Supporting Information for

Regioselective electrochemical 7-*endo-dig* selenocyclization of *N*-benzyl propiolamides to access selenated benzo[*c*]azepinones

Xian-Bing Luo,[a,b] Xia-Die Wu,[a] Lei Wang,*[,a,b] Zhifang Li,*[b] and Zhong-Wei Hou*[,a]

[a] School of Pharmaceutical Sciences, Taizhou University, Jiaojiang, Zhejiang, 318000, P. R. China

[b] Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, Zhejiang, 311121, P. R. China

**Corresponding Author(s): zhongwei.hou@tzc.edu.cn; leiwang88@hotmail.com*

Contents

1. General Information

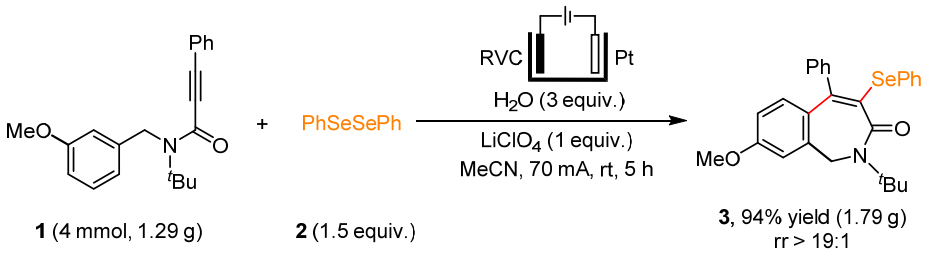
Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. The reticulated vitreous carbon (RVC) anode and Pt plate cathode are commercially available from Gaoss Union in China. XINRUI® DJS-292B potentiostat made in China was used as a power supply device. All the solvents were treated according to the general methods. Flash column chromatography was performed with silica gel (200–300 mesh). 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 $CDCl_3$ (7.26 ppm) for ^1H NMR and $CDCl_3$ (77.2 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. High resolution mass spectra (ESI HRMS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). X-Ray data were collected on a Bruker SMART APEX Ⅱ instrument with an IμS Mo microsource (λ = 0.7107 A).

2. General Procedure for the Electrolysis

2.1 General Procedure for the Model Reaction

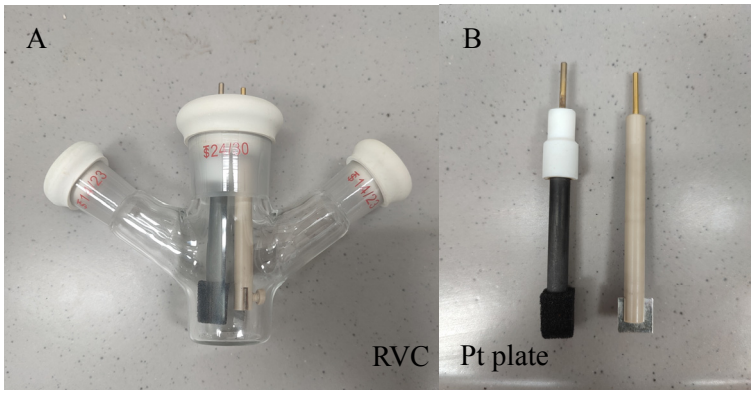
A 20 mL three-necked beaker-type cell (Figure S1A) was charged with *N*-benzyl propiolamide (0.2 mmol, 1 equiv.), diselenide (0.3 mmol, 1.5 equiv.), $LiClO_4$ (0.2 mmol, 1 equiv.). The cell was equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1 cm × 1 cm × 0.1 mm) cathode (Figure S1B), MeCN (7 mL) and H_2O (3 equiv.) were added. The RVC was fixed on a sharpened graphite rod (diameter: 0.6 cm) and the distance between RVC electrode and platinum electrode was about 0.5 cm. The electrolysis was carried out at room temperature using a constant current of 7 mA (0.14 mA/cm^2) for 2.5 h (3.3 F/mol). The reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:30) to ethyl acetate/petroleum ether (1:10) to give the desired product.

2.2 General Procedure for the Gram-Scale Synthesis of 3



1 (4 mmol, 1.29 g) **2** (1.5 equiv.) **3**, 94% yield (1.79 g)
rr > 19:1

The gram-scale electrosynthesis of **3** was conducted in a 100 mL electrolytic cell (Figure S1C) with a piece of RVC (2.4 cm × 2.4 cm × 1.2 cm) as the anode, a Pt plate as the cathode (1.5 cm × 1.5 cm × 0.3 mm), and a constant current of 70 mA for 5 h at room temperature. The reaction mixture consisted *N*-(*tert*-butyl)-*N*-(3-methoxybenzyl)-3-phenylpropiolamide (**1**, 4 mmol, 1 equiv.), PhSeSePh (**2**, 6 mmol, 1.5 equiv.), $LiClO_4$ (4 mmol, 1 equiv.), MeCN (80 mL) and H_2O (3 equiv.). 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 (1:30) to ethyl acetate/petroleum ether (1:10) to give the desired product **3** (1.79 g, 94% yield).



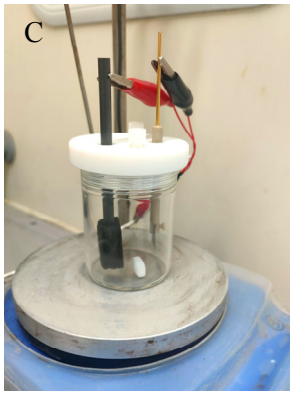
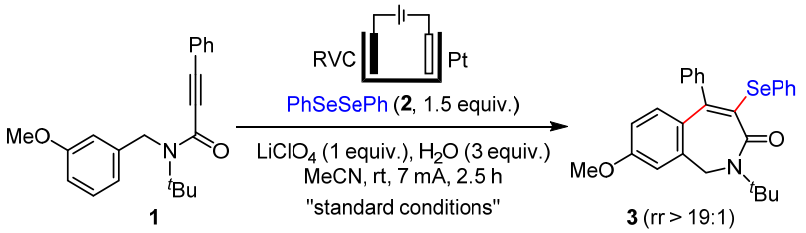


Figure S1. The electrolysis setup
[**A**: Setup for the model reaction; **B**: Electrodes for the model reaction;
C: Setup for the gram-scale electrosynthesis]

3. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions[a]



Entry	Variation from the standard conditions	Yield (%)[b]
1	none	92
2	PhSeSePh (1 equiv.)	85
3	$LiClO_4$ (0.5 equiv.)	81
4	no H_2O	73
5	H_2O (5 equiv.)	79
6	H_2O (10 equiv.)	71
7	H_2O (1 mL)	n.d.
8	5 mA, 3.5 h	87
9	10 mA, 1.75 h	90
10	no electricity	n.d.
11	no $LiClO_4$	n.d.
12	$^nBu_4NOAc$	n.d.
13	KPF_6	90
14	$^nBu_4NBF_4$	83
15	$^nBu_4NPF_6$	88
16	IKA Electrasyn 2.0 (graphite anode, Pt plate cathode) as electrolysis device	74

[a]Reaction conditions: RVC anode, Pt cathode, undivided cell, **1** (0.2 mmol), PhSeSePh (**2**, 0.3 mmol), $LiClO_4$ (0.2 mmol), H_2O (0.6 mmol), MeCN (7 mL), rt, 7 mA (0.14 mA/cm^2), 2.5 h (3.3 F/mol). [b] Isolated yield. rr = regioisomeric ratio. n.d. = not detected.

Initially, the reaction conditions for the electrochemical selenocyclization of *N*-(*tert*-butyl)-*N*-(3-methoxybenzyl)-3-phenyl propiolamide (**1**) with PhSeSePh (**2**) were systematically examined. The reaction was conducted in an undivided cell at a constant current of 7 mA for 2.5 h, utilizing a reticulated vitreous carbon (RVC) anode and a platinum sheet cathode (Table S1). Benzo[*c*]azepinone **3** was obtained in an 92% yield with a regioisomeric ratio exceeding 19:1 under standard conditions by employing $LiClO_4$ (1 equiv.) as the electrolyte in the presence of H_2O (3 equiv.) in MeCN at room temperature (Table S1, entry 1). When the equivalent amount of PhSeSePh (**2**) was reduced to 1, the formation of product **3** was slightly diminished (Table S1, entry 2). The reaction yield was decreased to 81% yield due to the reduction of electrolytes (Table S1, entry 3). Removal of H_2O resulted in a decrease in the yield of **3** to 73% (Table S1, entry 4). An increase in the water content of the reaction system substantially inhibited the selenocyclization reaction (Table S1, entries 5–7).

Modulating the reaction current to 5 mA or 10 mA led to the formation of benzo[*c*]azepinone **3** in yields ranging from 87% to 90% (Table S1, entries 8–9). Notably, the presence of electricity was imperative for the smooth progression of the reaction (Table S1, entry 10). When the reaction was carried out in the absence of $LiClO_4$ or with $^nBu_4NOAc$ (1 equiv.) as the electrolyte, significant amounts of starting materials remained unreacted, and the desired product **3** was not detected (Table S1, entries 11–12). Employing KPF_6 (1 equiv.), $^nBu_4NBF_4$ (1 equiv.), or $^nBu_4NPF_6$ (1 equiv.) as electrolytes had minimal impact on the efficiency of the electrochemical cyclization reaction (Table S1, entries 13–15). Furthermore, the electrochemical selenocyclization of **1** with PhSeSePh (**2**) could be achieved in 74% yield when performed using an IKA Electrasyn 2.0 system (graphite anode, Pt plate cathode) as the electrolysis device (Table S1, entry 16).

4. Cyclic Voltammetry Studies

Cyclic voltammograms were obtained on a CHI 660E potentiostat (CH Instruments, INS). The cyclic voltammograms were recorded with $LiClO_4$ (0.1 M) in MeCN (5 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. All CVs were plotted according to the IUPAC convention at room temperature. The scan rate was 50 mV/s.

The cyclic voltammetry studies indicates that PhSeSePh (**2**, $E_{p/2}$ = 1.16 V vs. Ag/AgCl) possesses a lower oxidation potential compared to substrate **1** ($E_{p/2}$ = 1.52 V vs. Ag/AgCl), enabling its preferential oxidation at the anode.

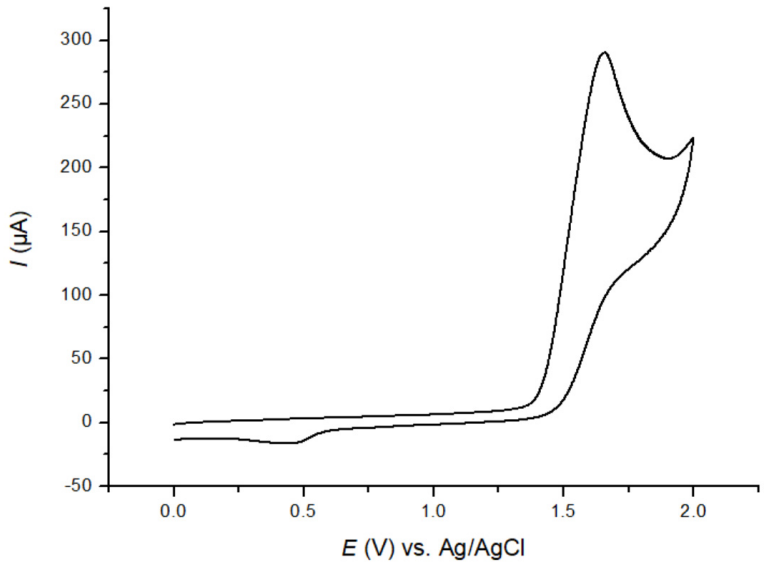


Figure S2. Cyclic voltammogram of **1** (10 mM) with $LiClO_4$ (0.1 M) in MeCN (5 mL) [$E_{p/2}$ = 1.52 V]

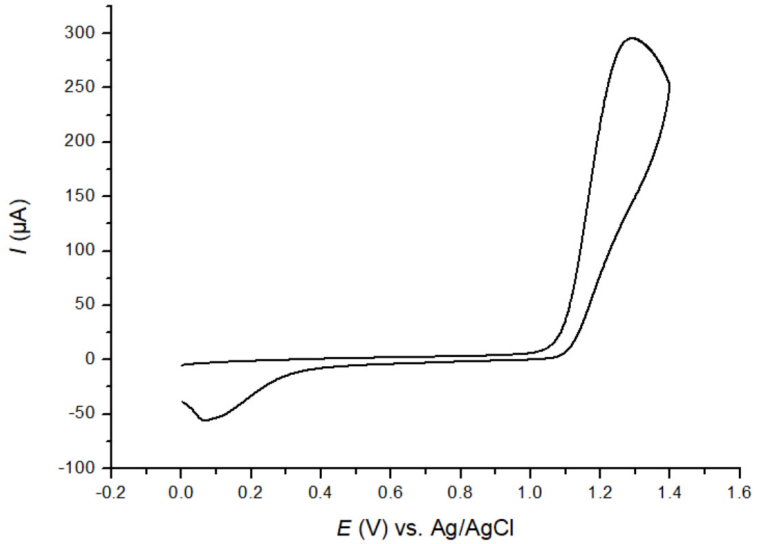
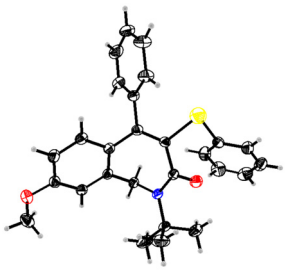


Figure S3. Cyclic voltammogram of PhSeSePh (**2**, 10 mM) with $LiClO_4$ (0.1 M) in MeCN (5 mL) [$E_{p/2}$ = 1.16 V]

5. X-Ray Crystallography

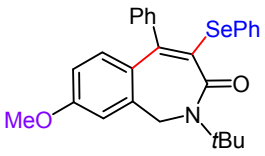
Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3**, **25** and **52** in petroleum ether/CH_2Cl_2 in a loosely capped vial. The ellipsoid contour 30% probability level was used for X-ray single crystal diffraction analysis.

5.1 X-Ray Single Crystal Diffraction Analysis of Compound 3 (CCDC: 2454821)



X-ray of **3**
CCDC 2454821

≡



3

Datablock: 1

Bond precision: C-C = 0.0030 A Wavelength=1.54178

Cell: a=24.2397(4) b=6.6540(1) c=30.0658(4)
alpha=90 beta=100.312(1) gamma=90
Temperature: 297 K

	Calculated	Reported
Volume	4771.01(13)	4771.01(12)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C27 H27 N O2 Se	C27 H27 N O2 Se
Sum formula	C27 H27 N O2 Se	C27 H27 N O2 Se
Mr	476.46	476.48
Dx,g cm-3	1.327	1.327
Z	8	8
Mu (mm-1)	2.302	2.301
F000	1968.0	1967.1
F000'	1966.30	
h,k,lmax	28,8,36	28,8,36
Nref	4352	4324
Tmin,Tmax	0.663,0.676	0.467,0.753
Tmin'	0.601	

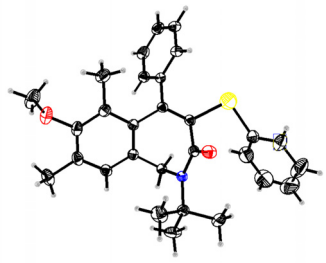
Correction method= # Reported T Limits: Tmin=0.467 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 68.330

R(reflections)= 0.0288(4067) wR2(reflections)= 0.0753(4324)

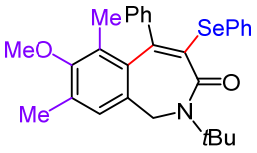
S = 1.043 Npar= 284

5.2 X-Ray Single Crystal Diffraction Analysis of Compound 25 (CCDC: 2386489)



X-ray of **25**
CCDC 2386489

≡

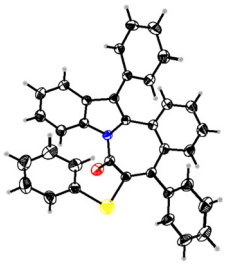


25

Datablock: 1

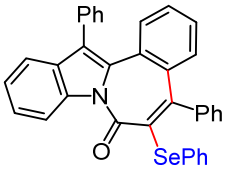
```
Bond precision:   C-C = 0.0032 A           Wavelength=0.71073

Cell:           a=6.6419(1)        b=11.9656(3)      c=17.5698(4)
                alpha=107.138(1)   beta=90.007(1)    gamma=100.861(1)
Temperature:    273 K

                 Calculated                 Reported
Volume           1308.14(5)                 1308.14(5)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C29 H31 N O2 Se            C29 H31 N O2 Se
Sum formula      C29 H31 N O2 Se            C29 H31 N O2 Se
Mr               504.51                     504.51
Dx,g cm-3        1.281                      1.281
Z                2                          2
Mu (mm-1)        1.460                      1.460
F000             524.0                      524.0
F000'            523.99
h,k,lmax         8,15,23                    8,15,23
Nref             6457                       6418
Tmin,Tmax        0.737,0.780                0.664,0.746
Tmin'            0.718

Correction method= # Reported T Limits: Tmin=0.664 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994           Theta(max)= 28.241

R(reflections)= 0.0323( 5243)                wR2(reflections)=
                                             0.0924( 6418)
S = 1.027                  Npar= 304
```

5.3 X-Ray Single Crystal Diffraction Analysis of Compound 52 (CCDC: 2470806)



X-ray of **52**
CCDC 2470806

≡

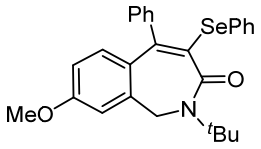


52

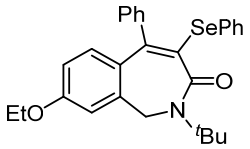
Datablock: 1

```
Bond precision:   C-C = 0.0041 A          Wavelength=1.54178

Cell:             a=19.5813(4)     b=8.5064(2)         c=32.0053(6)
                  alpha=90         beta=98.372(2)      gamma=90
Temperature:      299 K

                  Calculated                Reported
Volume            5274.20(19)               5274.20(19)
Space group       C 2/c                     C 1 2/c 1
Hall group        -C 2yc                    -C 2yc
Moiety formula    C35 H23 N O Se            C35 H23 N O Se
Sum formula       C35 H23 N O Se            C35 H23 N O Se
Mr                552.50                    552.50
Dx,g cm-3         1.392                     1.392
Z                 8                         8
Mu (mm-1)         2.145                     2.145
F000              2256.0                    2256.0
F000'             2255.02
h,k,lmax          23,10,38                  23,10,38
Nref              4858                      4803
Tmin,Tmax         0.655,0.651               0.442,0.753
Tmin'             0.594

Correction method= # Reported T Limits: Tmin=0.442 Tmax=0.753
AbsCorr = NONE

Data completeness= 0.989          Theta(max)= 68.458

R(reflections)= 0.0431( 4571)                wR2(reflections)=
                                             0.1257( 4803)
S = 1.109                 Npar= 343
```

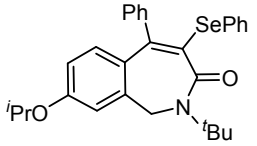
6. Characterization Data for Products



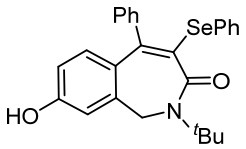
2-(*tert*-Butyl)-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (3). rr > 19:1; White solid (87.9 mg, 92% yield); m.p. = 195.5–197.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H), 7.38–7.35 (m, 3H), 7.24–7.14 (m, 5H), 6.82–6.79 (m, 1H), 6.77–6.73 (m, 1H), 6.72–6.68 (m, 1H), 4.40 (s, 2H), 3.80 (s, 3H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 159.4, 142.4, 142.0, 140.5, 135.0, 133.2, 132.2, 131.9, 131.0, 130.0, 128.8, 128.4, 127.7, 112.6, 112.2, 58.1, 55.5, 47.6, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_2Se^+$ 478.1280; Found 478.1278.



2-(*tert*-Butyl)-8-ethoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (4). rr > 19:1; White solid (79.4 mg, 81% yield); m.p. = 198.9–200.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.37–7.34 (m, 3H), 7.23–7.14 (m, 5H), 6.81–6.80 (m, 1H), 6.74–6.72 (m, 1H), 6.69–6.67 (m, 1H), 4.39 (s, 2H), 4.03 (dd, J = 7.0, 2.1 Hz, 1H), 4.00 (dd, J = 7.0, 2.1 Hz, 1H), 1.41 (t, J = 7.0 Hz, 3H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 158.9, 142.5, 142.1, 140.5, 135.1, 133.2, 132.3, 131.8, 131.1, 130.1, 128.8, 128.4, 127.7, 113.2, 112.6, 63.8, 58.2, 47.7, 28.9, 14.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2Se^+$ 492.1436; Found 492.1433.

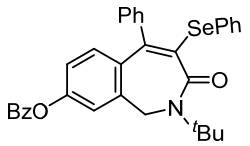


2-(*tert*-Butyl)-8-isopropoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (5). rr > 19:1; White solid (87.0 mg, 86% yield); m.p. = 183.1–186.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.38–7.34 (m, 3H), 7.23–7.14 (m, 5H), 6.80–6.78 (m, 1H), 6.73–6.71 (m, 1H), 6.69–6.66 (m, 1H), 4.59–4.49 (m, 1H), 4.38 (s, 2H), 1.33 (m, 6H) , 1.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 157.8, 142.5, 142.0, 140.5, 135.0, 133.1, 132.2, 131.5, 131.0, 130.0, 128.8, 128.3, 127.7, 114.4, 113.7, 70.1, 58.1, 47.6, 28.9, 22.2, 22.0. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{29}H_{32}NO_2Se^+$ 506.1593; Found 506.1589.

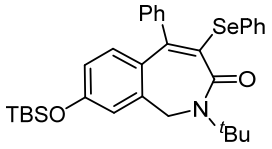


2-(*tert*-Butyl)-8-hydroxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-

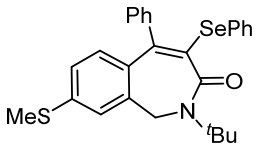
one (6). rr > 19:1; White solid (83.3 mg, 90% yield); m.p. = 194.5–196.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.57–7.54 (m, 2H), 7.30–7.26 (m, 1H), 7.25–7.16 (m, 6H), 6.92–6.90 (m, 1H), 6.46–6.42 (m, 1H), 6.33–6.29 (m, 1H), 4.36 (d, J = 15.1 Hz, 1H), 4.32 (d, J = 15.1 Hz, 1H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 157.8, 143.5, 141.7, 140.5, 135.5, 132.2, 131.0, 130.5, 130.2, 129.9, 128.9, 128.5, 128.4, 128.1, 115.3, 113.5, 58.6, 47.9, 28.9. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2Se^+$ 464.1123; Found 464.1123.



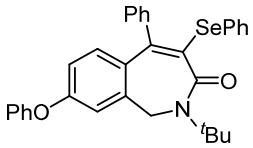
2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl benzoate (7). rr > 19:1; White solid (59.1 mg, 52% yield); m.p. = 177.7–179.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.4, 1.4 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.59–7.55 (m, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.41–7.37 (m, 3H), 7.27–7.17 (m, 6H), 7.04 (dd, J = 8.6, 2.4 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 4.50–4.42 (m, 2H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 165.0, 150.3, 141.4, 141.1, 140.1, 136.5, 135.8, 135.3, 133.9, 131.9, 130.4, 130.2, 130.0, 129.2, 128.8, 128.7, 128.5 (2C), 127.9, 121.0, 119.5, 58.2, 47.3, 28.8. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{33}H_{30}NO_3Se^+$ 568.1385; Found 568.1387.



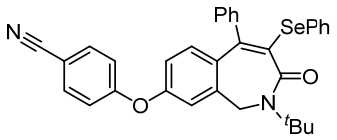
2-(*tert*-Butyl)-8-((*tert*-butyldimethylsilyl)oxy)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (8). rr > 19:1; White solid (40.5 mg, 35% yield); m.p. = 208.5–210.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.38–7.34 (m, 3H), 7.25–7.11 (m, 5H), 6.75–6.73 (m, 1H), 6.70–6.67 (m, 1H), 6.65–6.62 (m, 1H), 4.37 (d, J = 15.1 Hz, 1H), 4.34 (d, J = 15.1 Hz, 1H), 1.21 (s, 9H), 0.97 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 155.8, 142.4, 142.0, 140.4, 135.1, 133.4, 132.5, 132.2, 131.0, 130.0, 128.8, 128.4, 127.8, 119.6, 117.7, 58.1, 47.5, 28.9, 25.8, 18.4, –4.2. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{32}H_{40}NO_2SeSi^+$ 578.1988; Found 578.1983.



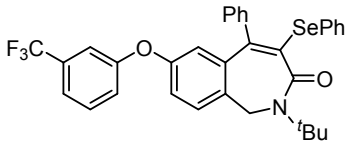
2-(*tert*-Butyl)-8-(methylthio)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (9). rr = 6:1; White solid (32.5 mg, 33% yield); m.p. = 188.3–190.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68–7.51 (m, 2H), 7.40–7.33 (m, 3H), 7.25–7.18 (m, 4H), 7.18–7.11 (m, 2H), 7.04–7.00 (m, 1H), 6.74 (d, J = 8.3 Hz, 1H), 4.42–4.30 (m, 2H), 2.31 (m, 3H), 1.11 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 141.8, 141.6, 139.4, 139.2, 136.8, 135.7, 135.2, 131.1, 130.7, 130.0, 128.8, 128.5 (2C), 127.9, 125.1, 123.8, 58.2, 47.5, 28.9, 15.6. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{28}NOSSe^+$ 494.1051; Found 494.1045.



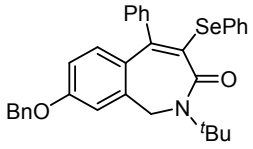
2-(*tert*-Butyl)-8-phenoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (10). rr > 19:1; White solid (72.1 mg, 67% yield); m.p. = 186.2–188.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 2H), 7.39–7.36 (m, 3H), 7.36–7.32 (m, 2H), 7.23–7.18 (m, 4H), 7.17–7.10 (m, 2H), 7.02–6.99 (m, 2H), 6.95–6.93 (m, 1H), 6.80–6.78 (m, 2H), 4.42 (d, J = 15.1 Hz, 1H), 4.37 (d, J = 15.1 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 157.2, 156.6, 141.7, 140.7, 135.2, 134.5, 134.0, 132.3, 130.7, 130.0 (2C), 128.8, 128.5 (2C), 127.9, 124.0, 119.2, 117.7, 116.2, 58.2, 47.4, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{32}H_{30}NO_2Se^+$ 540.1436; Found 540.1431.



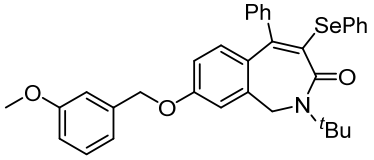
4-((2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl)oxy)benzonitrile (11). rr > 19:1; White solid (63.2 mg, 56% yield); m.p. = 214.5–217.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.58–7.54 (m, 2H), 7.42–7.37 (m, 3H), 7.26–7.14 (m, 5H), 7.01–6.97 (m, 3H), 6.89–6.83 (m, 2H), 4.44 (d, J = 12.9 Hz, 1H), 4.41 (d, J = 12.9 Hz, 1H), 1.17 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 161.2, 154.5, 141.4, 141.1, 141.0, 135.9, 135.5, 134.4, 132.7, 130.4, 130.0, 128.9, 128.7, 128.6, 128.1, 119.4, 118.3, 117.9, 106.6, 58.3, 47.3, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{33}H_{29}N_2O_2Se^+$ 565.1389; Found 565.1387.



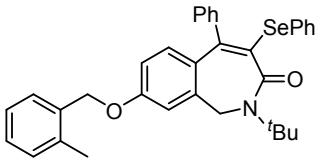
2-(*tert*-Butyl)-5-phenyl-4-(phenylselanyl)-7-(3-(trifluoromethyl)phenoxy)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (12). rr = 16:1; White solid (106.0 mg, 87% yield); m.p. = 192.0–194.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2H), 7.47–7.42 (m, 1H), 7.40–7.35 (m, 4H), 7.24–7.18 (m, 5H), 7.18–7.14 (m, 2H), 6.97–6.94 (m, 1H), 6.86–6.81 (m, 2H), 4.43 (d, J = 15.3 Hz, 1H), 4.38 (d, J = 15.0 Hz, 1H), 1.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 157.3, 155.9, 141.5, 141.3, 140.9, 135.3, 135.2, 134.9, 132.6, 130.6 (2C), 130.0, 128.9, 128.6, 128.5, 128.0, 123.7 (q, $J_{C–F}$ = 272.6 Hz), 122.0, 120.3 (q, $J_{C–F}$ = 3.5 Hz), 118.4, 116.6, 115.5 (q, $J_{C–F}$ = 3.5 Hz), 58.3, 47.4, 28.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.7. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{33}H_{29}F_3NO_2Se^+$ 608.1310; Found 608.1309.



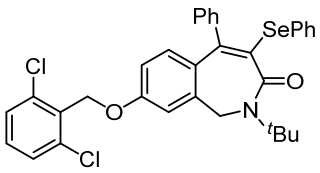
8-(Benzyloxy)-2-(*tert*-butyl)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (13). rr > 19:1; White solid (83.9 mg, 76% yield); m.p. = 192.4–194.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.42–7.37 (m, 3H), 7.37–7.34 (m, 4H), 7.33–7.30 (m, 1H), 7.23–7.13 (m, 5H), 6.87–6.84 (m, 1H), 6.80–6.76 (m, 1H), 6.75–6.72 (m, 1H), 5.08 (d, J = 11.8 Hz, 1H), 5.03 (d, J = 11.8 Hz, 1H), 4.37 (d, J = 3.1 Hz, 2H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 158.5, 142.3, 142.0, 140.5, 136.6, 135.1, 133.4, 132.2, 132.1, 130.9, 130.0, 128.8 (2C), 128.4, 128.3, 127.7, 127.5, 113.9, 112.9, 70.2, 58.1, 47.6, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{33}H_{32}NO_2Se^+$ 554.1593; Found 554.1588.



2-(*tert*-Butyl)-8-((3-methoxybenzyl)oxy)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (14). rr > 19:1; White solid (107.5 mg, 92% yield); m.p. = 165.3–167.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.36–7.32 (m, 3H), 7.29–7.25 (m, 1H), 7.25–7.21 (m, 1H), 7.20–7.13 (m, 4H), 6.97–6.93 (m, 2H), 6.86–6.82 (m, 2H), 6.79–6.75 (m, 1H), 6.74–6.71 (d, J = 8.7 Hz, 1H), 5.05 (d, J = 11.9 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 4.36 (d, J = 3.0 Hz, 2H), 3.76 (s, 3H), 1.15 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.9, 158.3, 142.2, 141.9, 140.4, 138.1, 135.0, 133.3, 132.1, 131.9, 130.8, 129.9, 129.8, 128.7, 128.3, 127.7, 119.6, 113.9, 113.6, 112.9, 112.8, 70.0, 58.0, 55.3, 47.5, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{34}H_{34}NO_3Se^+$ 584.1698; Found 584.1694.

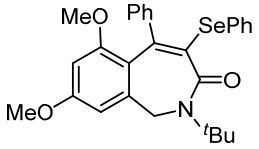


2-(*tert*-Butyl)-8-((4-methoxybenzyl)oxy)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (15). rr > 19:1; White solid (107.5 mg, 95% yield); m.p. = 194.7–196.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.37–7.33 (m, 4H), 7.25–7.20 (m, 3H), 7.20–7.13 (m, 5H), 6.89–6.85 (m, 1H), 6.81–6.77 (m, 1H), 6.77–6.73 (m, 1H), 5.02 (d, J = 1.7 Hz, 2H), 4.38 (s, 2H), 2.35 (s, 3H), 1.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 158.6, 142.3, 141.9, 140.5, 136.7, 135.0, 134.3, 133.4, 132.2, 132.0, 130.9, 130.6, 130.0, 128.8, 128.6, 128.4, 127.7, 126.2, 113.5, 113.0, 68.8, 58.1, 47.6, 28.8, 19.0. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{34}H_{34}NO_2Se^+$ 568.1749; Found 568.1746.

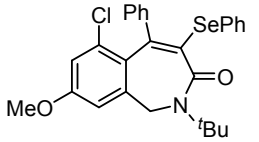


2-(*tert*-Butyl)-8-((2,6-dichlorobenzyl)oxy)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-be

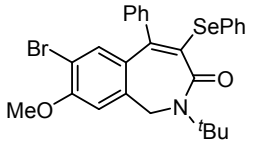
nzo[*c*]azepin-3-one (16). rr > 19:1; White solid (67.7 mg, 54% yield); m.p. = 196.5–198.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.38–7.34 (m, 5H), 7.26–7.23 (m, 1H), 7.23–7.14 (m, 5H), 6.93–6.91 (m, 1H), 6.86–6.83 (m, 1H), 6.79–6.76 (m, 1H), 5.30 (d, J = 10.0 Hz, 1H), 5.24 (d, J = 10.0 Hz, 1H), 4.40 (s, 2H), 1.20 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 158.7, 142.3, 142.0, 140.5, 137.0, 135.1, 133.5, 132.5, 132.2, 131.9, 130.9, 130.7, 130.0, 128.8, 128.7, 128.4, 127.8, 113.7, 113.2, 65.5, 58.2, 47.6, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{33}H_{30}Cl_2NO_2Se^+$ 622.0813; Found 622.0812.



2-(*tert*-Butyl)-6,8-dimethoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (17). White solid (42.7 mg, 42% yield); m.p. = 240.1–243.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 2H), 7.34–7.27 (m, 3H), 7.25–7.13 (m, 5H), 6.43 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 4.35 (d, J = 14.9 Hz, 1H), 4.27 (d, J = 15.0 Hz, 1H), 3.82 (s, 3H), 3.26 (s, 3H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 160.7, 159.5, 143.3, 142.7, 139.3, 136.0, 133.4, 130.1, 128.8, 128.5, 128.1, 127.7, 127.5, 121.2, 103.7, 98.8, 57.8, 55.6, 55.5, 48.2, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_3Se^+$ 508.1385; Found 508.1382.

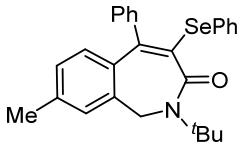


2-(*tert*-Butyl)-6-chloro-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (18). rr > 19:1; White solid (64.2 mg, 63% yield); m.p. = 236.8–238.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.60 (m, 2H), 7.36–7.32 (m, 3H), 7.26–7.23 (m, 1H), 7.23–7.17 (m, 3H), 7.17–7.13 (m, 1H), 6.79–6.74 (m, 2H), 4.35 (d, J = 15.1 Hz, 1H), 4.28 (d, J = 15.1 Hz, 1H), 3.78 (s, 3H), 1.03 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 159.3, 143.9, 141.6, 137.8, 136.7, 136.1, 136.0, 129.7, 129.4, 129.1, 128.9, 128.6, 128.2, 128.1, 115.2, 111.7, 58.0, 55.8, 48.5, 28.7. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}ClNO_2Se^+$ 512.0890; Found 512.0888.

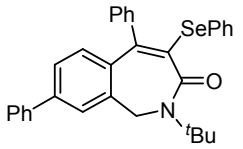


7-Bromo-2-(*tert*-butyl)-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (19). rr > 19:1; White solid (72.5 mg, 65% yield); m.p. = 246.6–248.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.42–7.34 (m, 4H), 7.26–7.09 (m, 5H), 6.99 (s, 1H), 6.78 (s, 1H), 4.43–4.34 (m, 2H), 3.91 (s, 3H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 155.5, 141.1, 140.7, 139.6, 135.3, 135.1, 134.9, 132.9, 130.5, 129.9, 128.8, 128.7,

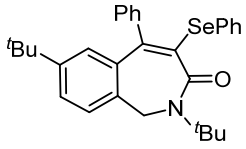
128.6, 127.9, 111.0, 109.3, 58.1, 56.5, 47.4, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}BrNO_2Se^+$ 556.0385; Found 556.0383.



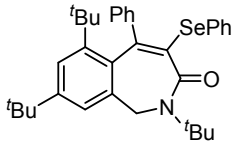
2-(*tert*-Butyl)-8-methyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (20). rr = 3:1; White solid (53.6 mg, 58% yield); m.p. = 162.5–164.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67–7.52 (m, 2H), 7.39–7.30 (m, 3H), 7.24–7.13 (m, 5H), 7.09 (d, J = 1.8 Hz, 1H), 7.03–6.91 (m, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.44–4.34 (m, 2H), 2.01 (m, 3H), 1.11 (m, 9H). **^{13}C NMR for isomer 1** (101 MHz, $CDCl_3$) δ 165.7, 142.4, 141.9, 139.0, 138.4, 136.7, 136.3, 135.2, 130.8, 130.6, 130.0, 128.8, 128.6, 128.4, 127.8, 126.9, 58.2, 47.5, 28.9, 21.4. **^{13}C NMR for isomer 2** (101 MHz, $CDCl_3$) δ 165.4, 142.1, 141.0, 139.9, 138.7, 137.9, 135.5, 134.5, 131.4, 129.5, 129.2, 128.5, 128.2 (2C), 128.0, 124.1, 57.8, 48.5, 28.7, 22.3. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{28}NOSe^+$ 462.1331; Found 462.1329.



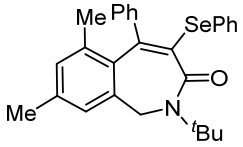
2-(*tert*-Butyl)-5,8-diphenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (21). rr = 4:1; White solid (68.9 mg, 66% yield); m.p. = 195.7–198.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.52 (m, 4H), 7.50 (d, J = 1.9 Hz, 1H), 7.46–7.40 (m, 2H), 7.40–7.35 (m, 4H), 7.24–7.18 (m, 4H), 7.06–7.00 (m, 1H), 6.94–6.90 (m, 1H), 6.89–6.55 (m, 1H), 4.56–4.39 (m, 2H), 1.16 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 144.1, 142.0, 141.9, 141.8, 141.7 (2C), 141.0, 140.5, 140.2, 139.5, 138.2, 137.9, 136.5, 135.8, 135.3, 135.2, 131.1, 130.7, 130.4, 130.0, 129.2, 129.1, 129.0, 128.8 (2C), 128.5, 128.4, 127.9, 127.8 (2C), 127.2, 127.1, 126.6, 126.5, 125.0, 124.8, 58.3, 57.9, 48.4, 47.7, 28.9, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{32}H_{30}NOSe^+$ 524.1487; Found 524.1482.



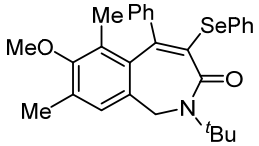
2,7-di-*tert*-Butyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (22). White solid (76.6 mg, 76% yield); m.p. = 208.2–210.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.7, 1.8 Hz, 2H), 7.38–7.35 (m, 3H), 7.28–7.26 (m, 1H), 7.25–7.17 (m, 6H), 6.81 (d, J = 2.0 Hz, 1H), 4.44 (d, J = 15.1 Hz, 1H), 4.38 (d, J = 15.1 Hz, 1H), 1.19 (s, 9H), 1.12 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 150.6, 142.8, 141.9, 138.6, 136.3, 135.3, 135.0, 130.8, 130.1, 128.9, 128.5, 128.4, 128.1, 127.9, 125.9, 125.2, 58.1, 47.2, 34.6, 31.2, 28.9; **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{30}H_{34}NOSe^+$ 504.1800; Found 504.1795.



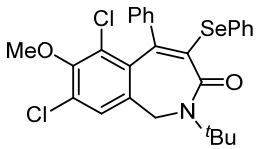
2,7-di-*tert*-Butyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (23). White solid (90.8 mg, 81% yield); m.p. = 167.6–169.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.42–7.40 (m, 1H), 7.31–7.27 (m, 4H), 7.24–7.20 (m, 2H), 7.11–7.09 (m, 1H), 6.98–6.91 (m, 2H), 4.40 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 15.3 Hz, 1H), 1.33 (s, 9H), 0.97 (s, 9H), 0.93 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 151.0, 149.9, 143.2, 142.9, 140.3, 137.3, 134.6, 131.6, 130.0, 128.8, 128.7, 128.4, 128.2, 127.7, 125.3, 120.9, 57.3, 49.9, 36.7, 34.8, 31.9, 31.5, 28.5. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{34}H_{42}NOSe^+$ 560.2426; Found 560.2426.



2-(*tert*-Butyl)-6,8-dimethyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (24). White solid (90.1 mg, 95% yield); m.p. = 171.5–172.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.62 (m, 2H), 7.35–7.30 (m, 3H), 7.27–7.12 (m, 5H), 6.95–6.92 (m, 1H), 6.85–6.82 (m, 1H), 4.36 (d, J = 15.0 Hz, 1H), 4.27 (d, J = 15.0 Hz, 1H), 2.30 (s, 3H), 1.64 (s, 3H), 1.04 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 142.3, 141.0, 140.0, 138.4, 137.8, 136.5, 135.2, 134.8, 132.1, 129.4 (2C), 128.8, 128.4, 128.2, 128.1, 124.7, 57.7, 48.4, 28.7, 22.1, 21.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NOSe^+$ 476.1487; Found 476.1483.

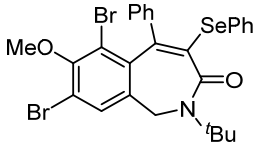


2-(*tert*-Butyl)-7-methoxy-6,8-dimethyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (25). White solid (92.1 mg, 91% yield); m.p. = 184.2–186.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.63 (m, 2H), 7.36–7.27 (m, 4H), 7.25–7.14 (m, 4H), 6.94 (s, 1H), 4.31 (d, J = 15.1 Hz, 1H), 4.24 (d, J = 15.1 Hz, 1H), 3.56 (s, 3H), 2.28 (s, 3H), 1.63 (s, 3H), 1.03 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 157.4, 142.4, 140.0, 137.6, 136.9, 136.7, 135.2, 131.7, 130.9, 129.5, 129.3, 128.9, 128.5, 128.2, 128.1, 126.4, 59.9, 57.8, 48.2, 28.8, 16.5, 15.3. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{29}H_{32}NO_2Se^+$ 506.1593; Found 506.1583.

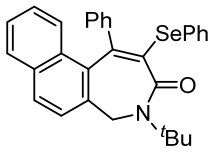


2-(*tert*-Butyl)-6,8-dichloro-7-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (26). White solid (69.5 mg, 64% yield); m.p. = 183.3–185.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.62 (m, 2H), 7.38–7.34 (m, 3H), 7.31–7.27 (m, 2H), 7.26–7.14 (m,

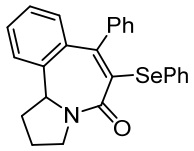
4H), 4.35 (d, J = 15.3 Hz, 1H), 4.29 (d, J = 15.3 Hz, 1H), 3.78 (s, 3H), 1.03 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 153.1, 140.8, 138.7, 138.6, 137.3, 136.9 (2C), 131.0, 129.4, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 126.0, 60.8, 58.2, 47.8, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{26}Cl_2NO_2Se^+$ 492.1436; Found 492.1433.



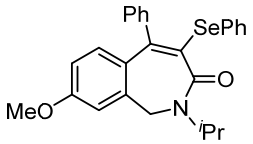
6,8-Dibromo-2-(*tert*-butyl)-7-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (27). White solid (66.0 mg, 52% yield); m.p. =180.1–182.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67–7.63 (m, 2H), 7.46 (s, 1H), 7.37–7.34 (m, 3H), 7.31–7.28 (m, 1H), 7.25–7.07 (m, 4H), 4.35 (d, J = 15.3 Hz, 1H), 4.29 (d, J = 15.3 Hz, 1H), 3.78 (s, 3H), 1.01 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 155.0, 140.7, 140.0, 139.8, 138.4, 137.9, 137.1, 129.8, 129.0 (2C), 128.5 (2C), 128.2, 121.8, 117.3, 60.8, 58.1, 47.8, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{26}Br_2NO_2Se^+$ 633.9490; Found 633.9487.



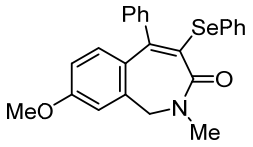
4-(*tert*-Butyl)-1-phenyl-2-(phenylselanyl)-4,5-dihydro-3*H*-naphtho[2,1-*c*]azepin-3-one (28). rr > 19:1; White solid (70.8 mg, 71% yield); m.p. = 354.2–356.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 1H), 7.76–7.70 (m, 3H), 7.53 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.33–7.28 (m, 4H), 7.28–7.24 (m, 3H), 7.23–7.17 (m, 2H), 7.13–7.09 (m, 1H), 4.58 (d, J = 15.2 Hz, 1H), 4.46 (d, J = 15.2 Hz, 1H), 1.02 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 142.8, 139.4, 138.9, 137.1, 136.8, 135.1, 134.0, 132.0, 129.5, 129.3, 129.2, 128.9, 128.7, 128.4, 128.3 (2C), 127.9, 126.0, 125.6, 124.5, 57.7, 48.7, 28.7. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{30}H_{28}NOSe^+$ 498.1331; Found 498.1326.



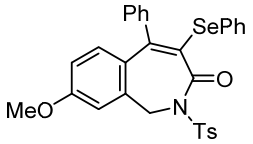
7-Phenyl-6-(phenylselanyl)-1,2,3,11b-tetrahydro-5*H*-benzo[*c*]pyrrolo[1,2-*a*]azepin-5-one (29). White solid (37.8 mg, 44% yield); m.p. = 189.9–191.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2H), 7.40–7.35 (m, 3H), 7.31–7.27 (m, 2H), 7.25–7.10 (m, 6H), 6.89–6.82 (m, 1H), 4.90 (dd, J = 7.8, 1.6 Hz, 1H), 3.64–3.53 (m, 1H), 3.05–2.94 (m, 1H), 2.78–2.68 (m, 1H), 2.35–2.21 (m, 1H), 2.17–2.04 (m, 1H), 2.03–1.96 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 145.5, 142.6, 139.6, 138.9, 134.3, 134.2, 131.9, 131.3, 129.8, 128.9, 128.6, 128.5, 128.4, 127.8, 127.4, 121.9, 57.4, 45.9, 27.7, 23.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{25}H_{22}NOSe^+$ 432.0861; Found 432.0863.



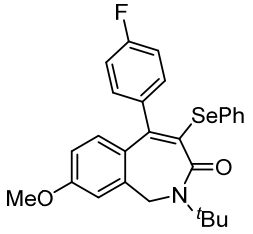
2-Isopropyl-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-on e (30). rr = 15:1; White solid (86.3 mg, 93% yield); m.p. = 175.3–177.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.39–7.34 (m, 3H), 7.18 (d, J = 6.8 Hz, 5H), 6.80 (d, J = 2.5 Hz, 1H), 6.73 (d, J = 8.6 Hz, 1H), 6.70–6.66 (m, 1H), 4.61–4.54 (m, 1H), 4.36 (d, J = 14.6 Hz, 1H), 4.07 (d, J = 14.6 Hz, 1H), 3.81–3.23 (m, 3H), 1.10–0.92 (m, 3H), 0.87–0.67 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 159.5, 144.7, 142.4, 140.4, 134.6, 132.5, 131.8, 131.7, 131.3, 129.9, 128.9, 128.5, 128.4, 127.7 (2C), 112.7, 55.5, 45.5, 45.3, 21.0, 20.1. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2Se^+$ 464.1123; Found 464.1125.



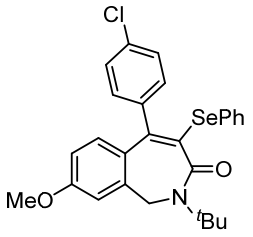
8-Methoxy-2-methyl-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (31). rr > 19:1; White solid (78.1 mg, 90% yield); m.p. = 181.9–184.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.37–7.32 (m, 3H), 7.23–7.12 (m, 5H), 6.80–6.78 (m, 1H), 6.76–6.72 (m, 1H), 6.72–6.68 (m, 1H), 4.74 (d, J = 14.3 Hz, 1H), 3.84 (d, J = 14.4 Hz, 1H), 3.79 (s, 3H), 2.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 159.7, 145.3, 142.1, 138.4, 134.2, 132.7, 131.5, 131.2, 130.8, 129.8, 128.9, 128.4, 128.3, 127.7, 113.0, 112.5, 55.5, 53.6, 34.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{24}H_{22}NO_2Se^+$ 436.0810; Found 436.0811.



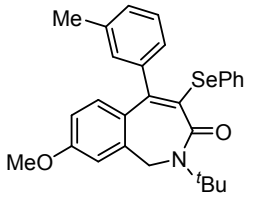
8-Methoxy-5-phenyl-4-(phenylselanyl)-2-tosyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (32). rr = 15:1; White solid (45.1 mg, 39% yield); m.p. = 230.7–233.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.39–7.34 (m, 5H), 7.17–7.13 (m, 2H), 7.11–7.06 (m, 6H), 6.75 (dd, J = 8.8, 2.6 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 5.31 (d, J = 15.0 Hz, 1H), 4.65 (d, J = 14.9 Hz, 1H), 3.88–3.22 (m, 3H), 2.38–2.31 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 160.3, 148.0, 144.5, 141.9, 138.3, 135.7, 134.1, 133.2, 130.8, 130.3, 129.6, 129.2, 129.1, 129.0 (2C), 128.7, 128.5, 128.0, 114.5, 112.7, 55.8, 48.5, 21.7. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{30}H_{26}NO_4SSe^+$ 576.0742; Found 576.0739.



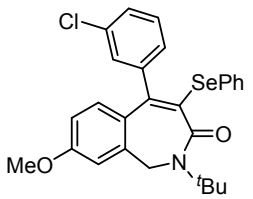
(*tert*-Butyl)-5-(4-fluorophenyl)-8-methoxy-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (33). rr = 15:1; White solid (83.5 mg, 84% yield); m.p. = 217.7–219.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.48 (m, 2H), 7.25–7.08 (m, 5H), 7.05–6.98 (m, 2H), 6.83–6.79 (m, 1H), 6.73–6.68 (m, 2H), 4.44–4.34 (m, 2H), 3.81–3.28 (m, 3H), 1.26–1.06 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 162.6 (d, J_{C-F} = 248.0 Hz), 159.5, 141.2, 140.5, 137.9 (d, J_{C-F} = 3.1 Hz), 135.0, 133.4, 132.1, 131.8 (d, J_{C-F} = 8.1 Hz), 131.7, 130.8, 128.8, 127.8, 115.3 (d, J_{C-F} = 21.7 Hz), 112.7, 112.2, 58.2, 55.5, 47.5, 28.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –113.0, –114.4. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}FNO_2Se^+$ 496.1186; Found 496.1182.



2-(*tert*-Butyl)-5-(4-chlorophenyl)-8-methoxy-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (34). rr = 17:1; White solid (94.8 mg, 93% yield); m.p. = 207.6–209.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.32–7.26 (m, 2H), 7.24–7.13 (m, 4H), 7.13–7.05 (m, 1H), 6.84–6.79 (m, 1H), 6.73–6.69 (m, 2H), 4.41 (d, J = 15.2 Hz, 1H), 4.36 (d, J = 14.9 Hz, 1H), 3.83–3.29 (m, 3H), 1.26–1.06 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 159.5, 141.1, 140.6, 140.3, 135.0, 134.2, 133.5, 132.0, 131.4 (2C), 130.7, 128.8, 128.5, 127.8, 112.7, 112.3, 58.2, 55.5, 47.5, 28.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}ClNO_2Se^+$ 512.0890; Found 512.0890.

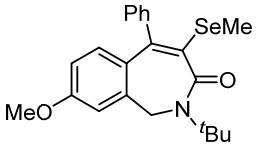


2-(*tert*-Butyl)-8-methoxy-4-(phenylselanyl)-5-(*m*-tolyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (35). rr = 15:1; White solid (89.6 mg, 91% yield); m.p. = 193.1–195.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.28–7.24 (m, 1H), 7.24–7.11 (m, 6H), 6.81 (d, J = 2.5 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 6.69 (dd, J = 8.7, 2.6 Hz, 1H), 4.42–4.35 (m, 2H), 3.80–3.25 (m, 3H), 2.36–2.07 (m, 3H), 1.24–1.06 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 159.3, 142.5, 141.9, 140.4, 135.0, 133.0, 132.2, 131.8, 130.9, 129.1, 128.7, 127.6, 112.6, 112.0, 58.0, 55.4, 47.5, 28.8, 21.5. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2Se^+$ 492.1436; Found 492.1435.

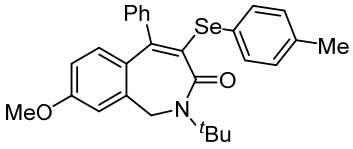


2-(*tert*-Butyl)-5-(3-chlorophenyl)-8-methoxy-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]a

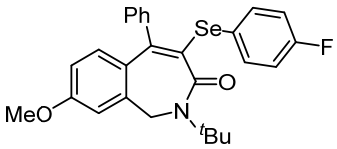
zepin-3-one (36). rr = 15:1; White solid (67.7 mg, 66% yield); m.p. = 205.9–209.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.46 (m, 3H), 7.30–7.37 (m, 2H), 7.22–7.13 (m, 4H), 6.83–6.80 (m, 1H), 6.73–6.69 (m, 2H), 4.41 (d, J = 15.1 Hz, 1H), 4.36 (d, J = 15.1 Hz, 1H), 3.81–3.30 (m, 3H), 1.26–1.06 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 159.6, 143.6, 141.0, 140.5, 135.1, 134.3, 133.8, 132.0, 131.3, 130.6, 130.0, 129.6, 128.9, 128.4, 128.3, 127.9, 112.8, 112.3, 58.3, 55.5, 47.6, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}ClNO_2Se^+$ 512.0890; Found 512.0890.



3-(*tert*-Butyl)-8-methoxy-4-(methylselanyl)-5-phenyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (37). rr > 19:1; White solid (49.9 mg, 60% yield); m.p. = 177.6–178.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 3H), 7.29–7.15 (m, 2H), 6.87–6.83 (m, 1H), 6.77–6.74 (m, 1H), 6.73–6.69 (m, 1H), 4.48 (d, J = 15.1 Hz, 1H), 4.34 (d, J = 15.1 Hz, 1H), 3.81 (s, 3H), 2.08 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 159.2, 142.0, 141.4, 140.4, 132.1, 131.9, 131.6, 129.9, 128.5, 128.4, 112.7, 112.1, 58.7, 55.5, 47.7, 29.3, 8.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_2Se^+$ 416.1123; Found 416.1119.

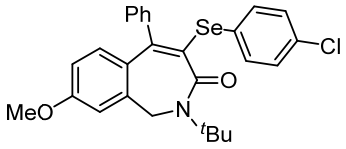


2-(*tert*-Butyl)-8-methoxy-5-phenyl-4-(*p*-tolylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (38). rr > 19:1; White solid (90.2 mg, 92% yield); m.p. = 197.8–198.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.38–7.32 (m, 3H), 7.32–7.21 (m, 1H), 7.21–7.13 (m, 1H), 7.01–6.97 (m, 2H), 6.82–6.79 (m, 1H), 6.76–6.72 (m, 1H), 6.71–6.66 (m, 1H), 4.37 (s, 2H), 3.78 (s, 3H), 2.27 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 159.3, 142.0, 141.9, 140.6, 137.7, 135.3, 133.6, 132.1, 131.9, 130.0, 129.5, 128.3, 127.2, 112.6, 112.1, 58.0, 55.5, 47.6, 28.9, 21.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2Se^+$ 492.1436; Found 492.1435.

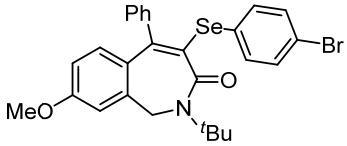


2-(*tert*-Butyl)-4-((4-fluorophenyl)selanyl)-8-methoxy-5-phenyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (39). rr = 15:1; White solid (70.5 mg, 71% yield); m.p. = 203.3–205.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.38–7.34 (m, 3H), 7.28–7.11 (m, 2H), 6.90–6.85 (m, 2H), 6.82–6.80 (m, 1H), 6.76–6.73 (m, 1H), 6.71–6.68(m, 1H), 4.39 (d, J = 15.0 Hz, 1H), 4.33 (d, J = 15.0 Hz, 1H), 3.81–3.25 (m, 3H), 1.26–1.09 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 162.8 (d, $J_{C–F}$ = 247.4 Hz), 159.5, 142.2, 141.9, 140.5, 137.5 (d, $J_{C–F}$ = 8.0 Hz), 133.3, 132.2, 131.7, 130.0, 128.5 (d, $J_{C–F}$ = 4.3 Hz), 125.6, 125.5, 115.9 (d,

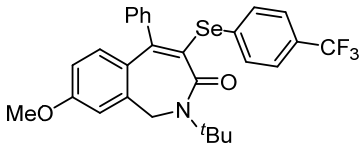
$J_{C–F}$ = 21.4 Hz), 112.7, 112.2, 58.2, 55.5, 47.6, 28.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –113.3, –113.8. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}FNO_2Se^+$ 496.1186; Found 496.1182.



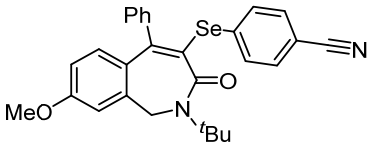
2-(*tert*-Butyl)-4-((4-chlorophenyl)selanyl)-8-methoxy-5-phenyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (40). rr = 17:1; White solid (81.9 mg, 80% yield); m.p. = 189.8–190.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.38–7.33 (m, 3H), 7.33–7.24(m, 1H), 7.19–7.11 (m, 3H), 6.83–6.80 (m, 1H), 6.75–6.75 (m, 1H), 6.72–6.68 (m, 1H), 4.42 (d, J = 15.1 Hz, 1H), 4.35 (d, J = 14.8 Hz, 1H), 3.82–3.24 (m, 3H), 1.28–1.10 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.5, 142.7, 141.9, 140.4, 136.4, 134.0, 132.8, 132.3, 131.7, 129.9, 129.2, 128.9, 128.5, 128.4, 112.7, 112.2, 58.3, 55.5, 47.6, 28.9. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}ClNO_2Se^+$ 512.0890; Found 512.0886.



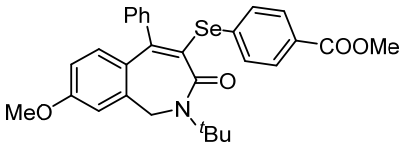
4-((4-Bromophenyl)selanyl)-2-(*tert*-butyl)-8-methoxy-5-phenyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (41). rr = 16:1; White solid (102.9 mg, 93% yield); m.p. = 176.8–179.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 1H), 7.38–7.32 (m, 5H), 7.30–7.26 (m, 3H), 6.83–6.81 (m, 1H), 6.75–6.72 (m, 1H), 6.71–6.68 (m, 1H), 4.42 (d, J = 15.1 Hz, 1H), 4.35 (d, J = 14.8 Hz, 1H), 3.81–3.24 (m, 3H), 1.29–1.10 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.5, 142.8, 141.8, 140.4, 136.6, 132.6, 132.2, 131.8, 131.6, 129.9, 128.4 (2C), 122.1, 112.7, 112.1, 58.3, 55.5, 47.6, 28.9. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{27}BrNO_2Se^+$ 556.0385; Found 556.0385.



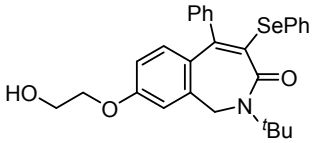
2-(*tert*-Butyl)-8-methoxy-5-phenyl-4-((4-(trifluoromethyl)phenyl)selanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (42). rr = 17:1; White solid (66.7 mg, 61% yield); m.p. = 181.0–182.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.42–7.38 (m, 2H), 7.38–7.27 (s, 4H), 7.22–7.11 (m, 1H), 6.86–6.82 (m, 1H), 6.76–6.69 (m, 2H), 4.48 (d, J = 15.1 Hz, 1H), 4.41 (d, J = 15.3 Hz, 1H), 3.85–3.24 (m, 3H), 1.33–1.09 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 159.7, 143.8, 141.9, 140.4, 136.3, 134.6, 132.4, 132.2, 131.6, 129.9, 129.6 (q, $J_{C–F}$ = 32.3 Hz) 128.5 (2C), 125.5 (q, $J_{C–F}$ = 3.8 Hz), 124.2 (q, $J_{C–F}$ = 272.4 Hz), 112.8, 112.3, 58.5, 55.5, 47.7, 28.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.7. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{28}H_{27}F_3NO_2Se^+$ 546.1154; Found 546.1149.



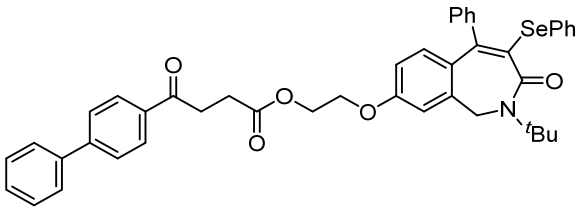
4-((2-(*tert*-Butyl)-8-methoxy-3-oxo-5-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepin-4-yl)selanyl)benzonitrile (43). rr = 15:1; White solid (86.6 mg, 86% yield); m.p. = 193.3–195.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.43–7.39 (m, 2H), 7.36–7.31 (m, 3H), 7.29–7.26 (m, 1H), 7.20–7.08(m, 1H), 6.88–6.84 (m, 1H), 6.75–6.70 (m, 2H), 4.53 (d, J = 15.1 Hz, 1H), 4.43 (d, J = 15.3 Hz, 1H), 3.85–3.24 (m, 3H), 1.31–1.14 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.9, 144.8, 141.8, 140.3, 138.9, 133.8, 132.5, 132.0, 131.4, 131.2, 129.7, 128.6, 128.4, 118.9, 112.9, 112.3, 110.5, 58.6, 55.5, 47.7, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{27}N_2O_2Se^+$ 503.1232; Found 503.1232.



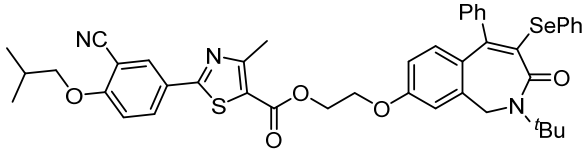
Methyl 4-((2-(*tert*-butyl)-8-methoxy-3-oxo-5-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepin-4-yl) selanyl)benzoate (44). rr = 17:1; White solid (101.7 mg, 95% yield); m.p. = 184.6–18 5.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.80 (m, 2H), 7.56–7.51 (m, 2H), 7.37–7. 31 (m, 3H), 7.31–7.25(m, 1H), 7.21–7.11 (m, 1H), 6.86–6.83 (m, 1H), 6.76–6.73(m,1 H), 6.72–6.69 (m, 1H), 4.50 (d, J = 15.0 Hz, 1H), 4.45 (d, J = 14.8 Hz, 1H), 3.88(s, 3H), 3.84–3.24 (m, 3H), 1.33–1.10 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9,1 65.8, 159.7, 144.2, 141.9, 140.4, 138.2, 133.4, 132.4, 131.9, 131.6, 129.8 (2C), 128.8, 128.5, 128.4, 112.8, 112.2, 58.5, 55.5, 52.2, 47.7, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{29}H_{30}NO_4Se^+$ 536.1335; Found 536.1331.



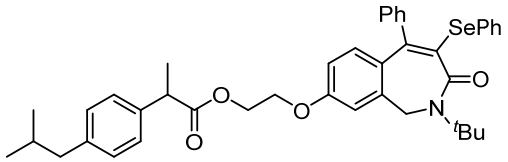
2-(*tert*-Butyl)-8-(2-hydroxyethoxy)-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]a zepin-3-one (45). rr > 19:1; White solid (92.1 mg, 91% yield); m.p. = 203.5–205.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.35 (m, 3H), 7.23–7.15 (m, 5H), 6.86–6.83 (m, 1H), 6.75–6.71 (m, 2H), 6.70–6.66 (m, 2H), 4.40–4.37 (s, 2H), 4.07 (dd, J = 7.3, 2.9 Hz, 2H), 3.96 (dd, J = 4.7 Hz, 2H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) 165.9, 158.6, 142.3, 141.9, 140.6, 135.1, 133.4, 132.3, 132.1, 130.8, 130.0, 128.8, 128.4 (2C), 127.8, 113.3, 112.7, 69.5, 61.3, 58.2, 47.6, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_3Se^+$ 508.1385; Found 508.1387.



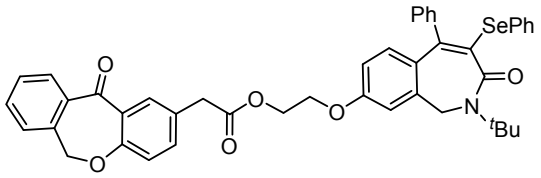
2-((2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl) oxy)ethyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (46). rr > 19:1; White solid (97.8 mg, 66% yield); m.p. = 137.3–140.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–8.04 (m, 2H), 7.69–7.65 (m, 2H), 7.63–7.60 (m, 2H), 7.57–7.53 (m, 2H), 7.49–7.44 (m, 2H), 7.44–7.28 (m, 5H), 7.24–7.16 (m, 4H), 6.88–6.84 (m, 1H), 6.76–6.71 (m, 1H), 6.71–7.66 (m, 1H), 4.47 (dd, J = 5.8, 3.7 Hz, 2H), 4.40 (s, 2H), 4.21–4.14 (m, 2H), 3.35 (t, J = 6.5 Hz, 2H), 2.83 (t, J = 6.5 Hz, 2H), 1.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.7, 173.0, 165.8, 158.3, 146.1, 142.2, 142.0, 140.6, 139.9, 135.3, 135.1, 133.6, 132.3 (2C), 130.9, 130.0, 129.1, 128.8 (2C), 128.4 (2C), 127.8, 127.4 (2C), 113.3, 112.8, 66.1, 62.9, 58.2, 47.6, 33.5, 28.9, 28.4. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{44}H_{42}NO_5Se^+$ 744.2223; Found 744.2221.



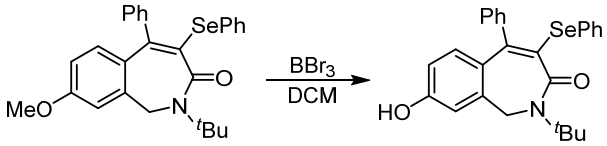
2-((2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl) oxy)ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (47). rr > 19:1; White solid (128.8 mg, 80% yield); m.p. = 140.9–142.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16–8.11 (m, 1H), 8.05–8.01 (m, 1H), 7.54–7.49 (m, 2H), 7.36–7.31 (m, 3H), 7.24–7.07 (m, 5H), 7.03–7.98 (m, 1H), 6.86 (s, 1H), 6.73 (s, 2H), 4.65–4.59 (m, 2H), 4.39 (s, 2H), 4.27 (q, J = 4.4 Hz, 2H), 3.88 (d, J = 6.6 Hz, 2H), 2.74 (s, 3H), 2.17 (m, 1H), 1.20 (s, 9H), 1.07 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 165.7, 162.6, 161.8 (2C), 158.2, 142.0, 141.8, 140.6, 135.0, 133.5, 132.7, 132.3, 132.2, 132.0, 130.7, 129.9, 128.8, 128.4, 128.3, 127.8, 125.9, 121.2, 115.4, 113.3, 112.8 (2C), 103.0, 75.8, 66.0, 63.4, 58.1, 47.5, 28.8, 28.2, 19.1, 17.6. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{44}H_{44}N_3O_5SSe^+$ 806.2161; Found 806.2159.



2-((2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl) oxy)ethyl 2-(4-isobutylphenyl)propanoate (48). rr > 19:1; White solid (110.0 mg, 79% yield); m.p. = 148.6–149.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2H), 7.40–7.34 (m, 3H), 7.24–7.15 (m, 7H), 7.08–7.03 (m, 2H), 6.84–6.80 (m, 1H), 6.76–6.71 (m, 1H), 6.67–6.62 (m, 1H), 4.49–4.40 (m, 2H), 4.40–4.34 (m, 2H), 4.12 (dd, J = 5.9, 4.1 Hz, 2H), 3.74 (q, J = 7.1 Hz, 1H), 2.43 (d, J = 7.1 Hz, 2H), 1.83 (dt, J = 13.5, 6.7 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.22 (s, 9H), 0.90 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 165.8, 158.3, 142.2, 141.9, 140.7, 140.5, 137.6, 137.5, 135.1, 133.5, 132.3, 132.2, 130.9, 130.0, 129.4, 128.8, 128.4, 127.8, 127.2, 113.3, 112.7, 66.1, 62.8, 58.1, 47.5, 45.1 (2C), 30.3, 28.9, 22.5, 18.8. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{41}H_{46}NO_4Se^+$ 696.2587; Found 696.2581.

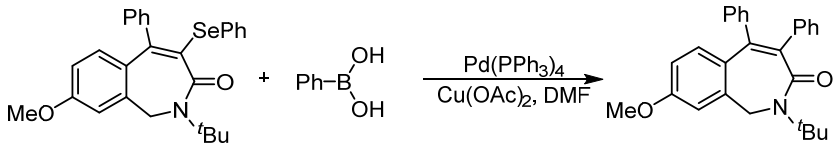


2-((2-(*tert*-Butyl)-3-oxo-5-phenyl-4-(phenylselanyl)-2,3-dihydro-1*H*-benzo[*c*]azepin-8-yl) oxy)ethyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (49). rr > 19:1; White solid (113.1 mg, 75% yield); m.p. = 156.0–159.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13–8.10 (m, 1H), 7.88–7.83 (m, 1H), 7.57–7.52 (m, 3H), 7.47–7.43 (m, 1H), 7.42–7.38 (m, 1H), 7.37–7.32 (m, 4H), 7.26–7.09 (m, 5H), 7.01–6.99 (m, 1H), 6.85–6.82 (m, 1H), 6.75–6.71 (m, 1H), 6.70–6.65 (m, 1H), 5.14 (s, 2H), 4.50–4.41 (m, 2H), 4.38 (s, 2H), 4.19–4.11 (m, 2H), 3.68 (s, 2H), 1.20 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) 190.9, 171.5, 160.6, 158.2, 142.2, 141.9, 140.6, 140.5, 136.4, 135.7, 135.1, 133.6, 133.0, 132.6, 132.4, 132.3, 130.9, 130.0, 129.6, 129.4, 128.8, 128.4, 128.0, 127.8, 127.6, 125.3, 121.2, 113.3, 112.8, 73.7, 66.0, 63.1, 58.2, 47.5, 40.1, 28.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{44}H_{40}NO_6Se^+$ 758.2015; Found 758.2014.



3 **6**

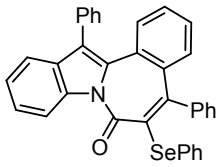
2-(*tert*-Butyl)-8-hydroxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (6). To a solution of **3** (72 mg, 0.15 mmol, 1.0 equiv.) in DCM (5.0 mL), then the mixture was added BBr_3 (1.5 mL) and stirred at 0 ºC for 3.0 h. After the reaction, it was cooled to room temperature, quenched with $NaHCO_3$ saturated solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **6** as a white solid (49.4 mg, 71% yield).



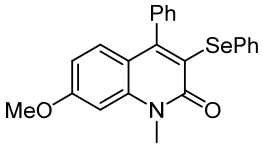
3 **50**

2-(*tert*-Butyl)-8-methoxy-4,5-diphenyl-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (50). To a solution of **3** (72 mg, 0.15 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 20 mol %) and $Cu(OAc)_2$ (33 mg, 0.18 mmol, 1.2 equiv.) in DMF (3.0 mL), then the mixture was added phenylboronic acid (55 mg, 0.45 mmol, 3.0 equiv.) and stirred at 80 ºC for 24 h. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **50** as a white solid (40.1 mg, 67% yield); m.p. = 185.0–187.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.13–7.07 (m, 6H), 6.99–6.95 (m, 2H), 6.91–6.88 (m, 2H), 6.76–6.72 (m, 1H), 4.63 (d, J = 15.1 Hz, 1H), 4.50 (d, J = 15.1 Hz, 1H), 3.84 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz,

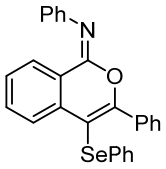
$CDCl_3$) δ 168.9, 159.4, 141.8, 141.3, 140.3, 138.7, 137.2, 132.8, 132.5, 131.4, 131.0, 127.8, 127.5, 127.0, 126.8, 112.7, 112.0, 58.1, 55.5, 47.5, 29.4. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_2^+$ 398.2115; Found 398.2113.



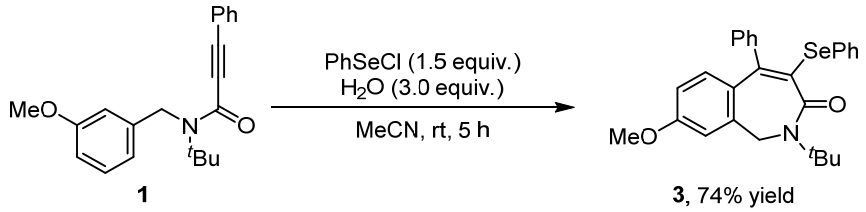
5,13-Diphenyl-6-(phenylselanyl)-7*H*-benzo[3,4]azepino[1,2-*a*]indol-7-one (52). Yellow solid (100.7 mg, 91% yield); m.p. = 188.2–190.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 1H), 7.65–7.60 (m, 2H), 7.54–7.46 (m, 5H), 7.44–7.33 (m, 3H), 7.28–7.26 (m, 1H), 7.17–7.10 (m, 4H), 7.09–7.05 (m, 2H), 7.04–6.95 (m, 3H), 6.80–6.74 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 145.4, 142.1, 136.4, 135.3, 134.2, 133.9, 133.5, 131.9, 131.5, 131.3, 130.8, 130.6, 129.6, 129.2, 129.0, 128.9, 128.8, 128.5, 128.3, 128.0, 127.9, 127.7, 125.9, 124.1, 123.6, 119.5, 113.1. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{35}H_{24}NO_2Se^+$ 554.1018; Found 554.1019.



7-Methoxy-1-methyl-4-phenyl-3-(phenylselanyl)quinolin-2(1*H*)-one (54).[1] rr > 19:1; White solid (51.5 mg, 60% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.36 (m, 3H), 7.28–7.24 (m, 2H), 7.15–7.09 (m, 5H), 7.08–7.05 (m, 1H), 6.83–6.80 (m, 1H), 6.69–6.65 (m, 1H), 3.89 (s, 3H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 161.2, 155.8, 141.9, 138.5, 132.4, 131.8, 130.6, 128.9, 128.7, 128.3, 128.1, 126.6, 122.1, 115.9, 109.6, 98.6, 55.8, 31.1.

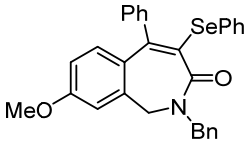


(*E*)-*N*,3-Diphenyl-4-(phenylselanyl)-1*H*-isochromen-1-imine (56).[2] Yellow solid (50.0 mg, 55% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (dd, J = 7.9, 1.5 Hz, 1H), 7.89 (dd, J = 8.0, 1.2 Hz, 1H), 7.54–7.48 (m, 3H), 7.45–7.41 (m, 1H), 7.36–7.28 (m, 5H), 7.26–7.23 (m, 4H), 7.21–7.14 (m, 3H), 7.09–7.04 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 148.8, 146.1, 134.8, 134.3, 132.9, 132.5, 130.0, 129.6 (2C), 128.8, 128.7, 128.0, 127.8, 127.5, 126.3, 124.2, 124.0, 123.0, 103.5.

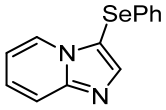


1 **3**, 74% yield

2-(*tert*-Butyl)-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (3). To a solution of **1** (64 mg, 0.2 mmol, 1.0 equiv.), PhSeCl (58 mg, 0.3 mmol, 1.5 equiv.) and H_2O (3.0 equiv.) in MeCN (7.0 mL), then the mixture was stirred at room temperature for 5.0 h. 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 (1:30) to ethyl acetate/petroleum ether (1:10) to give the desired product **3** as a white solid (70.6 mg, 74% yield).



2-Benzyl-8-methoxy-5-phenyl-4-(phenylselanyl)-1,2-dihydro-3*H*-benzo[*c*]azepin-3-one (58). rr = 15:1; White solid (82.7 mg, 81% yield); m.p. = 175.9–177.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.59 (m, 2H), 7.41–7.37 (m, 3H), 7.34–7.31 (m, 1H), 7.27–7.22 (m, 3H), 7.22–7.16 (m, 4H), 6.77–6.72 (m, 3H), 6.70 (dd, J = 8.7, 2.6 Hz, 1H), 6.58 (d, J = 2.6 Hz, 1H), 5.05 (d, J = 15.1 Hz, 1H), 4.47 (d, J = 14.5 Hz, 1H), 3.87 (d, J = 15.1 Hz, 1H), 3.75 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 159.7, 145.3, 142.2, 138.5, 136.7, 135.3, 132.8, 131.4, 131.3, 130.9, 129.8, 129.2, 128.6, 128.5, 128.4, 128.1, 128.0, 127.4, 113.0, 112.4, 55.5, 50.2, 49.1. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{30}H_{26}NO_2Se^+$ 512.1123; Found 512.1125.



3-(Phenylselanyl)imidazo[1,2-*a*]pyridine (62).[3] White solid (47.0 mg, 86% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28–8.24 (m, 1H), 7.98 (s, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.29–7.24 (m, 1H), 7.18–7.12 (m, 5H), 6.87–6.81 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 143.1, 130.6, 129.6, 129.1, 127.0, 125.9, 125.3, 118.0, 113.2, 106.6.

References

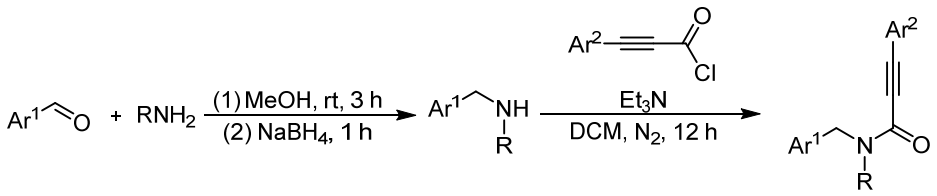
[1] X. Li, B. Zhang, Z. Yu, D. Zhang, H. Shi, L. Xu, Y. Du, *Synthesis* **2022**, *54*, 1375–1387.

[2] J. S. S. Neto, D. F. Back, G. Zeni, *Eur. J. Org. Chem.* **2015**, *7*, 1583–1590.

[3] X. He, W. Song, X. Liu, J. Huang, R. Feng, S. Zhou, J. Hong, X. Ge, *Green Chem.* **2023**, *25*, 1311–1321.

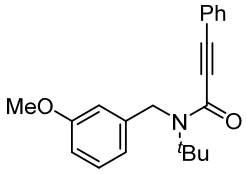
7. Synthesis and Characterization of Substrates

General Procedure for the Synthesis of *N*-Benzyl propiolamides

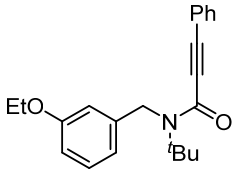


Step 1: To a solution of aldehyde (10 mmol) in methanol (20 mL) was added amine (12 mmol, 1.2 equiv.), and then the resulting solution was stirred for 3.0 h at room temperature. Next, the mixture was added $NaBH_4$ (20 mmol, 2.0 equiv.) at 0 ºC, and then warmed to room temperature and continue to be stirred 1.0 h. The solvent was evaporated under reduced pressure and extracted with EtOAc. The organic layer was dried over Na_2SO_4, and concentrated to afford the crude amine product. The crude product was directly used in the next step without purification.

Step 2: To a solution of amine obtained above and Et_3N (2.8 mL, 20 mmol, 2.0 equiv.) in dry DCM (20 mL) was added phenylpropioloyl chloride (1.5 equiv.) at 0 ºC. Then the resulting mixture was warmed to room temperature and continued to stir for overnight. The solution was diluted with an equal volume of DCM, washed with saturated $NaHCO_3$ aqueous solution (30 mL) two times and brine (30 mL), dried (Na_2SO_4), and purified by column chromatography (petroleum ether/ethyl acetate) to afford *N*-benzyl propiolamide.

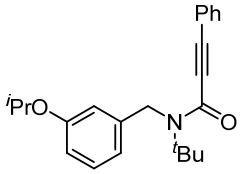


N*-(*tert*-Butyl)-*N*-(3-methoxybenzyl)-3-phenylpropiolamide (S1).** White solid (2.18 g, 68% yield); m.p. = 95.1–97.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 3H), 7.30–7.28 (m, 1H), 7.27–7.25 (m, 2H), 6.92 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 2.0 Hz, 1H), 6.81 (dd, J = 8.3, 2.5 Hz, 1H), 4.99 (s, 2H), 3.80 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 156.3, 141.1, 132.5, 129.9, 128.5, 120.9, 118.8, 112.7, 112.1, 88.0, 84.0, 58.6, 55.4, 51.4, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO_2^+$ 322.1802; Found 322.1796.

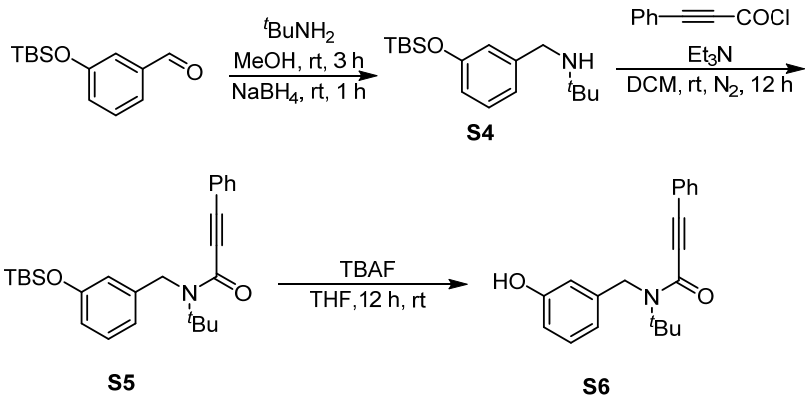


***N*-(*tert*-Butyl)-*N*-(3-ethoxybenzyl)-3-phenylpropiolamide (S2).** White solid (2.19 g, 65% yield); m.p. = 86.0–88.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 3H), 7.29–7.26 (m, 2H), 7.25 (d, J = 7.9 Hz, 1H), 6.92–6.85 (m, 2H), 6.79 (dd, J = 8.2, 2.5 Hz, 1H), 4.98 (s, 2H),

4.01 (q, J = 7.0 Hz, 2H), 1.45 (s, 9H), 1.40 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 156.3, 141.0, 132.5, 129.8 (2C), 128.5, 120.9, 118.6, 113.3, 112.5, 87.9, 84.0, 63.5, 58.5, 51.4, 28.5, 14.9. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_2^+$ 336.1958; Found 336.1952.



N*-(*tert*-Butyl)-*N*-(3-isopropoxybenzyl)-3-phenylpropiolamide (S3).** Yellow solid (1.91 g, 55% yield); m.p. = 77.2–79.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 3H), 7.27–7.21 (m, 3H), 6.88 (d, J = 4.0 Hz, 2H), 6.81–6.77 (m, 1H), 4.97 (s, 2H), 4.56–4.50 (m, 1H), 1.46 (s, 9H), 1.33–1.27 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 156.2, 140.9, 132.3, 129.8, 129.7, 128.4, 120.8, 118.5, 114.7, 113.8, 87.8, 84.0, 69.9, 58.4, 51.3, 28.5, 22.1. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{23}H_{28}NO_2^+$ 350.2115; Found 350.2108.

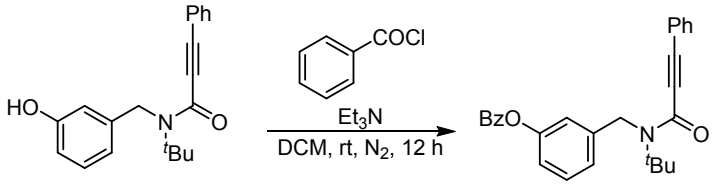


***N*-(3-((*tert*-Butyldimethylsilyl)oxy)benzyl)-2-methylpropan-2-amine (S4).** To a solution of 3-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (10 mmol) in methanol (20 mL) was added *tert*-butylamine (1.2 equiv.), and then the resulting solution was stirred for 3.0 h at room temperature. Next, the mixture was added $NaBH_4$ (2.0 equiv.) at 0 ºC, and then warmed to room temperature and continue to be stirred 1.0 h. The solvent was evaporated under reduced pressure and extracted with EtOAc. The organic layer was dried over Na_2SO_4, and concentrated to afford the crude product **S4**. The crude product was directly used in the next step without purification.

***N*-(*tert*-Butyl)-*N*-(3-((*tert*-butyldimethylsilyl)oxy)benzyl)-3-phenylpropiolamide (S5).** To a solution of **S4** obtained above and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added 3-phenylpropioloyl chloride (1.5 equiv.) at 0 ºC. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S5** as a yellow solid (2.57 g, 61% yield); m.p. = 71.3–73.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 3H), 7.28–7.25 (m, 2H), 7.23–7.18 (m, 1H), 6.91 (d, J = 7.6 Hz, 1H),

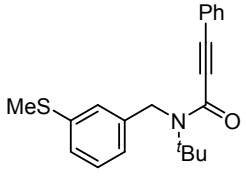
6.85–6.82 (m, 1H), 6.76–6.73 (m, 1H), 4.95 (s, 2H), 1.45 (s, 9H), 0.96 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 156.2, 141.0, 132.5, 129.8 (2C), 128.5, 120.9, 119.5, 119.0, 118.1, 87.8, 84.0, 58.5, 51.2, 28.6, 25.8, 18.3, –4.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{26}H_{36}NO_2Si^+$ 422.2510; Found 422.2508.

N*-(*tert*-Butyl)-*N*-(3-hydroxybenzyl)-3-phenylpropiolamide (S6).** To a solution of **S5** in THF (15 mL) was added TBAF (2.0 equiv.), and then the resulting solution was stirred for 12 h at room temperature. The resulting crude was diluted with water (20 mL), extracted with EtOAc (30×3 mL) and the combined organic phase was dried over Na_2SO_4, filtered and concentrated. After related work-up, the residue was purified by flash chromatography (petroleum ether/ethyl acetate) on silica gel to afford the corresponding product **S6** as a yellow solid (1.42 g, 76% yield). m.p. = 149.0–150.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.24–7.20 (m, 1H), 7.19–7.14 (m, 1H), 7.11–7.07 (m, 1H), 7.03–6.99 (m, 2H), 6.98–6.93 (m, 2H), 6.84 (dd, J = 8.0, 2.6 Hz, 1H), 6.72 (d, J = 7.5 Hz, 1H), 4.99 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 157.2, 140.2, 132.5, 130.0, 129.8, 128.2, 120.3, 117.3, 114.9, 113.3, 90.0, 82.9, 59.2, 51.8, 28.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO_2^+$ 308.1645; Found 308.1645.

