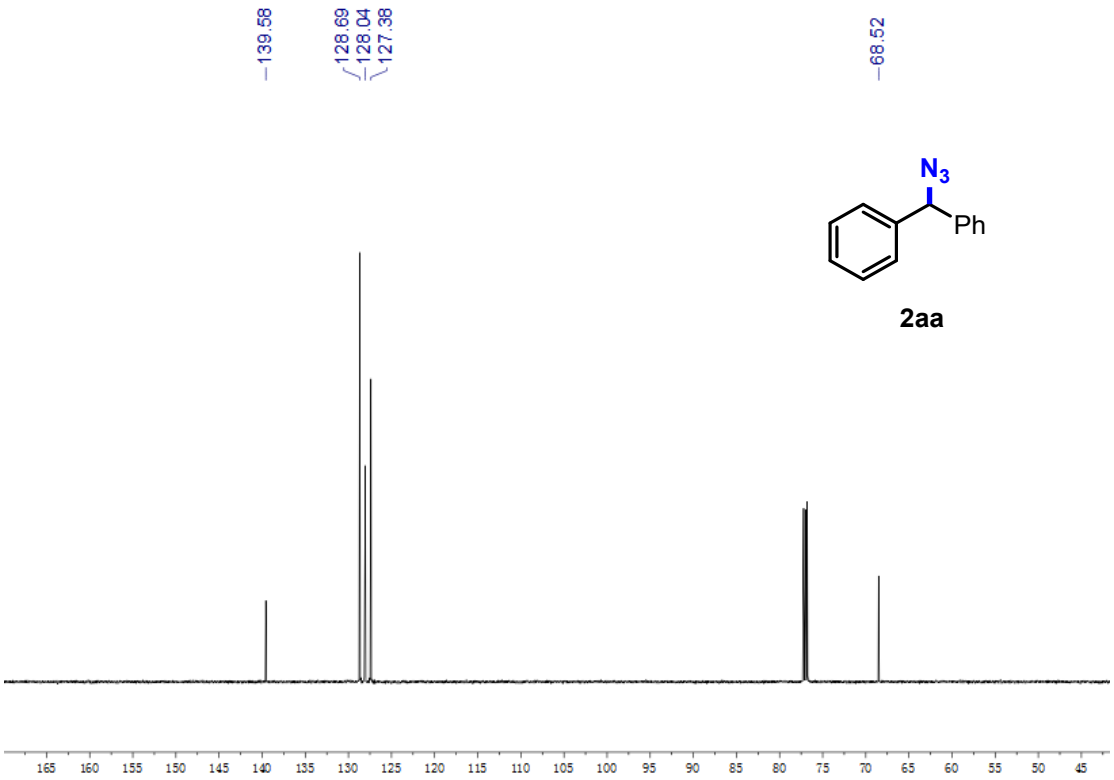
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2z**



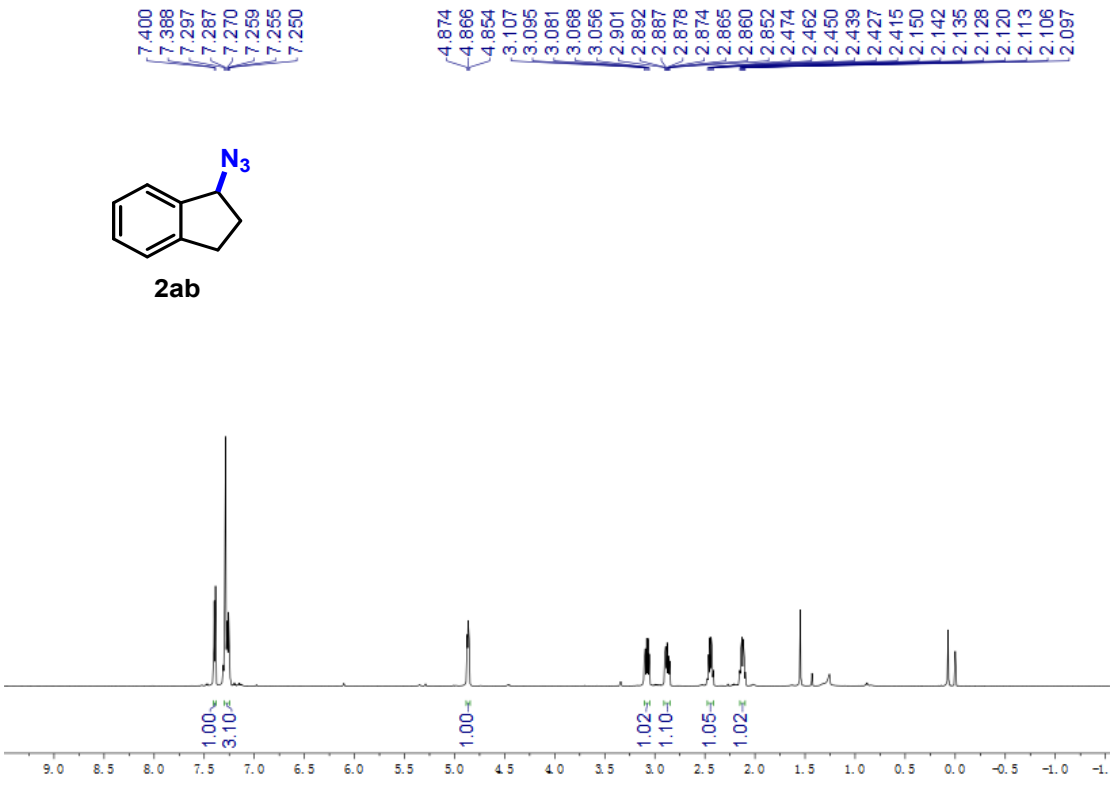
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2z**



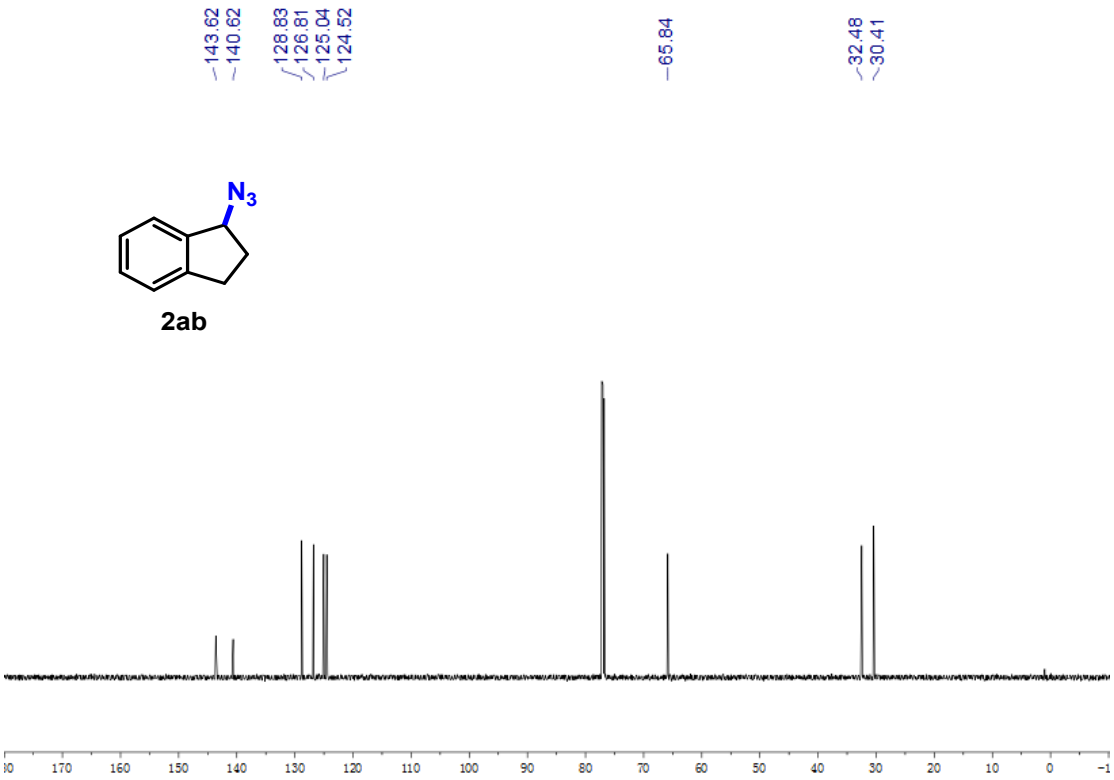
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aa**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2aa**

