Supporting Information

For

Copper-Catalyzed Monochloromethylazidation to Access Transformable Terminal Alkyl Chlorides Using Stoichiometric $BrCH_2Cl$

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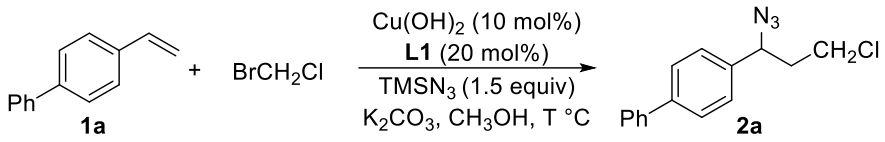
General Information:

NMR spectra were recorded on Bruker-400 MHz or Bruker-500 MHz NMR spectrometer (400 MHz or 500 MHz for 1H; 101 MHz or 126 MHz for ^{13}C and 376 MHz or 471 MHz for ^{19}F {^{1}H, $^{1}3C$ decoupled}). ^{1}H NMR spectra were referenced relative to internal $Si(Me)_4$ (TMS) at δ 0.00 ppm or $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were recorded at ambient temperature on Bruker-400 (101 MHz) or Bruker-500 (126 MHz) spectrometers and are referenced relative to $CDCl_3$ at δ 77.16 ppm. The ^{13}C NMR spectra were obtained with ^{1}H de-coupling. Data for ^{1}H, ^{13}C, ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). Bromochloromethane was obtained from Energy and used as received. Cupric acetylacetonate was obtained from Energy and used as received. Tris(2-dimethylaminoethyl)amine (**L1, Me$_6$TREN**) was obtained from Energy and used as received. Azidotrimethylsilane was obtained from Energy and used as received. Potassium carbonate was purchased from Sinopharm and used as received. Diisopropylamine was purchased from Adamas and used as received. Anhydrous methanol was purchased from Infinity Scientific and used as received.

Tables of the Optimization of Reaction Conditions

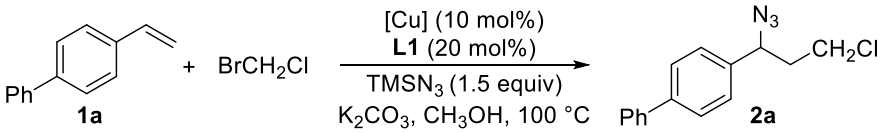
Table S1. Temperature Screening[a], related to **Table 1**.



entry	T (°C)	yield (%)[b]	entry	T (°C)	yield (%)[b]
1	40	nd	5	80	30
2	50	nd	6	90	38
3	60	nd	**7**	**100**	**47**
4	70	25	8	110	44 (46[c])

[a] Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (0.4 mmol, 2.0 equiv), $Cu(OH)_2$ (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol%), $TMSN_3$ (0.3 mmol, 1.5 equiv), K_2CO_3 (0.24 mmol, 1.2 equiv), CH_3OH (1.0 mL), 12 h, N_2. [b] Yield determined by ^1H NMR using dibromomethane as internal standard. [c] Isolated yield. **L1**= Me_6TREN.

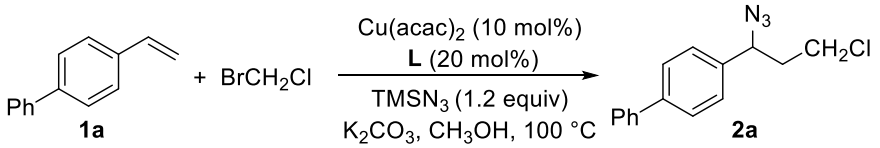
Table S2. Copper Catalyst Screening[a], related to **Table 1**.



entry	[Cu]	yield (%)[b]	entry	[Cu]	yield (%)[b]
1	CuCN	63	18	CuO	nd
2	Cu_2O	57	19	$CuSO_4$	nd
3	CuOAc	53	20	CuF_2	43
4	CuSCN	72	21	$CuCl_2$	26
5	CuCl	49	22	$CuBr_2$	9
6	CuBr	51	23	$Cu_2(OH)_2CO_3$	39
7	CuI	38	24	$Cu(COO^sOct)_2$	29
8	$Cu(PPh_3)_3Br$	44	25	$Cu(COO^sBu)_2$	41
9	$CuBr{\bullet}Me_2S$	48	26	$Cu(hfacac)_2{\bullet}xH_2O$	75
10	CuTc	53	27	$Cu(CF_3CO_2)_2{\bullet}H_2O$	33
11	$Cu(CH_3CN)_4PF_6$	39	28	$CuSO_4{\bullet}5H_2O$	nd
12	$Cu(acac)_2$	79 (78[c])	29	$CuF_2{\bullet}2H_2O$	48
13[d]	**$Cu(acac)_2$**	**79 (78[c])**	30	$CuCl_2{\bullet}2H_2O$	37
14	$Cu(hfacac)_2$	43	31	$Cu(ClO_4)_2{\bullet}6H_2O$	30
15	$Cu(CF_3COCH_2COCH_3)_2$	67	32	$Cu(NO_3)_2{\bullet}H_2O$	28
16	$Cu(OAc)_2$	trace	33	$Cu(BF_4)_2{\bullet}6H_2O$	40
17	$Cu(OTf)_2$	nd	34	$Cu(OAc)_2{\bullet}H_2O$	39
18	$Cu(OH)_2$	47			

[a] Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (0.4 mmol, 2.0 equiv), [Cu] (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol%), $TMSN_3$ (0.3 mmol, 1.5 equiv), K_2CO_3 (0.24 mmol, 1.2 equiv), CH_3OH (1.0 mL),100 °C, 12 h, N_2. [b] Yield determined by ^1H NMR using dibromomethane as internal standard. [c] Isolated yield. [d] $TMSN_3$ (0.24 mmol, 1.2 equiv) was used. **L1**= Me_6TREN.

Table S3. Ligand Screening[a], related to **Table 1**.



entry	L	yield (%)[b]	entry	L	yield (%)[b]
1	NEt_3	nd	7	bpy	nd
2	TMEDA	trace	8	dtbpy	nd
3	PMDTA	trace	9	phen	nd
4	**L1**	**79**	10	PPh_3	nd
5	**L2**	trace	11	dppp	nd
6	**L3**	32			

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (0.4 mmol, 2.0 equiv), $Cu(acac)_2$ (0.02 mmol, 10 mol%), **L** (0.04 mmol, 20 mol%), $TMSN_3$ (0.24 mmol, 1.2 equiv), K_2CO_3 (0.24 mmol, 1.2 equiv), CH_3OH (1.0 mL),100 °C, 12 h, N_2. [b]Yield determined by ^1H NMR using dibromomethane as internal standard.

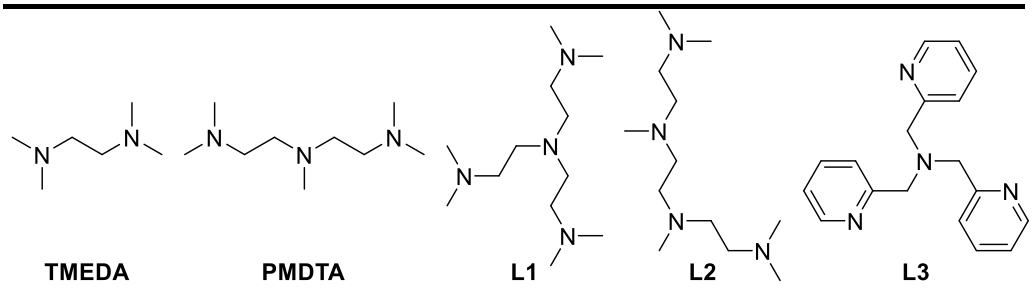
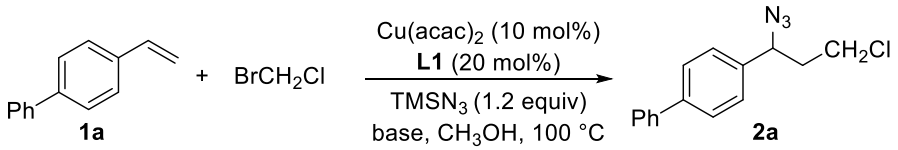


Table S4. Base Screening[a], related to **Table 1**.



entry	base	yield (%)[b]	entry	base	yield (%)[b]
1	LiOAc	31	18	*t*BuOLi	65
2	NaOAc	22	19	*t*BuONa	45
3	KOAc	39	20	*t*BuOK	58
4	CsOAc	33	21	CH_3OLi	62
5	$NaHCO_3$	58	22	CH_3ONa	38
6	$KHCO_3$	50	23	CH_3OK	32
7	Na_2HPO_4	13	24	CsF	26
8	K_2HPO_4	57	25	Et_3N	47
9	Li_2CO_3	44	26	TMEDA	36
10	Na_2CO_3	72	27	DIPEA	61
11	**K_2CO_3**	**79**	28	DABCO	6
12	Cs_2CO_3	78	29	DMAP	15
13	Na_3PO_4	15	30	TMG	68
14	K_3PO_4	62	31	DBU	61
15	$LiOH•H_2O$	67	32	PMP	54
16	NaOH	66	33	HMTA	29
17	KOH	55	34	proton sponge	47

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (0.4 mmol, 2.0 equiv), $Cu(acac)_2$ (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol %), $TMSN_3$ (0.24 mmol, 1.2 equiv), base (0.24 mmol, 1.2 equiv), CH_3OH (1.0 mL),100 °C , 12 h, N_2. [b]Yield determined by ^1H NMR using dibromomethane as internal standard.

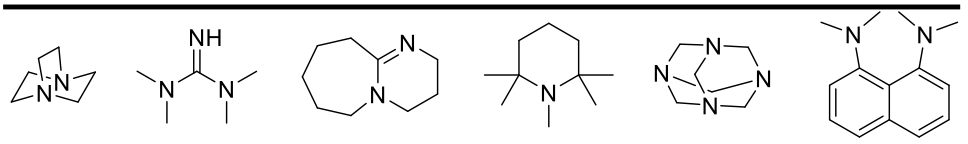
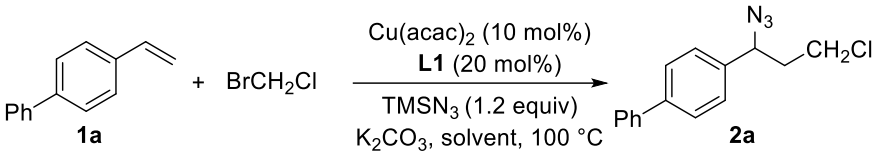


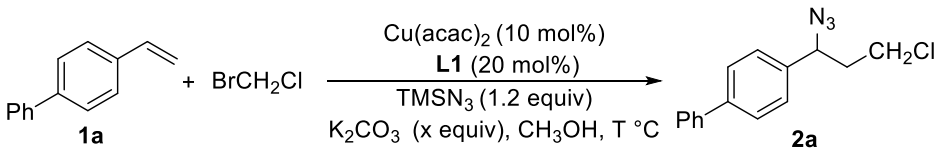
Table S5. Solvent Screening[a], related to **Table 1**.



entry	solvent	yield (%)[b]	entry	solvent	yield (%)[b]
1	DCE	nd	7	CH_3CN	5
2	MeOH	79	8	DME	nd
3	EtOH	61	9	DMF	nd
4	HFIP	nd	10	DMA	nd
5	THF	nd	11	DMSO	nd
6	1,4-dioxane	nd	12	NMP	nd

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (0.4 mmol, 2.0 equiv), $Cu(acac)_2$ (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol %), $TMSN_3$ (0.24 mmol, 1.2 equiv), K_2CO_3 (0.24 mmol, 1.2 equiv), solvent (1.0 mL),100 °C, 12 h, N_2. [b]Yield determined by ^1H NMR using dibromomethane as internal standard.

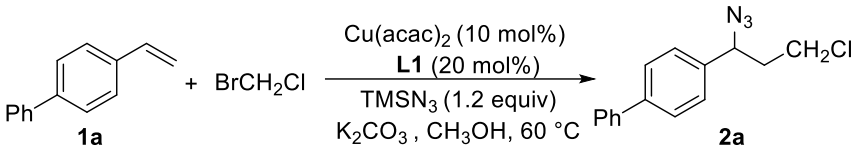
Table S6. Reaction Conditions Screening[a], related to **Table 1**.



entry	x	T (°C)	yield (%)[b]
1	1.2	100	79
2	2.0	100	80
3	2.0	90	85
4	2.0	80	84
5	2.0	70	85
6	2.0	60	86

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $Cu(acac)_2$ (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol%), $TMSN_3$ (0.24 mmol, 1.2 equiv), CH_3OH (1.0 mL), 12 h, N_2. [b]Yield determined by ^1H NMR using dibromomethane as internal standard.

Table S7. Final Variation[a], related to **Table 1**.



entry	conditions	yield (%)[b]
1	standard conditons	86
2	$Cu(acac)_2$ (5 mol%) was used	58
3	$BrCH_2Cl$ (1.5 equiv) was used.	85
4	t = 24 h	86
5	K_2CO_3 (3.0 equiv) was used.	87
6	**K_2CO_3 (3.0 equiv) and t = 24 h were used.**	**90 (90[c])**
7	NaN_3 instead of $TMSN_3$	83
8	TsN_3 instead of $TMSN_3$	61
9	$(PhO)_2P(O)N_3$ instead of $TMSN_3$	70

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.2 mmol, 1.0 equiv), $Cu(acac)_2$ (0.02 mmol, 10 mol%), **L1** (0.04 mmol, 20 mol%), $TMSN_3$ (0.24 mmol, 1.2 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CH_3OH (1.0 mL), 60 °C, 12 h, N_2. [b]Yield determined by ^1H NMR using dibromomethane as internal standard. [c]Isolated yield.

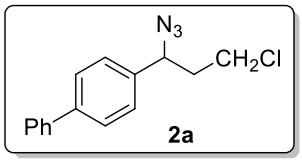
Preparation of Alkenes

The styrenes **1b-1d**, **1f-1h**, **1j, 1p-1r**, **1u**, **1ac-1ae** were purchased and used directly from commercial sources, and substrates **1a**, **1e**, **1i**, **1k-1l**, **1o**, **1s-1t**, **1v-1ab**, **1af-1ak** were prepared in accordance with method described in the reference.[1] **1m-1n**, **Estrone Derivative 6** were prepared in accordance with method described in the reference.[2] **1ap** was prepared in accordance with method described in the reference.[3]

General Procedure for Copper-Catalyzed Monochloromethylazidation of Alkenes

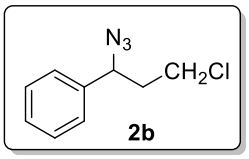
To a 25 mL of Schlenk tube was added $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) or DIPA（100 μL, 0.60 mmol, 3.0 equiv）under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times), then methanol (1.0 mL), **1** (0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol%) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 - 100 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel to give the product **2**.

4-(1-azido-3-chloropropyl)-1, 1'-biphenyl (2a)



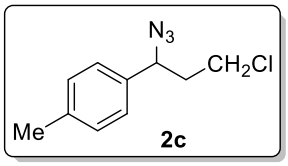
The product **2a** was purified with silica gel chromatography (PE/EA = 100:1) as a white solid (48.9 mg, 90% yield); **mp** 31-32 ˚C**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.55 (m, 4H), 7.50 – 7.35 (m, 5H), 4.82 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.70 (ddd, *J* = 11.1, 7.9, 5.3 Hz, 1H), 3.54 (dt, *J* = 11.3, 5.9 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.20 – 2.08 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 140.5, 137.6, 129.0, 127.9, 127.7, 127.5, 127.2, 63.0, 41.5, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{15}H_{15}ClN$: 244.0893; Found 244.0911.

(1-azido-3-chloropropyl)benzene (2b)



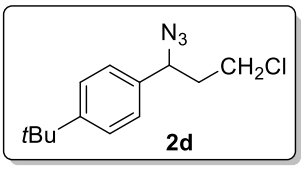
The product **2b** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (30.5 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 4.77 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.67 (ddd, *J* = 11.2, 8.0, 5.3 Hz, 1H), 3.49 (dt, *J* = 11.3, 5.9 Hz, 1H), 2.30 – 2.19 (m, 1H), 2.15 – 2.03 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8, 129.2, 128.8, 127.1, 63.2, 41.5, 39.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_9H_{11}ClN$: 168.0580; Found 168.0590.

1-(1-azido-3-chloropropyl)-4-methylbenzene (2c)



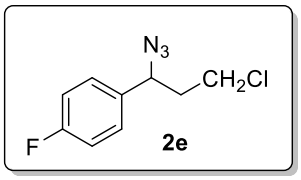
The product **2c** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (36.5 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 4.73 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.65 (ddd, *J* = 11.0, 7.9, 5.3 Hz, 1H), 3.49 (dt, *J* = 11.4, 5.9 Hz, 1H), 2.37 (s, 3H), 2.30 – 2.18 (m, 1H), 2.15 – 2.02 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 135.6, 129.8, 127.0, 63.0, 41.6, 39.0, 21.3. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClN$: 182.0737; Found 182.0746.

1-(1-azido-3-chloropropyl)-4-(tert-butyl)benzene (2d)



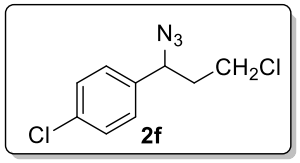
The product **2d** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (47.3 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 7.28 – 7.22 (m, 2H), 4.73 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.65 (ddd, *J* = 11.1, 7.9, 5.4 Hz, 1H), 3.49 (dt, *J* = 11.3, 5.9 Hz, 1H), 2.29 – 2.18 (m, 1H), 2.14 – 1.99 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 135.6, 126.7, 126.0, 62.9, 41.6, 39.0, 34.8, 31.4. **HRMS** (ESI) (m/z): $[M + H - N_2]^+$ Calcd for $C_{13}H_{19}ClN$: 224.1206; Found 224.1215.

1-(1-azido-3-chloropropyl)-4-fluorobenzene (2e)



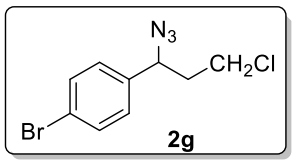
The product **2e** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (32.0 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.14 – 7.06 (m, 2H), 4.76 (dd, *J* = 8.7, 5.8 Hz, 1H), 3.66 (ddd, *J* = 11.2, 8.0, 5.1 Hz, 1H), 3.47 (ddd, *J* = 11.4, 6.3, 5.4 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.11 – 2.00 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (d, C-F, $1J_{C\text{-}F}$ = 247.6 Hz), 134.5 (d, C-F, $4J_{C\text{-}F}$ = 3.2 Hz), 128.8 (d, C-F, $3J_{C\text{-}F}$ = 8.2 Hz), 116.1 (d, *C-F*, $2J_{C\text{-}F}$ =21.6 Hz), 62.5, 41.4, 39.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calc for $C_9H_{10}ClFN$: 186.0486; Found 186.0498.

1-(1-azido-3-chloropropyl)-4-chlorobenzene (2f)



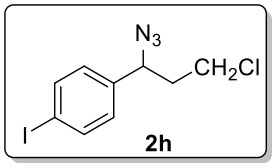
The product **2f** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (42.8 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.32 – 7.23 (m, 2H), 4.76 (dd, *J* = 8.7, 5.8 Hz, 1H), 3.66 (ddd, *J* = 11.2, 8.1, 5.1 Hz, 1H), 3.47 (ddd, *J* = 11.3, 6.2, 5.3 Hz, 1H), 2.28 – 2.14 (m, 1H), 2.12 – 1.98 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.3, 134.6, 129.4, 128.4, 62.5, 41.3, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_9H_{10}Cl_2N$: 202.0190; Found 202.0202.

1-(1-azido-3-chloropropyl)-4-bromobenzene (2g)



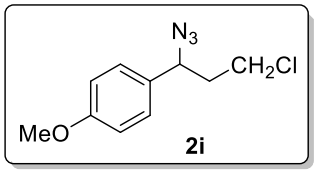
The product **2g** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (46.1 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.25 – 7.18 (m, 2H), 4.75 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.66 (ddd, *J* = 11.1, 8.1, 5.0 Hz, 1H), 3.47 (dt, *J* = 11.3, 5.8 Hz, 1H), 2.27 – 2.14 (m, 1H), 2.05 (ddt, *J* = 14.0, 8.1, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 132.3, 128.7, 122.7, 62.5, 41.3, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_9H_{10}BrClN$: 245.9685; Found 245.9693.

1-(1-azido-3-chloropropyl)-4-iodobenzene (2h)



The product **2h** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (51.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.13 – 7.02 (m, 2H), 4.73 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.66 (ddd, *J* = 11.2, 8.1, 5.1 Hz, 1H), 3.47 (ddd, *J* = 11.3, 6.2, 5.4 Hz, 1H), 2.26 – 2.13 (m, 1H), 2.04 (ddt, *J* = 14.0, 8.1, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 138.3, 128.9, 94.4, 62.6, 41.3, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_9H_{10}ClIN$: 293.9546; Found 293.9549.

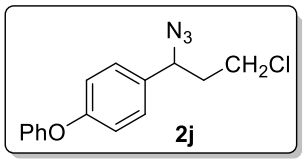
1-(1-azido-3-chloropropyl)-4-methoxybenzene (2i)



The product **2i** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (32.5 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.97 – 6.88 (m, 2H), 4.71 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.82 (s, 3H), 3.64 (ddd, *J* = 11.1, 7.8, 5.3 Hz, 1H), 3.47 (ddd, *J* = 11.1, 6.4, 5.5 Hz, 1H), 2.30 – 2.17 (m, 1H), 2.13 – 2.01 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 130.5, 128.4, 114.5,

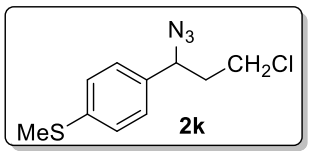
62.7, 55.4, 41.6, 38.9. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClNO$: 198.0686; Found 198.0696.

1-(1-azido-3-chloropropyl)-4-phenoxybenzene (2j)



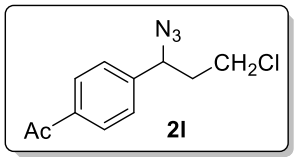
The product **2j** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (47.8 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.00 (m, 4H), 4.76 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.68 (ddd, *J* = 11.1, 7.9, 5.2 Hz, 1H), 3.51 (dt, *J* = 11.4, 5.9 Hz, 1H), 2.25 (ddt, *J* = 14.4, 8.6, 5.8 Hz, 1H), 2.10 (ddt, *J* = 13.9, 7.9, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.8, 156.7, 133.2, 130.0, 128.5, 123.9, 119.4, 119.0, 62.7, 41.5, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{15}H_{15}ClNO$: 260.0842; Found 260.0854.

(4-(1-azido-3-chloropropyl)phenyl)(methyl)sulfane (2k)



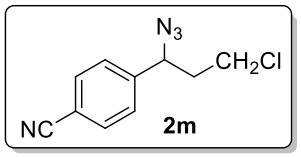
The product **2k** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (39.2 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 4H), 4.72 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.64 (ddd, *J* = 11.1, 7.9, 5.2 Hz, 1H), 3.47 (dt, *J* = 11.4, 5.9 Hz, 1H), 2.49 (s, 3H), 2.29 – 2.15 (m, 1H), 2.06 (ddt, *J* = 14.0, 7.9, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4, 135.2, 127.5, 126.9, 62.8, 41.4, 38.9, 15.7. HRMS (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClNS$: 214.0457; Found 214.0465.

1-(4-(1-azido-3-chloropropyl)phenyl)ethan-1-one (2l)



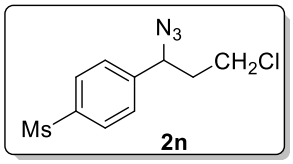
DIPA (3.0 equiv) was used as base. The product **2l** was purified with silica gel chromatography (PE/EA = 20:1) as a colorless oil (29.0 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.48 – 7.40 (m, 2H), 4.84 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.68 (ddd, *J* = 11.2, 8.3, 5.0 Hz, 1H), 3.49 (dt, *J* = 11.3, 5.7 Hz, 1H), 2.61 (s, 3H), 2.28 – 2.17 (m, 1H), 2.08 (ddt, *J* = 14.1, 8.3, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 143.9, 137.4, 129.2, 127.2, 62.7, 41.2, 39.0, 26.8. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{13}ClNO$: 210.0686; Found 210.0696.

4-(1-azido-3-chloropropyl)benzonitrile (2m)



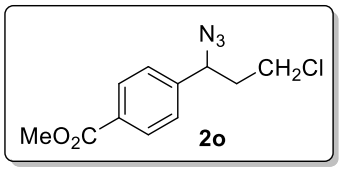
DIPA (3.0 equiv) was used as base. The product **2m** was purified with silica gel chromatography (PE/EA = 20:1) as a colorless oil (29.6 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 4.85 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.69 (ddd, *J* = 11.3, 8.4, 4.8 Hz, 1H), 3.49 (dt, *J* = 11.2, 5.5 Hz, 1H), 2.20 (ddt, *J* = 14.3, 9.0, 5.3 Hz, 1H), 2.06 (ddt, *J* = 14.0, 8.6, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 133.0, 127.7, 118.4, 112.7, 62.5, 41.0, 39.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{10}ClN_2$: 193.0533; Found 193.0542.

1-(1-azido-3-chloropropyl)-4-(methylsulfonyl)benzene (2n)



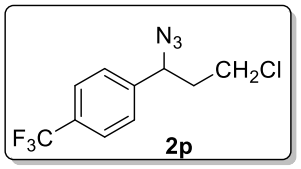
DIPA (3.0 equiv) was used as base. The product **2n** was purified with silica gel chromatography (PE/EA = 3:1) as a colorless oil (32.8 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.59 – 7.52 (m, 2H), 4.89 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.69 (ddd, *J* = 11.2, 8.4, 4.9 Hz, 1H), 3.49 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.07 (s, 3H), 2.28 – 2.14 (m, 1H), 2.07 (ddt, *J* = 14.1, 8.4, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 140.8, 128.3, 128.0, 62.4, 44.5, 41.1, 39.1. **HRMS** (ESI) m/z: $[M + H- N_2]^+$ Calcd. for $C_{10}H_{13}ClNO_2S$: 246.0356; Found 246.0368.

Methyl 4-(1-azido-3-chloropropyl)benzoate (2o)



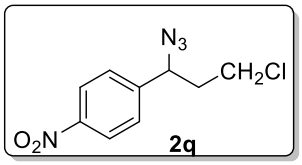
DIPA (3.0 equiv) was used as base. The product **2o** was purified with silica gel chromatography (PE/EA = 20:1) as a colorless oil (30.4 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.45 – 7.37 (m, 2H), 4.83 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.92 (s, 3H), 3.67 (ddd, *J* = 11.2, 8.2, 5.1 Hz, 1H), 3.48 (dt, *J* = 11.3, 5.7 Hz, 1H), 2.22 (dddd, *J* = 14.8, 8.9, 6.0, 5.1 Hz, 1H), 2.08 (ddt, *J* = 14.6, 8.3, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 143.8, 130.5, 130.4, 127.0, 62.7, 52.4, 41.2, 39.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{13}ClNO_2$: 226.0635; Found 226.0647.

1-(1-azido-3-chloropropyl)-4-(trifluoromethyl)benzene (2p)



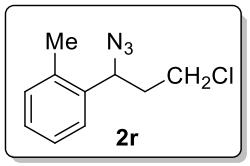
DIPA (3.0 equiv) was used as base. The product **2p** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (32.2 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 4.87 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.70 (ddd, *J* = 11.3, 8.2, 4.9 Hz, 1H), 3.50 (dt, *J* = 11.3, 5.7 Hz, 1H), 2.24 (ddt, *J* = 14.4, 8.9, 5.6 Hz, 1H), 2.09 (ddt, *J* = 14.1, 8.5, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) 142.9, 130.9 (q, C-F, $2J_{C-F}$ = 32.5 Hz), 127.4, 126.2 (q, C-F, $3J_{C-F}$ = 3.8 Hz), 124.0 (q, C-F, $1J_{C-F}$ = 272.3 Hz), 62.6, 41.2, 39.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{10}ClF_3N$: 236.0454; Found 236.0455.

1-(1-azido-3-chloropropyl)-4-nitrobenzene (2q)



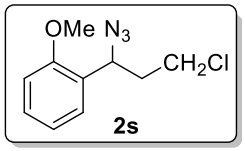
DIPA (3.0 equiv) was used as base. The product **2q** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (20.2 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 – 8.24 (m, 2H), 7.58 – 7.49 (m, 2H), 4.92 (dd, *J* = 9.0, 5.3 Hz, 1H), 3.71 (ddd, *J* = 11.3, 8.5, 4 .8 Hz, 1H), 3.51 (ddd, *J* = 11.2, 5.9, 5.3 Hz, 1H), 2.23 (dddd, *J* = 14.8, 9.0, 5.9, 4.7 Hz, 1H), 2.08 (ddt, *J* = 14.5, 8.5, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.2, 127.9, 124.4, 62.3, 41.0, 39.2. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_9H_{10}ClN_2O_2$ 213.0431; Found 213.0433.

1-(1-azido-3-chloropropyl)-2-methylbenzene (2r)



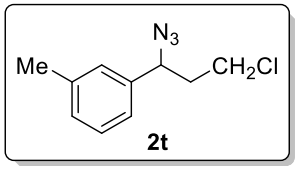
The product **2r** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (26.4 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.31 – 7.17 (m, 3H), 5.05 (dd, *J* = 9.1, 4.9 Hz, 1H), 3.72 (ddd, *J* = 11.1, 8.8, 4.9 Hz, 1H), 3.57 (dt, *J* = 11.0, 5.4 Hz, 1H), 2.41 (s, 3H), 2.19 (ddt, *J* = 14.4, 9.2, 5.1 Hz, 1H), 2.08 (ddt, *J* = 14.3, 8.8, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 135.7, 131.1, 128.4, 126.8, 126.3, 59.4, 41.8, 38.4, 19.3. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClN$: 182.0737; Found 182.0747.

1-(1-azido-3-chloropropyl)-2-methoxybenzene (2s)



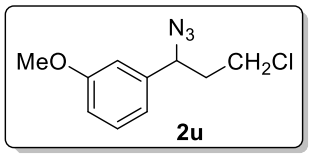
The product **2s** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (38.8 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.18 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.87 (s, 3H), 3.67 (ddd, *J* = 11.0, 8.0, 6.4 Hz, 1H), 3.58 (dt, *J* = 11.2, 6.0 Hz, 1H), 2.29 – 2.12 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9, 129.6, 127.4, 126.9, 121.0, 111.0, 57.5, 55.6, 41.8, 37.5. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClNO$: 198.0686; Found 198.0696.

1-(1-azido-3-chloropropyl)-3-methylbenzene (2t)



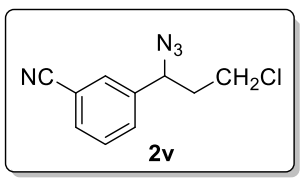
The product **2t** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (35.2 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 7.20 – 7.10 (m, 3H), 4.73 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.66 (ddd, *J* = 11.1, 8.0, 5.3 Hz, 1H), 3.50 (dt, *J* = 11.3, 5.9 Hz, 1H), 2.39 (s, 3H), 2.24 (ddt, *J* = 14.4, 8.7, 5.7 Hz, 1H), 2.10 (ddt, *J* = 14.0, 8.0, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.9, 138.6, 129.5, 129.0, 127.7, 124.1, 63.2, 41.6, 39.0, 21.6. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClN$: 182.0737; Found 182.0747.

1-(1-azido-3-chloropropyl)-3-methoxybenzene (2u)



The product **2u** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (37.0 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 1H), 6.94 – 6.85 (m, 3H), 4.73 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.83 (s, 3H), 3.66 (ddd, *J* = 11.1, 7.9, 5.2 Hz, 1H), 3.49 (dt, *J* = 11.4, 5.9 Hz, 1H), 2.22 (ddt, *J* = 14.3, 8.6, 5.9 Hz, 1H), 2.14 – 2.03 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 140.3, 130.2, 119.3, 114.0, 112.7, 63.1, 55.4, 41.5, 39.0. HRMS (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClNO$: 198.0686; Found 198.0694.

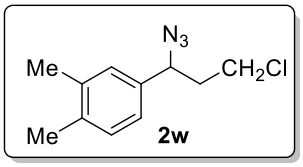
3-(1-azido-3-chloropropyl)benzonitrile (2v)



DIPA (3.0 equiv) was used as base. The product **2v** was purified with silica gel chromatography (PE/EA = 40:1) as a colorless oil (26.5 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.62 – 7.56 (m, 1H), 7.56 – 7.49 (m, 1H), 4.84 (dd, *J* =

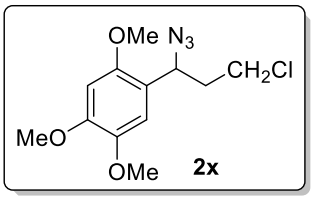
8.9, 5.4 Hz, 1H), 3.69 (ddd, *J* = 11.2, 8.4, 4.8 Hz, 1H), 3.49 (dt, *J* = 11.2, 5.6 Hz, 1H), 2.27 – 2.15 (m, 1H), 2.06 (ddt, *J* = 14.1, 8.4, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.7, 132.3, 131.4, 130.5, 130.1, 118.4, 113.4, 62.3, 41.0, 39.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{10}ClN_2$: 193.0533; Found 193.0540.

4-(1-azido-3-chloropropyl)-1,2-dimethylbenzene (2w)



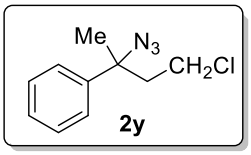
The product **2w** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (38.5 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 – 7.04 (m, 2H), 4.70 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.65 (ddd, *J* = 11.0, 7.9, 5.4 Hz, 1H), 3.50 (dt, *J* = 11.4, 5.9 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.27 – 2.19 (m, 1H), 2.09 (ddt, *J* = 14.0, 7.9, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 137.3, 136.0, 130.3, 128.3, 124.5, 63.1, 41.6, 39.0, 20.0, 19.6. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{15}ClN$: 196.0893; Found 196.0908.

1-(1-azido-3-chloropropyl)-2,4,5-trimethoxybenzene (2x)



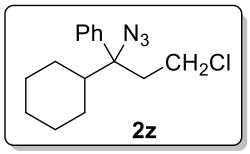
The product **2x** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (46.9 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 6.53 (s, 1H), 5.13 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.66 – 3.51 (m, 2H), 2.26 – 2.05 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 149.8, 143.3, 117.9, 111.1, 97.4, 57.2, 56.8, 56.5, 56.2, 41.7, 37.8. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{12}H_{17}ClNO_3$: 258.0897; Found 258.0903.

(2-azido-4-chlorobutan-2-yl)benzene (2y)



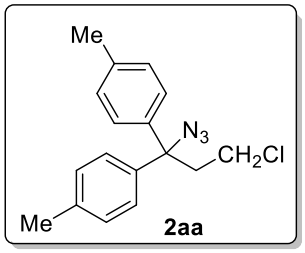
The product **2y** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (34.8 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.29 (m, 1H), 3.47 (ddd, *J* = 10.8, 9.4, 7.0 Hz, 1H), 3.23 (ddd, *J* = 10.7, 9.1, 7.1 Hz, 1H), 2.40 – 2.23 (m, 2H), 1.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 129.0, 127.9, 125.4, 66.1, 45.4, 39.8, 26.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClN$: 182.0737; Found 182.0746.

(1-azido-3-chloro-1-cyclohexylpropyl)benzene (2z)



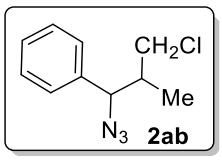
The product **2z** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (44.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.24 (m, 3H), 3.54 – 3.40 (m, 1H), 3.29 – 3.12 (m, 1H), 2.67 – 2.50 (m, 2H), 1.98 – 1.86 (m, 1H), 1.84 – 1.66 (m, 3H), 1.61 (d, *J* = 12.6 Hz, 1H), 1.56 – 1.49 (m, 1H), 1.28 – 1.09 (m, 2H), 1.08 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 128.4, 127.5, 126.6, 72.3, 48.9, 40.1, 39.9, 27.9, 27.6, 26.6, 26.6, 26.2. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{15}H_{21}ClN$: 250.1363; Found 250.1375.

4,4'-(1-azido-3-chloropropane-1,1-diyl)bis(methylbenzene) (2aa)



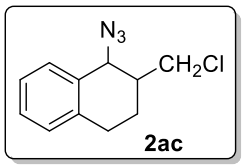
The product **2aa** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (58.8 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 8H), 3.39 – 3.32 (m, 2H), 2.89 – 2.81 (m, 2H), 2.36 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.0, 137.8, 129.4, 126.8, 71.6, 42.5, 40.2, 21.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{17}H_{19}ClN$: 272.1206; Found 272.1220.

(1-azido-3-chloro-2-methylpropyl) benzene (2ab)



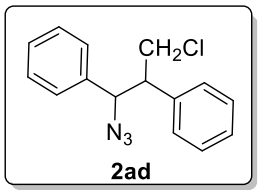
The product **2ab** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (22.2 mg, 53% yield，dr = 1:1.25). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 4.69 (d, *J* = 7.0 Hz, 0.42H), 4.49 (d, *J* = 9.1 Hz, 0.58H), 3.81 (dd, *J* = 10.9, 5.0 Hz, 0.58H), 3.61 (dd, *J* = 10.9, 3.9 Hz, 0.58H), 3.51 (dd, *J* = 11.0, 5.8 Hz, 0.42H), 3.27 (dd, *J* = 11.0, 5.0 Hz, 0.42H), 2.27 – 2.10 (m, 1.0H), 1.08 (d, *J* = 6.7 Hz, 1.26H), 0.85 (d, *J* = 6.8 Hz, 1.74H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 137.5, 129.0, 128.7, 128.5, 127.8, 127.3, 68.1, 68.0, 48.3, 48.1, 41.7, 40.4, 14.8, 13.9. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{10}H_{13}ClN$: 182.0737; Found 182.0743.

1-azido-2-(chloromethyl)-1,2,3,4-tetrahydronaphthalene (2ac)



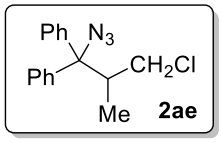
The product **2ac** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (25.7 mg, 58% yield，dr = 1.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.11 (m, 4H), 4.79 (d, *J* = 2.7 Hz, 0.53H), 4.50 (d, *J* = 7.3 Hz, 0.47H), 3.77 – 3.64 (m, 1.47H), 3.57 (dd, *J* = 10.9, 5.7 Hz, 0.52H), 2.99 – 2.75 (m, 2.0H), 2.29 – 2.08 (m, 1.41H), 1.90 – 1.67 (m, 1.59H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 136.6, 133.0, 132.9, 130.0, 129.7, 129.3, 129.0, 128.3, 126.7, 126.3, 61.8, 60.6, 46.6, 46.3, 41.7, 41.7, 28.6, 27.0, 24.0, 22.2. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{13}ClN$: 194.0737; Found 194.0745.

(1-azido-3-chloropropane-1,2-diyl)dibenzene (2ad)



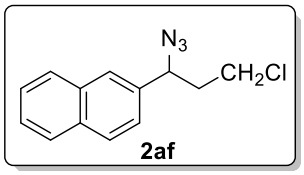
The product **2ad** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (30.0 mg, 55% yield, dr = 1:2.5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 -7.00 (m, 10H), 5.11 (d, *J* = 7.1 Hz, 0.29H), 4.93 (d, *J* = 8.5 Hz, 0.71H), 4.02 – 3.92 (m, 1.42H), 3.81 (dd, *J* = 11.1, 6.6 Hz, 0.29H), 3.61 (dd, *J* = 11.1, 6.4 Hz, 0.29H), 3.35 (ddd, *J* = 8.6, 7.5, 5.0 Hz, 0.71H), 3.24 (q, *J* = 6.6 Hz, 0.29H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 137.6, 137.5, 137.0, 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 128.4, 127.9, 127.8, 127.6, 127.5, 68.2, 67.2, 53.7, 53.0, 46.2, 46.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{15}H_{15}ClN$: 244.0893; Found 244.0902.

(1-azido-3-chloro-2-methylpropane-1,1-diyl)dibenzene (2ae)



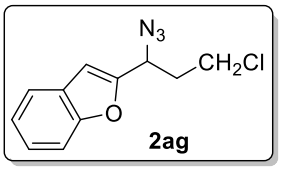
The product **2ae** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (30.3 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 10H), 3.85 (dd, *J* = 10.5, 2.2 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.98 (t, *J* = 10.4 Hz, 1H), 1.19 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.2, 139.9, 128.6, 128.5, 128.0, 127.9, 127.7, 75.8, 47.8, 43.9, 14.4. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{16}H_{17}ClN$: 258.1050; Found 258.1063.

2-(1-azido-3-chloropropyl)naphthalene (2af)



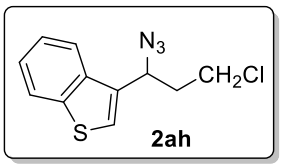
The product **2af** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (45.2 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 3H), 7.83 (s, 1H), 7.59 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.96 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.71 (ddd, *J* = 11.0, 7.9, 5.2 Hz, 1H), 3.52 (dt, *J* = 11.3, 5.9 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.20 (ddt, *J* = 13.9, 7.8, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 133.4, 133.3, 129.2, 128.1, 127.9, 126.7, 126.6, 126.5, 124.2, 63.4, 41.5, 38.9. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{13}H_{13}ClN$: 218.0737; Found 218.0742.

2-(1-azido-3-chloropropyl)benzofuran (2ag)



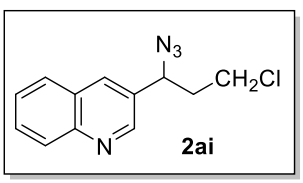
The product **2ag** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (37.2 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.32 (td, *J* = 8.3, 7.8, 1.4 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.74 (s, 1H), 4.90 (dd, *J* = 7.9, 6.5 Hz, 1H), 3.73 (ddd, *J* = 11.2, 7.6, 5.8 Hz, 1H), 3.60 (dt, *J* = 11.3, 5.7 Hz, 1H), 2.37 (dtd, *J* = 7.8, 5.8, 2.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 153.7, 127.6, 125.1, 123.3, 121.5, 111.6, 105.4, 56.5, 41.1, 35.4. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{11}ClNO$: 208.0529; Found 208.0539.

3-(1-azido-3-chloropropyl)benzo[*b*]thiophene (2ah)



The product **2ah** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (39.3 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.50 – 7.37 (m, 3H), 5.19 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.77 (ddd, *J* = 11.1, 8.3, 5.2 Hz, 1H), 3.60 (dt, *J* = 11.1, 5.5 Hz, 1H), 2.44 – 2.28 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 136.9, 133.5, 125.1, 124.6, 124.4, 123.3, 122.1, 58.0, 41.6, 37.4. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{11}ClNS$: 224.0301; Found 224.0307.

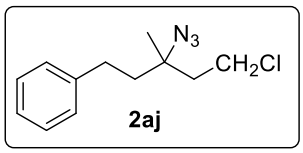
3-(1-azido-3-chloropropyl)quinolone (2ai)



The product **2ai** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (33.6 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.2 Hz, 1H), 8.17 – 8.09 (m, 2H), 7.85 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.80 – 7.70 (m, 1H), 7.59 (t, *J* = 7.5 Hz,

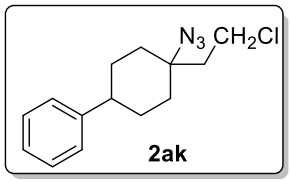
1H), 5.01 (dd, *J* = 8.9, 5.5 Hz, 1H), 3.74 (ddd, *J* = 11.2, 8.4, 4.8 Hz, 1H), 3.53 (dt, *J* = 11.2, 5.6 Hz, 1H), 2.35 (ddt, *J* = 14.5, 9.0, 5.4 Hz, 1H), 2.24 – 2.13 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 148.2, 134.2, 131.6, 130.2, 129.5, 128.0, 127.6, 127.5, 61.1, 41.2, 38.9. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{12}H_{12}ClN_2$: 219.0689; Found 219.0696.

(3-azido-5-chloro-3-methylpentyl)benzene (2aj)



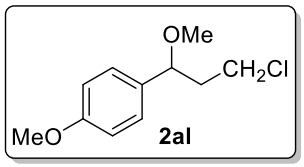
The product **2aj** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (19.0 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 3.61 (t, *J* = 8.0 Hz, 2H), 2.75 – 2.64 (m, 2H), 2.17 – 1.99 (m, 2H), 1.92 – 1.79 (m, 2H), 1.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 128.7, 128.4, 126.3, 63.2, 42.5, 41.9, 39.7, 30.5, 23.4. **HRMS** (ESI) (m/z): $[M + H - N_2]^+$ Calcd for $C_{12}H_{17}ClN$: 210.1050; Found 210.1058.

(4-azido-4-(2-chloroethyl)cyclohexyl)benzene (2ak)



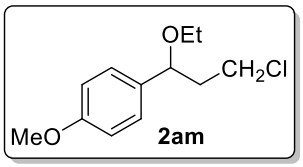
The product **2ak** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (21.1 mg, 40% yield, dr = 1:3.8). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 3.72 – 3.58 (m, 2H), 2.66 – 2.45 (m, 1H), 2.22 – 2.08 (m, 2H), 1.97 – 1.87 (m, 2H), 1.86 – 1.64 (m, 4H), 1.63 – 1.45 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 145.5, 128.7, 128.6, 126.9, 126.9, 126.5, 126.4, 63.0, 62.9, 44.5, 43.5, 43.1, 39.7, 39.4, 37.9, 35.0, 34.6, 30.1, 29.4. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for$C_{14}H_{19}ClN$:236.1206; Found 236.1215.

1-(3-chloro-1-methoxypropyl)-4-methoxybenzene (2al)



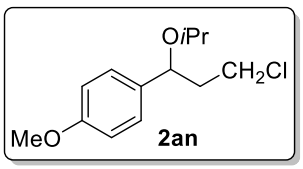
The product **2al** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (36.5 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 2H), 6.96 – 6.86 (m, 2H), 4.31 (dd, *J* = 8.2, 5.1 Hz, 1H), 3.81 (s, 3H), 3.64 – 3.73 (m, 1H), 3.48 (dddd, *J* = 11.9, 7.0, 4.3, 1.2 Hz, 1H), 3.20 (s, 3H), 2.31 – 2.17 (m, 1H), 2.05 – 1.93 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 133.1, 128.0, 114.1, 80.1, 56.6, 55.4, 41.9, 40.9. **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{11}H_{15}ClO_2$:214.0761; Found 214.0752.

1-(3-chloro-1-ethoxypropyl)-4-methoxybenzene (2am)



$Cu(OAc)_2$ (10 mol%) was used as catalyst, morpholine(3.0 equiv) was used as base. The product **2am** was purified with silica gelchromatography (PE/EA = 100:1) as a colorless oil (27.9 mg, 61%yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 6.93-6.85 (m, 2H), 4.43 (dd, *J* = 8.4, 5.0 Hz,1H), 3.81 (s, 3H), 3.71 (ddd, *J* = 10.8, 8.1, 5.6 Hz, 1H), 3.54 – 3.47 (m, 1H), 3.35 (ddq, *J* = 36.5, 9.3, 7.0 Hz, 2H), 2.29 – 2.17 (m, 1H), 1.98 (ddt, *J* = 11.0, 8.1, 5.8 Hz, 1H), 1.17 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 134.0, 127.8, 114.0, 78.1, 77.4, 77.2, 76.9, 64.2, 55.4, 42.0, 41.1, 15.4. **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{17}ClO_2$:228.0917; Found 228.0910.

1-(3-chloro-1-isopropoxypropyl)-4-methoxybenzene (2an)



The product **2an** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (25.7 mg, 53% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 2H), 6.94 – 6.84 (m, 2H), 4.55 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.81 (s, 3H), 3.71 (ddd, *J* = 10.8, 8.7, 5.3 Hz, 1H), 3.57 – 3.45 (m, 2H), 2.16 (ddt, *J* = 14.3, 8.9, 5.3 Hz, 1H), 1.94 (dddd, *J* = 14.4, 8.6, 5.7, 4.4 Hz, 1H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.06 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 134.9, 127.8, 114.0, 75.2, 69.0, 55.4, 42.1, 41.6, 23.6, 21.4. **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{19}ClO_2$:242.1074; Found 242.1068.

Large Scale Experiment

1a, 1 mmol **2a**, 89%

To a 50 mL of Schlenk tube were added 4-vinyl-1,1'-biphenyl **1a** (0.1805 g, 1.0 mmol, 1.0 equiv), $Cu(acac)_2$ (26.0 mg, 0.1 mmol, 10 mol%) and K_2CO_3 (414.5 mg, 3.0 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times), then methanol (5.0 mL), $BrCH_2Cl$ (130 μL, 2.0 mmol, 2.0 equiv), **L1** (55 μL, 0.2 mmol, 20 mol%) and $TMSN_3$ (160 μL, 2.4 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel (PE/ EA = 100:1) to give the product **2a** in 89% yield.

