Supporting Information

Accessing Illusive *E* Isomers of α-Ester Hydrazons via Visible Light-Induced Pd-catalyzed Heck-type Alkylation

Nikita Kvasovs and Vladimir Gevorgyan*

Department of Chemistry and Biochemistry, The University of Texas at Dallas,

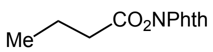
Richardson, Texas 75080-3021, United States, vlad@utdallas.edu

Table of Contents

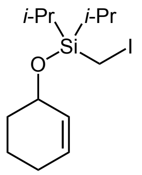
1. General Information

NMR spectra were recorded on Bruker Avance III HD (600 MHz) or DRX 500 (500 MHz) instrument. 1 H signals are referenced to residual $CHCl_3$ at 7.26 ppm. 13C signals are referenced to $CDCl_3$ at 77.16 ppm. GC/MS analysis was performed on Agilent 7890A gas chromatograph coupled with Agilent 5975C mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out using Silicycle Silica-P flash silica gel (40–63 μm). Silica gel was neutralized before use with 1% triethylamine in hexanes where applicable. Precoated silica gel plates F-254 were used for TLC analysis. HRMS analysis was performed on maXis plus mass spectrometer. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS400-4 by Innovative Technology, Inc. purification system. All starting materials were purchased from Strem Chemicals, Sigma Aldrich, Gelest Inc., TCI America, Alfa Aesar, Combi-Blocks, Oakwood Chemicals, Ambeed or synthesized via known literature procedures. 40 W Blue LED lamps (Kessil PR160L-427 nm) were purchased from Kessil. Light-induced reaction were performed in PhotoRedOx Box (HepatoChem, HCK1006-01-016). All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques.

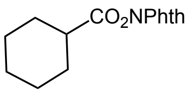
2. Synthesis of Starting Materials



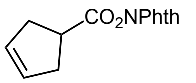
S1



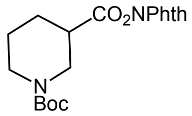
S2



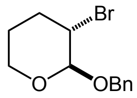
S3



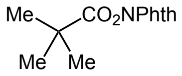
S4



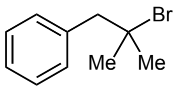
S5



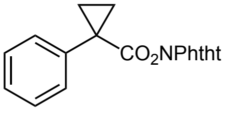
S6



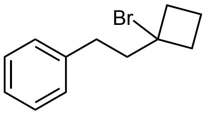
S7



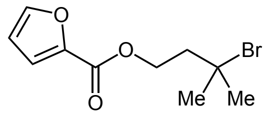
S8



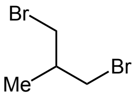
S9



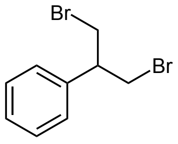
S10



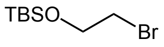
S11



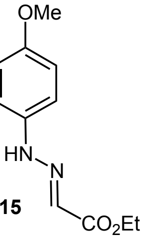
S12



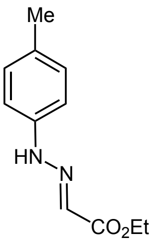
S13



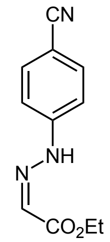
S14



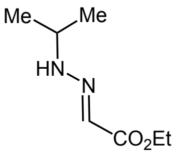
S15



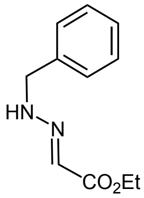
S16



S17

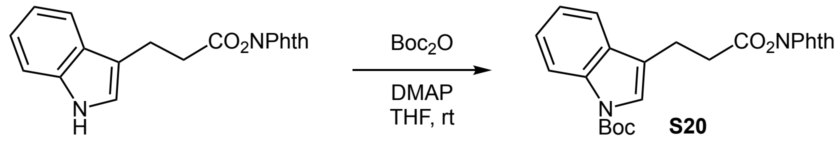


S18

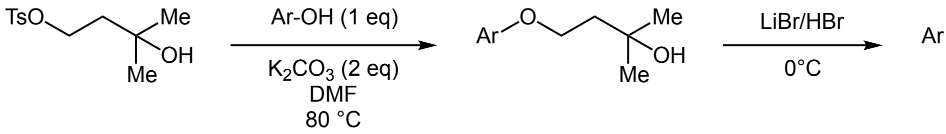


S19

Following starting materials were prepared according to known literature procedures: **S1**, **S3** and **S7**[1]; **S2**[2]; **S4**[3]; **S5**[4]; **S6**[5]; **S8**[6]; **S9**[7]; **S10**[8]; **S11**[9]; **S12**[10]; **S13**[11]; **S14**[12]; **S15**[13]; **S16**[14]; **S17-S19**[15].

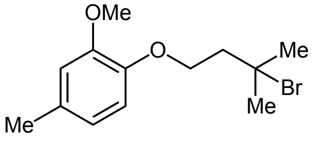


To a stirred solution of indole (344 mg, 1.03 mmol, 1 eq) and DMAP (2.5 mg, 20.6 μmol, 0.02 eq) in THF (8 mL) Boc_2O (225 mg, 1.03 mmol, 1 eq) was added in a single portion. Upon reaction completion (over night), solvent was removed *in vacuo*, crude product was purified using flash chromatography (Hex/EtOAc 9/1 to 4/1). White solid, 380 mg, 85%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.92 – 7.88 (m, 2H), 7.82 – 7.78 (m, 2H), 7.55 (ap. d, J = 7.7 Hz, 1H), 7.49 (s, 1H), 7.34 (ap. t, J = 7.6 Hz, 1H), 7.28 (ap. d, J = 7.5 Hz, 1H), 3.22 – 3.17 (m, 3H), 3.10 – 3.06 (m, 3H), 1.68 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.0, 161.9, 149.7, 135.6, 134.8, 129.9, 129.0, 124.6, 124.0, 123.1, 122.6, 118.7, 118.1, 115.4, 83.6, 31.0, 28.3, 20.2.

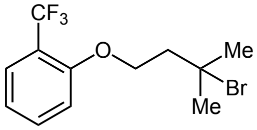


Mixture of 3-hydroxy-3-methylbutyl 4-methylbenzenesulfonate (620 mg, 2.4 mmol, 1.2 eq), phenol (2.0 mmol, 1.0 eq) and potassium carbonate (553 mg, 4 mmol, 2.0 eq) in DMF (4 mL, 0.5 M) was stirred at 80 °C overnight. Upon completion, reaction was quenched by addition of water (12-15 mL), extracted with EtOAc (20-25 mL). Organic phase was washed two times with water (20 mL) and brine (20 mL), dried over Na_2SO_4. Solvent was removed *in vacuo*, crude alcohol was used in the next step without additional purification.

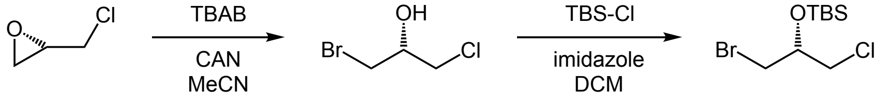
To a crude alcohol (2.0 mmol, 1 eq), dissolved in a minimal amount of DCM, solution of LiBr (347 mg , 2 eq, 4 mmol) in 48% HBr (4 mL) was added at 0 °C. Reaction mixture was allowed to warm up to room temperature and stirred overnight. Reaction mixture was diluted with EtOAc (15 mL), washed with saturated $NaHCO_3$ until neutralized. Organic phase was additionally washed with brine, dried over Na_2SO_4. Upon solvent removal *in vacuo*, crude product was purified using flash chromatography.



S21 was isolated as a white solid (267 mg, 47% over two steps). (Hex/EtOAc 9/1 to 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (ap. d, *J* = 8.1 Hz, 1H), 6.73 – 6.70 (m, 2H), 4.27 (t, *J* = 6.9 Hz, 2H), 3.85 (s, 3H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.86 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.3, 146.0, 131.0, 121.0, 113.5, 113.0, 67.3, 65.3, 56.0, 45.9, 34.9, 21.1.**HRMS** m/z (ESI) calcd. for $C_{13}H_{19}BrO_2$ $[M+H]^+$: 287.0641; found: 287.0639.



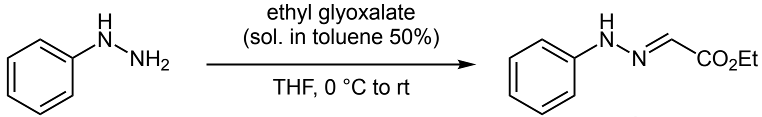
S22 was isolated as a colorless oil (184 mg, 30% over two steps). (Hex/EtOAc 9/1 to 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (ap. d, *J* = 7.7 Hz, 1H), 7.49 (ap. dd, *J* = 11.6, 4.1 Hz, 1H), 7.05 (ap. d, *J* = 8.4 Hz, 1H), 7.01 (ap. t, *J* = 7.6 Hz, 1H), 4.33 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 1.87 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.6, 133.4, 127.3 (q, *J* = 5.2 Hz), 123.8 (q, *J* = 272.3 Hz), 120.2, 119.0 (q, *J* = 30.8 Hz) 112.8, 67.0, 65.8, 45.9, 35.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.3.



S23

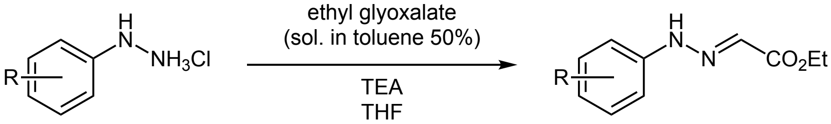
Literature protocol.[16] Cerium ammonium nitrate (467 mg, 0.8 mmol, 0.4 eq) was portion wise added to a solution of (S)-epichlorohydrin (0.157 mL, 2 mmol, 1 eq) and TBAB (1.9 g, 6 mmol, 3 eq) in MeCN (6 mL). Reaction progress was monitored using GC-MS. Upon completion, reaction mixture was filtered through a short pad of celite, washed with EtOAc. Solvent was removed *in vacuo*, crude product was partitioned between water and EtOAc. Organic phase was removed, aqueous layer was washed with EtOAc two times. Combined organic phase was dried over Na_2SO_4, concentrated *in vacuo*, crude product was used in next step without additional purification.

To a solution of crude alcohol (2.0 mmol, 1 eq) and imidiazole (272 mg, 4 mmol, 2 eq) in DCM (6 mL) portion wise was added TBS-Cl (332 mg, 2.2 mmol, 1.1 eq) at 0 °C. Reaction mixture was allowed to warp up to room temperature and stirred for 3 hours. Upon completion, reaction mixture was quenched with saturated $NaHCO_3$, organic phase was removed, and aqueous layer was washed with DCM 2 times. Combined organic phase was dried over Na_2SO_4, concentrated *in vacuo*, crude product was purified using flash chromatography to yield **S23** as colorless liquid (286 mg, 50% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.04 – 3.99 (m, 1H), 3.63 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.58 (dd, *J* = 11.2, 5.0 Hz, 1H), 3.47 (qd, *J* = 10.5, 5.2 Hz, 2H), 0.91 (s, 9H), 0.13 (d, *J* = 3.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 71.9, 46.7, 34.9, 25.8, 18.2, -4.5.



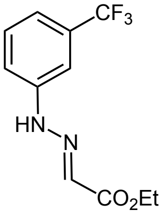
1

1 was synthesized according to literature protocol.[13] To a solution of phenylhydrazine (2 mL, 20 mmol, 1 eq) in THF (24 mL) ethyl glyoxalate (4 mL, 20 mmol, 1 eq) 50 % solution in toluene was added dropwise at 0 °C. Reaction mixture was allowed to warm up to a room temperature, stirred over night. Upon completion, reaction solvent was removed *in vacuo*, crude product was suspended in diethyl ether and filtered. Additional wash with diethyl ether resulted in a desired **2** in 75% yield.

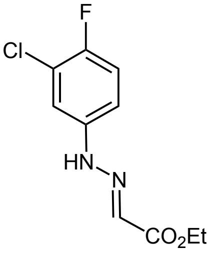


For synthesis of unknown hydrazones, a literature protocol was adopted.[13]

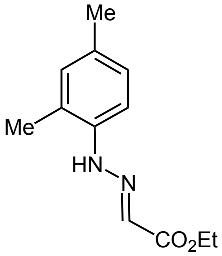
To a suspension of arylhydrazine•HCl (1.5 mmol, 1 eq) in THF (4 mL) triethylamine (0.25 mL, 1.8 mmol, 1.2 eq) and ethyl glyoxalate (0.3 mL, 1.5 mmol, 1 eq) 50 % solution in toluene were added sequentially. Reaction mixture was stirred over night. Upon completion, reaction solvent was removed *in vacuo*, crude product was subjected to flash chromatography directly (Hex/EtOAc 9/1 to 4/1). If obtained compound is not of desired purity, product can be suspended in cold diethyl ether and filtered off.



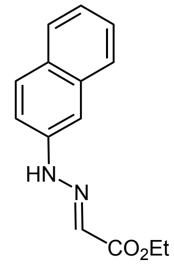
S24 was isolated as a white solid (324 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.39 – 7.30 (m, 3H), 7.20 (ap. d, *J* = 7.4 Hz, 1H), 7.15 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.3, 143.2, 131.9 (q, *J* = 32.4 Hz), 130.0, 127.3, 124.0 (q, *J* = 272.4 Hz), 118.9 (q, *J* = 3.7 Hz), 117.1, 110.7 (q, *J* = 3.9 Hz), 61.4, 14.4. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.9. **HRMS** m/z (ESI) calcd. for $C_{11}H_{11}F_3N_2O_2$ $[M+H]^+$: 261.0845; found: 261.0844.



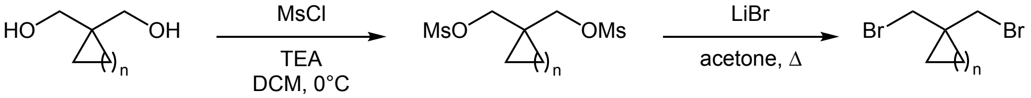
S25 was isolated as a yellow solid (140 mg, 38% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.26 – 7.24 (m, 1H), 7.09 (s, 1H), 7.05 (ap. t, *J* = 8.7 Hz, 1H), 6.98 – 6.94 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.1, 154.7, 153.1, 139.5, 127.0, 122.0 (d, J = 18.8 Hz), 117.2 (d, J = 22.6 Hz), 115.8 (s), 113.3 (d, J = 6.8 Hz), 100.1 (s), 61.3 (s), 14.4 (s). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -124.3. **HRMS** m/z (ESI) calcd. for $C_{10}H_{10}ClFN_2O_2$ $[M+H]^+$: 245.0488; found: 245.0485.



S26 was isolated as a yellow solid (169 mg, 51% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.39 (s, 1H), 7.12 (s, 1H), 6.99 (ap. d, J = 7.6 Hz, 1H), 6.75 (ap. d, J = 7.5 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.2, 140.8, 137.2, 130.6, 123.2, 119.6, 119.0, 113.6, 60.6, 21.5, 16.6, 14.4.

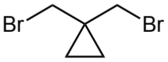


S27 was isolated as a yellow solid (270 mg, 74% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.80 (ap. d, J = 8.8 Hz, 1H), 7.75 (t, J = 9.2 Hz, 2H), 7.52 (s, 1H), 7.46 – 7.39 (m, 2H), 7.34 (ap. t, J = 7.4 Hz, 1H), 7.15 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.2, 140.2, 134.3, 130.2, 129.7, 128.0, 127.1, 126.9, 126.4, 124.3, 115.5, 109.4, 61.2, 14.5. **HRMS** m/z (ESI) calcd. for $C_{14}H_{14}N_2O_2$ $[M+H]^+$: 243.1128; found: 243.1125.

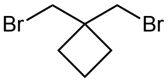


To a solution of corresponding diol (5 mmol, 1 eq) and triethylamine (2.8 mL, 20 mmol, 4 eq) in DCM (15 mL) methanesulfonyl chloride (1.2 mL, 15 mmol, 3 eq) was added dropwise at 0 °C. Reaction mixture was allowed to warm up to room temperature and left stirring over night. Upon completion, reaction mixture was quenched with saturated $NaHCO_3$, phases separated, aqueous layer was additionally washed with DCM two times. Combined organic phase was dried over Na_2SO_4, concentrated *in vacuo*, crude product was used in next step without additional purification.

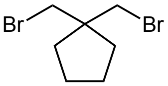
Crude mesylated diol (5 mmol, 1 eq) was dissolved in acetone (20 mL) (in case of n=2, DMA was used). LiBr (1.7 g, 20 mmol, 4 eq) was added in a single portion and reaction was heated over night (n=0 40 °C, n=1 60 °C, n=2 80-90 °C). Upon completion, reaction solvent was removed (in cases of DMA solvent was removed using water/EtOAc extraction), crude product was filtered through short pad of silica gel using Hex to Hex/EtOAc (99/1) and used in the next step without additional purification.



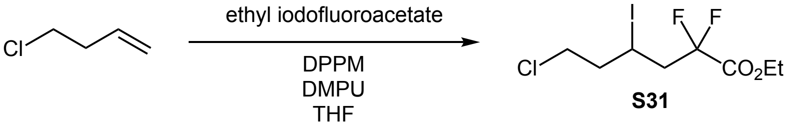
S28 was isolated as a colorless oil (184 mg, 30% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.53 (s, 2H), 0.93 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 40.8, 25.3, 18.0.



S29 was isolated as a colorless oil (160 mg, 22% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.67 (s, 1H), 1.96 (t, *J* = 7.4 Hz, 1H), 1.91 – 1.85 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 43.6, 41.5, 29.6, 13.4.

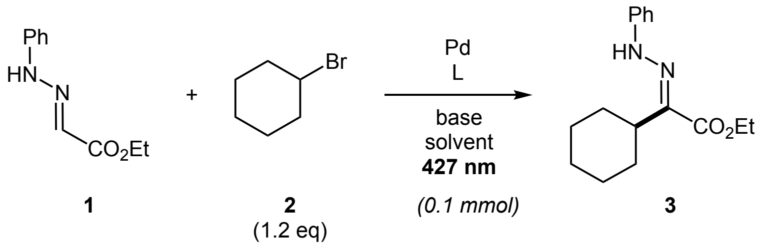


S30was isolated as a colorless oil (184 mg, 30% over two steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.55 (s, 4H), 1.72 – 1.65 (m, 8H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 48.5, 42.4, 36.1, 25.5.



Literature protocol was adopted.[17] 50 mL sealed tube equipped with stir bar was charge with bis(diphenylphosphino)methane (77 mg, 0.2 mmol, 0.1 eq) in glovebox. In sequence were added THF (13 mL), ethyl iododifluoroacetate (0.60 mL, 4 mmol, 2 eq) and DMPU (0.12 mL, 2 mmol, 0.5 eq). Tube was screw capped and heated at 90 °C for 24 hours. Upon completion, reaction mixture was cooled down, solvent was removed *in vacuo*, crude product was purified using flash chromatography. **S31** was isolated as a colorless oil (290 mg, 43%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.42 (ddd, *J* = 13.9, 10.4, 3.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.77 – 3.71 (m, 1H), 3.67 – 3.62 (m, 1H), 3.00 (dtd, *J* = 19.1, 15.6, 6.1 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.27 – 2.11 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.4 (t, *J* = 32.1 Hz), 117.1 – 113.3 (m), 63.6, 45.5 (t, *J* = 23.3 Hz), 44.9, 42.4, 18.9 (t, *J* = 3.9 Hz), 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -101.6 (d, *J* = 264.2 Hz), -106.1 (d, *J* = 264.3 Hz).

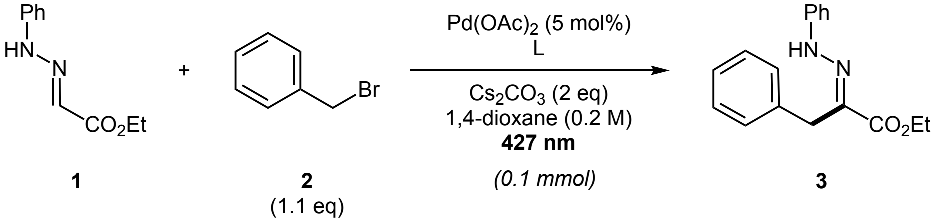
3. Reaction Optimization



Entry	Pd, (mol%)	L, (mol %)	Solvent	Base, eq	GC Yield, %[a]
1	$Pd(OAc)_2$ (5)	Xantphos (10) PPh_3 (20)	PhH (0.1 M)	Cs_2CO_3 (2)	10
2	$Pd(OAc)_2$ (5)	Xantphos (10) PPh_3 (20)	DMA (0.1 M)	Cs_2CO_3 (2)	-
3	$Pd(OAc)_2$ (5)	Xantphos (10) PPh_3 (20)	1,4-dioxane (0.1 M)	Cs_2CO_3 (2)	-
4	$Pd(PPh_3)_4$ (5)	-	PhH (0.1 M)	Cs_2CO_3 (2)	60
5	$Pd(PPh_3)_4$ (5)	-	DMA (0.1 M)	Cs_2CO_3 (2)	18
6	$Pd(PPh_3)_4$ (5)	-	1,4-dioxane (0.1 M)	Cs_2CO_3 (2)	57
7	$Pd(OAc)_2$ (5)	PPh_3 (30)	1,4-dioxane (0.1 M)	Cs_2CO_3 (2)	84
8	$Pd(OAc)_2$ (5)	PPh_3 (30)	THF (0.1 M)	Cs_2CO_3 (2)	80
9	$Pd(OAc)_2$ (5)	PPh_3 (30)	DMA (0.1 M)	Cs_2CO_3 (2)	42
10	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.1 M)	Cs_2CO_3 (2)	84
11	$Pd(OAc)_2$ (5)	PPh_3 (30)	PhH (0.1 M)	Cs_2CO_3 (2)	53
12	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	Cs_2CO_3 (2)	95
13	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	Cs_2CO_3 (1)	**99**
14	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	-	13
15	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	NEt_3 (1)	17
16	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	DBU (1)	**99**
17	$Pd(PPh_3)_4$ (5)	-	HMPA (0.2 M)	Cs_2CO_3 (1)	**99**
18	$Pd(OAc)_2$ (5)	PPh_3 (30)	1,4-dioxane	Cs_2CO_3 (1)	**99**

			(0.1 M)		
19	-	PPh_3 (30)	HMPA (0.2 M)	Cs_2CO_3 (1)	0
20[b]	$Pd(OAc)_2$ (5)	PPh_3 (30)	HMPA (0.2 M)	Cs_2CO_3 (1)	0

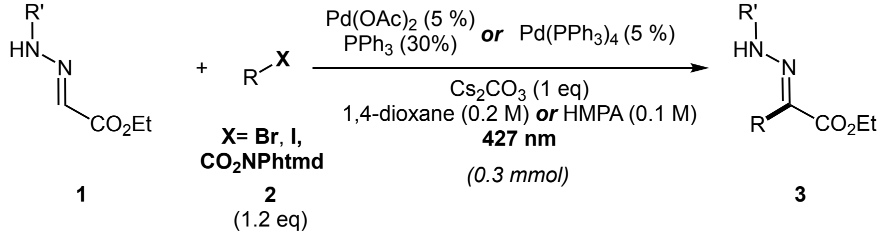
[a] pentadecane as internal standard [b] 80 °C, no light



Entry	L, (mol %)	GC Yield, %[a]
1	PPh_3 (30)	40
2[b]	PPh_3 (30)	28
3	(*p*-Cl-Ph)$_3$P (30)	40
4	(*p*-F_3C-Ph)$_3$P (30)	46
5	(*p*-F-Ph)$_3$P (30)	41
6	(*p*-MeO-Ph)$_3$P (30)	35
7	Xantphos (15)	**61**
8	BINAP (15)	37
9	M’L	34
10	PPh_3 (30)	13
11	-	16
12[c]	Xantphos (15)	0

[a] back calibrated, pentadecane as internal standard; [b] HMPA as solvent; [c] no light, rt

4. Alky-Heck-type Reaction of Hydrazones

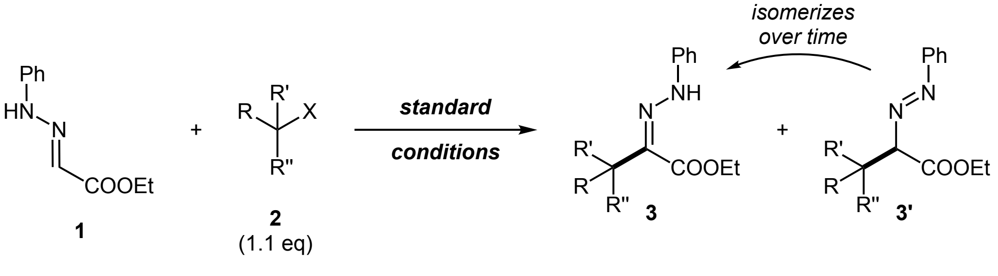


5 mL screw cap vial equipped with stir bar was charged with corresponding hydrazone (0.3 mmol, 1 eq). Vial was taken up in glove box and charged in sequence with Cs_2CO_3 (98 mg, 0.3 mmol, 1 eq), PPh_3 (23.6 mg, 0.09 mmol, 0.3 eq), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.05 eq) and screw capped using cap with septum. Outside of glovebox corresponding solvent was added following up by alkyl bromide/iodide or redox active ester (0.36 mmol, 1.2 eq). If alkyl bromide/iodide or redox active ester was solid or viscous liquid, it was introduced as a solution in corresponding reaction solvent. Reaction mixture was irradiated with Kessil 427 nm lamp (PR160L) in HepatoChem photoredox box equipped with a fan for 12-32 h. Stirring rate 400-500 rpm. Reaction progress was monitored using GC-MS. *In case of 1,4-dioxane as a solvent.* Reaction mixture was filtered through short pad of celite, washed with EtOAc. Solvent was removed *in vacuo*. *In case of HMPA as a solvent.* Reaction mixture was diluted with EtOAc (10 mL), washed with water (2 x 10 mL) and brine (10 mL). Organic phase was dried over Na_2SO_4, concentrated. Crude product was purified using flash chromatography.

1# Note: HMPA is used as solvent in case of redox-active esters (0.1 M) and secondary alkyl bromides (0.2 M). In all other cases 1,4-dioxane (0.2 M) is used.

2# Note: In cases of redox-active esters $Pd(PPh_3)_4$ (17.4 mg, 0.015 mmol, 0.05 eq) is used as a catalyst instead of $Pd(OAc)_2/PPh_3$ mixture.

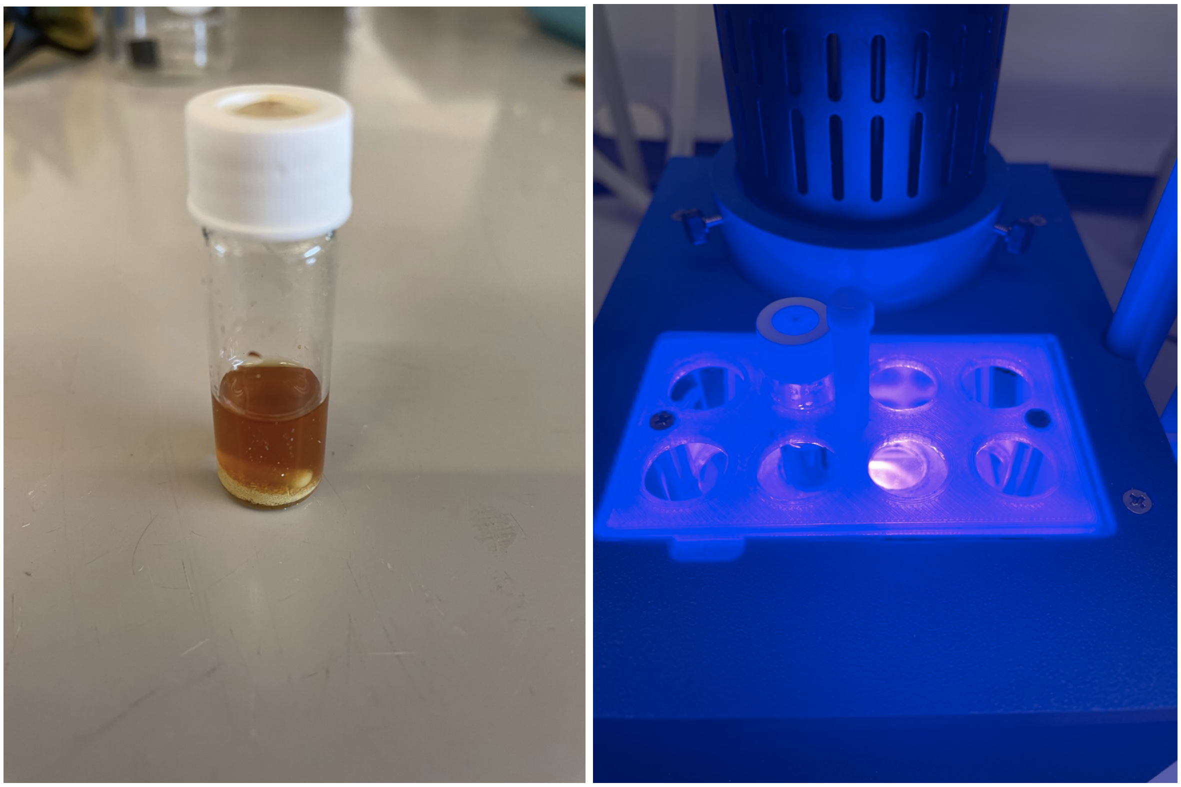
3# Note: In cases when tertiary electrophiles are used, most often mixture of corresponding diazene and hydrazone is formed. In such cases, prolonged stirring is necessary for isomerization of diazene into hydrazone.

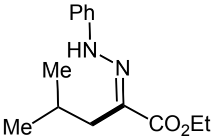


4# Note: In cases when tertiary electrophiles are used, some products may be inseparable from excess of triphenylphosphine. In such cases hydrogen peroxide work-up could be used. Product/triphenylphosphine mixture was dissolved in EtOAc (10 mL). Water was added (5 mL), followed by H_2O_2 (50% wt., 0.3 mL). Upon extraction, aqueous layer was removed, organic phase was washed with brine, dried over Na_2SO_4, concentrated. Filtration through short pad of silicagel using Hex/EtOAc (9/1) resulted in a pure product.

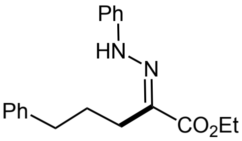
5# Note: In order to prevent product isomerization, $CDCl_3$ for NMR was neutralized via filtration through anhydrous K_2CO_3.

6# Note: For benzylic primary bromides, Xantphos (15 mol%) is used as ligand instead of PPh_3.

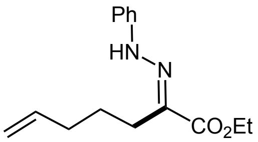




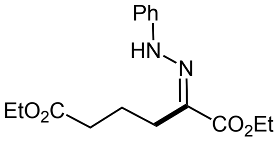
3a was prepared from corresponding alkyl bromide. Isolated as red oil, 56 mg, 75% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.32 – 7.27 (m, 2H), 7.21 – 7.17 (m, 2H), 6.96 (ap. t, *J* = 7.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.49 (d, *J* = 7.5 Hz, 2H), 2.10 – 2.00 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6, 143.3, 136.1, 129.4, 122.0, 114.1, 61.2, 33.3, 26.6, 23.0, 14.4. HRMS m/z (ESI) calcd. for $C_{14}H_{20}N_2O_2$ $[M+H]^+$: 249.1598; found: 249.1597.



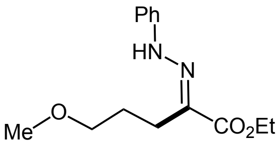
3b was prepared from corresponding alkyl bromide. Isolated as orange oil, 77 mg, 83% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.36 (ap. t, *J* = 7.5 Hz, 2H), 7.31 – 7.22 (m, 5H), 7.03 (ap. d, *J* = 7.7 Hz, 2H), 6.95 (ap. t, *J* = 7.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.55 (dd, *J* = 9.0, 7.0 Hz, 2H), 1.89 (dt, *J* = 10.0, 7.2 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.2, 143.2, 141.4, 135.9, 129.3, 128.8, 128.6, 126.4, 121.9, 113.9, 61.2, 35.2, 26.5, 23.1, 14.4. HRMS m/z (ESI) calcd. for $C_{19}H_{22}N_2O_2$ $[M+H]^+$: 311.1754; found: 311.1754.



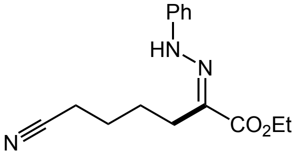
3c was prepared from corresponding alkyl bromide. Isolated as yellow oil, 59 mg, 76% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.30 (ap. t, *J* = 7.8 Hz, 2H), 7.18 (ap. d, *J* = 7.9 Hz, 2H), 6.96 (ap. t, *J* = 7.3 Hz, 1H), 5.87 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.15 – 5.05 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.60 – 2.56 (m, 2H), 2.15 (q, *J* = 6.9 Hz, 2H), 1.67 (dt, *J* = 14.7, 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.3, 143.3, 138.1, 136.3, 129.4, 122.0, 116.2, 114.0, 61.2, 33.3, 24.5, 23.4, 14.5. HRMS m/z (ESI) calcd. for $C_{15}H_{20}N_2O_2$ $[M+H]^+$: 261.1598; found: 261.1597.



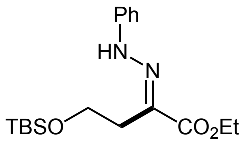
3d was prepared from corresponding alkyl bromide. Isolated as yellow solid, 85 mg, 93% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.34 (ap. d, *J* = 7.6 Hz, 2H), 7.30 (ap. t, *J* = 7.9 Hz, 2H), 6.94 (ap. t, *J* = 7.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.67 – 2.56 (m, 2H), 2.47 – 2.41 (m, 2H), 1.76 (ddd, *J* = 11.6, 8.0, 5.7 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.4, 165.5, 144.0, 134.5, 129.3, 121.6, 114.0, 61.2, 61.1, 32.4, 24.3, 19.5, 14.5, 14.3. **HRMS** m/z (ESI) calcd. for $C_{16}H_{22}N_2O_4$ $[M+H]^+$: 307.1652; found: 307.1652.



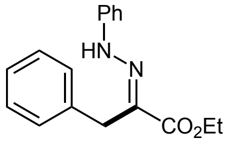
3e was prepared from corresponding alkyl bromide. Isolated as brown oil, 61 mg, 77% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.29 (ap. t, *J* = 7.9 Hz, 2H), 7.18 (ap. d, *J* = 7.7 Hz, 2H), 6.94 (ap. t, *J* = 7.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 3H), 3.37 – 3.34 (m, 2H), 2.70 (t, *J* = 6.7 Hz, 2H), 1.87 (td, *J* = 11.5, 6.0 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 143.9, 135.6, 129.4, 121.6, 113.8, 70.8, 61.1, 58.8, 26.3, 21.0, 14.5. HRMS m/z (ESI) calcd. for $C_{14}H_{20}N_2O_3$ $[M+H]^+$: 265.1547; found: 265.1546.



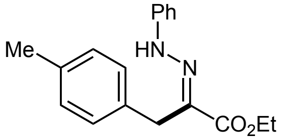
3f was prepared from corresponding alkyl bromide. Isolated as yellow solid, 70 mg, 85% yield. (Hex/EtOAc 4/1 to Hex/EtOAc 1/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.29 (ap. t, *J* = 7.9 Hz, 2H), 7.22 (ap. d, *J* = 7.7 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.66 (m, 5H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 143.3, 134.7, 129.4, 122.2, 119.7, 114.2, 61.3, 24.8, 24.2, 23.3, 16.9, 14.4. **HRMS** m/z (ESI) calcd. for $C_{15}H_{19}N_3O_2$ $[M+H]^+$: 274.1550; found: 274.1549.



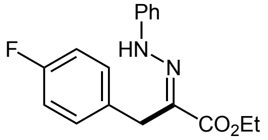
3g was prepared from corresponding alkyl bromide. Isolated as orange oil, 80 mg, 76% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, C_6D_6) δ 9.18 (s, 1H), 7.38 – 7.33 (m, 2H), 7.16 (ap. t, *J* = 7.9 Hz, 3H), 6.82 (ap. t, *J* = 7.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.60 (m, 2H), 2.71 – 2.65 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.76 (s, 10H), -0.12 (s, 6H). **^{13}C NMR** (151 MHz, C_6D_6) δ 165.8, 144.5, 135.8, 129.5, 128.1, 121.9, 114.4, 63.2, 60.9, 29.5, 26.1, 18.6, 14.5, -5.5. **HRMS** m/z (ESI) calcd. for $C_{18}H_{30}N_2O_3Si$ $[M+H]^+$: 351.2098; found: 351.2095.



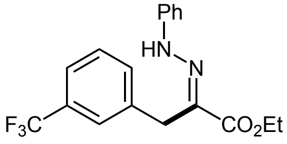
3h was prepared from corresponding benzyl bromide. Isolated as yellow solid, 52 mg, 61% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6, 143.0, 135.2, 133.9, 129.4, 128.1, 127.2, 122.3, 114.1, 61.5, 31.2, 14.5. **HRMS** m/z (ESI) calcd. for $C_{17}H_{18}N_2O_2$ $[M+H]^+$: 283.1441; found: 283.1439.



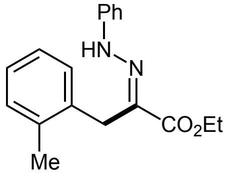
3i was prepared from corresponding benzyl bromide. Isolated as yellow solid, 54 mg, 61% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.37 (ap. t, *J* = 7.8 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.19 (ap. d, *J* = 7.9 Hz, 2H), 7.06 (ap. t, *J* = 7.3 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.11 (s, 2H), 2.44 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6, 143.1, 136.8, 134.2, 132.0, 130.0, 129.3, 128.0, 122.2, 114.1, 61.5, 30.9, 21.1, 14.5. **HRMS** m/z (ESI) calcd. for $C_{18}H_{20}N_2O_2$ $[M+H]^+$: 297.1598; found: 297.1595.



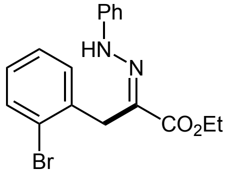
3j was prepared from corresponding benzyl bromide. Isolated as yellow solid, 49 mg, 54% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.31 (ap. t, *J* = 7.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.12 (ap. d, *J* = 8.0 Hz, 2H), 7.06 (ap. t, *J* = 8.5 Hz, 2H), 7.01 (ap. t, *J* = 7.3 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 162.8, 161.2, 142.9, 133.7, 130.8 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 8.0 Hz), 122.5,116.2 (d, *J* = 21.5 Hz), 114.2, 61.6, 30.3, 14.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.3. **HRMS** m/z (ESI) calcd. for $C_{17}H_{17}FN_2O_2$ $[M+H]^+$: 301.1347; found: 301.1343.



3k was prepared from corresponding benzyl bromide. Isolated as yellow solid, 70 mg, 67% yield **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (ap. d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.51 (ap. d, *J* = 7.6 Hz, 1H), 7.43 (ap. t, *J* = 7.6 Hz, 1H), 7.39 (ap. d, *J* = 7.7 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.11 (ap. d, *J* = 8.4 Hz, 2H), 6.97 (ap. t, *J* = 7.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 142.8, 136.3, 132.7, 131.6 (d, *J* = 32.4 Hz), 131.3, 129.8, 129.4, 125.0 (d, *J* = 3.7 Hz), 124.9, 124.1 (d, *J* = 3.7 Hz), 123.1, 122.7, 114.3, 61.7, 30.6, 14.4. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.6. **HRMS** m/z (ESI) calcd. for $C_{18}H_{17}F_3N_2O_2$ $[M+H]^+$: 351.1315; found: 351.1314.

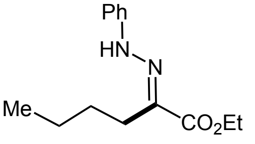


3l was prepared from corresponding benzyl bromide. Isolated as orange oil, 40 mg, 45% yield **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.27 – 7.21 (m, 3H), 7.19 (ap. t, *J* = 7.4 Hz, 1H), 7.14 (ap. t, *J* = 7.4 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.94 (ap. t, *J* = 7.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 2.39 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 143.1, 136.8, 133.6, 132.8, 131.3, 129.4, 127.5, 127.3, 126.9, 122.3, 114.1, 61.5, 29.7, 20.0, 14.5. **HRMS** m/z (ESI) calcd. for $C_{18}H_{20}N_2O_2$ $[M+H]^+$: 297.1598; found: 297.1594.

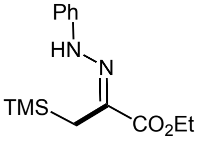


3m was prepared from corresponding benzyl bromide. Isolated as yellow solid, 91 mg, 84% yield **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.59 (ap.

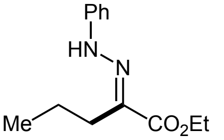
d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.24 – 7.22 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.08 (m, 1H), 6.95 (ap. t, *J* = 7.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 2.16 (s, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.7, 143.0, 134.6, 133.0, 133.0, 129.9, 129.4, 128.9, 128.4, 124.2, 122.4, 114.2, 61.6, 31.0, 14.5. **HRMS** m/z (ESI) calcd. for $C_{17}H_{17}BrN_2O_2$ $[M+H]^+$: 361.0546; found: 361.0544.



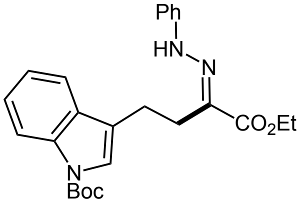
3n was prepared from corresponding alkyl iodide. Isolated as orange oil, 54 mg, 73% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.30 (ap. t, *J* = 7.9 Hz, 2H), 7.19 (ap. d, *J* = 7.8 Hz, 2H), 6.96 (ap. t, *J* = 7.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.62 – 2.55 (m, 2H), 1.57 – 1.48 (m, 2H), 1.46 – 1.40 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.3, 143.4, 136.7, 129.4, 122.0, 114.0, 61.2, 27.6, 24.1, 23.1, 14.4, 14.0. **HRMS** m/z (ESI) calcd. for $C_{14}H_{20}N_2O_2$ $[M+H]^+$: 249.1598; found: 249.1597.



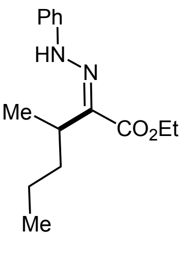
3o was prepared from corresponding alkyl iodide. Isolated as orange solid, 41 mg, 49% yield. (Hex to Hex/EtOAc 9/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.29 (ap. t, *J* = 7.9 Hz, 2H), 7.16 (ap. d, *J* = 7.7 Hz, 2H), 6.94 (ap. t, *J* = 7.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.17 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.14 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 143.6, 136.2, 129.4, 121.7, 113.8, 61.4, 17.1, 14.4, -0.3. **HRMS** m/z (ESI) calcd. for $C_{14}H_{22}N_2O_2Si$ $[M+H]^+$: 279.1523; found: 279.1521.



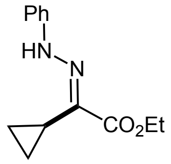
3p was prepared from corresponding alkyl iodide. Isolated as orange solid, 41 mg, 53% yield. (Hex to Hex/EtOAc 9/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.29 (ap. t, *J* = 7.2 Hz, 2H), 7.20 (ap. d, *J* = 8.0 Hz, 2H), 6.96 (ap. t, *J* = 7.3 Hz, 1H), 4.31 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.38 (td, *J* = 7.1, 1.4 Hz, 3H), 1.02 (td, *J* = 7.3, 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 143.4, 136.5, 129.1, 122.1, 114.0, 61.2, 26.3, 19.0, 14.4, 14.4. **HRMS** m/z (ESI) calcd. for $C_{13}H_{18}N_2O_2$ $[M+H]^+$: 235.1441; found: 235.1439.



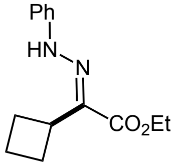
3q was prepared from corresponding alkyl redox-active ester (1.5 eq). Isolated as red solid, 66 mg, 51% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.69 (ap. d, *J* = 7.6 Hz, 1H), 7.40 (ap. dd, *J* = 13.9, 5.6 Hz, 3H), 7.34 (ap. t, *J* = 7.4 Hz, 1H), 7.15 (ap. t, *J* = 7.8 Hz, 2H), 6.87 (ap. t, *J* = 7.3 Hz, 1H), 6.62 (ap. d, *J* = 8.0 Hz, 2H), 4.34 (ap. q, *J* = 7.1 Hz, 2H), 2.99 (s, 4H), 1.60 (s, 9H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.3, 143.0, 135.5, 129.9, 129.2, 125.0, 123.4, 123.0, 122.0, 119.1, 118.5, 116.0, 113.8, 83.8, 61.3, 28.3, 25.0, 22.2, 14.5. **HRMS** m/z (ESI) calcd. for $C_{25}H_{29}N_3O_4$ $[M+H]^+$: 436.2231; found: 436.2227.



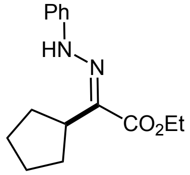
3r was prepared from corresponding alkyl bromide. Isolated as orange oil, 57 mg, 72% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.29 (ap. t, *J* = 7.8 Hz, 2H), 7.17 (ap. d, *J* = 8.1 Hz, 2H), 6.95 (ap. t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.92 (m, 1H), 1.88 – 1.79 (m, 1H), 1.66 – 1.58 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.36 – 1.25 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.9, 143.6, 139.7, 129.4, 121.8, 113.8, 60.9, 35.9, 30.8, 21.4, 17.1, 14.4, 14.2. **HRMS** m/z (ESI) calcd. for $C_{15}H_{22}N_2O_2$ $[M+H]^+$: 263.1754; found: 263.1752.



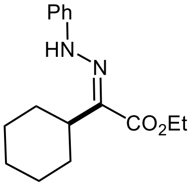
3s was prepared from corresponding alkyl bromide. Isolated as brown oil, 47 mg, 67% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.30 (ap. t, *J* = 7.9 Hz, 2H), 7.20 (ap. d, *J* = 7.7 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.39 – 1.31 (m, 4H), 1.08 – 1.03 (m, 2H), 0.75 – 0.70 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.8, 143.0, 134.9, 129.4, 122.1, 114.1, 77.2, 60.9, 14.4, 5.9, 5.5. HRMS m/z (ESI) calcd. for $C_{13}H_{16}N_2O_2$ $[M+H]^+$: 233.1285; found: 233.1284.



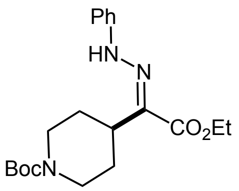
3t was prepared from corresponding alkyl bromide. Isolated as yellow solid, 72 mg, 97% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.28 (ap. t, *J* = 7.9 Hz, 2H), 7.13 (ap. d, *J* = 7.8 Hz, 2H), 6.94 (ap. t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.36 (m, 1H), 2.48 – 2.41 (m, 2H), 2.41 – 2.31 (m, 2H), 2.10 – 2.01 (m, 1H), 1.89 (dd, *J* = 19.4, 9.0 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.8, 143.5, 138.6, 129.4, 121.8, 113.8, 60.9, 33.7, 28.0, 19.7, 14.4. **HRMS** m/z (ESI) calcd. for $C_{14}H_{18}N_2O_2$ $[M+H]^+$: 247.1441; found: 247.1440.



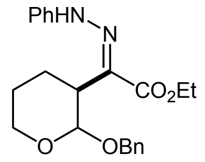
3u was prepared from corresponding alkyl bromide. Isolated as yellow solid, 56 mg, 72% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.29 (ap. t, *J* = 7.9 Hz, 2H), 7.16 (ap. d, *J* = 7.8 Hz, 2H), 6.95 (ap. t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.21 – 3.12 (m, 1H), 1.98 – 1.84 (m, 6H), 1.68 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.9, 143.6, 139.4, 129.4, 121.8, 113.8, 60.9, 35.4, 29.2, 26.9, 14.4.



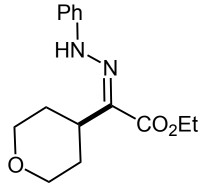
3v was prepared from corresponding alkyl bromide. Isolated as orange solid, 77 mg, 94% yield. From alkyl iodide (**3y**): 71 mg, 86%. From redox-active ester (**3ab**): 56 mg, 68%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.29 (ap. t, *J* = 7.9 Hz, 2H), 7.17 (ap. d, *J* = 7.8 Hz, 2H), 6.95 (ap. t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.66 (tt, *J* = 11.0, 2.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.86 (dd, *J* = 9.8, 2.1 Hz, 2H), 1.76 (d, *J* = 8.5 Hz, 1H), 1.70 (d, *J* = 13.5 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.36 – 1.25 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.0, 143.6, 139.8, 129.4, 121.8, 113.9, 60.9, 36.4, 28.4, 26.7, 26.0, 14.4. **HRMS** m/z (ESI) calcd. for $C_{16}H_{22}N_2O_2$ $[M+H]^+$: 275.1754; found: 275.1753.



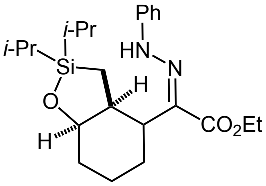
3w was prepared from corresponding alkyl bromide. Isolated as yellow solid, 80 mg, 71% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.27 (ap. dd, *J* = 10.9, 3.7 Hz, 2H), 7.18 (ap. d, *J* = 7.9 Hz, 2H), 6.94 (ap. t, *J* = 6.8 Hz, 1H), 4.32 – 4.14 (m, 4H), 2.87 (t, *J* = 11.6 Hz, 1H), 2.74 (s, 2H), 2.13 (d, *J* = 11.3 Hz, 2H), 1.60 (d, *J* = 12.4 Hz, 2H), 1.47 (s, 9H), 1.35 (dd, *J* = 9.0, 4.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.7, 154.8, 143.5, 137.1, 129.4, 122.0, 114.0, 79.8, 34.3, 28.5, 27.4, 14.3. **HRMS** m/z (ESI) calcd. for $C_{20}H_{29}N_3O_4$ $[M+H]^+$: 376.2231; found: 376.2229.



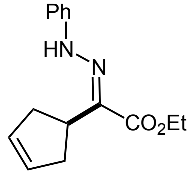
3x was prepared from corresponding alkyl bromide. Isolated as yellow solid, 94 mg, 82% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.24 – 7.17 (m, 7H), 6.97 (ap. d, *J* = 7.9 Hz, 2H), 6.92 (ap. t, *J* = 7.3 Hz, 1H), 4.96 (d, *J* = 7.9 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 11.4 Hz, 1H), 4.29 – 4.19 (m, 2H), 4.11 (d, *J* = 11.3 Hz, 1H), 3.65 (td, *J* = 11.3, 4.3 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.32 (ddd, *J* = 16.9, 11.6, 5.9 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.71 – 1.63 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.0, 144.0, 137.1, 136.1, 129.2, 128.5, 128.1, 127.9, 121.8, 114.3, 101.6, 70.8, 65.8, 61.0, 41.2, 25.0, 24.8, 14.4. **HRMS** m/z (ESI) calcd. for $C_{22}H_{26}N_2O_4$ $[M+H]^+$: 383.1893 not detected. $[M-OBn]^+$: 275.1396; found: 275.1392.



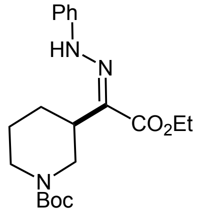
3z was prepared from corresponding redox-active ester. Isolated as white solid, 63 mg, 76% yield. (Hex/EtOAc 1/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.30 (ap. t, *J* = 7.8 Hz, 2H), 7.19 (ap. d, *J* = 8.2 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.08 (dd, *J* = 11.5, 4.1 Hz, 2H), 3.50 (t, *J* = 11.3 Hz, 2H), 3.03 (tt, *J* = 12.2, 3.6 Hz, 1H), 2.33 (qd, *J* = 12.6, 4.4 Hz, 2H), 1.57 (d, *J* = 13.0 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.8, 143.4, 137.0, 129.5, 122.2, 114.0, 68.2, 61.1, 33.5, 31.1, 28.0, 14.4.



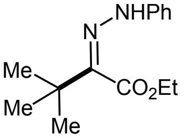
3aa was prepared from corresponding alkyl iodide (0.265 mmol scale). Isolated as yellow solid, 61 mg, 55% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.30 (ap. t, *J* = 7.8 Hz, 2H), 7.14 (ap. d, *J* = 8.1 Hz, 2H), 6.96 (ap. t, *J* = 7.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 1H), 2.88 (ddd, *J* = 11.5, 8.2, 3.7 Hz, 1H), 2.54 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.15 (d, *J* = 8.9 Hz, 1H), 1.84 (dt, *J* = 14.9, 10.6 Hz, 1H), 1.64 (ddd, *J* = 18.3, 12.8, 11.7 Hz, 5H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.22 – 0.96 (m, 16H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.7, 143.3, 138.5, 129.4, 121.9, 113.7, 76.5, 60.8, 38.3, 37.1, 30.8, 27.9, 19.9, 18.1, 18.1, 17.7, 17.5, 14.4, 14.1, 12.9, 12.3. **HRMS** m/z (ESI) calcd. for $C_{23}H_{36}N_2O_3Si$ $[M+H]^+$: 417.2568; found: 417.2569.



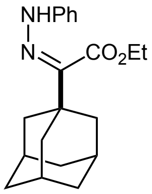
3ac was prepared from corresponding redox-active ester. Isolated as white solid, 35 mg, 45% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.14 (ddd, *J* = 15.7, 11.0, 4.6 Hz, 1H), 2.85 (dd, *J* = 14.0, 11.4 Hz, 2H), 2.45 (dd, *J* = 14.2, 4.4 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.8, 143.5, 138.1, 131.2, 129.4, 121.9, 113.6, 61.4, 35.6, 30.8, 14.5. **HRMS** m/z (ESI) calcd. for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441; found: 259.1439.



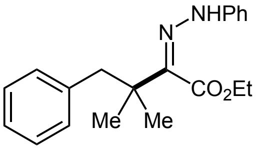
3ad was prepared from corresponding redox-active ester. Isolated as orange solid, 72 mg, 64% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.30 (ap. t, *J* = 7.8 Hz, 2H), 7.24 (ap. d, *J* = 8.0 Hz, 2H), 6.96 (ap. t, *J* = 7.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 3H), 4.06 (d, *J* = 12.3 Hz, 1H), 4.00 (d, *J* = 13.1 Hz, 1H), 3.09 (s, 1H), 2.87 (t, *J* = 12.6 Hz, 1H), 2.71 (t, *J* = 11.2 Hz, 1H), 2.29 (d, *J* = 8.1 Hz, 1H), 1.85 (d, *J* = 12.9 Hz, 1H), 1.75 (d, *J* = 13.5 Hz, 1H), 1.50 (s, 9H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.7, 143.7, 134.9, 129.4, 122.0, 114.1, 80.3, 60.9, 46.3, 35.8, 28.6, 27.1, 25.9, 14.4. **HRMS** m/z (ESI) calcd. for $C_{20}H_{29}N_3O_4$ $[M+H]^+$: 376.2231; found: 376.2228.



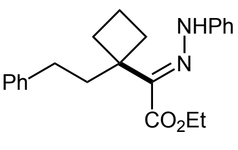
3ae was prepared from corresponding alkyl bromide. DBU (2 eq) used as base. Isolated as orange solid, 74 mg, 99% yield. From alkyl iodide (**3al**): 52 mg, 70% (1,4-dioxane (0.2 M) as solvent; DBU (2 eq) as base). From redox-active ester (**3am**): 49 mg, 66%. (Hex to Hex/EtOAc 20/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.78 (s, 1H), 7.28 (ap. t, *J* = 7.9 Hz, 2H), 7.17 (ap. d, *J* = 7.7 Hz, 2H), 6.93 (ap. t, *J* = 7.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.1, 144.3, 135.0, 129.4, 121.5, 113.7, 60.5, 37.4, 29.3, 14.3. HRMS m/z (ESI) calcd. for $C_{14}H_{20}N_2O_2$ $[M+H]^+$: 249.1598; found: 249.1599.



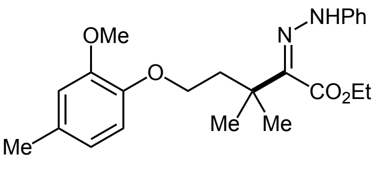
3af was prepared from corresponding alkyl bromide. Isolated as a mixture of diazene **3af'** and hydrazone **3af** (^{1}H NMR of mixture can be found in NMR spectra section). Isomerizes into hydrazone quantitatively in $CDCl_3$ overnight. Yellow solid, 97 mg, 99% yield. (Hex to Hex/EtOAc 20/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.68 (s, 1H), 7.28 – 7.20 (m, 2H), 7.13 (ap. d, *J* = 6.8 Hz, 2H), 6.89 (ap. t, *J* = 6.8 Hz, 1H), 4.29 (qd, *J* = 7.1, 2.6 Hz, 2H), 2.02 (s, 3H), 1.98 (s, 6H), 1.71 (q, *J* = 12.4 Hz, 6H), 1.37 (td, *J* = 7.1, 2.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.1, 144.4, 135.7, 129.4, 121.4, 113.7, 60.5, 40.5, 39.6, 37.1, 28.9, 14.3. **HRMS** m/z (ESI) calcd. for $C_{20}H_{26}N_2O_2$ $[M+H]^+$: 327.2067; found: 327.2066.



3ag was prepared from corresponding alkyl bromide. Isolated as orange solid, 82 mg, 84% yield. (Hex to Hex/EtOAc 20/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.86 (s, 1H), 7.27 – 7.20 (m, 4H), 7.16 (ap. t, *J* = 7.3 Hz, 1H), 7.09 – 7.04 (m, 4H), 6.91 (t, *J* = 7.3 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.06 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.1, 144.1, 139.3, 133.4, 130.5, 129.3, 127.8, 126.0, 121.6, 113.8, 60.7, 46.7, 41.6, 27.4, 14.4. **HRMS** m/z (ESI) calcd. for $C_{20}H_{24}N_2O_2$ $[M+H]^+$: 325.1911; found: 325.1915.

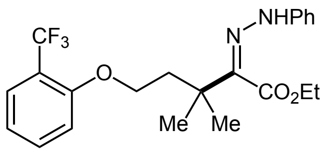


3ah was prepared from corresponding alkyl bromide. Isolated as yellow solid, 69 mg, 67% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.33 – 7.27 (m, 4H), 7.23 – 7.17 (m, 3H), 7.14 (ap. d, *J* = 8.0 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.72 (dd, *J* = 10.5, 6.6 Hz, 2H), 2.52 (dd, *J* = 21.5, 9.8 Hz, 2H), 2.29 (dd, *J* = 18.0, 10.0 Hz, 4H), 2.23 – 2.12 (m, 1H), 1.92 (dt, *J* = 11.3, 9.4 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.5, 143.3, 142.1, 139.5, 129.4, 128.5, 128.4, 126.1, 121.9, 113.7, 60.9, 44.9, 38.7, 32.2, 32.0, 17.3, 14.4. **HRMS** m/z (ESI) calcd. for $C_{22}H_{26}N_2O_2$ $[M+H]^+$: 351.2067; found: 351.2070.

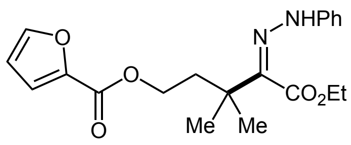


3ai was prepared from corresponding alkyl bromide. Isolated as yellow oil, 98 mg, 82% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.96 (s, 1H), 7.30 (ap. t, *J* = 7.9 Hz, 2H), 7.18 (ap. d, *J* = 7.7 Hz, 2H), 6.95 (ap. t, *J* = 7.3 Hz, 1H), 6.74 (ap. d, *J* = 8.1 Hz, 1H), 6.68 (ap. d, *J* = 1.4 Hz, 1H), 6.64 (ap. dd, *J* =

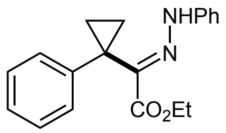
8.1, 1.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.01 (t, *J* = 7.4 Hz, 2H), 3.84 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.29 (s, 3H), 1.40 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.9, 149.3, 146.3, 144.1, 133.0, 130.5, 129.3, 121.6, 120.8, 113.7, 113.3, 112.9, 66.4, 60.6, 55.8, 39.8, 39.3, 27.9, 21.1, 14.2. **HRMS** m/z (ESI) calcd. for $C_{23}H_{30}N_2O_4$ [M+H]$^{+}$: 399.2278; found: 399.2279.



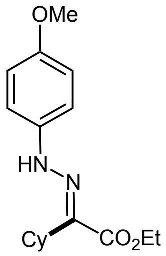
3aj was prepared from corresponding alkyl bromide. Isolated as yellow solid, 57 mg, 72% yield. (Hex to Hex/EtOAc 20/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 11.96 (s, 1H), 7.56 (ap. d, *J* = 7.7 Hz, 1H), 7.42 (ap. t, *J* = 7.5 Hz, 1H), 7.31 (ap. t, *J* = 7.9 Hz, 2H), 7.19 (ap. d, *J* = 7.7 Hz, 2H), 6.99 – 6.93 (m, *J* = 11.9, 4.5 Hz, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.08 (t, *J* = 7.1 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.42 (s, 6H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.0, 157.1, 144.1, 133.3, 132.8, 129.4, 127.1 (q, *J* = 5.2 Hz), 123.9 (q, *J* = 272.3 Hz), 121.7, 119.9, 119.1 (q, *J* = 30.5 Hz), 66.5, 60.8, 39.8, 39.4, 27.8, 14.1. **^{19}F NMR** (565 MHz, CDCl$_3$) δ -62.3. **HRMS** m/z (ESI) calcd. for $C_{22}H_{25}F_3N_2O_3$ [M+H]$^{+}$: 423.1890; found: 423.1891.



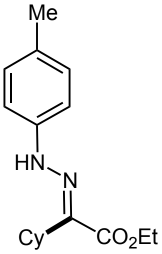
3ak was prepared from corresponding alkyl bromide. Isolated as yellow oil, 85 mg, 76% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 11.91 (s, 1H), 7.50 (ap. s, 1H), 7.25 (ap. dd, *J* = 11.3, 3.9 Hz, 2H), 7.12 (ap. d, *J* = 8.0 Hz, 2H), 7.05 (ap. d, *J* = 2.5 Hz, 1H), 6.91 (ap. t, *J* = 7.2 Hz, 1H), 6.47 – 6.41 (m, 1H), 4.31 (t, *J* = 6.7 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 2.19 (t, *J* = 6.7 Hz, 2H), 1.37 – 1.30 (m, 9H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.8, 158.7, 146.2, 144.9, 144.0, 132.6, 129.4, 121.7, 117.7, 113.8, 111.8, 62.6, 60.7, 39.4, 39.4, 27.8, 14.2. **HRMS** m/z (ESI) calcd. for $C_{20}H_{24}N_2O_5$ [M+H]$^{+}$: 373.1758; found: 373.1760.



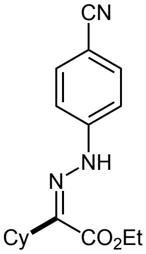
3an was prepared from corresponding redox-active ester. Isolated as white solid, 42 mg, 45% yield. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.59 (s, 1H), 7.30 – 7.26 (m, 4H), 7.20 (ap. t, *J* = 7.4 Hz, 1H), 7.16 (ap. d, *J* = 7.9 Hz, 2H), 7.13 (ap. d, *J* = 7.6 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.48 (q, *J* = 4.8 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.30 (q, *J* = 4.8 Hz, 2H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 164.7, 142.8, 140.0, 135.2, 129.4, 129.1, 126.6, 125.2, 122.4, 114.4, 61.1, 20.0, 18.1, 14.5. **HRMS** m/z (ESI) calcd. for $C_{19}H_{20}N_2O_2$ [M+H]$^{+}$: 309.1598; found: 309.1598.



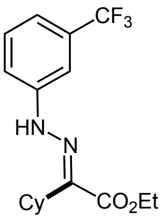
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.95 (s, 1H), 7.12 (ap. d, *J* = 8.9 Hz, 3H), 6.89 – 6.81 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 3H), 3.77 (s, 4H), 2.64 (ddt, *J* = 11.7, 8.5, 3.1 Hz, 1H), 1.99 – 1.64 (m, 7H), 1.41 – 1.28 (m, 6H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.9, 154.8, 138.1, 131.6, 114.8, 114.7, 60.4, 55.7, 40.6, 32.0, 26.8, 26.4, 14.4. **HRMS** m/z (ESI) calcd. for $C_{17}H_{24}N_2O_2$ [M+H]$^{+}$: 305.1860; found: 305.1857.



