Supporting Information

Cobalt-Catalyzed Carboxylation of Aryl and Vinyl Chlorides with CO_2

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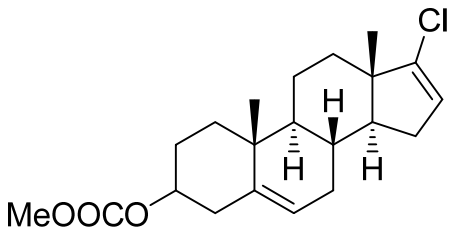
2. Experimental Section:

General Considerations: All the reactions were carried out under argon atmosphere using standard sealed Schlenk technique. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F (376 M Hz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ and DMSO-*d*$_6$ as solvent. Chemical shifts of ^{1}H, ^{13}C and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm; DMSO-*d*$_6$: δ H = 2.50 ppm, δ C = 39.43 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

3. Procedures for the Preparation of Substrates.

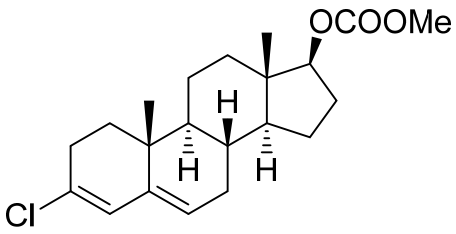
Aryl chlorides, aryl bromides and 2-chloropropene (**2g**) were purchased without any further purification. Vinyl chlorides (**2a-2f**) were prepared according to the literatures,[1] Vinyl chlorides (**2h**, **2i**) were prepared according to the following procedures: [2]

Solution of corresponding ketones (6.0 mmol), PCl_3 (11.3 mmol) in 20 mL of glacial acetic acid was allowed to stand in stoppered flasks at room temperature for about 5 h. Afterwards, it was evaporated under reduced pressure and the residue was washed with dilute sodium bicarbonate solution. The crude product was collected by gravity filtration and washed with dilute sodium bicarbonate solution. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/50 to 1/30).



(8R,9S,10R,13S,14S,17S)-3-Chloro-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[*a*]phenanthren-17-yl methyl carbonate

This compound is isolated as a white solid. M.p.: 133-135 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 6.05 (s, 1H), 5.38 (d, *J* = 3.1 Hz, 1H), 4.58 – 4.45 (m, 1H), 3.76 (s, 3H), 2.56 – 2.43 (m, 1H), 2.36 – 2.14 (m, 3H), 1.85 (dd, *J* = 12.6, 4.0 Hz, 2H), 1.73 – 1.57 (m, 5H), 1.46 – 1.28 (m, 3H), 1.23 (td, *J* = 12.9, 4.0 Hz, 1H), 1.14 – 1.07 (m, 1H), 1.06 – 0.98 (m, 1H), 0.96 (s, 3H), 0.85 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz)**: 155.8, 140.6, 130.4, 126.9, 123.6, 86.4, 54.6, 51.0, 47.8, 42.5, 36.6, 34.8, 34.5, 31.5, 31.2, 30.6, 27.4, 23.3, 20.6, 18.9, 11.9. **HRMS (ESI)**: Calcd for $C_{21}H_{29}ClO_3$ $[M+Na]^+$ 387.1697, found 387.1698.



(8R,9S,10R,13S,14S)-17-Chloro-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[*a*]phenanthren-3-yl methyl carbonate

This compound is isolated as a white solid. M.p.: 168-170 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 5.63 (s, 1H), 5.41 (d, *J* = 4.9 Hz, 1H), 4.55 – 4.41 (m, 1H), 3.77 (s, 3H), 2.48 – 2.32 (m, 2H), 2.16 (ddd, *J* = 14.8, 6.2, 3.1 Hz, 1H), 2.06 – 1.77 (m, 5H), 1.71 – 1.59 (m, 4H), 1.58 – 1.45 (m, 2H), 1.34 (td, *J* = 12.6, 4.6 Hz, 1H), 1.22 – 1.02 (m, 5H), 0.89 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz)**: 155.1, 144.6, 139.8, 124.5, 122.3, 77.6, 55.6, 54.5, 50.3, 47.4, 38.0, 36.7, 36.7, 33.6, 31.0, 30.5, 30.5, 27.6, 20.5, 19.1, 14.9. **HRMS (ESI)**: Calcd for $C_{21}H_{29}ClO_3$ $[M+Na]^+$ 387.1697, found 387.1699.

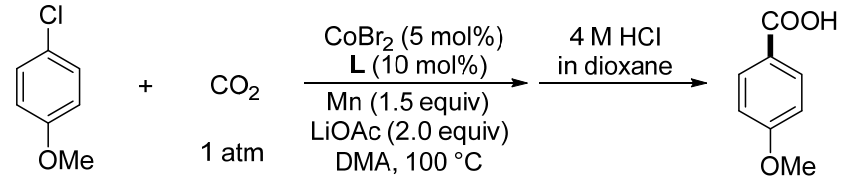
4. Optimization studies.

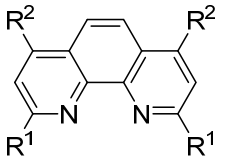
The effect of ligands on the carboxylation of aryl chlorides with CO_2

An oven-dried 50 mL schlenk tube containing a stirring bar was charged with $CoBr_2$ (5.5 mg, 5.0 mol %), ligand (10.0 mol%), Mn powder (41.2 mg, 0.75mmol, 1.5 equiv), and LiOAc (1.0 mmol, 66 mg, 2.0 equiv). The schlenk tube was evacuated and back-filled under CO_2 flow (this procedure was repeated three times). Then, anhydrous DMA (1.0 mL) and 1-chloro-4-methoxybenzene (0.5 mmol, 1.0 equiv.) was added under CO_2 flow, and the resulting mixture was stirred at 100 ºC for 12 h. The mixture was then allowed to cool to

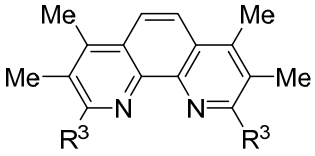
room temperature, carefully quenched with 4 M HCl (in 1,4-dioxane) and stirred for 10 minutes. The crude products were purified by flash chromatography (acetic acid/EtOAc/petroleum ether = 0/1/20 to 0.001/1/4).

Table S1 The effect of ligands on the carboxylation of aryl chlorides with CO_2.[a]



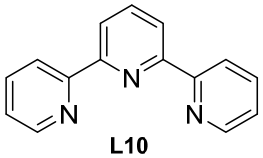


L1: $R^1 = R^2 = H$
L2: R^1 = Me, $R^2 = H$
L3: $R^1 = {}^n$Bu, $R^2 = H$
L4: R^1 = Ph, $R^2 = H$
L5: R^1 = Me, R^2 = Me
L6: $R^1 = {}^n$Bu, R^2 = Me
L7: $R^1 = {}^n$hex, R^2 = Me

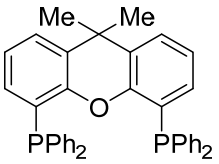


L8: $R^3 = H$
L9: $R^3 = {}^n$Bu

L11



L10

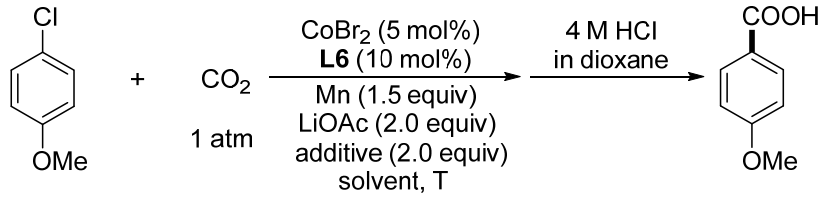


L12

Entry	Ligand (**L**)	Yield (%)
1	**L1**	trace
2	**L2**	10
3	**L3**	48
4	**L4**	0
5	**L5**	57
6	**L6**	59
7	**L7**	49
8	**L8**	trace
9	**L9**	53
10	**L10**	0
11	**L11**	0
12	**L12**	0

[a] Reaction conditions: 1-chloro-4-methoxybenzene (0.5 mmol, 1.0 equiv), CO_2 1 atm, $CoBr_2$ (5 mol%), ligand (10 mol%), Mn powder (1.5 equiv), LiOAc (2.0 equiv), DMA (1.0 mL), 100 °C for 12 h. Isolated yield.

Table S2 Optimization of the reaction conditions for the carboxylation of aryl chlorides.[a]

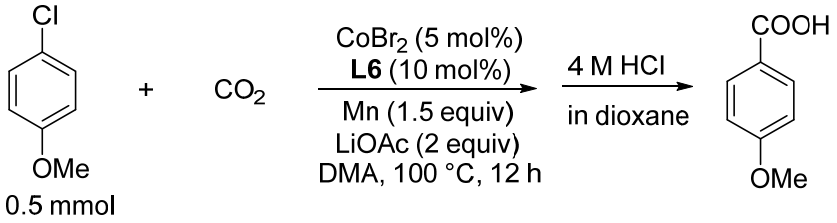


Entry	Additive	T (°C)	Solvent	Yield (%)
1		120	DMA	32
2		80	DMA	28
3		60	DMA	trace
4		RT	DMA	0
5		100	DMF	31
6		100	DMSO	0
7		100	CH_3CN	0
8	Bu_4NI	100	DMA	66
9	Et_4NI	100	DMA	71
10	Et_4NBr	100	DMA	65
11	Et_4NCl	100	DMA	0
12[b]	Et_4NI	100	DMA	19
13[c]	Et_4NI	100	DMA	34
14[d]	Et_4NI	100	DMA	59
15[e]	Et_4NI	100	DMA	0
16	Et_4NI	100	DMA	trace[f], 0[g]
17[h]	Et_4NI	100	DMA	0
18[i]	Et_4NI	100	DMA	12
19[j]	Et_4NI	100	DMA	0

[a] Reaction conditions: 1-chloro-4-methoxybenzene (0.5 mmol, 1.0 equiv), CO_2 1 atm, $CoBr_2$ (5 mol%), ligand (10 mol%), Mn powder (1.5 equiv), LiOAc (1.5 equiv), solvent (1.0 mL), 100 °C for 12 h. Isolated yield. [b] NaOAc instead of LiOAc. [c] KOAc instead of LiOAc. [d] Li_2CO_3 instead of LiOAc. [e] LiCl instead of

LiOAc. [f] Zn powder instead of Mn powder. [g] In powder instead of Mn powder. [h] $Co(PPh_3)_3Cl$ (5 mol %) as catalyst, without **L6**. [i] $Co(PPh_3)_3Cl$ (5 mol %) as catalyst, with **L6**. [j] Without $CoBr_2$.

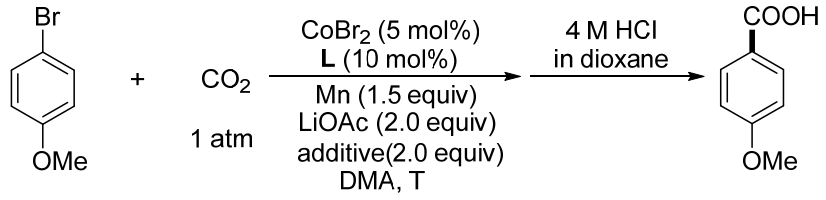
Table S3 Investigation Experiments about the Role of LiOAc.[a]



Entry	Aleration	Yield (%)
1	none	59
2	LiCl (2 equiv) + NaOAc (2 equiv) instead of LiOAc	51
3	LiCl (2 equiv) + KOAc (2 equiv) instead of LiOAc	49
4	LiCl (2 equiv) + K_2CO_3 (2 equiv) instead of LiOAc	53
5	LiCl (2 equiv) + Et_3N (2 equiv) instead of LiOAc	45
6	LiCl (2 equiv)	0

[a] Reaction conditions: 1-chloro-4-methoxybenzene (0.5 mmol, 1.0 equiv), CO_2 1 atm, $CoBr_2$ (5 mol%), ligand (10 mol%), Mn powder (1.5 equiv), LiOAc (2.0 equiv), DMA (1.0 mL), 100 °C for 12 h. Isolated yield.

Table S4 Optimization of the reaction conditions for the carboxylation of aryl bromides.[a]



Entry	Ligand (**L**)	Additive	T (°C)	Yield (%)
1	**L1**		60	trace
2	**L1**		80	trace
2	**L1**		RT	15
3	**L2**		RT	75
4	**L3**		RT	59

5	**L4**		RT	0
6	**L5**		RT	66
7	**L6**		RT	55
8	**L7**		RT	55
9	**L8**		RT	trace
10	**L9**		RT	53
11	**L10-12**		RT	0
12	**L2**	Et_4NI	RT	65
13	**L2**	Et_4NBr	RT	62
14[b]			RT	0
15[c]	**L2**		RT	59

[a] Reaction conditions: 1-bromo-4-methoxybenzene (0.5 mmol, 1.0 equiv), CO_2 1 atm, $CoBr_2$ (5 mol%), ligand (10 mol%), Mn powder (1.5 equiv), LiOAc (2.0 equiv), DMA (1.0 mL) for 12 h. Isolated yield. [b] $Co(PPh_3)_3Cl$ (10 mol %) as catalyst, without **L2**. [c] $Co(PPh_3)_3Cl$ (5 mol %) as catalyst.

5. Procedures for the Cobalt-Catalyzed Carboxylation

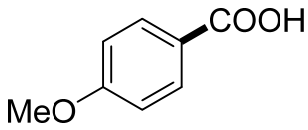
General Procedure for the Cobalt-Catalyzed Carboxylation of Aryl Chlorides with CO_2

An oven-dried 50 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (5.5 mg, 5.0 mol %), **L6** (16 mg, 10.0 mol%), Mn powder (41.2 mg, 0.75mmol, 1.5 equiv), Et_4NI (257 mg, 2.0 equiv) and LiOAc (1.0 mmol, 66 mg, 2.0 equiv). The Schlenk tube was evacuated and back-filled under CO_2 flow (this procedure was repeated three times). Then, anhydrous DMA (1.0 mL) and aryl chlorides (0.5 mmol, 1.0 equiv) was added under CO_2 flow, and the resulting mixture was stirred at 100 ºC for 12 h. The mixture was then allowed to cool to room temperature, carefully quenched with 4 M HCl (in 1,4-dioxane) and stirred for 10 minutes. The crude products were purified by flash chromatography (acetic acid/EtOAc/petroleum ether = 0/1/20 to 0.001/1/4).

General Procedure for the Cobalt-Catalyzed Carboxylation of Aryl Bromides with CO_2

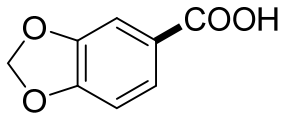
An oven-dried 50 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (5.5 mg, 10.0 mol %), **L2** (10.4 mg, 10.0 mol%), Mn powder (41.2 mg, 0.75mmol, 1.5 equiv), and LiOAc (1.0 mmol, 66 mg, 2.0 equiv). The Schlenk tube was evacuated and back-filled under CO_2 flow (this procedure was repeated three times). Then, anhydrous DMA (1.0 mL) and aryl bromides (0.5 mmol, 1.0 equiv) was added under CO_2 flow, and the resulting mixture was stirred at room temperature for 12 h. Then, the mixture was carefully quenched with 4 M HCl (in 1,4-dioxane) and stirred for 10 minutes. The crude products were purified by flash chromatography (acetic acid/EtOAc/petroleum ether = 0/1/20 to 0.001/1/4).

