Supporting Information

Electrocatalytic Conversion of ω-Azido Carboxylic Acids to 1-Pyrrolines *via* a Combined Process of Oxidative Decarboxylation and Intramolecular Schmidt Rearrangement

Kai Yang, Rui Li*, and Peiming Gu*

E-*State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, China.*
Rui Li, email: ruili@nxu.edu.cn;
Peiming Gu, email: gupm@nxu.edu.cn

Contents

Experimental Information..... S1

Reaction optimization Supplement..... S2

Cyclic Voltammetry Analysis..... S5

Additional Substrate Scope..... S7

Representative procedure for preparation of the pyrrolines..... S8

Experimental Data for the 1-pyrrolines..... S9

Representative procedure for preparation of the 5-azido-2-phenylpentanoic acid..... S17

Experimental Data for the azido carboxylic acid..... S18

Derivatization products..... S26

References..... S28

NMR spectra..... S29

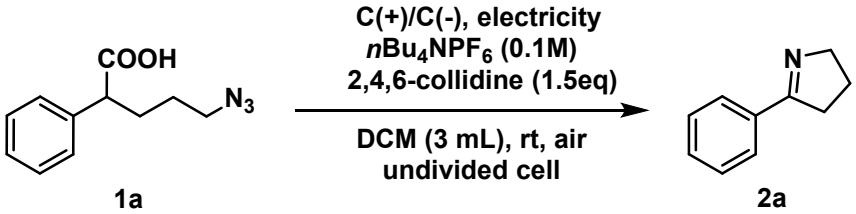
Experimental Information

All reagents were purchased from Titan, Innochem, Acros, Sigma-Aldrich, TCI, Energy chemical, Leyan or Adamas, DBU were purchased from Acros, and they were used as received. All solvents were purified by Vigor Solvent Purification System before used. The reactions were monitored by thin-layer chromatography (TLC) on 2.5 × 10 cm, 250 μm analytical plates coated with silica gel 60 F254, and they were purchased from Qingdao Haiyang Chemical Co. Ltd. Thin layer chromatography plates are observed by exposure to ultraviolet light (UV, 254 nm), using ninhydrin or phosphomolybdenic acid. Purification of the synthetic compounds by flash column chromatography employed neutral silica gel (200−300 mesh), which was purchased from Qingdao Haiyang Chemical Co. Ltd. The NMR spectra were recorded on a Bruker 400 MHz or 500MHz spectrometer, and $CDCl_3$ (δ = 7.26), acetone-d_6 (δ = 2.05) for ^1H NMR (400 MHz or 500MHz) and $CDCl_3$ (δ = 77.16), acetone-d_6 (δ = 29.84) for ^{13}C NMR (100MHz or 126 MHz). The ^{13}C NMR were obtained with an CPD technology. The IR spectra were recorded on a Beijing Beifen-Ruili Fourier transform infrared spectrometer, which was purchased from Beijing Beifen-Ruili Analytical Instrument (Group) CO. Ltd.

Reaction optimization Supplement

All optimization reactions were carried out on 0.1 mmol scale. Yield determined by ^{1}HNMR analysis using 1,3,5-Trimethoxybenzene as the internal standard.

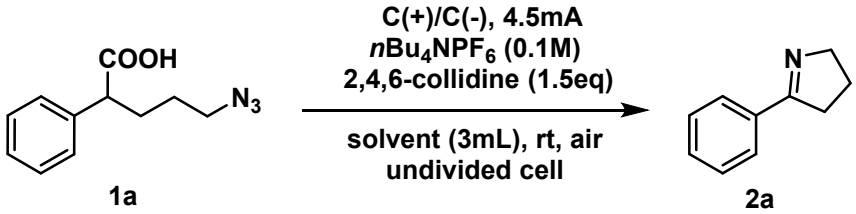
Table S1. Screening electricity for the reaction



1a 2a

entry	constant voltage/constant current	yield(%)
1	8mA	17
2	7mA	33
3	6mA	42
4	5mA	47
5	4mA	45
6	4.5mA	51
7	5V	24
8	4V	32
9	3V	38
10	2V	24
11	3.5V	35
12	no electricity	0

Table S2. Screening solvent for the reaction

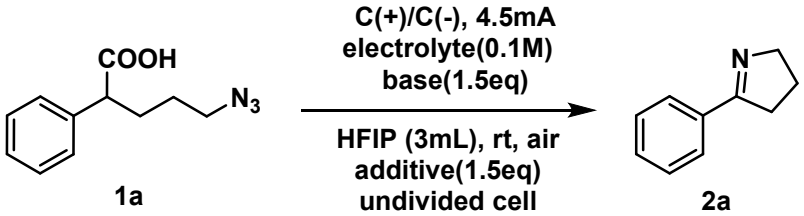


entry	solvent	yield(%)
1	Acetone	3
2	THF	10
3	DCE	40
4	$CHCl_3$	18
5	CCl_4	0
6	DCM	51
7	MeCN	9
8	HFIP [a]	84 (77) [b]
9	*i*PrOH	/ [c]
10	*t*BuOH	/
11	MeOH	0 [d]
12	HOAc	/
13		/
14		/

[a] 1,1,1,3,3,3-Hexafluoro-2-propanol. [b] Isolated yield.

[c] reactant did not dissolve. [d] The product is (4-azido-1-methoxybutyl) benzene, isolated yield = 96%.

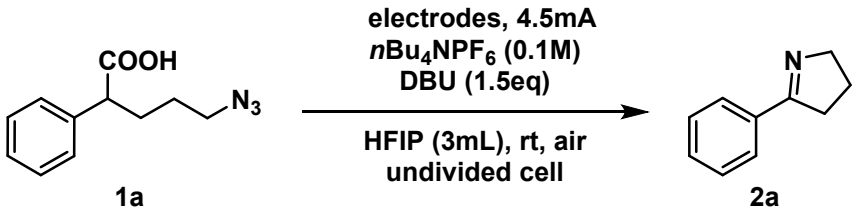
Table S3. Screening additive, eletrolyte and base for the reaction



entry	electrolyte	base	additive	yield(%)
1	nBu$_4$NPF$_6$	2,4,6-collidine	**AgPF$_6$**	22
2	nBu$_4$NPF$_6$	2,4,6-collidine	**AgClO$_4$**	28
3	nBu$_4$NPF$_6$	2,4,6-collidine	/	84
4	**Me$_4$NPF$_6$**	2,4,6-collidine	/	61
5	**LiClO$_4$**	2,4,6-collidine	/	3
6	***n*Bu$_4$NBr**	2,4,6-collidine	/	N.D.
7	***n*Bu$_4$NOH**	2,4,6-collidine	/	11
8	***n*Bu$_4$NF**	2,4,6-collidine	/	8
9	***n*Bu$_4$NBF$_4$**	2,4,6-collidine	/	trace
10	**Me$_4$NBF$_4$**	2,4,6-collidine	/	0
11	nBu$_4$NPF$_6$	**pyridine**	/	87
12	nBu$_4$NPF$_6$	**triethylenediamine**	/	68
13	nBu$_4$NPF$_6$	**piperridine**	/	65
14	nBu$_4$NPF$_6$	**2,6-lutidine**	/	79
15	nBu$_4$NPF$_6$	**limidazole**	/	80
16	nBu$_4$NPF$_6$	**3,5-lutidine**	/	77
17	nBu$_4$NPF$_6$	**DBU** [a]	/	91 (87) [b]
18	**no electrolyte**	DBU	/	0
19	nBu$_4$NPF$_6$	**no base**	/	0

[a] 1,8-Diazabicyclo[5.4.0]undec-7-ene. [b] Isolated yield.

Table S4. Screening eletrodes for the reaction



entry	electrodes	yield(%)
1	Pt (+) / C (-)	10
2	C (+) / Pt (-)	83
3	RVC (+) / C (-)	56
4	GC(+) / C (-)	40

Cyclic Voltammetry Analysis

Cyclic voltammetry was recorded with 3 mm disc glassy carbon working electrode, platinum plate counter electrode and aqueous Ag/AgCl reference electrode.

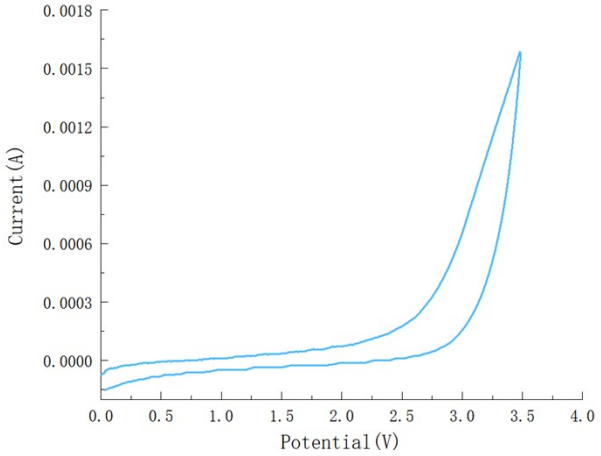


Figure 1: Cyclic voltammograms at 100 mV/s in HFIP. nBu$_4$NPF$_6$ (0.2 M).

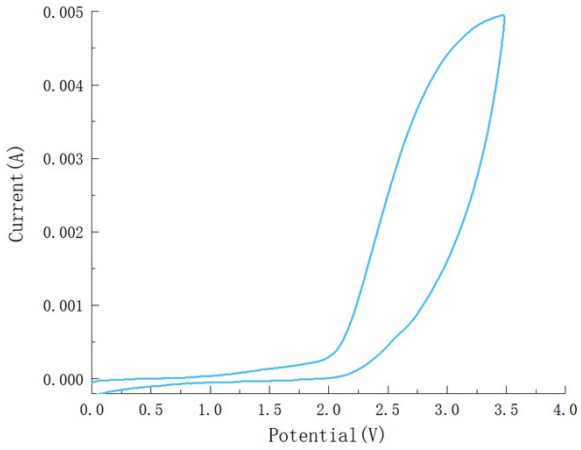


Figure 2: Cyclic voltammograms at 100 mV/s in HFIP. Azido carboxylic acid x (0.5 mmol) + nBu$_4$NPF$_6$ (0.2M).

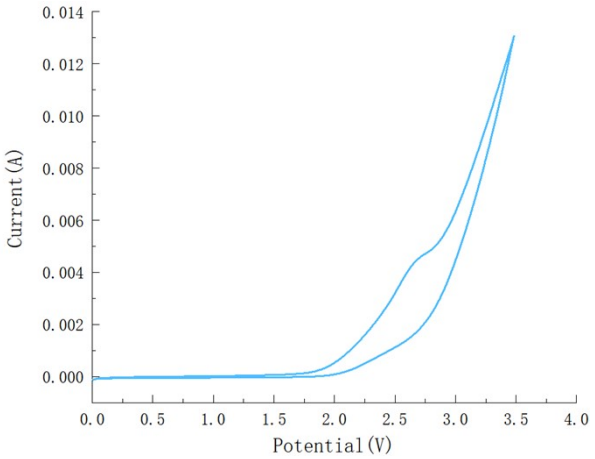


Figure 3: Cyclic voltammograms at 100 mV/s in HFIP. nBu$_4$NPF$_6$ (0.2 M) + DBU (0.75 mmol).

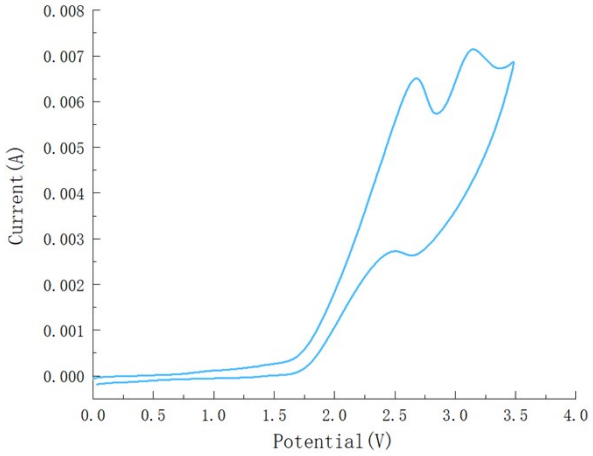


Figure 4: Cyclic voltammograms at 100 mV/s in HFIP. Azido carboxylic acid x (0.5 mmol) + nBu$_4$NPF$_6$ (0.2M) + DBU (0.75 mmol).

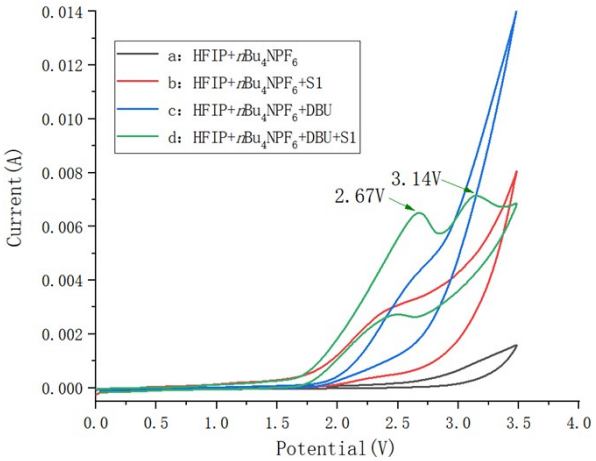
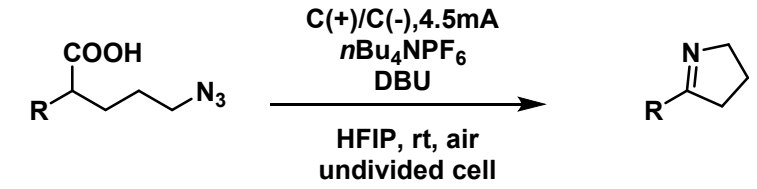
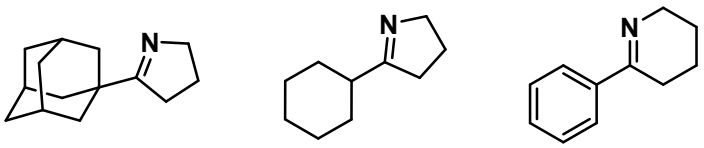


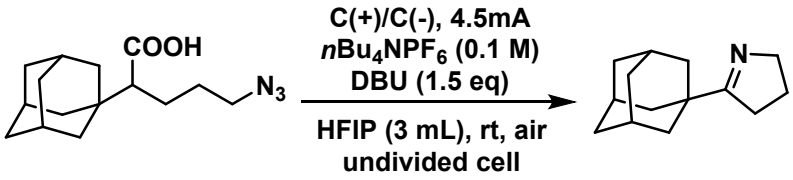
Figure 5: Comparison of cyclic voltammetry

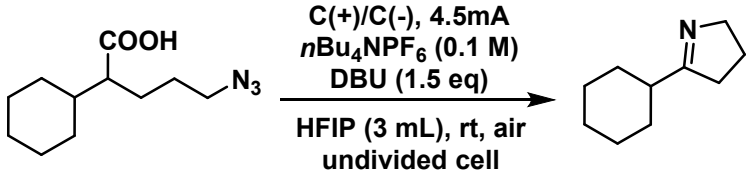
Additional Substrate Scope



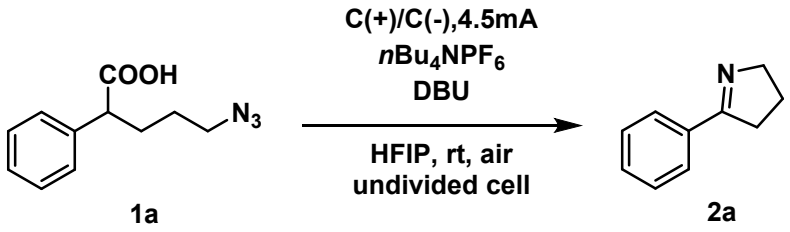


2aa,30% (nmr yield) 2ab,23% (nmr yield) 2ac, N.D.





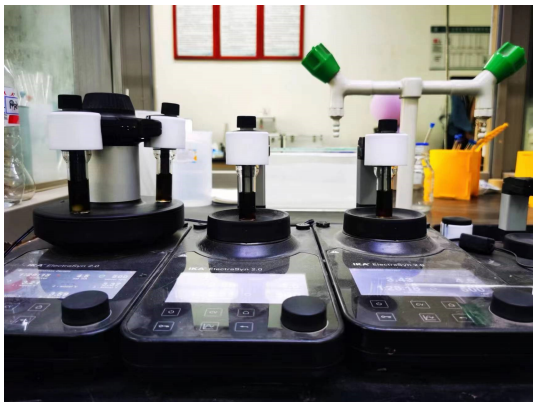
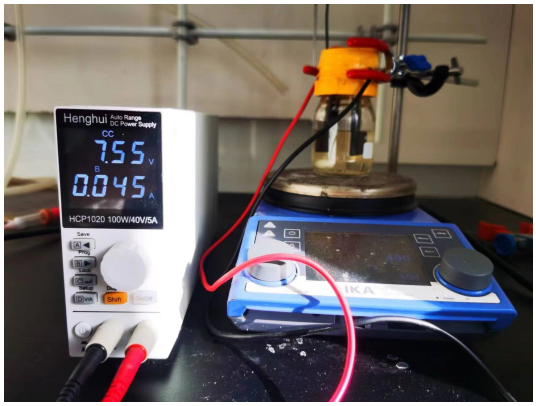
Representative procedure for preparation of the pyrroline



Air and moisture were not excluded. add 5-azido-2-phenylpentanoic acid **1a** (21.9 mg, 0.1 mmol, 1 eq), *n*-Bu_4NPF_6 (98%) (118 mg, 0.3 mmol/0.1 M), DBU (22.8 mg, 0.15 mmol, 1.5 eq), HFIP (3 mL) and a stir bar to the ElectraSyn vial (5 mL). The ElectraSyn vial cap equipped with anode (graphite) and cathode (graphite) were inserted into the mixture. Pre-stir until all reactants are dissolved, the reaction mixture was electrolyzed at a constant current of 4.5 mA for proper time in monitored by TLC (about 110 min). The ElectraSyn vial cap was removed, electrodes and ElectraSyn vial were rinsed with Et_2O (2 mL). Then, the crude mixture was further diluted with Et_2O (5 mL) , and the mixture was washed with saturated $NaHCO_3$ (3 ml), dried over Na_2SO_4, and concentrated in vacuo. Purification by flash chromatography on silica gel using Hexane/EtOAc (10:1) as eluent afforded 5-phenyl-3,4-dihydro-2H-pyrrole **2a** as a light yellow oil (12.6 mg, the yield was 87 %. R_f =0.68).

Setting up the IKA/ElectraSyn 2.0:

New Experiments→ Constant Current→ 4.5mA→ Run Continuous→ Do not alternate the polarity→ Start.

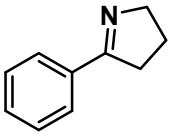



Left: Five 0.1 mmol scale experiments were performed simultaneously.
Right: 2 mmol scale experimental device.

Known compounds

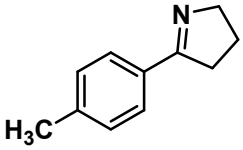
2a, 2b, 2c, 2h, 2i, 2m, 2n, 2q [1], 2f [2], 2o, 2r, 2s [3], 2g, 2t, 2y [4], 2z [5], 2e, 2j, 2x [6], 2l [7], 2d [8]

5-phenyl-3,4-dihydro-2H-pyrrole (2a)



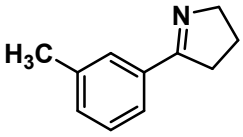
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.31 (m, 3H), 4.06 (d, *J* = 7.4 Hz, 2H), 2.94 (d, *J* = 8.8 Hz, 2H), 2.08 – 1.98 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.4, 134.8, 130.4, 128.5 (2), 127.7 (2), 61.7, 35.0, 22.8.

5-(p-tolyl)-3,4-dihydro-2H-pyrrole (2b)



5-(p-tolyl)-3,4-dihydro-2H-pyrrole **2b** (71.9 mg) was prepared from azide carboxylic acid **1b** (116.6 mg, 0.5 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 90 %, orange solid, M.p.=69-77 °C, R_f =0.70 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.05 (t, *J* = 7.3 Hz, 2H), 2.93 (t, *J* = 8.7 Hz, 2H), 2.38 (s, 3H), 2.07 – 1.97 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.3, 140.6, 132.1, 129.2 (2), 127.7 (2), 61.6, 35.0, 22.8, 21.5.

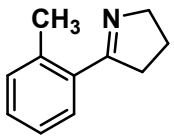
5-(m-tolyl)-3,4-dihydro-2H-pyrrole (2c)



5-(m-tolyl)-3,4-dihydro-2H-pyrrole **2c** (38.7 mg) was prepared from azide carboxylic acid **1c** (93.2 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was

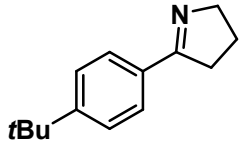
61 %, yellow oil, R_f =0.71 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.71 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.06 (t, *J* = 7.3 Hz, 2H), 2.95 (t, *J* = 8.2 Hz, 2H), 2.39 (s, 3H), 2.08 – 1.99 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.8, 138.2, 134.6, 131.3, 128.5, 128.3, 125.0, 61.5, 35.1, 22.8, 21.5.

5-(o-tolyl)-3,4-dihydro-2H-pyrrole (2d)



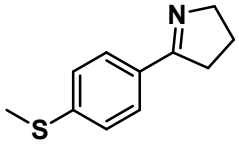
5-(o-tolyl)-3,4-dihydro-2H-pyrrole **2d** (37.3 mg) was prepared from azide carboxylic acid **1d** (93.2 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 59 %, orange oil, R_f =0.71 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.17 (m, 4H), 4.09 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 9.2 Hz, 1H), 2.51 (s, 3H), 2.05 – 1.95 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.3, 137.2, 135.3, 131.4, 129.1, 128.9, 125.7, 62.15, 38.5, 22.9, 21.7.

5-(4-(tert-butyl)phenyl)-3,4-dihydro-2H-pyrrole (2e)



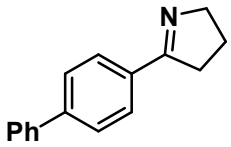
5-(4-(tert-butyl)phenyl)-3,4-dihydro-2H-pyrrole **2e** (70.5 mg) was prepared from azide carboxylic acid **1e** (110.1 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline x, the yield was 88 %, orange oil, R_f =0.78 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 4.05 (t, *J* = 7.4 Hz, 2H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.06 – 1.97 (m, 2H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.4, 153.9, 131.9, 127.6 (2), 125.5 (2), 61.5, 35.1, 31.3 (3), 22.8.

5-(4-(methylthio)phenyl)-3,4-dihydro-2H-pyrrole (2f)



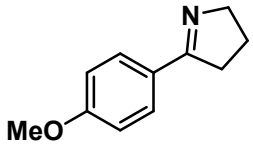
5-(4-(methylthio)phenyl)-3,4-dihydro-2H-pyrrole **2f** (41.4 mg) was prepared from azide carboxylic acid **1f** (106.1 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 54 %, white solid, M.p.=93-98^{o}C, R_f =0.73 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.06 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 8.7 Hz, 2H), 2.50 (s, 3H), 2.09 – 1.99 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.3, 142.3, 130.8, 128.3 (2), 125.8 (2), 61.1, 35.0, 22.7, 15.4.

5-([1,1'-biphenyl]-4-yl)-3,4-dihydro-2H-pyrrole (2g)



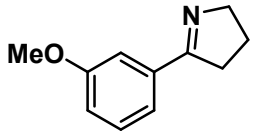
5-([1,1'-biphenyl]-4-yl)-3,4-dihydro-2H-pyrrole **2g** (31.3 mg) was prepared from azide carboxylic acid **1g** (88.6 mg, 0.3 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 47 %, white solid, M.p.=154-159 °C, R_f =0.82 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)**δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 4.10 (t, *J* = 7.4 Hz, 2H), 2.98 (t, *J* = 8.9 Hz, 2H), 2.11 – 2.01 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.1, 143.1, 140.6, 133.7, 128.9 (2), 128.2 (2), 127.8, 127.3 (2), 127.2 (2), 61.8, 35.1, 22.9.

5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole (2h)



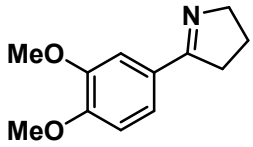
5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole **2h** (55.6 mg) was prepared from azide carboxylic acid **1h** (99.7 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 79 %, light yellow solid, M.p.=57-63 °C, R_f =0.57 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.03 (t, *J* = 7.3 Hz, 2H), 3.83 (s, 3H), 2.91 (d, *J* = 9.3 Hz, 2H), 2.06 – 1.97 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.8, 161.5, 129.4 (2), 127.6, 113.9 (2), 61.4, 55.4, 35.0, 22.8.

5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole (2i)



5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole **2i** (42.7 mg) was prepared from azide carboxylic acid **1i** (99.7 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 61 %, orange oil, R_f =0.76 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.46 (s, 1H), 7.38 – 7.26 (m, 3H), 4.07 (d, *J* = 7.8 Hz, 2H), 3.85 (s, 3H), 2.93 (t, *J* = 9.1 Hz, 2H), 2.08 – 1.98 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.4, 159.8, 136.2, 129.5, 120.6, 117.1, 111.9, 61.7, 55.5, 35.2, 22.9.

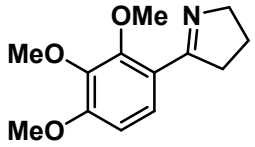
5-(3,4-dimethoxyphenyl)-3,4-dihydro-2H-pyrrole (2j)



5-(3,4-dimethoxyphenyl)-3,4-dihydro-2H-pyrrole **2j** (40.4 mg) was prepared from azide carboxylic acid **1j** (111.6 mg，0.4 mmol), according to the procedure for preparation of the

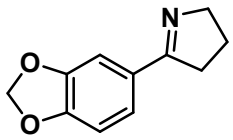
pyrroline **2a**, the yield was 49 %, yellow solid, M.p.=72-74 °C, R_f =0.76 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.63 (s, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.07 (t, *J* = 7.3, 2H), 3.97 (s, 3H), 3.94 (s, 3H), 2.97 (t, *J* = 8.8, 2H), 2.12 – 2.02 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.8, 151.8, 149.2, 126.7, 122.3, 110.4, 110.1, 60.4, 56.2, 56.0, 34.9, 22.6. **HRMS (APCI)**: calcd for $C_{12}H_{15}NO_2$+H (M^+ + H), 206.1175; found, 206.1172. **IR (KBr)**: 1587, 1515, 762, cm^{-1}.

5-(2,3,4-trimethoxyphenyl)-3,4-dihydro-2H-pyrrole (2k)



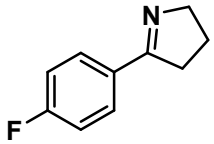
5-(2,3,4-trimethoxyphenyl)-3,4-dihydro-2H-pyrrole **2k** (26.7 mg) was prepared from azide carboxylic acid **2k** (92.7 mg, 0.3 mmol) according to the procedure for preparation of the pyrroline 2a, the yield was 38 %, yellow solid, M.p.=68-73 °C, R_f =0.73 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.07 (s, 1H), 4.03 (t, J = 8.2 Hz, 1H), 3.89 (s, 2H), 3.87 (s, 1H), 2.92 (t, J = 9.2 Hz, 1H), 2.06 – 1.98 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.40, 153.26 (2), 140.50, 130.03, 105.24 (2), 61.39, 61.02, 56.40 (2), 35.14, 22.87. **HRMS (APCI)**: calcd for $C_{13}H_{17}NO_3$+H (M^+ + H), 236.1278; found, 236.1281. **IR (KBr)**: 2931, 1584, 1219, 864 cm^{-1}.

5-(benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-2H-pyrrole (2l)



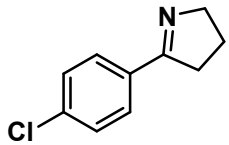
5-(benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-2H-pyrrole **2l** (35 mg) was prepared from azide carboxylic acid **1l** (105.3 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 46 %, light yellow solid, M.p.=92-94 °C, R_f =0.76 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.42 (d, *J* = 1.7 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H), 4.02 (t, *J* = 7.3 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H), 2.06 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.6, 149.6, 148.1, 122.7, 108.0, 107.6, 101.5, 61.4, 35.1, 22.9.

5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole (2m)



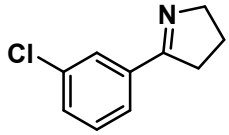
5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole **2m** (65.5 mg) was prepared from azide carboxylic acid **1m** (118.6 mg, 0.5 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 80 %, orange solid, M.p.=32-38 °C, R_f =0.79 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.84 (dd, *J* = 8.7 Hz, 2H), 7.08 (t, *J* = 8.7 Hz, 2H), 4.06 (t, *J* = 7.3 Hz, 2H), 2.97 – 2.89 (m, 2H), 2.10 – 2.00 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.4, 164.3 (d, *J* = 250.7 Hz), 130.9 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 8.6 Hz) (2), 115.6 (d, *J* = 21.6 Hz) (2), 61.5, 35.1, 22.9.

5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrole (2n)



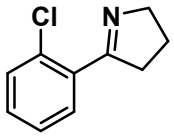
5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrole **2n** (83.8 mg) was prepared from azide carboxylic acid **1n** (126.8 mg, 0.5 mmol) according to the procedure for preparation of the pyrroline **2n**, the yield was 93 %, colorless oil, R_f =0.68 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 4.06 (t, *J* = 7.5 Hz, 2H), 2.93 – 2.89 (m, 2H), 2.09 – 1.99 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.4, 136.5, 133.3, 129.1 (2), 128.8 (2), 61.8, 35.0, 22.9.

5-(3-chlorophenyl)-3,4-dihydro-2H-pyrrole (2o)



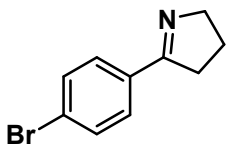
5-(3-chlorophenyl)-3,4-dihydro-2H-pyrrole **2o** (48.3 mg) was prepared from azide carboxylic acid **1o** (126.8 mg, 0.5 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 54 %, light yellow solid, M.p.=50-52 ºC, R_f =0.68 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 4.07 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.10 – 2.00 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.3, 136.5, 134.7, 130.4, 129.8, 127.9, 125.9, 61.8, 35.1, 22.8.

5-(2-chlorophenyl)-3,4-dihydro-2H-pyrrole (2p)



5-(2-chlorophenyl)-3,4-dihydro-2H-pyrrole **2p** (26.8 mg) was prepared from azide carboxylic acid **1p** (101.6 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 37 %, colorless oil, R_f =0.82 (MeOH/DCM =1/20), **^{1}H-NMR (500MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 4.04 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 8.1 Hz, 2H), 2.14 – 1.98 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.3, 135.7, 132.6, 130.4, 130.4, 130.3, 126.9, 61.4, 38.6, 23.6. **HRMS (APCI)**: calcd for $C_{10}H_{10}ClN$+H (M^+ + H), 180.0574; found, 180.0572. **IR (KBr)**: 1474, 1607, 754 cm^{-1}.

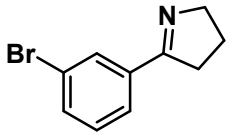
5-(4-bromophenyl)-3,4-dihydro-2H-pyrrole (2q)



5-(4-bromophenyl)-3,4-dihydro-2H-pyrrole **2q** (76.6 mg) was prepared from azide carboxylic acid **1q** (119.2 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the

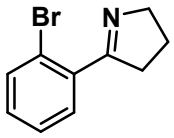
yield was 85 %, light yellow solid, M.p.=82-84 °C, R_f =0.79 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 4.05 (t, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz, 2H), 2.04 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.4, 133.7, 131.8 (2), 129.3 (2), 124.9, 61.8, 35.0, 22.9.

5-(3-bromophenyl)-3,4-dihydro-2H-pyrrole (2r)



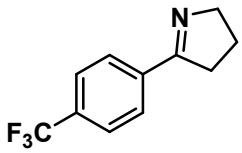
5-(3-bromophenyl)-3,4-dihydro-2H-pyrrole **2r** (57.7 mg) was prepared from azide carboxylic acid **1r** (119.2 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 64 %, light yellow solid, M.p.=41-43 °C, R_f =0.8 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 4.07 (t, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz 2H), 2.16 – 1.94 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.2, 136.8, 133.3, 130.8, 130.1, 126.3, 122.8, 61.8, 35.04, 22.83.

5-(2-bromophenyl)-3,4-dihydro-2H-pyrrole (2s)



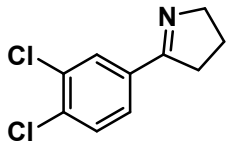
5-(2-bromophenyl)-3,4-dihydro-2H-pyrrole **2s** (31.2 mg) was prepared from azide carboxylic acid **1s** (119.2 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 35 %, orange liquid, R_f =0.81 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.36 (m, 3H), 4.08 (t, *J* = 7.4 Hz, 2H), 2.96 (t, *J* = 8.1, 8.4 Hz 2H), 2.11 – 2.00 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.6, 134.7, 130.5, 128.6 (2), 127.8 (2), 61.6, 35.1, 22.8.

5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole (2t)



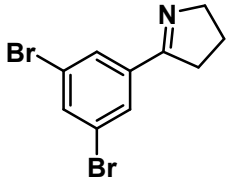
5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole **2t** (69.4 mg) was prepared from azide carboxylic acid **1t** (114.9 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 81 %, white solid, R_f =0.87 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 4.10 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 8.4 Hz, 2H), 2.12 – 2.02 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.3, 137.9, 132.1 (q, *J* = 32.6 Hz), 128.0 (2), 125.5 (d, *J* = 3.7 Hz), 123.9 (q, J = 269.5 Hz),62.0, 35.2, 22.8.

5-(3,4-dichlorophenyl)-3,4-dihydro-2H-pyrrole (2u)



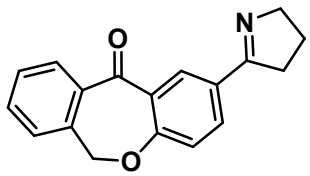
5-(3,4-dichlorophenyl)-3,4-dihydro-2H-pyrrole **2u** (63.9 mg) was prepared from azide carboxylic acid **1u** (115.3 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 75 %, light yellow solid, M.p.=108-110 °C, R_f =0.83 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 4.07 (t, *J* = 7.5 Hz, 2H), 2.90 (t, *J* = 8.3 Hz 2H), 2.11 – 2.01 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.4, 134.7, 134.6, 132.9, 130.6, 129.70, 126.9, 61.9, 35.0, 22.9. **HRMS (APCI)**: calcd for $C_{10}H_9Cl_2N$+H (M^+ + H), 214.0184; found, 214.0181. **IR (KBr)**: 1621, 1560, 823, 661 cm^{-1}.

5-(3,5-dibromophenyl)-3,4-dihydro-2H-pyrrole (2v)



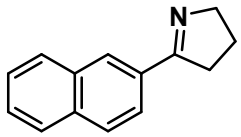
5-(3,5-dibromophenyl)-3,4-dihydro-2H-pyrrole **2v** (73.7 mg) was prepared from azide carboxylic acid **1v** (150.8 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 61 %, white solid, M.p.=89-93 °C, R_f =0.87 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.91 (d, *J* = 1.8 Hz, 2H), 7.71 (t, *J* = 1.8 Hz, 1H), 4.08 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 8.1 Hz, 2H), 2.11 – 2.01 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 178.7, 178.6, 141.6, 133.7, 130.1, 123.4, 51.1, 50.6, 30.2, 26.9. **HRMS (APCI)**: calcd for $C_{10}H_9Br_2N$+H (M^+ + H), 301.9174; found, 301.9169. **IR (KBr)**: 1626, 1551 734 cm^{-1}.

2-(3,4-dihydro-2H-pyrrol-5-yl)dibenzo[b,e]oxepin-11(6H)-one (2w)



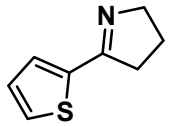
2-(3,4-dihydro-2H-pyrrol-5-yl)dibenzo[b,e]oxepin-11(6H)-one **2w** (55.3 mg) was prepared from azide carboxylic acid **1w** (140.4 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline 2a, the yield was 50 %, yellow oil, R_f =0.77 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 8.49 (d, J = 2.3 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 5.22 (s, 2H), 4.05 (t, J = 7.2 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.05 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.9, 172.3, 163.0, 140.7, 135.3, 134.2, 133.0, 132.1, 129.5 (d, J = 3.3 Hz), 129.1, 128.0, 124.7, 121.4, 73.7, 61.7, 35.1, 22.9. **HRMS (APCI)**: calcd for $C_{18}H_{15}NO_2$+H (M^+ + H), 278.1175; found, 278.1171. **IR (KBr)**: 1726, 1649, 1487, 1141, 756 cm^{-1}.

5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrole (2x)



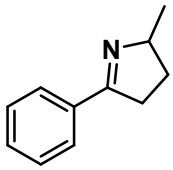
5-(naphthalen-2-yl)-3,4-dihydro-2H-pyrrole **2x** (24.8 mg) was prepared from azide carboxylic acid **1x** (108 mg,0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 32 %, orange solid, M.p.=86-91 °C, R_f =0.8 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 8.17 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.82 (m, 3H), 7.56 – 7.45 (m, 2H), 4.13 (t, *J* = 7.4 Hz, 2H), 3.08 (t, *J* = 9.0 Hz, 2H), 2.14 – 2.05 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.5, 134.1, 132.7, 131.3, 130.3, 128.4, 127.4, 127.1, 126.8, 126.1, 124.8, 62.7, 38.8, 22.7.

5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole (2y)



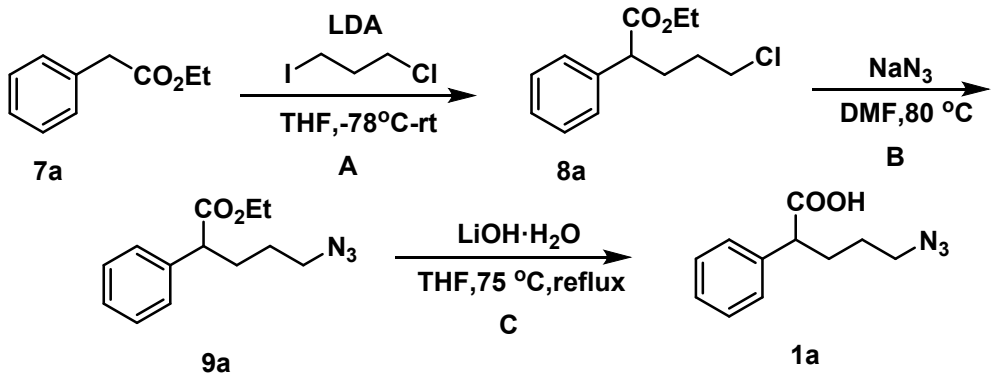
5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole **2y** (13.5 mg) was prepared from azide carboxylic acid **1y** (67.5 mg, 0.3 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 30 %, light yellow solid, M.p.=41- 45 °C, R_f =0.79 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.40 (d, *J* = 5.1, Hz, 1H), 7.32 (d, *J* = 3.7, Hz, 1H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.02 (t, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.10 – 2.00 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.0, 139.9, 129.1, 129.1, 127.5, 61.5, 35.8, 23.2. **HRMS (APCI)**: calcd for C_8H_9NS+H (M^+ + H), 152.0528; found, 152.0528. **IR (KBr)**: 1432, 1610, 692 cm^{-1}.

2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole (2z)



2-methyl-5-phenyl-3,4-dihydro-2H-pyrrole **2z** (28.8 mg) was prepared from azide carboxylic acid **1z** (93.3 mg, 0.4 mmol) according to the procedure for preparation of the pyrroline **2a**, the yield was 45 %, colorless oil, R_f =0.81 (MeOH/DCM =1/20), **^{1}H NMR (500MHz, $CDCl_3$)** δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.46 – 7.33 (m, 3H), 4.34 – 4.21 (m, 1H), 3.11 – 3.01 (m, 1H), 2.94 – 2.83 (m, 1H), 2.30 – 2.20 (m, 1H), 1.61 – 1.50 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.9, 134.9, 130.4, 128.5 (2), 127.8 (2), 68.6, 35.3, 30.8, 22.3. **HRMS (APCI)**: calcd for $C_{11}H_{13}N$+H (M^+ + H), 160.1120; found, 160.1118. **IR (KBr)**: 1609, 1453, 756, 684 $cm^{-1.}$

Representative procedure for preparation of the 5-azido-2-phenylpentanoic acid



Procedure A

Under nitrogen atmosphere, to a stirred solution of Diisopropylamine (926 mg, 9.15 mmol, 1.5 eq) in THF (15 ml) was slowly added a solution of *n*BuLi (3.2 ml, 2.5 M in hexane, 7.93 mmol, 1.3 eq) at 0 °C. The mixture was kept for 30 min at 0 °C, then it was cooled to -78 °C, and a solution of Ethyl phenylacetate **7a** (1 g, 6.1 mmol, 1 eq) in THF (2 ml) and 10 ml THF was added over a period of 5 min. After 1 hour, a solution of 1-Chloro-3-iodopropane (1.37 g, 6.71 mmol, 1.1 eq) was added dropwise over 5 min. The reaction mixture was slowly warmed to room temperature. The reaction was stirred overnight, and complete consumption of the starting material was confirmed by TLC. The mixture was quenched by addition of saturated NH_4Cl (20 ml) and extracted with EtOAc (25 ml×3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated. The organic phase was purified by flash chromatography (eluent: EtOAc/PE = 1/100) to give ethyl 5-chloro-2-phenylpentanoate **8a** (1.37 g, the yield was 93 %, light yellow liquid, R_f =0.64, EA/PE=1/10).

Procedure B

To astirred solution of **8a** (1.37 g, 5.7 mmol, 1 eq) in DMF (28 mL)was added NaN_3 (1.11 g, 17.1 mmol, 3 eq) at room temperature. The mixture was kept at 80 °C. The reaction was stirred overnight, and complete consumption of the starting material was confirmed by TLC.Then the resulting mixture was cooled to room temperature, and the reaction was quenched by H_2O (10 mL), extracted with ethyl acetate (20 mL×3). The organic phase was separated. Then the combined extract was washed with water (20mL×7) and brine, dried over anhydrous Na_2SO_4, and concentrated. The organic phase was purified by flash chromatography (eluent: EtOAc/PE = 1/100) to give ethyl 5-azido-2-phenylpentanoate **9a** (1.27 g, the yield was 90 %, light yellow liquid, R_f =0.62, EA/PE=1/10).

Procedure C

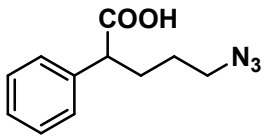
To a stirred solution of azido ester **9a** (1.27 g, 5.14 mmol, 1 eq) in THF/H_2O (V/V = 1/1, 26 mL) was added LiOH. H_2O (2.17 g, 51.4 mmol 10 eq) at room temperature. The mixture was heated to 75 °C. The reaction was stirred overnight, and complete consumption of the starting material was confirmed by TLC, then the mixture was cooled to room temperature and the pH of the mixture was adjusted to 1-2 with 2.0 M HCl. The reaction mixture was extracted by EtOAc (25 mL × 3) and the combined organic layers were dried over Na_2SO_4 and concentrated. The organic phase

was purified by flash chromatography to afford the 5-azido-2-phenylpentanoic acid **1a** (1.0 g, the yield was 88 %, light yellow oil, R_f =0.43, EA/PE=1/11).

Known compounds

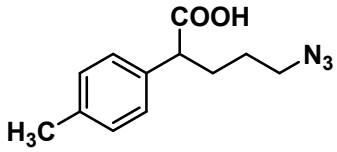
1a, 1b, 1h, 1i, 1j, 1m, 1n, 1o, 1r, 1x [9].

5-azido-2-phenylpentanoic acid (1a)



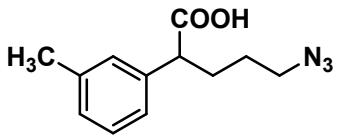
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 3.57 (t, *J* = 7.7 Hz, 1H), 3.31 – 3.25 (m, 2H), 2.21 – 2.09 (m, 1H), 1.94 – 1.83 (m, 1H), 1.65 – 1.47 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.9, 137.3, 129.0 (2), 128.1 (2), 127.9, 51.2, 51.2, 30.2, 27.0.

5-azido-2-(p-tolyl)pentanoic acid (1b)



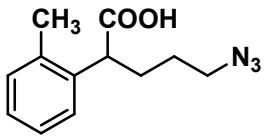
5-azido-2-(p-tolyl)pentanoic acid **1b** (518.6 mg) was prepared from azido ester **5b** (622 mg, 2.4 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 93 %, white solid, M.p.=59- 62 °C, R_f =0.5 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.19 – 2.05 (m, 1H), 1.92 – 1.79 (m, 1H), 1.65 – 1.44 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.9, 137.6, 134.9, 129.7 (2), 128.0 (2), 51.3, 50.8, 30.2, 27.0, 21.2.

5-azido-2-(m-tolyl)pentanoic acid (1c)



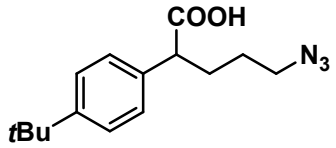
5-azido-2-(m-tolyl)pentanoic acid **1c** (667 mg) was prepared from azido ester **5c** (850 mg, 3.3 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 88 %, yellow oil, R_f =0.52 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 3H), 3.58 (t, *J* = 7.7 Hz, 1H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 2.21 – 2.11 (m, 1H), 1.98 – 1.87 (m, 1H), 1.74 – 1.51 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.2, 138.6, 137.8, 128.8, 128.8, 128.6, 125.1, 51.2, 51.1, 30.1, 26.9, 21.5. **HRMS (APCI)**: calcd for $C_{12}H_{15}N_3O_2$-H (M^+ - H), 232.1091; found, 232.1088. **IR (KBr)**:2195, 1704, 1247, 718 cm^{-1}.

5-azido-2-(o-tolyl)pentanoic acid (1d)



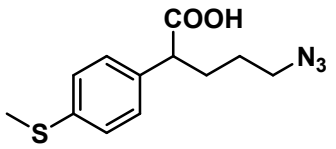
5-azido-2-(o-tolyl)pentanoic acid **1d** (2.1 g) was prepared from azido ester **5d** (2.4 g, 9.5 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 94 %, yellow oil, R_f =0.51 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.29 (m, 1H), 7.25 – 7.13 (m, 3H), 3.87 (t, *J* = 7.6 Hz, 1H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 2.24 – 2.12 (m, 1H), 1.91 – 1.80 (m, 1H), 1.70 – 1.50 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.1, 136.6, 136.4, 130.8, 127.6, 126.8, 126.7, 51.3, 46.4, 29.8, 27.0, 19.9. **HRMS (APCI)**: calcd for $C_{12}H_{15}N_3O_2$-H (M^+ - H), 232.1091; found, 232.1087. **IR (KBr)**:2100, 1698, 1242, 750, 723 cm^{-1}.

5-azido-2-(4-(tert-butyl)phenyl)pentanoic acid (1e)



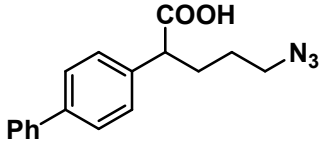
5-azido-2-(4-(tert-butyl)phenyl)pentanoic acid **1e** (1.2 g) was prepared from azido ester **5e** (1.5 g, 5.1 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 88 %, white solid, M.p.=61-65 °C, R_f =0.34 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.19 – 2.08 (m, 1H), 1.92 – 1.81 (m, 1H), 1.65 – 1.48 (m, 2H), 1.31 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.0, 150.7, 134.9, 127.7 (2), 125.9 (2), 51.3, 50.8, 34.6, 31.4 (3), 30.2, 27.0. **HRMS (APCI)**: calcd for $C_{15}H_{21}N_3O_2$-H (M^+ - H), 274.1561; found, 274.1562. **IR (KBr)**: 2083, 1687, 1275, 1063 cm^{-1}.

5-azido-2-(4-(methylthio)phenyl)pentanoic acid (1f)



5-azido-2-(4-(methylthio)phenyl)pentanoic acid **1f** (806.7 mg) was prepared from azido ester **5f** (933.8 mg, 3.2 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 96 %, yellow oil, R_f =0.43 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)**δ 7.22 (s, 4H), 3.52 (t, *J* = 7.7 Hz, 1H), 3.30 – 3.15 (m, 2H), 2.47 (s, 3H), 2.18 – 2.07 (m, 1H), 1.91 – 1.80 (m, 1H), 1.64 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.8, 138.3, 134.7, 128.6 (2), 127.1 (2), 51.2, 50.6, 30.1, 26.9, 15.9. **HRMS (APCI)**: calcd for $C_{12}H_{15}N_3O_2S$-H (M^+ - H), 264.0812; found, 264.0811. **IR (KBr)**: 2095, 1693, 1258, 1214, 768 cm^{-1}.

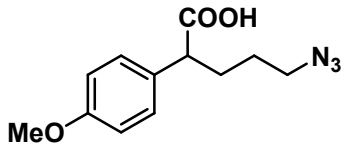
2-([1,1'-biphenyl]-4-yl)-5-azidopentanoic acid (1g)



2-([1,1'-biphenyl]-4-yl)-5-azidopentanoic acid **1g** (2.3 g) was prepared from azido ester **5g** (2.8 g, 8.5 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 90 %, white solid, M.p.=67-70 °C, R_f =0.49 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.33 (m, 1H), 3.64 (t, *J* =

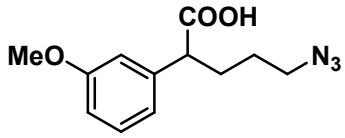
7.7 Hz, 1H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.26 – 2.15 (m, 1H), 2.00 – 1.89 (m, 1H), 1.70 – 1.52 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 179.8, 140.9, 140.7, 136.9, 128.9, (2) 128.5 (2), 127.7 (2), 127.5, 127.2 (2), 51.2, 50.9, 30.2, 27.0. **HRMS (APCI)**: calcd for $C_{17}H_{17}N_3O_2$-H (M^+ - H), 294.1248; found, 294.1246. **IR (KBr)**: 2089, 1687, 1258, 756 cm^{-1}.

5-azido-2-(4-methoxyphenyl)pentanoic acid (1h)



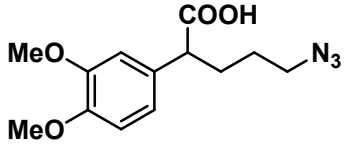
5-azido-2-(4-methoxyphenyl)pentanoic acid **1h** (1.6 g) was prepared from azido ester **5h** (1.9 g, 6.9 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 93 %, light yellow oil, R_f =0.56 (EA/PE=1/1), **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.51 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.17 – 2.06 (m, 1H), 1.91 – 1.79 (m, 1H), 1.63 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 180.1, 159.3, 130.0, 129.1 (2), 114.4 (2), 55.4, 51.2, 50.3, 30.2, 26.9.

5-azido-2-(3-methoxyphenyl)pentanoic acid (1i)



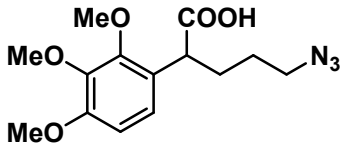
5-azido-2-(3-methoxyphenyl)pentanoic acid **1i** (1.9 g) was prepared from azido ester **5i** (2.2 g, 7.9 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 94 %, colorless oil, R_f =0.45 (EA/PE=1/1), **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.25 (t, *J* = 7.9 Hz, 1H), 6.92 – 6.80 (m, 3H), 3.80 (s, 3H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.18 – 2.07 (m, 1H), 1.93 – 1.82 (m, 1H), 1.65 – 1.47 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 179.6, 160.0, 139.4, 129.9, 120.5, 114.0, 113.1, 55.4, 51.2, 30.2, 26.9.