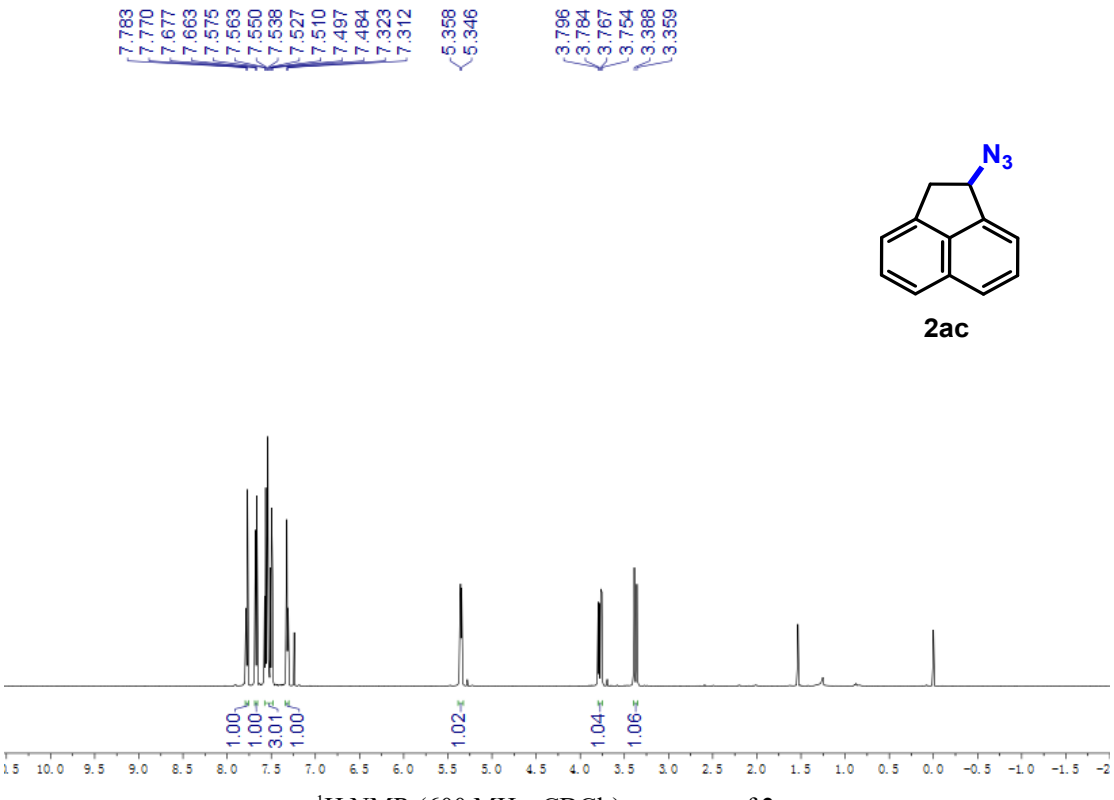


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ab**



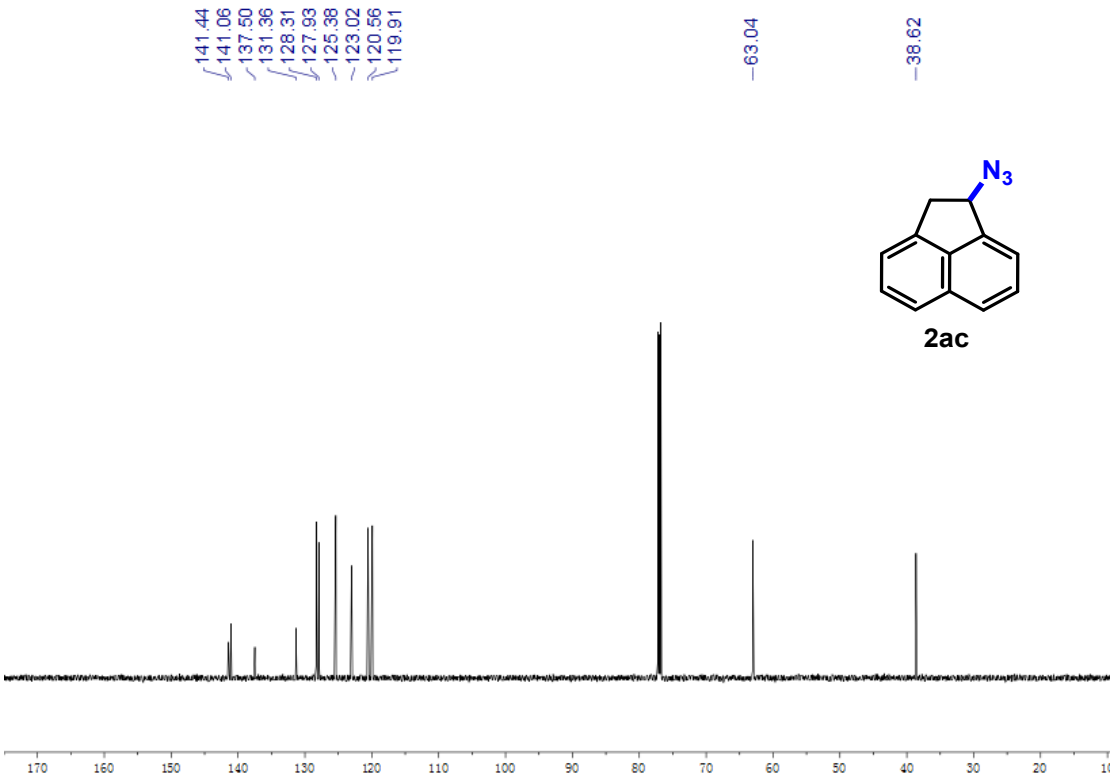
2ab

^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ab**

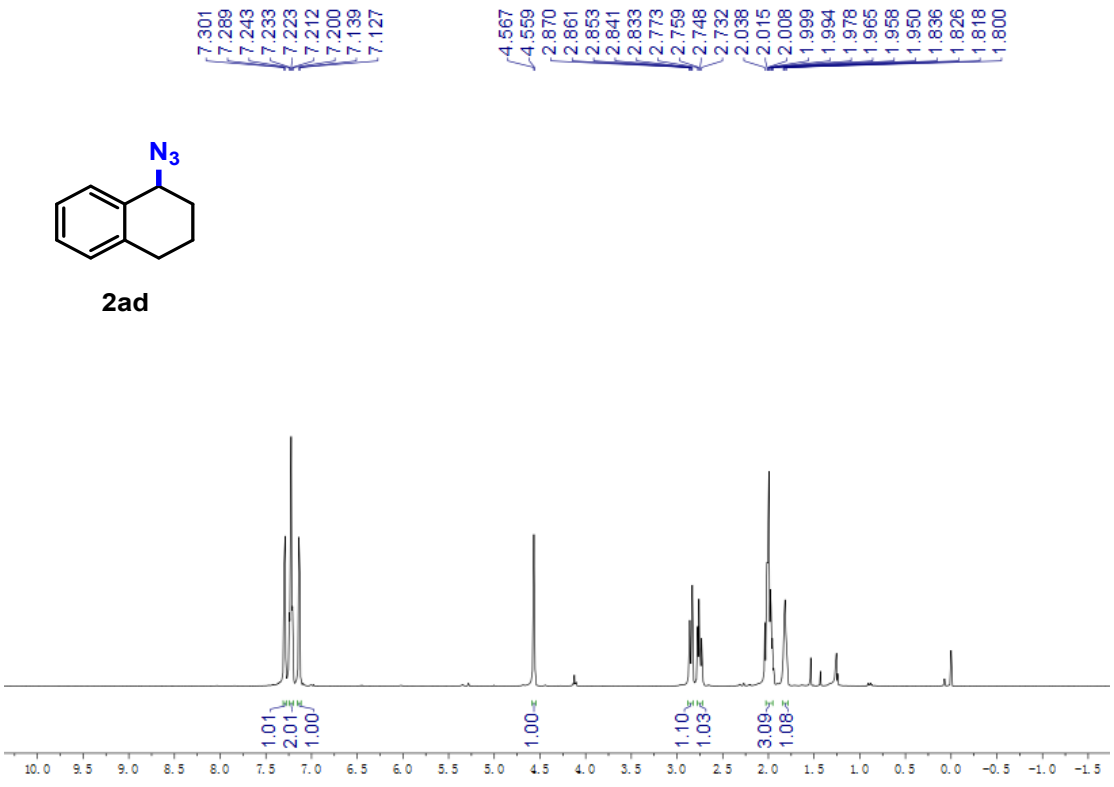


2ac

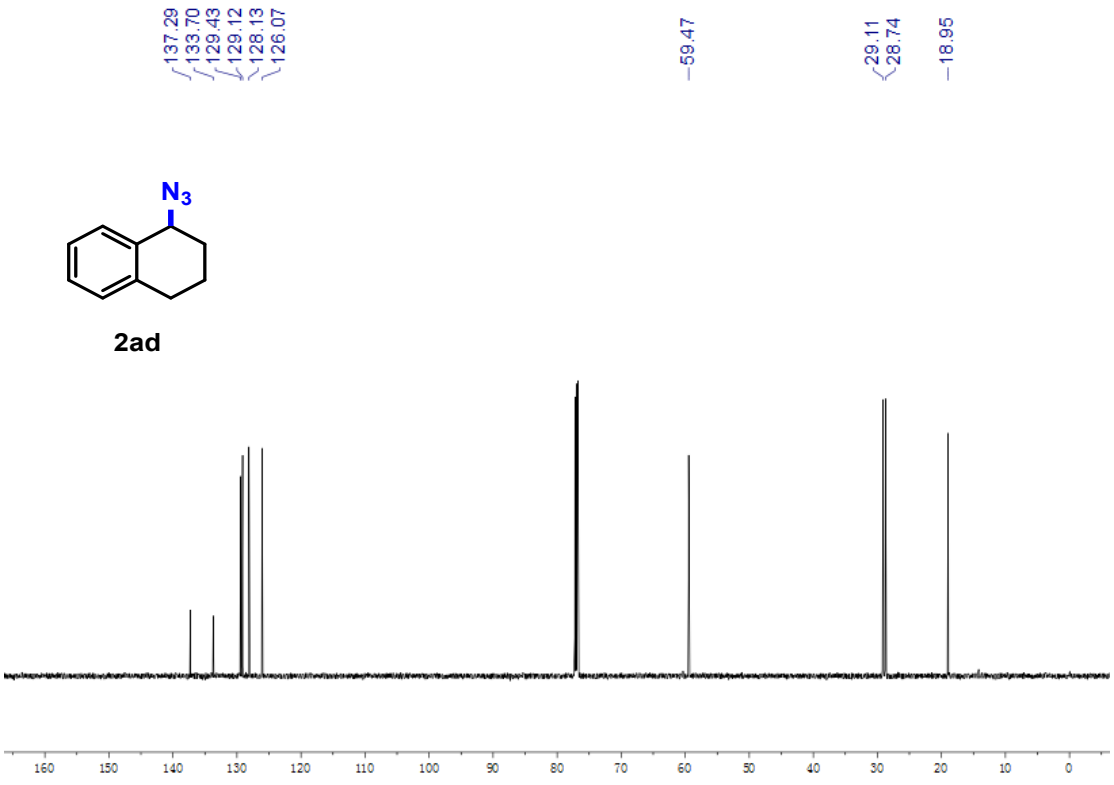
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ac**



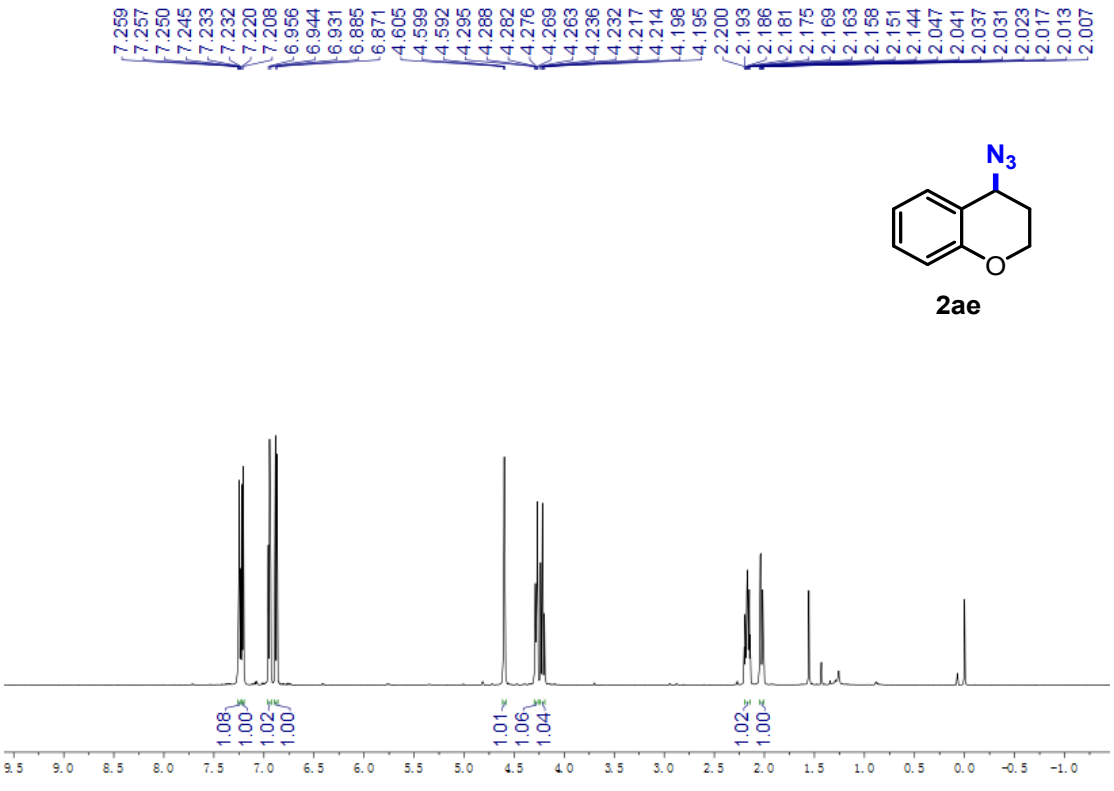
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ac**



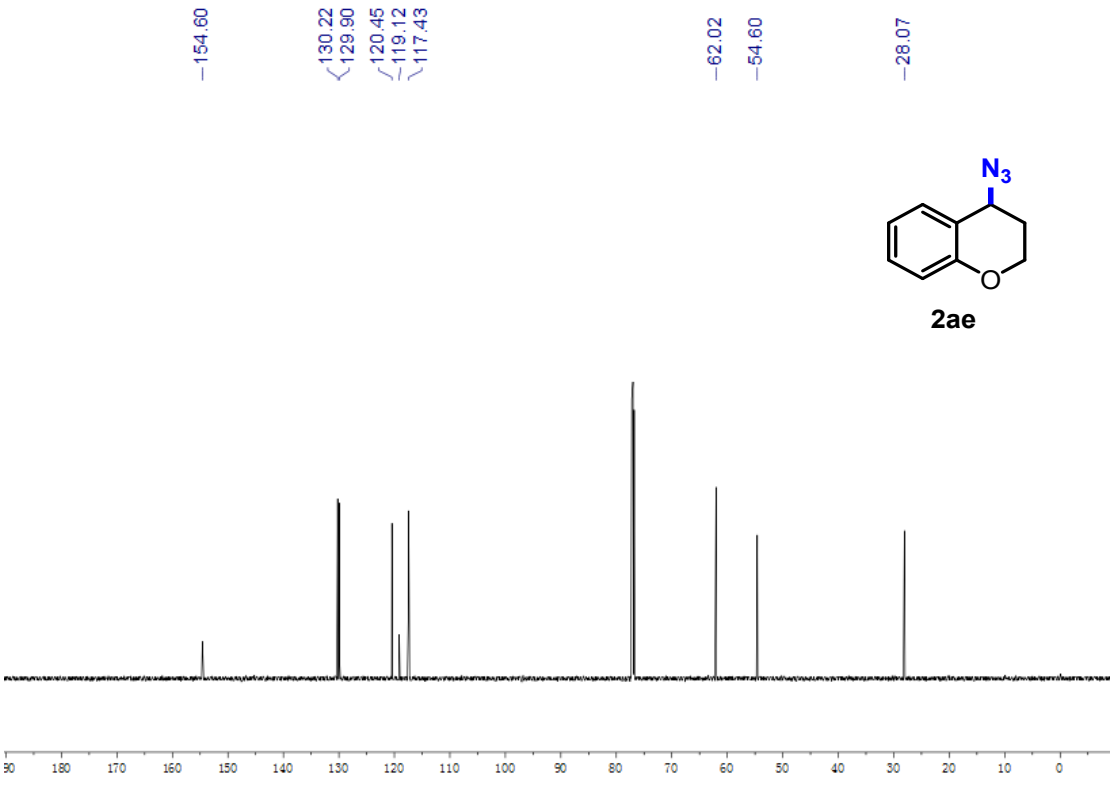
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ad**



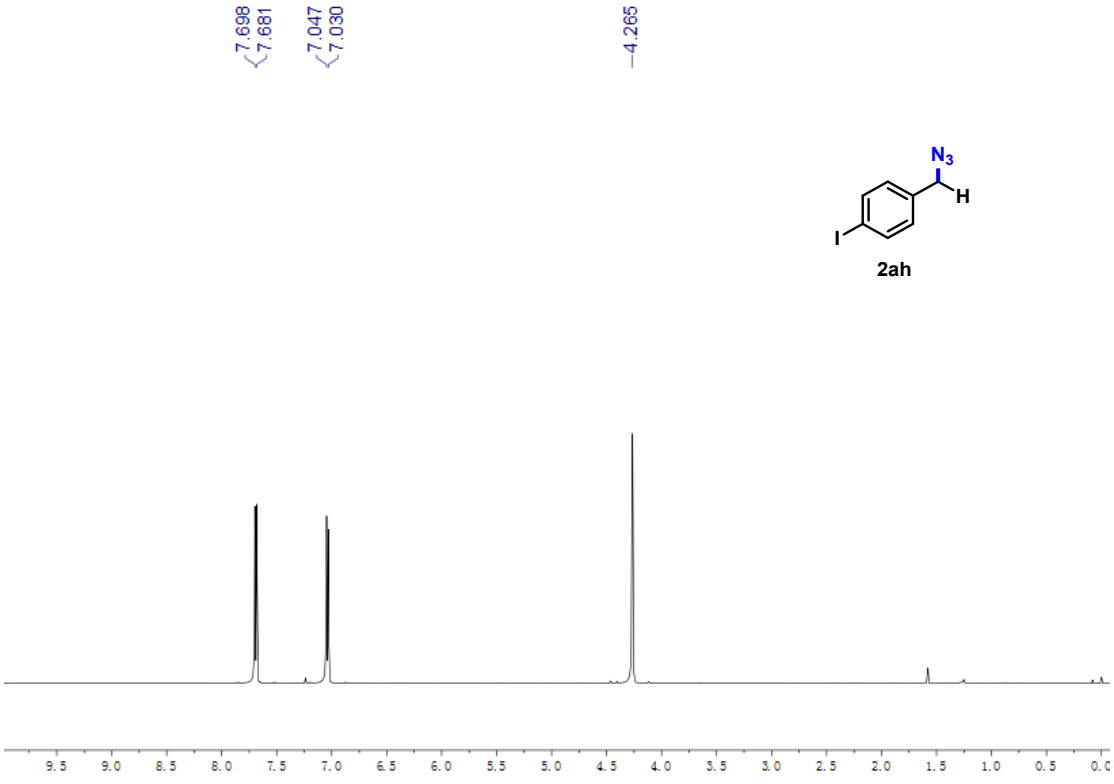
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ad**