6. Characterization of the Carboxylation Products



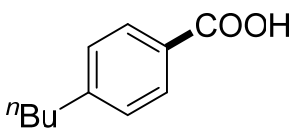
4-Methoxybenzoic acid (1)

The title compound was isolated as a white solid, 54 mg, 71% (from 1-chloro-4-methoxybenzene); 57 mg, 75% (from 1-bromo-4-methoxybenzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.64 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.0, 162.8, 131.3, 122.9, 113.8, 55.4. Spectroscopic data for **1** match those previously reported in the literature.[1]



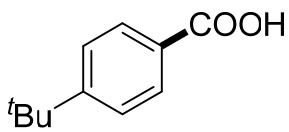
Benzo[*d*][1,3]dioxole-5-carboxylic acid (2)

The title compound was isolated as a white solid, 62.3 mg, 75% (from 5-chlorobenzo[*d*][1,3]dioxole); 67.2 mg, 81% (from 5-bromobenzo[*d*][1,3]dioxole). **^{1}H NMR (DMSO-*d*$_{63}$, 400 MHz)**: δ 12.77 (s, 1H), 7.54 (d, *J* = 6.6 Hz, 1H), 7.36 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.12 (s, 2H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.6, 151.1, 147.4, 124.9, 124.6, 108.7, 108.0, 101.9. Spectroscopic data for **2** match those previously reported in the literature.[6]



4-Butylbenzoic acid (3)

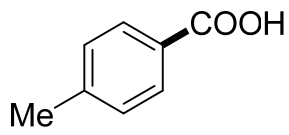
The title compound was isolated as a white solid, 68.5 mg, 77% (from 1-chloro-4-butylbenzene); 72.1 mg, 81% (from 1-bromo-4-butylbenzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.77 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.36 – 1.23 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ167.2, 147.6, 129.3, 128.4, 128.2, 34.7, 32.7, 21.6, 13.6. Spectroscopic data for **3** match those previously reported in the literature.[1]



4-(*tert*-Butyl)benzoic acid (4)

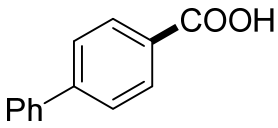
The title compound was isolated as a white solid, 65 mg, 73% (from 1-chloro-4-(*tert*-butyl)benzene); 71.2 mg, 80% (from 1-bromo-4-(*tert*-butyl)benzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.78 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 1.29 (s, 9H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.1, 155.7, 129.1,

127.9, 125.2, 34.7, 30.8. Spectroscopic data for **4** match those previously reported in the literature.[1]



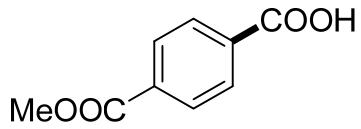
4-Methylbenzoic acid (5)

The title compound was isolated as a white solid, 49.6 mg, 73% (from 1-chloro-4-methylbenzene); 51 mg, 75% (from 1-bromo-4-methylbe -nzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.79 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.2, 142.9, 129.2, 129.0, 127.9, 21.0. Spectroscopic data for **5** match those previously reported in the literature.[6]



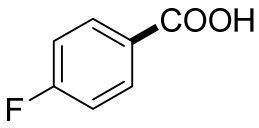
[1,1'-Biphenyl]-4-carboxylic acid (6)

The title compound was isolated as a white solid, 72.3 mg, 73% (from 4-chloro-1,1'-biphenyl); 67.3 mg, 68% (from 4-bromo-1,1'-biphenyl). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.00 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.46 – 7.39 (m, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.1, 144.3, 139.0, 129.9, 129.5, 129.0, 128.3, 126.9, 126.8. Spectroscopic data for **6** match those previously reported in the literature.[6]



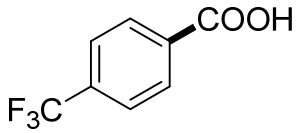
4-(Methoxycarbonyl)benzoic acid (7)

The title compound was isolated as a white solid, 60.3 mg, 67% (from methyl 4-chlorobenzoate); 55.8 mg, 62% (from methyl 4-bromobenzoate). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.34 (s, 1H), 8.06 (s, 4H), 3.88 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.5, 165.5, 134.7, 133.1, 129.5, 129.3, 52.4. Spectroscopic data for **7** match those previously reported in the literature.[1]



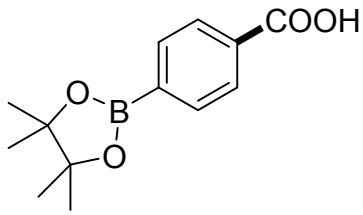
4-Fluorobenzoic acid (8)

The title compound was isolated as a white solid, 43.4 mg, 62% (from 1-chloro-4-fluorobenzene); 47.6 mg, 68% (from 1-bromo-4-fluorobenzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.05 (s, 1H), 8.00 (s, 2H), 7.31 (s, 2H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.3, 164.9 (d, *J* = 250.4 Hz), 132.0 (d, *J* = 9.4 Hz), 127.3, 115.5 (d, *J* = 22.1 Hz). **^{19}F NMR (DMSO-*d*$_6$, 376 MHz)**: δ -106.90. Spectroscopic data for **8** match those previously reported in the literature.[1]



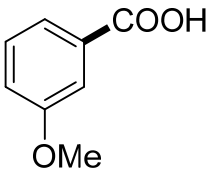
4-(Trifluoromethyl)benzoic acide (9)

The title compound was isolated as a white solid, 65.6 mg, 69% (from 1-chloro-4-(trifluoromethyl)benzene); 55.1 mg, 58% (from 1-bromo-4-(trifluoromethyl)benzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.48 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.6, 135.0, 132.9 (q, *J* = 31.6 Hz), 130.5, 126.0 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.6 Hz). **^{19}F NMR (DMSO-*d*$_6$, 376 MHz)**: δ -61.58. Spectroscopic data for **9** match those previously reported in the literature.[1]



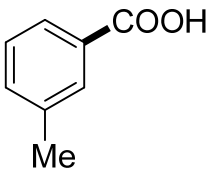
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (10)

The title compound was isolated as a white solid, 79.4 mg, 64% (from 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol -ane); 62 mg, 50% (from 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.09 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 1.30 (d, *J* = 1.2 Hz, 12H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.1, 134.4, 133.1, 128.5, 83.9, 24.6. Spectroscopic data for **10** match those previously reported in the literature.[1]



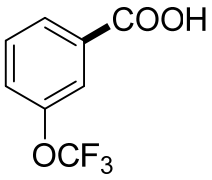
3-Methoxybenzoic acid (11)

The title compound was isolated as a white solid, 62.3 mg, 82% (from 1-chloro-3-methoxybenzene); 50.2 mg, 66% (from 1-bromo-3-methoxybenzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.00 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.18 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.1, 159.2, 132.1, 130.0, 121.5, 118.9, 113.8, 55.2. Spectroscopic data for **11** match those previously reported in the literature.[3]



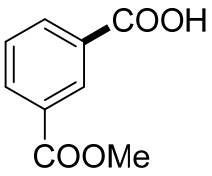
3-Methylbenzoic acid (12)

The title compound was isolated as a white solid, 42.8 mg, 63% (from 1-chloro-3-methylbenzene); 59.8 mg, 88% (from 1-bromo-3-methylbenzene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.88 (s, 1H), 7.83 – 7.67 (m, 2H), 7.51 – 7.27 (m, 2H), 2.35 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.4, 137.9, 133.4, 130.7, 129.7, 128.4, 126.4, 20.8. Spectroscopic data for **12** match those previously reported in the literature.[4]



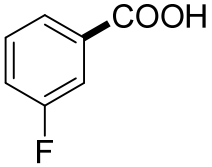
3-(Trifluoromethoxy)benzoic acid (13)

The title compound was isolated as a white solid, 65.9 mg, 64% (from 1-chloro-3-(trifluoromethoxy)benzene); 87.6 mg, 85% (from 1-bromo-3-(trifluoromethoxy)benzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 13.43 (s, 1H), 8.03 – 7.93 (m, 1H), 7.80 (s, 1H), 7.72 – 7.55 (m, 2H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 165.9, 148.3, 133.1, 130.8, 128.3, 125.4, 121.2, 120.0 (q, J = 256.5 Hz). **^{19}F NMR (DMSO-d_6, 376 MHz)**: δ -57.0. Spectroscopic data for **13** match those previously reported in the literature.[5]



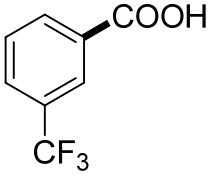
3-(Methoxycarbonyl)benzoic acid (14)

The title compound was isolated as a white solid, 67.5 mg, 75% (from methyl 3-chlorobenzoate); 59.4 mg, 66% (from methyl 3-bromobenzoate). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 13.32 (s, 1H), 8.47 (s, 1H), 8.21 – 8.14 (m, 2H), 7.66 (t, J = 7.8 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 166.4, 165.5, 133.7, 133.2, 131.3, 130.0, 129.7, 129.3, 52.4. Spectroscopic data for **14** match those previously reported in the literature.[6]



3-Fluorobenzoic acid (15)

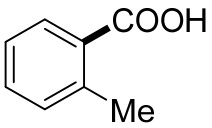
The title compound was isolated as a white solid, 49.7 mg, 71% (from 1-chloro-3-fluorobenzene); 44.8 mg, 64% (from 1-bromo-3-fluorobenzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 13.28 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 9.4 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.51 – 7.42 (m, 1H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 166.1, 161.9 (d, J = 244.5 Hz), 133.2 (d, J = 7.3 Hz), 130.7 (d, J = 7.9 Hz), 125.3 (d, J = 2.8 Hz), 119.7 (d, J = 21.1 Hz), 115.6 (d, J = 22.7 Hz). **^{19}F NMR (DMSO-d_6, 376 MHz)**: δ -112.6. Spectroscopic data for **15** match those previously reported in the literature.[4]



3-(Trifluoromethyl)benzoic acid (16)

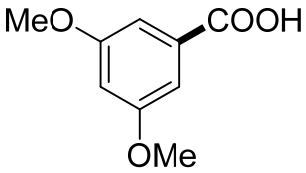
The title compound was isolated as a white solid, 62.7 mg, 66% (from 1-chloro-3-(trifluoromethyl)benzene); 62.7 mg, 66% (from 1-bromo-3-(trifluoromethyl)benzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 13.51 (s, 1H), 8.22 (d, J = 7.7 Hz, 1H), 8.17 (s, 1H), 7.98 (d, J = 6.3 Hz, 1H), 7.80 – 7.71 (m, 1H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 166.0, 133.1, 131.9, 130.0, 129.4 (q, J = 32.1 Hz), 129.3 (q, J = 3.5

Hz), 125.4 (q, J = 3.8 Hz), 123.7 (q, J = 272.4 Hz). **^{19}F NMR (DMSO-d_6, 376 MHz)**: δ -61.4. Spectroscopic data for **16** match those previously reported in the literature.[3]



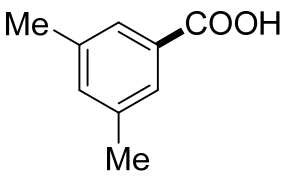
2-Methylbenzoic acid (17)

The title compound was isolated as a white solid, 41.5 mg, 61% (from 1-chloro-2-methylbenzene); 57.8 mg, 85% (from 1-bromo-2-methylbenzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.81 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.34 – 7.23 (m, 2H), 2.52 (s, 3H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 169.1, 139.5, 132.2, 132.0, 130.9, 130.7, 126.3, 21.7. Spectroscopic data for **17** match those previously reported in the literature.[6]



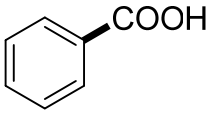
3,5-dimethoxybenzoic acid (18)

The title compound was isolated as a white solid, 60.1 mg, 66% (from 1-chloro-3,5-dimethoxybenzene); 54.6 mg, 60% (from 1-bromo-3,5-dimethoxybenzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.99 (s, 1H), 7.06 (d, J = 2.3 Hz, 2H), 6.73 (t, J = 2.2 Hz, 1H), 3.79 (s, 6H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 166.9, 160.3, 132.8, 106.8, 104.8, 55.3. Spectroscopic data for **18** match those previously reported in the literature.[7]



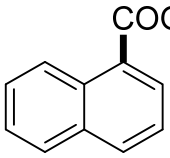
3,5-Dimethylbenzoic acid (19)

The title compound was isolated as a white solid, 63 mg, 84% (from 1-chloro-3,5-dimethylbenzene); 62.3 mg, 83% (from 1-bromo-3,5-dimethylbenzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.78 (s, 1H), 7.55 (s, 2H), 7.22 (s, 1H), 2.31 (s, 6H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 167.5, 137.6, 134.1, 130.6, 126.9, 20.6. Spectroscopic data for **19** match those previously reported in the literature.[8]



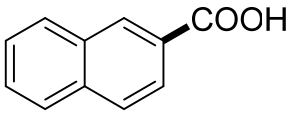
Benzoic acid (20)

The title compound was isolated as a white solid, 41.5 mg, 68% (from chlorobenzene); 39.7 mg, 65% (from bromobenzene). **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.96 (s, 1H), 7.95 (d, J = 7.3 Hz, 2H), 7.61 (t, J = 7.0 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 167.3, 132.8, 130.7, 129.2, 128.5. Spectroscopic data for **1** match those previously reported in the literature.[6]



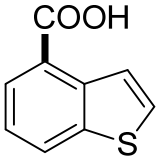
1-Naphthoic acid (21)

The title compound was isolated as a white solid, 62.8 mg, 73% (from 1-chloronaphthalene); 58.5 mg, 68% (from 1-bromonaphthalene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.15 (s, 1H), 8.88 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.10 (m, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.55 (m, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 168.6, 133.4, 132.8, 130.6, 129.8, 128.5, 127.6, 127.5, 126.1, 125.4, 124.8. Spectroscopic data for **21** match those previously reported in the literature.[3]



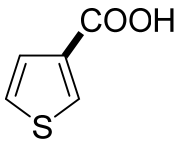
2-Naphthoic acid (22)

The title compound was isolated as a white solid, 49.9 mg, 58% (from 2-chloronaphthalene); 47.3 mg, 55% (from 2-bromonaphthalene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.09 (s, 1H), 8.62 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 – 7.94 (m, 3H), 7.70 – 7.56 (m, 2H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.9, 135.4, 132.6, 131.0, 129.8, 128.8, 128.6, 128.5, 128.1, 127.3, 125.6. Spectroscopic data for **22** match those previously reported in the literature.[3]



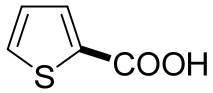
Benzo[*b*]thiophene-4-carboxylic acid (23)

The title compound was isolated as a white solid, 58.7 mg, 66% (from 4-chlorobenzo[*b*]thiophene); 55.2 mg, 62% (from 4-bromobenzo[*b*]thiophene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.14 (s, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 5.5 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 5.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ167.6, 140.7, 138.3, 129.8, 127.5, 127.4, 125.2, 124.1, 123.7. Spectroscopic data for **23** match those previously reported in the literature.[8]



Thiophene-3-carboxylic acid (24)

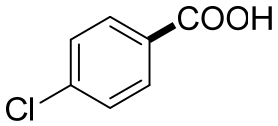
The title compound was isolated as a white solid, 32.6 mg, 51% (from 3-chlorothiophene); 41.6 mg, 65% (from 3-bromothiophene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.71 (s, 1H), 8.26 (s, 1H), 7.65 – 7.55 (m, 1H), 7.42 (d, *J* = 4.7 Hz, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 164.0, 134.8, 133.8, 128.2, 127.7. Spectroscopic data for **24** match those previously reported in the literature.[3]



Thiophene-2-carboxylic acid (25)

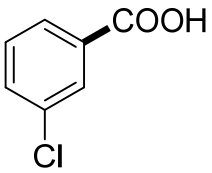
The title compound was isolated as a white solid, 22.4 mg, 35% (from 2-chlorothiophene); 14.7 mg, 23% (from 2-bromothiophene). **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**:

δ 13.04 (s, 1H), 7.88 (d, *J* = 3.9 Hz, 1H), 7.73 (d, *J* = 2.6 Hz, 1H), 7.23 – 7.15 (t, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 162.8, 134.6, 133.2, 133.1, 128.1. Spectroscopic data for **25** match those previously reported in the literature.[3]



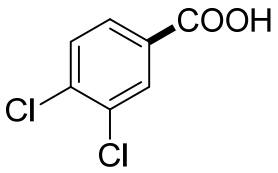
4-Chlorobenzoic acid (26)

The title compound was isolated as a white solid, 46.8 mg, 60%. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.18 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.4, 137.7, 131.1, 129.6, 128.7. Spectroscopic data for **26** match those previously reported in the literature.[3]



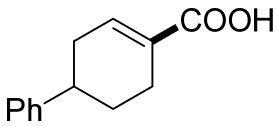
3-Chlorobenzoic acid (27)

The title compound was isolated as a white solid, 49.9 mg, 64%. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.27 (s, 1H), 7.89 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.0, 133.3, 132.8, 132.6, 130.6, 128.8, 127.8. Spectroscopic data for **27** match those previously reported in the literature.[3]



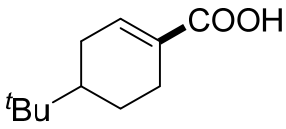
3-Chlorobenzoic acid (28)

The title compound was isolated as a white solid, 66.5 mg, 70%. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 13.48 (s, 1H), 8.05 (d, *J* = 1.9 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 165.3, 135.7, 131.4, 131.3, 130.9, 130.8, 129.2. Spectroscopic data for **28** match those previously reported in the literature.[9]



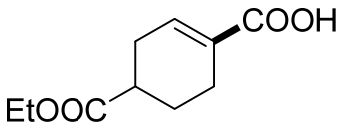
1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxylic acid (29)

The title compound was isolated as a white solid, 74.7 mg, 74%. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.17 (s, 1H), 7.36 – 7.16 (m, 5H), 6.95 (s, 1H), 2.73 (d, *J* = 8.9 Hz, 1H), 2.51 (s, 1H), 2.47 – 2.32 (m, 2H), 2.33 – 2.19 (m, 2H), 1.89 (d, *J* = 11.2 Hz, 1H), 1.78 – 1.61 (m, 1H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 167.9, 145.9, 138.3, 130.1, 128.3, 126.6, 126.0, 38.3, 33.0, 29.0, 24.5. **HRMS (ESI)**: Calcd for $C_{13}H_{14}O_2$ $[M-H]^-$ 201.0921, found 201.0918. Spectroscopic data for **29** match those previously reported in the literature.[1]



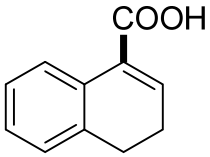
4-(*tert*-Butyl)cyclohex-1-ene-1-carboxylic acid (30)

The title compound was isolated as a white solid, 69.7 mg, 83%. **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.04 (s, 1H), 6.90 – 6.80 (m, 1H), 2.37 (d, *J* = 17.6 Hz, 1H), 2.19 (d, *J* = 18.9 Hz, 1H), 2.06 – 1.79 (m, 3H), 1.24 – 1.15 (m, 1H), 1.09 – 0.97 (m, 1H), 0.85 (s, 9H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 168.5, 139.6, 130.6, 43.2, 32.3, 27.4, 25.7, 23.7. Spectroscopic data for **30** match those previously reported in the literature.[10]



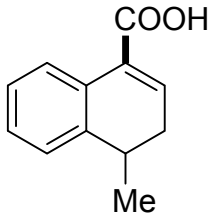
4-(Ethoxycarbonyl)cyclohex-1-ene-1-carboxylic acid (31)

The title compound was isolated as a white solid, 75.2 mg, 76%. **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.21 (s, 1H), 6.84 (s, 1H), 4.18 – 3.98 (m, 2H), 2.57 – 2.50 (m, 1H), 2.46 – 2.22 (m, 3H), 2.22 – 2.08 (m, 1H), 2.03 – 1.89 (m, 1H), 1.65 – 1.52 (m, 1H), 1.19 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 164.5, 155.6, 142.8, 135.2, 130.0, 127.9, 75.8, 53.6, 47.1, 45.5, 40.8, 34.2, 31.4, 26.4, 23.5, 22.0, 21.6, 20.7, 16.4. Spectroscopic data for **31** match those previously reported in the literature.[10]



