Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

N-Heterocyclic Nitrenium Charge Transfer Catalysis via Inner-Sphere Electron Transfer Concerted with Halogen-Atom Dissociation

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1. General Information

Chemicals were purchased from Heowns,Innochem or Bidepharm and used without further purification unless otherwise noted. Solvents were purified using a solvent-purification system (VSPS-8, Vigor) that contained activated alumina and molecular sieves. N-methacryloyl-N-methylbenzamide[1], N-arylacrylamides[2], phenylcinnamamide[3], enamides[4], nitrenium salt [5,6] were prepared according to literature methods.

Analytical thin layer chromatography was carried out with silica gel pre-coated glass plates (TLC-Silica gel GF254, coating thickness: 0.25 mm) purchased from Xinnuo Chemical (Yantai, China). Chromatographic purification of the products was performed on silica gel 200-300 mesh. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.

High-resolution mass spectra (HRMS) were obtained with the mass analyzer of an orbitrap. The calculated values are based on the most abundant isotope.

IR spectra were taken on a Vertex 70 spectrophotometer and reported as wave numbers (cm^{-1}).

The WRS-2 microcomputer melting point meter was used to measure the melting point of solids.

The GC-MS TQ8040 was used in the detection of the reaction mixture.

UV-vis absorption spectra were acquired on UV-1900 spectrophotometer (Shimadzu, Japan).

Fluorescecespectra were recorded on a Edingburg FS5 Fluorescent Spectrophotometer.

The luminescence decays were measured on an Edingburg FLS980 spectrometer.

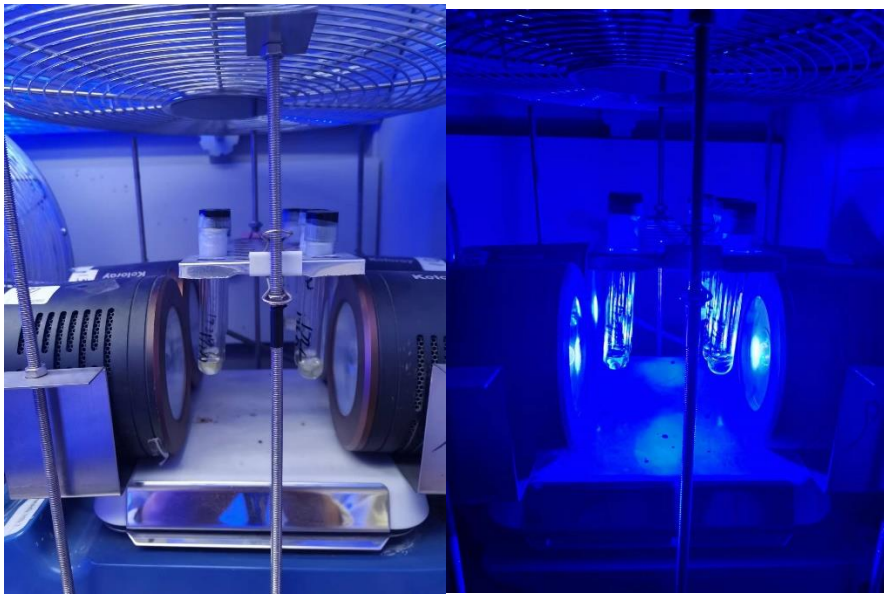
Cyclic voltammetry studies were carried out on a Shanghai Chen Hua CHI660E electrochemical workstation.

EPR spectra were recorded at room temperature, using a Bruker EMXplus spectrometer.

^{1}H- and ^{13}C- NMR spectra were recorded at ambient temperature on a Shimadzu Avance 400/500 Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet, bs = broad signal), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).

Photochemical experiments were performed magnetically stirred in 10 mL glass tubes, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm,) using a LED lamp with a power output of 100 W (see below pictures). The distance from the light source to the irradiation vessel is 2.0 cm to keep the reaction temperature at 50 ± 5 °C.

(The purchase link of LED lamp is https://item.taobao.com/item.htm?spm=a1z10.5-c-s.w4002-21207510047.14.dbef5298YBVk03&id=522759747619).



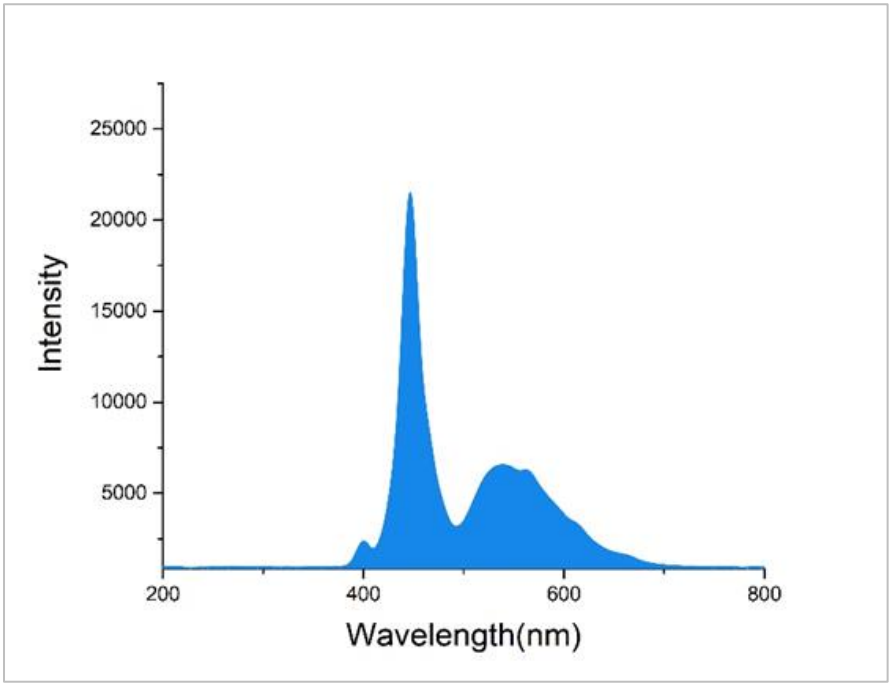
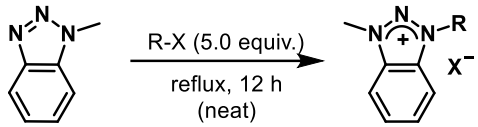
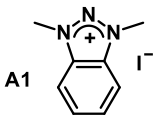


Figure S1. The spectrum of blue LEDs employed in the reaction

2. Synthesis of N-Heterocyclic Nitrenium Salts

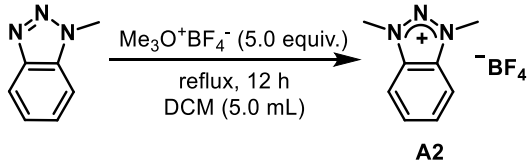


The preparation of nitrenium salt **A-C** was performed according to previously reported procedure[5]. 1-methylbenzotriazole (266.0 mg, 2.0 mmol, 1.0 equiv.) was dissolved in methylating reagent (R-X, 10.0 mmol, 5.0 equiv.) which was warmed to reflux for 12 h. After cooling to room temperature, removal of alkyl iodide and recrystallization of the crude crystals from ethanol led to nitrenium salt.

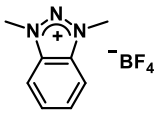


A1

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.30 – 8.25 (m, 2H), 8.04 – 7.94 (m, 2H), 4.65 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 135.6, 131.1, 113.5, 37.4. **IR** (ATR): 2981, 1603, 1437, 1313, 1012, 774 cm^{-1} **HRMS** (ESI)**:** *m/z* [M]$^+$ calcd for $C_8H_{10}N_3^+$:148.0869; found 148.0866. **Melting Point:** 184 - 186 ˚C. These data are in agreement with those reported previously in the literature[5].

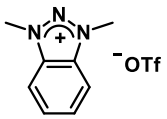


A2



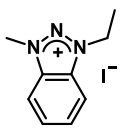
A2

^{1}H NMR (400 MHz, D_2O) δ 7.99 (dd, J = 6.6, 3.1 Hz, 1H), 7.84 (dd, J = 6.6, 3.1 Hz, 1H), 4.47 (s, 3H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 135.3, 131.2, 113.1, 37.2. **^{19}F NMR** (471 MHz, Methanol-d_4) δ -150.6 (major), -150.5 (minor). **IR** (ATR): 2987, 2911, 1092, 1039, 1017, 779, 521 cm^{-1}. **HRMS** (ESI)**:** *m/z* [M]$^+$ calcd for $C_8H_{10}N_3^+$:148.0869; found 148.0867. **Melting Point:** 169 - 170 ˚C.



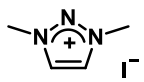
A3

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.24 – 8.18 (m, 2H), 7.99 – 7.93 (m, 2H), 4.61 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 135.5, 131.0, 120.5 (q, *J* = 323.2 Hz), 113.3, 36.9. **^{19}F NMR** (471 MHz, Methanol-d_4) δ -79.99. **IR** (ATR): 2988, 1439, 1323, 1265, 1023, 775 cm^{-1} **HRMS** (ESI)**:** *m/z* [M]$^+$ calcd for $C_8H_{10}N_3^+$:148.0869; found 148.0867. **Melting Point:** 125 - 127 ˚C.



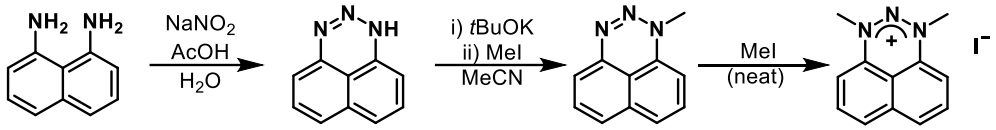
B

^{1}H NMR (500 MHz, Methanol-d_4) δ 8.35 – 8.31 (m, 1H), 8.29 – 8.24 (m, 1H), 8.00 – 7.96 (m, 2H), 5.06 (q, *J* = 7.3 Hz, 2H), 4.66 (s, 3H), 1.77 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 135.7, 134.8, 131.1, 131.0, 113.7, 113.5, 37.6, 13.2, 13.1. **IR** (ATR): 2980, 1606, 1440, 1365, 1069,1026, 767 cm^{-1}. **HRMS** (ESI)**:** *m/z* [M]$^+$ calcd for $C_9H_{12}N_3^+$:162.1026; found 162.1023. **Melting Point:** 145 - 147 ˚C.



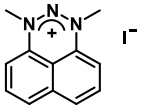
C

^{1}H NMR (500 MHz, Methanol-d_4) δ 8.74 (s, 2H), 4.38 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 131.5, 39.8. **IR** (ATR): 3156, 1537, 1289, 1210, 1099, 750, 665 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M]^+$ calcd for $C_4H_8N_3^+$: 98.0713; found 98.0716. **Melting Point:** 194 - 196 ˚C.



D

The preparation of nitrenium salt **D** was performed according to previously reported procedure[6].



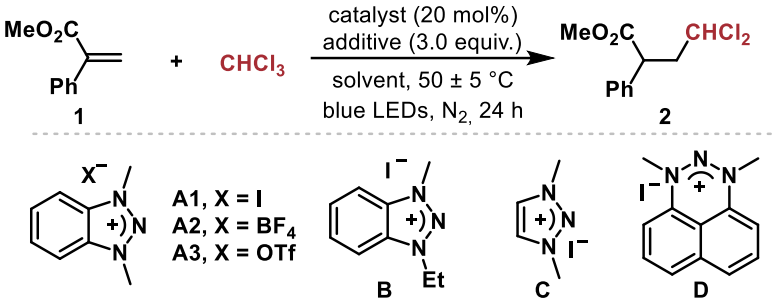
D

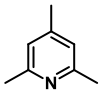
^{1}H NMR (500 MHz, Methanol-d_4) δ 7.67 (dd, *J* = 8.5, 0.7 Hz, 2H), 7.5 (dd, *J* = 8.6, 7.7 Hz, 2H), 7.10 (dd, *J* = 7.7, 0.7 Hz, 2H), 3.94 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 133.9, 131.3, 128.9, 126.1, 122.3, 107.9, 43.5. **IR** (ATR): 3472, 1639, 1599, 1527, 1459, 1391, 984, 819, 698 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M]^+$ calcd for $C_{12}H_{12}N_3^+$:198.1026; found 198.1023.

Melting Point: 201 - 203 ˚C.

3. General Procedure for the Optimization of the Reaction Conditions

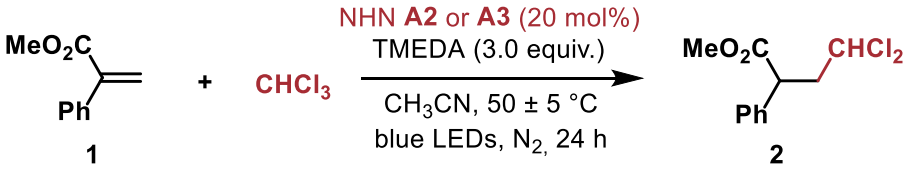
Table S1. Optimization of the reaction conditions for activation of chloroform [a]



Entry	Catalyst	Additive	Solvent	Yield (%)[b]
1	**A1**	TMEDA	CH_3CN	69 (62)[c]
2	**A2**	TMEDA	CH_3CN	38
3	**A3**	TMEDA	CH_3CN	44
4	**B**	TMEDA	CH_3CN	38
5	**C**	TMEDA	CH_3CN	24
6	**D**	TMEDA	CH_3CN	52
7	**A1**	TMEDA	DMSO	52
8	**A1**	TMEDA	DMA	50
9	**A1**	TMEDA	DMF	48
10	**A1**	TMEDA	DCM	61
11	**A1**	TMEDA	THF	30
12	**A1**	TMEDA	Acetone	56
13	**A1**	TMEDA	Toluene	28
14	**A1**	DMAP	CH_3CN	26
15	**A1**	Quinuclidine	CH_3CN	14
16	**A1**	DABCO	CH_3CN	21
17	**A1**	DIPEA	CH_3CN	50
18	**A1**	DBU	CH_3CN	44
19	**A1**	NEt_3	CH_3CN	34
20	**A1**	$PMPPh_2N$	CH_3CN	NR
21	**A1**		CH_3CN	NR
22	**A1**	$CyNMe_2$	CH_3CN	26
23	**A1**	NaOAc	CH_3CN	NR

24	**A1**	K_2CO_3	CH_3CN	NR
25	**A1**	$NaHCO_3$	CH_3CN	NR
26	**A1**	---	CH_3CN	NR
27	**---**	TMEDA	CH_3CN	NR
28	**---**	---	CH_3CN	NR
29[d]	**A1**	TMEDA	CH_3CN	NR
30[e]	**A1**	TMEDA	CH_3CN	58
31[f]	**A1**	TMEDA	CH_3CN	64
32[g]	**A1**	TMEDA	CH_3CN	44
33[h]	**A1**	TMEDA	CH_3CN	14
34[i]	**A1**	TMEDA	---	62
35[j]	**A1**	TMEDA	CH_3CN	51

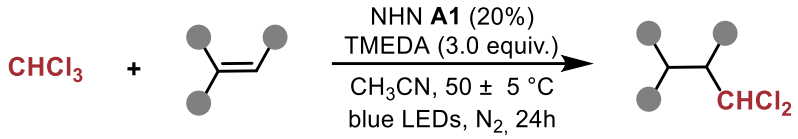
[a] Reaction carried out with **1** (0.1 mmol), $CHCl_3$ (0.1 mL), catalyst (20 mol%), additive (0.3 mmol) and solvent (0.25 mL). [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. [c] Reactions were performed on a 0.2 mmol scale with yield of isolated product given. [d] No irradiation, 60 °C. [e] $CHCl_3$ (0.2 mL). [f] $CHCl_3$ (0.15 mL). [g] $CHCl_3$ (0.05 mL). [h] $CHCl_3$ (2.0 equiv.). [i] $CHCl_3$ (0.5 mL). [j] catalyst (10 mol%). NR, No Reaction. DIPEA = N,N-Diisopropylethylamine. DMAP = 4-dimethylaminopyridine. TMEDA = N,N,N',N'-Tetramethylethylenediamine. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.



Entry	Catalyst	NaI	Yield (%)[a]
1	**A2**	**---**	38
2	**A2**	20 mol%	54
3	**A3**	**---**	44
4	**A3**	20 mol%	55
5	**---**	20 mol%	NR

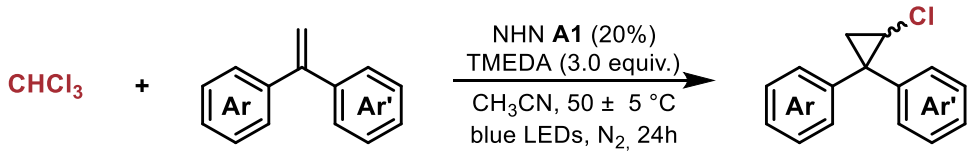
[a] Yields were determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard.

General procedure A:



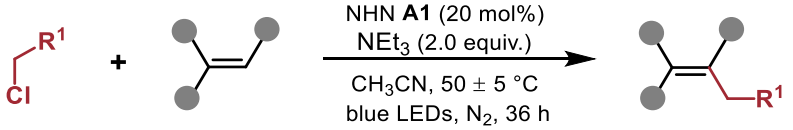
In a nitrogen-filled glove box, the olefin (0.2 mmol), NHN **A1** (0.04 mmol, 10.5 mg, 20 mol%), TMEDA (0.6 mmol, 69.7 mg, 90 μL) were added sequentially into a 10 mL dry tube, then CH_3CN (0.5 mL) and chloroform (0.2 mL) was added by syringe. The vial was closed and removed from the glove box, and the resulting mixture was allowed to stir under blue LED irradiation for 24 h, where the distance from the light source to the irradiation vessel is 2.0 cm to keep the reaction temperature at 50 ± 5 °C. Upon completion, solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired product.

General procedure B:



In a nitrogen-filled glove box, the olefin (0.2 mmol), NHN **A1** (0.04 mmol, 10.5 mg, 20 mol%), TMEDA (0.6 mmol, 69.7 mg, 90 μL) were added sequentially into a 10 mL dry tube under nitrogen, then DMF (0.5 mL) and chloroform (0.2 mL) was added by syringe. The vial was closed and removed from the glove box, and the resulting mixture was allowed to stir under blue LED irradiation for 24 h, where the distance from the light source to the irradiation vessel is 2.0 cm to keep the reaction temperature at 50 ± 5 °C. Upon completion, solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired product.

General procedure C



In a nitrogen-filled glove box, the alkyl chlorides (0.4 mmol), olefin (0.2 mmol), NHN **A1** (0.04 mmol, 10.5 mg, 20 mol%), NEt_3 (0.4 mmol, 40.5 mg, 55.6 μL) were added sequentially into a 10 mL dry tube under nitrogen, then CH_3CN (0.5 mL) was added by syringe. The vial was closed and removed from the glove box, and the resulting mixture was allowed to stir under blue LED irradiation for 36 h, where the distance from the light source to the irradiation vessel is 2.0 cm to keep the reaction temperature at 50 ± 5 °C. Upon completion, solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired product.

4. UV/vis Absorption Spectra Experiments

UV/vis absorption spectra were recorded using CH_3CN as solvent in 1 cm path quartz cuvettes using a UV-1900 UV/Vis spectrometer.

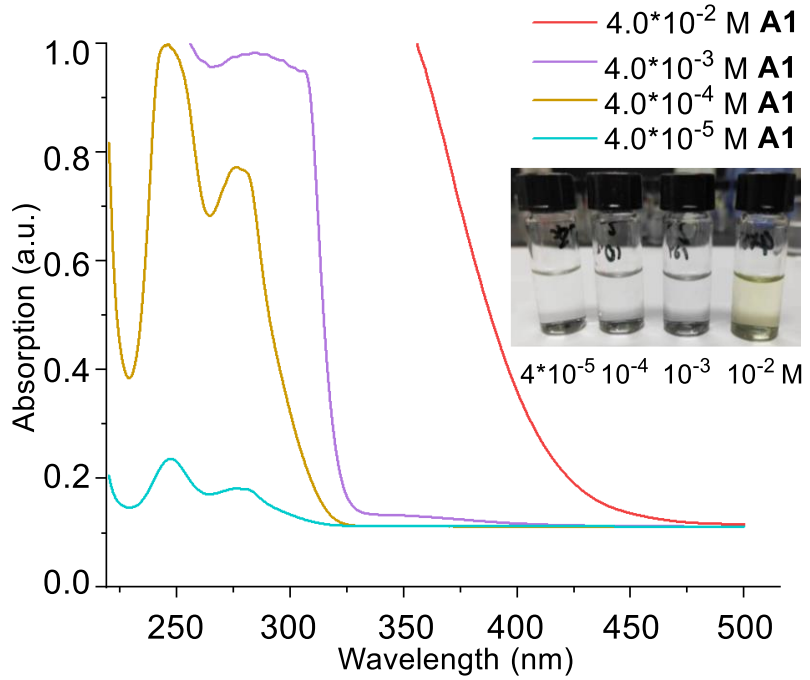


Figure S2. Absorption spectra of NHN salt **A1**, The UV/vis spectra of various concentrations of NHN **A1** (0.04 M, 0.004 M, 0.0004 M and 0.00004M in CH_3CN).

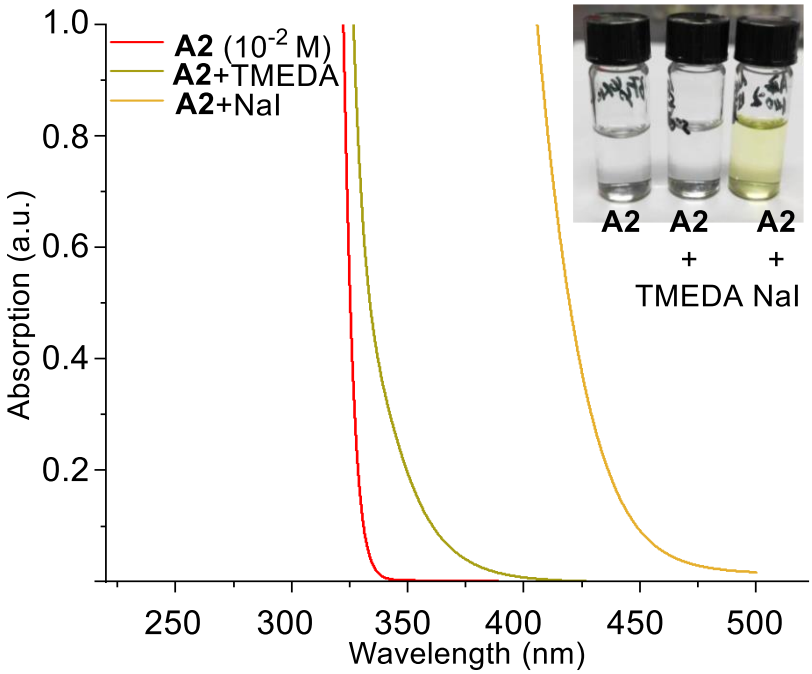


Figure S3. Absorption spectra of NHN salt **A2**, The UV/vis spectra of NHN **A2** (0.04 M in CH_3CN) and his mixture with TMEDA (0.6 M in CH_3CN), NaI (0.6 M in CH_3CN) were tested.

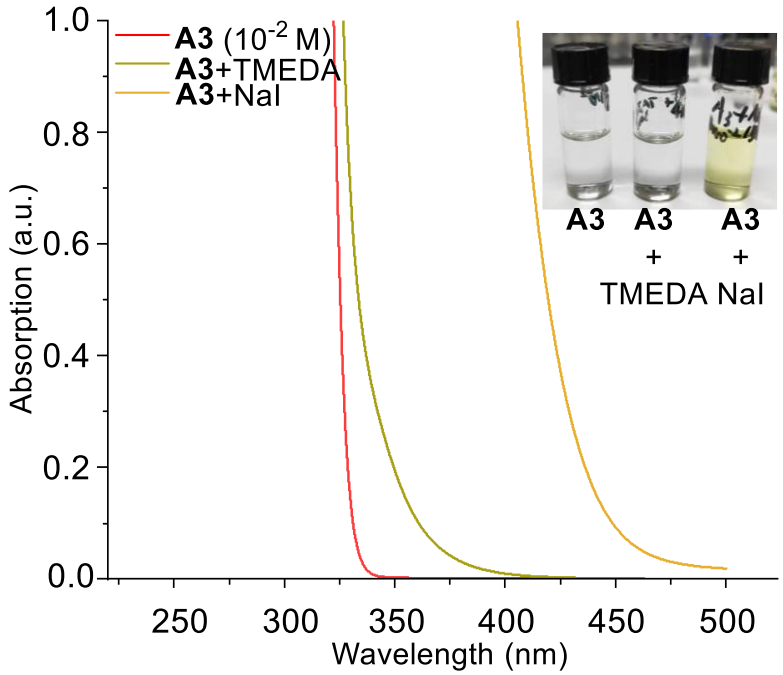


Figure S4. Absorption spectra of NHN salt **A3**, The UV/vis spectra of NHN **A3** (0.04 M in CH_3CN) and his mixture with TMEDA (0.6 M in CH_3CN), NaI (0.6 M in CH_3CN) were tested.

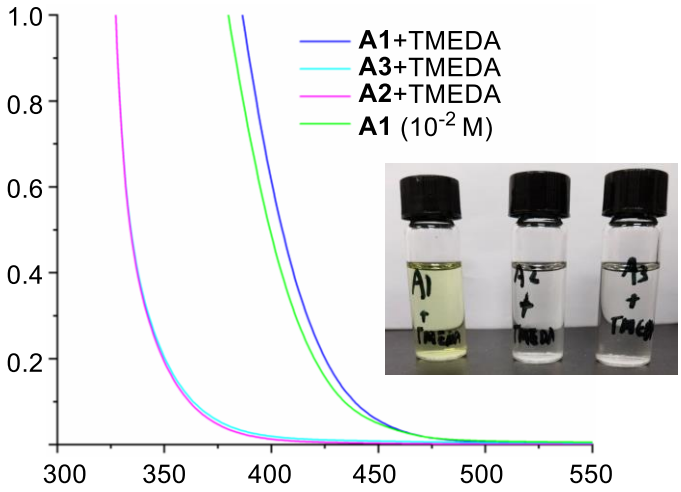


Figure S5. Absorption spectra of NHN salt **A1**, **A2**, **A3** and their mixture with TMEDA. The UV/vis spectra of NHN **A1** (0.04 M in CH_3CN) and his mixture with TMEDA (0.6 M in CH_3CN), **A2** + TMEDA (0.6 M in CH_3CN), **A3** + TMEDA (0.6 M in CH_3CN) were tested.

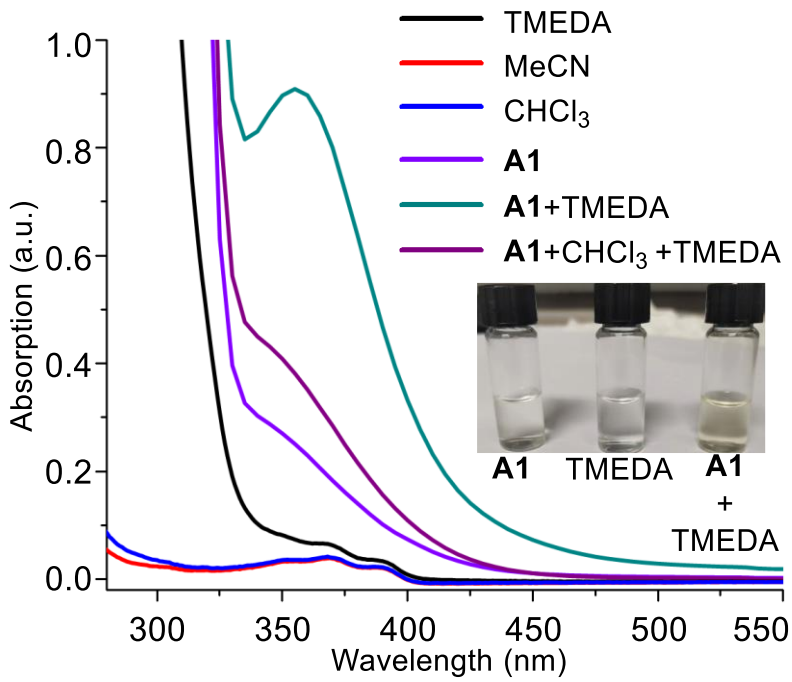


Figure S6. Absorption spectra of NHN salt **A1**, substrate **1**, $CHCl_3$, TMEDA and their mixture. The UV/vis spectra of methyl 2-phenylacrylate **1** (0.04 M in CH_3CN), NHN **A1** (0.008 M in CH_3CN), $CHCl_3$ (0.04 M in CH_3CN), TMEDA (0.04 M in CH_3CN) and their mixture were tested.

5. Determination of the Binding Ratio by Job's Plot

Job's plot was performed according to the literature method.[10] NHN **A1** and TMEDA were dissolved in DMSO-d_6 (0.5 mL), then the solutions of NHN **A1** and TMEDA were added to the NMR tube based on the specific ratio in Table S2. The $^1H(CH_3)$ chemical shift of NHN **A1** in DMSO-d_6 (0.04 mol/L) is 4.6251 ppm. The job's plot had a maximum when X (NHN **A1**) equals to 0.5, suggesting that the binding stoichiometry between TMEDA and NHN **A1** is 1:1.

Table S2. ^{1}H NMR experimental data for Job's plot

Entry	n (NHN **A1**, mmol)	n (TMEDA, mmol)	X (NHN **A1**)	δ (^{1}H(CH), ppm)	Δδ (ppm)	Δδ* X (**1**)
1	0.1	0.00	1.0	4.6251	0	0.000000
2	0.08	0.02	0.8	4.6233	0.0018	0.000288
3	0.07	0.03	0.7	4.6222	0.0029	0.000406
4	0.06	0.04	0.6	4.6209	0.0042	0.000504
5	0.05	0.05	0.5	4.6192	0.0059	0.000590
6	0.04	0.06	0.4	4.6177	0.0074	0.000592
7	0.03	0.07	0.3	4.6165	0.0086	0.000516
8	0.02	0.08	0.2	4.6145	0.0106	0.000424
9	0.00	0.10	0.0	0	0	0.000000

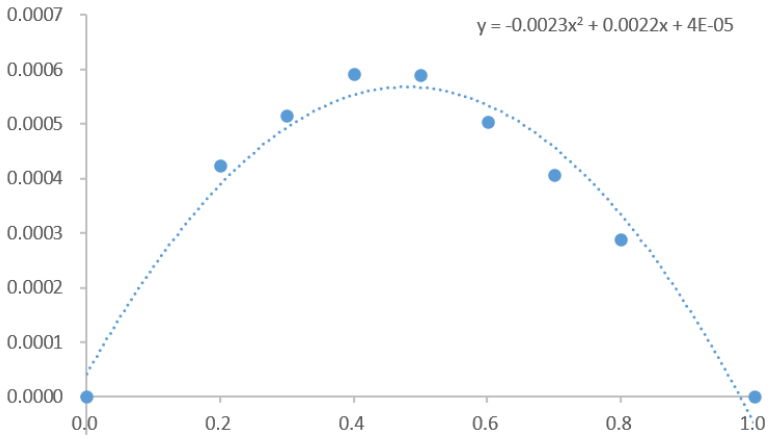


Figure S7. Job's plot for the determination of binding stoichiometry between NHN **A1** and TMEDA

^{1}H NMR Titrations of TMEDA with NHN **A1**

NHN **A1** (0.02 mmol) and TMEDA were mixed in DMSO-d_6 (0.5 mL), then the resulted mixture was injected into an NMR tube. The ^{1}H NMR (500 MHz, DMSO-d_6, 25 ^{o}C) spectra of the 0.04 M DMSO-d_6 solution of NHN **A1** with increasing concentration of TMEDA (corresponding concentration from bottom to top is 0.06, 0.12, 0.18, 0.24, 0.30, 0.36, 0.41, 0.48, 0.54 and 0.60 M) were recorded and shown in Figure S8. The titration curve was obtained with Bindfit program based on the ^{1}H titration experiment (Figure S9), and the association constant K_a between NHN **A1** and TMEDA was calculated to be 1.66±0.01 M^{-1}.[11]

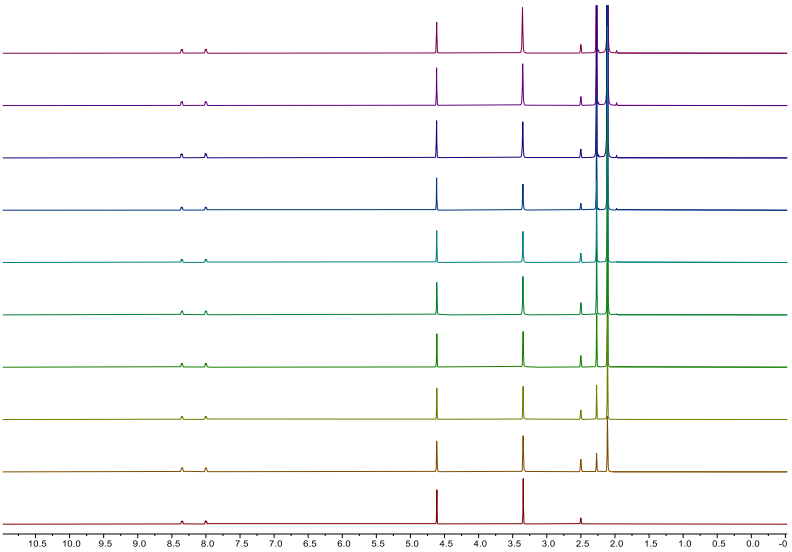
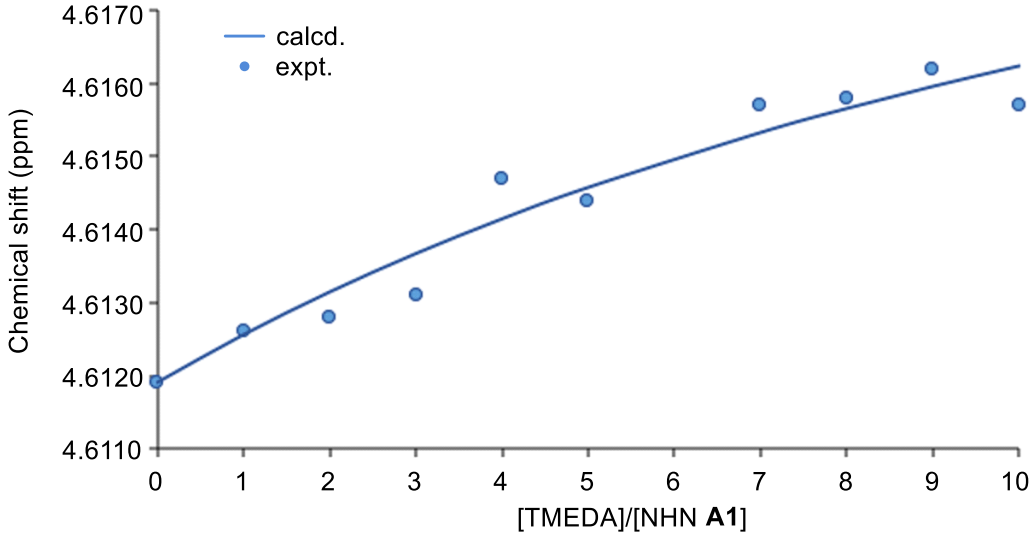


Figure S8. ^{1}H NMR spectra recorded during the titration of NHN **A1** (0.04 M) with variable concentrations (0.0-10.0 equiv.) of TMEDA in DMSO-d_6.



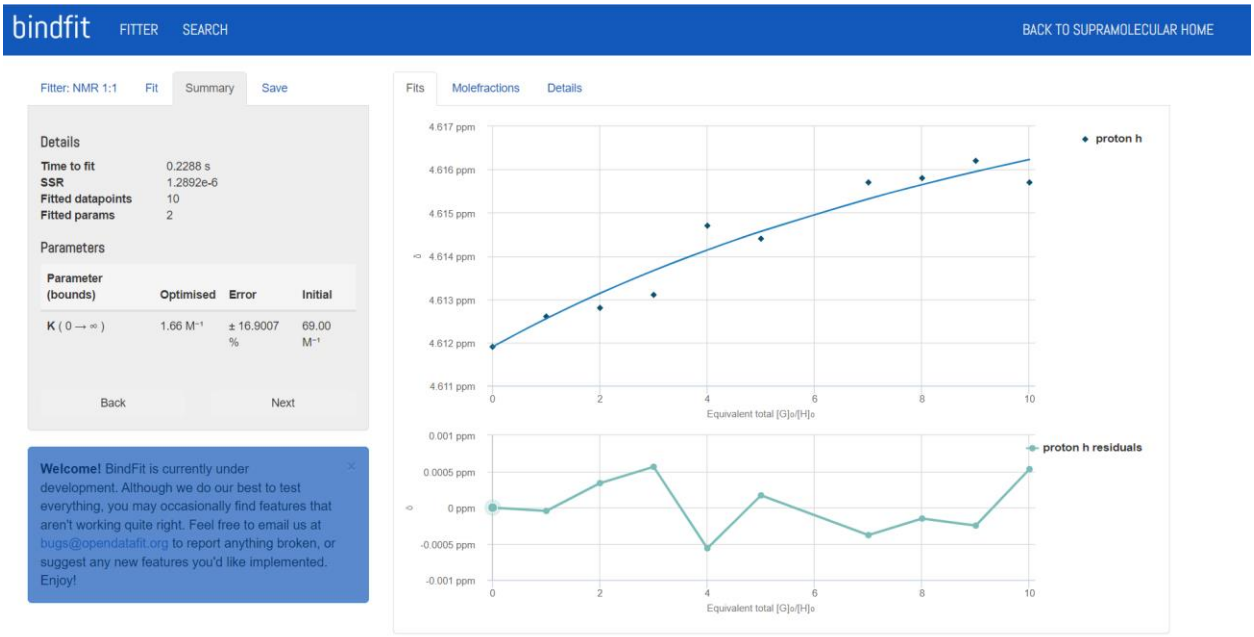


Figure S9. The curve fitting of the ^{1}H NMR titration data by Bindfit program, available online (http://supramolecular.org/); fitting output from Bindfit.

6. Quantum yield determination

According to the procedure of Xu[7]: 3 To an oven-dried 10 mL glass tube sealed with rubber septum. **1** (0.2 mmol), $CHCl_3$ (0.2 mL), catalyst (20 mol%) and additive (0.6 mmol) were combined in CH_3CN (0.5 mL) under N_2 atmosphere. The reaction mixture was stirred and irradiated (λ = 450 nm, PLS-LED100C) for 20 min. After irradiation, the solution was measured the unit area photon flux (MQ-500 photosynthetic active radiation meter). And the yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. The quantum yield is calculated using the following equation:

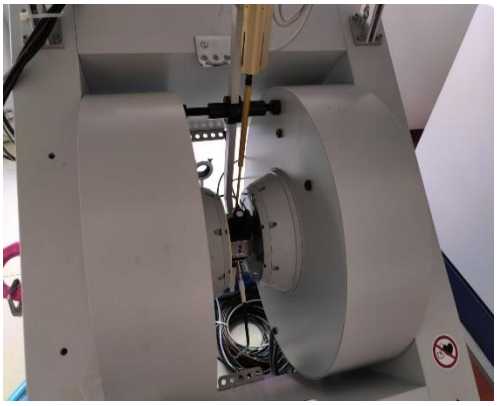
$$\phi = \frac{mol\ product}{flus \cdot S \cdot t}$$

Where, Φ is quantum yield, S (m^2) is the irradiation area and t (s) is the photoreaction time. Experiment: the unit photon flux was 310 μmol·s^{-1}·m^{-2}(average of three experiments), the irradiation area was 1.4×10^{-4} m^2, and the product yield was 14% after 20 min (1200 s).

Quantum yield calculation:

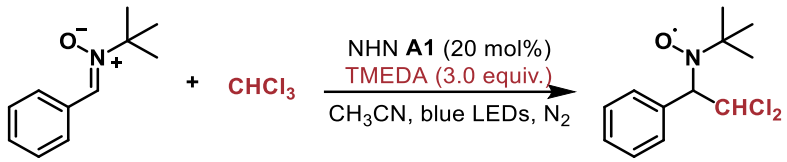
$$\phi = \frac{mol\ product}{flux \cdot S \cdot t} = \frac{0.14 \times 0.2 \times 10^{3}}{310 \times 1.4 \times 10^{-4} \times 1200} = 0.55$$

7. EPR Spectroscopy Experiments



Continuous-wave (CW) electron paramagnetic resonance (EPR) measurements were performed on acetonitrile solution in capillary tubes at ambient temperature with a Bruker EMXplus spectrometer at microwave frequencies of about 9.85 GHz. A Bruker super-high Q resonator (ER 4119HS) with slits in the cavity wall for optical excitation was used. As a light source, a 100 W blue LED (λ = 450 nm, PLS-LED100C) was placed outside the magnet 40 cm from the cavity wall. CW EPR spectra were measured with a microwave power of 2.518 mW and a modulation amplitude of 0.1 mT in order to avoid line broadening by saturation or overmodulation.

Characterization of the $CHCl_2$ radical



In a nitrogen-filled glove box, NHN **A1** (0.02 mmol, 5.3 mg, 20 mol%), TMEDA (0.3 mmol, 45 μL), PBN (0.3 mmol, 53.2mg) in dry CH_3CN (0.25 mL) and chloroform (0.1 mL). The solution was added to 3 mm EPR tube and sealed. The EPR tube was measured under blue light irradiation (λ = 450 nm). Upon irradiation, there was an immediate observation of the spin-trapped $CHCl_2$ radical adduct. Upon cessation of irradiation, the EPR signal vanished.

The hyperfine couplings of the PBN radical adduct are ^{α}N = 1.468 mT and ^{α}H = 0.221 mT (Figure S10a). After the light was switched off, a weak signal was still detectable in the first scan, but not thereafter. The simulated hyperfine coupling is consistent with the known report.[8]

When TMEDA was not added, the spin-trapped $CHCl_2$ radical adduct was not observed (Figure S10b).

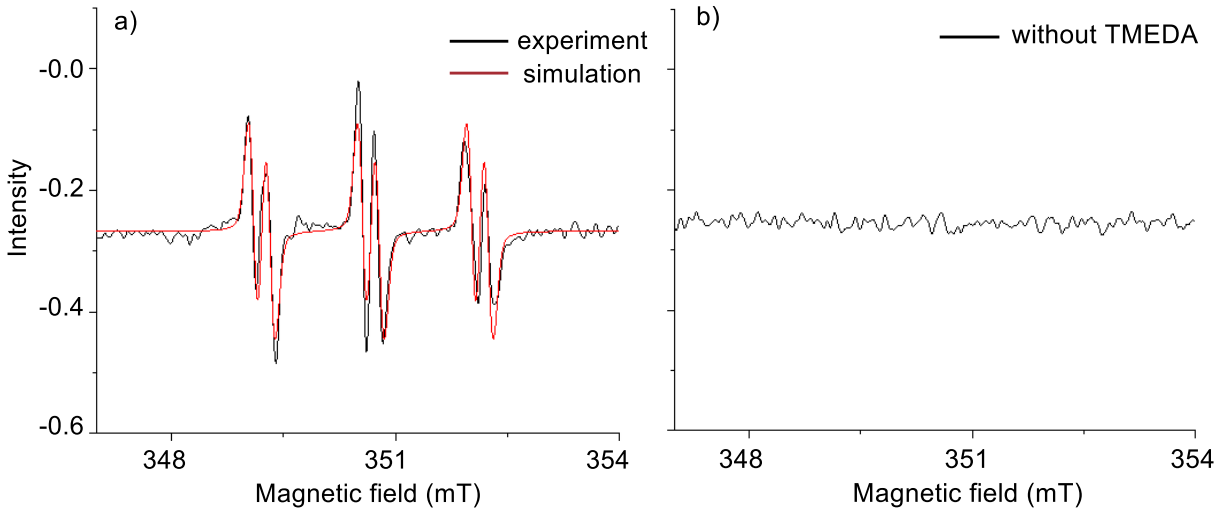
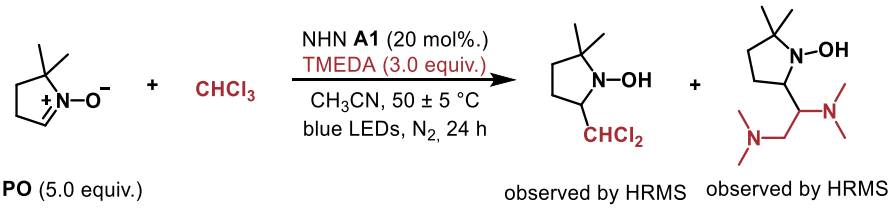
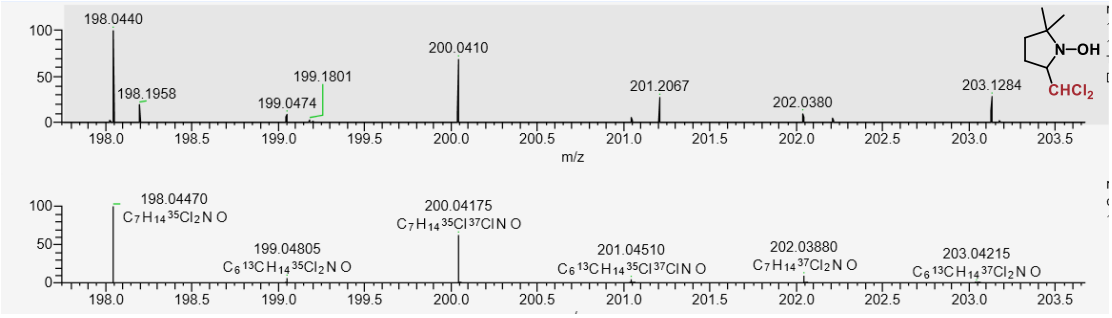


Figure S10. a) EPR spectrum of the PBN radical adduct. The hyperfine couplings are $^{\alpha}N$ = 1.468 mT for the nitroxide nitrogen, $^{\alpha}H$ = 0.221 mT for the hydrogen bound to the C atom. b) EPR spectrum of the PBN radical adduct without TMEDA.

8. Radical Trapping Experiments



The NHN **A1** (0.06 mmol, 16.5 mg, 20 mol%), TMEDA (0.3 mmol, 69.7 mg, 90 μL), DMPO (0.5 mmol, 56.6mg) were added sequentially into a 10 mL dry tube under nitrogen, then CH_3CN (0.5 mL) and chloroform (0.2 mL) was added by syringe. After degas, the resulting mixture was allowed to stir under blue LED irradiation for 24h as monitored by TLC, where the distance from the light source to the irradiation vessel is 2 cm to keep the reaction temperature with 50 ± 5 °C. Upon completion, the products of $CHCl_2$ and α-aminoalkyl radical trapped by DMPO are detected by HRMS.



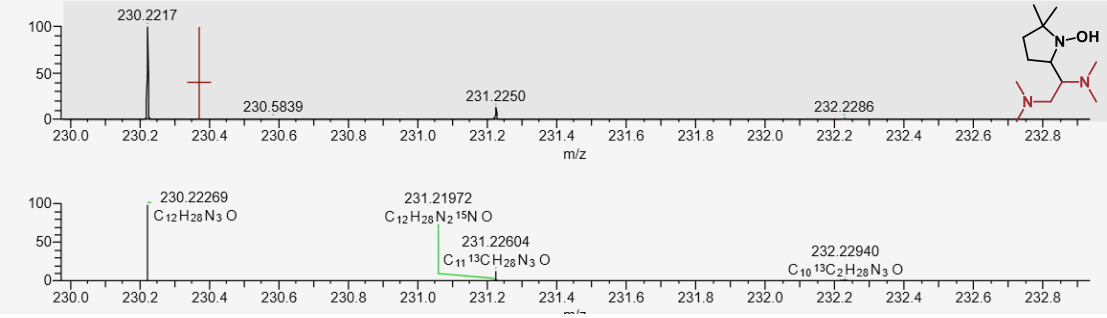
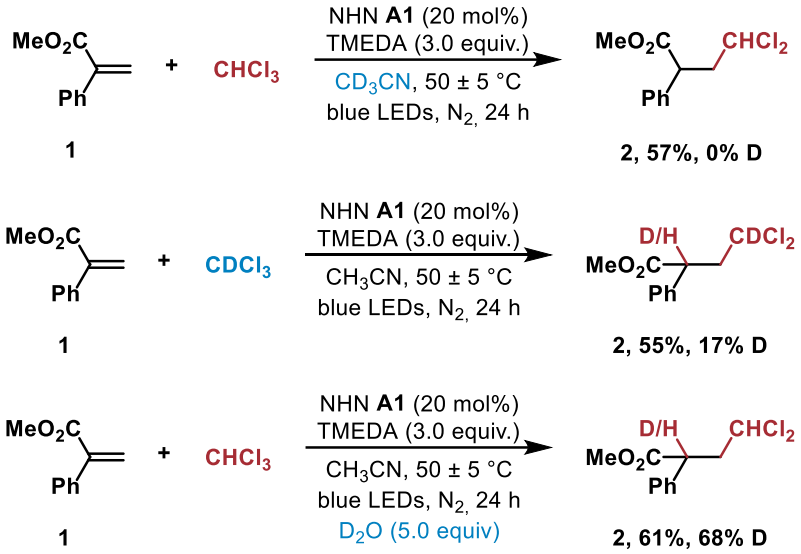


Figure S11. The HRMS results for $CHCl_2$ and α-aminoalkyl radical trapped by DMPO.

9. Deuterium incorporation experiments.



Following the general procedure A, the reaction was performed using CD_3CN instead of CH_3CN or $CDCl_3$ instead of $CHCl_3$ or adding 5.0 equiv. of D_2O.

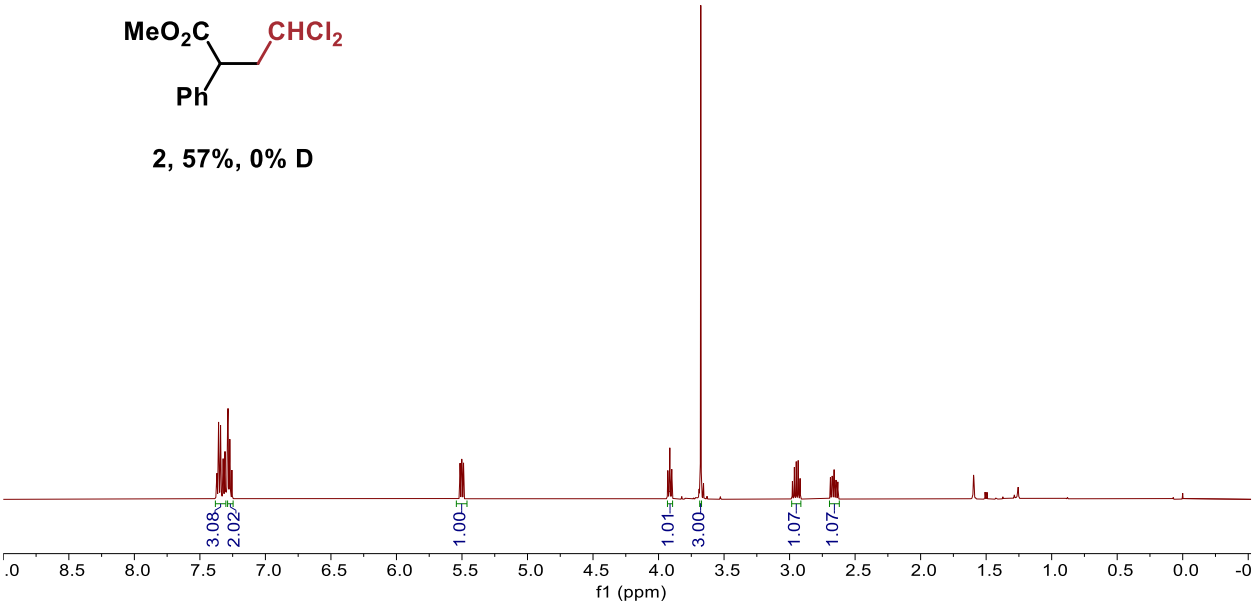


Figure S12. ^{1}H NMR spectrum of **2** using CD_3CN.

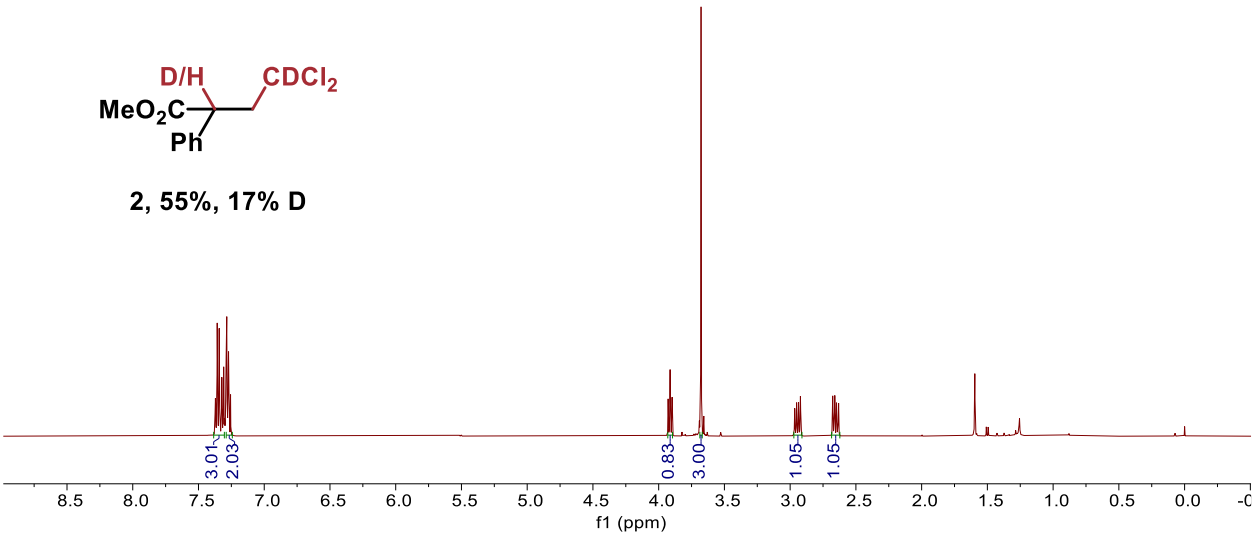


Figure S13. ^{1}H NMR spectrum of **2** using $CDCl_3$.

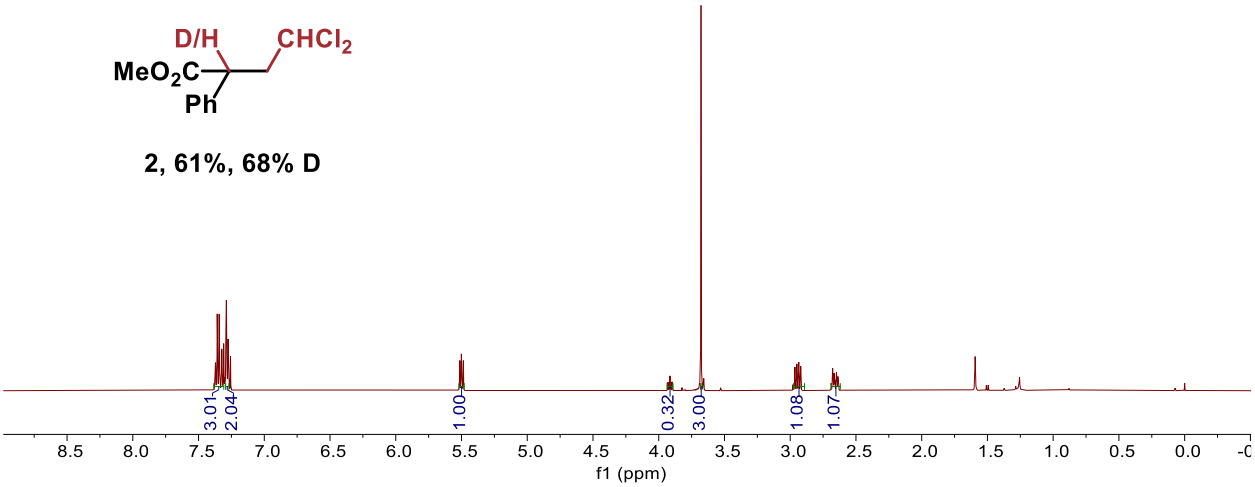


Figure S14. ^{1}H NMR spectrum of **2** with addition of D_2O.

10. Cyclic Voltammetry Analysis

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated Ag/AgCl reference electrode, Pt wire auxiliary electrode. All solutions used for the voltammetric experiments were performed in a Faraday cage at room temperature (23 ± 2 °C).

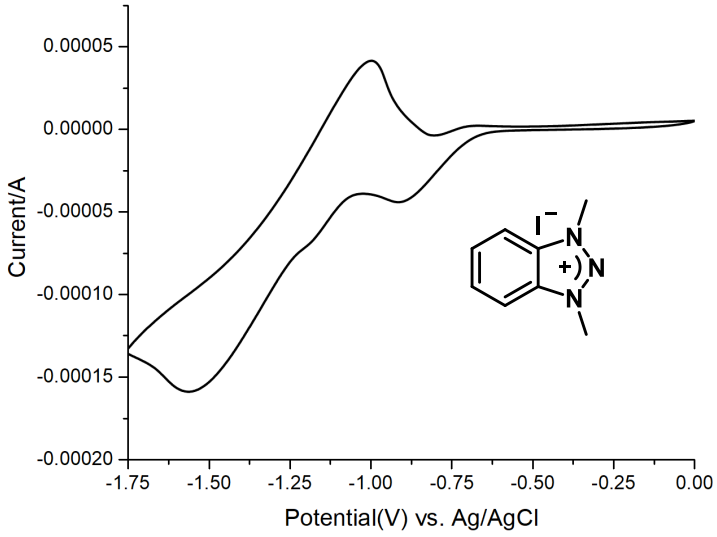


Figure S15. Cyclic voltammograms of NHN **A1** in CH_3CN (5.0 mM). Scan rate: 0.04 V/s. E^{red} = -1.56 V.

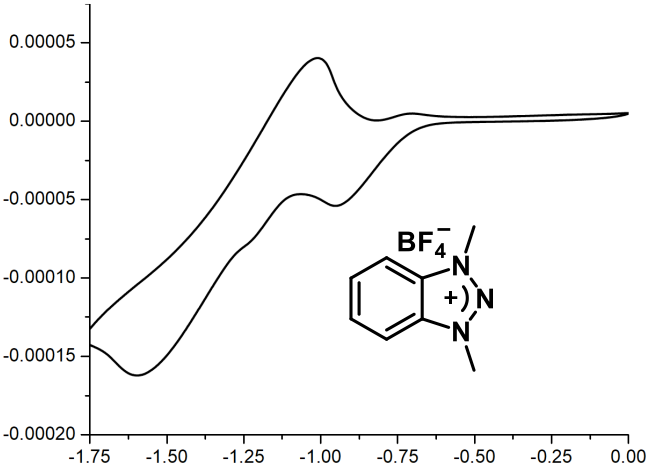


Figure S16. Cyclic voltammograms of NHN **A2** in CH_3CN (5.0 mM). Scan rate: 0.04 V/s. E^{red} = -1.56 V.

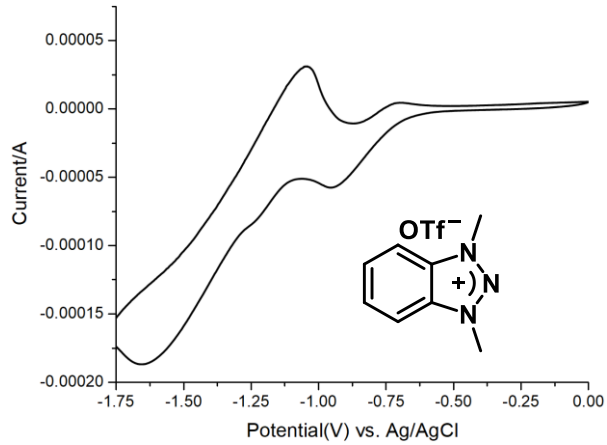


Figure S17. Cyclic voltammograms of NHN **A3** in CH_3CN (5.0 mM). Scan rate: 0.04 V/s. E^{red} = -1.56 V.

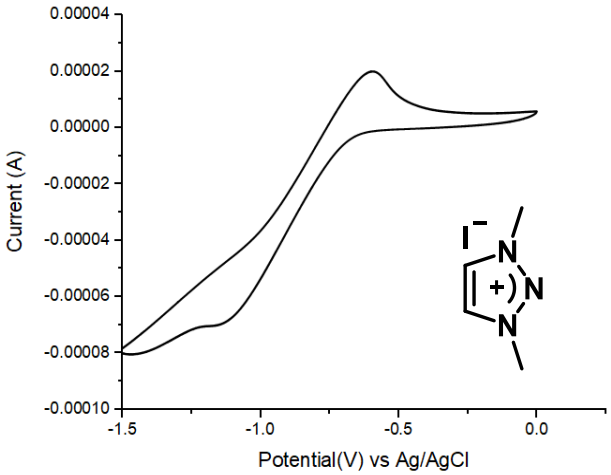


Figure S18. Cyclic voltammograms of NHN **C** in CH_3CN (5.0 mM). Scan rate: 0.04 V/s. E^{red} = -1.10 V.

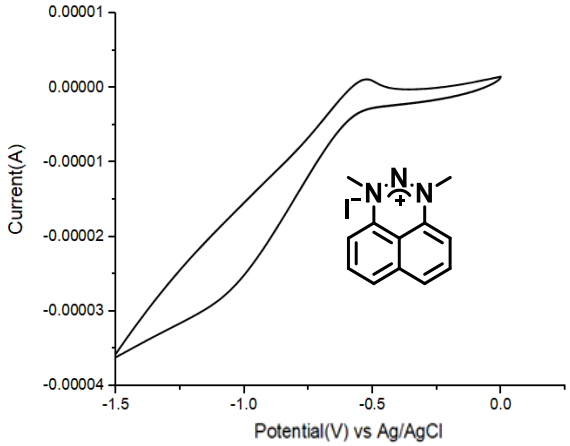


Figure S19. Cyclic voltammograms of NHN **D** in CH_3CN (5.0 mM). Scan rate: 0.04 V/s. E^{red} = -1.05 V.

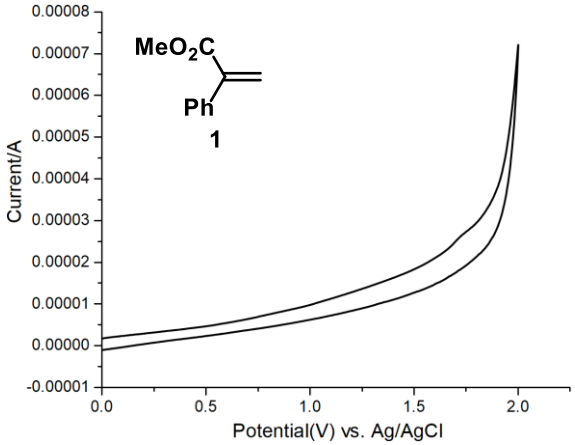


Figure S20. Cyclic voltammograms of **1** in CH_3CN (5.0 mM) containing 0.10M $TBAPF_6$ as supporting electrolyte. Scan rate: 0.04 V/s. E^{ox} = +1.75V.

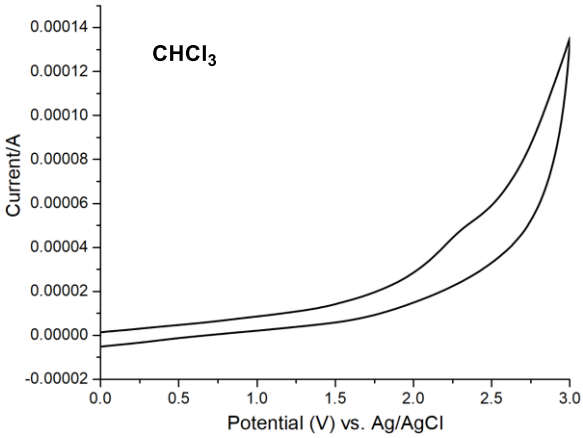


Figure S21. Cyclic voltammograms of $CHCl_3$ in CH_3CN (5.0 mM) containing 0.10M $TBAPF_6$ as supporting electrolyte. Scan rate: 0.04 V/s. E^{ox} = +2.25V.

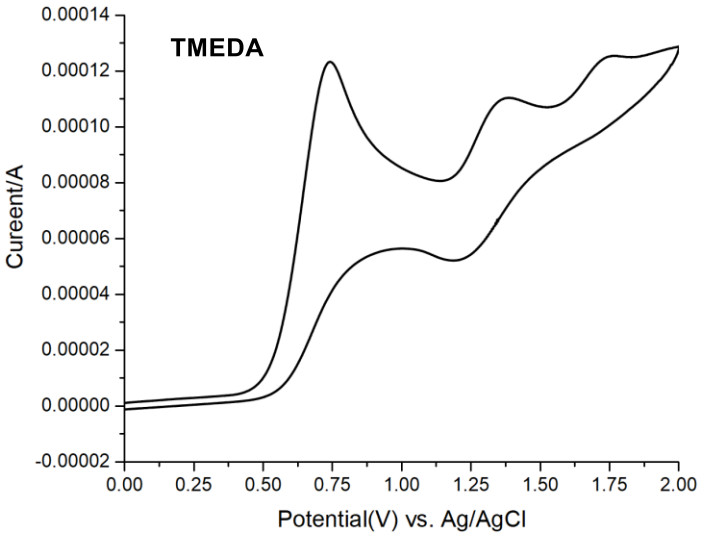


Figure S22. Cyclic voltammograms of TMEDA in CH_3CN (5.0 mM) containing 0.10M $TBAPF_6$ as supporting electrolyte. Scan rate: 0.04 V/s. E^{ox} = +0.75V.

11. Evaluation of Excited State Potential and Lifetime of the Photocatalyst

Fluorescence spectra were recorded on a Edingburg FS5 Fluorescent Spectrophotometer. The samples NHN **A1-A3** were prepared as a 0.01 mM solution in CH_3CN and used freshly for the measurement.

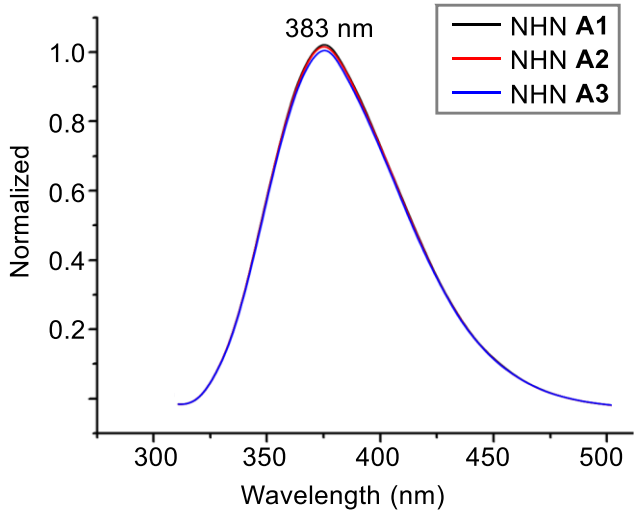


Figure S23. Fluorescence emission spectra of NHN **A1-A3** (excited at 300 nm). The $\lambda_{max,em}$ was estimated to be 383 nm. The $\lambda_{offset,em}$ was estimated to be 500 nm.

Remarks: Using, $\lambda_{max,em}$, $\lambda_{offset,em}$ and E^{red}, the excited state reduction potential was determined for E^*(**A1***/**A1**$^{\cdot-}$) according to the following equations: E^*(**A1***/**A1**$^{\cdot-}$) = E^{red} + $E^{0,0}$, where $E^{0,0} = hc/\lambda$ = 1240 nm/λ.

E^*(**A1***/**A1**$^{\cdot-}$) = 0.92 – 1.68V.

Estimating lifetime of excited state of the photocatalysts was based on the ultrafast transient absorption spectroscopic techniques. The luminescence decays were measured on an Edingburg FLS980 spectrometer. The sample compartment was home-built and designed as 10x10 mm cuvettes in 90° geometry between excitation and detection. The solution of NHN **A1** in CH_3CN (0.01 mM) was excited at 280 nm. All decay traces were fitted by iterative reconvolution with an experimental instrument response function recorded directly after decay acquisition.

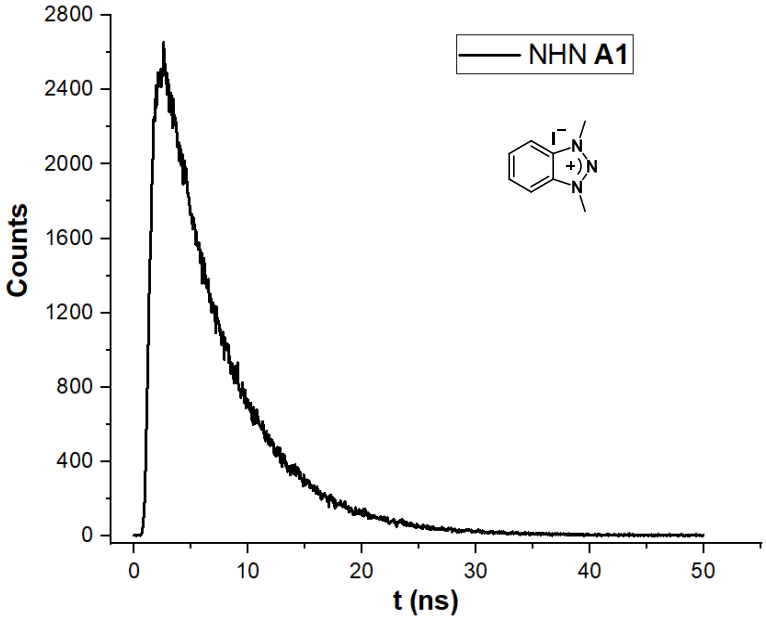


Figure S24. Luminescence decays of NHN **A1** in CH_3CN detected at 25 °C after excitation at 280 nm. τ = 5.65 ns.

12. Stern-Volmer Luminescence Quenching Studies

Luminescence intensities were recorded using an Edinburgh Instruments FS5 spectrofluorometer. All luminescence measurements were recorded using a screw-top quartz cuvette (fluorescence quartz cuvette, 10 x 10 mm, 3.5 mL).

Quenching was analyzed by plotting I_0/I according to the Stern-Volmer relationship:

$I_0/I = k_q\tau_0[Q]+1$ where I_0 represents the integral of the luminescence over the range of 310 to 500 nm in the absence of a quencher, I is the integral of luminescence over the range of 310 to 500 nm in the presence of a quencher, k_q represents the quenching rate constant, [Q] is the concentration of a given quencher.

NHN **A1**	**Quencher**	**Ratio (A1 : Q)**
0.00001M	**0.001M**	**1 : 100**
	0.002M	**1 : 200**
	0.003M	**1 : 300**
	0.004M	**1 : 400**

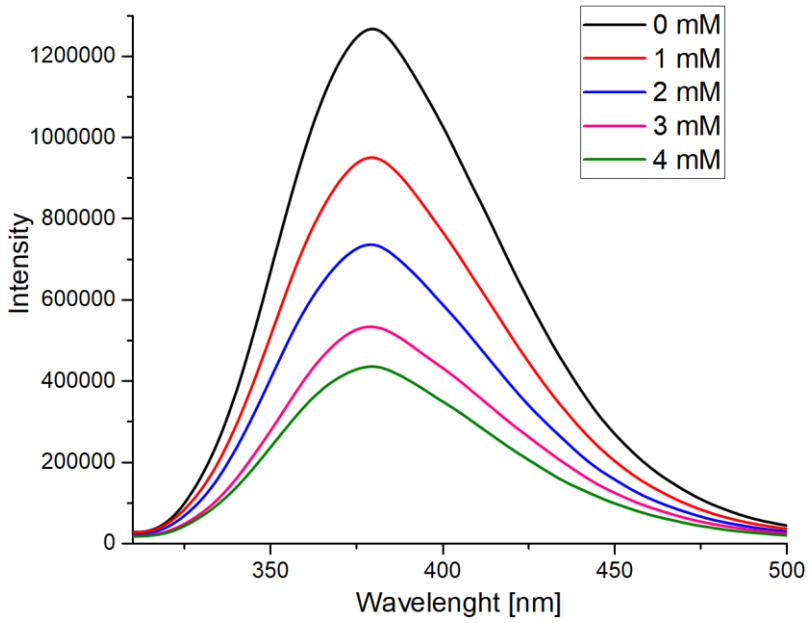


Figure S25. Fluorescence emission spectrum of NHN **A1** at different concentrations of NaI.

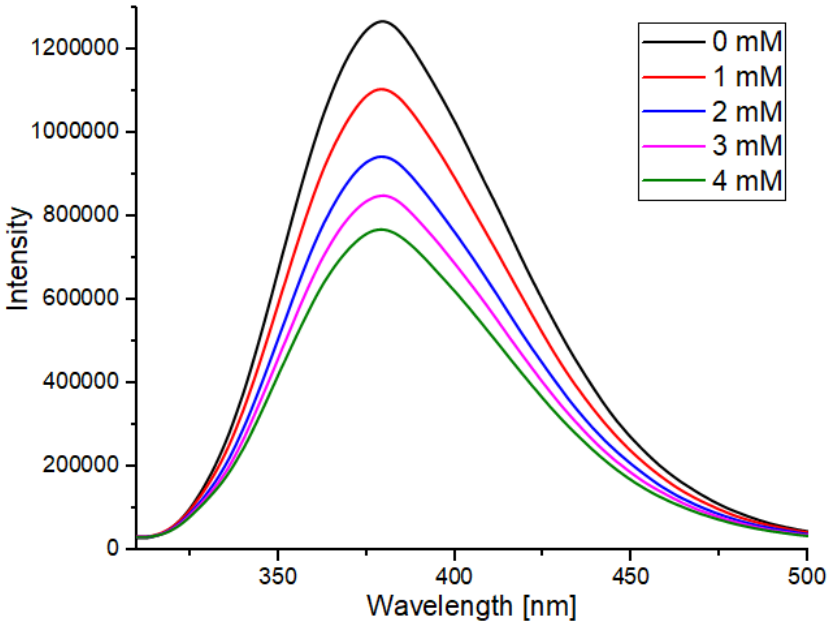


Figure S26. Fluorescence emission spectrum of NHN **A1** at different concentrations of TMEDA.

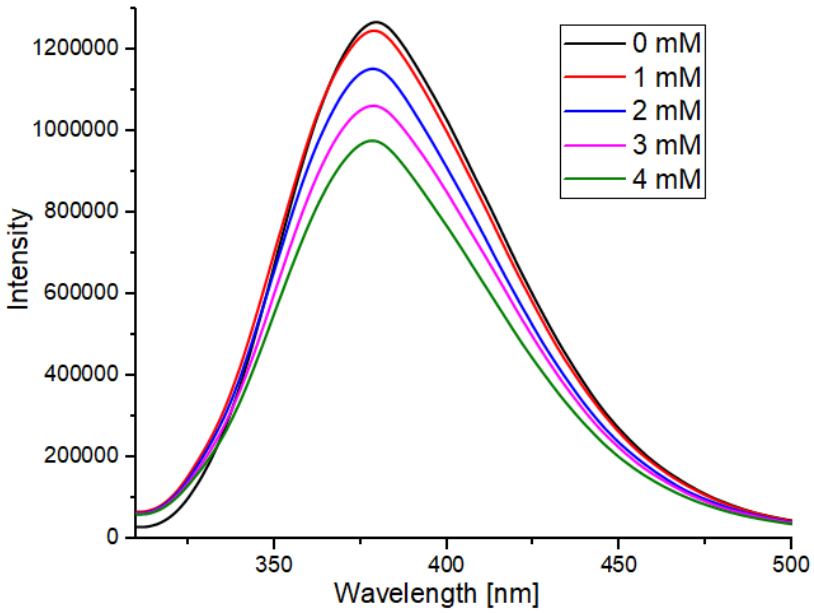


Figure S27. Fluorescence emission spectrum of NHN **A1** at different concentrations of substrate **1**.

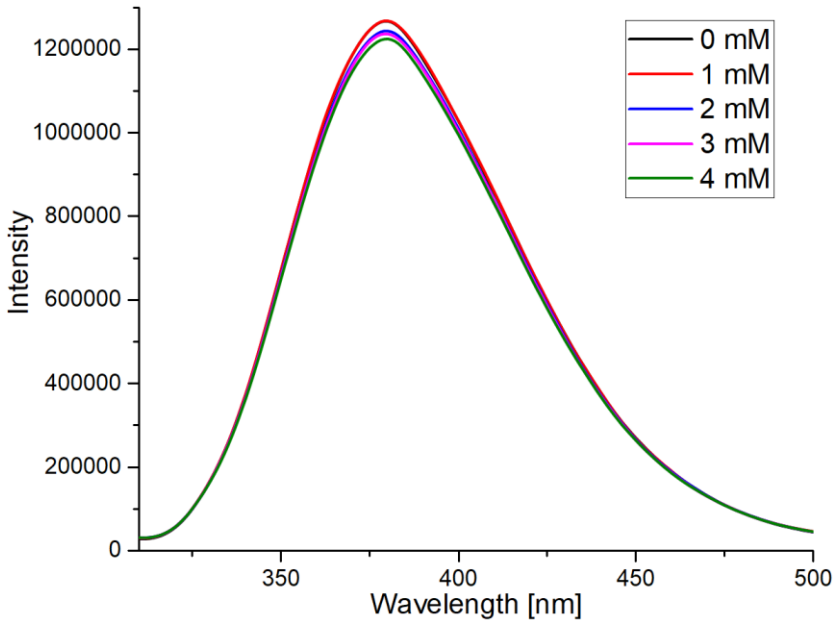


Figure S28. Fluorescence emission spectrum of NHN **A1** at different concentrations of $CHCl_3$.

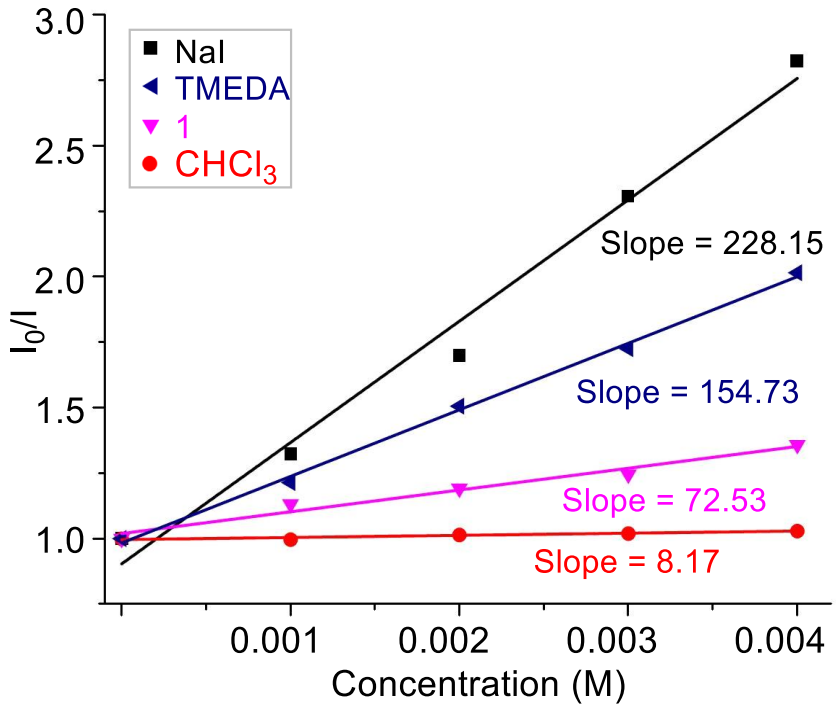
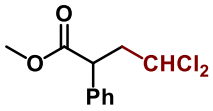


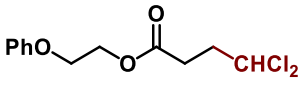
Figure S29. Stern-Volmer plot.

13. Compound Characterization Data



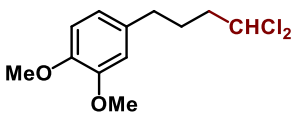
2

methyl 4,4-dichloro-2-phenylbutanoate (2) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a yellow oil (30.5 mg, 0.124 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.50 (dd, *J* = 7.6, 5.8 Hz, 1H), 3.91 (t, *J* = 7.6 Hz, 1H), 3.68 (s, 3H), 2.95 (ddd, *J* = 14.7, 7.6, 7.6 Hz, 1H), 2.66 (ddd, *J* = 14.7, 7.6, 5.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.0, 136.8, 129.3, 128.2, 128.0, 71.3, 52.6, 48.7, 46.6. **IR** (ATR): 2957, 1732, 1435, 1163, 782, 753, 699, 651 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+H]^+$ calcd for $C_{11}H_{13}O_2Cl_2^+$: 247.0287; found 247.0279.



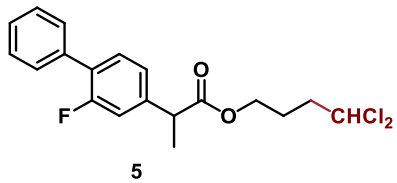
3

2-phenoxyethyl 4,4-dichlorobutanoate (3) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a brown oil (27.6 mg, 0.100 mmol, 50%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.01 – 6.95 (m, 1H), 6.95 – 6.88 (m, 2H), 5.92 (t, *J* = 5.8 Hz, 1H), 4.53 – 4.39 (m, 2H), 4.25 – 4.10 (m, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.58 – 2.43 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ172.0, 158.5, 129.7, 121.4, 114.7, 72.3, 65.8, 63.4, 38.4, 30.3. **IR** (ATR): 2923, 1735, 1599, 1497, 1244, 1171, 1087, 755, 692 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{12}H_{15}O_3Cl_2^+$: 277.0393; found 277.0397.



4

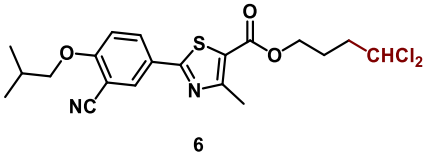
4-(4,4-dichlorobutyl)-1,2-dimethoxybenzene (4) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a colorless oil (21.0 mg, 0.080 mmol, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.76 – 6.64 (m, 2H), 5.75 (t, *J* = 6.1 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.28 – 2.14 (m, 2H), 1.94 – 1.76 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.0, 147.5, 133.9, 120.3, 111.6, 111.3, 73.6, 56.0, 56.0, 43.0, 34.4, 27.8. **IR** (ATR): 2935, 2850, 1515, 1464, 1262, 1236, 1139, 1028, 735 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{12}H_{17}O_2Cl_2^+$: 263.0600; found 263.0603.



5

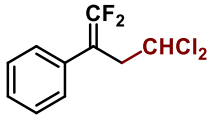
4,4-dichlorobutyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (5) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a colorless oil (31.7 mg, 0.086 mmol, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.34 (m, 6H), 7.16 - 7.10 (m, 2H), 5.70 (t, *J* = 5.9 Hz, 1H), 4.21 – 4.11 (m, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 2.19 – 2.14 (m, 2H), 1.93 – 1.82 (m, 2H), 1.55 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.0, 159.8 (d, *J* = 249.1), 141.7 (d, *J* = 7.6), 135.6, 131.1 (d, *J* = 4.2), 129.1 (d, *J* = 2.9), 128.6, 128.1 (d, *J* = 13.6), 127.8, 123.6 (d, *J* = 3.3), 115.3 (d, *J* = 23.7), 72.9, 63.7, 45.1, 40.2, 25.1, 18.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.35

- -117.31 (m, 1F). **IR** (ATR): 2921, 1732, 1484, 1418, 1265, 1173, 766, 734, 698 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M-H]^-$ calcd for $C_{19}H_{18}O_2Cl_2F^-$: 367.0673; found 367.0674.