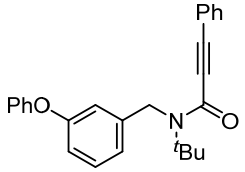


S6 **S7**

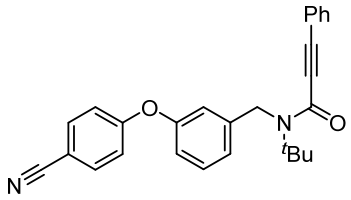
3-((*N*-(*tert*-Butyl)-3-phenylpropiolamido)methyl)phenyl benzoate (S7). To a solution of **S6** (10 mmol) and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added benzoyl chloride (1.5 equiv.) at 0 ℃. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S7** as a white solid (1.35 g, 44% yield); m.p. = 83.8–85.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22–8.18 (m, 2H), 7.67–7.61 (m, 1H), 7.54–7.49 (m, 2H), 7.48–7.40 (m, 2H), 7.38–7.32 (m, 3H), 7.30–7.7 (m, 2H), 7.24–7.20 (m, 1H), 7.18–7.13 (m, 1H), 5.06 (s, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 165.2, 156.4, 151.4, 141.3, 133.8, 133.6, 132.5, 130.3, 130.2, 129.9, 129.5, 128.7, 128.5, 123.9, 120.7, 120.0, 88.3, 83.8, 58.7, 51.1, 28.6. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{27}H_{26}NO_3^+$ 412.1907; Found 412.1899.



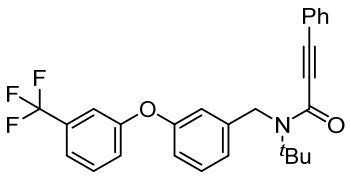
N*-(*tert*-Butyl)-*N*-(3-(methylthio)benzyl)-3-phenylpropiolamide (S8).** Yellow solid (2.39 g, 71% yield); m.p. = 83.9–85.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 3H), 7.30–7.24 (m, 3H), 7.22 (s, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 4.98 (s, 2H), 2.46 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 140.1, 139.2, 132.4, 129.8, 129.2, 128.5, 125.2, 124.2, 123.1, 120.7, 88.0, 83.9, 58.5, 51.2, 28.5, 15.8. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO_2^+$ 338.1573; Found 338.1567.



N*-(*tert*-Butyl)-*N*-(3-phenoxybenzyl)-3-phenylpropiolamide (S9).** Yellow solid (1.88 g, 49% yield); m.p. = 98.1–100.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.3 Hz, 3H), 7.31–7.24 (m, 5H), 7.10–7.05 (m, 2H), 7.00–6.95 (m, 3H), 6.91 (dd, J = 8.2, 2.3 Hz, 1H), 4.97 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 157.2, 156.2, 141.6, 132.4, 130.1, 129.9, 128.5, 123.5, 121.2, 120.8, 118.9, 117.7, 117.0, 87.9, 83.9, 58.5, 51.1, 28.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2^+$ 384.1958; Found 384.1950.

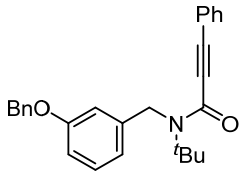


N*-(*tert*-Butyl)-*N*-(3-(4-cyanophenoxy)benzyl)-3-phenylpropiolamide (S10).** White solid (1.73 g, 42% yield); m.p. = 95.1–96.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.41–7.35 (m, 2H), 7.29 (d, J = 7.7 Hz, 4H), 7.20 (d, J = 7.7 Hz, 1H), 7.07 (s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.3 Hz, 2H), 5.01 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 156.2, 141.2, 132.4, 129.8, 128.5, 120.8, 119.7, 113.7, 113.0, 87.9, 83.9, 78.5, 75.8, 58.5, 55.9, 51.3, 28.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}N_2O_2^+$ 409.1911; Found 409.1903.

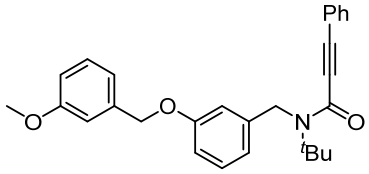


***N*-(*tert*-Butyl)-3-phenyl-*N*-(3-(3-(trifluoromethyl)phenoxy)benzyl)propiolamide (S11).** Yellow solid (2.19 g, 49% yield); m.p. = 83.1–85.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 3H), 7.34–7.32 (m, 3H), 7.31–7.27 (m, 2H), 7.20–7.19 (m, 1H), 7.17–7.14 (m, 1H), 7.14–7.11 (m, 1H), 7.04–7.01 (m, 1H), 6.96–6.92 (m, 1H), 5.00 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 156.7, 156.3, 142.1, 132.4, 132.4 (q, $J_{C–F}$ = 32.7 Hz), 130.5 (2C), 130.0, 128.6, 123.8 (q, $J_{C–F}$ = 272.5 Hz) 122.3, 121.7, 119.9 (q, $J_{C–F}$ = 3.8Hz), 118.3,

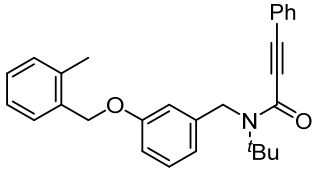
117.6, 115.3 (q, J_{C-F} = 3.7 Hz), 88.1, 83.8, 58.6, 51.1, 28.6. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.7. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{27}H_{25}F_3NO_2^+$ 452.1832; Found 452.1828.



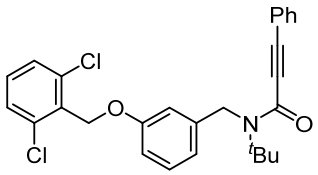
N*-(3-(Benzyloxy)benzyl)-*N*-(*tert*-butyl)-3-phenylpropiolamide (S12).** White solid (2.06 g, 52% yield); m.p. = 82.7–84.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.38–7.35 (m, 2H), 7.35–7.31 (m, 4H), 7.30–7.26 (m, 3H), 6.96–6.87 (m, 3H), 5.06 (s, 2H), 4.97 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 156.3, 141.1, 136.9, 132.5, 129.9, 129.8, 128.7, 128.5, 128.1, 127.6, 120.9, 119.1, 113.7, 113.0, 87.9, 84.0, 70.1, 58.5, 51.4, 28.5. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_2^+$ 398.2115; Found 398.2108.



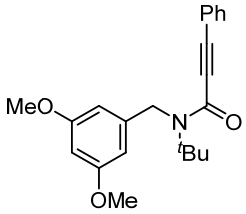
N*-(*tert*-Butyl)-*N*-(3-((3-methoxybenzyl)oxy)benzyl)-3-phenylpropiolamide (S13).** Yellow solid (2.40 g, 56% yield); m.p. = 66.0–69.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 3H), 7.29–7.26 (m, 2H), 7.26–7.24 (m, 2H), 7.00–6.96 (m, 2H), 6.96–6.91 (m, 2H), 6.88 (dd, J = 8.2, 2.5 Hz, 1H), 6.83 (dd, J = 8.2, 2.2 Hz, 1H), 5.03 (s, 2H), 4.97 (s, 2H), 3.79 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 159.1, 156.2, 141.1, 138.5, 132.4, 129.8 (3C), 128.5, 120.8, 119.7, 119.0, 113.7 (2C), 112.9, 112.8, 87.9, 83.9, 69.9, 58.5, 55.3, 51.3, 28.5. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_3^+$ 428.2220; Found 428.2218.



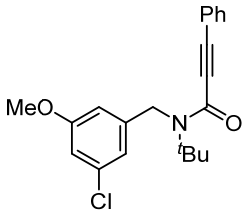
N*-(*tert*-Butyl)-*N*-(3-((2-methylbenzyl)oxy)benzyl)-3-phenylpropiolamide (S14).** Yellow solid (2.17 g, 53% yield); m.p. = 118.8–120.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 1H), 7.36–7.33 (m, 3H), 7.31–7.26 (m, 3H), 7.25–7.16 (m, 3H), 6.98–6.94 (m, 2H), 6.92–6.89 (m, 1H), 5.03 (s, 2H), 4.99 (s, 2H), 2.36 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 156.3, 141.2, 136.8, 134.8, 132.5, 130.6, 129.9 (2C), 128.7, 128.5 (2C), 126.2, 120.9, 119.1, 113.6, 113.0, 88.0, 84.0, 68.8, 58.6, 51.4, 28.6, 19.0. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; Found 412.2265.



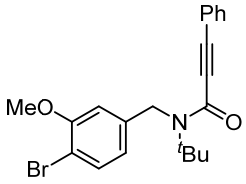
N*-(*tert*-Butyl)-*N*-(3-((2,6-dichlorobenzyl)oxy)benzyl)-3-phenylpropiolamide (S15).** Yellow solid (2.38 g, 51% yield); m.p. = 129.5–131.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 2H), 7.35–7.33 (m, 3H), 7.32–7.30 (m, 1H), 7.29–7.26 (m, 2H), 7.26–7.23 (m, 1H), 7.02–6.99 (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.94 (dd, J = 8.2, 2.4 Hz, 1H), 5.27 (s, 2H), 5.00 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 156.3, 141.2, 137.1, 132.5, 132.2, 130.6, 129.9, 129.8, 128.6, 128.5, 120.9, 119.5, 113.8, 113.2, 88.0, 84.0, 65.4, 58.6, 51.4, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}NO_2^+$ 466.1335; Found 466.1325.



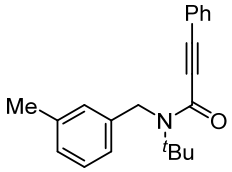
N*-(*tert*-Butyl)-*N*-(3,5-dimethoxybenzyl)-3-phenylpropiolamide (S16).** Yellow solid (1.89 g, 54% yield); m.p. = 82.2–84.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37– 7.32 (m, 3H), 7.28 (d, J = 7.3 Hz, 2H), 6.48 (d, J = 2.2 Hz, 2H), 6.37 (d, J = 2.3 Hz, 1H), 4.95 (s, 2H), 3.78 (s, 6H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 139.3, 138.3, 132.4, 129.8, 128.9, 128.5, 124.3, 121.0, 87.9, 84.1, 58.5, 51.4, 28.6, 21.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_3^+$ 352.1907; Found 352.1901.



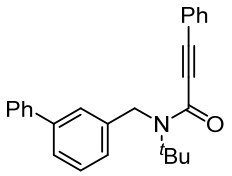
N*-(*tert*-Butyl)-*N*-(3-chloro-5-methoxybenzyl)-3-phenylpropiolamide (S17).** Yellow solid (2.19 g, 62% yield); m.p. = 76.4–79.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 3H), 7.29–7.27 (m, 1H), 7.26–7.23 (m, 1H), 6.90 (s, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.76 (t, J = 1.9 Hz, 1H), 4.93 (s, 2H), 3.76 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 156.3, 142.6, 135.3, 132.4, 130.0, 128.6, 120.7, 118.8, 113.0, 110.8, 88.3, 83.7, 58.6, 55.6, 51.0, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}ClNO_2^+$ 356.1412; Found 356.1406.



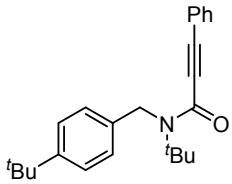
N*-(4-Bromo-3-methoxybenzyl)-*N*-(*tert*-butyl)-3-phenylpropiolamide (S18).** Yellow solid (2.67 g, 67% yield); m.p. = 95.6–96.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 1H), 7.38–7.31 (m, 3H), 7.31–7.26 (m, 2H), 6.89 (d, J = 1.9 Hz, 1H), 6.82 (dd, J = 8.2, 1.9 Hz, 1H), 4.97 (s, 2H), 3.87 (d, J = 2.5 Hz, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 156.1, 140.4, 133.4, 132.3, 129.9, 128.5, 119.7, 110.1, 109.9, 88.0, 83.6, 58.5, 56.2, 51.0, 28.4. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}BrNO_2^+$ 400.0907; Found 400.0900.



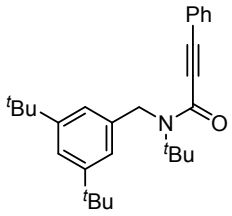
N*-(*tert*-Butyl)-*N*-(3-methylbenzyl)-3-phenylpropiolamide (S19).** White solid (2.04 g, 67% yield); m.p. = 80.2–82.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 3H), 7.29–7.25 (m, 2H), 7.25–7.22 (m, 1H), 7.16–7.11 (m, 2H), 7.10–7.06 (m, 1H), 4.98 (s, 2H), 2.35 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 139.3, 138.4, 132.5, 129.8, 128.7, 128.5, 128.0, 127.2, 123.6, 121.0, 87.9, 84.1, 58.5, 51.5, 28.6, 21.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO^+$ 306.1852; Found 306.1846.



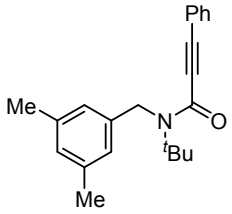
N*-([1,1'-Biphenyl]-3-ylmethyl)-*N*-(*tert*-butyl)-3-phenylpropiolamide (S20).** Yellow solid (1.76 g, 48% yield); m.p. = 71.2–73.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 3H), 7.53–7.49 (m, 1H), 7.45–7.40 (m, 3H), 7.37–7.28 (m, 5H), 7.25–7.23 (m, 2H), 5.08 (s, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 141.7, 140.9, 139.9, 132.4, 129.8, 129.2, 128.9, 128.4, 127.6, 127.2, 126.1, 125.4, 125.2, 120.8, 88.0, 84.0, 58.5, 51.4, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO^+$ 368.2009; Found 368.2002.



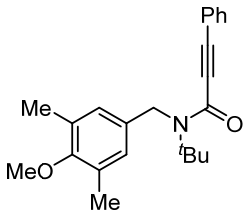
N*-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)benzyl)-3-phenylpropiolamide (S21).** Yellow solid (2.26 g, 65% yield); m.p. = 82.2–83.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 7H), 7.25 (d, J = 5.9 Hz, 2H), 4.98 (s, 2H), 1.45 (s, 9H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 150.2, 136.2, 132.5, 129.8, 128.4, 126.3, 125.6, 121.0, 87.9, 84.2, 58.4, 51.1, 34.6, 31.5, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}NO_2^+$ 348.2322; Found 348.2320.



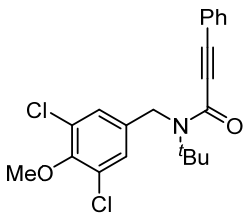
N*-(*tert*-Butyl)-*N*-(3,5-di-*tert*-butylbenzyl)-3-phenylpropiolamide (S22)** Yellow solid (2.85 g, 71% yield); m.p. = 79.1–81.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.26–7.21 (m, 2H), 7.18–7.15 (m, 2H), 5.00 (s, 2H), 1.47 (s, 9H), 1.32 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 151.2, 138.3, 132.4, 129.7, 128.4, 121.0, 120.8, 87.9, 84.2, 58.5, 51.9, 35.0, 31.6, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 404.2948; Found 404.2943.



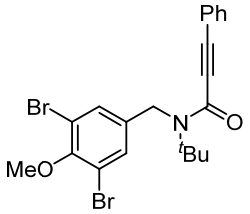
N*-(*tert*-Butyl)-*N*-(3,5-dimethylbenzyl)-3-phenylpropiolamide (S23).** Yellow solid (1.97 g, 62% yield); m.p. = 81.6–83.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 3H), 7.29–7.24 (m, 2H), 6.91 (d, J = 14.6 Hz, 3H), 4.95 (s, 2H), 2.30 (s, 6H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 139.3, 138.3, 132.4, 129.8, 128.9, 128.5, 124.3, 121.0, 87.9, 84.1, 58.5, 51.4, 28.6, 21.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}NO^+$ 320.2009; Found 320.2003.



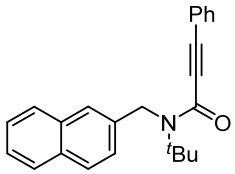
N*-(*tert*-Butyl)-*N*-(4-methoxy-3,5-dimethylbenzyl)-3-phenylpropiolamide (S24).** Yellow solid (2.24 , 64% yield); m.p. = 67.7–69.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 6.94 (s, 2H), 4.90 (s, 2H), 3.71 (s, 3H), 2.27 (s, 6H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 156.1, 134.4, 132.5, 131.1, 129.8, 128.5, 126.9, 121.1, 87.9, 84.2, 59.9, 58.5, 51.1, 28.6, 16.4. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{23}H_{28}NO_2^+$ 350.2115; Found 350.2112.



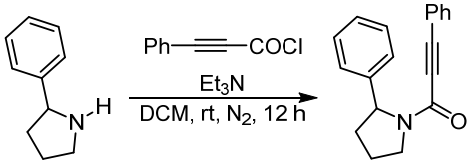
N*-(*tert*-Butyl)-*N*-(3,5-dichloro-4-methoxybenzyl)-3-phenylpropiolamide (S25).** Yellow solid (2.14 g, 55% yield); m.p. = 103.6–105.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 7H), 4.91 (s, 2H), 3.89 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 151.5, 137.1, 132.4, 130.1, 129.9, 128.6, 126.8, 120.5, 88.6, 83.5, 60.9, 58.7, 50.2, 28.6. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}Cl_2NO_2$ 390.1022; Found 390.1021.



N*-(tert-Butyl)-*N*-(3,5-dibromo-4-methoxybenzyl)-3-phenylpropiolamide (S26).** Yellow solid (2.56 g, 54% yield); m.p. = 76.8–80.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.38–7.28 (m, 5H), 4.91 (s, 2H), 3.88 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 153.4, 138.2, 132.4, 130.6, 130.1, 128.6, 120.5, 118.6, 88.6, 83.5, 60.8, 58.7, 50.0, 28.7. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}Br_2NO_2^+$ 478.0012; Found 478.0013.



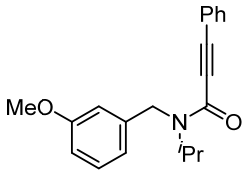
N*-(*tert*-Butyl)-*N*-(naphthalen-2-ylmethyl)-3-phenylpropiolamide (S27).** Yellow solid (2.02 g, 59% yield); m.p. = 126.3–127.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 3H), 7.77 (s, 1H), 7.50–7.44 (m, 3H), 7.33–7.26 (m, 3H), 7.24–7.18 (m, 2H), 5.18 (s, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 136.9, 133.5, 132.7, 132.3, 129.8, 128.6, 128.4, 127.8 (2C), 126.4, 125.9, 125.2, 124.6, 120.7, 87.9, 84.0, 58.5, 51.5, 28.5. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO^+$ 342.1852; Found 342.1846.



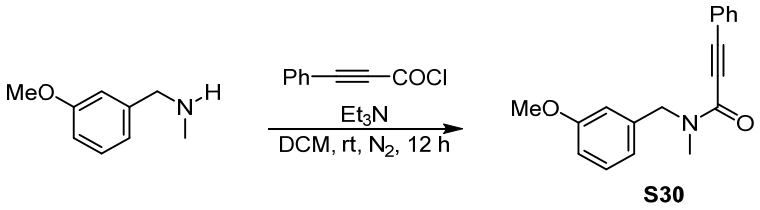
S28

3-Phenyl-1-(2-phenylpyrrolidin-1-yl)prop-2-yn-1-one (S28). To a solution of 2-phenylpyrrolidine (10 mmol) and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added 3-phenylpropioloyl chloride (1.5 equiv.) at 0 ºC. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with $NaHCO_3$ saturated solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S28** as a white solid (1.24 g, 45% yield); m.p. = 94.9–96.8 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.57–7.23 (m, 5H), 7.22–7.10 (m, 5H), 5.30–5.22 (m, 1H), 3.98–3.75 (m, 2H), 2.42–1.89 (m, 4H). **^{13}C NMR for isomer 1** (101 MHz, $CDCl_3$) δ 153.6, 143.3, 132.2, 129.8, 128.5, 128.2, 127.0, 125.5, 120.3, 89.2, 82.9, 62.9, 46.7, 35.5, 22.3. **^{13}C NMR for isomer 2** (101 MHz, $CDCl_3$) δ 152.8, 141.9, 132.4, 130.0, 128.5, 128.4, 126.8, 125.4, 120.5, 88.9, 82.8, 60.1, 49.1, 34.5, 23.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{19}H_{18}NO^+$ 276.1383; Found 276.1379.

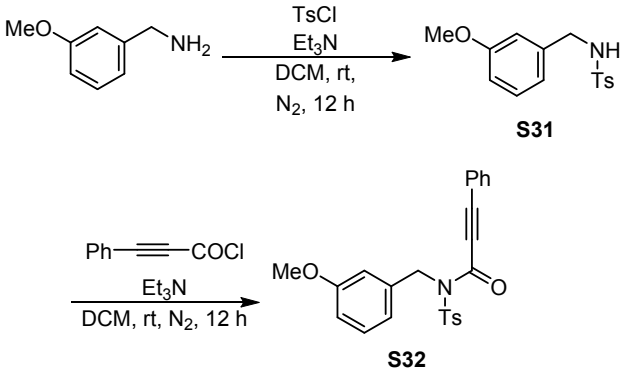


N*-Isopropyl-*N*-(3-methoxybenzyl)-3-phenylpropiolamide (S29).** Yellow oil (1.17 g, 38% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 1H), 7.43–7.33 (m, 3H), 7.31–7.27 (m, 1H), 7.26–7.18 (m, 1H), 6.96–6.89 (m, 1H), 6.89–6.84 (m, 1H), 6.83–6.75 (m, 1H), 4.88–4.62 (m, 1H), 4.80 (s, 1H), 4.61 (s, 1H), 3.80–3.77 (m, 3H), 1.24–1.20 (m, 3H), 1.15–1.12 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 159.8, 155.4, 155.1, 140.4, 140.2, 132.5, 130.1, 130.0, 129.8, 129.5, 128.6, 128.5, 120.8, 120.6, 119.6, 119.3, 113.1, 112.8, 112.6, 112.4, 90.8, 89.6, 82.7, 81.9, 55.3 (2C), 51.2, 49.1, 46.7, 43.9, 21.6, 20.3. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO_2^+$ 308.1645; Found 308.1640.



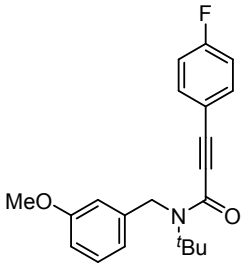
S30

N*-(3-Methoxybenzyl)-*N*-methyl-3-phenylpropiolamide (S30).** To a solution of 1-(3-methoxyphenyl)-*N*-methylmethanamine (10 mmol) and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added 3-phenylpropioloyl chloride (1.5 equiv.) at 0 ºC. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S30** as a yellow oil (1.36 g, 49% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 1H), 7.51–7.48 (m, 1H), 7.41–7.31 (m, 3H), 7.31–7.26 (m, 1H), 7.26–7.21 (m, 1H), 6.91–6.86 (m, 1H), 6.85–6.80 (m, 2H), 4.83–4.61 (m, 2H), 3.80–3.75 (m, 3H), 3.20–2.92 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 160.0, 154.8, 154.8, 137.9, 137.8, 132.4, (2C), 130.1 (2C), 130.0, 129.7, 128.6, 128.5, 120.5, 120.4, 119.7, 113.7, 113.2 (2C), 90.8, 90.3, 81.6 (2C), 55.2, 54.9, 49.8, 35.9, 32.0. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2^+$ 280.1332; Found 280.1328.



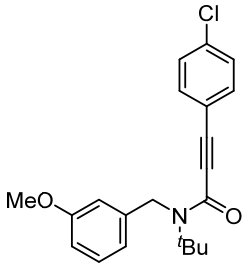
***N*-(3-Methoxybenzyl)-4-methylbenzenesulfonamide (S31).** To a solution of (3-methoxyphenyl)methanamine (10 mmol) and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (1.5 equiv.) at 0 ℃. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S31**.

N*-(3-Methoxybenzyl)-3-phenyl-*N*-tosylpropiolamide (S32).** To a solution of **S31** obtained above and Et_3N (2 equiv.) in dry DCM (20 mL) was added 3-phenylpropioloyl chloride (1.5 equiv.) at 0 ℃. Then warmed to room temperature and continue to be stirred for 12 h. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S32** as a yellow solid (2.01 g, 48% yield); m.p. = 56.8–59.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.45–7.41 (m, 3H), 7.36–7.31 (m, 2H), 7.28–7.25 (m, 1H), 7.22–7.18 (m, 2H), 7.03–7.00 (m, 1H), 6.97–6.95 (m, 1H), 6.87–6.83 (m, 1H), 5.27 (s, 2H), 3.74 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 153.0, 145.2, 137.9, 135.8, 132.8, 131.1, 129.8, 129.4, 128.8, 120.3, 119.3, 113.7, 113.4, 93.8, 81.7, 55.3, 50.4, 21.7. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NOS^+$ 338.1573; Found 338.1567.

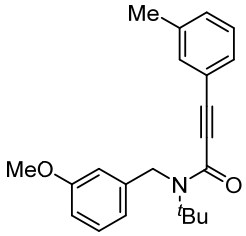


***N*-(*tert*-Butyl)-3-(4-fluorophenyl)-*N*-(3-methoxybenzyl)propiolamide (S33).** Yellow solid (1.85 g, 55% yield); m.p. = 63.5–65.9 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.28–7.26 (m, 1H), 6.99–5.93 (m, 2H), 6.93–6.90 (m, 1H), 6.88–6.86 (m, 1H), 6.83–6.79 (m, 1H), 4.98 (s, 2H), 3.80 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4 (d, J_{C-F} =

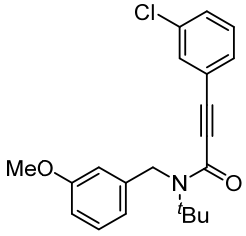
252.1 Hz), 160.0, 156.2, 141.0, 134.6 (d, $J_{C–F}$ = 8.7 Hz), 129.9, 118.7, 116.9 (d, $J_{C–F}$ = 3.6 Hz), 115.9 (d, $J_{C–F}$ = 22.1 Hz), 112.6, 112.1, 86.9, 83.8, 58.5, 55.3, 51.3, 28.5. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –108.0. **HRMS (ESI)** ***m/z***: $[M + H]^+$ Calcd for $C_{21}H_{23}FNO_2^+$ 340.1707; Found 340.1701.



N*-(*tert*-Butyl)-3-(4-chlorophenyl)-*N*-(3-methoxybenzyl)propiolamide (S34).** Yellow solid (2.40 g, 68 yield)%; m.p. = 81.4–83.0 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.25–7.23 (m, 3H), 6.93–6.88 (m, 1H), 6.88–6.85(m, 1H), 6.83–7.79 (m 1H), 4.97 (s, 2H), 3.80 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 156.1, 141.0, 136.1, 133.7, 129.9, 128.9, 119.3, 118.7, 112.6, 112.1, 86.7, 84.8, 58.6, 55.4, 51.4, 28.5. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}ClNO_2^+$ 356.1412; Found 356.1406.

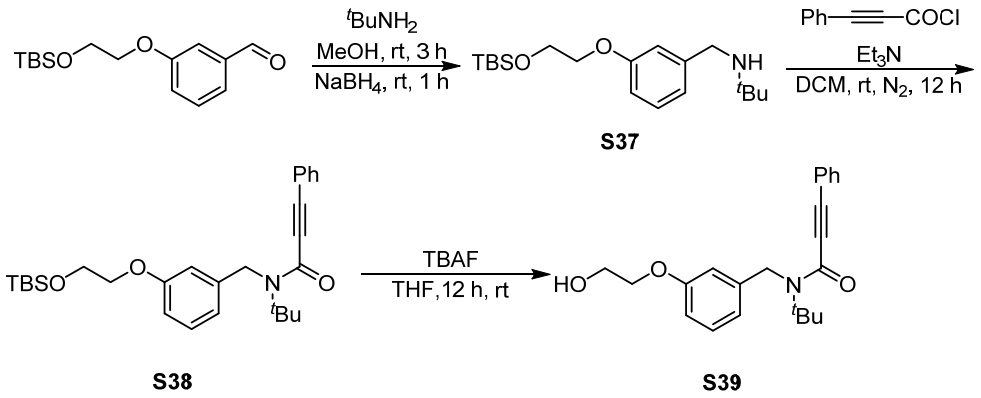


N*-(*tert*-Butyl)-*N*-(3-methoxybenzyl)-3-(*m*-tolyl)propiolamide (S35).** Yellow solid (2.09g, 62% yield); m.p. = 46.0–48.1 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 1H), 7.16–7.11 (m, 4H), 6.94–6.90 (m, 1H), 6.89–6.87 (m, 1H), 6.83–6.78 (m, 1H), 4.98 (s, 2H), 3.79 (s, 3H), 2.26 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 156.3, 141.2, 138.2, 132.9, 130.7, 129.8, 129.5, 128.4, 120.6, 118.8, 112.6, 112.1, 88.2, 83.7, 58.5, 55.3, 51.4, 28.5, 21.2. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_2^+$ 336.1958; Found 336.1951.



N*-(*tert*-Butyl)-3-(3-chlorophenyl)-*N*-(3-methoxybenzyl)propiolamide (S36).** Yellow solid (2.01 g, 57% yield); m.p. = 82.1–84.5 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.22–7.18 (m, 2H), 6.93–6.78 (m, 4H), 4.95 (s, 2H), 3.79 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 155.9, 140.9, 134.3, 132.1, 130.5, 130.1, 129.9, 129.8, 122.6, 118.7, 112.6, 112.1, 86.2, 84.8, 58.6, 55.4, 51.3, 28.5. **HRMS (ESI)** ***m/z: $[M + H]^+$ Calcd for

$C_{21}H_{23}ClNO_2^+$ 356.1412; Found 356.1404.

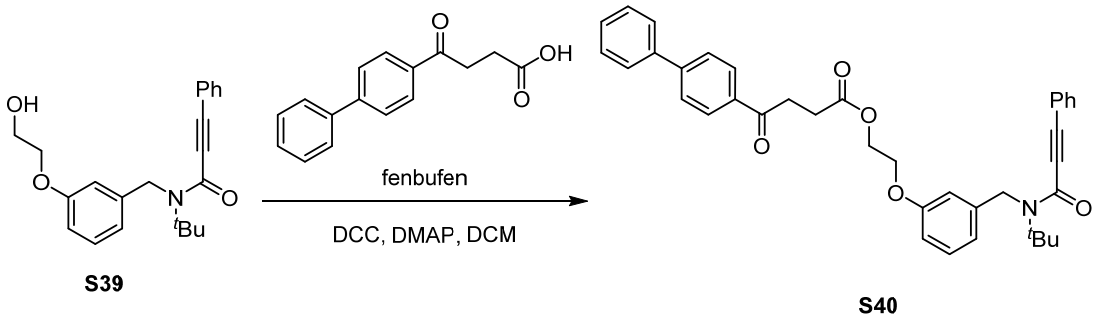


***N*-(3-(2-((*tert*-Butyldimethylsilyl)oxy)ethoxy)benzyl)-2-methylpropan-2-amine (S37).** To a solution of 3-(2-((*tert*-butyldimethylsilyl)oxy)ethoxy)benzaldehyde (10 mmol) in methanol (20 mL) was added *tert*-butylamine (1.2 equiv.), and then the resulting solution was stirred for 3 h at room temperature. Next, the mixture was added $NaBH_4$ (2.0 equiv.) at 0 ºC, and then warmed to room temperature and continue to be stirred 1.0 h. The solvent was evaporated under reduced pressure and extracted with EtOAc. The organic layer was dried over Na_2SO_4, and concentrated to afford the crude product **S37**. The crude product was directly used in the next step without purification.

N*-(*tert*-Butyl)-*N*-(3-(2-((*tert*-butyldimethylsilyl)oxy)ethoxy)benzyl)-3-phenylpropiolamid e (S38).** To a solution of **S37** obtained above and Et_3N (2.0 equiv.) in dry DCM (20 mL) was added 3-phenylpropioloyl chloride (1.5 equiv.) at 0 ºC. Then warmed to room temperature and continue to be stirred for overnight. After the reaction, it was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extracted with EtOAc (20×3 mL). The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding product **S38** as a yellow oil (2.43 g, 52% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 3H), 7.28 (s, 1H), 7.26–7.23 (m, 2H), 6.93–6.86 (m, 2H), 6.83–6.80 (m, 1H), 4.98 (s, 2H), 4.04–4.01 (m, 2H), 3.98–3.95 (m, 2H), 1.45 (s, 9H), 0.90 (s, 9H), 0.09 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 156.4, 141.1, 132.5, 129.9, 129.8, 128.5, 120.9, 118.8, 113.3, 112.7, 88.0, 84.0, 69.4, 62.1, 58.6, 51.4, 28.6, 26.1, 18.6, –5.0. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{28}H_{40}NO_3Si^+$ 465.2699; Found 465.2692.

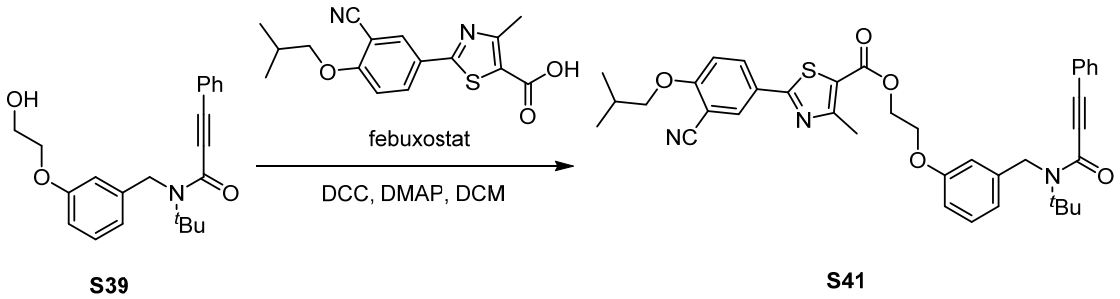
***N*-(*tert*-Butyl)-*N*-(3-(2-hydroxyethoxy)benzyl)-3-phenylpropiolamide (S39).** To a solution of **S38** in THF (15 mL) was added TBAF (2.0 equiv.), and then the resulting solution was stirred for 12 h at room temperature. The resulting crude was diluted with water (20 mL), extracted with EtOAc (30×3 mL) and the combined organic phase was dried over Na_2SO_4, filtered and concentrated. After related work-up, the residue was purified by flash chromatography (petroleum ether/ethyl acetate) on silica gel to afford the corresponding product **S39** as a yellow oil (2.21 g, 91% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 3H), 7.19–7.14 (m, 3H), 6.86–6.79 (m, 2H), 6.73 (dd, J = 8.2, 2.5 Hz, 1H), 4.89 (s, 2H), 3.98

(t, J = 4.7 Hz, 2H), 3.86 (t, J = 4.7 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 156.3, 141.0, 132.3, 129.8 (2C), 128.4, 120.6, 119.0, 113.2, 112.6, 88.1, 83.8, 69.3, 61.2, 58.5, 51.3, 28.4. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{22}H_{26}NO_3^+$ 352.1907; Found 352.1901.



S39 **S40**

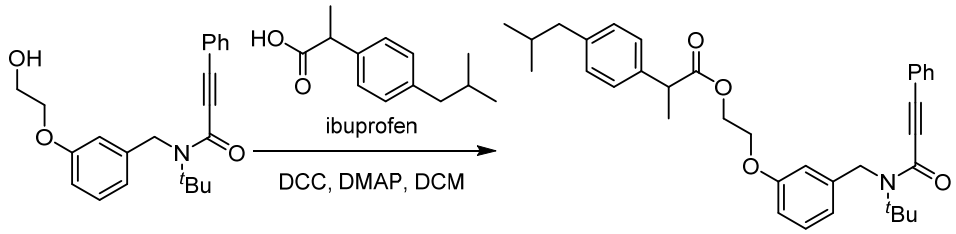
2-(3-((*N*-(*tert*-Butyl)-3-phenylpropiolamido)methyl)phenoxy)ethyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (S40). To a solution of fenbufen (381 mg, 1.5 mmol, 1.0 equiv.), **S39** (580 mg, 1.65 mmol, 1.1 equiv.) and DMAP (92 mg, 0.75 mmol, 0.5 equiv.) in DCM (10 mL) was added DCC (464 mg, 2.25 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **S40** as a white oil (537.2 mg, 61% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H), 7.68–7.65 (m, 2H), 7.63–7.60 (m, 2H), 7.48–7.44 (m, 2H), 7.41–7.38 (m, 1H), 7.35–7.29 (m, 3H), 7.27–7.26 (m, 1H), 7.26–7.22 (m, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.91–6.88 (m, 1H), 6.83–6.79 (m, 1H), 4.98 (s, 2H), 4.47–4.44 (m, 2H), 4.17 (t, J = 4.8 Hz, 2H), 3.34 (t, J = 6.6 Hz, 2H), 2.83 (t, J = 6.6 Hz, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 172.9, 158.9, 156.2, 145.9, 141.1, 139.8, 135.2, 132.3, 129.8 (2C), 129.0, 128.7, 128.4, 128.3, 127.3 (2C), 120.7, 119.2, 113.2, 112.8, 87.9, 83.9, 65.9, 63.0, 58.4, 51.3, 33.4, 28.5, 28.2. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{38}H_{38}NO_5^+$ 588.2744; Found 588.2734.



S39 **S41**

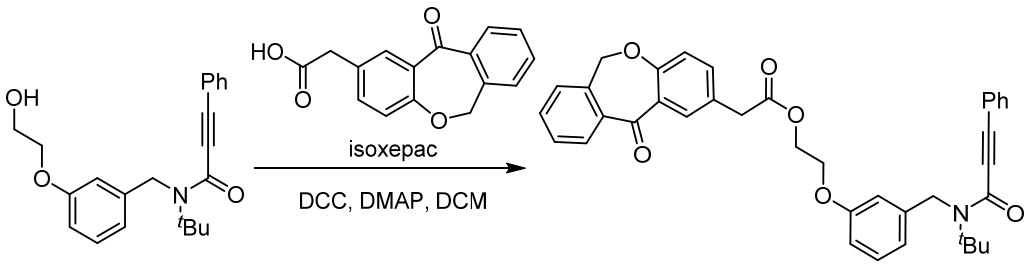
2-(3-((*N*-(*tert*-Butyl)-3-phenylpropiolamido)methyl)phenoxy)ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (S41). To a solution of febuxostat (475 mg, 1.5 mmol, 1.0 equiv.), **S39** (580 mg, 1.65 mmol, 1.1 equiv.) and DMAP (37 mg, 0.3 mmol, 0.2 equiv.) in DCM (10 mL) was added DCC (464 mg, 2.25 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel

eluting with ethyl acetate/petroleum ether to give the desired product **S41** as a white solid (537.2 mg, 55% yield). m.p. = 140.9–142.2 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 2.3 Hz, 1H), 8.06 (dd, J = 8.8, 2.3 Hz, 1H), 7.33–7.28 (m, 4H), 7.26–7.22 (m, 2H), 6.99 (d, J = 8.9 Hz, 1H), 6.96–6.91 (m, 2H), 6.84 (dd, J = 8.3, 2.4 Hz, 1H), 4.98 (s, 2H), 4.62 (t, J = 4.7 Hz, 2H), 4.26 (t, J = 4.7 Hz, 2H), 3.88 (d, J = 6.4 Hz, 2H), 2.74 (s, 3H), 2.22–2.16 (m, 1H), 1.45 (s, 9H), 1.09 (s, 3H), 1.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 162.5, 161.9, 161.7, 158.9, 156.2, 141.2, 132.7, 132.3, 132.0, 129.9, 129.8, 128.4, 125.9, 121.3, 120.7, 119.3, 115.4, 113.2, 112.9, 112.7, 102.9, 87.9, 83.9, 75.7, 65.9, 63.5, 58.5, 51.2, 28.5, 28.2, 19.1, 17.6. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{38}H_{40}N_3O_5S^+$ 650.2683; Found 650.2675.



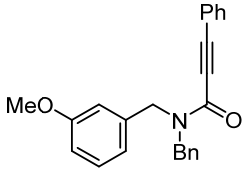
S39 **S42**

2-(3-((*N*-(*tert*-Butyl)-3-phenylpropiolamido)methyl)phenoxy)ethyl 2-(4-isobutylphenyl)propanoate (S42). To a solution of ibuprofen (309 mg, 1.5 mmol, 1.0 equiv.), **S39** (580 mg, 1.65 mmol, 1.1 equiv.) and DMAP (92 mg, 0.75 mmol, 0.5 equiv.) in DCM (10 mL) was added DCC (464 mg, 2.25 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **S42** as a colorless oil (503.1 mg, 62%; yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 3H), 7.28–7.26 (m, 3H), 7.22–7.19 (m, 2H), 7.07 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 6.77 (dd, J = 8.2, 2.5 Hz, 1H), 4.99 (s, 2H), 4.45 (dt, J = 12.0, 5.0 Hz, 1H), 4.36 (dt, J = 12.0, 4.7 Hz, 1H), 4.12 (t, J = 4.9 Hz, 2H), 3.74 (q, J = 7.1 Hz, 1H), 2.43 (d, J = 7.1 Hz, 2H), 1.85–1.81 (m, 1H), 1.49 (d, J = 7.2 Hz, 3H), 1.46 (s, 9H), 0.89 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 159.0, 156.3, 141.2, 140.6, 137.6, 132.4, 129.9, 129.8, 129.4, 128.5, 127.3, 120.8, 119.2, 113.3, 112.9, 88.0, 83.9, 66.0, 63.0, 58.5, 51.3, 45.1 (2C), 30.3, 28.5, 22.5, 18.7. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{35}H_{42}NO_4^+$ 540.3108; Found 540.3103.

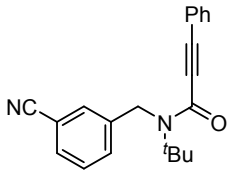


S39 **S43**

2-(3-((*N*-(*tert*-Butyl)-3-phenylpropiolamido)methyl)phenoxy)ethyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (S43). To a solution of isoxepac (402 mg, 1.5 mmol, 1.0 equiv.), **S39** (580 mg, 1.65 mmol, 1.5 equiv.) and DMAP (92 mg, 0.75 mmol, 0.5 equiv.) in DCM (10 mL) was added DCC (464 mg, 2.25 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **S43** as a colorless oil (605.6 mg, 67%; yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.5 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.46–7.39 (m, 3H), 7.35–7.31 (m, 4H), 7.26–7.22 (m, 2H), 6.99 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 6.87 (s, 1H), 6.80 (d, J = 8.3 Hz, 1H), 5.15 (s, 2H), 4.97 (s, 2H), 4.44 (t, J = 4.8 Hz, 2H), 4.16 (t, J = 4.7 Hz, 2H), 3.67 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 171.5, 160.6, 158.9, 156.3, 141.2, 140.5, 136.4, 135.6, 132.9, 132.6, 132.4, 129.9 (2C), 129.5, 129.3, 128.5, 127.9, 127.6, 125.2, 121.2, 120.8, 119.3, 113.3, 112.9, 88.0, 83.9, 73.7, 65.9, 63.3, 58.5, 51.3, 40.0, 28.5. **HRMS (ESI) *m/z***: $[M + H]^+$ Calcd for $C_{38}H_{36}NO_6^+$ 602.2537; Found 602.2526.



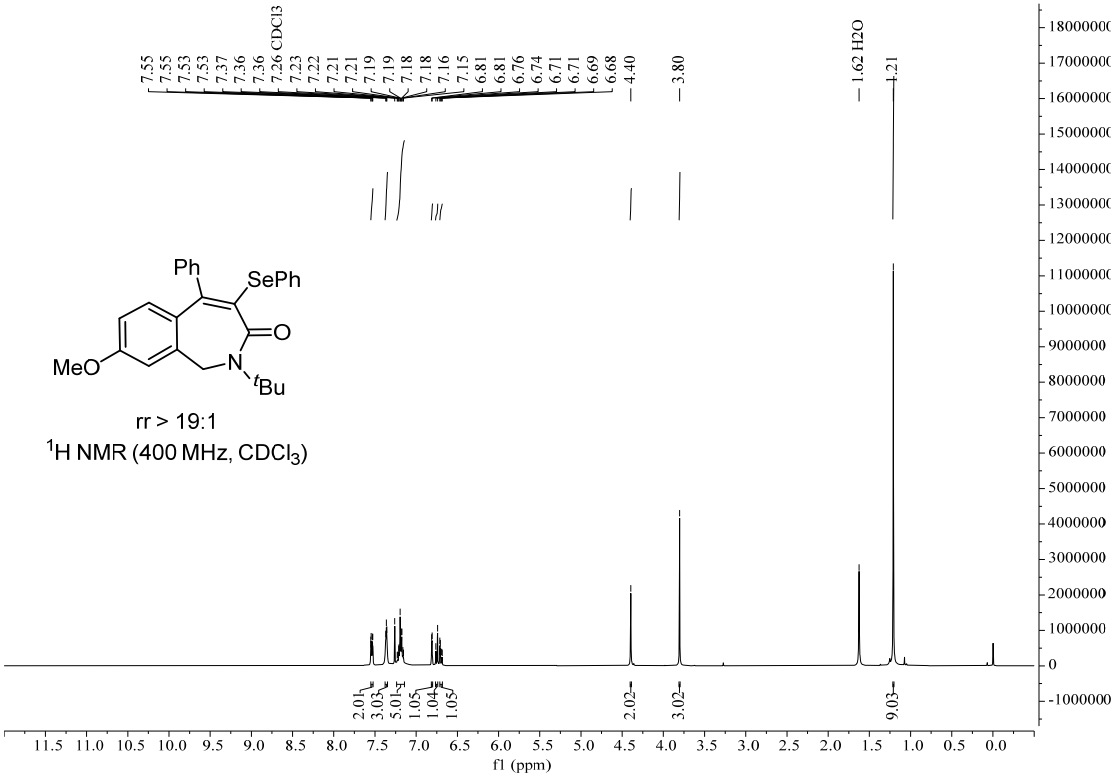
N*-(*tert*-Butyl)-*N*-(3-cyanobenzyl)-3-phenylpropiolamide (57).** Yellow oil (1.67 g, 47% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.42–7.37 (m, 2H), 7.37–7.31 (m, 5H), 7.31–7.26 (m, 2H), 6.92–6.82 (m, 3H), 4.77 (d, J = 15.0 Hz, 2H), 4.58 (d, J = 16.2 Hz, 2H), 3.80 (d, J = 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 160.0, 155.1, 137.9, 137.8, 136.3, 136.1, 132.5, 130.3, 130.0, 129.8, 129.0, 128.8, 128.6 (2C), 128.1, 127.8 (2C), 120.8, 120.4, 120.1, 114.0, 113.4 (2C), 113.3, 90.9, 81.7, 55.3, 51.6, 51.5, 46.5, 46.4. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}NO_2^+$ 356.1645; Found 356.1637.



N*-(*tert*-Butyl)-*N*-(3-cyanobenzyl)-3-phenylpropiolamide (59).** White solid (1.56 g, 49% yield); m.p. = 87.9–90.6 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65–7.57 (m, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.36–7.27 (m, 5H), 5.06 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 141.0, 132.2, 132.1, 130.9, 130.7, 129.9, 129.7, 129.6, 128.4, 120.1, 118.5, 112.7, 88.1, 83.3, 58.4, 50.4, 28.3. **HRMS (ESI) *m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O^+$ 317.1648; Found 317.1642.

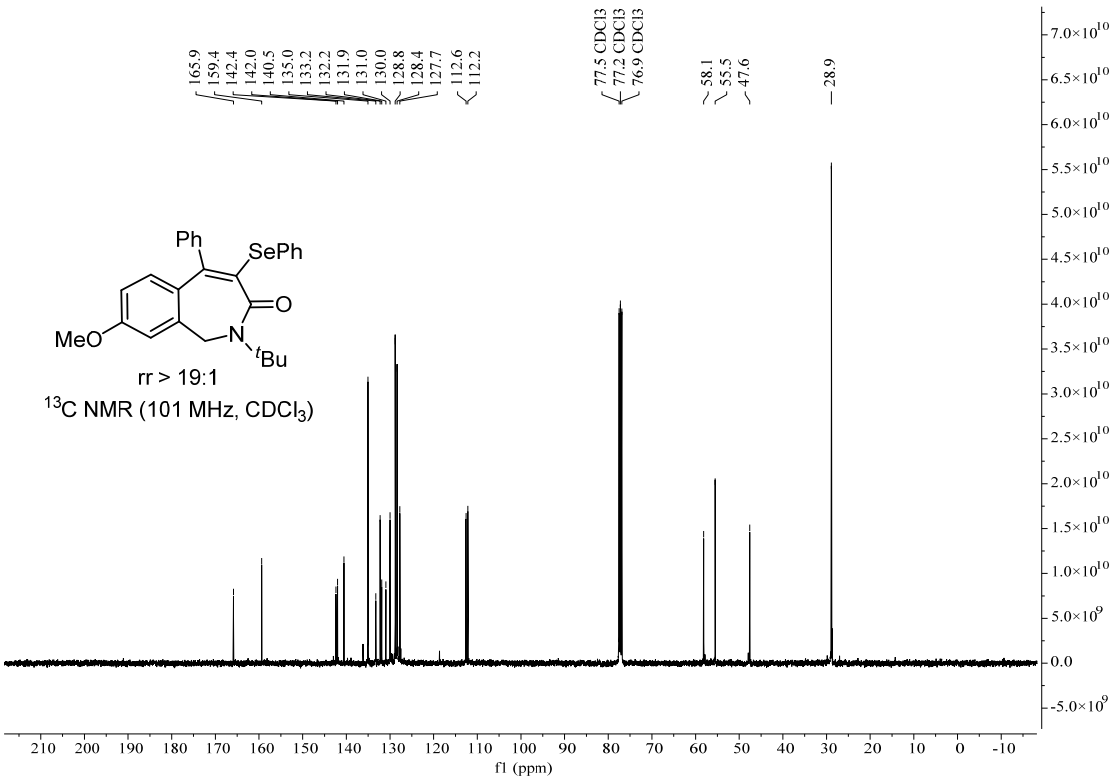
8. NMR Spectra for Compounds

Compound 3



rr > 19:1

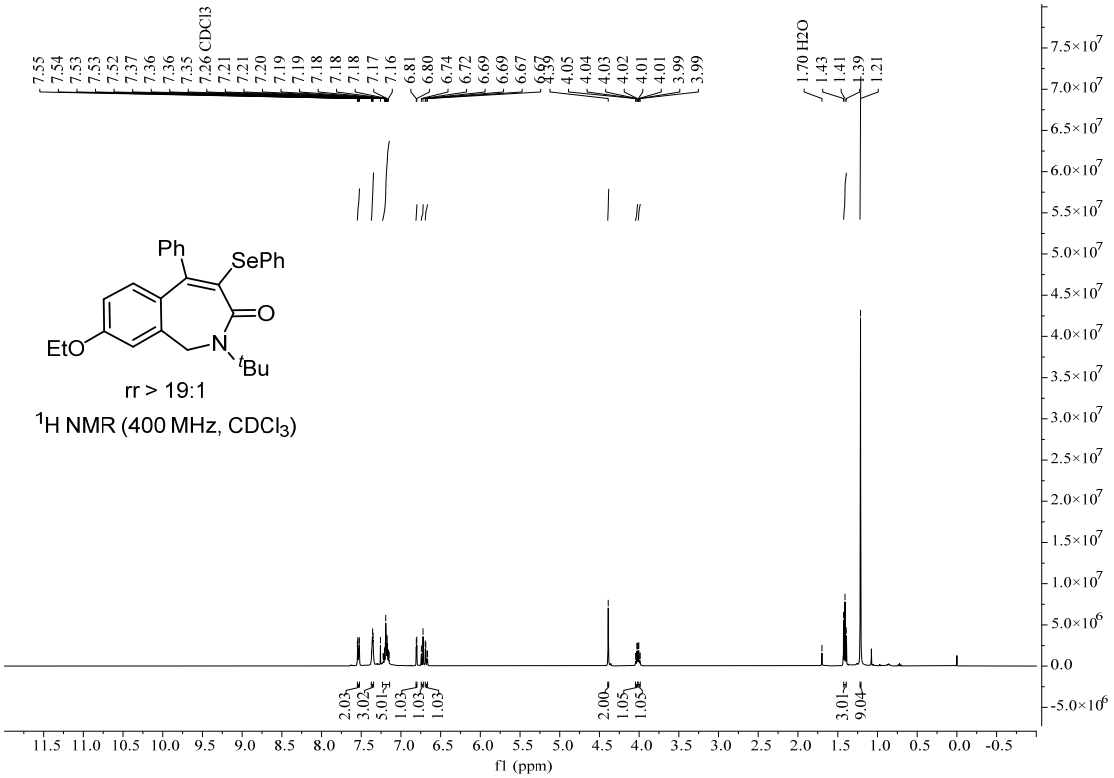
^{1}H NMR (400 MHz, $CDCl_3$)

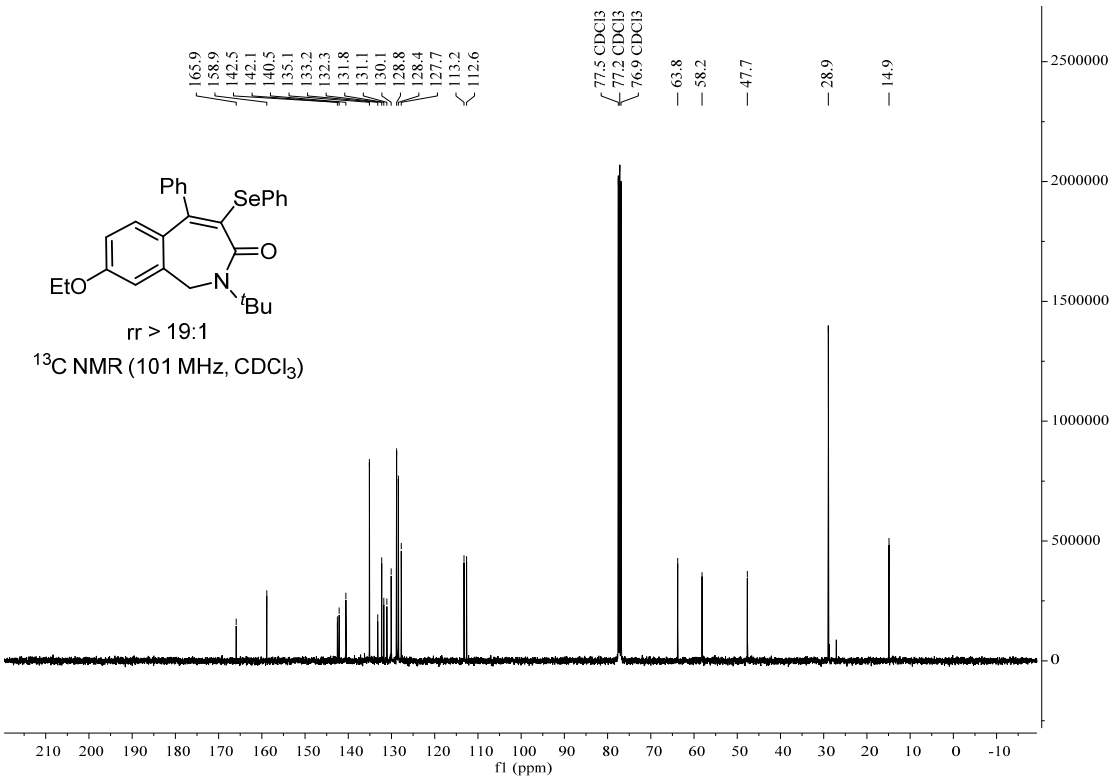


rr > 19:1

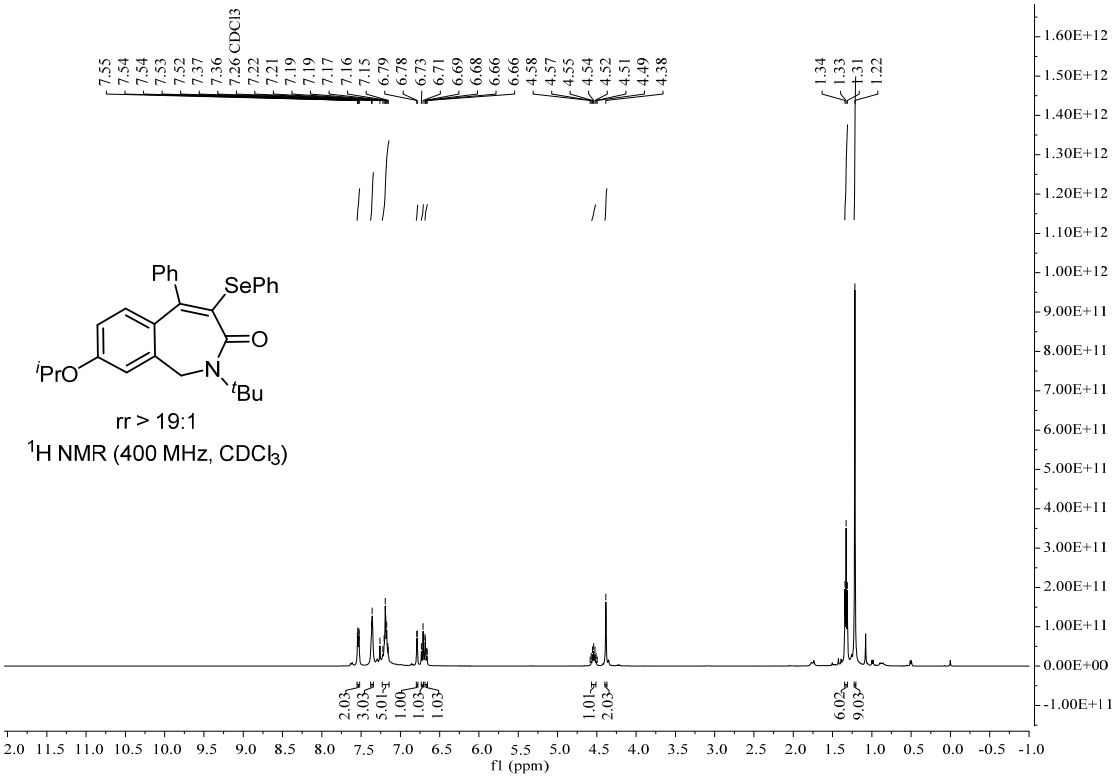
^{13}C NMR (101 MHz, $CDCl_3$)

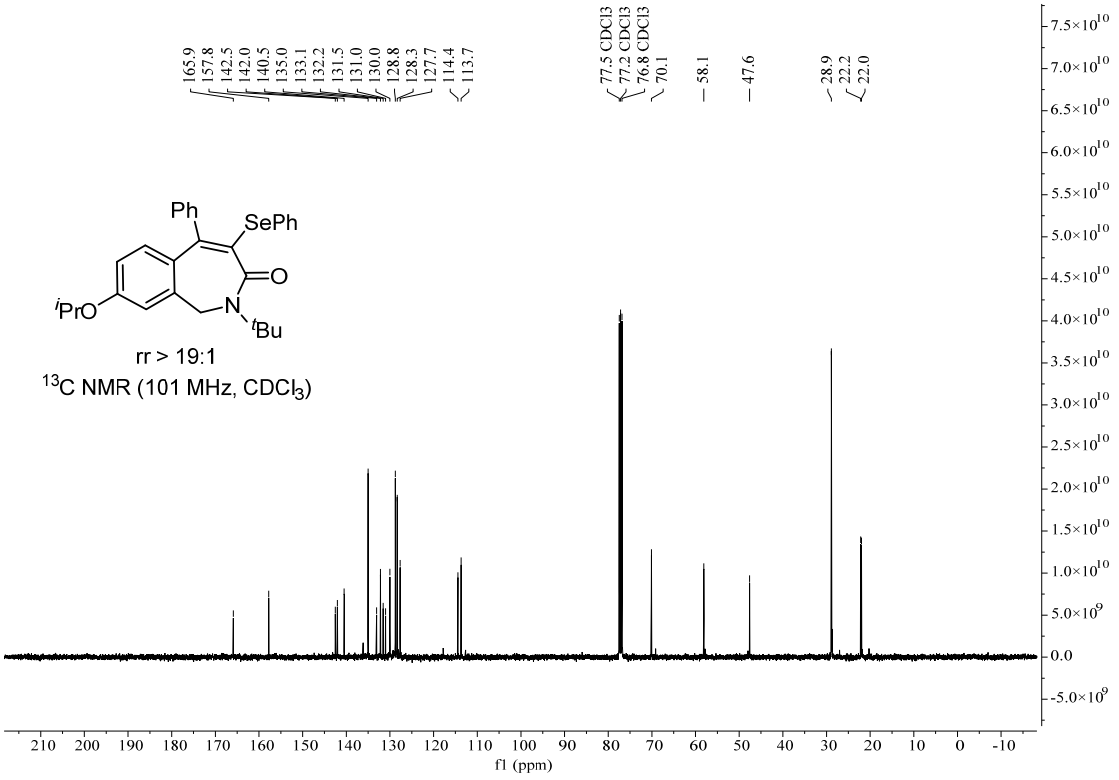
Compound 4


7.55 7.54 7.53 7.53 7.52 7.37 7.36 7.36 7.35 7.26 CDCl3 7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.16 6.81 6.80 6.74 6.72 6.69 6.69 6.67 6.67 4.39 4.05 4.04 4.03 4.02 4.01 4.01 3.99 3.99
1.70 H2O 1.43 1.41 1.39 1.21
Ph SePh O EtO N tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.03 3.02 5.01 1.03 1.03 1.03 2.00 1.05 1.05 3.01 9.04
f1 (ppm)

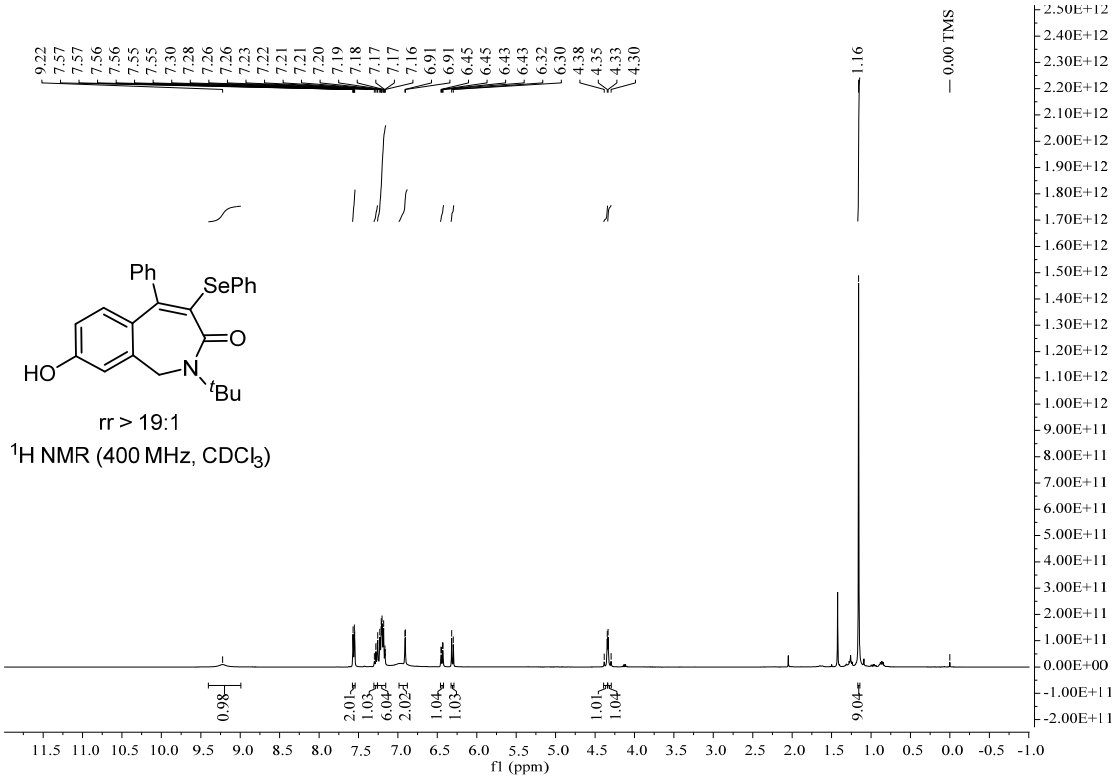

165.9 158.9 142.5 142.1 140.5 135.1 133.2 132.3 131.8 131.1 130.1 128.8 128.4 127.7 113.2 112.6
77.5 CDCl3 77.2 CDCl3 76.9 CDCl3 63.8 58.2 47.7 28.9 14.9
Ph SePh O EtO N tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

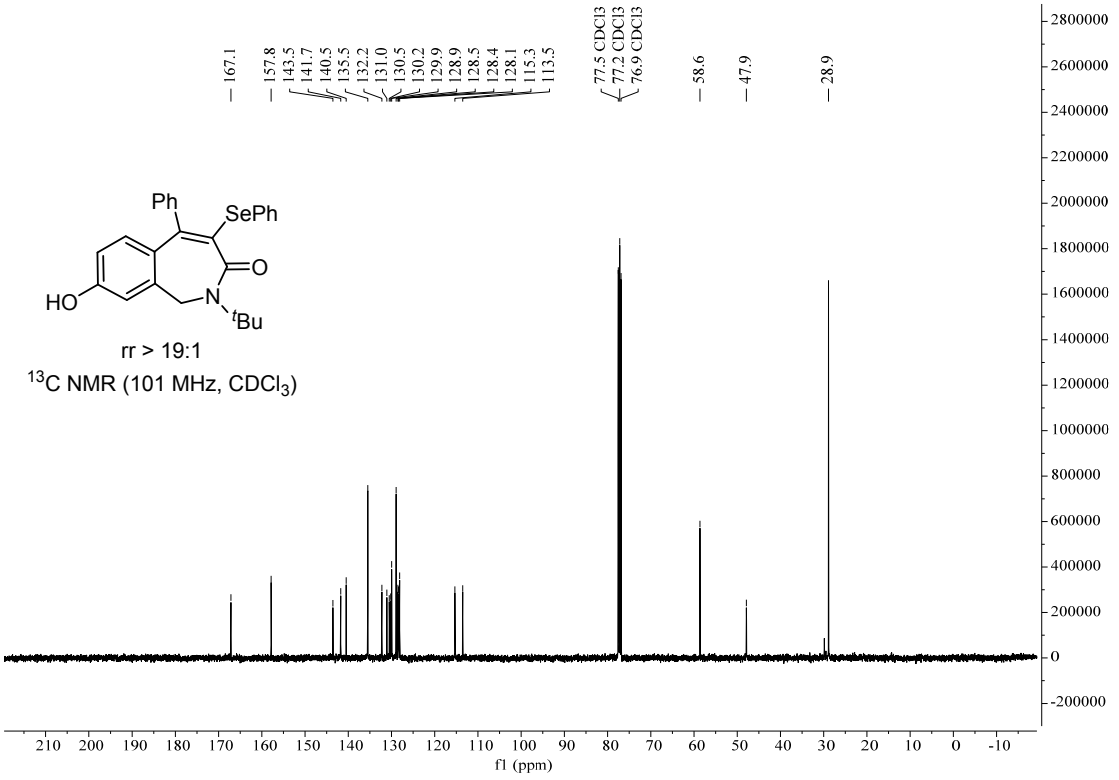
Compound 5


7.55
7.54
7.54
7.53
7.52
7.37
7.36
7.26 CDCl3
7.22
7.21
7.19
7.19
7.17
7.16
7.15
6.79
6.78
6.73
6.71
6.69
6.68
6.66
6.66
4.58
4.57
4.55
4.54
4.52
4.51
4.49
4.38
1.34
1.33
1.31
1.22
Ph
SePh
O
iPrO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.03
3.03
5.01
1.00
1.03
1.03
1.01
2.03
6.02
9.03
f1 (ppm)

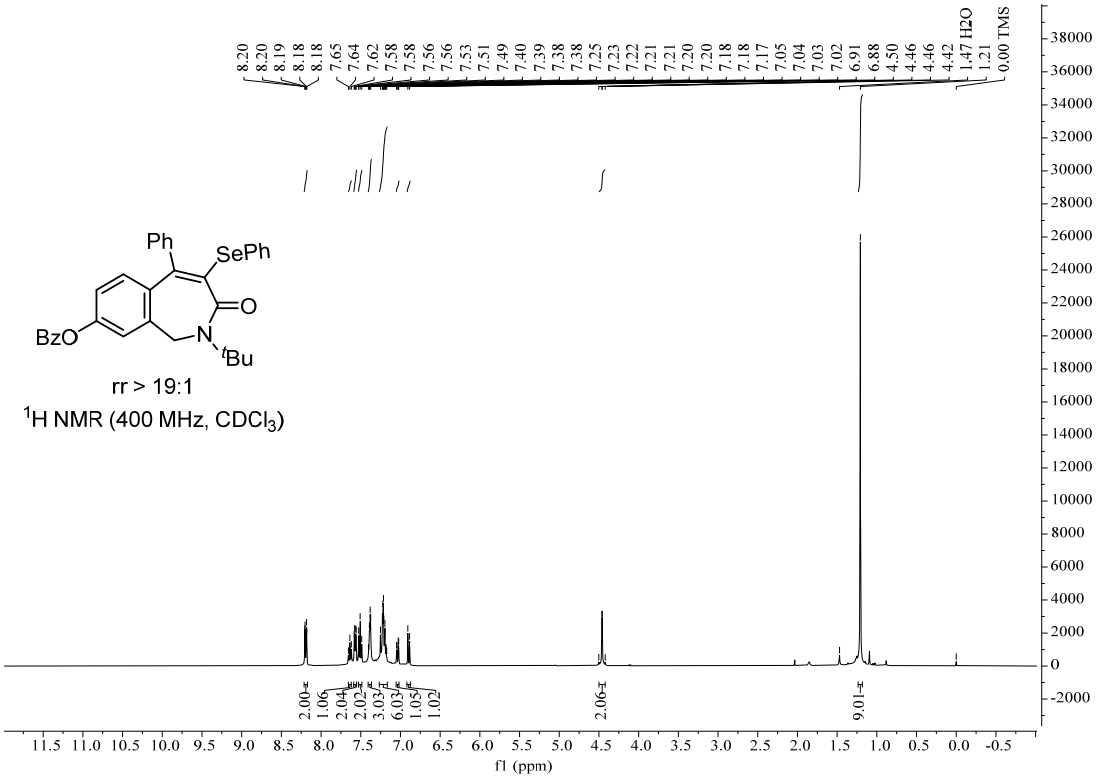

165.9
157.8
142.5
142.0
140.5
135.0
133.1
132.2
131.5
131.0
130.0
128.8
128.3
127.7
114.4
113.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.1
58.1
47.6
28.9
22.2
22.0
Ph
SePh
O
iPrO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

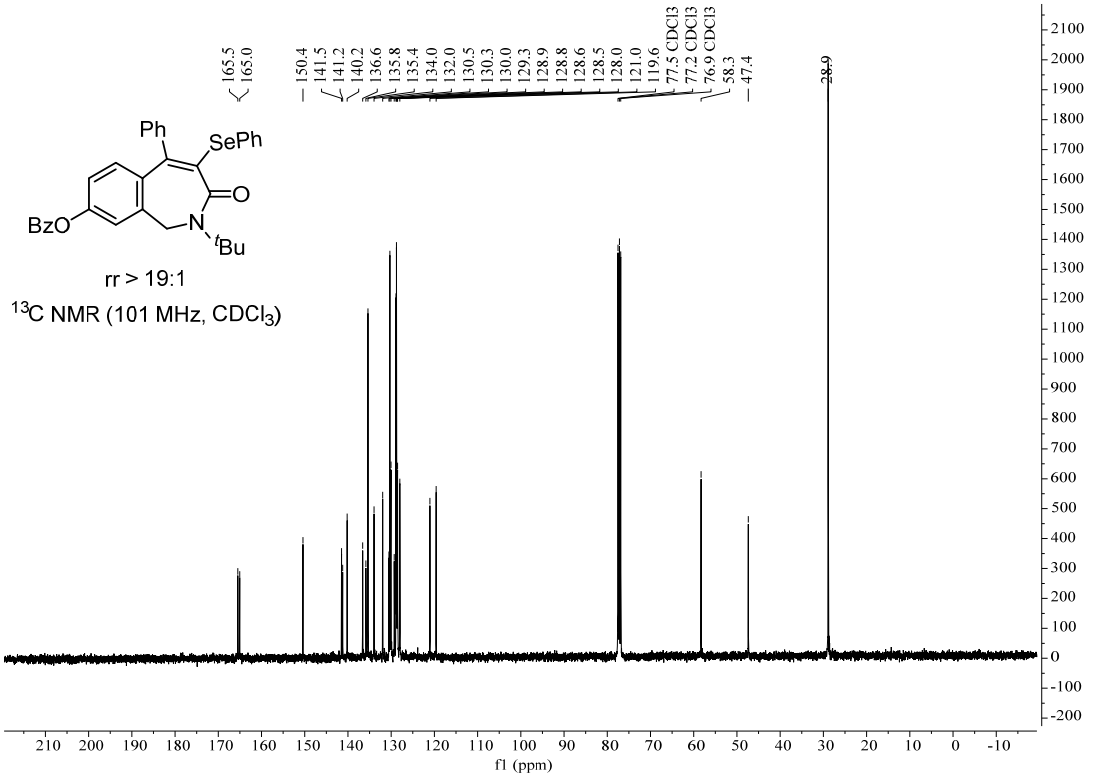
Compound 6


9.22
7.57
7.57
7.56
7.56
7.55
7.55
7.30
7.28
7.26
7.26
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.16
6.91
6.91
6.45
6.45
6.43
6.43
6.32
6.30
4.38
4.35
4.33
4.30
1.16
0.00 TMS
Ph
SePh
O
HO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
0.98
2.01
1.03
6.04
2.02
1.04
1.03
1.01
1.04
9.04
f1 (ppm)

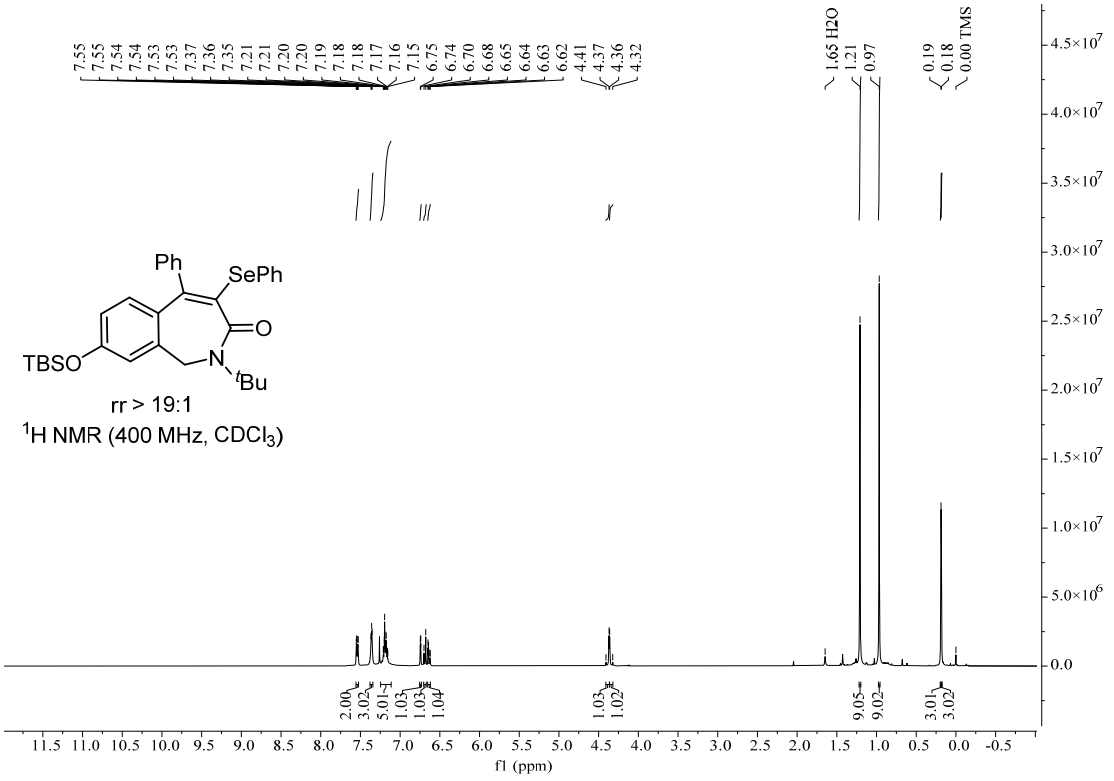

167.1
157.8
143.5
141.7
140.5
135.5
132.2
131.0
130.5
130.2
129.9
128.9
128.5
128.4
128.1
115.3
113.5
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.6
47.9
28.9
Ph
SePh
O
HO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

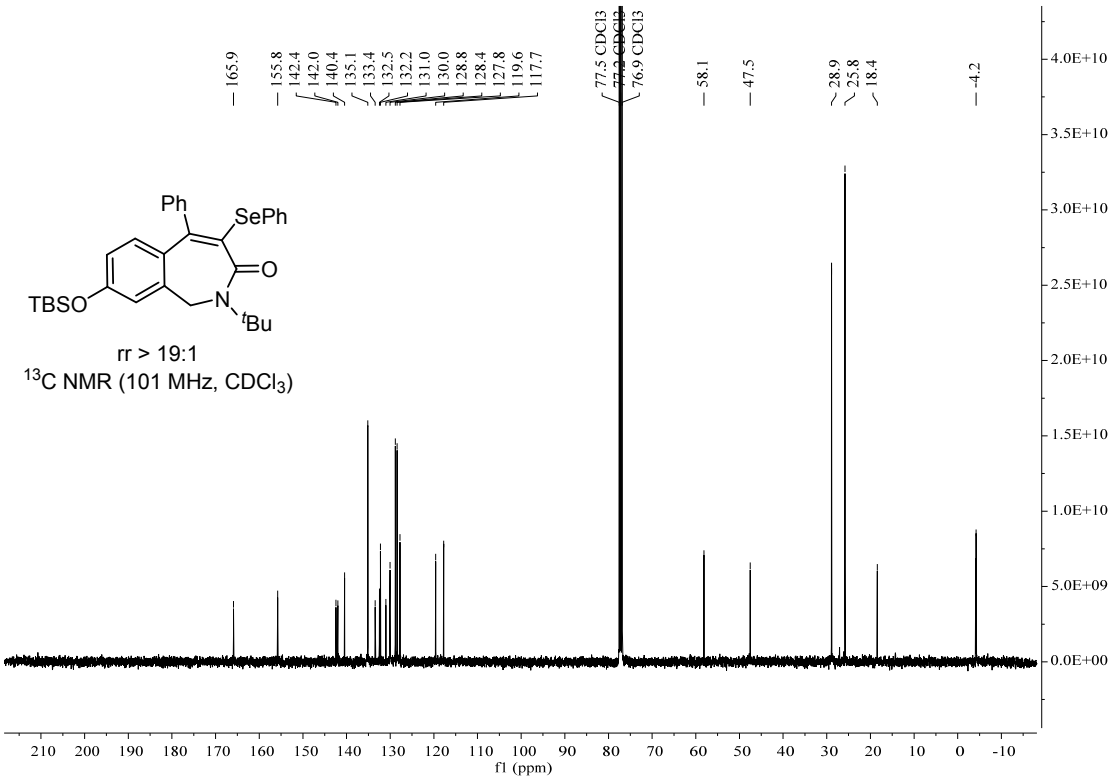
Compound 7


Ph
SePh
O
BzO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)

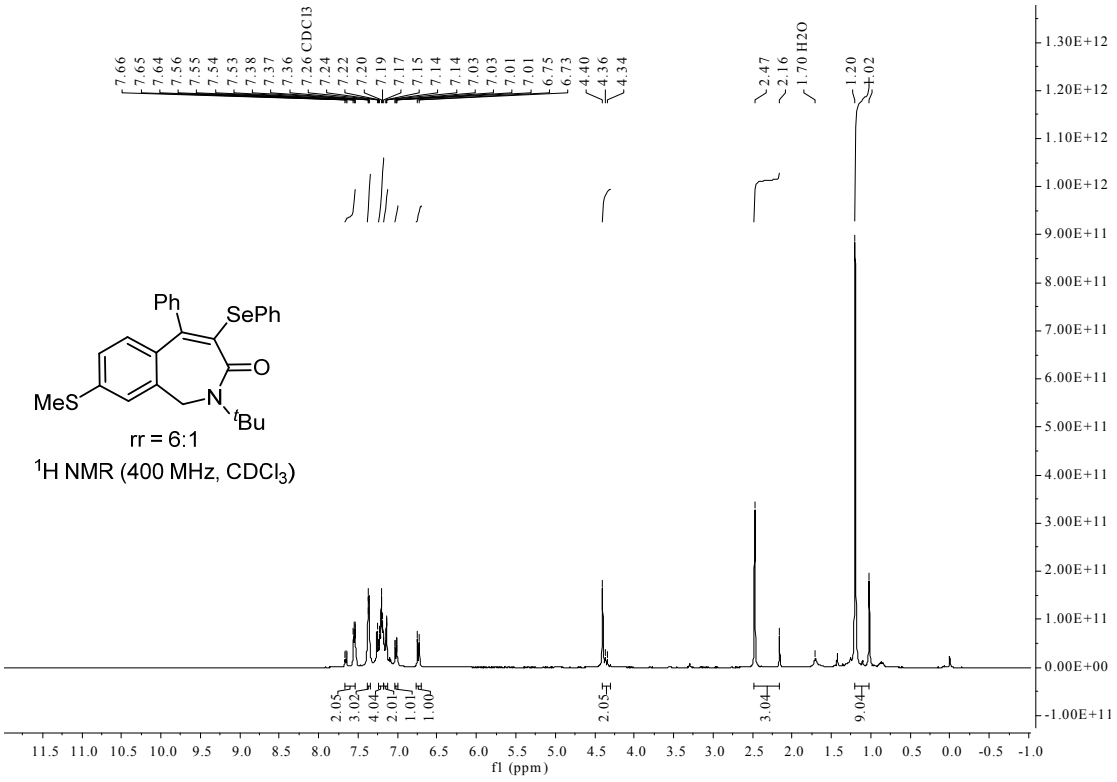

Ph
SePh
O
BzO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

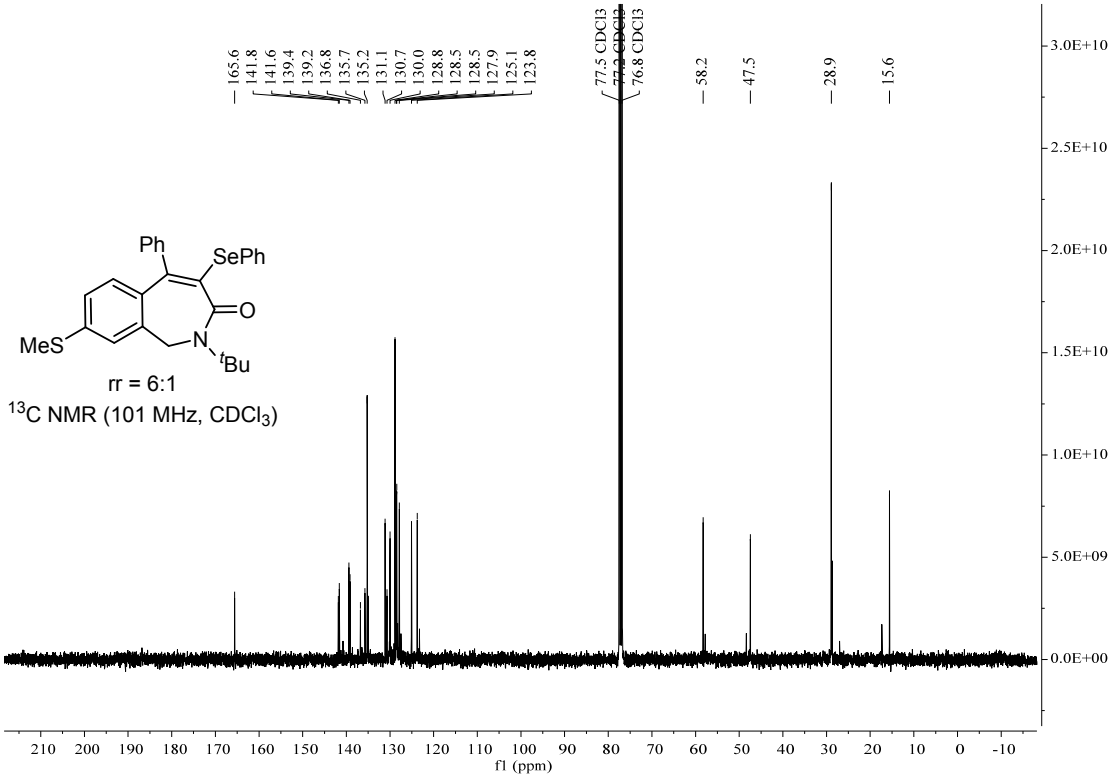
Compound 8


7.55
7.55
7.54
7.54
7.53
7.53
7.37
7.36
7.35
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.15
6.75
6.74
6.70
6.68
6.65
6.64
6.63
6.62
4.41
4.37
4.36
4.32
1.65 H2O
1.21
0.97
0.19
0.18
0.00 TMS
Ph
SePh
O
TBSO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.00
3.02
5.01
1.03
1.03
1.04
1.03
1.02
9.05
9.02
3.01
3.02
f1 (ppm)