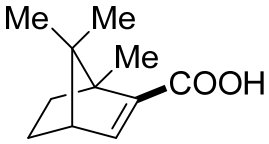
3,4-Dihydronaphthalene-1-carboxylic acid (32)

The title compound was isolated as a white solid, 45.6 mg, 57%. **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.59 (s, 1H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 28.2 Hz, 4H), 2.76 – 2.62 (m, 2H), 2.34 (s, 2H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 167.3, 139.5, 136.0, 130.8, 130.4, 127.4, 127.3, 126.1, 125.7, 26.8, 22.9. Spectroscopic data for **32** match those previously reported in the literature.[10]



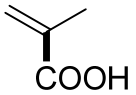
4-Methyl-3,4-dihydronaphthalene-1-carboxylic acid (33)

The title compound was isolated as a white solid, 51.7 mg, 55%. **^{1}H NMR (DMSO-d_6, 400 MHz)**: δ 12.61 (s, 1H), 7.86 – 7.74 (m, 1H), 7.22 (s, 3H), 7.05 (t, *J* = 4.5 Hz, 1H), 2.95 – 2.81 (m, 1H), 2.54 – 2.48 (m, 1H), 2.27 – 2.13 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (DMSO-d_6, 101 MHz)**: δ 167.4, 140.8, 138.0, 129.9, 127.7, 126.0, 30.9, 30.6, 19.7. Spectroscopic data for **33** match those previously reported in the literature.[11]



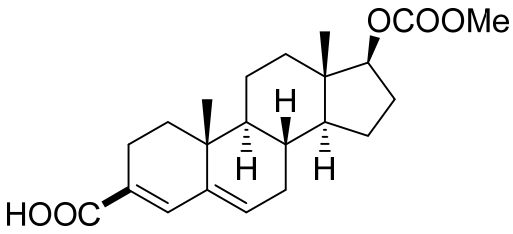
(1S,4S)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ene-2-carboxylic acid (34)

The title compound was isolated as a white solid, 63 mg, 70%. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 11.88 (s, 1H), 6.80 (d, *J* = 3.3 Hz, 1H), 2.42 (t, *J* = 3.5 Hz, 1H), 1.94 – 1.82 (m, 1H), 1.60 – 1.51 (m, 1H), 1.16 (s, 3H), 1.04 – 0.97 (m, 1H), 0.94 – 0.88 (m, 1H), 0.74 (d, *J* = 8.6 Hz, 6H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 166.0, 145.6, 141.0, 56.1, 53.2, 51.2, 30.8, 24.2, 19.1, 18.8, 11.8. Spectroscopic data for **34** match those previously reported in the literature.[1]



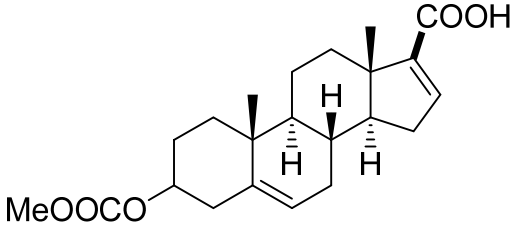
Methacrylic acid (35)

The title compound was isolated as a colorless liquid, 29.2 mg, 68%. **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 6.25 (s, 1H), 5.68 (s, 1H), 1.96 (s, 3H). **^{13}C NMR (CDCl$_3$, 101 MHz)**: δ 172.9, 135.7, 127.8, 17.8. Spectroscopic data for **35** match those previously reported in the literature.[12]



(8R,9S,10R,13S,14S,17S)-17-((Methoxycarbonyl) oxy)-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16, 17-dodecahydro-1H-cyclopenta[a]phenanthrene-3-carboxylic acid (36)

The title compound was isolated as a white solid, 134.6 mg, 72%, M.p.: 201-203 °C. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.12 (s, 1H), 6.92 (s, 1H), 5.83 (s, 1H), 4.47 – 4.41 (m, 1H), 3.67 (s, 3H), 2.38 (dd, *J* = 18.3, 4.7 Hz, 1H), 2.28 – 2.08 (m, 3H), 1.84 (dd, *J* = 12.7, 4.3 Hz, 1H), 1.74 – 1.55 (m, 5H), 1.40 – 1.30 (m, 2H), 1.26 – 1.09 (m, 3H), 1.08 – 0.96 (m, 2H), 0.85 (s, 3H), 0.77 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 168.3, 155.0, 140.6, 137.2, 130.8, 126.0, 85.5, 54.3, 50.0, 47.3, 42.0, 36.0, 34.1, 32.9, 31.1, 30.9, 26.9, 22.7, 21.4, 20.06, 18.6, 11.7. **HRMS (ESI)**: Calcd for $C_{22}H_{30}O_5$ $[M-H]^-$ 373.2020, found 373.2018.

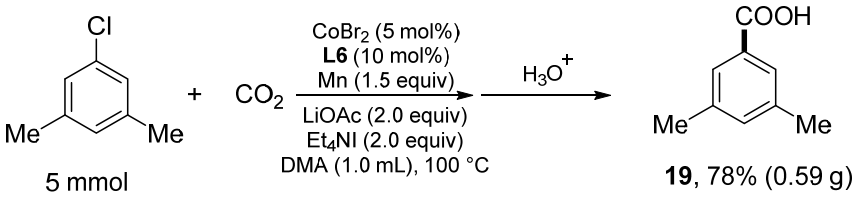


(8R,9S,10R,13S,14S)-3-((Methoxycarbonyl)oxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthrene-17-carboxylic acid (37)

The title compound was isolated as a white solid, 108.5 mg, 58%, M.p.: 209-211 °C. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ 12.03 (s, 1H), 6.69 – 6.61 (m, 1H), 5.38 (d, *J* = 4.8 Hz, 1H), 4.40 –

4.26 (m, 1H), 3.67 (s, 3H), 2.42 – 2.15 (m, 4H), 2.08 (s, 1H), 2.05 – 1.93 (m, 2H), 1.89 – 1.79 (m, 2H), 1.69 – 1.47 (m, 5H), 1.43 – 1.27 (m, 2H), 1.12 – 1.04 (m, 1H), 1.01 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (DMSO-*d*$_6$, 101 MHz)**: δ 165.6, 154.4, 146.9, 142.6, 139.5, 122.0, 77.0, 55.9, 54.3, 49.7, 45.0, 37.5, 36.2, 34.2, 31.3, 30.8, 30.6, 29.7, 27.2, 20.1, 18.8, 15.6. **HRMS (ESI)**: Calcd for $C_{22}H_{30}O_5$ $[M-H]^-$ 373.2020, found 373.2023.

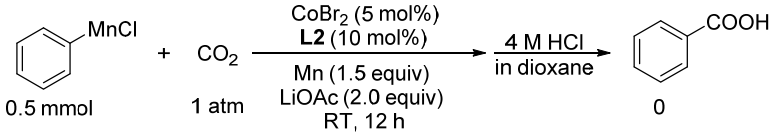
7. Procedure for 5 mmol Aryl Chlolide Carboxylation



An oven-dried 500 mL Schlenk flask containing a stirring bar was charged with $CoBr_2$ (55 mg, 5.0 mol %), **L6** (160 mg, 10.0 mol%), Mn powder (412 mg, 0.75mmol, 1.5 equiv), Et_4NI (2.57 g, 2.0 equiv) and LiOAc (660 mg, 2.0 equiv). The Schlenk flask was evacuated and back-filled under CO_2 flow (this procedure was repeated three times). Then, anhydrous DMA (20 mL) and aryl chlorides (5 mmol, 1.0 equiv) was added under CO_2 flow, and the resulting mixture was stirred at 100 ºC for 24 h. The mixture was then allowed to cool to room temperature. Then HCl aq. (2 M) was added into the flask to quench this reaction and stirred for another 10 minutes at room temperature. The mixture was extracted with Et_2O. The collected organic layer was combined and dried over anhydrous $MgSO_4$. After removal of solvent, the crude products were purified by flash chromatography (acetic acid/EtOAc/petroleum ether = 0/1/20 to 0.001/1/4) affording 3,5-dimethylbenzoic acid (**19**) in 78% yield (0.59 g).

8. Control Experiment

Procedure for the preparation of phenyl manganese chloride:[13] A solution of $MnCl_4Li_2$ was prepared by stirring anhydrous $MnCl_2$ (1.98g, 15.75 mmol) and anhydrous LiCl (1.33g, 31.5 mmol) in 25 ml of THF at room temperature until all $MnCl_2$ and LiCl dissolved. Then, PhMgCl (15 mmol, 1 M solution in THF) was added at -10°C. The solution was stirred at -10 °C to 0 °C for 15 minutes, then for 1 h at 0 °C. The concentration of phenyl manganese chloride solution was determined by titration with I_2/LiCl,[14] which was used immediately for next step.

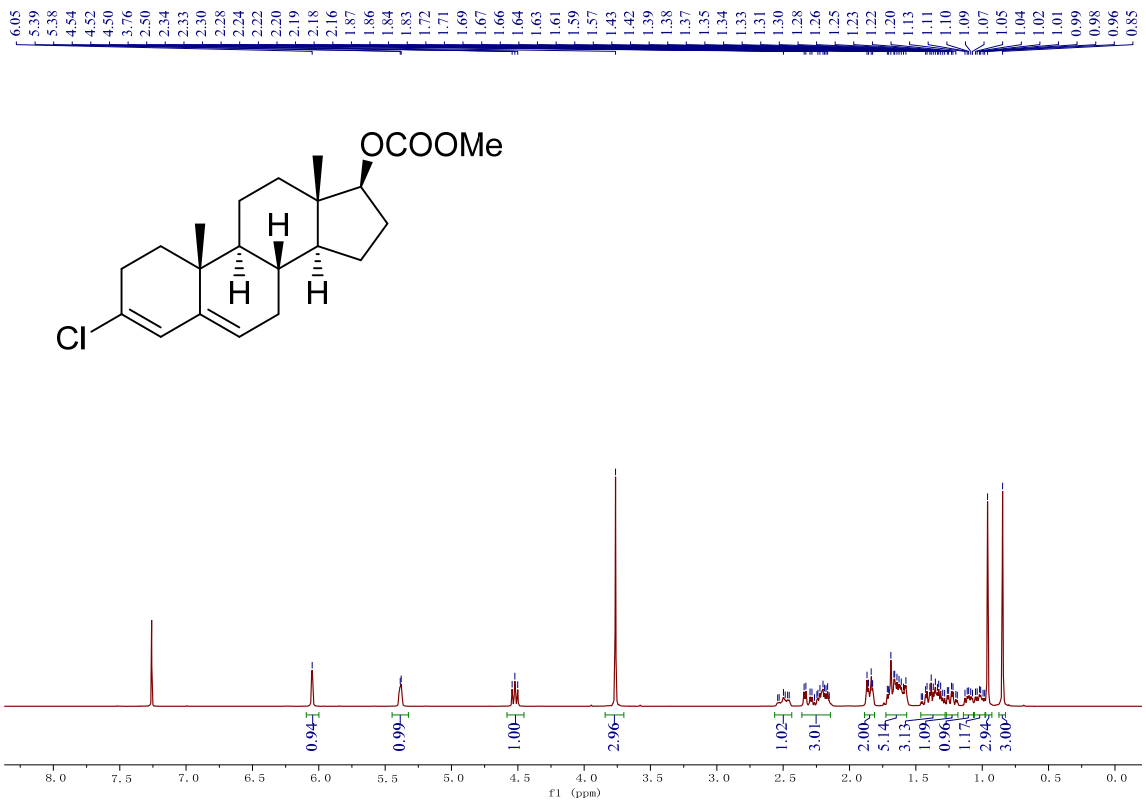


An oven-dried 50 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (5.5 mg, 5.0 mol %), **L2** (10.4 mg, 10.0 mol%), Mn powder (41.2 mg, 1.5 equiv) and LiOAc (66

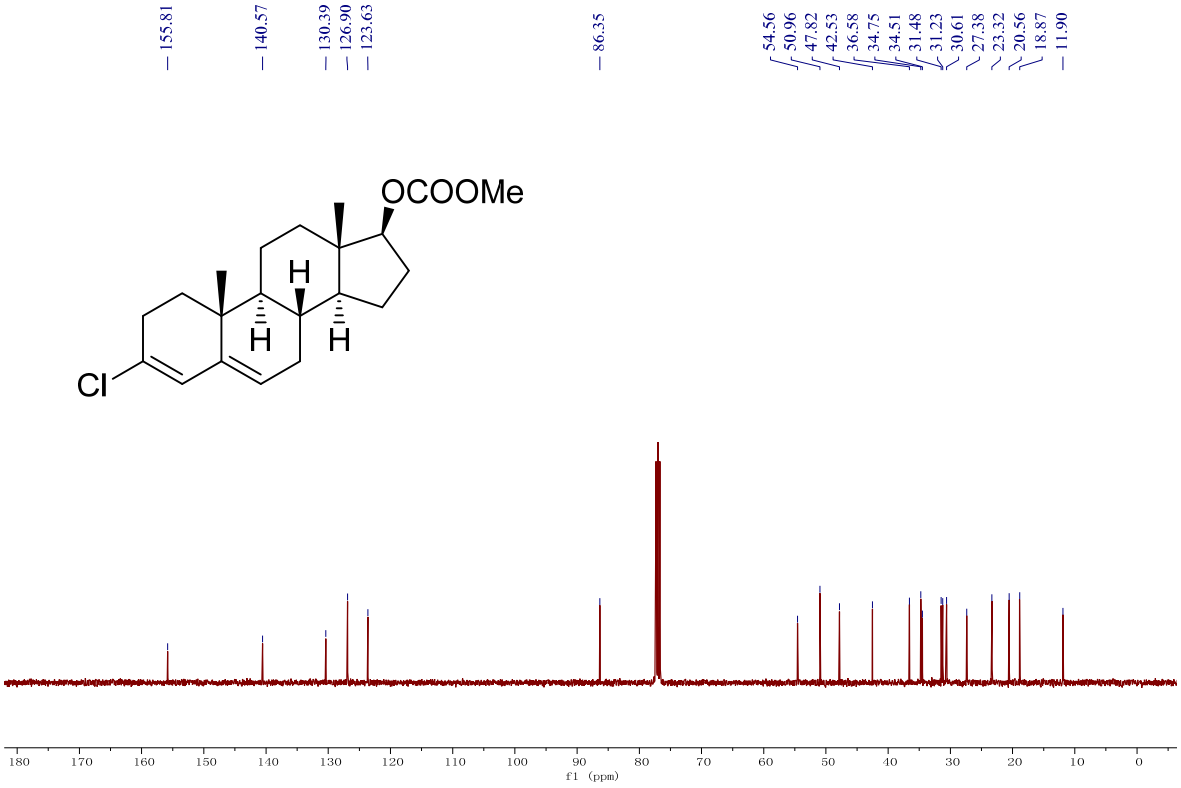
mg, 2.0 equiv). The Schlenk tube was evacuated and back-filled under CO_2 flow (this procedure was repeated three times). Then, anhydrous DMA (1.0 mL) and PhMnCl (0.5 mmol, 1.0 equiv, 0.32 M in THF) was added under CO_2 flow, and the resulting mixture was stirred at room temperature for 12 h. Then, the mixture was carefully quenched with 4 M HCl (in 1,4-dioxane) and stirred for 10 minutes. No desired product was detected. This result indicated ArMnCl may not serve as an intermediate in the catalytic cycle.

9. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra for Compounds

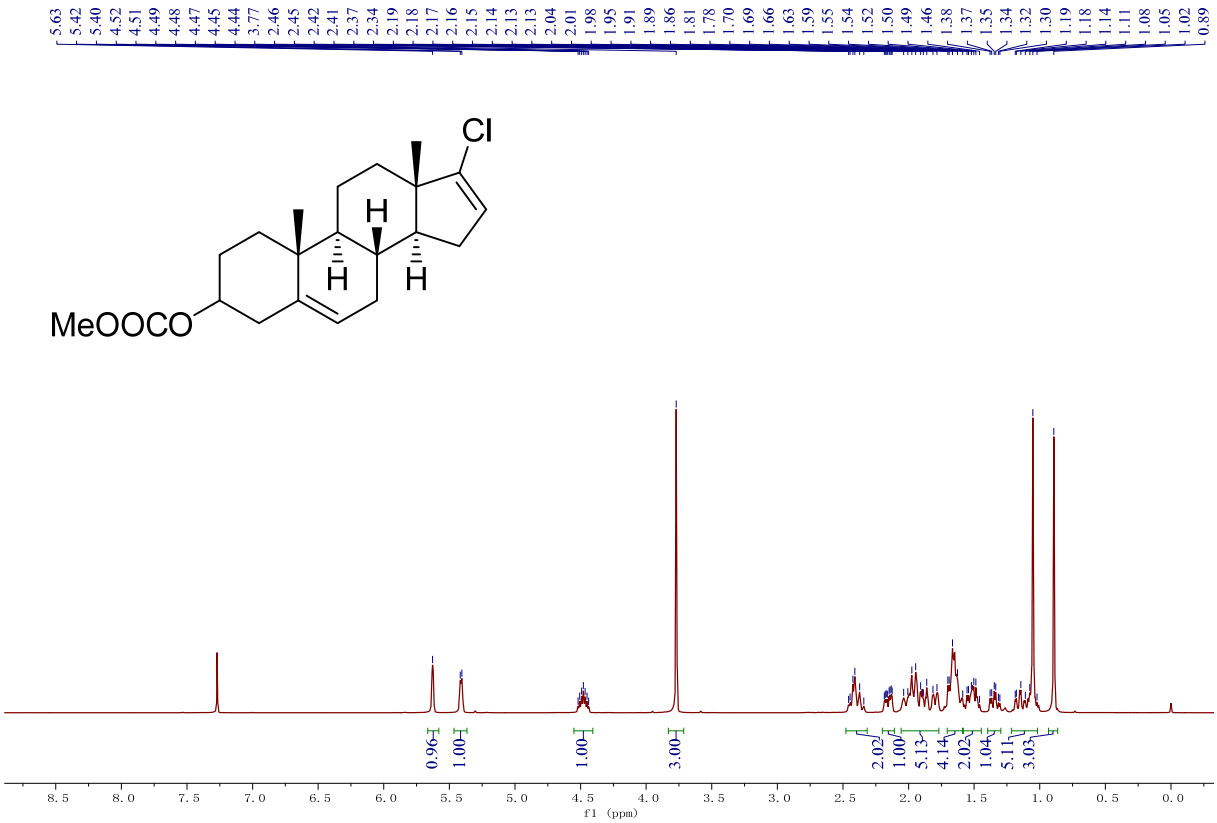
^{1}H NMR spectrum of **2h**



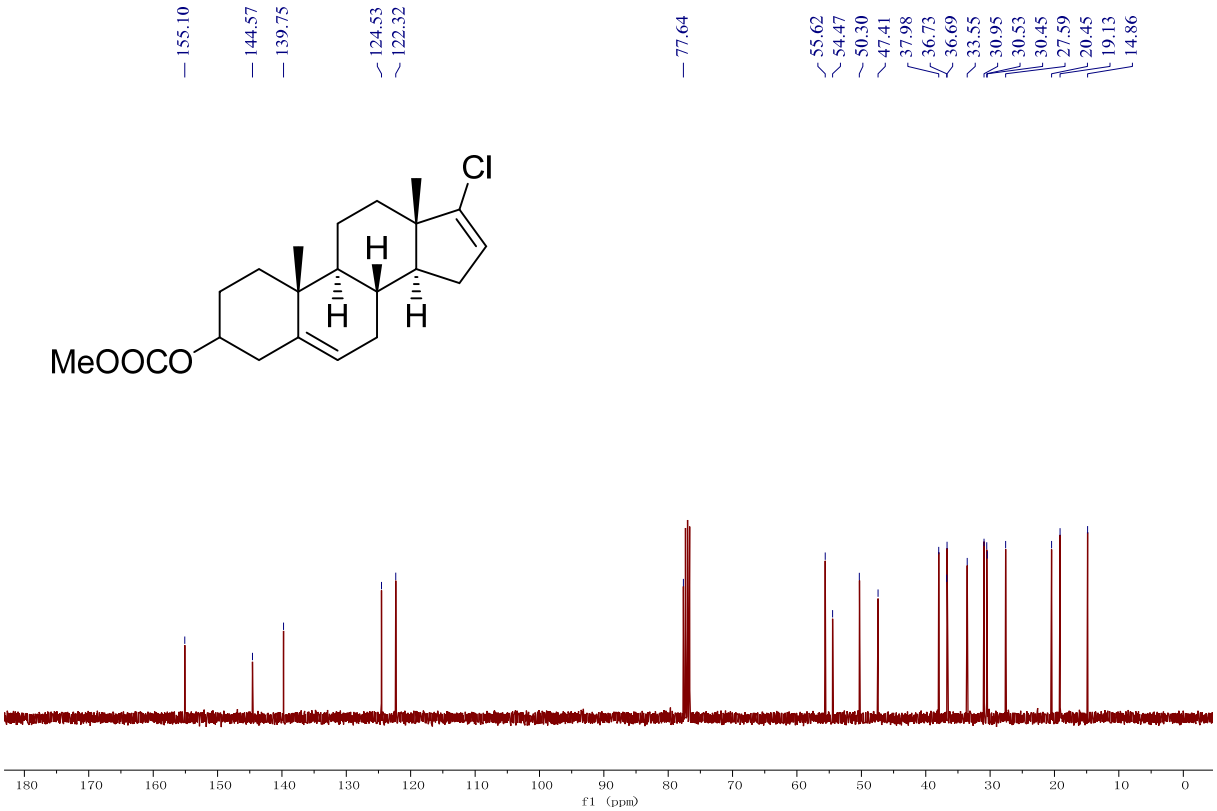
^{13}C NMR spectrum of **2h**



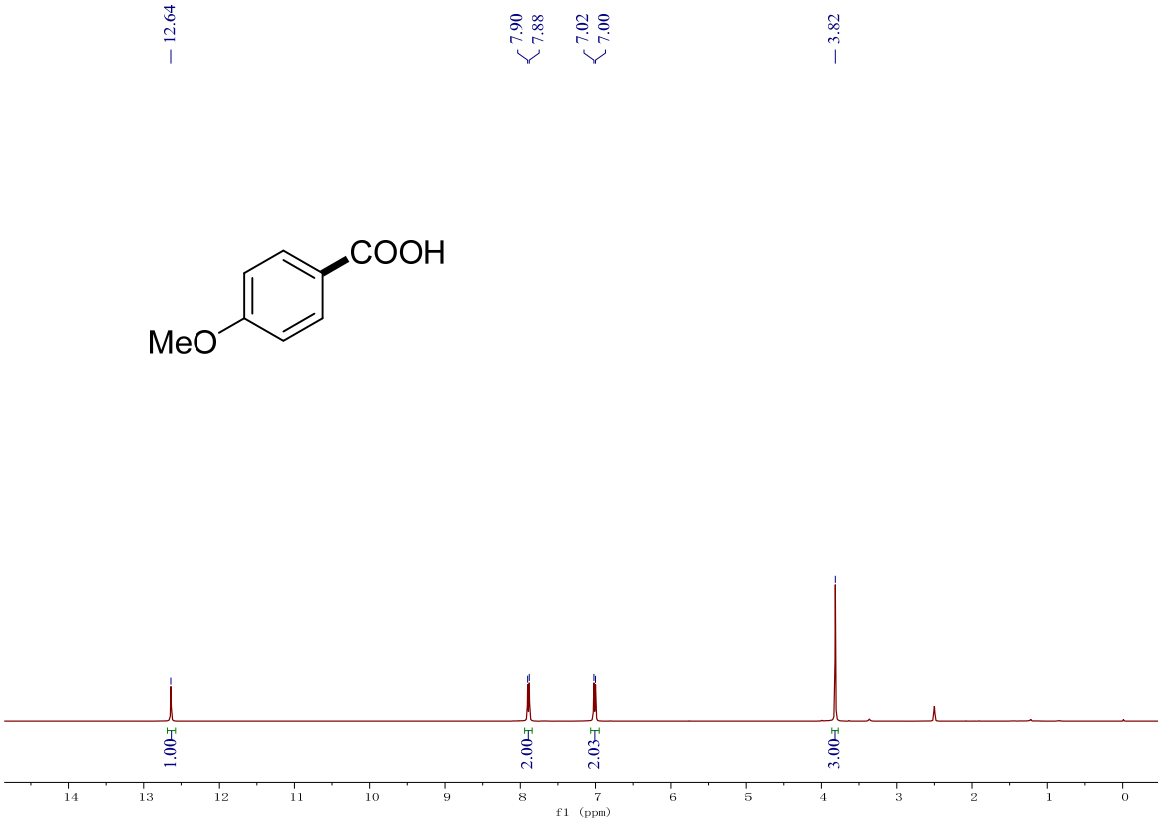
^{1}H NMR spectrum of **2i**



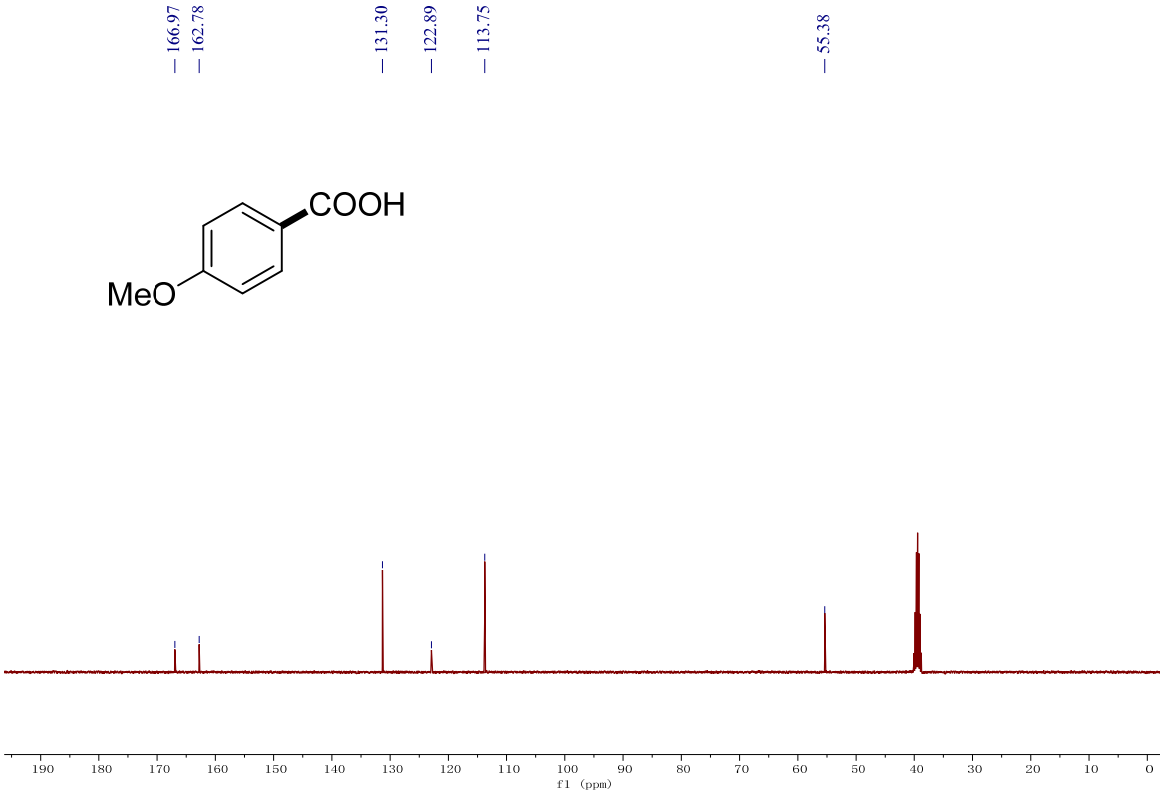
^{13}C NMR spectrum of **2i**



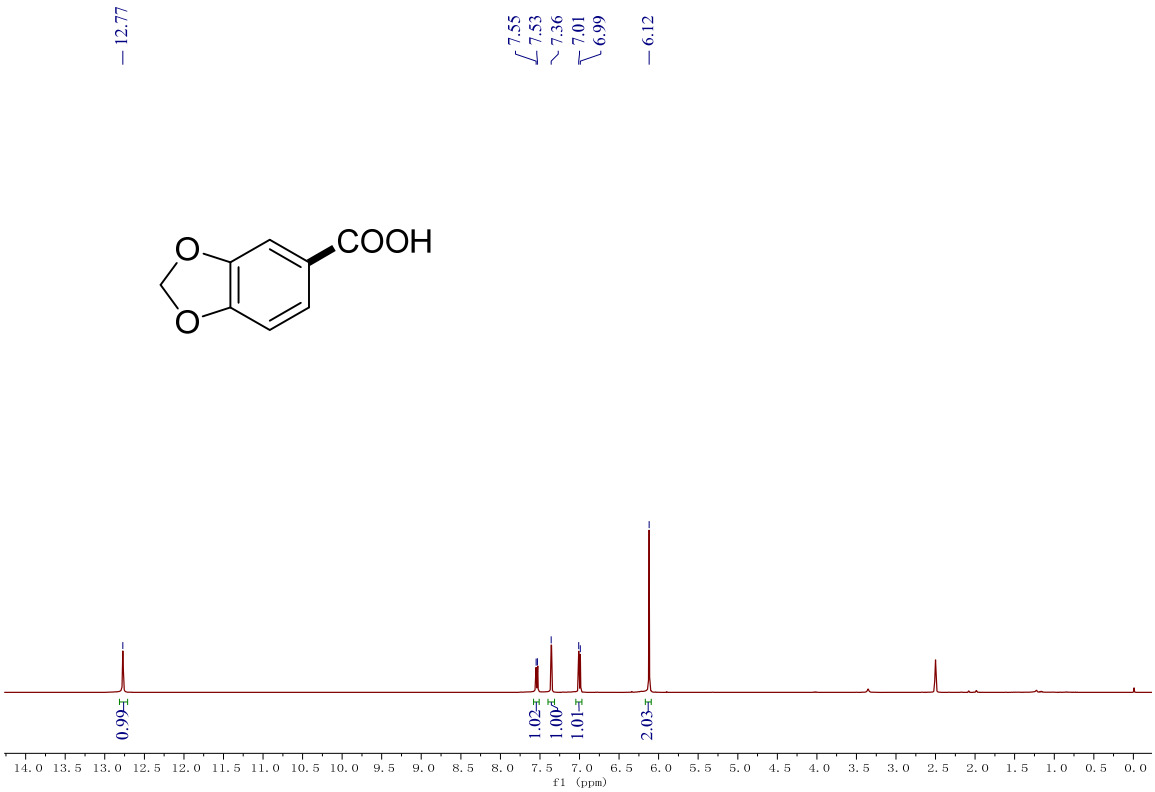
^{1}H NMR spectrum of **1**