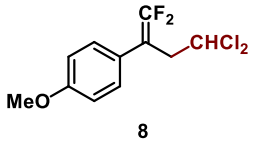
6

4,4-dichlorobutyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (6) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a white solid (39.6 mg, 0.090 mmol, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.3 Hz, 1H), 8.10 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 5.87 (t, *J* = 5.8 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 3H), 2.43 – 2.33 (m, 2H), 2.26 – 2.16 (m, 1H), 2.13 – 2.00 (m, 2H), 1.10 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 162.7, 162.0, 161.7, 132.7, 132.3, 125.9, 121.4, 115.5, 112.7, 103.1, 72.9, 64.1, 40.3, 28.3, 25.3, 19.2, 17.7. **IR** (ATR): 2923, 1712, 1606, 1509, 1261, 1106, 1012, 736 cm^{-1}**. HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{20}H_{23}O_3N_2Cl_2S^+$: 441.0801; found 441.0802. **Melting Point** (Experimental): 100 – 102 °C



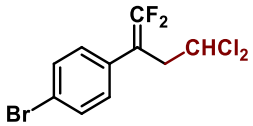
7

(4,4-dichloro-1,1-difluorobut-1-en-2-yl)benzene (7) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a colorless oil (22.7 mg, 0.096mmol, 48%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.27 (m, 5H), 5.51 (t, *J* = 6.8 Hz, 1H), 3.29 (dt, *J* = 6.8, 2.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (t, *J* = 292.9 Hz), 131.6 (t, *J* = 3.4 Hz), 129.0, 128.5(t, *J* = 3.0 Hz), 128.3, 89.0 (dd, *J* = 20.5 Hz, 18.8 Hz), 70.5 (t, *J* = 4.8 Hz), 42.4 (d, *J* = 2.6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -87.7 (d, *J* = 34.8 Hz, 1F), -88.4 (d, *J* = 34.8 Hz, 1F). **IR (ATR)**: 2923, 1737, 1247, 1125, 985, 794, 757, 714, 697 cm^{-1}. **HRMS (ESI):** *m/z* $[M+K]^+$ calcd for $C_{10}H_8F_2Cl_3K^+$: 274.9603; found 274.9608.



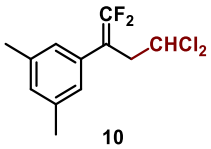
8

1-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)-4-methoxybenzene (8) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a yellow oil (36.9 mg, 0.138 mmol, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 6.94 – 6.87 (m, 2H), 5.51 (t, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 3.25 (dt, *J* = 6.8, 2.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 155.1 (t, *J* = 363.8 Hz), 129.7 (t, *J* = 3.2 Hz), 123.6 (t, *J* = 3.5 Hz), 114.5, 88.5 (dd, *J* = 20.9 Hz, 19.1 Hz), 70.6 (t, *J* = 4.5 Hz), 55.43, 42.6 (d, *J* = 2.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -88.6 (d, *J* = 36.2 Hz, 1F), -89.3 (d, *J* = 36.2 Hz, 1F). **IR** (ATR): 2915, 1732, 1611, 1513, 1242, 1179, 983, 832, 684 cm^{-1}**. HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{11}H_{11}OCl_2F_2^+$: 267.0149; found 267.0152.



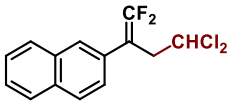
9

1-bromo-4-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)benzene (9) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a colorless oil (31.4 mg, 0.100 mmol, 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 2H), 7.22 – 7.14 (m, 2H), 5.51 (t, *J* = 6.8 Hz, 1H), 3.26 (dt, *J* = 6.8, 2.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2 (t, *J* = 292.8 Hz), 132.2, 130.6 (t, *J* = 3.4 Hz), 130.1 (t, *J* = 3.1 Hz), 122.40, 88.3 (dd, *J* = 21.1 Hz, 18.2 Hz), 70.3 (t, *J* = 4.1 Hz), 42.2 (d, *J* = 2.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -86.5 (d, *J* = 31.2 Hz, 1F), -87.4 (d, *J* = 31.2 Hz, 1F). **IR** (ATR): 2915, 1728, 1489, 1316, 1249, 983, 828, 729, 583 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+OH]^-$ calcd for $C_{10}H_8BrF_2Cl_2O^-$: 330.9109; found 330.9126.



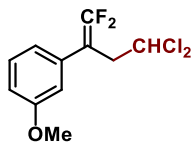
10

1-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)-3,5-dimethylbenzene (10) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 100:1) as a colorless oil (27.6 mg, 0.104 mmol, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.82 (s, 2H), 5.42 (t, *J* = 6.8 Hz, 1H), 3.17 (dt, *J* = 6.8, 2.1 Hz, 2H), 2.25 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2 (t, *J* = 291.3 Hz), 138.6, 131.4 (t, *J* = 3.3 Hz), 130.0, 126.3 (t, *J* = 3.0 Hz), 89.0 (t, *J* = 19.5 Hz), 70.6 (t, *J* = 4.7 Hz), 42.6 (d, *J* = 2.5 Hz), 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.3 (d, *J* = 34.4 Hz, 1F), -88.6 (d, *J* = 33.8 Hz, 1F). **IR** (ATR): 2957, 1737, 1604, 1261, 1213, 1126, 765, 704, 672 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{12}H_{13}F_2Cl_2^+$: 265.0368; found 265.0370.



11

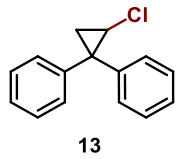
2-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)naphthalene (11) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 100:1) as a colorless oil (32.2 mg, 0.112 mmol, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 4H), 7.56 – 7.48 (m, 2H), 7.42 - 7.39 (m, 1H), 5.53 (t, *J* = 6.8 Hz, 1H), 3.38 (dt, *J* = 6.9, 2.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.5 (t, *J* = 293.2 Hz), 133.3, 132.9, 128.9 (t, *J* = 3.3 Hz), 128.8, 128.1, 127.9 (t, *J* = 2.7Hz), 127.8, 126.8, 125.9 (t, *J* = 2.9 Hz), 89.1 (dd, *J* = 20.8 Hz, 18.3 Hz), 70.6 (t, *J* = 4.2 Hz), 42.5 (d, *J* = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.2 (d, *J* = 30.4 Hz, 1F), -88.1 (d, *J* = 30.4 Hz, 1F). **IR** (ATR): 3070, 2953, 1728, 1253, 1230, 1111, 817, 746, 686, 476 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{14}H_{10}F_2Cl_2Na^+$: 309.0020; found 309.0018.



12

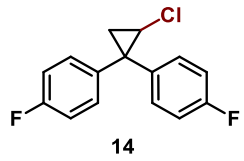
1-(4,4-dichloro-1,1-difluorobut-1-en-2-yl)-3-methoxybenzene (12) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 100:1) as a yellow oil (32.6 mg, 0.122 mmol, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 6.90 – 6.82 (m, 3H), 5.52 (t, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 3.26 (dt, *J* = 6.8, 2.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 155.2 (t, *J* = 292.5 Hz), 132.9 (t, *J* = 2.9 Hz), 130.1, 120.8 (t, *J* = 2.8 Hz), 114.6 (t, *J* = 3.2 Hz), 113.4, 88.9 (dd, *J* = 20.6 Hz, 19.1 Hz), 70.5(t, *J* = 4.4 Hz), 55.4, 42.4 (d, *J* = 2.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.5 (d, *J* = 33.5 Hz, 1F), -87.8 (d, *J* = 33.5 Hz,

1F). **IR** (ATR): 2937, 2851, 1735, 1580, 1255, 1223, 785, 703, 671 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{11}H_{11}OCl_2F_2^+$: 267.0149; found 267.0152.



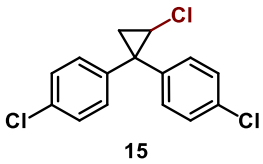
13

(2-chlorocyclopropane-1,1-diyl)dibenzene (13) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (39.8 mg, 0.174 mmol, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.19 (m, 6H), 3.73 (dd, *J* = 7.5, 4.6 Hz, 1H), 1.83 – 1.69 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 139.7, 130.7, 128.7, 128.4, 127.8, 127.2, 126.8, 39.5, 37.0, 23.8. **IR** (ATR): 3027, 2925, 1600, 1495, 1446, 758, 695, 610, 546 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}Cl^+$: 229.0778; found 229.0781.



14

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(fluorobenzene) (14) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (42.2 mg, 0.160 mmol, 80%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.20 – 7.14 (m, 2H), 7.06 – 6.99 (m, 2H), 6.97 – 6.91 (m, 2H), 3.67 (dd, *J* = 7.7, 4.5 Hz, 1H), 1.74 (dd, *J* = 7.7, 6.5 Hz, 1H), 1.69 (dd, *J* = 6.5, 4.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.7 Hz), 161.7 (d, *J* = 246.6 Hz), 139.9 (d, *J* = 3.3 Hz), 135.5 (d, *J* = 3.2 Hz), 132.1 (d, *J* = 8.0 Hz), 129.4 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 27.7 Hz), 115.4 (d, *J* = 27.4 Hz), 39.4, 35.8, 24.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.01 (t, *J* = 6.6 Hz), -115.46 (t, *J* = 6.6 Hz). **IR** (ATR): 3042, 1603, 1506, 1218, 1157, 825, 579, 549 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}F_2Cl^+$: 265.0590; found 265.0593.

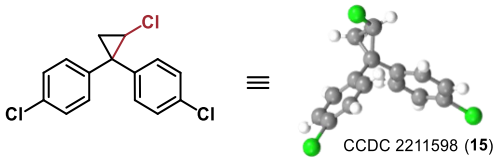


15

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(chlorobenzene) (15) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a white solid (50.6 mg, 0.170 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.26 – 7.20 (m, 2H), 7.16 – 7.10 (m, 2H), 3.68 (dd, *J* = 7.6, 4.6 Hz, 1H), 1.75 (dd, *J* = 7.6, 6.5 Hz, 1H), 1.71 (dd, *J* = 6.5, 4.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.3, 137.9, 133.4, 132.9, 131.9, 129.1, 129.0, 128.8, 39.2, 36.0, 24.0. **IR** (ATR): 3025, 2923, 1491, 1090, 1011, 807, 634, 645, 502 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}Cl_3^+$: 296.9999; found 297.0007.

The crystal suitable for X-ray analysis was prepared by slow evaporation of the solvent of the solution of **15** in PE about -8 ℃.

The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition numbers CCDC 2211598.



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2_pl

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2_pl

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Bond precision:   C-C = 0.0066 A          Wavelength=0.71073

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                  alpha=90        beta=108.793(3)     gamma=90
Temperature:      150 K

                 Calculated                  Reported
Volume           2733.0(4)                   2733.0(4)
Space group      C c                         C 1 c 1
Hall group       C -2yc                      C -2yc
Moiety formula   C15 H11 Cl3                 2(C15 H11 Cl3)
Sum formula      C15 H11 Cl3                 C30 H22 Cl6
Mr               297.59                      595.17
Dx,g cm-3        1.446                       1.446
Z                8                           4
Mu (mm-1)        0.648                       0.648
F000             1216.0                      1216.0
F000'            1219.88
h,k,lmax         12,23,18                    12,23,18
Nref             5379[ 2695]                 5277
Tmin,Tmax        0.907,0.937                 0.604,0.745
Tmin'            0.907

Correction method= # Reported T Limits: Tmin=0.604 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.96/0.98        Theta(max)= 25.986

R(reflections)= 0.0411( 4959)                wR2(reflections)=
                                             0.1022( 5277)
S = 1.120                  Npar= 326
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00659 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
            C15 H11 C13
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        15 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....          7 Note
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Alert level G

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PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...          2 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
            C15 H11 C13
PLAT792_ALERT_1_G Model has Chirality at C13         (Polar  SPGR)          R Verify
PLAT792_ALERT_1_G Model has Chirality at C27         (Polar  SPGR)          R Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

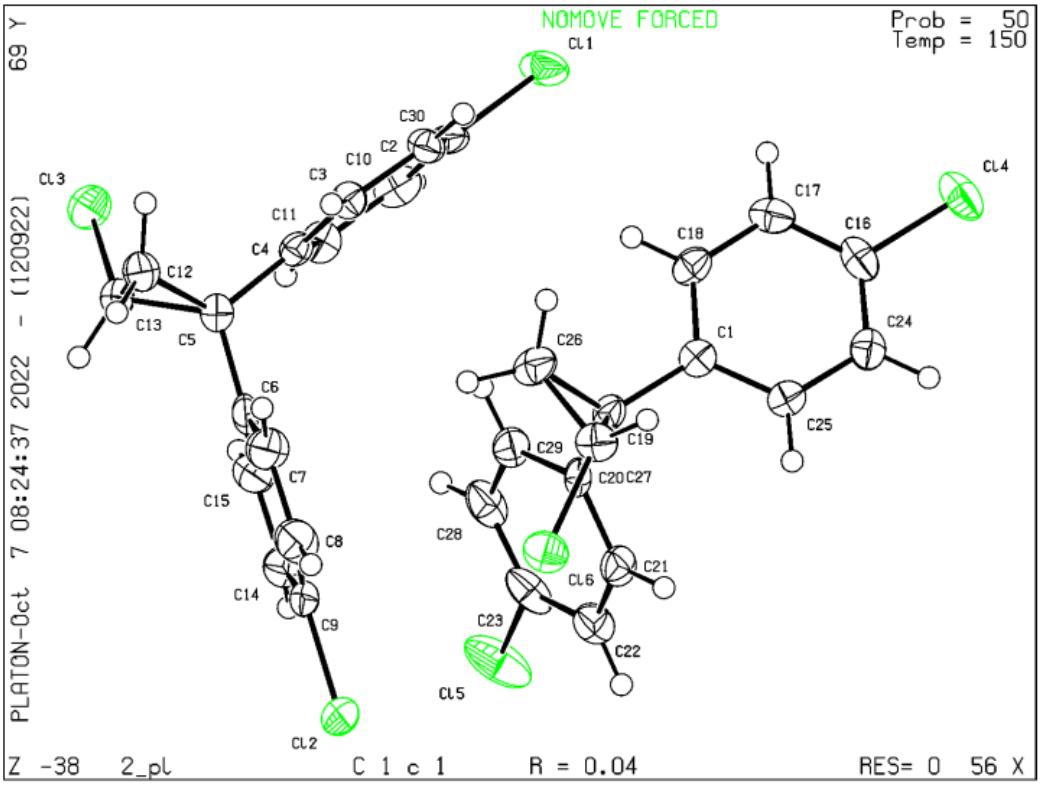
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

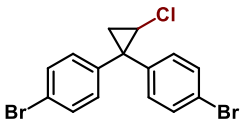
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 12/09/2022; check.def file version of 09/08/2022

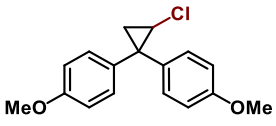
Datablock 2_pl - ellipsoid plot





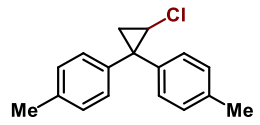
16

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(bromobenzene) (16) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a white solid (48.7 mg, 0.126 mmol, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.27 – 7.22 (m, 2H), 7.09 – 7.04 (m, 2H), 3.67 (dd, *J* = 7.6, 4.6 Hz, 1H), 1.83 – 1.65 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 138.3, 132.3, 131.9, 131.7, 129.5, 121.6, 121.0, 39.1, 36.1, 23.9. **IR** (ATR): 3083, 2925, 1600, 1495, 1446, 758, 695, 610, 546 cm^{-1}. **Elem. Anal.** calcd for $C_{15}H_{11}Br_2Cl$ (386.51): C, 46.61; H, 2.87. found C, 46.64; H, 2.98.



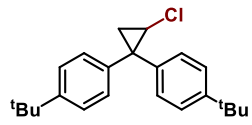
17

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(methoxybenzene) (17) Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white wax (43.9 mg, 0.152 mmol, 76%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.66 (dd, *J* = 7.6, 4.5 Hz, 1H), 1.71 (dd, *J* = 7.6, 6.3 Hz, 1H), 1.66 (dd, *J* = 6.3, 4.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.6, 158.3, 136.9, 132.4, 131.5, 128.8, 114.1, 113.8, 55.4, 55.3, 39.8, 35.7, 23.8. **IR** (ATR): 2921, 2850, 1610, 1512, 1290, 1247, 1179, 1032, 829, 558 cm^{-1} **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{17}H_{18}O_2Cl^+$: 289.0989; found 289.0991.



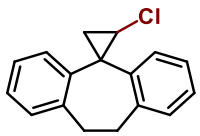
18

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(methylbenzene) (18) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (40.1 mg, 0.156 mmol, 78%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.25 (m, 2H), 7.17 – 7.02 (m, 6H), 3.69 (dd, *J* = 7.4, 4.7 Hz, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 1.74 – 1.68 (m 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 137.0, 136.8 136.4, 130.4, 129.4 129.1, 127.7 39.6, 36.4 23.7, 21.3 21.1. **IR** (ATR): 2988, 2921, 1513, 1407, 1044, 809, 727, 693, 582, 546 cm^{-1} **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{17}H_{17}ClNa^+$: 279.0911; found 279.0920.



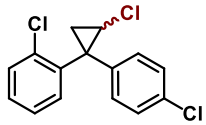
19

4,4'-(2-chlorocyclopropane-1,1-diyl)bis(tert-butylbenzene) (19) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a white solid (55.2 mg, 0.162 mmol, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 7.18 – 7.14 (m, 2H), 3.69 (dd, *J* = 7.6, 4.5 Hz, 1H), 1.79 (dd, *J* = 7.6, 6.3 Hz, 1H), 1.71 (dd, *J* = 6.3, 4.5 Hz, 1H), 1.33 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 149.5, 141.6, 136.8, 130.2, 127.4, 125.6, 125.3, 39.9, 36.2, 34.6, 34.5, 31.5, 31.4, 23.8. **IR** (ATR): 2962, 2902, 2866, 1509, 1462, 1401, 1362, 1266, 1031, 834 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{23}H_{29}ClNa^+$: 363.1850; found 363.1853. **Melting Point** (Experimental): 102 – 104 °C



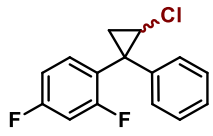
20

2-chloro-10',11'-dihydrospiro[cyclopropane-1,5'-dibenzo[a,d][7]annulene] (20) Following the general procedure B, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (38.2 mg, 0.15 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.05 (m, 8H), 3.81 – 3.62 (m, 2H), 3.31 (dd, J = 7.7, 4.3 Hz, 1H), 3.04 – 2.82 (m, 2H), 2.11 (t, J = 7.4 Hz, 1H), 1.79 (dd, J = 7.1, 4.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 140.6 (2C), 137.4, 130.2, 129.9, 128.5, 127.7, 127.5, 126.6, 126.3, 126.0, 42.0, 35.4, 32.4, 31.8, 19.5. **IR** (ATR):3063, 3018, 2932, 2897, 1487, 1446, 1305, 752, 688, 447 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{17}H_{15}ClNa^+$: 277.0755; found 230.0745.



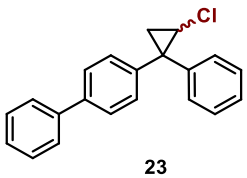
21

1-chloro-2-(2-chloro-1-(4-chlorophenyl)cyclopropyl)benzene (21) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (51.8 mg, 0.174 mmol, 87%, d:r = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers)** δ 7.56 – 7.56 (m, 1H), 7.42 – 7.28(m, 3H), 7.22 – 7.20 (m, 2H), 7.07 – 7.05 (m, 2H), 3.82 – 3.74 (m, 1H), 1.86 – 1.91 (m, 1H) 1.76 – 1.71 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) (mixture of diastereomers)** δ 140.8, 140.7, 136.9, 136.8, 136.7, 135.4, 133.3, 133.0, 132.5, 131.5, 131.4, 130.5, 129.8, 129.2, 128.9, 128.7, 128.4, 128.3, 127.3, 126.9, 40.1, 39.6, 35.5, 34.7, 26.0, 23.0. **IR** (ATR):3057, 2988, 2901, 1490, 1432, 1094, 1038, 1012, 817, 755 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}Cl_3^+$: 296.9999; found 297.0007.



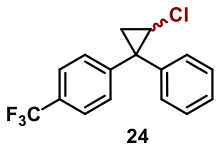
22

1-(2-chloro-1-phenylcyclopropyl)-2,4-difluorobenzene (22) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (38.1 mg, 0.144 mmol, 72%, d:r = 6:1). **^{1}H NMR (500 MHz, $CDCl_3$) major isomer:** δ 7.47 – 7.41 (m, 1H), 7.28 – 7.19 (m, 5H), 6.9 – 6.78 (m, 1H), 6.83 – 6.78 (m, 1H), 3.75 (dd, *J* = 7.6, 4.6 Hz, 1H), 1.84 (dd, *J* = 7.6, 6.6 Hz, 1H), 1.64 (dd, *J* = 6.6, 4.6 Hz, 1H); **minor isomer:** 7.41 – 7.36 (m, 1H), 7.33 – 7.30 (m, 3H), 7.18 – 7.16 (m, 3H), 6.76 – 6.69 (m, 1H), 3.67 (dd, *J* = 7.7, 4.5 Hz, 1H), 1.78 (dd, *J* = 6.7, 4.5 Hz, 1H), 1.69 (dd, *J* = 7.7, 6.6 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) major isomer:** δ 163.5 (dd, *J* = 13.9, 12.7 Hz), 142.6, 133.3 (dd, *J* = 9.7, 5.5 Hz), 130.0, 128.8, 127.4, 123.5 (d, *J* = 3.8 Hz), 111.4 (d, *J* = 3.6 Hz), 111.2 (d, *J* = 3.8 Hz), 104.5 (t, *J* = 25.5 Hz), 38.8, 32.3, 24.6; **minor isomer:** 161.5 (dd, *J* = 17.0, 11.8 Hz), 139.0, 131.6 (dd, *J* = 9.6, 5.3 Hz), 129.1, 128.4, 127.1, 123.4 (d, *J* = 3.8 Hz), 111.7 (d, *J* = 3.6 Hz), 111.5 (d, *J* = 3.8 Hz), 104.5 (t, *J* = 25.5 Hz), 38.7, 32.2, 22.2. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -108.56 – -108.61 (m, 1F), -110.63 – -110.70 (m, 1F). **IR (ATR)**: 3026, 2923, 2361, 1598, 1504, 1423, 1139, 850, 695, 534 cm^{-1}**. HRMS (APCI):** *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}F_2Cl^+$: 265.0590; found 265.0593.



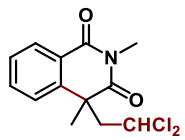
23

4-(2-chloro-1-phenylcyclopropyl)-1,1'-biphenyl (23) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a yellow oil (49.4 mg, 0.162 mmol, 81%, d:r = 1.5:1). **^{1}H NMR (500 MHz, $CDCl_3$) (mixture of diastereomers)** δ 7.59 – 7.27 (m, 14H), 3.77 – 3.74 (m, 1H), 1.84 – 1.80 (m, 1H), 1.79 – 1.76 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) (mixture of diastereomers)** δ 144.3, 143.4, 140.9, 140.7, 140.0, 139.8, 139.7, 138.9, 131.0, 130.8, 128.91, 128.86, 128.8, 128.5, 128.2, 128.0, 127.47, 127.45, 127.4, 127.3, 127.22, 127.15, 126.9, 39.6, 36.84, 36.78, 24.0, 23.8. **IR (ATR)**: 3027, 2360, 1599, 1486, 1446, 836, 760, 730, 693 cm^{-1}. **HRMS (APCI):** *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}Cl^+$: 305.1091; found 305.1093.



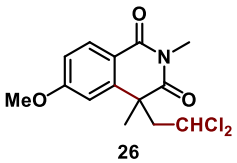
24

1-(2-chloro-1-phenylcyclopropyl)-4-(trifluoromethyl)benzene (24) Following the general procedure B, the title product was obtained after purification by column chromatography (PE) as a colorless oil (40.8 mg, 0.138 mmol, 69%, d:r = 3:1). **^{1}H NMR (500 MHz, $CDCl_3$) (mixture of diastereomers)** δ 7.61 – 7.50 (m, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.26 (m, 3H), 7.24 – 7.19 (m, 1H), 3.80 – 3.71 (m, 1H), 1.88 – 1.73 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$) (mixture of diastereomers)** δ 148.3, 143.8, 143.4, 138.8, 131.0, 130.8, 129.0, 128.8 (q, *J* = 32.7 Hz), 128.7, 128.1, 128.0, 127.7, 127.2, 125.7 (q, *J* = 3.6 Hz), 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.6 Hz) 39.4, 39.2, 37.0, 36.8, 24.2, 23.8. **^{19}F NMR (471 MHz, $CDCl_3$) (mixture of diastereomers)** δ -62.1 (s, 3F), -62.2 (s, 3F). **IR (ATR)**: 2957, 2361, 1598, 1504, 1424, 1269, 1139, 850, 695 cm^{-1}. **HRMS (APCI):** *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}Cl^+$: 305.1091; found 305.1093.



25

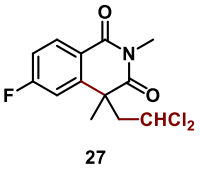
4-(2,2-dichloroethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (25) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (41.0 mg, 0.144 mmol, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.53 -7.49 (m, 1H), 7.41 - 7.39 (m, 1H), 5.20 (dd, *J* = 10.0, 3.9 Hz, 1H), 3.49 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.39 (s, 3H), 2.87 (dd, *J* = 14.8, 3.9 Hz, 1H), 1.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 163.9, 140.7, 134.4, 129.7, 128.3, 125.3, 125.1, 69.7, 53.3, 46.3, 31.7, 27.6. **IR** (ATR): 2935, 1713, 1661, 1467, 1317, 1058, 1431, 775, 703, 560 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{13}H_{14}NO_2Cl_2^+$: 286.0396; found 286.04398.



26

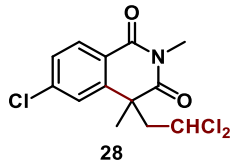
4-(2,2-dichloroethyl)-6-methoxy-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (26) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (41.1 mg, 0.130 mmol, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 5.27 (dd, *J* = 9.9, 3.9 Hz, 1H), 3.92 (s, 3H), 3.48 (dd, *J* = 14.8, 9.9 Hz, 1H), 3.36 (s, 3H), 2.82 (dd, *J* = 14.8, 3.9 Hz, 1H), 1.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.4, 164.4, 163.6, 142.9, 132.1, 118.0, 113.5,

110.9, 69.7, 55.8, 53.4, 46.5, 31.8, 27.4. **IR** (ATR): 2935, 1709, 1661, 1606, 1434, 1359, 1313, 780 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}NO_3Cl_2^+$: 316.0502; found 316.0504. **Melting Point** (Experimental): 158 – 160 °C



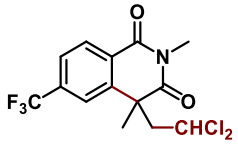
27

4-(2,2-dichloroethyl)-6-fluoro-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (27) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (42.0 mg, 0.138 mmol, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 8.8, 5.8 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.11 – 7.09 (m, 1H), 5.27 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.49 (dd, *J* = 14.9, 9.6 Hz, 1H), 3.38 (s, 3H), 2.83 (dd, *J* = 14.9, 4.4 Hz, 1H), 1.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 166.5 (d, *J* = 258.0 Hz), 162.9, 143.8 (d, *J* = 81.8 Hz), 132.8 (d, *J* = 9.8 Hz), 121.5 (d, *J* = 2.4 Hz), 116.3 (d, *J* = 22.2 Hz), 112.3 (d, *J* = 23.1 Hz), 69.4, 53.2, 46.6, 31.7, 27.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.2. **IR** (ATR): 2935, 1715, 1661, 1614, 1357, 1311, 1056, 780, 699 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{13}H_{13}NO_2Cl_2F^+$: 304.0302; found 304.0305. **Melting Point** (Experimental): 108 – 110 °C



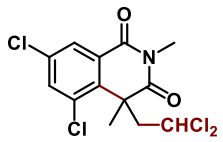
28

6-chloro-4-(2,2-dichloroethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (28) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (31.9 mg, 0.100 mmol, 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 5.27 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.48 (dd, *J* = 14.9, 9.6 Hz, 1H), 3.38 (s, 3H), 2.84 (dd, *J* = 14.9, 4.4 Hz, 1H), 1.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 163.1, 142.5, 141.0, 131.3, 128.9, 125.5, 123.5, 69.4, 53.1, 46.4, 31.7, 27.6. **IR** (ATR): 2935, 1713, 1660, 1597, 1427, 1354, 1057, 849, 780, 697 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{13}H_{13}NO_2Cl_3^+$: 320.0006; found 320.0009. **Melting Point** (Experimental): 126 – 128 °C



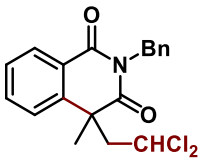
29

4-(2,2-dichloroethyl)-2,4-dimethyl-6-(trifluoromethyl)isoquinoline-1,3(2H,4H)-dione (29) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a yellow-white solid (39.7 mg, 0.112 mmol, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.65 (s, 1H), 5.24 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.51 (dd, *J* = 15.0, 9.1 Hz, 1H), 3.41 (s, 3H), 2.92 (dd, *J* = 14.9, 4.8 Hz, 1H), 1.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5, 162.8, 141.8, 135.9 (q, *J* = 33.3 Hz), 130.6, 128.0, 125.9 (d, *J* = 3.4 Hz), 123.3 (q, *J* = 274.1 Hz), 122.5 (q, *J* = 4.1 Hz), 69.3, 53.1, 46.6, 31.7, 27.8. **^{19}F NMR** (376 MHz, $CDCl_3$) **δ** -62.9. **IR** (ATR): 2935, 1716, 1665, 1431, 1272, 1128, 1076, 855, 789, 702 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+H]^+$ calcd for $C_{14}H_{13}NO_2Cl_2F_3^+$: 354.0260; found 354.0270. **Melting Point** (Experimental): 73 – 75 °C



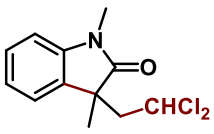
30

5,7-dichloro-4-(2,2-dichloroethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (30) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (36.9 mg, 0.104 mmol, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.3 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 5.24 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.71 (dd, *J* = 15.3, 3.7 Hz, 1H), 3.54 (dd, *J* = 15.3, 10.6 Hz, 1H), 3.40 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3, 161.8, 136.6, 135.3, 135.1, 133.2, 129.3, 129.1, 70.2, 49.3, 47.7, 28.2, 26.8. **IR** (ATR): 2935, 1718, 1668, 1587, 1434, 1323, 1261, 1061, 728, 425 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{13}H_{11}NO_2Cl_4Na^+$: 377.9391; found 377.9406.



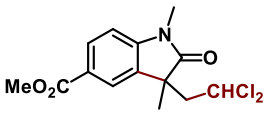
31

2-benzyl-4-(2,2-dichloroethyl)-4-methylisoquinoline-1,3(2H,4H)-dione (31) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (51.4 mg, 0.142 mmol, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.76 – 7.65 (m, 1H), 7.54 – 7.34 (m, 3H), 7.31 – 7.26 (m, 3H), 7.24 (dd, *J* = 9.9, 4.2 Hz, 1H), 5.26 (d, *J* = 13.8 Hz, 1H), 5.15 (d, *J* = 13.8 Hz, 1H), 5.14 (dd, *J* = 9.9, 4.2 Hz 1H), 3.48 (dd, *J* = 14.8, 9.9 Hz, 1H), 2.86 (dd, *J* = 14.8, 4.2 Hz, 1H), 1.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0, 163.7, 140.8, 136.7, 134.4, 130.0, 129.2, 128.5, 128.3, 127.7, 125.3, 125.1, 69.6, 52.9, 46.5, 44.1, 32.0. **IR** (ATR): 3065, 2923, 1713, 1667, 1466, 1385, 1352, 1159, 737, 707 cm^{-1}**.** **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_2Cl_2^+$: 362.0709; found 362.0709.



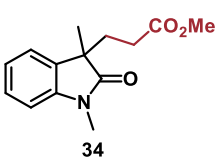
32

3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (32) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (44.2 mg, 0.172 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 1H), 7.21 – 7.19 (m, 1H), 7.12 - 7.09 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.39 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.21 (s, 3H), 3.04 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.71 (dd, *J* = 14.9, 4.1 Hz, 1H), 1.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.1, 143.6, 131.2, 128.8, 122.8, 108.8, 69.8, 50.3, 47.3, 26.6, 25.6.
These data are in agreement with those reported previously in the literature[9].



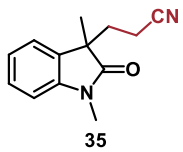
33

methyl 3-(2,2-dichloroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (33) Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (40.3 mg, 0.128 mmol, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.37 (dd, *J* = 9.4, 4.2 Hz, 1H), 3.94 (s, 3H), 3.25 (s, 3H), 3.07 (dd, *J* = 14.8, 9.4 Hz, 1H), 2.77 (dd, *J* = 14.8, 4.2 Hz, 1H), 1.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 166.8, 147.7, 131.5, 131.2, 124.7, 124.1, 108.3, 69.6, 52.3, 49.9, 47.1, 26.8, 25.6. **IR** (ATR): 2957, 1713, 1668, 1466, 1385, 1352, 1159, 737, 707 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}NO_3Cl_2^+$: 316.0502; found 316.0504. **Melting Point** (Experimental): 134 – 136 °C



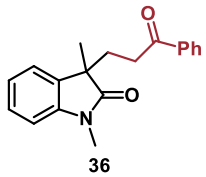
34

methyl 3-(1,3-dimethyl-2-oxoindolin-3-yl)propanoate (34) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (32.1 mg, 0.130 mmol, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.19 – 7.17 (m, 1H), 7.10 – 7.06 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.54 (s, 3H), 3.22 (s, 3H), 2.28 – 2.19 (m, 1H), 2.17 – 2.03 (m, 2H), 1.93 – 1.81 (m, 1H), 1.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.0, 173.3, 143.3, 132.9, 128.2, 122.82, 122.77, 108.2, 51.7, 47.7, 33.1, 29.5, 26.3, 23.7. These data are in agreement with those reported previously in the literature[10].



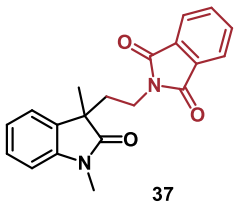
35

3-(1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (35) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (33.0 mg, 0.154 mmol, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 1H), 7.23 – 7.21 (m, 1H), 7.16 – 7.12 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.39 – 2.33 (m, 1H), 2.15 – 1.98 (m, 3H), 1.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.9, 143.2, 131.7, 128.8, 123.1, 122.7, 118.9, 108.6, 47.4, 33.5, 26.4, 23.6, 12.9. These data are in agreement with those reported previously in the literature[11].



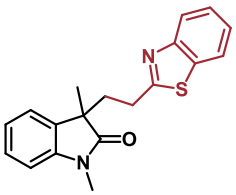
36

1,3-dimethyl-3-(3-oxo-3-phenylpropyl)indolin-2-one (36) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (26.4 mg, 0.090 mmol, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.31 (m, 2H), 7.30 - 7.20 (m, 2H), 7.10 – 7.06 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.26 (s, 3H), 2.84 – 2.76 (m, 1H), 2.52 – 2.44 (m, 1H), 2.38 – 2.20 (m, 2H), 1.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.5, 180.3, 143.2, 136.7, 133.4, 133.1, 128.6, 128.2, 128.1, 122.9, 122.8, 108.2, 47.7, 33.6, 32.5, 26.3, 23.9. These data are in agreement with those reported previously in the literature[12].



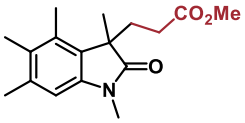
37

2-(2-(1,3-dimethyl-2-oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (37) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a colorless oil (31.4 mg, 0.094 mmol, 47%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.78 – 6.65 (m, 2H), 3.59 (ddd, *J* = 14.5, 8.8, 5.9 Hz, 1H), 3.44 (dt, *J* = 14.5, 5.7 Hz, 1H), 3.20 (s, 3H), 2.46 (ddd, *J* = 14.8, 8.8, 6.2 Hz, 1H), 2.31 (dt, *J* = 14.8, 5.6 Hz, 1H), 1.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.6, 167.9, 143.1, 133.7, 132.9, 131.9, 127.6, 122.9, 122.4, 122.1, 108.4, 47.1, 34.64, 34.6, 26.3, 25.2. These data are in agreement with those reported previously in the literature[12].



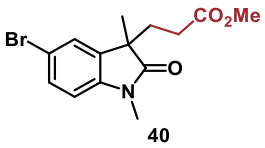
38

3-(2-(benzo[d]thiazol-2-yl)ethyl)-1,3-dimethylindolin-2-one (38) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 100:1) as a colorless oil (38.6 mg, 0.120 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 1H), 7.81 - 7.79 (m, 1H), 7.44 – 7.40 (m, 1H), 7.35 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.09 – 7.05 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.84 (ddd, *J* = 15.0, 12.2, 5.1 Hz, 1H), 2.72 (ddd, *J* = 15.0, 11.9, 4.8 Hz, 1H), 2.52 (ddd, *J* = 13.3, 11.9, 5.1 Hz, 1H), 2.37 (ddd, *J* = 13.3, 12.2, 4.8 Hz, 1H), 1.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.0, 170.9, 153.2, 143.4, 135.2, 133.1, 128.3, 126.0, 124.8, 123.0, 122.9, 122.6, 121.6, 108.3, 48.2, 37.4, 29.7, 26.4, 23.8. **IR** (ATR): 2925, 1703, 1612, 1492, 1377, 1346, 1123, 1095, 755 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}ON_2S^+$: 323.1213; found 323.1215.



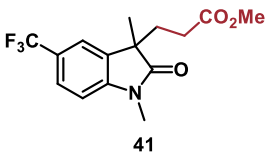
39

methyl 3-(1,3,4,5,6-pentamethyl-2-oxoindolin-3-yl)propanoate (39) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (46.8 mg, 0.162 mmol, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.55 (s, 1H), 3.51 (s, 3H), 3.18 (s, 3H), 2.39 – 2.30 (m, 1H), 2.32 (s, 3H), 2.29 – 2.24 (m, 1H), 2.28 (s, 3H), 2.14 (s, 3H), 1.97 – 1.91 (m, 1H), 1.81 – 1.74 (m, 1H), 1.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.1, 173.3, 141.1, 136.1, 133.3, 129.8, 127.1, 107.8, 51.6, 48.9, 31.7, 29.9, 26.2, 22.6, 21.4, 15.7, 14.9. **IR** (ATR): 2931, 1703, 1614, 1455, 1381, 1339, 1171, 1062, 838 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{17}H_{24}O_3N^+$: 290.1751; found 290.1753.



40

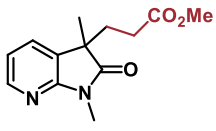
methyl 3-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanoate (40) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (33.1 mg, 0.102 mmol, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 6.80 (dd, *J* = 7.2, 1.5 Hz, 1H), 3.56 (s, 3H), 3.21 (s, 3H), 2.67 (ddd, *J* = 13.8, 10.9, 5.8 Hz, 1H), 2.23 (ddd, *J* = 13.8, 10.9, 5.5 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.53 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.3, 172.9, 145.4, 130.4, 129.7, 127.0, 119.1, 107.3, 51.7, 50.1, 30.0, 29.8, 26.5, 21.2. **IR** (ATR): 2931, 1710, 1602, 1578, 1451, 1297, 1172, 1120, 776, 561, 499 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{14}H_{17}O_3NBr^+$: 326.0386; found 326.0385.



41

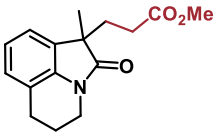
methyl 3-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)propanoate (41) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as white solid (32.8 mg, 0.104 mmol, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 1H), 7.41 (d, *J* = 1.3 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.55 (s, 3H), 3.26 (s, 3H), 2.28 (ddd, *J* = 13.1, 10.4, 5.2 Hz, 1H), 2.19 – 2.06 (m, 2H), 1.90 (ddd, *J* = 15.9, 10.4, 5.2 Hz, 1H), 1.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.9, 172.9, 146.4, 133.6, 126.1 (q, *J* = 4.0 Hz), 125.0 (q, *J* = 32.3 Hz), 124.5 (q, *J* = 272.2 Hz), 119.9 (q, *J* = 3.2 Hz), 108.0, 51.8, 47.7, 32.9, 29.5, 26.5, 23.6. **^{19}F**

NMR (471 MHz, $CDCl_3$) δ -61.2. **IR** (ATR): 2957, 1721, 1623, 1505, 1460, 1328, 1115, 823, 537 cm^{-1}. **HRMS** (APCI)**:** *m/z* $[M+H]^+$ calcd for $C_{15}H_{17}O_3NF_3^+$: 316.1155; found 316.1157.



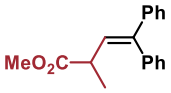
42

methyl 3-(1,3-dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl) propanoate (42) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (28.8 mg, 0.116 mmol, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.98 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.55 (s, 3H), 3.31 (s, 3H), 2.30 – 2.22 (m, 1H), 2.19 – 2.09 (m, 2H), 1.98 – 1.89 (m, 1H), 1.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.6, 173.1, 156.9, 147.2, 130.4, 127.3, 118.3, 51.8, 47.4, 32.5, 29.4, 25.4, 23.2. **IR** (ATR): 2925, 1714, 1592, 1467, 1345, 1133, 1020, 780 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}N_2O_3Na^+$:271.1053; found 271.1050.



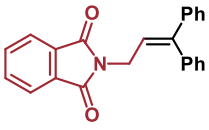
43

methyl 3-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)propanoate (43) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as white solid (41.5 mg, 0.152 mmol, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 – 6.93 (m, 3H), 3.77 – 3.67 (m, 2H), 3.55 (s, 3H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.26 – 1.90 (m, 6H), 1.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 173.4, 139.1, 131.4, 126.9, 122.2, 120.6, 120.3, 51.7, 49.0, 38.8, 32.9, 29.6, 24.7, 23.4, 21.3. **IR** (ATR): 2924, 1734, 1694, 1599, 1483, 1385, 1166, 1060, 787 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{16}H_{19}NO_3Na^+$:296.1257; found 296.1255. **Melting Point:** 184 - 186 ˚C.



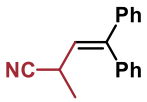
44

methyl 2-methyl-4,4-diphenylbut-3-enoate (44) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (38.3 mg, 0.146 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 3H), 7.28 – 7.25 (m, 2H), 7.24 – 7.19 (m, 5H), 6.12 (d, *J* = 10.3 Hz, 1H), 3.68 (s, 3H), 3.33 – 3.27 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 143.2, 141.9, 139.4, 129.9, 128.5, 128.3, 127.8, 127.54, 127.49, 52.1, 40.4, 18.7. These data are in agreement with those reported previously in the literature[13].



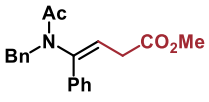
45

4,4-diphenylbut-3-enenitrile (45) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (38.3 mg, 0.146 mmol, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.70 – 7.68 (m, 2H), 7.47 – 7.39 (m, 2H), 7.37 – 7.32 (m, 3H), 7.28 – 7.19 (m, 5H), 6.07 (t, J = 6.6 Hz, 1H), 4.39 (d, *J* = 6.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 144.8, 141.5, 138.8, 134.0, 132.2, 129.9, 128.6, 128.5, 128.2, 127.7, 127.7, 127.5, 123.3, 122.4, 37.7. These data are in agreement with those reported previously in the literature[14].



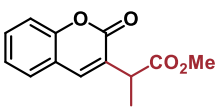
46

2-methyl-4,4-diphenylbut-3-enenitrile (46) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (27.5 mg, 0.118 mmol, 59%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.32 – 7.29 (m, 2H), 7.25 – 7.18 (m, 5H), 5.97 (d, *J* = 9.9 Hz, 1H), 3.39 (dq, *J* = 9.9, 7.0 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ145.7, 140.7, 138.3, 129.4, 128.9, 128.5, 128.3, 128.2, 127.6, 123.5, 121.8, 25.9, 19.6. These data are in agreement with those reported previously in the literature[15].



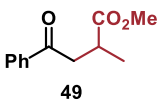
47

methyl (*E*)-4-(N-benzylacetamido)-4-phenylbut-3-enoate (47) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (52.3 mg, 0.162 mmol, 81%, *E:Z* = 5/1). **^{1}H NMR (400 MHz, $CDCl_3$)** major *E*-isomer: δ 7.43 – 7.38 (m, 3H), 7.29 – 7.18 (m, 7H), 5.53 (t, *J* = 7.6 Hz, 1H), 4.49 (s, 2H), 3.63 (s, 3H), 3.21 (d, *J* = 7.6 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** major *E*-isomer: δ 171.3, 170.9, 141.6, 137.4, 134.2, 129.2, 129.0, 128.9, 128.8, 128.4, 127.3, 123.2, 52.1, 49.0, 33.9, 22.4. **IR (ATR)**: major *E*-isomer: 2915, 1735, 1644, 1493, 1386, 1169, 980, 780 cm^{-1}. **HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{20}H_{21}NO_3Na^+$:346.1413; found 346.1406.



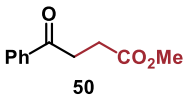
48

methyl 2-(2-oxo-2*H*-chromen-3-yl)propanoate (48) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as white solid (32.0 mg, 0.138 mmol, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.53 – 7.49 (m, 2H), 7.34 – 7.29 (m, 2H), 3.92 (q, *J* = 7.3 Hz, 1H), 3.73 (s, 3H), 1.54 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 161.1, 153.3, 139.1, 131.5, 128.6, 127.9, 124.6, 119.2, 116.6, 52.5, 40.1, 16.4. **IR** (ATR): 2920, 1736, 1708, 1459, 1382, 1191, 1085, 788 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{13}H_{12}O_4Na^+$:255.0628; found 255.0626. **Melting Point:** 87 - 89 ˚C.



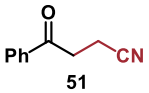
49

methyl 2-methyl-4-oxo-4-phenylbutanoate (49) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (25.1 mg, 0.122 mmol, 61%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.59 – 7.55 (m, 1H), 7.48 – 7.45 (m, 2H), 3.71 (s, 3H), 3.49 (dd, *J* = 17.7, 7.9 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.04 (dd, *J* = 17.7, 5.5 Hz, 1H), 1.29 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.2, 176.6, 136.7, 133.4, 128.7, 128.2, 52.1, 42.1, 35.0, 17.4. These data are in agreement with those reported previously in the literature[16].



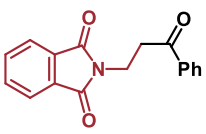
50

methyl 4-oxo-4-phenylbutanoate (50) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (28.0 mg, 0.146 mmol, 73%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.99 (m, 2H), 7.59 – 7.56 (m, 1H), 7.49 – 7.46 (m, 2H), 3.71 (s, 3H), 3.33 (t, *J* = 6.6 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.2, 173.5, 136.6, 133.4, 128.8, 128.2, 52.0, 33.5, 28.1. These data are in agreement with those reported previously in the literature[17].



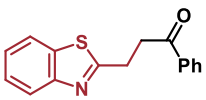
51

4-oxo-4-phenylbutanenitrile (51) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (21.0 mg, 0.132 mmol, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.65 – 7.60 (m, 1H), 7.52 – 7.48 (m, 2H), 3.41 – 3.38 (m, 2H), 2.80 – 2.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5, 135.7, 134.1, 129.0, 128.2, 119.4, 34.4, 11.9. These data are in agreement with those reported previously in the literature[18].



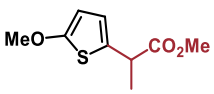
52

2-(3-oxo-3-phenylpropyl)isoindoline-1,3-dione (52) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (28.5 mg, 0.102 mmol, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.96 (m, 2H), 7.87 – 7.84 (m, 2H), 7.74 – 7.71 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 - 7.43 (m, 2H), 4.17 – 4.13 (m, 2H), 3.46 – 3.42 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 168.3, 136.4, 134.1, 133.5, 132.2, 128.8, 128.1, 123.4, 36.9, 33.6. These data are in agreement with those reported previously in the literature[18].



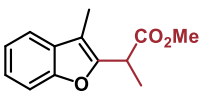
53

3-(benzo[d]thiazol-2-yl)-1-phenylpropan-1-one (53) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (31.0 mg, 0.116 mmol, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.79 (m, 4H), 7.60 – 7.33 (m, 5H), 3.68 – 3.64 (m, 2H), 3.56 – 3.59 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.0, 170.6, 153.3, 136.6, 135.3, 133.5, 128.8, 128.2, 126.0, 124.9, 122.6, 121.6, 37.6, 28.3. These data are in agreement with those reported previously in the literature[18].



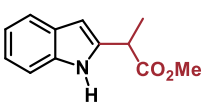
54

methyl 2-(5-methoxythiophen-2-yl)propanoate (54) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (20.8 mg, 0.104 mmol, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.53 (d, *J* = 3.8 Hz, 1H), 6.02 (d, *J* = 3.8 Hz, 1H), 3.85 (s, 3H), 3.82 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 165.5, 128.9, 122.1, 103.1, 60.3, 52.4, 41.2, 19.1. **IR** (ATR): 2951, 1734, 1560, 1504, 1432, 1196, 1060, 767 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_9H_{12}O_3SNa^+$:223.0399; found 223.0399.



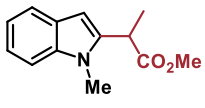
55

methyl 2-(3-methylbenzofuran-2-yl)propanoate (55) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a colorless oil (28.3 mg, 0.130 mmol, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.26 – 7.19 (m, 2H), 4.00 (q, *J* = 7.3 Hz, 1H), 3.69 (s, 3H), 2.21 (s, 3H), 1.59 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.7, 154.0, 150.8, 130.1, 124.0, 122.3, 119.2, 111.3, 111.1, 52.5, 37.8, 15.5, 8.0. **IR** (ATR): 2949, 1737, 1454, 1189, 1066, 876 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{13}H_{14}O_3Na^+$:241.0835; found 241.0833.



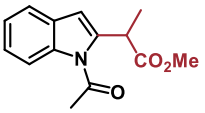
56

methyl 2-(1*H*-indol-2-yl)propanoate (56) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as pale yellow solid (17.5 mg, 0.086 mmol, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (bs, 1H), 7.56 – 7.54 (m, 1H), 7.35 – 7.33 (m, 1H), 7.17 – 7.06 (m, 2H), 6.37 – 6.36 (m, 1H), 3.96 (q, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.2, 136.7, 136.3, 128.2, 122.0, 120.4, 120.0, 110.9, 100.3, 52.6, 39.2, 17.6. **IR** (ATR): 3355, 2920, 1712, 1455, 1330, 1197, 1068, 780 cm^{-1} **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{12}H_{13}NO_2Na^+$:226.0838; found 226.0836 **Melting Point:** 84 - 86 ˚C.



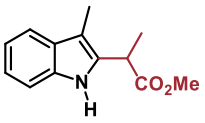
57

methyl 2-(1-methyl-1H-indol-2-yl)propanoate (57) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a colorless oil (19.1 mg, 0.088 mmol, 44%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.56 (m, 1H), 7.30 – 7.28 (m, 1H), 7.22 – 7.18 (m, 1H), 7.12 – 7.07 (m, 1H), 6.43 (s, 1H), 3.96 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.7, 138.9, 137.6, 127.6, 121.5, 120.5, 119.7, 109.2, 99.6, 52.5, 37.9, 29.9, 17.0. **IR** (ATR): 2917, 1731, 1467, 1316, 1163, 1064, 775 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{13}H_{15}NO_2Na^+$:240.0995; found 240.0994.



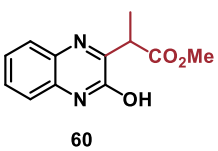
58

methyl 2-(1-acetyl-1H-indol-2-yl)propanoate (58) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as white solid (20.6 mg, 0.084 mmol, 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H), 7.32 – 7.23 (m, 2H), 6.63 (s, 1H), 4.39 (q, *J* = 7.3, 1H), 3.71 (s, 3H), 2.80 (s, 3H), 1.65 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 170.7, 141.2, 136.0, 130.0, 124.2, 123.2, 121.4, 114.3, 109.5, 52.2, 41.2, 27.7, 16.8. **IR** (ATR): 2952, 1731, 1697, 1428, 1369, 1210, 979 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{14}H_{15}NO_3Na^+$:268.0944; found 268.0942. **Melting Point:** 98 - 100 ˚C.



59

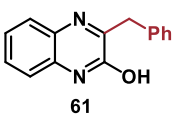
methyl 2-(3-methyl-1H-indol-2-yl)propanoate (59) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as white solid (29.5 mg, 0.136 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 (bs, 1H), 7.52 – 7.50 (m, 1H), 7.32 – 7.30 (m, 1H), 7.17 – 7.07 (m, 2H), 4.06 (q, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 2.27 (s, 3H), 1.54 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.0, 135.6, 132.1, 128.9, 121.9, 119.3, 118.6, 110.8, 107.9, 52.4, 37.0, 18.9, 8.5. These data are in agreement with those reported previously in the literature[19].



60

methyl 2-(3-hydroxyquinoxalin-2-yl)propanoate (60) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as whiter solid (40.4 mg, 0.174 mmol, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.89 (bs, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.37 – 7.34 (m, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3, 158.6, 156.3, 132.8, 131.3,

130.5, 129.3, 124.4, 116.0, 52.4, 43.7, 14.5. **IR** (ATR): 2839, 1731, 1660, 1561, 1432, 1085, 763 cm^{-1}. **HRMS** (ESI)**:** *m/z* $[M+Na]^+$ calcd for $C_{12}H_{12}N_2O_3Na^+$:255.0740; found 255.0737. **Melting Point:** 184 - 186 ˚C.

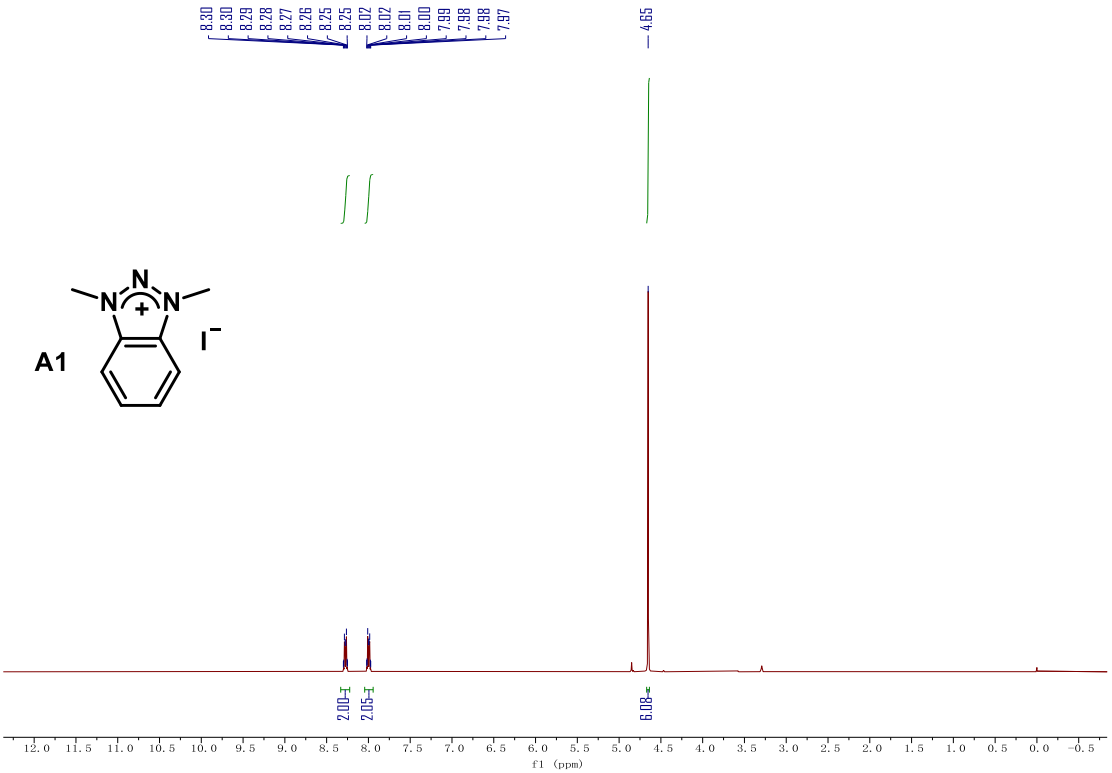


61

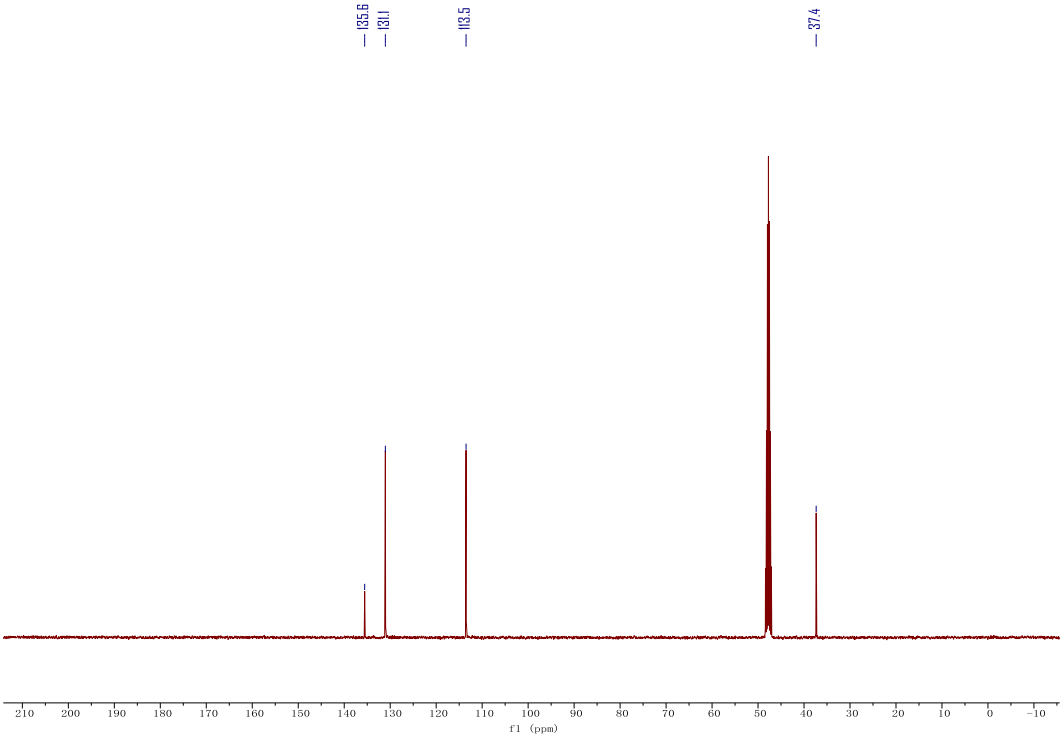
3-benzylquinoxalin-2-ol (61) Following the general procedure C, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as whiter solid (29.7 mg, 0.126 mmol, 63%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.40 (bs, 1H), 7.85 – 7.83 (m, 1H), 7.50 – 7.46 (m, 3H), 7.34 – 7.25 (m, 4H), 7.22 – 7.19 (m, 1H), 4.30 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 156.6, 137.1, 133.0, 131.3, 130.1, 129.7, 129.1, 128.5, 126.8, 124.3, 115.8, 40.1. These data are in agreement with those reported previously in the literature[20].

14. NMR Spectrum

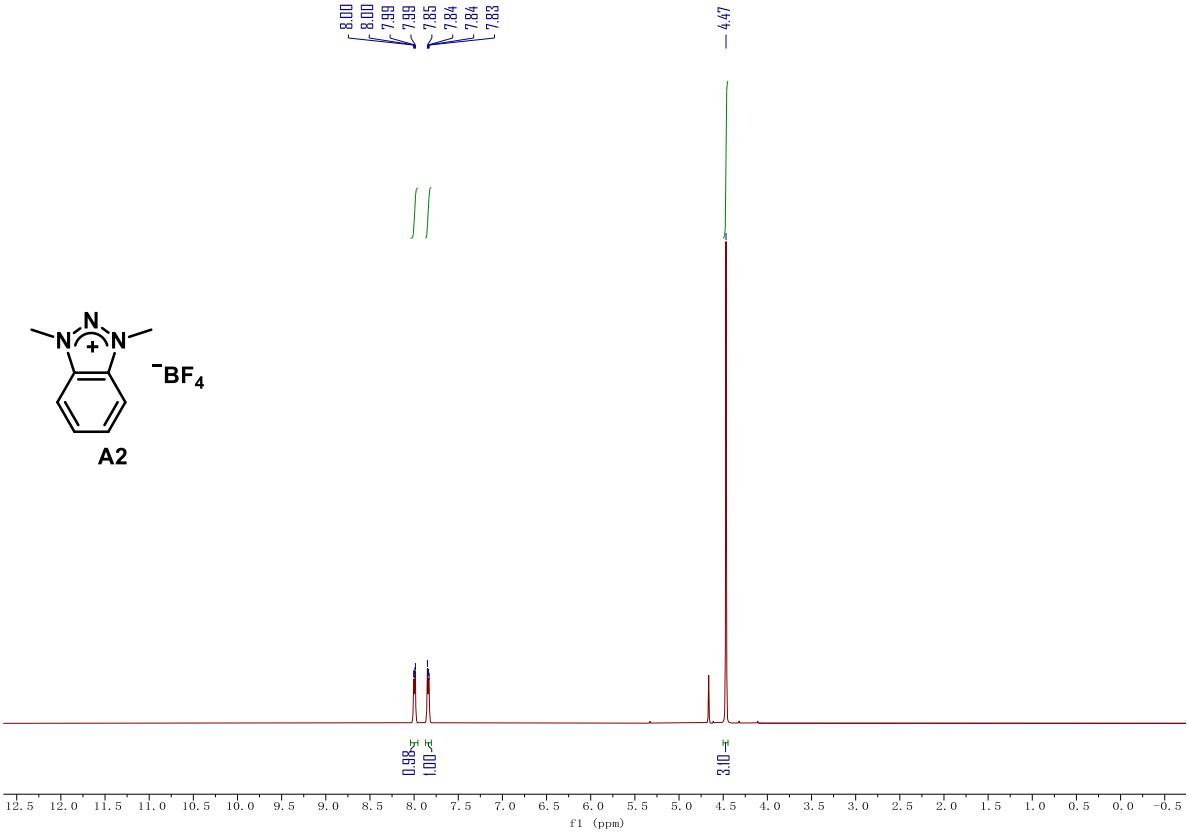
^{1}H NMR of Nitrenium Salt A1 (400 MHz, Methanol-d_4)



^{13}C NMR of Nitrenium Salt A1 (101 MHz, Methanol-d_4)

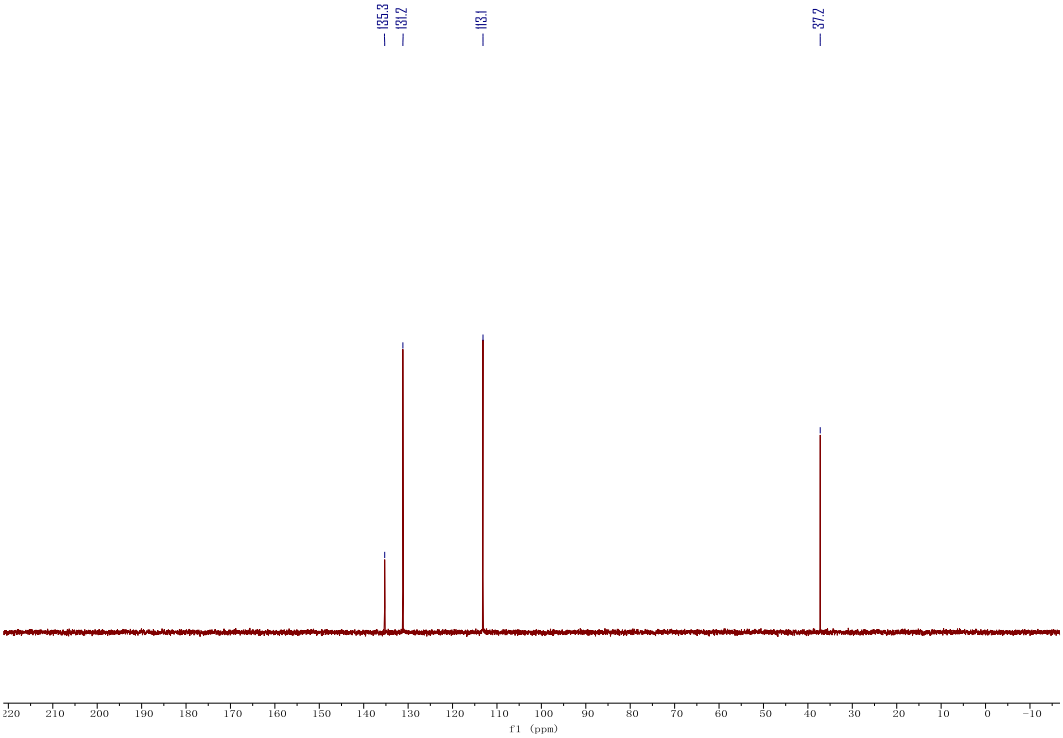


^{1}H NMR of Nitrenium Salt A2 (500 MHz, D_2O)

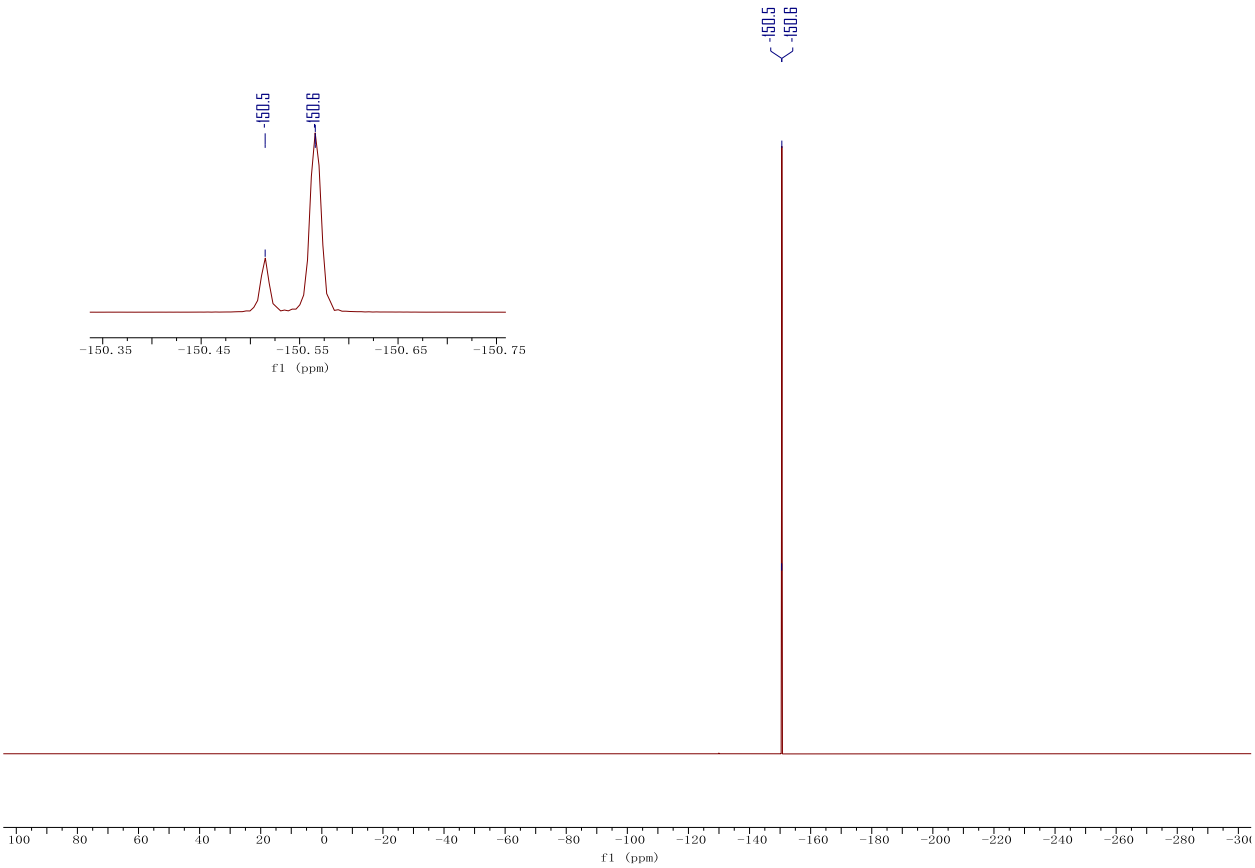


A2

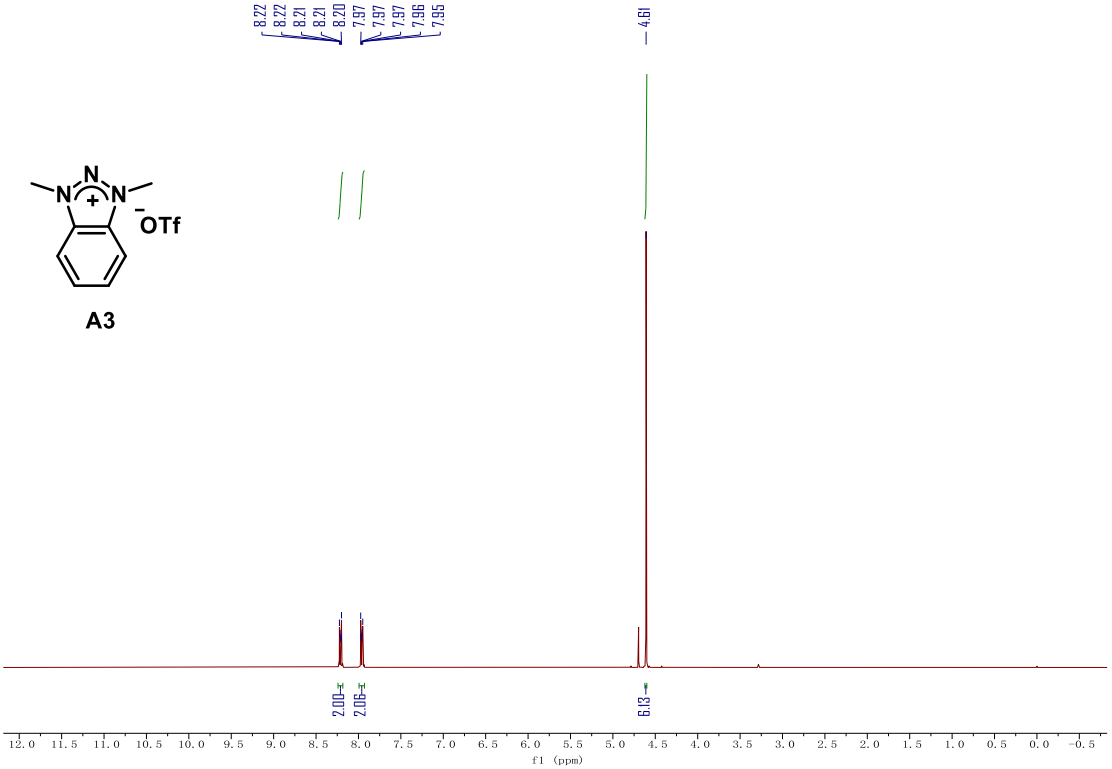
^{13}C NMR of Nitrenium Salt A2 (126 MHz, D_2O)



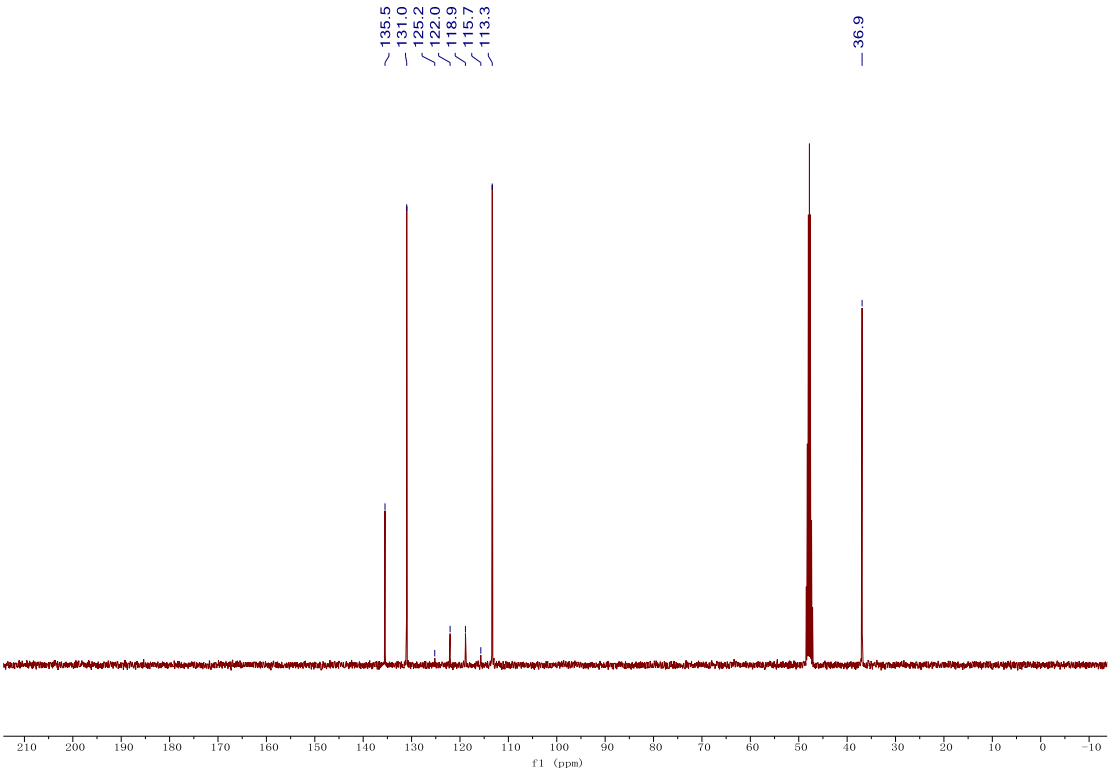
^{19}F NMR of Nitrenium Salt A2 (471 MHz, D_2O)



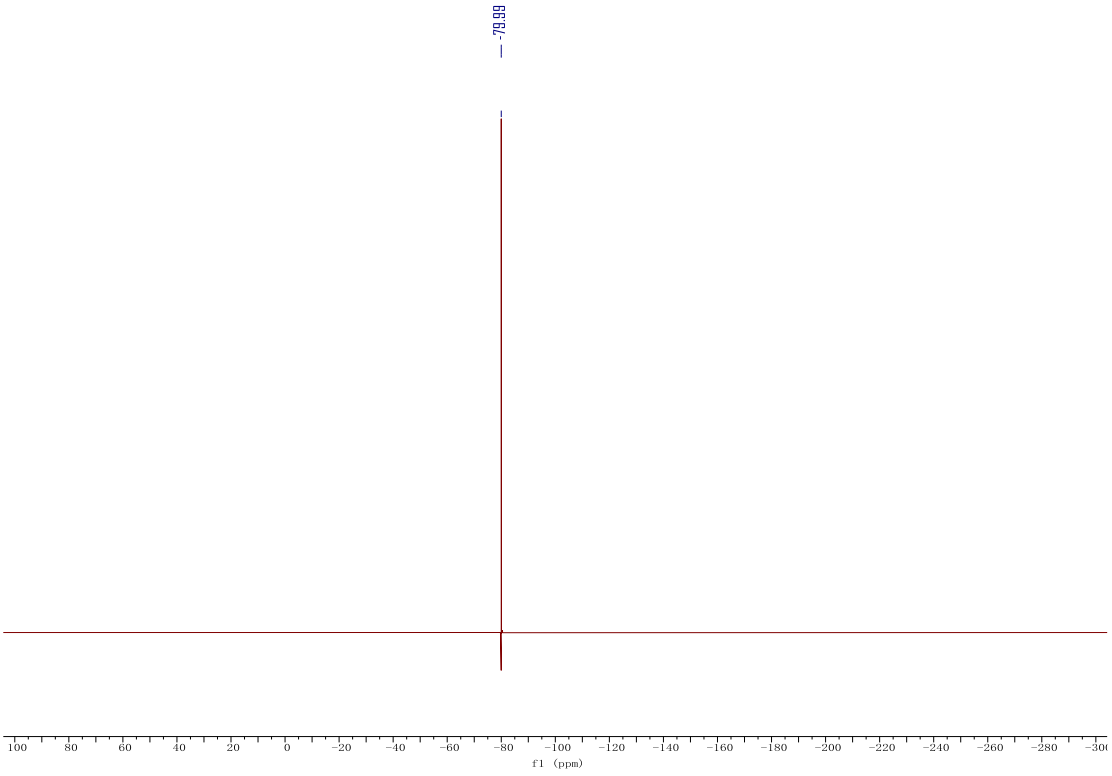
^{1}H NMR of Nitrenium Salt A3 (400 MHz, Methanol-d_4)



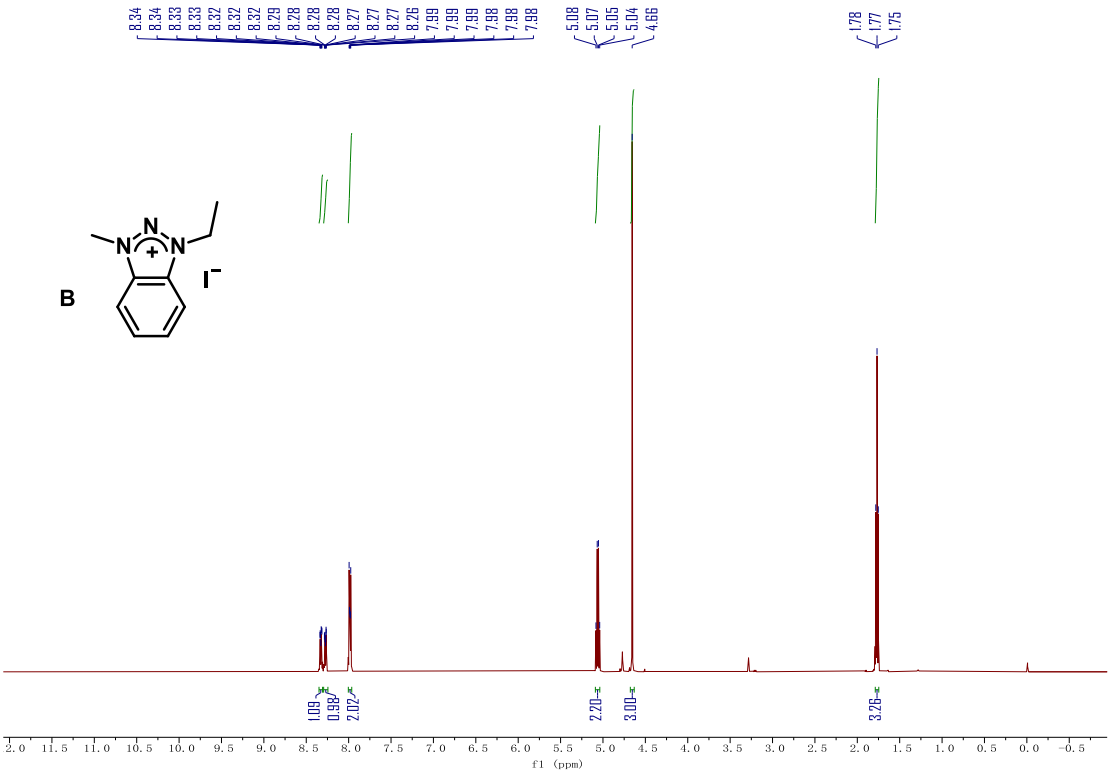
^{13}C NMR of Nitrenium Salt A3 (101 MHz, Methanol-d_4)



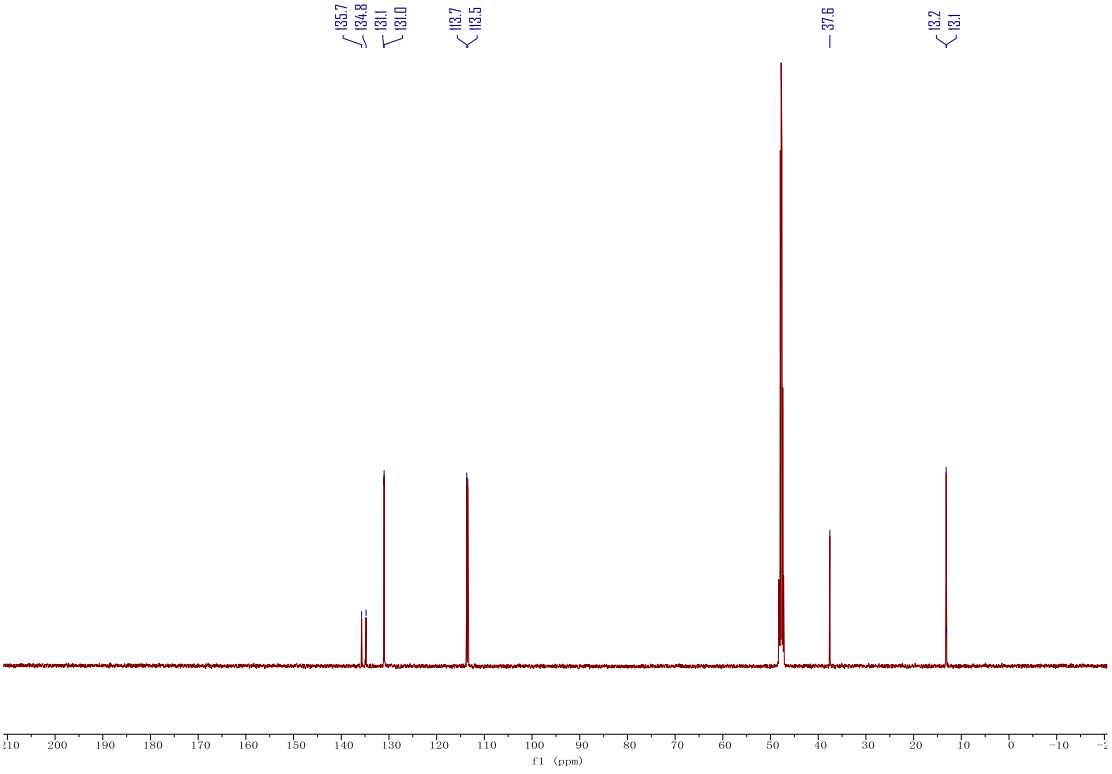
^{19}F NMR of Nitrenium Salt A3 (471 MHz, Methanol-d_4)