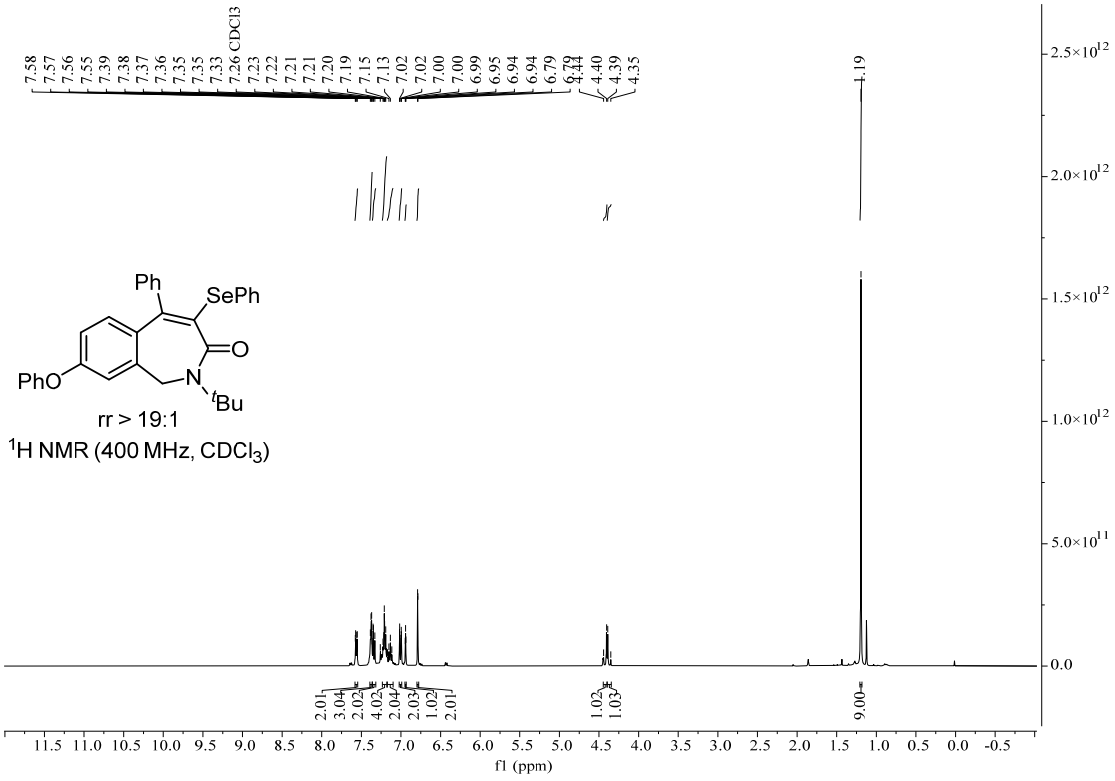

165.9
155.8
142.4
142.0
140.4
135.1
133.4
132.5
132.2
131.0
130.0
128.8
128.4
127.8
119.6
117.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.1
47.5
28.9
25.8
18.4
-4.2
Ph
SePh
O
TBSO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

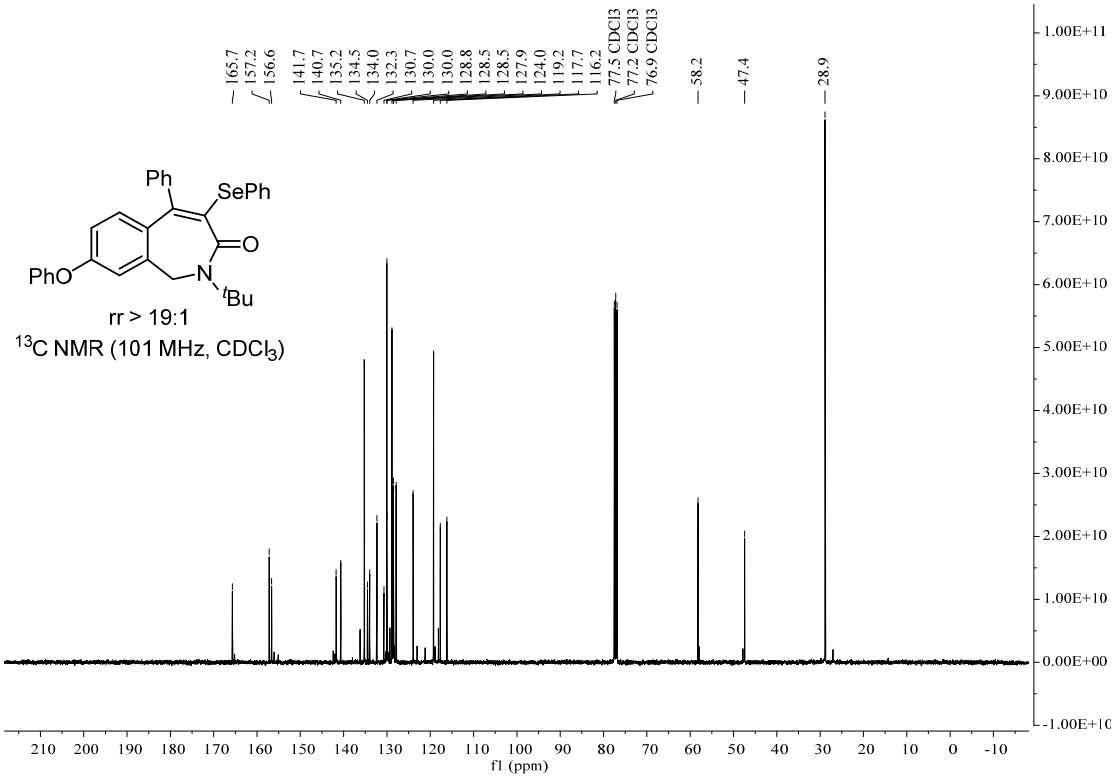
Compound 9


Ph
SePh
O
MeS
N
tBu
rr = 6:1
1H NMR (400 MHz, CDCl3)
7.66
7.65
7.64
7.56
7.55
7.54
7.53
7.38
7.37
7.36
7.26 CDCl3
7.24
7.22
7.20
7.19
7.17
7.15
7.14
7.14
7.03
7.03
7.01
7.01
6.75
6.73
4.40
4.36
4.34
2.47
2.16
1.70 H2O
1.20
1.02
2.05
3.02
4.04
2.01
1.01
1.00
2.05
3.04
9.04
f1 (ppm)

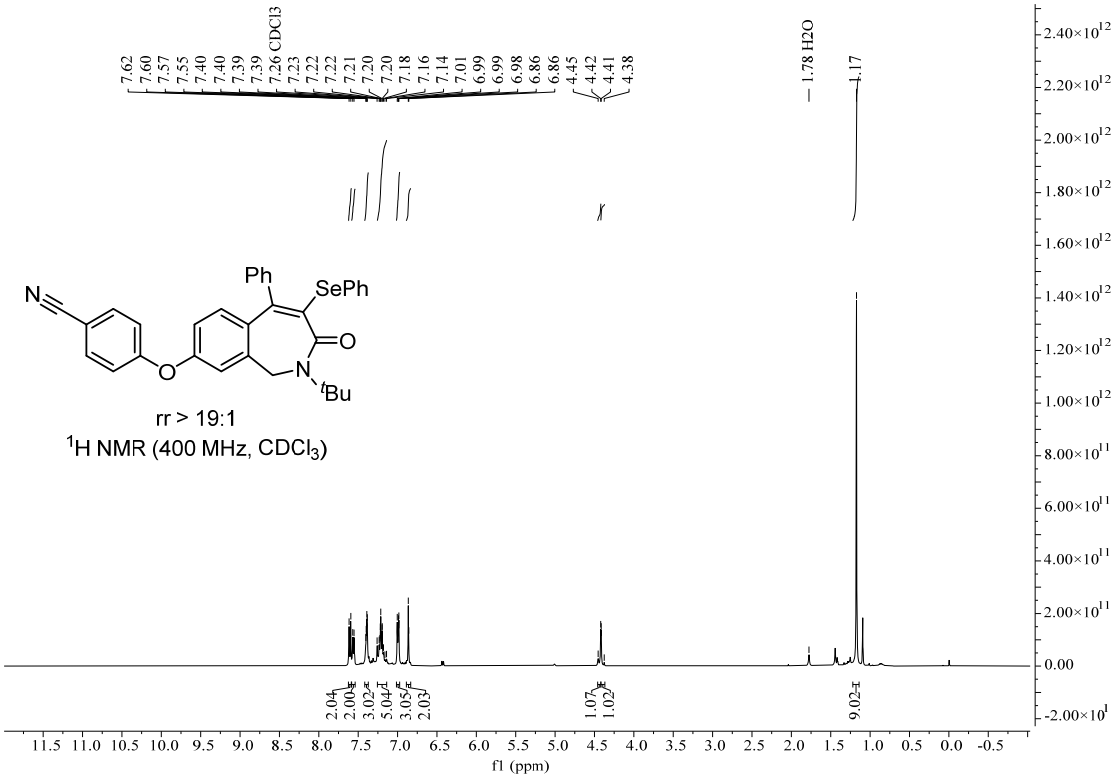

Ph
SePh
O
MeS
N
tBu
rr = 6:1
13C NMR (101 MHz, CDCl3)
165.6
141.8
141.6
139.4
139.2
136.8
135.7
135.2
131.1
130.7
130.0
128.8
128.5
128.5
127.9
125.1
123.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
58.2
47.5
28.9
15.6
f1 (ppm)

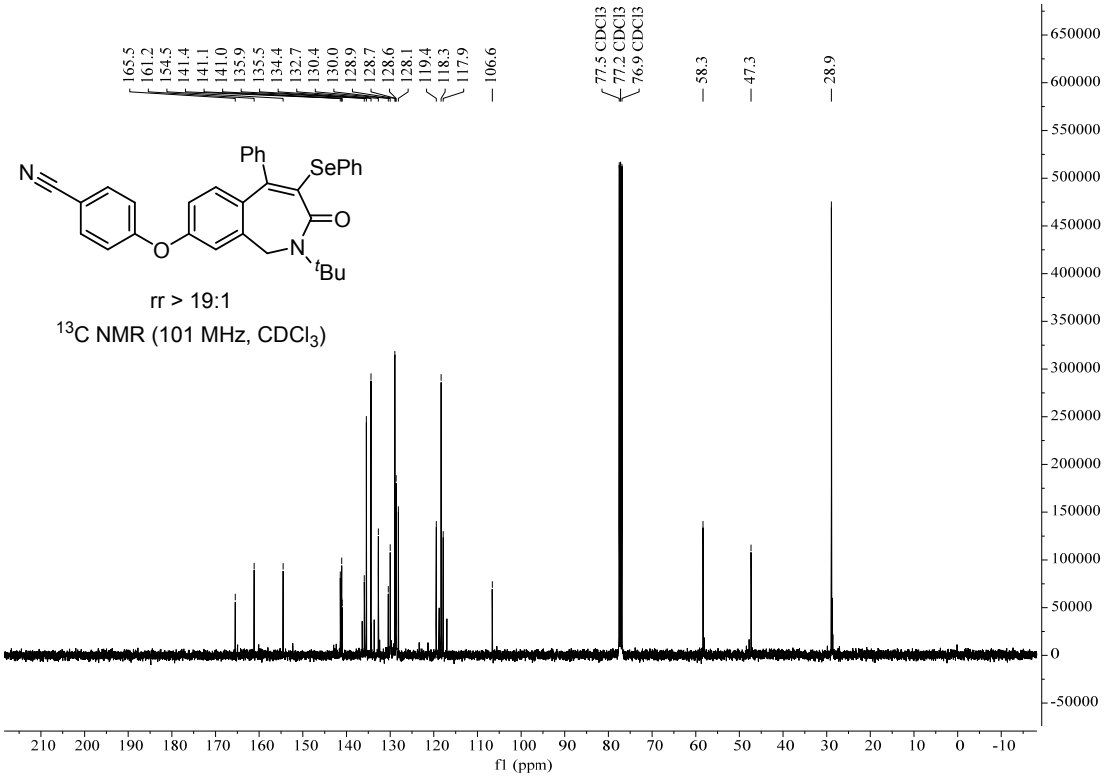
Compound 10


Ph
SePh
O
PhO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)

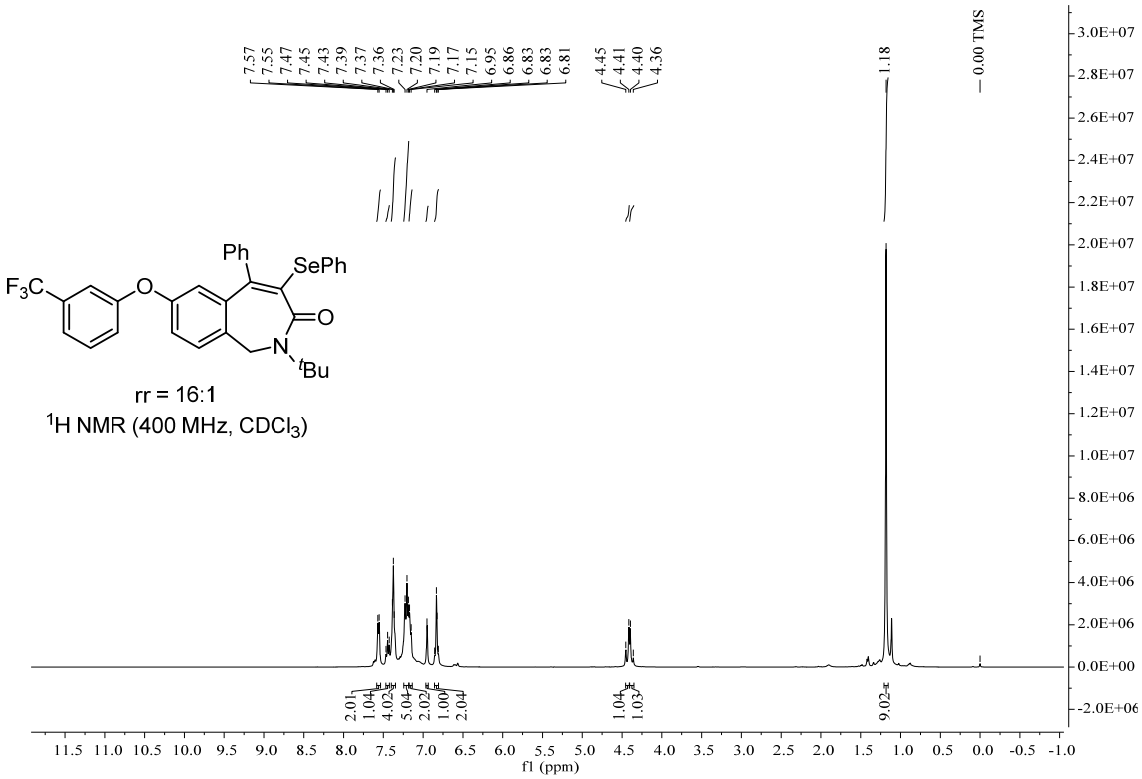

Ph
SePh
O
PhO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 11


7.62
7.60
7.57
7.55
7.40
7.40
7.39
7.39
7.26 CDCl3
7.23
7.22
7.22
7.21
7.20
7.20
7.18
7.16
7.14
7.01
6.99
6.99
6.98
6.86
6.86
4.45
4.42
4.41
4.38
1.78 H2O
1.17
Ph
SePh
O
N
tBu
O
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.04
2.00
3.02
5.04
3.05
2.03
1.07
1.02
9.02
f1 (ppm)

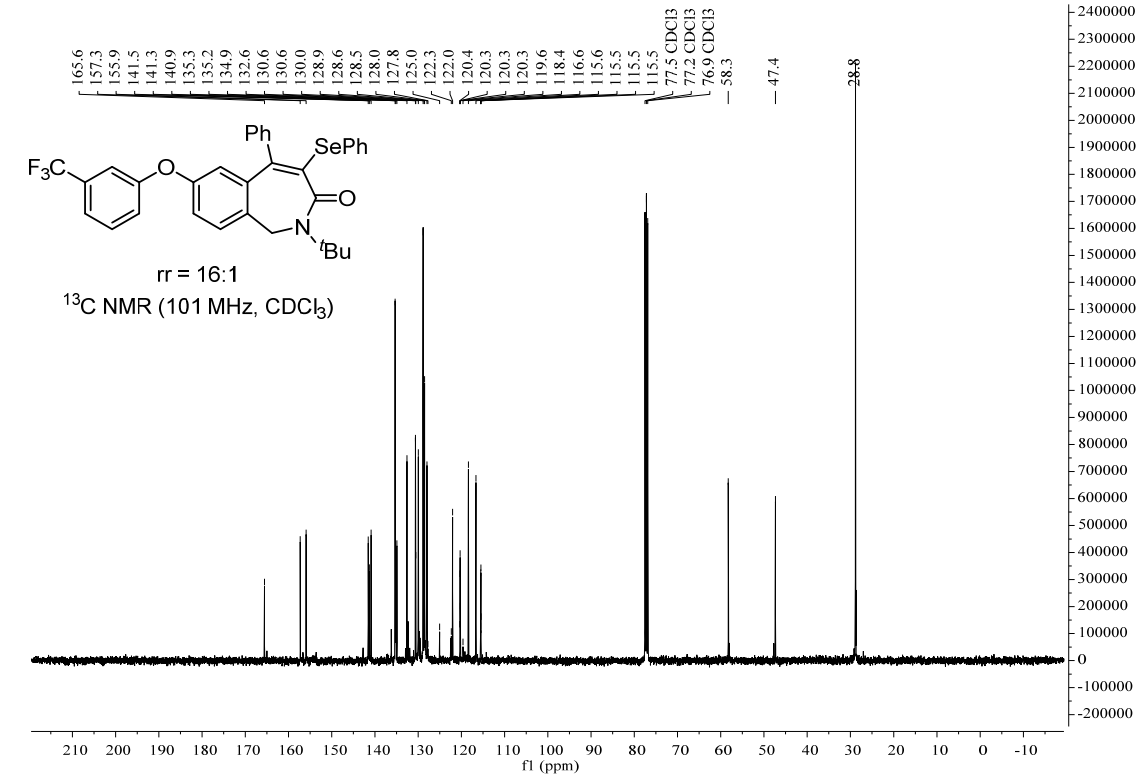

165.5
161.2
154.5
141.4
141.1
141.0
135.9
135.5
134.4
132.7
130.4
130.0
128.9
128.7
128.6
128.1
119.4
118.3
117.9
106.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.3
47.3
28.9
Ph
SePh
O
N
tBu
O
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 12



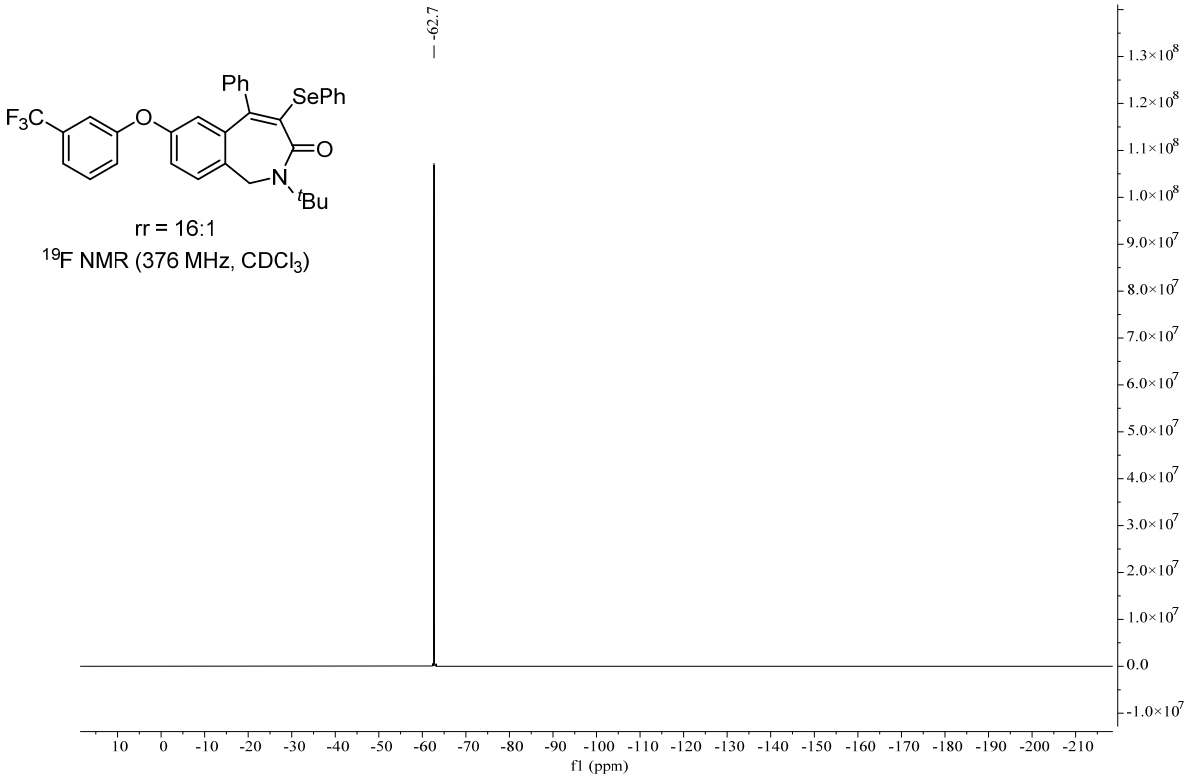
rr = 16:1

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



rr = 16:1

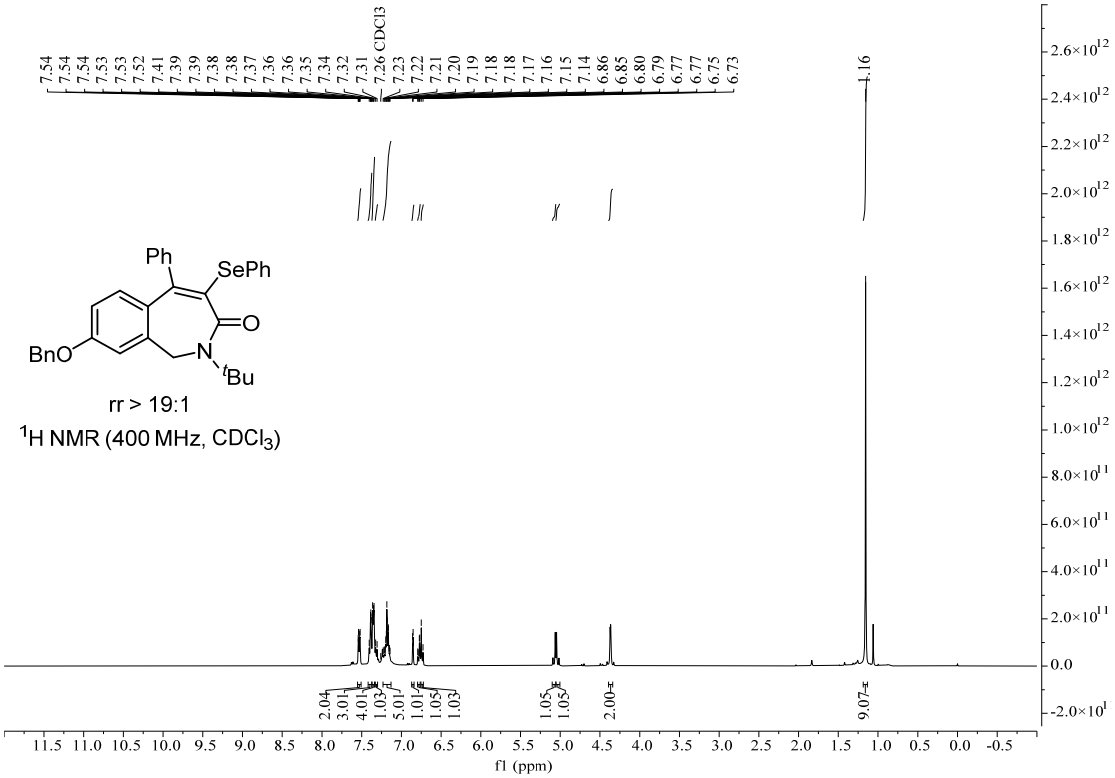
^{13}C NMR (101 MHz, $CDCl_3$)

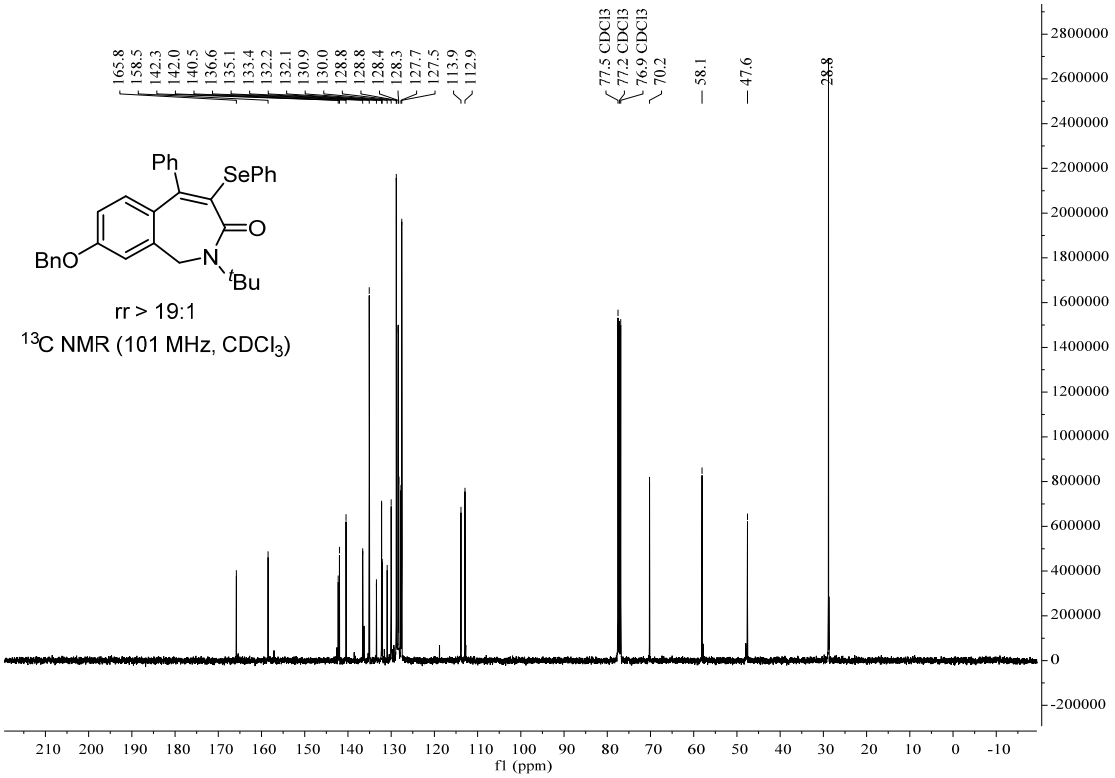


rr = 16:1

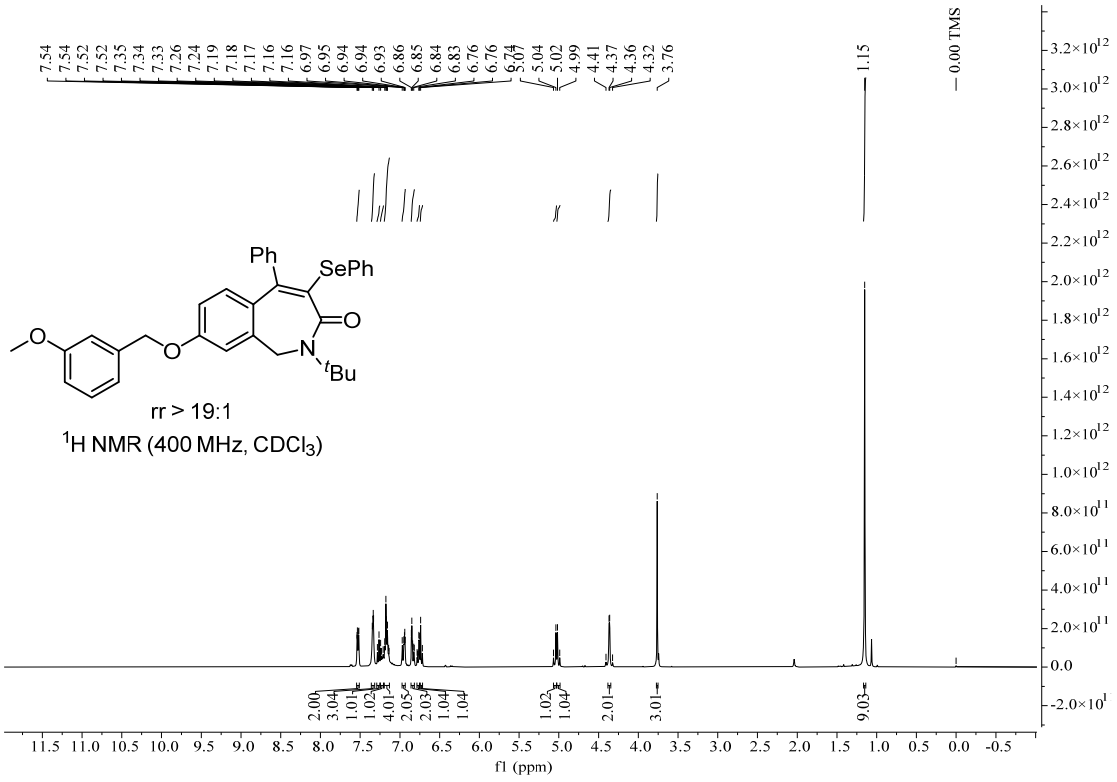
^{19}F NMR (376 MHz, $CDCl_3$)

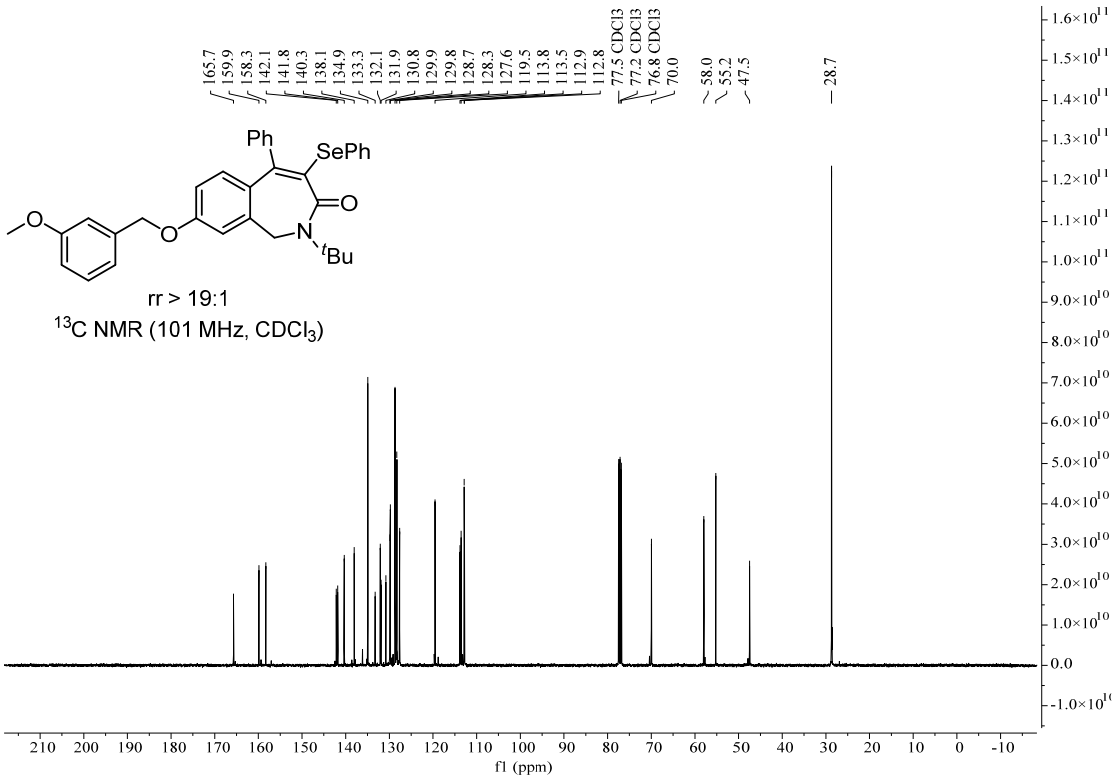
Compound 13


Ph
SePh
O
BnO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)

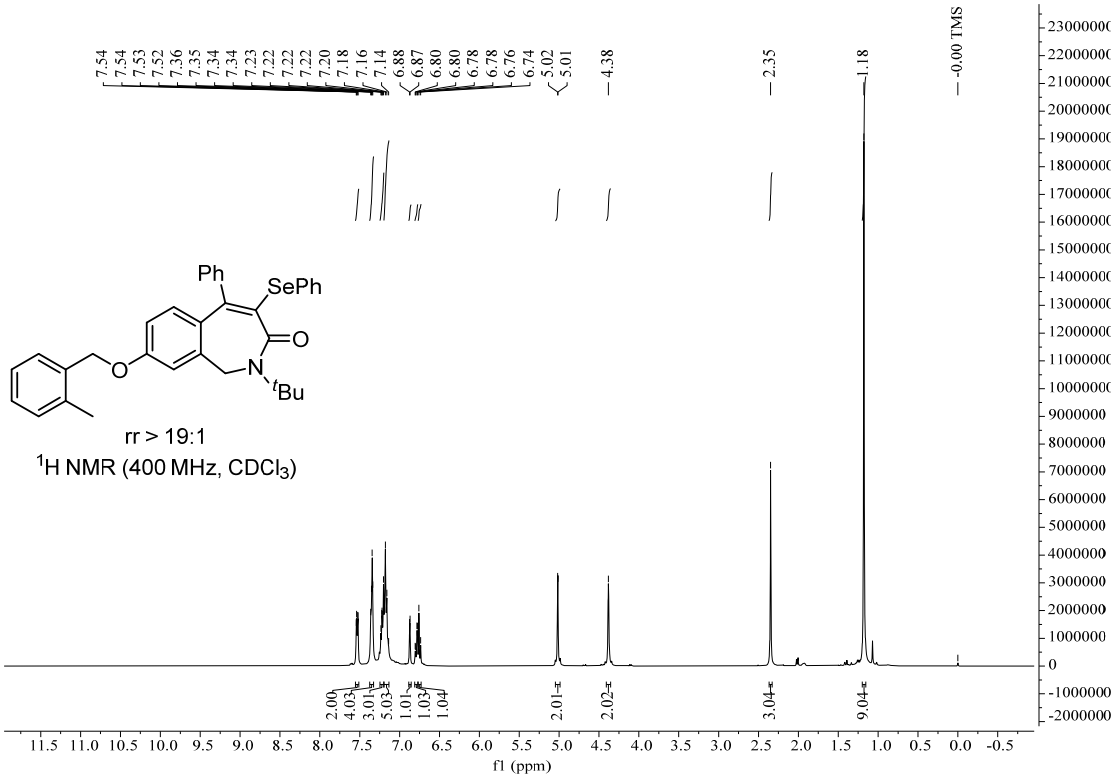

Ph
SePh
O
BnO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

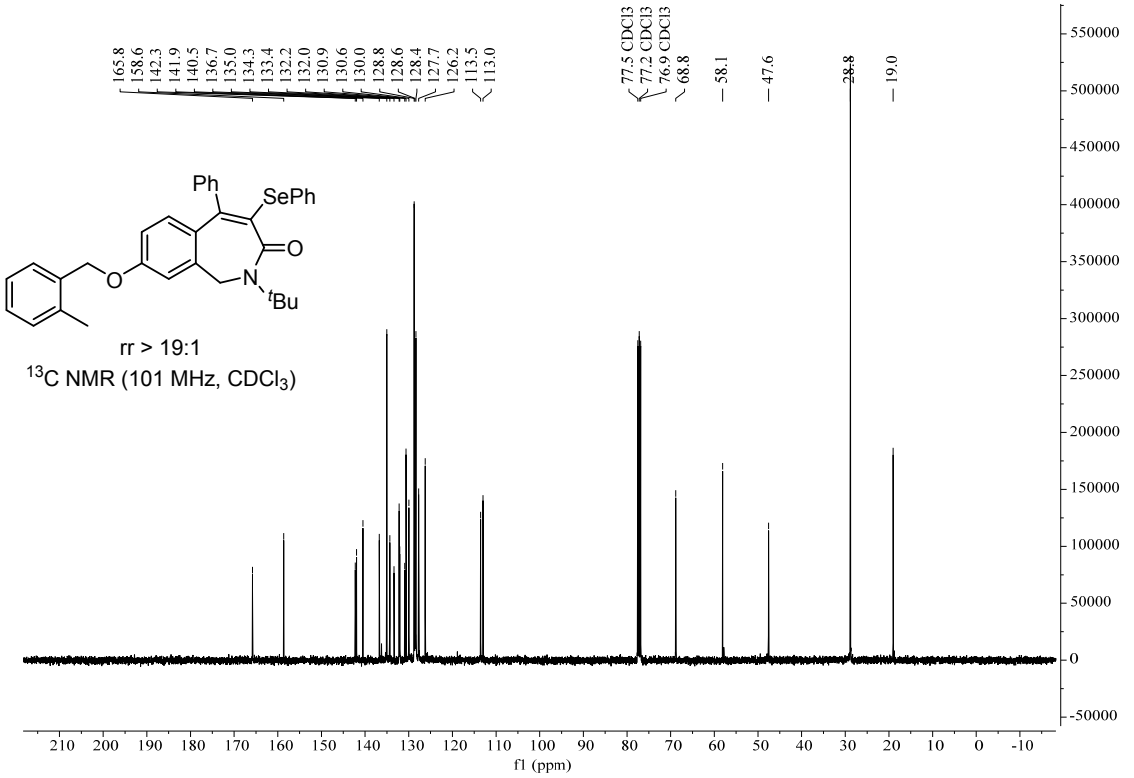
Compound 14


Ph
SePh
O
O
O
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
0.00 TMS
1.15
f1 (ppm)

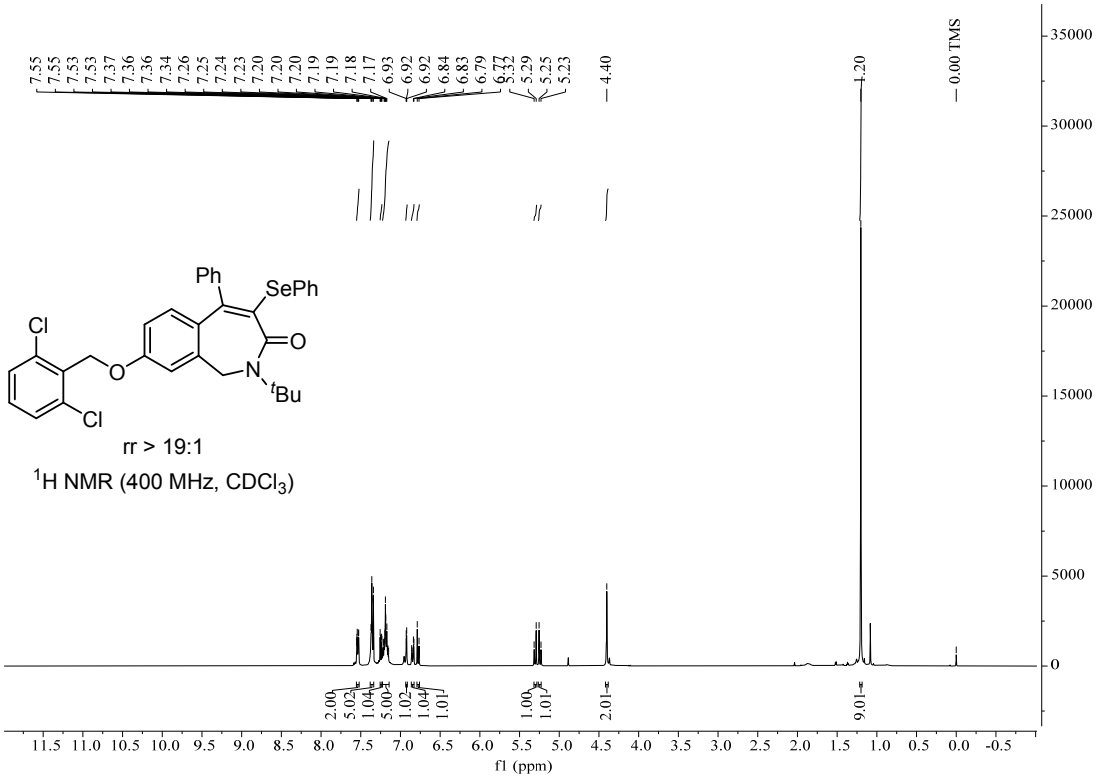

Ph
SePh
O
O
O
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
28.7
f1 (ppm)

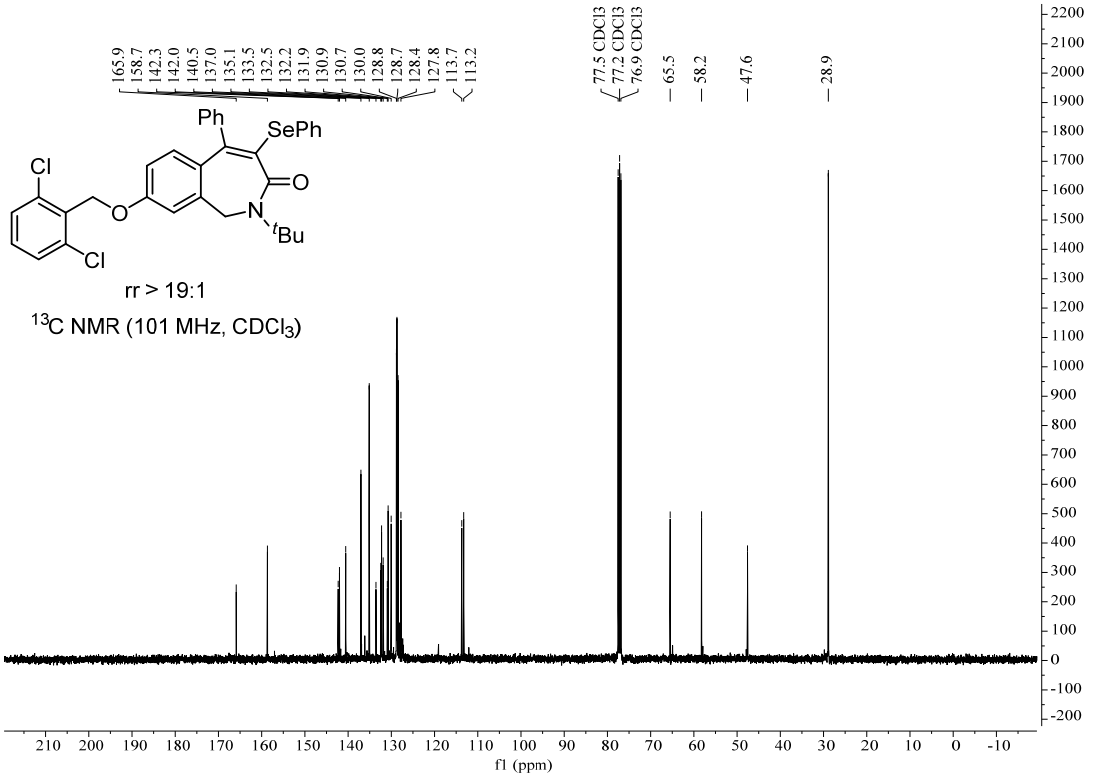
Compound 15


Ph
SePh
O
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
fl (ppm)

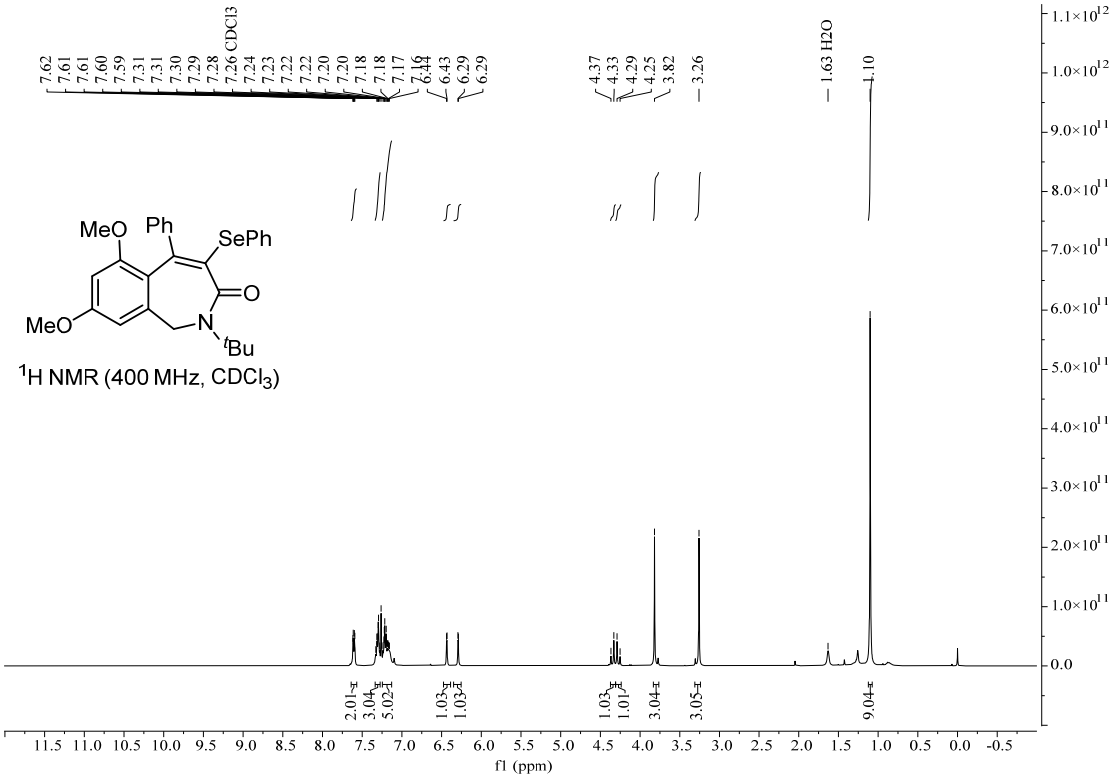

Ph
SePh
O
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
fl (ppm)

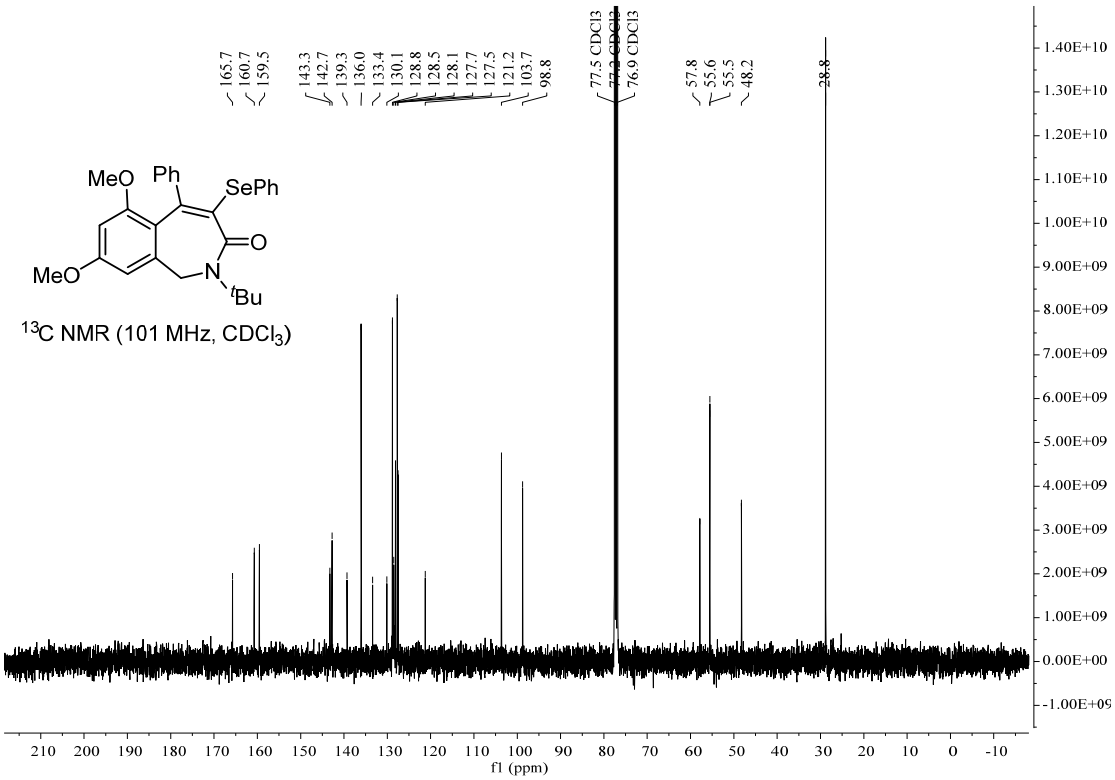
Compound 16


7.55
7.55
7.53
7.53
7.37
7.36
7.36
7.34
7.26
7.25
7.24
7.23
7.20
7.20
7.20
7.19
7.19
7.18
7.17
6.93
6.92
6.92
6.84
6.83
6.79
6.77
5.32
5.29
5.25
5.23
4.40
1.20
0.00 TMS
Ph
SePh
Cl
O
N
tBu
Cl
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.00
5.03
1.04
5.00
1.02
1.04
1.01
1.00
1.01
2.01
9.01
f1 (ppm)

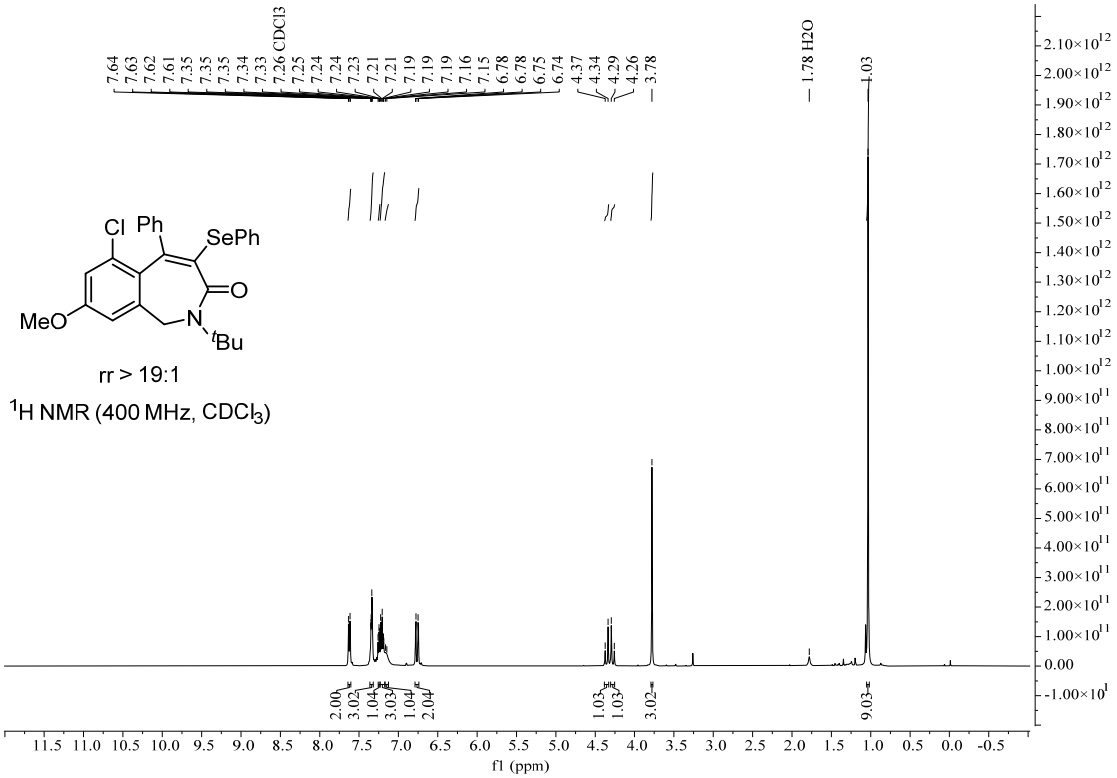

165.9
158.7
142.3
142.0
140.5
137.0
135.1
133.5
132.5
132.2
131.9
130.9
130.7
130.0
128.8
128.7
128.4
127.8
113.7
113.2
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
65.5
58.2
47.6
28.9
Ph
SePh
Cl
O
N
tBu
Cl
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 17


MeO
Ph
SePh
O
MeO
N
tBu
1H NMR (400 MHz, CDCl3)
7.62
7.61
7.61
7.60
7.59
7.31
7.31
7.30
7.29
7.28
7.26 CDCl3
7.24
7.23
7.22
7.22
7.20
7.20
7.18
7.18
7.17
7.16
6.44
6.43
6.29
6.29
4.37
4.33
4.29
4.25
3.82
3.26
1.63 H2O
1.10
2.01
3.04
5.02
1.03
1.03
1.03
1.01
3.04
3.05
9.04
f1 (ppm)

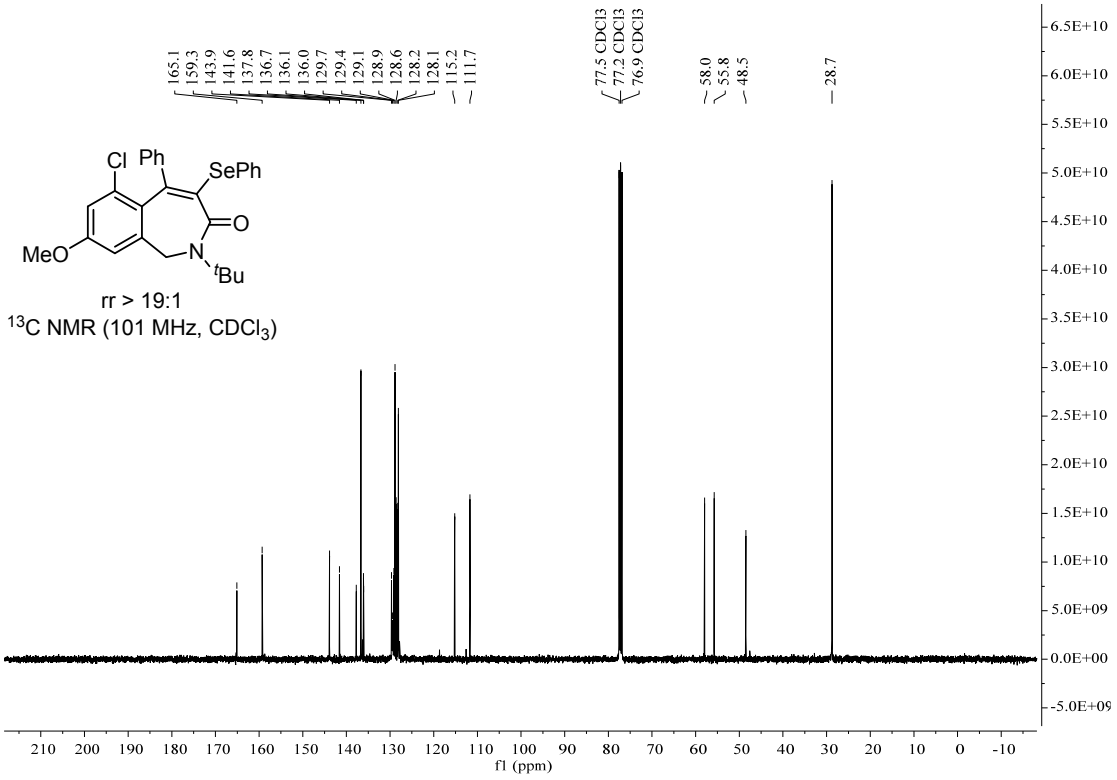

MeO
Ph
SePh
O
MeO
N
tBu
13C NMR (101 MHz, CDCl3)
165.7
160.7
159.5
143.3
142.7
139.3
136.0
133.4
130.1
128.8
128.5
128.1
127.7
127.5
121.2
103.7
98.8
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
57.8
55.6
55.5
48.2
28.8
f1 (ppm)

Compound 18



rr > 19:1

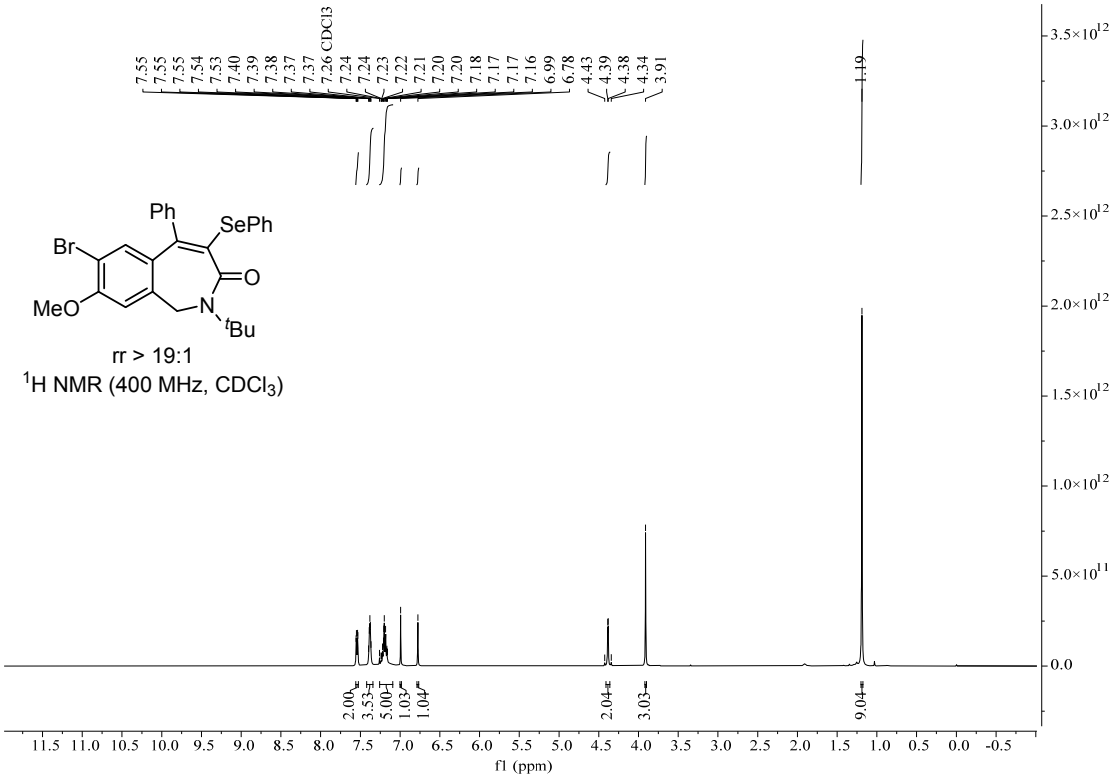
^{1}H NMR (400 MHz, $CDCl_3$)

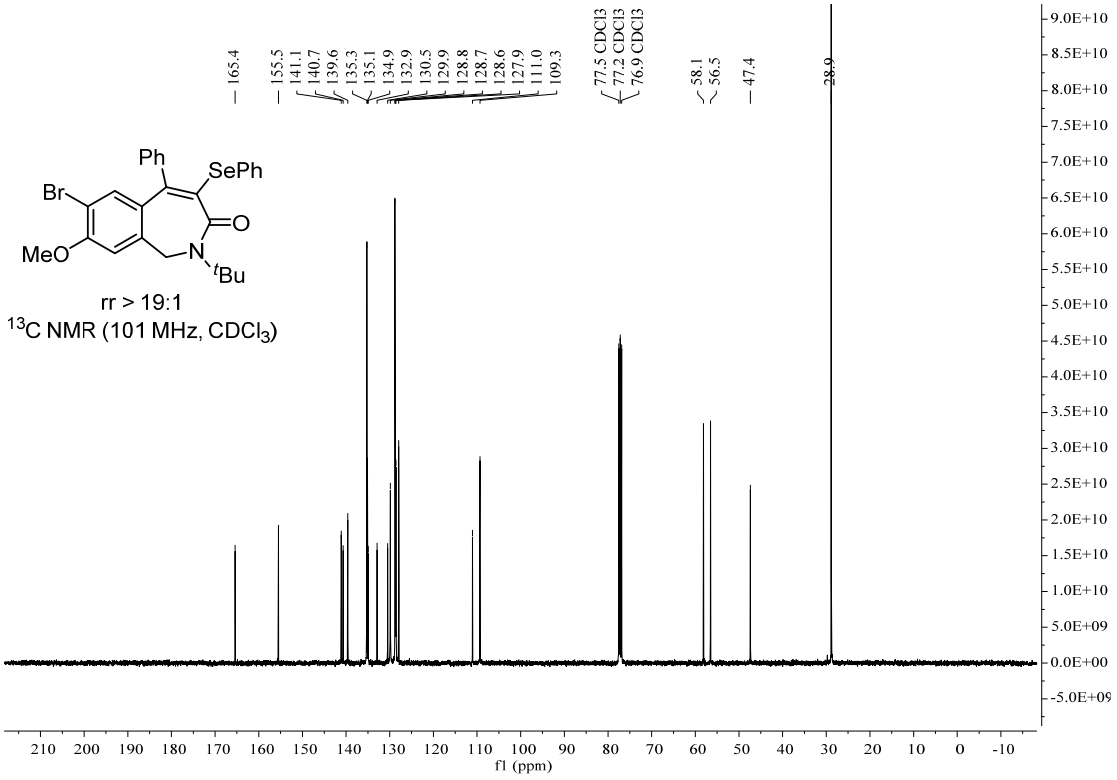


rr > 19:1

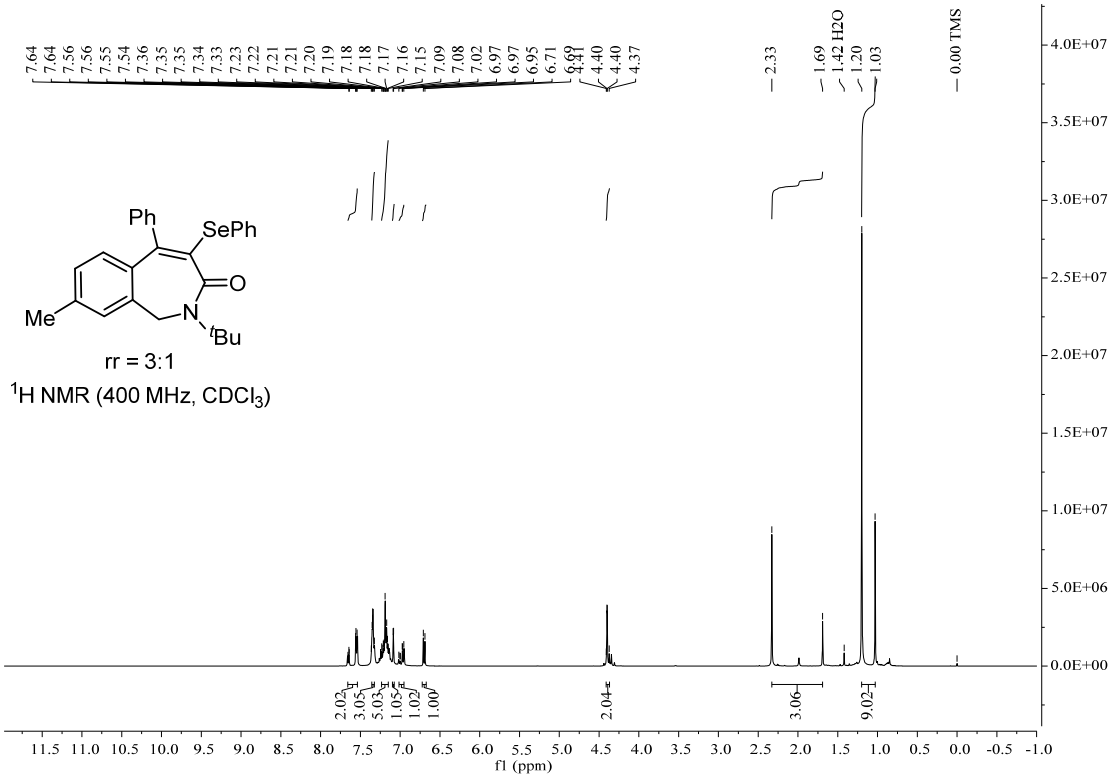
^{13}C NMR (101 MHz, $CDCl_3$)

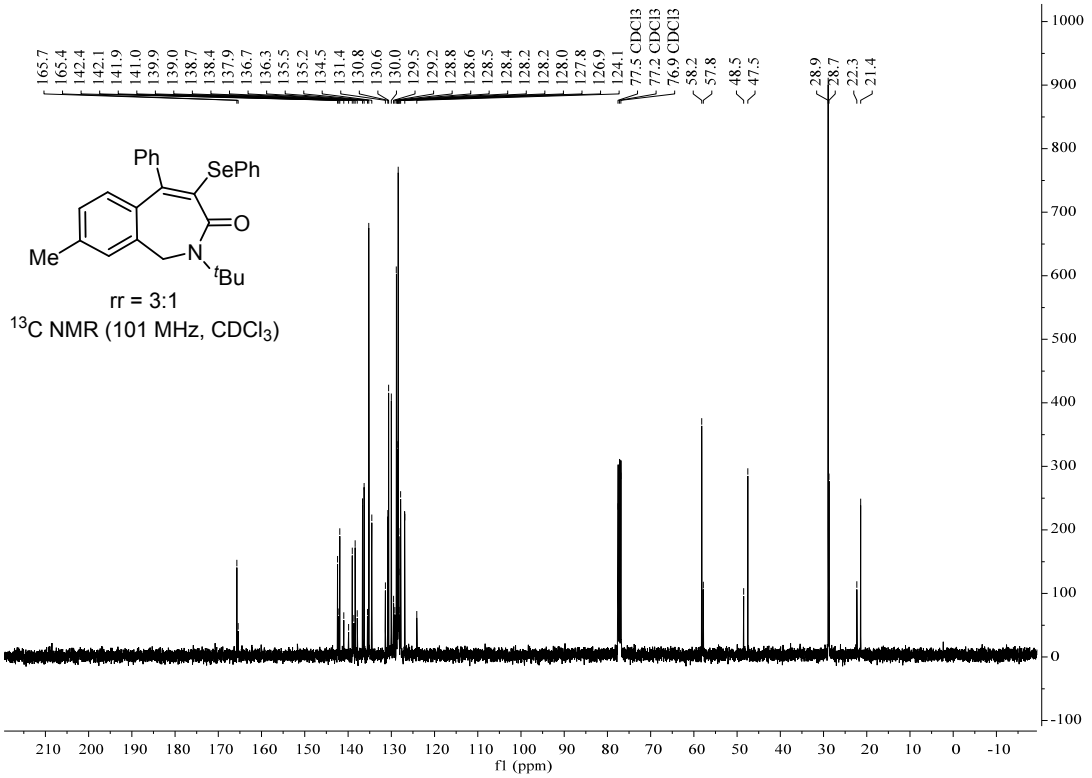
Compound 19


7.55
7.55
7.55
7.54
7.53
7.40
7.39
7.38
7.37
7.37
7.26 CDCl3
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.18
7.17
7.17
7.16
6.99
6.78
4.43
4.39
4.38
4.34
3.91
1.19
Ph
SePh
Br
O
MeO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.00
3.53
5.00
1.03
1.04
2.04
3.03
9.04
f1 (ppm)

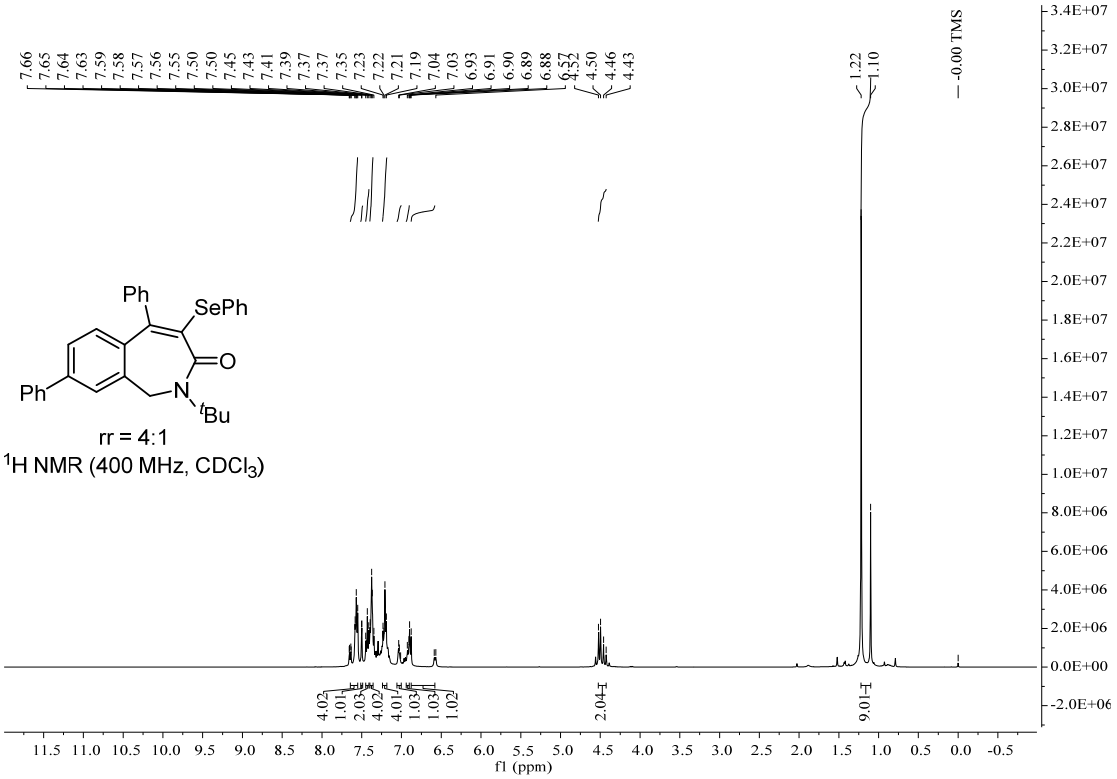

165.4
155.5
141.1
140.7
139.6
135.3
135.1
134.9
132.9
130.5
129.9
128.8
128.7
128.6
127.9
111.0
109.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.1
56.5
47.4
28.9
Ph
SePh
Br
O
MeO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

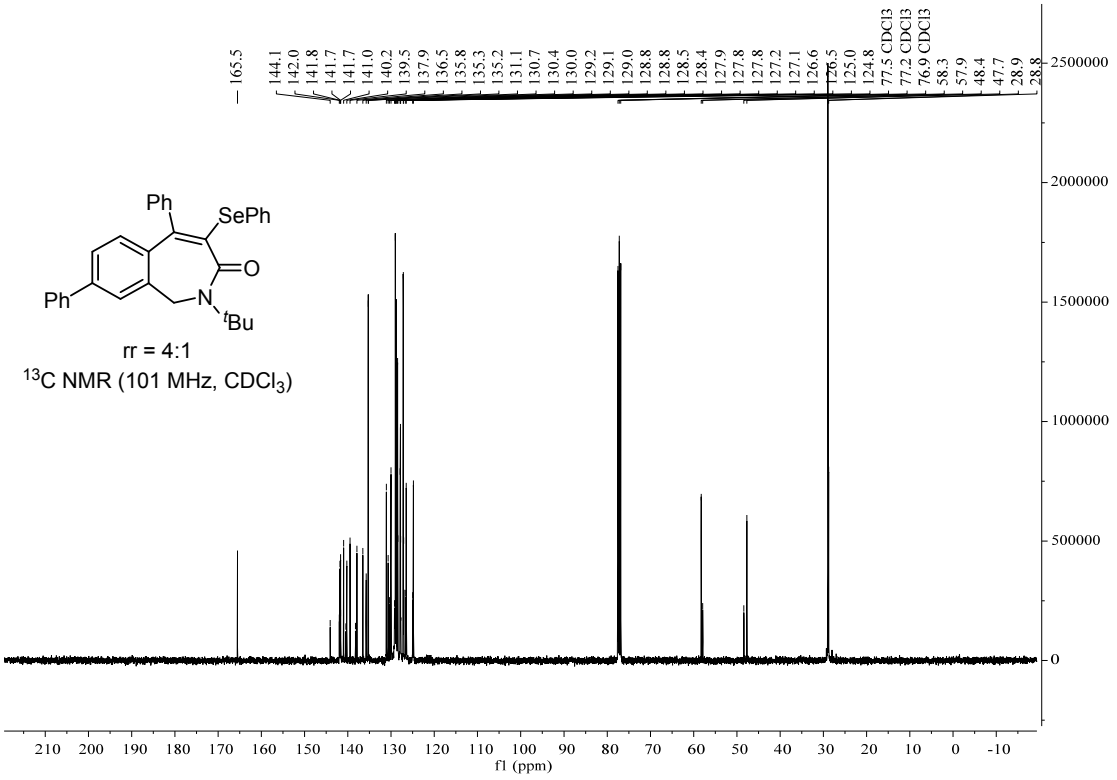
Compound 20


Ph
SePh
O
Me
N
tBu
rr = 3:1
1H NMR (400 MHz, CDCl3)
7.64
7.64
7.56
7.56
7.55
7.54
7.36
7.35
7.35
7.34
7.33
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.15
7.09
7.08
7.02
6.97
6.95
6.71
6.69
4.41
4.40
4.40
4.37
2.33
1.69
1.42 H2O
1.20
1.03
0.00 TMS
2.02
3.05
5.03
1.05
1.02
1.00
2.04
3.06
9.02
f1 (ppm)

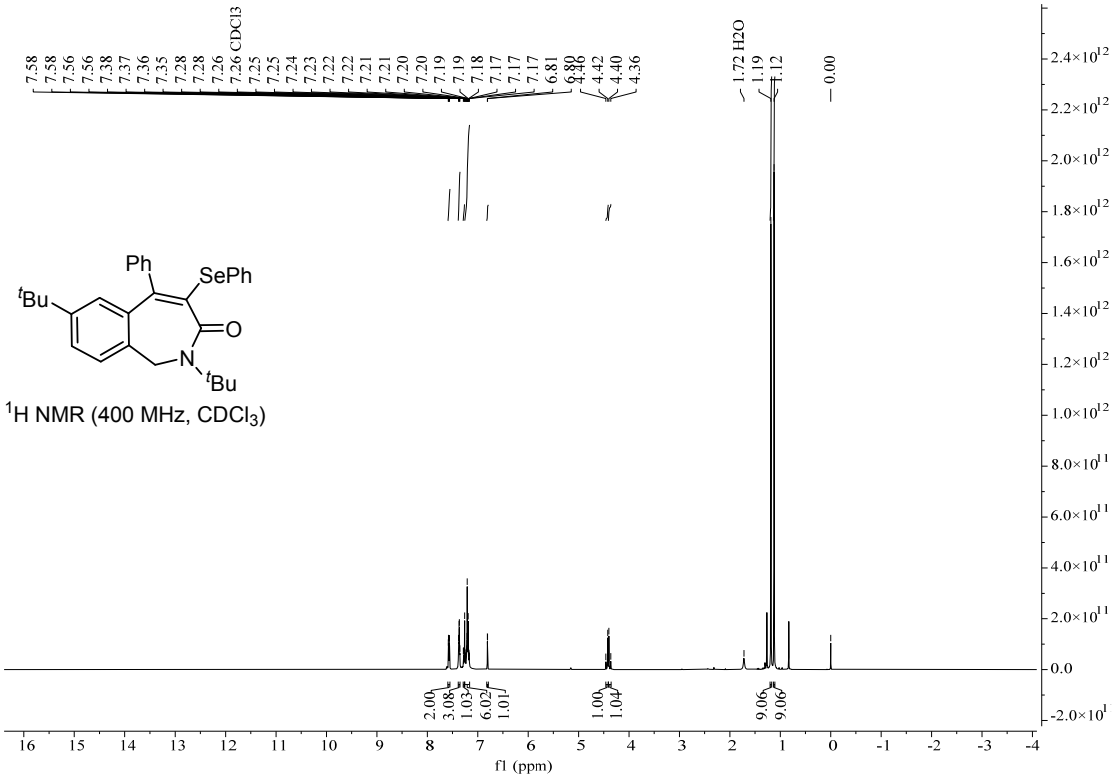

Ph
SePh
O
Me
N
tBu
rr = 3:1
13C NMR (101 MHz, CDCl3)
165.7
165.4
142.4
142.1
141.9
141.0
139.9
139.0
138.7
138.4
137.9
136.7
136.3
135.5
135.2
134.5
131.4
130.8
130.6
130.0
129.5
129.2
128.8
128.6
128.5
128.4
128.2
128.2
128.0
127.8
126.9
124.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.2
57.8
48.5
47.5
28.9
28.7
22.3
21.4
f1 (ppm)

Compound 21

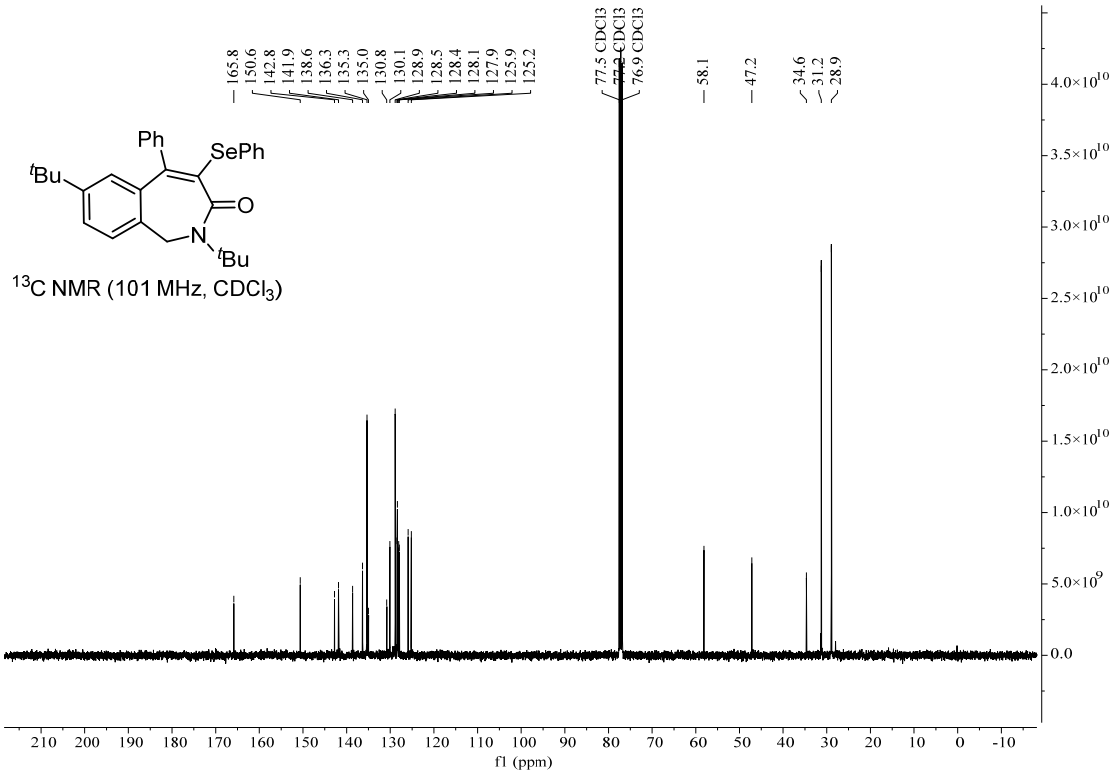

Ph
SePh
O
Ph
N
tBu
rr = 4:1
1H NMR (400 MHz, CDCl3)
-0.00 TMS
f1 (ppm)


Ph
SePh
O
Ph
N
tBu
rr = 4:1
13C NMR (101 MHz, CDCl3)
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
f1 (ppm)

Compound 22

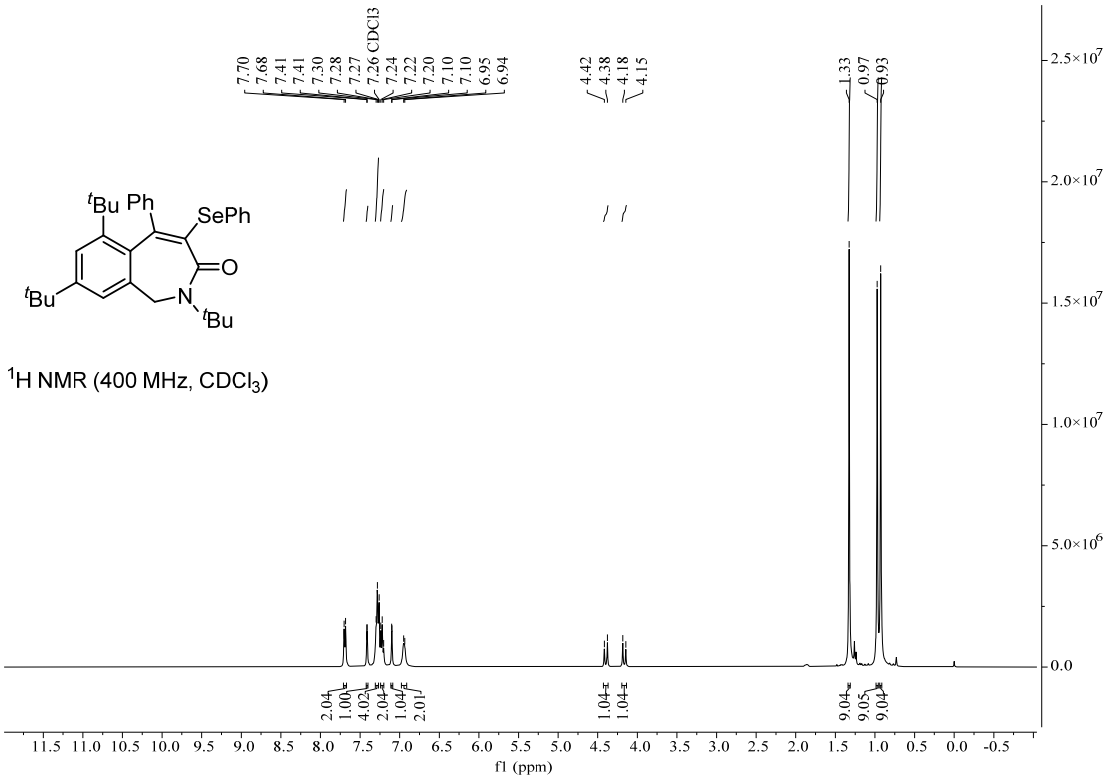


^{1}H NMR (400 MHz, $CDCl_3$)

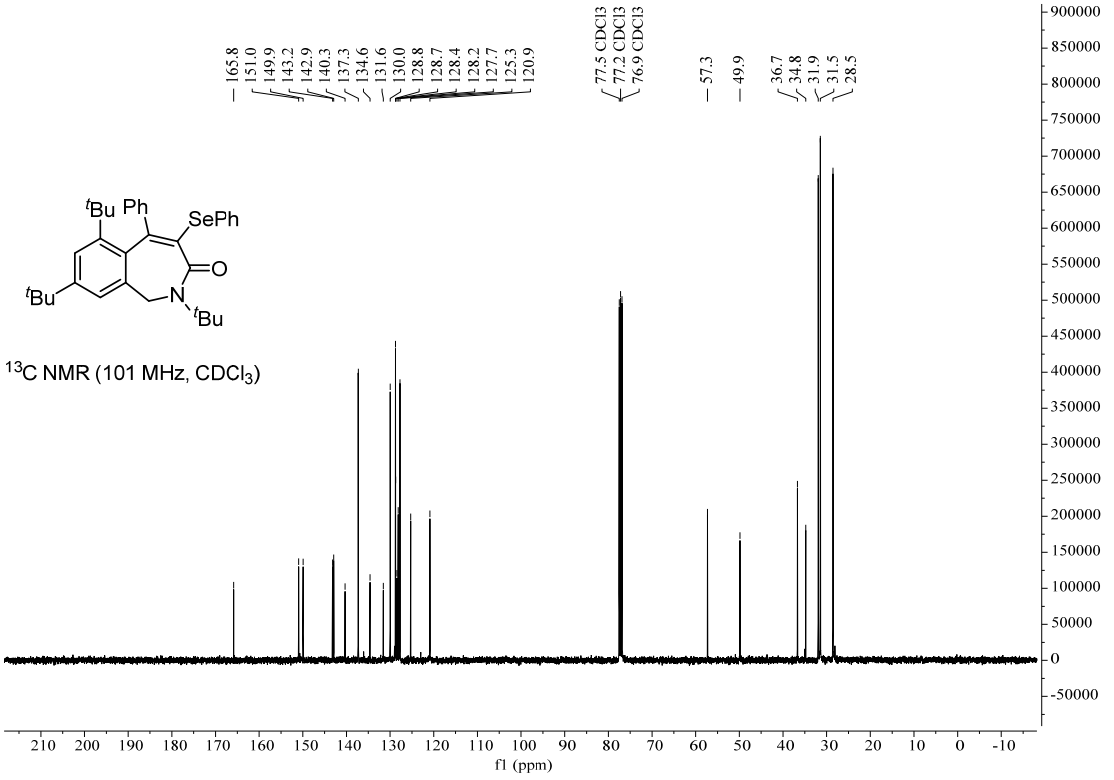


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 23

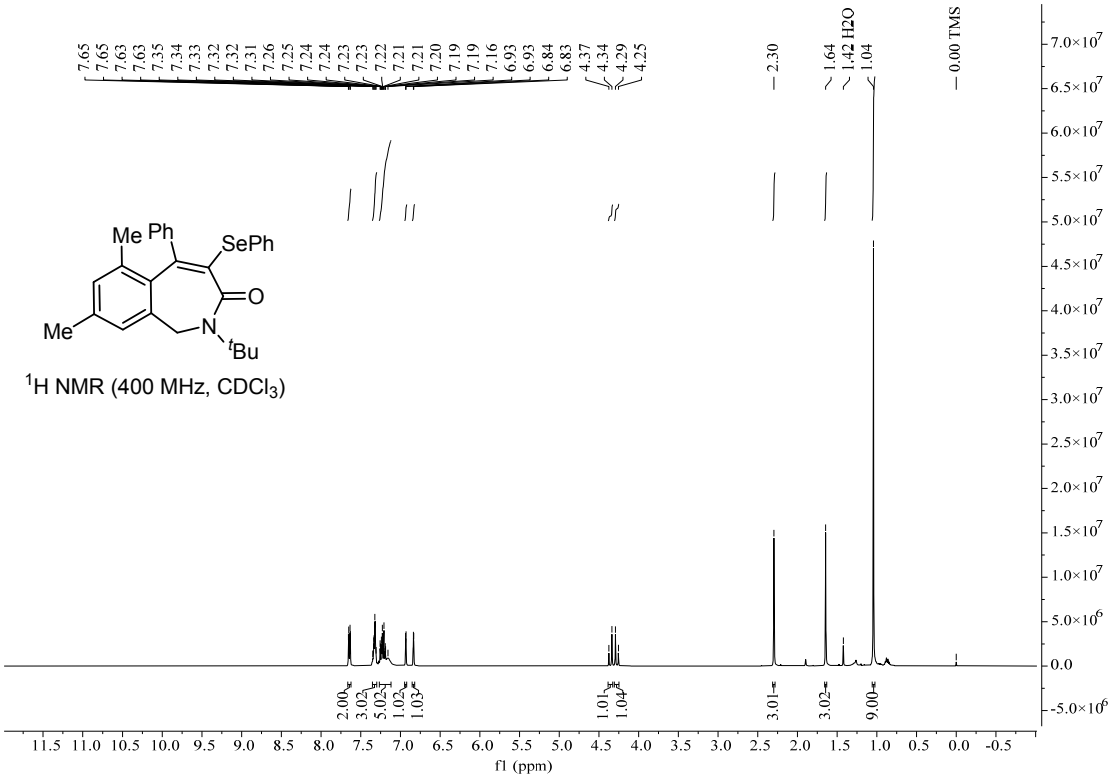


^{1}H NMR (400 MHz, $CDCl_3$)