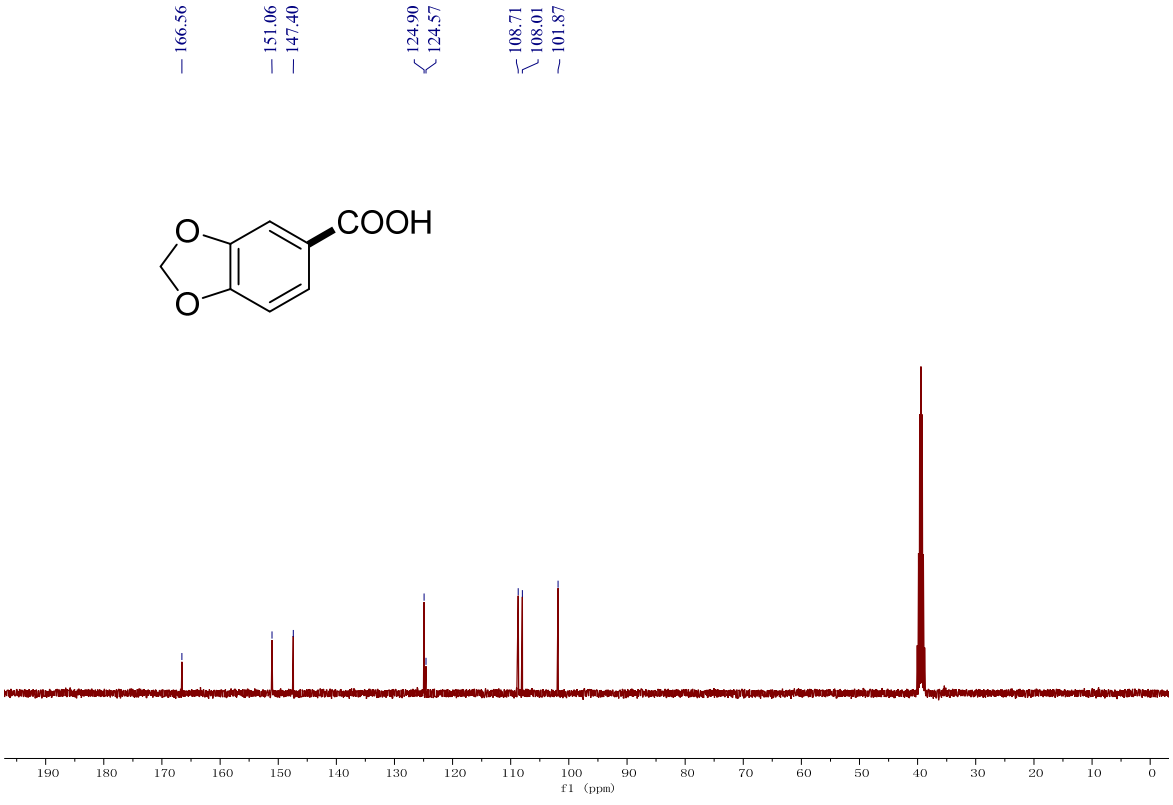
^{13}C NMR spectrum of



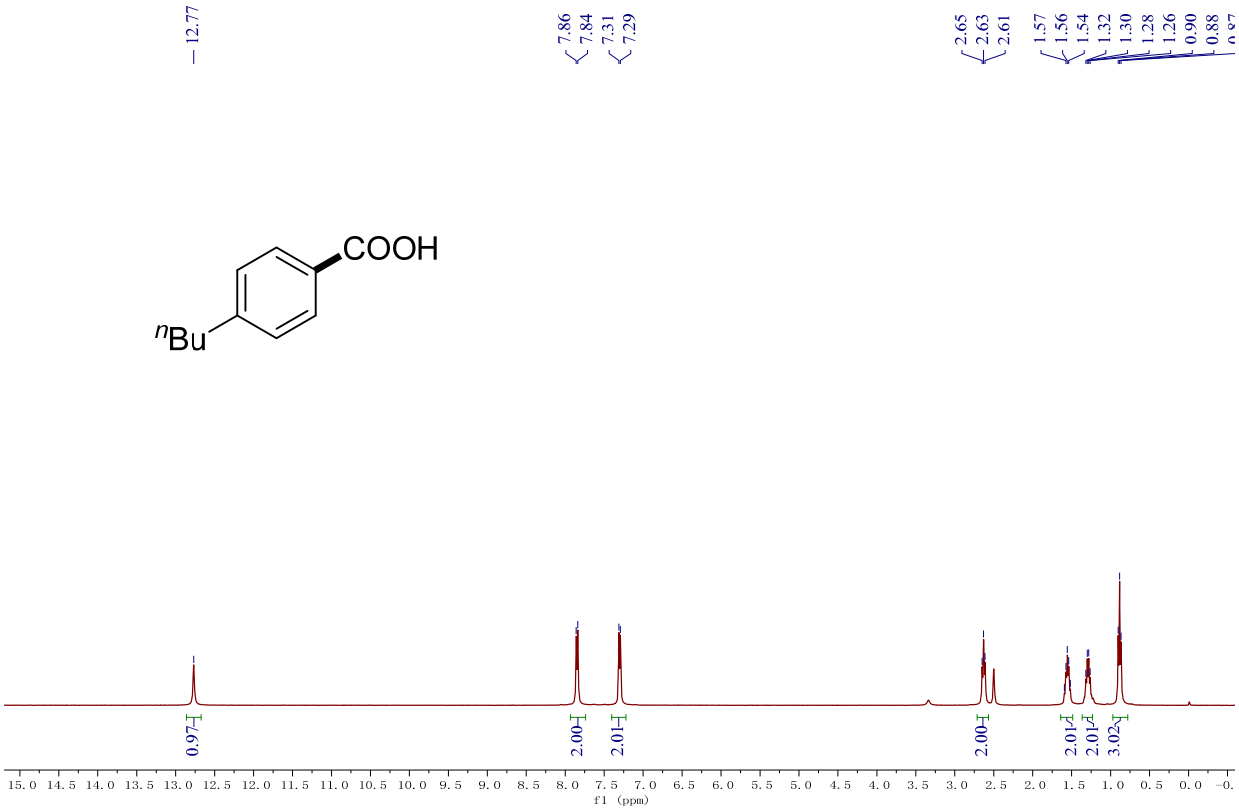
^{1}H NMR spectrum of **2**



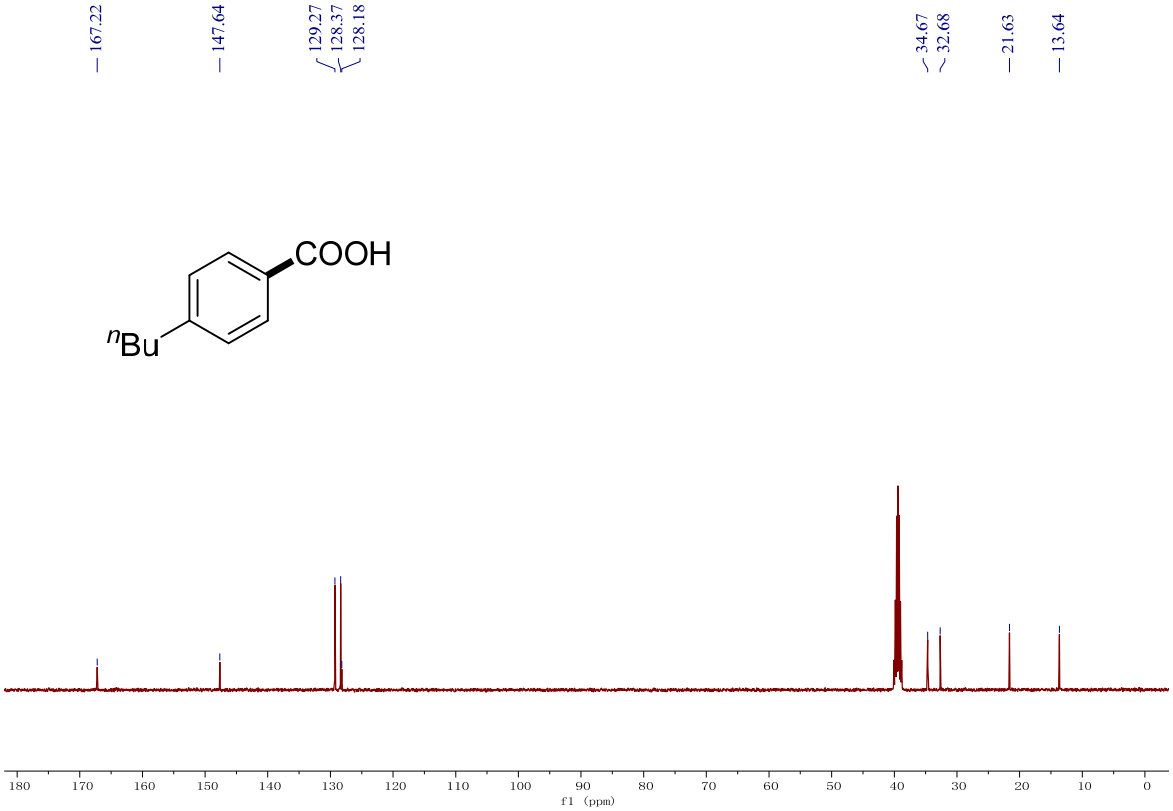
^{13}C NMR spectrum of **2**



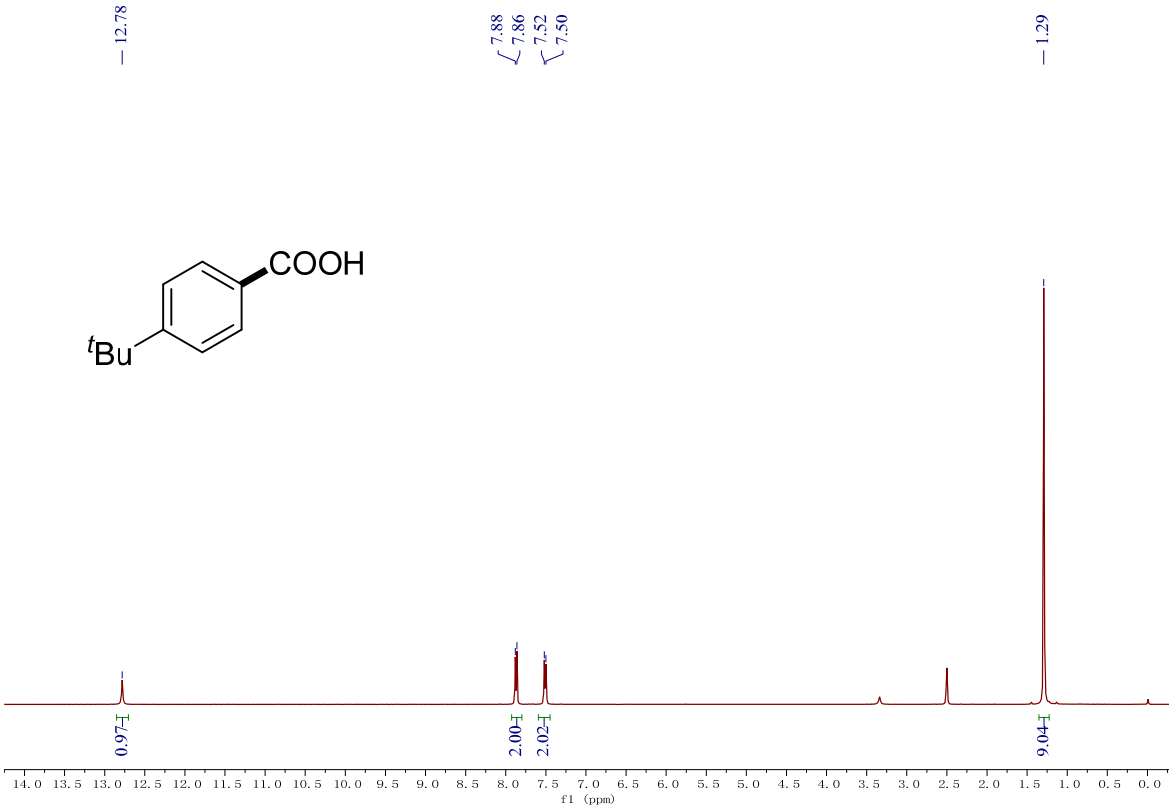
^{1}H NMR spectrum of **3**



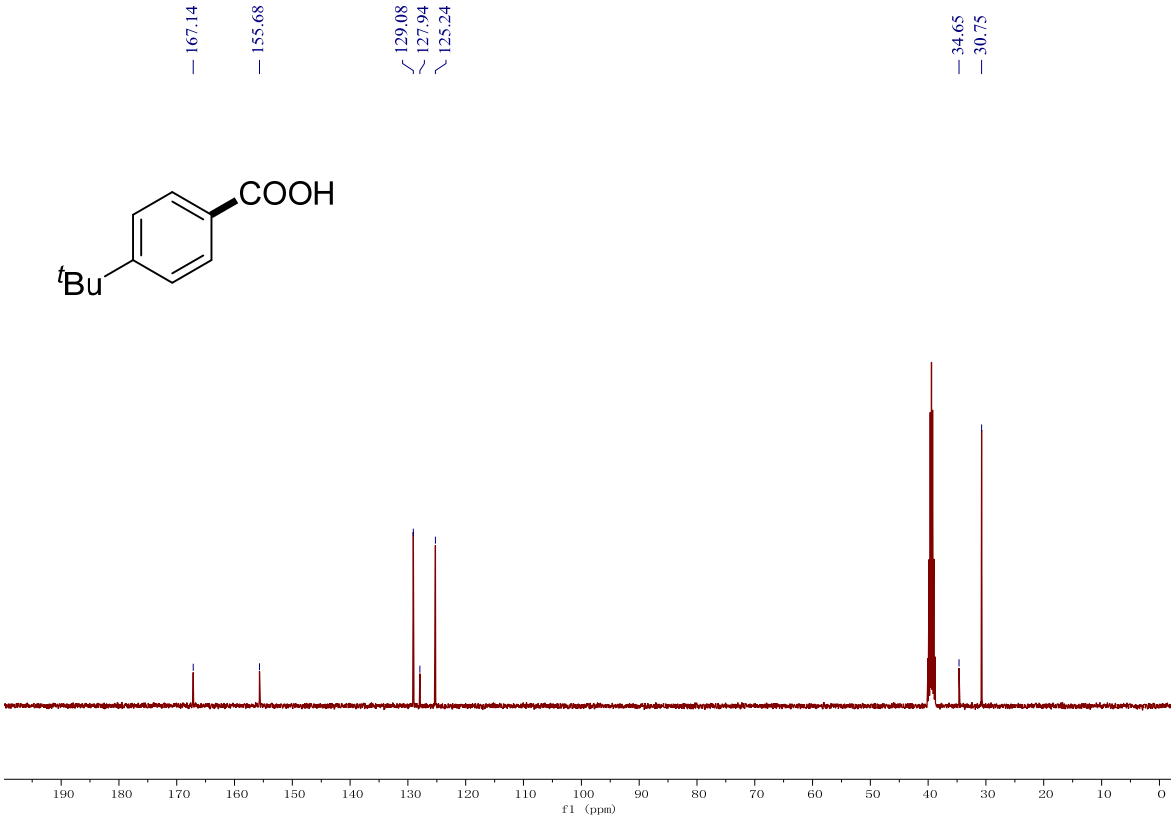
^{13}C NMR spectrum of **3**



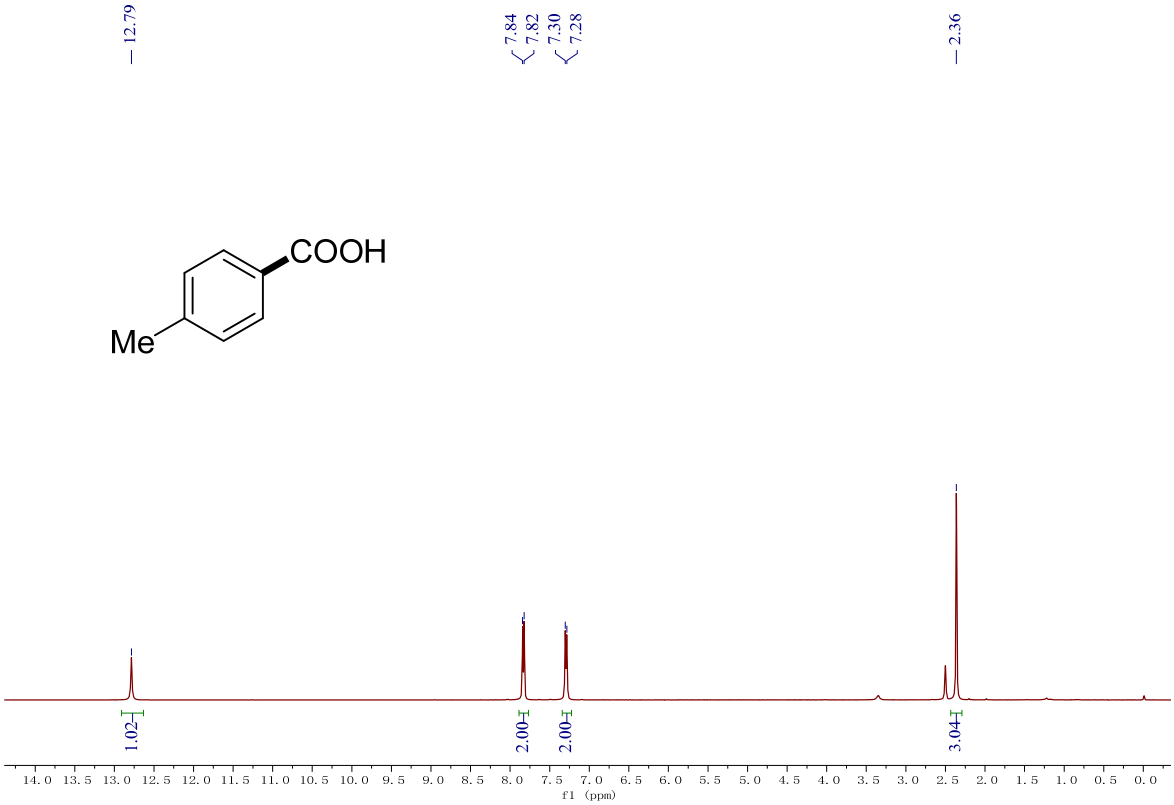
^{1}H NMR spectrum of **4**



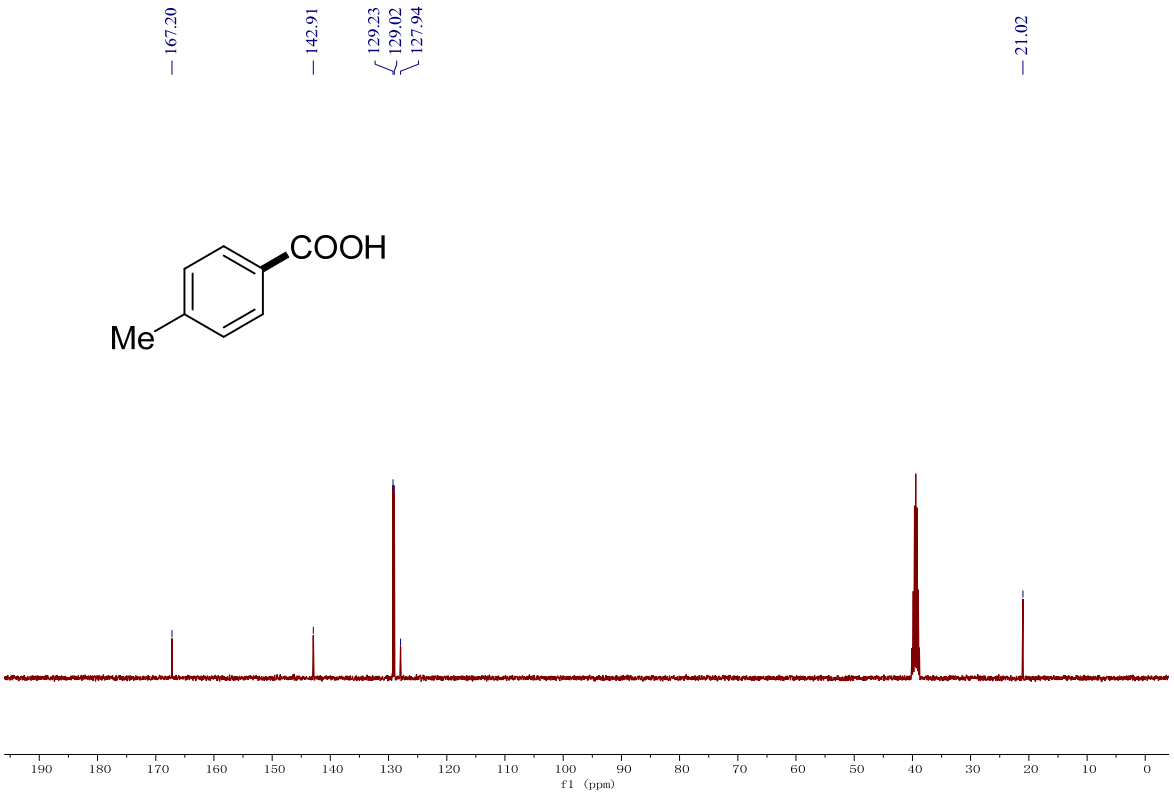