-79.99
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

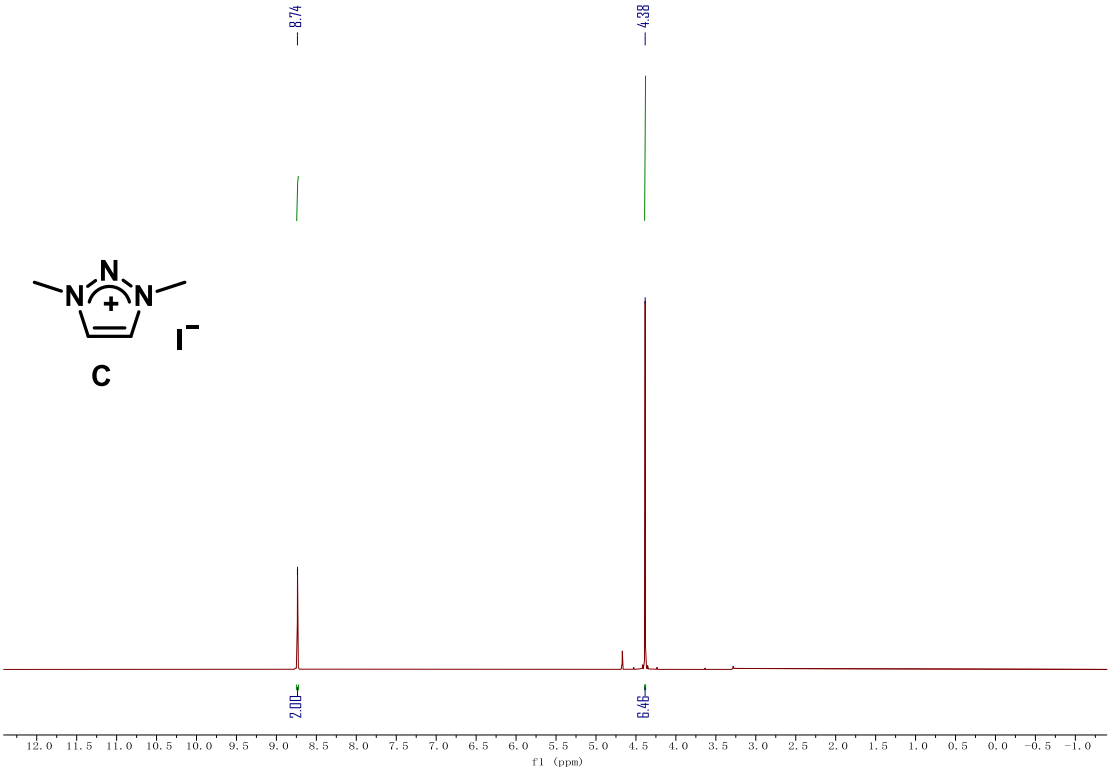
^{1}H NMR of Nitrenium Salt B (500 MHz, Methanol-d_4)



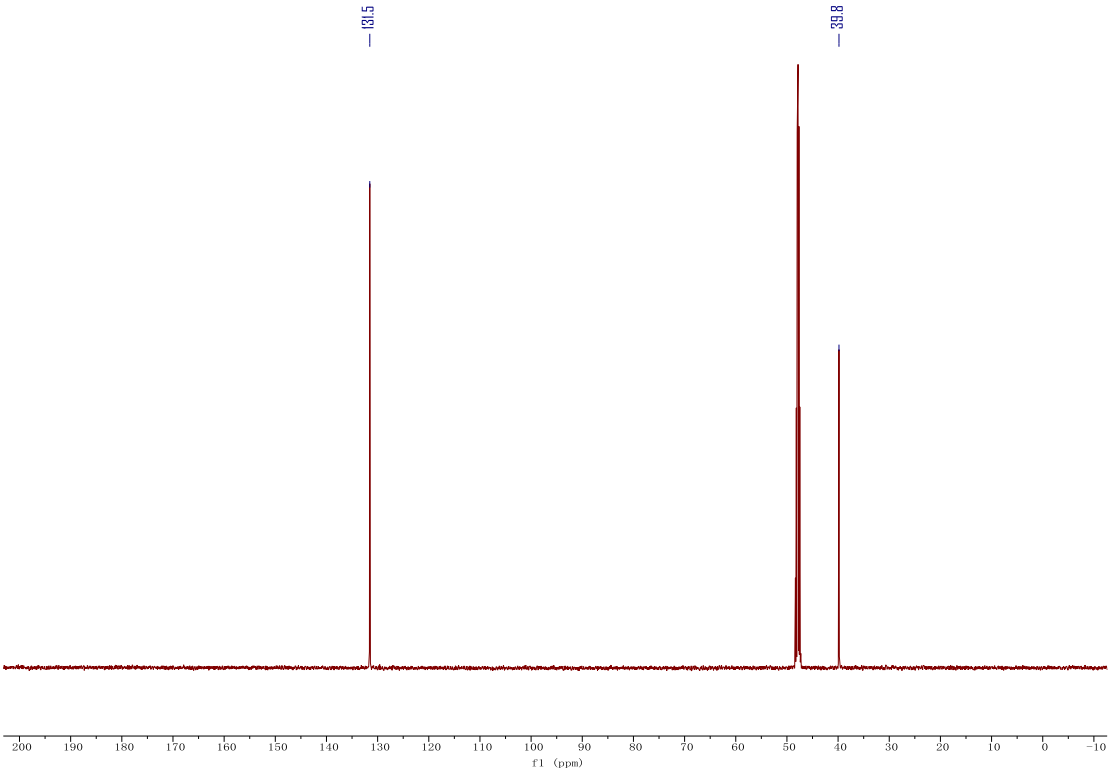
^{13}C NMR of Nitrenium Salt B (126 MHz, Methanol-d_4)



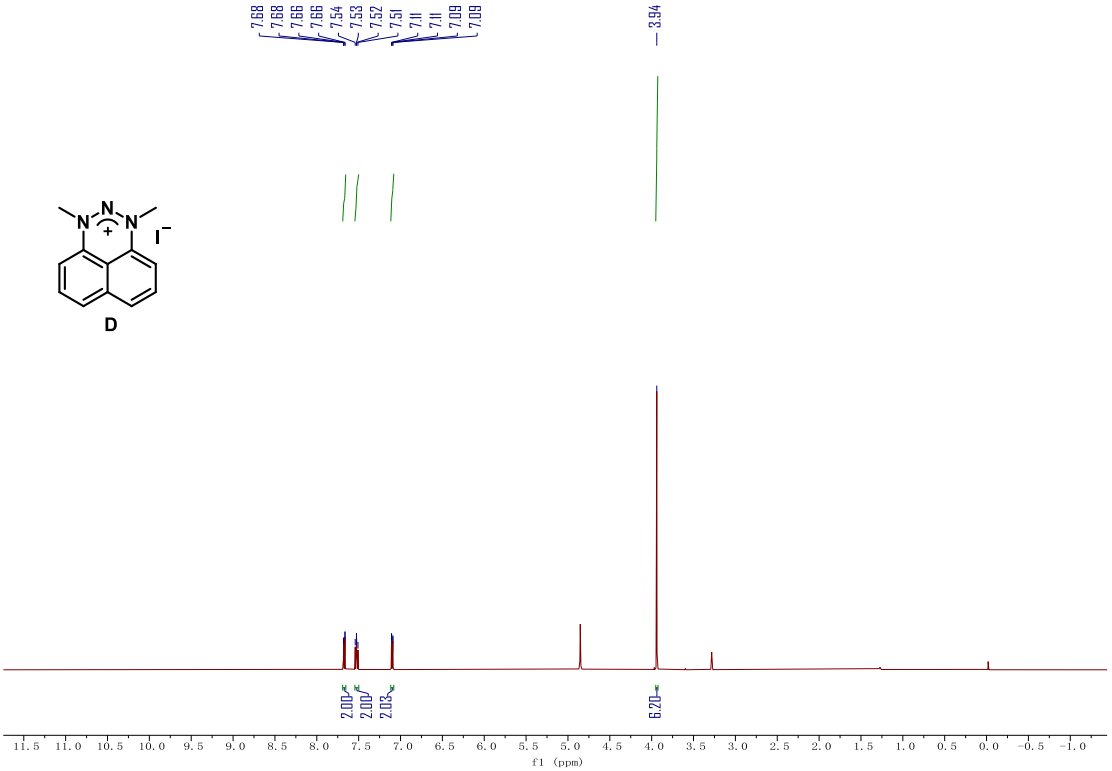
^{1}H NMR of Nitrenium Salt C (500 MHz, Methanol-d_4)



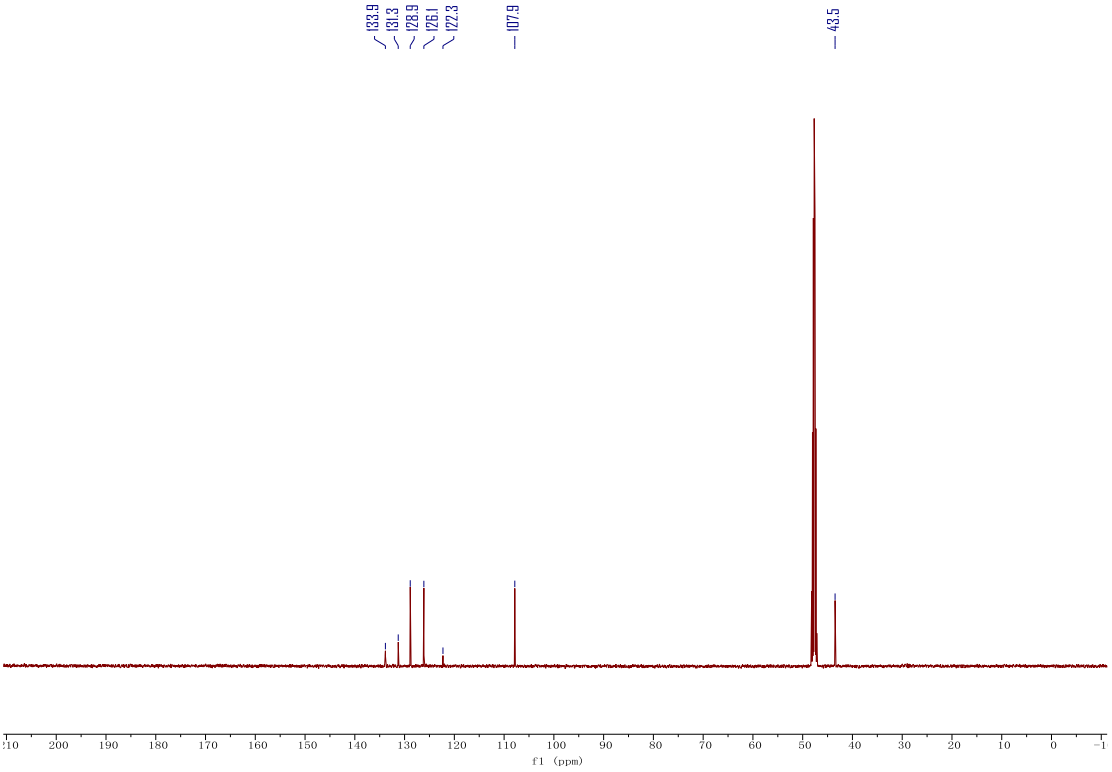
^{13}C NMR of Nitrenium Salt B1 (126 MHz, Methanol-d_4)



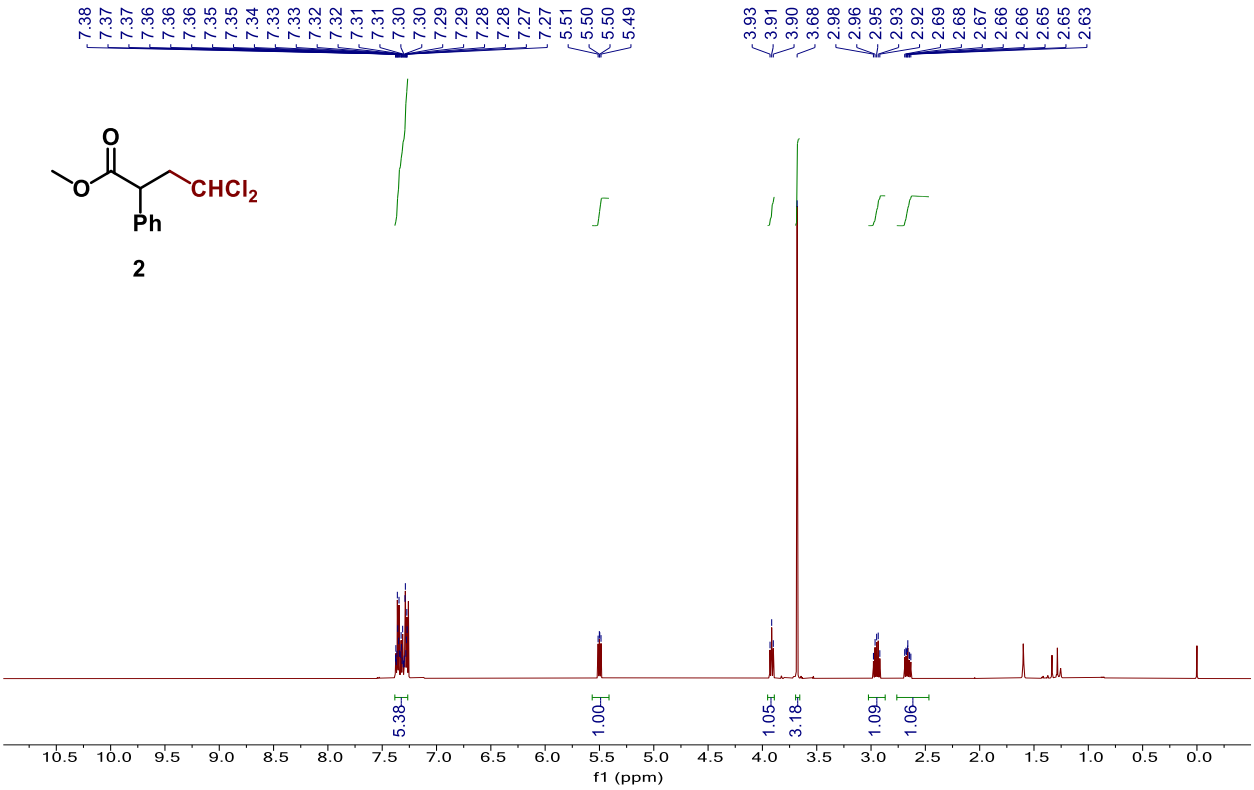
^{1}H NMR of Nitrenium Salt D (500 MHz, Methanol-d_4)



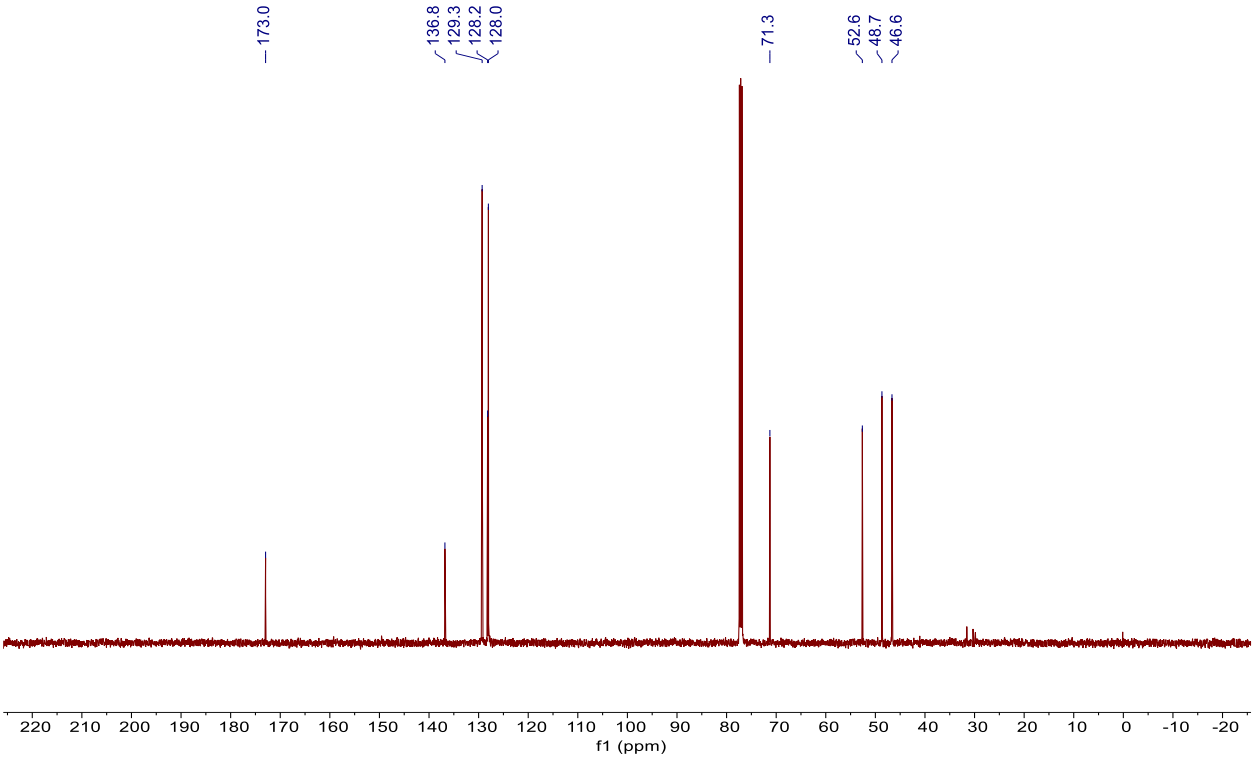
^{13}C NMR of Nitrenium Salt D (126 MHz, Methanol-d_4)



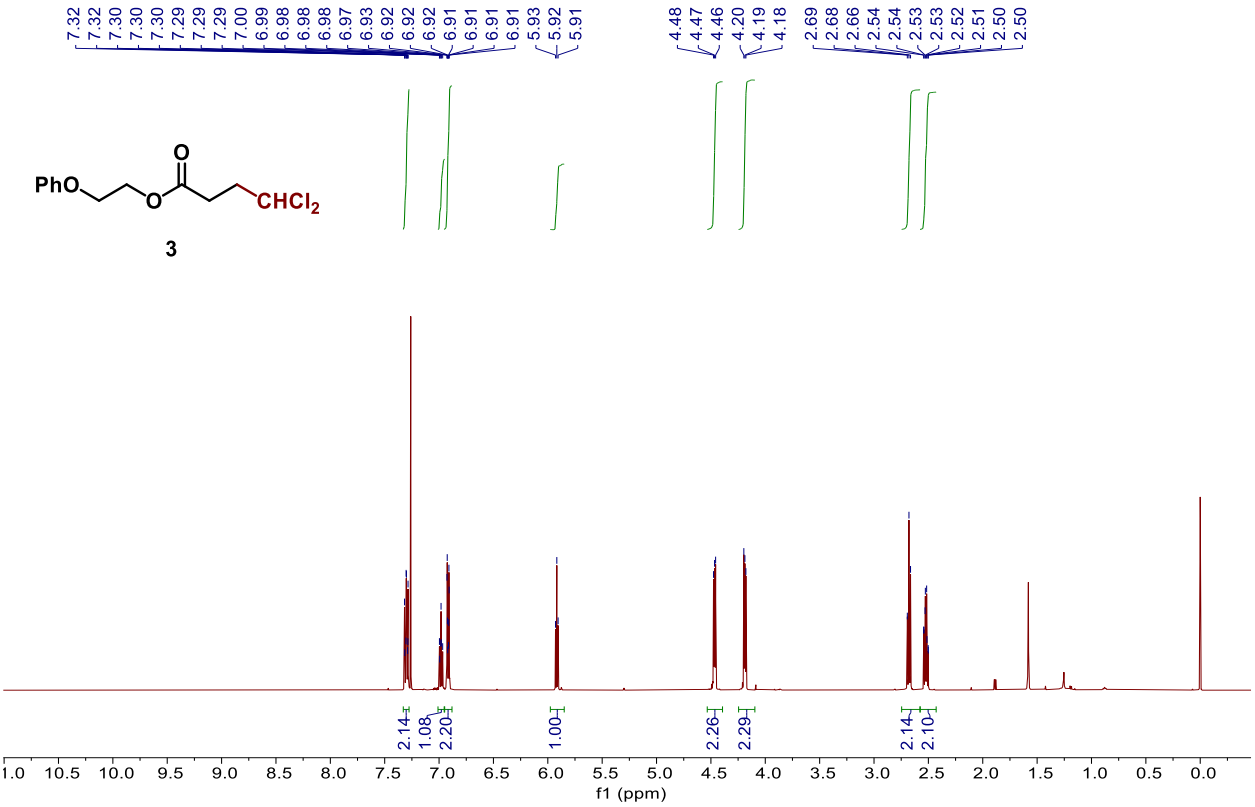
^{1}H NMR of 2 (500 MHz, $CDCl_3$)



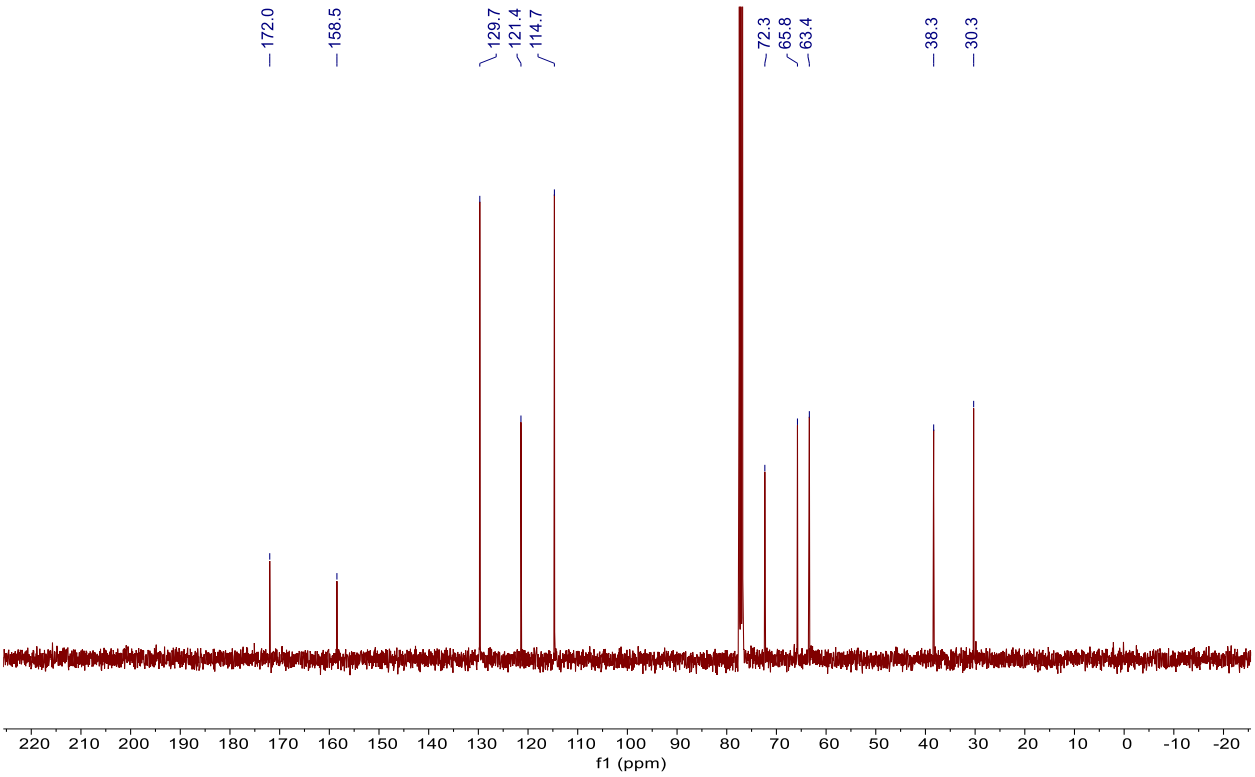
^{13}C NMR of 2 (126 MHz, $CDCl_3$)



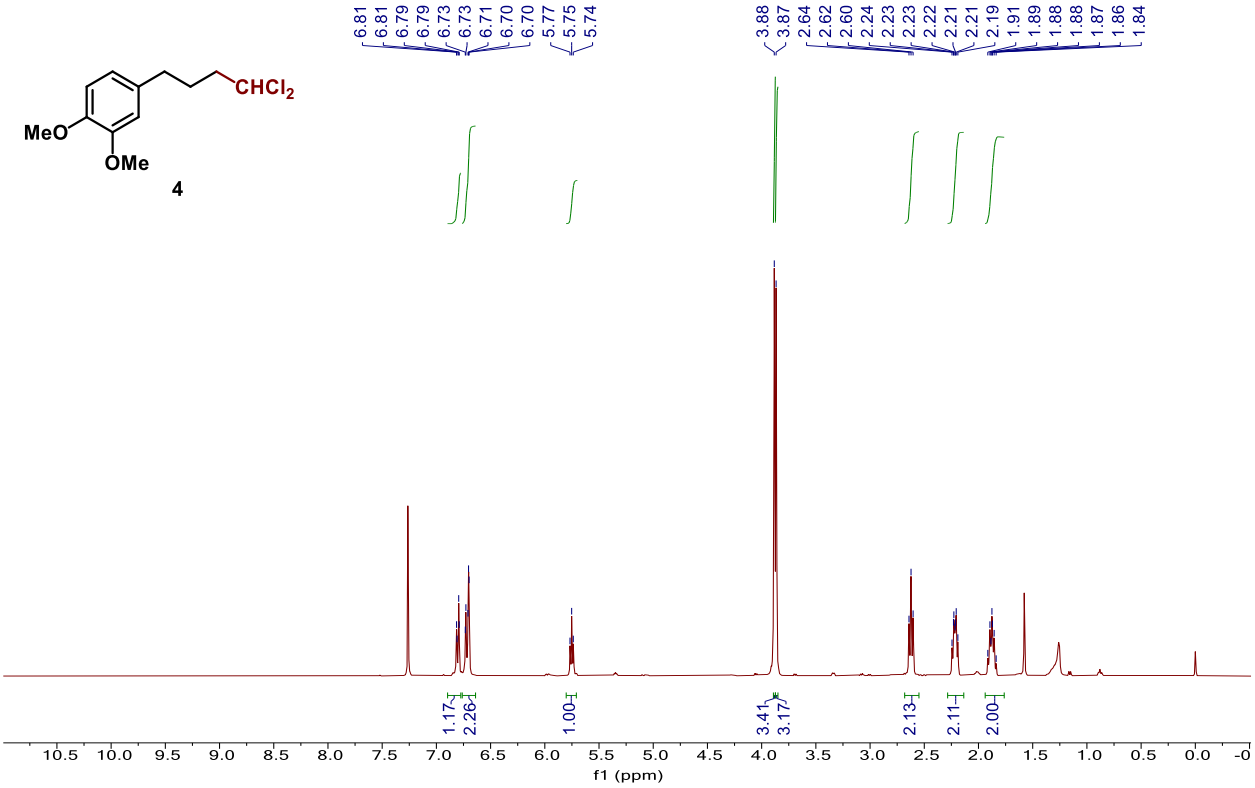
^{1}H NMR of 3 (500 MHz, $CDCl_3$)



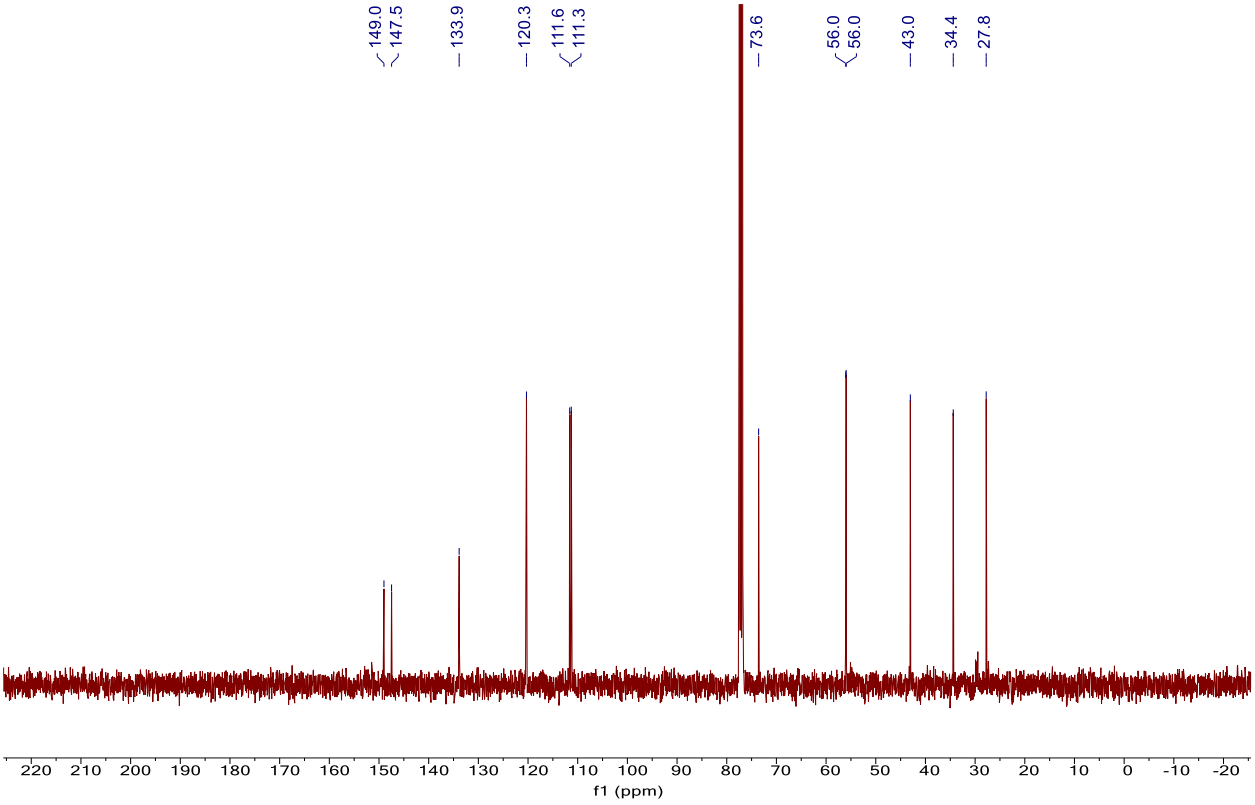
^{13}C NMR of 3 (101 MHz, $CDCl_3$)



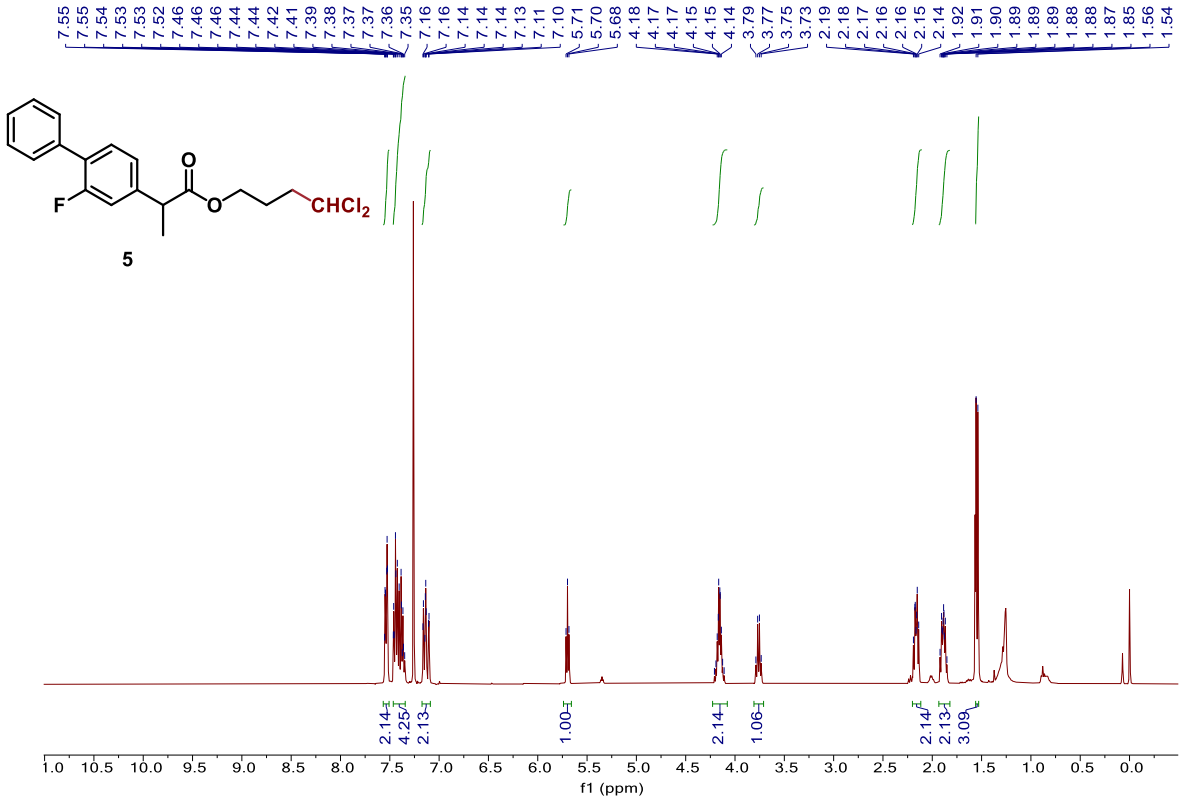
^{1}H NMR of 4 (500 MHz, $CDCl_3$)



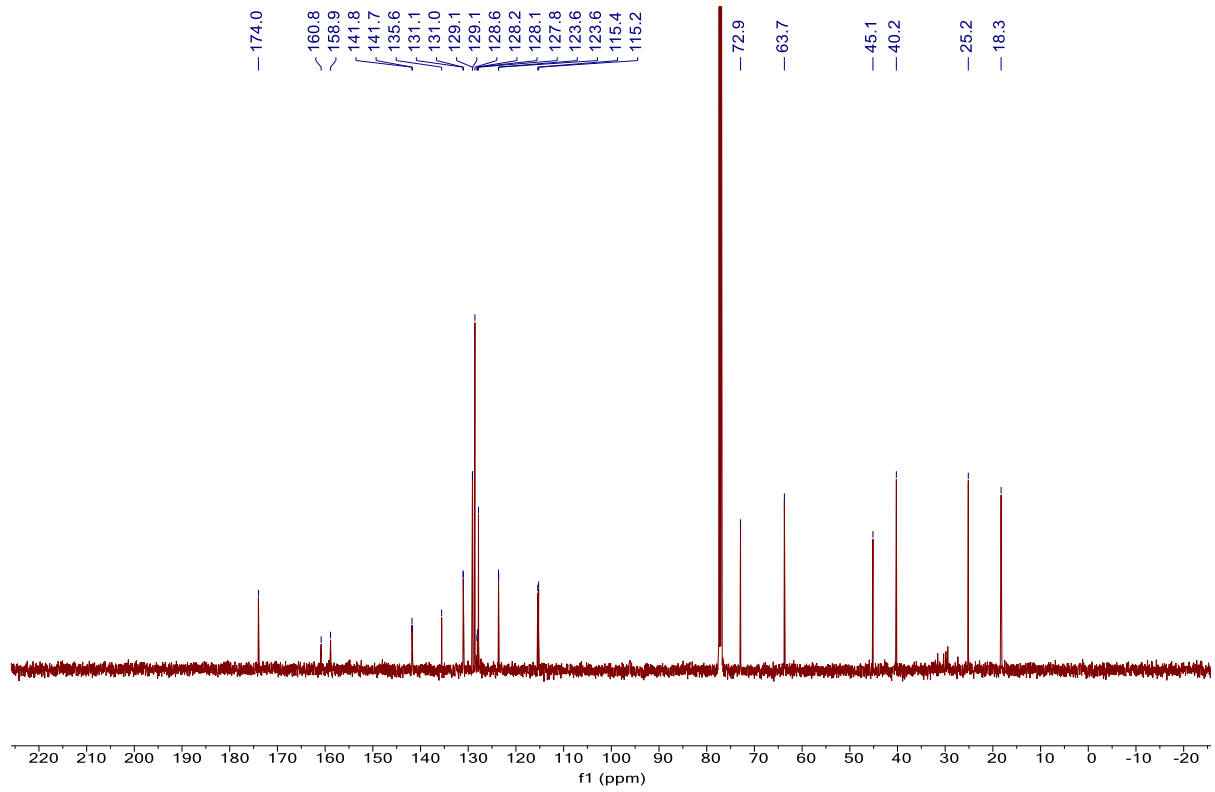
^{13}C NMR of 4 (101 MHz, $CDCl_3$)



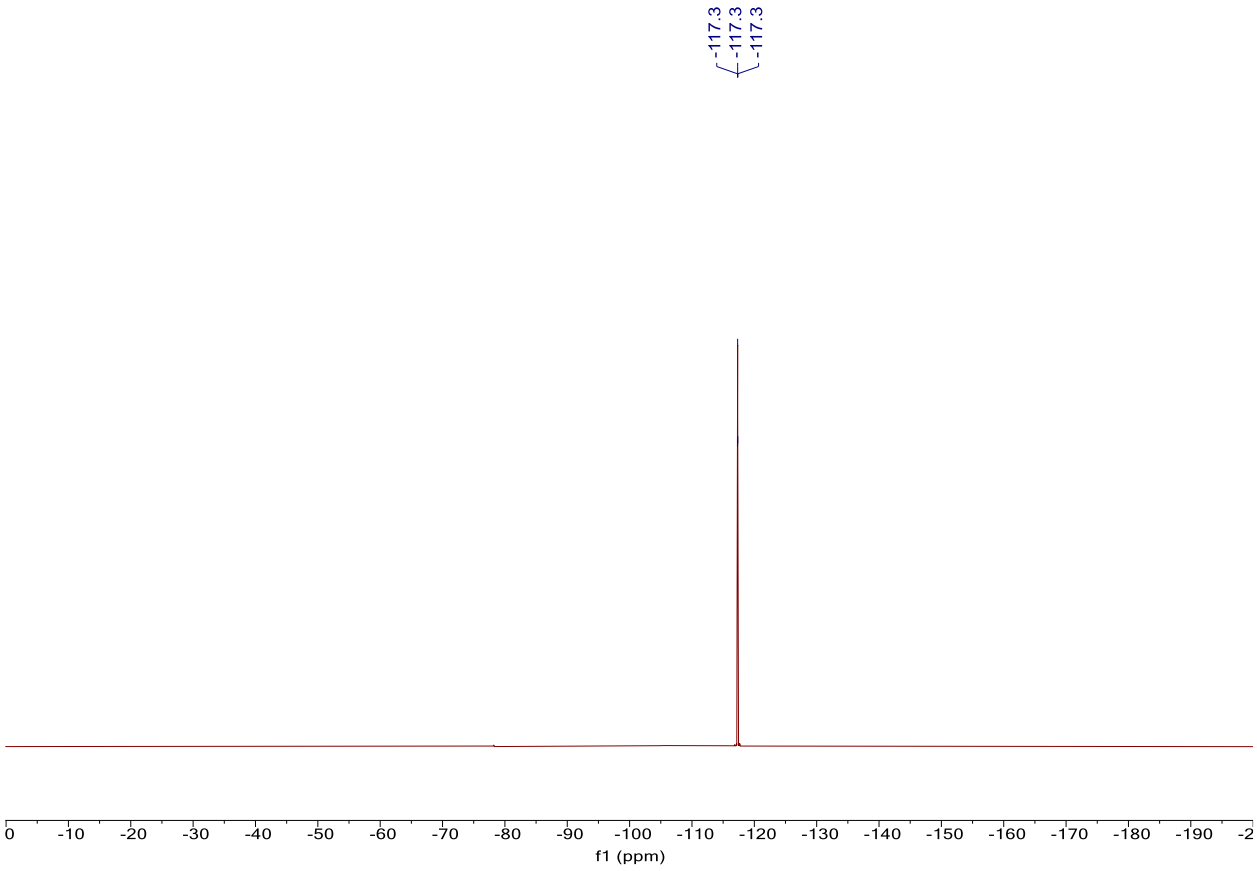
^{1}H NMR of 5 (400 MHz, $CDCl_3$)



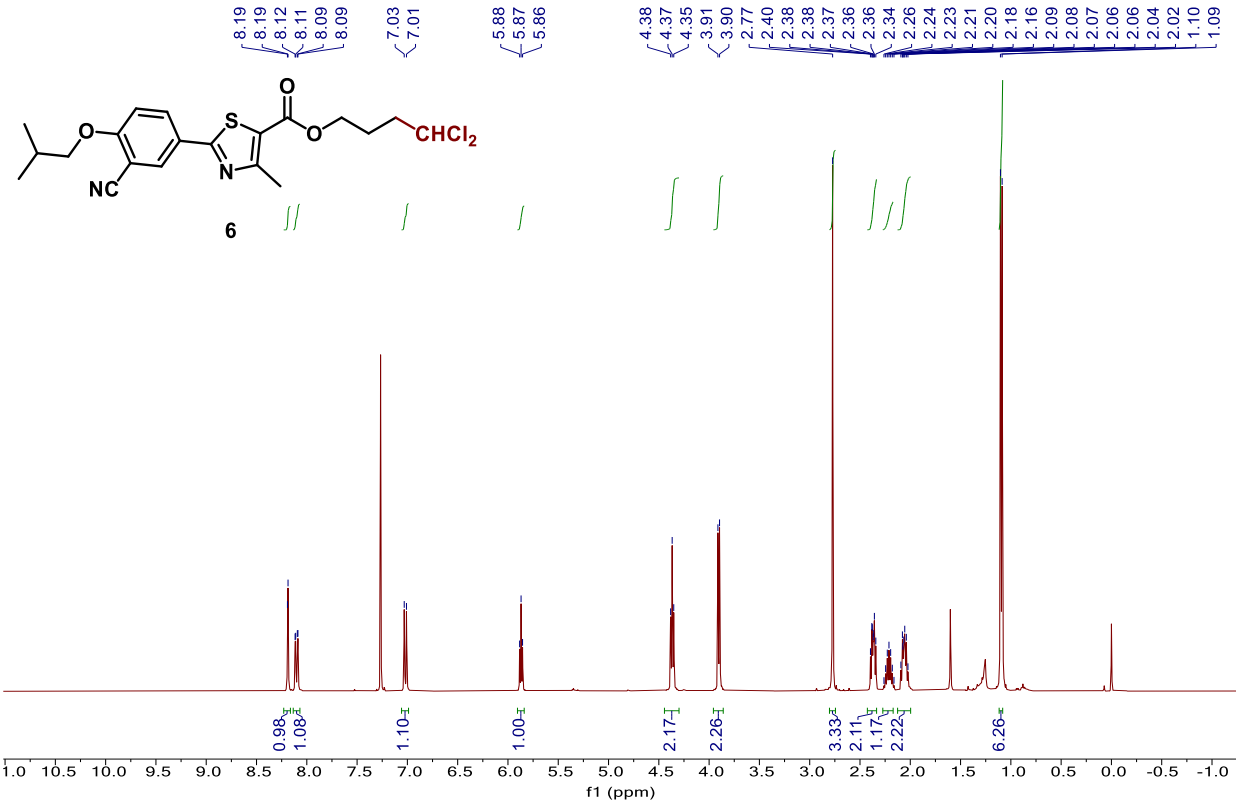
^{13}C NMR of 5 (126 MHz, $CDCl_3$)



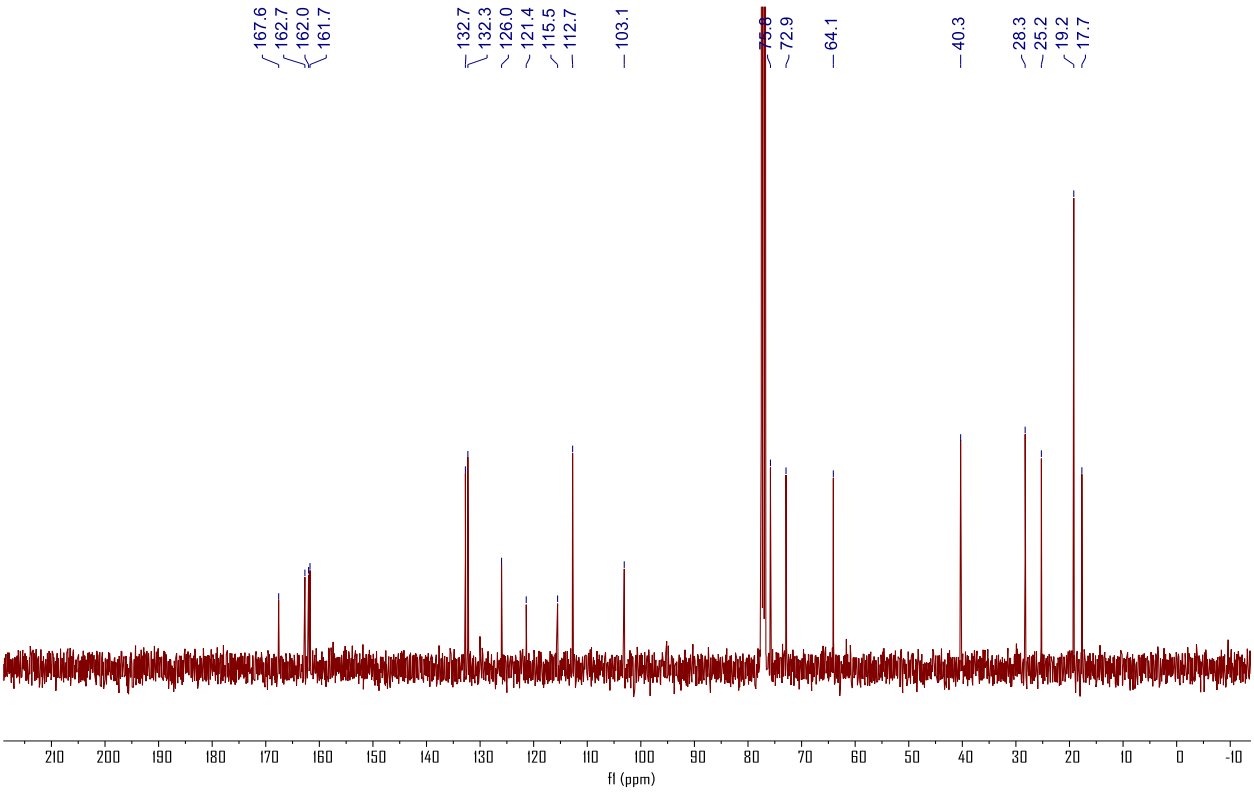
^{19}F NMR of 5 (471 MHz, $CDCl_3$)



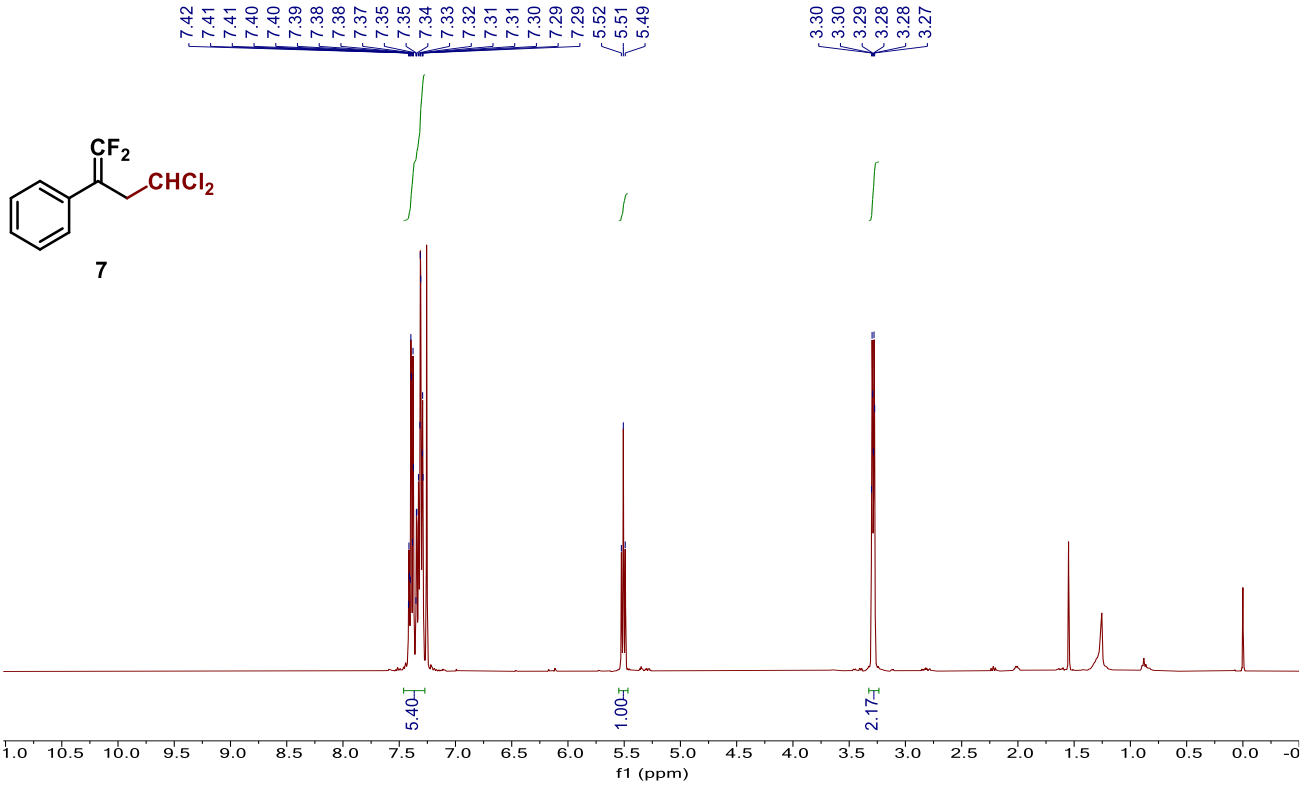
^{1}H NMR of 6 (400 MHz, $CDCl_3$)



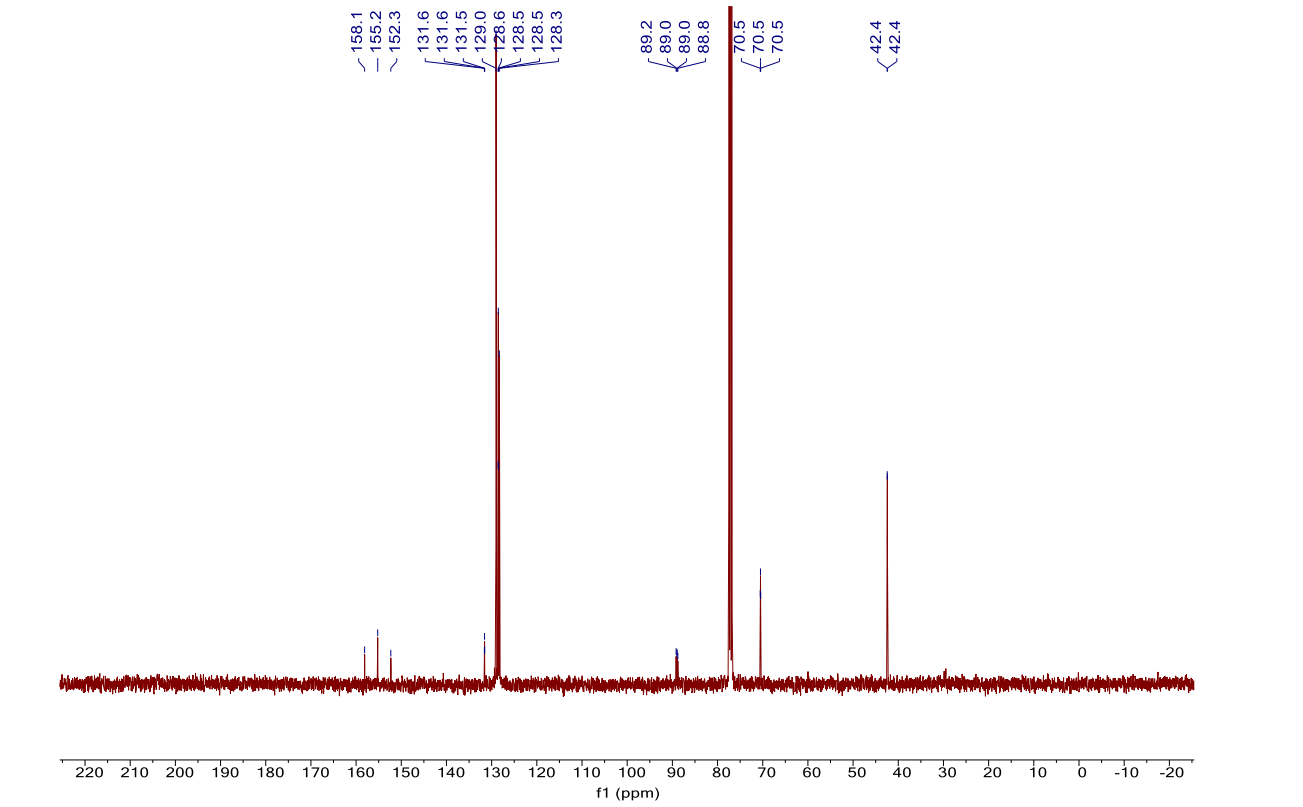
^{13}C NMR of 6 (101 MHz, $CDCl_3$)



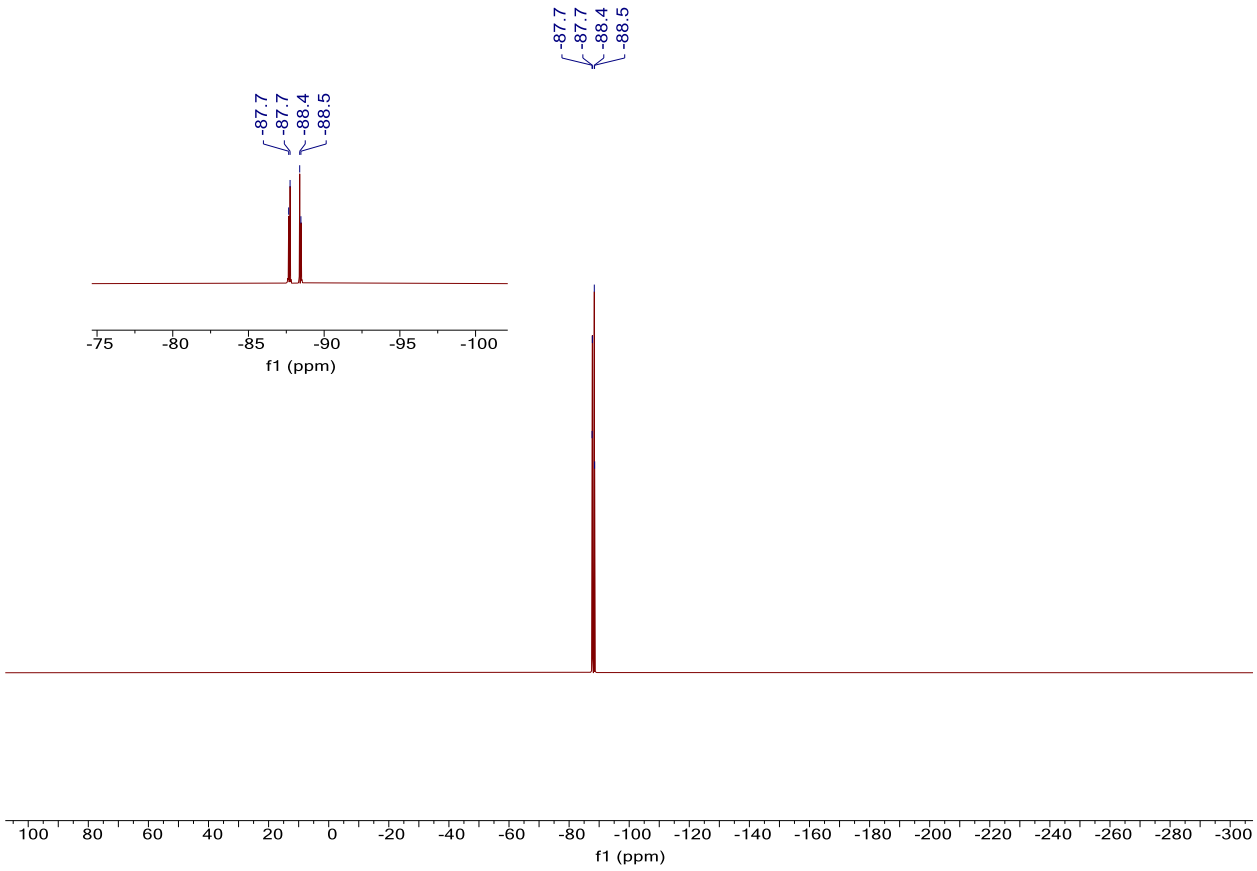
^{1}H NMR of 7 (500 MHz, $CDCl_3$)



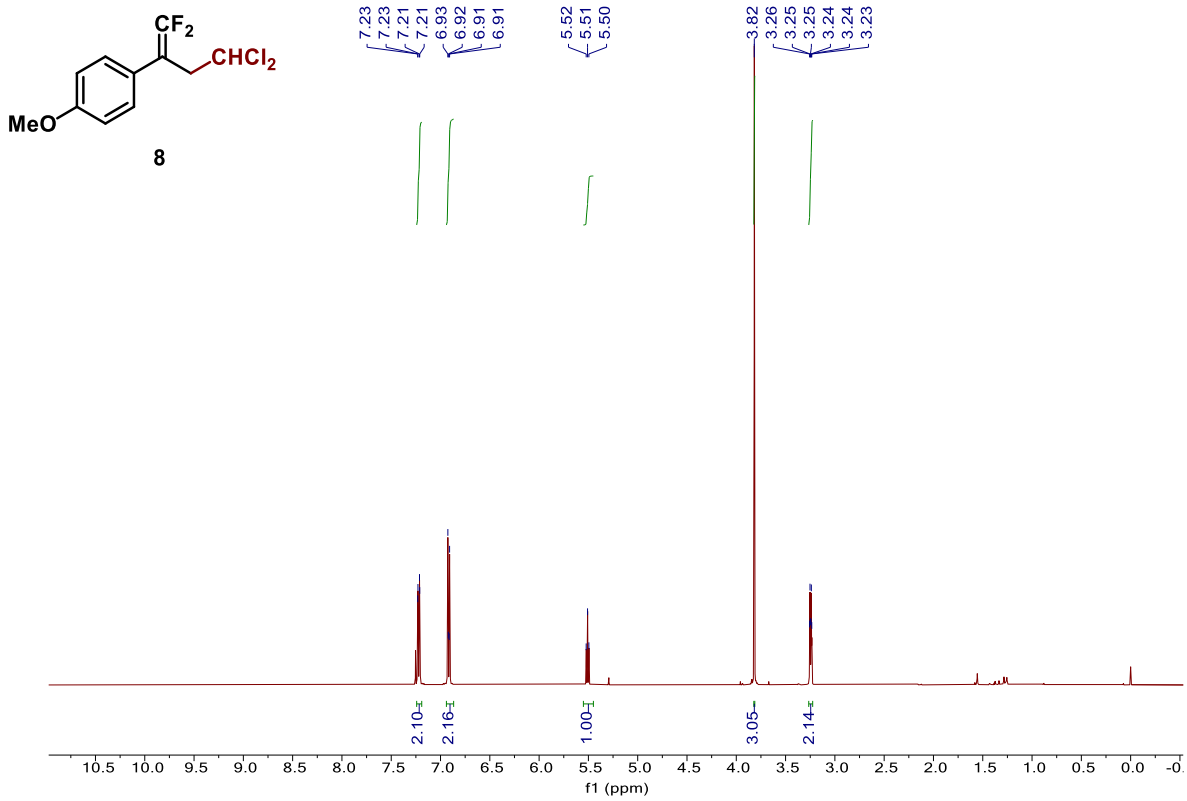
^{13}C NMR of 7 (126 MHz, $CDCl_3$)



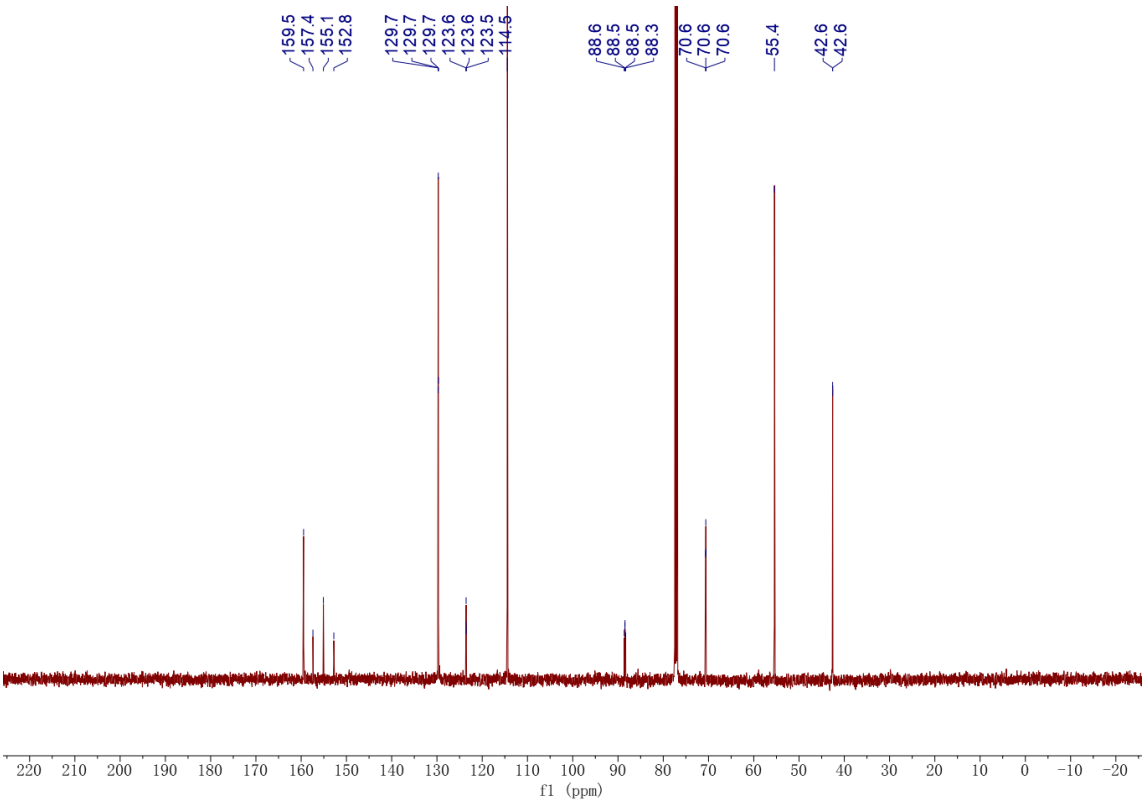
^{19}F NMR of 7 (376 MHz, $CDCl_3$)


-87.7
-87.7
-88.4
-88.5
-87.7
-87.7
-88.4
-88.5
-75
-80
-85
-90
-95
-100
f1 (ppm)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

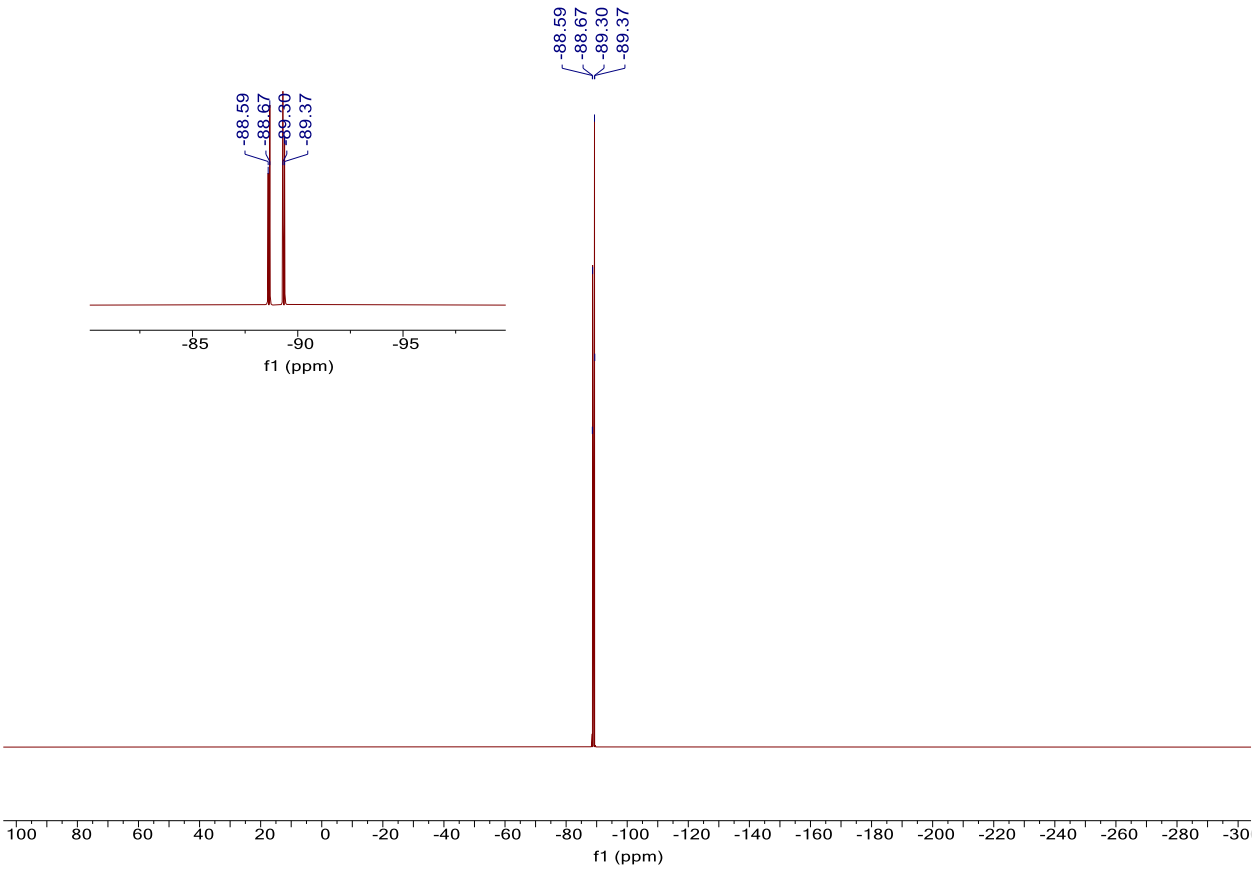
^{1}H NMR of 8 (500 MHz, $CDCl_3$)



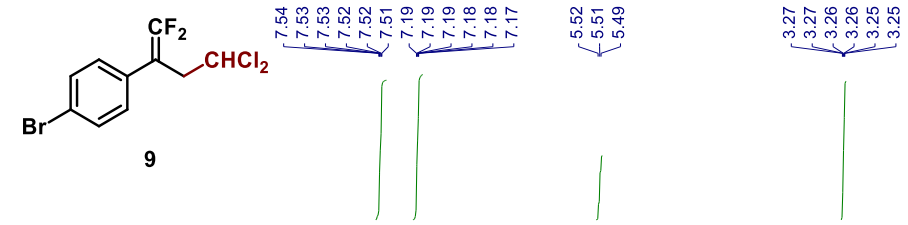
^{13}C NMR of 8 (126 MHz, $CDCl_3$)

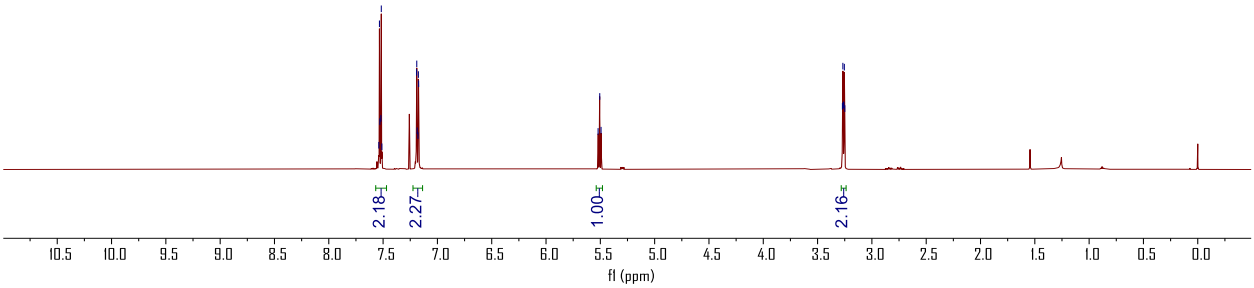


^{19}F NMR of 8 (471 MHz, $CDCl_3$)

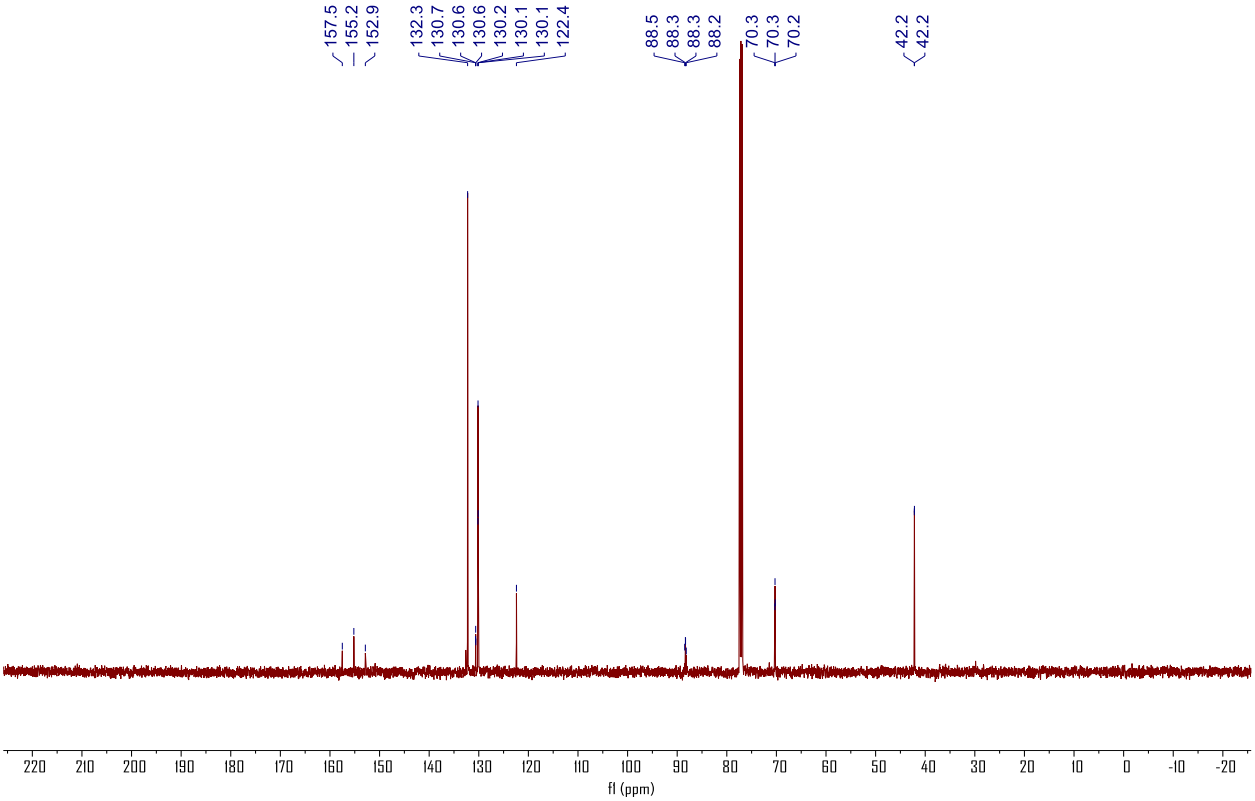


^{1}H NMR of 9 (500 MHz, $CDCl_3$)

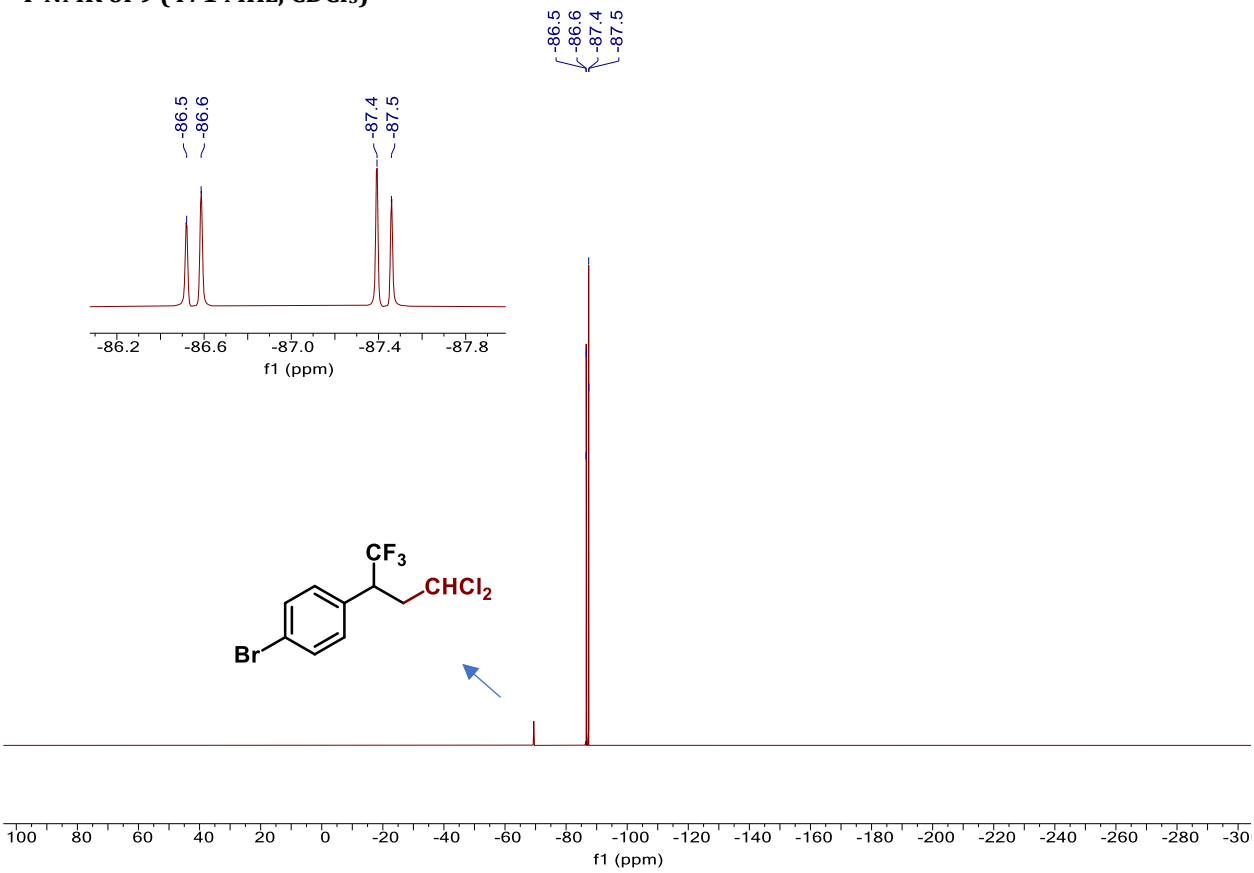




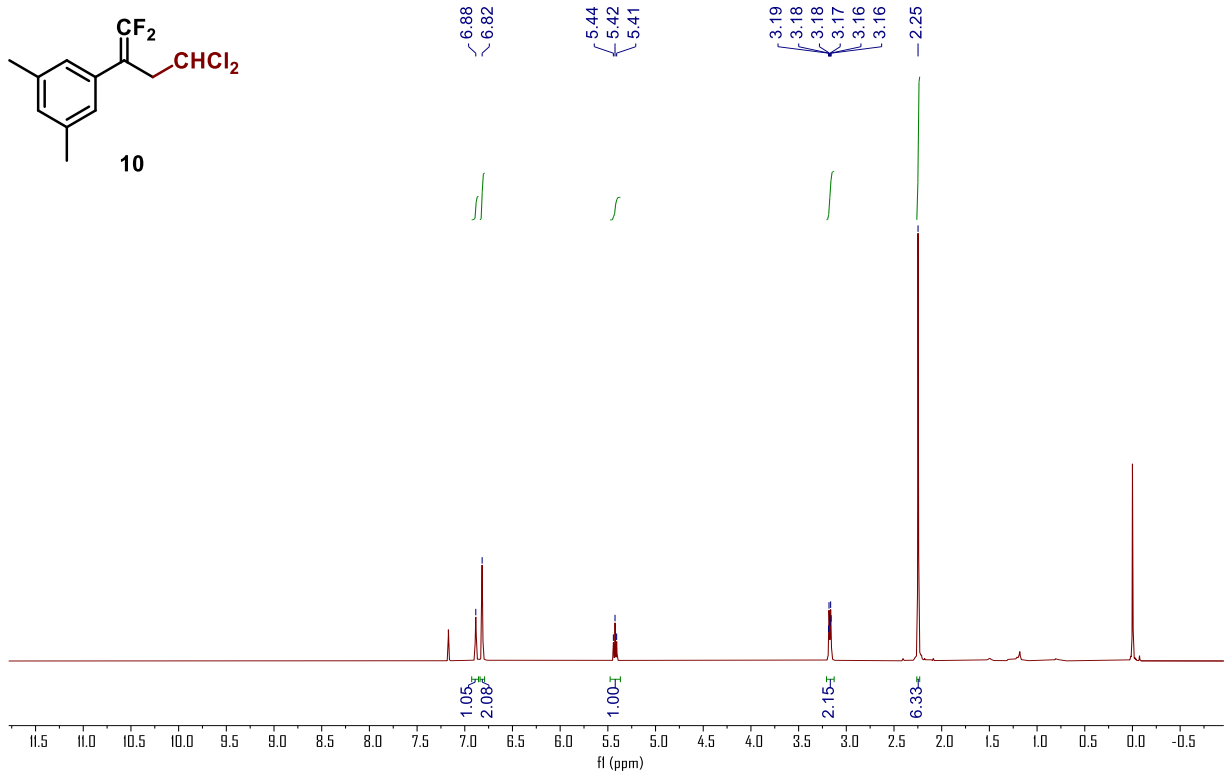
^{13}C NMR of 9 (126 MHz, $CDCl_3$)



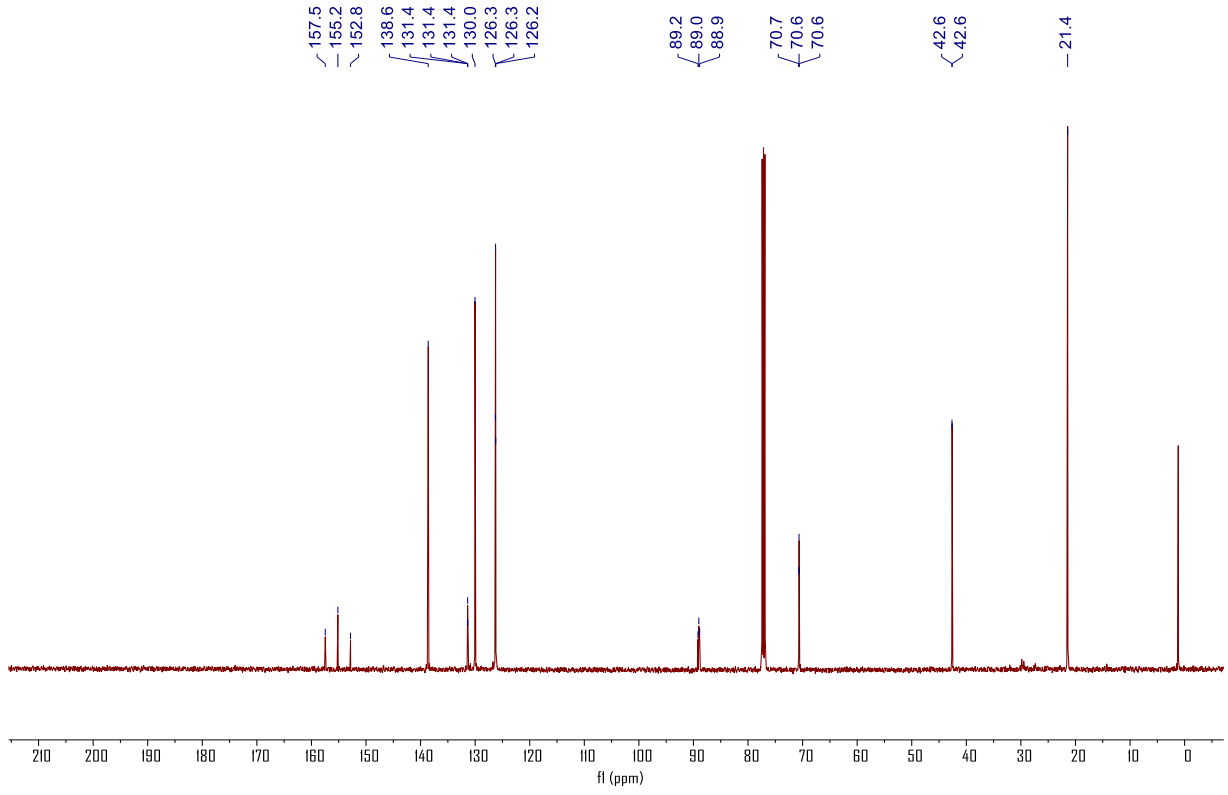
^{19}F NMR of 9 (471 MHz, $CDCl_3$)



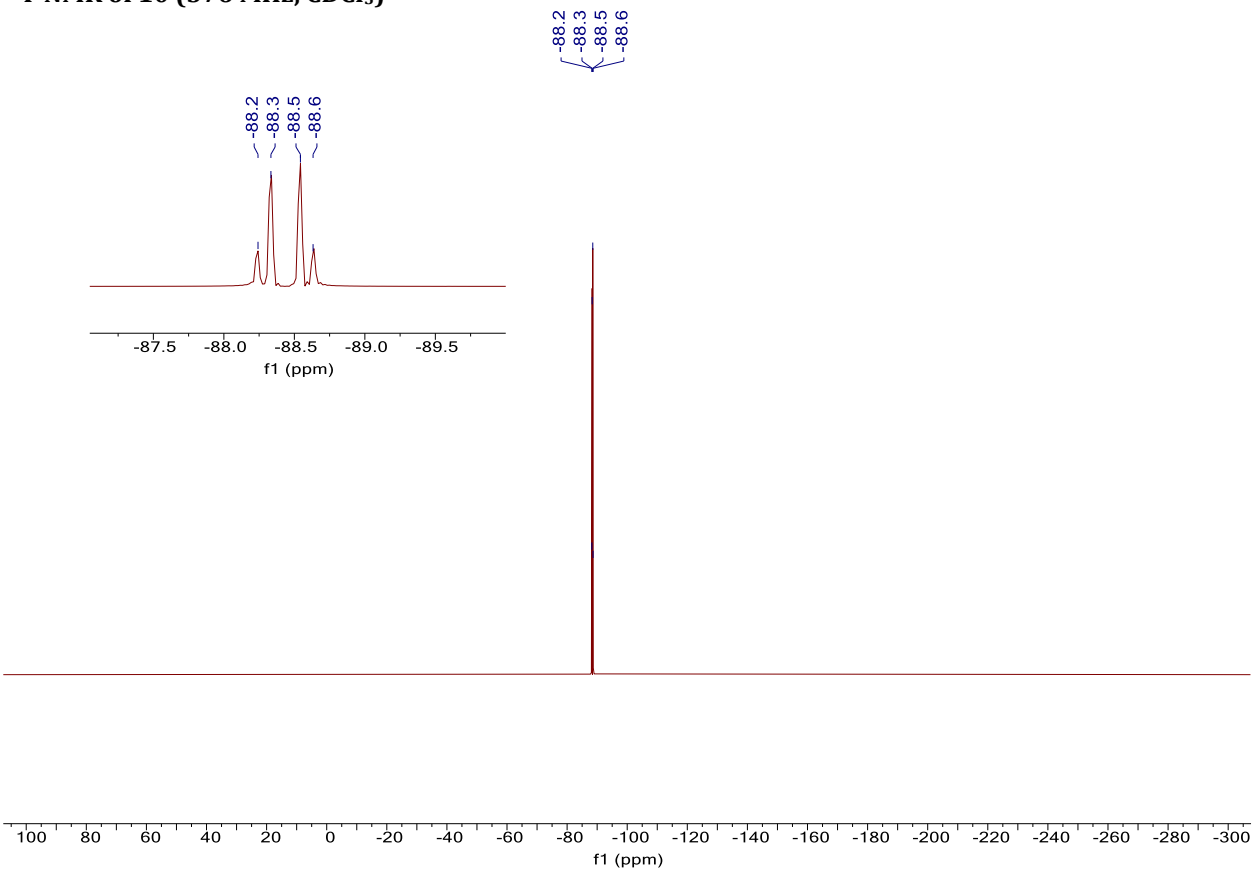
^{1}H NMR of 10 (400 MHz, $CDCl_3$)



