Supporting Information

Visible Light-induced Metal-free Cascade Denitrogenative Borylation and Iodination of Nitroarenes

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Contents

1. General Information

General Methods. All reagents were bought from commercial sources and used as received without further purification. All reactions were carried out under under N_2 atmosphere unless otherwise noted. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. ^{1}H NMR was recorded on Bruker instrument (500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker instrument (126 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to either the center line of a triplet at 77.0 ppm of chloroform-*d* or referenced to the center line of a septet at 39.52 ppm of DMSO-d_6. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

General Instrumental Data. The photoreactors used in this research were bought from GeAo Chem and KeTai Chem: 10 W for every light bulb; every glass vessel was irradiated by 2 light bulbs from the side.

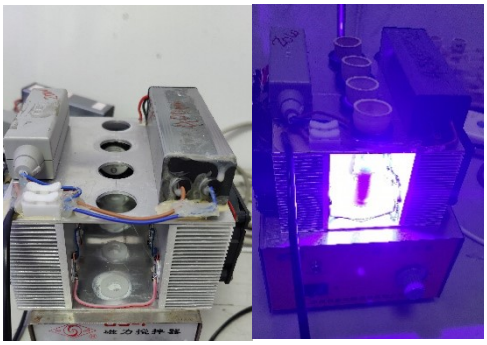
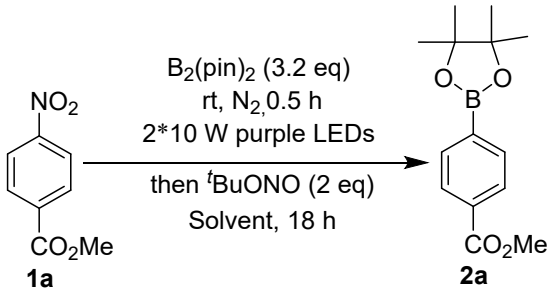


Figure S1. Experimental Apparatus

2. Borylation Reaction Conditions

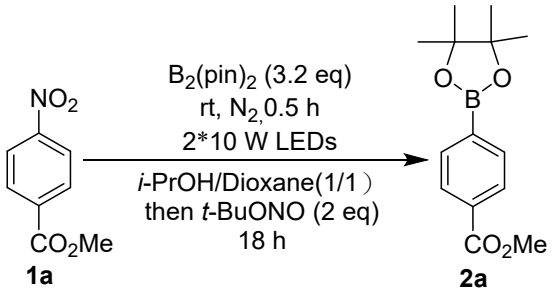
2.1 Screening of Solvent



Entry	Solvent	Yield **2a** (%)[b]
1	MeOH	28
2	EtOH	33
3	^{i}PrOH	55
4	1-butanol	20
5	THF	15
6	1,4-dioxane	17
7	CH_3CN	10
8	DMF	N.D
9	Toluene	6
10	^{i}PrOH/1,4-dioxane(1/1)	59
11	^{i}PrOH/THF(1/1)	50
12	^{i}PrOH/CH3CN(1/1)	56

Table S1: Screening of solvent. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (3.2 eq) in solvent (3 mL, 0.1 M) stirred under 2 x 10 W purple LEDs at rt for 0.5 h. Then t-BuONO (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

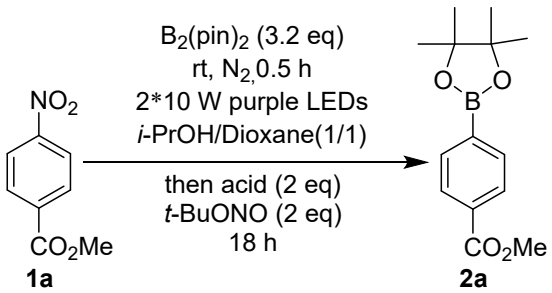
2.2 Screening of light source



Entry	Light source	Yield **2a** (%)[b]
1	2×10 W purple LEDs	59
2	2×10 W blue LEDs	8
3	Dark	N.R.

Table S2: Screening of light source. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (3.2 eq) in ^{i}PrOH/1,4-dioxane (3 mL, 1/1) stirred under 2 x 10 W LEDs at rt for 0.5 h. Then t-BuONO (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

2.3 Screening of acid

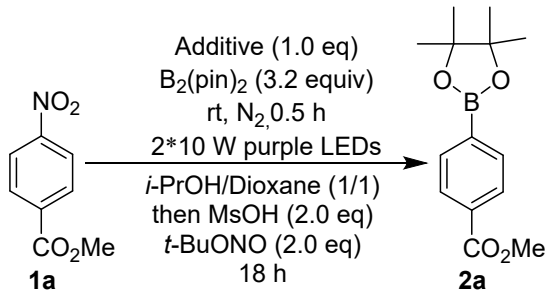


Entry	Acid	Yield **2a** (%)[b]
1	HBF_4	64
2	CH_3COOH	60
3	MsOH	70
5	CF_3SO_3H	67
6	HCl	58

Table S3: Screening of acid. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (3.2 eq) in ^{i}PrOH/1,4-dioxane (3 mL, 1/1) stirred under 2 x 10 W purple LEDs at rt for 0.5

h. Then t-BuONO (2.0 eq) and acid (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

2.4 Screening of additive



Entry	Additive	Yield **2a** (%)[b]
1	$NaBF_4$	75
2	NaF	70
3	KF	68
4	AgF	60

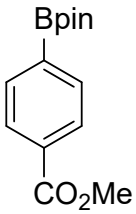
Table S4: Screening of additive. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (3.2 eq) and additive (1.0 eq) in ^{i}PrOH/1,4-dioxane (3 mL, 1/1) stirred under 2 x 10 W purple LEDs at rt for 0.5 h. Then t-BuONO (2.0 eq) and MsOH (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

2.5 General procedure for the synthesis of 2a – 2d

A sealed tube with magnetic stir bar was charged with **1** (0.3 mmol,1.0 eq), Bis(pinacolato)diboron (0.96 mmol, 3.2 eq), $NaBF_4$ (0.3 mmol, 1.0 eq) in nitrogen atmosphere, followed by *i*-PrOH/1,4-Dioxane (1/1, 3 mL). MsOH (0.6 mmol, 2.0 eq) and t-BuONO (0.6 mmol, 2.0 eq) were added to the reaction solution half an hour after irradiation by the photoreaction device (380 nm light). The mixture was stirred until complete conversion of the **2** (monitored by TLC). The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 40:1 to 10:1).

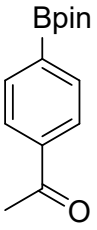
2.6 Characterization of products

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2a)



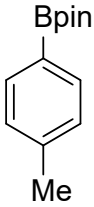
White solid, yield 76%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 134.7, 132.3, 128.6, 84.2, 52.2, 24.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{20}BO_4$ 263.1449, found 263.1445.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (2b)



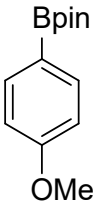
White solid, yield 37%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 4H), 2.60 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.4, 139.0, 134.9, 127.3, 83.5, 25.0, 24.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{20}BO_3$ 247.1205, found 247.1207.

4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (2c)



White solid, yield 20%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.5, 135.0, 128.7, 83.8, 25.0, 21.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_{20}BO_2$ 219.1551, found 219.1547.

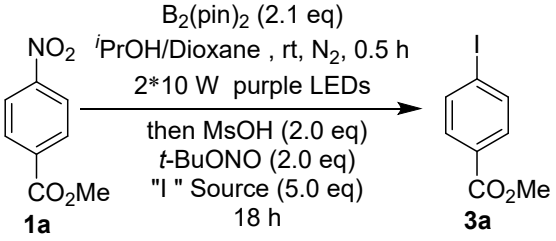
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



White solid, yield 53%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.1 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 136.6, 113.5, 83.7, 55.2, 25.0. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_{20}BO_3$ 235.1500, found 235.1504.

3. Iodization Reaction Conditions

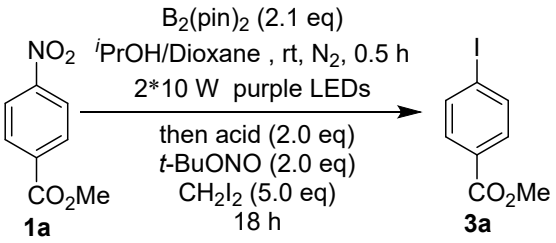
3.1 Screening of iodizing reagent



Entry	Iodizing reagent	Yield **3a** (%)[b]
1	NIS	46
2	CH_2I_2	72
3	NaI	34
4	NH_4I	28

Table S5: Screening of iodizing reagent. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (2.1 eq) in ^{i}PrOH/1,4-dioxane (3 mL, 1/1) stirred under 2 x 10 W purple LEDs at rt for 0.5 h. Then t-BuONO (2.0 eq), Iodizing reagent (5.0 eq) and MsOH (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

3.2 Screening of acid



Entry	Acid	Yield **6a** (%)[b]
1	HBF_4	77
2	CH_3COOH	70
3	CH_3SO_3H	72
4	CF_3SO_3H	70

Table S6: Screening of acid. [a]Reaction conditions: **1a** (0.3 mmol,1.0 eq), $B_2(pin)_2$ (2.1 eq) in ^{i}PrOH/1,4-dioxane (3 mL, 1/1) stirred under 2 x 10 W purple LEDs at rt for 0.5 h. Then t-BuONO (2.0 eq), CH_2I_2 (5.0 eq) and acid (2.0 eq) was added and stirred for 18 h. [b]Isolated yields.

3.3 General procedure for the synthesis of 3a – 3r

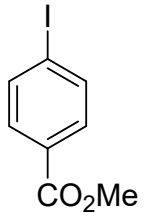
A sealed tube with magnetic stir bar was charged with **1** (0.3 mmol,1.0 eq), Bis(pinacolato)diboron (0.63 mmol, 2.1 eq), CH_2I_2 (1.5 mmol, 5.0 eq) in nitrogen atmosphere, followed by ^{i}PrOH/1,4-dioxane (1/1, 2 mL). HBF_4 (0.6 mmol, 2.0 eq) and t-BuONO (0.6 mmol, 2.0 eq) were added to the reaction solution half an hour after irradiation by the photoreaction device (380 nm light). The mixture was stirred until complete conversion of the **3** (monitored by TLC). The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 40:1 to 10:1).

3.4 General procedure for the synthesis of 3s – 3u

A sealed tube with magnetic stir bar was charged with **1** (0.3 mmol,1.0 eq), Bis(pinacolato)diboron (0.63 mmol, 2.1 eq), CCl_3Br (1.5 mmol, 5.0 eq) in nitrogen atmosphere, followed by ^{i}PrOH/1,4-dioxane (1/1, 2 mL). HBF_4 (0.6 mmol, 2.0 eq) and t-BuONO (0.6 mmol, 2.0 eq) were added to the reaction solution half an hour after irradiation by the photoreaction device (380 nm light). The mixture was stirred until complete conversion of the **3** (monitored by TLC). The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 40:1 to 10:1).

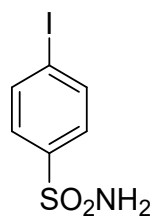
3.5 Characterization of products

Methyl 4-iodobenzoate (3a)



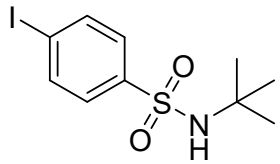
White solid, yield 77%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 137.8, 131.1, 129.7, 100.7, 52.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_8IO_2$ 292.9563, found 292.9568.

4-iodobenzenesulfonamide (3b)



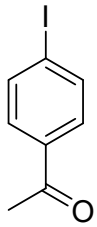
White solid, yield 90%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.40 (s, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 144.2, 138.3, 127.9, 99.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_6H_7INO_2S$ 283.9237, found 283.9239.

N-(tert-butyl)-4-iodobenzenesulfonamide (3c)



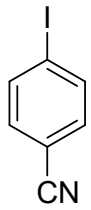
White solid, yield 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 2.8 Hz, 2H), 7.58 (s, 1H), 1.09 (s, 9H). **^{13}C NMR** (126 MHz, DMSO) δ 144.5, 138.4, 128.5, 100.0, 53.9, 30.2. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{15}INO_2S$ 339.9863, found 339.9867.

4-Iodoacetophenone (3d)



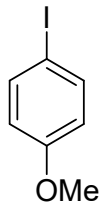
Yellow solid, yield 72%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 2.56 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.3, 137.9, 136.4, 129.7, 101.1, 26.5. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_8H_8IO 246.9614, found 246.9612.

4-iodobenzonitrile (3e)



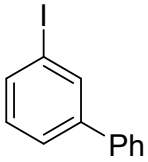
Yellow solid, yield 60%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.5, 133.2, 118.2, 111.8, 100.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_7H_5IN 229.9461, found 229.9455.

4-Iodoanisole (3f)



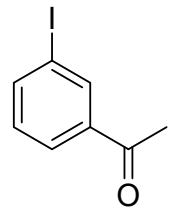
White solid, yield 56%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5, 138.2, 116.4, 82.7, 55.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_7H_8IO 234.9614, found 234.9618.

3-iodo-1,1'-biphenyl (3g)



White solid, yield 21%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 140.0, 136.2, 136.2, 130.4, 128.9, 127.9, 127.1, 126.4, 94.8. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_{10}I$ 280.9822, found 280.9823.

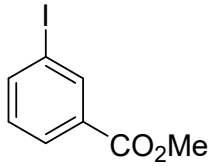
1-(3-iodophenyl)ethan-1-one (3h)



Yellow oil, yield 41%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.90 – 7.83 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 2.55 (s, 3H). **^{13}C NMR** (126

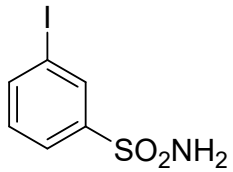
MHz, DMSO) δ 191.8, 137.1, 134.0, 132.5, 125.6, 122.7, 89.7, 21.8. **HRMS (ESI)** *m/z*: $[M+H]^+$ calculated for C_8H_8IO 246.9614, found 246.9618.

Methyl 3-iodobenzoate (3i)



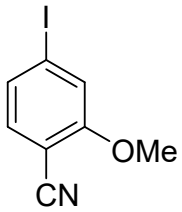
White solid, yield 56%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.6, 141.7, 138.5, 132.0, 130.1, 128.7, 93.8, 52.4. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_8IO_2$ 262.9563, found 262.9567.

3-iodobenzenesulfonamide (3j)



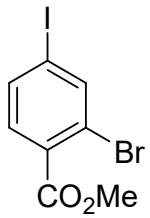
White solid, yield 66%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.46 (s, 2H), 7.38 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 146.3, 140.8, 134.4, 131.6, 125.3, 95.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_6H_7INO_2S$ 282.9237, found 282.9235.

4-iodo-2-methoxybenzonitrile (3k)



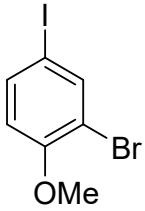
White solid, yield 53%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 3.1 Hz, 1H), 6.75 (d, *J* = 9.5 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 143.1, 141.6, 114.8, 113.5, 104.2, 81.3, 56.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_8H_7INO 259.9567, found 259.9567

Methyl 2-bromo-4-iodobenzoate (3l)



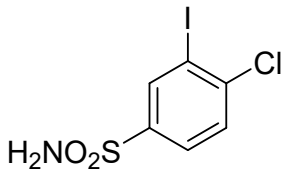
White solid, yield 54%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.7 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 142.5, 136.4, 132.4, 131.4, 122.6, 98.7, 52.6. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_6BrIO_2$ 340.8669, found 340.8665.

2-bromo-4-iodo-1-methoxybenzene (3m)



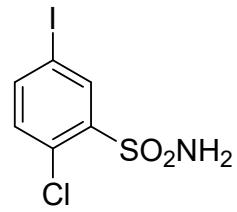
White solid, yield 40%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.1 Hz, 1H), 7.54 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0, 141.0, 137.3, 113.9, 113.0, 82.4, 56.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_7H_7BrIO 312.8719, found 312.8719.

4-chloro-3-iodobenzenesulfonamide (3n)



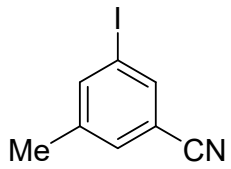
White solid, yield 70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 144.3, 141.4, 137.4, 130.4, 127.5, 99.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_6H_6ClINO_2S$ 317.8847, found 317.8847.

2-chloro-5-iodobenzenesulfonamide (3o)



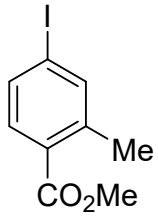
White solid, yield 61%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.95 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.72 (s, 2H), 7.43 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 143.0, 142.3, 137.3, 133.9, 130.8, 93.0. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_6H_6ClINO_2S$ 317.8847, found 317.8846.

3-iodo-5-methylbenzonitrile (3p)



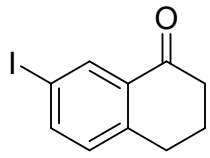
White solid, yield 51%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.42 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 141.2, 137.5, 131.8, 117.3, 113.9, 93.8, 20.8. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for C_8H_7IN 243.9618, found 243.9617.

Methyl 4-iodo-2-methylbenzoate (3q)



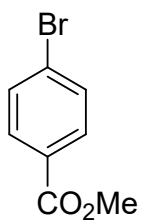
White solid, yield 38%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.62 – 7.57 (m, 2H), 3.88 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 142.2, 140.6, 135.0, 131.9, 129.0, 99.5, 52.0, 21.4. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_{10}IO_2$ 276.9720, found 276.9725.

7-iodo-3,4-dihydronaphthalen-1(2H)-one (3r)



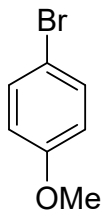
Yellow solid, yield 30%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 2.90 (t, *J* = 6.1 Hz, 2H), 2.66 – 2.62 (m, 2H), 2.13 (p, *J* = 6.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.9, 143.7, 141.9, 136.1, 134.2, 130.8, 91.6, 38.8, 29.3, 22.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{10}IO$ 272.9771, found 272.9765.

Methyl 4-bromobenzoate (3s)



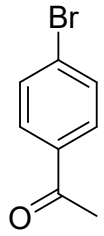
White solid, yield 60%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 131.7, 131.1, 129.1, 128.0, 52.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calculated for $C_8H_8BrO_2$ 214.9702, Found 214.9705.

1-bromo-4-methoxybenzene (3t)



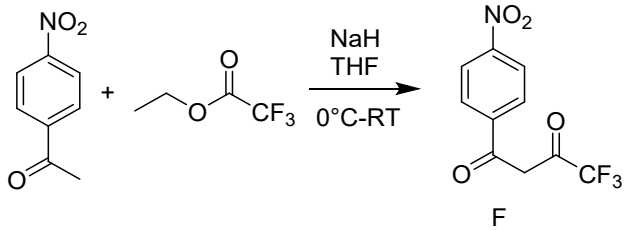
Yellow, yield39%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 158.73, 132.25, 115.75, 112.84, 55.45. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.7, 132.3, 115.8, 112.8, 55.5. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calculated for C_7H_8BrO 186.9753, Found 186.9754.

1-(4-bromophenyl)ethan-1-one (3u)



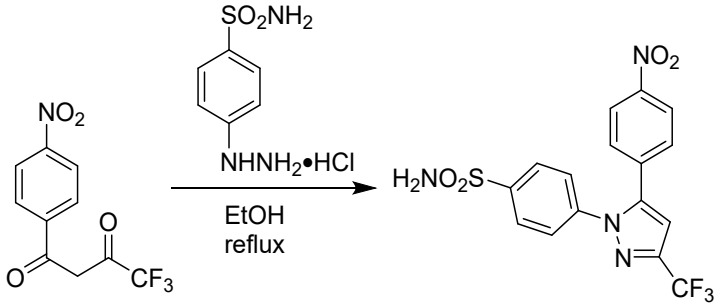
White solid, yield 43%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 2.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.0, 135.9, 131.9, 129.8, 128.3, 26.5. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calculated for C_8H_8BrO 198.9753, Found 198.9758.

3.5 Synthesis of 5



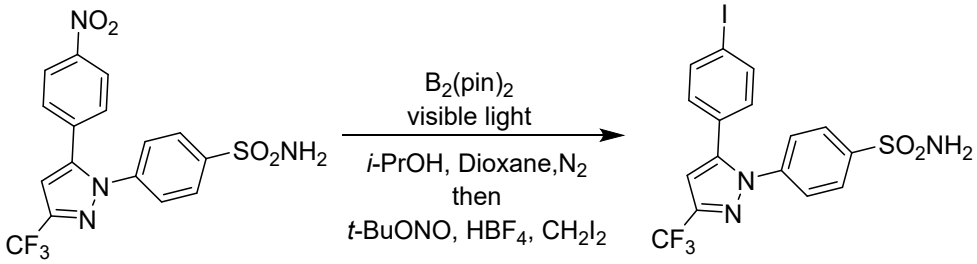
F

Synthesis of 4,4,4-Trifluoro-1-(4-nitrophenyl)-1,3-butanedione: Add a solution of acetophenone (825.7 mg, 5 mmol) in dry THF (20 mL) dropwise over 0.5 h to a mixture of NaH (480 mg, 20 mmol) and ethyl trifluoroacetate (2840 mg, 20 mmol) in dry THF (20 mL) and reflux the reaction mixture for 8 h. The reaction was quenched with dilute acetic acid aqueous solution (20 mL) and extracted into DCM (3 x 15 mL). The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by column chromatography (PE/EtOAc 3:1) afforded 4,4,4-Trifluoro-1-(4-nitrophenyl)-1,3-butanedione as gray-green solid (562 mg, yield 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.5 Hz, 2H), 8.14 (d, J = 8.5 Hz, 2H), 6.64 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.4, 179.2,178.9(d, J = 37.8 Hz), 150.7, 138.2, 128.6, 124.1, 120.2, 117.9(q, J = 284.8 Hz), 115.7, 113.4, 93.4. **^{19}F NMR** (471 MHz, CDCl3) δ -76.7. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_7F_3NO_4$ 262.0322, found 262.0330.



F **Celecoxib-G**
4

Synthesis of 4-(5-(4-nitrophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (Celecoxib-G): To a solution of 4,4,4-trifluoro-1-(4-bromophenyl)butane-1,3-dione (261 mg, 1 mmol) in EtOH (20 mL) at r.t. was added 4-Hydrazinylbenzenesulfonamide hydrochloride (246 mg, 1.1 mmol), the mixture was let to stir for 24 h at 70 °C, The reaction was quenched with H_2O (20 mL) and extracted into DCM (3 x 15 mL). The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by column chromatography (PE/ EtOAc 2:1) afforded 4-(5-(4-nitrophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide as White solid(164 mg, yield 40%). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.23 (d, J = 8.9 Hz, 2H), 7.87 (d, J = 8.6 Hz, 2H), 7.58 (dd, J = 13.7, 8.8 Hz, 4H), 7.50 (s, 2H), 7.41 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 148.1, 144.8, 143.6, 143.4, 143.1, 142.8(q, J= 37.8 Hz), 142.5, 141.1, 135.0, 130.8, 127.5, 127.2, 126.6, 124.8, 124.4, 122.7, 120.5, 108.2. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -60.3. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{12}F_3N_4O_4S$ 413.0526, found 413.0531.

