Supporting Information

Electrochemical electrophilic bromination/spirocyclization of *N*-benzyl-acrylamides to brominated 2-azaspiro[4.5]decanes

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1. General Considerations

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) or DMSO-d_6 (2.50 ppm) for ^{1}H NMR and $CDCl_3$ (77.0 ppm) or DMSO-d_6 (40.0 ppm) for ^{13}C NMR. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Thermofisher Q Exactive Accurate-Mass Q-Orbitrap LC/MS (HESI). X-Ray data were collected on a Bruker SMART APEXII instrument with an IμS Mo microsource (λ = 0.7107 A). XINRUI® DJS-292B potentiostat made in China was used as a power supply device. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

2. General Procedure for the Electrosynthesis

2.1 General Procedure for the Model Reaction: A 20 mL three-necked beaker-type cell (Figure S1A) was charged with *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**, 0.20 mmol), 2-bromoethan-1-ol (**2**, 0.60 mmol), KPF_6 (0.10 mmol). The cell was equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1.0 cm x 1.0 cm x 0.1 mm) cathode. Then MeCN (6.0 mL) and H_2O (1.0 mL) were added (Figure S1B). The electrolysis was carried out at room temperature using a constant current of 10 mA for 2.5 h. The reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product.

2.2 General Procedure for the Gram-Scale Synthesis of 3: The gram-scale electrolysis was conducted in a 100 mL three-necked round-bottomed flask with a piece of RVC (1.2 cm x 2.0 cm x 2.0 cm) as the anode, a Pt plate as the cathode (1.5 cm x 1.5 cm x 0.3 mm), and a constant current of 62 mA for 10 h at room temperature (Figure S1C). The reaction mixture consisted **1** (1.16 g, 5.0 mmol) or **4** (1.31 g, 5.0 mmol), 2-bromoethan-1-ol (**2**, 1.87 g, 15 mmol), KPF_6 (0.46 g, 2.5 mmol), MeCN (72 mL) and H_2O (12 mL). When the reaction was

complete, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **3** (1.21 g, 74% yield or 1.24 g, 76% yield).

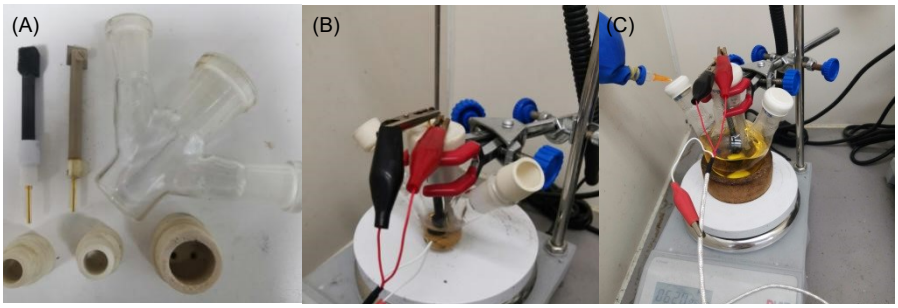
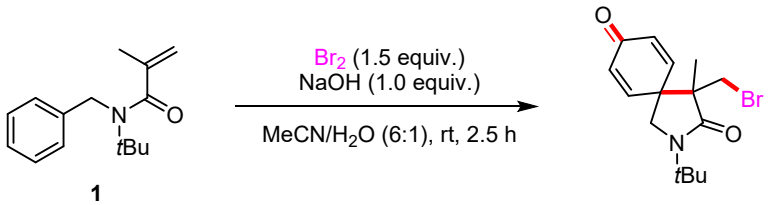


Figure S1. The electrolysis setup [The RVC is fixed on a sharpened graphite rod (⌀ 6 mm)].

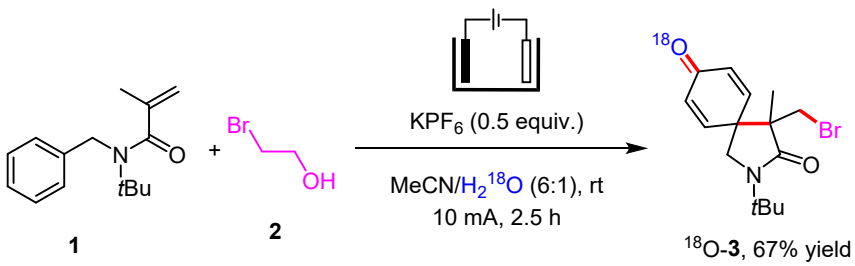
3. Mechanistic Studies

3.1 Electrophilic Bromination/Spirocyclization of 1 with Br_2



When Br_2 was added to the solution of *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**) in MeCN/H_2O (6:1) with NaOH (1.5 equiv.), the electrophilic bromination/spirocyclization could be achieved in 46% yield at room temperature for 2.5 h, indicating that the reaction may involve Br_2 as the intermediate.

3.2 Electrochemical Electrophilic Bromination/Spirocyclization of 1 in MeCN/$H_2{}^{18}O$



The ^{18}O-**3** was formed by electrolyzing **1** and **2** with MeCN/$H_2{}^{18}O$ (6:1) as solvent, indicating that the oxygen atom in product **3** was derived from H_2O.

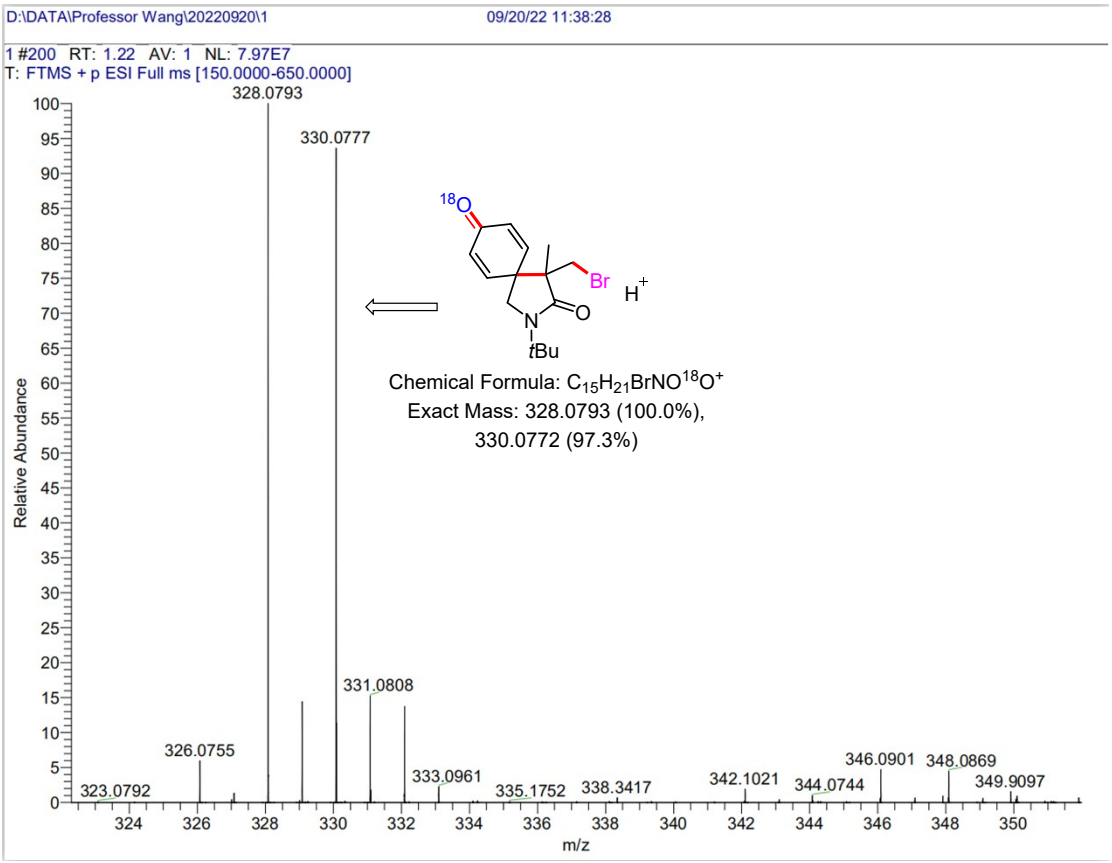
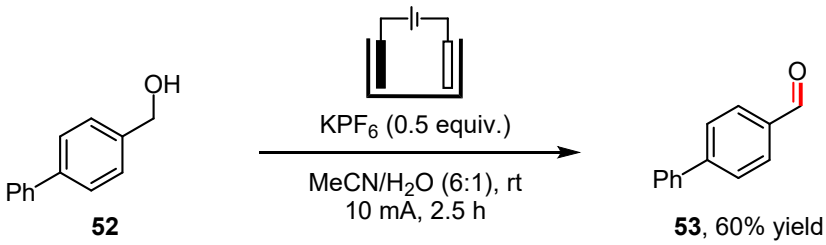


Figure S2. High resolution mass spectroscopy (HRMS) of ^{18}O-**3**.

3.3 Electrochemical Oxidation of Benzyl Alcohol 52 to Aldehyde 53



The electrochemical oxidation of benzyl alcohol **52** gave aldehyde **53** in 60% yield, showing that the direct electrooxidation of **56** is feasible to produce product **3** at the anode.

3.4 Cyclic Voltammograms Studies

The cyclic voltammograms were recorded in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN/H_2O (6:1, 5.0 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a

Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 100 mV/s.

The cyclic voltammograms (CVs) of *n*-Bu_4NBr, *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**) and *N*-(tert-butyl)-*N*-(4-methoxybenzyl)methacrylamide (**4**) were recorded in an electrolyte of nBu_4NBF_4 (0.10 M) in MeCN/H_2O (6:1, 5.0 mL) (Figure S3–S5). The oxidation potential of Br^- ($E_{p/2}$ = 1.05 V vs. Ag/AgCl) was significantly lower than that of the substrate **1** ($E_{p/2}$ = 1.99 V vs. Ag/AgCl) and substrate **4** ($E_{p/2}$ = 1.72 V vs. Ag/AgCl), indicating the anodic oxidation of Br^- were preferentially carried out. The studies of cyclic voltammograms support our proposed mechanism in Scheme 6 of the main text.

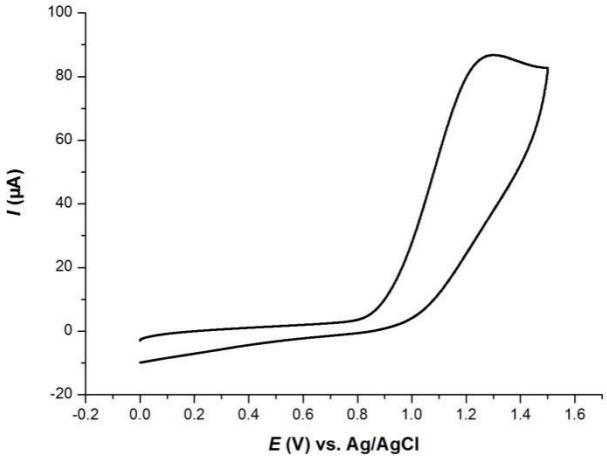


Figure S3. Cyclic voltammogram of nBu_4NBr (10 mM) in an electrolyte of nBu_4NBF_4 (0.1 M) in MeCN/H_2O (6:1, 5 mL). $E_{p/2}$ = 1.05 V.

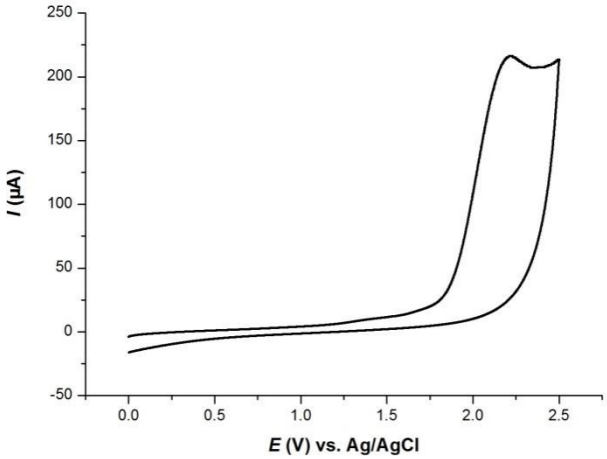


Figure S4. Cyclic voltammogram of *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**, 10 mM) in an electrolyte of nBu_4NBF_4 (0.1 M) in MeCN/H_2O (6:1, 5 mL). $E_{p/2}$ = 1.99 V.

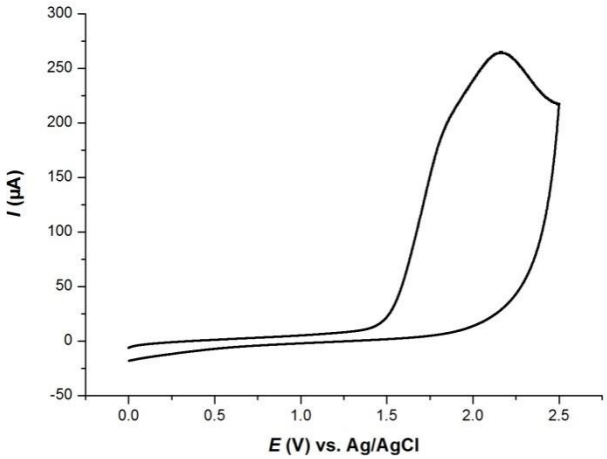
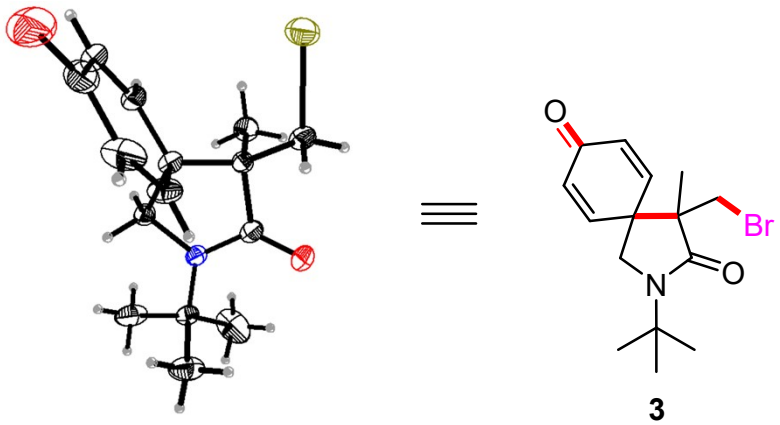


Figure S5. Cyclic voltammogram of *N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)methacrylamide (**4**, 10 mM) in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN/H$_2$O (6:1, 5 mL). $E_{p/2}$ = 1.72 V.

4. X-Ray Crystallography

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3** and **45** in petroleum ether/CH_2Cl_2) in a loosely capped vial.

4.1 X-Ray Single Crystal Diffraction Analysis of Compound 3 (CCDC: 2213723)



3

CCDC 2213723
X-ray of **3**

Datablock: 1

Bond precision: C-C = 0.0057 A Wavelength=0.71073

Cell: a=7.079(2) b=9.363(3) c=11.864(3)
alpha=93.881(5) beta=97.142(5) gamma=100.629(4)
Temperature: 296 K

	Calculated	Reported
Volume	763.6(4)	763.5(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H20 Br N O2	?
Sum formula	C15 H20 Br N O2	C15 H20 Br N O2
Mr	326.22	326.23
Dx,g cm-3	1.419	1.419
Z	2	2
Mu (mm-1)	2.690	2.690
F000	336.0	336.0
F000'	335.56	
h,k,lmax	8,11,14	8,11,14
Nref	2705	2672
Tmin,Tmax	0.502,0.524	
Tmin'	0.492	

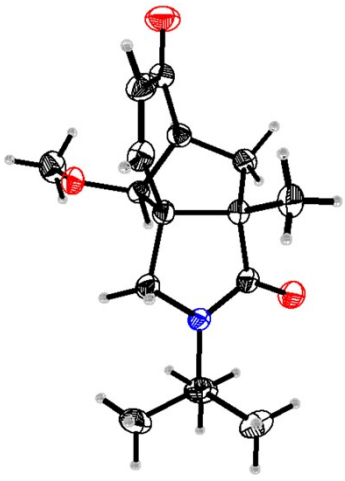
Correction method= Not given

Data completeness= 0.988 Theta(max)= 25.000

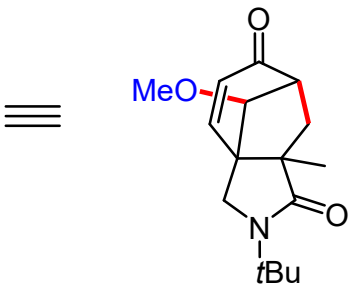
R(reflections)= 0.0443(2034) wR2(reflections)= 0.1155(2672)

S = 0.996 Npar= 176

4.2 X-Ray Single Crystal Diffraction Analysis of Compound 45 (CCDC: 2213724)



CCDC 2213724
X-ray of **45**



45

Datablock: a

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=6.6760(17) b=23.100(6) c=9.948(3)
alpha=90 beta=94.562(4) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1529.3(7)	1529.2(7)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C16 H23 N O3	?
Sum formula	C16 H23 N O3	C16 H23 N O3
Mr	277.35	277.35
Dx,g cm-3	1.205	1.205
Z	4	4
Mu (mm-1)	0.083	0.083
F000	600.0	600.0
F000'	600.28	
h,k,lmax	7,27,11	7,27,11
Nref	2686	2683
Tmin,Tmax	0.971,0.982	0.971,0.982
Tmin'	0.971	

Correction method= # Reported T Limits: Tmin=0.971 Tmax=0.982
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.000

R(reflections)= 0.0398(2181) wR2(reflections)= 0.1081(2683)

S = 1.019 Npar= 182

5. Unsuccessful Substrates

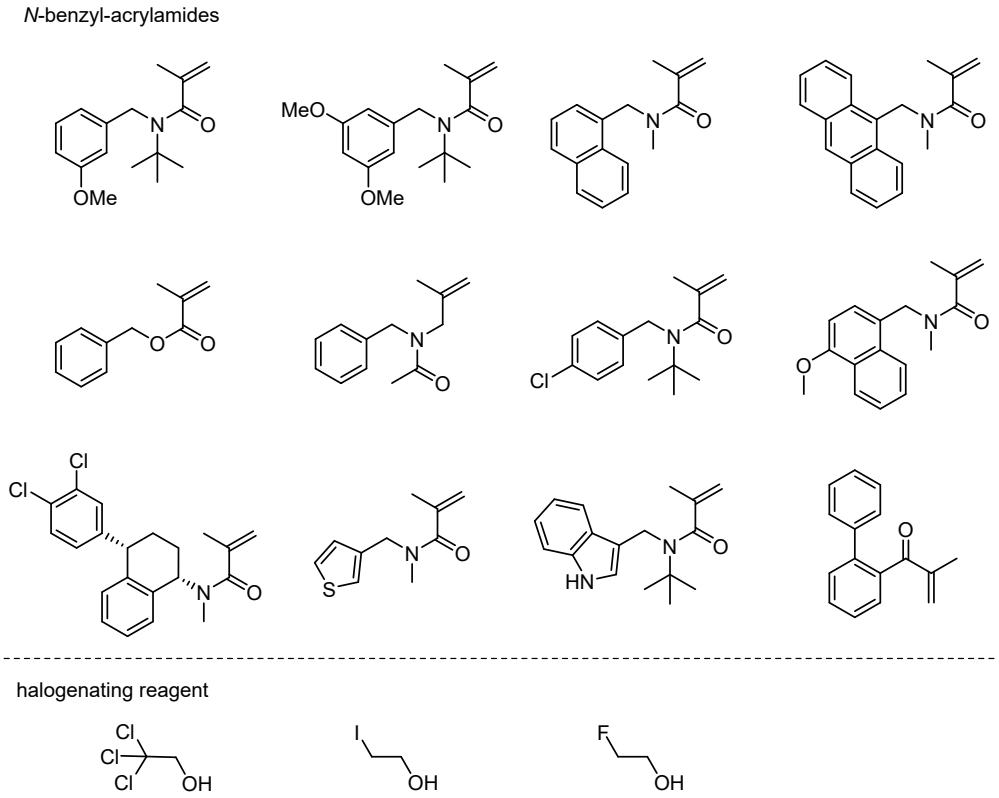
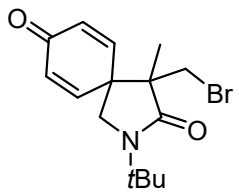
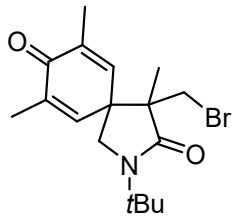


Figure S6. Unsuccessful substrates in the reactions.

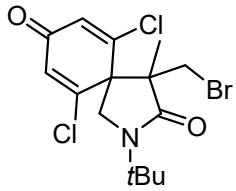
6. Characterization Data for the Electrolysis Products



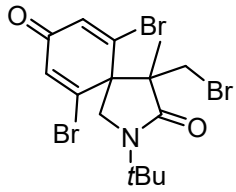
4-(Bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (3). White solid (46 mg, 71% yield); m.p. = 103.6−106.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, J = 10.0, 2.8 Hz, 1H), 6.91 (dd, J = 10.4, 2.8 Hz, 1H), 6.46 (dd, J = 10.4, 2.0 Hz, 1H), 6.40 (dd, J = 10.0, 2.0 Hz, 1H), 3.52–3.44 (m, 3H), 3.37 (d, J = 10.4 Hz, 1H), 1.43 (s, 9H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 173.6, 148.1, 146.7, 131.2, 131.0, 54.9, 52.9, 50.3, 46.6, 37.4, 27.5, 18.5; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{21}BrNO_2^+$: 326.0750, Found: 326.0753.



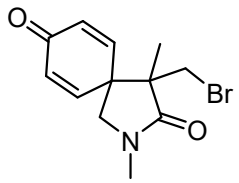
4-(Bromomethyl)-2-(*tert*-butyl)-4,7,9-trimethyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (15). White solid (51 mg, 72% yield); m.p. = 102.7−104.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.62 (s, 1H), 3.46 (s, 2H), 3.42 (d, J = 10.4 Hz, 1H), 3.31 (d, J = 10.4 Hz, 1H), 1.96 (s, 3H), 1.93 (s, 3H), 1.43 (s, 9H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 174.2, 142.9, 141.6, 137.1 (2C) , 54.7, 52.6, 50.5, 45.9, 37.5, 27.5, 18.5, 16.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{25}BrNO_2^+$: 354.1063, Found: 354.1062.



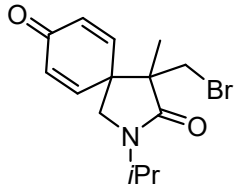
4-(Bromomethyl)-2-(*tert*-butyl)-6,10-dichloro-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (16). White solid (45 mg, 57% yield); m.p. = 134.4−136.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, J = 1.6 Hz, 1H), 6.62 (d, J = 1.6 Hz, 1H), 4.19 (d, J = 11.4 Hz, 1H), 3.73–3.69 (m, 2H), 3.63 (d, J = 11.4 Hz, 1H), 1.61 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.7, 171.9, 153.8, 153.6, 133.1, 131.2, 55.4, 52.3, 49.5, 38.3, 27.4, 23.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}BrCl_2NO_2^+$: 393.9971, Found: 393.9971.



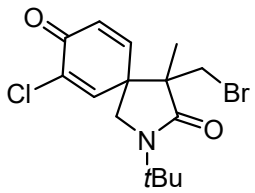
6,10-Dibromo-4-(bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (17). White solid (36 mg, 37% yield); m.p. = 138.4−140.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (d, J = 1.8 Hz, 1H), 6.91 (d, J = 1.8 Hz, 1H), 4.28 (d, J = 11.4 Hz, 1H), 3.76 (d, J =4.8 Hz, 1H), 3.74 (d, J =4.8 Hz, 1H), 3.63 (d, J = 11.4 Hz, 1H), 1.65 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 171.8, 145.7, 145.1, 137.7, 135.6, 55.5, 54.9, 52.8, 52.4, 38.6, 27.4, 24.1; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}BrNO_2^+$: 481.8960, Found: 481.8961.



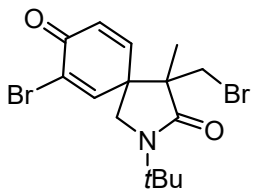
4-(Bromomethyl)-2,4-dimethyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (18). Colorless oil (11 mg, 19% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, J = 10.4, 3.2 Hz, 1H), 6.90 (dd, J = 10.4, 3.2 Hz, 1H), 6.46 (dd, J = 10.0, 2.0 Hz, 1H), 6.40 (dd, J = 10.0, 2.0 Hz, 1H), 3.52 (s, 2H), 3.41 (d, J = 10.4 Hz, 1H), 3.33 (d, J = 10.4 Hz, 1H), 2.96 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 173.8, 147.9, 146.4, 131.4, 130.9, 54.2, 52.3, 47.4, 37.1, 30.1, 18.9; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_{15}BrNO_2^+$: 284.0281, Found: 284.0285.



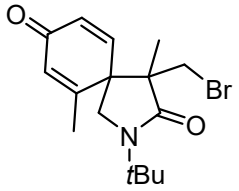
4-(Bromomethyl)-2-(*iso*-propyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (19). White solid (9 mg, 14% yield); m.p. = 112.4−114.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, J = 10.4, 3.2 Hz, 1H), 6.90 (dd, J = 10.4, 3.2 Hz, 1H), 6.46 (dd, J = 10.4, 2.0 Hz, 1H), 6.40 (dd, J = 10.4, 2.0 Hz, 1H), 4.50–4.39 (m, 1H), 4.53–4.50 (m, 2H), 3.33 (dd, J = 14.8, 10.4 Hz, 2H), 1.33 (s, 3H), 1.20 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 172.7, 148.0, 146.4, 131.4, 130.9, 52.6, 47.2, 47.1, 43.3, 37.1, 19.6, 19.5, 18.7; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{19}BrNO_2^+$: 312.0594, Found: 312.0595.



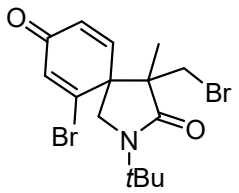
4-(Bromomethyl)-2-(*tert*-butyl)-7-chloro-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (20). White solid (67 mg, 93% yield, d:r = 1.3:1); m.p. = 103.8−105.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.10 (m, 1H), 7.08–6.93 (m, 1H), 6.55–6.47 (m, 1H), 3.56–3.49 (m, 2H), 3.47–3.36 (m, 2H), 1.44–1.43 (m, 9H), 1.36–1.32 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9 (2C), 173.2, 173.1, 148.3, 147.0, 143.8, 142.6, 134.9, 134.7, 129.8 (2C), 55.0 (2C), 53.3, 53.1, 49.8 (2C), 49.1, 37.2, 37.1, 27.4, 18.6, 18.4; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{20}ClBrNO_2^+$: 360.0360, Found: 360.0363.



7-Bromo-4-(bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (21). White solid (71 mg, 88% yield, d:r = 1.5:1); m.p. = 112.4−114.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52–7.32 (m, 1H), 7.13–6.91 (m, 1H), 6.55–6.48 (m, 1H), 3.53–3.37 (m, 4H), 1.44–1.43 (m, 9H), 1.36–1.31 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 173.2 (2C), 148.2, 148.1, 147.0, 146.9, 129.5, 129.4, 127.0, 126.8, 55.2, 55.1, 53.2, 53.1, 50.1, 49.7 (2C), 37.1, 27.5, 18.8, 18.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{20}Br_2NO_2^+$: 403.9855, Found: 403.9855.

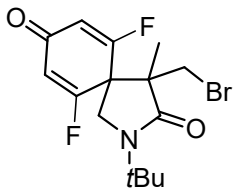


4-(Bromomethyl)-2-(*tert*-butyl)-4,7-dimethyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (22). Yellow oil (51 mg, 75% yield, d:r = 1.5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–6.64 (m, 2H), 6.45–6.36 (m, 1H), 3.51–3.31 (m, 4H), 1.97–1.93 (m, 3H), 1.44–1.43 (m, 9H), 1.31–1.28 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6, 173.9, 147.9, 146.6, 143.0, 141.8, 137.7, 137.6, 130.7, 130.6, 54.8 (2C), 52.8, 52.6, 50.4, 50.3, 46.6, 46.5, 37.4, 27.5, 18.6, 18.4, 16.2; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{23}BrNO_2^+$: 340.0907, Found: 340.0912.

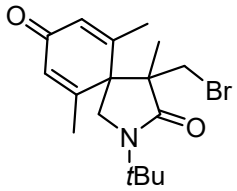


6-Bromo-4-(bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (23). Isomer I: White solid (39 mg, 48% yield); m.p. = 112.4−114.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 10.0 Hz, 1H), 6.71 (s, 1H), 6.44 (d, J = 10.0 Hz, 1H), 3.79 (d, J = 11.2 Hz, 1H), 3.54 (d, J = 12.0 Hz, 2H), 3.23 (d, J = 11.2 Hz, 1H), 1.44 (s, 9H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.8, 172.3, 148.8, 147.5, 134.9, 130.5, 55.7, 54.7, 51.9, 50.6, 38.3, 27.6, 18.9; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{20}Br_2NO_2^+$: 403.9855, Found: 403.9855. **Isomer I':** White solid (25 mg, 31% yield); m.p. = 140.5−142.8 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 10.4 Hz, 1H), 6.88 (s, 1H), 6.43 (d, J = 10.4, 1H), 3.89 (d, J = 11.2 Hz, 1H), 3.60–3.56 (m, 2H), 3.51 (d, J = 11.2 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 173.4, 149.2, 145.8, 136.2, 130.2, 55.2, 52.4, 50.9, 50.4,

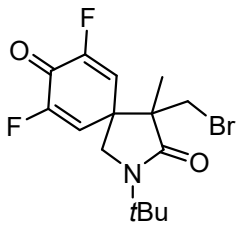
36.9, 27.3, 21.6; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{20}Br_2NO_2^+$: 403.9855, Found: 403.9855.



4-(Bromomethyl)-2-(*tert*-butyl)-6,10-difluoro-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (24). White solid (64 mg, 88% yield); m.p. = 128.2−130.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (s, 1H), 5.99 (s, 1H), 3.82 (d, J = 10.4 Hz, 1H), 3.60 (d, J = 10.4 Hz, 1H), 3.57–3.48 (m, 2H), 1.44 (d, J = 6.0 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.5 (t, $J_{C–F}$ = 18.2 Hz), 172.6 (dd, $J_{C–F}$ = 284.2, 14.2 Hz), 171.8, 171.3 (dd, $J_{C–F}$ = 284.2, 14.2 Hz), 112.2 (d, $J_{C–F}$ = 14.2 Hz), 110.6 (d, $J_{C–F}$ = 12.5 Hz), 55.3, 52.0 (t, $J_{C–F}$ = 3.2 Hz), 50.7 (t, $J_{C–F}$ = 20.9 Hz), 45.9 (d, $J_{C–F}$ = 2.7 Hz), 37.0 (d, $J_{C–F}$ = 4.2 Hz), 27.2, 20.7 (d, $J_{C–F}$ = 8.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ –91.1, –98.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}BrF_2NO_2^+$: 362.0562, Found: 362.0564.

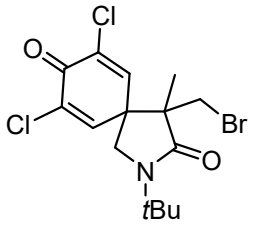


4-(Bromomethyl)-2-(*tert*-butyl)-4,6,10-trimethyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (25). White solid (22 mg, 31% yield); m.p. = 164.4−166.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 6.24 (s, 1H), 3.79 (d, J = 10.8 Hz, 1H), 3.53 (t, J = 11.2 Hz, 2H), 3.32 (d, J = 11.2 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 1.47 (s, 9H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.5, 173.8, 157.6, 157.3, 132.5, 131.0, 55.1, 52.0, 51.9, 47.5, 38.3, 27.5, 24.0, 23.4, 22.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{25}BrNO_2^+$: 354.1063, Found: 354.1063.

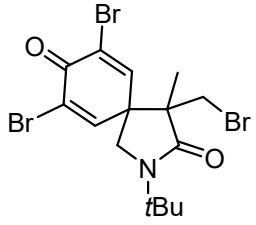


4-(Bromomethyl)-2-(*tert*-butyl)-7,9-difluoro-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (26). White solid (30 mg, 41% yield); m.p. = 120.1−122.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (dd, J = 12.0, 2.8 Hz, 1H), 6.53 (dd, J = 12.0, 2.8 Hz, 1H), 3.56 (dd, J = 10.4, 2.0 Hz, 1H), 3.51 (d, J = 11.6 Hz, 1H), 3.46 (d, J = 11.2 Hz, 1H), 3.41 (d, J = 10.4 Hz, 1H), 1.43 (s, 9H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 171.0 (t, $J_{C–F}$ = 24.6 Hz),

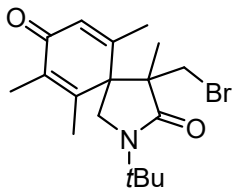
154.5 (dd, $J_{C–F}$ = 265.6, 8.3 Hz), 154.1 (dd, $J_{C–F}$ = 265.6, 8.3 Hz), 124.6 (d, $J_{C–F}$ = 16.9 Hz), 123.4 (d, $J_{C–F}$ = 14.8 Hz), 55.2, 53.1, 50.4 (t, $J_{C–F}$ = 3.0 Hz), 45.9 (t, $J_{C–F}$ = 6.0 Hz), 37.3, 27.5, 18.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –125.2 (t, J = 13.5 Hz, 1F), –126.1(t, J = 13.5 Hz, 1F) ; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}BrNO_2^+$: 362.0562, Found: 362.0565.



4-(Bromomethyl)-2-(*tert*-butyl)-7,9-dichloro-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dion (27). White solid (51 mg, 65% yield); m.p. = 217.1−219.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 2.8 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 3.55 (d, J = 10.8 Hz, 1H), 3.50 (d, J = 11.2 Hz, 1H), 3.47–3.42 (m, 2H), 1.44 (s, 9H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.3, 144.0, 142.8, 133.9, 133.7, 55.3, 53.6, 49.9, 49.7, 37.0, 27.5, 18.7; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}BrCl_2NO2^+$: 393.9971, Found: 393.9972.

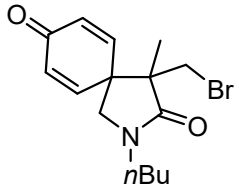


7,9-Dibromo-4-(bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (28). White solid (45 mg, 46% yield); m.p. = 250.3−252.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 2.8 Hz, 1H), 7.34 (d, J = 2.8 Hz, 1H), 3.55–3.43 (m, 4H), 1.44 (s, 9H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 171.9, 148.4, 147.2, 124.3, 124.2, 55.3, 53.4, 52.4, 49.1, 36.9, 27.5, 18.7; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{19}Br_3NO_2^+$: 481.8960, Found: 481.8961.

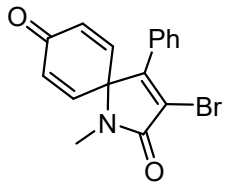


4-(Bromomethyl)-2-(*tert*-butyl)-4,6,7,10-tetramethyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (29). White solid (24 mg, 33% yield, d:r = 1.2;1); m.p. = 155.6−157.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1H), 3.90–3.70 (m, 1H), 3.68–3.39 (m, 2H), 3.30–3.25 (m, 1H), 2.13–2.11 (m, 3H), 2.10–1.93 (m, 3H), 1.90–1.74 (m, 3H), 1.48–1.47 (m, 9H), 1.36–1.25 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.1, 185.0, 174.2, 173.9, 156.7, 156.5, 150.6, 149.9,

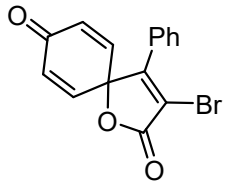
136.9, 135.3, 131.2, 130.3, 55.1, 55.0, 52.6, 51.7, 51.6, 51.5, 48.1, 47.9, 38.8, 38.7, 27.5, 27.4, 23.8, 23.6, 22.9, 22.5, 21.0, 19.0, 11.9, 11.6; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{27}BrNO_2^+$: 368.1220, Found: 368.1223.



4-(Bromomethyl)-2-butyl-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (30). Colorless oil (20 mg, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, J = 10.4, 3.2 Hz, 1H), 6.84 (dd, J = 10.4, 3.2 Hz, 1H), 6.39 (dd, J = 10.0, 2.0 Hz, 1H), 6.33 (dd, J = 10.0, 2.0 Hz, 1H), 3.48–3.42 (m, 2H), 3.36–3.22 (m, 4H), 1.50–1.43 (m, 2H), 1.31–1.24 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 173.5, 147.9, 146.5, 131.3, 131.0, 52.5, 52.1, 47.4, 42.8, 37.1, 29.2, 20.1, 18.8, 13.7; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{21}BrNO_2^+$: 326.0750, Found: 326.0754.



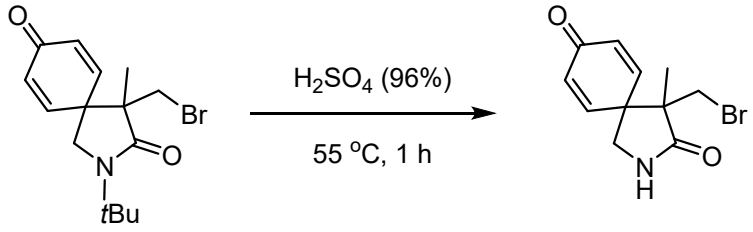
3-Bromo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (31).[1] White solid (60 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.36 (m, 5H), 6.55–6.49 (m, 4H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 165.7, 151.2, 144.1, 133.4, 130.2, 130.1, 128.7, 127.7, 119.8, 68.2, 26.6.



3-Bromo-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (32).[2] White solid (21 mg, 33% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 3H), 7.45–7.40 (m, 2H), 6.71–6.67 (m, 2H), 6.46–6.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.4, 166.9, 159.7, 141.6, 132.2, 131.3, 129.0, 128.5, 127.4, 112.2, 82.9.

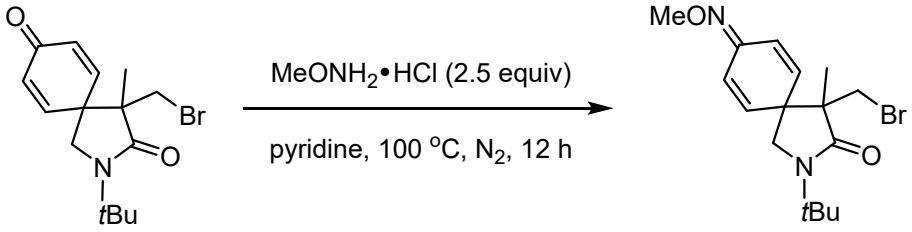
7. Synthetic Applications

7.1 Conversions of 3 to Compounds 33, 34 and 36



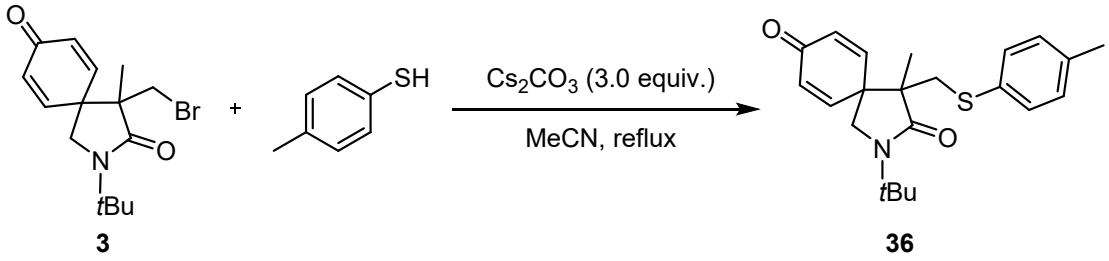
3 **33**

4-(Bromomethyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (33). A mixture of **3** (0.1 mmol, 1.0 equiv.) and H_2SO_4 96% (0.50 mL) was heated at 55 °C for 1 h. Then the reaction was cooled to room temperature, diluted with cold water and extracted with CH_2Cl_2. The organic phase was concentrated and the residue purified by chromatography (CH_2Cl_2/ ethyl acetate = 3:1, v/v) to provide product **33** (19 mg, 70% yield) as a white solid. m.p. = 187.8−190.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 (s, 1H), 7.34 (dd, J = 10.4, 3.2 Hz, 1H), 7.19 (dd, J = 10.4, 3.2 Hz, 1H), 6.37 (s, 1H), 6.35 (s, 1H), 3.71 (d, J = 11.2 Hz, 1H), 3.57 (d, J = 11.2 Hz, 1H), 3.52 (d, J = 10.4 Hz, 1H), 3.17 (dd, J = 10.4, 1.6 Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.1, 175.8, 150.2, 149.4, 130.6, 129.9, 51.5, 50.0, 46.4, 39.3, 18.7; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{11}H_{13}BrNO_2^+$: 270.0124, Found: 270.0125.



3 **34**

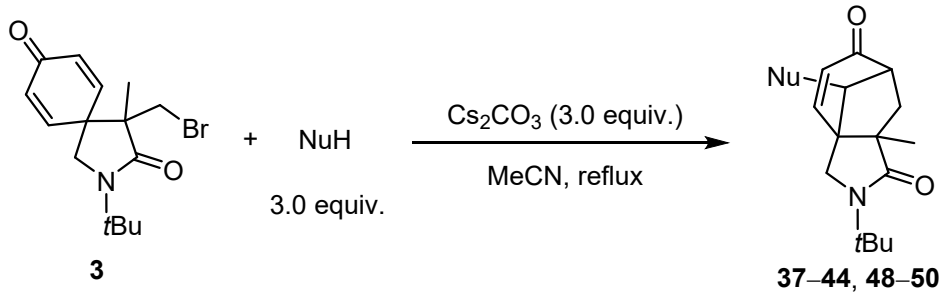
4-(Bromomethyl)-2-(*tert*-butyl)-8-(methoxyimino)-4-methyl-2-azaspiro[4.5]deca-6,9-dien-3-one (34). Pyridine (1.0 mL) was added to a solution of compound **3** (0.1 mmol, 1.0 equiv) and methoxyamine hydrochloride (0.25 mmol, 2.5 equiv) under a N_2 atmosphere. Then, the mixture was stirred at 100 °C for 12 h. After completion of the reaction, pyridine was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) to provide ketoxime **34** (30 mg, 84% yield) as a white solid. m.p. = 97.3−100.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–6.91 (m, 1H), 6.45–6.22 (m, 2H), 6.20–6.04 (m, 1H), 3.94 (s, 3H), 3.66–3.27 (m, 4H), 1.41 (s, 9H), 1.23–1.15 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 174.3, 147.7, 138.6, 138.2, 137.0, 134.3, 133.9, 132.8, 132.7, 125.8, 125.6, 125.2, 124.5, 118.2, 118.1, 117.6, 116.9, 62.1, 54.6 (2C), 53.7, 53.0, 52.9, 52.8, 52.7, 52.6, 52.5, 49.0, 46.4 (2C), 37.5 (2C), 27.6, 18.3, 18.2, 17.3, 17.2; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{12}H_{16}BrN_2O_2^+$: 299.0390, Found: 299.0392.



2-(*tert*-Butyl)-4-methyl-4-((*p*-tolylthio)methyl)-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (36). To a solution of **3** (0.1 mmol, 1.0 equiv) in MeCN (1.5 mL), 4-methylthiophenol (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.3 mmol, 3.0 equiv.) was added. The mixture is heated to reflux and stirred overnight. The crude reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 4/1, v/v) to afford the product **36** (34 mg, 92% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.17 (m, 2H), 7.07–7.04 (m, 3H), 6.92 (dd, J = 10.0, 3.2 Hz, 1H), 6.42–6.36 (m, 2H), 3.44 (d, J = 10.4 Hz, 1H), 3.36 (d, J = 10.4 Hz, 1H), 3.22 (d, J = 12.8 Hz, 1H), 3.03 (d, J = 12.8 Hz, 1H), 2.29 (s, 3H), 1.43 (s, 9H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0, 175.2, 148.3, 147.8, 136.5, 133.0, 131.0, 130.9, 130.1, 129.7, 54.7, 54.1, 50.2, 47.0, 41.6, 27.6, 21.0, 18.3; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{22}H_{28}NO_2S^+$: 370.1835, Found: 370.1840.

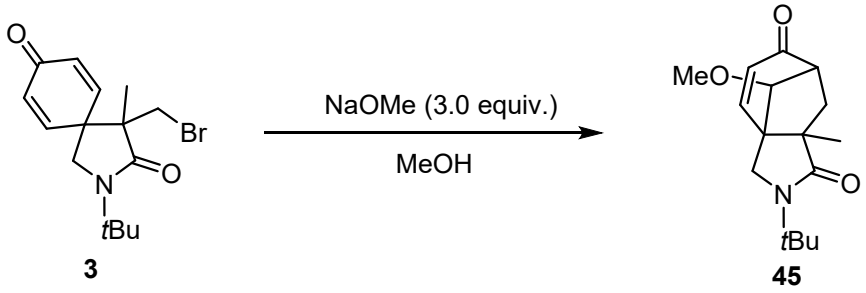
7.2 Tandem Cyclizations of 3 to Compounds 37–51

Synthesis of 37–44 and **48–50**



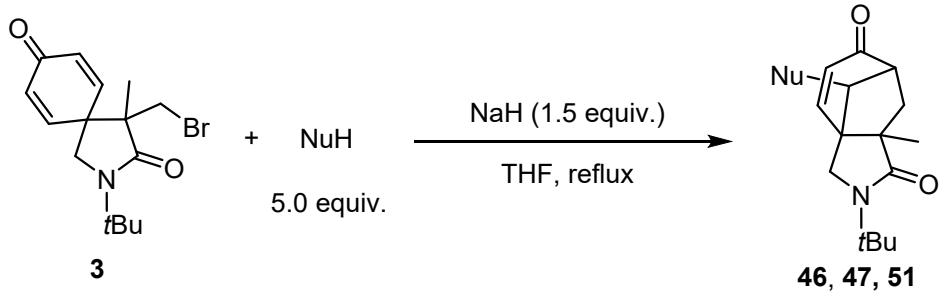
To a solution of **3** (0.1 mmol, 1.0 equiv.) in MeCN (1.5 mL), Nucleophile (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.3 mmol, 3.0 equiv.) was added. The mixture is heated to reflux and stirred overnight. The crude reaction mixture was concentrated and purified by column chromatography on silica gel to afford the products **37–44** and **48–50**.

Synthesis of 45

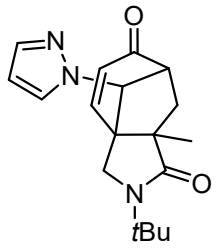


To a solution of **3** (0.1 mmol, 1.0 equiv.) in MeOH (1.5 mL), NaOMe (0.3 mmol, 3.0 equiv.) was added. The mixture is heated to reflux and stirred 16 h. The crude reaction mixture was concentrated and purified by column chromatography on silica gel to afford the product **45**.

Synthesis of 46, **47 and 51**

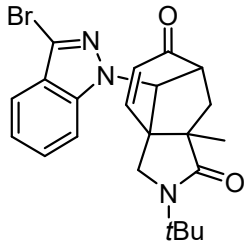


To a solution of **3** (0.1 mmol, 1.0 equiv.) in dry THF (1.5 mL), the mixture was added NaH (60% in mineral oil, 0.15 mmol, 1.5 equiv.) at 0 °C and stirred 10 minutes. Then, the corresponding alcohol (0.5 mmol, 5.0 equiv.) was added. The mixture is heated to reflux and stirred 16 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic phase was washed with brine (10 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under reduced pressure to afford the crude mixture. The crude was purified over silica gel column chromatography to afford **46**, **47** and **51**, respectively.

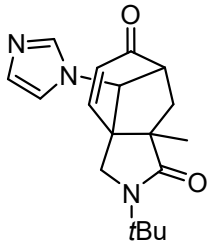


2-(*tert*-Butyl)-8a-methyl-9-(1*H*-pyrazol-1-yl)-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (37). White solid (29 mg, 93% yield); m.p. = 141.3−143.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 2.0 Hz,

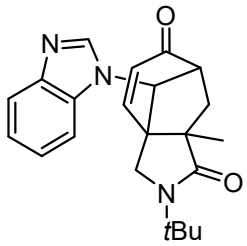
1H), 6.74 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.13 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.68 (d, *J* = 10.8 Hz, 1H), 4.59–4.57 (m, 1H), 3.60 (d, *J* = 10.8 Hz, 1H), 3.40 (t, *J* = 6.0 Hz, 1H), 2.85 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.48 (s, 9H), 1.42 (d, *J* = 15.2 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 177.3, 148.6, 139.5, 130.7, 129.8, 105.7, 68.0, 57.7, 54.3, 53.6, 53.5, 48.4, 33.5, 27.7, 20.0; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{24}N_3O_2^+$: 314.1863, Found: 314.1860.



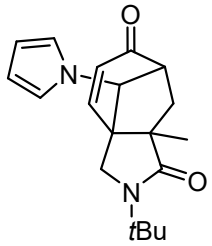
9-(3-Bromo-1*H*-indazol-1-yl)-2-(*tert*-butyl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (38). White solid (41 mg, 93% yield); m.p. = 208.6−211.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 1H), 7.48–7.43 (m, 1H), 7.39–7.36 (m, 1H), 7.26–7.22 (m, 1H), 6.80 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.28 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.87 (dd, *J* = 4.0, 1.6 Hz, 1H), 3.91 (d, *J* = 11.2 Hz, 1H), 3.60 (d, *J* = 11.2 Hz, 1H), 3.53–3.50 (m, 1H), 2.90 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.49–1.46 (m, 10H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 178.0, 147.2, 141.4, 131.5, 127.9, 124.2, 122.0, 121.1, 120.8, 108.8, 67.0, 57.1, 54.3, 53.5, 52.7, 48.4, 33.6, 27.7, 19.8; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{22}H_{25}BrN_3O_2^+$: 442.1125, Found: 442.1126.



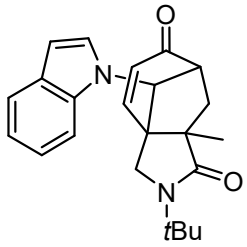
2-(*tert*-Butyl)-9-(1*H*-imidazol-1-yl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (39). White solid (28 mg, 89% yield); m.p. = 172.8−175.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.04 (t, *J* = 1.2 Hz, 1H), 6.86–6.83 (m, 2H), 6.36 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.43 (dd, *J* = 4.0, 2.0 Hz, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.61 (d, *J* = 11.2 Hz, 1H), 3.35–3.32 (m, 1H), 2.83 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.46 (s, 9H), 1.40 (d, *J* = 14.8 Hz, 1H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 177.0, 148.1, 137.0, 132.3, 129.6, 119.1, 65.3, 57.8, 54.4, 54.3, 52.1, 47.1, 33.3, 27.6, 19.9; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{24}N_3O_2^+$: 314.1863, Found: 314.1859.