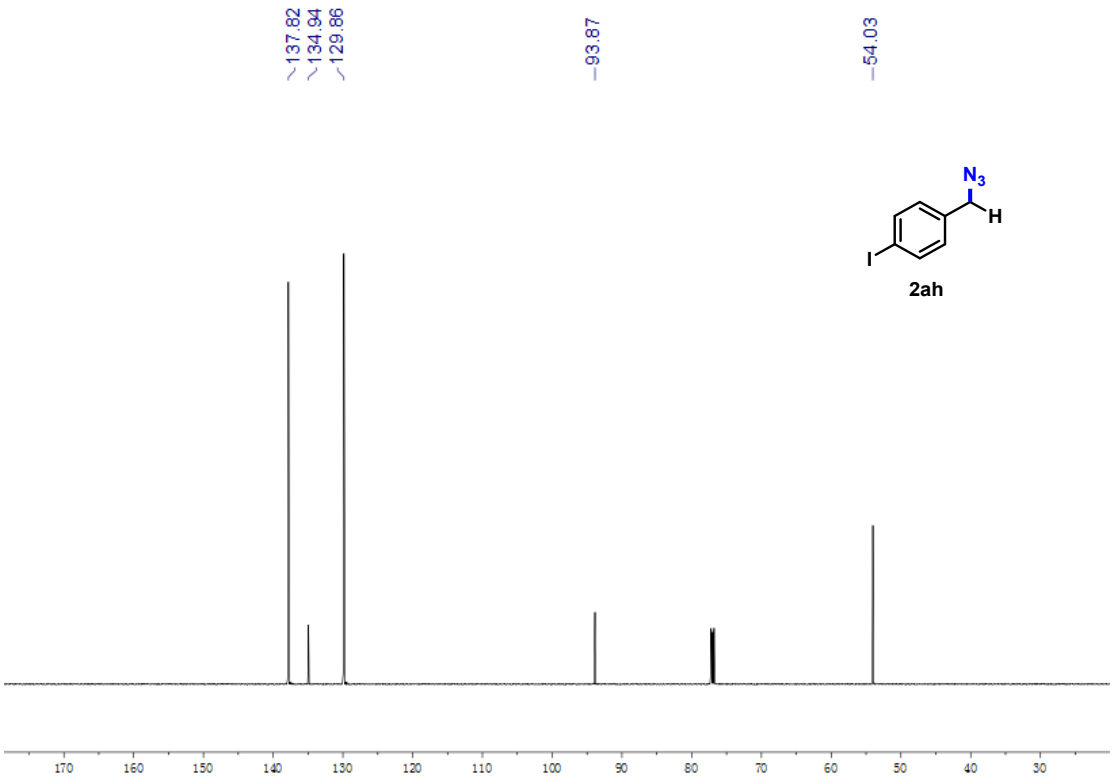
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ae**



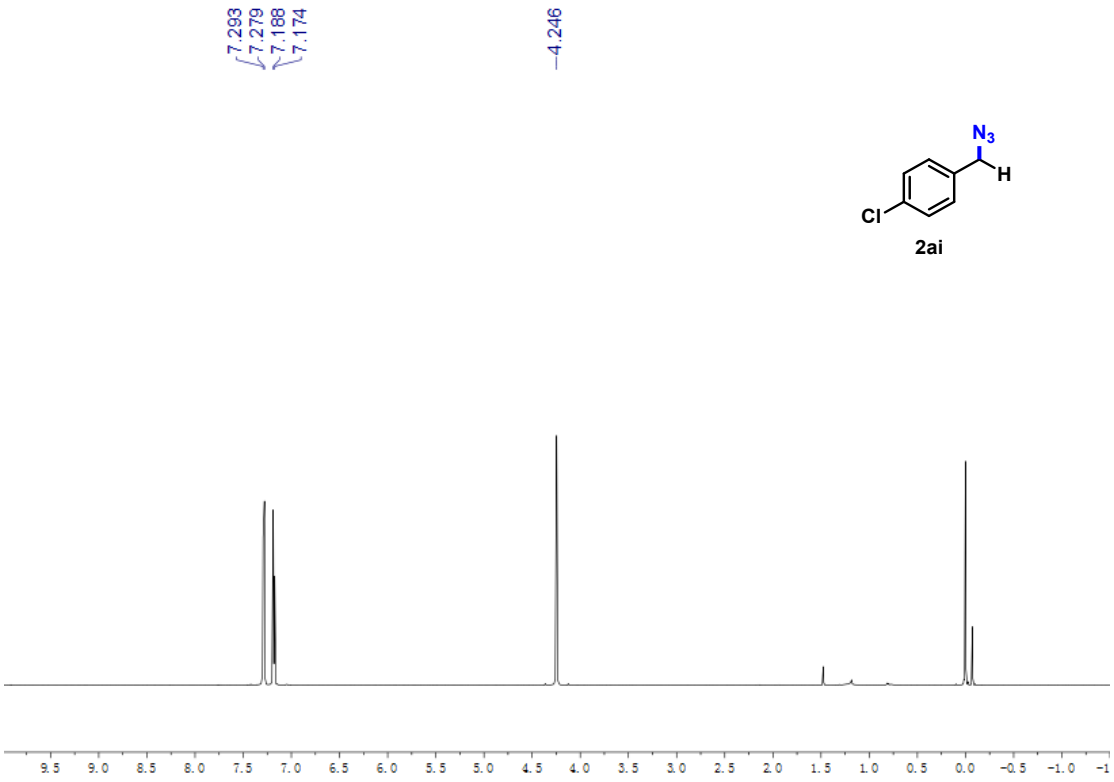
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ae**



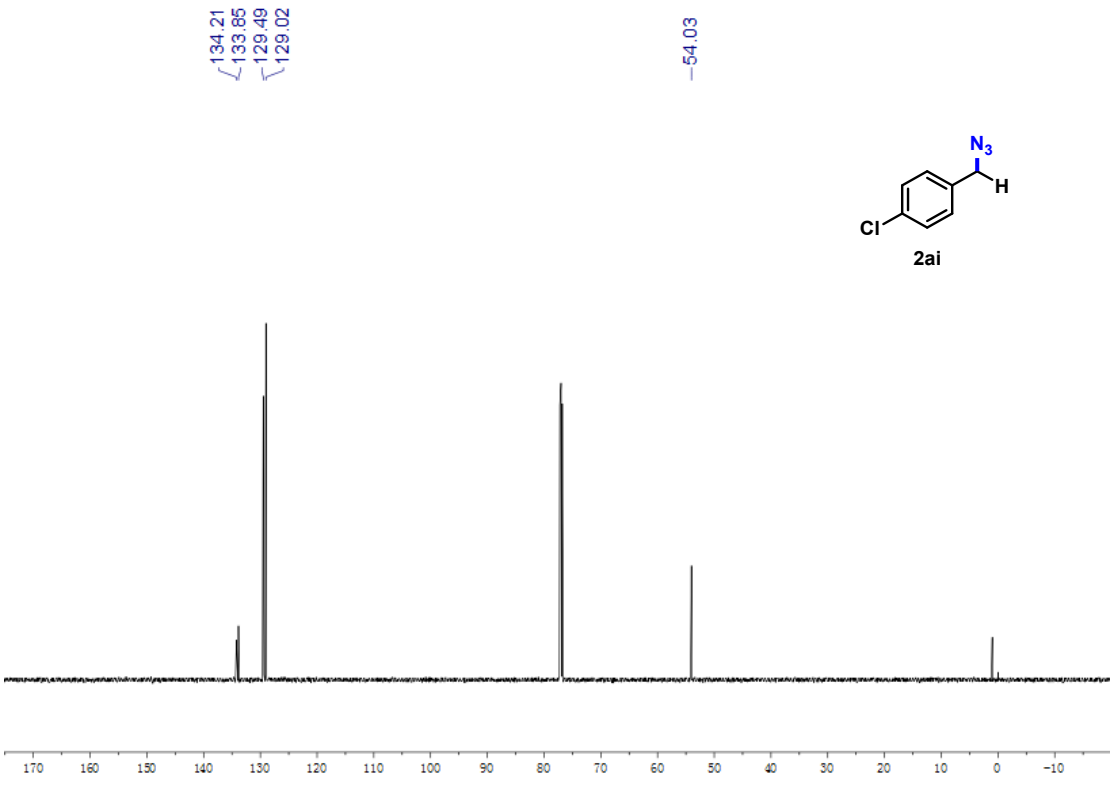
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2ah**



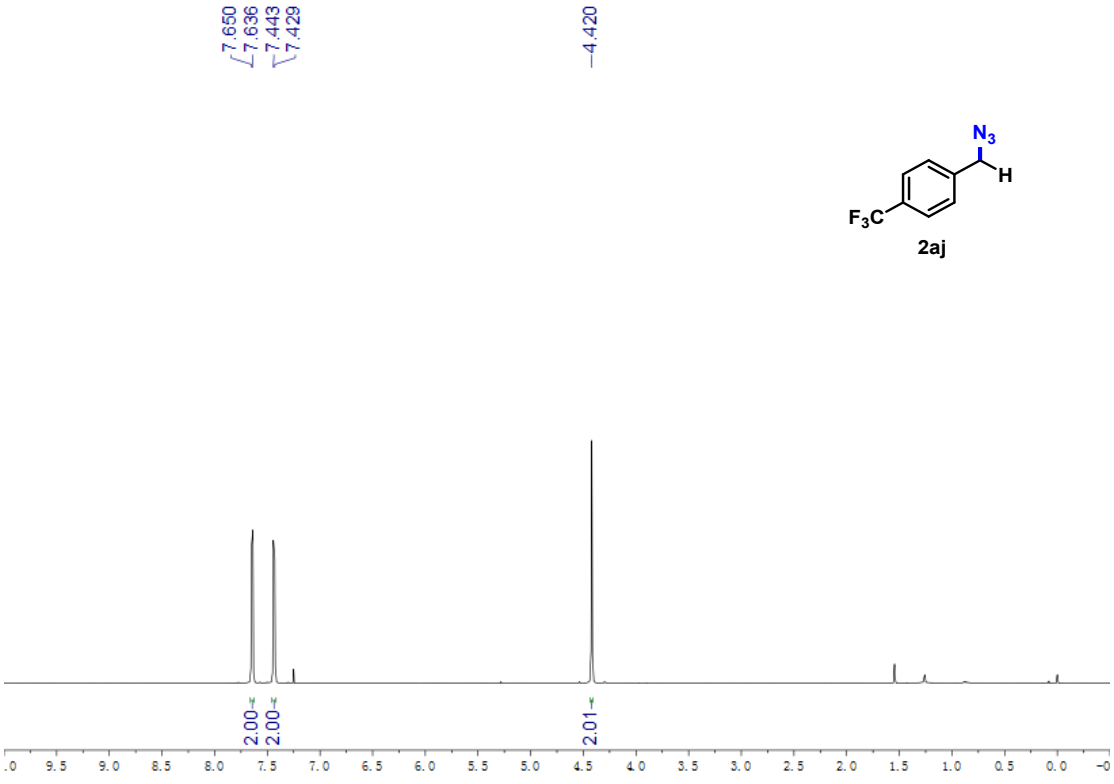
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ah**



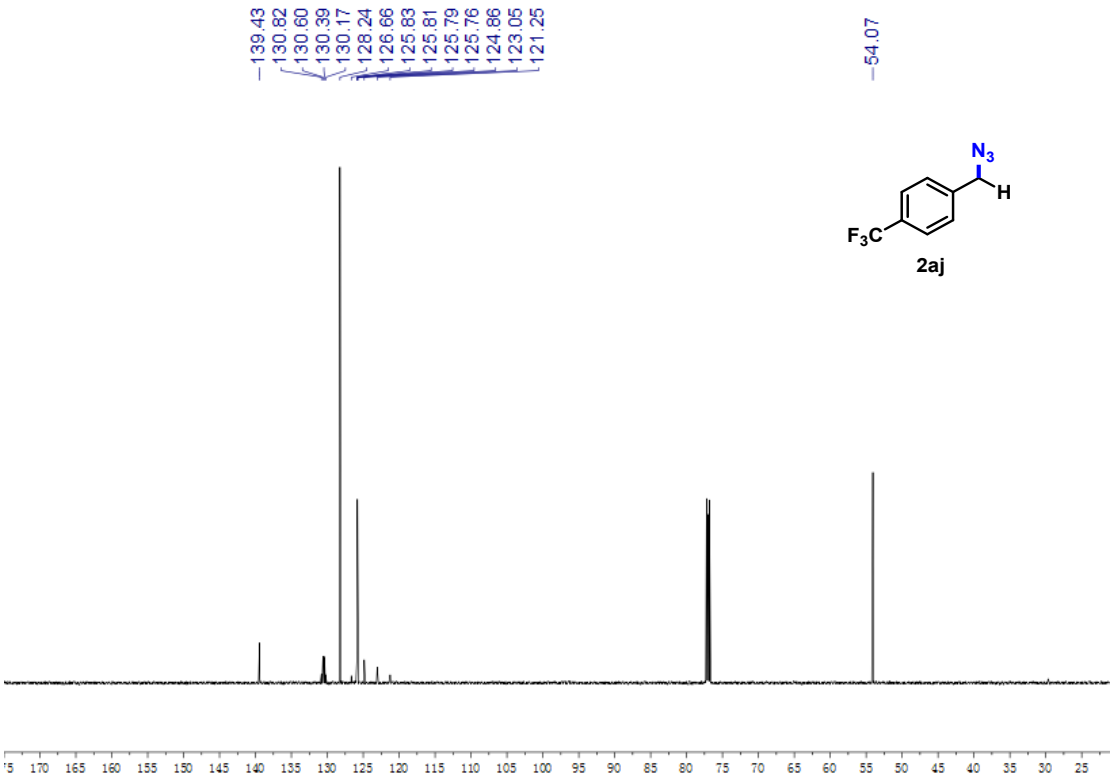
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ai**