5-azido-2-(3,4-dimethoxyphenyl)pentanoic acid (1j)



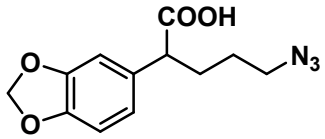
5-azido-2-(3,4-dimethoxyphenyl)pentanoic acid **1j** (1.6 g) was prepared from azido ester **5j** (2.2 g, 7.2 mmol), replace LiOH·H_2O/THF with NaOH/MeOH, proceed at room temperature, the yield was 82 %, white solid, M.p.=64-68 °C, R_f =0.21 (EA/PE=1/1), **^{1}H NMR (500 MHz, CDCl$_3$)** δ 6.88 – 6.79 (m, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.50 (t, *J* = 7.7 Hz, 1H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.18 – 2.07 (m, 1H), 1.92 – 1.81 (m, 1H), 1.65 – 1.47 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 178.9, 149.2, 148.7, 130.3, 120.3, 111.4, 111.0, 56.0, 55.9, 51.1, 50.5, 30.2, 26.8.

5-azido-2-(2,3,4-trimethoxyphenyl)pentanoic acid (1k)



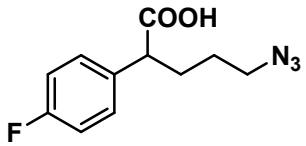
5-azido-2-(2,3,4-trimethoxyphenyl)pentanoic acid **1k** (706 mg) was prepared from azido ester **5k** (1.0g, 4.2 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 72 %, yellow oil, R_f =0.52 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.52 (s, 2H), 3.84 (s, 6H), 3.82 (s, 3H), 3.47 (t, *J* = 7.7 Hz, 1H), 3.29 (t, *J* = 6.6 Hz, 2H), 2.18 – 2.06 (m, 1H), 1.86 (m, 1H), 1.65 – 1.48 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.3, 153.4 (2), 137.6, 133.4, 105.1 (2), 60.8, 56.2 (2), 51.3, 51.1, 30.2, 26.8. **HRMS (APCI)**: calcd for $C_{14}H_{19}N_3O_5$-H (M^+ - H), 308.1251; found, 308.1253. **IR (KBr)**: 2089, 1693, 1448, 1247, 1108 cm^{-1}.

5-azido-2-(benzo[d][1,3]dioxol-5-yl)pentanoic acid (1l)



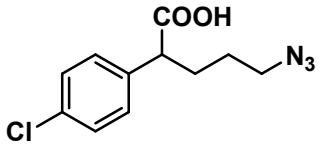
5-azido-2-(benzo[d][1,3]dioxol-5-yl)pentanoic acid **1l** (498.4 mg) was prepared from azido ester **5l** (546.4 mg, 2.0 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 97 %, yellow oil, R_f =0.38 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.82 (d, *J* = 1.5 Hz, 1H), 6.75 (dd, *J* = 1.9, 1.1 Hz, 2H), 5.95 (s, 2H), 3.48 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.14 – 2.03 (m, 1H), 1.88 – 1.77 (m, 1H), 1.63 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.8, 148.2, 147.3, 131.6, 121.7, 108.6, 108.2, 101.3, 51.2, 50.76, 30.28, 26.88. **HRMS (APCI)**: calcd for $C_{12}H_{13}N_3O_4$-H (M^+ - H), 262.0833; found, 262.0831. **IR (KBr)**: 2090, 1704, 1481, 1224, 912 cm^{-1}.

5-azido-2-(4-fluorophenyl)pentanoic acid (1m)



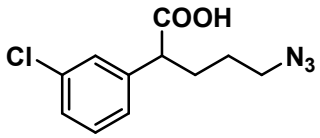
5-azido-2-(4-fluorophenyl)pentanoic acid **1m** (2.2 g) was prepared from azido ester **5m** (2.5 g, 9.3 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 99 %, white solid, M.p.=41-44 °C, R_f =0.45 (EA/PE=1/1), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.23 (m, 3H), 7.01 (t, *J* = 8.4 Hz, 2H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.18 – 2.05 (m, 1H), 1.90 – 1.76 (m, 1H), 1.63 – 1.41 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.6, 162.5 (d, *J* = 252 Hz), 133.6 (d, *J* = 15 Hz), 129.7 (d, *J* = 30 Hz) (2), 115.9 (d, *J* = 21.4 Hz) (2), 51.2, 50.4, 30.4, 26.9.

5-azido-2-(4-chlorophenyl)pentanoic acid (1n)



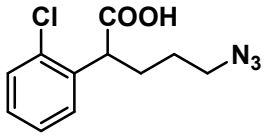
5-azido-2-(4-chlorophenyl)pentanoic acid **1n** (911 mg) was prepared from azido ester **5n** (1.2 g, 4.2 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 98 %, white solid, M.p.=30-35 °C, R_f =0.48 (EA/PE=1/1), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.32 – 3.25 (m, 2H), 2.18 – 2.07 (m, 1H), 1.90 – 1.79 (m, 1H), 1.63 – 1.44 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.5, 136.4, 133.8, 129.5 (2), 129.1 (2), 51.1, 50.6, 30.2, 26.9.

5-azido-2-(3-chlorophenyl)pentanoic acid (1o)



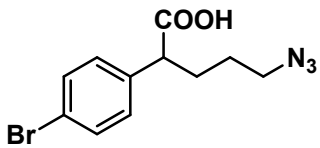
5-azido-2-(3-chlorophenyl)pentanoic acid **1o** (1.5 g) was prepared from azido ester **5o** (2.1 g, 7.6 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 80 %, white solid, M.p.=53-55 °C, R_f =0.53 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 (s, 1H), 7.27 (t, *J* = 4.6 Hz, 2H), 7.19 (t, *J* = 4.6 Hz, 1H), 3.55 (t, *J* = 7.7 Hz, 1H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.07 (m, 1H), 1.92 – 1.81 (m, 1H), 1.65 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.2, 139.8, 134.8, 130.2, 128.3, 128.2, 126.4, 51.2, 50.9, 30.2, 26.9.

5-azido-2-(2-chlorophenyl)pentanoic acid (1p)



5-azido-2-(2-chlorophenyl)pentanoic acid **1p** (1.1 g) was prepared from azido ester 5**p** (1.3 g, 4.6 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 98 %, yellow oil, R_f =0.56 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.05 (m, 2H), 3.93 (t, *J* = 7.5 Hz, 1H), 3.14 (t, *J* = 6.7 Hz, 2H), 1.99 – 1.89 (m, 1H), 1.74 – 1.66 (m, 1H), 1.50 – 1.31 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.9, 138.2, 134.3, 129.7, 128.94, 128.2, 127.3, 51.4, 48.9, 30.1, 26.9. **HRMS (APCI)**: calcd for $C_{11}H_{12}ClN_3O_2$-H (M^+ - H), 252.0545; found, 252.0543. **IR (KBr)**:2094, 1587, 1247, 751 cm^{-1}.

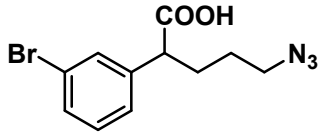
5-azido-2-(4-bromophenyl)pentanoic acid (1q)



5-azido-2-(4-bromophenyl)pentanoic acid **1q** (546 mg) was prepared from azido ester **5q** (626.5 mg, 1.9 mmol) according to the procedure for preparation of the azido acids **1a**, the yield

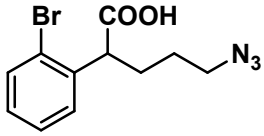
was 95 %, white solid, M.p.=37-42 °C, R_f =0.61 (EA/PE=1/1), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.53 (t, *J* = 7.7 Hz, 1H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.22 – 2.07 (m, 1H), 1.92 – 1.78 (m, 1H), 1.65 – 1.43 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.1, 136.9, 132.1 (2), 129.9 (2), 122.0, 51.2, 50.6, 30.2, 26.9. **HRMS (APCI)**: calcd for $C_{11}H_{12}BrN_3O_2$-H (M^+ - H), 296.0040; found, 296.0039. **IR (KBr)**:2089, 1693, 1252, 750 cm^{-1}.

5-azido-2-(3-bromophenyl)pentanoic acid (1r)



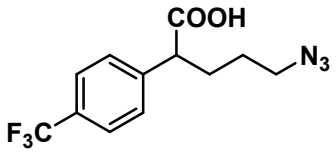
5-azido-2-(3-bromophenyl)pentanoic acid **1r** (2.1 g) was prepared from azido ester **5r** (2.5 g, 7.6 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 93 %, white solid, M.p.=43- 49 °C, R_f =0.46 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.18 (m, 2H), 3.54 (t, *J* = 7.7 Hz, 1H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.08 (m, 1H), 1.92 – 1.81 (m, 1H), 1.66 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.2, 137.7, 133.3, 129.2, 128.78, 128.1, 125.1, 51.2, 49.5, 30.0, 26.7.

5-azido-2-(2-bromophenyl)pentanoic acid (1s)



5-azido-2-(2-bromophenyl)pentanoic acid **1s** (2.0 g) was prepared from azido ester **5s** (2.3 g, 7 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 91 %, light yellow oil, R_f =0.55 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.0, 1.3 Hz, 1H), 7.24 (d, *J* = 7.8, 1.7 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.7, 1.6 Hz, 1H), 3.89 (t, *J* = 7.5 Hz, 1H), 3.15 (t, *J* = 6.7 Hz, 2H), 1.99 – 1.88 (m, 1H), 1.74 – 1.63 (m, 1H), 1.48 – 1.29 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.0, 140.4, 133.0, 129.0, 128.4, 127.9, 125.4, 51.8, 51.5, 30.6, 26.9. **HRMS (APCI)**: calcd for $C_{11}H_{12}BrN_3O_2$-H (M^+ - H), 296.0040; found, 296.0037. **IR (KBr)**: 2094, 1582, 1247, 750 cm^{-1}.

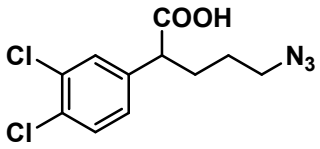
5-azido-2-(4-(trifluoromethyl)phenyl)pentanoic acid (1t)



5-azido-2-(4-(trifluoromethyl)phenyl)pentanoic acid **1t** (543.4 mg) was prepared from azido ester **5t** (765.2 mg, 2.4 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 78 %, white solid, M.p.=48-51 °C, R_f =0.41 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 3.65 (t, *J* = 7.7 Hz, 1H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.24 – 2.13 (m, 1H), 1.95 – 1.84 (m, 1H), 1.66 – 1.46 (m, 2H).. **^{13}C NMR (126 MHz, $CDCl_3$)** δ 178.7, 141.7, 130.2 (dd, *J* = 32.6 Hz), 128.5 (2), 125.8 (q, *J* = 3.8 Hz) (2), 124 (dd, *J* =

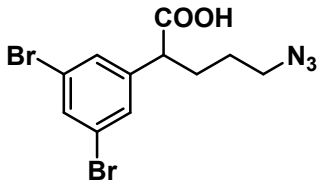
272.2 Hz) (2), 51.0, 50.9, 30.1, 26.8. **HRMS (APCI)**: calcd for $C_{12}H_{12}F_3N_3O_2$-H (M^+ - H), 286.0808; found, 286.0807. **IR (KBr)**: 2089, 1698, 1325, 1135, 1063 cm^{-1}.

5-azido-2-(3,4-dichlorophenyl)pentanoic acid (1u)



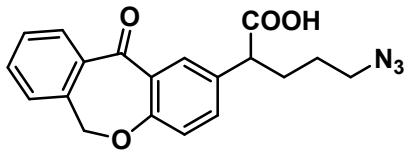
5-azido-2-(3,4-dichlorophenyl)pentanoic acid **1u** (2.2 g) was prepared from azido ester **5u** (2.4 g, 7.9 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 97 %, yellow oil, R_f =0.41 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (d, *J* = 2.1 Hz, 1H), 7.24 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.24 – 3.11 (m, 3H), 1.93 – 1.82 (m, 1H), 1.64 – 1.53 (m, 1H), 1.41 – 1.19 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.3, 140.7, 132.5, 131.1, 130.5, 129.8, 127.3, 52.6, 51.2, 30.4, 26.8. **HRMS (APCI)**: calcd for $C_{11}H_{11}Cl_2N_3O_2$-H (M^+ - H), 286.0155; found, 286.0155. **IR (KBr)**: 2100, 1598, 1370, 1258, 1030 cm^{-1}.

5-azido-2-(3,5-dibromophenyl)pentanoic acid (1v)



5-azido-2-(3,5-dibromophenyl)pentanoic acid **1v** (622 mg) was prepared from azido ester **5v** (667.3 mg, 1.7 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 84 %, white solid, M.p.=73-77 °C, R_f =0.47 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 (t, *J* = 1.8 Hz, 1H), 7.41 (s, 1H), 7.40 (s, 1H), 3.51 (t, *J* = 7.7 Hz, 1H), 3.31 (t, *J* = 6.6 Hz, 2H), 2.19 – 2.08 (m, 1H), 1.90 – 1.79 (m, 1H), 1.67 – 1.46 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.5, 142.6, 133.3, 130.0, 123.3, 61.5, 50.6, 44.4, 30.8, 30.5, 14.2. **HRMS (APCI)**: calcd for $C_{11}H_{11}Br_2N_3O_2$-H (M^+ - H), 373.9145; found, 373.9143. **IR (KBr)**: 1726, 1560, 1180, 740 cm^{-1}.

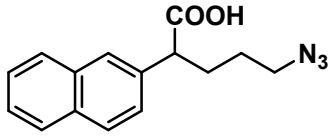
5-azido-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)pentanoic acid (1w)



5-azido-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)pentanoic acid **1w** (1.7 g) was prepared from azido ester **5w** (1.9 g, 5.2 mmol), In an air atmosphere, add 26 mL of MeOH to ethyl 5-azido-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl) pentanoate (1.9 g, 5.2 mmol), then add NaOH (2 g, 52 mmol), heat to 60 °C for reaction. The yield was 93 %, brown viscous oil, R_f =0.44 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.48 – 7.41 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.15 (s, 2H), 3.62 (t, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.16 (m, 1H), 1.88 (m, 1H), 1.72 – 1.44 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.9, 179.3, 160.8, 140.4, 135.5, 134.7, 132.9, 131.7, 131.6, 129.6, 129.3, 127.8, 125.3, 121.5, 73.6, 51.1, 50.2, 30.0, 26.9. **HRMS**

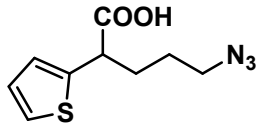
(APCI): calcd for $C_{19}H_{17}N_3O_4$-H (M^+ - H), 350.1146; found, 350.1145. **IR (KBr)**:2100, 1704, 1498, 1135, 762 cm^{-1}.

5-azido-2-(naphthalen-2-yl)pentanoic acid (1x)



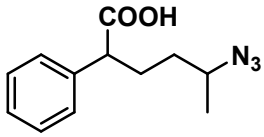
5-azido-2-(naphthalen-2-yl)pentanoic acid **1x** (2.4 g) was prepared from azido ester **5x** (2.9 g, 9.8 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 92 %, white solid, M.p.=60-65 °C, R_f =0.54 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 7.9 Hz, 3H), 7.76 (s, 1H), 7.50 – 7.42 (m, 3H), 3.74 (t, *J* = 7.7 Hz, 1H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.29 – 2.18 (m, 1H), 2.04 – 1.88 (m, 1H), 1.68 – 1.50 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.4, 135.2, 133.4, 132.9, 128.7, 127.8, 127.7, 127.1, 126.4, 126.1, 125.6, 51.11, 30.0, 26.9.

5-azido-2-(thiophen-2-yl)pentanoic acid (1y)



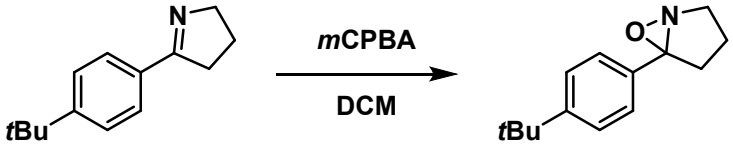
5-azido-2-(thiophen-2-yl)pentanoic acid **1y** (1.0 g) was prepared from azido ester **5y** (1.5 g, 6.1 mmol), replace $LiOH{\cdot}H_2O$/THF with KOH/EtOH (1.7g/31mL), reaction at room temperature, the yield was 68 %, brown oil, R_f =0.28 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 5.0, 1.3 Hz, 1H), 7.01 – 6.94 (m, 2H), 3.90 (t, *J* = 7.7 Hz, 1H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.23 – 2.12 (m, 1H), 2.01 – 1.90 (m, 1H), 1.71 – 1.56 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 177.8, 140.0, 127.0, 126.1, 125.2, 51.1, 46.2, 31.5, 26.9. **HRMS (APCI)**: calcd for $C_9H_{11}N_3O_2S$-H (M^+ - H), 224.0499; found, 224.0495. **IR (KBr)**: 2941, 2089, 1704, 1247, 701 cm^{-1}.

5-azido-2-phenylhexanoic acid (1z)



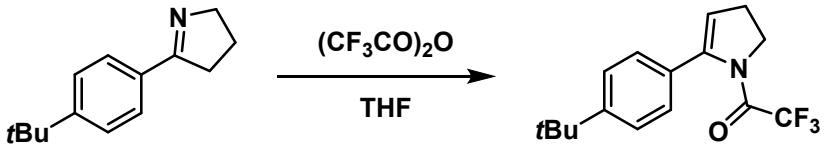
5-azido-2-phenylhexanoic acid **1z** (781.2 mg) was prepared from azido ester **5z** (1.1 g, 3.8 mmol) according to the procedure for preparation of the azido acids **1a**, the yield was 88 %, light yellow oil, R_f =0.43 (EA/PE=1/1), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.26 (m, 10H), 3.54 (td, *J* = 7.7, 1.0 Hz, 2H), 3.47 – 3.39 (m, 2H), 2.26 – 2.16 (m, 1H), 2.15 – 2.04 (m, 1H), 2.01 – 1.89 (m, 1H), 1.88 – 1.78 (m, 1H), 1.55 – 1.33 (m, 4H), 1.24 (dd, *J* = 6.5, 5.1 Hz, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.3, 139.9 (d, *J* = 12.1 Hz), 128.7 (2), 128.1 (2), 127.2, 57.9 (d, *J* = 31.2 Hz), 52.9, 34.2 (d, *J* = 14.1 Hz), 29.7 (d, *J* = 33.2 Hz), 19.4 (d, *J* = 6.7 Hz). **HRMS (APCI)**: calcd for $C_{12}H_{15}N_3O_2$-H (M^+ - H), 232.1091; found, 232.1087. **IR (KBr)**: 2100, 1236, 695 cm^{-1}.

Derivatization products



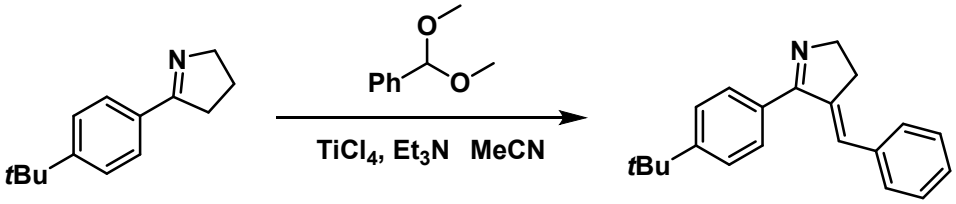
2e **3**

To astirred solution of **2e** (202 mg, 1 mmol, 1 eq) in DCM (3 mL)was added *m*CPBA (225 mg, 1.3 mmol, 1.3 eq) at room temperature. The reaction was stirred overnight. The Et_3N (0.21 mL, 1.5 mmol, 1.5 eq) was added and complete consumption of the starting material was confirmed by TLC.Then the resulting mixture was purified by flash chromatography (eluent: EA/PE = 1/10) to give 5-(4-(tert-butyl)phenyl)-6-oxa-1-azabicyclo[3.1.0]hexane **6** (145.6 mg, the yield was 67 %, R_f =0.89, EA/PE=1/1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.59 – 3.51 (m, 1H), 3.12 – 3.02 (m, 1H), 2.71 – 2.63 (m, 1H), 2.42 – 2.31 (m, 1H), 2.00 – 1.65 (m, 2H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 152.7, 132.4, 127.2, 125.5, 88.1, 55.9, 34.8, 31.4, 28.1, 19.9.



2e **4**

Under nitrogen atmosphere, to a stirred solution of **2e** (202 mg, 1 mmol, 1 eq) in THF (3.3 ml) was slowly added $(CF_3CO)_2O$ (174 uL, 1.25 mmol, 1.25 eq) at 0 °C. The mixture was kept for 30 min at 0 °C, then the reaction mixture was slowly warmed to room temperature and complete consumption of the starting material was confirmed by TLC. The mixture was purified by flash chromatography (eluent: EA/PE = 1/5) to give ethyl 5-chloro-2-phenylpentanoate **7** (279.9 g, the yield was 94 %, black solid, R_f =0.87, MeOH/DCM=1/20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.67 (t, *J* = 3.0 Hz, 1H), 4.34 – 4.00 (m, 2H), 2.76 (t, *J* = 8.0, 3.0 Hz, 2H), 1.32 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 151.5, 144.3, 129.0, 126.8, 124.9, 117.6 (d, *J* = 11.0 Hz), 49.2, 34.8, 31.4, 29.3.



2e **5**

Under nitrogen atmosphere, to a stirred solution of **2e** (202 mg, 1 mmol, 1 eq) in MeCN (10 ml) was added Benzaldehyde dimethyl acetal (304 mg, 2 mmol, 2 eq), and the Et_3N (0.42 mL, 3 mmol, 3 eq) was added, $TiCl_4$ (0.33 mL, 3 mmol, 3 eq) was added dropfold at 0 °C. The mixture was moved to at 85 °C and complete consumption of the starting material was confirmed by TLC. The mixture was quenched by addition of saturated Na_2HCO_3 (10 ml) and extracted with DCM (8

ml×3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated. The organic phase was purified by flash chromatography (eluent: MeOH/DCM = 1/200) to give (E)-4-benzylidene-5-(4-(tert-butyl)phenyl)-3,4-dihydro-2H-pyrrole **8** (213.6 mg, the yield was 92 %, brown solid, R_f =0.52, MeOH/DCM = 1/20). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 2.9 Hz, 1H), 4.30 – 4.10 (m, 2H), 3.15 – 2.95 (m, 2H), 1.38 (s, 9H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 174.8, 152.9, 142.3, 137.3, 131.7, 129.0, 128.7, 128.6, 127.9, 127.8, 125.5, 59.6, 35.0.

References

[1]. W. Li, G. Hou, X. M. Zhang, Iridium-Catalyzed Enantioselective Hydrogenation of Cyclic Imines, *Adv. Synth. Catal*., 2010, **352**,3121 – 3125.

[2]. WO2006/124447A2, "Substituted N-arylpyrrolidines as Selective Androgen Receptor Modulators" World Intellectual Property Organization, published on 23 November 2006, applied by K. Gavardinas, P. K. Jadhav, D. R. Stack and I. R. Clemens.

[3]. H. Huang, Q. Yang, Q. Zhang, J. Wu, Y. Liu, C. Song, J. Chang, A Hofmann Rearrangement–Ring Expansion Cascade for the Synthesis of 1-Pyrrolines: Application to the Synthesis of 2,3-Dihydro-1H-pyrrolo[2,1-a]isoquinolinium Salts, *Adv. Synth. Catal*., 2016, **358**, 1130 – 1135.

[4]. Y. Miki, N. Tomita, K. Ban, H. Sajiki, Y. Sawama, Synthesis of 1-Pyrroline by Denitrogenative Ring Expansion of Cyclobutyl Azides under Thermal Conditions, *Adv. Synth. Catal*., 2021, **363**, 3481 –3484.

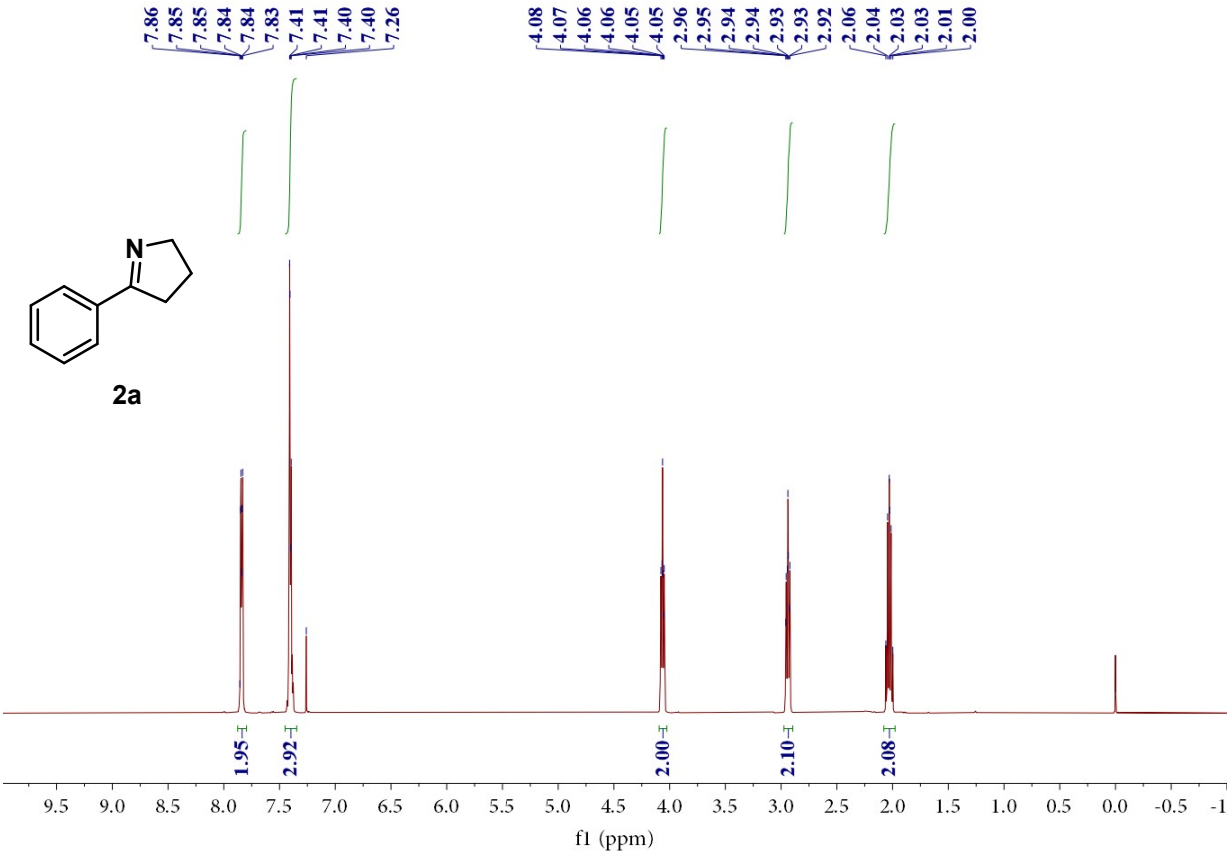
[5]. J. Zhou, M. Jia, M. Song, Dr. Z. Huang, Dr. A. Steiner, Q. An, J. Ma, Z. Guo, Q. Zhang, Dr. H. Sun, Dr. C. Robertson, Dr. J. Bacsa, Prof. Dr. J. Xiao, Prof. Dr. C. Li, Chemoselective Oxyfunctionalization of Functionalized Benzylic Compounds with a Manganese Catalyst, *Angew. Chem., Int. Ed*., 2022, **61**, e202205983.

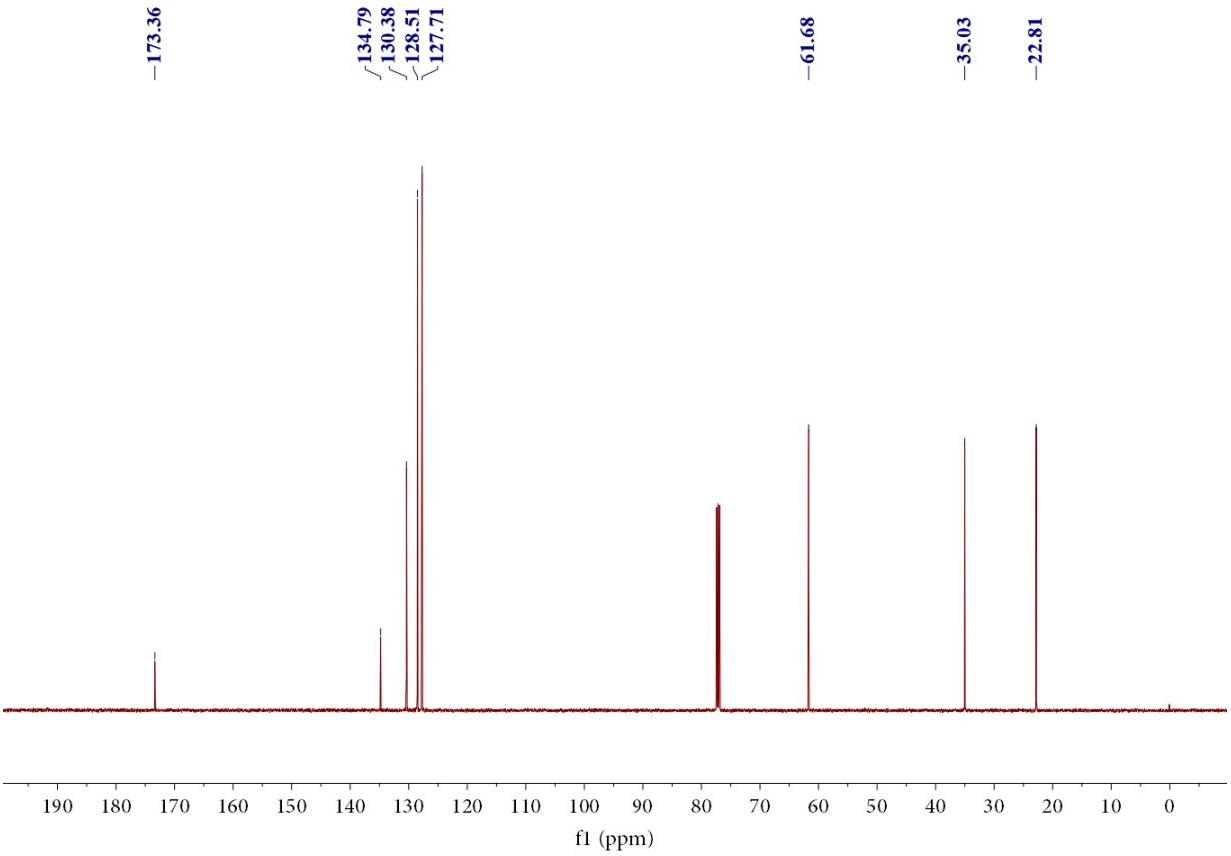
[6]. Y.Wang, F. Huang, Dr. S. Zhang, Intramolecular Cyclization of Brominated Oxime Ether Promoted with Ytterbium(0) to the Synthesis of Cyclic Imines, *Eur. J. Org. Chem.,* 2020, **2020**, 5178-5181.

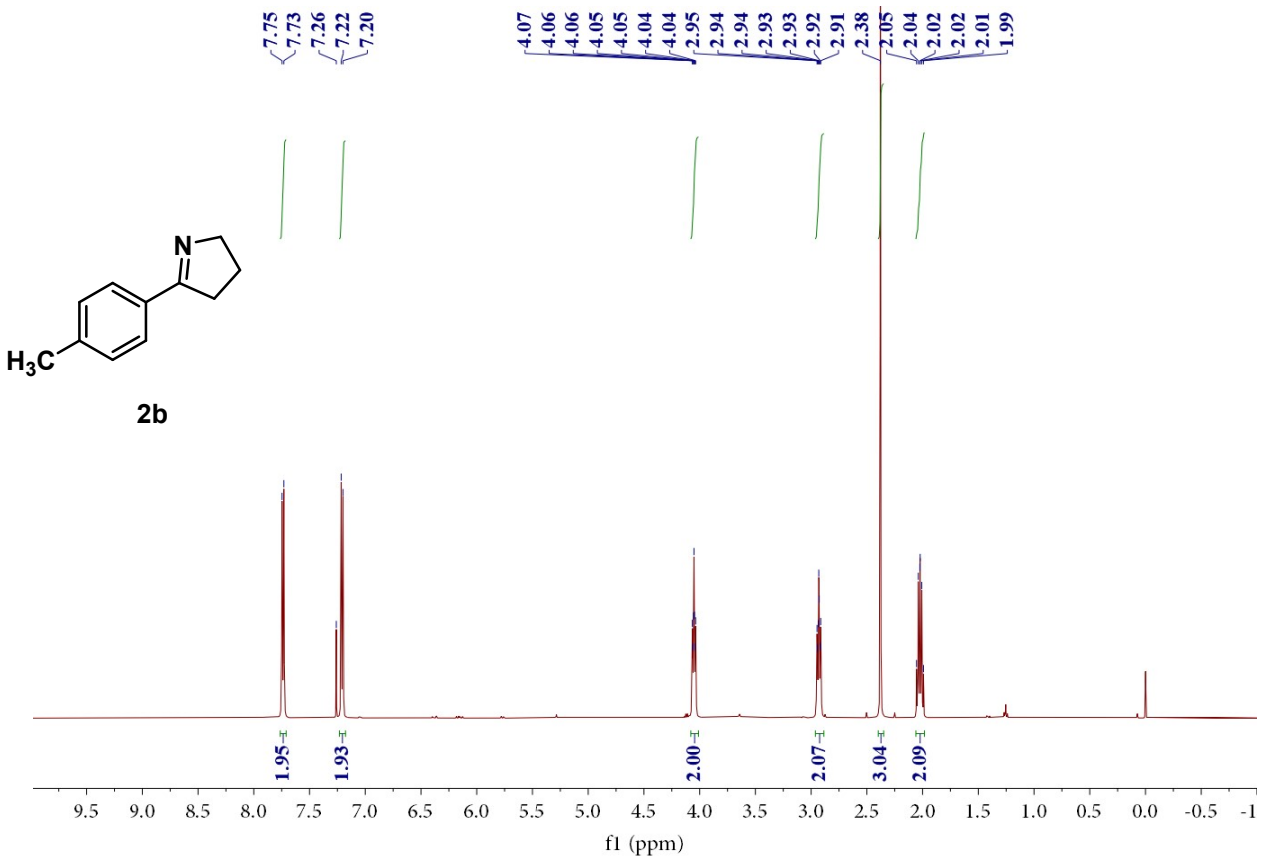
[7]. D. Zhuang, T. Gatera, Z. An, R. Yan, Iron-Catalyzed Ring Expansion of Cyclobutanols for the Synthesis of 1-Pyrrolines by Using $MsONH_3OTf$, *Org.Le*tt., 2022, **24**, 771−775.

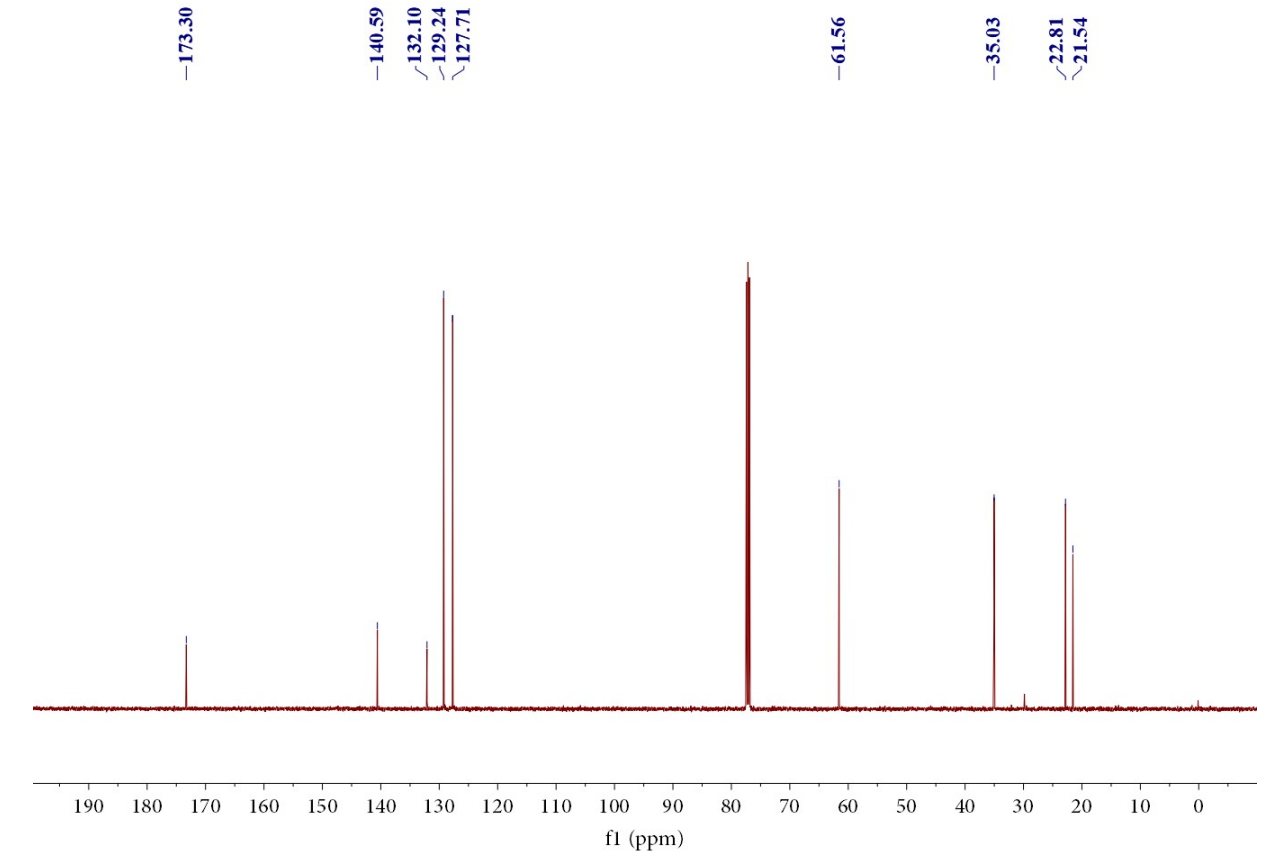
[8]. X. Wen, X. Li, X. Luo, W. Wang, S. Song, N. Jiao, Intramolecular Csp3–H/C–C bond amination of alkyl azides for the selective synthesis of cyclic imines and tertiary amines, *Chem. Sci.*, 2020, **11**, 4482–4487.

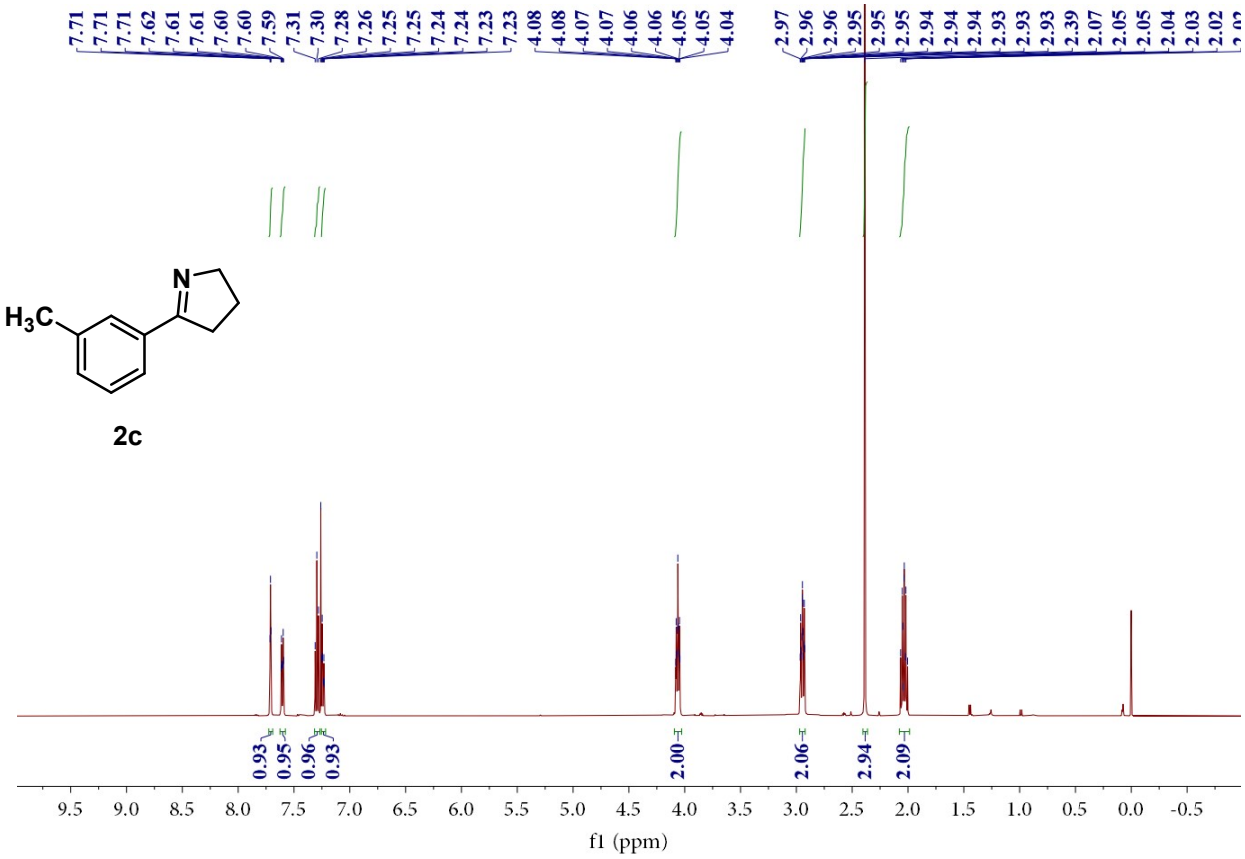
[9]. Q. Li, R. Li, X.. Li, P. Gu, Preparation of Aryl Fused Pyrrolizidines via Intramolecular Schmidt Reaction of Acyl Chlorides with Alkyl Azides, *Chin. J.Org. Chem.*, 2015, **35(11)**: 2326-2332.

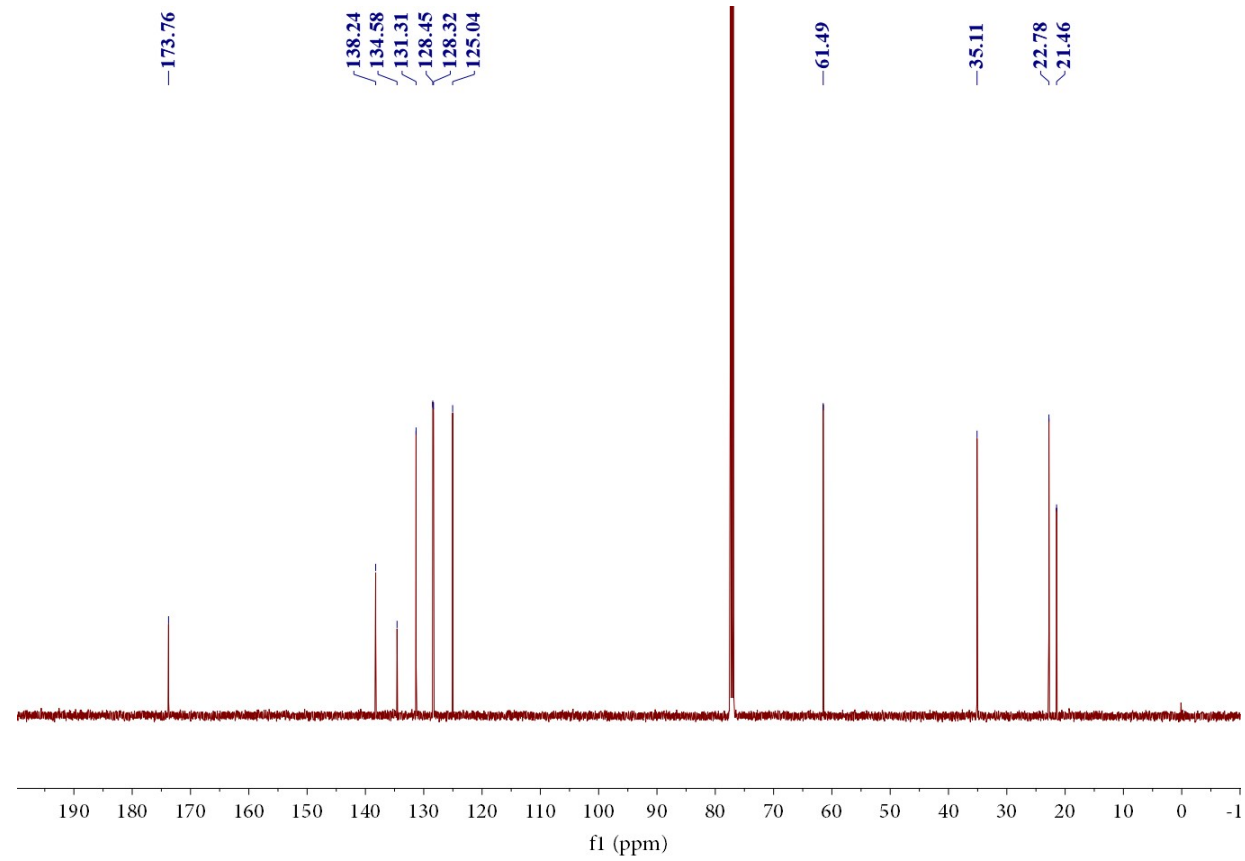

7.86
7.85
7.85
7.84
7.84
7.83
7.41
7.41
7.40
7.40
7.26
4.08
4.07
4.06
4.06
4.05
4.05
2.96
2.95
2.94
2.94
2.93
2.93
2.92
2.06
2.04
2.03
2.03
2.01
2.00
N
2a
1.95
2.92
2.00
2.10
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

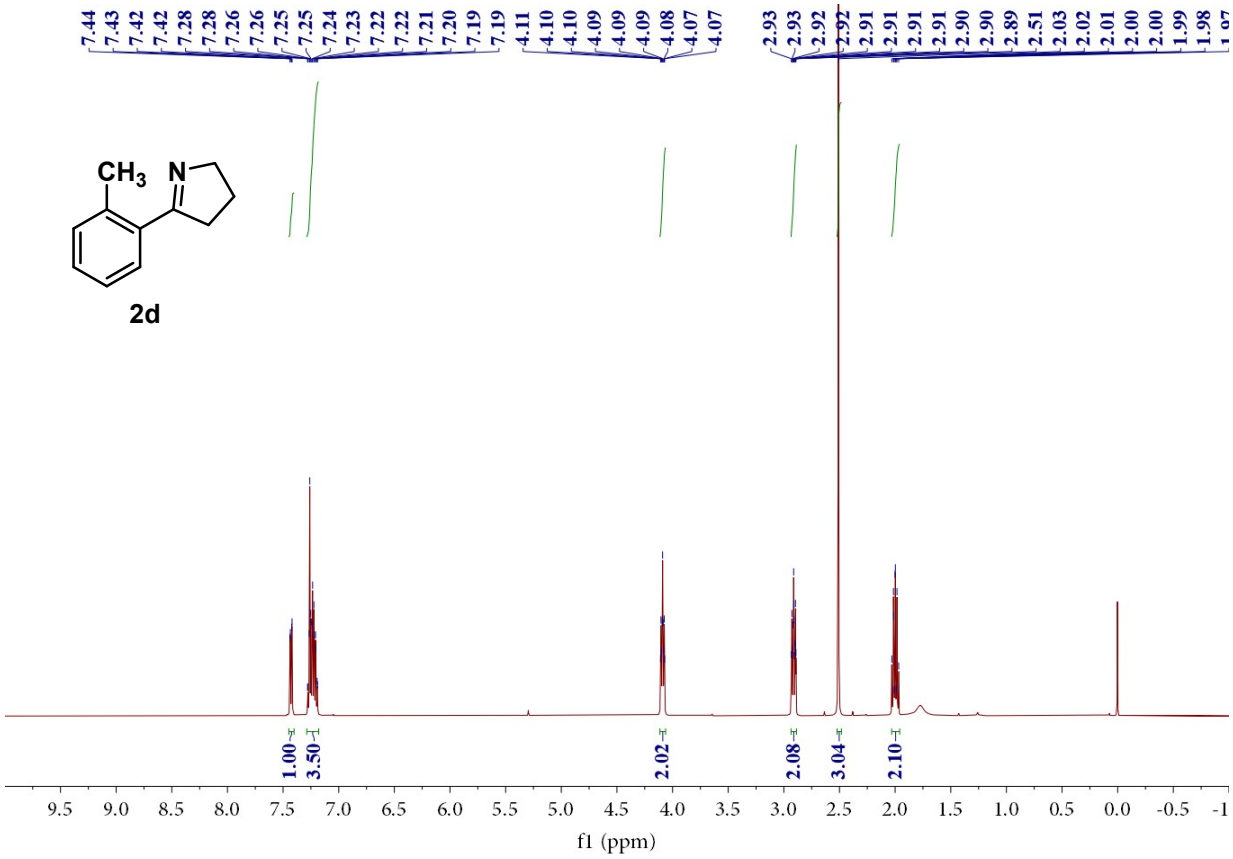

173.36
134.79
130.38
128.51
127.71
61.68
35.03
22.81
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

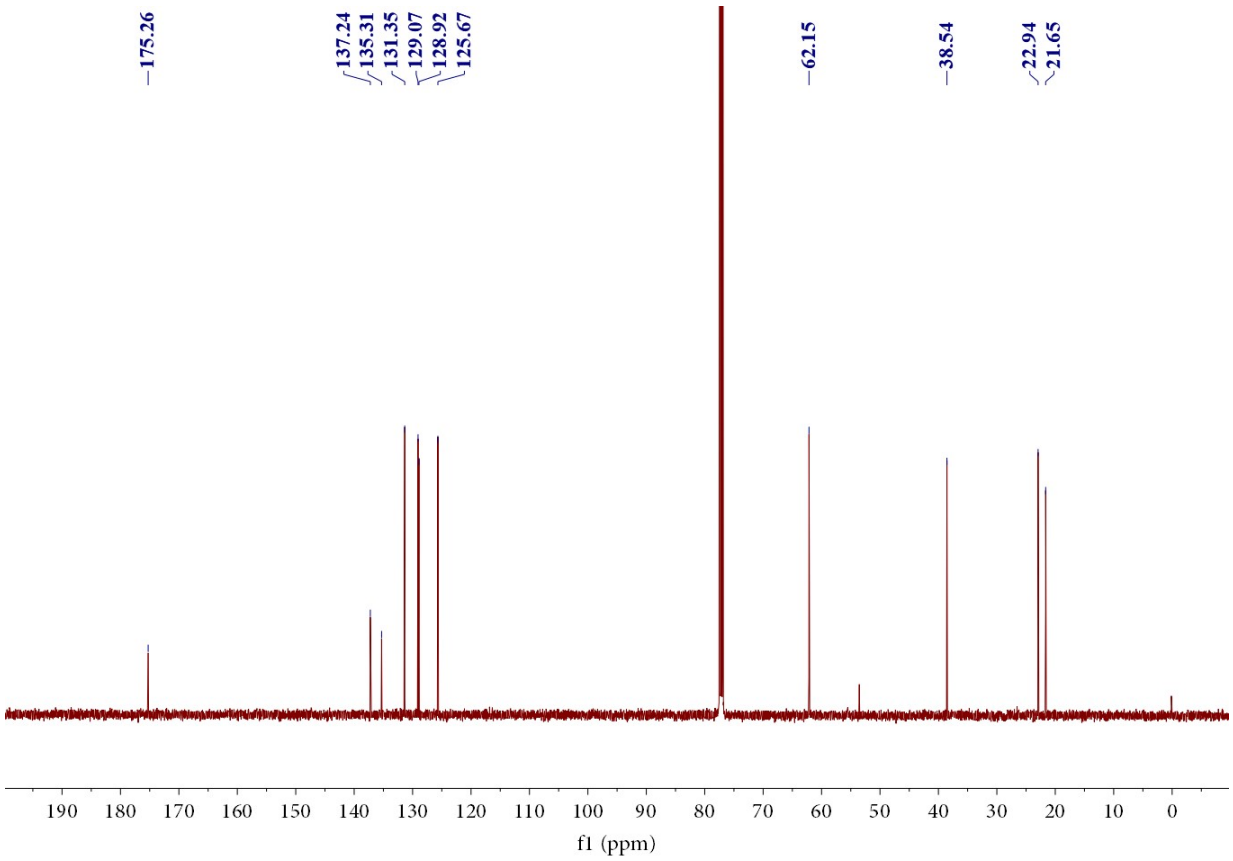

7.75
7.73
7.26
7.22
7.20
4.07
4.06
4.06
4.05
4.05
4.04
4.04
2.95
2.94
2.94
2.93
2.93
2.92
2.91
2.38
2.05
2.04
2.02
2.02
2.01
1.99
N
H3C
2b
1.95
1.93
2.00
2.07
3.04
2.09
f1 (ppm)