9-(1*H*-Benzo[*d*]imidazol-1-yl)-2-(*tert*-butyl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (40). White solid (35 mg, 96% yield); m.p. = 309.6−311.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.37–7.30 (m, 3H), 6.97 (dd, J = 10.0, 2.0 Hz, 1H), 6.50 (dd, J = 9.6, 1.2 Hz, 1H), 4.82 (dd, J = 4.0, 1.6 Hz, 1H), 3.67 (d, J = 10.8 Hz, 1H), 3.56 (d, J = 10.8 Hz, 1H), 3.48–3.45 (m, 1H), 2.95 (dd, J = 14.4, 7.2 Hz, 1H), 1.51–1.46 (m, 10H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 177.6, 148.9, 142.9, 141.3, 134.7, 132.5, 123.5, 123.1, 120.8, 109.1, 64.0, 57.7, 54.6, 53.9, 52.3, 47.4, 33.6, 27.6, 20.0; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{22}H_{26}N_3O_2^+$: 364.2020, Found: 364.2022.

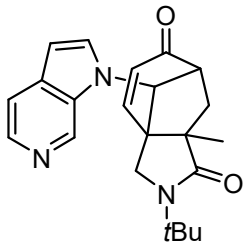


2-(*tert*-Butyl)-8a-methyl-9-(1*H*-pyrrol-1-yl)-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (41). White solid (22 mg, 70% yield); m.p. = 162.3−164.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, J = 10.0, 2.0 Hz, 1H), 6.56 (t, J = 2.4 Hz, 2H), 6.34 (dd, J = 10.0, 1.2 Hz, 1H), 6.16–6.13 (m, 2H), 4.37 (dd, J = 4.0, 2.0 Hz, 1H), 3.82 (d, J = 10.8 Hz, 1H), 3.56 (d, J = 10.8 Hz, 1H), 3.34–3.31 (m, 1H), 2.80 (dd, J = 14.4, 7.2 Hz, 1H), 1.47 (s, 9H), 1.35 (d, J = 14.8 Hz, 1H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 177.5, 148.3, 132.1, 121.1, 108.9, 67.3, 57.8, 54.5, 54.3, 52.5, 47.5, 33.5, 27.7, 20.0; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{19}H_{25}N_2O_2^+$: 313.1911, Found: 313.1908.

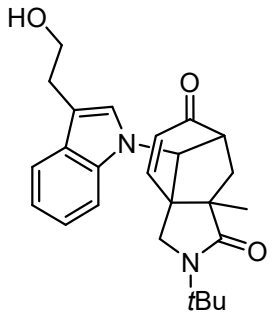


2-(*tert*-Butyl)-9-(1*H*-indol-1-yl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (42). White solid (30 mg, 83% yield); m.p. =

229.2−231.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.24–7.20 (m, 1H), 7.15–7.11 (m, 1H), 6.99 (d, J = 3.2 Hz, 1H), 6.88 (dd, J = 10.0, 2.0 Hz, 1H), 6.50–6.45 (m, 2H), 4.90 (dd, J = 4.0, 2.0 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 3.47 (d, J = 10.8 Hz, 1H), 3.38–3.35 (m, 1H), 2.92 (dd, J = 14.4, 7.2 Hz, 1H), 1.46 (s, 9H), 1.42 (d, J = 14.4 Hz, 1H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 178.1, 149.5, 137.5, 132.4, 128.0, 126.8, 121.9, 121.2, 120.3, 108.8, 102.7, 64.3, 57.6, 54.5, 54.2, 52.6, 47.6, 33.9, 27.6, 20.0; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{23}H_{27}BrN_2O_2^+$: 363.2067, Found: 363.2063.

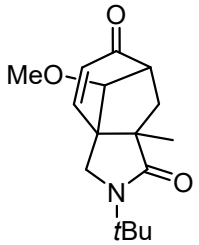


2-(*tert*-Butyl)-8a-methyl-9-(1*H*-pyrrolo[2,3-*c*]pyridin-1-yl)-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (43). White solid (35 mg, 96% yield); m.p. = 211.7−213.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.21 (d, J = 5.6 Hz, 1H), 7.43 (dd, J = 5.6, 1.2 Hz, 1H), 7.08 (d, J = 3.2 Hz, 1H), 6.83 (dd, J = 10.0, 2.0 Hz, 1H), 6.43–6.40 (m, 2H), 4.94 (dd, J = 4.0, 1.6 Hz, 1H), 3.59 (d, J = 11.2 Hz, 1H), 3.45 (d, J = 11.2 Hz, 1H), 3.35–3.31 (m, 1H), 2.88 (dd, J = 14.4, 7.2 Hz, 1H), 1.41 (s, 9H), 1.37 (d, J = 14.4 Hz, 1H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 177.8, 149.2, 139.5, 134.7, 132.9, 132.5, 131.9, 130.2, 115.4, 102.3, 64.4, 57.7, 54.7, 54.3, 52.6, 47.5, 33.7, 27.6, 19.9; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{22}H_{26}N_3O_2^+$: 364.2020, Found: 364.2017.

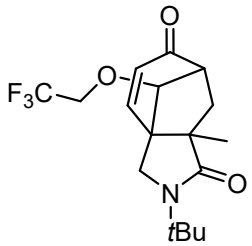


2-(*tert*-Butyl)-9-(3-(2-hydroxyethyl)-1*H*-indol-1-yl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (44). White solid (26 mg, 64% yield); m.p. = 212.9−214.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.18–7.14 (m, 1H), 7.09–7.05 (m, 1H), 6.81 (dd, J = 10.0, 1.6 Hz, 1H), 6.79 (s, 1H), 6.40 (dd, J = 10.0, 1.6 Hz, 1H), 4.79 (dd, J = 4.0, 1.6 Hz, 1H), 3.76 (t, J = 6.4 Hz, 2H), 3.58 (d, J = 10.8 Hz, 1H), 3.40 (d, J = 10.8 Hz, 1H), 3.28–3.25 (m, 1H), 2.88–2.81 (m, 3H), 1.39 (s, 9H), 1.33 (d, J = 14.8 Hz, 1H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 178.1, 149.6, 138.0, 132.5, 127.6, 125.0, 122.2, 120.0, 119.4, 112.7, 108.9, 64.3, 62.6, 57.6,

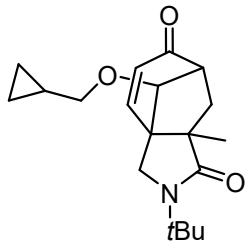
54.5, 54.2, 52.5, 47.6, 33.9, 28.6, 27.6, 20.0; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{22}H_{25}BrN_3O_2^+$: 442.1125, Found: 442.1126.



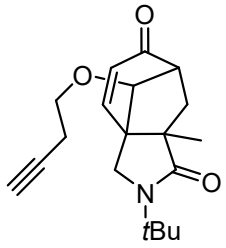
2-(*tert*-Butyl)-9-methoxy-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (45). White solid (22 mg, 79% yield); m.p. = 106.4−108.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, J = 10.0, 1.8 Hz, 1H), 6.25 (dd, J = 10.0, 1.8 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 3.60 (dd, J = 4.4, 2.0 Hz, 1H), 3.49 (d, J = 10.4 Hz, 1H), 3.35 (s, 3H), 3.16–3.12 (m, 1H), 2.58 (dd, J = 14.8, 7.2 Hz, 1H), 1.43 (s, 9H), 1.31 (d, J = 14.8 Hz, 1H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 177.9, 148.1, 131.5, 88.4, 58.2, 55.4, 54.0, 51.9, 51.7, 47.3, 32.2, 27.5, 19.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{24}NO_3^+$: 278.1751, Found: 278.1749.



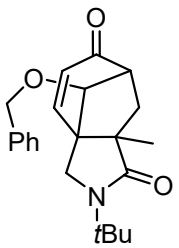
2-(*tert*-Butyl)-8a-methyl-9-(2,2,2-trifluoroethoxy)-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (46). White solid (16 mg, 46% yield); m.p. = 106.4−108.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, J = 10.0, 1.8 Hz, 1H), 6.26 (dd, J = 10.0, 1.8 Hz, 1H), 3.98–3.88 (m, 2H), 3.78–3.68 (m, 2H), 3.50 (d, J = 10.8 Hz, 1H), 3.09–3.05 (m, 1H), 2.59 (dd, J = 14.8, 6.8 Hz, 1H), 1.42 (s, 9H), 1.33 (d, J = 14.8 Hz, 1H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 177.5, 147.6, 131.5, 123.7 (q, $J_{C–F}$ = 279.9 Hz), 87.8, 67.1 (q, $J_{C–F}$ = 34.4 Hz), 55.2, 54.2, 51.9 (2C), 47.0, 32.1, 27.4, 19.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –74.2; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{23}F_3NO_3^+$: 346.1625, Found: 346.1622.



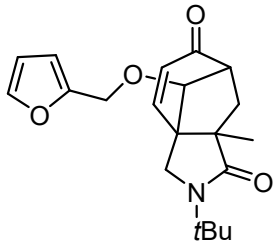
2-(*tert*-Butyl)-9-(cyclopropylmethoxy)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (47). White solid (22 mg, 69% yield); m.p. = 58.2−60.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (dd, J = 9.6, 2.0 Hz, 1H), 6.09 (dd, J = 9.6, 1.6 Hz, 1H), 3.60 (dd, J = 4.4, 2.0 Hz, 1H), 3.53 (d, J = 10.4 Hz, 1H), 3.33 (d, J = 10.4 Hz, 1H), 3.19–3.07 (m, 2H), 2.94–2.91 (m, 1H), 2.41 (dd, J = 14.8, 7.2 Hz, 1H), 1.26 (s, 9H), 1.14 (d, J = 14.4 Hz, 1H), 0.90 (s, 3H), 0.85–0.78 (m, 1H), 0.41–0.31 (m, 2H), 0.04 – –0.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 178.0, 148.3, 131.5, 86.2, 74.9, 55.3, 54.0, 52.3, 52.0, 47.4, 32.3, 27.5, 19.8, 10.5, 3.3, 2.9; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{19}H_{28}NO_3^+$: 318.2064, Found: 318.2069.



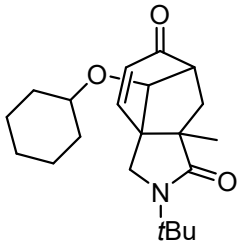
9-(But-3-yn-1-yloxy)-2-(*tert*-butyl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (48). Colorless oil (26 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, J = 9.6, 2.0 Hz, 1H), 6.24 (dd, J = 9.6, 1.6 Hz, 1H), 3.75 (dd, J = 4.4, 2.0 Hz, 1H), 3.72 (d, J = 10.4 Hz, 1H), 3.68–3.64 (m, 1H), 3.51–3.45 (m, 2H), 3.10–3.07 (m, 1H), 2.58 (dd, J = 14.4, 7.2 Hz, 1H), 2.41–2.37 (m, 2H), 1.97 (t, J = 2.8 Hz, 1H), 1.43 (s, 9H), 1.30 (d, J = 14.8 Hz, 1H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 177.9, 148.1, 131.5, 86.8, 80.8, 69.6, 68.2, 55.3, 54.0, 52.2, 51.9, 47.3, 32.3, 27.5, 19.8 (2C); HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{19}H_{26}NO_3^+$: 316.1907, Found: 316.1914.



9-(Benzyloxy)-2-(*tert*-butyl)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (49). White solid (30 mg, 85% yield); m.p. = 93.8−95.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 3H), 7.27–7.25 (m, 2H), 6.79 (dd, J = 10.0, 2.0 Hz, 1H), 6.29 (dd, J = 10.0, 1.6 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.33 (d, J = 12.4 Hz, 1H), 3.72 (dd, J = 4.4, 2.0 Hz, 1H), 3.52 (d, J = 10.4 Hz, 1H), 3.41 (d, J = 10.4 Hz, 1H), 3.12–3.08 (m, 1H), 2.52 (dd, J = 14.4, 7.2 Hz, 1H), 1.29 (d, J = 14.8 Hz, 1H), 1.23 (s, 9H), 1.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 177.8, 148.3, 137.1, 131.5, 128.6, 128.2, 128.1, 84.8, 71.7, 55.3, 53.8, 51.8, 47.2, 32.2, 27.2, 19.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{22}H_{28}NO_3^+$: 354.2064, Found: 354.2068.



2-(*tert*-Butyl)-9-(furan-2-ylmethoxy)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta [*c*]pyrrole-1,6(7*H*)-dione (50). White solid (22 mg, 64% yield); m.p. = 144.9−147.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.33 (m, 1H), 6.69 (dd, J = 9.6, 2.0 Hz, 1H), 6.27 (dd, J = 3.2, 2.0 Hz, 1H), 6.23 (d, J = 3.2 Hz, 1H), 6.19 (dd, J = 9.6, 1.6 Hz, 1H), 4.49 (d, J = 13.6 Hz, 1H), 4.28 (d, J = 13.6 Hz, 1H), 3.68 (dd, J = 4.4, 2.0 Hz, 1H), 3.43 (d, J = 10.4 Hz, 1H), 3.33 (d, J = 10.4 Hz, 1H), 2.98–2.94 (m, 1H), 2.48 (dd, J = 14.8, 7.2 Hz, 1H), 1.24 (s, 9H), 1.20 (d, J = 2.4 Hz, 1H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 177.8, 150.7, 148.1, 143.2, 131.5, 110.5, 110.2, 84.8, 63.5, 55.2, 53.9, 51.8 (2C), 47.1, 32.3, 27.3, 19.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{20}H_{26}BrNO_4^+$: 344.1856, Found: 344.1853.

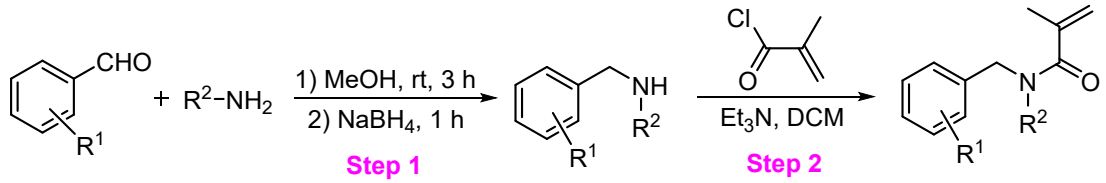


2-(*tert*-Butyl)-9-(cyclohexyloxy)-8a-methyl-2,3,8,8a-tetrahydro-1*H*-3a,7-methanocyclohepta[*c*]pyrrole-1,6(7*H*)-dione (51). White solid (24 mg, 69% yield); m.p. = 119.7−122.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (dd, J = 10.0, 2.0 Hz, 1H), 6.17 (dd, J = 10.0, 1.6 Hz, 1H), 3.72 (dd, J = 4.4, 2.0 Hz, 1H), 3.55 (d, J = 10.4 Hz, 1H), 3.40 (d, J = 10.4 Hz, 1H), 3.20–3.14 (m, 1H), 2.96–2.93 (m, 1H), 2.49 (dd, J = 14.8, 7.2 Hz, 1H), 1.64–1.58 (m, 4H), 1.35 (s, 9H), 1.23–1.10 (m, 7H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5,

178.1, 148.3, 131.6, 84.4, 55.2, 54.0, 53.0, 51.9, 47.3, 33.2, 32.3, 31.9, 27.6, 25.5, 24.0, 23.9, 19.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{21}H_{32}BrNO_3^+$: 346.2377, Found: 346.2375.

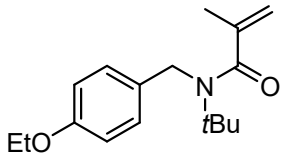
8. Synthesis of *N*-Benzylacrylamides

The substrates **1**[3], **4**[4], **6**[4] and **12**[3] have been reported.

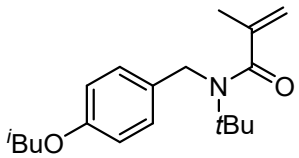


Step 1: To a solution of benzaldehyde (10 mmol) in methanol (20 mL) was added alkyl amine (1.0 equiv.), and then the resulting solution was stirred for 3 h at room temperature. Next, the mixture was added $NaBH_4$ (1.2 equiv.) at 0 °C, and then warmed to room temperature and continue to be stirred 1 h. After related work-up and purification by flash chromatography, the *N*-alkylbenzylamine was thereby obtained, which is used for next synthetic step.

Step 2: To a solution of *N*-alkylbenzylamine obtained above and Et_3N (1.5 equiv) in dry CH_2Cl_2 (15 mL) was added methacryloyl chloride (1.2 equiv.) at 0 °C. Then the resulting mixture was warmed to r.t. and continue to stir for overnight. After related work-up, the residue was purified by flash chromatography (petroleum ether/ethyl acetate as the eluent) on silica gel to afford the corresponding *N*-benzylacrylamide.

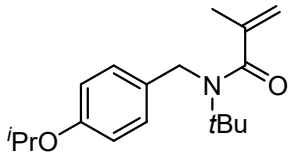


***N*-(*tert*-Butyl)-*N*-(4-ethoxybenzyl)methacrylamide (5).** Colorless oil (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.02–4.93 (m, 2H), 4.61 (s, 2H), 4.05–3.99 (m, 2H), 1.93 (s, 3H), 1.43–1.39 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 157.8, 143.1, 131.8, 127.1, 114.4, 113.3, 63.4, 57.5, 50.1, 28.5, 20.8, 14.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{26}NO_2^+$: 276.1958, Found: 276.1961.

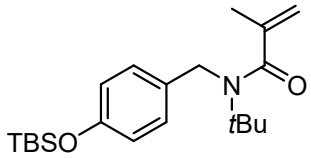


***N*-(*tert*-Butyl)-*N*-(4-*iso*-butoxybenzyl)methacrylamide (7).** White solid (61% yield); m.p. = 57.0−59.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz,

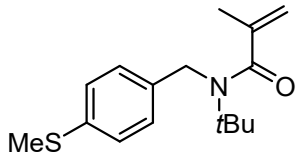
2H), 5.02–4.93 (m, 2H), 4.61 (s, 2H), 3.70 (d, J = 6.8 Hz, 2H), 2.11–2.04 (m, 1H), 1.94 (s, J = 1.4 Hz, 3H), 1.42 (s, 9H), 1.02 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 158.1, 143.0, 131.6, 127.0, 114.3, 113.2, 74.3, 57.4, 50.1, 28.5, 28.2, 20.8, 19.2; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{19}H_{30}NO_2^+$: 304.2271, Found: 304.2273.



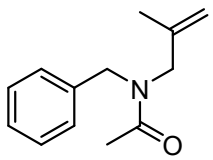
***N*-(*tert*-Butyl)-*N*-(4-*iso*-propoxybenzyl)methacrylamide (8).** Colorless oil (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.03–4.93 (m, 2H), 4.60 (s, 2H), 4.56–4.50 (m, 1H), 1.93 (s, 3H), 1.42 (s, 9H), 1.33 (d, J = 6.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 156.7, 143.1, 131.7, 127.2, 115.7, 113.3, 69.8, 57.5, 50.2, 28.5, 22.0, 20.8; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{28}NO_2^+$: 290.2115, Found: 290.2117.



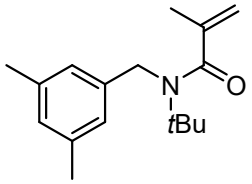
***N*-(*tert*-Butyl)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)benzyl)methacrylamide (9).** White solid (24% yield); m.p. = 65.0−66.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 4.83–4.75 (m, 2H), 4.41 (s, 2H), 1.73 (s, 3H), 1.22 (s, 9H), 0.79 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 154.5, 143.1, 132.6, 127.2, 120.0, 113.4, 57.5, 50.3, 28.6, 25.6, 20.8, 18.1, –4.5; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{21}H_{36}NO_2Si^+$: 362.2510, Found: 362.2511.



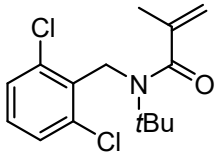
***N*-(*tert*-Butyl)-*N*-(4-(methylthio)benzyl)methacrylamide (10).** White solid (89% yield); m.p. = 98.1−100.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.01 (s, 1H), 4.93 (s, 1H), 4.63 (s, 2H), 2.48 (s, 3H), 1.93 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 143.0, 137.0, 136.8, 126.6, 113.3, 57.6, 50.3, 28.5, 20.8, 15.8; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{24}NOS^+$: 278.1573, Found: 278.1572.



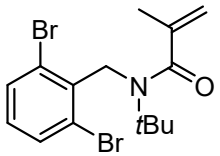
***N*-Benzyl-*N*-(2-methylallyl)acetamide (14).** Colorless oil (67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 3H), 7.26–7.16 (m, 2H), 4.97–4.89 (m, 1H), 4.83–4.73 (m, 1H), 4.58–4.49 (m, 2H), 3.98–3.70 (m, 2H), 2.18–2.14 (m, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.9, 140.4, 139.5, 137.5, 136.5, 128.8, 128.5, 128.1, 127.5, 127.2, 126.2, 112.2, 111.3, 52.9, 50.4, 50.2, 48.0, 21.5, 21.3, 20.0 (2C); HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{13}H_{18}NO^+$: 204.1383, Found: 204.1384.



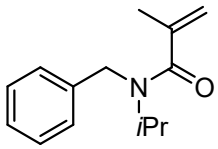
***N*-(*tert*-Butyl)-*N*-(3,5-dimethylbenzyl)methacrylamide (S1).** White solid (63% yield); m.p. = 90.8−92.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.82 (s, 2H), 5.02 (s, 1H), 4.92 (s, 1H), 4.61 (s, 2H), 2.30 (s, 6H), 1.94 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 143.0, 140.0, 138.0, 128.4, 123.8, 113.2, 57.6, 50.6, 28.5, 21.3, 20.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{26}NO^+$: 260.2009, Found: 260.2011.



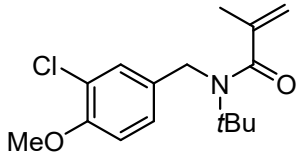
***N*-(*tert*-Butyl)-*N*-(2,6-dichlorobenzyl)methacrylamide (S2).** White solid (55% yield); m.p. = 74.1−76.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 5.22 (s, 1H), 5.20 (s, 1H) 5.01 (s, 2H), 1.95 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 143.4, 135.8, 133.9, 129.2, 128.8, 116.5, 57.6, 48.2, 28.4, 19.5; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{20}Cl_2NO^+$: 300.0916, Found: 300.0919.



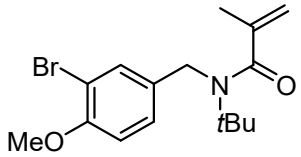
***N*-(*tert*-Butyl)-*N*-(2,6-dibromobenzyl)methacrylamide (S3).** White solid (61% yield); m.p. = 108.3−110.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 2H), 6.97 (t, J = 7.8 Hz, 1H), 5.23–5.21 (m, 2H), 5.00 (s, 2H), 1.95 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 143.4, 136.3, 133.4, 129.6, 125.7, 116.8, 58.0, 53.1, 28.7, 19.6; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{20}Br_2NO^+$: 387.9906, Found: 387.9907.



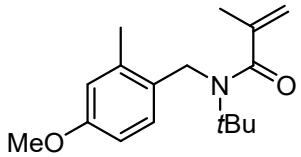
***N*-Benzyl-*N*-*iso*-propylmethacrylamide (S4).** Colorless oil (58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5H), 5.15–5.09 (m, 2H), 4.56 (s, 2H), 4.35 (s, 1H), 2.03–1.98 (m, 3H), 1.13 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 141.5, 139.2, 128.3, 126.8, 114.0, 50.1, 42.8, 21.5, 20.7; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_{20}NO^+$: 218.1539, Found: 218.1541.



***N*-(*tert*-Butyl)-*N*-(3-chloro-4-methoxybenzyl)methacrylamide (S5).** White solid (77% yield); m.p. = 80.2−82.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 2.0 Hz, 1H), 7.11 (dd, J = 8.4, 2.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 5.01 (s, 1H), 4.94(s, 1H), 4.60 (s, 2H), 3.89 (s, 3H), 1.94 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 153.6, 142.8, 133.0, 127.6, 125.1, 122.3, 113.2, 111.8, 57.4, 55.9, 49.5, 28.4, 20.6; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{23}ClNO_2^+$: 296.1412, Found: 296.1414.

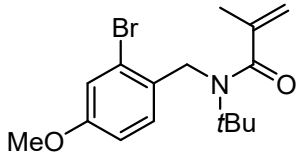


***N*-(3-Bromo-4-methoxybenzyl)-*N*-(*tert*-butyl)methacrylamide (S6).** White solid (72% yield); m.p. = 90.4−92.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, J = 2.4 Hz, 1H), 7.14 (dd, J = 8.4, 2.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 4.59 (s, 2H), 3.89 (s, 3H), 1.93 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 154.8, 143.0, 133.6, 130.9, 126.0, 113.4, 111.8, 111.7, 57.6, 56.2, 49.5, 28.6, 20.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{23}BrNO^+$: 340.0907, Found: 340.0910.

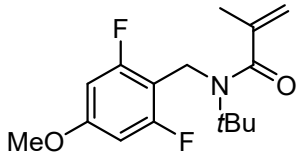


***N*-(*tert*-Butyl)-*N*-(4-methoxy-2-methylbenzyl)methacrylamide (S7).** White solid (64% yield); m.p. = 63.7−66.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, J = 8.4, 2.0 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 5.03–4.92 (m, 2H), 4.58 (s, 2H), 3.82 (s, 3H), 2.20 (s, 3H), 1.94 (t, J = 1.2 Hz, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6,

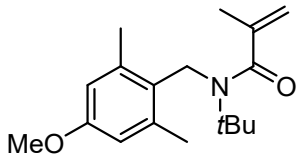
156.6, 143.2, 131.5, 128.4, 126.7, 124.4, 113.2, 109.7, 57.5, 55.3, 50.2, 28.6, 20.9, 16.3; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{17}H_{26}NO_2^+$: 276.1958, Found: 276.1960.



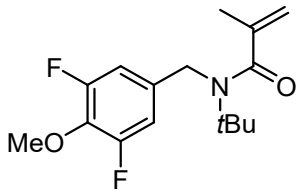
***N*-(2-Bromo-4-methoxybenzyl)-*N*-(*tert*-butyl)methacrylamide (S8).** White solid (69% yield); m.p. = 97.2−99.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 8.4, 2.4 Hz, 1H), 4.92–4.87 (m, 2H), 4.56 (s, 2H), 3.80 (s, 3H), 1.92 (t, J = 1.2 Hz, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 158.9, 142.7, 130.6, 128.5, 121.5, 118.1, 113.2, 113.0, 57.7, 55.5, 50.4, 28.4, 20.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{23}BrNO_2^+$: 340.0907, Found: 340.0910.



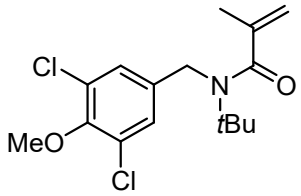
***N*-(*tert*-Butyl)-*N*-(2,6-difluoro-4-methoxybenzyl)methacrylamide (S9).** White solid (65% yield); m.p. = 74.8−76.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 6.42 (s, 1H), 5.17–5.13 (m, 1H), 4.75 (s, 2H), 3.78 (s, 3H), 1.97 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 161.6 (dd, $J_{C–F}$ = 246.7, 11.6 Hz),160.2 (t, $J_{C–F}$ = 14.5 Hz), 143.4, 115.4, 107.1 (t, $J_{C–F}$ = 17.0 Hz), 98.1 (d, $J_{C–F}$ = 13.2, 8.3 Hz), 56.8, 55.6, 40.3 (t, $J_{C–F}$ = 2.9 Hz), 28.2, 19.8 (t, $J_{C–F}$ = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.9, –113.0; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{22}F_2NO_2^+$: 298.1613, Found: 298.1614.



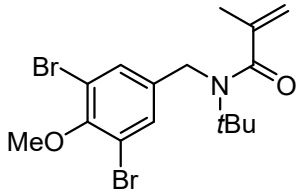
***N*-(*tert*-Butyl)-*N*-(4-methoxy-2,6-dimethylbenzyl)methacrylamide (S10).** White solid (56% yield); m.p. = 78.2−80.9 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 2H), 5.18–5.12 (m, 2H), 4.61 (s, 2H), 3.76 (s, 3H), 2.30 (s, 6H), 1.75 (t, J = 1.2 Hz, 3H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 158.1, 144.0, 138.4, 127.7, 116.1, 114.3, 57.7, 55.0, 47.0, 28.4, 21.2, 19.1; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{18}H_{28}NO_2^+$: 290.2115, Found: 290.2116.



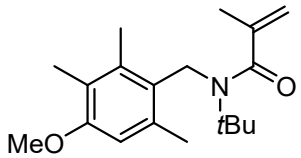
***N*-(*tert*-butyl)-*N*-(3,5-difluoro-4-methoxybenzyl)methacrylamide (S11).** White solid (70% yield); m.p. = 63.6−66.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.77 (s, 1H), 4.99–4.95 (m, 2H), 4.58 (s, 2H), 3.99 (s, 3H), 1.93 (t, J = 1.2 Hz, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 155.7 (dd, $J_{C–F}$ = 249.2, 6.4 Hz), 142.7, 135.8 (t, $J_{C–F}$ = 7.3 Hz), 135.0 (t, $J_{C–F}$ = 14.1 Hz), 113.6, 109.7 (dd, $J_{C–F}$ = 23.7, 10.1 Hz), 61.9 (t, $J_{C–F}$ = 3.2 Hz), 57.8, 49.7, 28.5, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –127.5 (2F); HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{22}F_2NO_2^+$: 298.1613, Found: 298.1615.



***N*-(*tert*-Butyl)-*N*-(3,5-dichloro-4-methoxybenzyl)methacrylamide (S12).** White solid (78% yield); m.p. = 93.0−95.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 4.99–4.95 (m, 2H), 4.57 (s, 2H), 3.90 (s, 3H), 1.93 (t, J = 1.2 Hz, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 151.1, 142.8, 137.8, 129.6, 126.3, 113.6, 60.7, 57.8, 49.5, 28.7, 20.8; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{22}Cl_2NO_2^+$: 330.1022, Found: 330.1024.



***N*-(*tert*-Butyl)-*N*-(3,5-dibromo-4-methoxybenzyl)methacrylamide (S13).** White solid (69% yield); m.p. = 57.5−60.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 4.99–4.95 (m, 2H), 4.59 (s, 2H), 3.89 (s, 3H), 1.94 (t, J = 1.2 Hz, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 152.9, 142.7, 138.9, 130.0, 118.3, 113.5, 60.6, 57.8, 49.2, 28.6, 20.7; HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{22}Br_2NO_2^+$: 418.0012, Found: 418.0014.



***N*-(*tert*-Butyl)-*N*-(4-methoxy-2,3,6-trimethylbenzyl)methacrylamide (S14).** White solid (52% yield); m.p. = 77.5−79.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55–6.49 (m, 1H), 5.17–5.10 (m, 2H), 4.65 (s, 2H), 3.79–3.78 (m, 3H), 2.37–2.31 (m, 3H), 2.28–2.21 (m, 3H), 2.12–2.11 (m, 3H), 1.73 (t, J = 1.2 Hz, 3H), 1.36–1.19 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 156.2, 156.0, 144.1, 137.0, 136.8, 134.8, 134.5, 129.4, 127.5, 123.2, 122.9, 115.9,

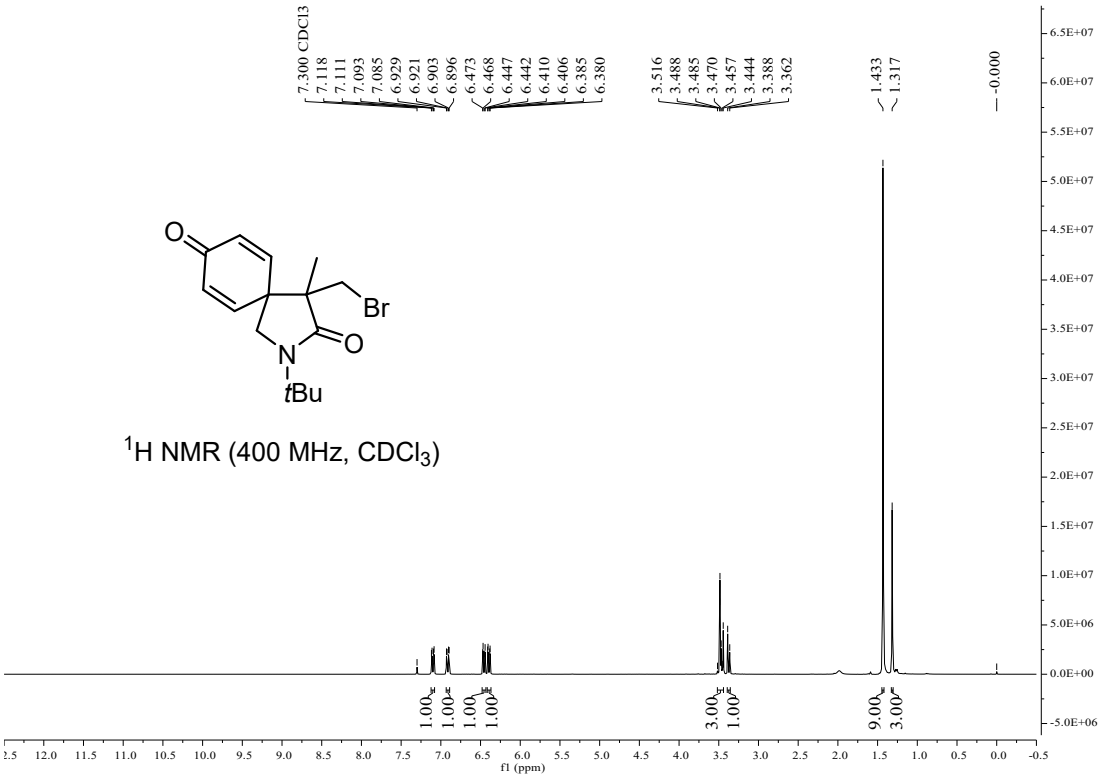
110.7, 110.3, 57.6, 55.5, 55.4, 50.4, 47.4, 40.7, 28.9, 28.5, 26.9, 21.4, 19.9, 19.0, 16.8, 15.4, 11.9, 11.8; HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{19}H_{30}NO_2^+$: 304.2271, Found: 304.2271.

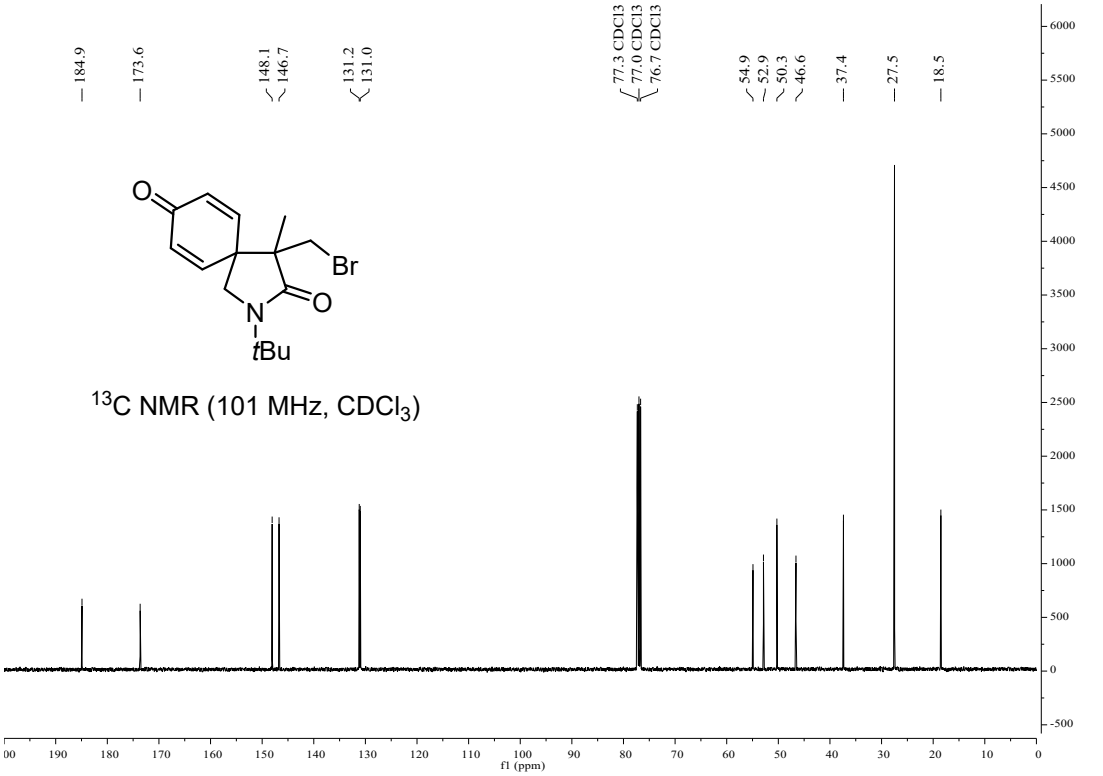
References

1. K. Yu, X. Kong, J. Yang, G. Li, B. Xu and Q. Chen, *J. Org. Chem.*, 2021, **86**, 917−928.
2. T. Liu, Y. Li, L. Jiang, J. Wang, K. Jin, R. Zhang and C. Duan, *Org. Biomol. Chem.*, 2020, **18**, 1933–1939.
3. L. Yuan, S. Jiang, Z. Li, Y. Zhu, J. Yu, L. Li, M. Li, S. Tang and R. Sheng, *Org. Biomol. Chem.*, 2018, **16**, 2406–2410.
4. Z. Zhang, X. Tang and W. R. Dolbier, Jr., *Org. Lett.*, 2016, **18**, 1048−1051.

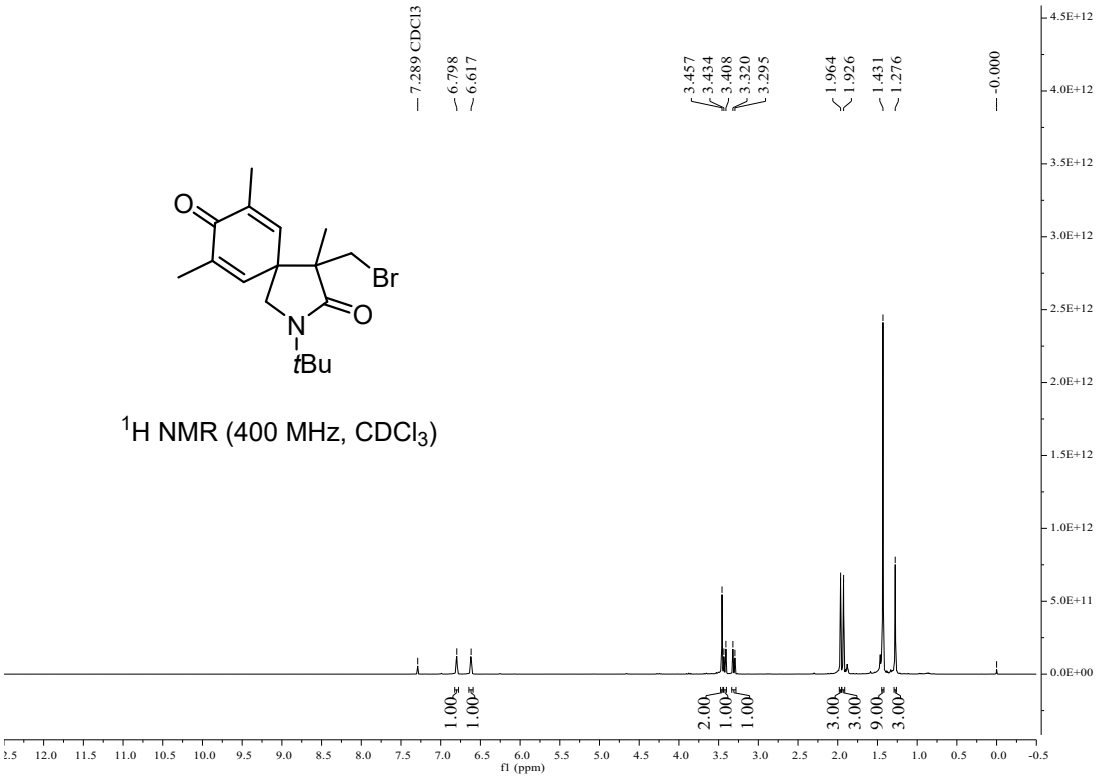
9. NMR Spectra for the Obtained Compounds

Compound 3

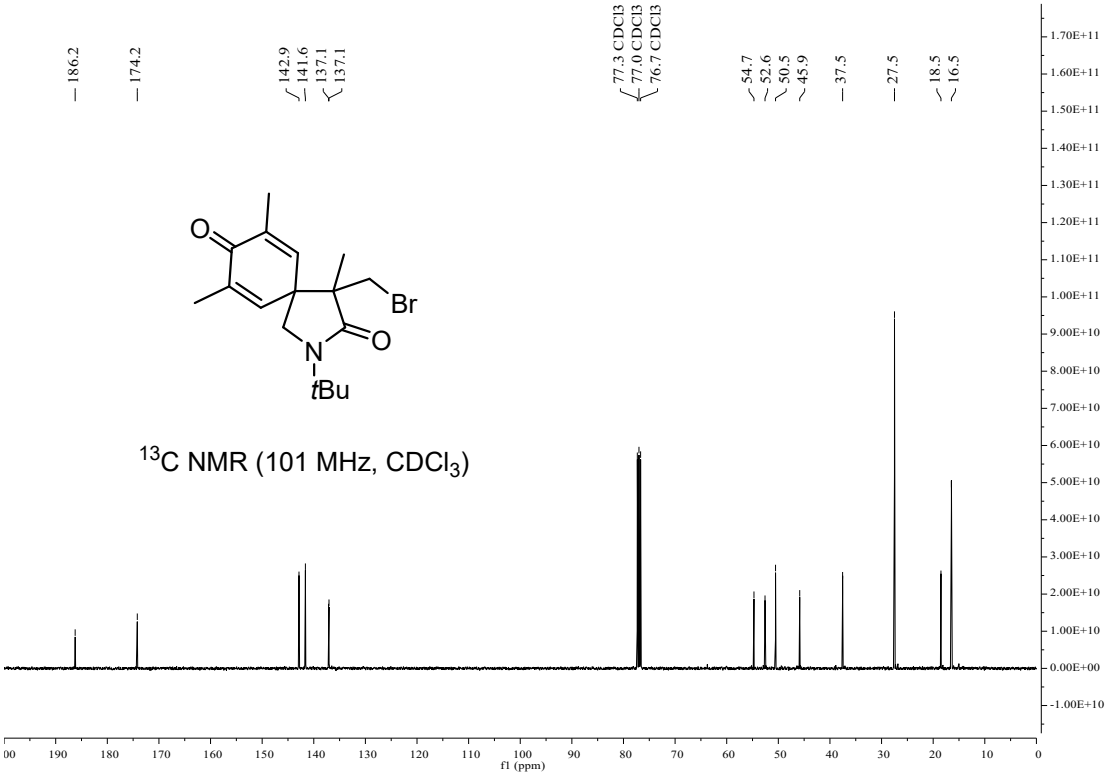




Compound 15

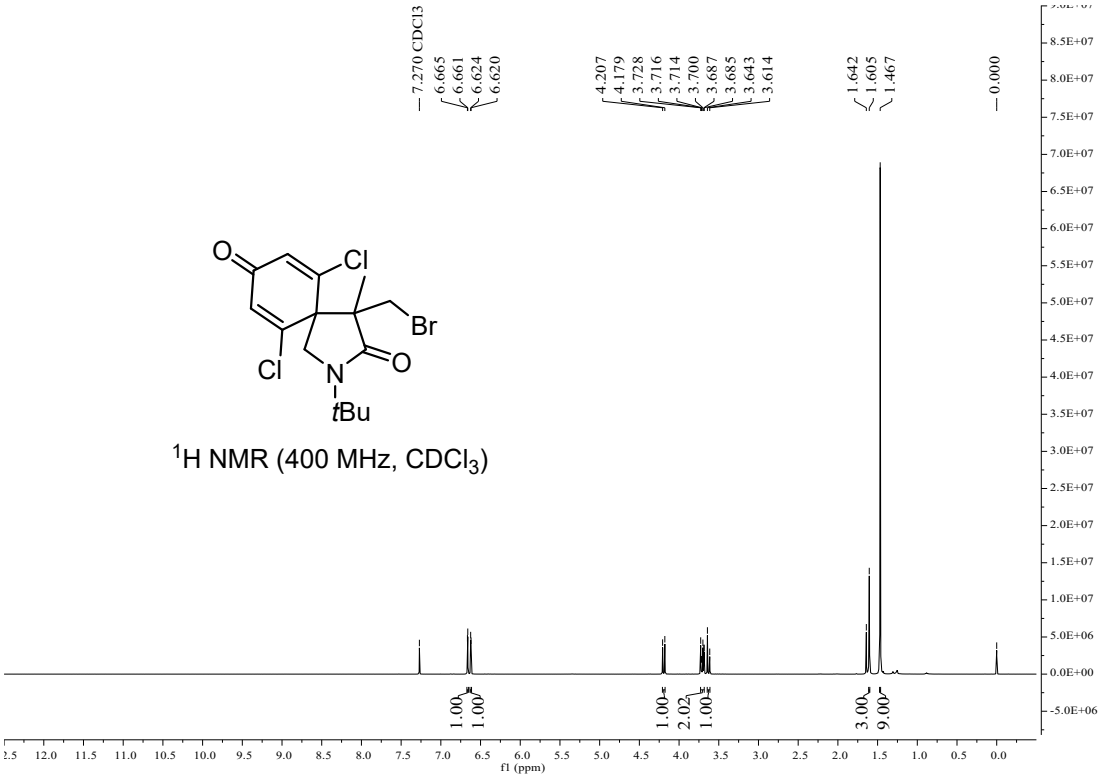


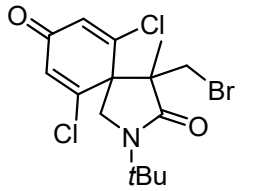
^{1}H NMR (400 MHz, $CDCl_3$)



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

Compound 16

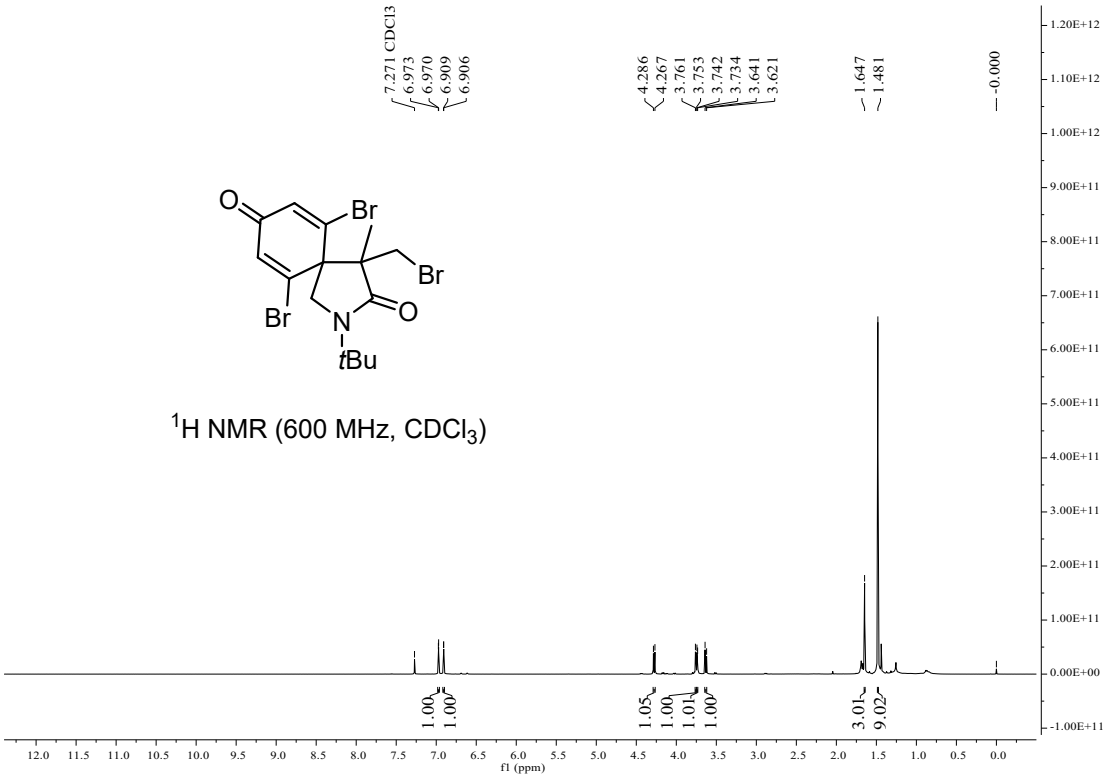




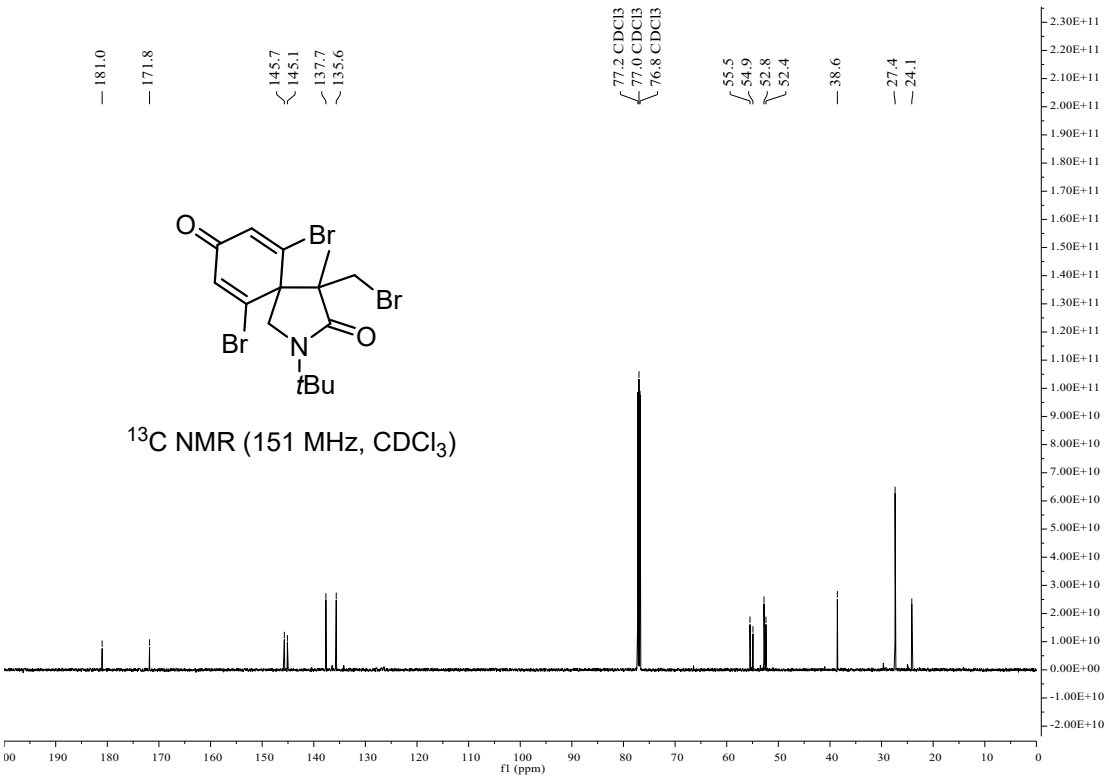
^{1}H NMR (400 MHz, $CDCl_3$)