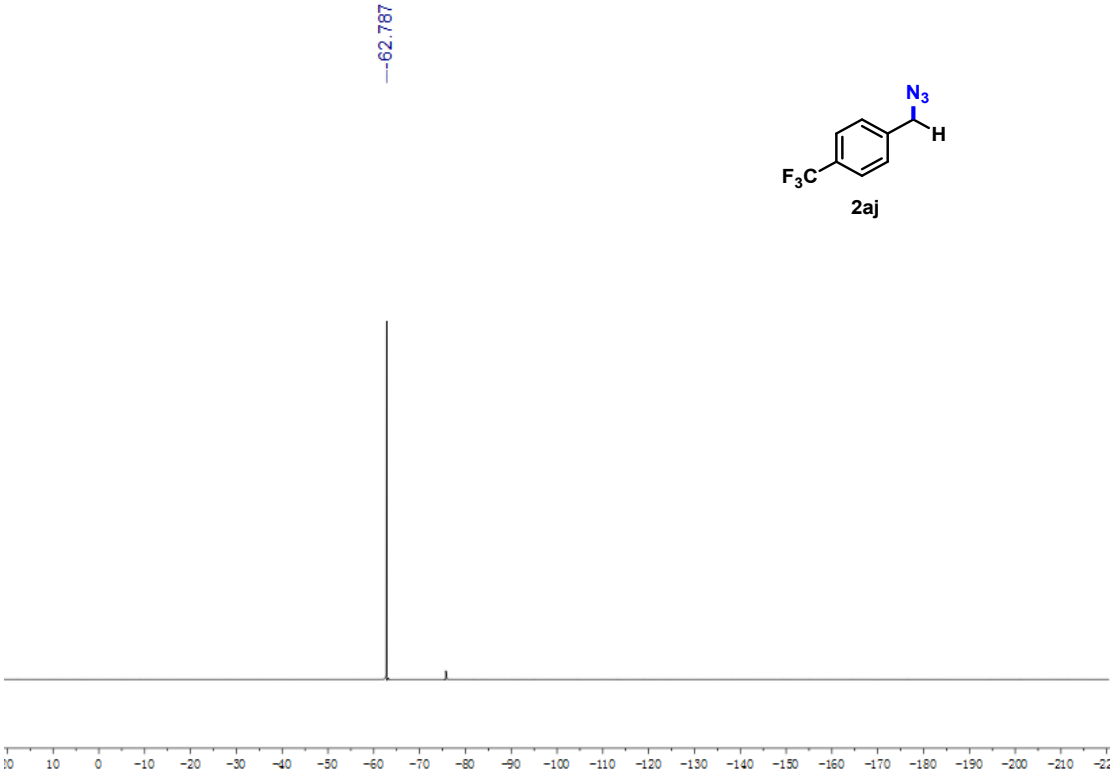
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ai**



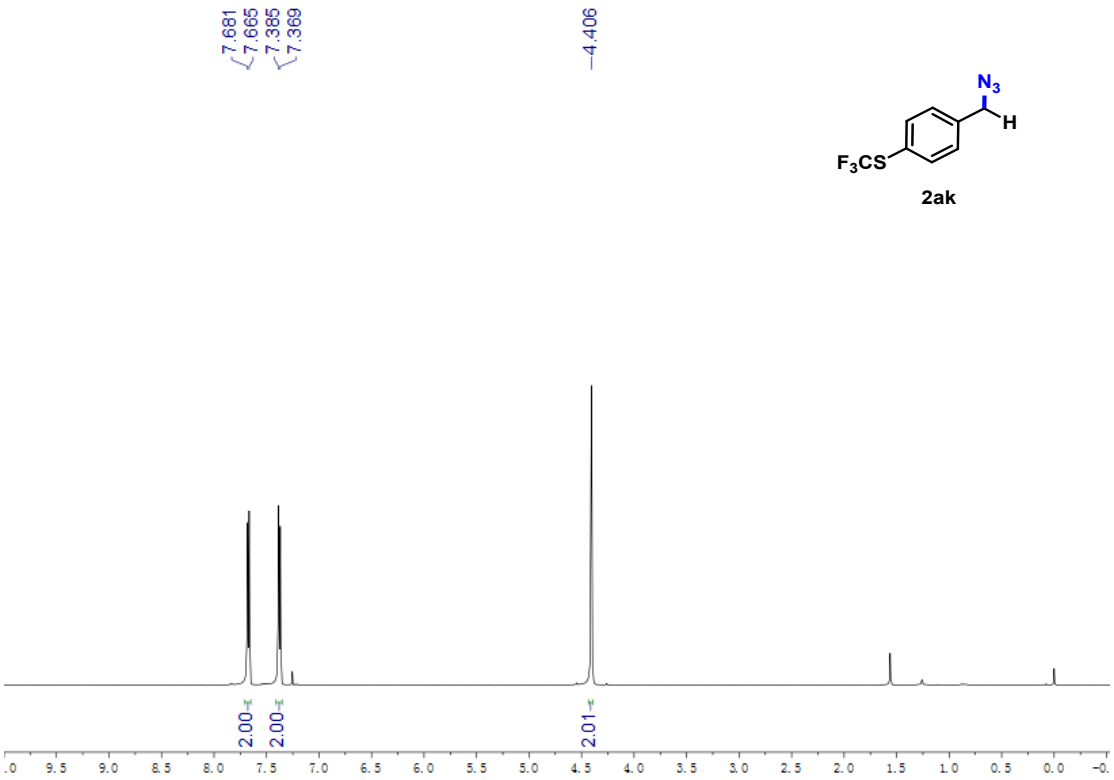
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aj**



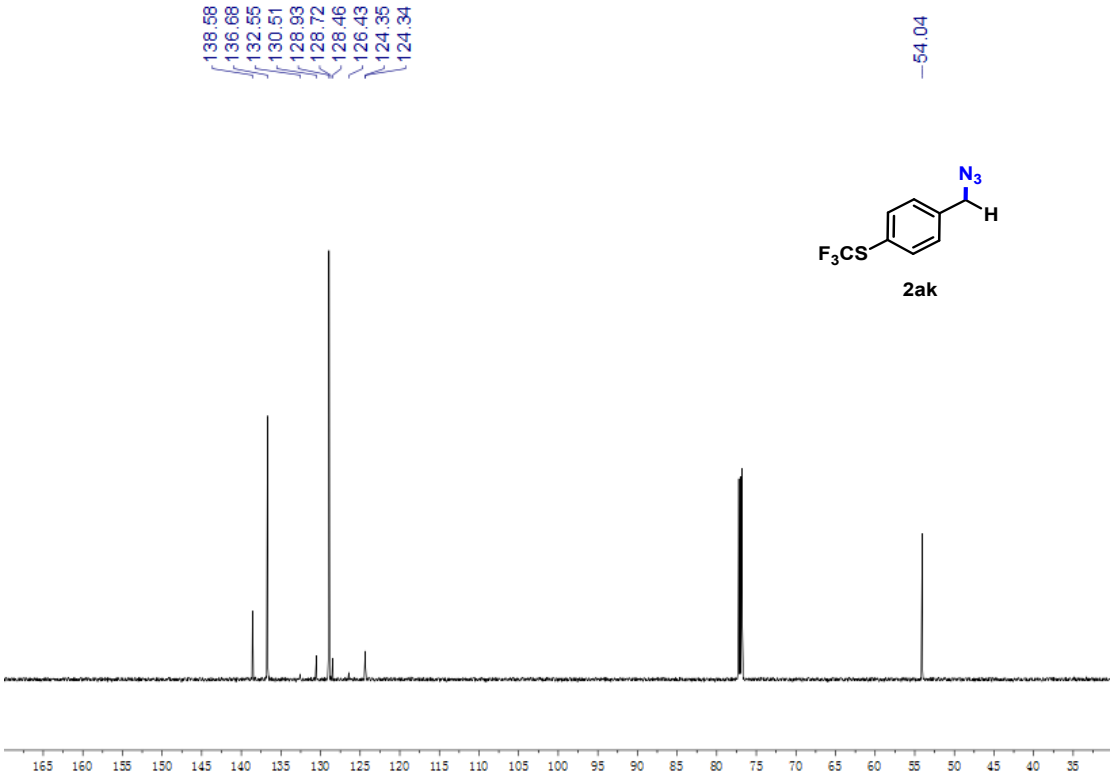
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2aj**



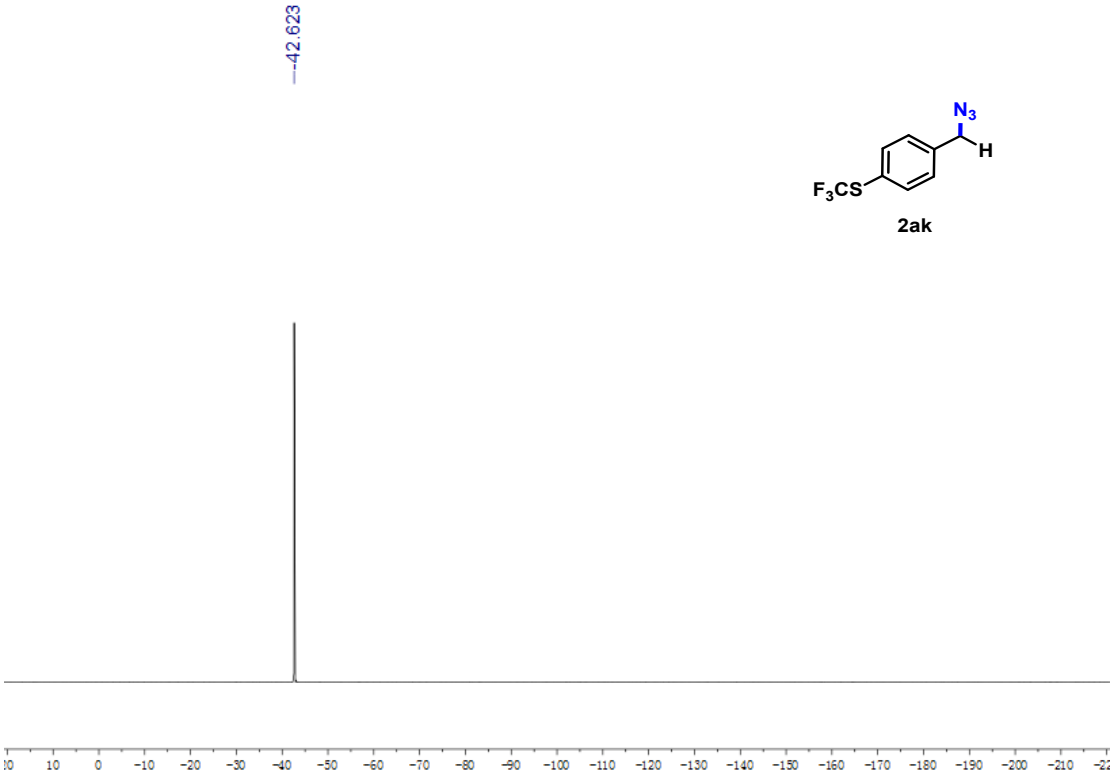
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2aj**.



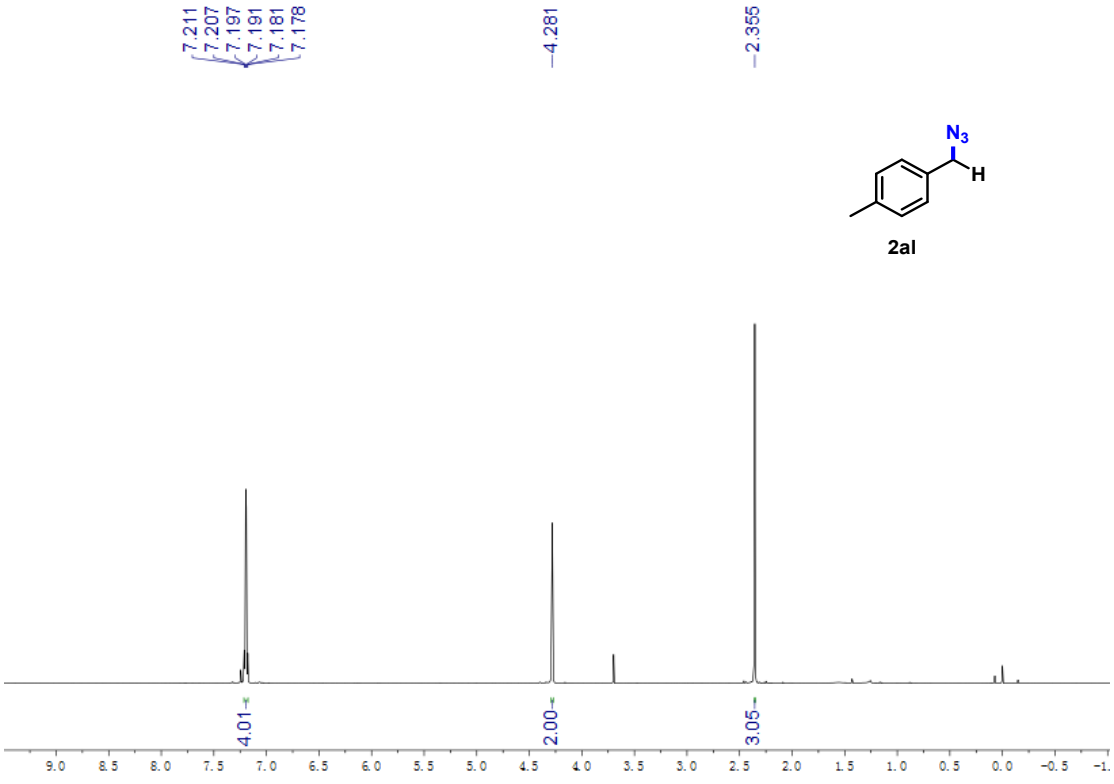
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ak**