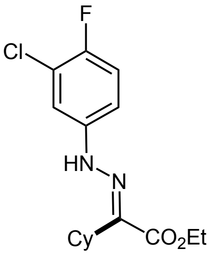
3ap was isolated as brown solid, 81 mg, 94%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.15 – 7.03 (m, 4H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 12.0 Hz, 1H), 2.29 (s, 3H), 1.93 (dd, *J* = 24.5, 12.2 Hz, 2H), 1.85 (d, *J* = 9.7 Hz, 2H), 1.76 – 1.72 (m, 1H), 1.68 (d, *J* = 13.3 Hz, 2H), 1.41 – 1.29 (m, 6H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 165.0, 141.4, 139.1, 131.1, 129.9, 129.9, 113.8, 60.8, 36.3, 31.0, 28.4, 26.7, 26.0, 20.8, 14.4. **HRMS** m/z (ESI) calcd. for $C_{17}H_{24}N_2O_2$ [M+H]$^+$: 289.1911; found: 289.1906.



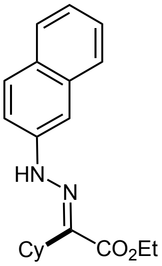
3aq was isolated as white solid, 73 mg, 81%. (Hex to Hex/EtOAc 4/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 12.16 (s, 1H), 7.53 (ap. d, *J* = 8.7 Hz, 2H), 7.17 (ap. d, *J* = 8.6 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.66 (ddd, *J* = 11.2, 8.5, 2.9 Hz, 1H), 1.91 – 1.78 (m, 4H), 1.72 (d, *J* = 12.8 Hz, 1H), 1.42 – 1.32 (m, 7H), 1.26 – 1.18 (m, 1H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.5, 147.4, 136.6, 133.7, 119.9, 113.7, 103.5, 61.2, 40.9, 31.7, 26.6, 26.3, 14.2. **HRMS** m/z (ESI) calcd. for $C_{17}H_{21}N_3O_2$ [M+H]$^+$: 300.1707; found: 300.1705.



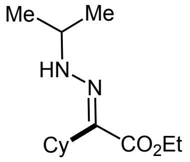
3ar was isolated as yellow solid, 81 mg, 79%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.40 (ap. s, 1H), 7.39 – 7.33 (m, 2H), 7.17 (ap. d, *J* = 6.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.71 – 2.63 (m, 1H), 1.96 – 1.81 (m, 4H), 1.77 – 1.66 (m, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.35 – 1.28 (m, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 164.8, 144.2, 141.6, 131.7 (q, *J* = 32.3 Hz), 129.9, 124.2 (q, *J* = 272.3 Hz), 118.1, 116.9, 110.6 (q, *J* = 3.9 Hz), 61.1, 36.6, 28.4, 26.5, 25.9, 14.3. **^{19}F NMR** (565 MHz, CDCl$_3$) δ -62.8. **HRMS** m/z (ESI) calcd. for $C_{17}H_{21}F_3N_2O_2$ [M+H]$^+$: 343.1628; found: 343.1624.



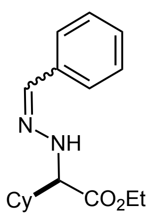
3as was isolated as orange solid, 71 mg, 72%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.24 (ap. dd, *J* = 6.3, 2.7 Hz, 1H), 7.05 (ap. t, *J* = 8.7 Hz, 1H), 7.01 – 6.96 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.61 (tt, *J* = 12.0, 3.2 Hz, 1H), 1.95 – 1.80 (m, 4H), 1.78 – 1.63 (m, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.35 – 1.23 (m, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 163.7, 154.1, 152.5, 141.1, 141.0, 134.1, 121.7 (d, *J* = 18.8 Hz), 117.0 (d, *J* = 22.4 Hz), 115.0, 112.8 (d, *J* = 6.6 Hz), 60.8, 40.8, 31.8, 26.7, 26.3, 14.3. **^{19}F NMR** (565 MHz, CDCl$_3$) δ -125.6. **HRMS** m/z (ESI) calcd. for $C_{16}H_{20}ClFN_2O_2$ [M+H]$^+$: 327.1270; found: 327.1267.



3at was isolated as orange solid, 63 mg, 65%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.21 (s, 1H), 7.79 (ap. d, *J* = 8.8 Hz, 1H), 7.75 (ap. dd, *J* = 10.8, 8.5 Hz, 2H), 7.52 (ap. d, *J* = 1.7 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 (ap. t, *J* = 7.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.73 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.03 – 1.91 (m, 2H), 1.91 – 1.83 (m, 2H), 1.81 – 1.70 (m, 3H), 1.45 – 1.40 (m, 3H), 1.40 – 1.32 (m, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 165.0, 141.3, 140.3, 134.5, 129.8, 129.5, 127.9, 127.0, 126.7, 123.8, 115.7, 108.8, 61.0, 36.5, 28.5, 26.7, 26.0, 14.5.

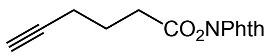


3au was prepared according to the general procedure using 1,4-dioxane (0.2 M) as a solvent. Isolated as colorless oil, 42 mg, 58%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.61 (ap. d, *J* = 5.6 Hz, 1H), 4.21 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.72 – 3.63 (m, 1H), 2.47 (t, *J* = 11.9 Hz, 1H), 1.90 – 1.74 (m, 5H), 1.73 – 1.66 (m, 1H), 1.58 (d, *J* = 13.0 Hz, 2H), 1.32 – 1.23 (m, 6H), 1.19 (dd, *J* = 6.5, 1.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.1, 139.0, 60.5, 51.5, 36.0, 28.2, 26.8, 26.1, 22.5, 14.5. **HRMS** m/z (ESI) calcd. for $C_{13}H_{24}N_2O_2$ $[M+H]^+$: 241.1911; found: 241.1908.

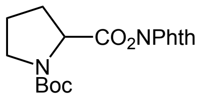


3av was prepared according to the general procedure using 1,4-dioxane (0.2 M) as a solvent. Isolated as colorless oil, 62 mg, 72%. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.53 (ap. d, *J* = 7.4 Hz, 2H), 7.32 (ap. t, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, *J* = 7.2 Hz, 1H), 5.75 (s, 1H), 4.18 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.97 (s, 1H), 1.89 – 1.64 (m, 6H), 1.32 – 1.11 (m, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.9, 140.7, 135.4, 128.5, 128.5, 126.3, 67.5, 60.8, 40.2, 29.8, 29.4, 26.3, 26.2, 26.2, 14.5.

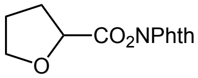
Failed substrates (decomposition or less than 20% yield)



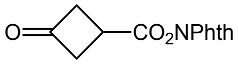
F1



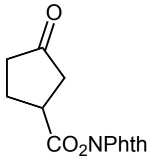
F2



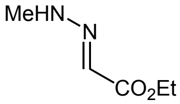
F3



F4

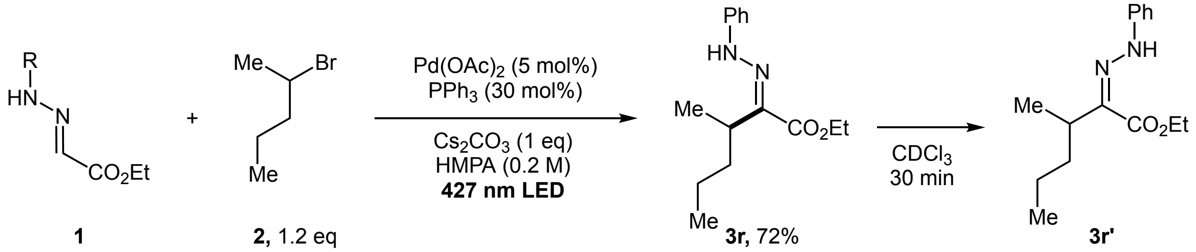


F5

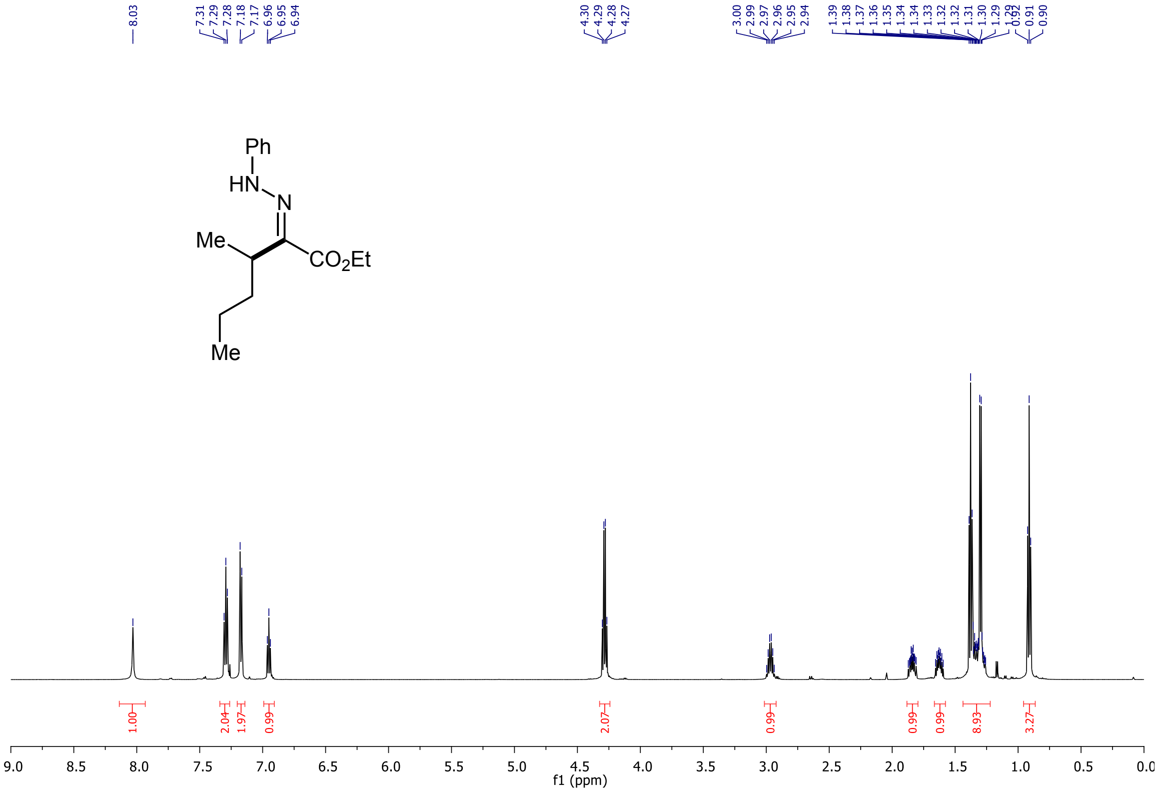


F6

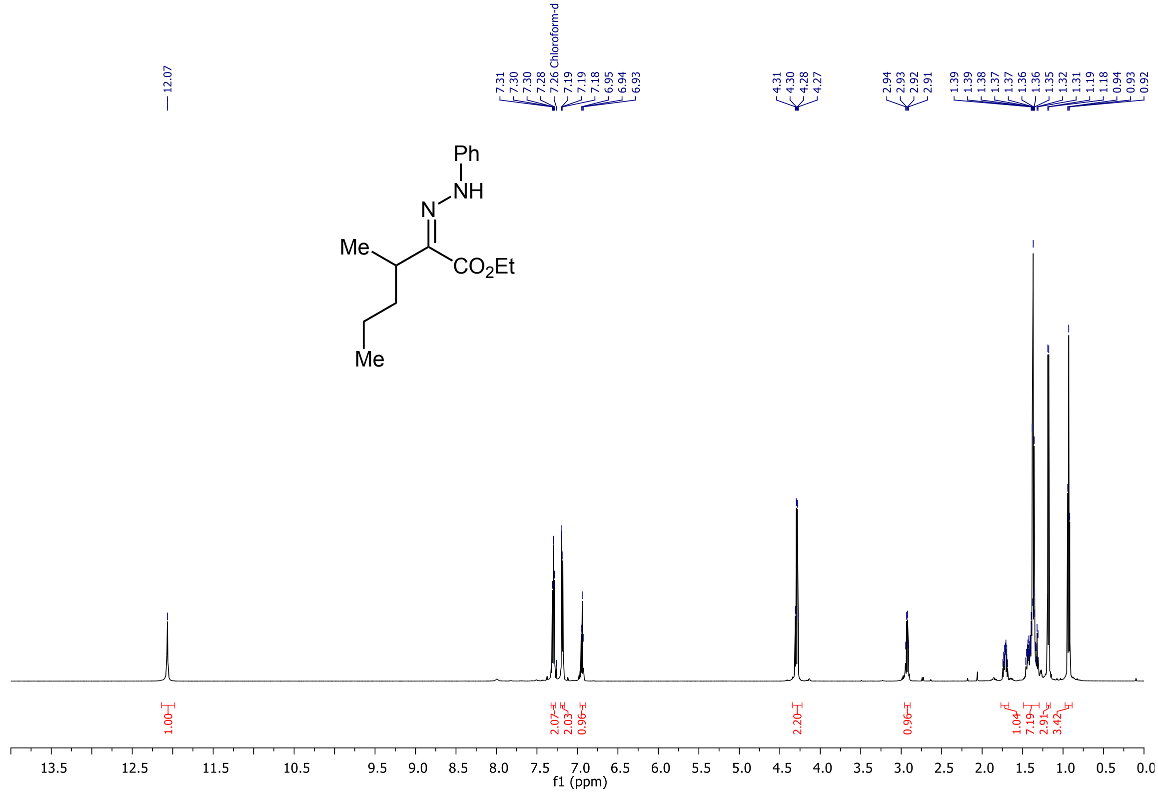
Isomerization in non-neutralized $CDCl_3$



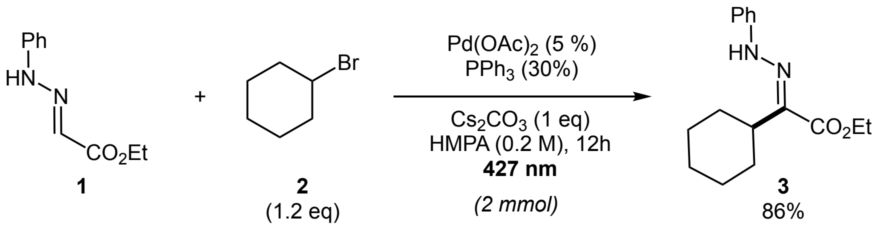
^{1}**H NMR** of initially isolated **3r**



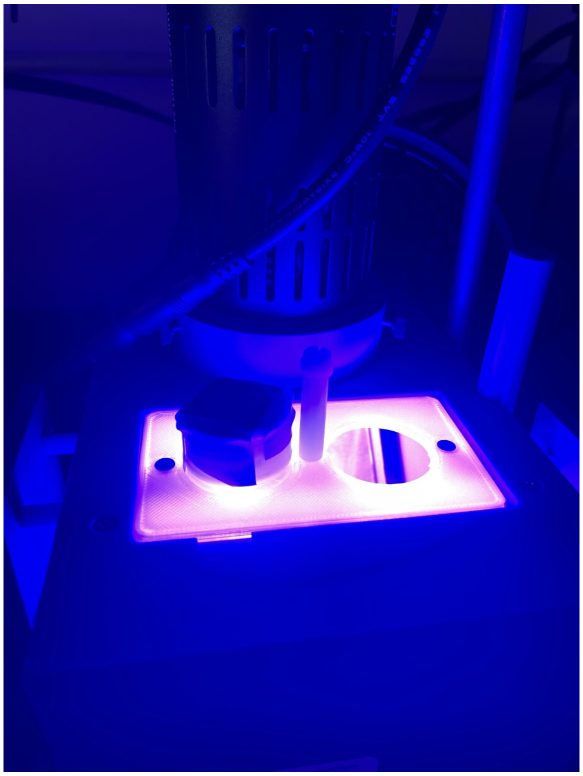
^{1}**H NMR** of the same sample after 30 min



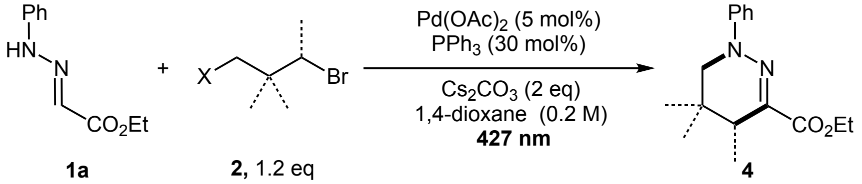
Scaleup Experiment



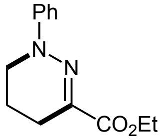
20 mL screw cap vial equipped with stir bar was charged with hydrazine **1** (384 mg, 2 mmol, 1 eq). Vial was taken up in glove box and charged in sequence with Cs_2CO_3 (652 mg, 2 mmol, 1 eq), PPh_3 (157 mg, 0.3 mmol, 0.3 eq), $Pd(OAc)_2$ (24 mg, 0.1 mmol, 0.05 eq) and screw capped using cap with septum. Outside of glovebox HMPA (10 mL) was added following up by cycloheylbromide (0.294 mL, 2.4 mmol, 1.2 eq). Reaction mixture was irradiated with Kessil 427 nm lamp (PR160L) in HepatoChem photoredox box equipped with a fan for 12 h. Stirring rate 400-500 rpm. Reaction completion was monitored using GC-MS. Mixture was diluted with EtOAc (70 mL), washed with water (2 x 70mL) and brine (50 mL). Organic phase was dried over Na_2SO_4, concentrated. Crude product was purified using flash chromatography (Hex to Hex/EtOAc 9/1). Obtained 470 mg (86 %) of **3v**.



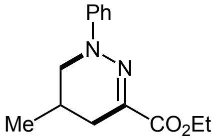
5. Sequential *C*,*N*-Alkylation



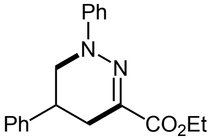
5 mL screw cap vial equipped with stir bar was charged with corresponding hydrazone (0.3 mmol, 1 eq). Vial was taken up in glove box and charged in sequence with Cs_2CO_3 (195 mg, 0.6 mmol, 2 eq) (unless DBU is used as a base), PPh_3 (23.6 mg, 0.09 mmol, 0.3 eq), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.05 eq) and screw capped using cap with septum. Outside of glovebox 1,4-dioxane (1.5 mL) was added following up by DBU (90 µL, 0.6 mmol, 2 eq) and dihalide (0.36 mmol, 1.2 eq). Dihalide could also be added as a solution in 1,4-dioxane, in case microsyringe cannot be used. Reaction mixture was irradiated with Kessil 427 nm lamp (PR160L) in HepatoChem photoredox box equipped with a fan for 12-32 h. Stirring rate 400-500 rpm. Reaction progress was monitored using GC-MS. Reaction mixture was filtered through short pad of celite, washed with EtOAc. Solvent was removed *in vacuo*. Crude reaction mixture was purified using flash chromatography.



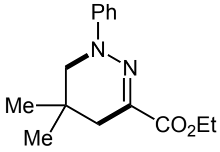
4a was prepared from corresponding dibromide, usind DBU as base. Isolated as orange solid, 47 mg, 67.4% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 6.99 (ap. ddd, *J* = 8.4, 6.0, 2.4 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.66 (m, 2H), 2.54 (t, *J* = 6.5 Hz, 2H), 2.06 – 2.00 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 146.6, 131.9, 129.2, 122.1, 115.1, 61.0, 43.5, 20.8, 17.5, 14.5. **HRMS** m/z (ESI) calcd. for $C_{13}H_{16}N_2O_2$ $[M+H]^+$: 233.1285; found: 233.1279.



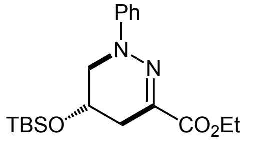
4b was prepared from corresponding dibromide (1.5 eq) using Cs_2CO_3 as base. Isolated as yellow solid, 58 mg, 79% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.00 (ap. dd, *J* = 8.9, 4.4 Hz, 1H), 4.36 – 4.25 (m, 2H), 3.81 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.76 (dd, *J* = 13.1, 2.4 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.4, 146.7, 131.7, 129.2, 122.1, 115.2, 61.0, 50.0, 29.0, 23.0, 19.3, 14.5. **HRMS** m/z (ESI) calcd. for $C_{14}H_{18}N_2O_2$ $[M+H]^+$: 247.1441; found: 247.1437.



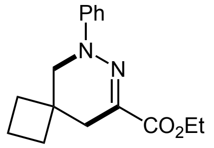
4c was prepared from corresponding dibromide using Cs_2CO_3 as base. Isolated as brown solid, 45 mg, 49% yield. (Hex to Hex/EtOAc 9/1) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 7H), 7.25 – 7.23 (m, 2H), 7.01 (tt, *J* = 7.0, 1.3 Hz, 1H), 4.38 – 4.27 (m, 2H), 4.06 (ddd, *J* = 12.1, 4.3, 2.7 Hz, 1H), 3.44 (t, *J* = 11.4 Hz, 1H), 3.12 (ddd, *J* = 15.5, 10.7, 4.7 Hz, 1H), 3.04 (ddd, *J* = 18.0, 5.1, 2.3 Hz, 1H), 2.55 (dd, *J* = 17.8, 11.0 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 146.4, 141.7, 132.5, 129.2, 129.1, 127.6, 127.3, 122.4, 115.4, 61.1, 49.8, 34.2, 28.4, 14.5. **HRMS** m/z (ESI) calcd. for $C_{19}H_{20}N_2O_2$ $[M+H]^+$: 309.1598; found: 309.1592.



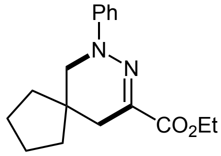
4d was prepared from corresponding dibromide using DBU as base. Isolated as orange solid, 50 mg, 64% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.01 (ap. dd, *J* = 9.3, 4.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.31 (s, 2H), 2.31 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.06 – 1.02 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6, 147.0, 131.5, 129.2, 122.2, 115.5, 61.0, 55.0, 35.2, 27.0, 26.0, 14.5. **HRMS** m/z (ESI) calcd. for $C_{15}H_{20}N_2O_2$ $[M+H]^+$: 261.1598; found: 261.1592.



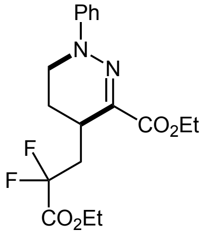
4e was prepared from corresponding chloro-bromide **S23** using DBU as base. Isolated as yellow solid, 78 mg, 72% yield. (Hex to Hex/EtOAc 95/5) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 4H), 7.01 (ap. ddd, *J* = 8.4, 5.2, 3.3 Hz, 1H), 4.35 – 4.27 (m, 2H), 4.23 – 4.18 (m, 1H), 3.82 – 3.77 (m, 1H), 3.34 (ddd, *J* = 11.8, 7.7, 0.9 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.3, 146.6, 130.7, 129.2, 122.3, 115.5, 61.2, 61.1, 50.3, 31.3, 25.8, 18.1, 14.5, -4.5, -4.6. **HRMS** m/z (ESI) calcd. for $C_{19}H_{30}N_2O_3Si$ $[M+H]^+$: 363.2098; found: 363.2092



4f was prepared from corresponding dibromide using Cs_2CO_3 as base. Isolated as yellow oil, 60 mg, 73% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.03 – 6.98 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 2H), 2.58 (s, 2H), 2.07 – 1.96 (m, 2H), 1.90 (t, *J* = 7.3 Hz, 4H), 1.41 – 1.35 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 146.9, 131.4, 129.2, 122.2, 115.3, 61.0, 53.6, 34.3, 33.1, 31.6, 15.1, 14.5. **HRMS** m/z (ESI) calcd. for $C_{16}H_{20}N_2O_2$ $[M+H]^+$: 273.1598; found: 273.1591.

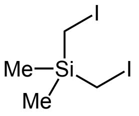


4g was prepared from corresponding dibromide (1.5 eq) using Cs_2CO_3 as base. Isolated as yellow oil, 58 mg, 68% yield. (Hex to Hex/EtOAc 9/1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 4H), 7.06 – 6.96 (m, 1H), 4.36 – 4.25 (m, 2H), 3.39 (s, 2H), 2.42 (s, 2H), 1.80 – 1.65 (m, 4H), 1.53 – 1.41 (m, 4H), 1.41 – 1.35 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.6, 146.9, 132.0, 129.2, 122.2, 115.4, 61.0, 53.8, 37.7, 36.9, 34.5, 25.2, 14.5. **HRMS** m/z (ESI) calcd. for $C_{17}H_{22}N_2O_2$ $[M+H]^+$: 287.1754; found: 287.1747.

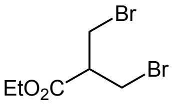


4h was prepared from corresponding chloro-iodide using Cs_2CO_3 as base. Isolated as yellow solid, 87 mg, 79% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.03 (ap. t, *J* = 6.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.35 – 4.24 (m, 2H), 3.94 (d, *J* = 12.6 Hz, 1H), 3.48 (td, *J* = 13.0, 3.8 Hz, 1H), 3.28 – 3.22 (m, 1H), 2.47 (td, *J* = 17.5, 8.7 Hz, 1H), 2.27 (d, *J* = 13.9 Hz, 1H), 2.16 – 2.03 (m, 1H), 1.96 – 1.88 (m, 1H), 1.37 (q, *J* = 6.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.4, 164.3 – 163.7 (m), 146.1, 131.7, 129.2, 122.6, 115.3 (dd, *J* = 467.8, 215.6 Hz), 115.1, 63.3, 61.0, 39.6, 37.0 (t, *J* = 22.2 Hz), 24.0, 21.4, 14.5, 14.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -101.5 (d, *J* = 259.9 Hz), -106.3 (d, *J* = 259.9 Hz).

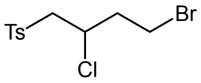
Failed substrates



F7
hydrazone consumed
but no product obtained

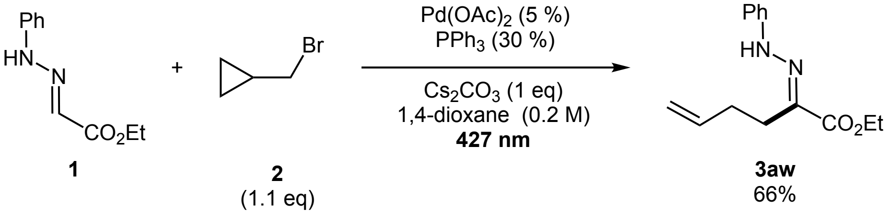


F8
dihalide prematuraly
decomposes

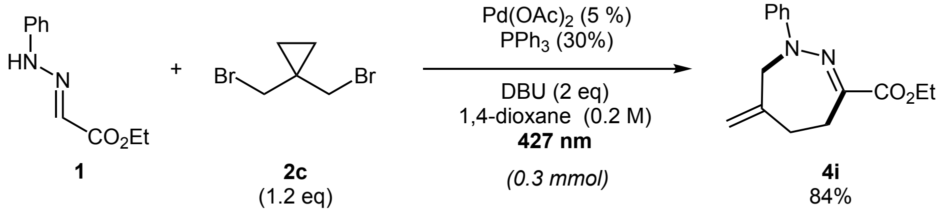


F9
no reaction

6. Ring-opening Experiments



5 mL screw cap vial equipped with stir bar was charged with corresponding hydrazone (57.7 mg, 0.3 mmol, 1 eq). Vial was taken up in glove box and charged in sequence Cs_2CO_3 (98 mg, 0.3 mmol, 1 eq), PPh_3 (23.6 mg, 0.09 mmol, 0.3 eq), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.05 eq) and screw capped using cap with septum. Outside of glovebox 1,4-dioxane (1.5 mL) was added following up (bromomethyl)cyclopropane (32 µL, 0.33 mmol, 1.1 eq). Reaction mixture was irradiated with Kessil 427 nm lamp (PR160L) in HepatoChem photoredox box equipped with a fan for 12-32 h. Stirring rate 400-500 rpm. Reaction progress was monitored using GC-MS. Reaction mixture was filtered through short pad of celite, washed with EtOAc. Solvent was removed *in vacuo*. Crude reaction mixture was purified using flash chromatography (Hex to Hex/EtOAc 9/1). Yellow oil 49 mg, 66%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.30 (ap. t, *J* = 7.8 Hz, 2H), 7.18 (ap. d, *J* = 8.0 Hz, 2H), 6.97 (ap. t, *J* = 7.3 Hz, 1H), 5.88 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.32 (dd, *J* = 14.6, 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.2, 143.3, 137.2, 135.8, 129.5, 122.2, 116.4, 114.1, 61.3, 29.8, 24.2, 14.5. **HRMS** m/z (ESI) calcd. for $C_{14}H_{18}N_2O_2$ $[M+H]^+$: 247.1441; found: 247.1438.



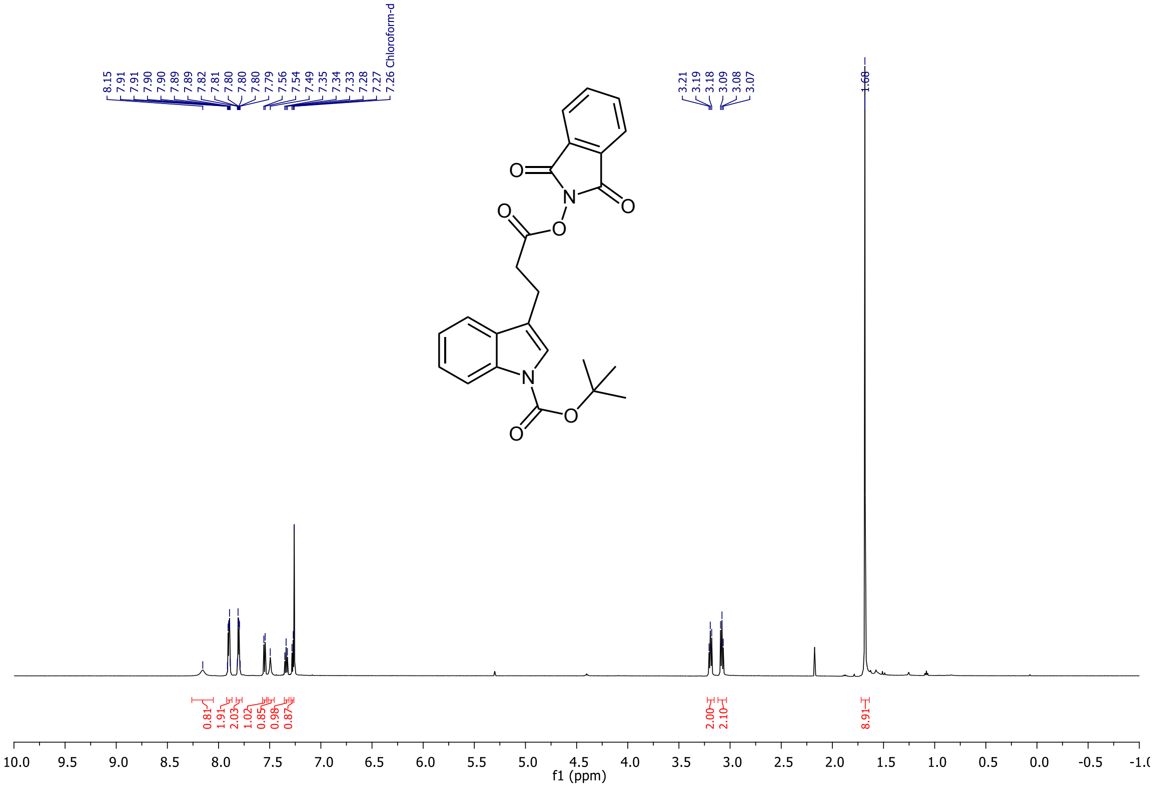
5 mL screw cap vial equipped with stir bar was charged with corresponding hydrazone (57.7 mg, 0.3 mmol, 1 eq). Vial was taken up in glove box and charged in sequence PPh_3 (23.6 mg, 0.09 mmol, 0.3 eq), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.05 eq) and screw capped using cap with septum. Outside of glovebox dihalide (75.2 mg, 0.36 mmol, 1.2 eq) in 1,4-dioxane (1.5 mL) was added following up by DBU (90 µL, 0.6 mmol, 2 eq). Reaction mixture was irradiated with Kessil 427 nm lamp (PR160L) in HepatoChem photoredox box equipped with a fan for 12-32 h. Stirring rate 400-500 rpm. Reaction progress was monitored using GC-MS. Reaction mixture was filtered through short pad of celite, washed with EtOAc. Solvent was removed *in vacuo*. Crude reaction mixture was purified using flash chromatography (Hex to Hex/EtOAc 9/1). **Nk4619** Yellow oil 65 mg, 84%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 6.98 (ap. ddd, *J* = 6.9, 2.8, 1.3 Hz, 1H), 5.00 (d, *J* = 0.6 Hz, 1H), 4.93 (s, 1H), 4.55 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.06 – 2.99 (m, 2H), 2.71 – 2.66 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.2, 148.3, 143.7, 137.0, 129.1, 122.0, 115.8, 110.8, 61.4, 59.2, 31.3, 27.5, 14.4. **HRMS** m/z (ESI) calcd. for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441; found: 259.1436.

7. References

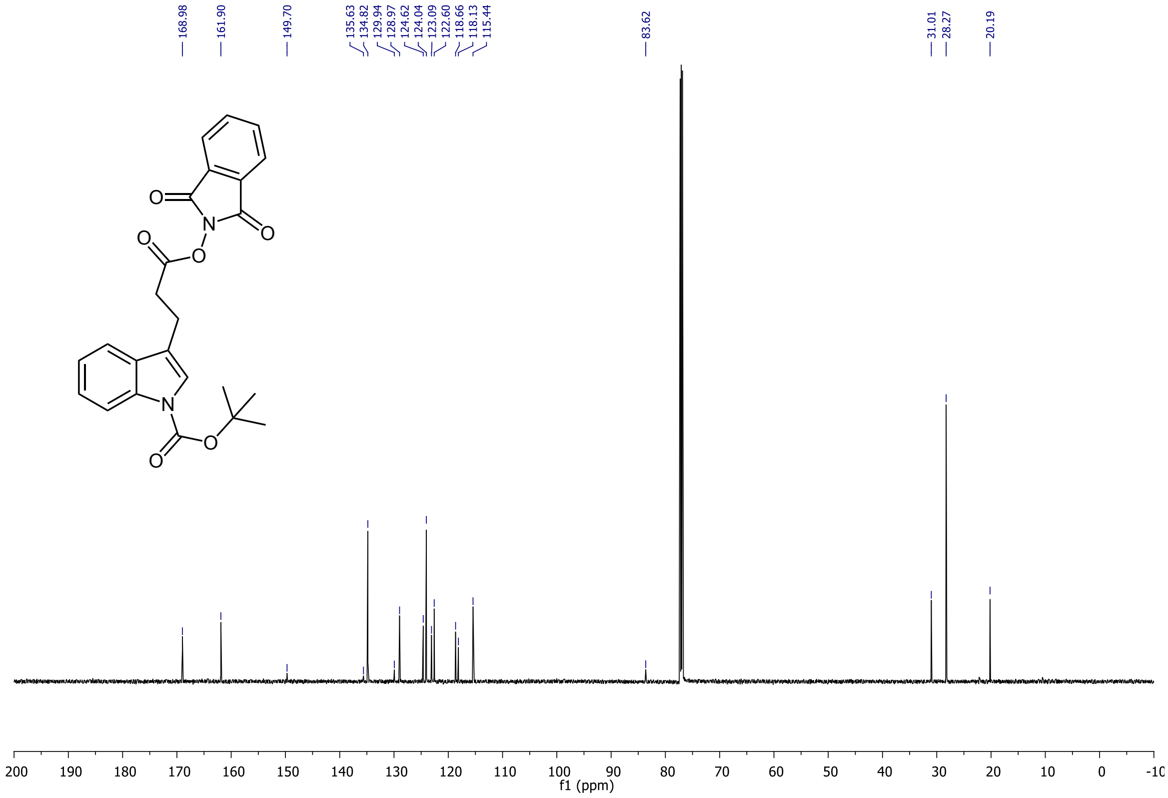
[1] C.-M. Chan, Q. Xing, Y.-C. Chow, S.-F. Hung, W.-Y. Yu, *Org. Lett.* **2019**, *21*, 8037-8043.
[2] C. M. McMahon, M. S. Renn, E. J. Alexanian, *Org. Lett.* **2016**, *18*, 4148-4150.
[3] L. Yu, M.-L. Tang, C.-M. Si, Z. Meng, Y. Liang, J. Han, X. Sun, *Org. Lett.* **2018**, *20*, 4579-4583.
[4] S. J. Ton, K. T. Neumann, P. Nørby, T. Skrydstrup, *J. Am. Chem. Soc.* **2021**, *143*, 17816-17824.
[5] J. Gui, X. Cai, L. Chen, Y. Zhou, W. Zhu, Y. Jiang, M. Hu, X. Chen, Y. Hu, S. Zhang, *Org. Chem. Front.* **2021**, *8*, 4685-4692.
[6] S. Kyasa, R. N. Meier, R. A. Pardini, T. K. Truttmann, K. T. Kuwata, P. H. Dussault, *J. Org. Chem.* **2015**, *80*, 12100-12114.
[7] F. Toriyama, J. Cornella, L. Wimmer, T.-G. Chen, D. D. Dixon, G. Creech, P. S. Baran, *J. Am. Chem. Soc.* **2016**, *138*, 11132-11135.
[8] H.-M. Huang, P. Bellotti, P. M. Pflüger, J. L. Schwarz, B. Heidrich, F. Glorius, *J. Am. Chem. Soc.* **2020**, *142*, 10173-10183.
[9] H. Chen, X. Jia, Y. Yu, Q. Qian, H. Gong, *Angew. Chem. Int. Ed.* **2017**, *56*, 13103-13106.
[10] A. Westerbeek, J. G. E. van Leeuwen, W. Szymański, B. L. Feringa, D. B. Janssen, *Tetrahedron* **2012**, *68*, 7645-7650.
[11] J. Borrel, G. Pisella, J. Waser, *Org. Lett.* **2020**, *22*, 422-427.
[12] J. Vader, H. Sengers, A. de Groot, *Tetrahedron* **1989**, *45*, 2131-2142.
[13] M. Fernández, U. Uria, J. L. Vicario, E. Reyes, L. Carrillo, *J. Am. Chem. Soc.* **2012**, *134*, 11872-11875.
[14] W. Wu, X. Yuan, J. Hu, X. Wu, Y. Wei, Z. Liu, J. Lu, J. Ye, *Org. Lett.* **2013**, *15*, 4524-4527.
[15] J.-N. Zhu, W.-K. Wang, J. Zheng, H.-P. Lin, Y.-X. Deng, S.-Y. Zhao, *J. Org. Chem.* **2019**, *84*, 11032-11041.
[16] N. Iranpoor, F. Kazemi, P. Salehi, *Synth. Commun.* **1997**, *27*, 1247-1258.
[17] L. Zhao, Y. Huang, Z. Wang, E. Zhu, T. Mao, J. Jia, J. Gu, X.-F. Li, C.-Y. He, *Org. Lett.* **2019**, *21*, 6705-6709.