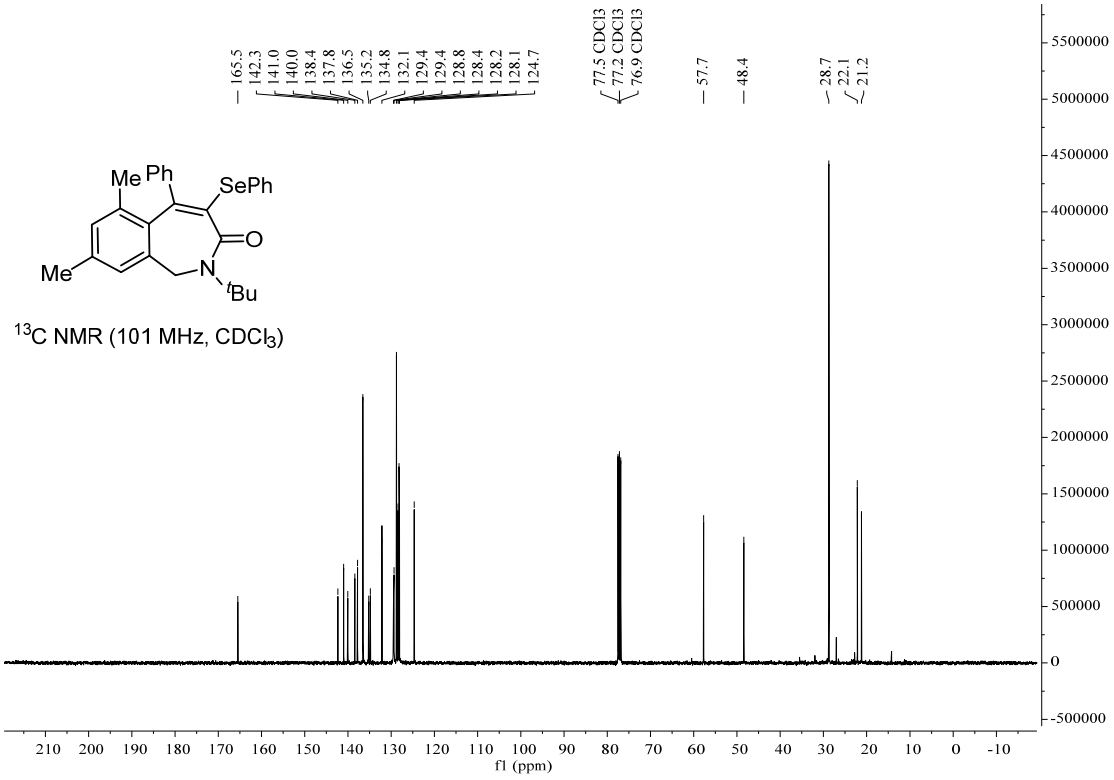


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 24

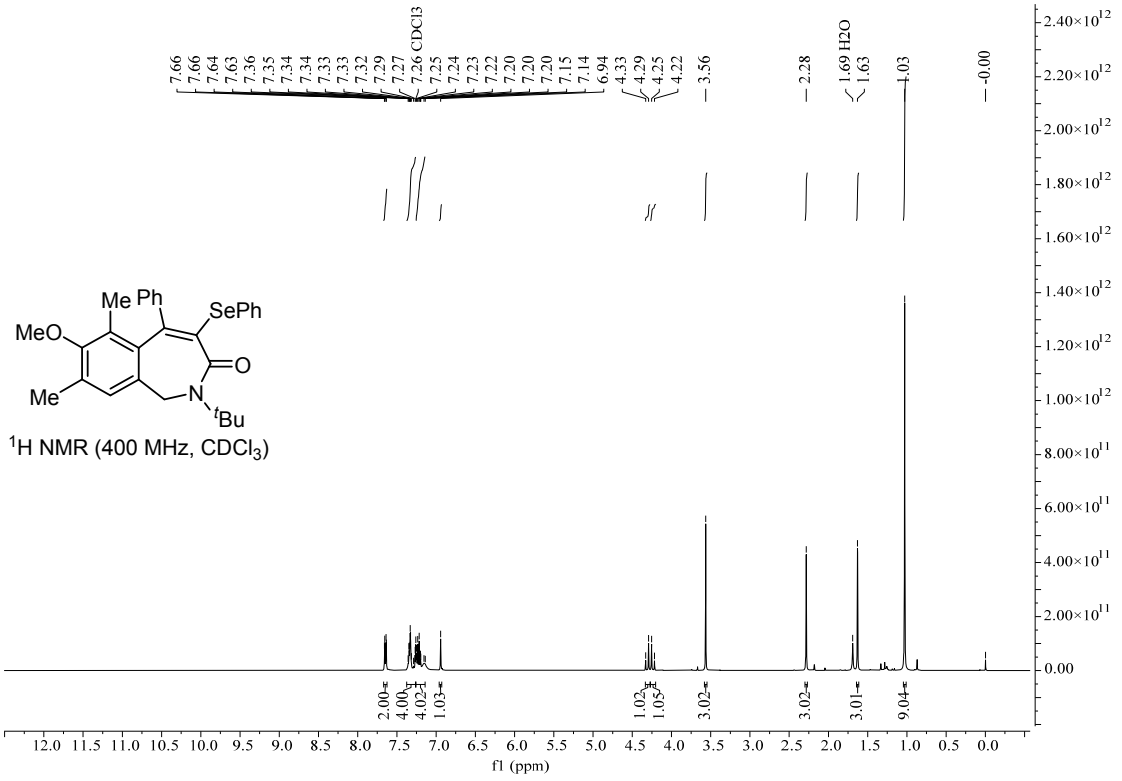


^{1}H NMR (400 MHz, $CDCl_3$)

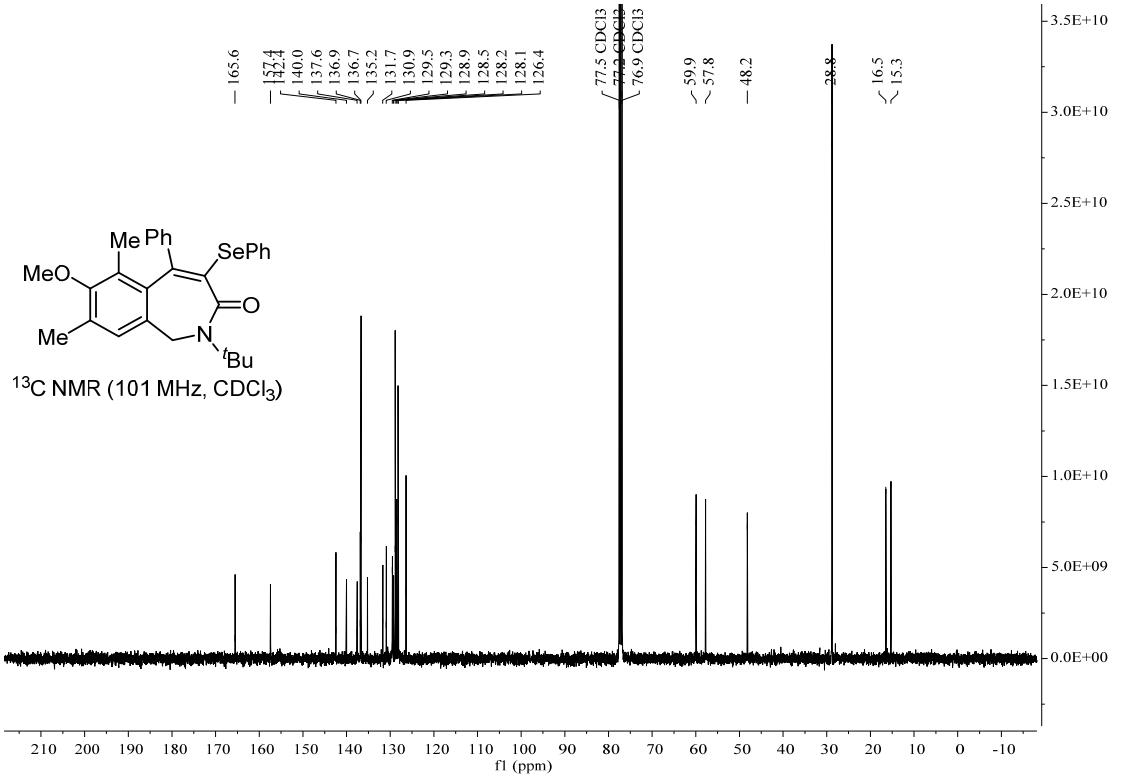


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 25

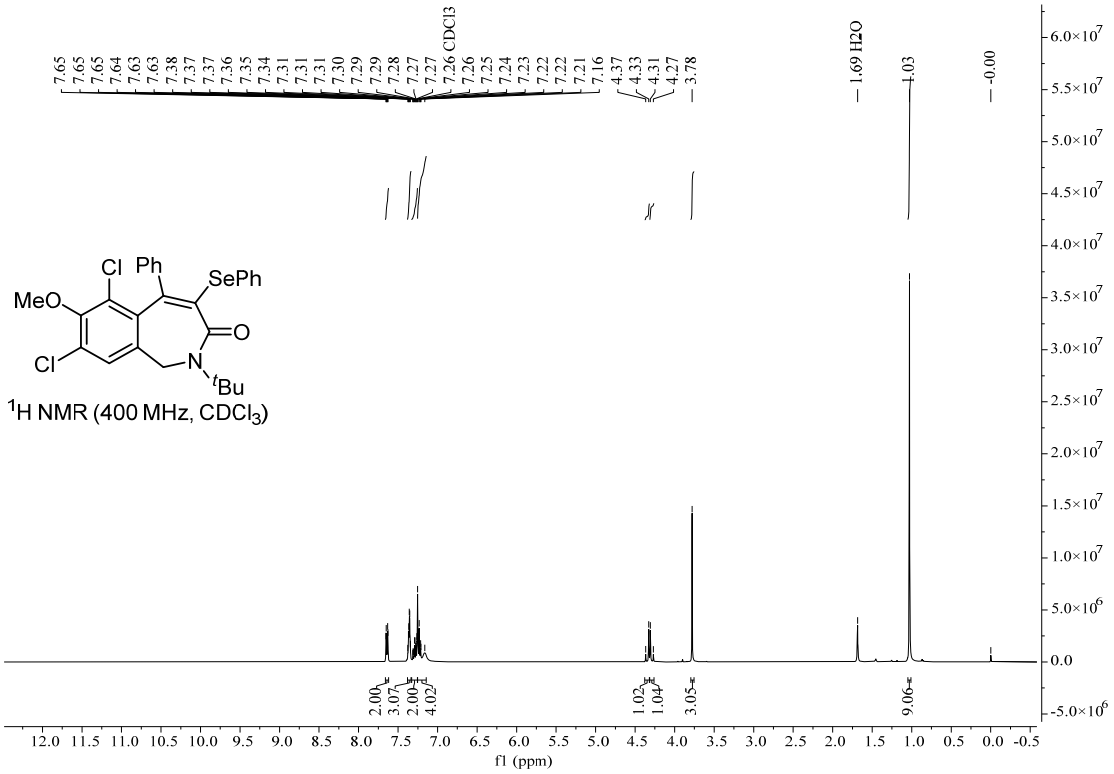


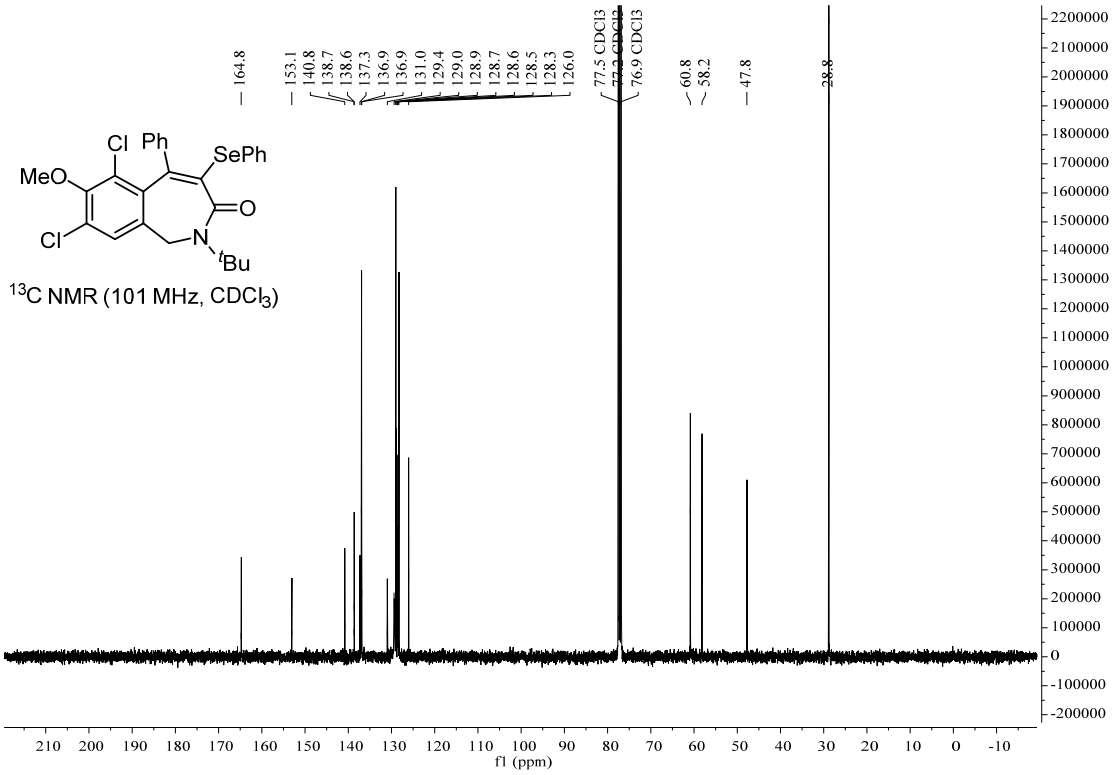
^{1}H NMR (400 MHz, $CDCl_3$)



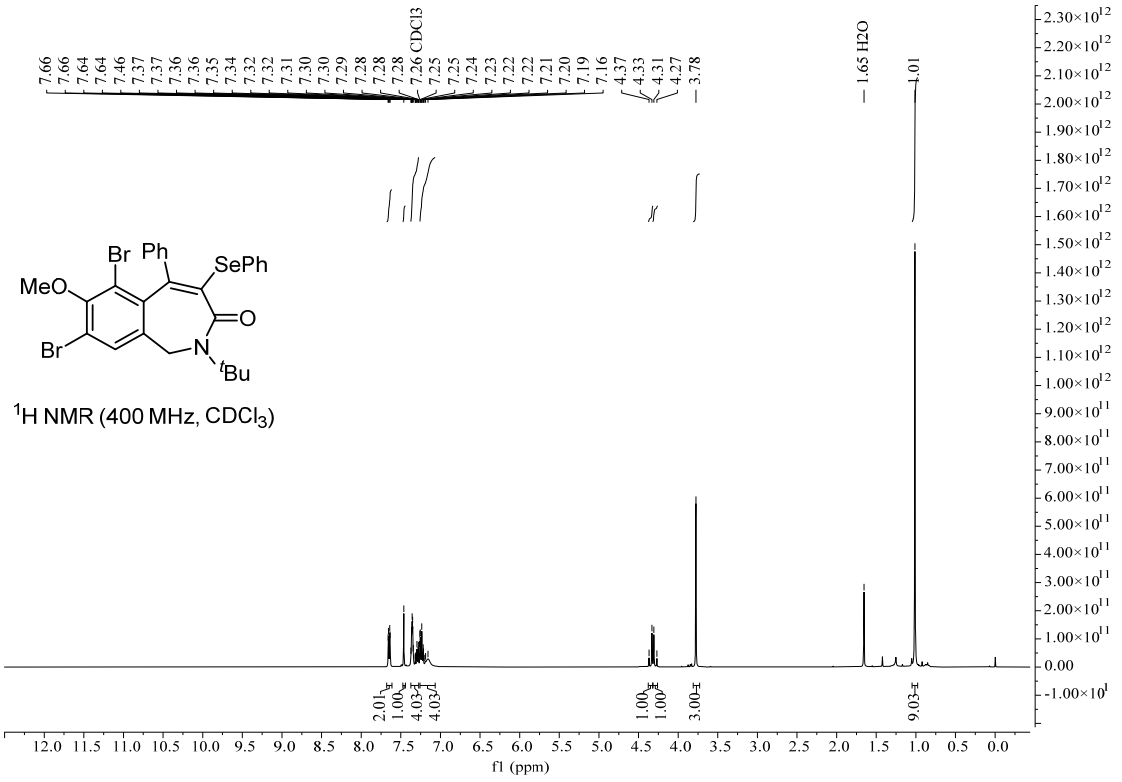
^{13}C NMR (101 MHz, $CDCl_3$)

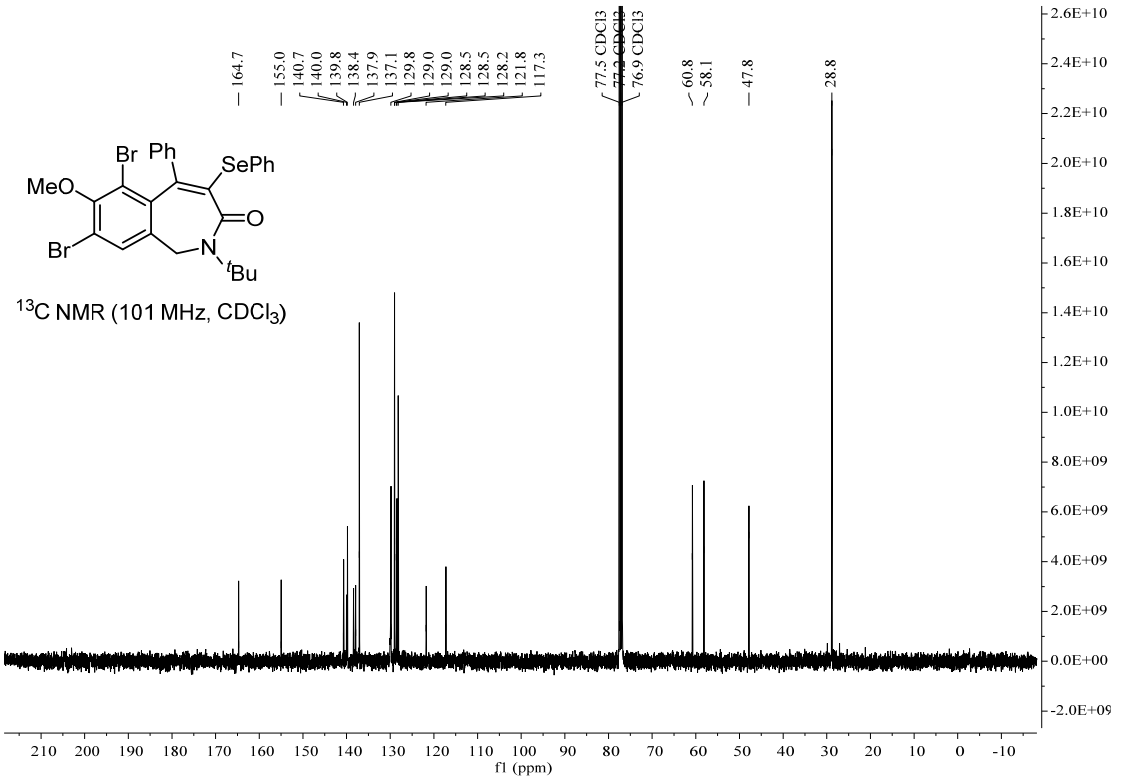
Compound 26


Cl Ph
SePh
MeO
O
Cl
N
tBu
1H NMR (400 MHz, CDCl3)
7.65 7.65 7.65 7.64 7.63 7.63 7.38 7.37 7.37 7.36 7.35 7.34 7.31 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 CDCl3 7.26 7.25 7.24 7.23 7.22 7.22 7.21 7.16 4.37 4.33 4.31 4.27 3.78
1.69 H2O
1.03
-0.00
2.00 3.07 2.00 4.02 1.02 1.04 3.05 9.06
f1 (ppm)

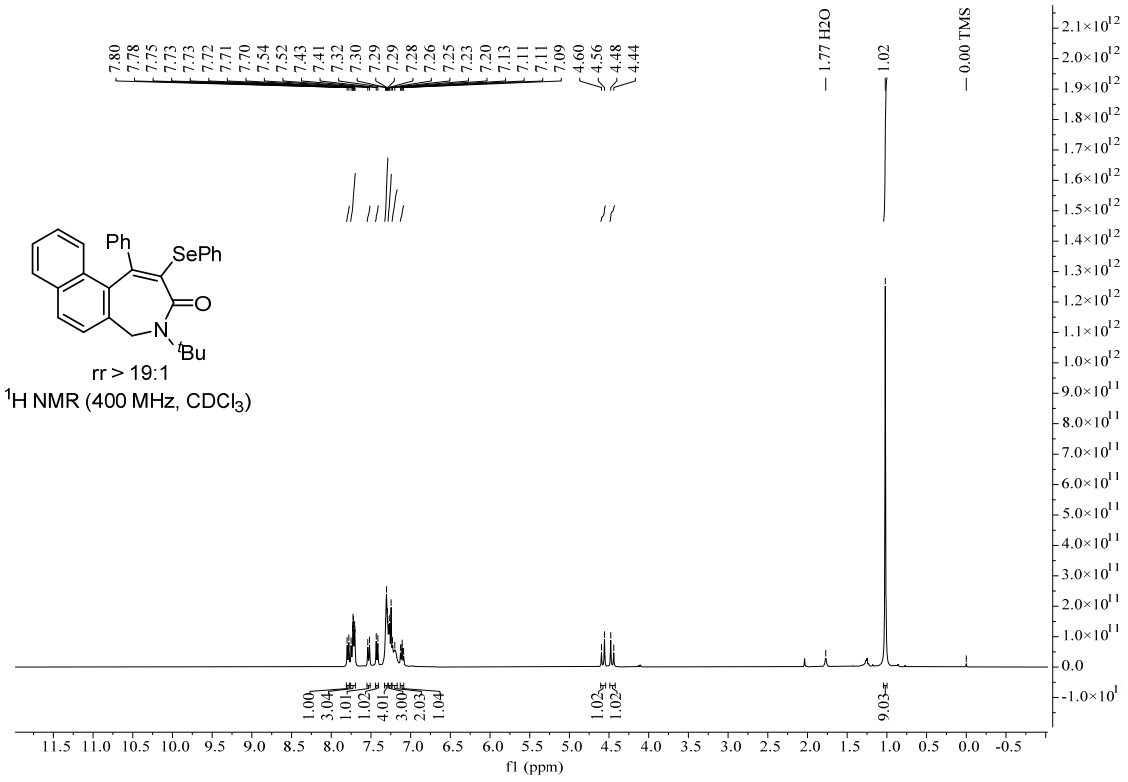

Cl Ph
SePh
MeO
O
Cl
N
tBu
13C NMR (101 MHz, CDCl3)
164.8 153.1 140.8 138.7 138.6 137.3 136.9 136.9 131.0 129.4 129.0 128.9 128.7 128.6 128.5 128.3 126.0
77.5 CDCl3 77.2 CDCl3 76.9 CDCl3
60.8 58.2 47.8 28.8
f1 (ppm)

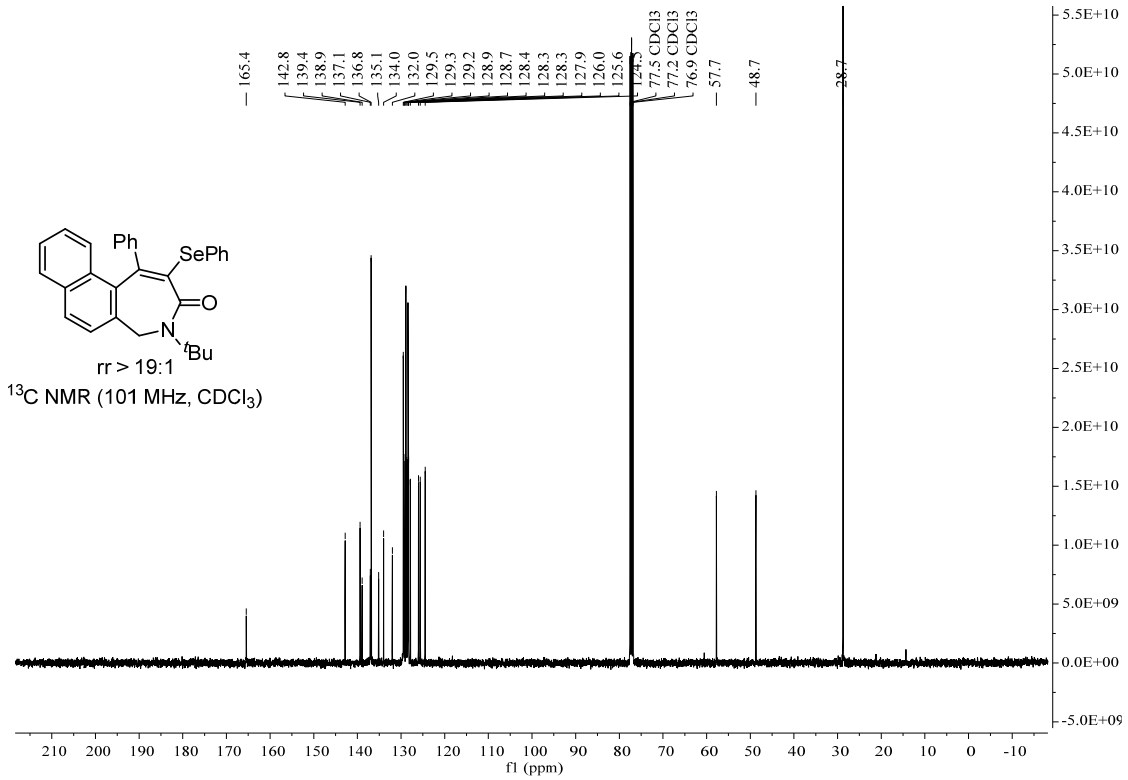
Compound 27


Br Ph
SePh
MeO
O
Br
N
tBu
1H NMR (400 MHz, CDCl3)
7.66 7.66 7.64 7.64 7.46 7.37 7.37 7.36 7.36 7.35 7.34 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.28 7.26 CDCl3 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.16 4.37 4.33 4.31 4.27 3.78 1.65 H2O 1.01
2.01 1.00 4.03 4.03 1.00 1.00 3.00 9.03
f1 (ppm)

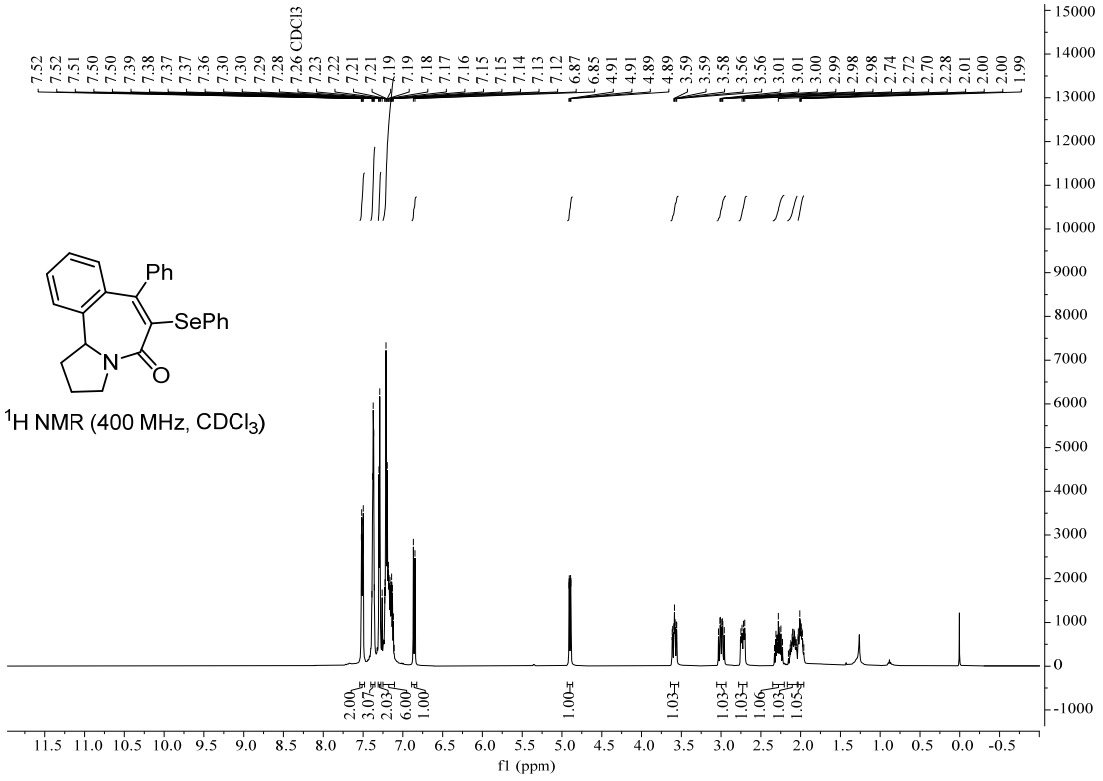

Br Ph
SePh
MeO
O
Br
N
tBu
13C NMR (101 MHz, CDCl3)
164.7 155.0 140.7 140.0 139.8 138.4 137.9 137.1 129.8 129.0 129.0 128.5 128.5 128.2 121.8 117.3 77.5 CDCl3 77.2 CDCl3 76.9 CDCl3 60.8 58.1 47.8 28.8
f1 (ppm)

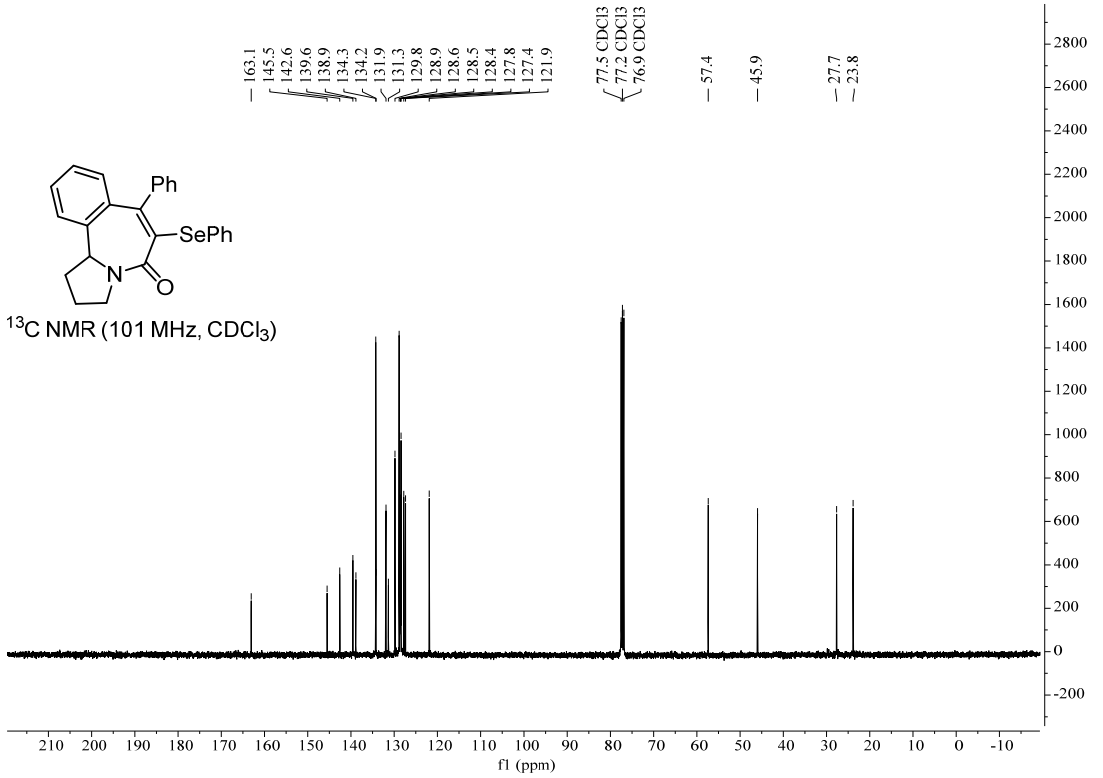
Compound 28


Ph
SePh
O
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
7.80
7.78
7.75
7.73
7.73
7.72
7.71
7.70
7.54
7.52
7.43
7.41
7.32
7.30
7.29
7.29
7.28
7.26
7.25
7.23
7.20
7.13
7.11
7.11
7.09
4.60
4.56
4.48
4.44
1.77 H2O
1.02
0.00 TMS
1.00
3.04
1.01
1.02
4.01
3.00
2.03
1.04
1.02
1.02
9.03
f1 (ppm)

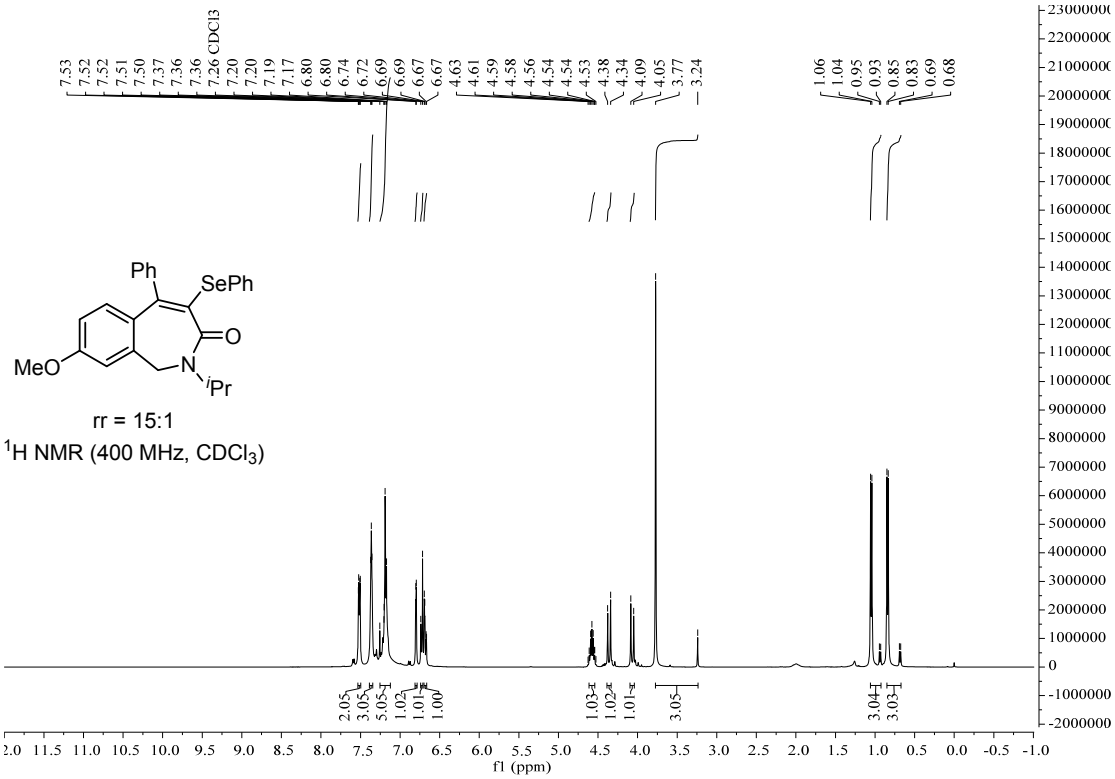

Ph
SePh
O
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
165.4
142.8
139.4
138.9
137.1
136.8
135.1
134.0
132.0
129.5
129.3
129.2
128.9
128.7
128.4
128.3
128.3
127.9
126.0
125.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
57.7
48.7
28.7
f1 (ppm)

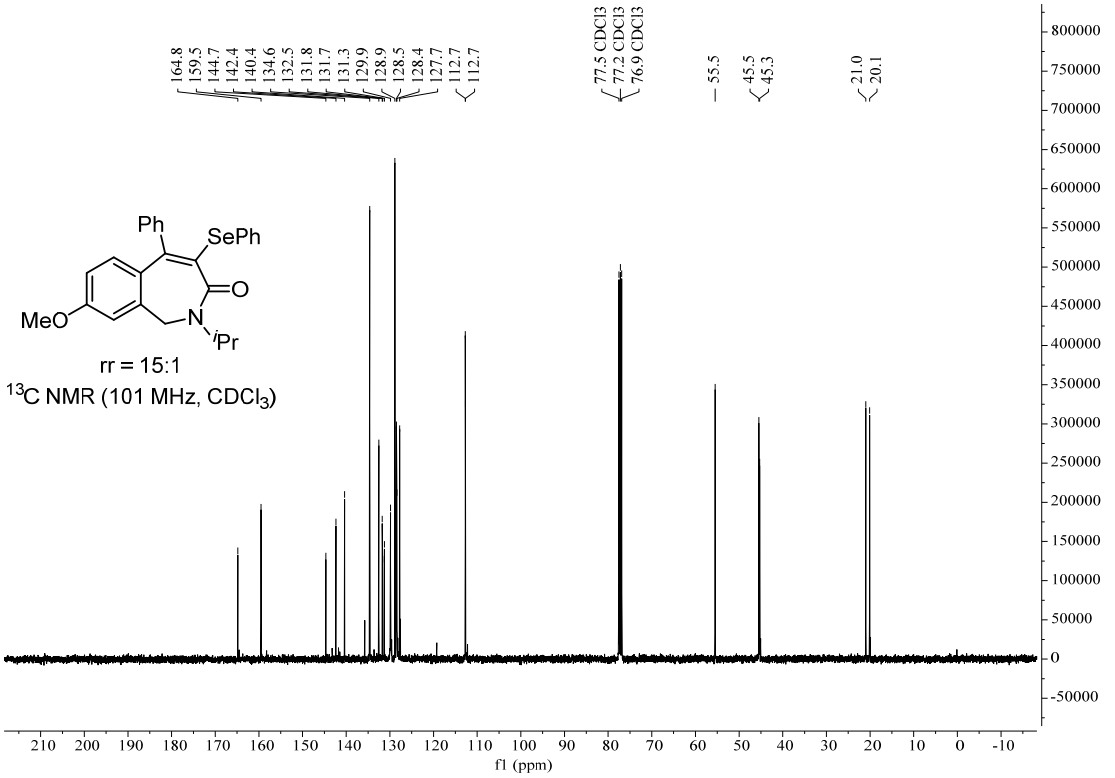
Compound 29


Ph
SePh
N
O
1H NMR (400 MHz, CDCl3)
f1 (ppm)

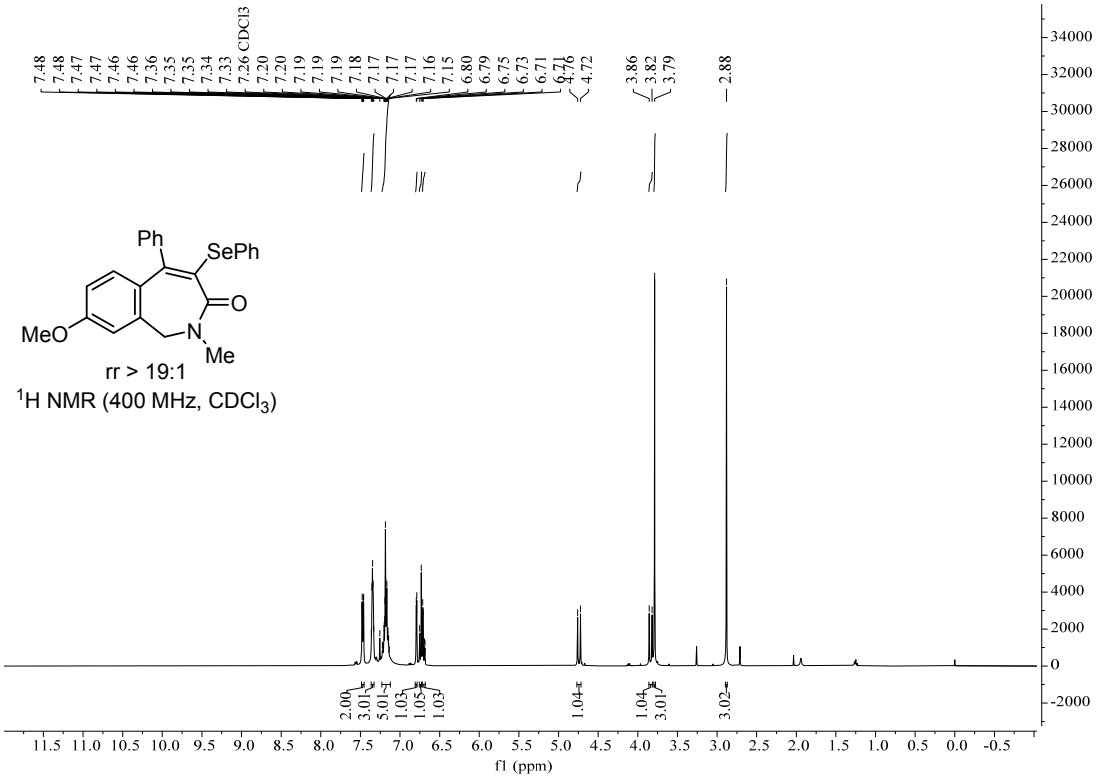

Ph
SePh
N
O
13C NMR (101 MHz, CDCl3)
f1 (ppm)

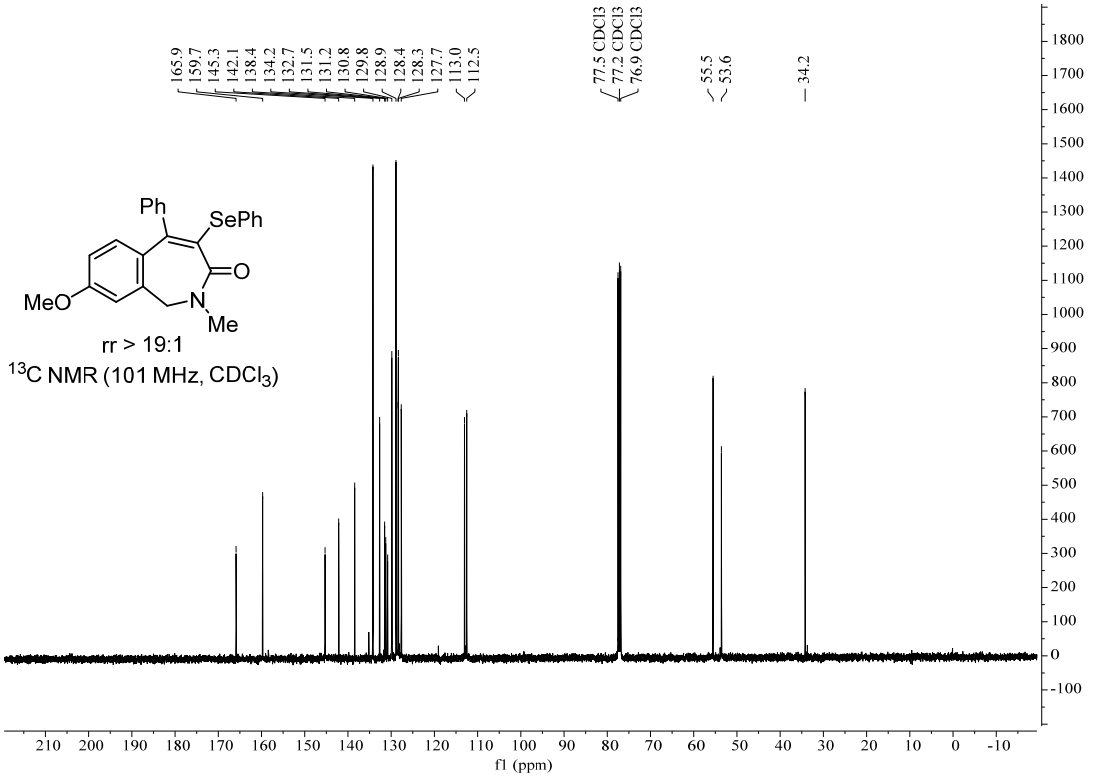
Compound 30


Ph
SePh
O
MeO
N
iPr
rr = 15:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)

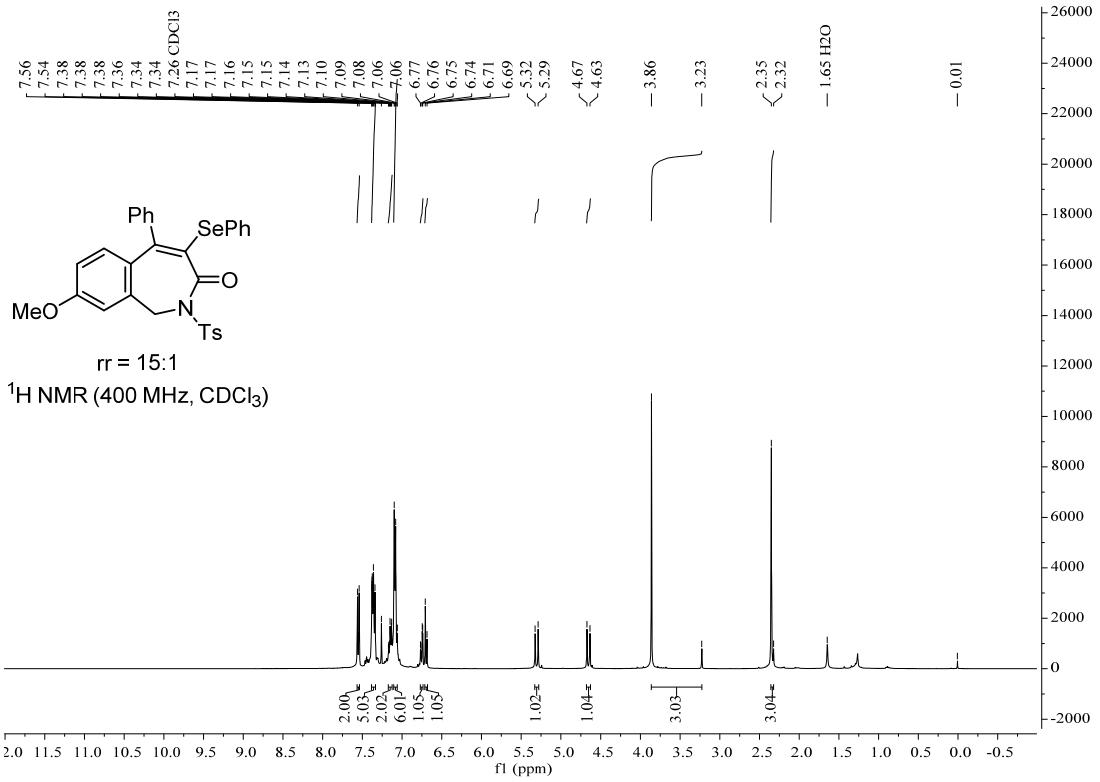

Ph
SePh
O
MeO
N
iPr
rr = 15:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

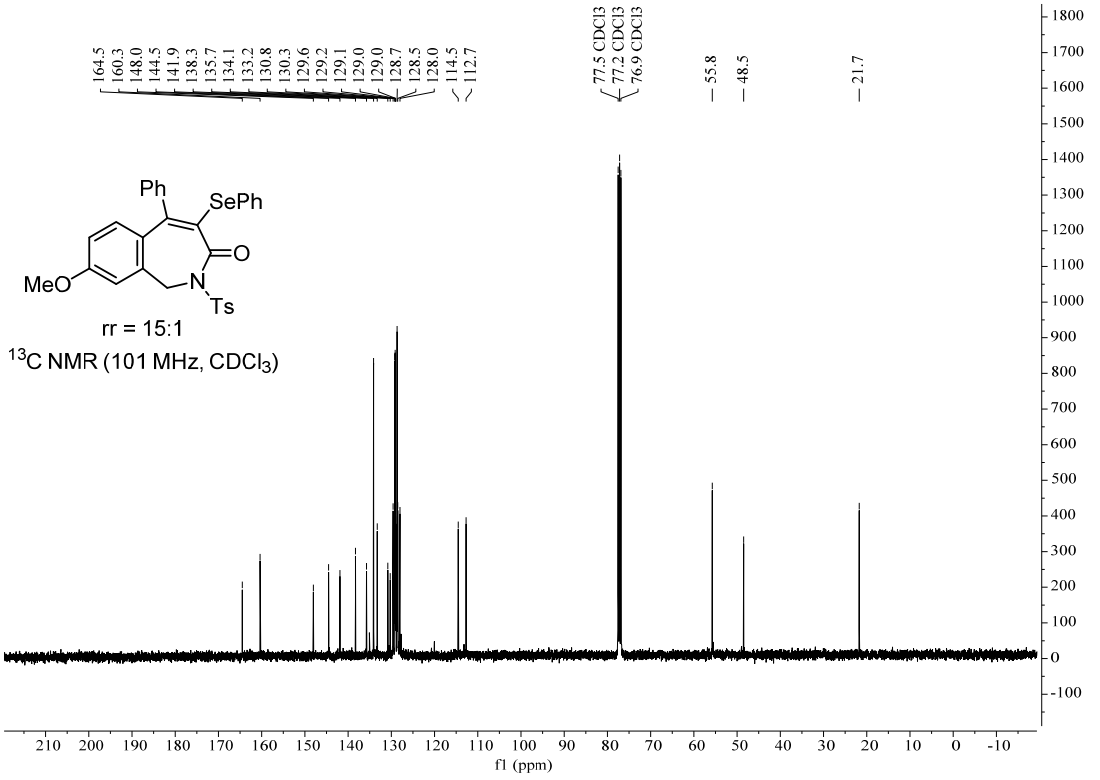
Compound 31


7.48
7.48
7.47
7.47
7.46
7.46
7.36
7.35
7.35
7.34
7.33
7.26 CDCl3
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
6.80
6.79
6.75
6.73
6.71
6.71
4.76
4.72
3.86
3.82
3.79
2.88
Ph
SePh
O
MeO
N
Me
rr > 19:1
1H NMR (400 MHz, CDCl3)
2.00
3.01
5.01
1.03
1.05
1.03
1.04
1.04
3.01
3.02
f1 (ppm)

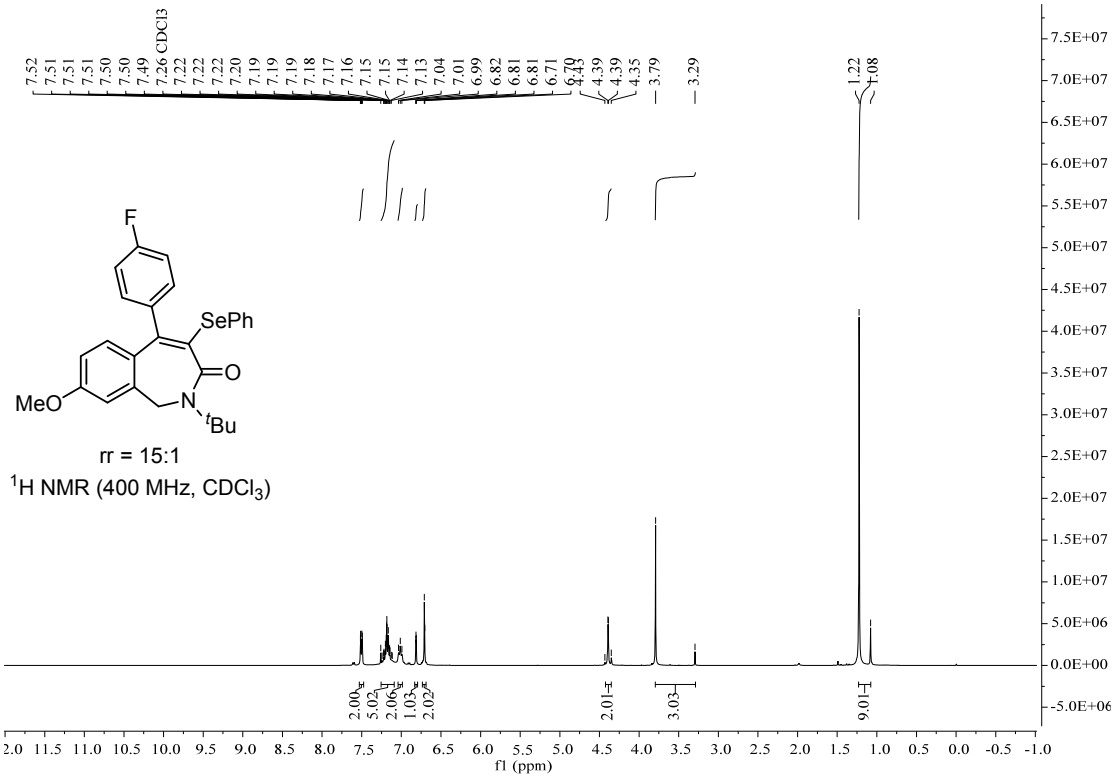

165.9
159.7
145.3
142.1
138.4
134.2
132.7
131.5
131.2
130.8
129.8
128.9
128.4
128.3
127.7
113.0
112.5
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.5
53.6
34.2
Ph
SePh
O
MeO
N
Me
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

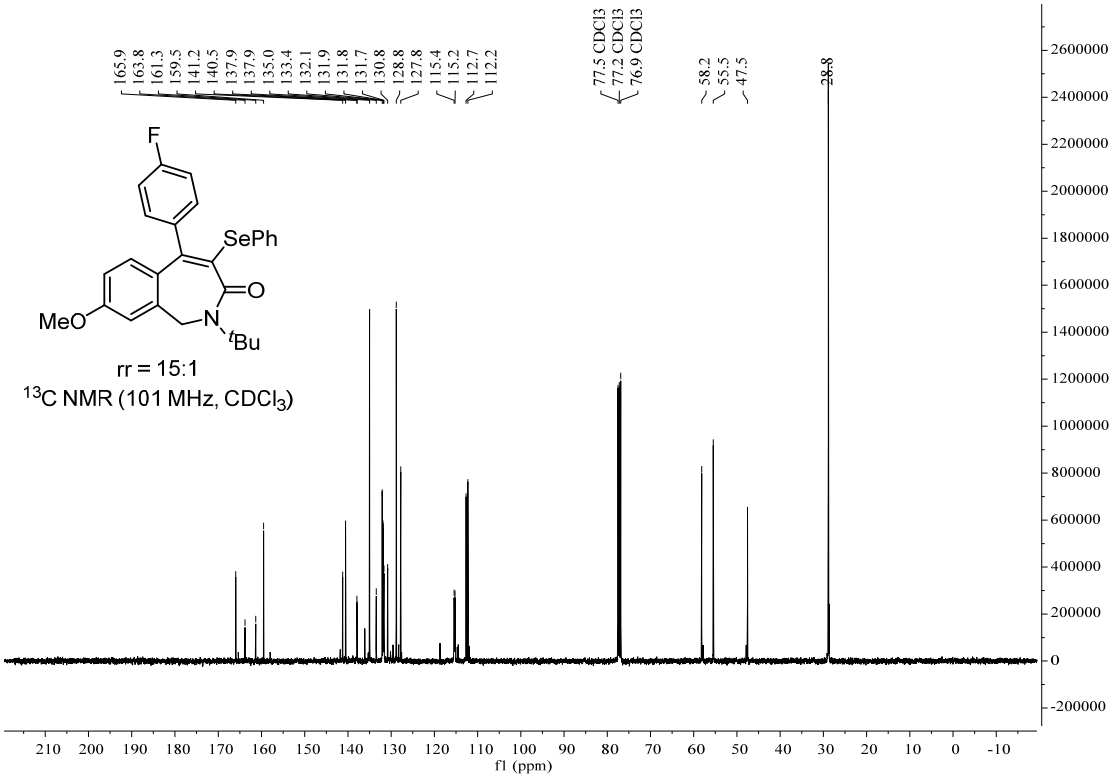
Compound 32

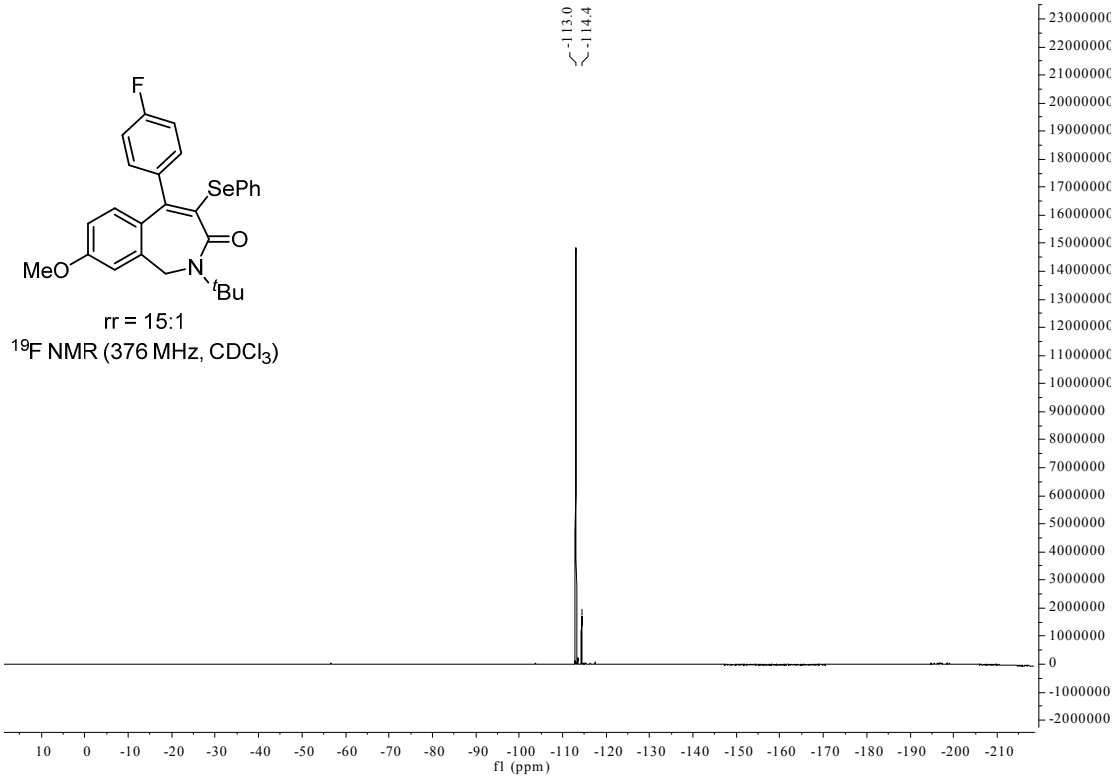

7.56
7.54
7.38
7.38
7.38
7.36
7.34
7.34
7.26 CDCl3
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.10
7.09
7.08
7.06
7.06
6.77
6.76
6.75
6.74
6.71
6.69
5.32
5.29
4.67
4.63
3.86
3.23
2.35
2.32
1.65 H2O
0.01
Ph
SePh
O
MeO
N
Ts
rr = 15:1
1H NMR (400 MHz, CDCl3)
2.00
5.03
2.02
6.01
1.05
1.05
1.02
1.04
3.03
3.04
f1 (ppm)


164.5
160.3
148.0
144.5
141.9
138.3
135.7
134.1
133.2
130.8
130.3
129.6
129.2
129.1
129.0
129.0
128.7
128.5
128.0
114.5
112.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.8
48.5
21.7
Ph
SePh
O
MeO
N
Ts
rr = 15:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 33


F
SePh
O
MeO
N
tBu
rr = 15:1
1H NMR (400 MHz, CDCl3)
fl (ppm)

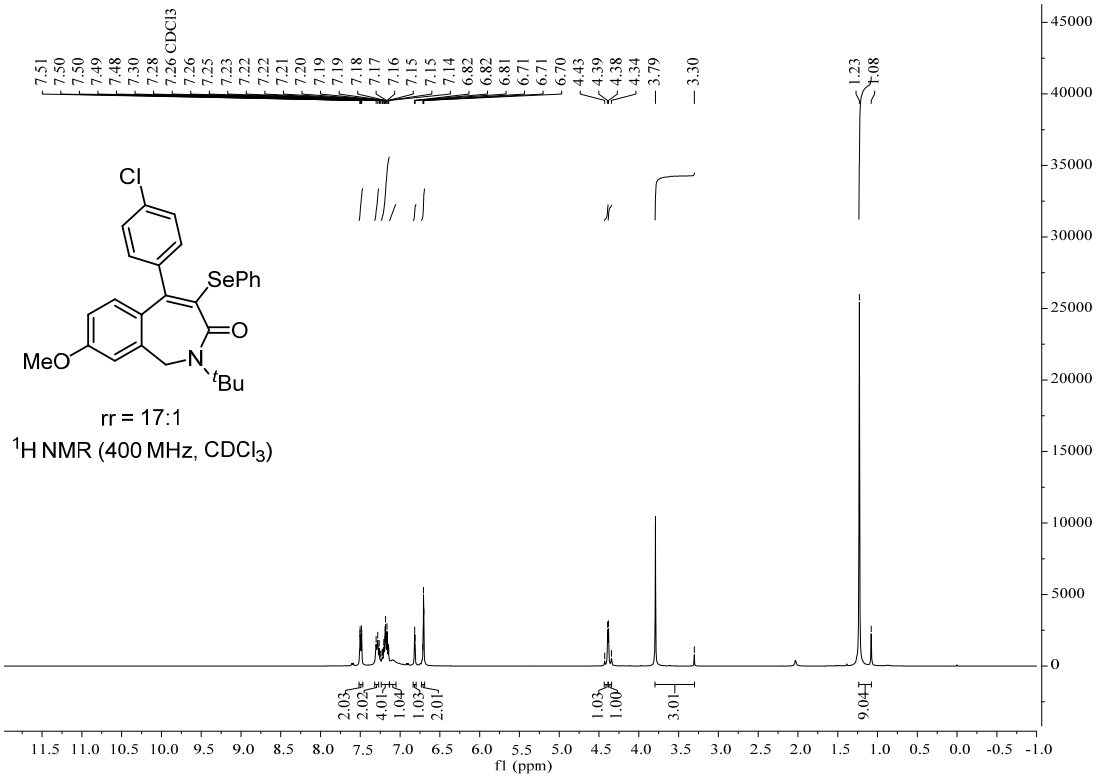

F
SePh
O
MeO
N
tBu
rr = 15:1
13C NMR (101 MHz, CDCl3)
fl (ppm)

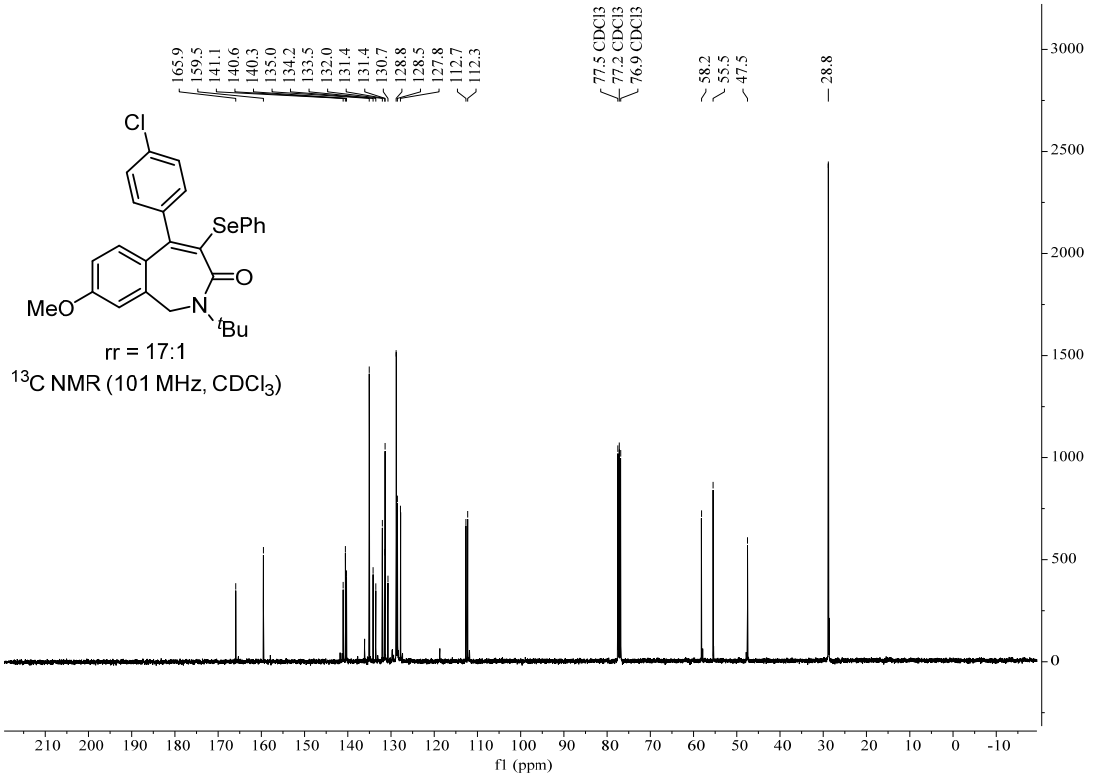


rr = 15:1

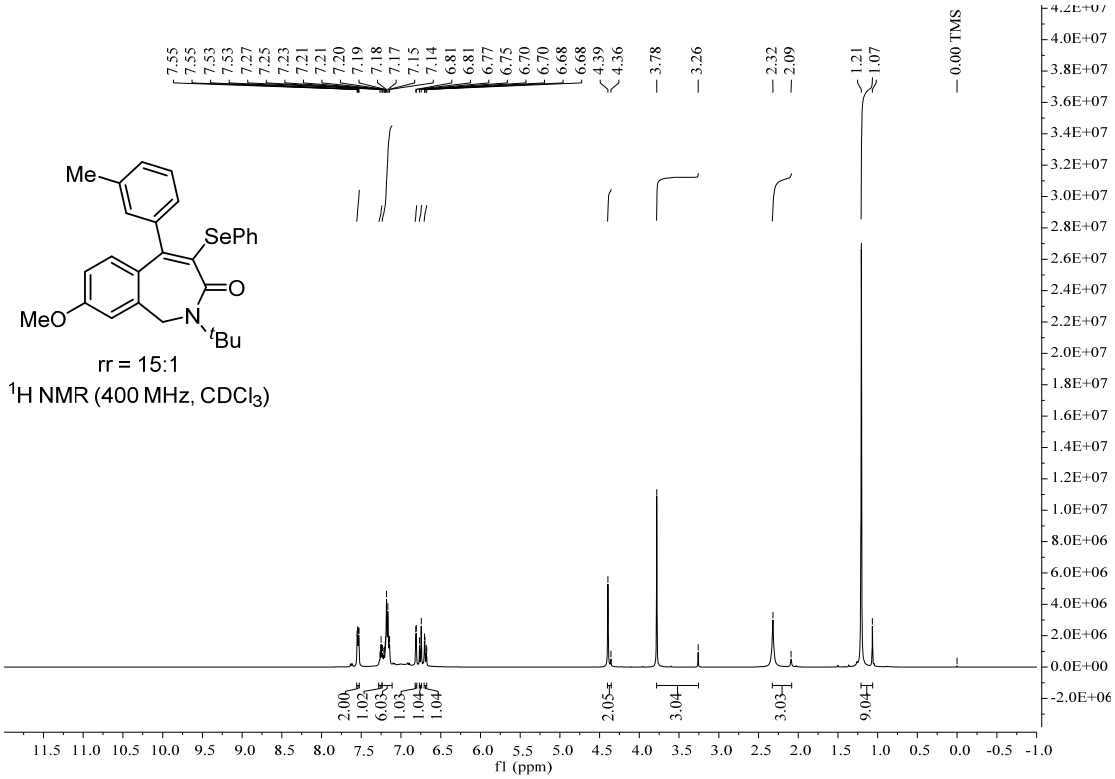
^{19}F NMR (376 MHz, $CDCl_3$)

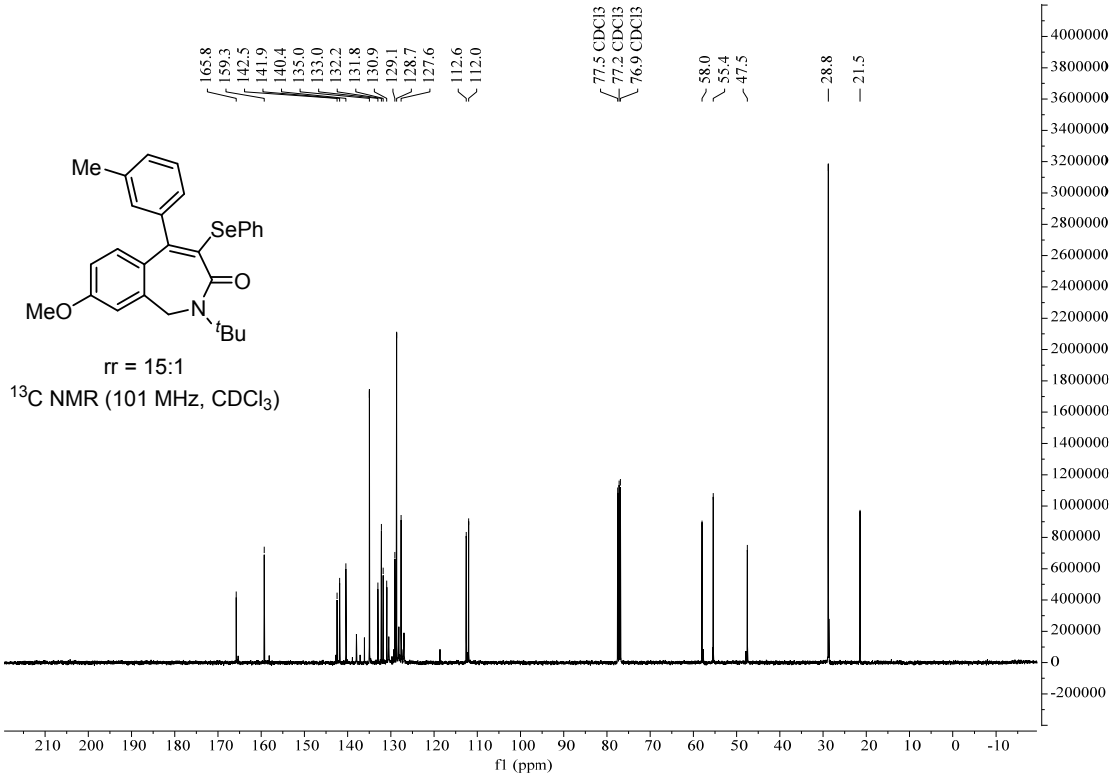
Compound 34


7.51
7.50
7.50
7.49
7.48
7.30
7.28
7.26 CDCl3
7.26
7.25
7.23
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.14
6.82
6.82
6.81
6.71
6.71
6.70
4.43
4.39
4.38
4.34
3.79
3.30
1.23
1.08
Cl
SePh
O
MeO
N
tBu
rr = 17:1
1H NMR (400 MHz, CDCl3)
2.03
2.02
4.01
1.04
1.03
2.01
1.03
1.00
3.01
9.04
f1 (ppm)

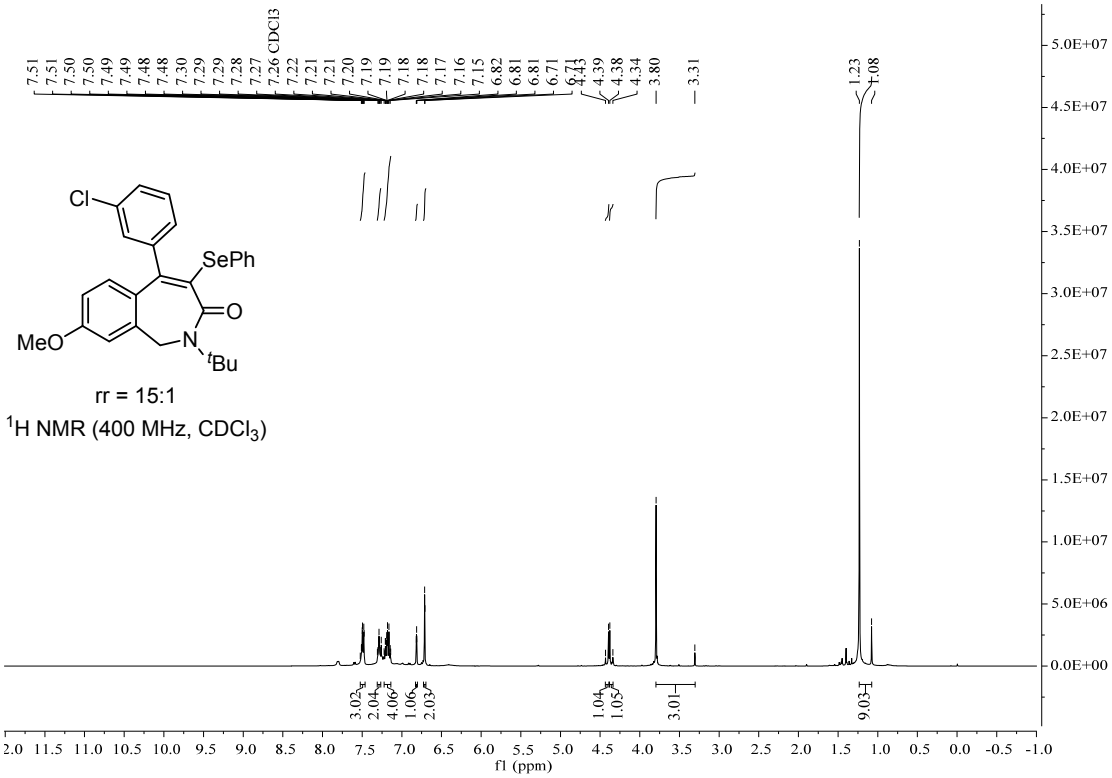

165.9
159.5
141.1
140.6
140.3
135.0
134.2
133.5
132.0
131.4
131.4
130.7
128.8
128.5
127.8
112.7
112.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.2
55.5
47.5
28.8
Cl
SePh
O
MeO
N
tBu
rr = 17:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

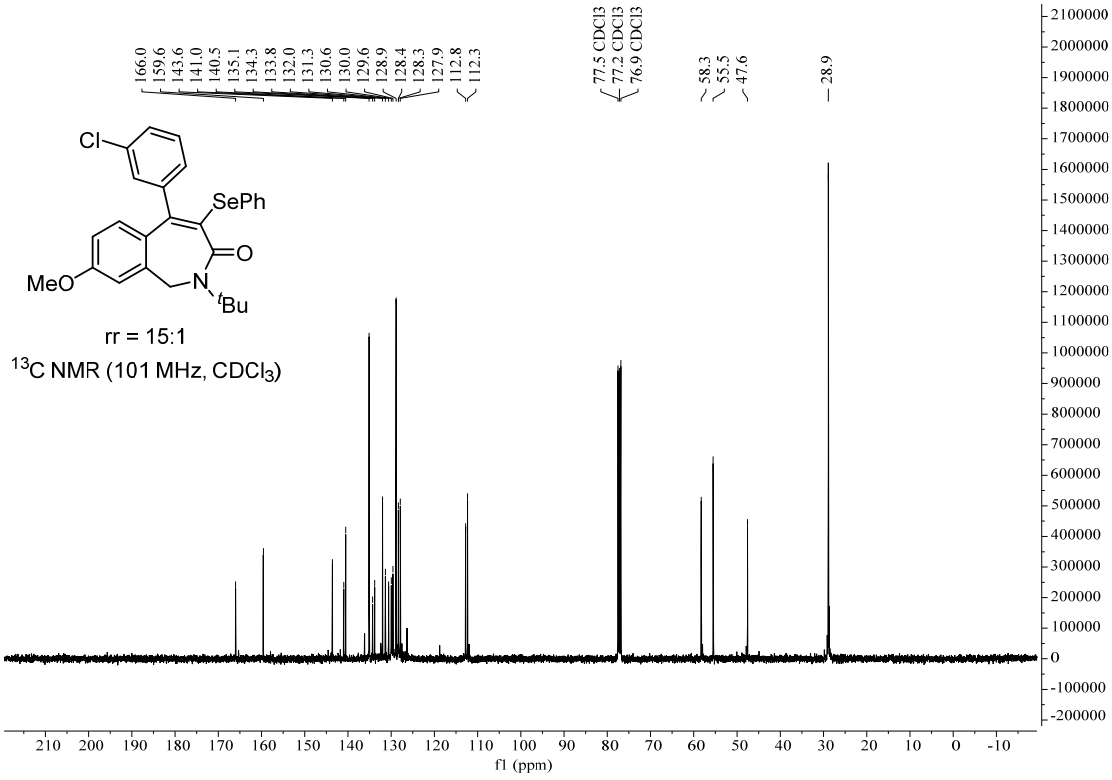
Compound 35


Me
SePh
O
MeO
N
tBu
rr = 15:1
1H NMR (400 MHz, CDCl3)
7.55
7.55
7.53
7.53
7.27
7.25
7.23
7.21
7.21
7.20
7.19
7.18
7.17
7.15
7.14
6.81
6.81
6.77
6.75
6.70
6.70
6.68
6.68
4.39
4.36
3.78
3.26
2.32
2.09
1.21
1.07
0.00 TMS
2.00
1.02
6.03
1.03
1.04
1.04
2.05
3.04
3.03
9.04
f1 (ppm)

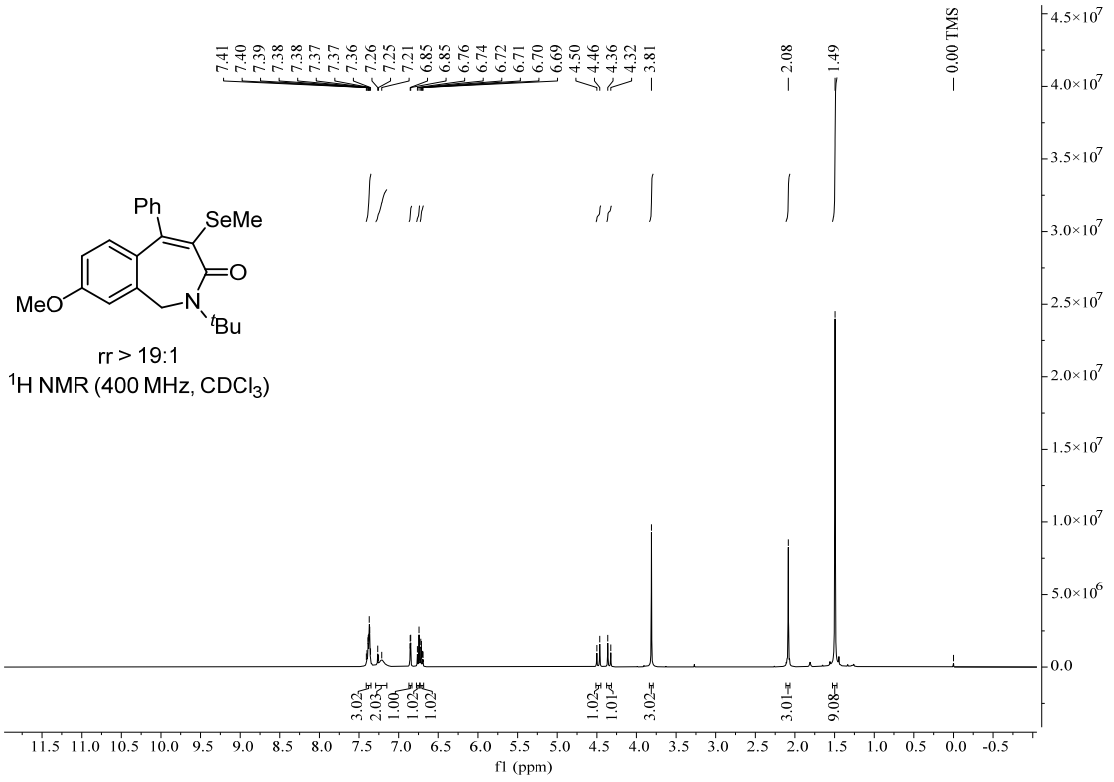

Me
SePh
O
MeO
N
tBu
rr = 15:1
13C NMR (101 MHz, CDCl3)
165.8
159.3
142.5
141.9
140.4
135.0
133.0
132.2
131.8
130.9
129.1
128.7
127.6
112.6
112.0
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.0
55.4
47.5
28.8
21.5
f1 (ppm)

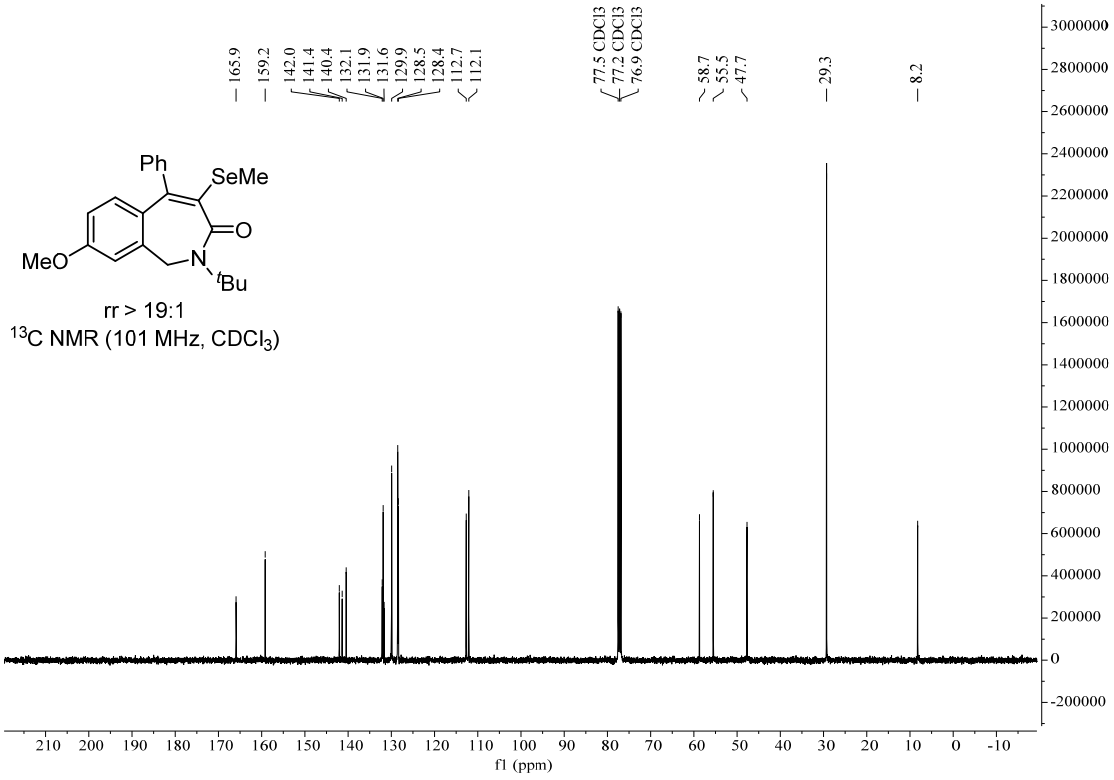
Compound 36


7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.30
7.29
7.29
7.28
7.27
7.26 CDCl3
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.15
6.82
6.81
6.81
6.71
6.71
4.43
4.39
4.38
4.34
3.80
3.31
1.23
1.08
Cl
SePh
O
MeO
N
tBu
rr = 15:1
1H NMR (400 MHz, CDCl3)
3.02
2.04
4.06
1.06
2.03
1.04
1.05
3.01
9.03
f1 (ppm)

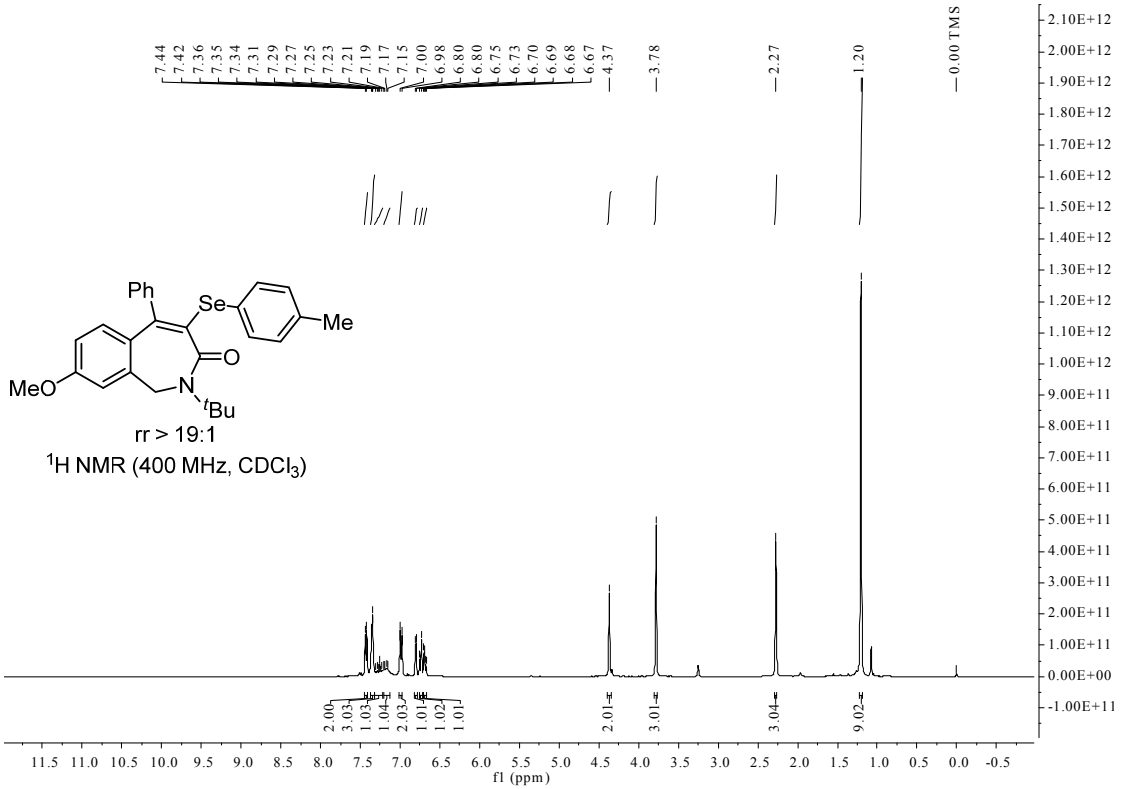

166.0
159.6
143.6
141.0
140.5
135.1
134.3
133.8
132.0
131.3
130.6
130.0
129.6
128.9
128.4
128.3
127.9
112.8
112.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.3
55.5
47.6
28.9
Cl
SePh
O
MeO
N
tBu
rr = 15:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 37