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

Compound 17

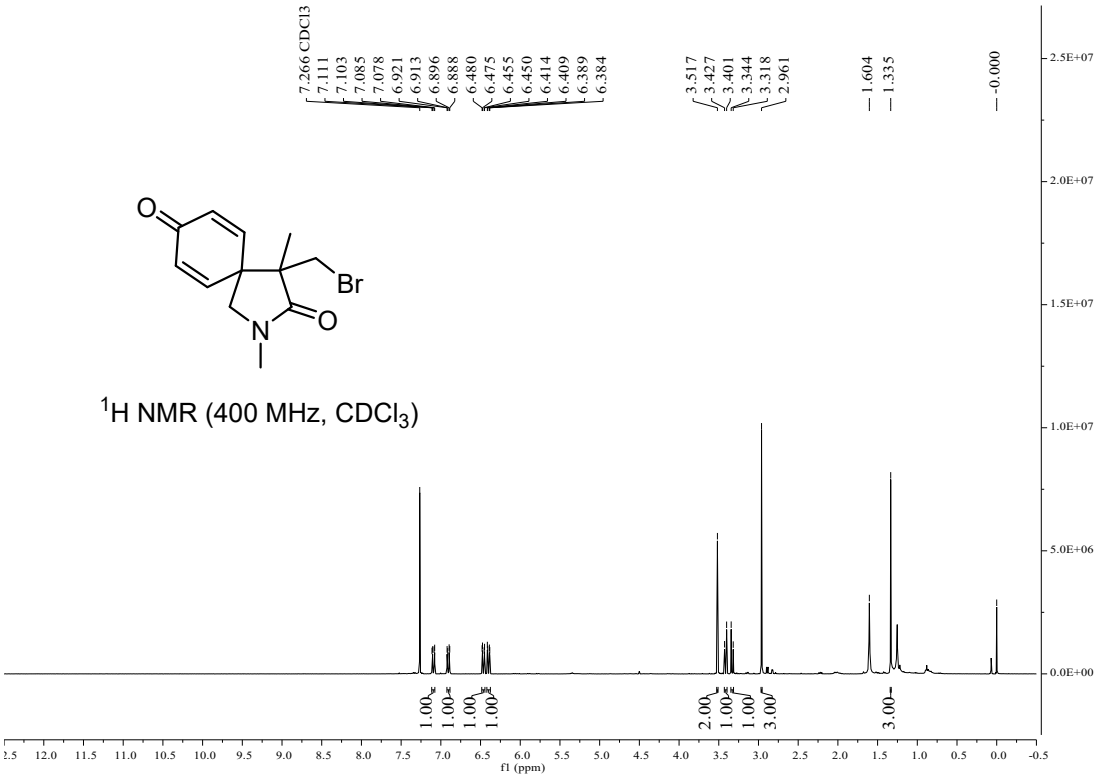


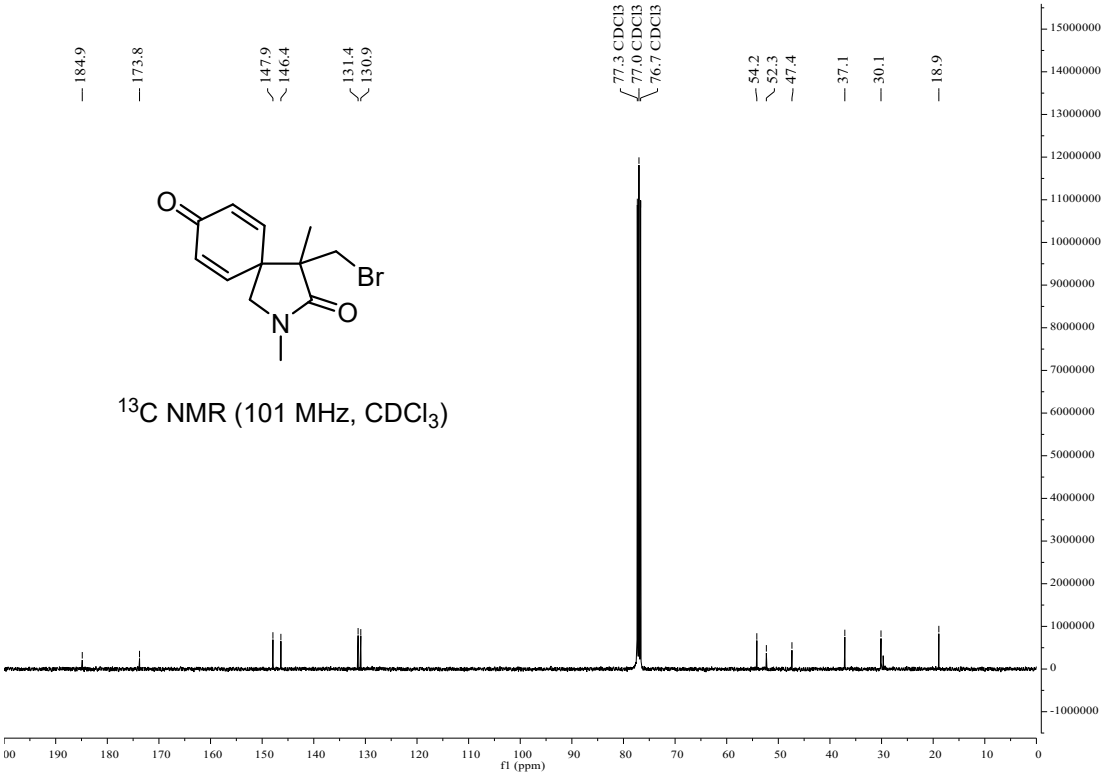
^{1}H NMR (600 MHz, $CDCl_3$)



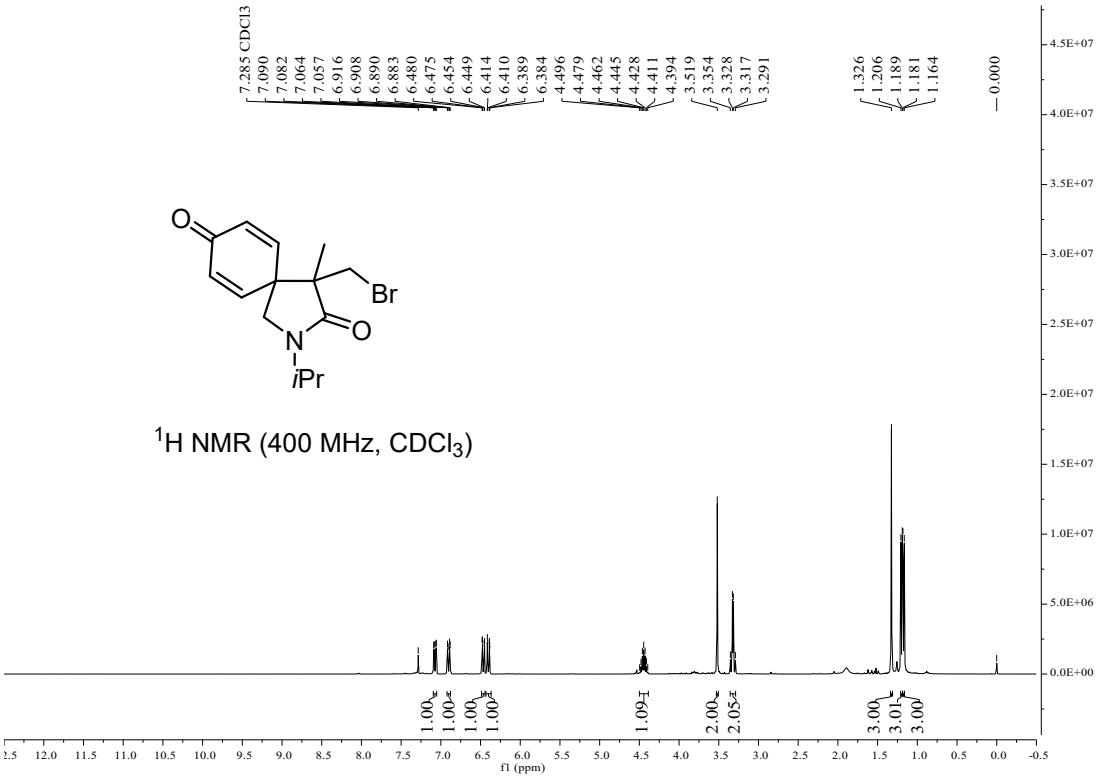
^{13}C NMR (151 MHz, $CDCl_3$)

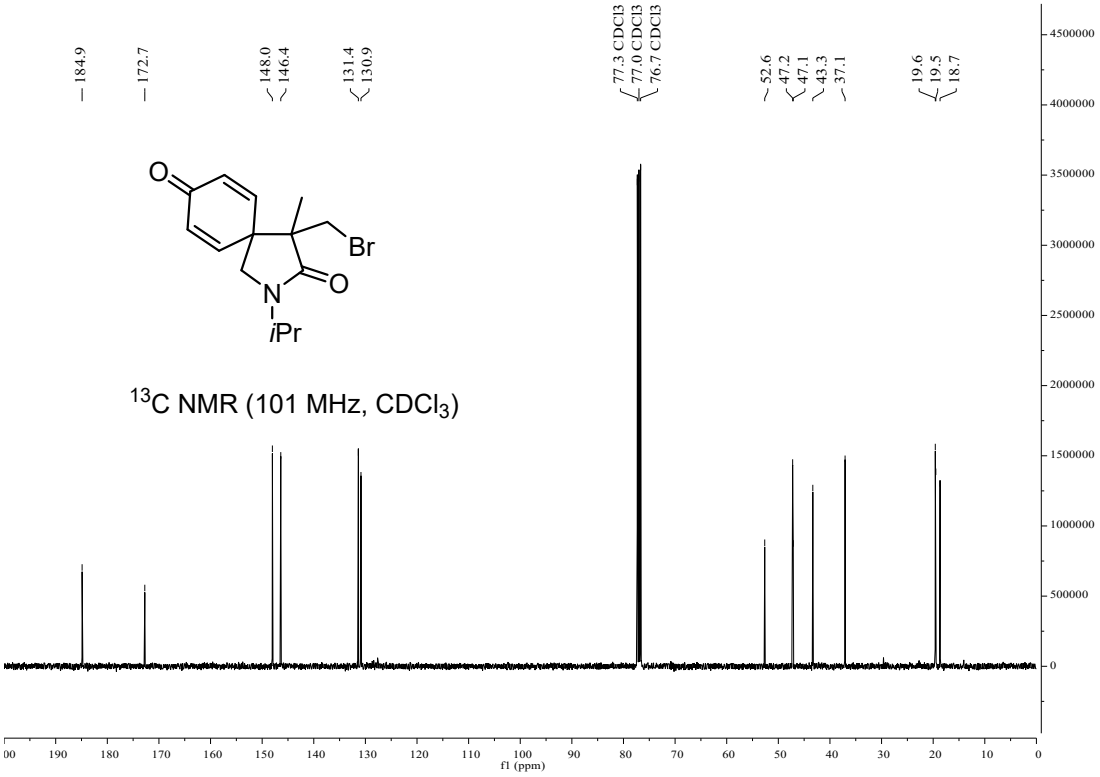
Compound 18


7.266 CDCl3
7.111
7.103
7.085
7.078
6.921
6.913
6.896
6.888
6.480
6.475
6.455
6.450
6.414
6.409
6.389
6.384
3.517
3.427
3.401
3.344
3.318
2.961
1.604
1.335
-0.000
O
Br
N
O
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

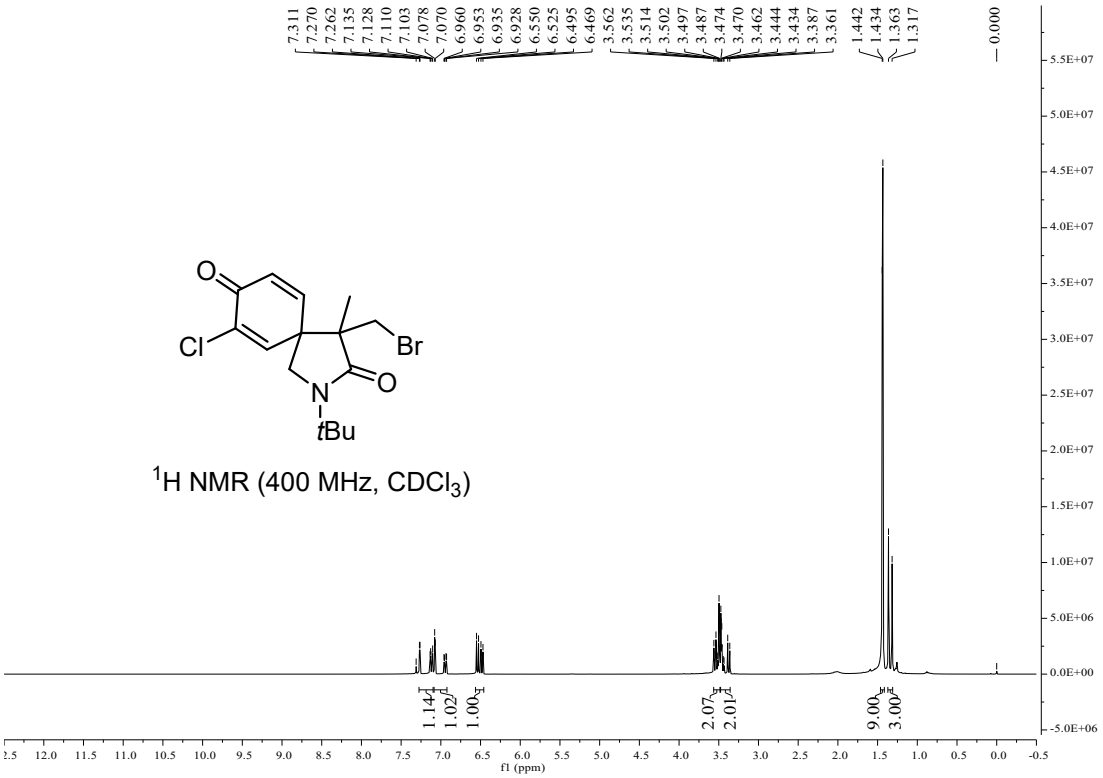

184.9
173.8
147.9
146.4
131.4
130.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
54.2
52.3
47.4
37.1
30.1
18.9
O
Br
N
O
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 19

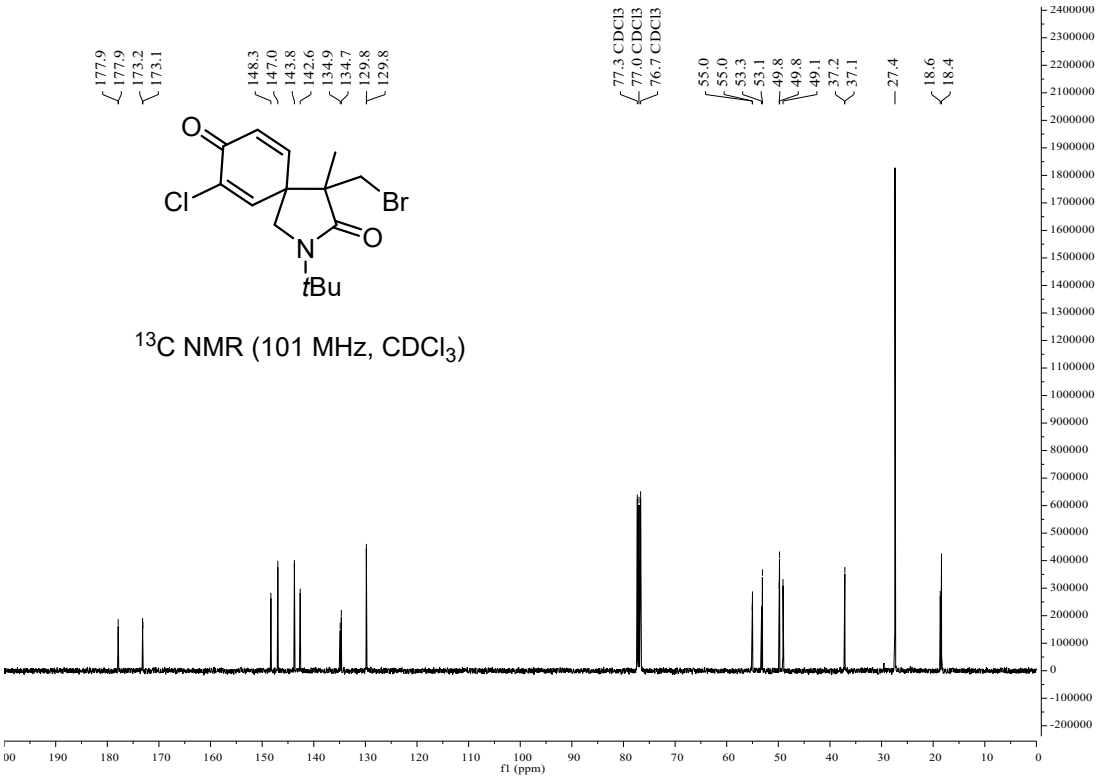

7.285 CDCl3
7.090
7.082
7.064
7.057
6.916
6.908
6.890
6.883
6.480
6.475
6.454
6.449
6.414
6.410
6.389
6.384
4.496
4.479
4.462
4.445
4.428
4.411
4.394
3.519
3.354
3.328
3.317
3.291
1.326
1.206
1.189
1.181
1.164
0.000
O
Br
O
N
iPr
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.09
2.00
2.05
3.00
3.01
3.00
f1 (ppm)


184.9
172.7
148.0
146.4
131.4
130.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
52.6
47.2
47.1
43.3
37.1
19.6
19.5
18.7
O
Br
O
N
iPr
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 20

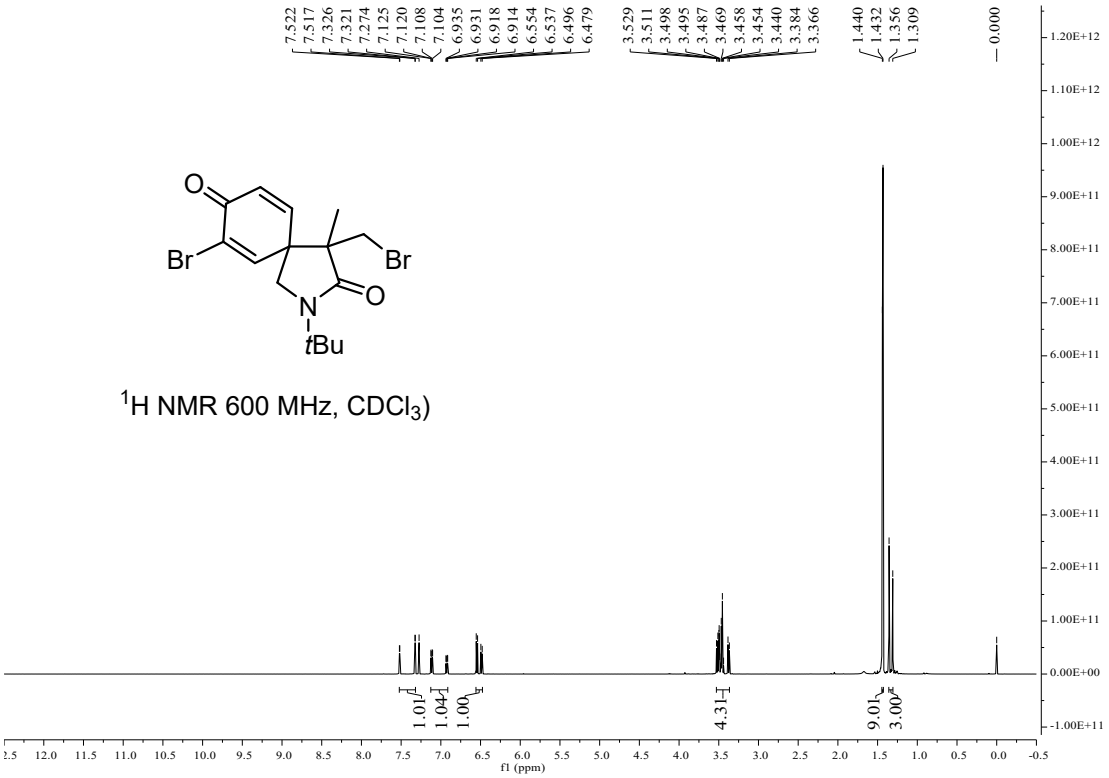


^{1}H NMR (400 MHz, $CDCl_3$)

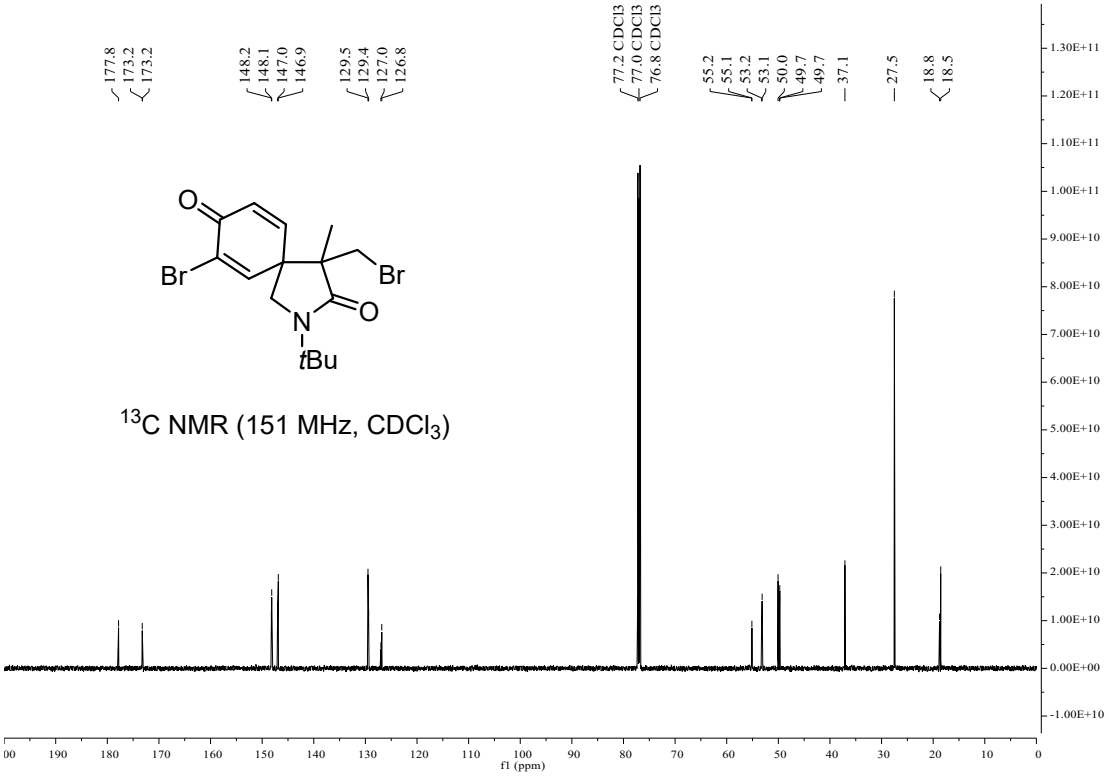


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 21

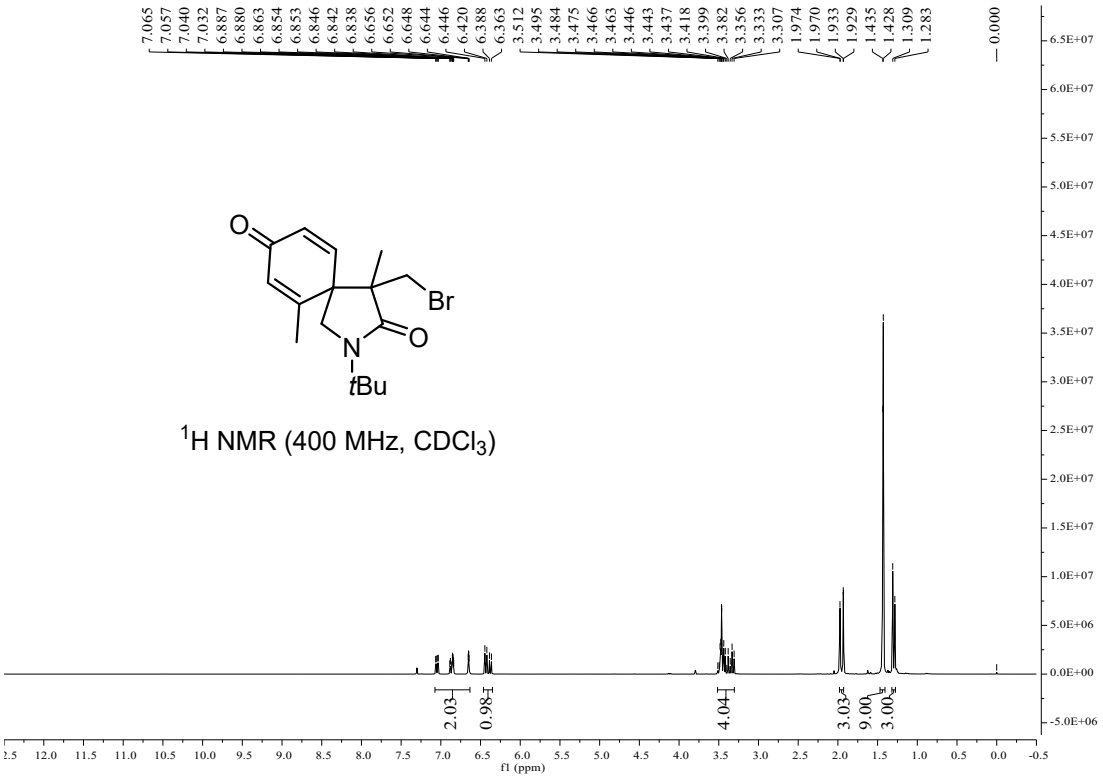


^{1}H NMR 600 MHz, $CDCl_3$)

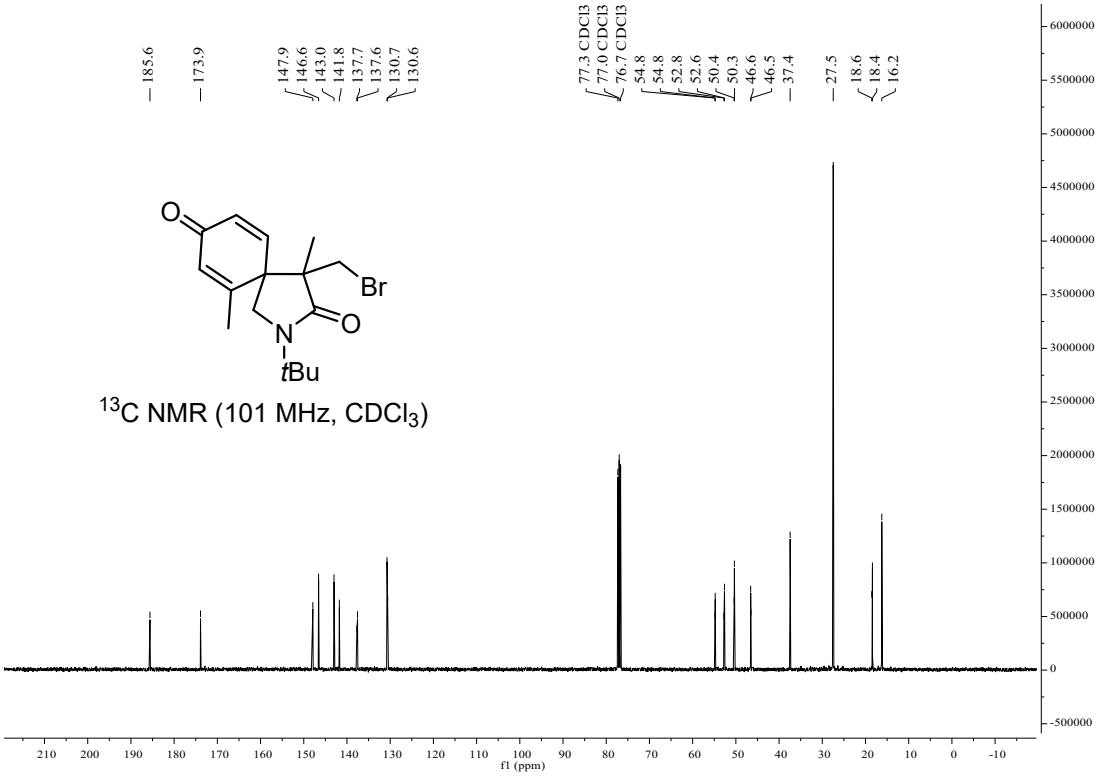


^{13}C NMR (151 MHz, $CDCl_3$)

Compound 22

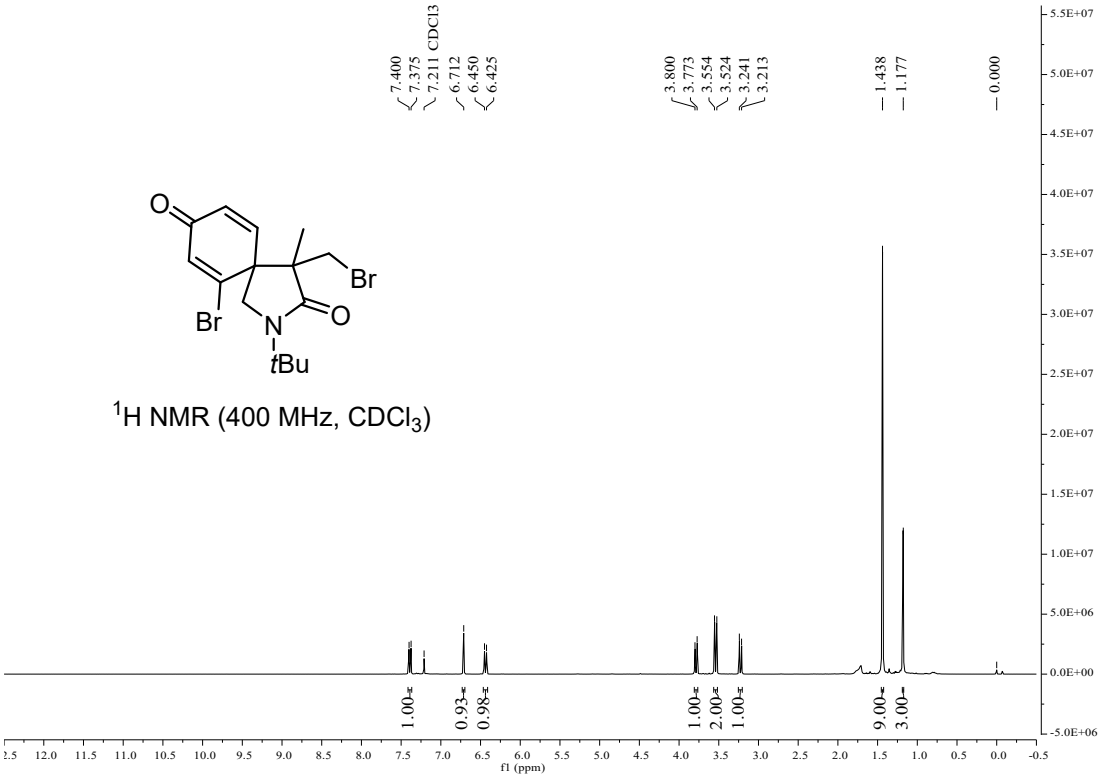


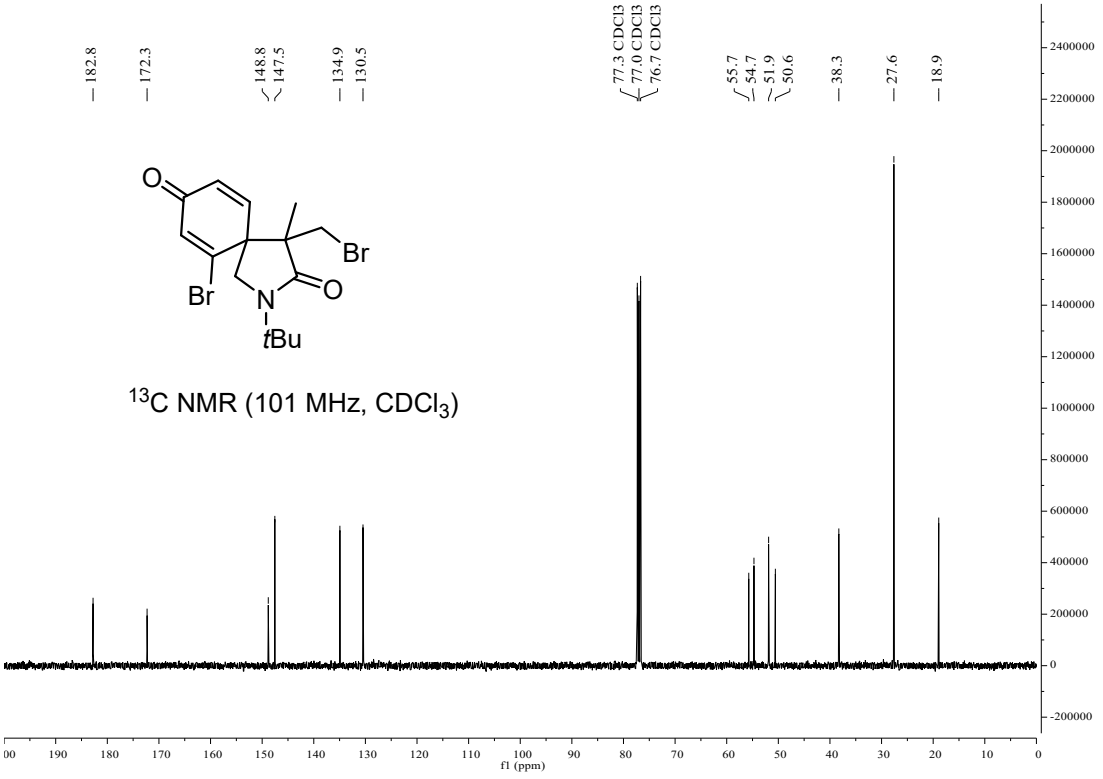
^{1}H NMR (400 MHz, $CDCl_3$)



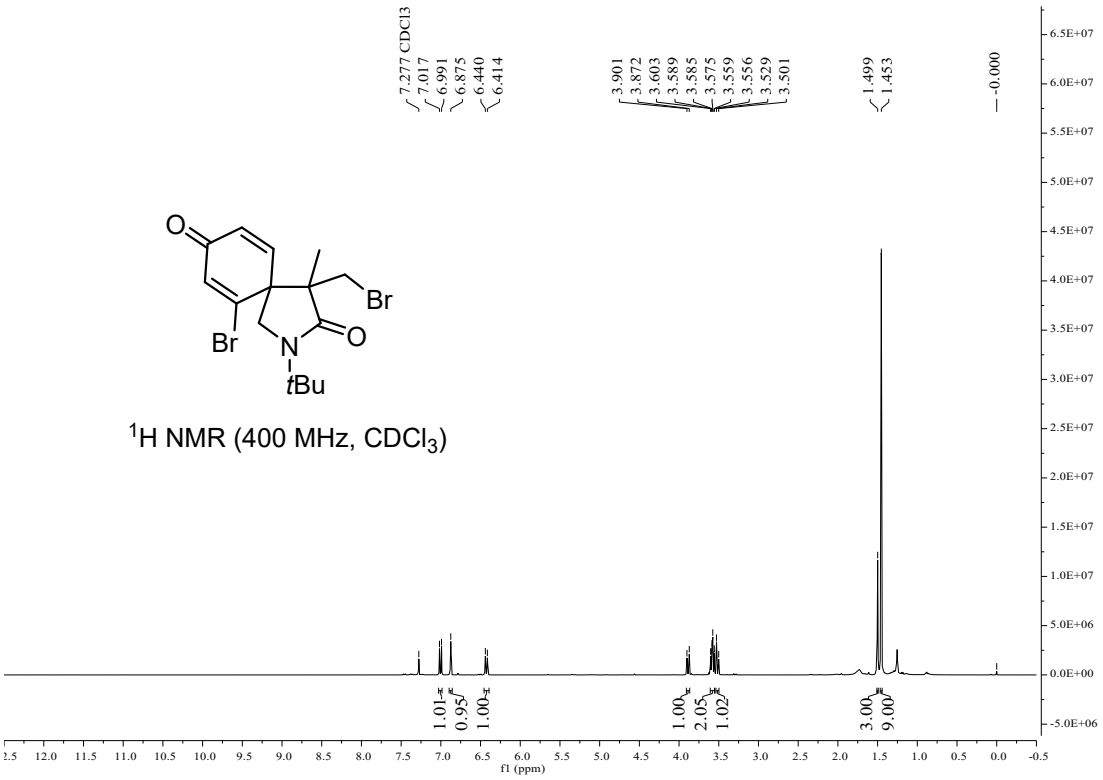
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 23

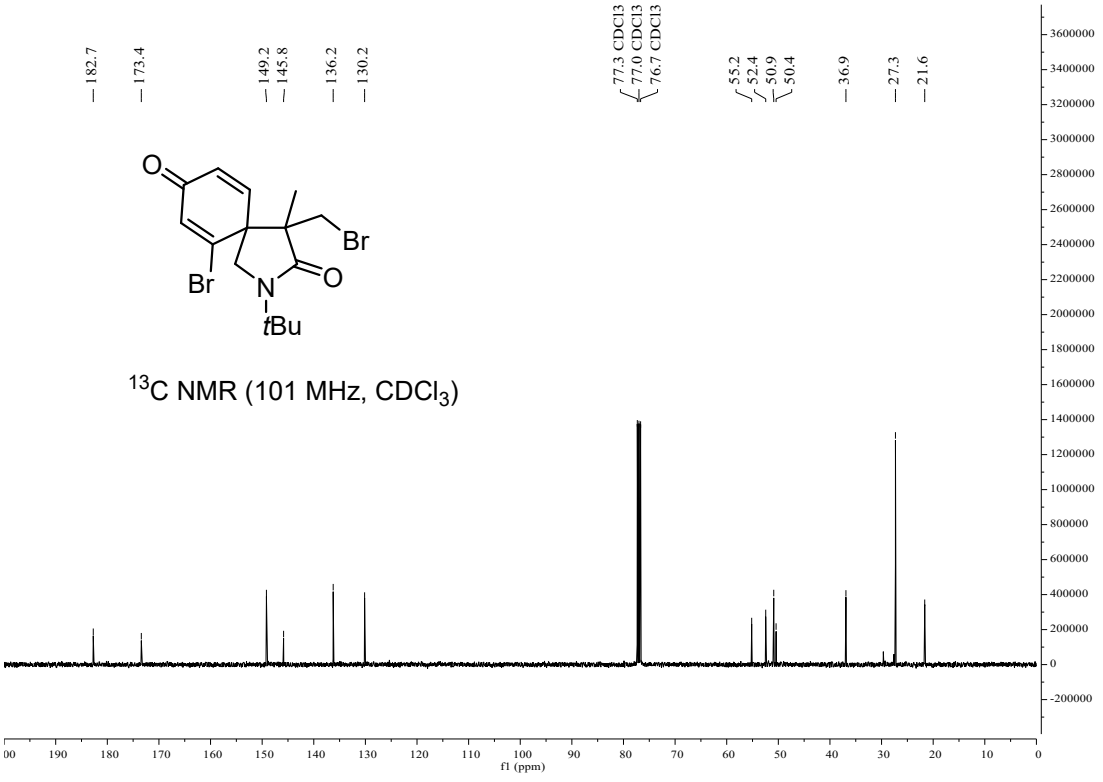

7.400
7.375
7.211 CDCl3
6.712
6.450
6.425
3.800
3.773
3.554
3.524
3.241
3.213
1.438
1.177
0.000
1.00
0.93
0.98
1.00
2.00
1.00
9.00
3.00
f1 (ppm)


182.8
172.3
148.8
147.5
134.9
130.5
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
55.7
54.7
51.9
50.6
38.3
27.6
18.9
f1 (ppm)

Compound 23’

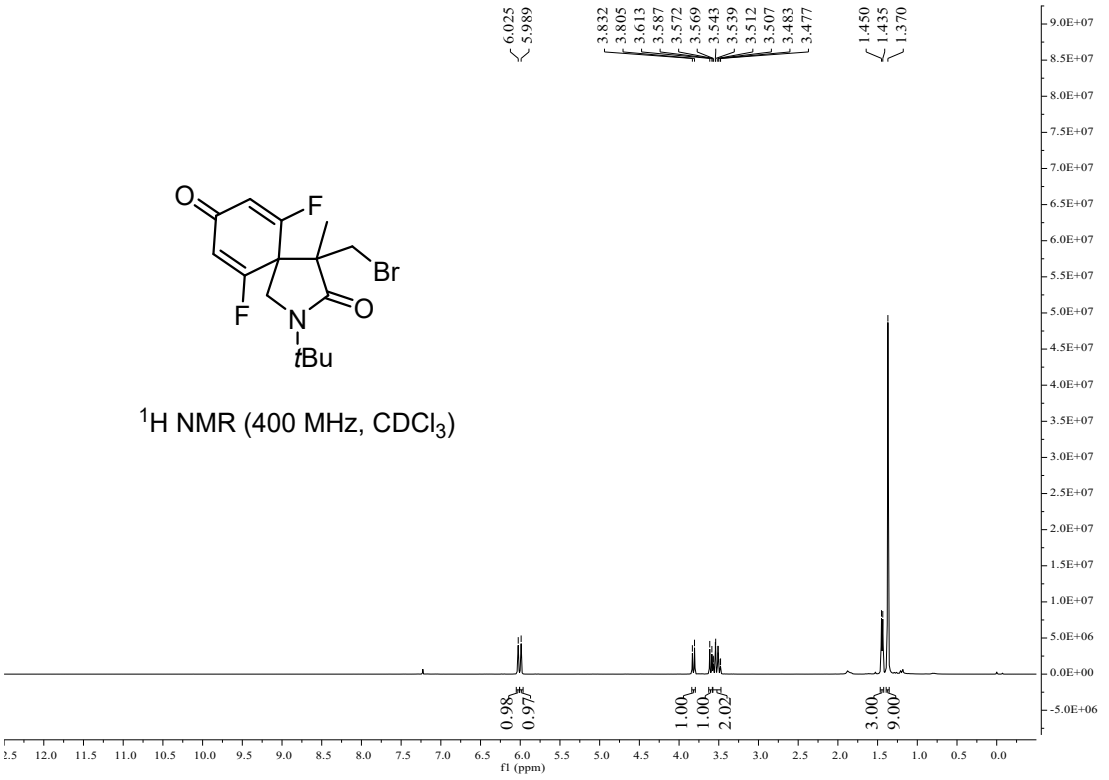


^{1}H NMR (400 MHz, $CDCl_3$)

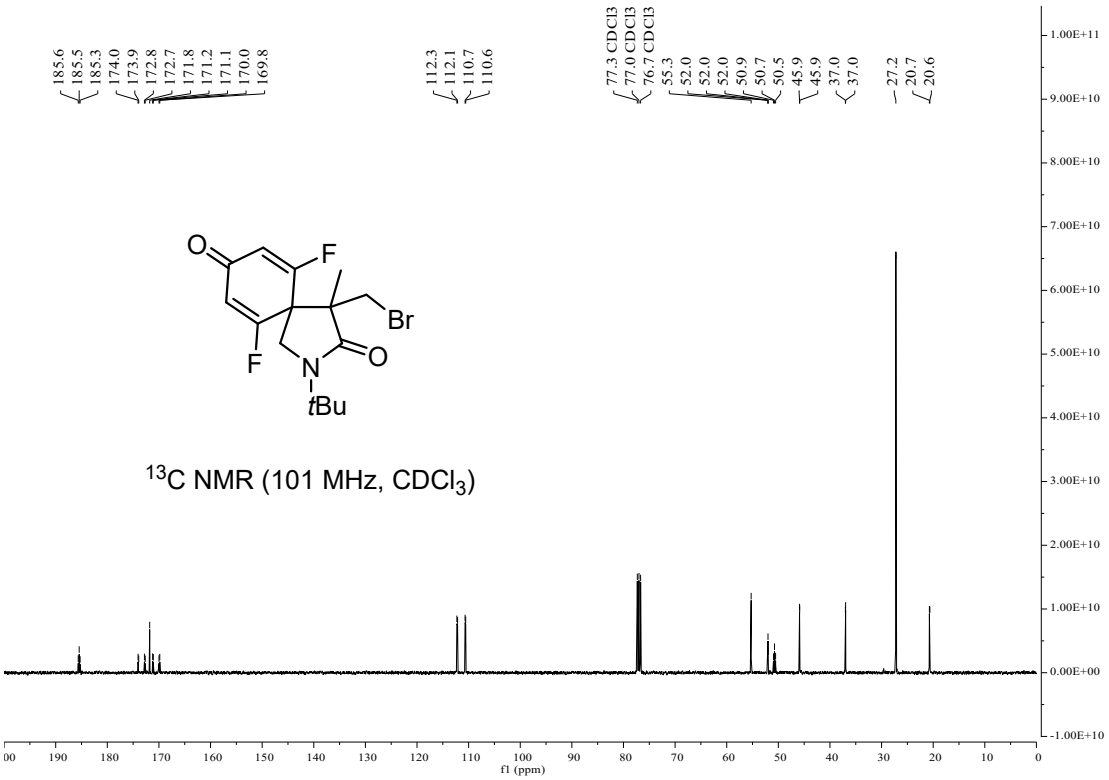


^{13}C NMR (101 MHz, $CDCl_3$)

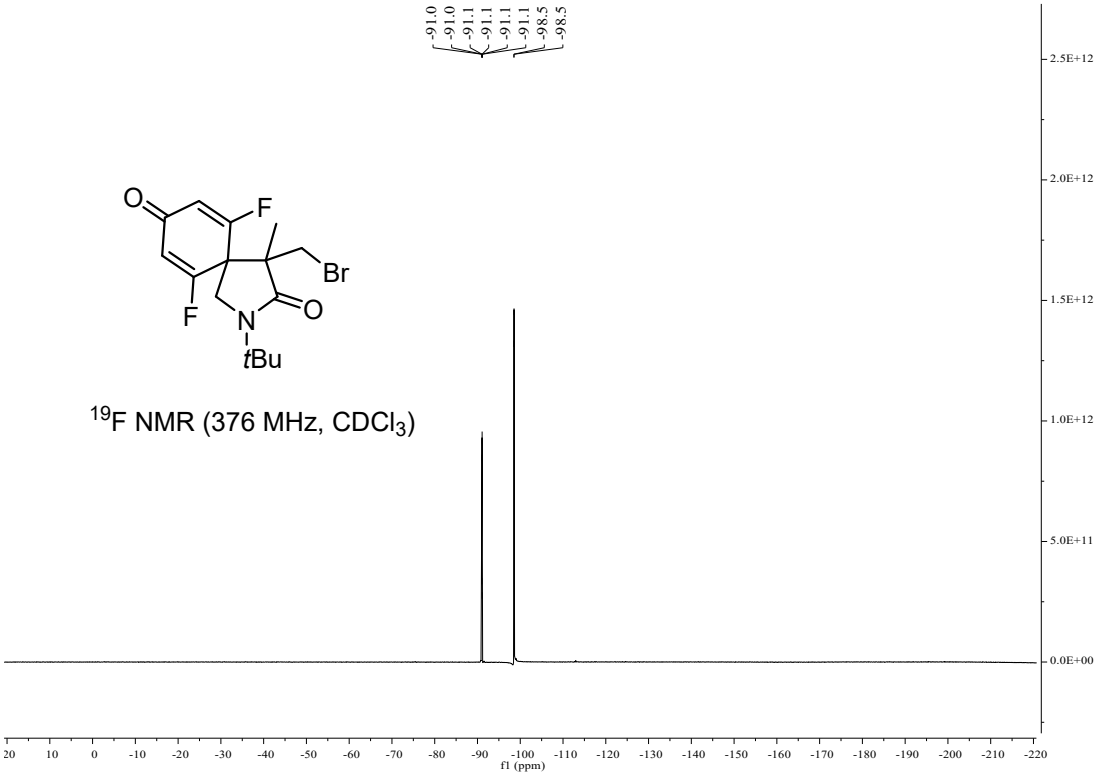
Compound 24



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

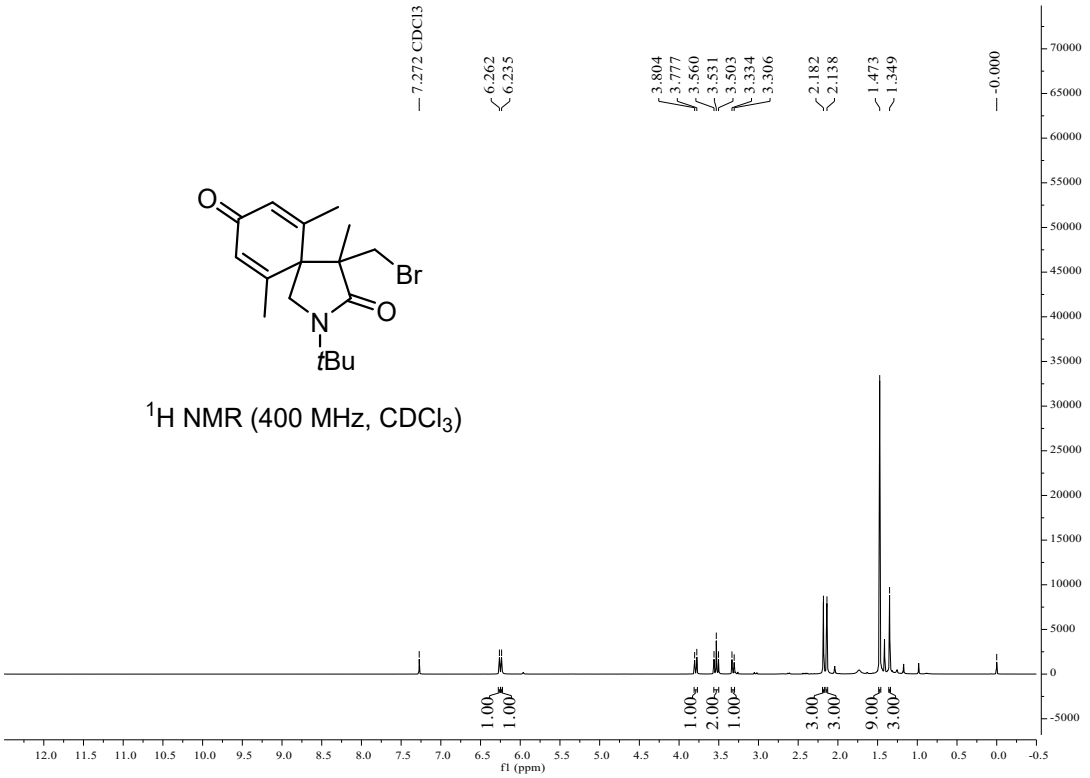


^{13}C NMR (101 MHz, $CDCl_3$)