8. NMR Spectra

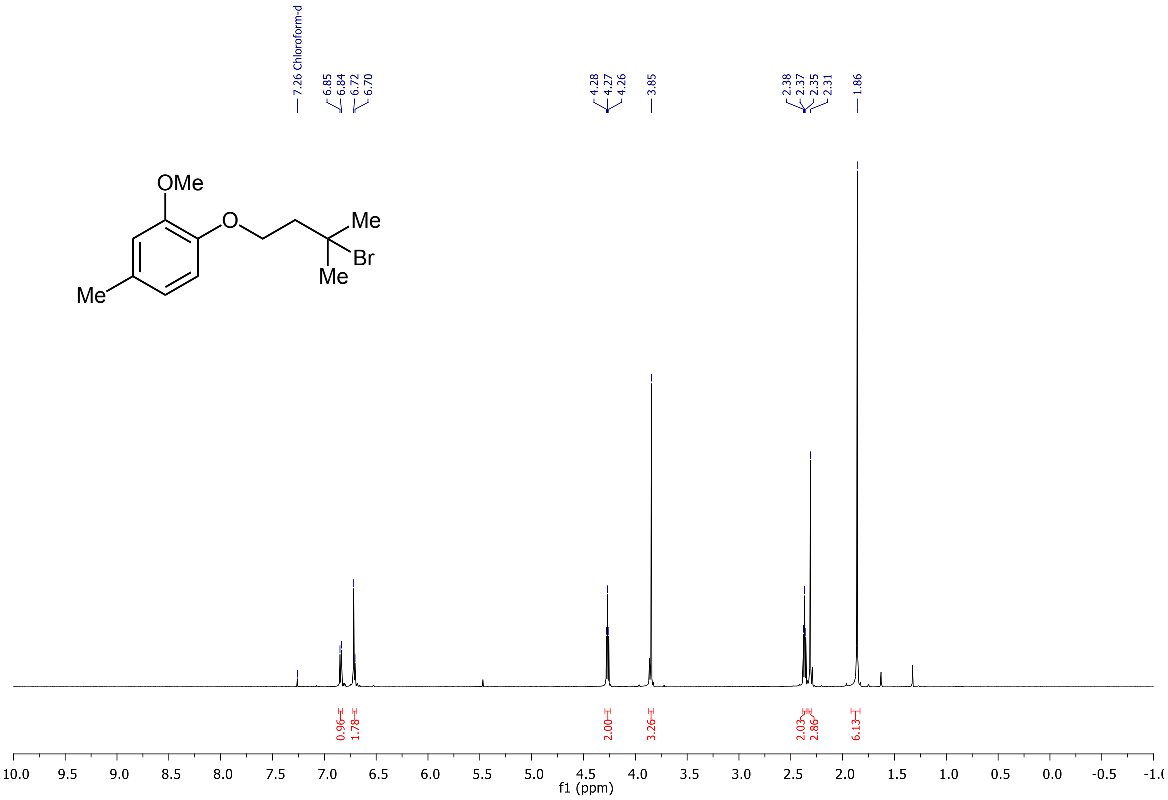
^{1}H NMR spectrum of **S20**



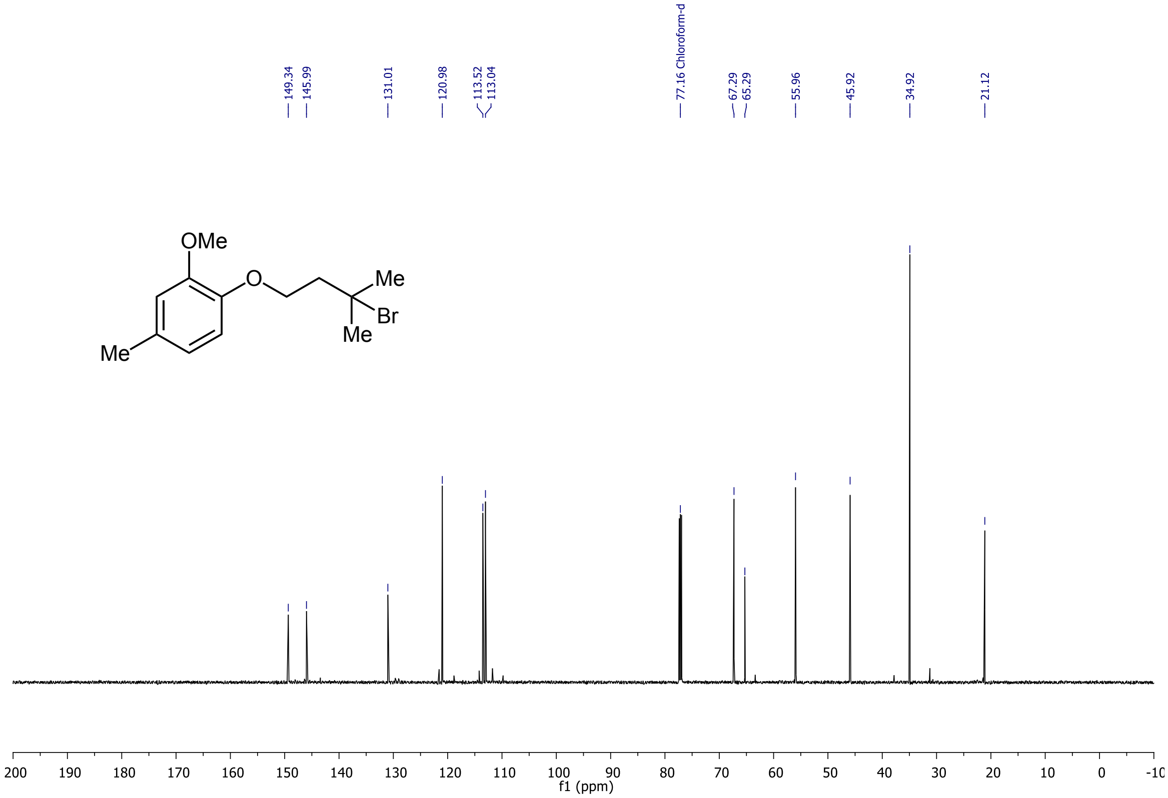
^{13}C NMR spectrum of **S20**



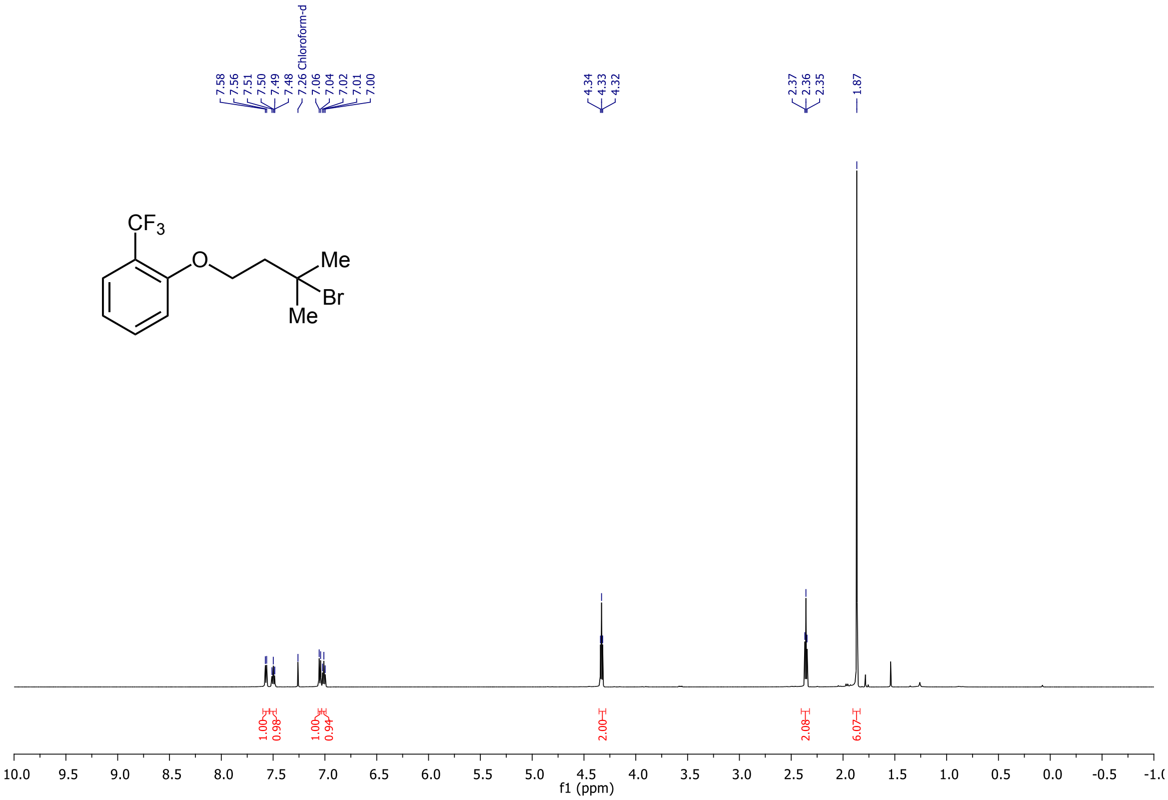
^{1}H NMR spectrum of **S21**



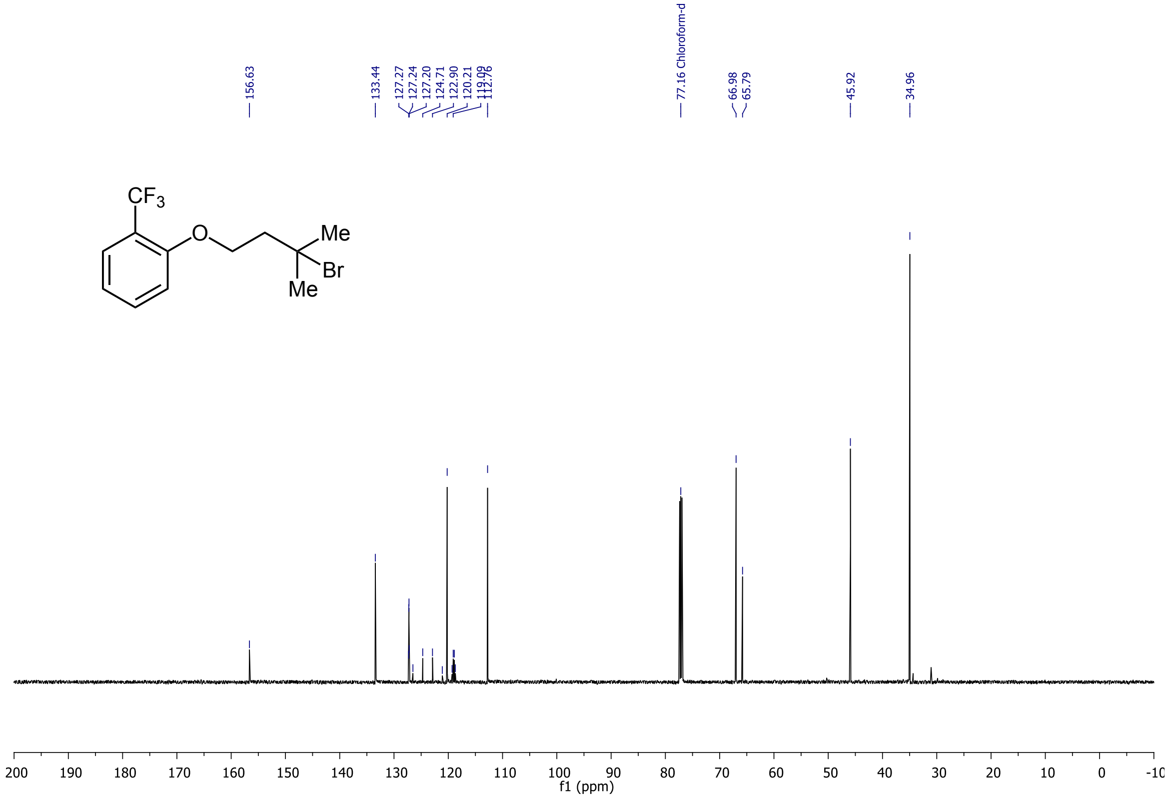
^{13}C NMR spectrum of **S21**



^{1}H NMR spectrum of **S22**

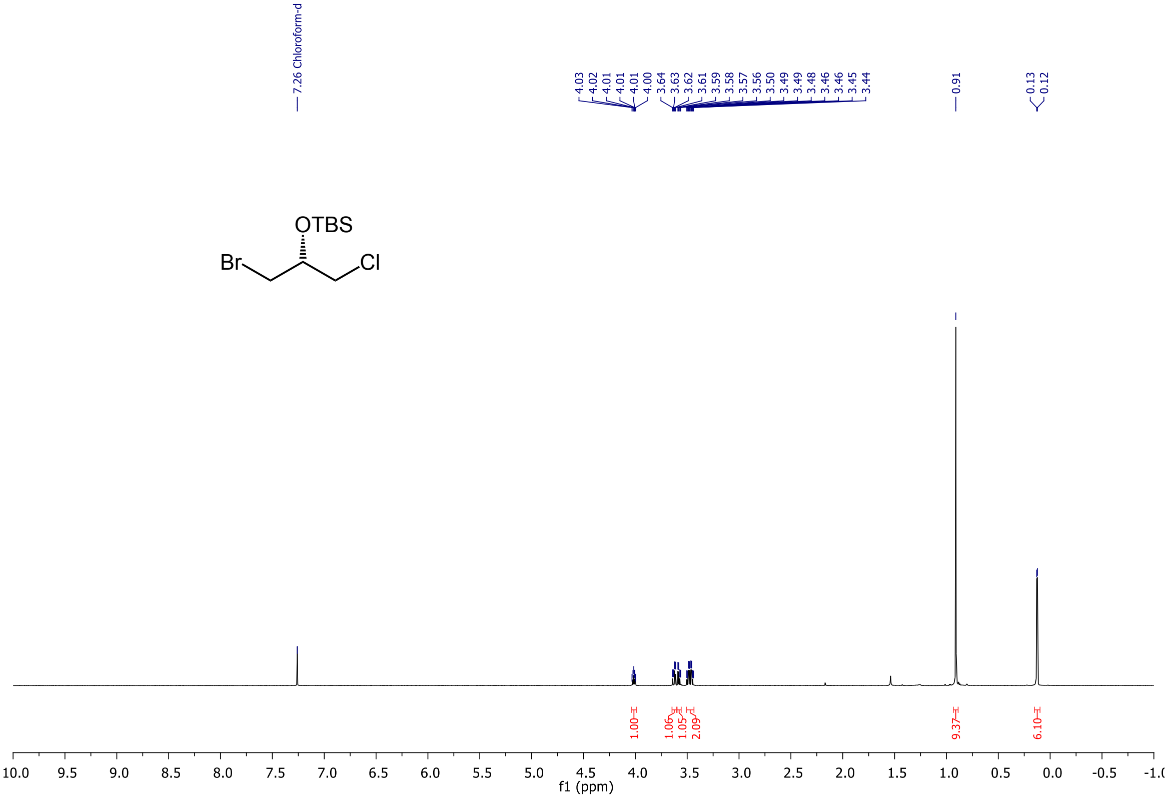


^{13}C NMR spectrum of **S22**

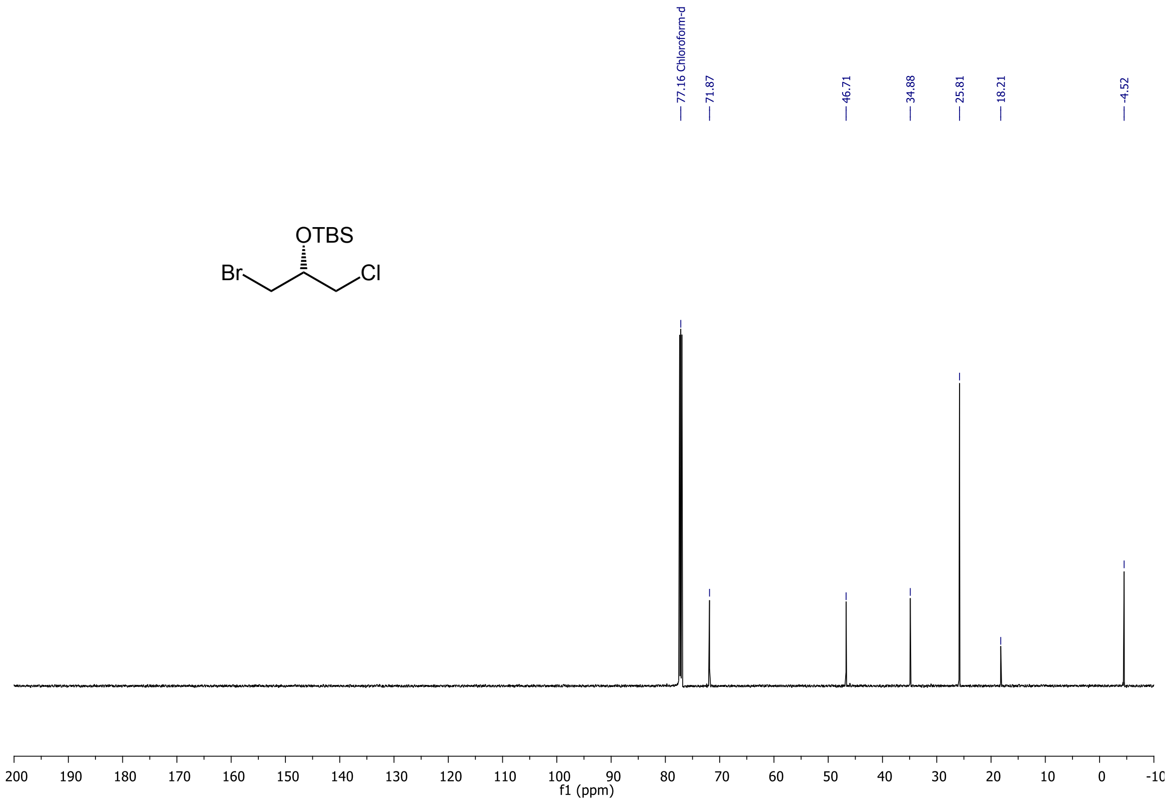


^{19}F NMR spectrum of **S22**

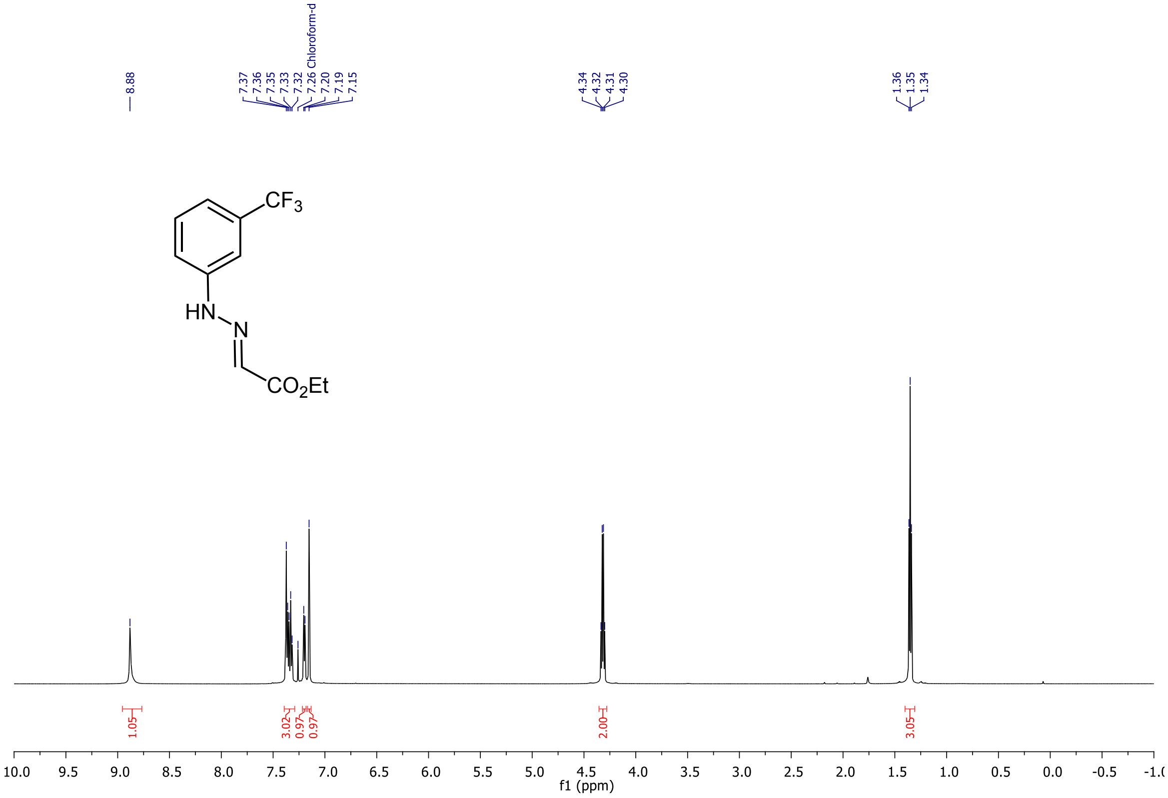
^{1}H NMR spectrum of **S23**



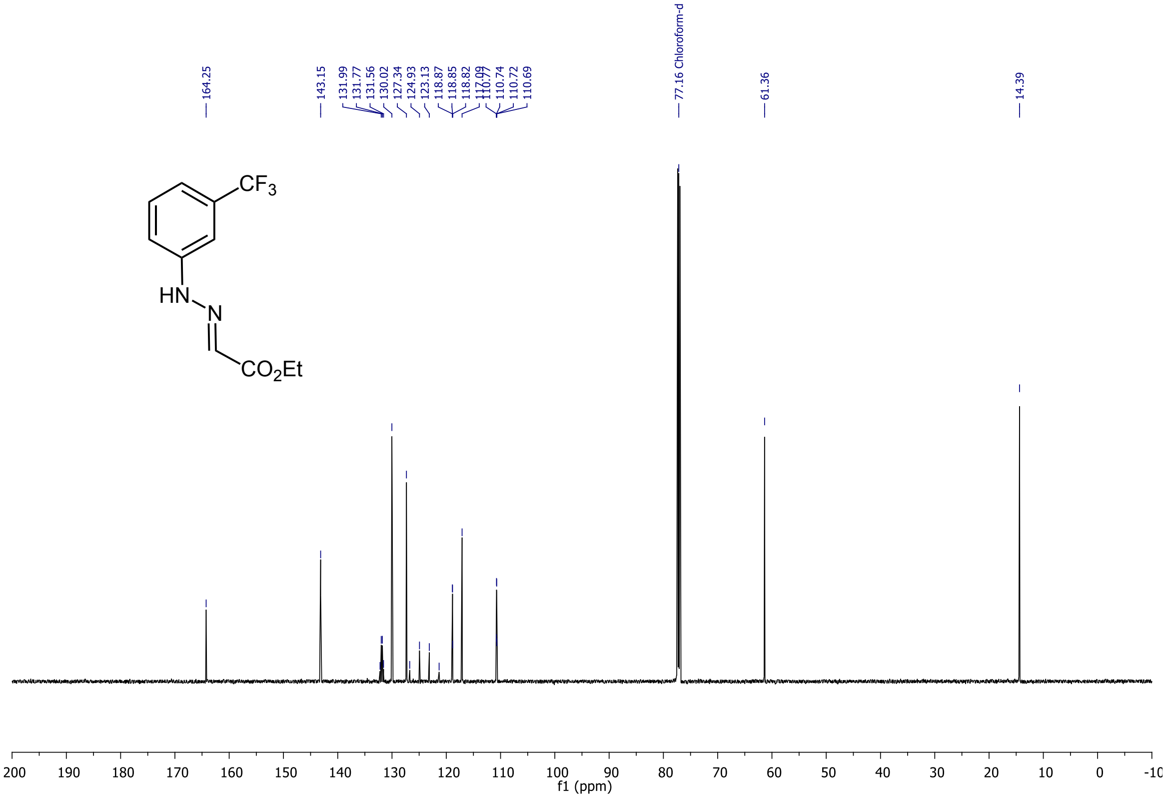
^{13}C NMR spectrum of **S23**



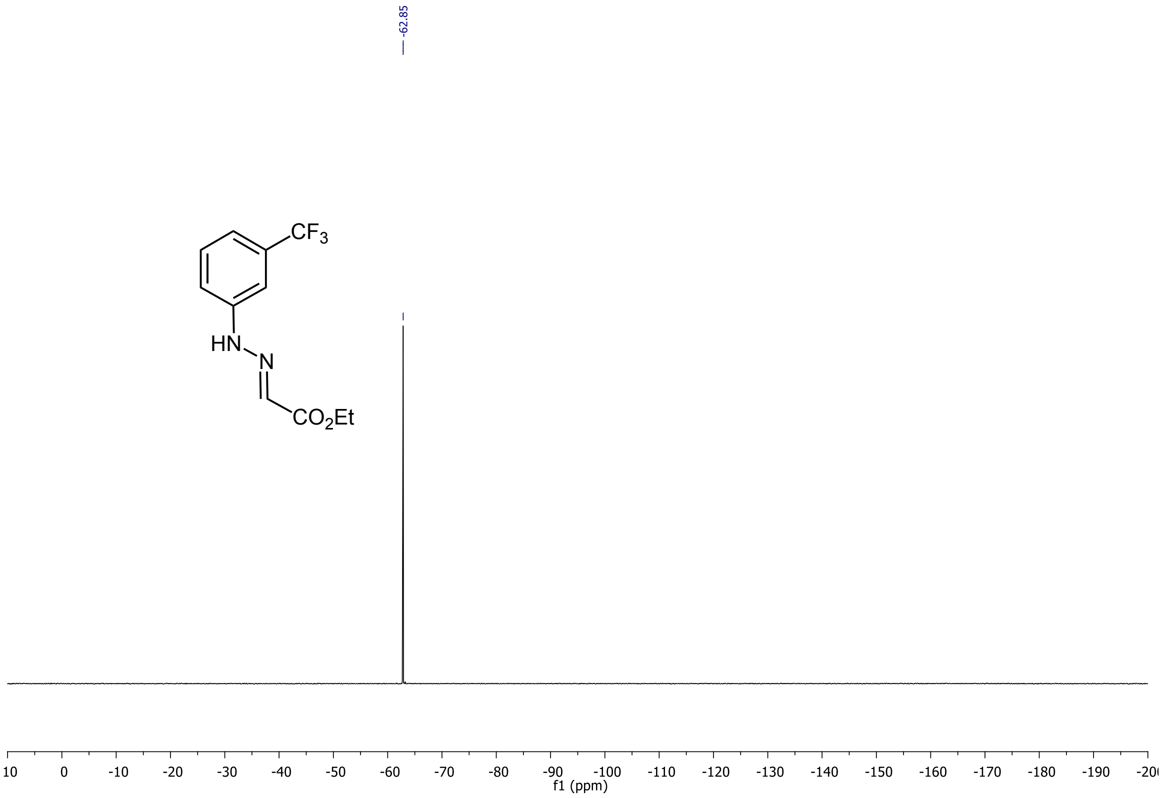
^{1}H NMR spectrum of **S24**



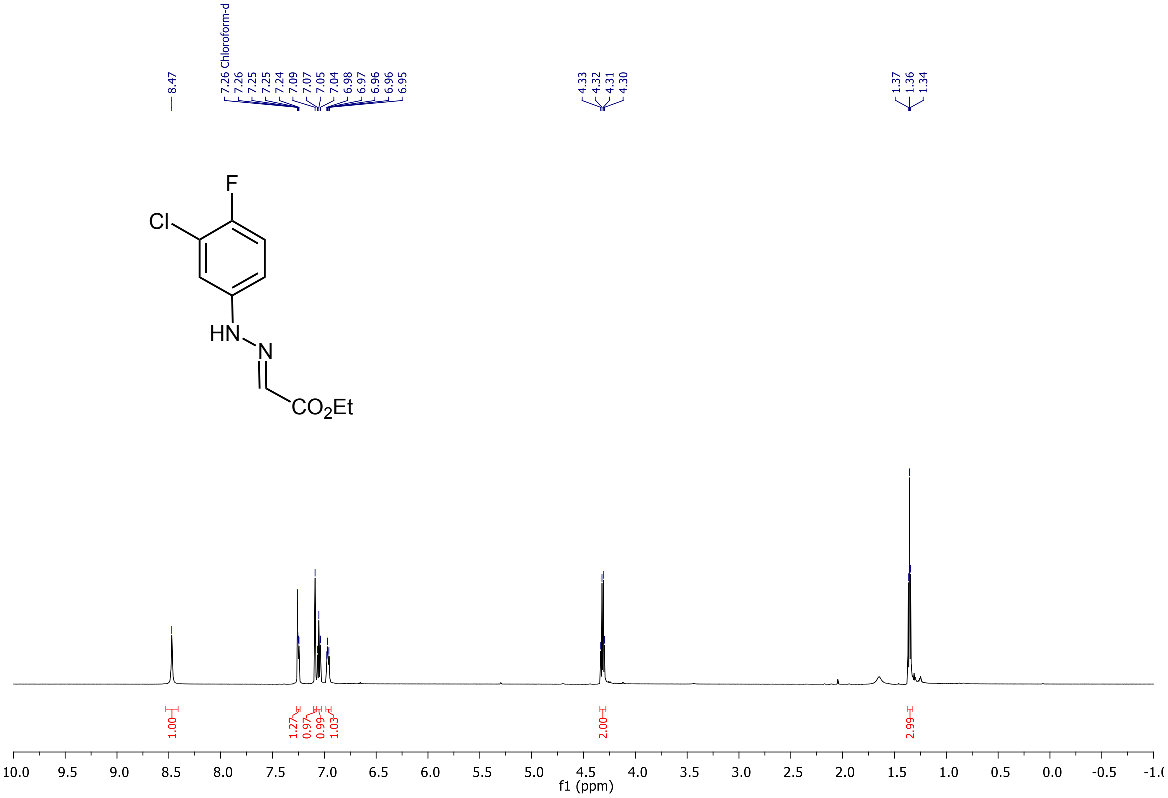
^{13}C NMR spectrum of **S24**



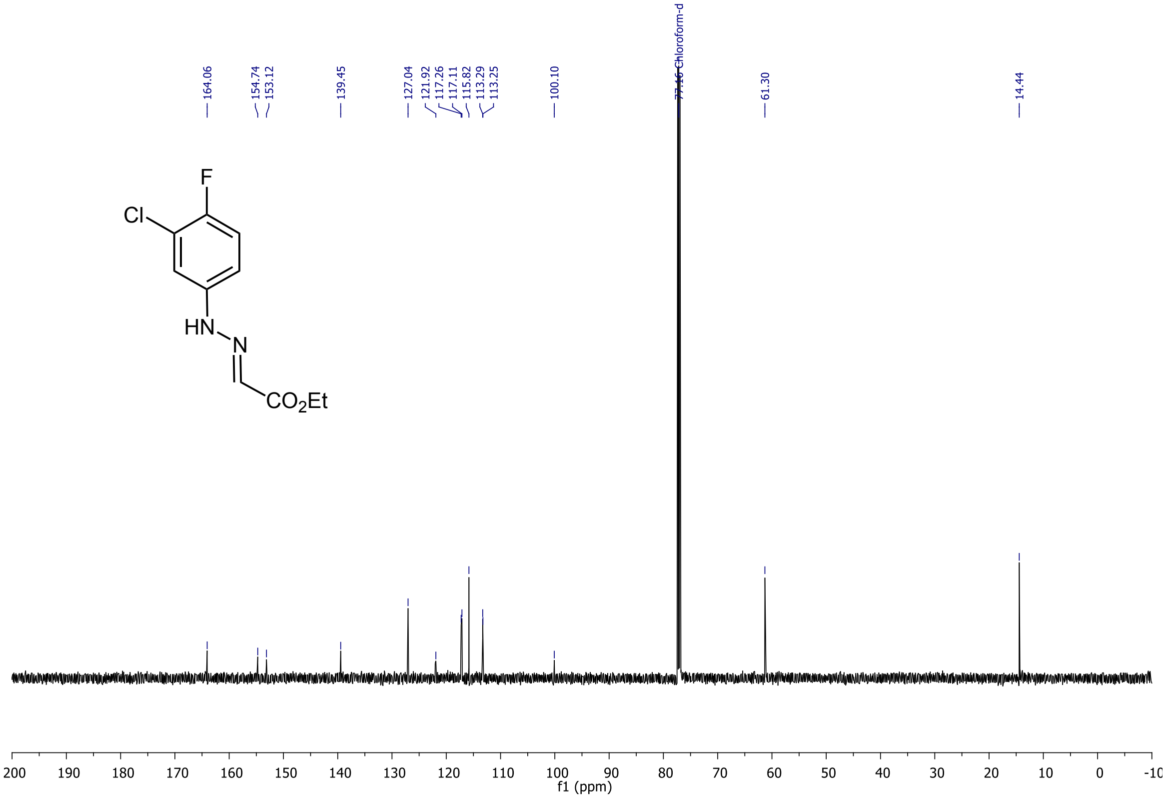
^{19}F NMR spectrum of **S24**



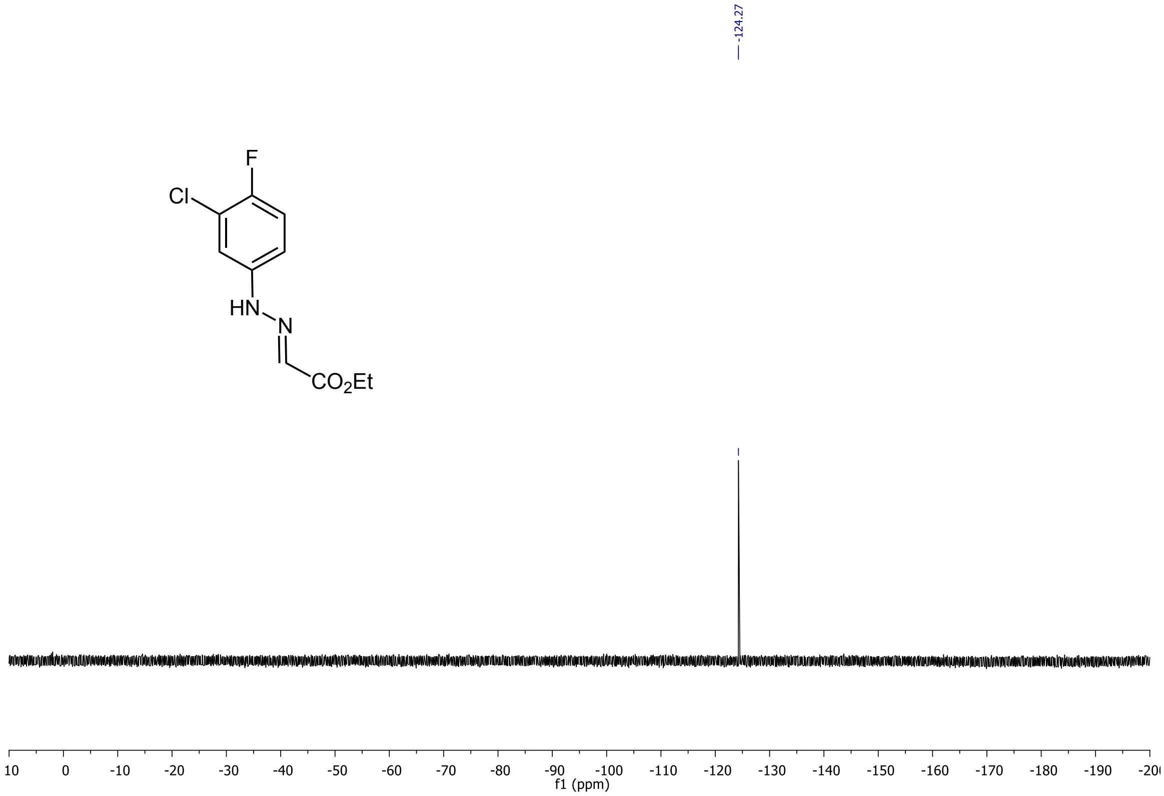
^{1}H NMR spectrum of **S25**



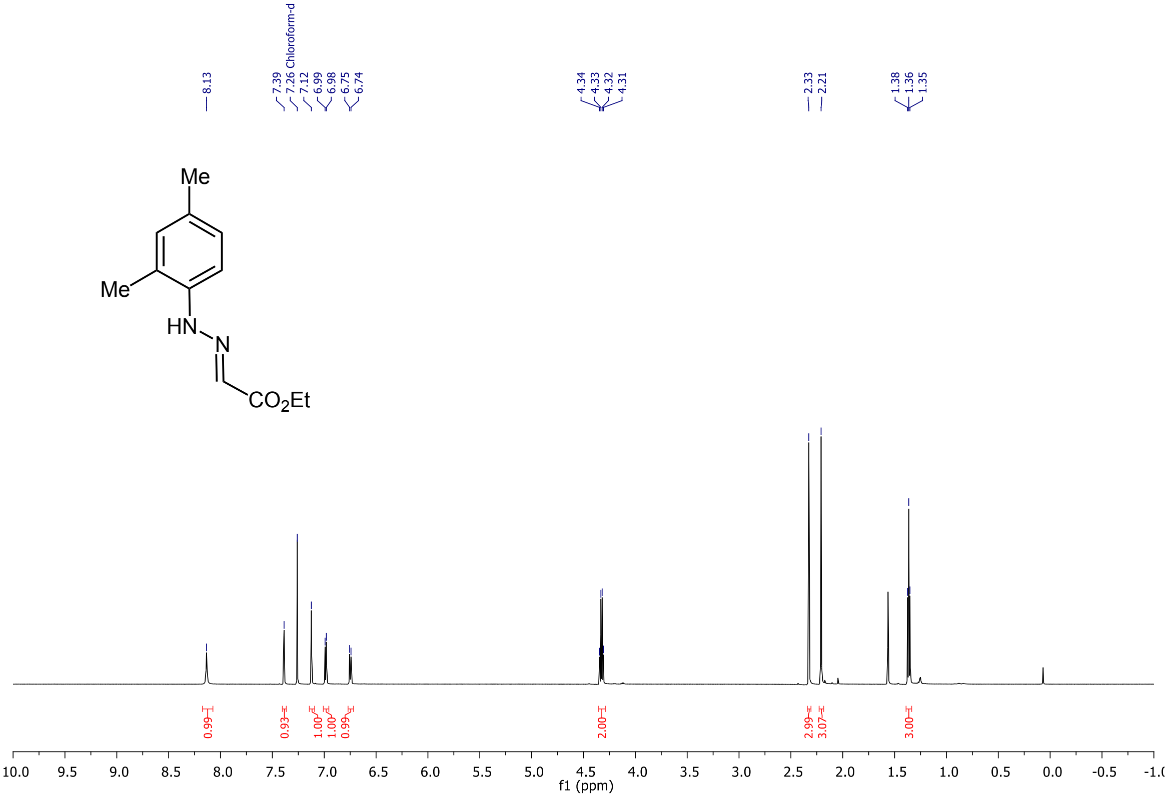
^{13}C NMR spectrum of **S25**



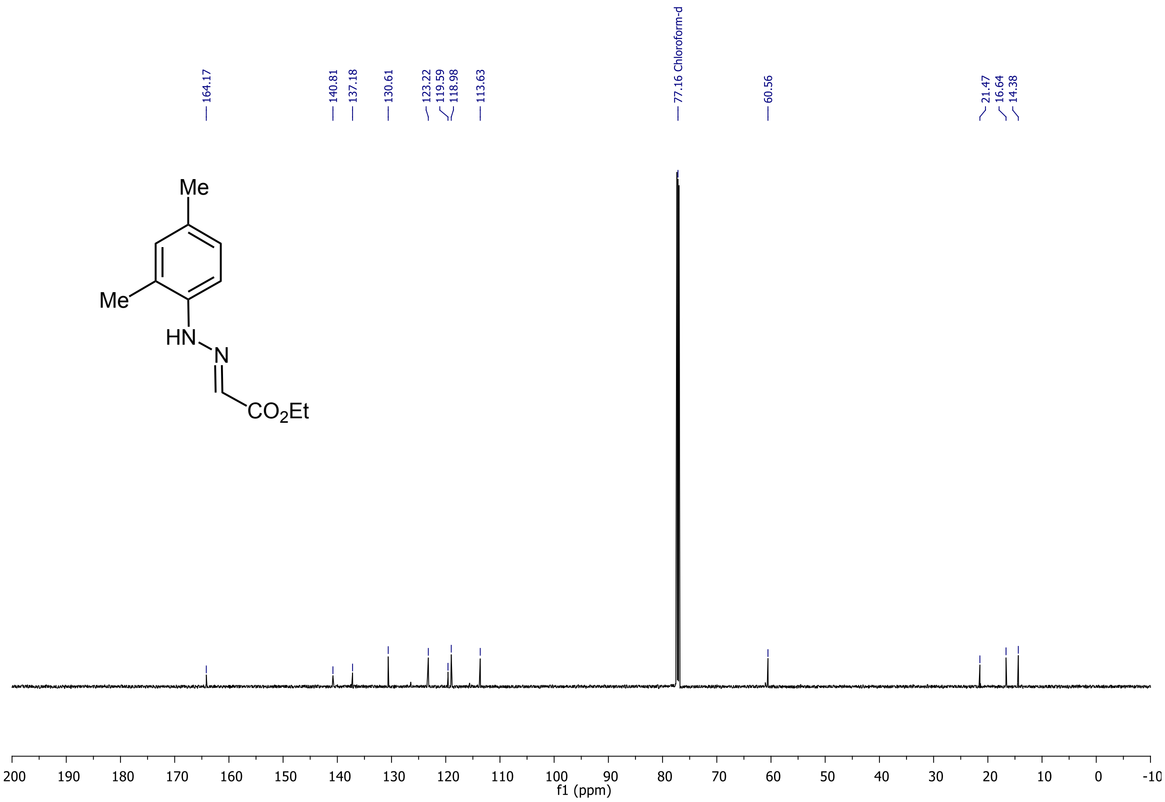
^{19}F NMR spectrum of **S25**



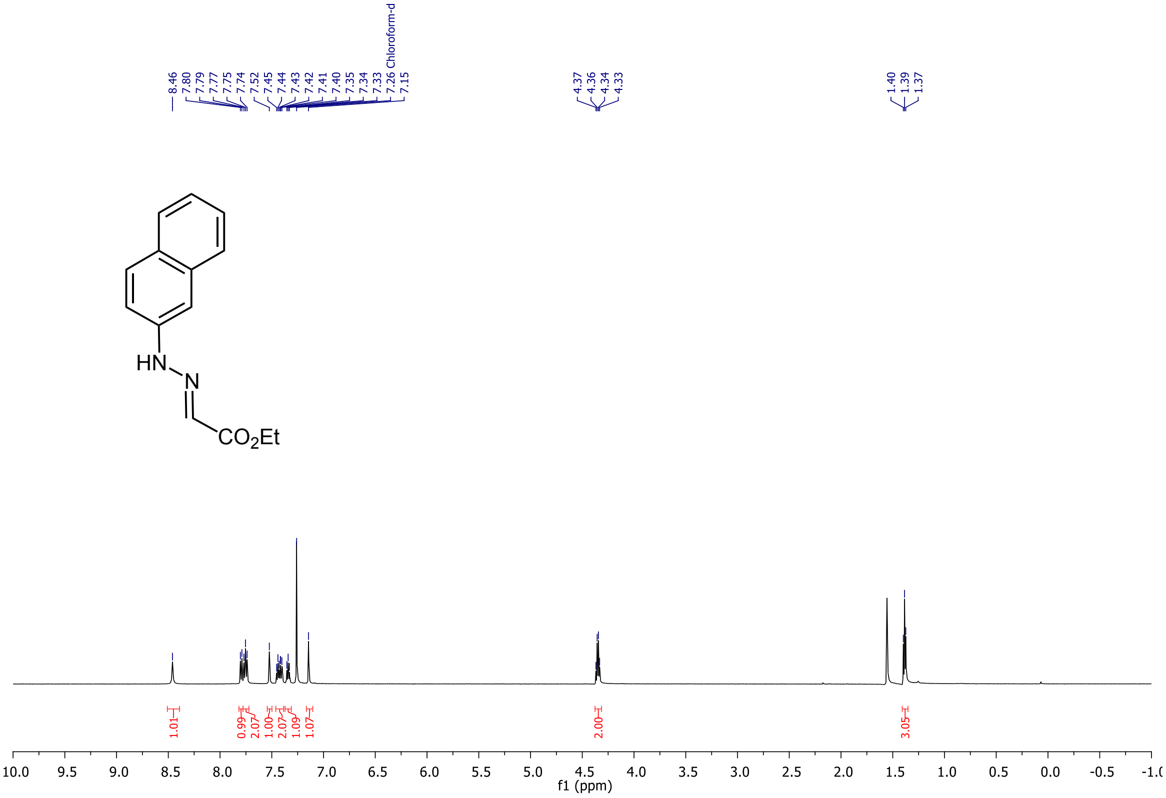
^{1}H NMR spectrum of **S26**



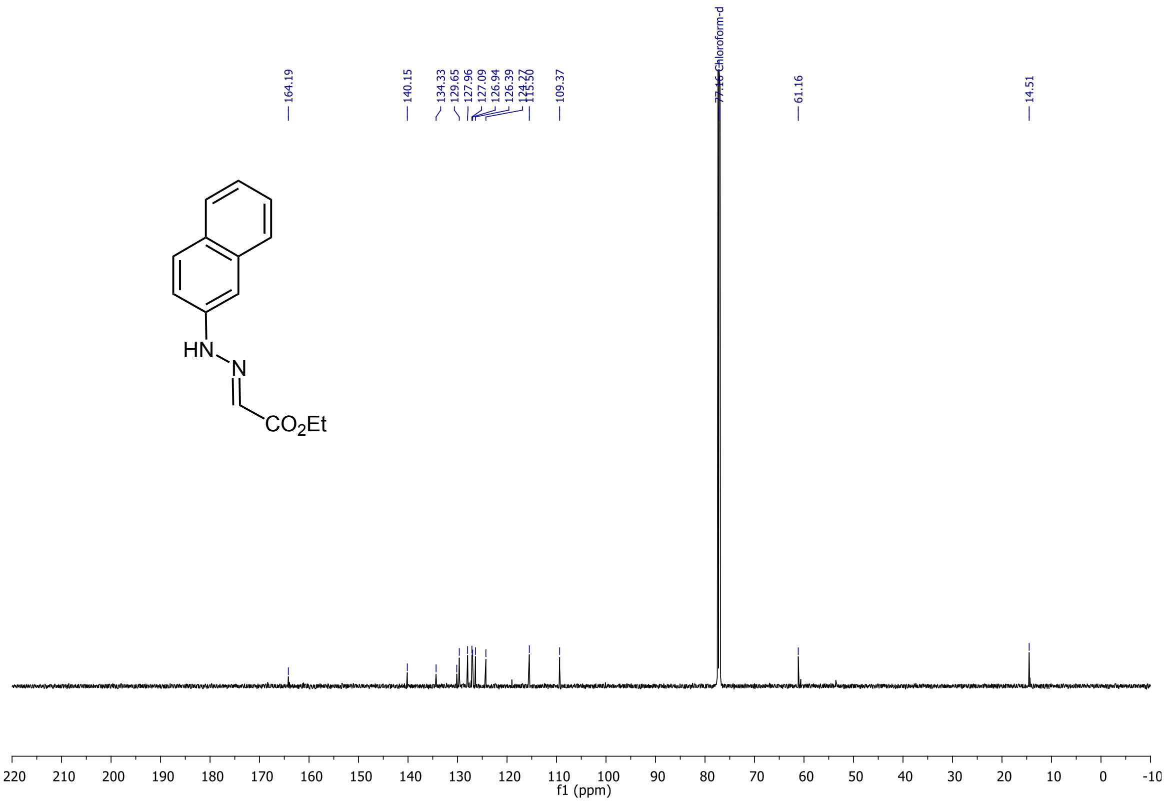
^{13}C NMR spectrum of **S26**



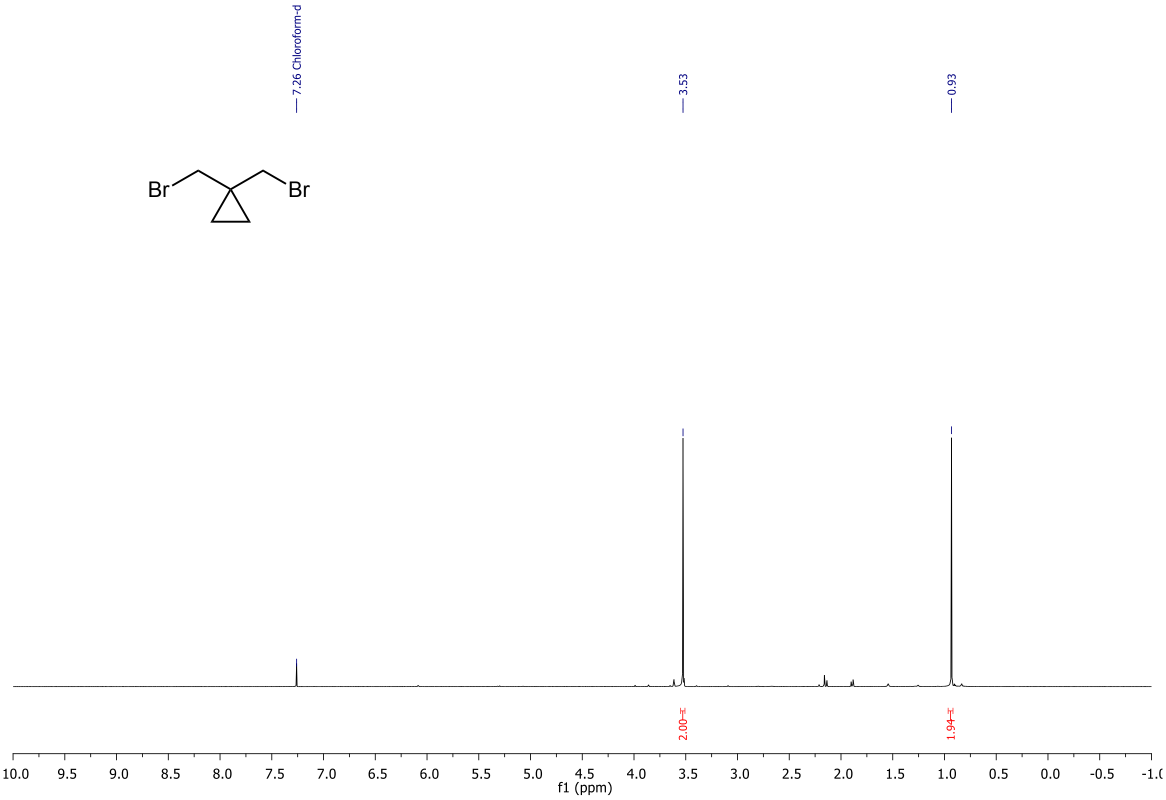
^{1}H NMR spectrum of **S27**



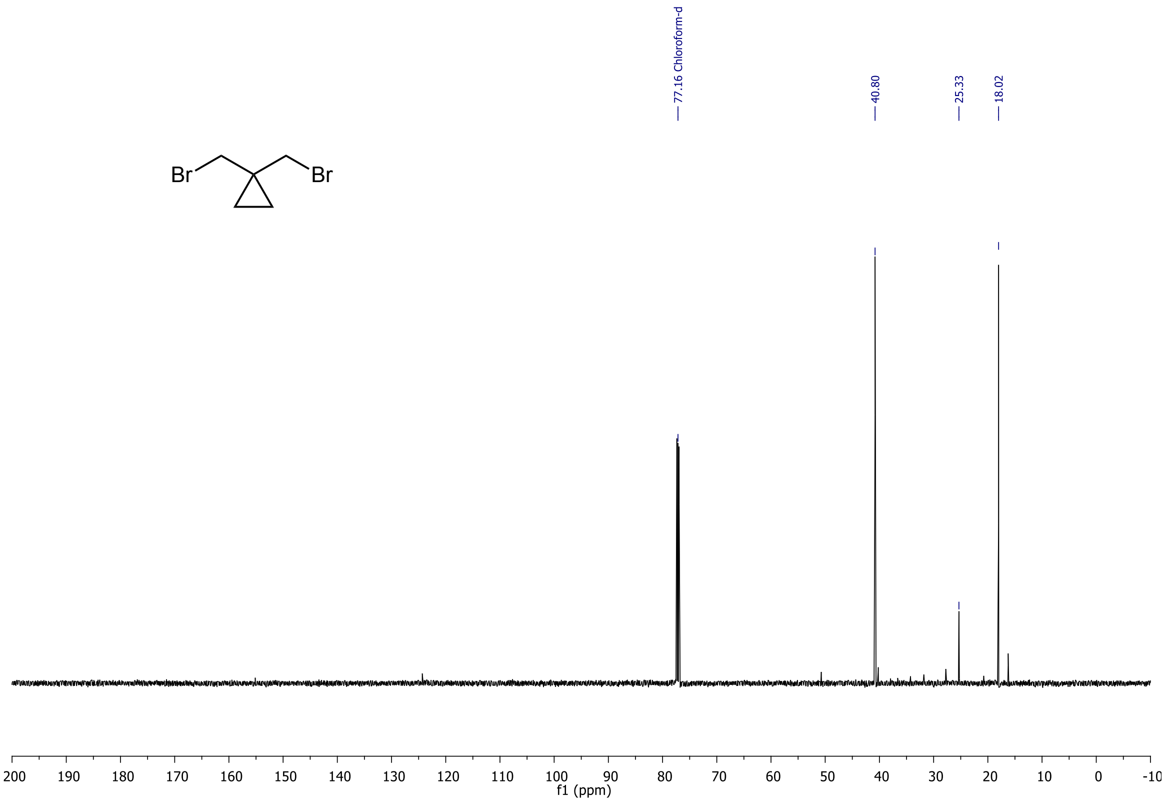
^{13}C NMR spectrum of **S27**



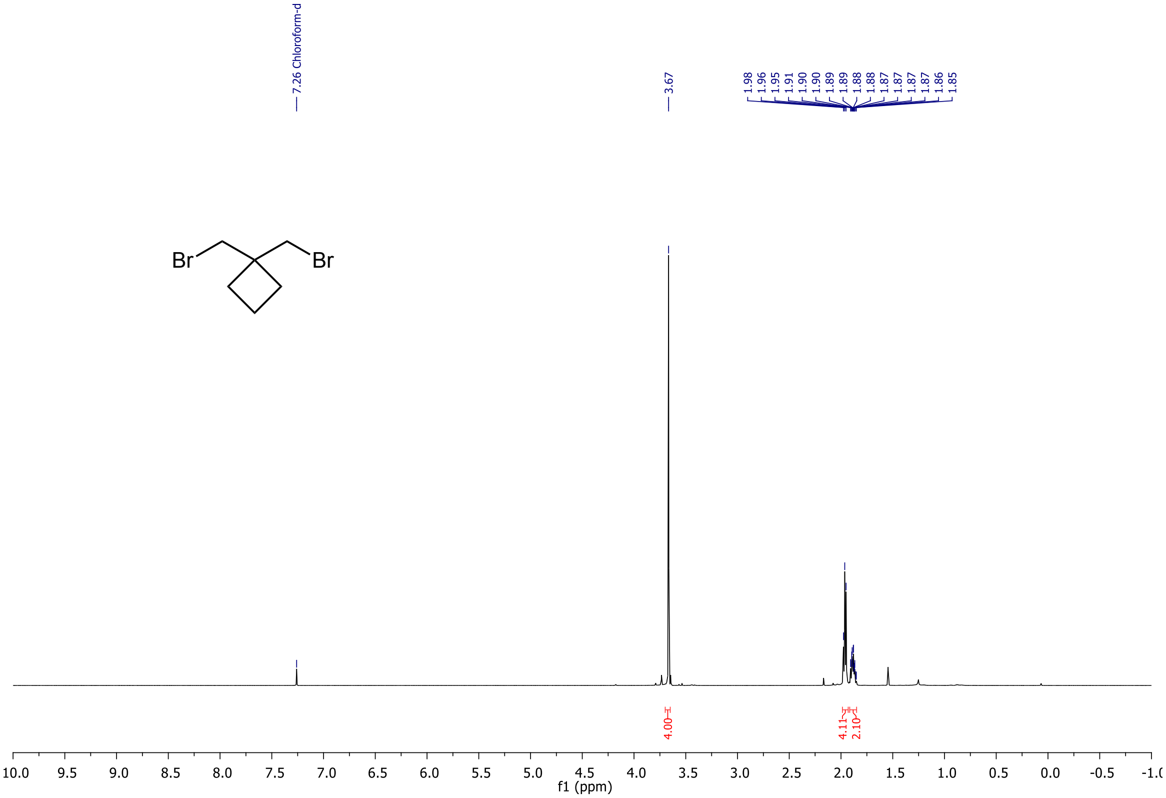
^{1}H NMR spectrum of **S28**



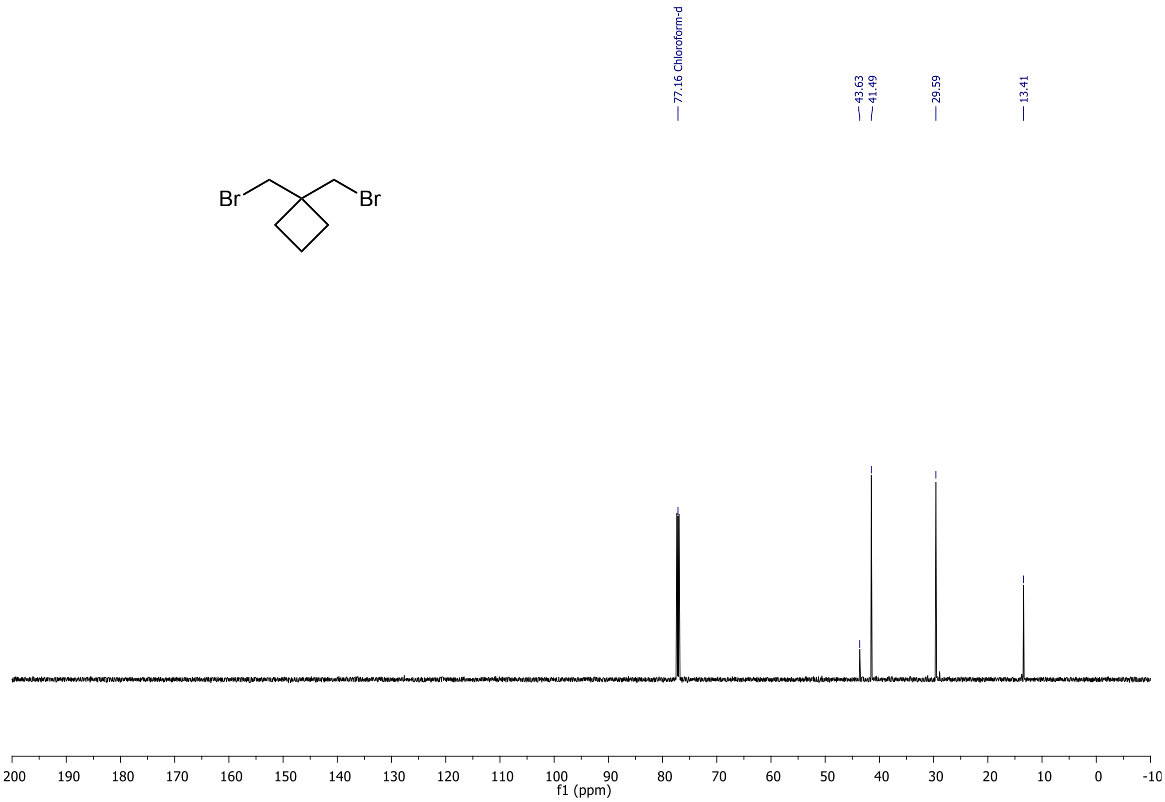
^{13}C NMR spectrum of **S28**



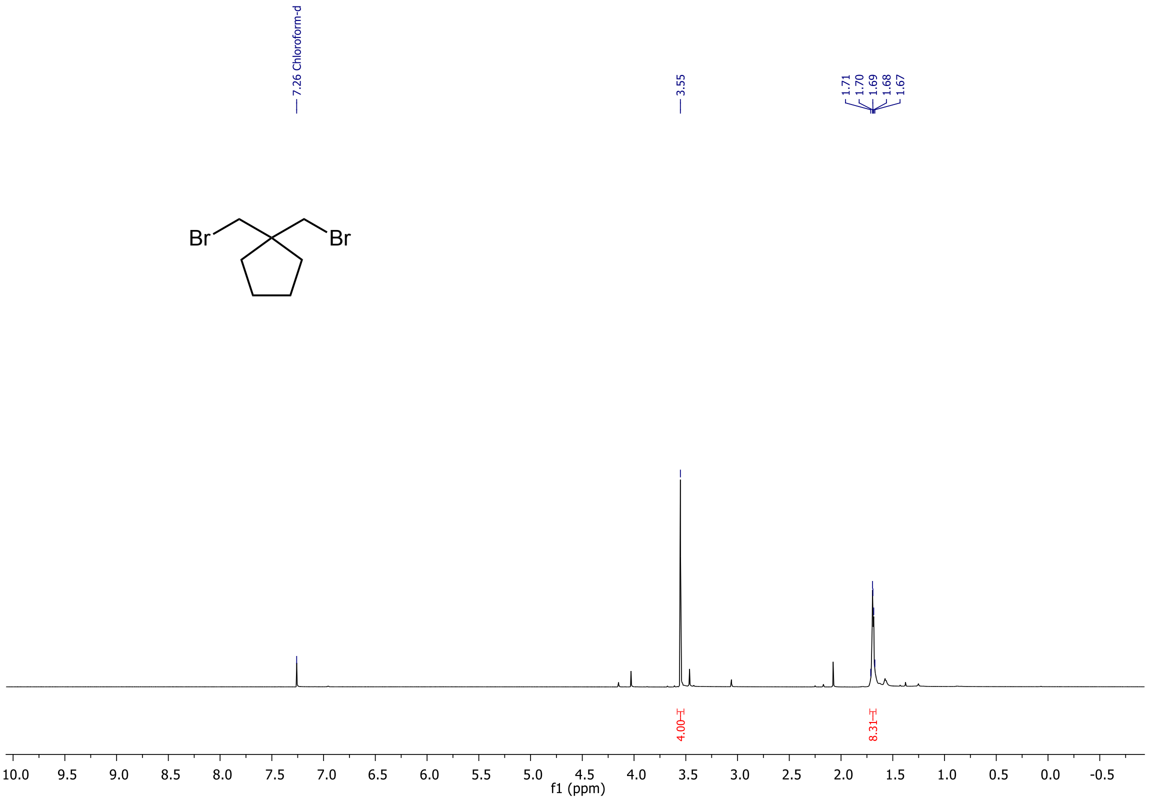
^{1}H NMR spectrum of **S29**



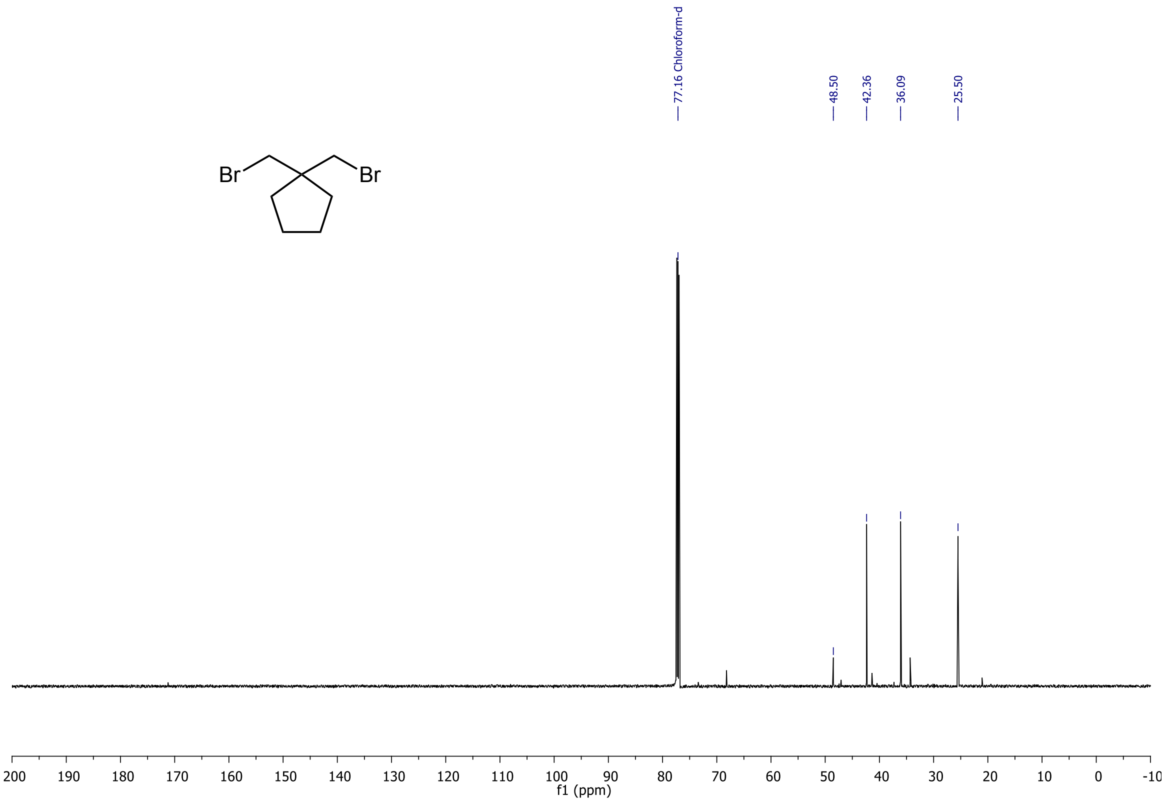
^{13}C NMR spectrum of **S29**



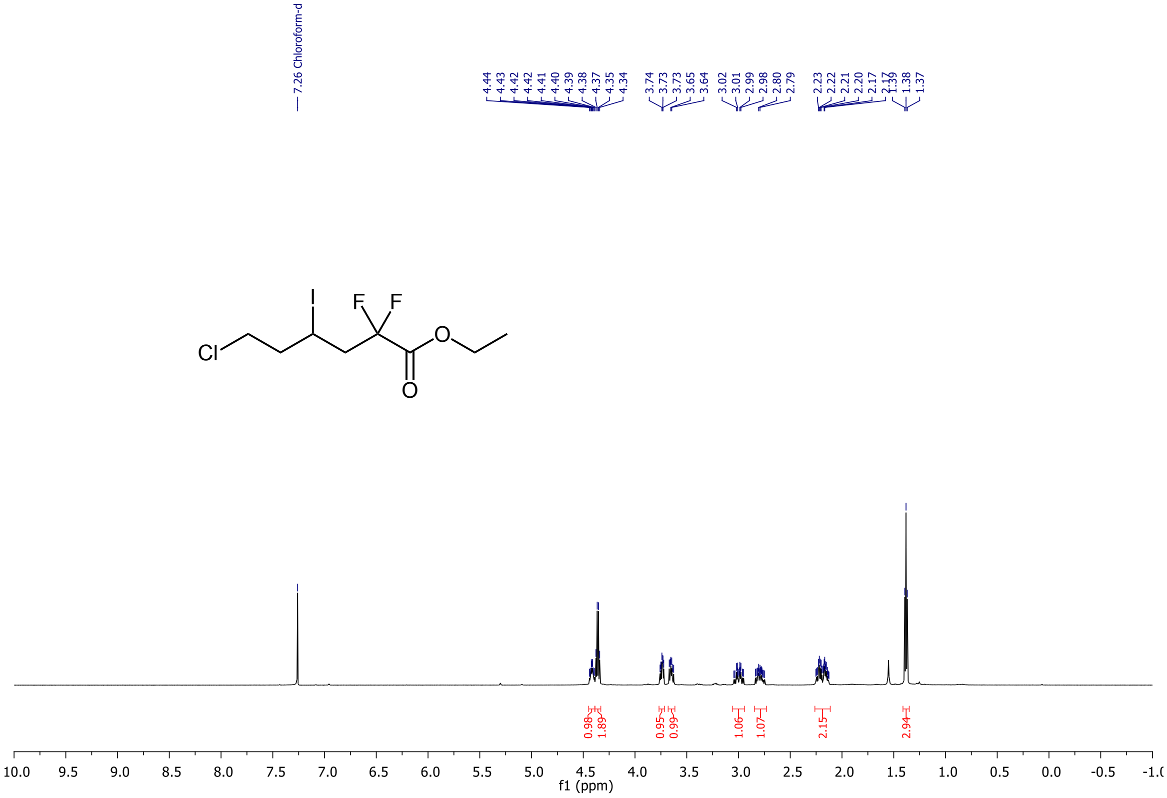