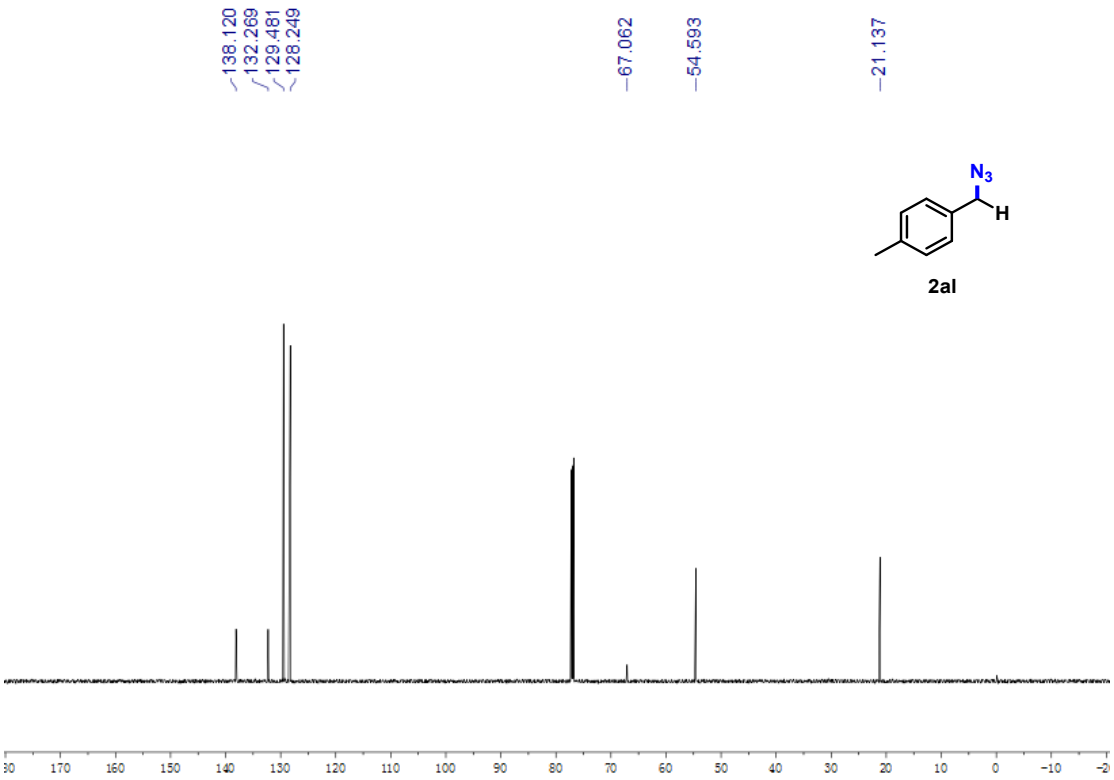
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ak**



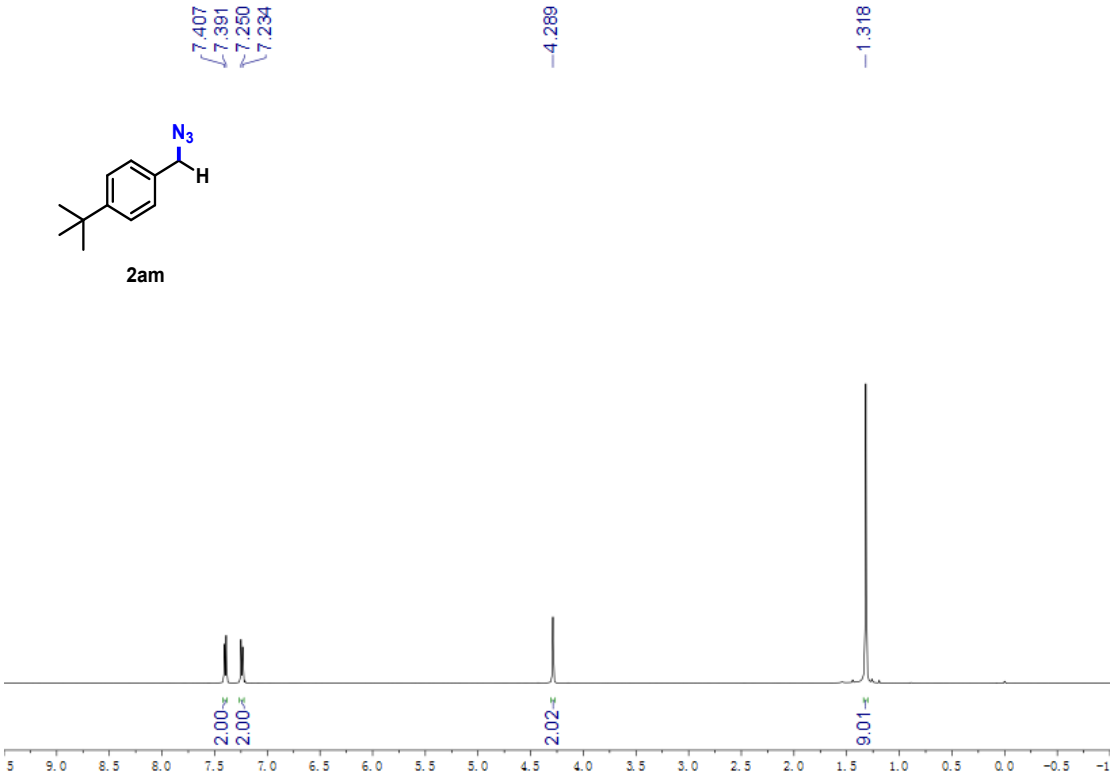
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2ak**



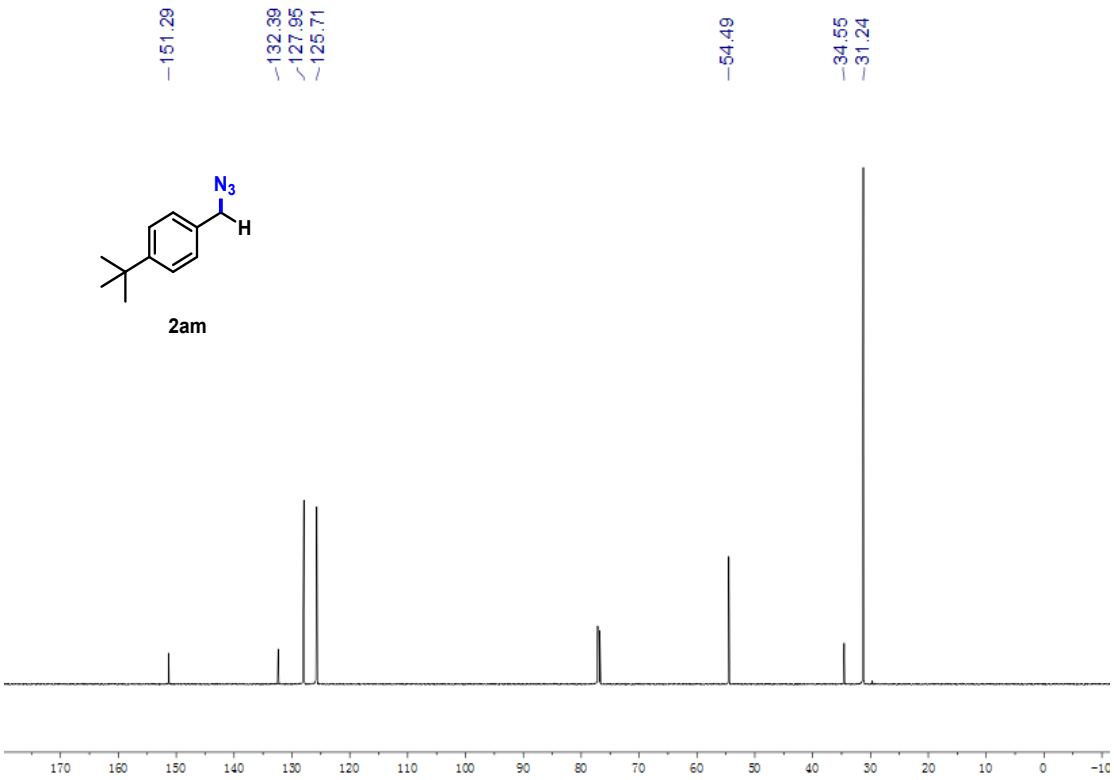
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2al**



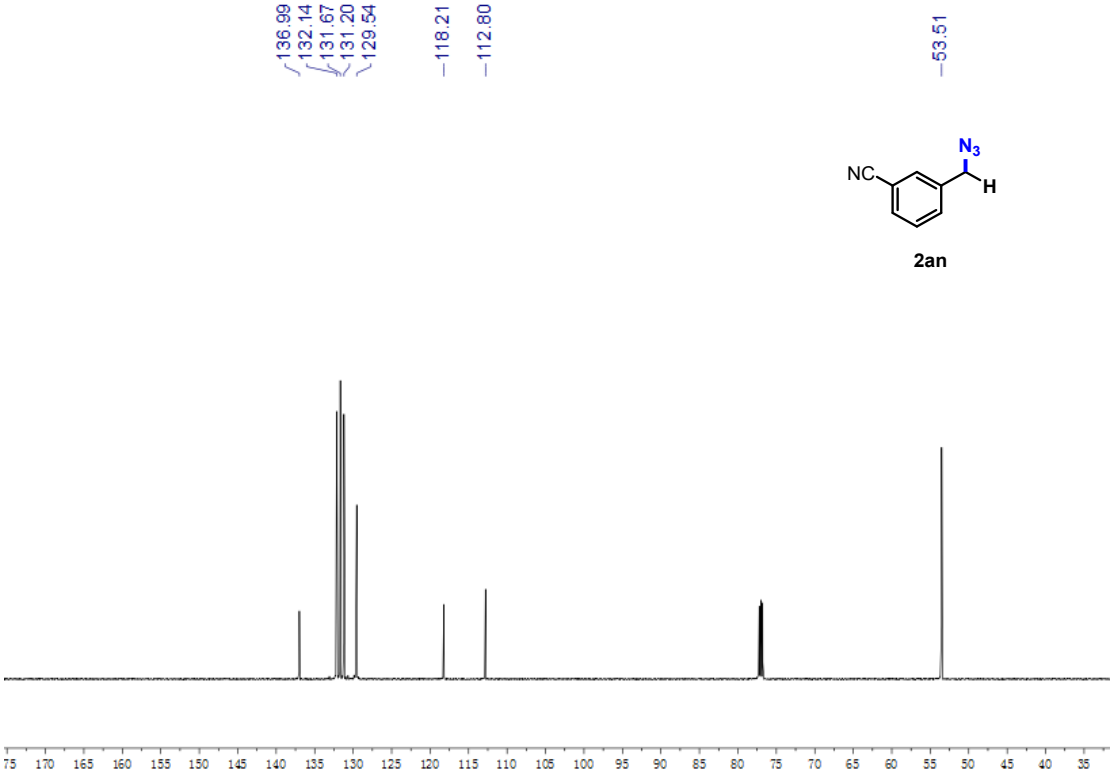
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2al**



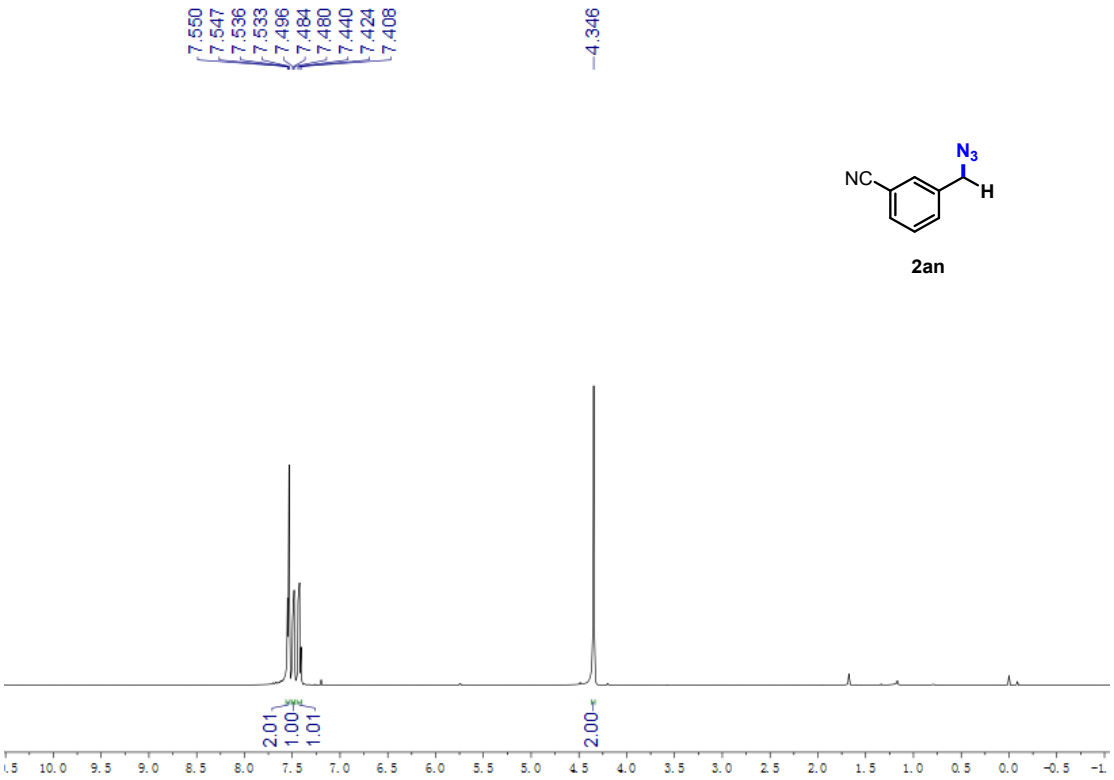
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2am**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2am**