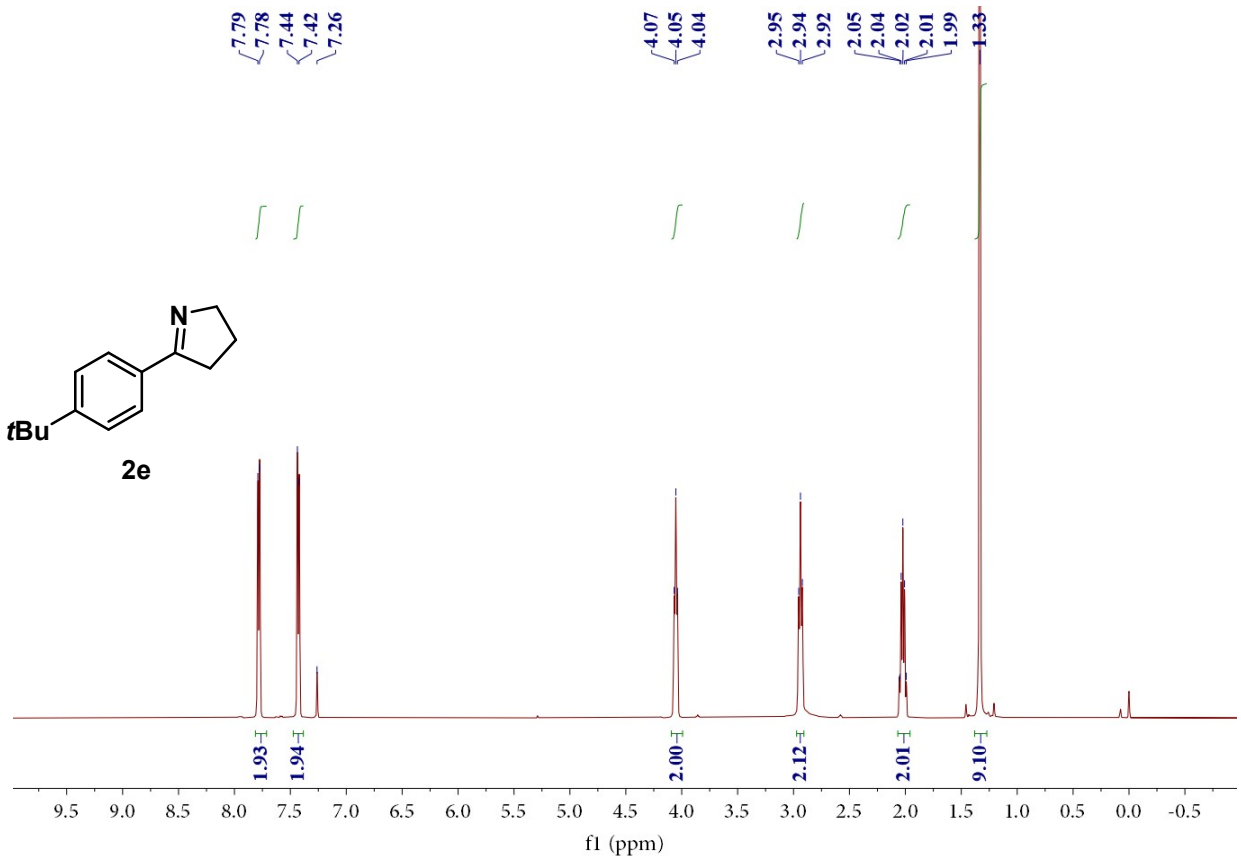

173.30
140.59
132.10
129.24
127.71
61.56
35.03
22.81
21.54
f1 (ppm)

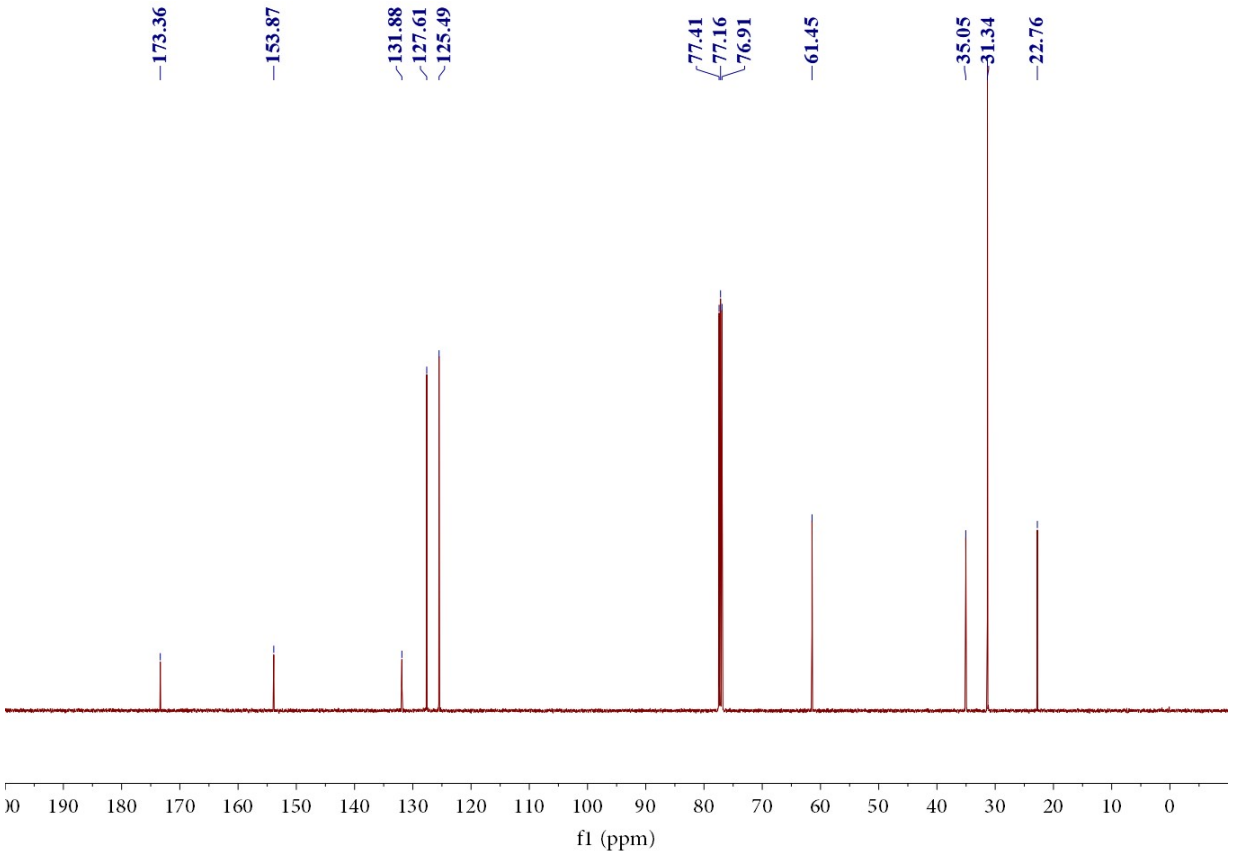

7.71 7.71 7.71 7.62 7.61 7.61 7.60 7.60 7.59 7.31 7.30 7.28 7.26 7.25 7.25 7.24 7.24 7.23 7.23
4.08 4.08 4.07 4.07 4.06 4.06 4.05 4.05 4.04
2.97 2.96 2.96 2.95 2.95 2.95 2.94 2.94 2.94 2.93 2.93 2.93 2.39 2.07 2.05 2.05 2.04 2.03 2.02
N
H3C
2c
0.93 0.95 0.96 0.93 2.00 2.06 2.94 2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

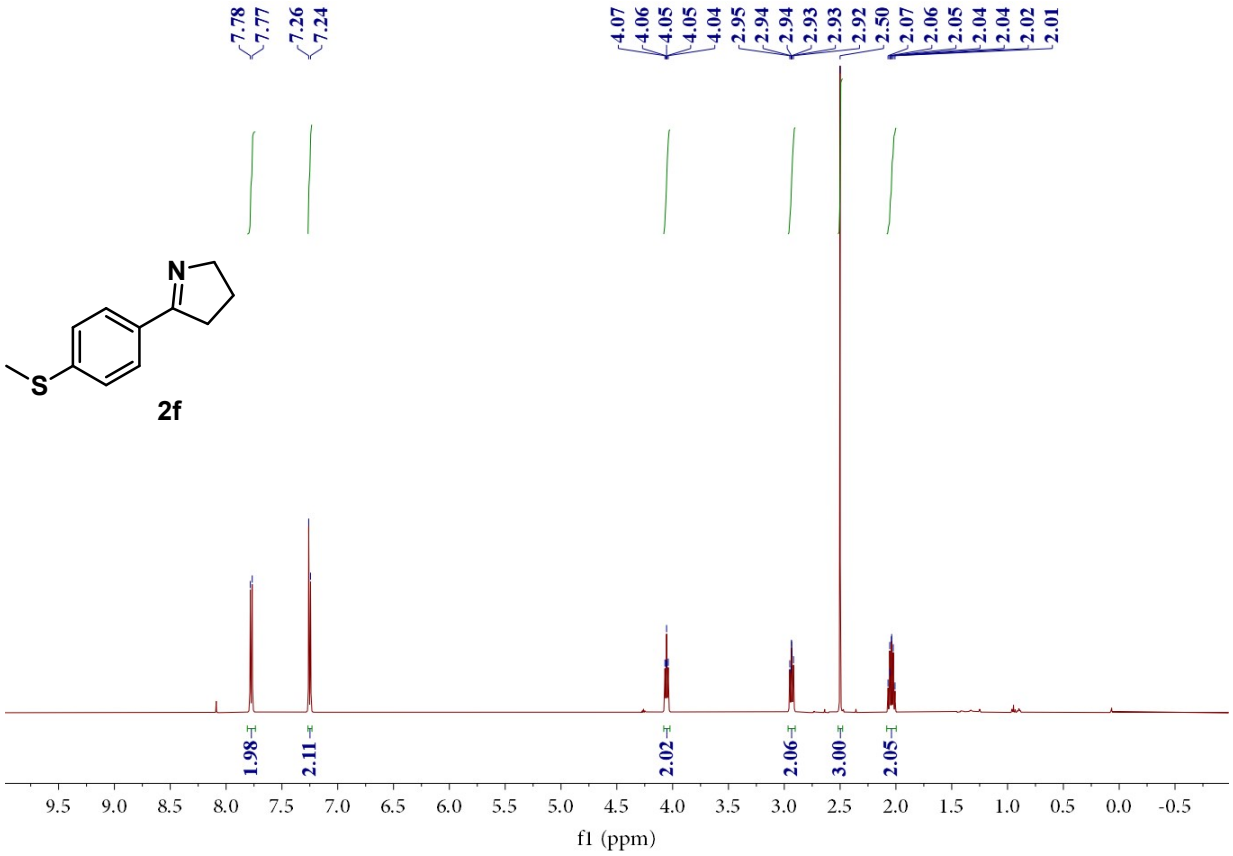

173.76
138.24 134.58 131.31 128.45 128.32 125.04
61.49
35.11
22.78 21.46
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.44 7.43 7.42 7.42 7.28 7.28 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.19
4.11 4.10 4.10 4.09 4.09 4.09 4.08 4.07 4.07
2.93 2.93 2.92 2.92 2.91 2.91 2.91 2.91 2.90 2.90 2.89 2.51 2.03 2.02 2.01 2.00 2.00 1.99 1.98
CH3
N
2d
1.00
3.50
2.02
2.08
3.04
2.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

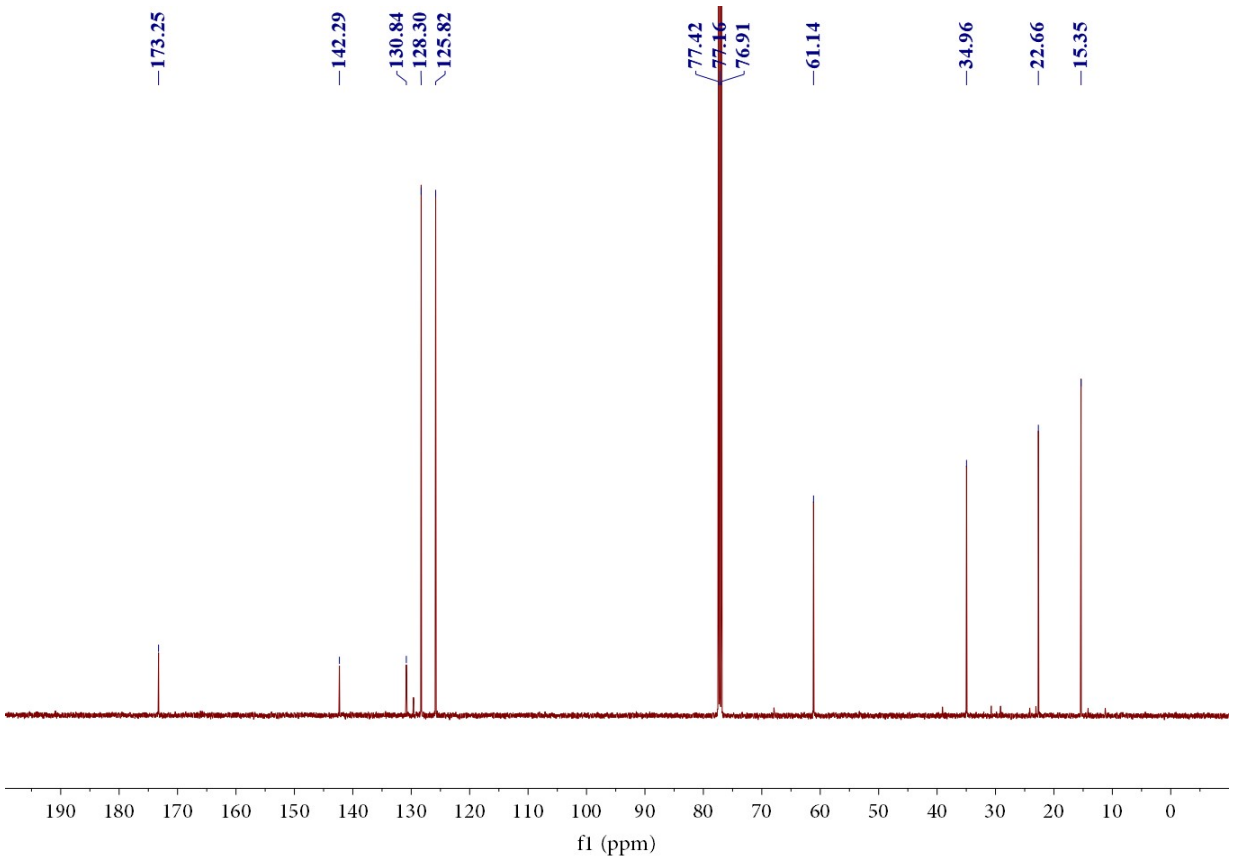

175.26
137.24
135.31
131.35
129.07
128.92
125.67
62.15
38.54
22.94
21.65
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

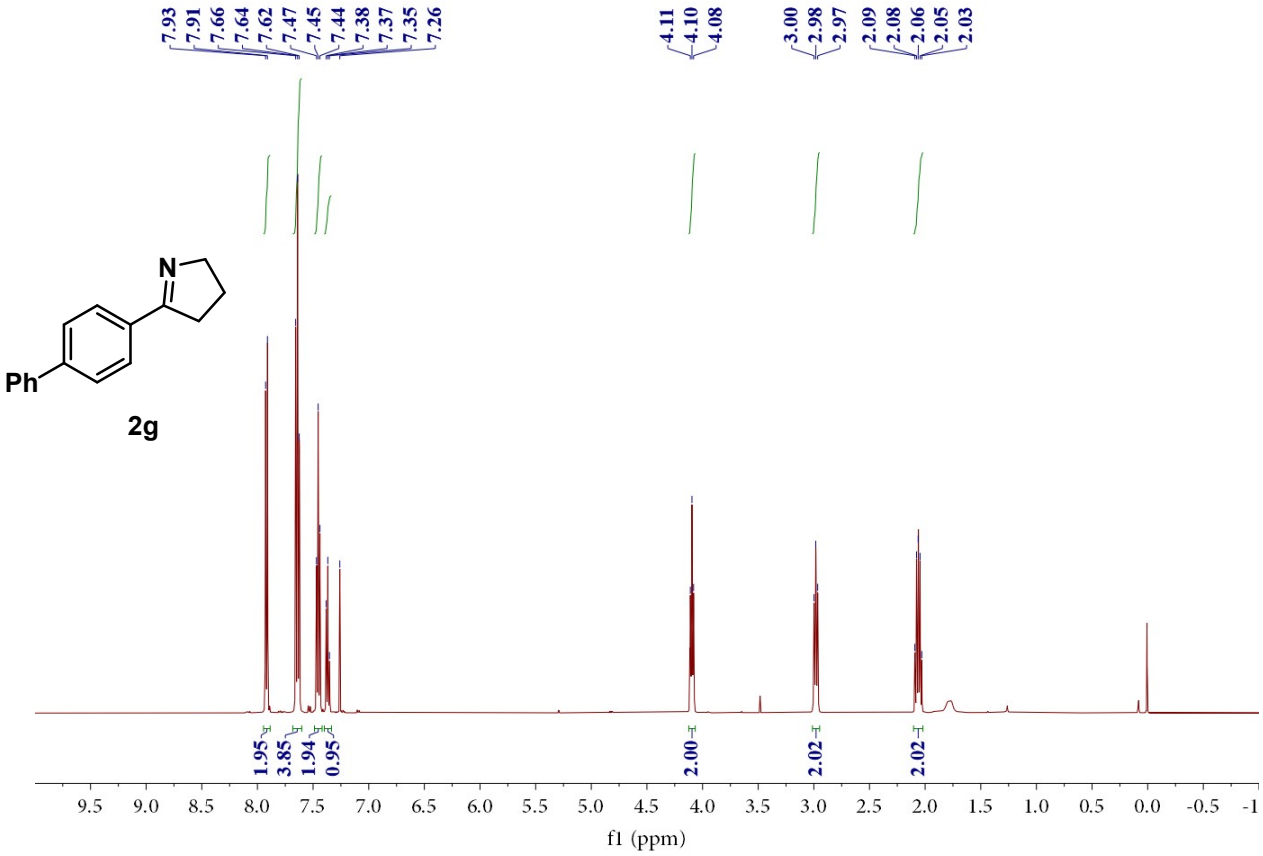

7.79
7.78
7.44
7.42
7.26
4.07
4.05
4.04
2.95
2.94
2.92
2.05
2.04
2.02
2.01
1.99
1.33
N
tBu
2e
1.93
1.94
2.00
2.12
2.01
9.10
f1 (ppm)

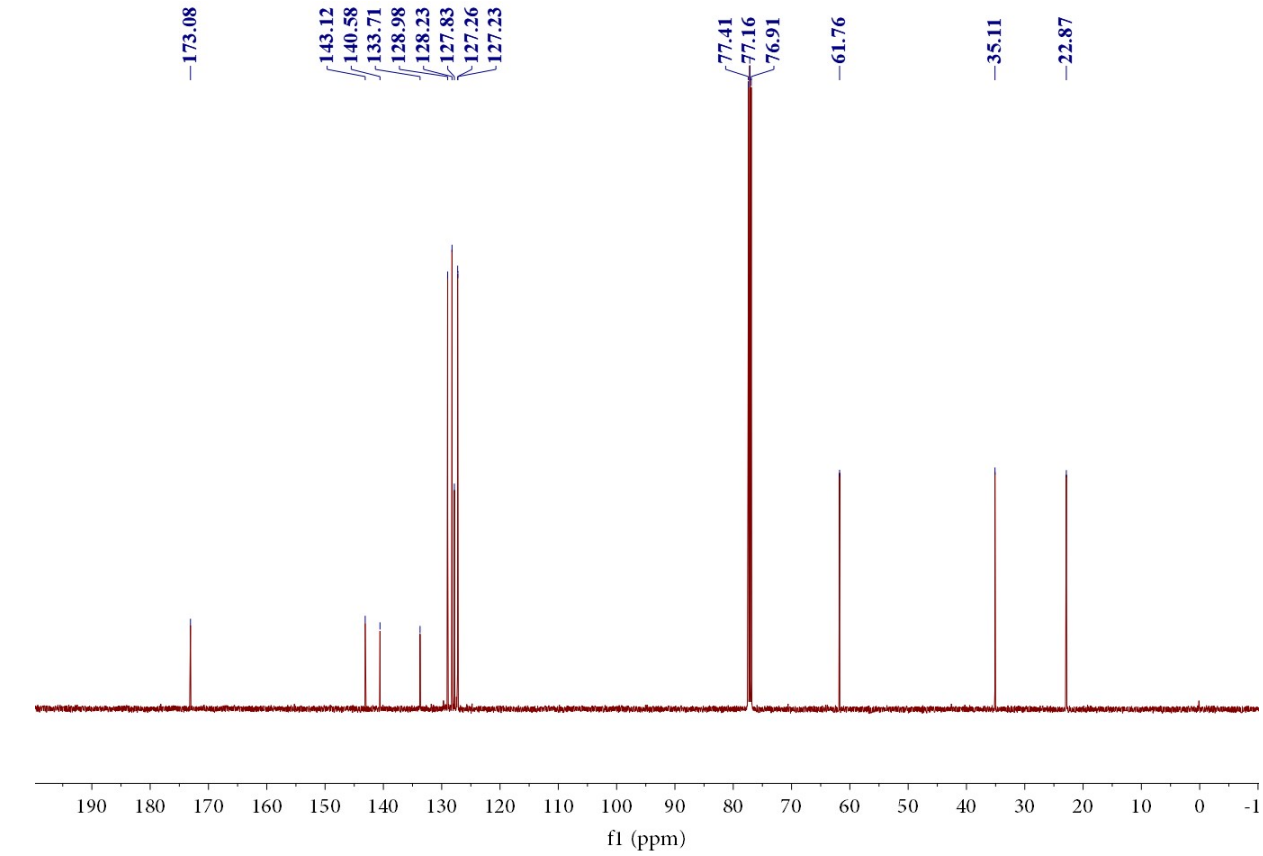

173.36
153.87
131.88
127.61
125.49
77.41
77.16
76.91
61.45
35.05
31.34
22.76
f1 (ppm)

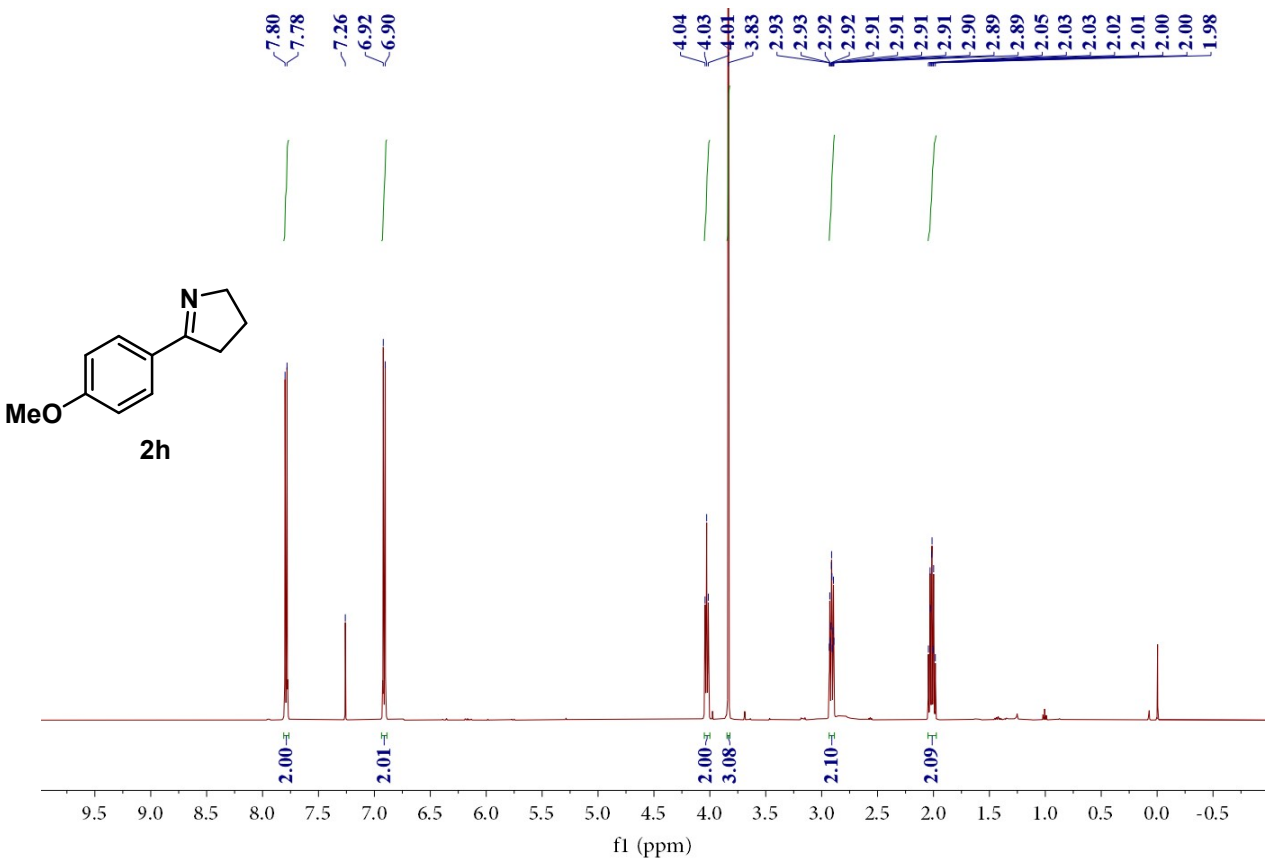

7.78
7.77
7.26
7.24
4.07
4.06
4.05
4.05
4.04
2.95
2.94
2.94
2.93
2.93
2.92
2.50
2.07
2.06
2.05
2.04
2.04
2.02
2.01
N
S
1.98
2.11
2.02
2.06
3.00
2.05
f1 (ppm)

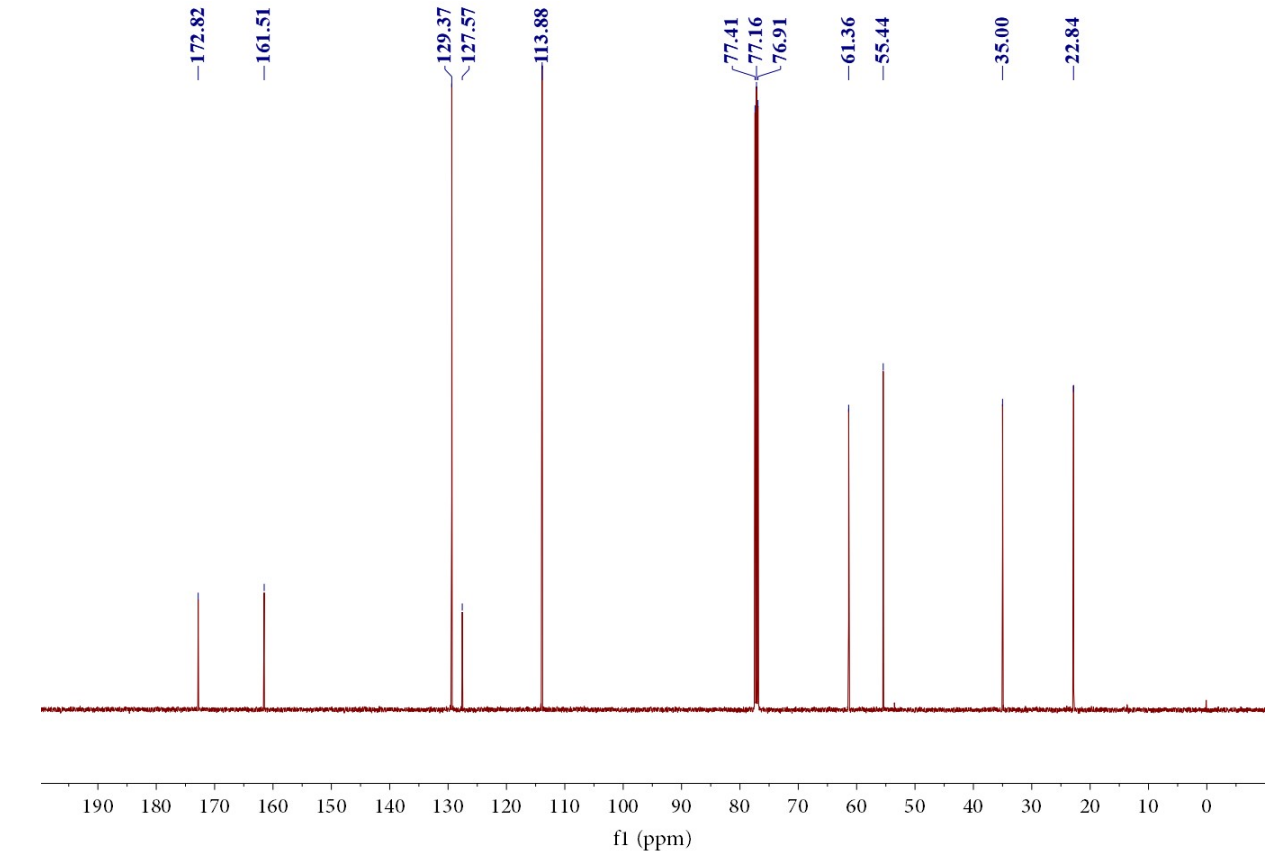
2f

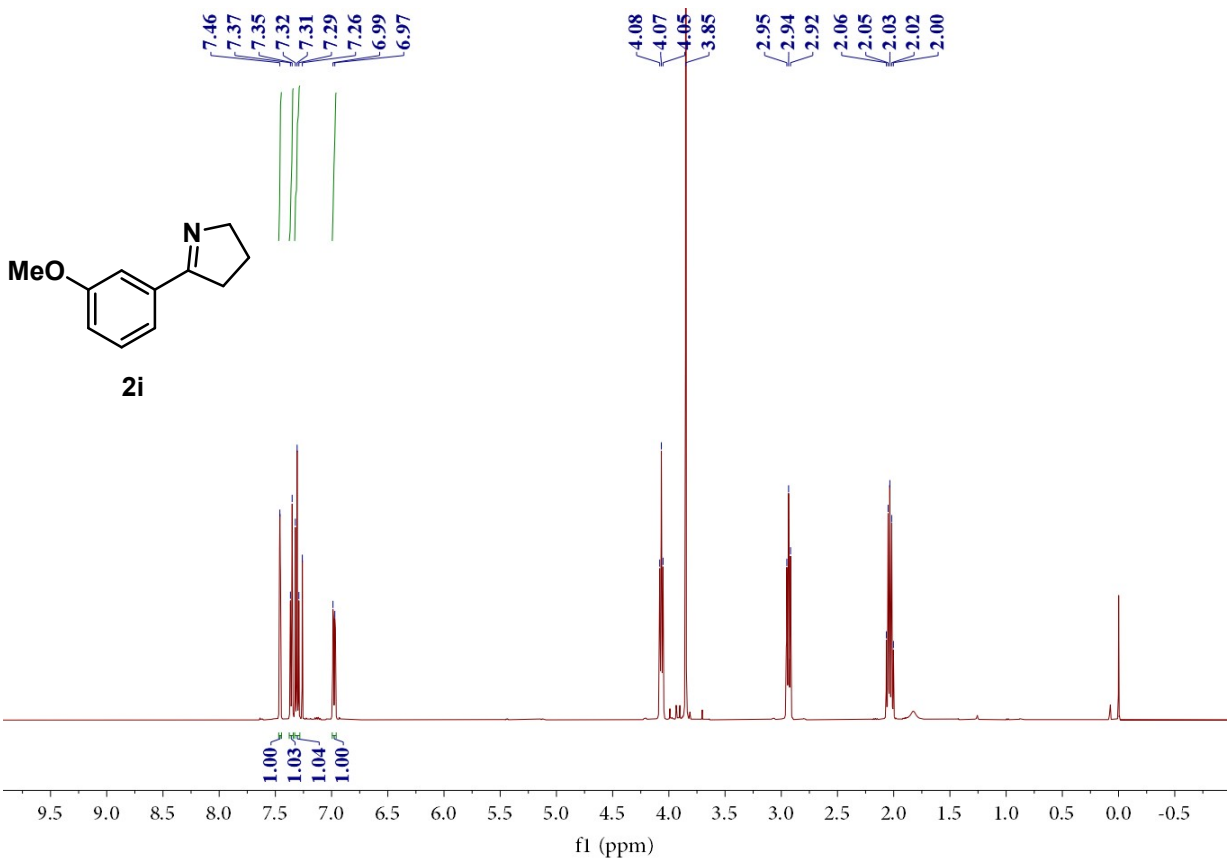

173.25
142.29
130.84
128.30
125.82
77.42
77.16
76.91
61.14
34.96
22.66
15.35
f1 (ppm)


7.93
7.91
7.66
7.64
7.62
7.47
7.45
7.44
7.38
7.37
7.35
7.26
4.11
4.10
4.08
3.00
2.98
2.97
2.09
2.08
2.06
2.05
2.03
N
Ph
2g
1.95
3.85
1.94
0.95
2.00
2.02
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

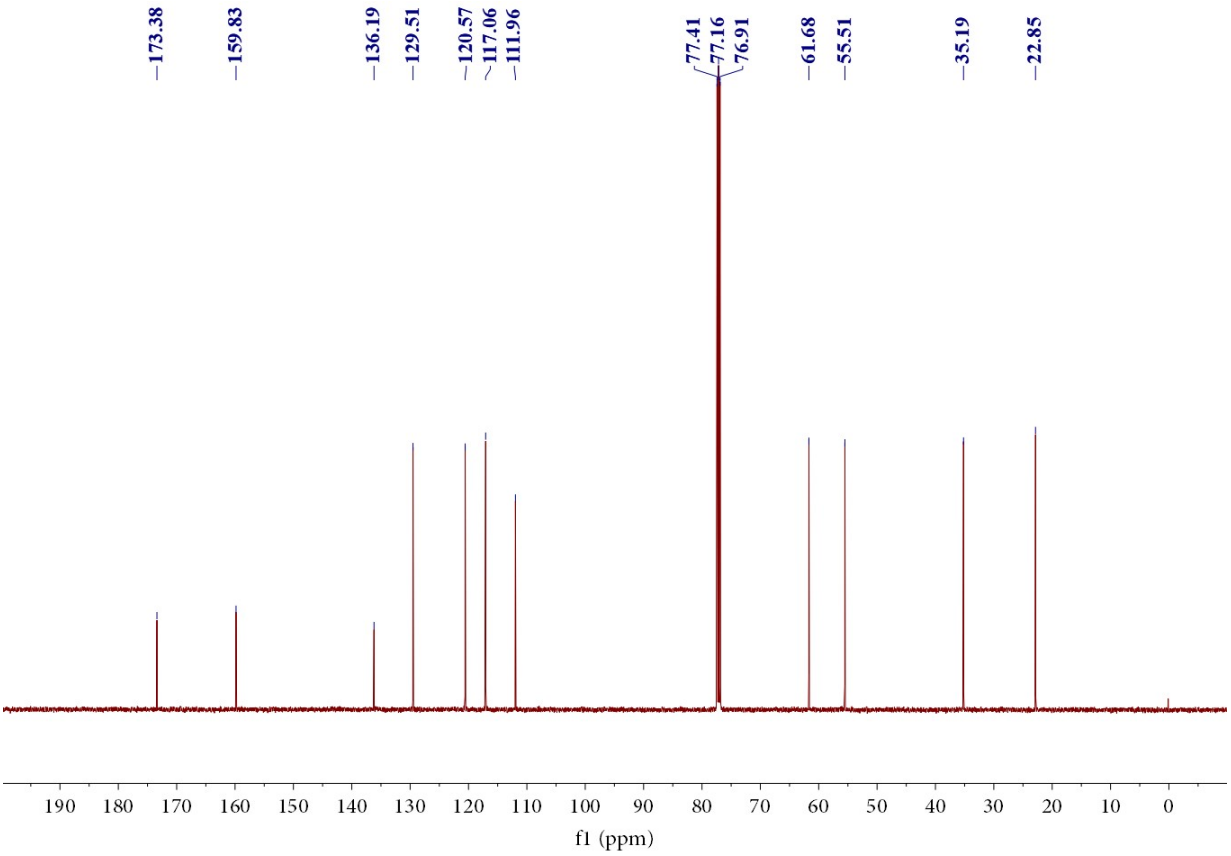

173.08
143.12
140.58
133.71
128.98
128.23
127.83
127.26
127.23
77.41
77.16
76.91
61.76
35.11
22.87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

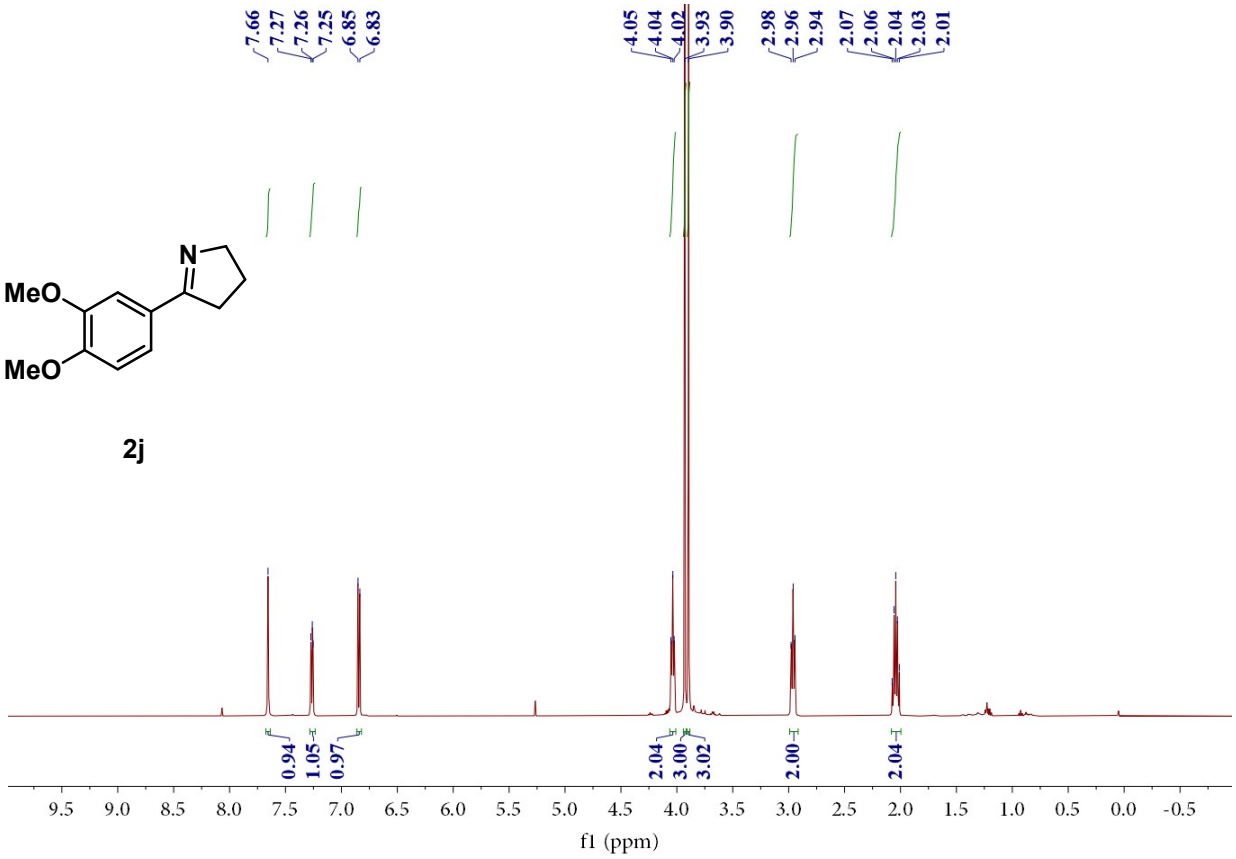

7.80
7.78
7.26
6.92
6.90
4.04
4.03
4.01
3.83
2.93
2.93
2.92
2.92
2.91
2.91
2.91
2.91
2.90
2.89
2.89
2.05
2.03
2.03
2.02
2.01
2.00
2.00
1.98
N
MeO
2h
2.00
2.01
2.00
3.08
2.10
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.82
161.51
129.37
127.57
113.88
77.41
77.16
76.91
61.36
55.44
35.00
22.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

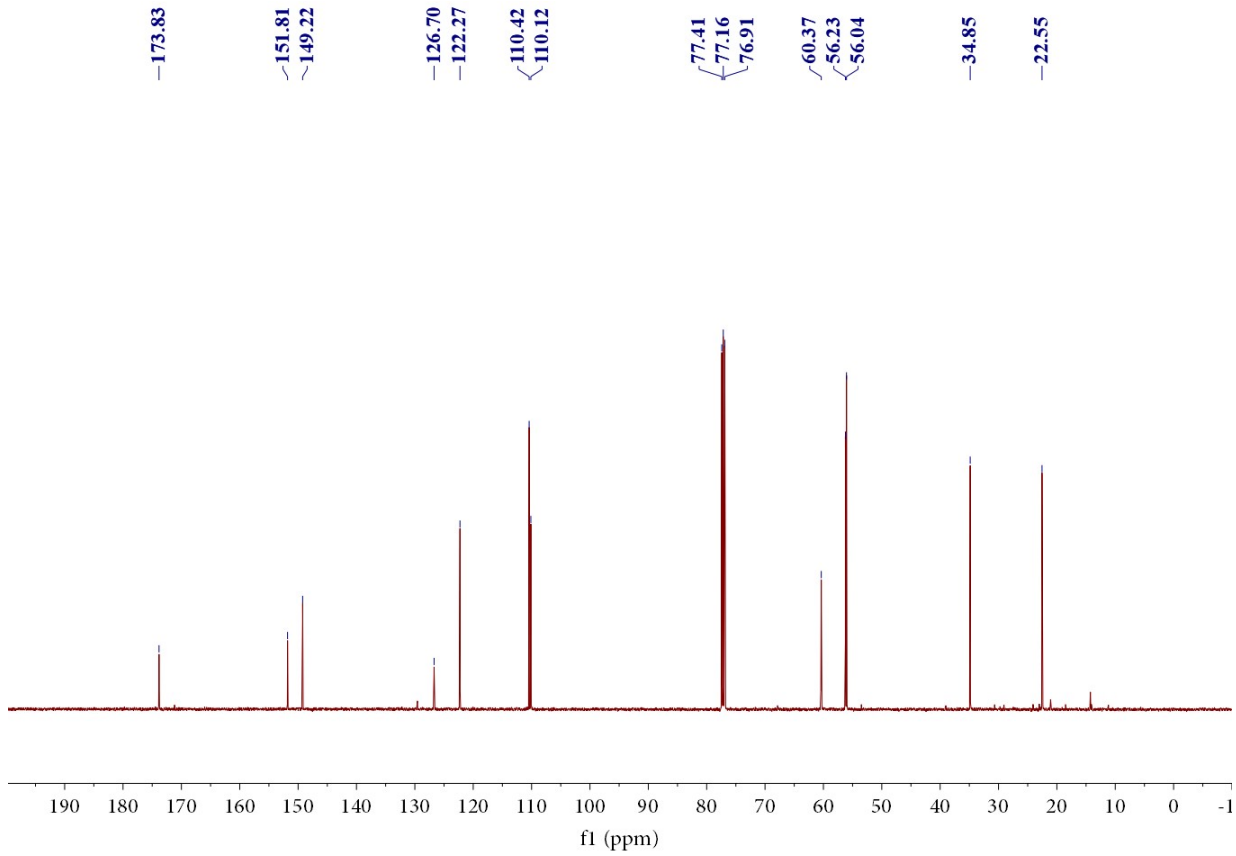

7.46
7.37
7.35
7.32
7.31
7.29
7.26
6.99
6.97
4.08
4.07
4.05
3.85
2.95
2.94
2.92
2.06
2.05
2.03
2.02
2.00
N
MeO
1.00
1.03
1.04
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

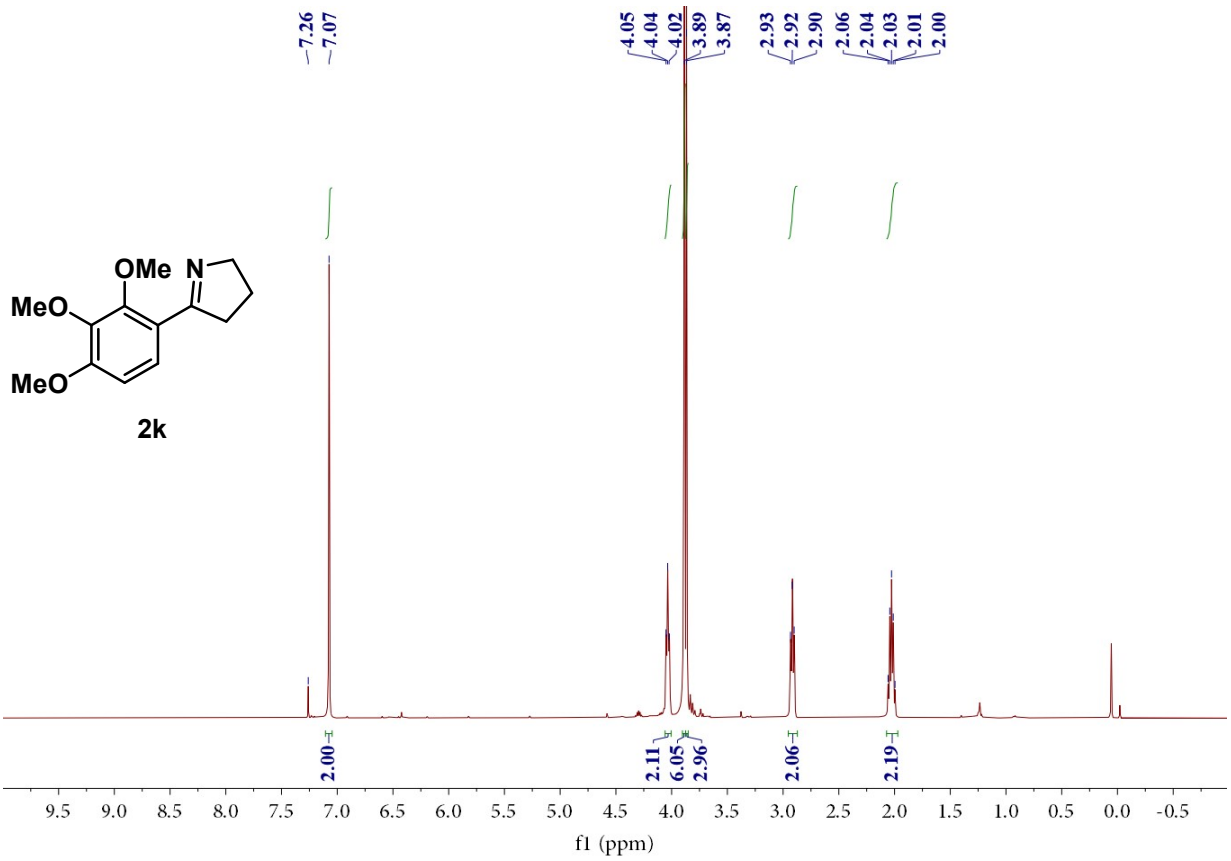
2i

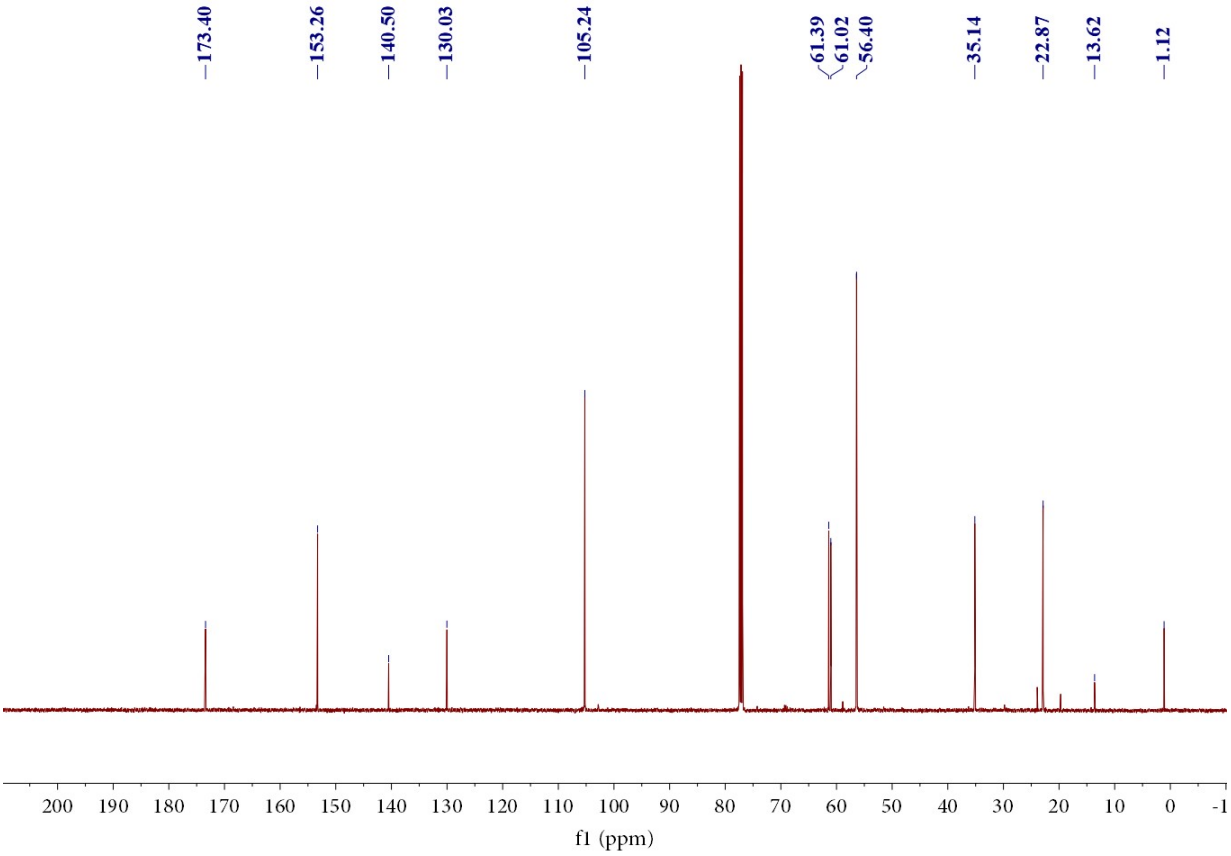

173.38
159.83
136.19
129.51
120.57
117.06
111.96
77.41
77.16
76.91
61.68
55.51
35.19
22.85
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