^{1}H NMR spectrum of **S30**



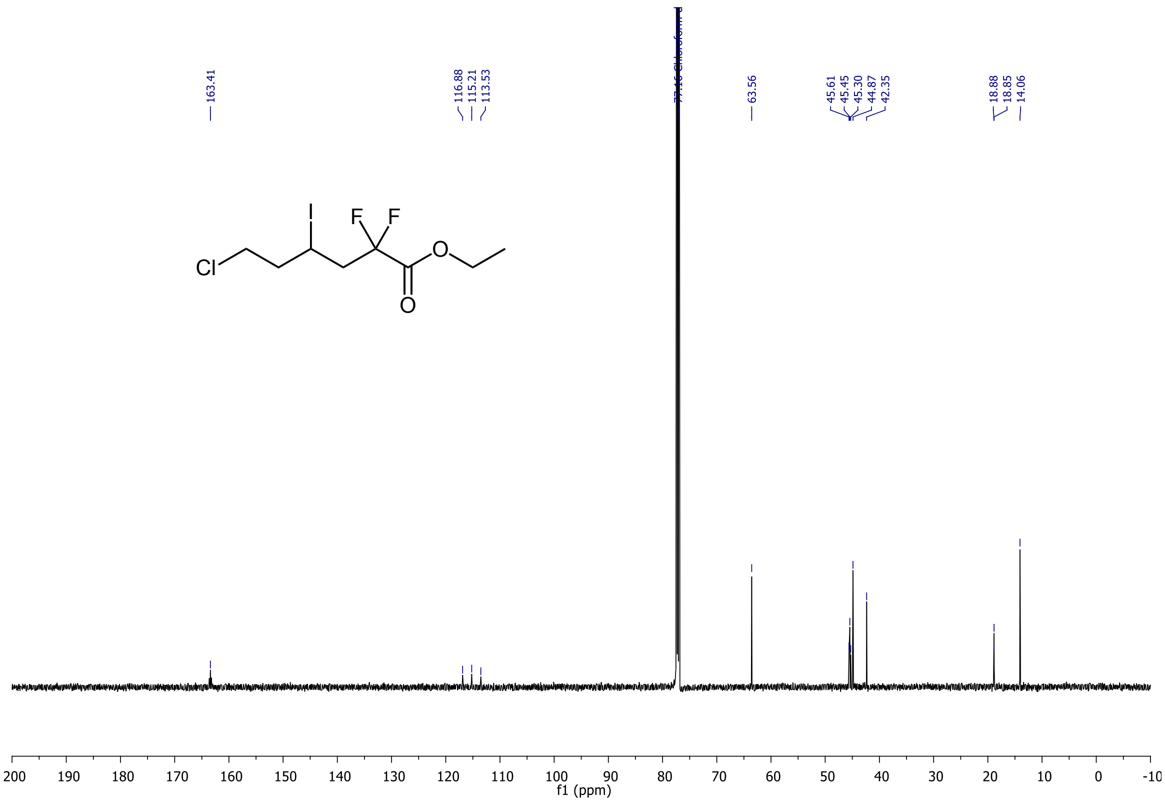
^{13}C NMR spectrum of **S30**



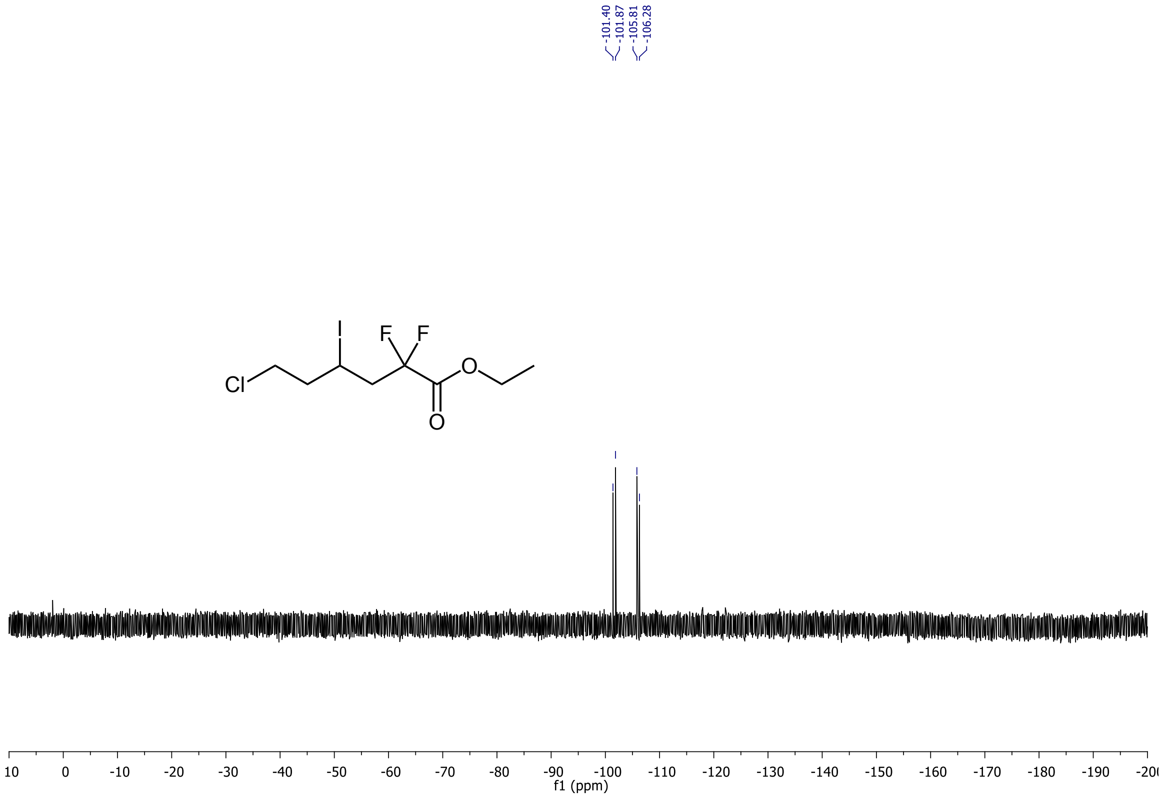
^{1}H NMR spectrum of **S31**



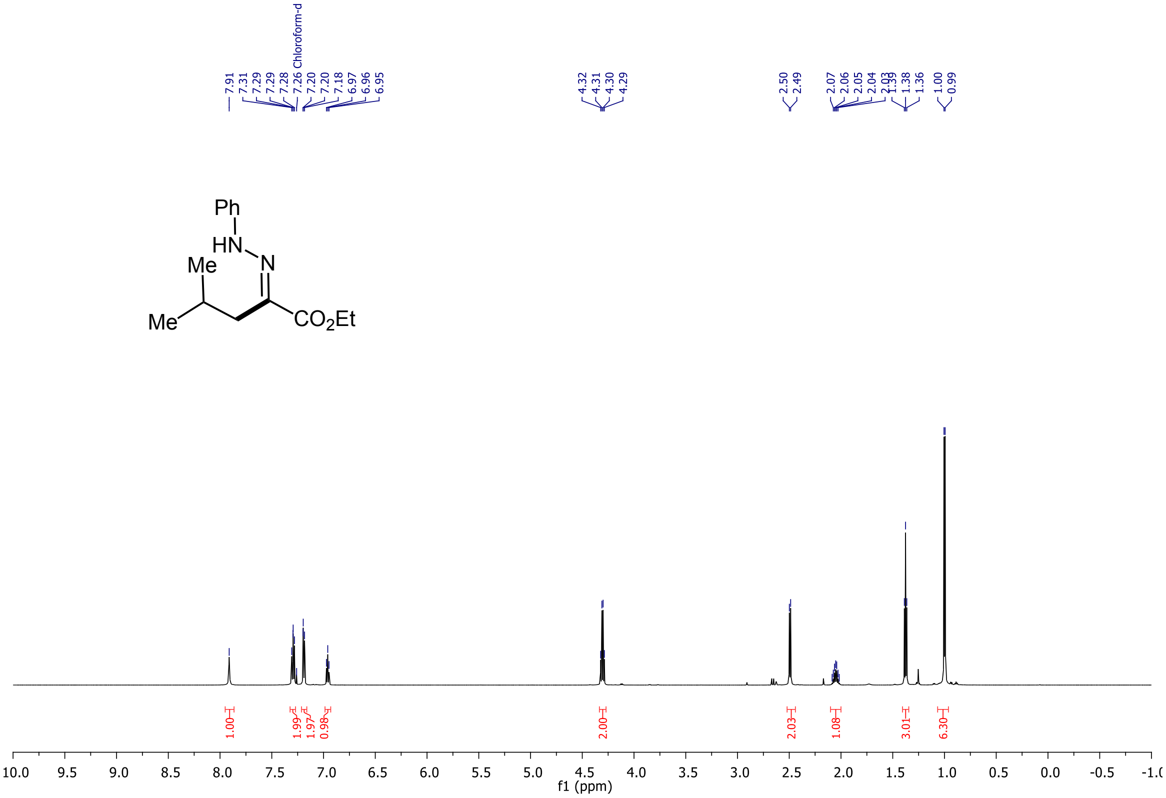
^{13}C NMR spectrum of **S31**



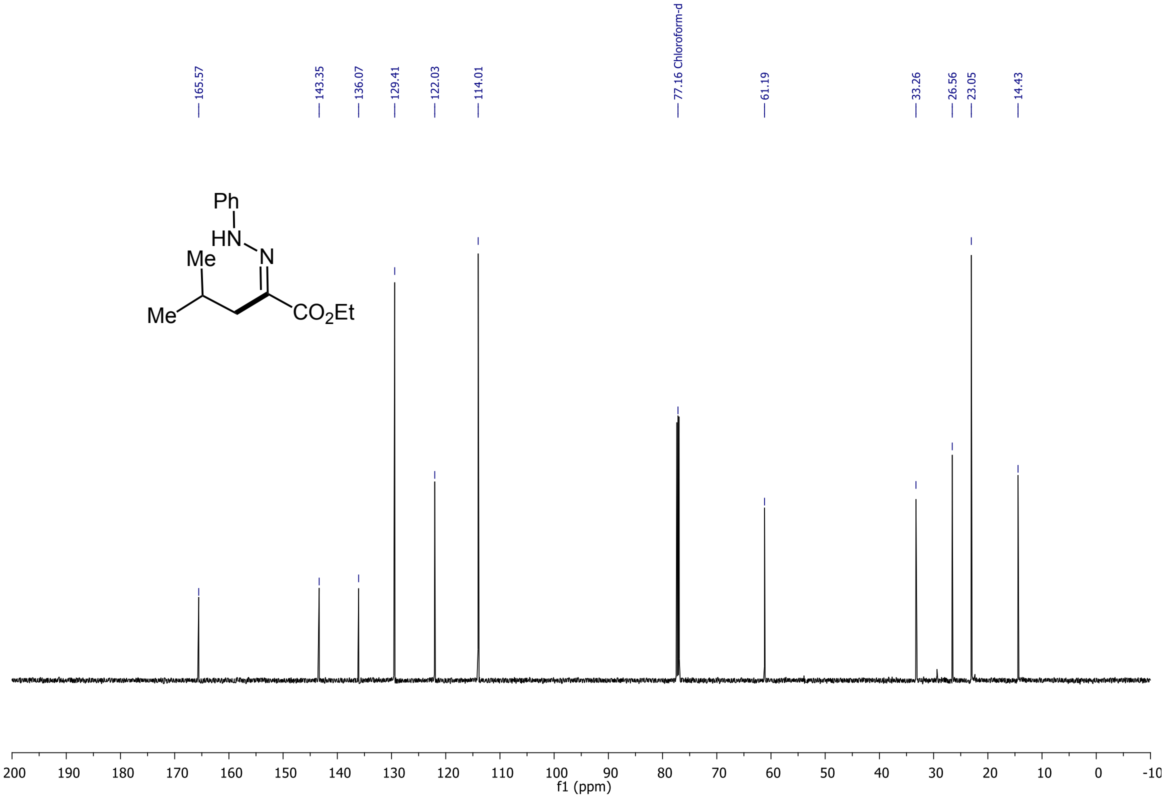
^{19}F NMR spectrum of **S31**



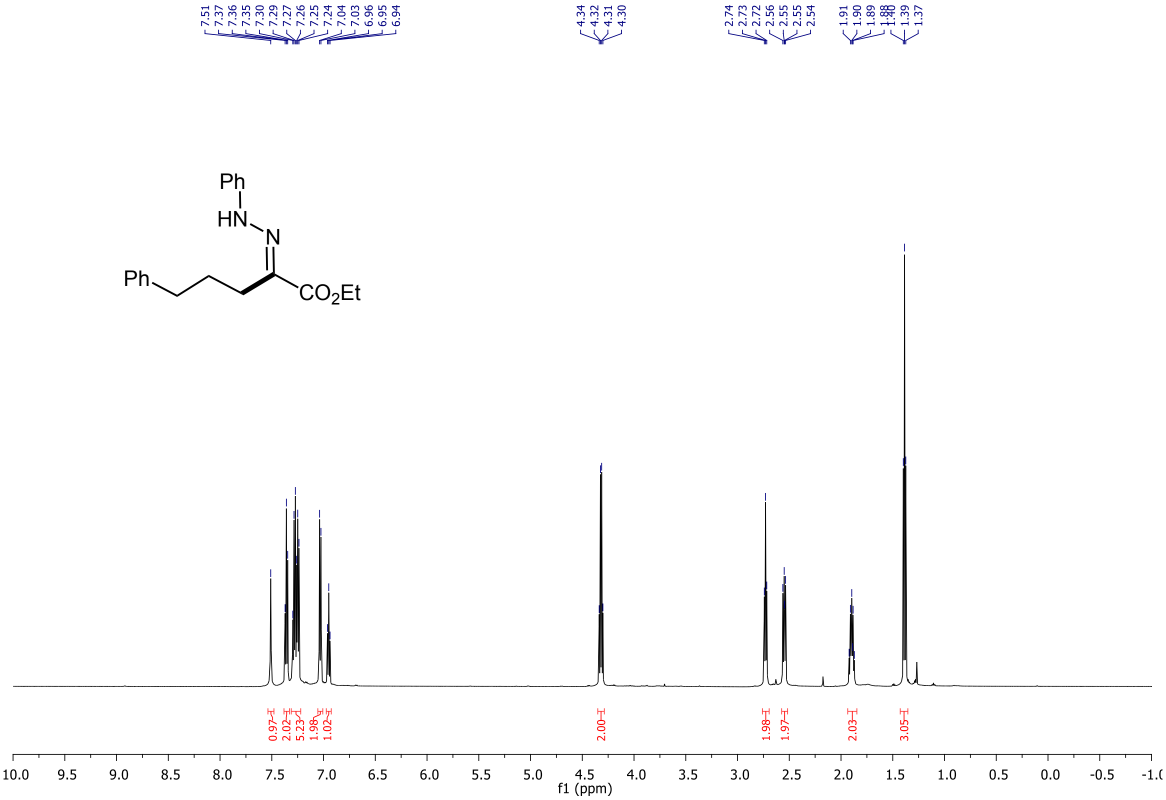
^{1}H NMR spectrum of **3a**



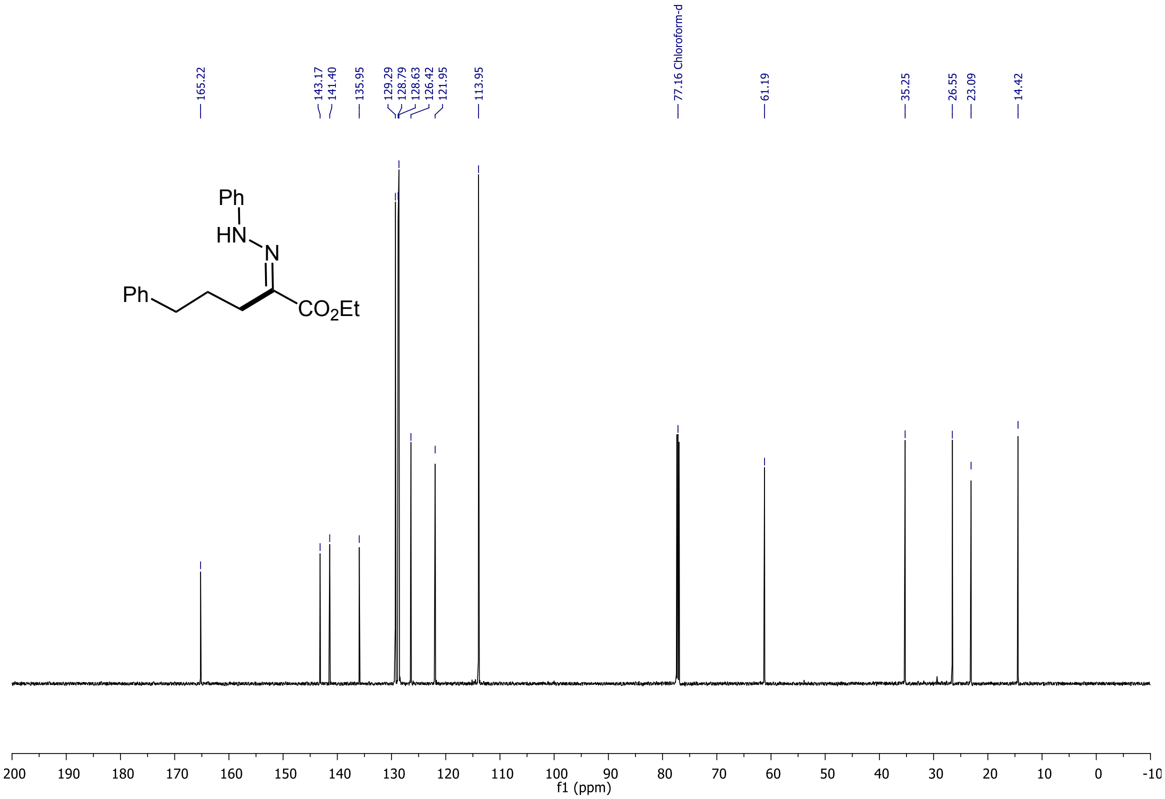
^{13}C NMR spectrum of **3b**



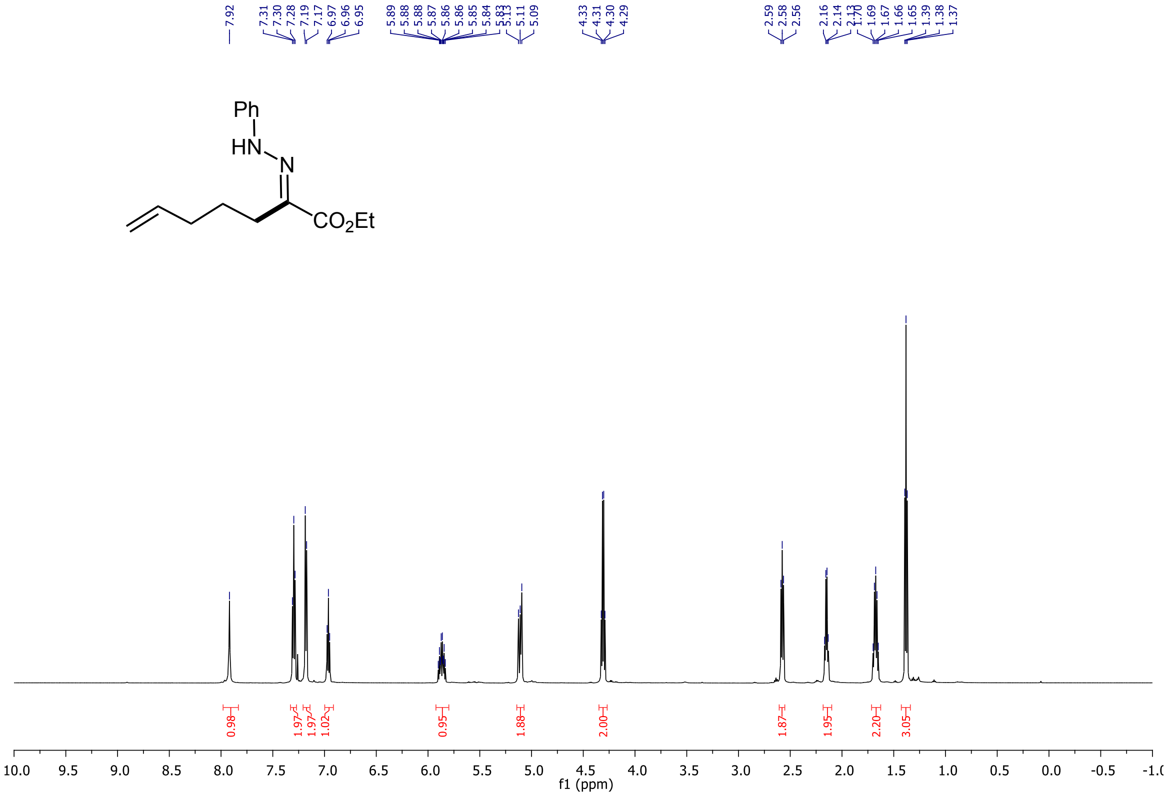
^{1}H NMR spectrum of **3b**



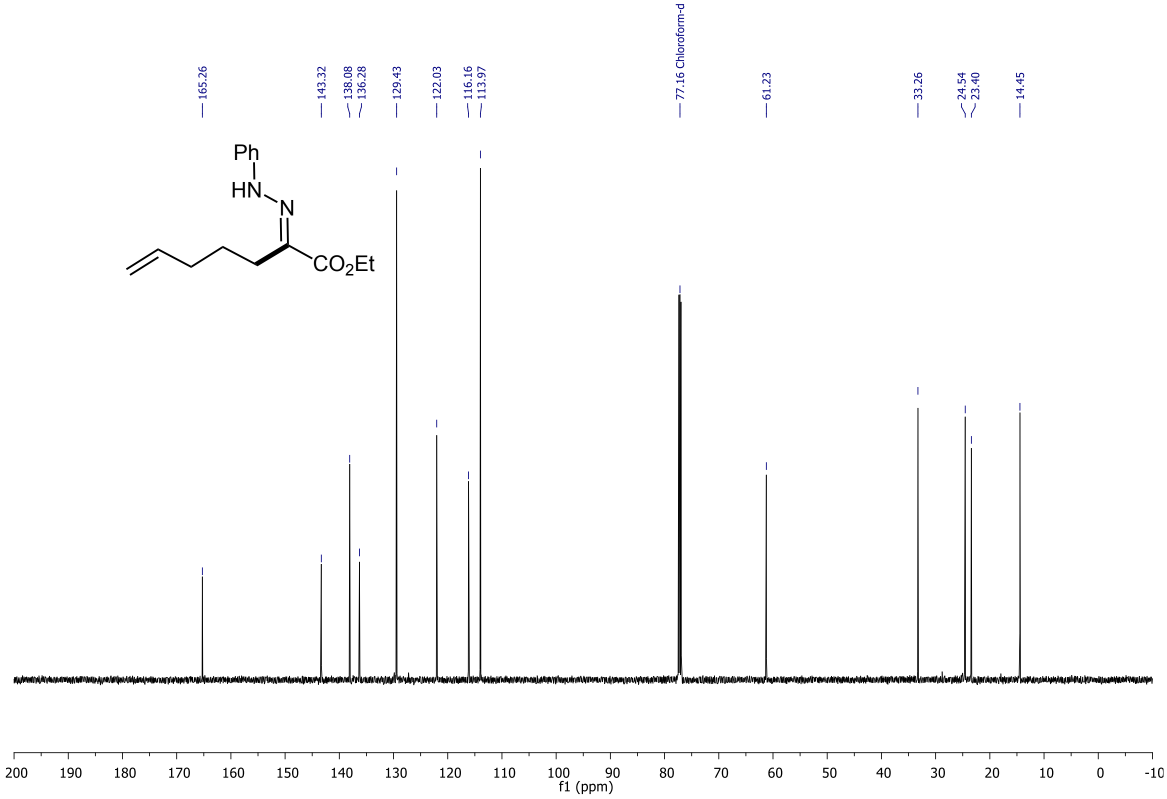
^{13}C NMR spectrum of **3b**



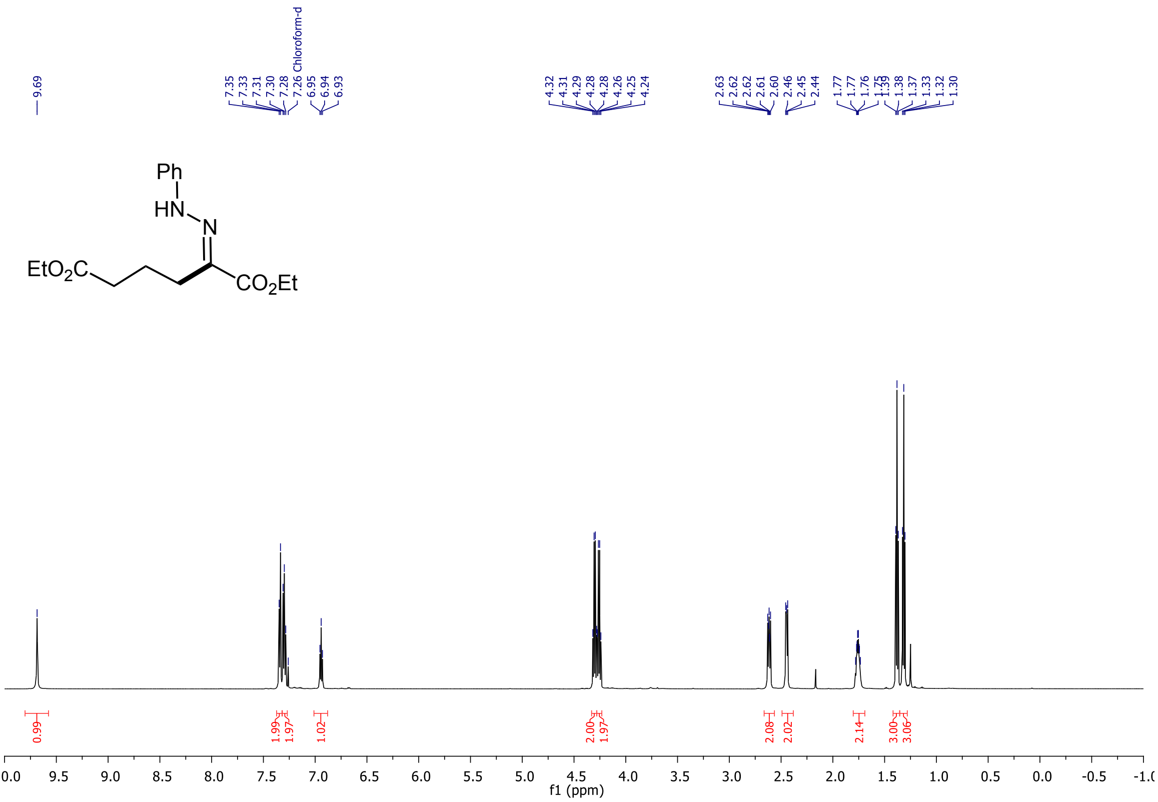
^{1}H NMR spectrum of **3c**



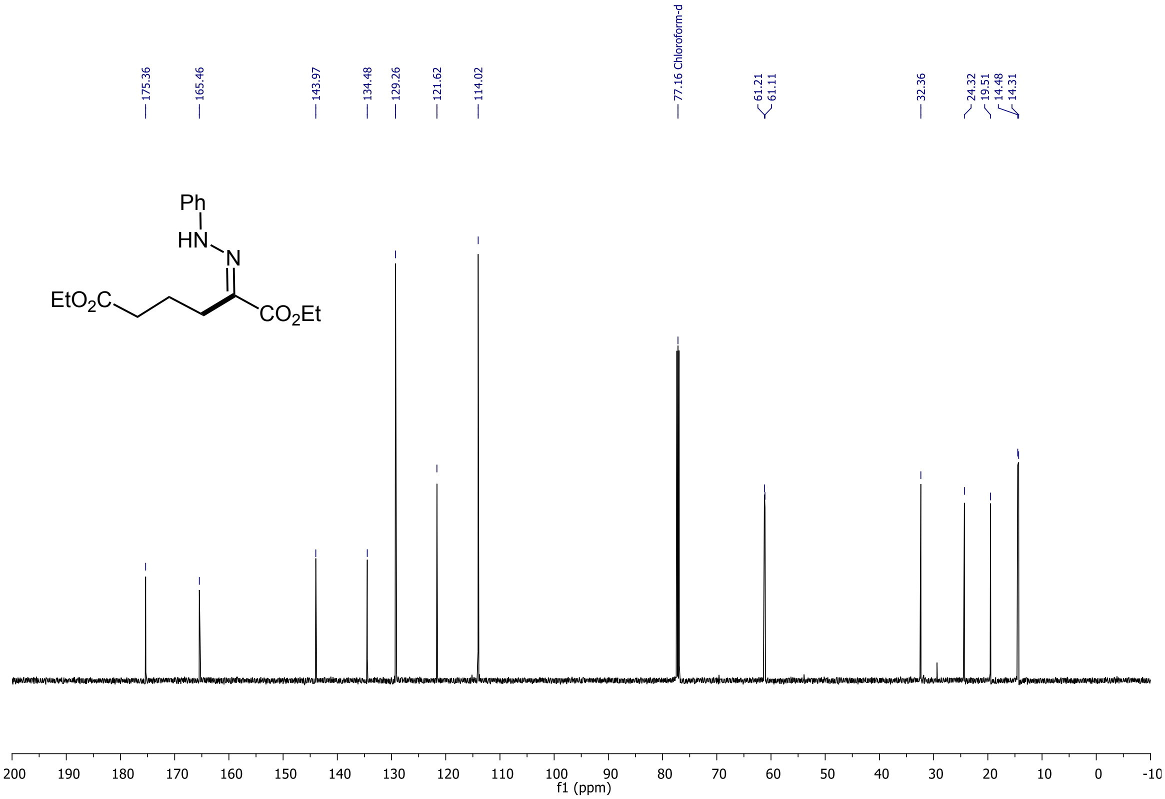
^{13}C NMR spectrum of **3c**



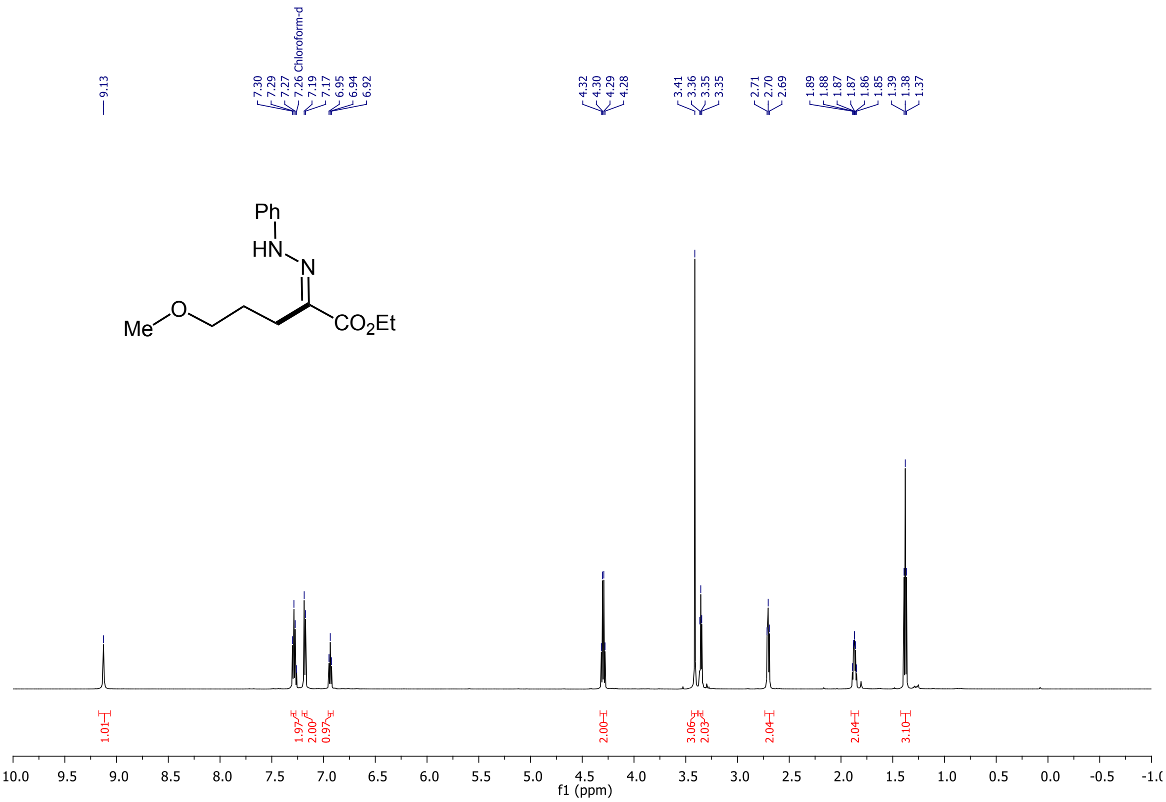
^{1}H NMR spectrum of **3d**



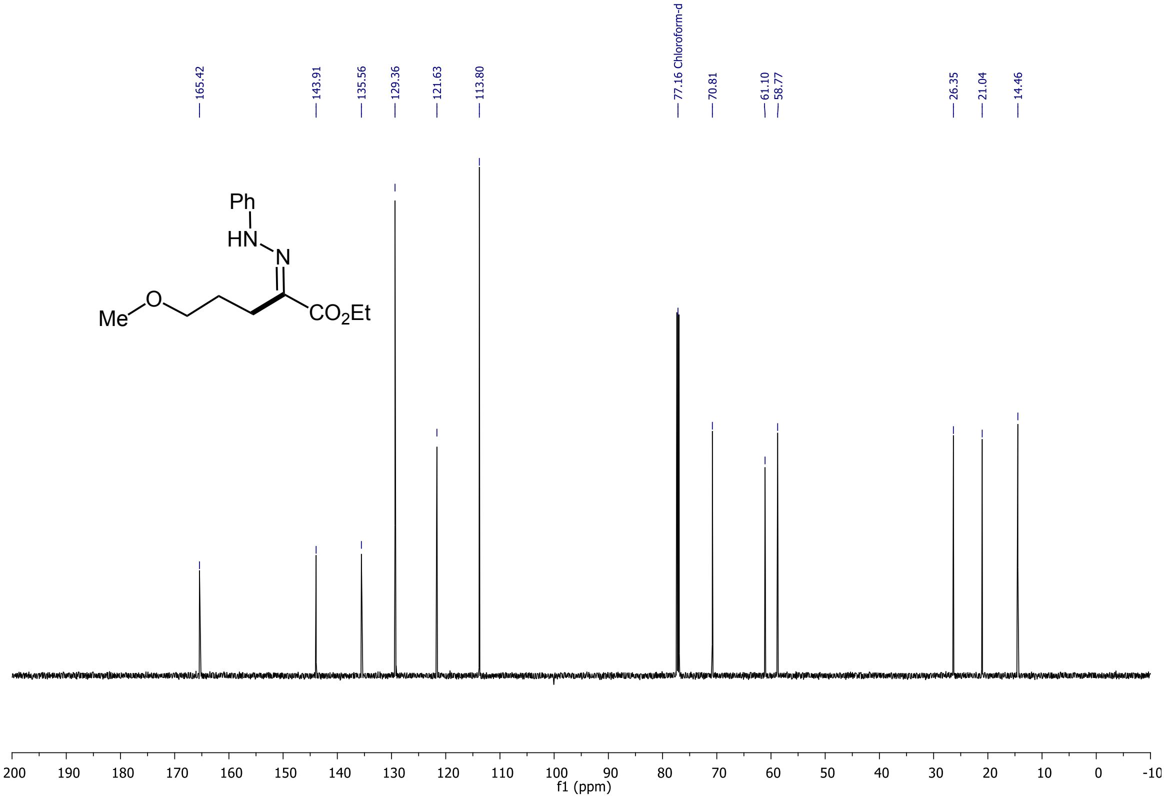
^{13}C NMR spectrum of **3d**



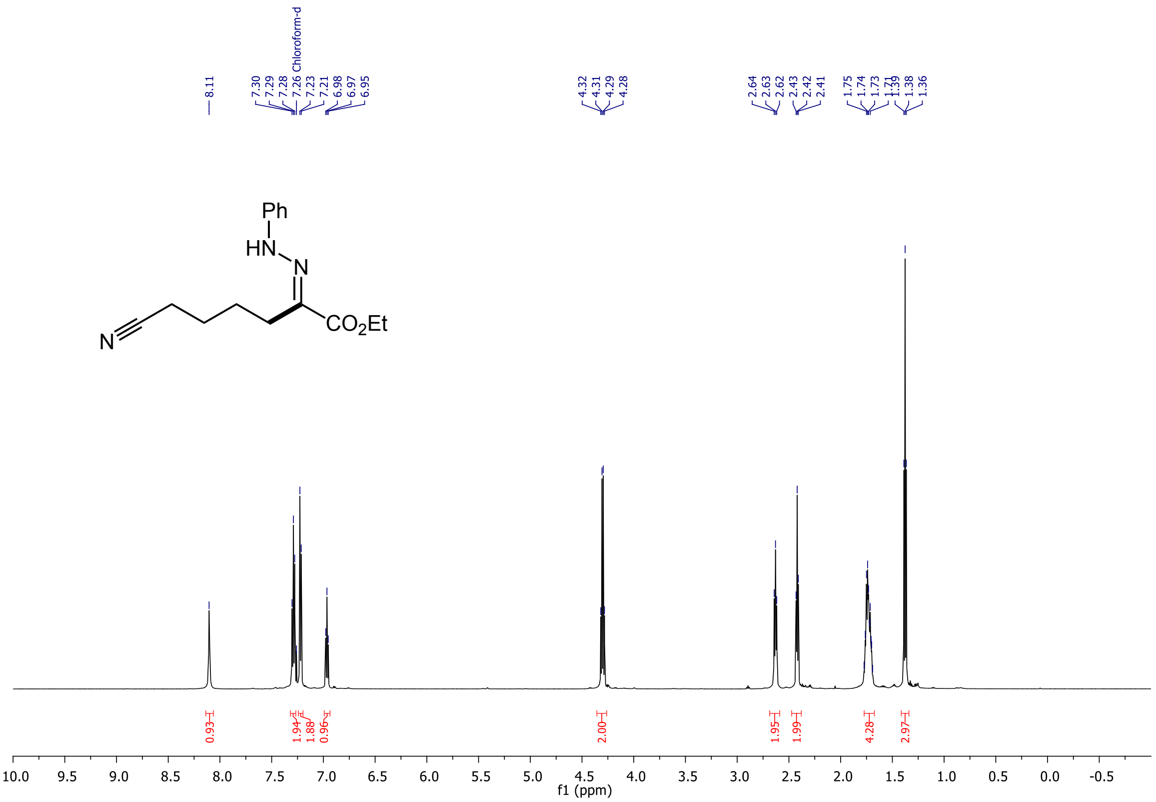
^{1}H NMR spectrum of **3e**



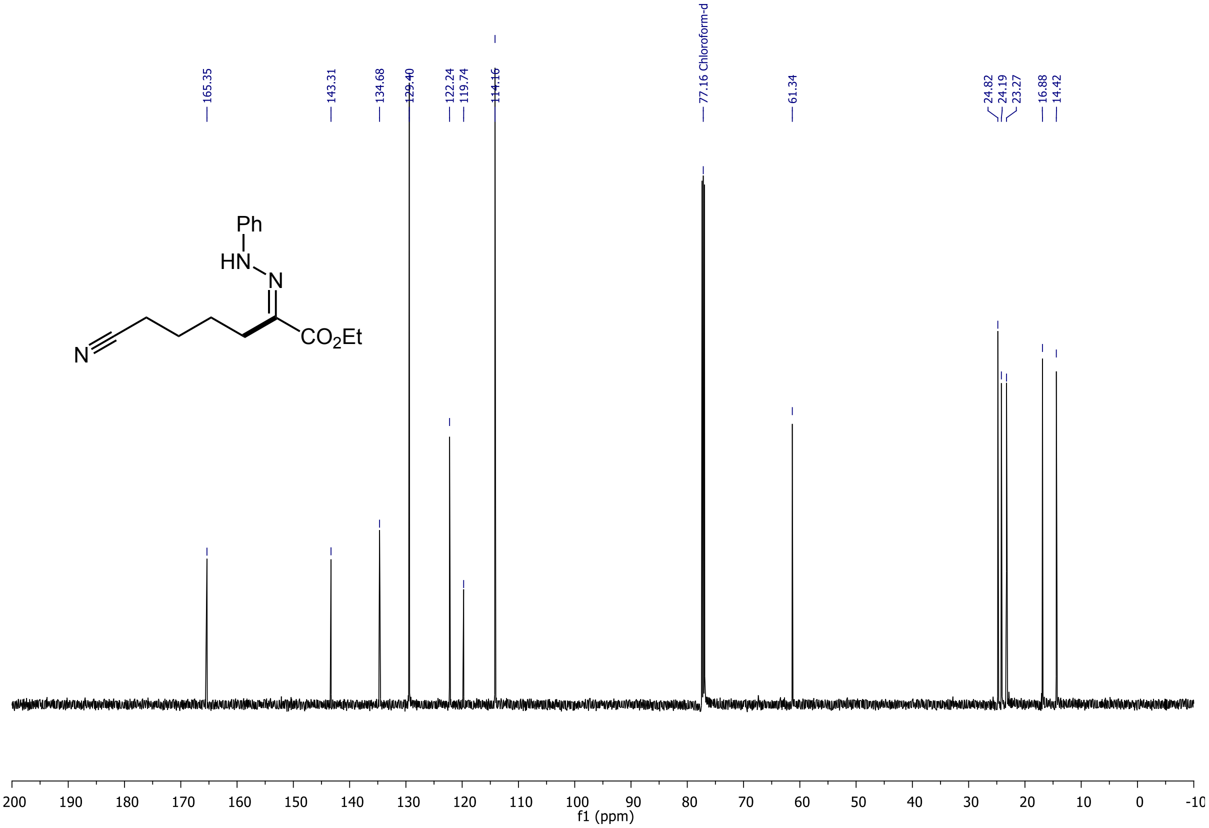
^{13}C NMR spectrum of **3e**



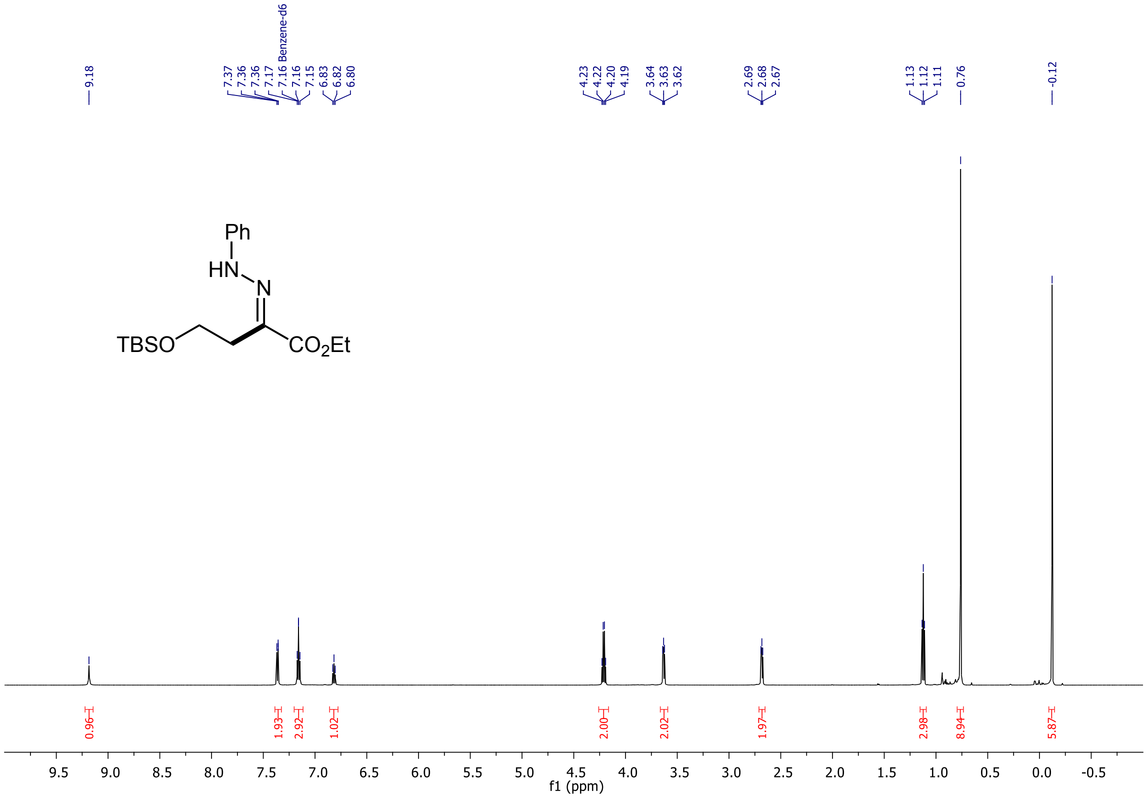
^{1}H NMR spectrum of **3f**



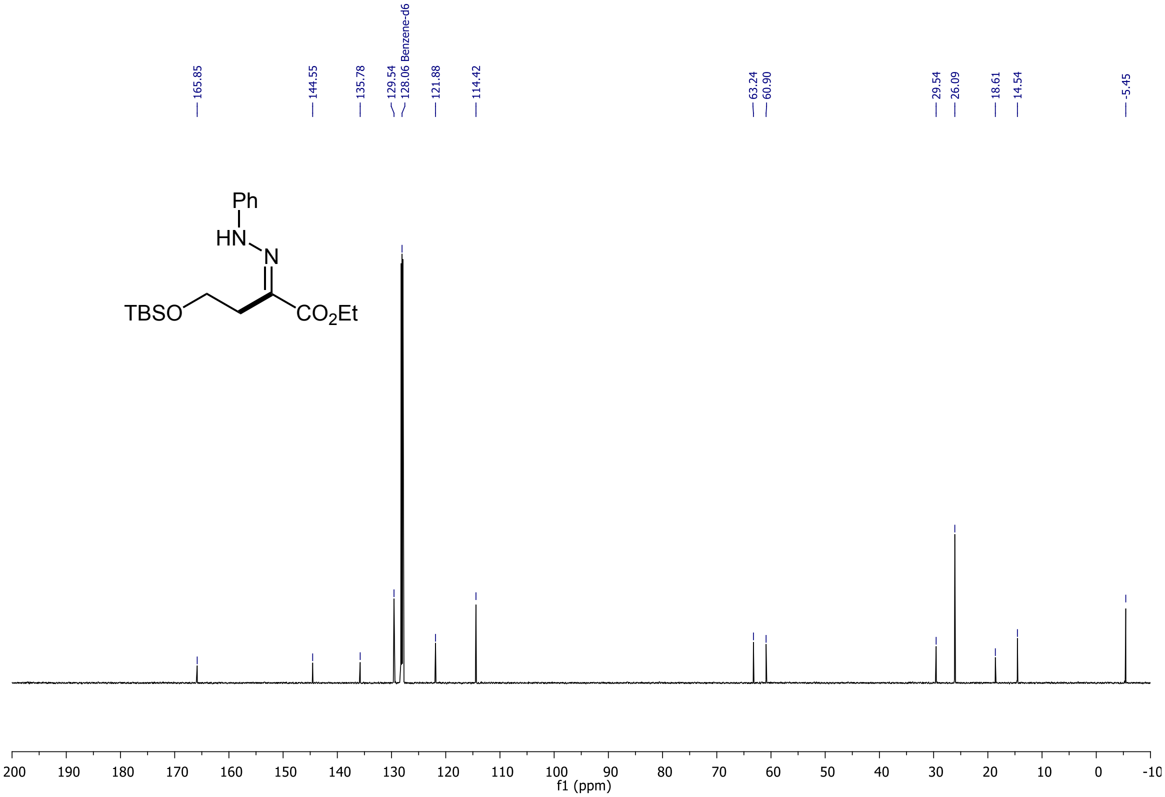
^{13}C NMR spectrum of **3f**



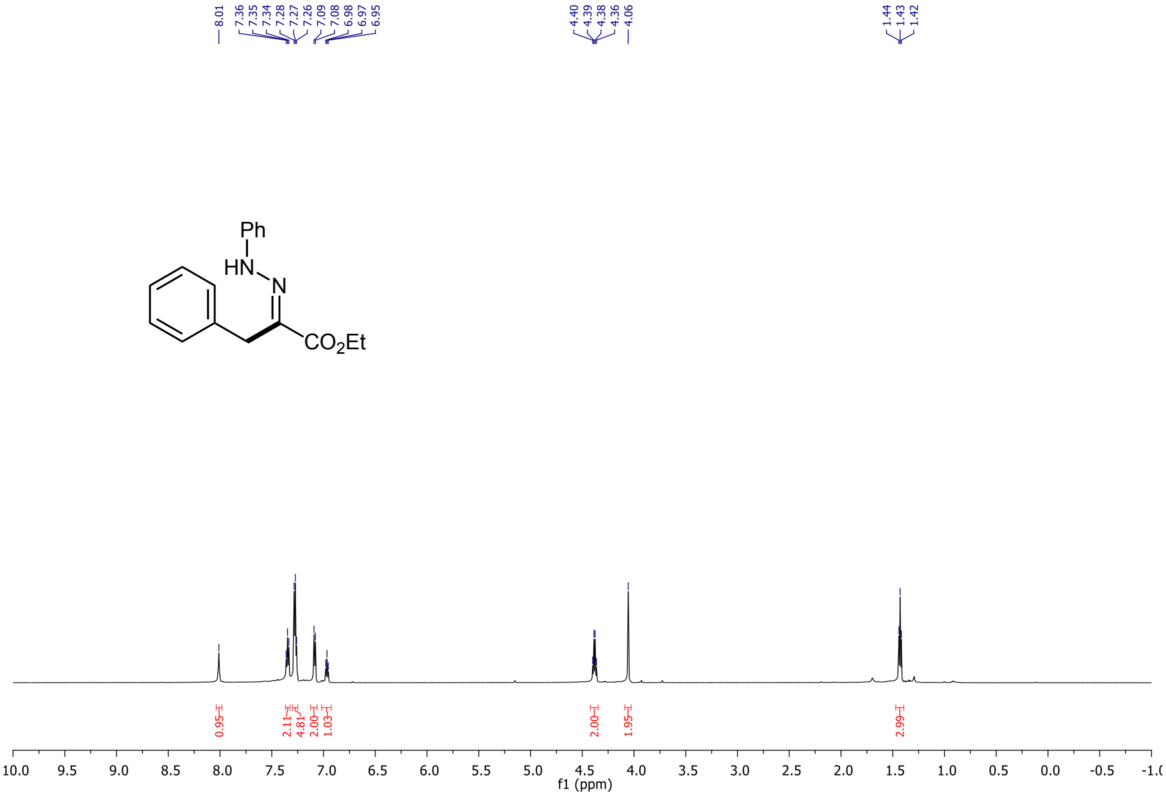
^{1}H NMR spectrum of **3g**



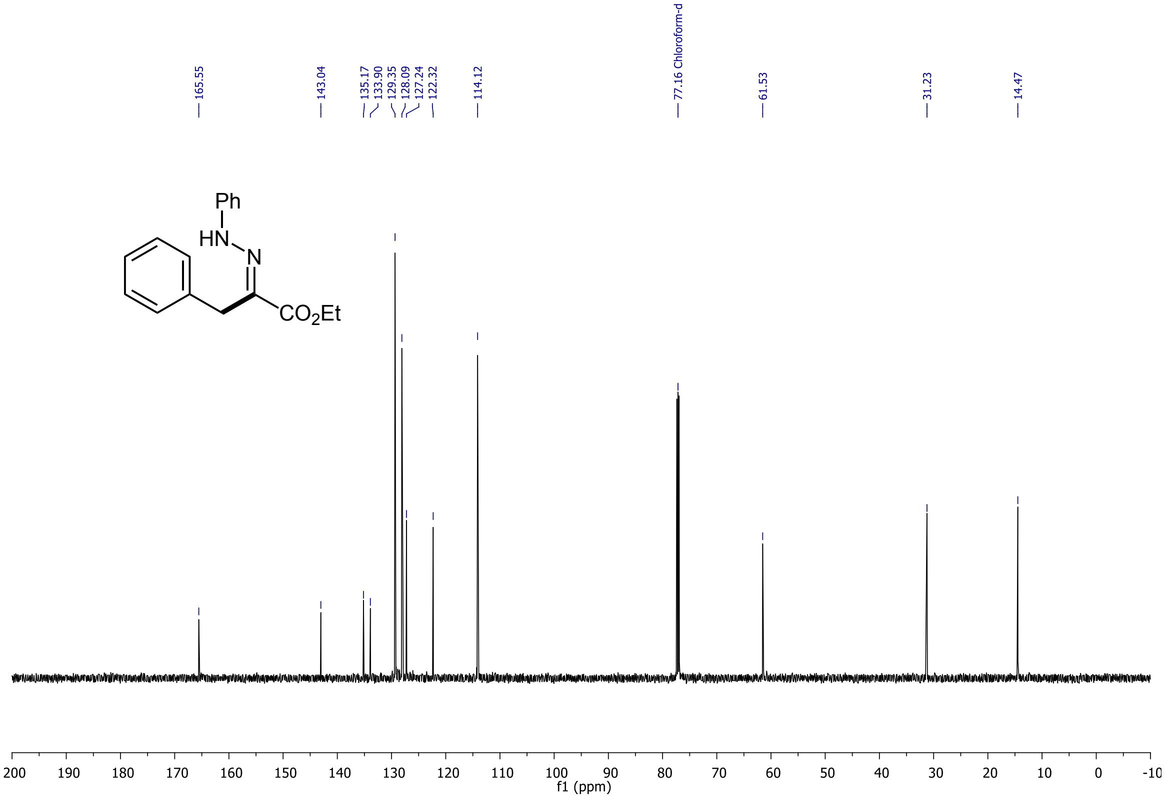
^{13}C NMR spectrum of **3g**



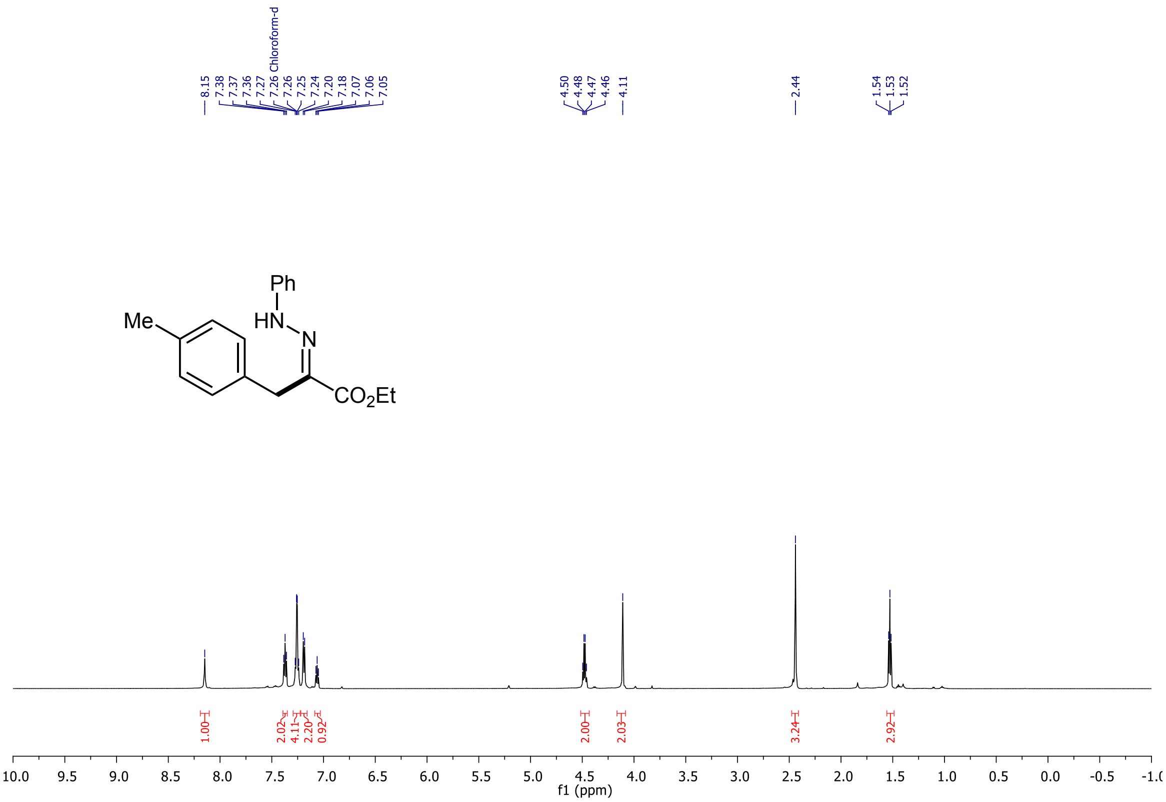
^{1}H NMR spectrum of **3h**



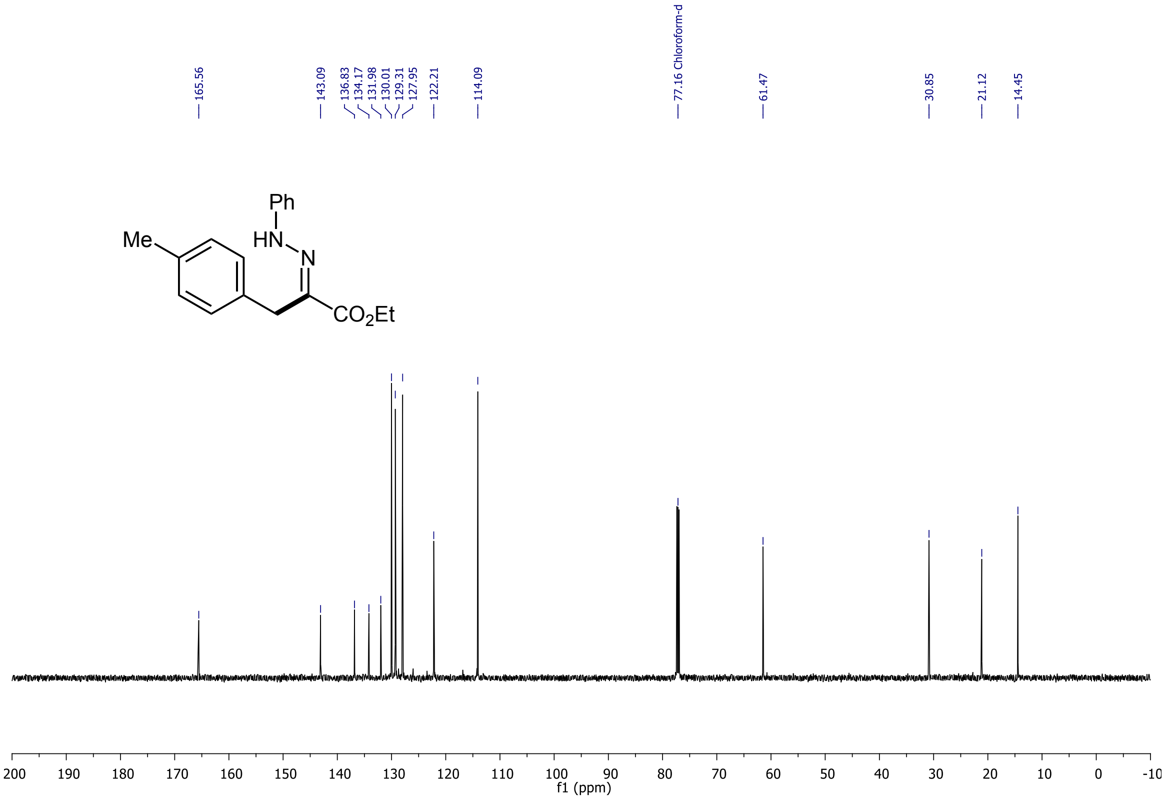
^{13}C NMR spectrum of **3h**



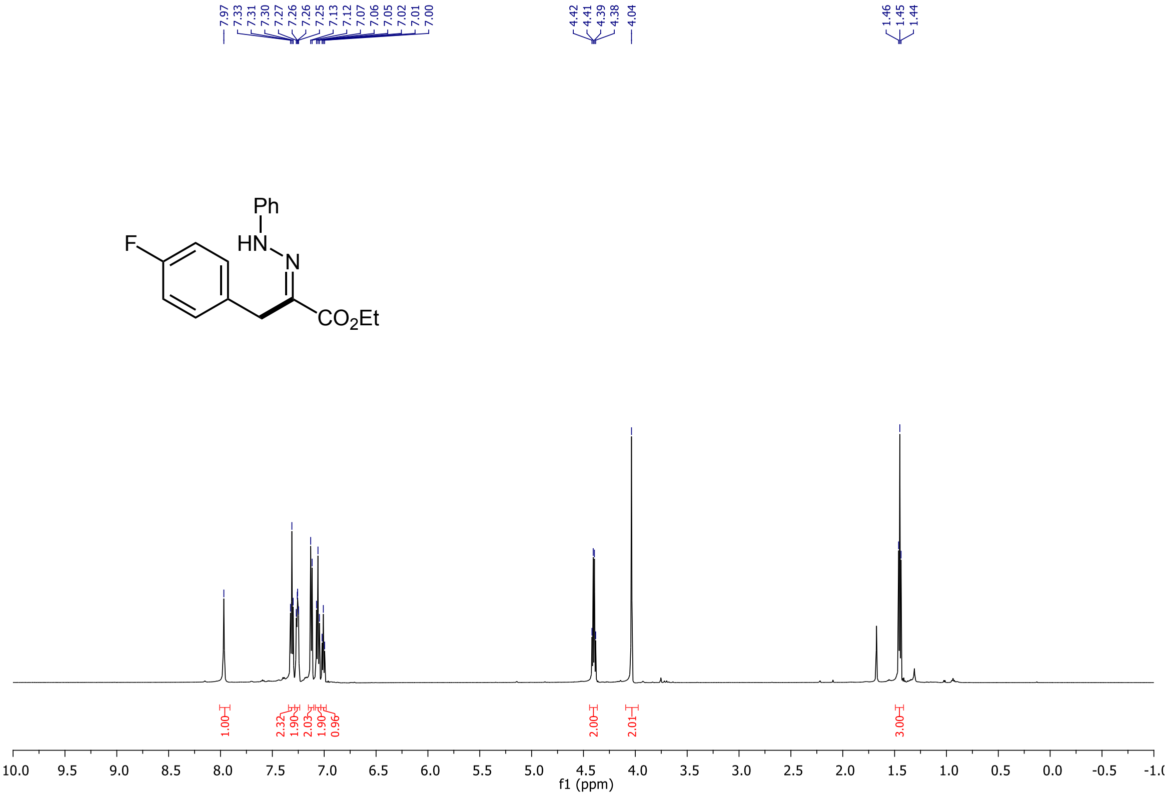
^{1}H NMR spectrum of **3i**



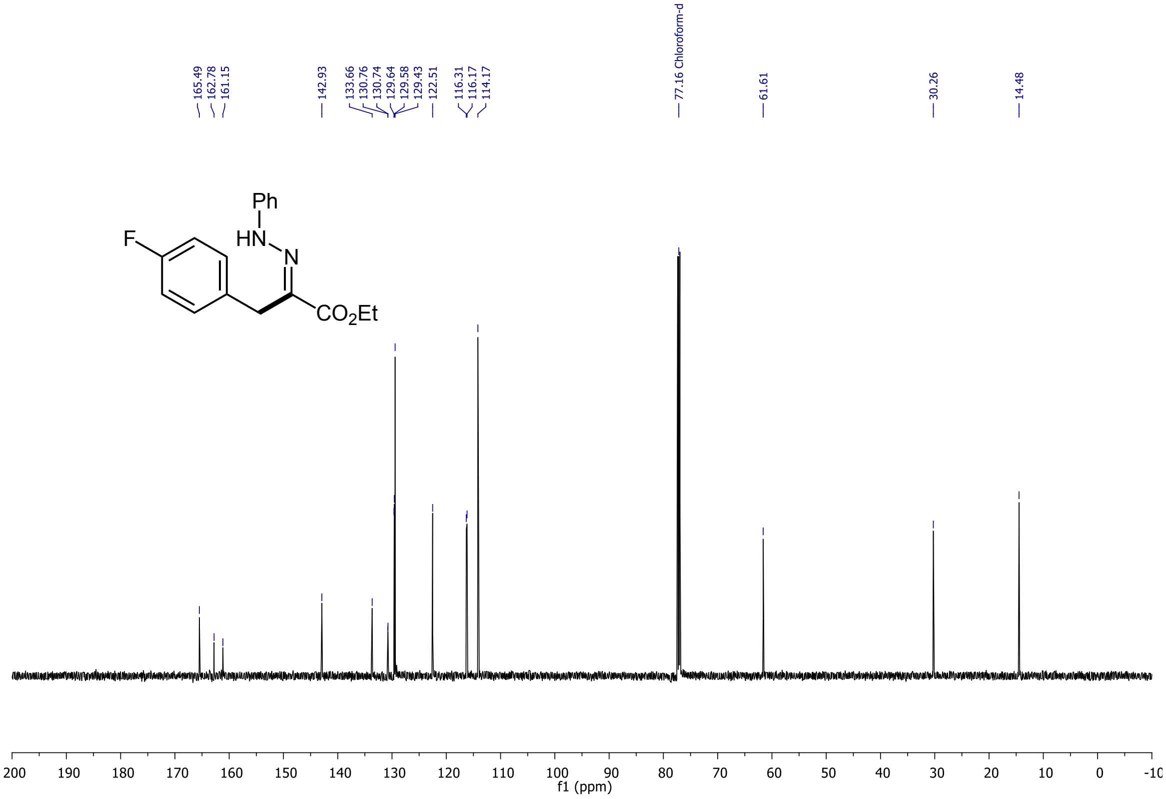
^{13}C NMR spectrum of **3i**



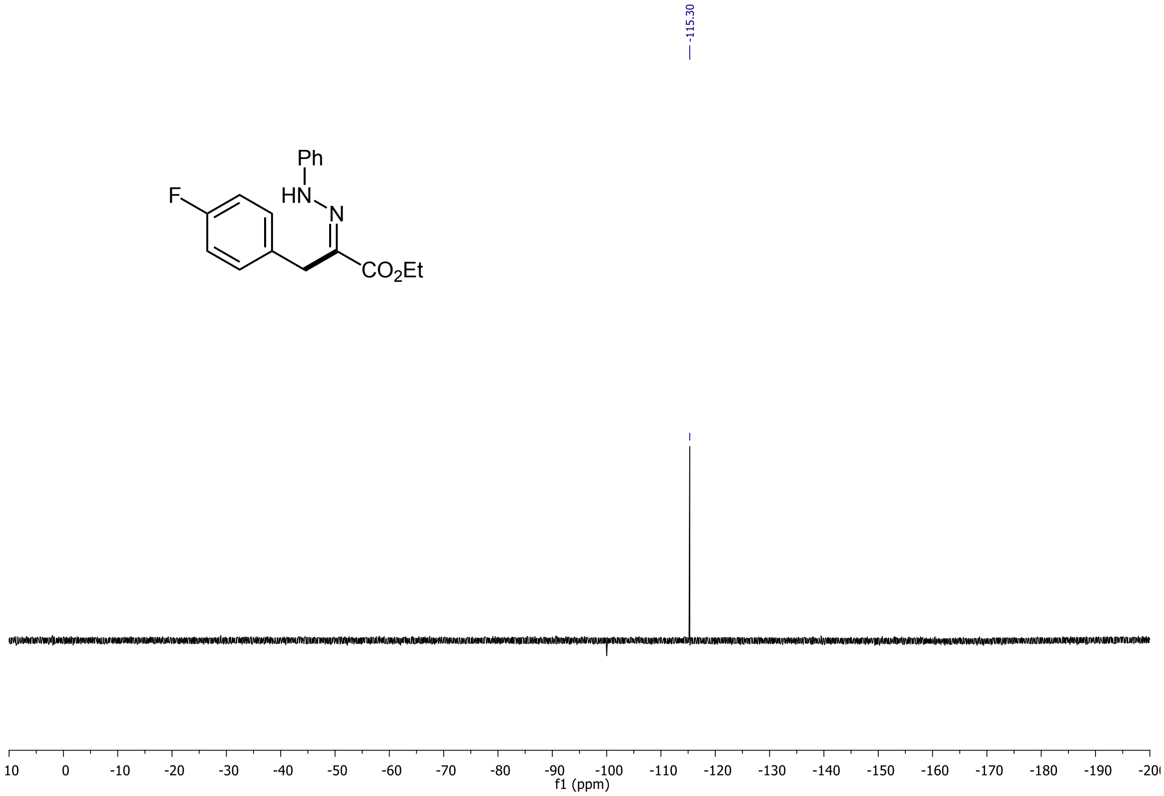
^{1}H NMR spectrum of **3j**



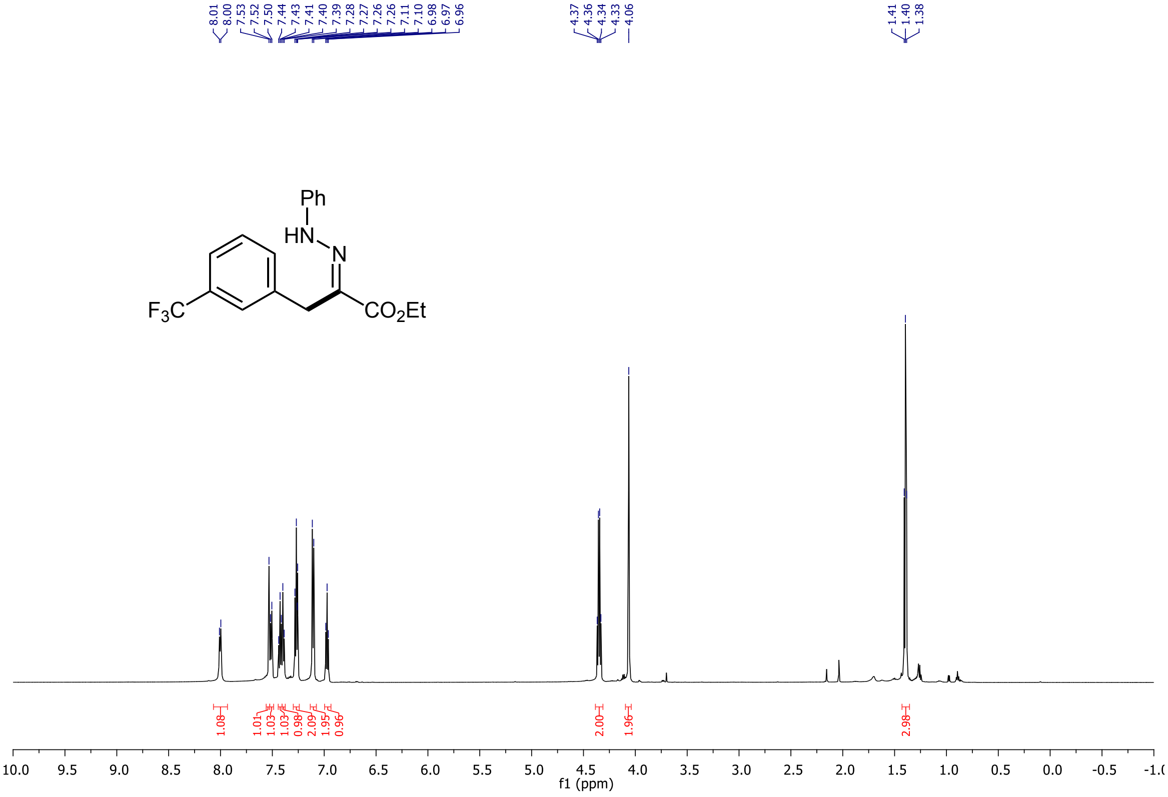