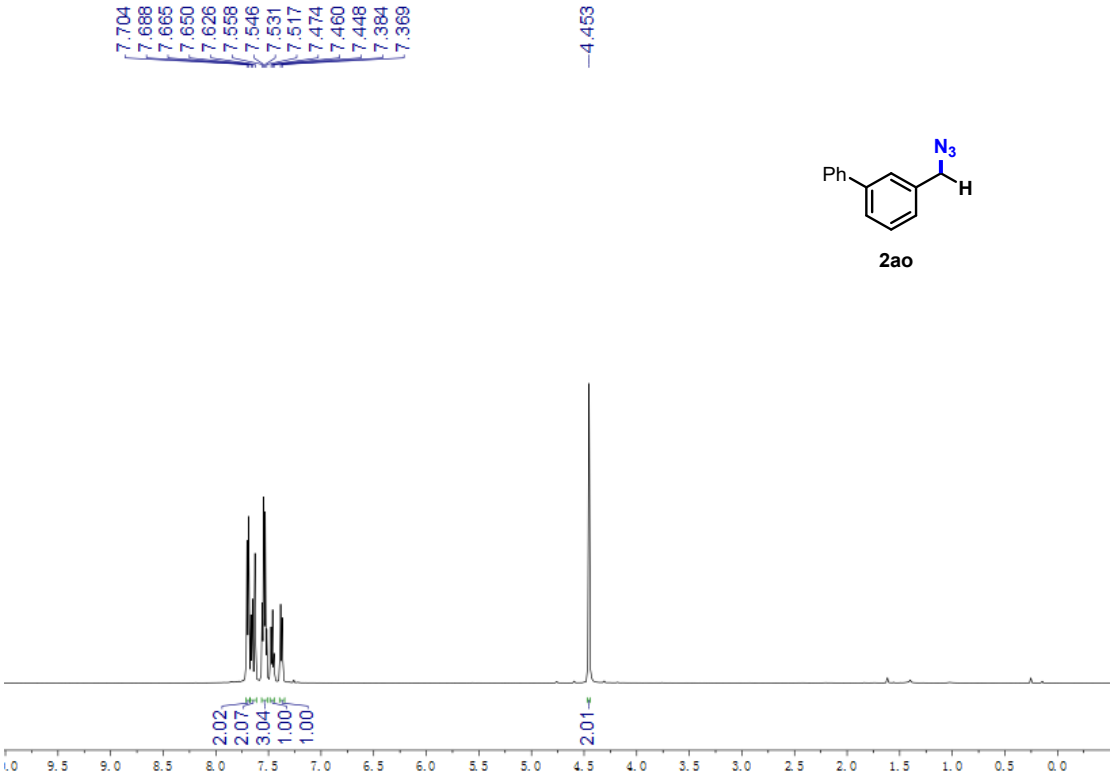


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2an**



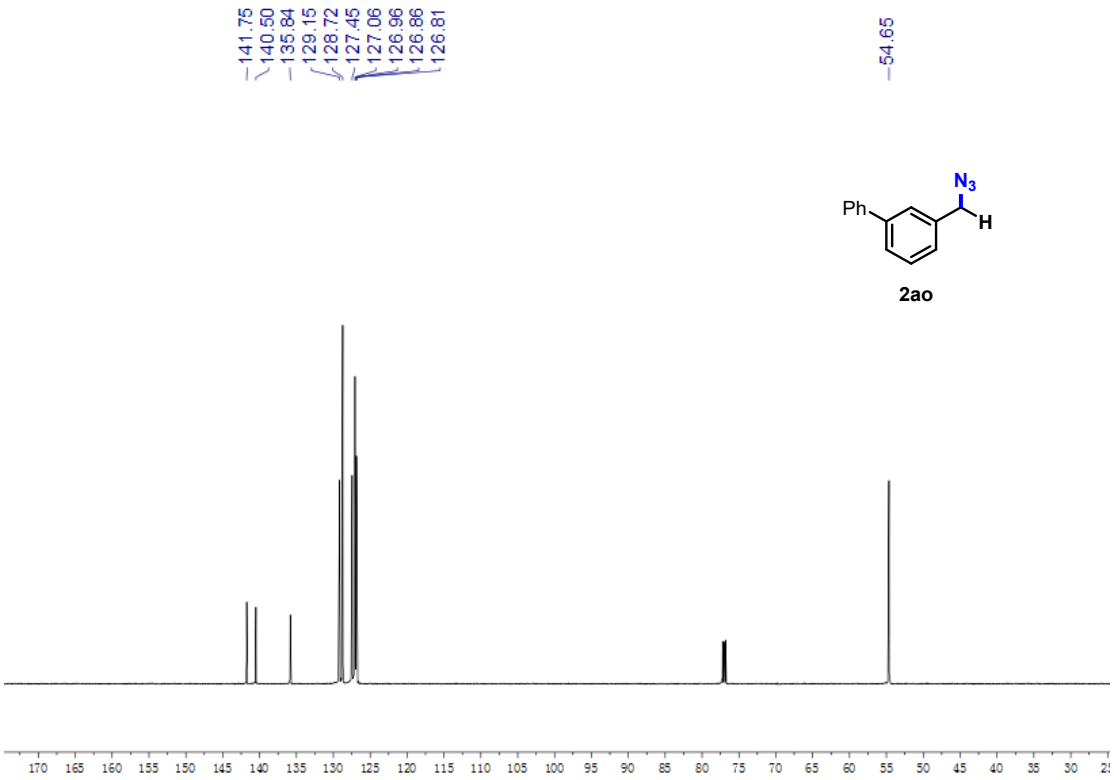
2an

^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2an**

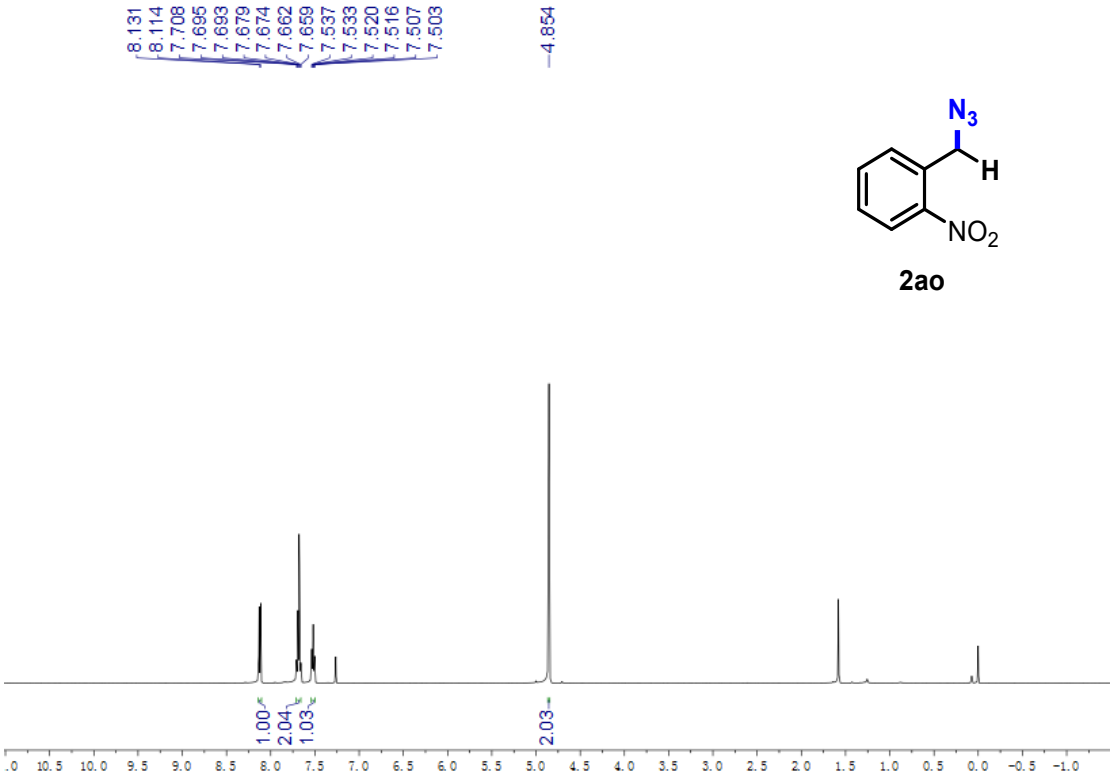


2ao

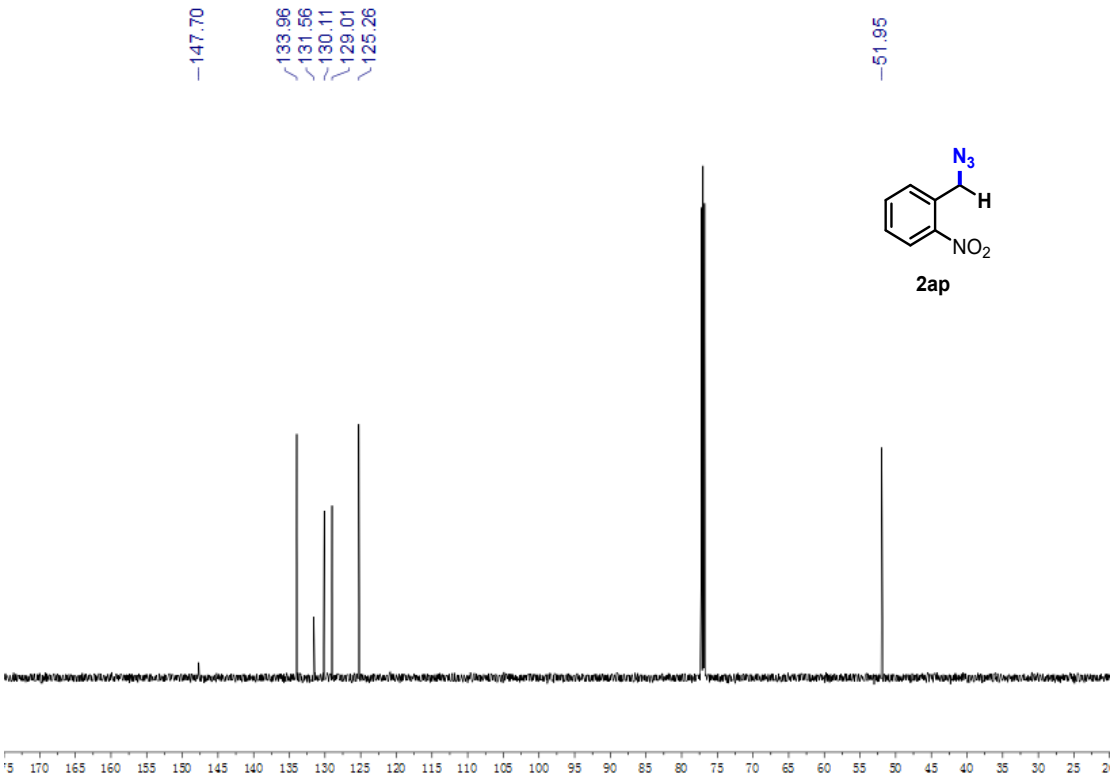
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ao**



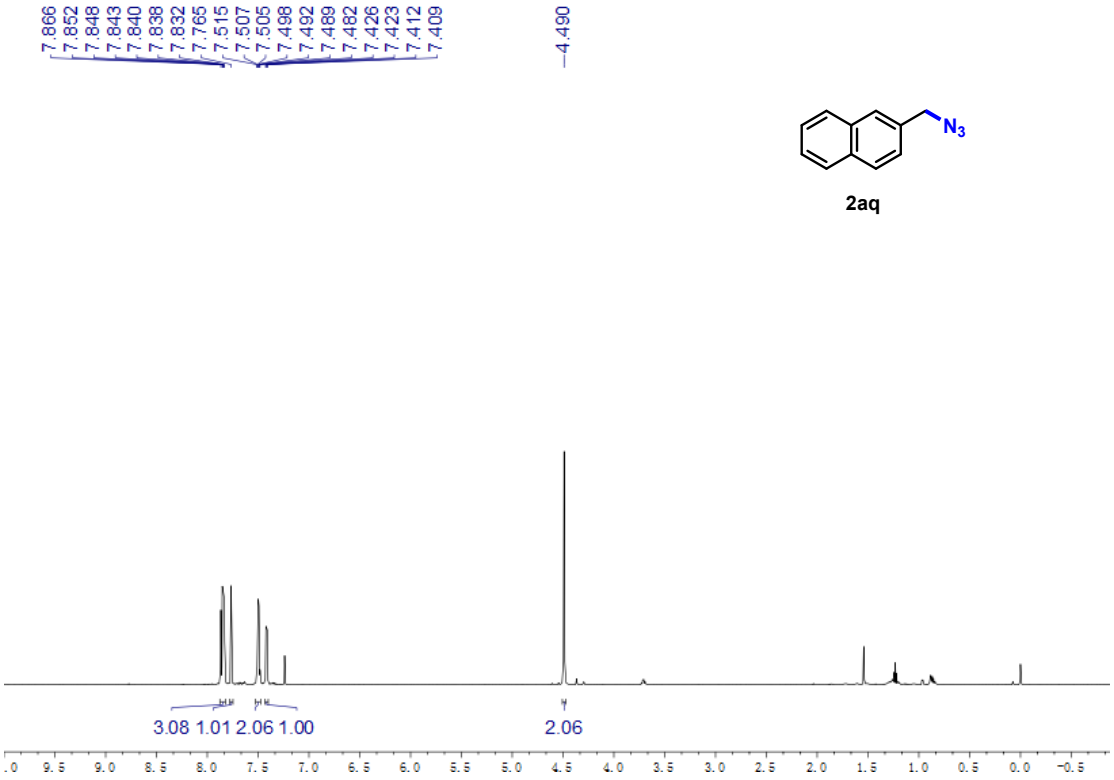
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ao**



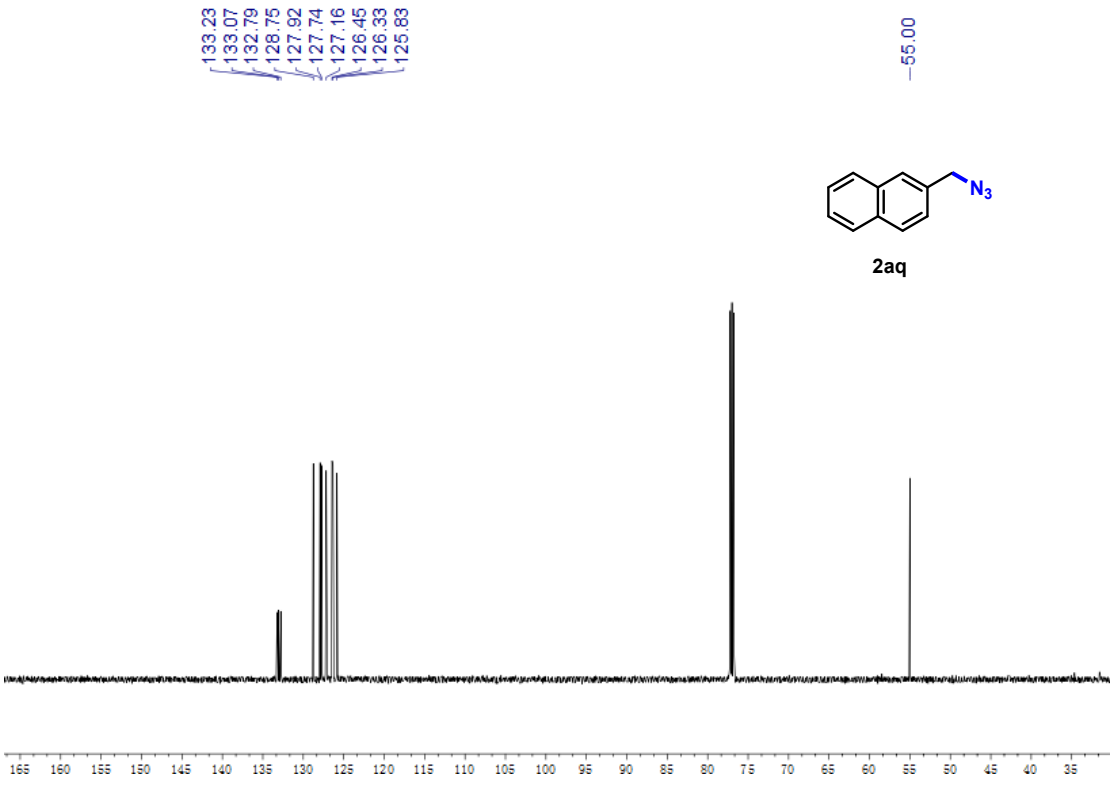
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ao**