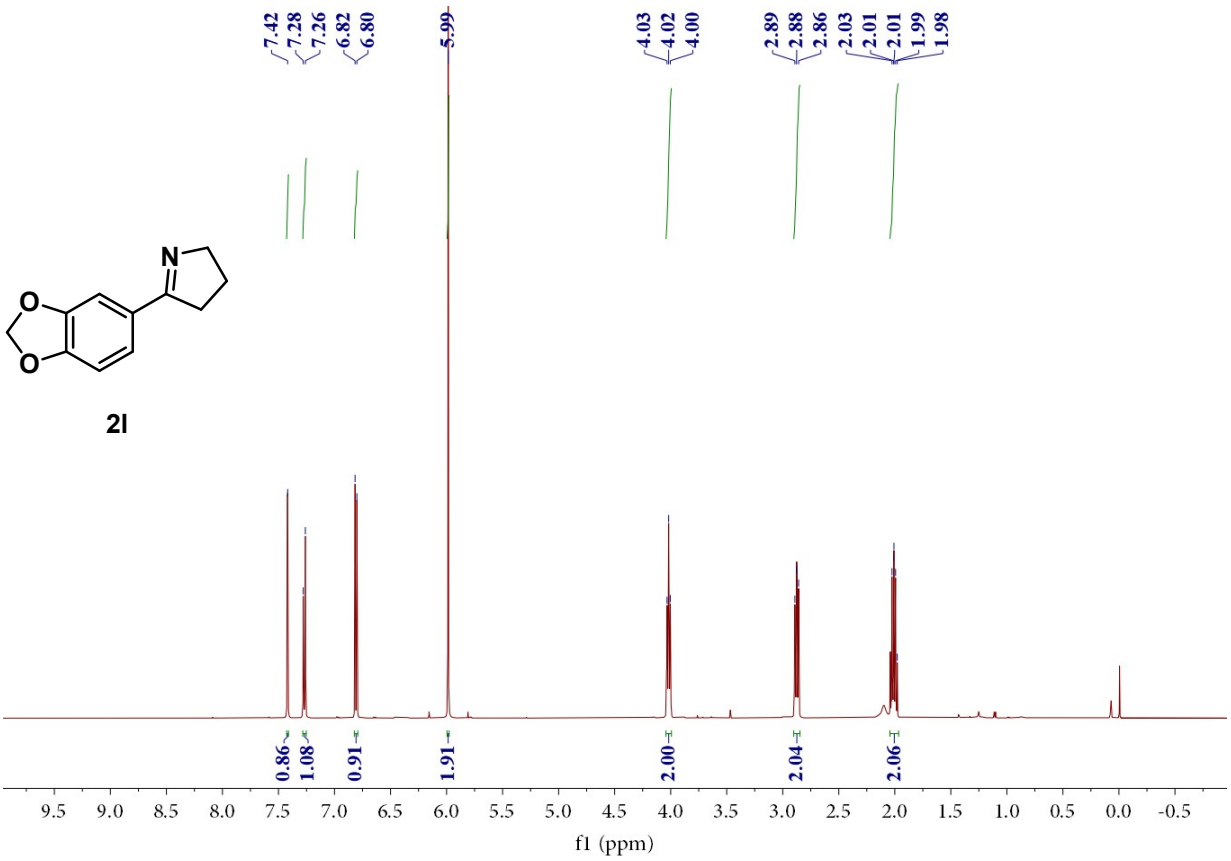

7.66
7.27
7.26
7.25
6.85
6.83
4.05
4.04
4.02
3.93
3.90
2.98
2.96
2.94
2.07
2.06
2.04
2.03
2.01
N
MeO
MeO
0.94
1.05
0.97
2.04
3.00
3.02
2.00
2.04
f1 (ppm)

2j

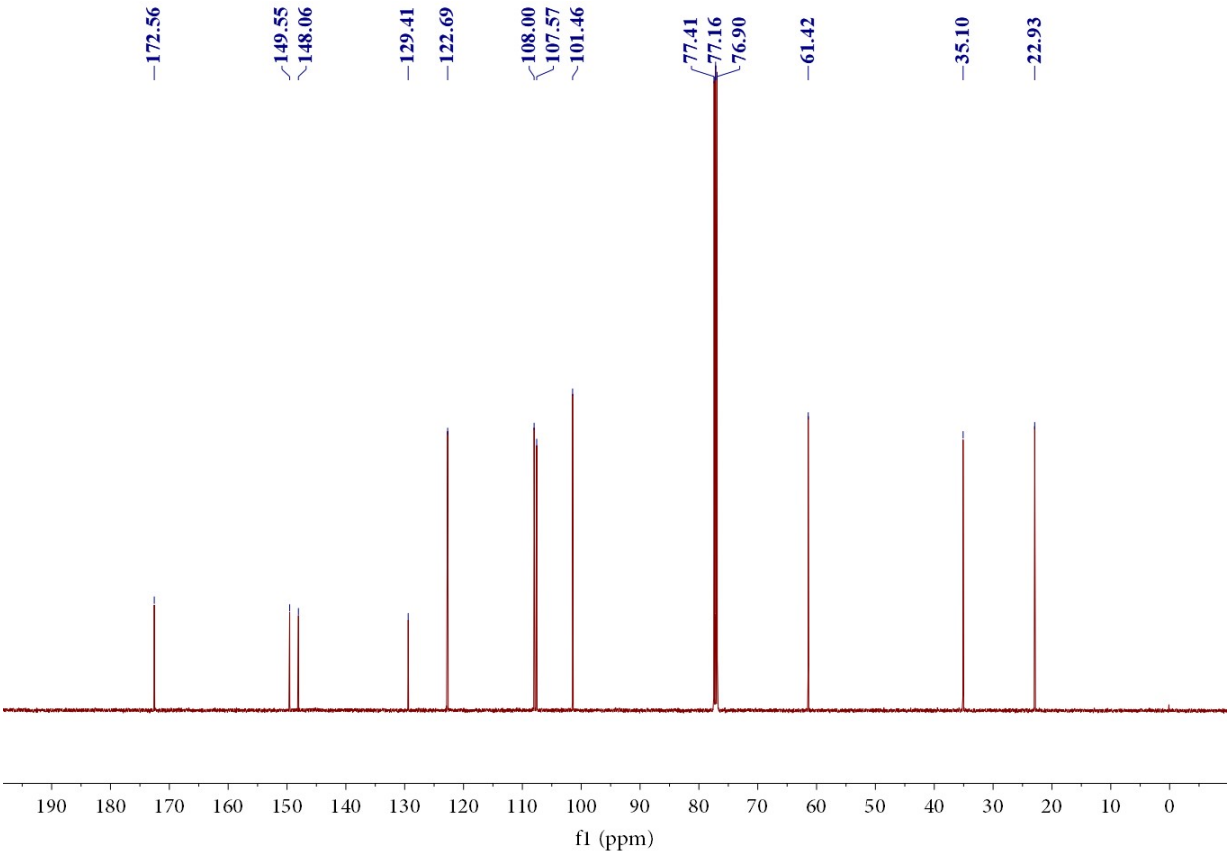

173.83
151.81
149.22
126.70
122.27
110.42
110.12
77.41
77.16
76.91
60.37
56.23
56.04
34.85
22.55
f1 (ppm)

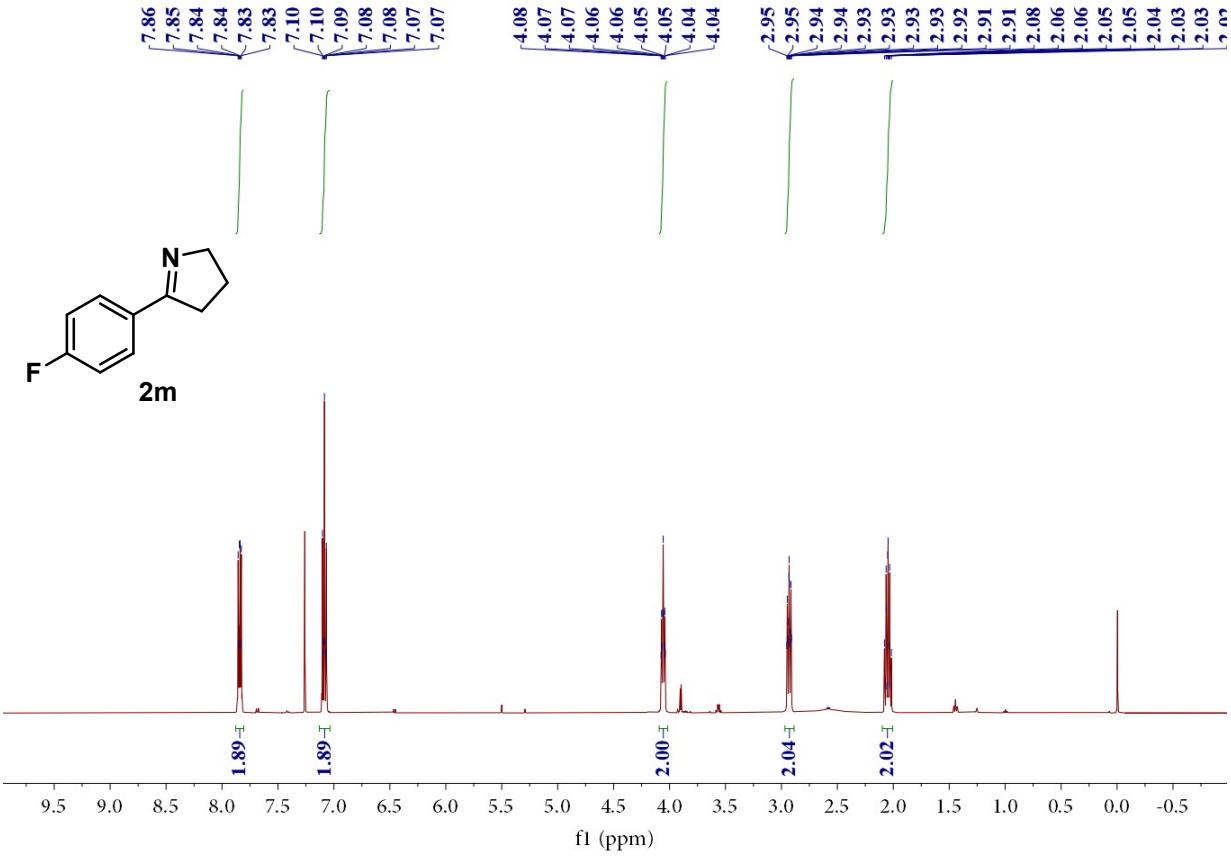

7.26
7.07
4.05
4.04
4.02
3.89
3.87
2.93
2.92
2.90
2.06
2.04
2.03
2.01
2.00
OMe
N
MeO
MeO
2k
2.00
2.11
6.05
2.96
2.06
2.19
f1 (ppm)

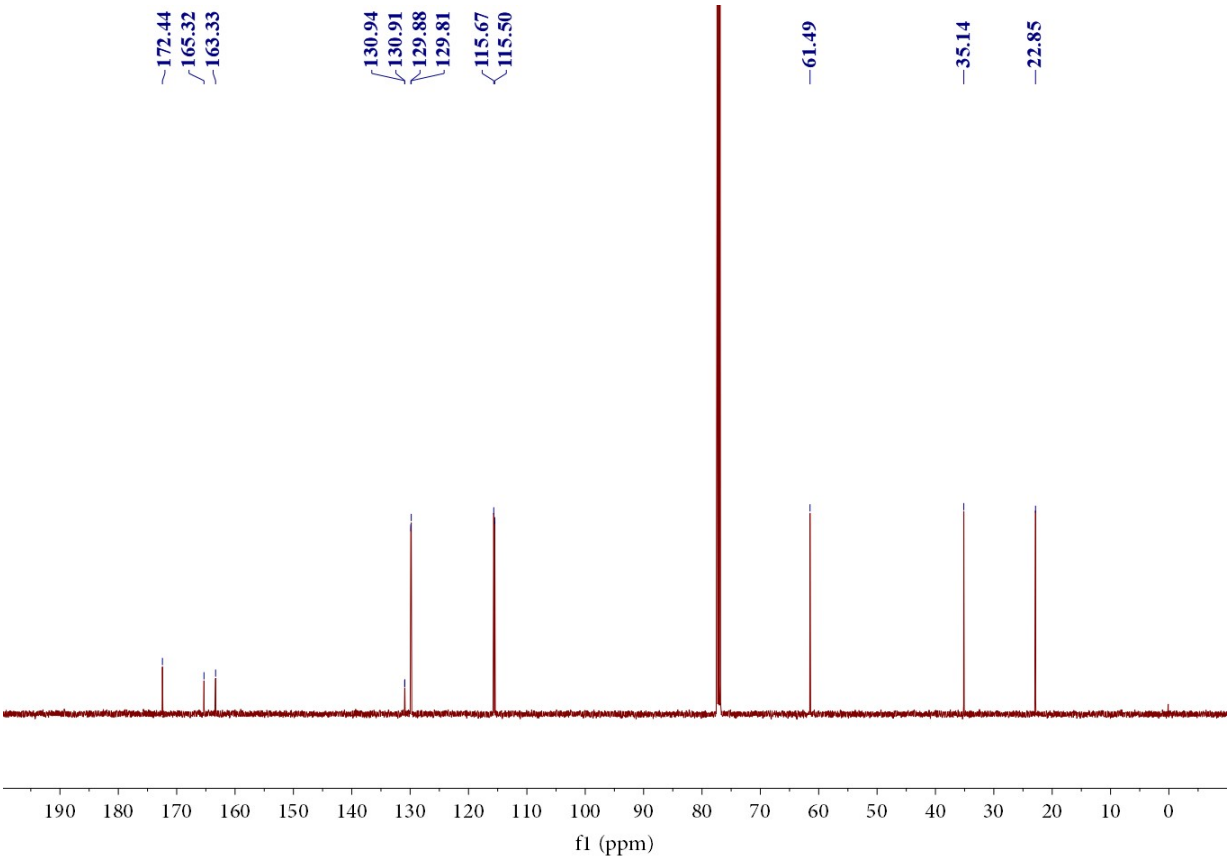

173.40
153.26
140.50
130.03
105.24
61.39
61.02
56.40
35.14
22.87
13.62
1.12
f1 (ppm)


7.42
7.28
7.26
6.82
6.80
5.99
4.03
4.02
4.00
2.89
2.88
2.86
2.03
2.01
2.01
1.99
1.98
N
O
O
0.86
1.08
0.91
1.91
2.00
2.04
2.06
f1 (ppm)

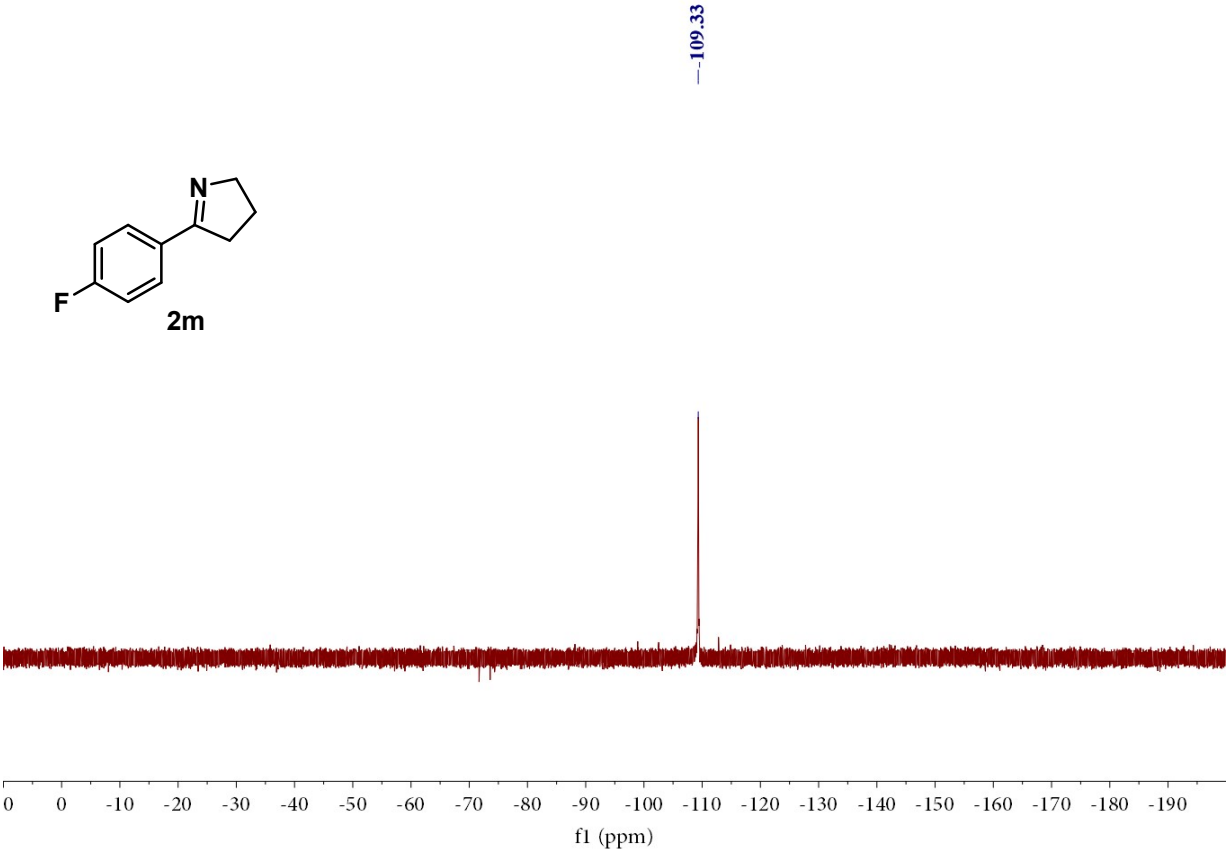
2l

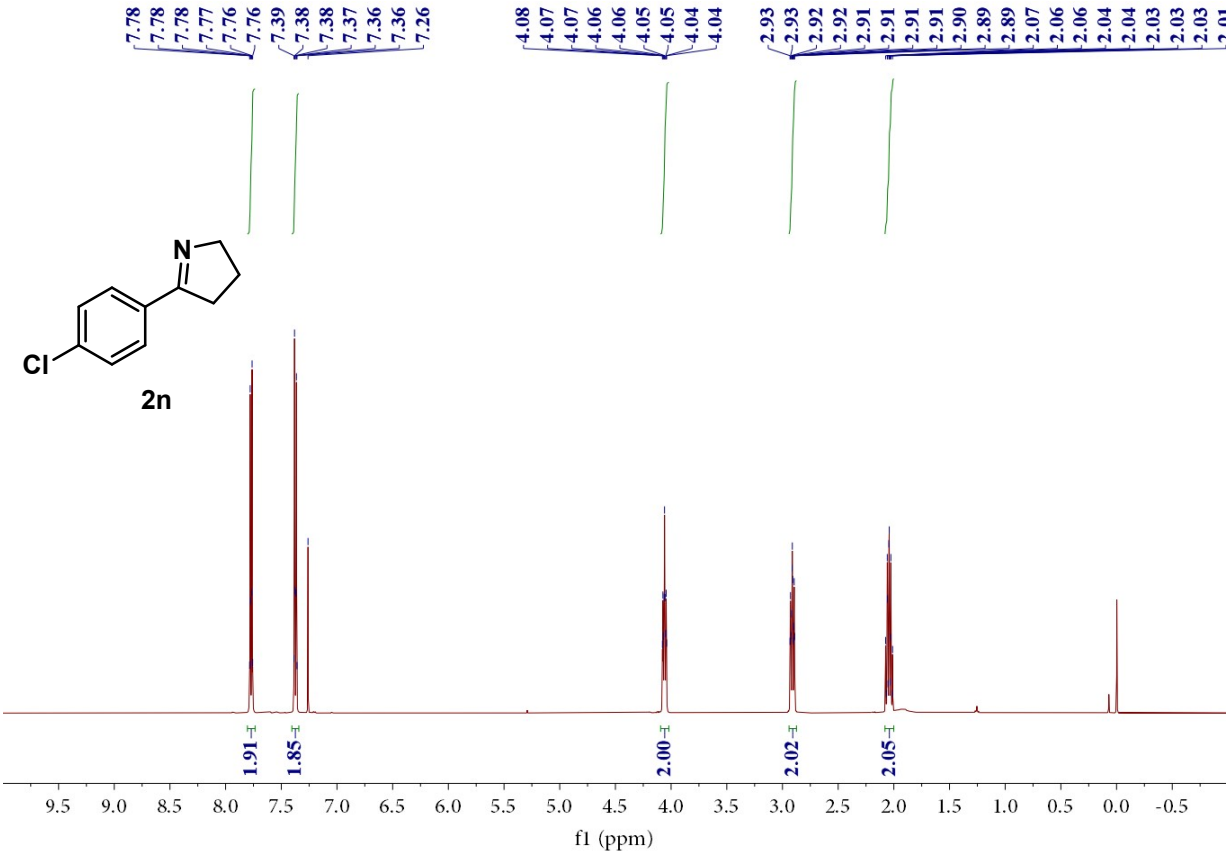

172.56
149.55
148.06
129.41
122.69
108.00
107.57
101.46
77.41
77.16
76.90
61.42
35.10
22.93
f1 (ppm)

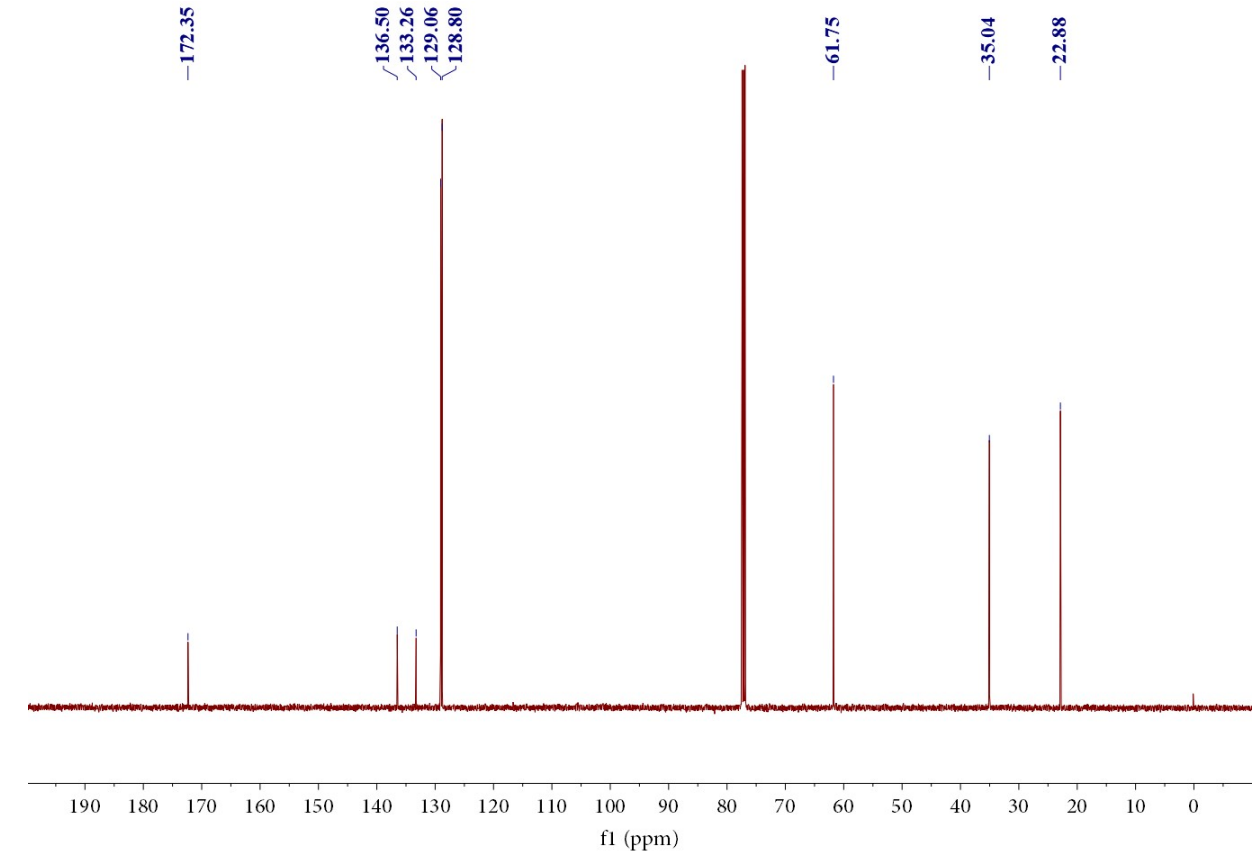

7.86
7.85
7.84
7.84
7.83
7.83
7.10
7.10
7.09
7.08
7.08
7.07
7.07
4.08
4.07
4.07
4.06
4.06
4.05
4.05
4.04
4.04
2.95
2.95
2.94
2.94
2.93
2.93
2.93
2.93
2.92
2.91
2.91
2.08
2.06
2.06
2.05
2.05
2.04
2.03
2.03
N
F
2m
1.89
1.89
2.00
2.04
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

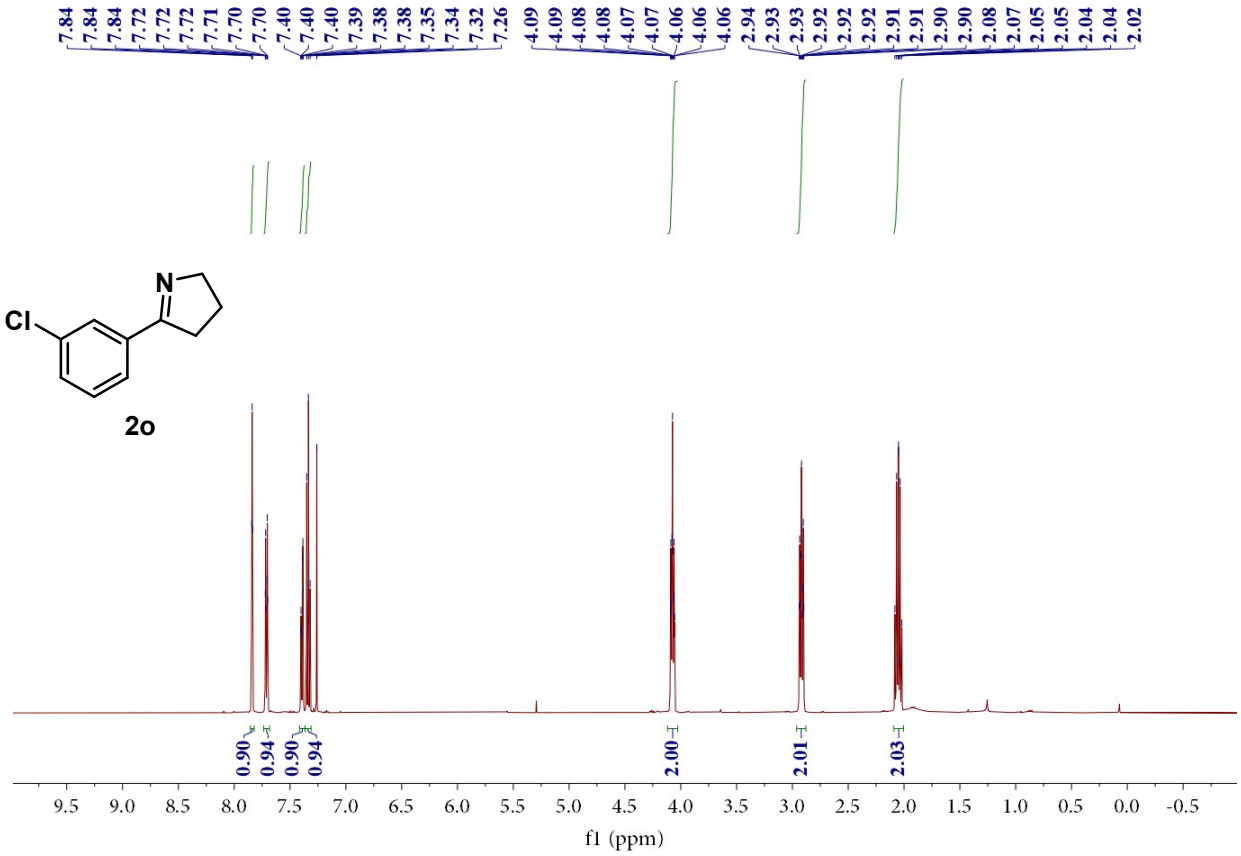

172.44
165.32
163.33
130.94
130.91
129.88
129.81
115.67
115.50
61.49
35.14
22.85
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

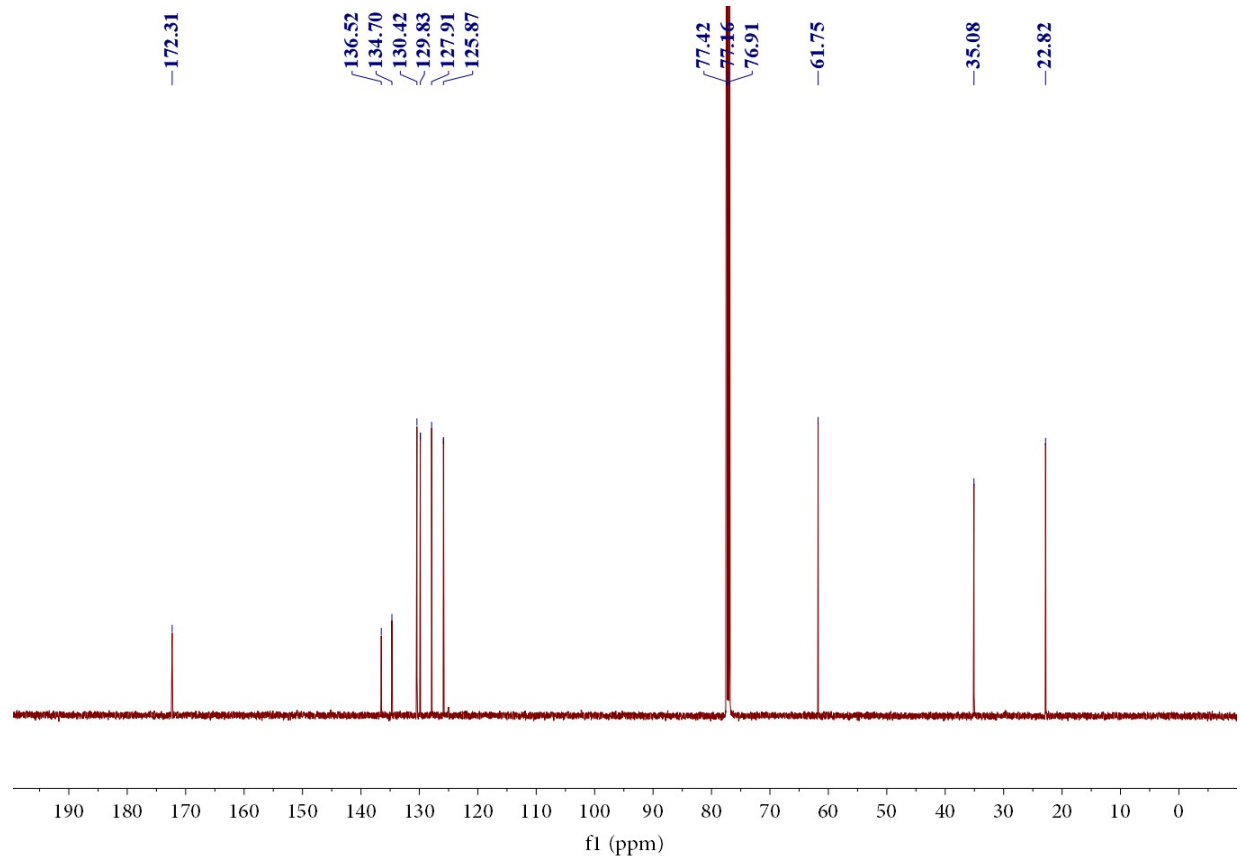
19F-NMR of 2m

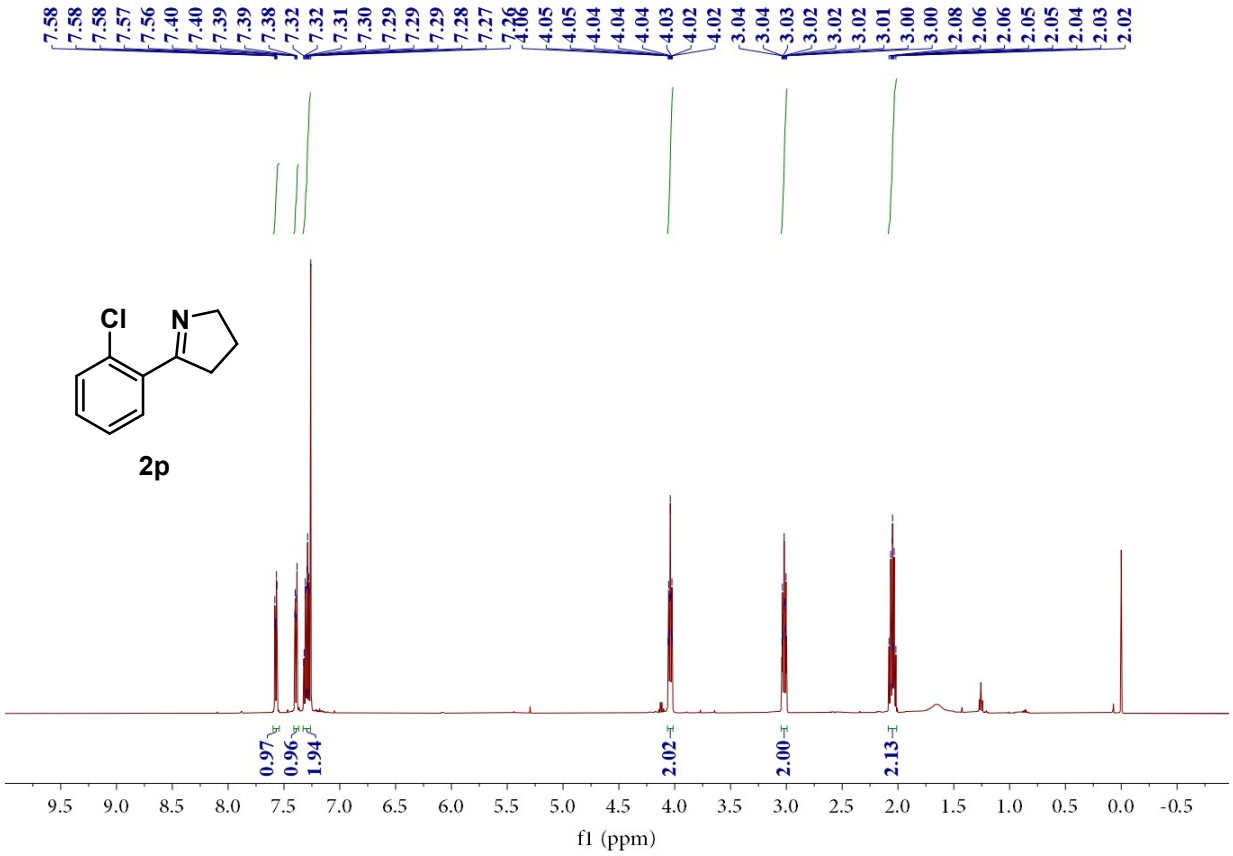

-109.33
N
F
2m
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

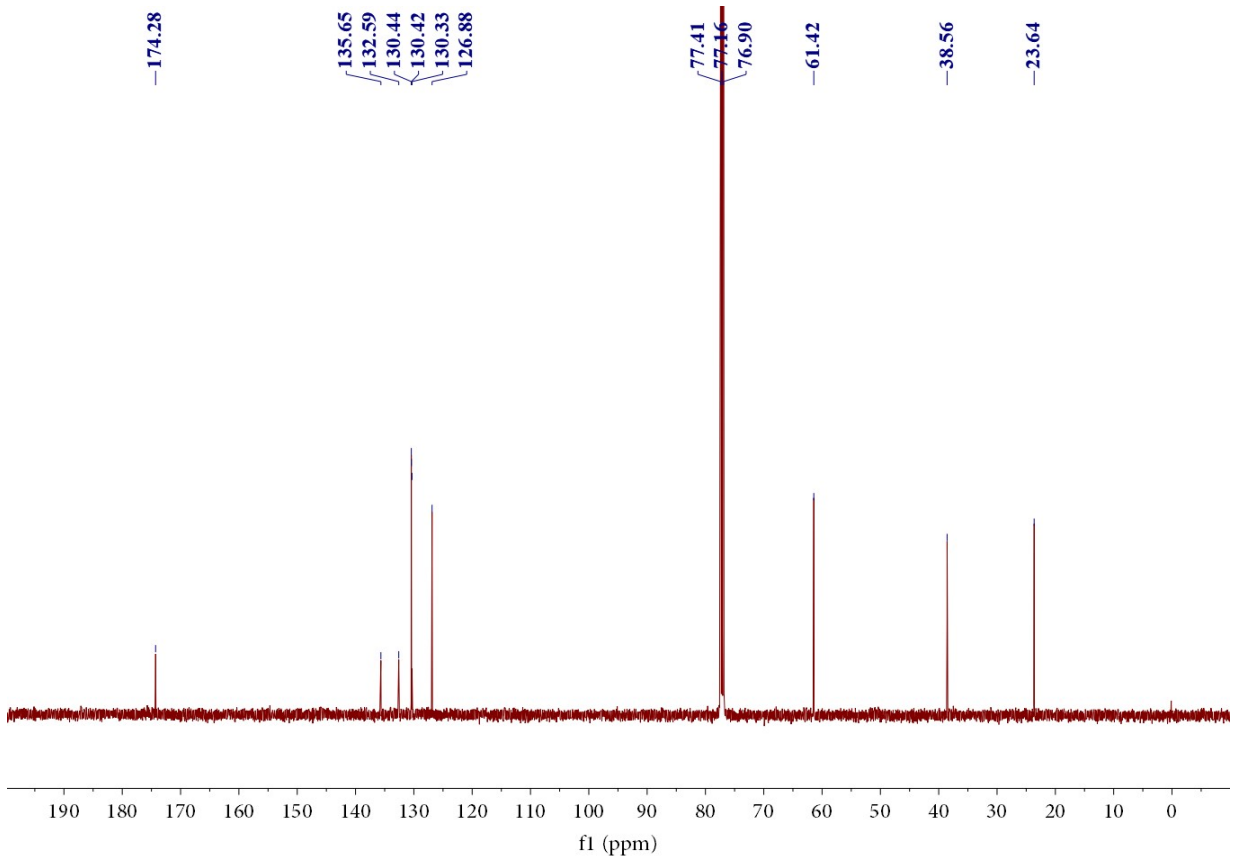

7.78
7.78
7.78
7.77
7.76
7.76
7.39
7.38
7.38
7.37
7.36
7.36
7.26
4.08
4.07
4.07
4.06
4.06
4.05
4.05
4.04
4.04
2.93
2.93
2.92
2.92
2.91
2.91
2.91
2.91
2.90
2.89
2.89
2.07
2.06
2.06
2.04
2.04
2.03
2.03
N
Cl
2n
1.91
1.85
2.00
2.02
2.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

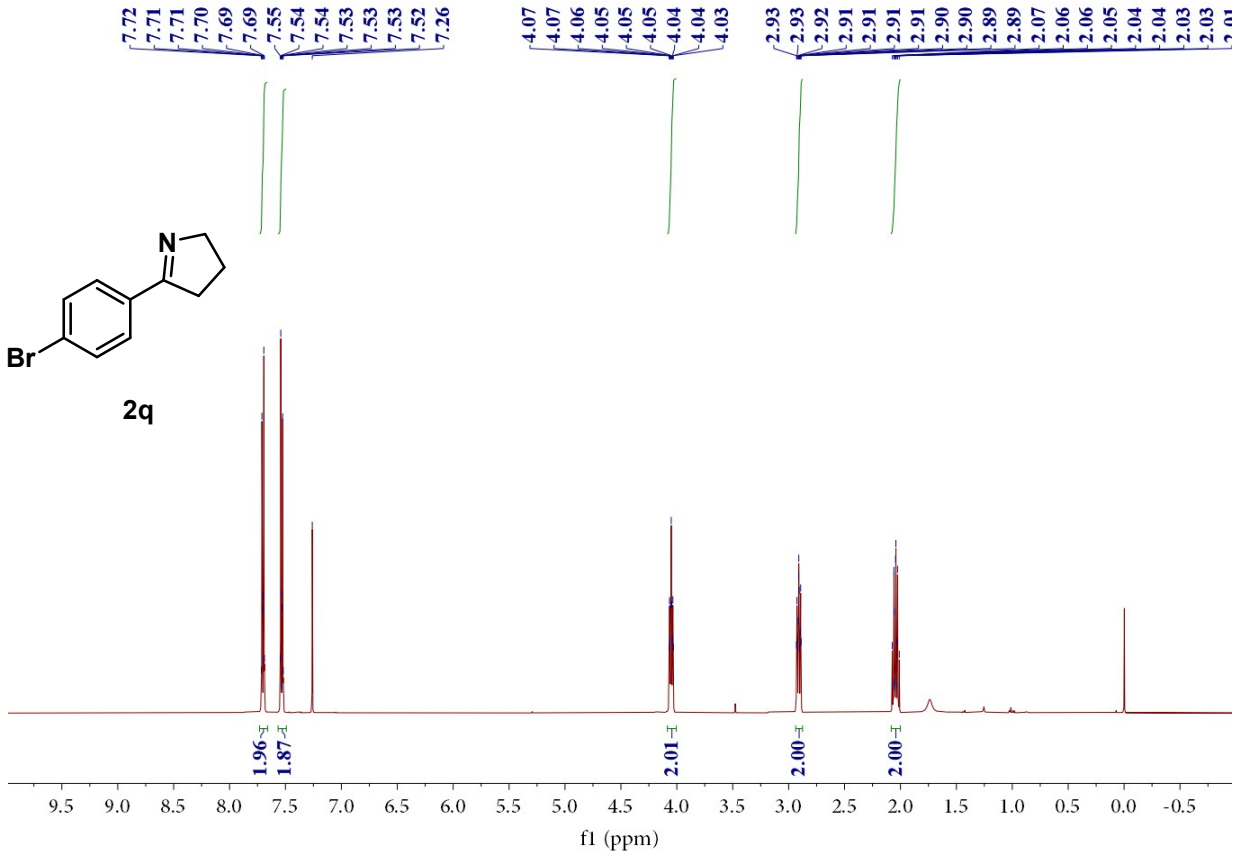

172.35
136.50
133.26
129.06
128.80
61.75
35.04
22.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

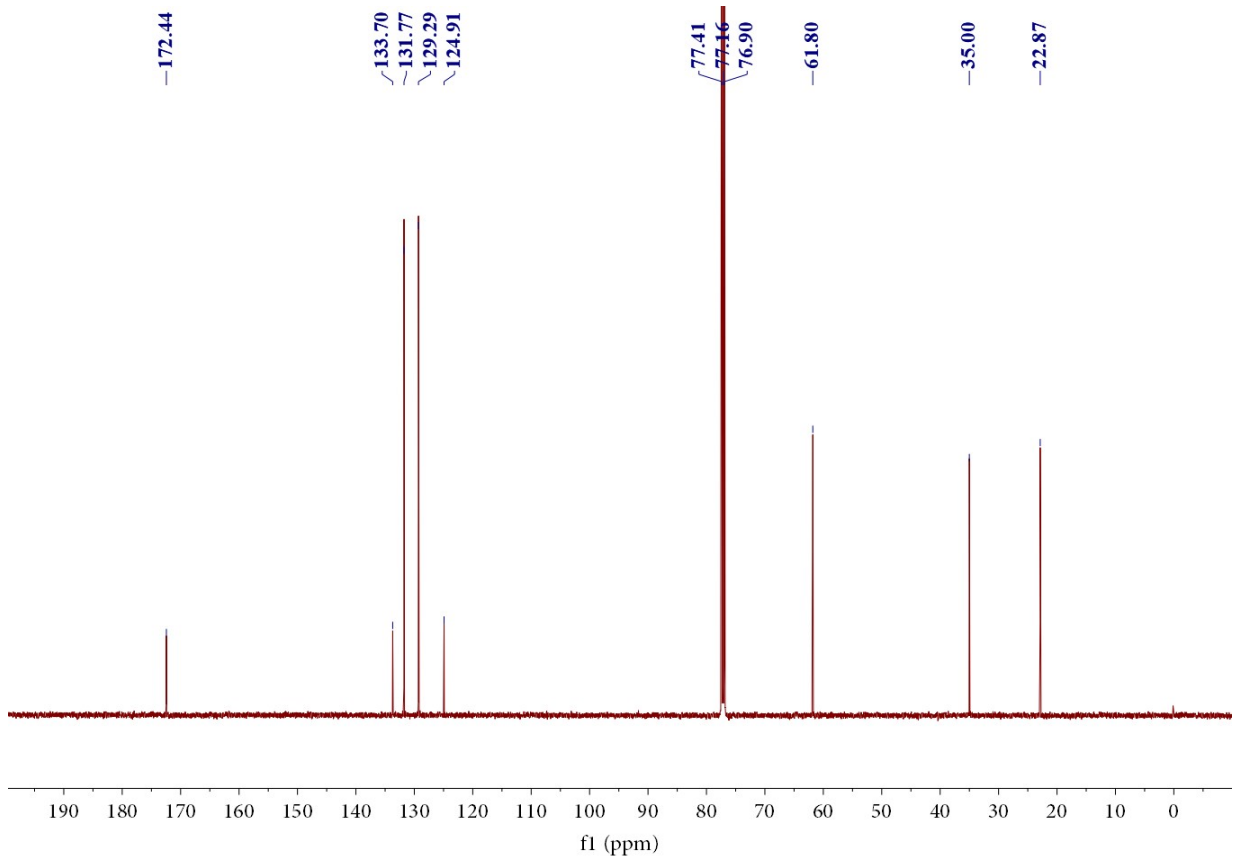

7.84 7.84 7.84 7.72 7.72 7.72 7.71 7.70 7.70 7.40 7.40 7.40 7.39 7.38 7.38 7.35 7.34 7.32 7.26
4.09 4.09 4.08 4.08 4.07 4.07 4.06 4.06 4.06
2.94 2.93 2.93 2.92 2.92 2.92 2.91 2.91 2.90 2.90 2.08 2.07 2.05 2.05 2.04 2.04 2.02
N
Cl
2o
0.90 0.94 0.90 0.94 2.00 2.01 2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

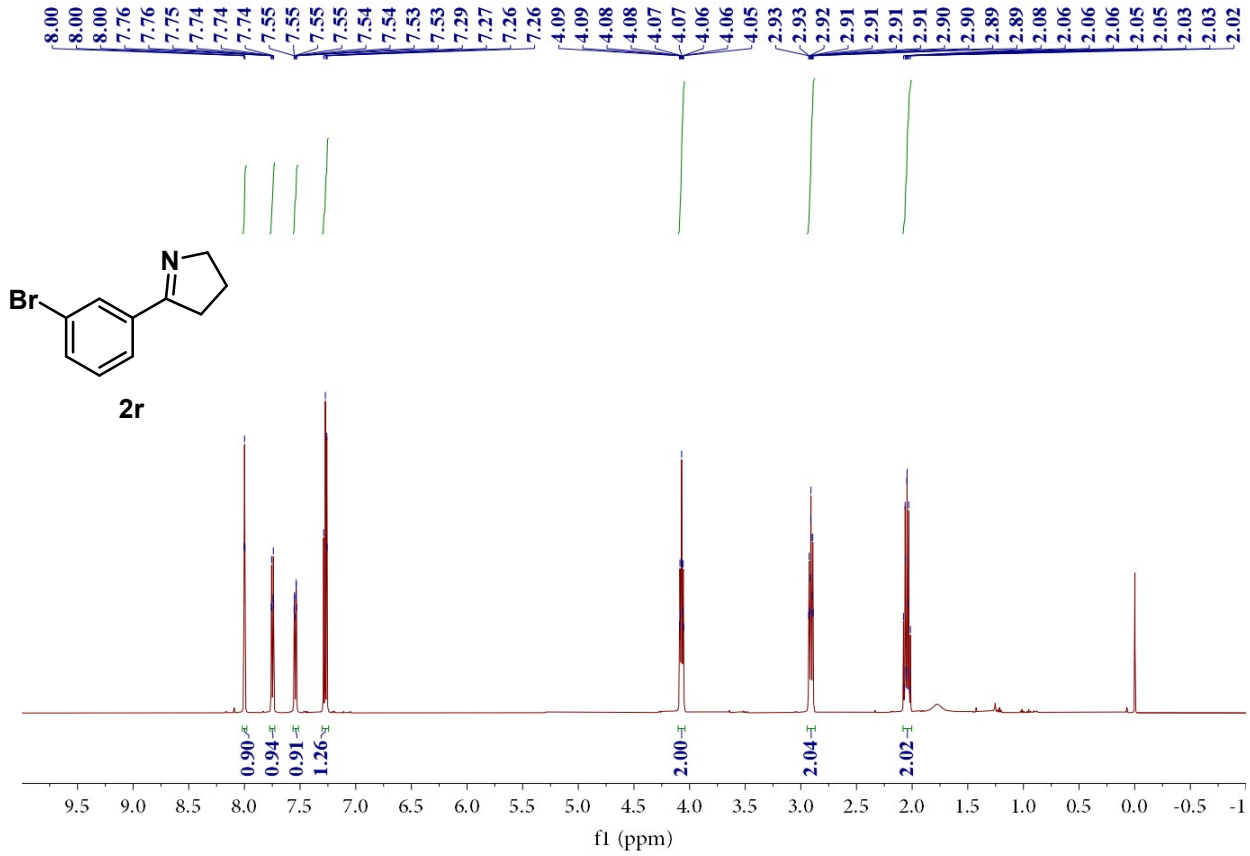

172.31
136.52 134.70 130.42 129.83 127.91 125.87
77.42 77.16 76.91
61.75
35.08
22.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

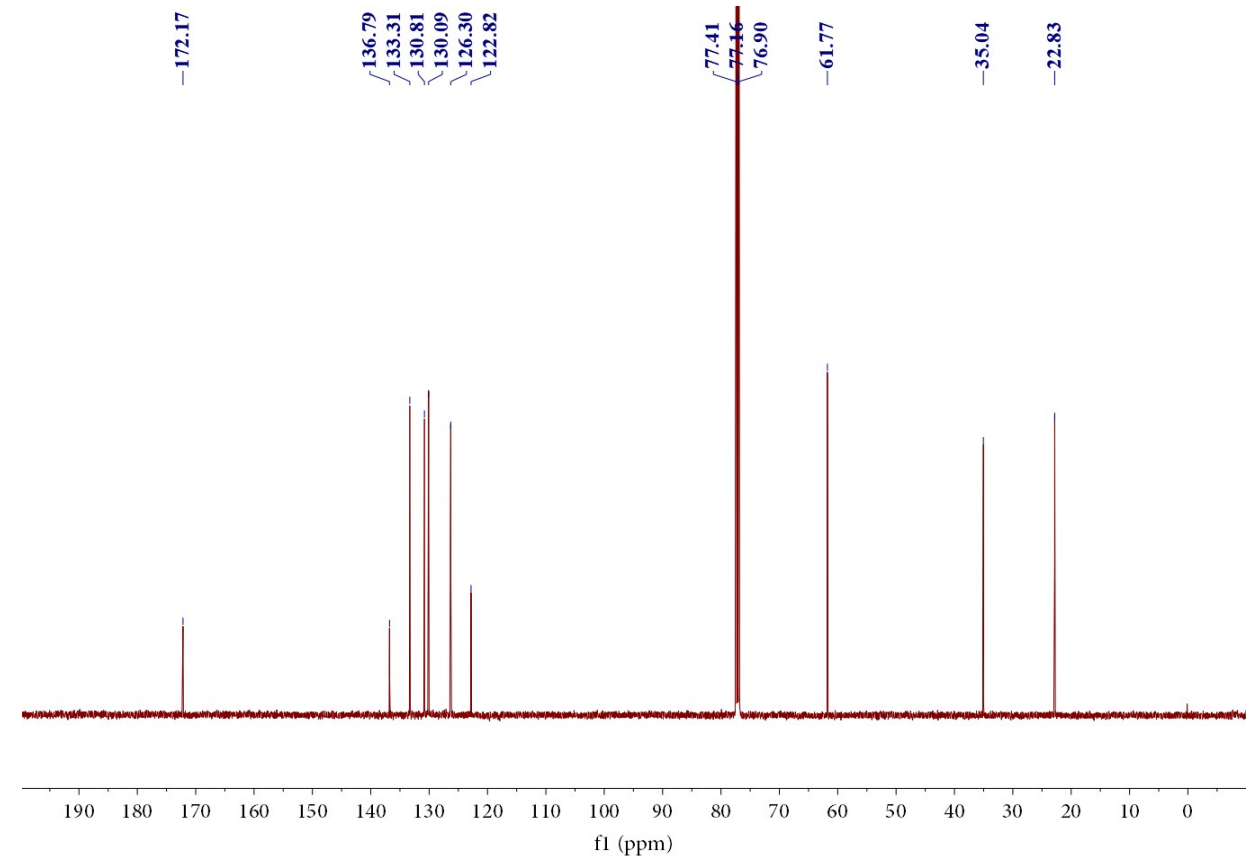

7.58 7.58 7.58 7.57 7.56 7.40 7.40 7.39 7.39 7.38 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26 4.06 4.05 4.05 4.04 4.04 4.04 4.03 4.02 4.02 3.04 3.04 3.03 3.02 3.02 3.02 3.01 3.00 3.00 2.08 2.06 2.06 2.05 2.05 2.04 2.03 2.02
Cl
N
2p
0.97
0.96
1.94
2.02
2.00
2.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