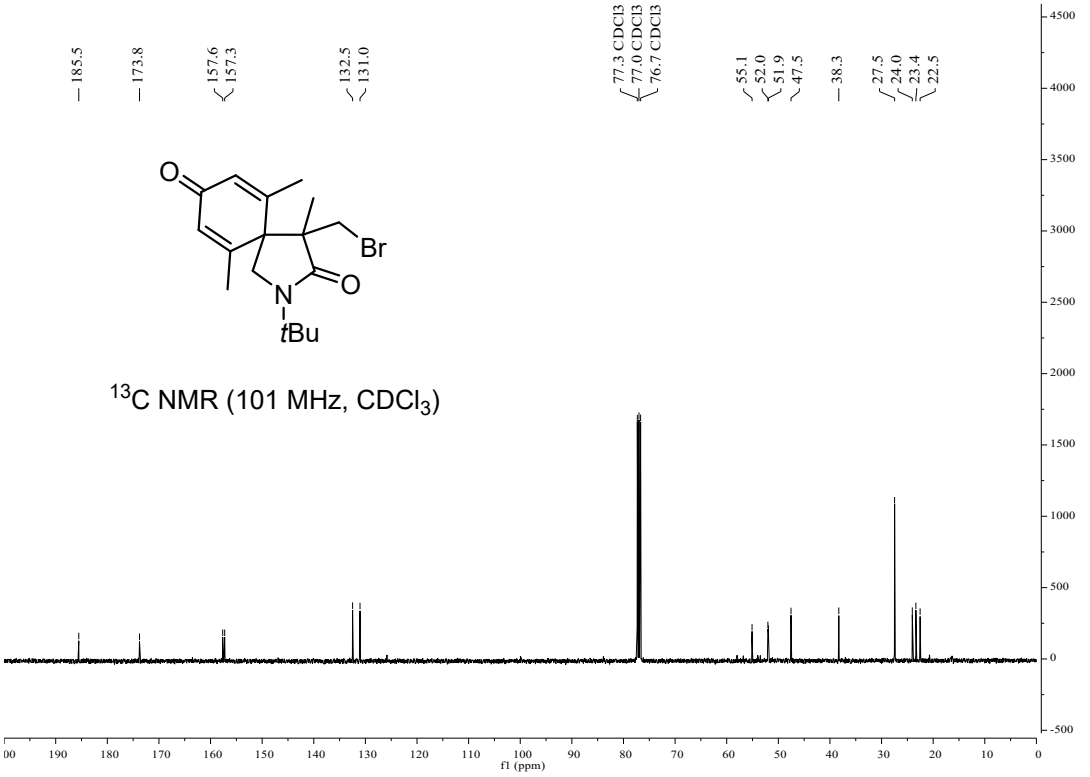


^{19}F NMR (376 MHz, $CDCl_3$)

Compound 25

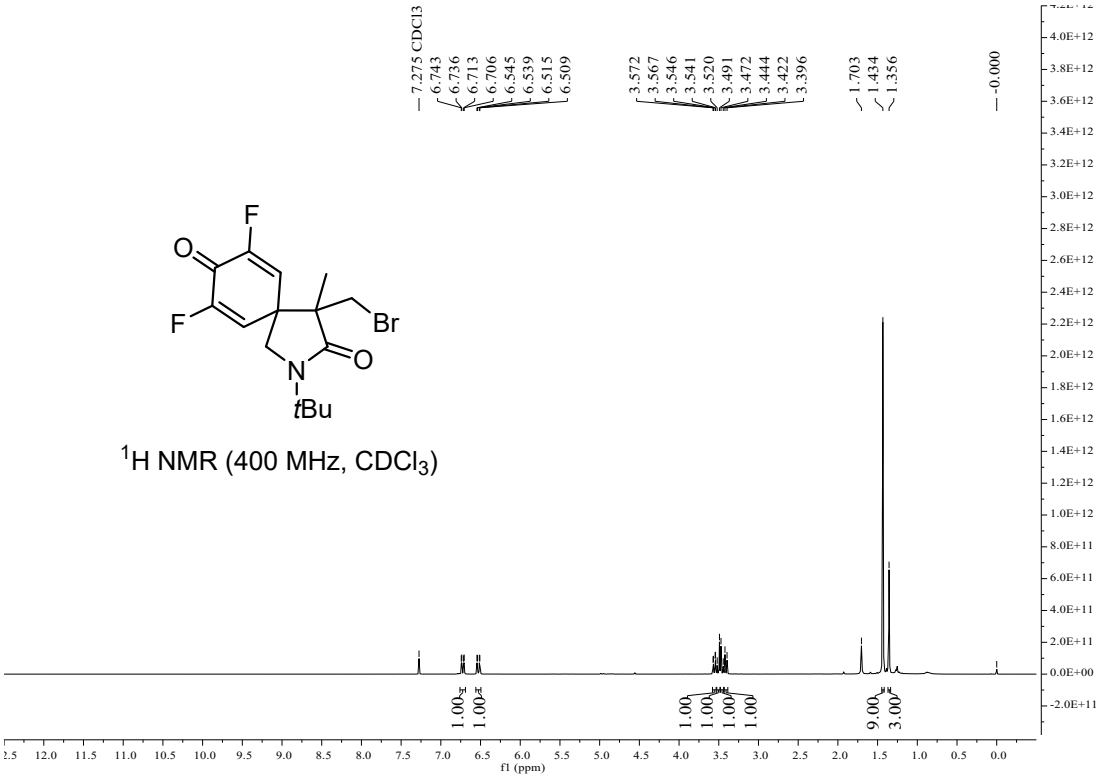


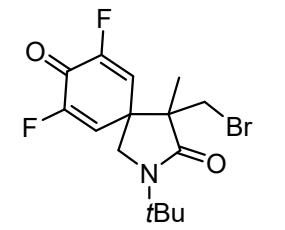
^{1}H NMR (400 MHz, $CDCl_3$)



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

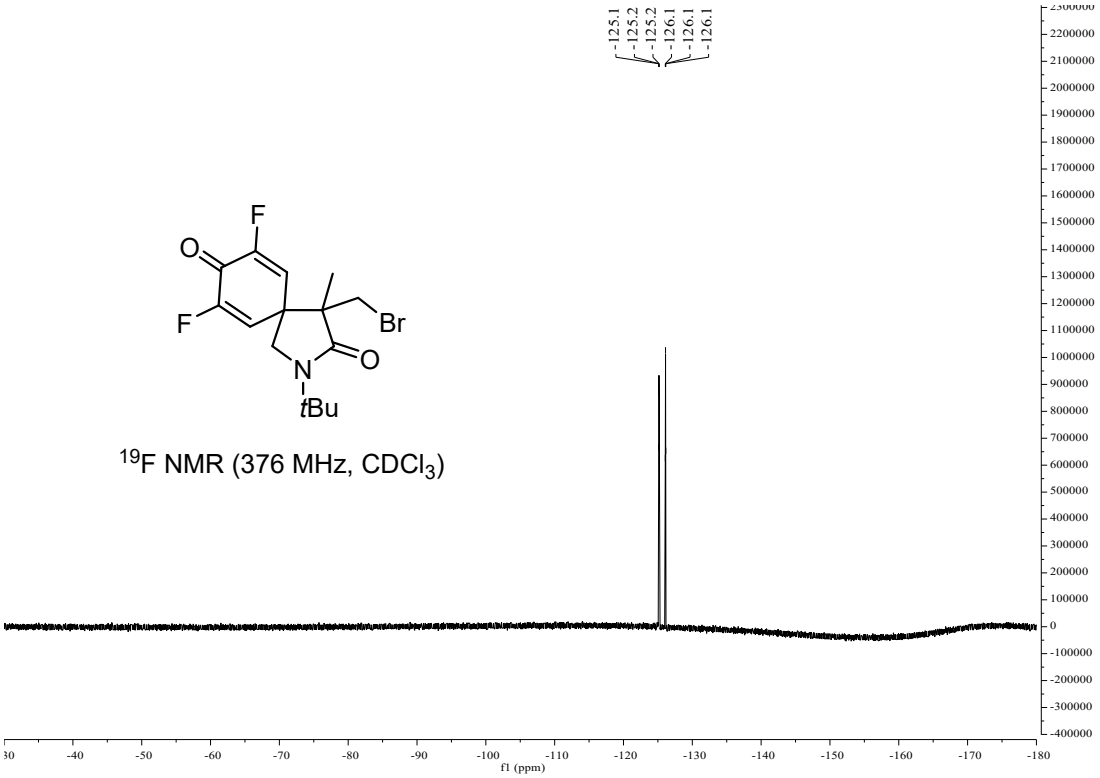
Compound 26





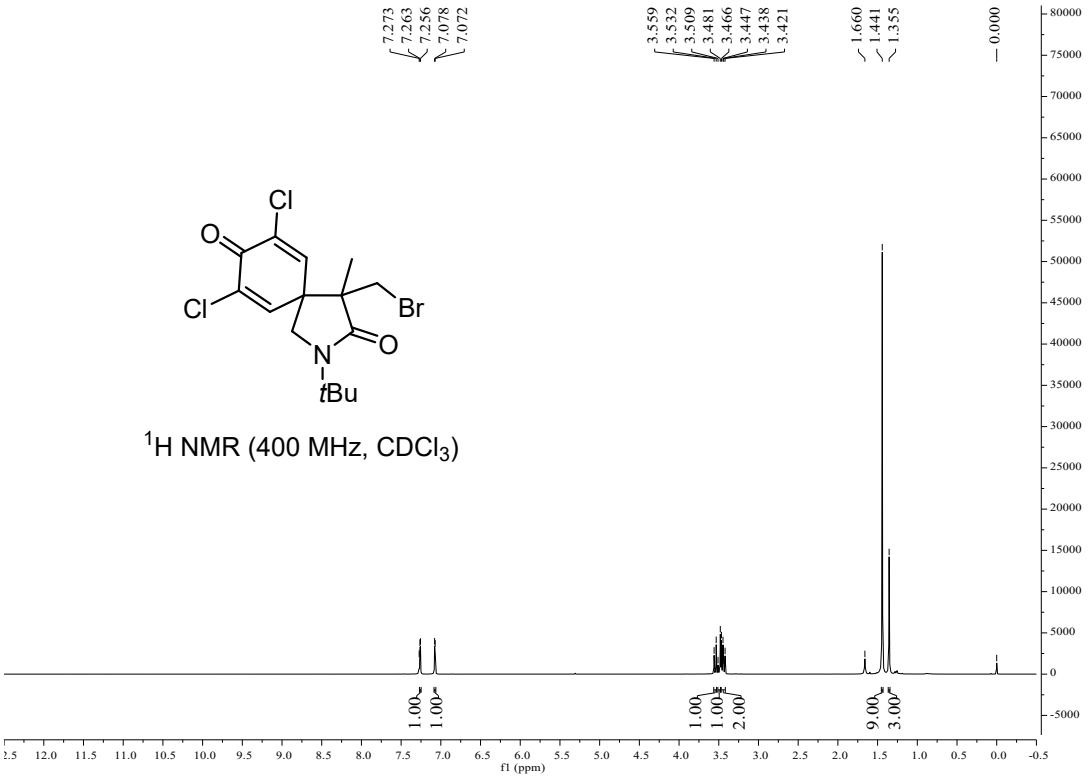
^{1}H NMR (400 MHz, $CDCl_3$)

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

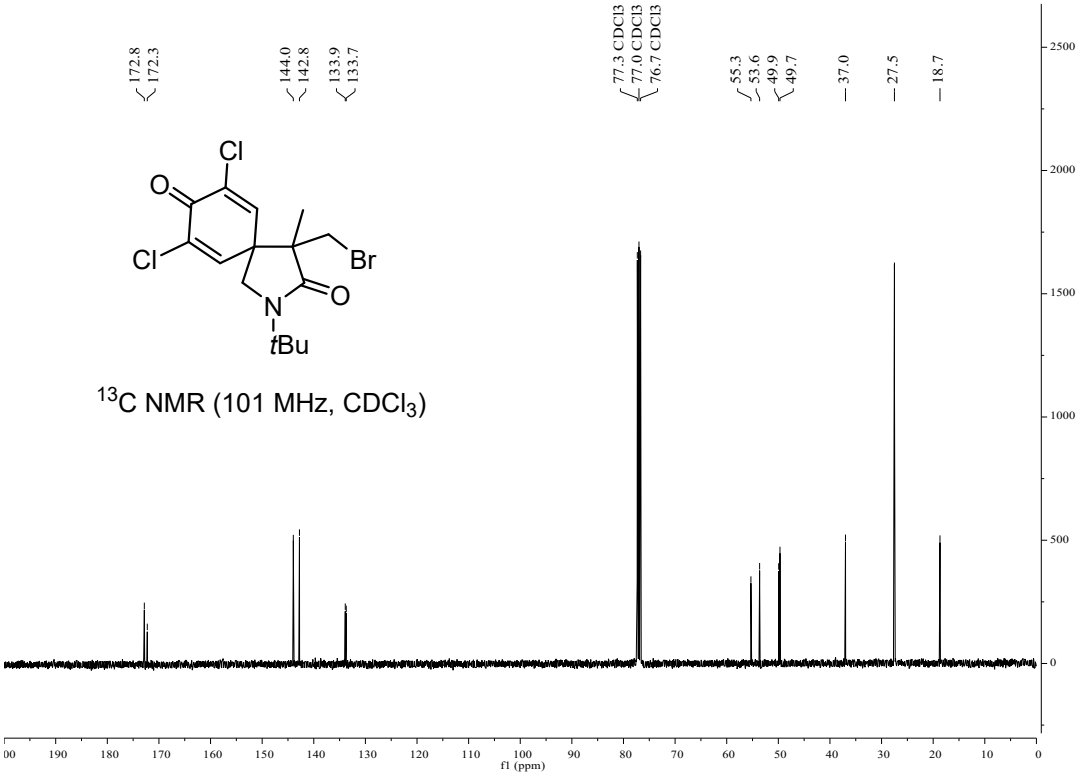


^{19}F NMR (376 MHz, $CDCl_3$)

Compound 27

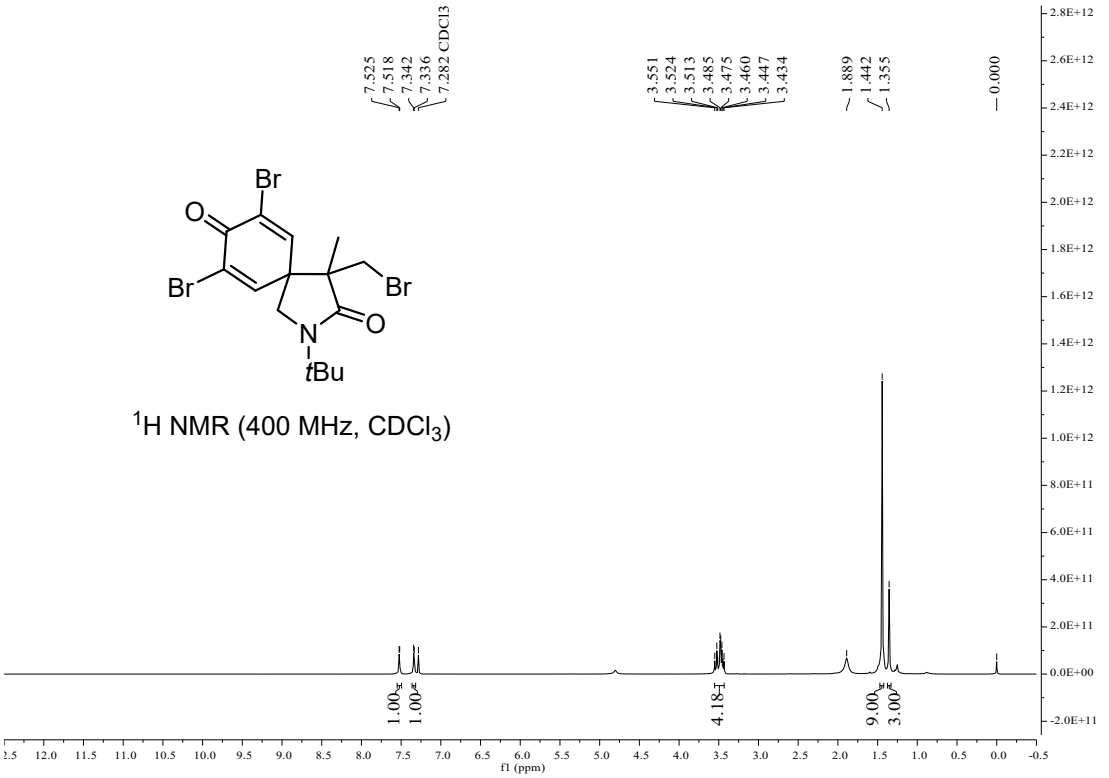


^{1}H NMR (400 MHz, $CDCl_3$)

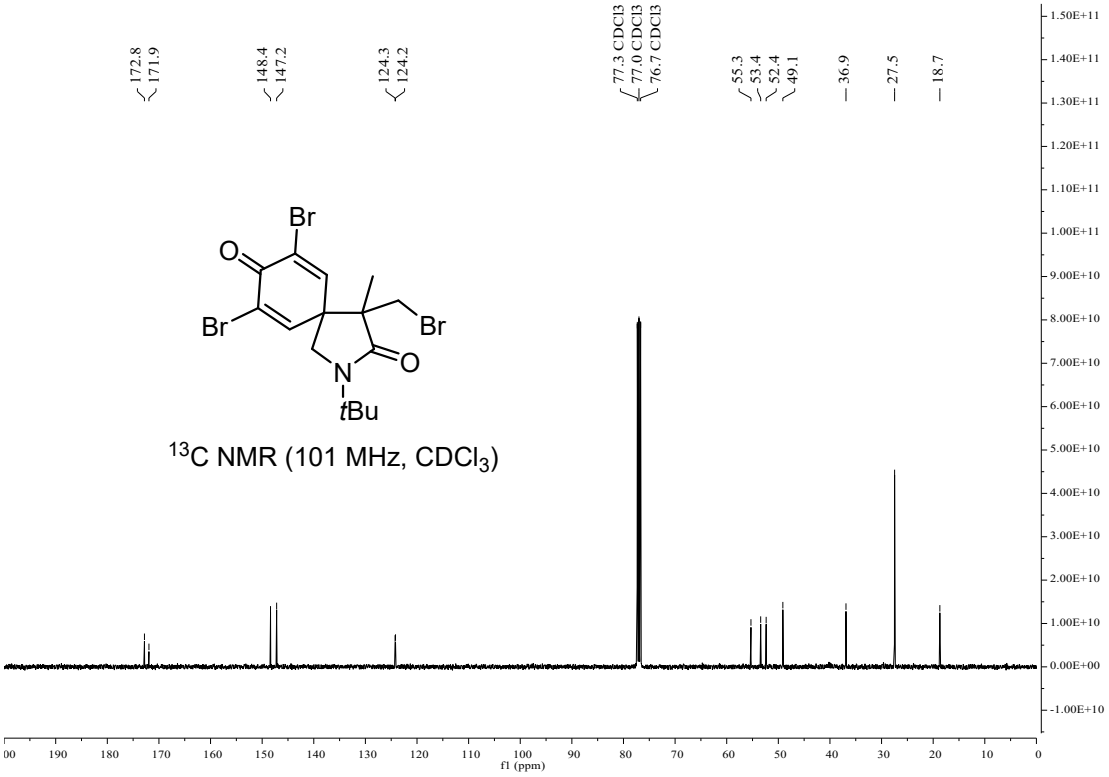


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 28

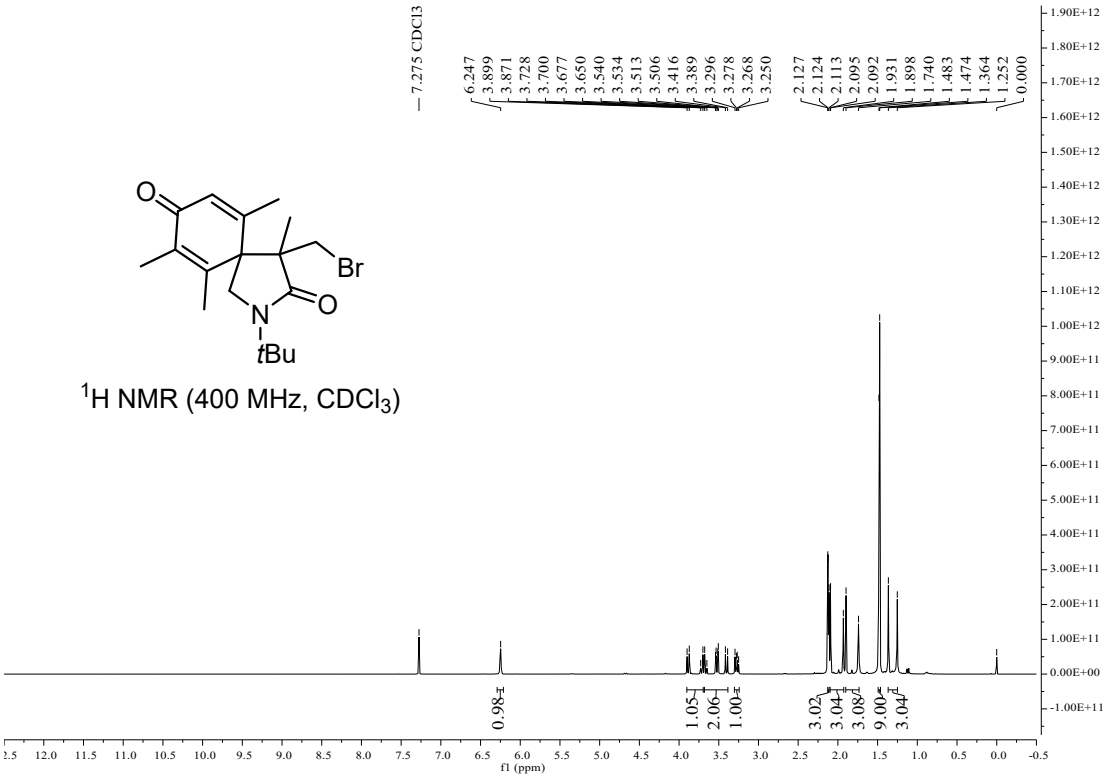


^{1}H NMR (400 MHz, $CDCl_3$)



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

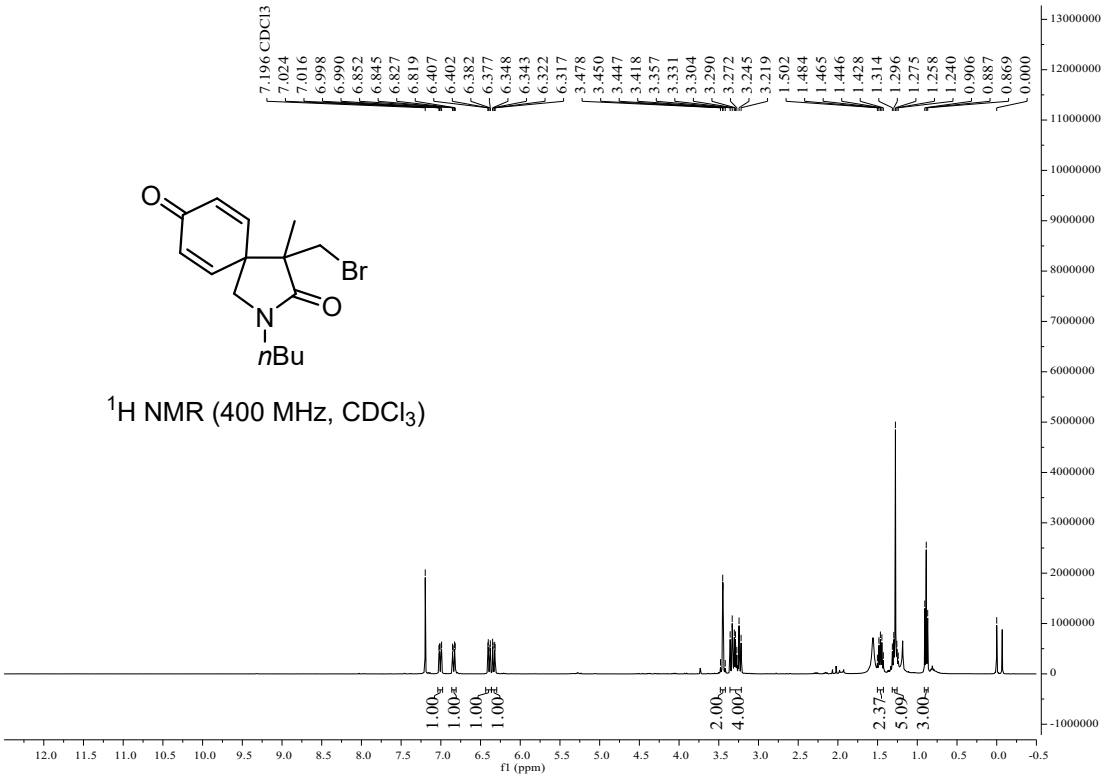
Compound 29



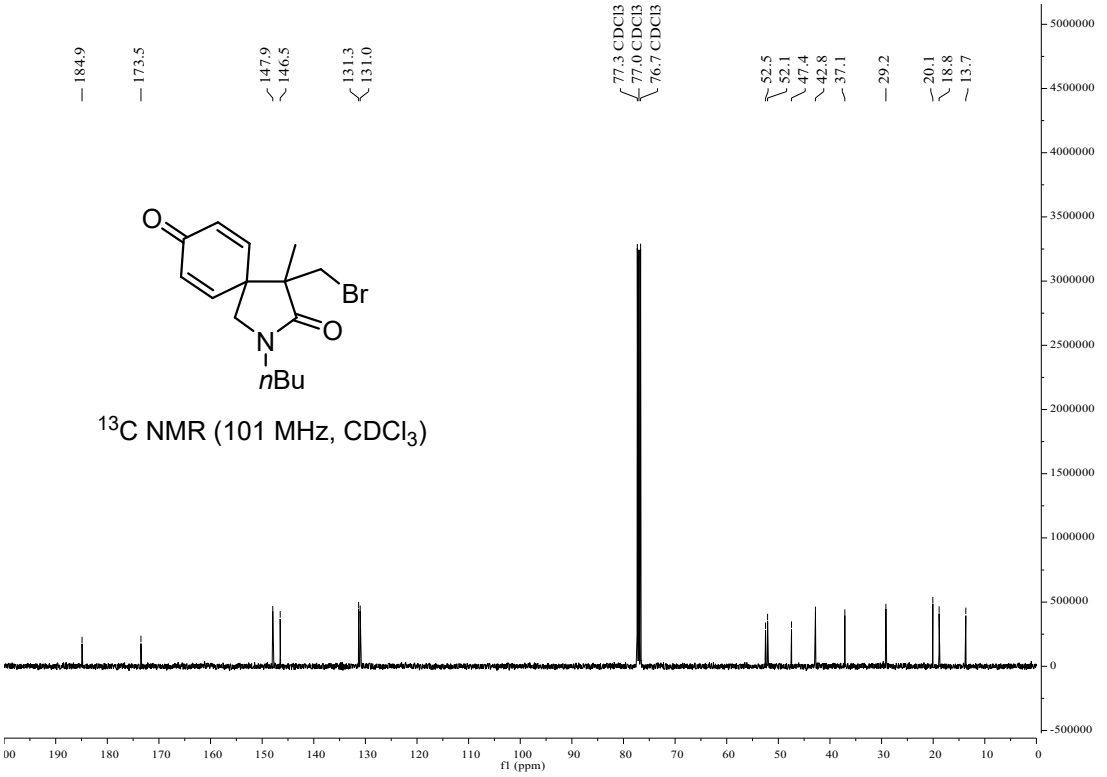
^{1}H NMR (400 MHz, $CDCl_3$)

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

Compound 30

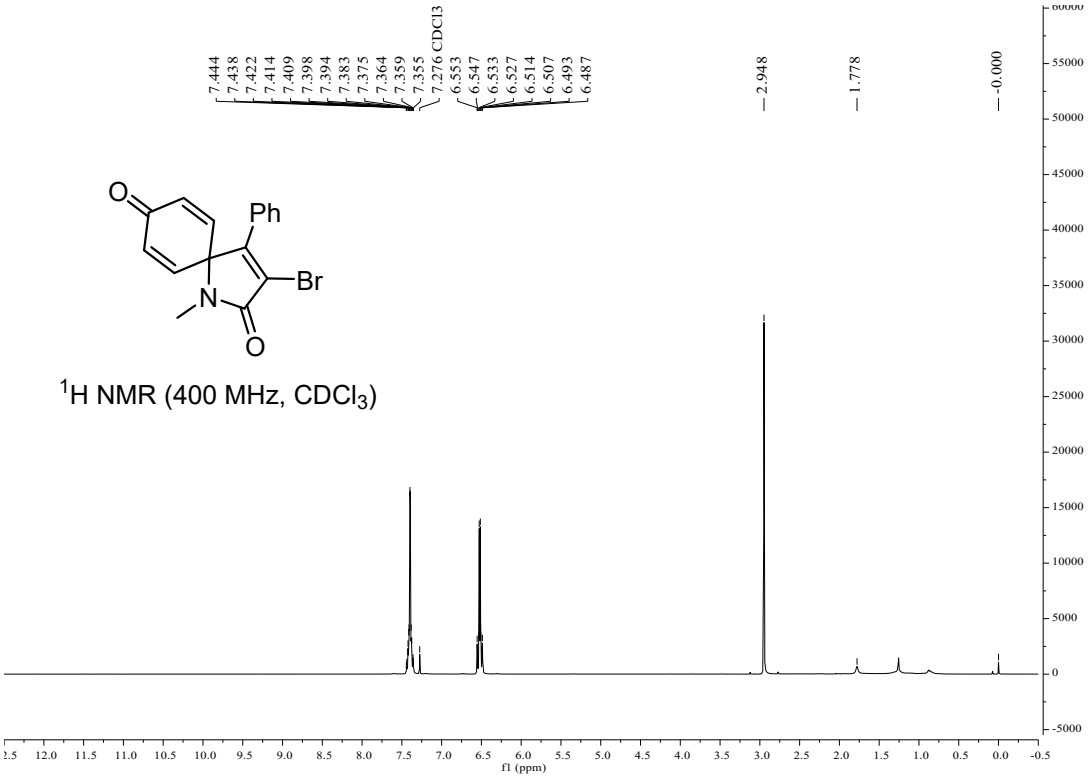


^{1}H NMR (400 MHz, $CDCl_3$)

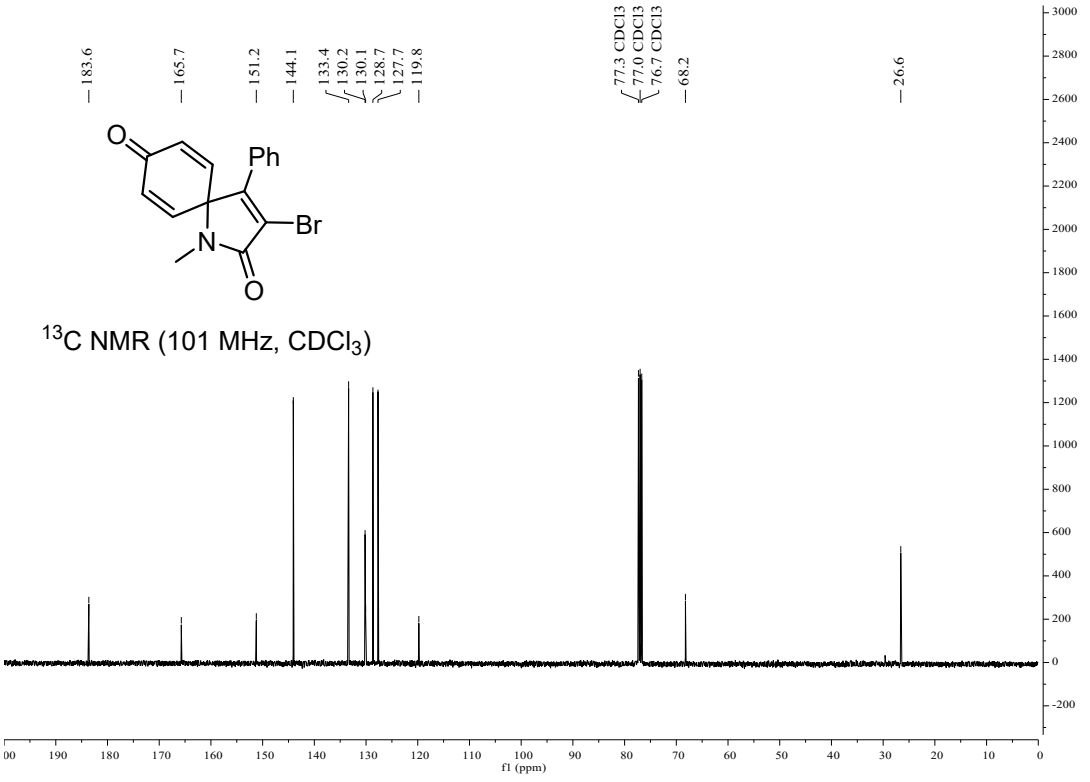


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 31

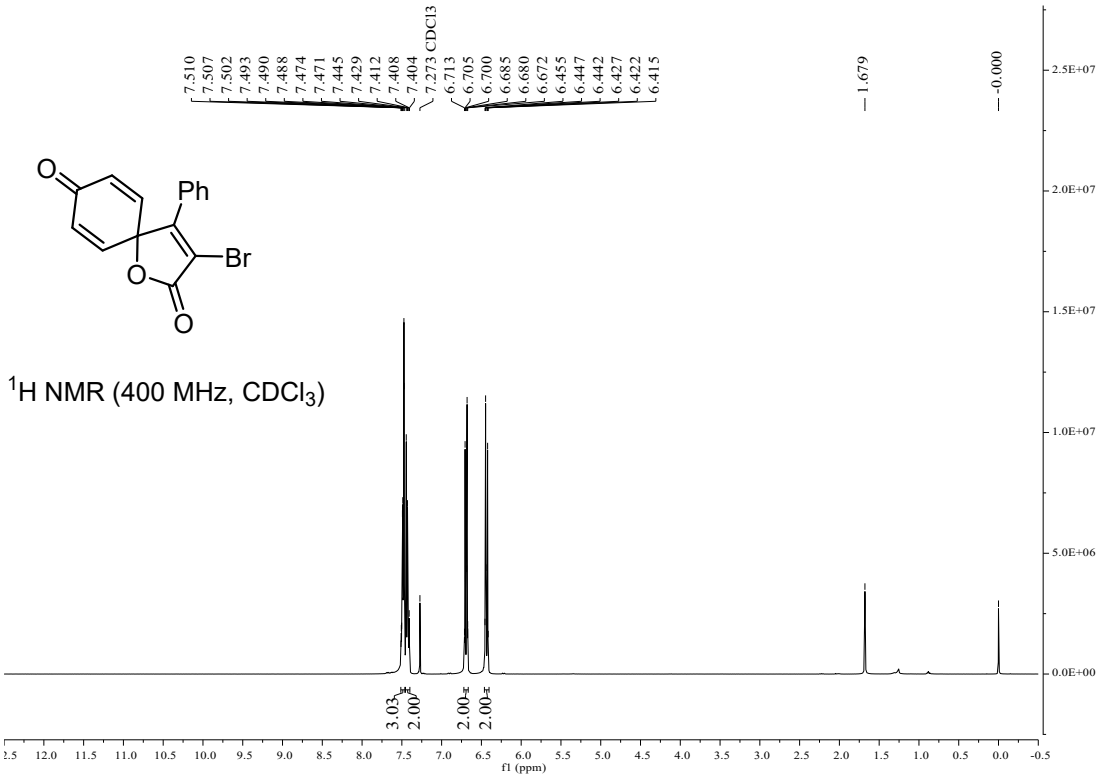


^{1}H NMR (400 MHz, $CDCl_3$)

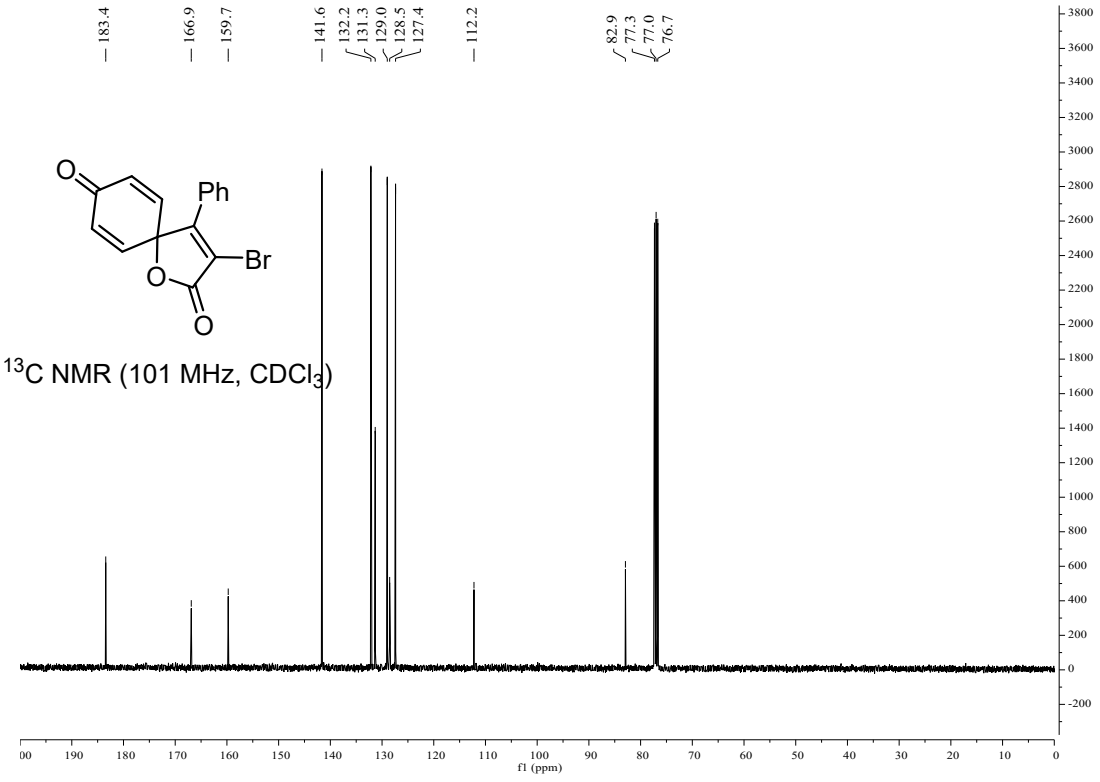


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 32

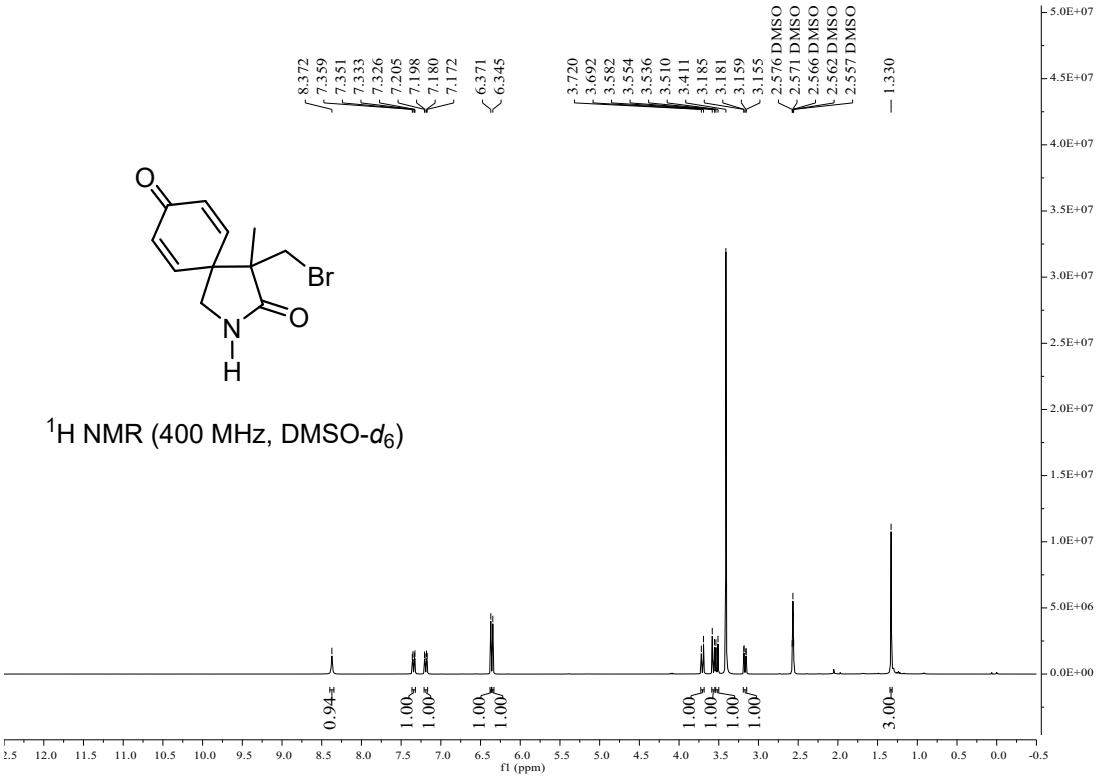


^{1}H NMR (400 MHz, $CDCl_3$)

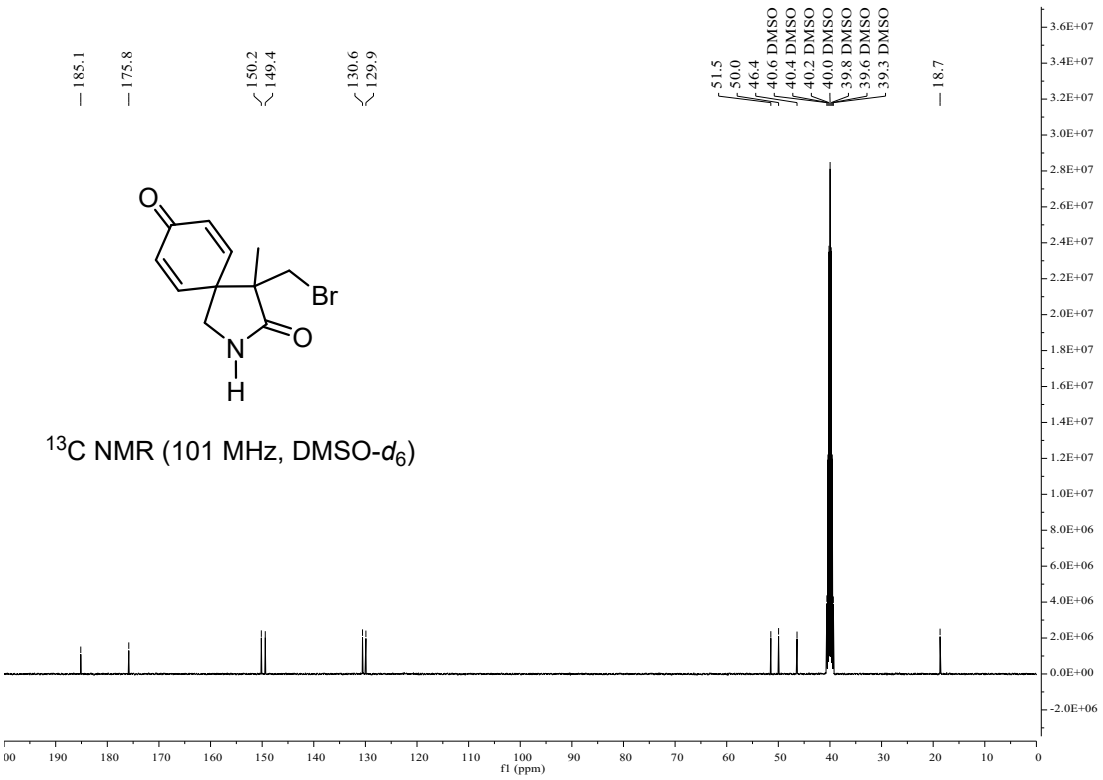


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 33

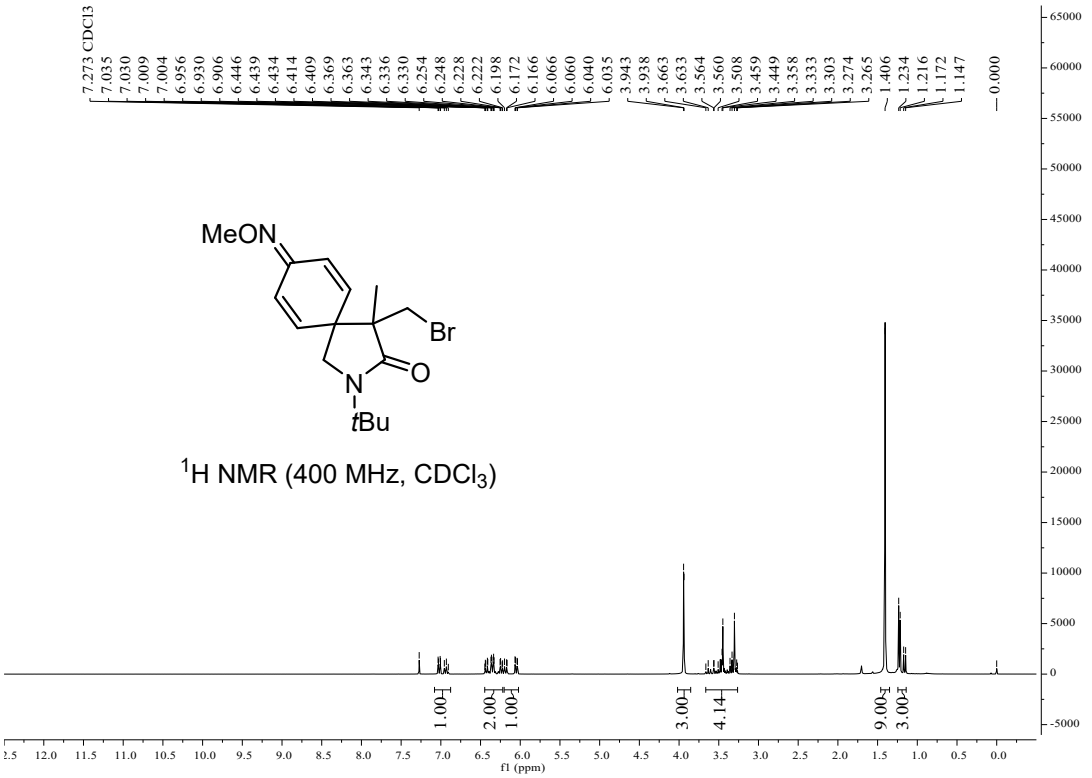


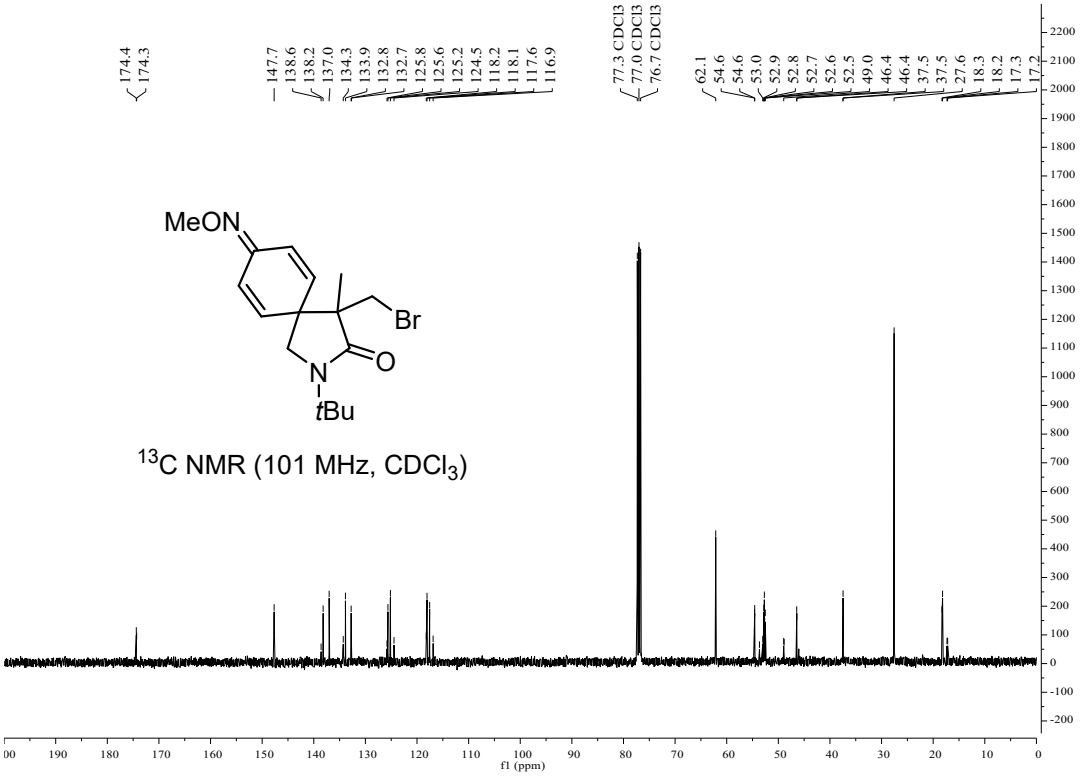
^{1}H NMR (400 MHz, DMSO-d_6)