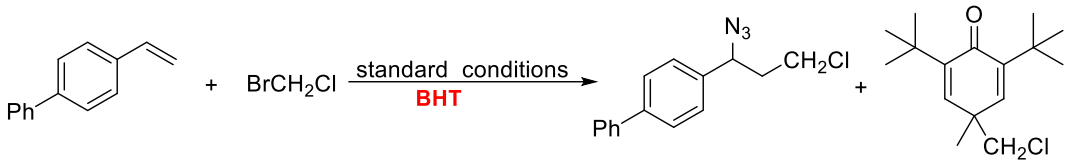
Mechanistic Studies

1. Radical Inhibiting Experiment with TEMPO

1a **2a**, 0%

To a 25 mL of Schlenk seal tube were added 4-vinyl-1,1'-biphenyl **1a** (36.0 mg, 0.2 mmol, 1.0 equiv), $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%), TEMPO (15.7 mg, 0.1 mmol, 0.5 equiv) and K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times). Methanol (1.0 mL), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol%) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum, no product **2a** can be detected by ^{1}H NMR and GC-MS.

2. Radical Trapping Experiment with BHT



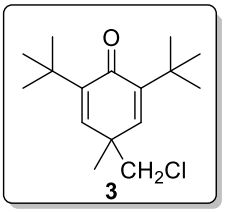
1a **2a**, 29% **3**, 25%

without **1a**, 61%

To a 25 mL of Schlenk seal tube were added 4-vinyl-1,1'-biphenyl **1a** (36.0 mg, 0.2 mmol, 1.0 equiv), $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol %), BHT (66.1 mg, 0.3 mmol, 1.5 equiv) and K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times). Methanol (1.0 mL), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol %) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography (PE/EA = 100:1) on silica gel to

give the product **3** in 25% yield. When this reaction was performed without **1a**, the product **3** could be obtained in 61% yield.

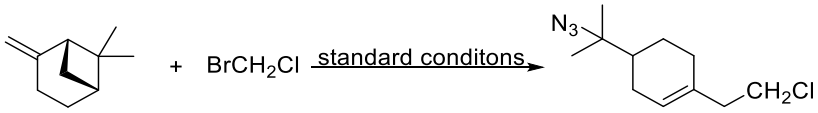
2,6-di-tert-butyl-4-(chloromethyl)-4-methylcyclohexa-2,5-dien-1-one (3)



3

The product **3** was purified with silica gel chromatography (PE/EA = 100:1) as a pale yellow solid (32.8 mg, 61% yield); **mp** 71-72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.46 (s, 2H), 3.48 (s, 2H), 1.29 (s, 3H), 1.23 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.2, 148.2, 142.7, 52.6, 40.7, 35.0, 29.6, 24.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{26}ClO$: 269.1672; Found 269.1683.

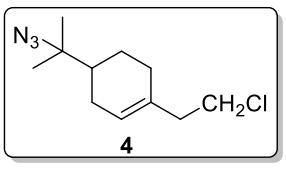
3. Radical Clock Experiment



1ao **4**, 26%

To a 25 mL of Schlenk seal tube were added $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%) and K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times). Methanol (1.0 mL), *β*-pinene **1ao** (31 μL, 0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol%) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography (PE/EA = 100:1) on silica gel to give the product **4** in 26% yield.

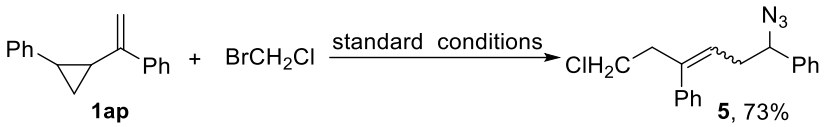
4-(2-azidopropan-2-yl)-1-(2-chloroethyl)cyclohex-1-ene (4)



4

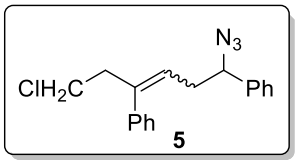
The product **4** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (11.8 mg, 26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50 – 5.48 (m, 1H), 3.60-3.53 (m, 2H), 2.46 – 2.37 (m, 2H), 2.15 – 1.98 (m, 3H), 1.93-1.81 (m, 2H), 1.61 – 1.51 (m, 1H), 1.36 – 1.19 (m, 1H), 1.27 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.1,

123.3, 64.2, 43.5, 43.1, 40.5, 29.0, 26.9, 24.1, 24.0, 23.2. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{11}H_{19}ClN$: 200.1206; Found: 200.1218.



To a 25 mL of Schlenk seal tube were added $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%) and K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times). Methanol (1.0 mL), (1-(2-phenylcyclopropyl)vinyl)benzene **1ap** (44 μL, 0.2 mmol, 1.0 equiv), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol%) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography (PE/EA = 100:1) on silica gel to give the product **5** in 73% yield.

(1-azido-6-chlorohex-3-ene-1,4-diyl)dibenzene (5)

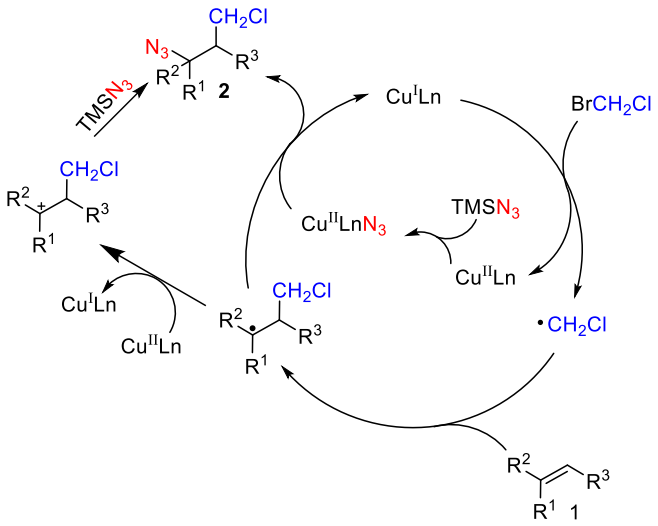


The product **5** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (45.5 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 9.2H), 7.24 – 7.19 (m, 0.4H), 7.06 – 7.01 (m, 0.4H), 5.76 (t, *J* = 7.4 Hz, 0.8H), 5.57 (t, *J* = 7.3 Hz, 0.2H), 4.64 (dd, *J* = 7.7, 6.5 Hz, 0.8H), 4.48 (t, *J* = 7.1 Hz, 0.2H), 3.46 – 3.26 (m, 2.0H), 2.92 (t, *J* = 7.4 Hz, 1.6H), 2.85 – 2.64 (m, 2.0H), 2.55 – 2.38 (m, 0.4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 140.4, 139.32, 139.26, 139.2, 139.1, 129.0, 128.8, 128.6, 128.5, 128.3, 128.3, 127.5, 127.3, 127.0, 127.0, 126.6, 126.5, 125.3, 66.22, 66.19, 42.8, 42.6, 42.5, 36.0, 35.9, 33.5. **HRMS** ESI (m/z): $[M + H - N_2]^+$ Calcd for $C_{18}H_{19}ClN$: 284.1206; Found 284.1210.

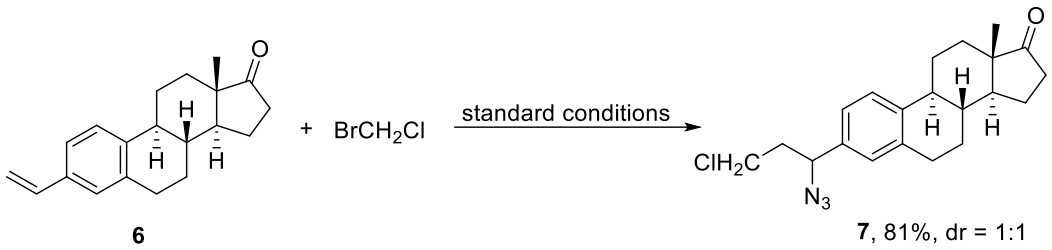
4. Proposed mechanism

On the basis of our preliminary study and previous reports,[4] a possible mechanism

was proposed as below. The single electron reduction of $BrCH_2Cl$ by Cu(I)Ln generated Cu(II)Ln species and monochloromethyl radical, which was captured by the terminal alkene **1** to afford the corresponding alkyl radical. The final azidation of this alkyl radical may process *via* two possible paths: a direct trap of cationic intermediate by $TMSN_3$ or a reductive elimination from benzyl Cu(III)N_3 intermediate.



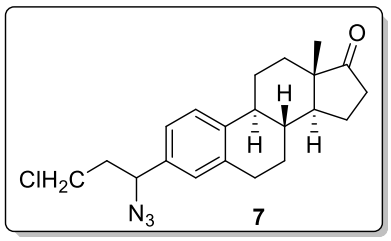
Monochloromethylazidation of the estrone derivative



6 **7**, 81%, dr = 1:1

To a 25 mL of Schlenk seal tube were added **estrone derivative 6** (56.1 mg, 0.2 mmol, 1.0 equiv), $Cu(acac)_2$ (5.2 mg, 0.02 mmol, 10 mol%) and K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) under air atmosphere. The mixture was evacuated and backfilled with N_2 (3 times). Methanol (1.0 mL), $BrCH_2Cl$ (26 μL, 0.4 mmol, 2.0 equiv), **L1** (11 μL, 0.04 mmol, 20 mol%) and $TMSN_3$ (32 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The Schlenk tube was then sealed with a Teflon lined cap and put into a preheated oil bath (60 ˚C). After stirring for 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was concentrated under vacuum and purified by flash column chromatography (PE/EA = 20:1) on silica gel to give the product **7** in 81% yield.

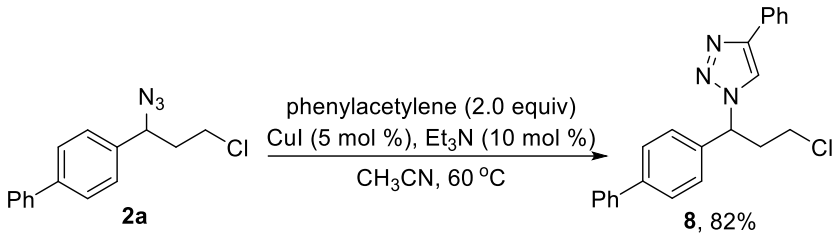
(8R,9S,13S,14S)-3-(1-azido-3-chloropropyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (7)



The product **7** was purified with silica gel chromatography (PE/EA = 20:1) as a colorless oil (60.2 mg, 81% yield, dr = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 4.69 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.65 (ddd, *J* = 11.1, 8.0, 5.3 Hz, 1H), 3.50 (dt, *J* = 11.3, 5.8 Hz, 1H), 2.93 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.56-2.47 (m, 1H), 2.46-2.39 (m, 1H), 2.38-2.28 (m, 1H), 2.26 – 2.12 (m, 2H), 2.11 – 2.01 (m, 3H), 2.00 – 1.93 (m, 1H), 1.75 – 1.39 (m, 6H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.8, 140.3, 137.3, 136.0, 127.6, 127.6, 126.1, 124.4, 124.3, 62.9, 62.9, 50.6, 48.1, 44.5, 41.6, 38.93, 38.88, 38.1, 35.9, 31. 7, 29.53, 29.51, 26.5, 25.8, 21.7, 13.9. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{21}H_{27}ClNO$: 344.1781; Found 344.1780.

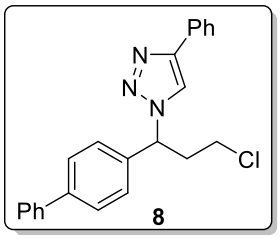
Derivatizations of the Products

1. The Click reaction of 2a with phenylacetylene



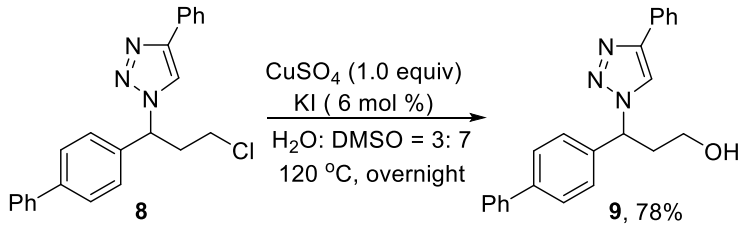
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), phenylacetylene (44 μL, 0.4 mmol, 2.0 equiv), CuI (2.0 mg, 0.01 mmol, 5 mol%), Et_3N (3 μL, 0.02 mmol, 10 mol%) in CH_3CN (2.0 mL) were stirred at 60 ˚C for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 10:1) on silica gel to give the product **8** in 82% yield.

1-(1-([1,1'-biphenyl]-4-yl)-3-chloropropyl)-4-phenyl-1H-1,2,3-triazole (8)



The product **8** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (61.3 mg, 82% yield); **mp** 168-169 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 3H), 7.59 (dd, *J* = 17.4, 7.6 Hz, 4H), 7.51 – 7.28 (m, 8H), 5.93 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.23-3.08 (m, 1H), 2.83 – 2.68 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 142.0, 140.3, 137.1, 130.5, 129.0, 129.0, 128.4, 128.0, 127.8, 127.5, 127.2, 125.8, 120.0, 62.0, 41.4, 37.9. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}ClN_3$: 374.1424; Found 374.1425.

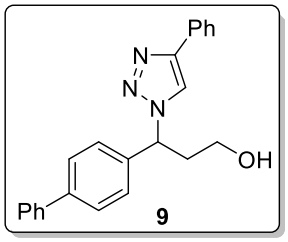
2. The Reaction of 8 with H_2O



The mixture of **8** (74.8 mg, 0.2 mmol, 1.0 equiv), $CuSO_4$ (31.9 mg, 0.2 mmol, 1.0 equiv) and KI (2.0 mg, 0.12 mmol, 6 mol%) in H_2O (0.3 mL) and DMSO (0.7 mL) were stirred at 120 ˚C overnight. After completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM

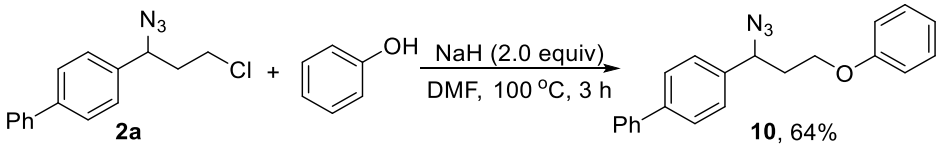
three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA =5:1) on silica gel to give the product **9** in 78% yield.

3-([1,1'-biphenyl]-4-yl)-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-1-ol (9)



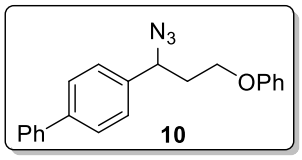
The product **9** was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (55.4 mg, 78% yield); **mp** 99-100 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.81 – 7.78 (m, 2H), 7.61 – 7.55 (m, 4H), 7.48-7.41 (m, 6H), 7.39 – 7.33 (m, 2H), 4.83 – 4.69 (m, 2H), 4.62 (dt, *J* = 13.8, 6.1 Hz, 1H), 2.53 – 2.38 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 142.8, 140.8, 140.7, 131.0, 130.3, 129.0, 128.9, 128.6, 127.4, 127.4, 127.2, 126.3, 126.0, 71.2, 52.0, 38.8. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O$: 356.1763; Found 356.1741.

3. The Reaction of 2a with Phenol



The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), Phenol (37.6 mg, 0.4 mmol, 2.0 equiv) and NaH (16.0 mg, 60%, dispersion in mineral oil, 0.40 mmol, 2.0 equiv) in DMF (1.0 mL) were stirred at 100 ˚C for 3 h. After completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 100:1) on silica gel to give the product **10** in 64% yield.

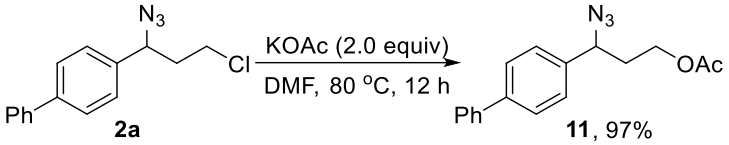
4-(1-azido-3-phenoxypropyl)-1,1'-biphenyl (10)



The product **10** was purified with silica gel chromatography (PE/EA = 100:1) as a white solid (42.2 mg, 64% yield); **mp** 57-58 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 4H), δ 7.52 – 7.43 (m, 4H), 7.42 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.03 – 6.90 (m, 3H), 4.89 (dd, *J* = 8.5, 6.1 Hz, 1H), 4.14 (ddd, *J* = 9.5, 7.4, 4.9 Hz, 1H), 3.97 (dt, *J* = 9.5, 5.6 Hz, 1H), 2.39 – 2.17 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 141.4, 140.6,

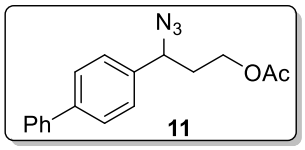
138.3, 129.6, 129.0, 127.7, 127.6, 127.5, 127.2, 121.1, 114.6, 64.1, 62.7, 36.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{21}H_{20}NO$: 302.1545; Found 302.1544.

4. The Reaction of 2a with KOAc



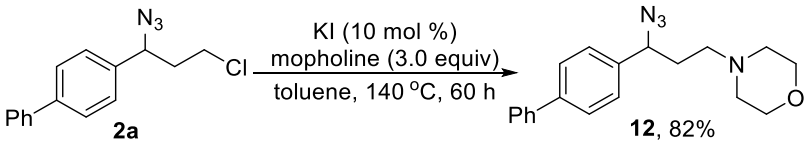
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), and KOAc (39.3 mg, 0.40 mmol, 2.0 equiv) in DMF (1.0 mL) were stirred at 80 ˚C for 12 h. After completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 10:1) on silica gel to give the product **11** in 97% yield.

3-([1,1'-biphenyl]-4-yl)-3-azidopropyl acetate (11)



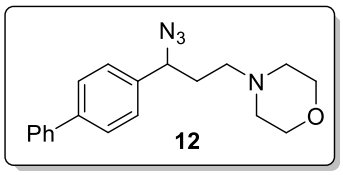
The product **11** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (57.3 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 4H), 7.51 – 7.35 (m, 5H), 4.66 (t, *J* = 7.3 Hz, 1H), 4.27 – 4.07 (m, 2H), 2.26 – 2.02 (m, 2H), 2.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 141.5, 140. 5, 137.9, 128.9, 127.7, 127.6, 127.4, 127.2, 62.8, 61.2, 35.2, 21.0. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{17}H_{18}NO_2$: 268.1338; Found 268.1344.

5. The Reaction of 2a with Morpholine



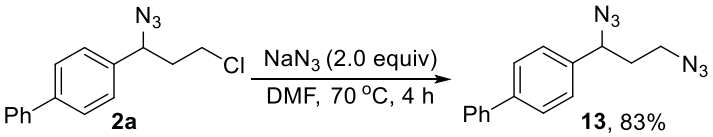
2a (54.3 mg, 0.2 mmol, 1.0 equiv) was dissolved in toluene (10.0 mL, dry), morpholine (53 μL, 0.6 mmol, 3.0 equiv), KI (4.0 mg, 0.02 mmol, 0.01 equiv) were added in the mixture and stirred at 140 ˚C for 60 h. After completion of the reaction, the solvent and excess morpholine were removed under reduced pressure and purified by flash column chromatography (PE/EA = 3:1) on silica gel to give the product **12** in 82% yield.

4-(3-([1,1'-biphenyl]-4-yl)-3-azidopropyl)morpholine (12)



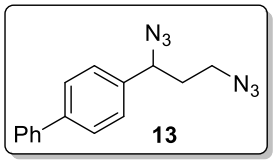
The product **12** was purified with silica gel chromatography (PE/EA = 3:1) as a colorless oil (52.9 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.48 – 7.42 (m, 2H), 7.41 – 7.33 (m, 3H), 4.64 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.72 (t, *J* = 4.7 Hz, 4H), 2.49 – 2.33 (m, 6H), 2.10 – 1.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 140.6, 138.7, 128.9, 127.62, 127.60, 127.4, 127.2, 67.1, 64.0, 55.3, 53. 8, 33.3. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ calcd. for $C_{19}H_{23}N_2O$: 295.1810; Found 295.1826.

6. The Reaction of 2a with NaN_3



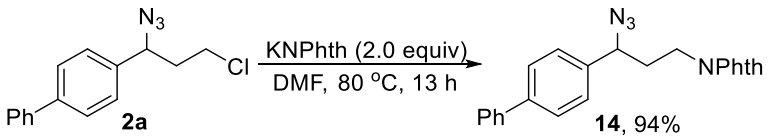
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), and NaN_3 (26.0 mg, 0.4 mmol, 2.0 equiv) in DMF (2.0 mL) were stirred at 70 ˚C for 4 h. After completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 100:1) on silica gel to give the product **13** in 83% yield.

4-(1,3-diazidopropyl)-1,1'-biphenyl (13)



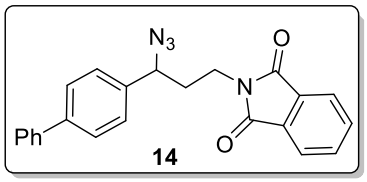
The product **13** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (46.2 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 4H), 7.50-7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 4.67 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.48 (ddd, *J* = 12.4, 7.7, 6.0 Hz, 1H), 3.37 (dt, *J* = 12.4, 6.2 Hz, 1H), 2.09 (ddt, *J* = 14.7, 8.7, 6.1 Hz, 1H), 1.98 (ddt, *J* = 14.0, 7.7, 6.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 140.5, 137.7, 129.0, 127.8, 127.7, 127.4, 127.2, 63.1, 48.3, 35.6. **HRMS** (ESI) m/z: $[M + H - 2N_2]^+$ Calcd for $C_{15}H_{15}N_2$: 223.1235; Found 223.1232.

7. The Reaction of 2a with KNPhth



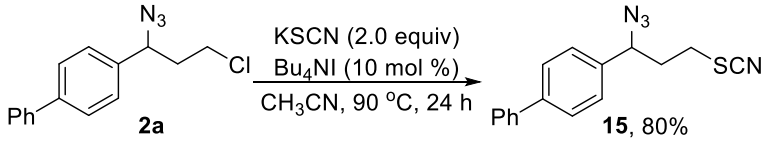
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), and KNPhth (74.1 mg, 0.40 mmol, 2.0 equiv) in DMF (1.0 mL) were stirred at 80 ˚C for 13 h. After completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 10:1) on silica gel to give the product **14** in 94% yield.

2-(3-([1,1'-biphenyl]-4-yl)-3-azidopropyl)isoindoline-1,3-dione (14)



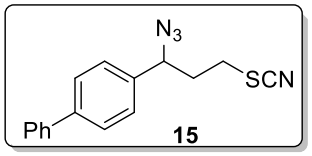
The product **14** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (71.9 mg, 94% yield); **mp** 121-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.70 – 7.63 (m, 2H), 7.59 – 7.50 (m, 4H), 7.47 – 7.30 (m, 5H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.29 – 2.14 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 141.4, 140.3, 137.6, 134.0, 132.0, 128.8, 127.6, 127.5, 127.4, 127.1, 123.2, 63.9, 35.3, 34.5. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ calcd. for $C_{23}H_{19}N_2O_2$: 355.1447, Found 355.1452.

8. The Reaction of 2a with KSCN



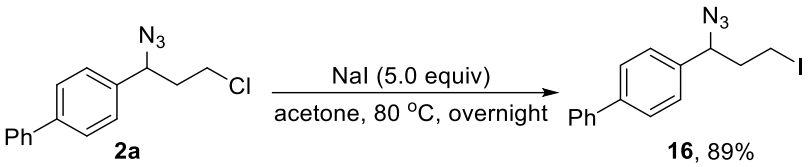
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), TBAI (7.4 mg, 0.02 mmol, 10 mol %) and KSCN (38.9 mg, 0.40 mmol, 2.0 equiv) in CH_3CN (1.0 mL) were stirred at 90 ˚C for 24 h. After completion of the reaction, the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 20:1) on silica gel to give the product **15** in 80% yield.

4-(1-azido-3-thiocyanatopropyl)-1,1'-biphenyl (15)



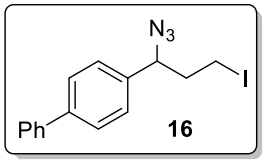
The product **15** was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (47.1 mg, 80% yield); **mp** 73-73 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 4H), 7.53 – 7.35 (m, 5H), 4.74 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.11 – 2.96 (m, 2H), 2.40 – 2.17 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 140.3, 136.9, 129.0, 127.9, 127.8, 127.4, 127.2, 111.7, 63.7, 36.4, 30.5. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{16}H_{15}N_2S$: 267.0956; Found 267.0966.

9. The Reaction of 2a with NaI



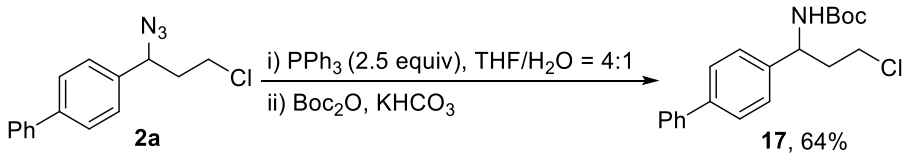
The mixture of **2a** (54.3 mg, 0.2 mmol, 1.0 equiv), and NaI (149.9 mg, 1.0 mmol, 5.0 equiv) in acetone (1.0 mL) were stirred under reflux overnight. After completion of the reaction, the solvent was removed under reduced pressure and purified by flash column chromatography (PE/EA = 100:1) on silica gel to give the product **16** in 89% yield.

4-(1-azido-3-iodopropyl)-1,1'-biphenyl (16)



The product **16** was purified with silica gel chromatography (PE/EA = 100:1) as a white solid (64.7 mg, 89% yield); **mp** 49-50 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 4H), 7.51 – 7.36 (m, 5H), 4.71 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.28 (ddd, *J* = 10.0, 7.6, 6.4 Hz, 1H), 3.16 (dt, *J* = 9.9, 6.5 Hz, 1H), 2.26 (dddt, *J* = 41.0, 14.4, 7.7, 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 140.4, 137.4, 129.0, 127.8, 127.7, 127.5, 127.2, 66.0, 39.7, 2.1. **HRMS** (ESI) m/z: $[M + H - N_2]^+$ Calcd for $C_{15}H_{15}IN$: 336.0249; Found 336.0264.

10. The Reduction reaction of azide with PPh_3

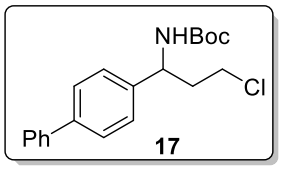


i) 2a (54.3 mg, 0.2 mmol, 1.0 equiv) and PPh_3 (131.1 mg, 0.5 mmol, 2.5 equiv) were dissolved in a mixture of THF (2.0 mL), H_2O (0.5 mL). The reaction was stirred for 4 h at 60 ˚C under N_2. After completion of the reaction, the residue was transferred into

a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was directly used in the next step without further purification.

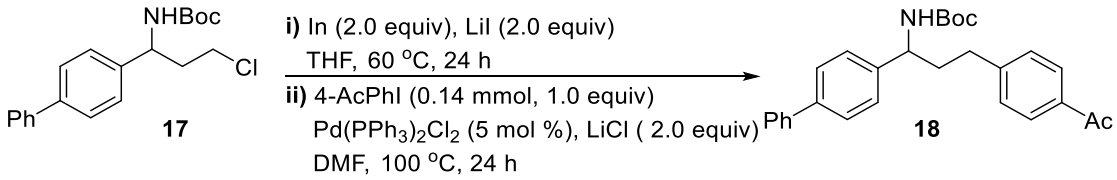
ii) To the above residue was added Boc_2O (55 μL, 0.24 mmol, 1.2 equiv), $KHCO_3$ (24.0 mg, 0.24 mmol, 1.2 equiv) and THF (1.0 mL), and the reaction mixture was stirring at the room temperature overnight. After completion of the reaction, the solvent was removed under reduced pressure and the product was purified by flash column chromatography (PE/EA = 20:1) on silica gel to give the product **17** in 64% yield.

***tert*-butyl (1-([1,1'-biphenyl]-4-yl)-3-chloropropyl)carbamate (17)**



The product **17** was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (44.3 mg, 64% yield); **mp** 133-134 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.72 – 7.51 (m, 5H), 7.45 (t, J = 7.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 4.72 (dd, J = 8.3, 7.9 Hz, 1H), 3.73-3.60 (m, 1H), 3.60-3.46(m, 1H), 2.23 – 1.95 (m, 2H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, DMSO) δ 155.0, 142.5, 139.9, 138.8, 128.9, 127.3, 126.9, 126.7, 126.6, 77.9, 51.4, 42.3, 38.9, 28.2. **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}ClNO_2$: 346.1574; Found 346.1574.

11. The Reaction of 17 with 4'-Iodoacetophenone

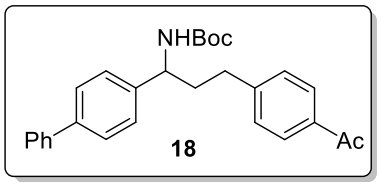


The insertion step 1: **17** (69.2 mg, 0.2 mmol), indium (45.9 mg, 0.4 mmol), LiI (53.5 mg, 0.4 mmol), and THF (1.0 mL) was added in a flask equipped with a septum and a magnetic stir bar. The reaction mixture was vigorously stirred at 60 ˚C for 24 h. Then the solution was carefully separated by filtration. The remaining black precipitate was additionally stirred with THF (3.0 mL), and the THF layer was carefully separated by filtration. The combined organic layers were concentrated under vacuum. The crude mixture was directly used in the next step without further purification.

The cross-coupling step 2: To the above residue was added 4'-Iodoacetophenone (34.4

mg, 0.7 mmol), LiCl (17.0 mg, 0.4 mmol), and Pd $(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol), and DMF (1.0 mL), and the reaction mixture was stirred at 100 ˚C for 24 h. Upon completion of the reaction, the residue was transferred into a separatory funnel and added water (1.0 mL), extracted with DCM three times. The last combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure and the product was purified by flash column chromatography (PE/EA =10:1) on silica gel to give the product **18** in 85% yield.

***tert*-butyl (1-([1,1'-biphenyl]-4-yl)-3-(4-acetylphenyl)propyl)carbamate (18)**

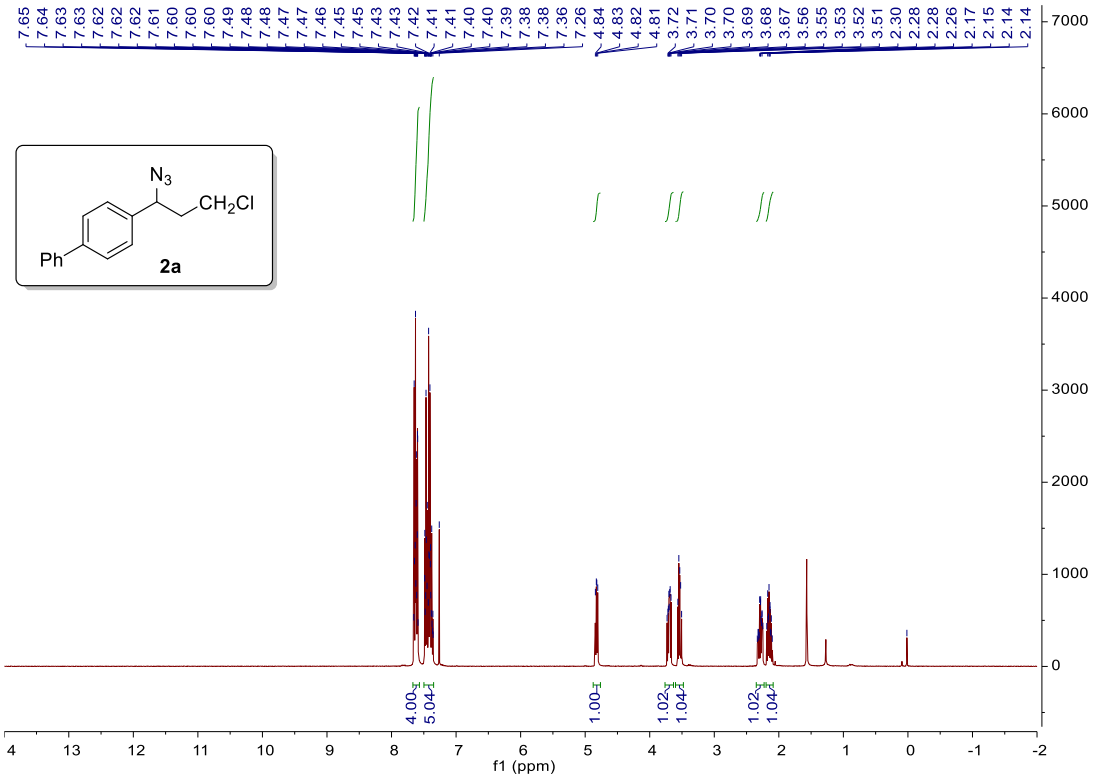


The product **18** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (51.1 mg, 85% yield); **mp** 118-119 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.62 – 7.53 (m, 4H), 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 3H), 7.29 – 7.25 (m, 2H), 4.92 (d, *J* = 8.2 Hz, 1H), 4.72 (s, 1H), 2.81 – 2.62 (m, 2H), 2.58 (s, 3H), 2.25 – 2.03 (m, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.9, 155.4, 147.3, 140.8, 140.5, 135.4, 128.9, 128.8, 127.6, 127. 5, 127.2, 127.0, 79.8, 54.4, 38.2, 32. 8, 28.5, 26.7. **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{31}NNaO_3$: 452.2202; Found 452.2198.

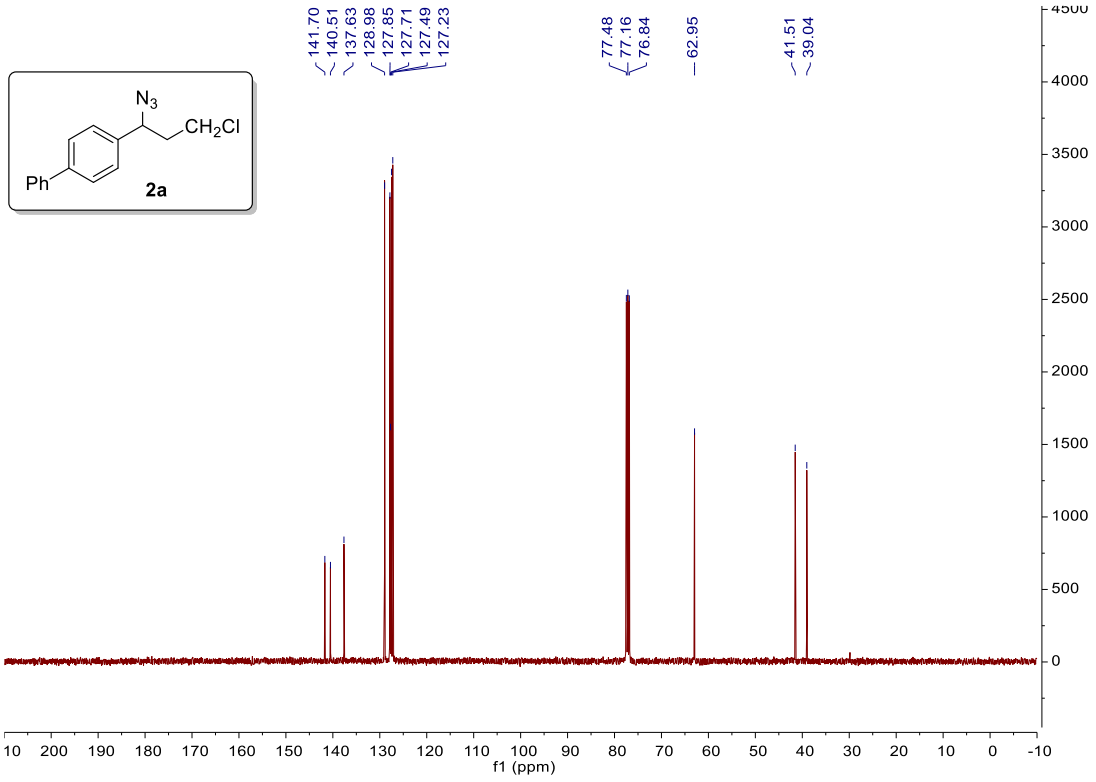
References:

1. N. Fu, G. S. Sauer, A. Saha, A. Loo and S. Lin, *Science* 2017, **357**, 575.
2. L. Crespin, L. Biancalana, T. Morack, D. C. Blakemore and S. V. Ley, *Org. Lett.,* 2017, **19**, 1084.
3. K. Miyazawa, T. Koike and M. Akita, *Chem*. *Eur*. *J*. 2015, **21**, 11677.
4. (a) B. Zhang and A. Studer, *Org*. *Lett*., 2014, **16**, 1790; (b) A. Bunescu, T. M. Ha, Q. Wang and J. Zhu, *Angew*. *Chem*. *Int*., *Ed*. 2017, **56**, 10555; (c) H. Zhou, W. Jian, B. Qian, C. Ye, D. Li, J. Zhou and H. Bao, *Org*. *Lett*., 2017, **19**, 6120; (d) F. Wang, X. Qi, Z. Liang, P. Chen and G. Liu, *Angew*. *Chem*. *Int*. *Ed*., 2014, **53**, 1881; (e) B. Chen, C. Fang, P. Liu and J. M. Ready, *Angew*. *Chem*. *Int*. *Ed*., 2017, **56**, 8780; (f) C.-L. Zhu, C. Wang, Q.-X. Qin, S. Yruegas, C. D. Martin and H. Xu, *ACS Catal*., 2018, **8**, 5032.

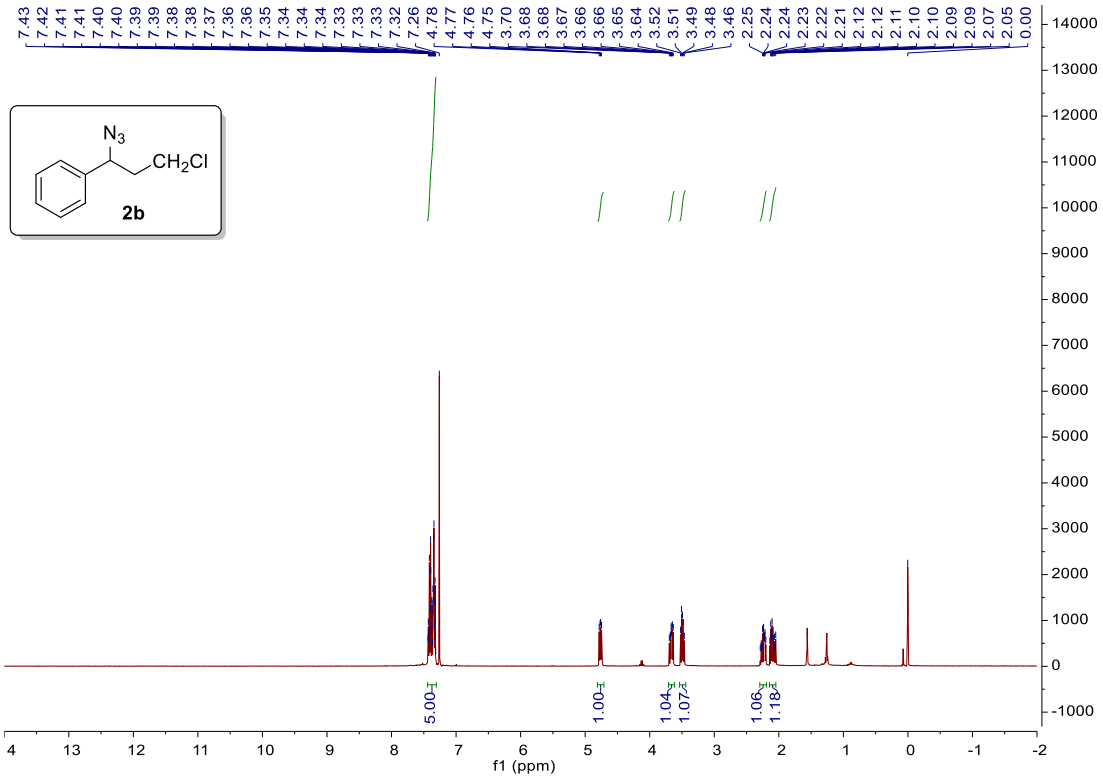
NMR Spectra of New Compounds (^{1}H NMR, ^{13}C NMR, ^{19}F NMR)



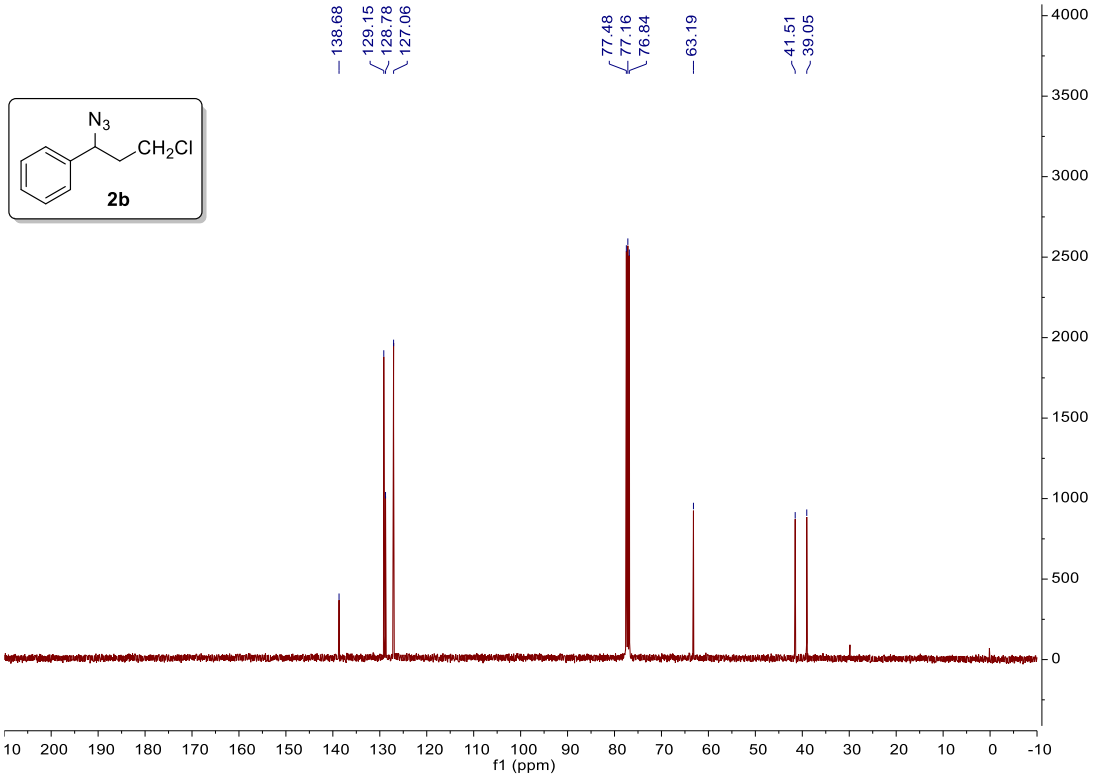
^{1}H NMR Spectrum of **2a** ($CDCl_3$, 400 MHz)



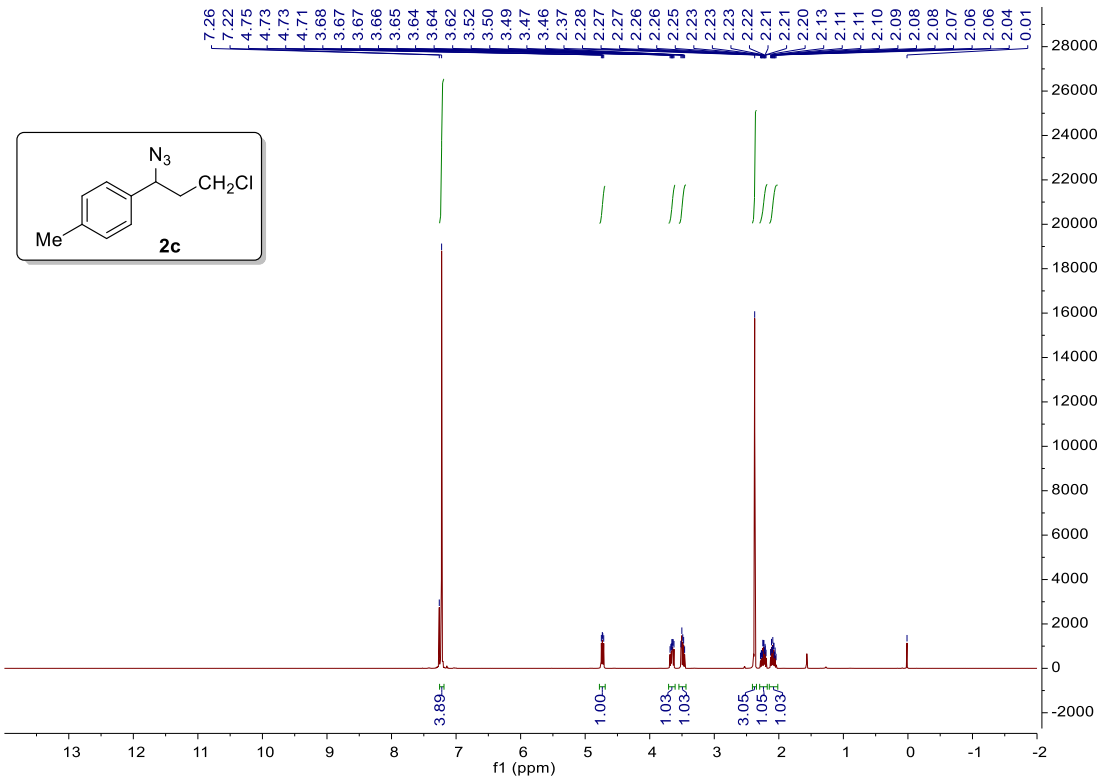
^{13}C NMR Spectrum of **2a** ($CDCl_3$, 101 MHz)



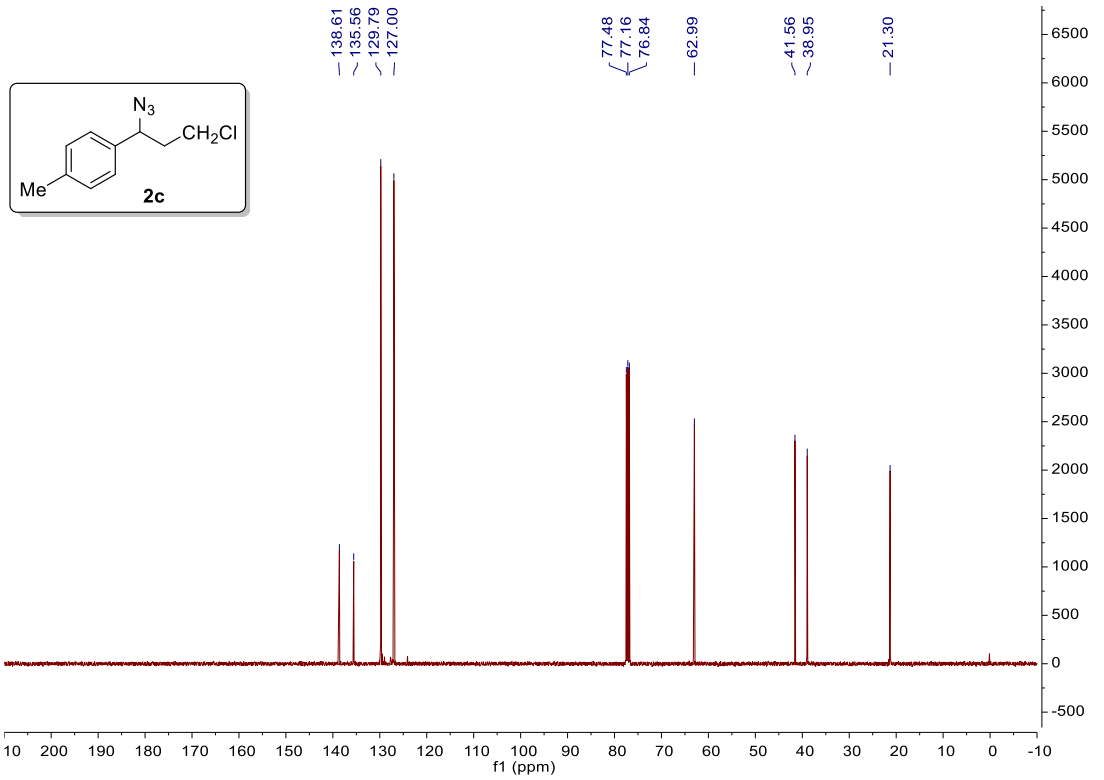
^{1}H NMR Spectrum of **2b** ($CDCl_3$, 400 MHz)