^{13}C NMR spectrum of **4**



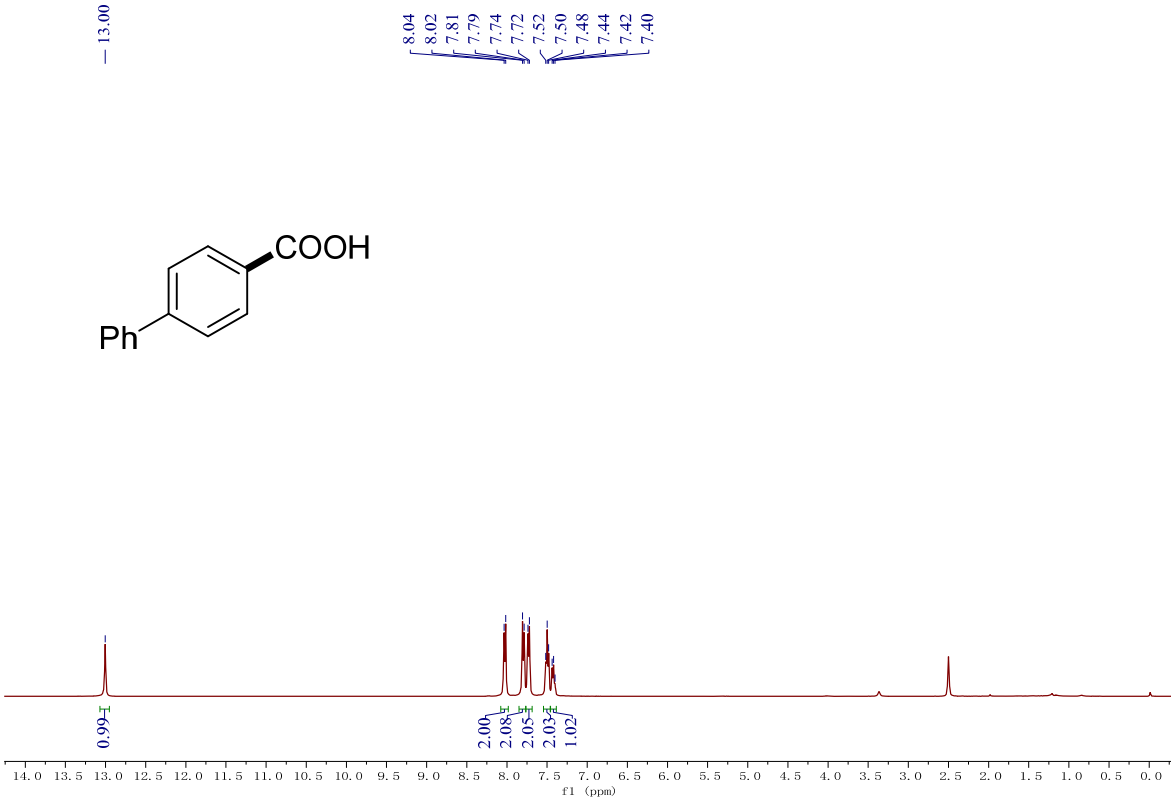
^{1}H NMR spectrum of **5**



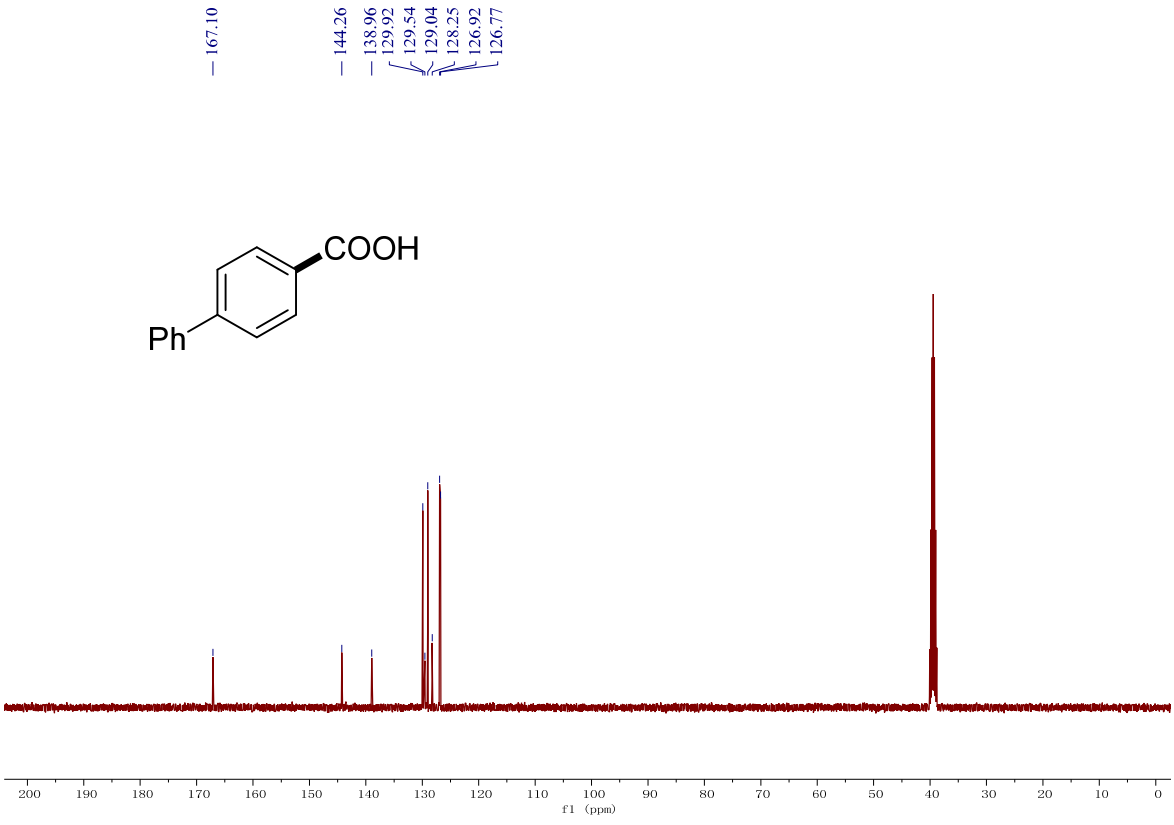
^{13}C NMR spectrum of **5**



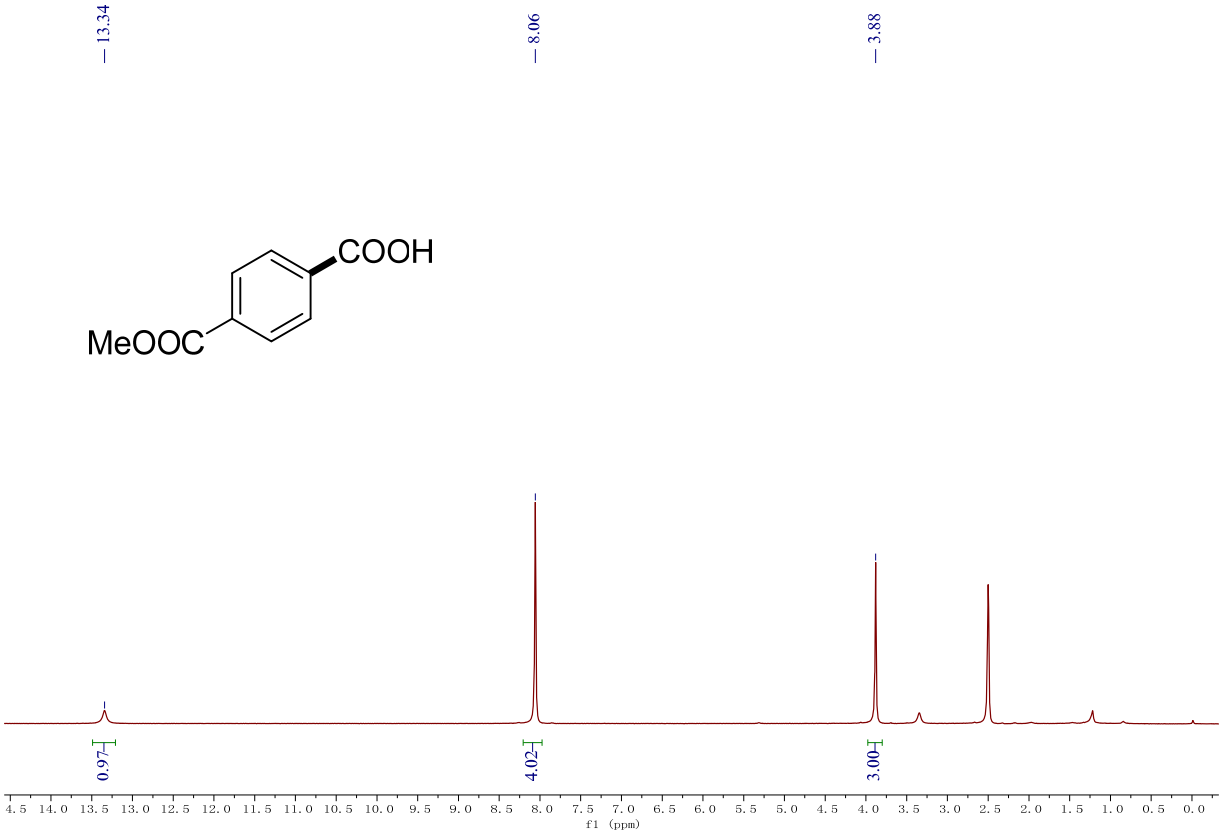
^{1}H NMR spectrum of **6**



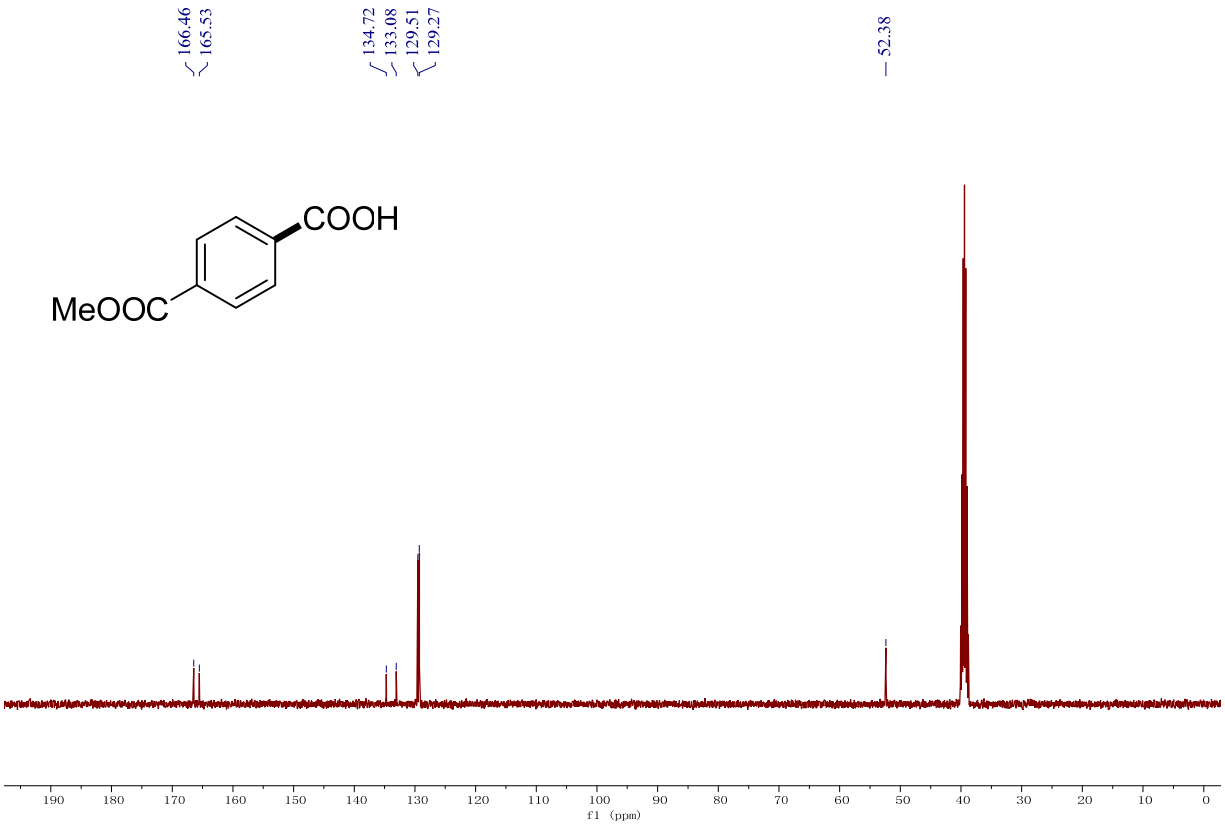
^{13}C NMR spectrum of **6**



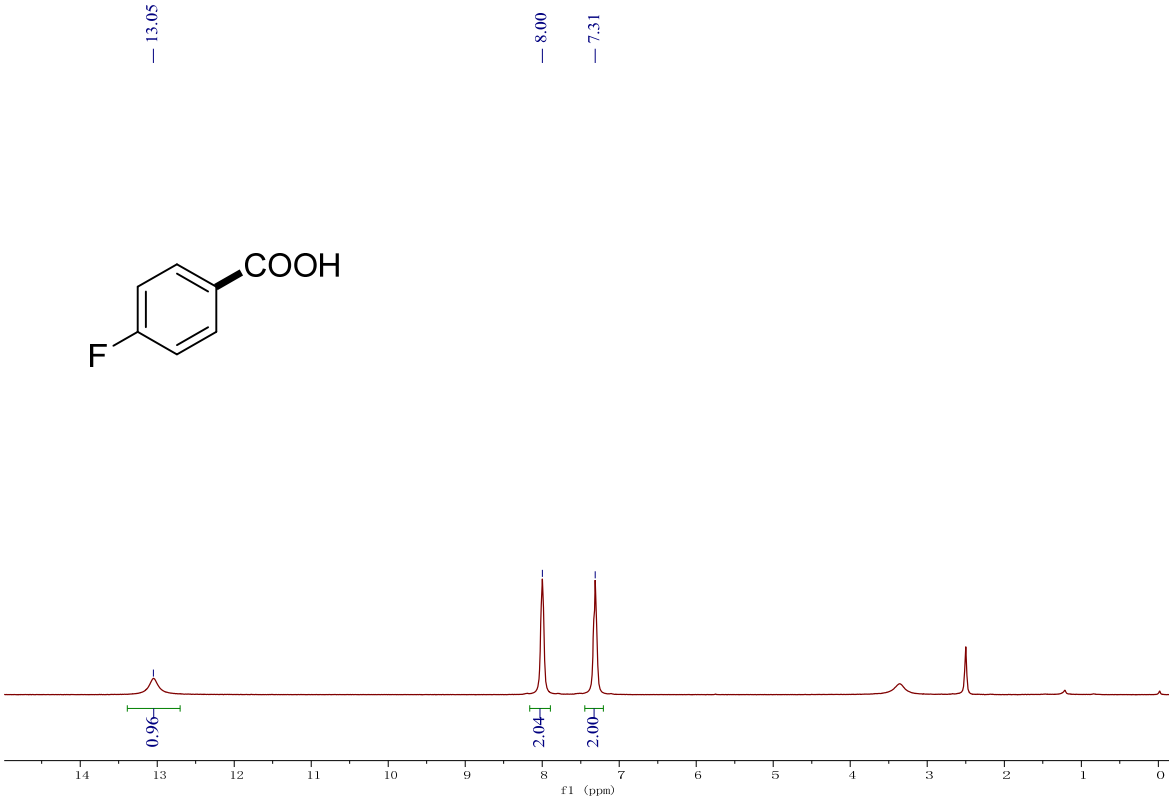
^{1}H NMR spectrum of **7**



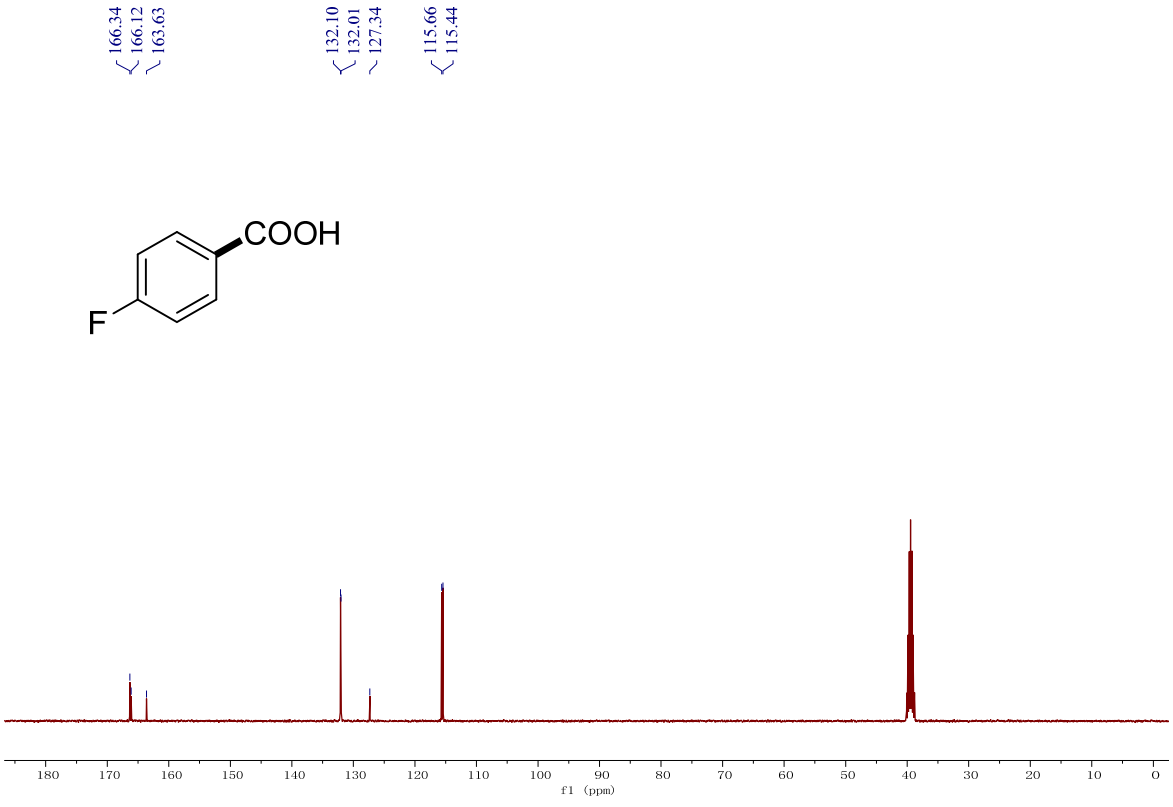