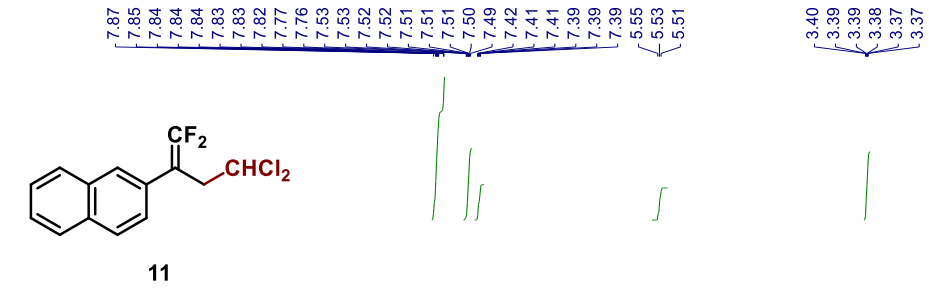
^{13}C NMR of 10 (126 MHz, $CDCl_3$)



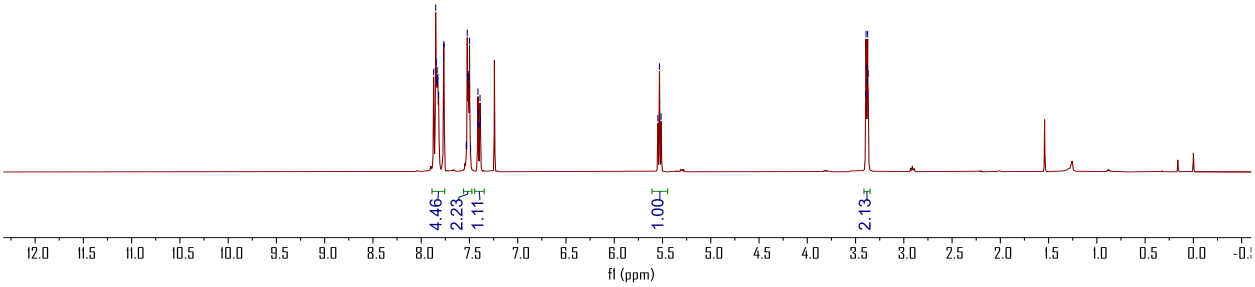
^{19}F NMR of 10 (376 MHz, $CDCl_3$)



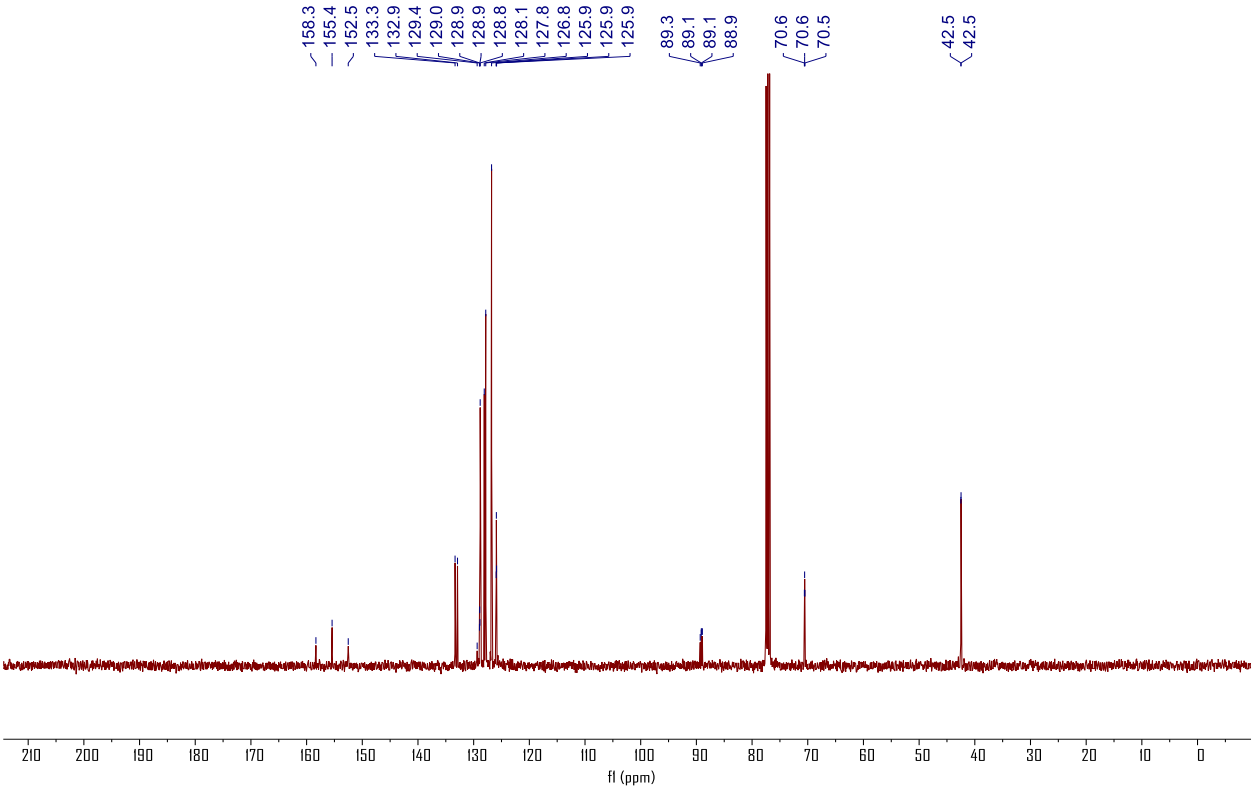
^{1}H NMR of 11 (400 MHz, $CDCl_3$)



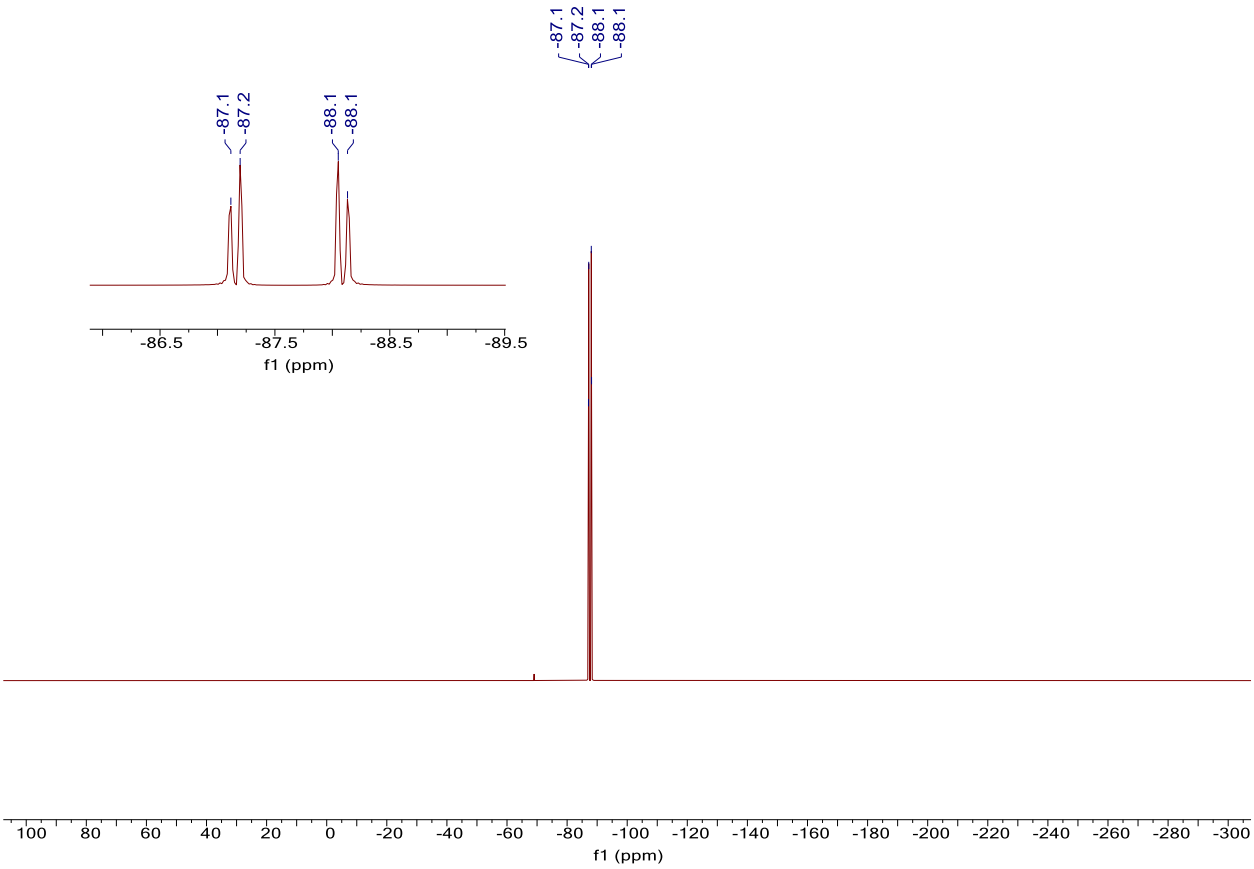
11



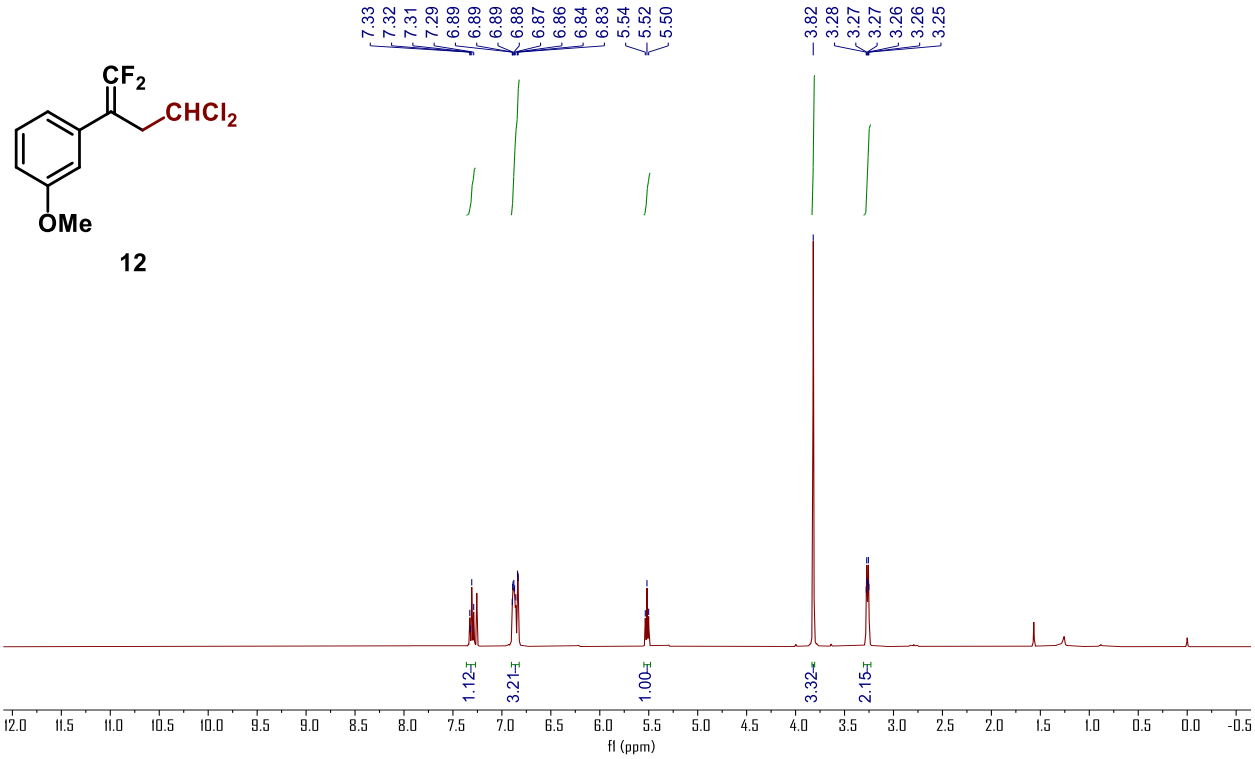
^{13}C NMR of 11 (101 MHz, $CDCl_3$)



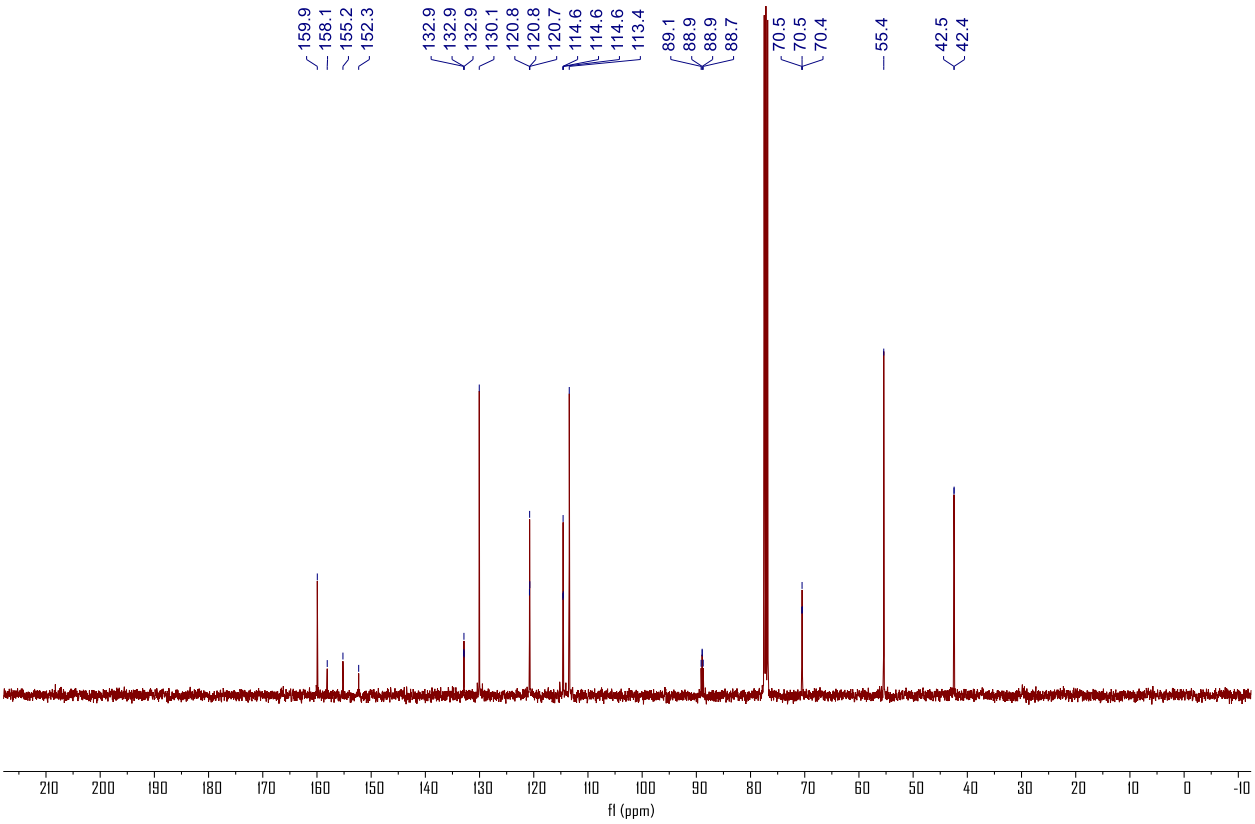
^{19}F NMR of 11 (376 MHz, $CDCl_3$)



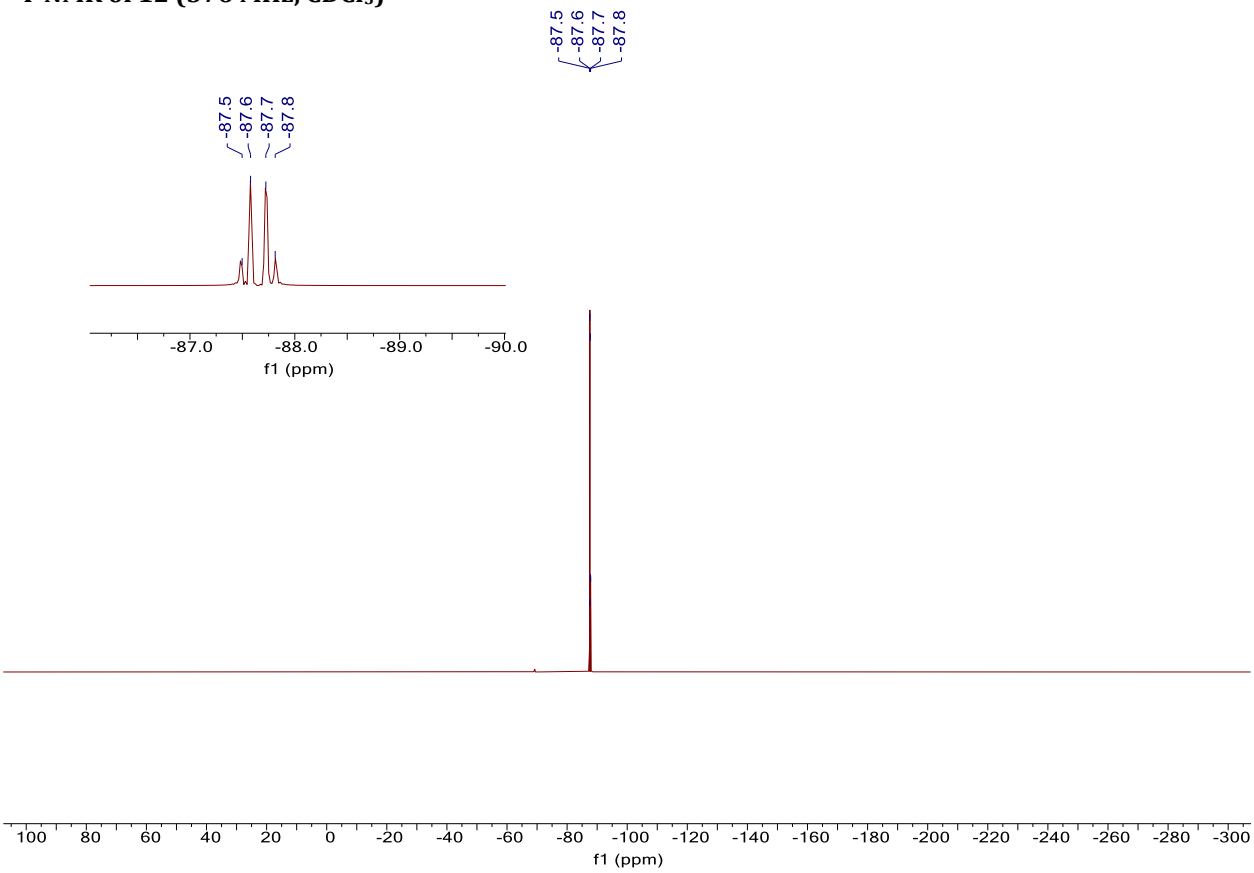
^{1}H NMR of 12 (400 MHz, $CDCl_3$)



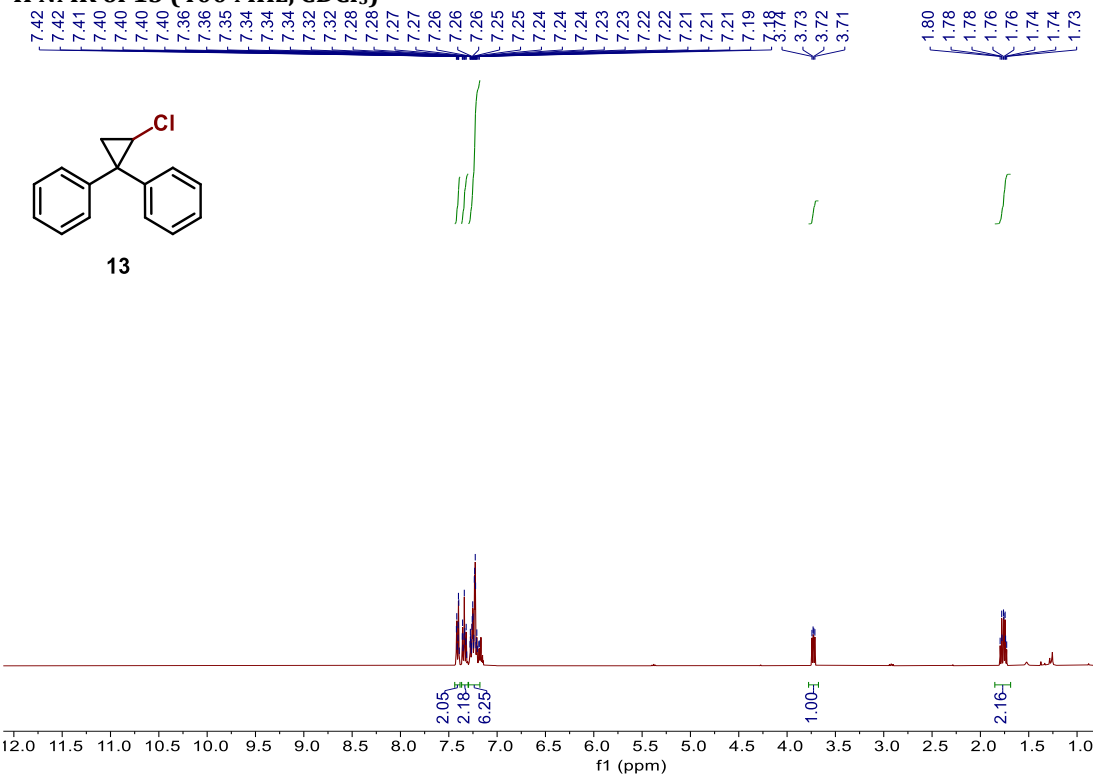
^{13}C NMR of 12 (101 MHz, $CDCl_3$)



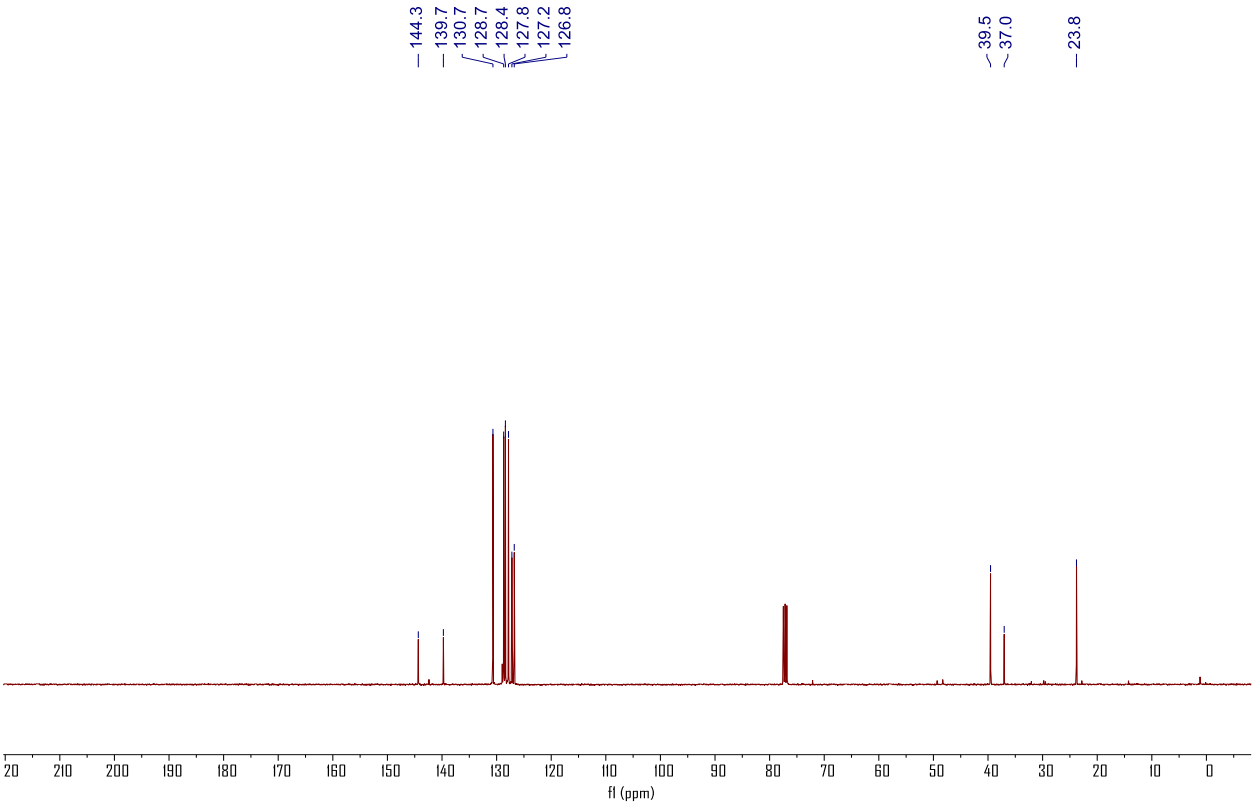
^{19}F NMR of 12 (376 MHz, $CDCl_3$)



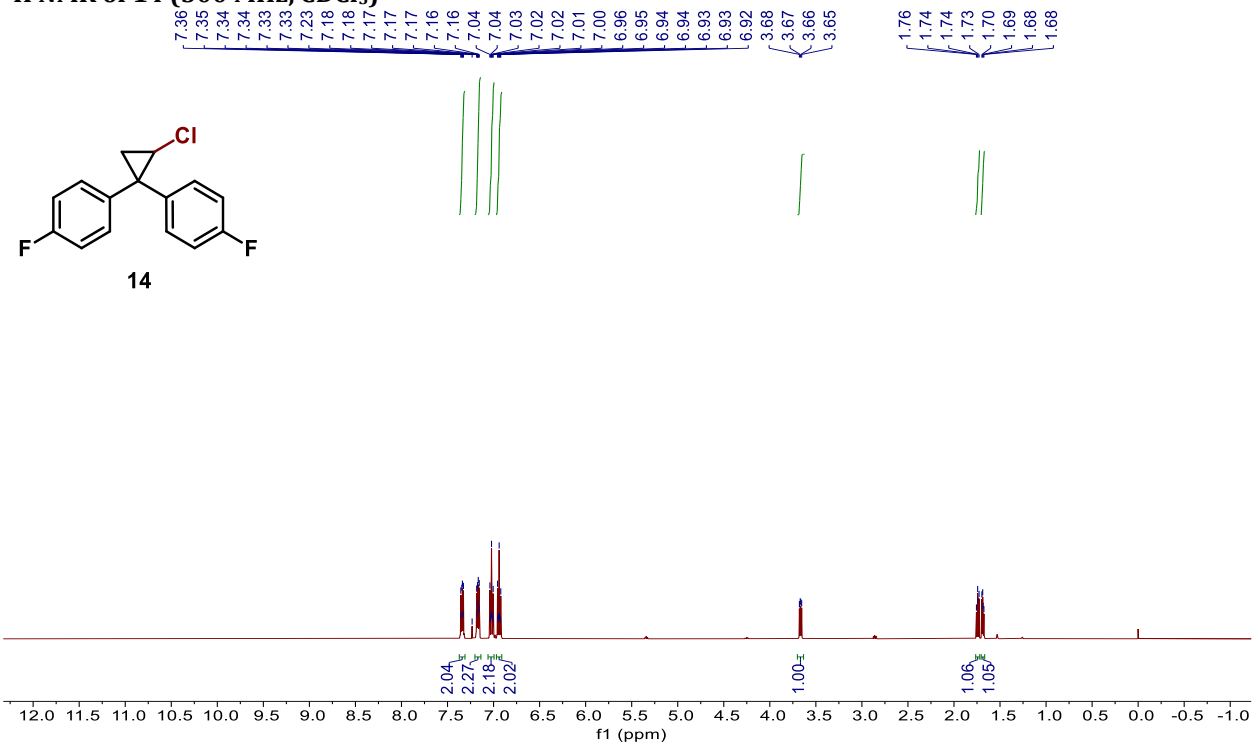
^{1}H NMR of 13 (400 MHz, $CDCl_3$)



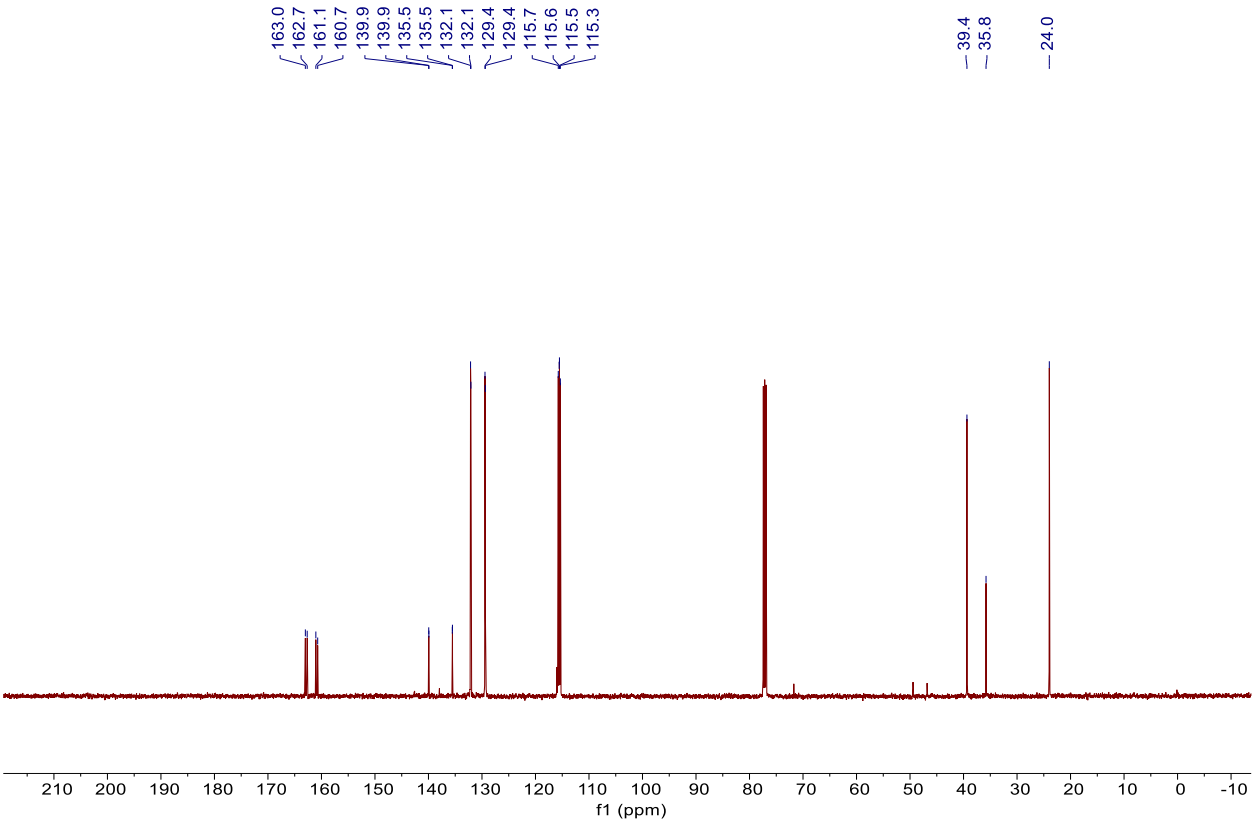
^{13}C NMR of 13 (101 MHz, $CDCl_3$)



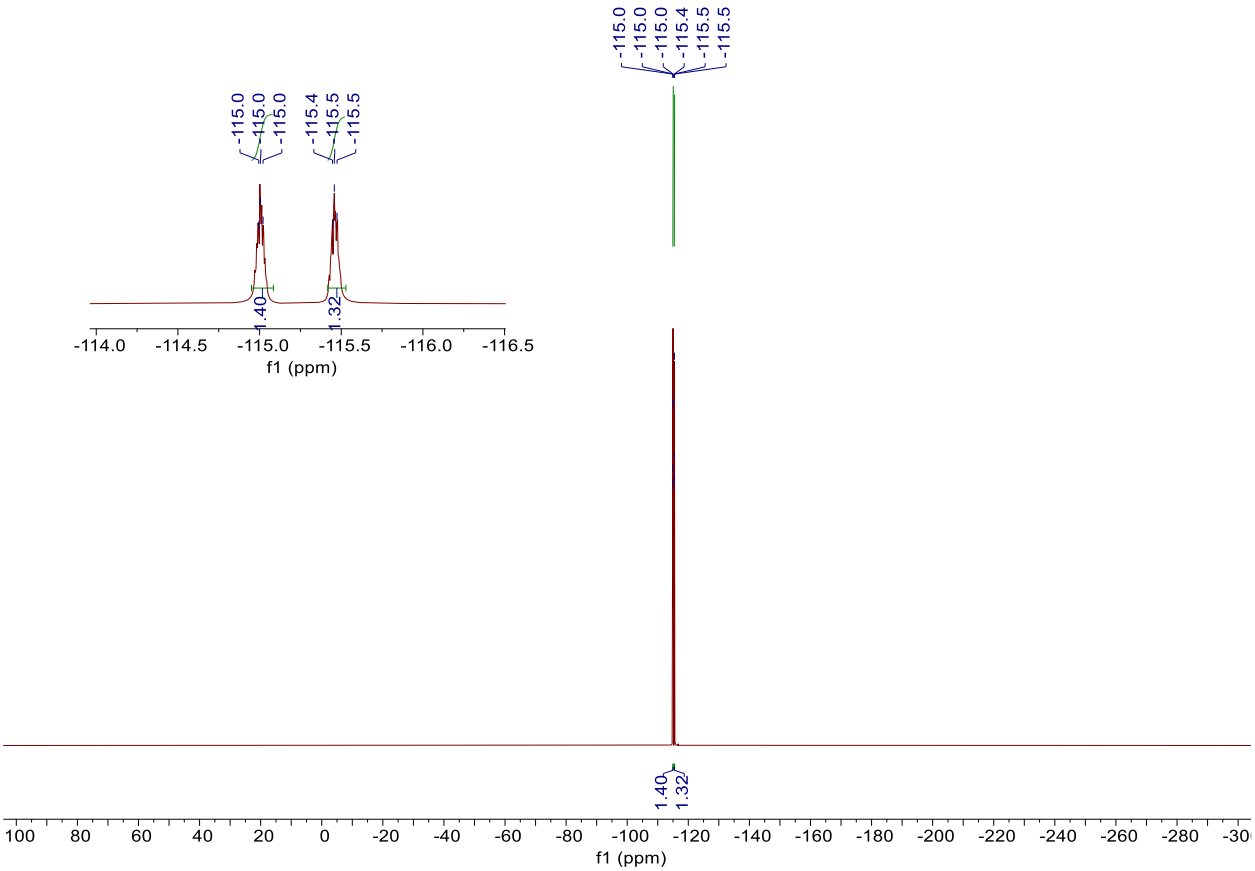
^{1}H NMR of 14 (500 MHz, $CDCl_3$)



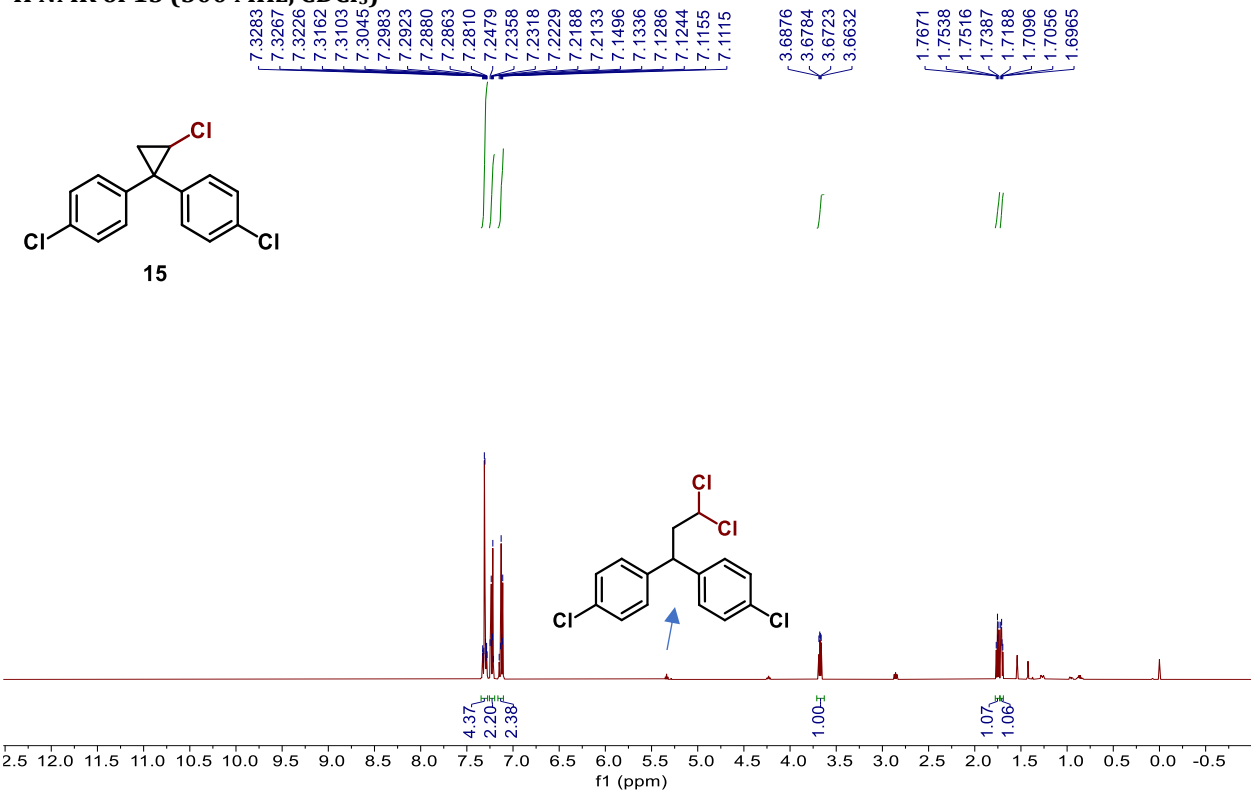
^{13}C NMR of 14 (126 MHz, $CDCl_3$)



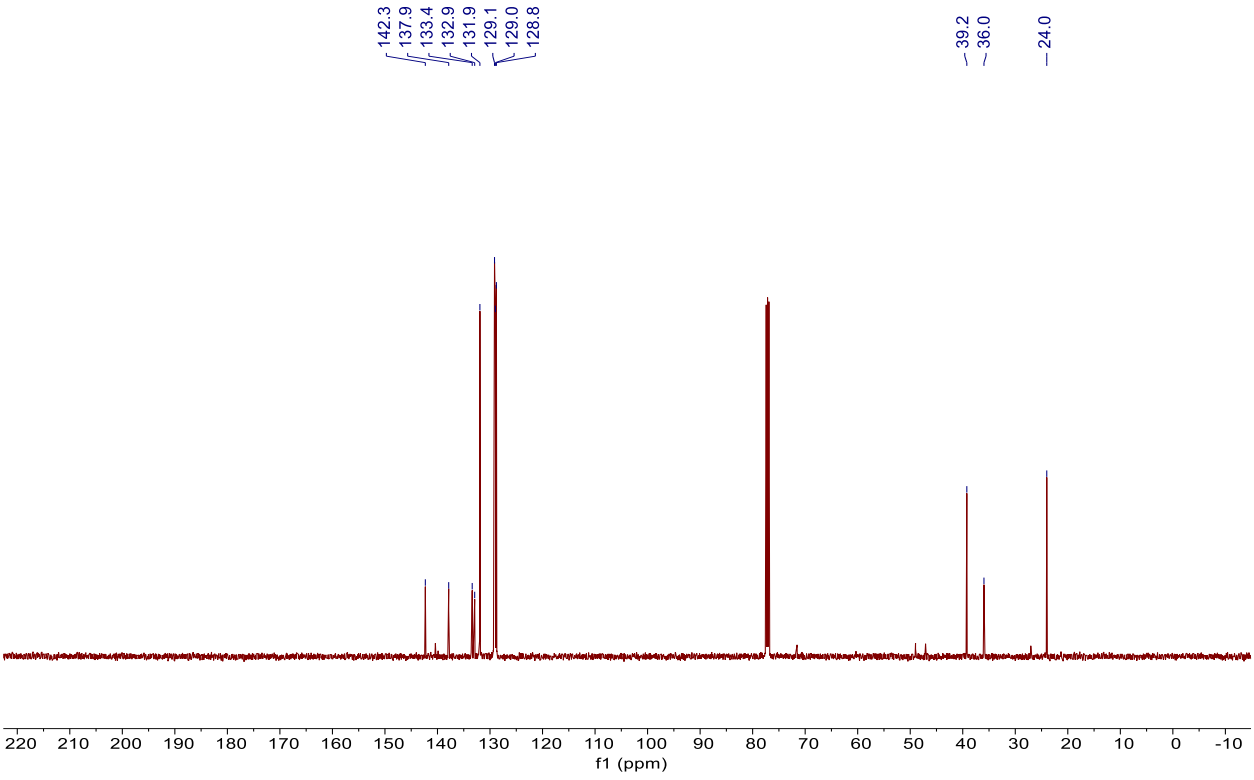
^{19}F NMR of 14 (471 MHz, $CDCl_3$)



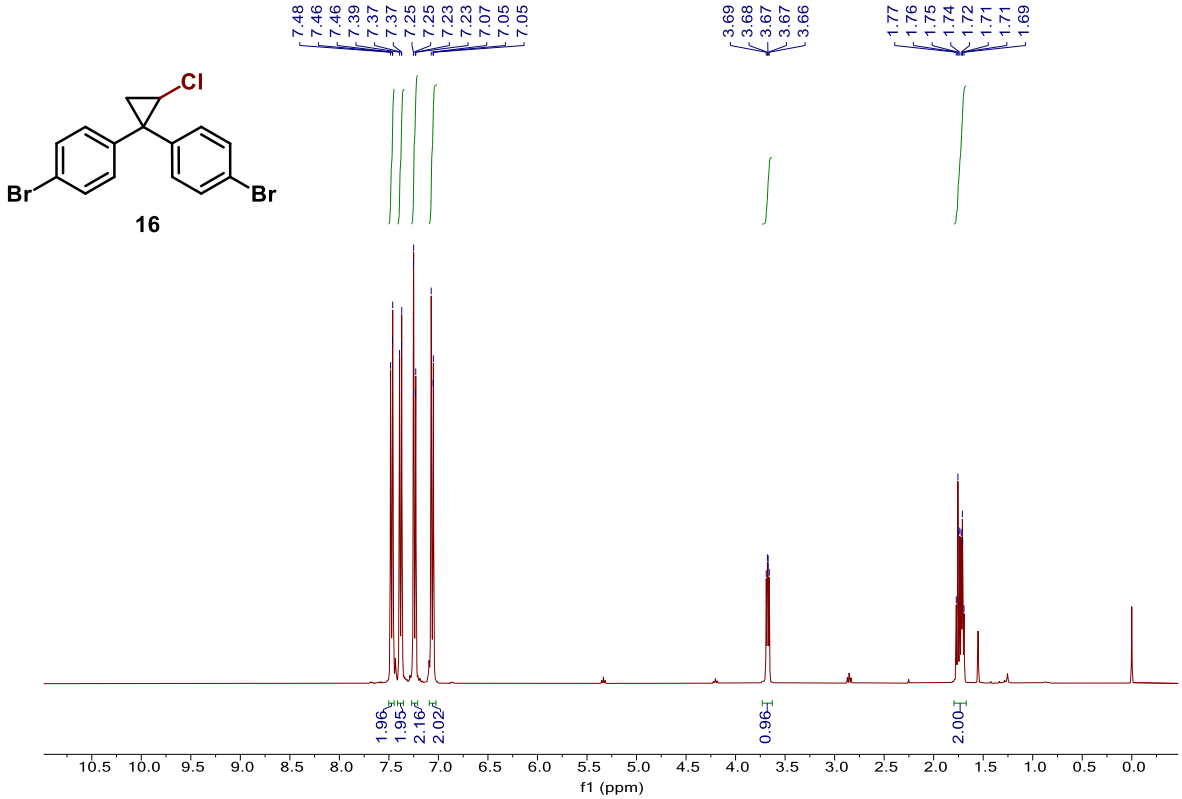
^{1}H NMR of 15 (500 MHz, $CDCl_3$)



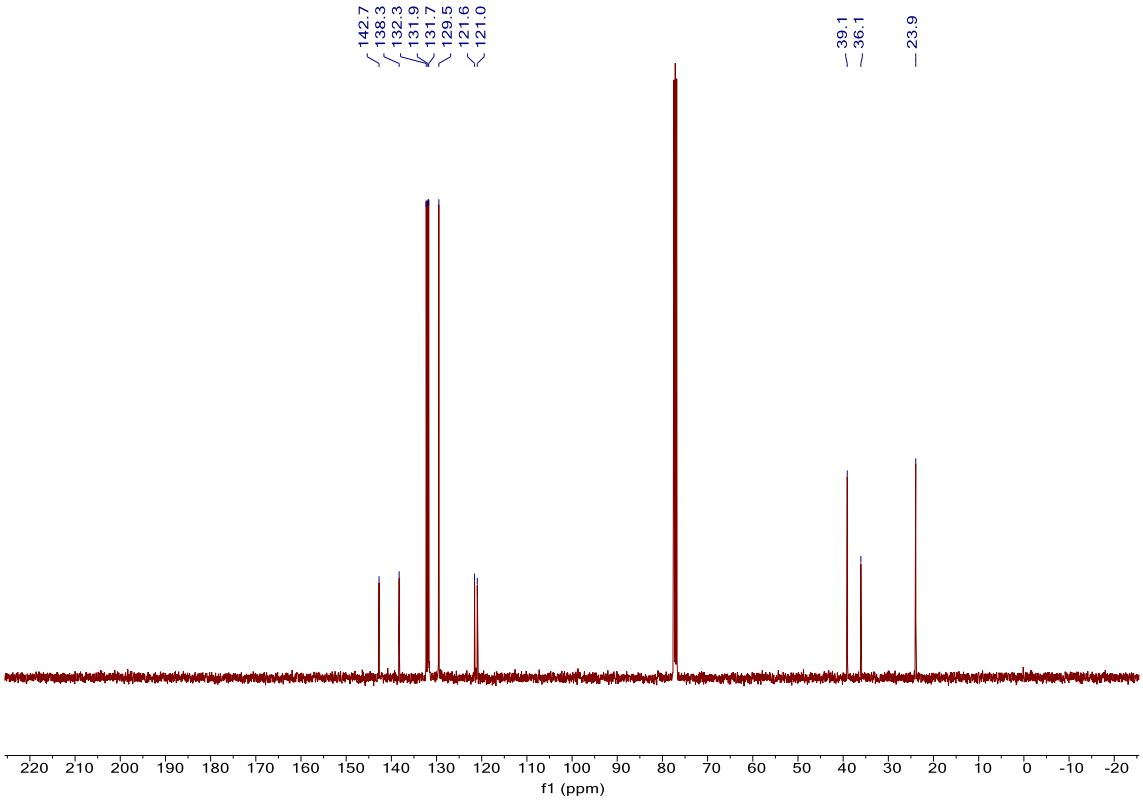
^{13}C NMR of 15 (126 MHz, $CDCl_3$)



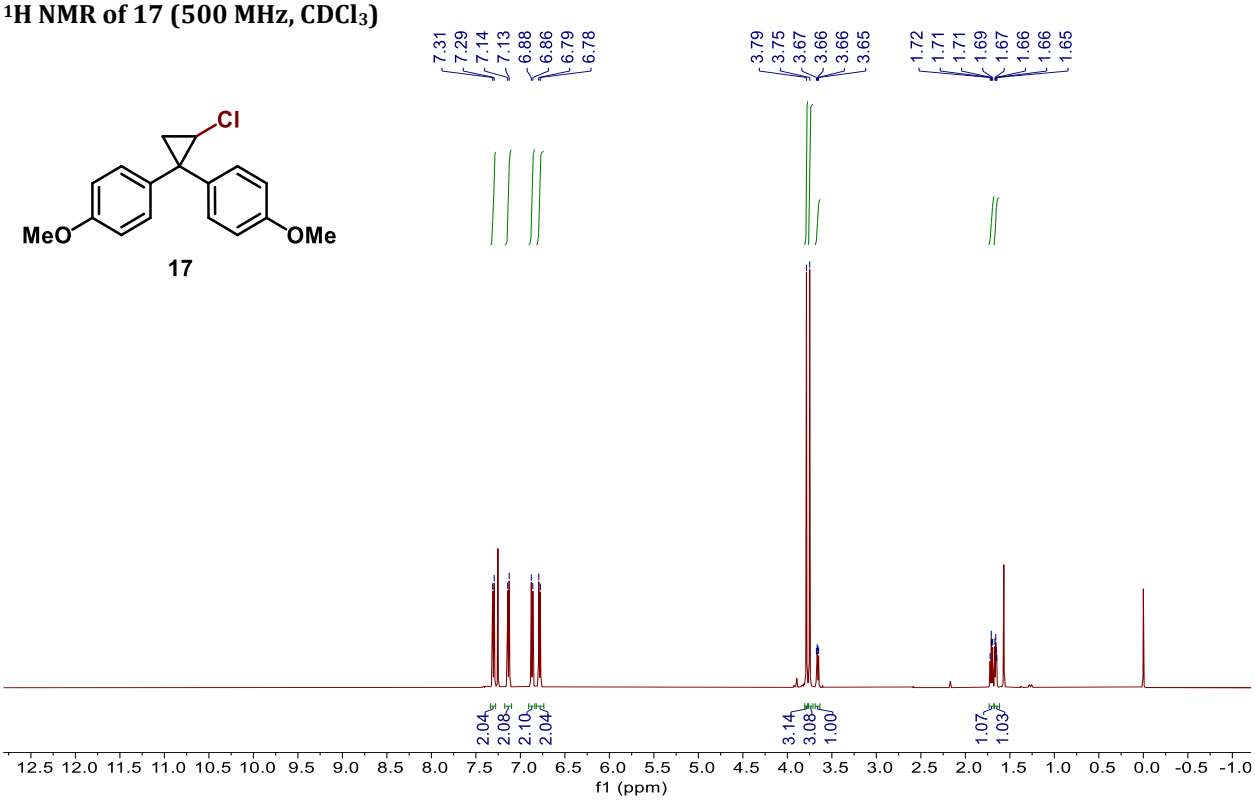
^{1}H NMR of 16 (500 MHz, $CDCl_3$)



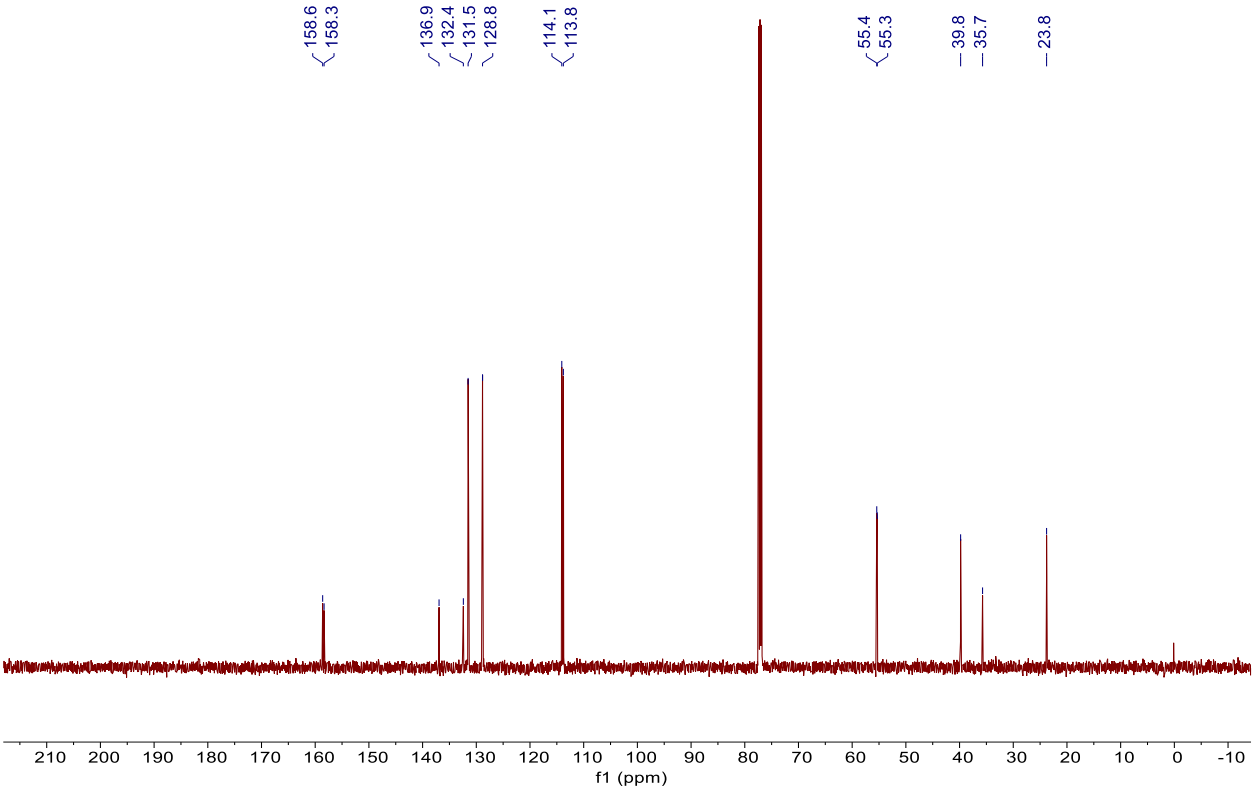
^{13}C NMR of 16 (126 MHz, $CDCl_3$)



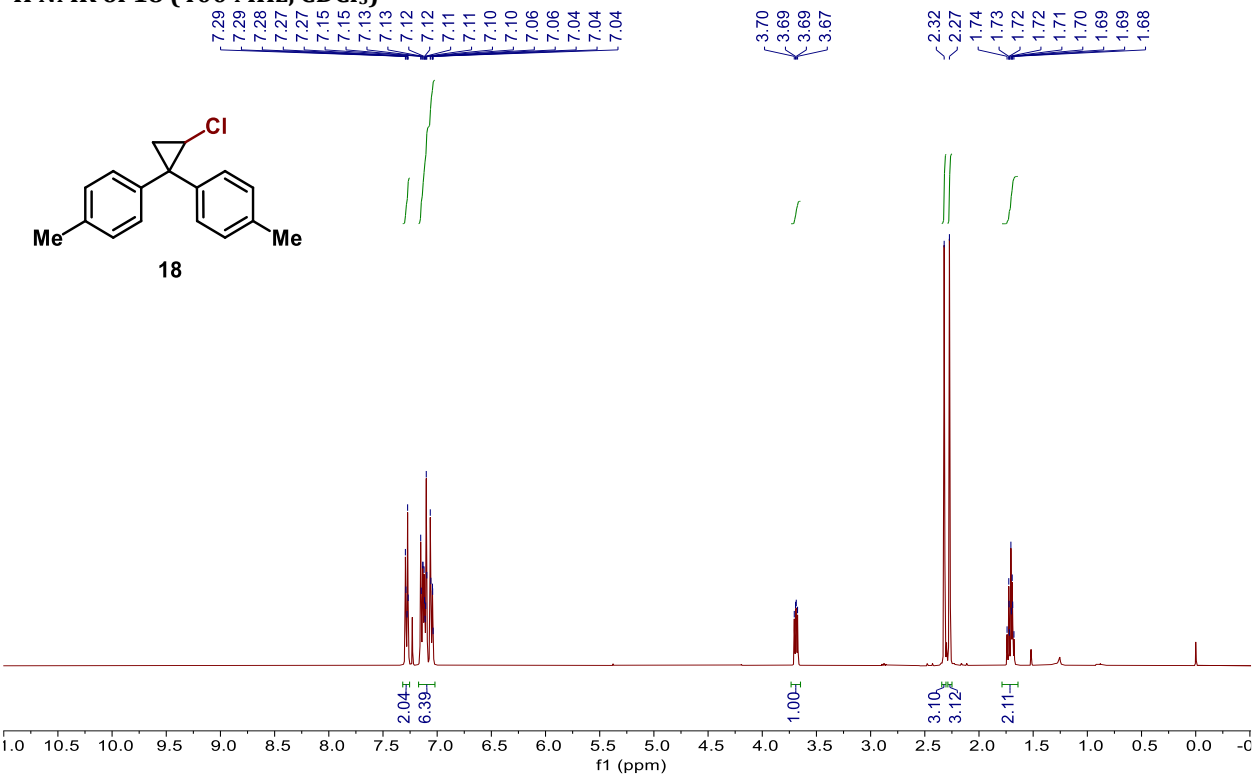
^{1}H NMR of 17 (500 MHz, $CDCl_3$)



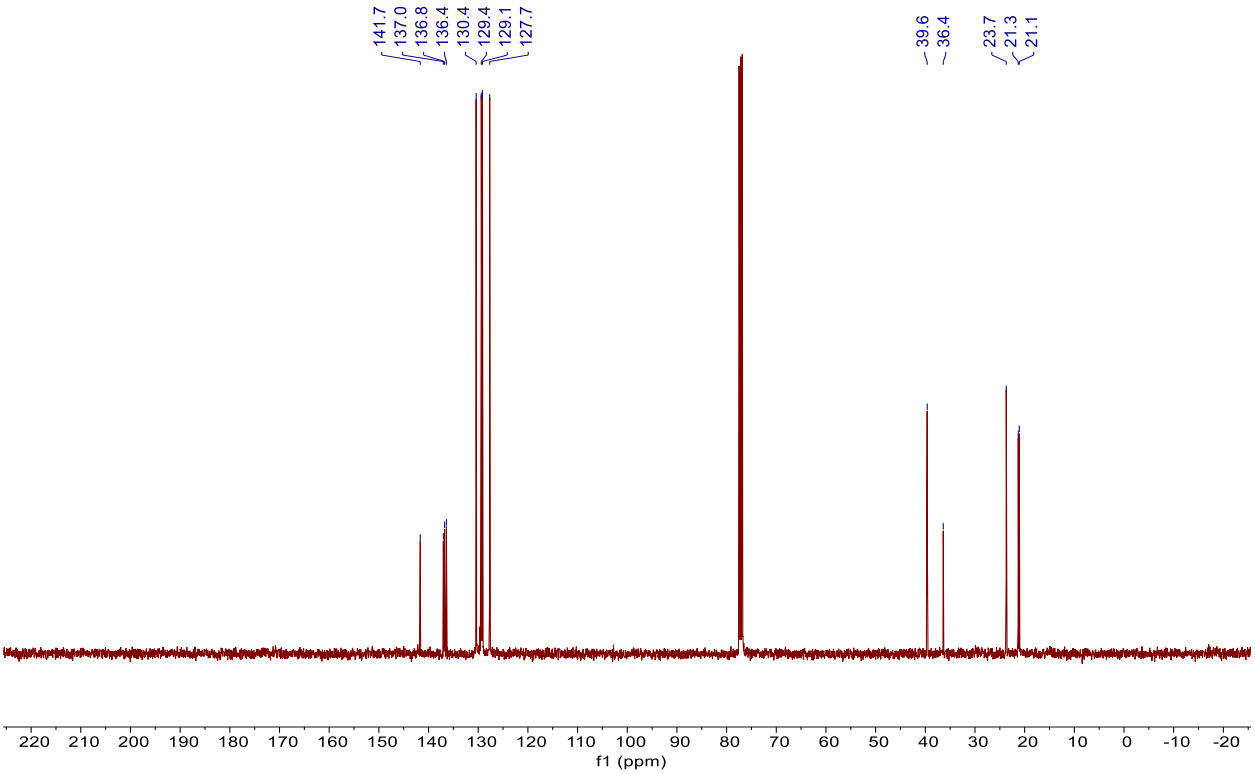
^{13}C NMR of 17 (126 MHz, $CDCl_3$)



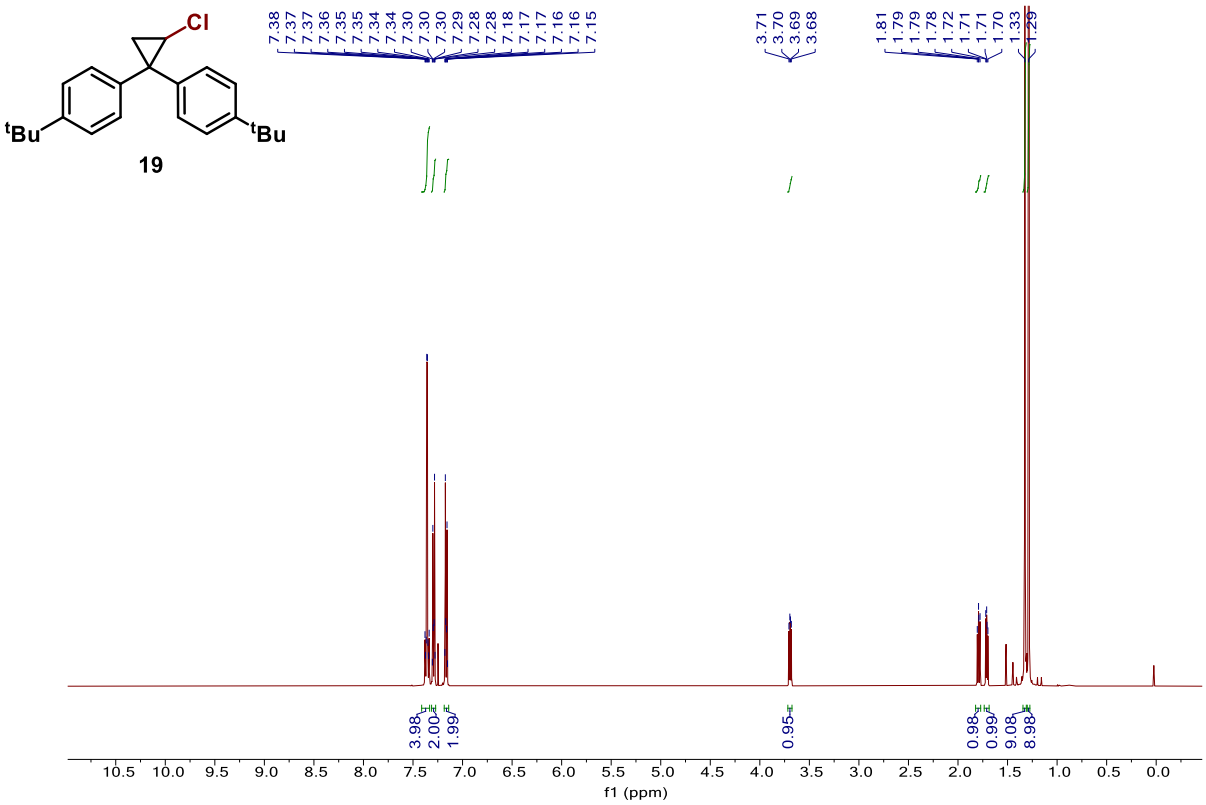
^{1}H NMR of 18 (400 MHz, $CDCl_3$)



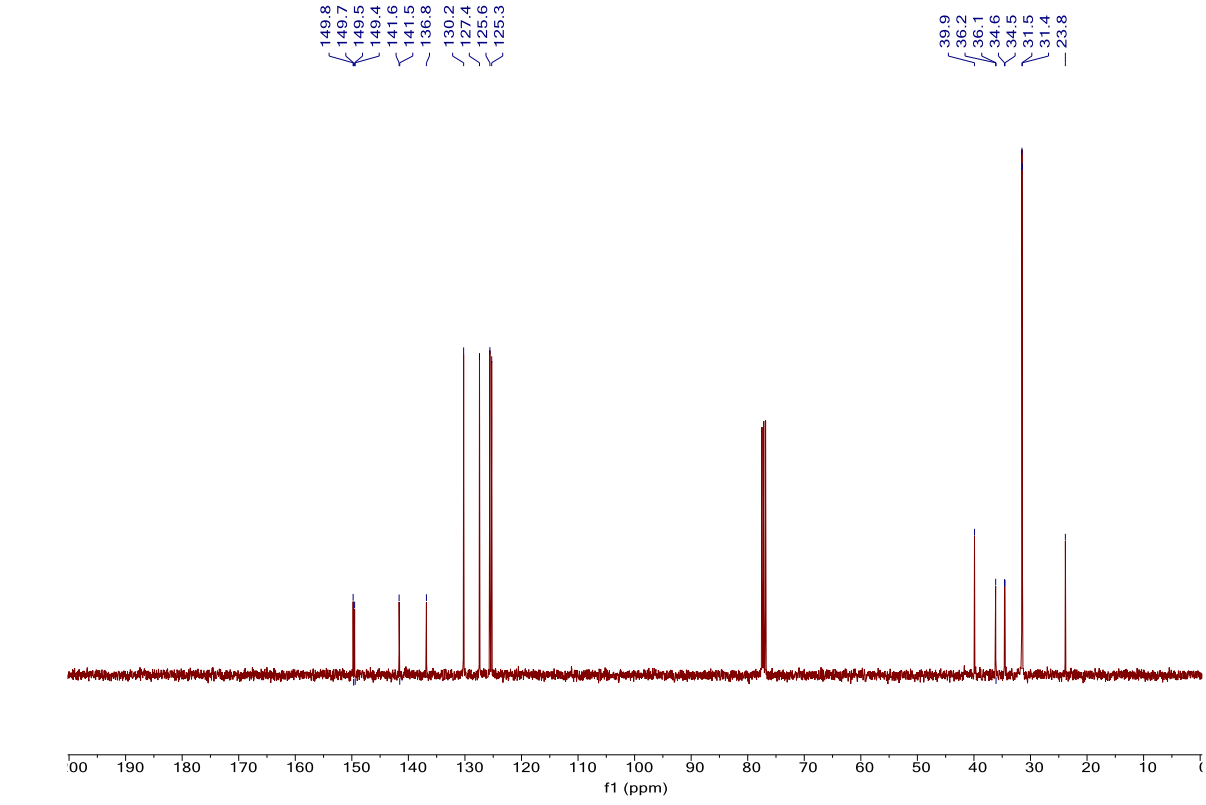
^{13}C NMR of 18 (101Hz, $CDCl_3$)



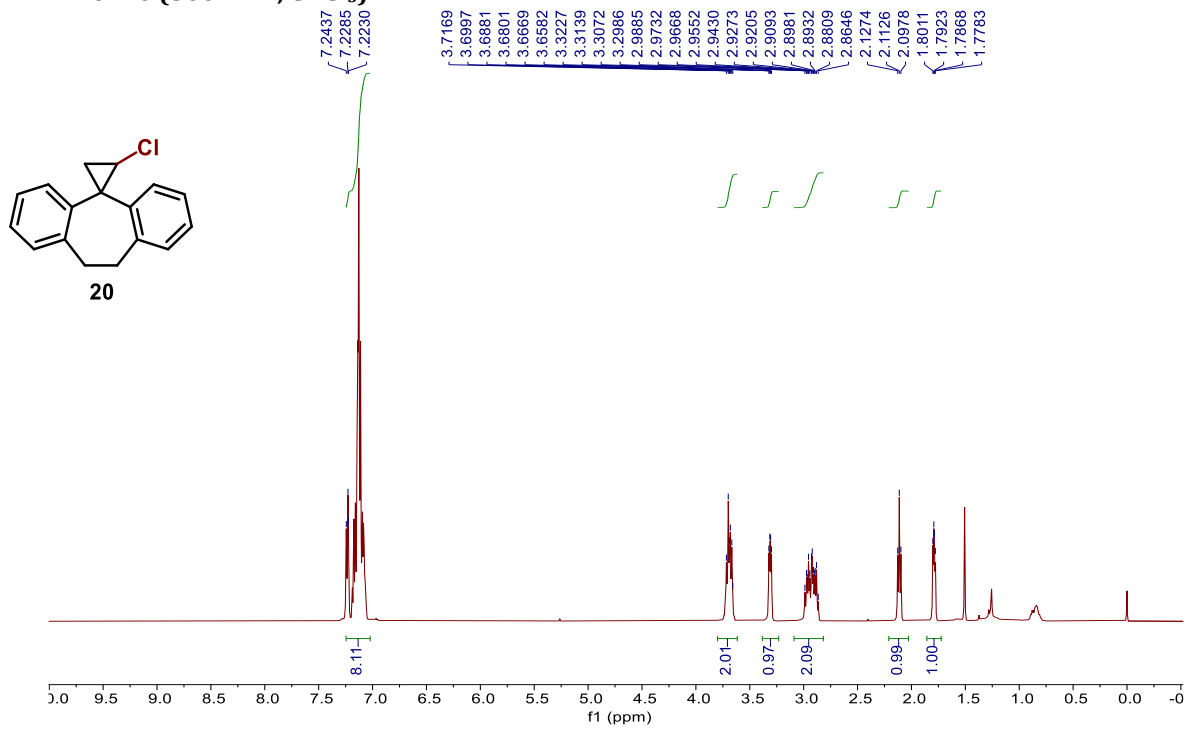
^{1}H NMR of 19 (500 MHz, $CDCl_3$)



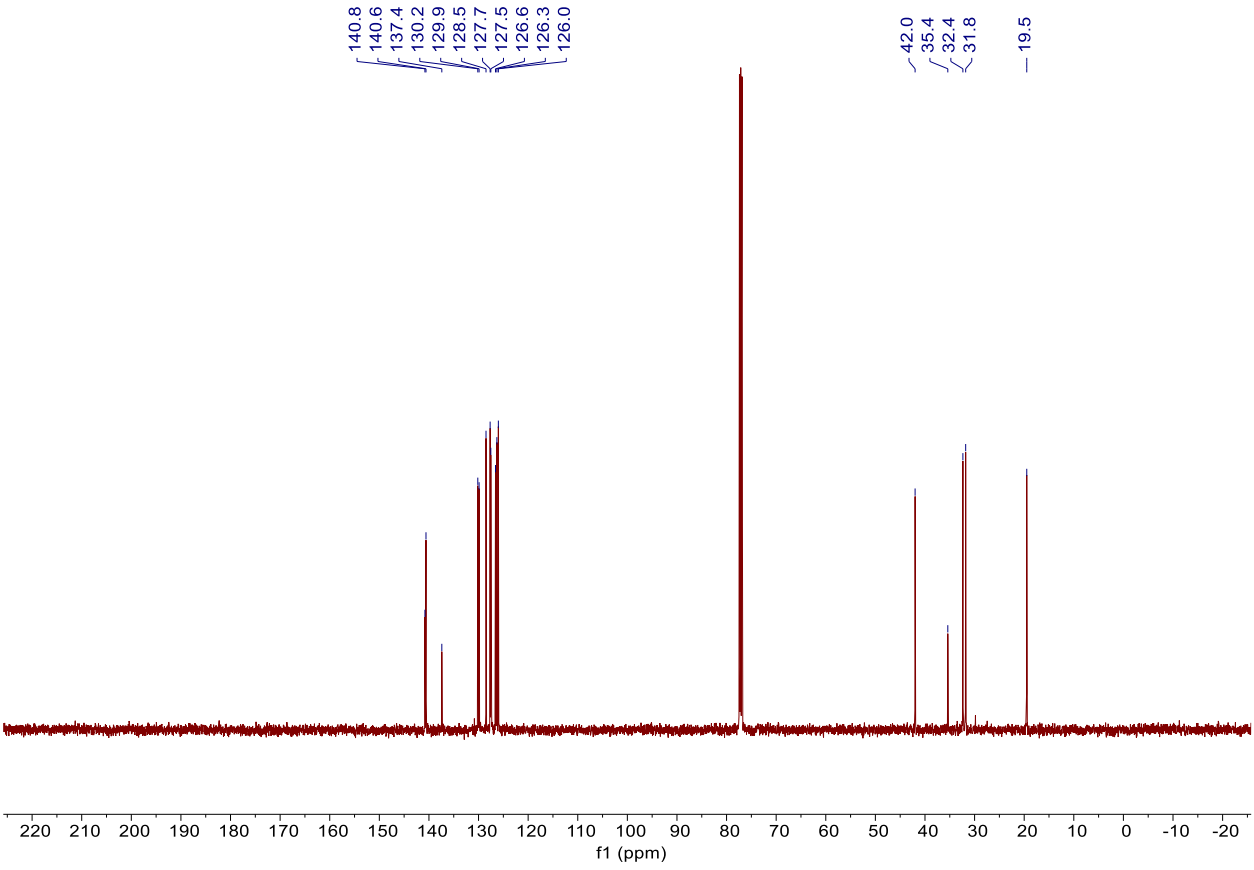
^{13}C NMR of 19 (126 Hz, $CDCl_3$)



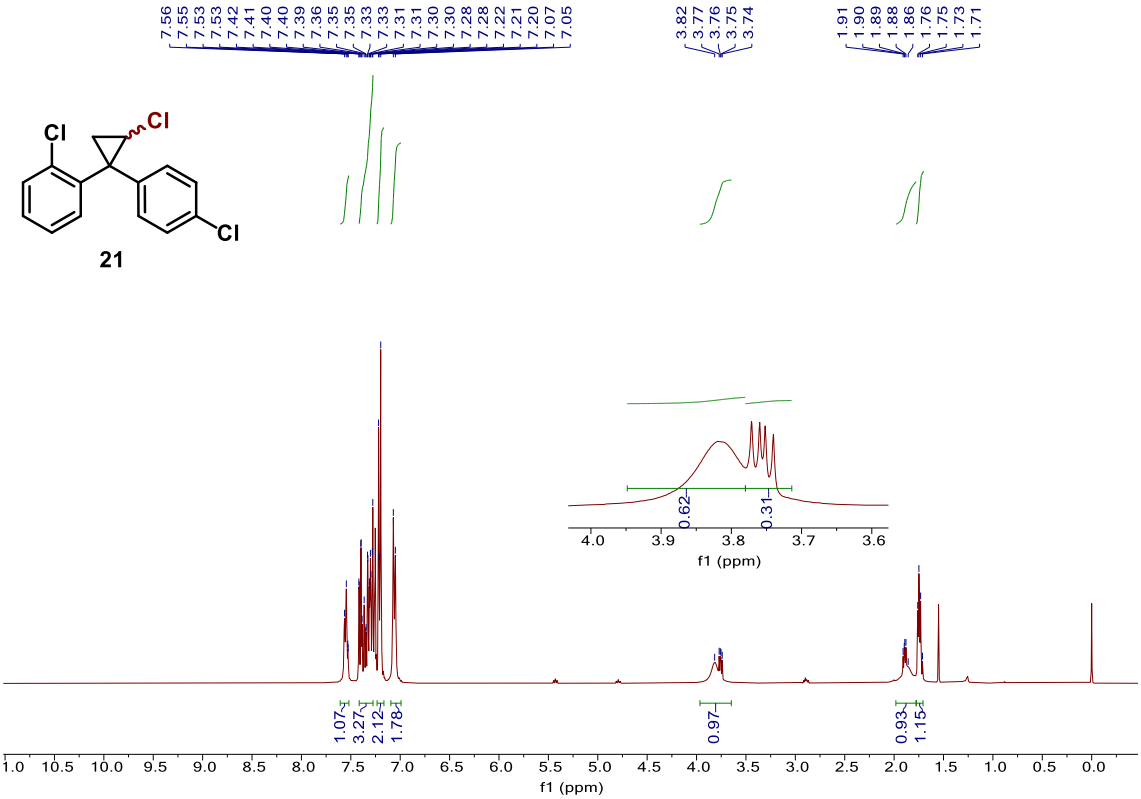
^{1}H NMR of 20 (500 MHz, $CDCl_3$)



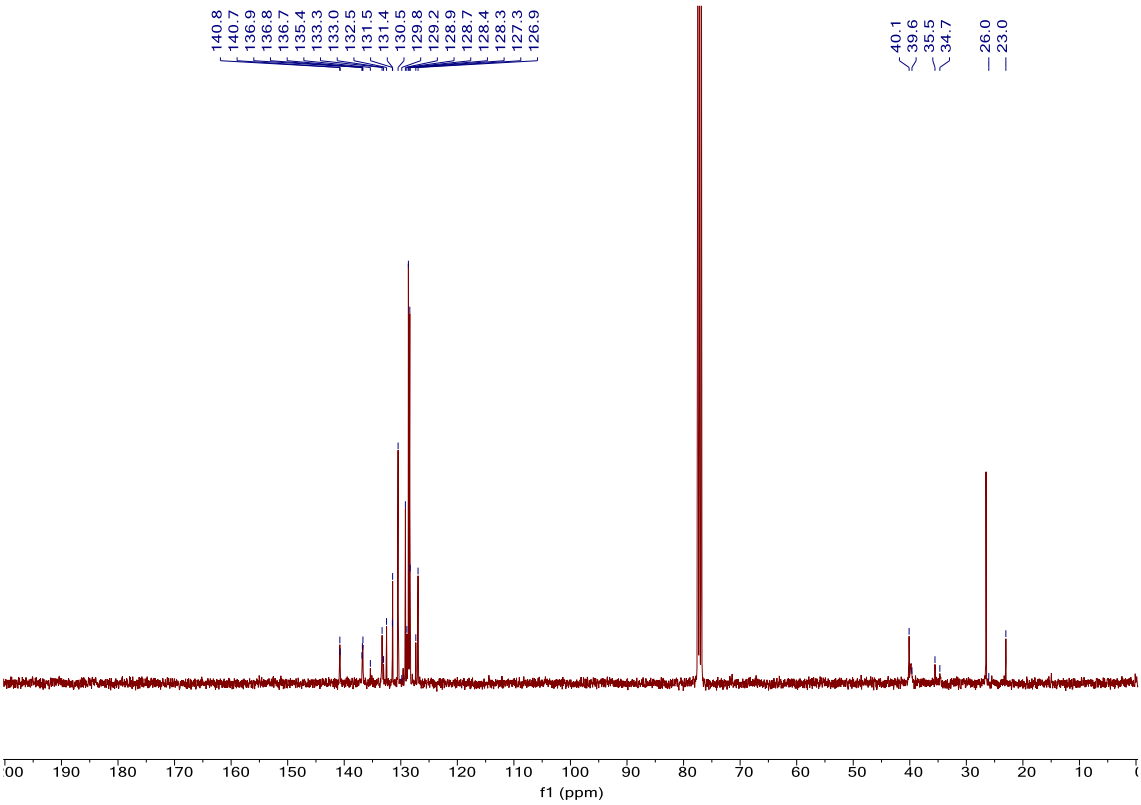
^{13}C NMR of 20 of (126 Hz, $CDCl_3$)



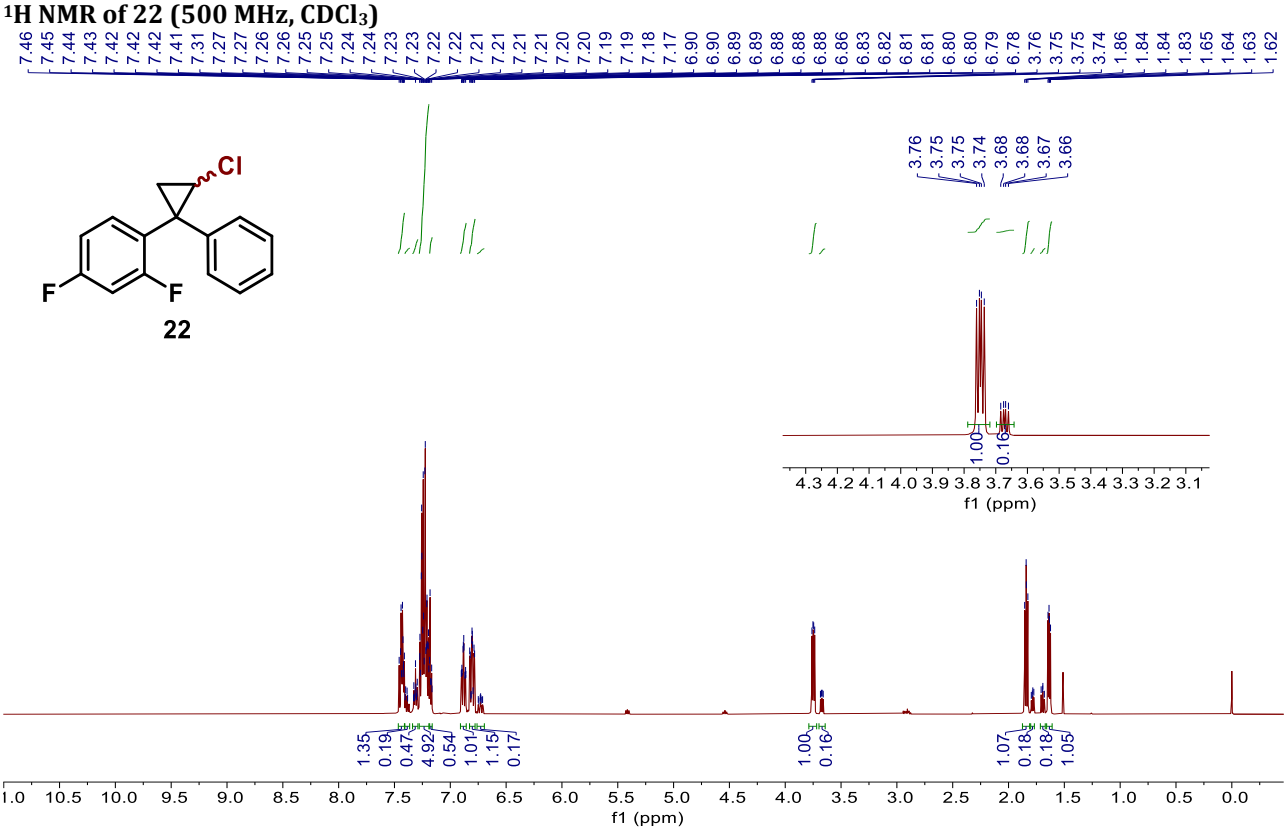
^{1}H NMR of 21 (400 MHz, $CDCl_3$)



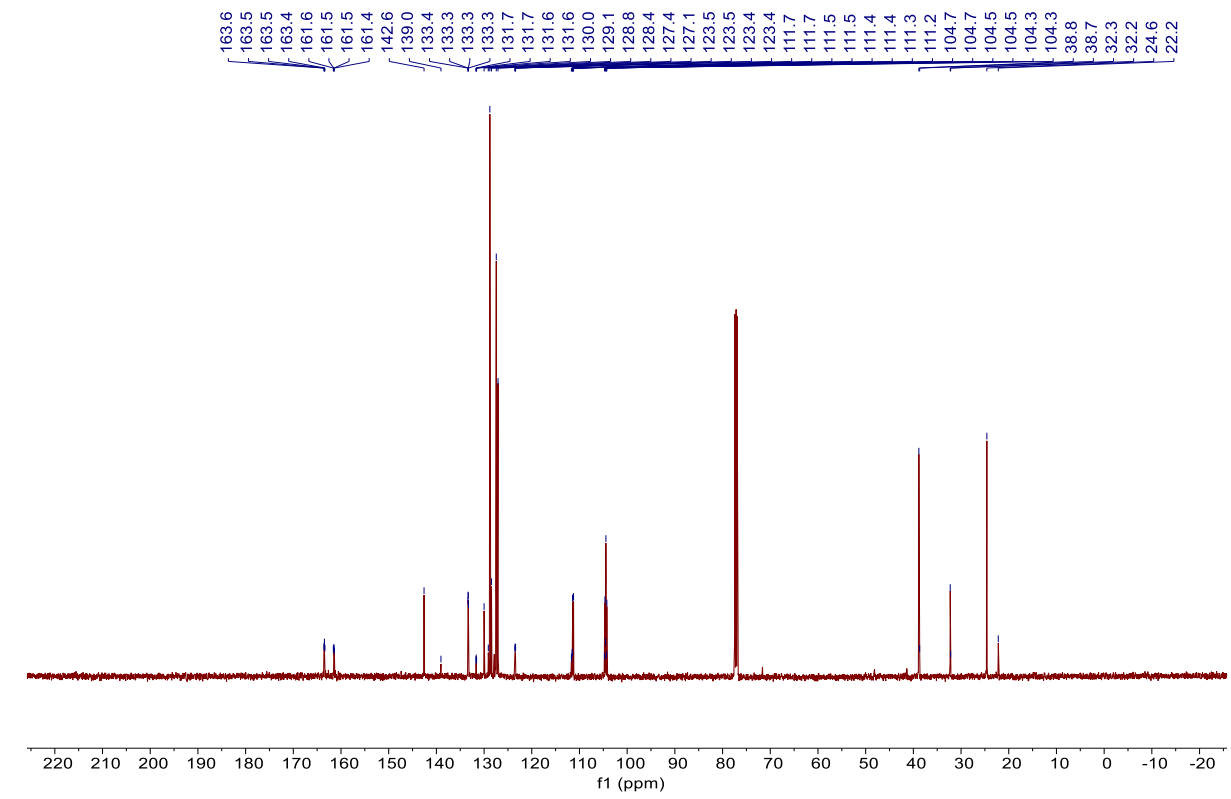
^{13}C NMR of 21 (126 Hz, $CDCl_3$)