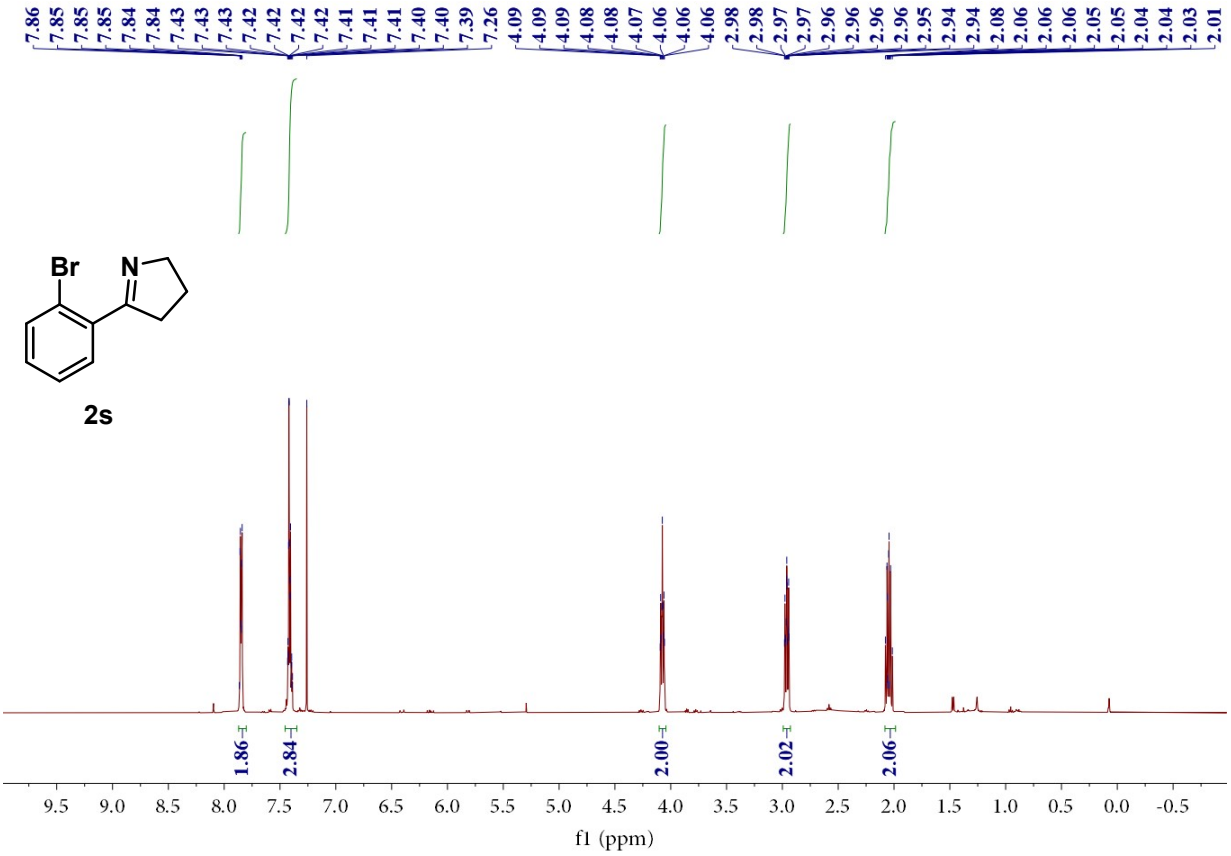

174.28
135.65
132.59
130.44
130.42
130.33
126.88
77.41
77.16
76.90
61.42
38.56
23.64
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

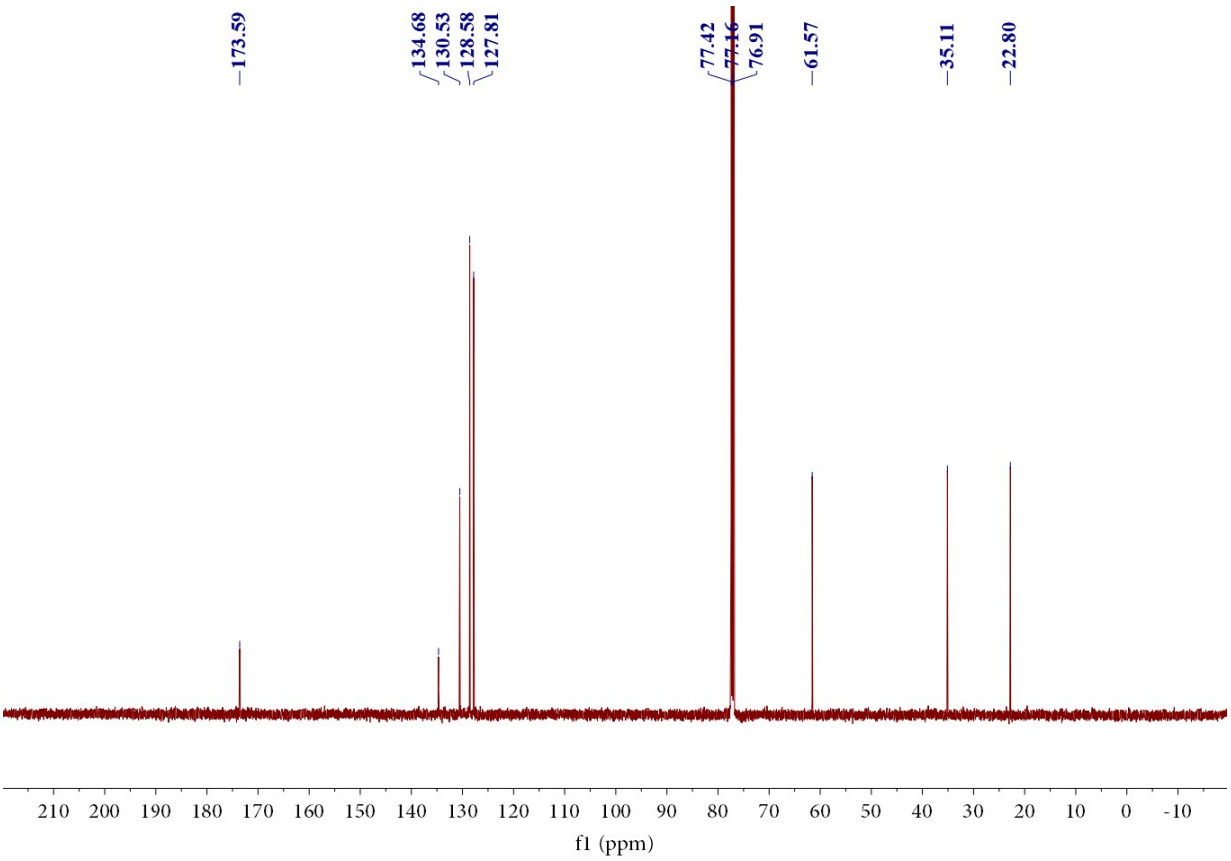

7.72
7.71
7.71
7.70
7.69
7.69
7.55
7.54
7.54
7.54
7.53
7.53
7.53
7.52
7.26
4.07
4.07
4.06
4.05
4.05
4.05
4.04
4.04
4.03
2.93
2.93
2.92
2.91
2.91
2.91
2.91
2.90
2.90
2.89
2.89
2.07
2.06
2.06
2.05
2.04
2.04
2.03
2.03
N
Br
2q
1.96
1.87
2.01
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

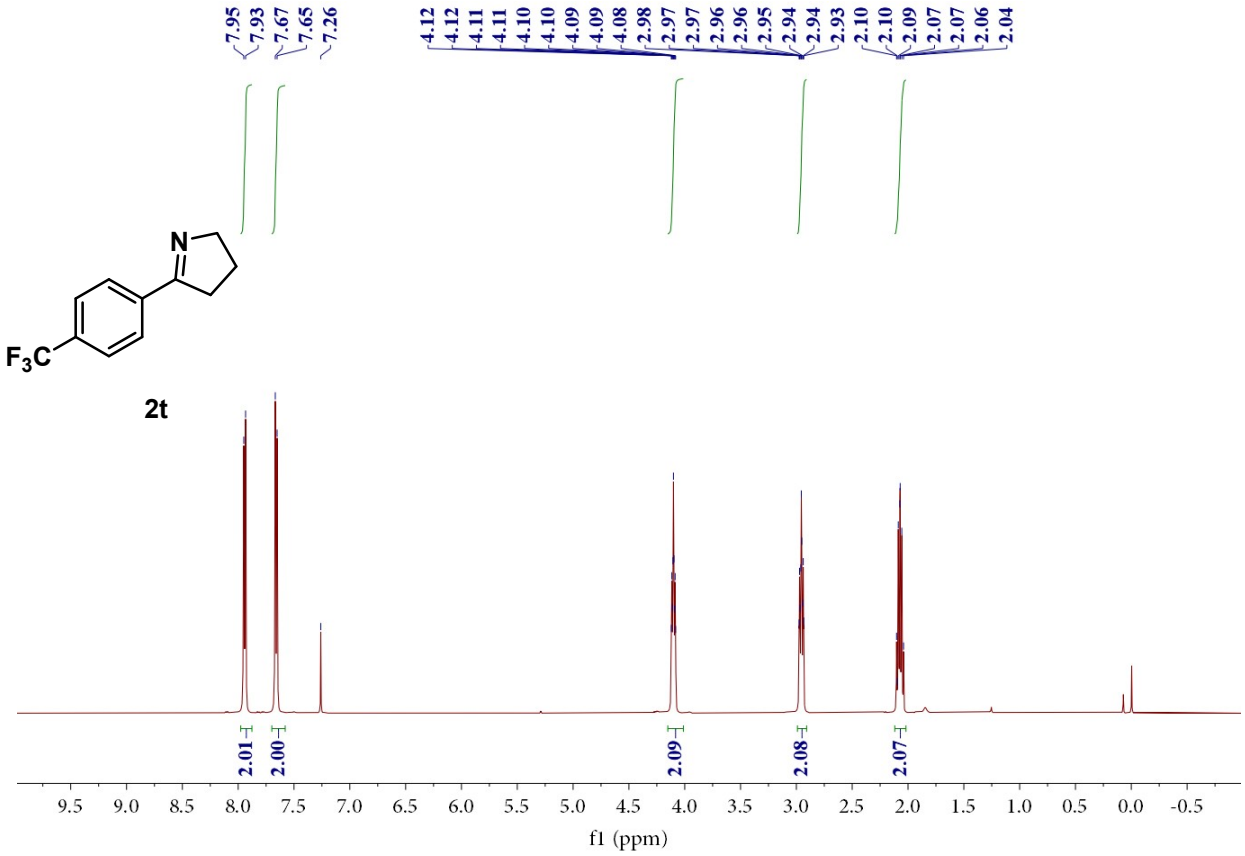

172.44
133.70
131.77
129.29
124.91
77.41
77.16
76.90
61.80
35.00
22.87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

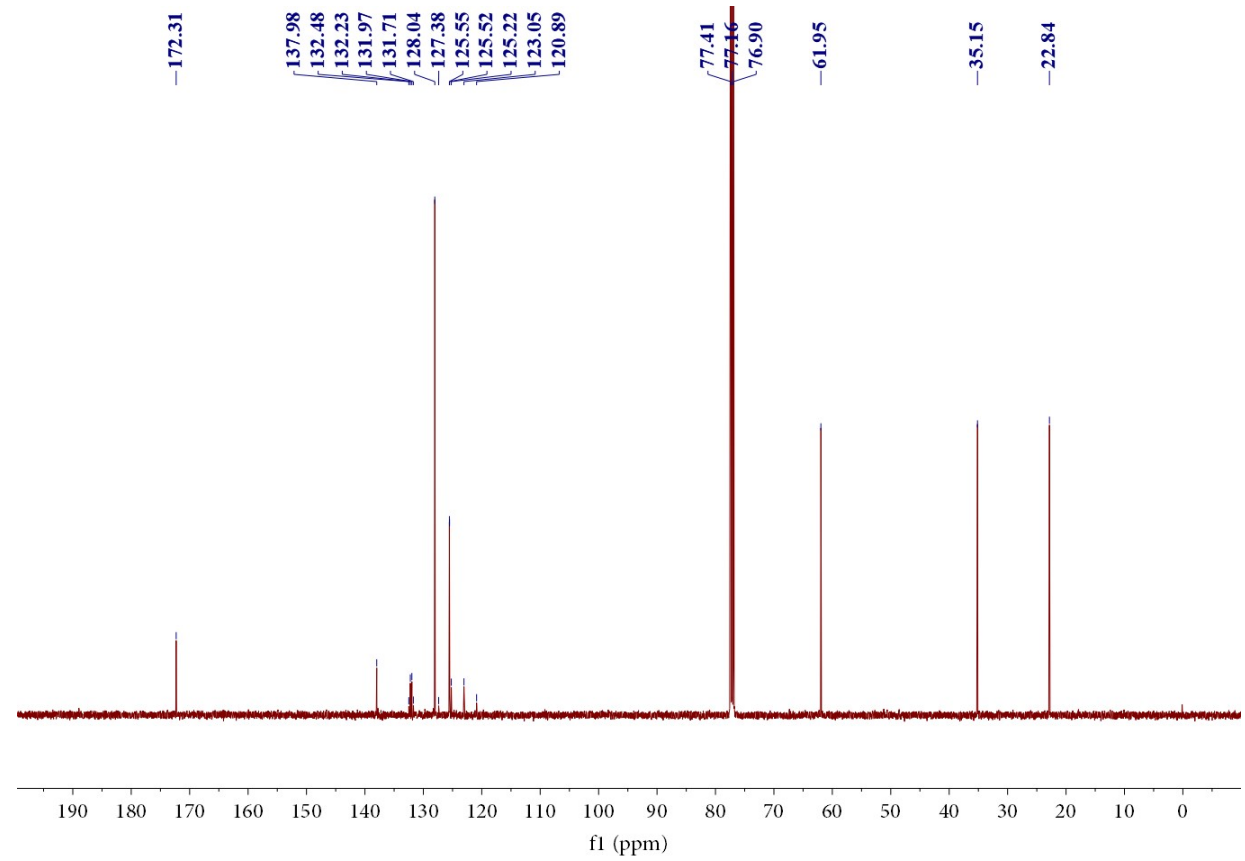

8.00 8.00 8.00 7.76 7.76 7.75 7.74 7.74 7.74 7.55 7.55 7.55 7.54 7.54 7.53 7.53 7.29 7.27 7.26 7.26
4.09 4.09 4.08 4.08 4.07 4.07 4.06 4.06 4.05
2.93 2.93 2.92 2.91 2.91 2.91 2.91 2.90 2.90 2.89 2.89 2.08 2.06 2.06 2.06 2.05 2.05 2.03 2.03 2.02
N
Br
2r
0.90 0.94 0.91 1.26 2.00 2.04 2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


172.17
136.79 133.31 130.81 130.09 126.30 122.82
77.41 77.16 76.90
61.77
35.04
22.83
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

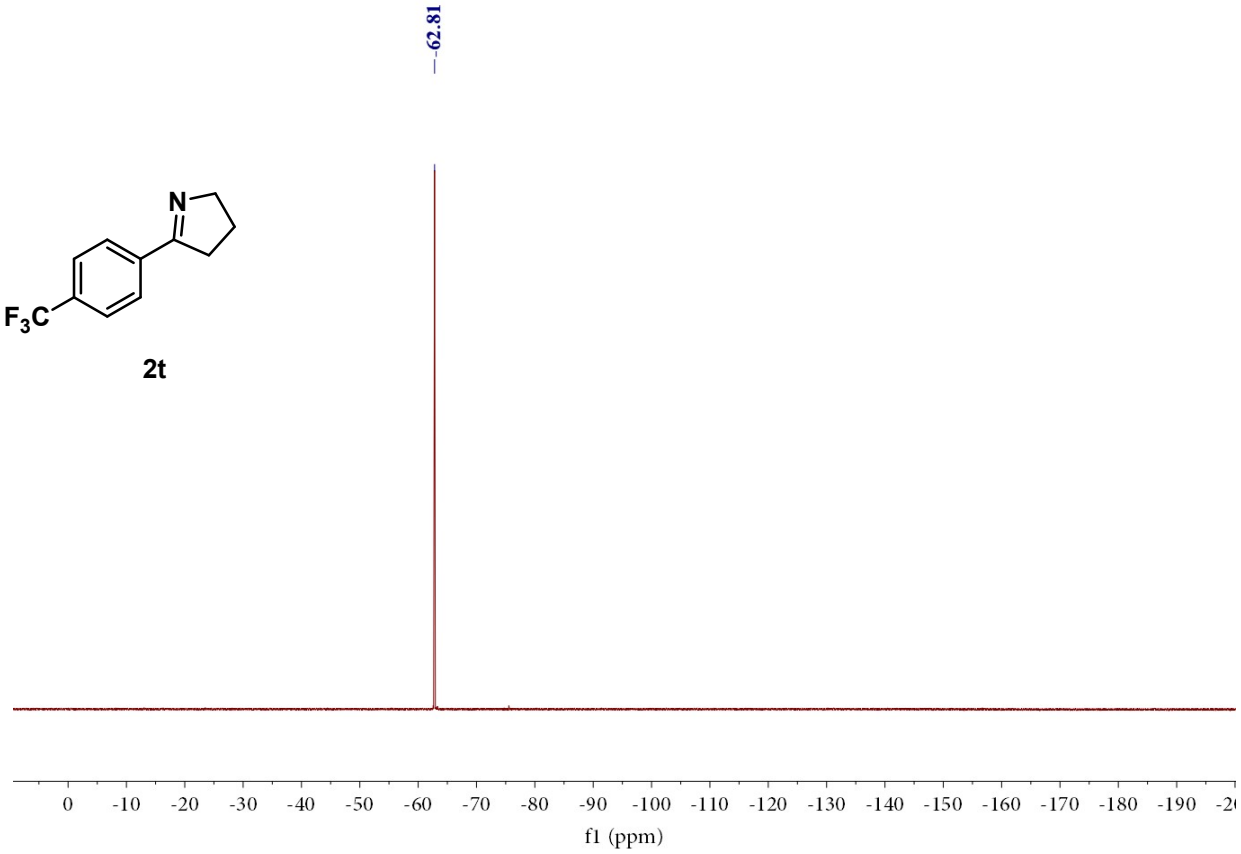

7.86 7.85 7.85 7.84 7.84 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.26
4.09 4.09 4.09 4.08 4.08 4.07 4.06 4.06 4.06
2.98 2.98 2.97 2.97 2.96 2.96 2.96 2.96 2.95 2.94 2.94 2.08 2.06 2.06 2.06 2.05 2.05 2.04 2.04 2.03 2.01
Br
N
2s
1.86
2.84
2.00
2.02
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

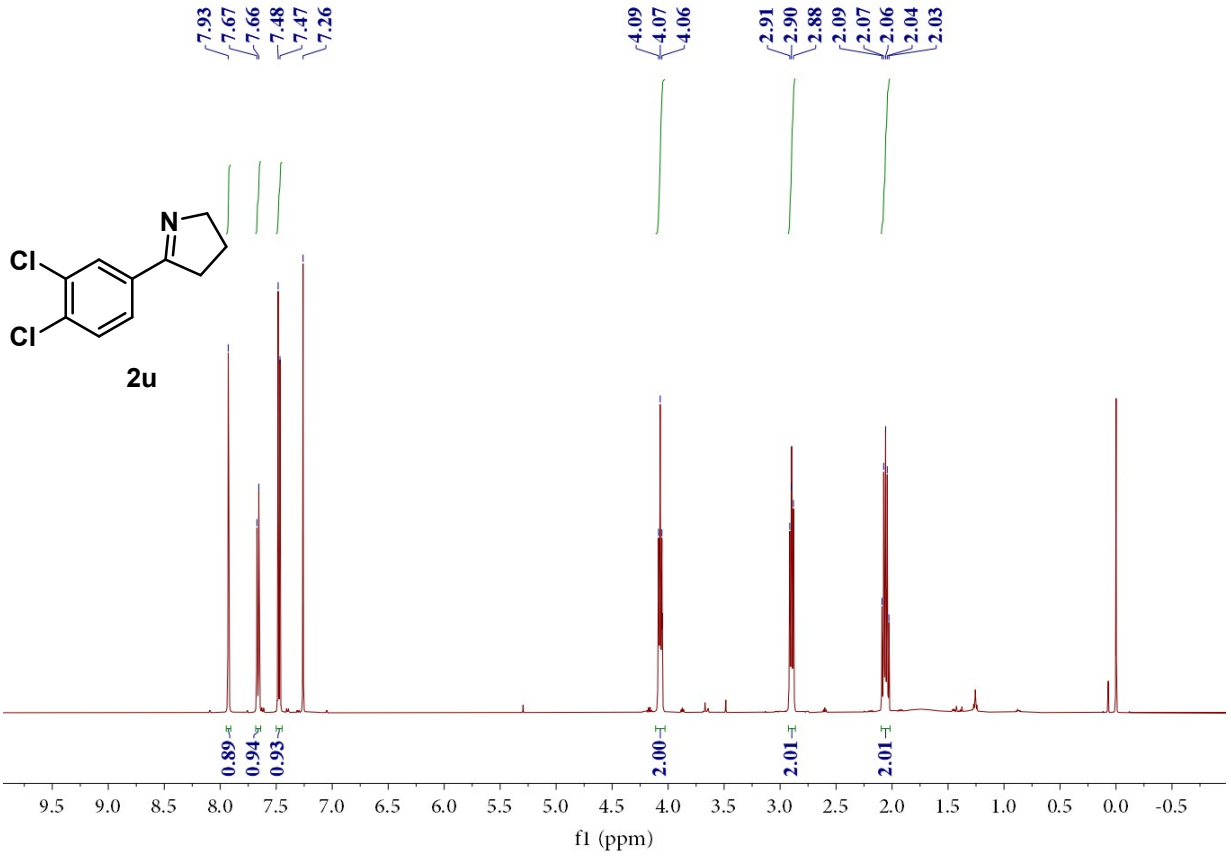

173.59
134.68
130.53
128.58
127.81
77.42
77.16
76.91
61.57
35.11
22.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

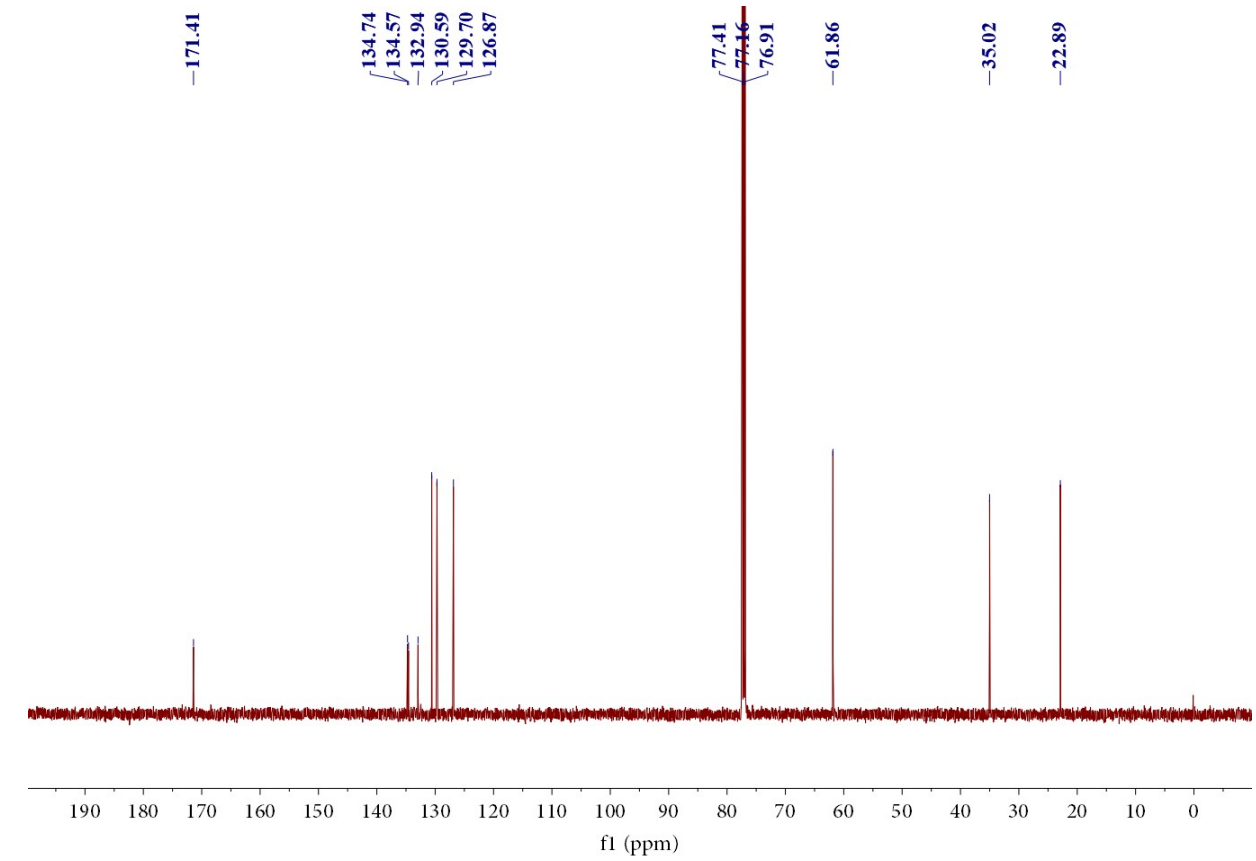

7.95
7.93
7.67
7.65
7.26
4.12
4.12
4.11
4.11
4.10
4.10
4.09
4.09
4.08
2.98
2.97
2.97
2.96
2.96
2.95
2.94
2.94
2.93
2.10
2.10
2.09
2.07
2.07
2.06
2.04
N
F3C
2t
2.01
2.00
2.09
2.08
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

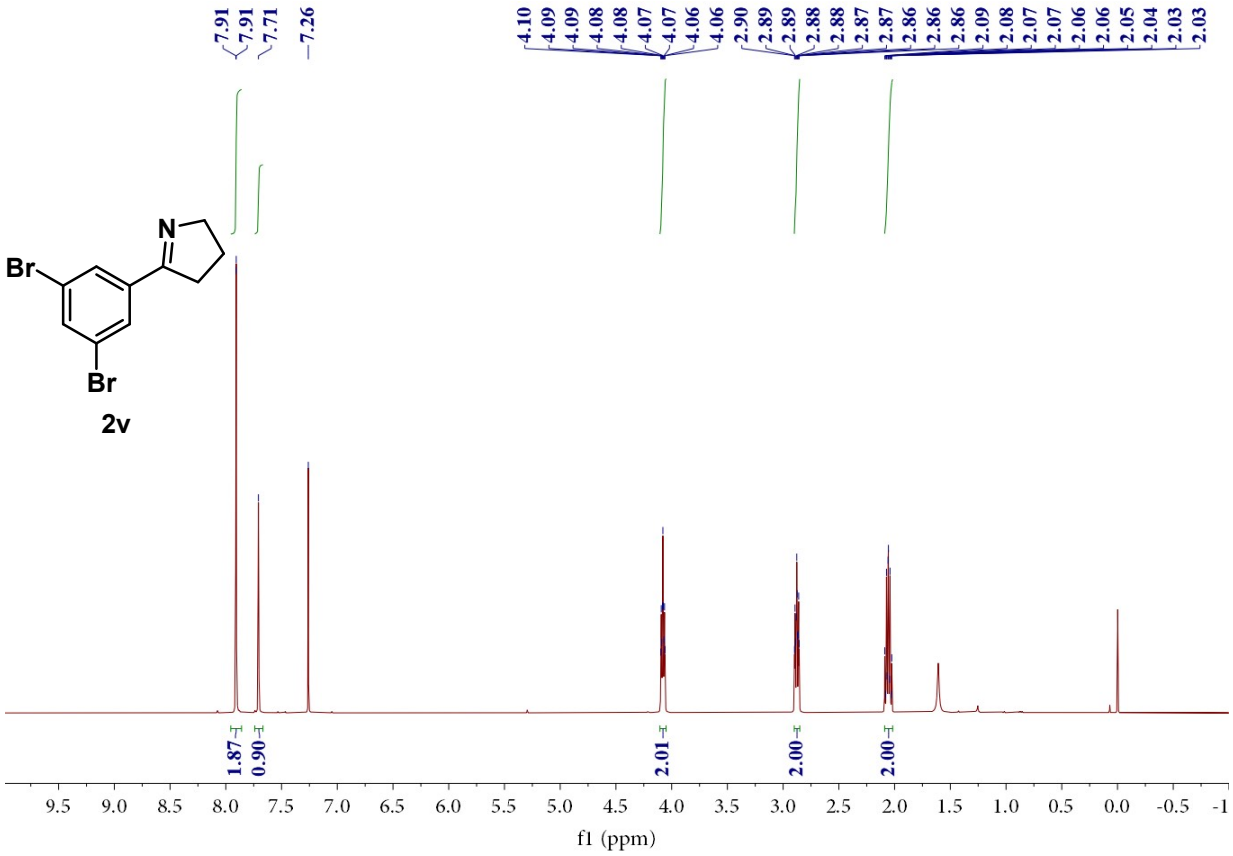

172.31
137.98
132.48
132.23
131.97
131.71
128.04
127.38
125.55
125.52
125.22
123.05
120.89
77.41
77.16
76.90
61.95
35.15
22.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

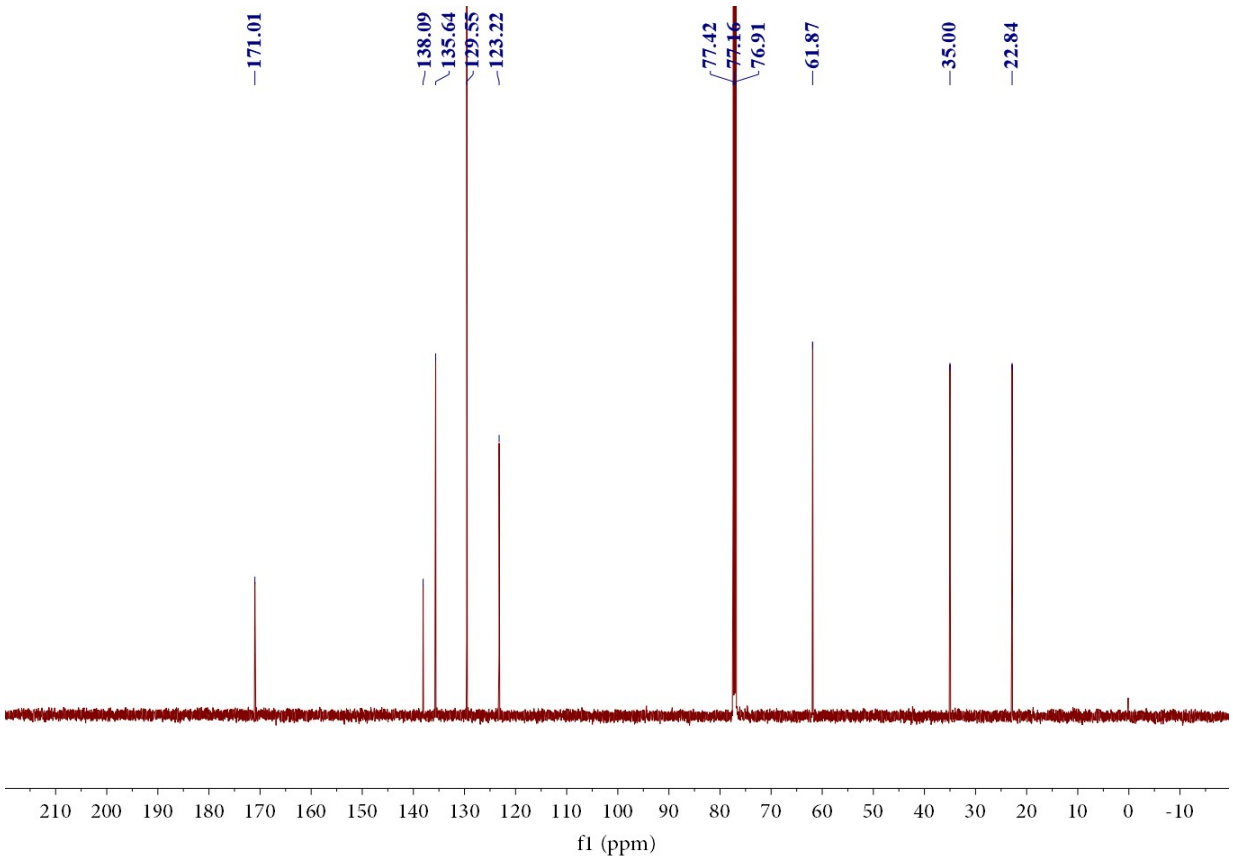
19F NMR of 2t

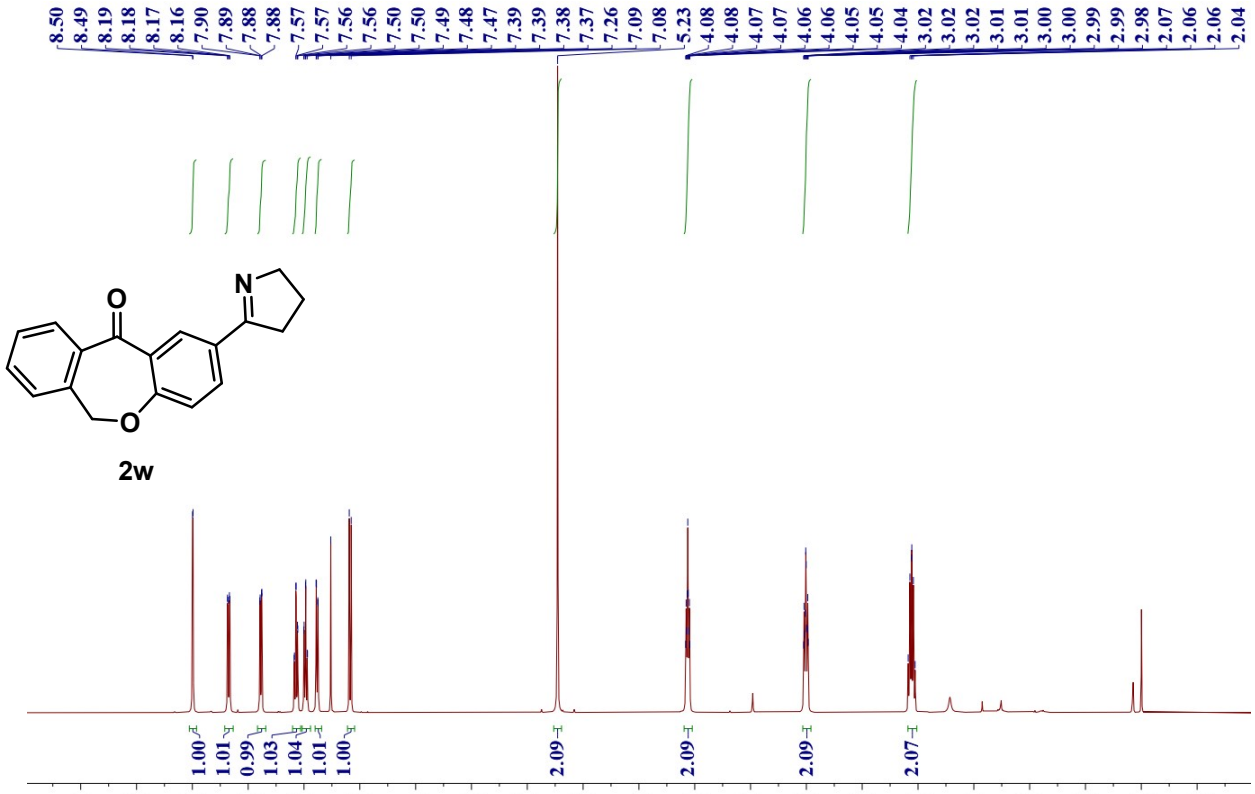

-62.81
N
F3C
2t
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

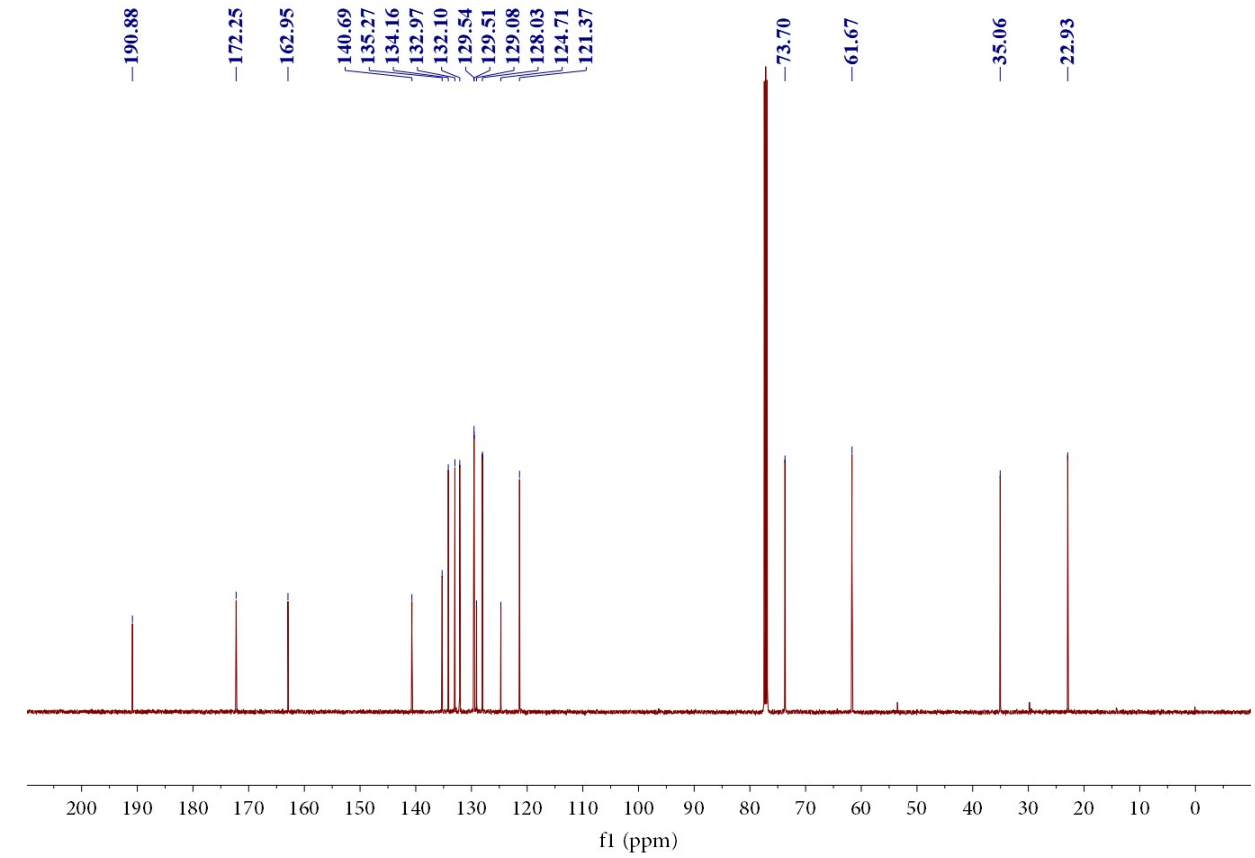

7.93
7.67
7.66
7.48
7.47
7.26
4.09
4.07
4.06
2.91
2.90
2.88
2.09
2.07
2.06
2.04
2.03
N
Cl
Cl
2u
0.89
0.94
0.93
2.00
2.01
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

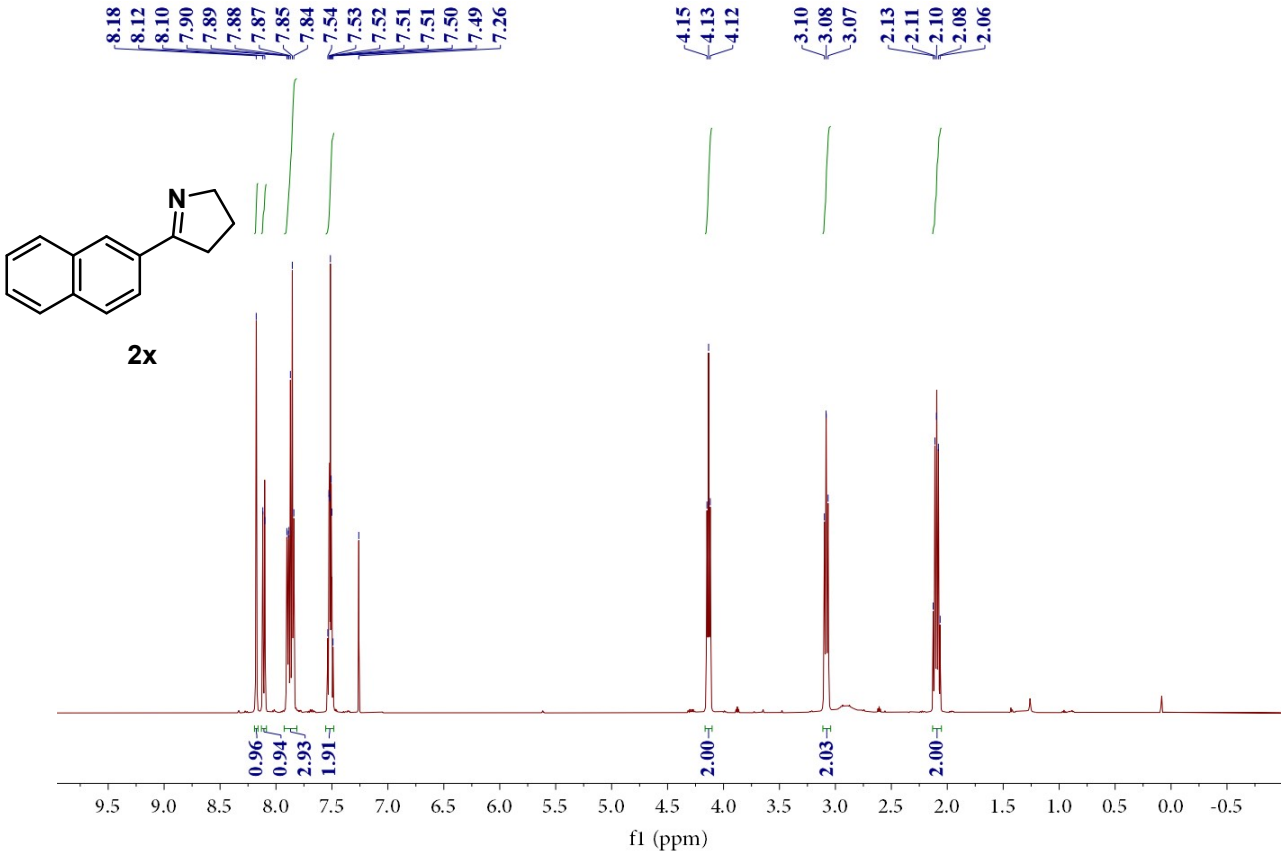

171.41
134.74
134.57
132.94
130.59
129.70
126.87
77.41
77.16
76.91
61.86
35.02
22.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

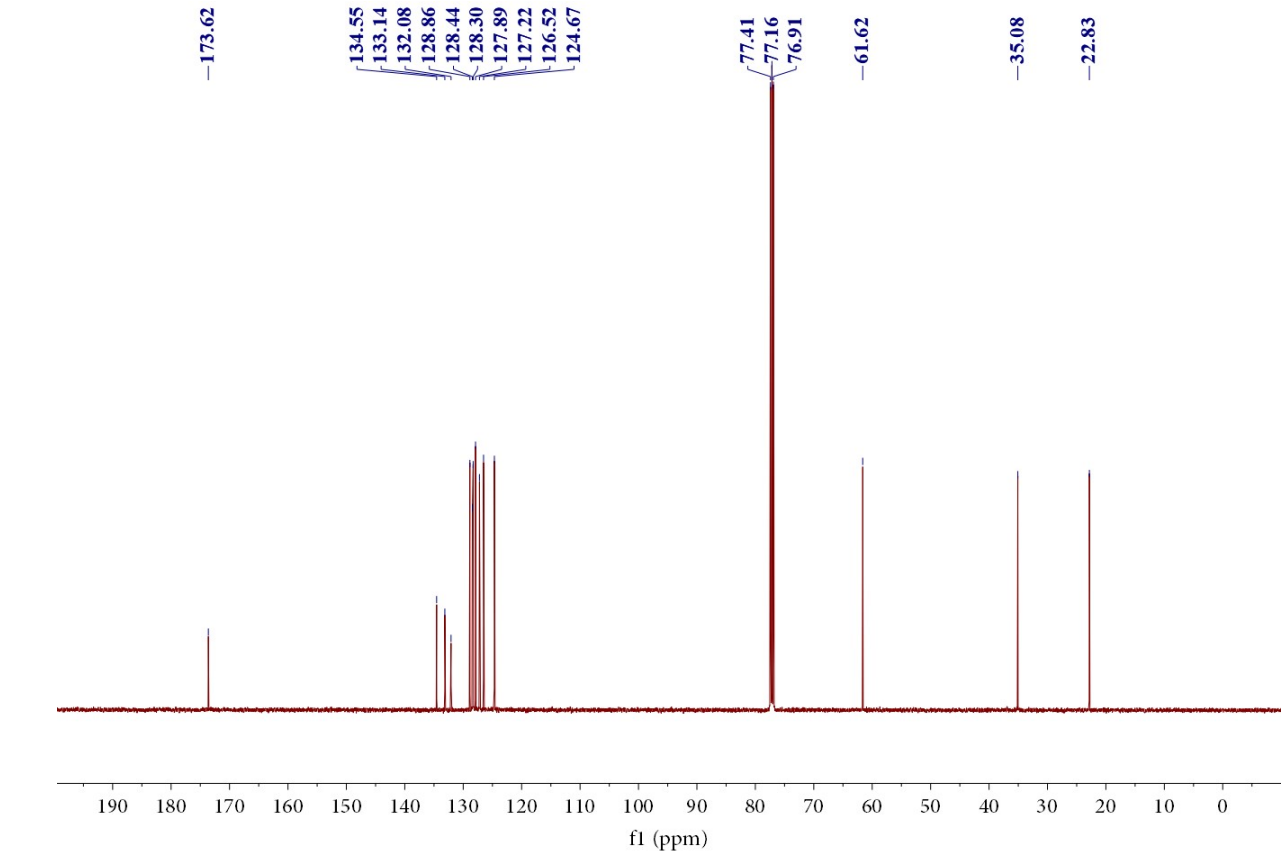

7.91
7.91
7.71
7.26
4.10
4.09
4.09
4.08
4.08
4.07
4.07
4.06
4.06
2.90
2.89
2.89
2.88
2.88
2.87
2.87
2.86
2.86
2.86
2.09
2.08
2.07
2.07
2.06
2.06
2.05
2.04
2.03
2.03
N
Br
Br
2v
1.87
0.90
2.01
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

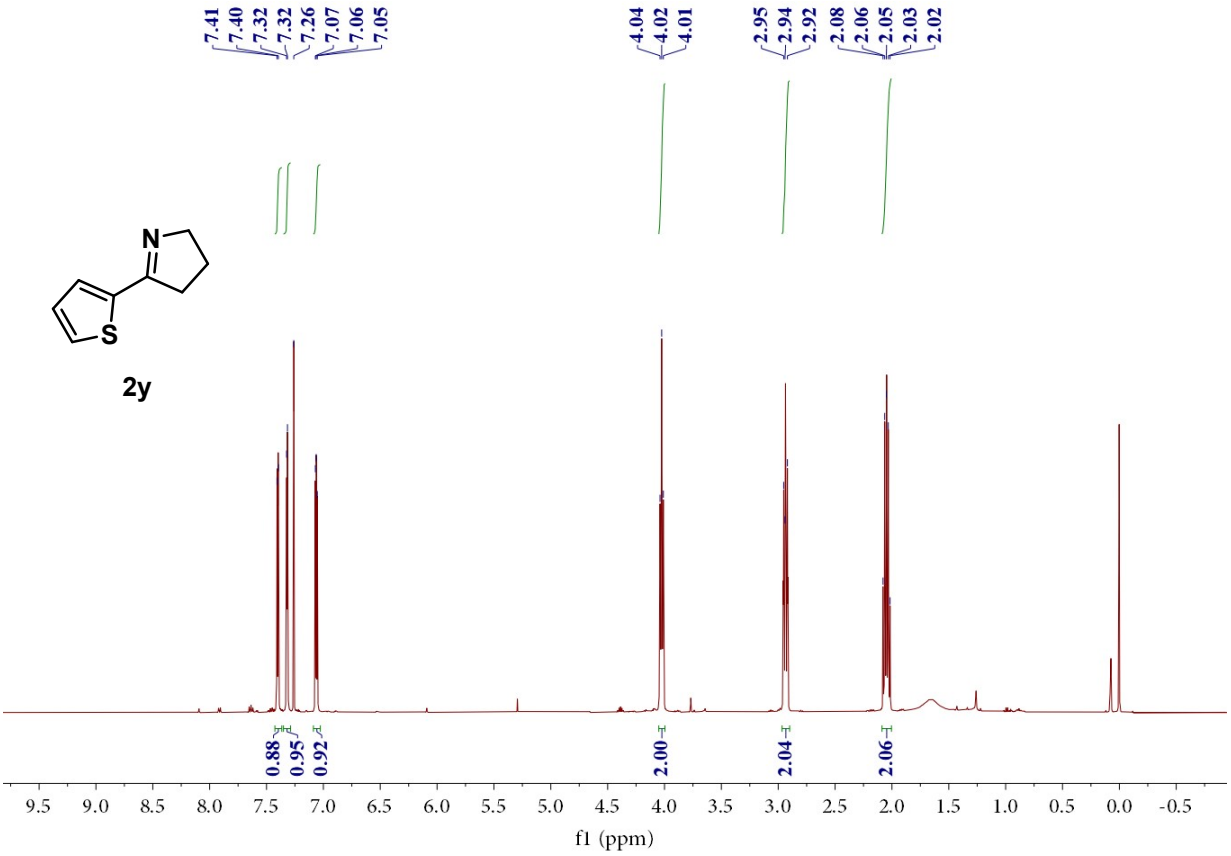

171.01
138.09
135.64
129.55
123.22
77.42
77.16
76.91
61.87
35.00
22.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