^{13}C NMR spectrum of **3j**



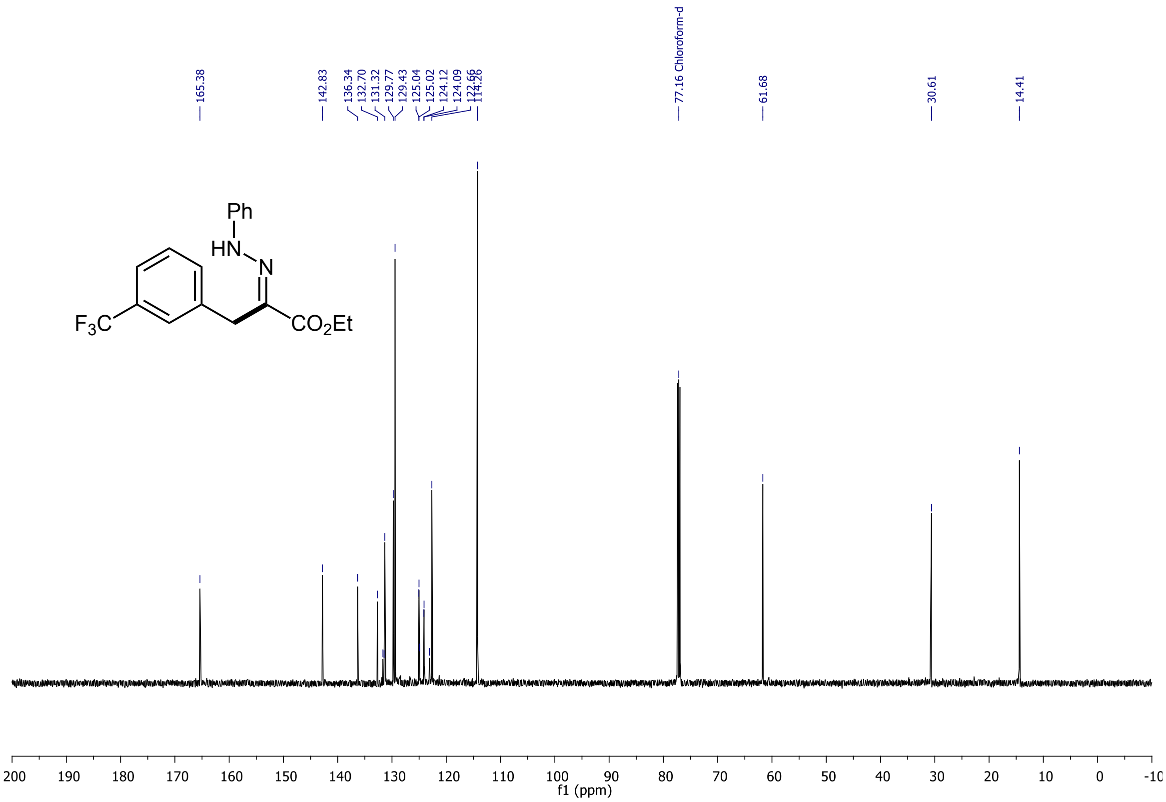
^{19}F NMR spectrum of **3j**



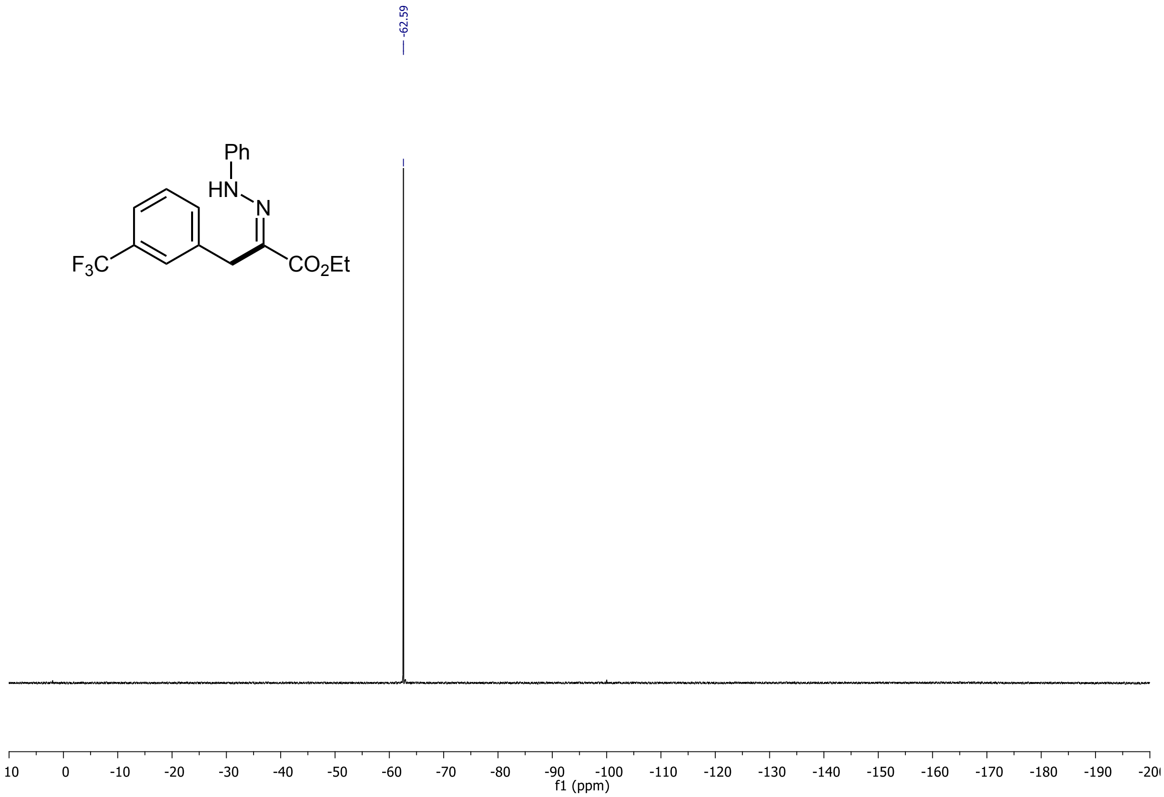
^{1}H NMR spectrum of **3k**



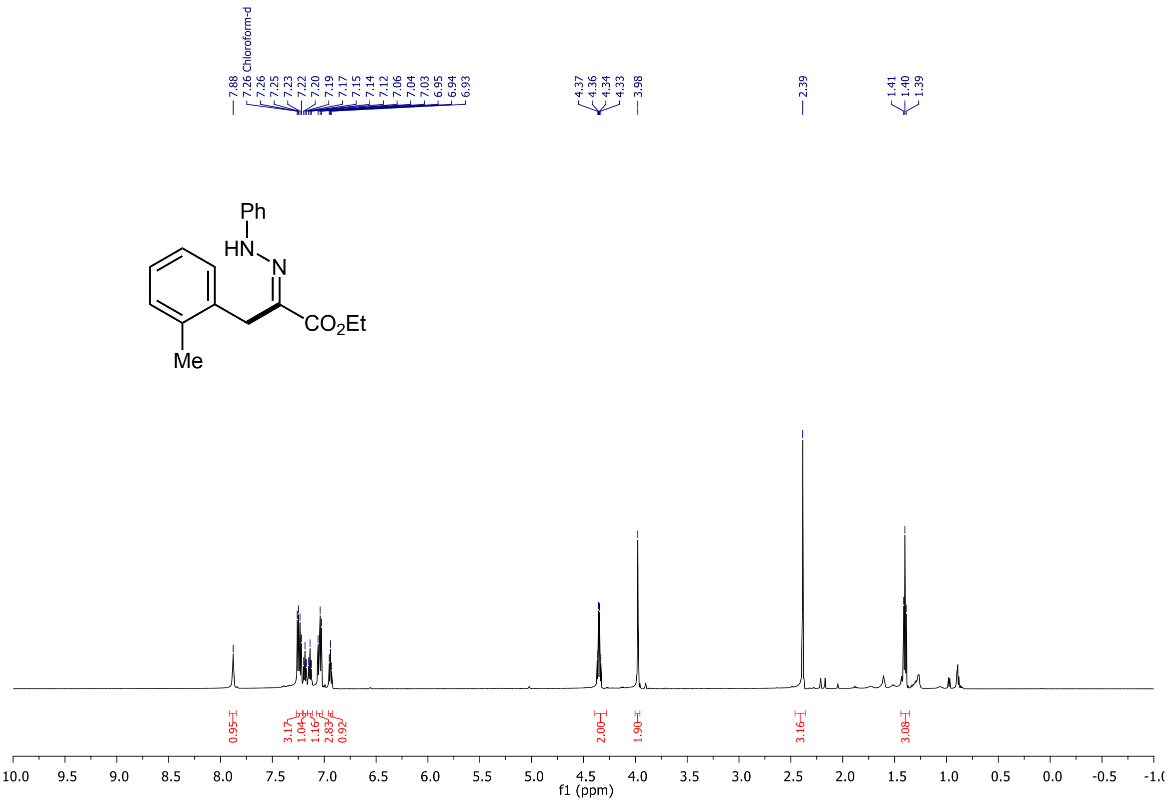
^{13}C NMR spectrum of **3k**



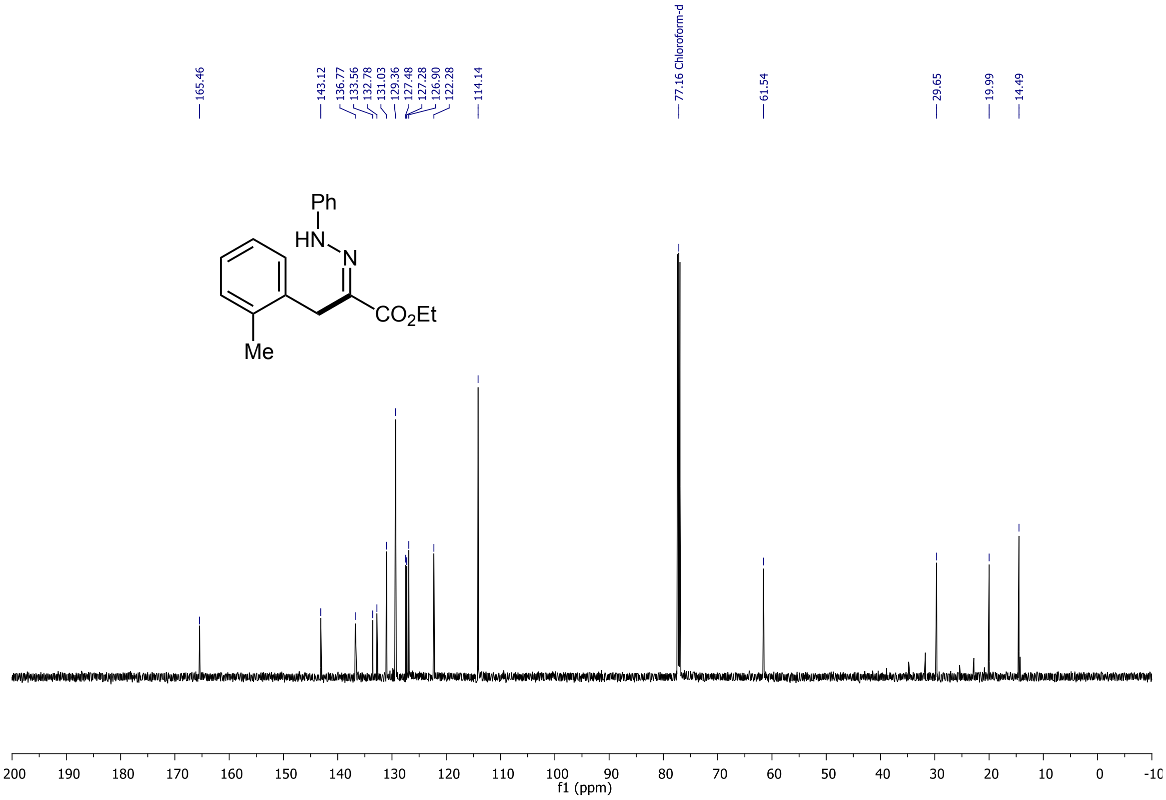
^{19}F NMR spectrum of **3k**



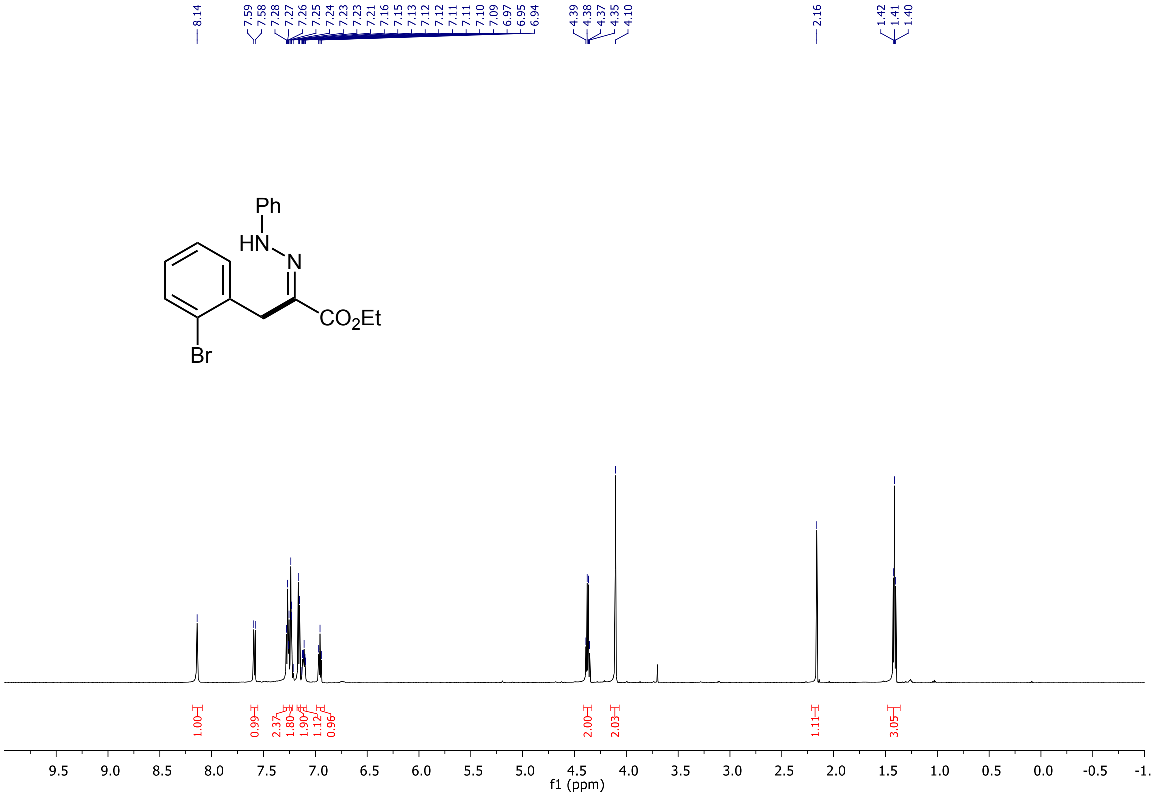
^{1}H NMR spectrum of **3l**



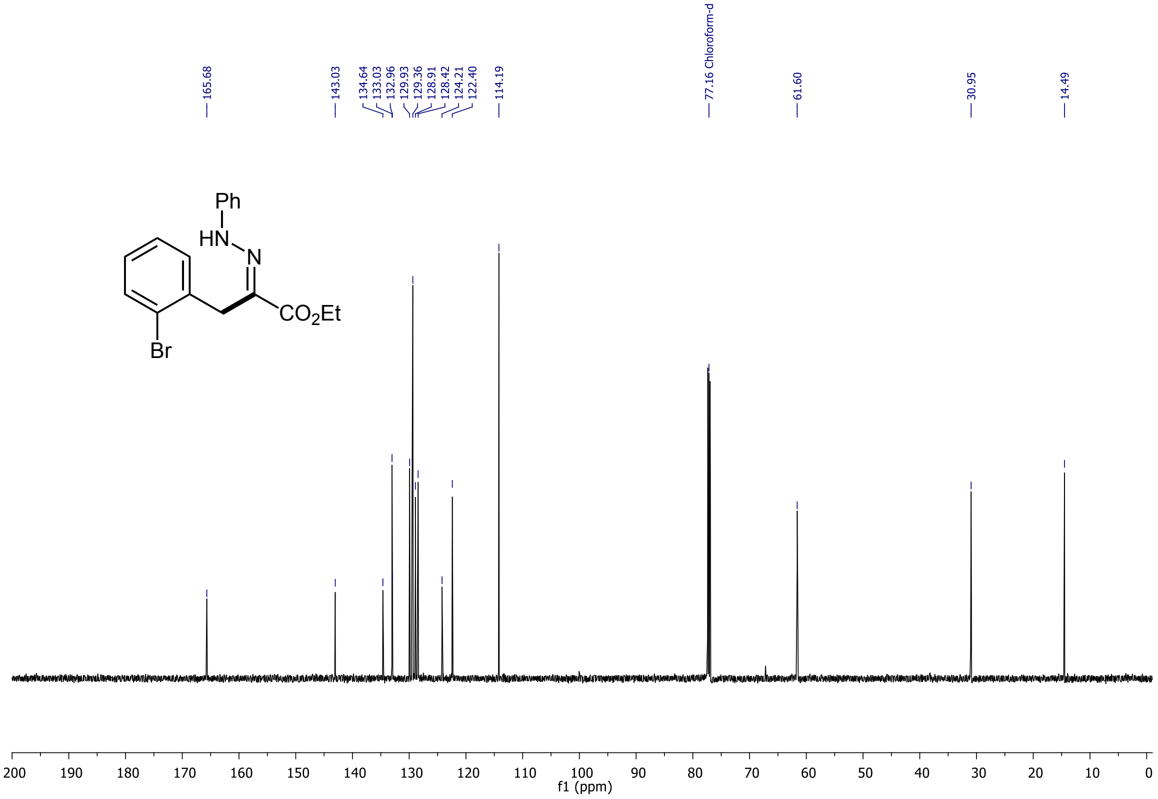
^{13}C NMR spectrum of **3l**



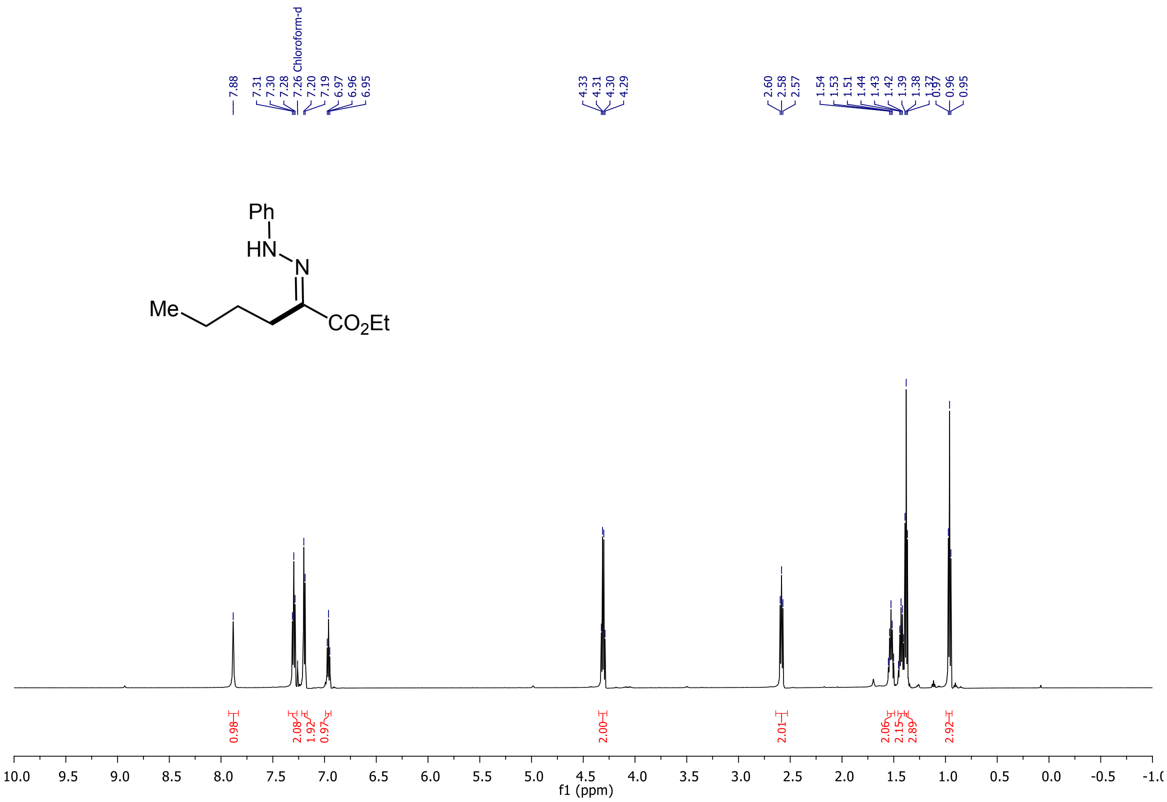
^{1}H NMR spectrum of **3m**



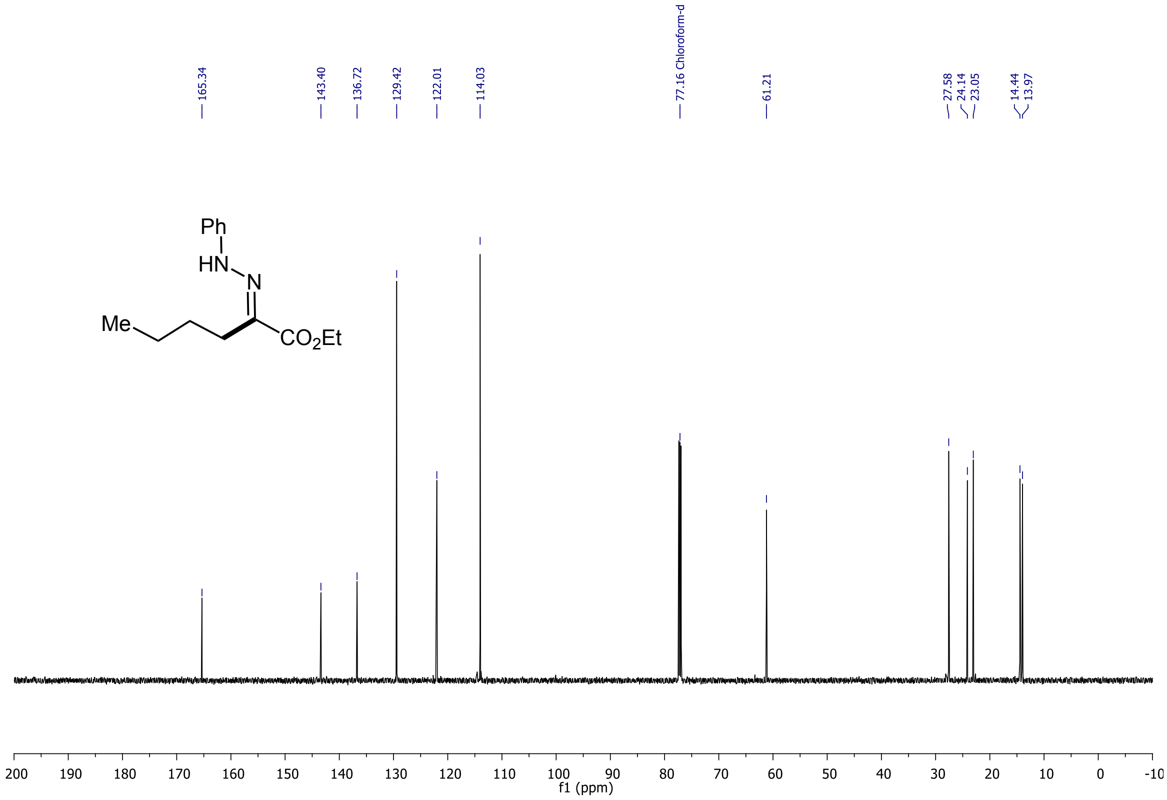
^{13}C NMR spectrum of **3m**



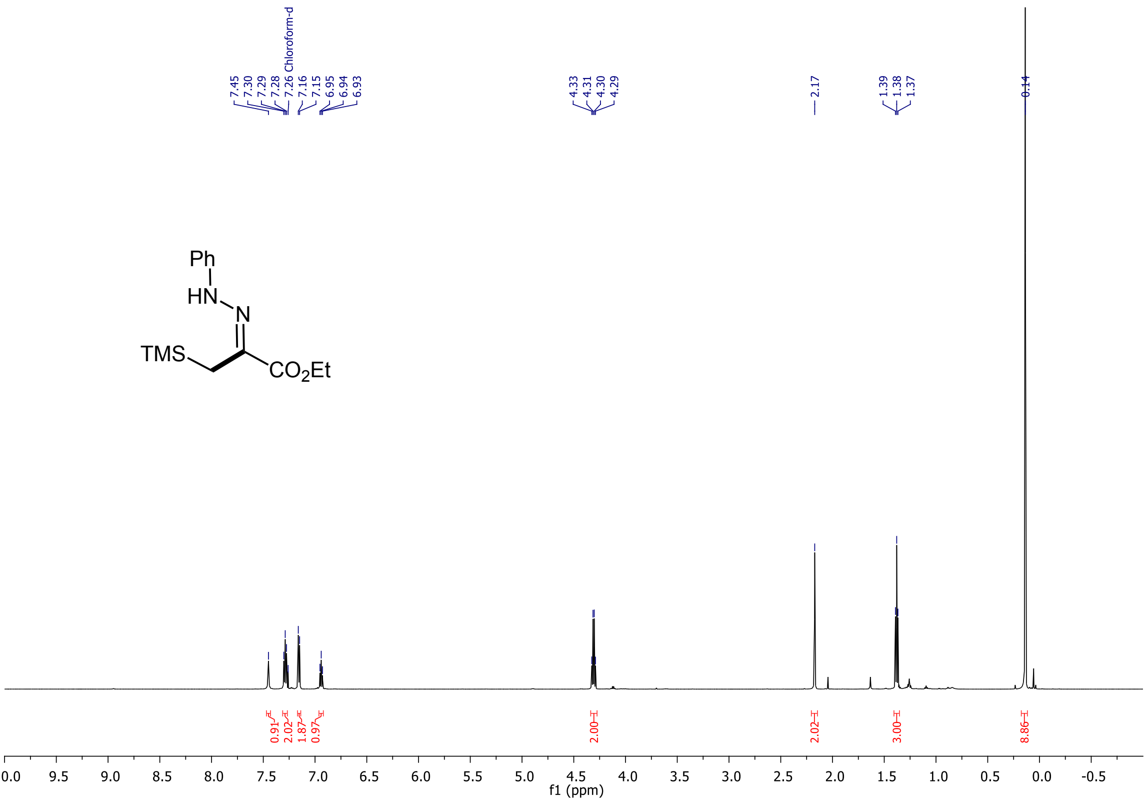
^{1}H NMR spectrum of **3n**



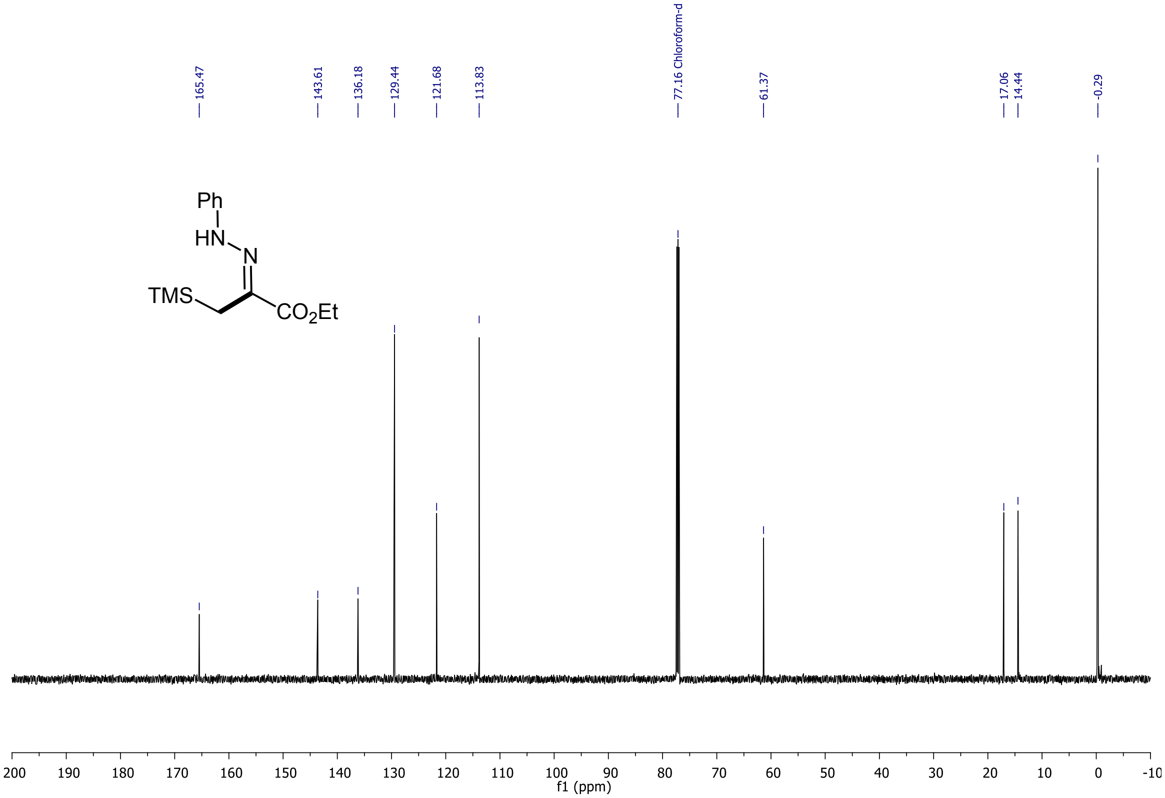
^{13}C NMR spectrum of **3n**



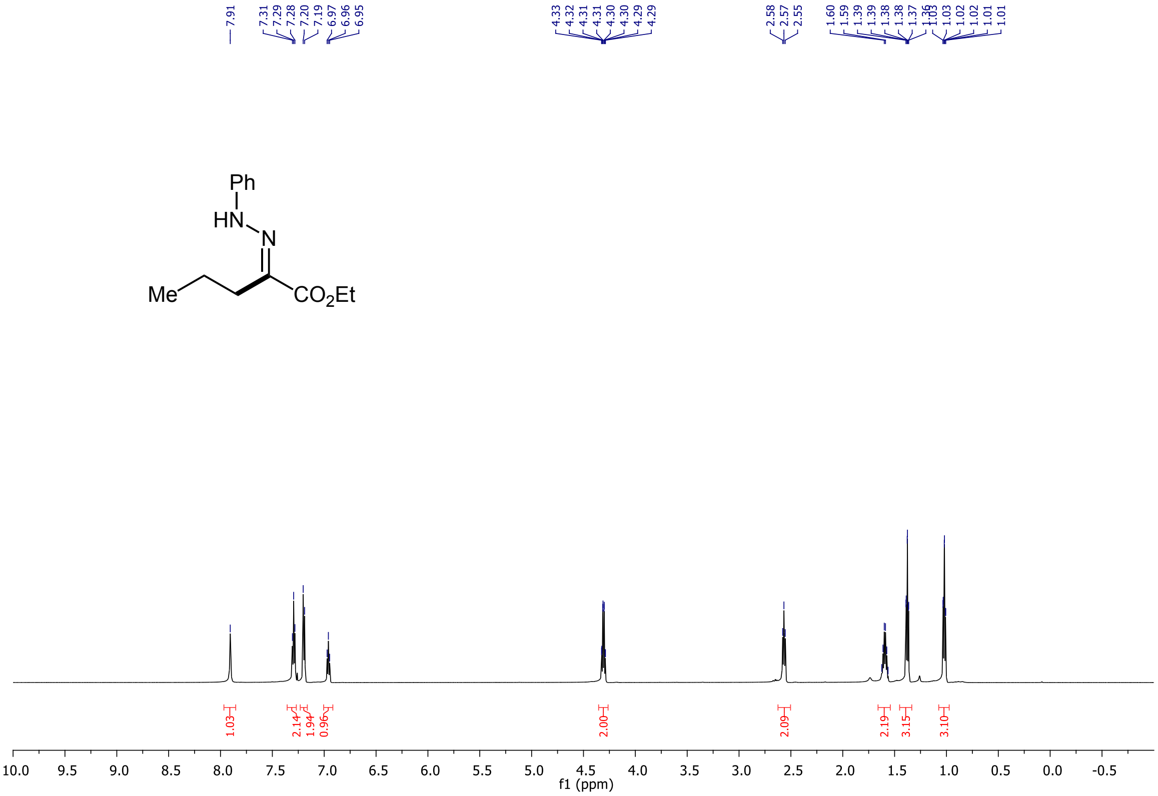
^{1}H NMR spectrum of **3o**



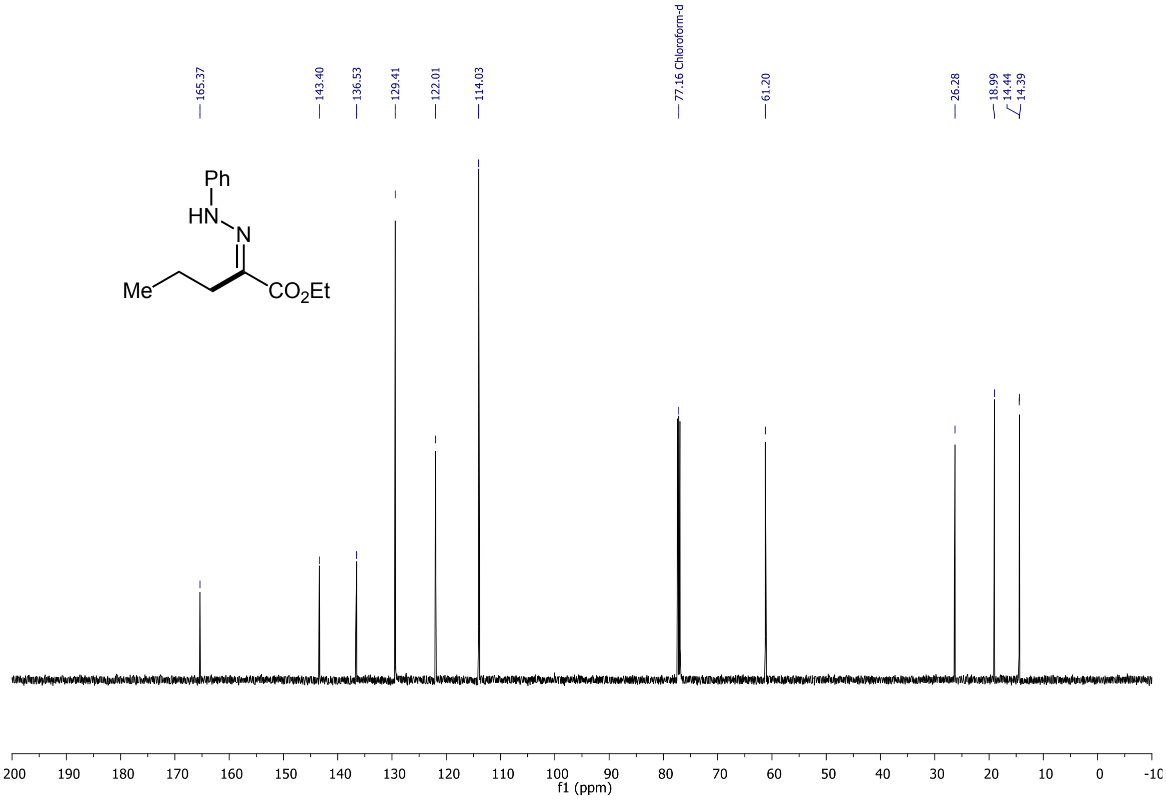
^{13}C NMR spectrum of **3o**



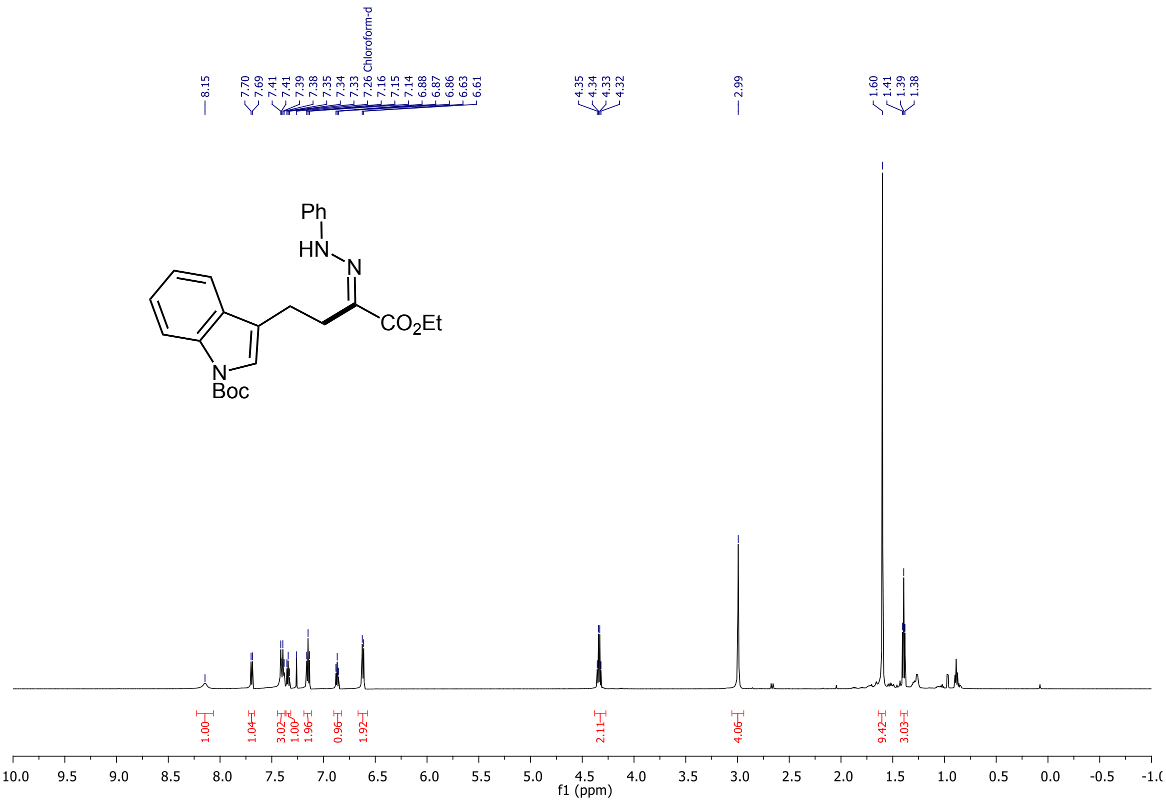
^{1}H NMR spectrum of **3p**



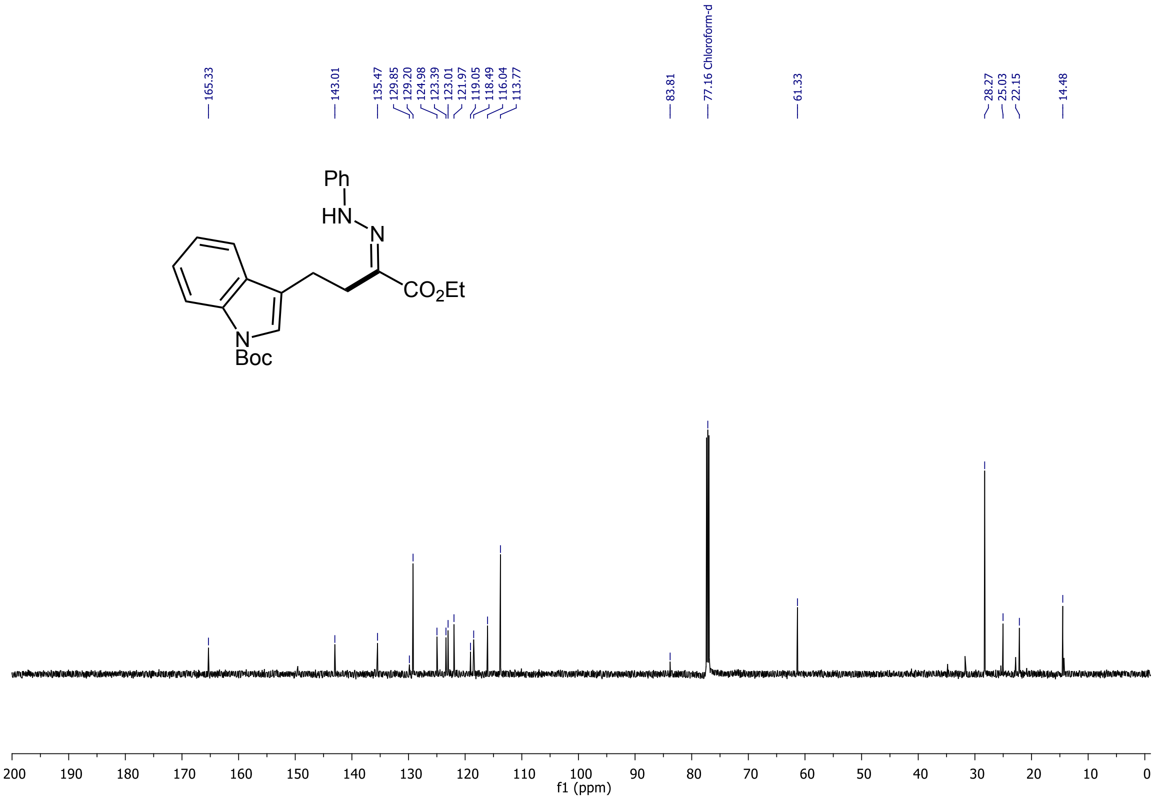
^{13}C NMR spectrum of **3p**



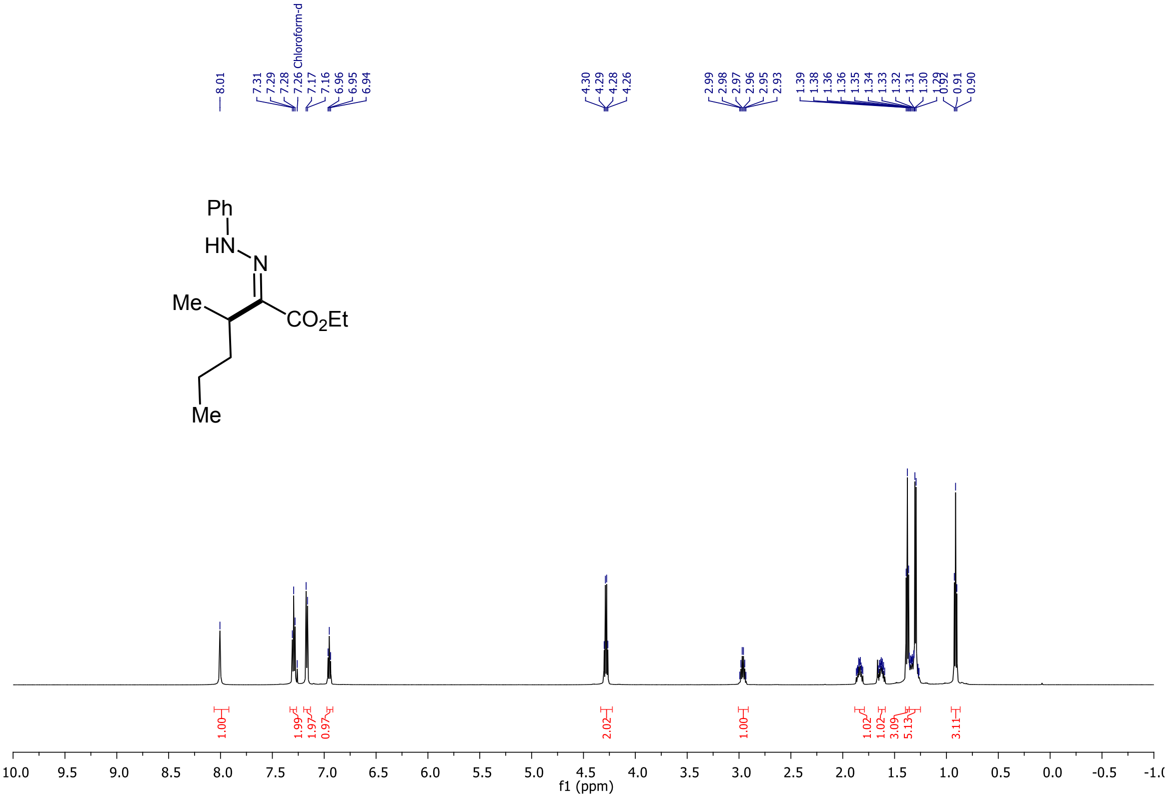
^{1}H NMR spectrum of **3q**



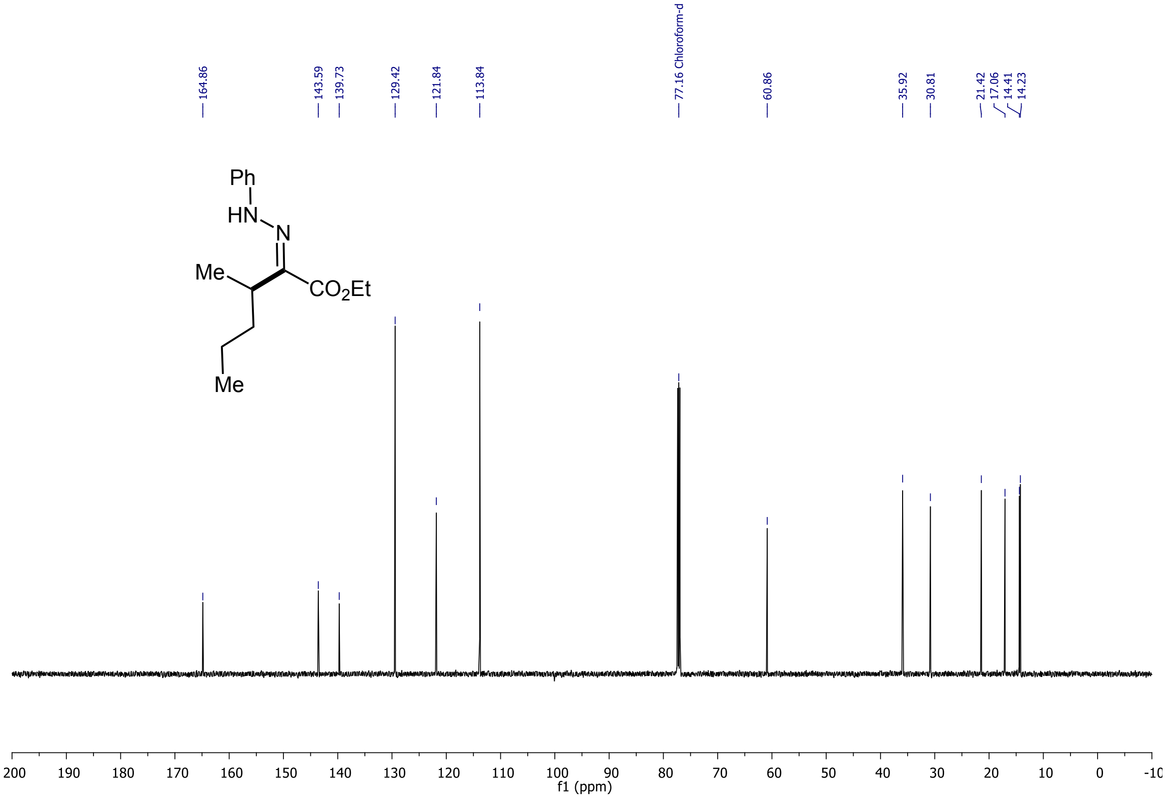
^{13}C NMR spectrum of **3q**



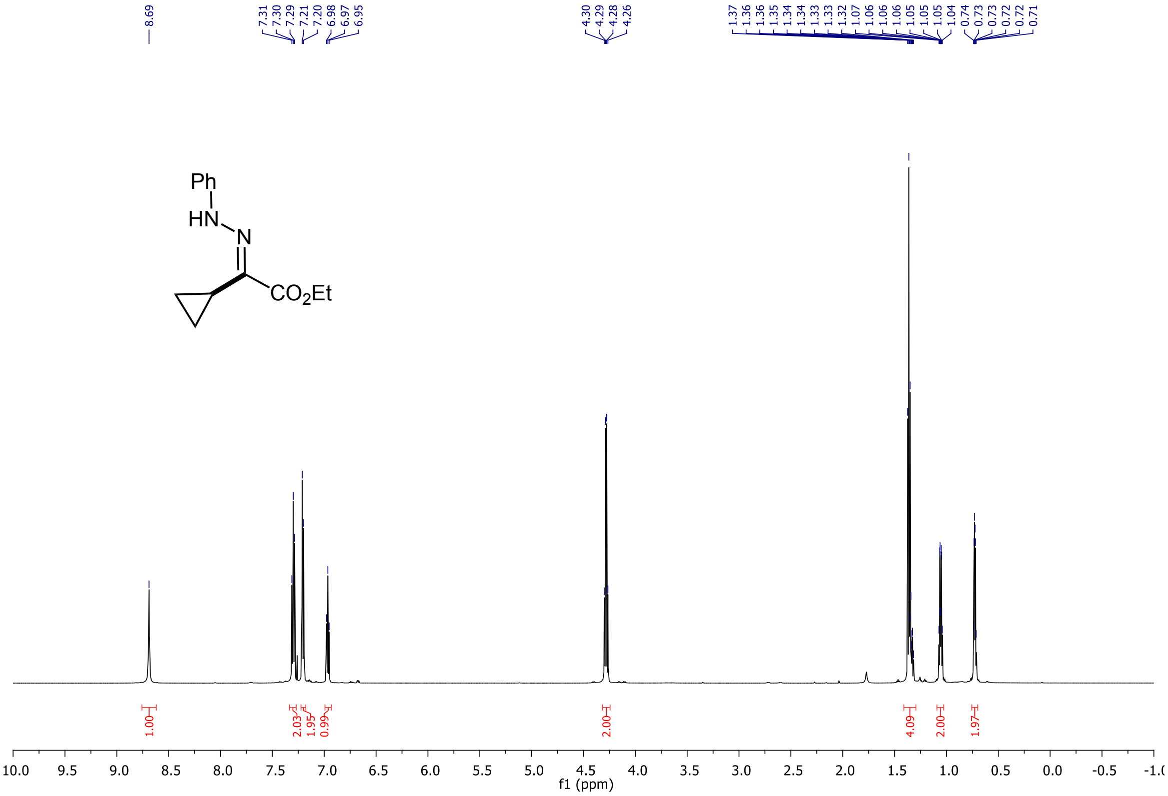
^{1}H NMR spectrum of **3r**



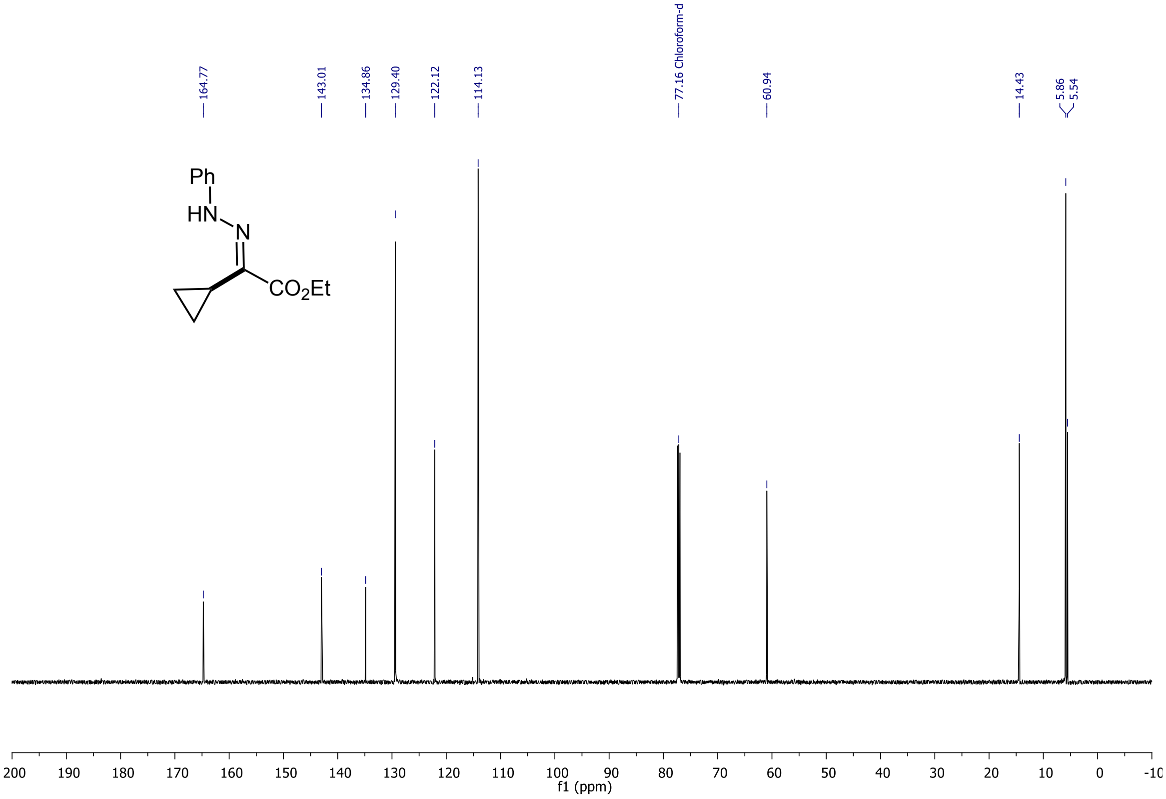
^{13}C NMR spectrum of **3r**



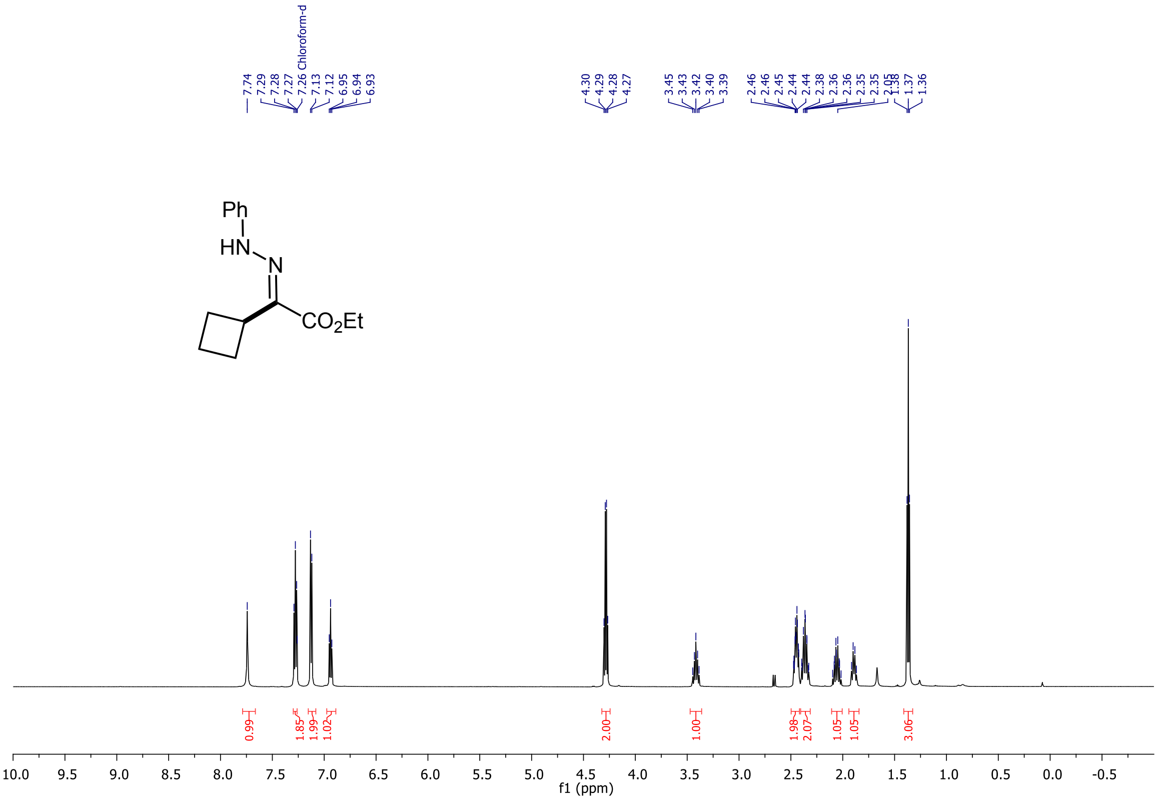
^{1}H NMR spectrum of **3s**



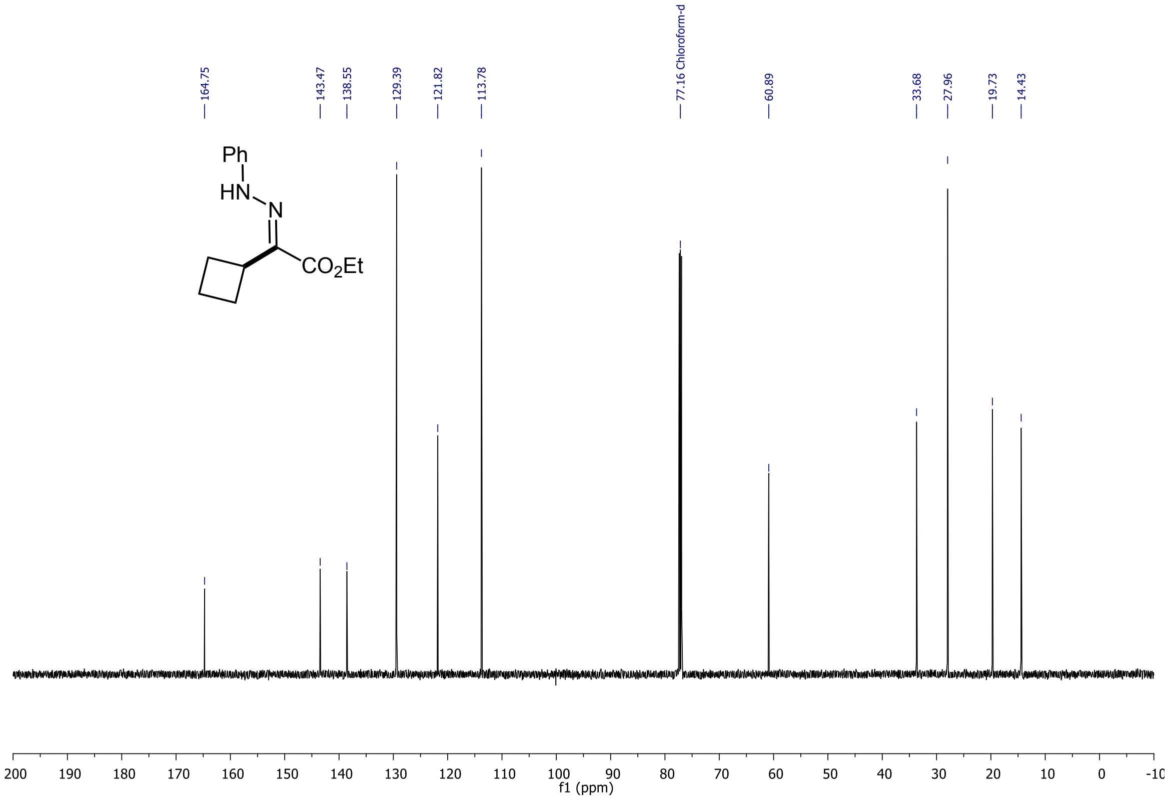
^{13}C NMR spectrum of **3s**



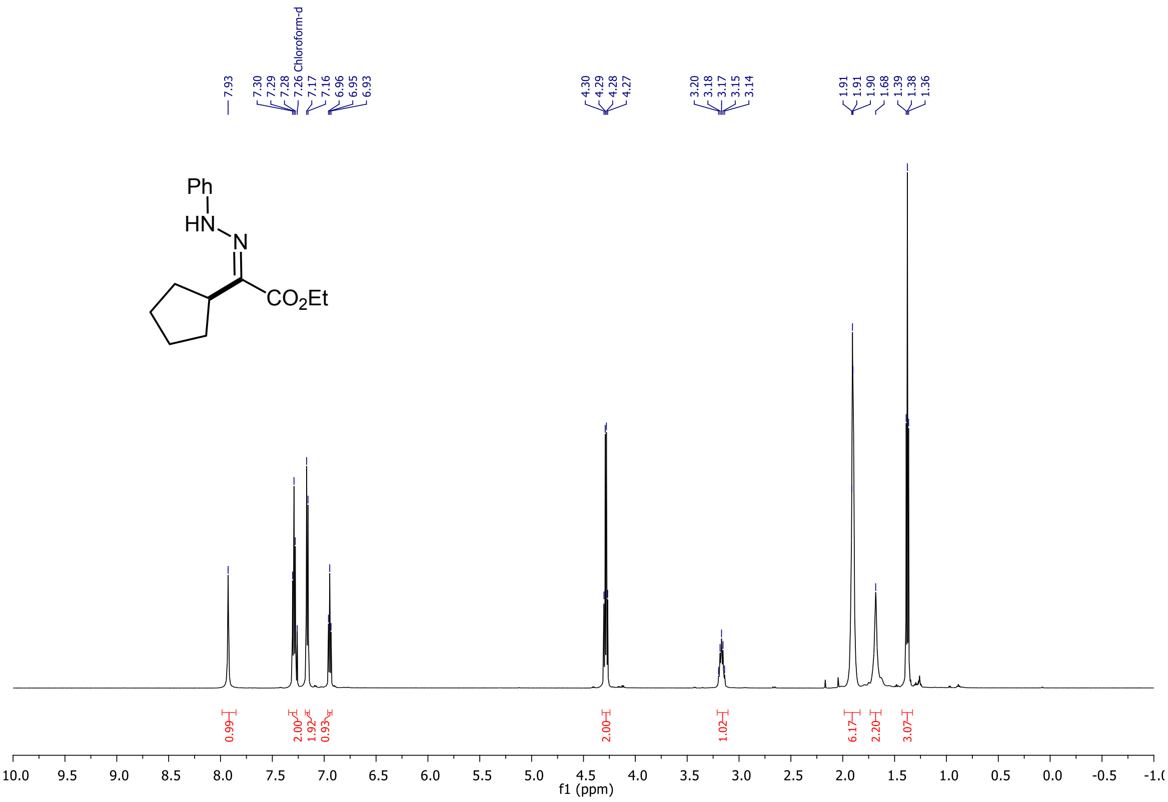
^{1}H NMR spectrum of **3t**



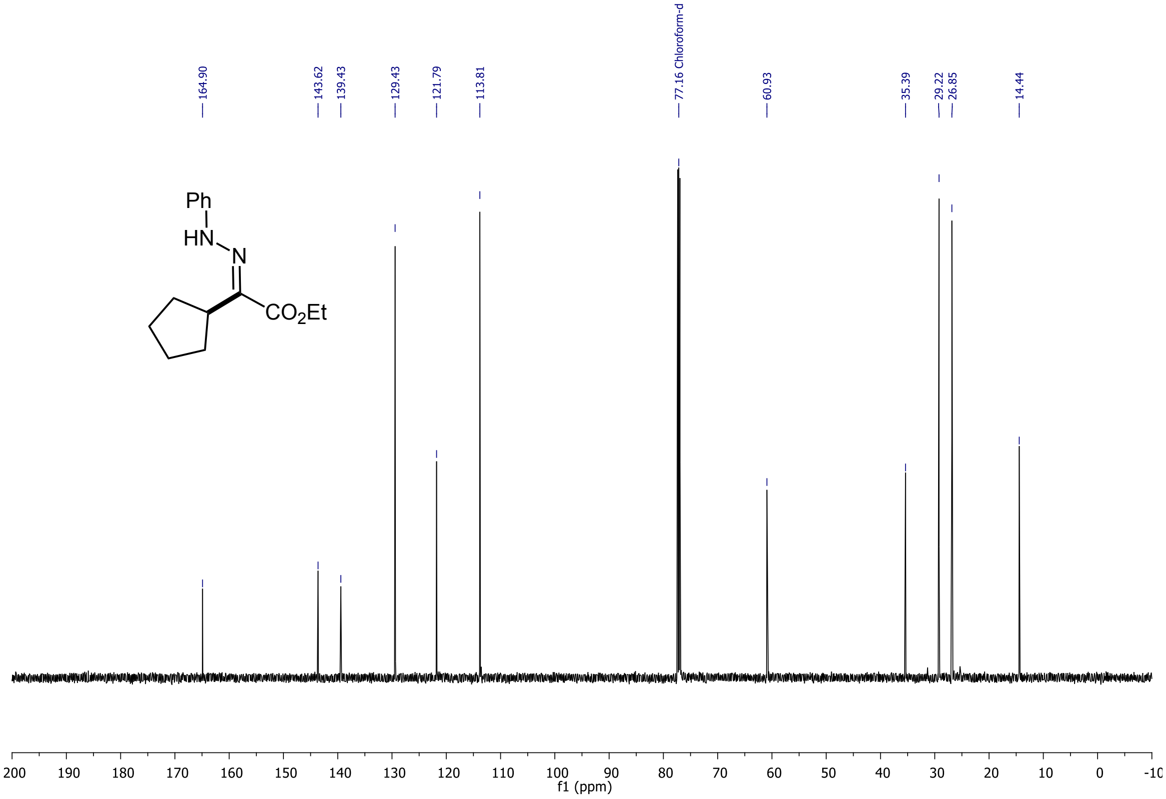
^{13}C NMR spectrum of **3t**



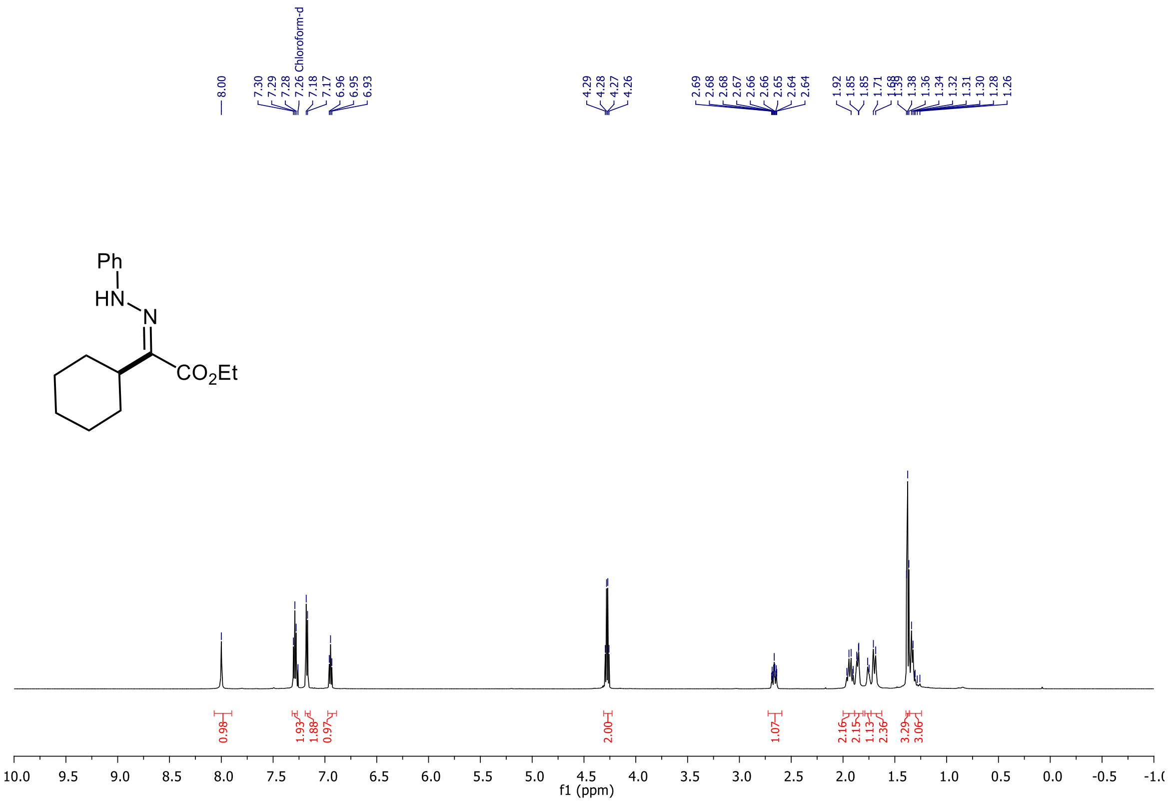
^{1}H NMR spectrum of **3u**