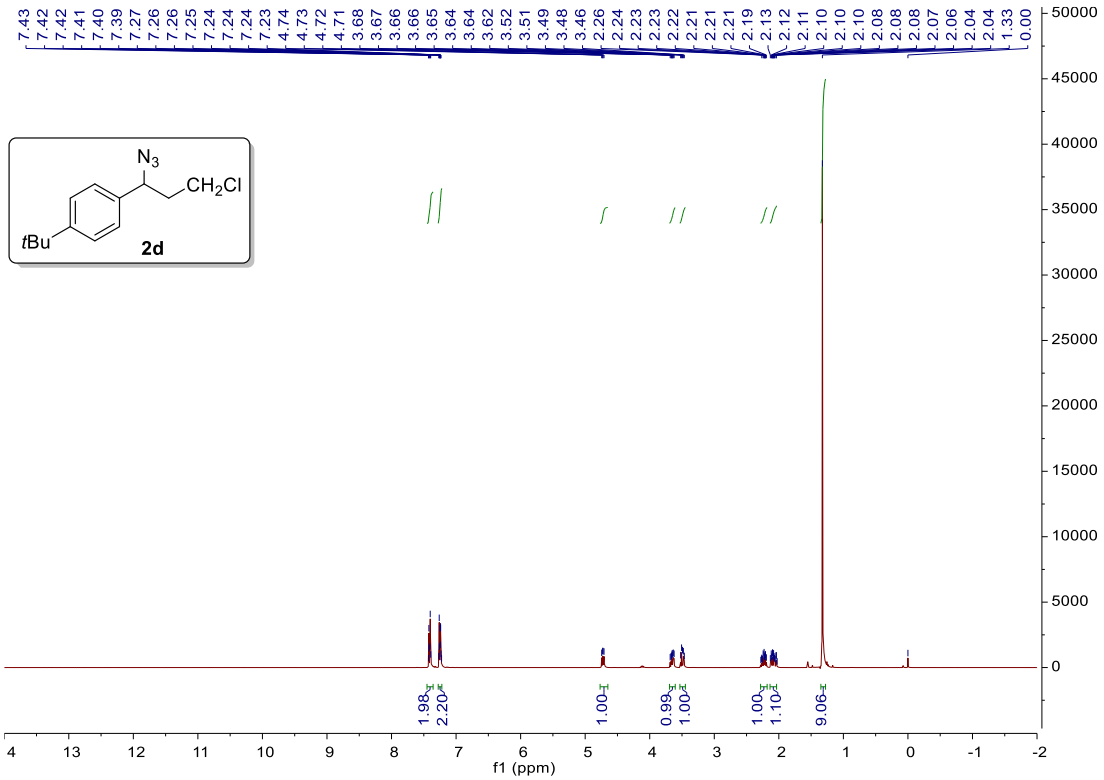
^{13}C NMR Spectrum of **2b** ($CDCl_3$, 101 MHz)



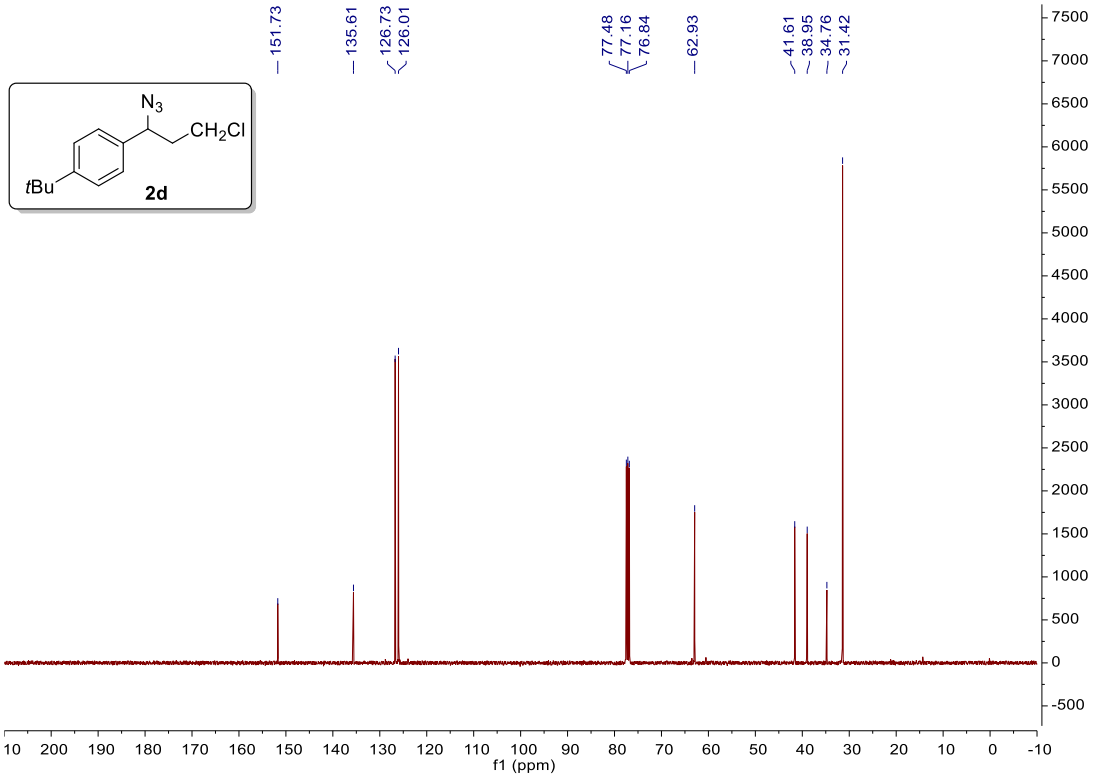
^{1}H NMR Spectrum of **2c** ($CDCl_3$, 400 MHz)



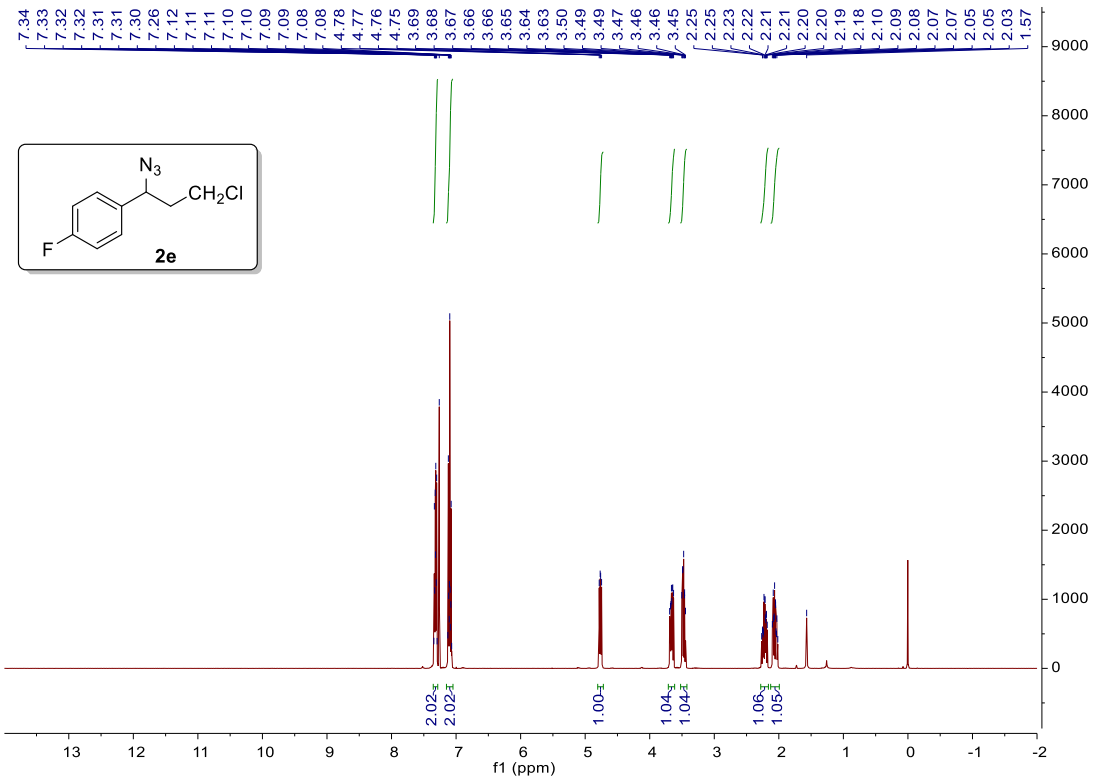
^{13}C NMR Spectrum of **2c** ($CDCl_3$, 101 MHz)



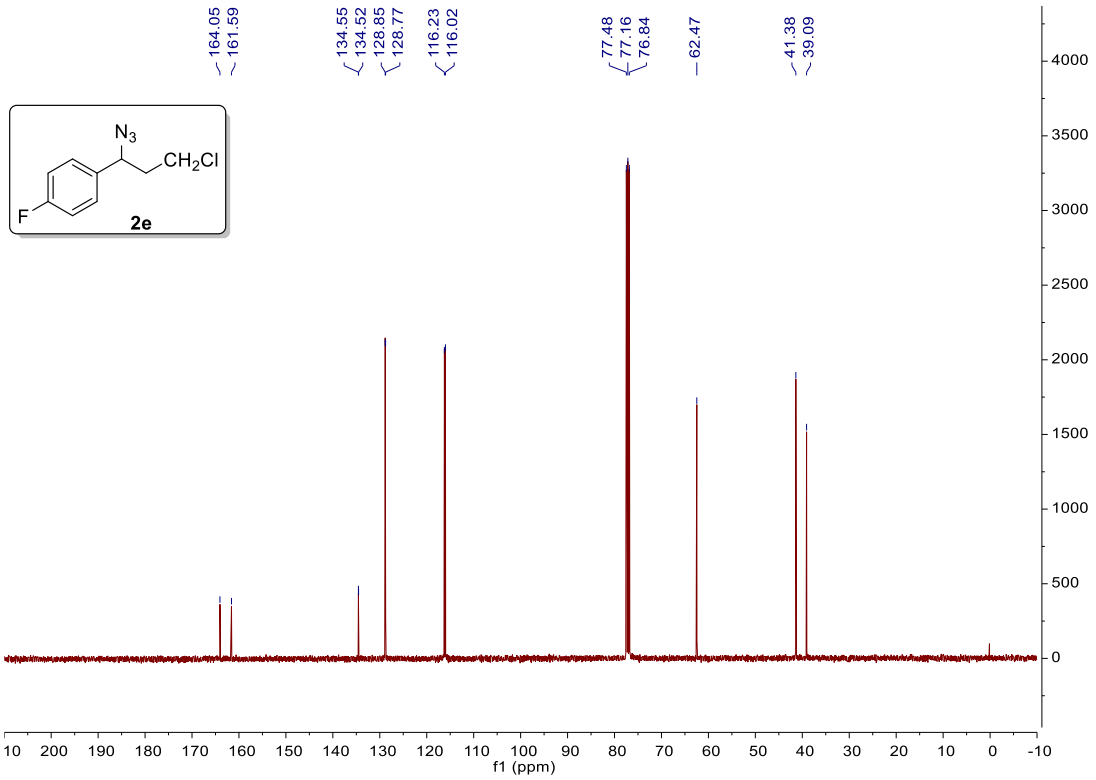
^{1}H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz)



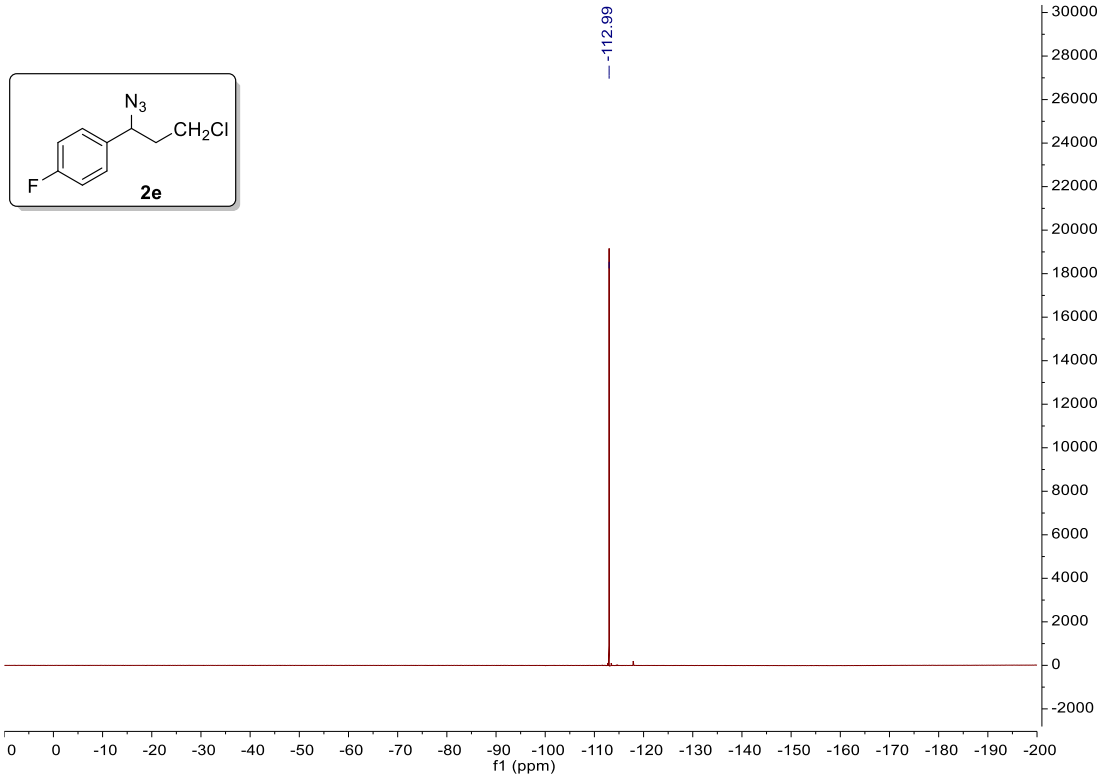
^{13}C NMR Spectrum of **2d** ($CDCl_3$, 101 MHz)



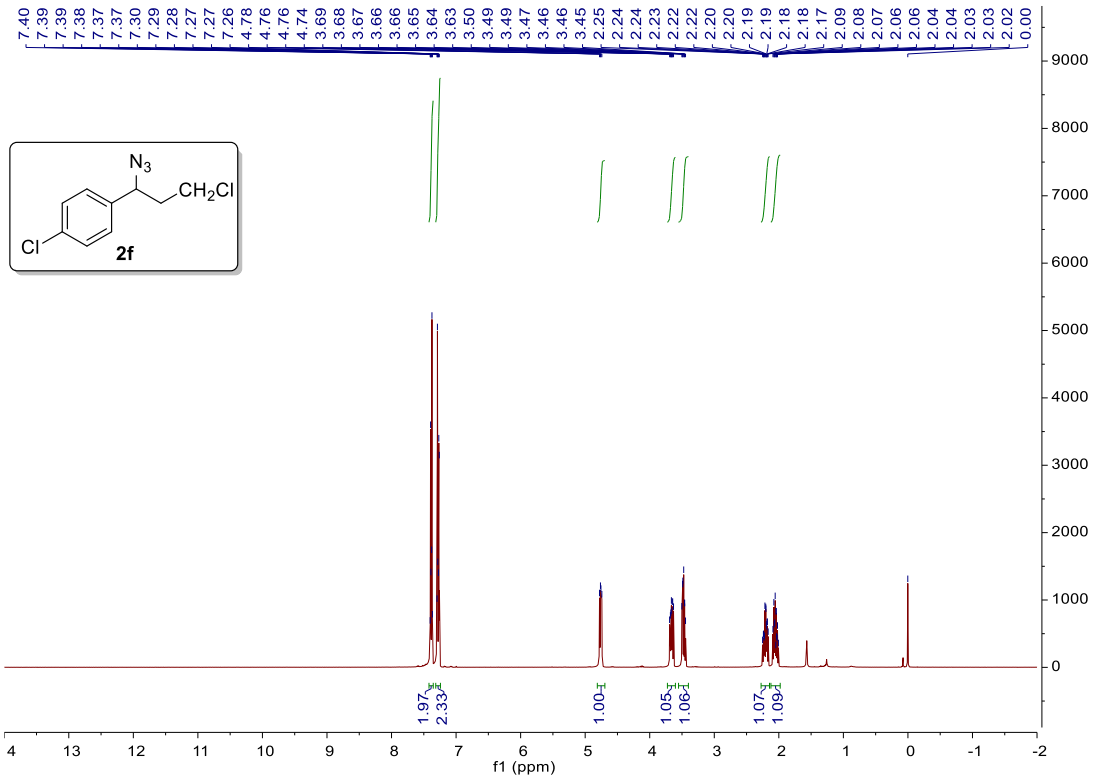
^{1}H NMR Spectrum of **2e** ($CDCl_3$, 400 MHz)



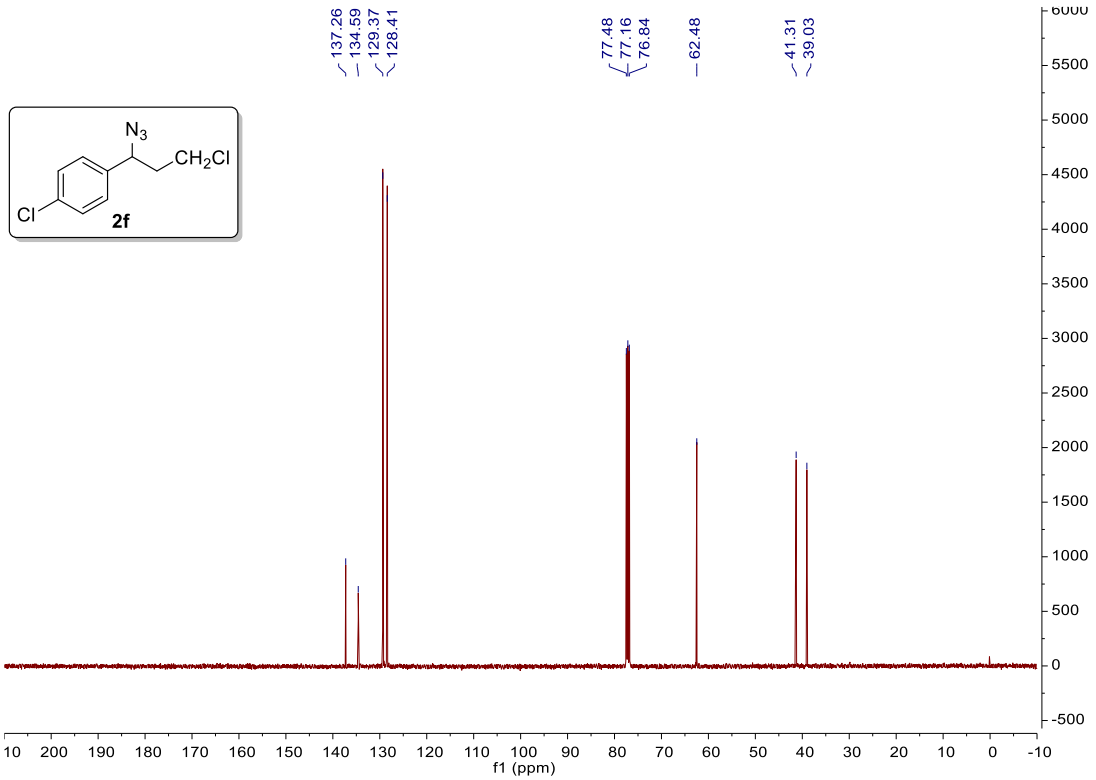
^{13}C NMR Spectrum of **2e** ($CDCl_3$, 101 MHz)



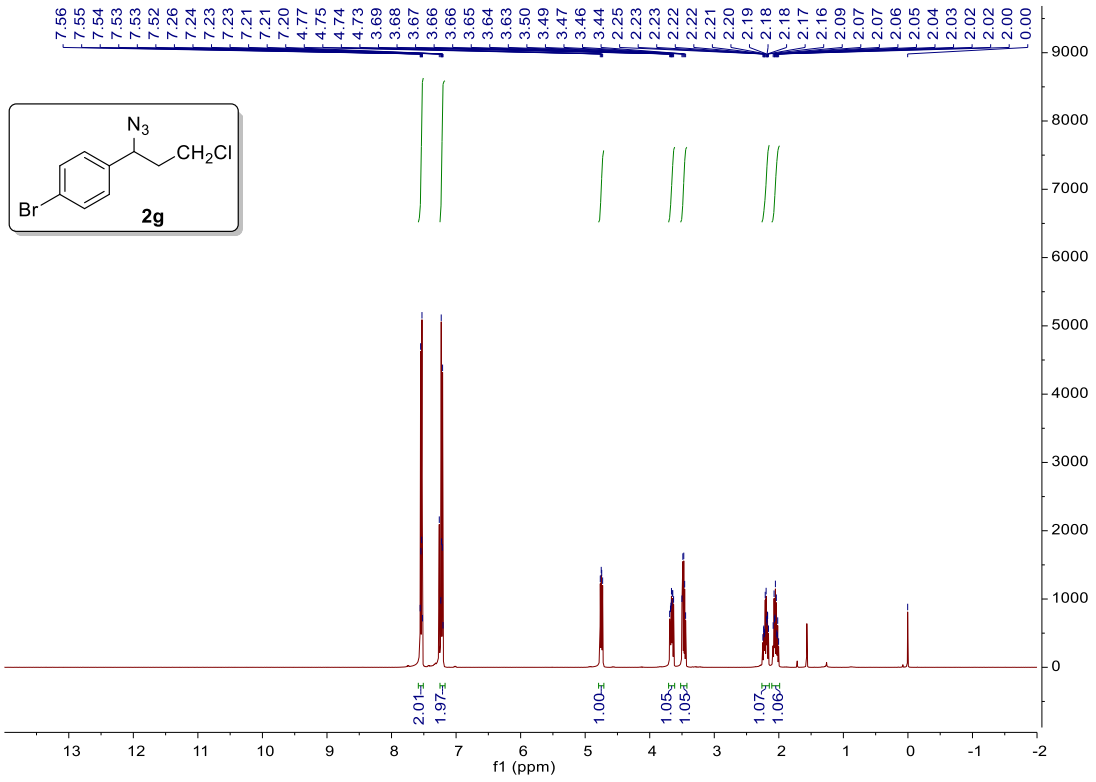
^{19}F NMR Spectrum of **2e** ($CDCl_3$, 376 MHz)



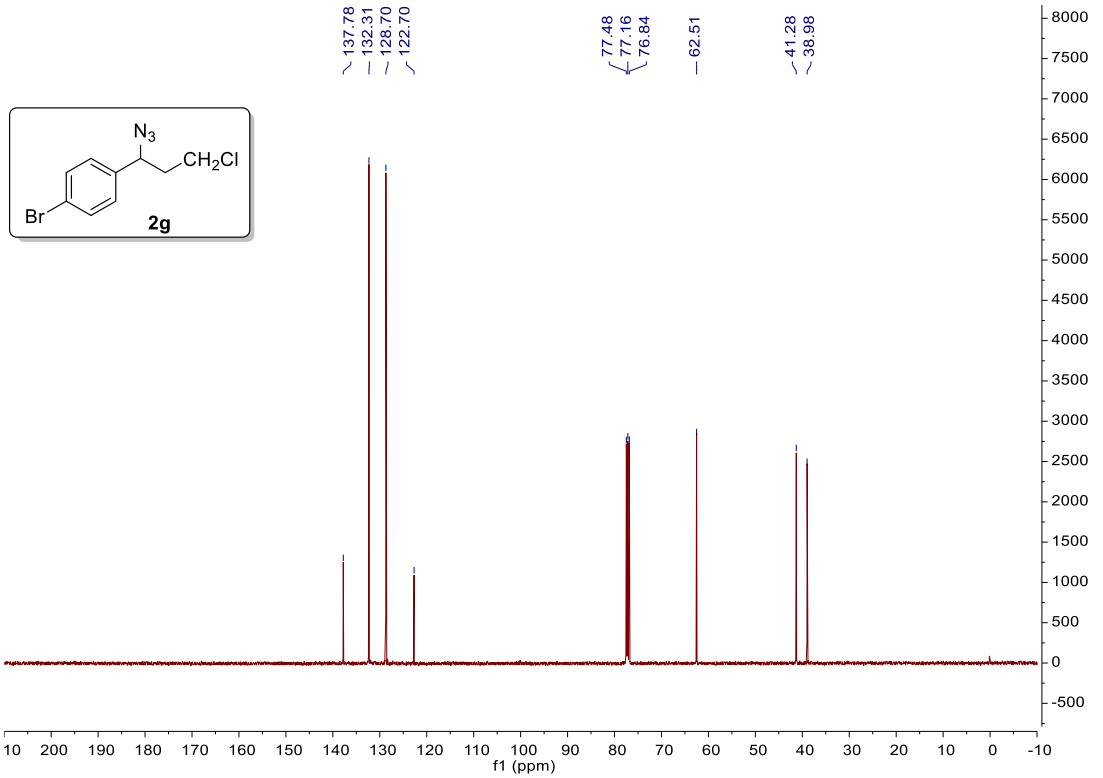
^{1}H NMR Spectrum of **2f** ($CDCl_3$, 400 MHz)



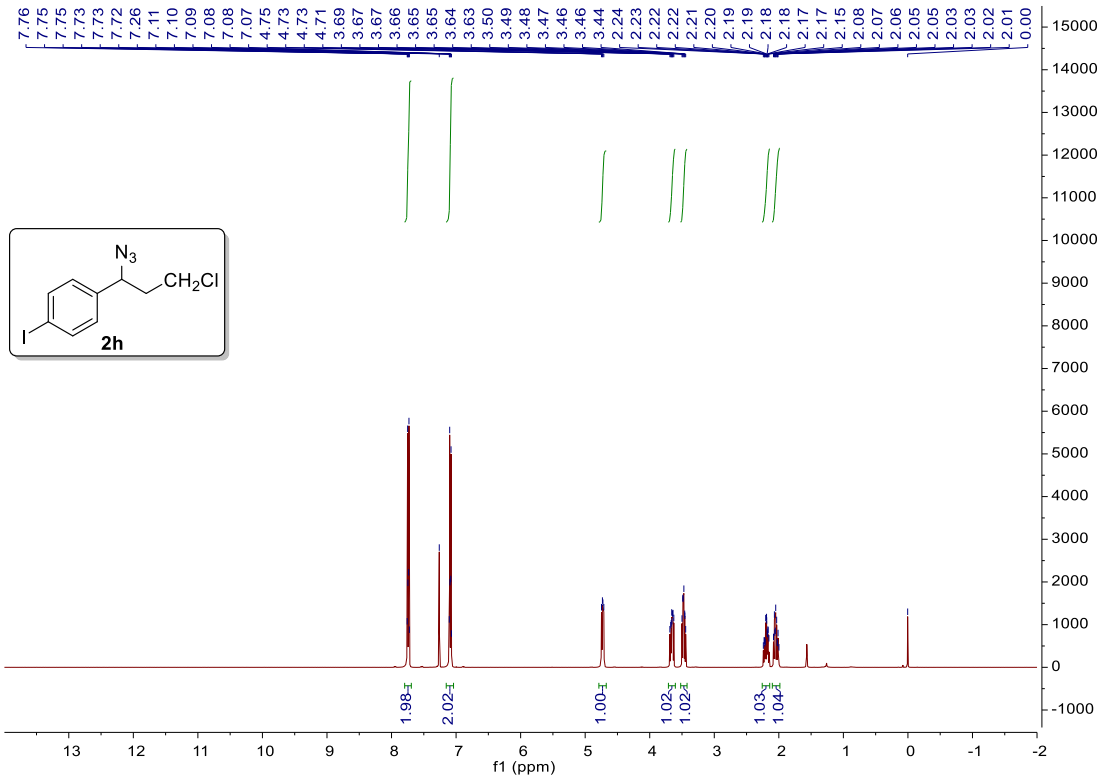
^{13}C NMR Spectrum of **2f** ($CDCl_3$, 101 MHz)



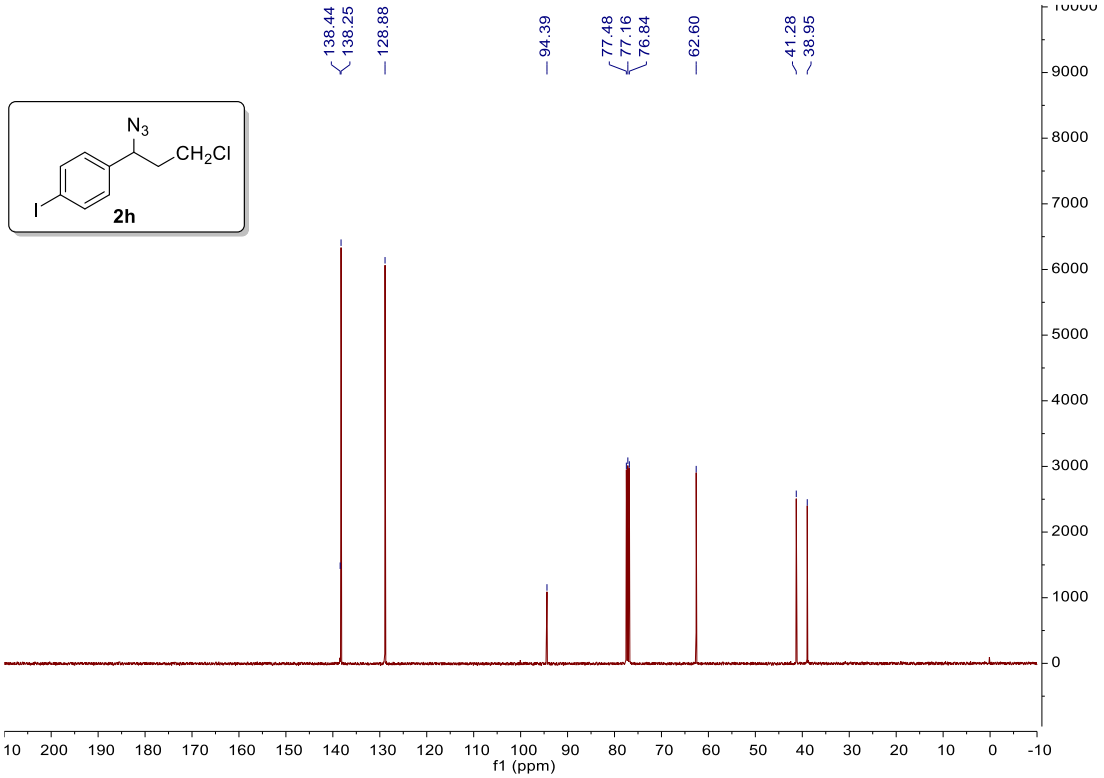
^{1}H NMR Spectrum of **2g** ($CDCl_3$, 400 MHz)



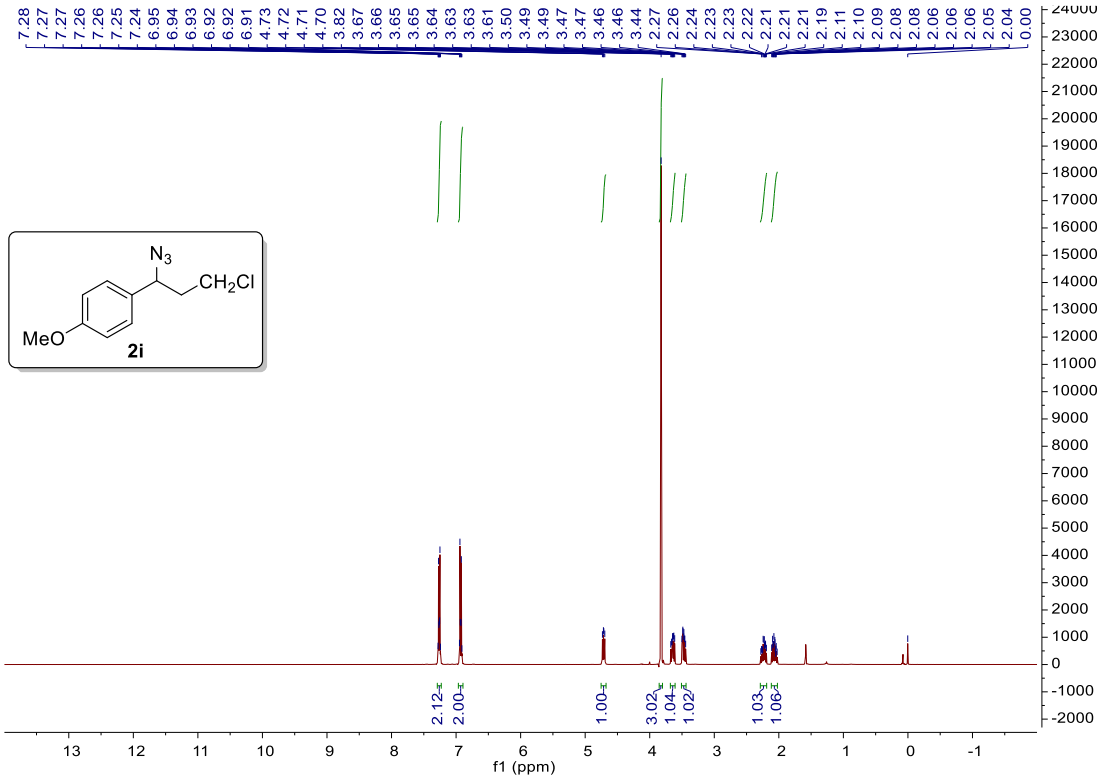
^{13}C NMR Spectrum of **2g** ($CDCl_3$, 101 MHz)



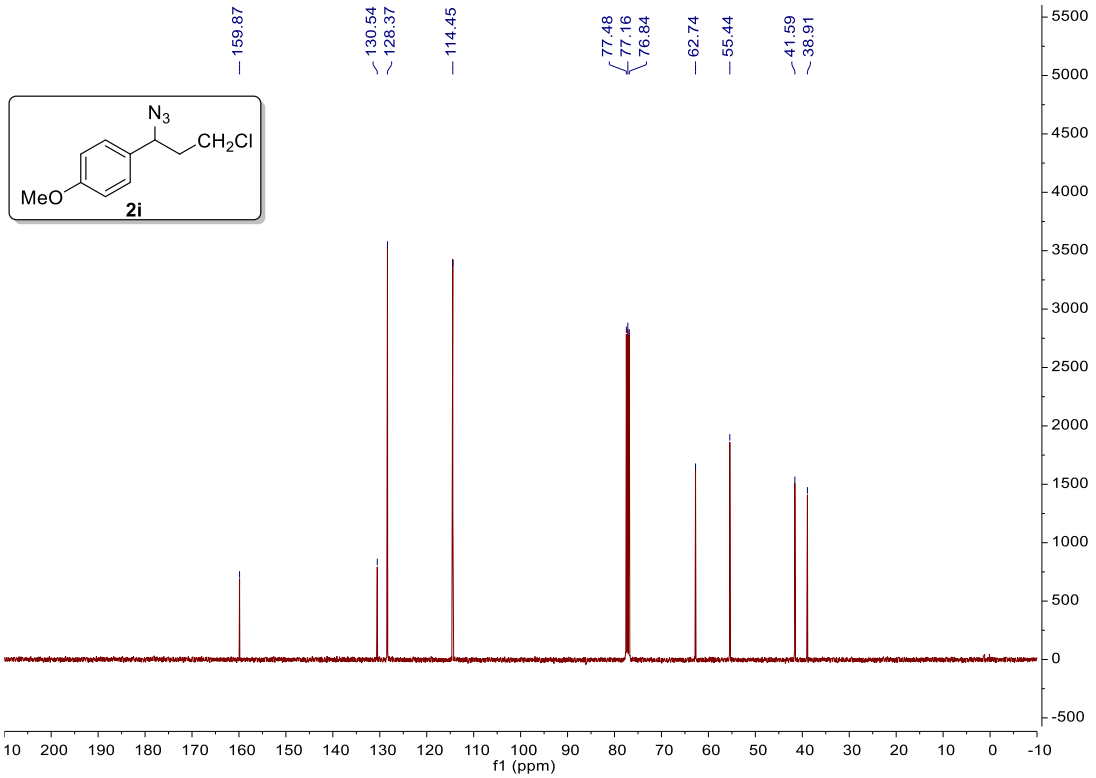
^{1}H NMR Spectrum of **2h** ($CDCl_3$, 400 MHz)



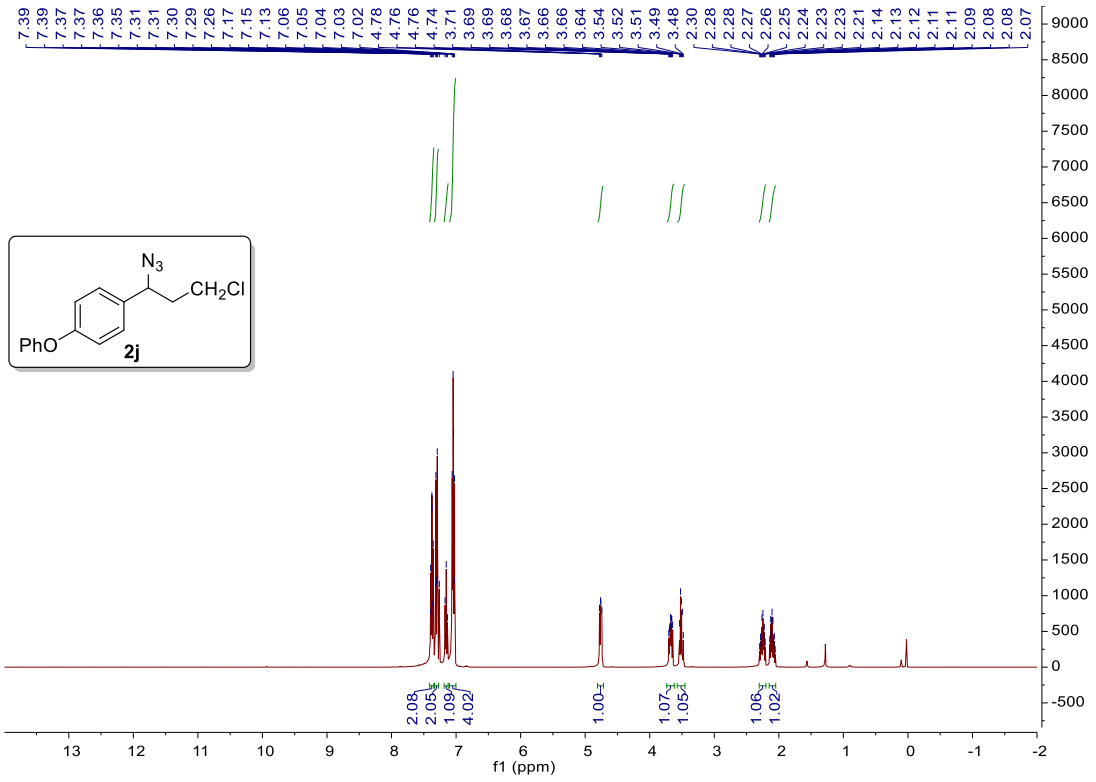
^{13}C NMR Spectrum of **2h** ($CDCl_3$, 101 MHz)



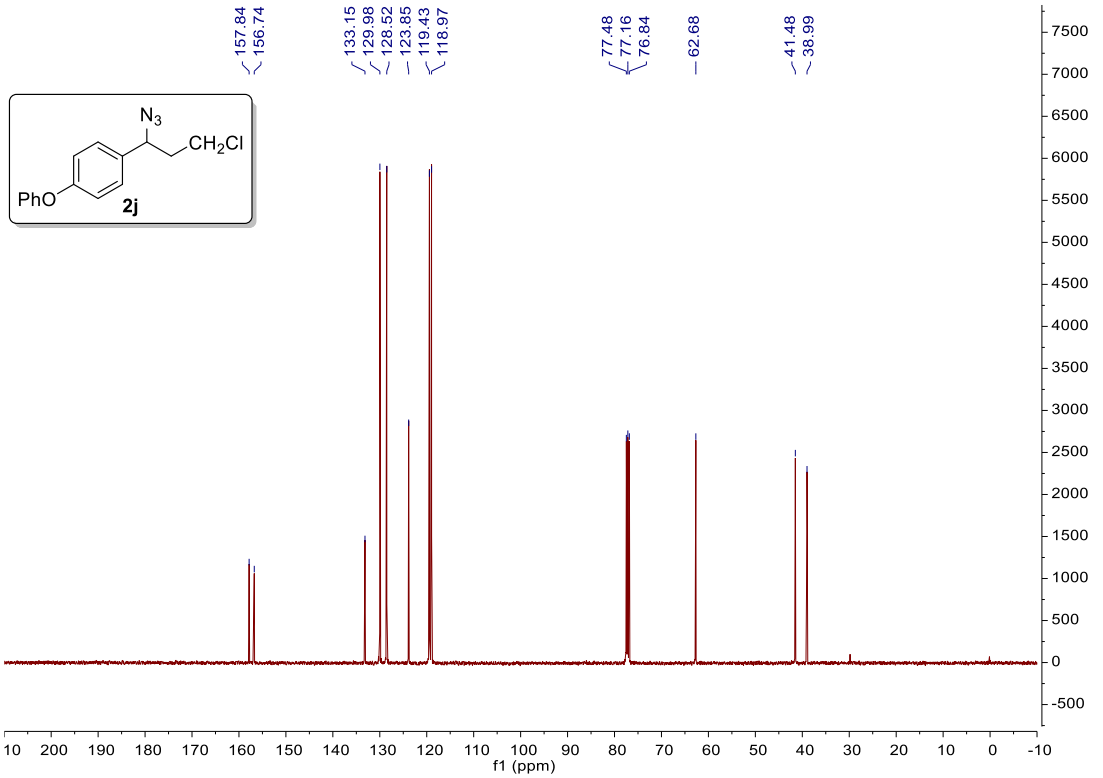
^{1}H NMR Spectrum of **2i** ($CDCl_3$, 400 MHz)



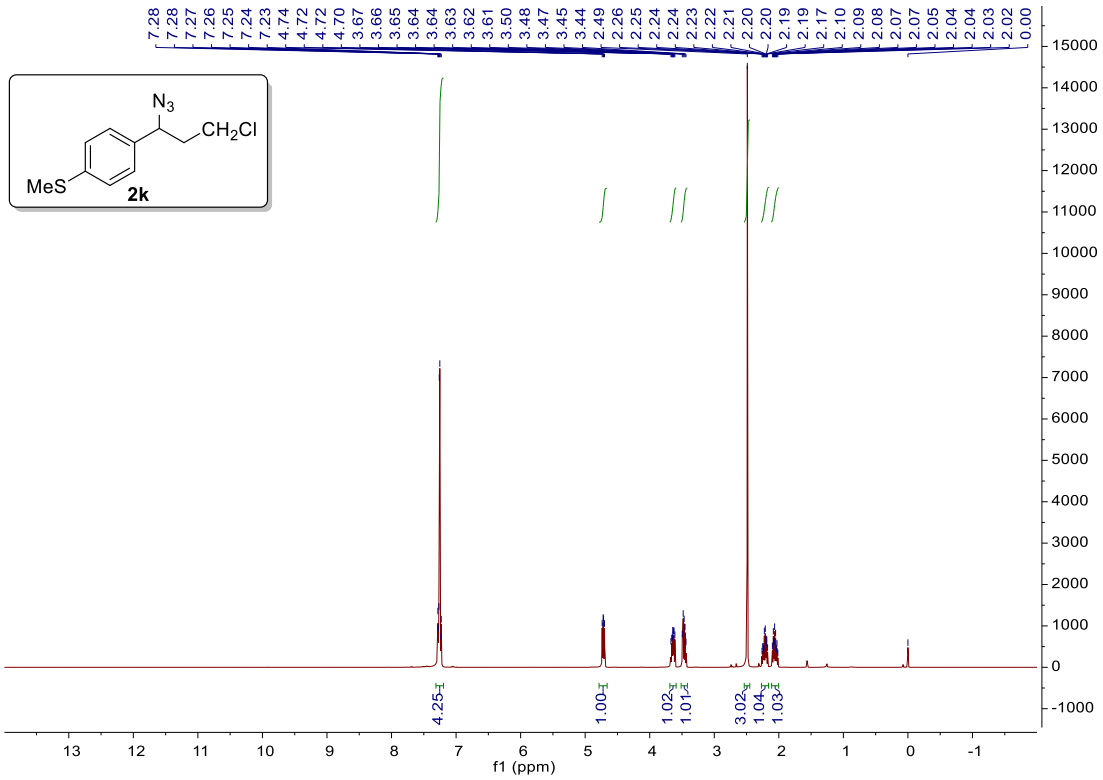
^{13}C NMR Spectrum of **2i** ($CDCl_3$, 101 MHz)



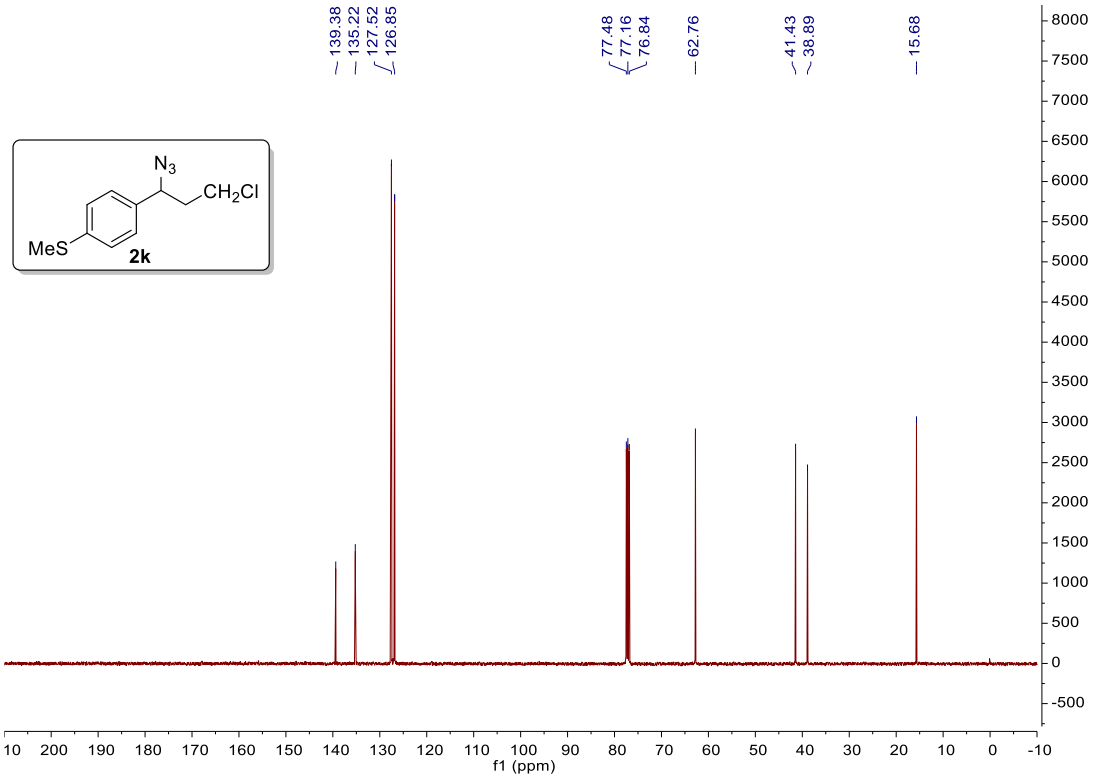
^{1}H NMR Spectrum of **2j** ($CDCl_3$, 400 MHz



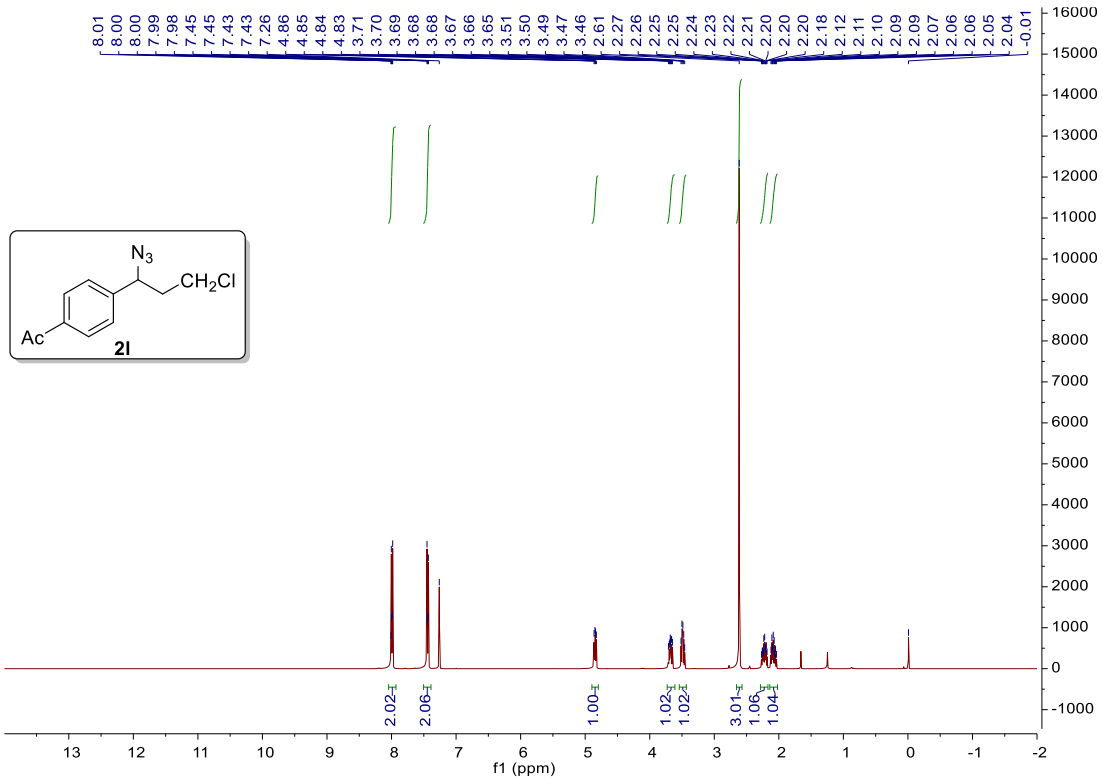
^{13}C NMR Spectrum of **2j** ($CDCl_3$, 101 MHz)