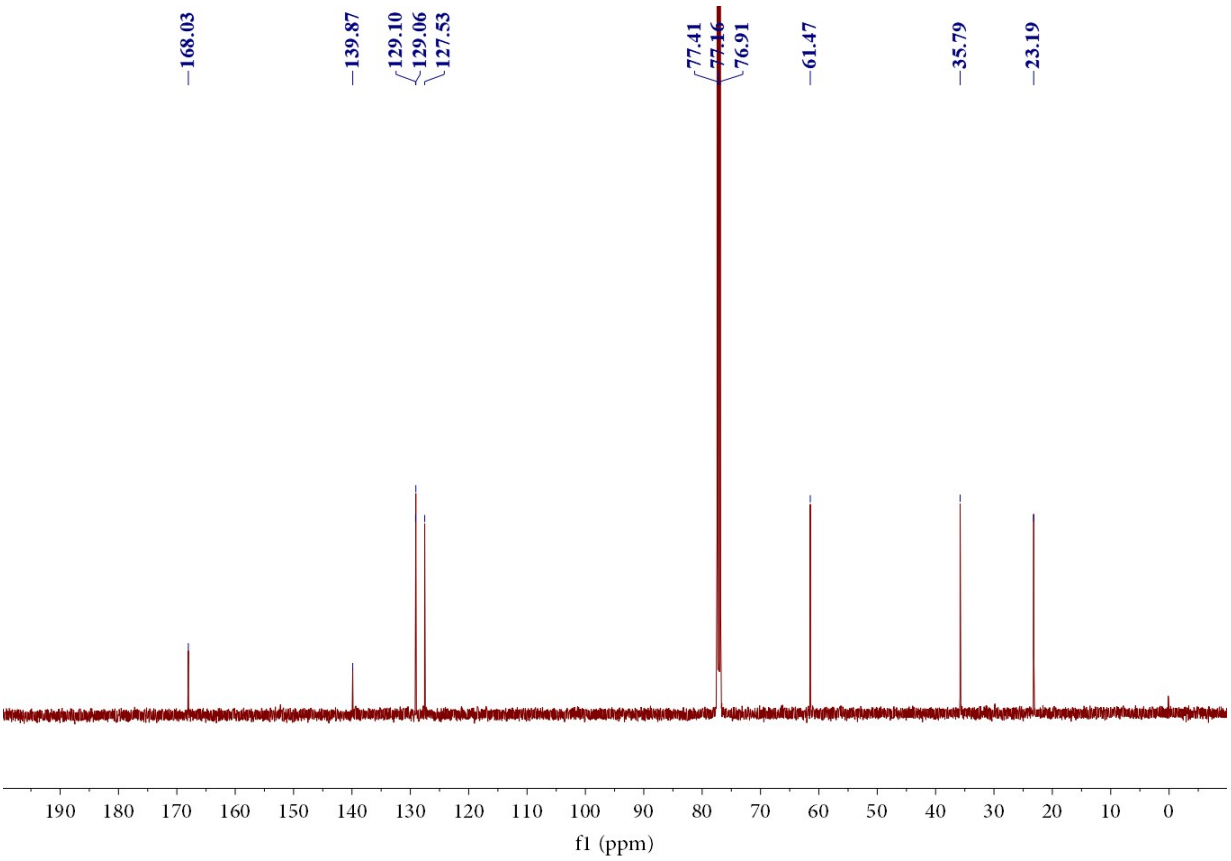

8.50 8.49 8.19 8.18 8.17 8.16 7.90 7.89 7.88 7.88 7.57 7.57 7.56 7.56 7.50 7.50 7.49 7.48 7.47 7.39 7.39 7.38 7.37 7.26 7.09 7.08 5.23 4.08 4.08 4.07 4.07 4.06 4.06 4.05 4.05 4.04 3.02 3.02 3.02 3.01 3.01 3.00 3.00 2.99 2.99 2.98 2.07 2.06 2.06 2.04
O
N
O
2w
1.00 1.01 0.99 1.03 1.04 1.01 1.00 2.09 2.09 2.09 2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

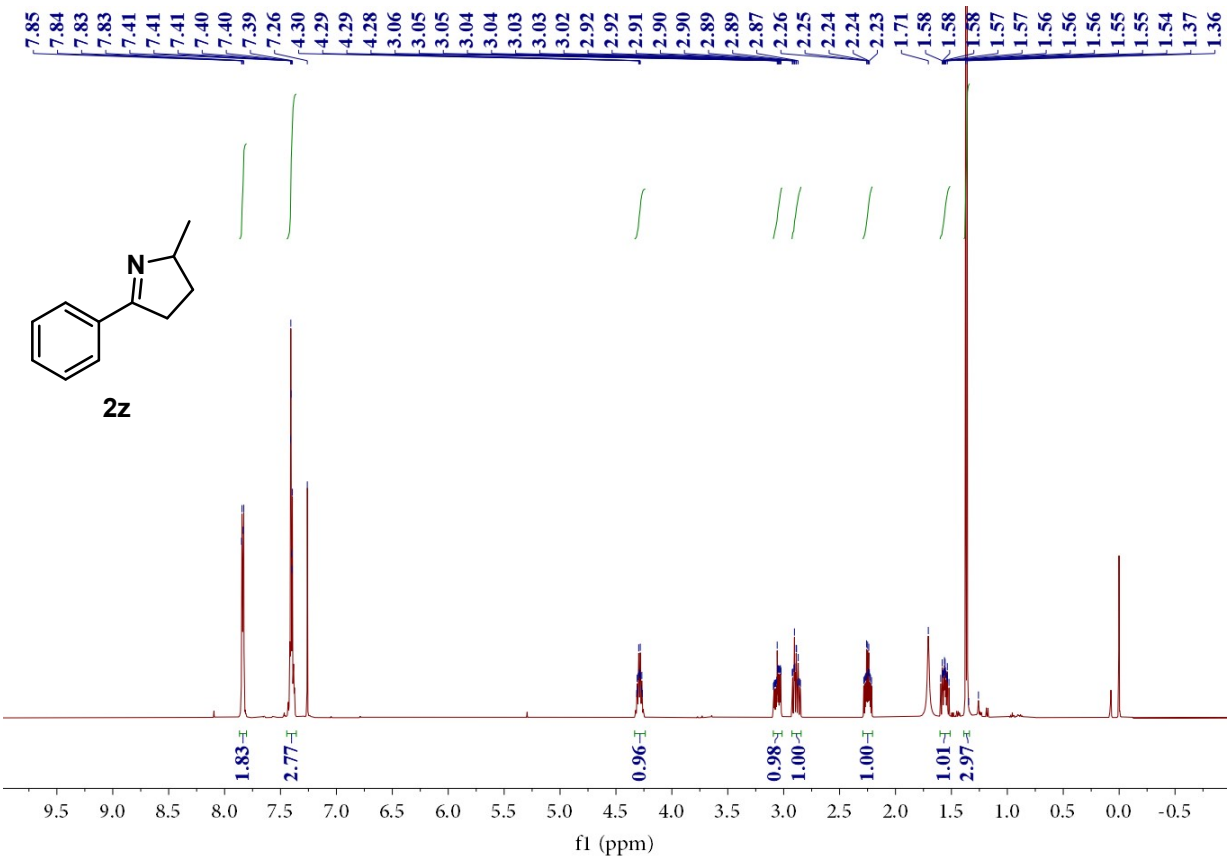

190.88 172.25 162.95 140.69 135.27 134.16 132.97 132.10 129.54 129.51 129.08 128.03 124.71 121.37 73.70 61.67 35.06 22.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

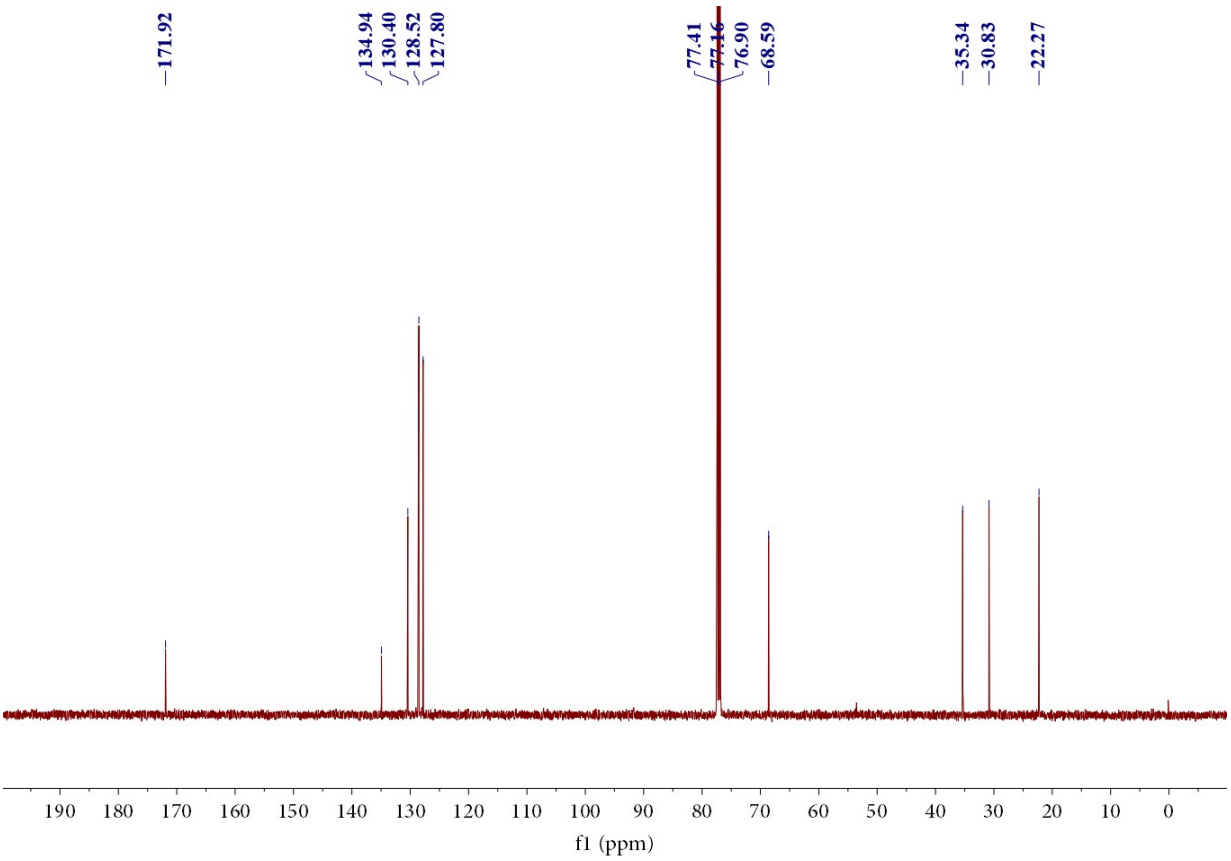

8.18
8.12
8.10
7.90
7.89
7.88
7.87
7.85
7.84
7.54
7.53
7.52
7.51
7.51
7.50
7.49
7.26
4.15
4.13
4.12
3.10
3.08
3.07
2.13
2.11
2.10
2.08
2.06
N
2x
0.96
0.94
2.93
1.91
2.00
2.03
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

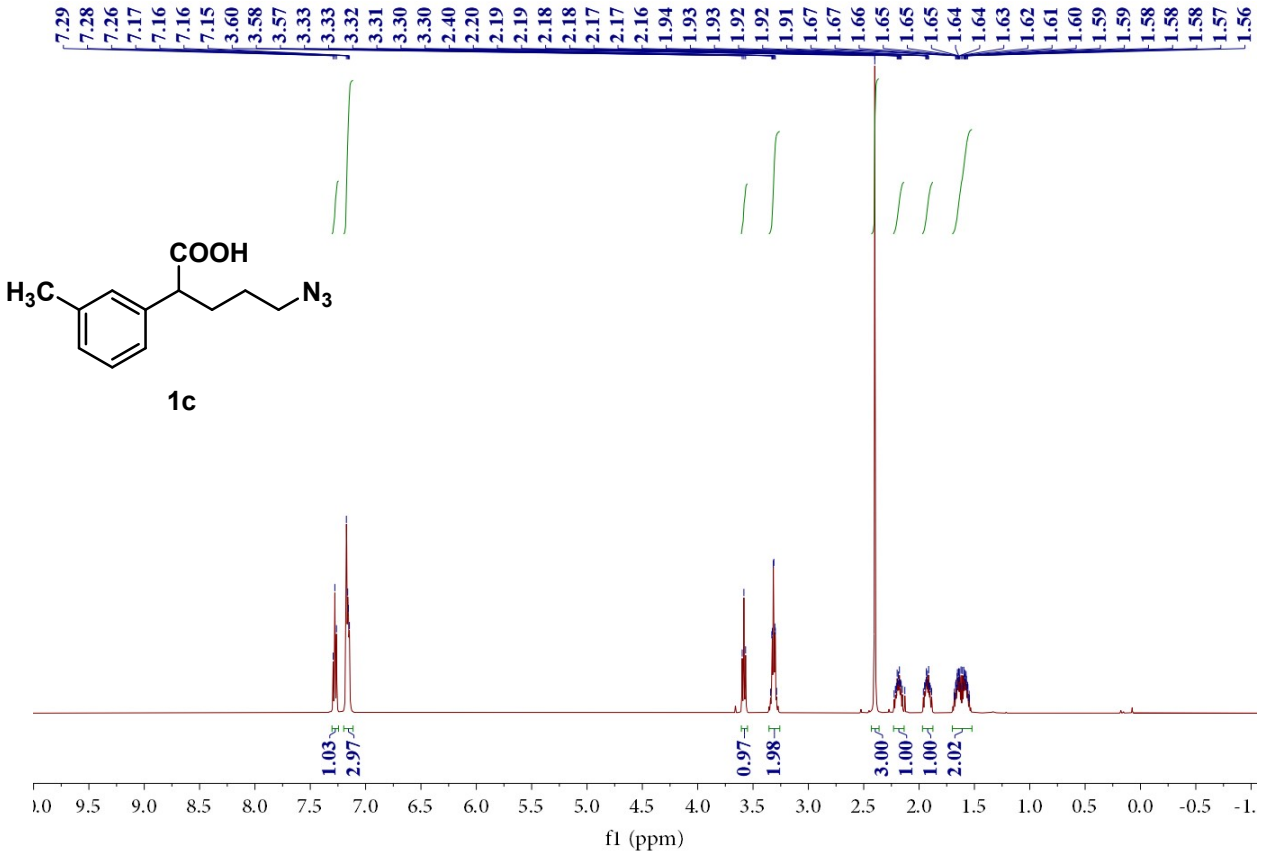

173.62
134.55
133.14
132.08
128.86
128.44
128.30
127.89
127.22
126.52
124.67
77.41
77.16
76.91
61.62
35.08
22.83
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

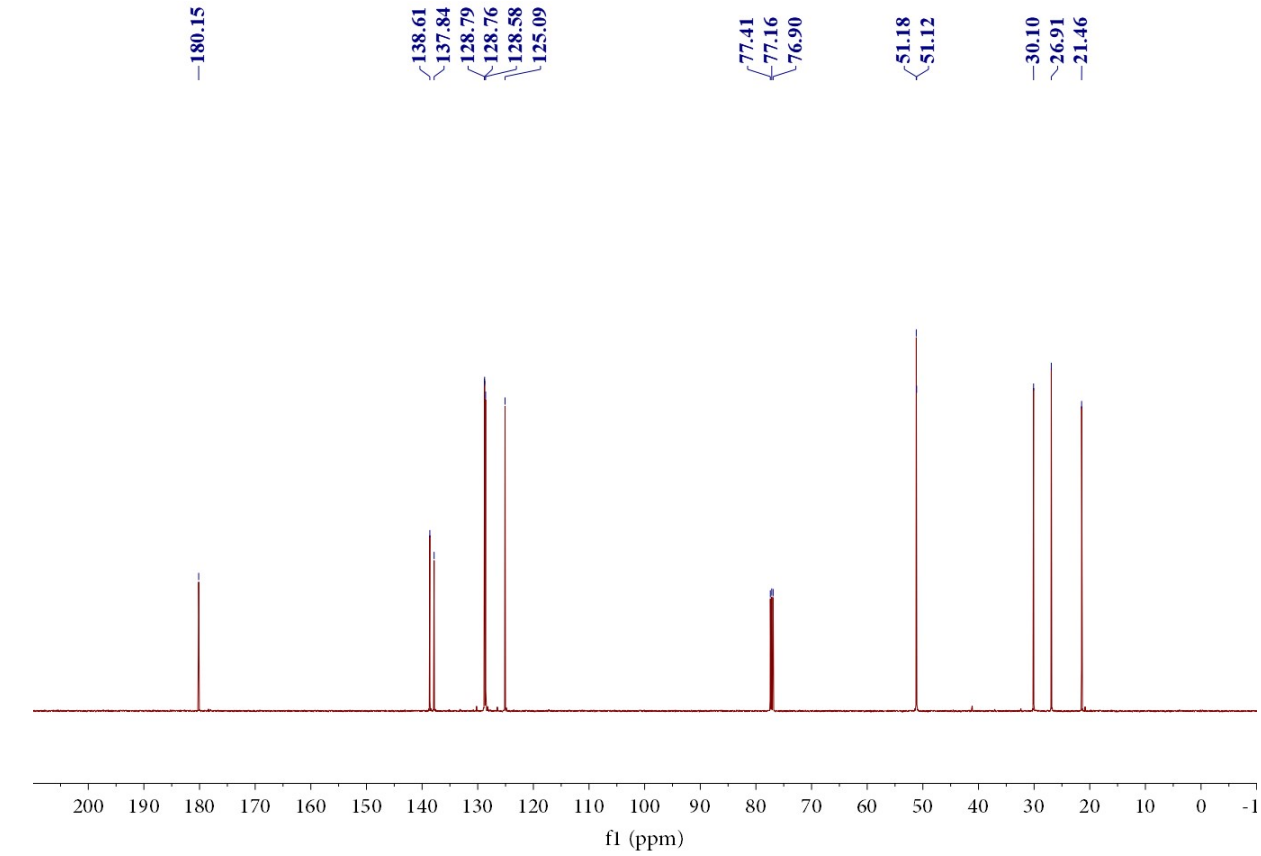

7.41
7.40
7.32
7.32
7.26
7.07
7.06
7.05
4.04
4.02
4.01
2.95
2.94
2.92
2.08
2.06
2.05
2.03
2.02
N
S
2y
0.88
0.95
0.92
2.00
2.04
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

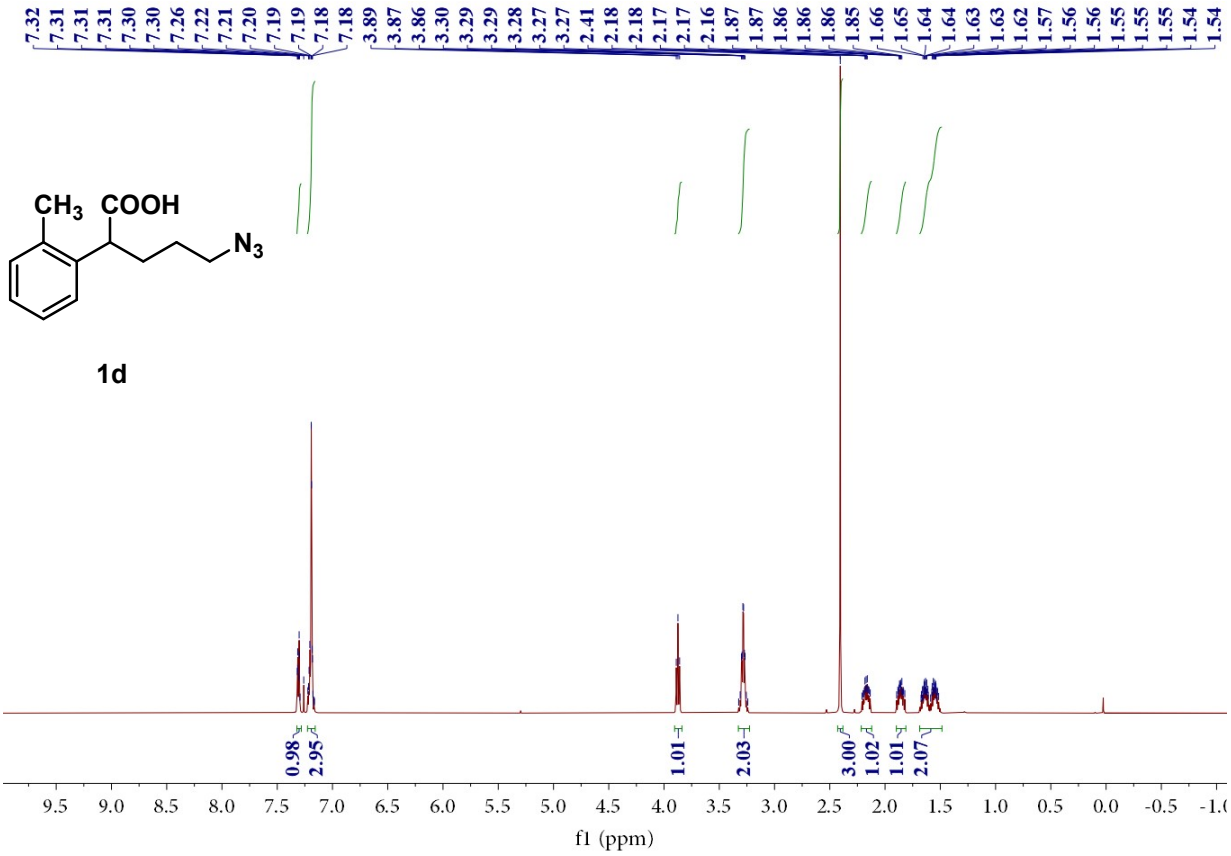

168.03
139.87
129.10
129.06
127.53
77.41
77.16
76.91
61.47
35.79
23.19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

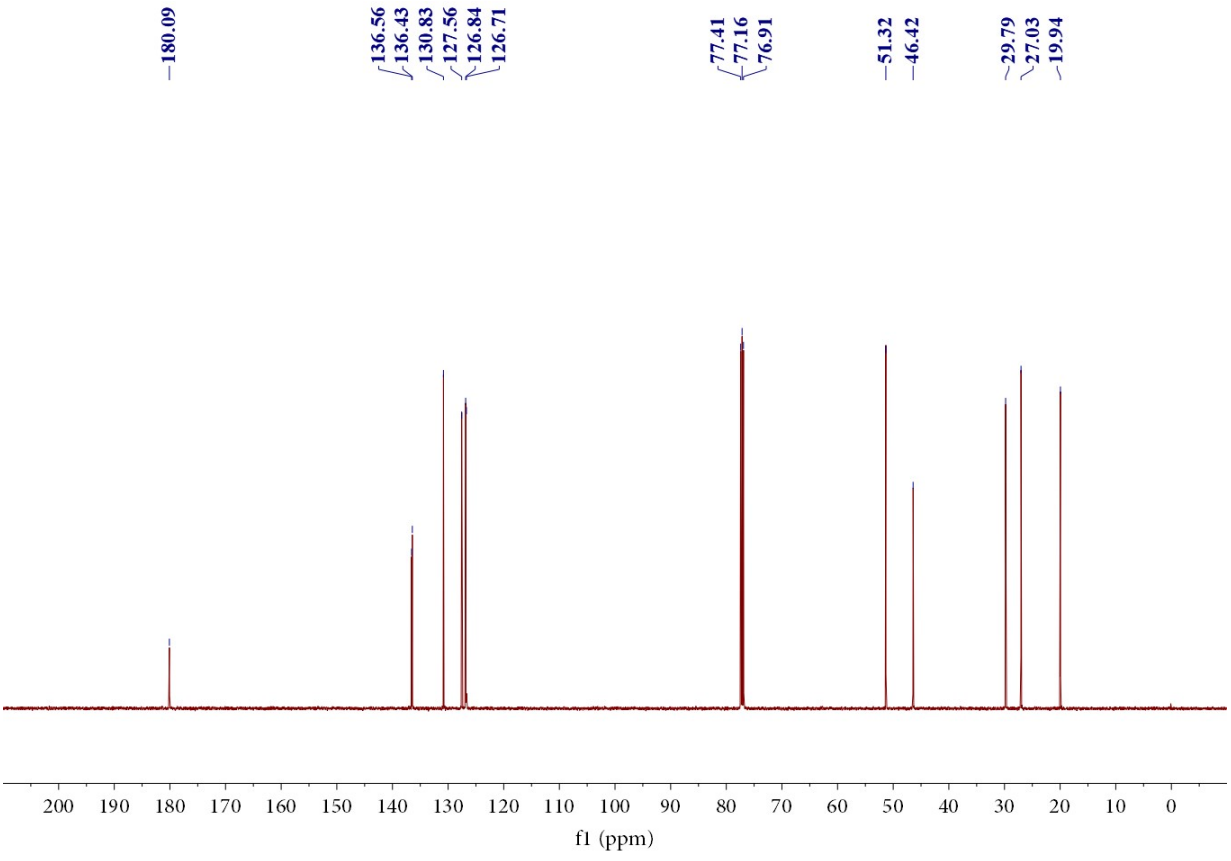

7.85 7.84 7.83 7.83 7.41 7.41 7.41 7.40 7.40 7.39 7.26 4.30 4.29 4.29 4.28 3.06 3.05 3.05 3.04 3.04 3.03 3.03 3.02 2.92 2.92 2.91 2.90 2.90 2.89 2.89 2.87 2.26 2.25 2.24 2.24 2.23 1.71 1.58 1.58 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.55 1.54 1.37 1.36
N
2z
1.83 2.77 0.96 0.98 1.00 1.00 1.01 2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

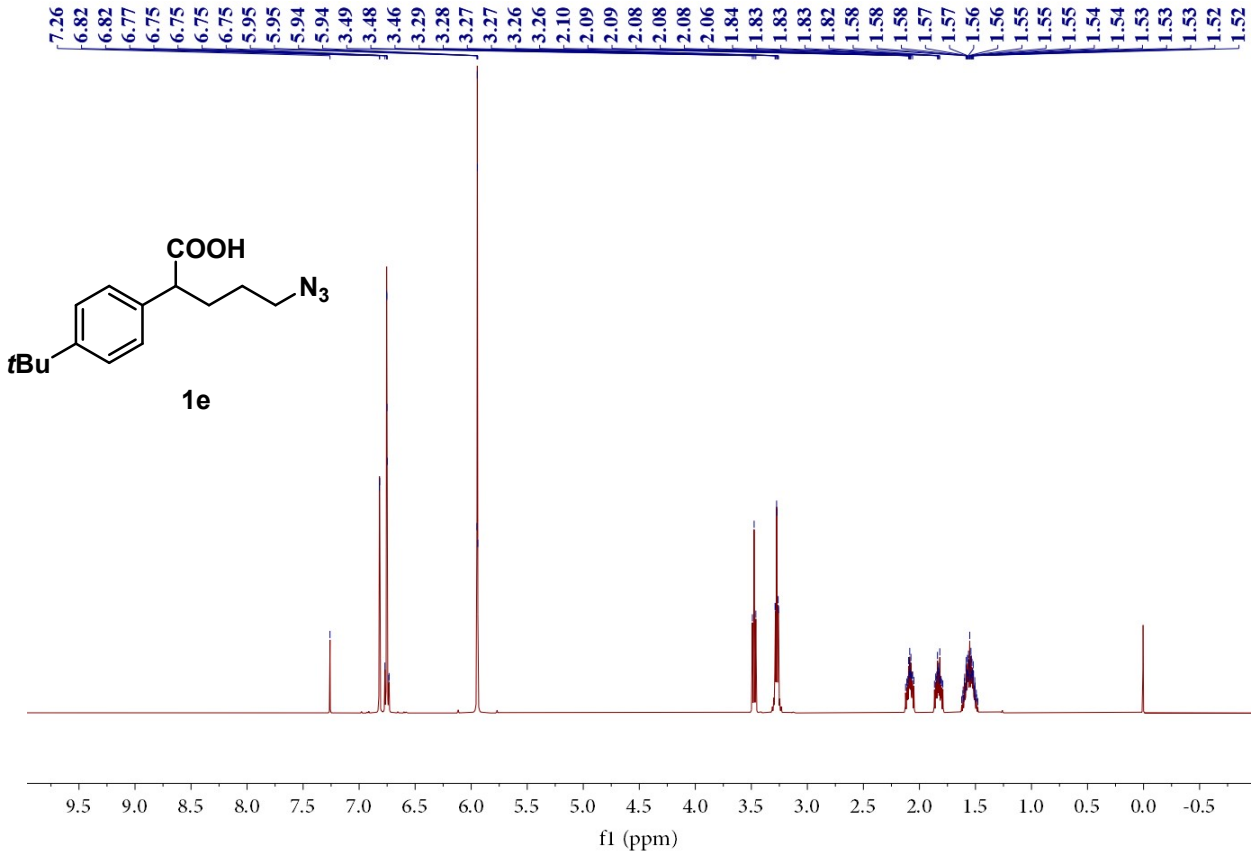

171.92
134.94 130.40 128.52 127.80
77.41 77.16 76.90 68.59
35.34 30.83 22.27
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

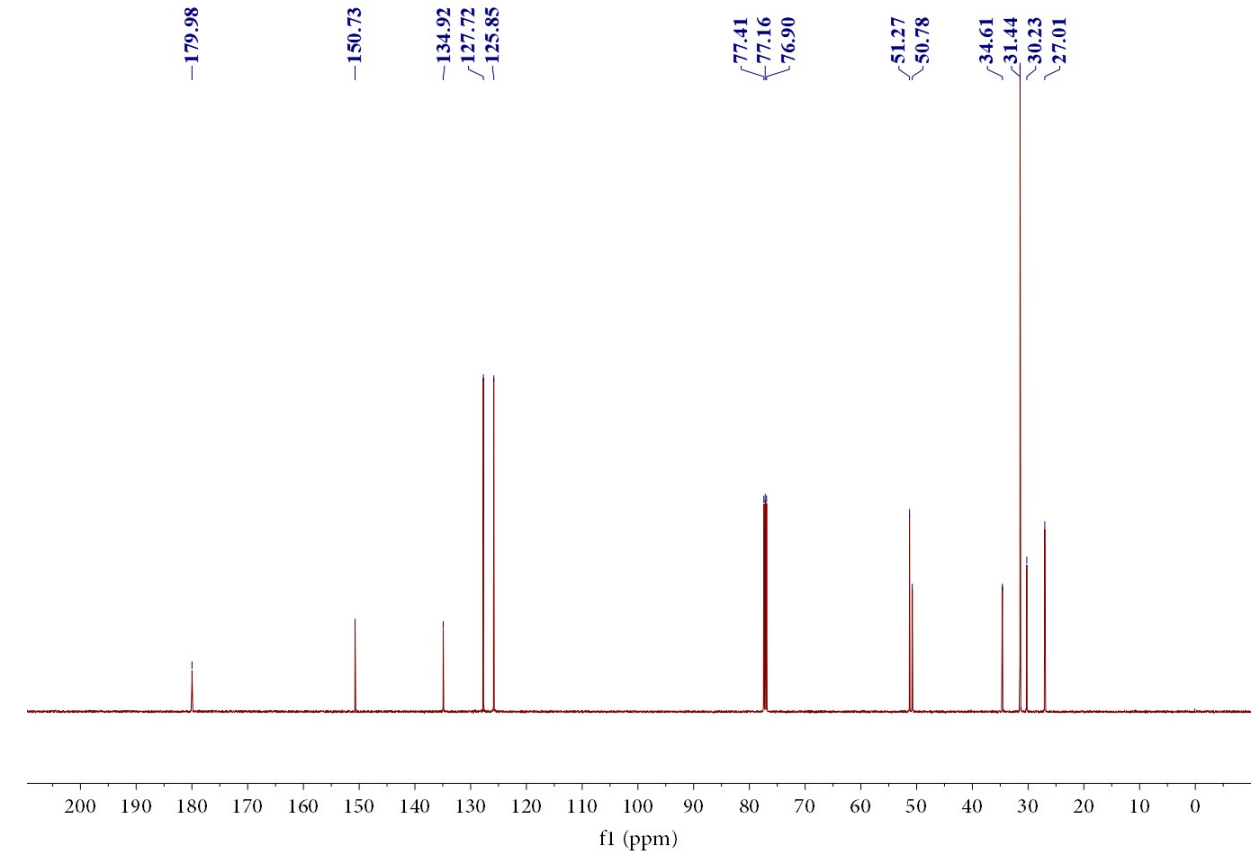

7.29 7.28 7.26 7.17 7.16 7.16 7.15 3.60 3.58 3.57 3.33 3.33 3.32 3.31 3.30 3.30 2.40 2.20 2.19 2.19 2.18 2.18 2.17 2.17 2.16 1.94 1.93 1.93 1.92 1.92 1.91 1.67 1.67 1.66 1.65 1.65 1.65 1.64 1.64 1.63 1.62 1.61 1.60 1.59 1.59 1.58 1.58 1.58 1.57 1.56
COOH
H3C
N3
1c
1.03 2.97 0.97 1.98 3.00 1.00 1.00 2.02
f1 (ppm)

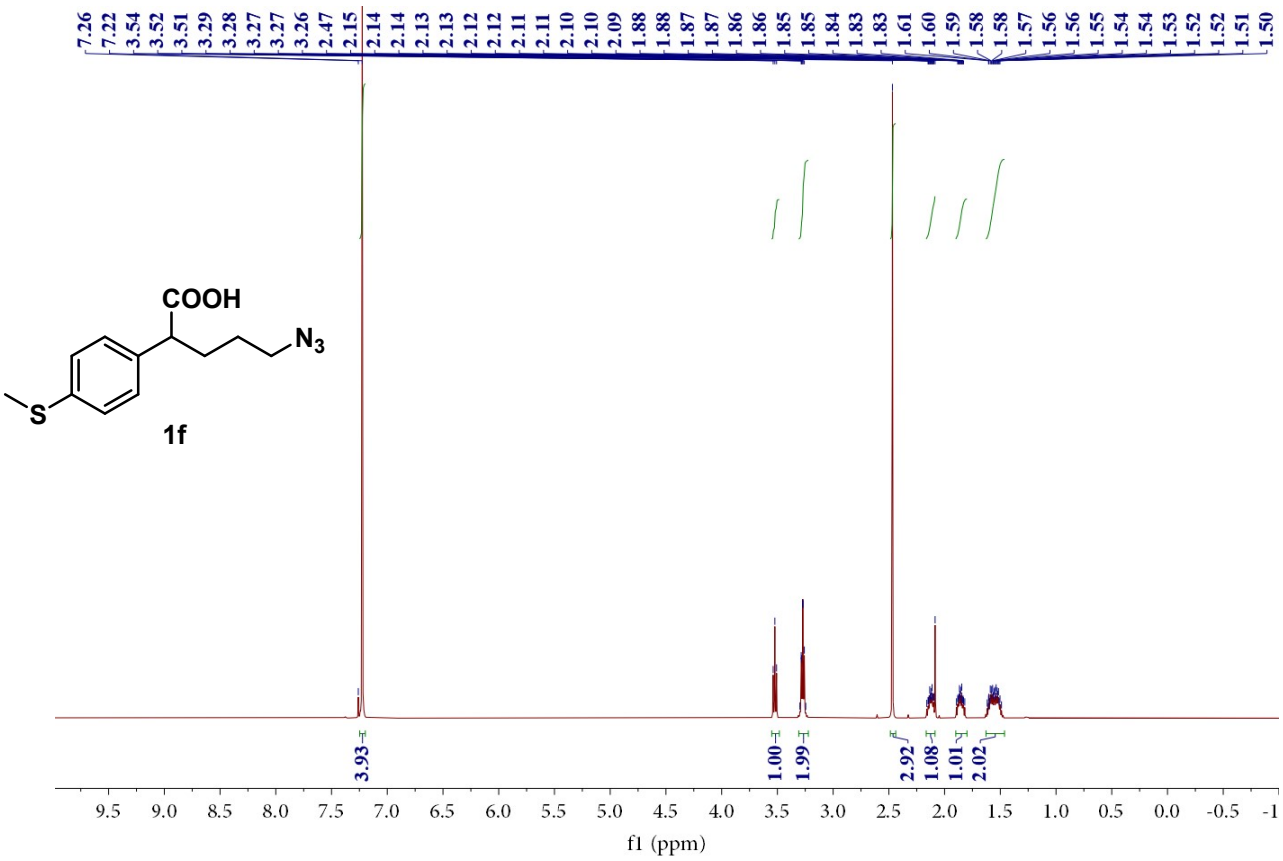

180.15
138.61 137.84 128.79 128.76 128.58 125.09
77.41 77.16 76.90
51.18 51.12
30.10 26.91 21.46
f1 (ppm)

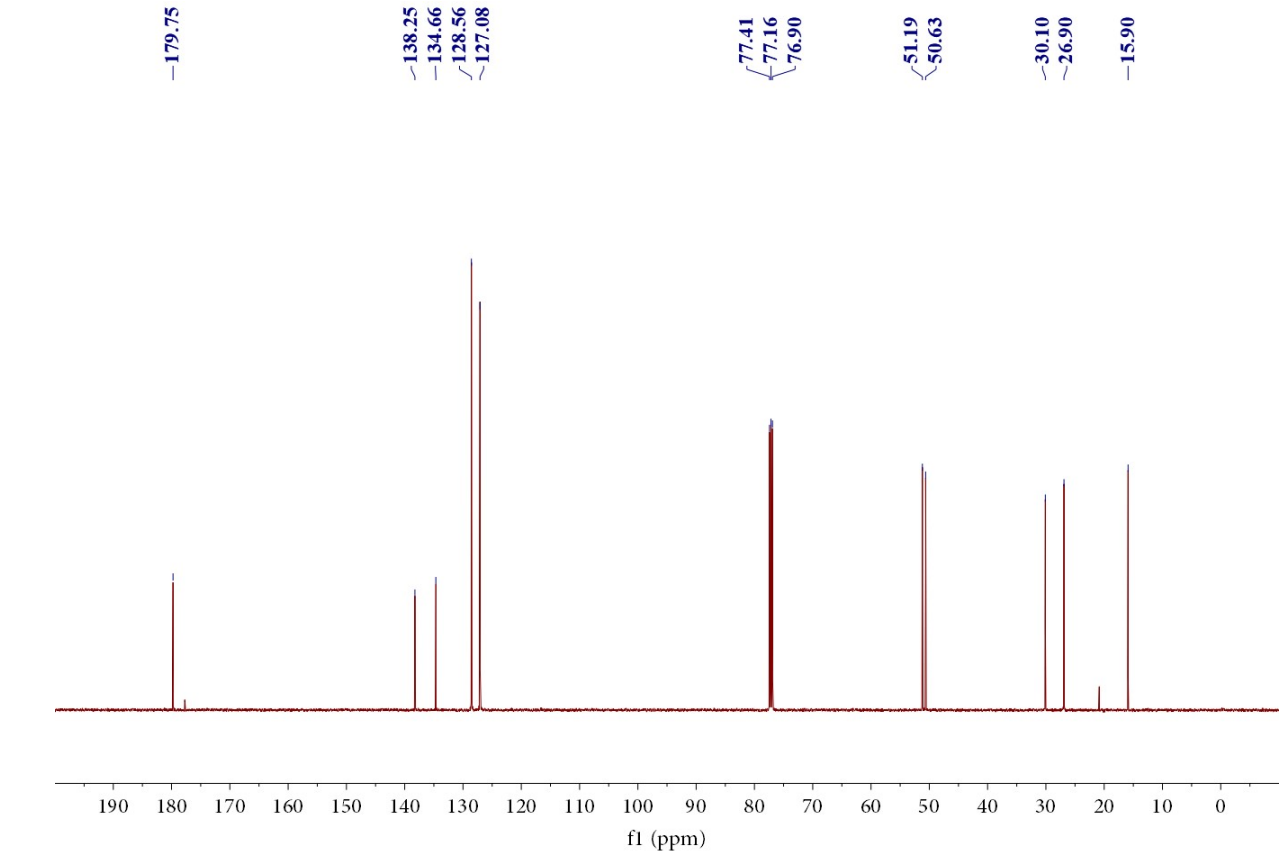

7.32 7.31 7.31 7.31 7.30 7.30 7.26 7.22 7.21 7.20 7.19 7.19 7.18 7.18
3.89 3.87 3.86 3.30 3.29 3.29 3.28 3.27 3.27 2.41 2.18 2.18 2.17 2.17 2.16 1.87 1.87 1.86 1.86 1.86 1.85 1.66 1.65 1.64 1.64 1.63 1.63 1.62 1.57 1.56 1.56 1.55 1.55 1.55 1.54 1.54
CH3 COOH
N3
1d
0.98 2.95 1.01 2.03 3.00 1.02 1.01 2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

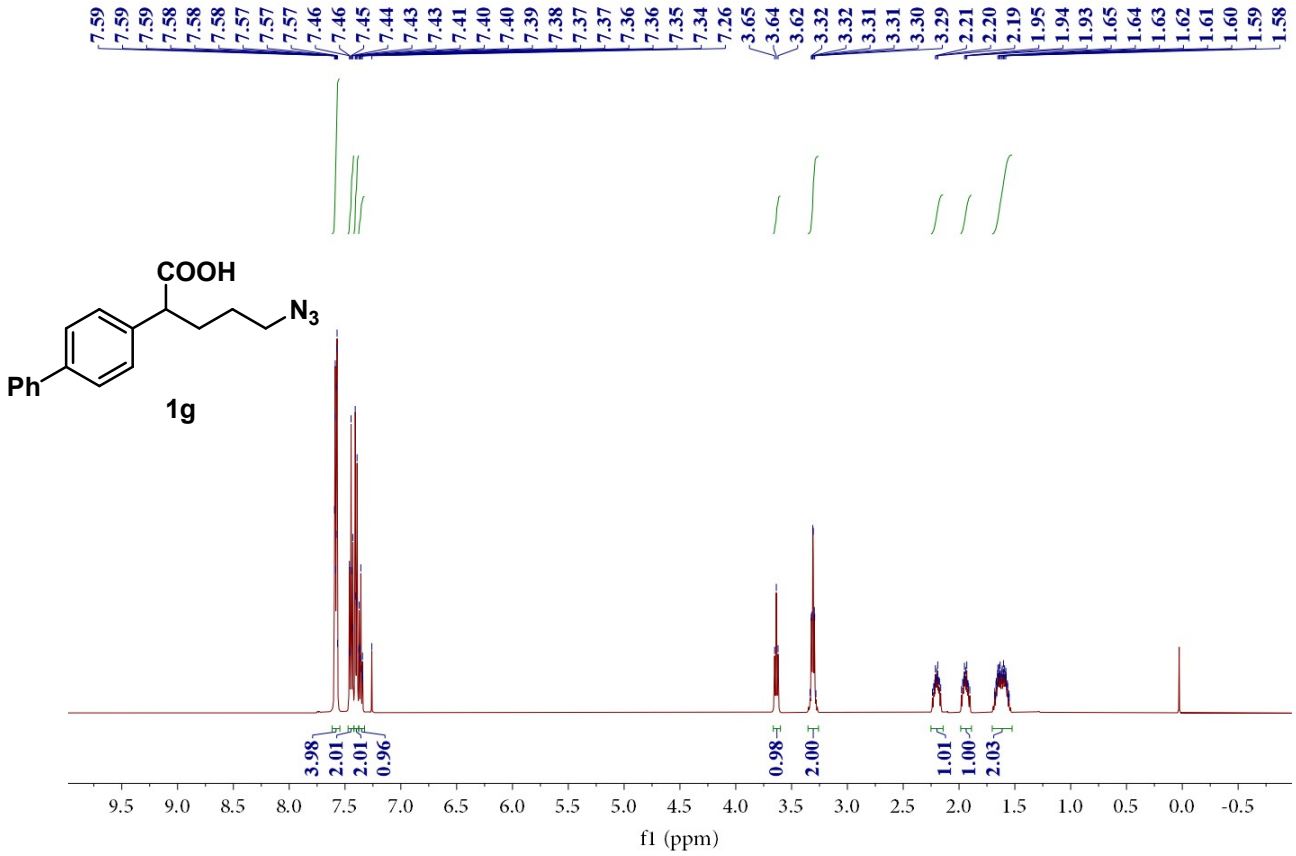

180.09
136.56 136.43 130.83 127.56 126.84 126.71
77.41 77.16 76.91
51.32 46.42
29.79 27.03 19.94
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

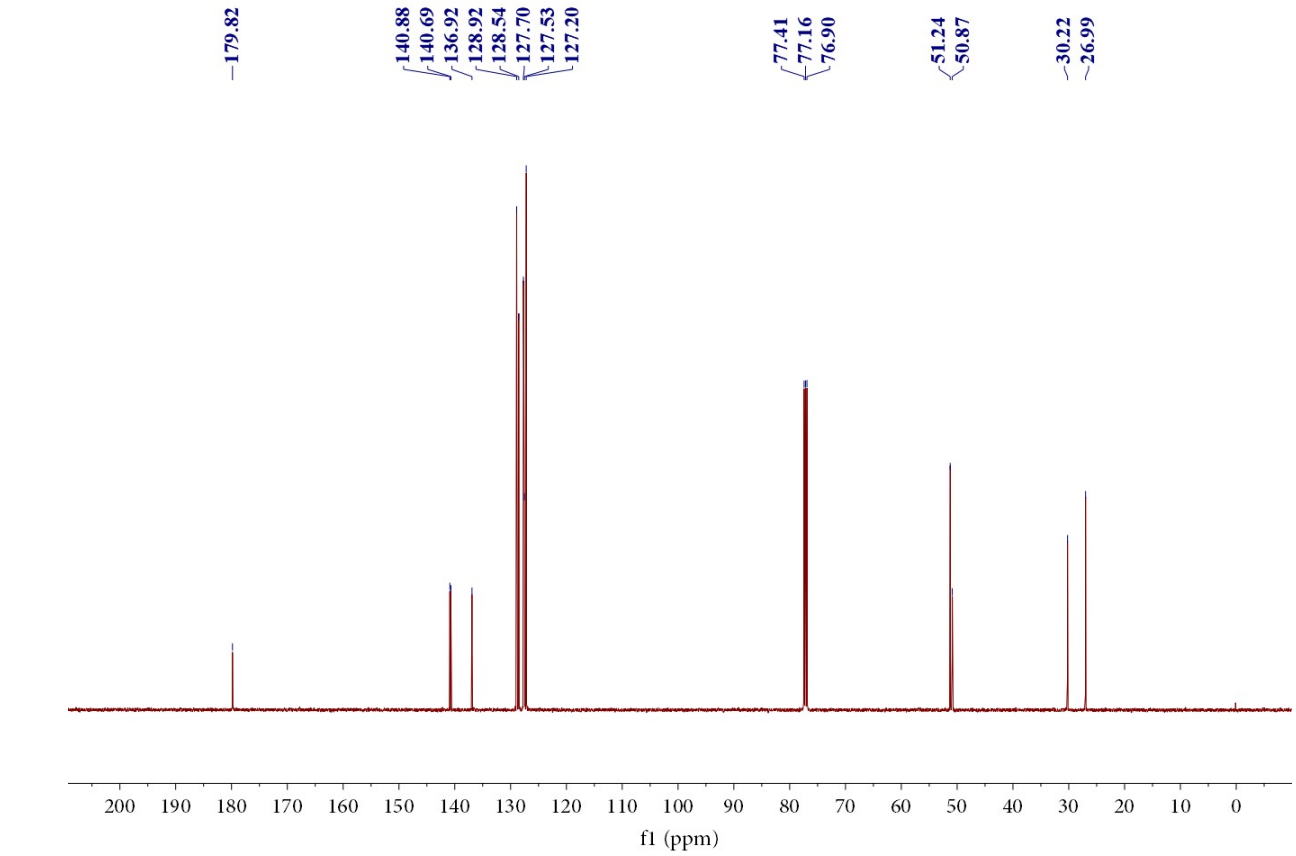

7.26
6.82
6.82
6.77
6.75
6.75
6.75
6.75
5.95
5.95
5.94
5.94
3.49
3.48
3.46
3.29
3.28
3.27
3.27
3.26
3.26
2.10
2.09
2.09
2.08
2.08
2.08
2.06
1.84
1.83
1.83
1.83
1.82
1.58
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
COOH
N3
tBu
1e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

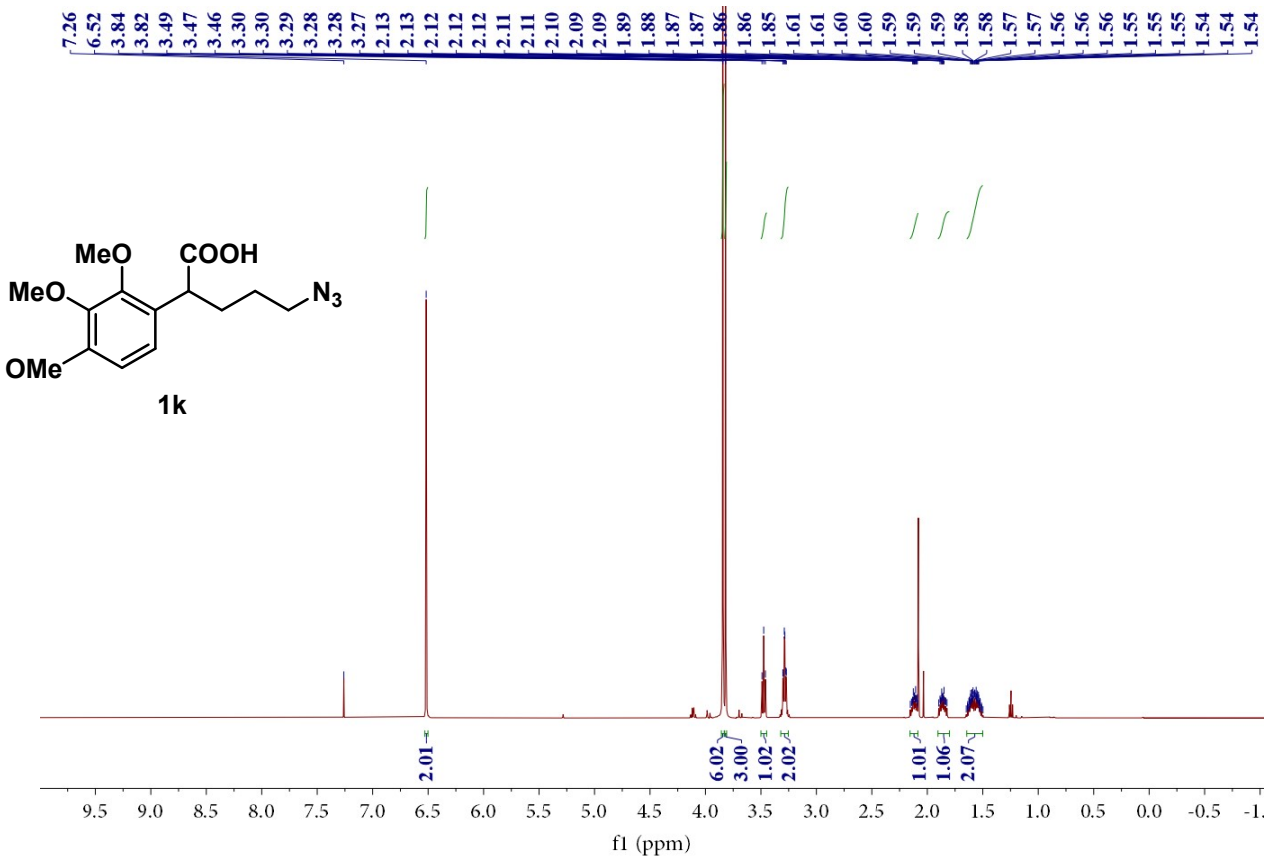

179.98
150.73
134.92
127.72
125.85
77.41
77.16
76.90
51.27
50.78
34.61
31.44
30.23
27.01
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