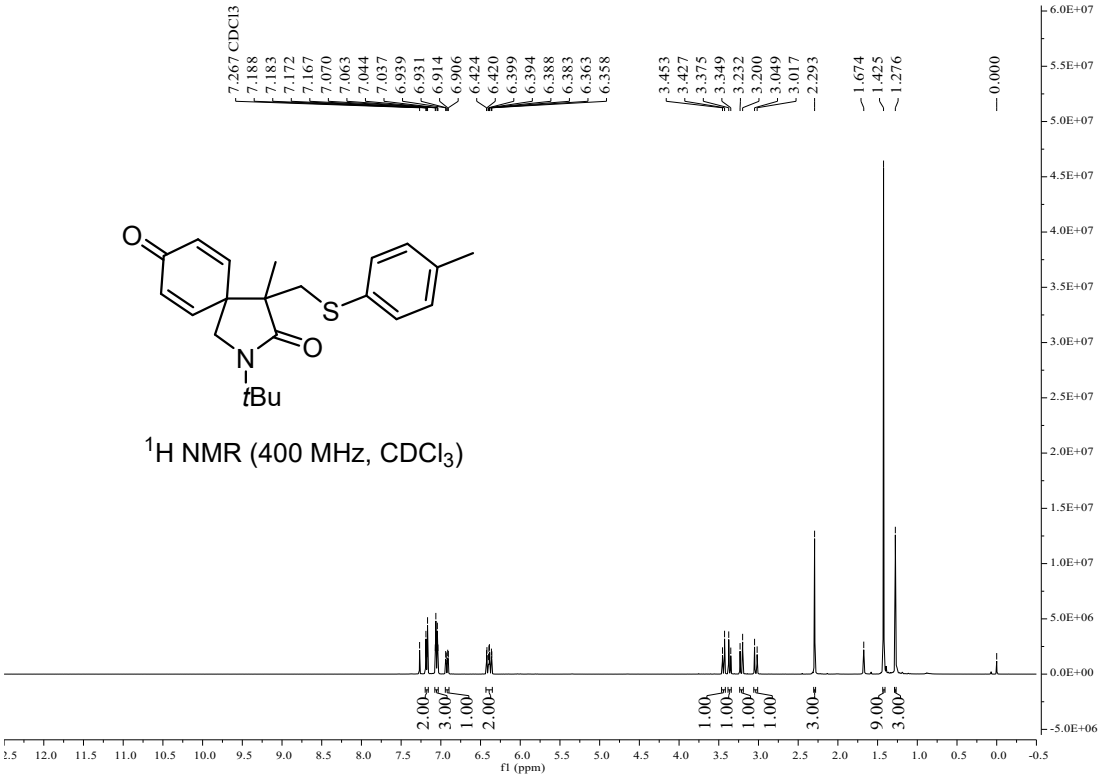
^{13}C NMR (101 MHz, DMSO-d_6)

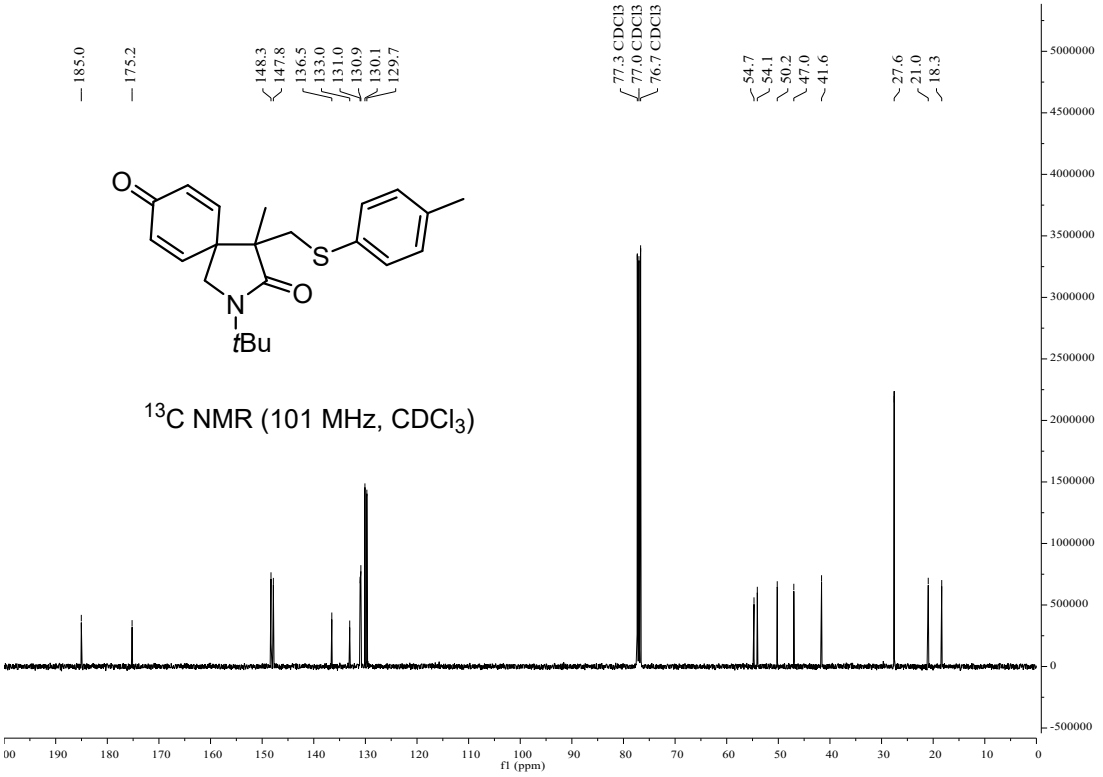
Compound 34


MeON
Br
O
N
tBu
1H NMR (400 MHz, CDCl3)
f1 (ppm)

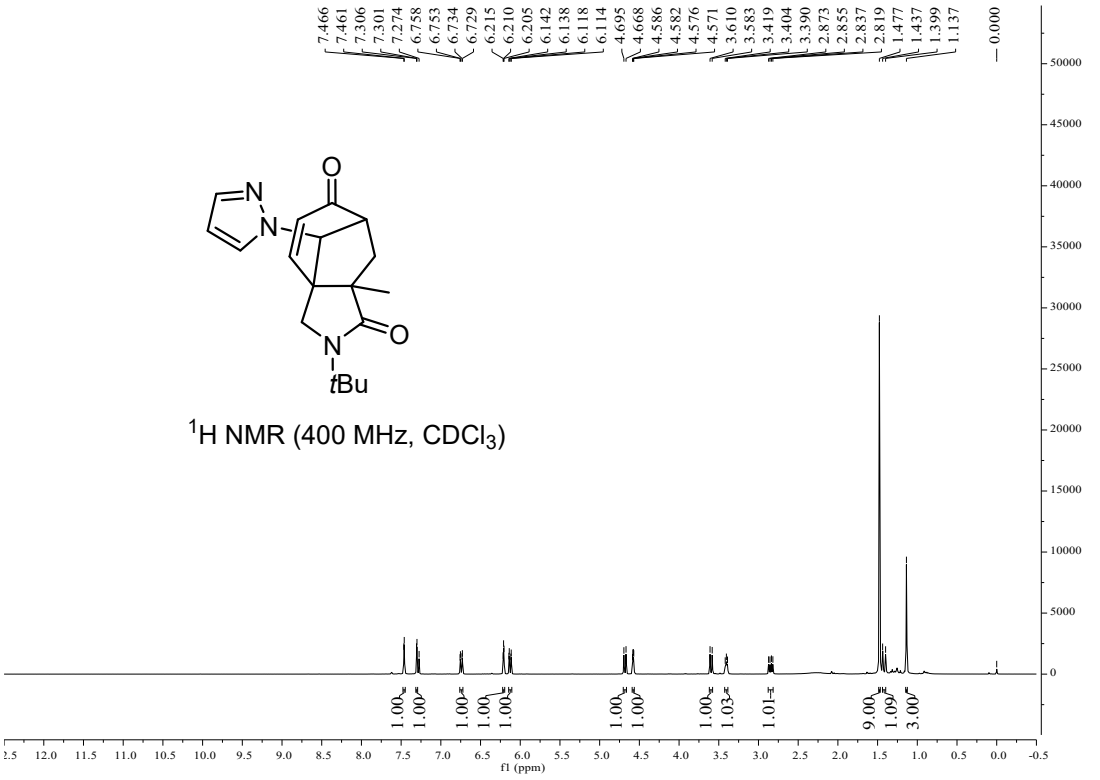

MeON
Br
O
N
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 36

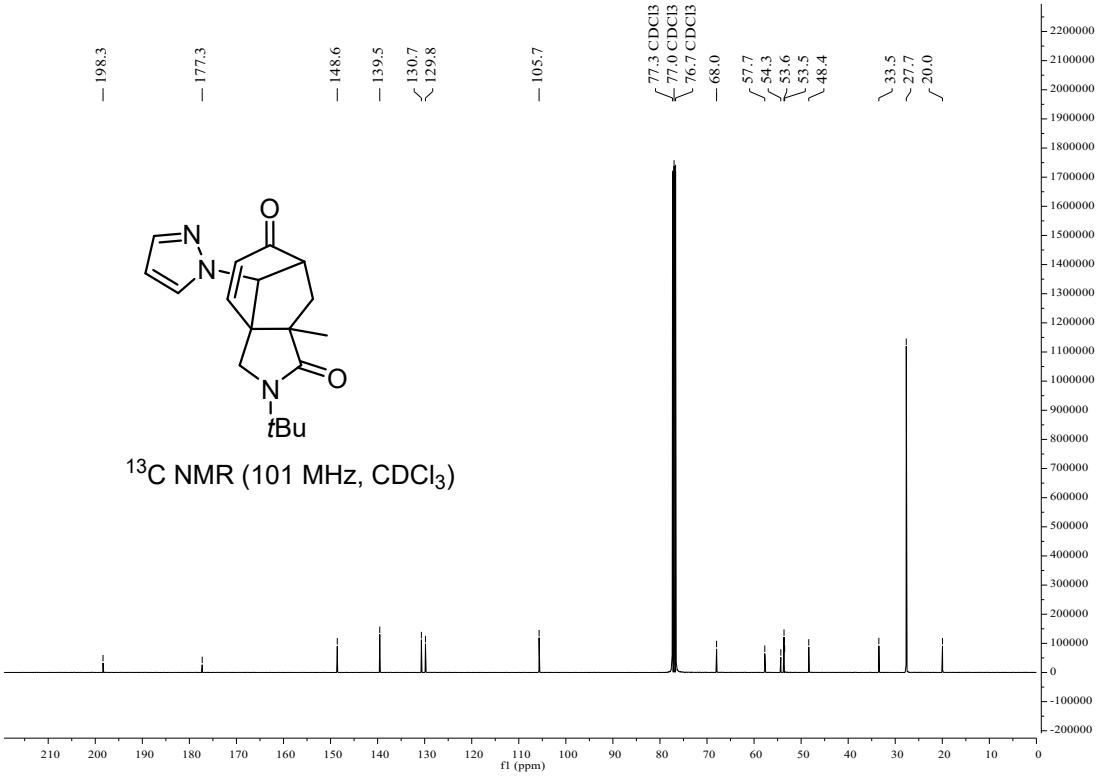

7.267 CDCl3
7.188
7.183
7.172
7.167
7.070
7.063
7.044
7.037
6.939
6.931
6.914
6.906
6.424
6.420
6.399
6.394
6.388
6.383
6.363
6.358
3.453
3.427
3.375
3.349
3.232
3.200
3.049
3.017
2.293
1.674
1.425
1.276
0.000
O
S
N
O
tBu
1H NMR (400 MHz, CDCl3)
2.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
9.00
3.00
f1 (ppm)


185.0
175.2
148.3
147.8
136.5
133.0
131.0
130.9
130.1
129.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
54.7
54.1
50.2
47.0
41.6
27.6
21.0
18.3
O
S
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 37

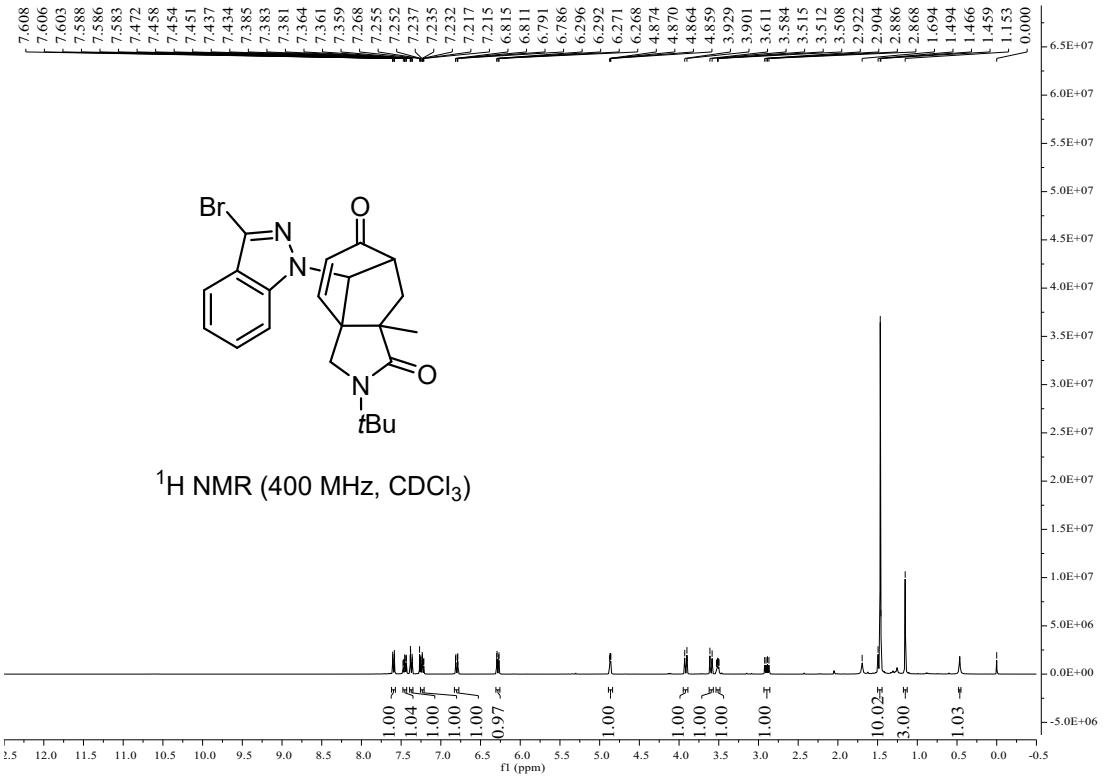


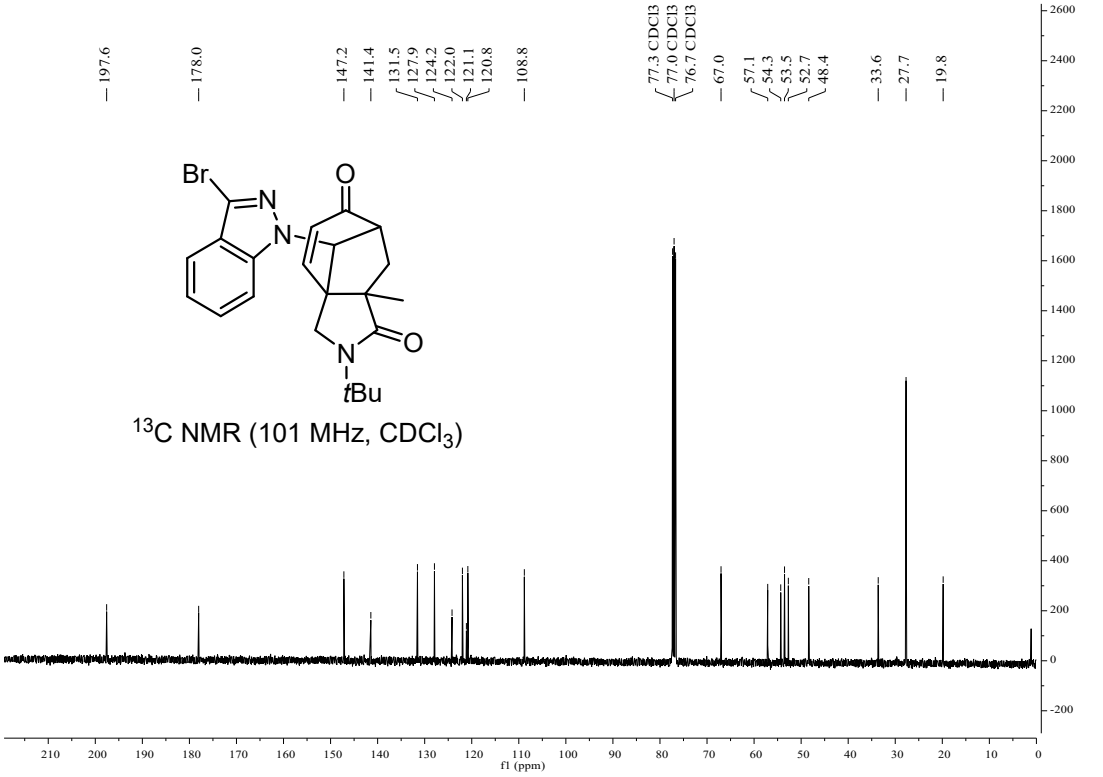
^{1}H NMR (400 MHz, $CDCl_3$)



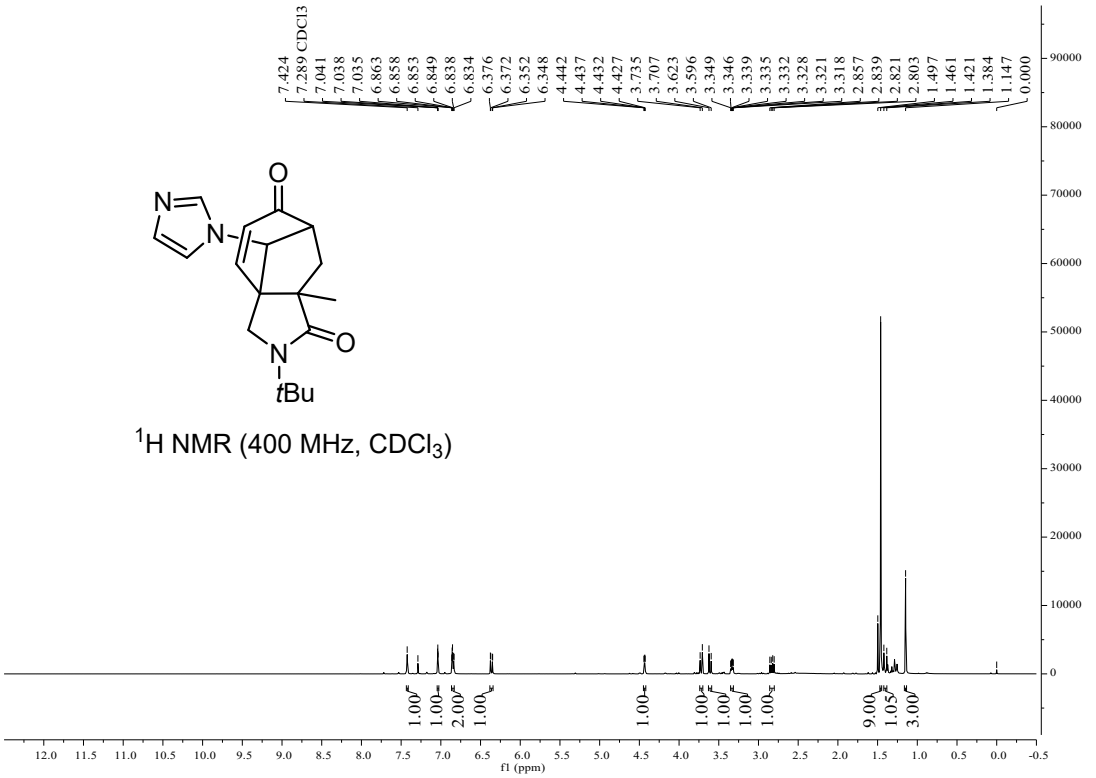
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 38

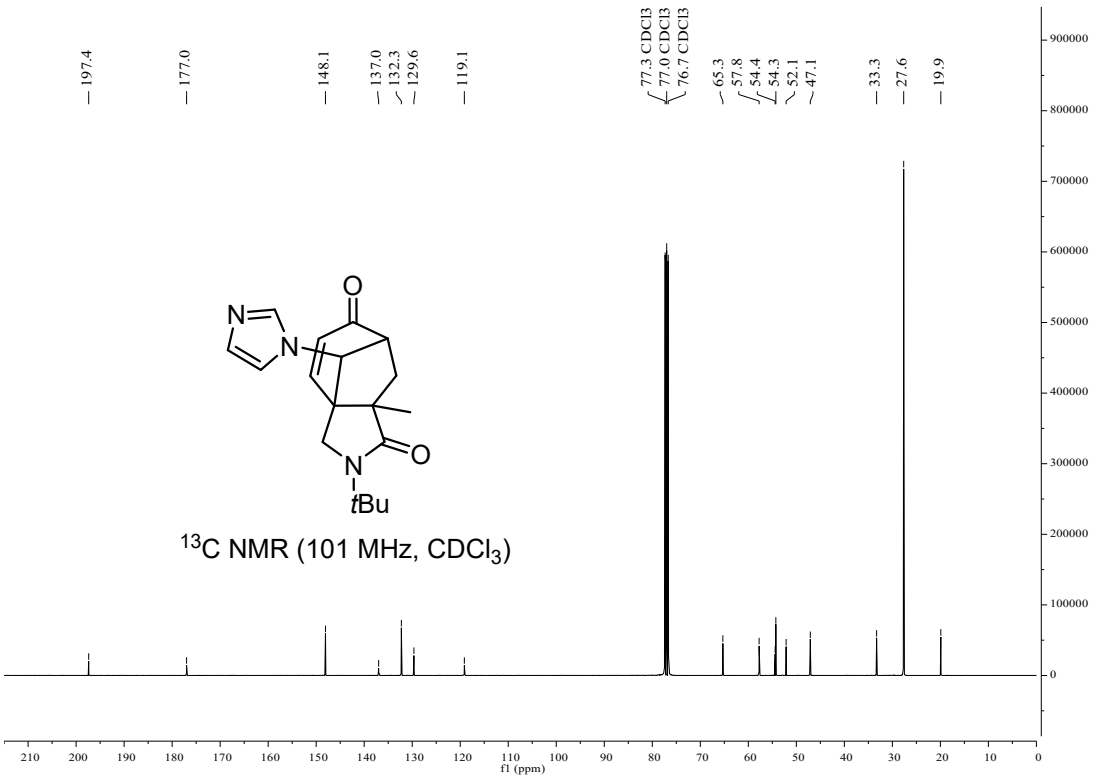

Br
N
N
O
O
N
tBu
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Br
N
N
O
O
N
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 39

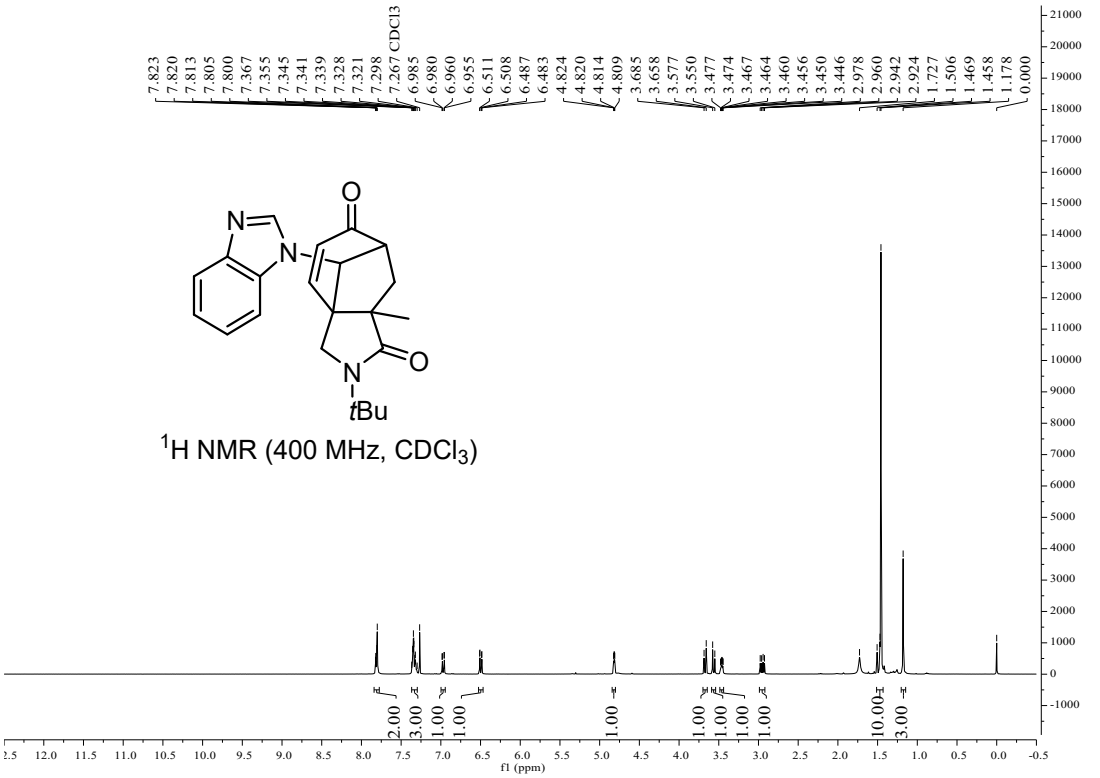


^{1}H NMR (400 MHz, $CDCl_3$)

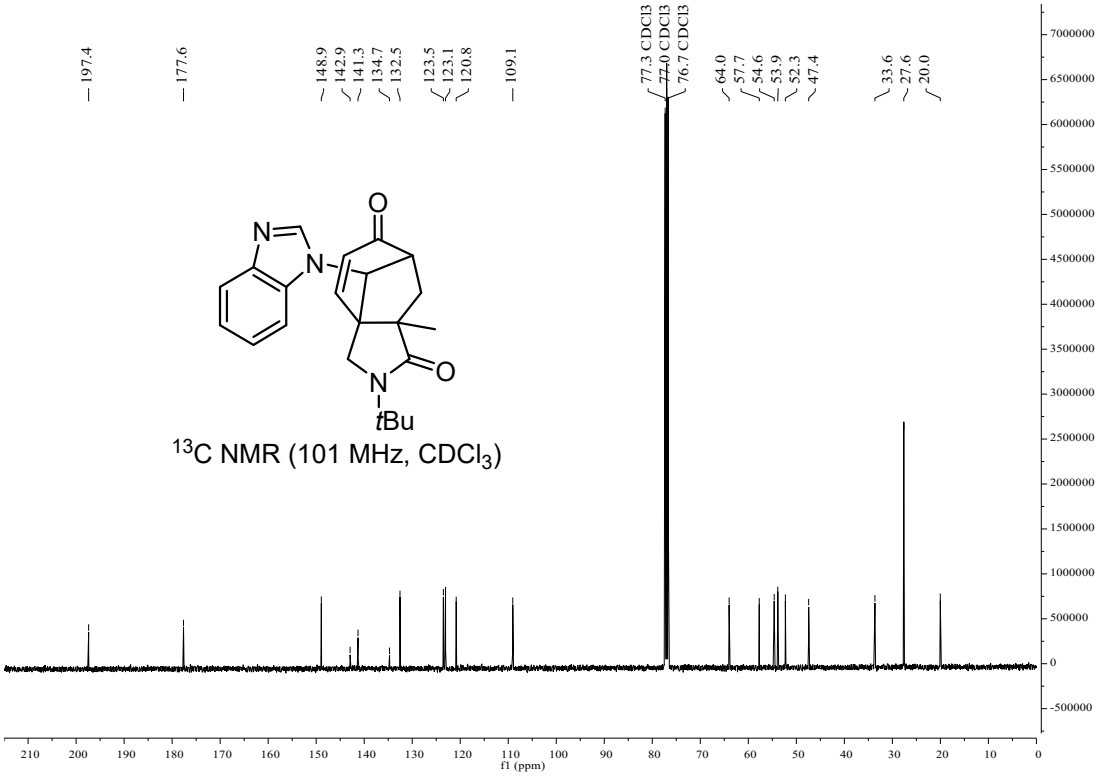


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 40

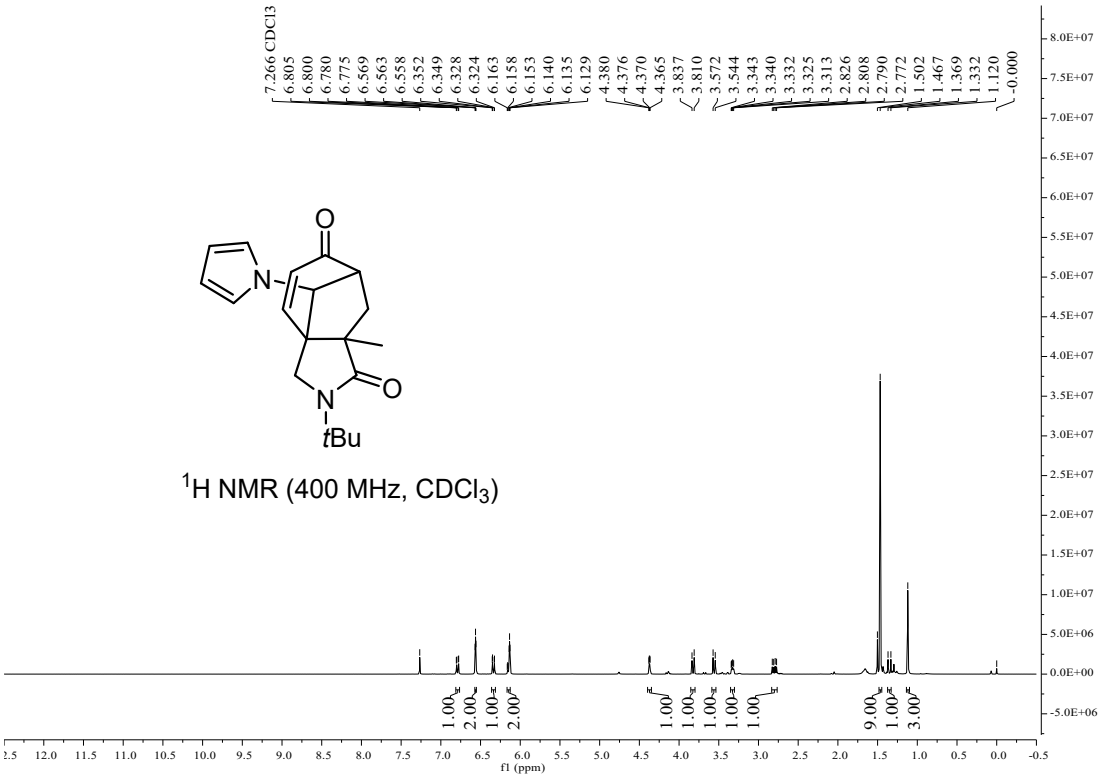


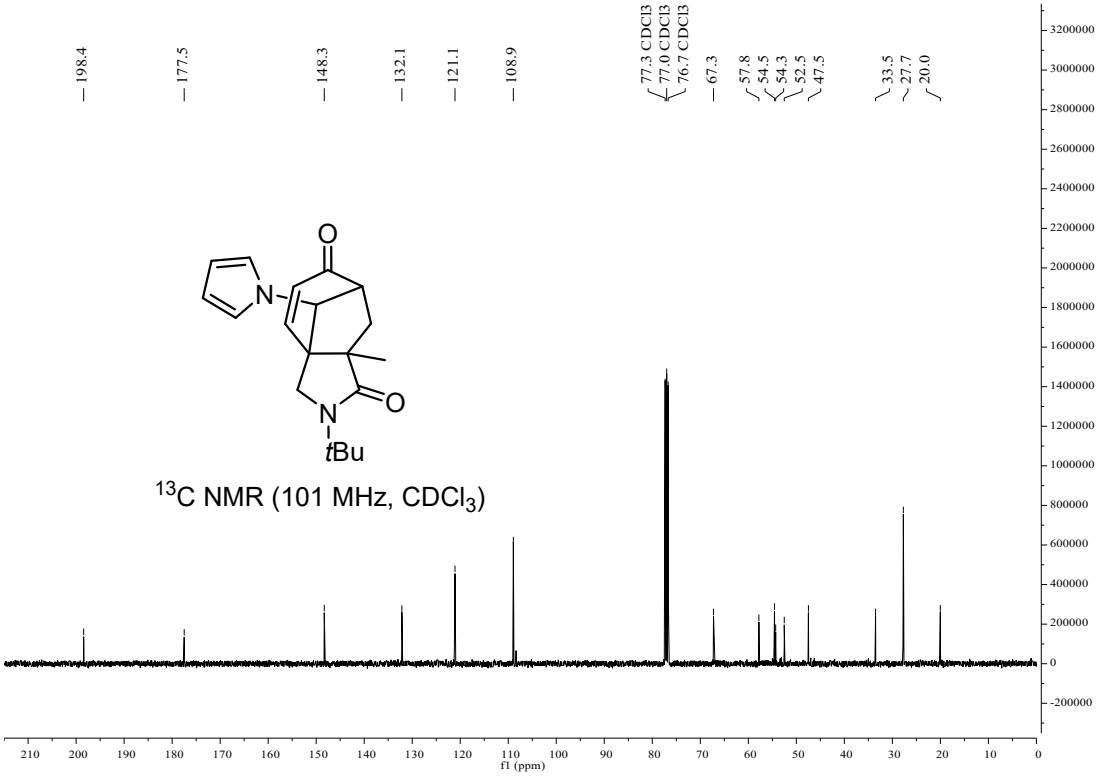
^{1}H NMR (400 MHz, $CDCl_3$)



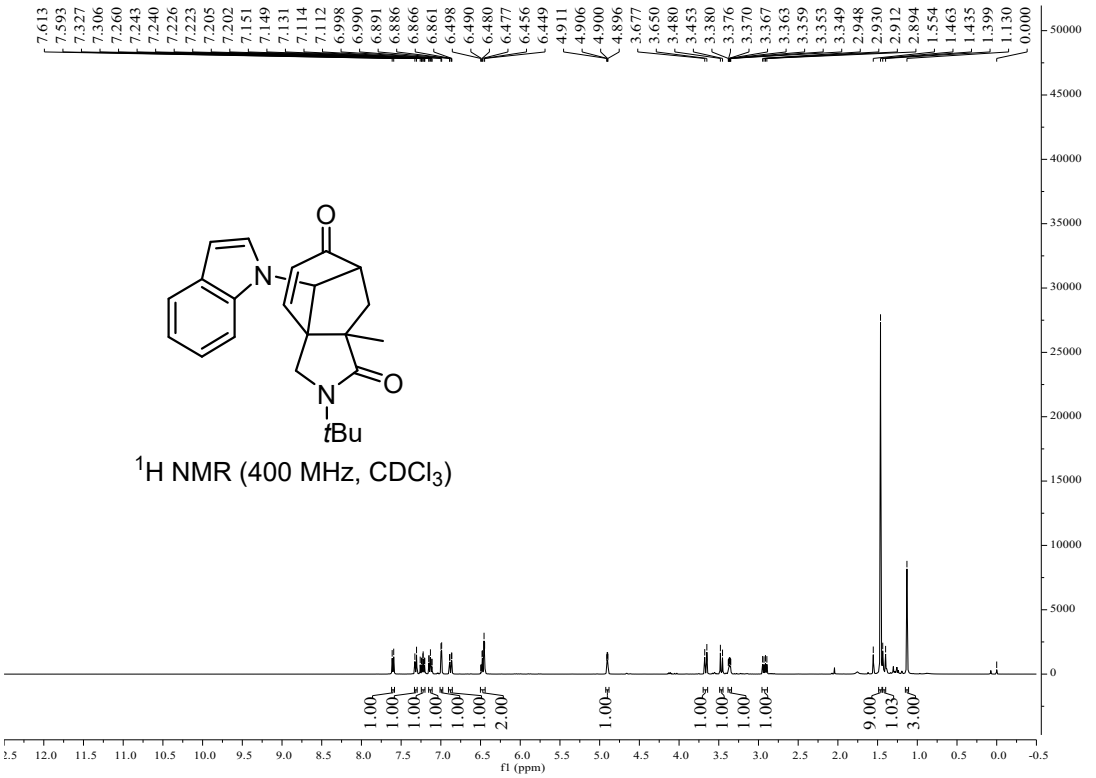
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 41

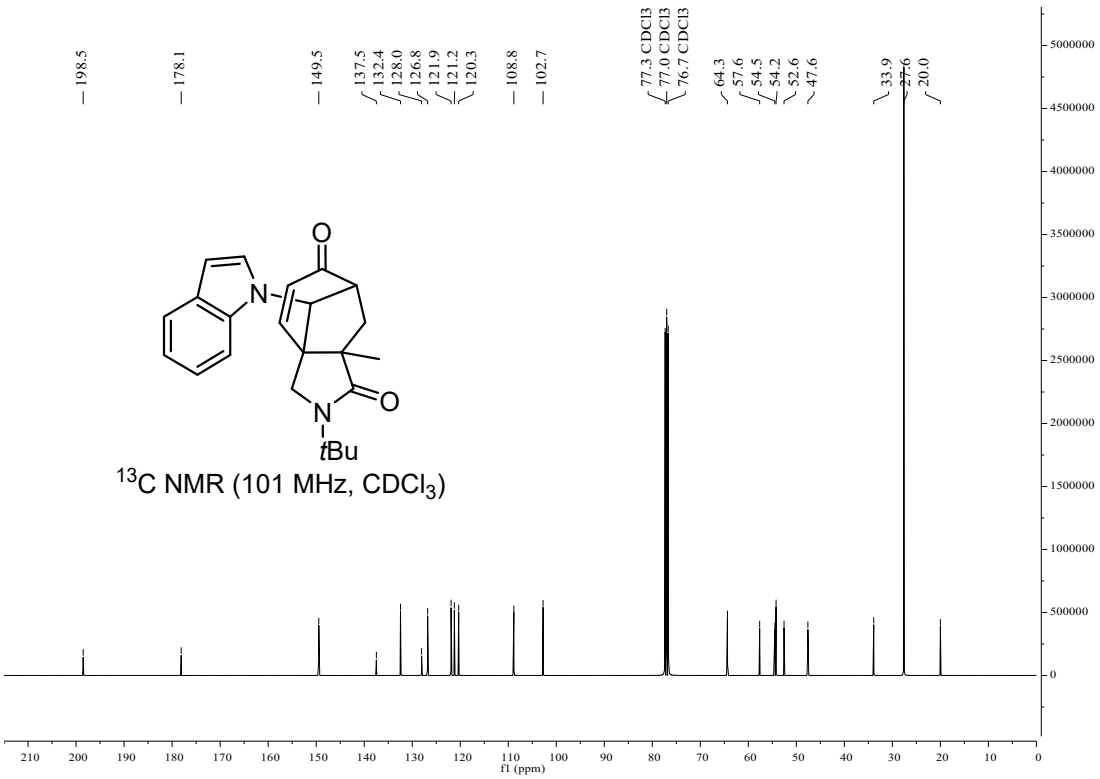

7.266 CDCl3
6.805
6.800
6.780
6.775
6.569
6.563
6.558
6.352
6.349
6.328
6.324
6.163
6.158
6.153
6.140
6.135
6.129
4.380
4.376
4.370
4.365
3.837
3.810
3.572
3.544
3.343
3.340
3.332
3.325
3.313
2.826
2.808
2.790
2.772
1.502
1.467
1.369
1.332
1.120
-0.000
O
N
O
N
tBu
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
9.00
1.00
3.00
f1 (ppm)


198.4
177.5
148.3
132.1
121.1
108.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
67.3
57.8
54.5
54.3
52.5
47.5
33.5
27.7
20.0
O
N
O
N
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 42

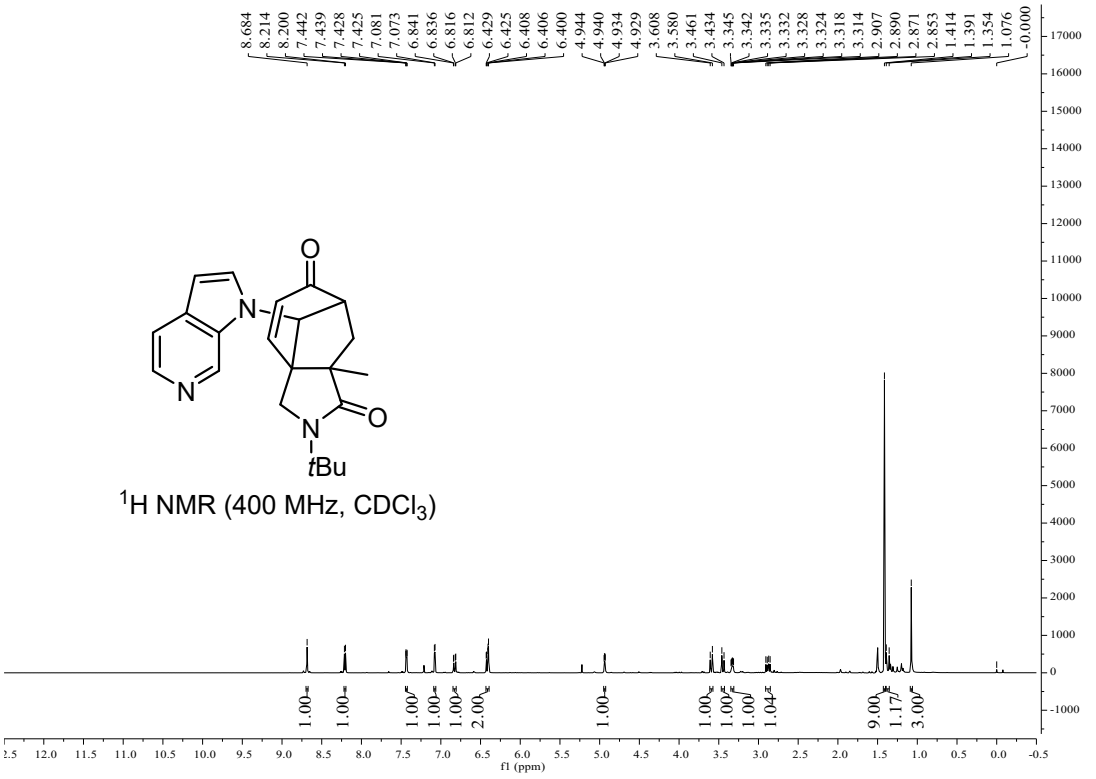


^{1}H NMR (400 MHz, $CDCl_3$)

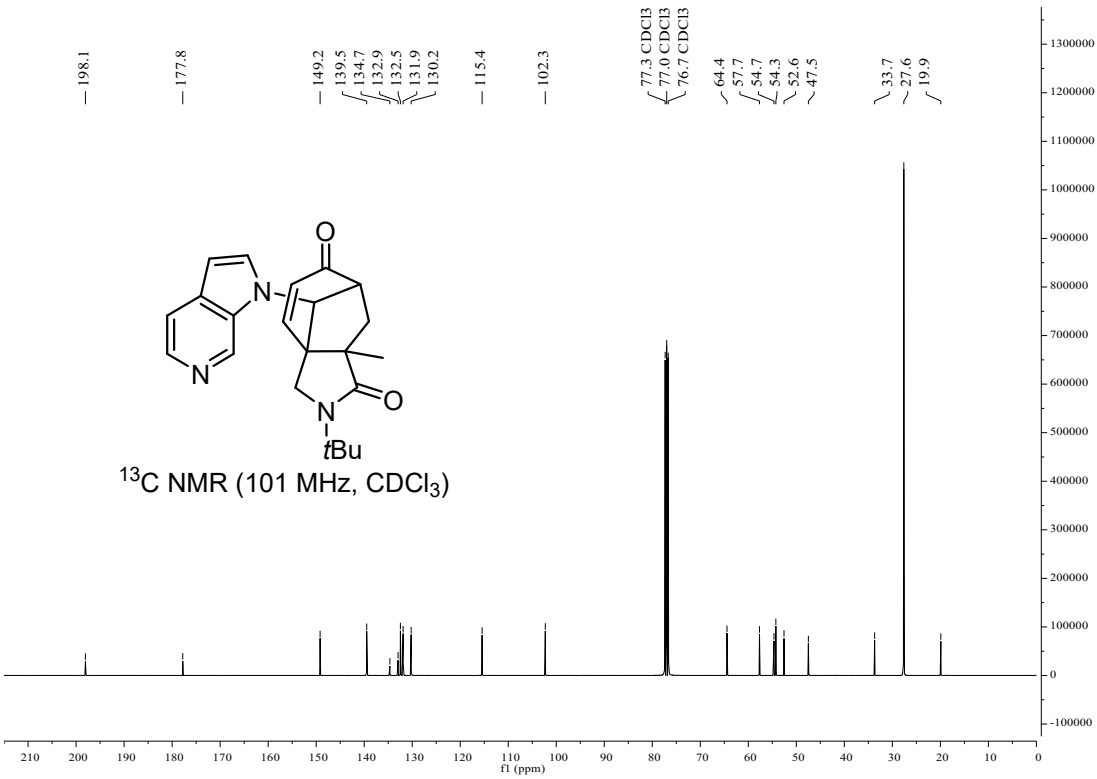


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 43

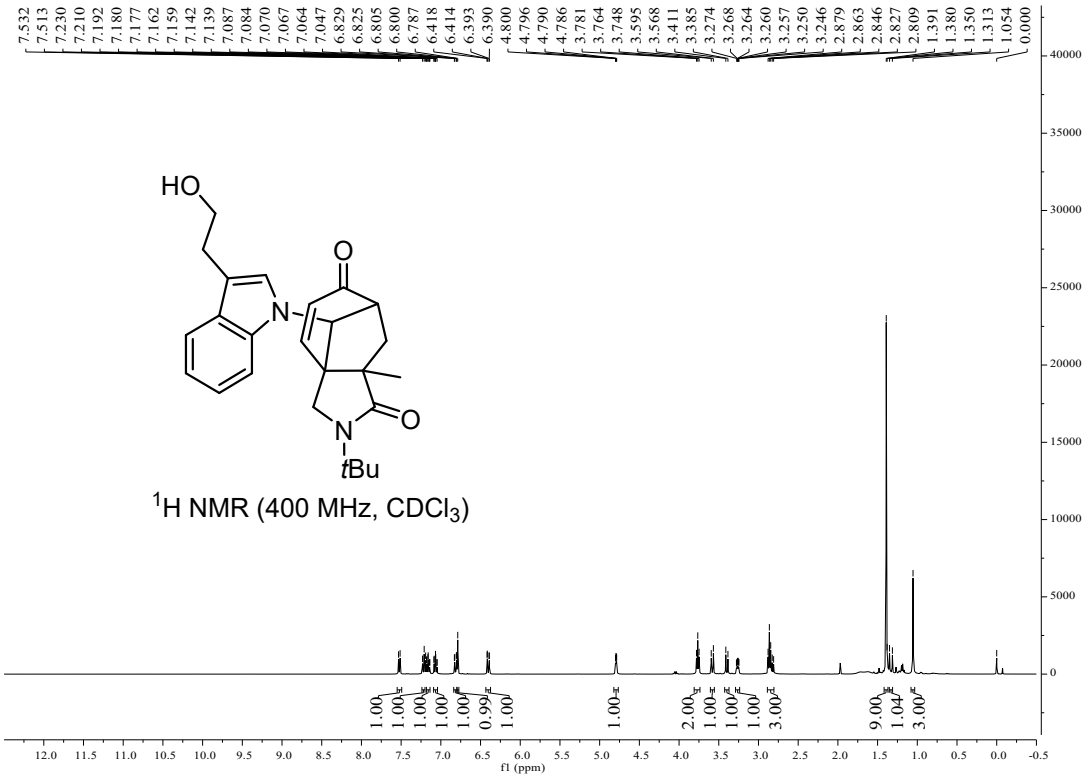


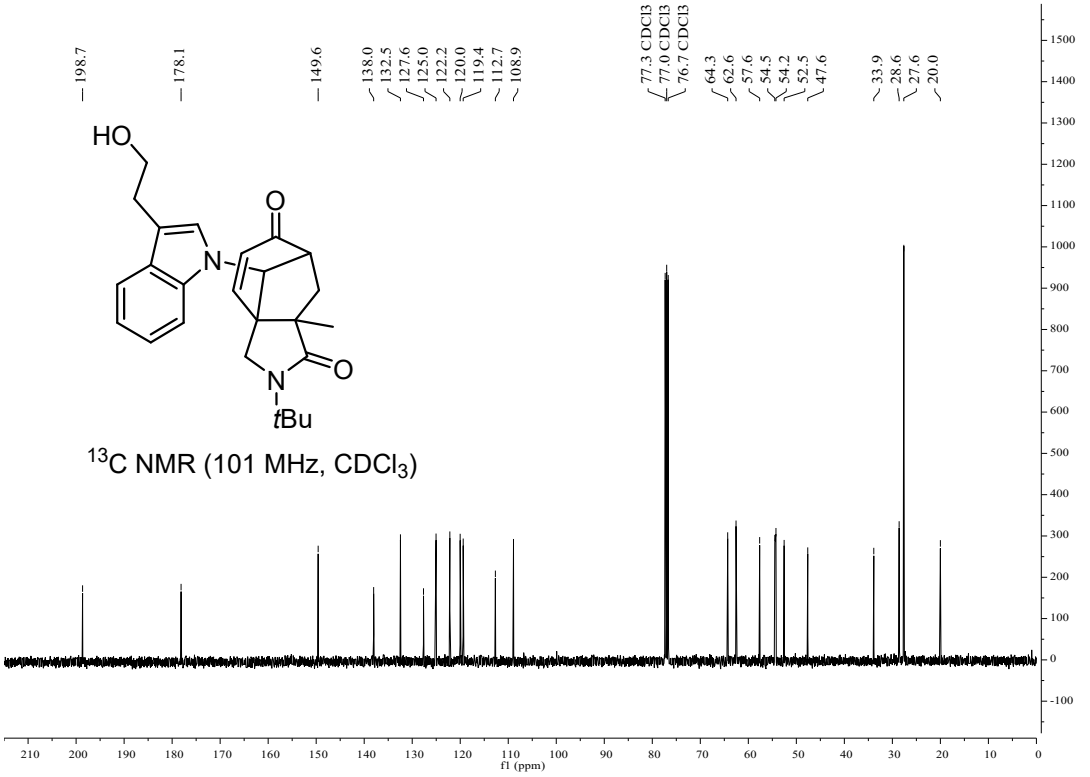
^{1}H NMR (400 MHz, $CDCl_3$)