^{13}C NMR spectrum of **7**



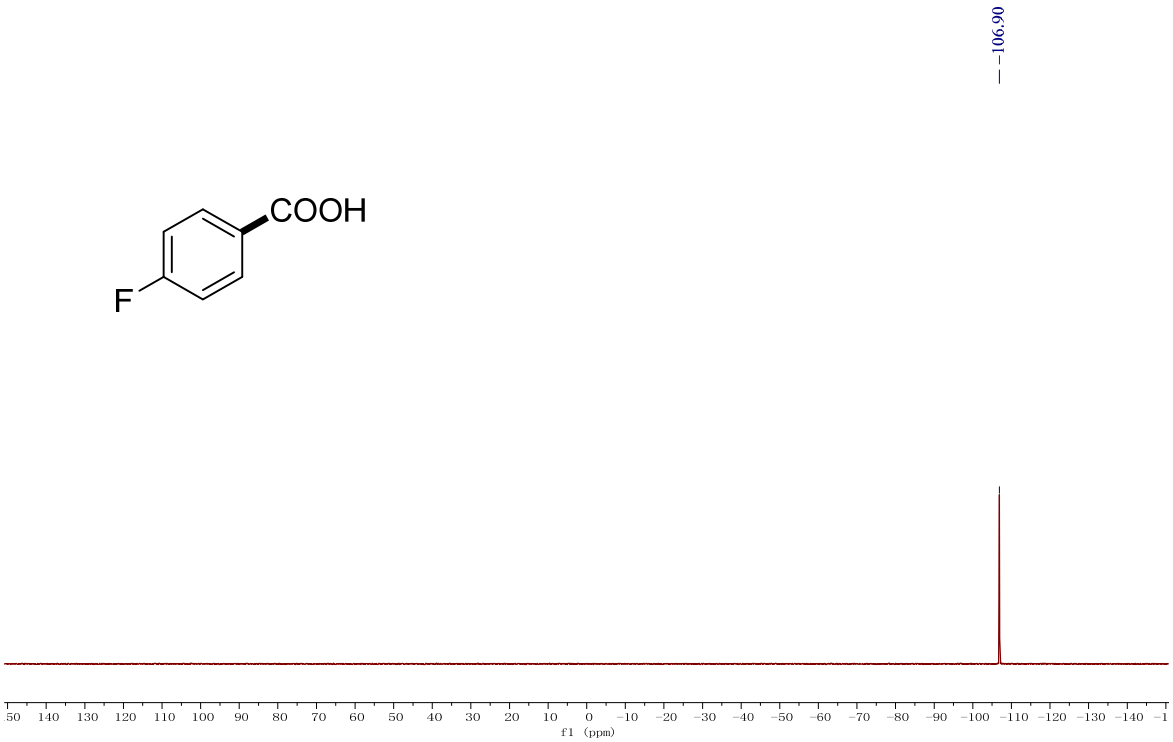
^{1}H NMR spectrum of **8**



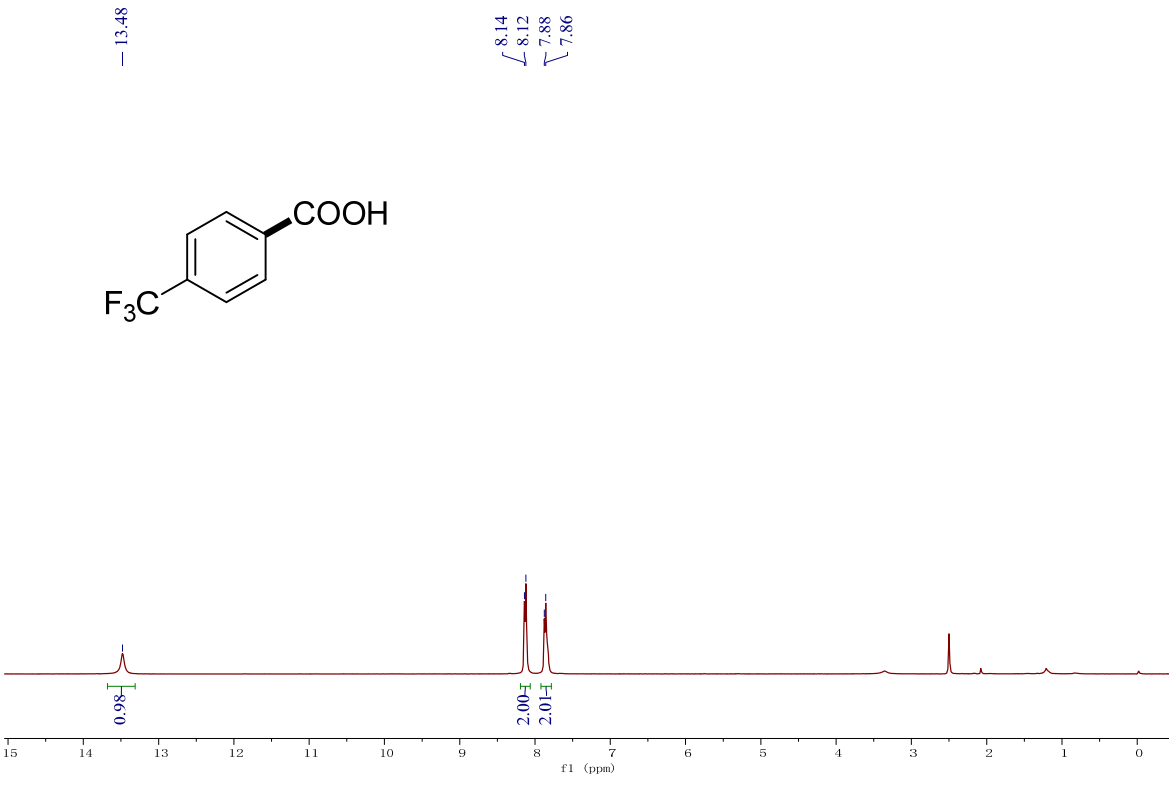
^{13}C NMR spectrum of **8**



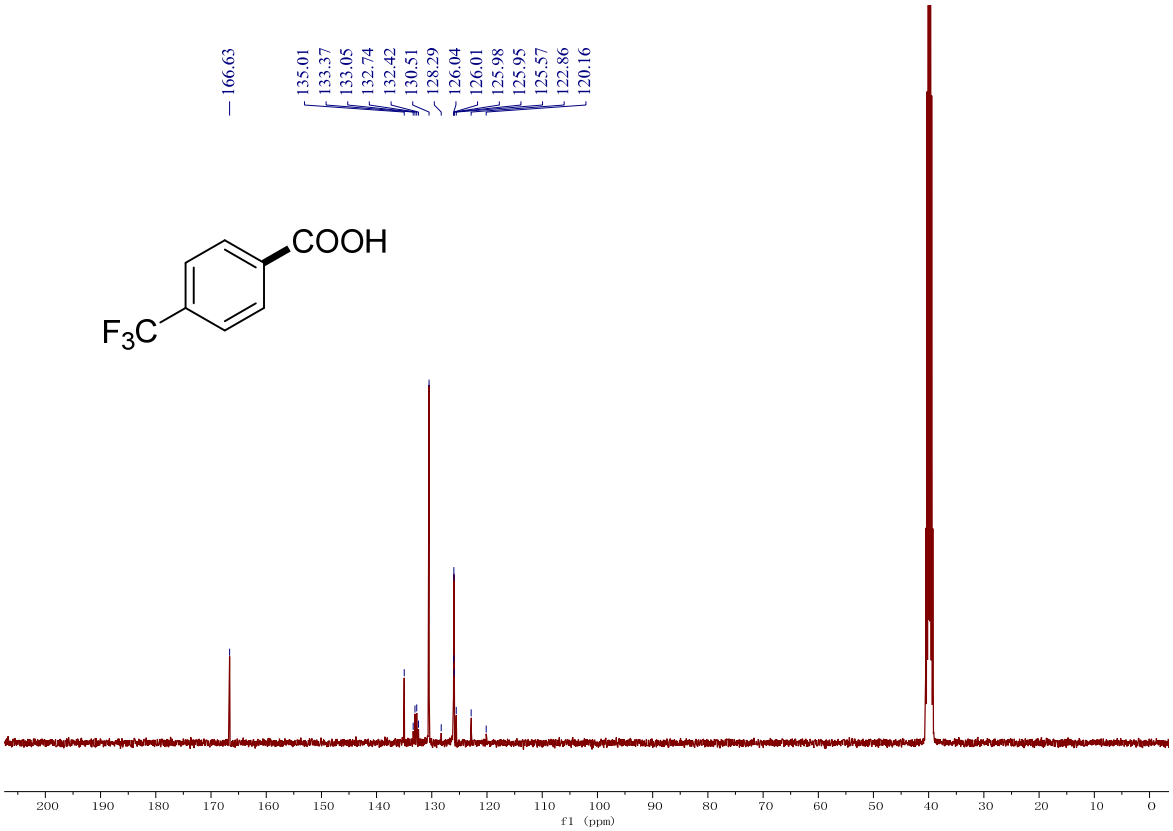
^{19}F NMR spectrum of **8**



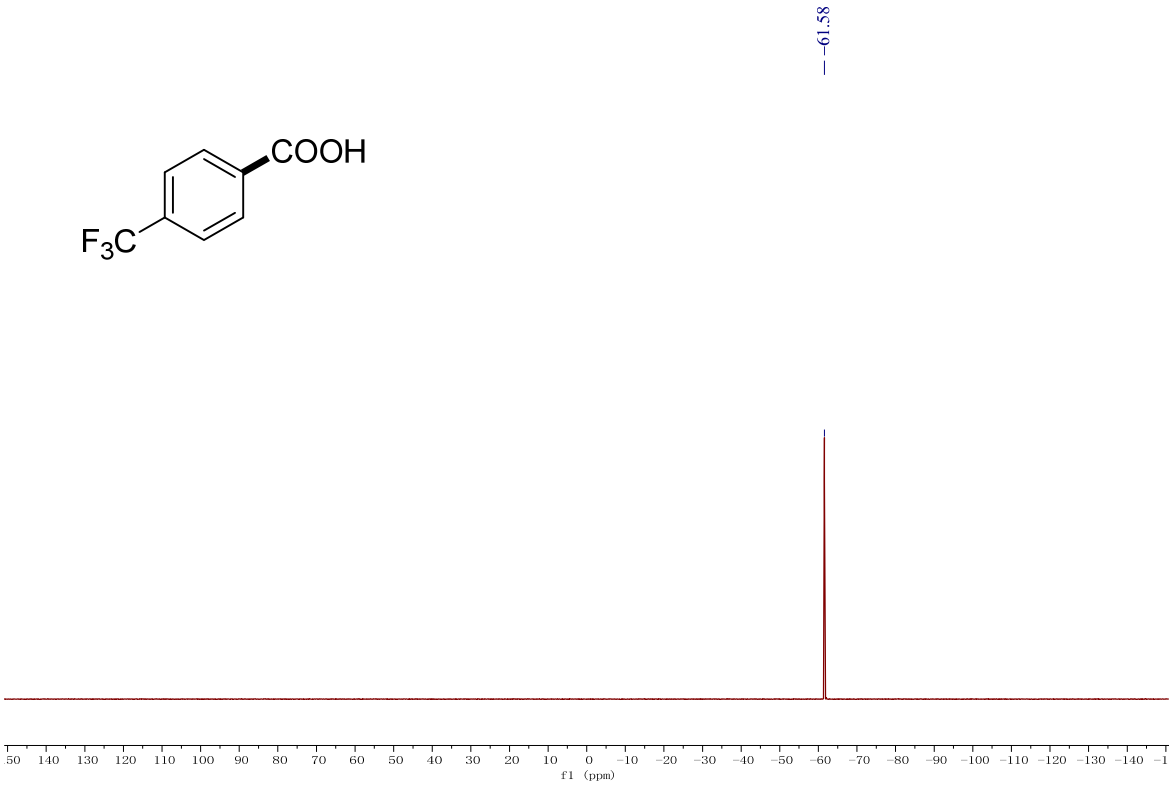
^{1}H NMR spectrum of **9**



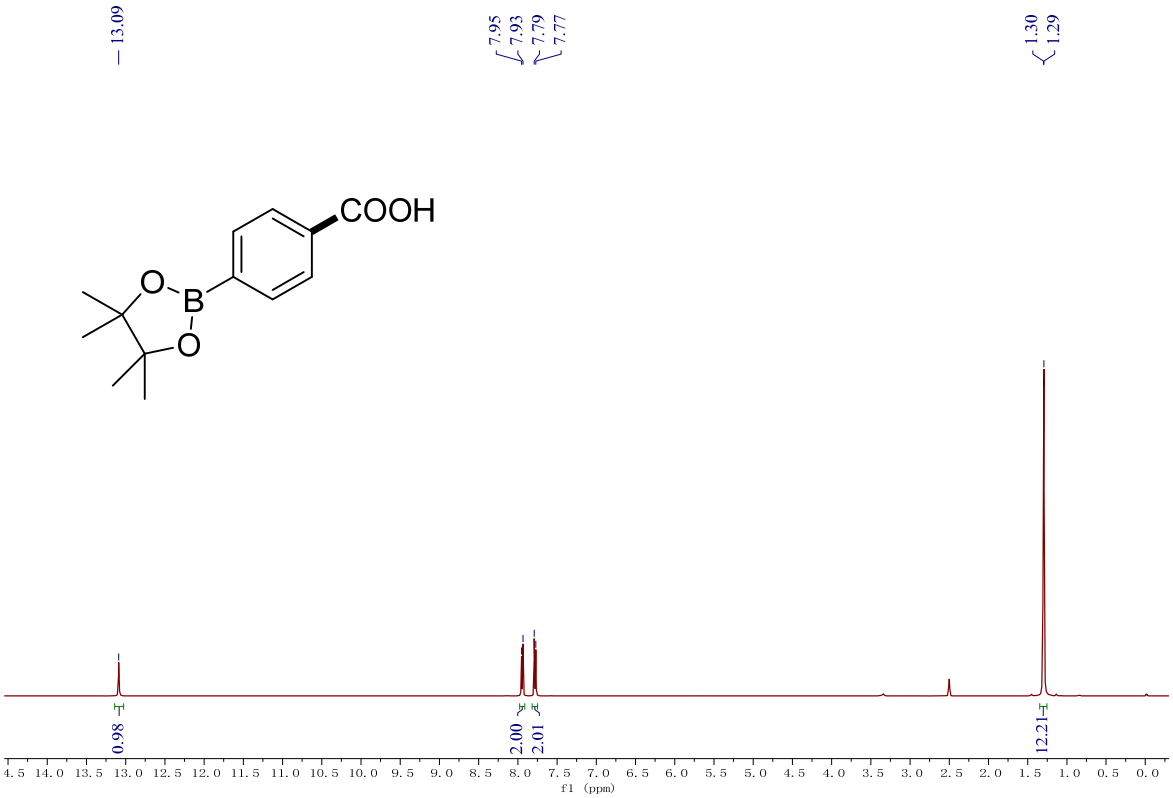
^{13}C NMR spectrum of **9**



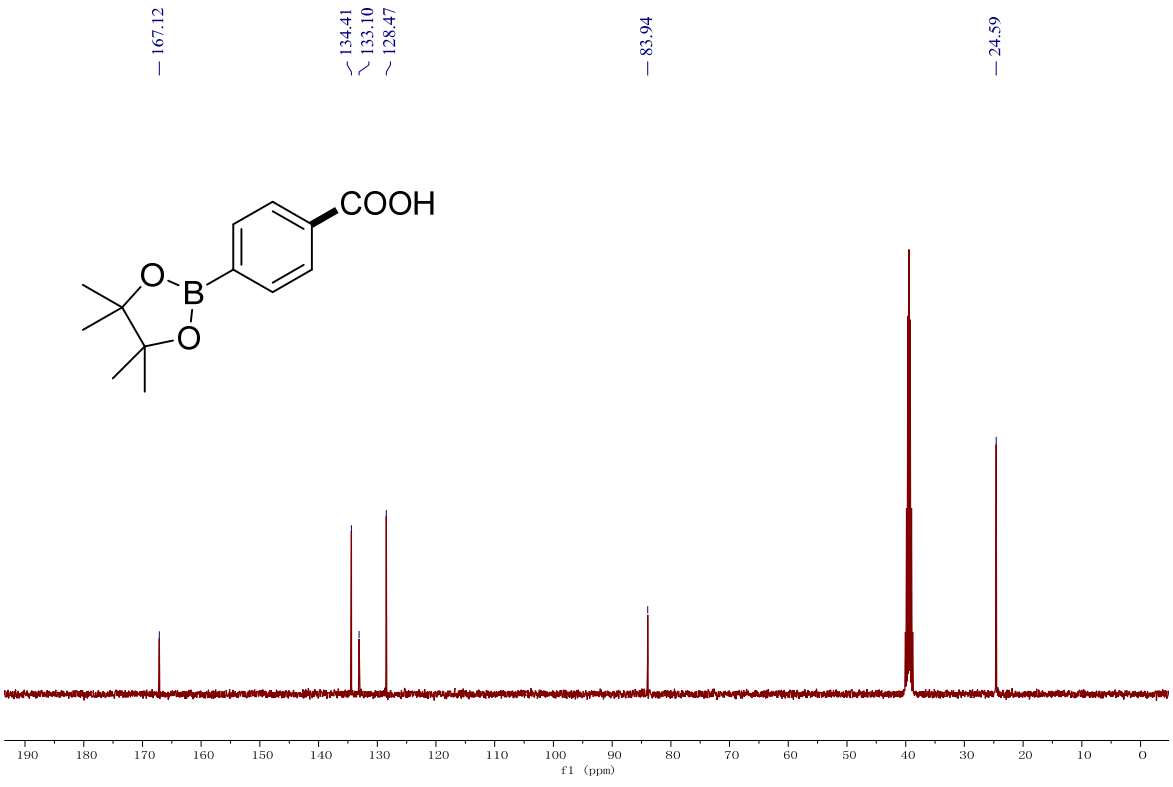
^{19}F NMR spectrum of **9**