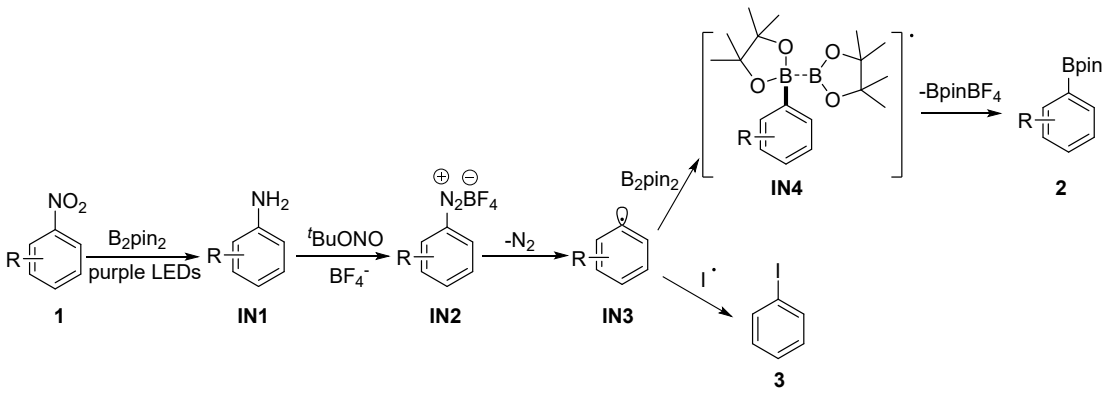


Celecoxib-G **Celecoxib-H**
4 **5**

Synthesis of 4-(5-(4-iodophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (Celecoxib-H): Prepared from **Celecoxib-G** (123.7 mg, 0.3 mmol) as starting materials according to *General Procedure II* and purified by flash

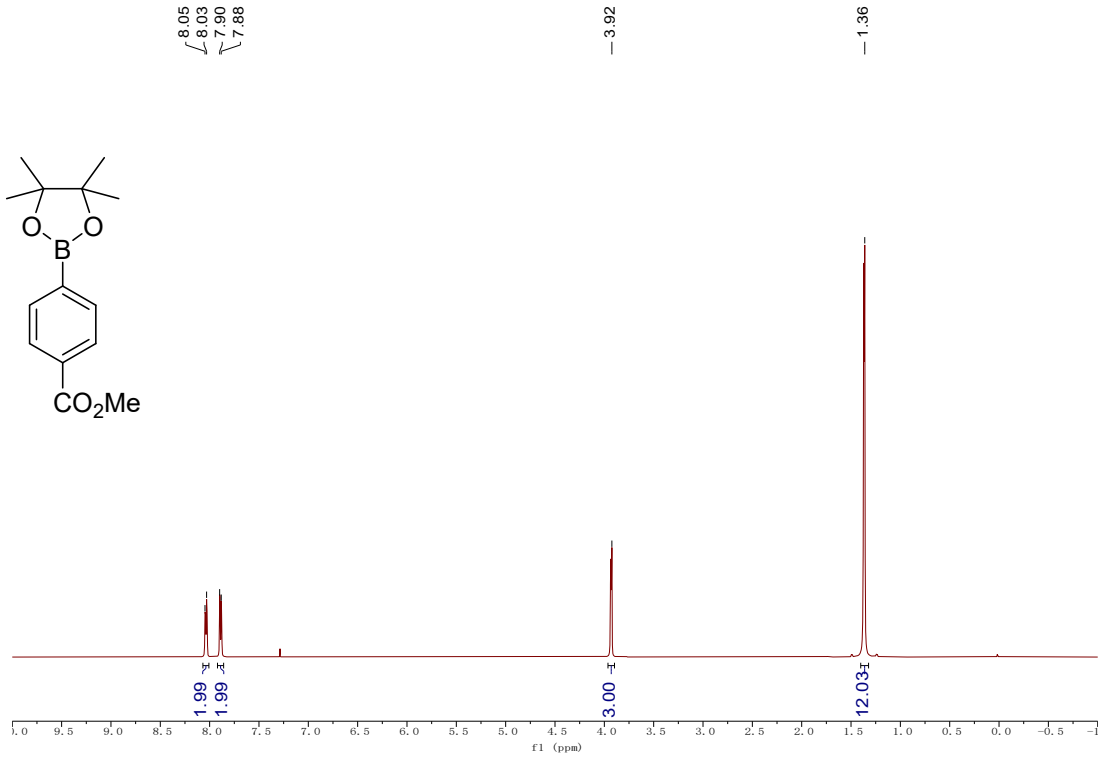
column chromatography (PE/EA 1:1) afforded **Celecoxib-H** as White solid, yield 35%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H), 5.28 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.7, 144.4,(q, *J* = 37.8 Hz), 144.1, 143.8, 142.1, 141.8, 138.3, 130.4, 128.0, 127.7, 125.6, 124.1, 122.0(q, *J* = 269.6 Hz), 119.8, 117.7, 106.7, 95.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.9. **HRMS** (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{12}F_3IN_3O_2S$ 493.9642, found 493.9645.

4. Plausible Pathway for the Reaction

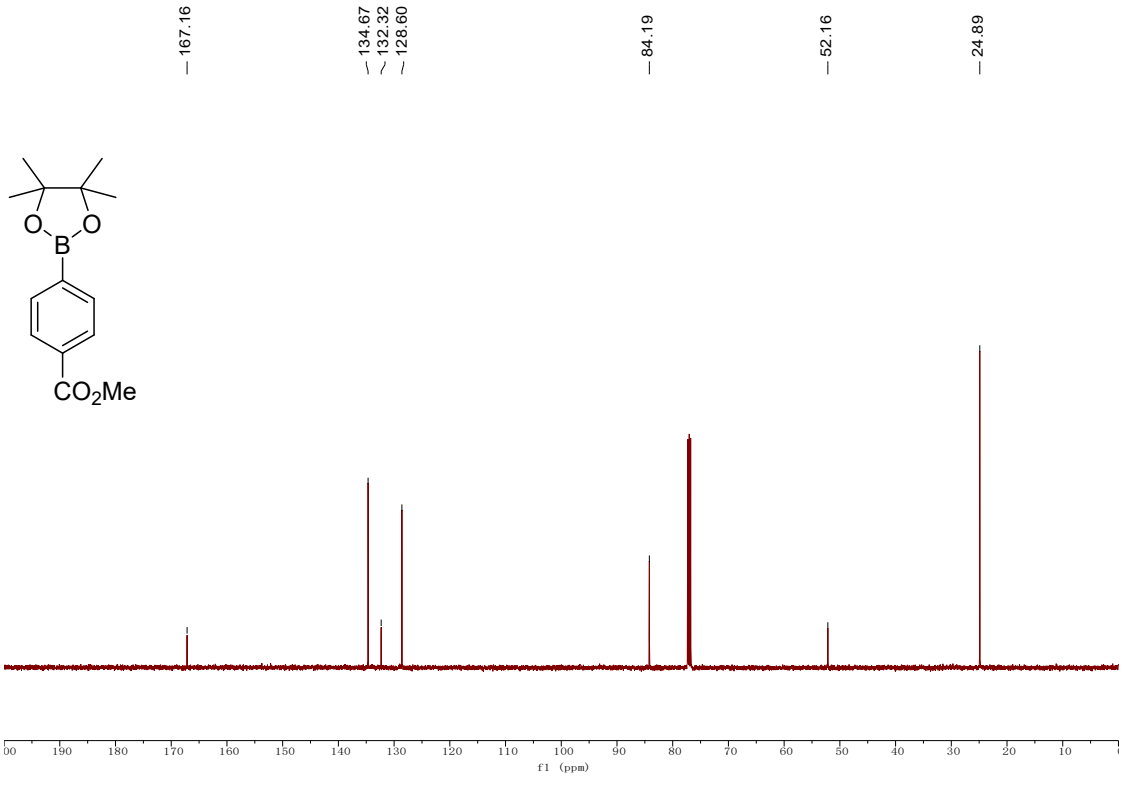


Based on the mechanism of Májek et al. and combined with our experimental results, we propose a possible reaction pathway.[1-3] Nitroarenes are treated with B_2pin_2 and purple LEDs to produce aniline **IN1**, followed by tert-butyl nitrite and fluoroborate to produce diazonium salt **IN2**. Diazo salts **IN2** easily lose nitrogen to form aryl radicals **IN3**. Then, the aryl radical **IN3** is trapped by B_2pin_2 to form radical intermediates **IN4**. Finally, the transition state **IN4** leads to B-B bond fission, and the final product 2 is formed. The way of forming iodine products is similar to the boration reaction.