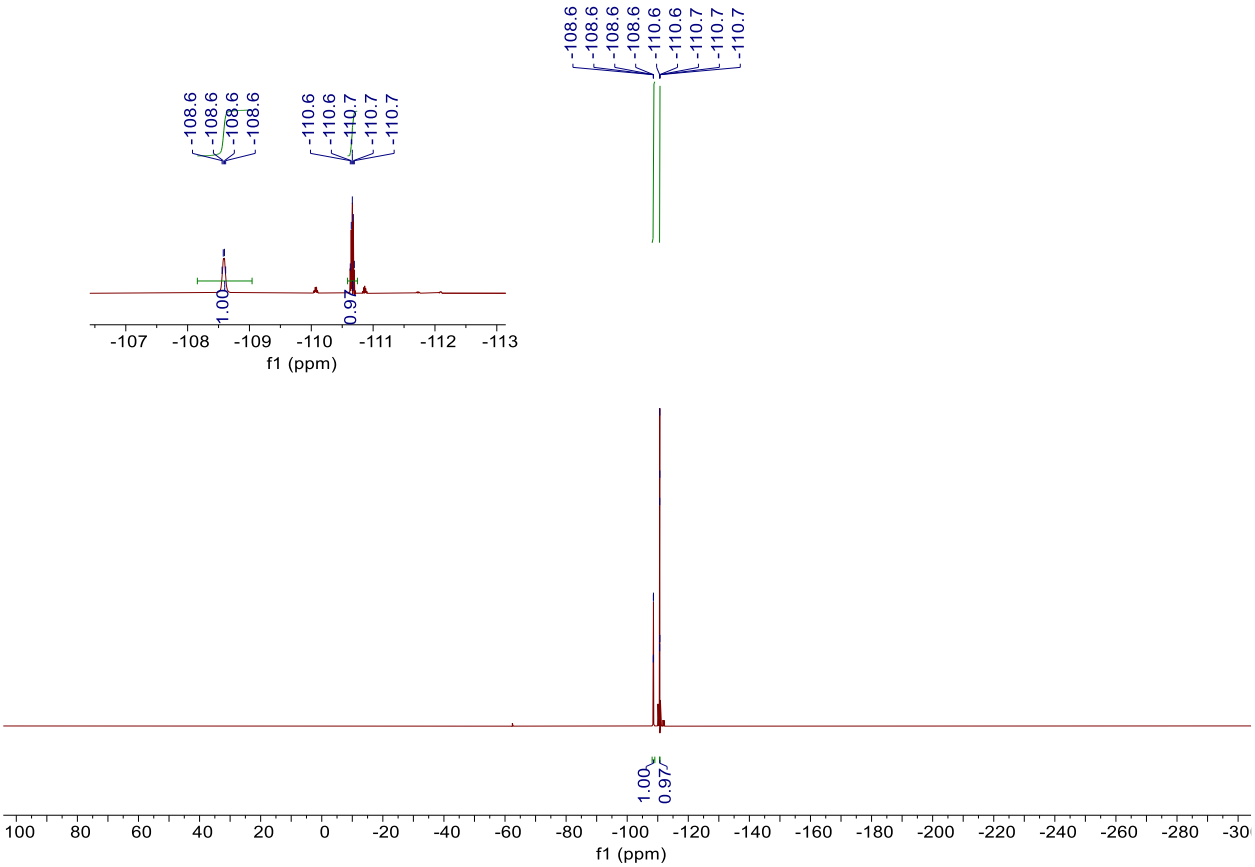
^{1}H NMR of 22 (500 MHz, $CDCl_3$)



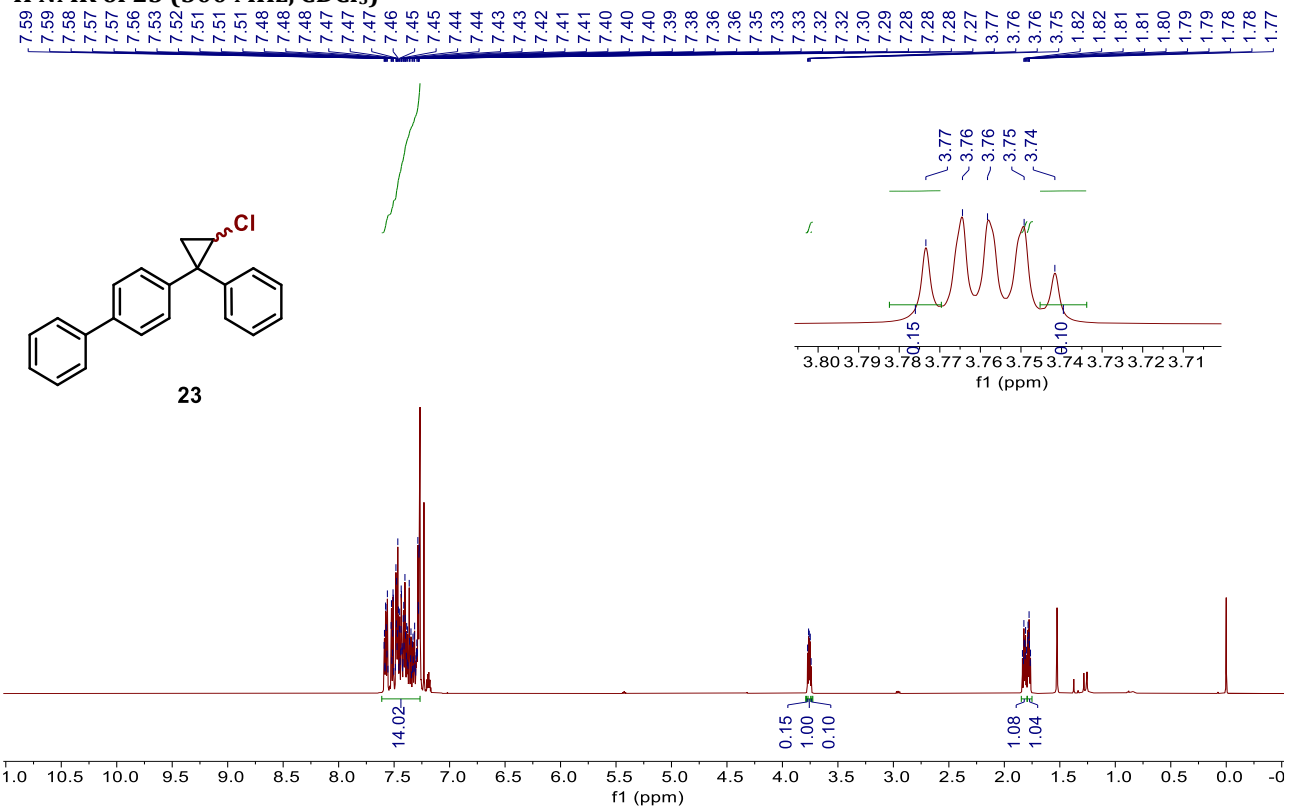
^{13}C NMR of 22 (126 Hz, $CDCl_3$)



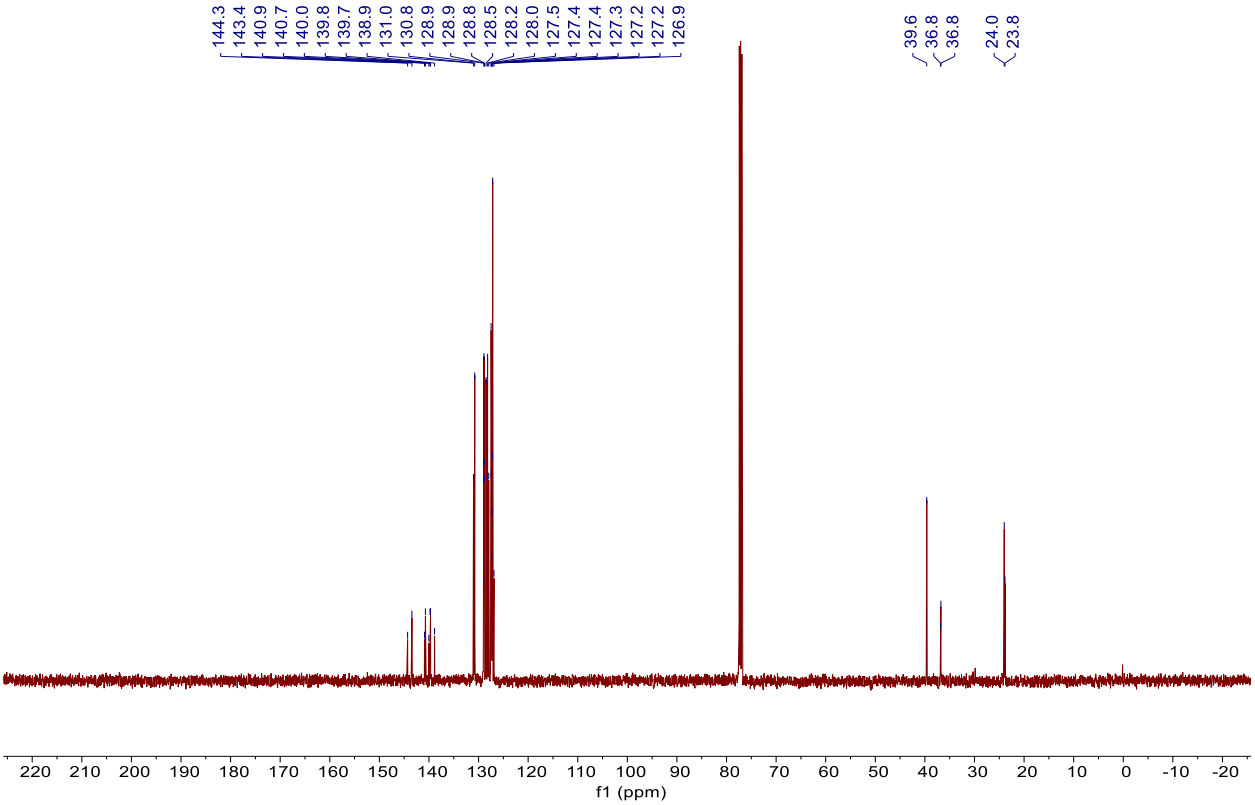
^{19}F NMR of 22 (471 Hz, $CDCl_3$)



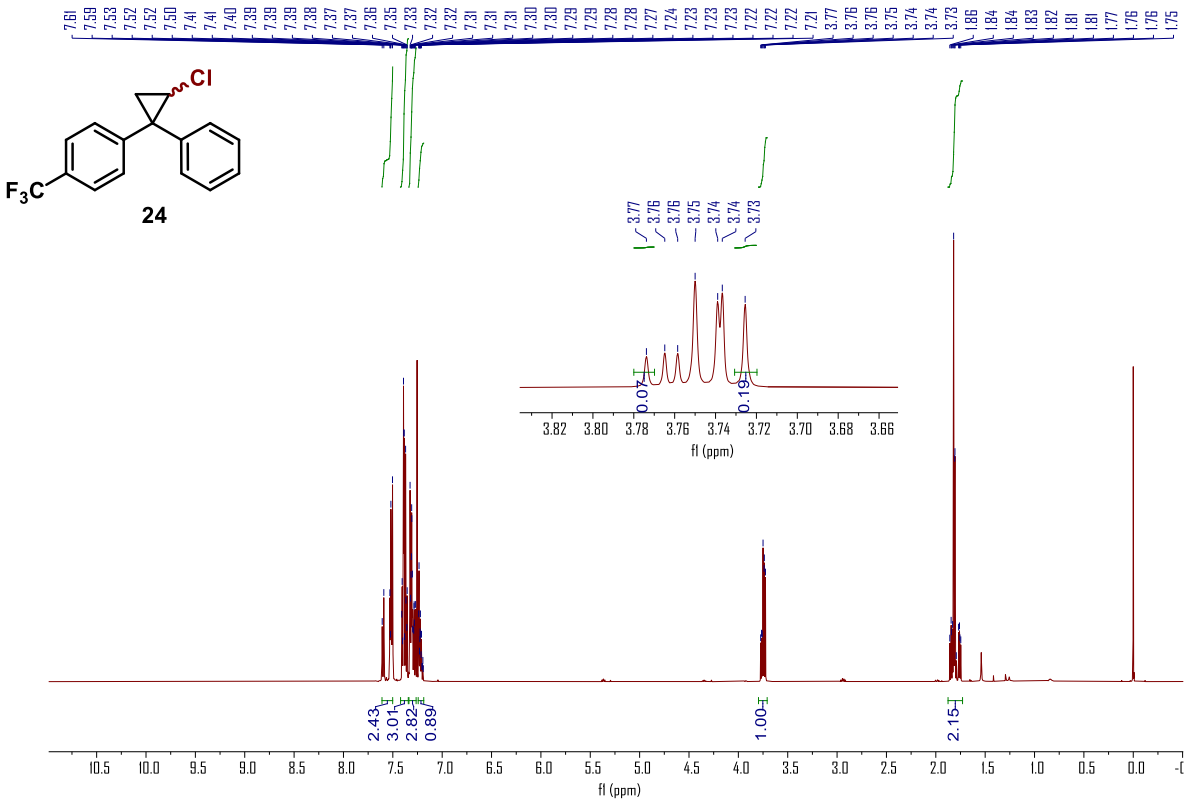
^{1}H NMR of 23 (500 MHz, $CDCl_3$)



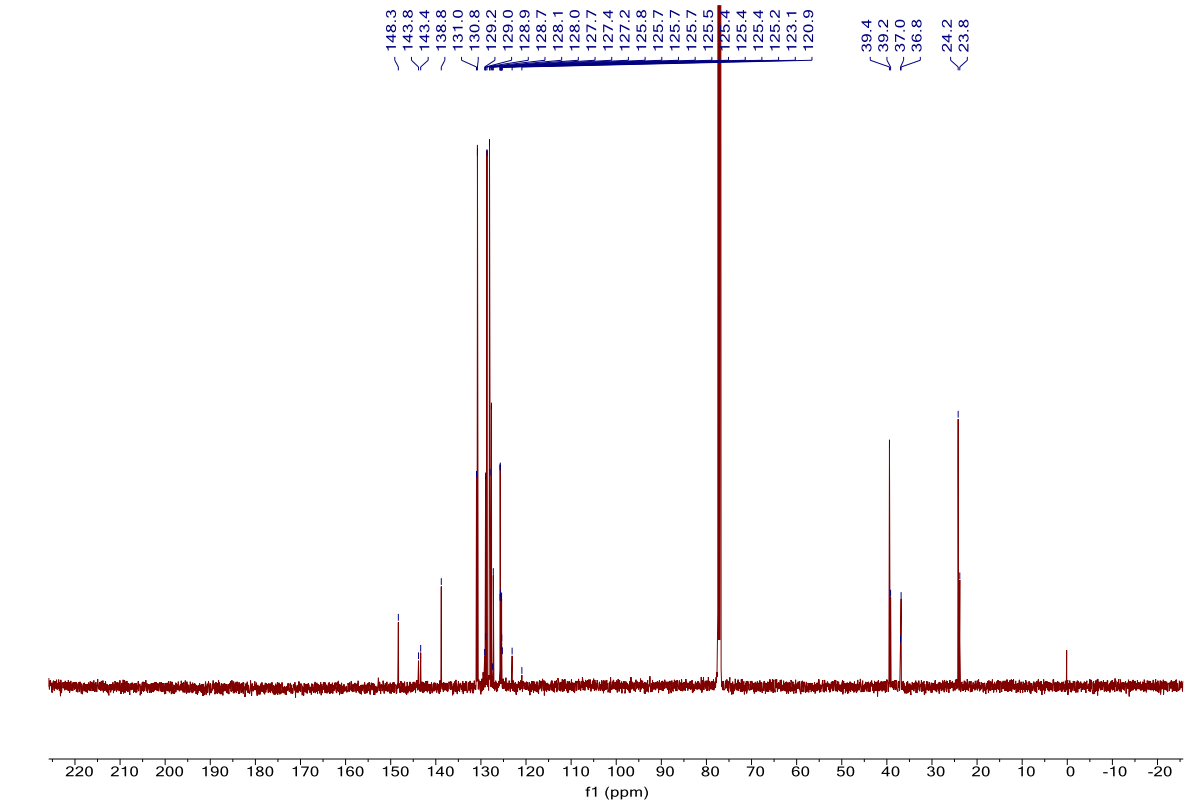
^{13}C NMR of 23 (126 Hz, $CDCl_3$)



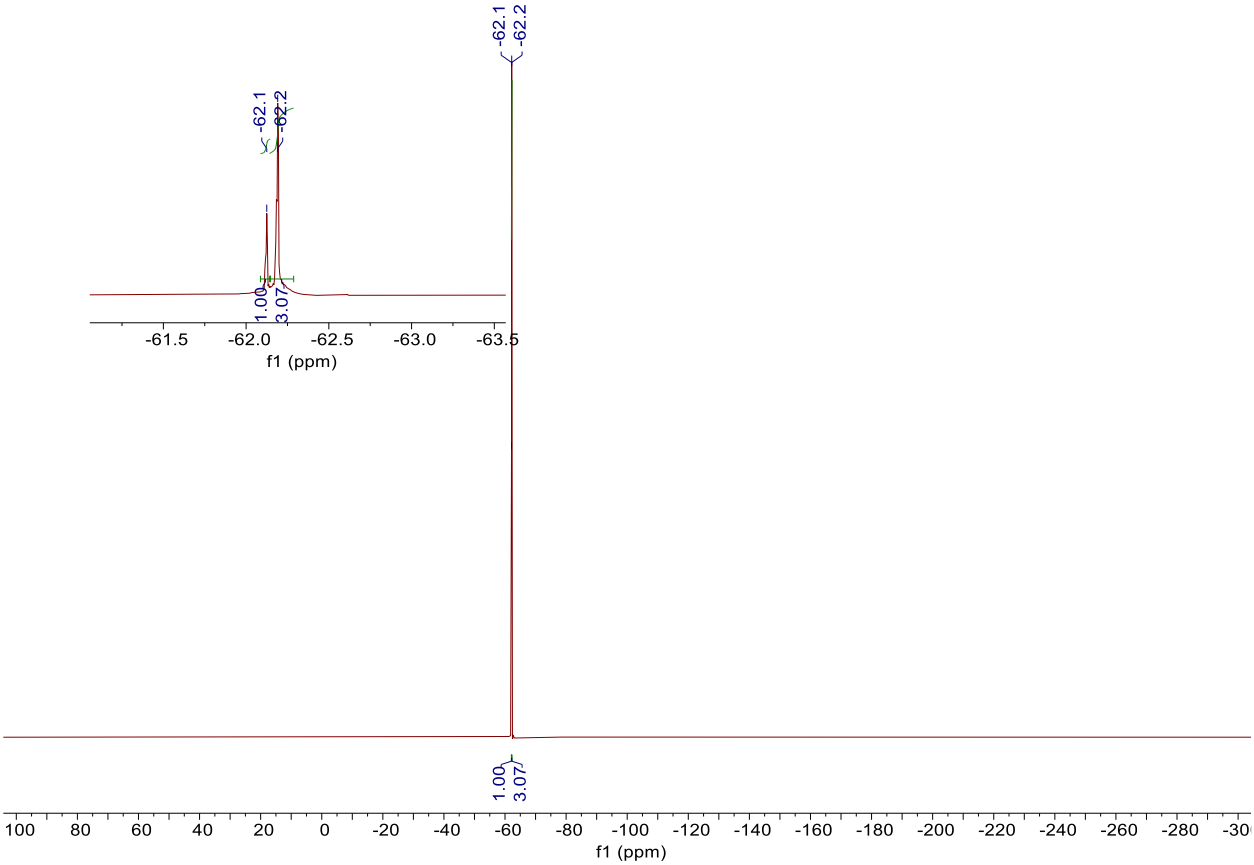
^{1}H NMR of 24 (500 MHz, $CDCl_3$)



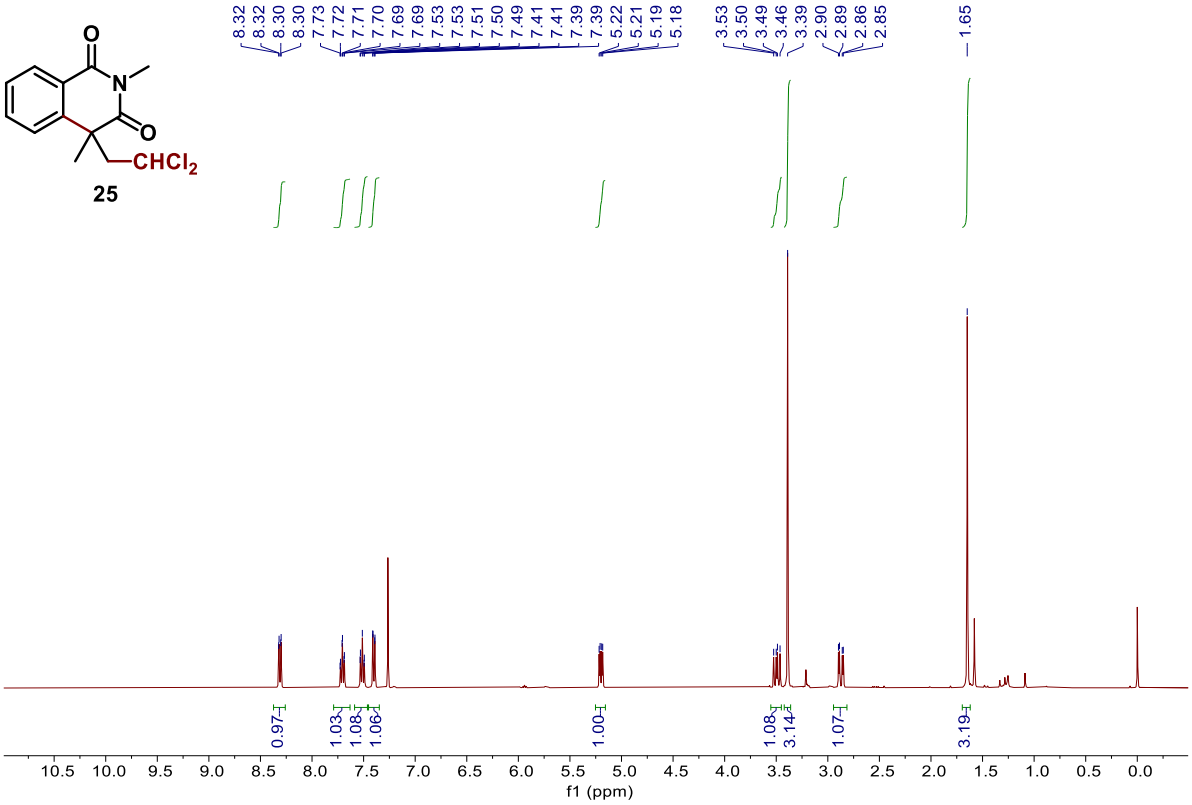
^{13}C NMR of 24 (126 Hz, $CDCl_3$)



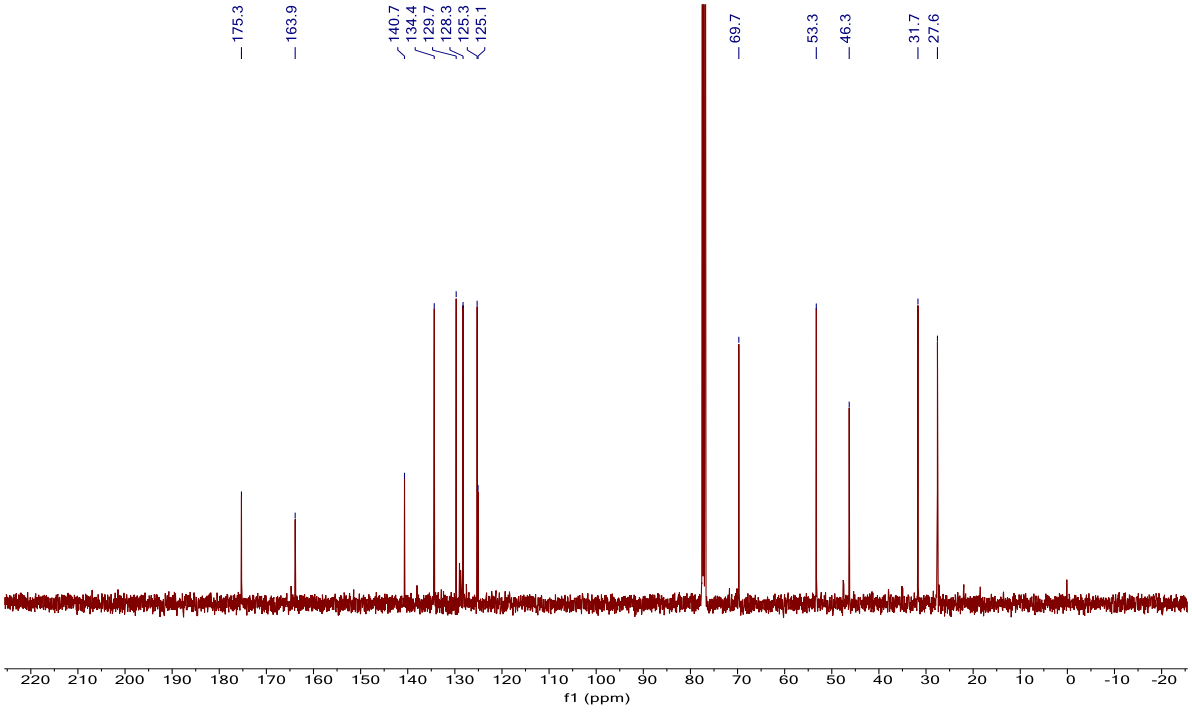
^{19}F NMR of 24 (471 Hz, $CDCl_3$)



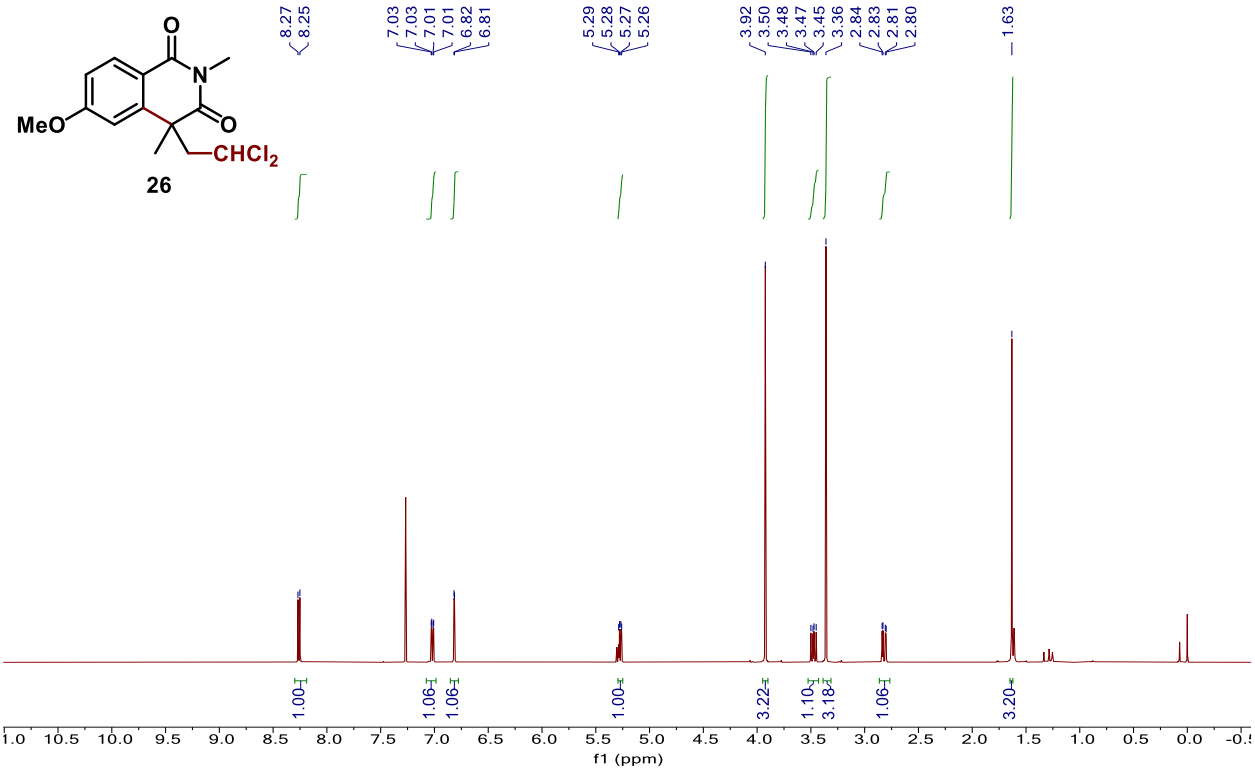
^{1}H NMR of 25 (400 MHz, $CDCl_3$)



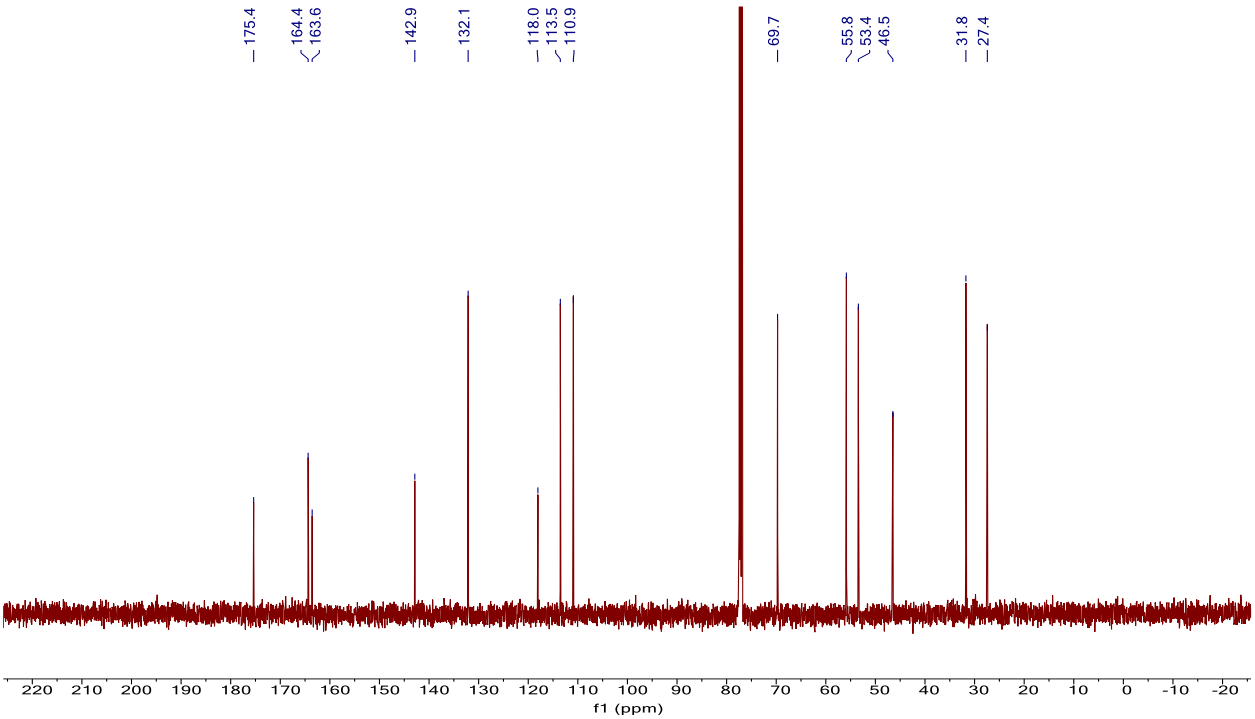
^{13}C NMR of 25 (101 MHz, $CDCl_3$)



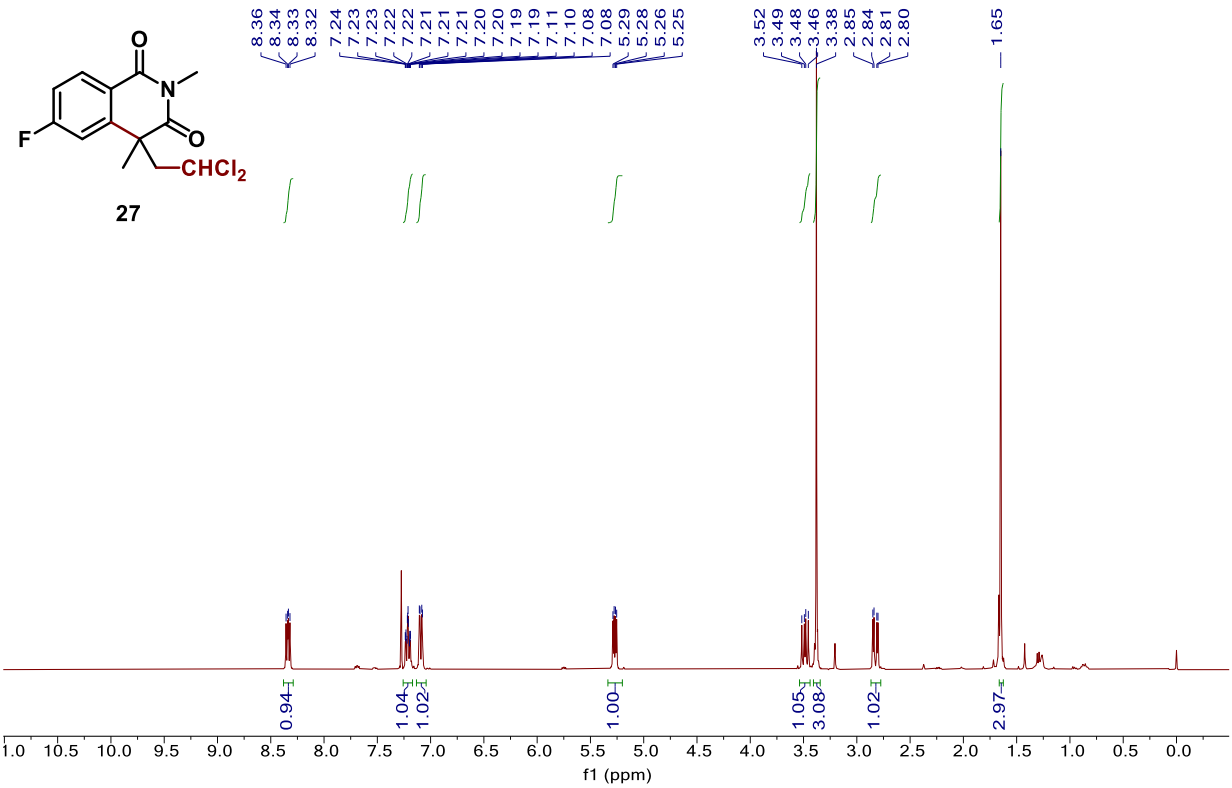
^{1}H NMR of 26 (500 MHz, $CDCl_3$)



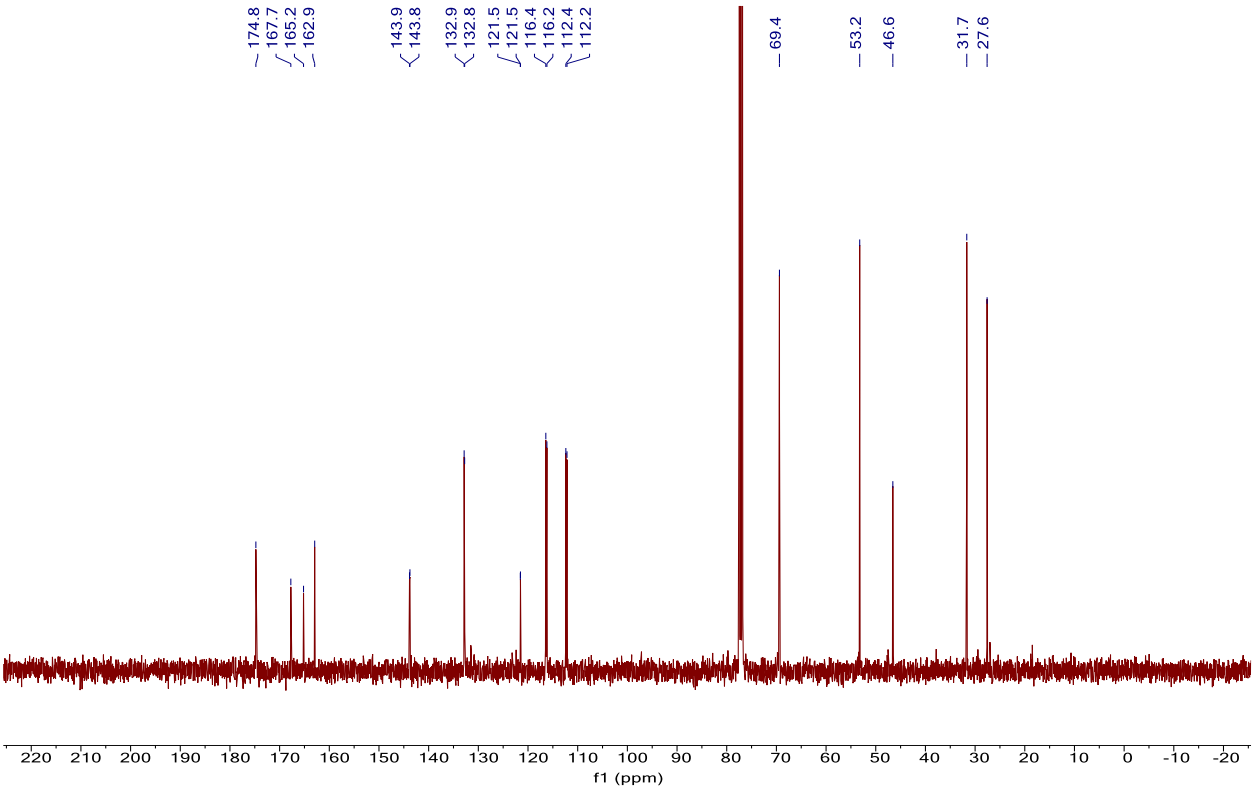
^{13}C NMR of 26 (126 MHz, $CDCl_3$)



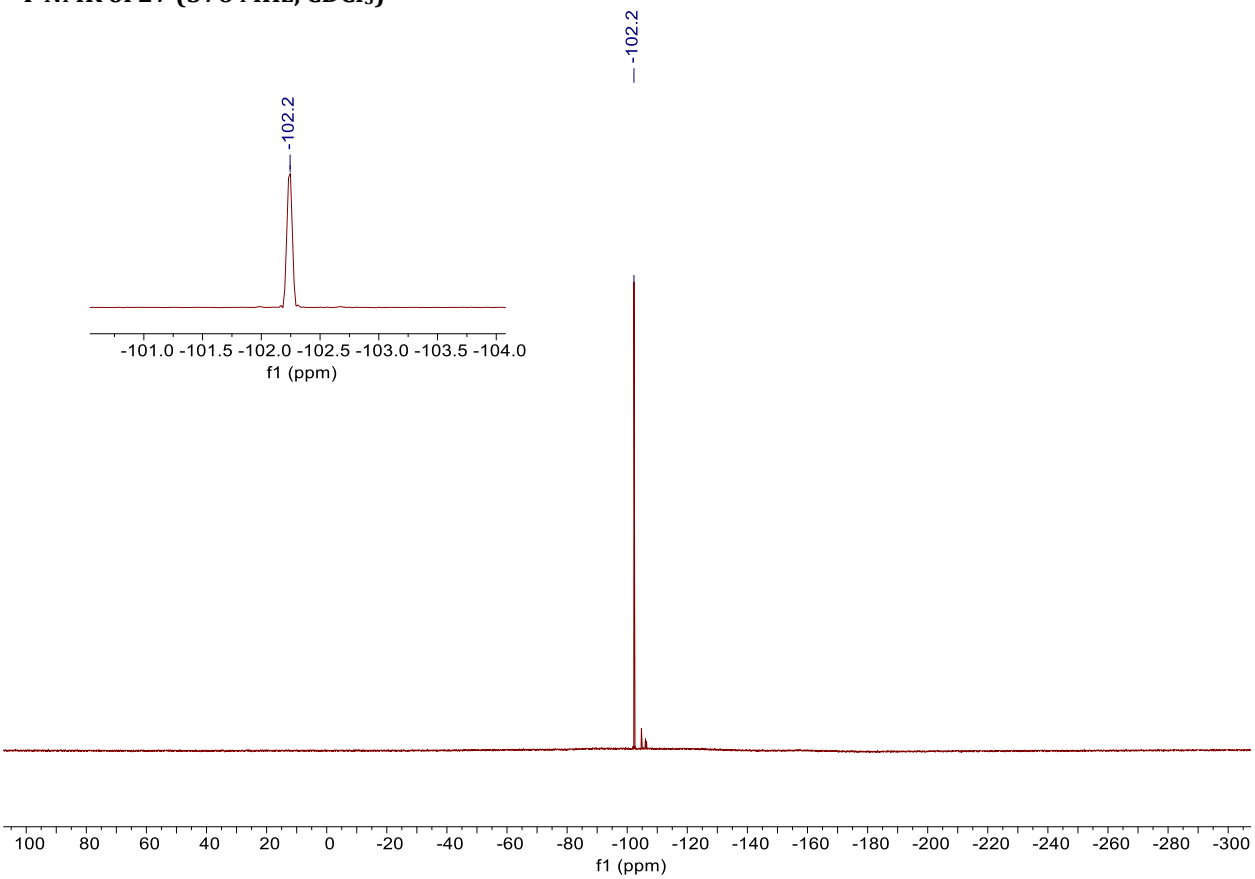
^{1}H NMR of 27 (400 MHz, $CDCl_3$)



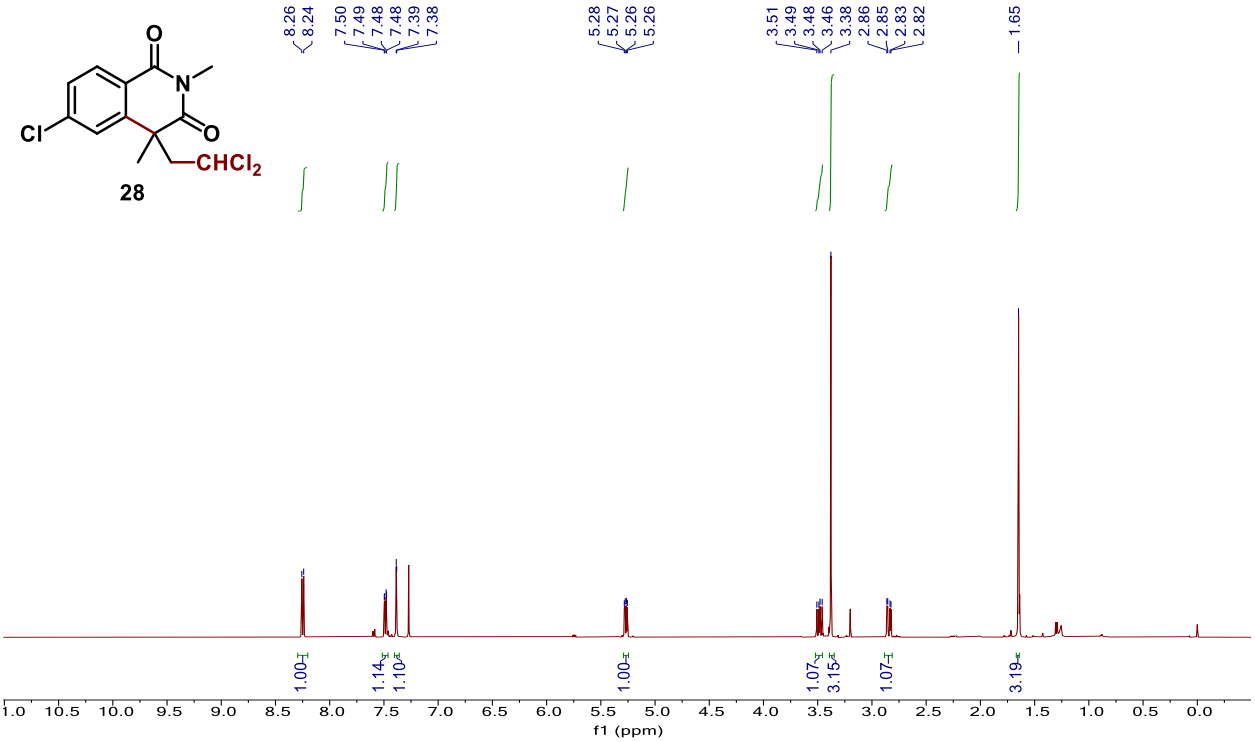
^{13}C NMR of 27 (101 MHz, $CDCl_3$)



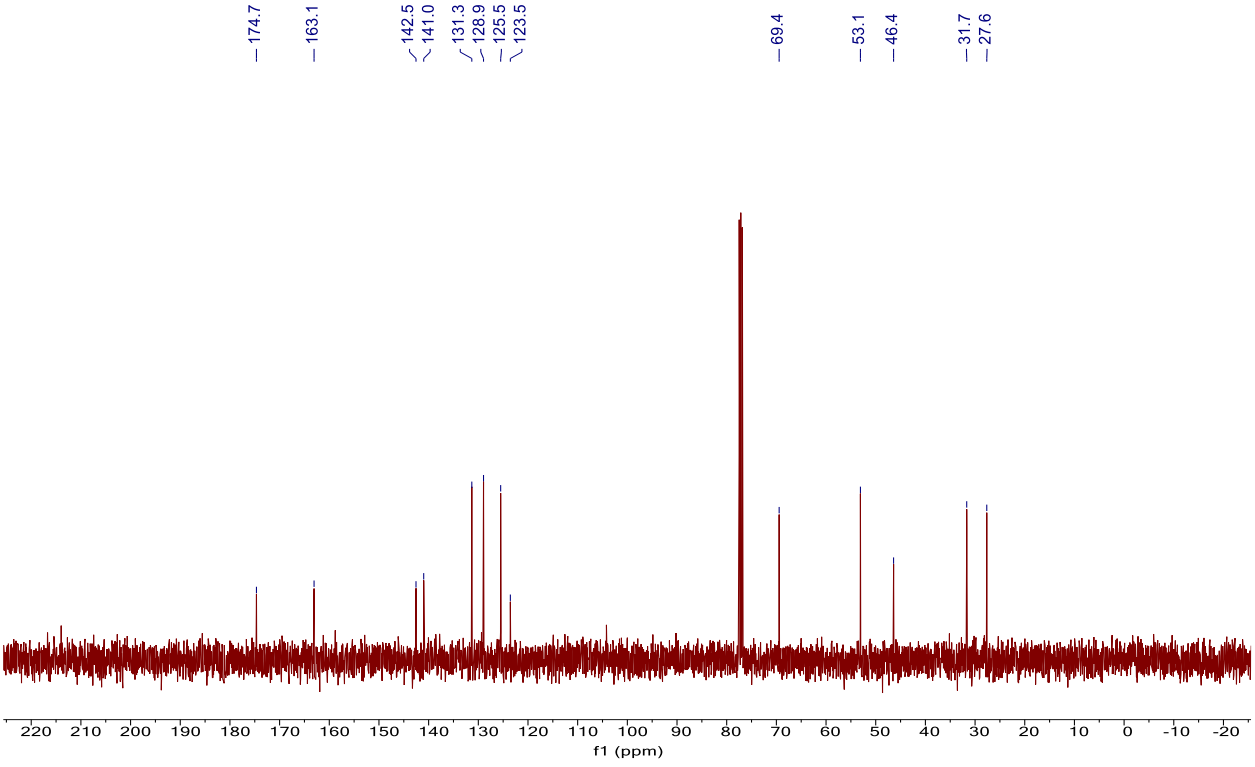
^{19}F NMR of 27 (376 MHz, $CDCl_3$)



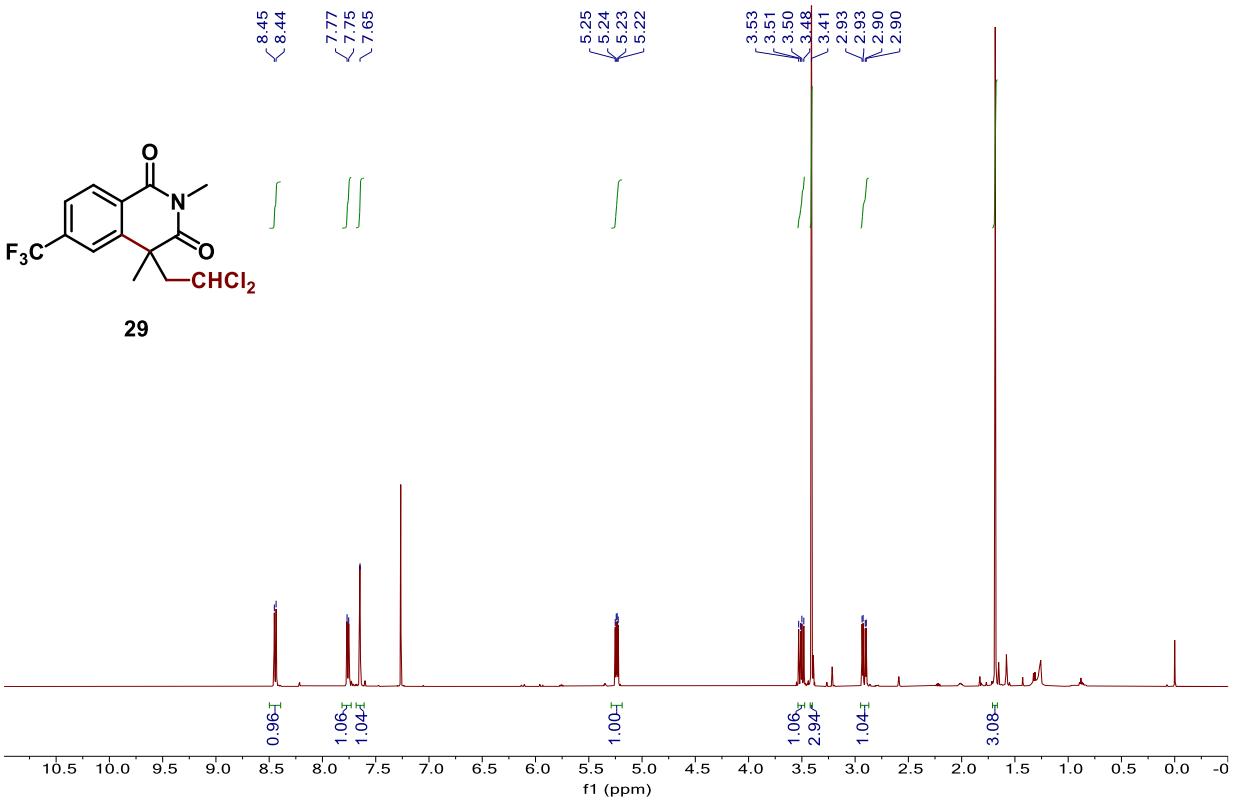
^{1}H NMR of 28 (500 MHz, $CDCl_3$)



^{13}C NMR of 28 (101 MHz, $CDCl_3$)

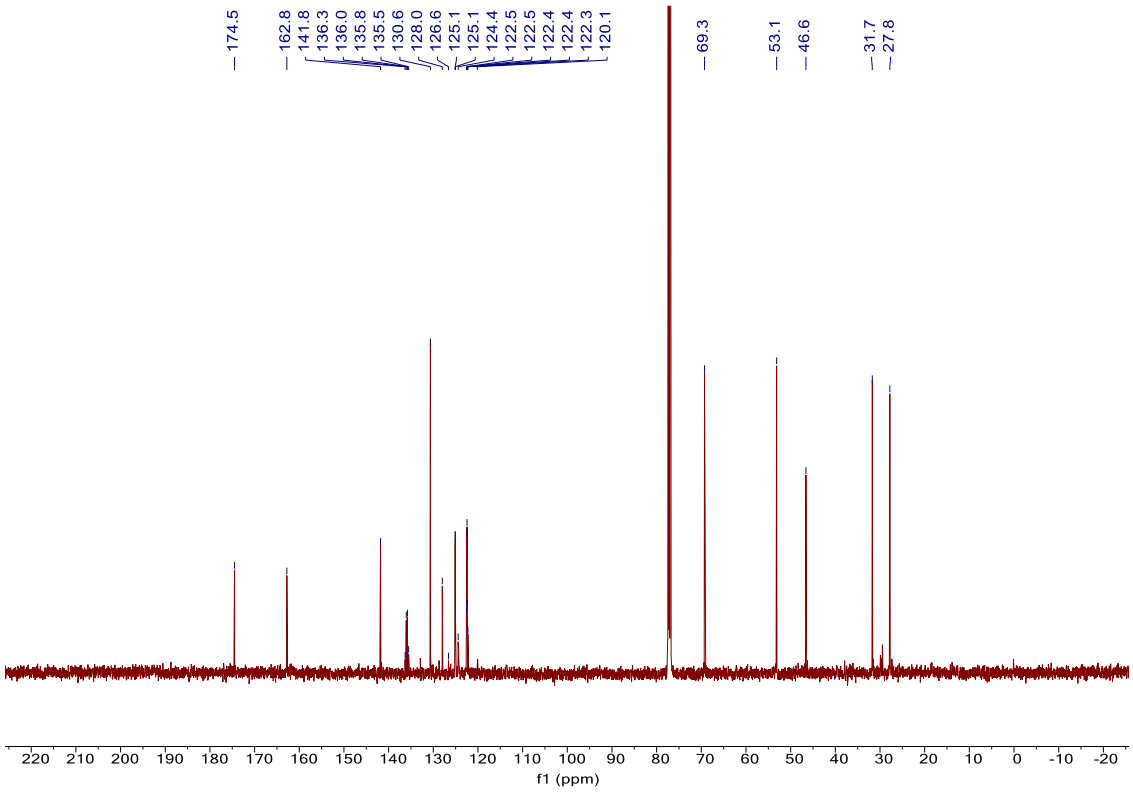


^{1}H NMR of 29 (500 MHz, $CDCl_3$)

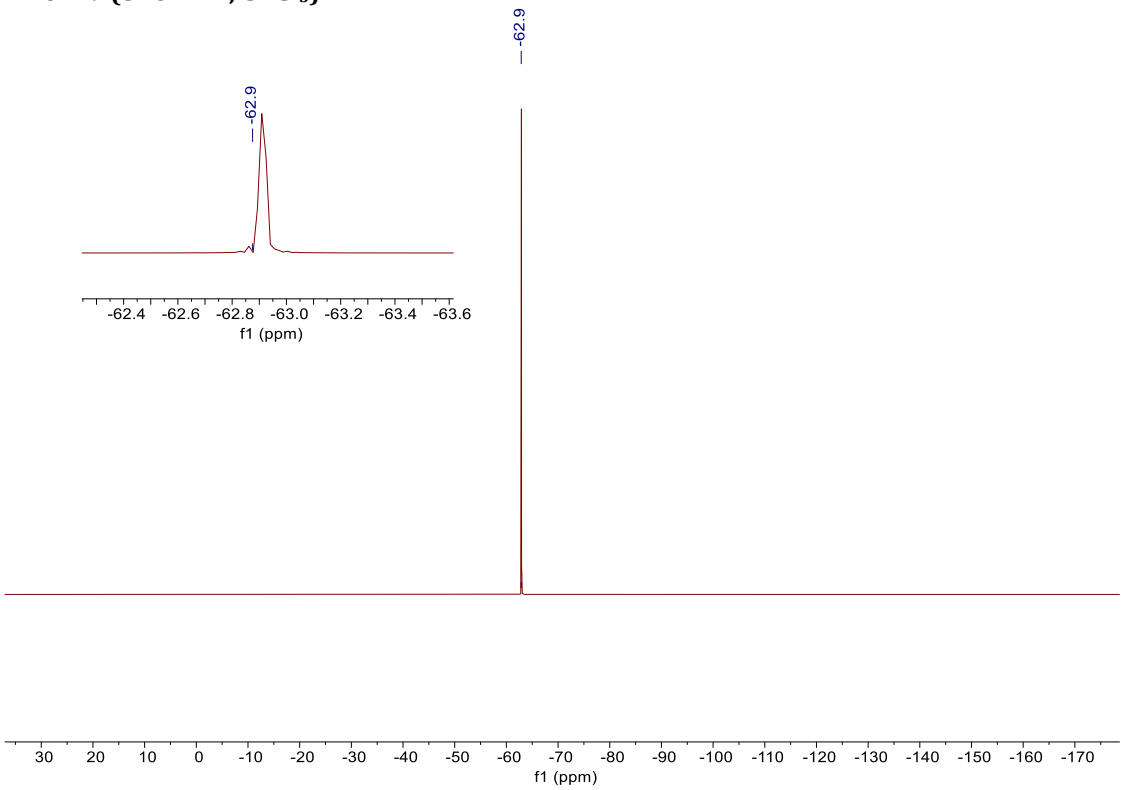


29

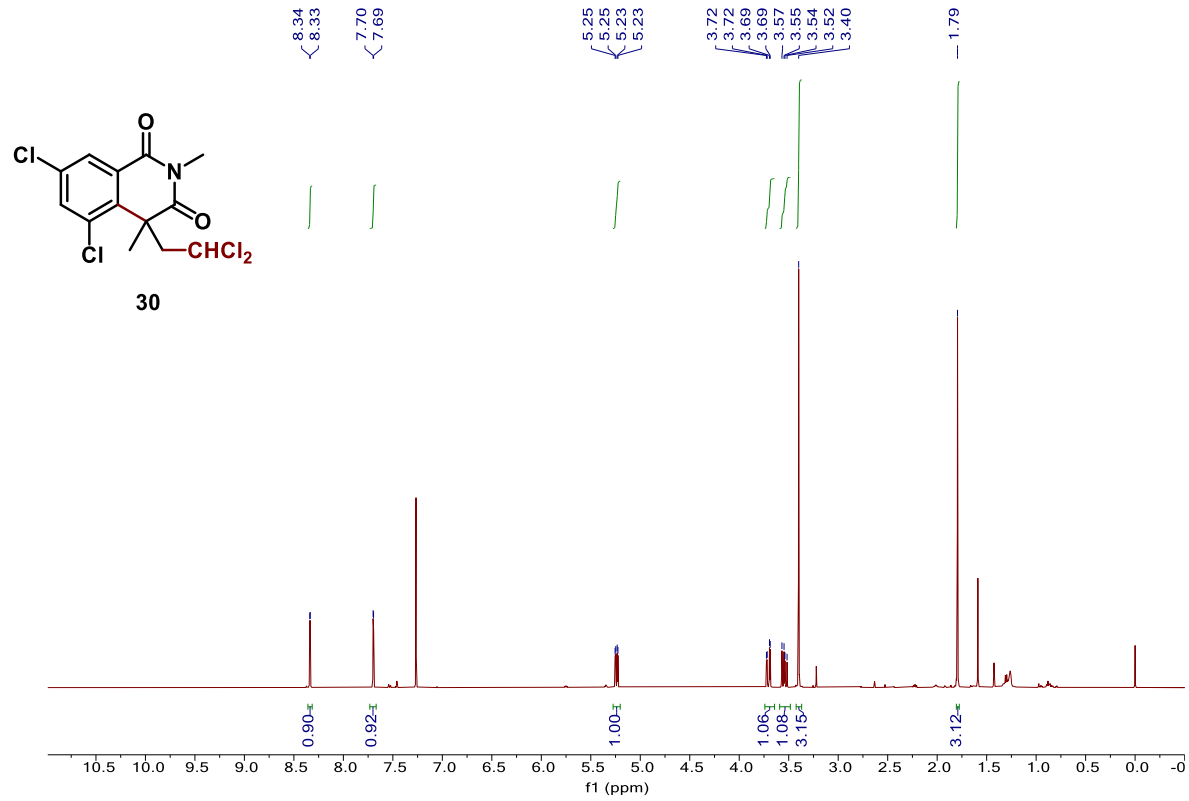
^{13}C NMR of 29 (126 MHz, $CDCl_3$)



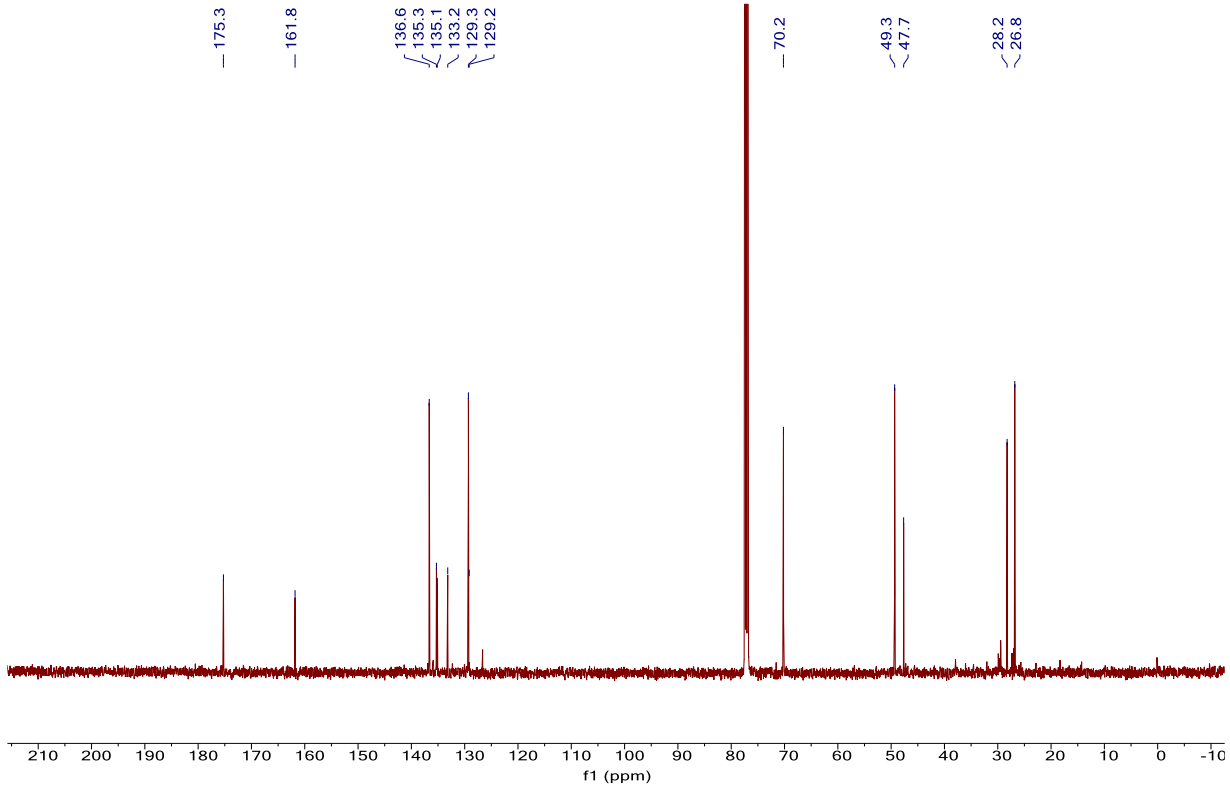
^{19}F NMR of 29 (376 MHz, $CDCl_3$)



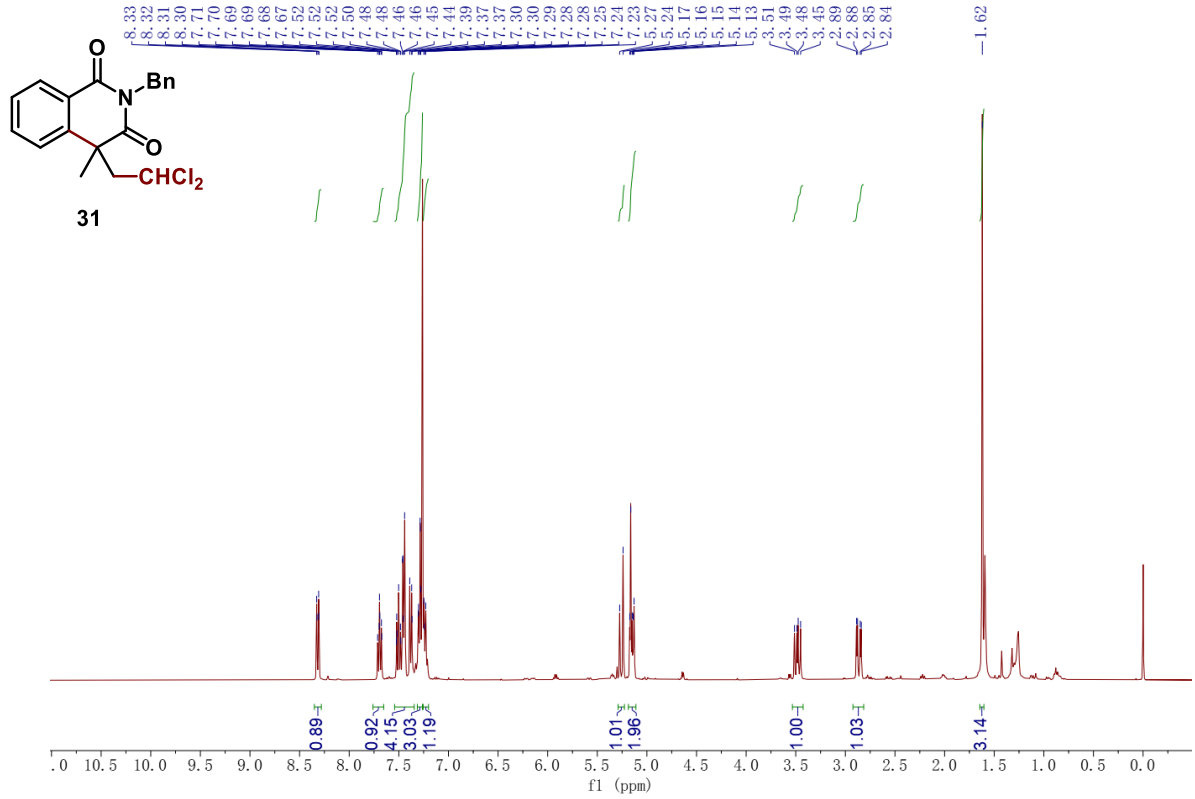
^{1}H NMR of 30 (500 MHz, $CDCl_3$)



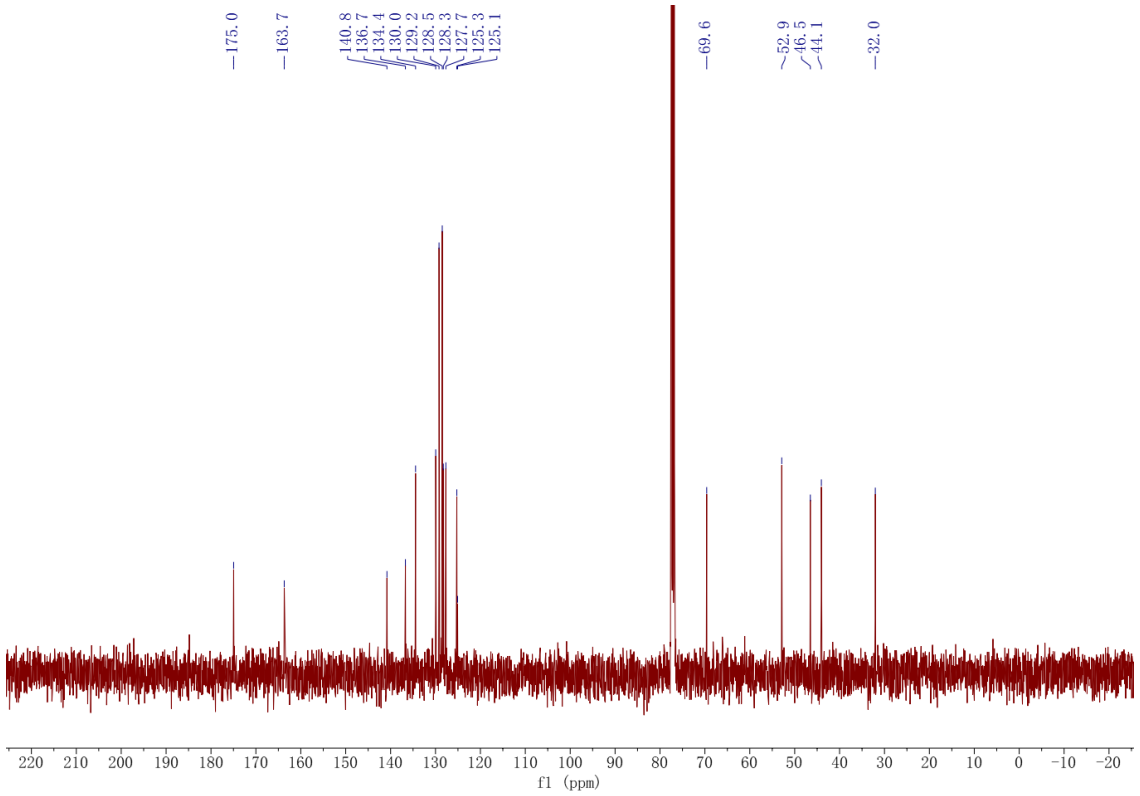
^{13}C NMR of 30 (126 MHz, $CDCl_3$)



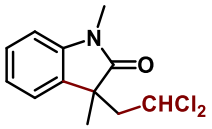
^{1}H NMR of 31 (400 MHz, $CDCl_3$)



^{13}C NMR of 31 (101 MHz, $CDCl_3$)

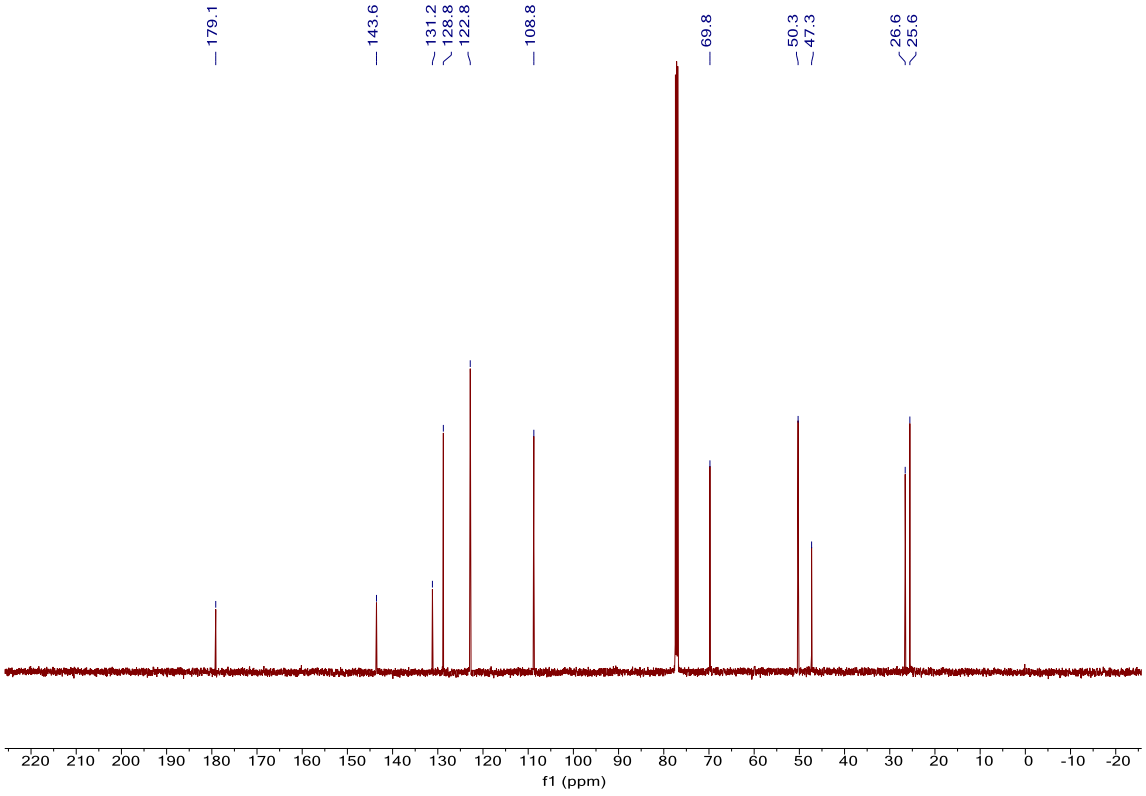


^{1}H NMR of 32 (500 MHz, $CDCl_3$)

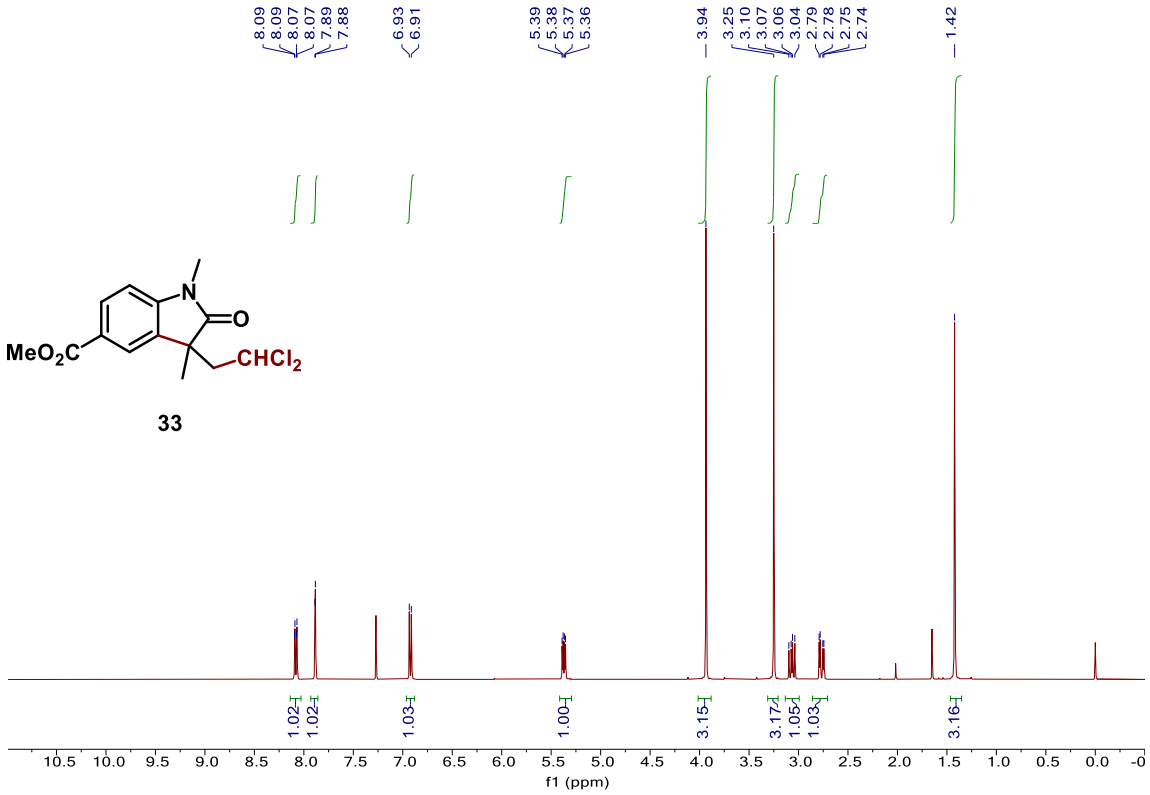


32

^{13}C NMR of 32 (126 MHz, $CDCl_3$)

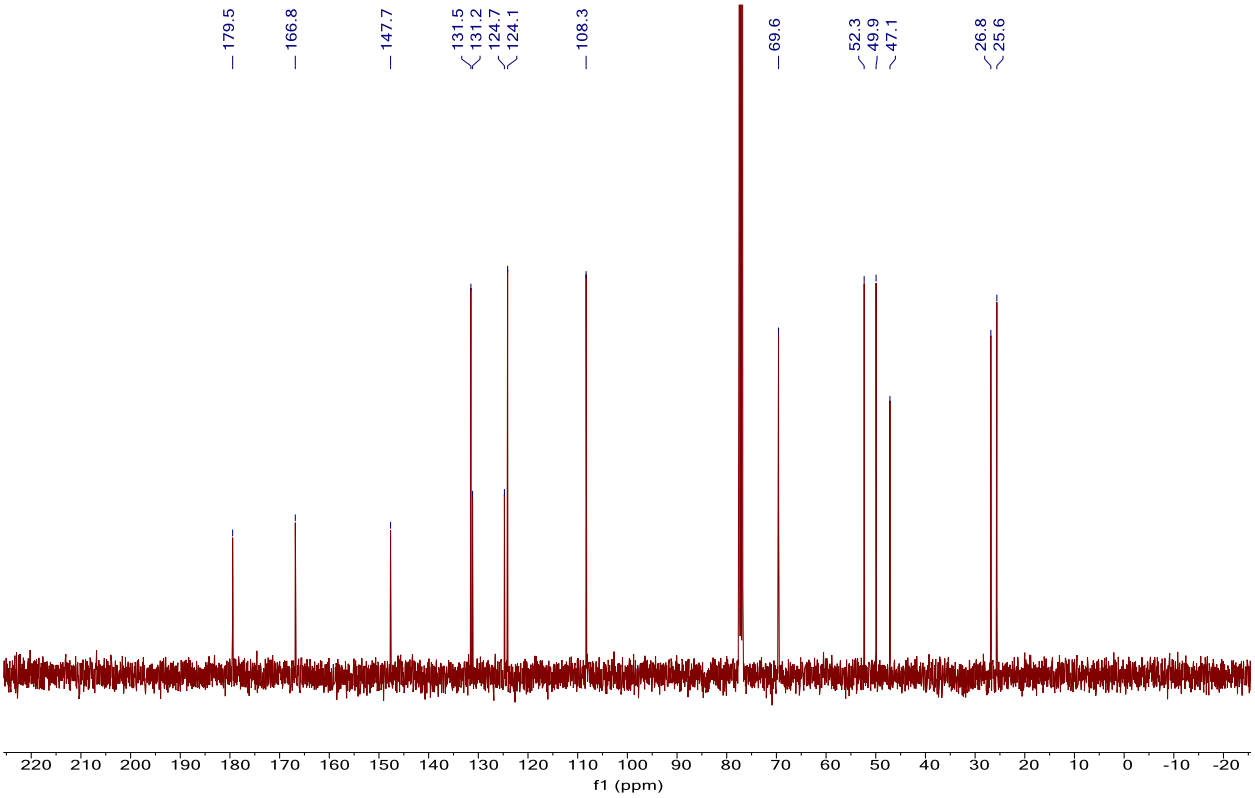


^{1}H NMR of 33 (400 MHz, $CDCl_3$)

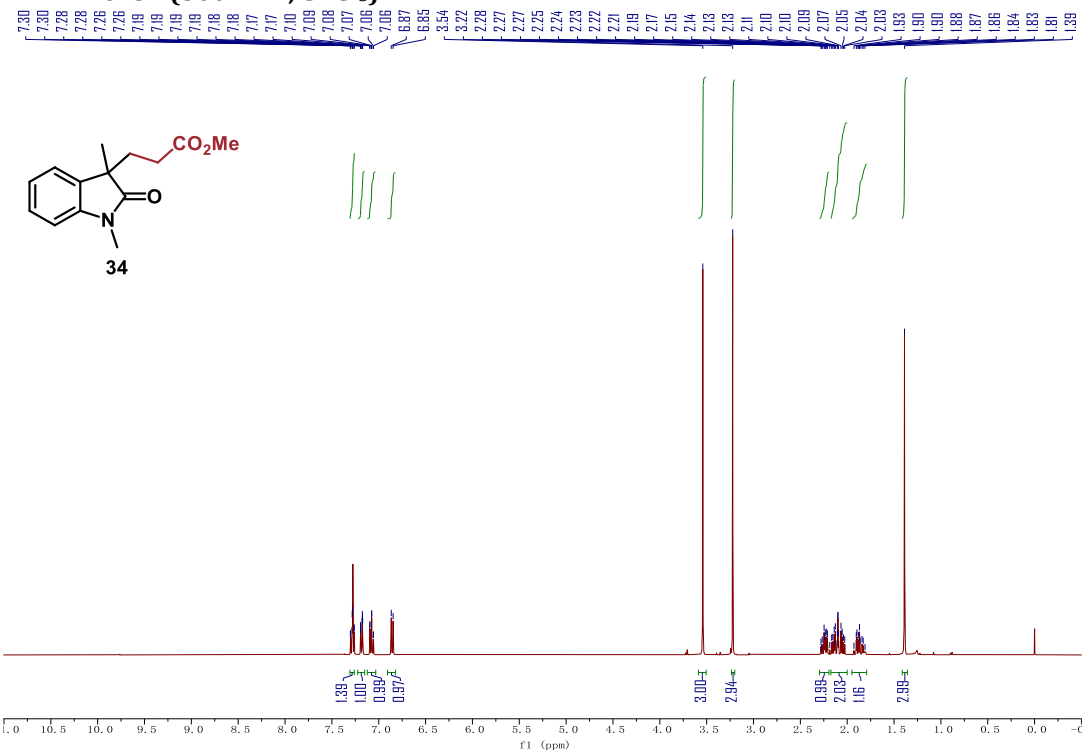


33

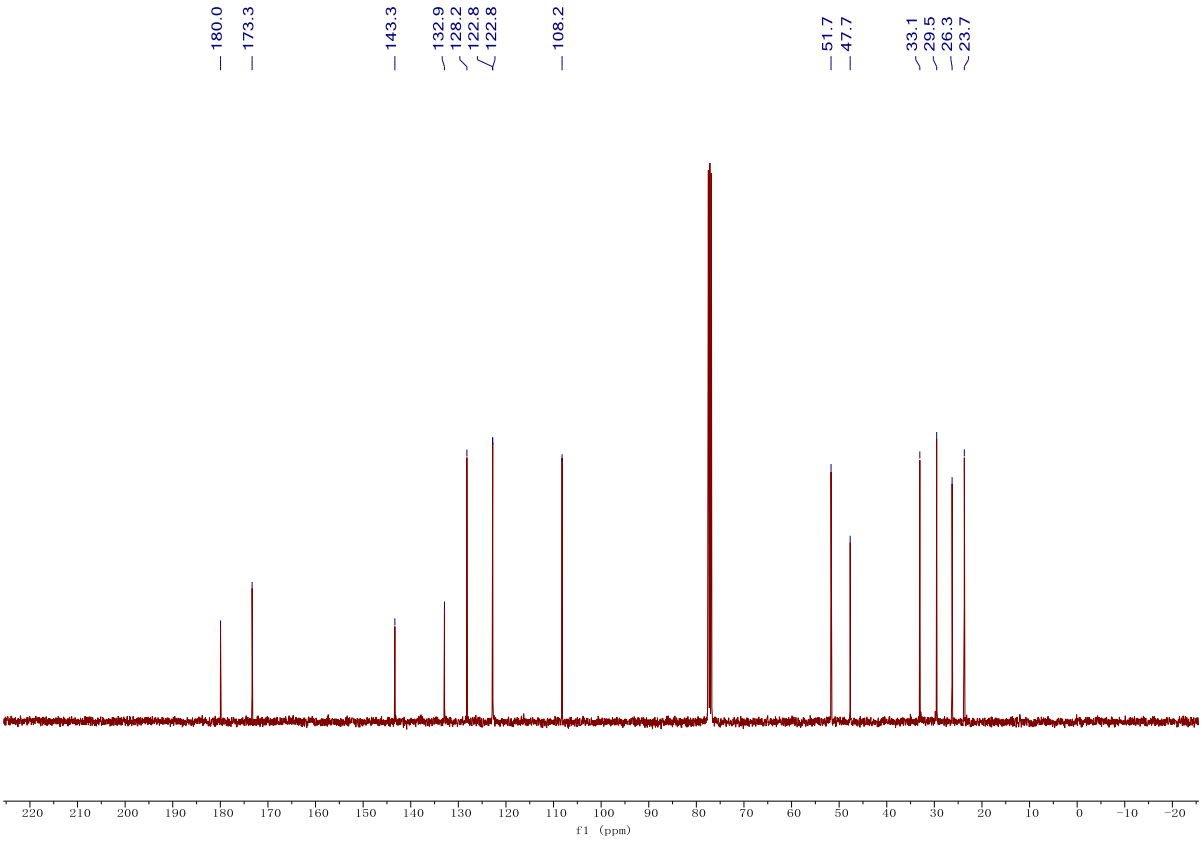
^{13}C NMR of 33 (101 MHz, $CDCl_3$)