7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.26
7.25
7.21
6.85
6.85
6.76
6.74
6.72
6.71
6.70
6.69
4.50
4.46
4.36
4.32
3.81
2.08
1.49
0.00 TMS
Ph
SeMe
O
MeO
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
3.02
2.03
1.00
1.02
1.02
1.02
1.01
3.02
3.01
9.08
f1 (ppm)

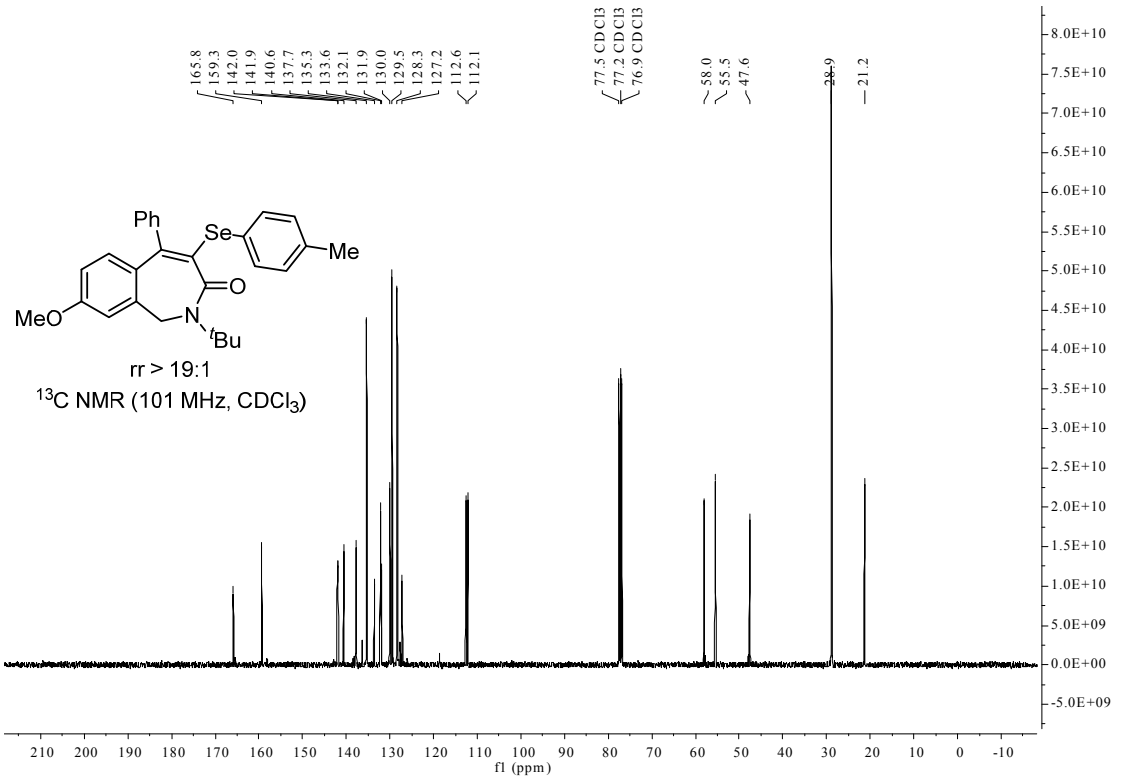

165.9
159.2
142.0
141.4
140.4
132.1
131.9
131.6
129.9
128.5
128.4
112.7
112.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.7
55.5
47.7
29.3
8.2
Ph
SeMe
O
MeO
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 38



rr > 19:1

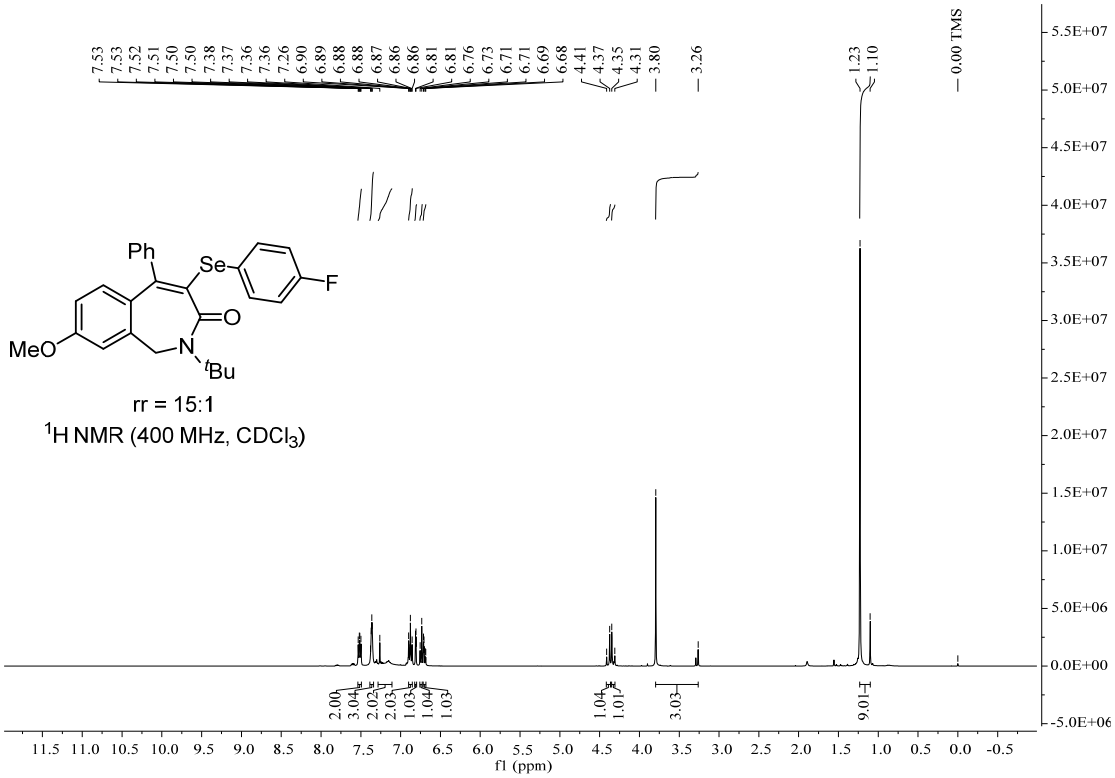
^{1}H NMR (400 MHz, $CDCl_3$)

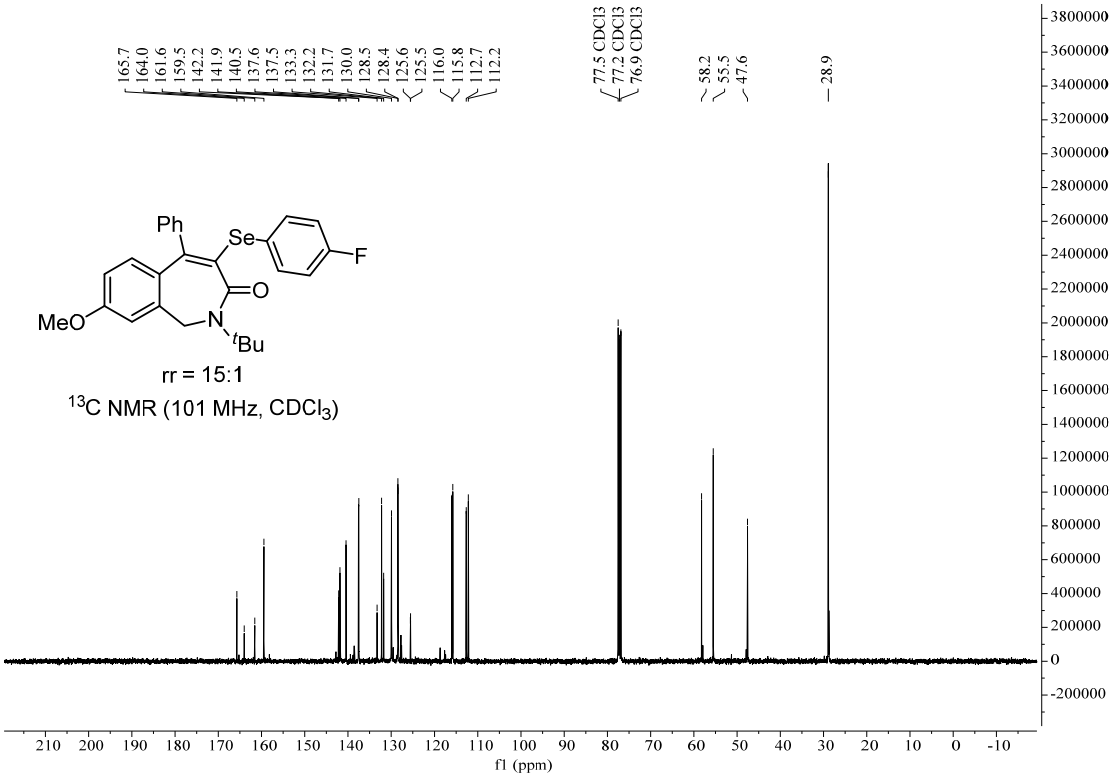


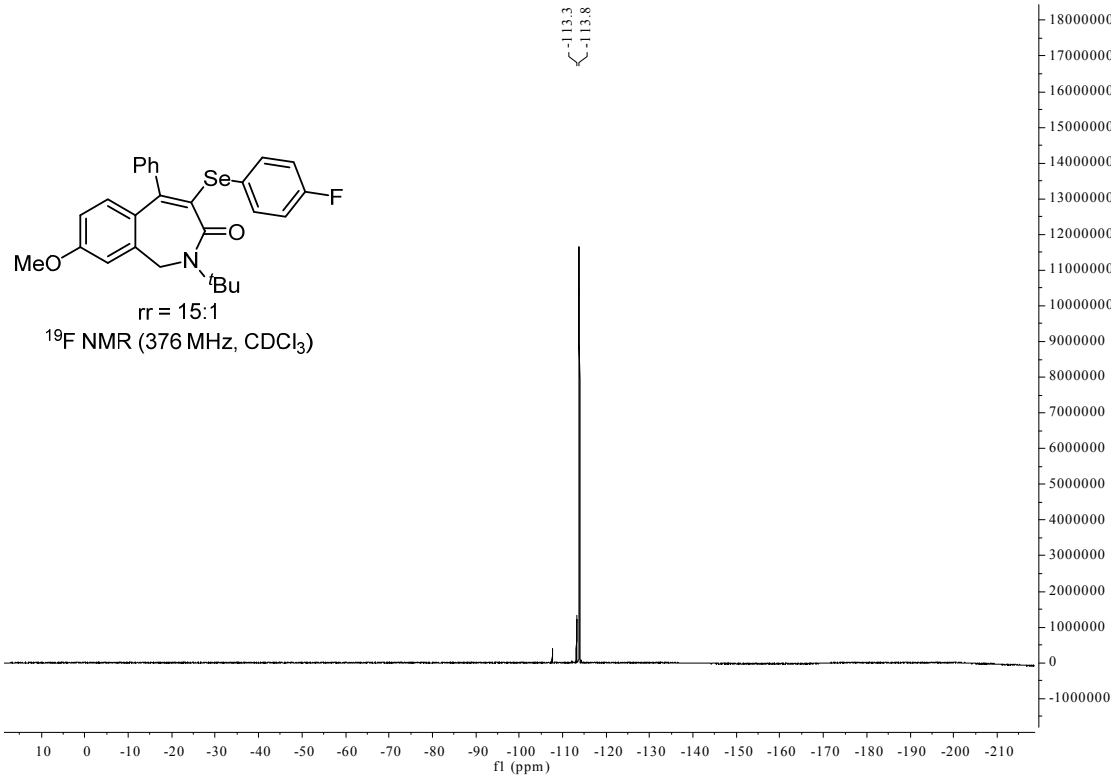
rr > 19:1

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

Compound 39


Ph
Se
F
O
MeO
N
tBu
rr = 15:1
1H NMR (400 MHz, CDCl3)
fl (ppm)

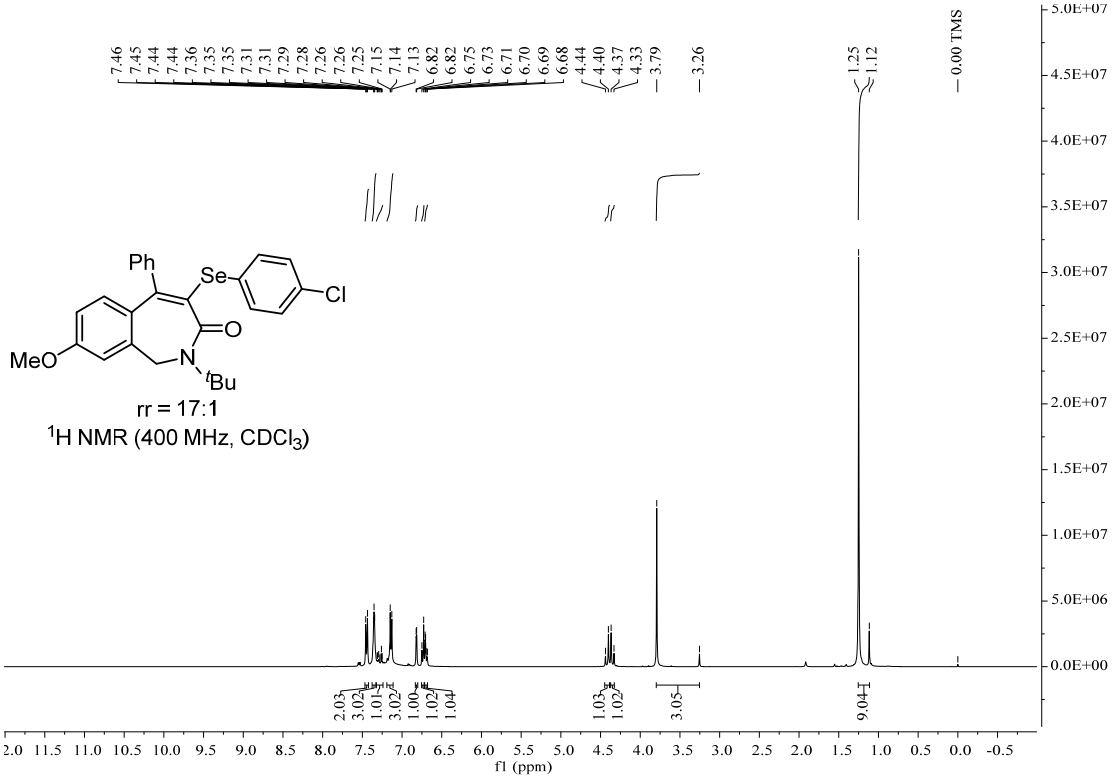

Ph
Se
F
O
MeO
N
tBu
rr = 15:1
13C NMR (101 MHz, CDCl3)
fl (ppm)

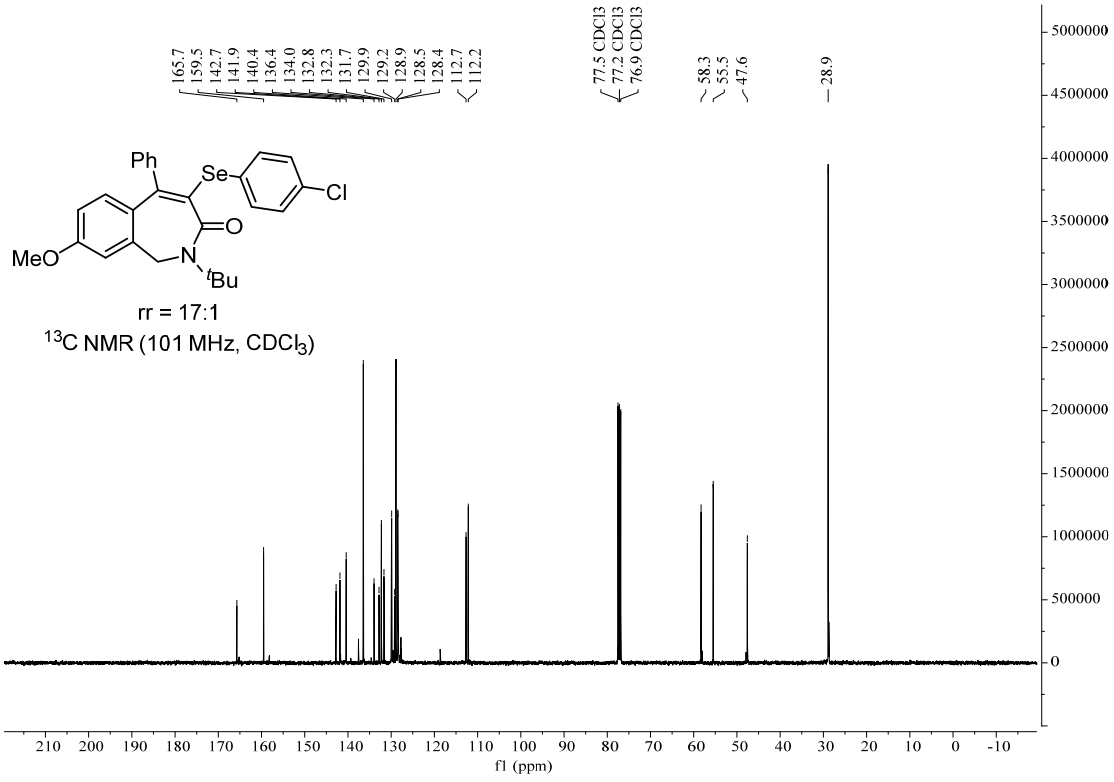


rr = 15:1

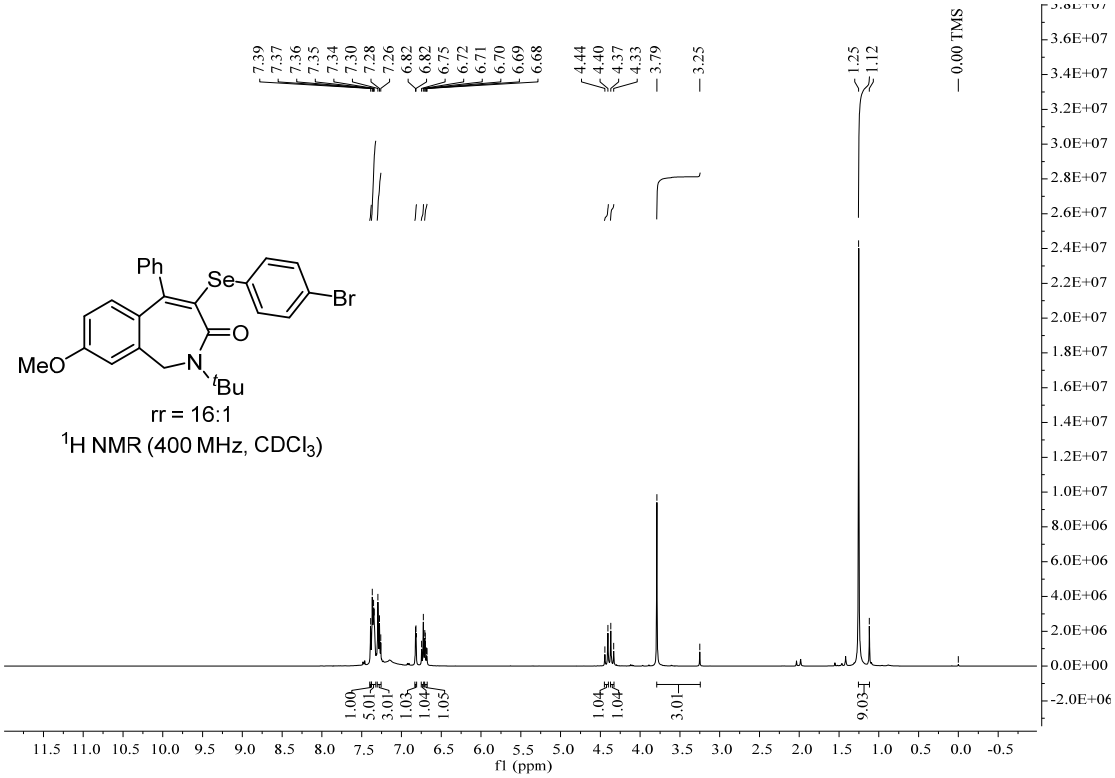
^{19}F NMR (376 MHz, $CDCl_3$)

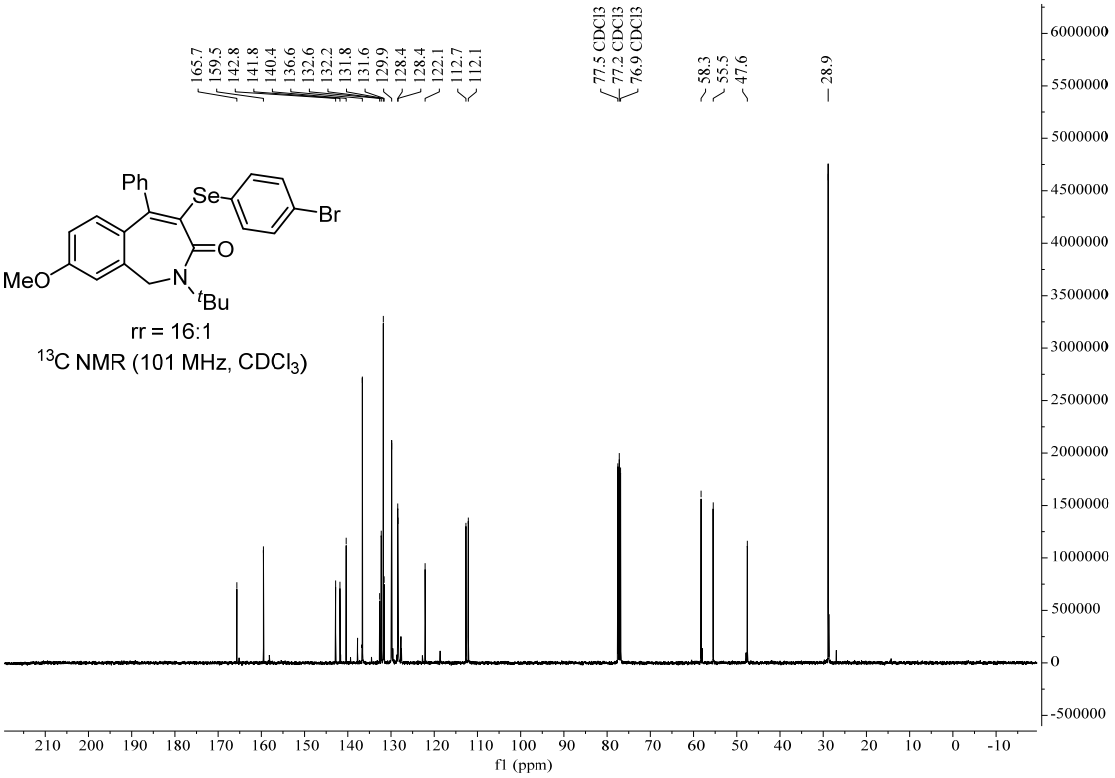
Compound 40


7.46
7.45
7.44
7.44
7.36
7.35
7.35
7.31
7.31
7.29
7.28
7.26
7.26
7.25
7.15
7.14
7.13
6.82
6.82
6.75
6.73
6.71
6.70
6.69
6.68
4.44
4.40
4.37
4.33
3.79
3.26
1.25
1.12
0.00 TMS
Ph
Se
Cl
O
MeO
N
tBu
rr = 17:1
1H NMR (400 MHz, CDCl3)
2.03
3.02
1.01
3.02
1.00
1.02
1.04
1.03
1.02
3.05
9.04
f1 (ppm)

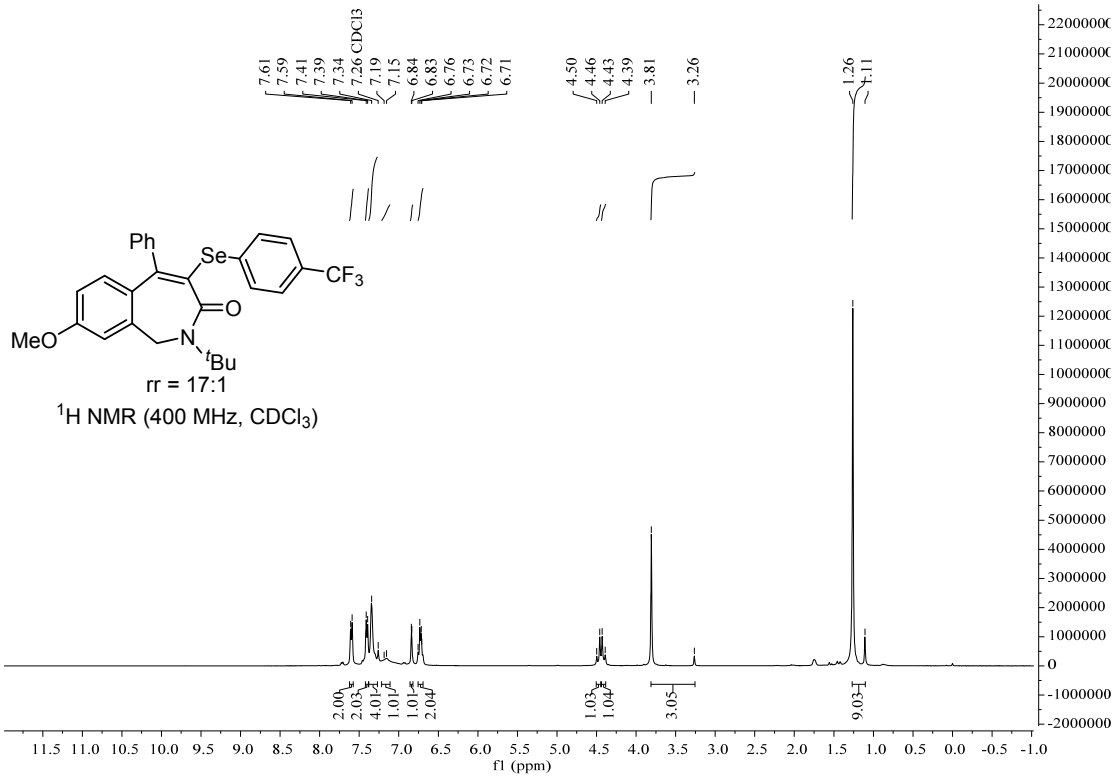

165.7
159.5
142.7
141.9
140.4
136.4
134.0
132.8
132.3
131.7
129.9
129.2
128.9
128.5
128.4
112.7
112.2
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.3
55.5
47.6
28.9
Ph
Se
Cl
O
MeO
N
tBu
rr = 17:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

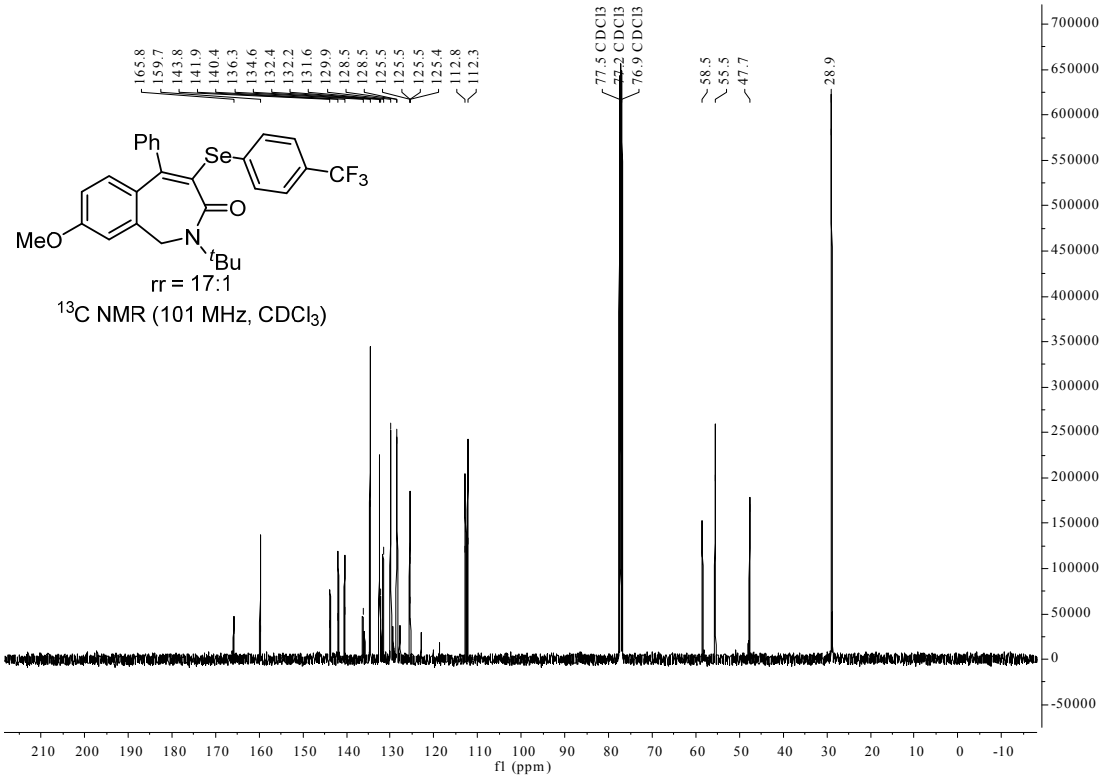
Compound 41

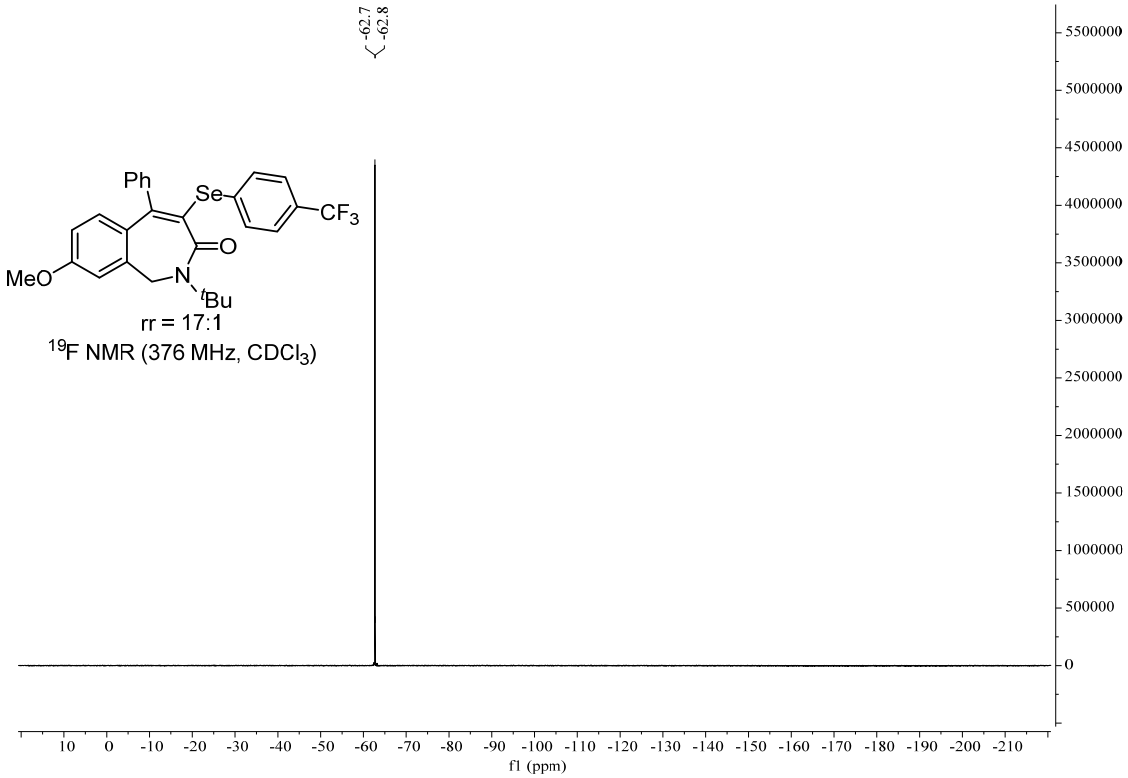

7.39
7.37
7.36
7.35
7.34
7.30
7.28
7.26
6.82
6.82
6.75
6.72
6.71
6.70
6.69
6.68
4.44
4.40
4.37
4.33
3.79
3.25
1.25
1.12
0.00 TMS
Ph
Se
Br
O
MeO
N
tBu
rr = 16:1
1H NMR (400 MHz, CDCl3)
1.00
5.01
3.01
1.03
1.04
1.05
1.04
1.04
3.01
9.03
f1 (ppm)


165.7
159.5
142.8
141.8
140.4
136.6
132.6
132.2
131.8
131.6
129.9
128.4
128.4
122.1
112.7
112.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.3
55.5
47.6
28.9
Ph
Se
Br
O
MeO
N
tBu
rr = 16:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

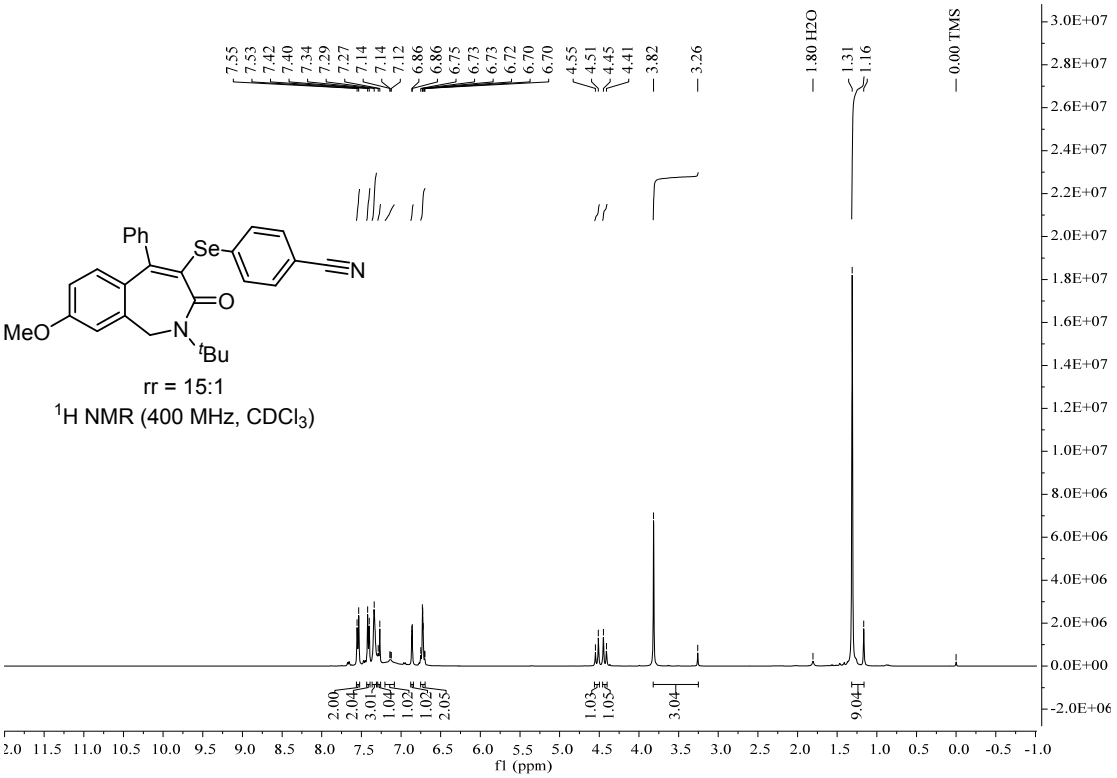
Compound 42


Ph
Se
CF3
O
MeO
N
tBu
rr = 17:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ph
Se
CF3
O
MeO
N
tBu
rr = 17:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

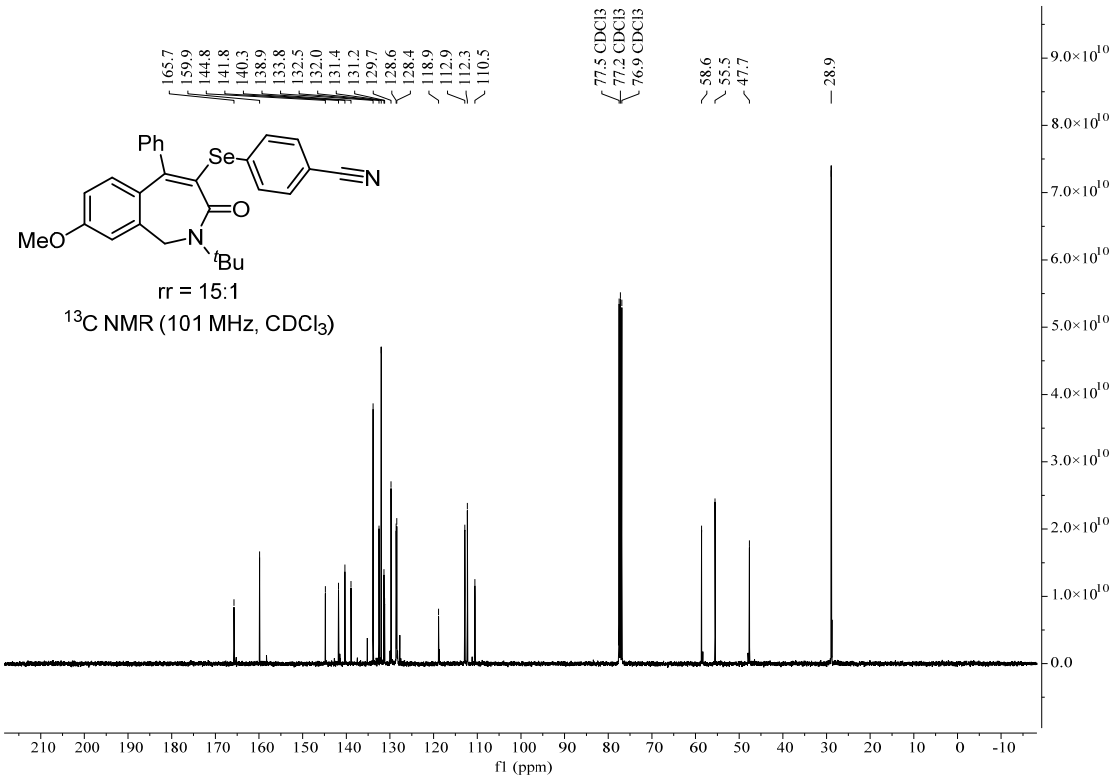

-62.7
-62.8
Ph
Se
CF3
O
MeO
N
tBu
rr = 17:1
19F NMR (376 MHz, CDCl3)
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound 43



rr = 15:1

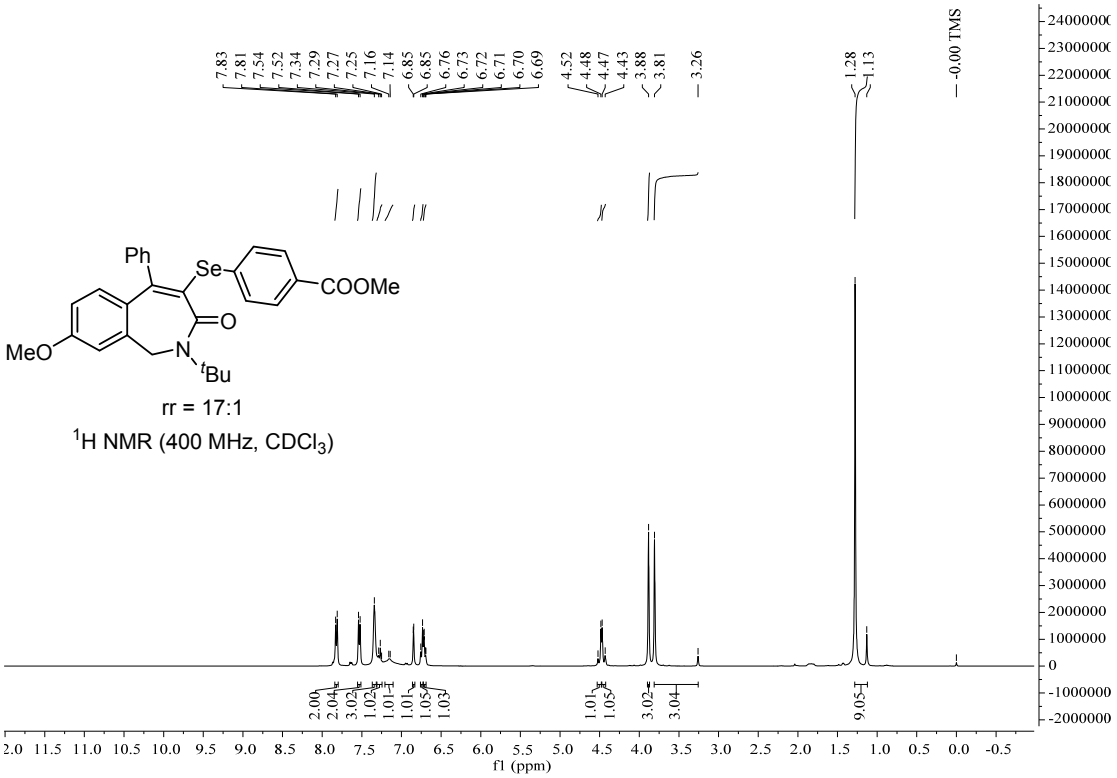
^{1}H NMR (400 MHz, $CDCl_3$)



rr = 15:1

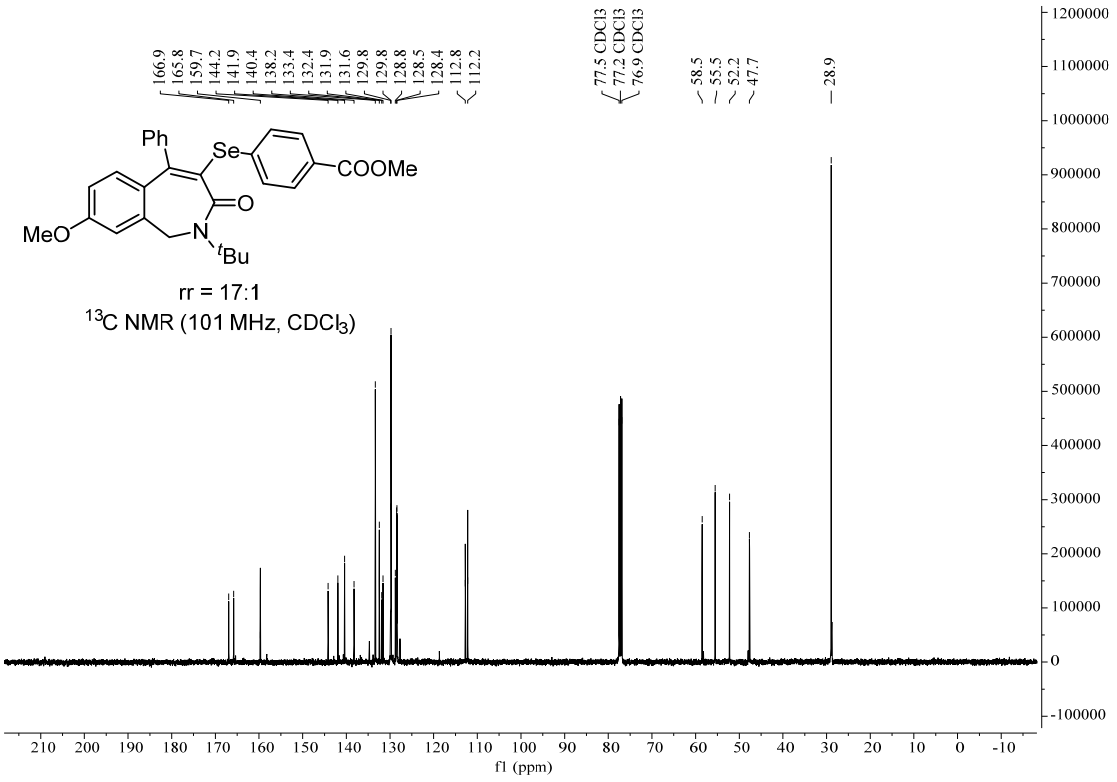
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 44



rr = 17:1

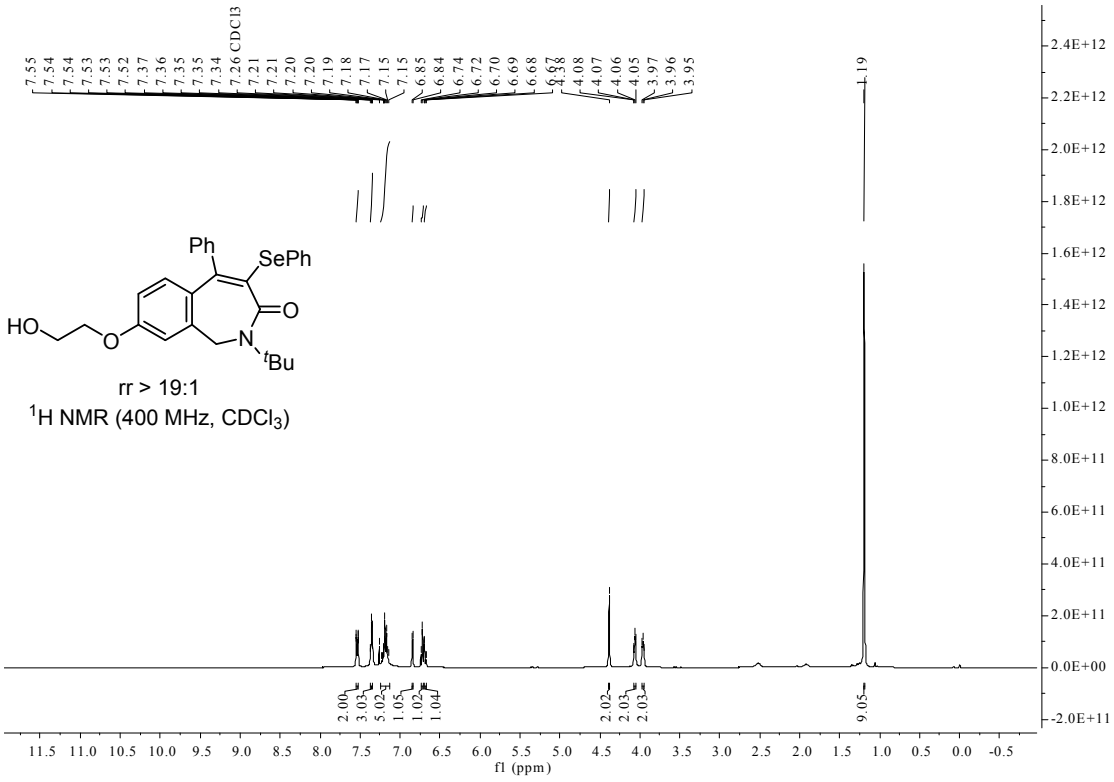
^{1}H NMR (400 MHz, $CDCl_3$)

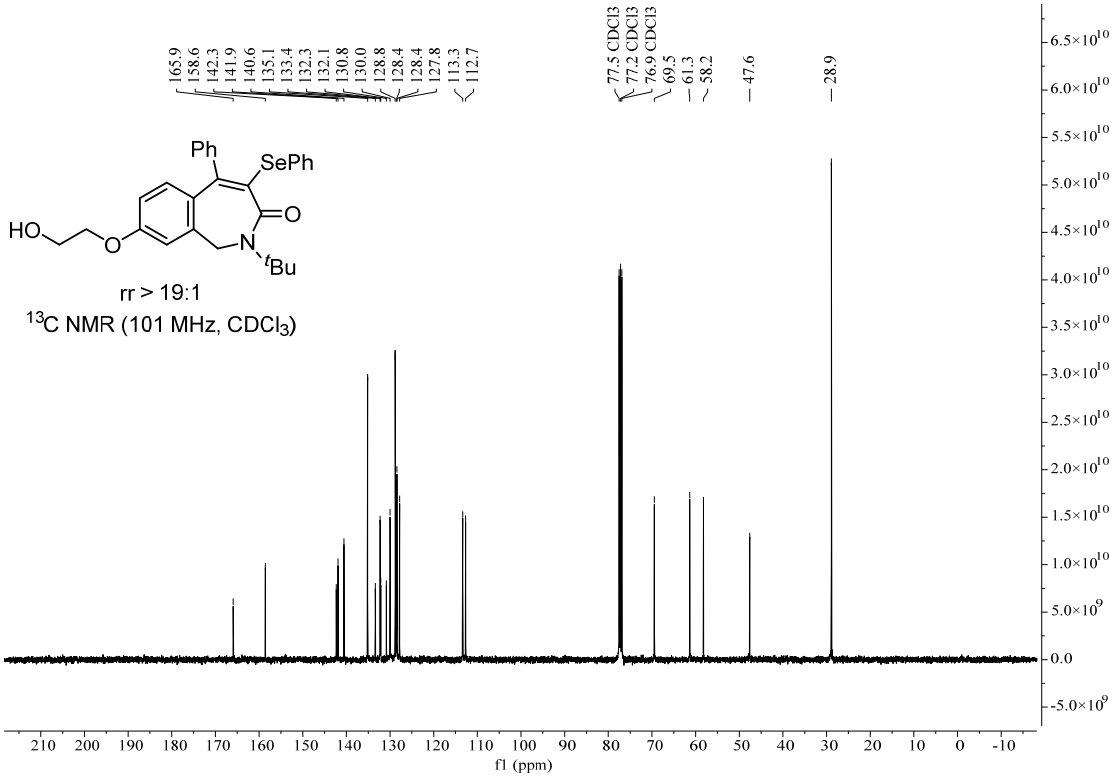


rr = 17:1

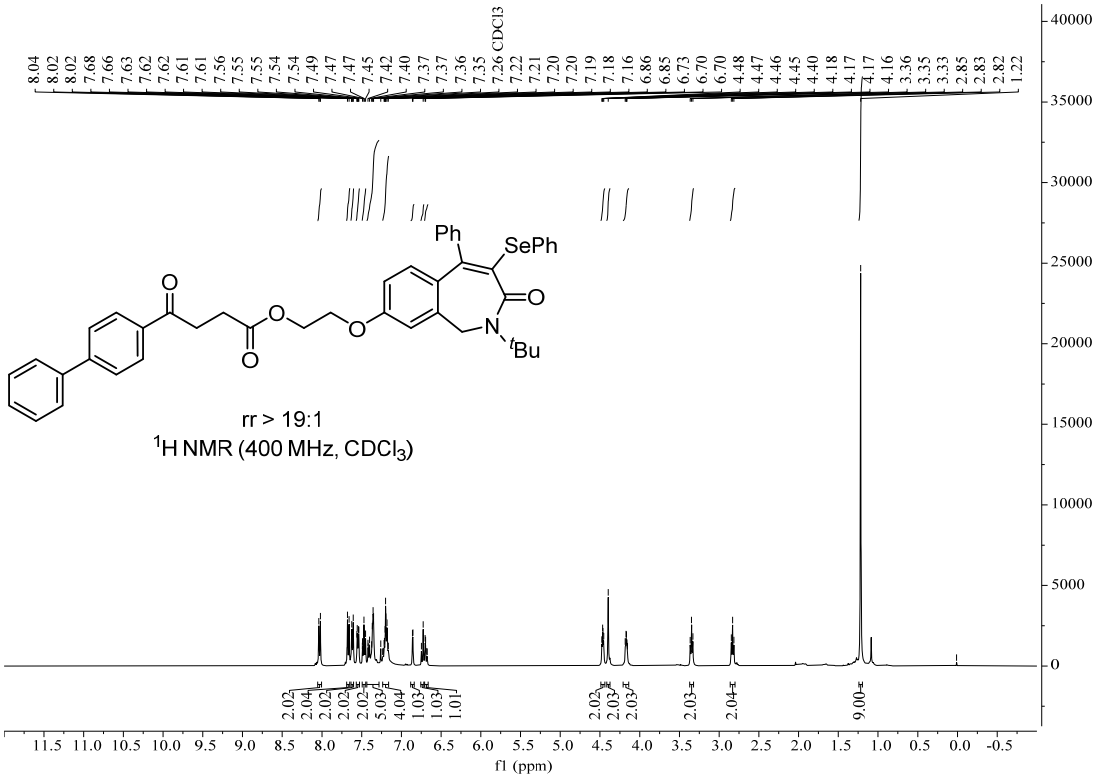
^{13}C NMR (101 MHz, $CDCl_3$)

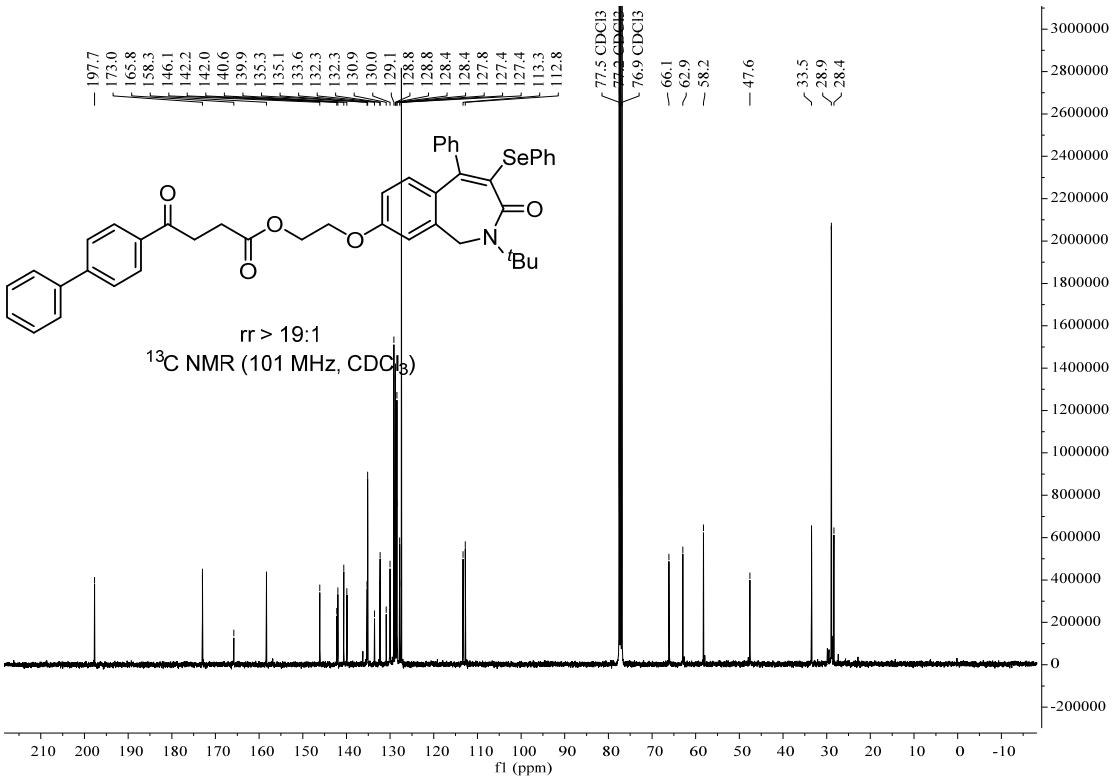
Compound 45


Ph
SePh
O
HO
O
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
fl (ppm)

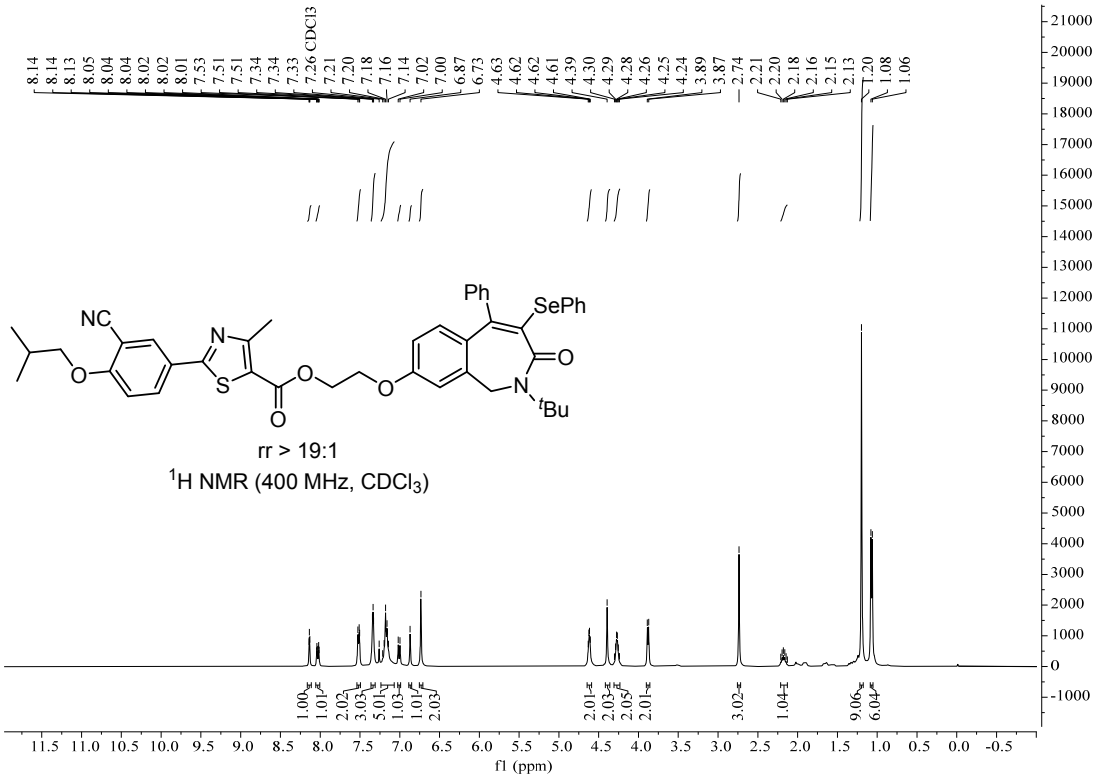

Ph
SePh
O
HO
O
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
fl (ppm)

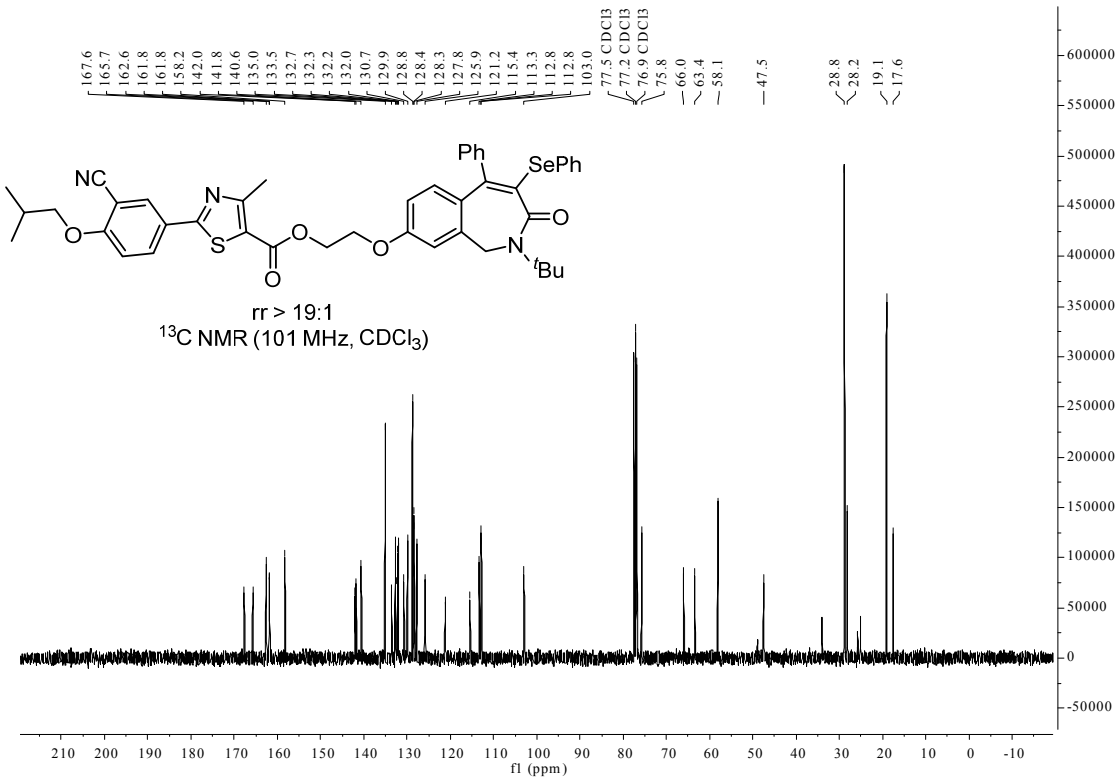
Compound 46


rr > 19:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)

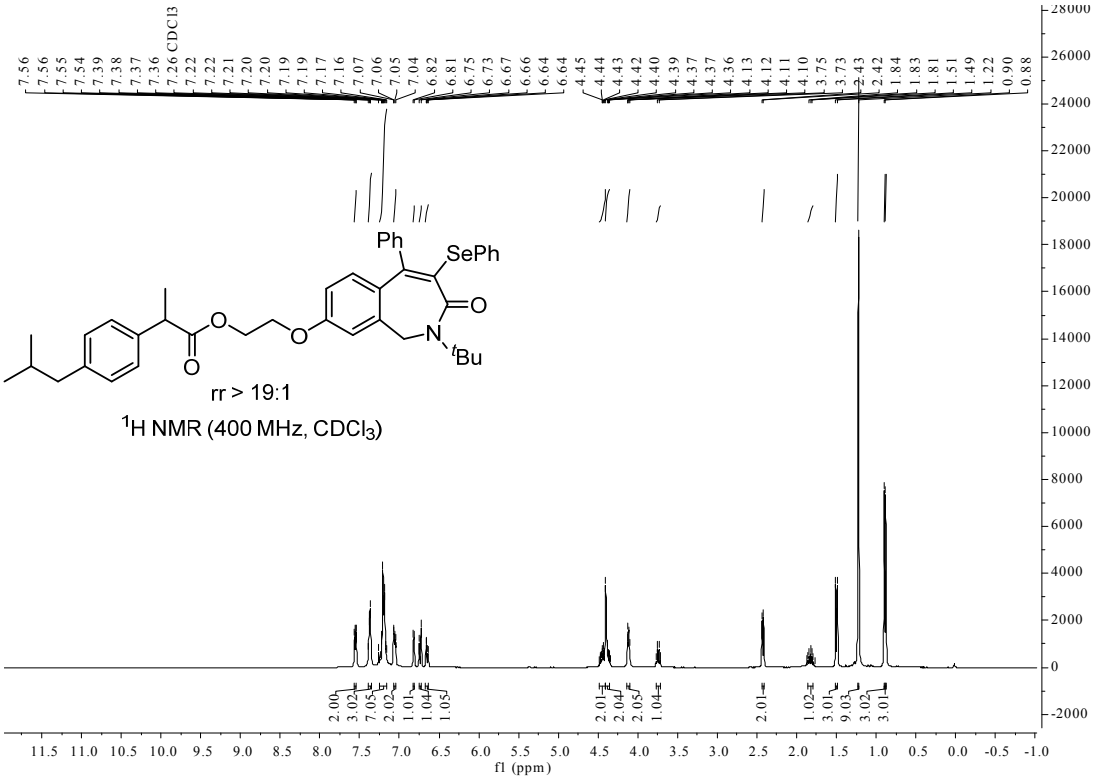

rr > 19:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

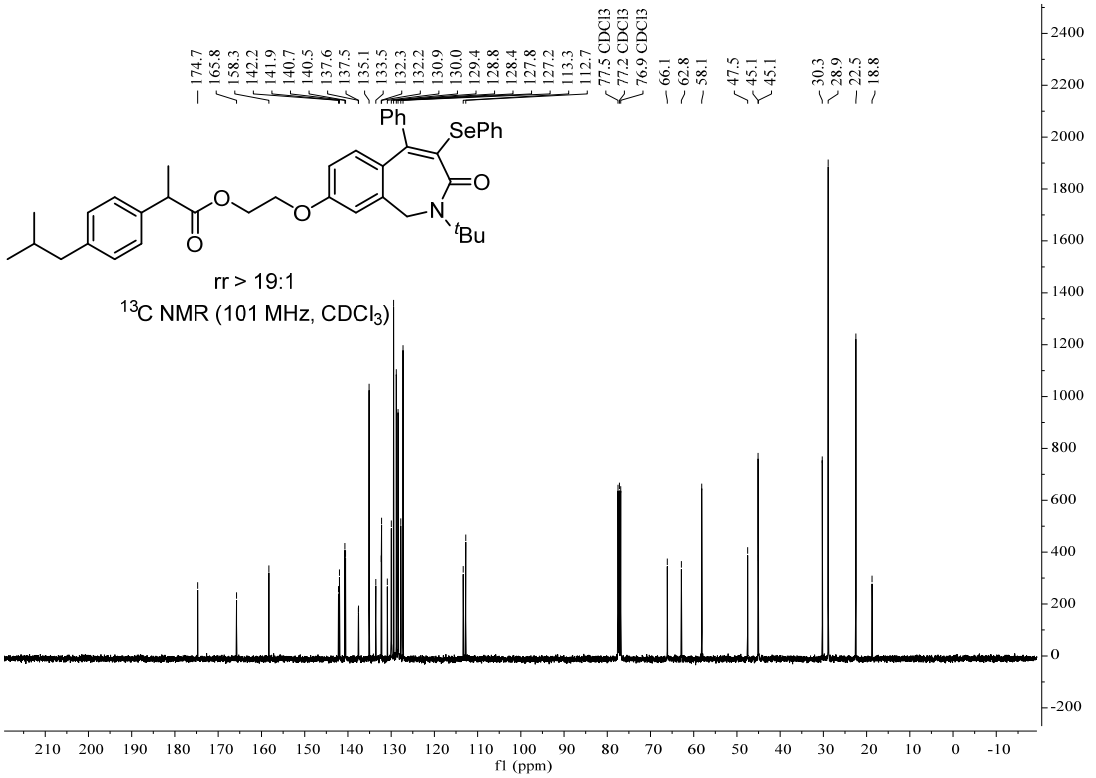
Compound 47


rr > 19:1
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

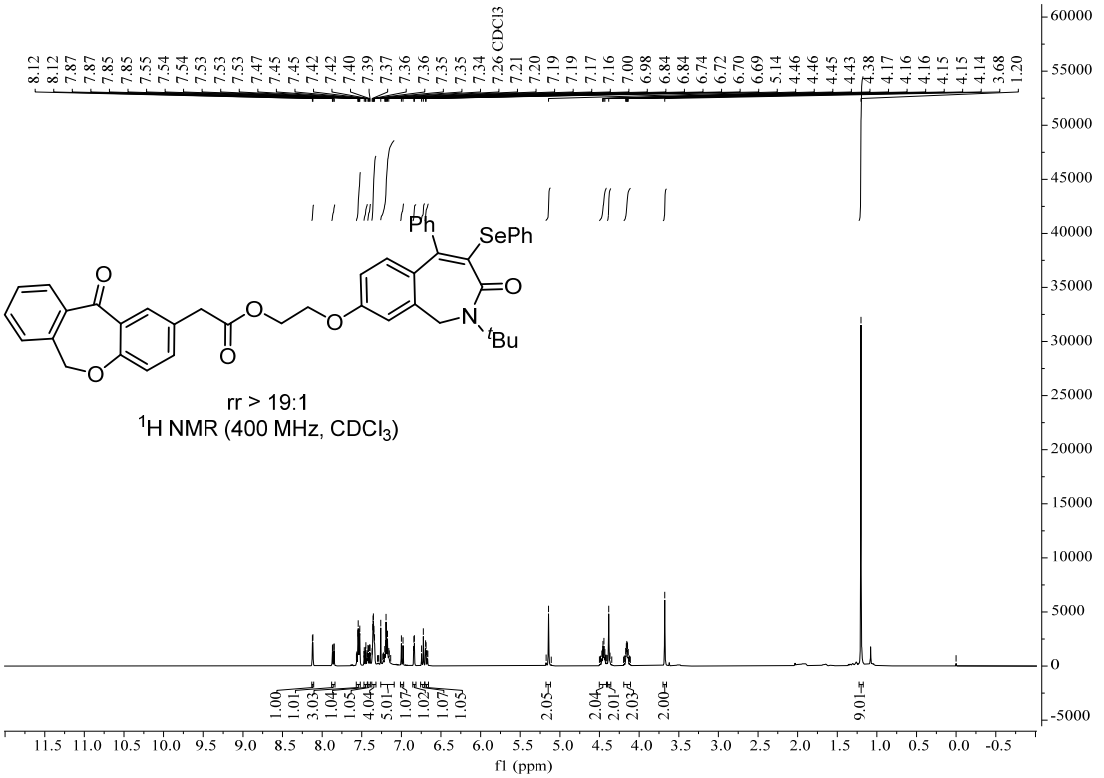

rr > 19:1
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

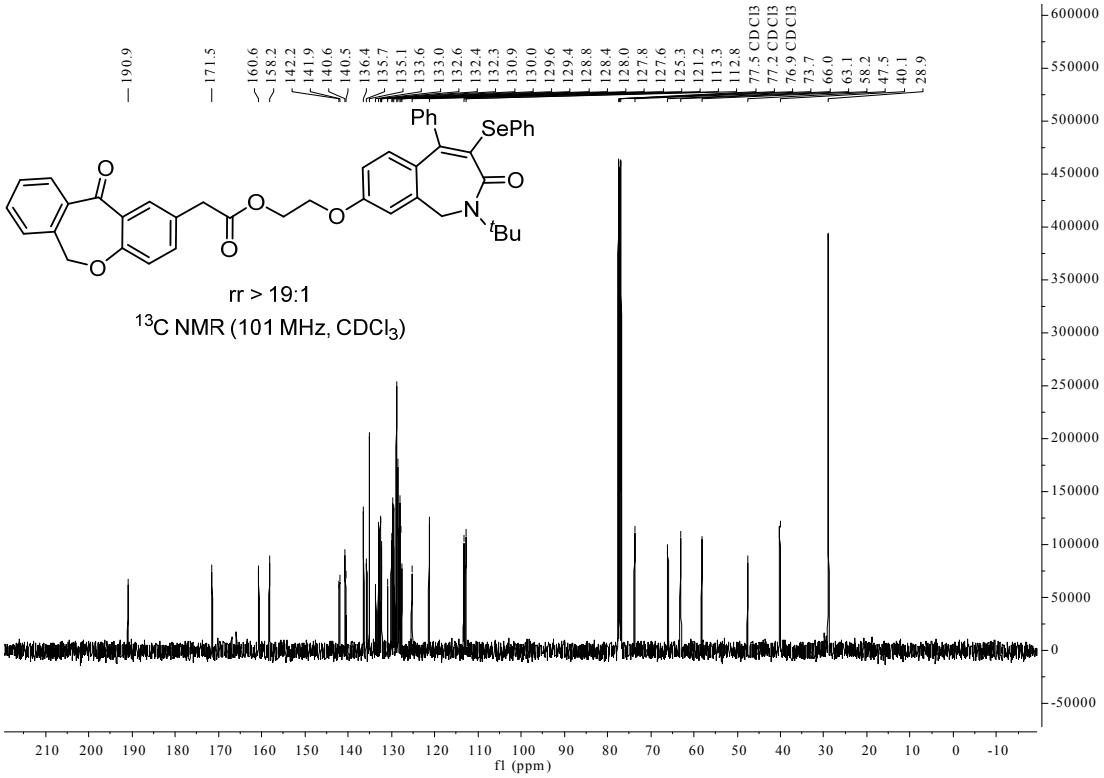
Compound 48


Ph
SePh
O
O
O
O
N
tBu
rr > 19:1
1H NMR (400 MHz, CDCl3)
fl (ppm)

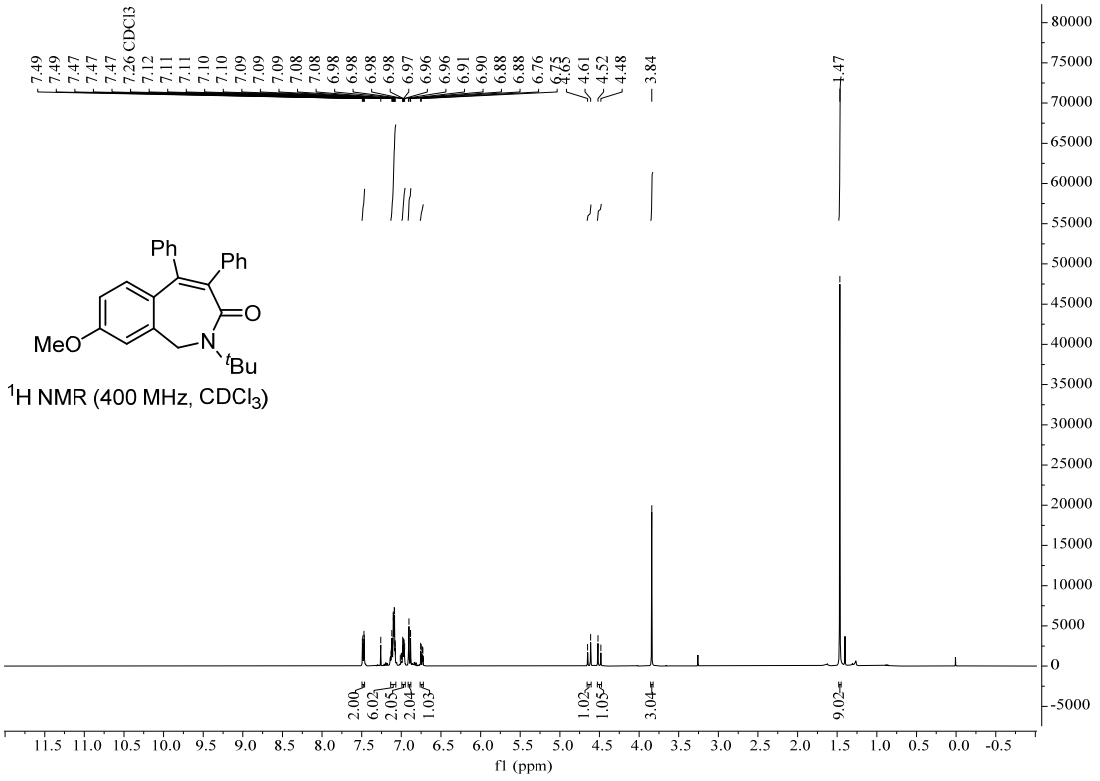

Ph
SePh
O
O
O
O
N
tBu
rr > 19:1
13C NMR (101 MHz, CDCl3)
fl (ppm)

Compound 49

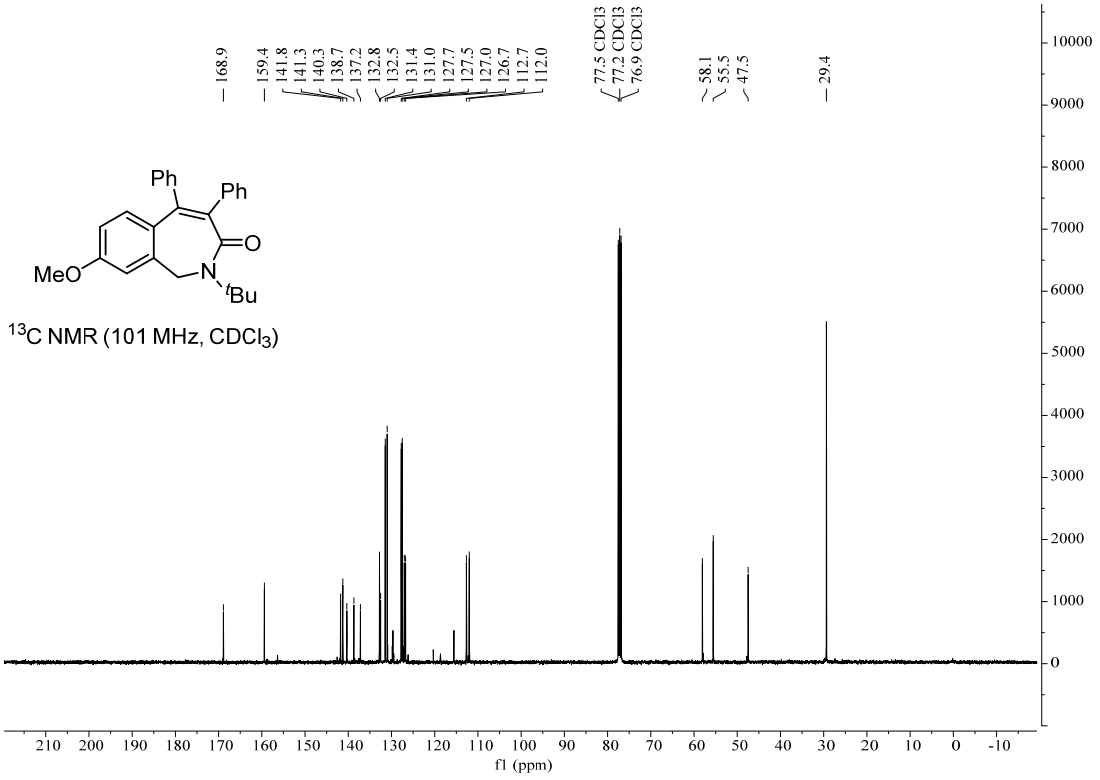

rr > 19:1
^{1}H NMR (400 MHz, $CDCl_3$)
fl (ppm)


rr > 19:1
^{13}C NMR (101 MHz, $CDCl_3$)
fl (ppm)

Compound 50

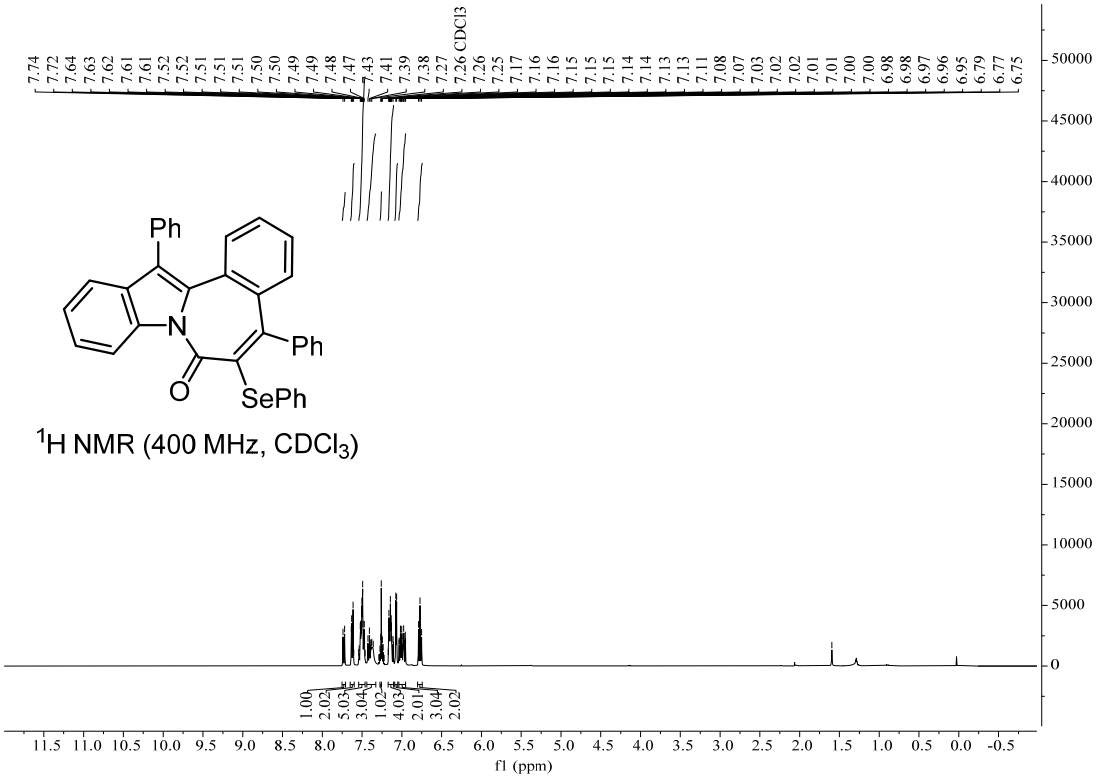


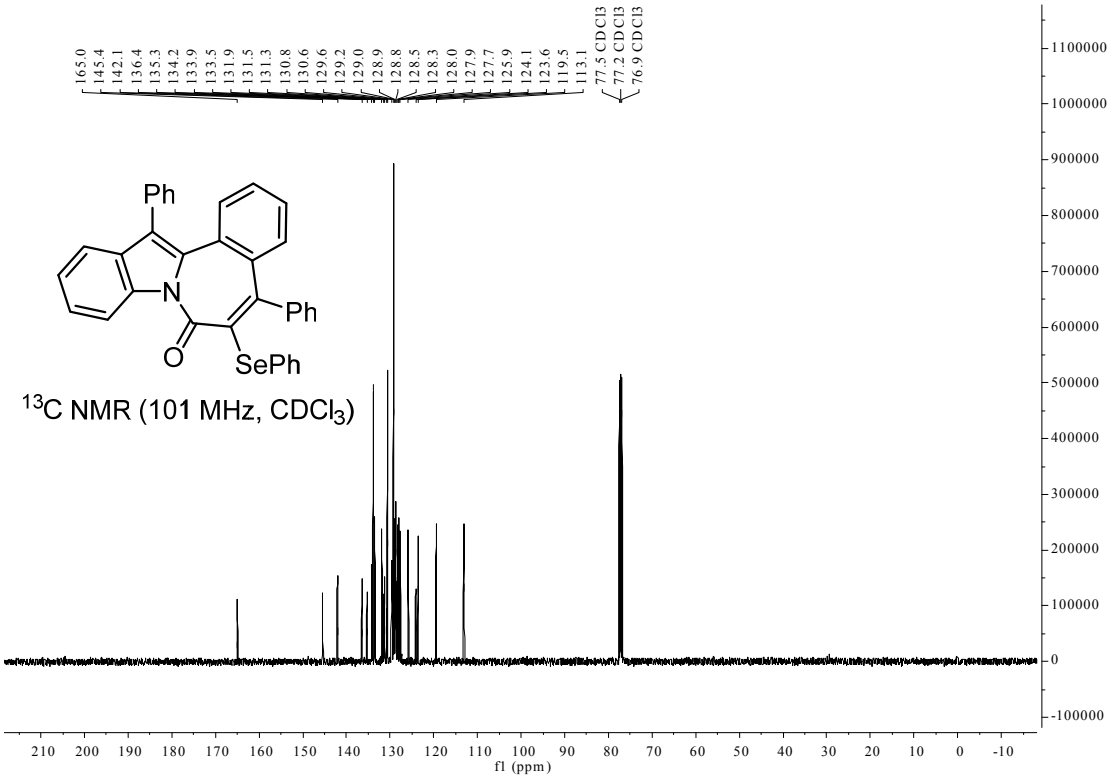
^{1}H NMR (400 MHz, $CDCl_3$)



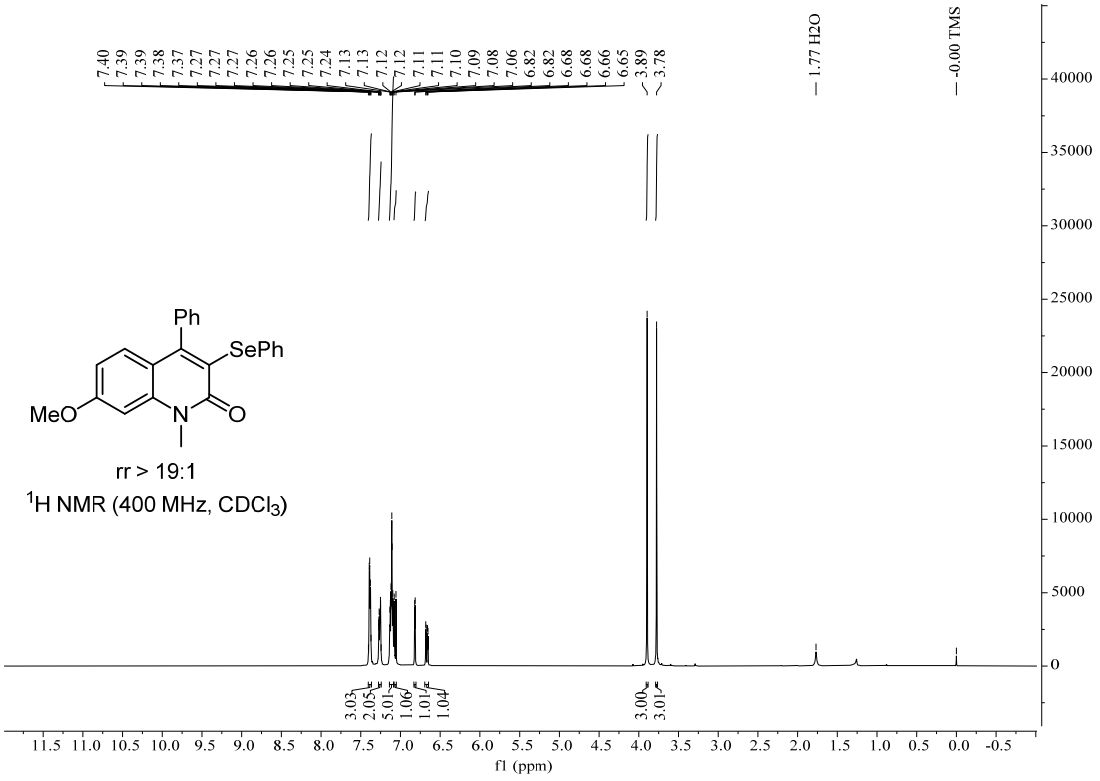
^{13}C NMR (101 MHz, $CDCl_3$)