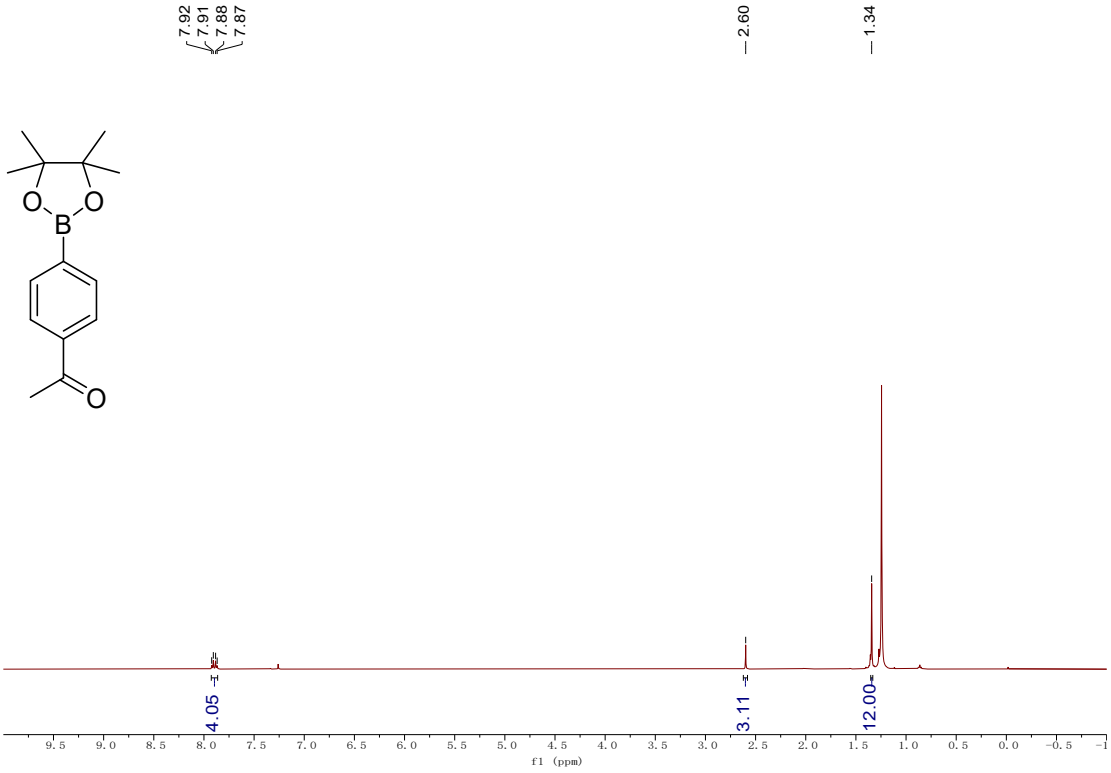
5. NMR Spectra



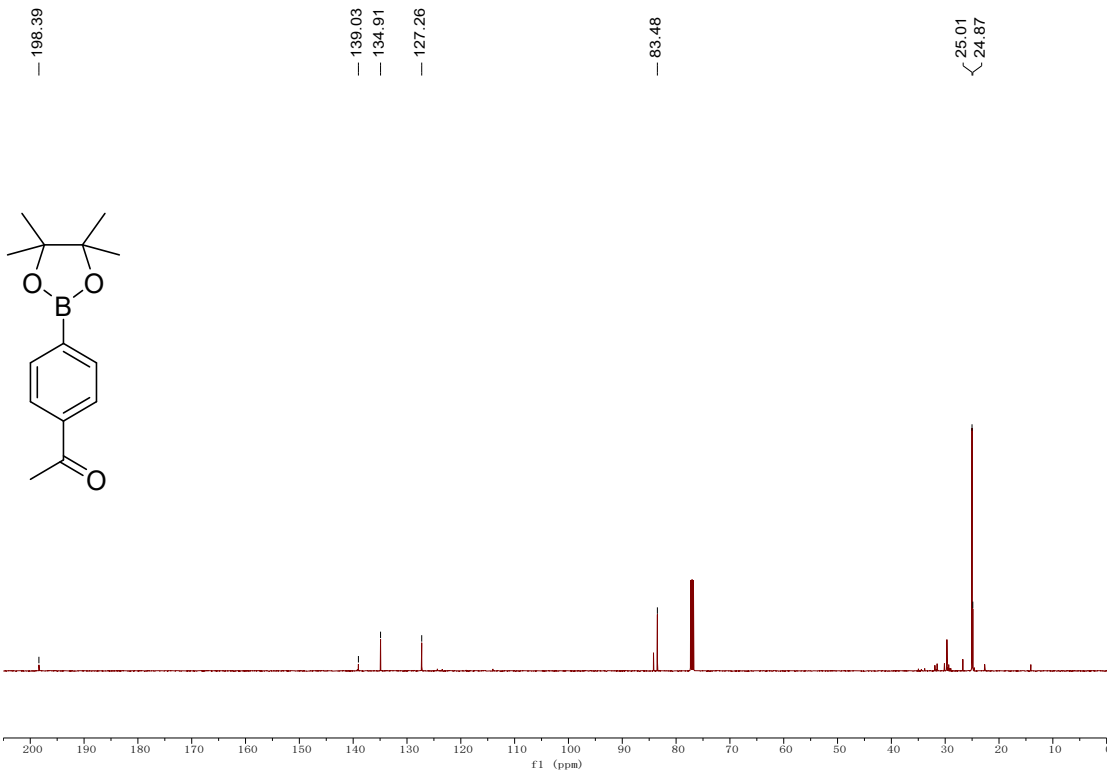
^{1}H NMR Spectrum of **2a**



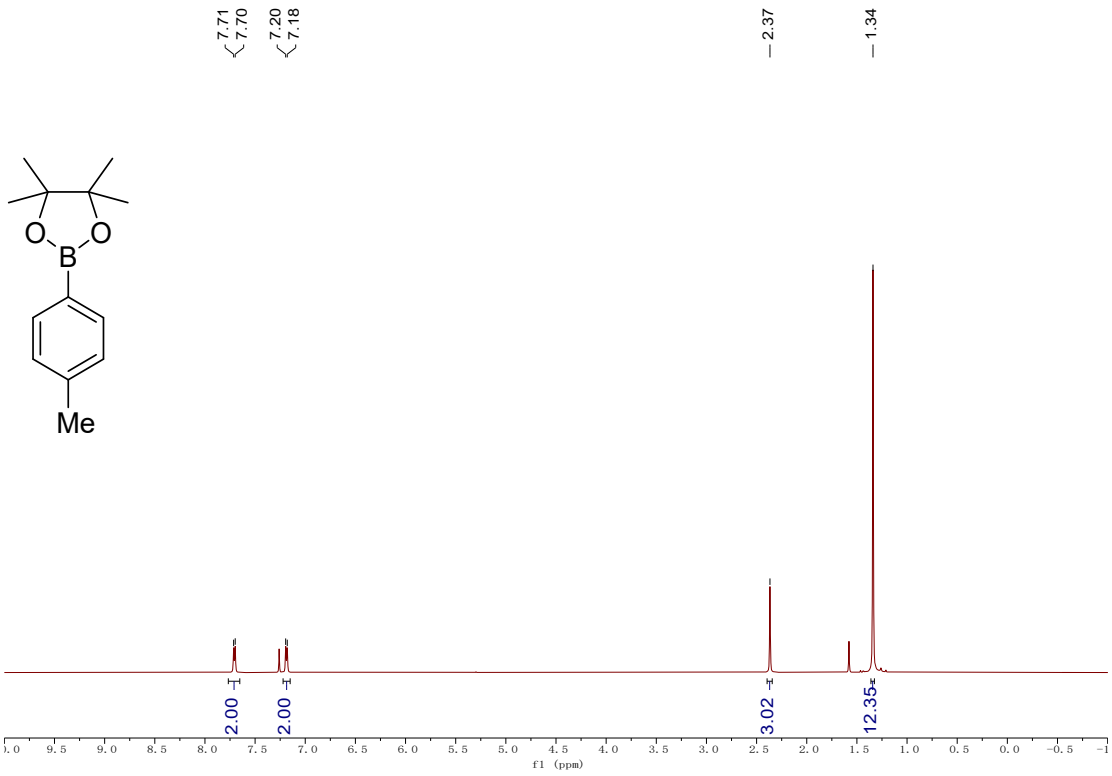
^{13}C NMR Spectrum of **2a**



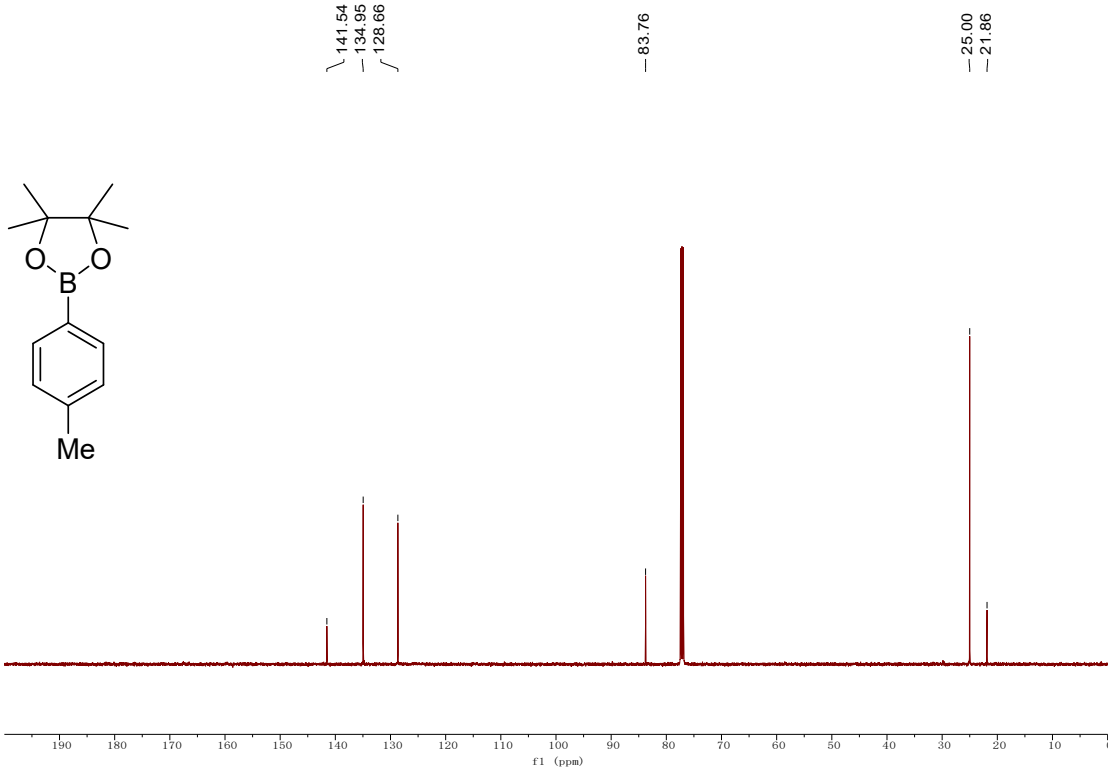
^{1}H NMR Spectrum of **2b**



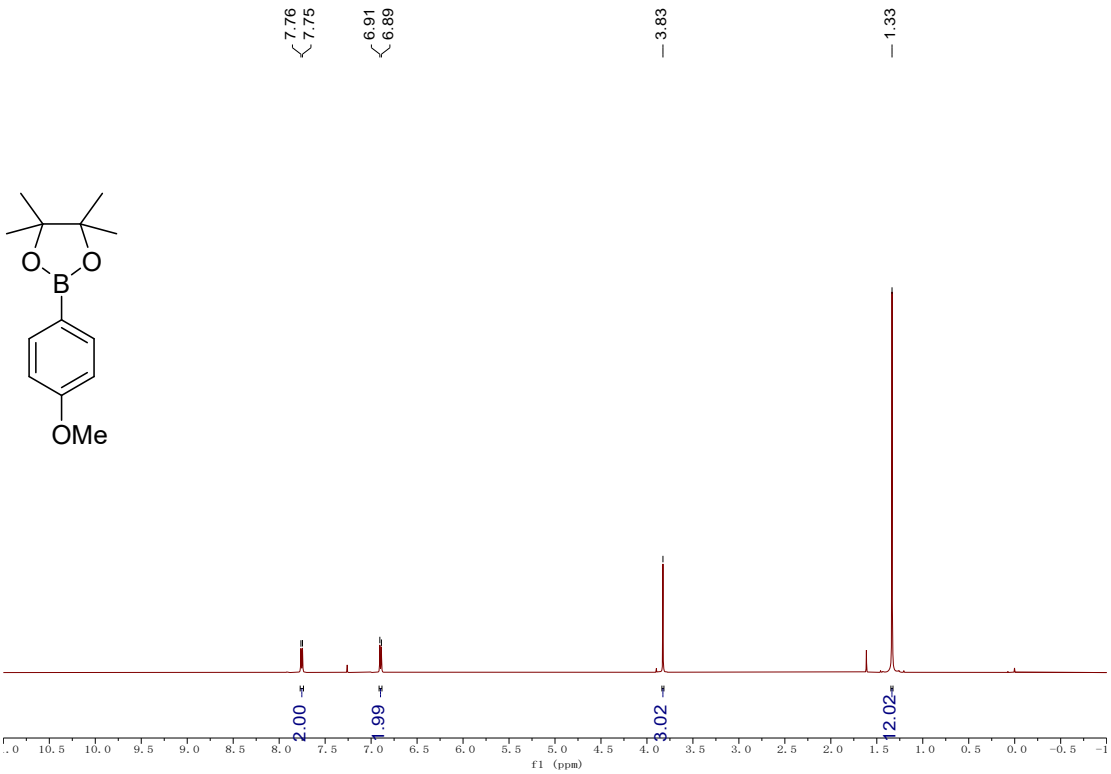
^{13}C NMR Spectrum of **2b**



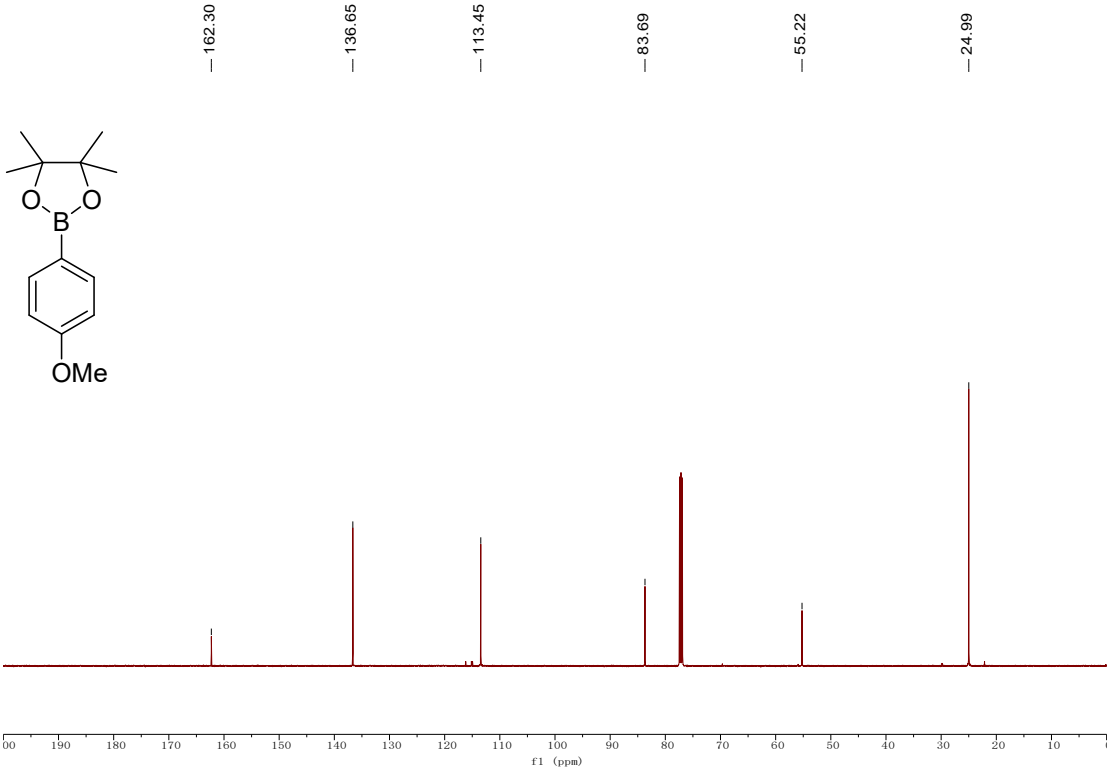
^{1}H NMR Spectrum of **2c**



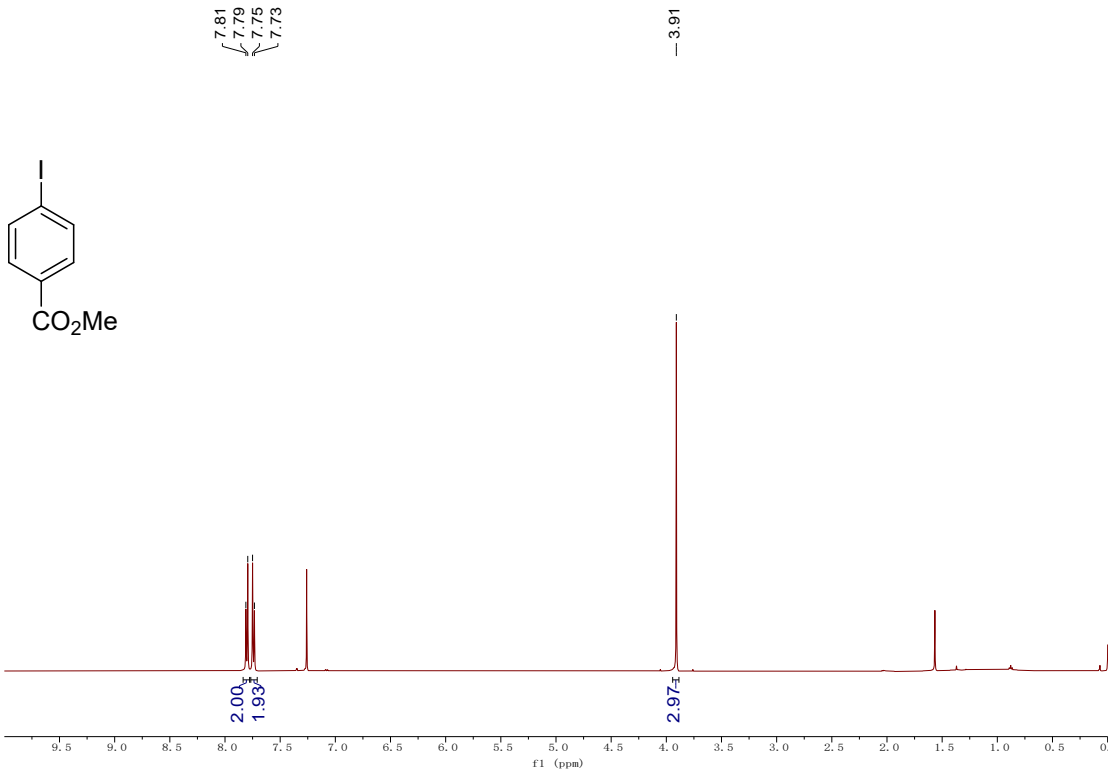
^{13}C NMR Spectrum of **2c**



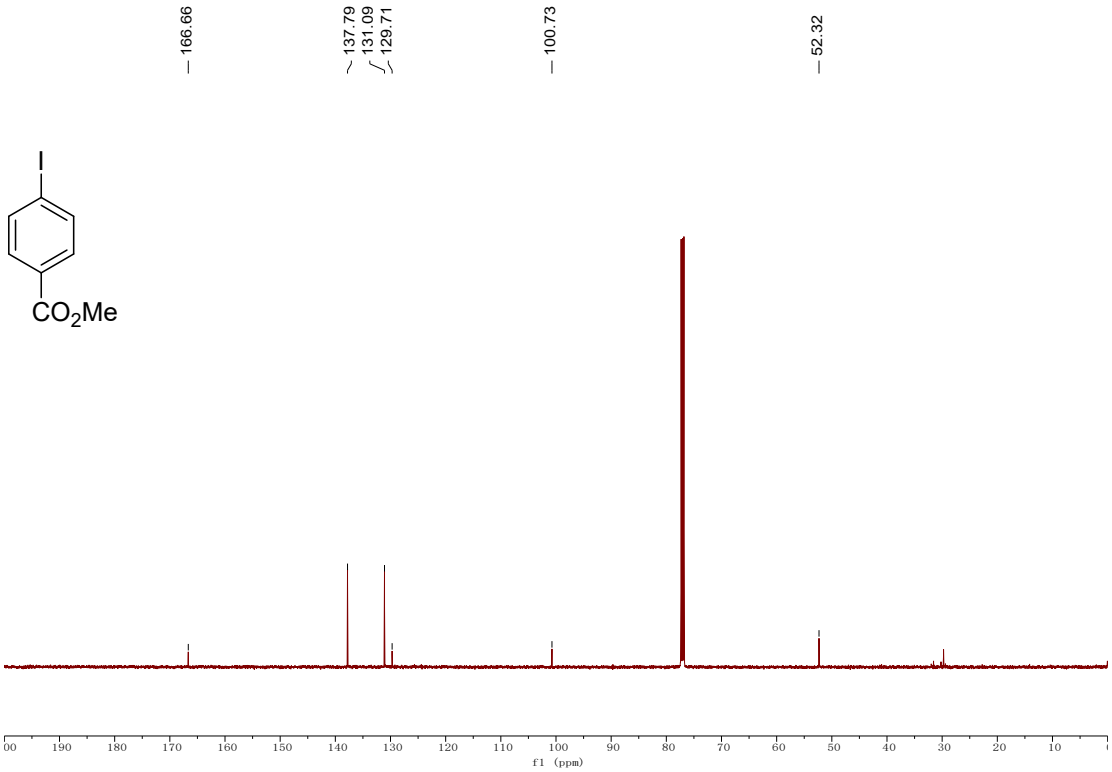
^{1}H NMR Spectrum of **2d**



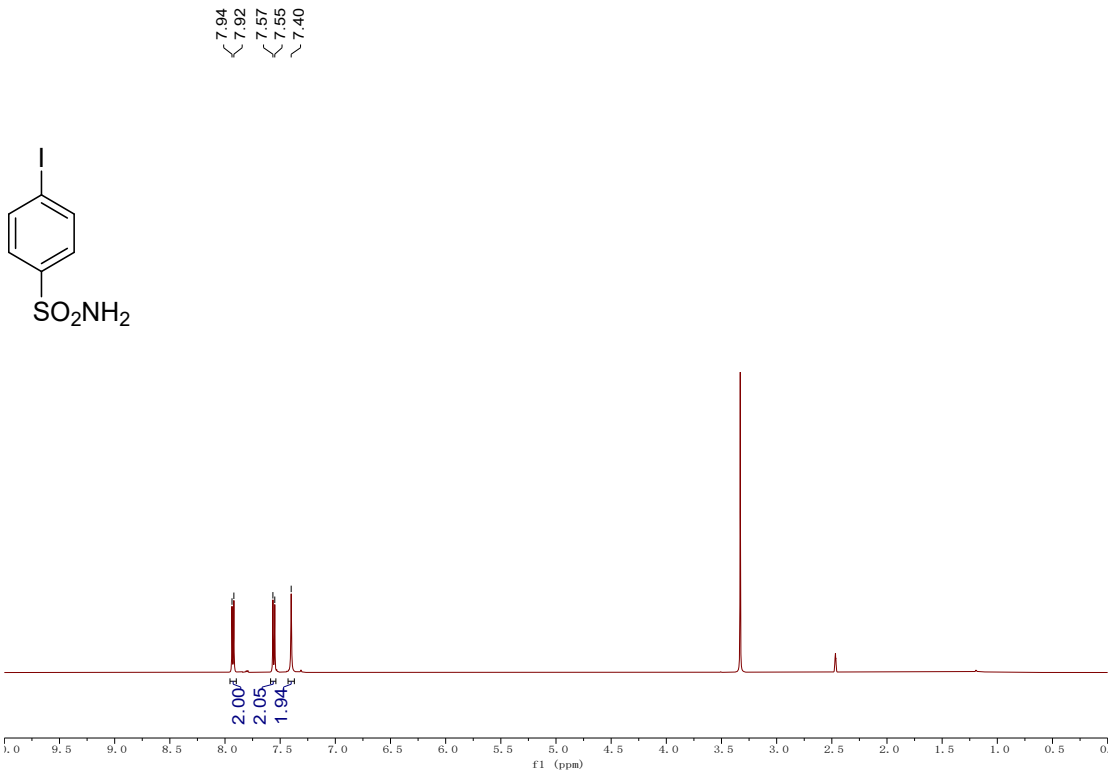
^{13}C NMR Spectrum of **2d**



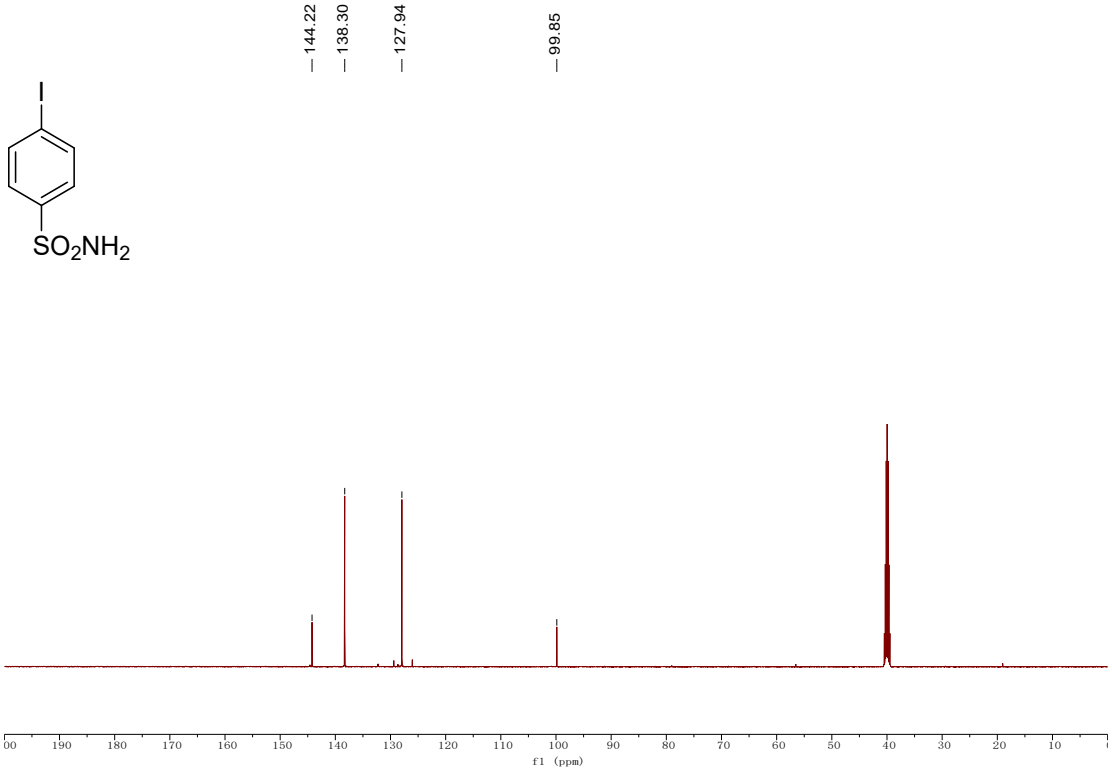
^{1}H NMR Spectrum of **3a**



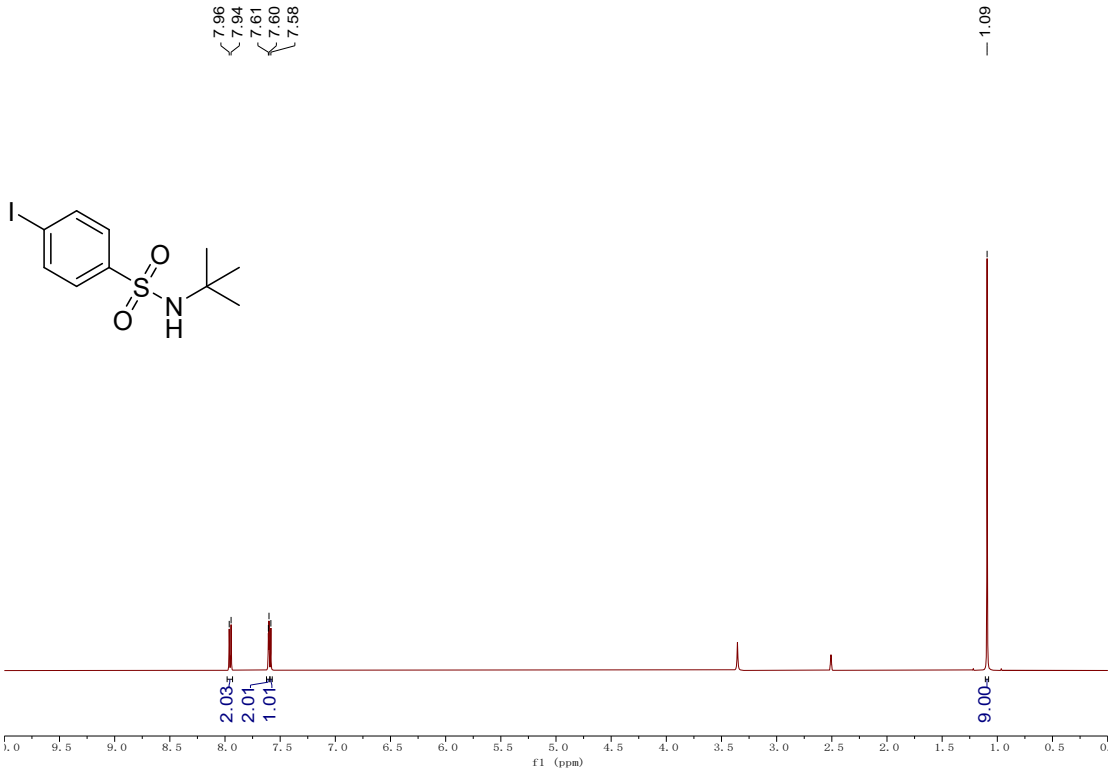