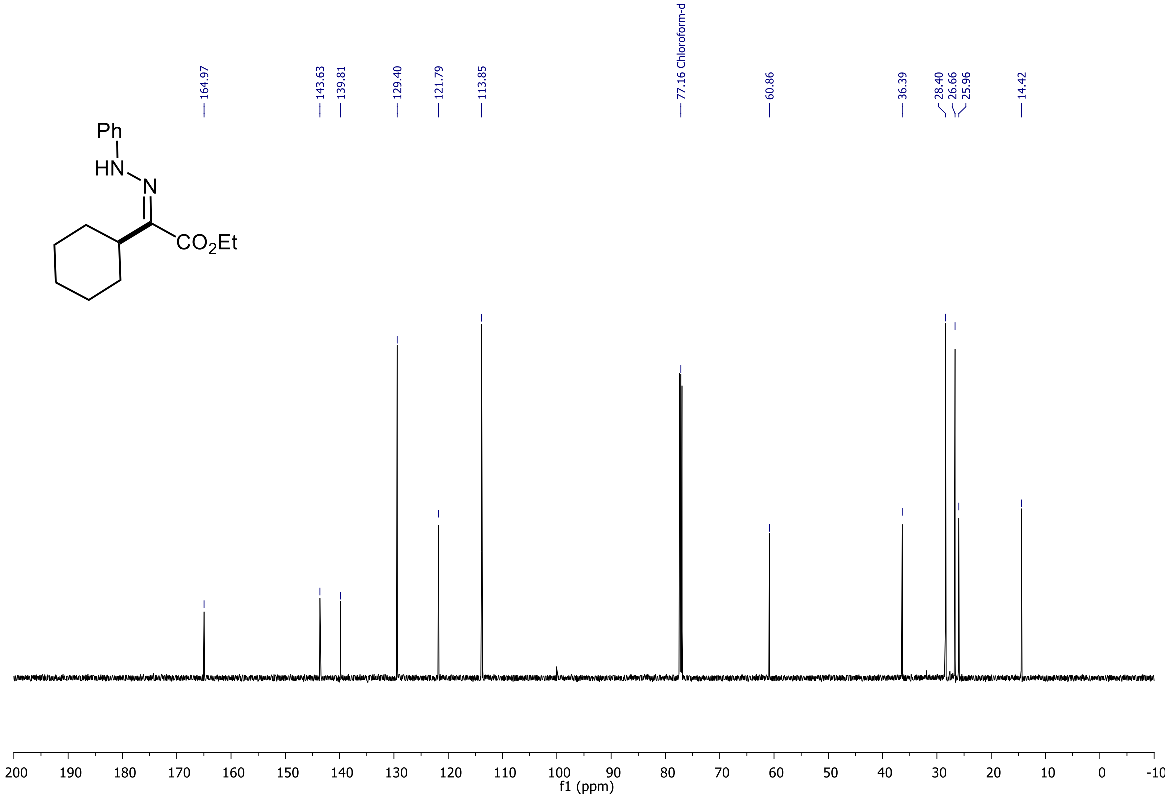
^{13}C NMR spectrum of **3u**



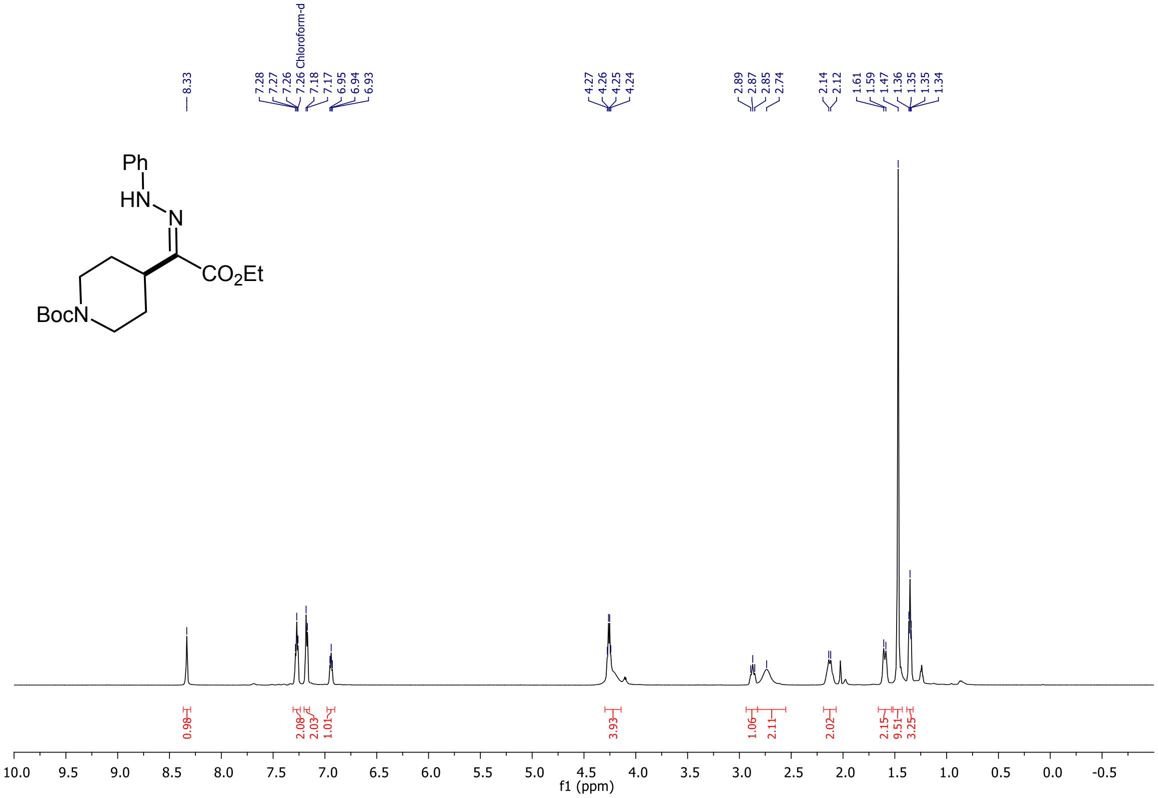
^{1}H NMR spectrum of **3v**



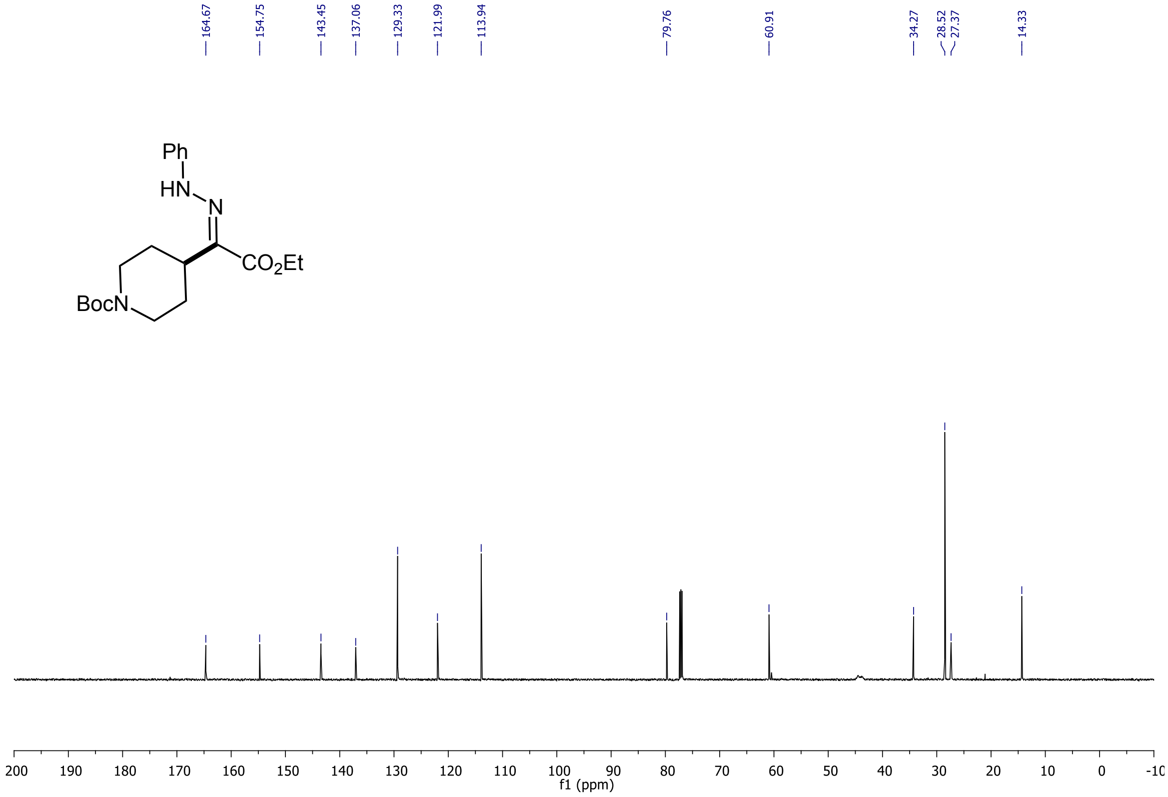
^{13}C NMR spectrum of **3v**



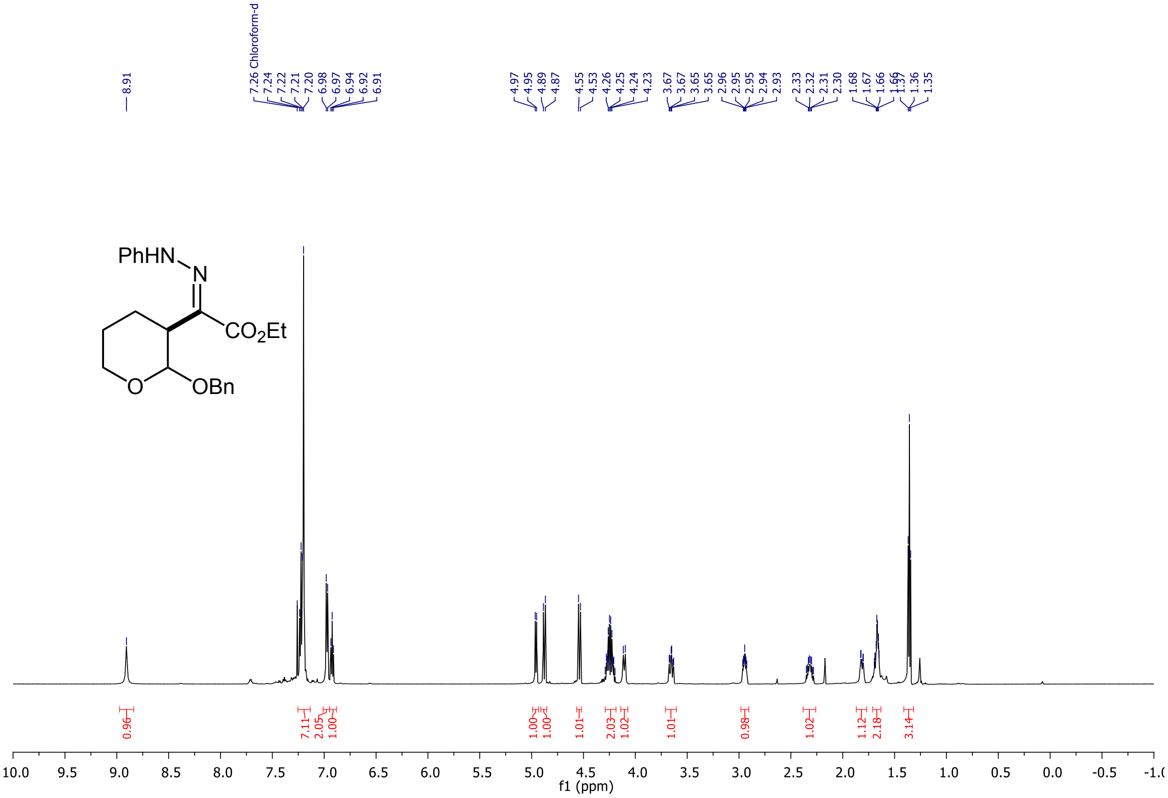
^{1}H NMR spectrum of **3w**



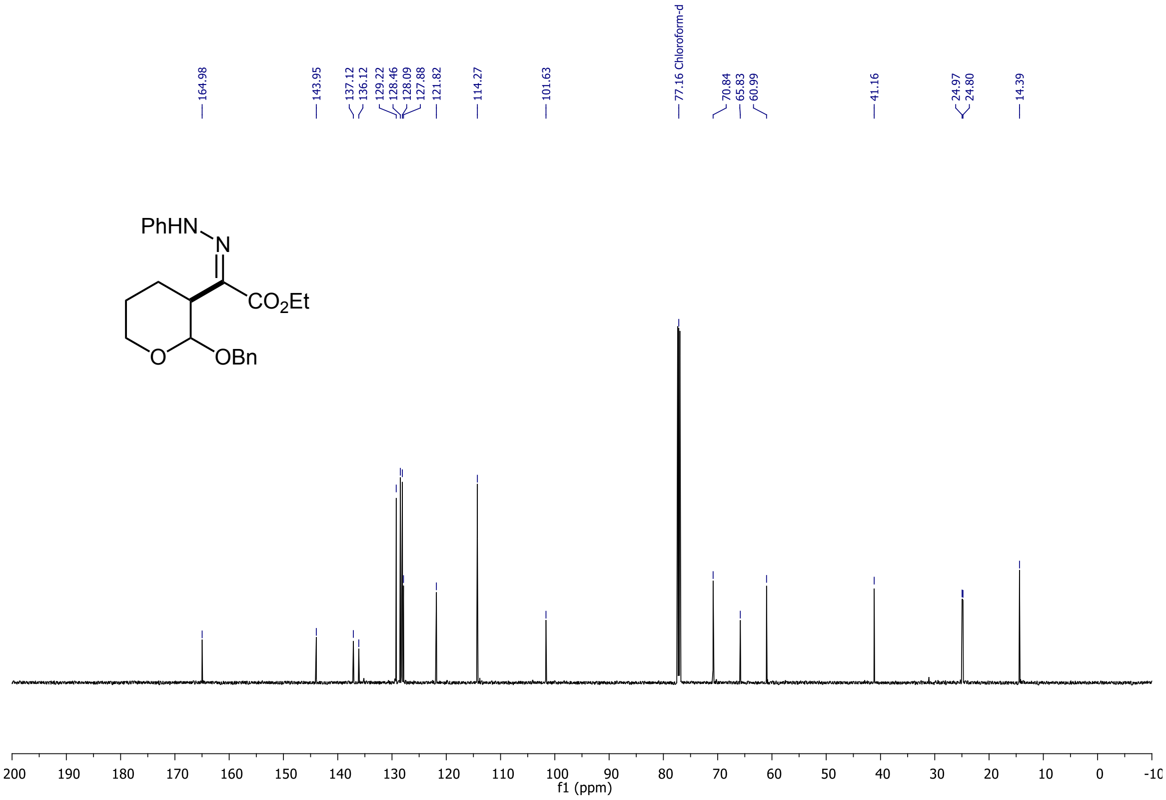
^{13}C NMR spectrum of **3w**



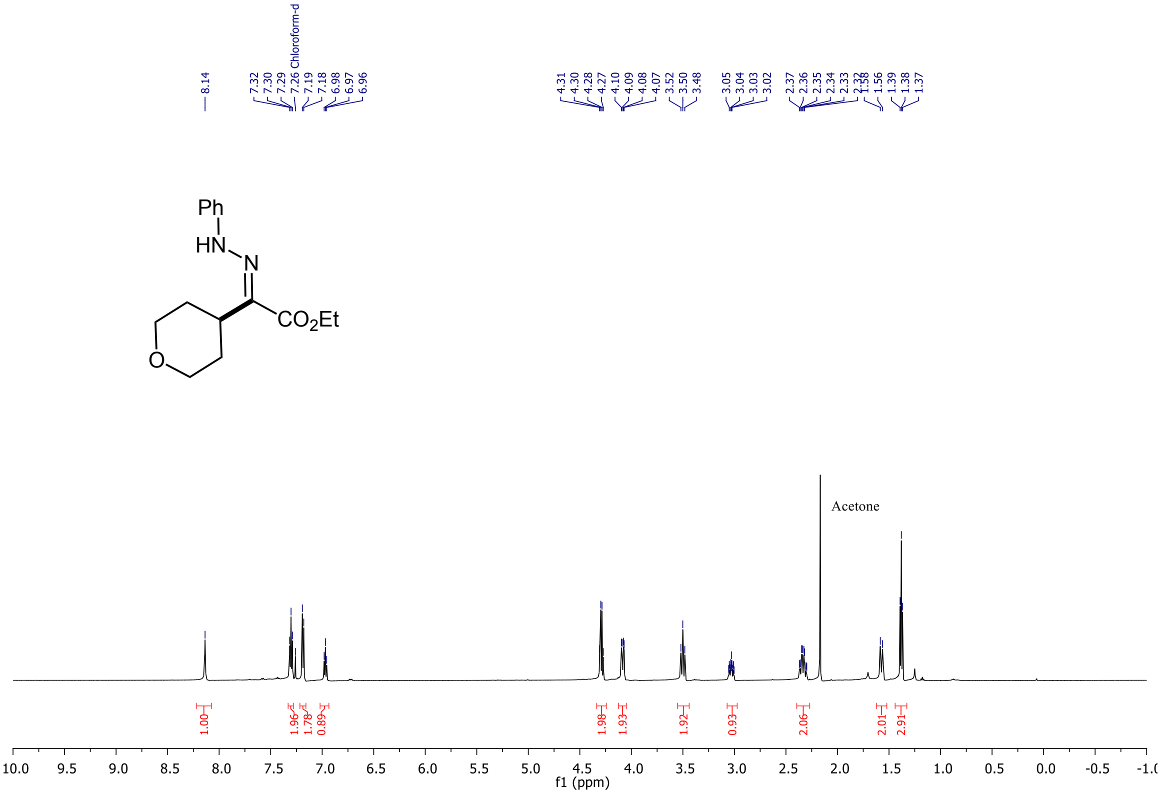
^{1}H NMR spectrum of **3x**



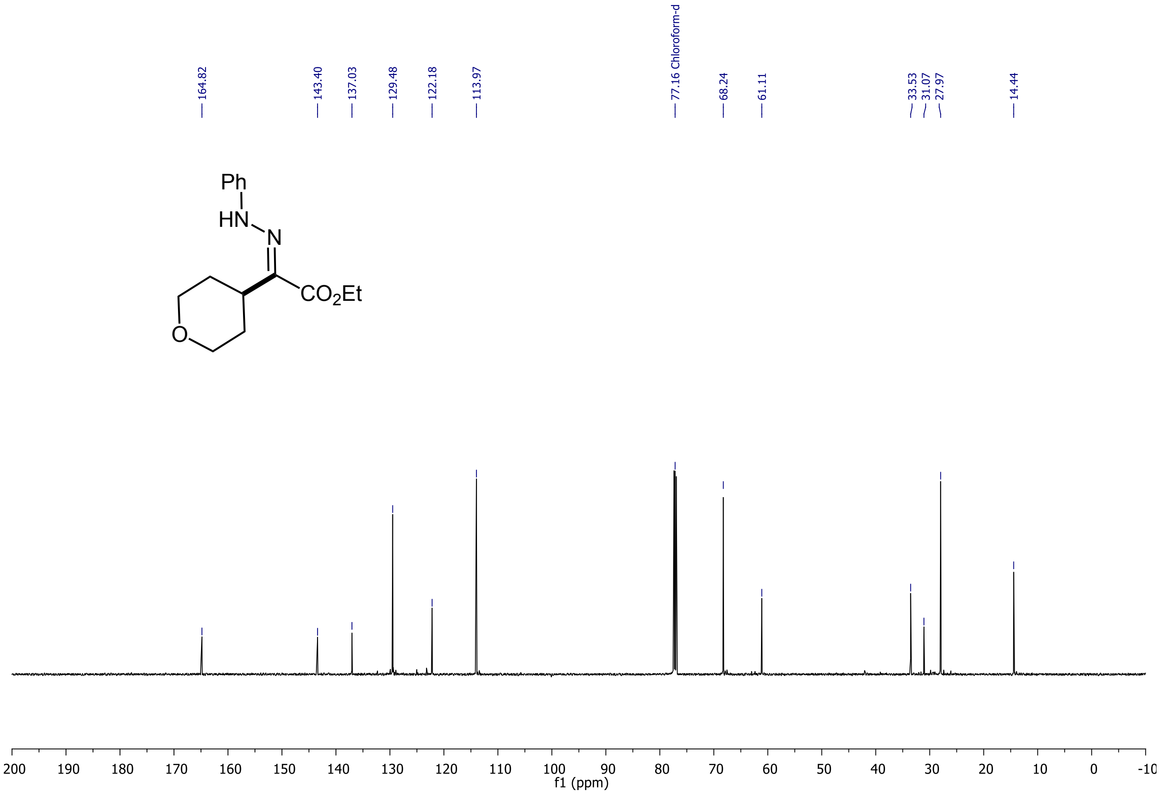
^{13}C NMR spectrum of **3x**



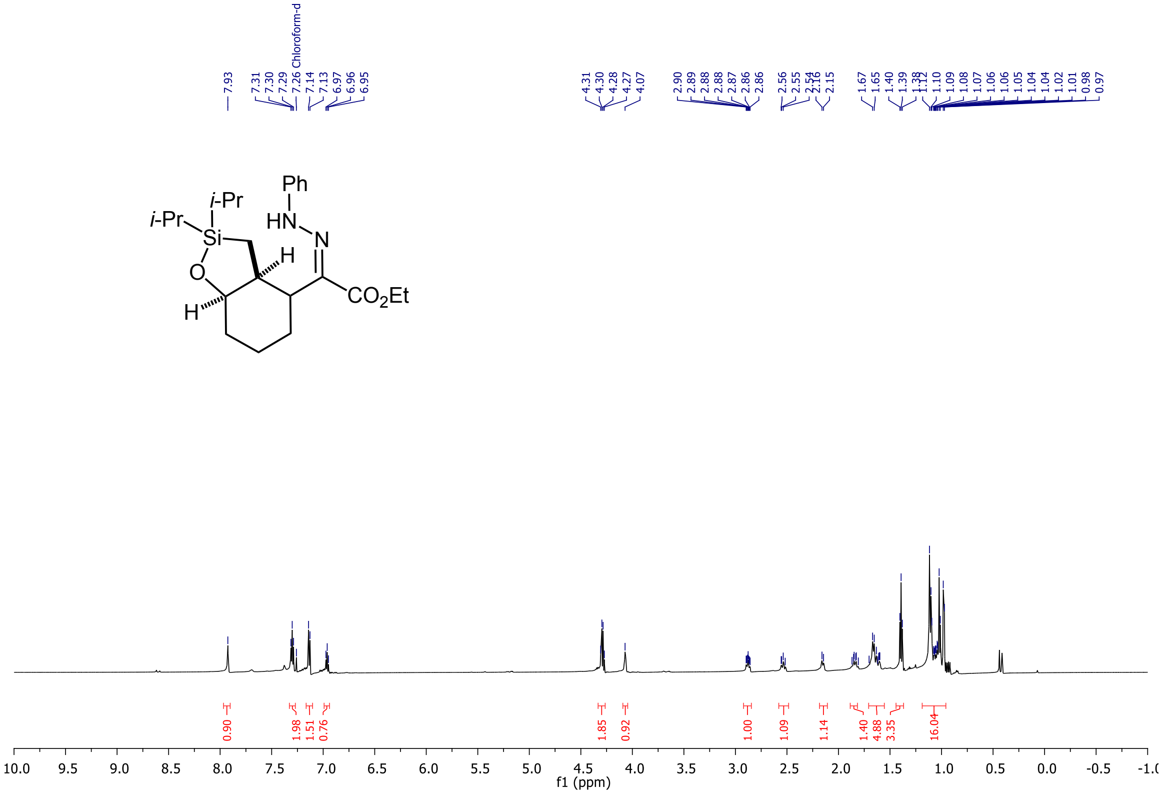
^{1}H NMR spectrum of **3z**



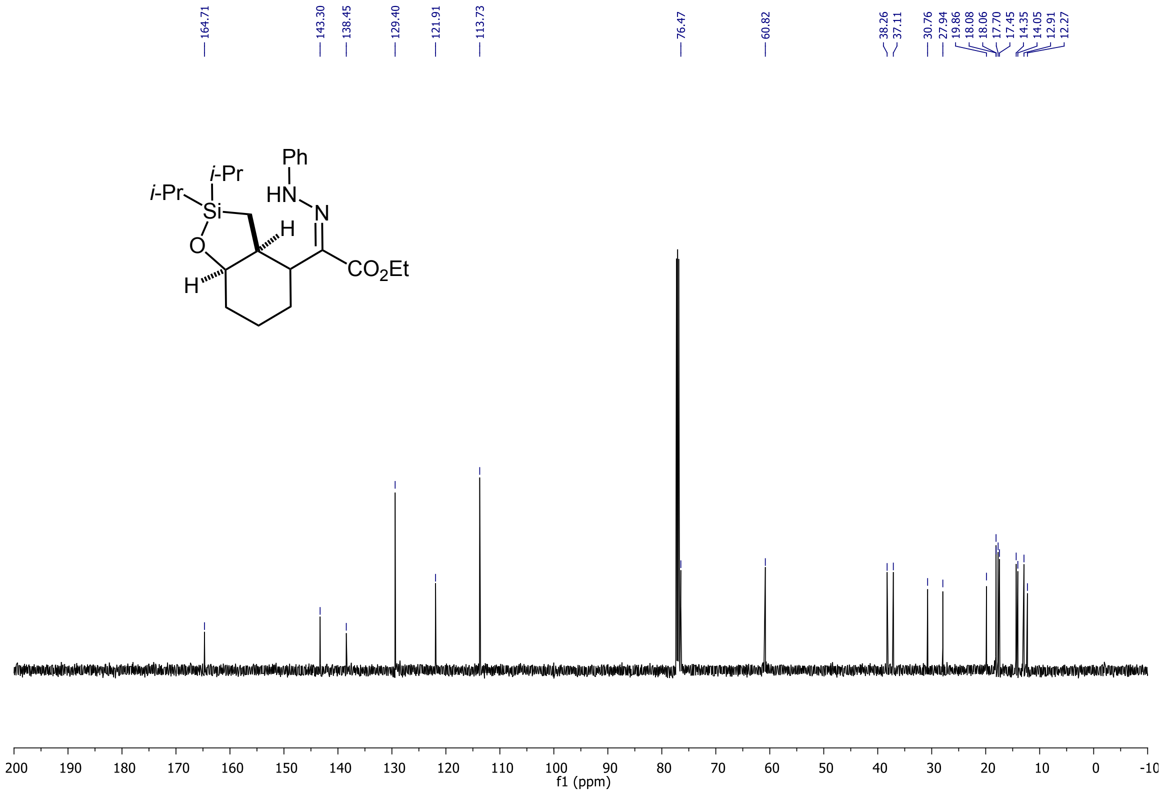
^{13}C NMR spectrum of **3z**



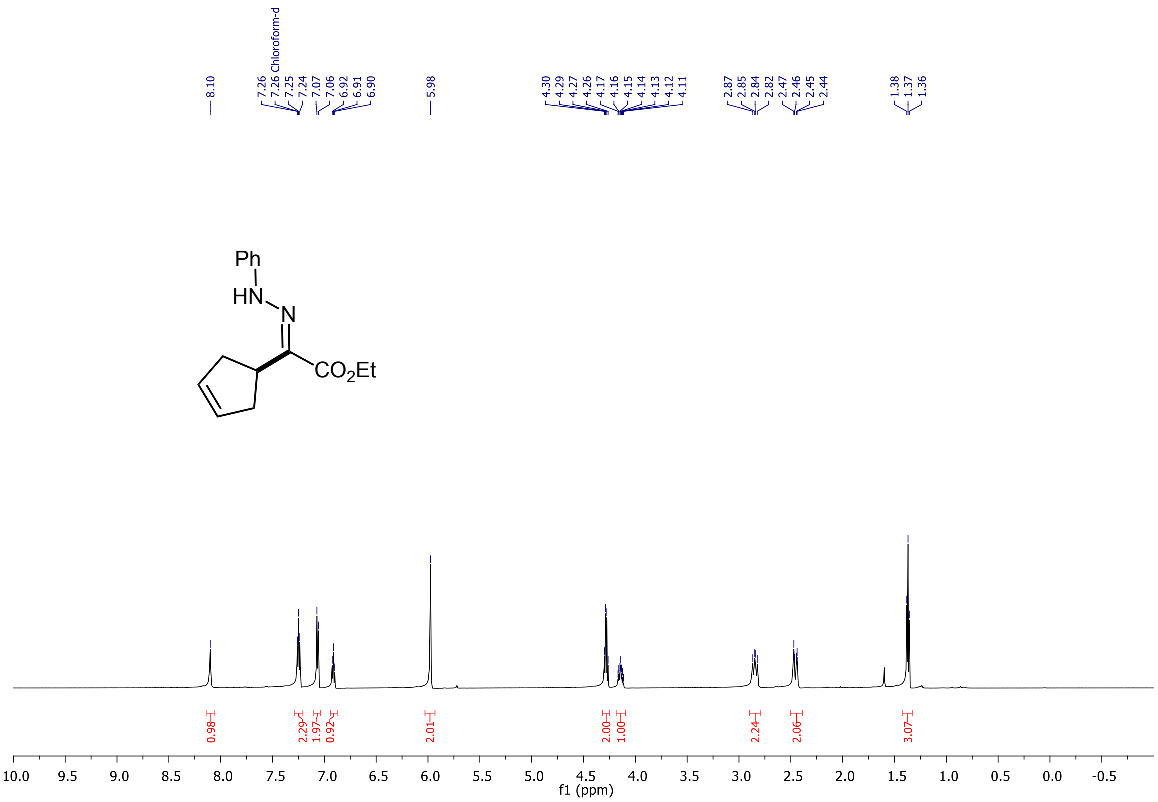
^{1}H NMR spectrum of **3aa**



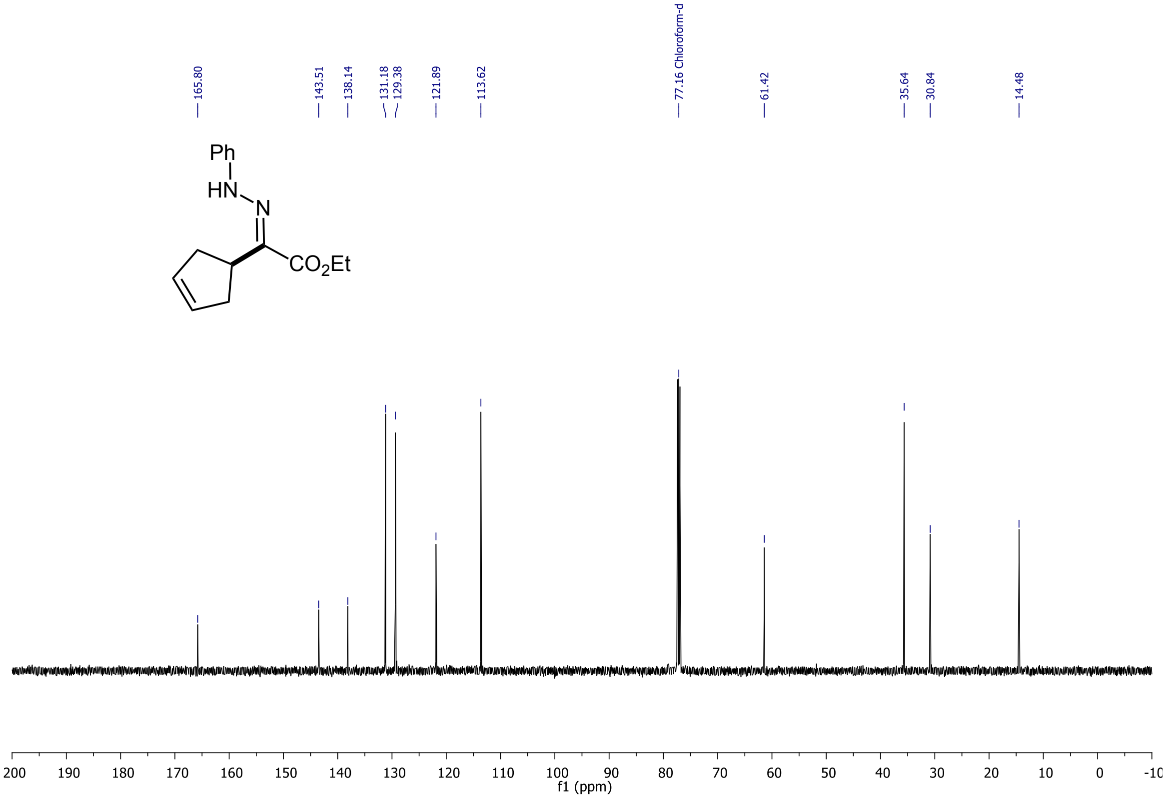
^{13}C NMR spectrum of **3aa**



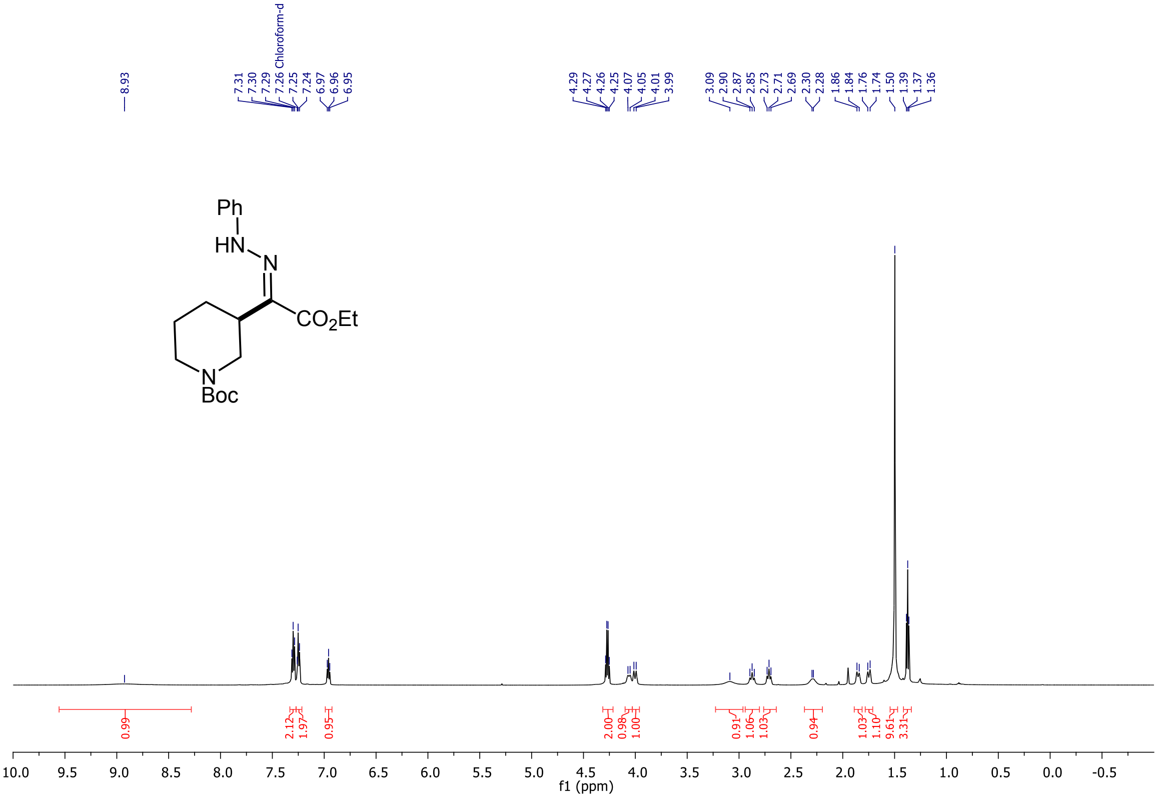
^{1}H NMR spectrum of **3ac**



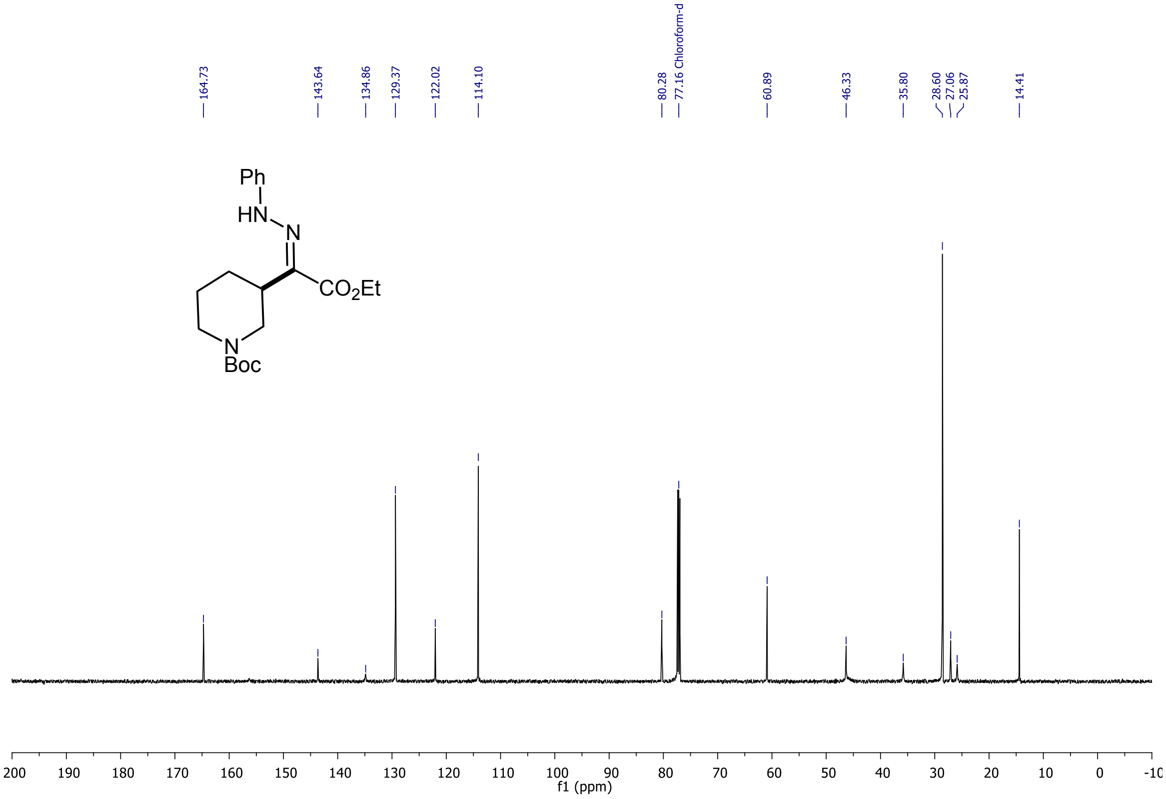
^{13}C NMR spectrum of **3ac**



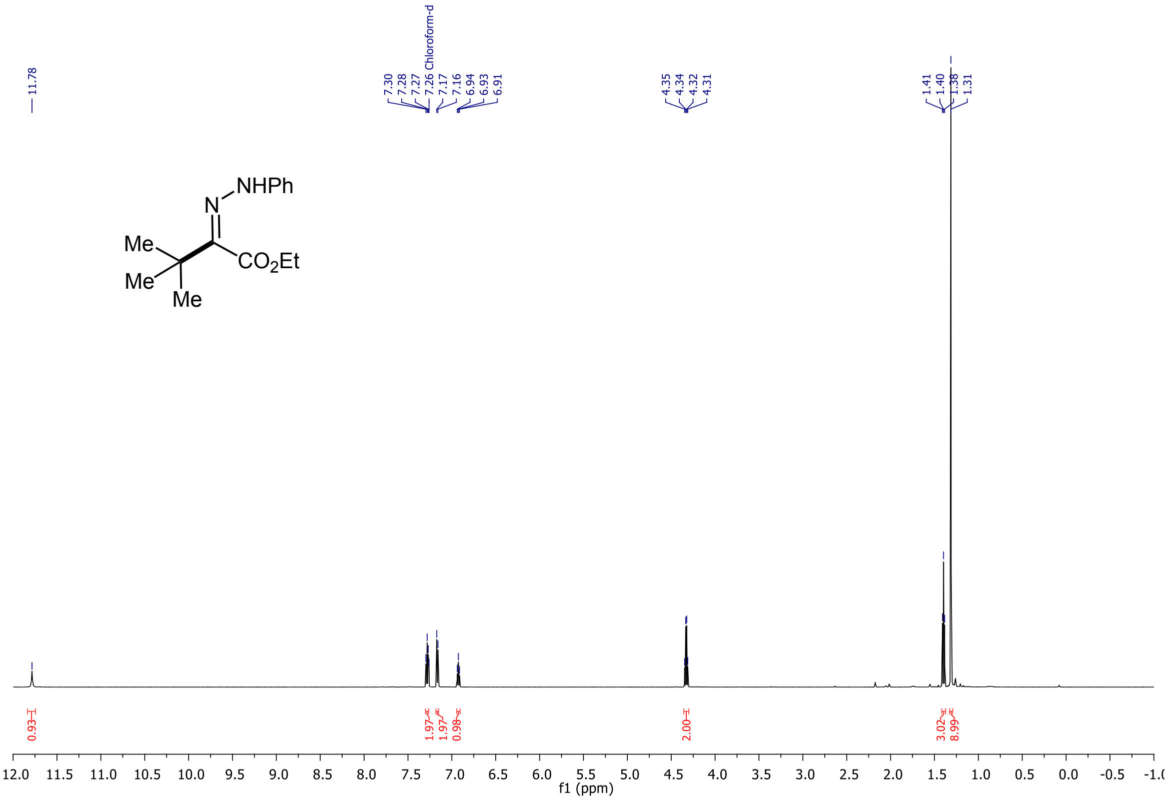
^{1}H NMR spectrum of **3ad**



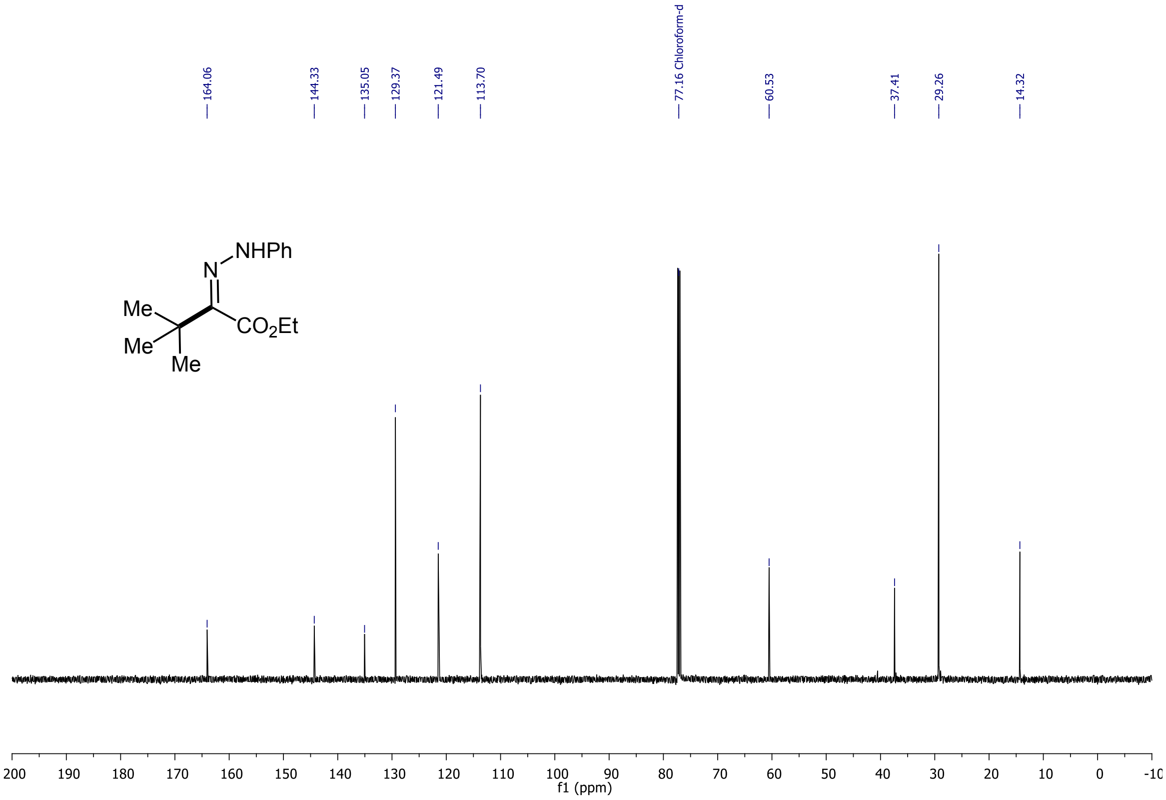
^{13}C NMR spectrum of **3ad**



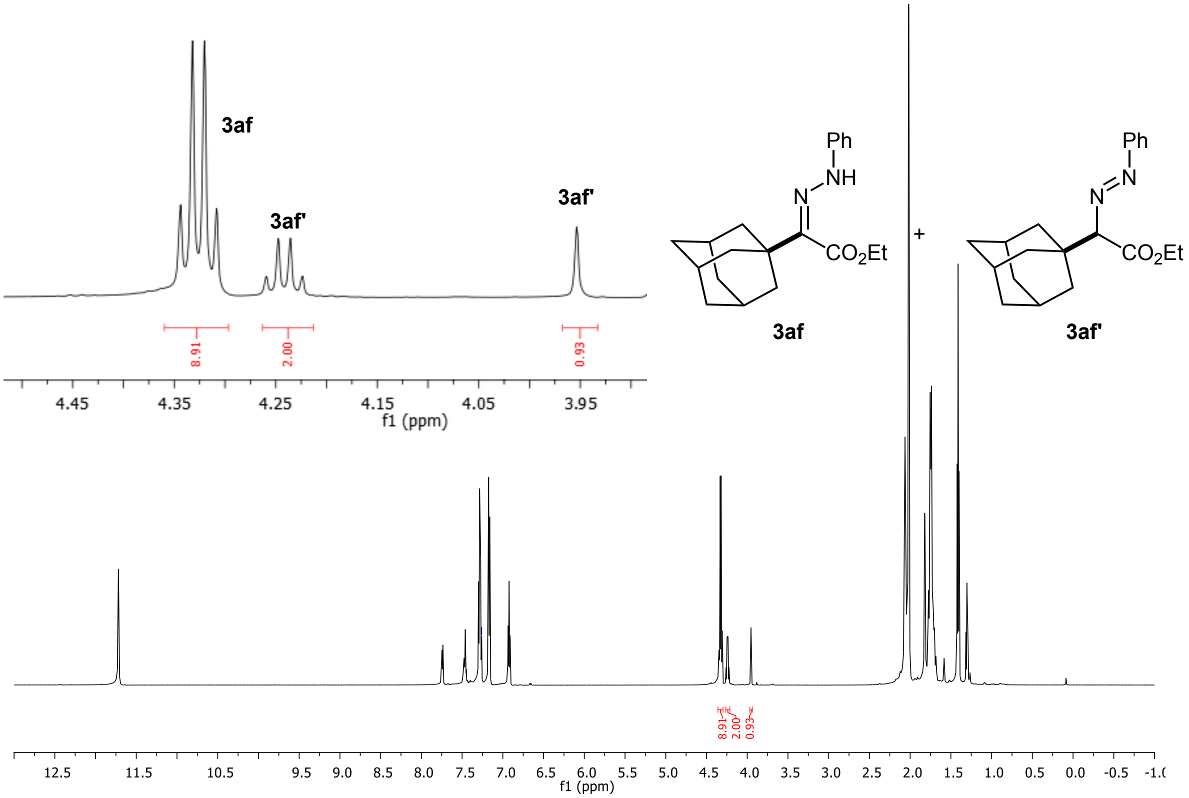
^{1}H NMR spectrum of **3ae**



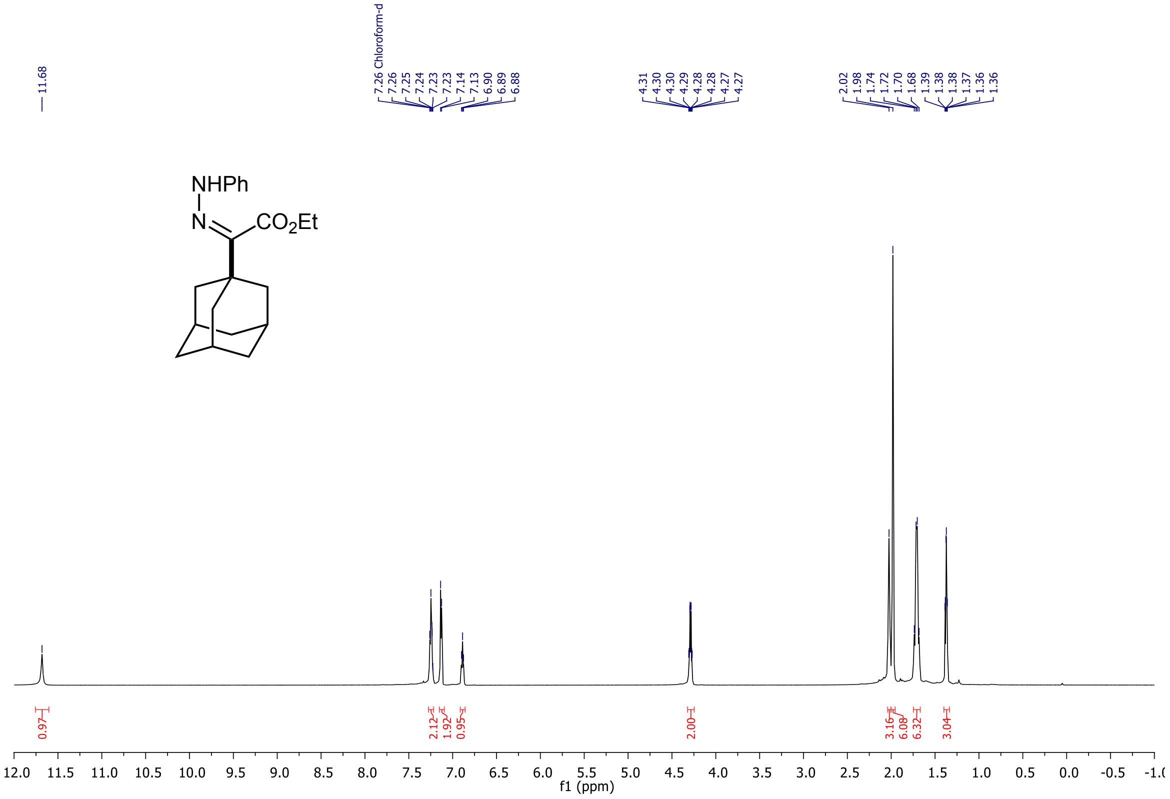
^{13}C NMR spectrum of **3ae**



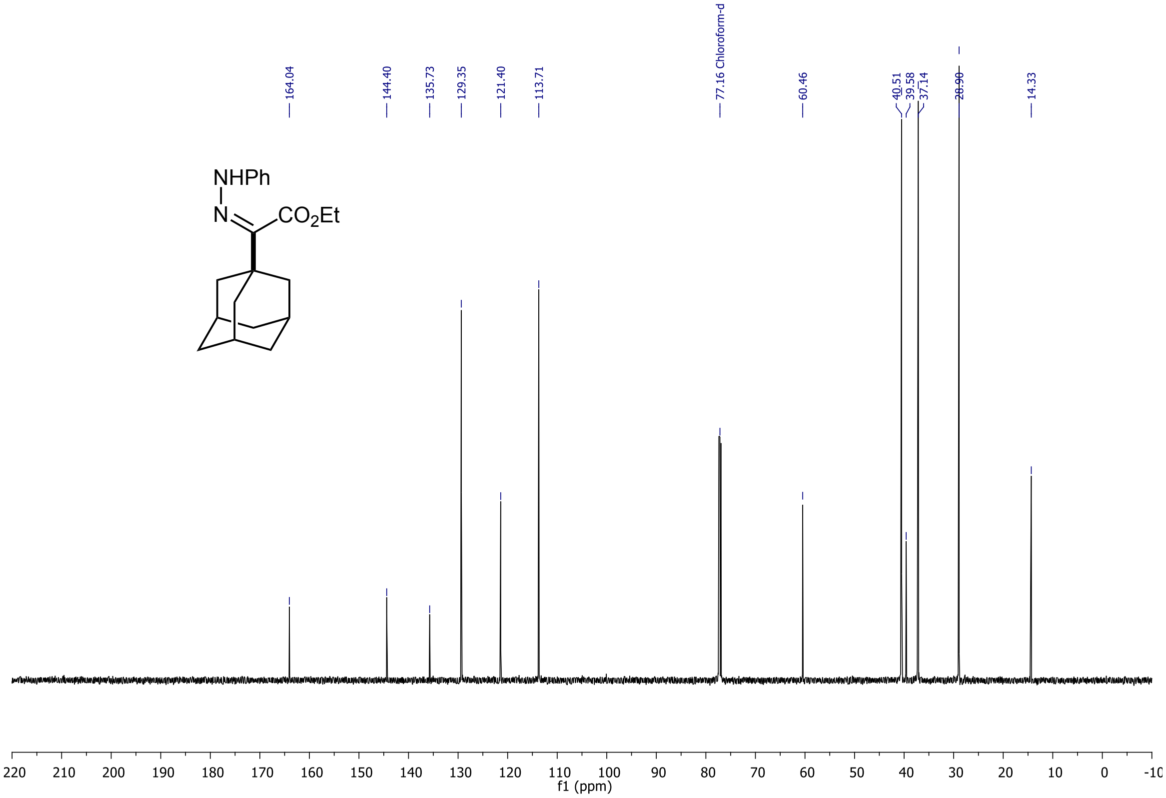
^{1}H NMR spectrum of **3af+3af'**



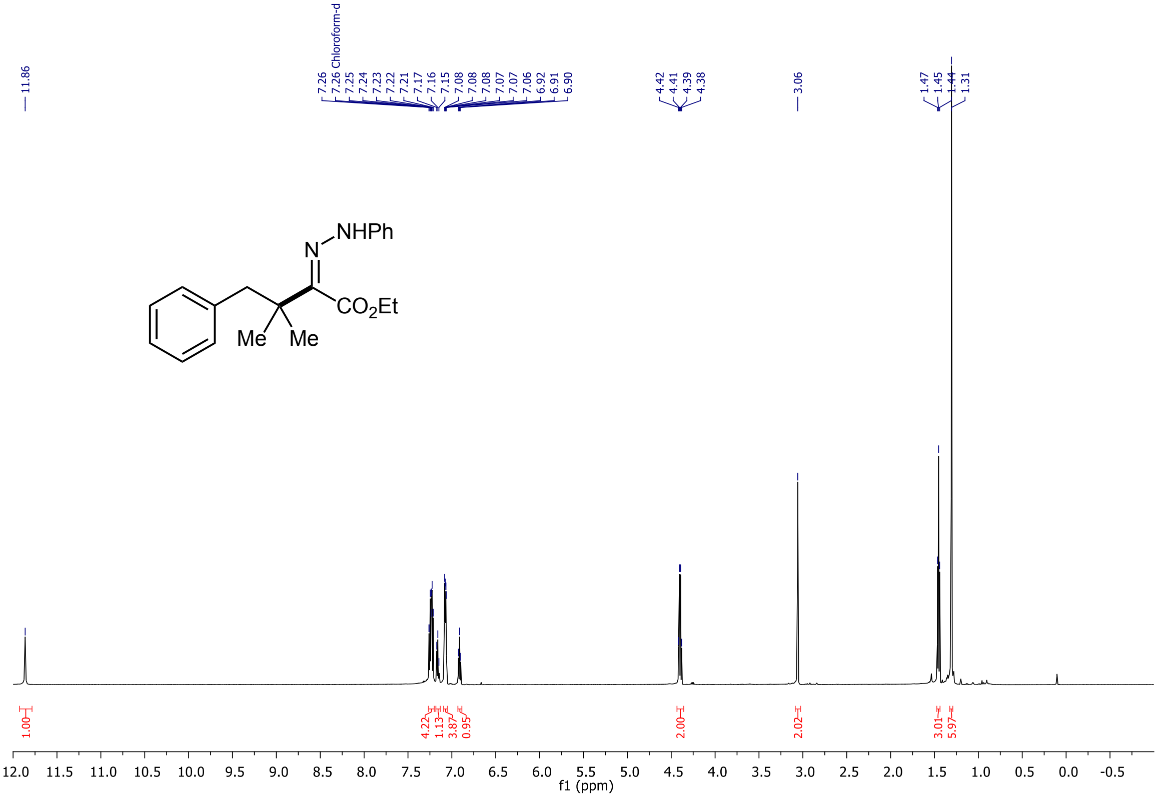
^{1}H NMR spectrum of **3af**



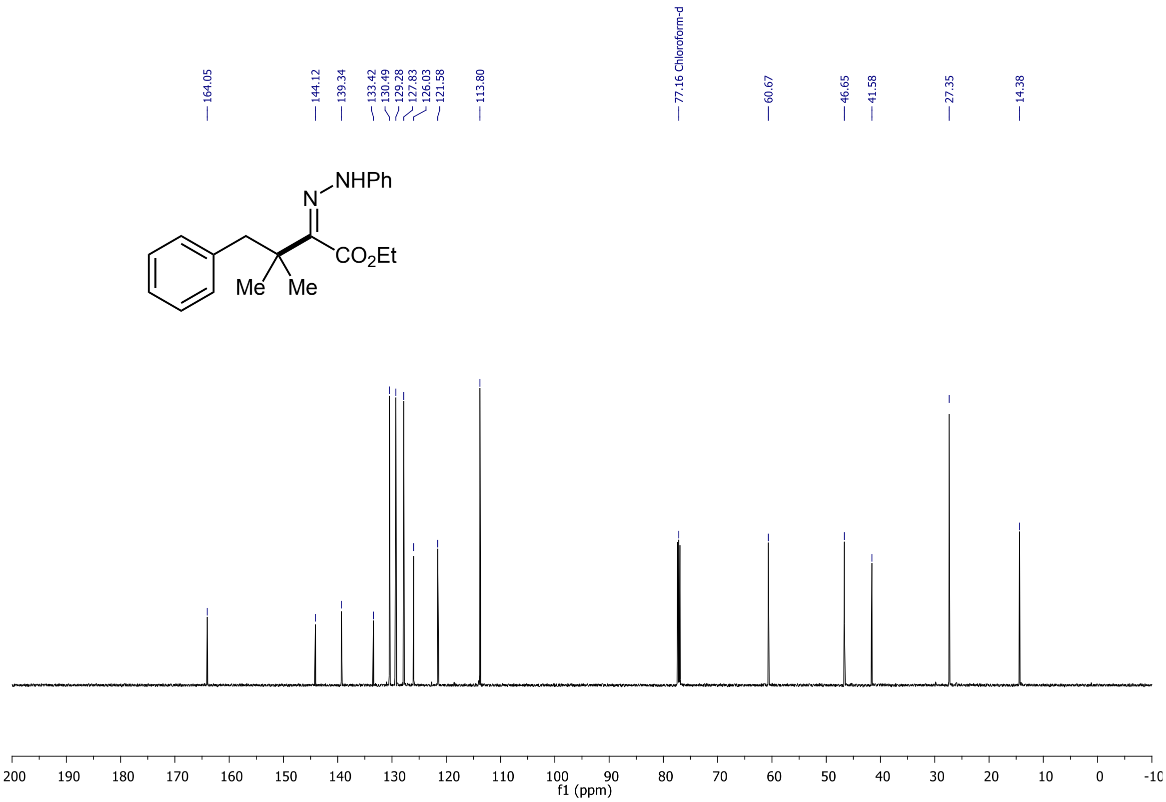
^{13}C NMR spectrum of **3af**



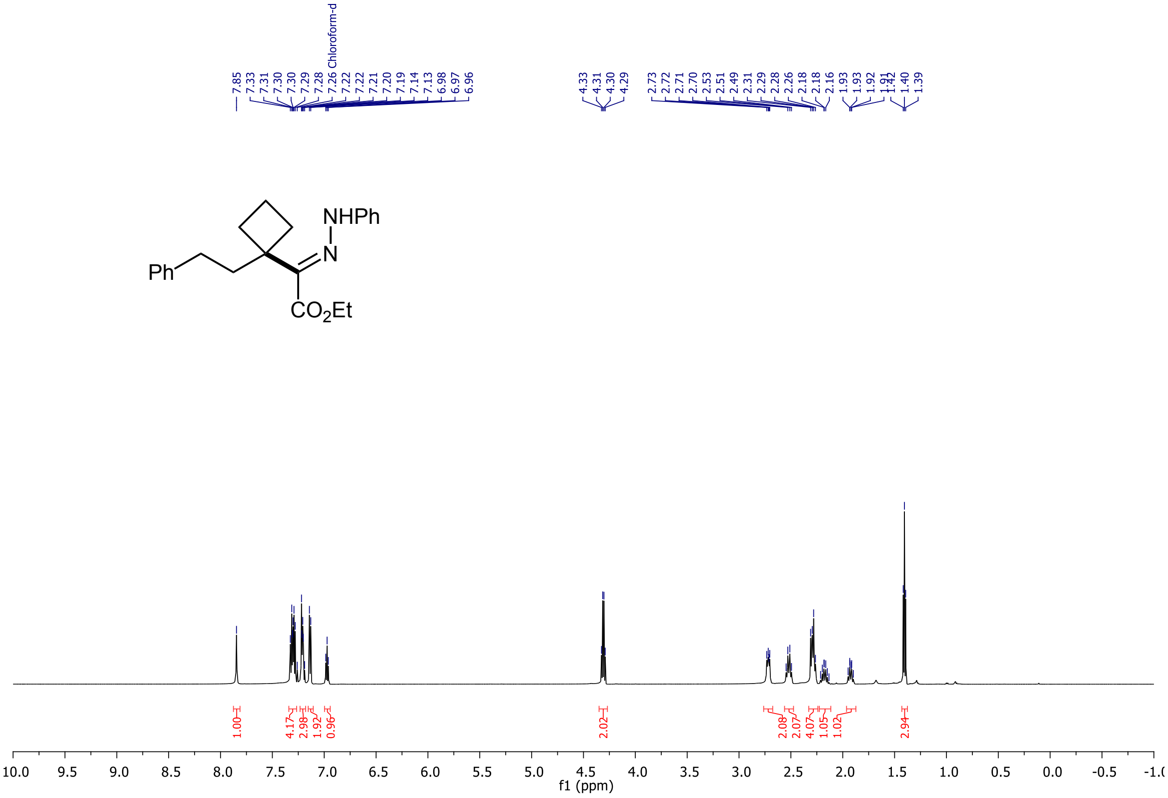
^{1}H NMR spectrum of **3ag**



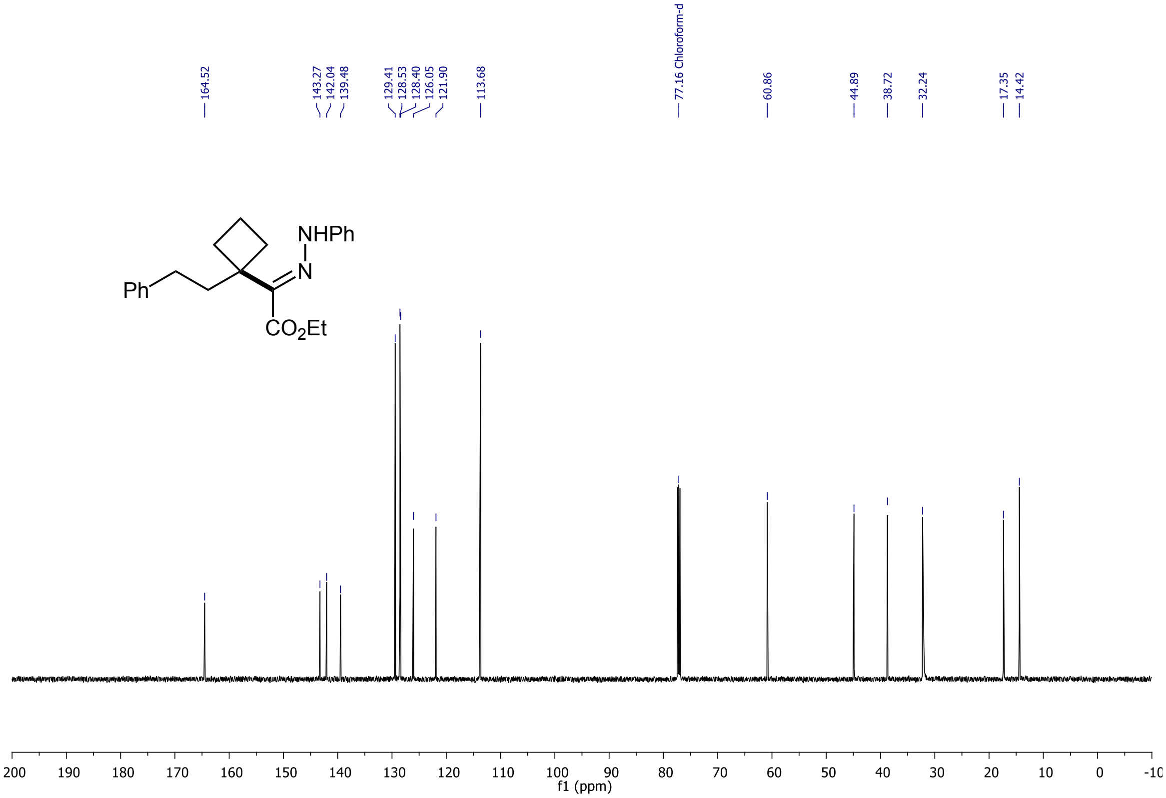
^{13}C NMR spectrum of **3ag**



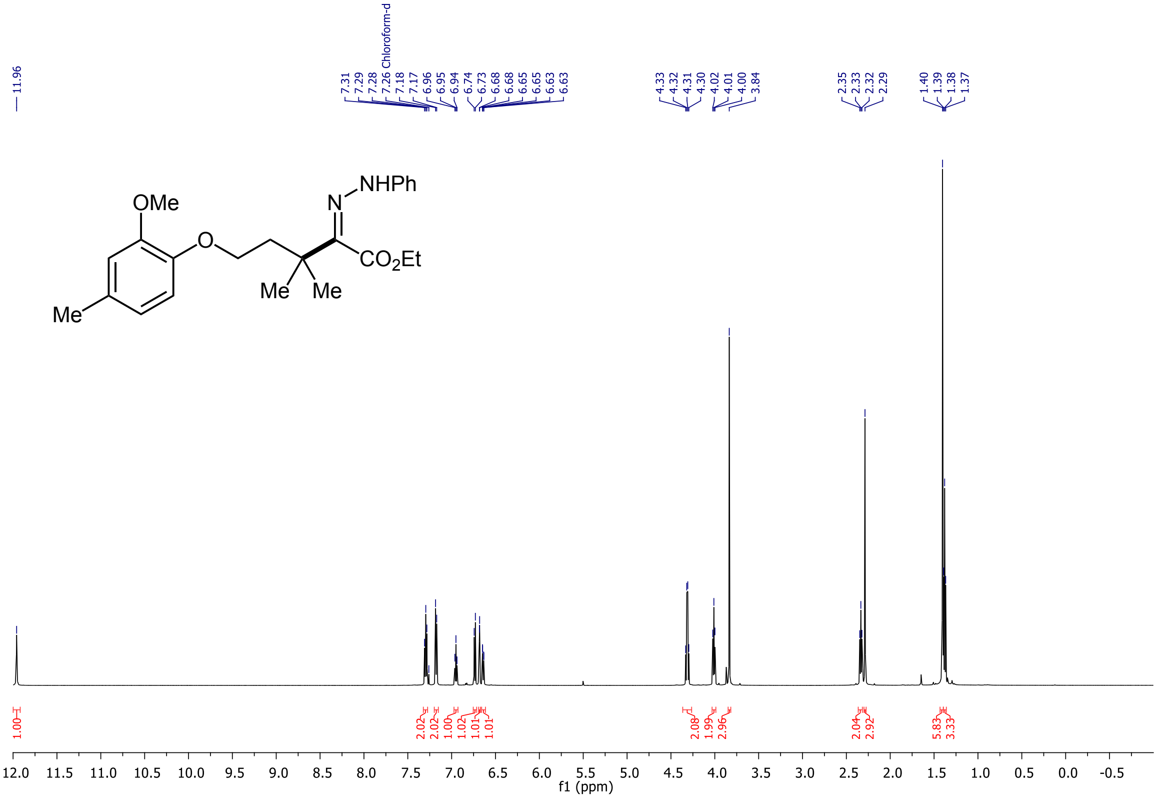
^{1}H NMR spectrum of **3ah**



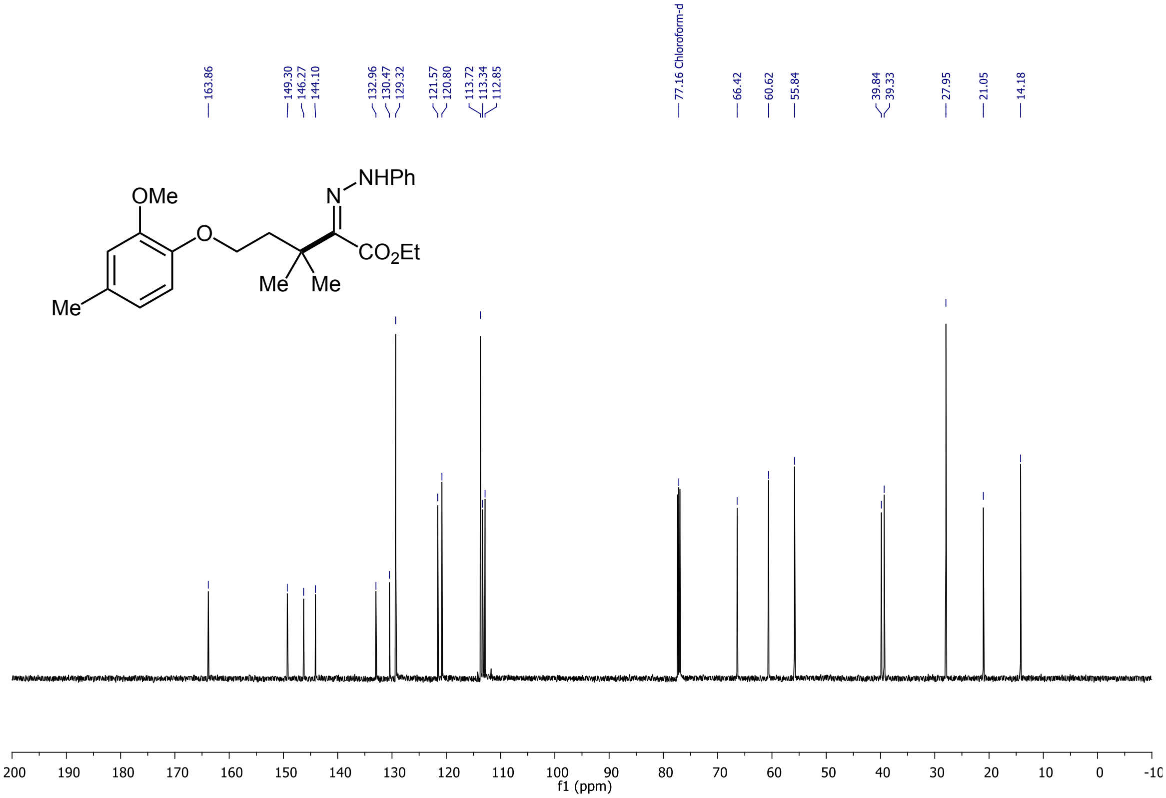