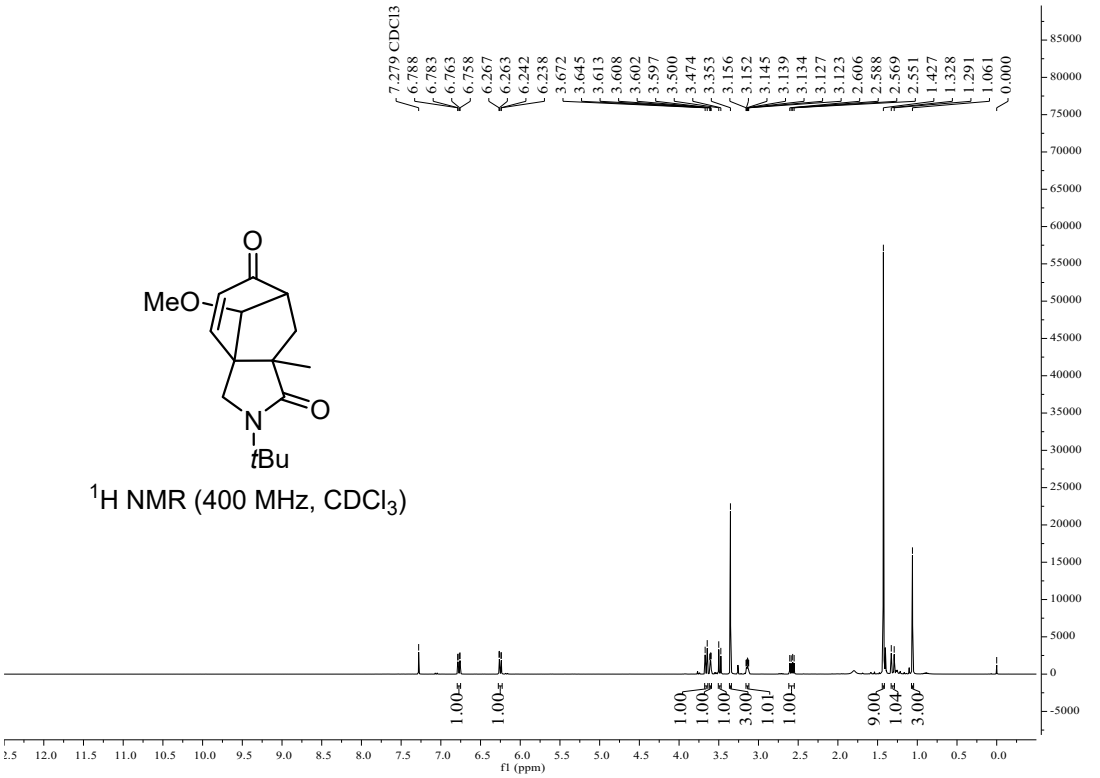
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 44

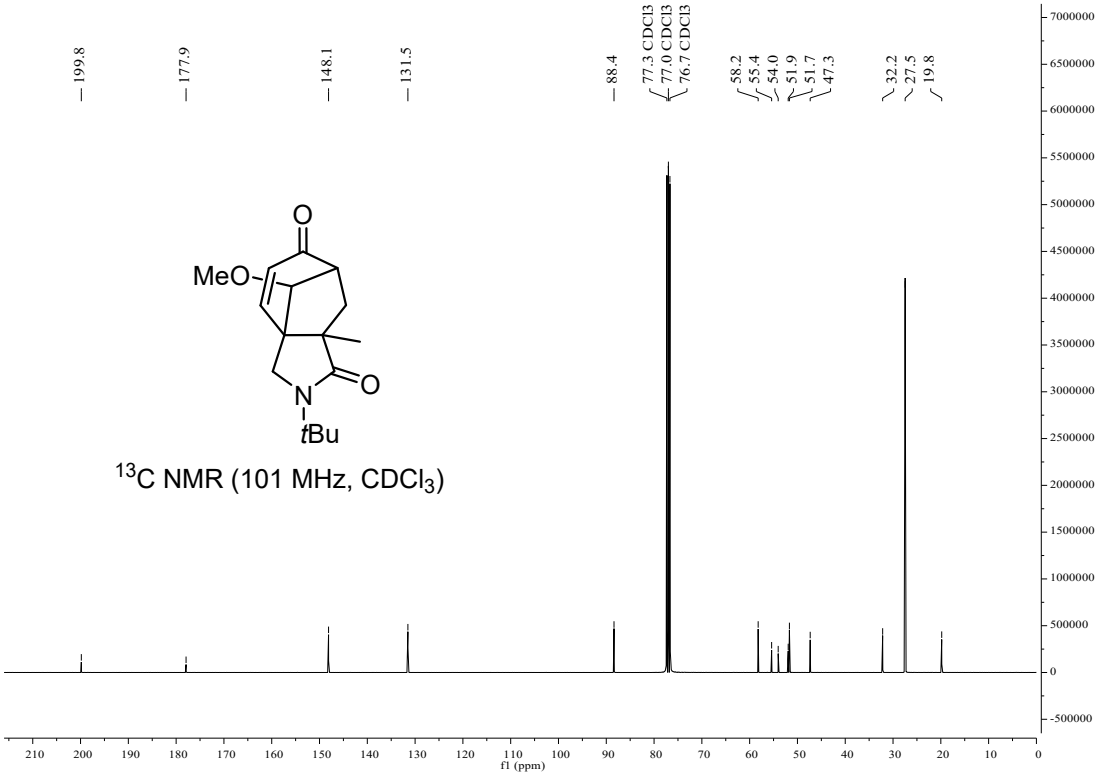

HO
O
N
O
N
tBu
1H NMR (400 MHz, CDCl3)
f1 (ppm)


HO
O
N
O
N
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 45

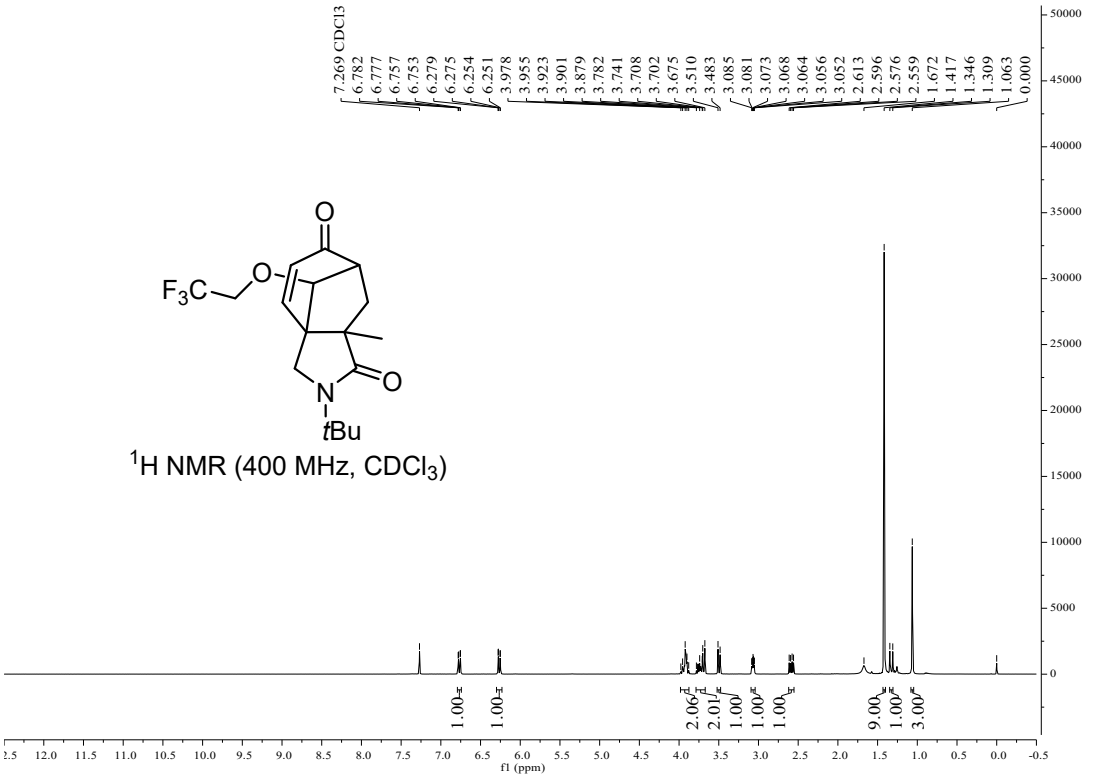


^{1}H NMR (400 MHz, $CDCl_3$)

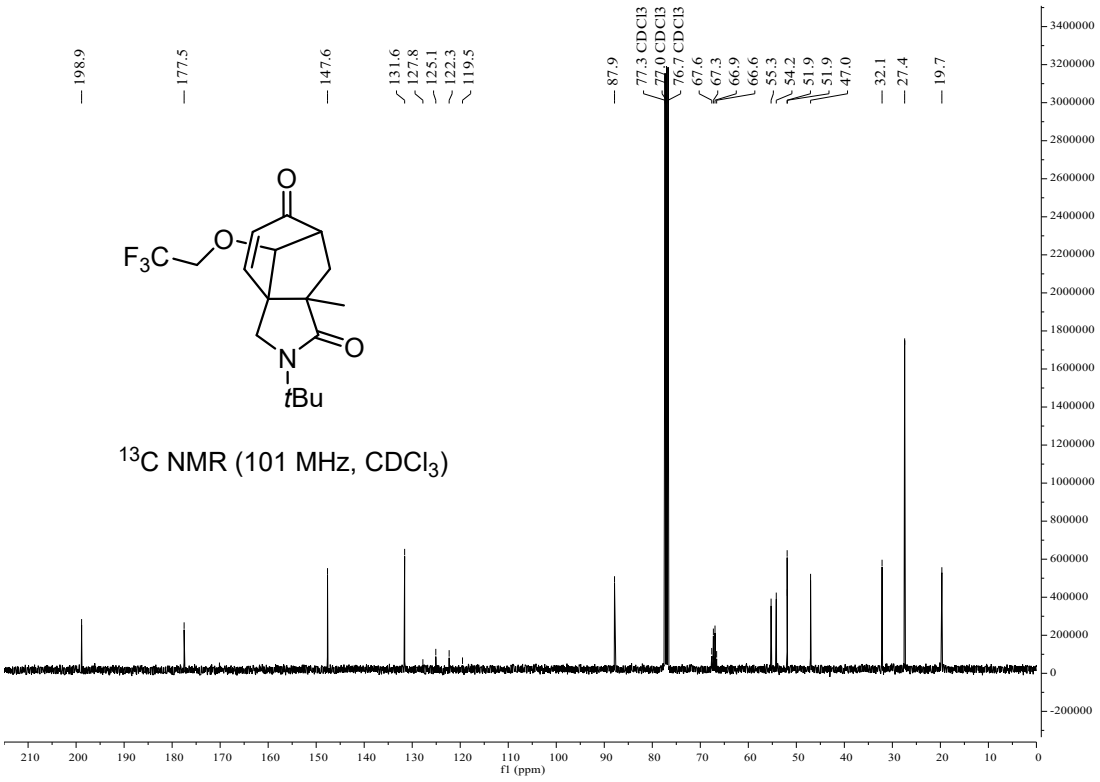


^{13}C NMR (101 MHz, $CDCl_3$)

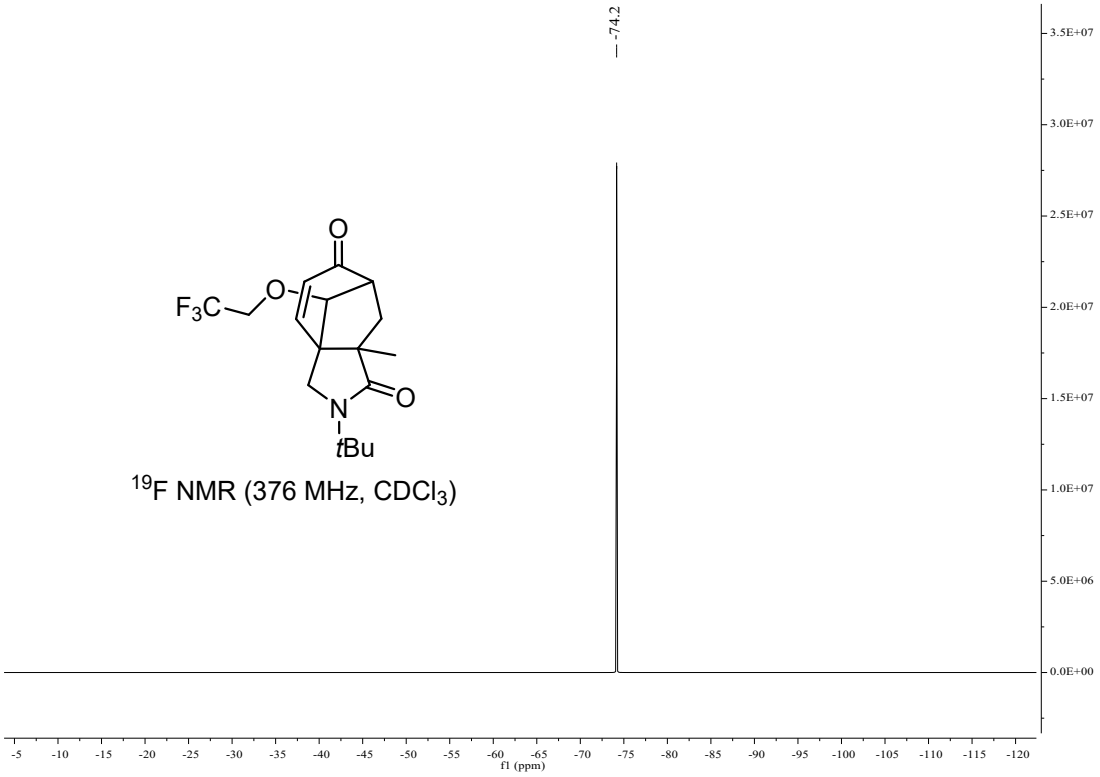
Compound 46



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

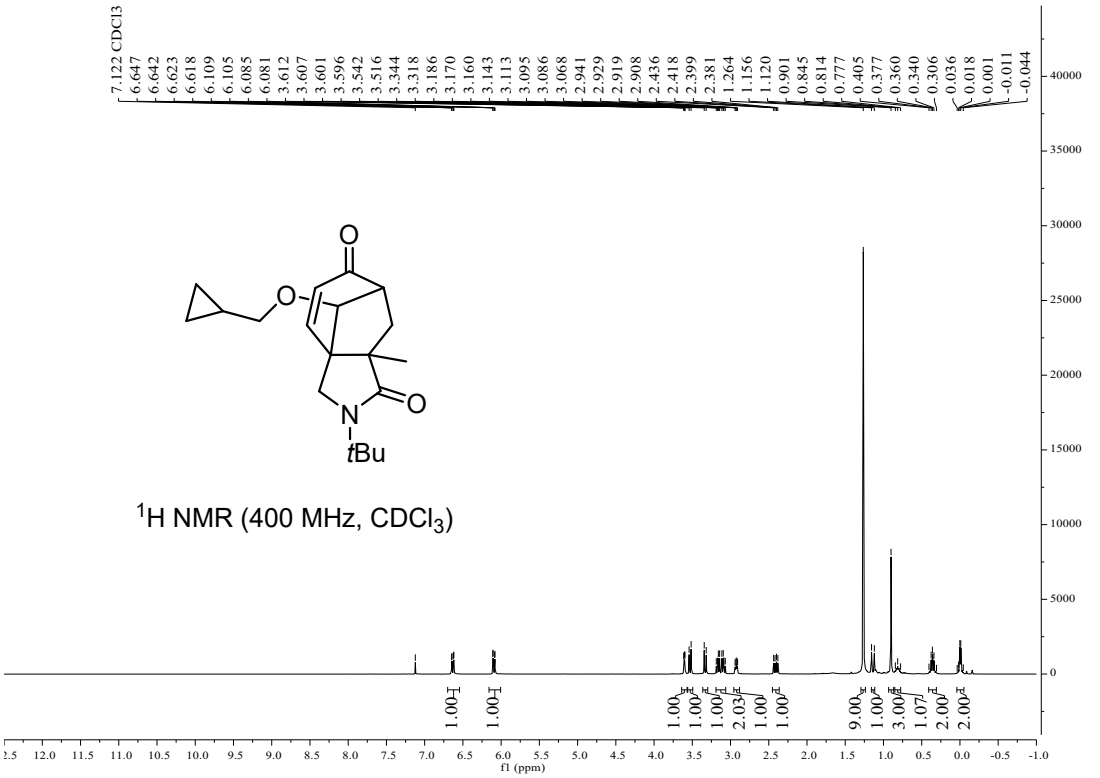


^{13}C NMR (101 MHz, $CDCl_3$)

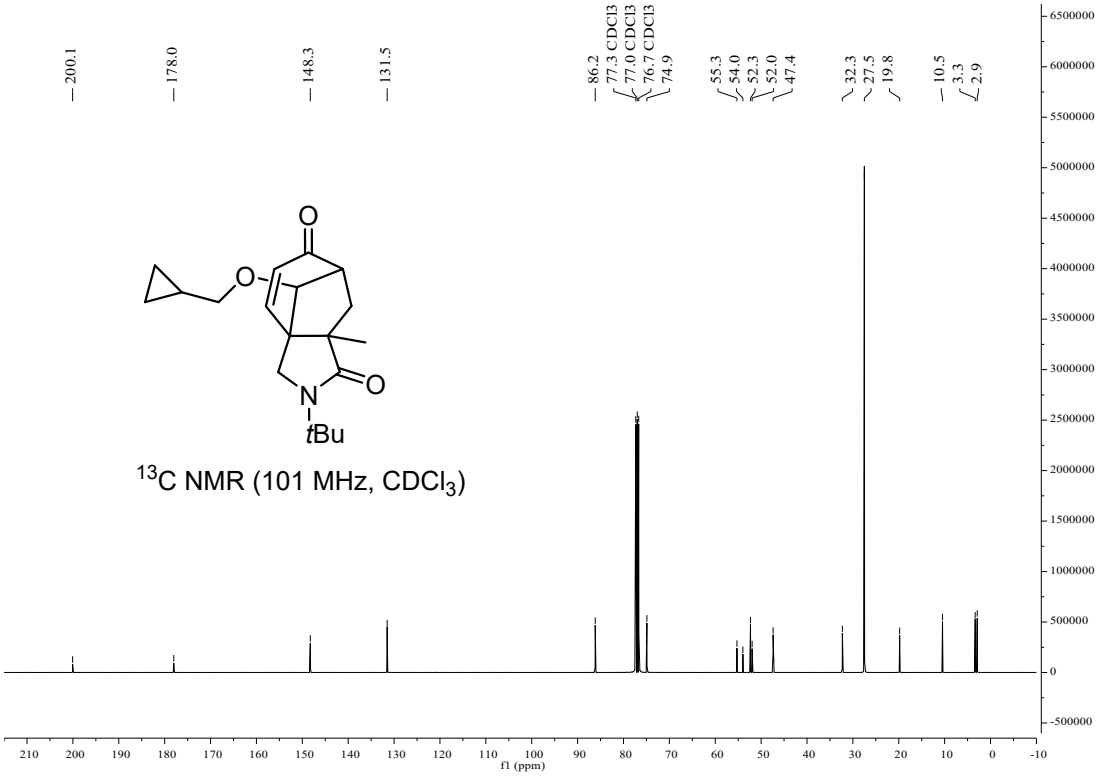


^{19}F NMR (376 MHz, $CDCl_3$)

Compound 47

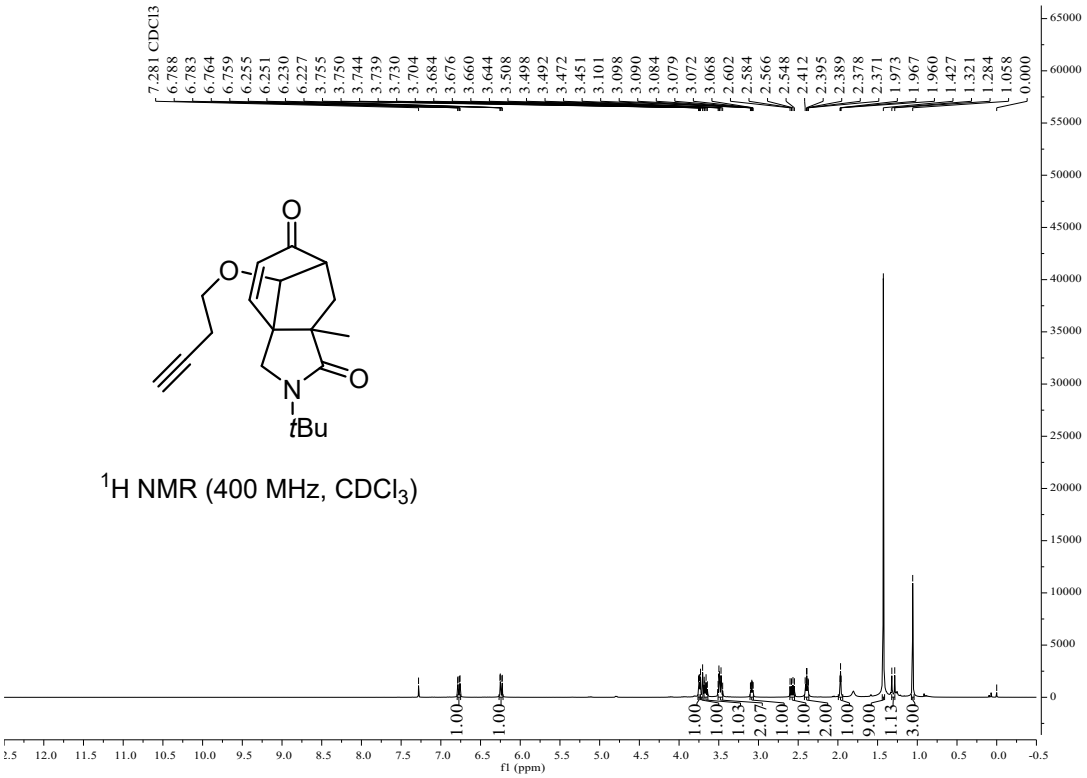


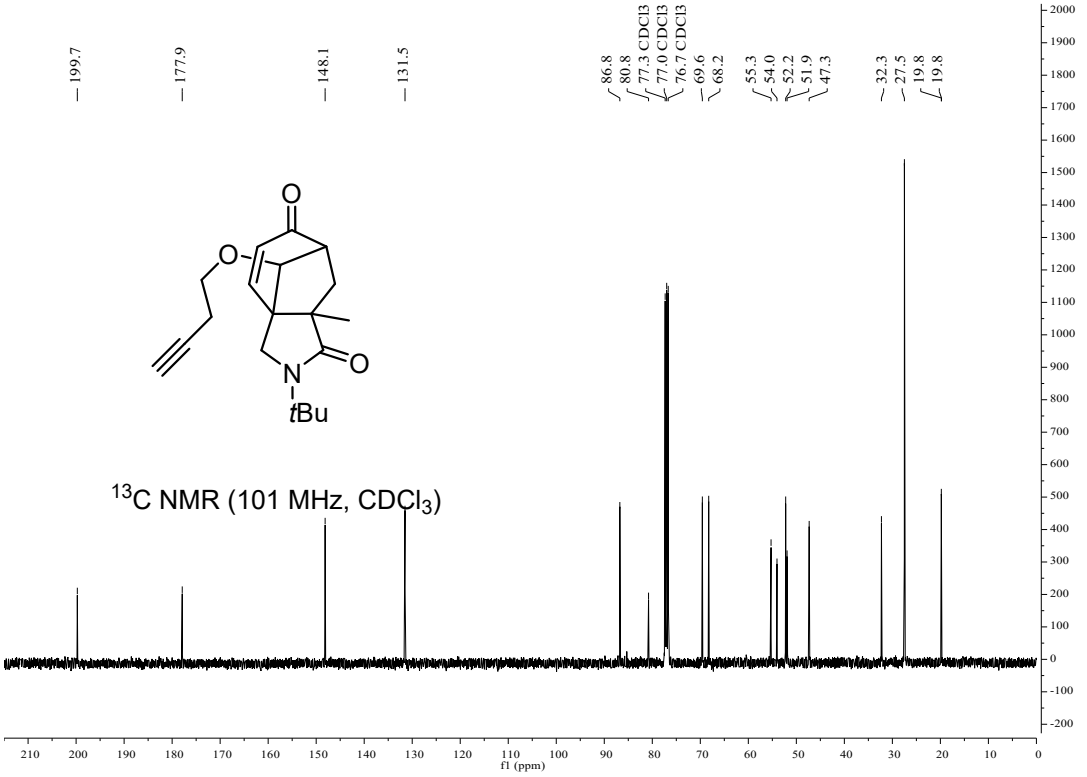
^{1}H NMR (400 MHz, $CDCl_3$)



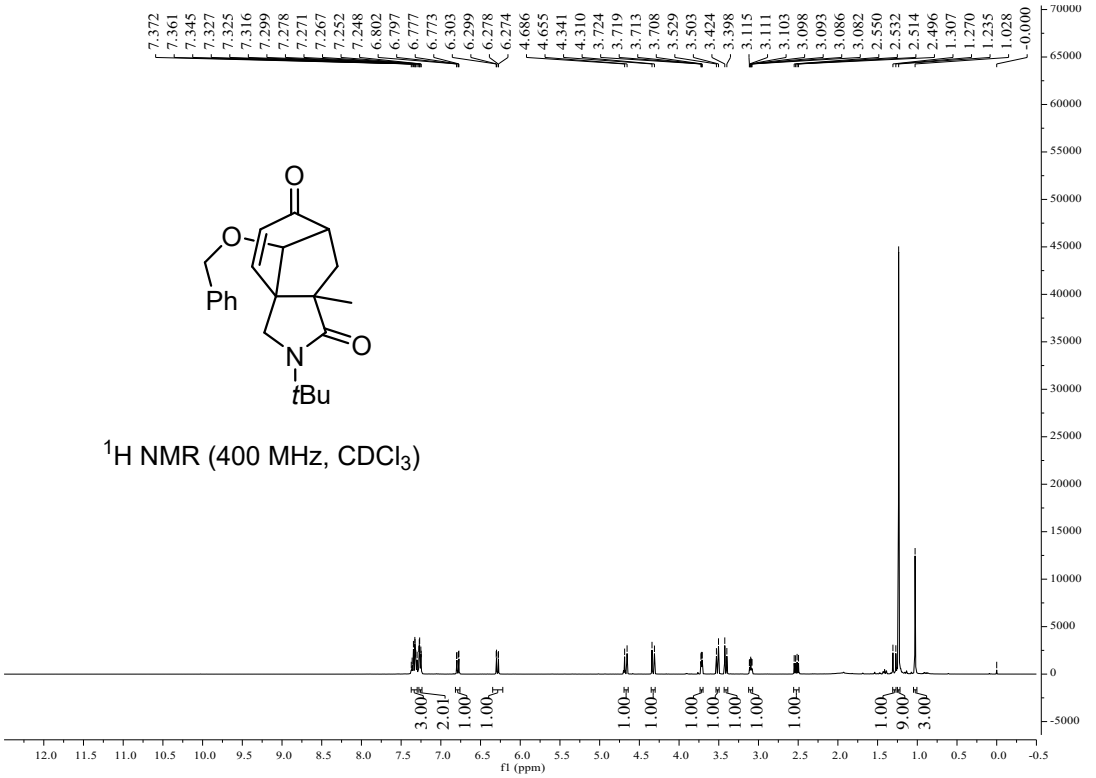
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 48

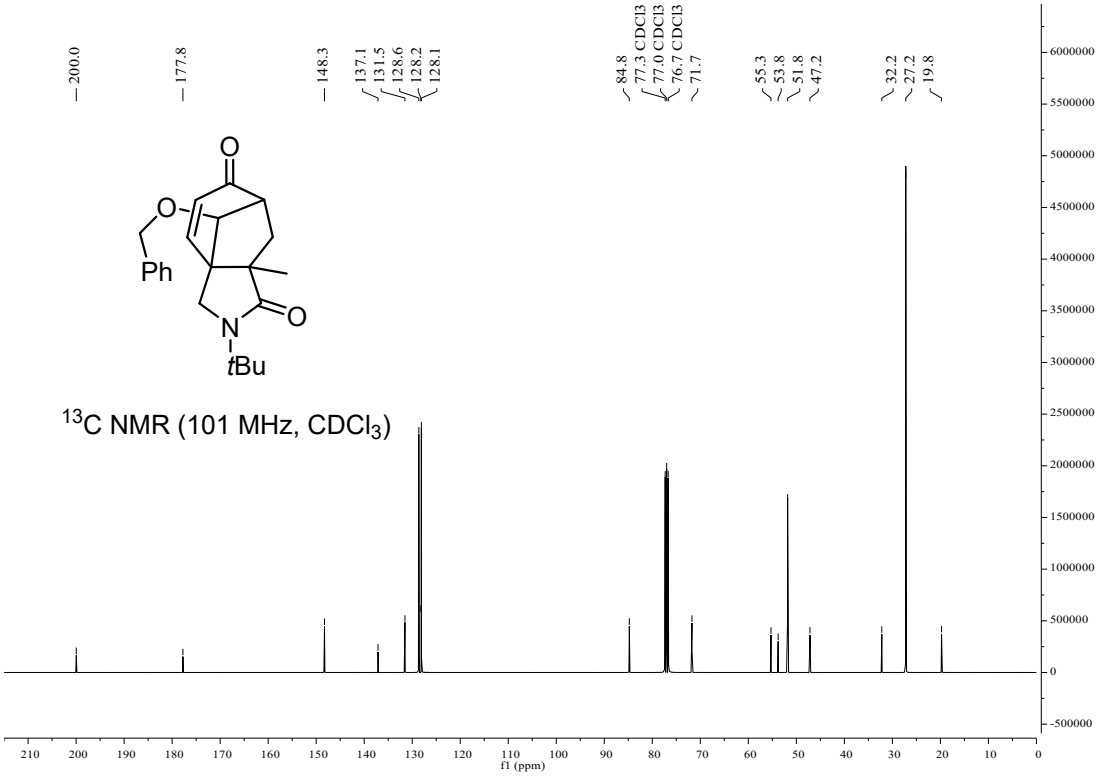

7.281 CDCl3
6.788
6.783
6.764
6.759
6.255
6.251
6.230
6.227
3.755
3.750
3.744
3.739
3.730
3.704
3.684
3.676
3.660
3.644
3.508
3.498
3.492
3.472
3.451
3.101
3.098
3.090
3.084
3.079
3.072
3.068
2.602
2.584
2.566
2.548
2.412
2.395
2.389
2.378
2.371
1.973
1.967
1.960
1.427
1.321
1.284
1.058
0.000
O
O
N
O
tBu
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.03
2.07
1.00
1.00
2.00
1.00
9.00
1.13
3.00
f1 (ppm)


199.7
177.9
148.1
131.5
86.8
80.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
69.6
68.2
55.3
54.0
52.2
51.9
47.3
32.3
27.5
19.8
19.8
O
O
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 49

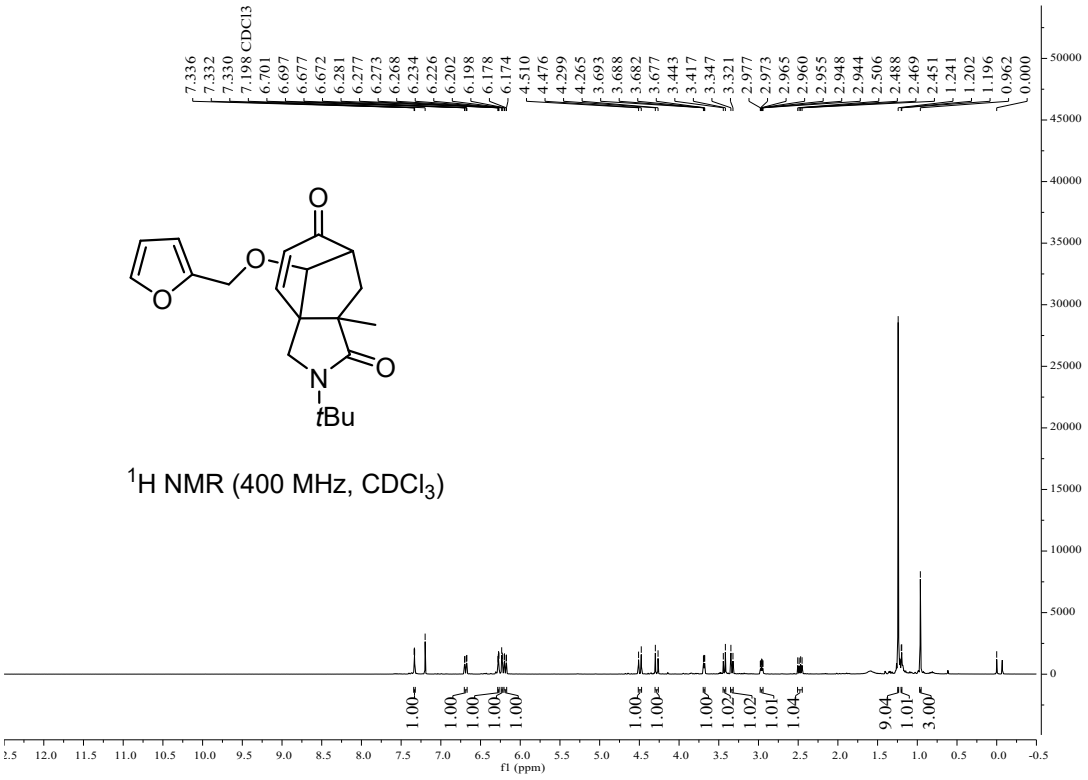


^{1}H NMR (400 MHz, $CDCl_3$)

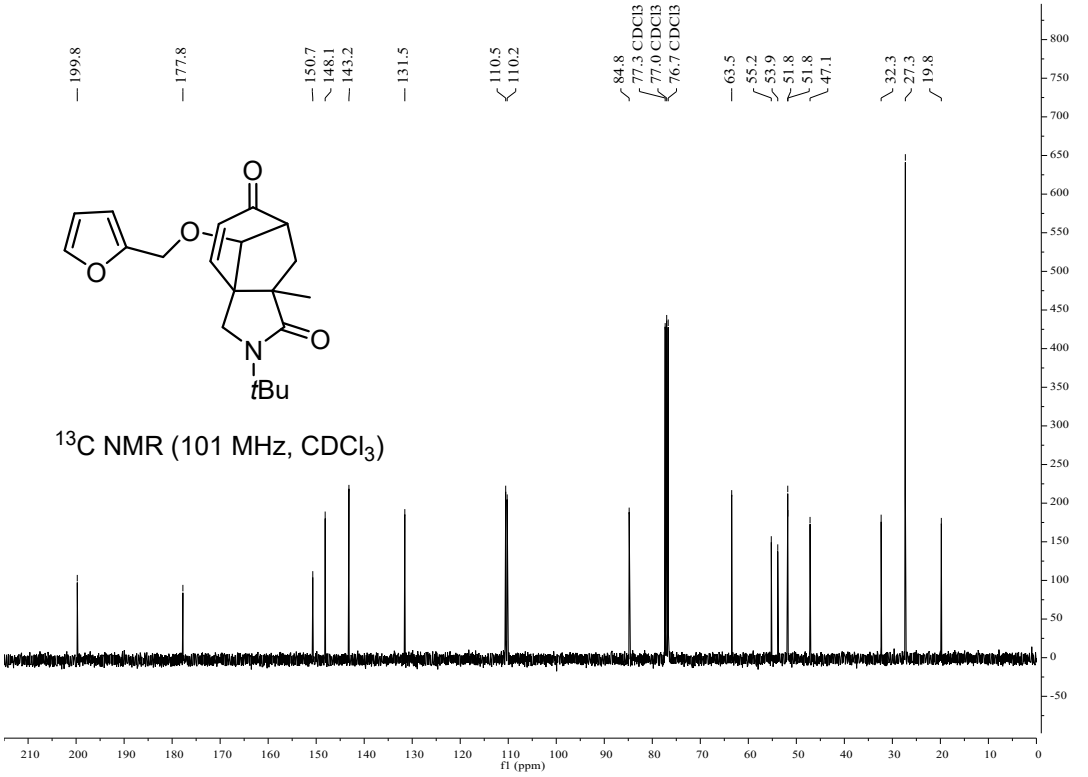


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 50

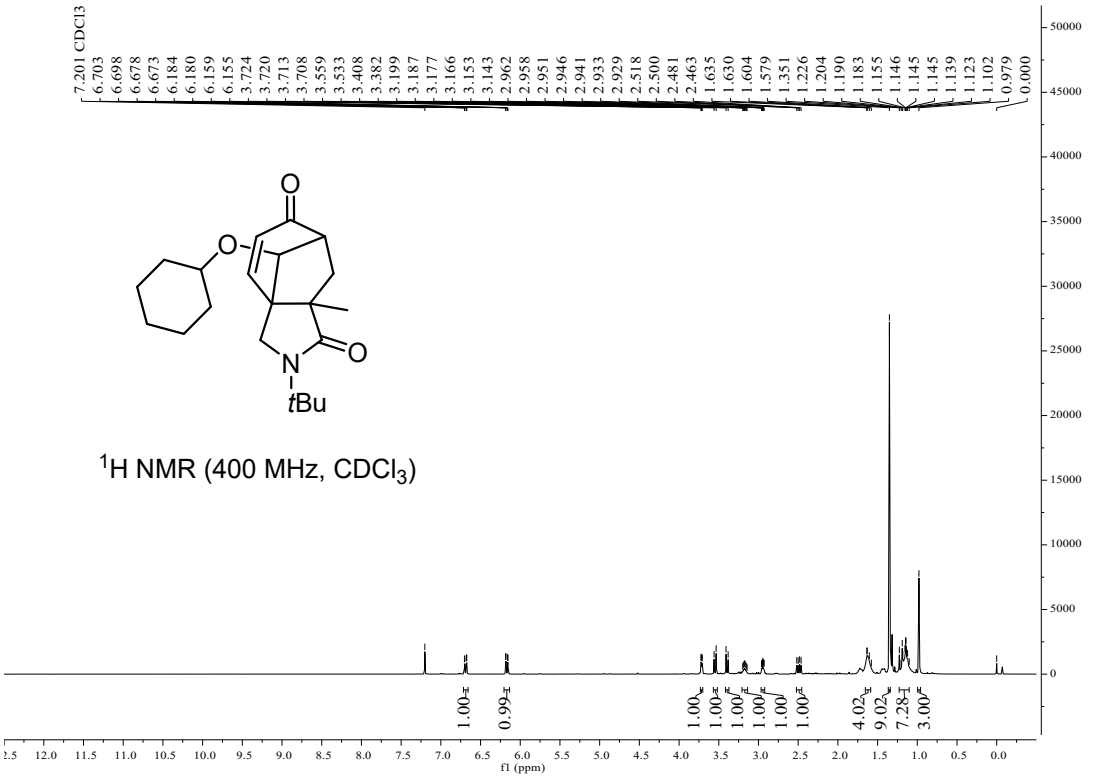


^{1}H NMR (400 MHz, $CDCl_3$)

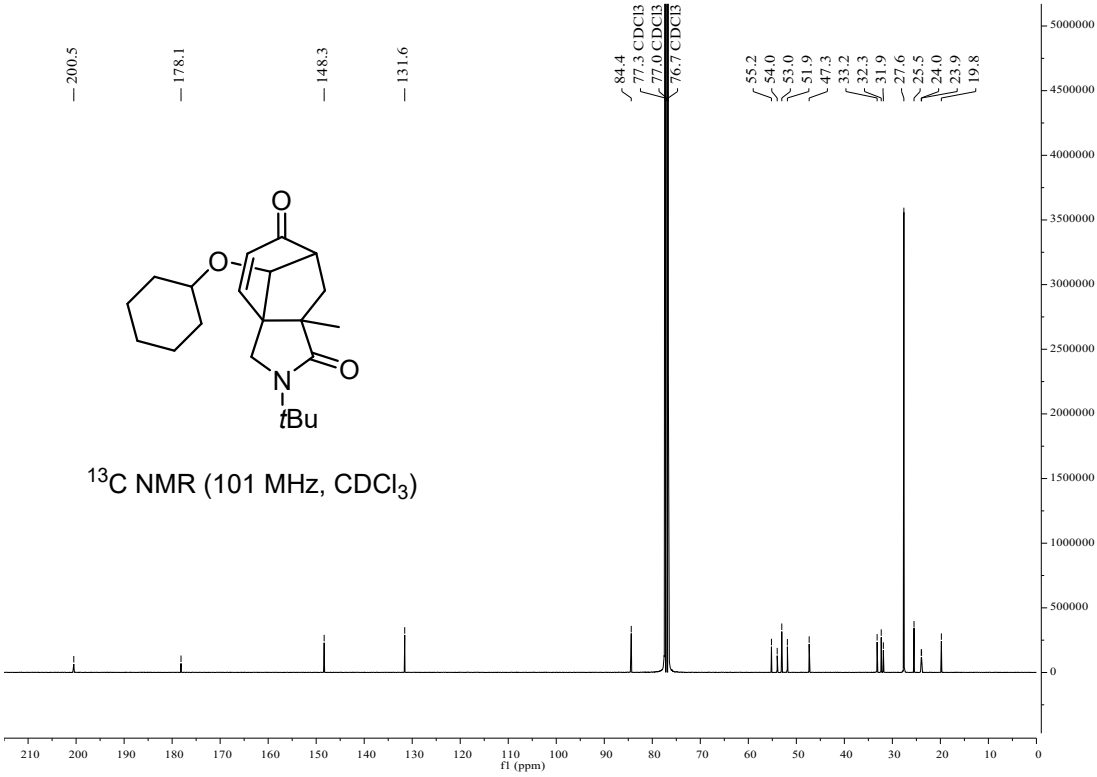


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 51

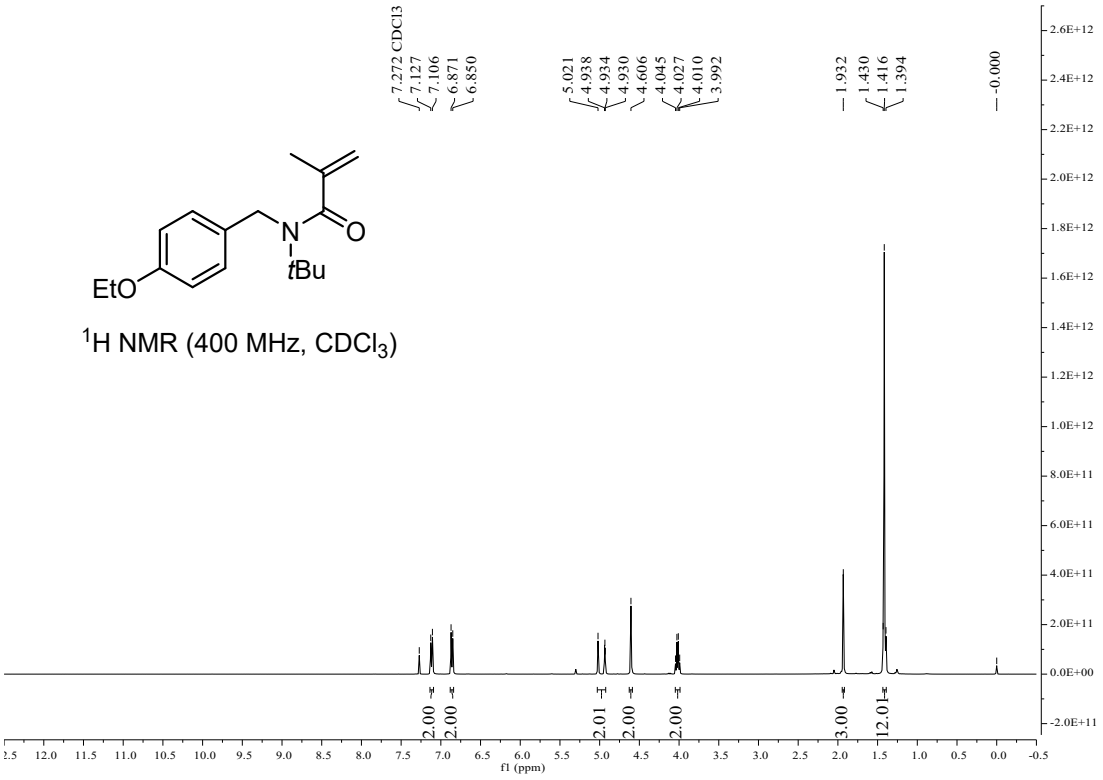


^{1}H NMR (400 MHz, $CDCl_3$)

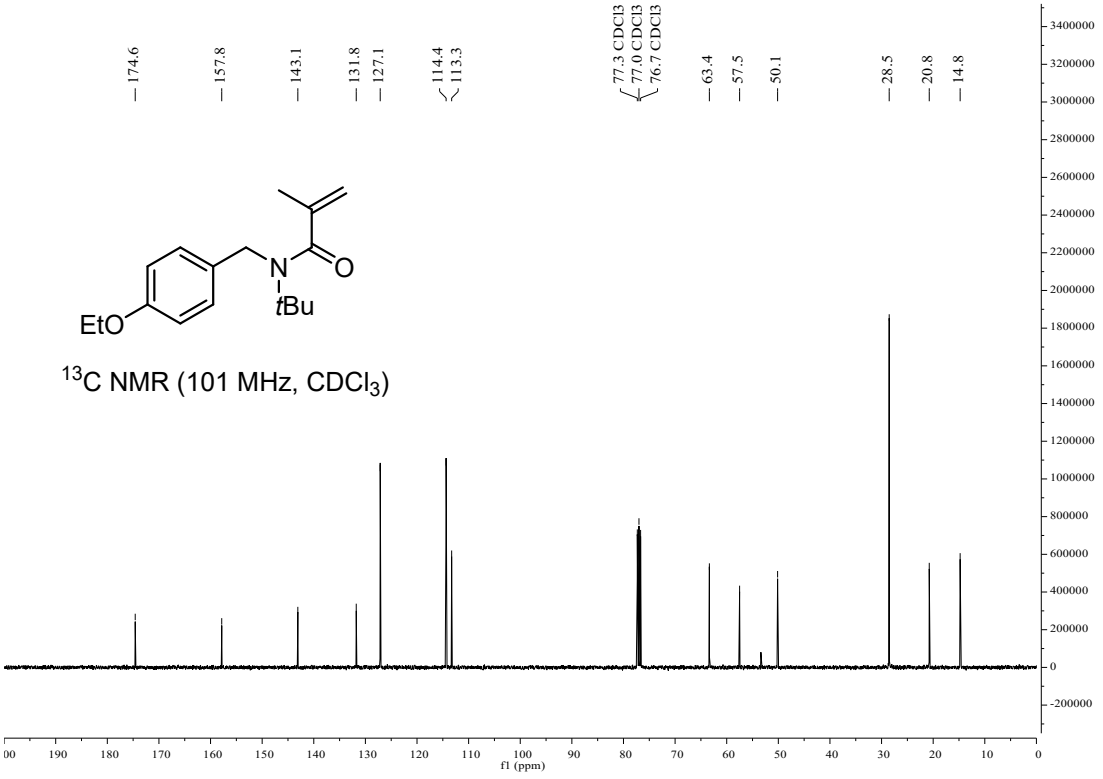


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 5

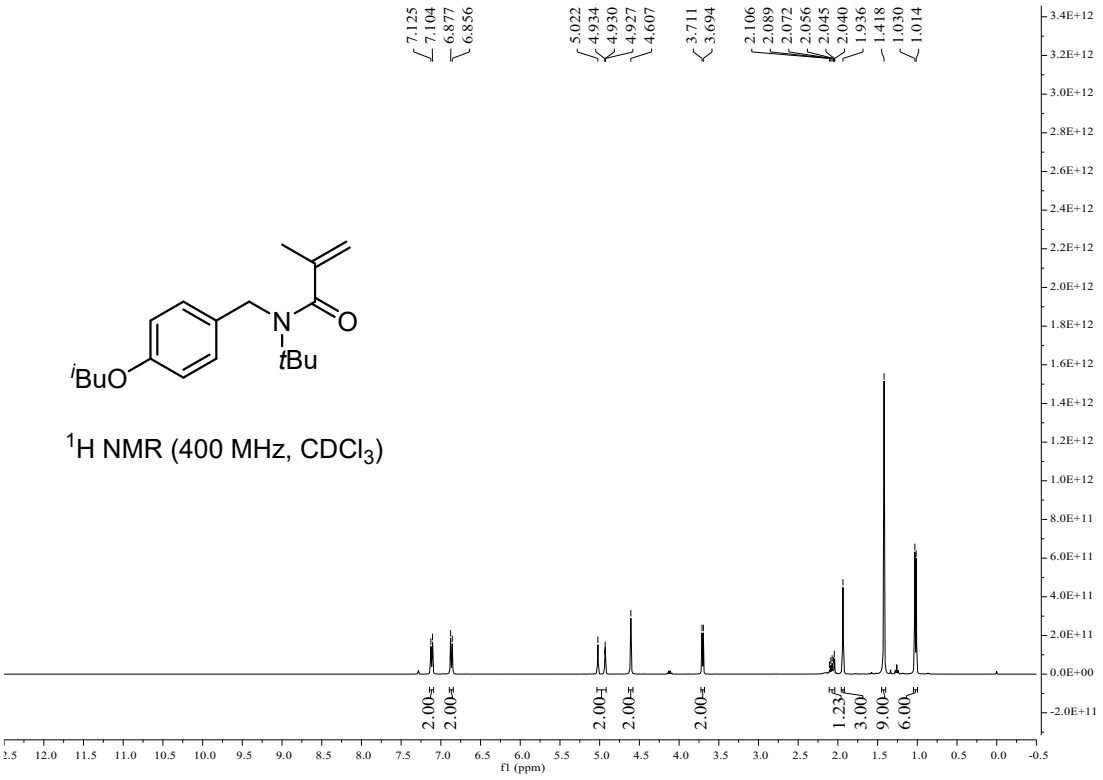


^{1}H NMR (400 MHz, $CDCl_3$)