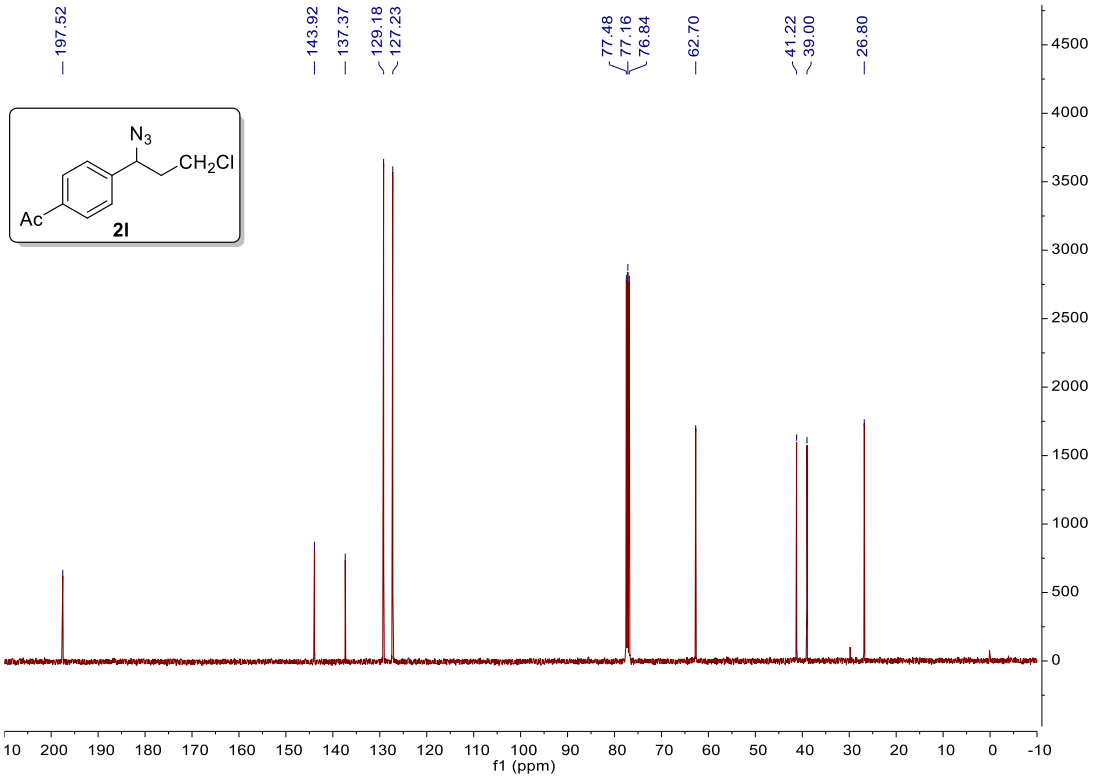
^{1}H NMR Spectrum of **2k** ($CDCl_3$, 400 MHz)



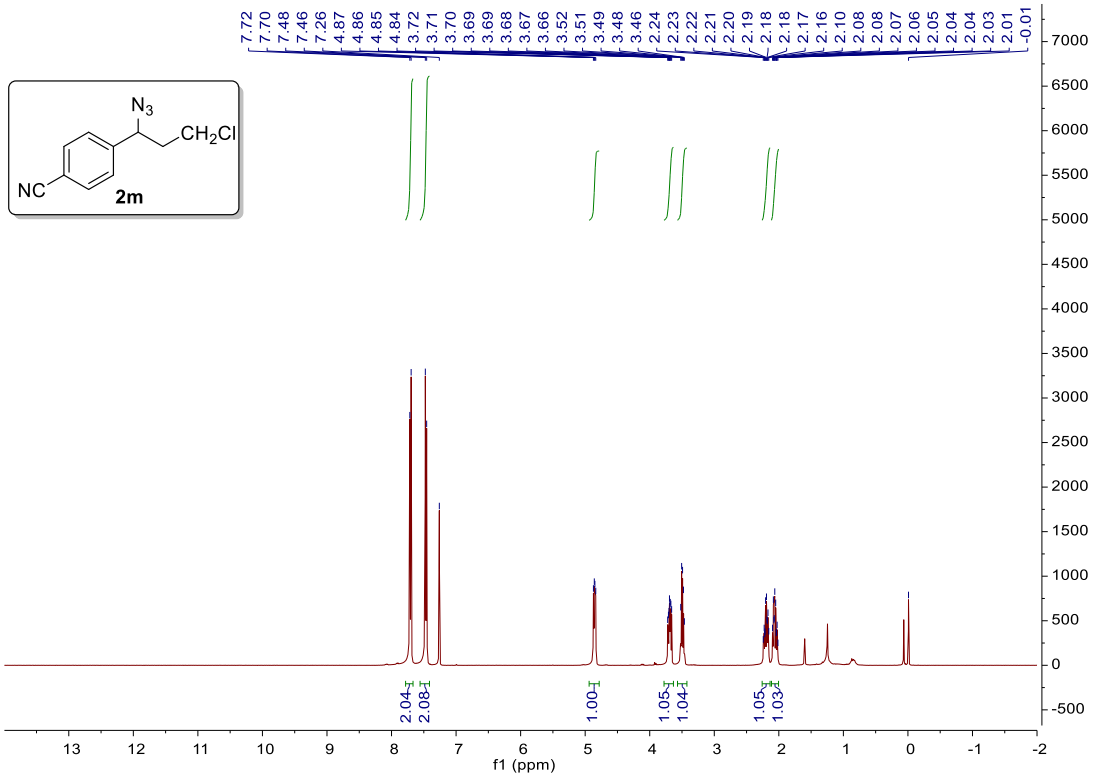
^{13}C NMR Spectrum of **2k** ($CDCl_3$, 101 MHz)



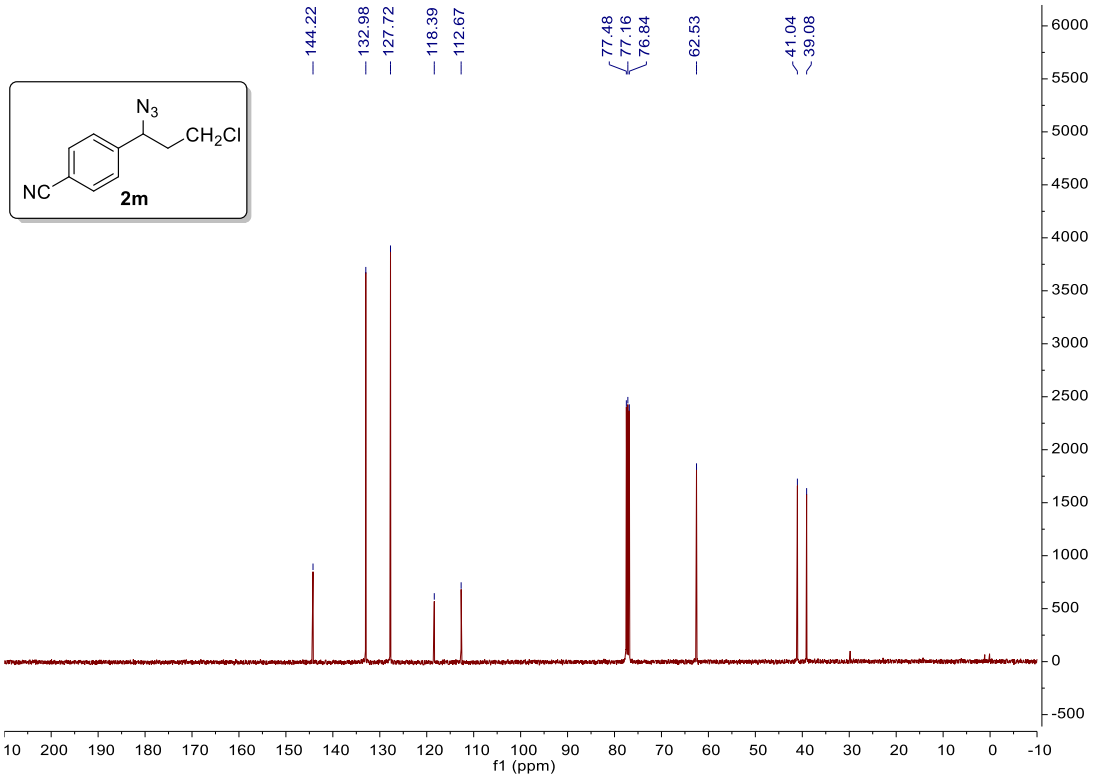
^{1}H NMR Spectrum of **2l** ($CDCl_3$, 400 MHz)



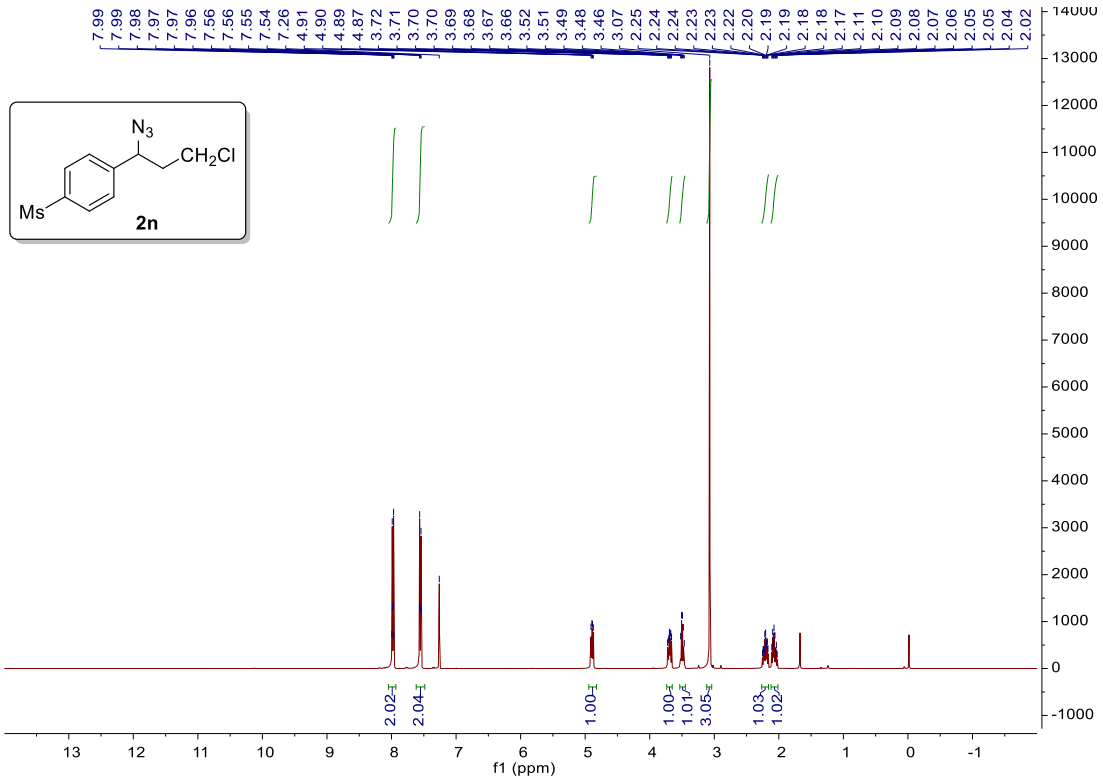
^{13}C NMR Spectrum of **2l** ($CDCl_3$, 101 MHz)



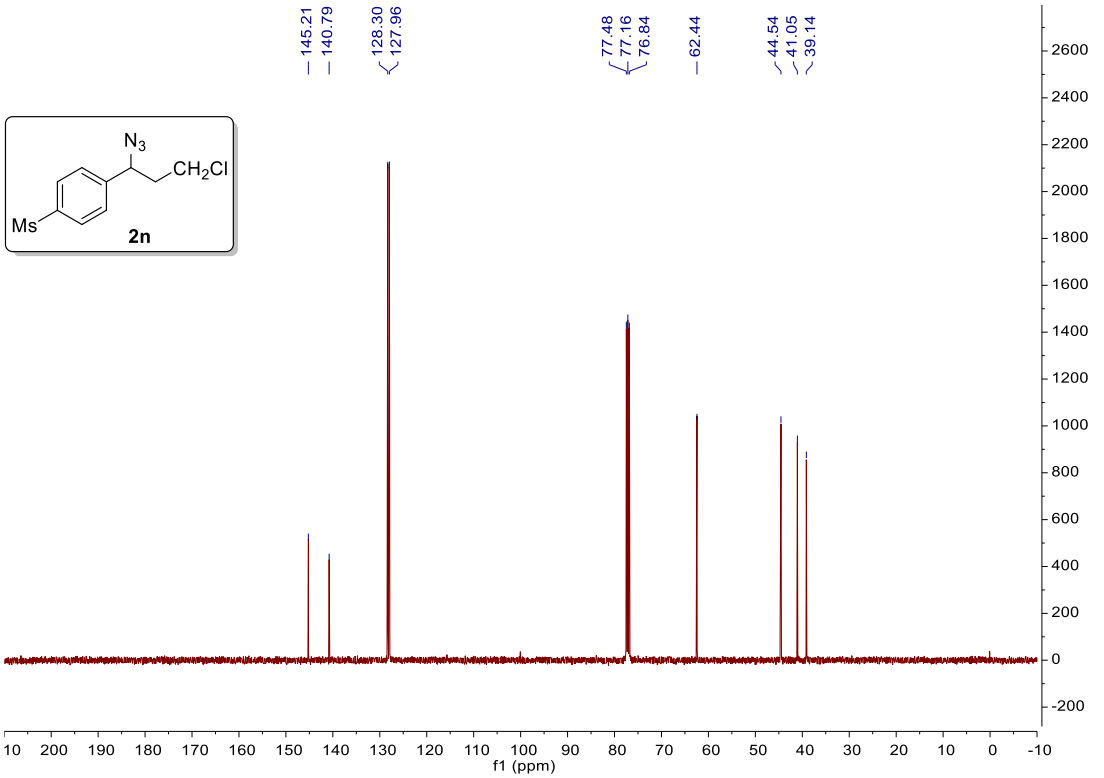
^{1}H NMR Spectrum of **2m** ($CDCl_3$, 400 MHz)



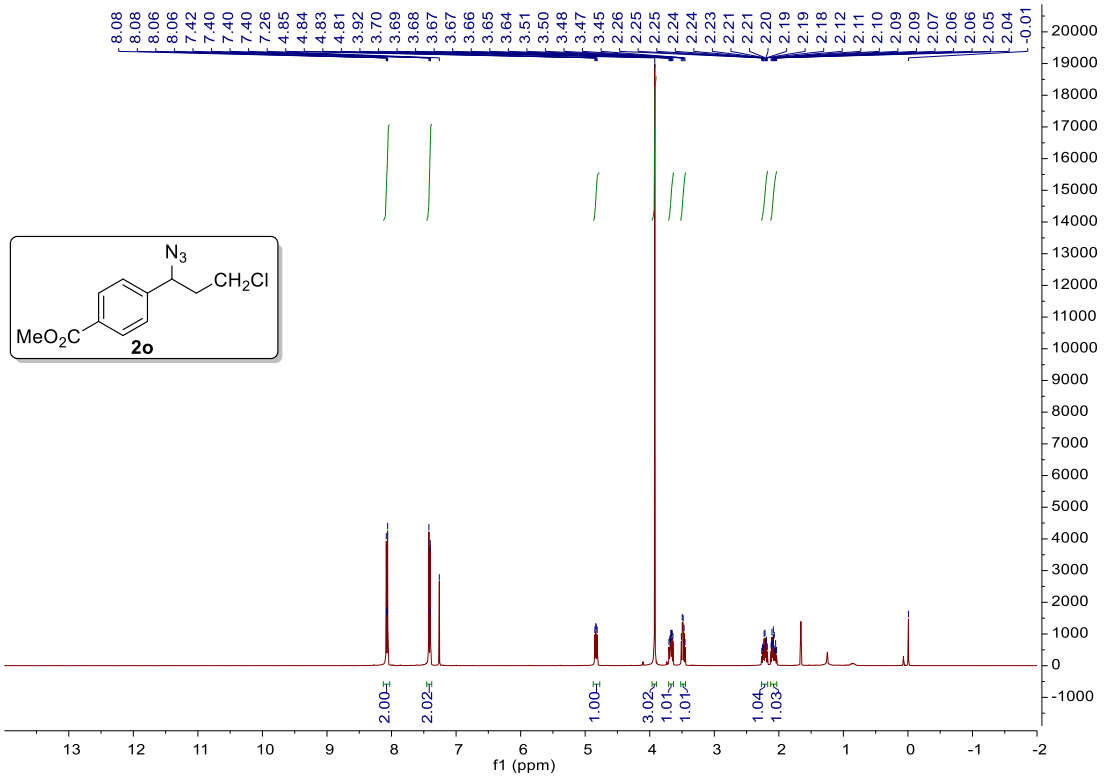
^{13}C NMR Spectrum of **2m** ($CDCl_3$, 101 MHz)



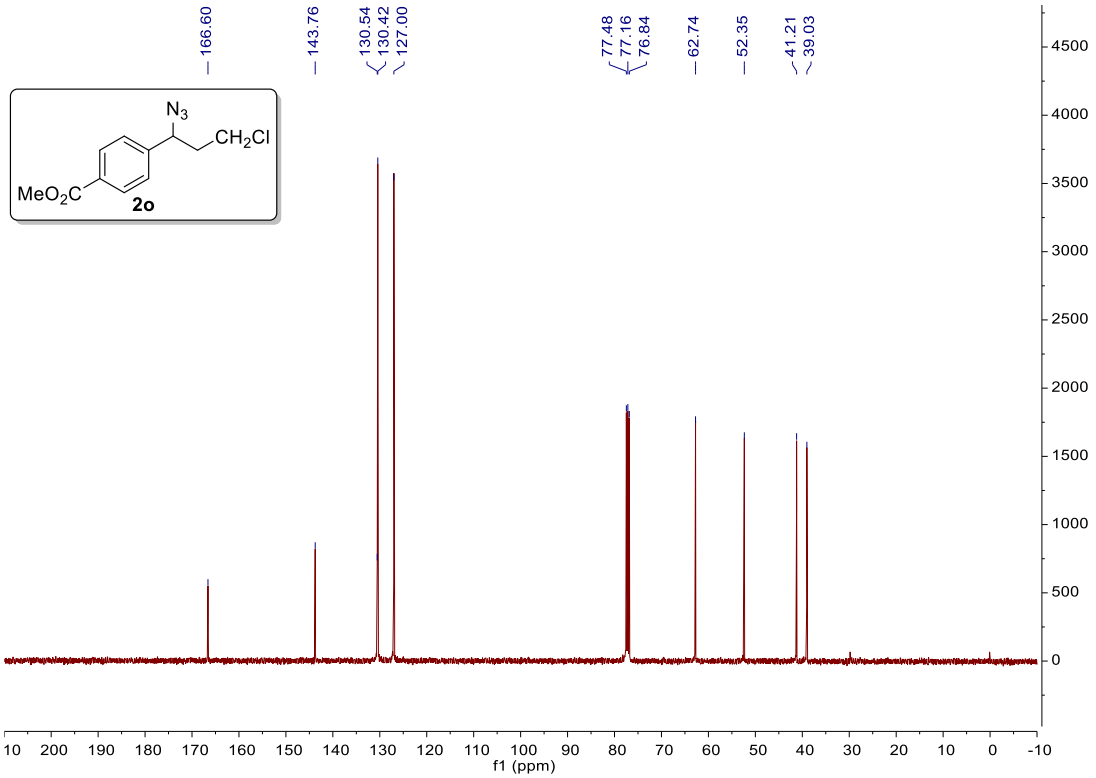
^{1}H NMR Spectrum of **2n** ($CDCl_3$, 400 MHz)



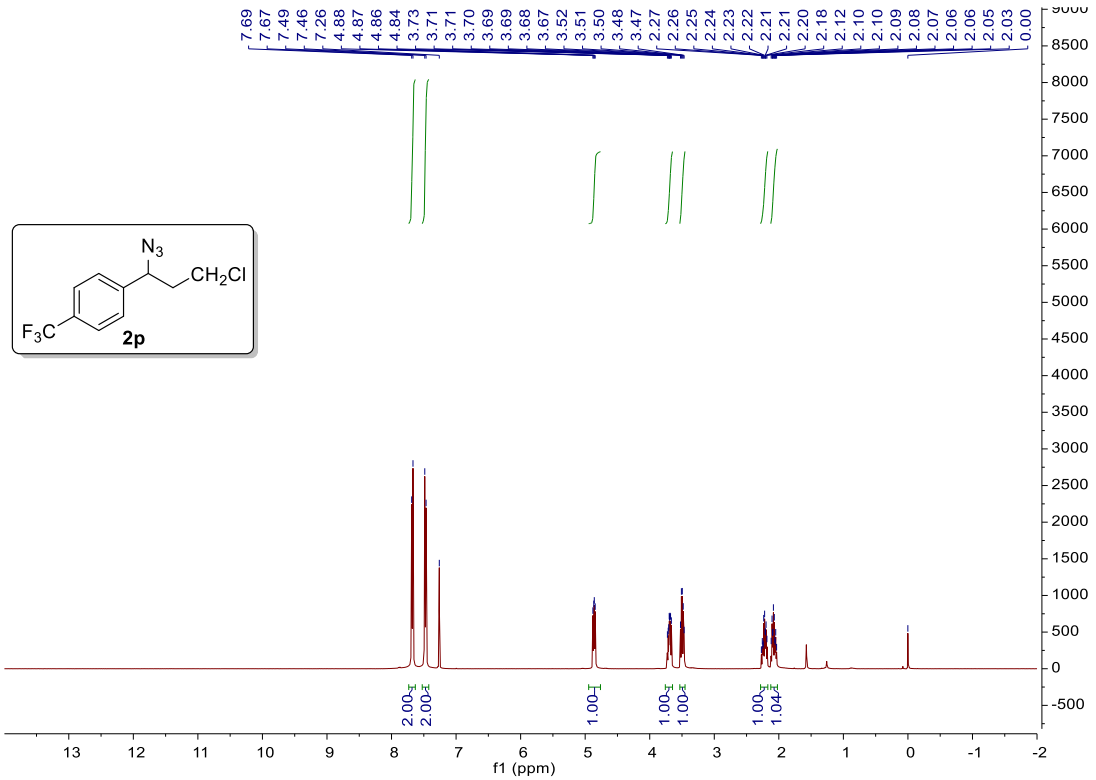
^{13}C NMR Spectrum of **2n** ($CDCl_3$, 101 MHz)



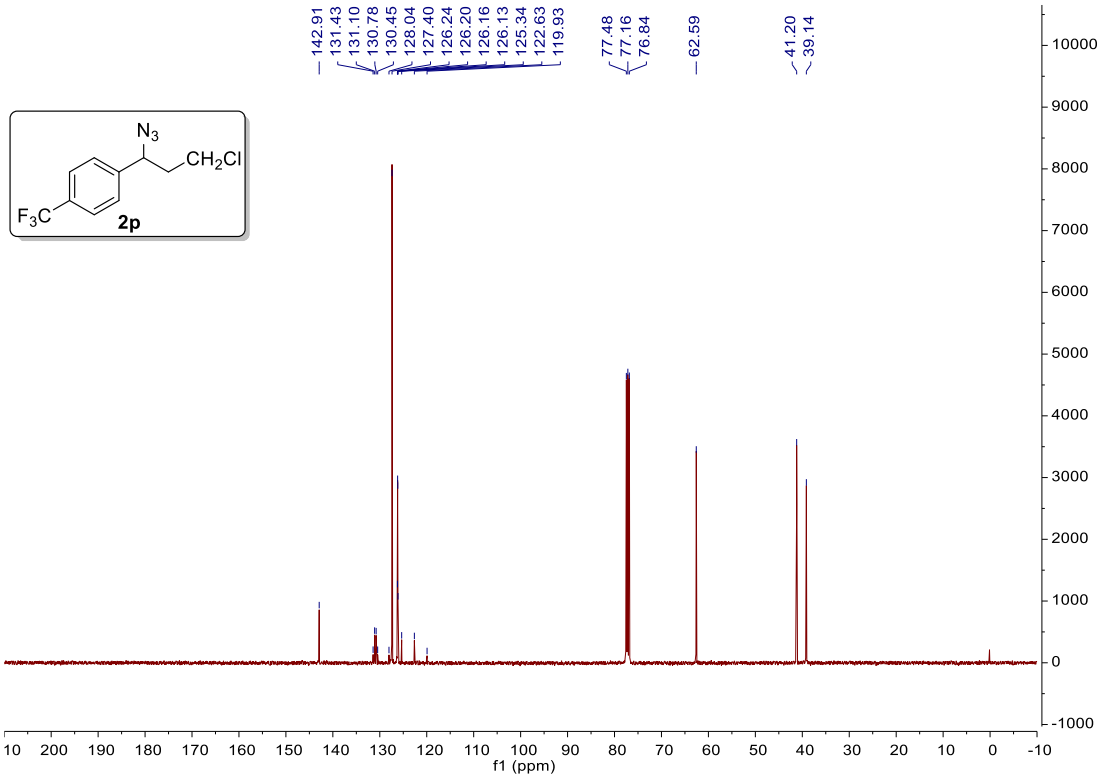
^{1}H NMR Spectrum of **2o** ($CDCl_3$, 400 MHz)



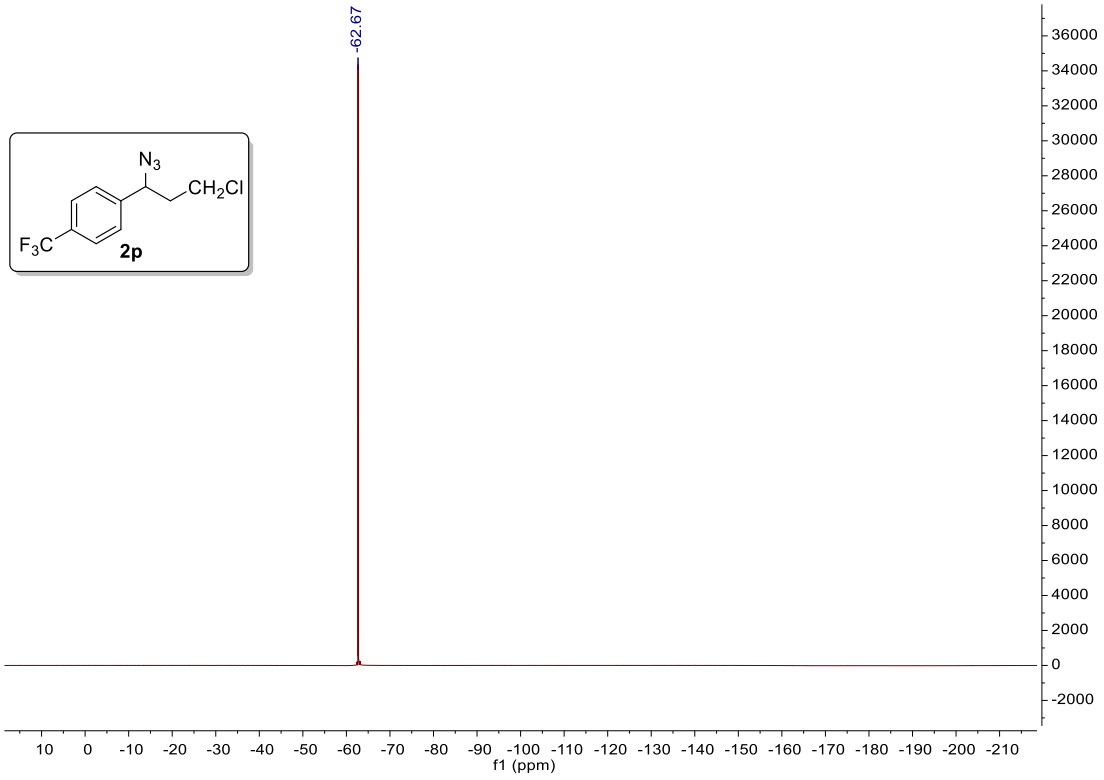
^{13}C NMR Spectrum of **2o** ($CDCl_3$, 101 MHz)



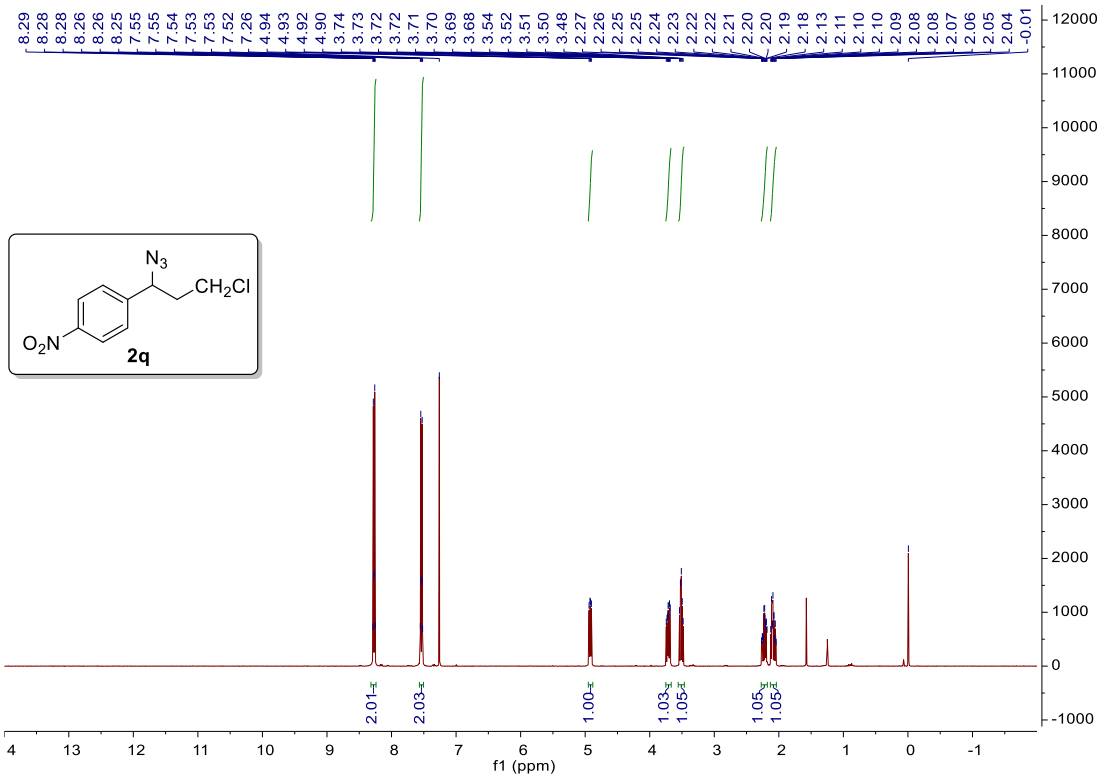
^{1}H NMR Spectrum of **2p** ($CDCl_3$, 400 MHz)



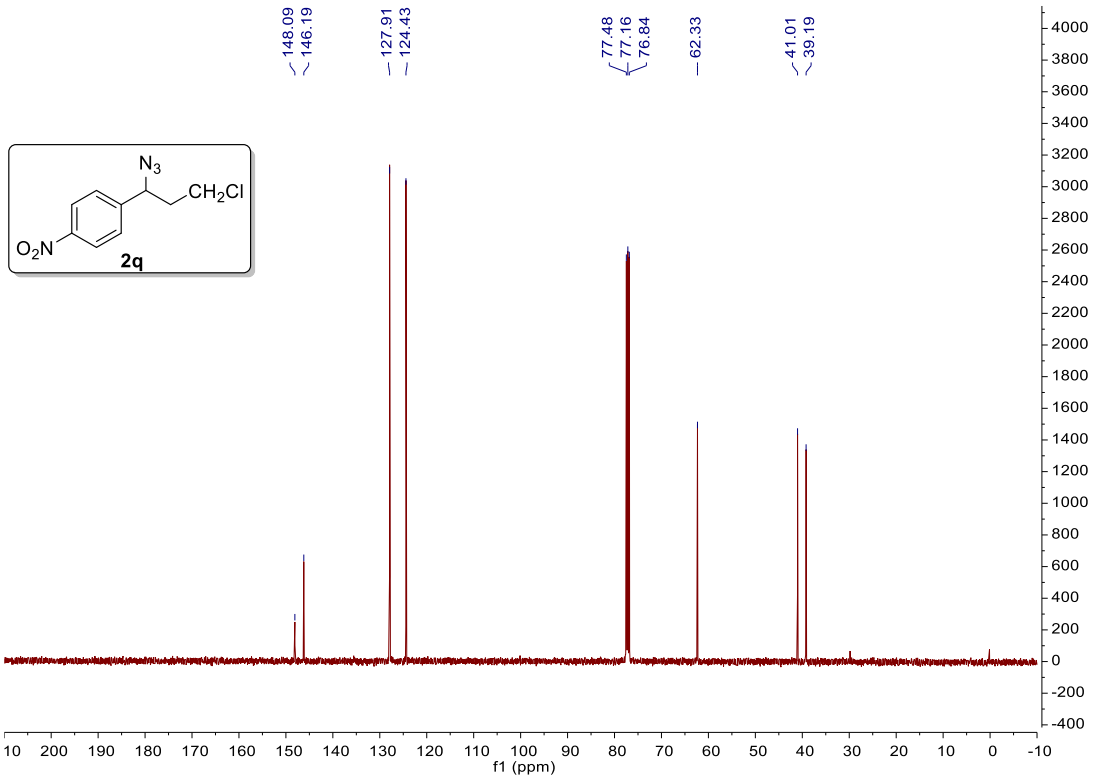
^{13}C NMR Spectrum of **2p** ($CDCl_3$, 101 MHz)



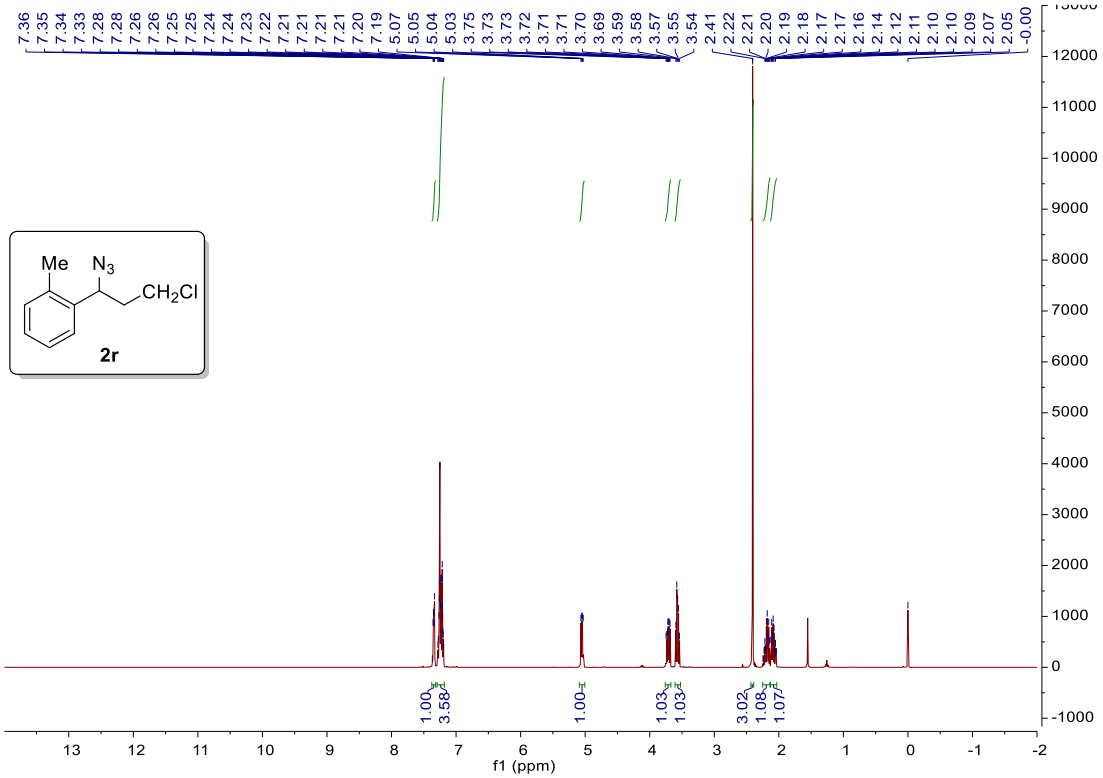
^{19}F NMR Spectrum of **2p** ($CDCl_3$, 376 MHz)



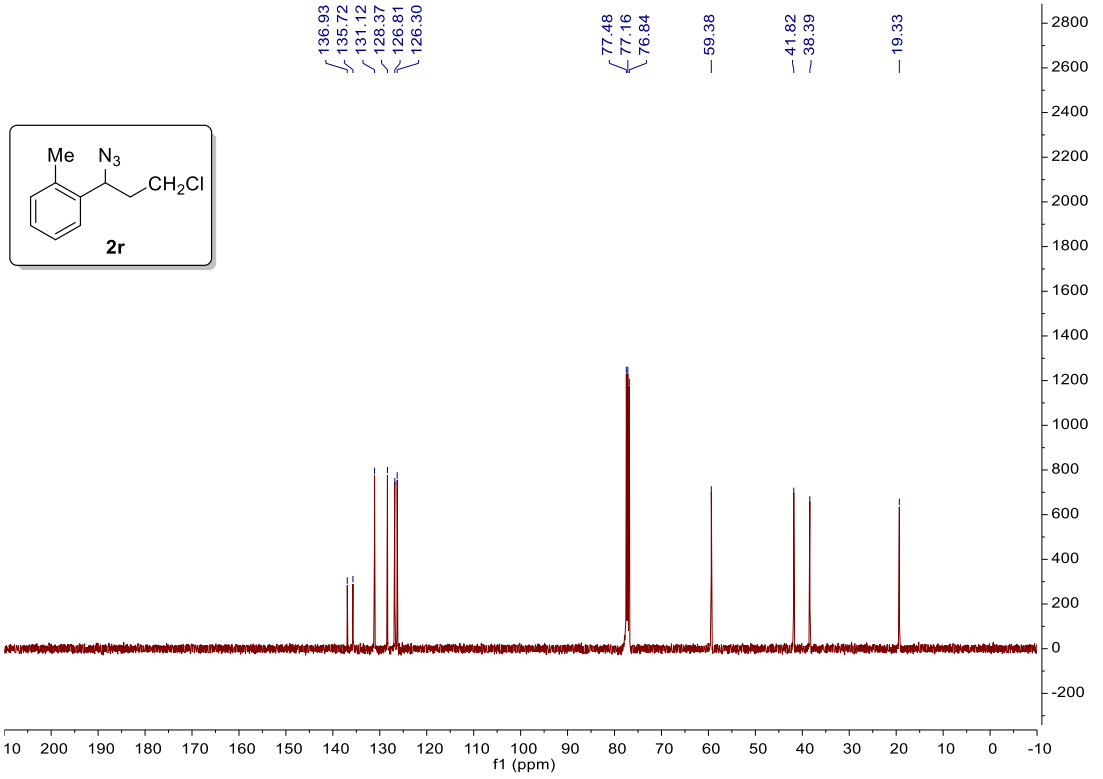
^{1}H NMR Spectrum of **2q** ($CDCl_3$, 400 MHz)



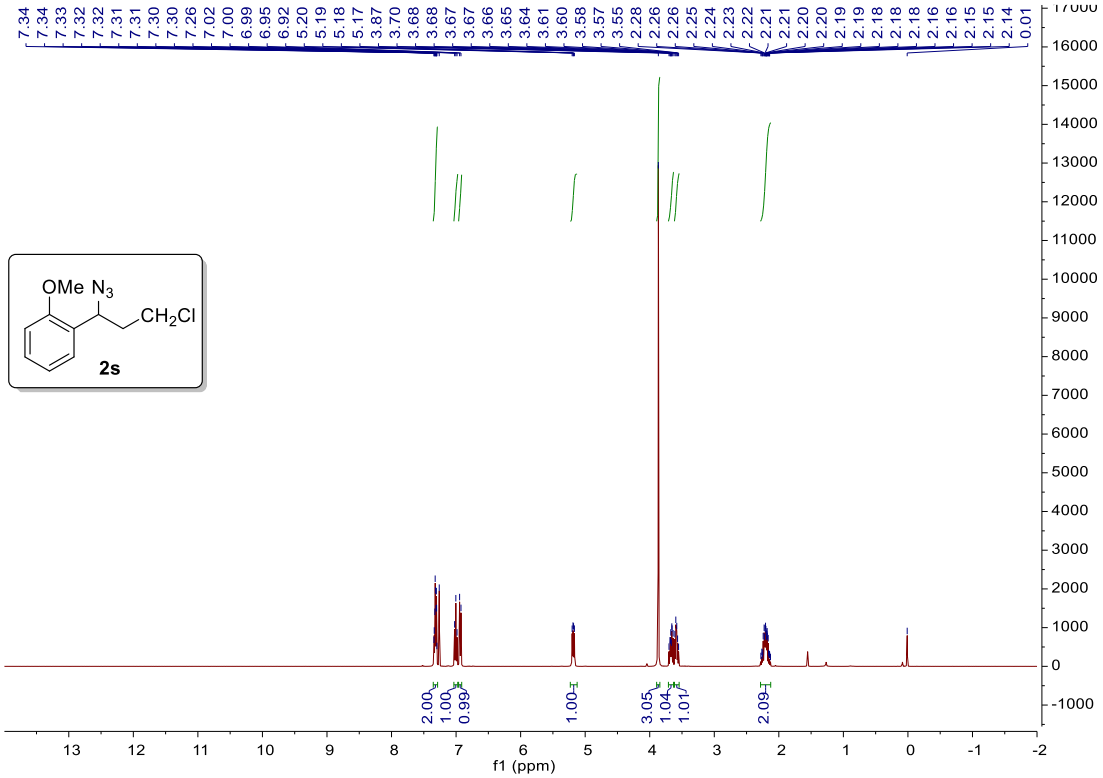
^{13}C NMR Spectrum of **2q** ($CDCl_3$, 101 MHz)



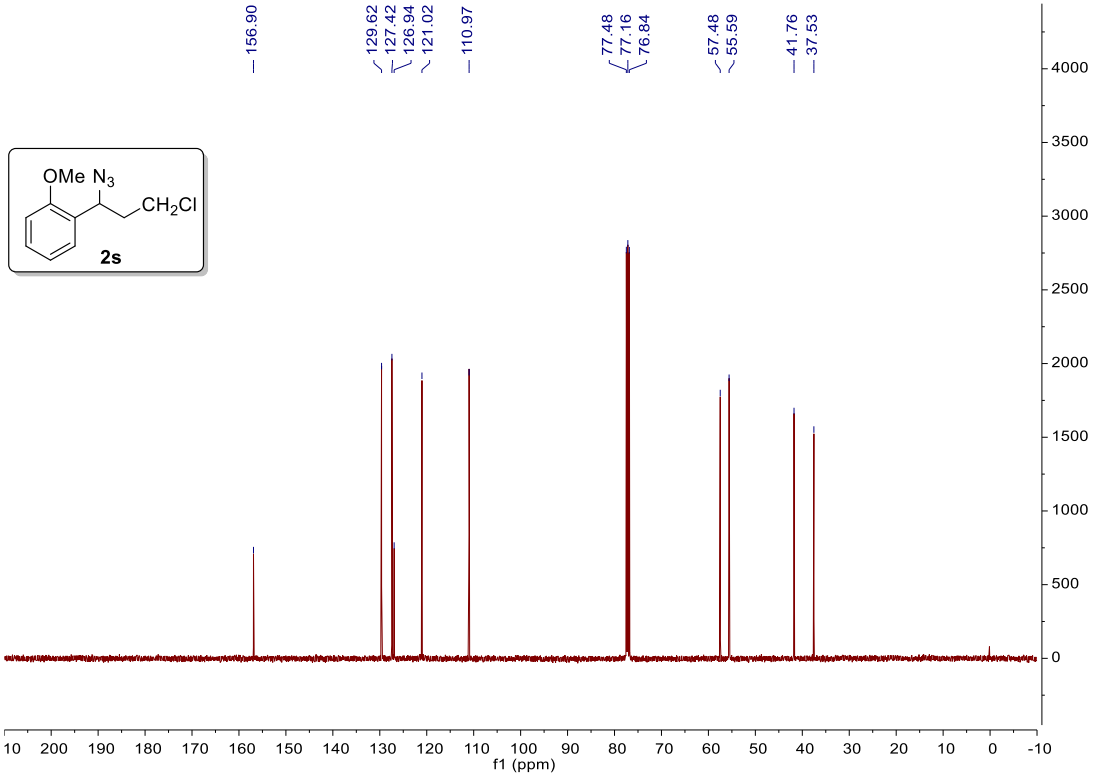
^{1}H NMR Spectrum of **2r** ($CDCl_3$, 400 MHz)



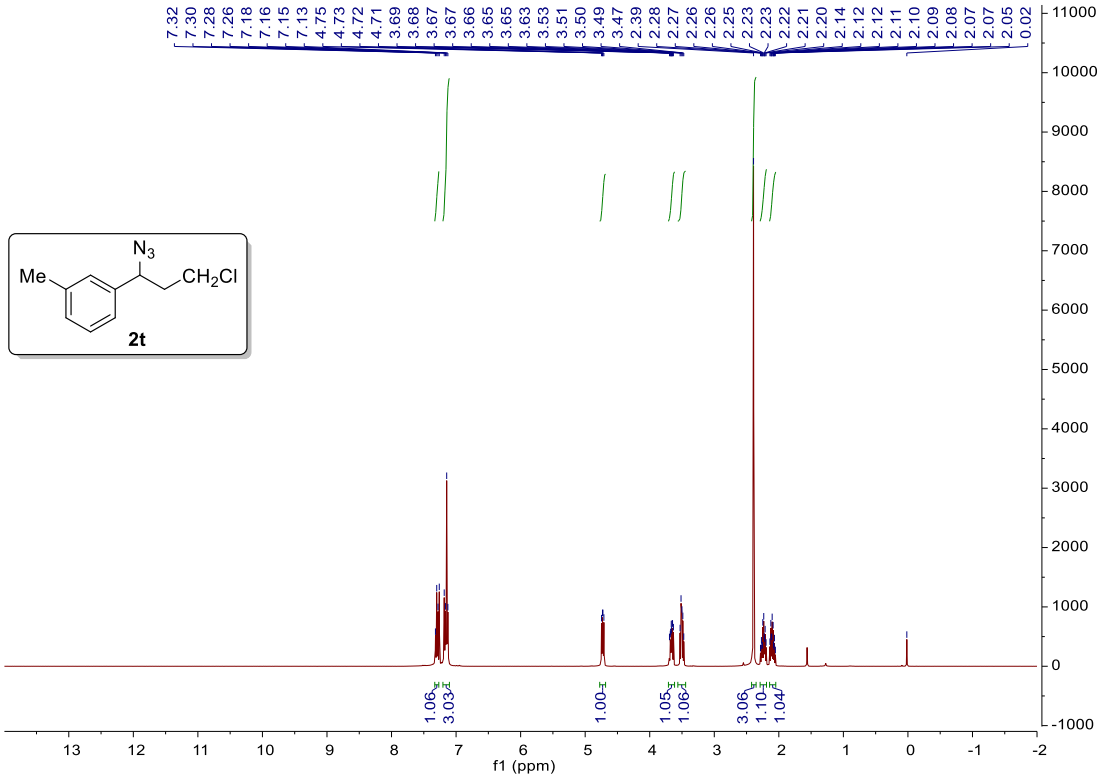
^{13}C NMR Spectrum of **2r** ($CDCl_3$, 101 MHz)



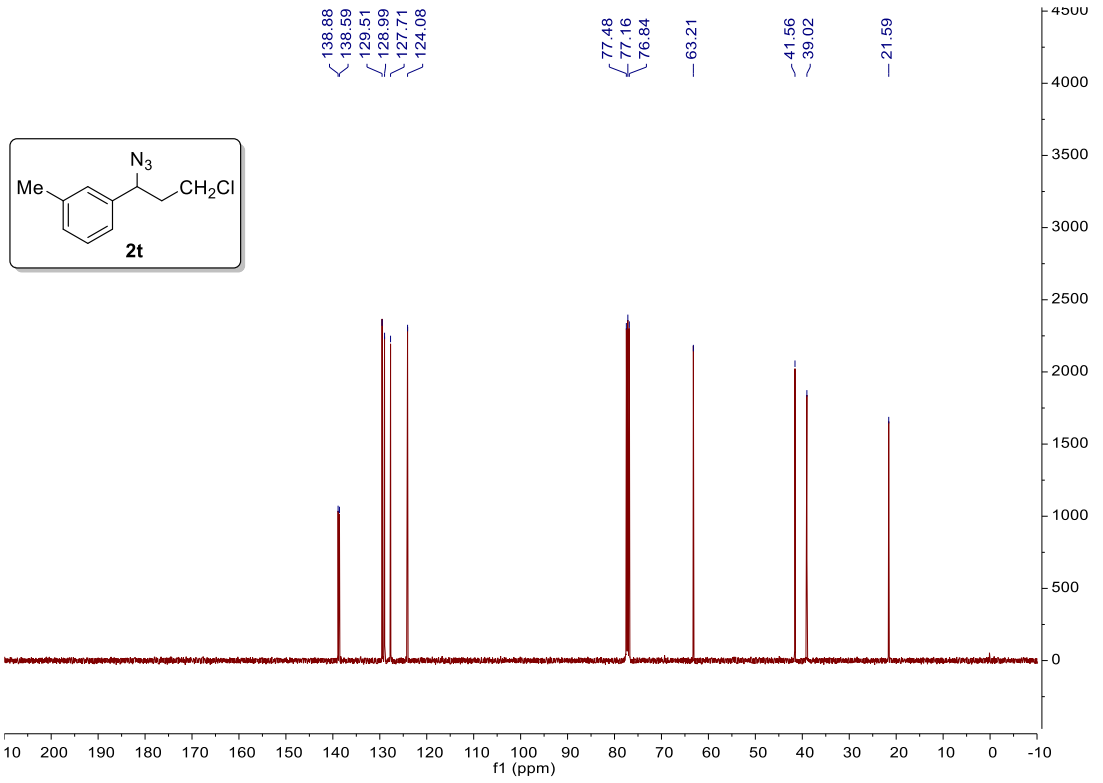
^{1}H NMR Spectrum of **2s** ($CDCl_3$, 400 MHz)