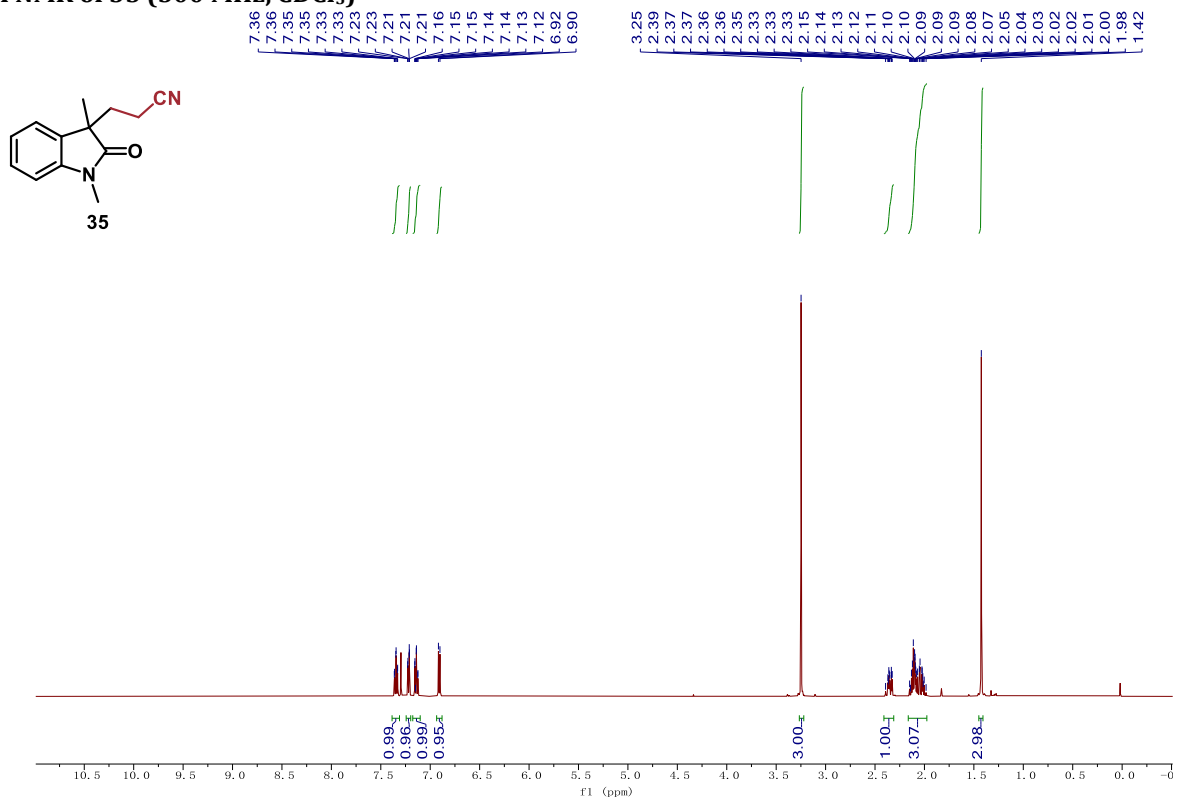
^{1}H NMR of 34 (500 MHz, $CDCl_3$)



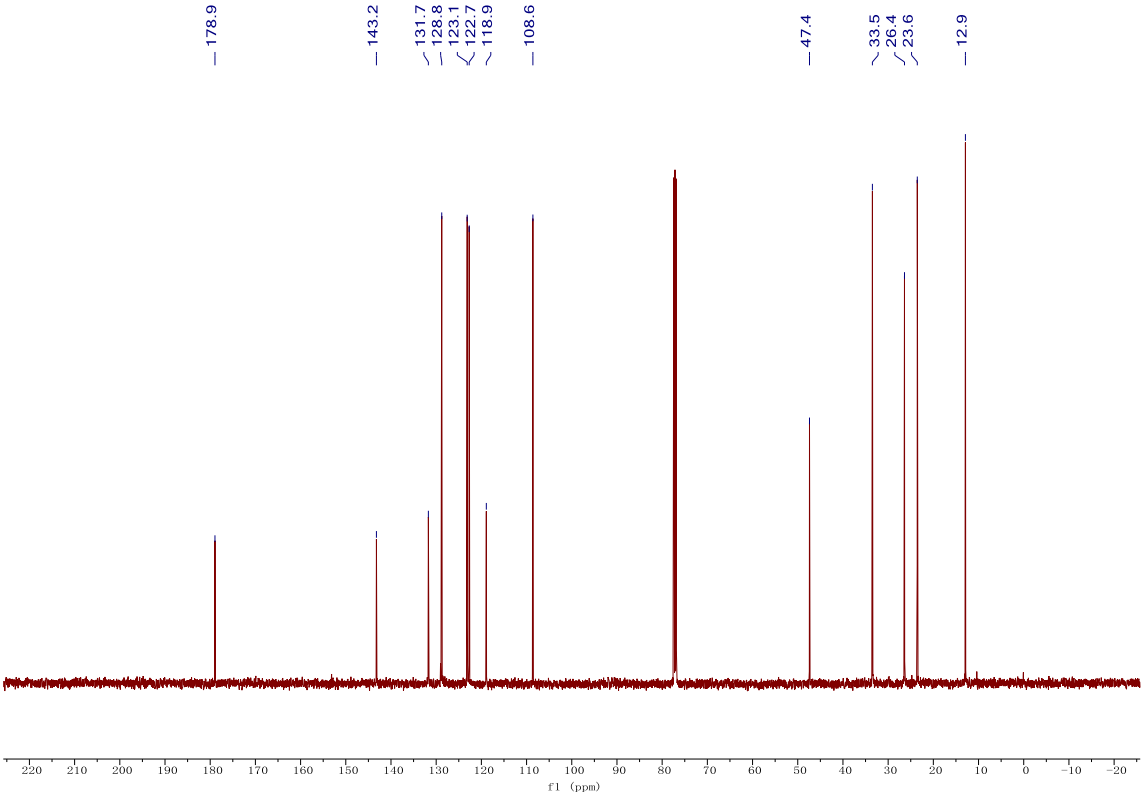
^{13}C NMR of 34 (101 MHz, $CDCl_3$)



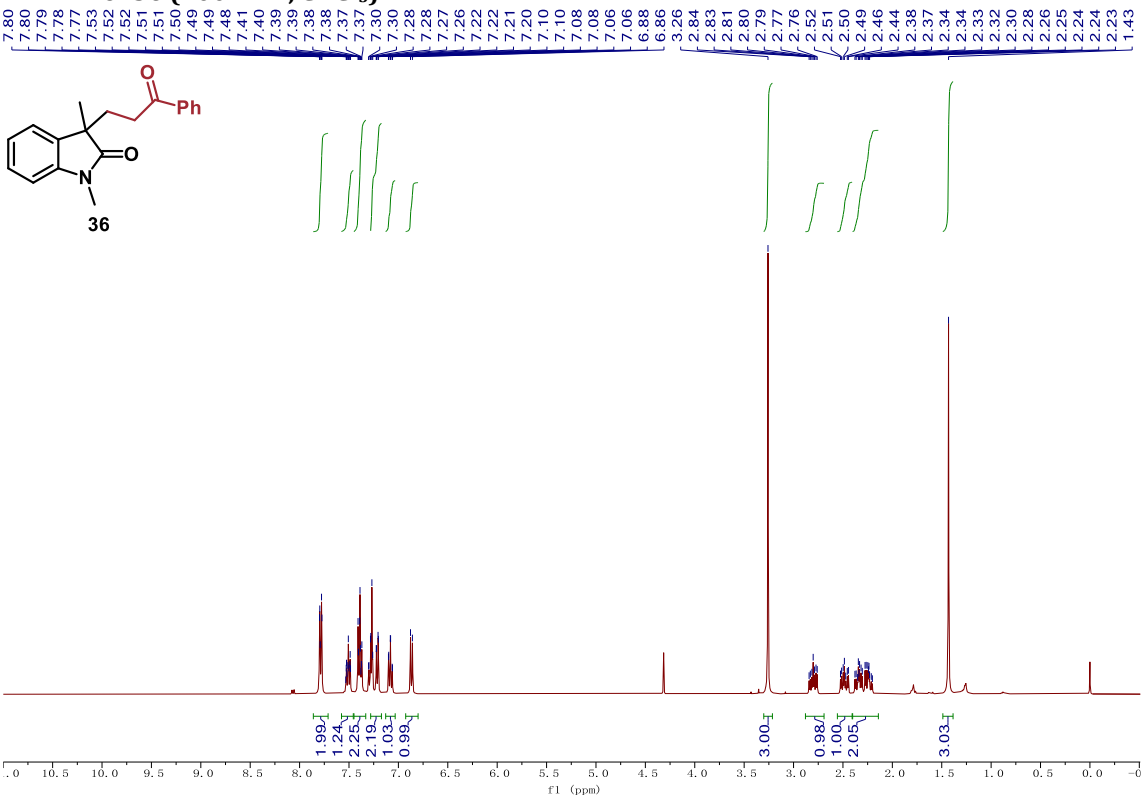
^{1}H NMR of 35 (500 MHz, $CDCl_3$)



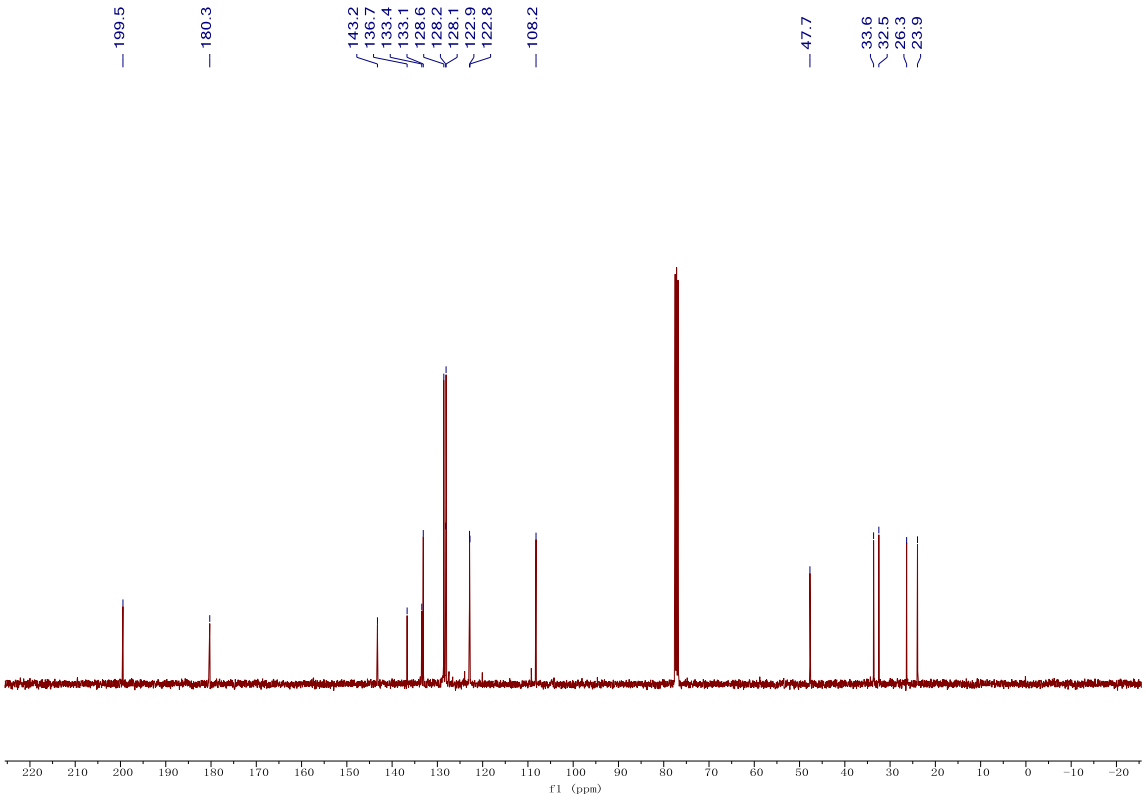
^{13}C NMR of 35 (126 MHz, $CDCl_3$)



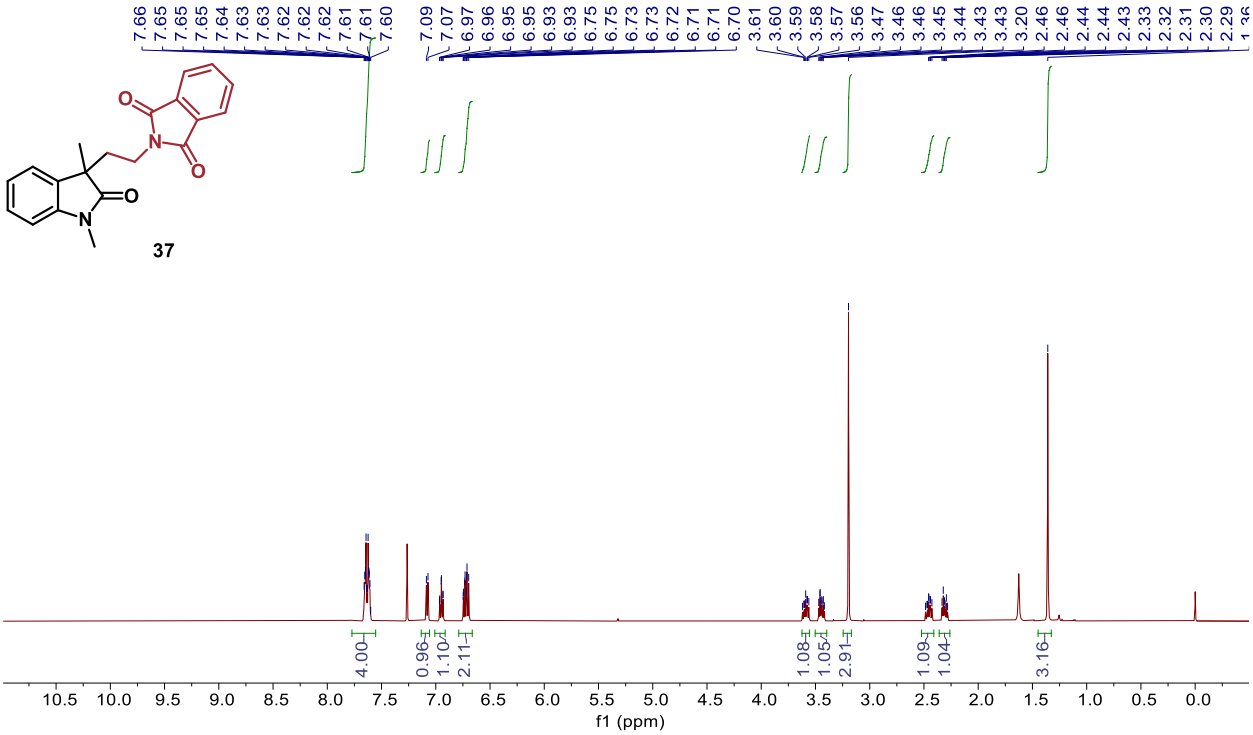
^{1}H NMR of 36 (400 MHz, $CDCl_3$)



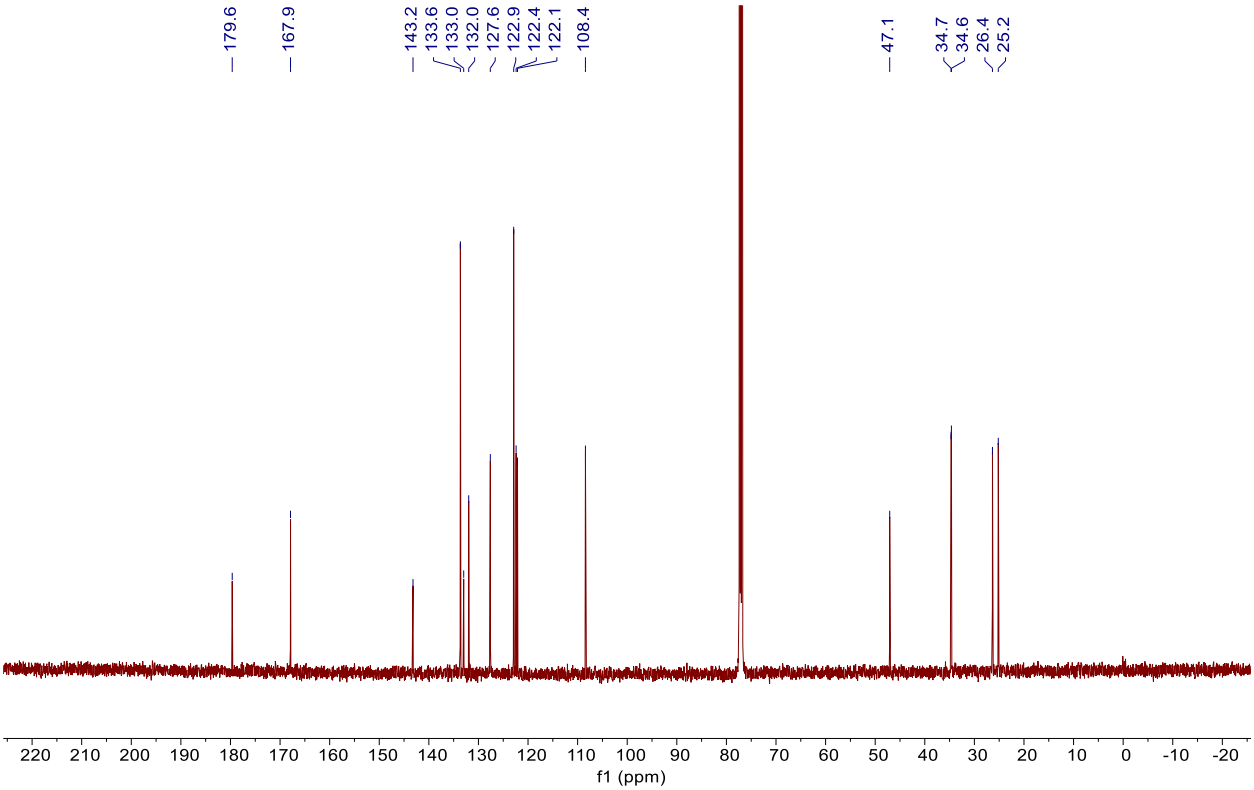
^{13}C NMR of 36 (101 MHz, $CDCl_3$)



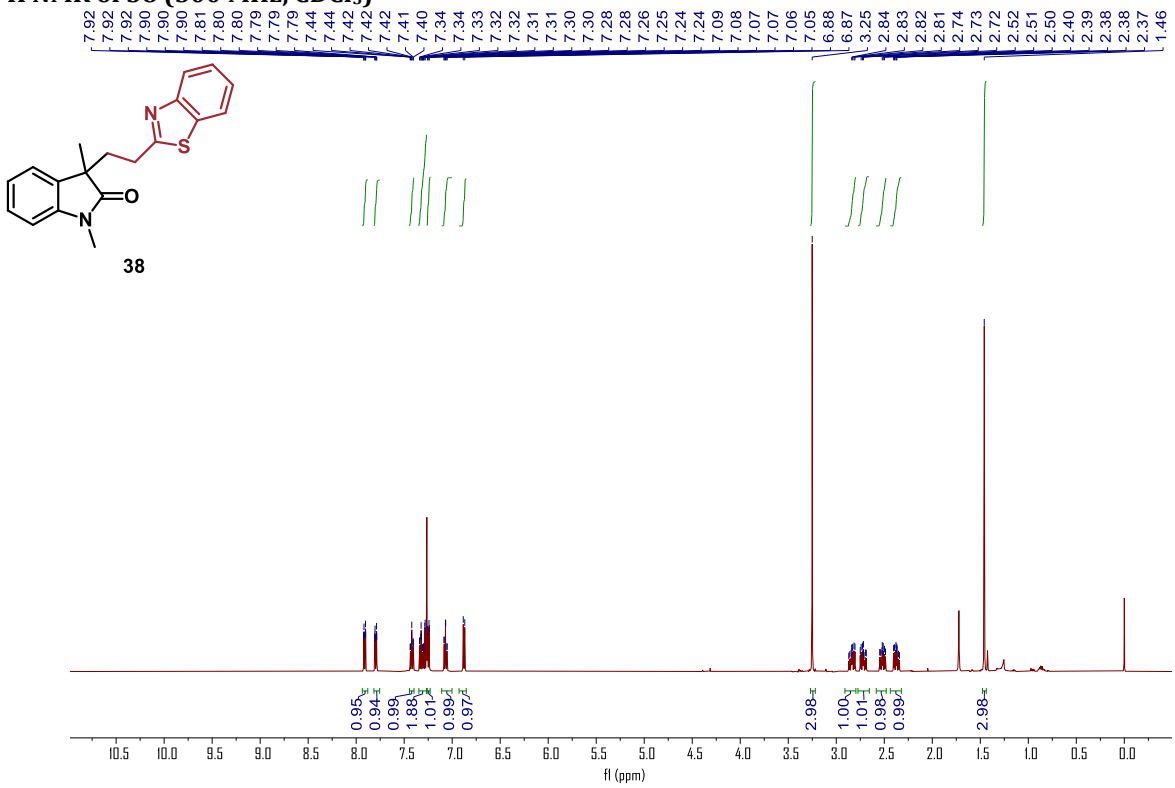
^{1}H NMR of 37 (500 MHz, $CDCl_3$)



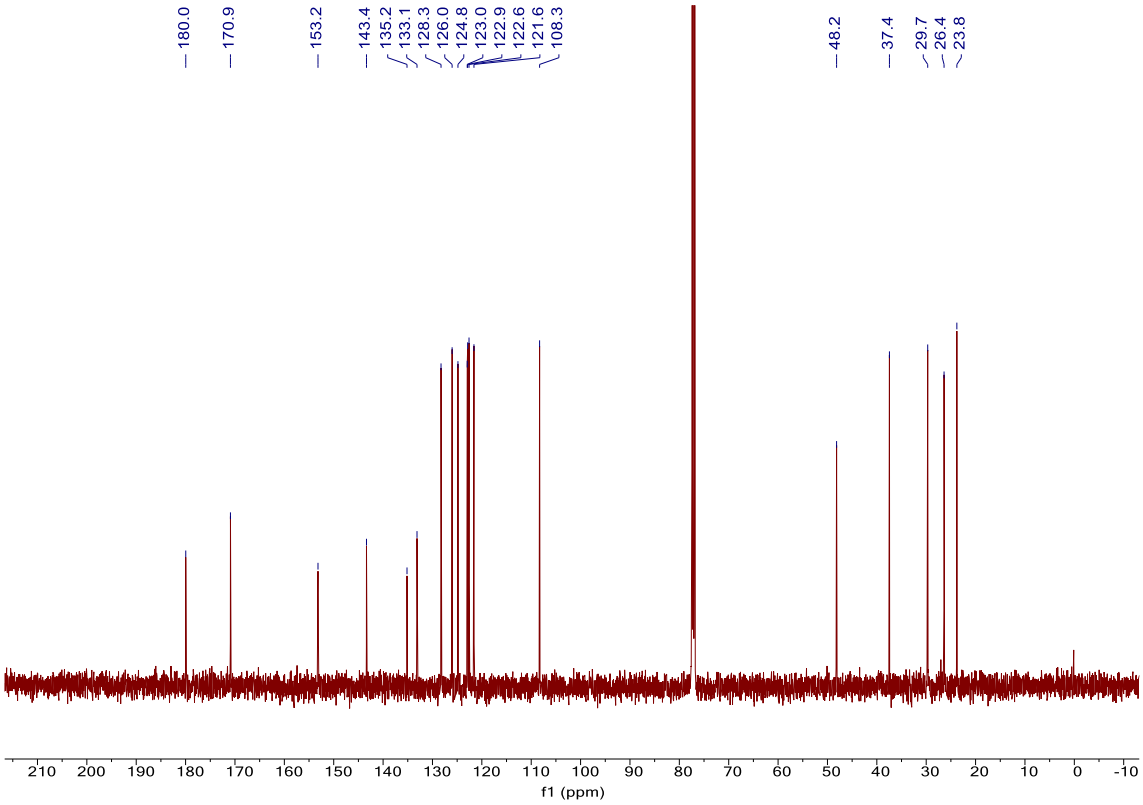
^{13}C NMR of 37 (126 MHz, $CDCl_3$)



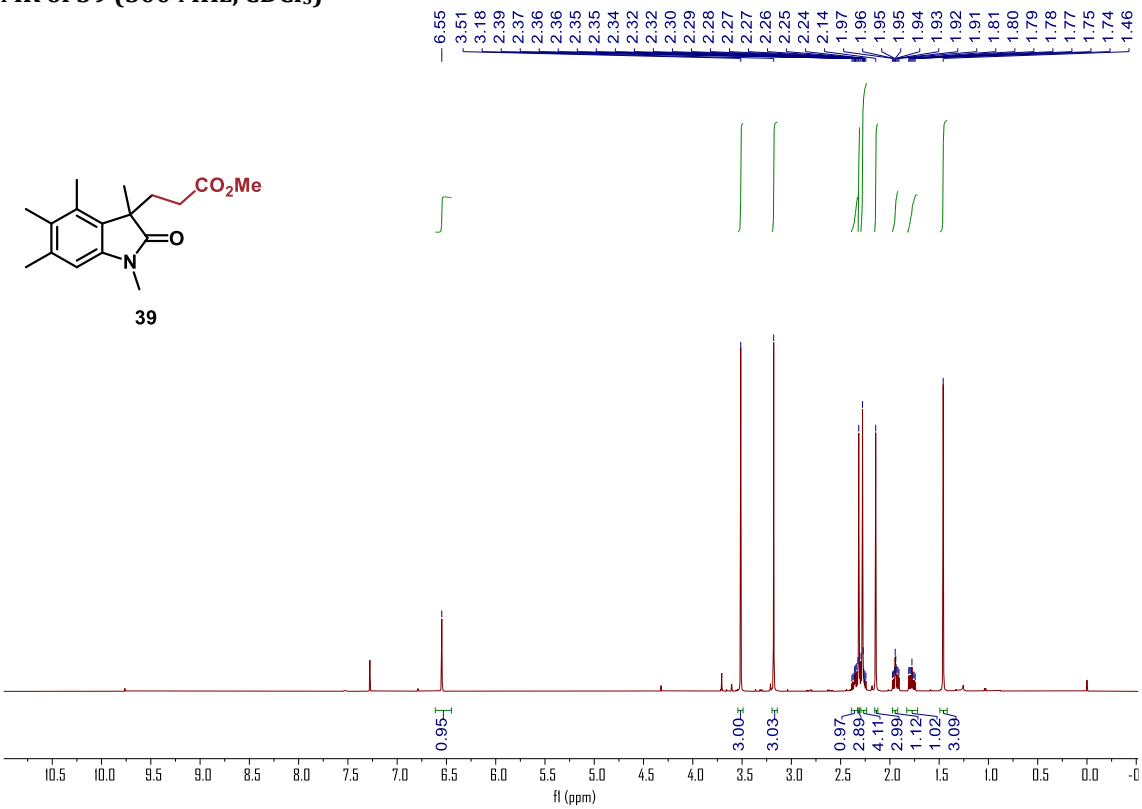
^{1}H NMR of 38 (500 MHz, $CDCl_3$)



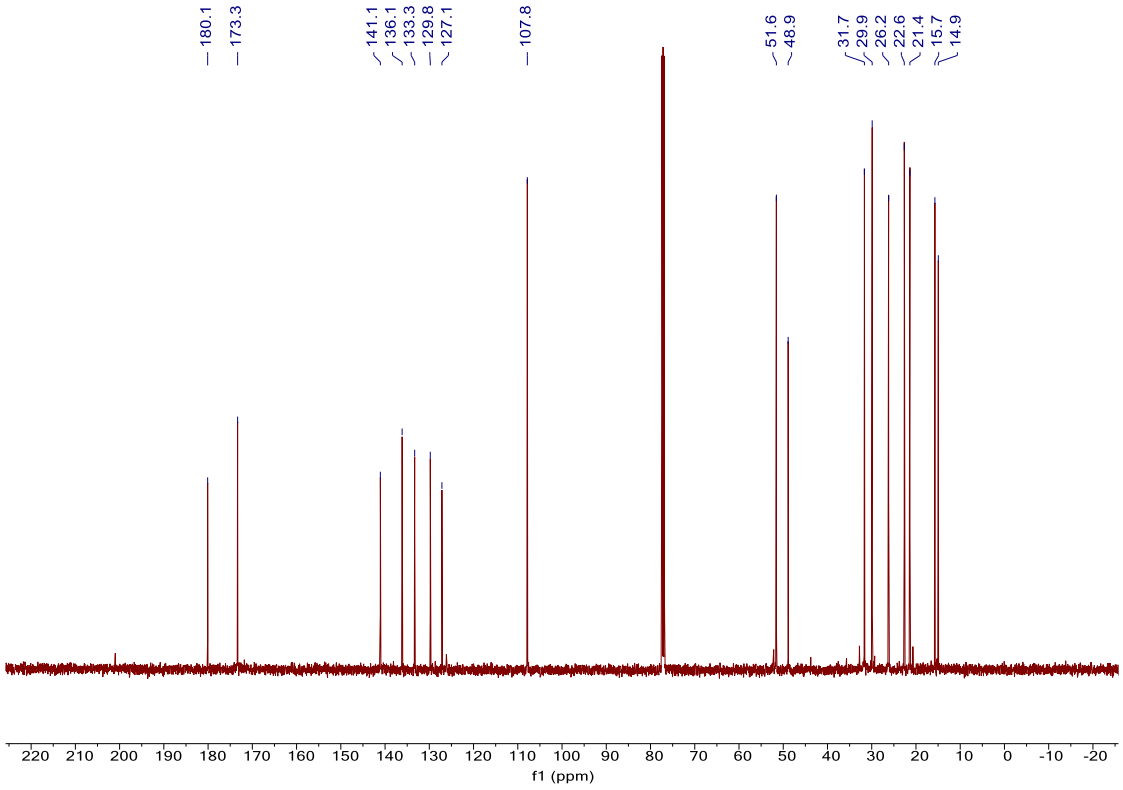
^{13}C NMR of 38 (126 MHz, $CDCl_3$)



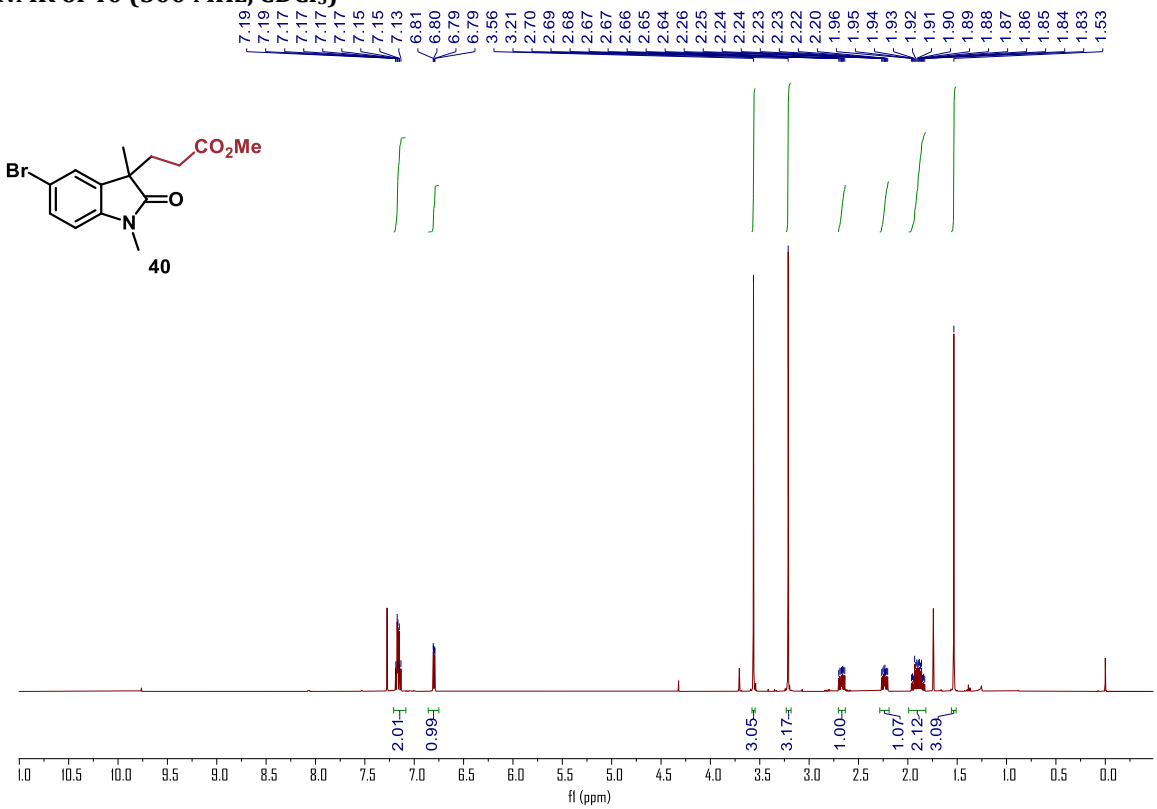
^{1}H NMR of 39 (500 MHz, $CDCl_3$)



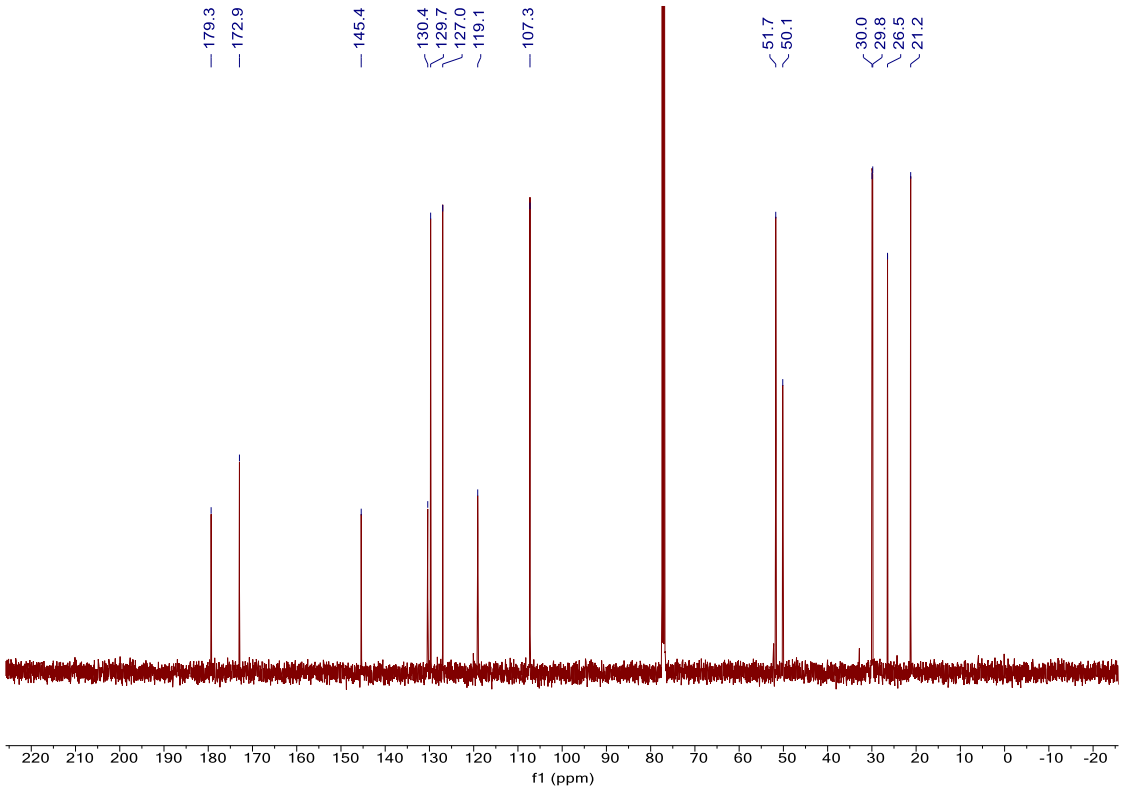
^{13}C NMR of 39 (126 MHz, $CDCl_3$)



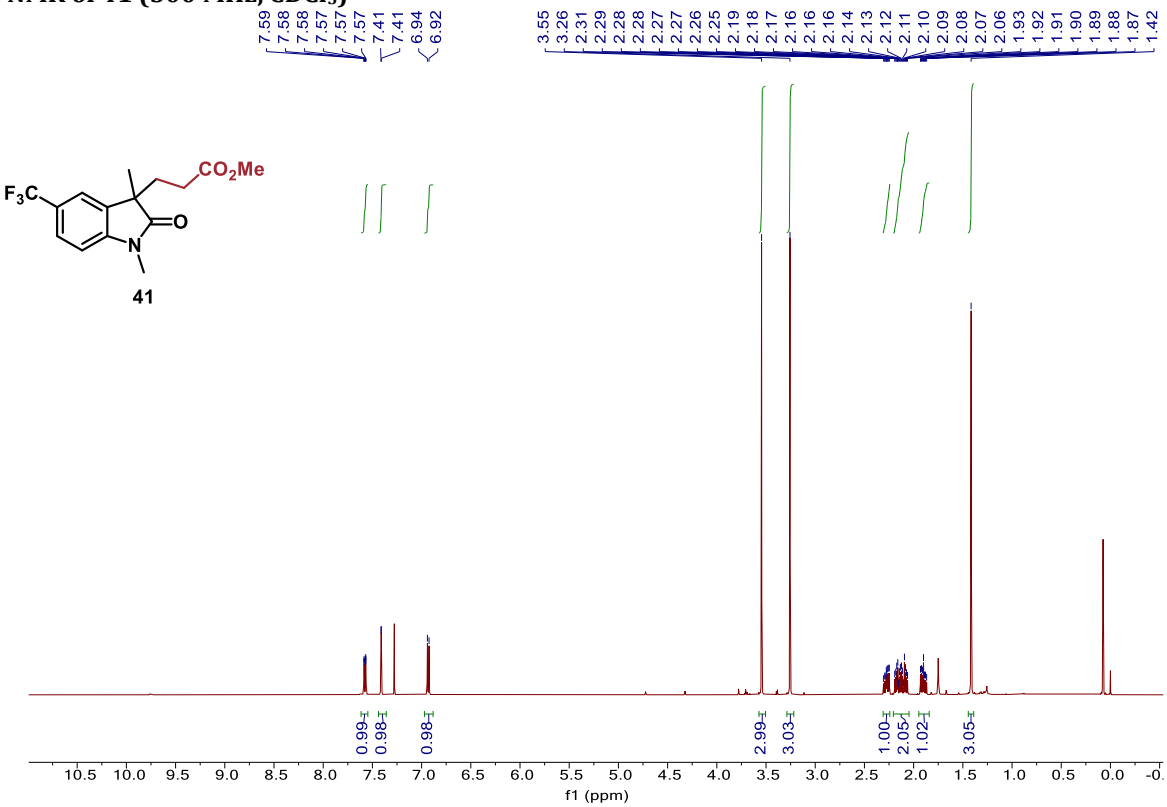
^{1}H NMR of 40 (500 MHz, $CDCl_3$)



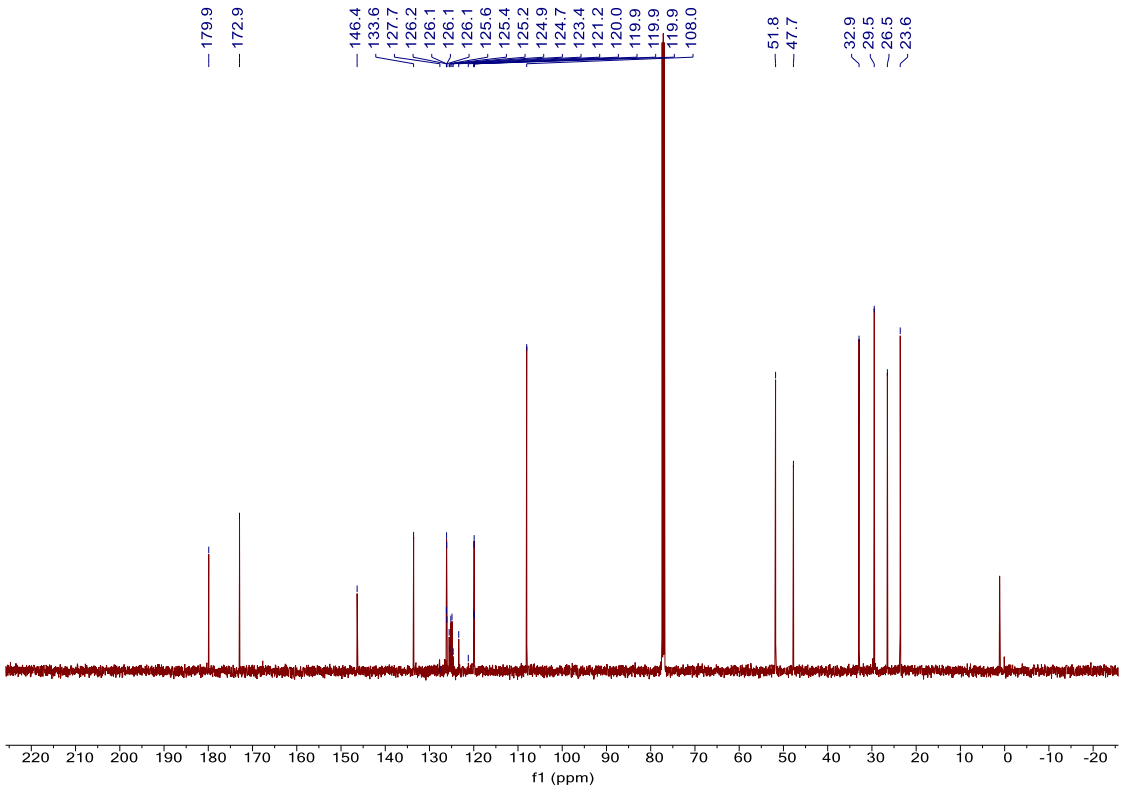
^{13}C NMR of 40 (126 MHz, $CDCl_3$)



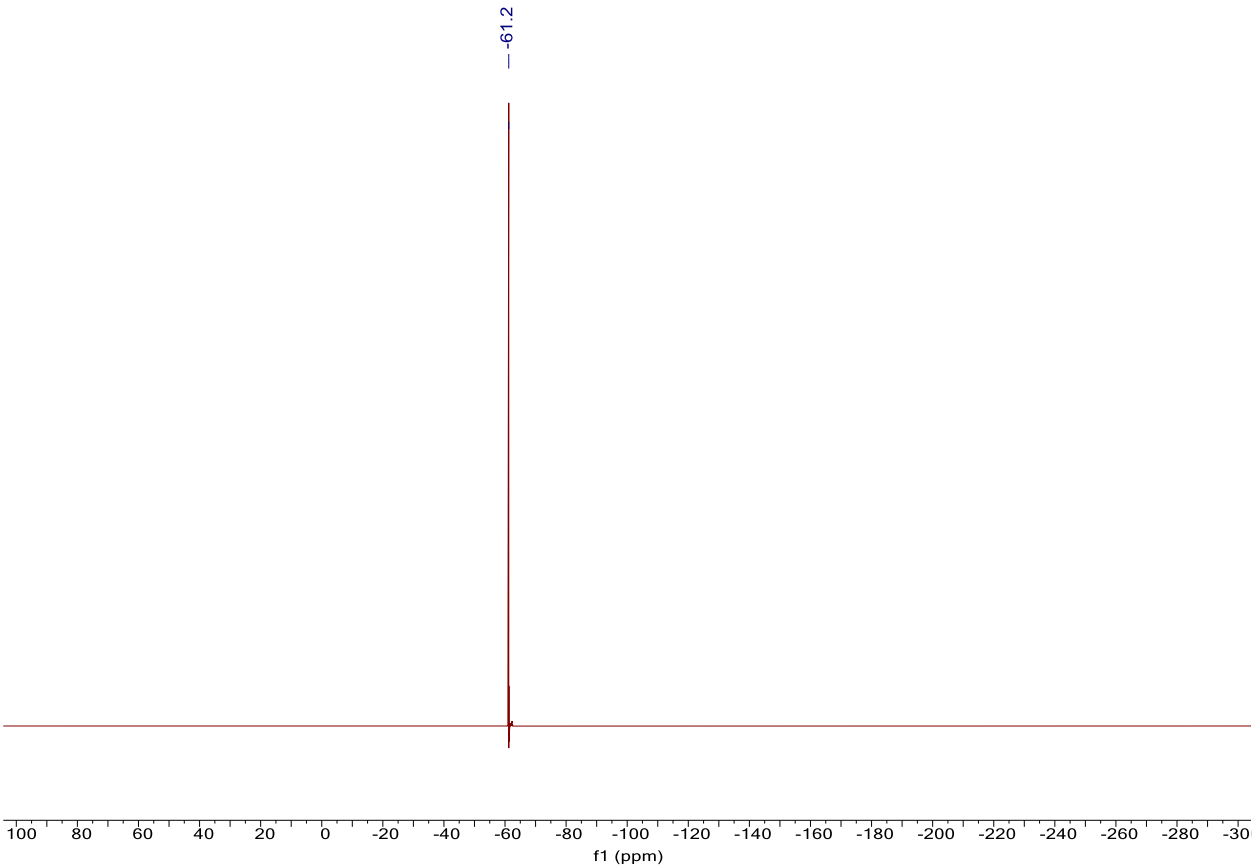
^{1}H NMR of 41 (500 MHz, $CDCl_3$)



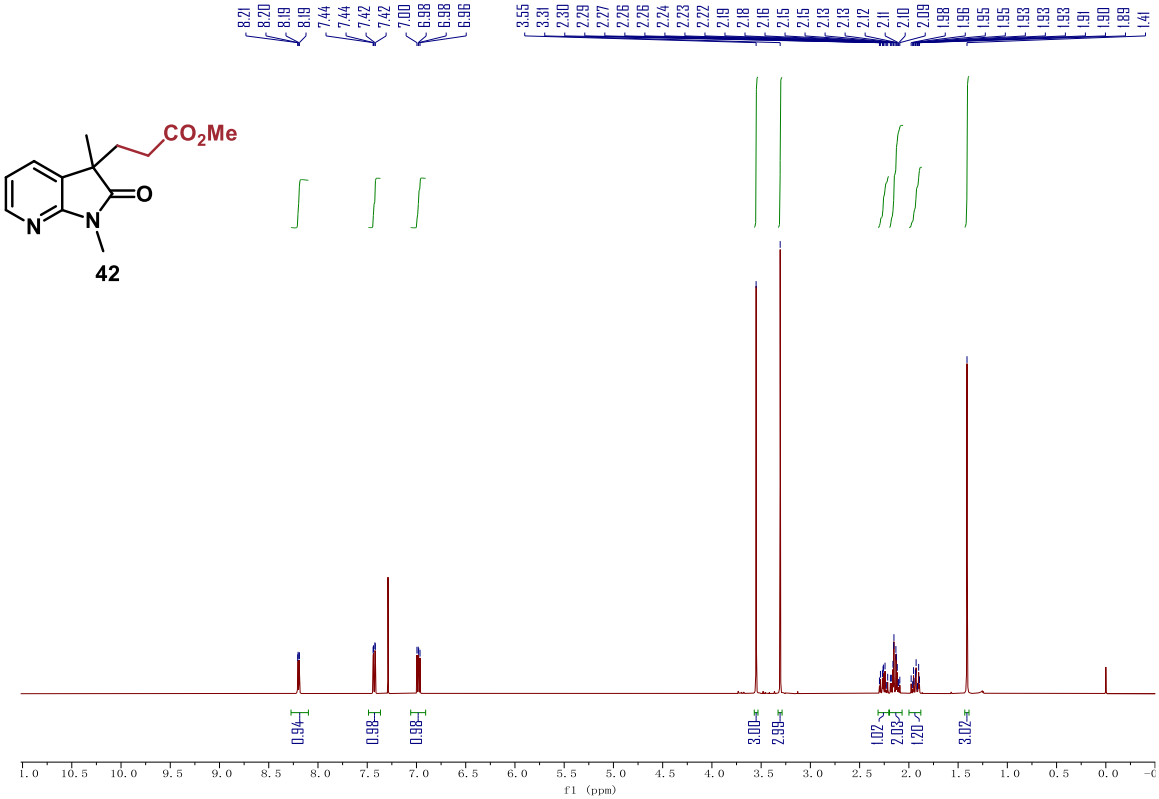
^{13}C NMR of 41 (126 MHz, $CDCl_3$)



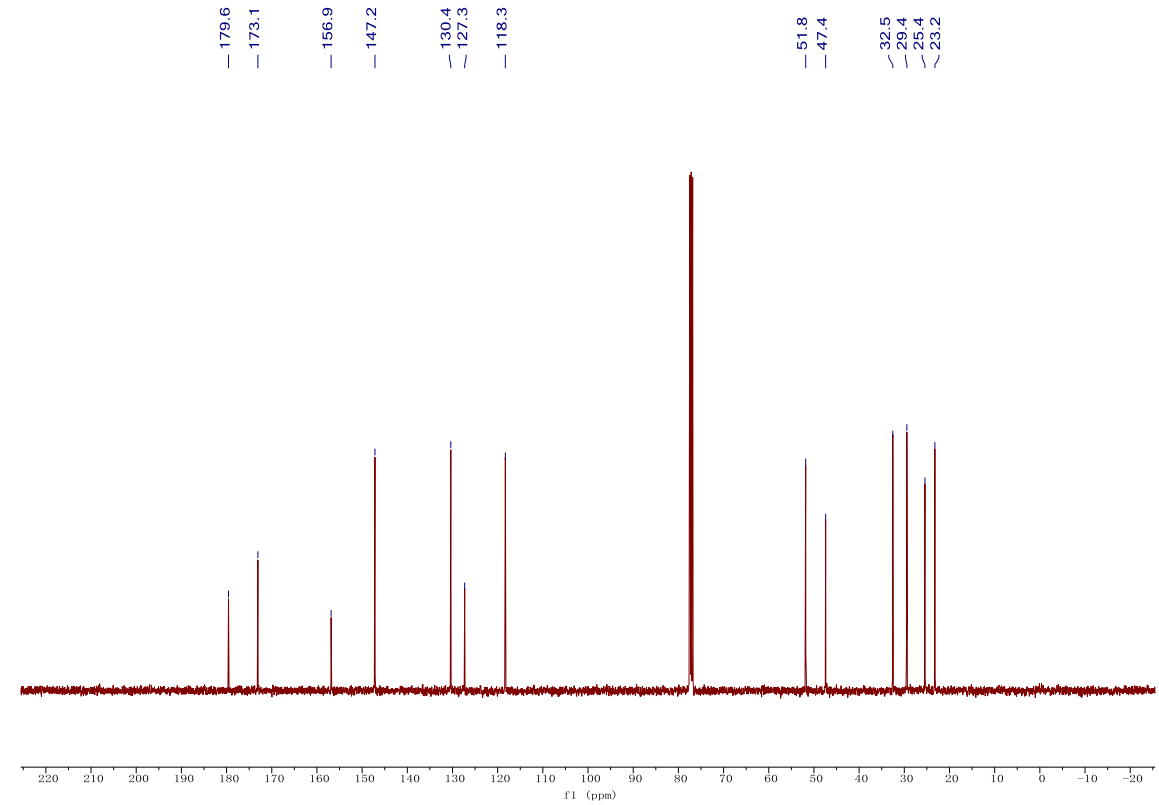
^{19}F NMR of 41 (471 MHz, $CDCl_3$)



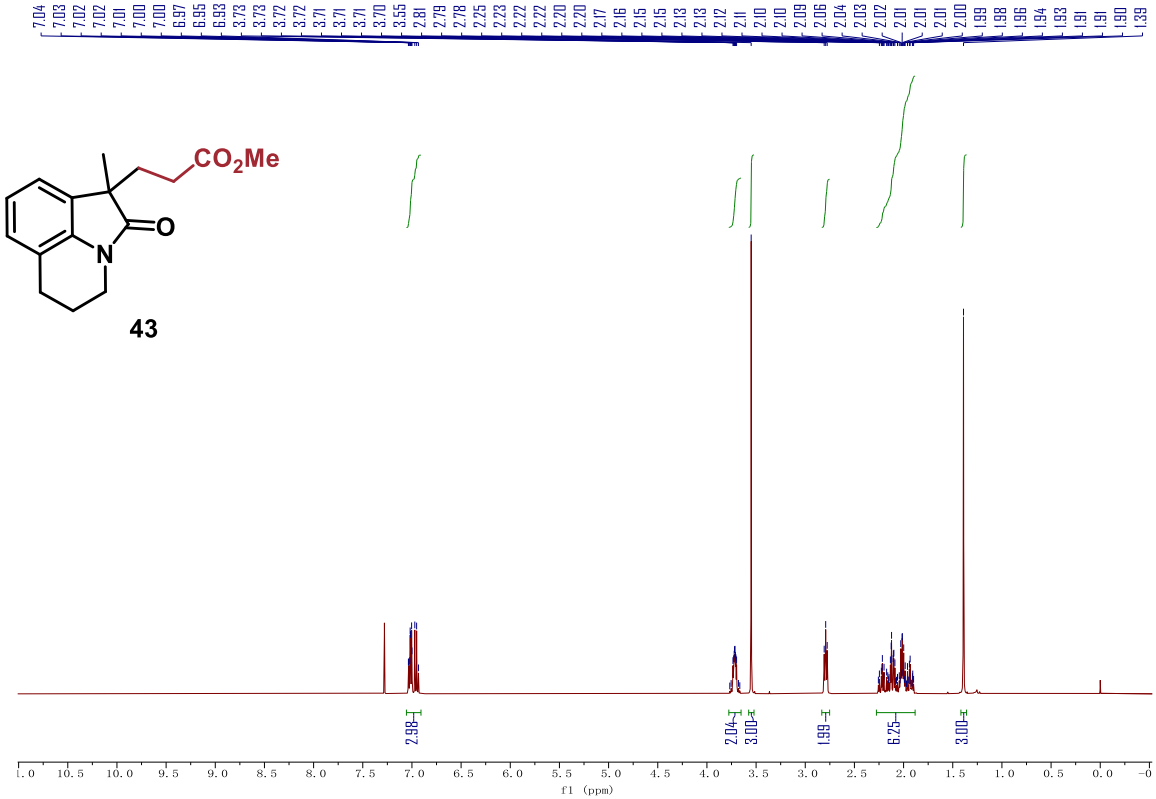
^{1}H NMR of 42 (400 MHz, $CDCl_3$)



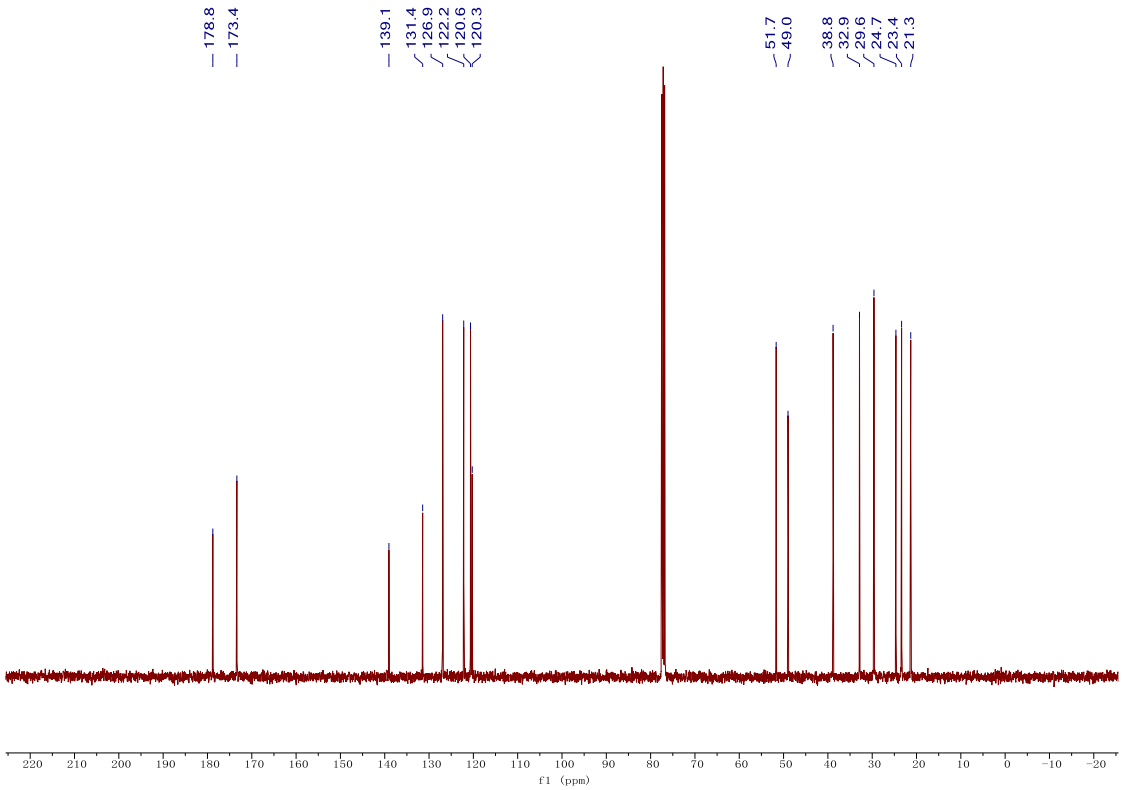
^{13}C NMR of 42 (101 MHz, $CDCl_3$)



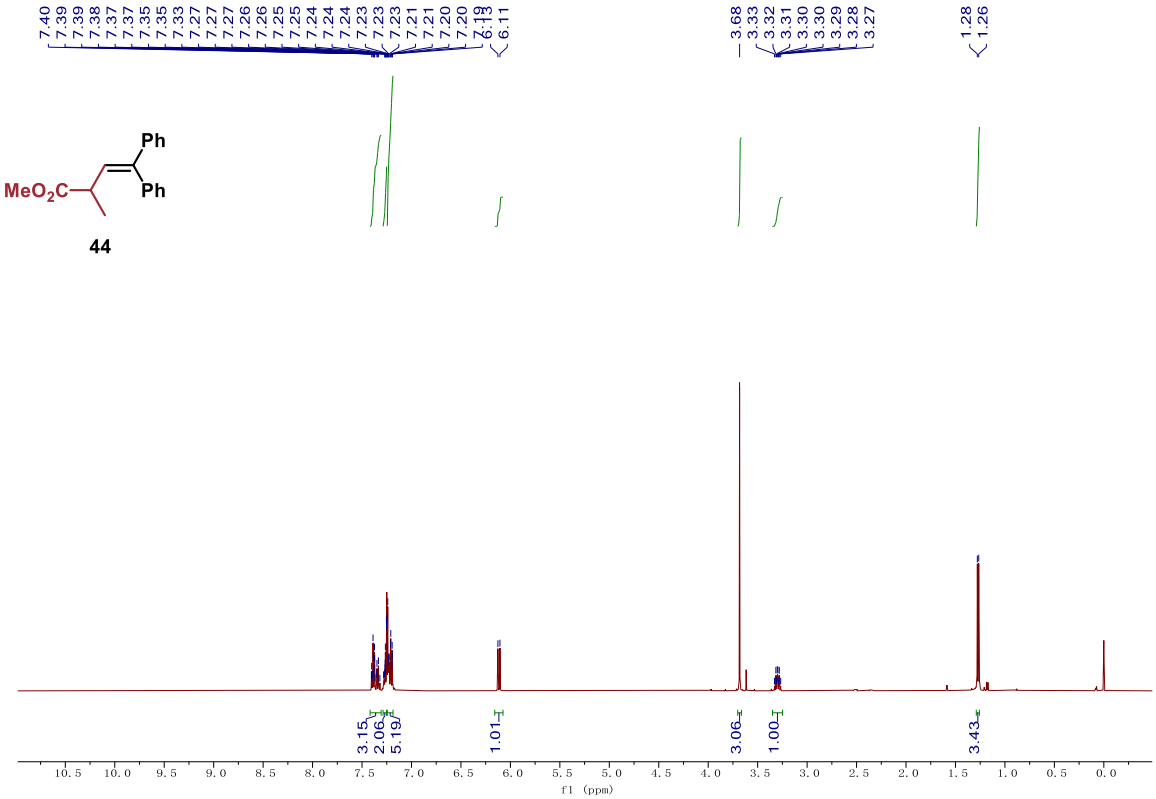
^{1}H NMR of 43 (400 MHz, $CDCl_3$)



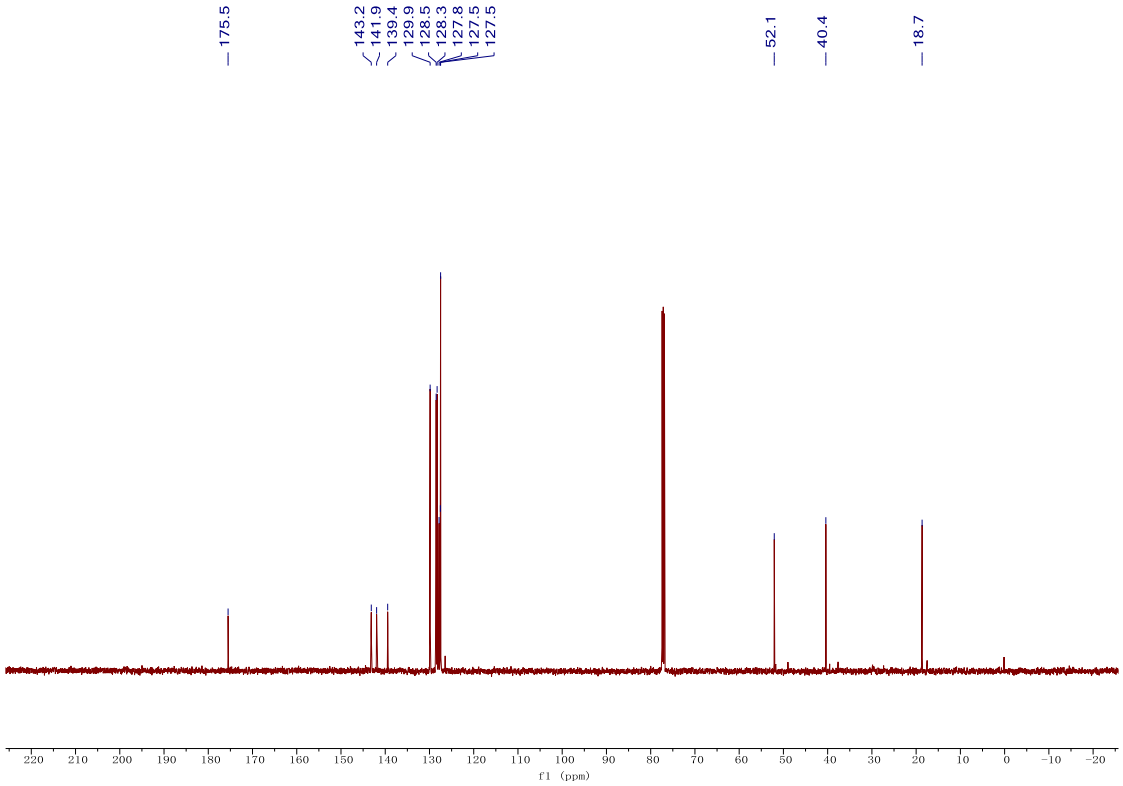
^{13}C NMR of 43 (101 MHz, $CDCl_3$)



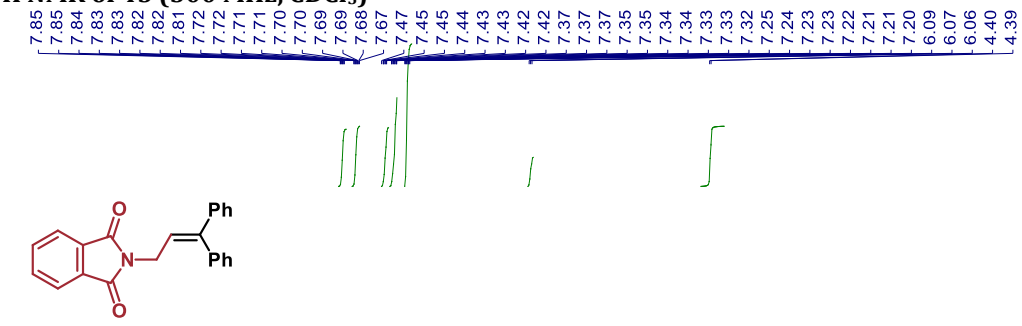
^{1}H NMR of 44 (500 MHz, $CDCl_3$)



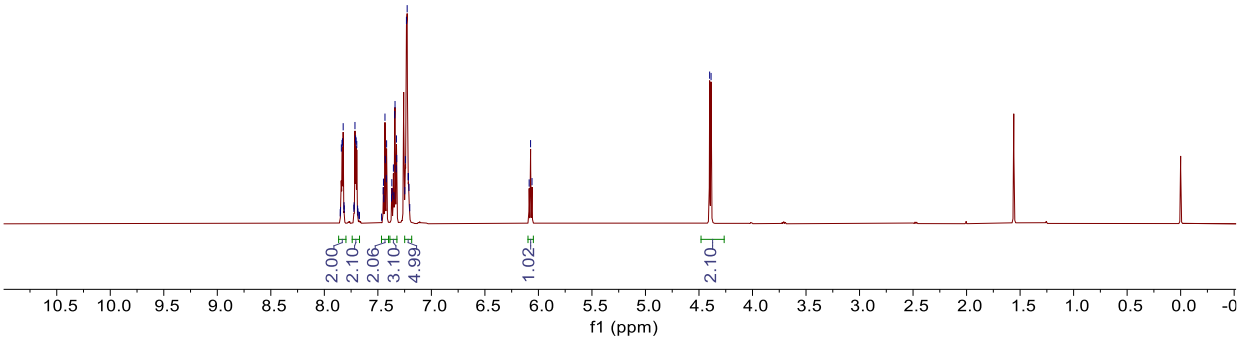
^{13}C NMR of 44 (126 MHz, $CDCl_3$)



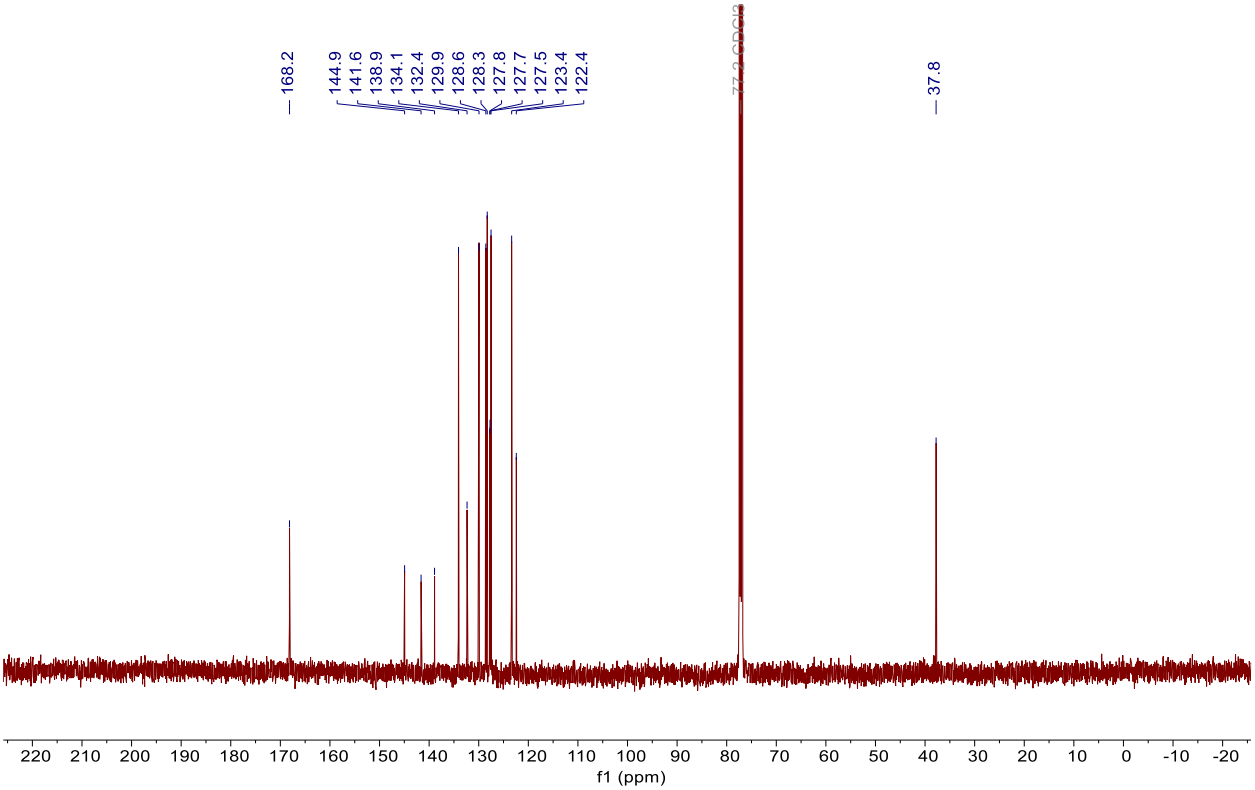
^{1}H NMR of 45 (500 MHz, $CDCl_3$)



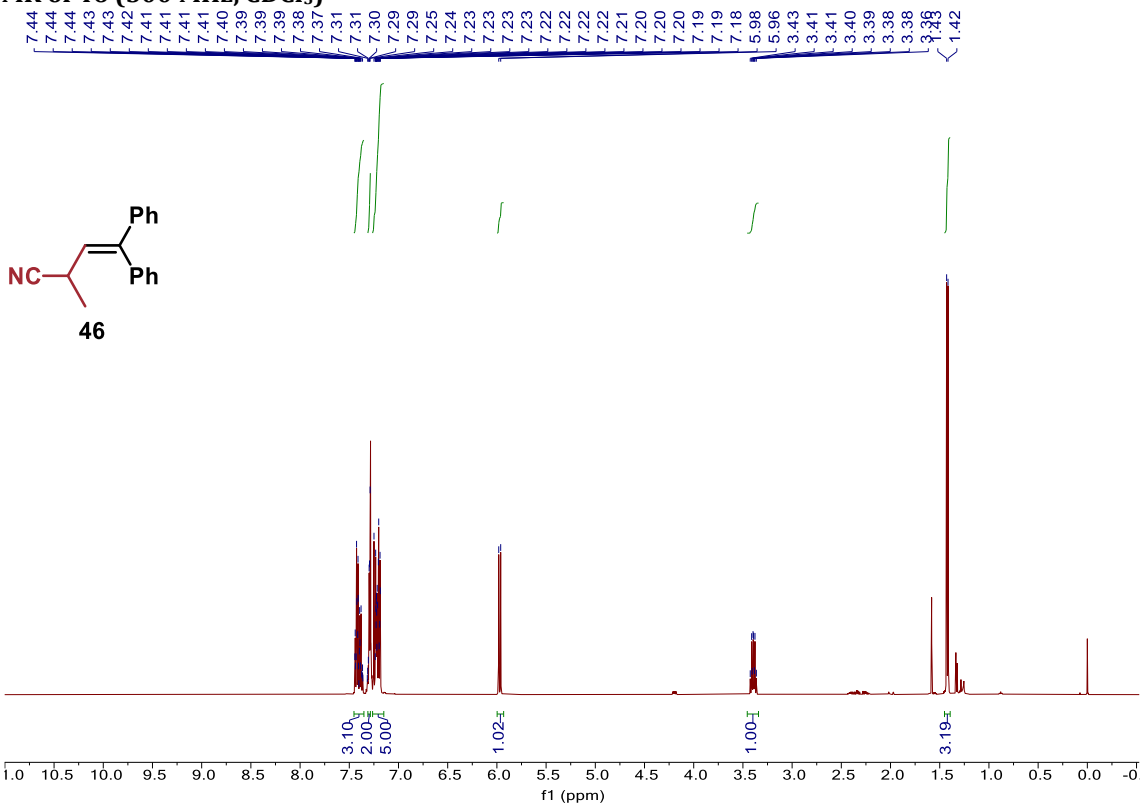
45



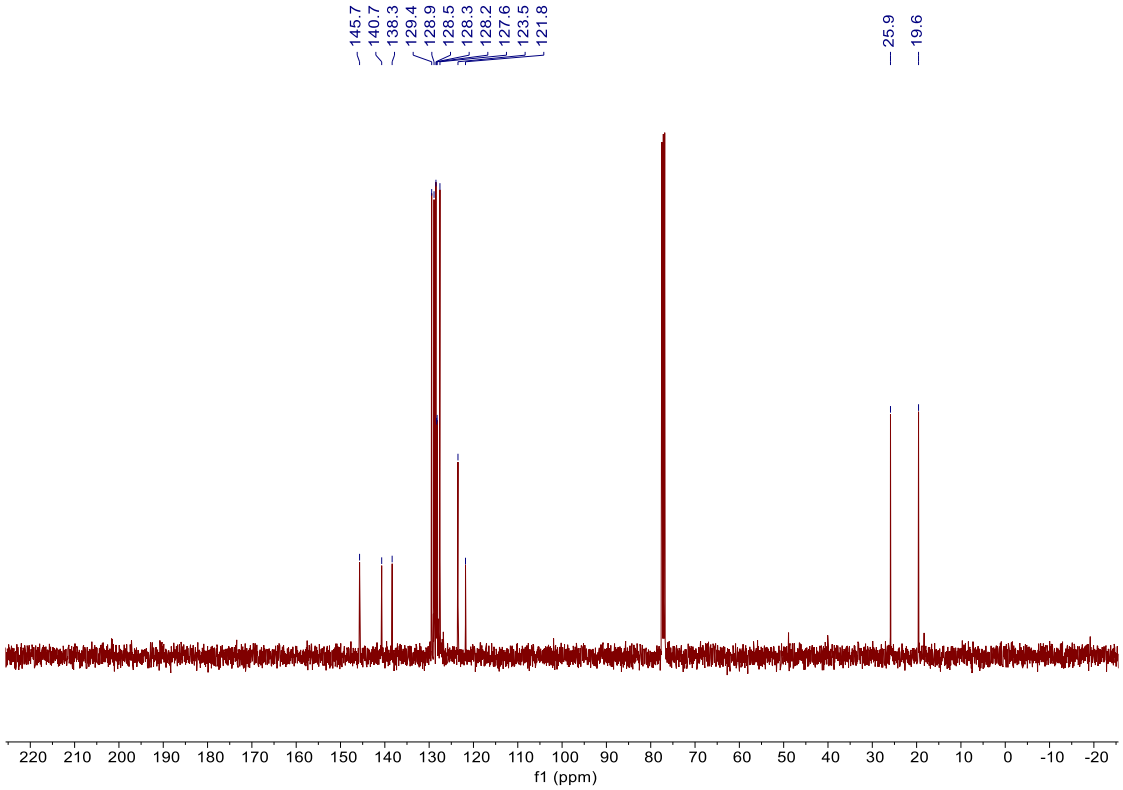
^{13}C NMR of 45 (126 MHz, $CDCl_3$)



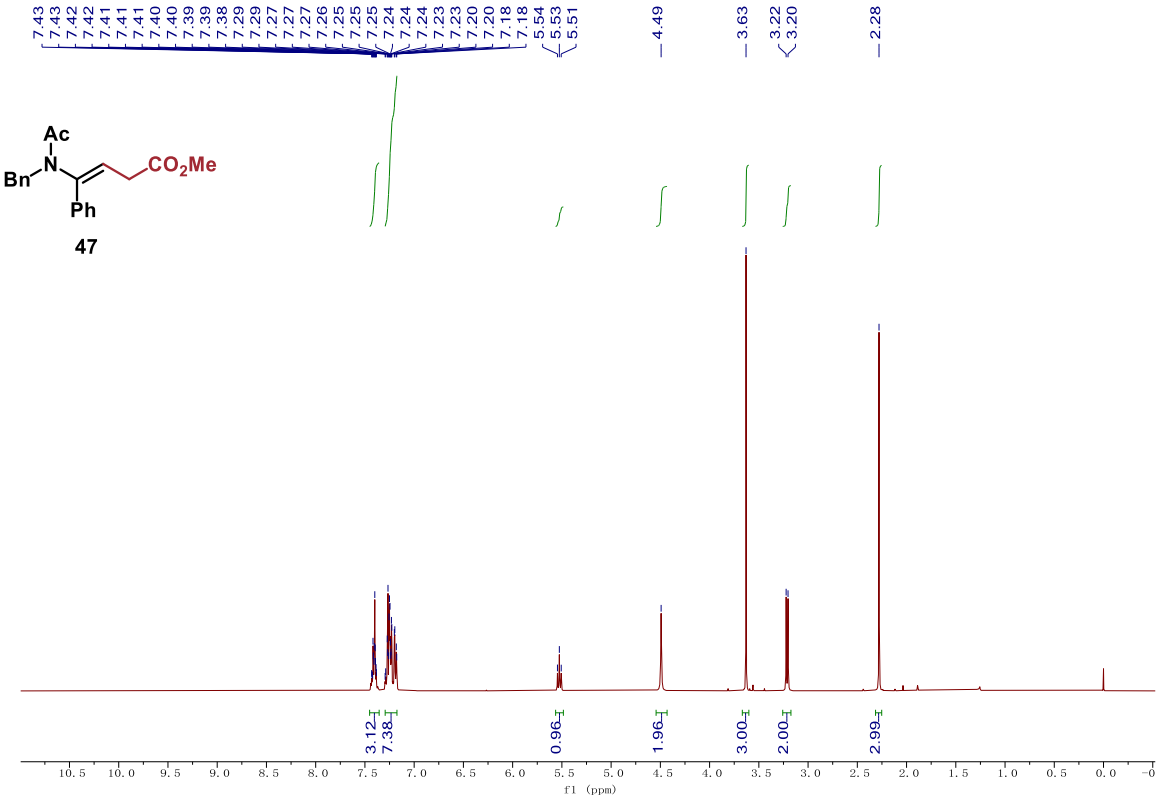
^{1}H NMR of 46 (500 MHz, $CDCl_3$)



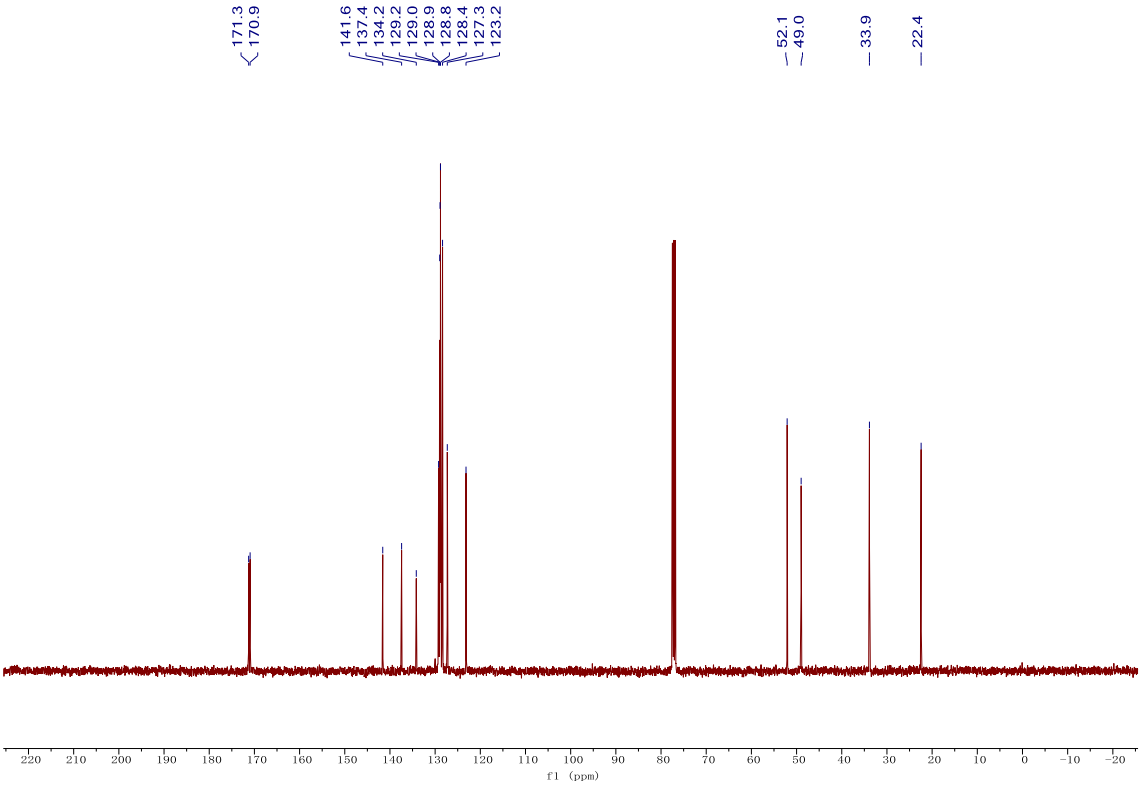
^{13}C NMR of 46 (101 MHz, $CDCl_3$)



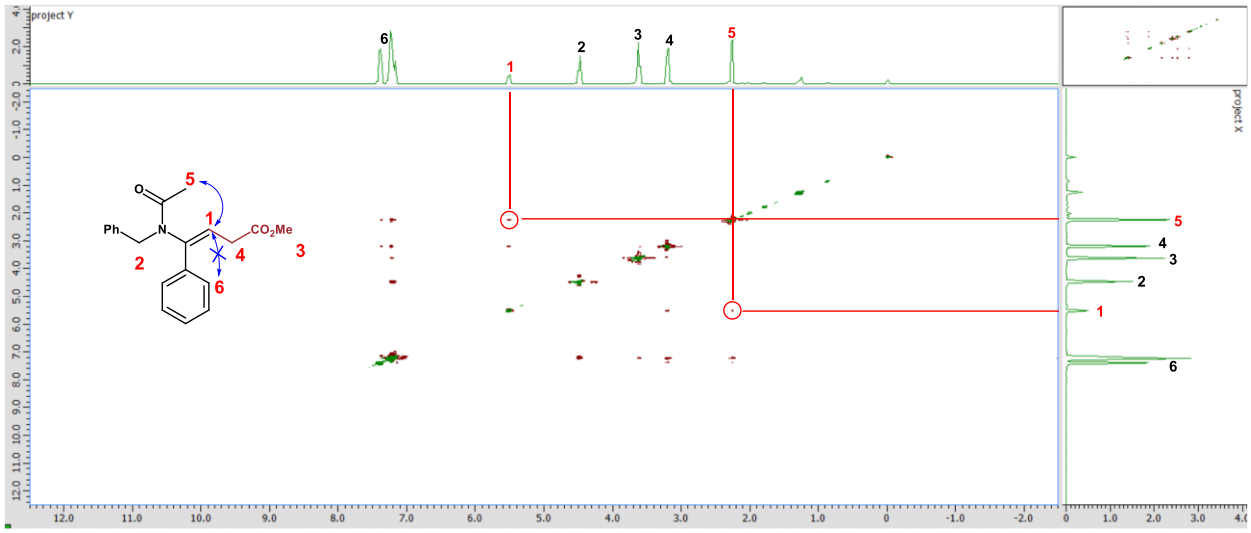
^{1}H NMR of 47 (400 MHz, $CDCl_3$)