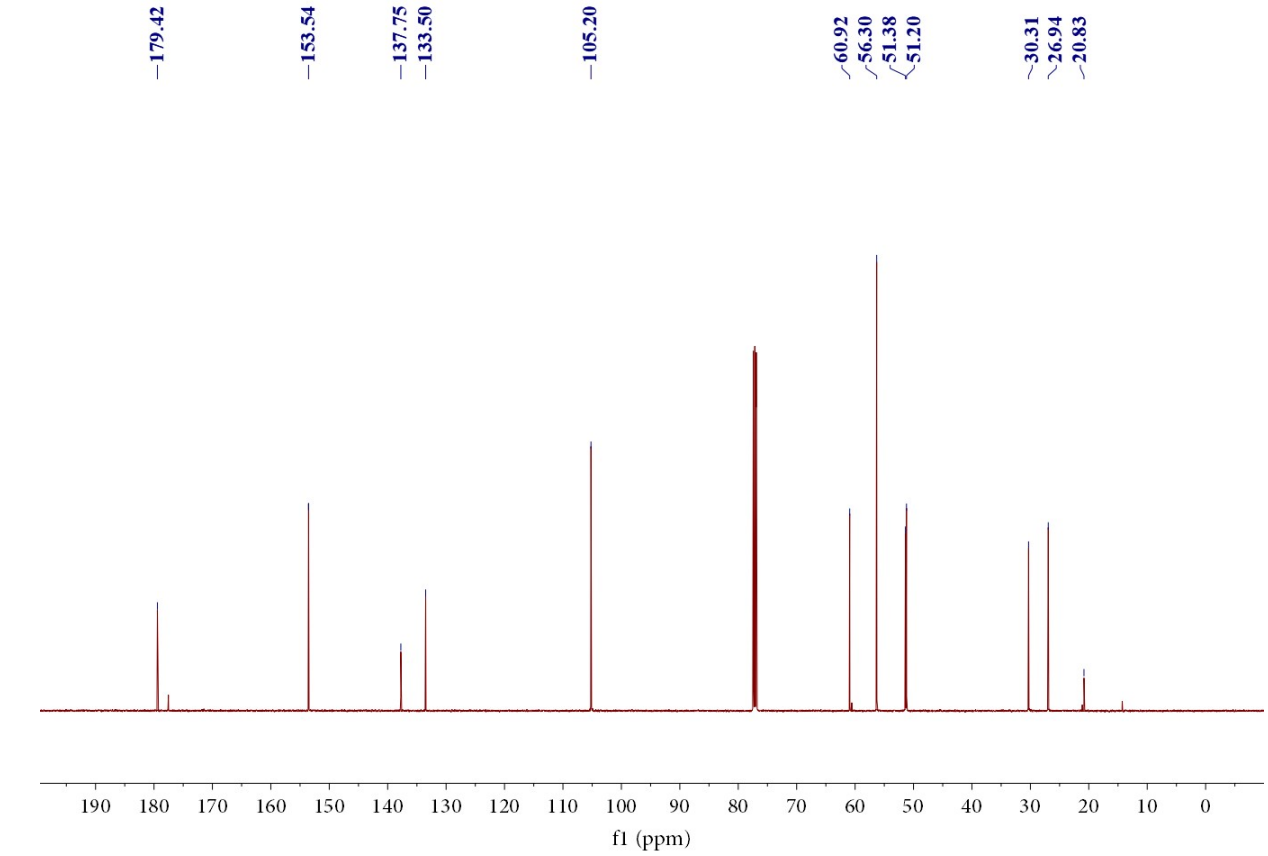

7.26
7.22
3.54
3.52
3.51
3.29
3.28
3.27
3.27
3.26
2.47
2.15
2.14
2.14
2.13
2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.83
1.83
1.61
1.60
1.59
1.58
1.58
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.52
1.52
1.51
1.50
COOH
N3
S
1f
3.93
1.00
1.99
2.92
1.08
1.01
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

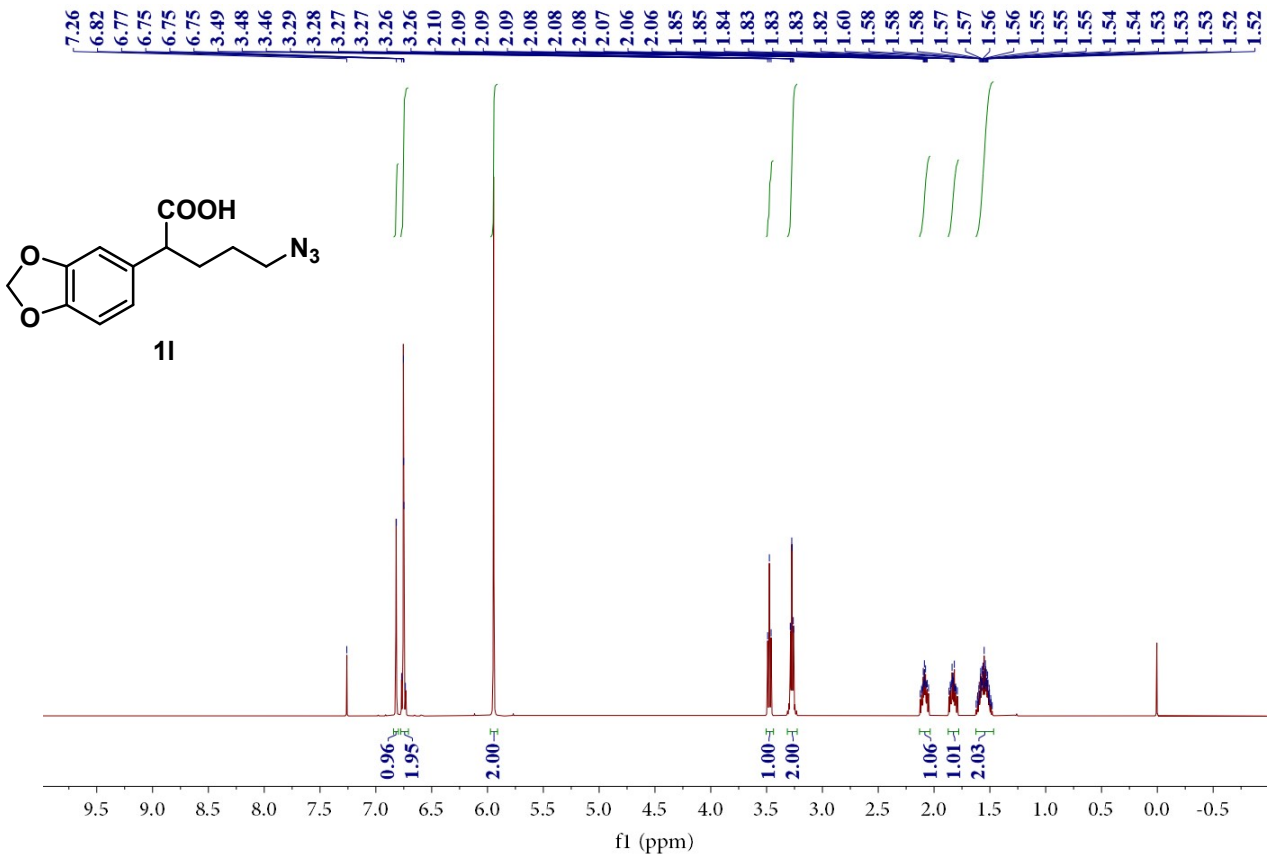

179.75
138.25
134.66
128.56
127.08
77.41
77.16
76.90
51.19
50.63
30.10
26.90
15.90
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

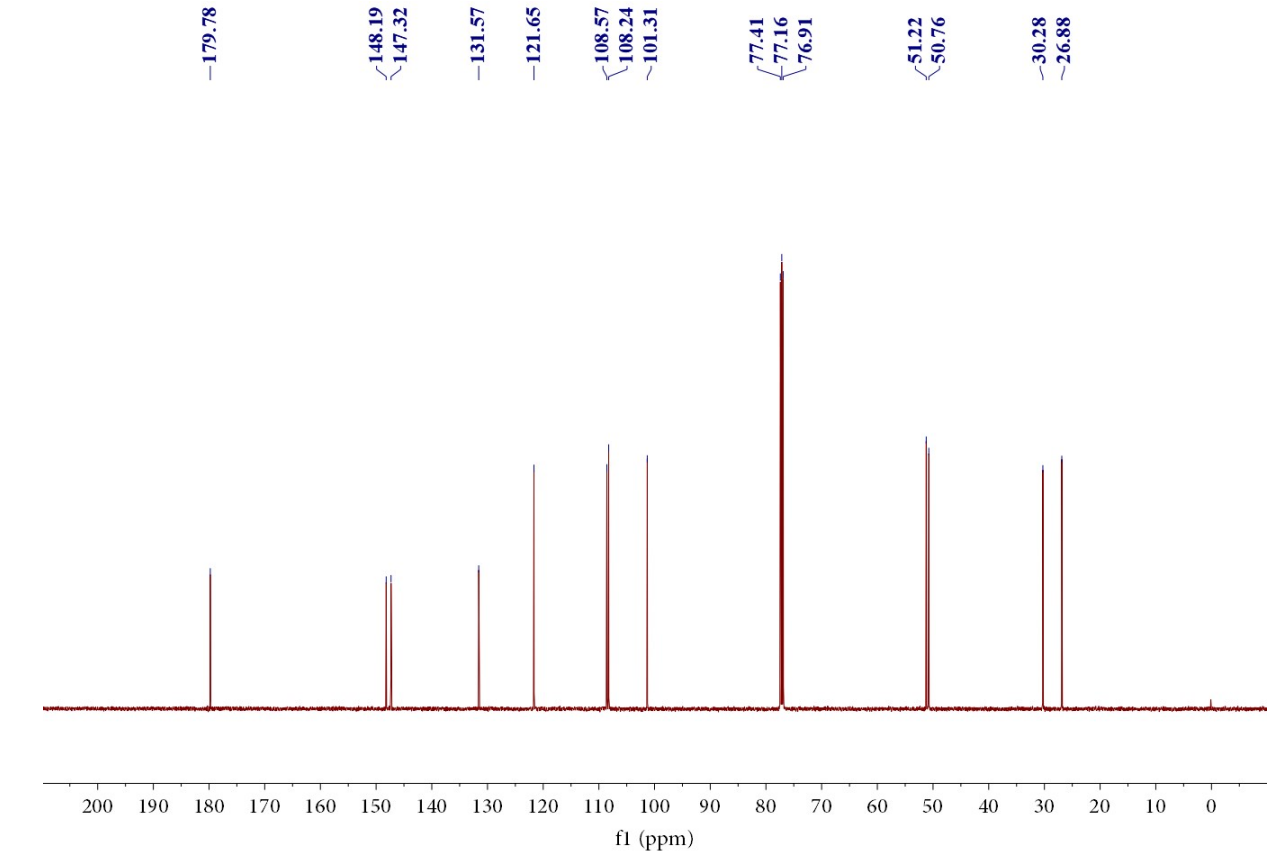

7.59 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.57 7.46 7.46 7.45 7.44 7.43 7.43 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.26 3.65 3.64 3.62 3.32 3.32 3.31 3.31 3.30 3.29 2.21 2.20 2.19 1.95 1.94 1.93 1.65 1.64 1.63 1.62 1.61 1.60 1.59 1.58
COOH
N3
Ph
1g
3.98 2.01 2.01 0.96 0.98 2.00 1.01 1.00 2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.82
140.88 140.69 136.92 128.92 128.54 127.70 127.53 127.20
77.41 77.16 76.90
51.24 50.87
30.22 26.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

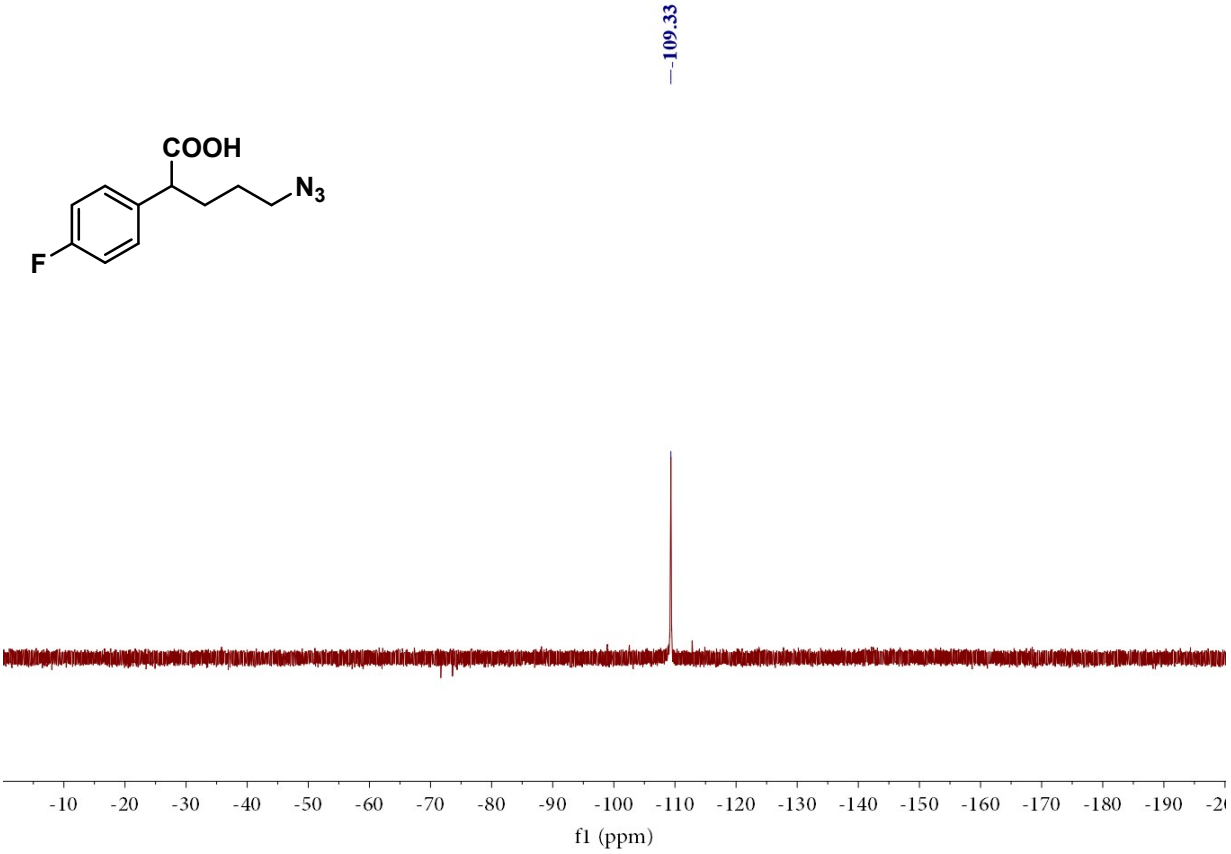

7.26 6.52 3.84 3.82 3.49 3.47 3.46 3.30 3.30 3.29 3.28 3.28 3.27 2.13 2.13 2.12 2.12 2.12 2.11 2.11 2.10 2.09 2.09 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.61 1.61 1.60 1.60 1.59 1.59 1.59 1.58 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.55 1.55 1.54 1.54 1.54
MeO
COOH
MeO
N3
OMe
1k
2.01
6.02
3.00
1.02
2.02
1.01
1.06
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

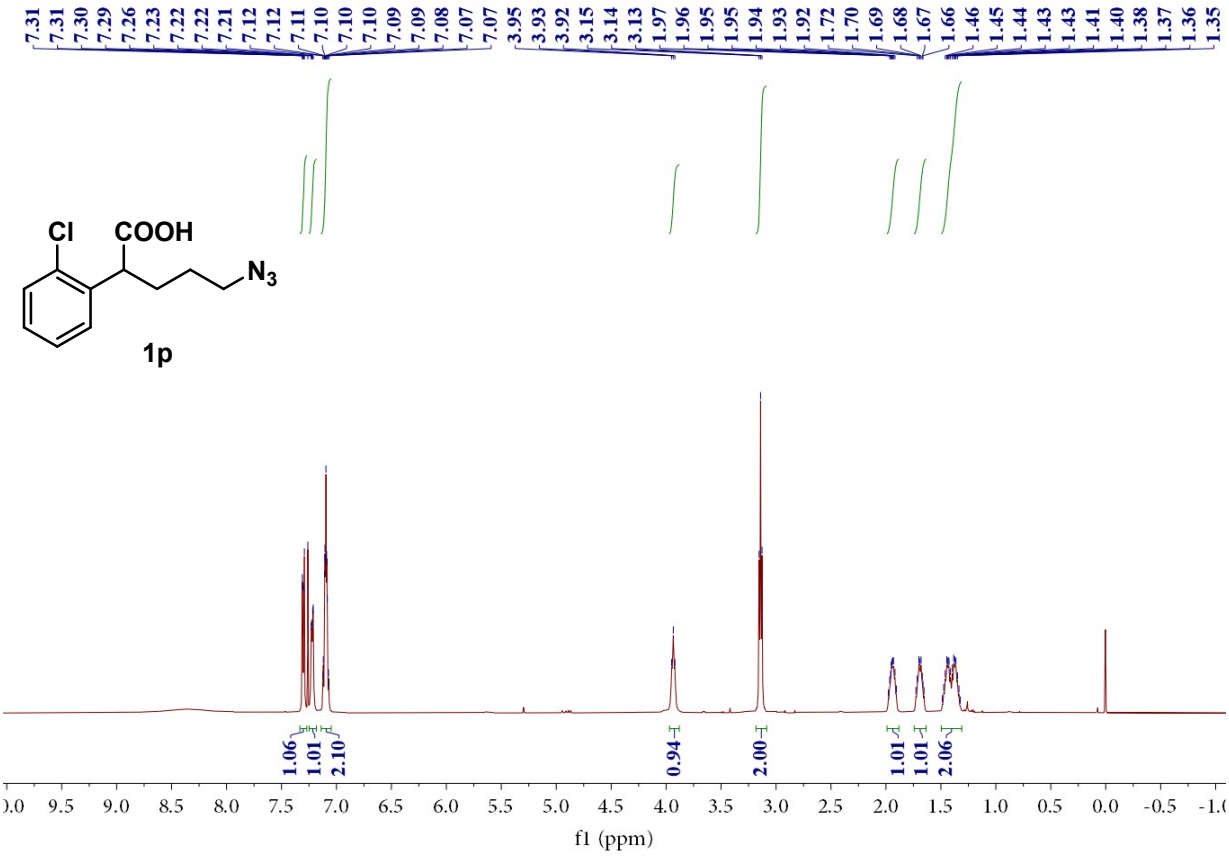

179.42
153.54
137.75
133.50
105.20
60.92
56.30
51.38
51.20
30.31
26.94
20.83
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

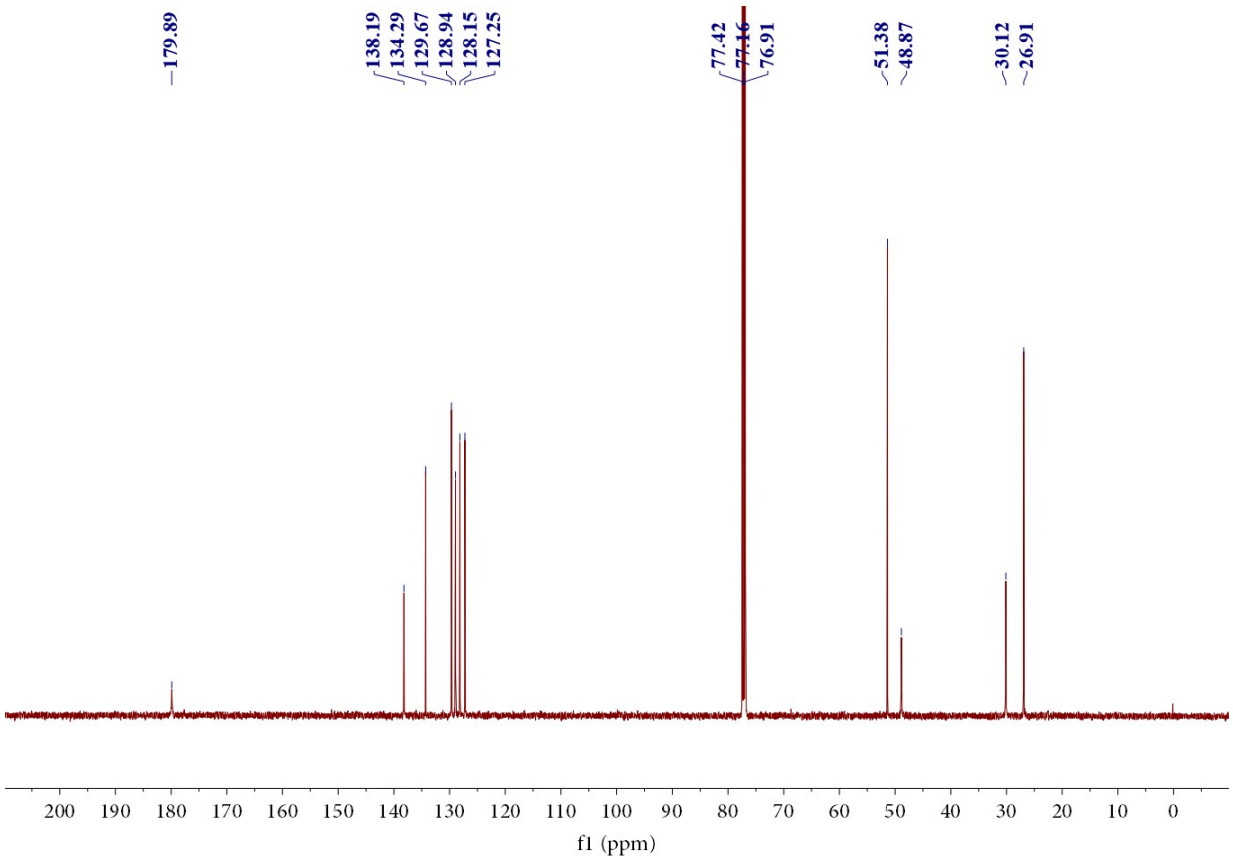

7.26 6.82 6.77 6.75 6.75 6.75 3.49 3.48 3.46 3.29 3.28 3.27 3.27 3.26 3.26 2.10 2.09 2.09 2.08 2.08 2.08 2.07 2.06 2.06 1.85 1.85 1.84 1.83 1.83 1.83 1.82 1.60 1.58 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.55 1.54 1.54 1.53 1.53 1.53 1.52 1.52
COOH
O
O
N3
1l
0.96
1.95
2.00
1.00
2.00
1.06
1.01
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

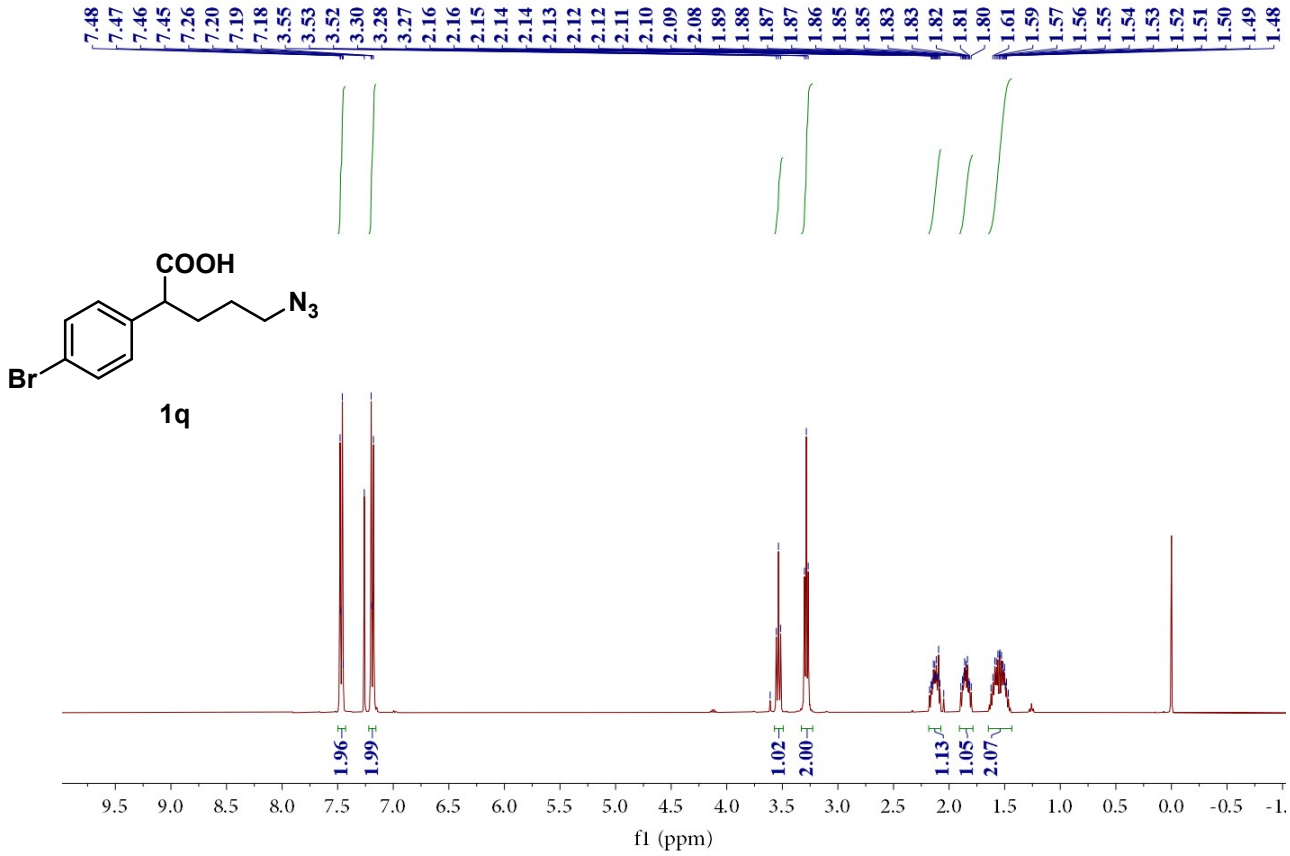

179.78
148.19
147.32
131.57
121.65
108.57
108.24
101.31
77.41
77.16
76.91
51.22
50.76
30.28
26.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

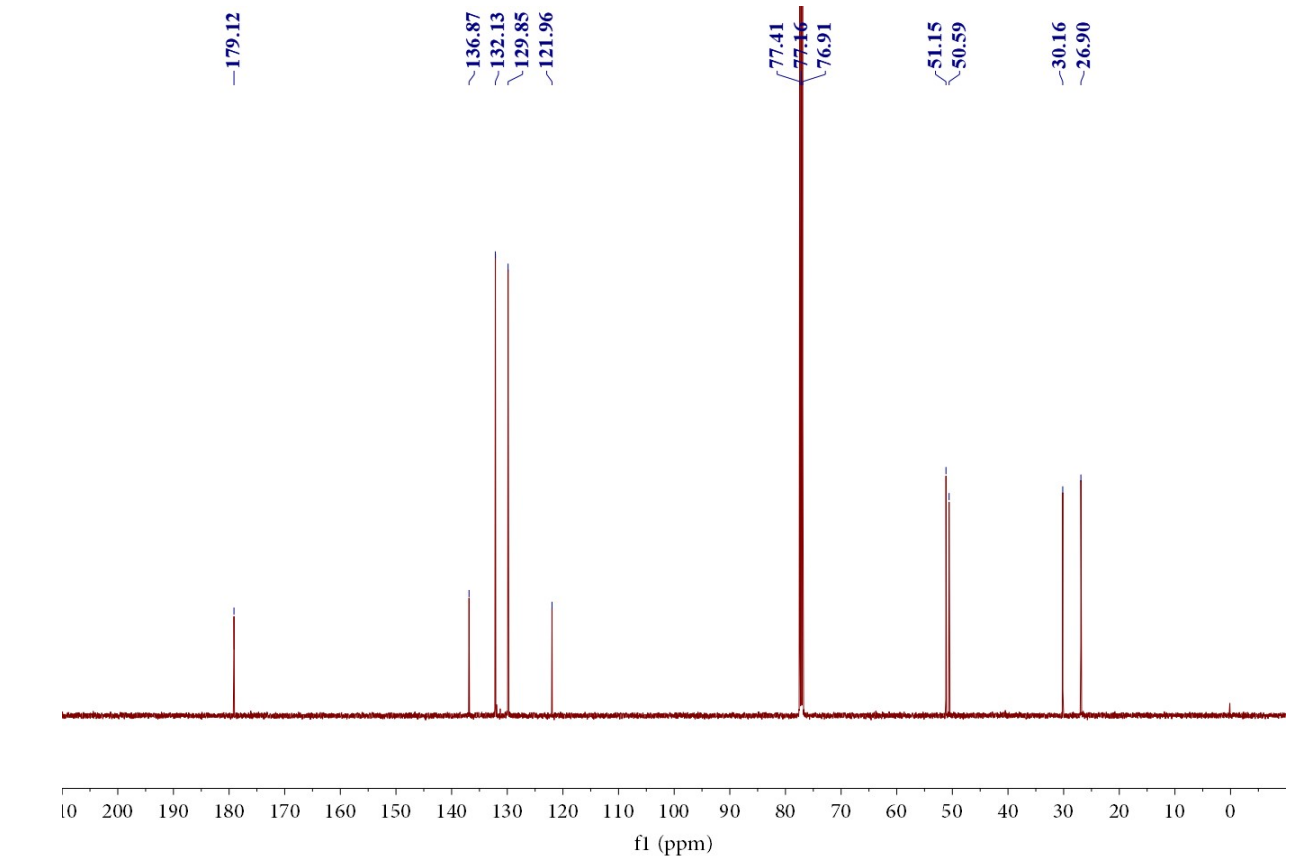
19F-NMR of 1m

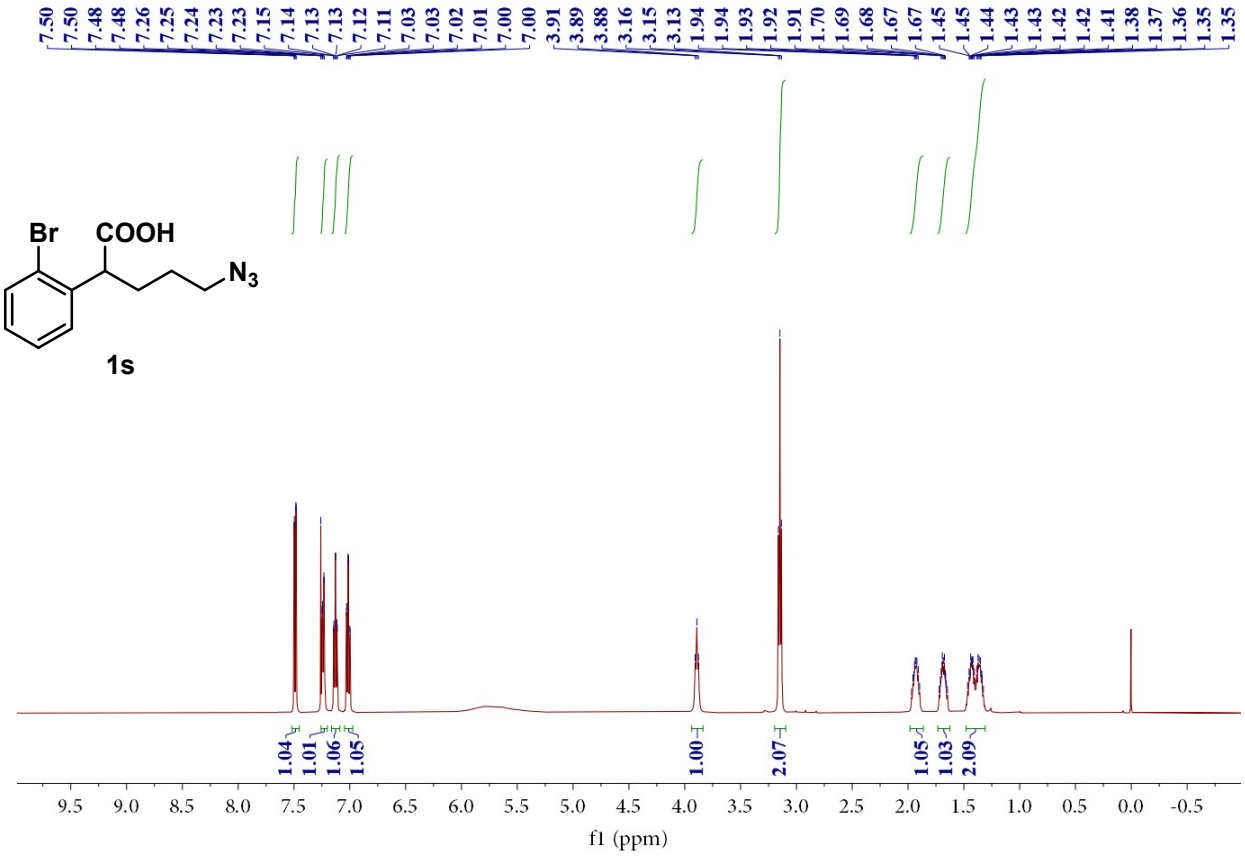

-109.33
COOH
N3
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

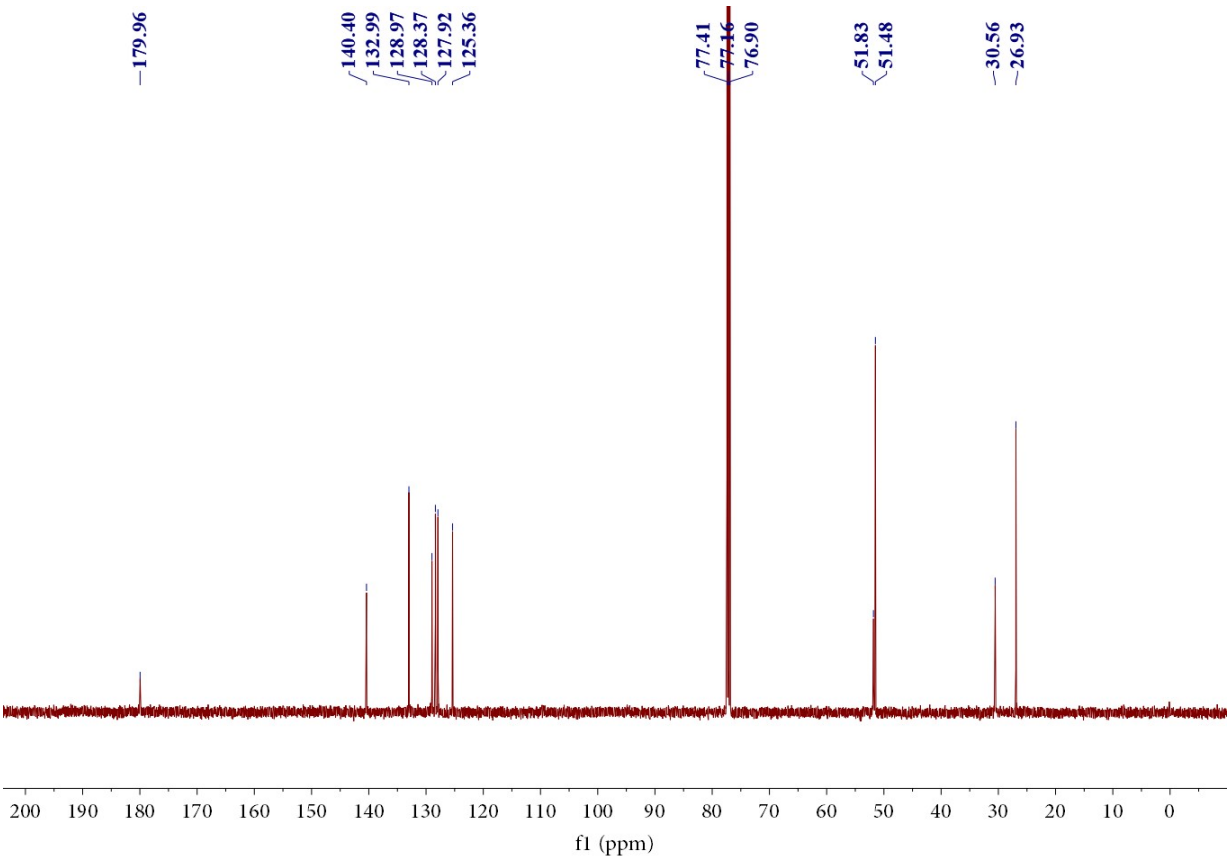

7.31 7.31 7.30 7.29 7.26 7.23 7.22 7.22 7.21 7.12 7.12 7.11 7.10 7.10 7.10 7.09 7.09 7.08 7.07 7.07
3.95 3.93 3.92 3.15 3.14 3.13 1.97 1.96 1.95 1.95 1.94 1.93 1.92 1.72 1.70 1.69 1.68 1.67 1.66 1.46 1.45 1.44 1.43 1.43 1.41 1.40 1.38 1.37 1.36 1.35
Cl
COOH
N3
1p
1.06
1.01
2.10
0.94
2.00
1.01
1.01
2.06
f1 (ppm)

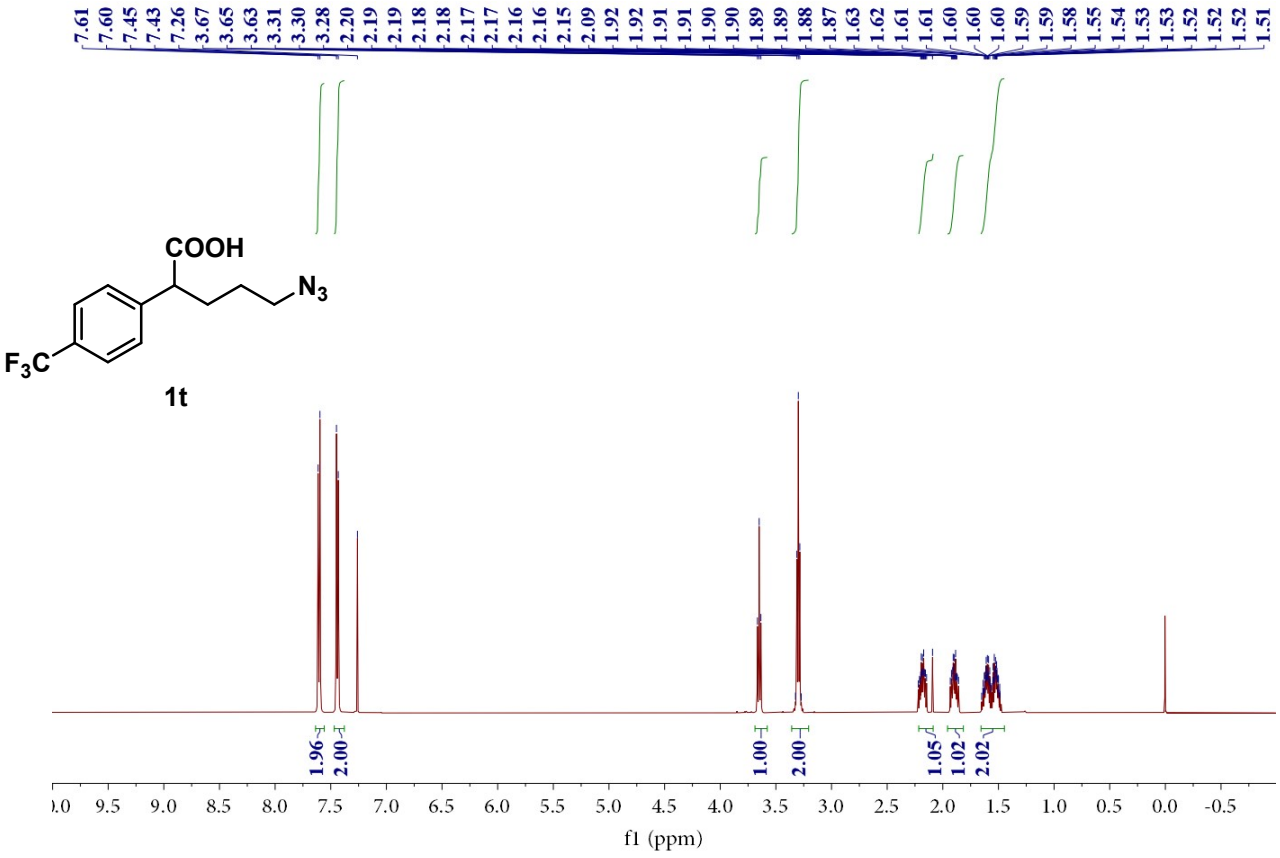

179.89
138.19
134.29
129.67
128.94
128.15
127.25
77.42
77.16
76.91
51.38
48.87
30.12
26.91
f1 (ppm)

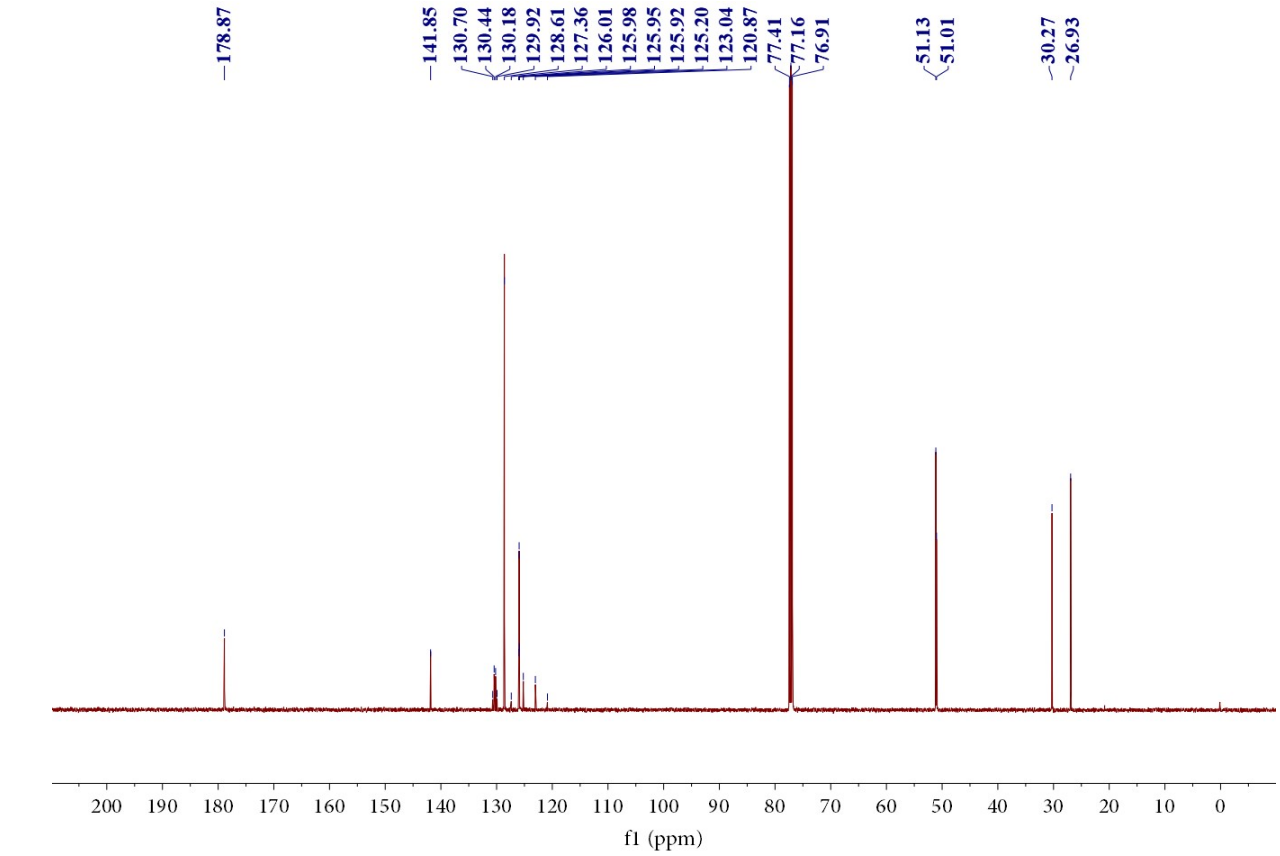

7.48
7.47
7.46
7.45
7.26
7.20
7.19
7.18
3.55
3.53
3.52
3.30
3.28
3.27
2.16
2.16
2.15
2.14
2.14
2.13
2.12
2.12
2.11
2.10
2.09
2.08
1.89
1.88
1.87
1.87
1.86
1.85
1.85
1.83
1.83
1.82
1.81
1.80
1.61
1.59
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
COOH
N3
Br
1q
1.96
1.99
1.02
2.00
1.13
1.05
2.07
f1 (ppm)


179.12
136.87
132.13
129.85
121.96
77.41
77.16
76.91
51.15
50.59
30.16
26.90
f1 (ppm)

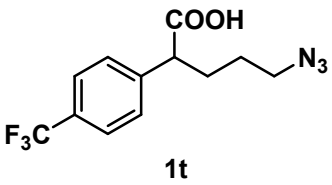

7.50 7.50 7.48 7.48 7.26 7.25 7.24 7.23 7.23 7.15 7.14 7.13 7.13 7.12 7.11 7.03 7.03 7.02 7.01 7.00 7.00
3.91 3.89 3.88 3.16 3.15 3.13 1.94 1.94 1.93 1.92 1.91 1.70 1.69 1.68 1.67 1.67 1.45 1.45 1.44 1.43 1.43 1.42 1.42 1.41 1.38 1.37 1.36 1.35 1.35
Br
COOH
N3
1s
1.04 1.01 1.06 1.05 1.00 2.07 1.05 1.03 2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.96
140.40 132.99 128.97 128.37 127.92 125.36
77.41 77.16 76.90
51.83 51.48
30.56 26.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

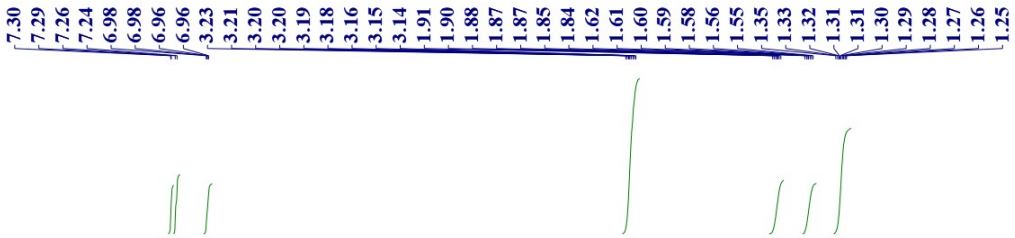

7.61 7.60 7.45 7.43 7.26 3.67 3.65 3.63 3.31 3.30 3.28 2.20 2.19 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15 2.09 1.92 1.92 1.91 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.63 1.62 1.61 1.61 1.60 1.60 1.60 1.59 1.59 1.58 1.55 1.54 1.53 1.53 1.52 1.52 1.52 1.51
COOH
N3
F3C
1t
1.96
2.00
1.00
2.00
1.05
1.02
2.02
f1 (ppm)

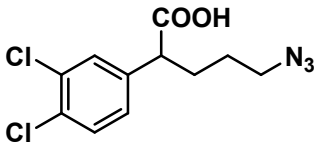

178.87
141.85
130.70
130.44
130.18
129.92
128.61
127.36
126.01
125.98
125.95
125.92
125.20
123.04
120.87
77.41
77.16
76.91
51.13
51.01
30.27
26.93
f1 (ppm)

19F-NMR of 1t

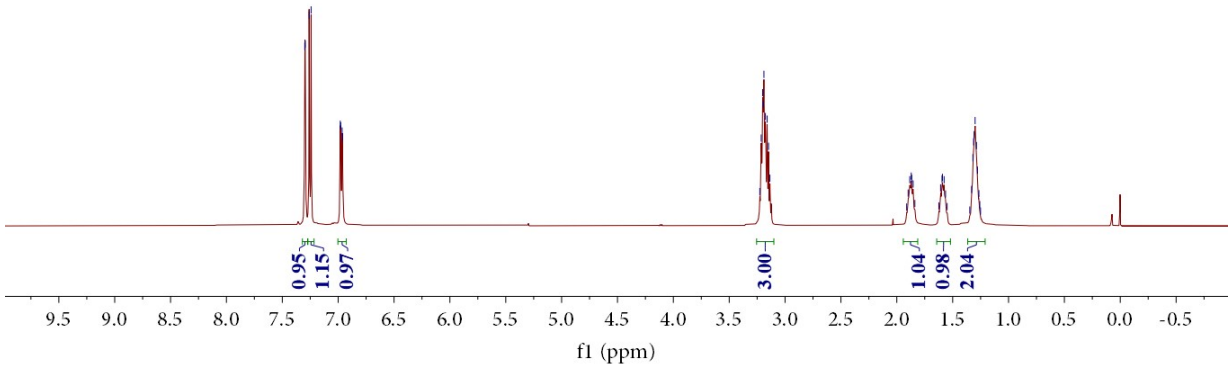


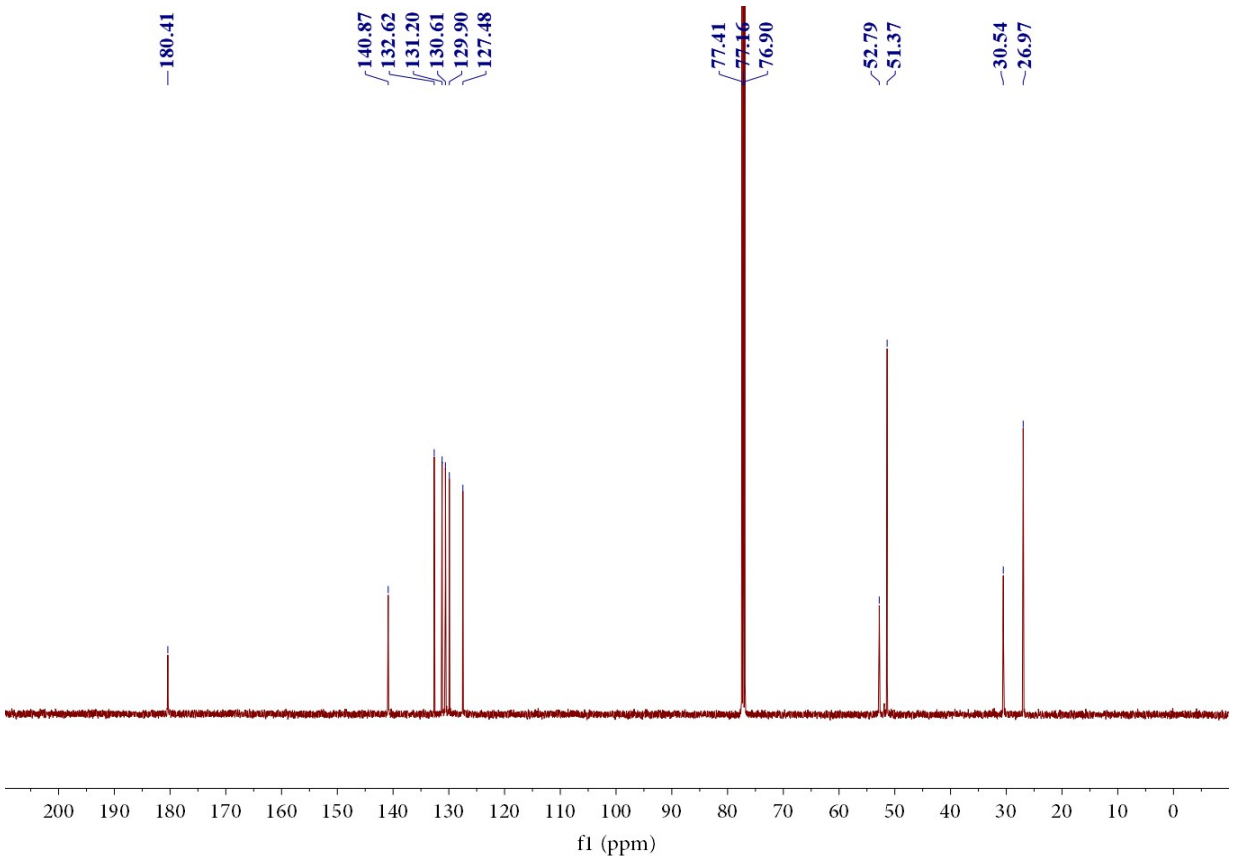
1t

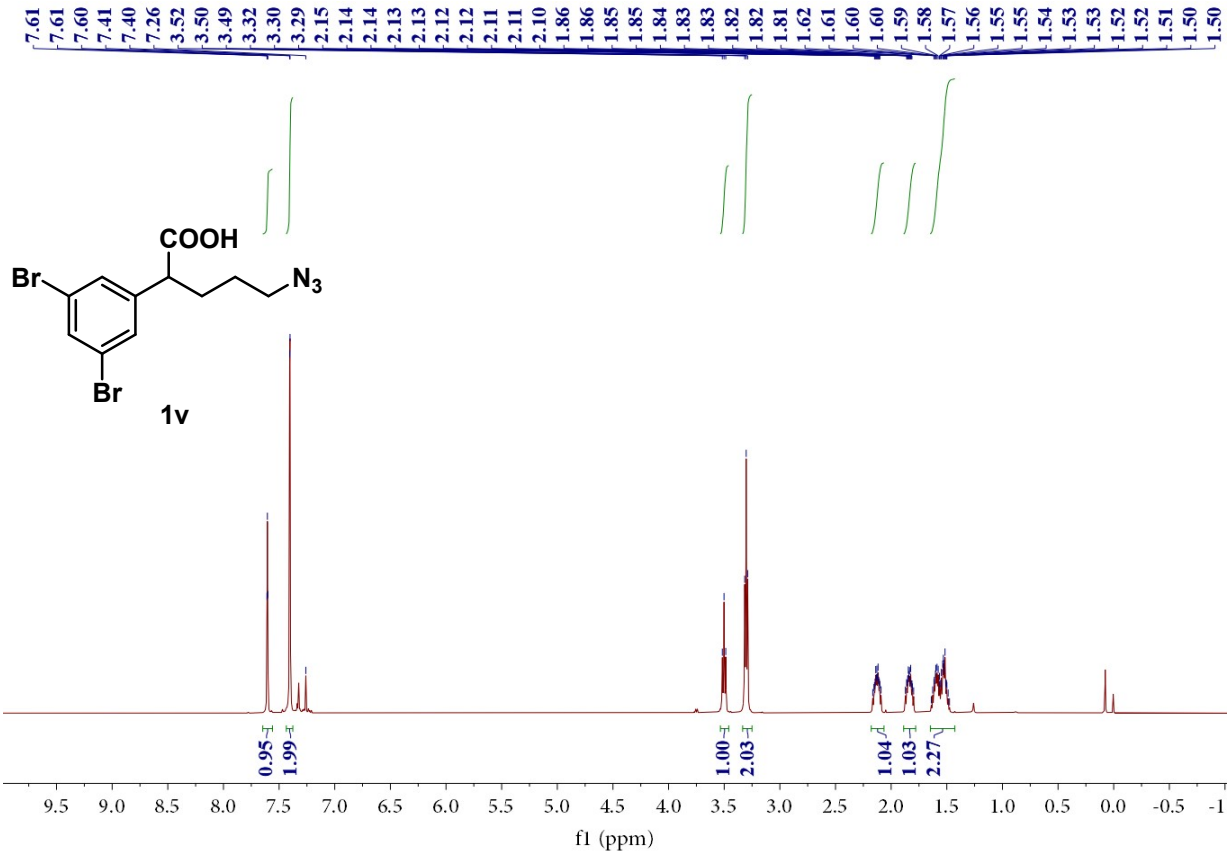

7.30
7.29
7.26
7.24
6.98
6.98
6.96
6.96
3.23
3.21
3.20
3.20
3.19
3.18
3.16
3.15
3.14
1.91
1.90
1.88
1.87
1.87
1.85
1.84
1.62
1.61
1.60
1.59
1.58
1.56
1.55
1.35
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.26
1.25