^{13}C NMR spectrum of **3ah**



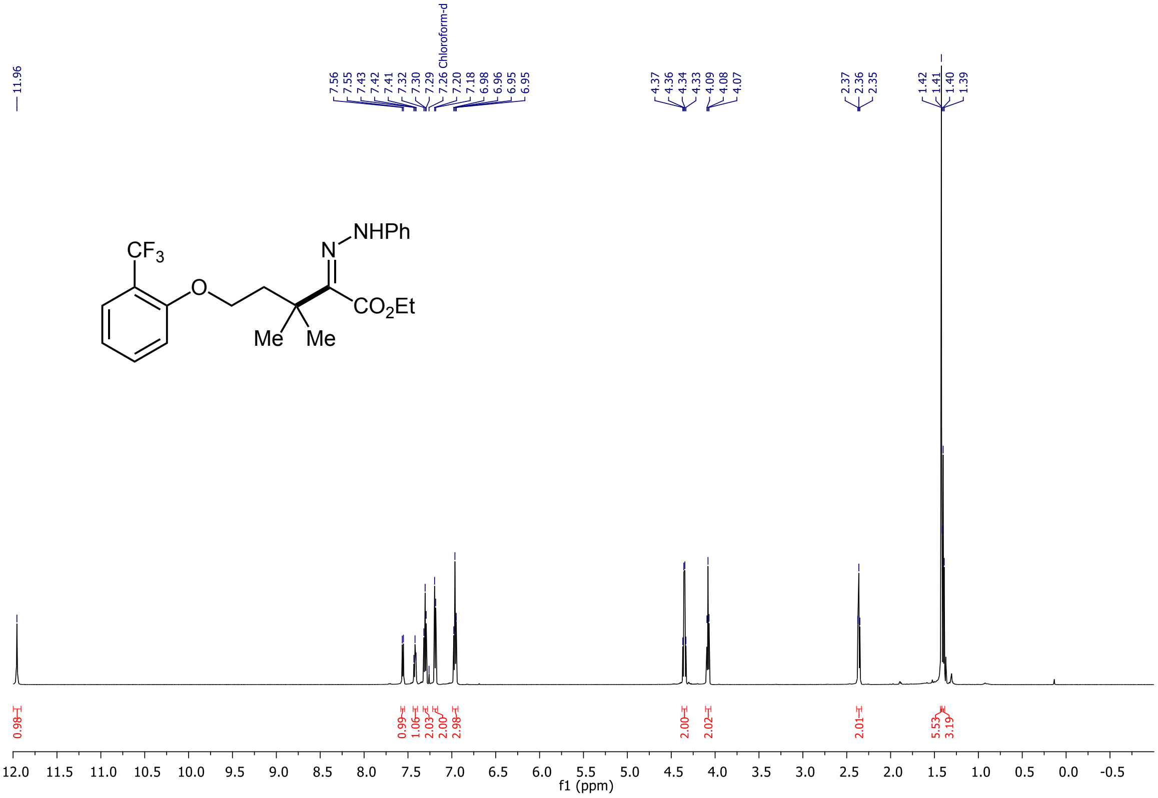
^{1}H NMR spectrum of **3ai**



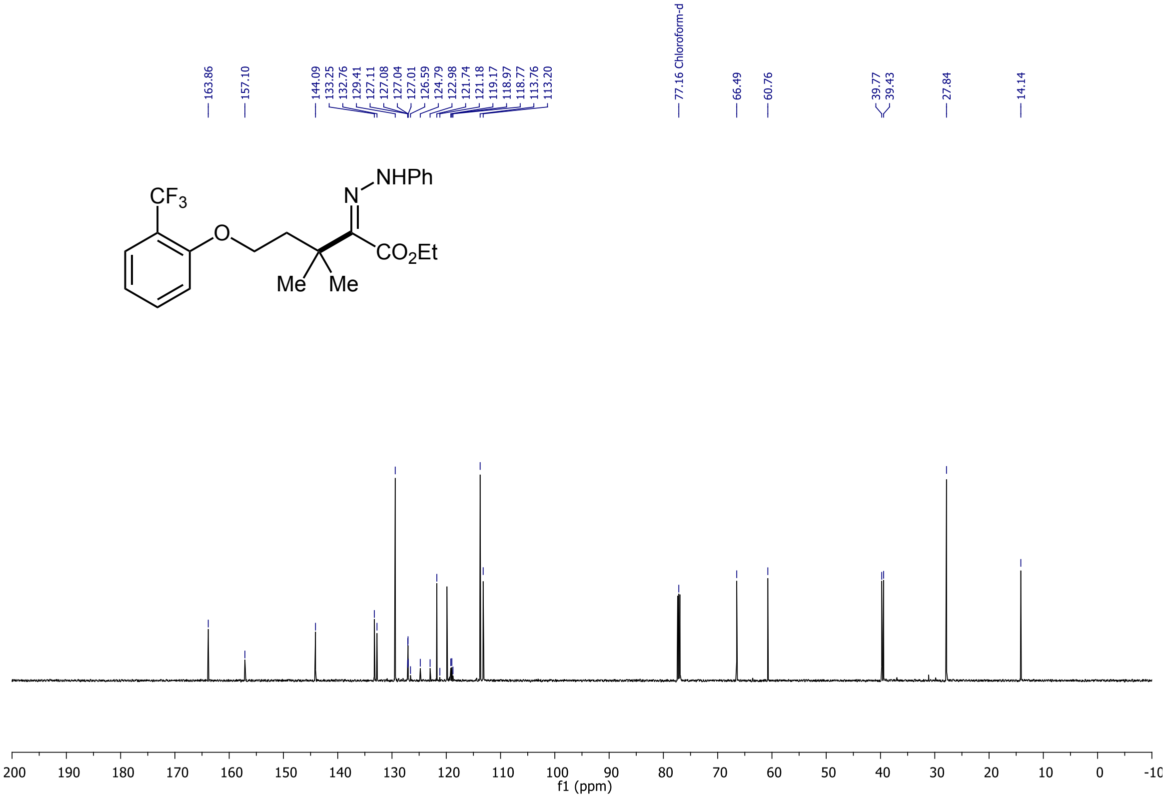
^{13}C NMR spectrum of **3ai**



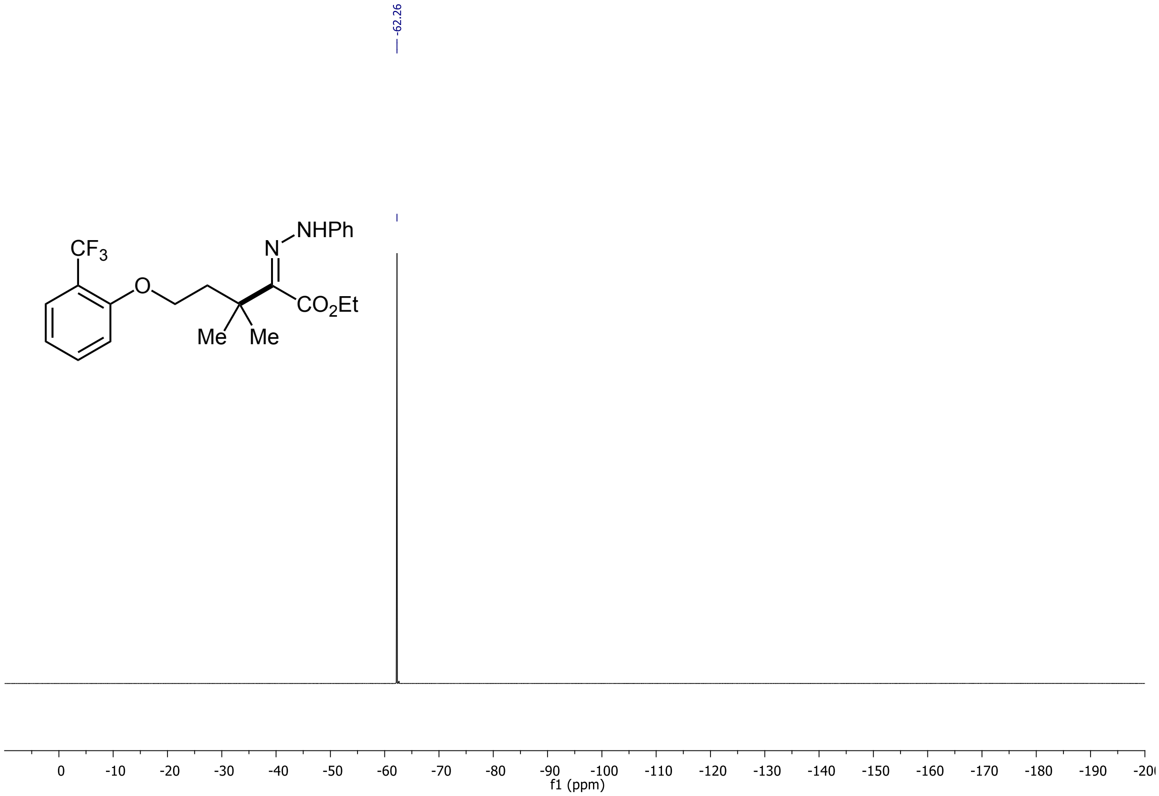
^{1}H NMR spectrum of **3aj**



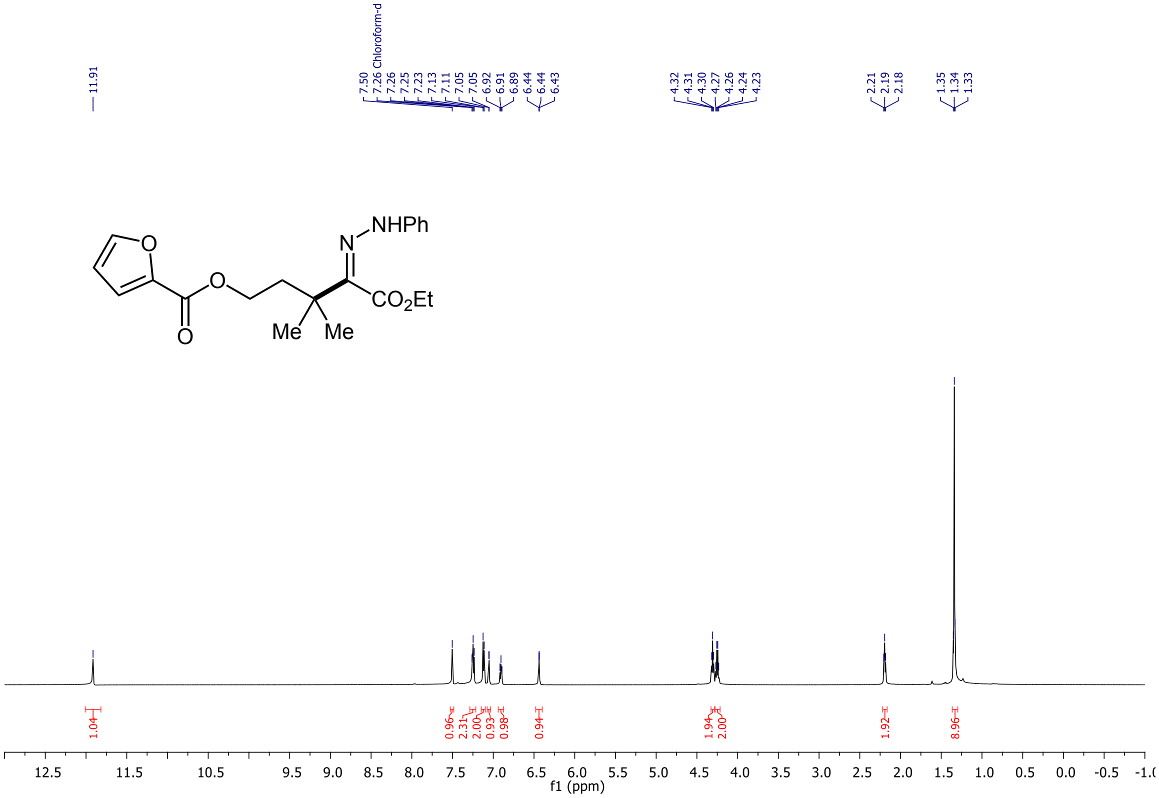
^{13}C NMR spectrum of **3aj**



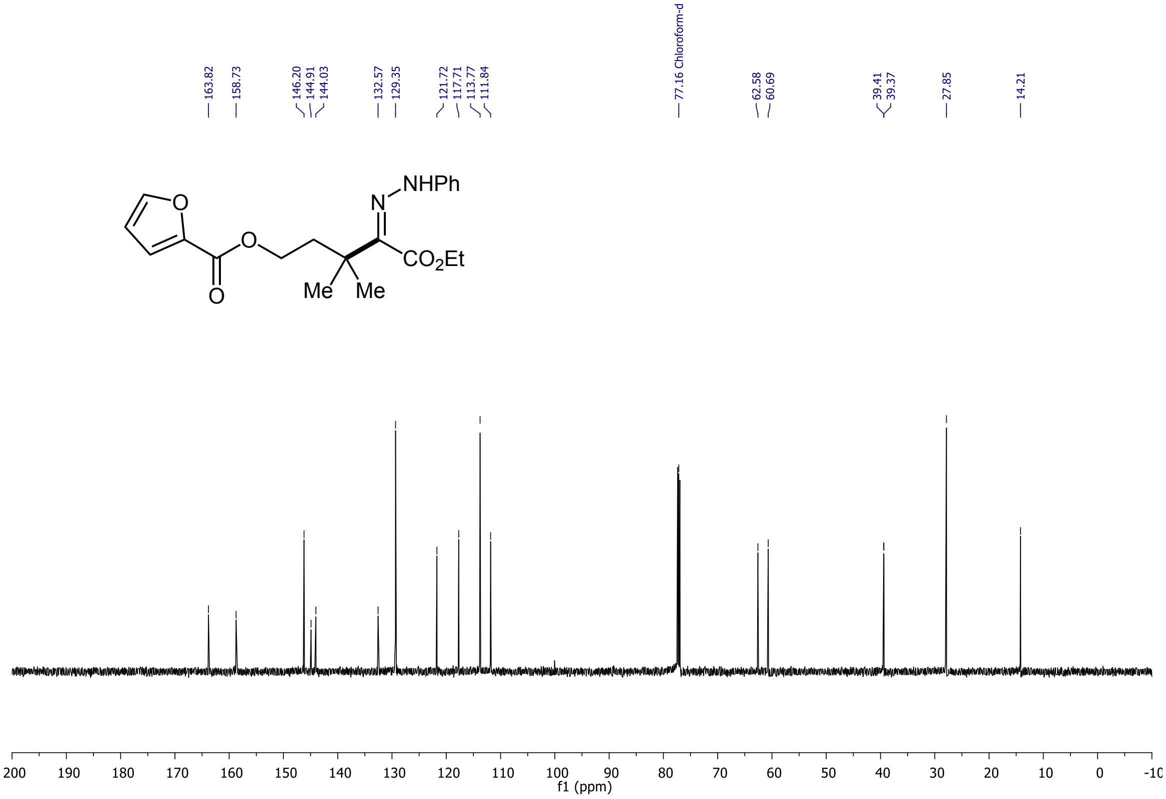
^{19}F NMR spectrum of **3aj**



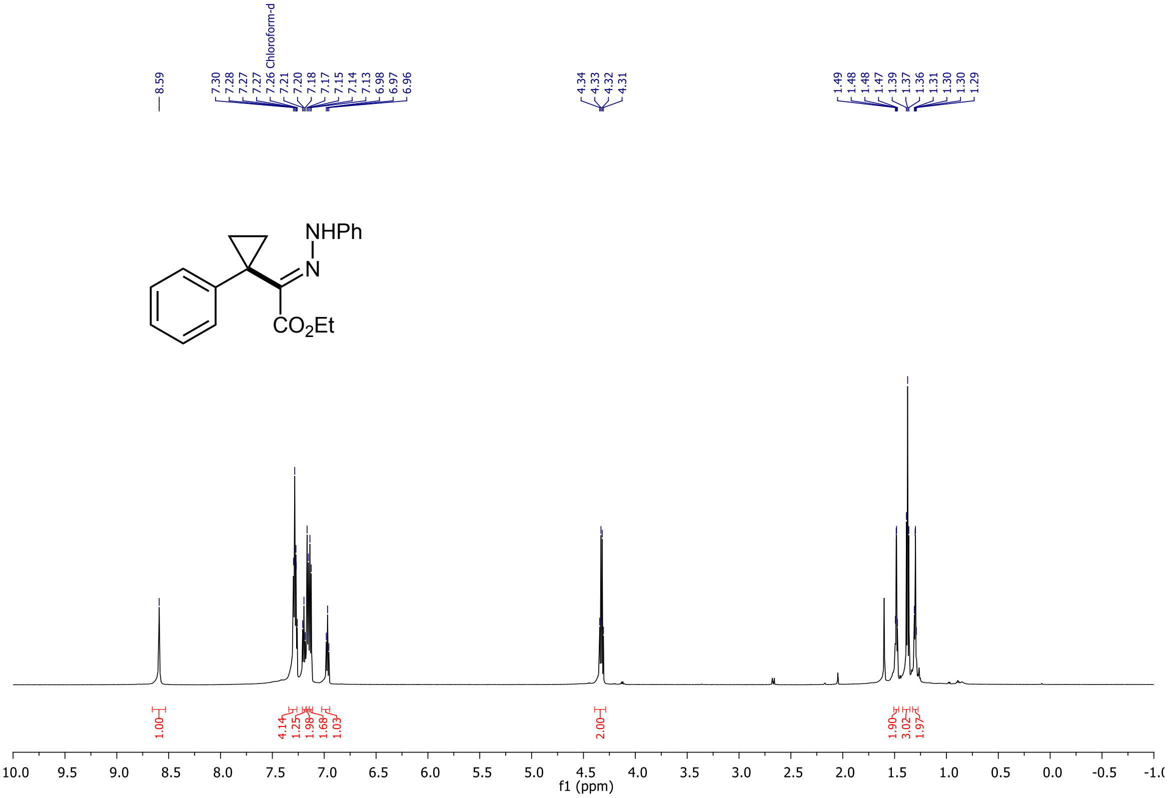
^{1}H NMR spectrum of **3ak**



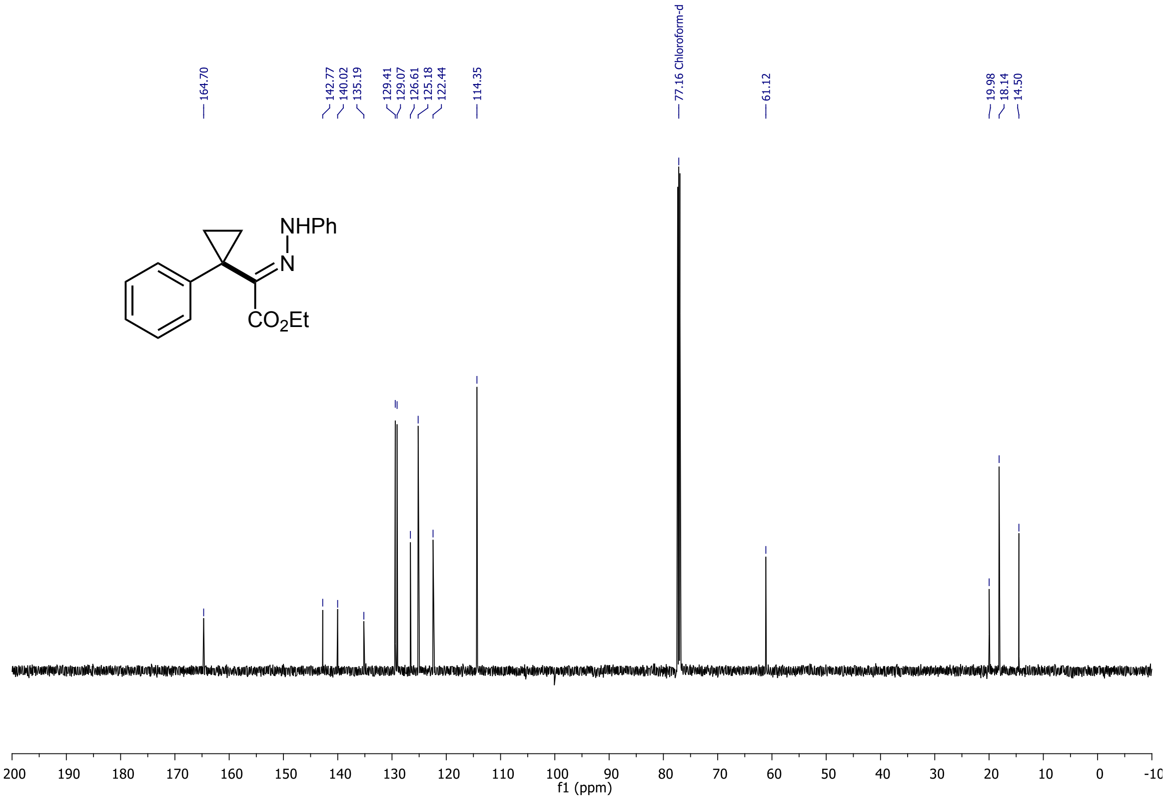
^{13}C NMR spectrum of **3ak**



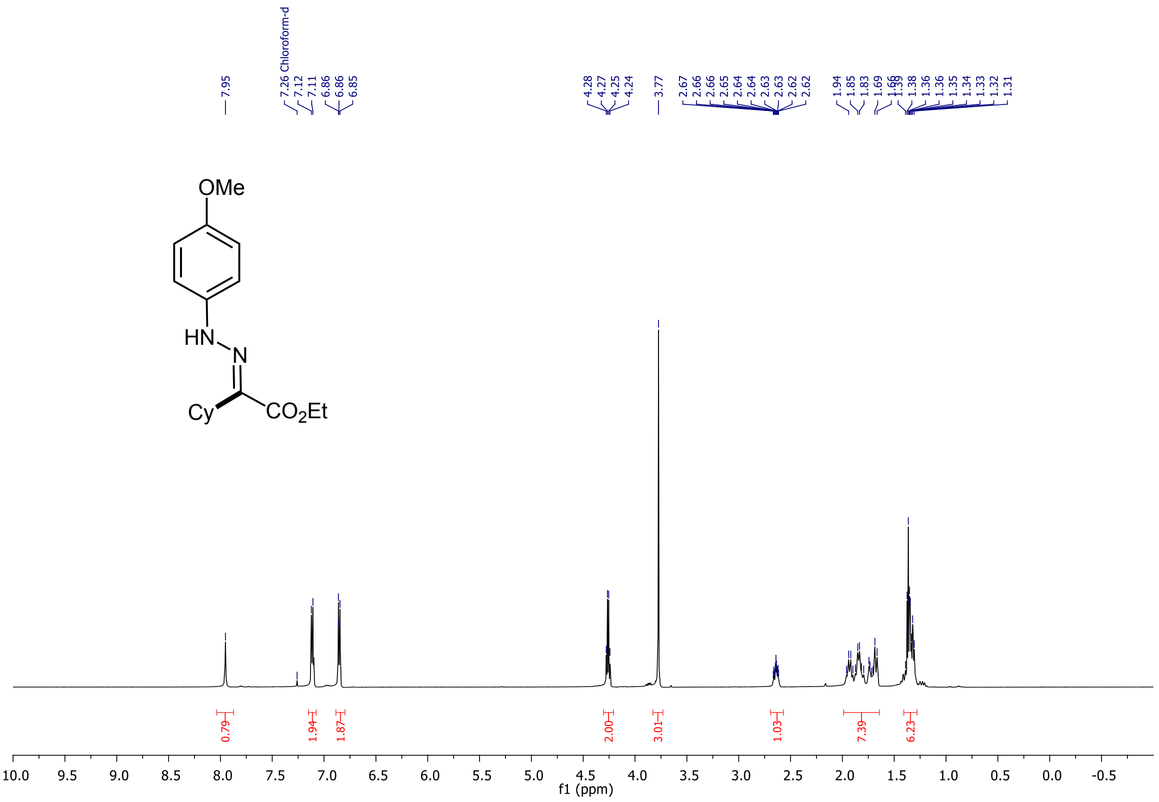
^{1}H NMR spectrum of **3an**



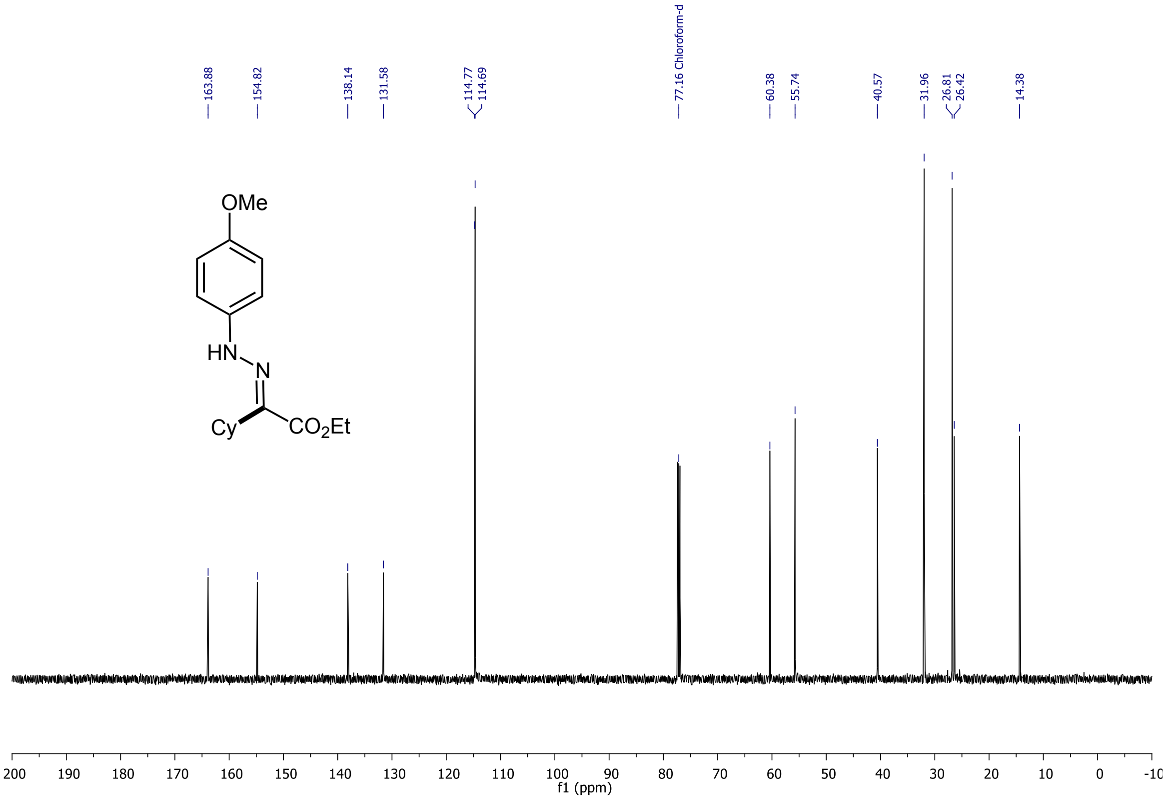
^{13}C NMR spectrum of **3an**



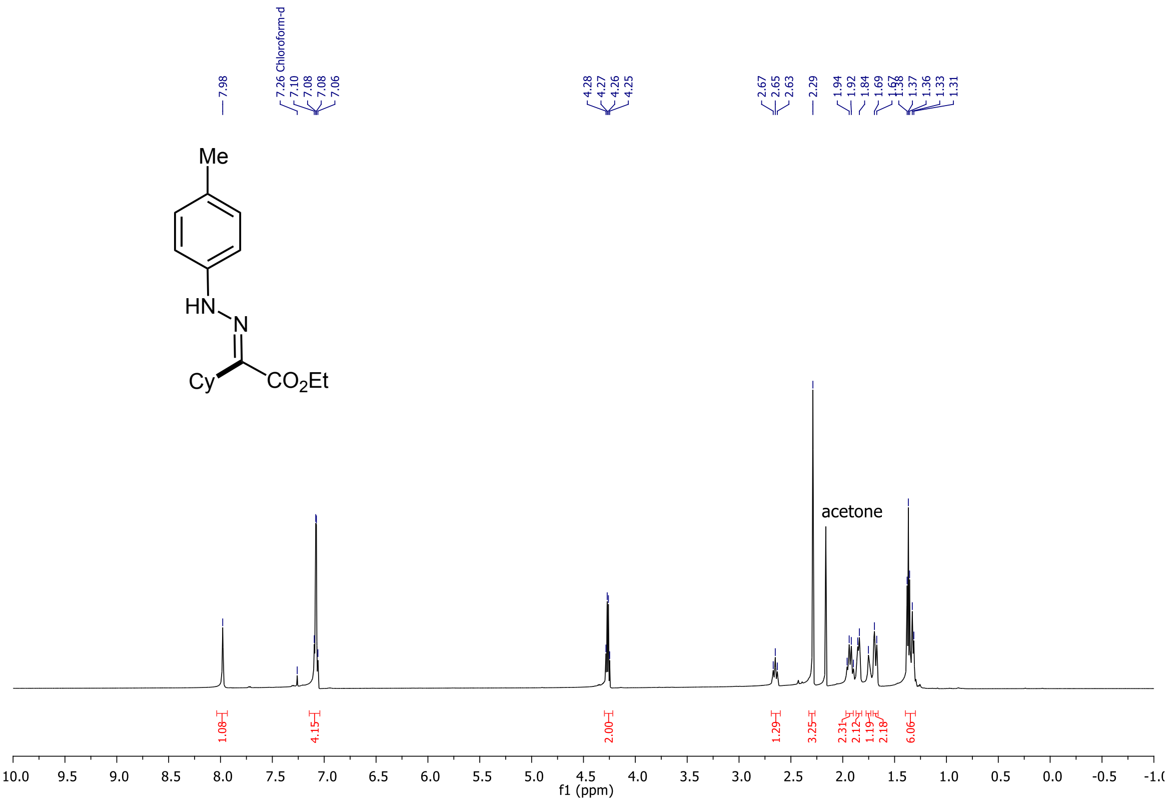
^{1}H NMR spectrum of **3ao**



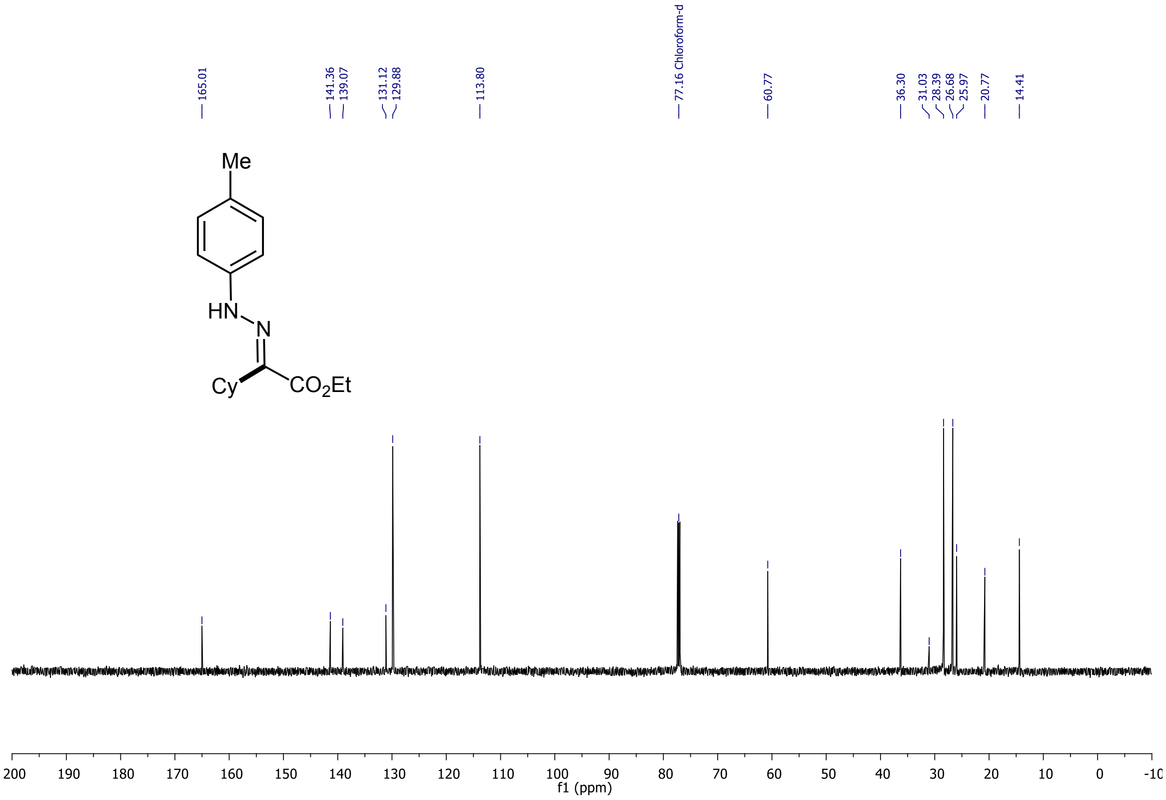
^{13}C NMR spectrum of **3ao**



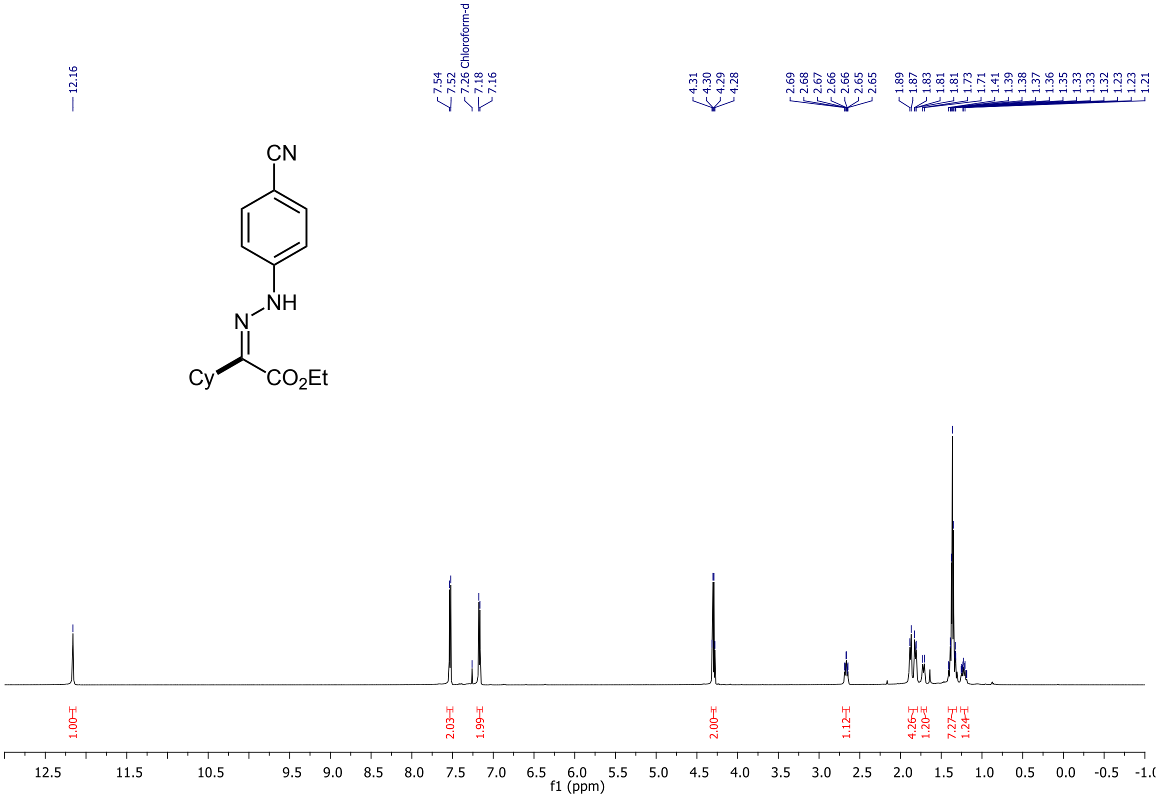
^{1}H NMR spectrum of **3ap**



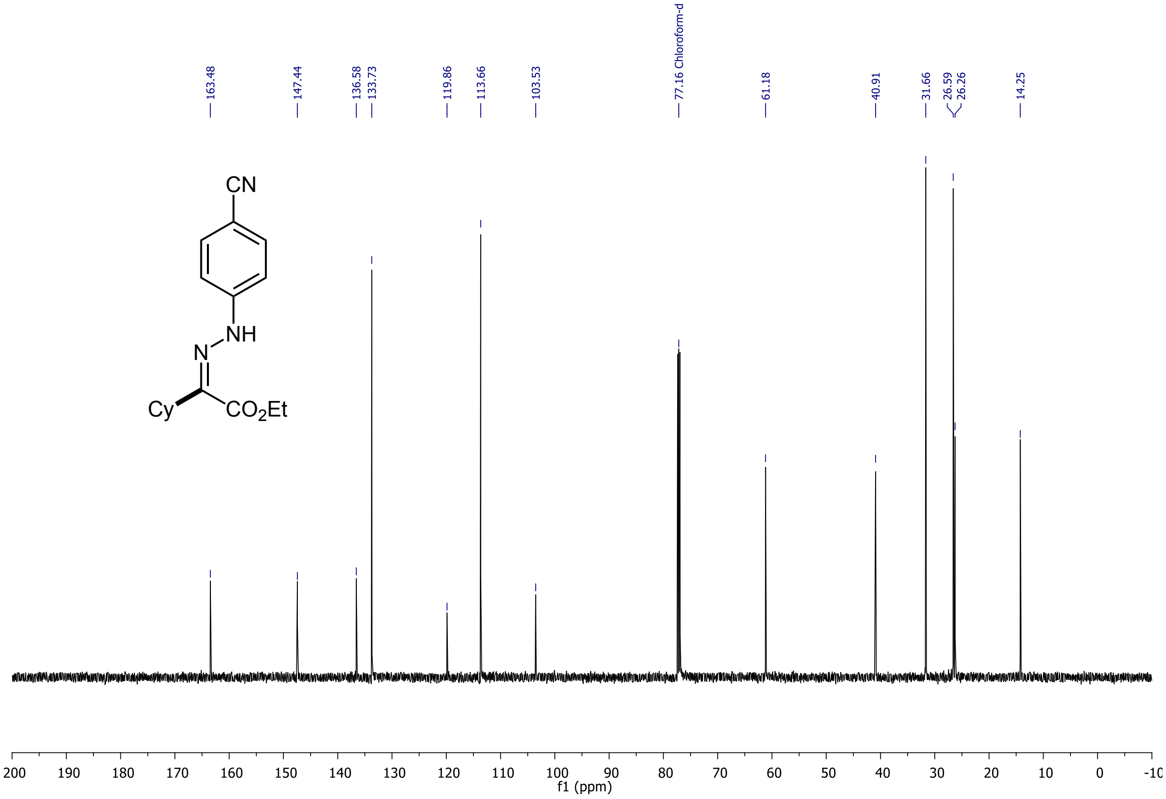
^{1}H NMR spectrum of **3ap**



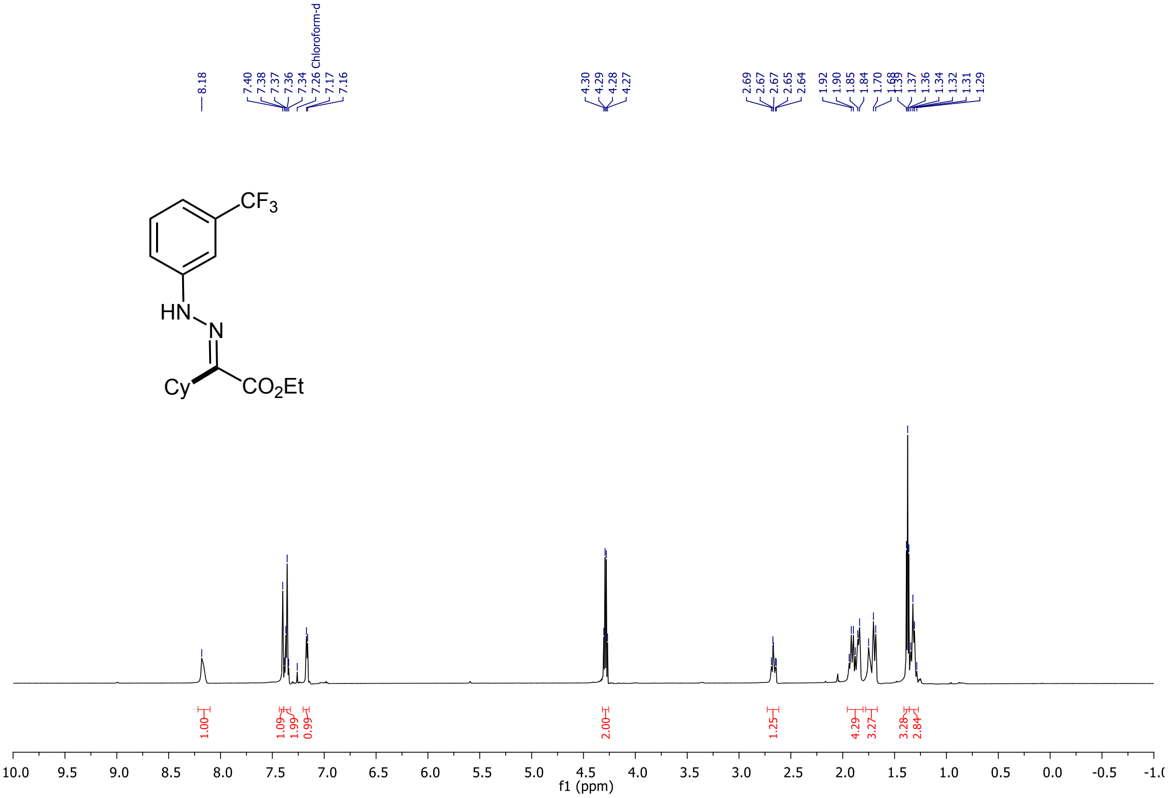
^{1}H NMR spectrum of **3aq**



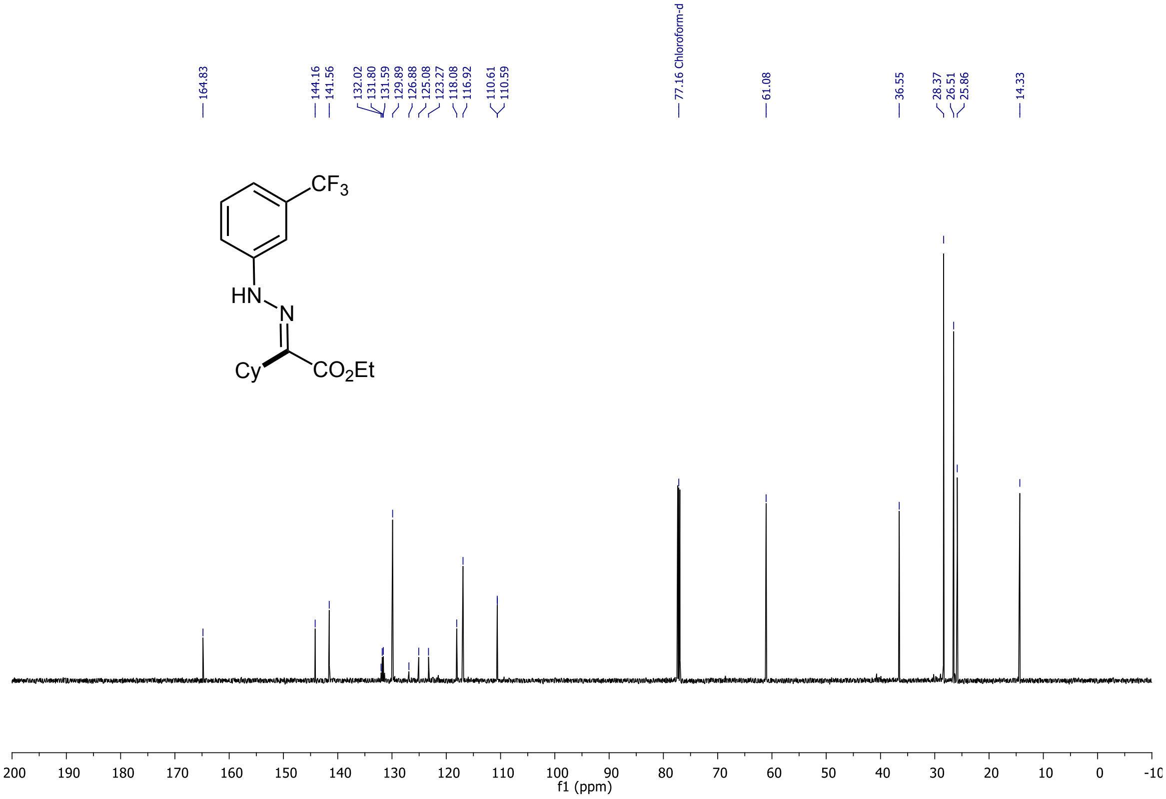
^{13}C NMR spectrum of **3aq**



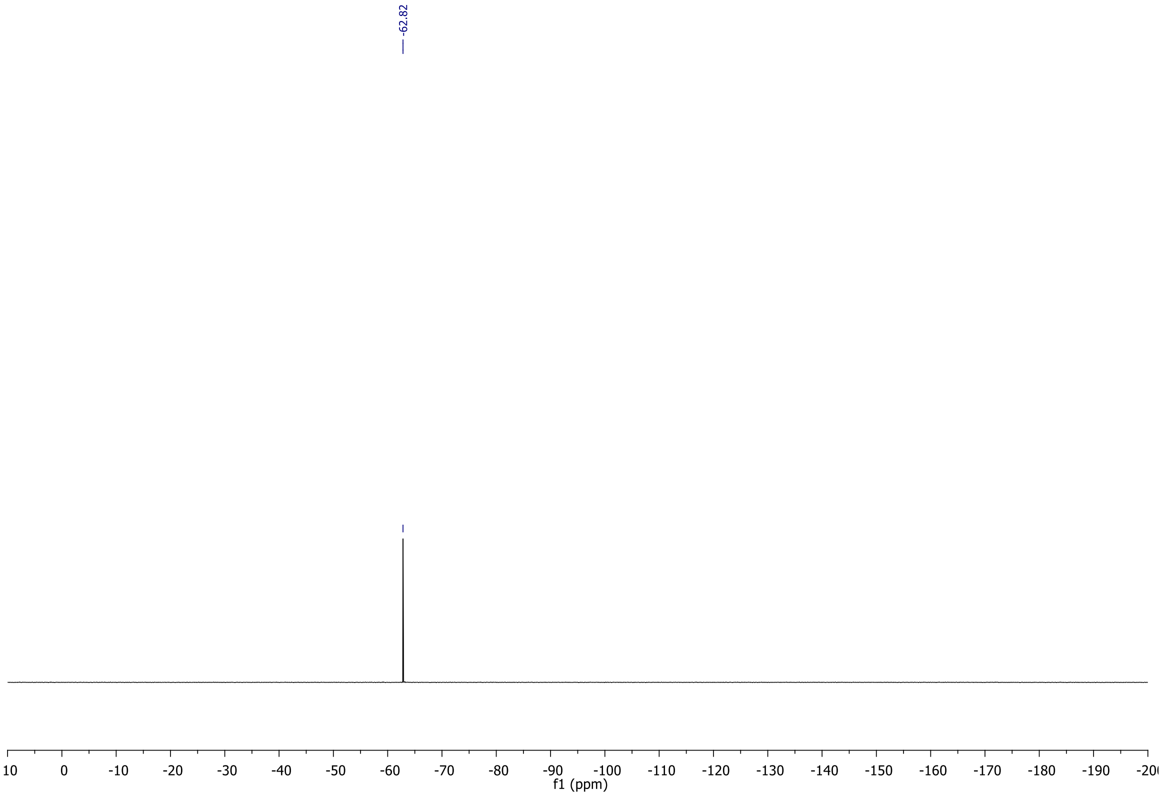
^{1}H NMR spectrum of **3ar**



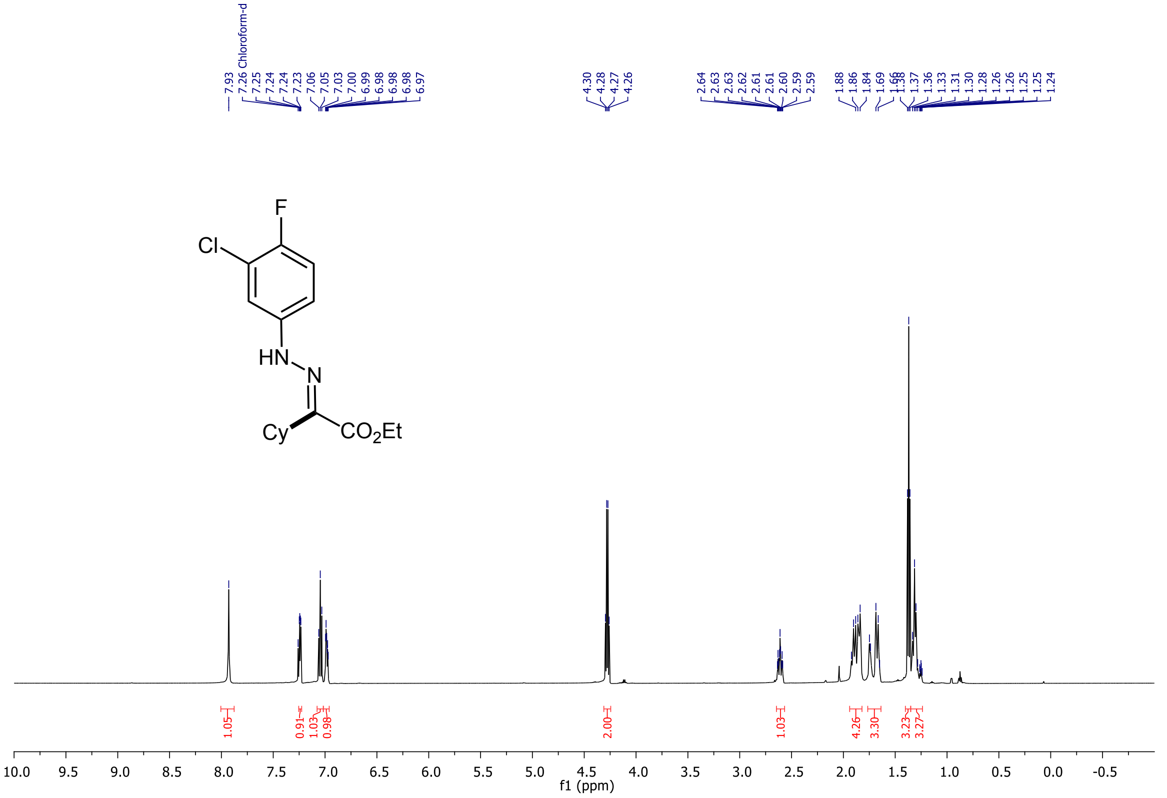
^{13}C NMR spectrum of **3ar**



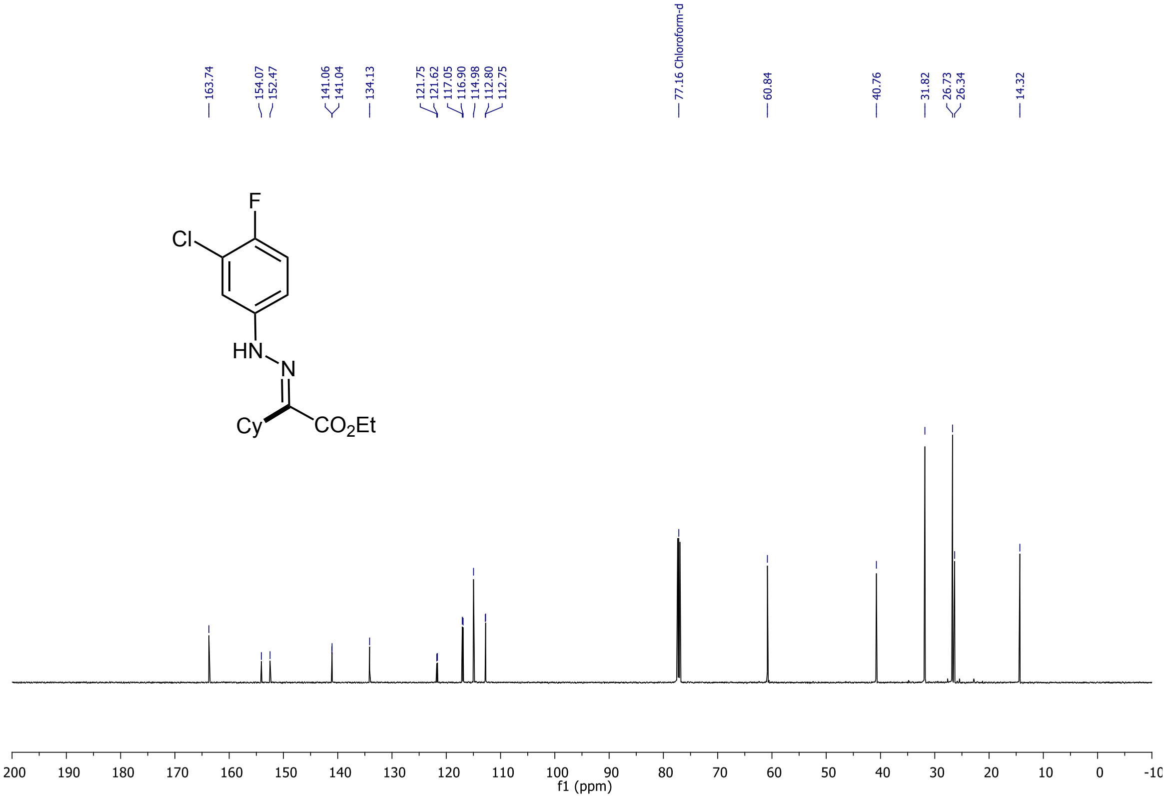
^{19}F NMR spectrum of **3ar**



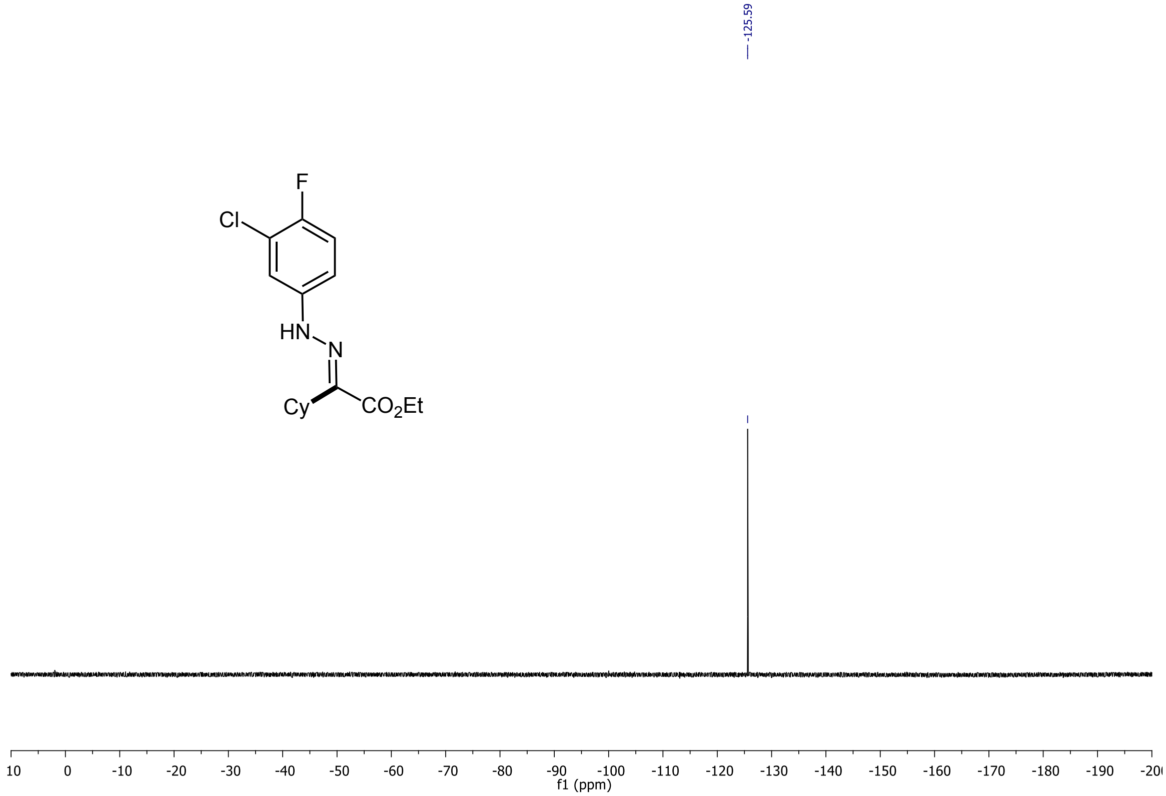
^{1}H NMR spectrum of **3as**



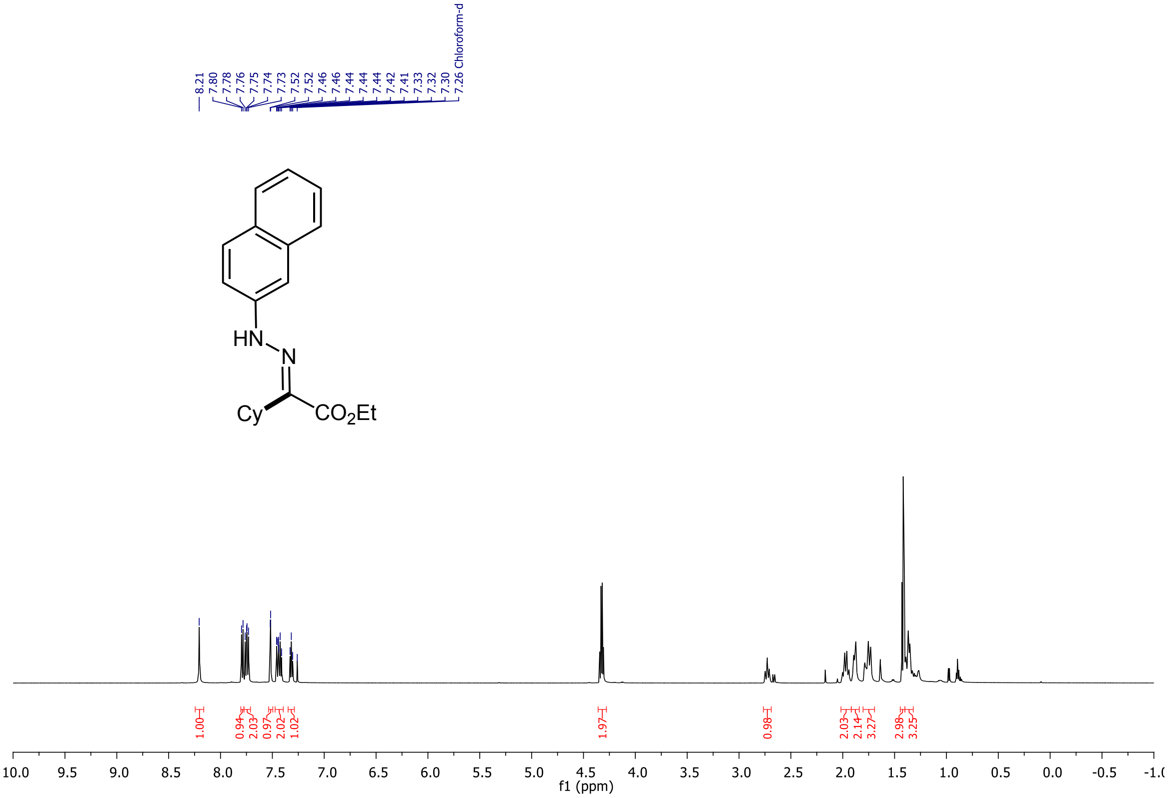
^{13}C NMR spectrum of **3as**



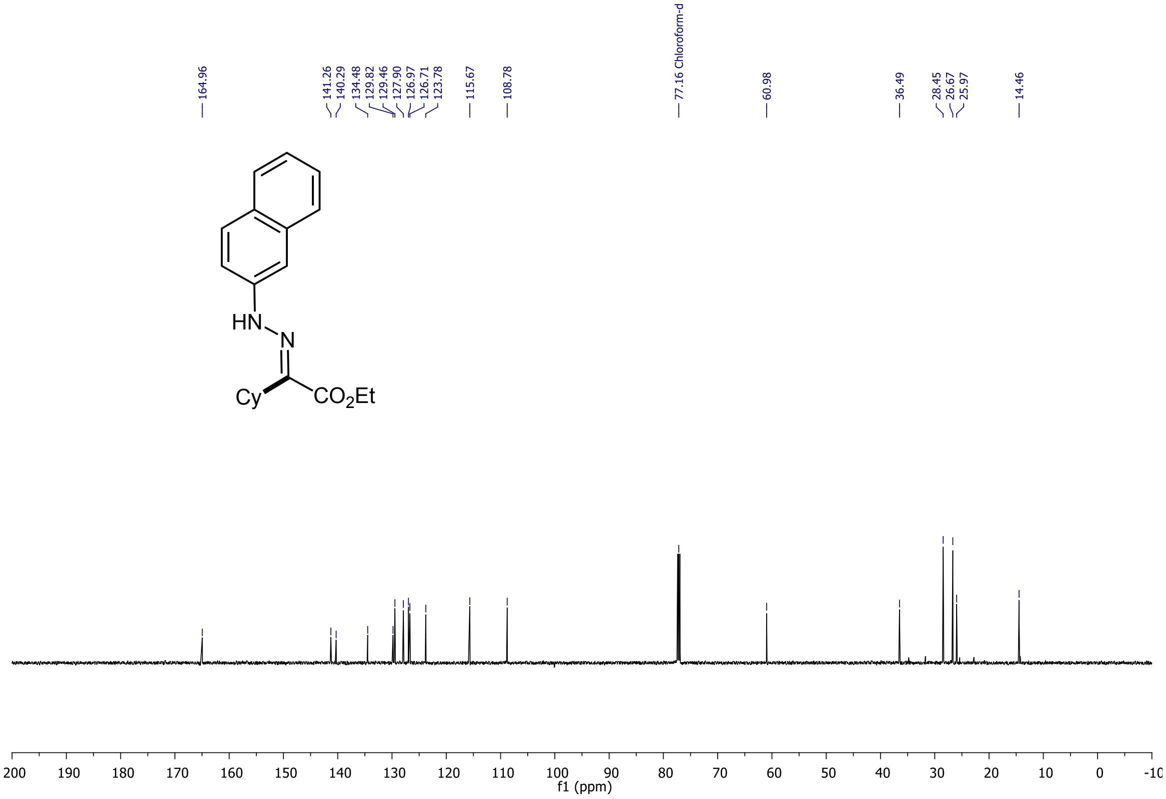
^{19}F NMR spectrum of **3as**



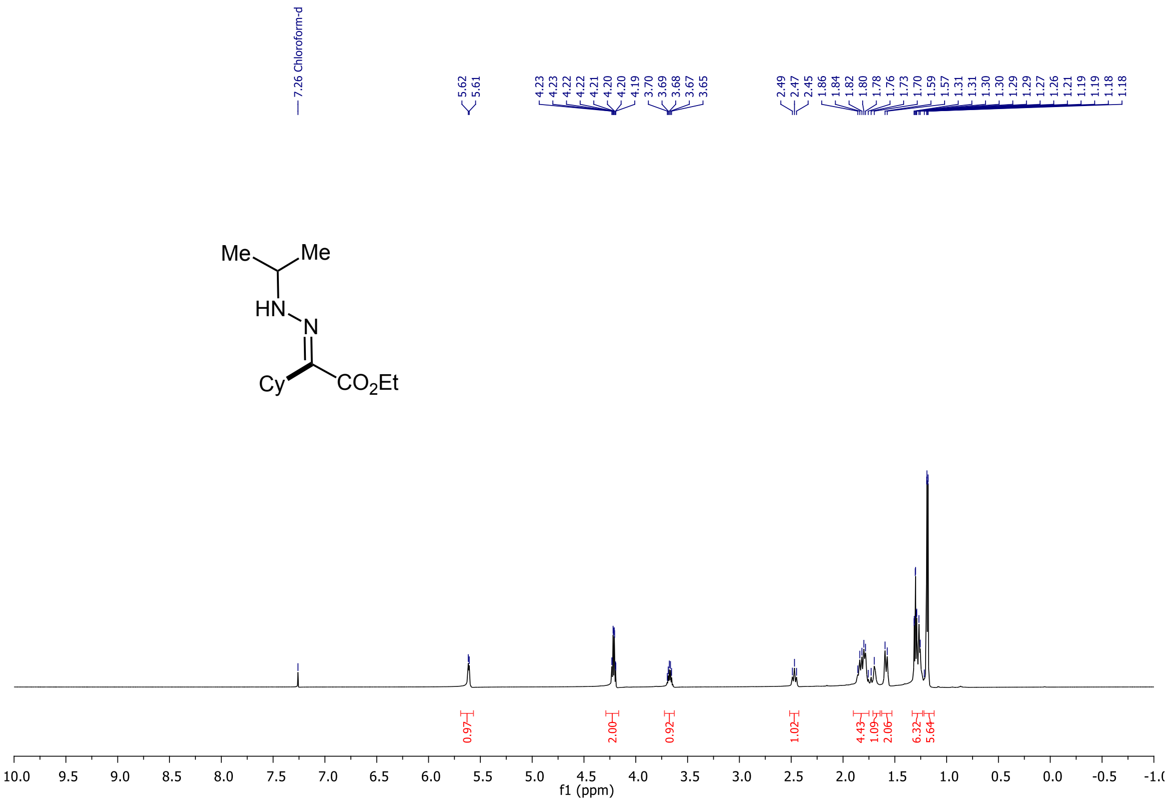
^{1}H NMR spectrum of **3at**



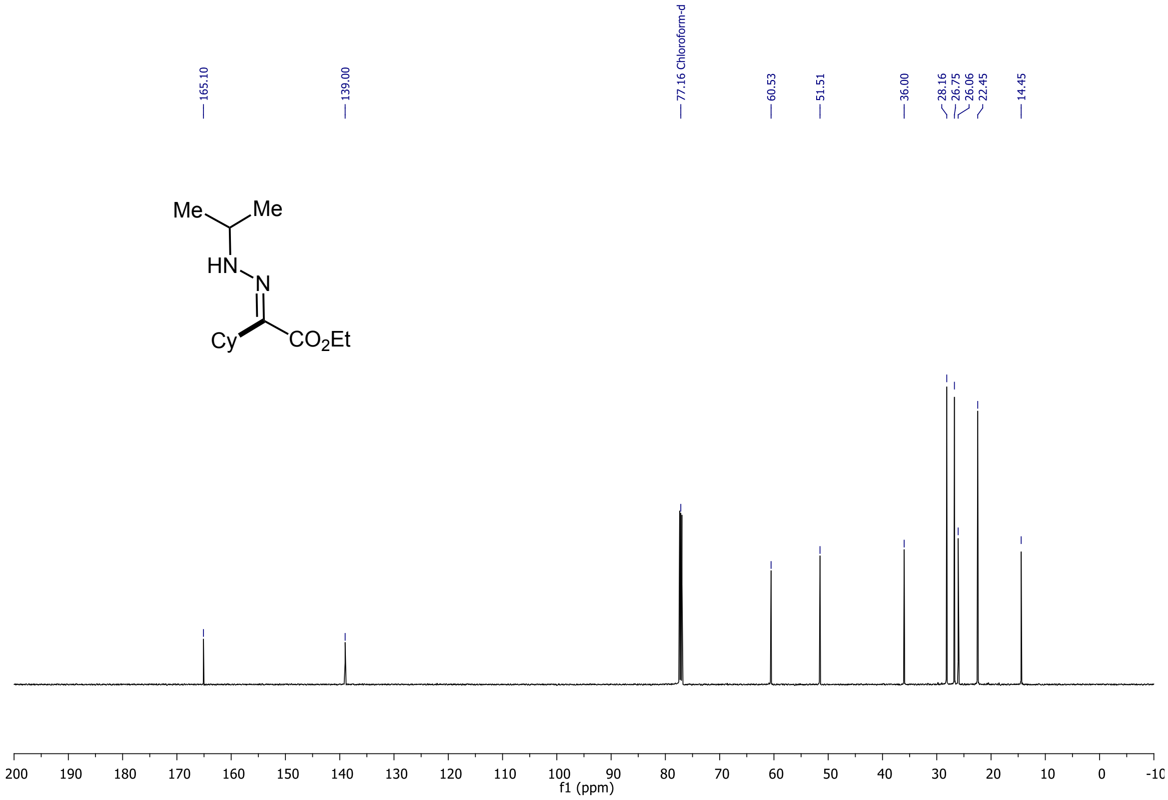