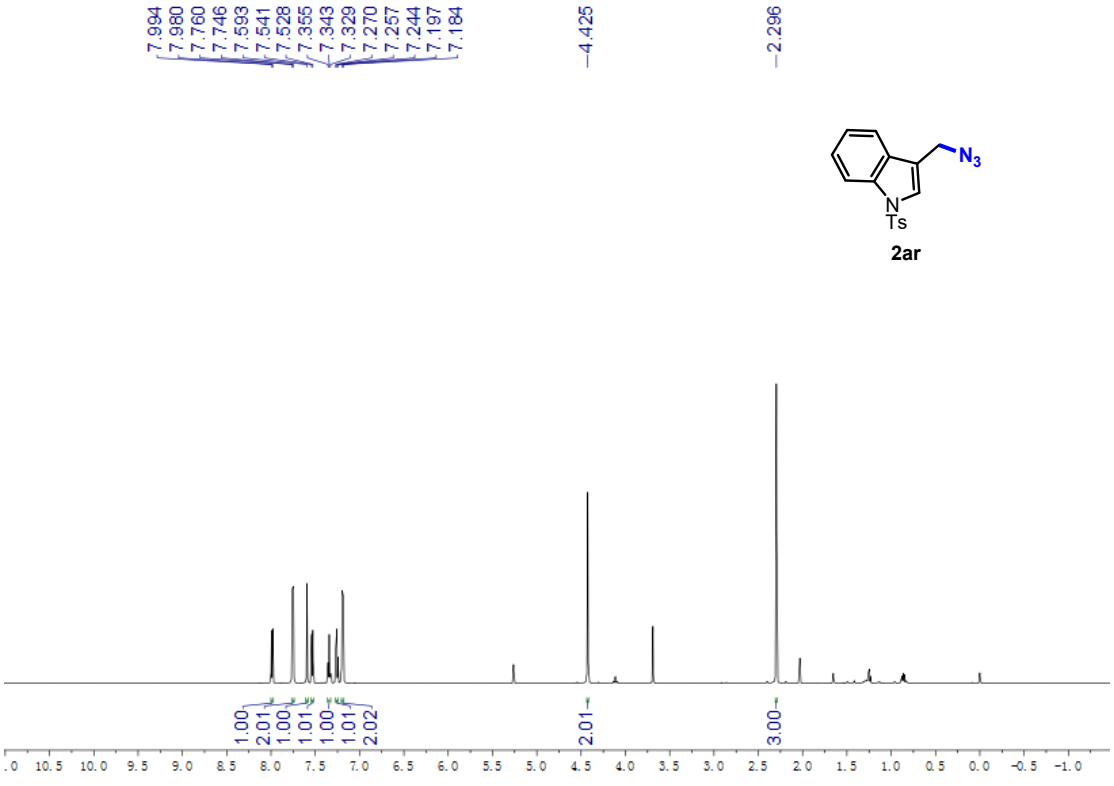
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ap**



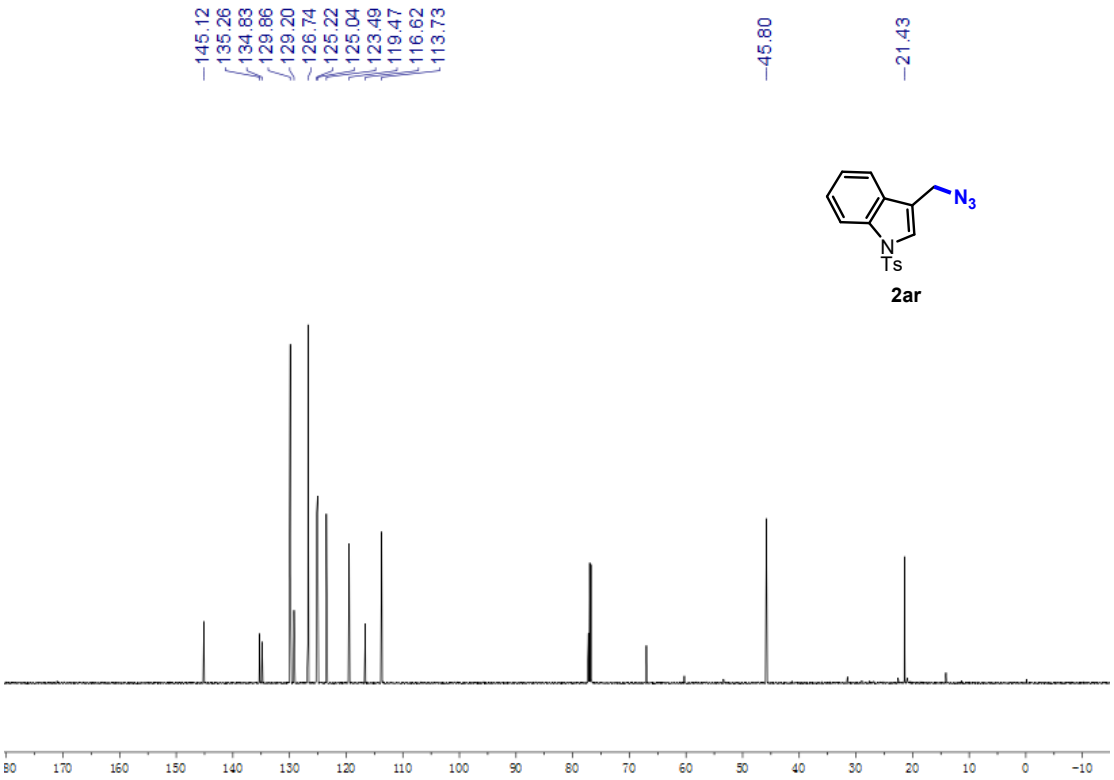
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aq**



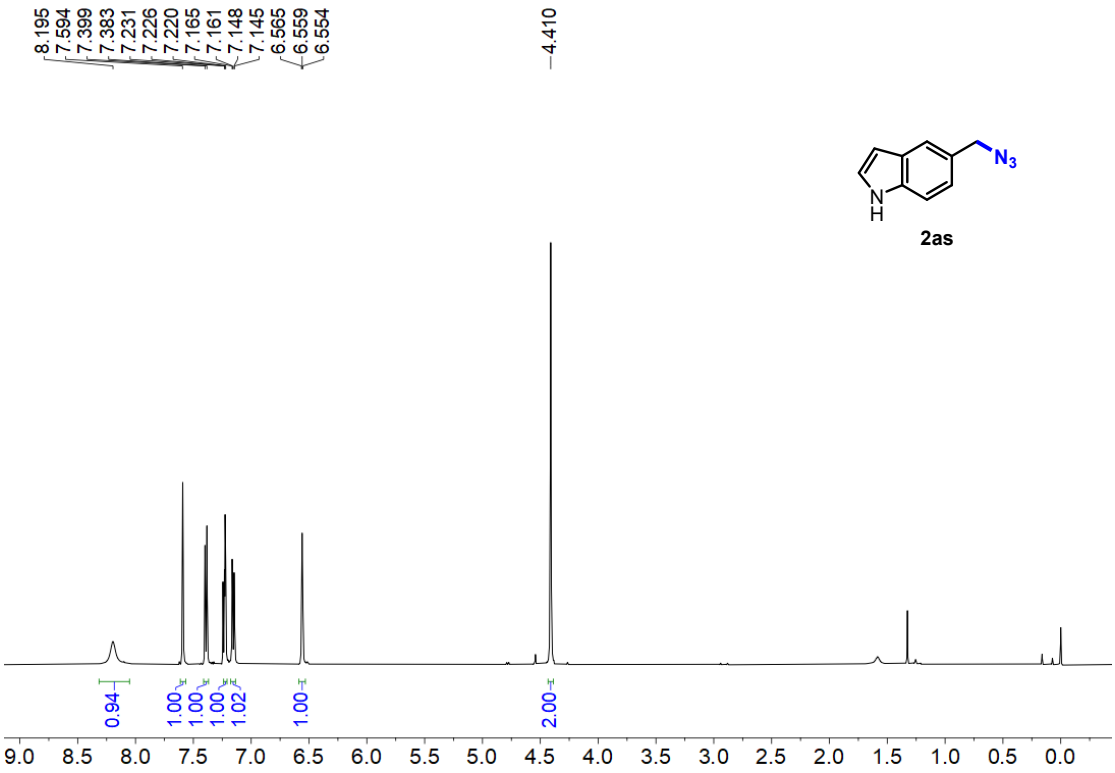
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2aq**

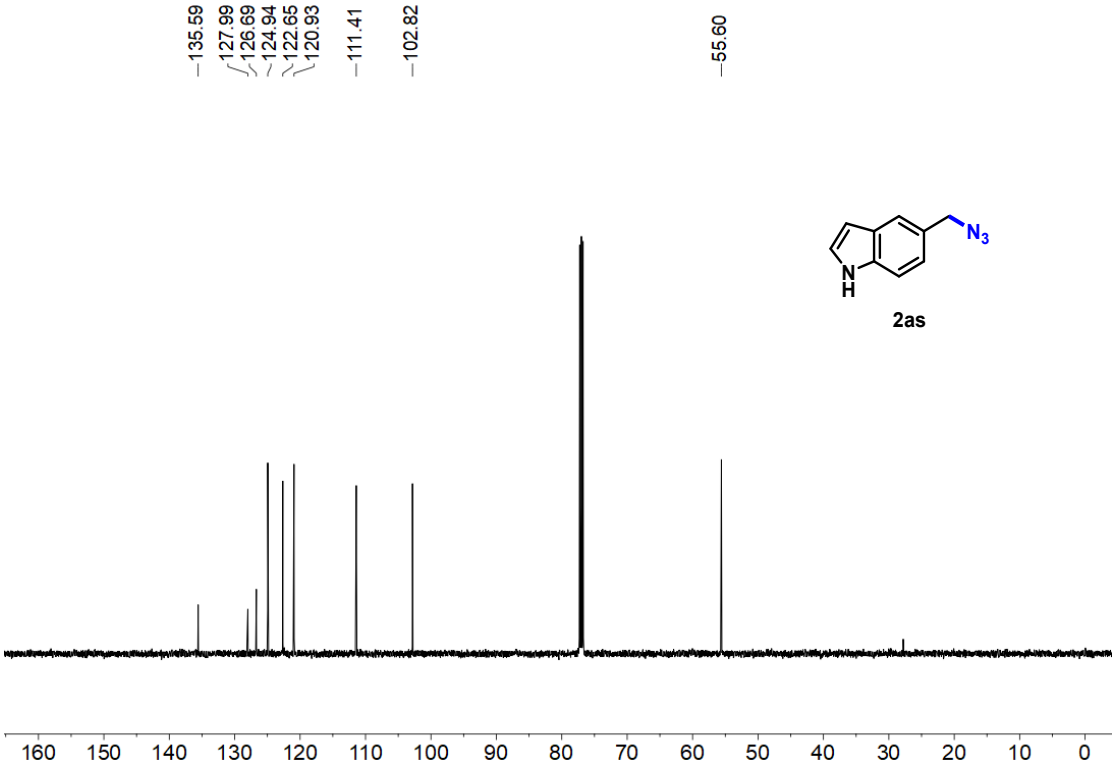


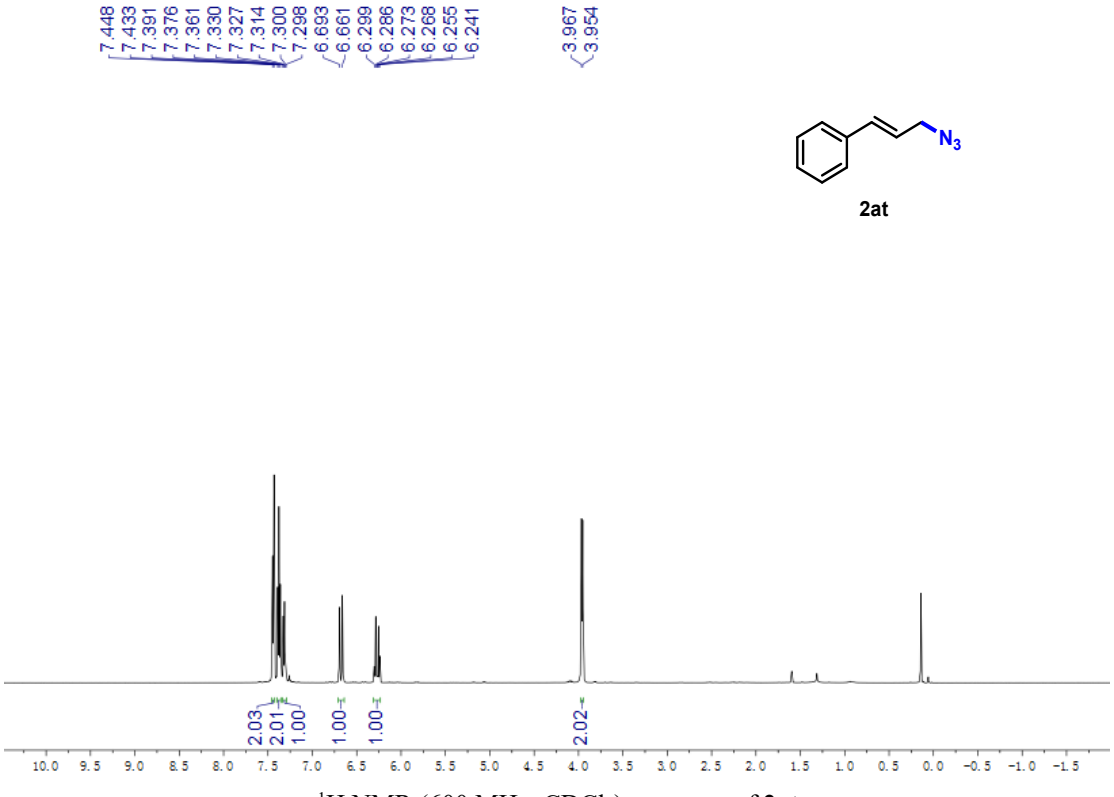
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ar**