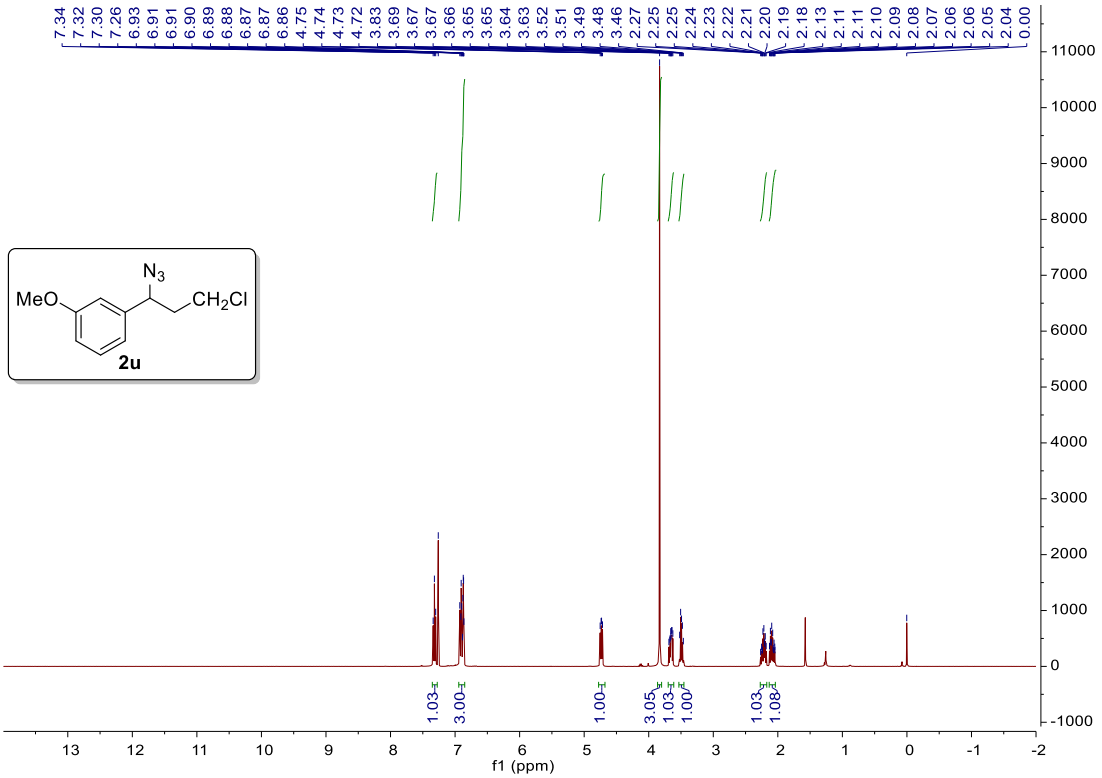
^{13}C NMR Spectrum of **2s** ($CDCl_3$, 101 MHz)



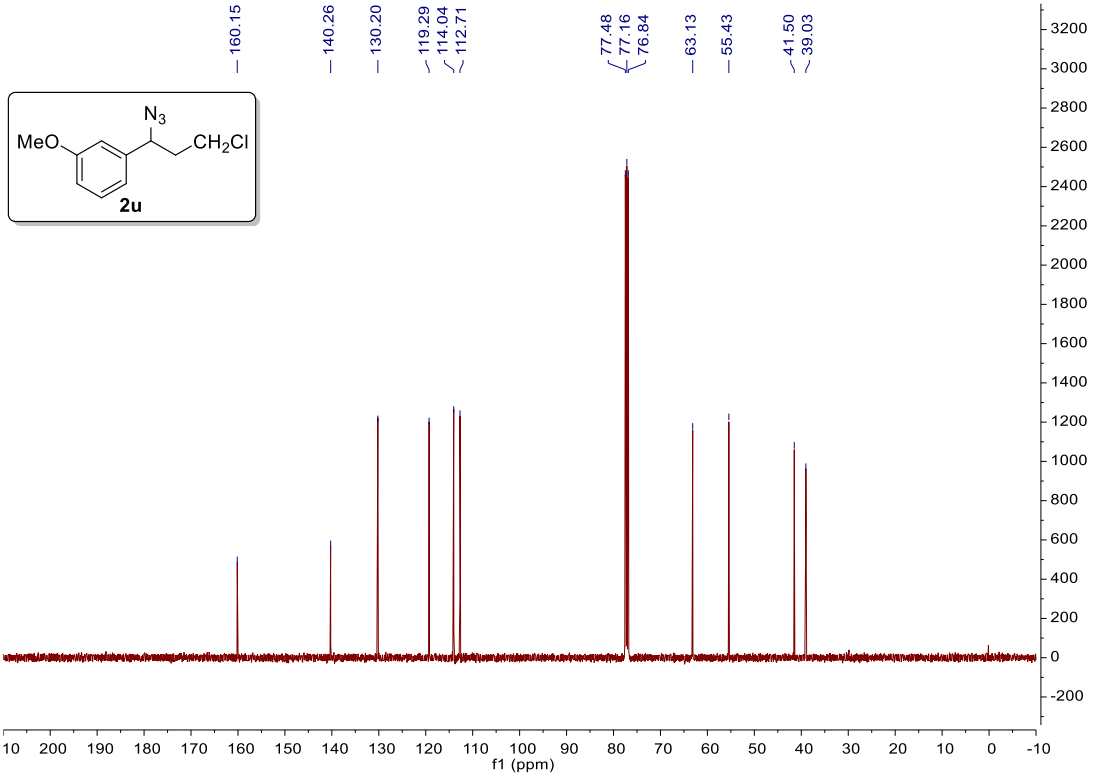
^{1}H NMR Spectrum of **2t** ($CDCl_3$, 400 MHz)



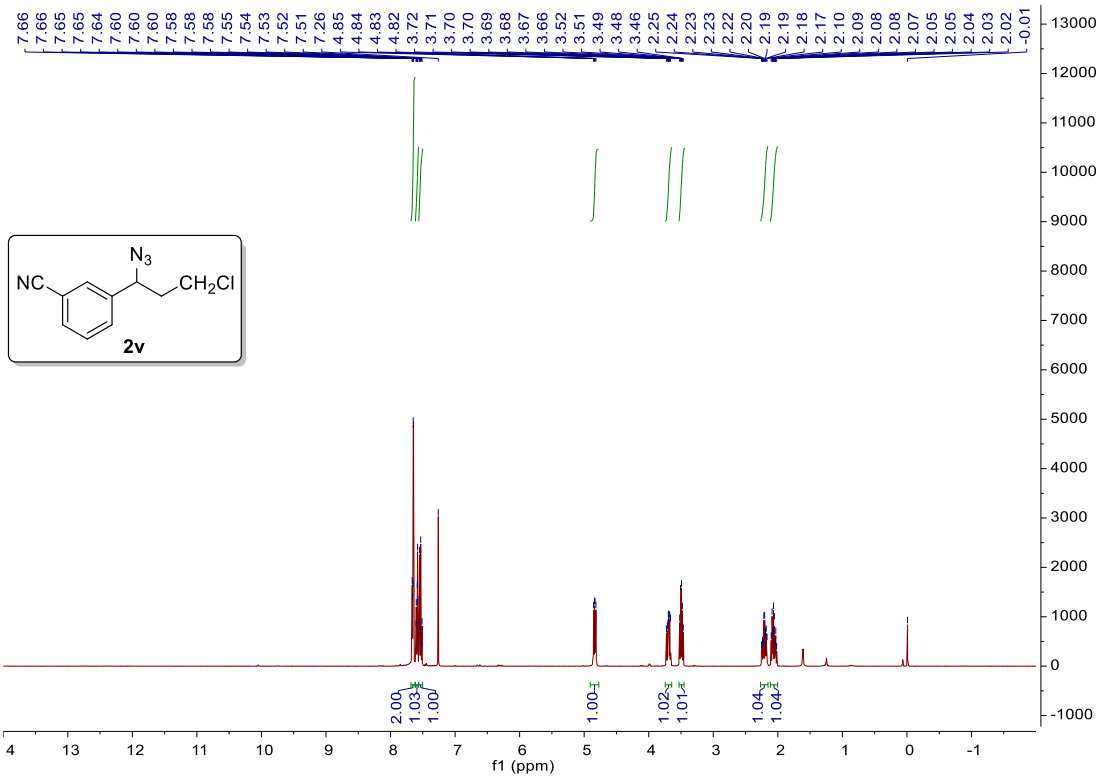
^{13}C NMR Spectrum of **2t** ($CDCl_3$, 101 MHz)



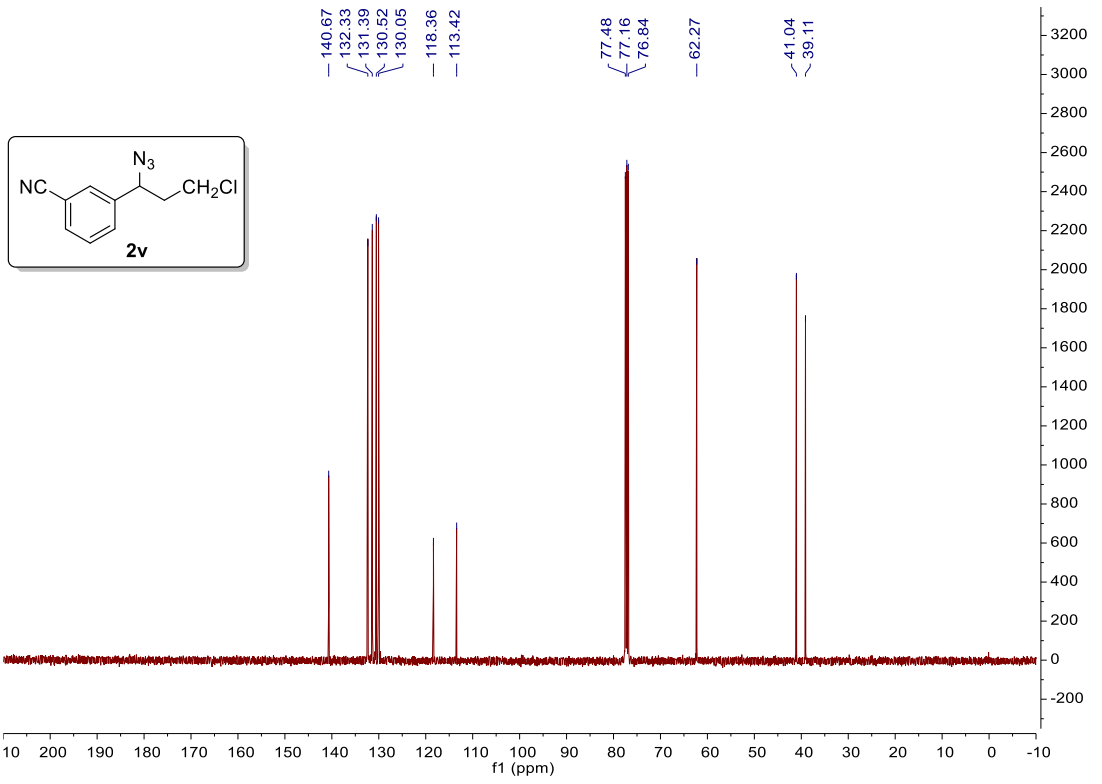
^{1}H NMR Spectrum of **2u** ($CDCl_3$, 400 MHz)



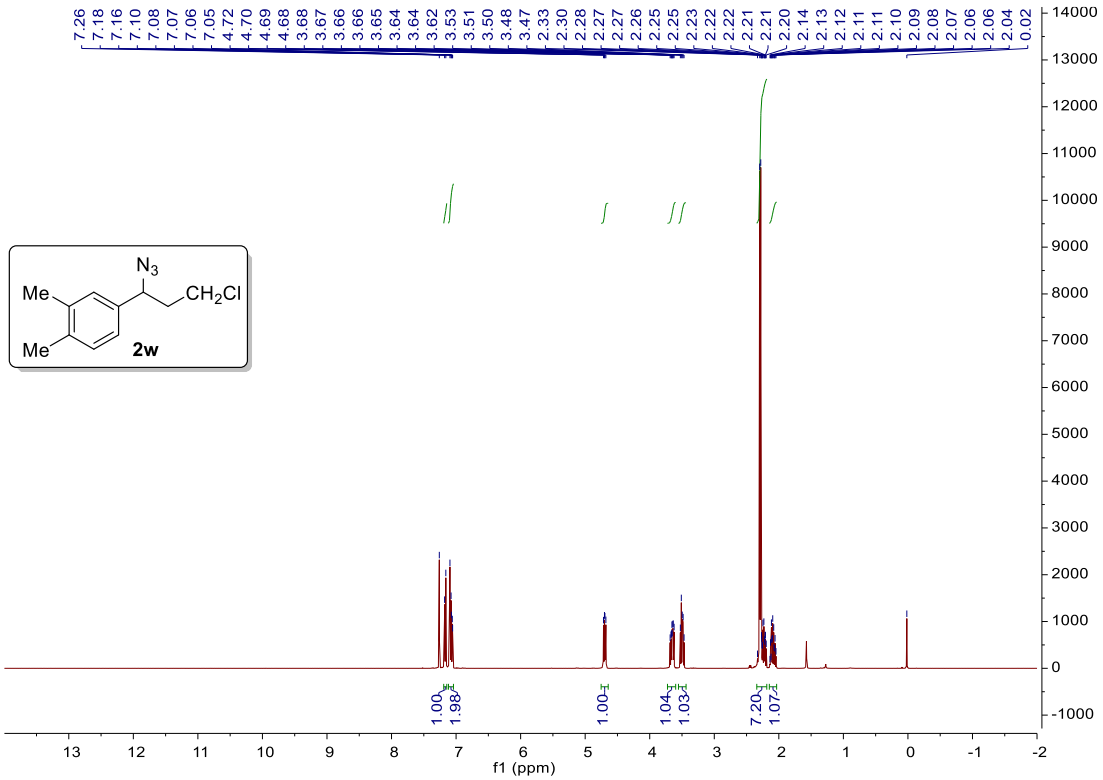
^{13}C NMR Spectrum of **2u** ($CDCl_3$, 101 MHz)



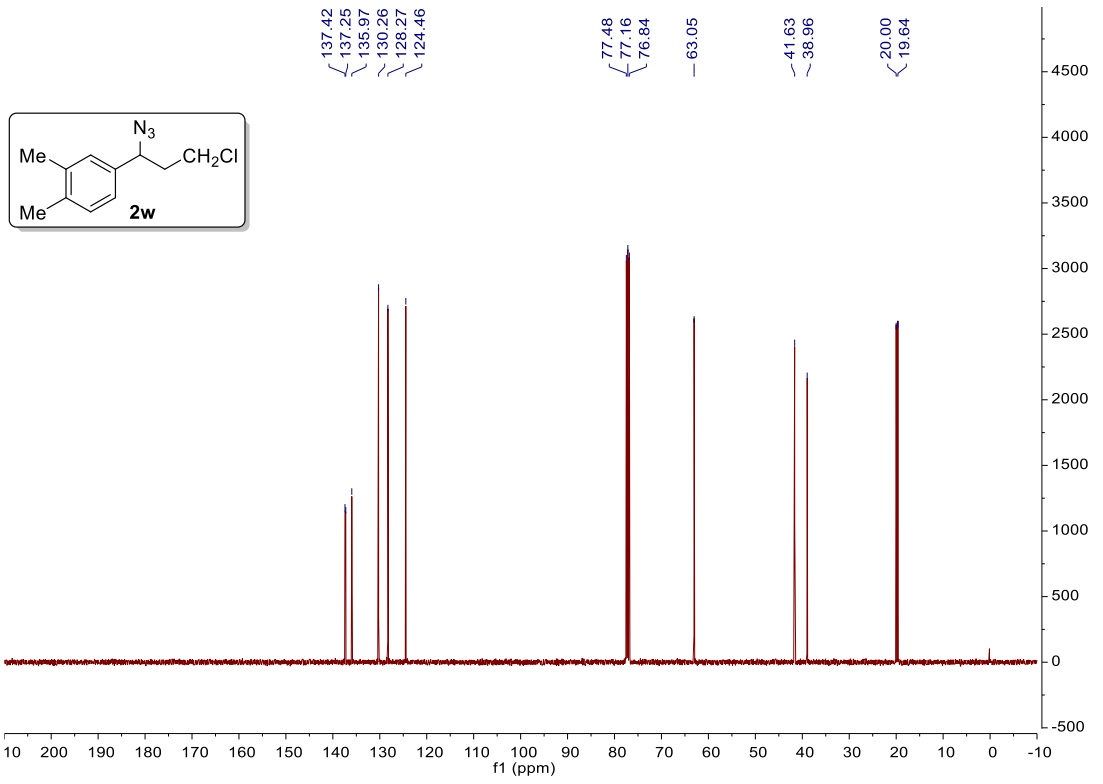
^{1}H NMR Spectrum of **2v** ($CDCl_3$, 400 MHz)



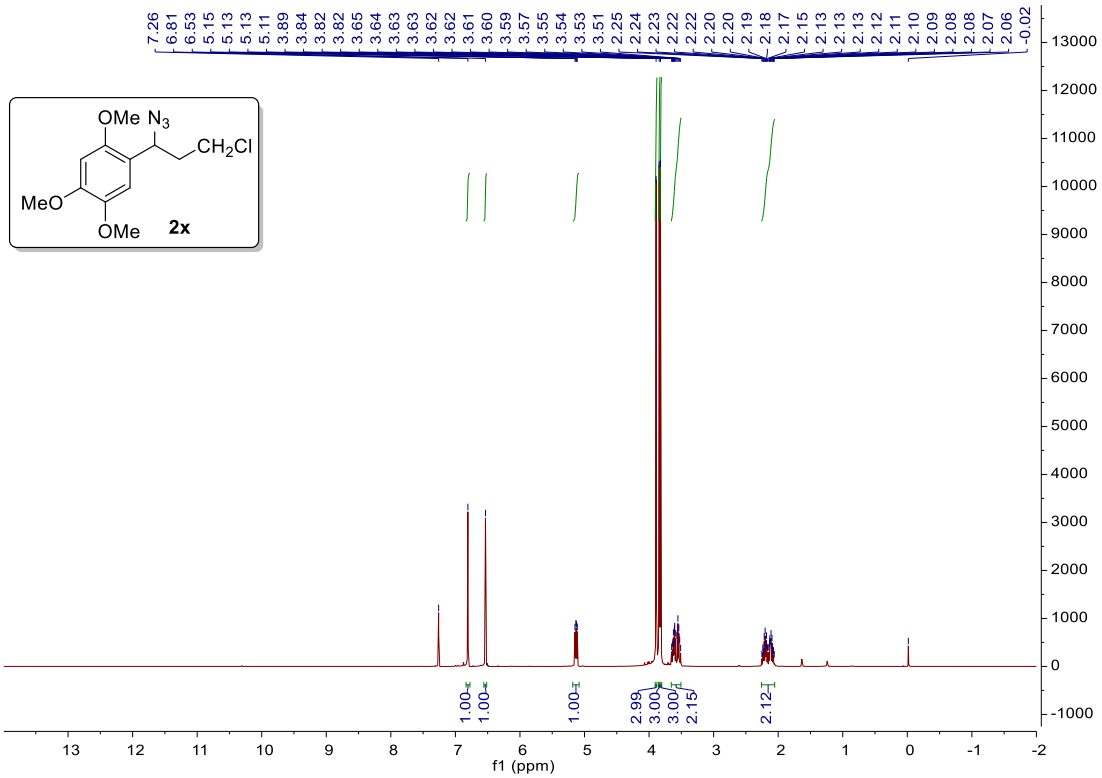
^{13}C NMR Spectrum of **2v** ($CDCl_3$, 101 MHz)



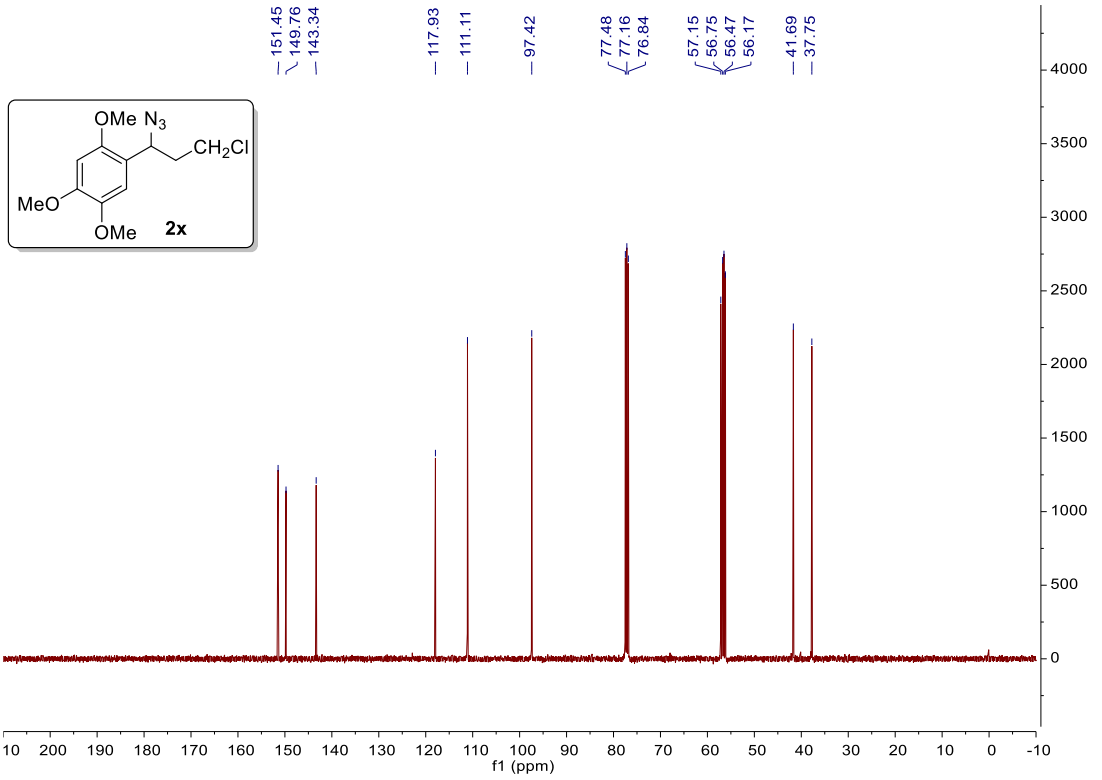
^{1}H NMR Spectrum of **2w** ($CDCl_3$, 400 MHz)



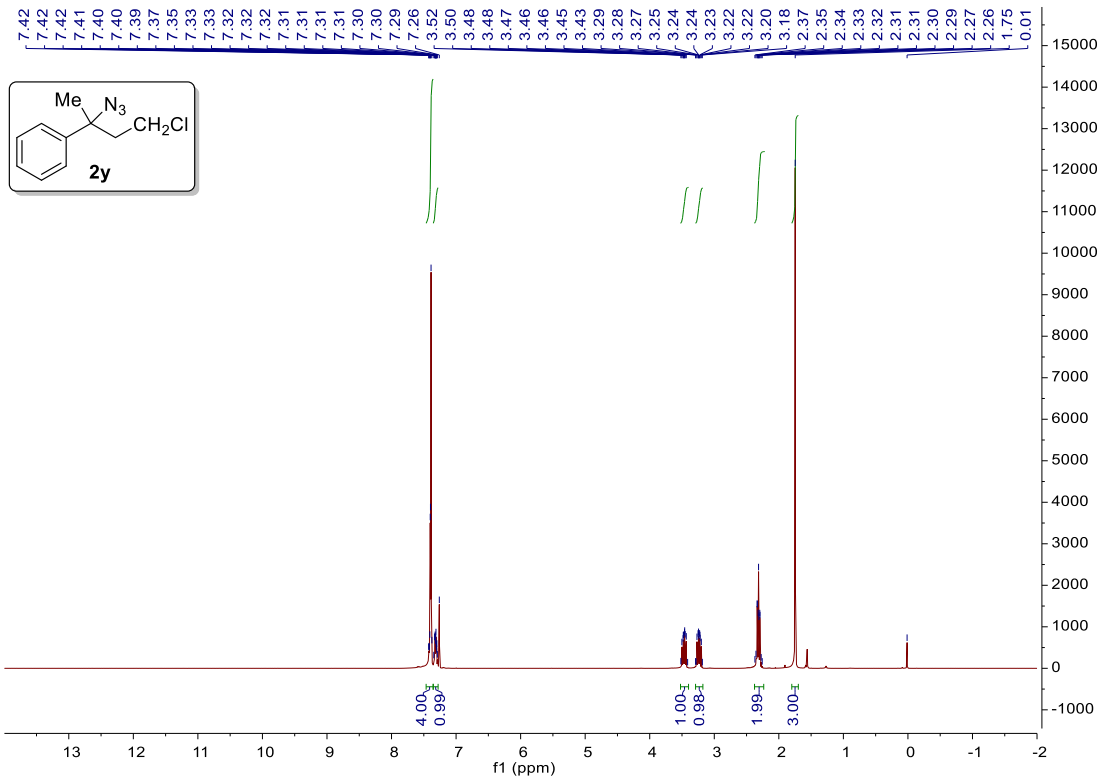
^{13}C NMR Spectrum of **2w** ($CDCl_3$, 101 MHz)



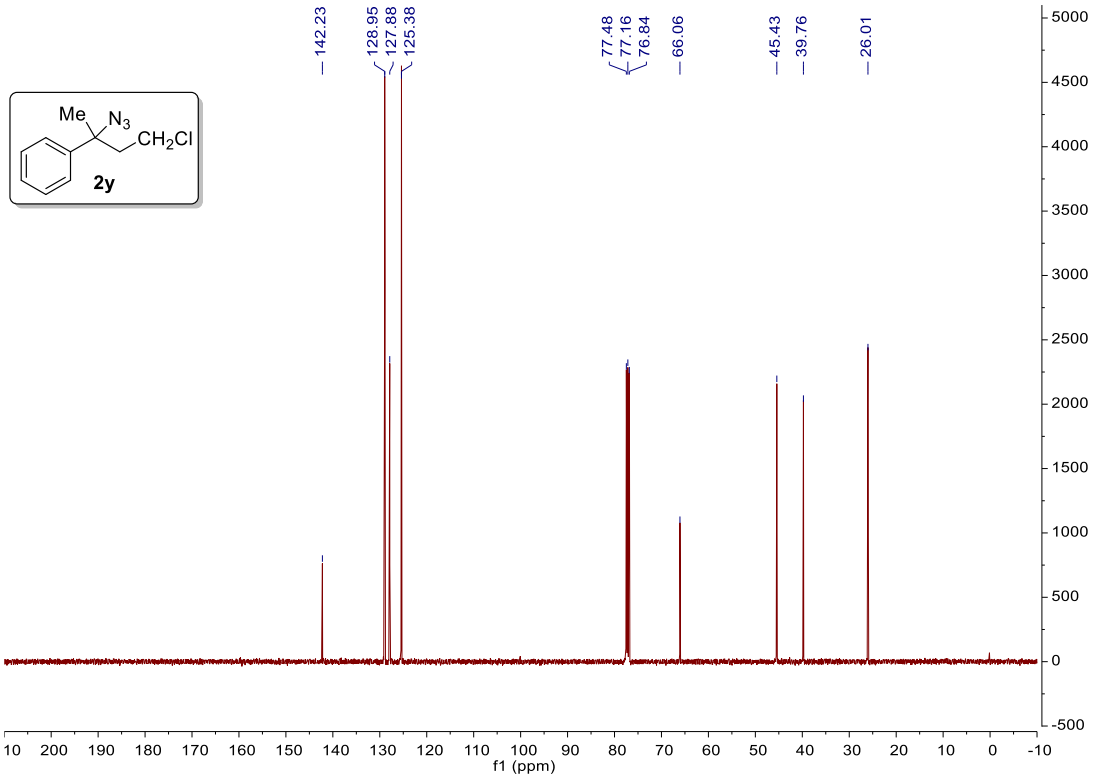
^{1}H NMR Spectrum of **2x** ($CDCl_3$, 400 MHz)



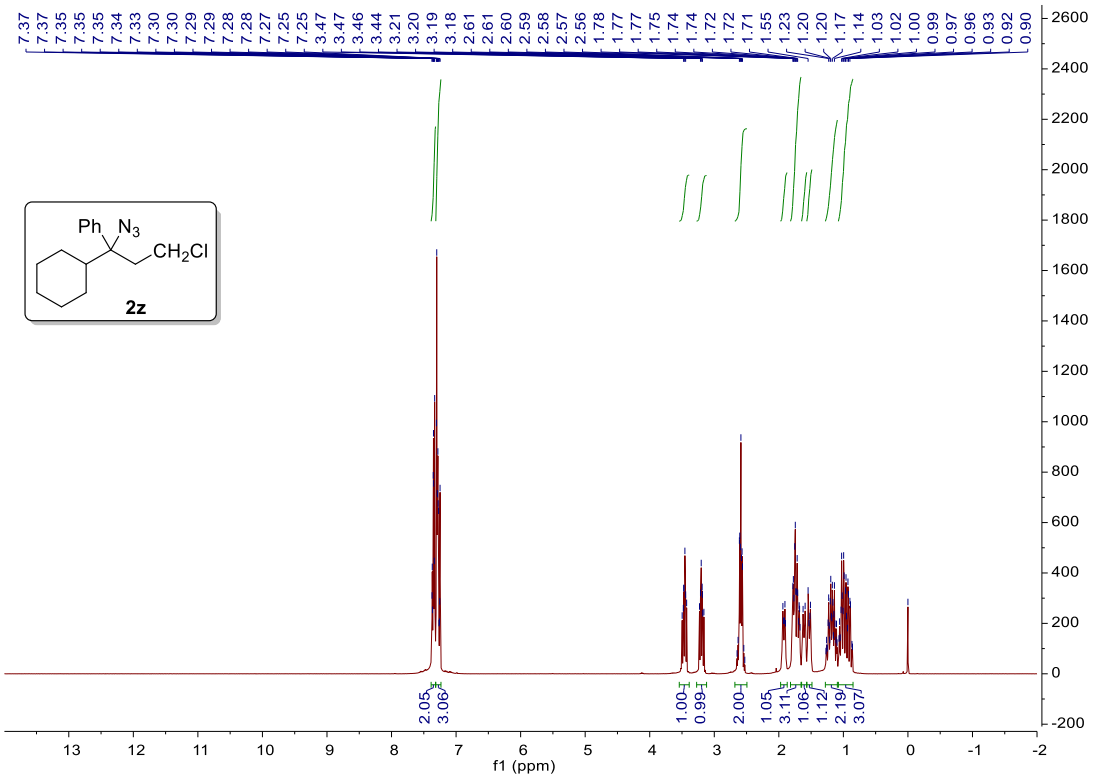
^{13}C NMR Spectrum of **2x** ($CDCl_3$, 101 MHz)



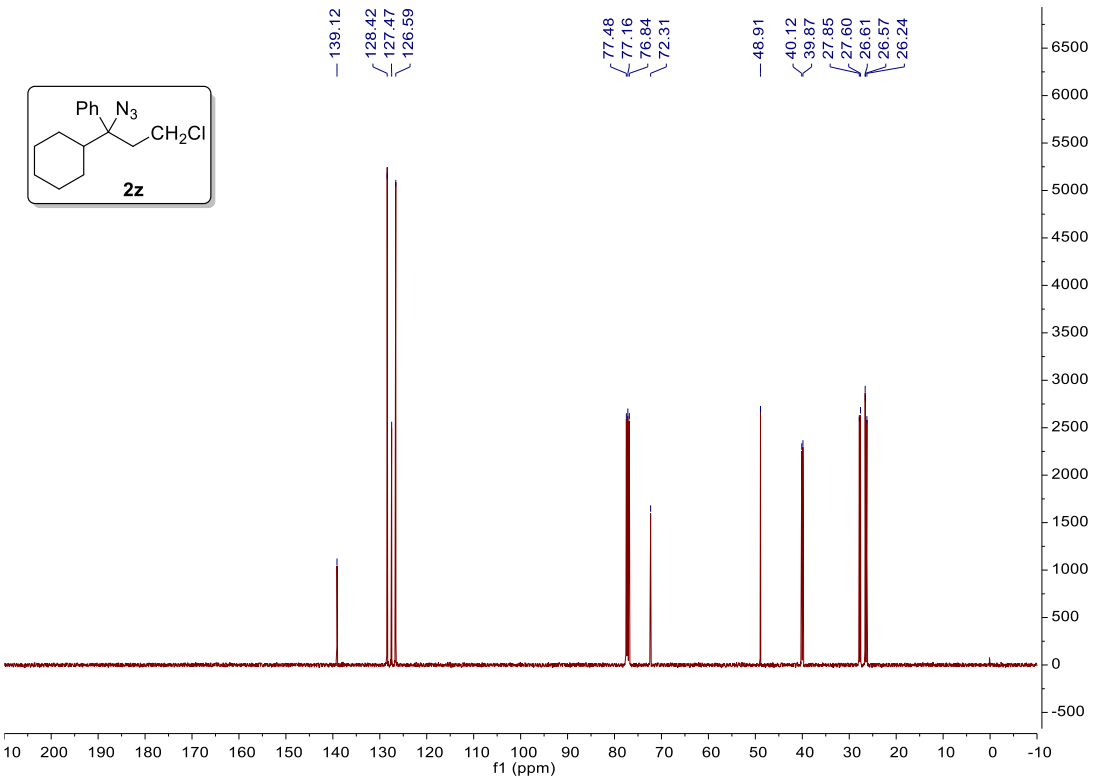
^{1}H NMR Spectrum of **2y** ($CDCl_3$, 400 MHz)



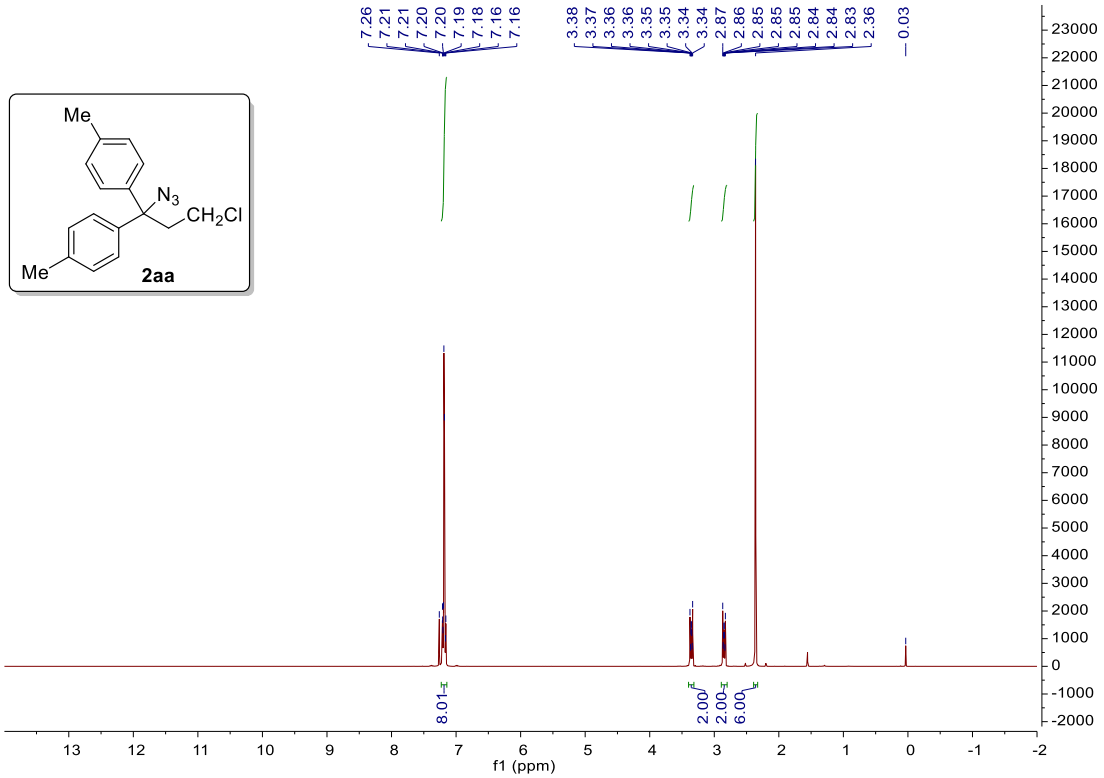
^{13}C NMR Spectrum of **2y** ($CDCl_3$, 101 MHz)



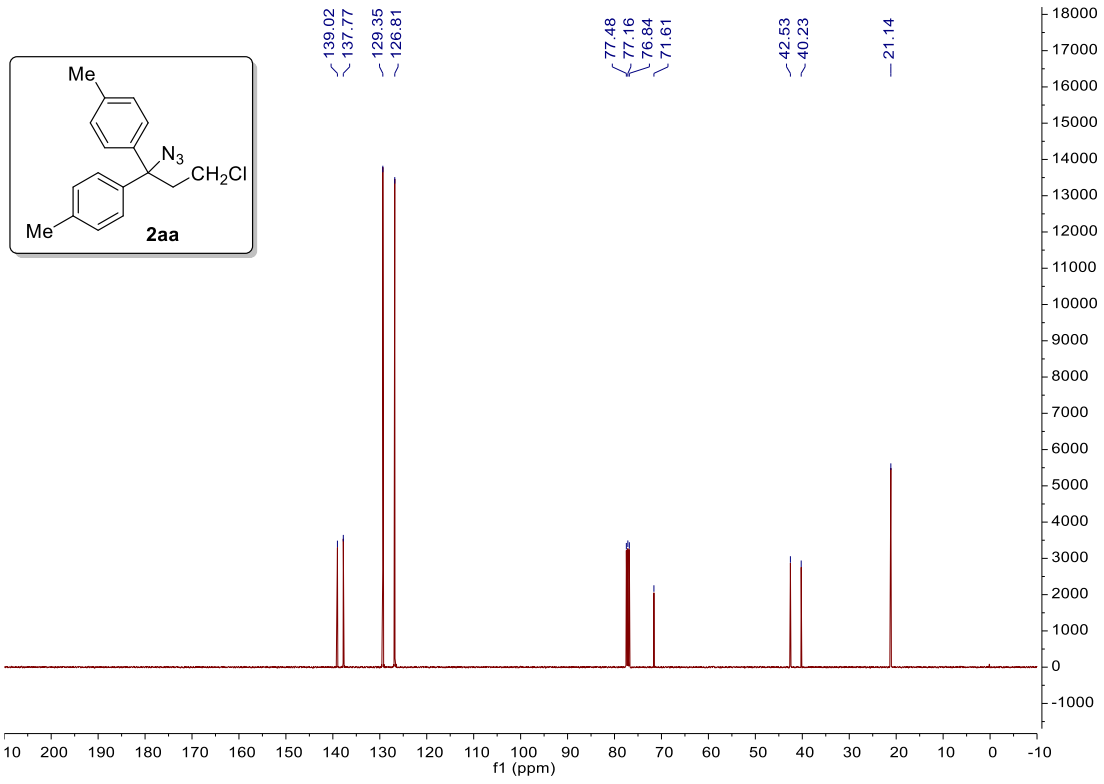
^{1}H NMR Spectrum of **2z** ($CDCl_3$, 400 MHz)



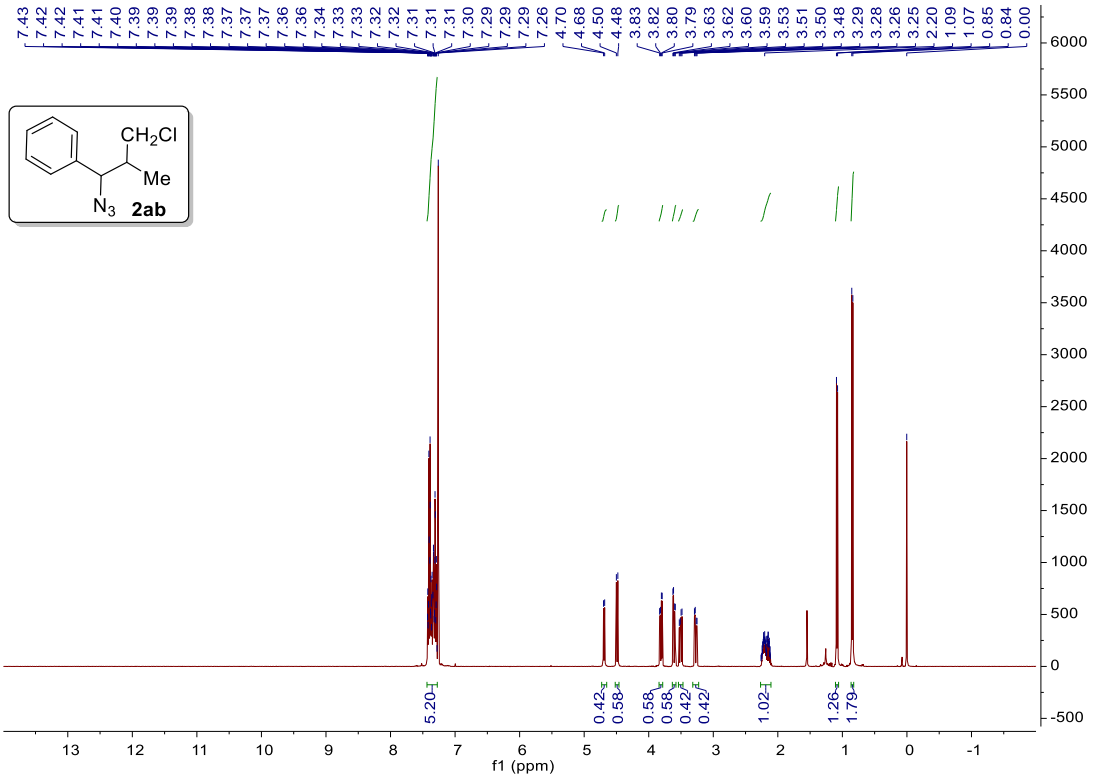
^{13}C NMR Spectrum of **2z** ($CDCl_3$, 10111111 MHz)



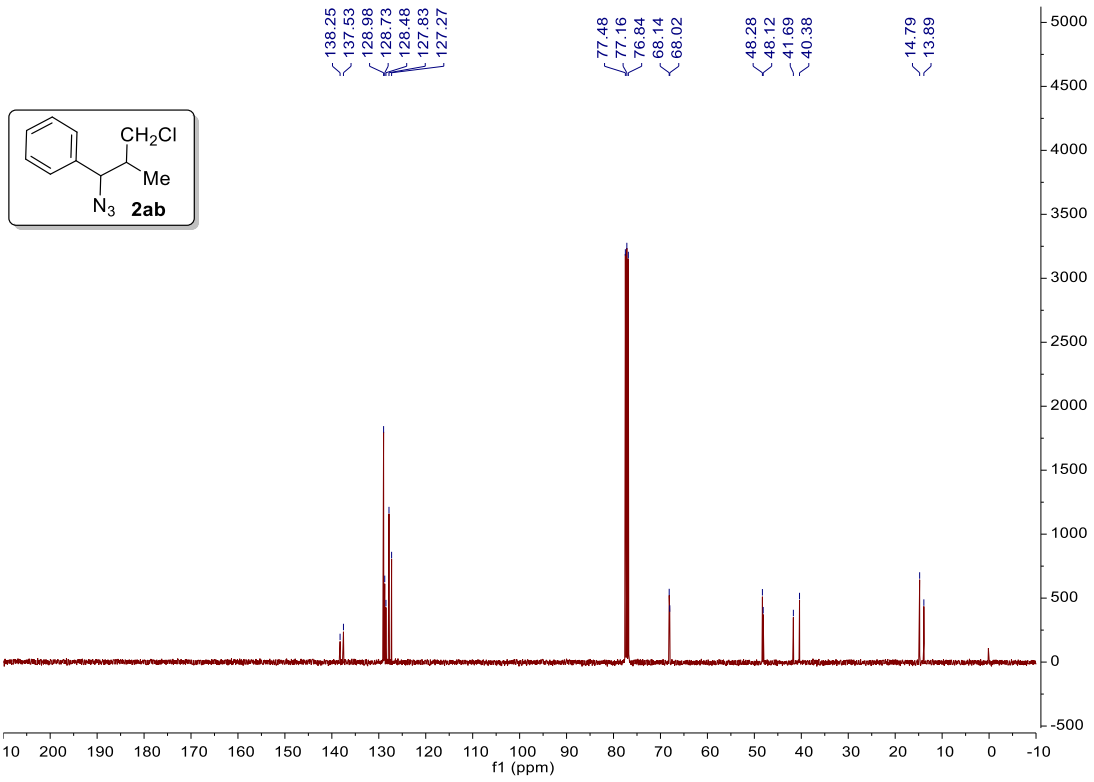
^{1}H NMR Spectrum of **2aa** ($CDCl_3$, 400 MHz)



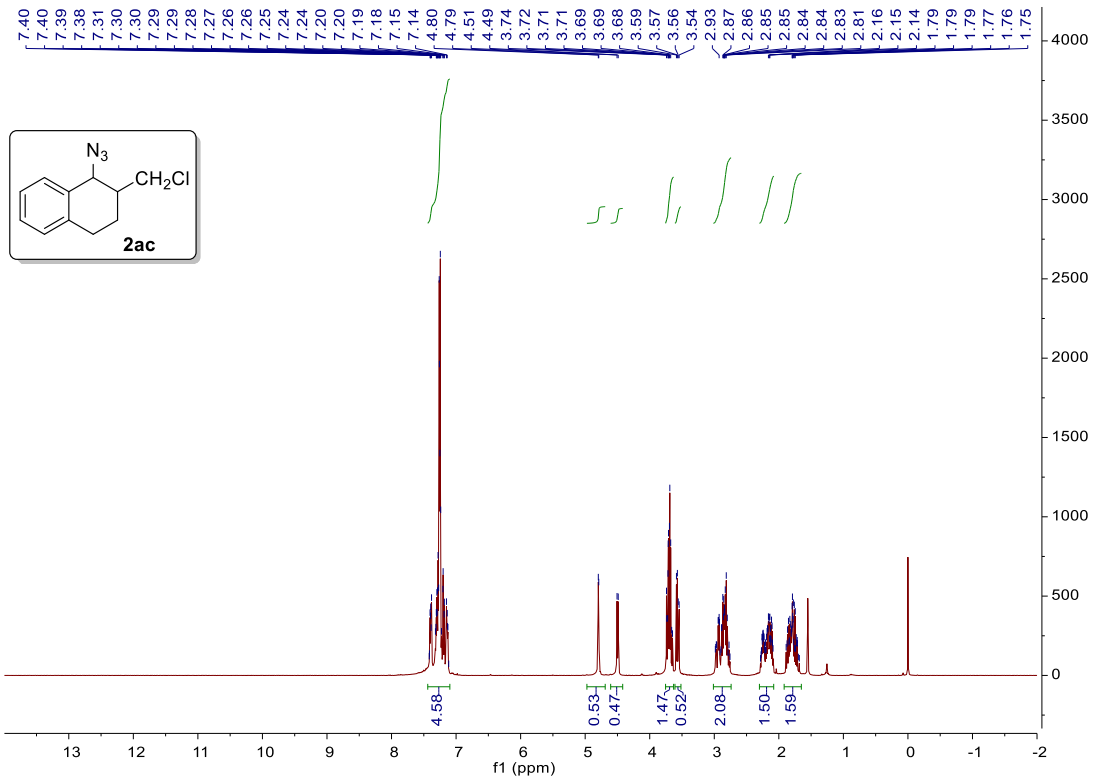
^{13}C NMR Spectrum of **2aa** ($CDCl_3$, 101 MHz)