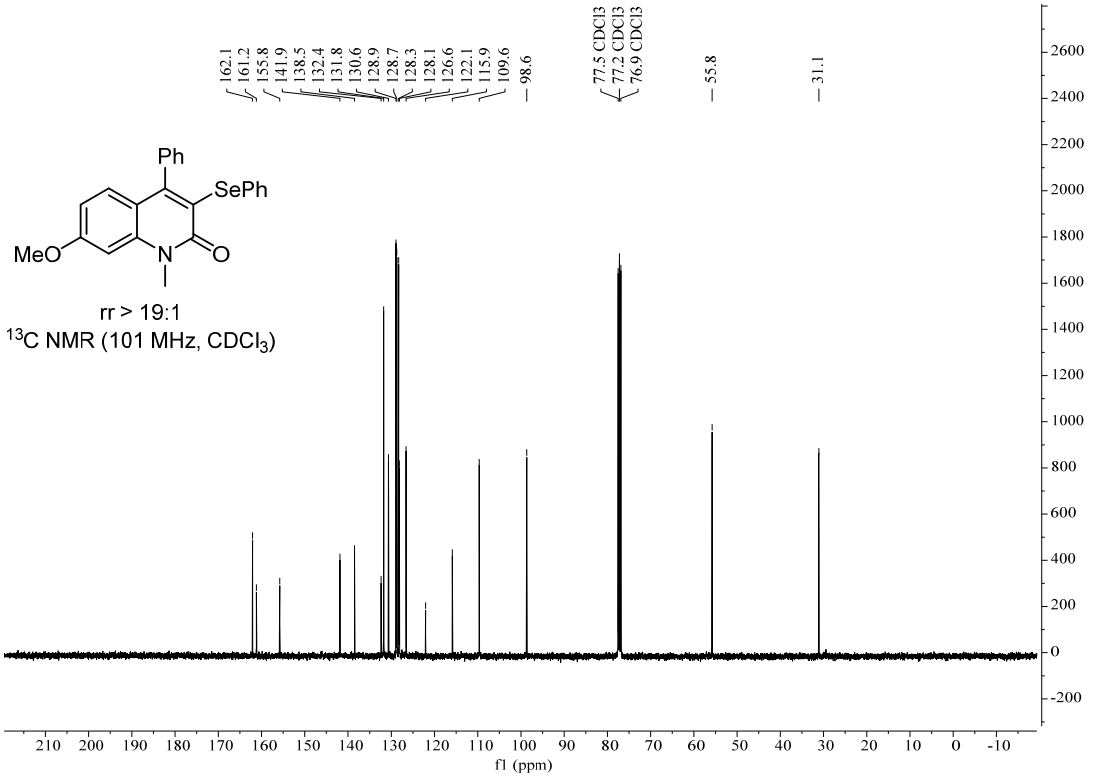
Compound 52


Ph
N
Ph
O
SePh
^{1}H NMR (400 MHz, $CDCl_3$)
fl (ppm)

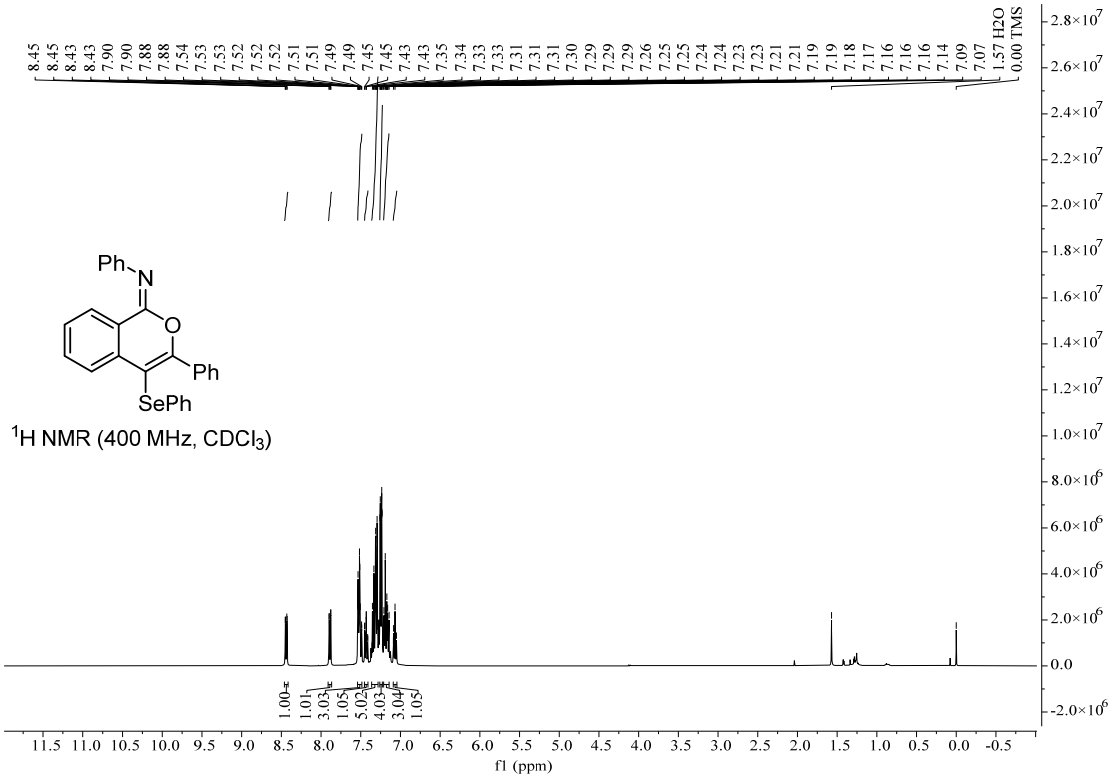

Ph
N
Ph
O
SePh
^{13}C NMR (101 MHz, $CDCl_3$)
fl (ppm)

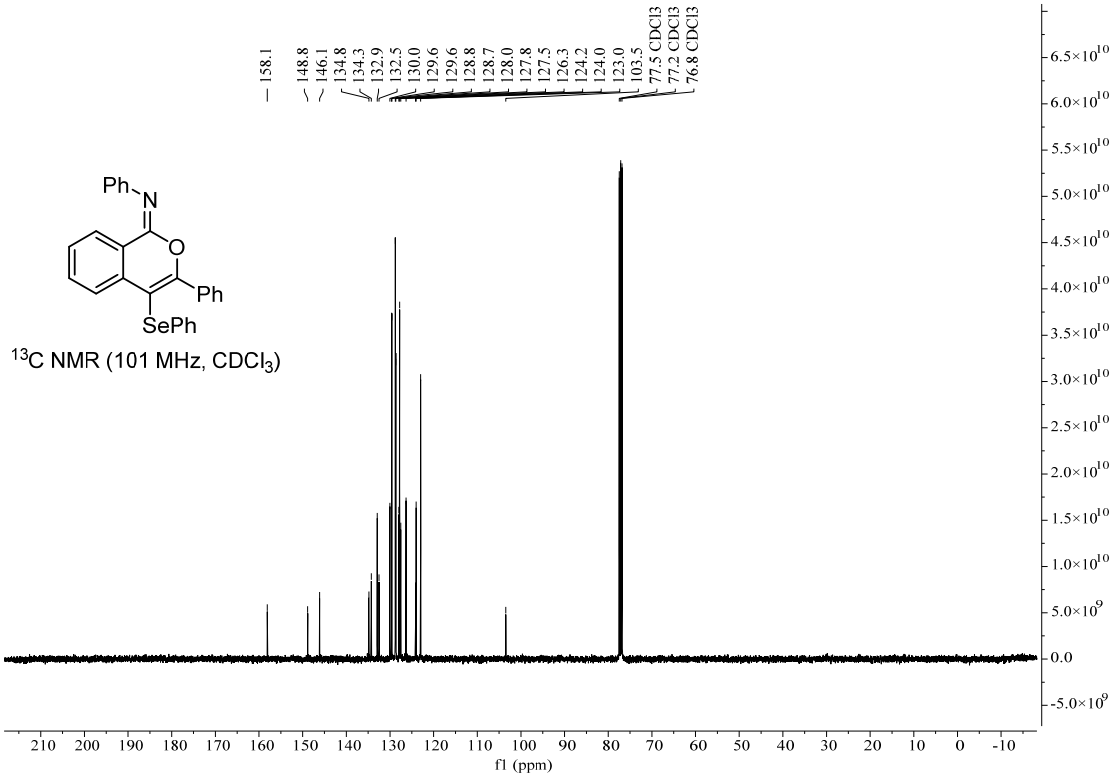
Compound 54


Ph
SePh
MeO
N
O
rr > 19:1
1H NMR (400 MHz, CDCl3)
7.40
7.39
7.39
7.38
7.37
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.08
7.06
6.82
6.82
6.68
6.68
6.66
6.65
3.89
3.78
1.77 H2O
-0.00 TMS
3.03
2.05
5.01
1.06
1.01
1.04
3.00
3.01
f1 (ppm)

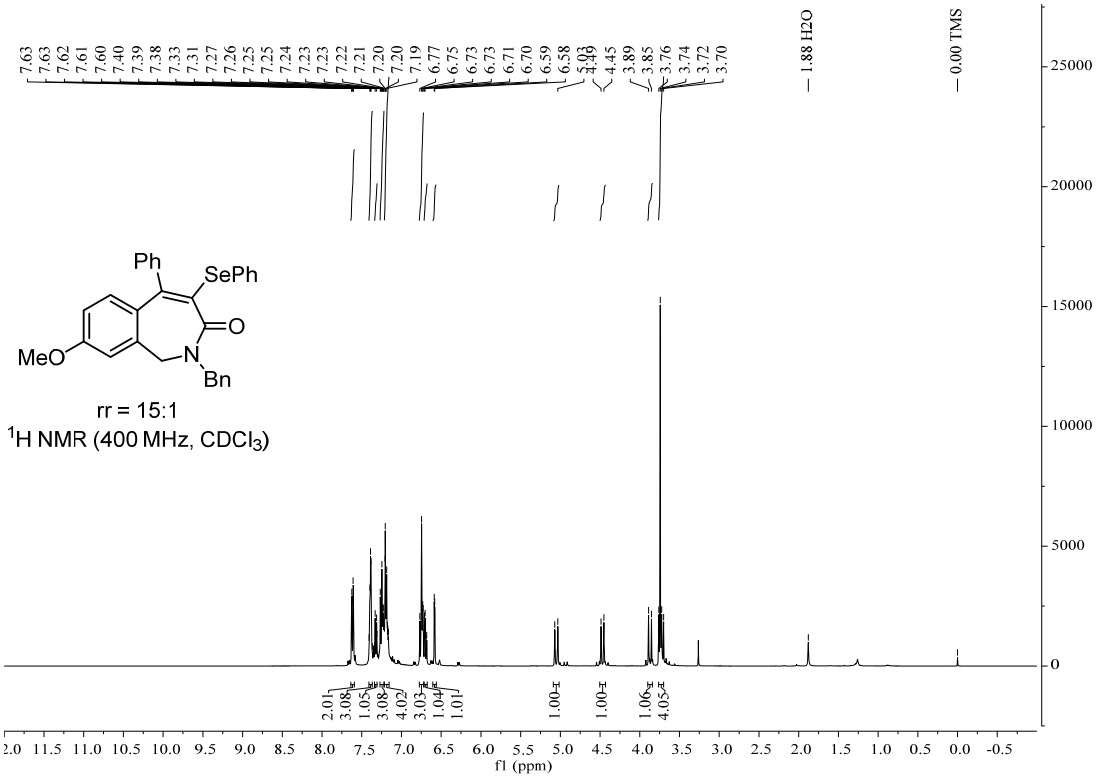

Ph
SePh
MeO
N
O
rr > 19:1
13C NMR (101 MHz, CDCl3)
162.1
161.2
155.8
141.9
138.5
132.4
131.8
130.6
128.9
128.7
128.3
128.1
126.6
122.1
115.9
109.6
98.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.8
31.1
f1 (ppm)

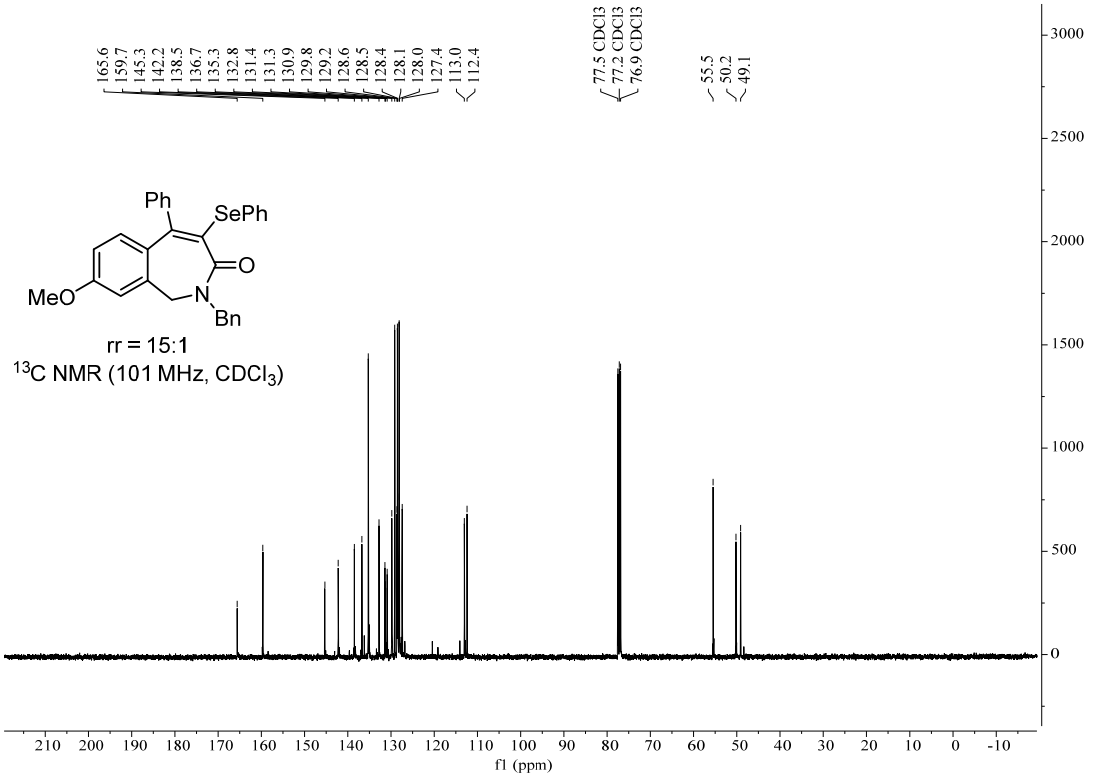
Compound 56


Ph
N
O
Ph
SePh
1H NMR (400 MHz, CDCl3)
f1 (ppm)

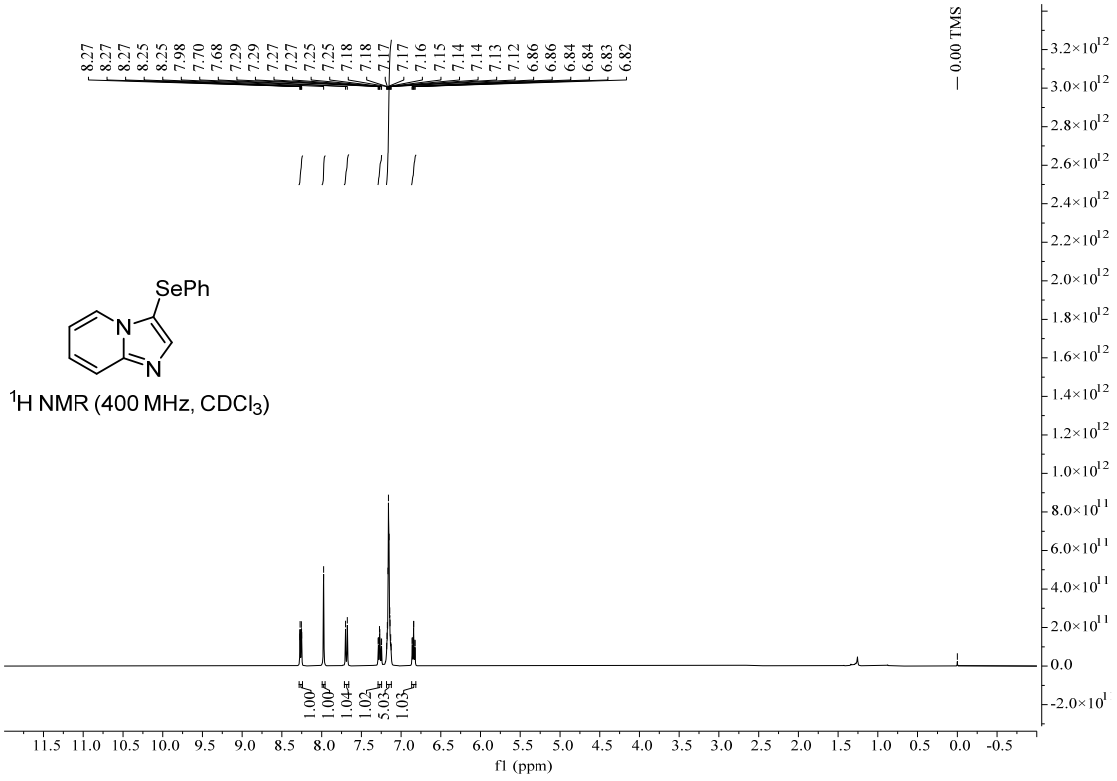

Ph
N
O
Ph
SePh
13C NMR (101 MHz, CDCl3)
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

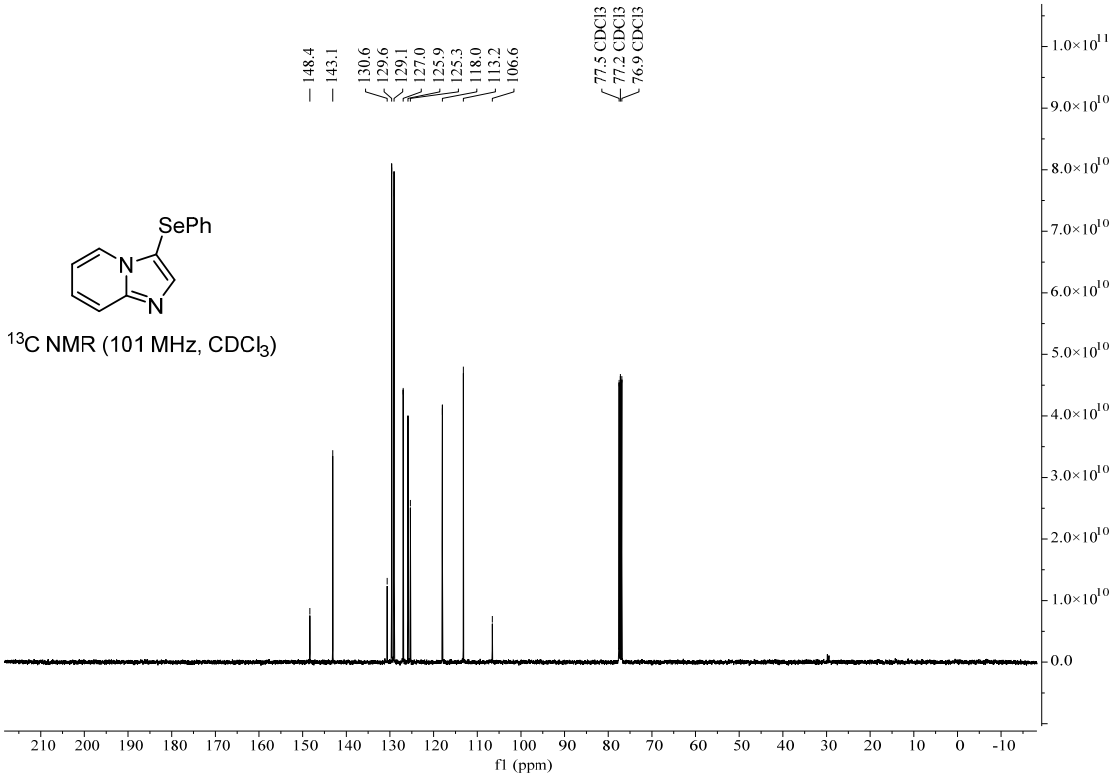
Compound 58


7.63
7.63
7.62
7.61
7.60
7.40
7.39
7.38
7.33
7.31
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
6.77
6.75
6.73
6.73
6.71
6.70
6.59
6.58
5.03
4.49
4.45
3.89
3.85
3.76
3.74
3.72
3.70
1.88 H2O
0.00 TMS
Ph
SePh
O
MeO
N
Bn
rr = 15:1
1H NMR (400 MHz, CDCl3)
2.01
3.08
1.05
3.08
4.02
3.03
1.04
1.01
1.00
1.00
1.06
4.05
f1 (ppm)

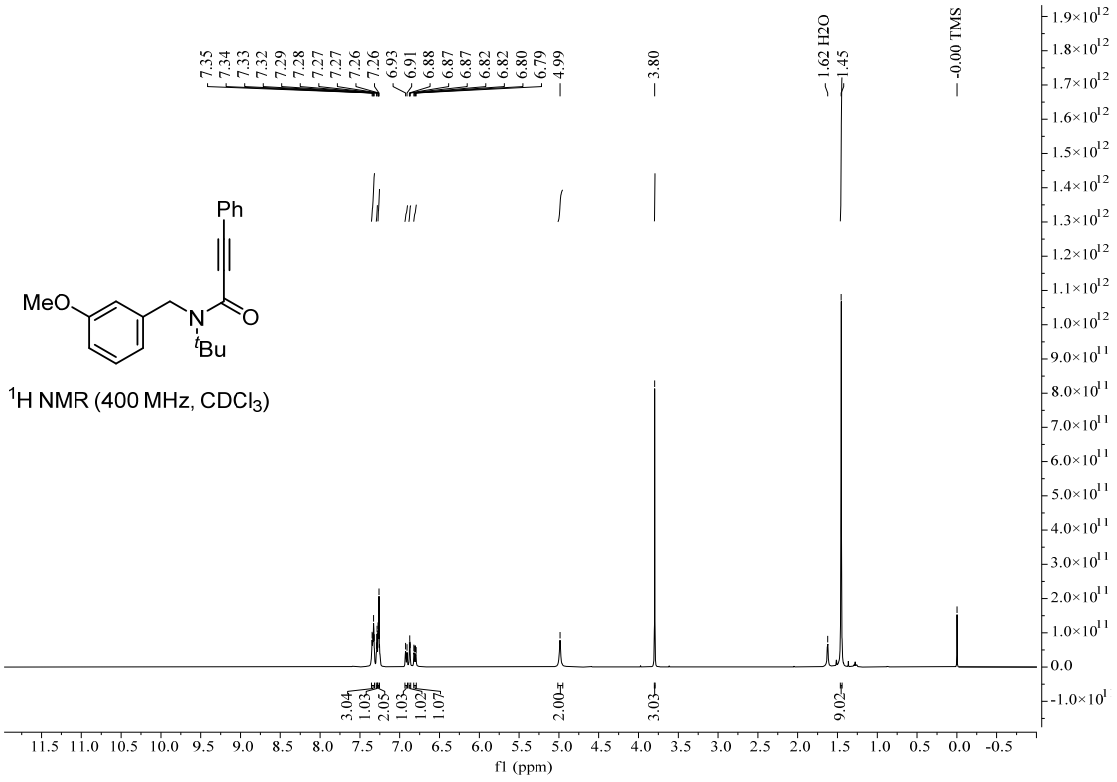

165.6
159.7
145.3
142.2
138.5
136.7
135.3
132.8
131.4
131.3
130.9
129.8
129.2
128.6
128.5
128.4
128.1
128.0
127.4
113.0
112.4
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.5
50.2
49.1
Ph
SePh
O
MeO
N
Bn
rr = 15:1
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 62

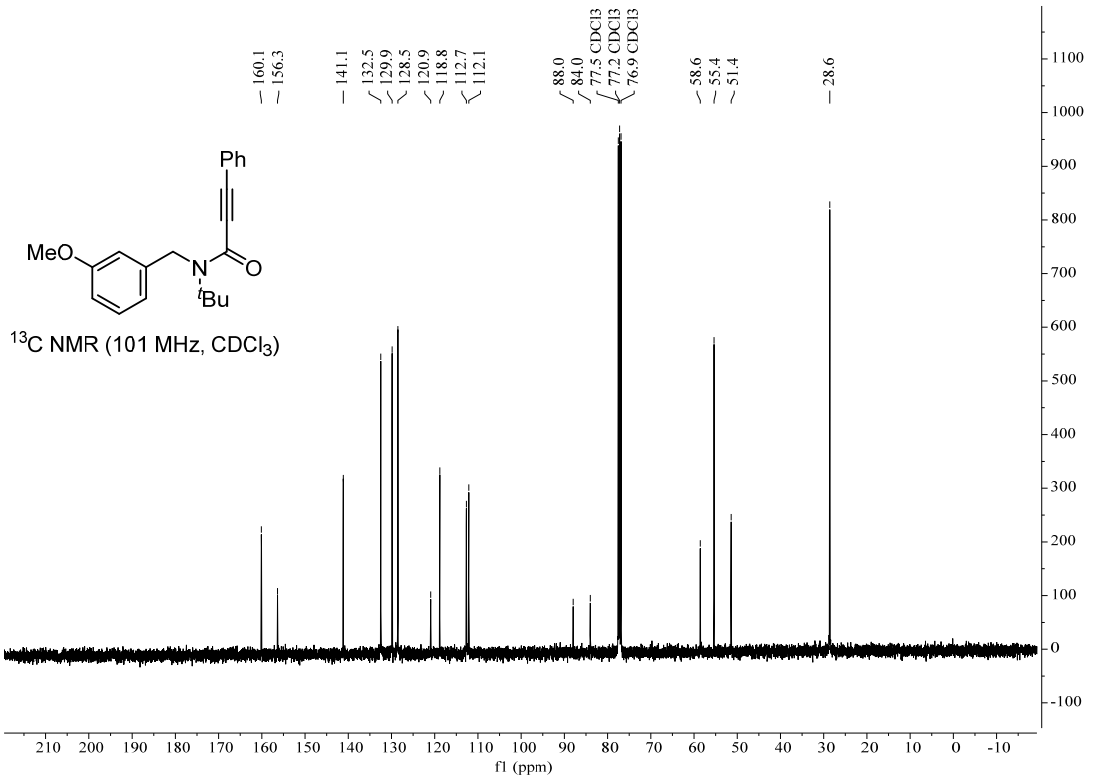

8.27
8.27
8.27
8.25
8.25
7.98
7.70
7.68
7.29
7.29
7.27
7.27
7.25
7.25
7.18
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
7.12
6.86
6.86
6.84
6.84
6.83
6.82
0.00 TMS
SePh
N
N
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.04
1.02
5.03
1.03
f1 (ppm)


148.4
143.1
130.6
129.6
129.1
127.0
125.9
125.3
118.0
113.2
106.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
SePh
N
N
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound S1

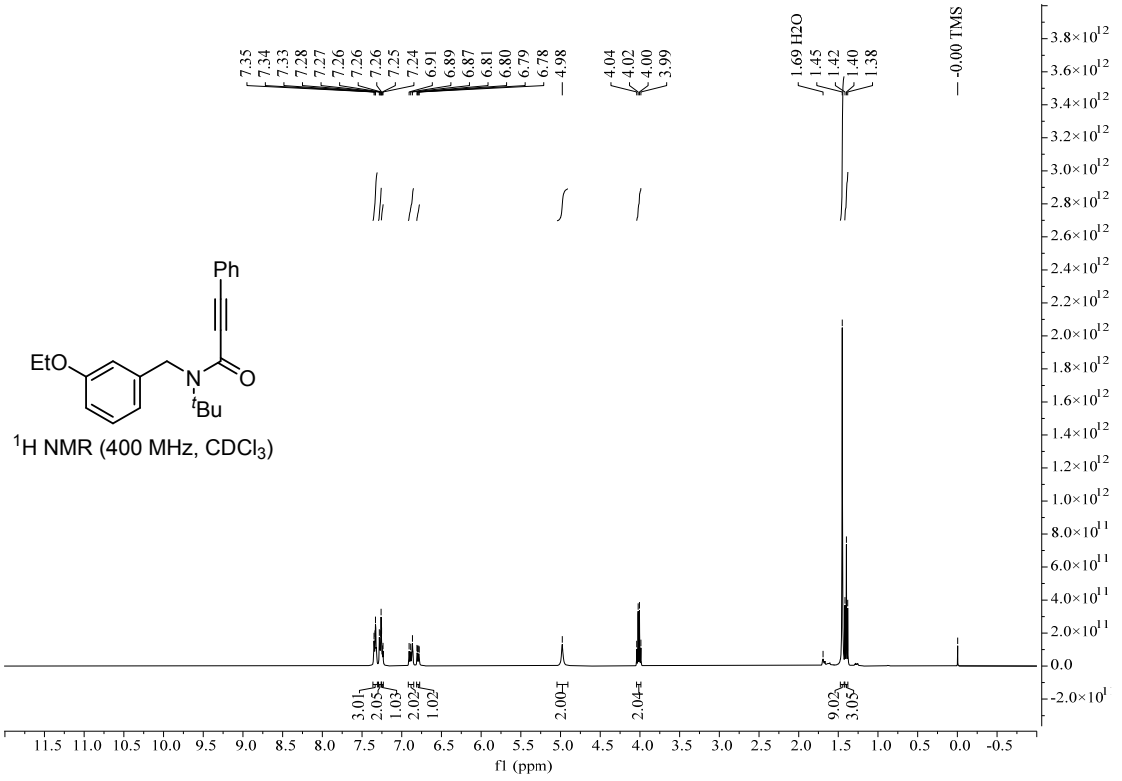


^{1}H NMR (400 MHz, $CDCl_3$)

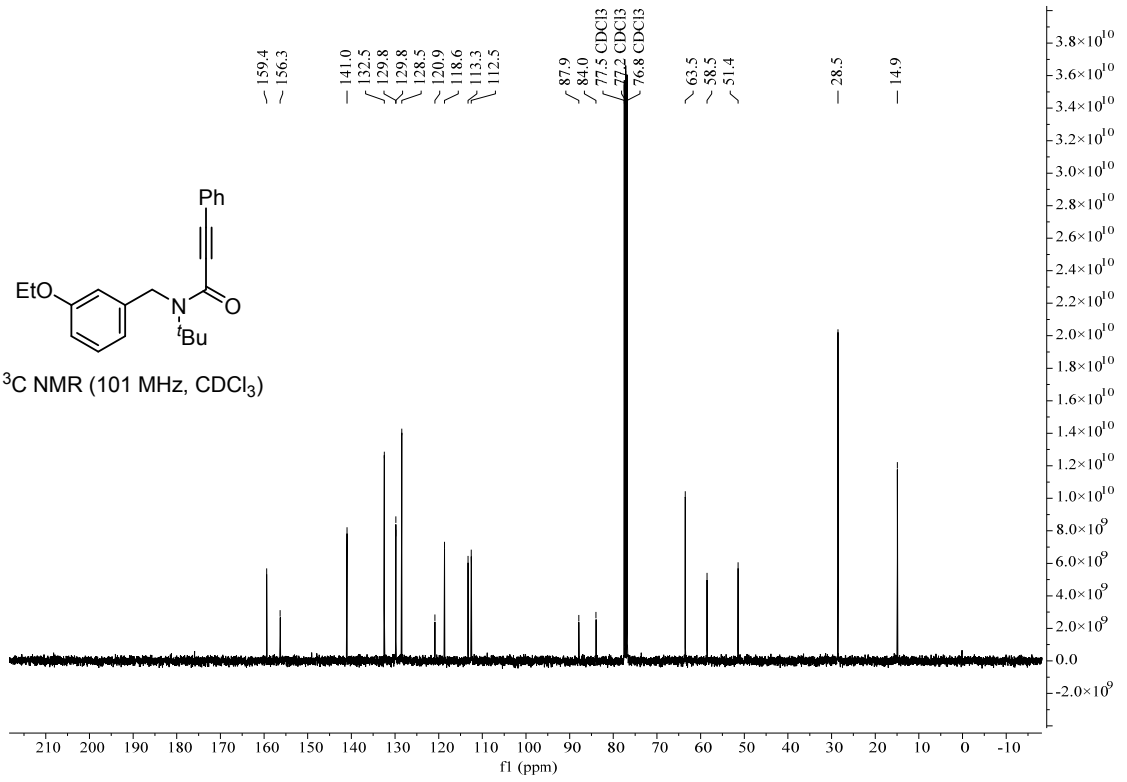


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S2

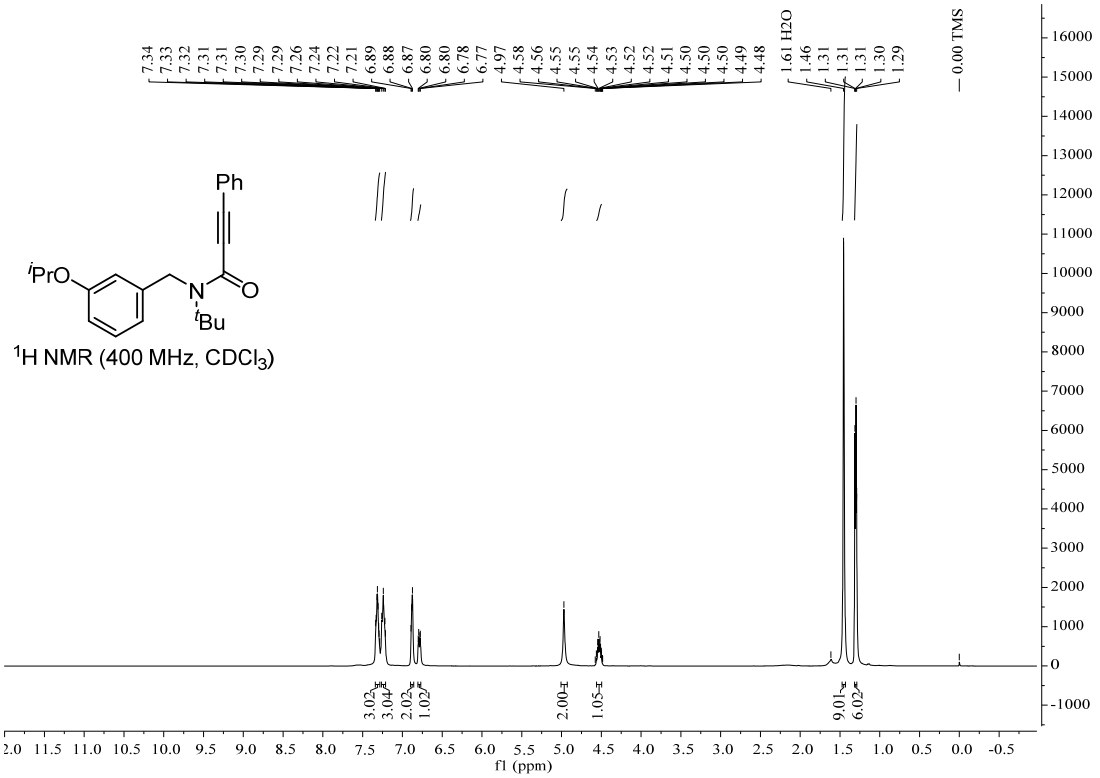


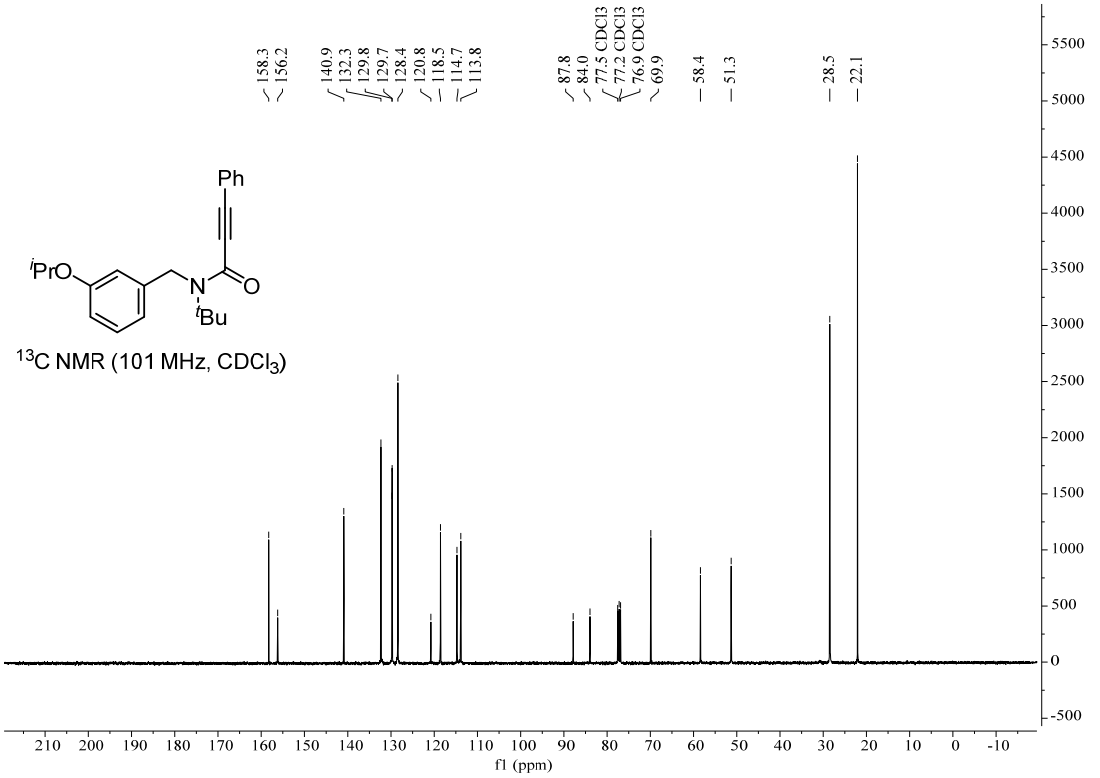
^{1}H NMR (400 MHz, $CDCl_3$)



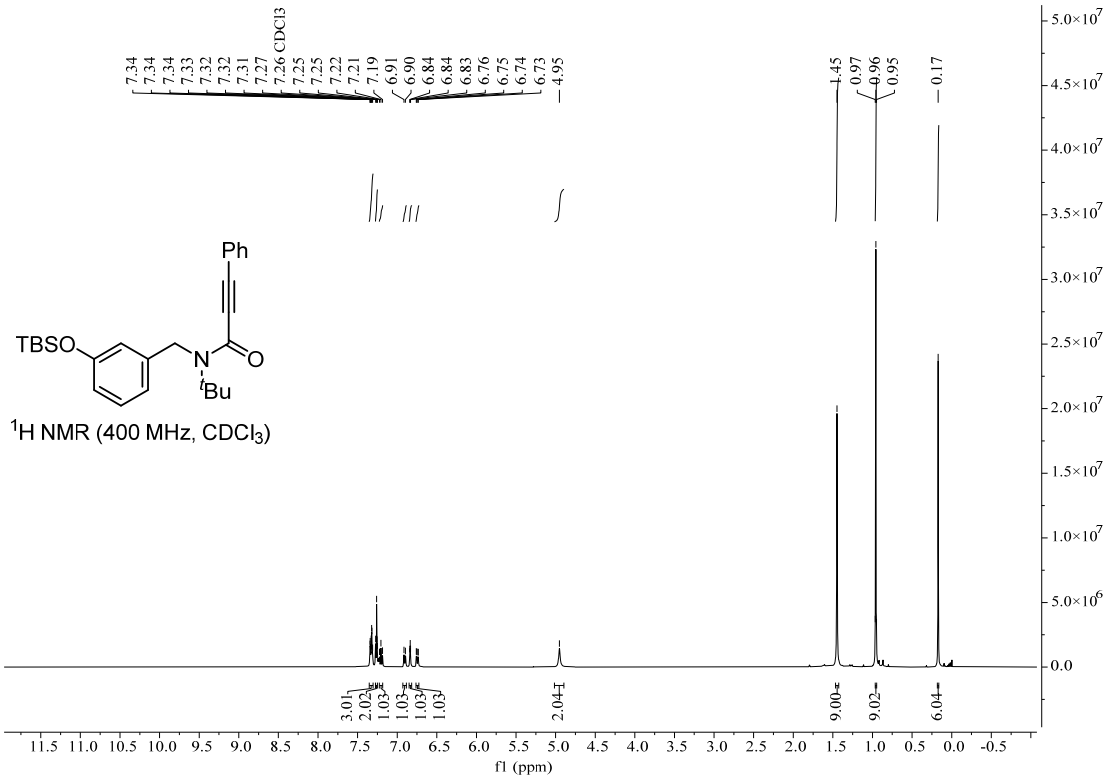
^{13}C NMR (101 MHz, $CDCl_3$)

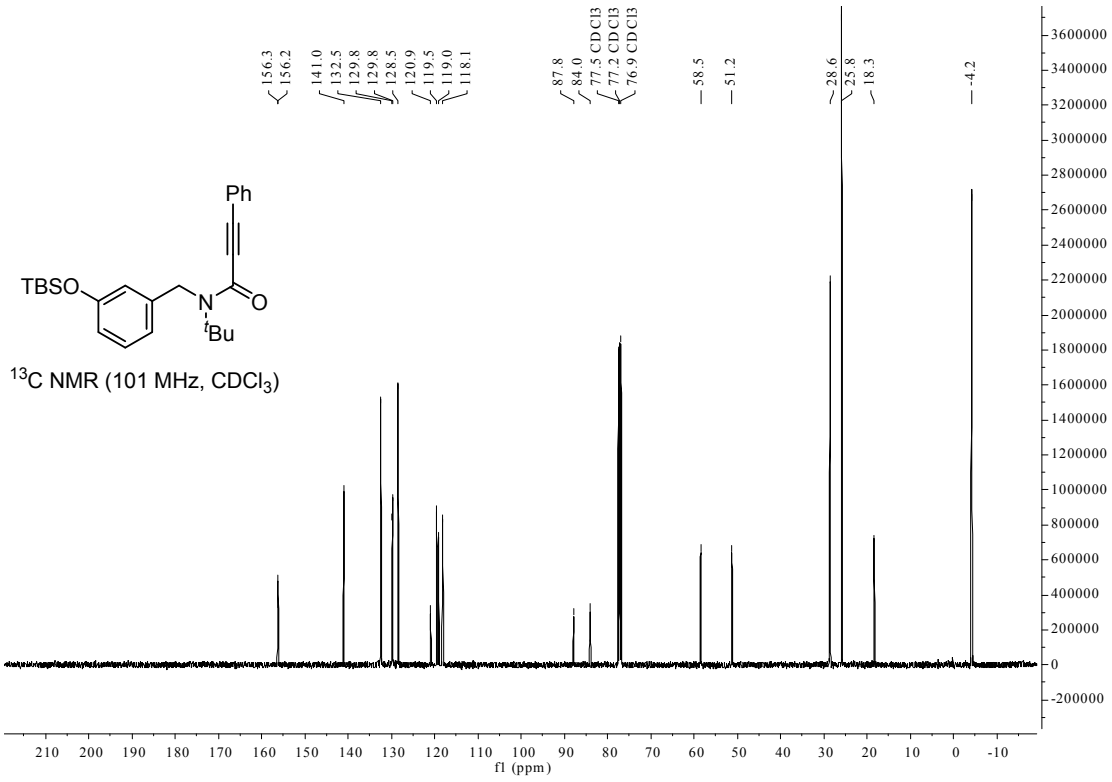
Compound S3


Ph
iPrO
N
O
tBu
1H NMR (400 MHz, CDCl3)
7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.26 7.24 7.22 7.21 6.89 6.88 6.87 6.80 6.80 6.78 6.77 4.97 4.58 4.56 4.55 4.55 4.54 4.53 4.52 4.52 4.51 4.50 4.50 4.50 4.49 4.48 1.61 H2O 1.46 1.31 1.31 1.31 1.30 1.29 0.00 TMS
3.02 3.04 2.03 1.02 2.00 1.05 9.01 6.02
f1 (ppm)

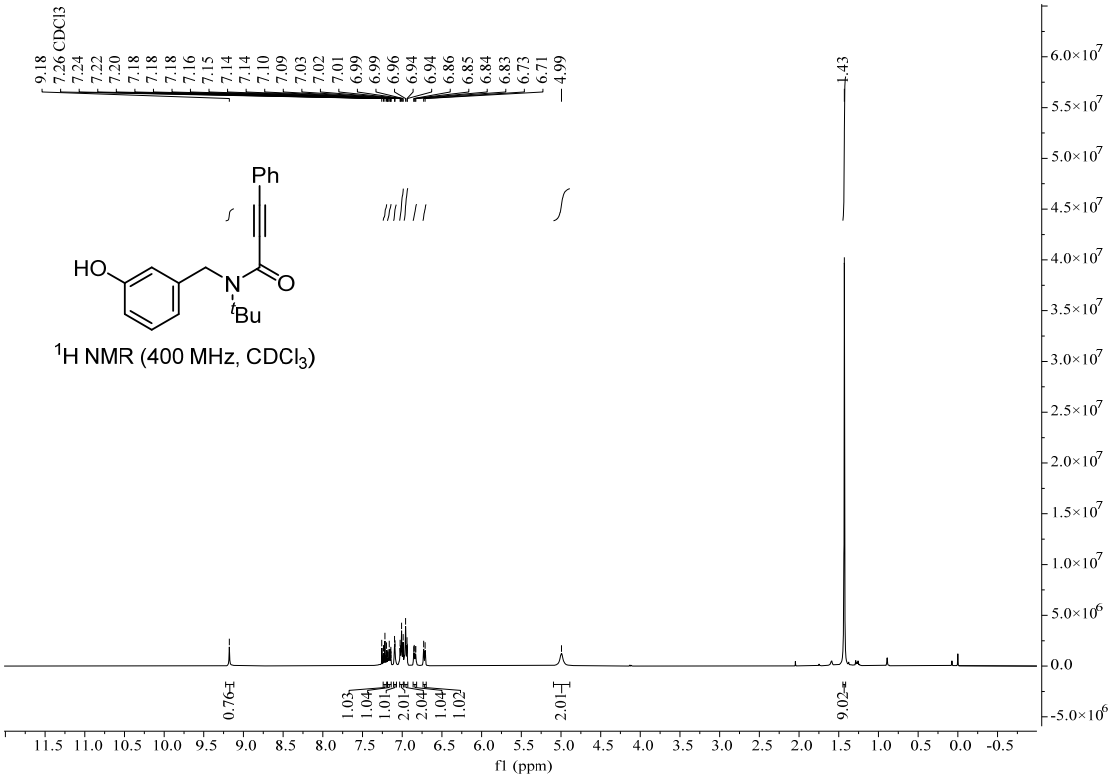

Ph
iPrO
N
O
tBu
13C NMR (101 MHz, CDCl3)
158.3 156.2 140.9 132.3 129.8 129.7 128.4 120.8 118.5 114.7 113.8 87.8 84.0 77.5 CDCl3 77.2 CDCl3 76.9 CDCl3 69.9 58.4 51.3 28.5 22.1
f1 (ppm)

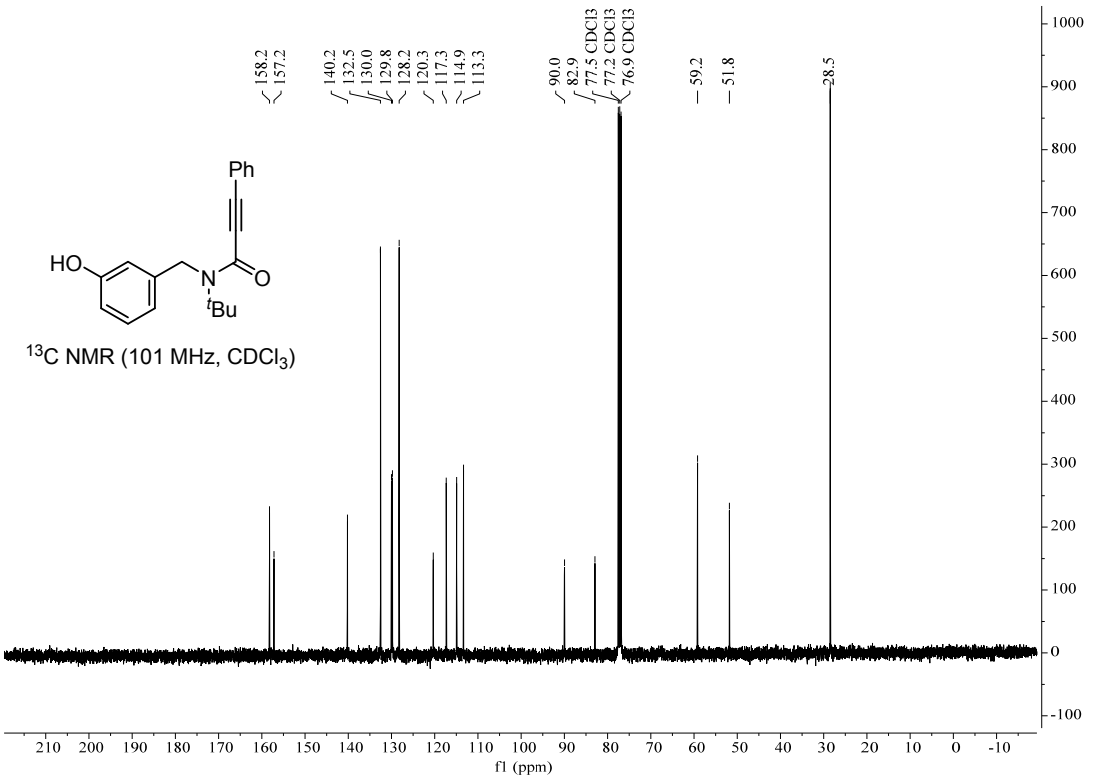
Compound S5


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

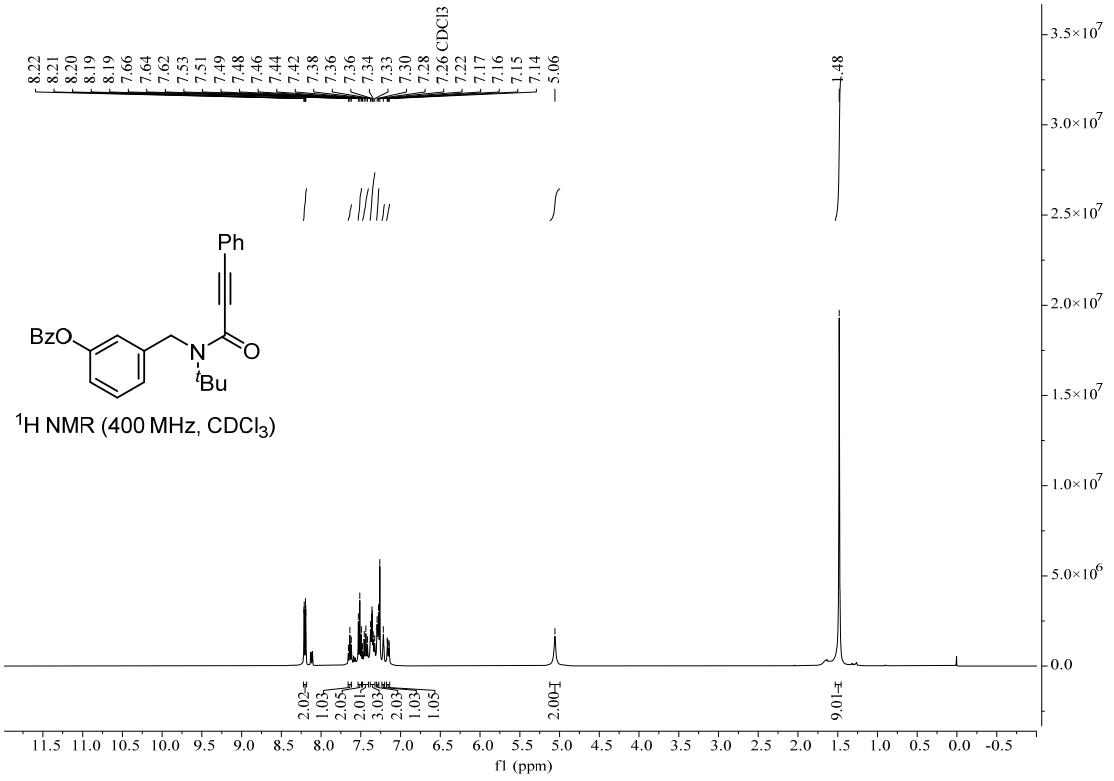

Ph
TBSO
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

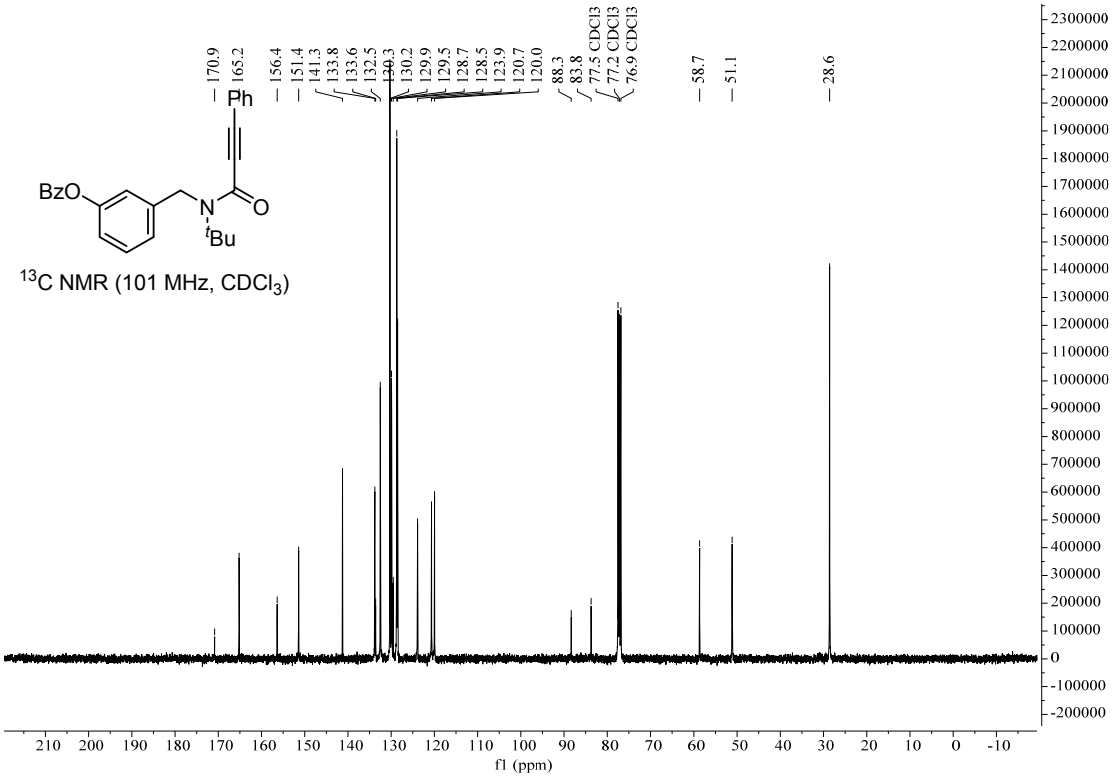
Compound S6


9.18
7.26 CDCl3
7.24
7.22
7.20
7.18
7.18
7.18
7.16
7.15
7.14
7.14
7.10
7.09
7.03
7.02
7.01
6.99
6.99
6.96
6.94
6.94
6.86
6.85
6.84
6.83
6.73
6.71
4.99
1.43
Ph
HO
N
O
tBu
1H NMR (400 MHz, CDCl3)
0.76
1.03
1.04
1.01
2.01
2.04
1.04
1.02
2.01
9.02
fl (ppm)

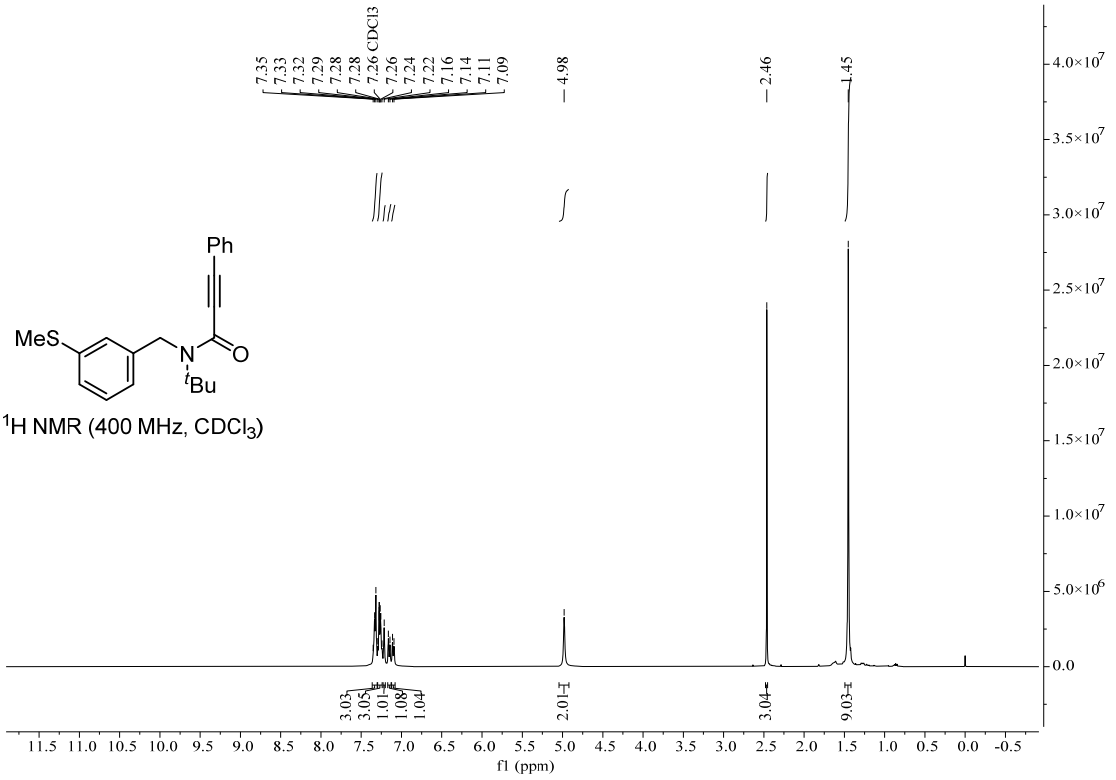

158.2
157.2
140.2
132.5
130.0
129.8
128.2
120.3
117.3
114.9
113.3
90.0
82.9
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
59.2
51.8
28.5
Ph
HO
N
O
tBu
13C NMR (101 MHz, CDCl3)
fl (ppm)

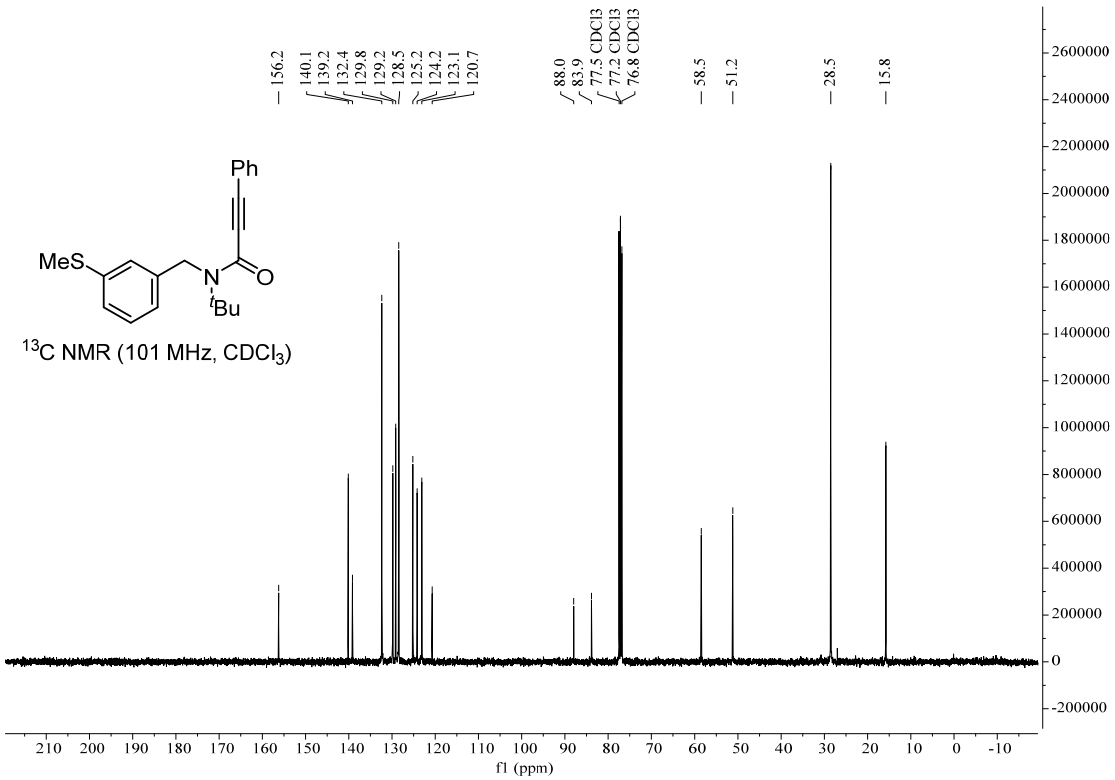
Compound S7


8.22
8.21
8.20
8.19
8.19
7.66
7.64
7.62
7.53
7.51
7.49
7.48
7.46
7.44
7.42
7.38
7.36
7.36
7.34
7.33
7.30
7.28
7.26 CDCl3
7.22
7.17
7.16
7.15
7.14
5.06
1.48
Ph
BzO
N
O
tBu
1H NMR (400 MHz, CDCl3)
2.02
1.03
2.05
2.01
3.03
2.03
1.03
1.05
2.00
9.01
f1 (ppm)

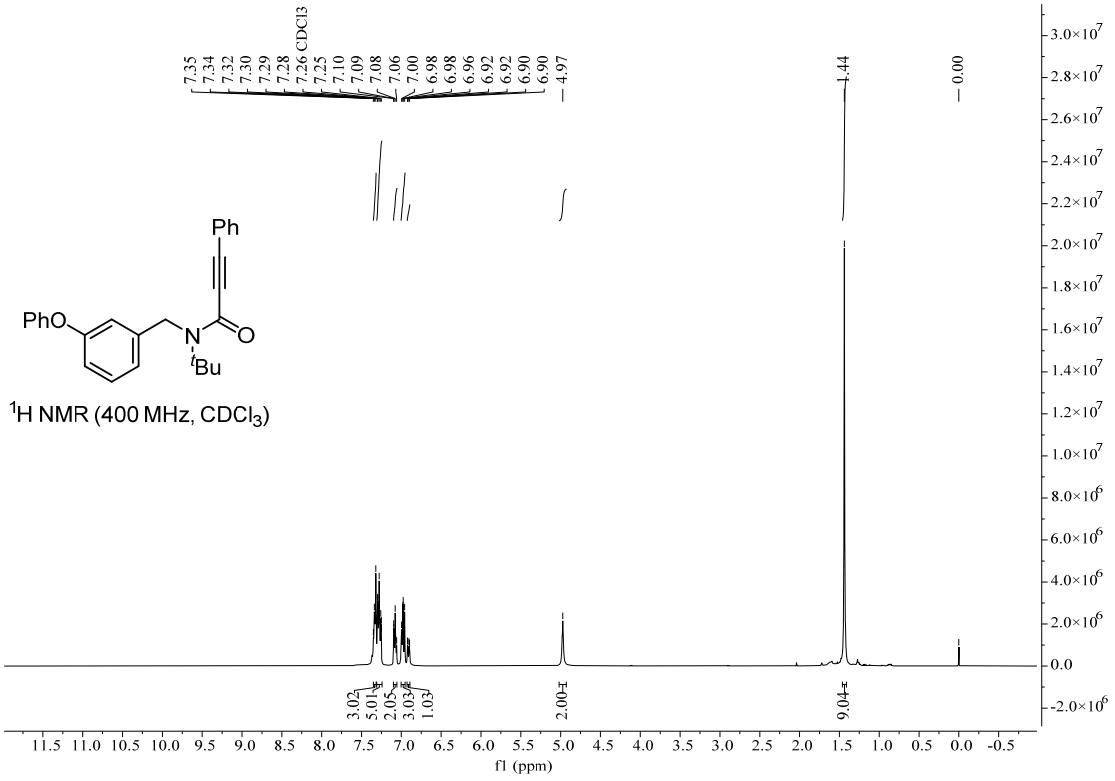

170.9
165.2
156.4
151.4
141.3
133.8
133.6
132.5
130.3
130.2
129.9
129.5
128.7
128.5
123.9
120.7
120.0
88.3
83.8
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
58.7
51.1
28.6
Ph
BzO
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

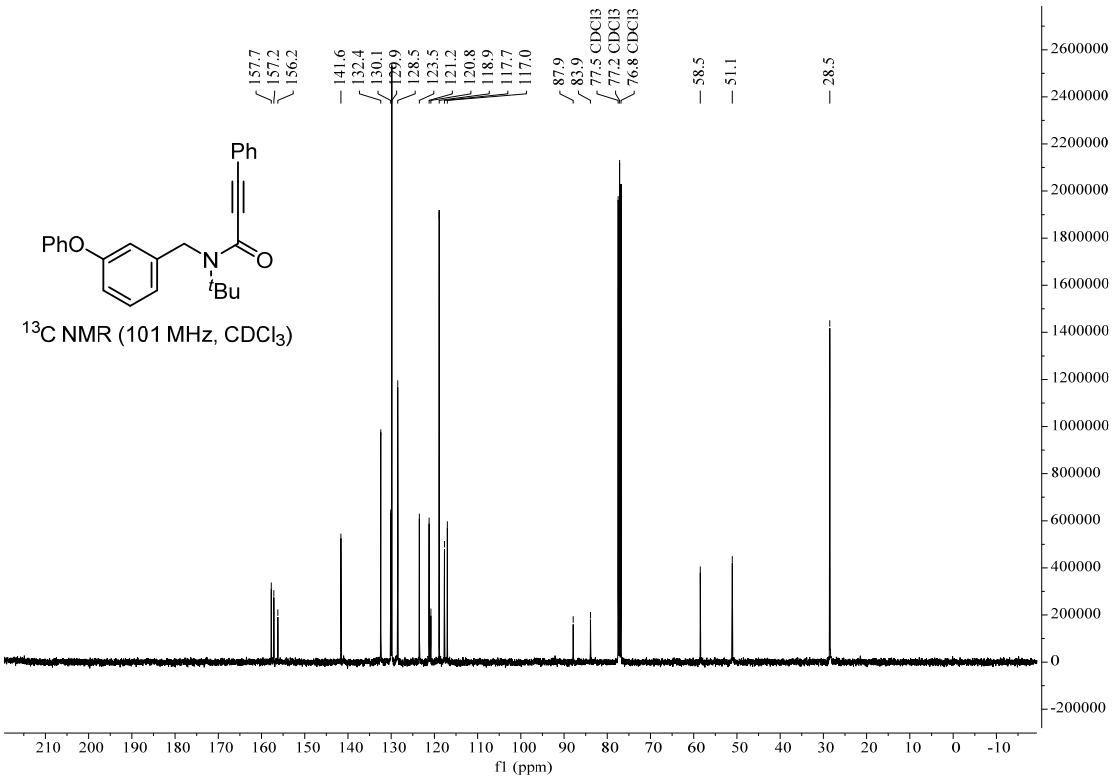
Compound S8


7.35
7.33
7.32
7.29
7.28
7.28
7.26 CDCl3
7.26
7.24
7.22
7.16
7.14
7.11
7.09
4.98
2.46
1.45
Ph
MeS
N
O
tBu
1H NMR (400 MHz, CDCl3)
3.03
3.05
1.01
1.08
1.04
2.01
3.04
9.03
f1 (ppm)

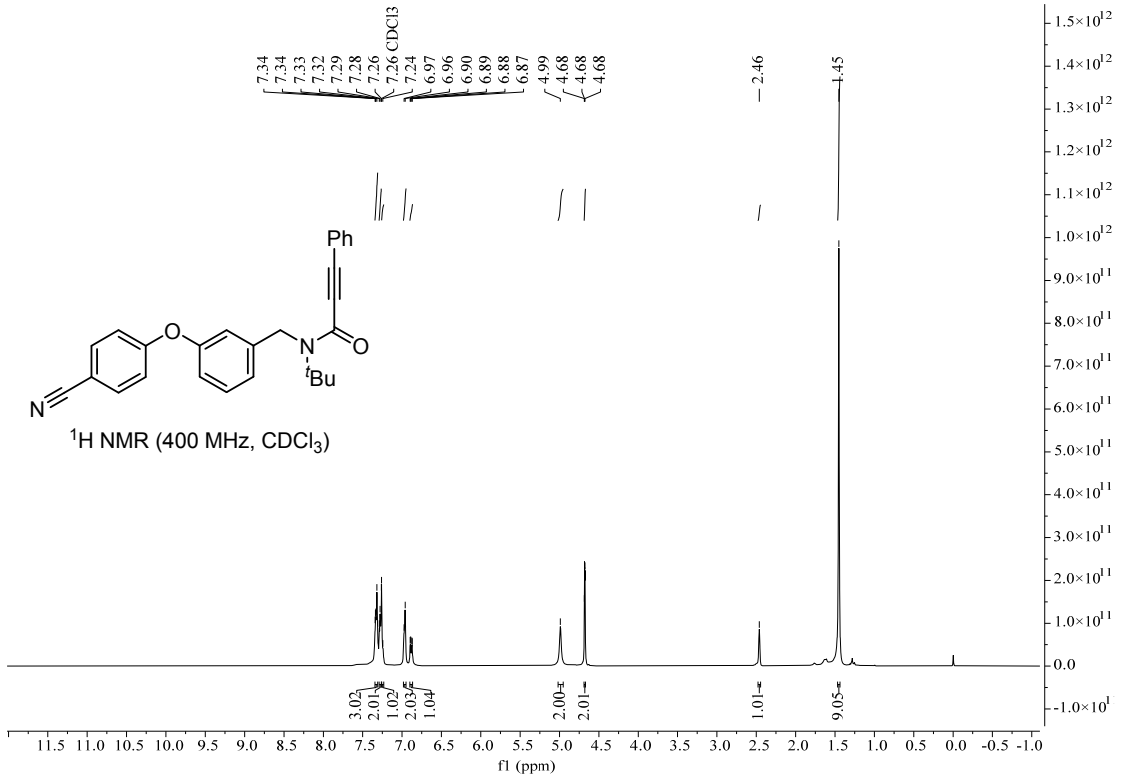

156.2
140.1
139.2
132.4
129.8
129.2
128.5
125.2
124.2
123.1
120.7
88.0
83.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
58.5
51.2
28.5
15.8
Ph
MeS
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

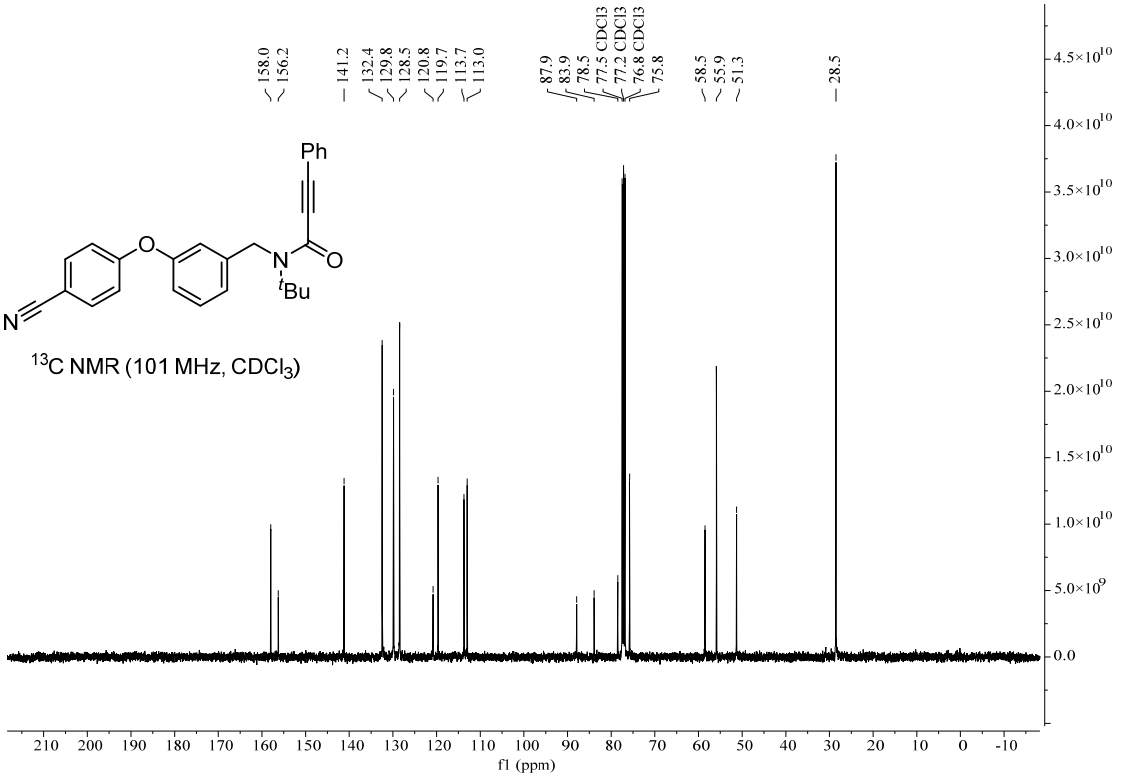
Compound S9


7.35
7.34
7.32
7.30
7.29
7.28
7.26 CDCl3
7.25
7.10
7.09
7.08
7.06
7.00
6.98
6.98
6.96
6.92
6.92
6.90
6.90
4.97
1.44
0.00
Ph
PhO
N
O
tBu
1H NMR (400 MHz, CDCl3)
3.02
5.01
2.05
3.03
1.03
2.00
9.04
f1 (ppm)

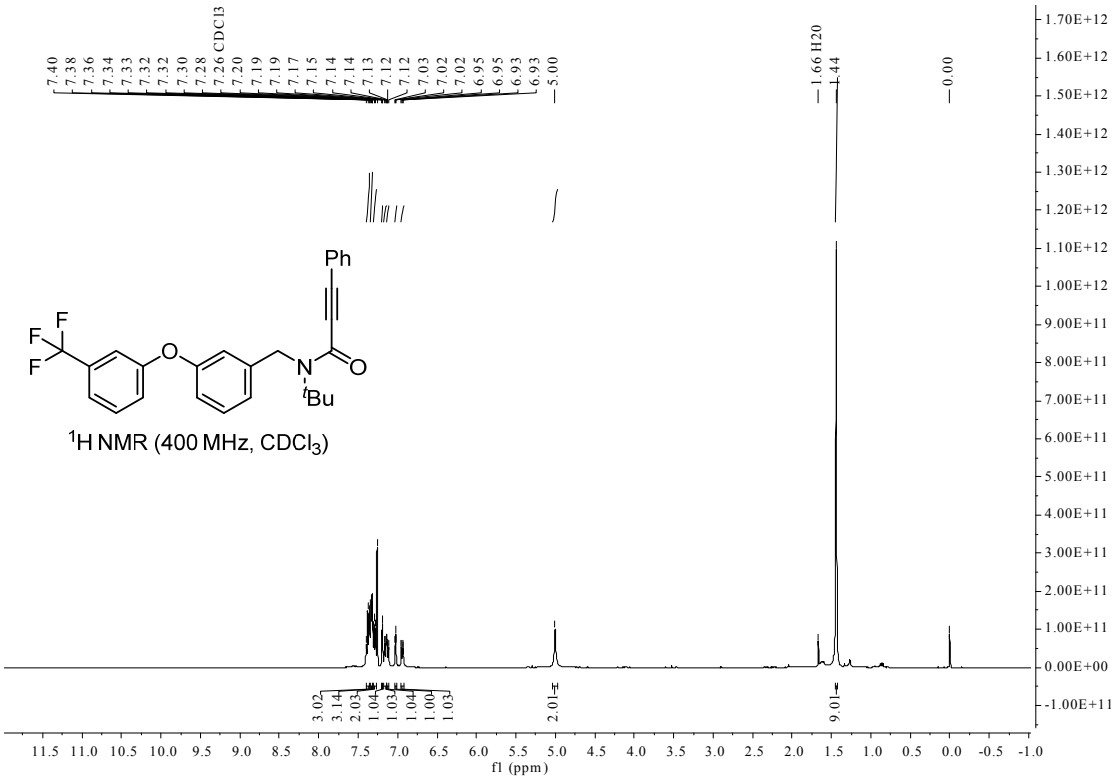

157.7
157.2
156.2
141.6
132.4
130.1
129.9
128.5
123.5
121.2
120.8
118.9
117.7
117.0
87.9
83.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
58.5
51.1
28.5
Ph
PhO
N
O
tBu
13C NMR (101 MHz, CDCl3)
f1 (ppm)

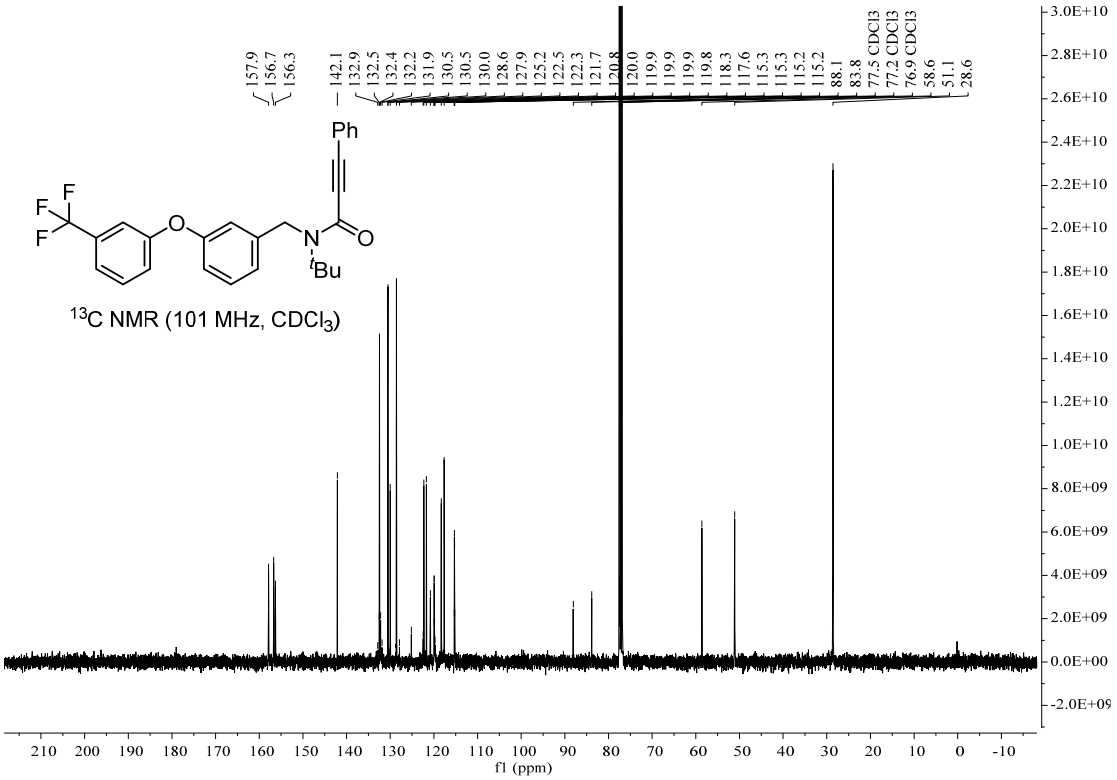
Compound S10

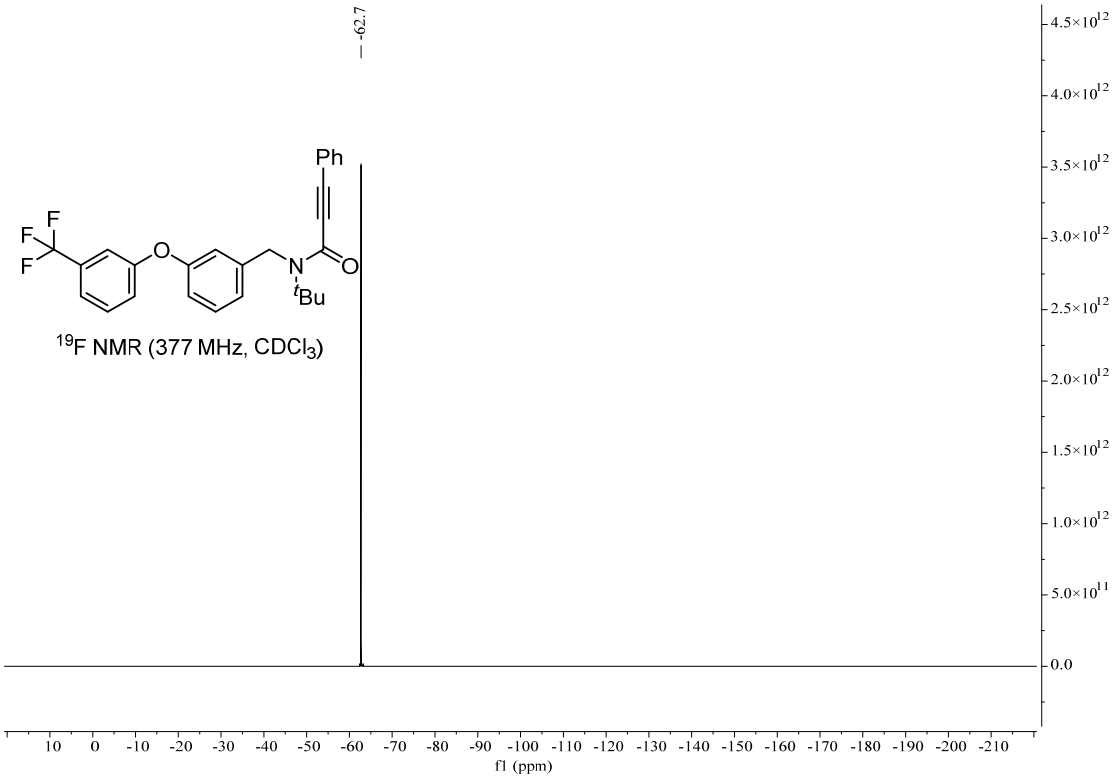




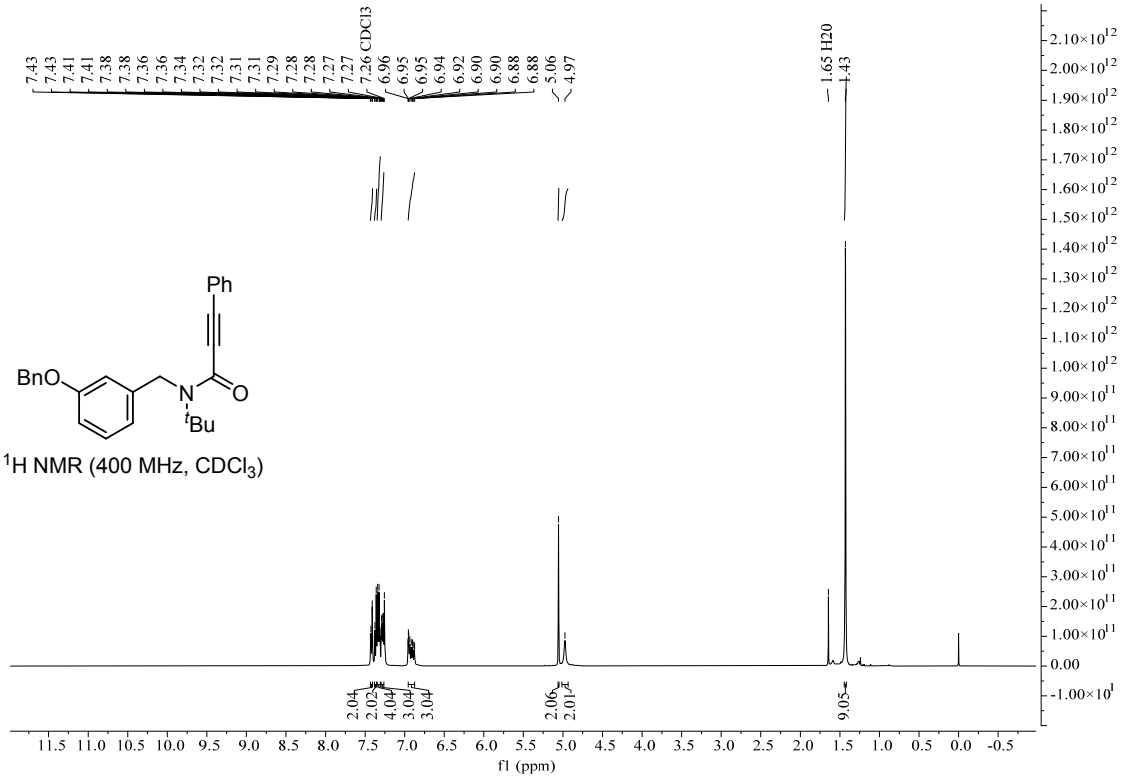
Compound S11



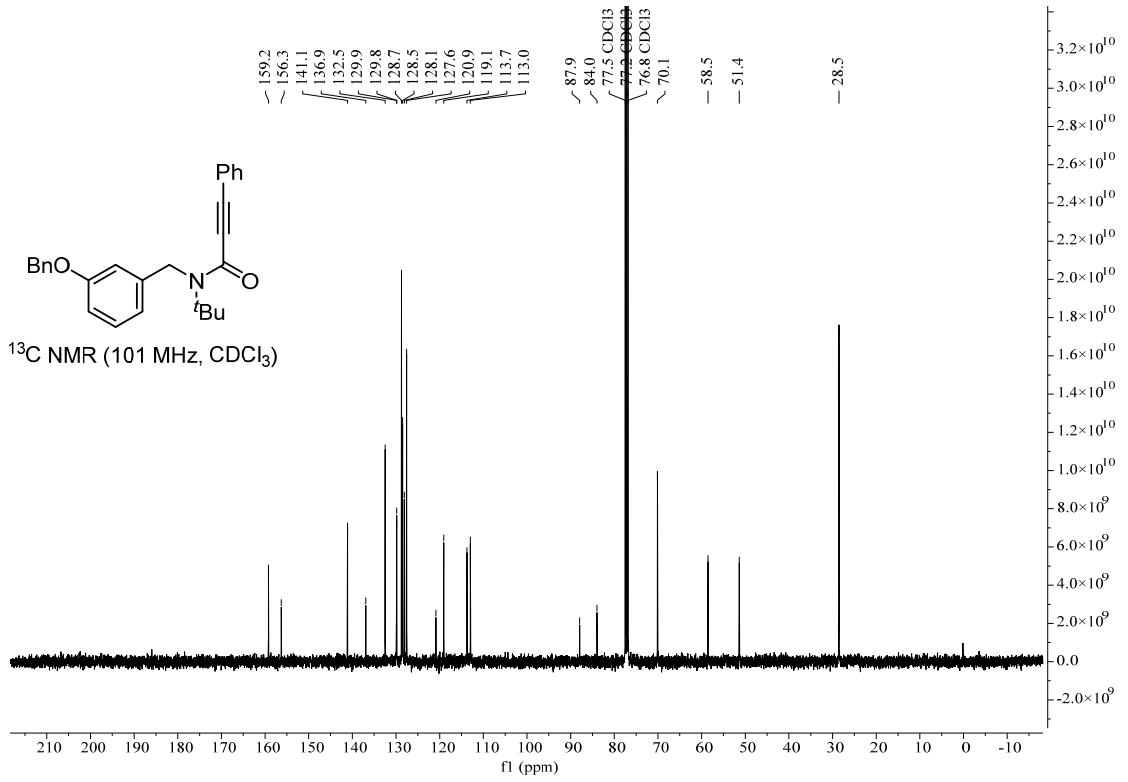



-62.7
Ph
F
F
F
O
N
O
tBu
19F NMR (377 MHz, CDCl3)
4.5×10^12
4.0×10^12
3.5×10^12
3.0×10^12
2.5×10^12
2.0×10^12
1.5×10^12
1.0×10^12
5.0×10^11
0.0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound S12