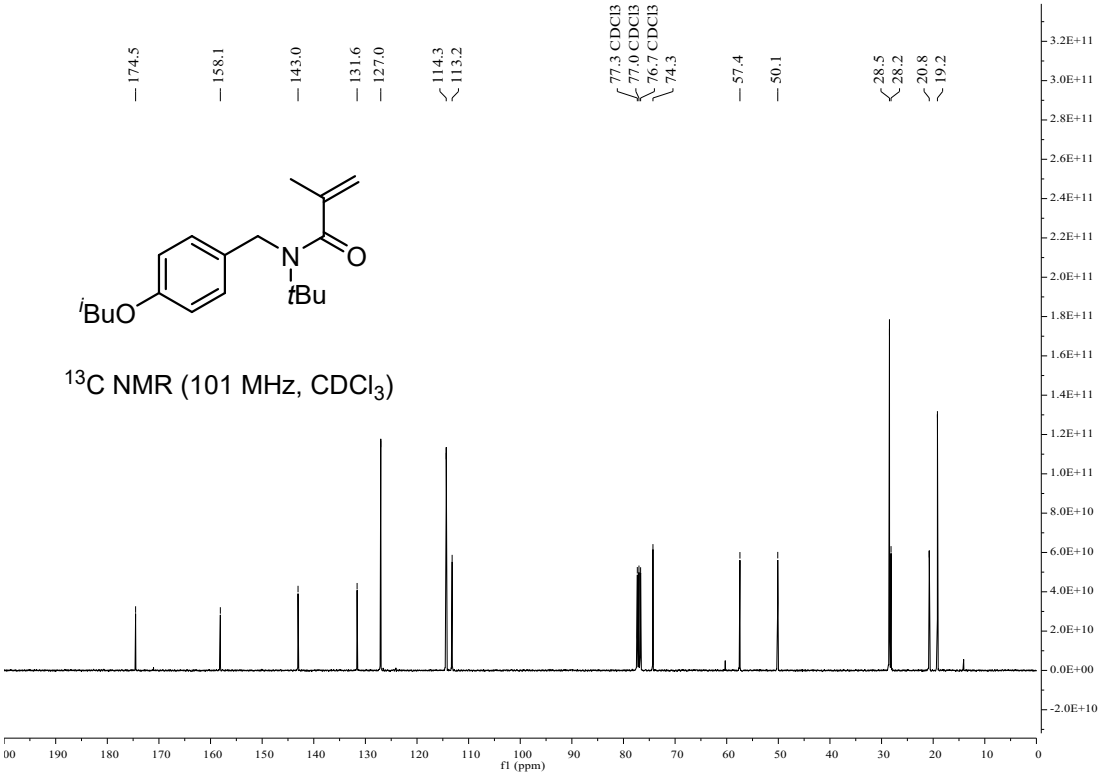


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 7

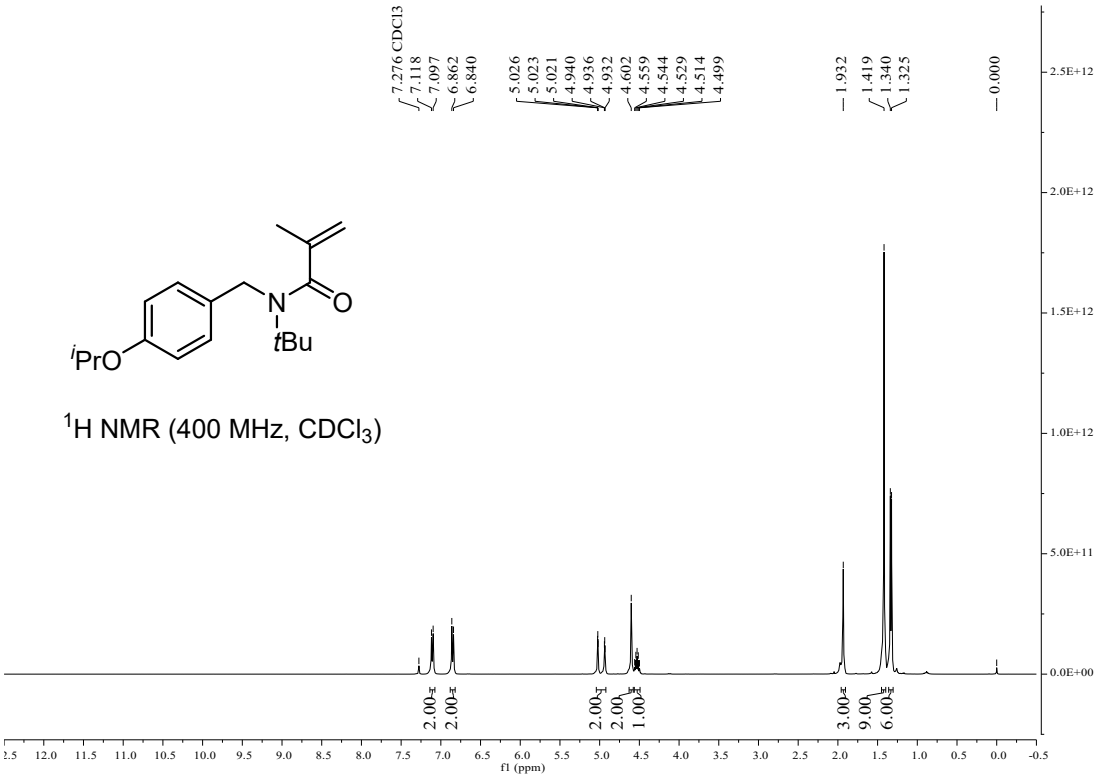


^{1}H NMR (400 MHz, $CDCl_3$)

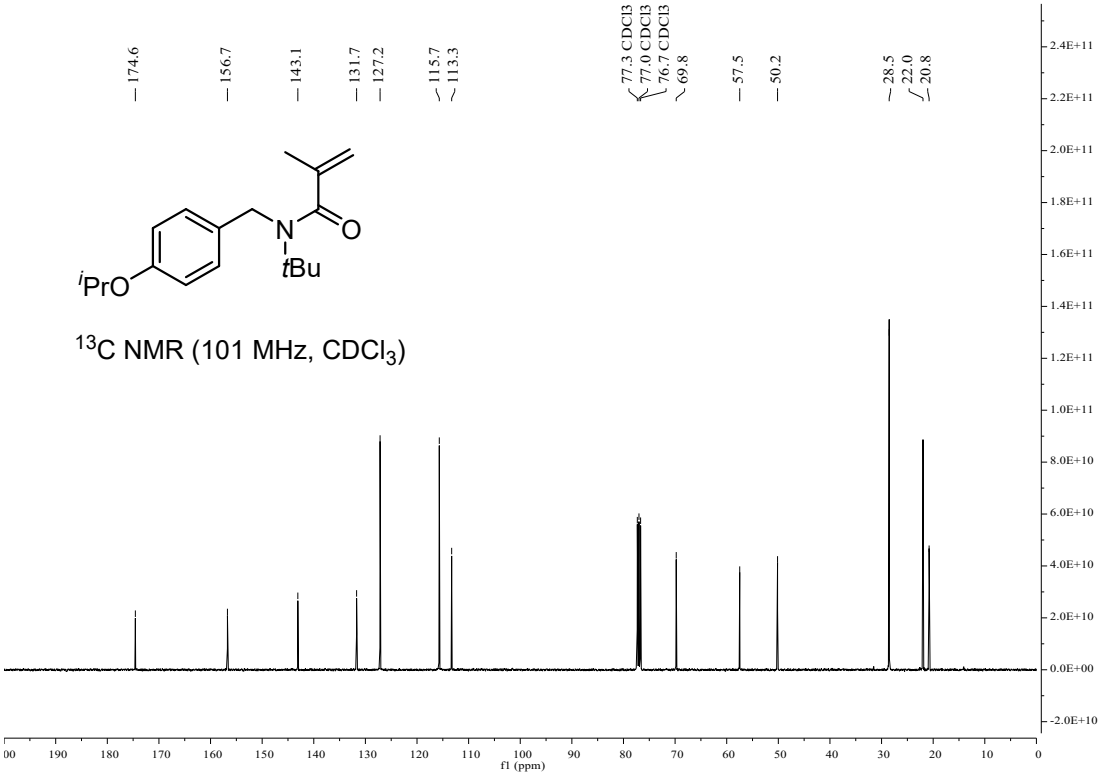


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 8

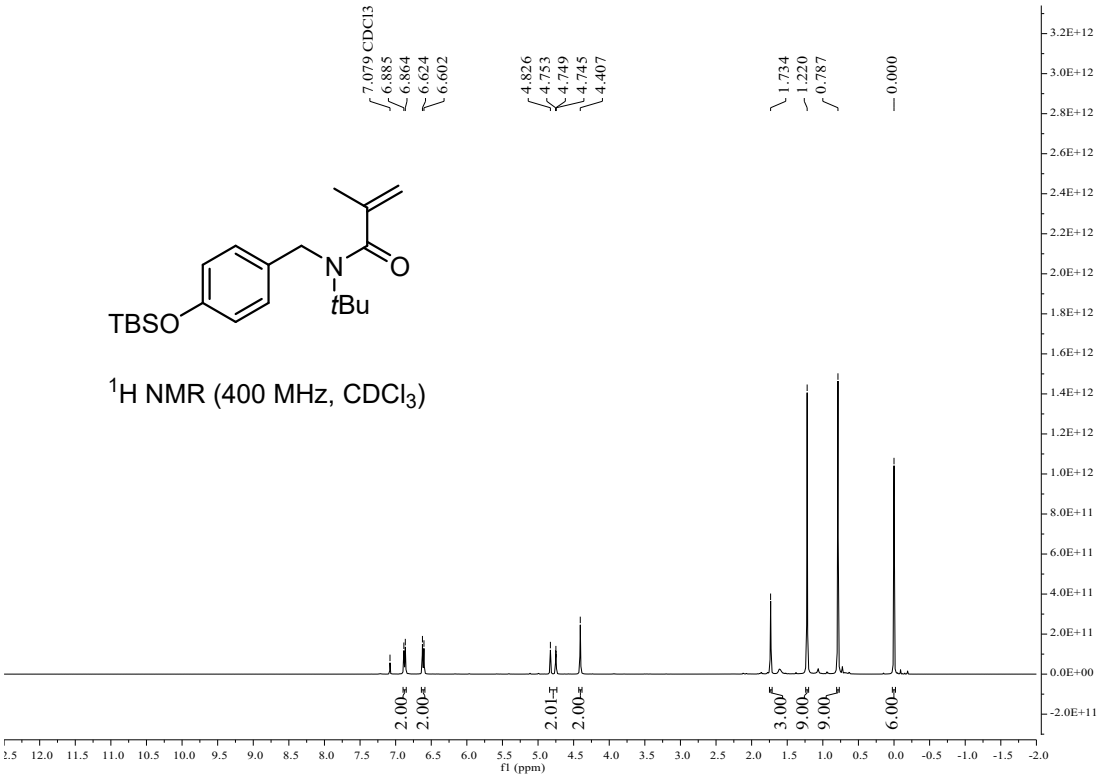


^{1}H NMR (400 MHz, $CDCl_3$)

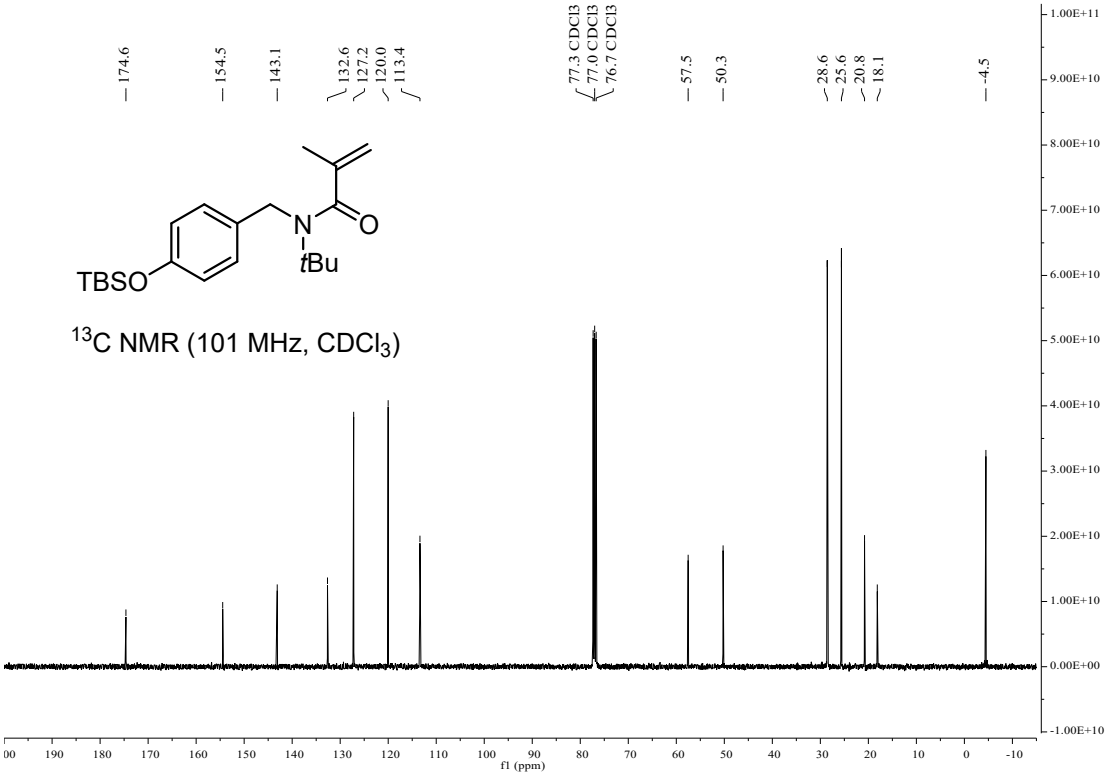


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 9

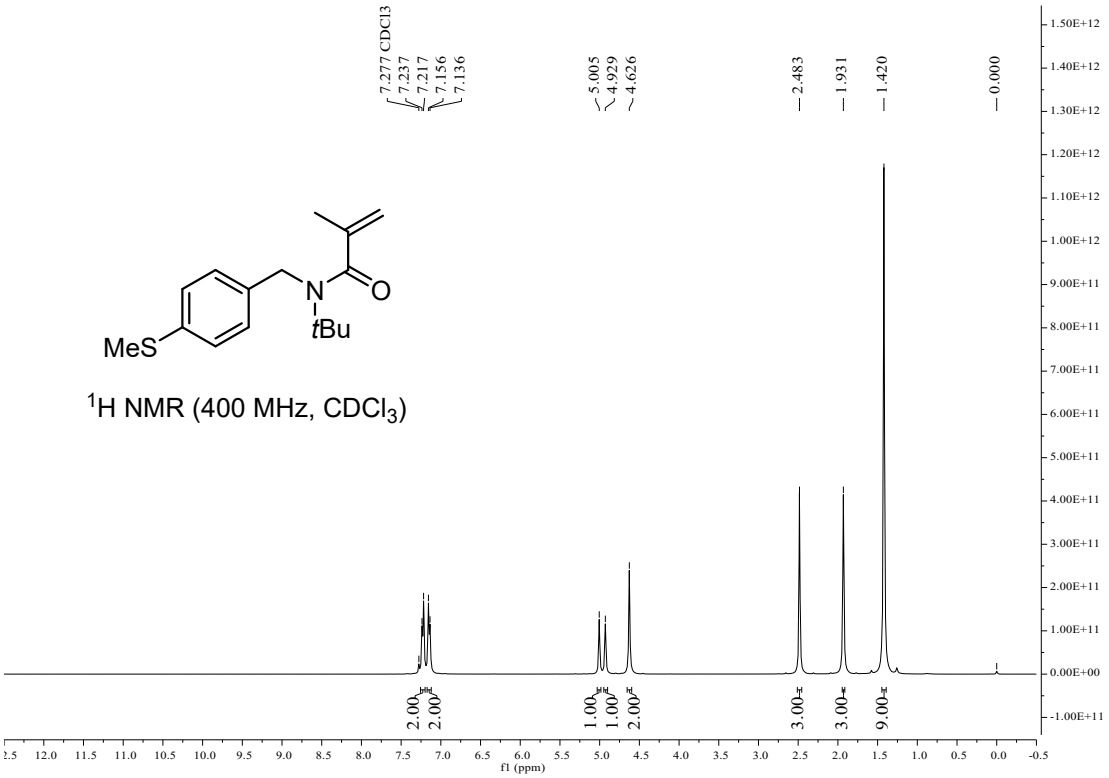


^{1}H NMR (400 MHz, $CDCl_3$)

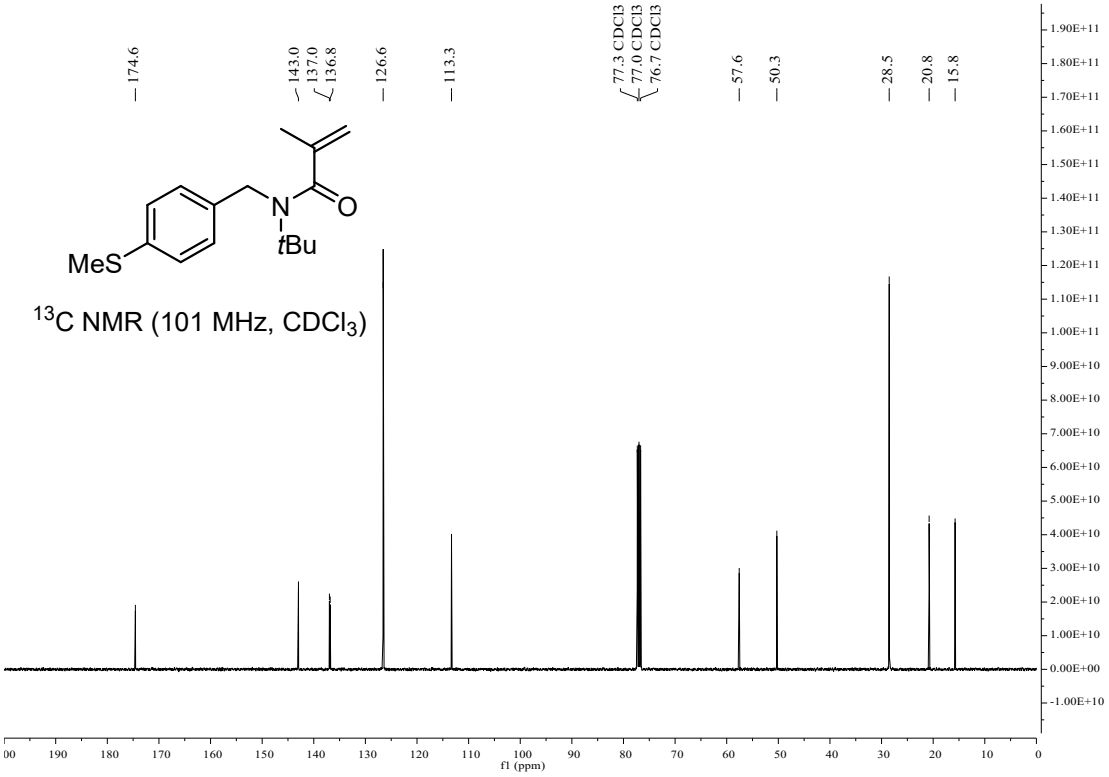


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 10

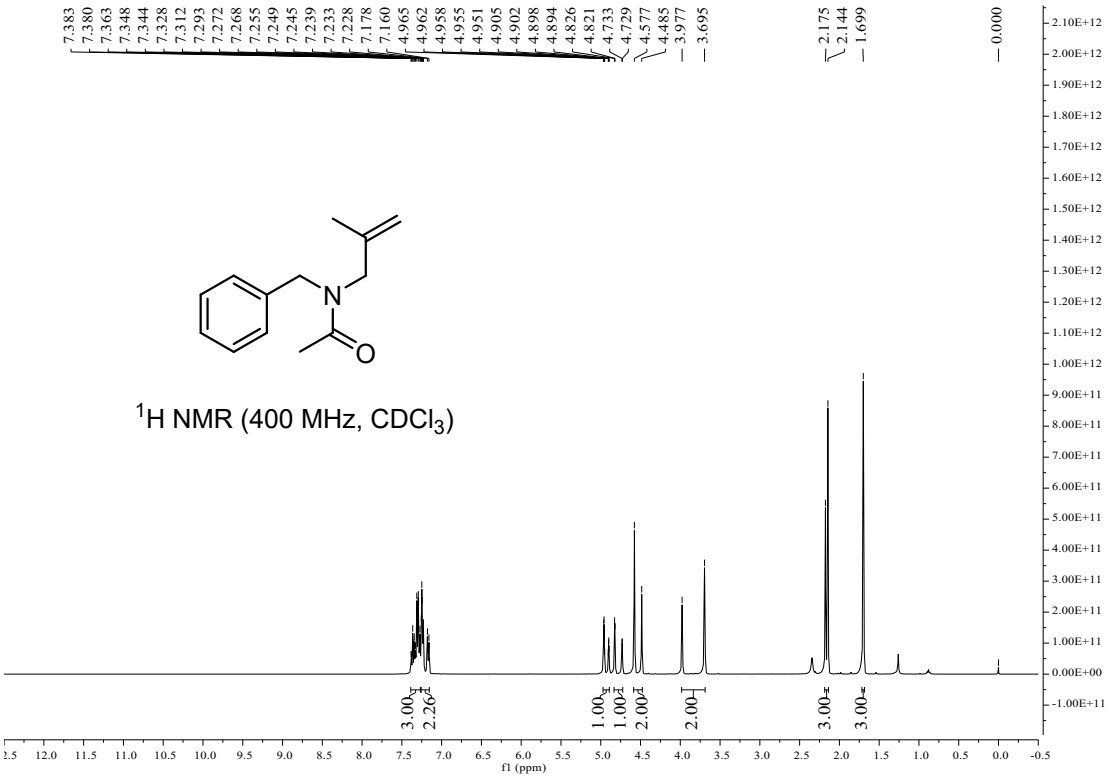


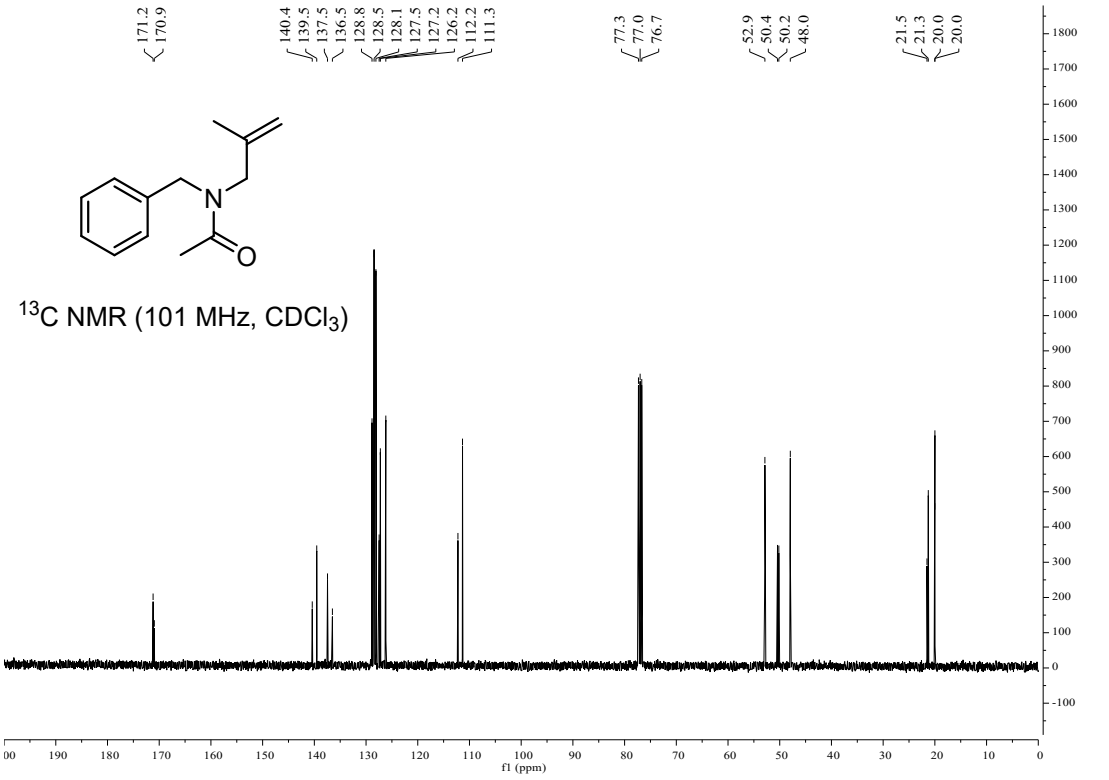
^{1}H NMR (400 MHz, $CDCl_3$)



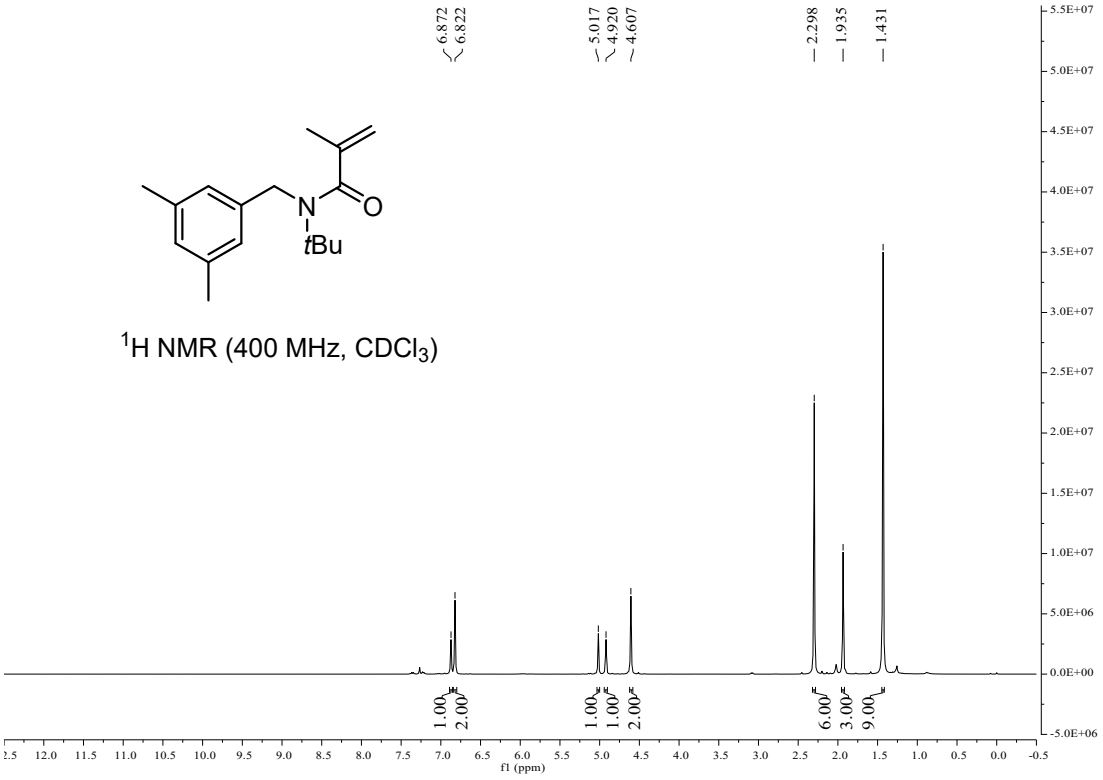
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 14

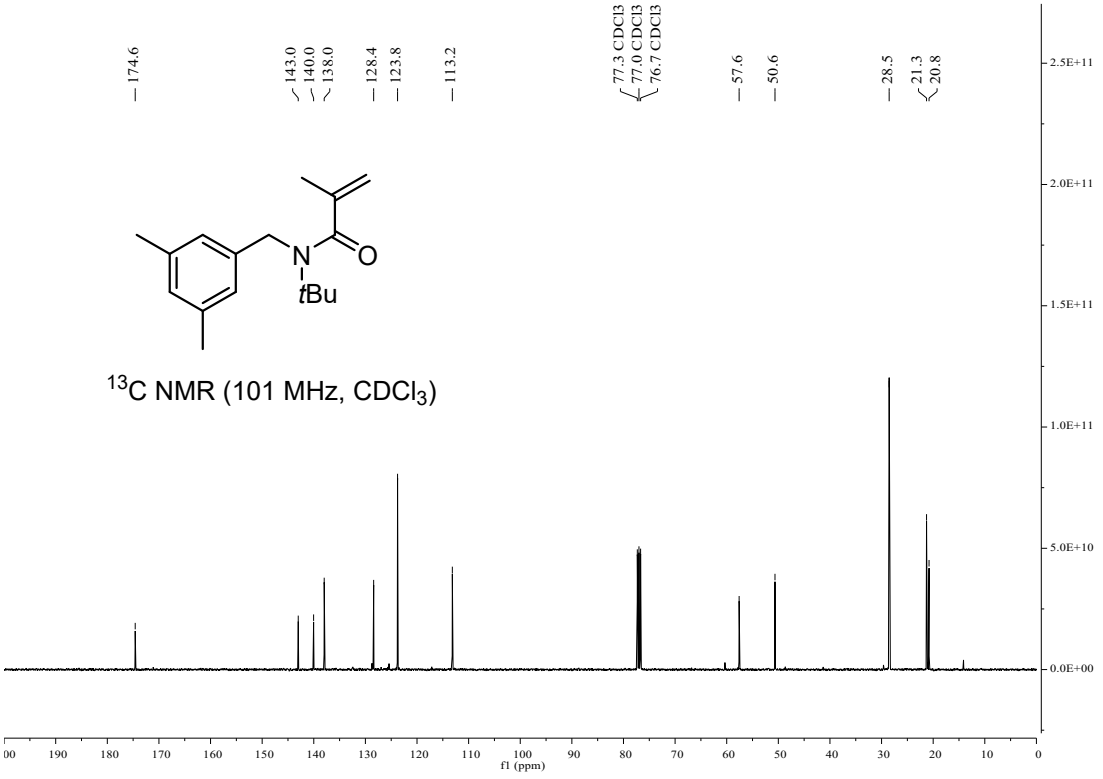

7.383
7.380
7.363
7.348
7.344
7.328
7.312
7.293
7.272
7.268
7.255
7.249
7.245
7.239
7.233
7.228
7.178
7.160
4.965
4.962
4.958
4.955
4.951
4.905
4.902
4.898
4.894
4.826
4.821
4.733
4.729
4.577
4.485
3.977
3.695
2.175
2.144
1.699
0.000
N
O
^{1}H NMR (400 MHz, $CDCl_3$)
3.00
2.26
1.00
1.00
2.00
2.00
3.00
3.00
f1 (ppm)


171.2
170.9
140.4
139.5
137.5
136.5
128.8
128.5
128.1
127.5
127.2
126.2
112.2
111.3
77.3
77.0
76.7
52.9
50.4
50.2
48.0
21.5
21.3
20.0
20.0
N
O
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound S1

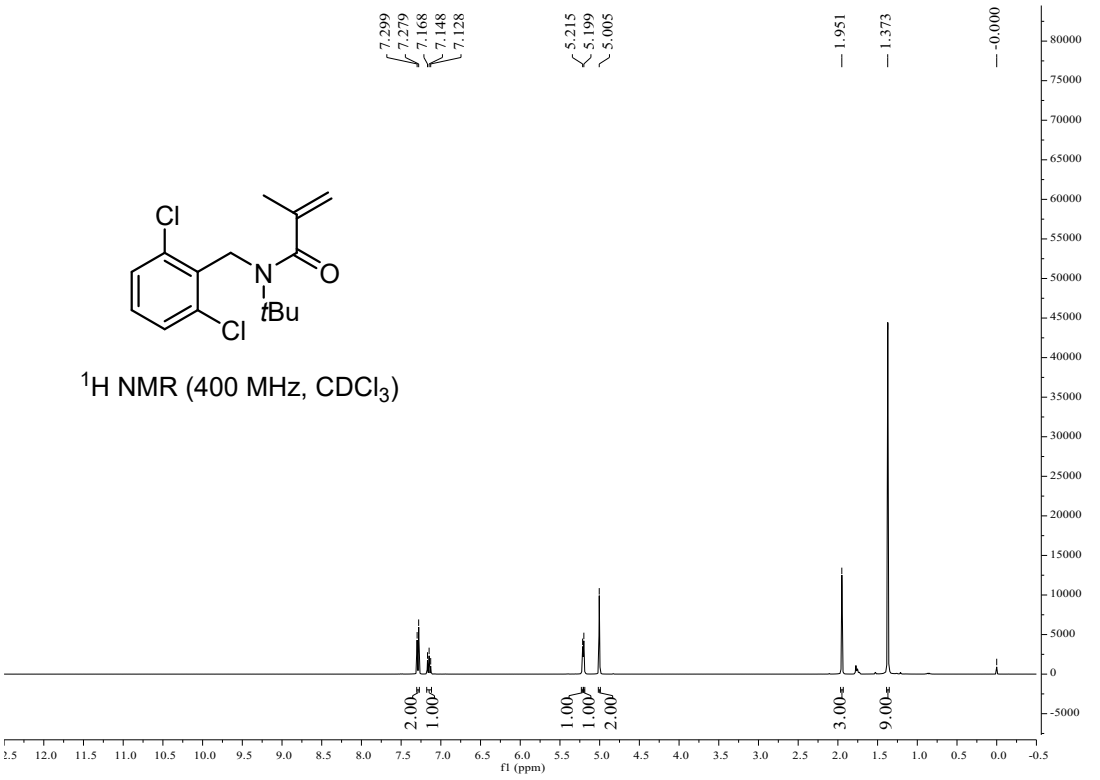


^{1}H NMR (400 MHz, $CDCl_3$)

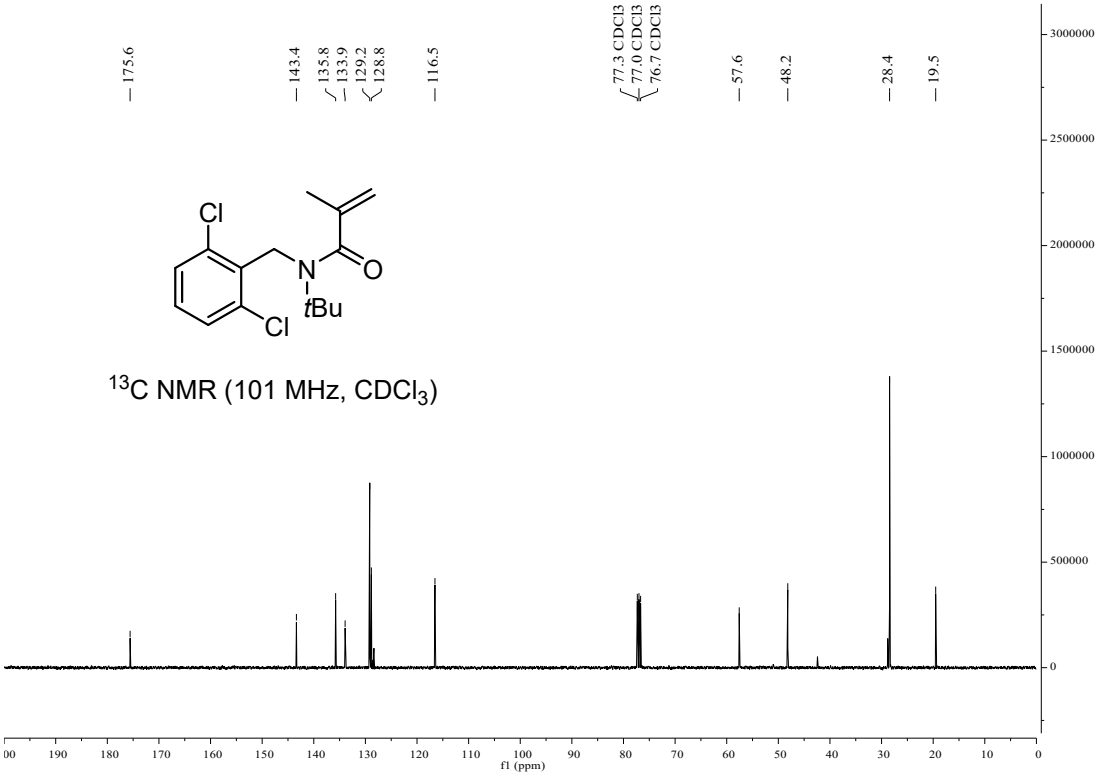


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S2

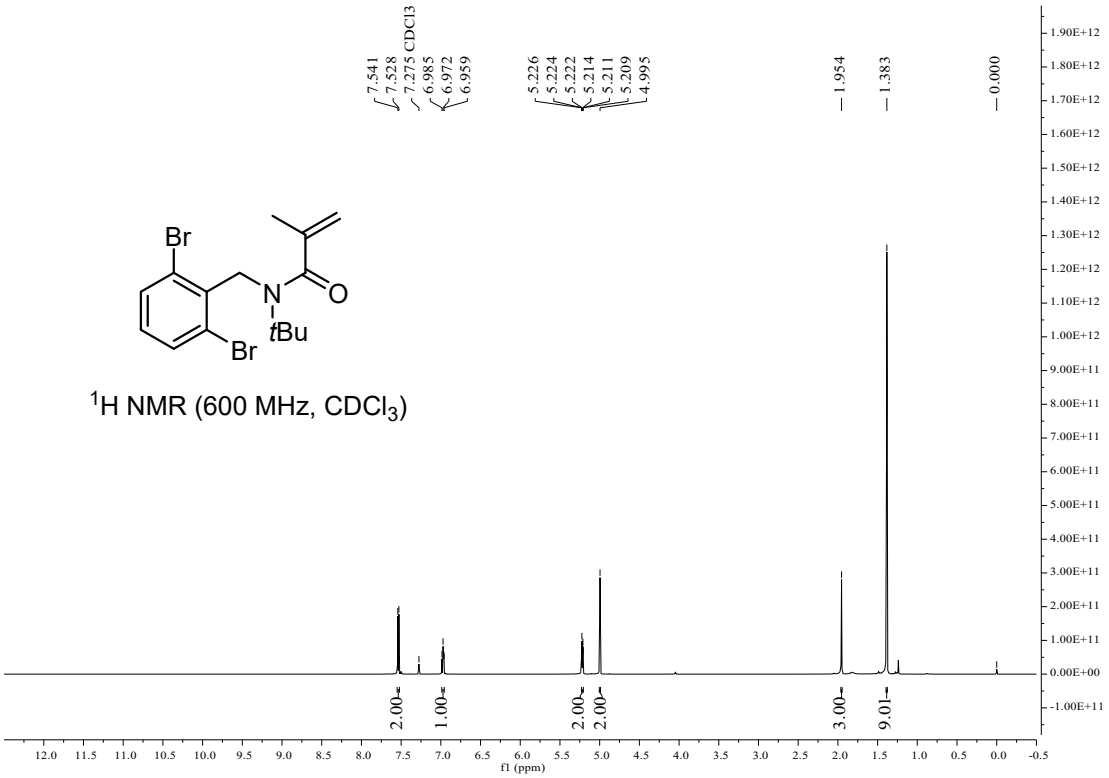


^{1}H NMR (400 MHz, $CDCl_3$)

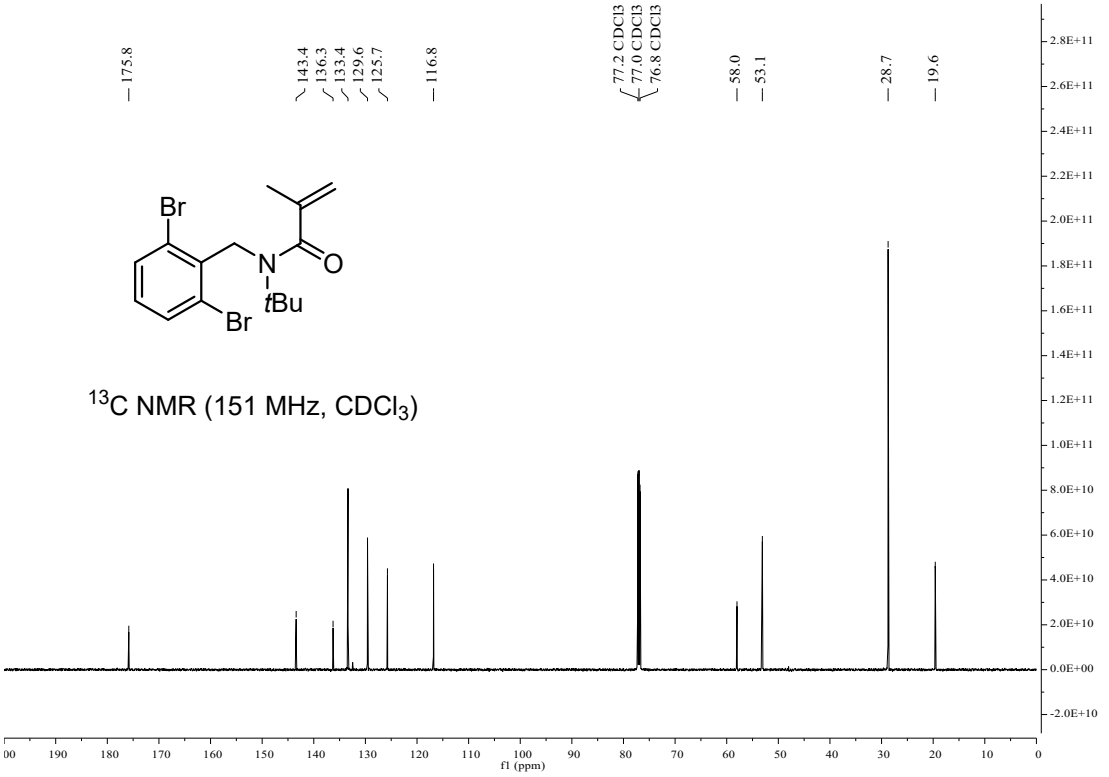


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S3

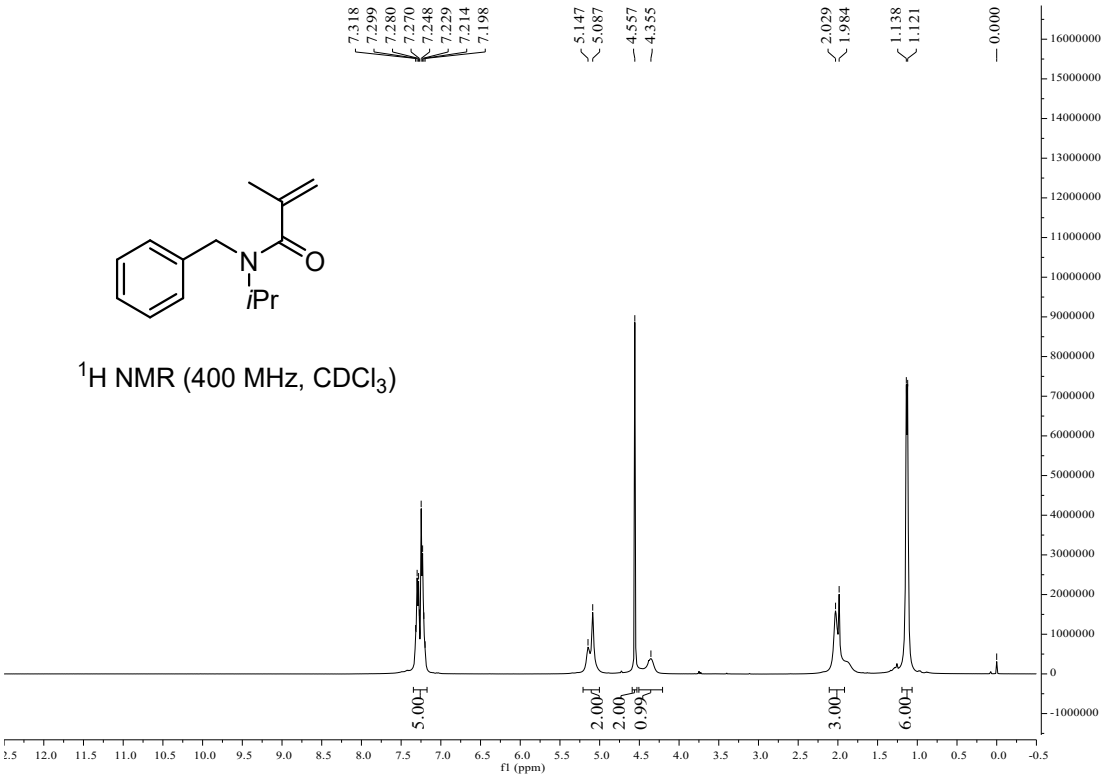


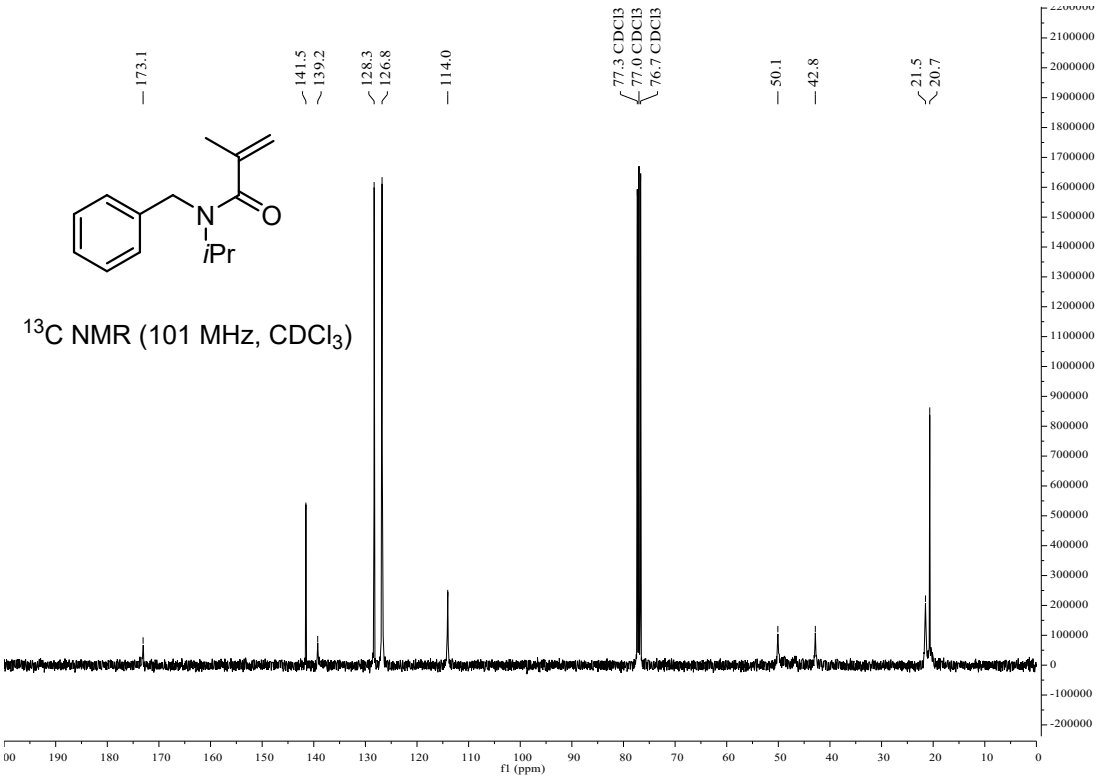
^{1}H NMR (600 MHz, $CDCl_3$)



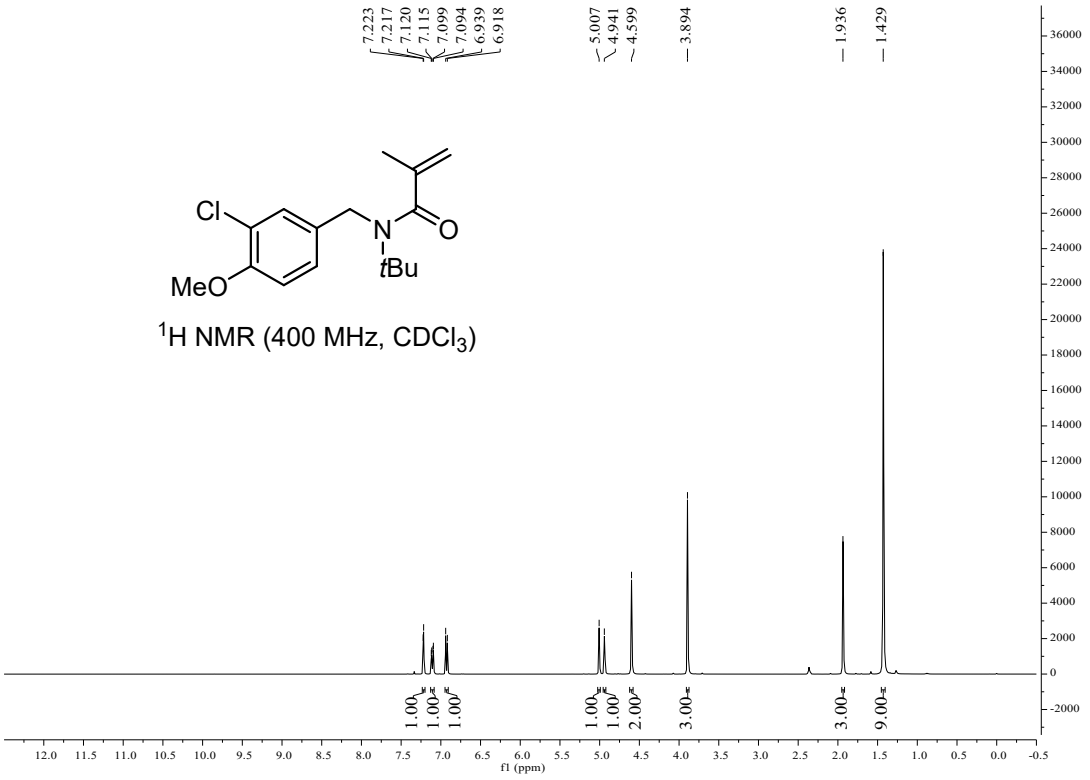
^{13}C NMR (151 MHz, $CDCl_3$)

Compound S4

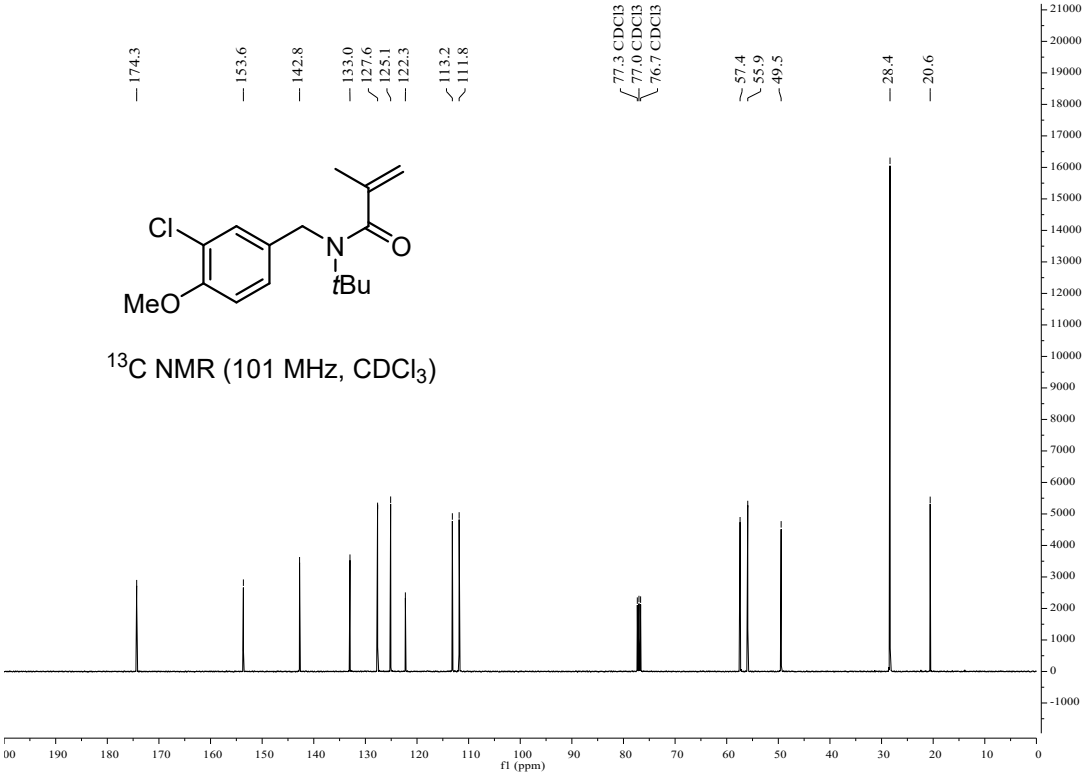

7.318
7.299
7.280
7.270
7.248
7.229
7.214
7.198
5.147
5.087
4.557
4.355
2.029
1.984
1.138
1.121
0.000
N
O
iPr
1H NMR (400 MHz, CDCl3)
5.00
2.00
2.00
0.99
3.00
6.00
f1 (ppm)