^{13}C NMR Spectrum of **3a**



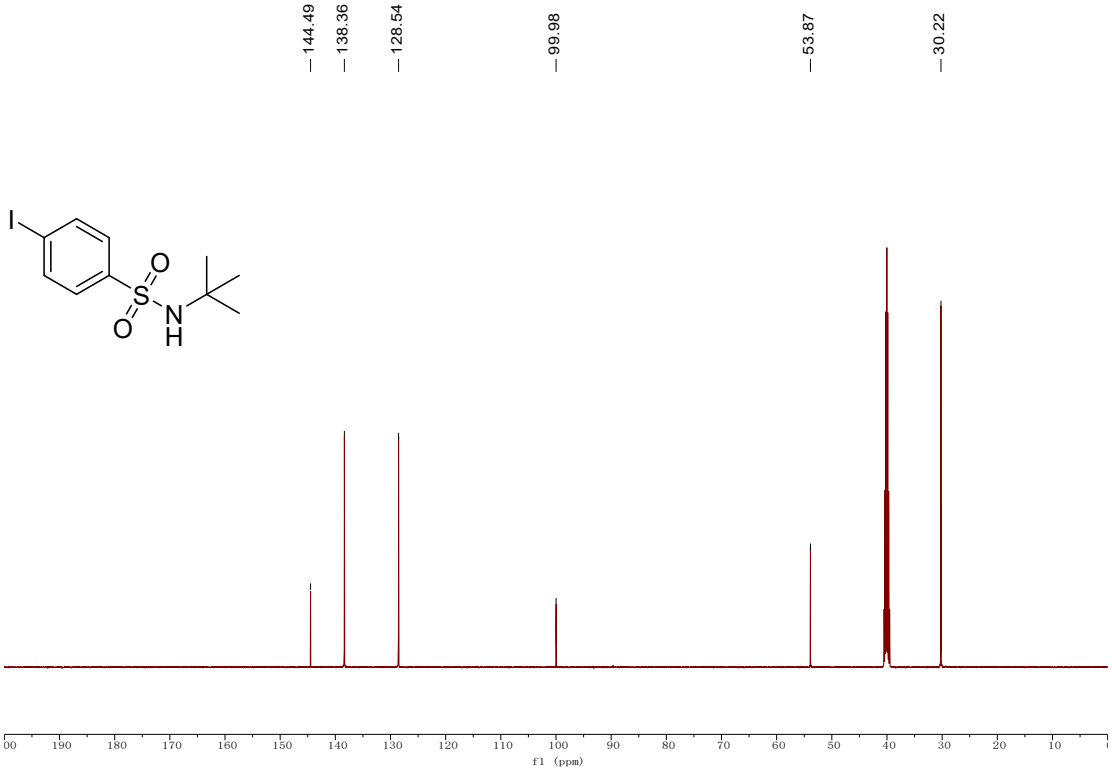
^{1}H NMR Spectrum of **3b**



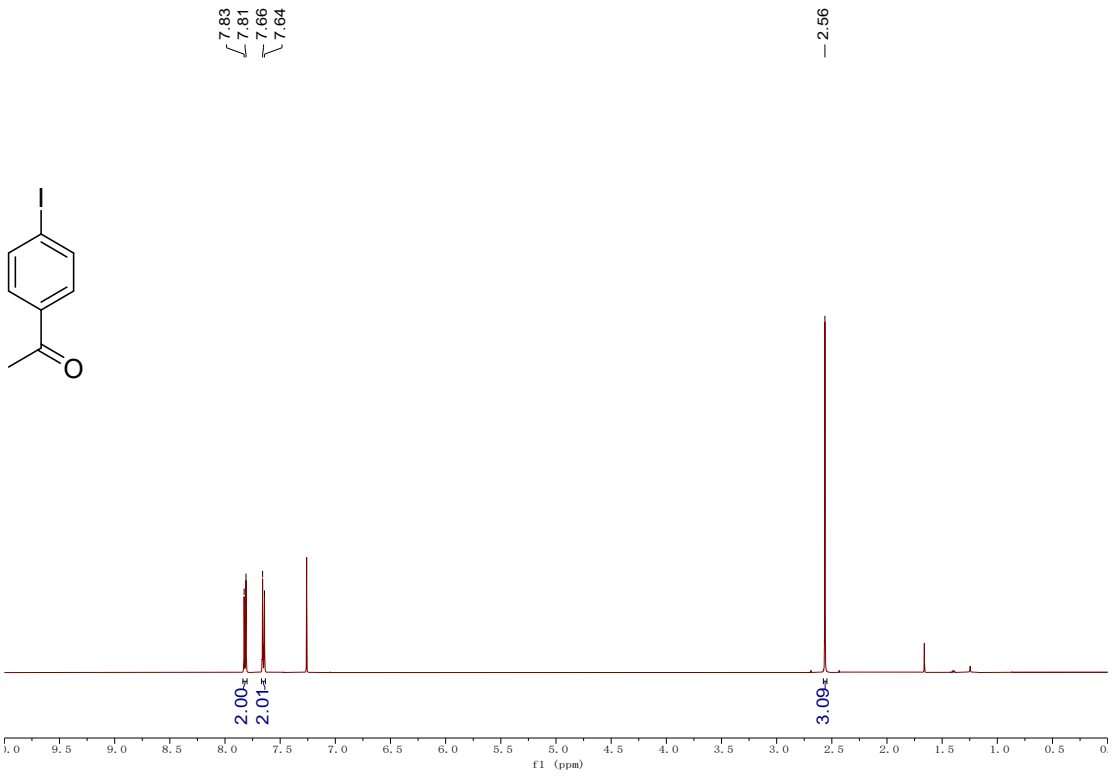
^{13}C NMR Spectrum of **3b**



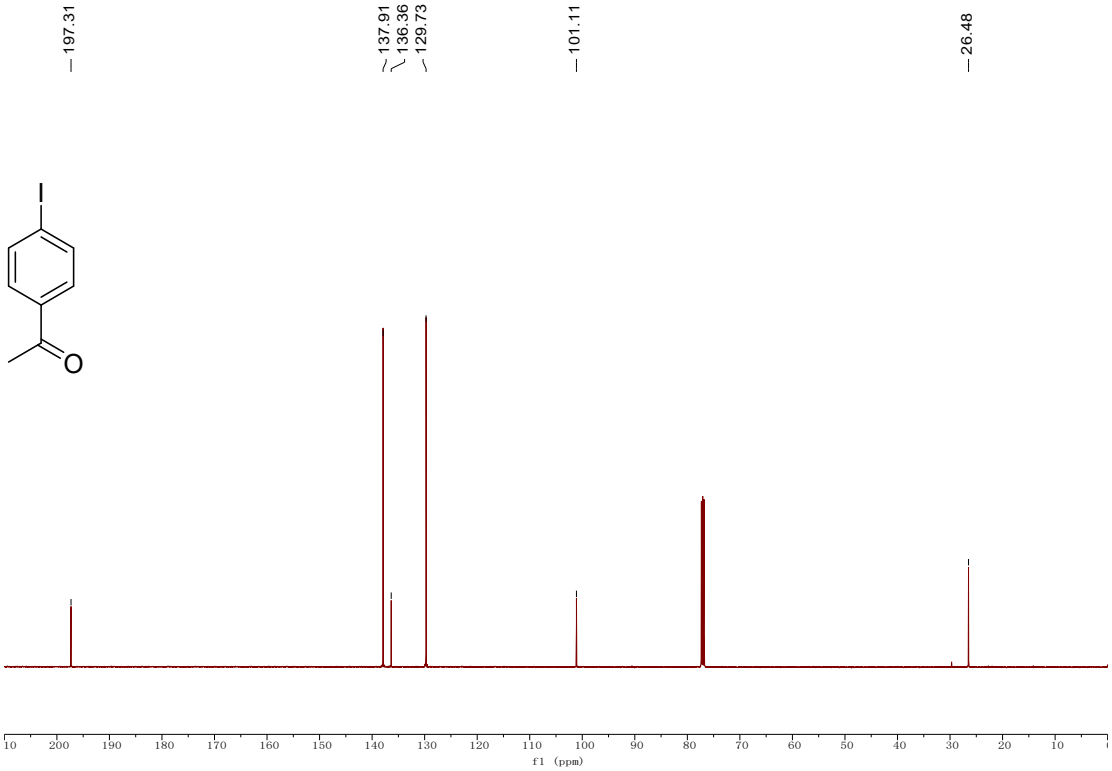
^{1}H NMR Spectrum of **3c**



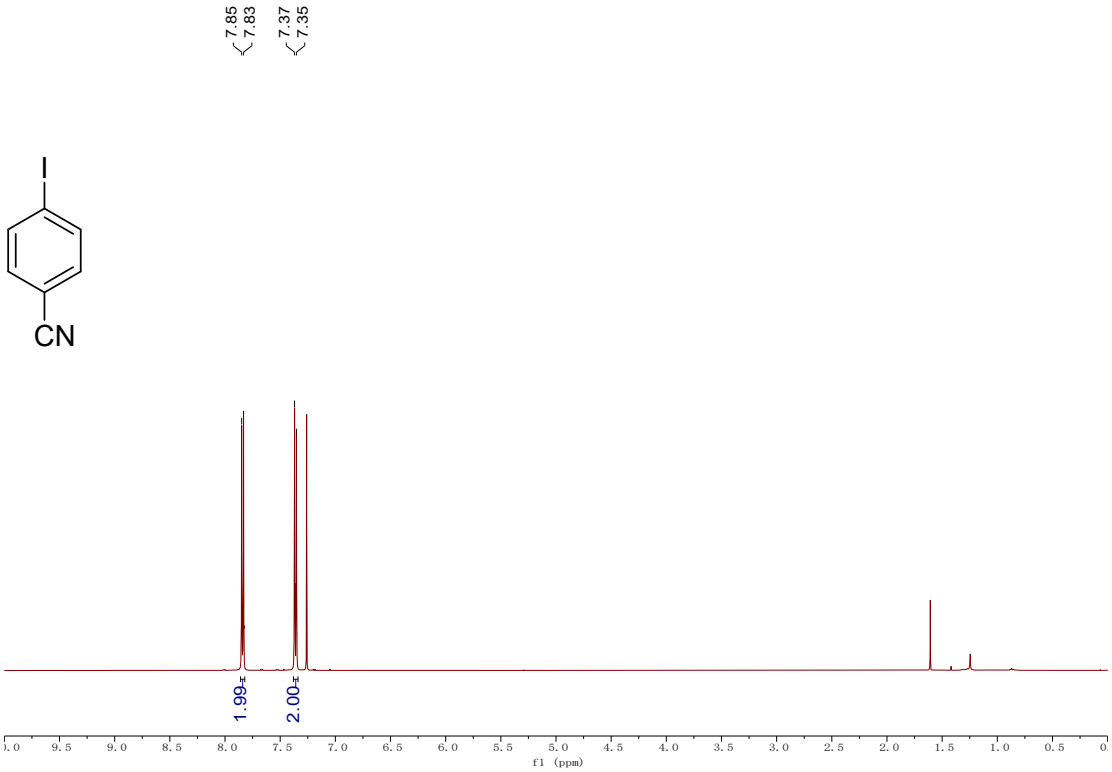
^{13}C NMR Spectrum of **3c**



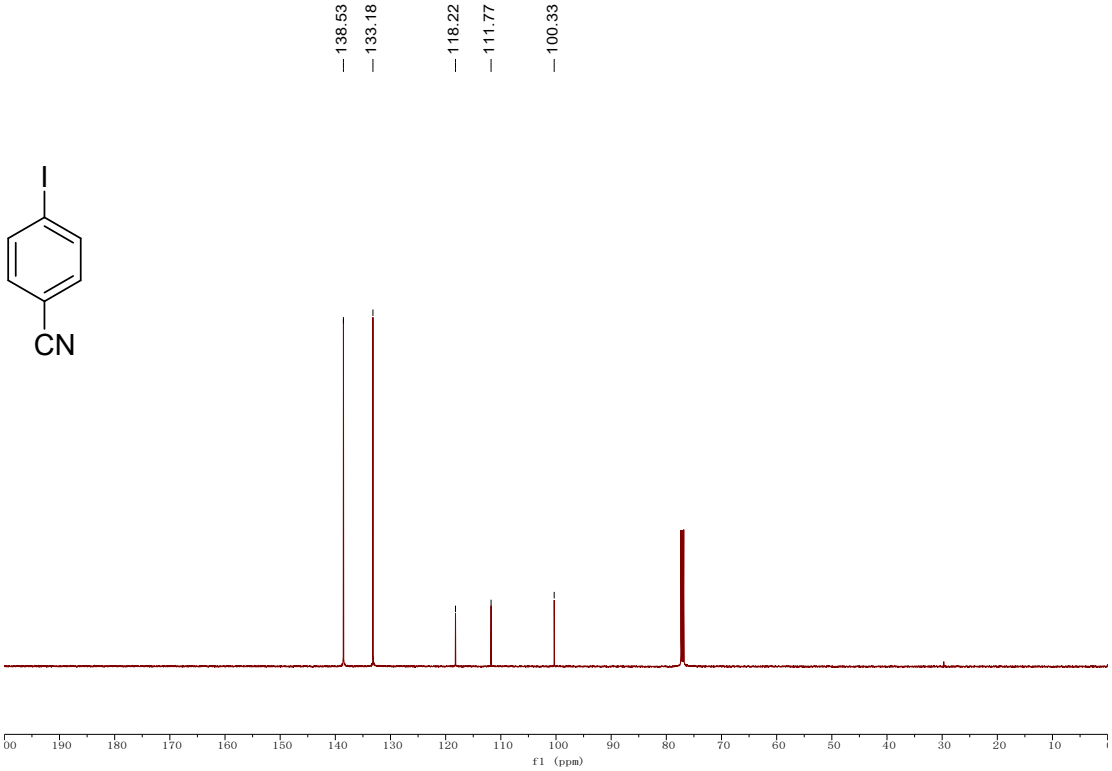
^{1}H NMR Spectrum of **3d**



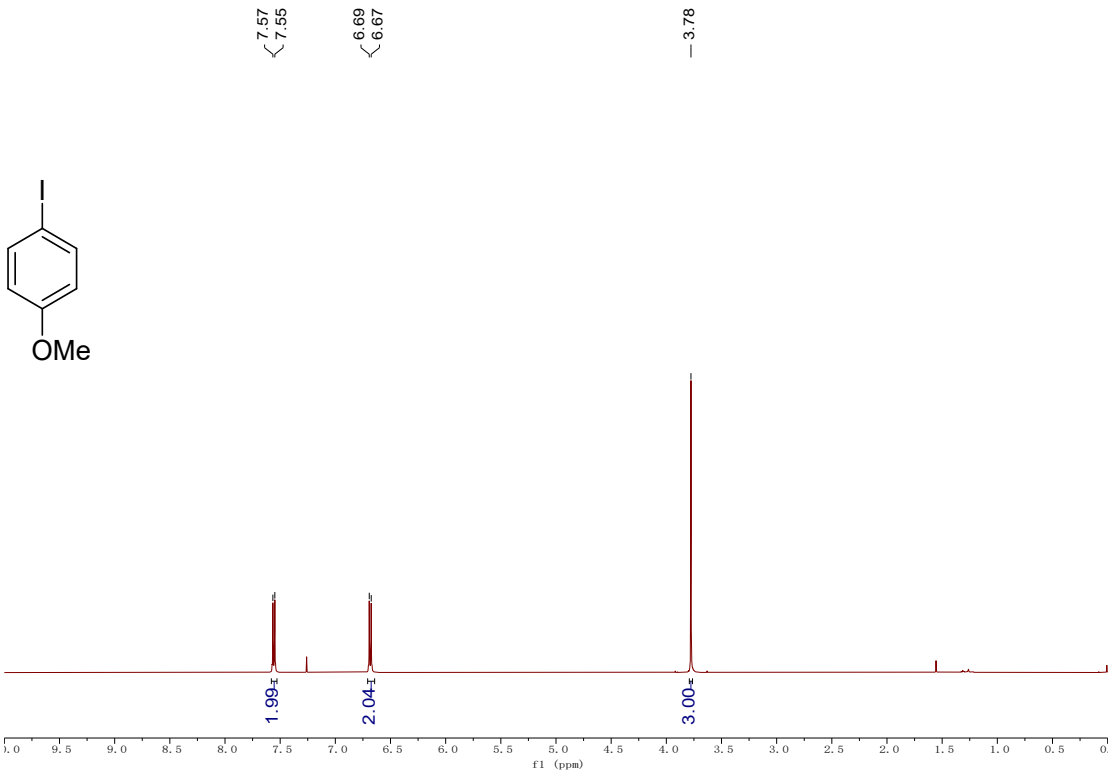
^{13}C NMR Spectrum of **3d**



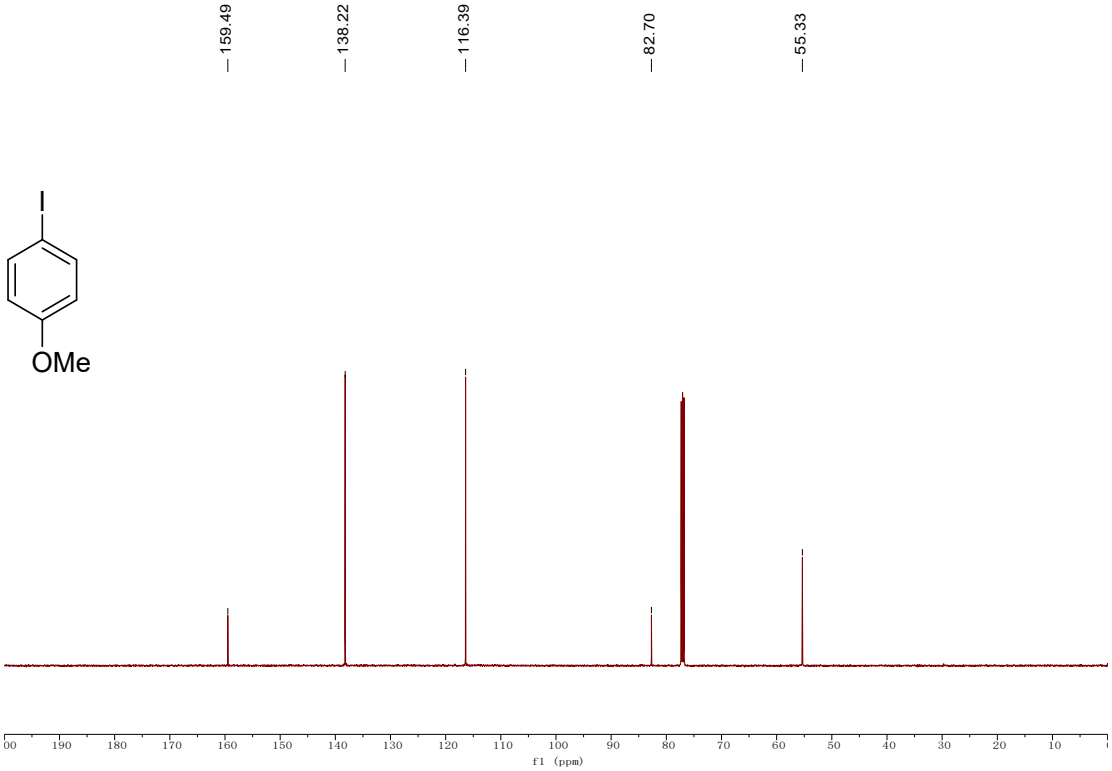
^{1}H NMR Spectrum of **3e**



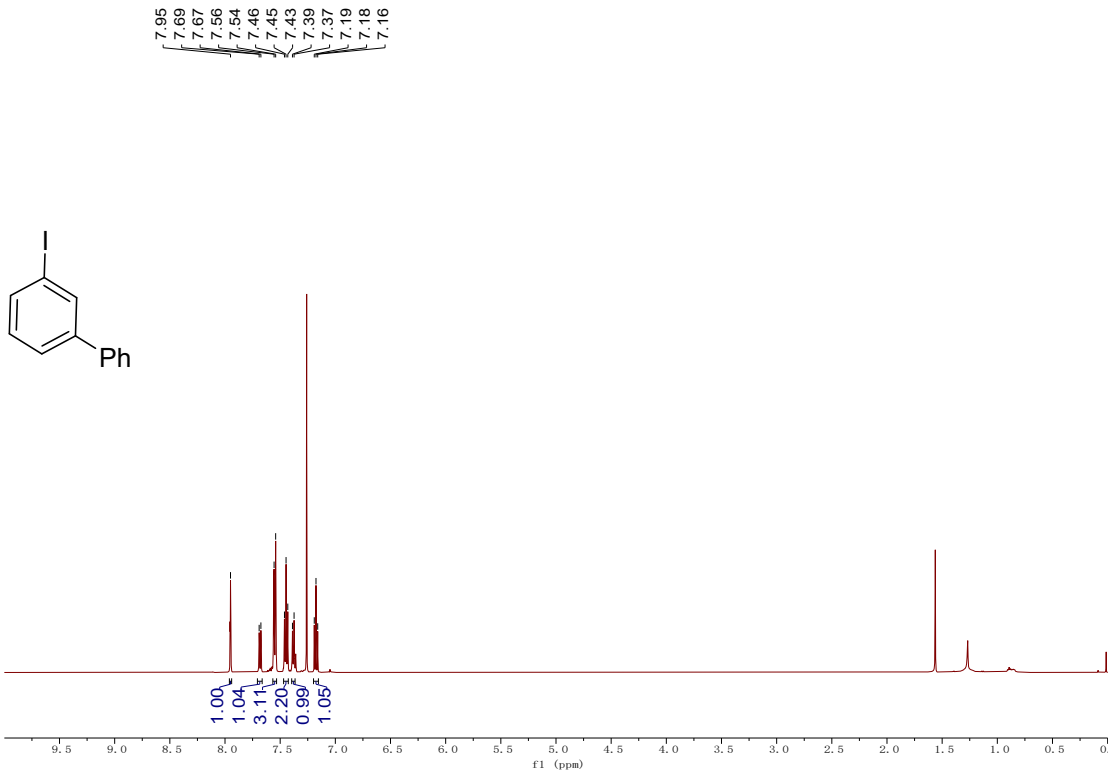
^{13}C NMR Spectrum of **3e**



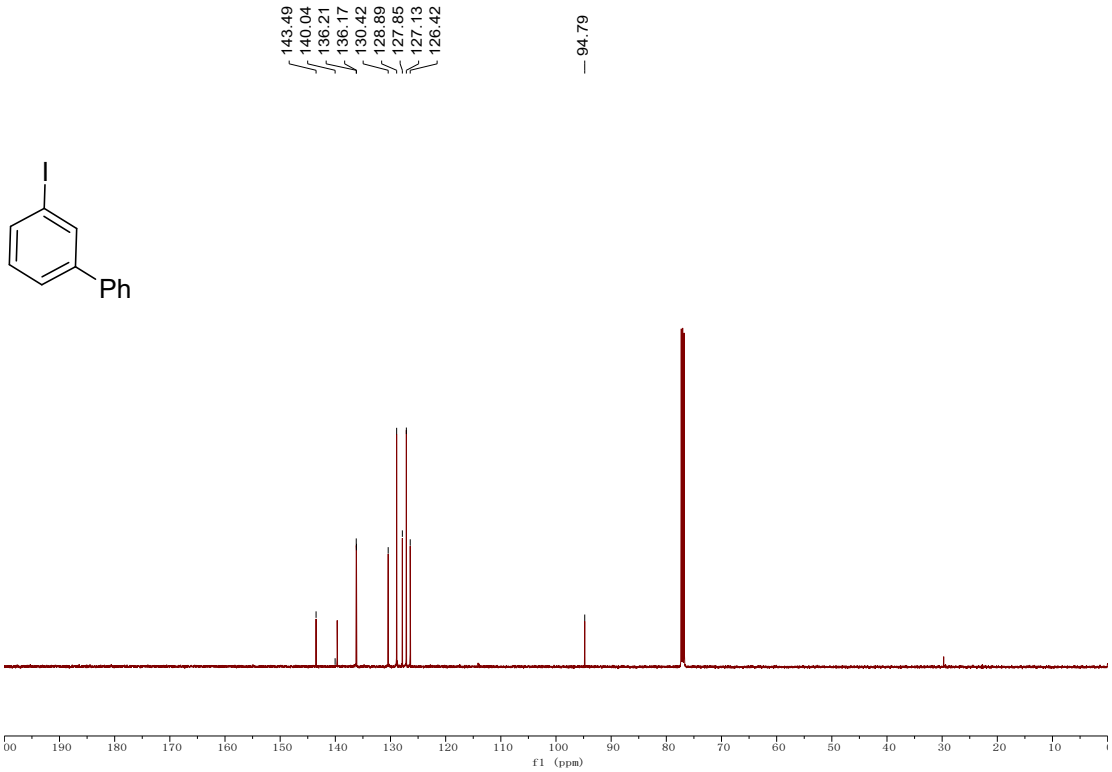
^{1}H NMR Spectrum of **3f**



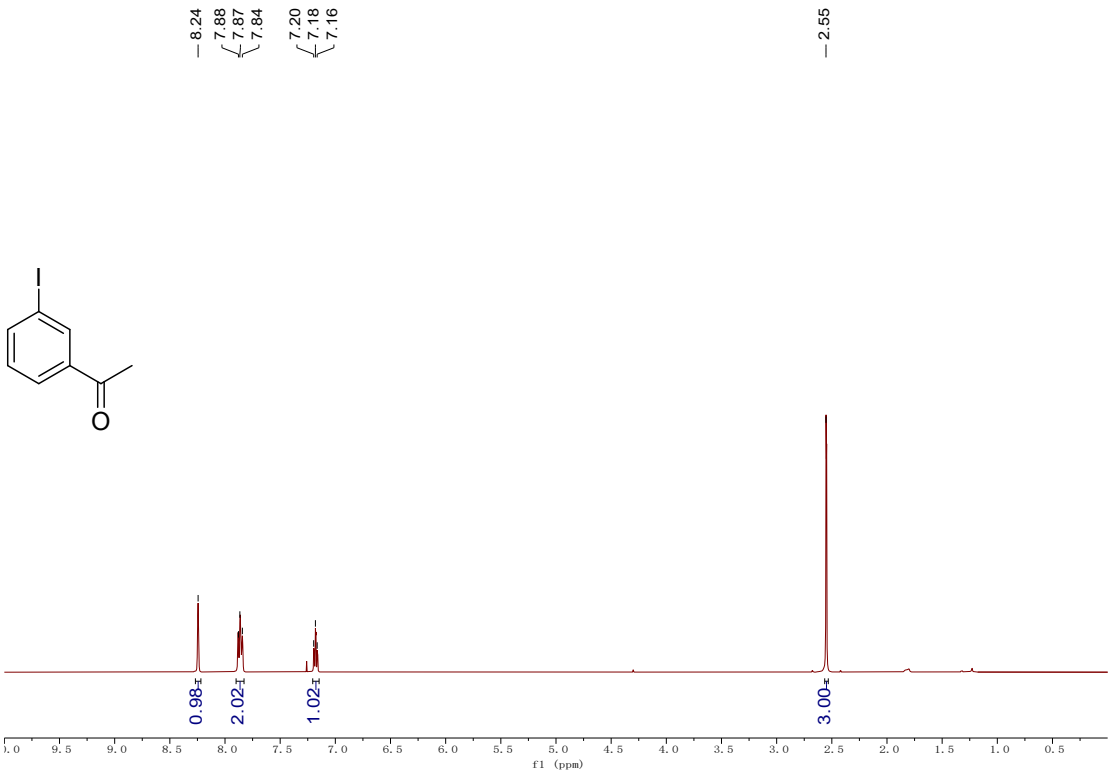