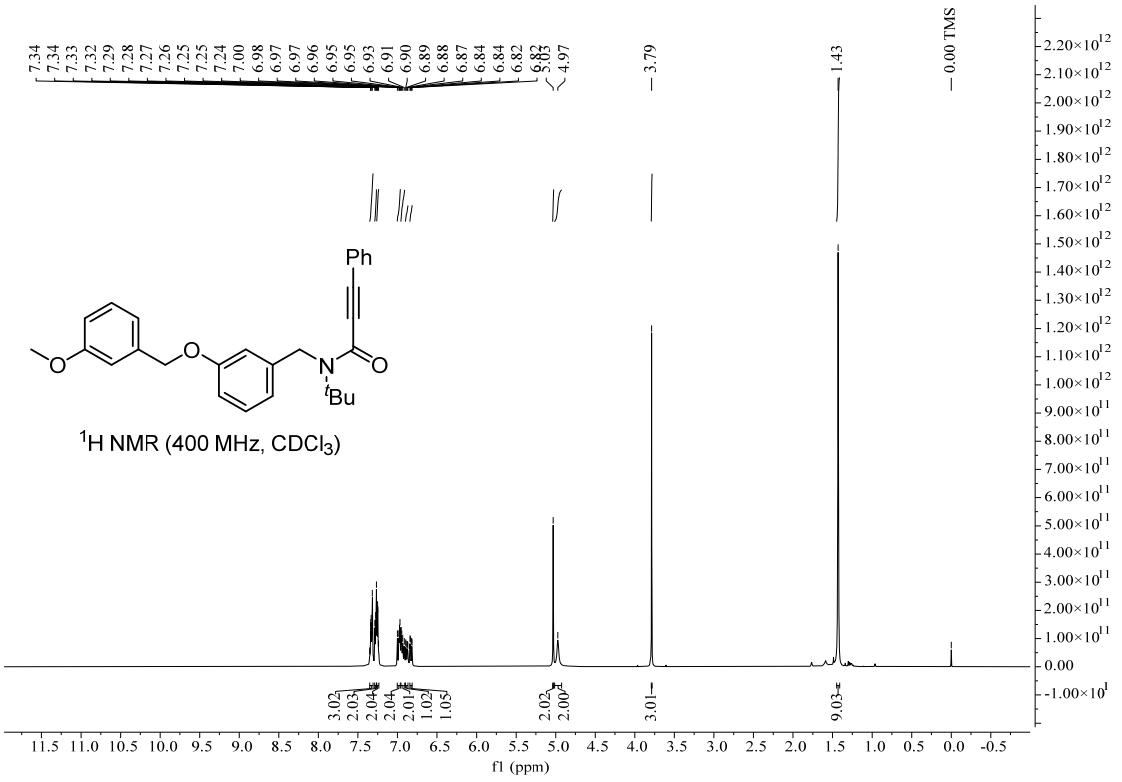


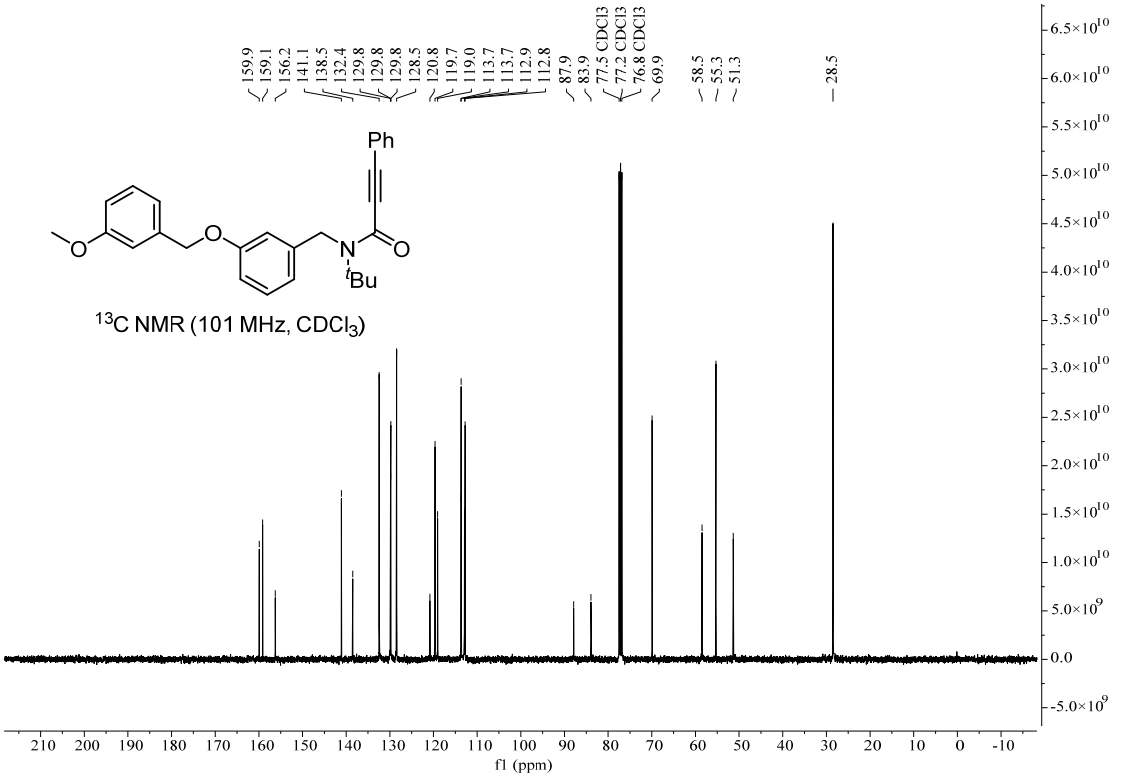
^{1}H NMR (400 MHz, $CDCl_3$)



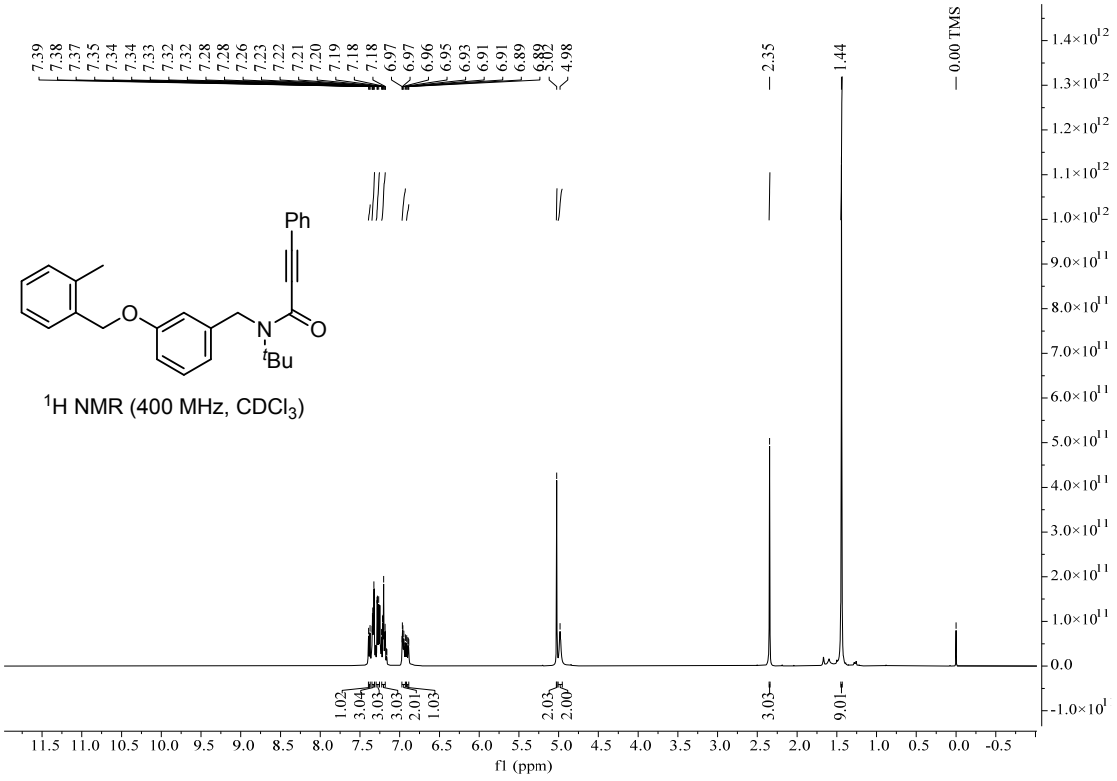
^{13}C NMR (101 MHz, $CDCl_3$)

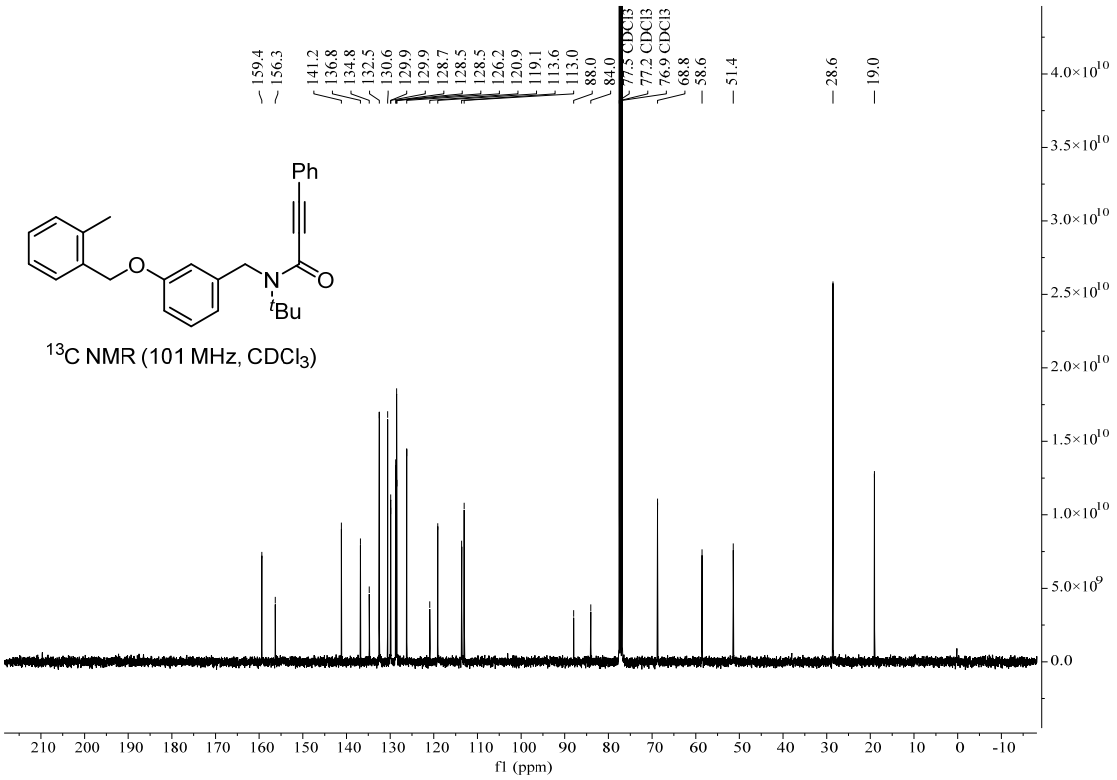
Compound S13



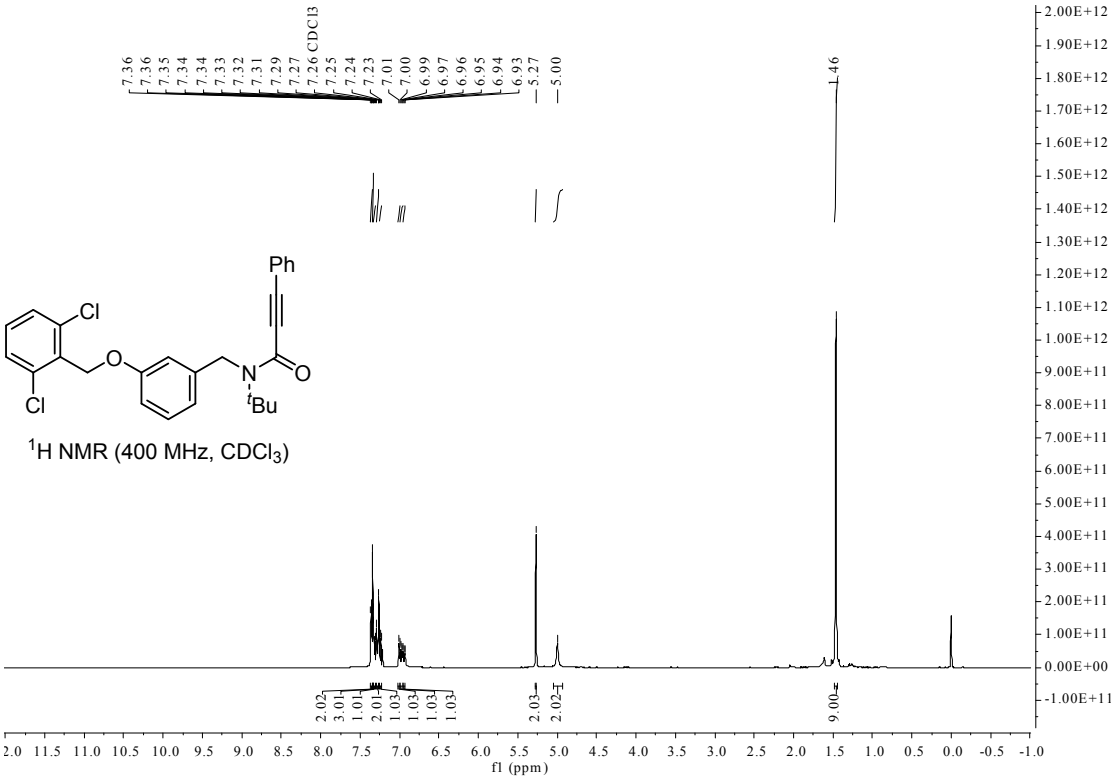


Compound S14

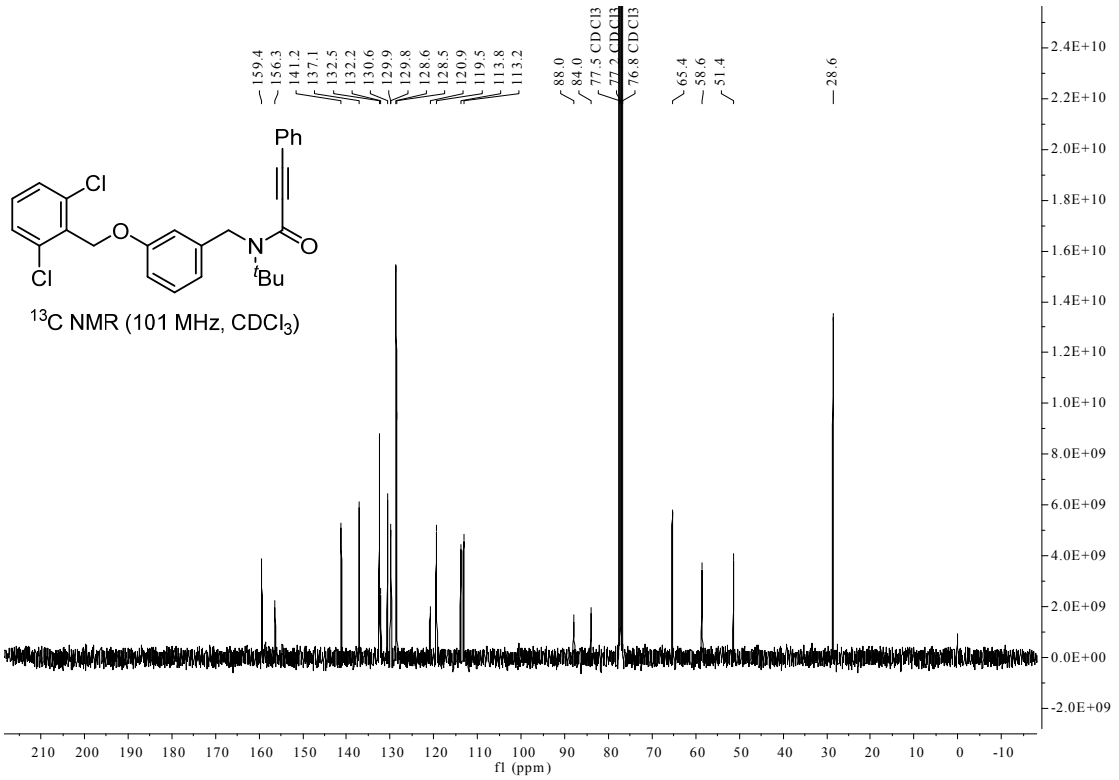




Compound S15

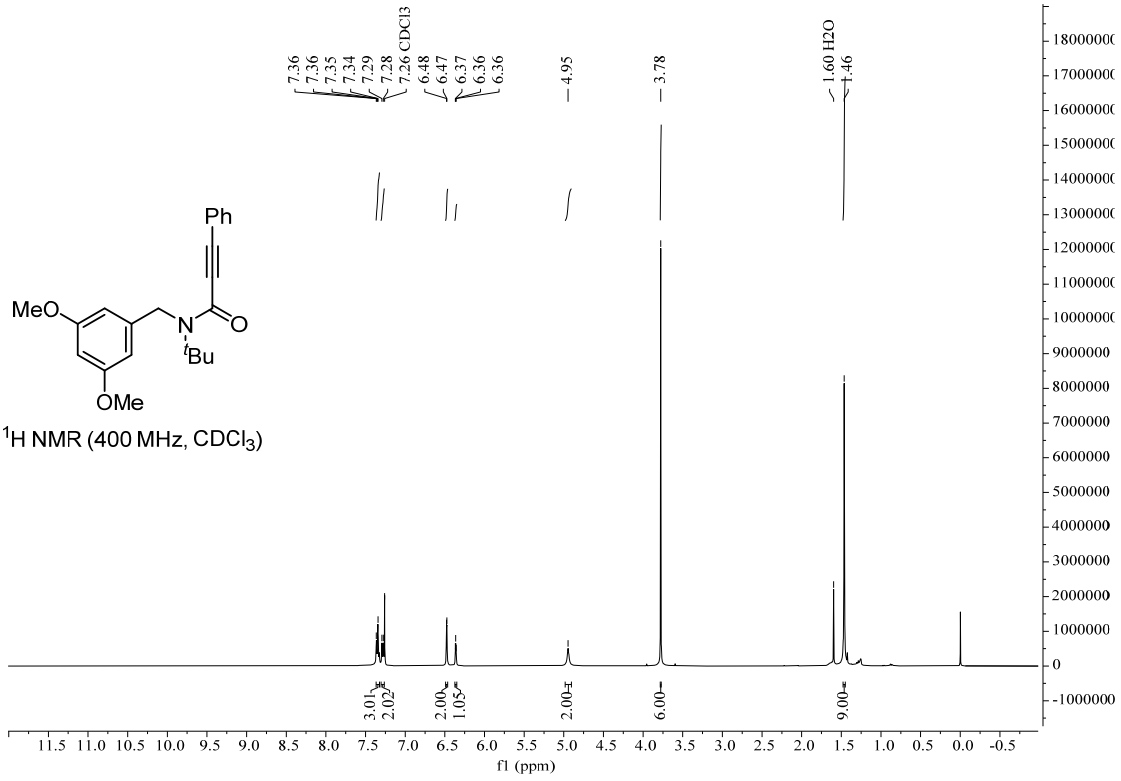


^{1}H NMR (400 MHz, $CDCl_3$)

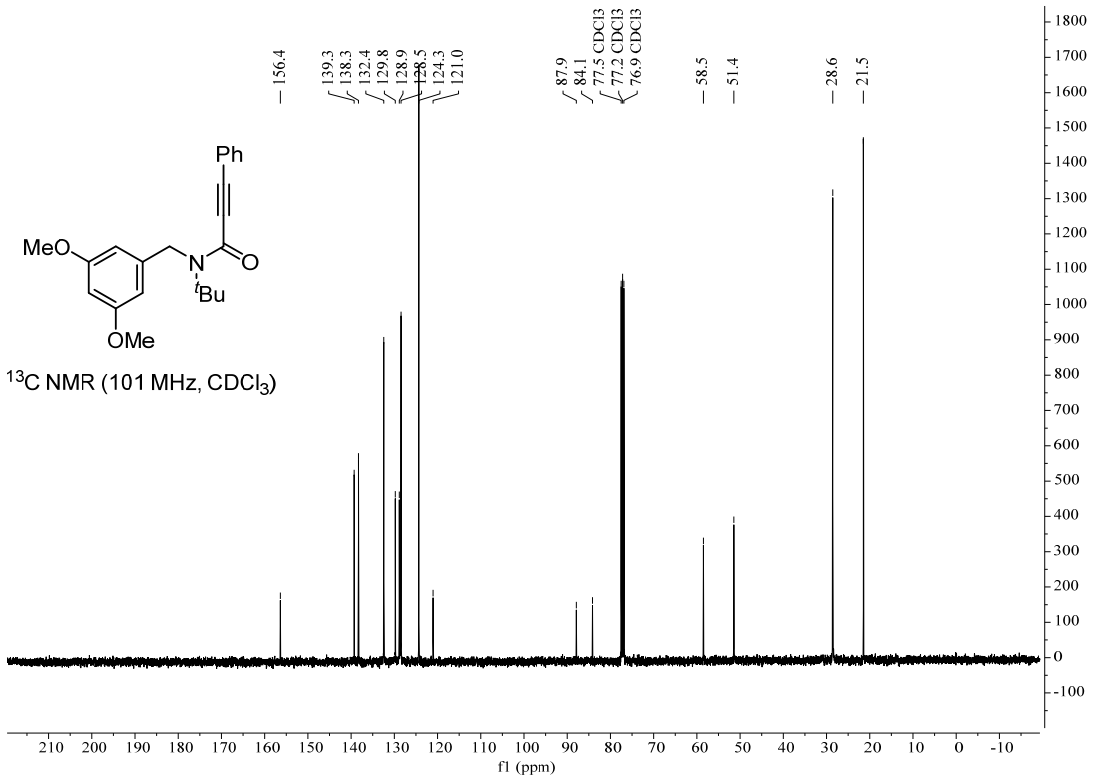


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S16

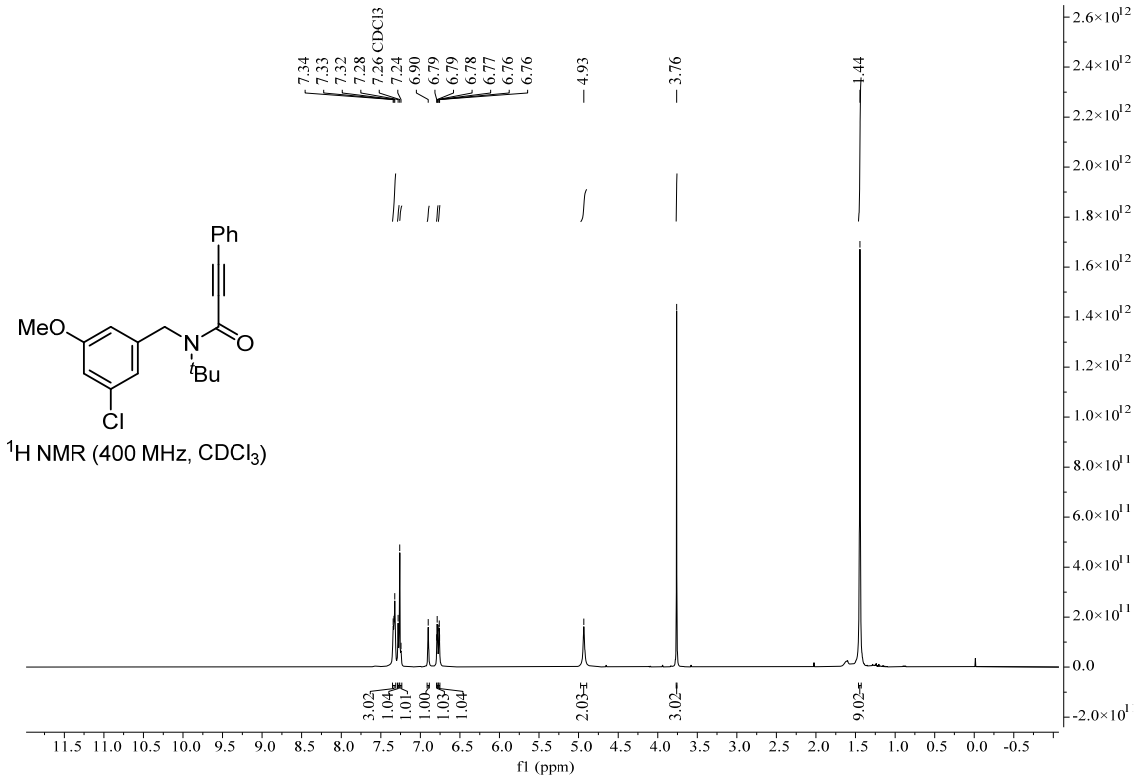


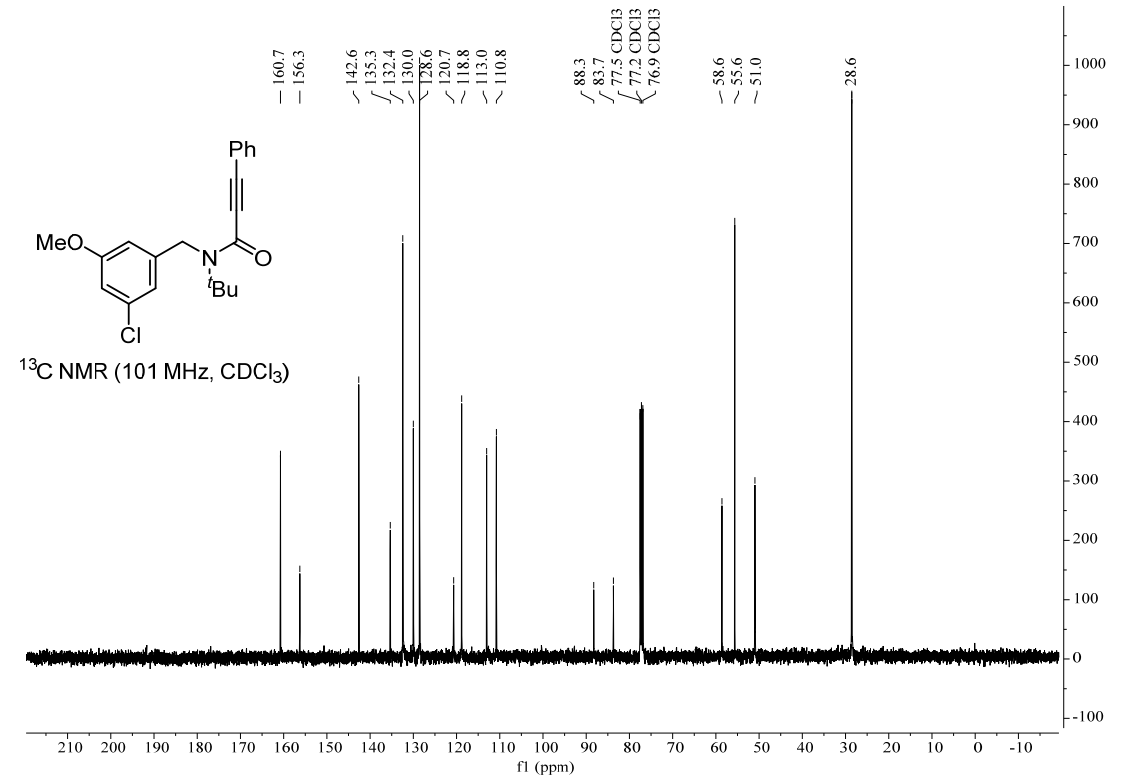
^{1}H NMR (400 MHz, $CDCl_3$)



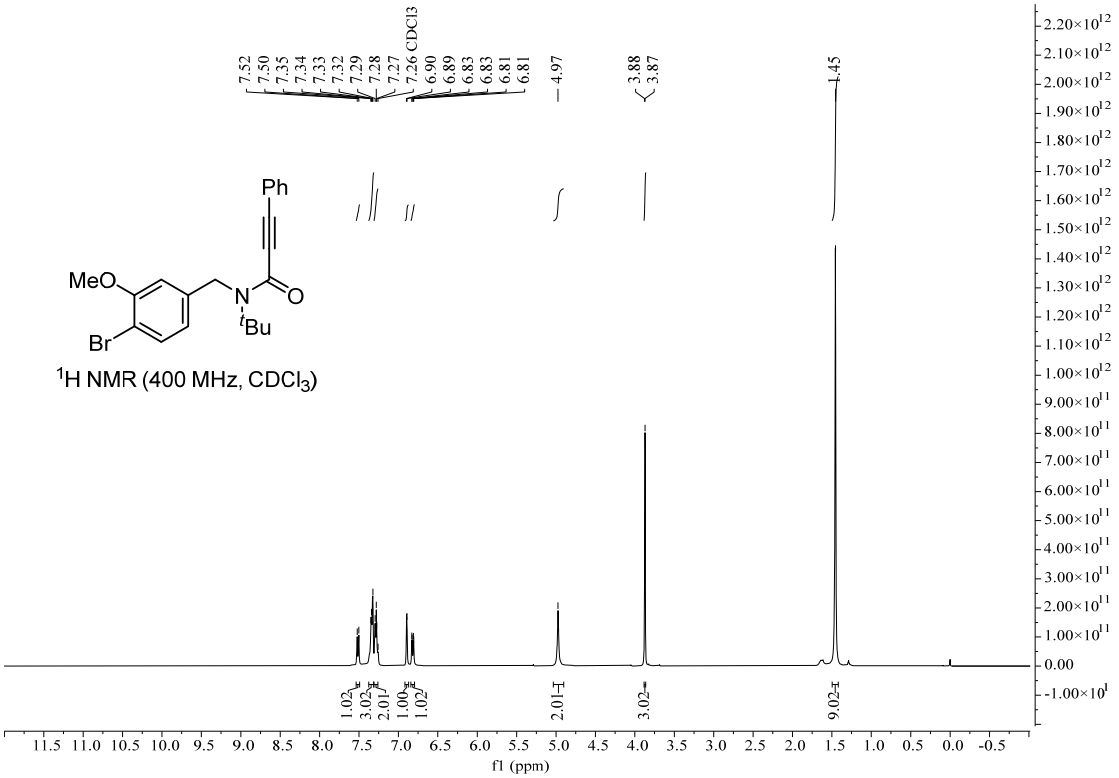
^{13}C NMR (101 MHz, $CDCl_3$)

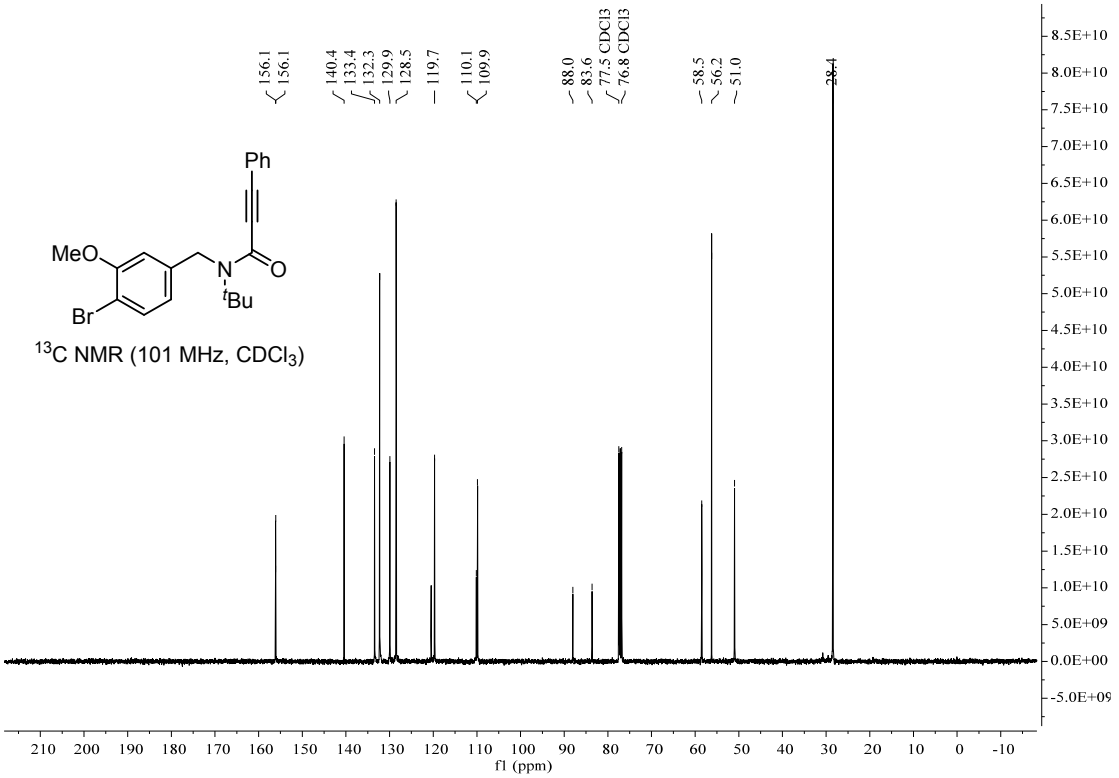
Compound S17



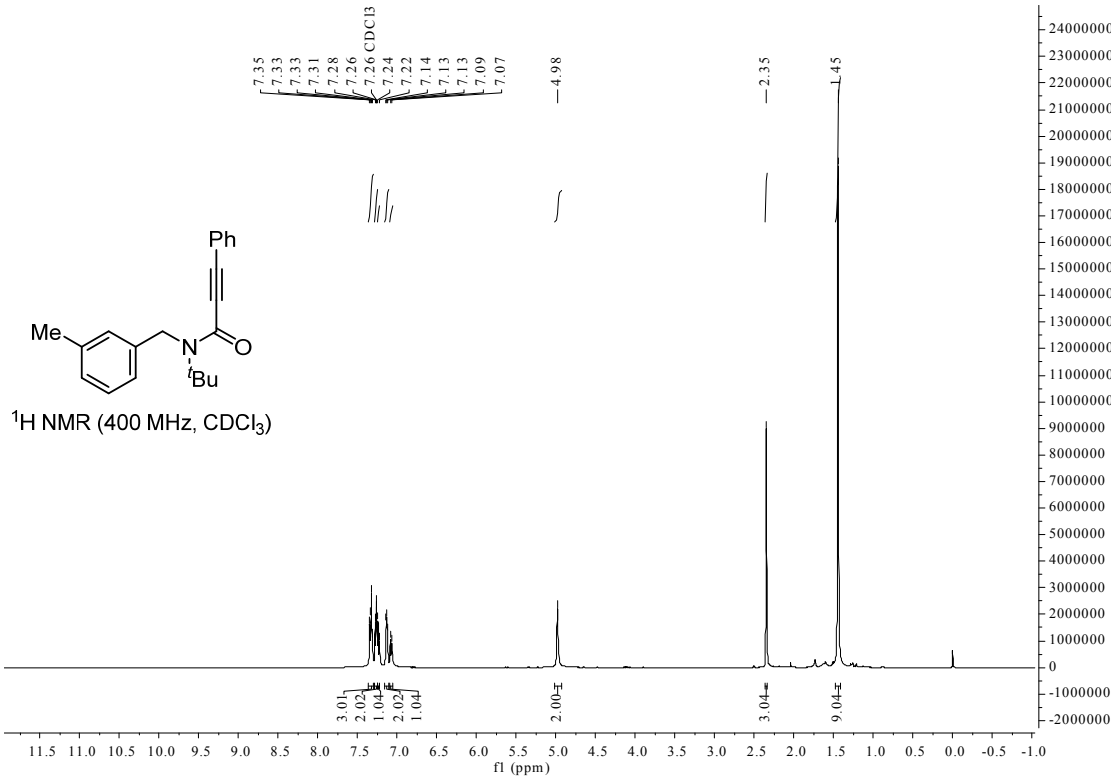


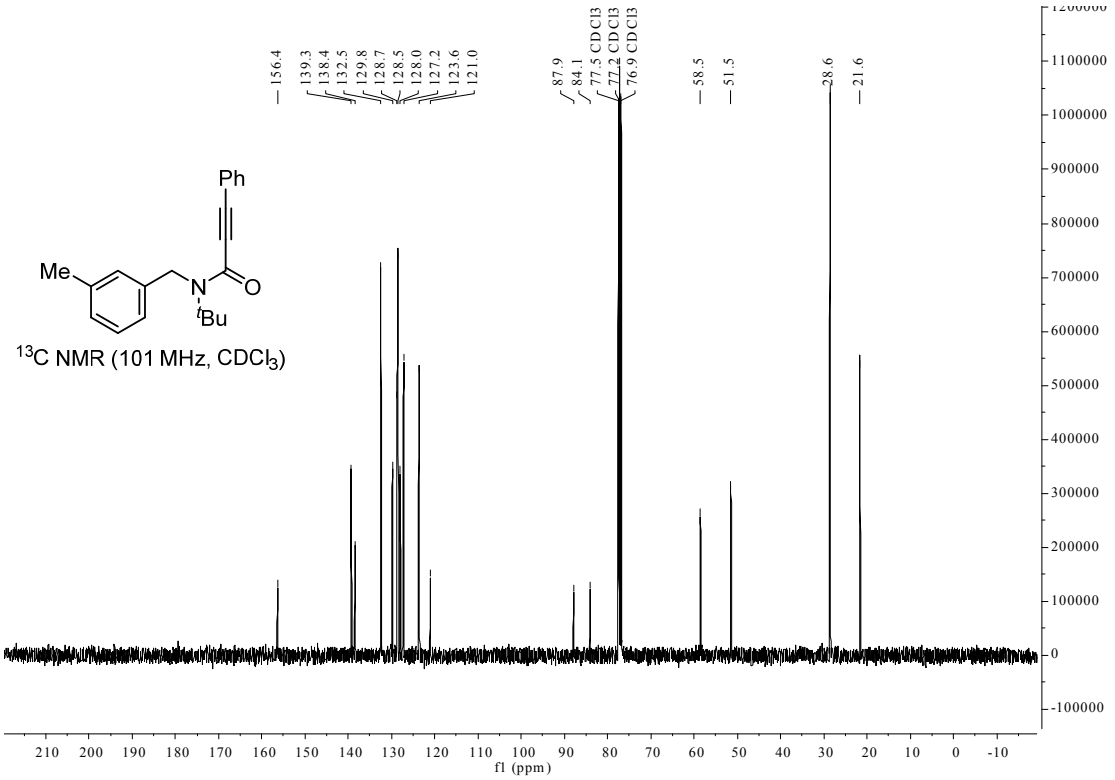
Compound S18



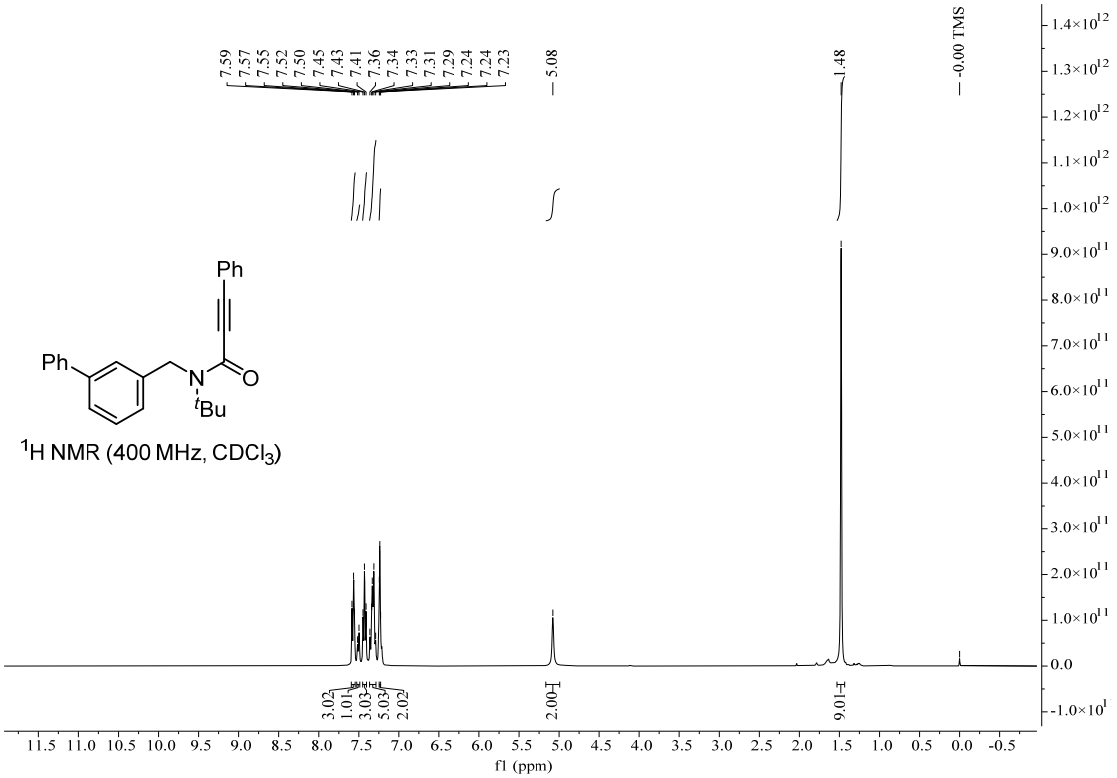


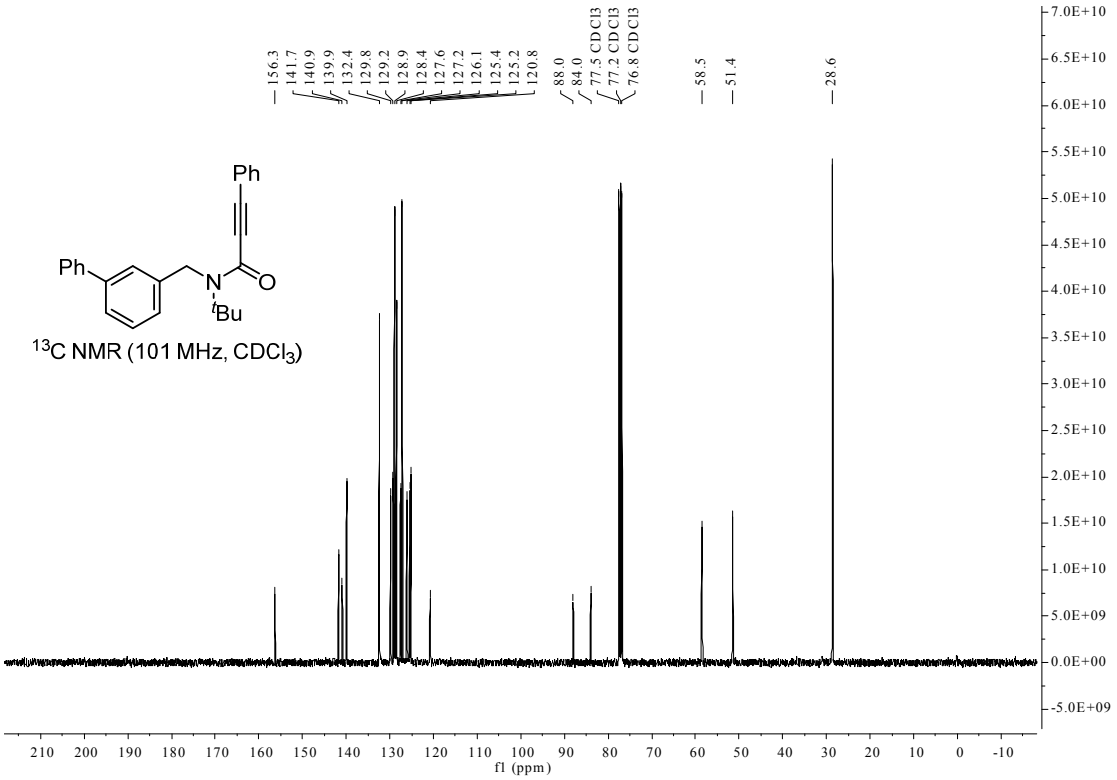
Compound S19



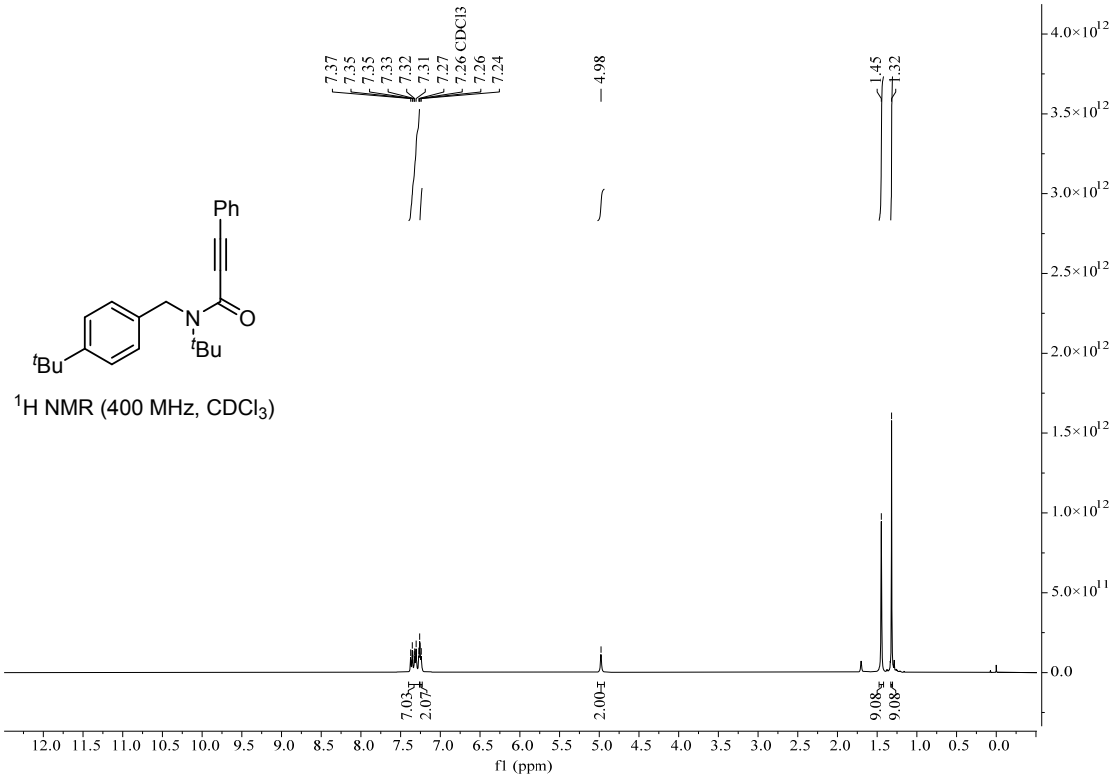


Compound S20

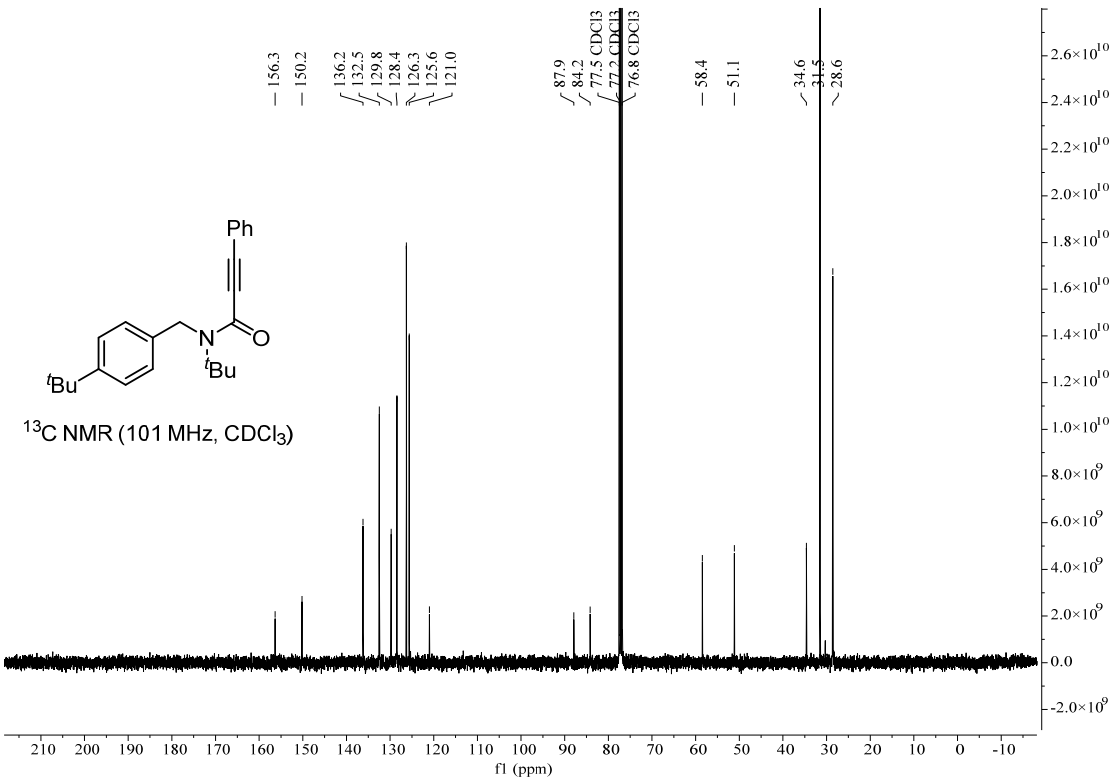




Compound S21

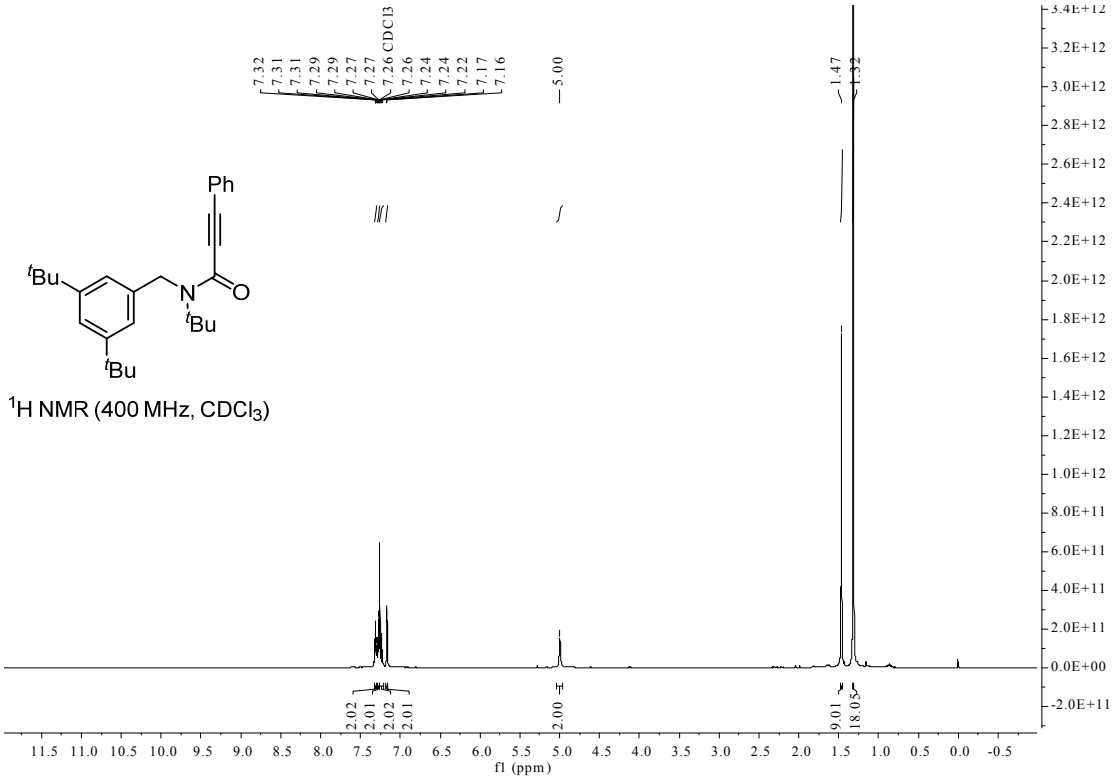


^{1}H NMR (400 MHz, $CDCl_3$)

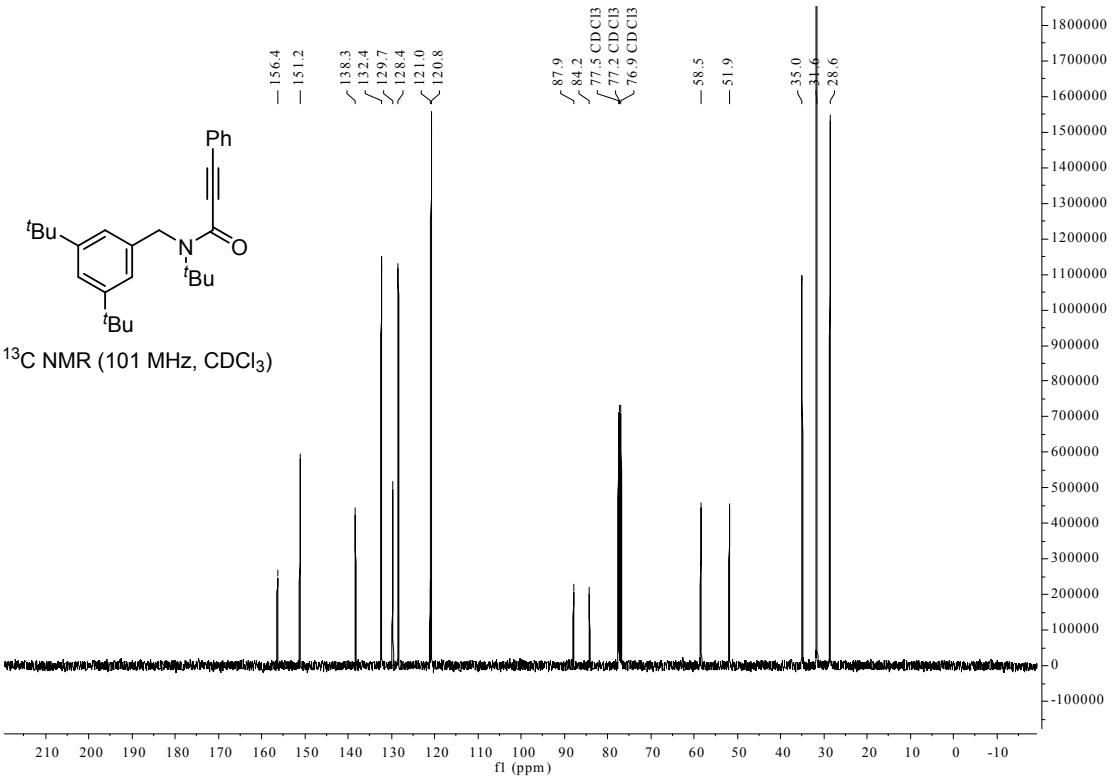


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S22

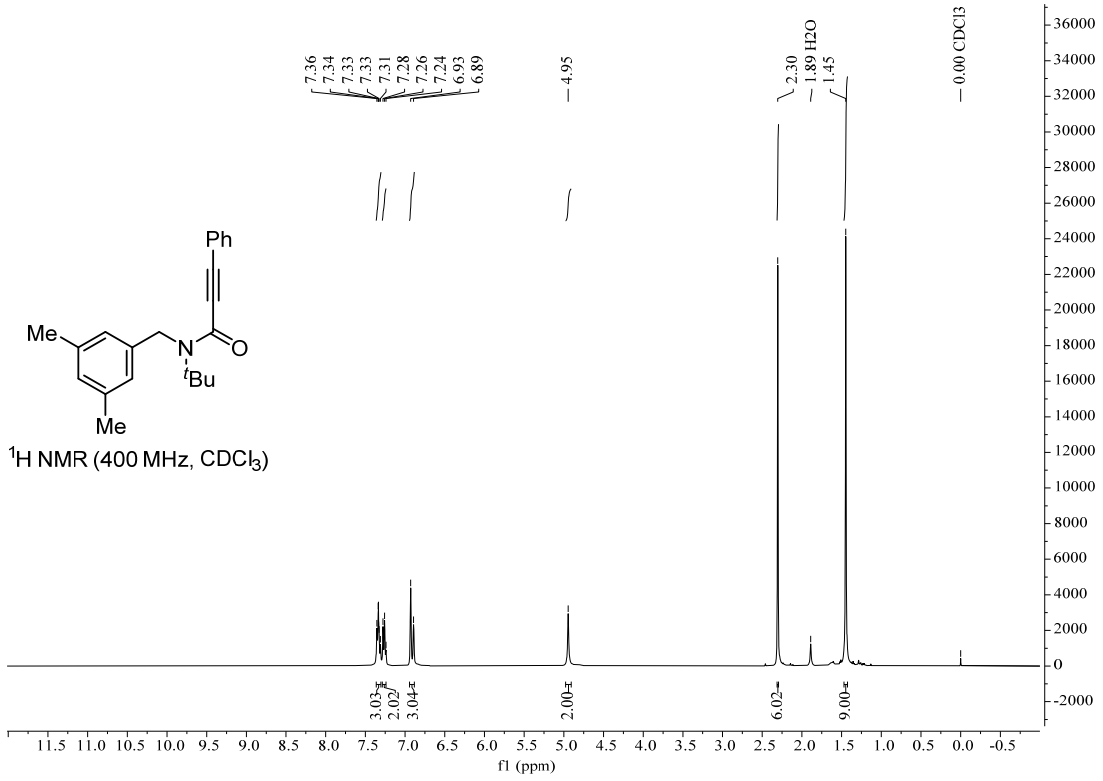


^{1}H NMR (400 MHz, $CDCl_3$)

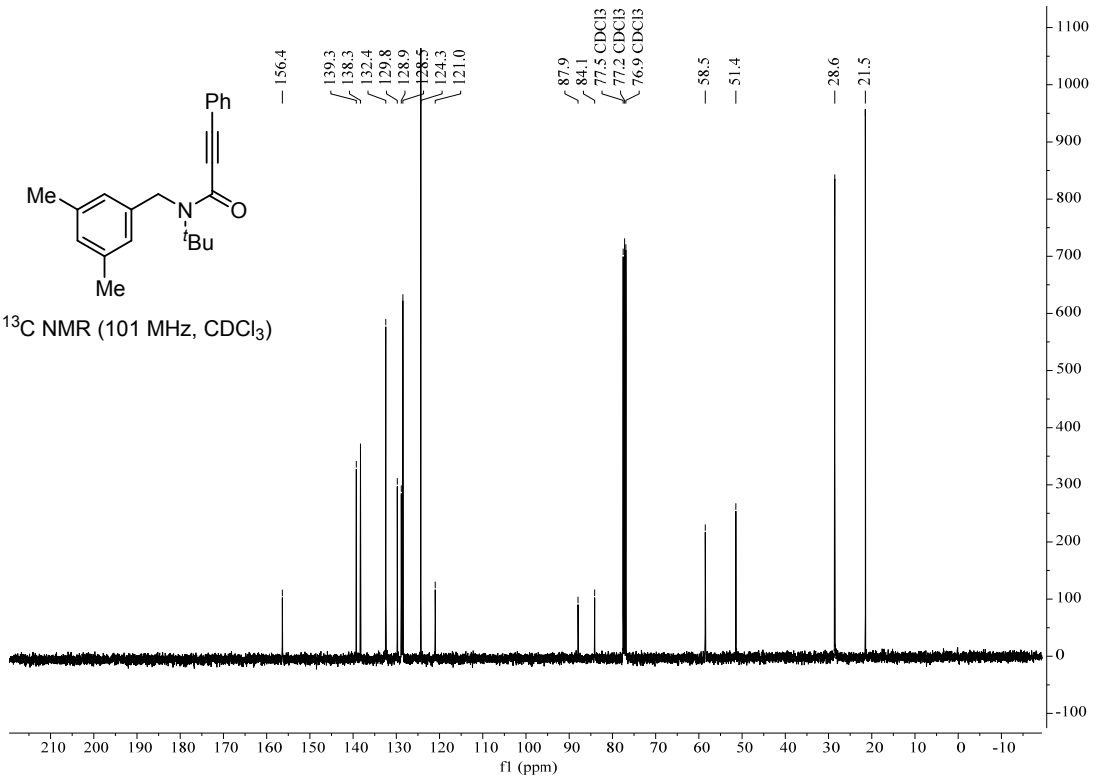


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S23

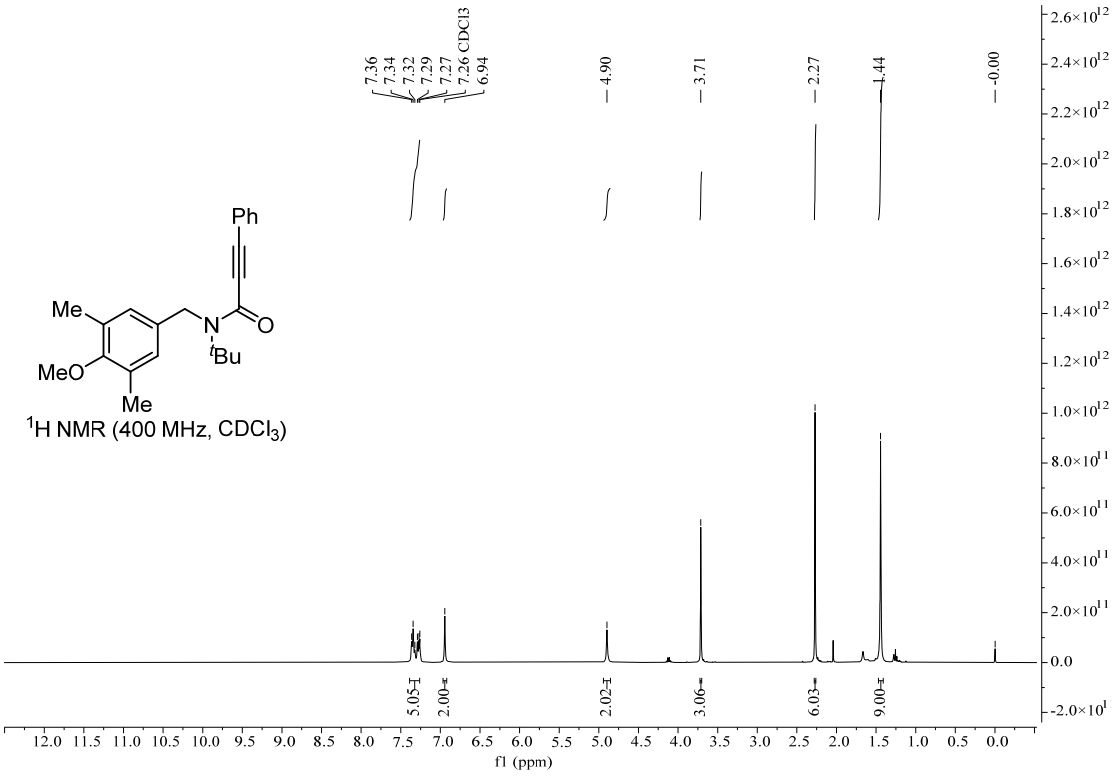


^{1}H NMR (400 MHz, $CDCl_3$)

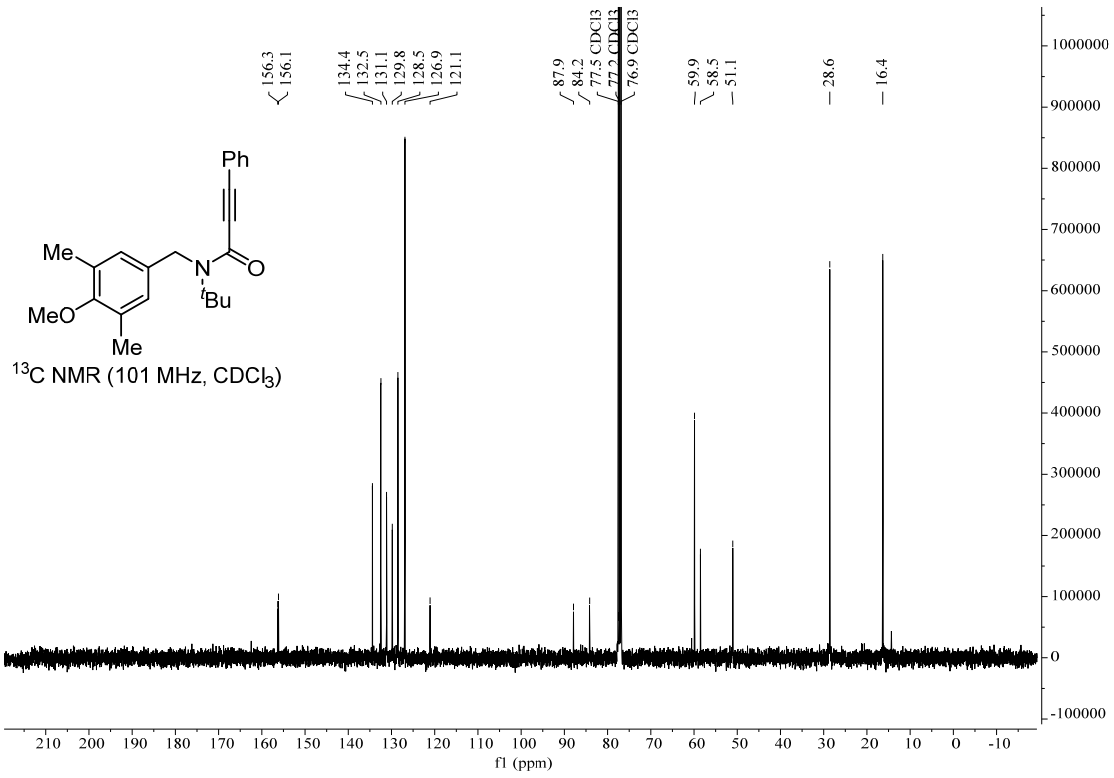


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S24

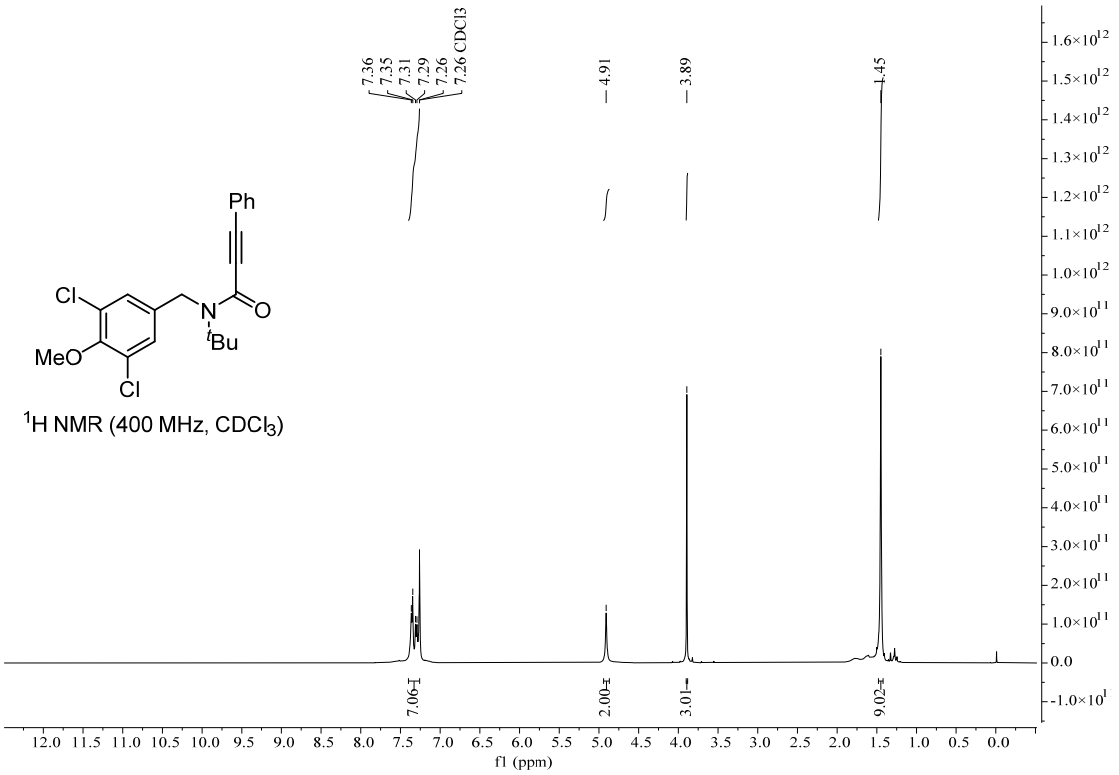


^{1}H NMR (400 MHz, $CDCl_3$)

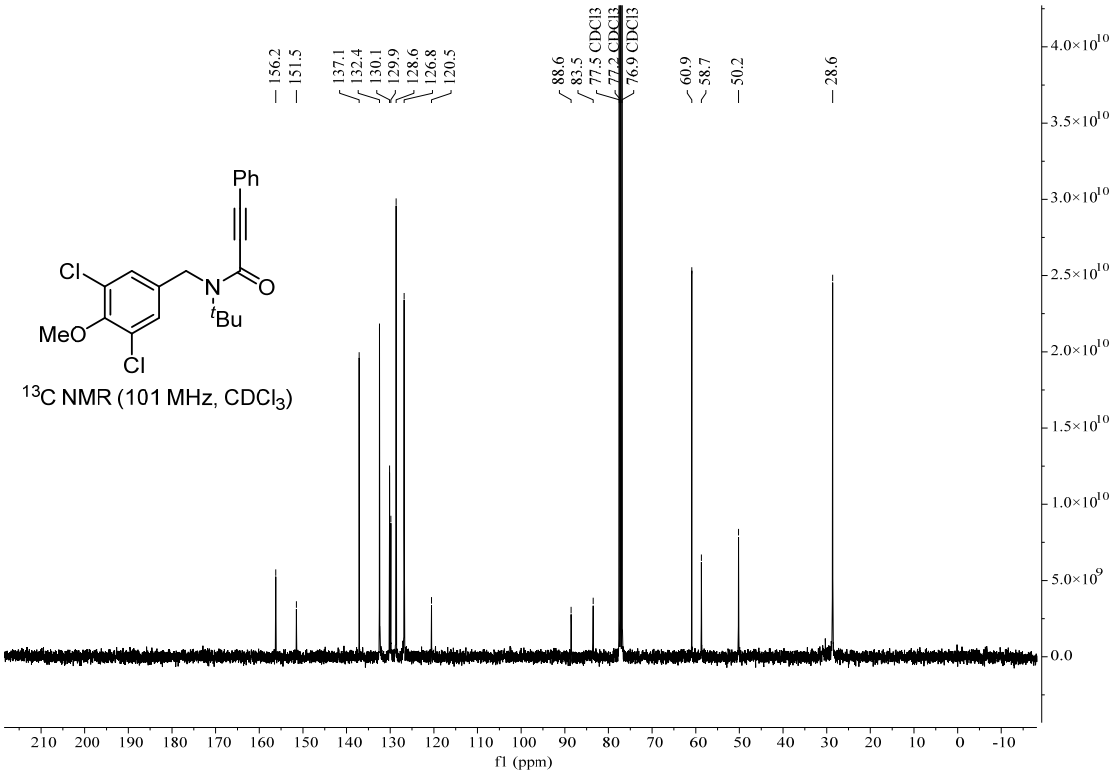


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S25

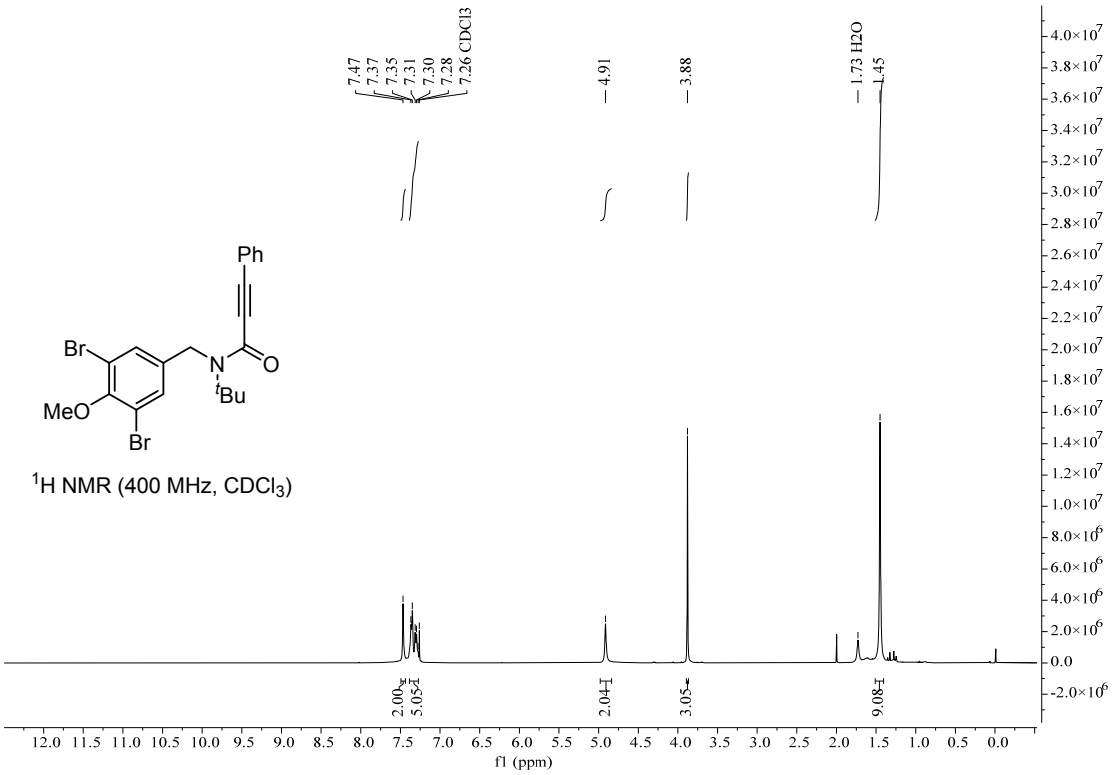


^{1}H NMR (400 MHz, $CDCl_3$)

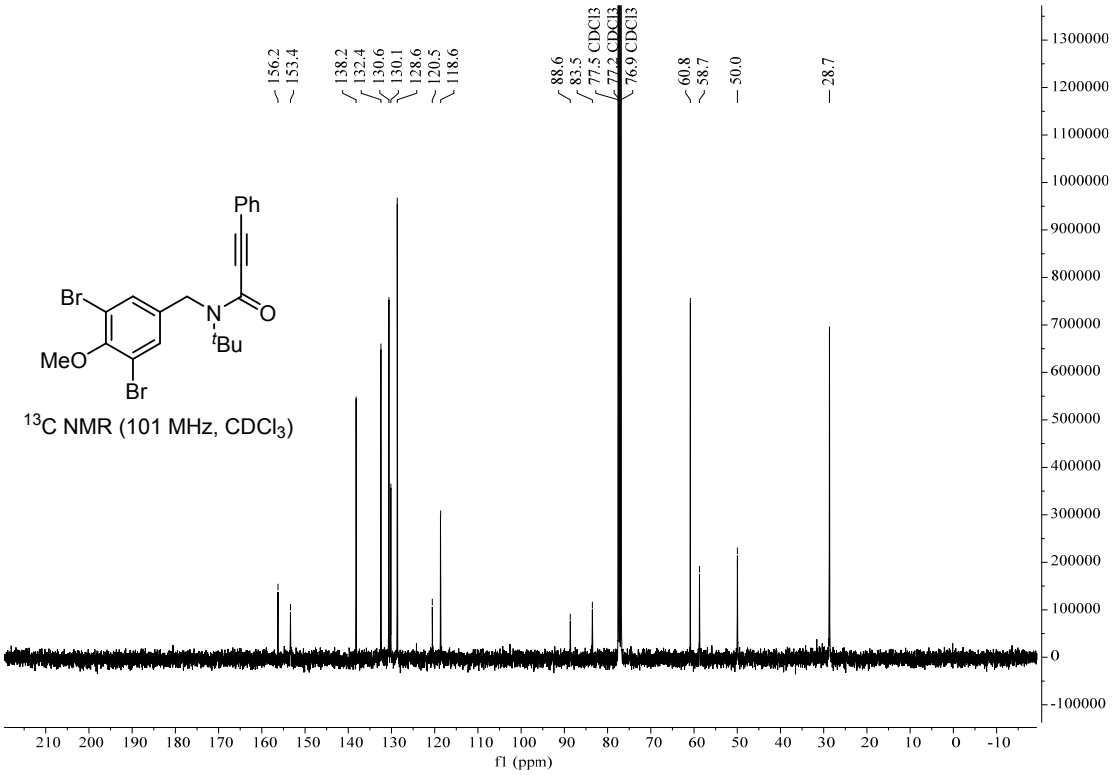


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S26

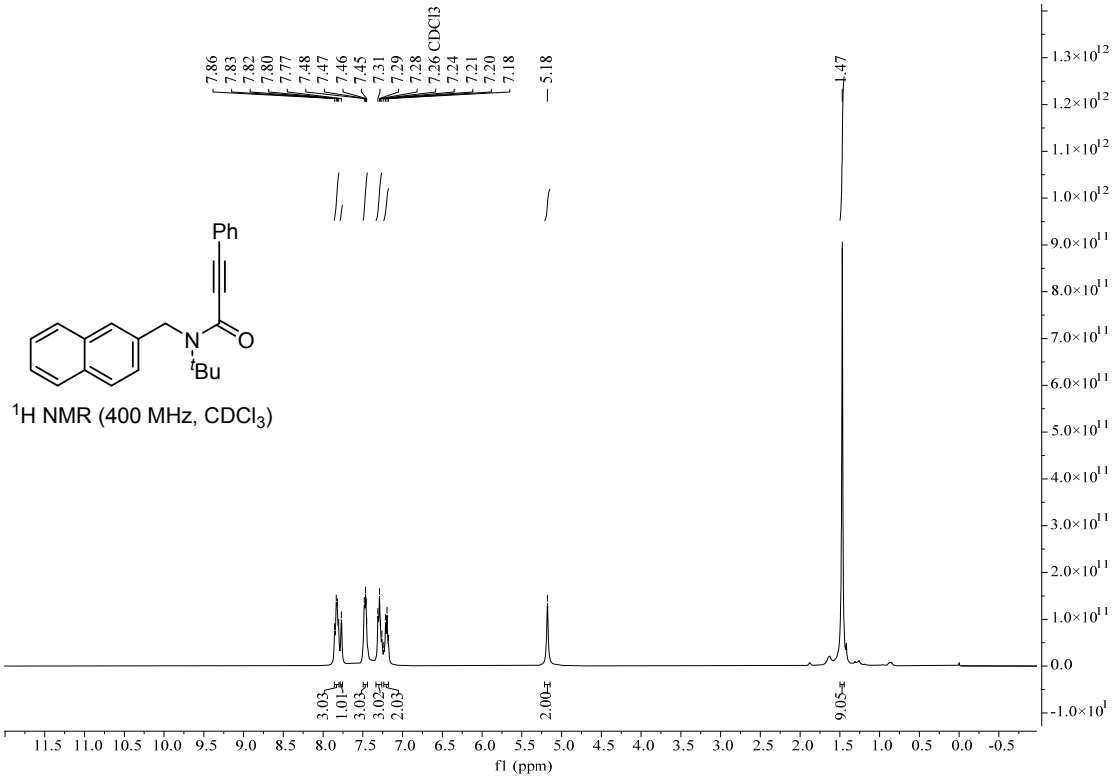


^{1}H NMR (400 MHz, $CDCl_3$)

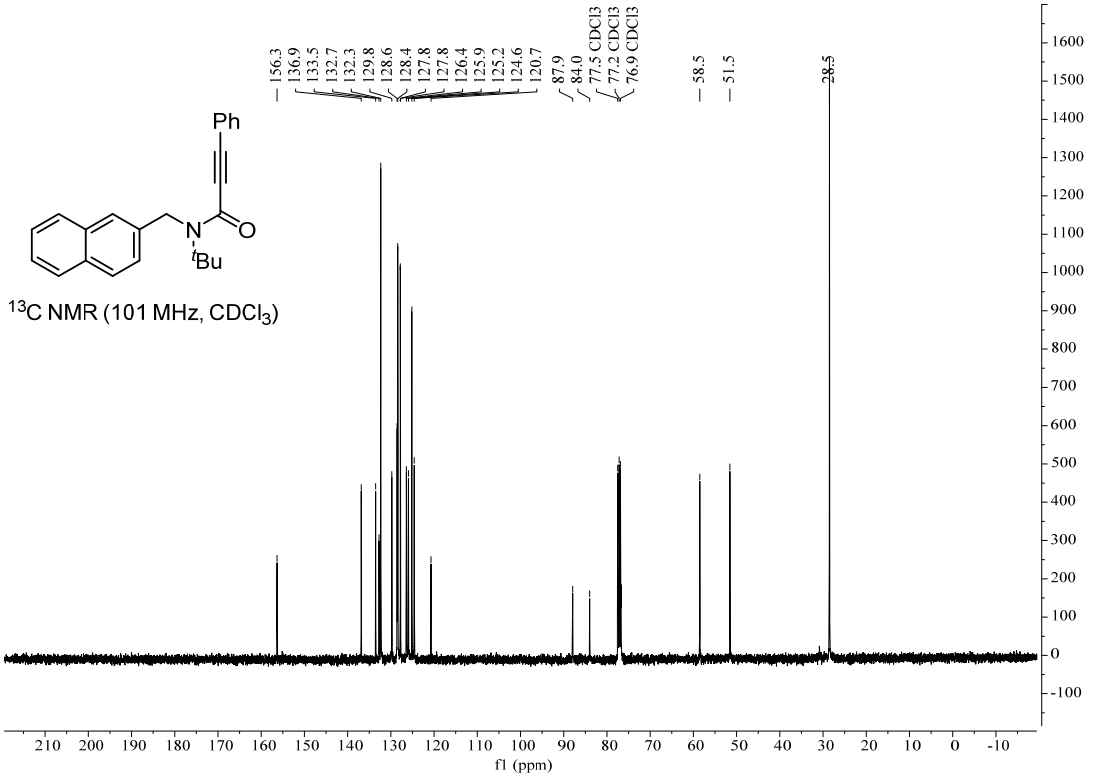


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S27

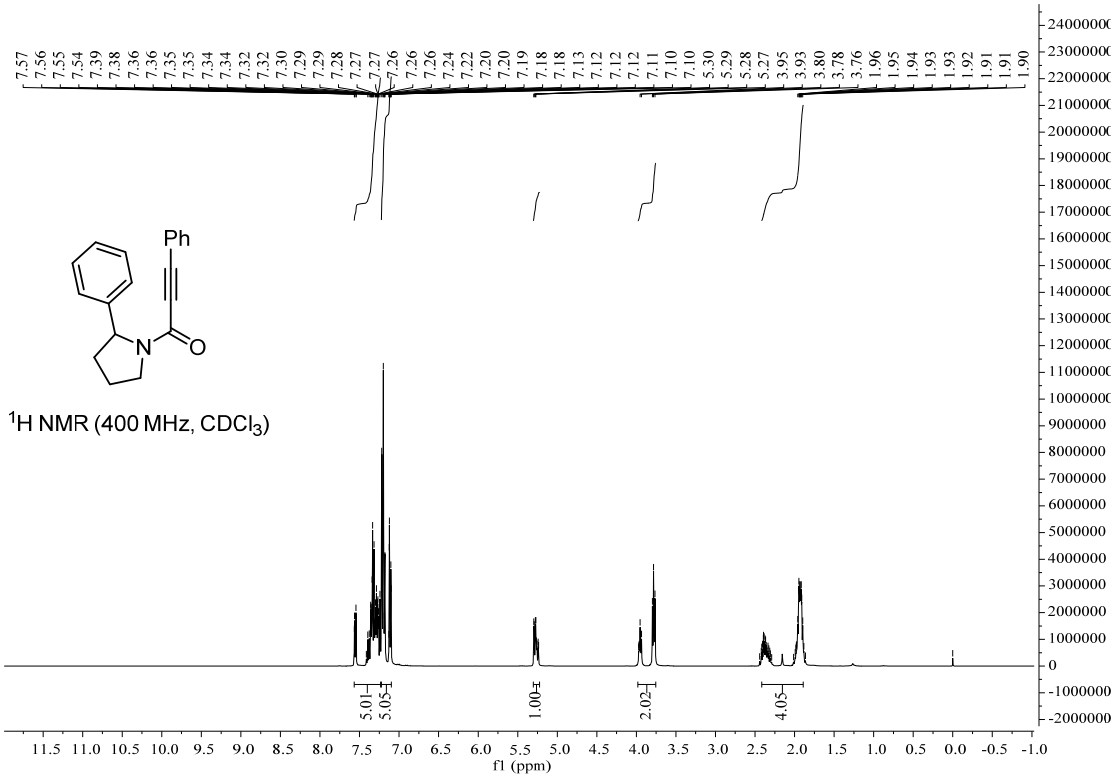


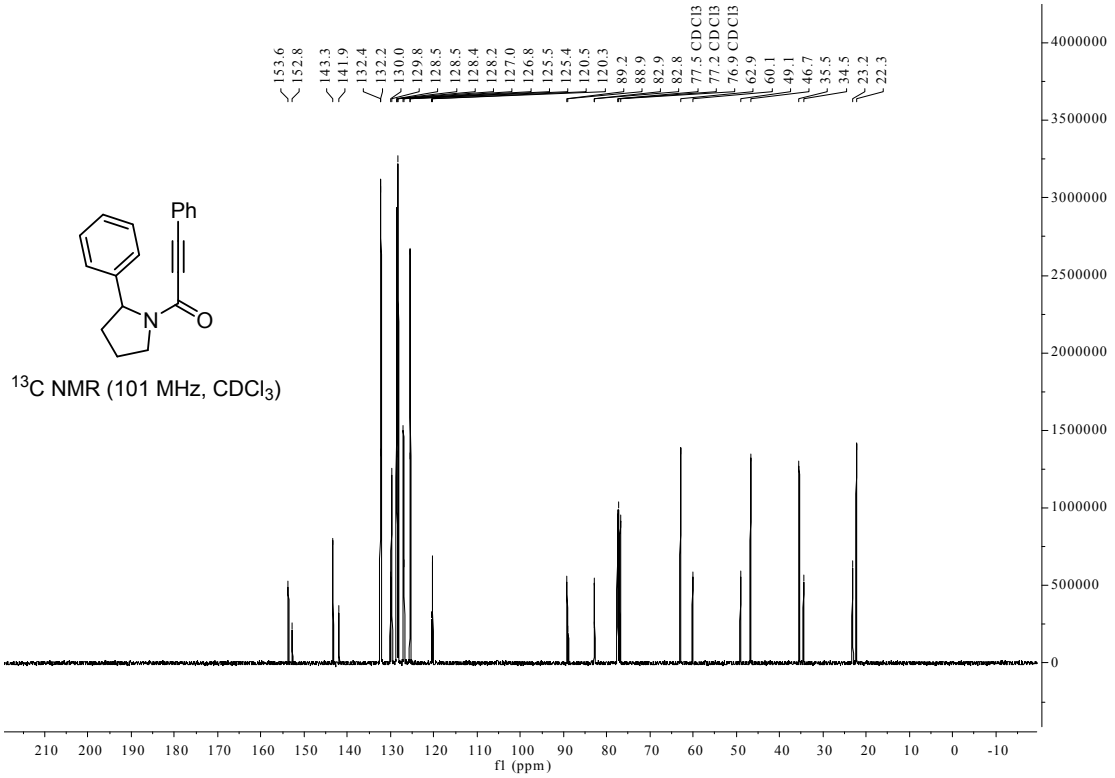
^{1}H NMR (400 MHz, $CDCl_3$)