^{13}C NMR spectrum of **3at**



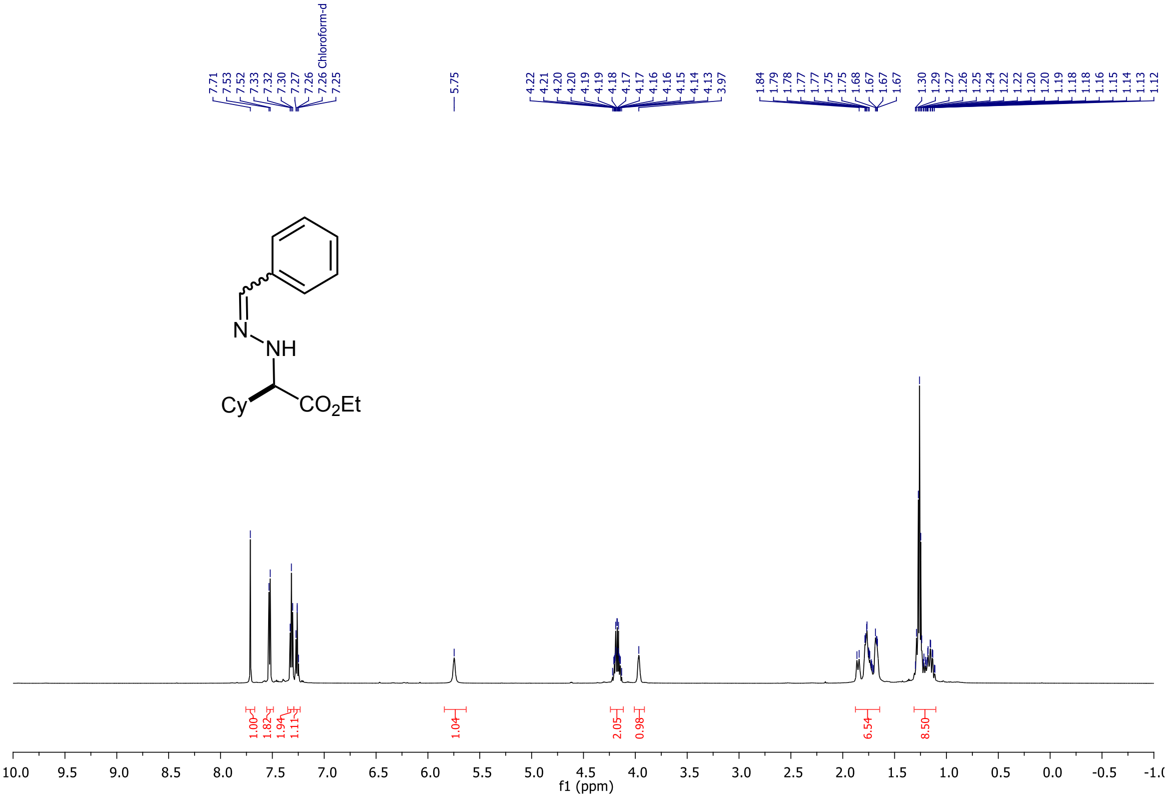
^{1}H NMR spectrum of **3au**



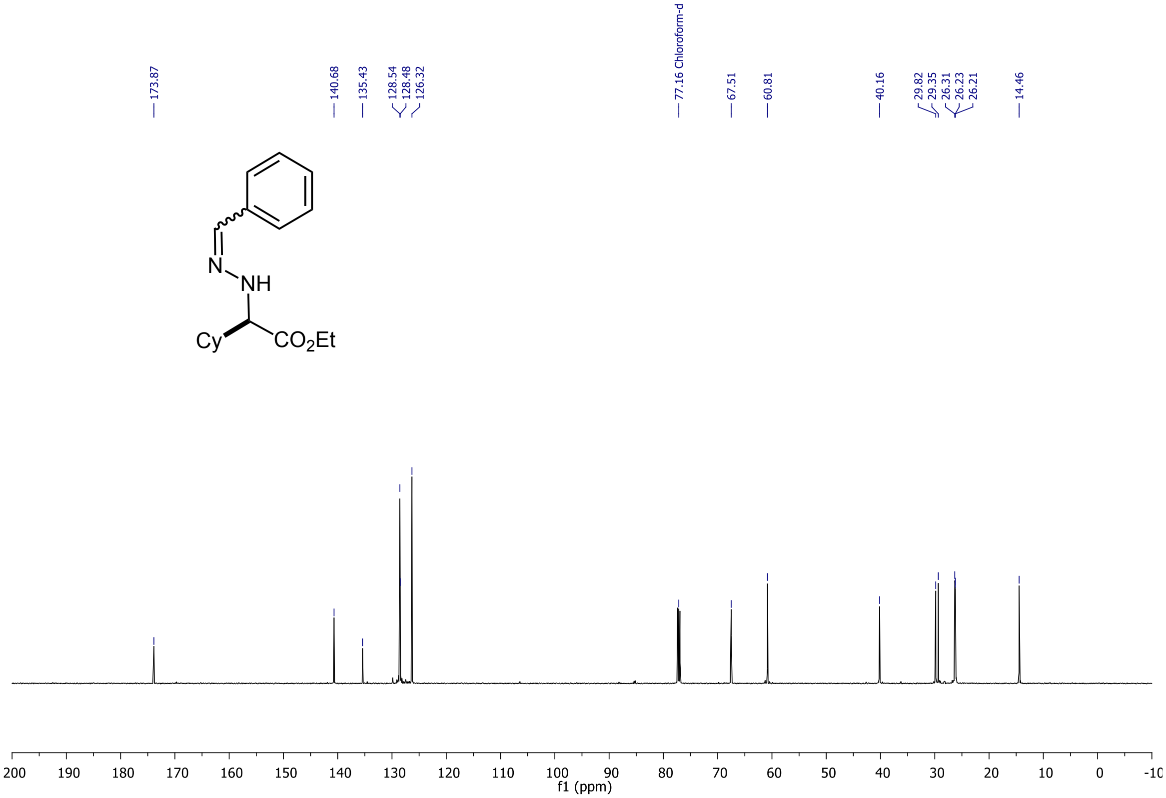
^{13}C NMR spectrum of **3au**



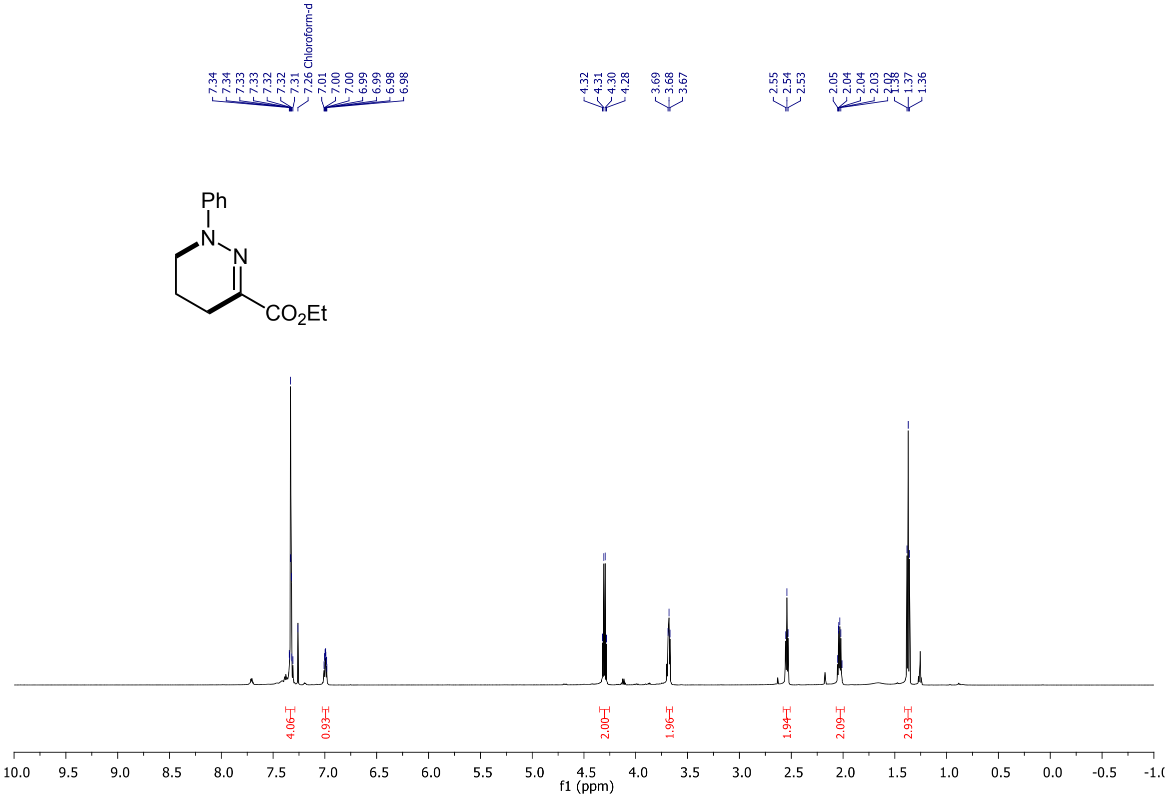
^{1}H NMR spectrum of **3av**



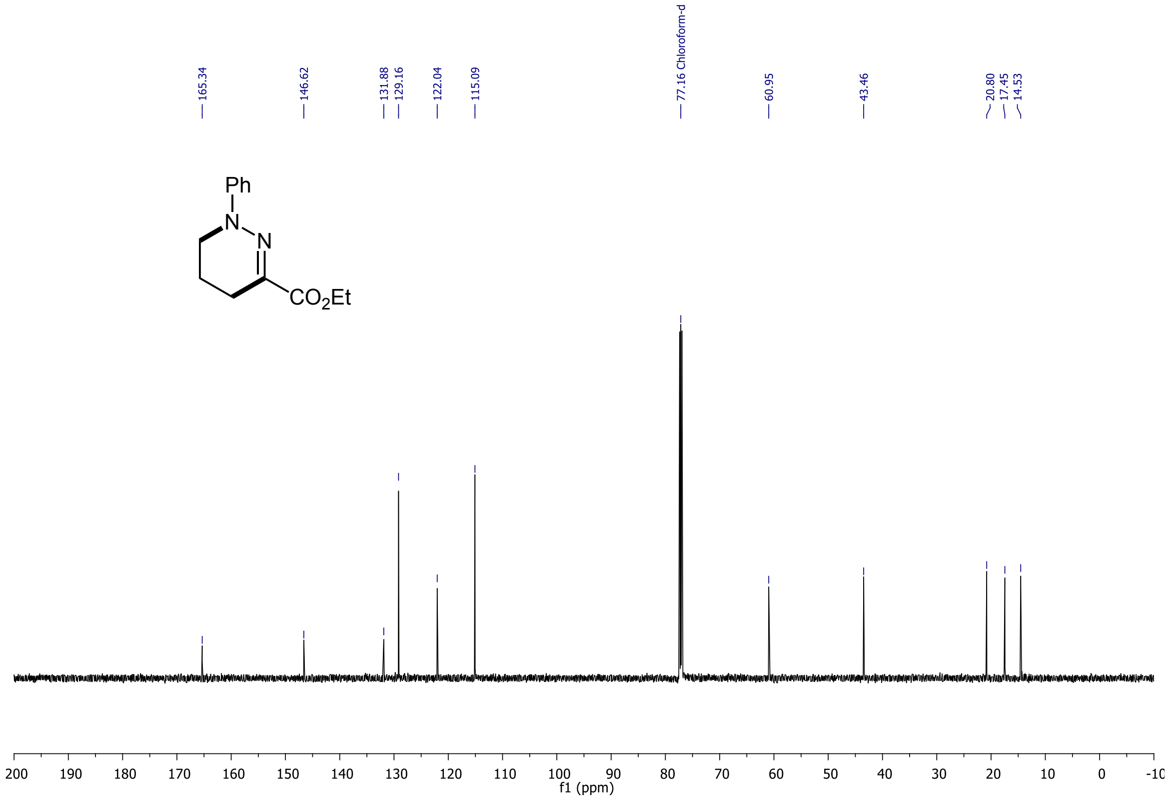
^{13}C NMR spectrum of **3av**



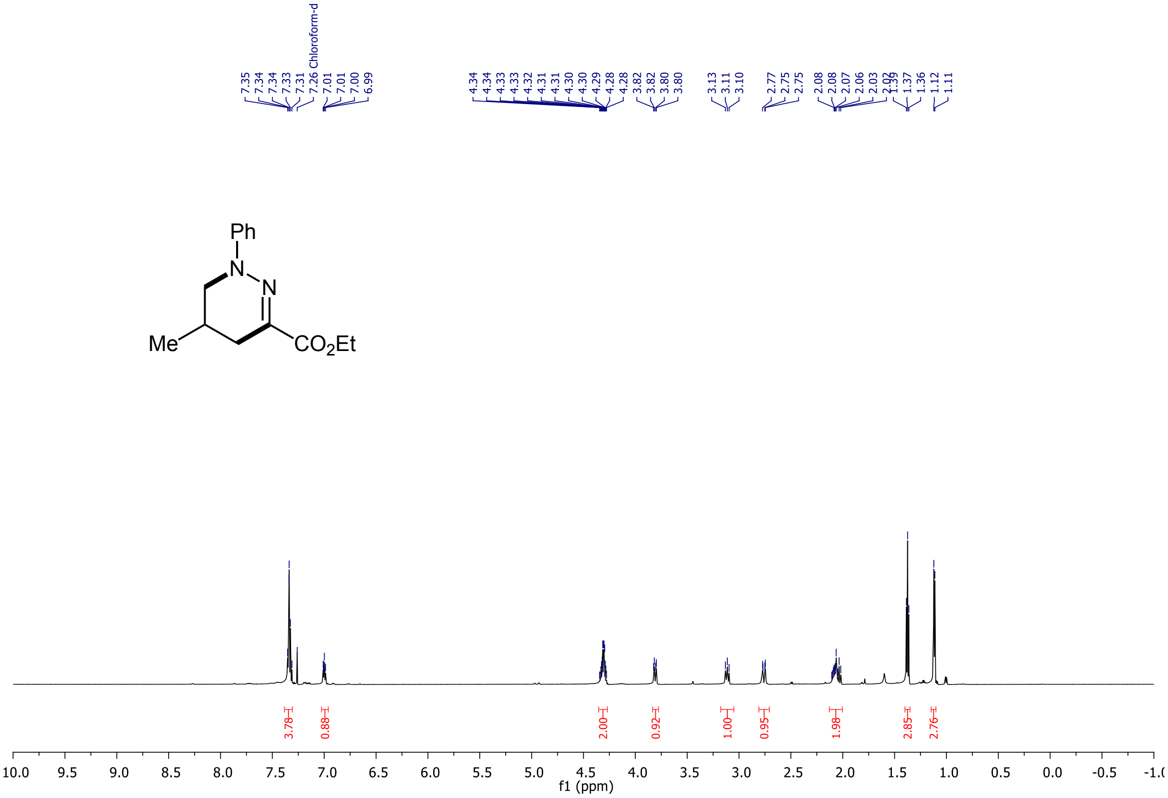
^{1}H NMR spectrum of **4a**



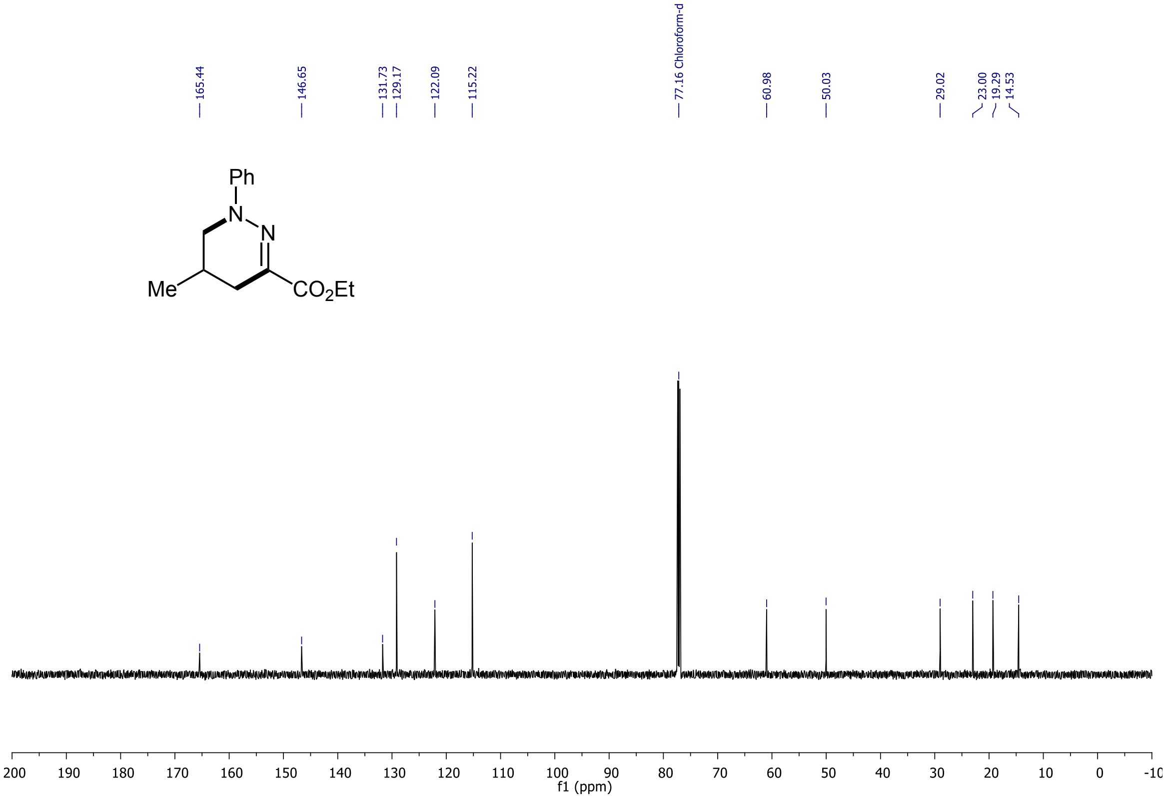
^{13}C NMR spectrum of **4a**



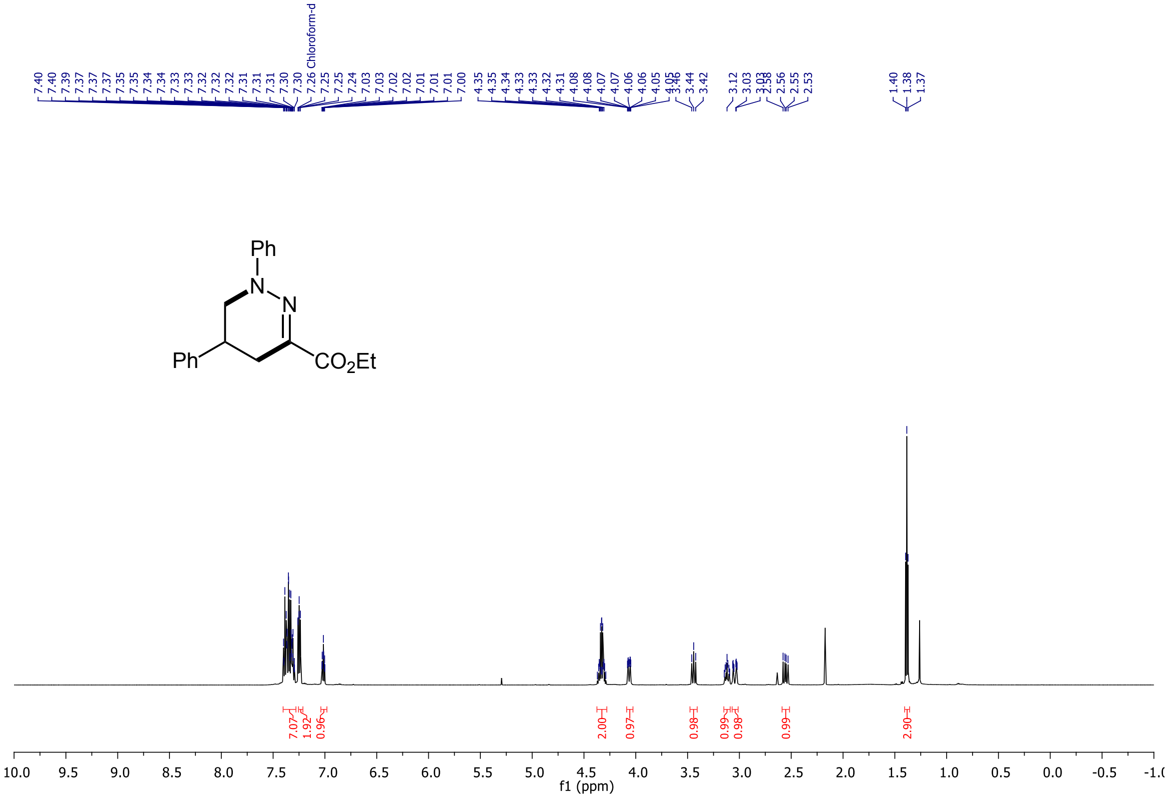
^{1}H NMR spectrum of **4b**



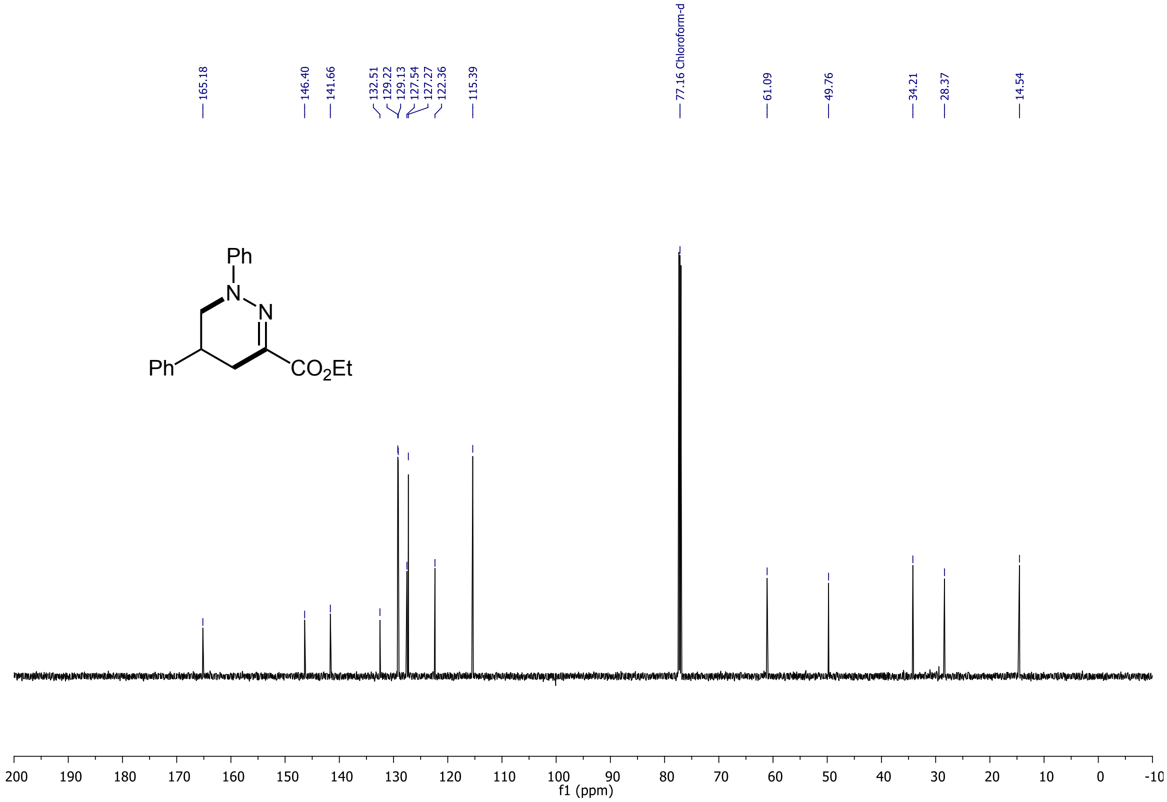
^{13}C NMR spectrum of **4b**



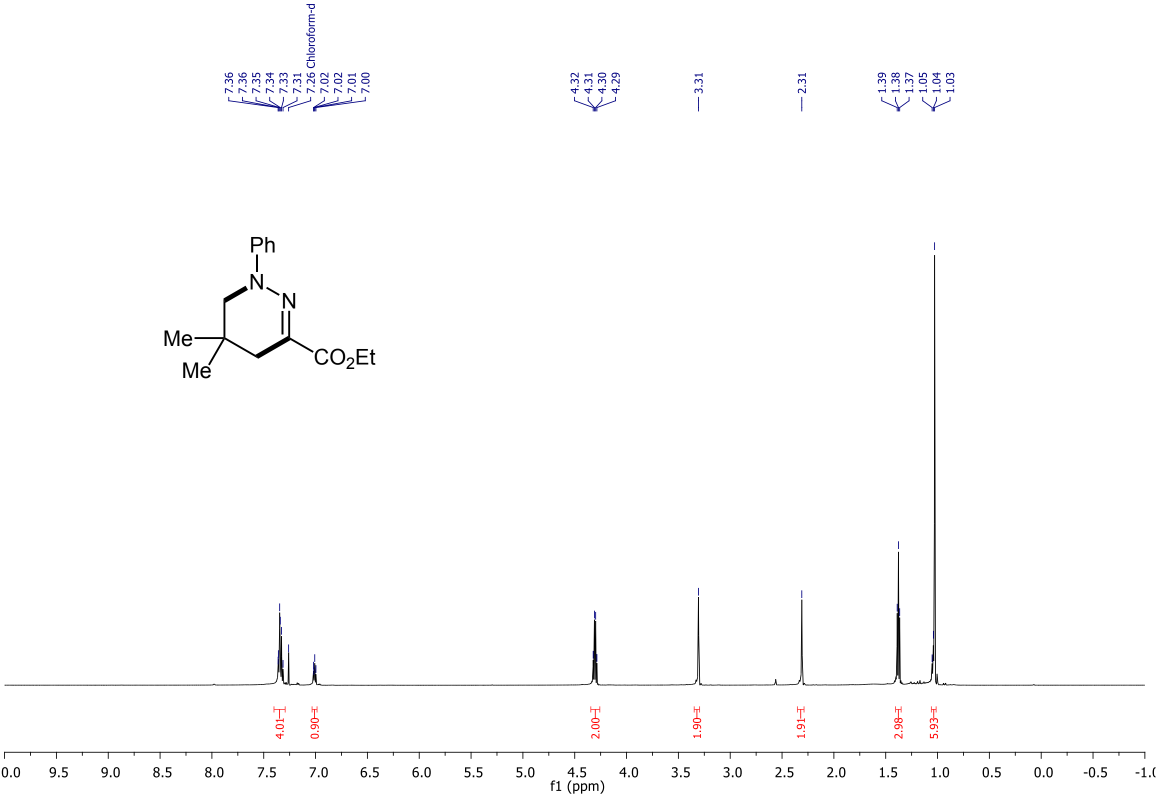
^{1}H NMR spectrum of **4c**



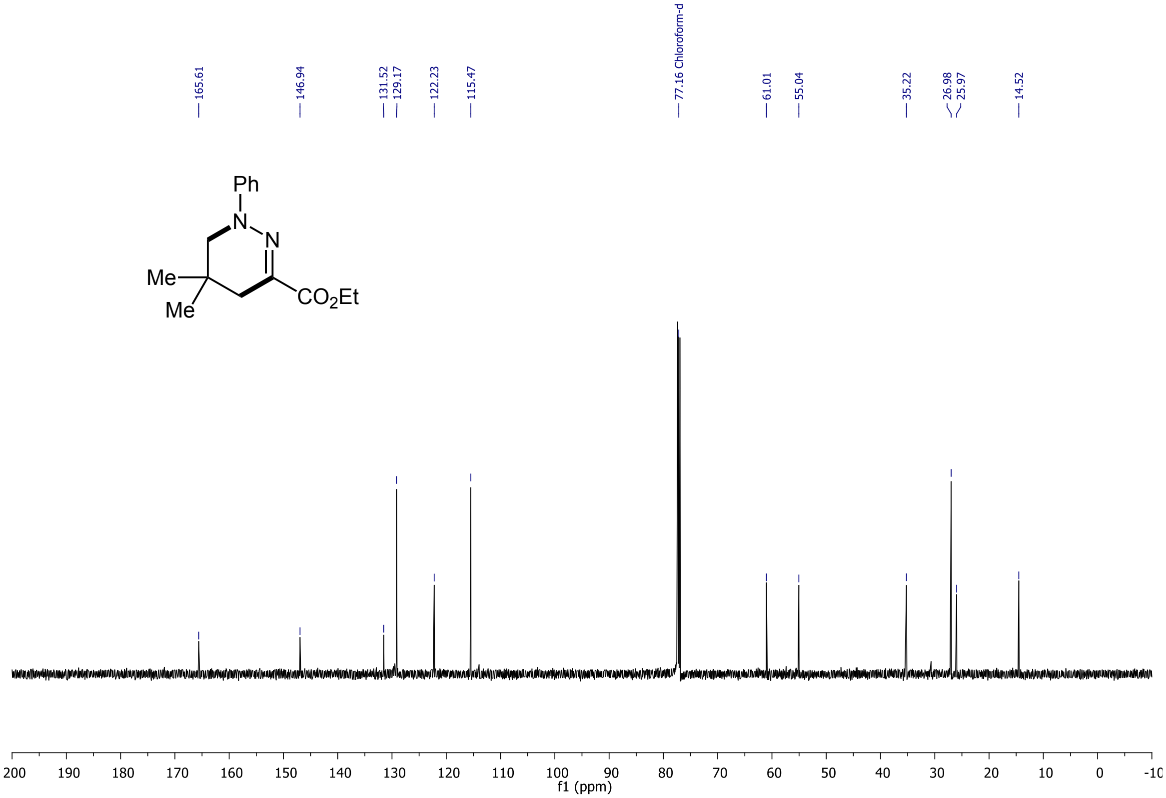
^{13}C NMR spectrum of **4c**



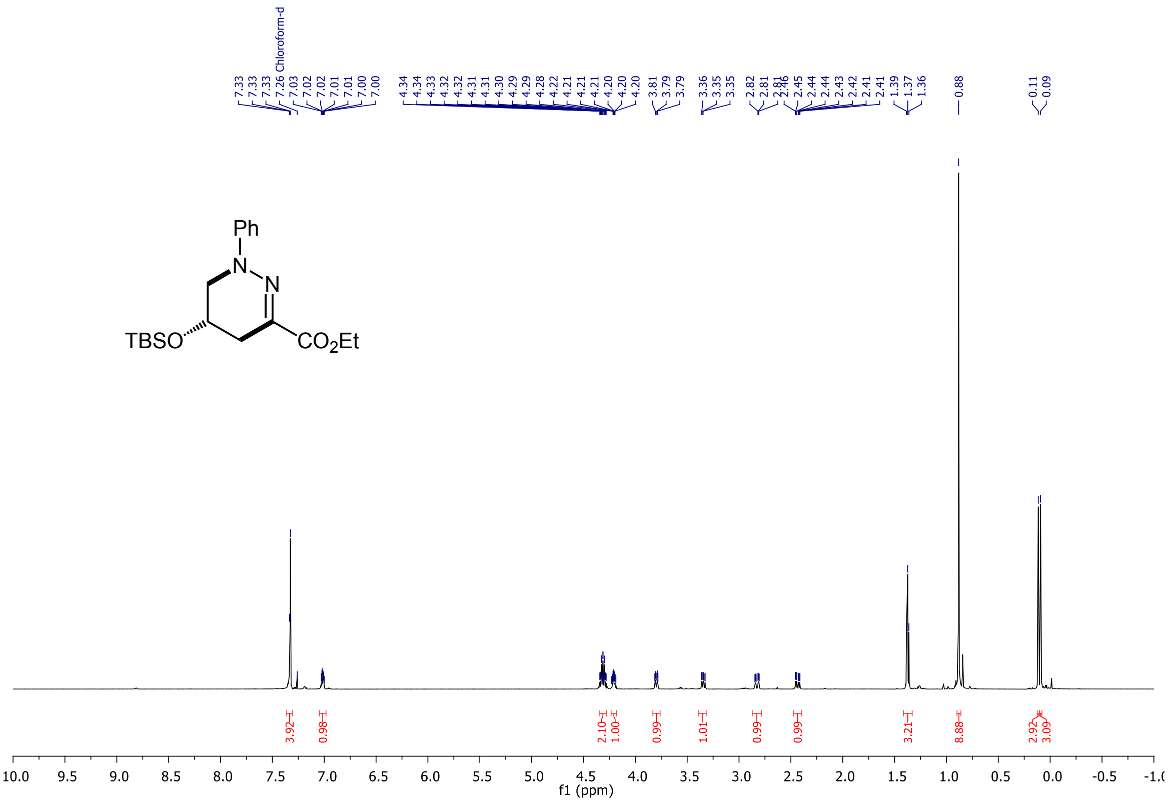
^{1}H NMR spectrum of **4d**



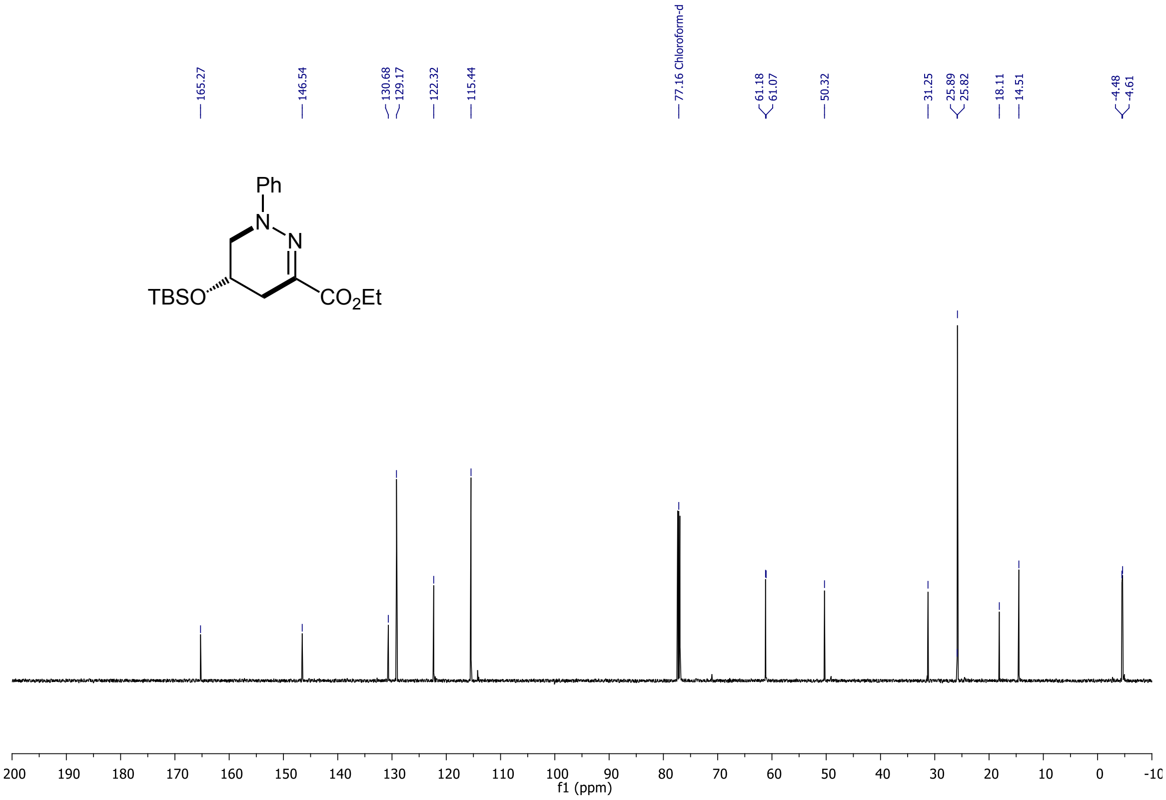
^{13}C NMR spectrum of **4d**



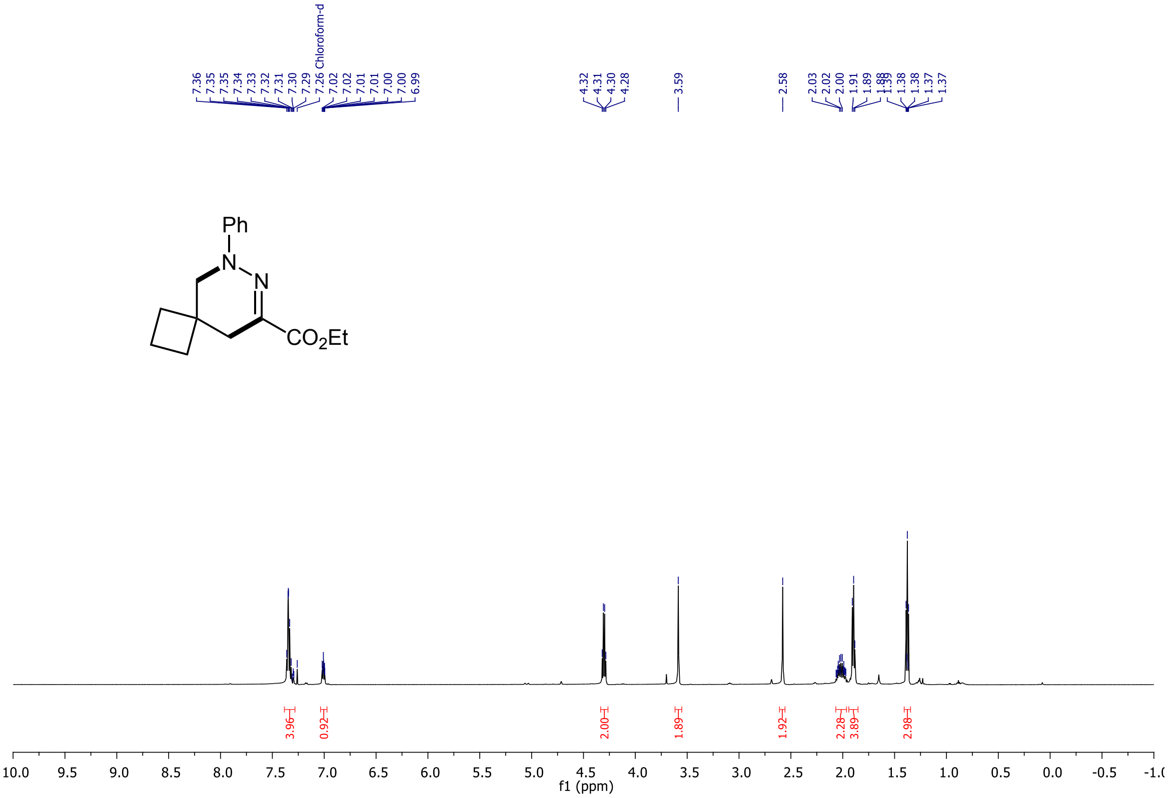
^{1}H NMR spectrum of **4e**



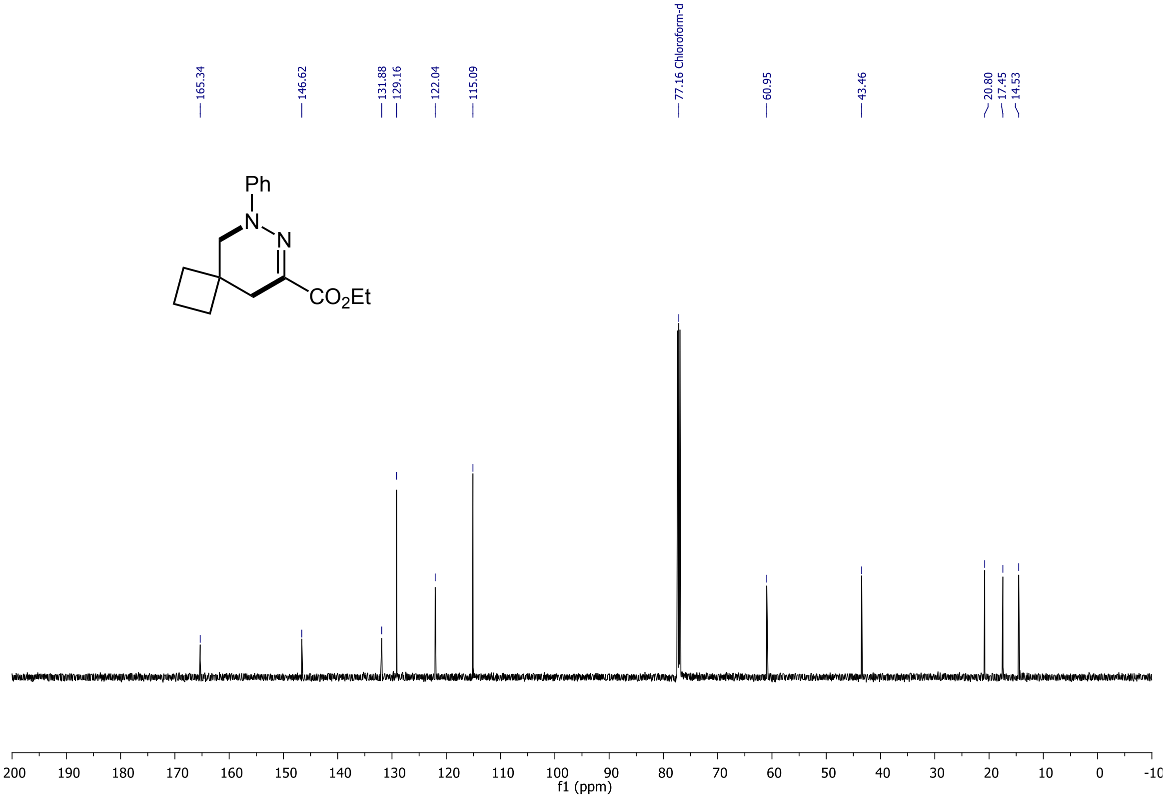
^{13}C NMR spectrum of **4e**



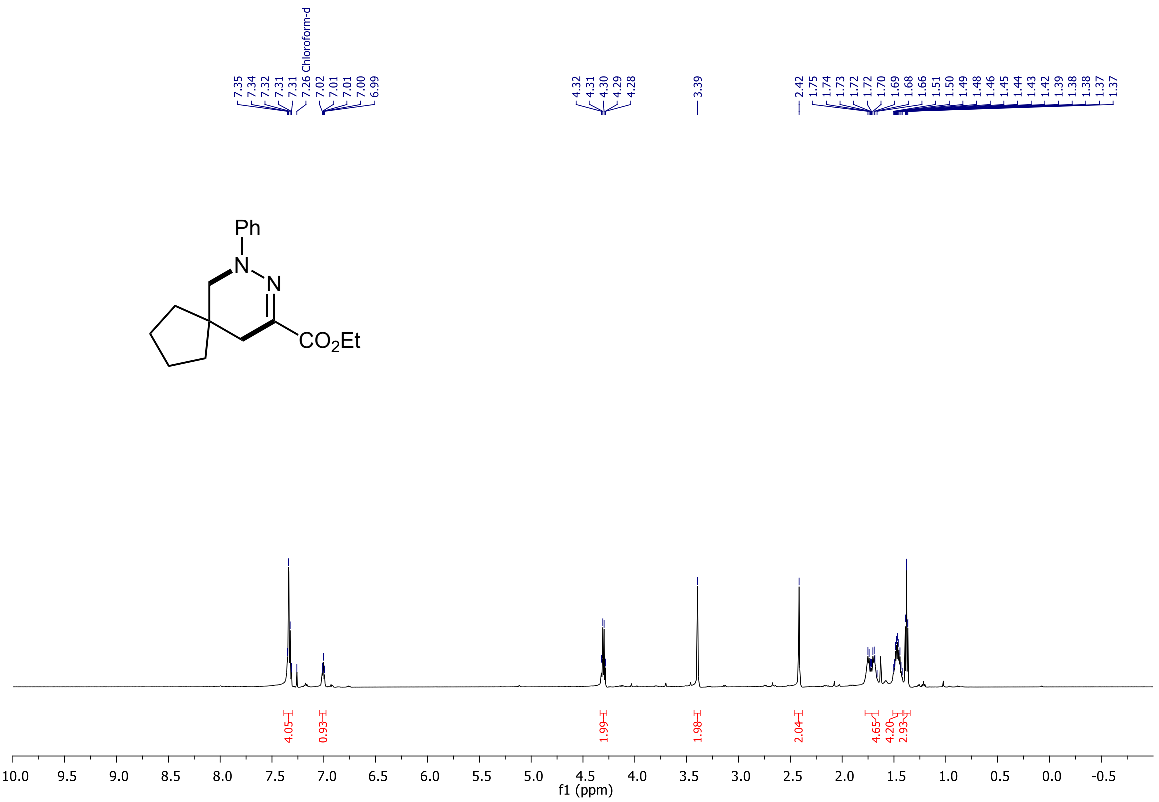
^{1}H NMR spectrum of **4f**



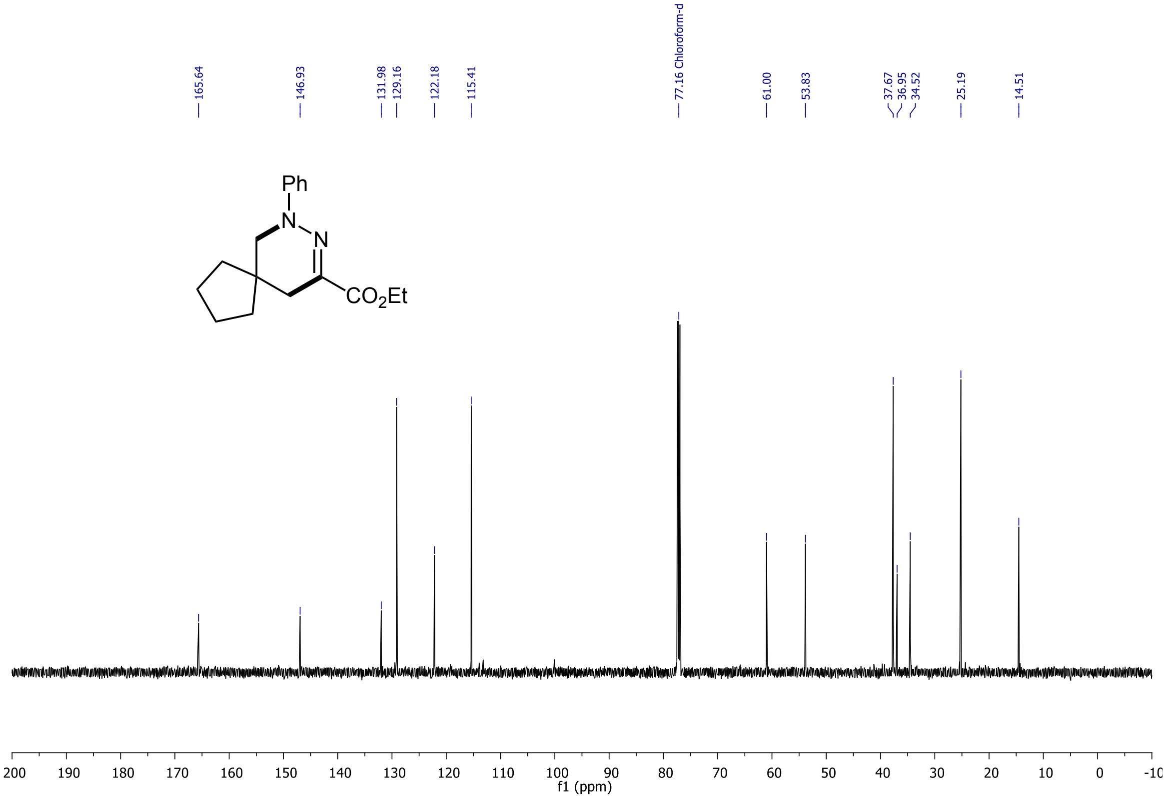
^{13}C NMR spectrum of **4f**



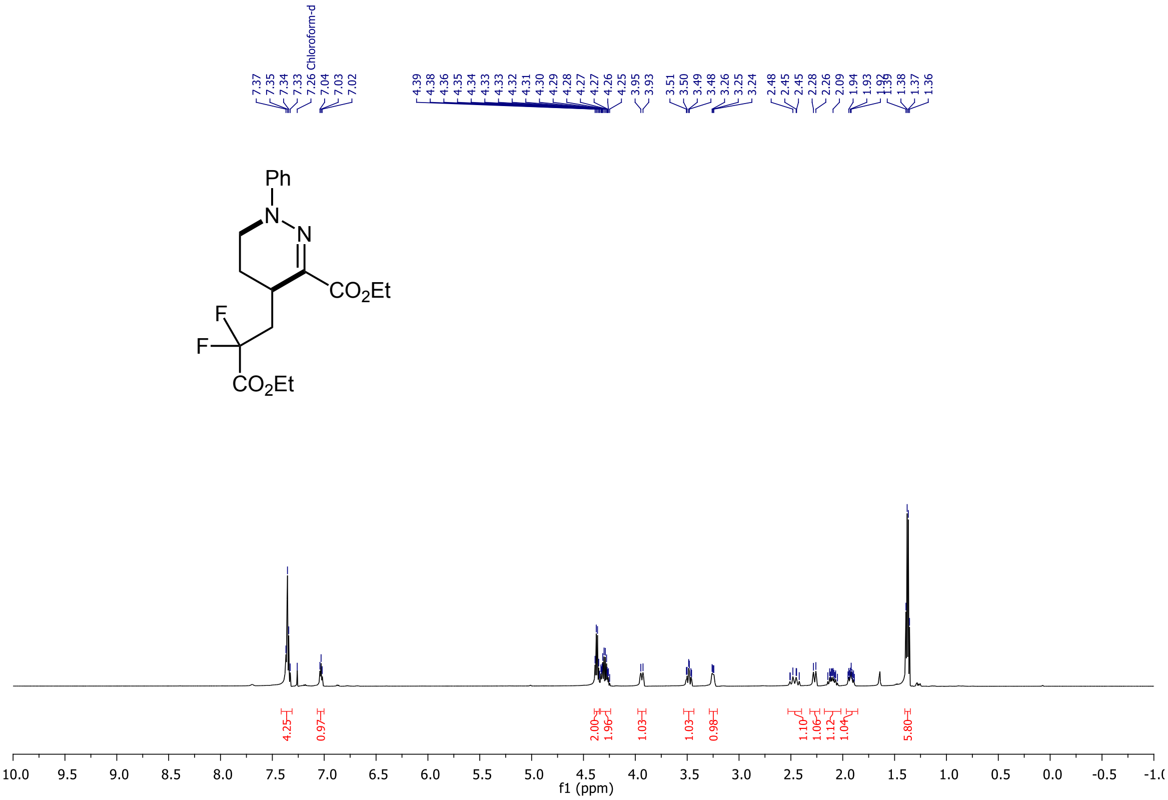
^{1}H NMR spectrum of **4g**



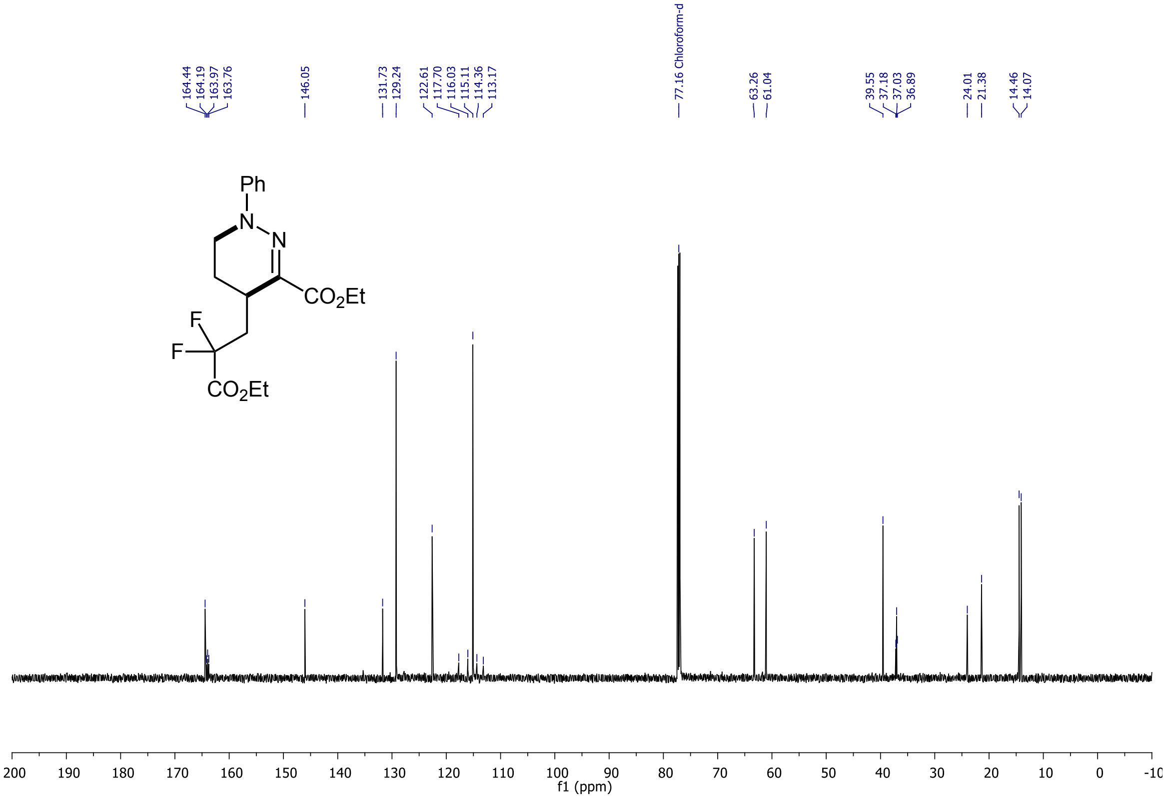
^{13}C NMR spectrum of **4g**



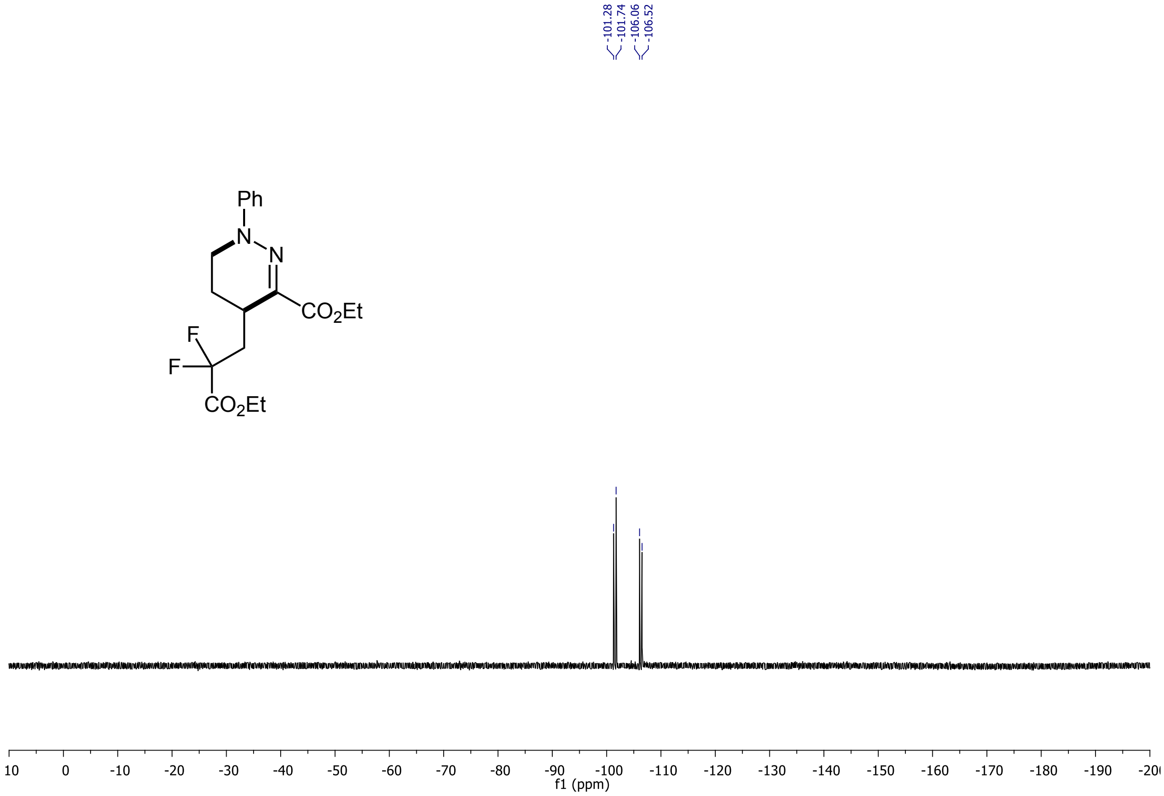
^{1}H NMR spectrum of **4h**



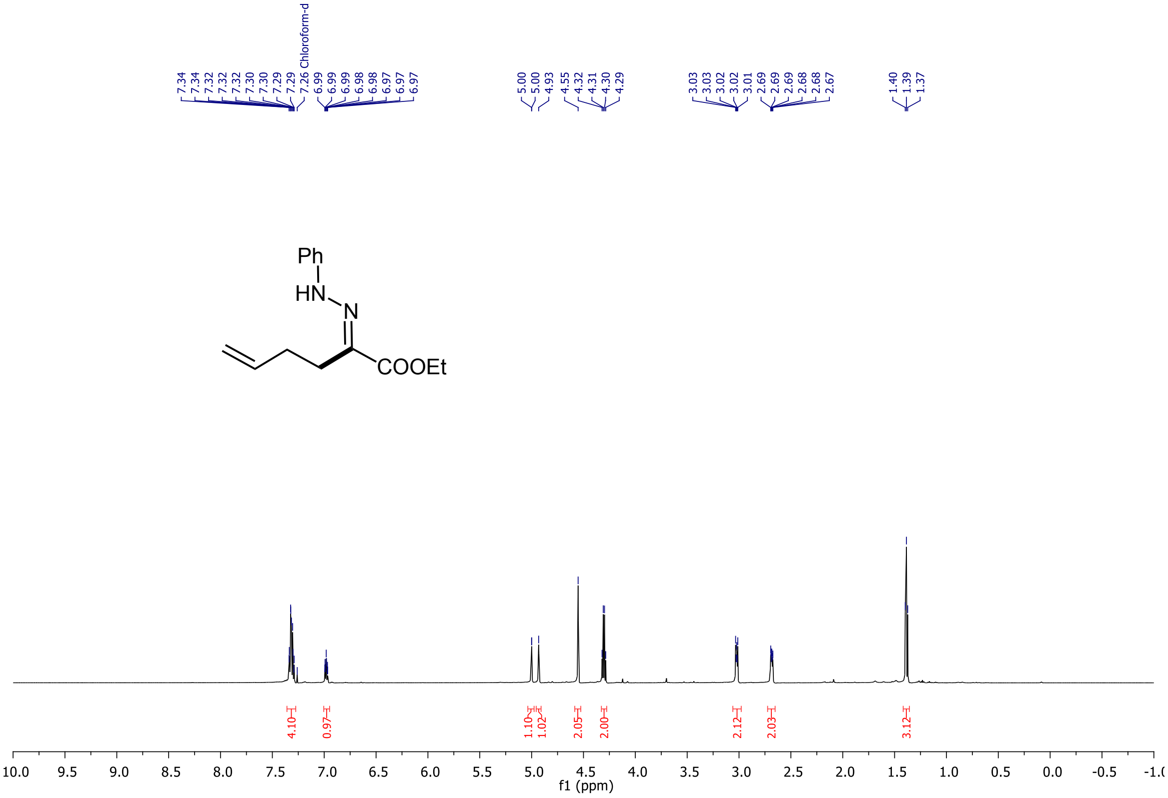
^{13}C NMR spectrum of **4h**



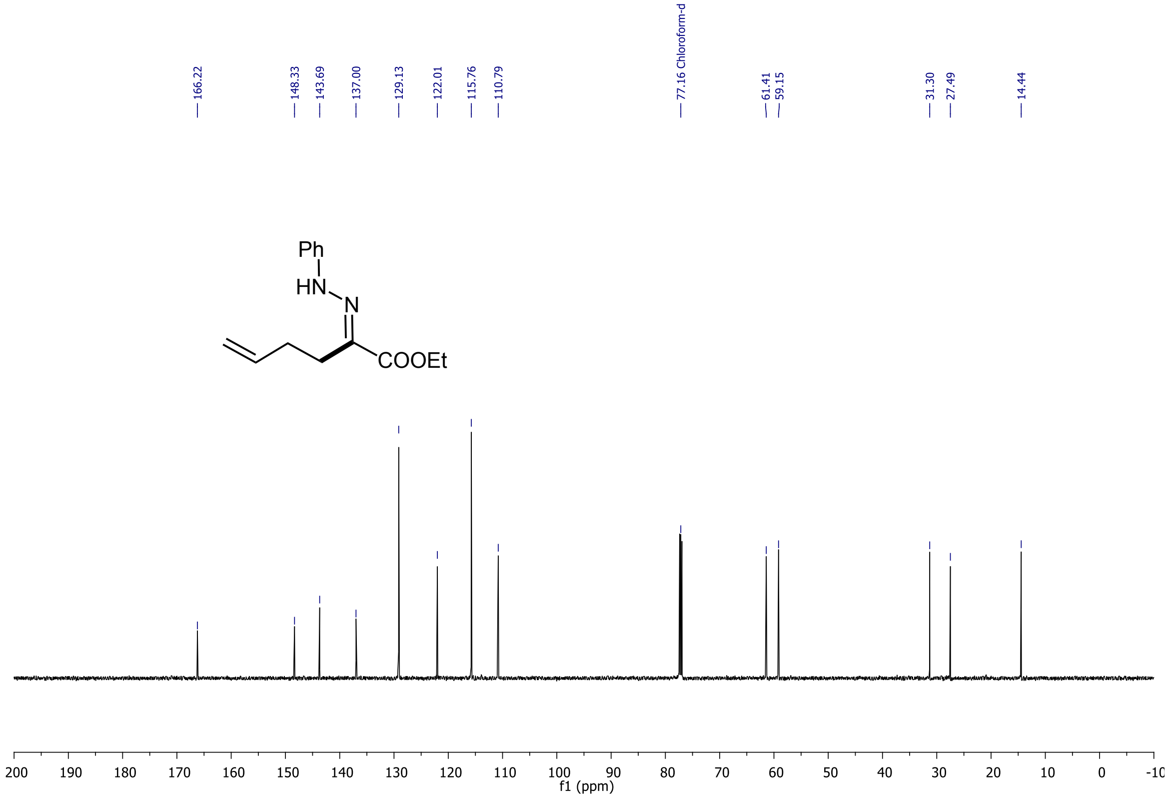
^{19}F NMR spectrum of **4h**



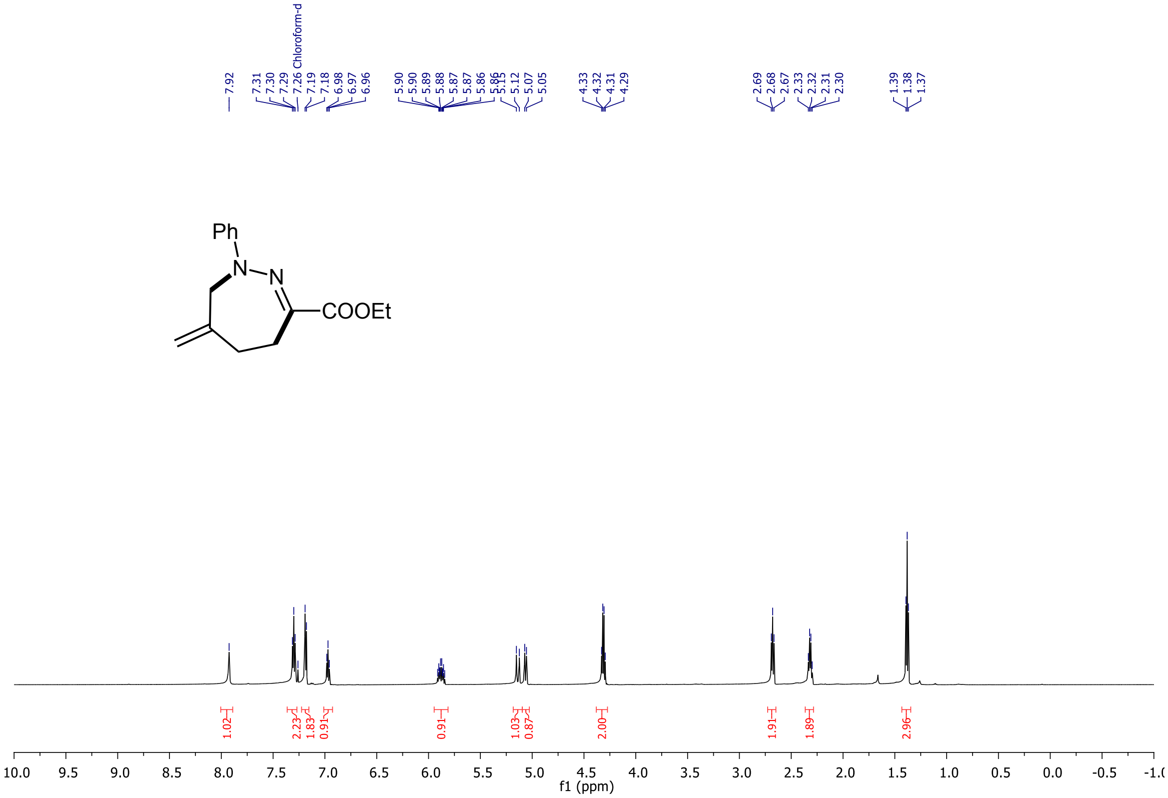
^{1}H NMR spectrum of **3aw**



^{13}C NMR spectrum of **3aw**



^{1}H NMR spectrum of **4i**



^{13}C NMR spectrum of **4i**