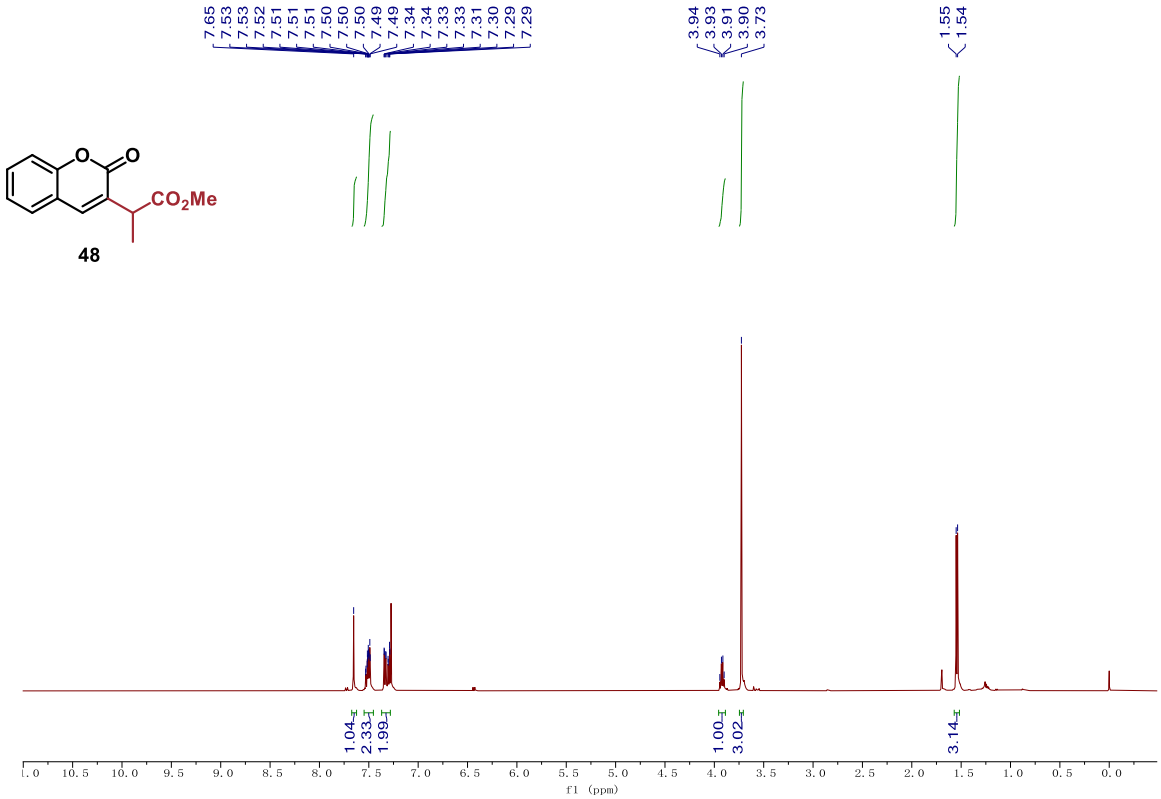
^{13}C NMR of 47 (101 MHz, $CDCl_3$)



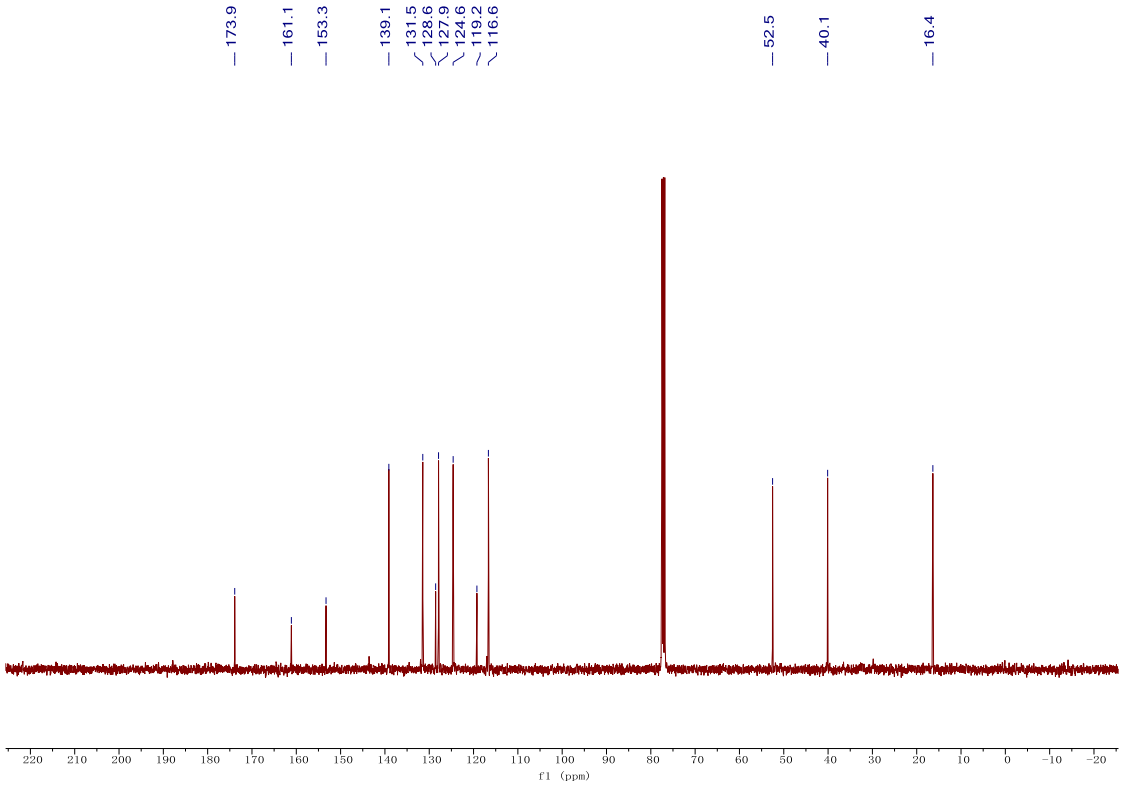
NOESY



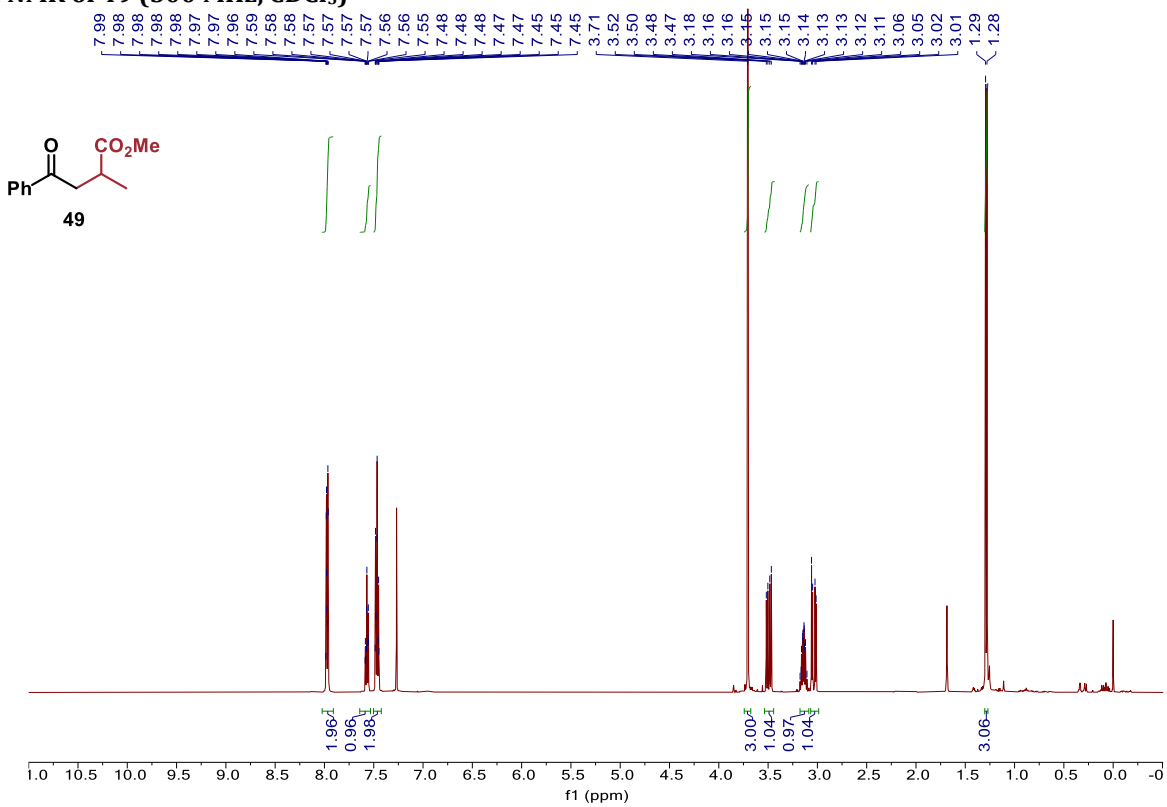
^{1}H NMR of 48 (500 MHz, $CDCl_3$)



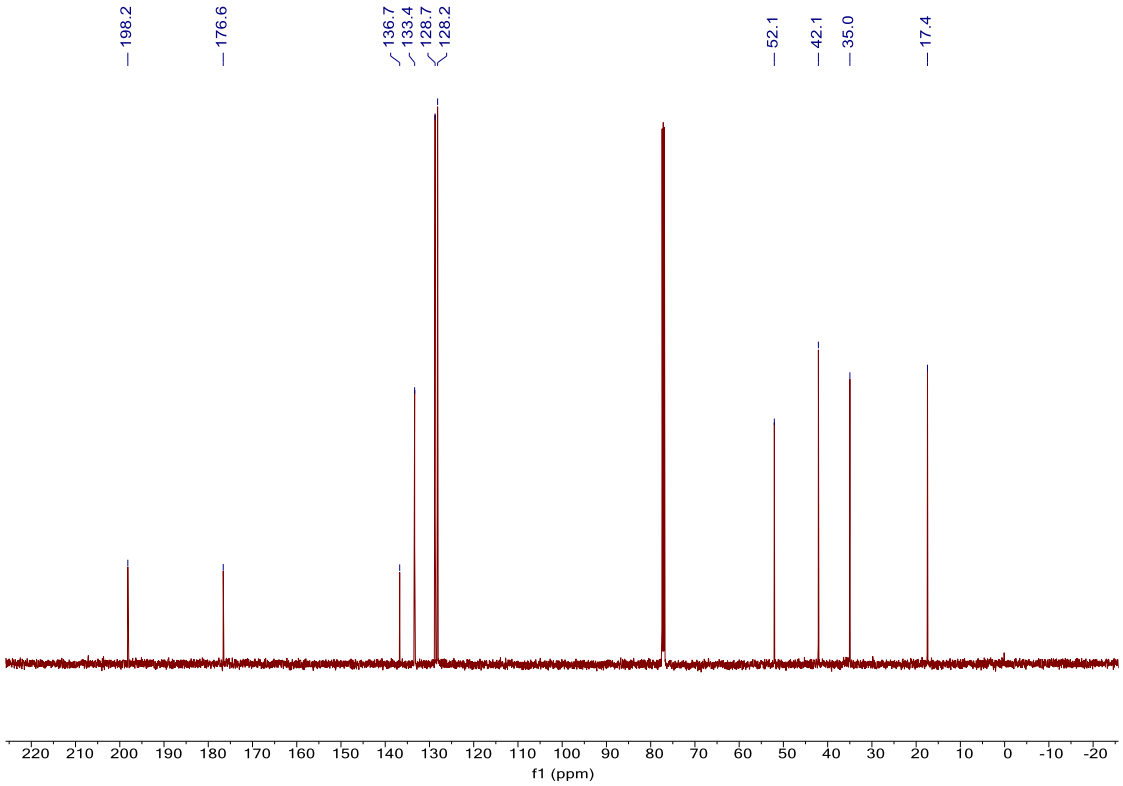
^{13}C NMR of 48 (101 MHz, $CDCl_3$)



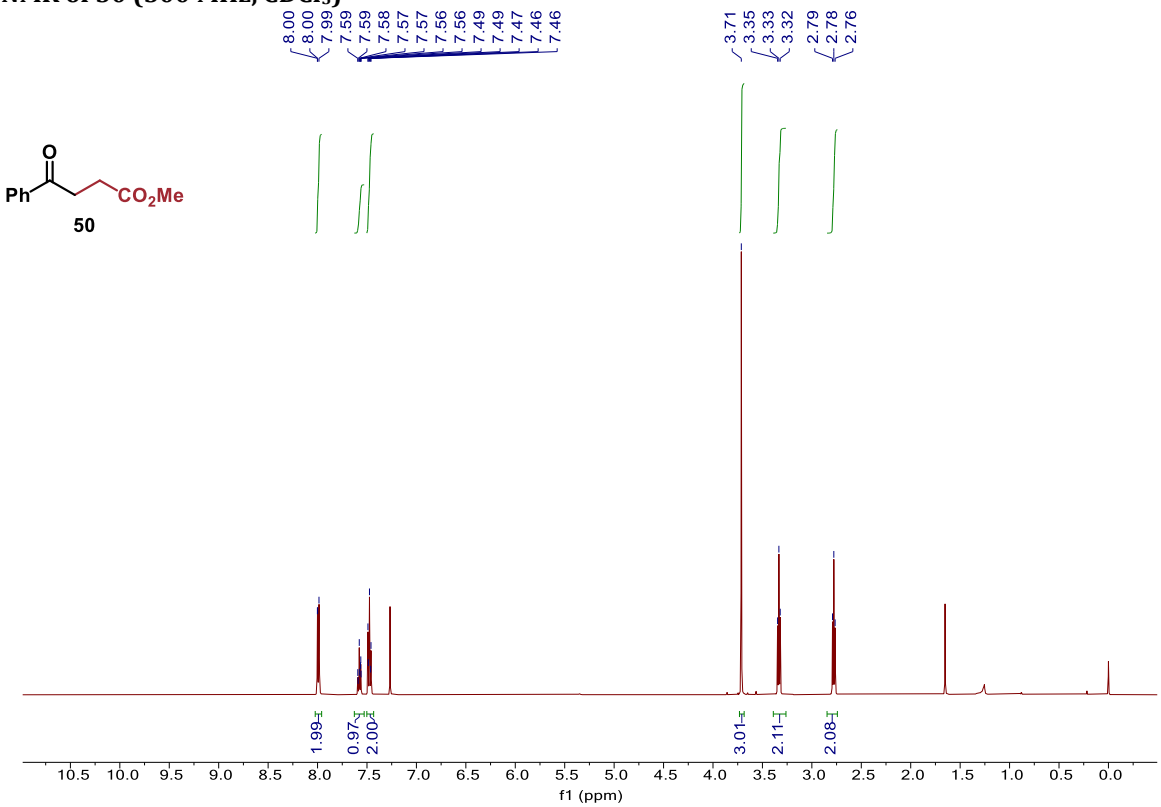
^{1}H NMR of 49 (500 MHz, $CDCl_3$)



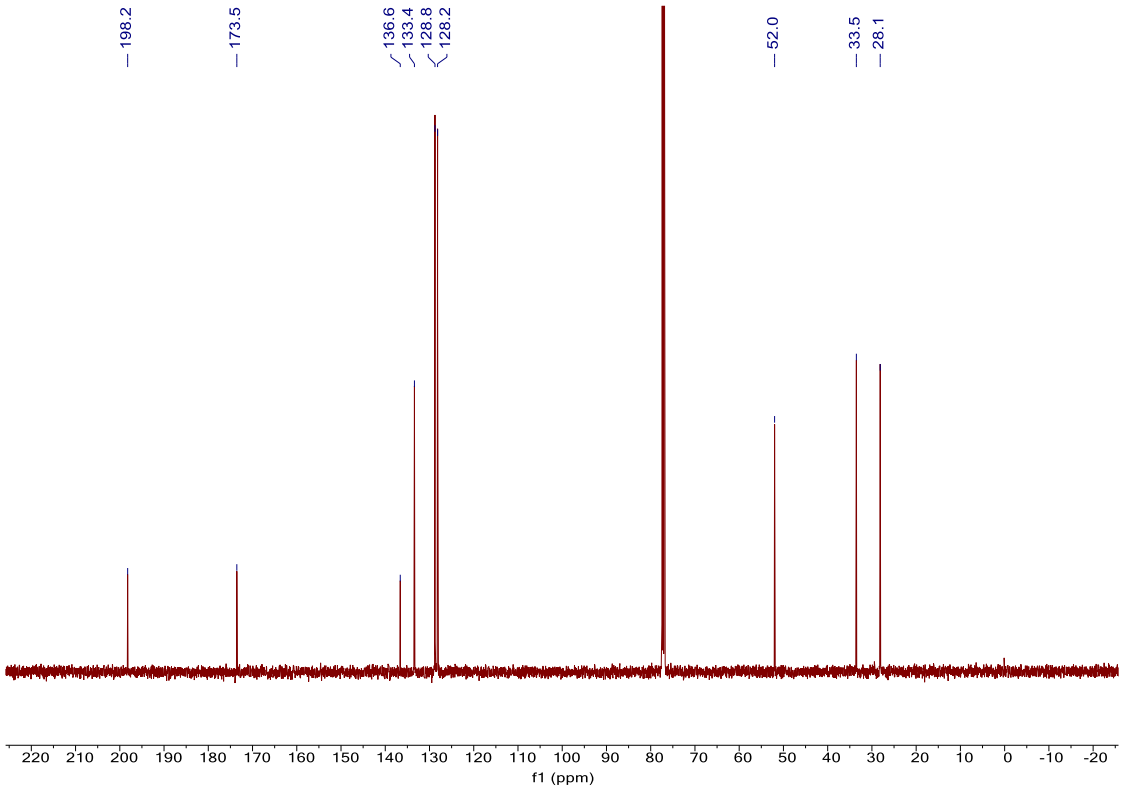
^{13}C NMR of 49 (126 MHz, $CDCl_3$)



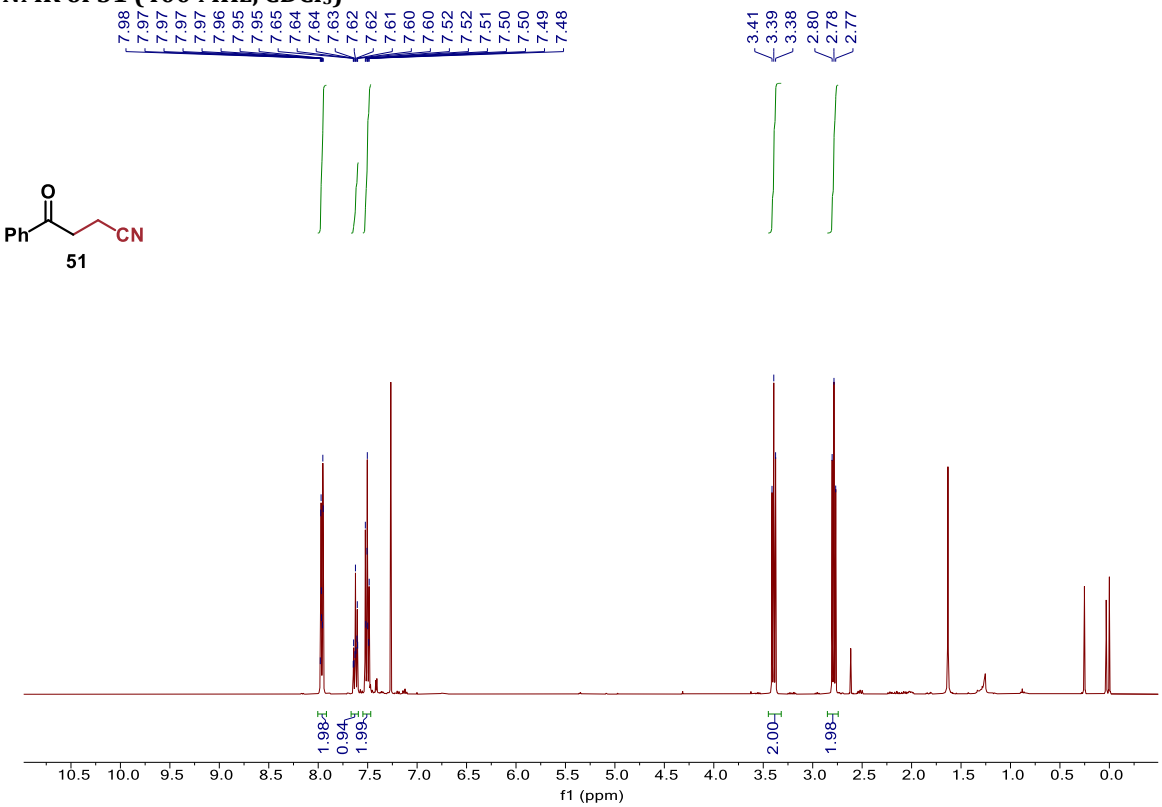
^{1}H NMR of 50 (500 MHz, $CDCl_3$)



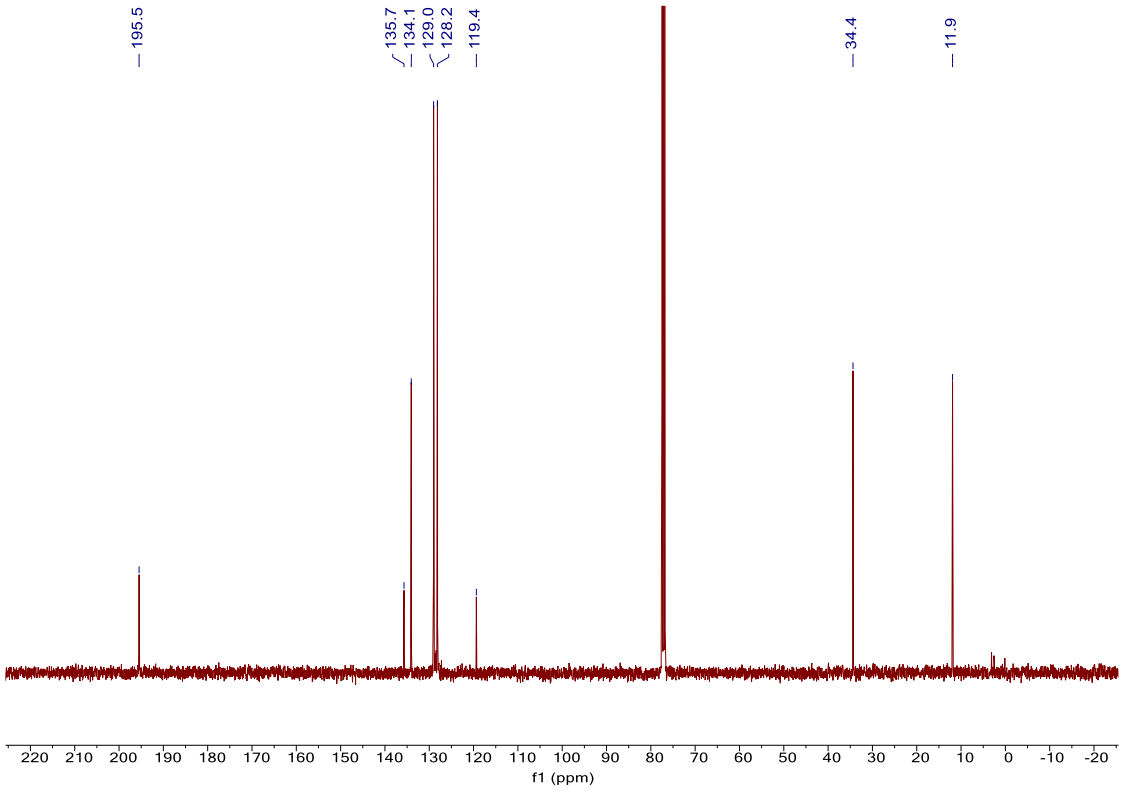
^{13}C NMR of 50 (126 MHz, $CDCl_3$)



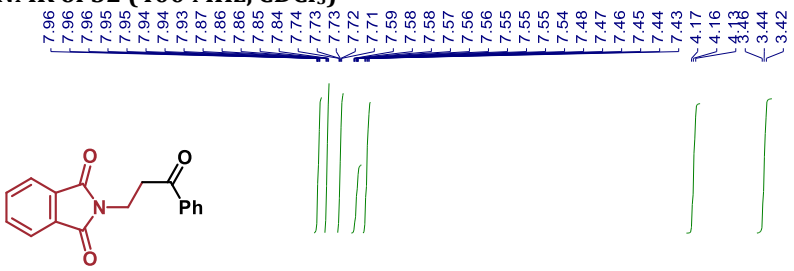
^{1}H NMR of 51 (400 MHz, $CDCl_3$)



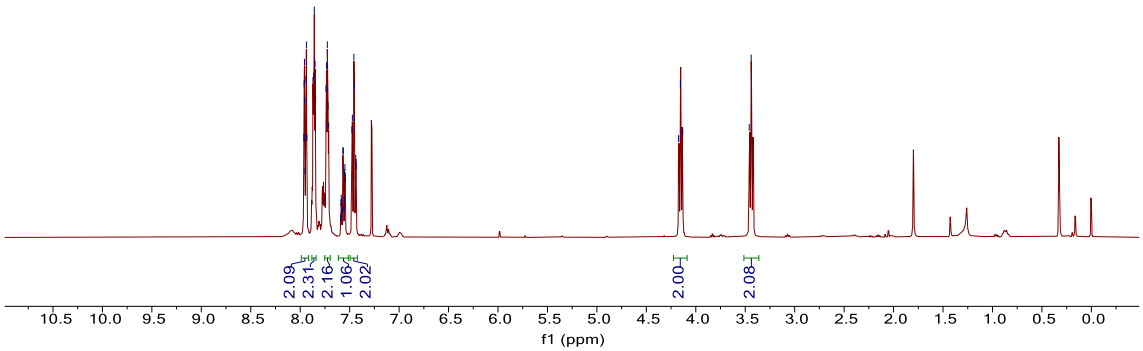
^{13}C NMR of 51 (101 MHz, $CDCl_3$)



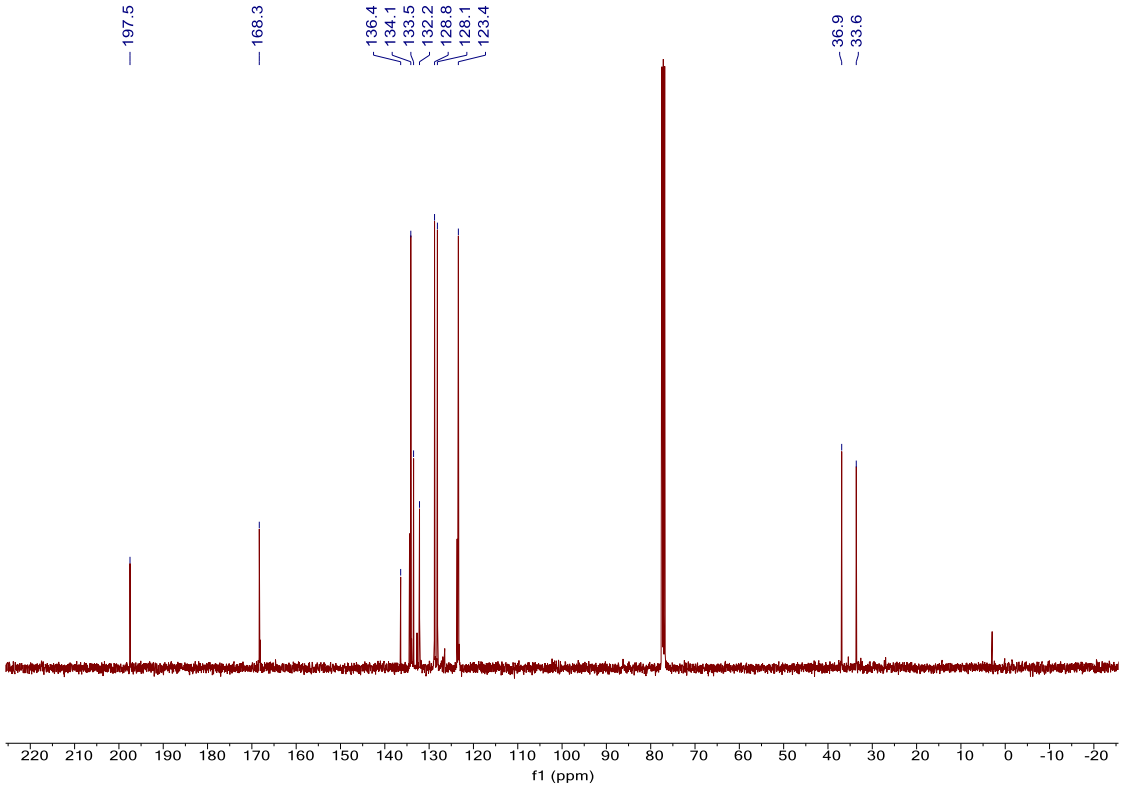
^{1}H NMR of 52 (400 MHz, $CDCl_3$)



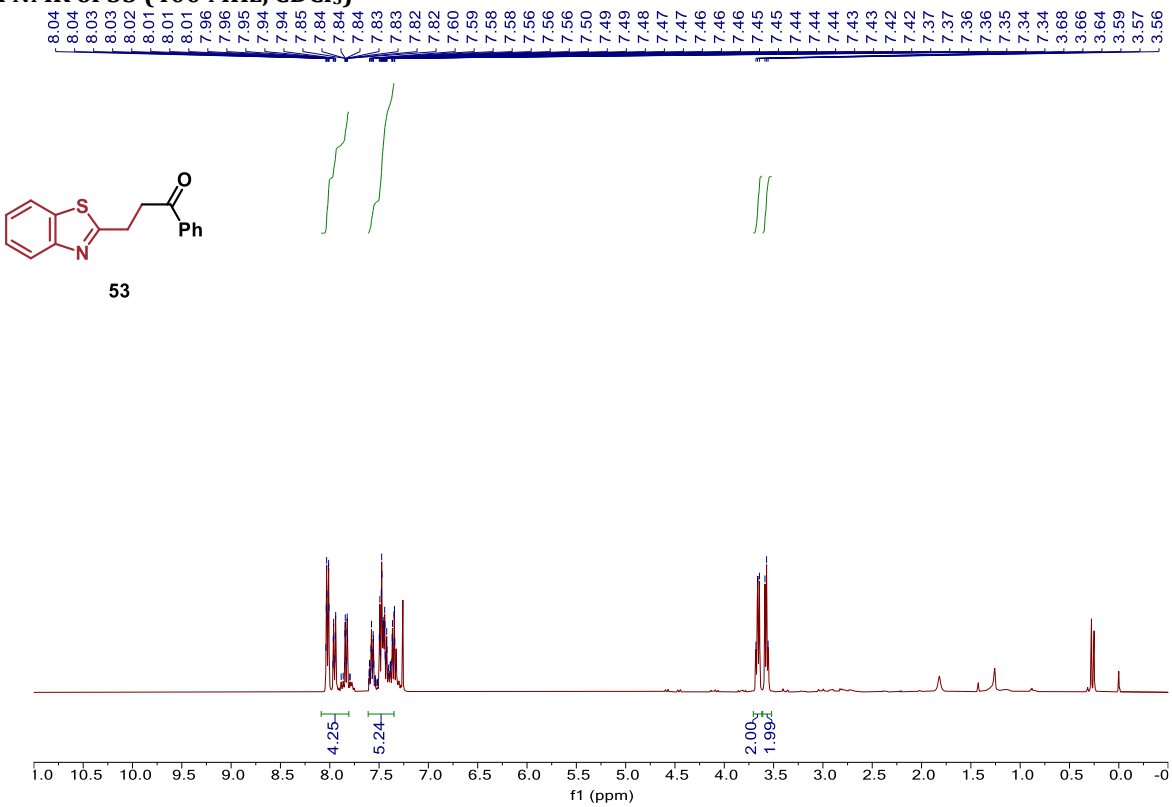
52



^{13}C NMR of 52 (101 MHz, $CDCl_3$)

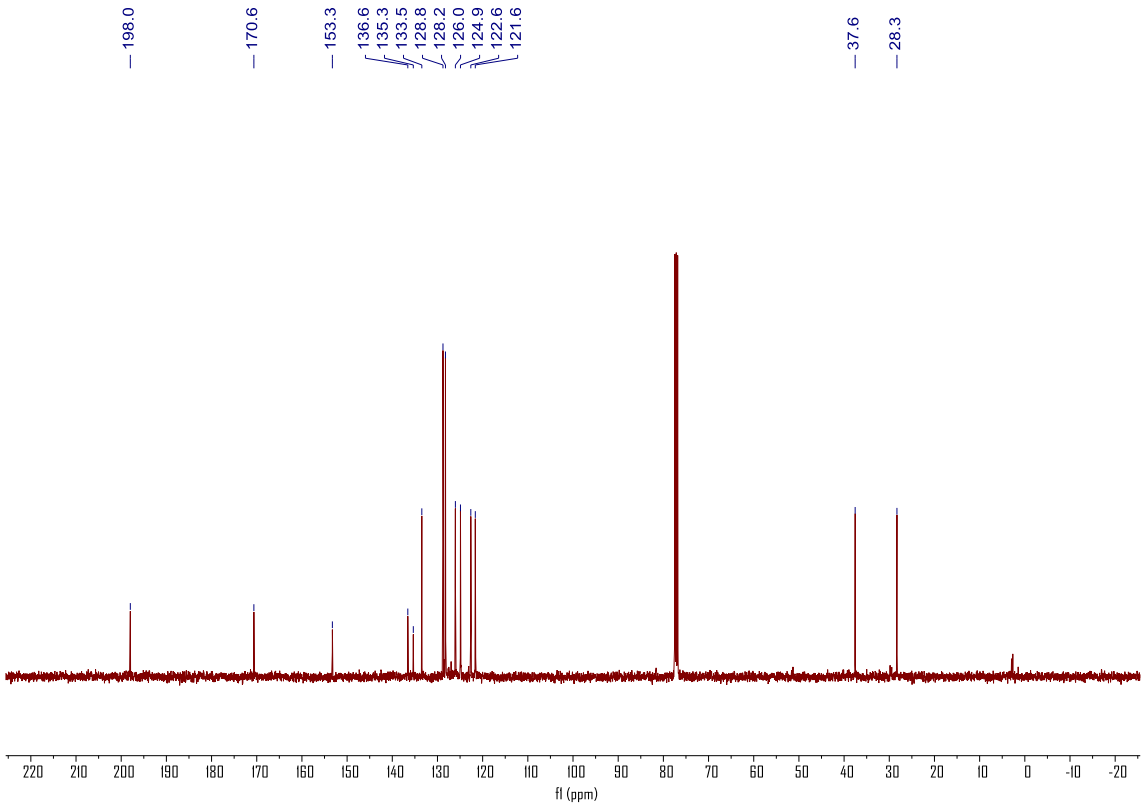


^{1}H NMR of 53 (400 MHz, $CDCl_3$)

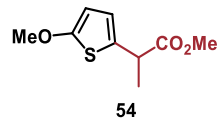


53

^{13}C NMR of 53 (101 MHz, $CDCl_3$)

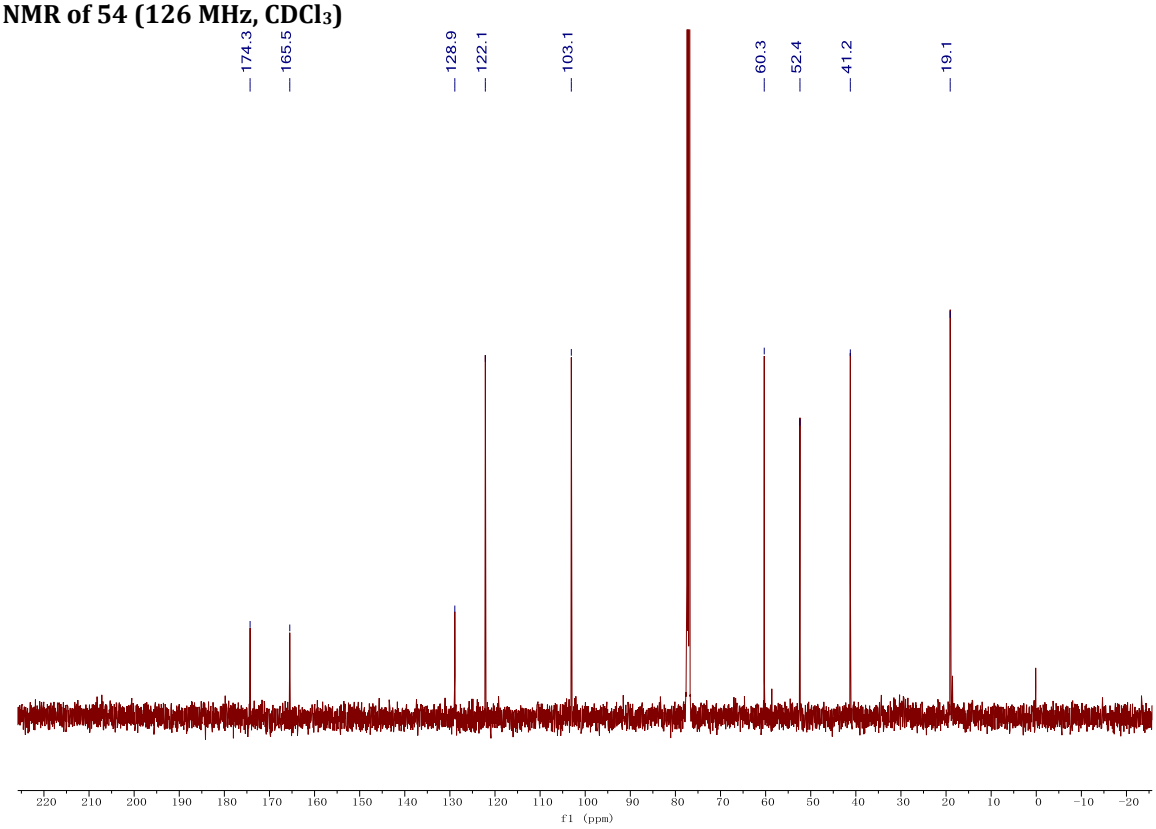


^{1}H NMR of 54 (500 MHz, $CDCl_3$)

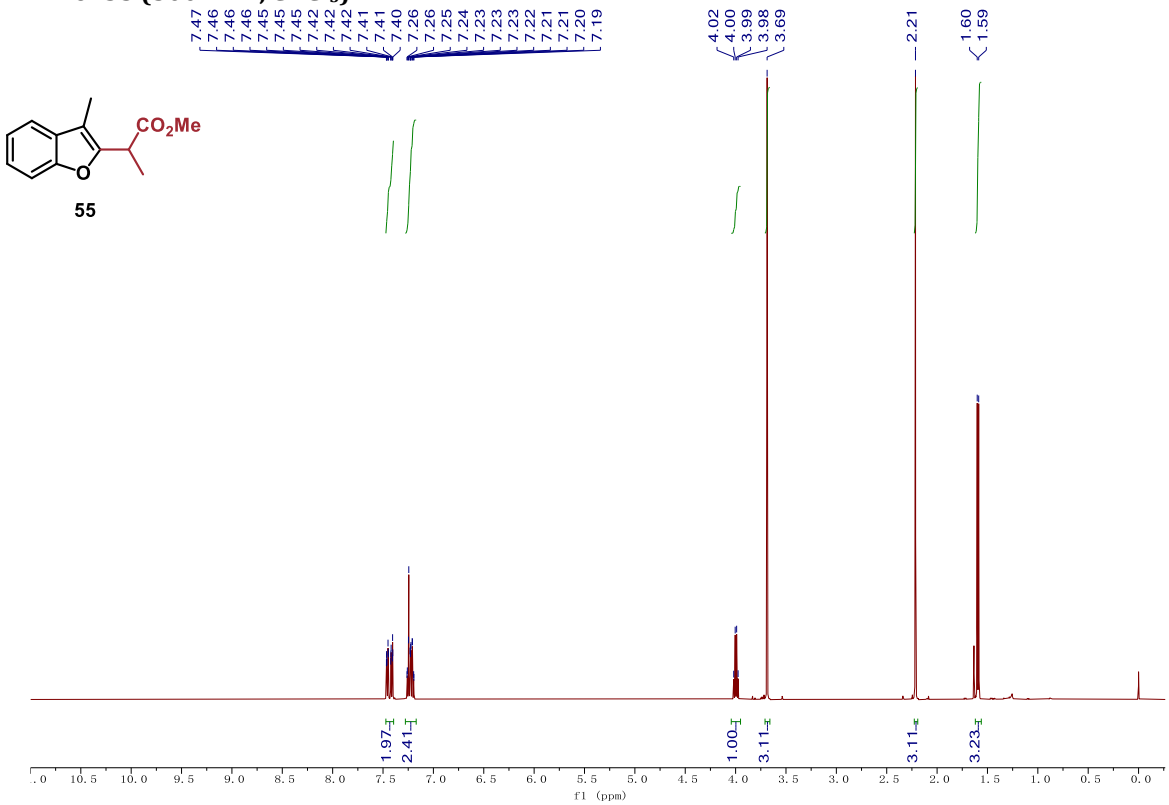


54

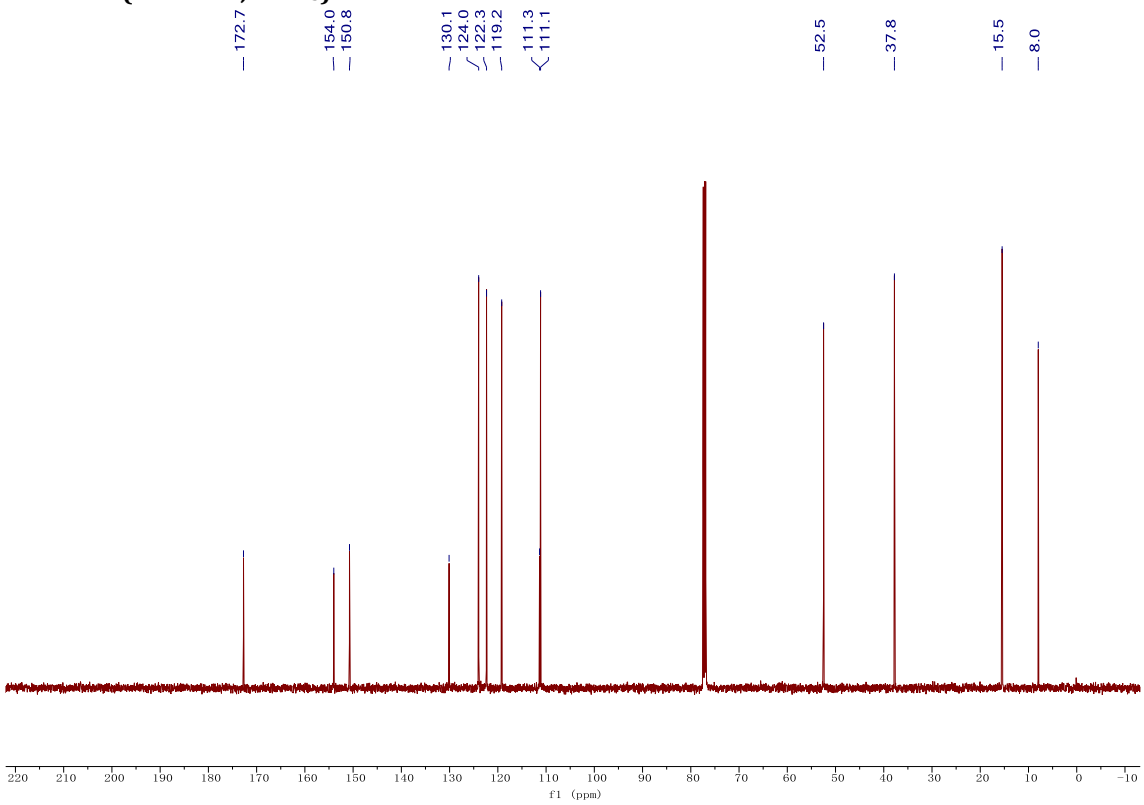
^{13}C NMR of 54 (126 MHz, $CDCl_3$)



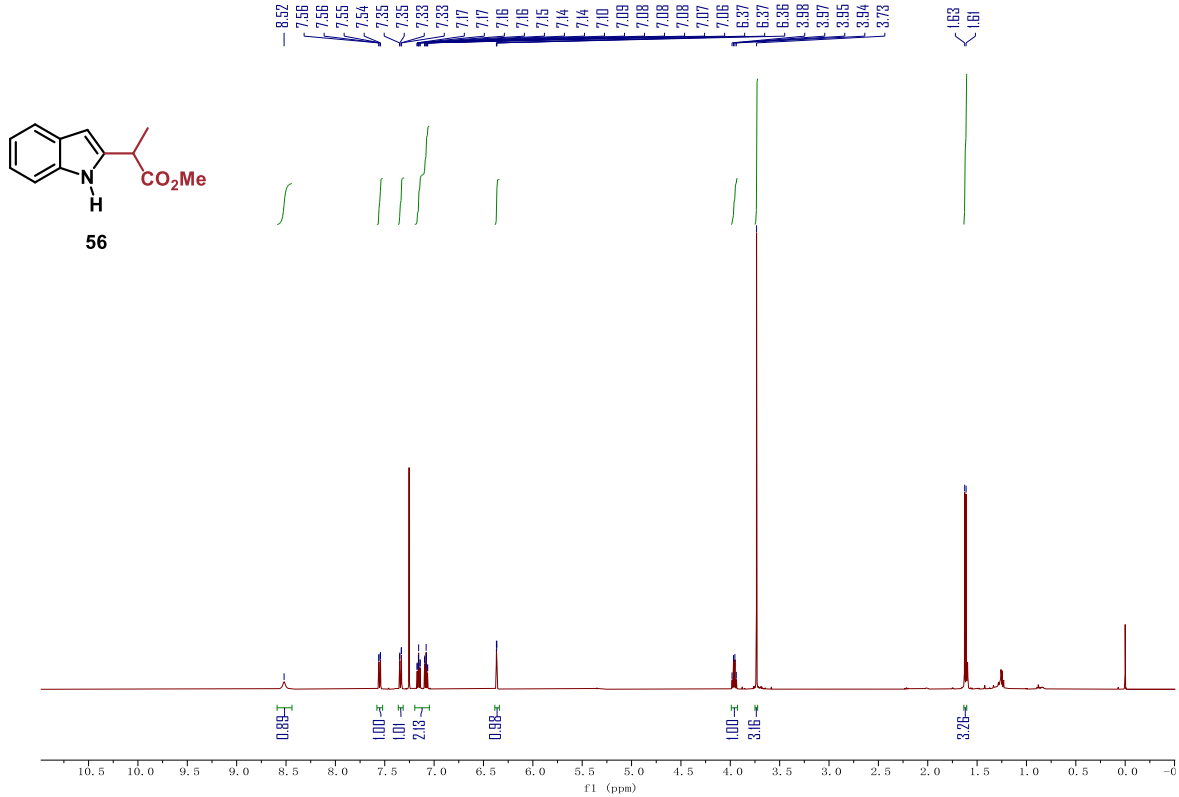
^{1}H NMR of 55 (500 MHz, $CDCl_3$)



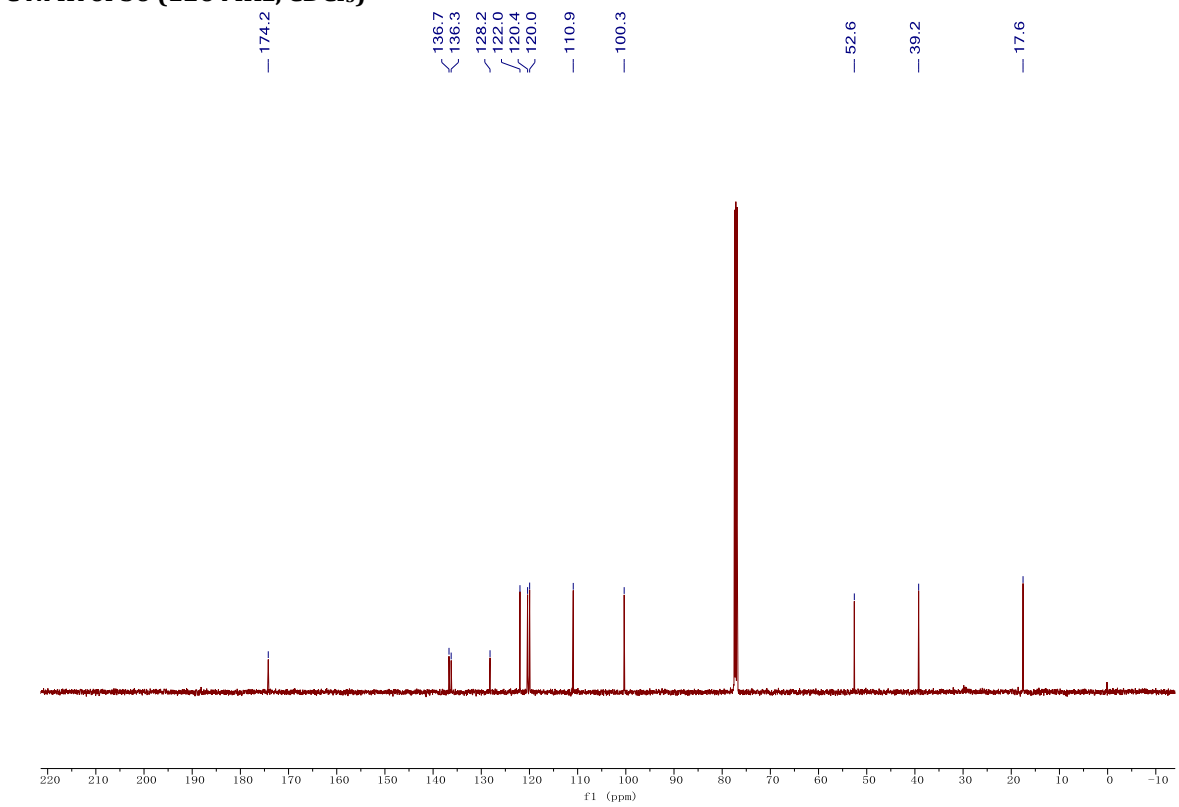
^{13}C NMR of 55 (126 MHz, $CDCl_3$)



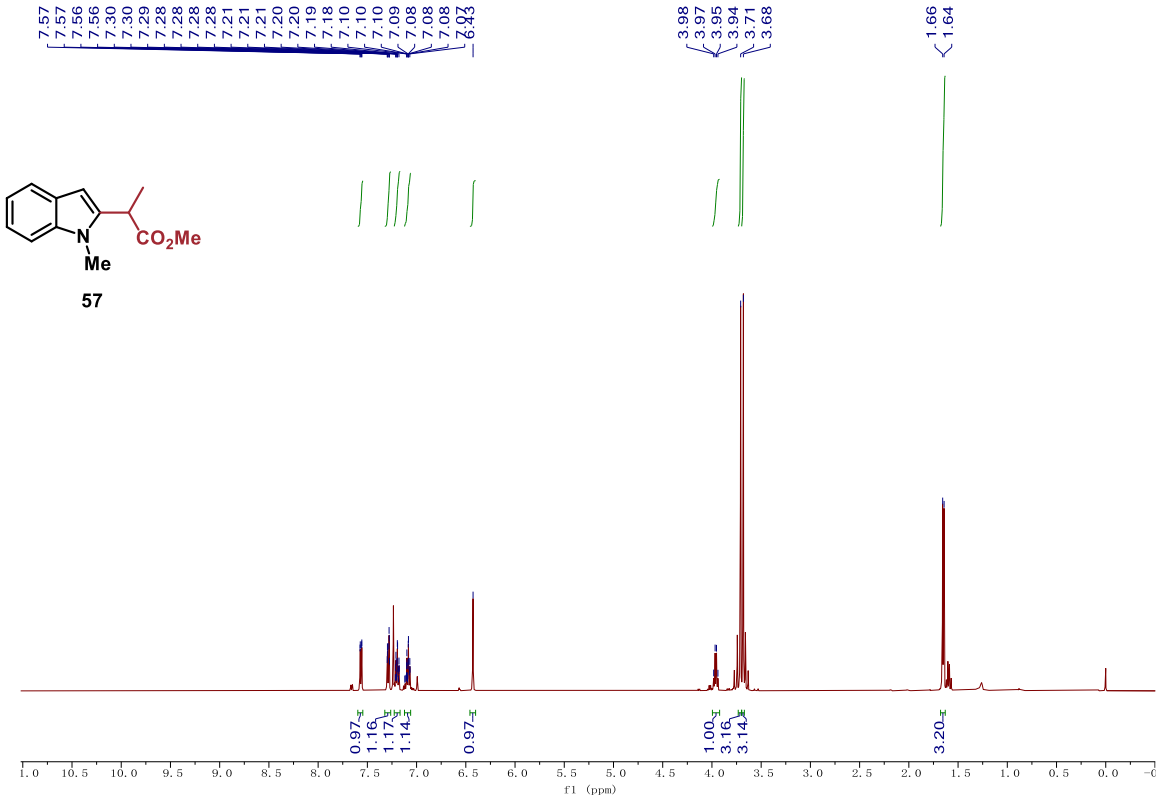
^{1}H NMR of 56 (500 MHz, $CDCl_3$)



^{13}C NMR of 56 (126 MHz, $CDCl_3$)

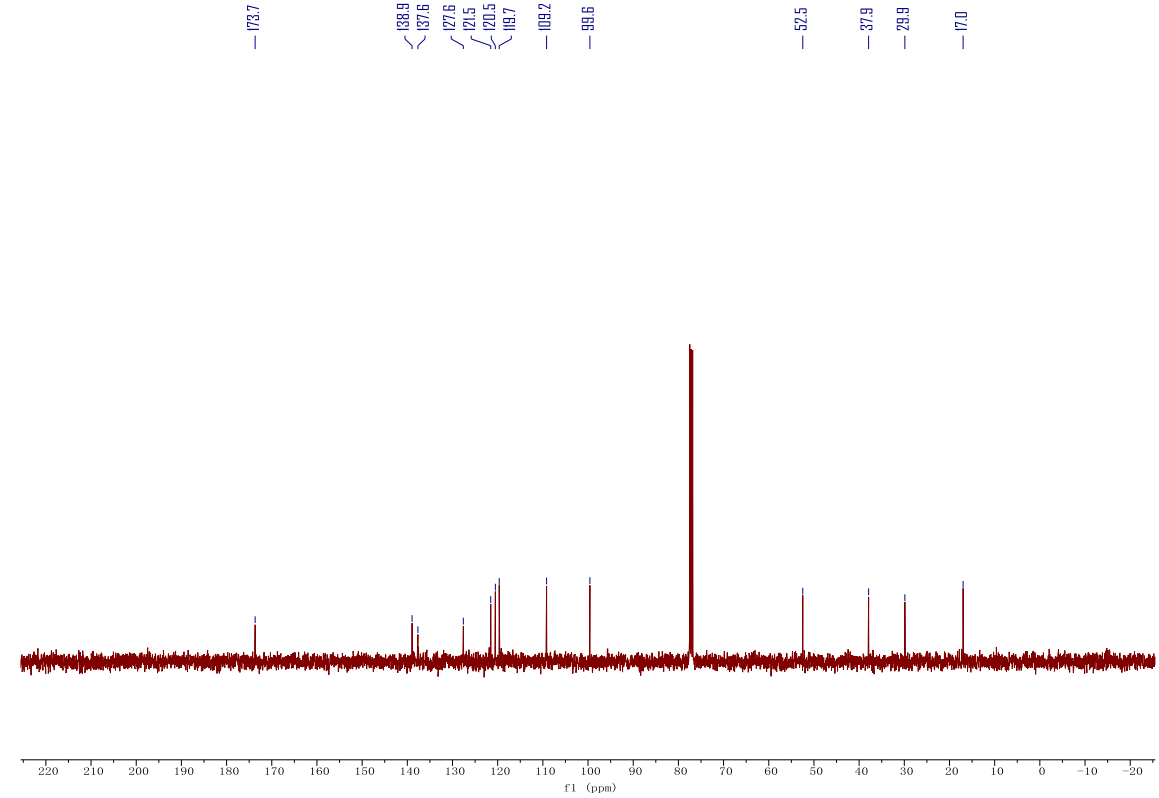


^{1}H NMR of 57 (500 MHz, $CDCl_3$)

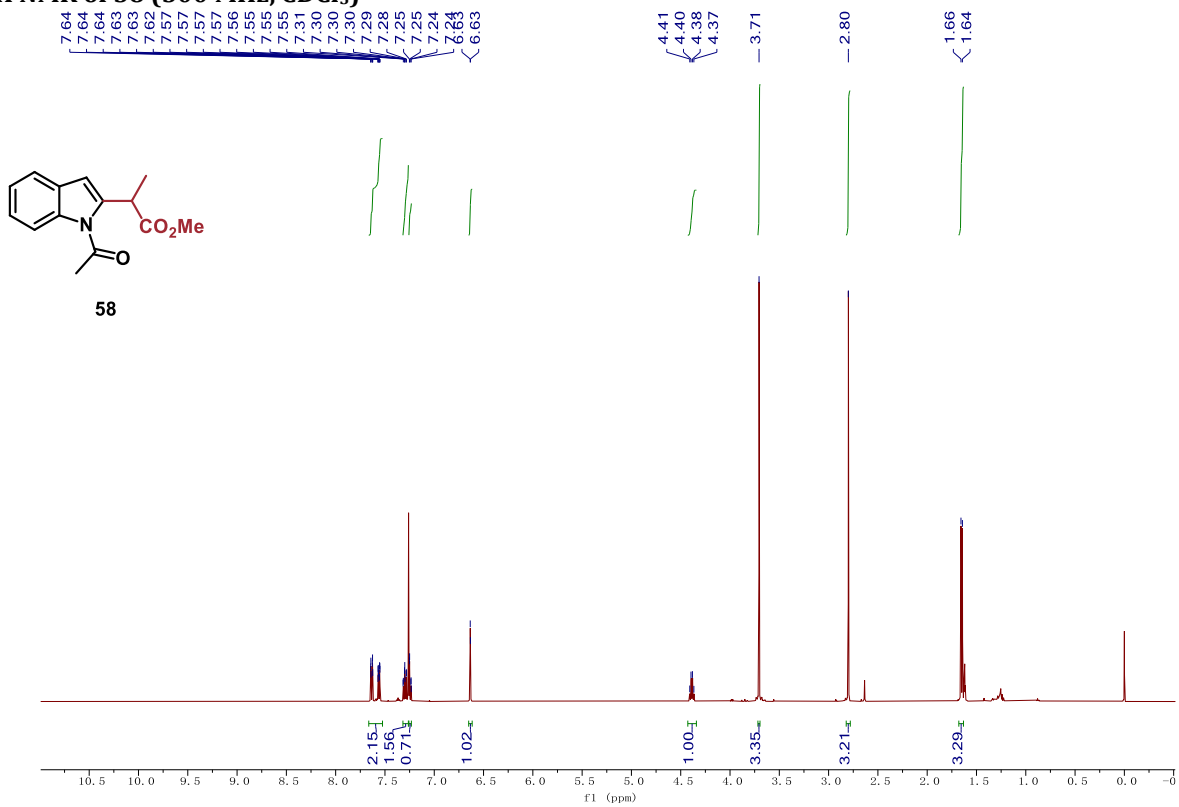


57

^{13}C NMR of 57 (101 MHz, $CDCl_3$)

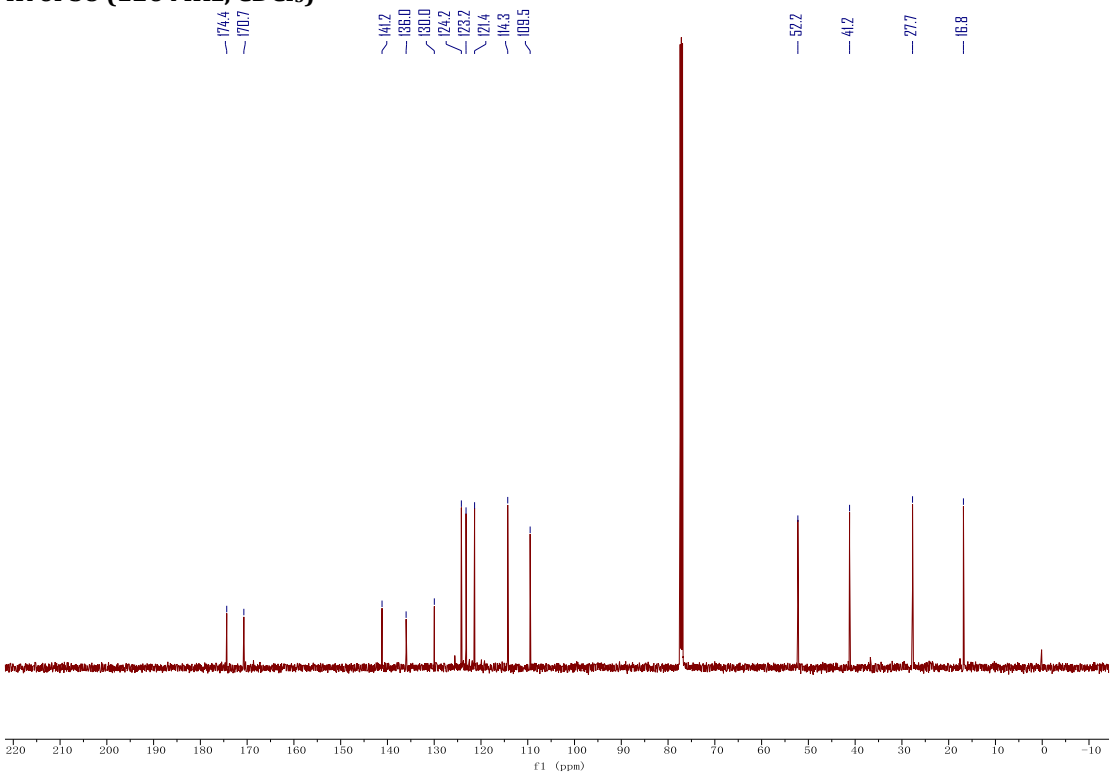


^{1}H NMR of 58 (500 MHz, $CDCl_3$)

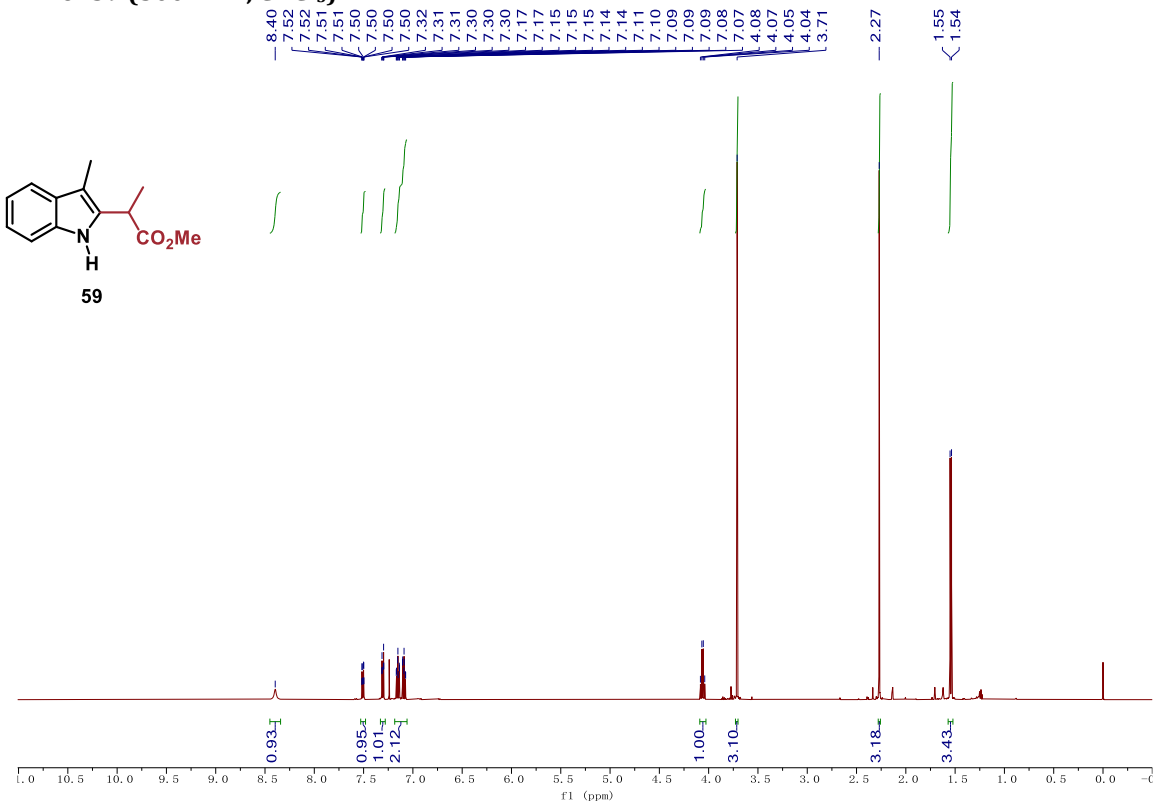


58

^{13}C NMR of 58 (126 MHz, $CDCl_3$)

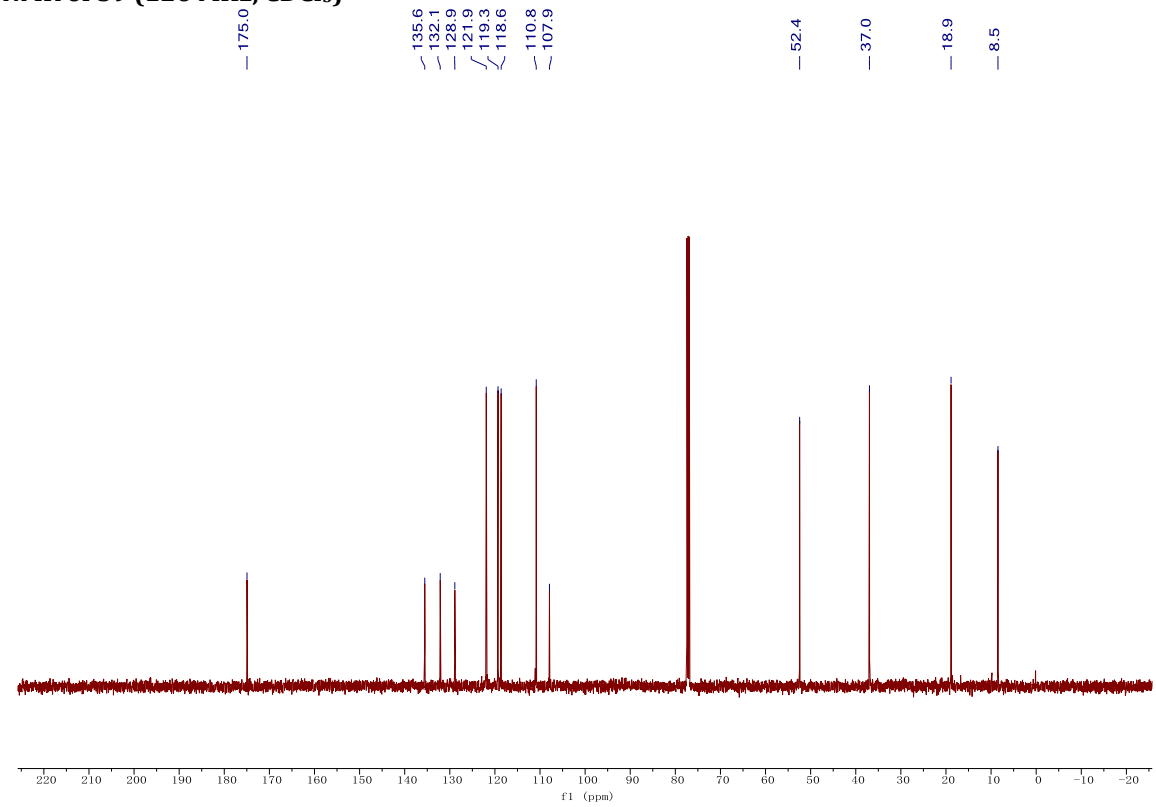


^{1}H NMR of 59 (500 MHz, $CDCl_3$)

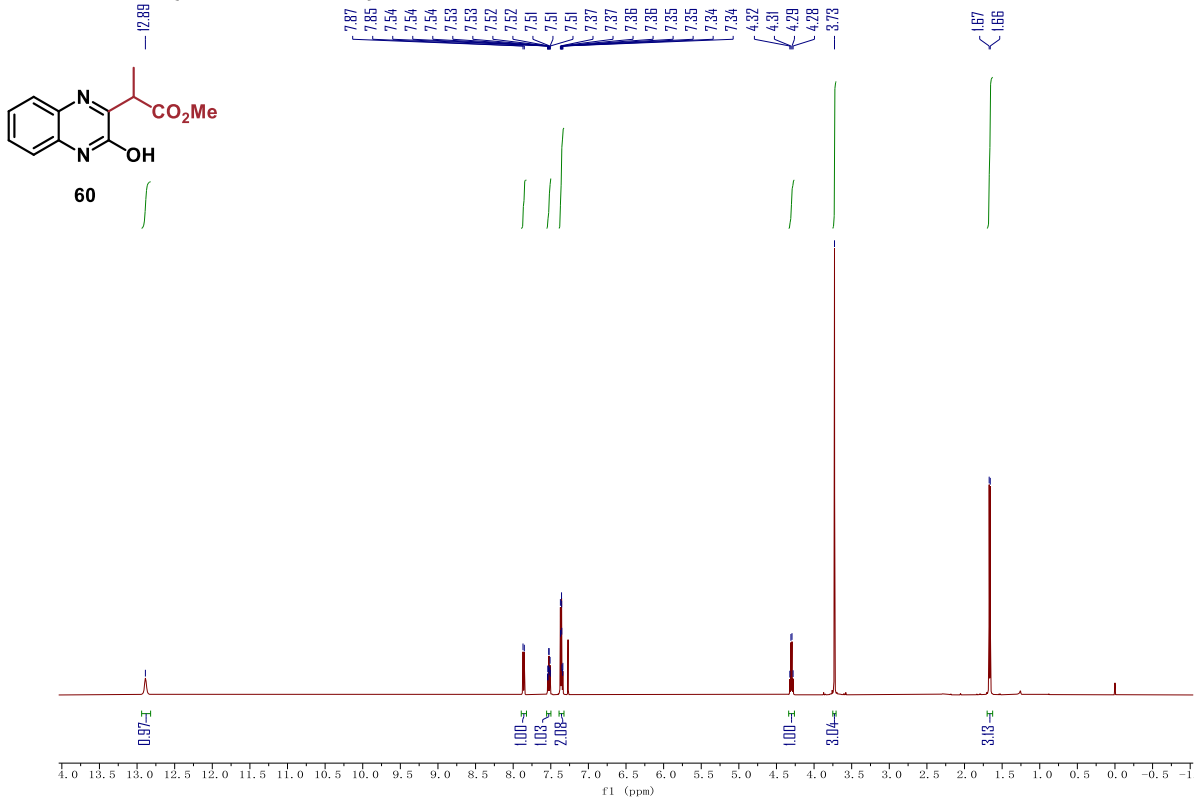


59

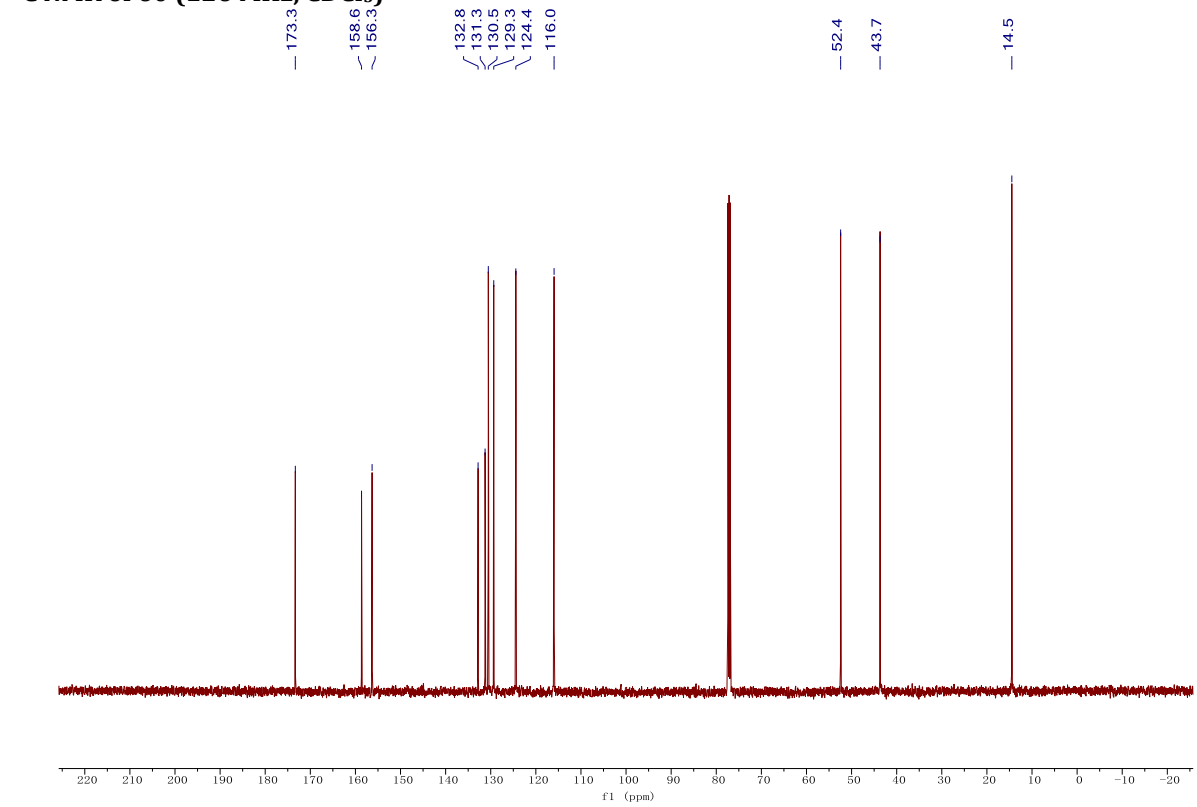
^{13}C NMR of 59 (126 MHz, $CDCl_3$)



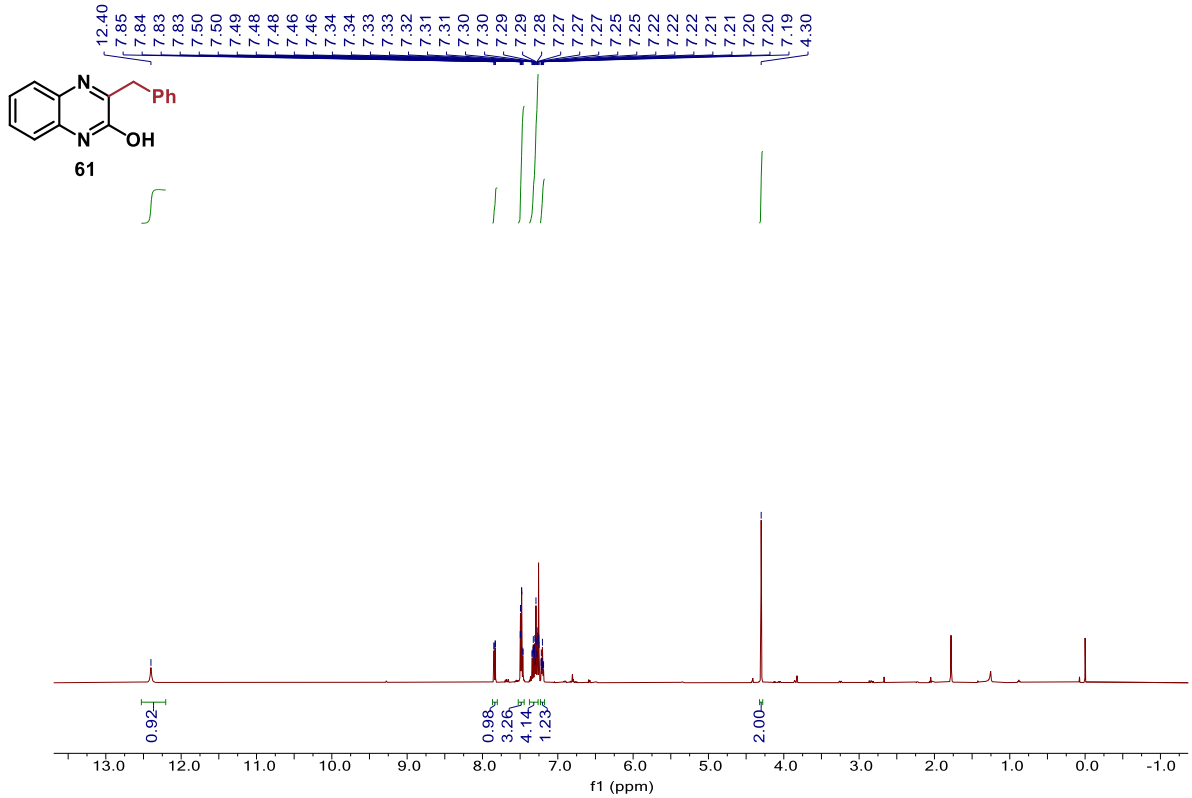
^{1}H NMR of 60 (500 MHz, $CDCl_3$)



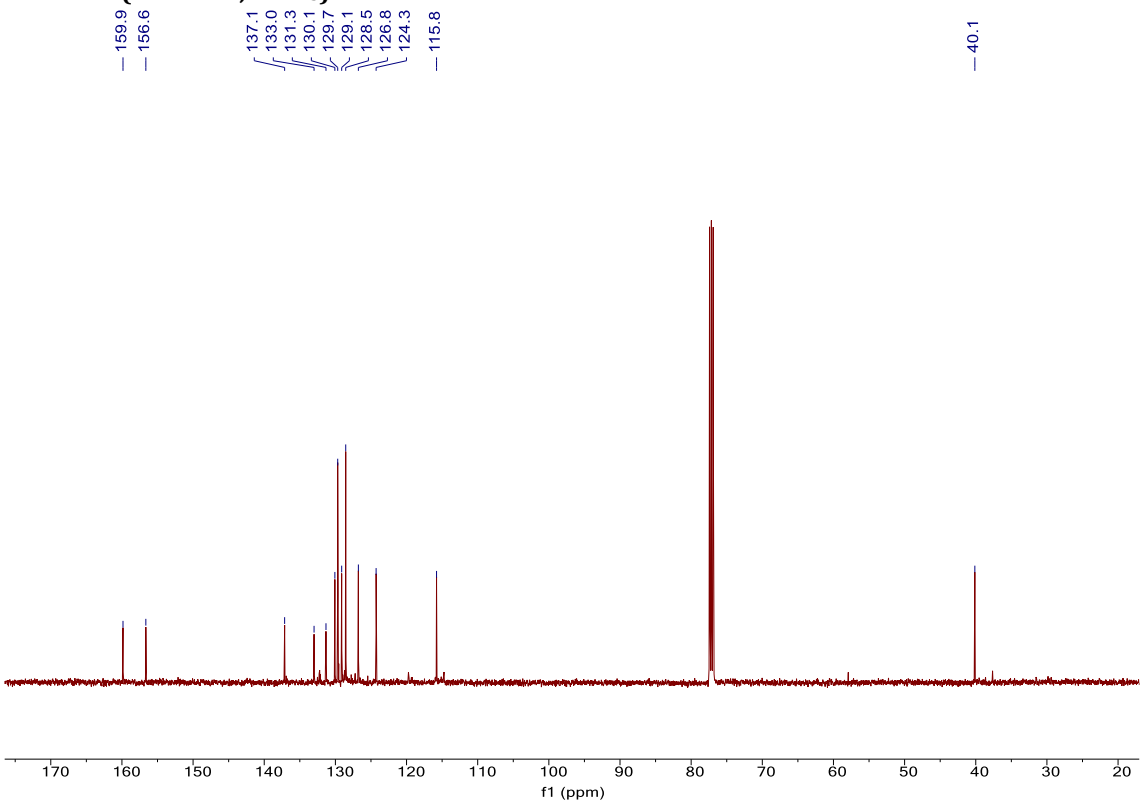
^{13}C NMR of 60 (126 MHz, $CDCl_3$)



^{1}H NMR of 61 (500 MHz, $CDCl_3$)



^{13}C NMR of 61 (126 MHz, $CDCl_3$)



15. Computational Details

Considering that acetonitrile (CH_3CN, ε = 35.7) is a strongly polar solvent , all structures were optimized and characterized in acetonitrile with the SMD[21] solvent model (SCRF=SMD) at B3LYP[22-24]-D3BJ[25]/BSI level, BSI representing a basis set with SDD[26-27] for I and 6-31G(d,p) for other atoms. Harmonic frequency analysis calculations at the same level were performed to verify the optimized geometries to be minima (no imaginary frequency) or transition states (TSs, having unique one imaginary frequency). The energies were further improved by M06[29-31]/BSII//B3LYP-D3BJ/BSI single-point calculations with solvent effects accounted by the SMD solvent model, using the experimental solvent (acetonitrile), BSII denotes a basis set with SDD for I and 6-311++G(d,p) for other atoms. The vertical excitation energies of **^{1}CT** complexes were calculated at TD[32-35]-M06/ BSII. When necessary, intrinsic reaction coordinate (IRC) calculations[36] were carried out at the B3LYP-D3BJ/BSI level to verify a TS correctly connecting with its nearby minima. To account for the overestimation of the entropy contributions estimated by the idea gas phase model for the solution system, which has been experimentally demonstrated[37,38], a correction factor of -1.9(or 1.9) kcal mol-1 for a 2:1 (or 1:2) process was applied to adjust 1atm to 1M standard state concentration[39-42]. Corrected free energies are discussed in the main text. All DFT and TD-DFT calculations were carried out using Gaussian 09 program[43]. Selected computed structures are illustrated using the CYLview[44].

On the basis of Marcus theory[45,46], the barriers for the outer-sphere single electron transfer (SET) were estimated by using the following equation:

$$\Delta G^{\ddagger} = \frac{(\Delta G + \lambda)^2}{4\lambda}$$

where ΔG is the reaction free energy for the SET process and λ is the reorganization energy of nuclei and solvent molecules. For the cross-reaction, the λ is estimated by using the average of those for the self-exchange reaction of acceptor and donor. The reorganization energy of a self-exchange reaction was calculated by using a standard method[47] which was modified to incorporate the solvent effect[48]. The non-equilibrium solvent cage implemented in Gaussian program was used for solvent effect.