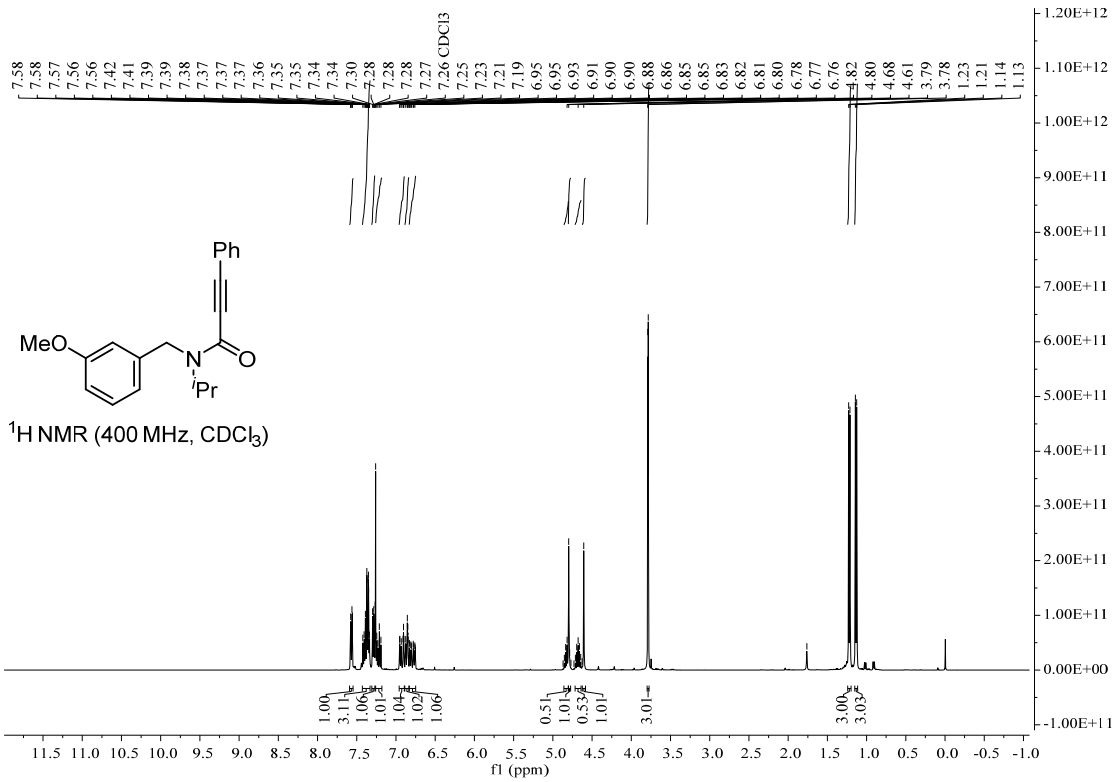
^{13}C NMR (101 MHz, $CDCl_3$)

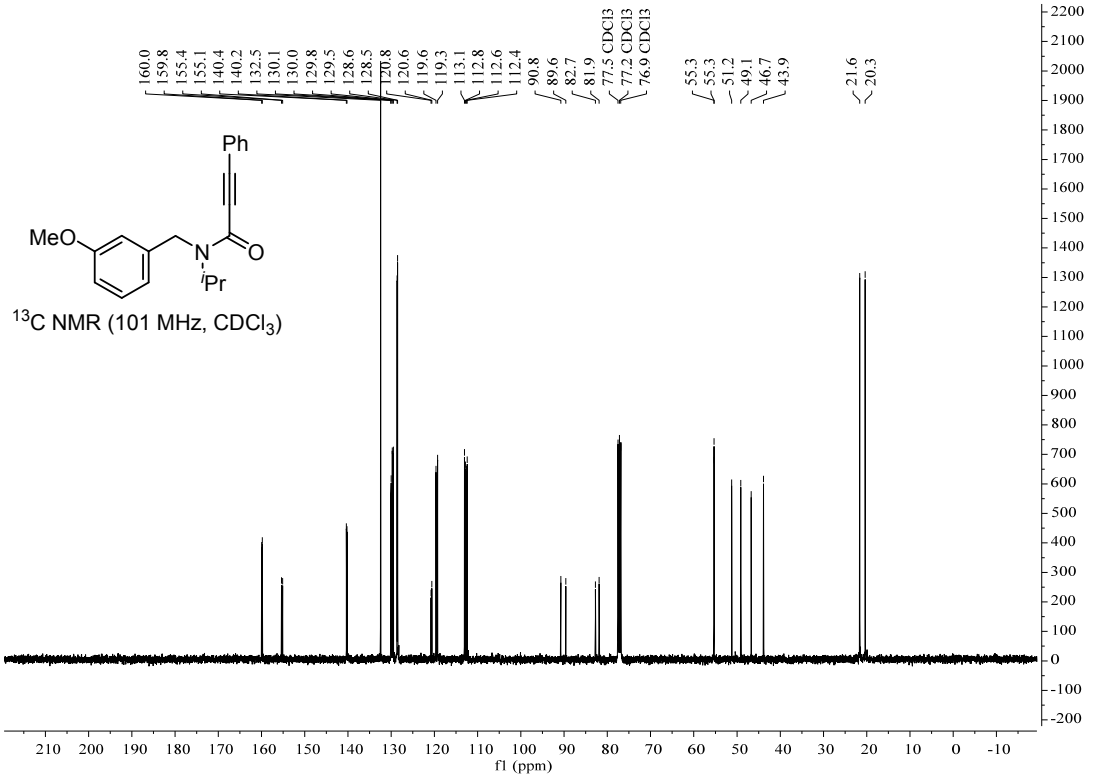
Compound S28



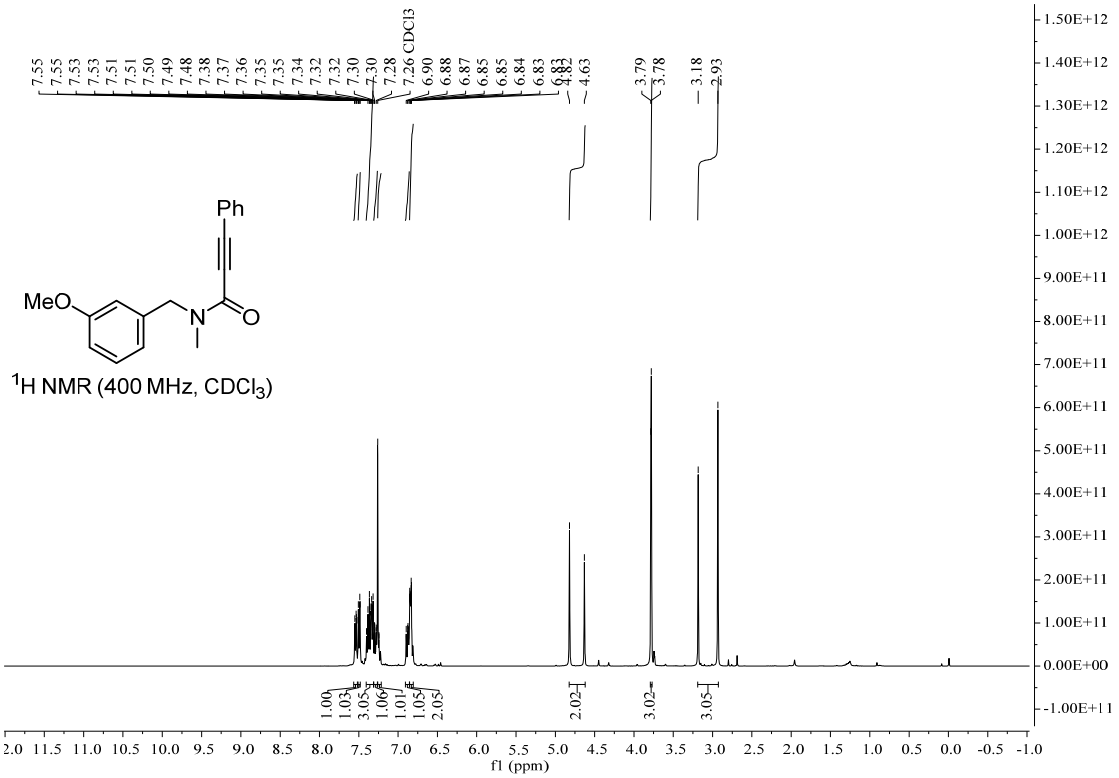


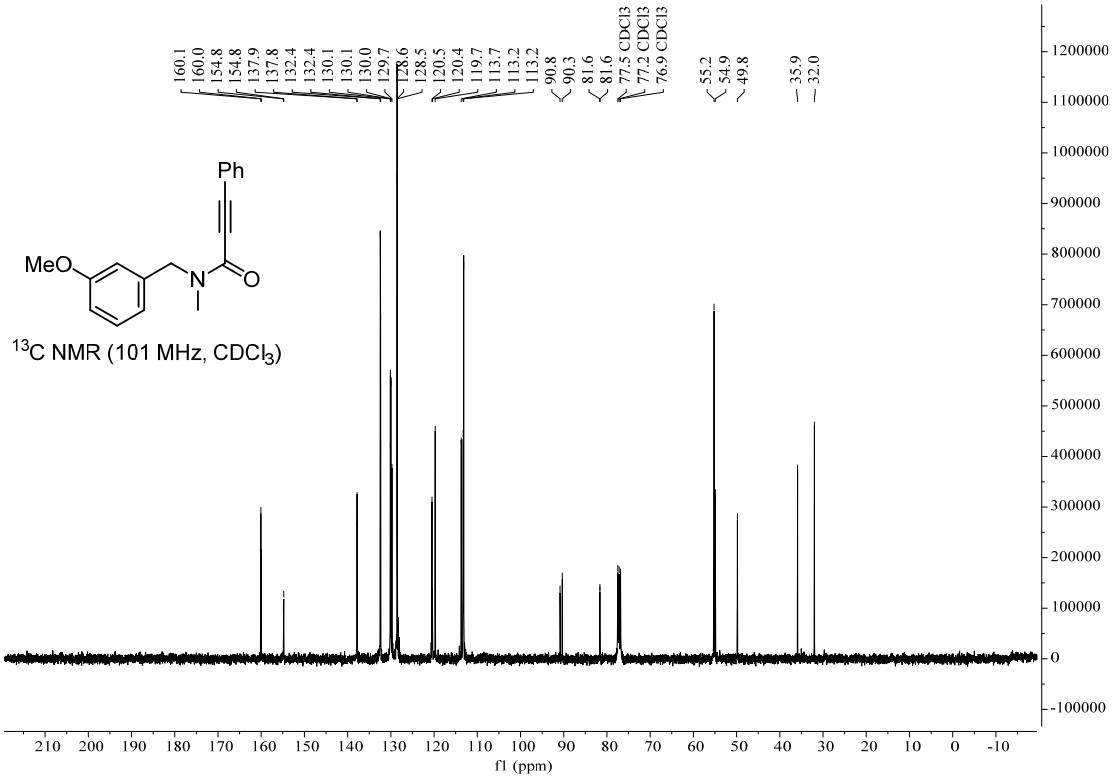
Compound S29



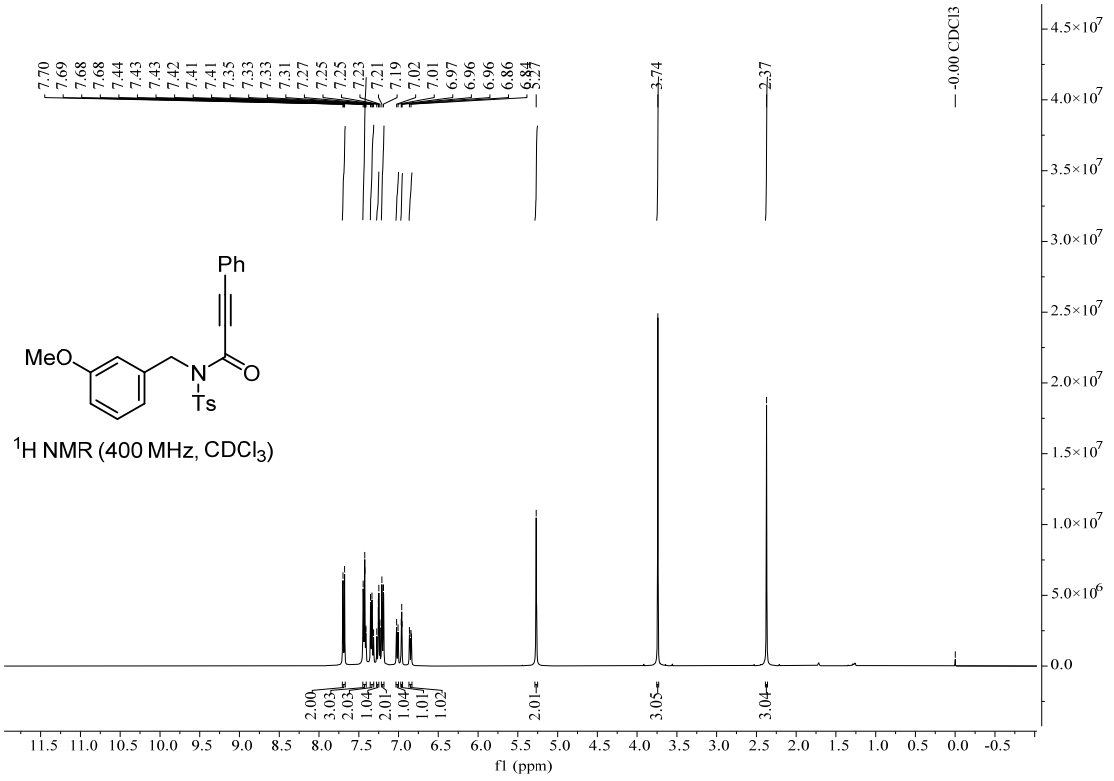


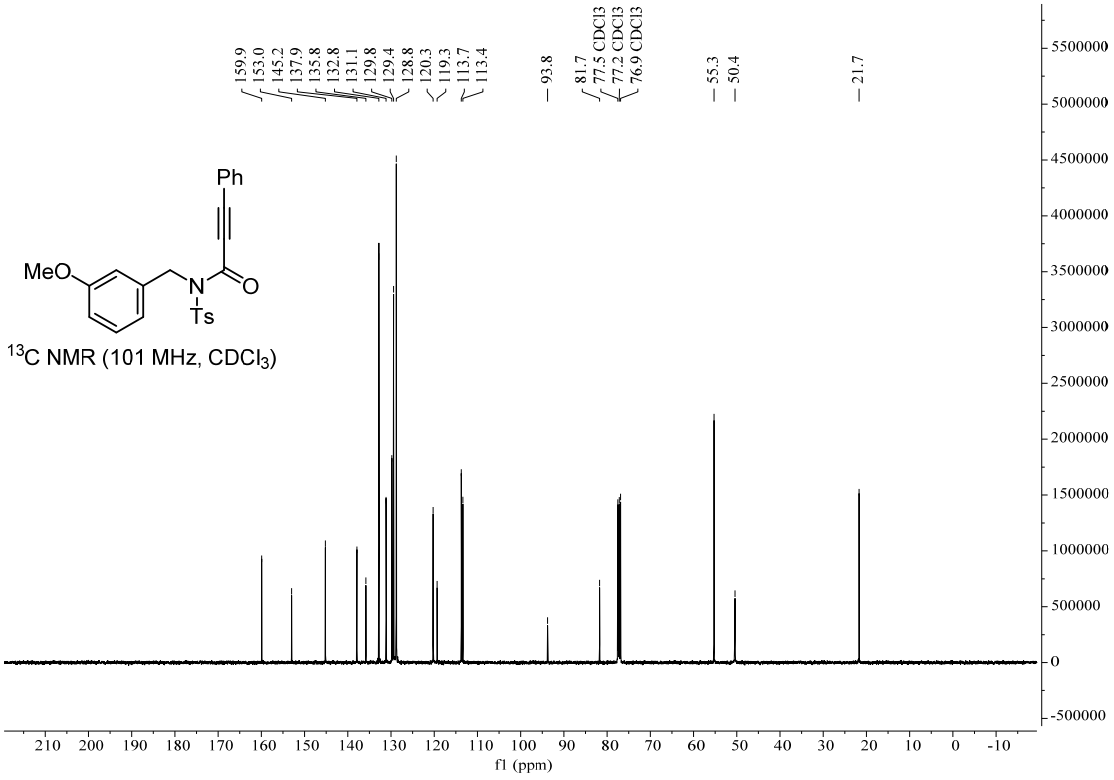
Compound S30



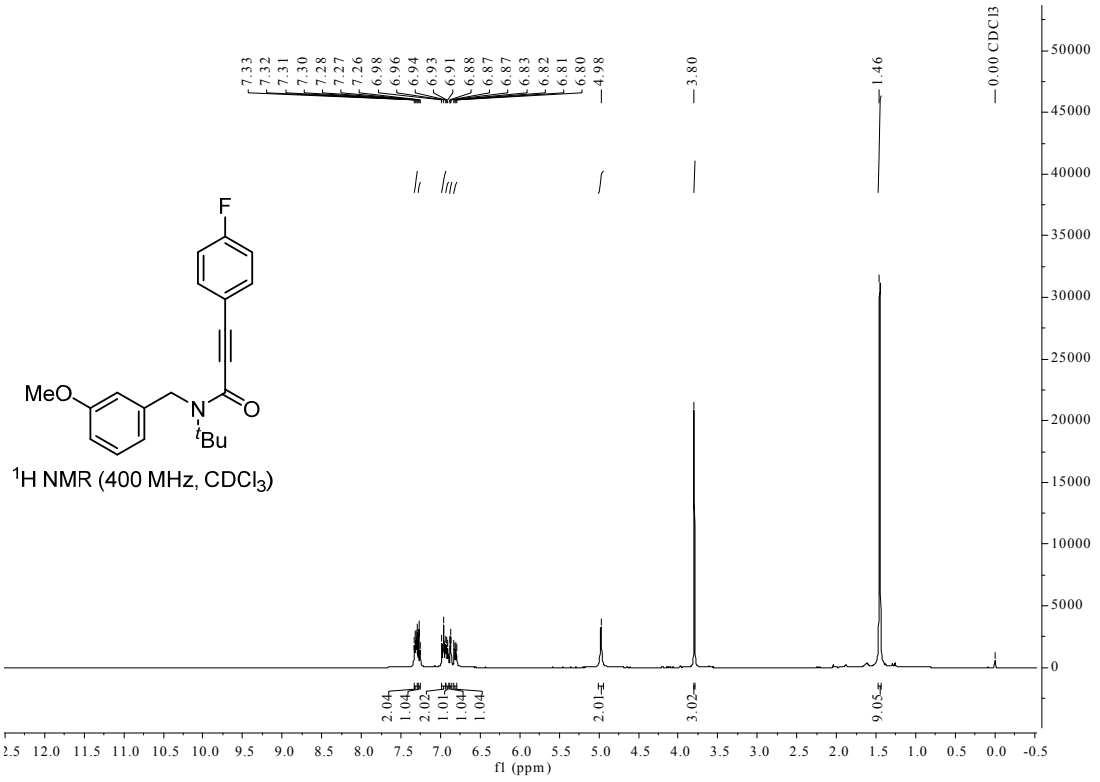


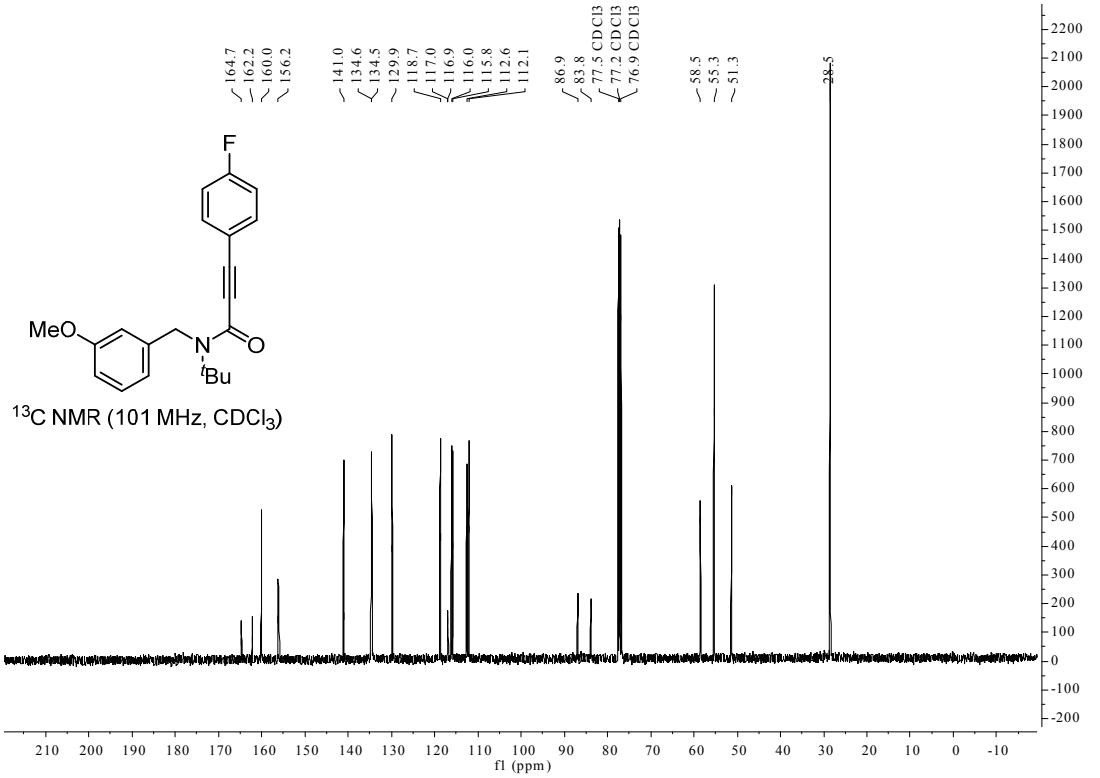
Compound S32

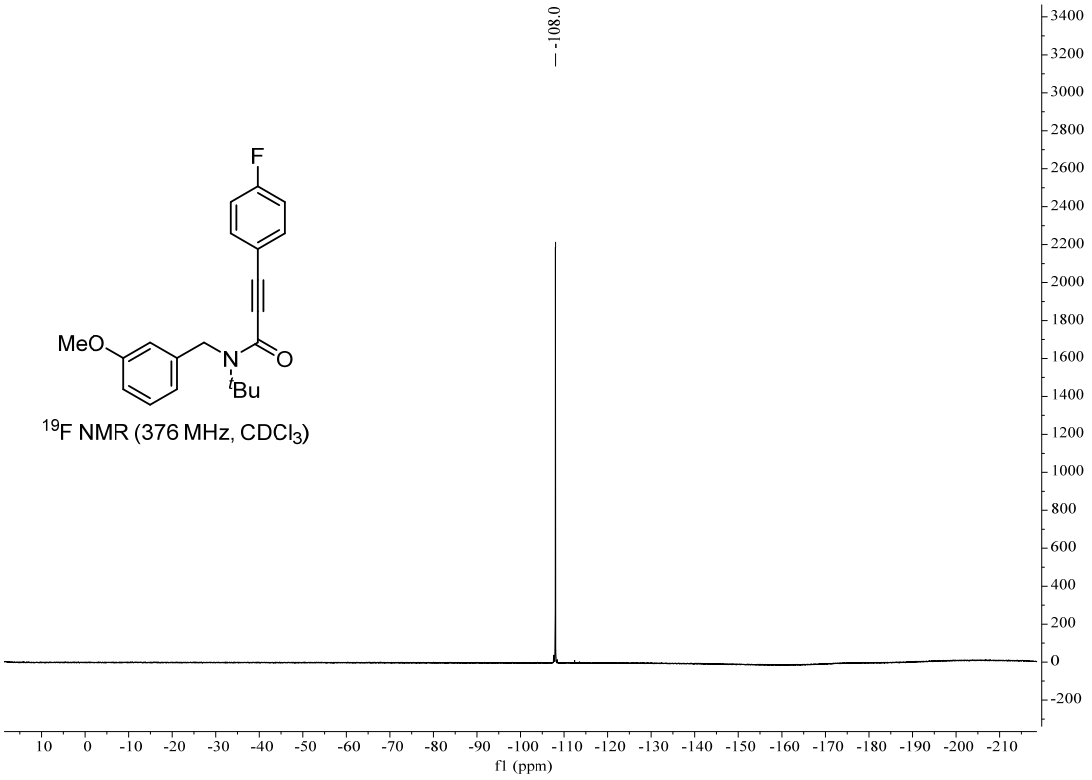




Compound S33

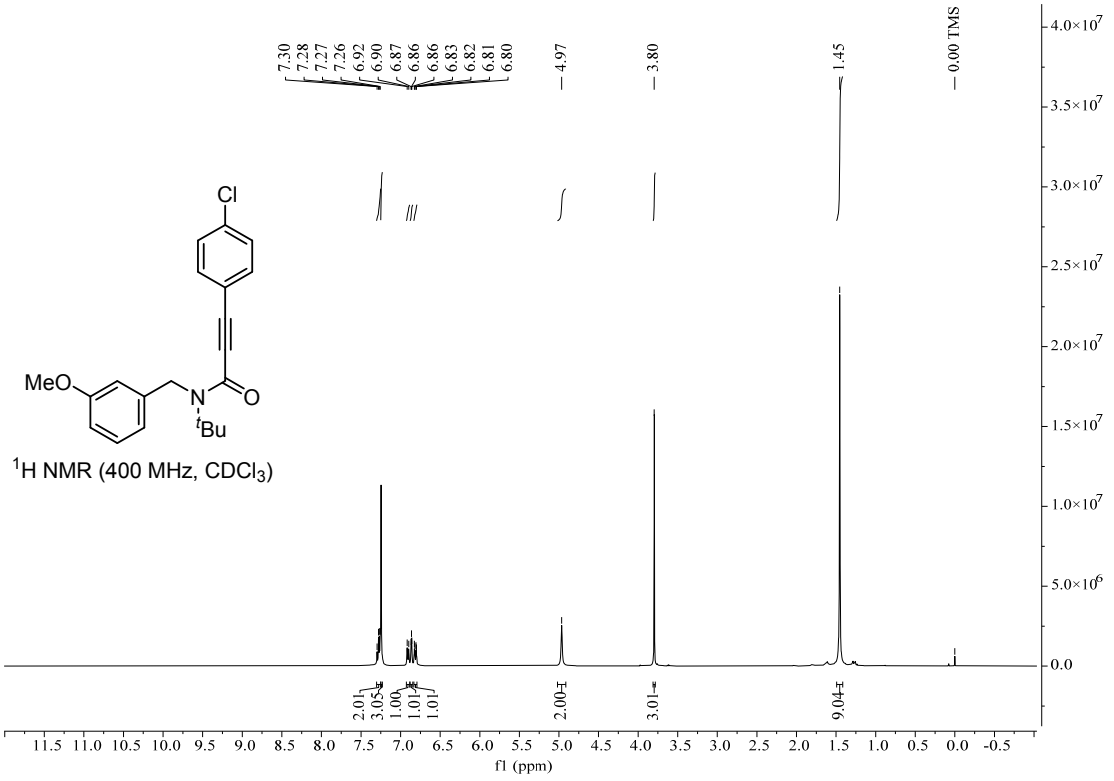


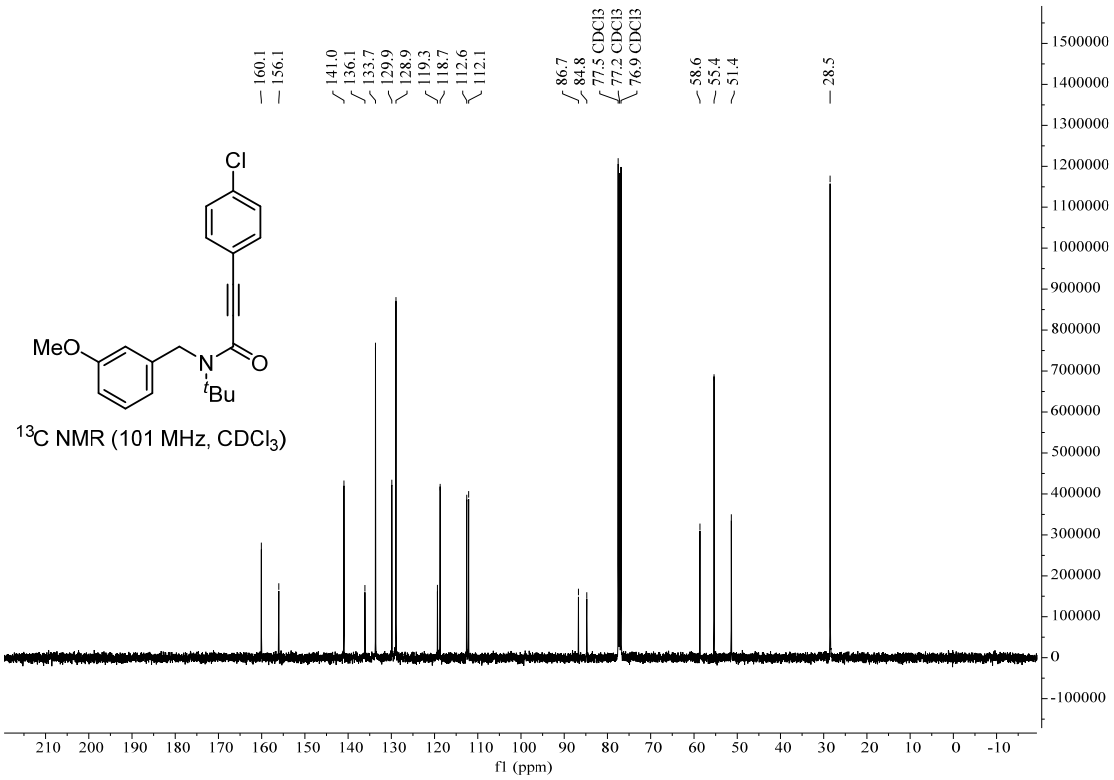




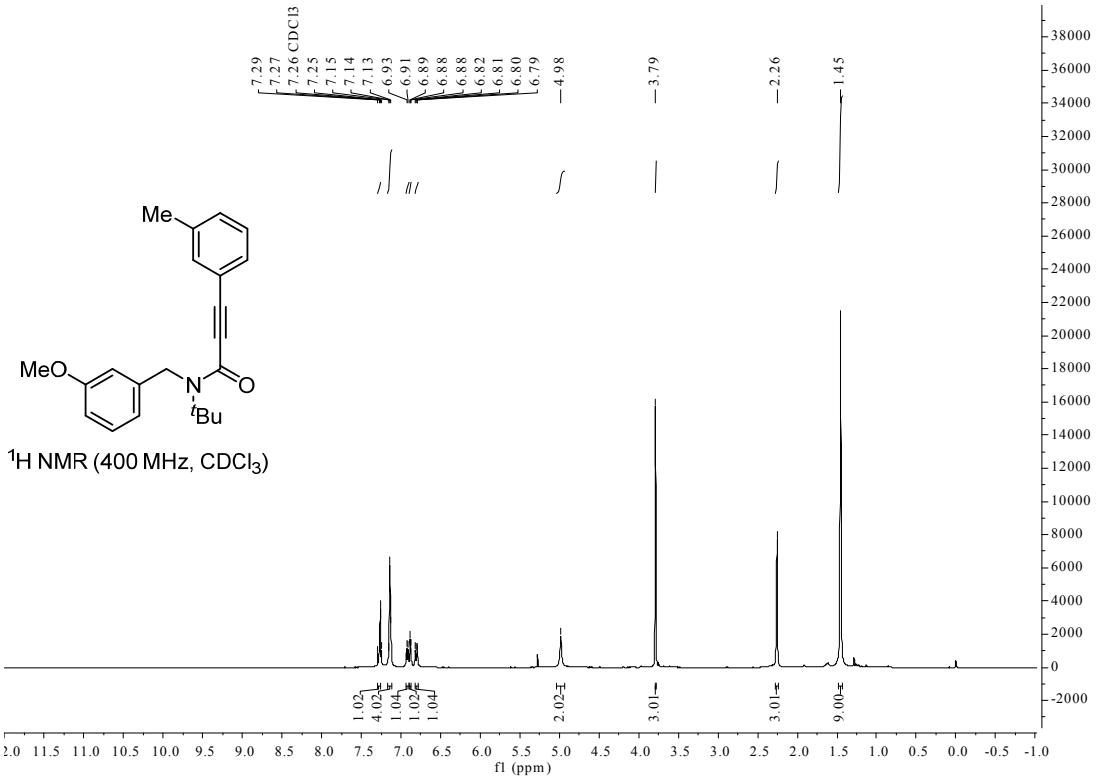
^{19}F NMR (376 MHz, $CDCl_3$)

Compound S34

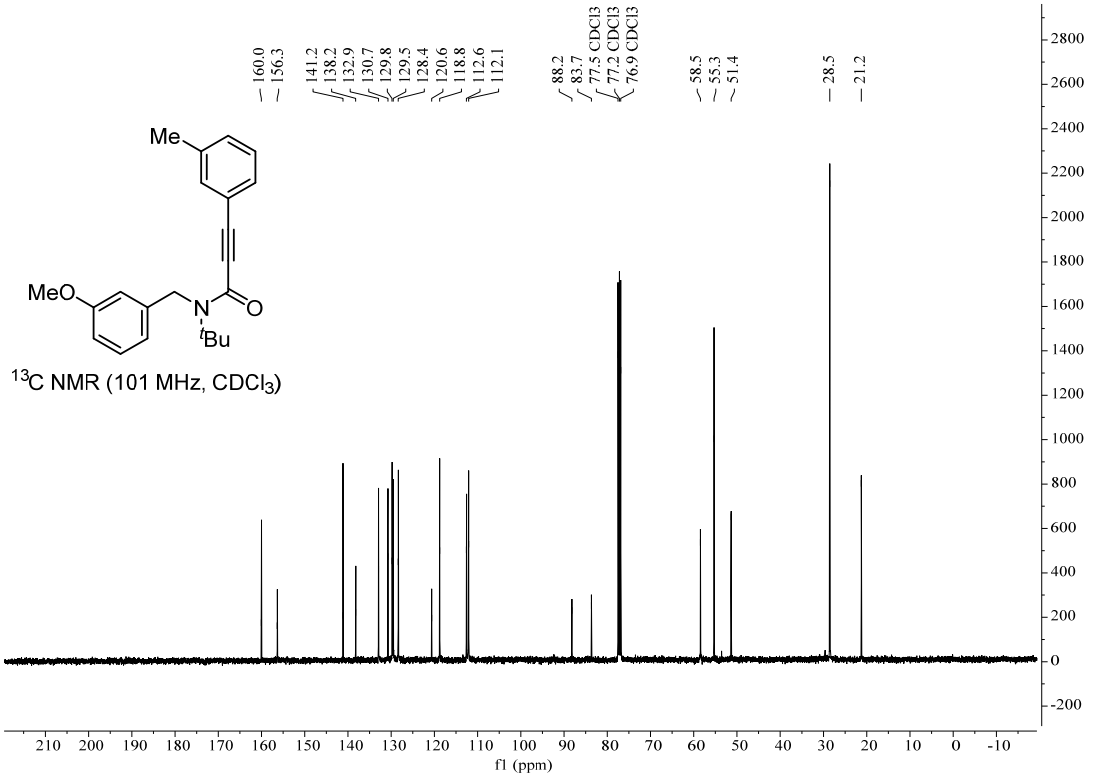




Compound S35

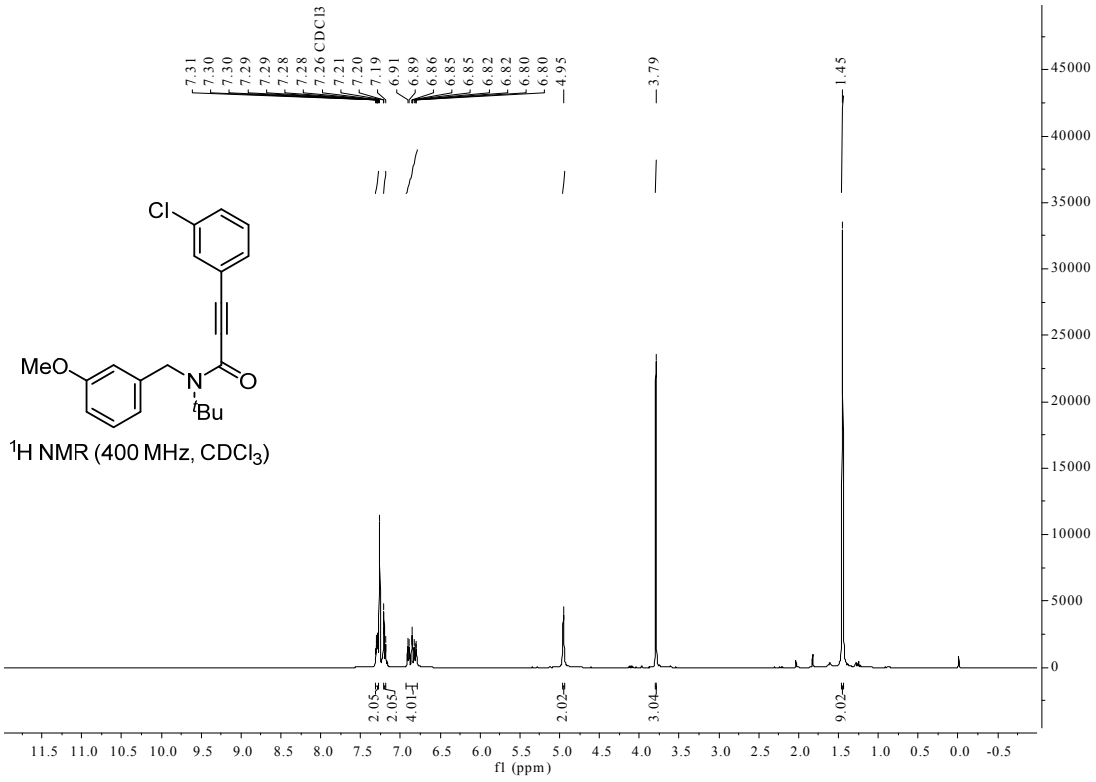


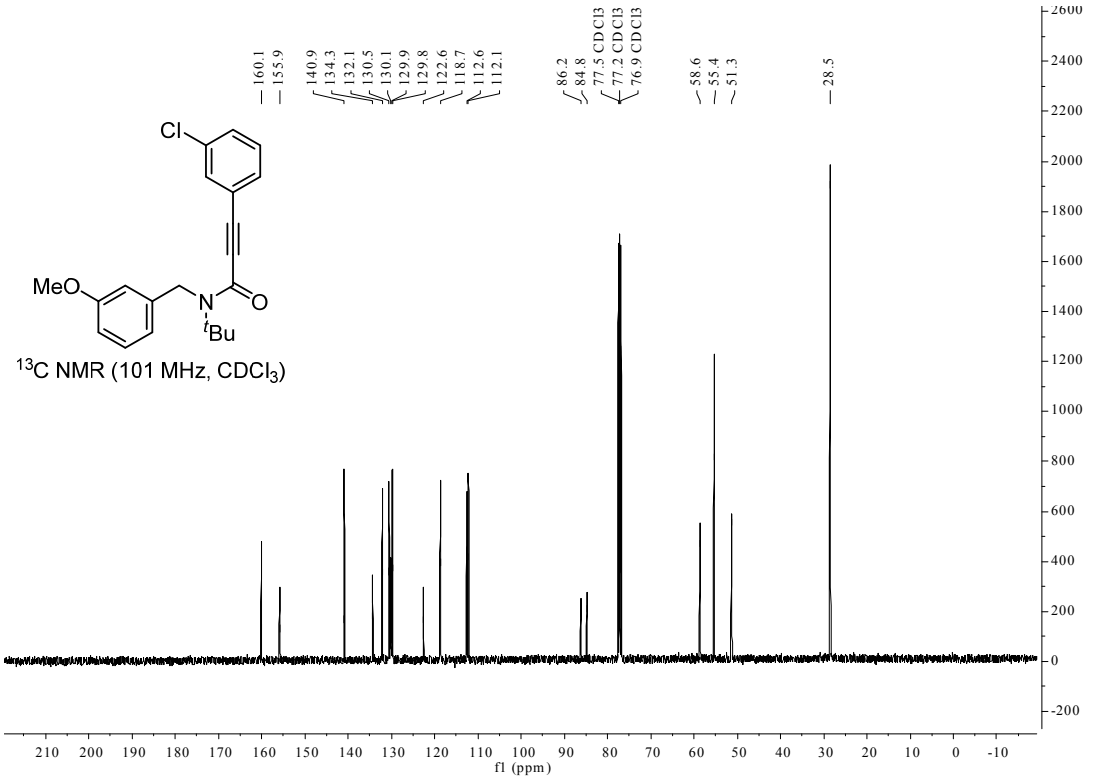
^{1}H NMR (400 MHz, $CDCl_3$)



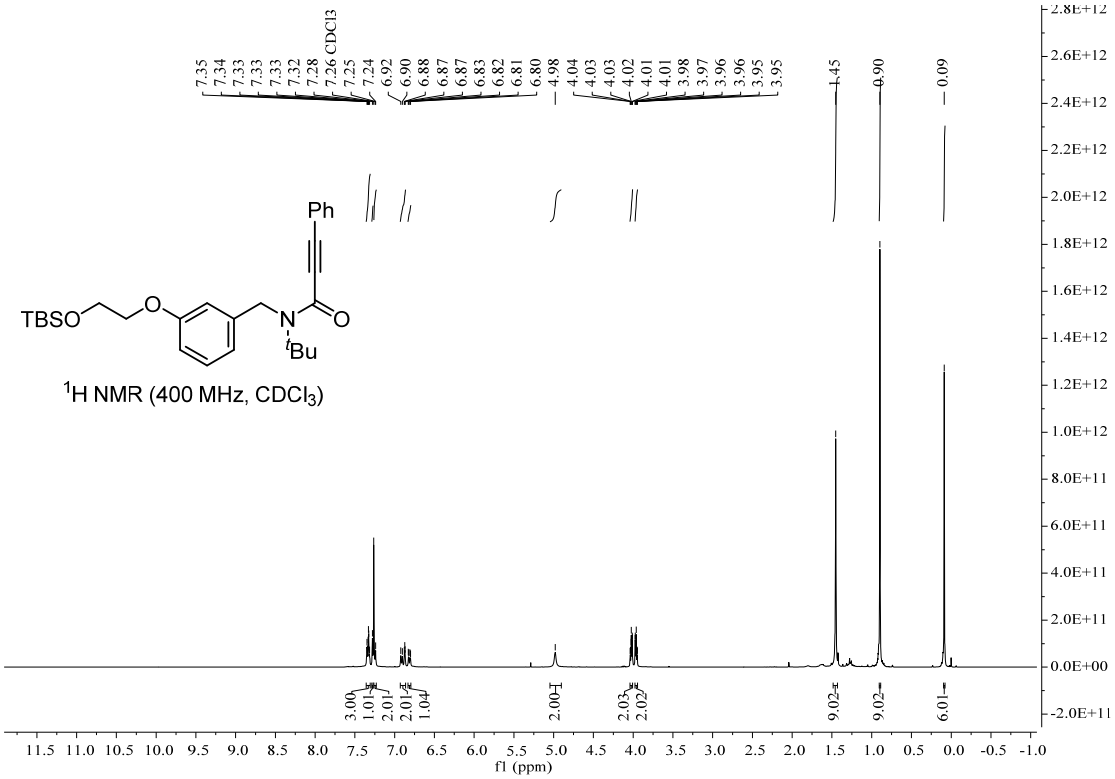
^{13}C NMR (101 MHz, $CDCl_3$)

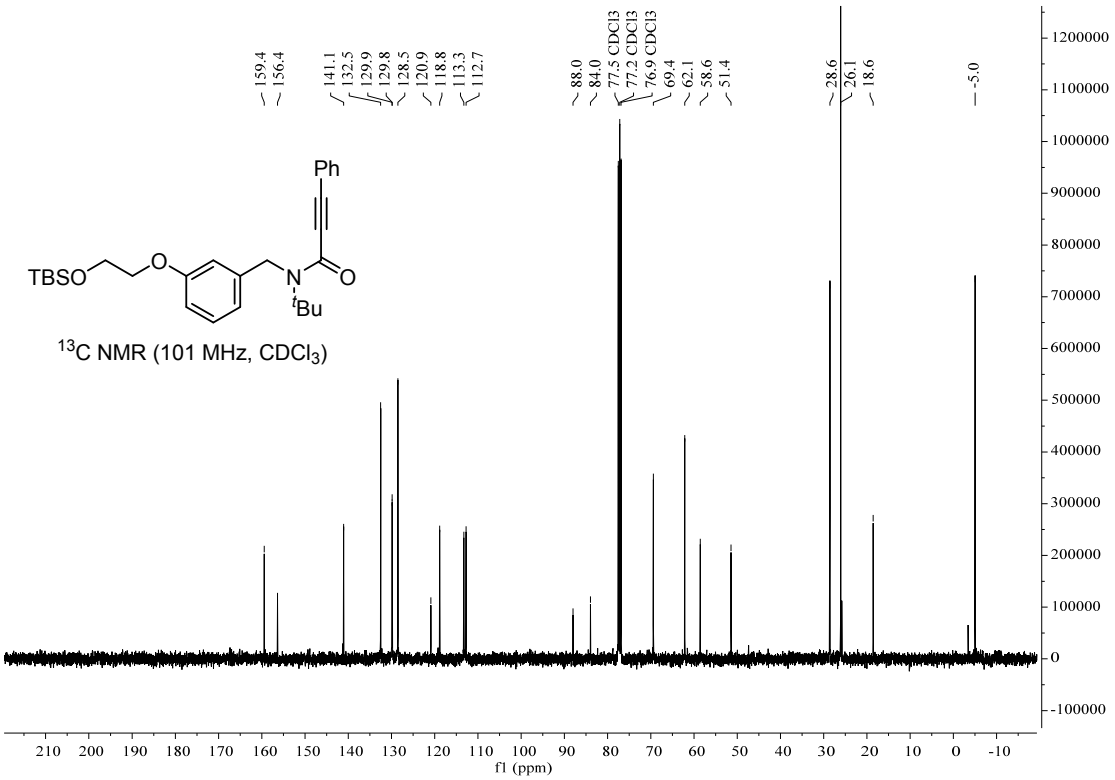
Compound S36



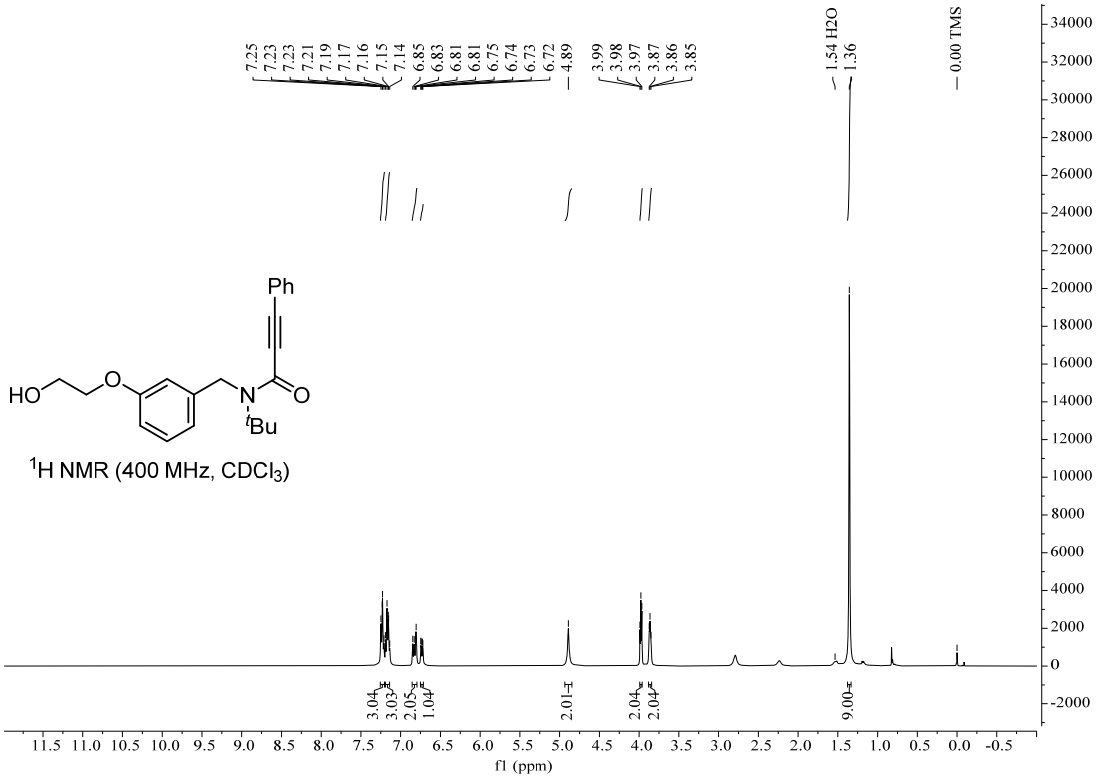


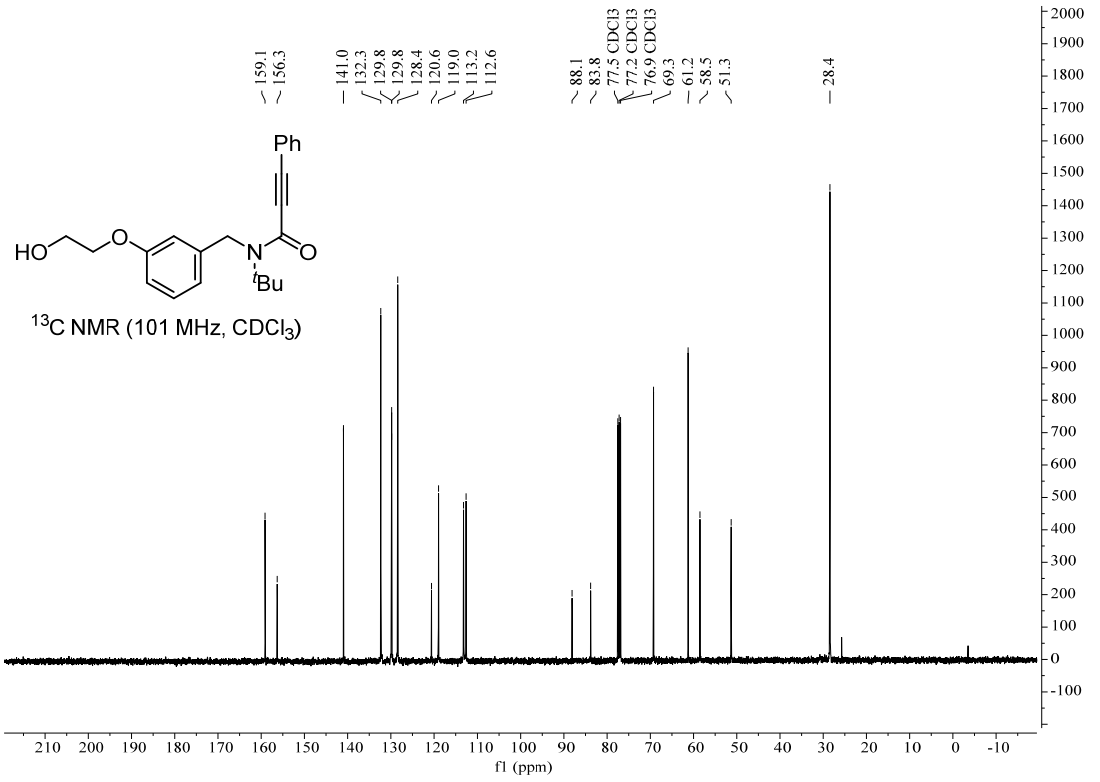
Compound S38



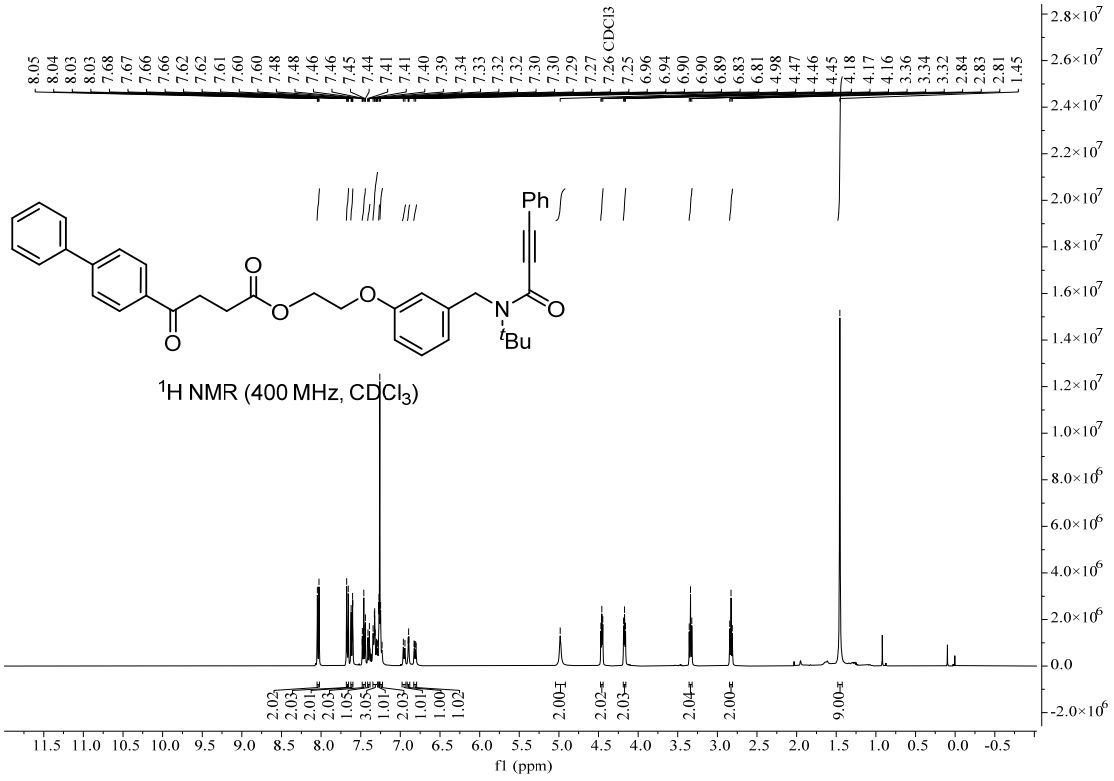


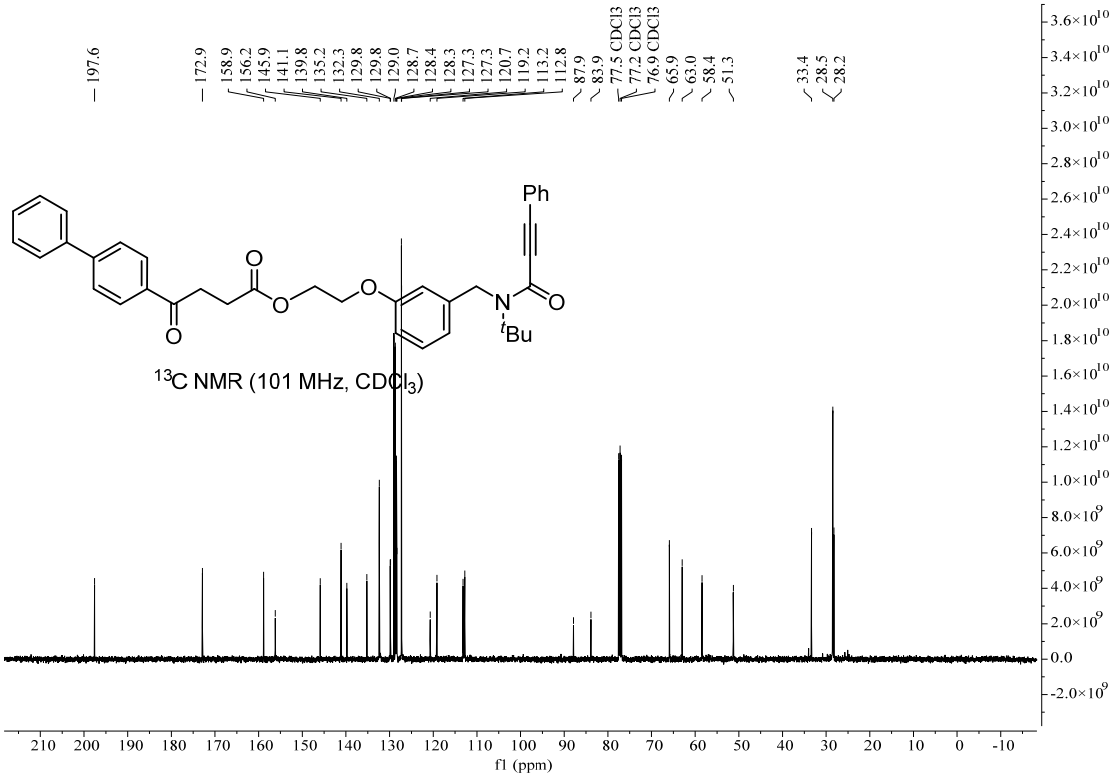
Compound S39



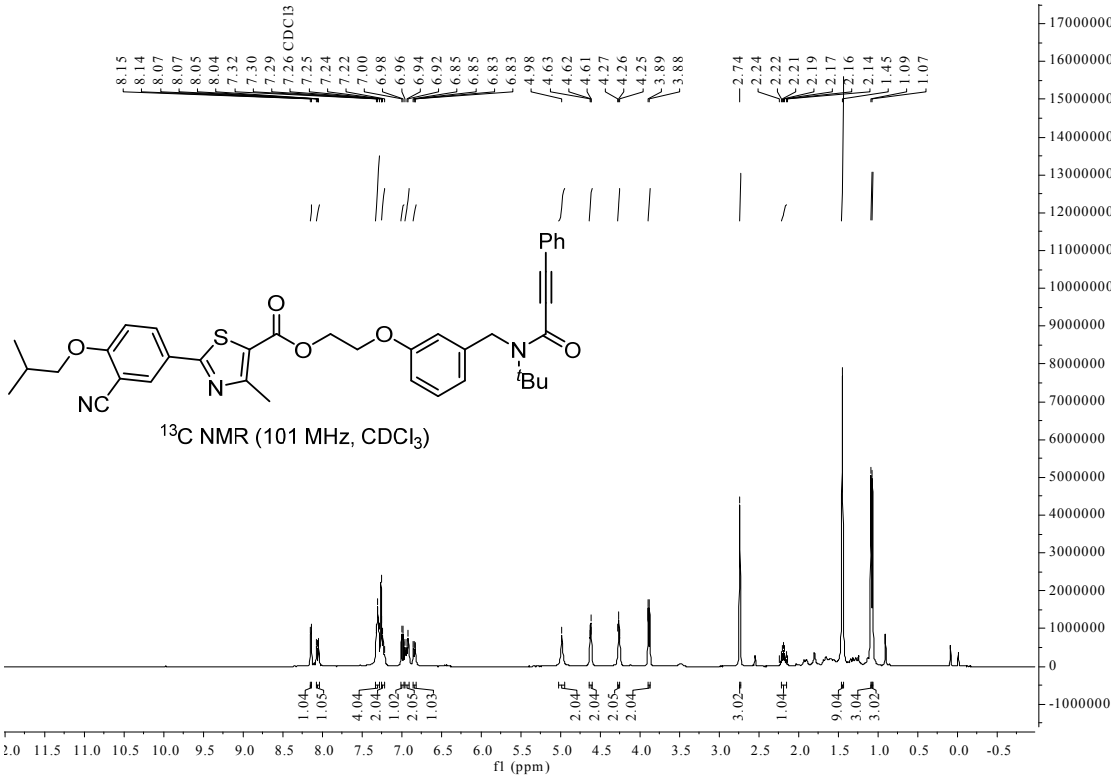


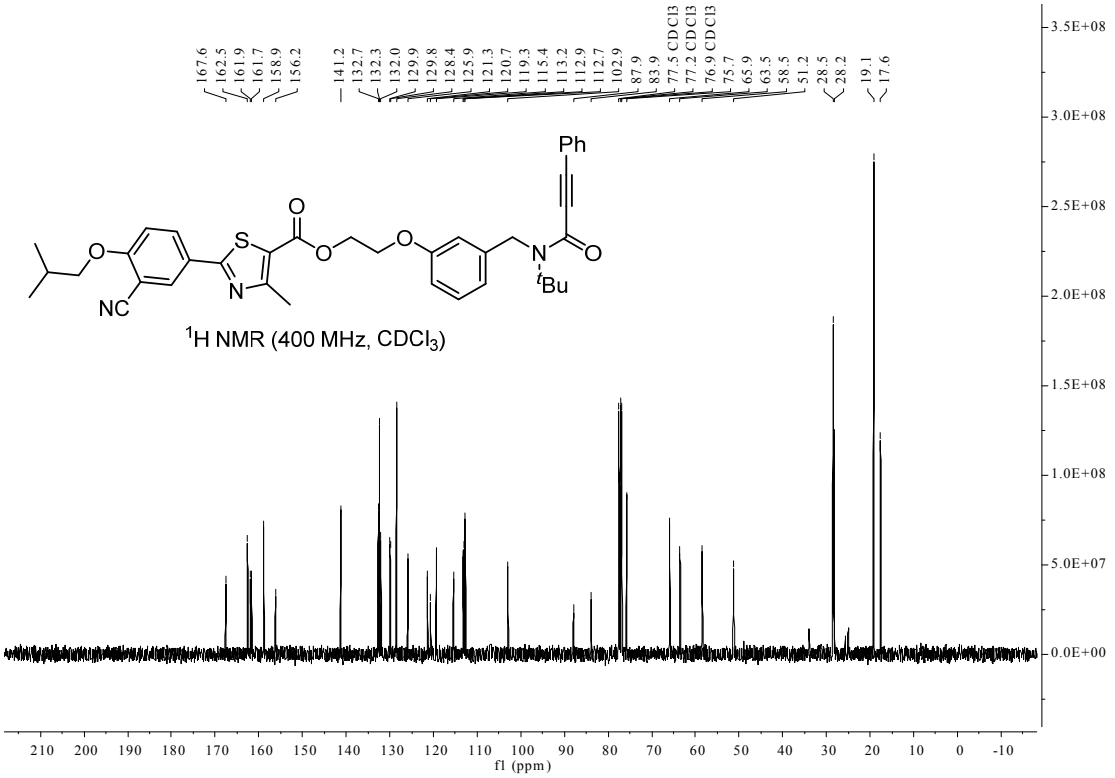
Compound S40



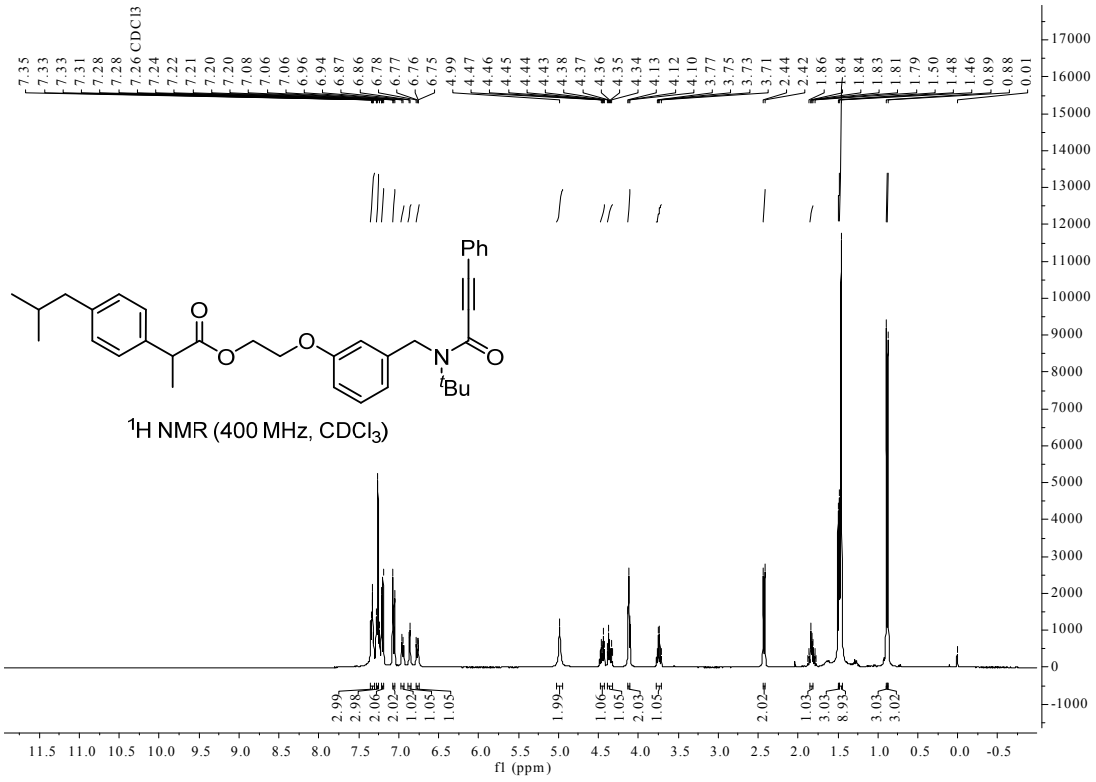


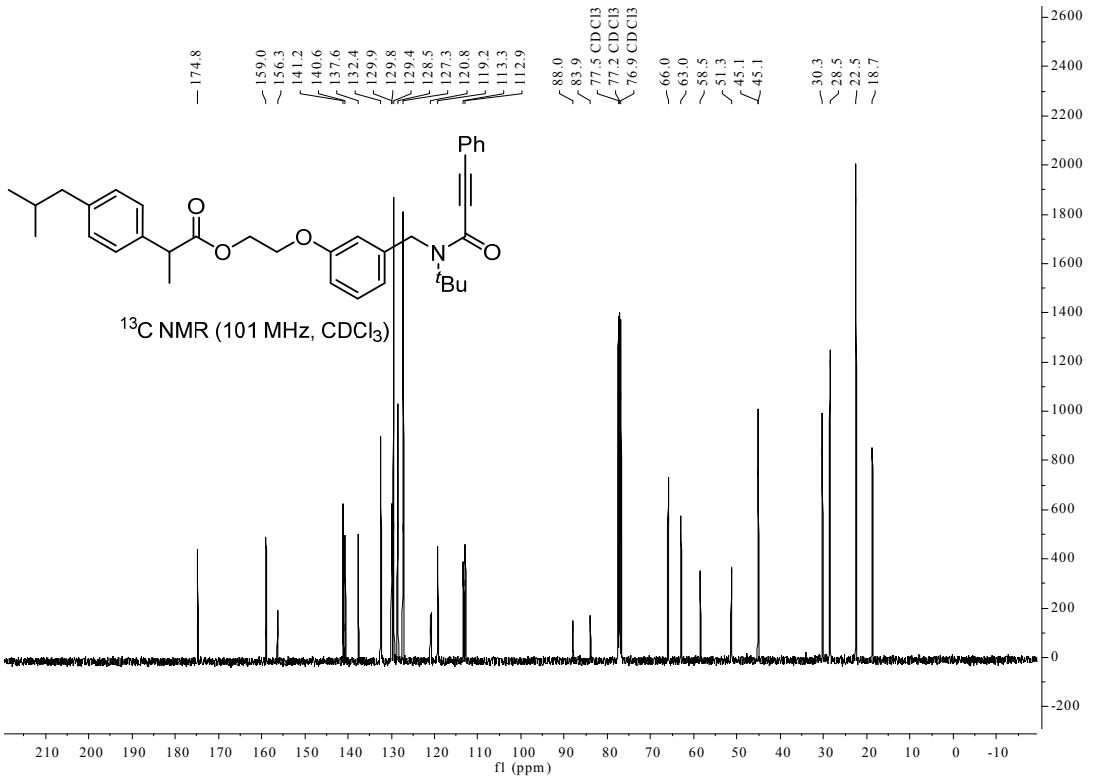
Compound S41



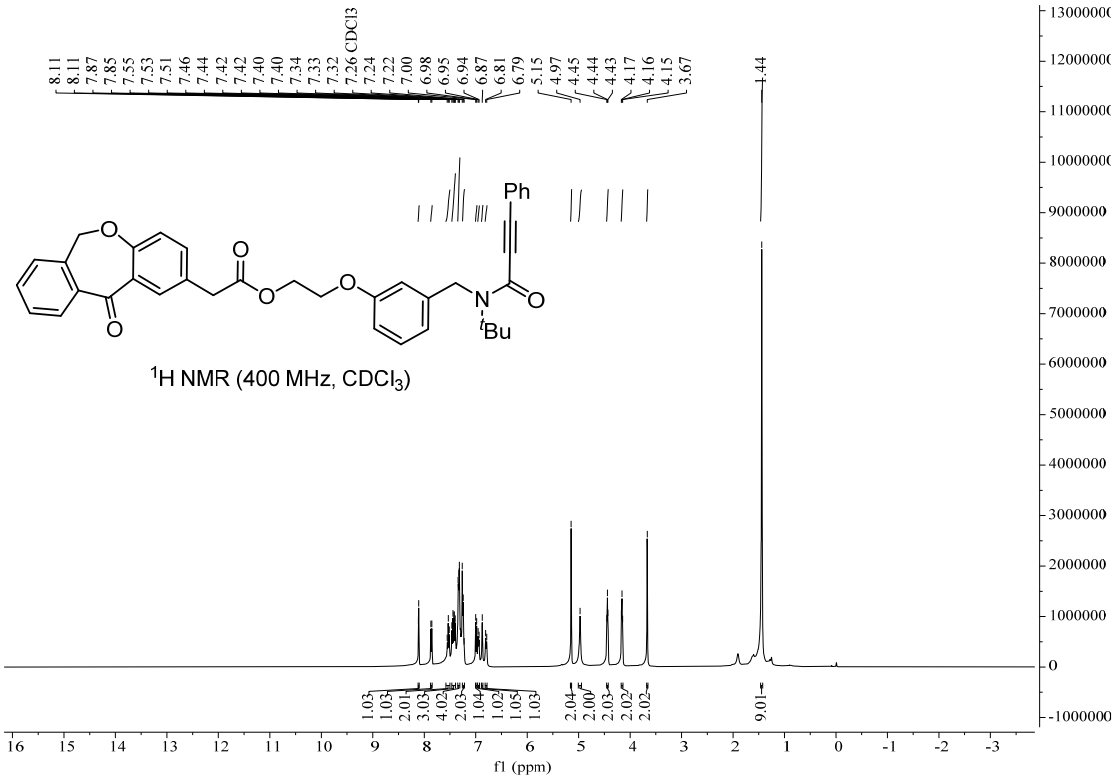


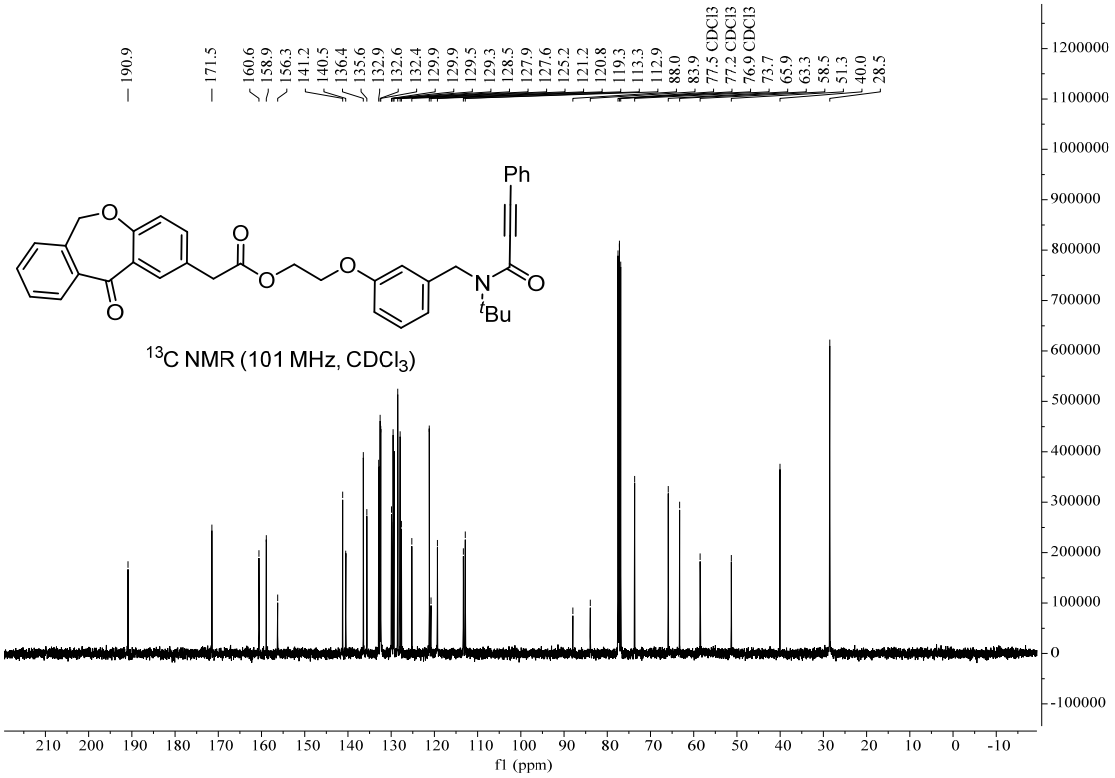
Compound S42



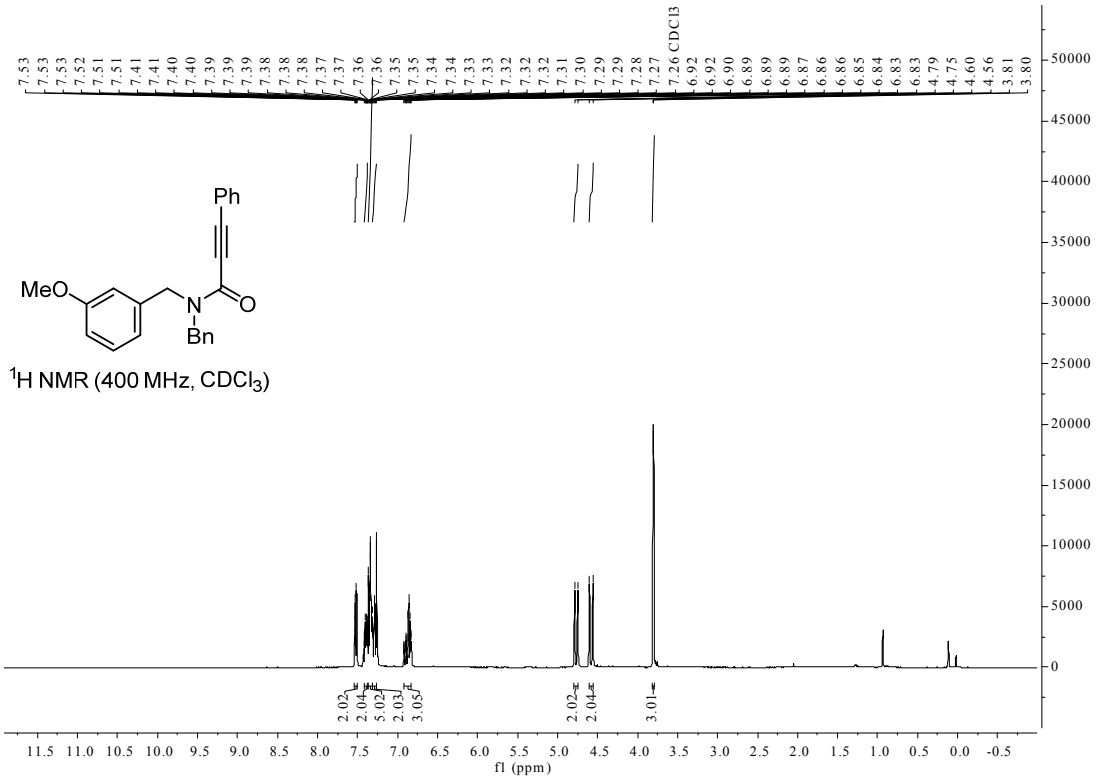


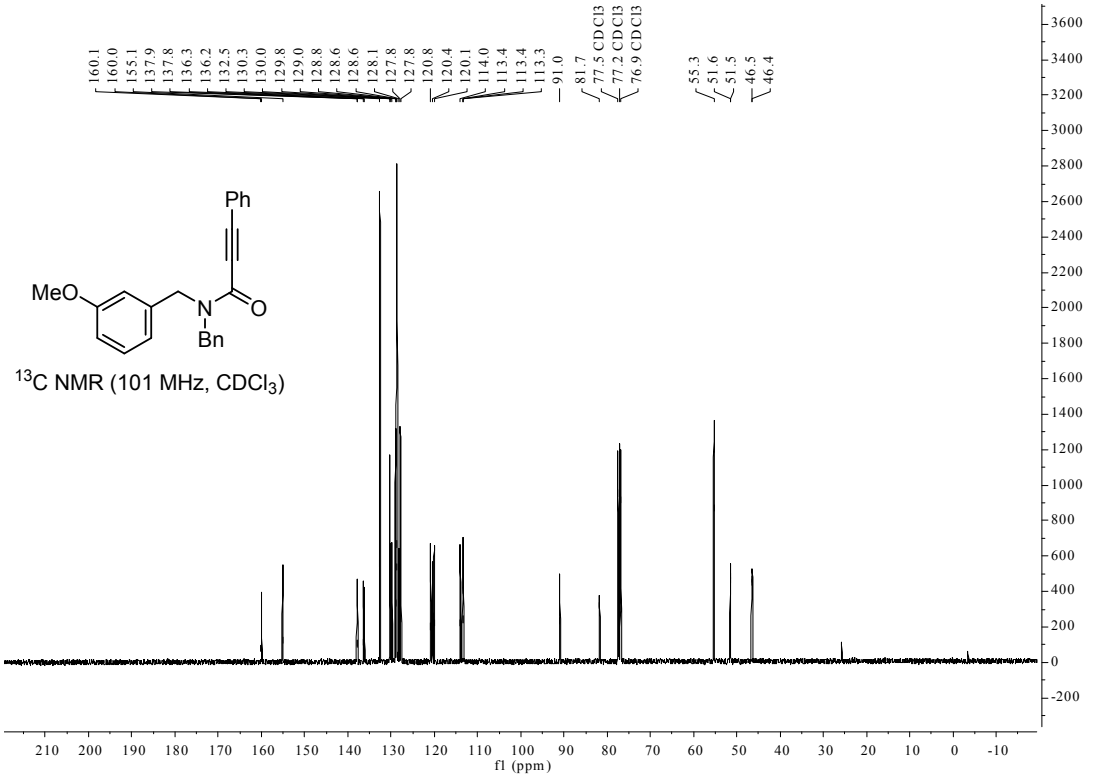
Compound S43



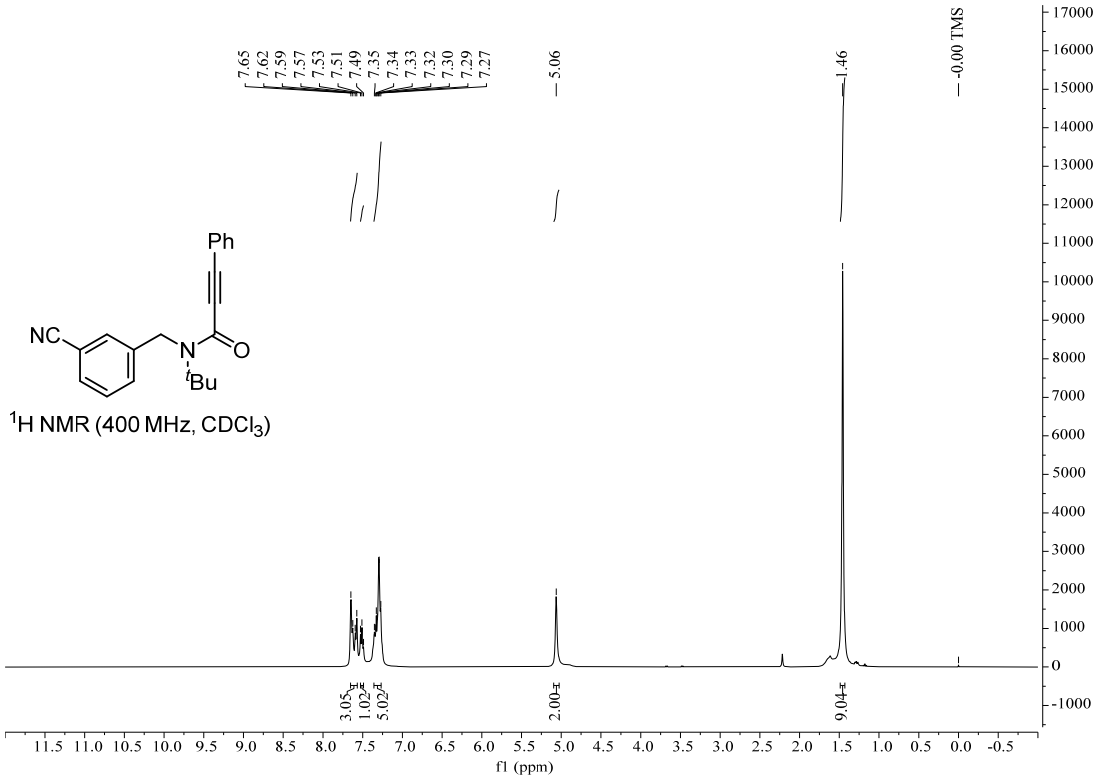


Compound 57

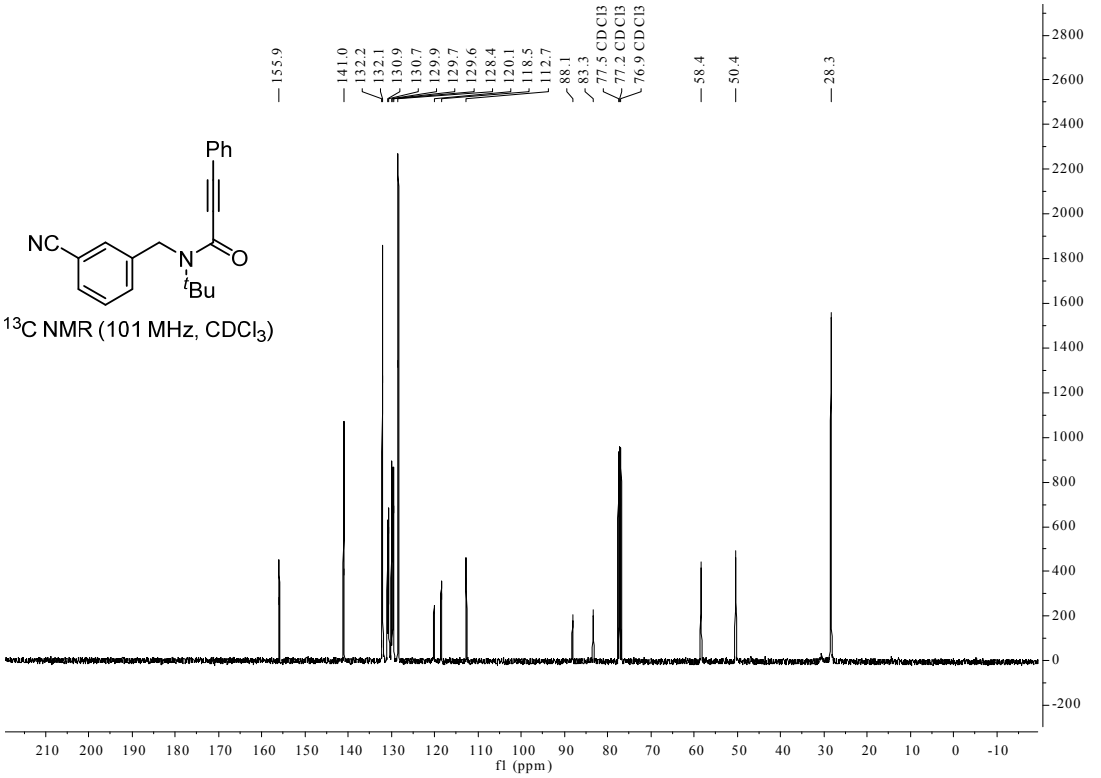

Ph
MeO
N
O
Bn
1H NMR (400 MHz, CDCl3)
fl (ppm)


Ph
MeO
N
O
Bn
13C NMR (101 MHz, CDCl3)
fl (ppm)

Compound 59



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



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