^{13}C NMR Spectrum of **3f**



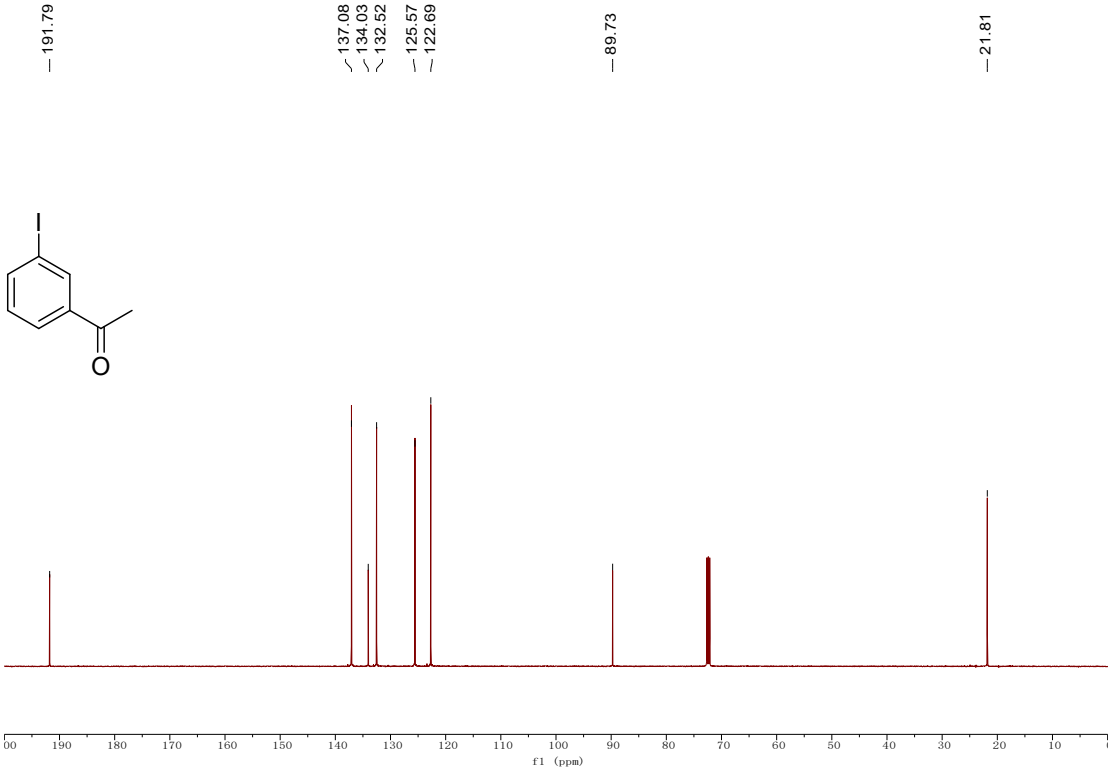
^{1}H NMR Spectrum of **3g**



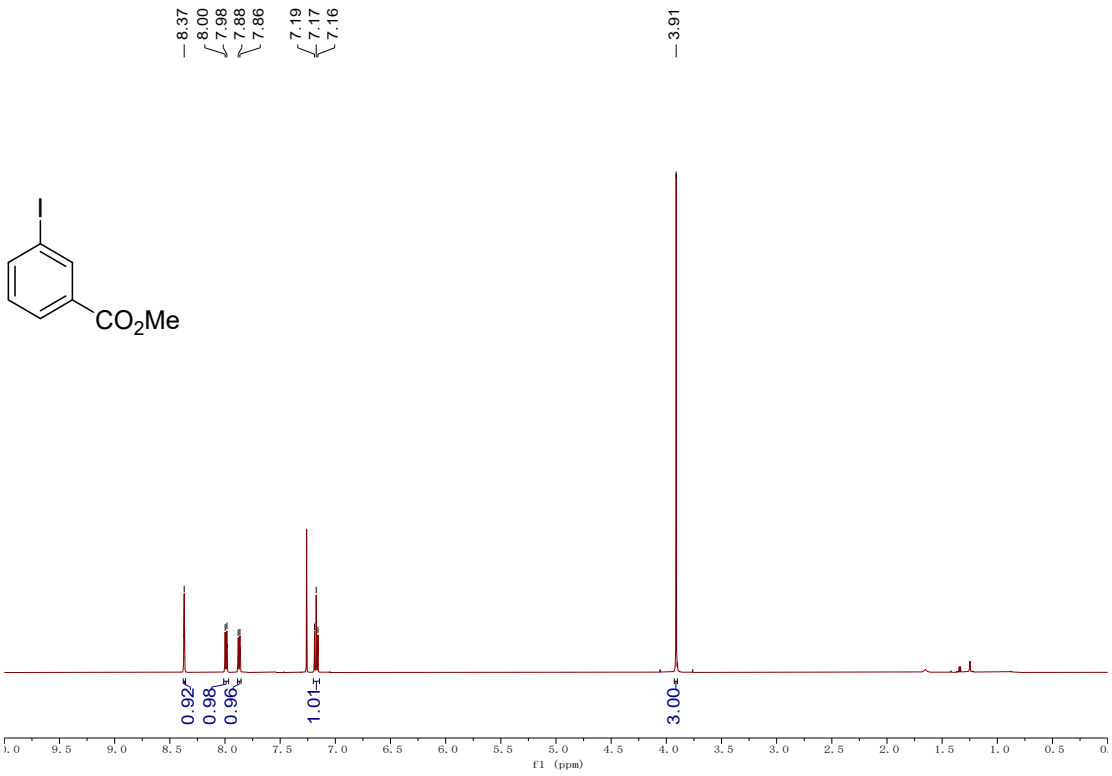
^{13}C NMR Spectrum of **3g**



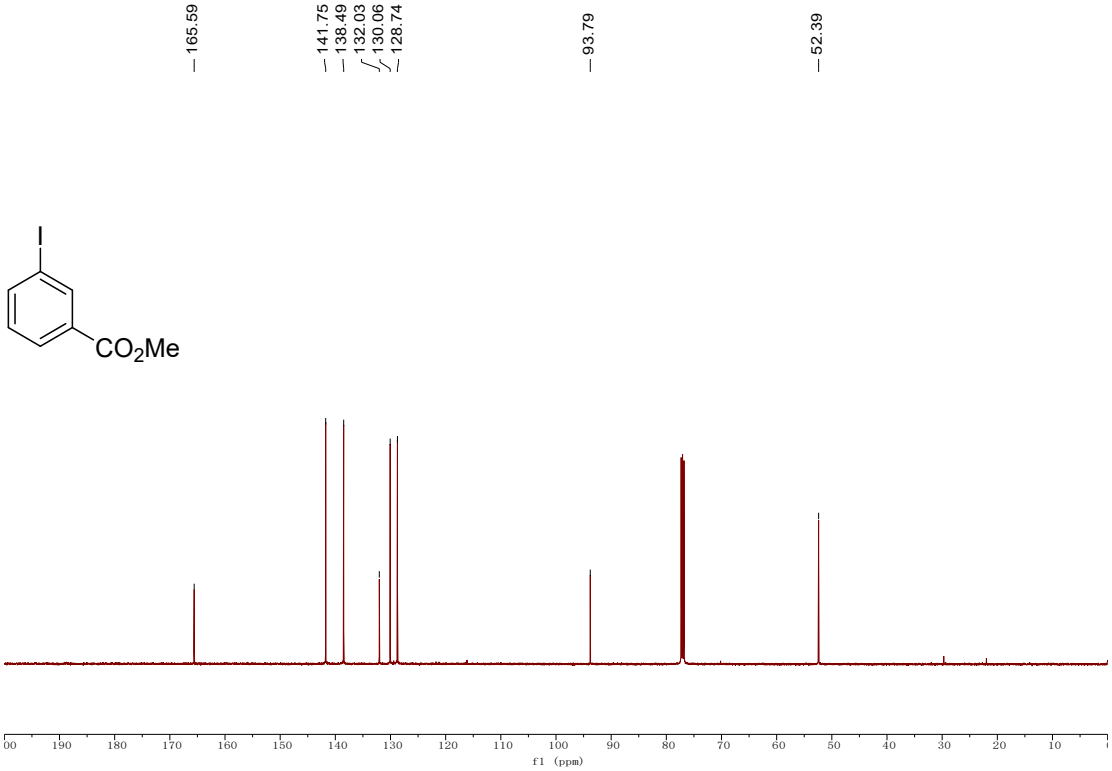
^{1}H NMR Spectrum of **3h**



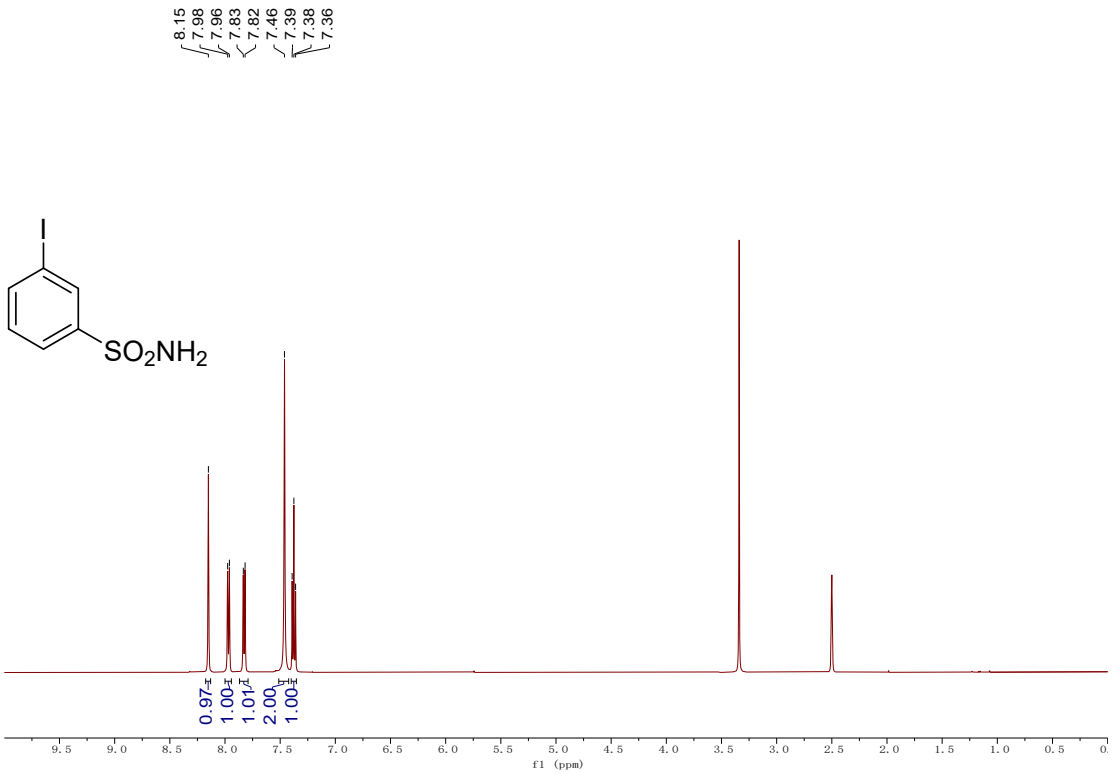
^{13}C NMR Spectrum of **3h**



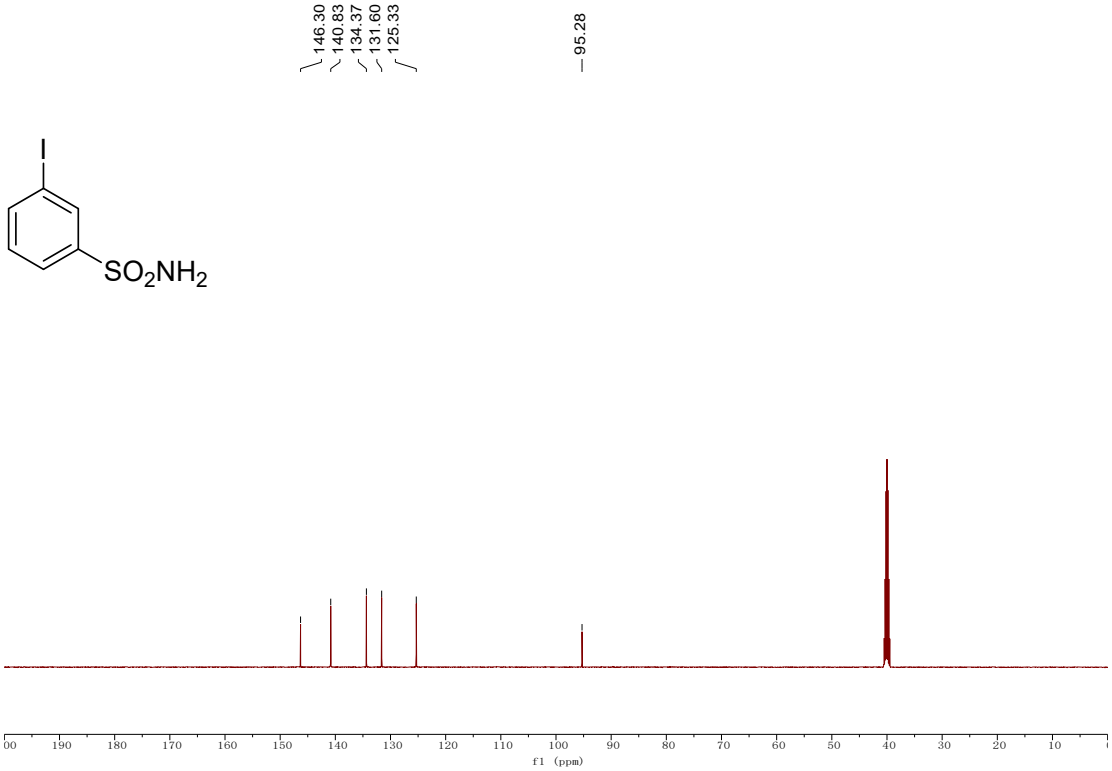
^{1}H NMR Spectrum of **3i**



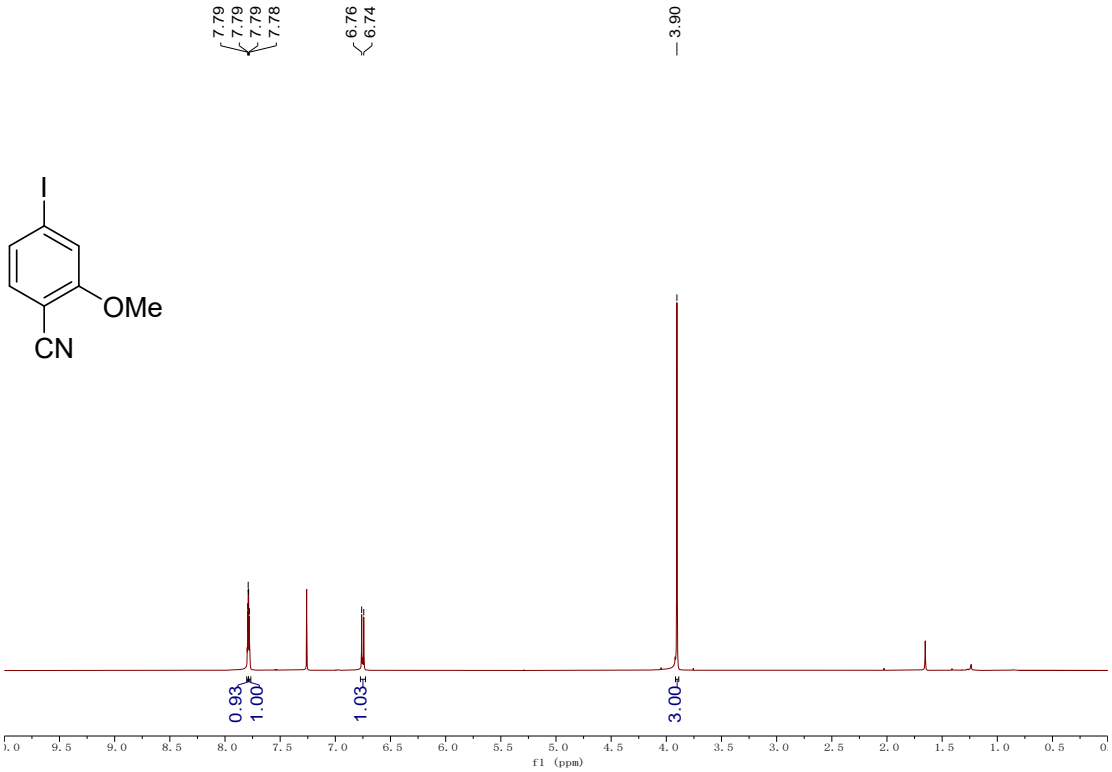
^{13}C NMR Spectrum of **3i**



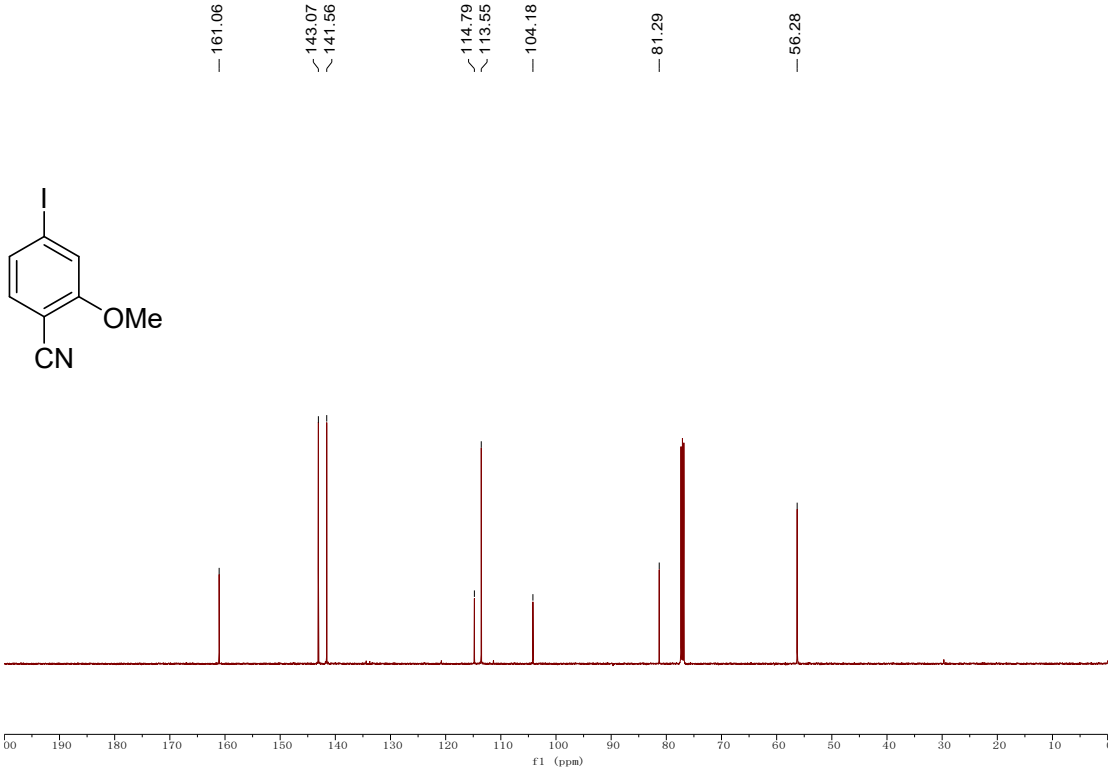
^{1}H NMR Spectrum of **3j**



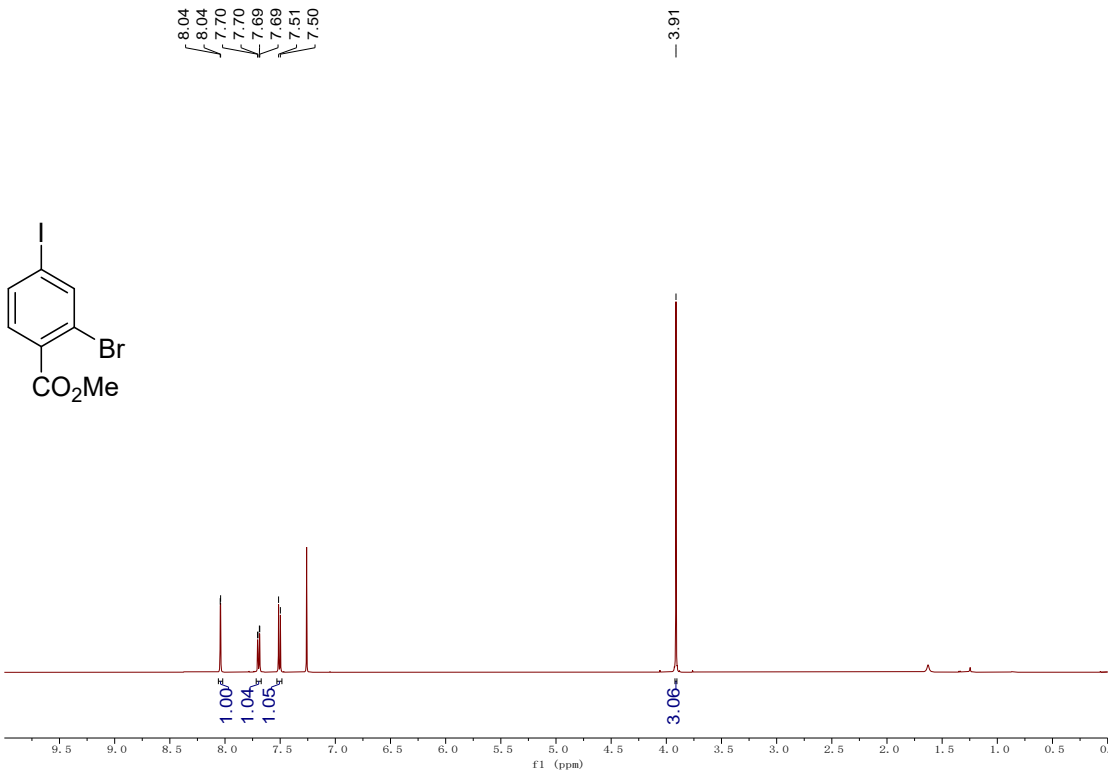
^{13}C NMR Spectrum of **3j**



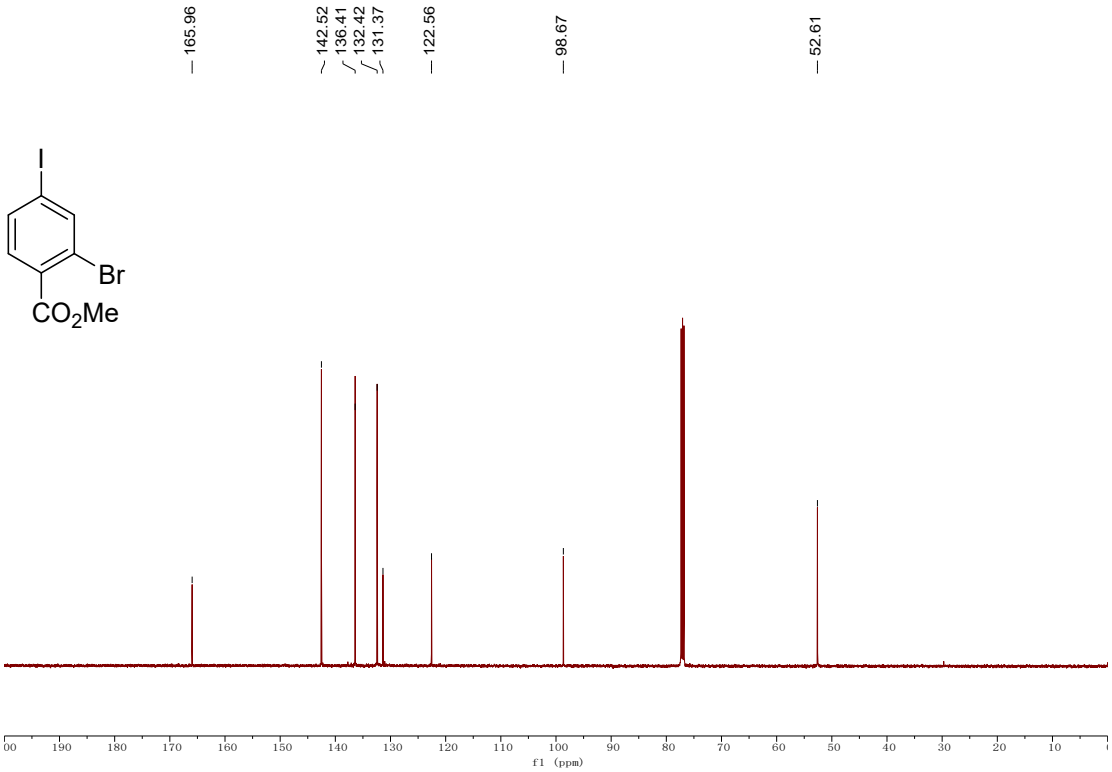
^{1}H NMR Spectrum of **3k**



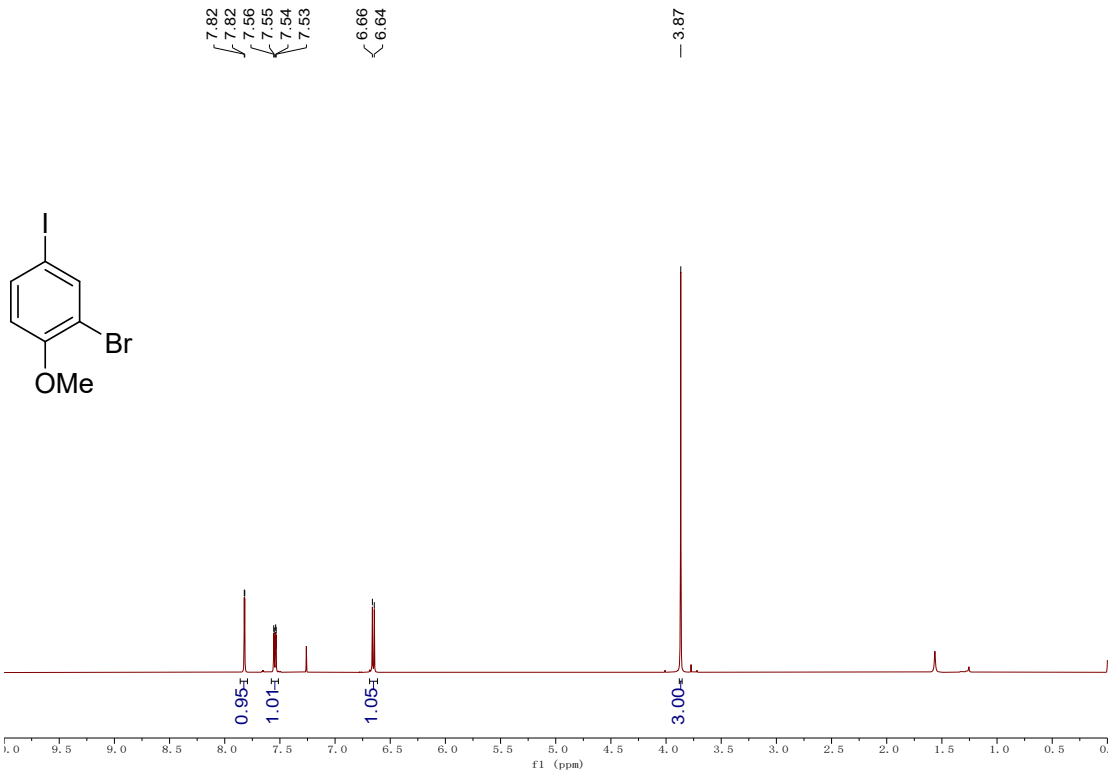
^{13}C NMR Spectrum of **3k**