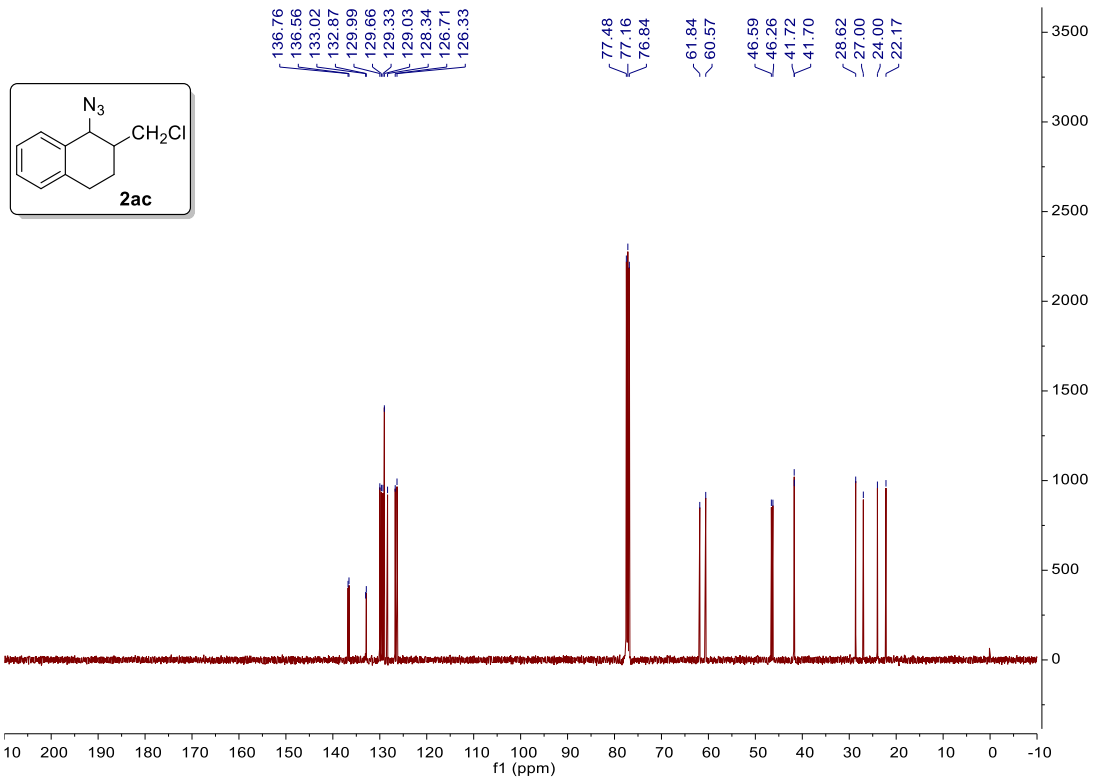
^{1}H NMR Spectrum of **2ab** ($CDCl_3$, 400 MHz)



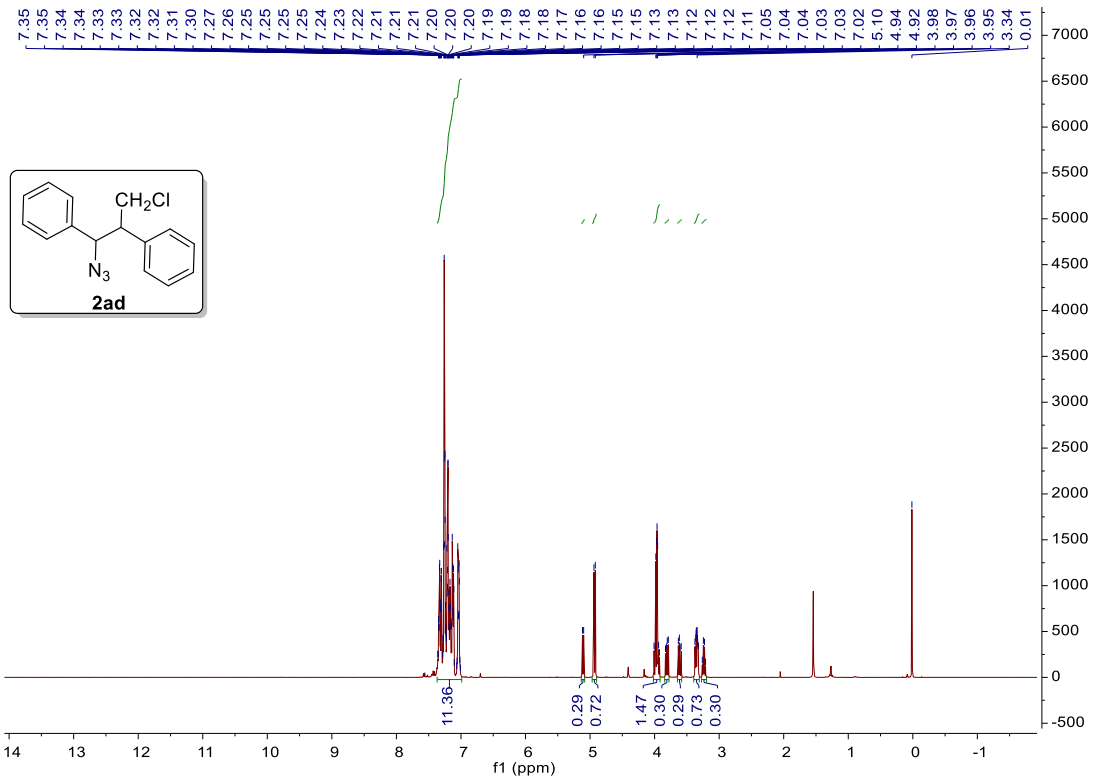
^{13}C NMR Spectrum of **2ab** ($CDCl_3$, 101 MHz)



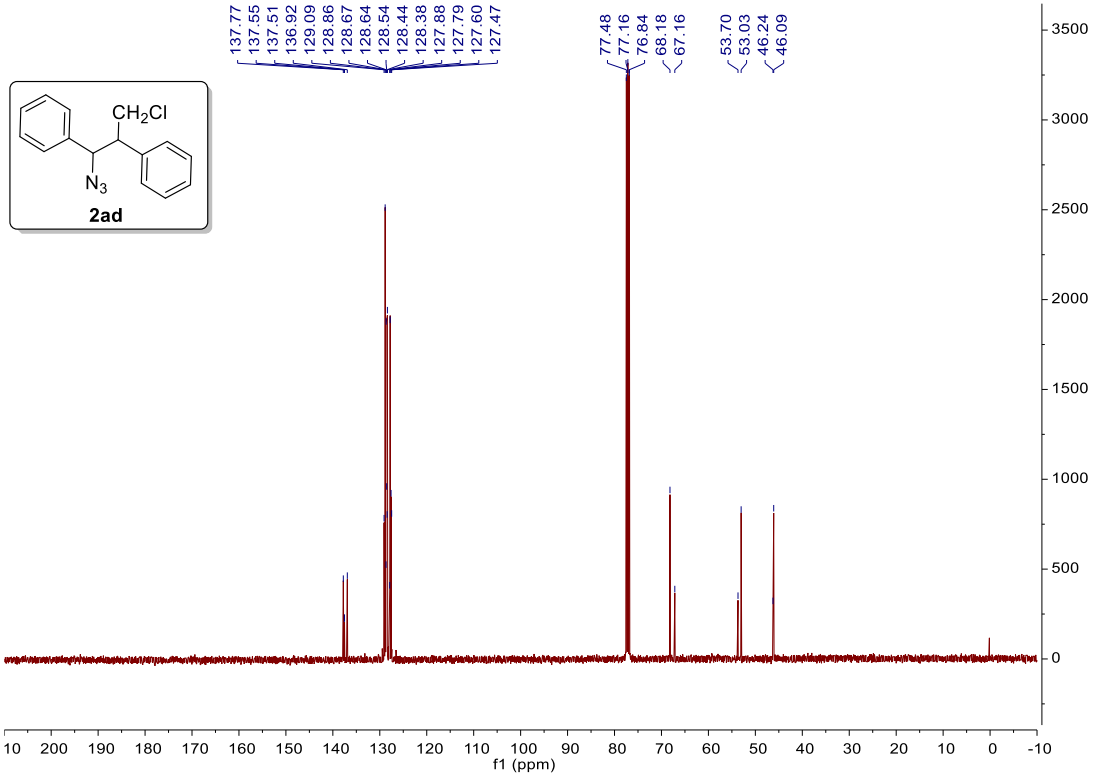
^{1}H NMR Spectrum of **2ac** ($CDCl_3$, 400 MHz)



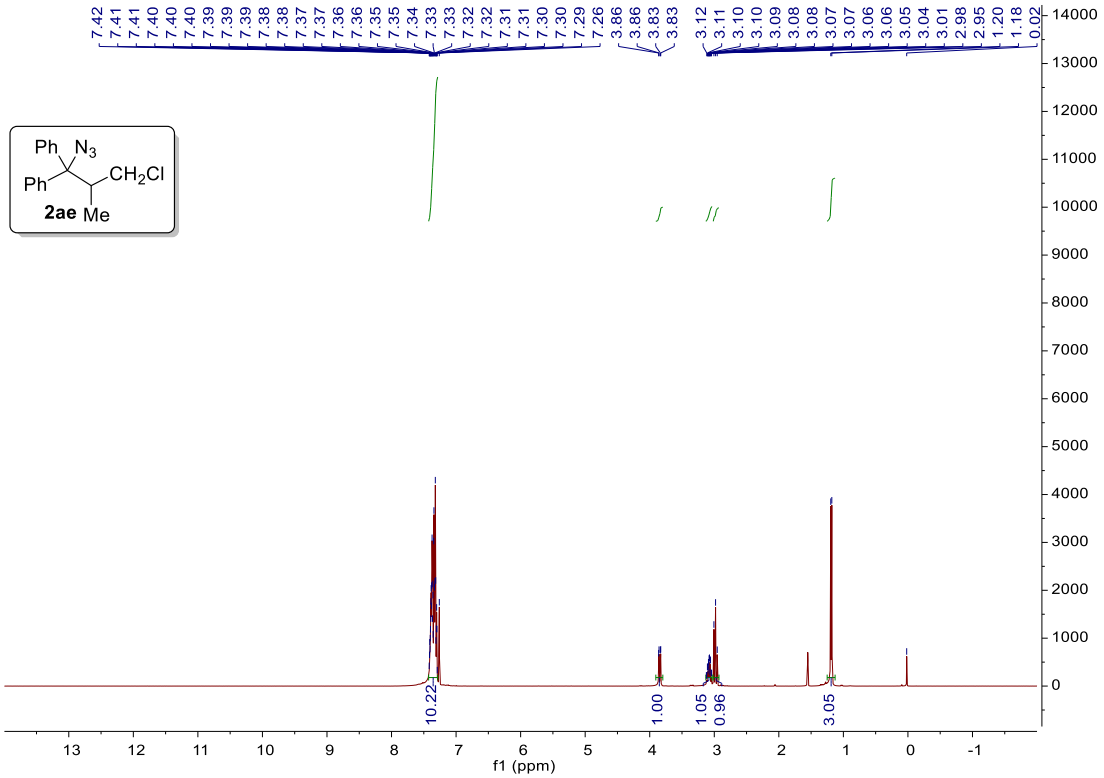
^{13}C NMR Spectrum of **2ac** ($CDCl_3$, 101 MHz)



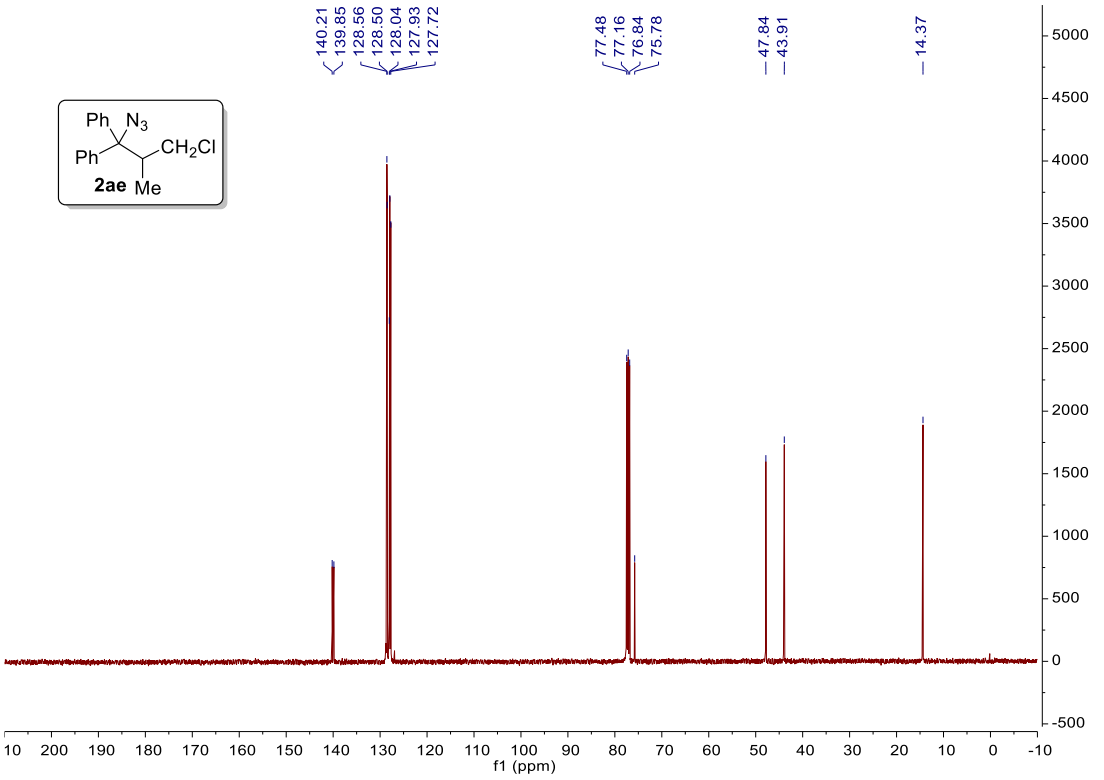
^{1}H NMR Spectrum of **2ad** ($CDCl_3$, 400 MHz)



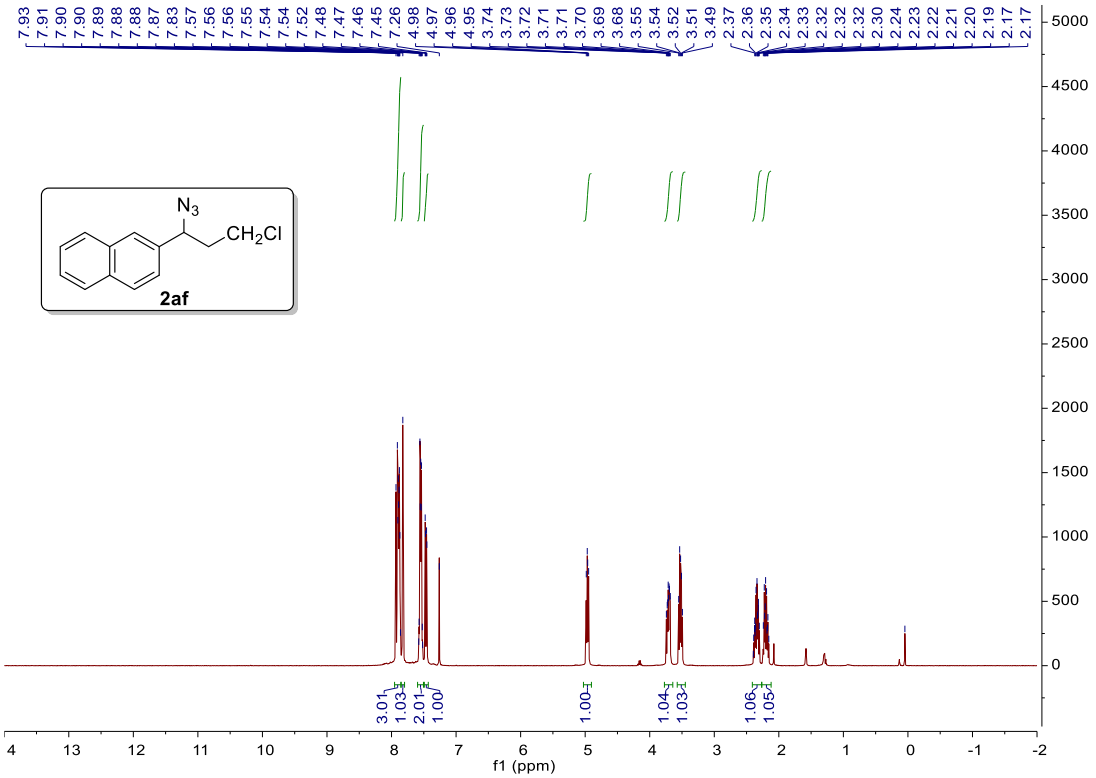
^{13}C NMR Spectrum of **2ad** ($CDCl_3$, 101 MHz)



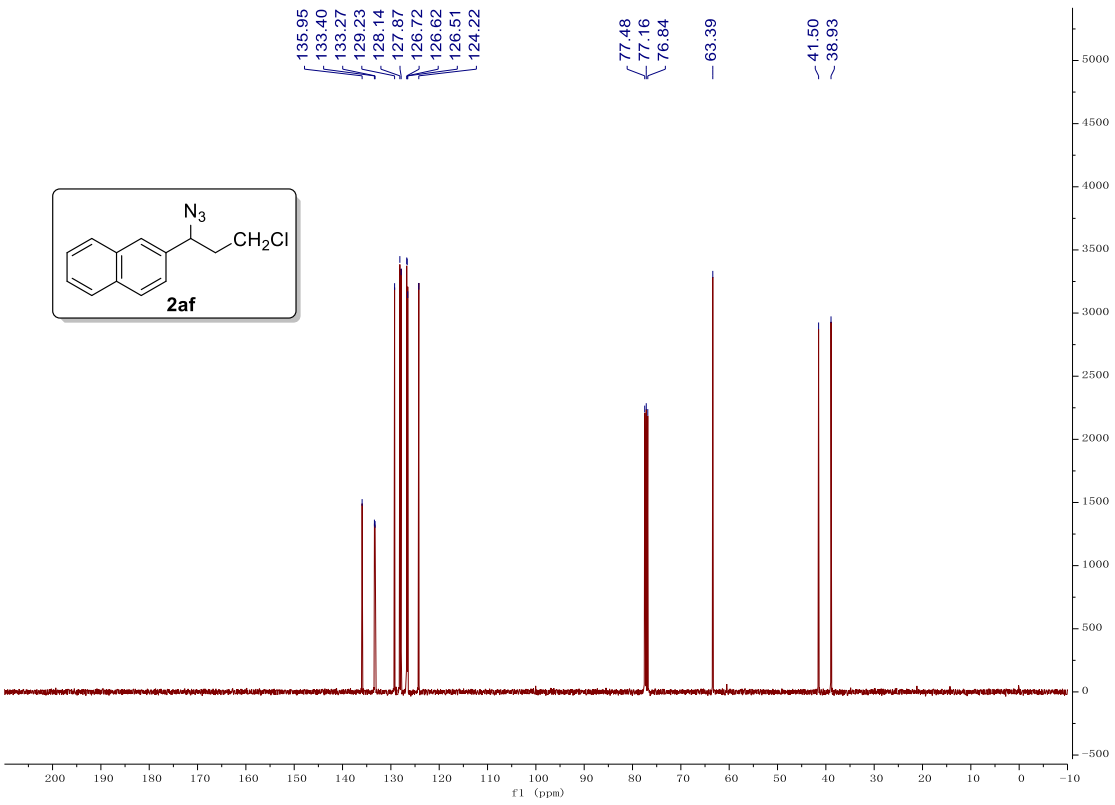
^{1}H NMR Spectrum of **2ae** ($CDCl_3$, 400 MHz)



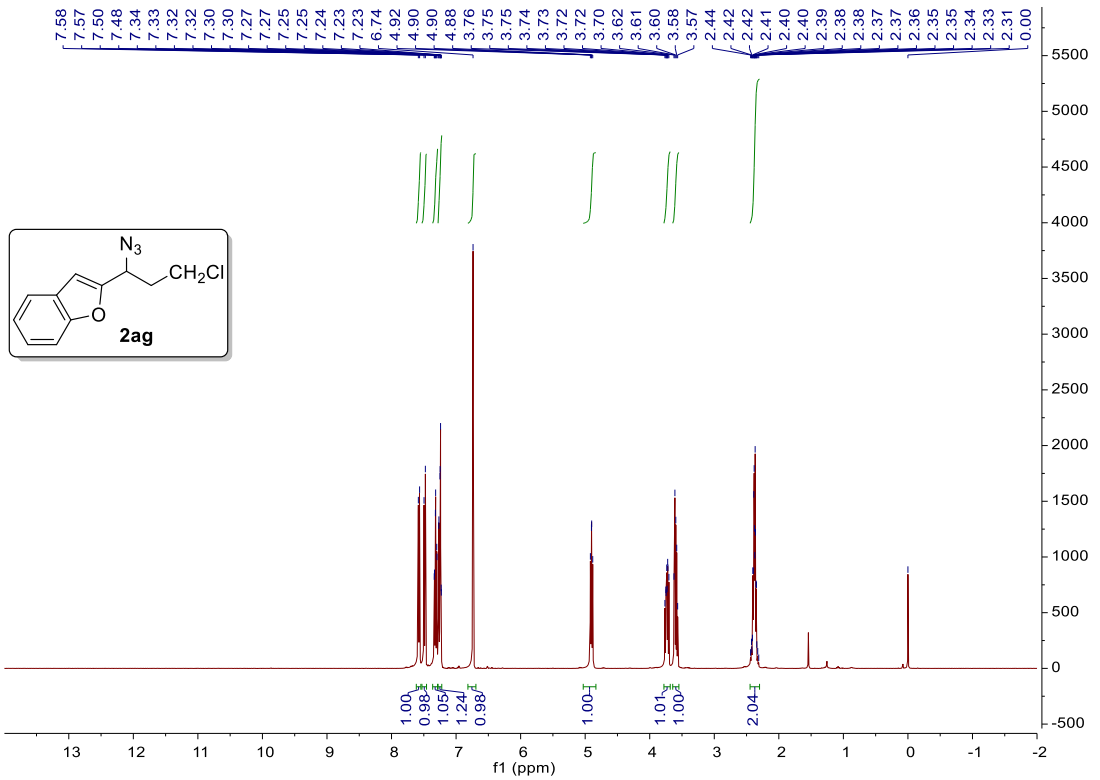
^{13}C NMR Spectrum of **2ae** ($CDCl_3$, 101 MHz)



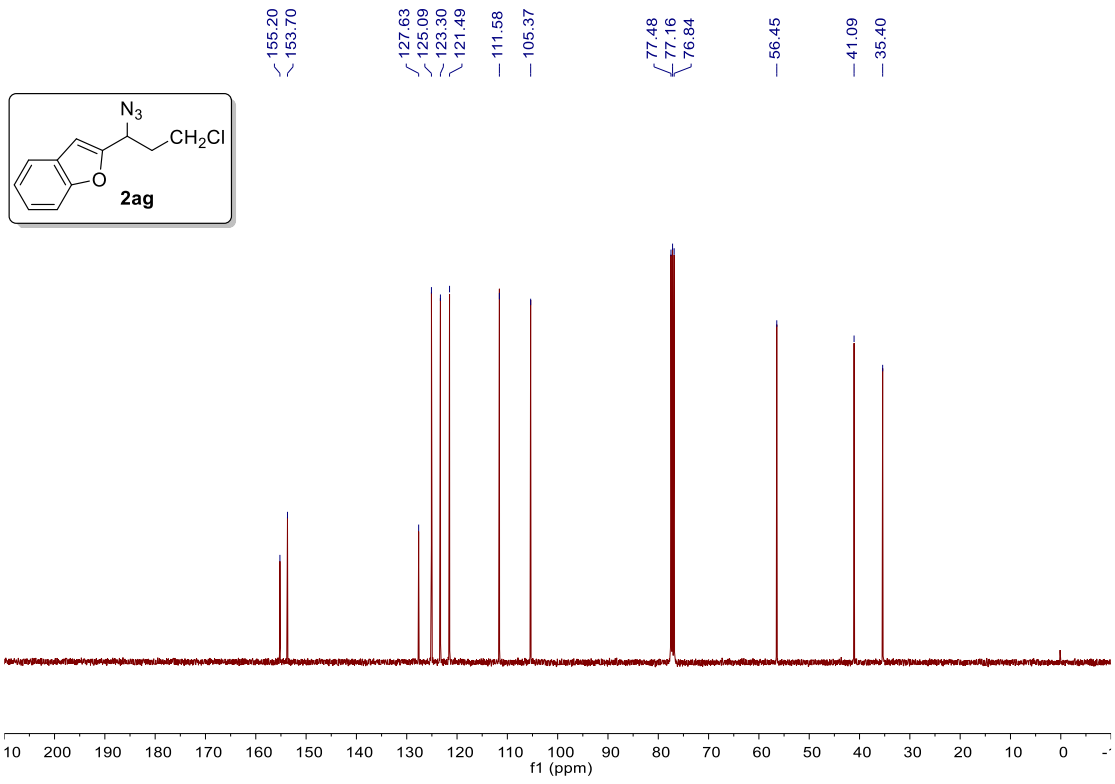
^{1}H NMR Spectrum of **2af** ($CDCl_3$, 400 MHz)



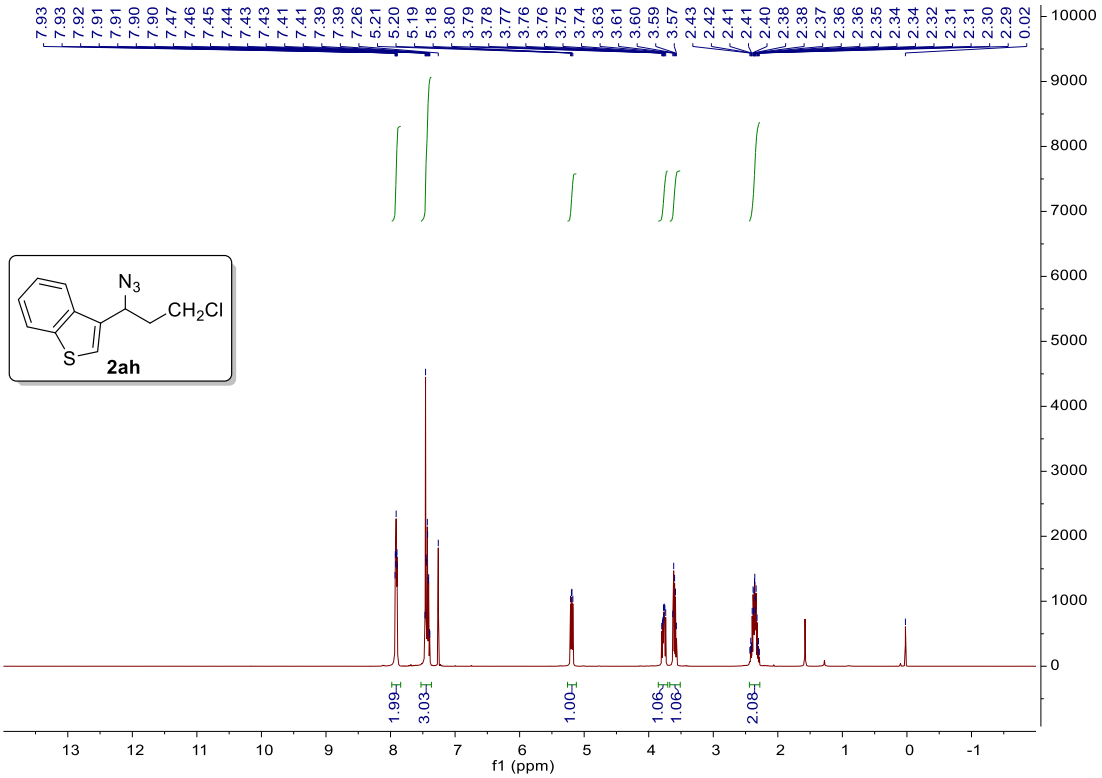
^{13}C NMR Spectrum of **2af** ($CDCl_3$, 101 MHz)



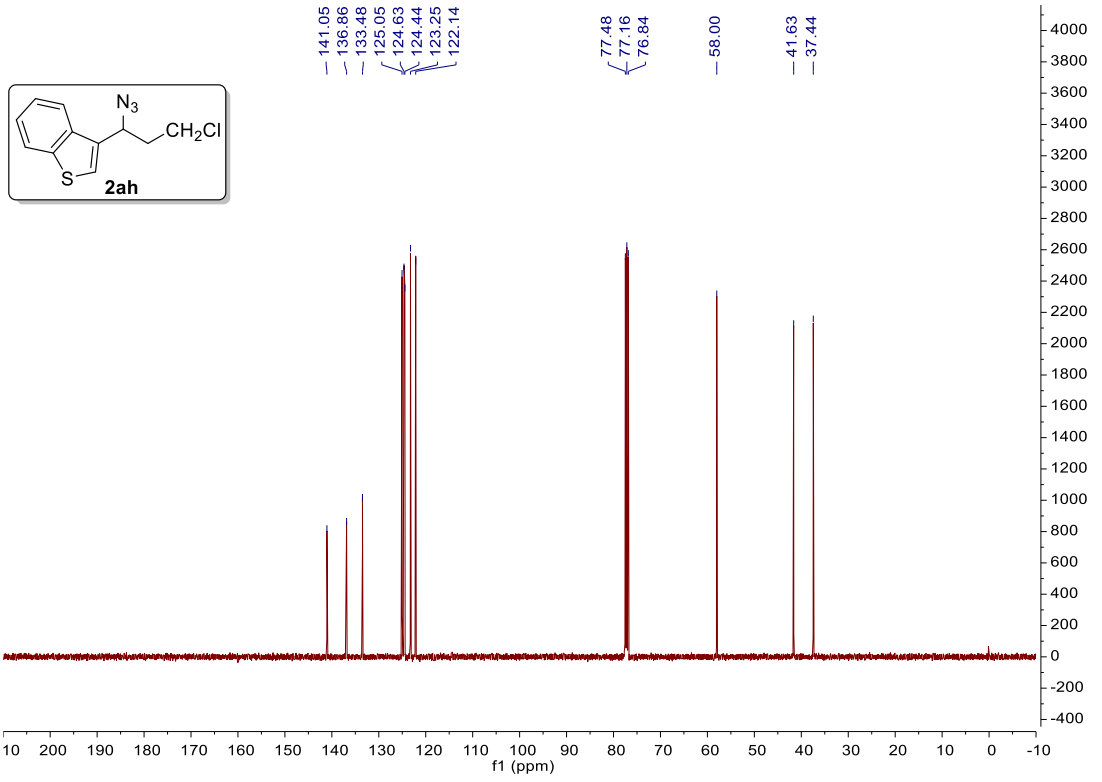
^{1}H NMR Spectrum of **2ag** ($CDCl_3$, 400 MHz)



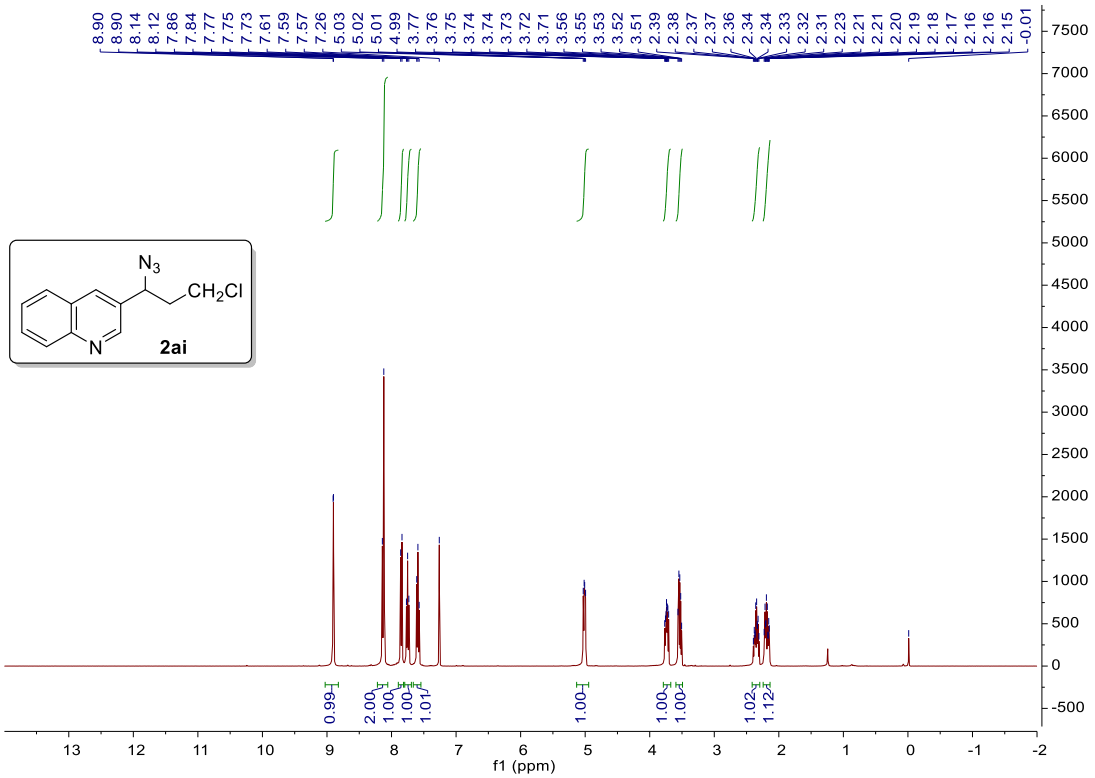
^{13}C NMR Spectrum of **2ag** ($CDCl_3$, 101 MHz)



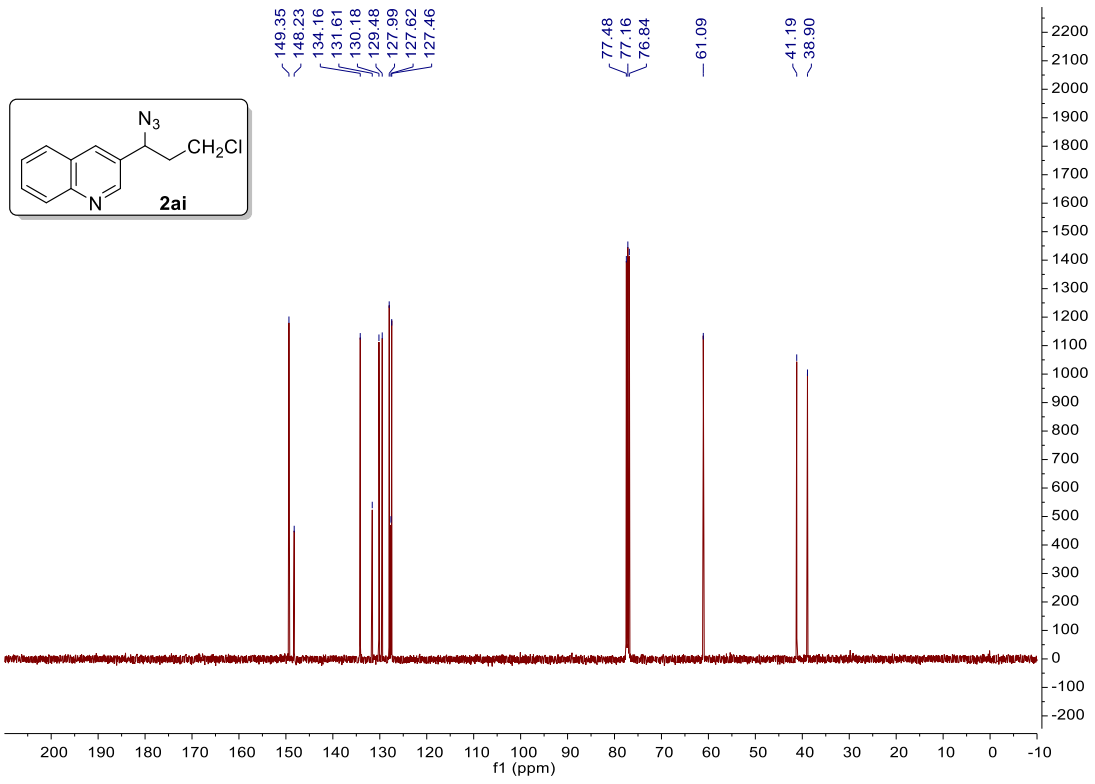
^{1}H NMR Spectrum of **2ah** ($CDCl_3$, 400 MHz)



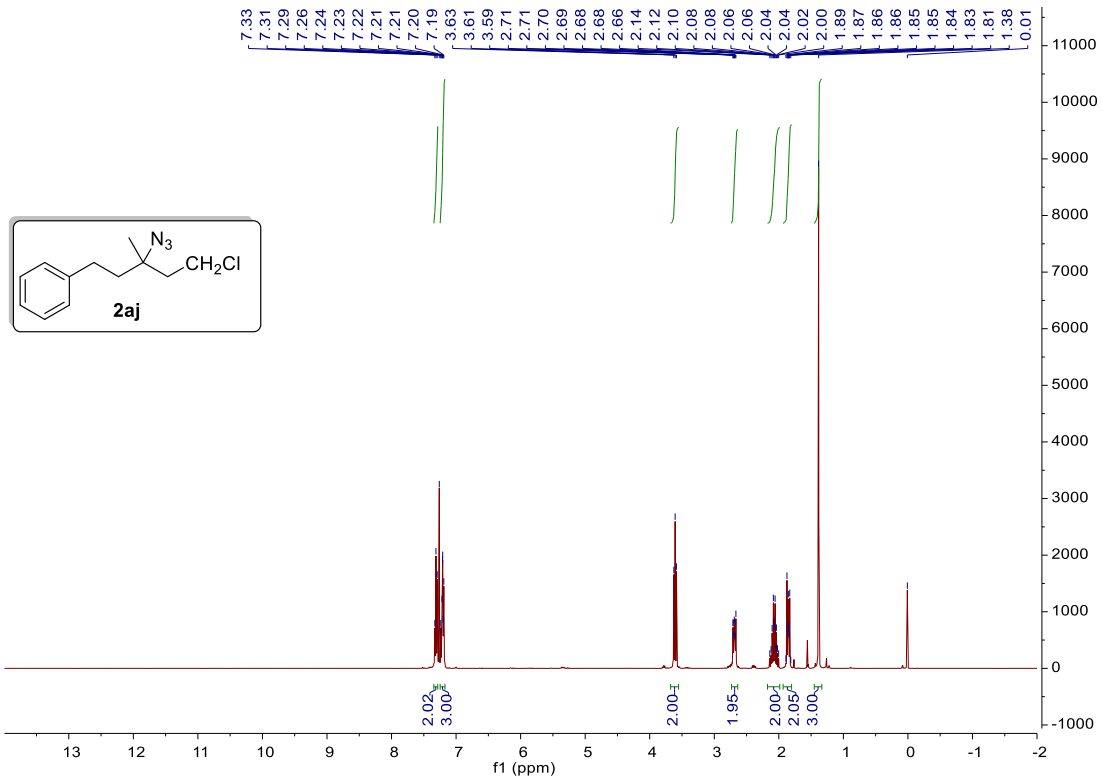
^{13}C NMR Spectrum of **2ah** ($CDCl_3$, 101 MHz)



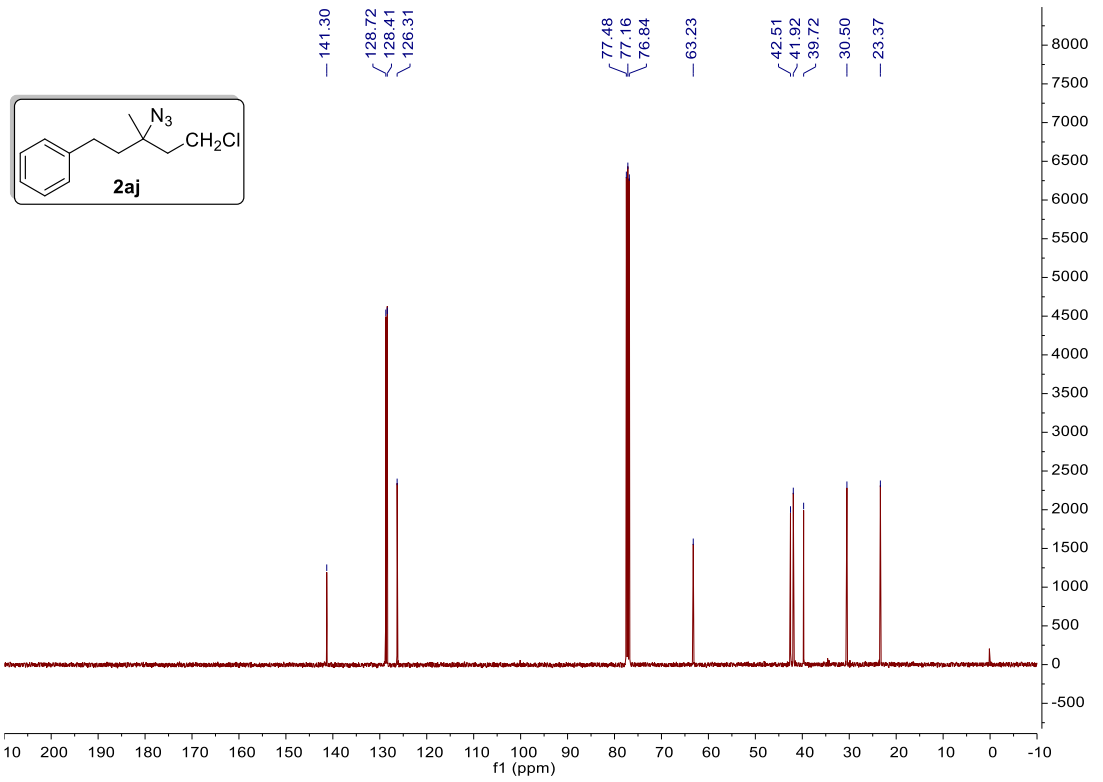
^{1}H NMR Spectrum of **2ai** ($CDCl_3$, 400 MHz)



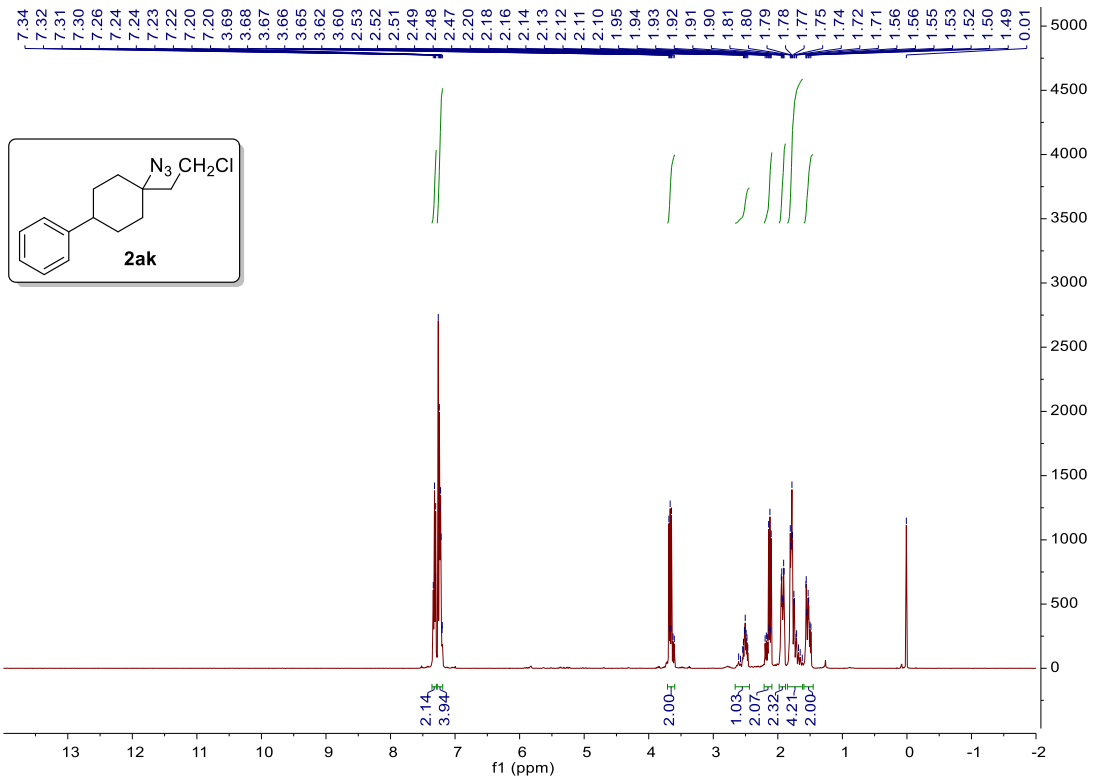
^{13}C NMR Spectrum of **2ai** ($CDCl_3$, 101 MHz)



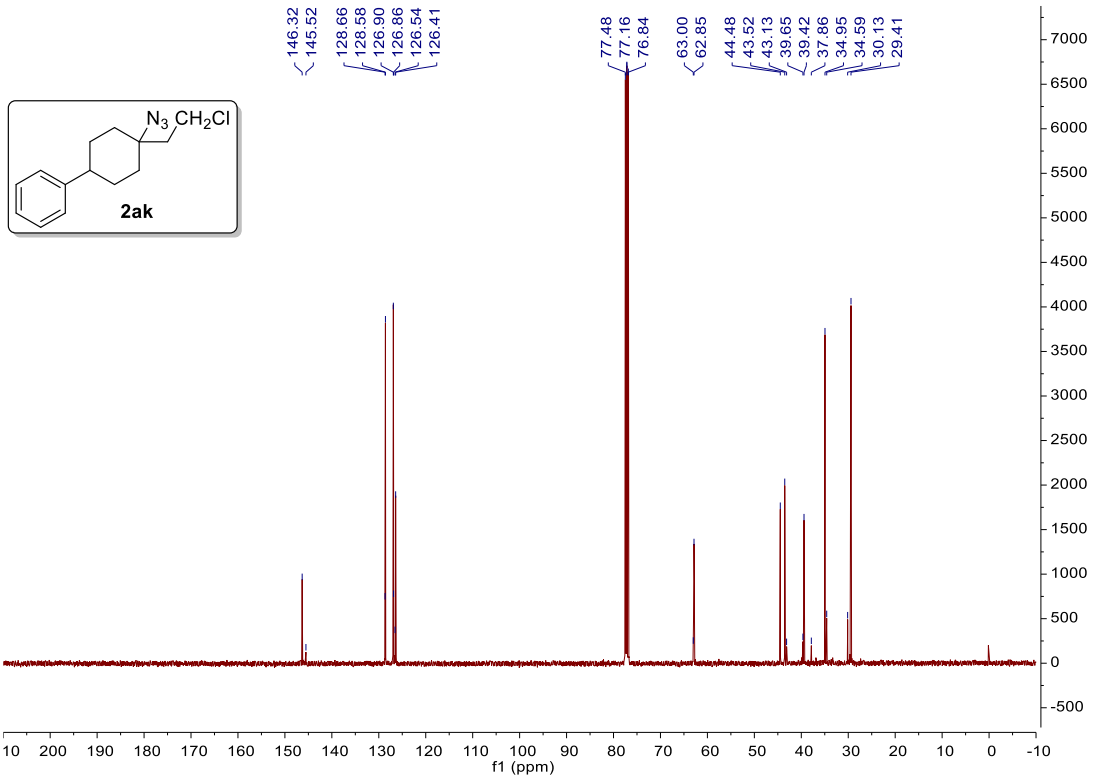
^{1}H NMR Spectrum of **2aj** ($CDCl_3$, 400 MHz)



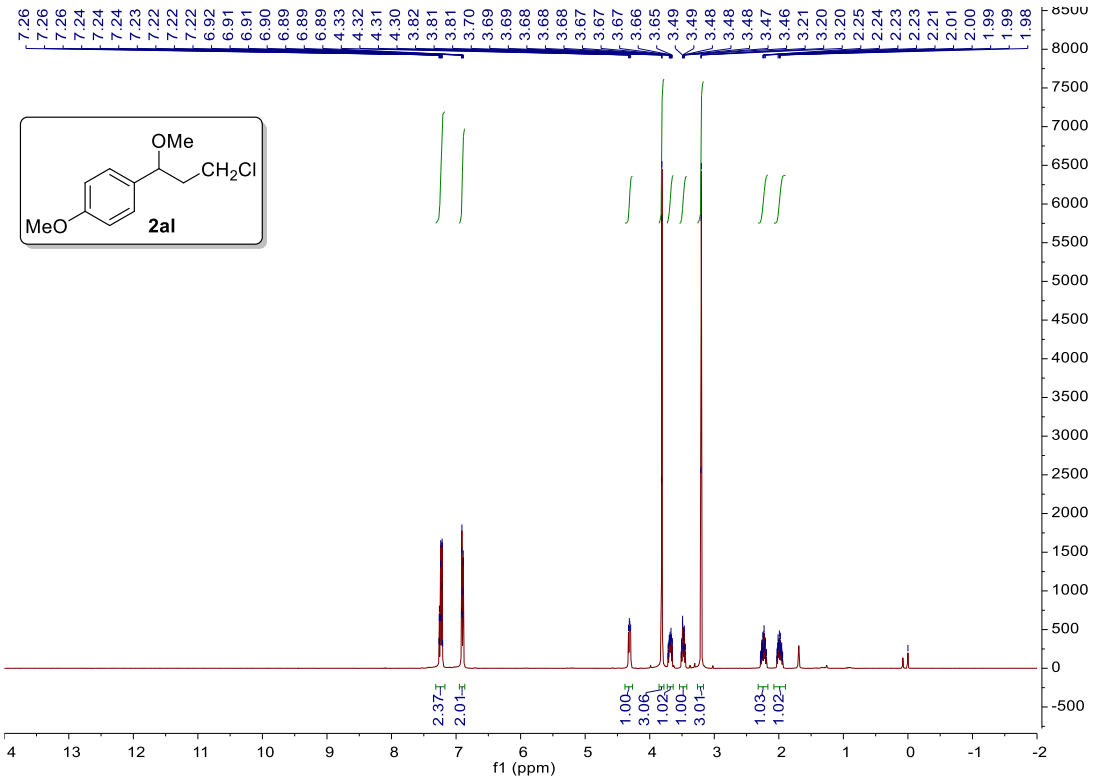
^{13}C NMR Spectrum of **2aj** ($CDCl_3$, 101 MHz)