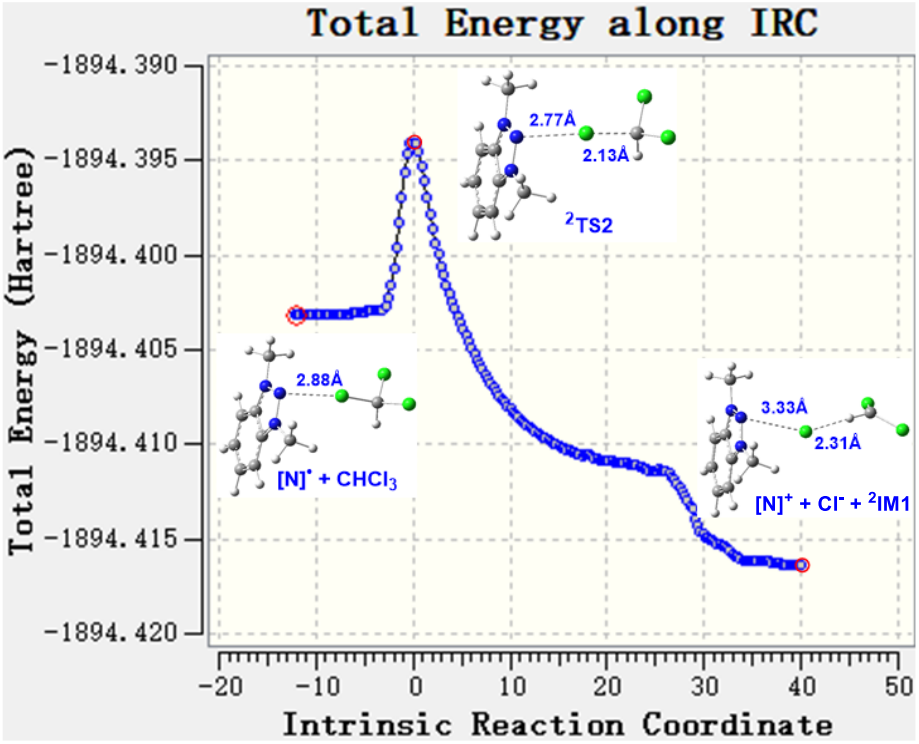


Figure S30. IRC results for confirming the right connections of **²TS2** with **²IM1** and **[N]•** + $CHCl_3$. Values are key bond lengths in angstroms.

Cartesian Coordinates in Å, SCF Energies and Free Energies (in a.u.) at 298.15 K and 1 atm for the Optimized Structures [BSI= 6-31G(d,p), BSII=6-311++G(d,p)]

NHN **A1**

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-486.622817 a.u.
M06/BSII SCF energy in acetonitrile:
-486.302401 a.u.
M06/BSII free energy in acetonitrile:
-486.169592 a.u.

C	-1.631950	0.181480	-0.671001
C	-1.590550	0.069908	0.728954
N	-0.670713	2.014874	0.151982
N	-0.995030	1.230661	1.157118
N	-1.054841	1.396931	-0.944005
C	-0.799611	1.994040	-2.250360
H	-1.728553	2.000662	-2.821704
H	-0.444343	3.010123	-2.090068
H	-0.041512	1.402073	-2.766677
C	-0.638246	1.606591	2.520564
H	-0.383248	2.664734	2.519905
H	-1.494762	1.421087	3.169118
H	0.217491	1.007425	2.838673
C	-2.162063	-0.829255	-1.484506
C	-2.642808	-1.944105	-0.819856
C	-2.603485	-2.056207	0.595673
C	-2.079910	-1.059029	1.400265
H	-2.183933	-0.738335	-2.563629
H	-3.062360	-2.762578	-1.394922
H	-2.995230	-2.956266	1.057209
H	-2.041552	-1.141697	2.479559
I	2.228185	-0.456321	-0.058519

NHN **A2**

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-899.616901 a.u.
M06/BSII SCF energy in acetonitrile:
-899.348573 a.u.
M06/BSII free energy in acetonitrile:
-899.203239a.u.

C	-1.353399	0.696978	0.313358
C	-1.371857	-0.706631	0.266751
H	-2.203684	2.561124	-0.416629
C	-2.228839	1.478719	-0.451404
C	-2.271468	-1.412554	-0.542424
C	-3.138430	-0.638965	-1.295746
C	-3.116693	0.779878	-1.251887
H	-2.279833	-2.495330	-0.575139
H	-3.857829	-1.129130	-1.943068
H	-3.819497	1.330390	-1.868171
N	0.230656	-0.071647	1.674500
N	-0.376729	-1.099685	1.126592
N	-0.350779	1.005915	1.198110
C	0.152831	2.326032	1.558209
H	0.719966	2.724126	0.716642
H	-0.693824	2.969942	1.796938
H	0.800041	2.210816	2.425318
C	0.089129	-2.453510	1.402720
H	-0.768822	-3.074723	1.661575
H	0.593135	-2.836508	0.515388
H	0.786904	-2.400419	2.235969

B	2.286826	0.021225	-0.795956
F	2.395888	-1.193308	-0.090500
F	2.493446	1.098529	0.088062
F	0.997425	0.120378	-1.353722
F	3.246532	0.060159	-1.817276

NHN **A3**

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1436.605168 a.u.

M06/BSII SCF energy in acetonitrile:

-1436.291511 a.u.

M06/BSII free energy in acetonitrile:

-1436.136878 a.u.

C	-1.877695	0.243521	0.694301
C	-1.874194	0.171677	-0.708334
N	-1.788917	-1.899370	0.101377
N	-1.827819	-1.170250	-0.991036
N	-1.828216	-1.062219	1.113215
C	-1.717585	-1.557830	2.478703
H	-2.524392	-1.132009	3.076546
H	-1.800037	-2.642797	2.447911
H	-0.743695	-1.262188	2.869587
C	-1.738121	-1.805550	-2.299589
H	-1.917365	-2.871120	-2.167001
H	-2.496525	-1.371618	-2.952105
H	-0.736253	-1.631513	-2.693239
C	-1.922538	1.466614	1.376919
C	-1.964016	2.598435	0.581351
C	-1.955373	2.526139	-0.836820
C	-1.908270	1.318894	-1.512416
H	-1.920815	1.515576	2.459069
H	-1.998285	3.574991	1.052441
H	-1.982387	3.449702	-1.405283
H	-1.895506	1.256475	-2.593800
O	1.116492	-1.056066	-1.312156
S	1.858945	-0.892037	-0.039715
O	3.228138	-1.450895	-0.032940
O	1.066474	-1.148662	1.186087
C	2.145947	0.936248	0.032780
F	2.873439	1.353136	-1.019433
F	2.807705	1.276286	1.153895
F	0.982082	1.611253	0.021885

[NHN]$^+$ ([N]$^+$)

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-475.00748 a.u.

M06/BSII SCF energy in acetonitrile:

-474.719807 a.u.

M06/BSII free energy in acetonitrile:

-474.578622 a.u.

C	-0.214197	-0.702655	-0.000015
C	-0.214180	0.702665	-0.000034
H	-1.393516	-2.531551	0.000062
C	-1.401288	-1.448318	0.000035
C	-1.401263	1.448345	-0.000027
C	-2.572479	0.710285	-0.000015
C	-2.572493	-0.710238	0.000016
H	-1.393473	2.531578	-0.000040
H	-3.524458	1.230194	-0.000020
H	-3.524482	-1.230128	0.000035
N	1.900736	-0.000019	0.000047
N	1.113974	1.054697	0.000018
N	1.113955	-1.054714	0.000071
C	1.686838	-2.397680	-0.000066

H	1.351891	-2.924882	0.894630
H	1.351465	-2.924859	-0.894612
H	2.770618	-2.298012	-0.000315
C	1.686909	2.397643	-0.000006
H	1.352018	2.924743	-0.894784
H	1.351512	2.924964	0.894450
H	2.770682	2.297920	0.000323

I^-

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-11.607332 a.u.
M06/BSII SCF energy in acetonitrile:
-11.572844 a.u.
M06/BSII free energy in acetonitrile:
-11.589692 a.u.

I	0.000000	0.000000	0.000000

TMEDA

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-347.8017 a.u.
M06/BSII SCF energy in acetonitrile:
-347.580305 a.u.
M06/BSII free energy in acetonitrile:
-347.392869 a.u.

N	1.864280	-0.035258	0.324696
C	0.597704	-0.365820	-0.332078
H	0.437072	-1.440231	-0.200574
H	0.639125	-0.179932	-1.422748
C	-0.591083	0.400947	0.253994
H	-0.480633	1.466528	0.033191
H	-0.580345	0.298596	1.355930
N	-1.865707	-0.034058	-0.323408
C	2.907933	-0.972212	-0.076854
H	3.835974	-0.744693	0.457905
H	2.609902	-1.995018	0.175655
H	3.126638	-0.939699	-1.161429
C	2.289069	1.334761	0.052578
H	2.421210	1.535683	-1.027997
H	1.564556	2.053823	0.443323
H	3.245871	1.525017	0.549100
C	-2.905474	0.966446	-0.106605
H	-3.838064	0.638534	-0.577582
H	-3.115680	1.149833	0.964443
H	-2.609898	1.918024	-0.559811
C	-2.296711	-1.325882	0.201611
H	-2.473237	-1.305058	1.294054
H	-3.229806	-1.627068	-0.285334
H	-1.551326	-2.098563	-0.003016

$CHCl_3$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1419.28761 a.u.
M06/BSII SCF energy in acetonitrile:
-1419.25325 a.u.
M06/BSII free energy in acetonitrile:
-1419.262596 a.u.

C	0.000242	-0.000095	0.466826
H	0.001751	-0.001349	1.552982
Cl	-0.319717	-1.671445	-0.085413
Cl	1.607799	0.559044	-0.085432
Cl	-1.288270	1.112514	-0.085269

1

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-670.370277 a.u.

M06/BSII SCF energy in acetonitrile:

-670.02241 a.u.

M06/BSII free energy in acetonitrile:

-669.83925 a.u.

C	-1.985110	1.055795	-0.483214
C	-1.642666	-0.254576	-0.125085
C	-2.637594	-1.133737	0.322503
C	-3.955433	-0.695750	0.445416
C	-4.293907	0.612993	0.090945
C	-3.309368	1.483592	-0.382145
H	-1.224735	1.733827	-0.857271
H	-2.371430	-2.154676	0.577303
H	-4.718738	-1.376792	0.809717
H	-5.322289	0.950922	0.177644
H	-3.571366	2.496280	-0.673517
C	-0.256344	-0.801179	-0.327587
O	-0.091280	-1.800126	-1.015380
N	0.792514	-0.096642	0.259607
C	0.556980	0.973292	1.249966
H	-0.308537	0.712545	1.859475
H	1.425535	1.038991	1.904812
H	0.392662	1.948800	0.789609
C	2.141007	-0.531721	0.077027
O	2.453395	-1.707524	0.059701
C	3.163680	0.544630	-0.112415
C	4.559609	0.202088	0.329448
H	4.589504	-0.003177	1.405864
H	4.911961	-0.702808	-0.175641
H	5.249241	1.020451	0.110415
C	2.839760	1.674221	-0.755371
H	3.592170	2.424134	-0.983442
H	1.827812	1.871319	-1.093713

^{1}CT1

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-834.440623591 a.u.

M06/BSII SCF energy in acetonitrile:

-833.8949838 a.u.

M06/BSII free energy in acetonitrile:

-833.5502968 a.u.

I	4.08792900	-0.35656700	-0.25242100
C	-0.00388300	-0.55570500	-0.31360400
C	0.14937200	-0.18755500	1.03291500
C	-0.17165400	-1.05689100	2.08355400
C	-0.63997500	-2.30565100	1.70872000
C	-0.79087500	-2.67862400	0.34693700
C	-0.48434500	-1.81581300	-0.69213100
H	-0.05251100	-0.76652500	3.12026200
H	-0.90126600	-3.02501500	2.47733400
H	-1.16319200	-3.67087800	0.11707500
H	-0.60201100	-2.09266600	-1.73250100
N	0.42027900	0.53776800	-1.02625300
N	0.64889800	1.08974500	0.99267600
N	0.81542200	1.51230500	-0.23877200
C	0.51561200	0.67678700	-2.47396600
H	1.23081800	-0.05556800	-2.85312300
H	-0.46869600	0.50470400	-2.91172200
H	0.85710100	1.68671100	-2.69155600
C	0.99950800	1.94889500	2.11603300
H	0.14404500	2.01113500	2.78944200
H	1.85968300	1.52289200	2.63581900

H	1.24474200	2.93254600	1.72029300
C	-3.63599000	-0.11849500	0.25096800
C	-3.20839200	1.08470100	-0.59395700
H	-2.77248000	-0.46870500	0.82388900
H	-4.40921900	0.18720800	0.98102100
H	-2.73231700	0.71073700	-1.50814000
H	-4.09925900	1.66332300	-0.90340800
N	-2.23917400	1.94784800	0.08594500
N	-4.10767600	-1.23829500	-0.56920700
C	-1.88162900	3.06644800	-0.77820500
H	-2.73687600	3.73682900	-0.98724700
H	-1.09165300	3.66092100	-0.30969700
H	-1.50752500	2.69604100	-1.73699800
C	-2.72893300	2.44304400	1.36856700
H	-1.98251400	3.11472900	1.80387900
H	-3.67893200	3.00404800	1.27952700
H	-2.88601800	1.61823200	2.06812000
C	-4.42014700	-2.38123200	0.28137200
H	-5.25270900	-2.18030500	0.98238200
H	-4.70195700	-3.23929400	-0.33785500
H	-3.54253600	-2.65728200	0.87272200
C	-5.27092500	-0.88058000	-1.37581000
H	-5.59883500	-1.75420500	-1.94799200
H	-6.12661300	-0.53354100	-0.76530200
H	-5.02018200	-0.08958600	-2.08699200

^{1}CT2

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1247.43216694 a.u.

M06/BSII SCF energy in acetonitrile:

-1246.939823 a.u.

M06/BSII free energy in acetonitrile:

-1246.585445 a.u.

C	-0.73968900	0.32375800	-0.85314500
C	-0.60122900	0.49046700	0.53338100
H	-0.53922900	1.20944200	-2.82922000
C	-0.42792800	1.34386000	-1.76004600
C	-0.14648900	1.68876000	1.09675300
C	0.15901200	2.69946300	0.20027700
C	0.02224200	2.52954700	-1.20249700
H	-0.04312700	1.81118400	2.16811900
H	0.51515200	3.65210000	0.57757800
H	0.27768300	3.35776900	-1.85485400
N	-1.35261900	-1.56627600	0.14543900
N	-0.99035500	-0.70830700	1.07106500
N	-1.20235900	-0.95674600	-1.00844000
C	-1.60923500	-1.61676100	-2.24140800
H	-2.55704200	-1.18627400	-2.56562700
H	-0.83563600	-1.46535300	-2.99373700
H	-1.72848500	-2.67772100	-2.02948200
C	-1.09134400	-1.06458200	2.47937000
H	-0.15055900	-0.82209300	2.97411800
H	-1.91645900	-0.50336900	2.91826400
H	-1.28645800	-2.13355300	2.54045100
N	1.77187300	-1.50264400	-0.13804200
C	2.57505000	-0.31117300	0.12697000
H	2.35602000	0.02725100	1.14622400
H	2.22325400	0.46983400	-0.55419700
C	4.09902300	-0.46932400	-0.00224400
H	4.37252400	-0.65477100	-1.05881600
H	4.41874600	-1.34879600	0.56735600
N	4.82113300	0.68718700	0.53614400
C	1.87833000	-1.98749100	-1.50511400
H	1.12027700	-2.75891300	-1.67896800
H	1.69542200	-1.16330500	-2.20249900

H	2.86039700	-2.42858900	-1.75140900
C	1.93766500	-2.56729000	0.83831800
H	2.90678700	-3.09412000	0.77529200
H	1.84211400	-2.15880700	1.84943500
H	1.14807100	-3.31453400	0.69860400
C	4.55403600	1.90617100	-0.22201400
H	5.14218200	2.73014800	0.19433800
H	4.81393000	1.81092200	-1.29409000
H	3.49913100	2.18427300	-0.15459900
C	6.25445500	0.42011500	0.57469100
H	6.69175600	0.25440000	-0.42863600
H	6.77860300	1.26580000	1.03223100
H	6.45093300	-0.47205200	1.17829300
B	-4.21133700	0.37924500	0.24753900
F	-4.06951800	-0.56241700	-0.79265600
F	-3.39359400	1.49217000	-0.01542600
F	-3.82100900	-0.21142700	1.46690300
F	-5.55103400	0.78470600	0.33175900

^{1}CT3

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1784.41916626 a.u.

M06/BSII SCF energy in acetonitrile:

-1783.881249 a.u.

M06/BSII free energy in acetonitrile:

-1783.518797 a.u.

C	0.20306600	-0.06730100	-1.01751100
C	0.17721900	0.20613100	0.35864800
H	0.49151400	0.70987500	-3.02887100
C	0.47663200	0.92539800	-1.96740200
C	0.42347300	1.48694300	0.86787500
C	0.69578300	2.46808400	-0.07074800
C	0.72254400	2.19211600	-1.46294900
H	0.39529200	1.69126100	1.93097900
H	0.89278300	3.48110800	0.26360800
H	0.93943200	3.00254200	-2.15064300
N	-0.25976400	-1.95402400	0.06537900
N	-0.10814800	-0.99746000	0.95023500
N	-0.07047700	-1.40779900	-1.11338900
C	-0.28755600	-2.19084400	-2.32131500
H	-1.25300000	-1.91222700	-2.74816400
H	0.51564800	-1.98071100	-3.02739000
H	-0.28348200	-3.24400900	-2.04681300
C	-0.30046200	-1.26832200	2.36813400
H	0.56712500	-0.90210700	2.91830900
H	-1.20839300	-0.75341000	2.68637600
H	-0.40110200	-2.34477300	2.49290700
N	2.85101100	-1.47207400	0.07272900
C	3.47899400	-0.16044100	0.21345100
H	3.13781600	0.27854100	1.15784700
H	3.08991600	0.46956400	-0.59260100
C	5.01593000	-0.13490900	0.20212000
H	5.39063100	-0.42503100	-0.79845000
H	5.39266000	-0.88063900	0.91077200
N	5.55244100	1.16732200	0.60886800
C	3.13320900	-2.12795200	-1.19432400
H	2.47610900	-2.99712600	-1.30920600
H	2.93369800	-1.43641500	-2.01958000
H	4.17334200	-2.48545000	-1.29615200
C	3.05062900	-2.35756600	1.20839200
H	4.07948800	-2.74912600	1.30570800
H	2.80286000	-1.82939200	2.13474800
H	2.37971600	-3.21936100	1.11785400
C	5.19642000	2.22650000	-0.33136600
H	5.65218900	3.16789600	-0.00891000

H	5.54043800	2.01754000	-1.36275700
H	4.11387700	2.37499600	-0.36024200
C	7.00122900	1.09430200	0.76123700
H	7.52403000	0.84499200	-0.18211200
H	7.38750500	2.05640700	1.11390700
H	7.26012700	0.32908200	1.50033600
O	-2.82470200	0.50439900	1.50417300
O	-3.09145900	1.68347100	-0.68712400
O	-2.87304800	-0.80815800	-0.62298000
S	-3.25898400	0.43447600	0.08717700
C	-5.09879500	0.26747600	0.23236600
F	-5.43061100	-0.85328500	0.89881100
F	-5.62955000	1.31270700	0.89285900
F	-5.67519000	0.21137700	-0.98225100

1···NHN^{+}···I^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1024.220081 a.u.

M06/BSII SCF energy in acetonitrile:

-1023.616018 a.u.

M06/BSII free energy in acetonitrile:

-1023.317716 a.u.

C	-0.27165800	-0.22429200	0.63146400
C	-0.55926700	1.07683700	0.18405800
H	0.23944200	-1.50641000	2.31112900
C	0.02678200	-0.50072700	1.97263200
C	-0.53814000	2.18196300	1.04663100
C	-0.22791200	1.90832500	2.36754400
C	0.04435900	0.59070500	2.82300000
H	-0.75226700	3.18325800	0.69397100
H	-0.19198400	2.72381500	3.08190300
H	0.27652800	0.43996900	3.87169800
N	-0.69097800	-0.30705700	-1.55326100
N	-0.81375400	0.93920800	-1.15715800
N	-0.36751400	-1.00989600	-0.49062600
C	-0.13871700	-2.44574100	-0.61628400
H	0.92331900	-2.62850200	-0.78421200
H	-0.46457000	-2.92514400	0.30601900
H	-0.72873600	-2.80729700	-1.45668600
C	-1.11722200	1.97985700	-2.13085600
H	-1.81958800	2.68063200	-1.67995600
H	-0.19030300	2.48460700	-2.40604300
H	-1.56546800	1.50442400	-3.00152400
C	3.09840800	0.64458600	0.52550500
C	3.39102800	1.09813900	1.75656600
H	3.24506200	2.13692900	2.02433300
H	3.78628500	0.43782300	2.52112000
C	3.23412600	-0.78565000	0.14868300
C	3.56998900	-1.17818700	-1.15829800
C	3.05786500	-1.78659700	1.12054000
C	3.73255200	-2.52660800	-1.47685100
H	3.70942200	-0.42628800	-1.92479600
C	3.22523300	-3.13313000	0.80237200
H	2.77189500	-1.50772900	2.12862100
C	3.56267500	-3.51030800	-0.49971800
H	3.99658800	-2.80790400	-2.49210400
H	3.07957600	-3.88798500	1.56941800
H	3.68556800	-4.55937300	-0.75172700
C	2.55542200	1.59725700	-0.49428200
O	2.01538200	1.26223100	-1.53703200
O	2.71538800	2.88165000	-0.13433700
C	2.16189200	3.86728200	-1.02593700
H	1.06991600	3.83030000	-1.00577000
H	2.50778200	4.82921400	-0.64822400
H	2.51775900	3.70875300	-2.04584100

I	-4.22039900	-0.53834300	-0.00742800

$CHCl_3$···NHN^+···I^-

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1905.914816 a.u.
M06/BSII SCF energy in acetonitrile:
-1905.558472 a.u.
M06/BSII free energy in acetonitrile:
-1905.417869 a.u.

C	1.81581000	-1.71703400	0.54621100
C	1.80577400	-1.56729400	-0.85072500
H	2.81726300	-2.54905600	2.28903000
C	2.81316400	-2.44323000	1.21107600
C	2.79062300	-2.13857900	-1.66829400
C	3.77497600	-2.85541000	-1.01000200
C	3.78656400	-3.00411400	0.40266100
H	2.77814500	-2.01845600	-2.74466100
H	4.56688300	-3.31945300	-1.58802400
H	4.58753900	-3.57570100	0.85910700
N	0.06681900	-0.45803000	-0.01252000
N	0.70468500	-0.79090800	-1.11363700
N	0.71955100	-1.01573200	0.98365200
C	0.29460200	-0.79340600	2.36187500
H	0.13723100	-1.75949400	2.84351400
H	1.07365900	-0.23306600	2.88206000
H	-0.63176800	-0.22320000	2.34145100
C	0.24834900	-0.29244200	-2.40645200
H	1.03871500	0.32079800	-2.84246500
H	0.02375300	-1.14041500	-3.05516600
H	-0.64355900	0.30750400	-2.23886600
C	-4.80272500	-0.33423000	-0.31293200
H	-5.05116400	-1.14683600	-0.98915300
Cl	-3.02750400	-0.29435400	-0.11809700
Cl	-5.61309800	-0.65586600	1.25177300
Cl	-5.40424200	1.18753100	-1.04028800
I	2.68802700	2.22698500	0.22665300

^{1}CT1eq*

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-834.3746157 a.u.
M06/BSII SCF energy in acetonitrile:
-833.8158036 a.u.
M06/BSII free energy in acetonitrile:
-833.4776066 a.u.

I	4.17279600	-0.25626500	-0.14826400
C	-0.04818200	-0.44614200	-0.60937400
C	0.08243000	-0.50908000	0.79308000
C	-0.17297500	-1.68476500	1.49471400
C	-0.57534600	-2.80349600	0.74247800
C	-0.71312100	-2.73819000	-0.64640600
C	-0.44737400	-1.55203300	-1.35393200
H	-0.05272900	-1.73754600	2.57045000
H	-0.77830600	-3.73745600	1.25655200
H	-1.02543900	-3.62037500	-1.19566600
H	-0.53841100	-1.50279200	-2.43281500
N	0.25333800	0.85486200	-0.96188400
N	0.45540700	0.75438400	1.19503500
N	0.66443200	1.60721700	0.12771400
C	0.62315300	1.31806200	-2.28174400
H	1.63825100	0.99903400	-2.54412800
H	-0.08360900	0.91906200	-3.01180000
H	0.57193300	2.40745200	-2.29742300
C	0.94359800	1.14810300	2.49694000

H	0.34737700	0.65363100	3.26607900
H	1.99775700	0.88056400	2.62869500
H	0.82887200	2.22812900	2.59961500
C	-3.62910000	-0.06128200	0.39980400
C	-3.20383600	1.05990600	-0.54325800
H	-2.74489000	-0.45066300	0.90973000
H	-4.31869500	0.32718800	1.17019900
H	-2.53778300	0.67238700	-1.31905000
H	-4.05901600	1.51042000	-1.05817400
N	-2.50836300	2.16854500	0.08551200
N	-4.22615900	-1.15595900	-0.36247200
C	-2.05761400	3.26105700	-0.74948400
H	-2.65692100	4.14280800	-0.50678300
H	-1.01380300	3.46122400	-0.50377400
H	-2.16880600	3.00229300	-1.79981500
C	-2.43646300	2.32107600	1.52140200
H	-1.82439100	3.18575600	1.76466800
H	-3.45128500	2.45453400	1.90491800
H	-2.01377200	1.41648200	1.95793500
C	-4.32876700	-2.35057400	0.47290700
H	-4.99165000	-2.20585900	1.34594600
H	-4.72959100	-3.17751300	-0.12106600
H	-3.33841900	-2.63565900	0.83622800
C	-5.53849800	-0.80496300	-0.90117200
H	-5.94946600	-1.66543800	-1.43695200
H	-6.25854000	-0.51524200	-0.11362700
H	-5.46488600	0.02021700	-1.61500700

^{1}TS1*

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-2253.658446 a.u.
M06/BSII SCF energy in acetonitrile:
-2253.056791 a.u.
M06/BSII free energy in acetonitrile:
-2252.707708 a.u.

C	-4.20460300	-1.21790700	-0.21397200
H	-4.07899600	-0.14364600	-0.11247500
Cl	-2.17941200	-1.90195600	-0.05012400
Cl	-4.90844400	-1.56826700	-1.82119500
Cl	-5.22296000	-1.81614400	1.12995500
I	-2.70846900	2.58732600	-0.02545500
C	1.09958800	0.19397500	-0.36202500
C	0.96086600	0.13537900	1.03686500
C	1.12787500	1.26534700	1.84043700
C	1.43923400	2.45316200	1.17898300
C	1.58281700	2.50962600	-0.22174900
C	1.41815600	1.38139500	-1.02380600
H	1.01448900	1.21844500	2.91688800
H	1.57330000	3.36019400	1.75878000
H	1.82803300	3.45734000	-0.68867300
H	1.52534600	1.41910900	-2.10099200
N	0.89707500	-1.09433100	-0.80106800
N	0.69471500	-1.18609200	1.31863300
N	0.58425600	-1.92947300	0.20511800
C	0.78494900	-1.55141400	-2.17363300
H	-0.12698700	-1.15254700	-2.62574500
H	1.65635600	-1.21140800	-2.73626600
H	0.74909200	-2.63931900	-2.16809000
C	0.31844100	-1.76604600	2.59359900
H	0.90742300	-1.29356300	3.38026900
H	-0.74754800	-1.60459500	2.77665400
H	0.53182000	-2.83399800	2.56382700
C	4.71591500	0.09532500	0.21147300
C	4.37444300	-1.12148400	-0.64259700
H	3.82953000	0.40224500	0.77243400

H	5.50350800	-0.16448400	0.94098300
H	3.65583800	-0.85389700	-1.42335900
H	5.25498900	-1.51937700	-1.15798500
N	3.81247600	-2.25033800	0.07727000
N	5.10691100	1.21278300	-0.64494000
C	3.46726700	-3.43693100	-0.67694300
H	4.16590200	-4.22992200	-0.39675400
H	2.45900800	-3.74277800	-0.39338500
H	3.52801600	-3.23423100	-1.74333800
C	3.80749000	-2.32426000	1.52155400
H	3.29125400	-3.22738600	1.83731600
H	4.84434700	-2.33954500	1.86768800
H	3.32055300	-1.43860100	1.92892200
C	5.19111900	2.44028900	0.14325000
H	5.98145300	2.39945300	0.91510200
H	5.40808100	3.28474800	-0.51784200
H	4.23679800	2.62883600	0.64094900
C	6.37117600	0.97276800	-1.33872000
H	6.62943600	1.85704100	-1.92836100
H	7.20661200	0.76811600	-0.64424100
H	6.28860800	0.13058100	-2.03135400

[TMEDA···I]$^{\cdot}$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-359.2418913 a.u.
M06/BSII SCF energy in acetonitrile:
-358.9746751 a.u.
M06/BSII free energy in acetonitrile:
-358.7921271 a.u.

I	1.87356800	-0.76762400	-0.08225900
C	-1.82819300	0.04898200	0.45880500
C	-1.13626700	1.09644300	-0.41531900
H	-1.07961200	-0.67752600	0.78675100
H	-2.25167600	0.52382800	1.36232900
H	-0.97463400	0.68726400	-1.41497500
H	-1.76180200	1.99617700	-0.51731800
N	0.16408600	1.53821700	0.09590100
N	-2.85040200	-0.67299200	-0.29764600
C	0.85523800	2.46486400	-0.79585000
H	0.32108200	3.42578700	-0.80563200
H	1.87317400	2.62345300	-0.44039300
H	0.87422000	2.05668800	-1.80664000
C	0.22182700	1.90822900	1.50613500
H	1.24580900	2.17882000	1.76364700
H	-0.43645500	2.77118600	1.68346500
H	-0.10225200	1.07833900	2.13215500
C	-3.30950600	-1.83467000	0.45798000
H	-3.79159500	-1.56412500	1.41607000
H	-4.03643700	-2.39638000	-0.13694100
H	-2.46323400	-2.49264200	0.67877700
C	-3.97921000	0.18244600	-0.65390300
H	-4.72058700	-0.40455100	-1.20451400
H	-4.47860700	0.62171400	0.23020300
H	-3.65564900	1.00172500	-1.30212900

^{3}CT1

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-834.3606709 a.u.
M06/BSII SCF energy in acetonitrile:
-833.8108703 a.u.
M06/BSII free energy in acetonitrile:
-833.4761613 a.u.

I	4.08763600	-0.29619200	-0.37571000

C	-0.07618500	-0.30119300	-0.37126000
C	0.15716300	-0.50327300	1.00598100
C	-0.04398200	-1.74552100	1.60080300
C	-0.49303100	-2.78842000	0.76727400
C	-0.71961300	-2.58821300	-0.59629600
C	-0.50936200	-1.33214600	-1.19732700
H	0.15224600	-1.90641000	2.65478100
H	-0.65723100	-3.77125600	1.19790900
H	-1.06105500	-3.41577700	-1.20979200
H	-0.66745200	-1.17721000	-2.25844100
N	0.18384500	1.03515300	-0.61349600
N	0.56353800	0.71656500	1.50570400
N	0.70165600	1.67286200	0.51493900
C	0.52599800	1.59007400	-1.90692800
H	1.50371000	1.22669300	-2.24599100
H	-0.23842800	1.30549600	-2.63299400
H	0.55497500	2.67680100	-1.82506100
C	1.20708500	0.95790900	2.77765200
H	0.68148600	0.40205600	3.55668300
H	2.25861400	0.64686900	2.75331000
H	1.14826900	2.02462800	2.99975200
C	-3.61091100	-0.12064300	0.29463900
C	-3.19594300	1.03276200	-0.61421700
H	-2.72349300	-0.52087600	0.79151400
H	-4.30106500	0.24280900	1.07712600
H	-2.55790600	0.66273900	-1.42700000
H	-4.06412500	1.50213900	-1.09828600
N	-2.47897100	2.11330100	0.03733300
N	-4.20160300	-1.19796900	-0.49729600
C	-2.15096200	3.27732100	-0.75535300
H	-2.93196700	4.03399200	-0.59221800
H	-1.19560200	3.68284800	-0.41949600
H	-2.11912300	3.01370300	-1.81167100
C	-2.31696000	2.18068500	1.46906100
H	-1.69833300	3.03763600	1.72511700
H	-3.30790000	2.27665800	1.93296300
H	-1.85573200	1.26028600	1.83578200
C	-4.32847400	-2.40535200	0.31553800
H	-5.00822000	-2.27126900	1.17724200
H	-4.72177200	-3.21968100	-0.30059300
H	-3.34730400	-2.70286600	0.69452000
C	-5.49911700	-0.83140100	-1.06082600
H	-5.90155200	-1.68184500	-1.61873800
H	-6.23640800	-0.54882100	-0.28672200
H	-5.40285300	0.00390200	-1.75977700

^{3}TS1

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-2253.645707 a.u.
M06/BSII SCF energy in acetonitrile:
-2253.05562 a.u.
M06/BSII free energy in acetonitrile:
-2252.711587 a.u.

C	-4.33495200	-1.08201200	-0.17329500
H	-4.14253600	-0.01263600	-0.13057000
Cl	-2.30558900	-1.85874500	-0.08091100
Cl	-5.12617000	-1.48496600	-1.71979500
Cl	-5.29134500	-1.57661600	1.24817100
I	-2.58874900	2.61452200	-0.06590400
C	1.09318000	0.10125500	-0.38122800
C	0.95833700	0.00754500	1.01748600
C	1.18383900	1.10376300	1.85336500
C	1.55169200	2.29478300	1.22611700
C	1.69291300	2.38577200	-0.17271800
C	1.46793900	1.29128800	-1.00782800

H	1.07060000	1.02999800	2.92844200
H	1.73304000	3.17604600	1.83235500
H	1.98327100	3.33385000	-0.61237800
H	1.56986000	1.35786400	-2.08420600
N	0.82209700	-1.16160700	-0.85624800
N	0.62155000	-1.30398200	1.26151200
N	0.46085100	-2.00737100	0.12704400
C	0.65121000	-1.56530500	-2.23875200
H	-0.31506200	-1.21496600	-2.61264600
H	1.45726800	-1.13456000	-2.83448800
H	0.69408400	-2.65231400	-2.28825700
C	0.24078000	-1.90412700	2.52496800
H	0.88326200	-1.50566400	3.31113600
H	-0.80594800	-1.67689300	2.74653100
H	0.37676600	-2.98239000	2.44932800
C	4.77809100	0.07236200	0.24305500
C	4.42652700	-1.10772300	-0.65807600
H	3.87753400	0.39461000	0.77259200
H	5.52410900	-0.23446400	0.99710900
H	3.75788600	-0.78960800	-1.46768000
H	5.31900100	-1.52432100	-1.15081800
N	3.79616300	-2.22998000	0.00655200
N	5.24254100	1.19544300	-0.56647500
C	3.35090500	-3.34285200	-0.80125700
H	4.06766000	-4.16639500	-0.67214300
H	2.37591900	-3.67775500	-0.43824200
H	3.30457300	-3.05287900	-1.84933300
C	3.78526000	-2.37362200	1.44387400
H	3.13833600	-3.20395000	1.72038100
H	4.81168400	-2.57508900	1.78166500
H	3.45170700	-1.44498000	1.91111200
C	5.31113700	2.40784700	0.24619600
H	6.05900700	2.33608900	1.05700300
H	5.58134000	3.25738100	-0.38821400
H	4.33615900	2.60883700	0.69653000
C	6.53429600	0.93652900	-1.19897100
H	6.84275300	1.82317000	-1.76021700
H	7.32751600	0.70077600	-0.46612800
H	6.46731300	0.10560800	-1.90715000

[N]·

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-475.107345 a.u.
M06/BSII SCF energy in acetonitrile:
-474.832051 a.u.
M06/BSII free energy in acetonitrile:
-474.69747 a.u.

C	0.205886	-0.707518	-0.048567
C	0.205887	0.707526	-0.048603
H	1.390816	-2.518761	0.010654
C	1.393789	-1.434486	-0.005604
C	1.393793	1.434488	-0.005666
C	2.594673	0.698294	0.025211
C	2.594670	-0.698295	0.025242
H	1.390825	2.518764	0.010543
H	3.538921	1.233555	0.057990
H	3.538917	-1.233558	0.058042
N	-1.979914	0.000004	-0.055578
N	-1.115694	1.082574	-0.105635
N	-1.115692	-1.082565	-0.105550
C	-1.658904	-2.404627	0.101303
H	-1.025506	-3.136614	-0.404497
H	-1.717491	-2.656656	1.167838
H	-2.659832	-2.442081	-0.332522
C	-1.658912	2.404613	0.101376

H	-1.717819	2.656392	1.167956
H	-1.025319	3.136669	-0.404059
H	-2.659707	2.442225	-0.332748

TMEDA$^{+\bullet}$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-347.639494 a.u.
M06/BSII SCF energy in acetonitrile:
-347.398088 a.u.
M06/BSII free energy in acetonitrile:
-347.211755 a.u.

N	1.828862	-0.008052	0.355124
C	0.462808	-0.064994	0.678131
H	0.166480	0.811858	1.256777
H	0.226834	-0.988170	1.211096
C	-0.462751	-0.064755	-0.678227
H	-0.226629	-0.987674	-1.211583
H	-0.166649	0.812440	-1.256438
N	-1.828786	-0.008060	-0.355083
C	2.384968	1.262508	-0.071430
H	2.213296	1.429796	-1.145776
H	1.921006	2.074898	0.490605
H	3.463797	1.263053	0.104730
C	2.470032	-1.200217	-0.167771
H	3.546185	-1.143305	0.016673
H	2.060073	-2.084373	0.323665
H	2.312999	-1.290727	-1.253384
C	-2.385272	1.262306	0.071515
H	-1.921042	2.074939	-0.489903
H	-3.464018	1.262729	-0.105301
H	-2.214471	1.429202	1.146068
C	-2.469770	-1.200360	0.167732
H	-2.314103	-1.290021	1.253605
H	-3.545753	-1.144270	-0.018102
H	-2.058625	-2.084509	-0.322716

Cl^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-460.357359 a.u.
M06/BSII SCF energy in acetonitrile:
-460.367097 a.u.
M06/BSII free energy in acetonitrile:
-460.38212 a.u.

Cl	0.000000	0.000000	0.000000

^{2}TS2

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1894.393927 a.u.
M06/BSII SCF energy in acetonitrile:
-1894.076498 a.u.
M06/BSII free energy in acetonitrile:
-1893.931983 a.u.

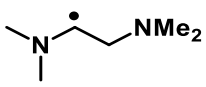
C	-2.410675	0.643974	0.302989
C	-2.500956	-0.670505	-0.197337
H	-3.000239	2.720187	0.079603
C	-3.078251	1.709868	-0.304535
C	-3.262756	-0.975085	-1.327574
C	-3.933045	0.090467	-1.931907
C	-3.843016	1.403151	-1.431726
H	-3.323926	-1.985678	-1.713980
H	-4.536125	-0.098836	-2.814066
H	-4.378368	2.199761	-1.938180
N	-1.112196	-0.687689	1.585659

N	-1.734761	-1.434207	0.652534
N	-1.597651	0.556717	1.408060
C	-1.063095	1.642548	2.205502
H	-0.218438	2.110001	1.690832
H	-1.850740	2.379013	2.372338
H	-0.732962	1.236198	3.161218
C	-1.361450	-2.827318	0.511132
H	-2.192467	-3.367698	0.056866
H	-0.469015	-2.917310	-0.116106
H	-1.157387	-3.234231	1.501875
C	3.103487	0.106166	-0.738042
H	2.736229	0.047131	-1.758574
Cl	1.378969	-0.364719	0.414497
Cl	3.656559	1.771384	-0.410187
Cl	4.395899	-1.105011	-0.508817

^{2}IM1

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-959.037198 a.u.
M06/BSII SCF energy in acetonitrile:
-959.003217 a.u.
M06/BSII free energy in acetonitrile:
-959.014626 a.u.

C	0.000533	0.695875	-0.100062
H	-0.000067	1.711750	0.276799
Cl	-1.482546	-0.173095	0.009510
Cl	1.482362	-0.173200	0.009524



B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-347.147555 a.u.
M06/BSII SCF energy in acetonitrile:
-346.927621 a.u.
M06/BSII free energy in acetonitrile:
-346.753977 a.u.

N	-1.616202	0.023618	-0.101189
C	-0.645722	-0.973736	0.020187
H	-0.719732	-1.743514	-0.744662
C	0.708775	-0.725818	0.596107
H	1.100572	-1.687437	0.950874
H	0.655970	-0.068935	1.483674
N	1.710323	-0.209768	-0.370917
C	-2.899117	-0.411807	-0.637078
H	-3.478880	0.458957	-0.956932
H	-2.734666	-1.057345	-1.504109
H	-3.494872	-0.971587	0.102493
C	-1.739767	1.022509	0.951944
H	-2.104449	0.589979	1.898258
H	-0.779817	1.505166	1.142274
H	-2.447071	1.791223	0.629855
C	3.046849	-0.257815	0.209874
H	3.784467	0.087665	-0.522427
H	3.150680	0.372508	1.114744
H	3.297452	-1.287143	0.488061
C	1.392778	1.145038	-0.805896
H	1.424686	1.881563	0.020834
H	2.112236	1.468415	-1.566077
H	0.391808	1.173298	-1.242944

^{2}TS3

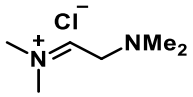
B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1766.44518 a.u.
M06/BSII SCF energy in acetonitrile:

-1766.185438 a.u.

M06/BSII free energy in acetonitrile:

-1766.004473 a.u.

N	-1.625829	1.559006	0.453292
C	-1.493392	0.210324	0.637575
H	-1.372539	-0.077910	1.677454
C	-2.138704	-0.809114	-0.253135
H	-1.565769	-1.735747	-0.151084
H	-2.079410	-0.520387	-1.316490
N	-3.525055	-1.119949	0.148157
C	-1.036942	2.437548	1.455445
H	-1.567796	3.393391	1.459771
H	-1.123370	1.979093	2.442464
H	0.025134	2.628542	1.246205
C	-1.688358	2.133906	-0.883980
H	-0.691301	2.172240	-1.345594
H	-2.348997	1.553601	-1.526941
H	-2.079518	3.151558	-0.813387
C	-3.977513	-2.349527	-0.494159
H	-4.990357	-2.591243	-0.155916
H	-3.997947	-2.279984	-1.598633
H	-3.317116	-3.179099	-0.221170
C	-4.442128	-0.023029	-0.140964
H	-4.518884	0.198433	-1.222639
H	-5.443670	-0.278465	0.220538
H	-4.116651	0.886520	0.369553
C	2.862135	-0.632325	-0.433766
H	2.824324	-1.375434	-1.225583
Cl	1.030883	-0.259840	0.059523
Cl	3.659996	0.834906	-1.082344
Cl	3.774383	-1.328314	0.942187



B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-807.423254 a.u.

M06/BSII SCF energy in acetonitrile:

-807.200861 a.u.

M06/BSII free energy in acetonitrile:

-807.027063 a.u.

N	-1.475924	-1.008435	-0.222412
C	-0.326499	-0.483931	-0.488113
H	-0.231508	0.036448	-1.433346
C	0.903153	-0.701097	0.335441
H	0.981210	-1.775905	0.538282
H	0.779134	-0.205267	1.314550
N	2.094841	-0.280363	-0.392285
C	-2.638500	-0.745783	-1.074175
H	-3.333179	-0.106723	-0.523522
H	-2.320251	-0.242628	-1.985760
H	-3.122397	-1.694756	-1.314508
C	-1.765871	-1.677677	1.048880
H	-2.582846	-2.381650	0.894144
H	-0.889730	-2.211321	1.413441
H	-2.066887	-0.919938	1.778725
C	3.283913	-0.953009	0.122777
H	4.153332	-0.653305	-0.470213
H	3.494907	-0.709862	1.180139
H	3.167395	-2.038151	0.038094
C	2.267988	1.170759	-0.366936
H	2.475779	1.551416	0.649951
H	3.105939	1.446528	-1.014767
H	1.361963	1.667246	-0.720643
Cl	-1.155905	2.211993	0.381828

^{2}TS3

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1496.623177 a.u.

M06/BSII SCF energy in acetonitrile:

-1496.311662 a.u.

M06/BSII free energy in acetonitrile:

-1496.164552 a.u.

C	1.834830	3.422515	0.289613
H	1.808045	3.539054	-0.796722
H	1.235693	4.210794	0.752425
H	2.862873	3.469589	0.648575
C	0.081532	1.844903	0.317699
O	-0.622746	2.638149	-0.286152
C	-0.352707	0.490785	0.762685
C	0.487830	-0.286562	1.490138
H	0.171792	-1.258195	1.852781
H	1.437197	0.092271	1.845461
C	1.680907	-1.568198	-0.312524
H	0.852296	-2.242225	-0.498228
Cl	3.043859	-2.297647	0.479499
Cl	2.018056	-0.471543	-1.611957
O	1.351490	2.123692	0.672685
C	-1.686379	0.004312	0.343608
C	-2.183408	0.237226	-0.951315
C	-2.464512	-0.757467	1.233177
C	-3.414637	-0.286279	-1.342817
H	-1.597668	0.820828	-1.650807
C	-3.697091	-1.276953	0.840593
H	-2.105082	-0.925486	2.243862
C	-4.177224	-1.044167	-0.450324
H	-3.778188	-0.103840	-2.349992
H	-4.285729	-1.856366	1.545907
H	-5.138596	-1.445610	-0.756954

^{2}IM2

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1496.682761 a.u.

M06/BSII SCF energy in acetonitrile:

-1496.371417 a.u.

M06/BSII free energy in acetonitrile:

-1496.217977 a.u.

C	-1.877983	3.477231	-0.520704
H	-2.016494	3.662198	0.547695
H	-1.185705	4.218151	-0.928470
H	-2.834969	3.529023	-1.039849
C	-0.181598	1.863987	-0.201731
O	0.453173	2.711332	0.415536
C	0.224186	0.468278	-0.454966
C	-0.843477	-0.484136	-0.933681
H	-0.450153	-1.159620	-1.697860
H	-1.673804	0.062779	-1.375236
C	-1.380767	-1.363105	0.196675
H	-0.608755	-1.955913	0.679729
Cl	-2.589394	-2.545307	-0.455930
Cl	-2.136322	-0.375745	1.515639
O	-1.389385	2.145401	-0.746024
C	1.563445	0.000577	-0.219988
C	2.612601	0.846472	0.246257
C	1.902064	-1.361994	-0.473234
C	3.894145	0.355382	0.448580
H	2.393092	1.883844	0.449948
C	3.186942	-1.840810	-0.263853
H	1.155023	-2.052216	-0.844941

C	4.195692	-0.988713	0.199813
H	4.669726	1.026839	0.805142
H	3.406424	-2.884522	-0.467252
H	5.200990	-1.365571	0.360953

^{2}TS4

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-2915.941526 a.u.
M06/BSII SCF energy in acetonitrile:
-2915.593899 a.u.
M06/BSII free energy in acetonitrile:
-2915.433276 a.u.

C	0.17254700	-2.77425400	2.82136400
H	0.60233300	-2.27667200	3.69332300
H	-0.90299100	-2.89985100	2.96349000
H	0.65105200	-3.73911400	2.65792800
C	-0.06495400	-0.75942900	1.61037900
O	-0.69869700	-0.27976300	2.53213900
C	0.16465300	-0.06862100	0.28884400
C	0.98540300	-0.84624200	-0.74581200
H	0.94018200	-0.34696300	-1.71523400
H	0.54813100	-1.83997200	-0.86375500
C	2.44723000	-1.05866300	-0.36085300
H	2.56208200	-1.46694800	0.63829000
Cl	3.41451300	0.46751800	-0.39776000
Cl	3.19811900	-2.27207300	-1.48595500
O	0.43465800	-2.00772900	1.62690100
C	0.35993200	1.41322300	0.33623400
C	0.69299600	2.10290000	1.51479800
C	0.22222800	2.15037400	-0.85523100
C	0.90030800	3.48085900	1.49375600
H	0.80433400	1.56080600	2.44476700
C	0.41807200	3.52778700	-0.87102100
H	-0.04569900	1.64278700	-1.77647400
C	0.76287100	4.20024900	0.30472600
H	1.17217800	3.99368800	2.41161100
H	0.30074500	4.07653200	-1.80055700
H	0.92129000	5.27438900	0.29397800
H	-1.00830600	-0.19994200	-0.17805200
C	-2.39243200	-0.35945500	-0.63458300
Cl	-2.33922300	-0.46210500	-2.39650000
Cl	-2.96807900	-1.84710300	0.12361300
Cl	-3.21392500	1.08251800	-0.04676300

^{1}IM3^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1496.810429 a.u.
M06/BSII SCF energy in acetonitrile:
-1496.514688 a.u.
M06/BSII free energy in acetonitrile:
-1496.362426 a.u.

C	-1.850710	3.541153	-0.418515
H	-1.748847	3.869305	0.621896
H	-1.263160	4.220161	-1.047243
H	-2.901957	3.592468	-0.714019
C	-0.137324	1.899427	-0.242444
O	0.569545	2.836679	0.174991
C	0.206958	0.537493	-0.449882
C	-0.858418	-0.413350	-0.930988
H	-0.485162	-1.087542	-1.713540
H	-1.707758	0.123516	-1.352197
C	-1.367515	-1.326194	0.182508
H	-0.570874	-1.843128	0.709898
Cl	-2.437286	-2.664205	-0.491017

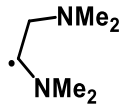
Cl	-2.290579	-0.428284	1.461516
O	-1.462153	2.186193	-0.590176
C	1.540115	0.026063	-0.199892
C	2.615390	0.827370	0.292598
C	1.873217	-1.340154	-0.449194
C	3.887701	0.306999	0.504313
H	2.410990	1.869387	0.497818
C	3.152318	-1.848768	-0.234958
H	1.119416	-2.023055	-0.826185
C	4.183898	-1.037272	0.245987
H	4.667045	0.967243	0.881110
H	3.341615	-2.898958	-0.448011
H	5.179481	-1.436661	0.416265

^{2}TS5

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1844.472069 a.u.
M06/BSII SCF energy in acetonitrile:
-1843.929126 a.u.
M06/BSII free energy in acetonitrile:
-1843.57145 a.u.

C	0.798258	3.792031	-1.434844
H	1.317318	3.687823	-2.390740
H	-0.232038	4.108667	-1.616396
H	1.308836	4.522525	-0.806850
C	0.282965	1.481395	-1.324267
O	-0.214262	1.576828	-2.440524
C	0.255862	0.290737	-0.445299
C	1.159449	0.359562	0.788904
H	0.983126	-0.501303	1.433440
H	0.901558	1.250717	1.366070
C	2.644006	0.475178	0.478869
H	2.872943	1.293386	-0.197025
Cl	3.323870	-1.017603	-0.287562
Cl	3.570191	0.832454	2.012274
O	0.830691	2.558883	-0.698603
C	0.091419	-1.052135	-1.090779
C	0.254576	-1.282443	-2.468035
C	-0.246267	-2.150869	-0.277724
C	0.090234	-2.560160	-3.005105
H	0.509430	-0.458209	-3.120327
C	-0.411795	-3.425570	-0.815850
H	-0.391319	-1.990916	0.785183
C	-0.244268	-3.640537	-2.186312
H	0.229928	-2.710133	-4.072349
H	-0.675041	-4.252908	-0.162258
H	-0.372900	-4.632832	-2.608811
N	-3.080875	1.269828	-0.197574
C	-2.177899	0.845252	0.784067
H	-1.870970	1.686743	1.405996
H	-0.943657	0.518915	0.154160
C	-2.570579	-0.387331	1.582944
H	-2.773056	-1.222065	0.907080
H	-3.520268	-0.171607	2.116400
N	-1.533728	-0.830301	2.516193
C	-2.980445	2.650811	-0.655125
H	-3.958576	2.983085	-1.019574
H	-2.681912	3.295166	0.174509
H	-2.257736	2.762537	-1.474467
C	-3.455685	0.346686	-1.264066
H	-2.669085	0.286340	-2.030209
H	-3.638178	-0.653885	-0.871345
H	-4.374716	0.701826	-1.739644
C	-1.907849	-2.113838	3.102339
H	-1.108256	-2.465111	3.761623

H	-2.840774	-2.060820	3.693728
H	-2.051749	-2.855966	2.310664
C	-1.259829	0.146572	3.565814
H	-2.156999	0.392863	4.164018
H	-0.500414	-0.255513	4.243101
H	-0.866665	1.073786	3.143418



B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-347.147555 a.u.
M06/BSII SCF energy in acetonitrile:
-346.927621 a.u.
M06/BSII free energy in acetonitrile:
-346.753977 a.u.

N	-1.616202	0.023618	-0.101189
C	-0.645722	-0.973736	0.020187
H	-0.719732	-1.743514	-0.744662
C	0.708775	-0.725818	0.596107
H	1.100572	-1.687437	0.950874
H	0.655970	-0.068935	1.483674
N	1.710323	-0.209768	-0.370917
C	-2.899117	-0.411807	-0.637078
H	-3.478880	0.458957	-0.956932
H	-2.734666	-1.057345	-1.504109
H	-3.494872	-0.971587	0.102493
C	-1.739767	1.022509	0.951944
H	-2.104449	0.589979	1.898258
H	-0.779817	1.505166	1.142274
H	-2.447071	1.791223	0.629855
C	3.046849	-0.257815	0.209874
H	3.784467	0.087665	-0.522427
H	3.150680	0.372508	1.114744
H	3.297452	-1.287143	0.488061
C	1.392778	1.145038	-0.805896
H	1.424686	1.881563	0.020834
H	2.112236	1.468415	-1.566077
H	0.391808	1.173298	-1.242944

2

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1497.320064 a.u.
M06/BSII SCF energy in acetonitrile:
-1497.009561 a.u.
M06/BSII free energy in acetonitrile:
-1496.844549 a.u.

C	-2.626247	-2.842435	-0.690405
H	-2.155786	-3.055041	-1.652948
H	-2.615702	-3.742313	-0.071288
H	-3.647838	-2.492555	-0.835329
C	-0.640505	-1.971329	0.250287
O	-0.054912	-2.996998	-0.031998
C	0.001515	-0.801868	0.994335
C	-0.927487	0.421566	1.171497
H	-0.471168	1.124425	1.872333
H	-1.856760	0.068828	1.621108
C	-1.288389	1.155512	-0.116177
H	-1.394833	0.495238	-0.971688
Cl	-0.047444	2.390149	-0.582584
Cl	-2.897461	1.986659	0.058941
O	-1.940279	-1.762969	-0.023204
C	1.380120	-0.470754	0.444763
C	1.682771	-0.568909	-0.918653
C	2.362942	0.001957	1.322081

C	2.941185	-0.198727	-1.394154
H	0.936127	-0.935966	-1.616172
C	3.620741	0.378281	0.849038
H	2.138021	0.077614	2.382791
C	3.913690	0.279093	-0.512868
H	3.160278	-0.280870	-2.454843
H	4.371680	0.742802	1.543994
H	4.892825	0.567807	-0.883658
H	0.146046	-1.190303	2.010779

7s

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-646.728163 a.u.
M06/BSII SCF energy in acetonitrile:
-646.510856 a.u.
M06/BSII free energy in acetonitrile:
-646.408102 a.u.

C	0.777397	0.748451	-0.227827
C	1.163453	1.972888	-0.605199
H	2.209261	2.254838	-0.635230
H	0.436630	2.721379	-0.901427
C	-0.640069	0.320771	-0.120121
C	-1.041407	-0.998018	-0.395300
C	-1.618365	1.253633	0.265346
C	-2.383988	-1.363824	-0.303688
H	-0.309941	-1.738468	-0.696154
C	-2.959409	0.885845	0.351803
H	-1.320878	2.266602	0.516705
C	-3.348602	-0.425337	0.067110
H	-2.674938	-2.386103	-0.526450
H	-3.698826	1.621139	0.654994
H	-4.392908	-0.713839	0.139996
C	1.834610	-0.267310	0.125102
F	1.552428	-0.902543	1.287029
F	1.946197	-1.237670	-0.823393
F	3.062474	0.274864	0.259054

^{1}IM3^{-}

B3LYP-DBJ/BSI SCF energy in acetonitrile:
-1496.810429 a.u.
M06/BSII SCF energy in acetonitrile:
-1496.514688 a.u.
M06/BSII free energy in acetonitrile:
-1496.362426 a.u.

^{2}TS6

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1605.771332 a.u.
M06/BSII SCF energy in acetonitrile:
-1605.518439 a.u.
M06/BSII free energy in acetonitrile:
-1605.407992 a.u.

C	0.362998	0.419807	-0.720346
C	-0.672321	-0.190800	-1.348093
H	-0.608441	-1.232160	-1.637060
H	-1.498277	0.379852	-1.752293
C	-2.140967	-1.008629	0.407528
H	-1.384858	-1.607345	0.903514
Cl	-3.365483	-1.944402	-0.402738
Cl	-2.690600	0.354421	1.333847
C	1.576824	-0.284761	-0.260765
C	2.349678	0.184473	0.819598
C	1.986723	-1.469343	-0.904401
C	3.478742	-0.514103	1.244076

H	2.063260	1.086729	1.345080
C	3.112321	-2.165800	-0.474475
H	1.433506	-1.834237	-1.763181
C	3.865147	-1.692685	0.603785
H	4.054923	-0.135443	2.083033
H	3.409617	-3.073401	-0.991258
H	4.746082	-2.233523	0.935882
C	0.246328	1.891302	-0.426237
F	-0.799176	2.469078	-1.054662
F	1.358233	2.569136	-0.802258
F	0.079249	2.146500	0.901743

^{2}IM4

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1605.827805 a.u.
M06/BSII SCF energy in acetonitrile:
-1605.577305 a.u.
M06/BSII free energy in acetonitrile:
-1605.460774 a.u.

C	0.209832	0.441054	-0.524823
C	-1.066413	-0.205882	-0.983148
H	-0.857781	-0.965018	-1.743013
H	-1.734465	0.528177	-1.432841
C	-1.806368	-0.917039	0.153383
H	-1.204189	-1.683598	0.633846
Cl	-3.276669	-1.756330	-0.488706
Cl	-2.276567	0.237846	1.467330
C	1.391063	-0.307217	-0.231332
C	2.569807	0.301968	0.293466
C	1.431746	-1.715350	-0.449718
C	3.697114	-0.452139	0.580838
H	2.595684	1.367092	0.480654
C	2.566568	-2.457091	-0.157039
H	0.569327	-2.225794	-0.861283
C	3.708351	-1.835381	0.362000
H	4.577558	0.040169	0.982582
H	2.564444	-3.527882	-0.336612
H	4.594450	-2.419079	0.590710
C	0.208270	1.927882	-0.334032
F	-0.962852	2.498557	-0.689150
F	1.174224	2.543370	-1.069490
F	0.437535	2.293110	0.957727

^{1}IM5^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1605.947971 a.u.
M06/BSII SCF energy in acetonitrile:
-1605.716144 a.u.
M06/BSII free energy in acetonitrile:
-1605.601627 a.u.

C	0.224003	0.484290	-0.534203
C	-1.048472	-0.162649	-0.988224
H	-0.861179	-0.953961	-1.727668
H	-1.728532	0.549616	-1.459528
C	-1.794283	-0.850829	0.158305
H	-1.158966	-1.516034	0.736780
Cl	-3.159848	-1.919375	-0.470008
Cl	-2.476769	0.335050	1.351094
C	1.378341	-0.298177	-0.216930
C	2.598423	0.263915	0.283076
C	1.398752	-1.720489	-0.383614
C	3.710548	-0.517119	0.570074
H	2.663227	1.333672	0.442920
C	2.522874	-2.488232	-0.094555

H	0.513156	-2.229738	-0.750670
C	3.700732	-1.907429	0.388737
H	4.607423	-0.029051	0.947532
H	2.473379	-3.564939	-0.246756
H	4.573520	-2.511021	0.618609
C	0.240229	1.919047	-0.329640
F	-0.916204	2.540270	-0.700207
F	1.243072	2.604982	-1.019789
F	0.467974	2.357083	0.980238

^{1}TS7$^-$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1605.929471 a.u.
M06/BSII SCF energy in acetonitrile:
-1605.715968 a.u.
M06/BSII free energy in acetonitrile:
-1605.600579 a.u.

C	-1.949671	0.284048	0.818366
C	-3.171383	-0.297590	1.151919
C	-3.867228	-1.067958	0.214327
C	-3.325014	-1.255455	-1.060151
C	-2.108340	-0.662367	-1.401160
C	-1.409314	0.125123	-0.471977
C	-0.105207	0.735180	-0.805590
C	0.205299	1.949484	-0.314997
F	0.838528	1.571961	1.701677
F	-0.690889	2.853436	0.070647
F	1.366183	2.551730	-0.573636
H	-1.351753	0.827115	1.544944
H	-3.574270	-0.169060	2.153388
H	-4.816254	-1.526462	0.477468
H	-3.853691	-1.859937	-1.792363
H	-1.695522	-0.806791	-2.396142
C	1.072538	-0.129145	-1.195223
H	0.780756	-0.973538	-1.824238
H	1.811024	0.457377	-1.748229
C	1.756542	-0.619675	0.087426
H	1.718249	0.157103	0.868581
Cl	3.504110	-1.073816	-0.217265
Cl	0.893992	-2.059702	0.793192

F$^-$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-99.900253 a.u.
M06/BSII SCF energy in acetonitrile:
-99.990886 a.u.
M06/BSII free energy in acetonitrile:
-100.005045 a.u.

F	0.000000	0.000000	0.000000

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B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1505.987588 a.u.
M06/BSII SCF energy in acetonitrile:
-1505.733862 a.u.
M06/BSII free energy in acetonitrile:
-1505.619063 a.u.

C	2.228766	0.257860	-0.807228
C	3.424181	-0.450642	-0.914864
C	3.795888	-1.361336	0.077040
C	2.960337	-1.556449	1.178702
C	1.764341	-0.847574	1.289496
C	1.382423	0.072866	0.299441

C	0.106100	0.816209	0.425517
C	0.010549	2.102246	0.086188
F	0.997911	2.877448	-0.343193
F	-1.117219	2.805833	0.156596
H	1.940571	0.948637	-1.592009
H	4.061168	-0.297173	-1.781076
H	4.725365	-1.916006	-0.009856
H	3.239896	-2.259959	1.957443
H	1.132774	-1.002512	2.158594
C	-1.148992	0.131357	0.928885
H	-0.894565	-0.761753	1.500822
H	-1.715878	0.796519	1.586204
C	-2.083305	-0.254593	-0.212598
H	-2.383028	0.600033	-0.814100
Cl	-3.615274	-0.969679	0.447558
Cl	-1.306741	-1.425438	-1.355212

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B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-540.779814 a.u.

M06/BSII SCF energy in acetonitrile:

-540.410329 a.u.

M06/BSII free energy in acetonitrile:

-540.233526 a.u.

C	-0.000109	2.505549	-0.000217
H	0.922331	3.072349	-0.079006
H	-0.922585	3.072298	0.078551
C	-0.000075	1.159766	-0.000182
C	-1.276814	0.395666	0.041050
C	-1.387819	-0.777519	0.807573
C	-2.406388	0.841109	-0.665607
C	-2.595916	-1.469809	0.881514
H	-0.525111	-1.140215	1.357088
C	-3.614049	0.147130	-0.593981
H	-2.327628	1.727738	-1.286908
C	-3.714462	-1.010393	0.181544
H	-2.663795	-2.369075	1.486934
H	-4.473956	0.504951	-1.152885
H	-4.653400	-1.553542	0.234449
C	1.276807	0.395799	-0.041193
C	1.388275	-0.776872	-0.808481
C	2.405899	0.840819	0.666390
C	2.596428	-1.469038	-0.882217
H	0.525876	-1.139181	-1.358739
C	3.613662	0.146914	0.594989
H	2.326819	1.727041	1.288237
C	3.714552	-1.010071	-0.181220
H	2.664766	-2.367880	-1.488220
H	4.473217	0.504410	1.154647
H	4.653518	-1.553198	-0.233926

^{2}TS8

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1499.8245 a.u.

M06/BSII SCF energy in acetonitrile:

-1499.419832 a.u.

M06/BSII free energy in acetonitrile:

-1499.23291 a.u.

C	-2.042354	1.561879	-0.378093
H	-1.282756	2.137389	-0.894179
C	-0.550502	0.646907	1.474266
H	-1.454332	0.151762	1.809280
H	-0.388644	1.659532	1.826377
C	0.409332	-0.032214	0.794893

C	0.192495	-1.456854	0.440587
C	0.544348	-1.946512	-0.830599
C	-0.414180	-2.339879	1.350809
C	0.282649	-3.269230	-1.183361
H	1.007124	-1.278773	-1.549733
C	-0.671872	-3.664268	0.998996
H	-0.667911	-1.985935	2.345326
C	-0.326623	-4.134223	-0.270407
H	0.551268	-3.624031	-2.174245
H	-1.135142	-4.331861	1.719766
H	-0.525767	-5.166122	-0.544220
C	1.652789	0.641279	0.350702
C	2.860422	-0.073459	0.240681
C	1.668275	2.017682	0.056151
C	4.039427	0.565932	-0.139504
H	2.875287	-1.134100	0.467671
C	2.846794	2.655304	-0.326674
H	0.747919	2.588507	0.115617
C	4.038849	1.933068	-0.426421
H	4.960886	-0.004893	-0.209453
H	2.832377	3.716846	-0.556514
H	4.956137	2.429828	-0.728318
Cl	-2.611059	0.182161	-1.269890
Cl	-3.251031	2.536038	0.414624

^{2}IM6

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1499.881969 a.u.

M06/BSII SCF energy in acetonitrile:

-1499.479758 a.u.

M06/BSII free energy in acetonitrile:

-1499.28907 a.u.

C	-1.025679	1.959287	-0.255131
H	-0.256719	2.210150	-0.980606
C	-0.494800	1.148140	0.930419
H	-1.340765	0.899786	1.574281
H	0.155281	1.819479	1.498024
C	0.256923	-0.087220	0.499919
C	-0.488507	-1.332489	0.328944
C	-0.200210	-2.219590	-0.735418
C	-1.555758	-1.676407	1.190393
C	-0.931443	-3.388866	-0.918952
H	0.582132	-1.963307	-1.440938
C	-2.278153	-2.852003	1.009802
H	-1.803781	-1.029506	2.024924
C	-1.972596	-3.716870	-0.045396
H	-0.695652	-4.041238	-1.754853
H	-3.082766	-3.096200	1.697443
H	-2.541592	-4.630542	-0.188321
C	1.673961	0.005930	0.236259
C	2.505336	-1.148347	0.213370
C	2.316543	1.260116	0.045117
C	3.871591	-1.053541	-0.016713
H	2.070266	-2.120390	0.411814
C	3.683723	1.345504	-0.189972
H	1.739095	2.177051	0.065701
C	4.474032	0.191853	-0.229660
H	4.475322	-1.956607	-0.017887
H	4.137423	2.320219	-0.344952
H	5.541779	0.262602	-0.412730
Cl	-2.302214	1.070963	-1.180463
Cl	-1.697186	3.548774	0.326946

^{1}IM7^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1499.98448 a.u.

M06/BSII SCF energy in acetonitrile:

-1499.597199 a.u.

M06/BSII free energy in acetonitrile:

-1499.407352 a.u.

C	-0.204581	-2.159910	0.248961
H	0.600004	-2.070189	0.972864
C	-0.074405	-1.198767	-0.932323
H	-0.965591	-1.315872	-1.552926
H	0.765142	-1.577011	-1.529194
C	0.159878	0.218020	-0.475762
C	-0.985401	1.093973	-0.319833
C	-1.022002	2.166335	0.622547
C	-2.189850	0.921804	-1.067159
C	-2.125654	3.000689	0.768572
H	-0.171828	2.317542	1.278140
C	-3.292297	1.755534	-0.914214
H	-2.255225	0.123228	-1.799282
C	-3.280761	2.817257	-0.000768
H	-2.090334	3.793963	1.512952
H	-4.175143	1.577160	-1.525135
H	-4.142372	3.468057	0.114764
C	1.517951	0.608854	-0.206150
C	1.949083	1.974475	-0.108433
C	2.585795	-0.345741	-0.106863
C	3.275630	2.332491	0.090068
H	1.220924	2.766978	-0.234193
C	3.912346	0.025664	0.090222
H	2.370911	-1.406189	-0.179592
C	4.288441	1.368522	0.205113
H	3.527922	3.390284	0.142787
H	4.666937	-0.755688	0.162942
H	5.322960	1.653449	0.371075
Cl	-1.735001	-1.915321	1.190104
Cl	-0.133195	-3.934145	-0.313579

^{1}TS9$^-$

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1499.980784 a.u.

M06/BSII SCF energy in acetonitrile:

-1499.587983 a.u.

M06/BSII free energy in acetonitrile:

-1499.399029 a.u.

C	0.343431	1.907524	-0.243655
H	1.051177	1.562415	-0.985415
C	0.265964	1.152925	1.047126
H	-0.546440	1.537730	1.665029
H	1.200343	1.294837	1.599417
C	0.072879	-0.249145	0.543056
C	-1.286075	-0.739375	0.340174
C	-1.631285	-1.618662	-0.721237
C	-2.361429	-0.326571	1.170380
C	-2.933619	-2.069778	-0.915196
H	-0.861114	-1.926694	-1.420151
C	-3.665077	-0.771992	0.969761
H	-2.166048	0.346049	1.999643
C	-3.969757	-1.655770	-0.070953
H	-3.145537	-2.736589	-1.747830
H	-4.450901	-0.431839	1.640226
H	-4.986504	-2.004862	-0.224775
C	1.255516	-1.026346	0.238828
C	1.226620	-2.446043	0.085330
C	2.557041	-0.441267	0.165100
C	2.374901	-3.193709	-0.145311

H	0.282124	-2.968552	0.183496
C	3.701831	-1.199540	-0.065262
H	2.677636	0.631146	0.272922
C	3.634293	-2.585801	-0.232878
H	2.286482	-4.273499	-0.245390
H	4.662970	-0.692824	-0.120496
H	4.528463	-3.172598	-0.420071
Cl	-1.196063	2.295096	-1.029483
Cl	1.311118	3.847055	0.136059

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B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1039.681766 a.u.
M06/BSII SCF energy in acetonitrile:
-1039.289279 a.u.
M06/BSII free energy in acetonitrile:
-1039.096221 a.u.

C	-0.055356	2.053846	-0.015241
H	0.785380	2.550560	-0.483724
C	-0.000794	1.697035	1.427459
H	-0.929884	1.734753	1.986102
H	0.885606	1.975667	1.989282
C	0.109982	0.591569	0.379179
C	-1.063699	-0.334387	0.224513
C	-1.520753	-0.679840	-1.055102
C	-1.679240	-0.908096	1.341748
C	-2.579085	-1.574282	-1.212577
H	-1.041939	-0.244610	-1.926850
C	-2.738766	-1.805188	1.187072
H	-1.326078	-0.651335	2.336065
C	-3.191749	-2.139501	-0.090408
H	-2.925878	-1.829928	-2.209650
H	-3.207483	-2.242742	2.063785
H	-4.016347	-2.835770	-0.212175
C	1.471212	-0.014866	0.129635
C	1.604721	-1.363312	-0.234846
C	2.644406	0.747987	0.268428
C	2.861975	-1.927239	-0.460989
H	0.721756	-1.981710	-0.342280
C	3.899508	0.185537	0.039497
H	2.593141	1.791140	0.563078
C	4.016974	-1.156758	-0.328065
H	2.933124	-2.974397	-0.741068
H	4.787939	0.799989	0.153490
H	4.994879	-1.594935	-0.503874
Cl	-1.584131	2.662841	-0.722000

25s

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-670.370277 a.u.
M06/BSII SCF energy in acetonitrile:
-670.02241 a.u.
M06/BSII free energy in acetonitrile:
-669.83925 a.u.

C	-1.985110	1.055795	-0.483214
C	-1.642666	-0.254576	-0.125085
C	-2.637594	-1.133737	0.322503
C	-3.955433	-0.695750	0.445416
C	-4.293907	0.612993	0.090945
C	-3.309368	1.483592	-0.382145
H	-1.224735	1.733827	-0.857271
H	-2.371430	-2.154676	0.577303
H	-4.718738	-1.376792	0.809717
H	-5.322289	0.950922	0.177644

H	-3.571366	2.496280	-0.673517
C	-0.256344	-0.801179	-0.327587
O	-0.091280	-1.800126	-1.015380
N	0.792514	-0.096642	0.259607
C	0.556980	0.973292	1.249966
H	-0.308537	0.712545	1.859475
H	1.425535	1.038991	1.904812
H	0.392662	1.948800	0.789609
C	2.141007	-0.531721	0.077027
O	2.453395	-1.707524	0.059701
C	3.163680	0.544630	-0.112415
C	4.559609	0.202088	0.329448
H	4.589504	-0.003177	1.405864
H	4.911961	-0.702808	-0.175641
H	5.249241	1.020451	0.110415
C	2.839760	1.674221	-0.755371
H	3.592170	2.424134	-0.983442
H	1.827812	1.871319	-1.093713

^{2}TS10

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1629.41952 a.u.
M06/BSII SCF energy in acetonitrile:
-1629.035751 a.u.
M06/BSII free energy in acetonitrile:
-1628.843334 a.u.

C	2.377204	0.752012	0.898164
C	1.825108	0.432285	-0.350418
C	2.573141	-0.314045	-1.270748
C	3.867375	-0.719137	-0.954841
C	4.415173	-0.398710	0.291242
C	3.667063	0.331203	1.218494
H	1.791208	1.309225	1.621636
H	2.127056	-0.571045	-2.225520
H	4.447789	-1.288101	-1.674706
H	5.421982	-0.720626	0.540186
H	4.086723	0.569872	2.190880
C	0.413946	0.766349	-0.693413
O	-0.252808	0.064068	-1.440953
N	-0.135607	1.918244	-0.096348
C	0.609676	3.187185	-0.112990
H	0.236196	3.827728	-0.915805
H	0.488232	3.706571	0.840187
H	1.664646	2.985857	-0.280826
C	-1.535592	2.037406	-0.000755
O	-2.079390	3.116985	-0.217406
C	-2.320376	0.896933	0.539077
C	-3.766935	0.858986	0.145028
H	-4.250375	1.821155	0.343570
H	-3.869237	0.670131	-0.930741
H	-4.299845	0.072568	0.683677
C	-1.799298	0.052944	1.477414
H	-2.479674	-0.493136	2.121051
H	-0.779280	0.164088	1.828671
C	-1.469210	-2.123094	0.677921
H	-1.960796	-2.582685	1.528552
Cl	0.233569	-2.508382	0.629463
Cl	-2.360712	-2.368654	-0.800907

^{2}IM8

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1629.478835 a.u.
M06/BSII SCF energy in acetonitrile:
-1629.099035 a.u.
M06/BSII free energy in acetonitrile:

-1628.901217 a.u.

C	2.521396	-0.140674	0.932872
C	2.147679	0.275943	-0.353793
C	2.553419	-0.468948	-1.469132
C	3.282242	-1.643711	-1.297874
C	3.639168	-2.064911	-0.013079
C	3.269056	-1.305964	1.099383
H	2.245763	0.450637	1.799606
H	2.278198	-0.128052	-2.461611
H	3.574832	-2.229254	-2.164032
H	4.210496	-2.978727	0.119372
H	3.561828	-1.619121	2.096632
C	1.391008	1.546015	-0.589699
O	1.708745	2.316579	-1.491852
N	0.356500	1.864553	0.279019
C	-0.105530	3.255648	0.279296
H	-0.516449	3.509422	-0.700483
H	-0.873163	3.359064	1.042955
H	0.721149	3.935082	0.501198
C	-0.240886	0.954701	1.191897
O	-0.591867	1.342818	2.307522
C	-0.484274	-0.416450	0.759773
C	-0.601397	-1.453047	1.825390
H	0.050233	-1.221119	2.671687
H	-1.627096	-1.510130	2.215394
H	-0.350158	-2.442093	1.432244
C	-0.812129	-0.758684	-0.663904
H	-0.423319	-1.751326	-0.914455
H	-0.371641	-0.050933	-1.368252
C	-2.301286	-0.765339	-1.021630
H	-2.435748	-0.944584	-2.085681
Cl	-3.059347	0.846907	-0.683025
Cl	-3.236315	-2.070048	-0.184037

^{2}TS11

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1629.463413 a.u.
M06/BSII SCF energy in acetonitrile:
-1629.080913 a.u.
M06/BSII free energy in acetonitrile:
-1628.881892 a.u.

C	1.885451	-0.221418	1.096965
C	2.115417	0.009241	-0.301180
C	2.554878	-1.019988	-1.127089
C	2.797382	-2.295900	-0.605452
C	2.601366	-2.537252	0.767569
C	2.196073	-1.519013	1.613230
H	1.982989	0.615938	1.783971
H	2.676887	-0.822665	-2.186976
H	3.131940	-3.095249	-1.258223
H	2.805061	-3.524239	1.172629
H	2.107673	-1.694801	2.679973
C	1.698650	1.282624	-0.926294
O	2.215809	1.710413	-1.953121
N	0.660193	1.994202	-0.296759
C	0.415986	3.370805	-0.743201
H	-0.656884	3.560794	-0.759518
H	0.890897	4.086227	-0.065711
H	0.833856	3.479914	-1.740884
C	-0.117435	1.555214	0.791188
O	-0.747287	2.380823	1.443558
C	-0.187222	0.096170	1.118272
C	-0.589033	-0.188904	2.541575
H	0.043458	0.356416	3.248018

H	-1.624402	0.113493	2.727965
H	-0.507250	-1.259250	2.748172
C	-0.740801	-0.829610	0.048685
H	-0.866565	-1.832555	0.463381
H	-0.046023	-0.906942	-0.791821
C	-2.053779	-0.367990	-0.575092
H	-1.989629	0.628601	-1.006051
Cl	-3.427966	-0.318449	0.601173
Cl	-2.490453	-1.469719	-1.957418

^{2}IM9

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1629.487668 a.u.
M06/BSII SCF energy in acetonitrile:
-1629.109316 a.u.
M06/BSII free energy in acetonitrile:
-1628.905896 a.u.

C	1.506235	0.650913	-0.863572
C	2.030143	-0.387214	0.085740
C	3.054306	-0.123378	0.974382
C	3.627529	1.152141	1.060313
C	3.142678	2.205332	0.231175
C	2.140612	1.996029	-0.667669
H	1.736692	0.327291	-1.896200
H	3.392291	-0.923200	1.625682
H	4.425815	1.343160	1.769271
H	3.587448	3.192492	0.320613
H	1.800666	2.806759	-1.302858
C	1.405761	-1.708157	0.076410
O	1.855874	-2.687111	0.671547
N	0.234069	-1.830491	-0.695564
C	-0.307452	-3.175948	-0.893616
H	-0.811433	-3.212666	-1.857475
H	0.513381	-3.888934	-0.860818
H	-1.027552	-3.422370	-0.106688
C	-0.545187	-0.759806	-1.131600
O	-1.580430	-0.966492	-1.747512
C	-0.064189	0.668357	-0.817087
C	-0.609691	1.601284	-1.907246
H	-0.117125	1.391021	-2.862119
H	-1.679348	1.456993	-2.040295
H	-0.427165	2.645957	-1.646342
C	-0.476205	1.134810	0.610031
H	-0.330506	2.219108	0.648590
H	0.214560	0.707352	1.343889
C	-1.855086	0.879146	1.195578
H	-1.928795	1.381334	2.156868
Cl	-2.150032	-0.875698	1.573415
Cl	-3.231597	1.535517	0.218792

I^{-}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-11.397842 a.u.
M06/BSII SCF energy in acetonitrile:
-11.36260072 a.u.
M06/BSII free energy in acetonitrile:
-11.38010072 a.u.

I	0.000000	0.000000	0.000000

^{1}IM10^{+}

B3LYP-D3BJ/BSI SCF energy in acetonitrile:
-1629.31759 a.u.
M06/BSII SCF energy in acetonitrile:

-1628.928557 a.u.

M06/BSII free energy in acetonitrile:

-1628.722525 a.u.

C	1.498796	0.703022	-0.754868
C	2.044936	-0.360189	0.101348
C	3.109944	-0.138750	0.931808
C	3.668454	1.155904	1.005367
C	3.180175	2.230710	0.244436
C	2.114769	2.027752	-0.598678
H	1.793995	0.420867	-1.792589
H	3.507091	-0.943992	1.537953
H	4.504297	1.323318	1.678102
H	3.642251	3.207156	0.328829
H	1.736052	2.840879	-1.207736
C	1.433709	-1.720102	0.042396
O	1.975914	-2.681466	0.567970
N	0.245303	-1.831819	-0.661059
C	-0.296062	-3.181521	-0.861887
H	-0.850645	-3.195783	-1.797211
H	0.531688	-3.886412	-0.892761
H	-0.966581	-3.443074	-0.038478
C	-0.535363	-0.752029	-1.101180
O	-1.564444	-0.958764	-1.714956
C	-0.077807	0.682395	-0.778512
C	-0.596081	1.608166	-1.887616
H	-0.080137	1.399260	-2.828986
H	-1.660459	1.448243	-2.040180
H	-0.437151	2.654614	-1.621758
C	-0.532934	1.151142	0.641692
H	-0.415251	2.238986	0.668974
H	0.144232	0.746092	1.400017
C	-1.926070	0.865700	1.182804
H	-2.032718	1.374614	2.137605
Cl	-2.188115	-0.891144	1.562142
Cl	-3.279200	1.486826	0.159556

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B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-1628.935218 a.u.

M06/BSII SCF energy in acetonitrile:

-1628.557001 a.u.

M06/BSII free energy in acetonitrile:

-1628.361711 a.u.

C	1.441585	-0.848892	0.190029
C	2.159508	0.305195	-0.155466
C	3.504915	0.225614	-0.538727
C	4.146738	-1.006685	-0.579279
C	3.437367	-2.161936	-0.239000
C	2.096097	-2.083988	0.137413
H	4.027112	1.141166	-0.793172
H	5.190146	-1.069697	-0.871434
H	3.928942	-3.129731	-0.266772
H	1.562622	-2.993200	0.388493
C	1.531641	1.646005	-0.102449
O	2.083826	2.657344	-0.521841
N	0.284947	1.736875	0.518970
C	-0.238137	3.084029	0.761976
H	-1.274824	2.996391	1.075830
H	0.337087	3.587373	1.544299
H	-0.164220	3.661537	-0.159105
C	-0.398462	0.646991	1.057970
O	-1.291688	0.813768	1.871885
C	-0.045002	-0.745536	0.514685
C	-0.464381	-1.792879	1.559716

H	0.228538	-1.771766	2.405497
H	-1.463386	-1.580766	1.931016
H	-0.457939	-2.796391	1.130644
C	-0.753508	-0.966400	-0.870301
H	-0.595566	-2.017493	-1.132690
H	-0.233314	-0.374110	-1.628948
C	-2.231263	-0.690253	-1.115863
H	-2.482263	-1.040767	-2.114084
Cl	-2.632606	1.081356	-1.141652
Cl	-3.370762	-1.564129	-0.015226

HCl···TMEDA

B3LYP-D3BJ/BSI SCF energy in acetonitrile:

-808.663058 a.u.

M06/BSII SCF energy in acetonitrile:

-808.429544 a.u.

M06/BSII free energy in acetonitrile:

-808.231333 a.u.

N	1.318706	-0.849212	0.104269
C	-0.095892	-0.912965	0.596028
H	-0.115284	-0.330026	1.517815
H	-0.317130	-1.955439	0.836786
C	-1.099172	-0.357392	-0.416005
H	-1.236027	-1.077743	-1.226158
H	-0.706264	0.572291	-0.864299
N	-2.392760	-0.151678	0.236829
C	2.266617	-1.313136	1.154597
H	3.284066	-1.169481	0.790707
H	2.106326	-0.718760	2.054327
H	2.084011	-2.368924	1.361028
C	1.534057	-1.577478	-1.176259
H	1.244359	-2.621831	-1.047738
H	0.938876	-1.112084	-1.960416
H	2.590815	-1.508991	-1.434953
C	-3.488127	-0.199144	-0.726850
H	-4.442073	-0.086093	-0.201865
H	-3.427724	0.597225	-1.491618
H	-3.492774	-1.165046	-1.241305
C	-2.428974	1.101960	0.986110
H	-2.319620	1.988483	0.334563
H	-3.381713	1.184527	1.518269
H	-1.627748	1.132807	1.729388
Cl	2.038761	2.059806	-0.323270
H	1.546292	0.177544	-0.072348

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