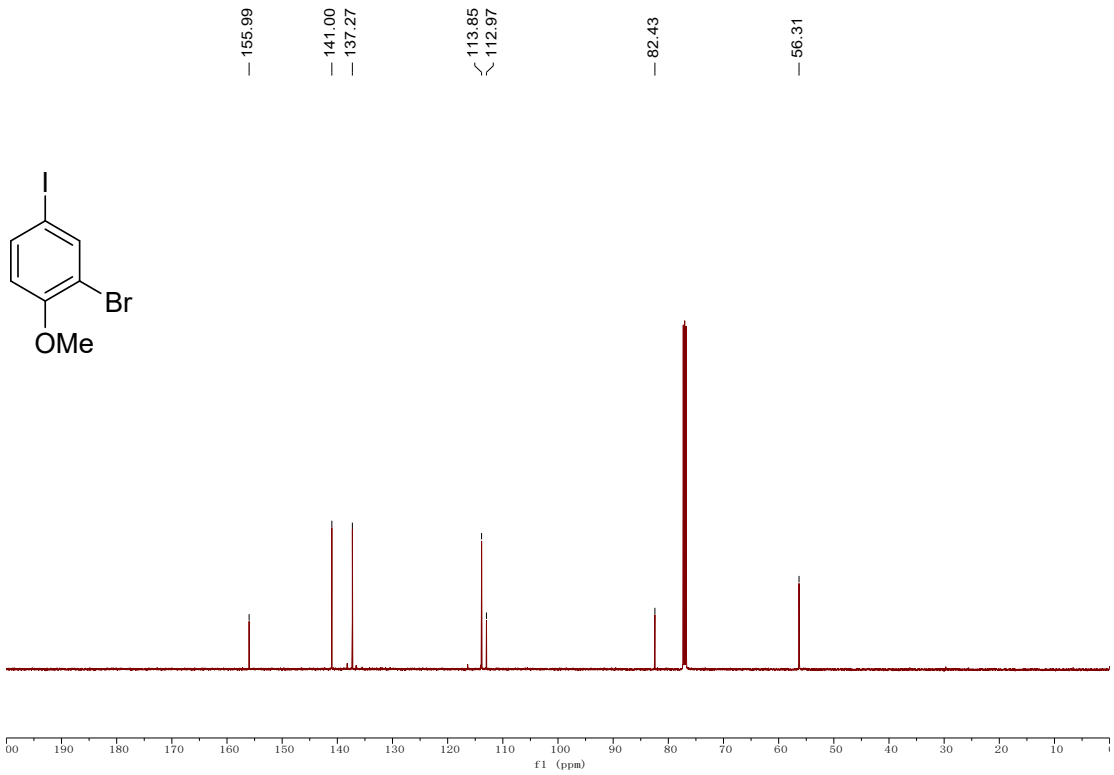
^{1}H NMR Spectrum of **3l**



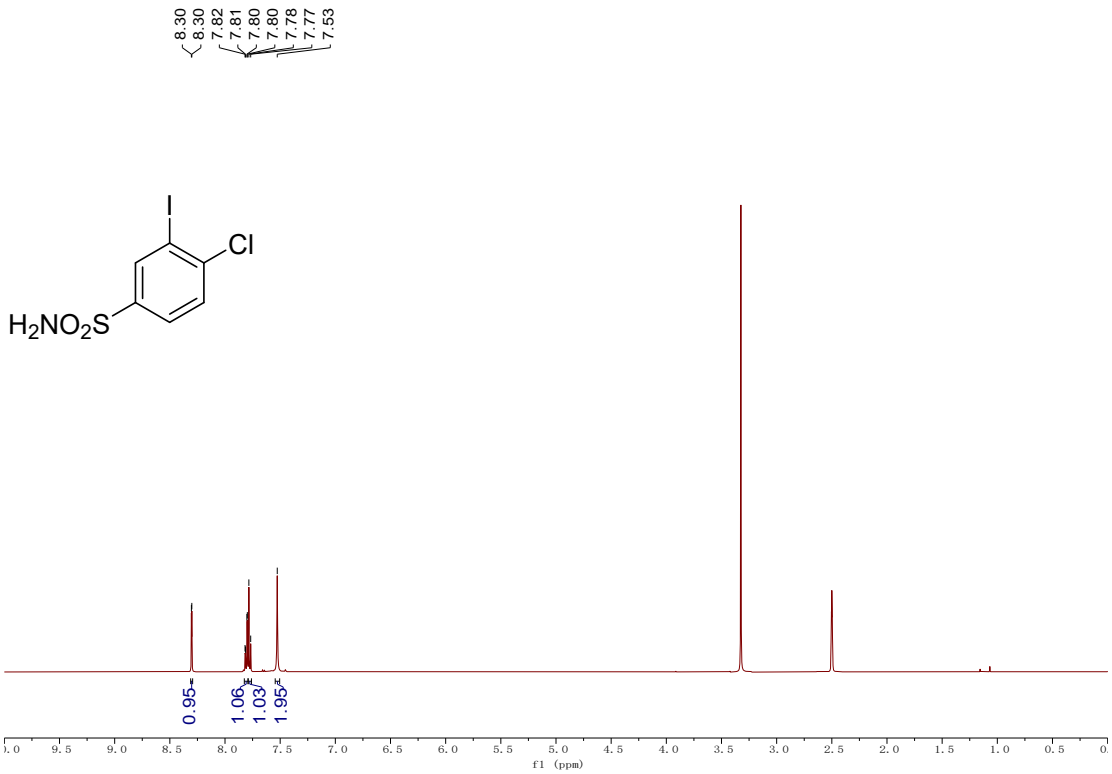
^{13}C NMR Spectrum of **3l**



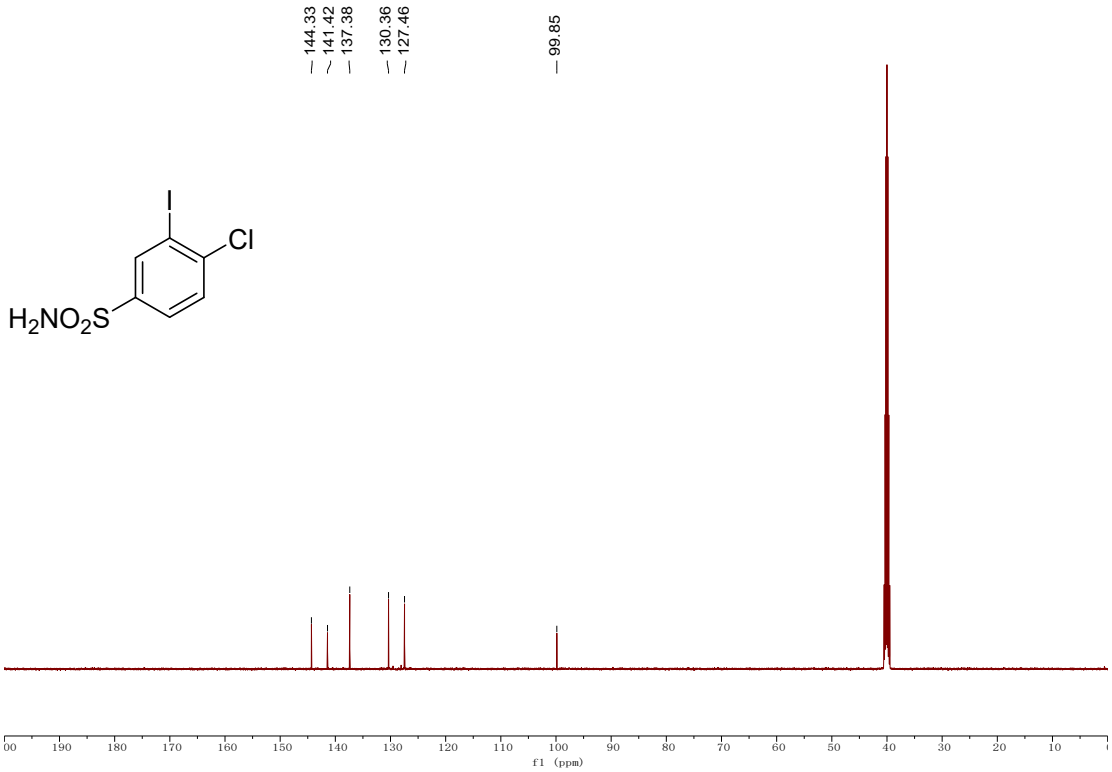
^{1}H NMR Spectrum of **3m**



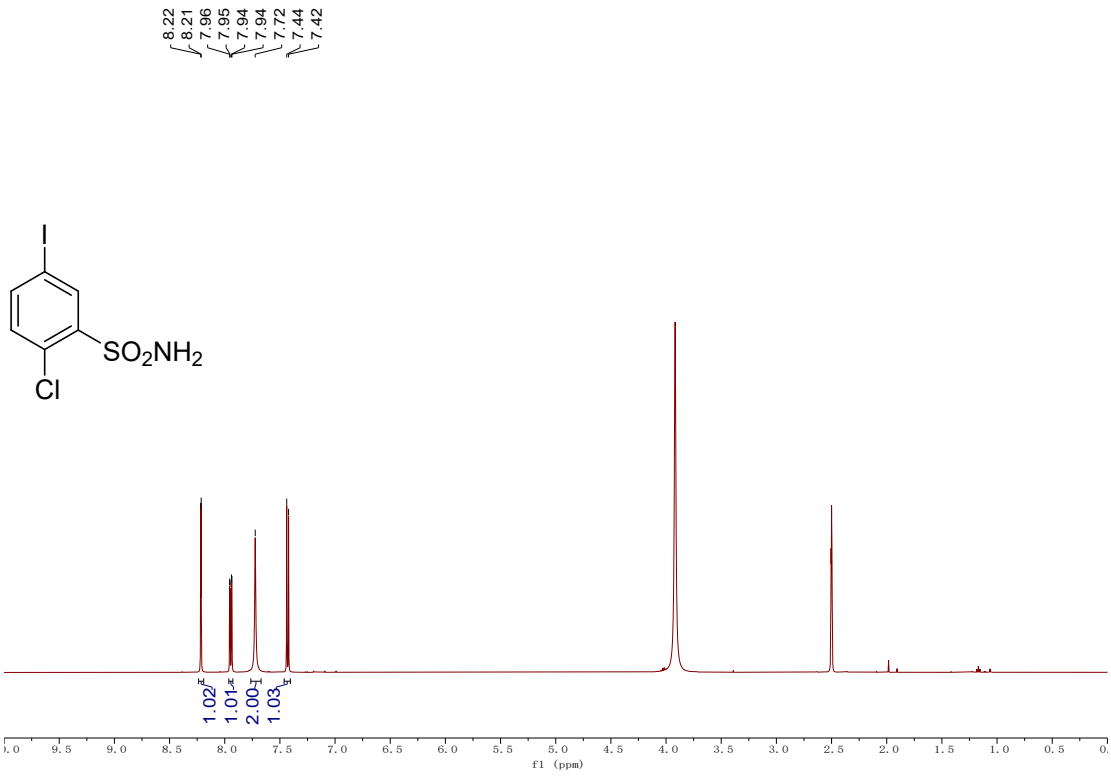
^{13}C NMR Spectrum of **3m**



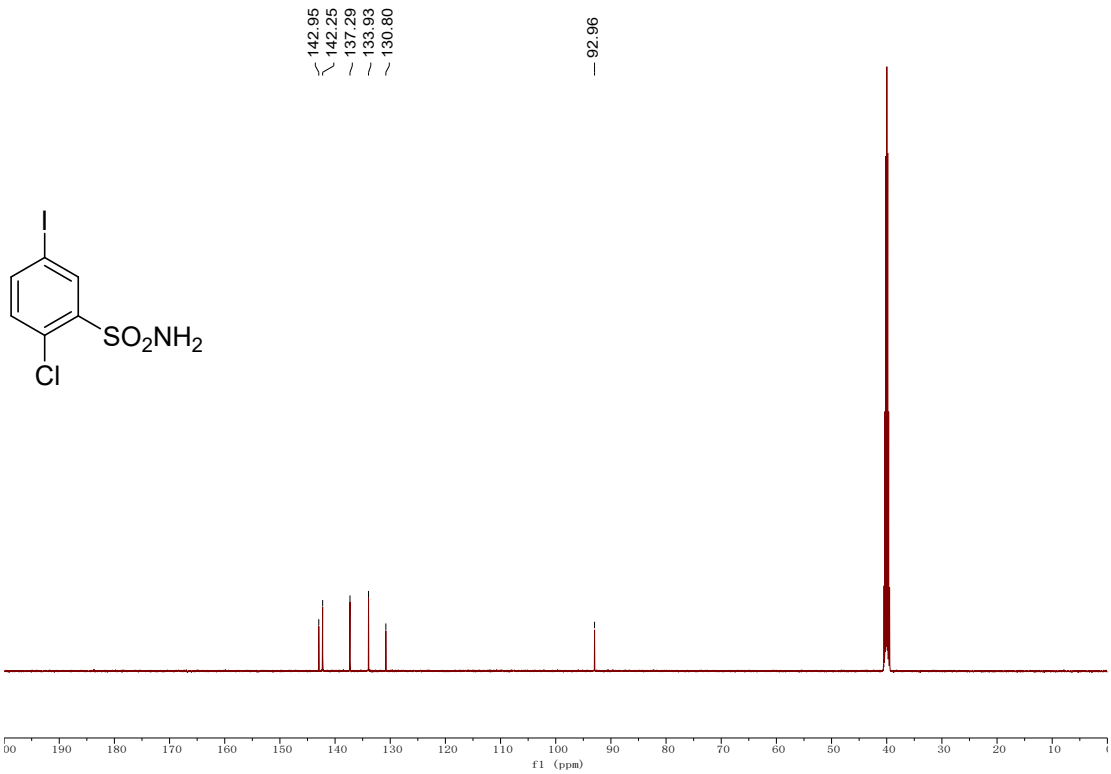
^{1}H NMR Spectrum of **3n**



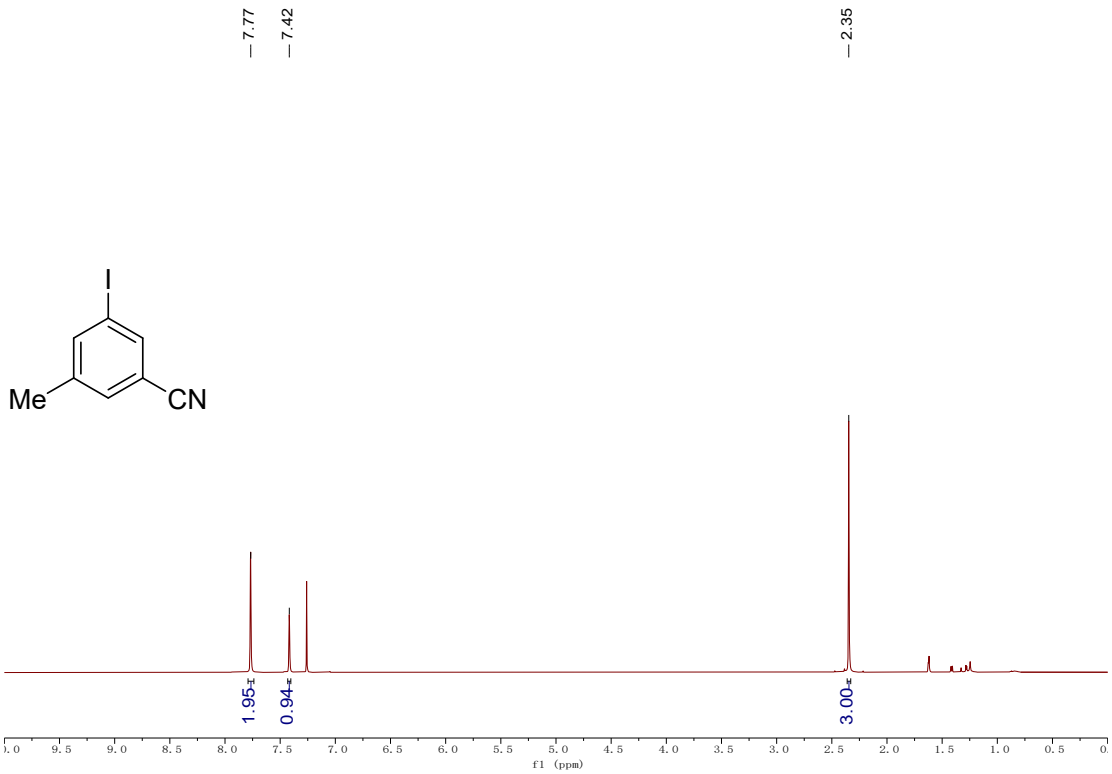
^{13}C NMR Spectrum of **3n**



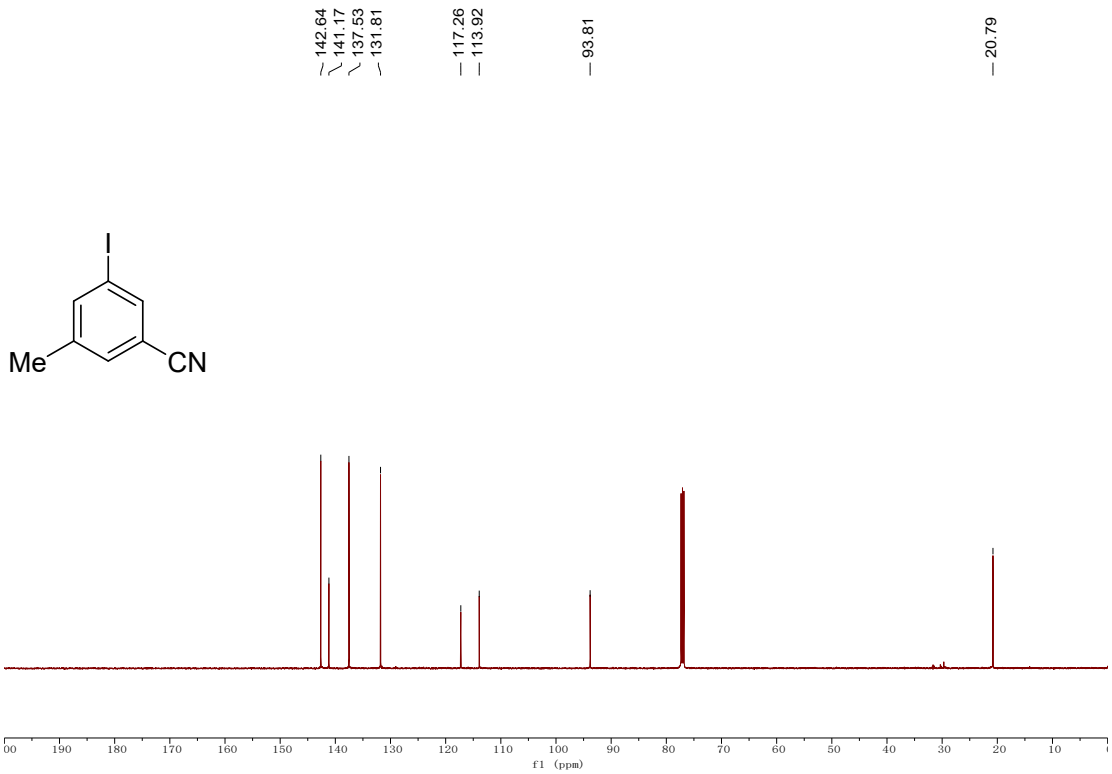
^{1}H NMR Spectrum of **3o**



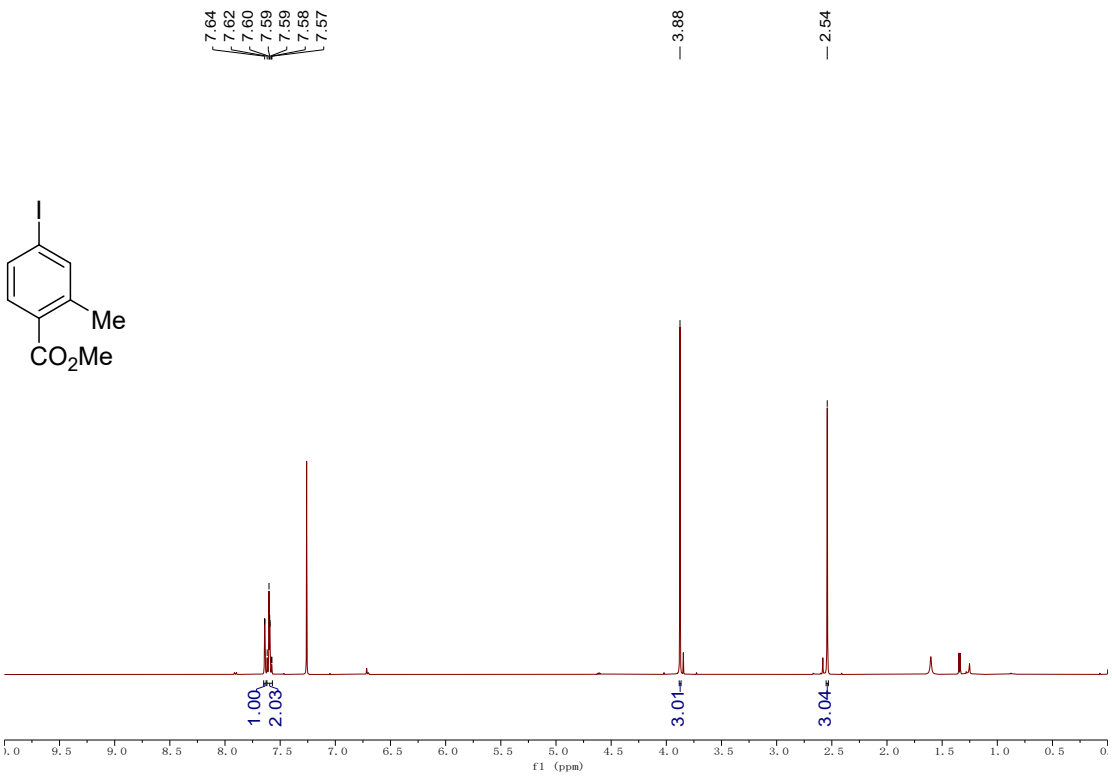
^{13}C NMR Spectrum of **3o**



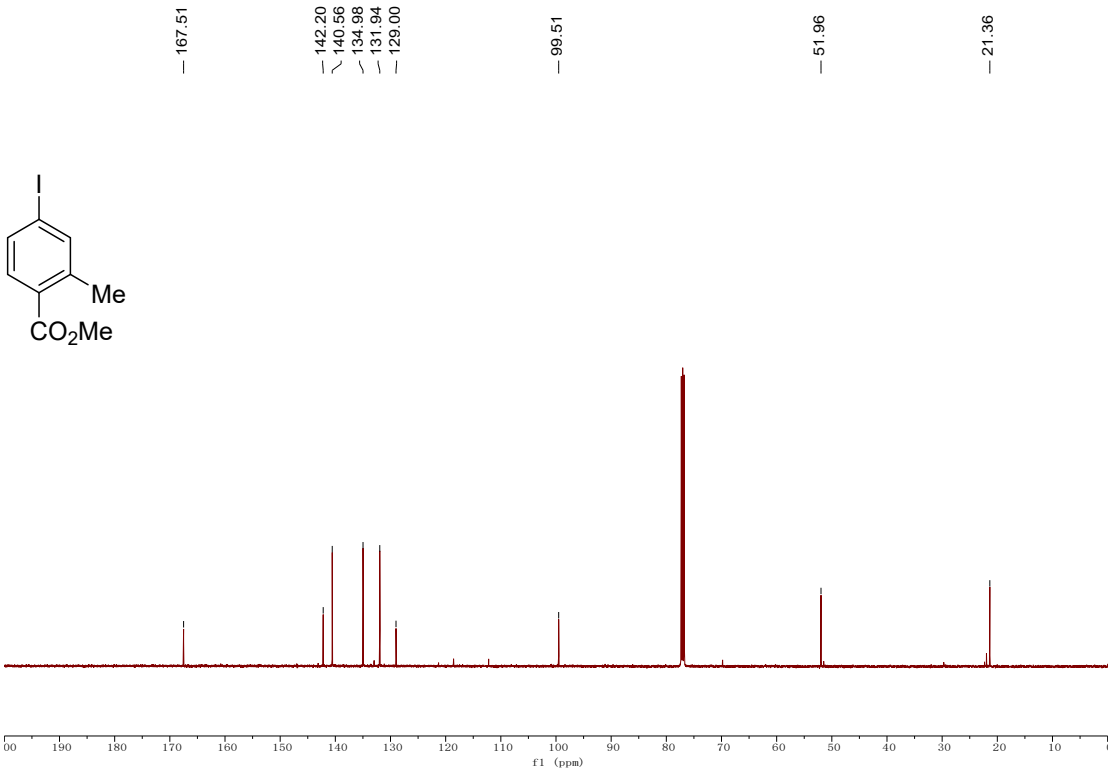
^{1}H NMR Spectrum of **3p**



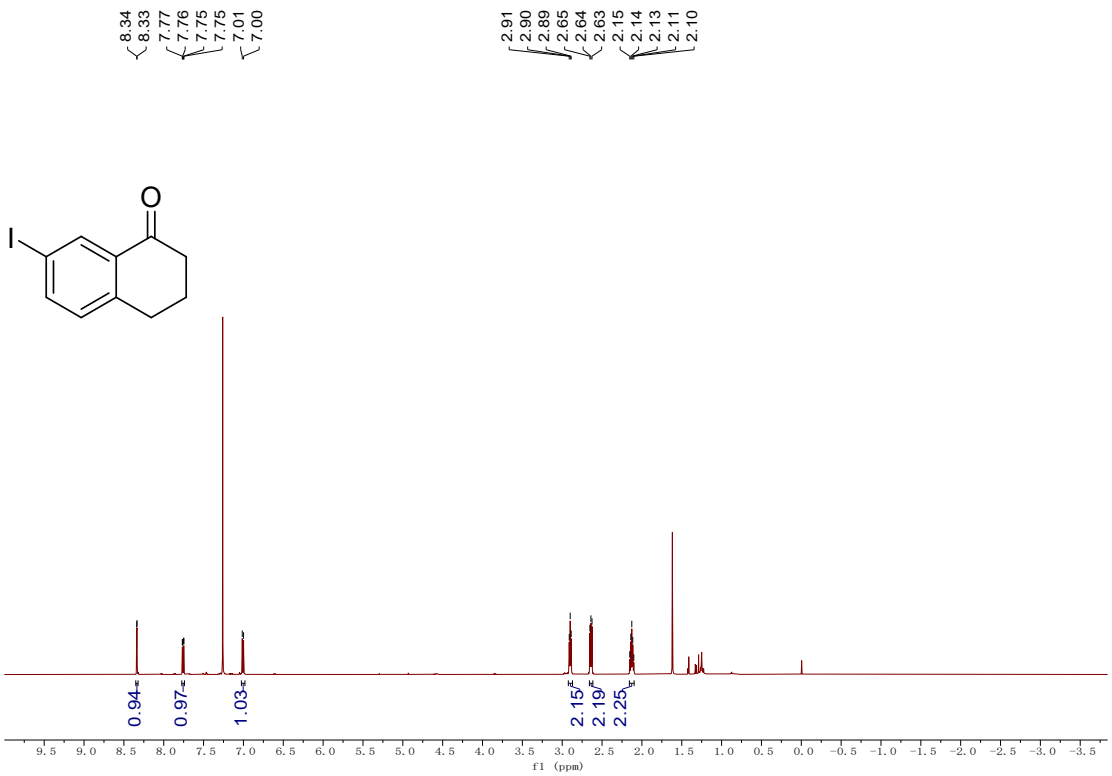
^{13}C NMR Spectrum of **3p**