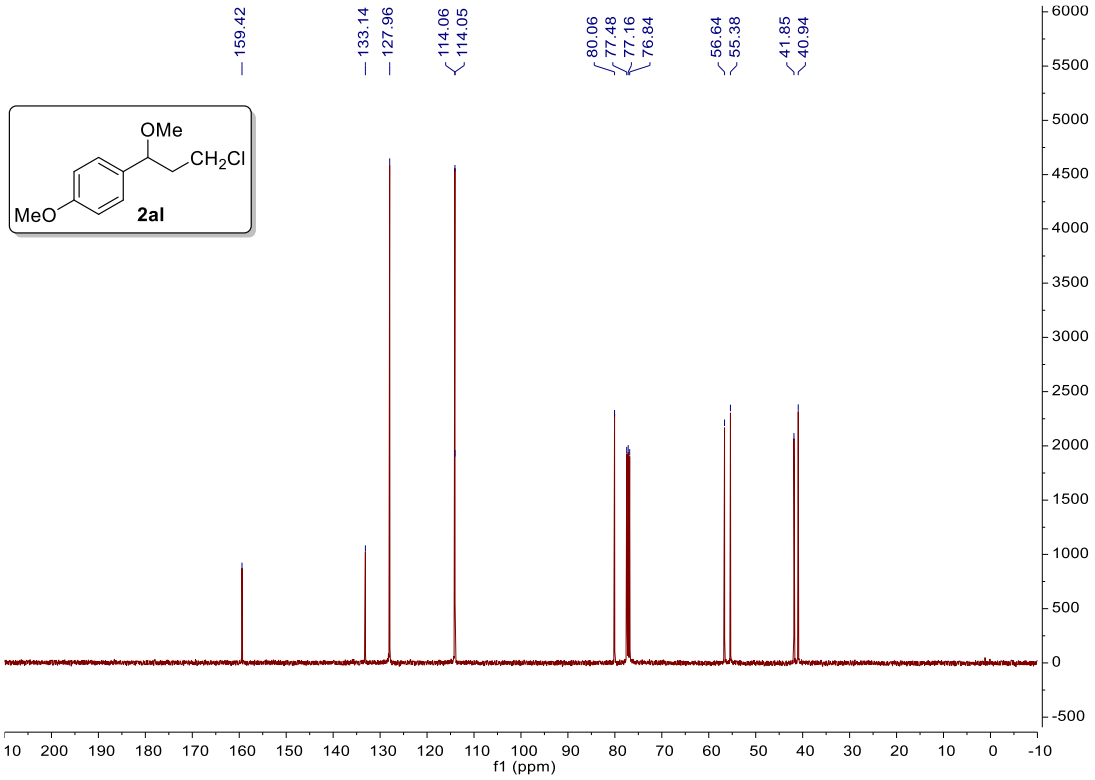
^{1}H NMR Spectrum of **2ak** ($CDCl_3$, 400 MHz)



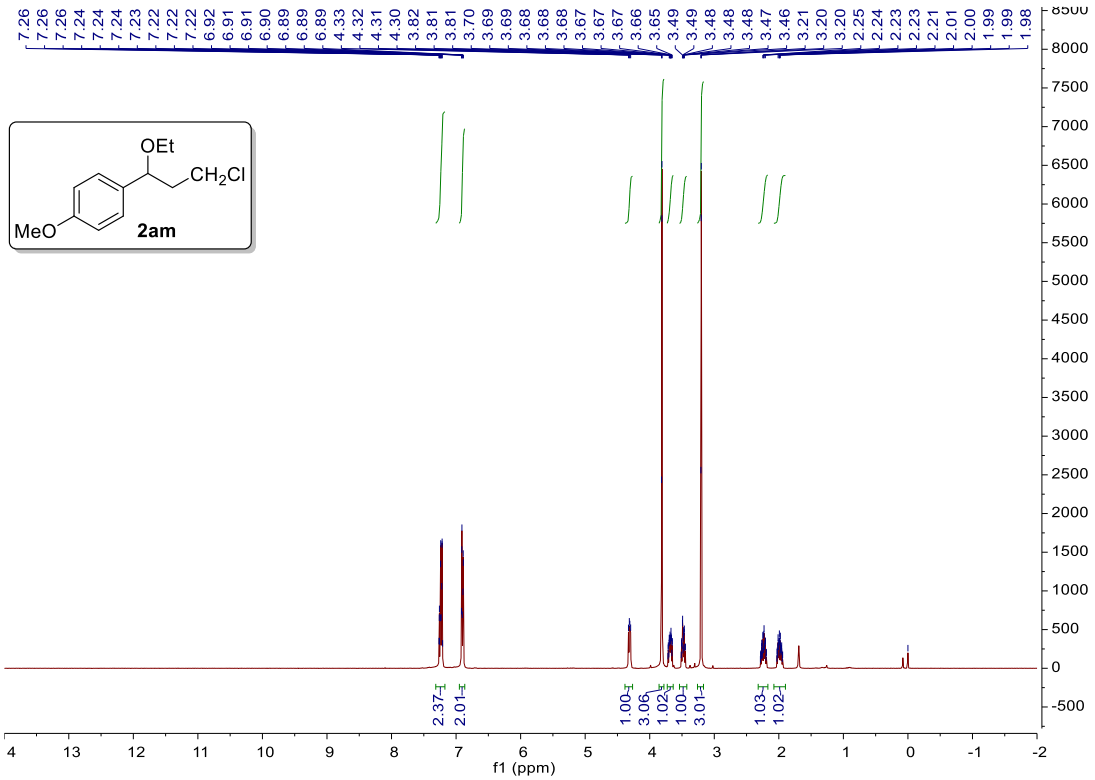
^{13}C NMR Spectrum of **2ak** ($CDCl_3$, 101 MHz)



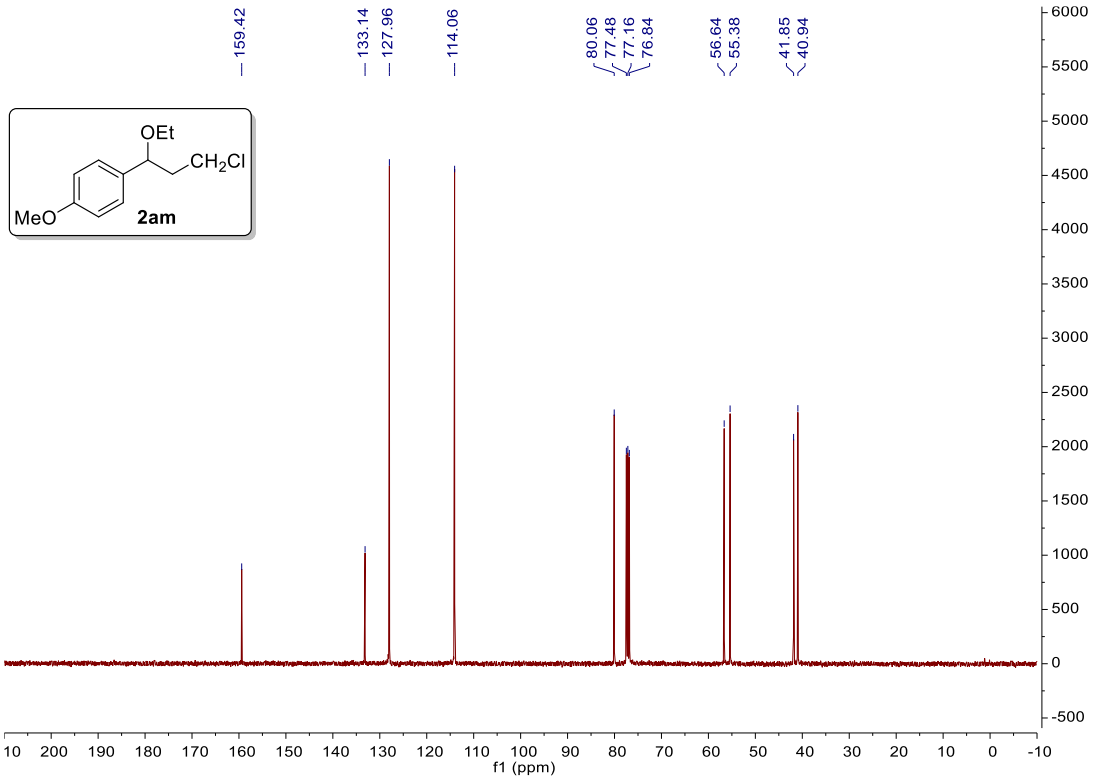
^{1}H NMR Spectrum of **2al** ($CDCl_3$, 400 MHz)



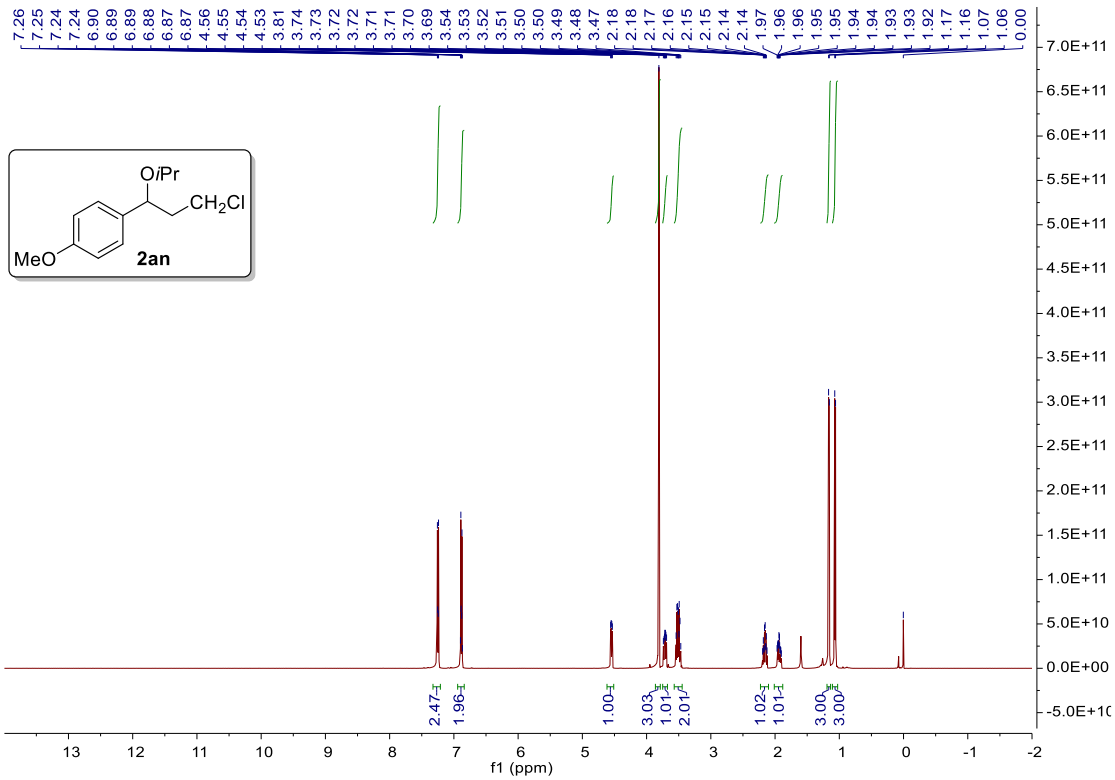
^{13}C NMR Spectrum of **2al** ($CDCl_3$, 101 MHz)



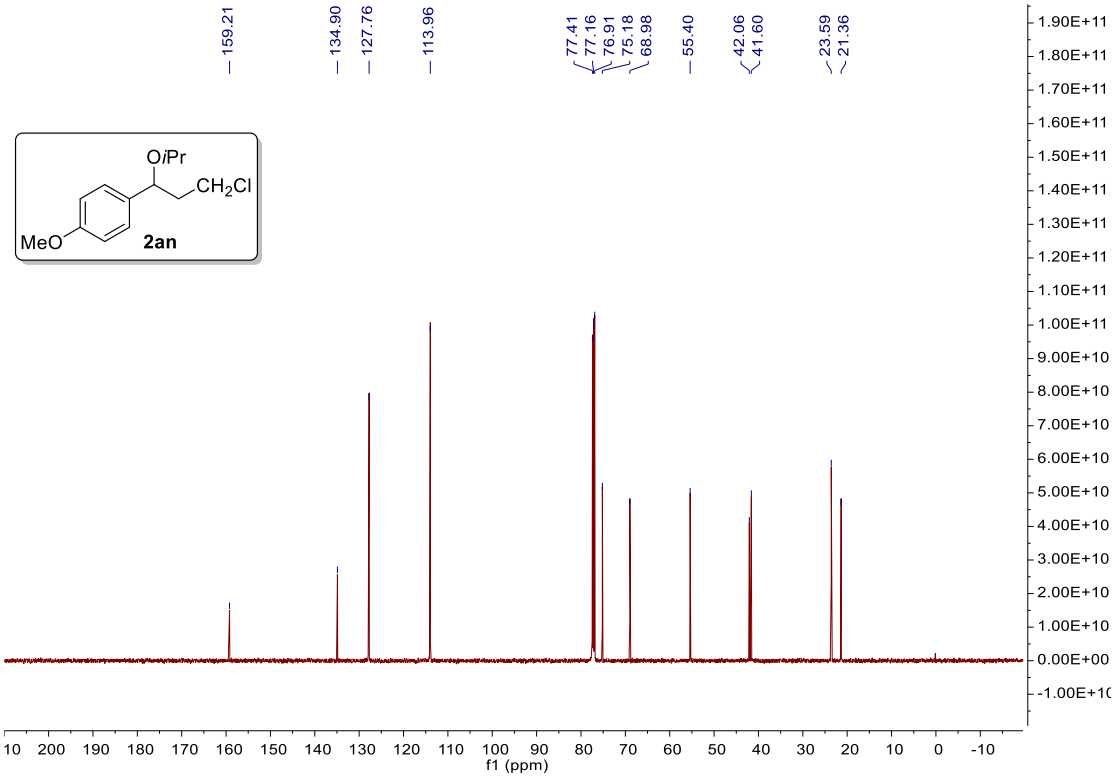
^{1}H NMR Spectrum of **2am** ($CDCl_3$, 500 MHz)



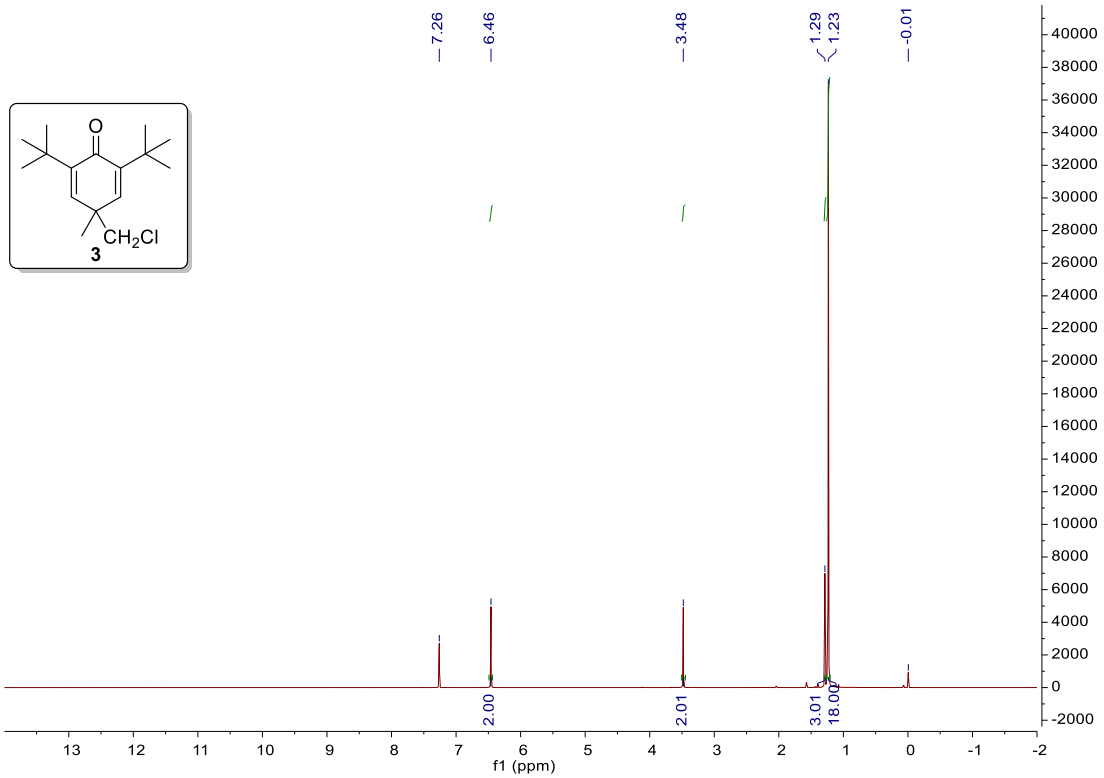
^{13}C NMR Spectrum of **2am** ($CDCl_3$, 127 MHz)



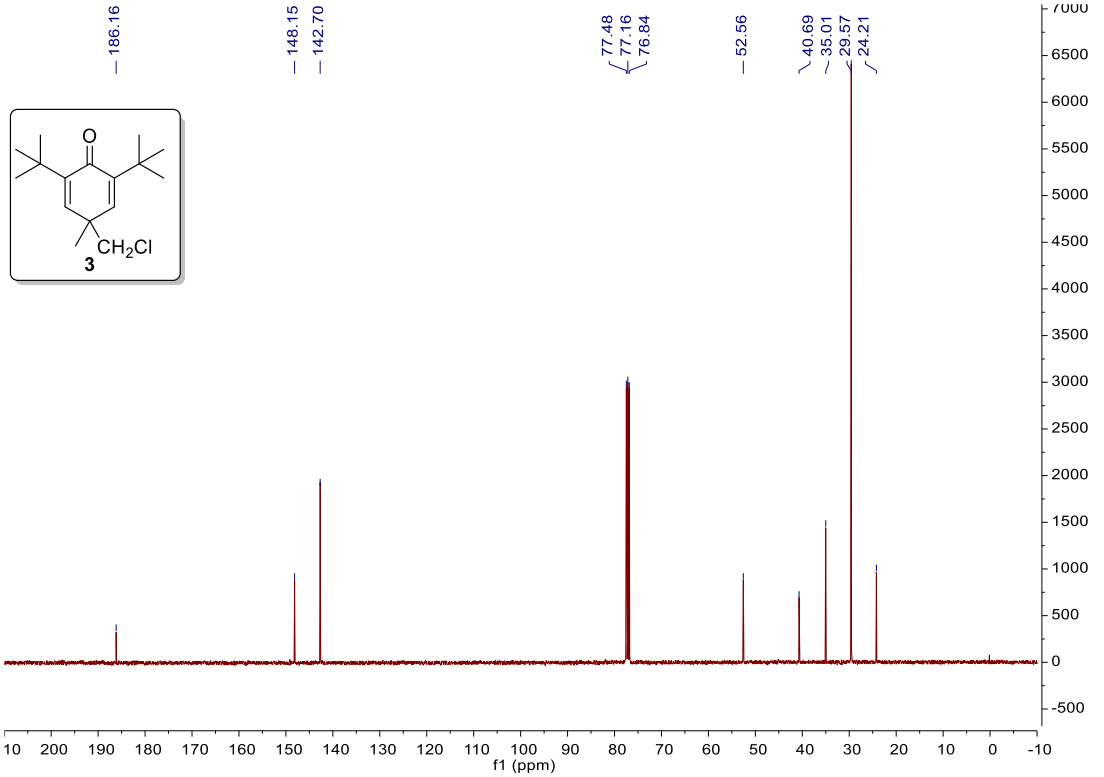
^{1}H NMR Spectrum of **2an** ($CDCl_3$, 500 MHz)



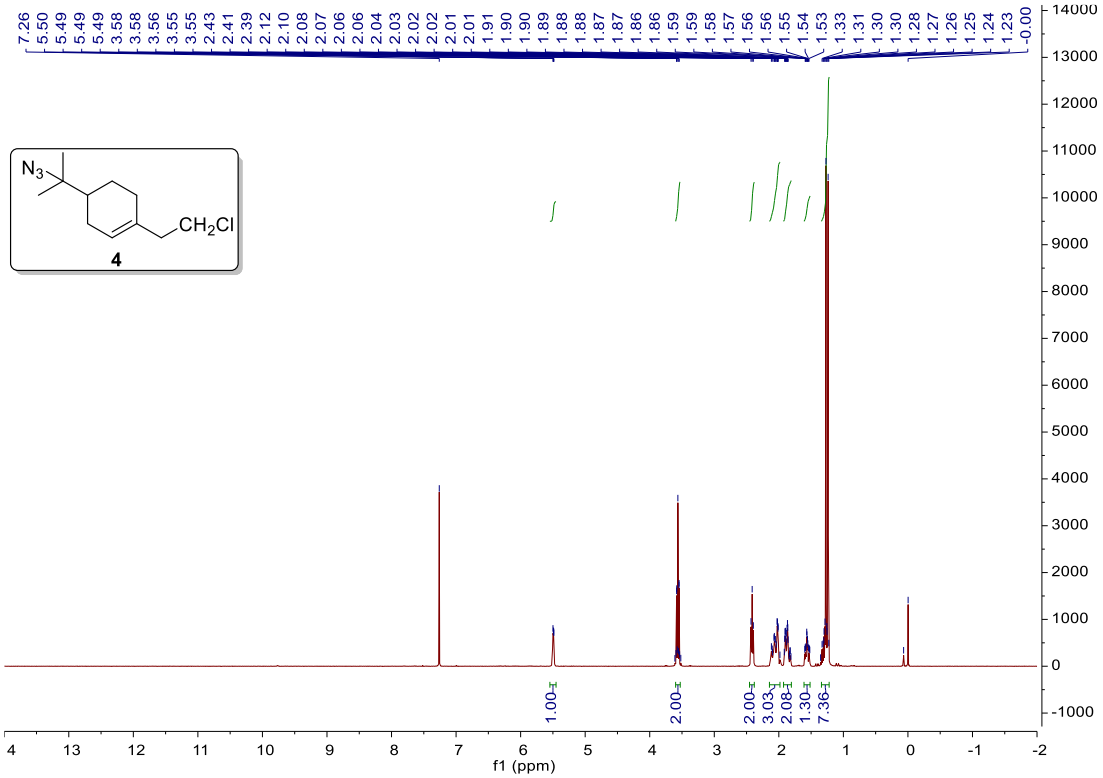
^{13}C NMR Spectrum of **2an** ($CDCl_3$, 127 MHz)



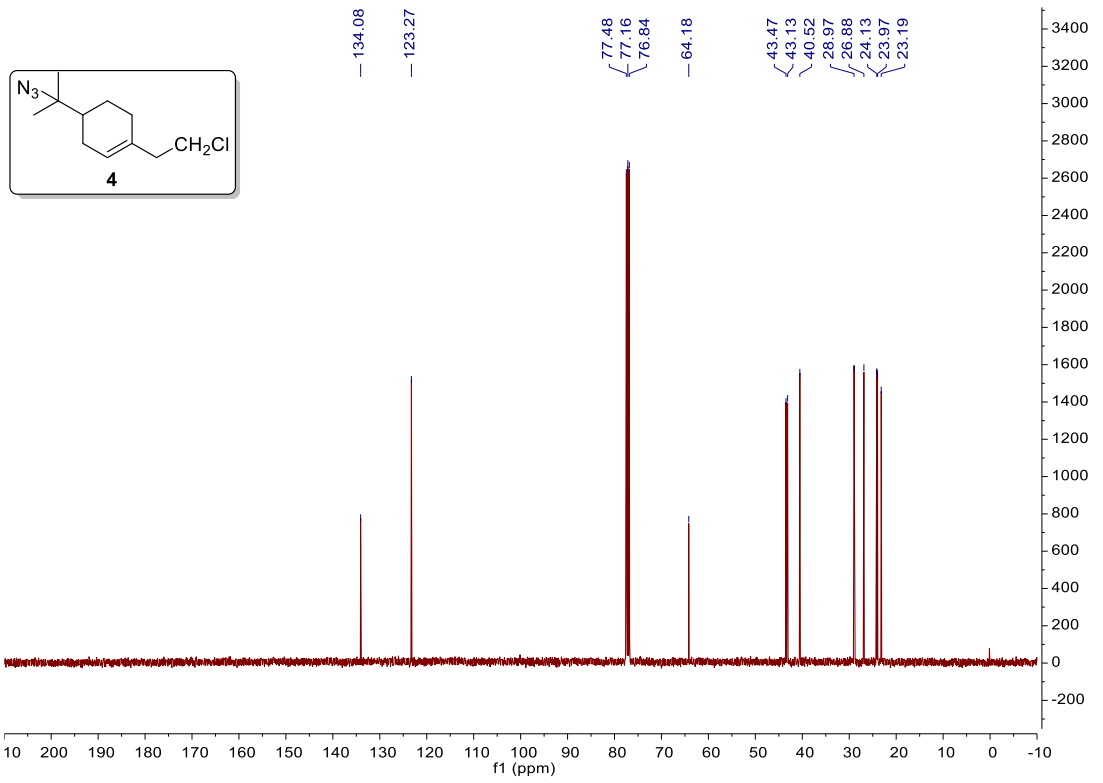
^{1}H NMR Spectrum of **3** ($CDCl_3$, 400 MHz)



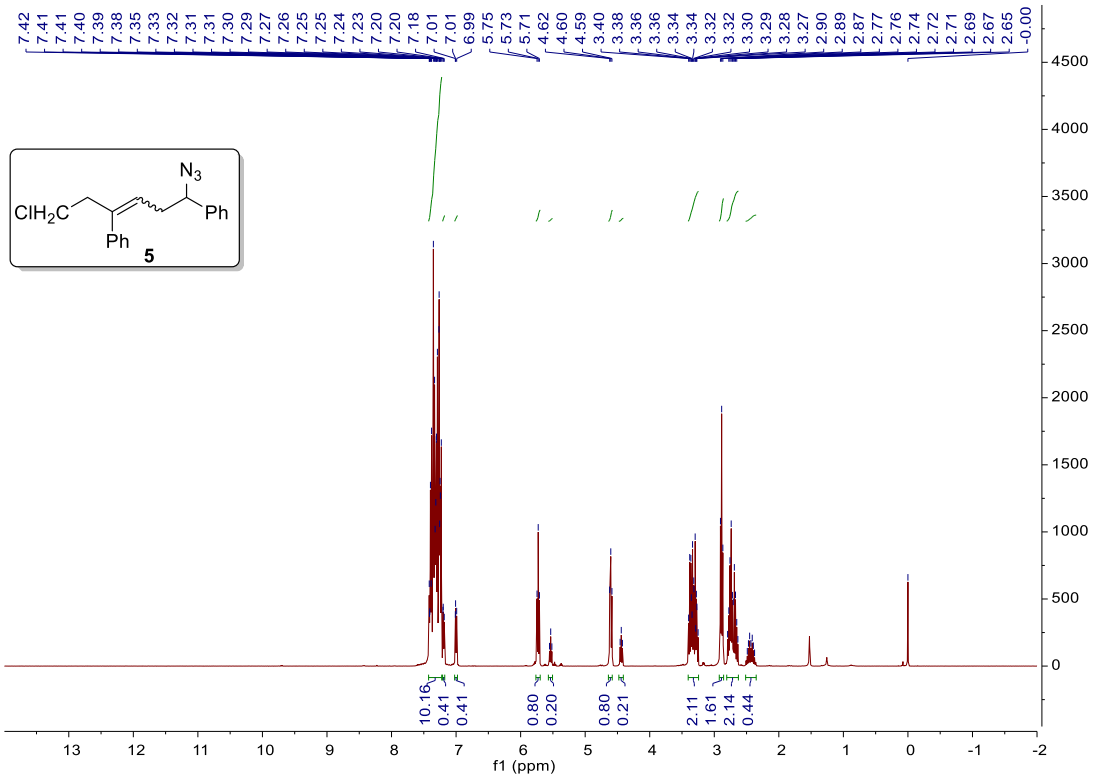
^{13}C NMR Spectrum of **3** ($CDCl_3$, 101 MHz)



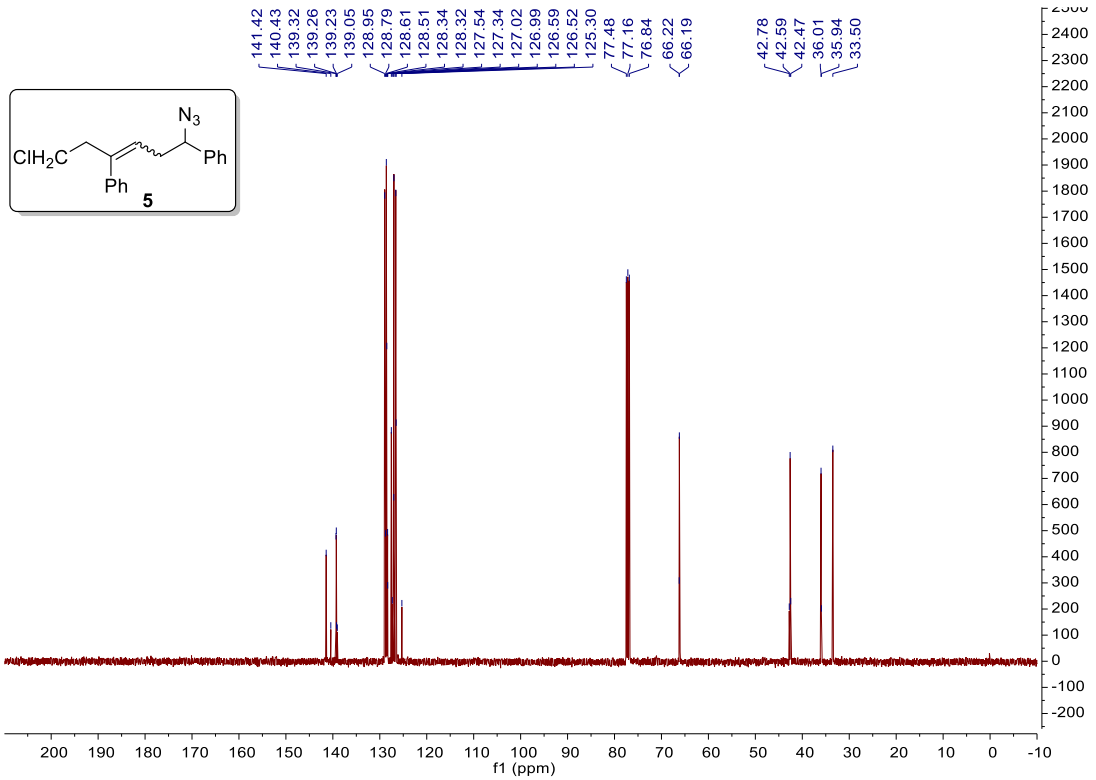
^{1}H NMR Spectrum of **4** ($CDCl_3$, 400 MHz)



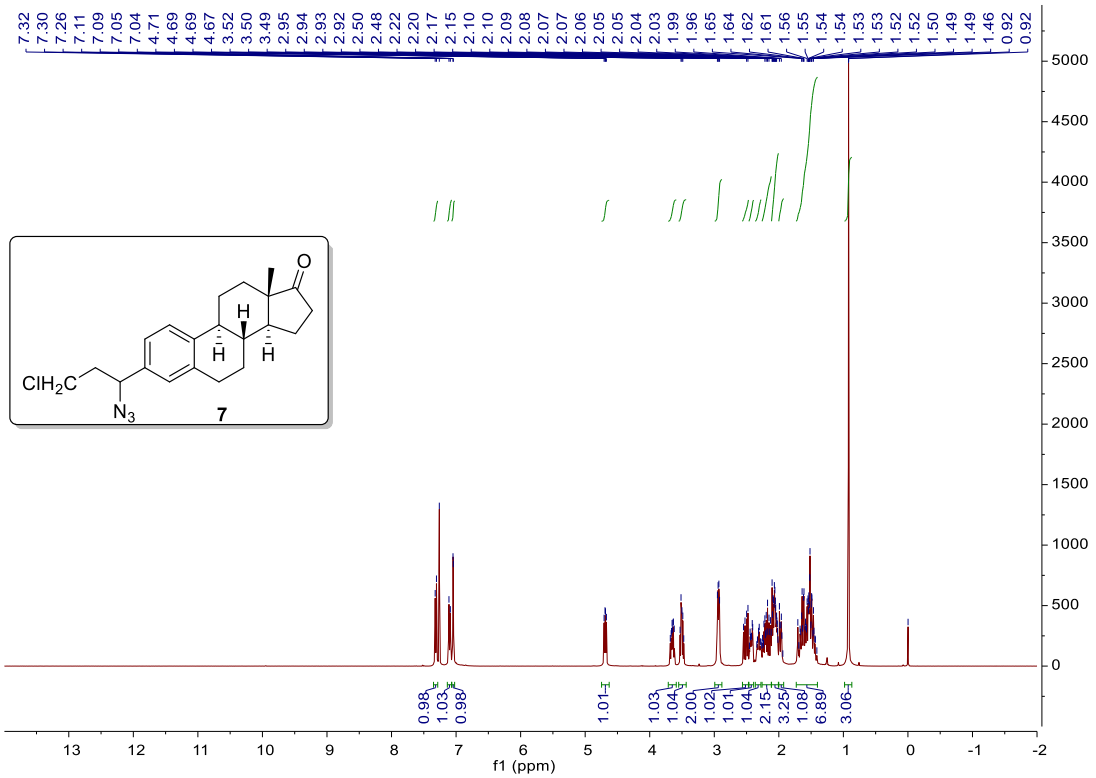
^{13}C NMR Spectrum of **4** ($CDCl_3$, 101 MHz)



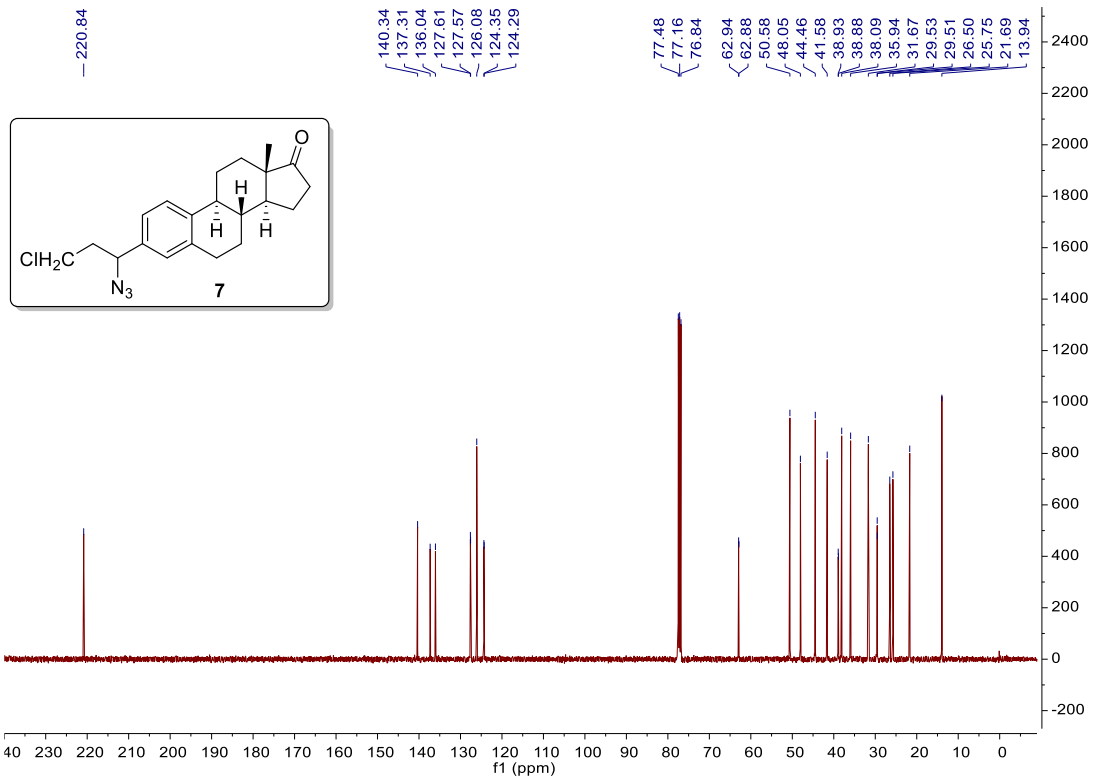
^{1}H NMR Spectrum of **5** ($CDCl_3$, 400 MHz)



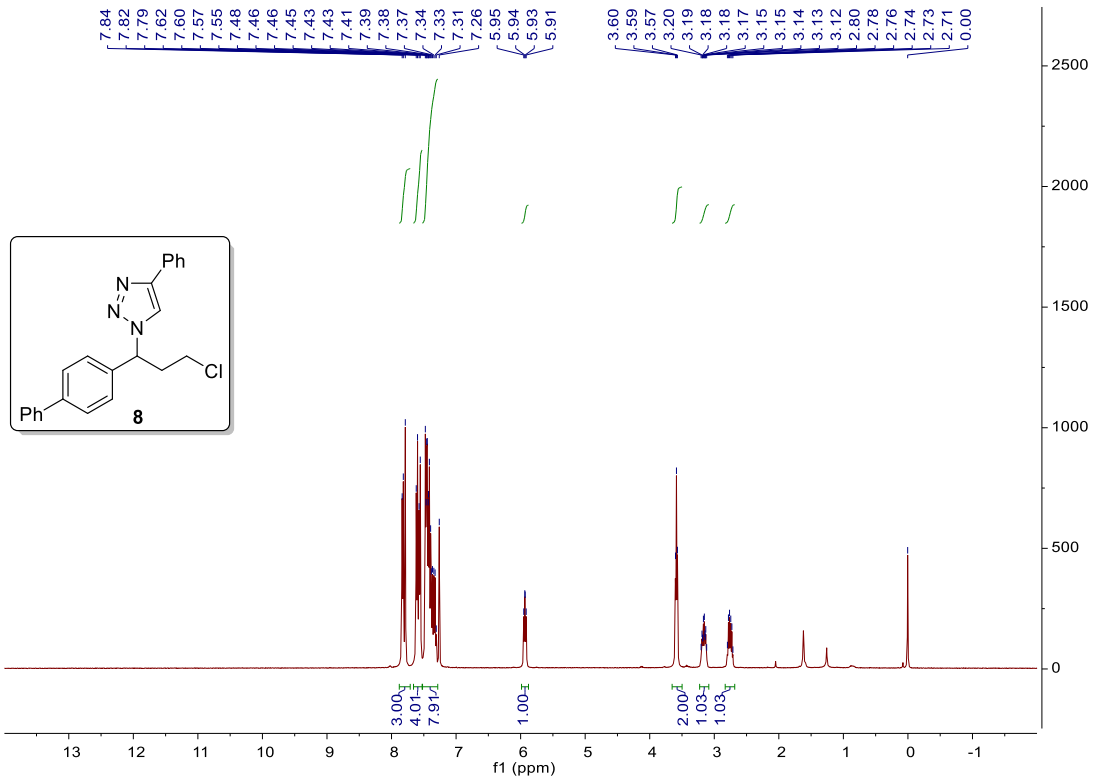
^{13}C NMR Spectrum of **5** ($CDCl_3$, 101 MHz)



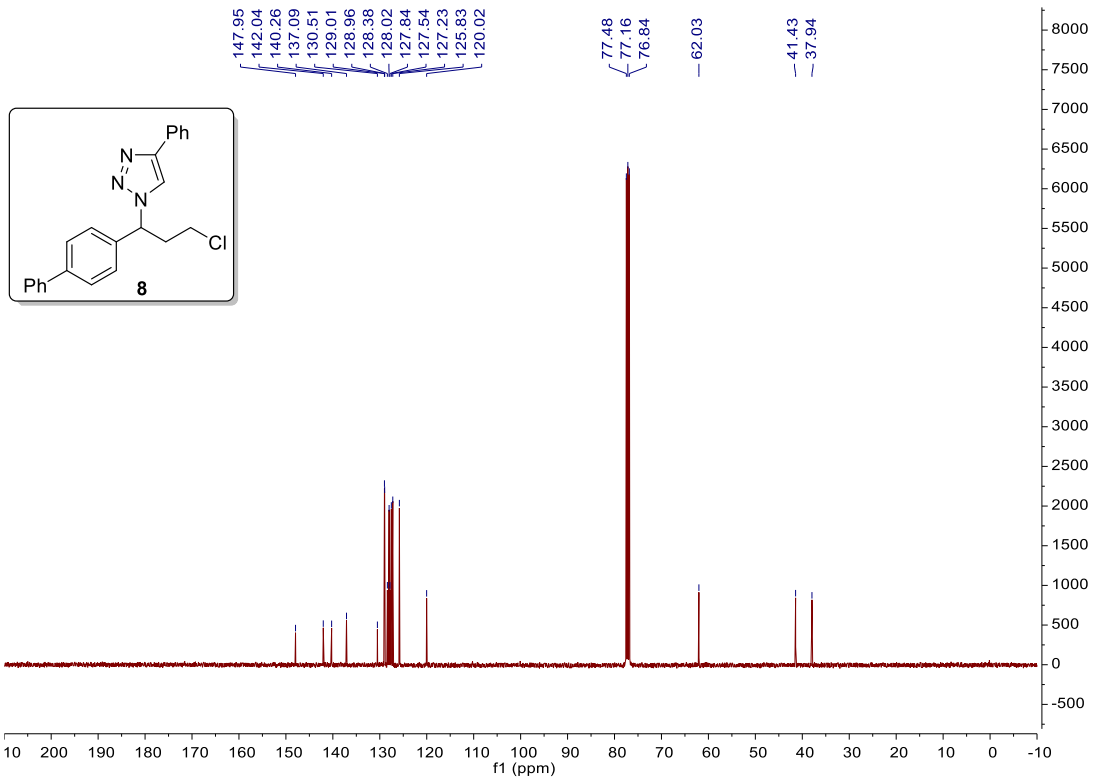
^{1}H NMR Spectrum of **7** ($CDCl_3$, 400 MHz)



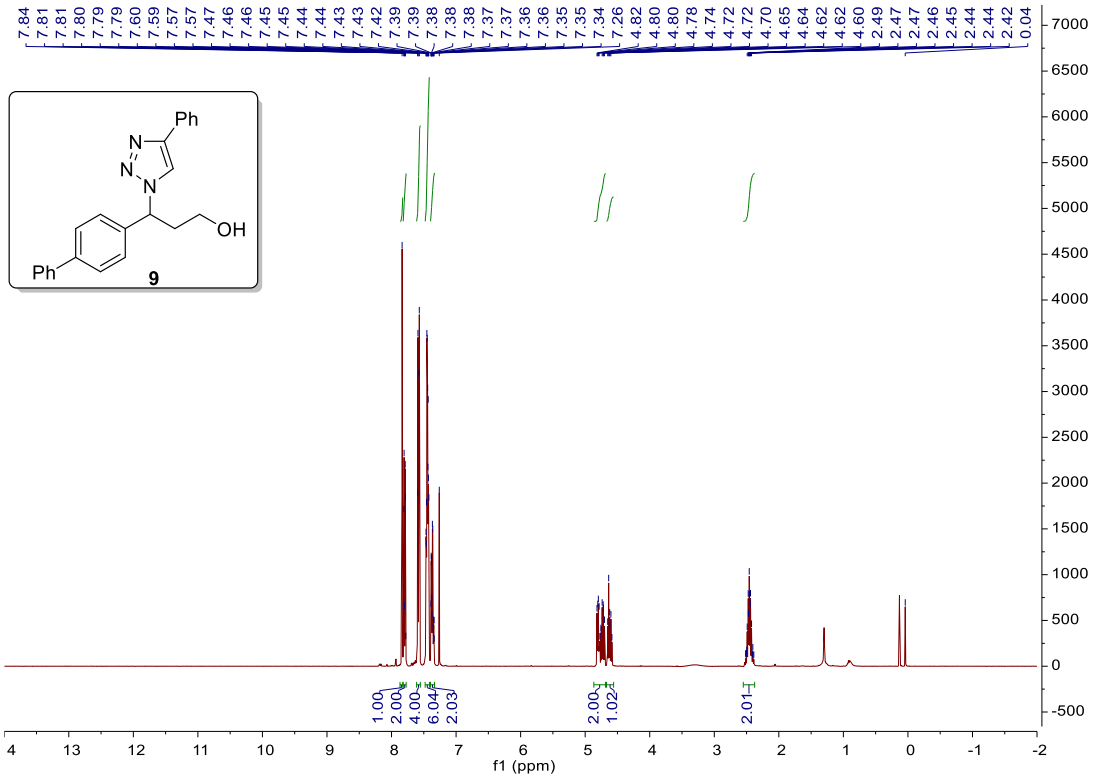
^{13}C NMR Spectrum of **7** ($CDCl_3$, 101 MHz)



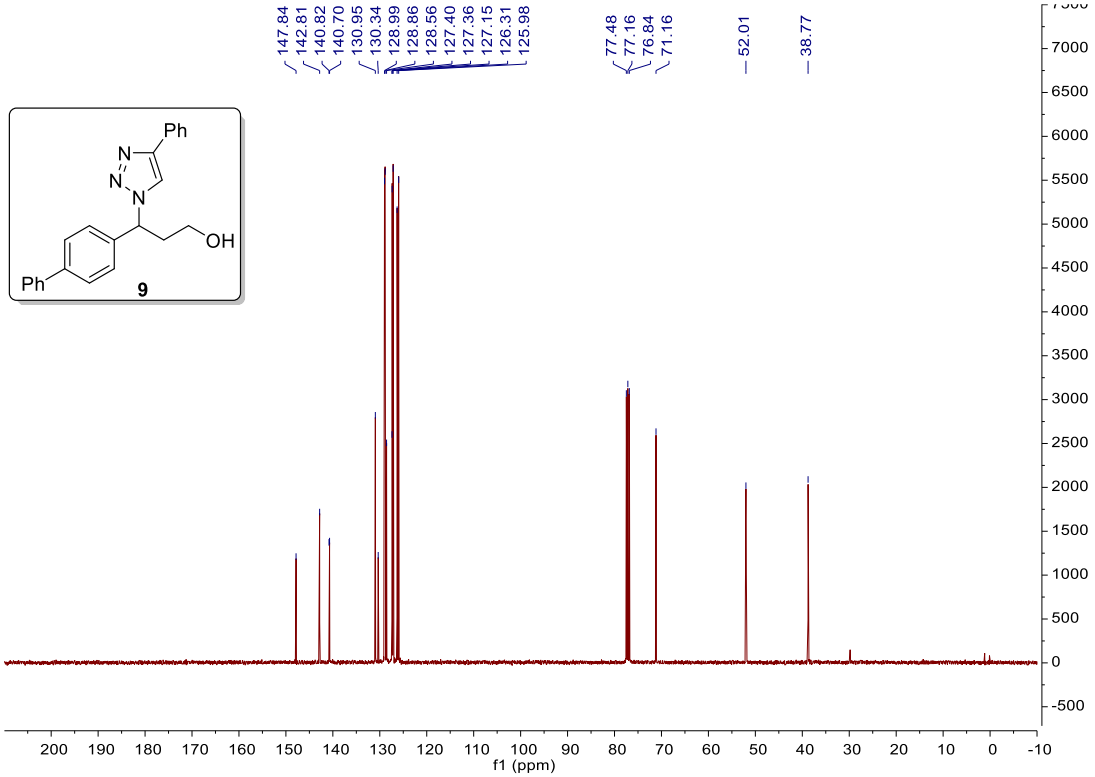
^{1}H NMR Spectrum of **8** ($CDCl_3$, 400 MHz)