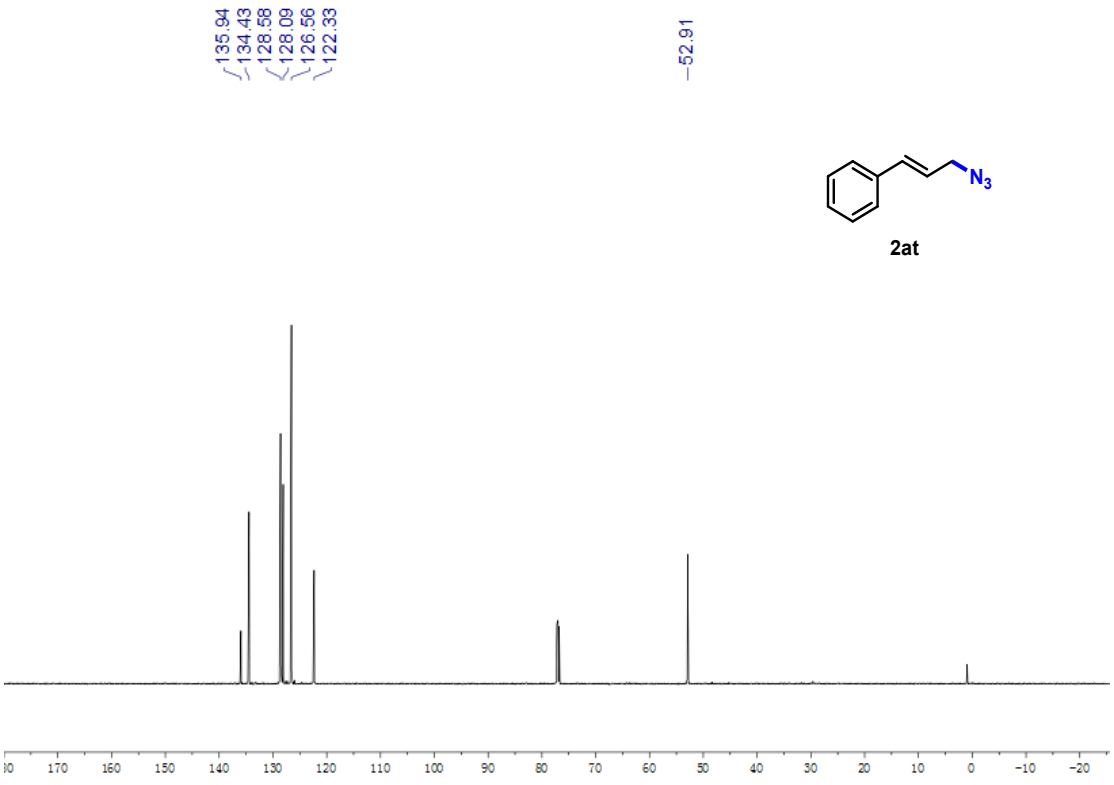
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2ar**



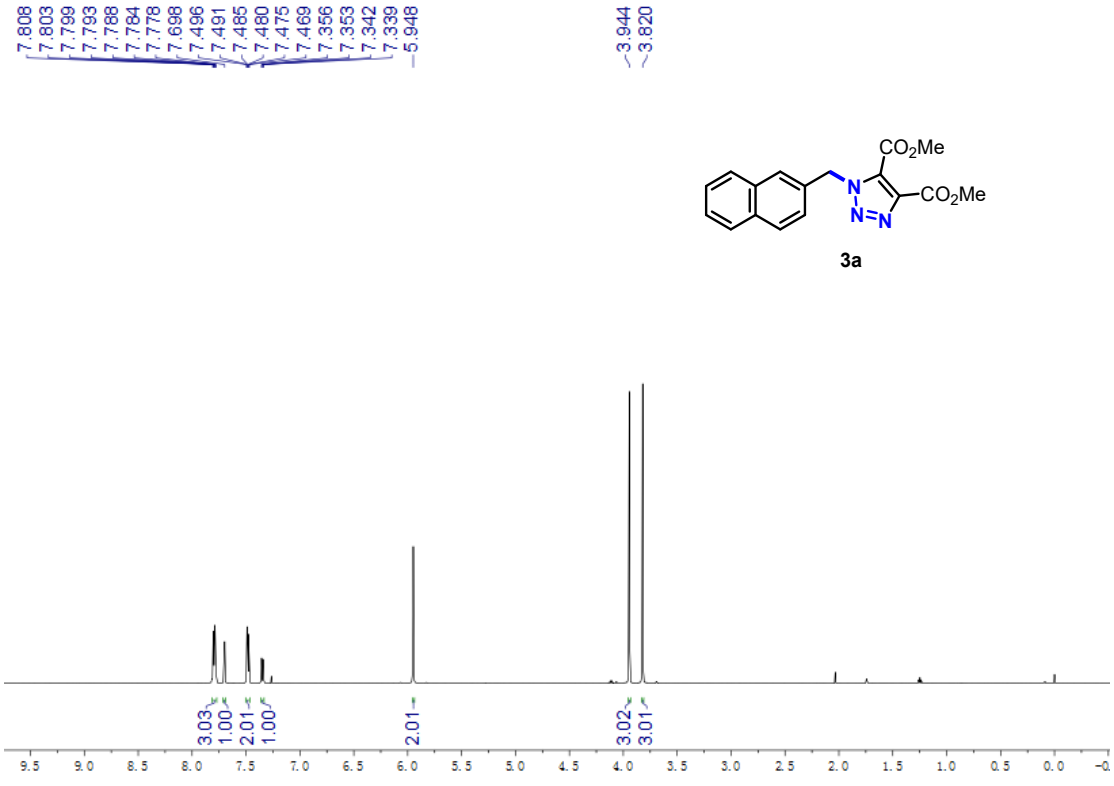




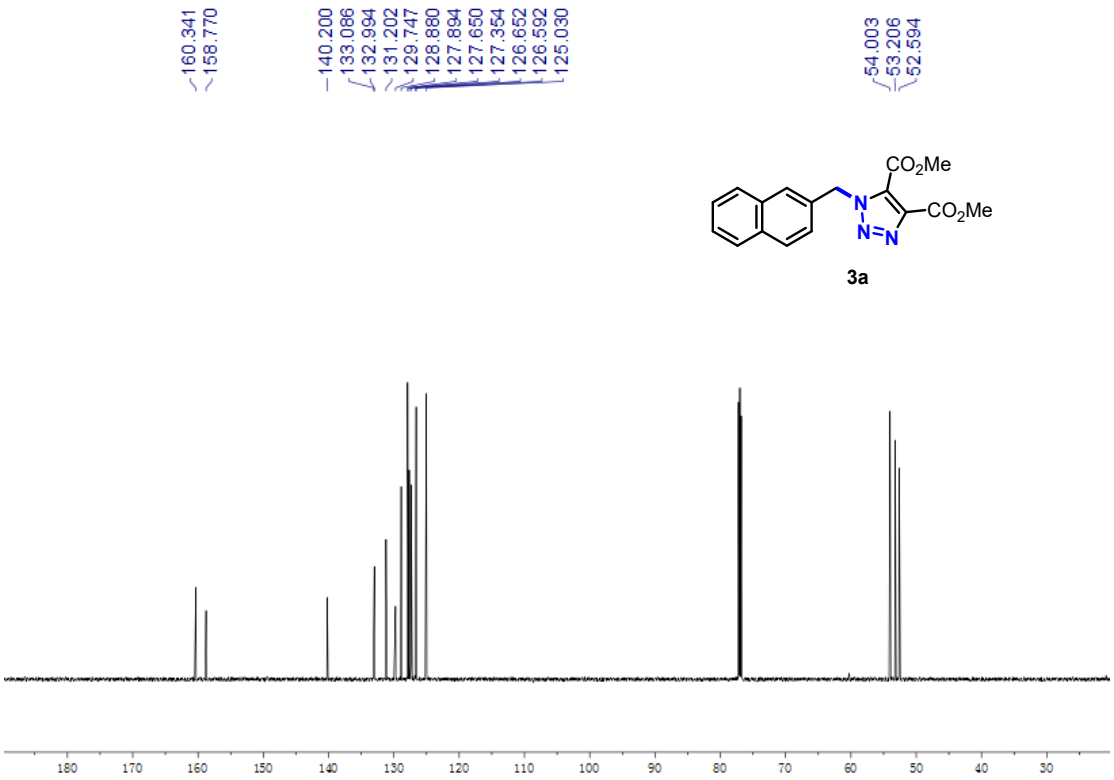
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2at**



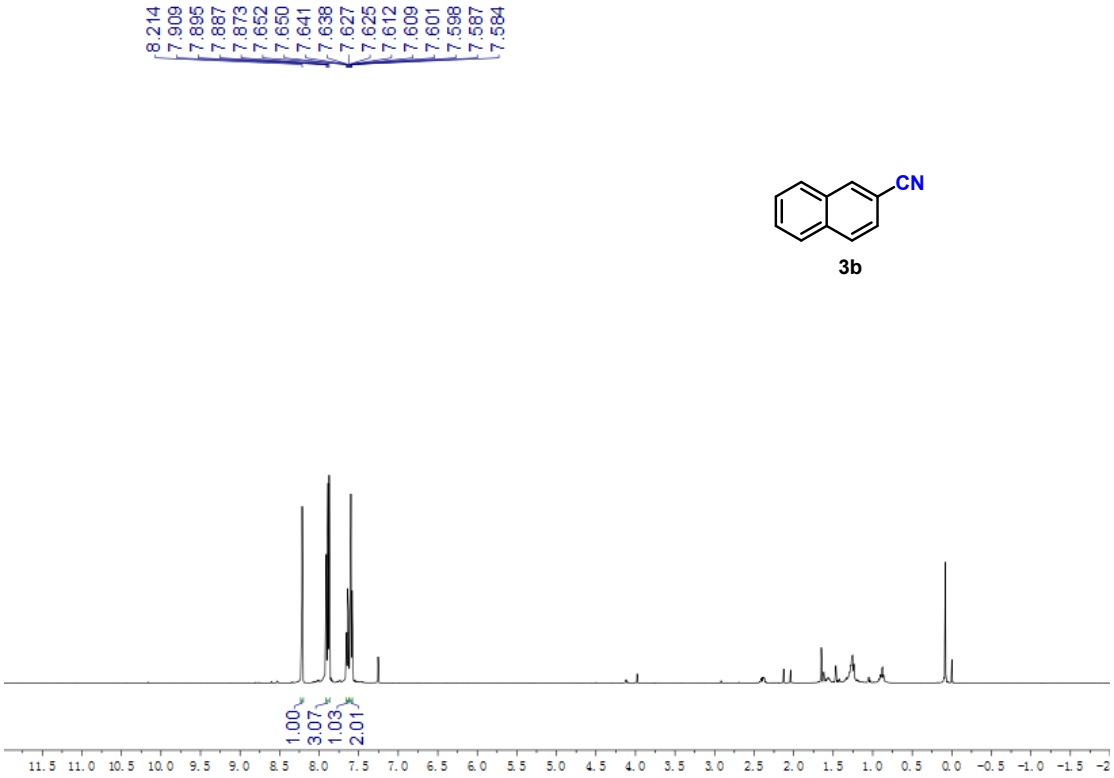
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2at**



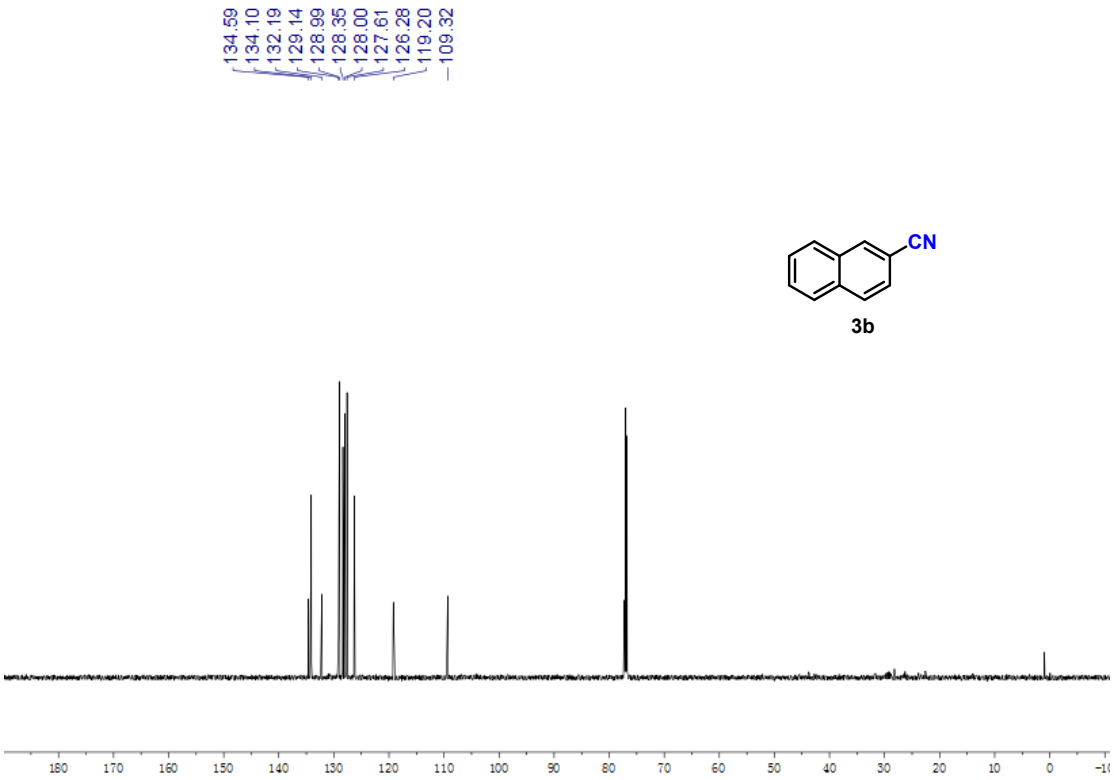
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3a**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **3a**



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



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **3b**

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