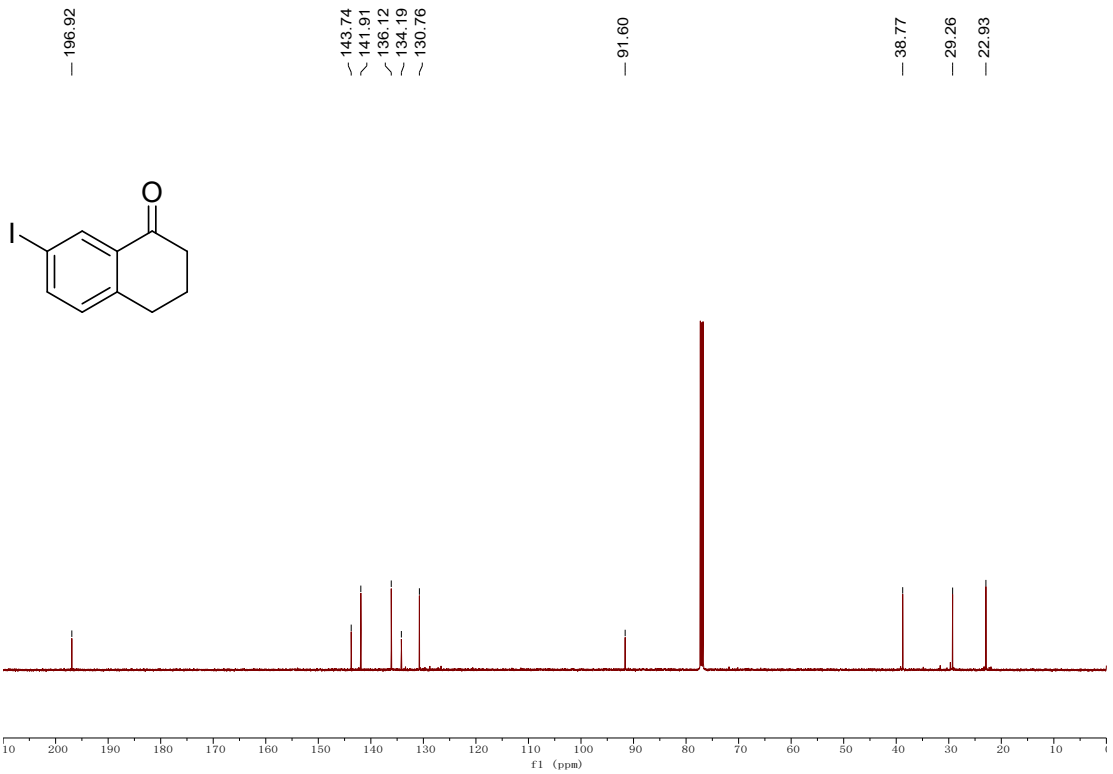
^{1}H NMR Spectrum of **3q**



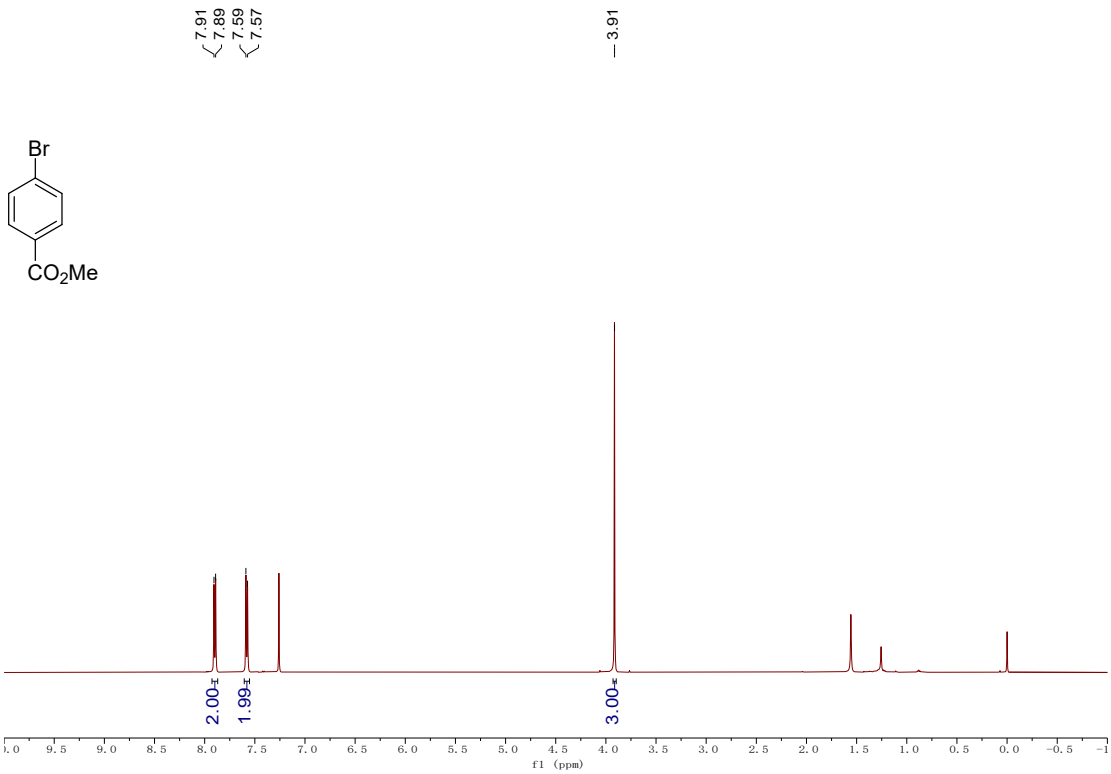
^{13}C NMR Spectrum of **3q**



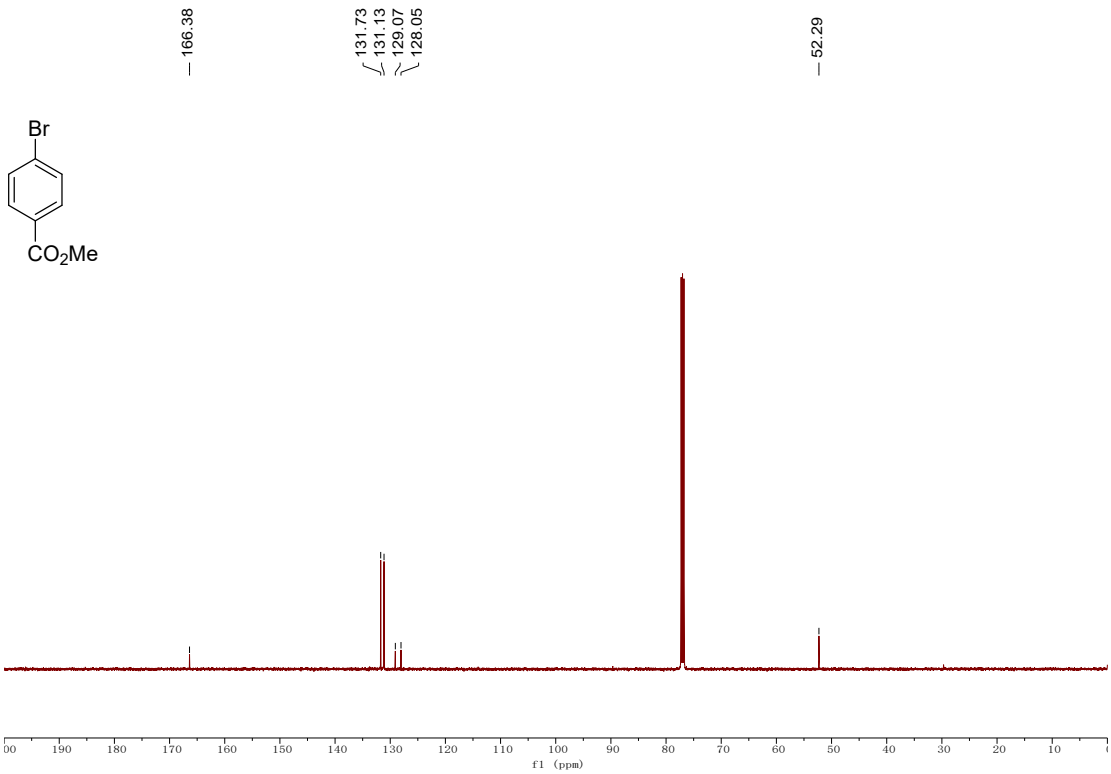
^{1}H NMR Spectrum of **3r**



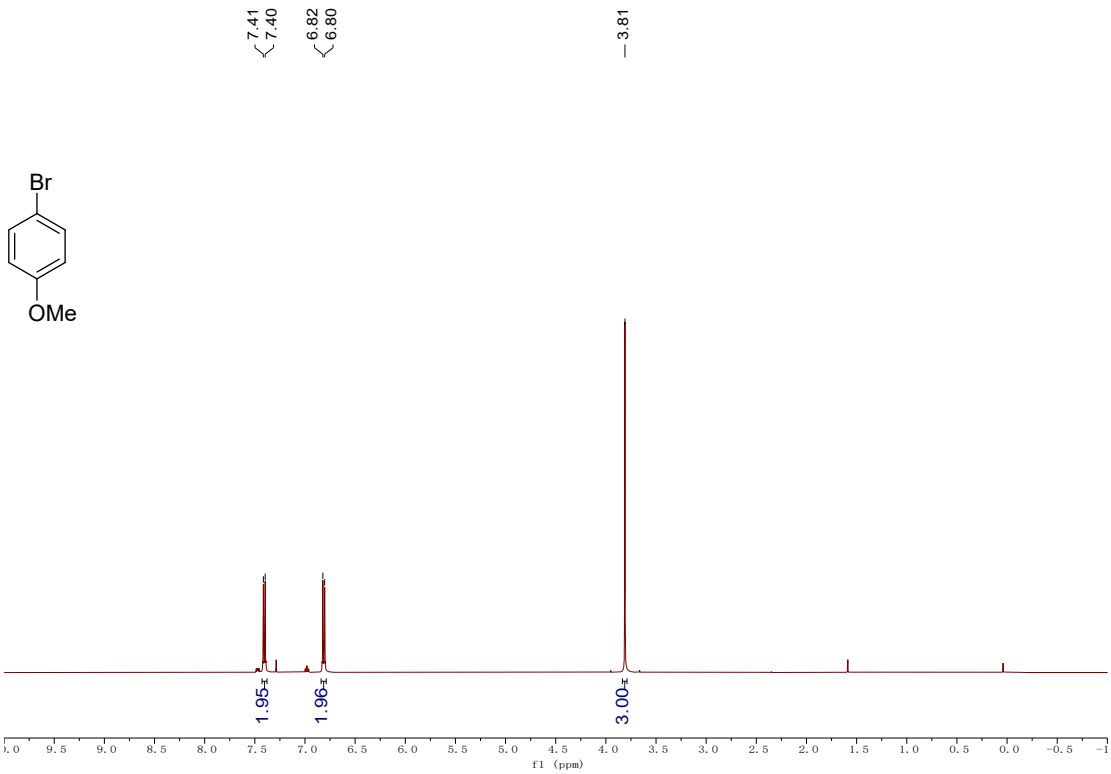
^{13}C NMR Spectrum of **3r**



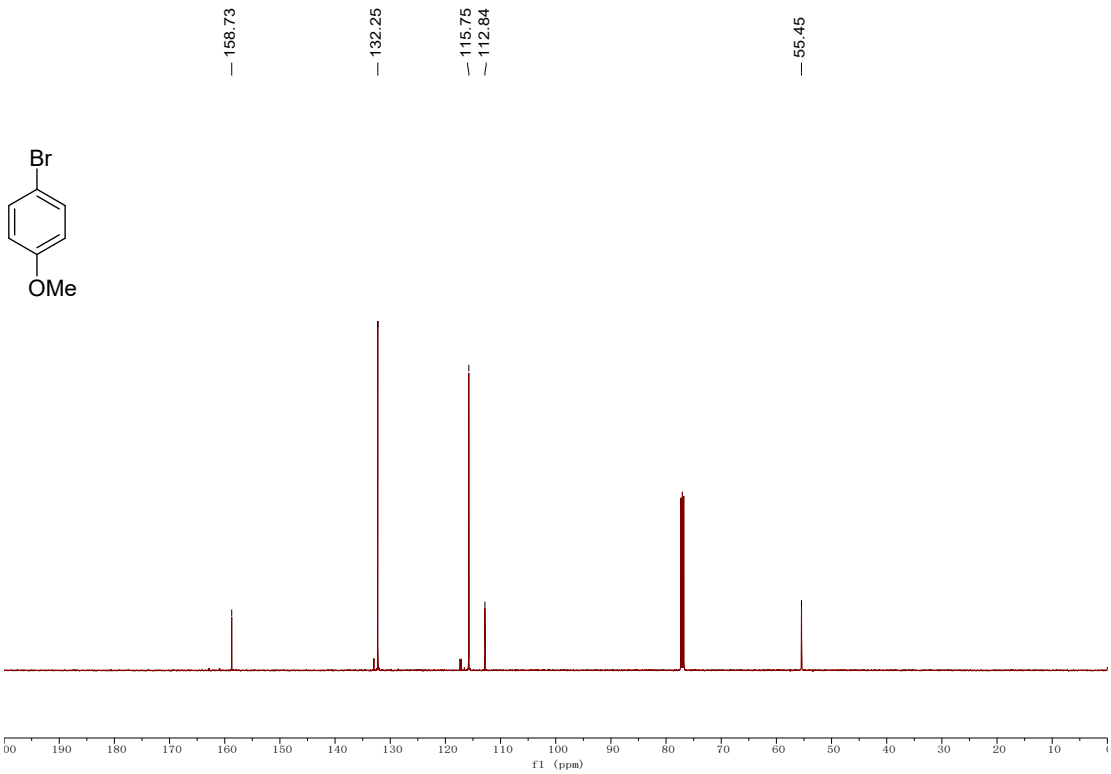
^{1}H NMR Spectrum of **3s**



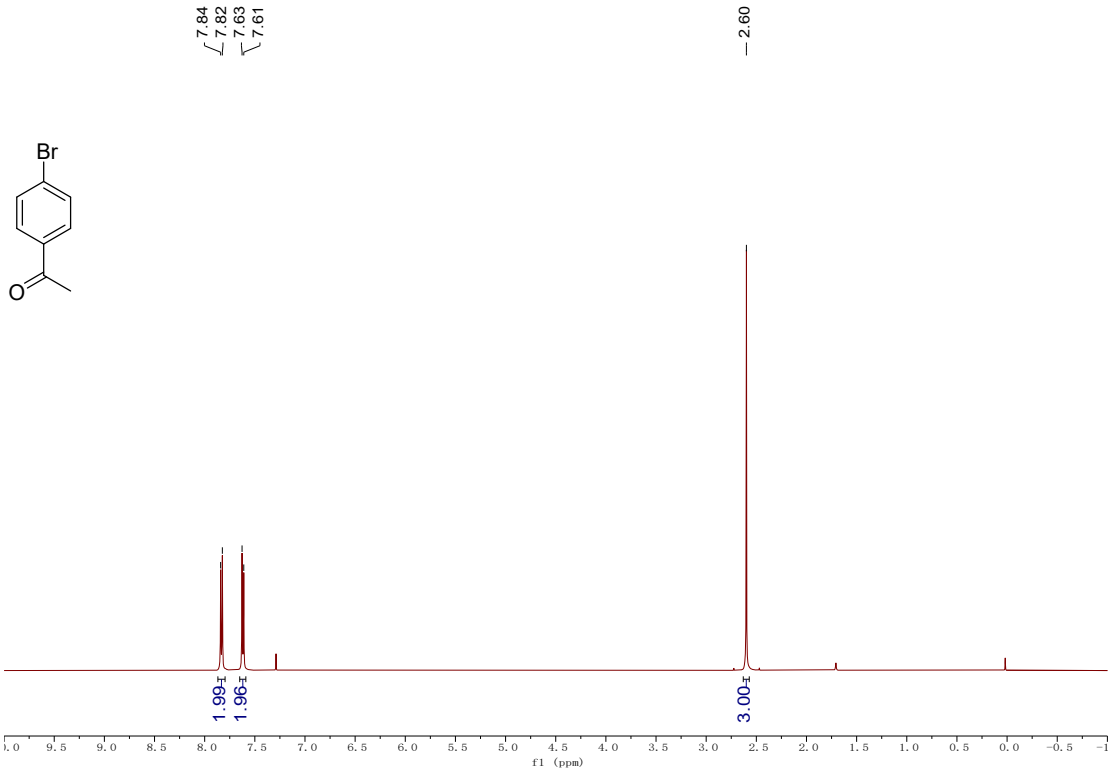
^{13}C NMR Spectrum of **3s**



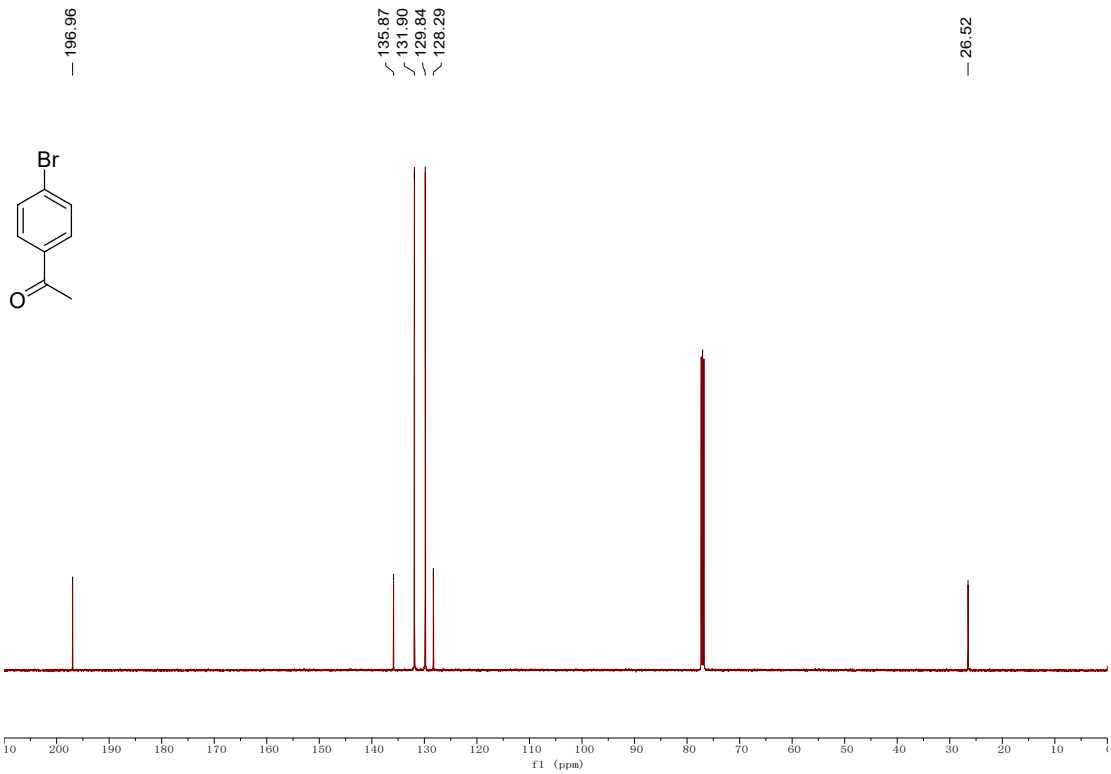
^{1}H NMR Spectrum of **3t**



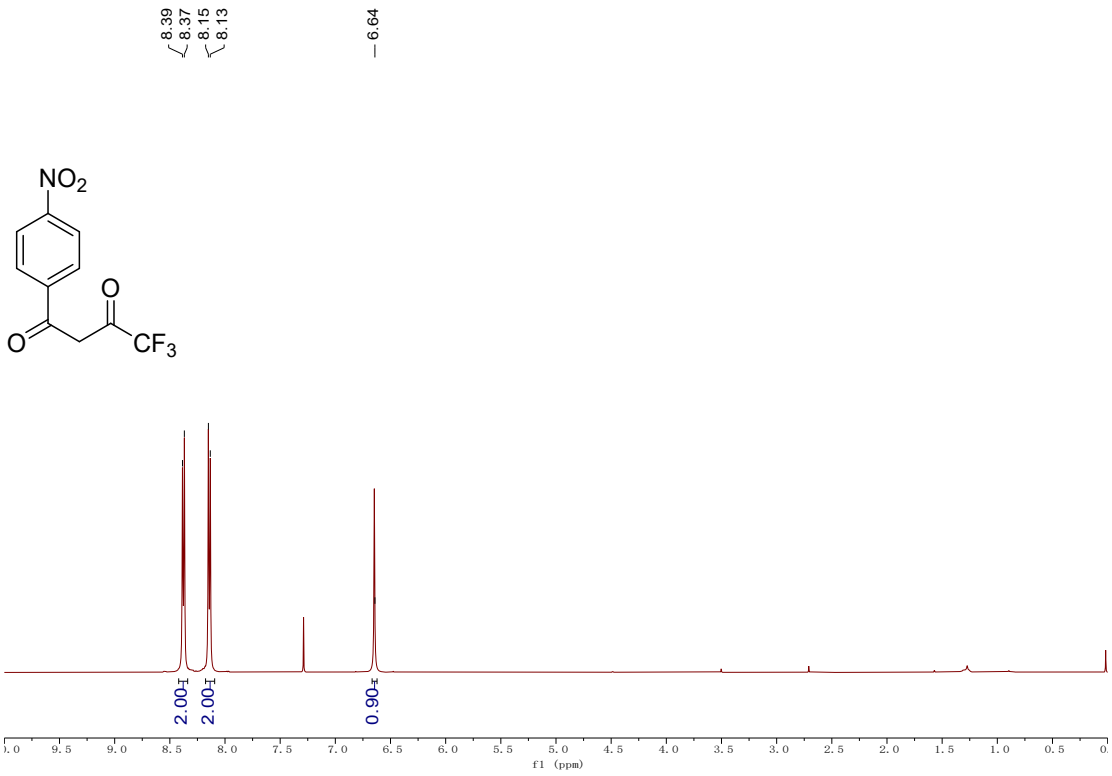
^{13}C NMR Spectrum of **3t**



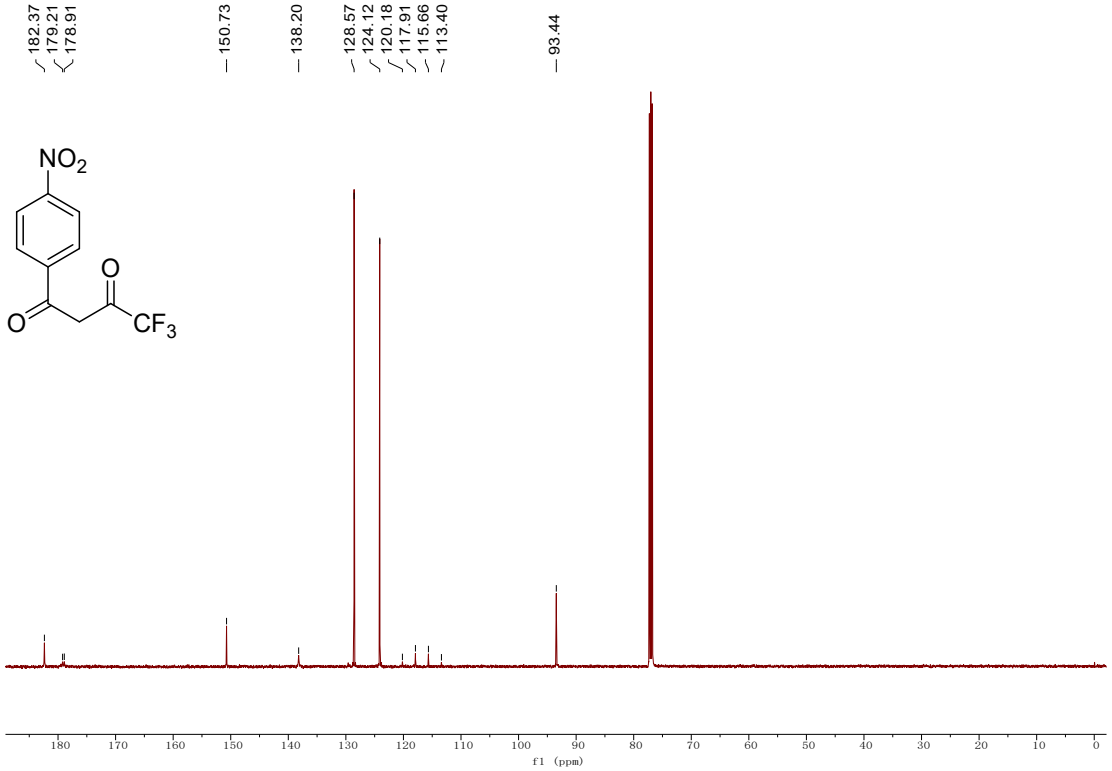
^{1}H NMR Spectrum of **3u**



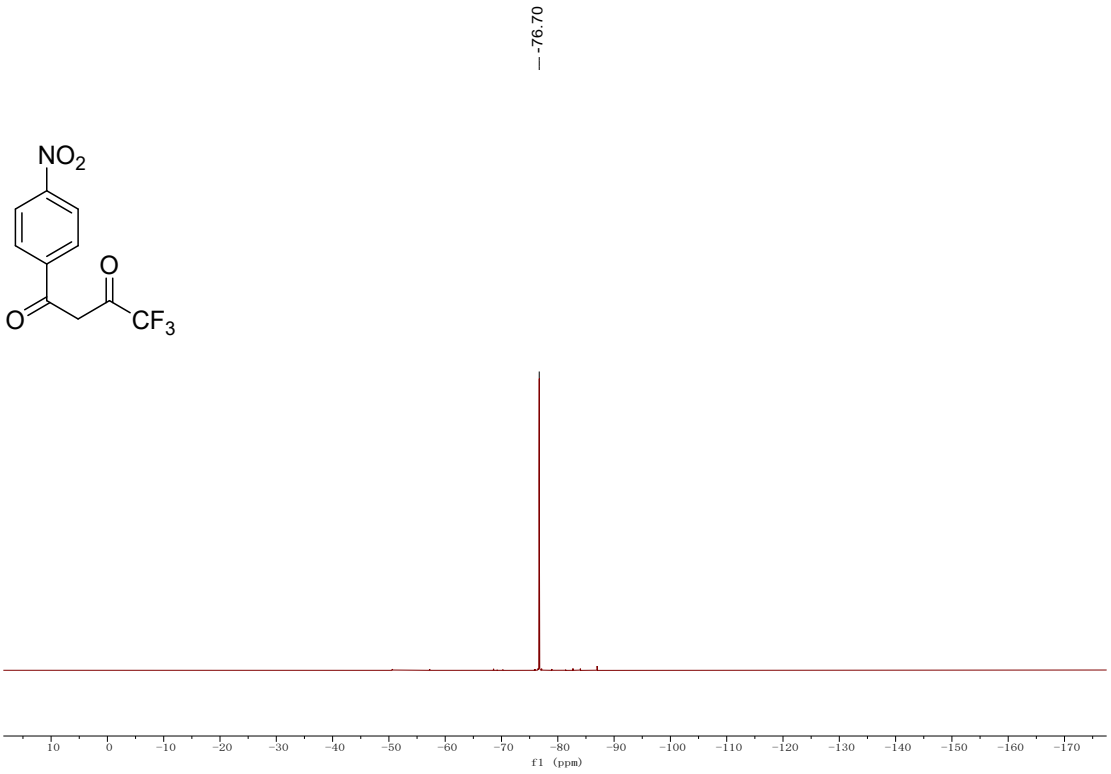
^{13}C NMR Spectrum of **3u**



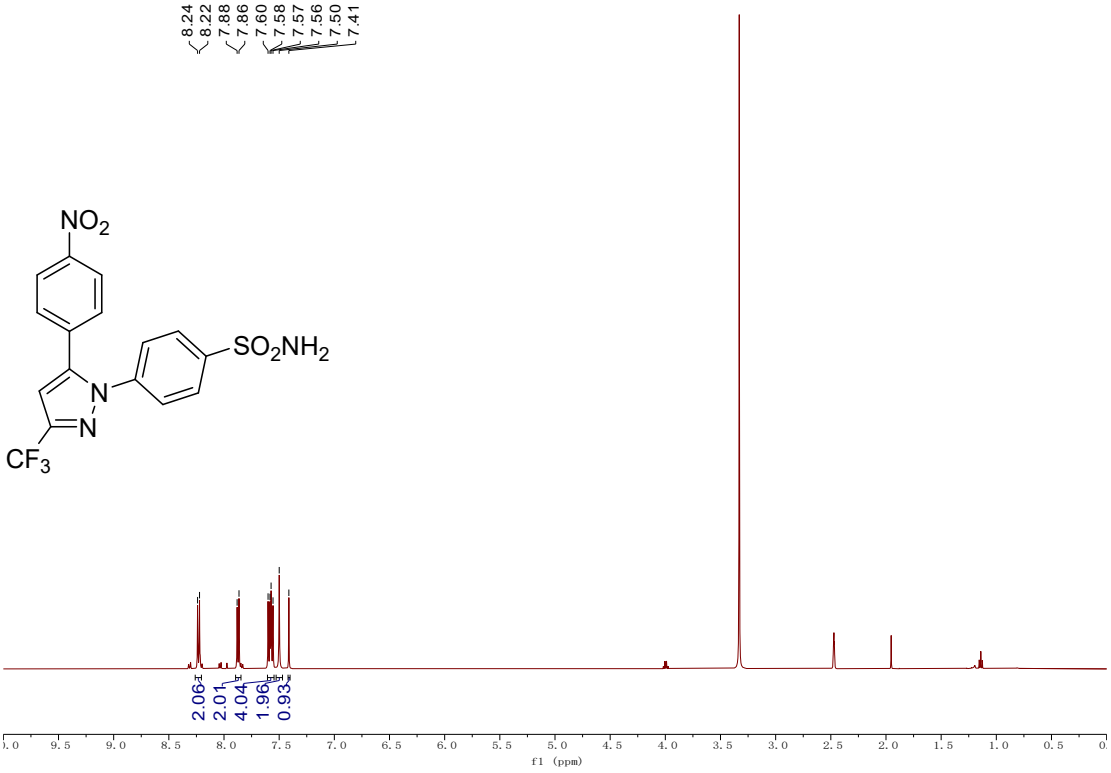