173.1
141.5
139.2
128.3
126.8
114.0
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
50.1
42.8
21.5
20.7
N
O
iPr
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound S5

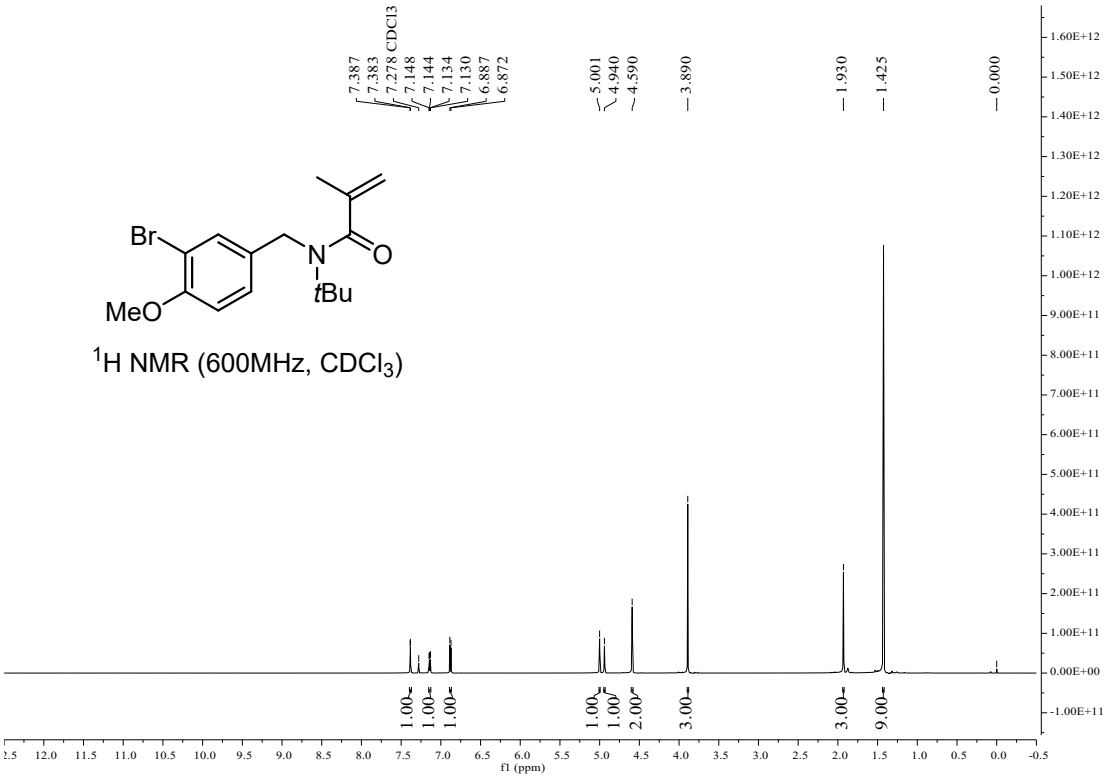


^{1}H NMR (400 MHz, $CDCl_3$)

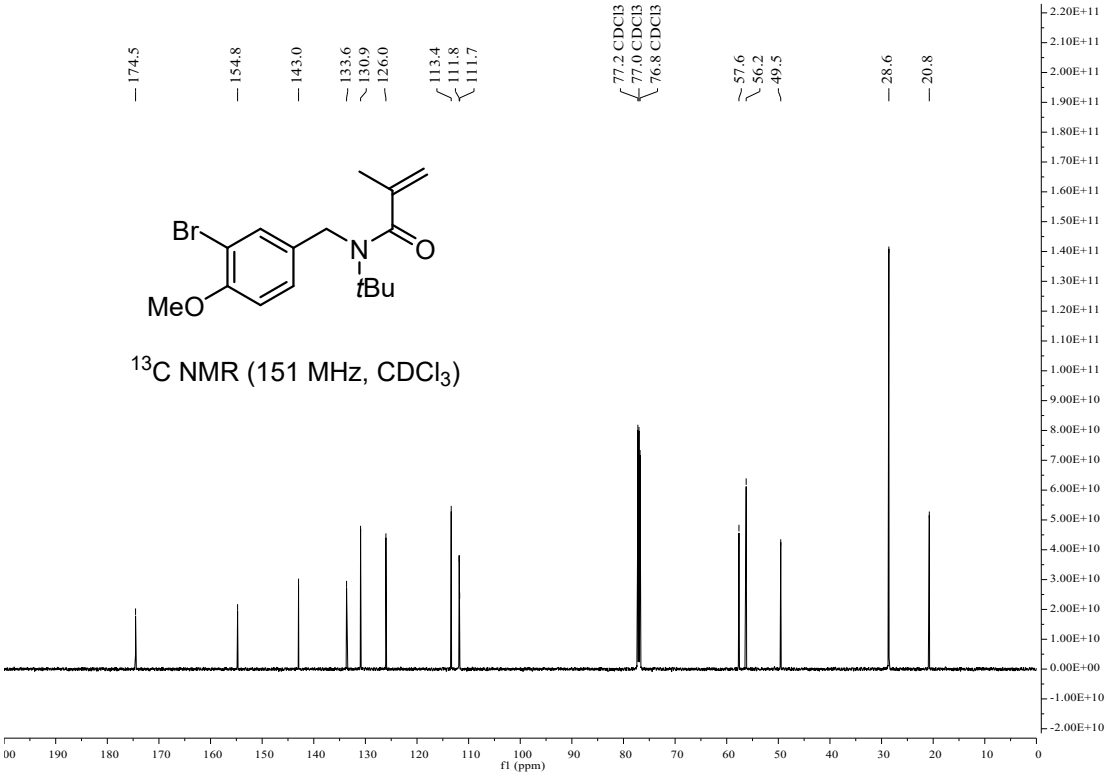


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S6

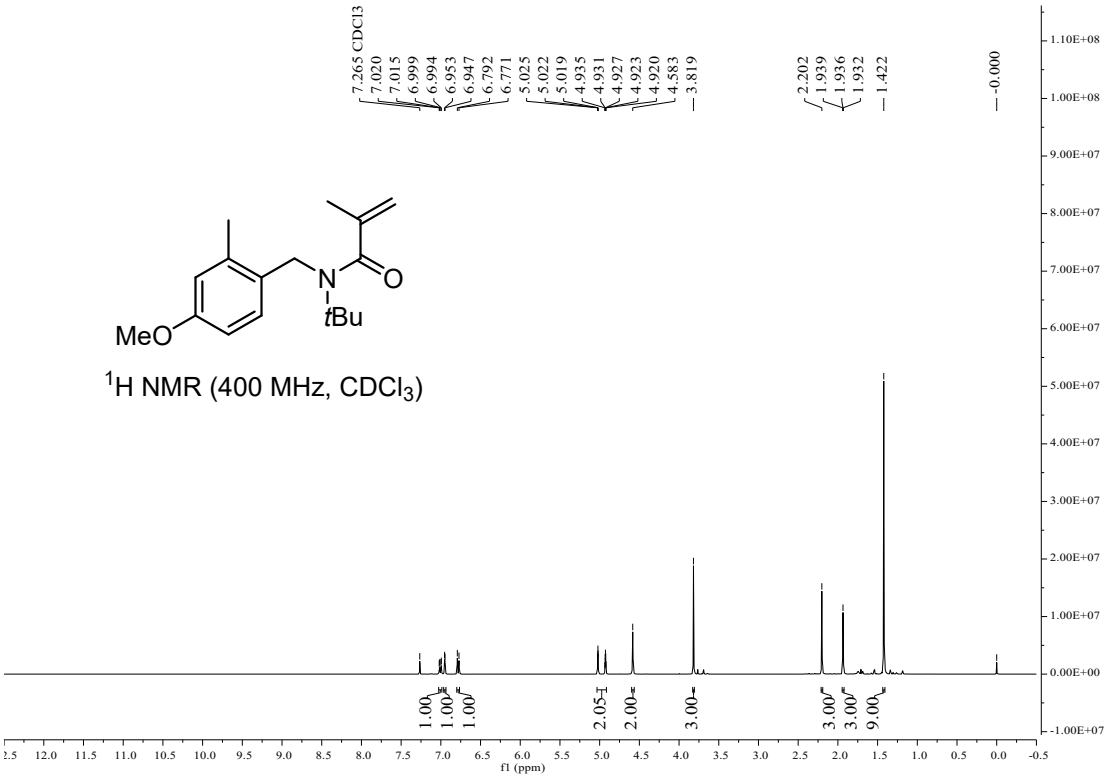


^{1}H NMR (600MHz, $CDCl_3$)

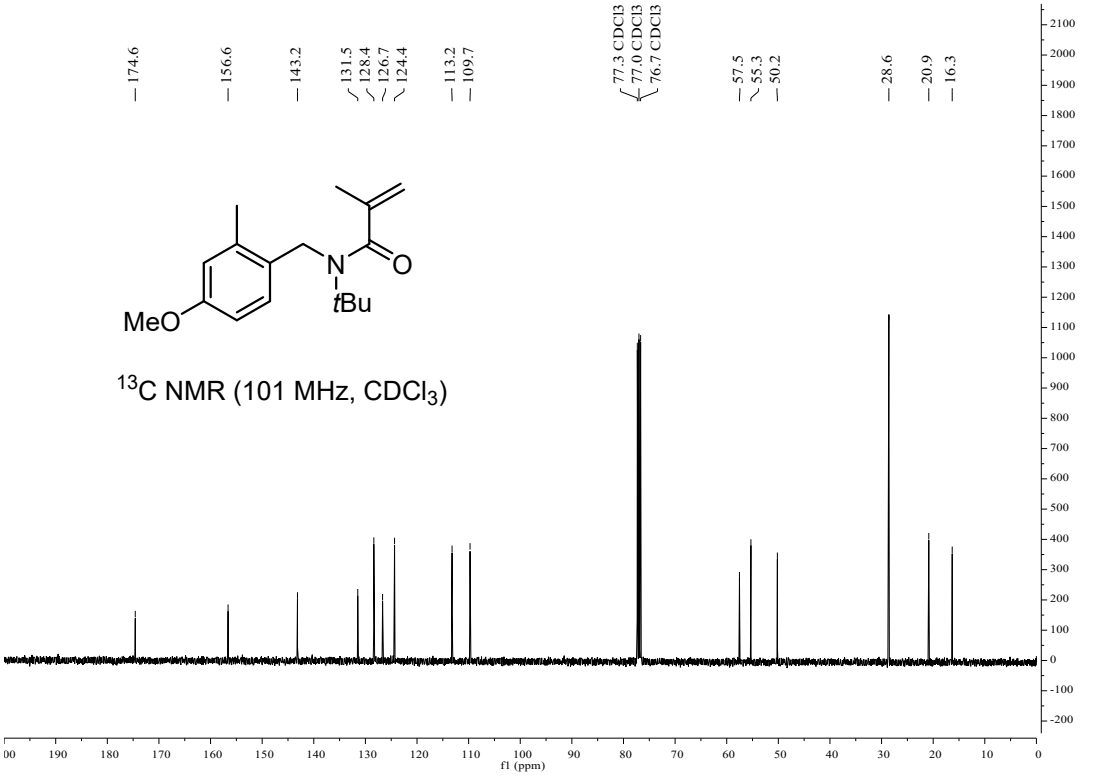


^{13}C NMR (151 MHz, $CDCl_3$)

Compound S7

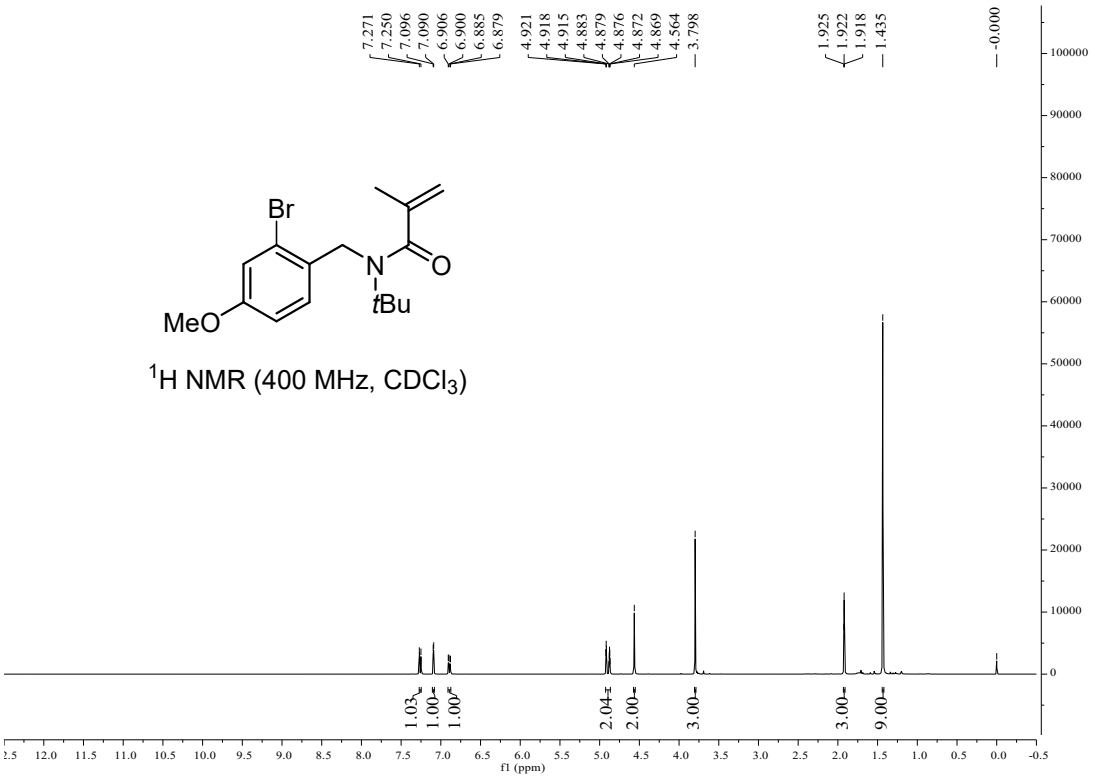


^{1}H NMR (400 MHz, $CDCl_3$)

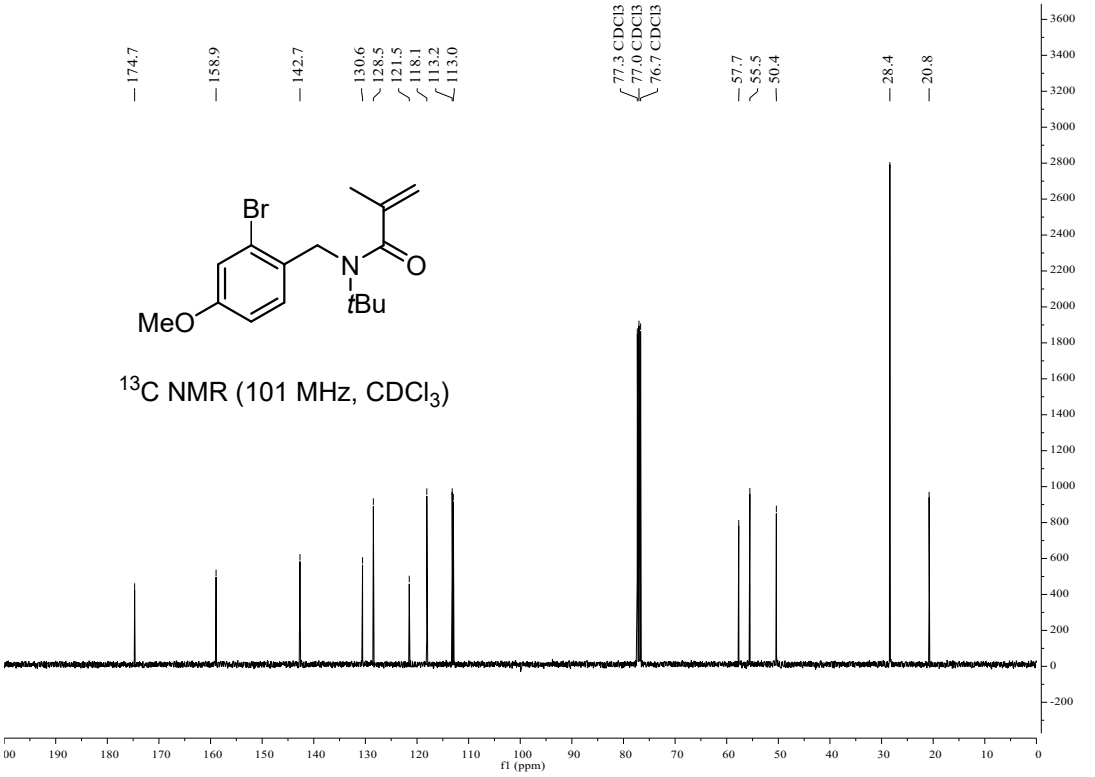


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S8

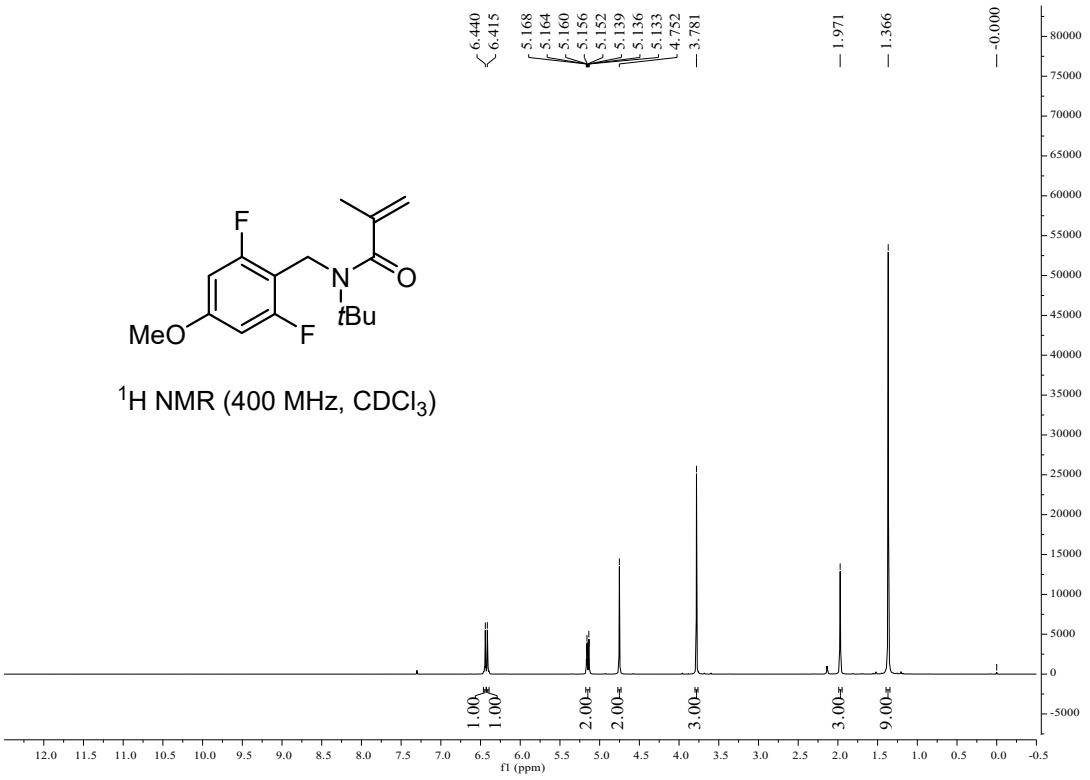


^{1}H NMR (400 MHz, $CDCl_3$)

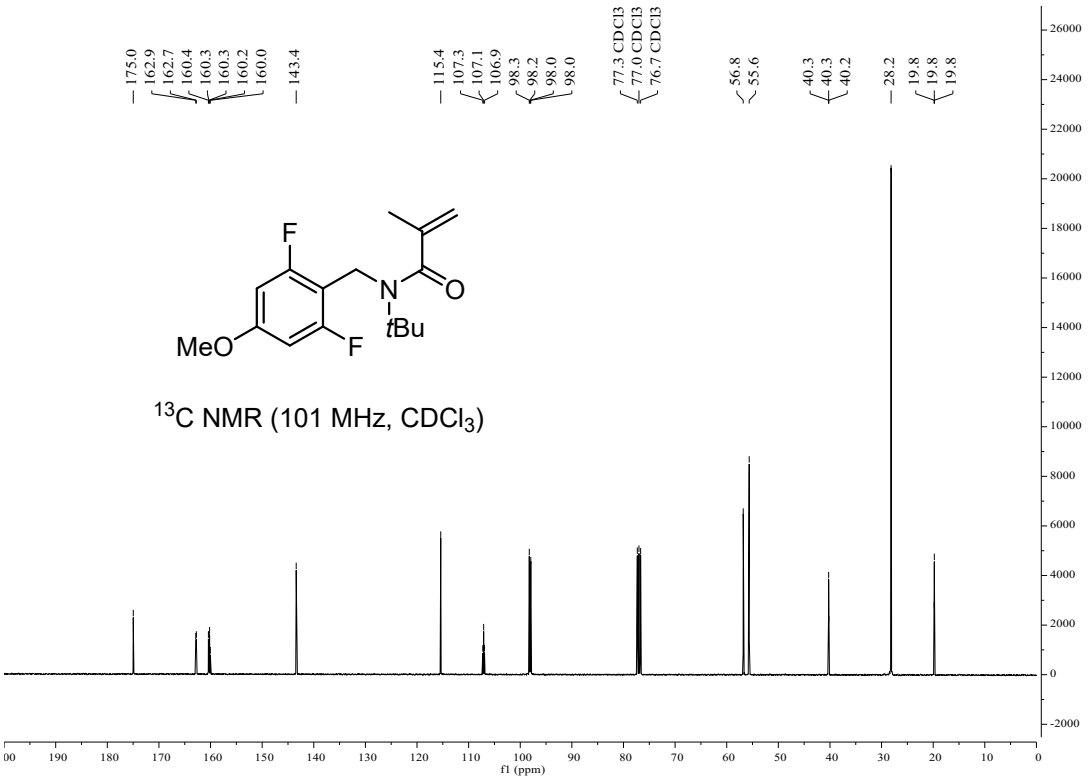


^{13}C NMR (101 MHz, $CDCl_3$)

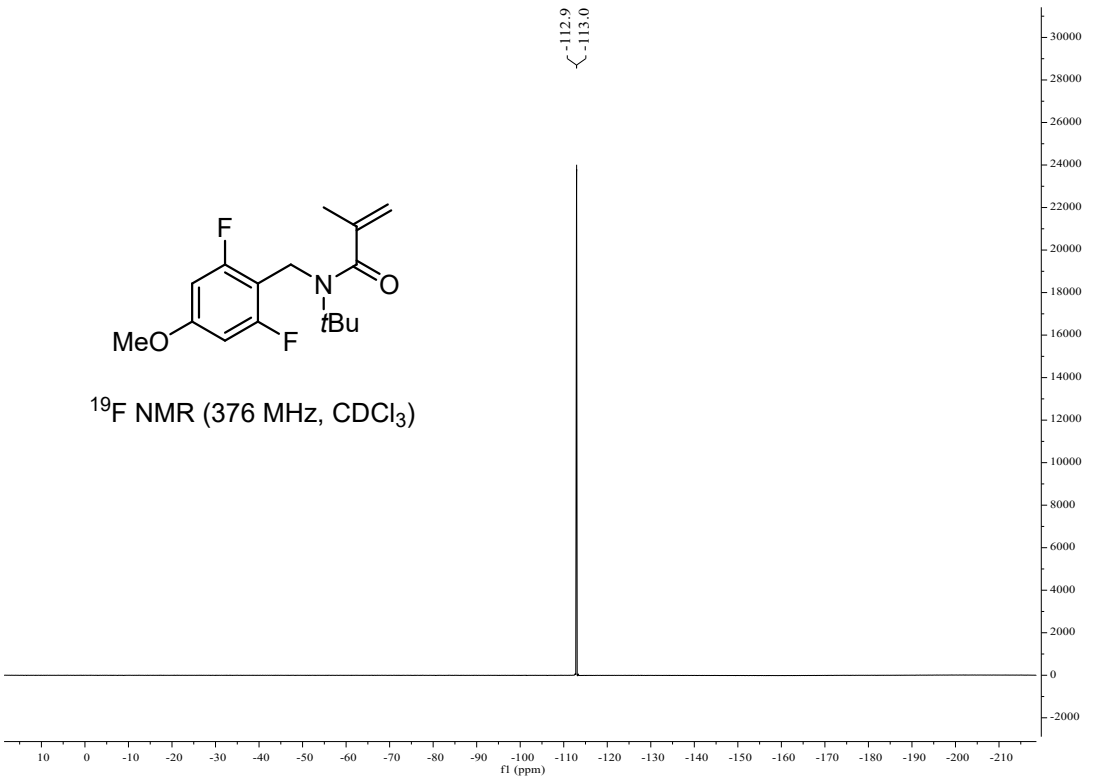
Compound S9



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

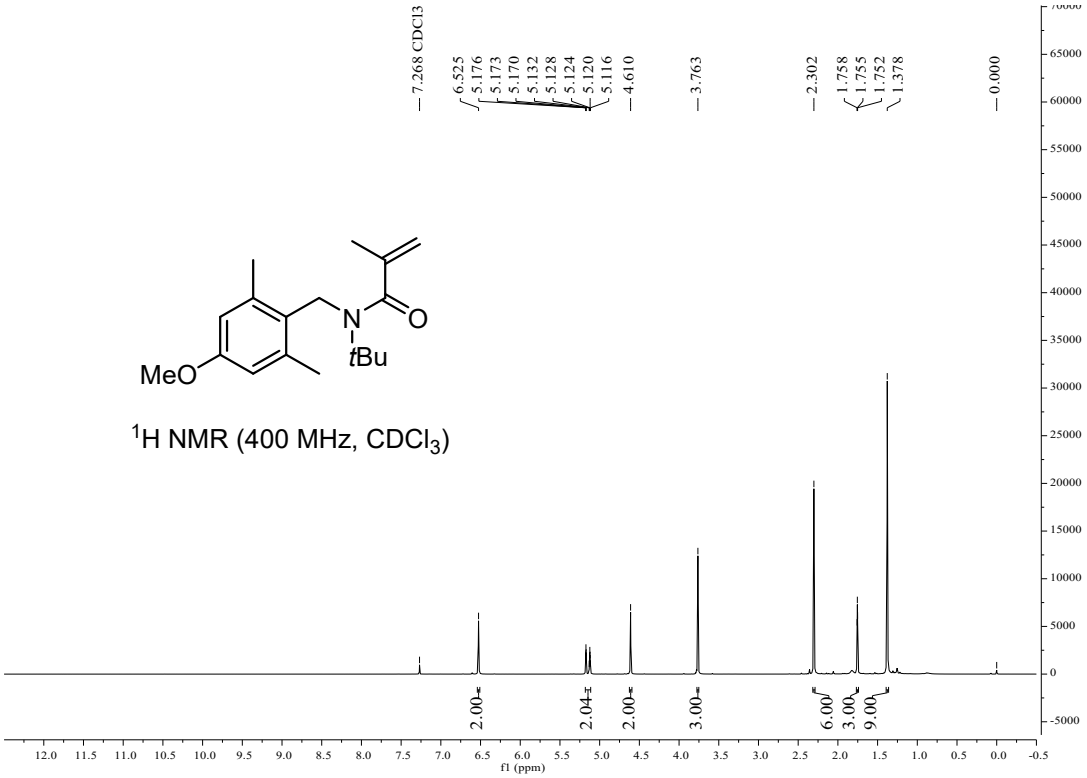


^{13}C NMR (101 MHz, $CDCl_3$)

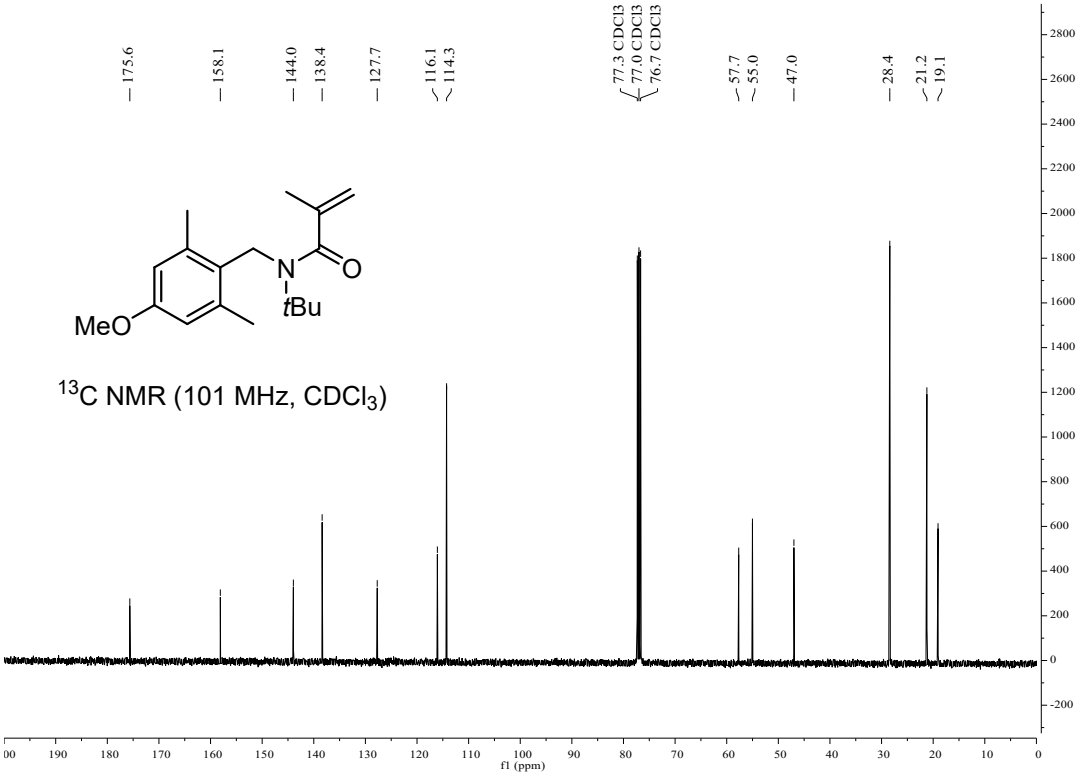


^{19}F NMR (376 MHz, $CDCl_3$)

Compound S10

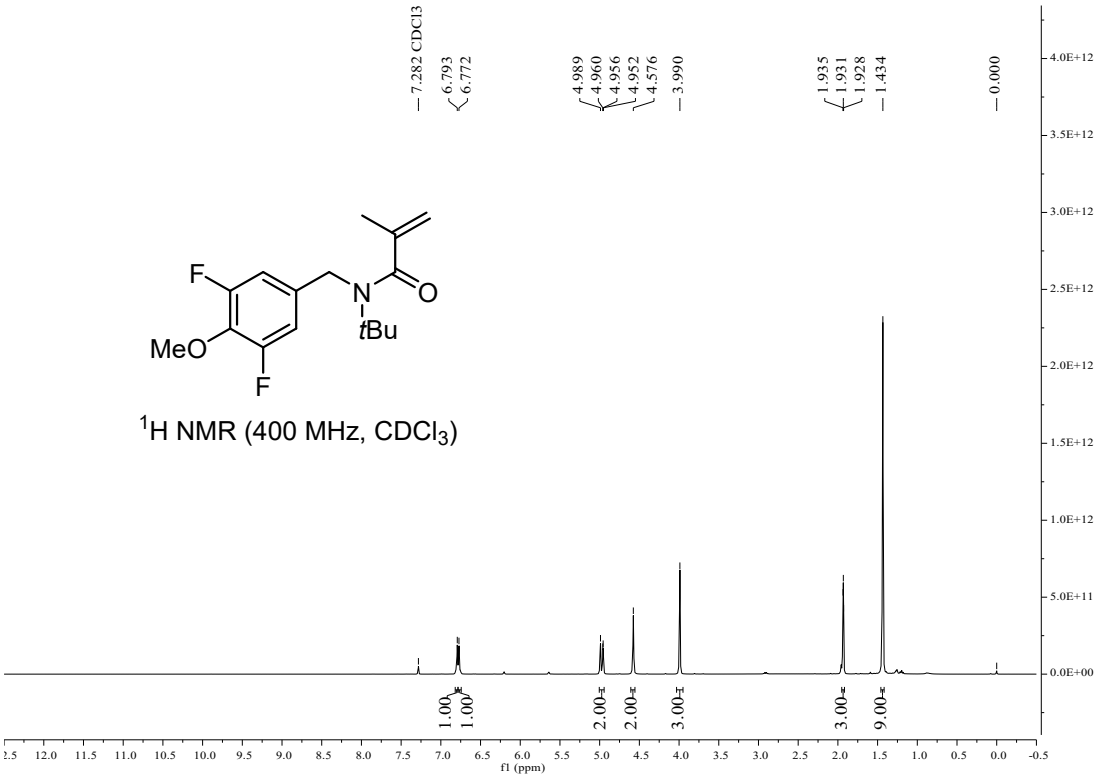


^{1}H NMR (400 MHz, $CDCl_3$)

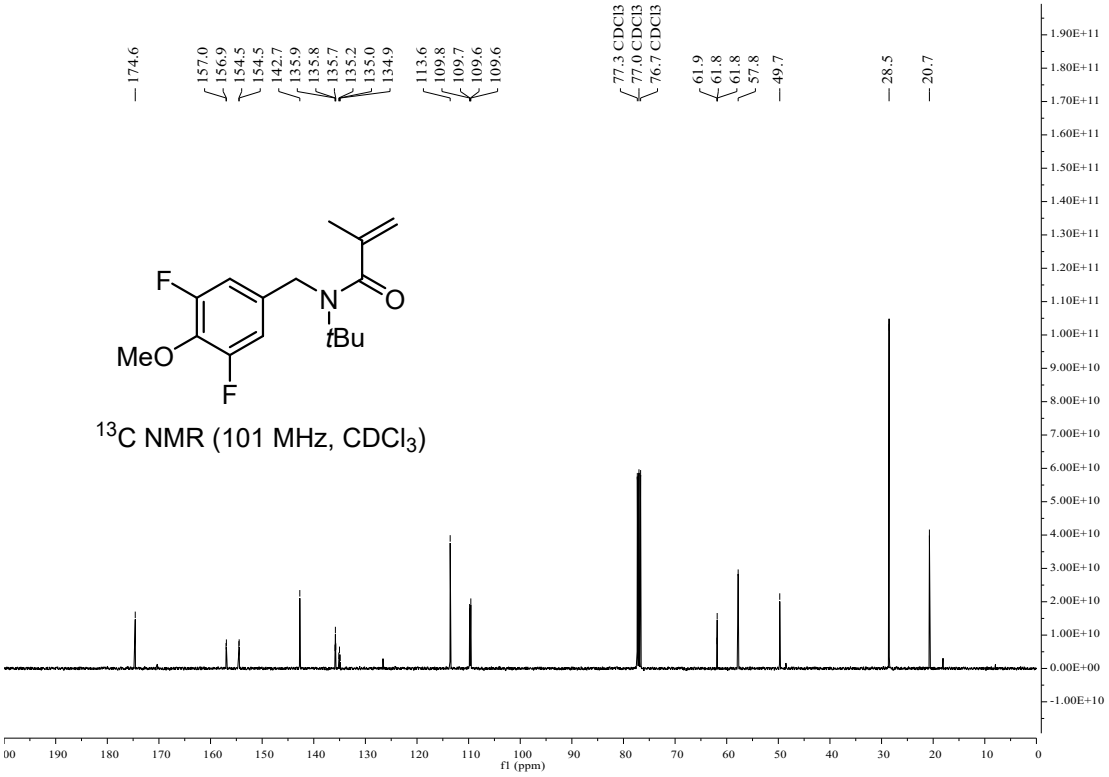


^{13}C NMR (101 MHz, $CDCl_3$)

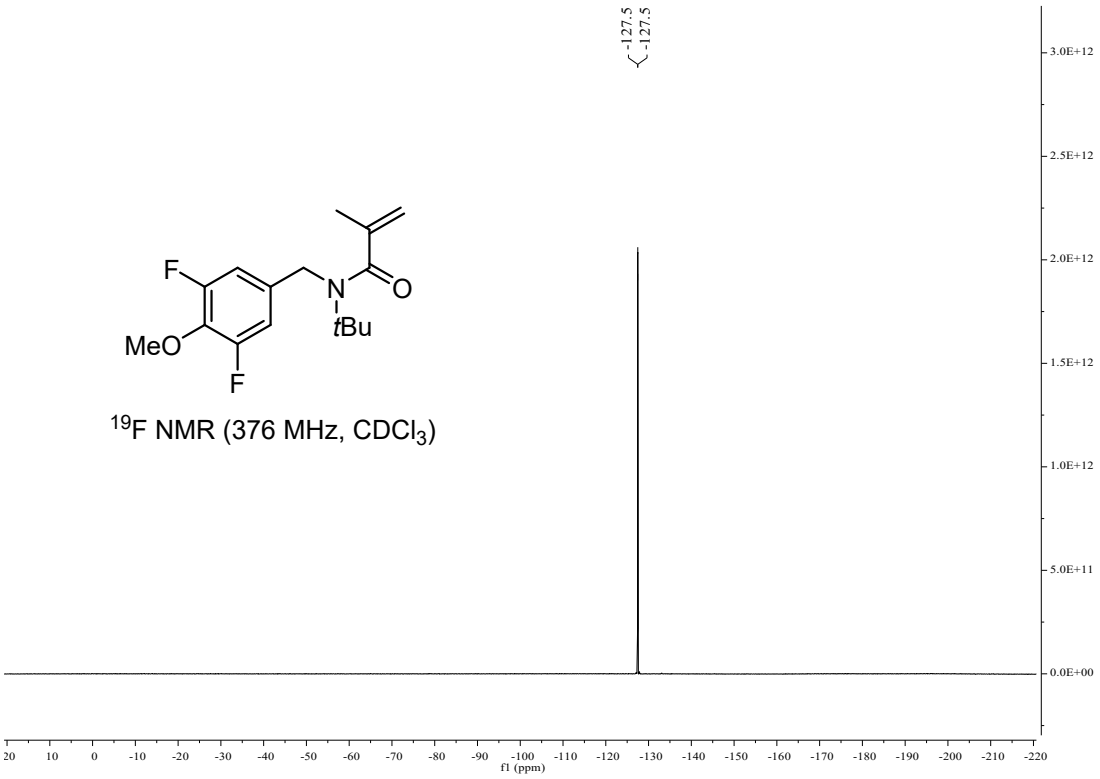
Compound S11



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

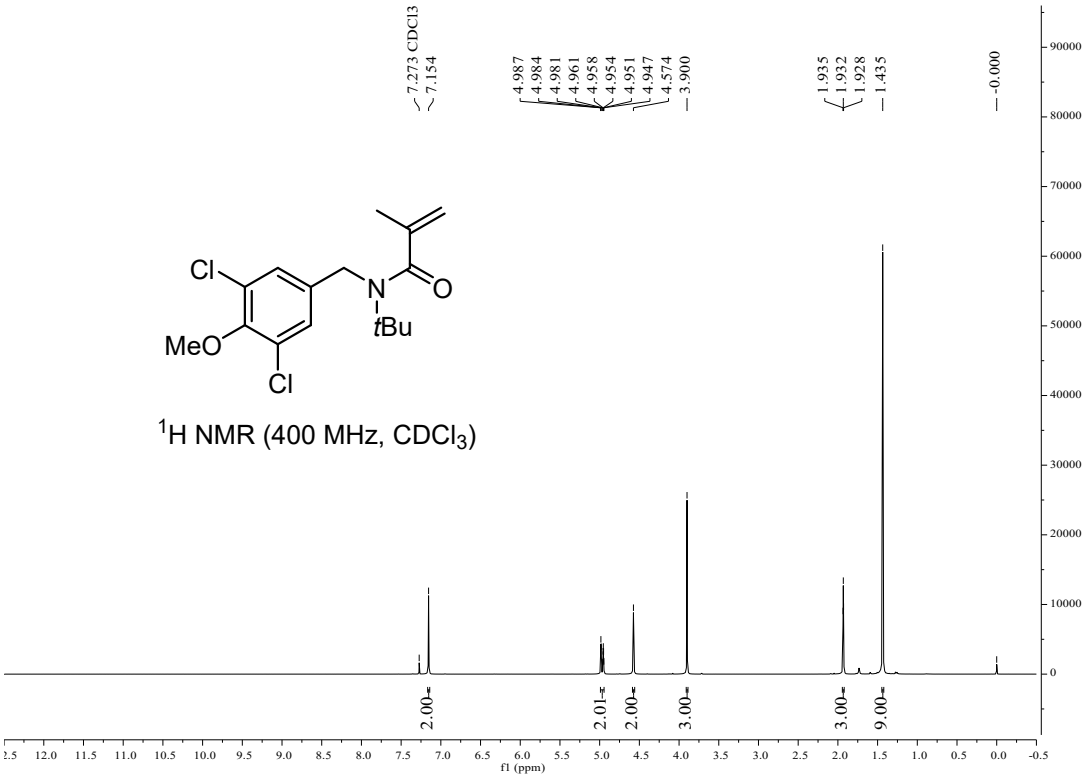


^{13}C NMR (101 MHz, $CDCl_3$)

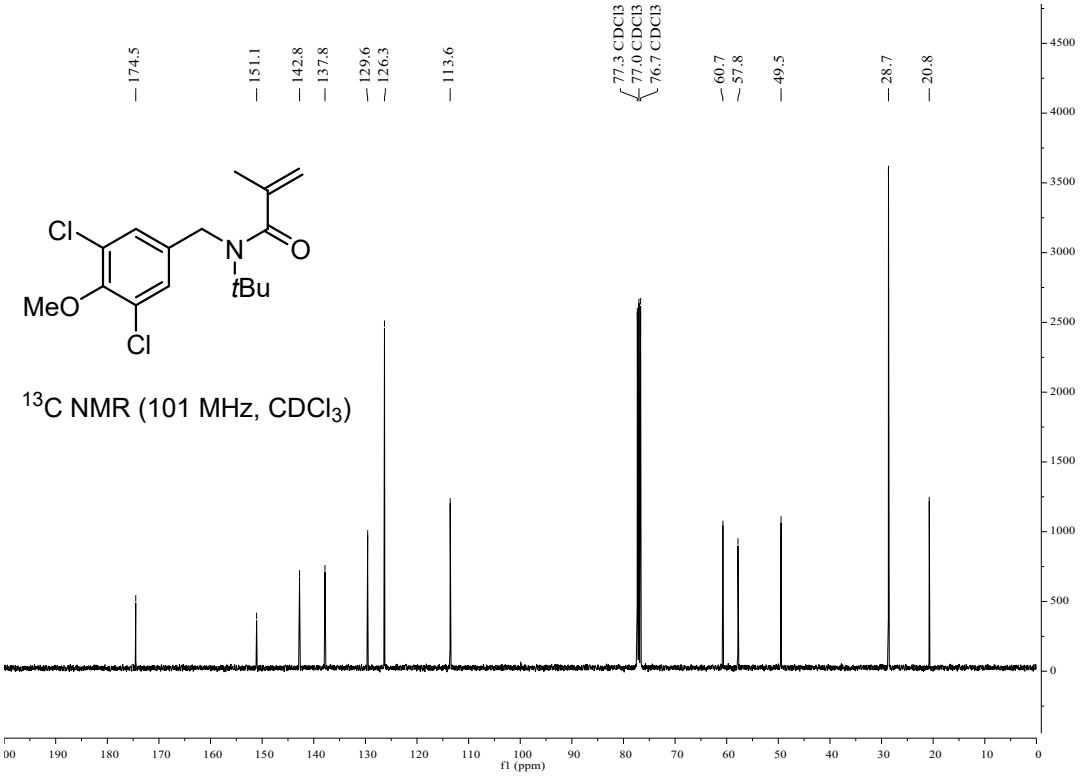


^{19}F NMR (376 MHz, $CDCl_3$)

Compound S12

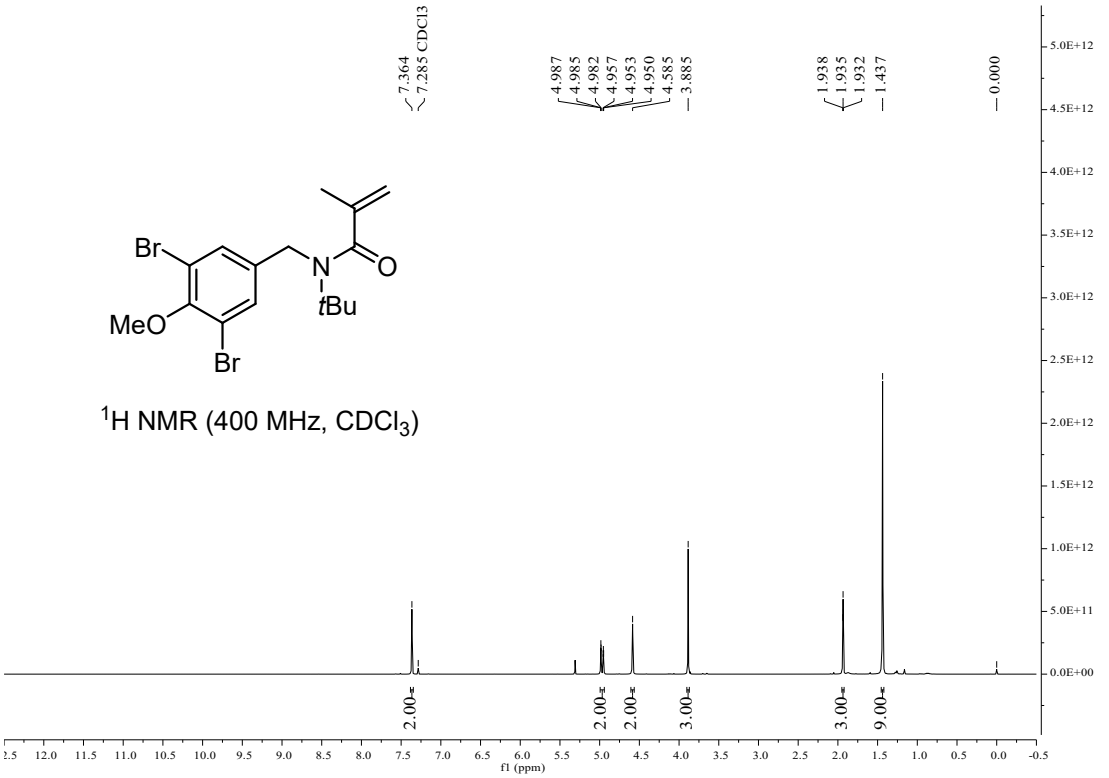


^{1}H NMR (400 MHz, $CDCl_3$)

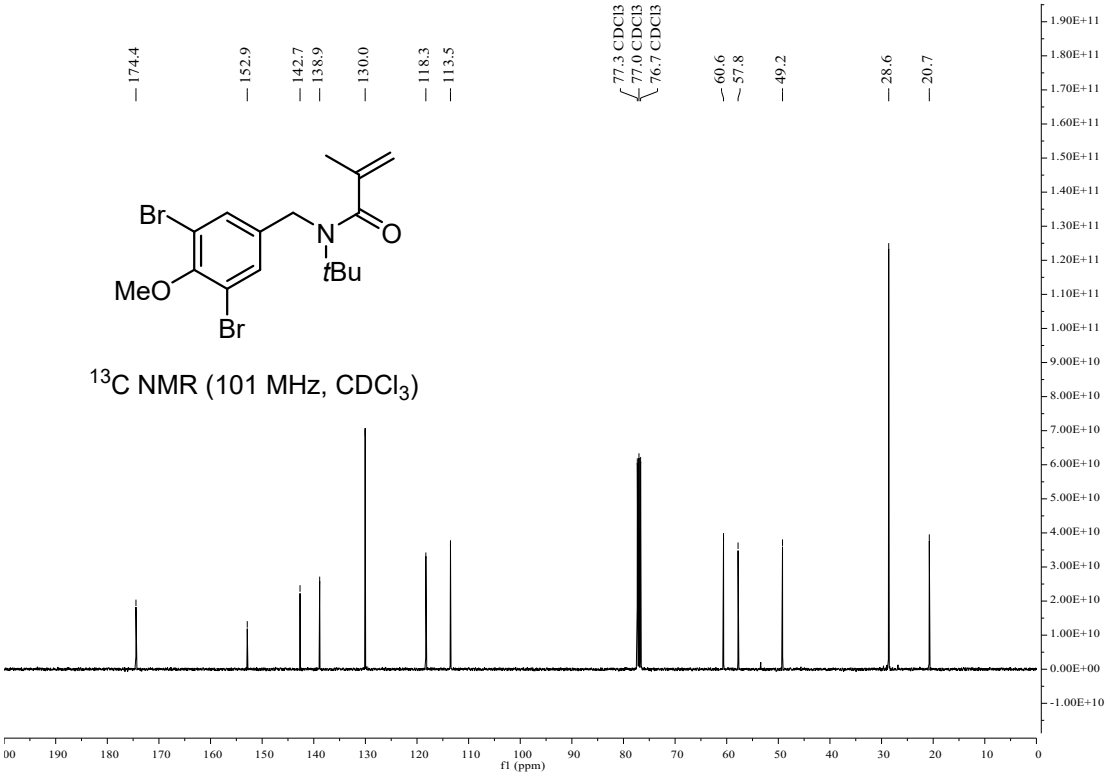


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S13



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



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

Compound S14