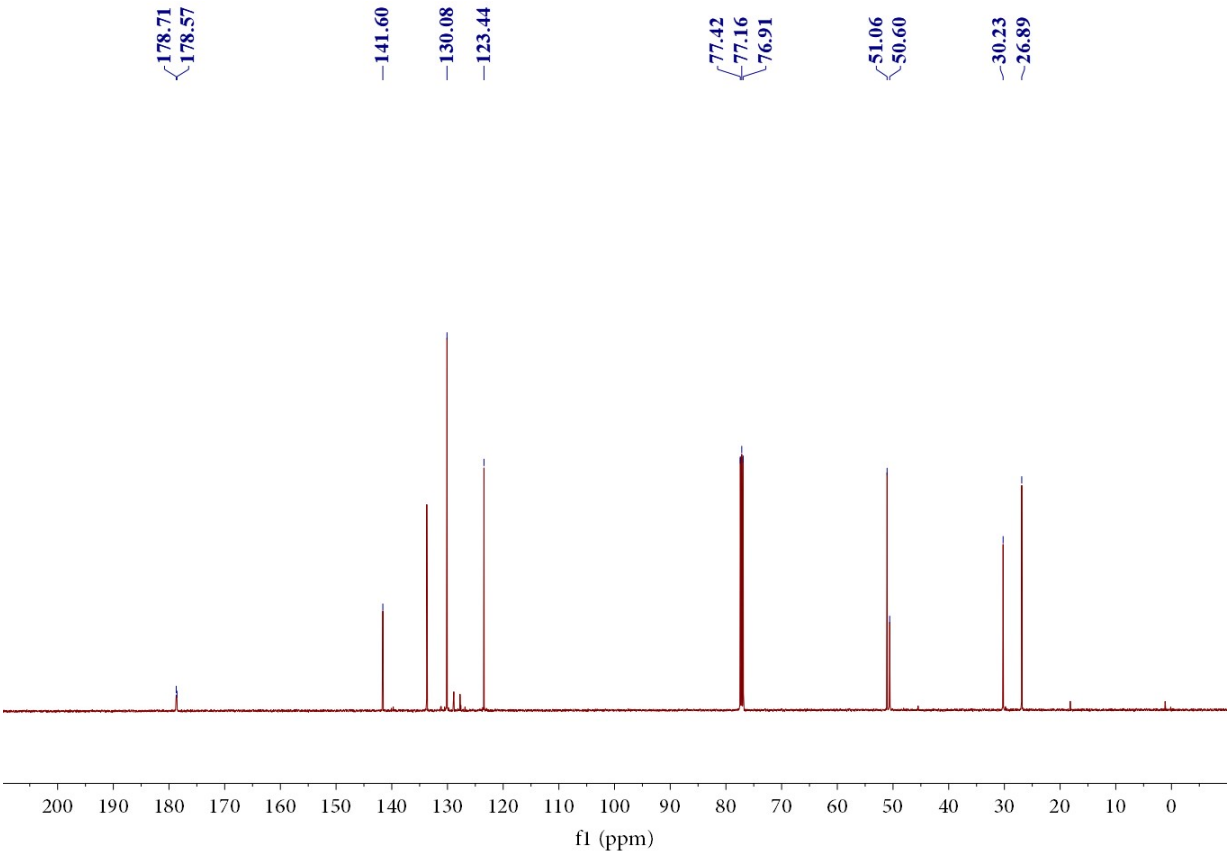

COOH
Cl
Cl
N3

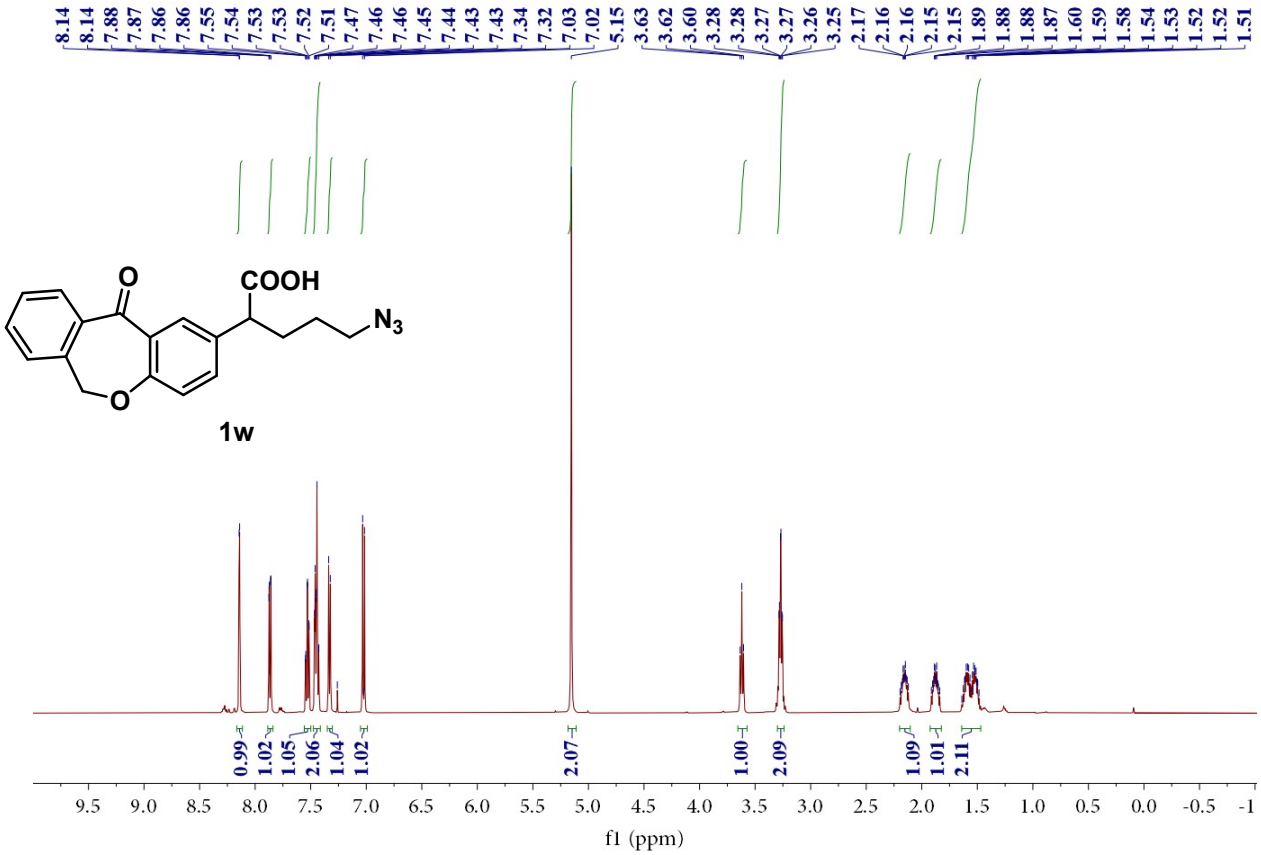
1u

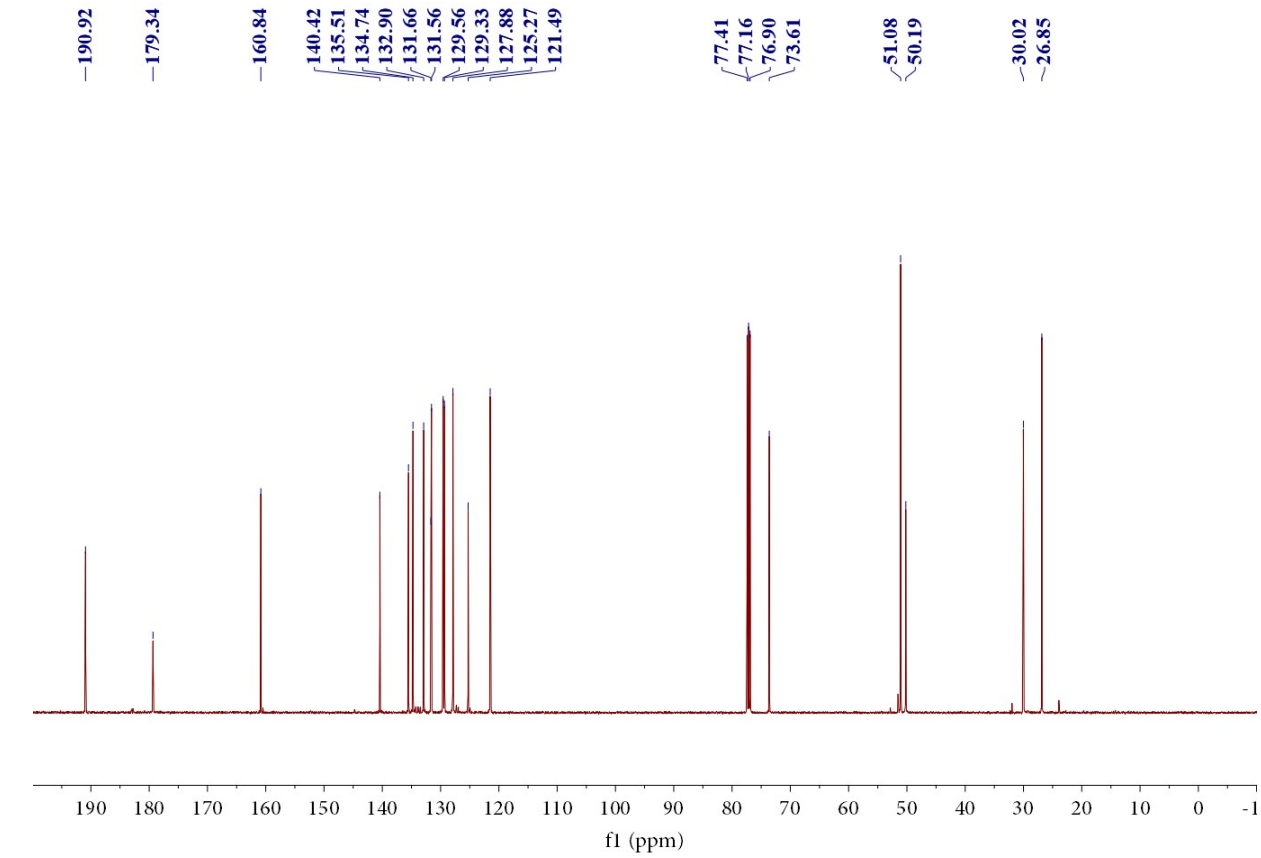

0.95
1.15
0.97
3.00
1.04
0.98
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

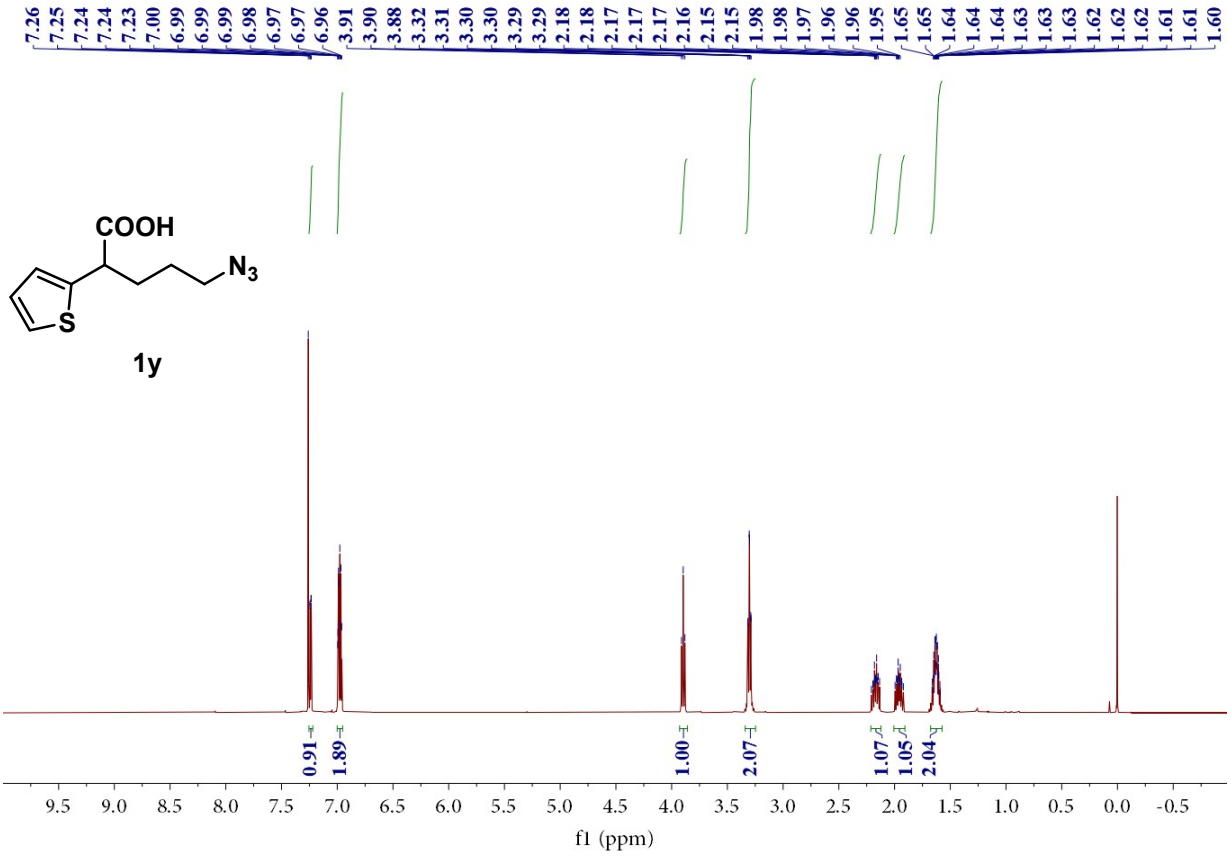

180.41
140.87
132.62
131.20
130.61
129.90
127.48
77.41
77.16
76.90
52.79
51.37
30.54
26.97
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

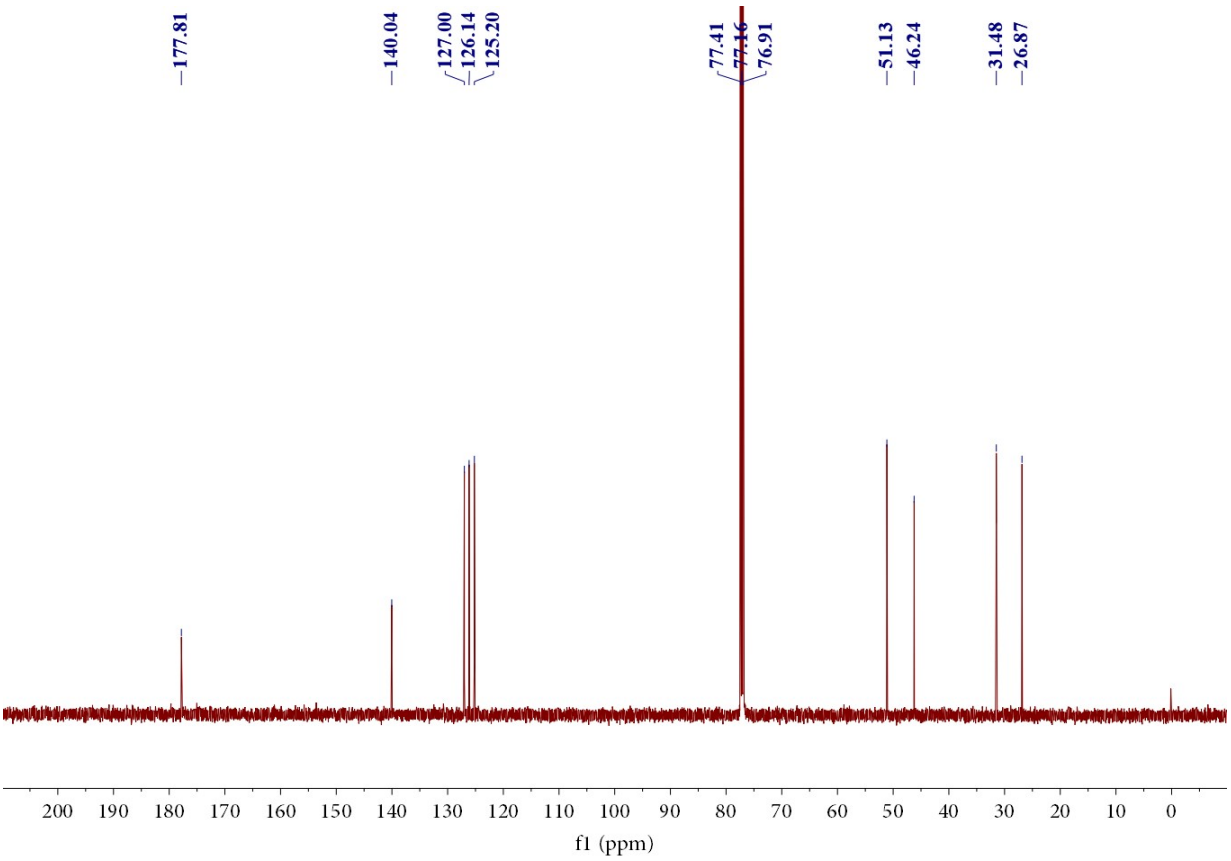

7.61 7.61 7.60 7.41 7.40 7.26 3.52 3.50 3.49 3.32 3.30 3.29 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.11 2.11 2.10 1.86 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.82 1.81 1.62 1.61 1.60 1.60 1.59 1.58 1.57 1.56 1.55 1.55 1.54 1.53 1.53 1.52 1.52 1.51 1.50 1.50
COOH
Br
N3
Br
1v
0.95 1.99 1.00 2.03 1.04 1.03 2.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

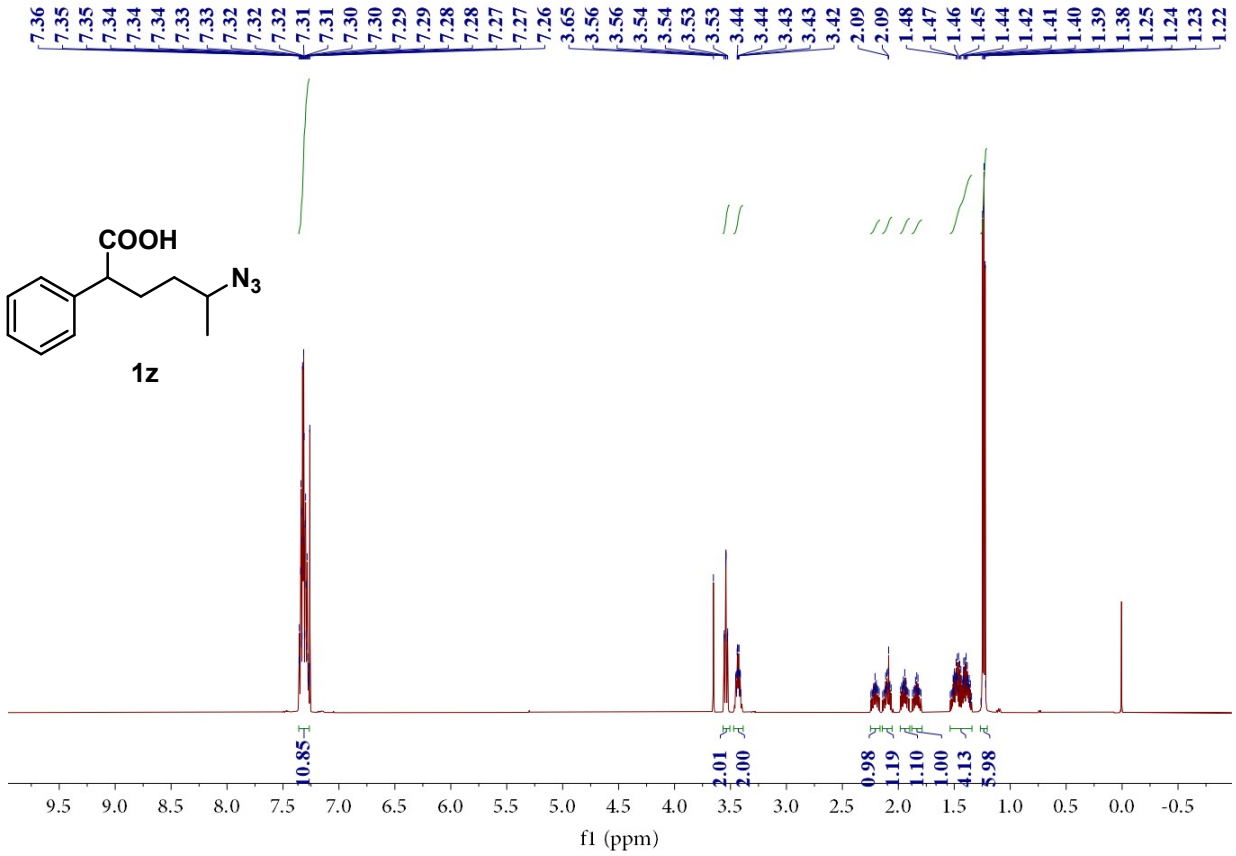

178.71 178.57 141.60 130.08 123.44 77.42 77.16 76.91 51.06 50.60 30.23 26.89
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

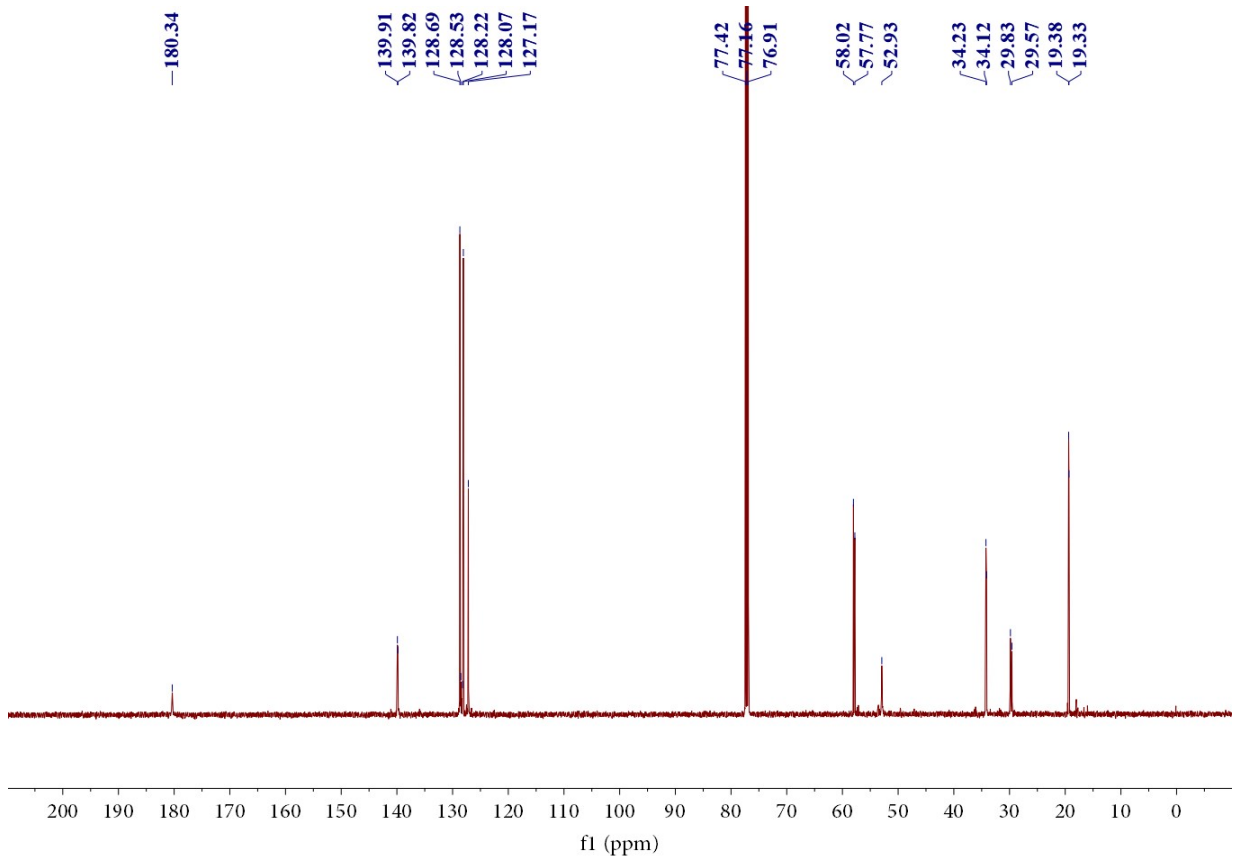

8.14 8.14 7.88 7.87 7.86 7.86 7.55 7.54 7.53 7.53 7.52 7.51 7.47 7.46 7.46 7.45 7.44 7.43 7.43 7.34 7.32 7.03 7.02 5.15 3.63 3.62 3.60 3.28 3.28 3.27 3.27 3.26 3.25 2.17 2.16 2.16 2.15 2.15 1.89 1.88 1.88 1.87 1.60 1.59 1.58 1.54 1.53 1.52 1.52 1.51
O
COOH
N3
O
1w
0.99 1.02 1.05 2.06 1.04 1.02 2.07 1.00 2.09 1.09 1.01 2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

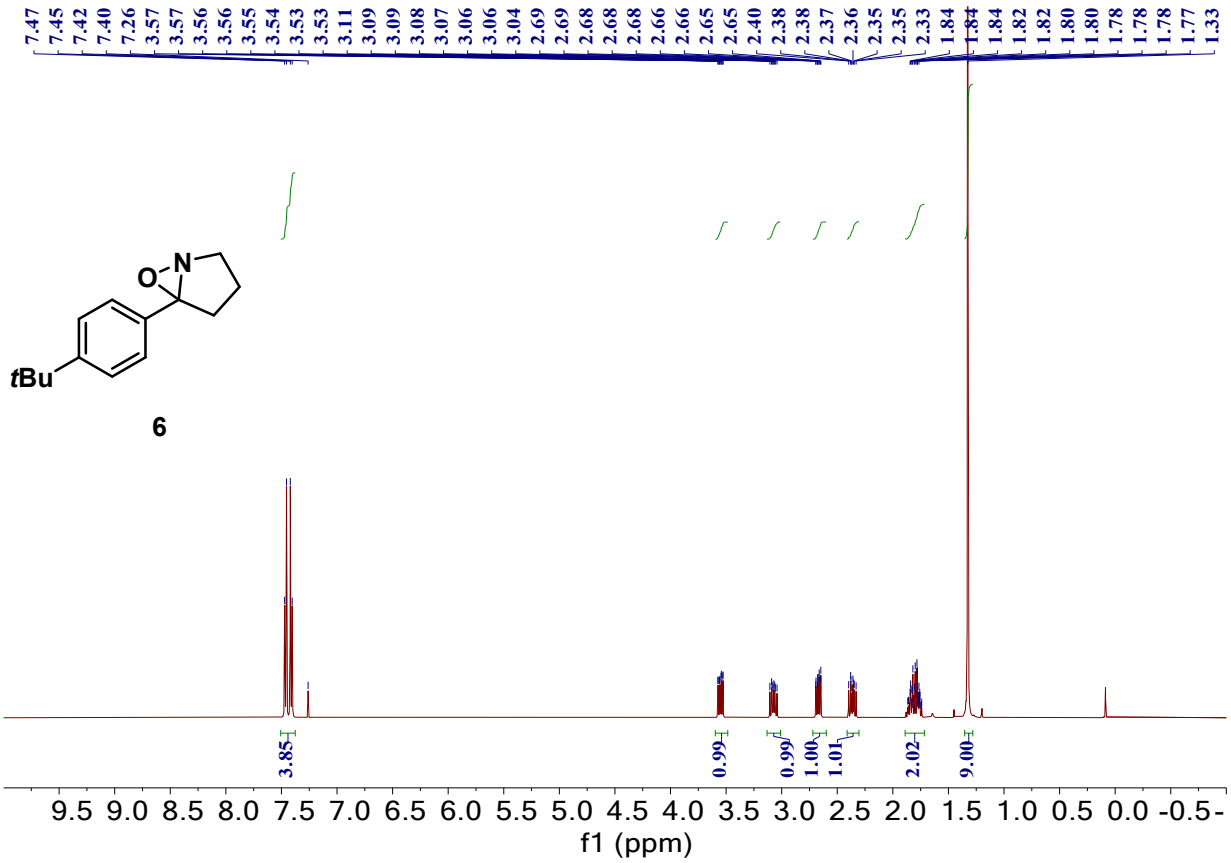

190.92 179.34 160.84 140.42 135.51 134.74 132.90 131.66 131.56 129.56 129.33 127.88 125.27 121.49 77.41 77.16 76.90 73.61 51.08 50.19 30.02 26.85
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

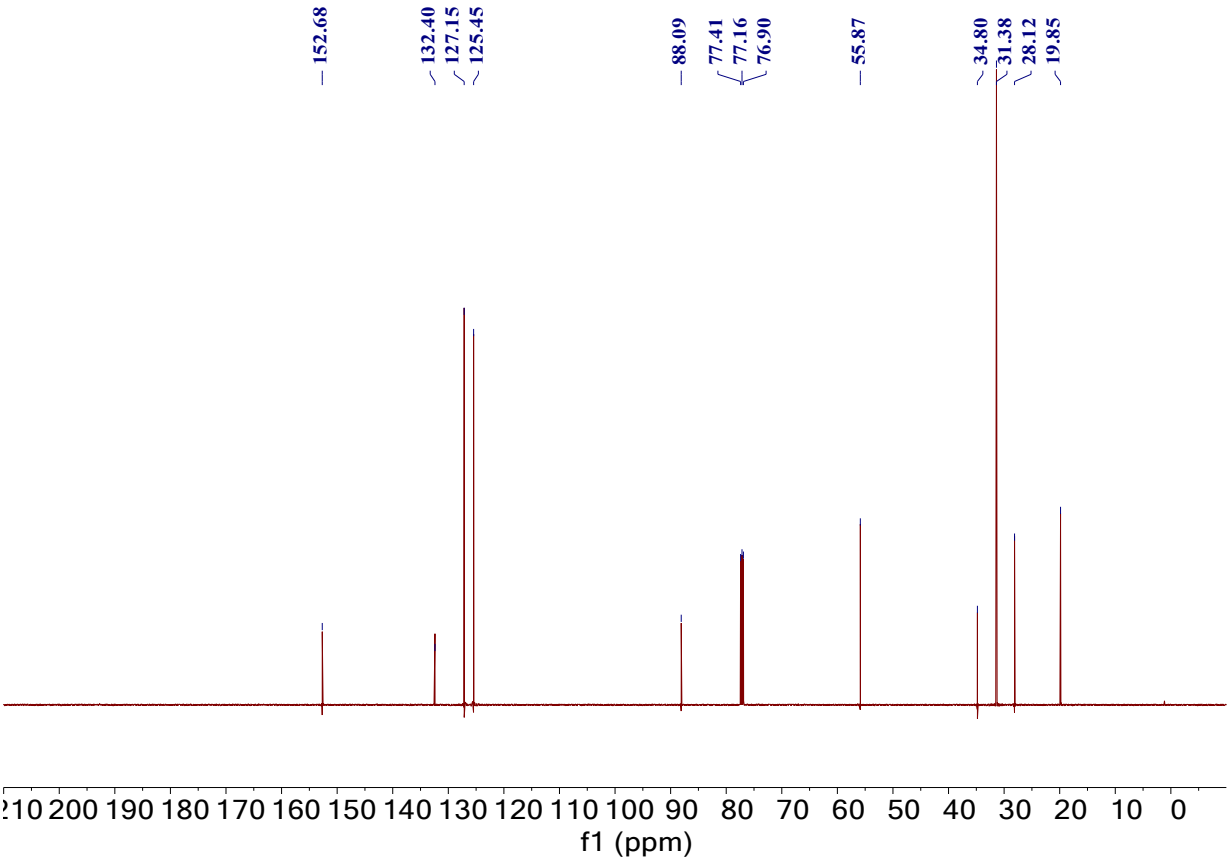

7.26 7.25 7.24 7.24 7.23 7.00 6.99 6.99 6.99 6.98 6.97 6.97 6.96 3.91 3.90 3.88 3.32 3.31 3.30 3.30 3.29 3.29 2.18 2.18 2.17 2.17 2.17 2.16 2.15 2.15 1.98 1.98 1.97 1.96 1.96 1.95 1.65 1.65 1.64 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.61 1.60
COOH
N3
S
1y
0.91
1.89
1.00
2.07
1.07
1.05
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

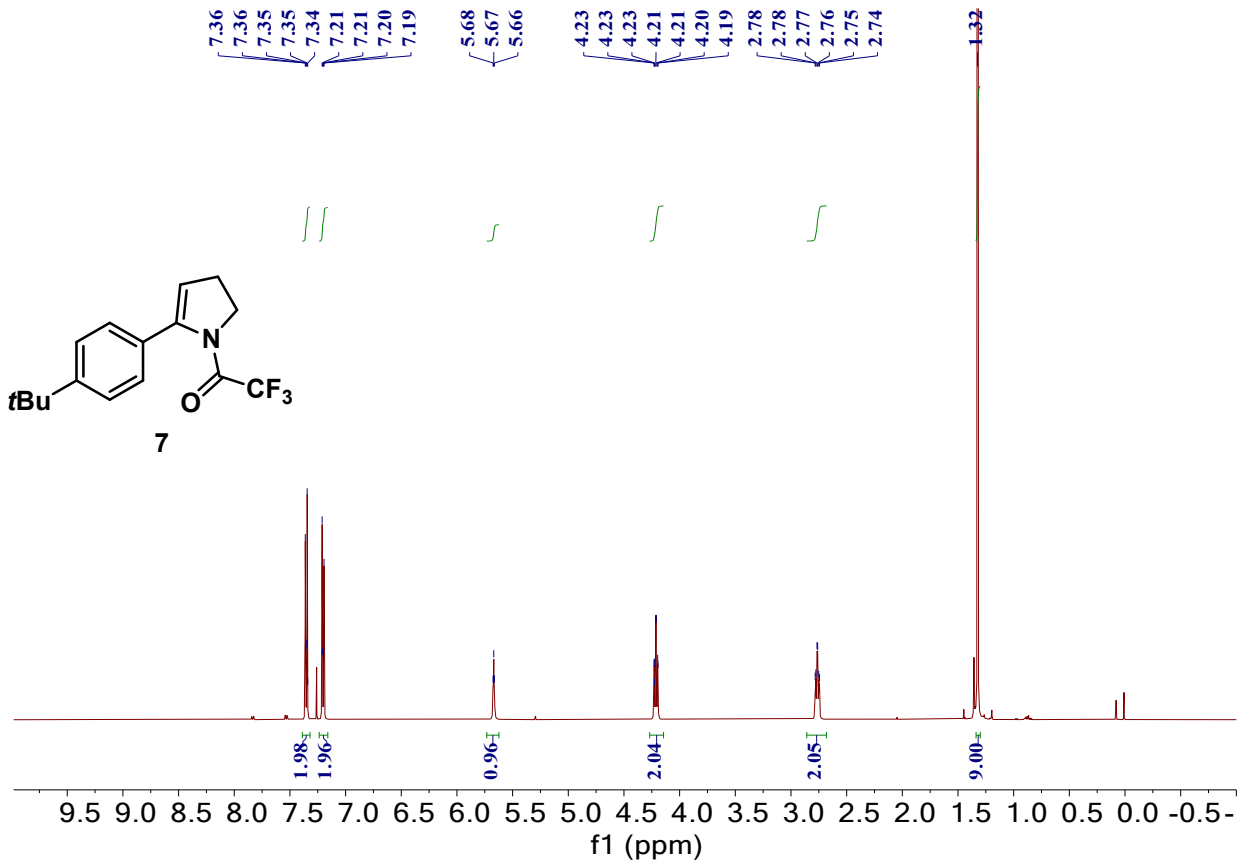

177.81
140.04
127.00
126.14
125.20
77.41
77.16
76.91
51.13
46.24
31.48
26.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 3.65 3.56 3.56 3.54 3.54 3.53 3.53 3.44 3.44 3.43 3.43 3.42 2.09 2.09 1.48 1.47 1.46 1.45 1.44 1.42 1.41 1.40 1.39 1.38 1.25 1.24 1.23 1.22
COOH
N3
1z
10.85
2.01
2.00
0.98
1.19
1.10
1.00
4.13
5.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


180.34
139.91
139.82
128.69
128.53
128.22
128.07
127.17
77.42
77.16
76.91
58.02
57.77
52.93
34.23
34.12
29.83
29.57
19.38
19.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

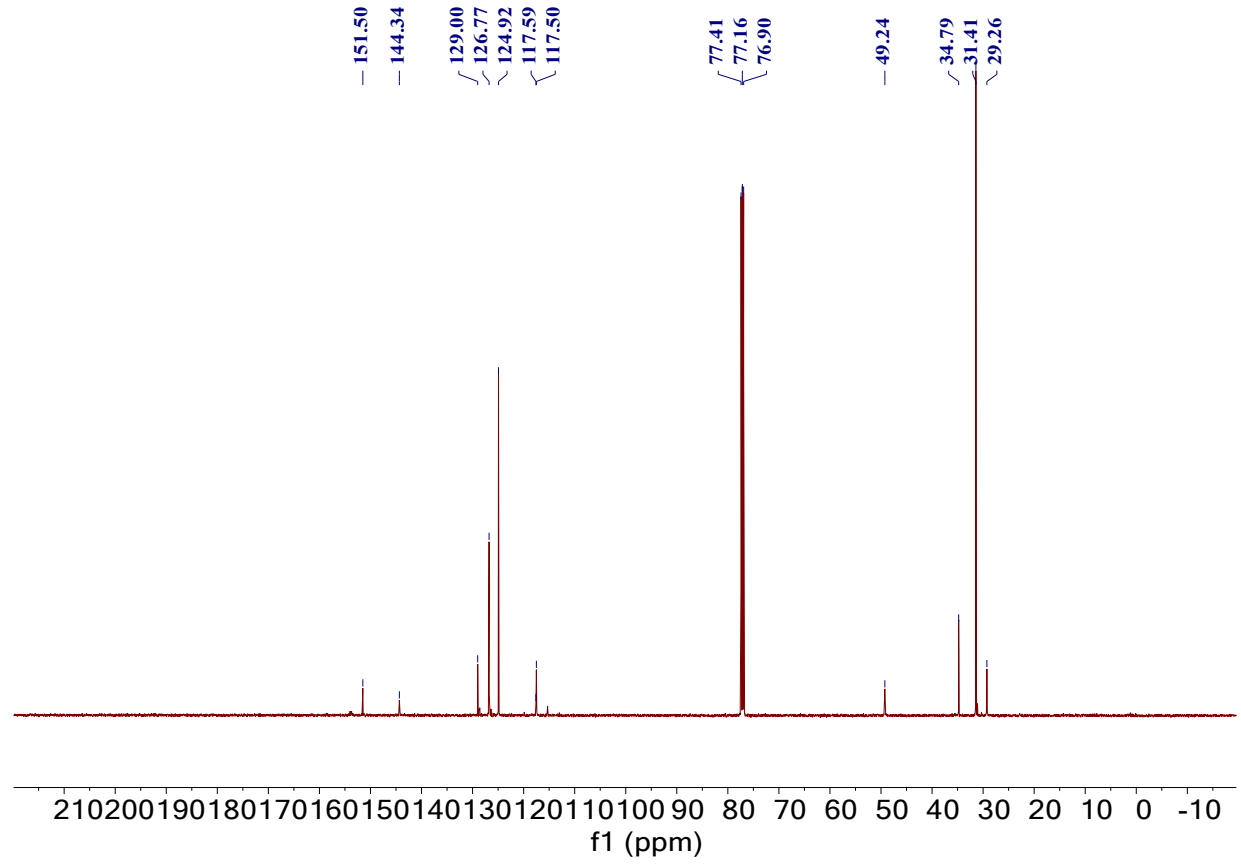

7.47
7.45
7.42
7.40
7.26
3.57
3.57
3.56
3.56
3.55
3.54
3.53
3.53
3.11
3.09
3.09
3.08
3.07
3.06
3.06
3.04
2.69
2.69
2.68
2.68
2.66
2.66
2.65
2.65
2.40
2.38
2.38
2.37
2.36
2.35
2.35
2.33
1.84
1.84
1.84
1.82
1.82
1.80
1.80
1.78
1.78
1.78
1.77
1.33
O
N
tBu
6
3.85
0.99
0.99
1.00
1.01
2.02
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

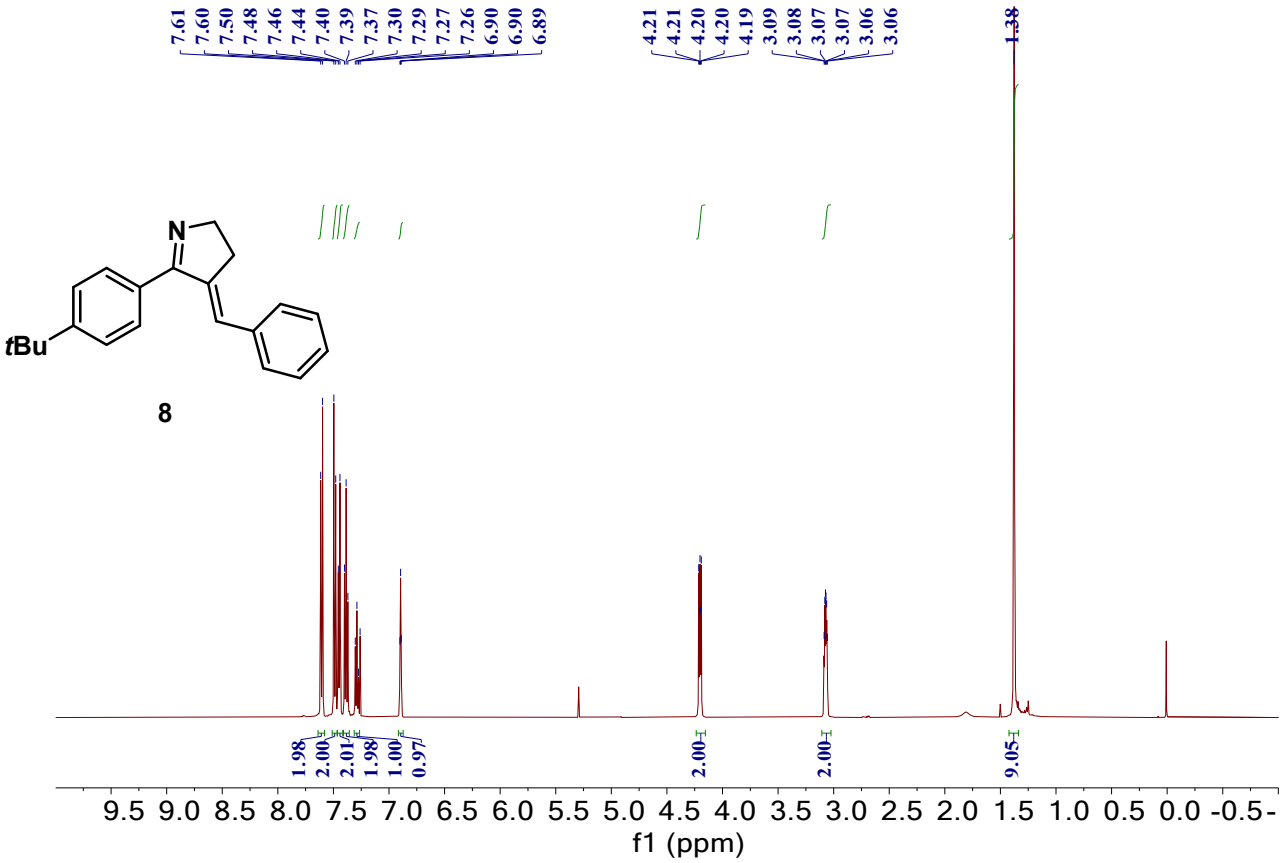

152.68
132.40
127.15
125.45
88.09
77.41
77.16
76.90
55.87
34.80
31.38
28.12
19.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

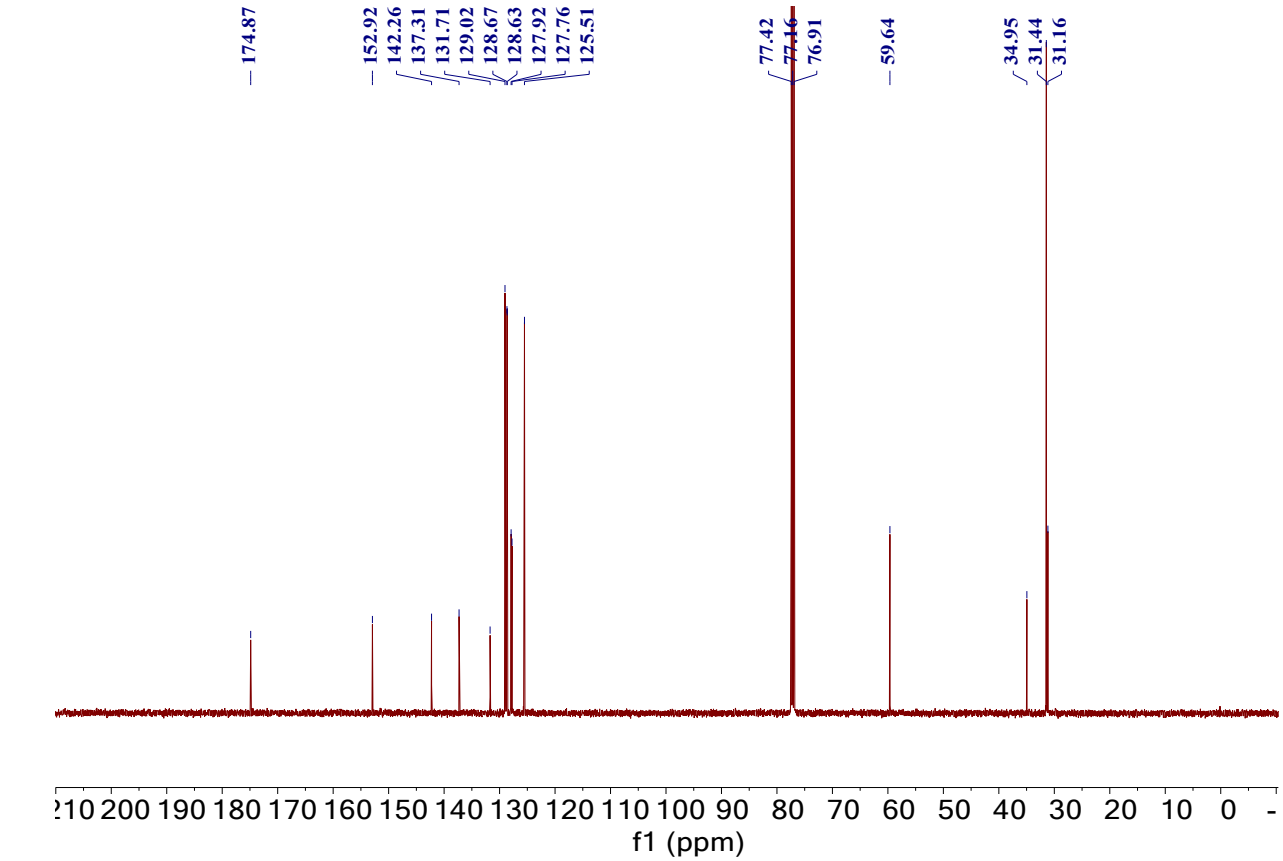

7.36
7.36
7.35
7.35
7.34
7.21
7.21
7.20
7.19
5.68
5.67
5.66
4.23
4.23
4.23
4.21
4.21
4.20
4.19
2.78
2.78
2.77
2.76
2.75
2.74
1.32
1.98
1.96
0.96
2.04
2.05
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

tBu
N
O
CF3

7


151.50
144.34
129.00
126.77
124.92
117.59
117.50
77.41
77.16
76.90
49.24
34.79
31.41
29.26
210200190180170160150140130120110100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.61
7.60
7.50
7.48
7.46
7.44
7.40
7.39
7.37
7.30
7.29
7.27
7.26
6.90
6.90
6.89
4.21
4.21
4.20
4.20
4.19
3.09
3.08
3.07
3.07
3.06
3.06
1.38
N
tBu
8
1.98
2.00
2.01
1.98
1.00
0.97
2.00
2.00
9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.87
152.92
142.26
137.31
131.71
129.02
128.67
128.63
127.92
127.76
125.51
77.42
77.16
76.91
59.64
34.95
31.44
31.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)