^{1}H NMR Spectrum of **F**



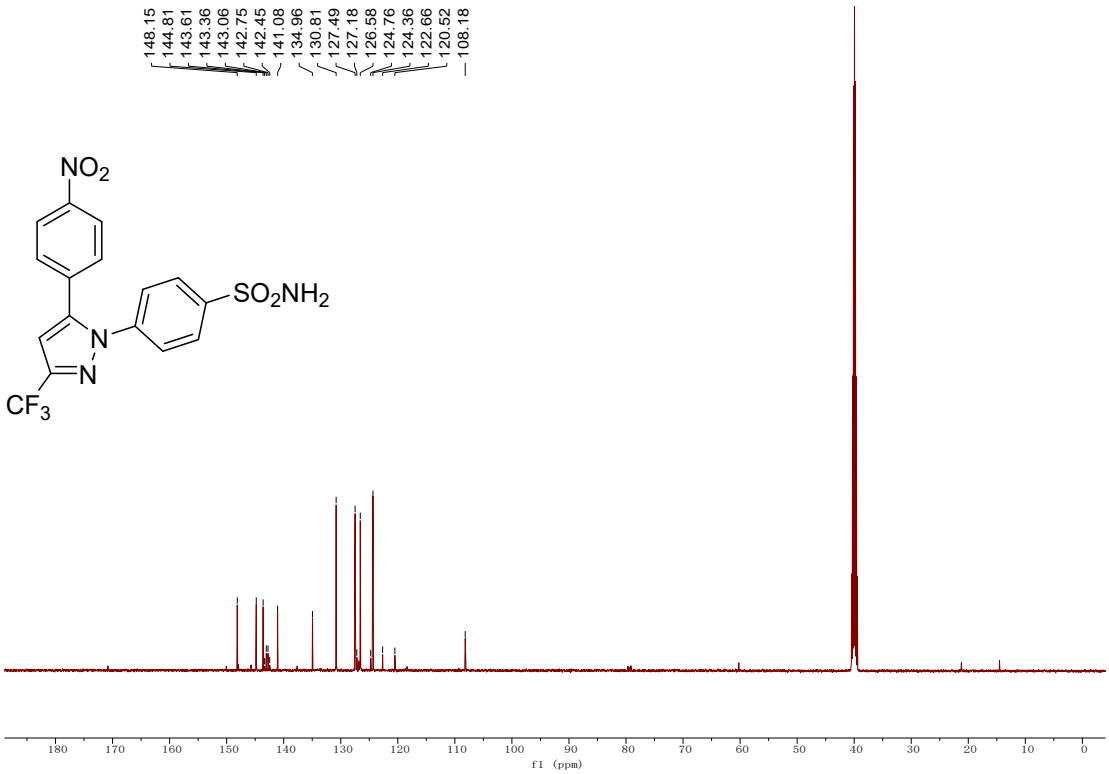
^{13}C NMR Spectrum of **F**



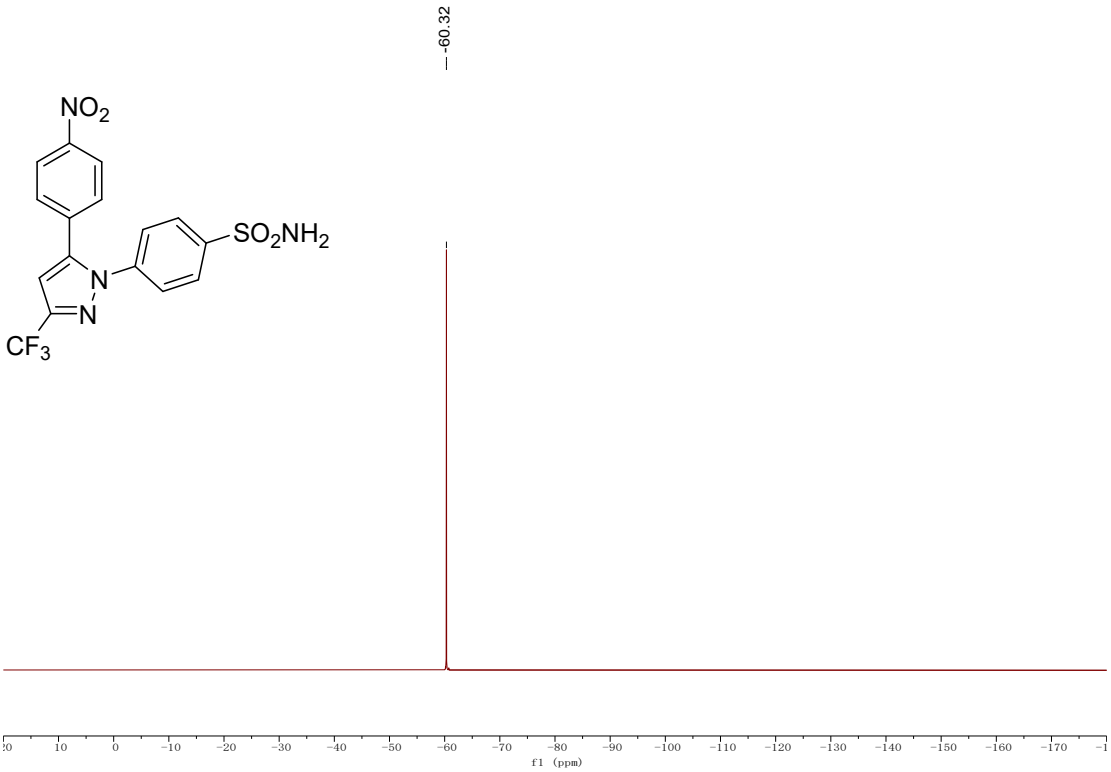
^{19}F NMR Spectrum of **F**



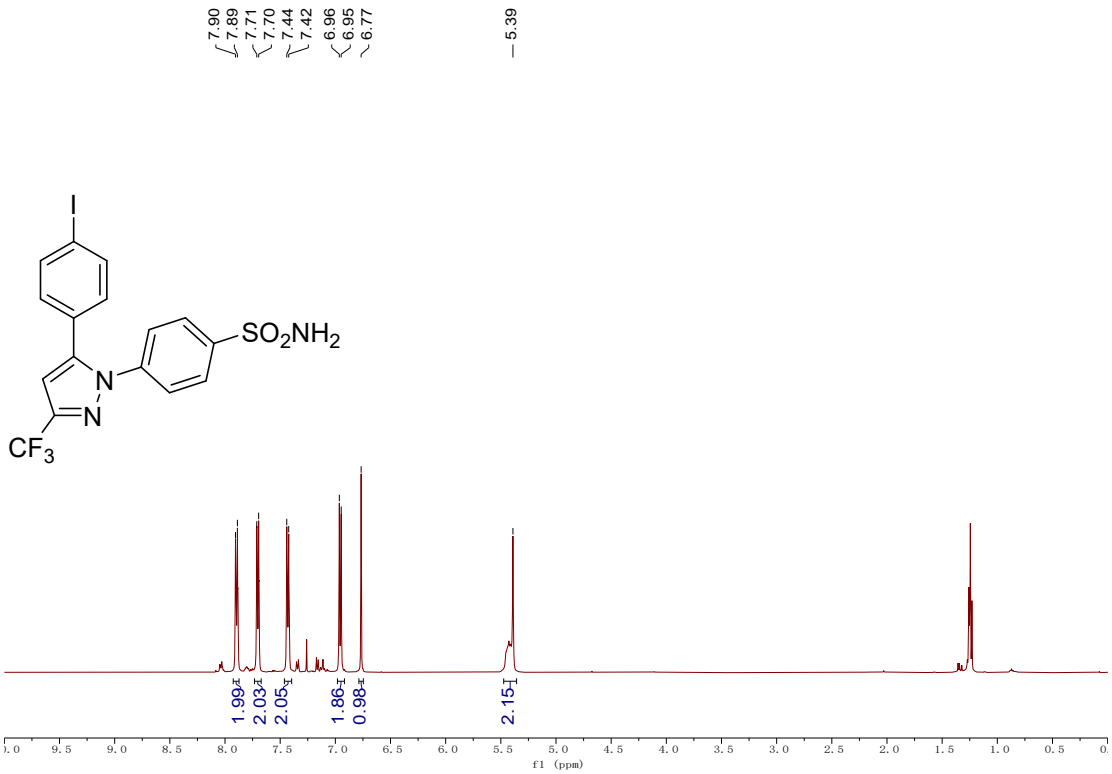
^{1}H NMR Spectrum of **4**



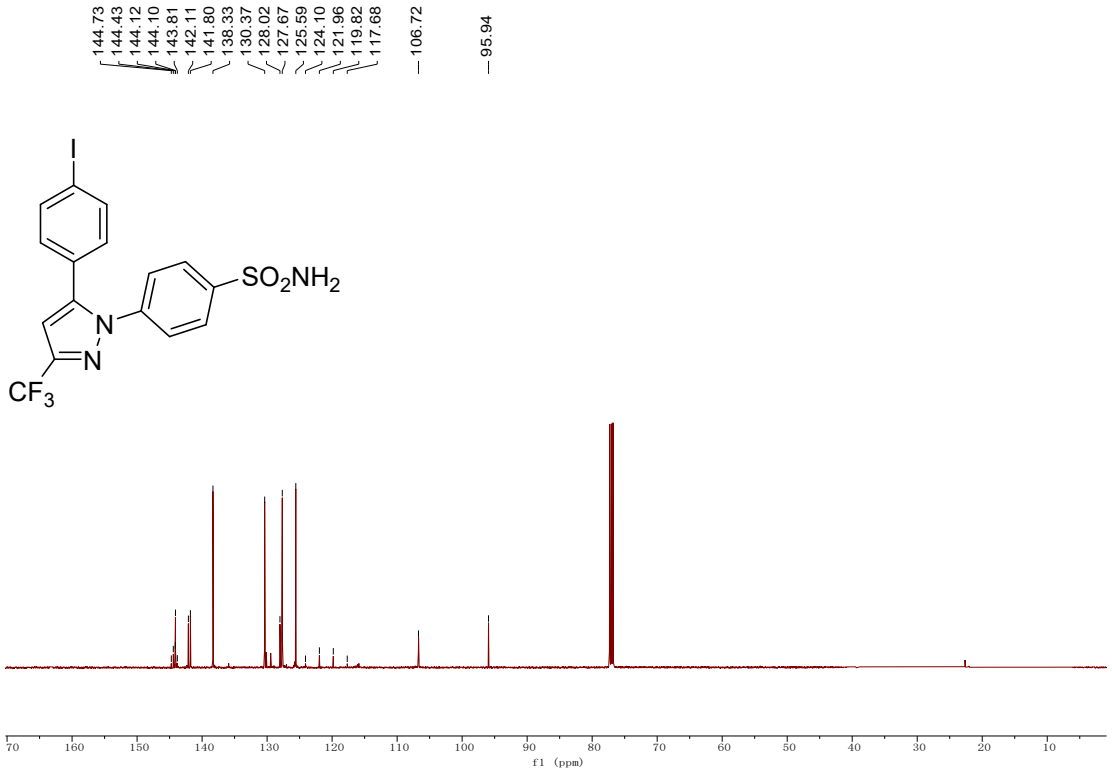
^{13}C NMR Spectrum of **4**



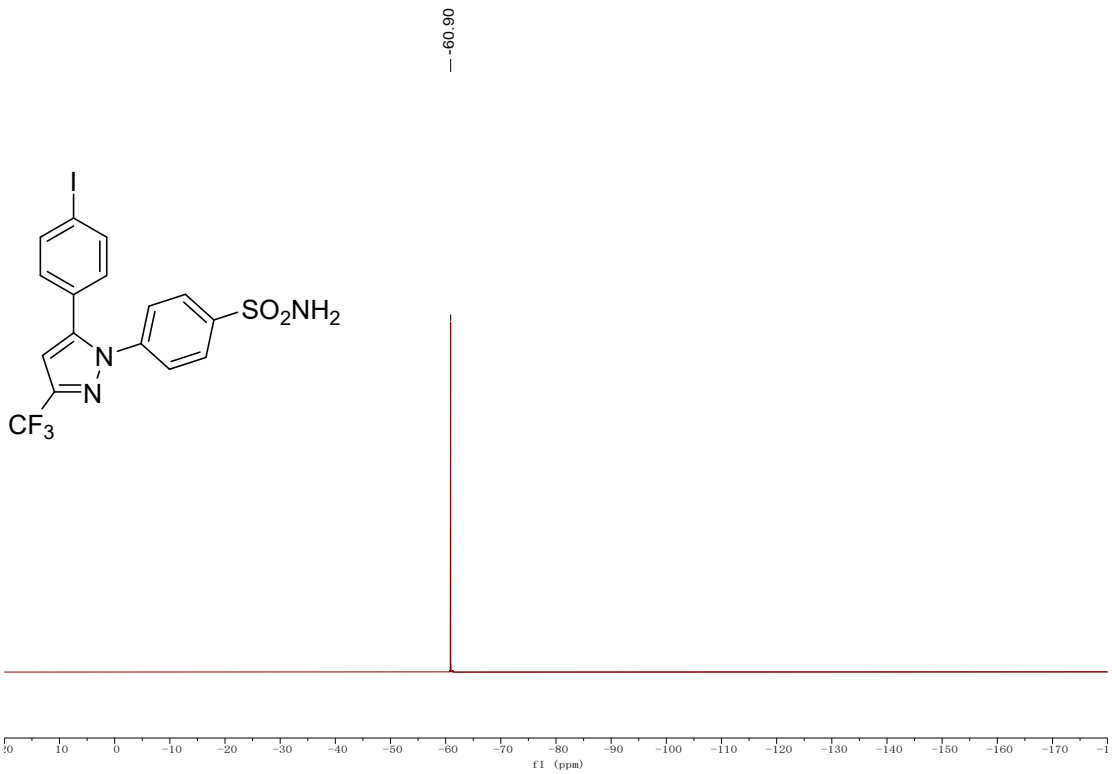
^{19}F NMR Spectrum of **4**



^{1}H NMR Spectrum of **5**



^{13}C NMR Spectrum of **5**



^{19}F NMR Spectrum of **5**

6. References

1. H.-S. Bao and L.-F. Wang, *Org. Lett.,* 2023, **25**, 8872−8876.
2. S. Andrejčák , P. Kisszékelyi, M. Májek, and R. Šebesta, *Eur. J. Org. Chem.,* 2023, **26**, e202201399.
3. S. S. Gholap, *Lett. Org. Chem.,* 2018, **15**, 594-599.