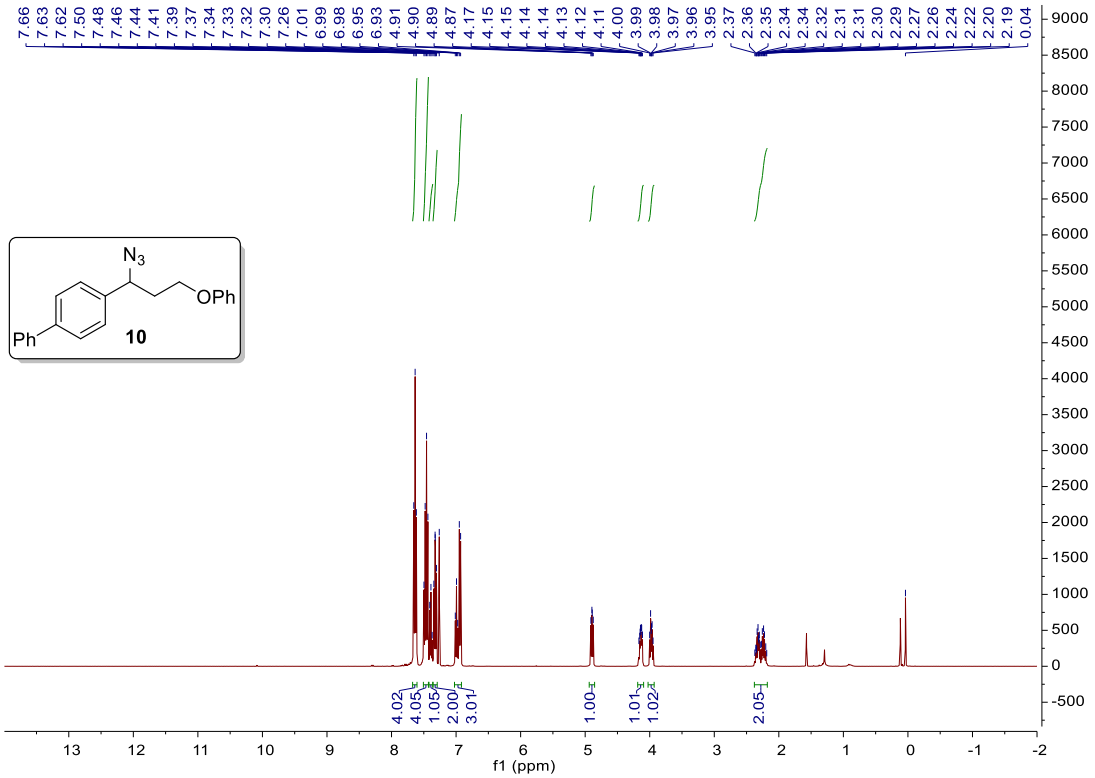
^{13}C NMR Spectrum of **8** ($CDCl_3$, 101 MHz)



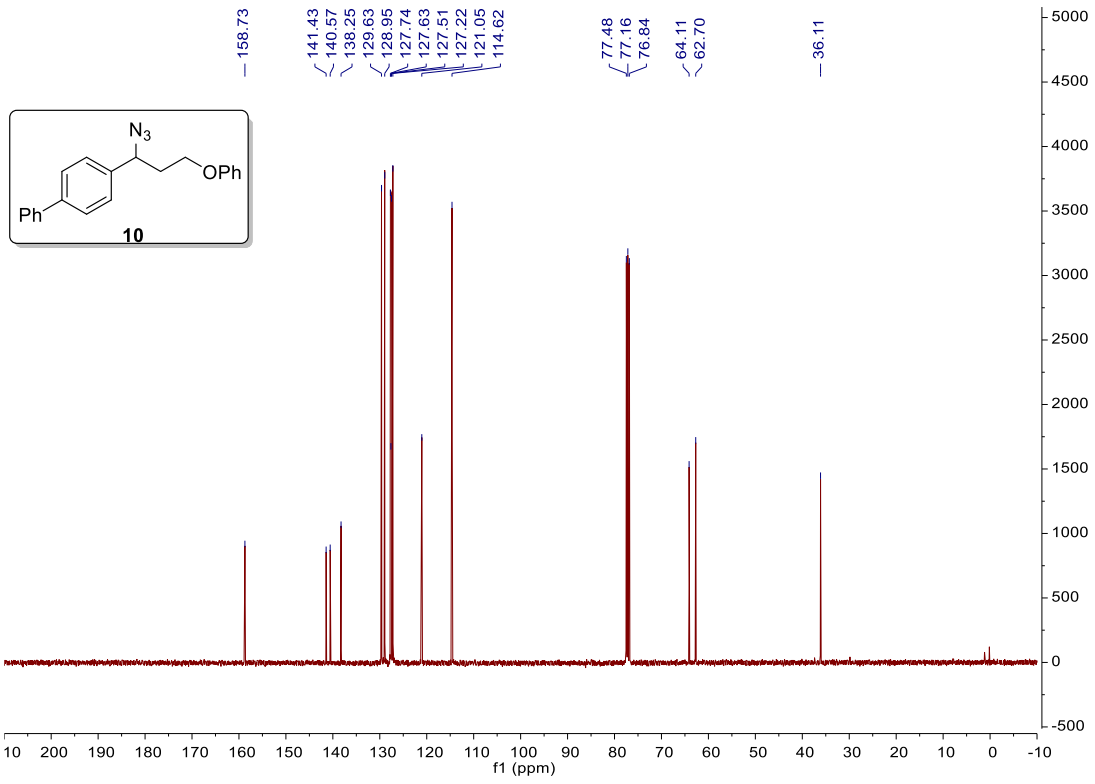
^{1}H NMR Spectrum of **9** ($CDCl_3$, 400 MHz)



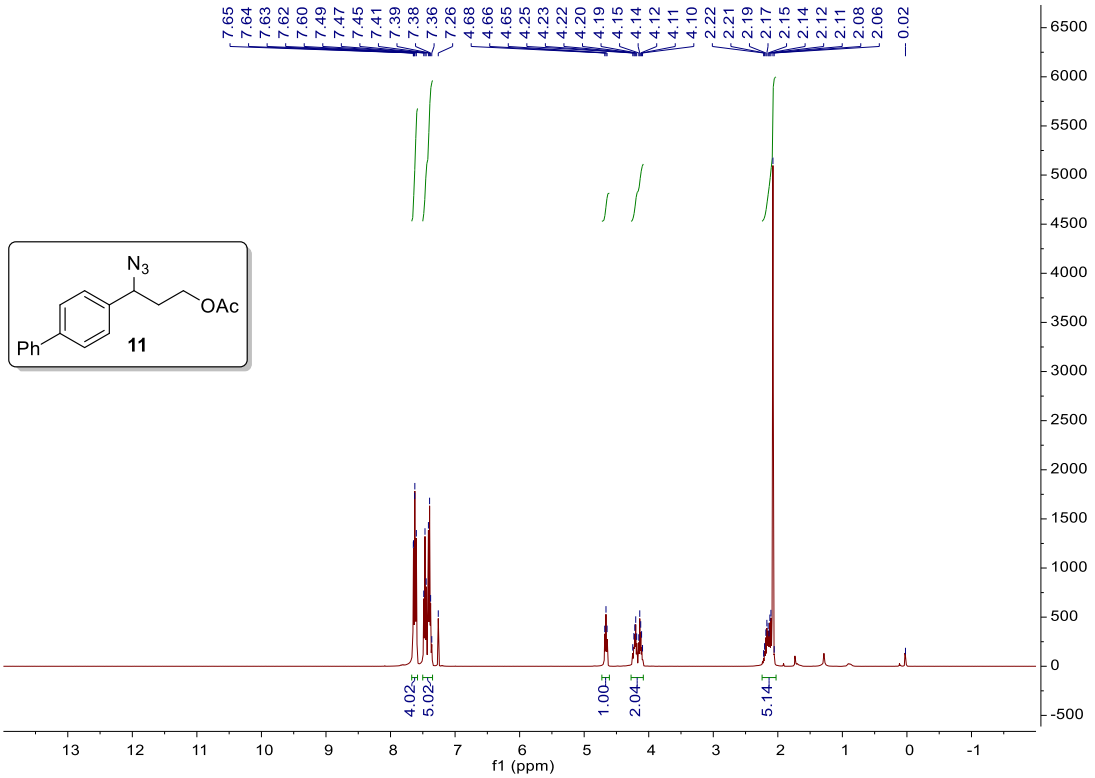
^{13}C NMR Spectrum of **9** ($CDCl_3$, 101 MHz)



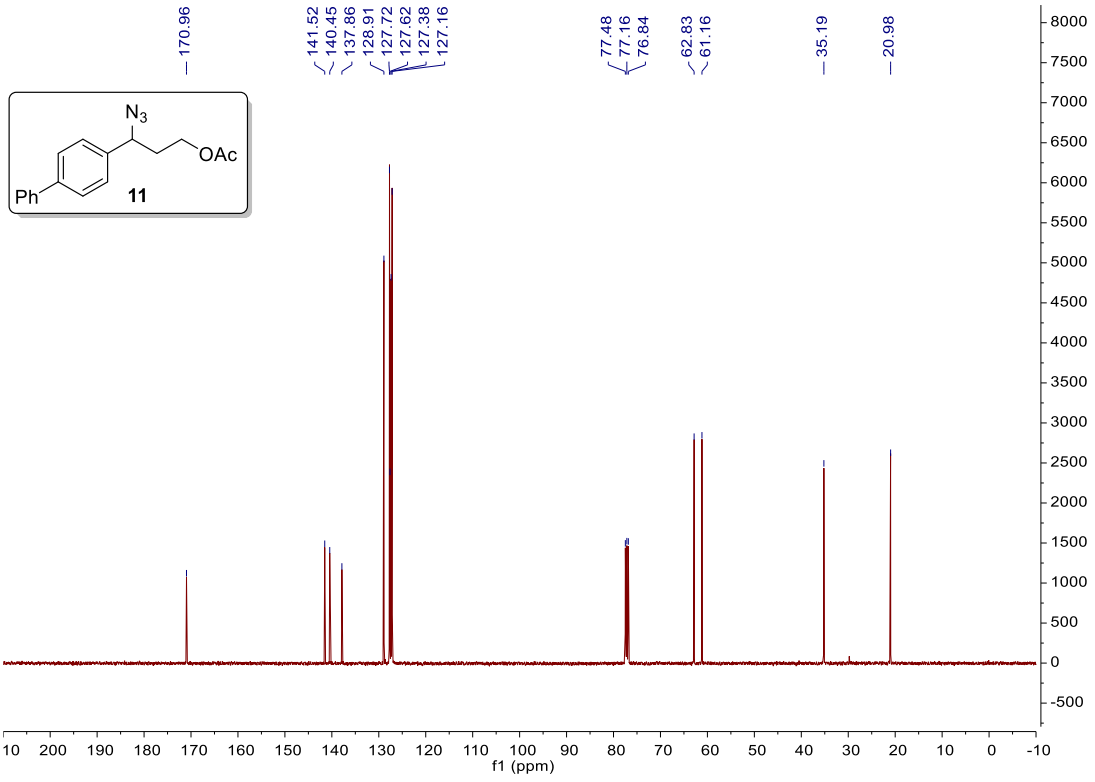
^{1}H NMR Spectrum of **10** ($CDCl_3$, 400 MHz)



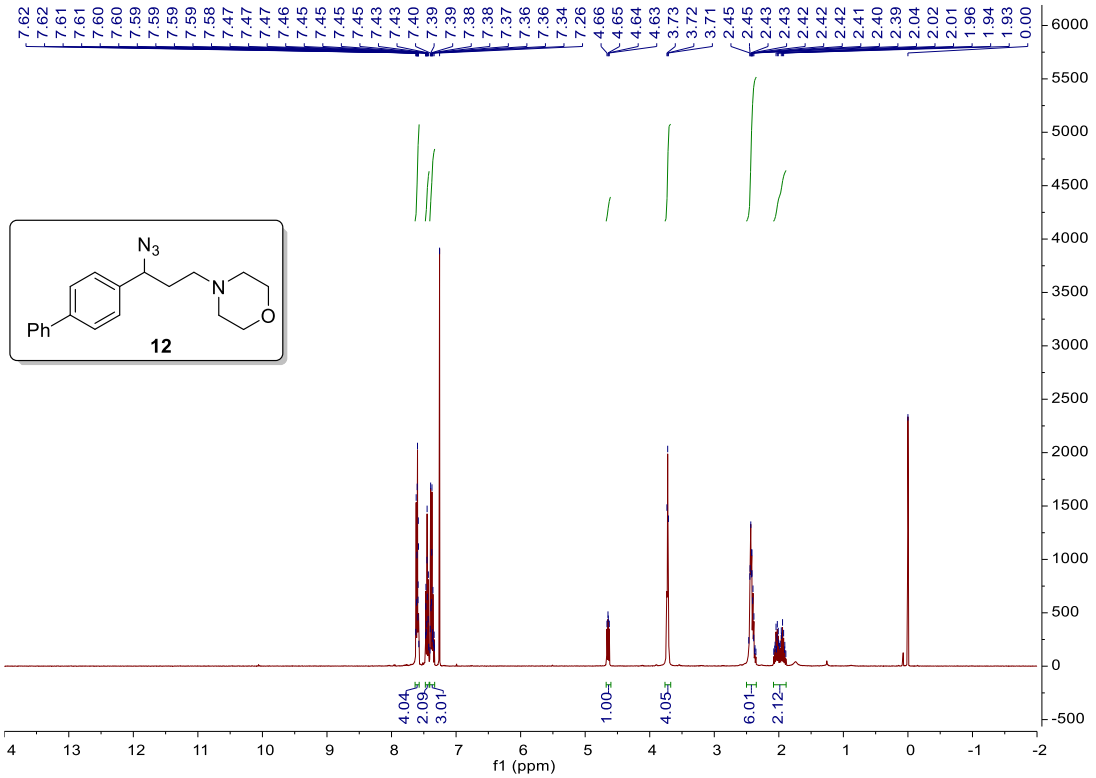
^{13}C NMR Spectrum of **10** ($CDCl_3$, 1011111 MHz)



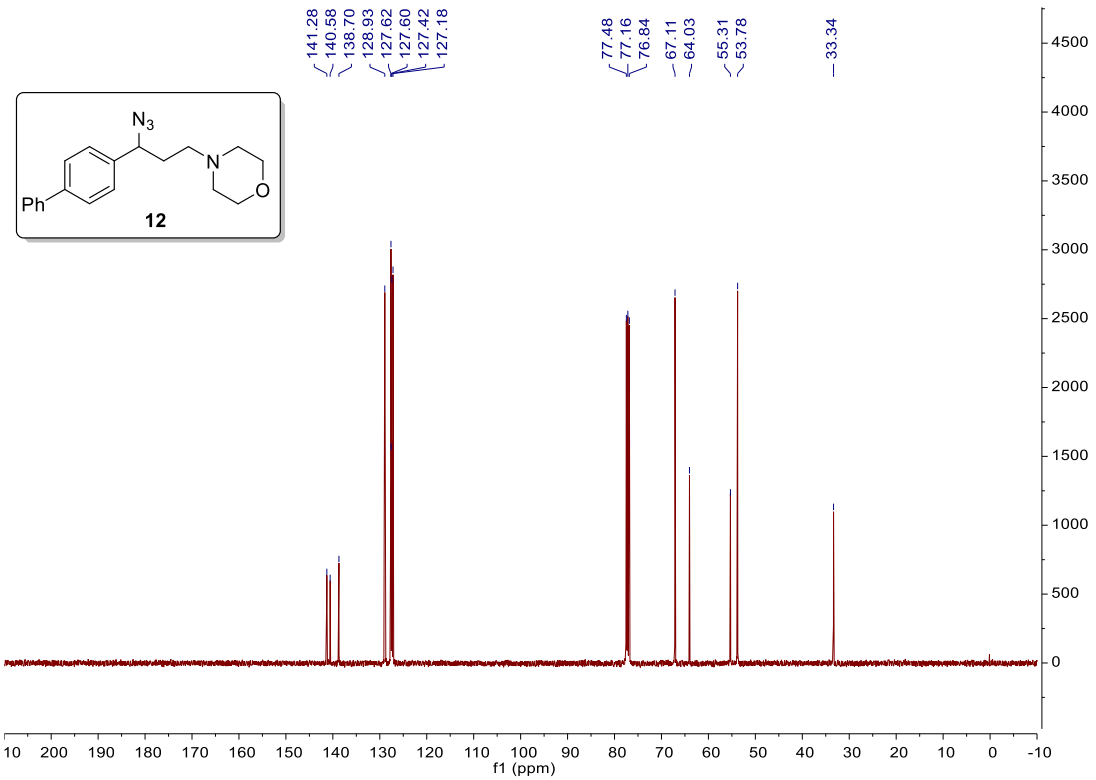
^{1}H NMR Spectrum of **11** ($CDCl_3$, 400 MHz)



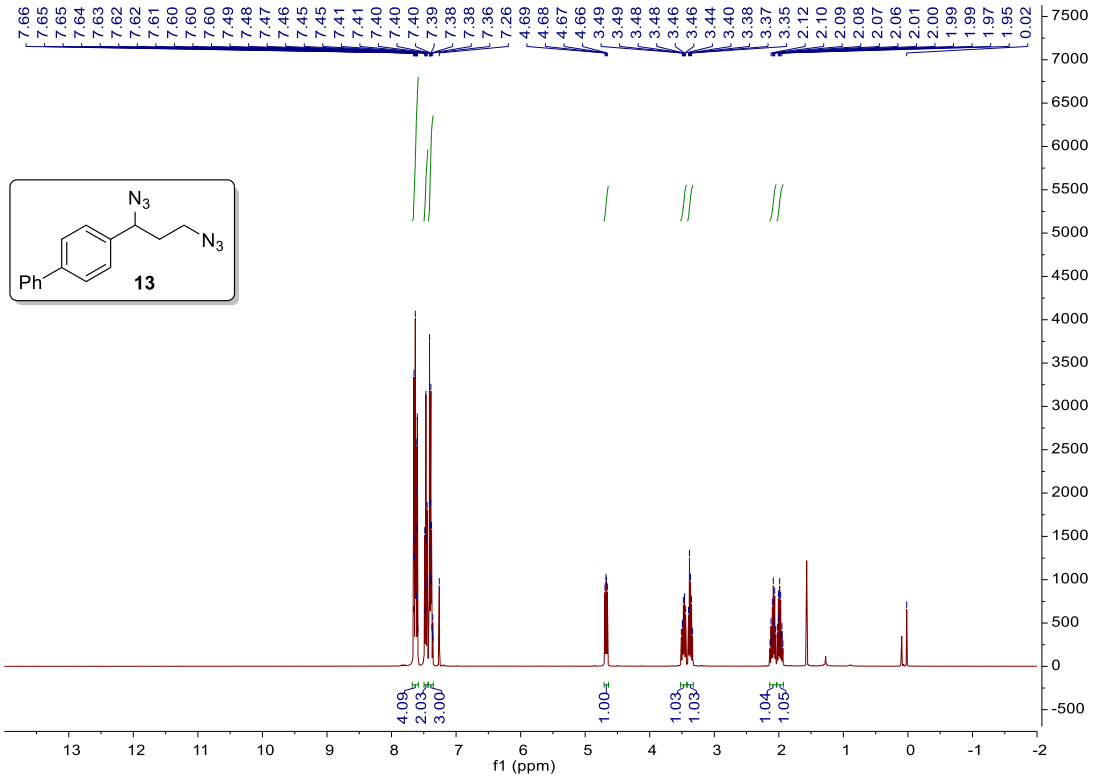
^{13}C NMR Spectrum of **11** ($CDCl_3$, 101 MHz)



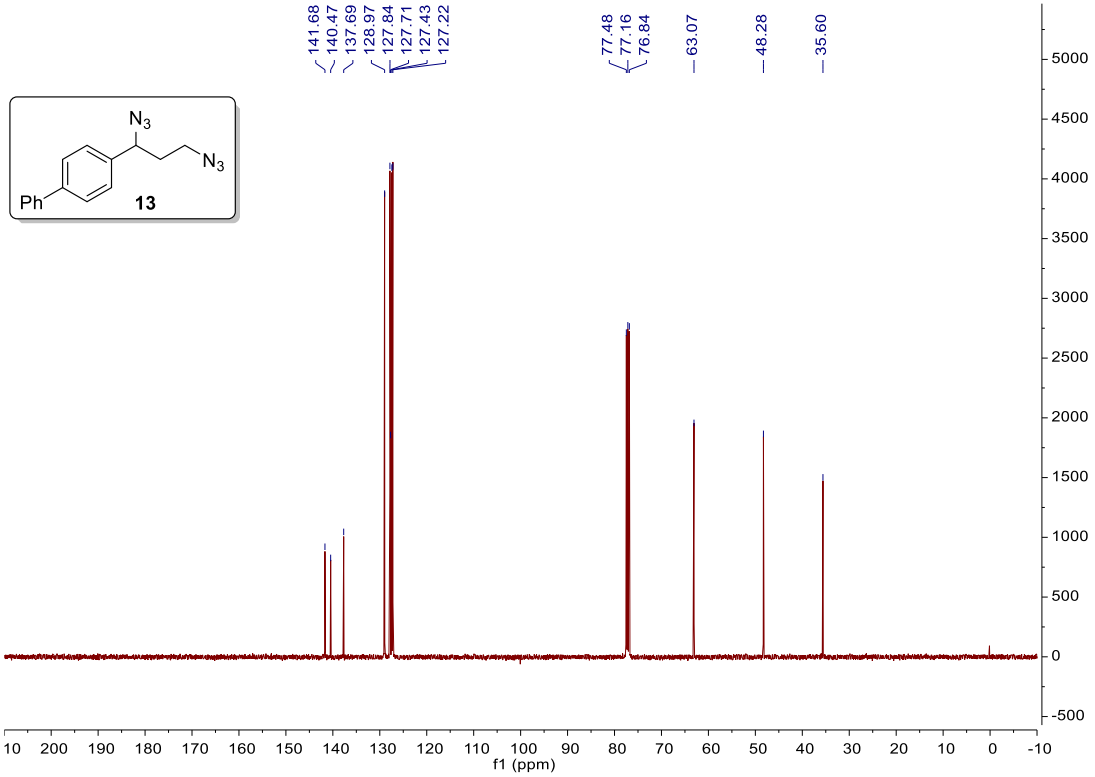
^{1}H NMR Spectrum of **12** ($CDCl_3$, 400 MHz)



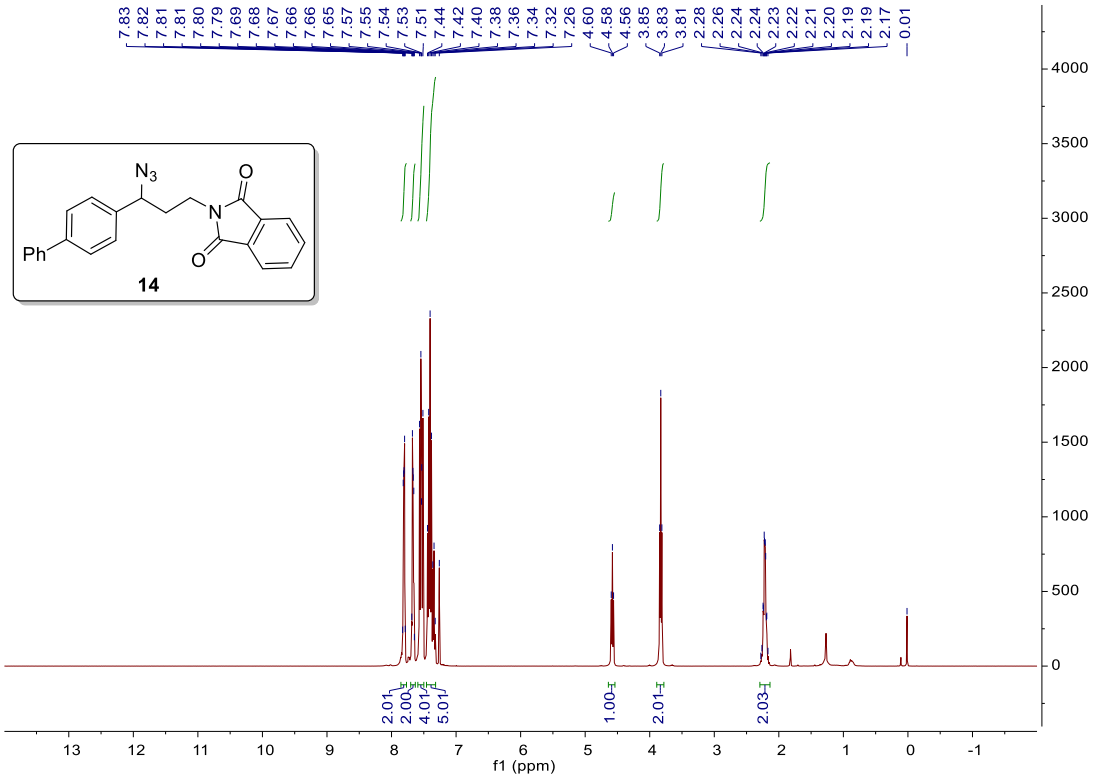
^{13}C NMR Spectrum of **12** ($CDCl_3$, 101 MHz)



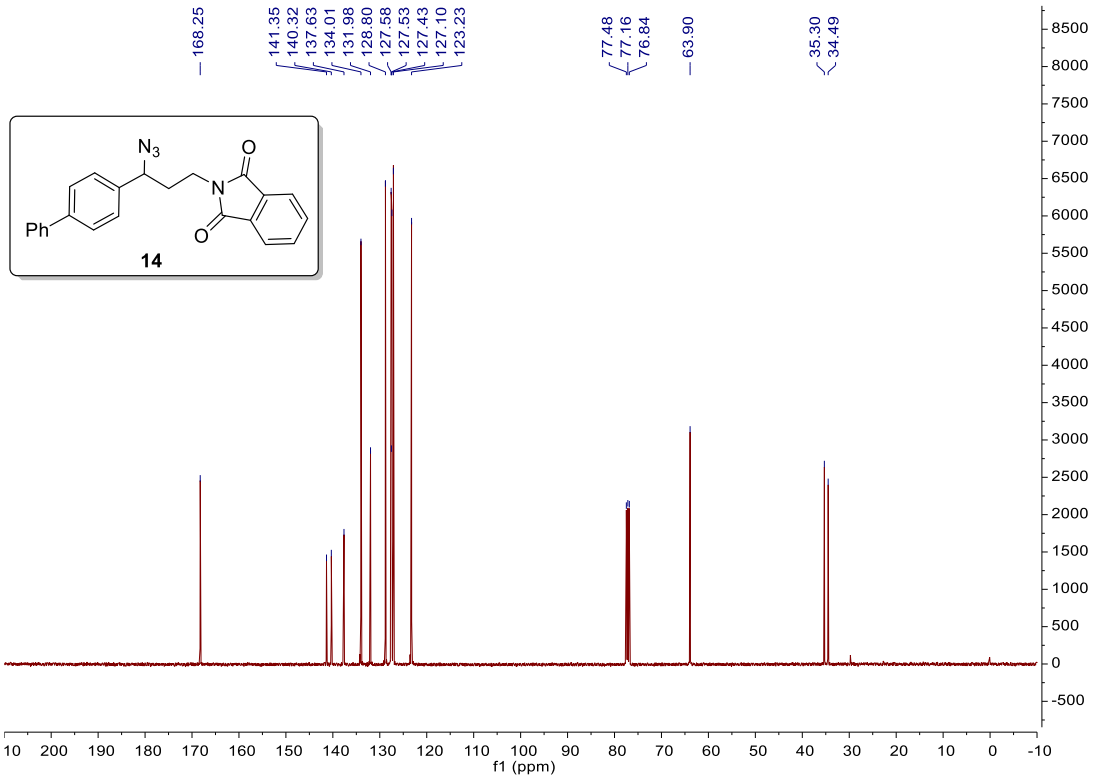
^{1}H NMR Spectrum of **13** ($CDCl_3$, 400 MHz)



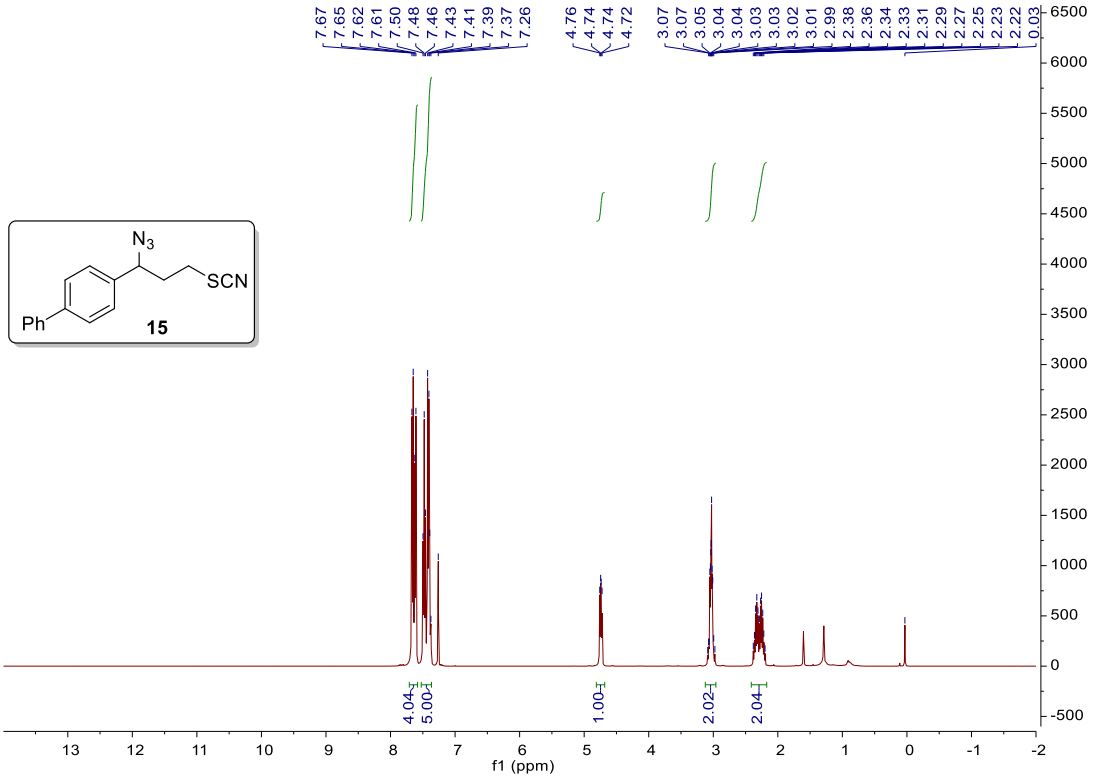
^{13}C NMR Spectrum of **13** ($CDCl_3$, 101 MHz)



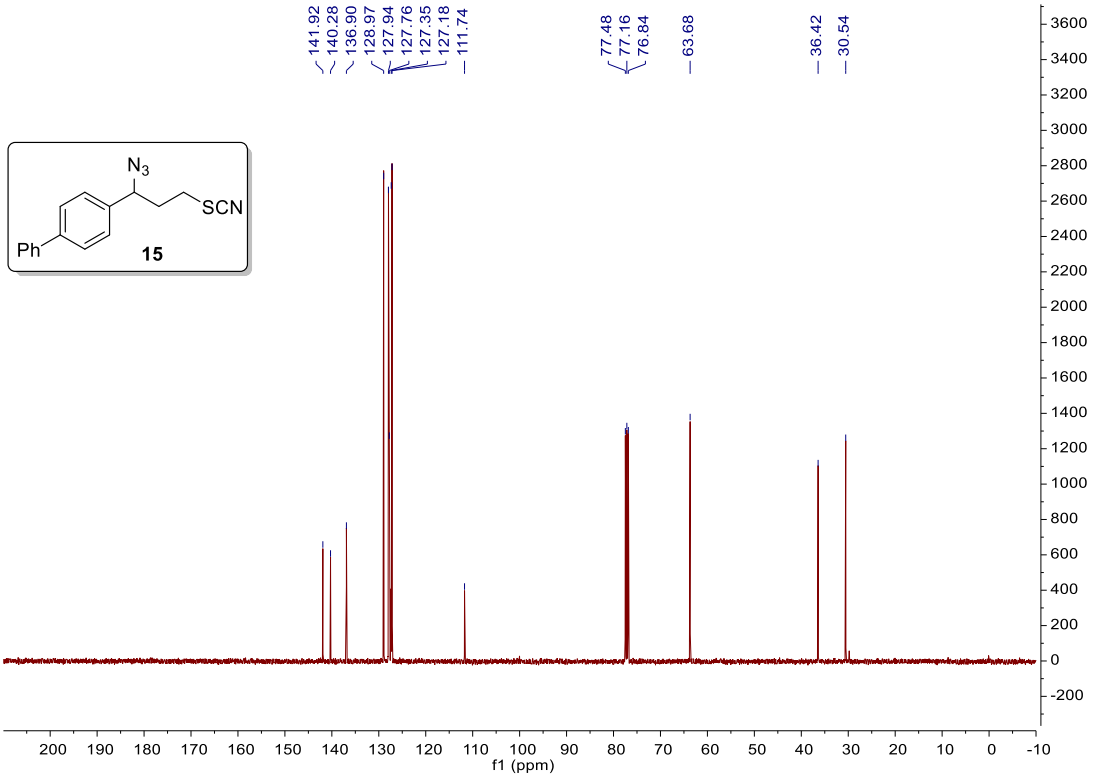
^{1}H NMR Spectrum of **14** ($CDCl_3$, 400 MHz)



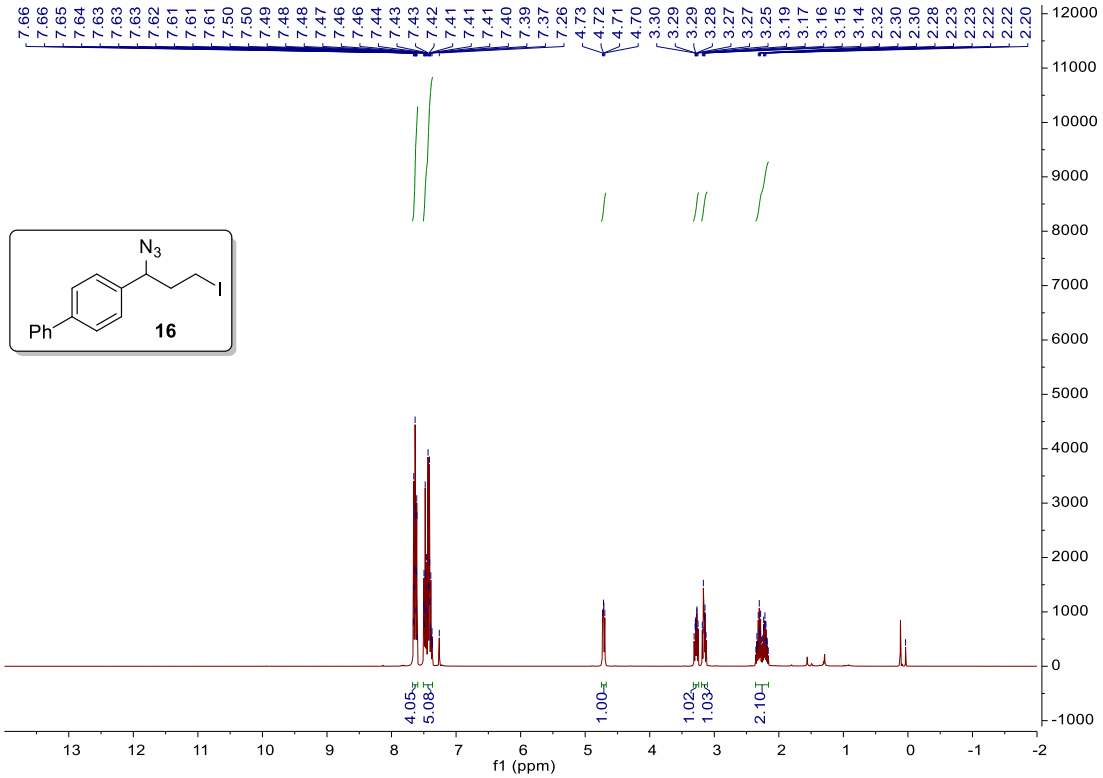
^{13}C NMR Spectrum of **14** ($CDCl_3$, 101 MHz)



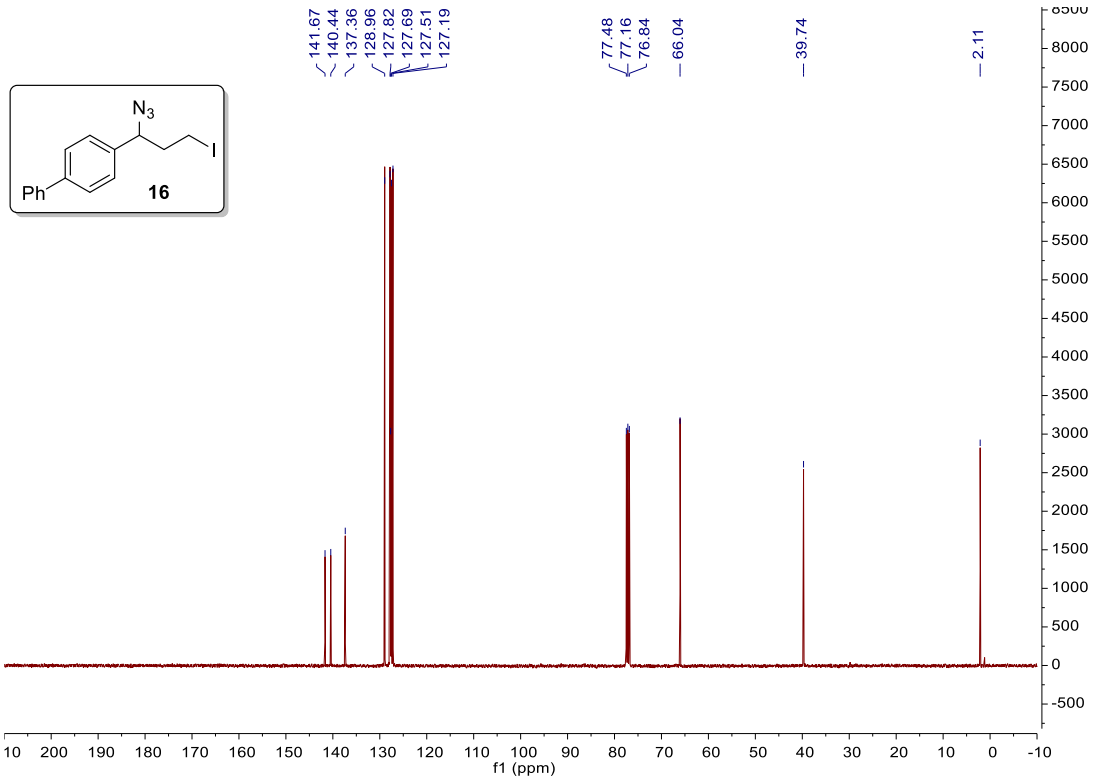
^{1}H NMR Spectrum of **15** ($CDCl_3$, 400 MHz)



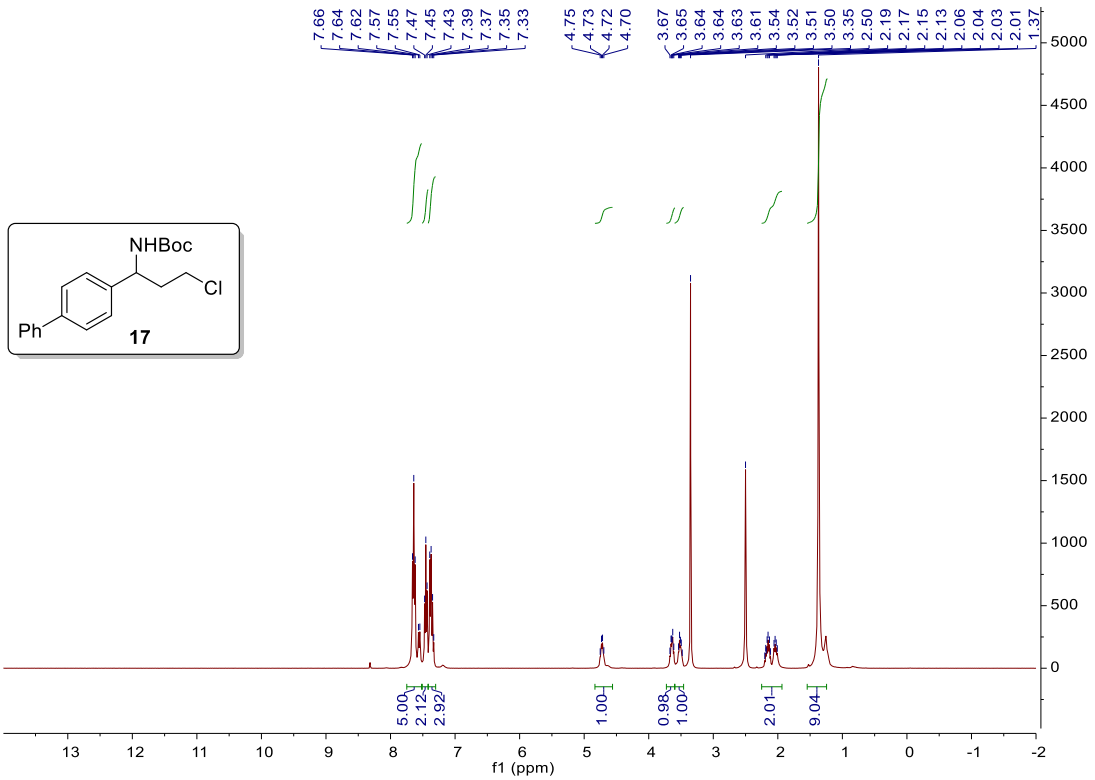
^{13}C NMR Spectrum of **15** ($CDCl_3$, 101 MHz)



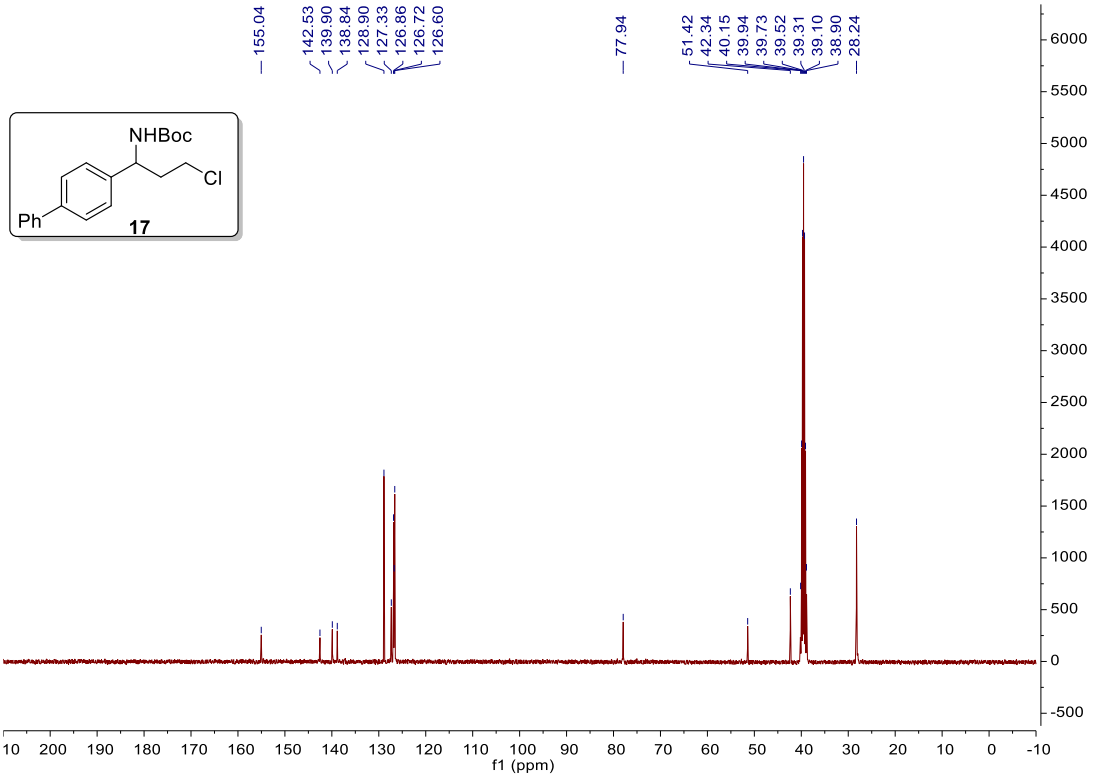
^{1}H NMR Spectrum of **16** ($CDCl_3$, 400 MHz)



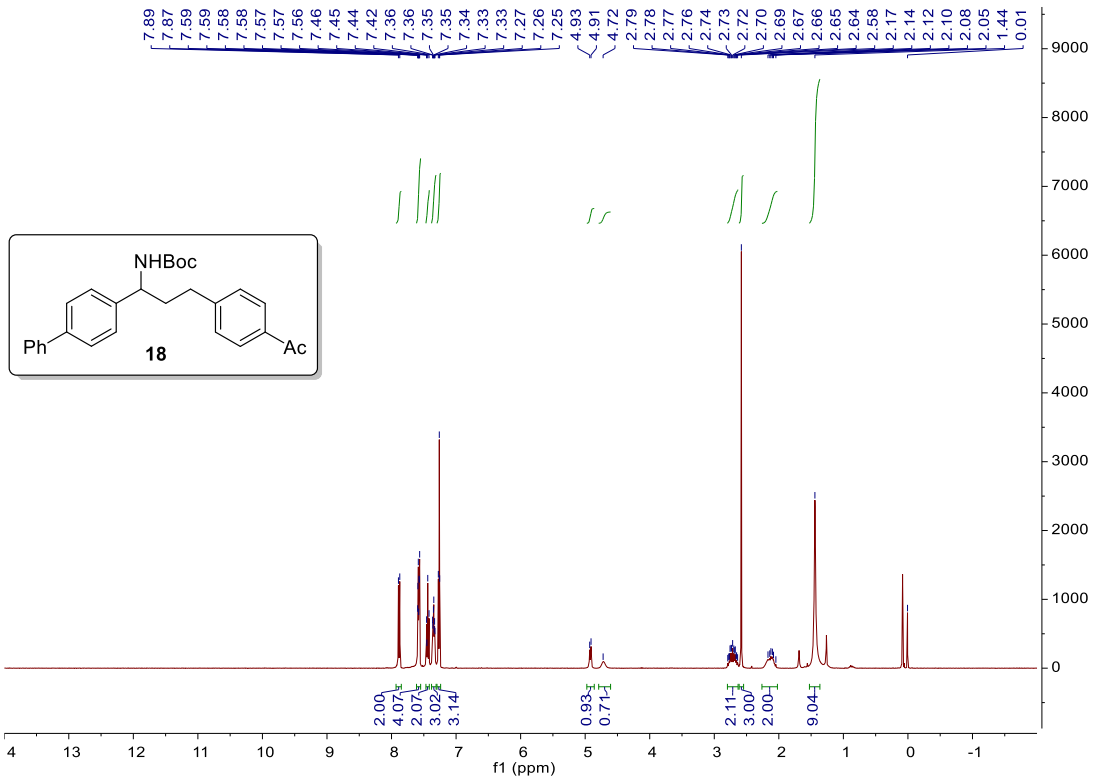
^{13}C NMR Spectrum of **16** ($CDCl_3$, 101 MHz)



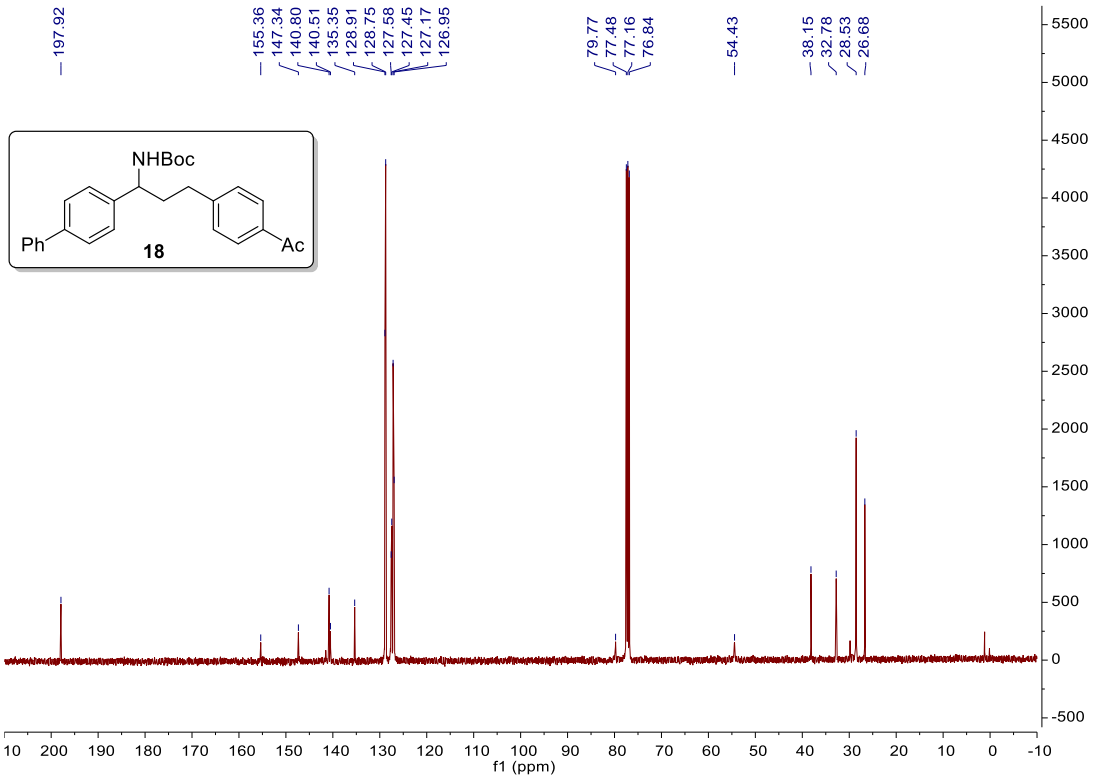
^{1}H NMR Spectrum of **17** (DMSO, 400 MHz)



^{13}C NMR Spectrum of **17** (DMSO, 101 MHz)



^{1}H NMR Spectrum of **18** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **18** ($CDCl_3$, 101 MHz)