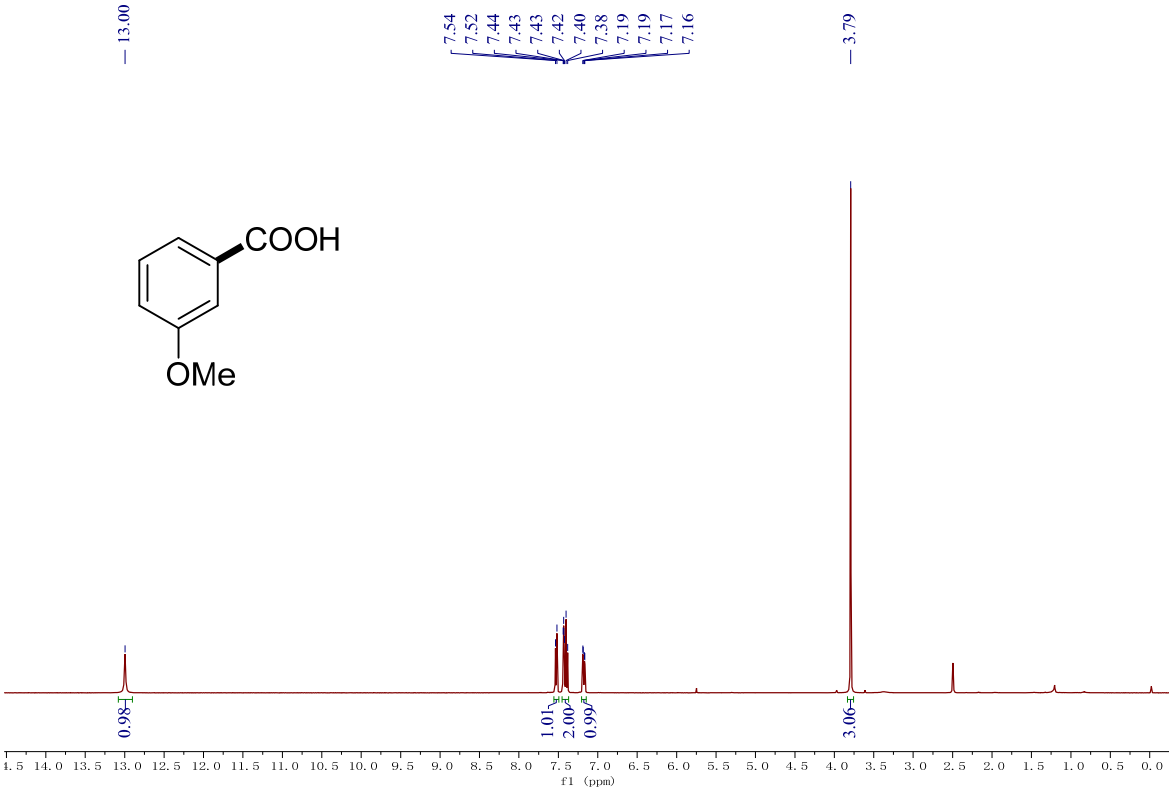
^{1}H NMR spectrum of **10**



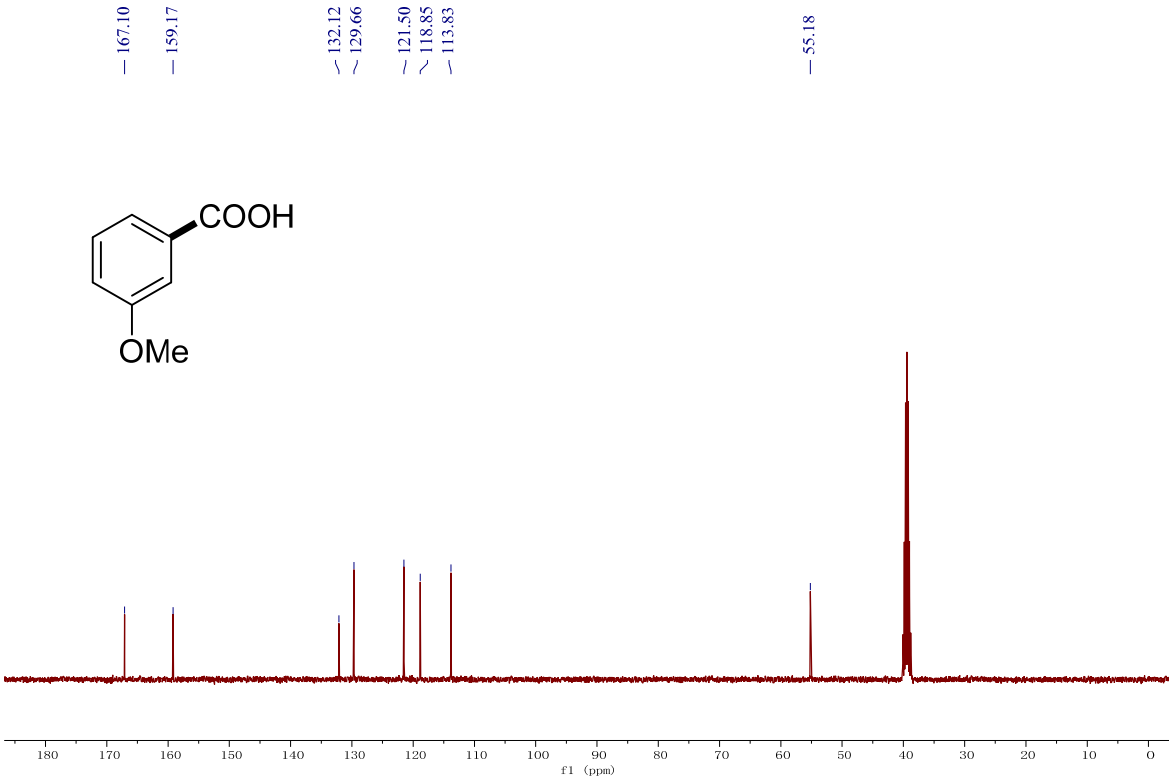
^{13}C NMR spectrum of **10**



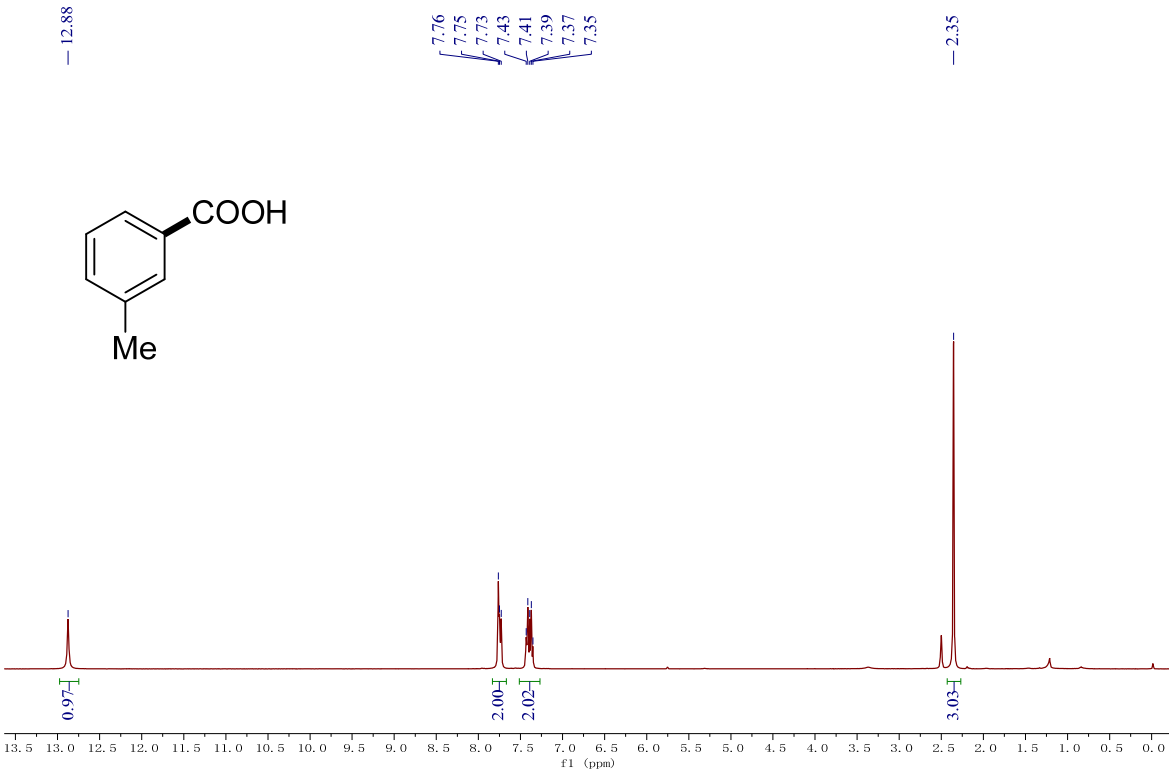
^{1}H NMR spectrum of **11**



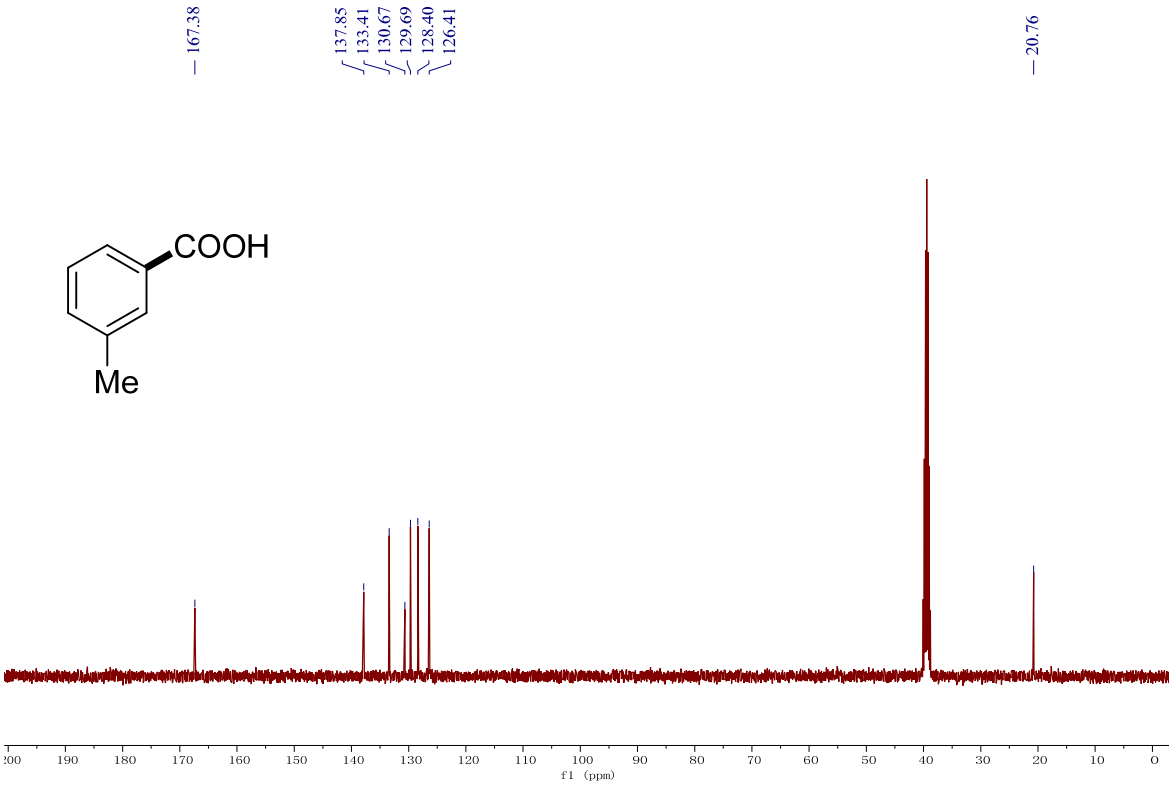
^{13}C NMR spectrum of **11**



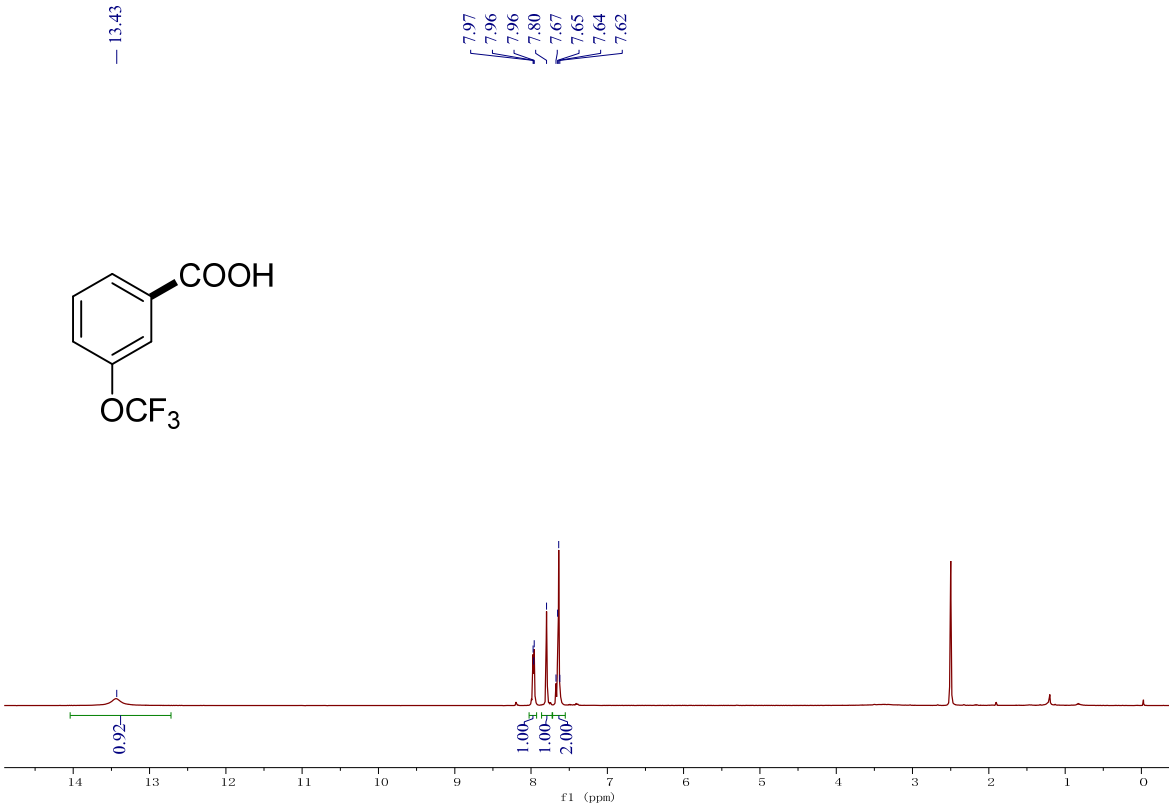
^{1}H NMR spectrum of **12**



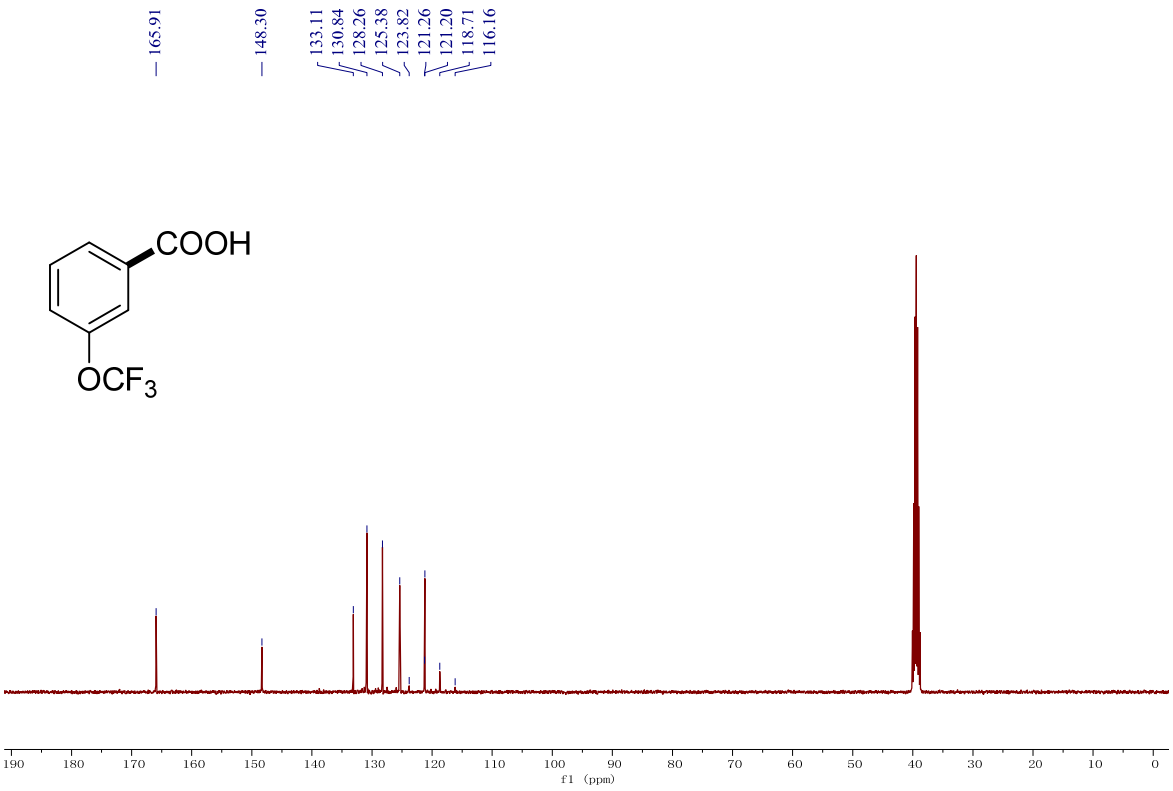
^{13}C NMR spectrum of **12**



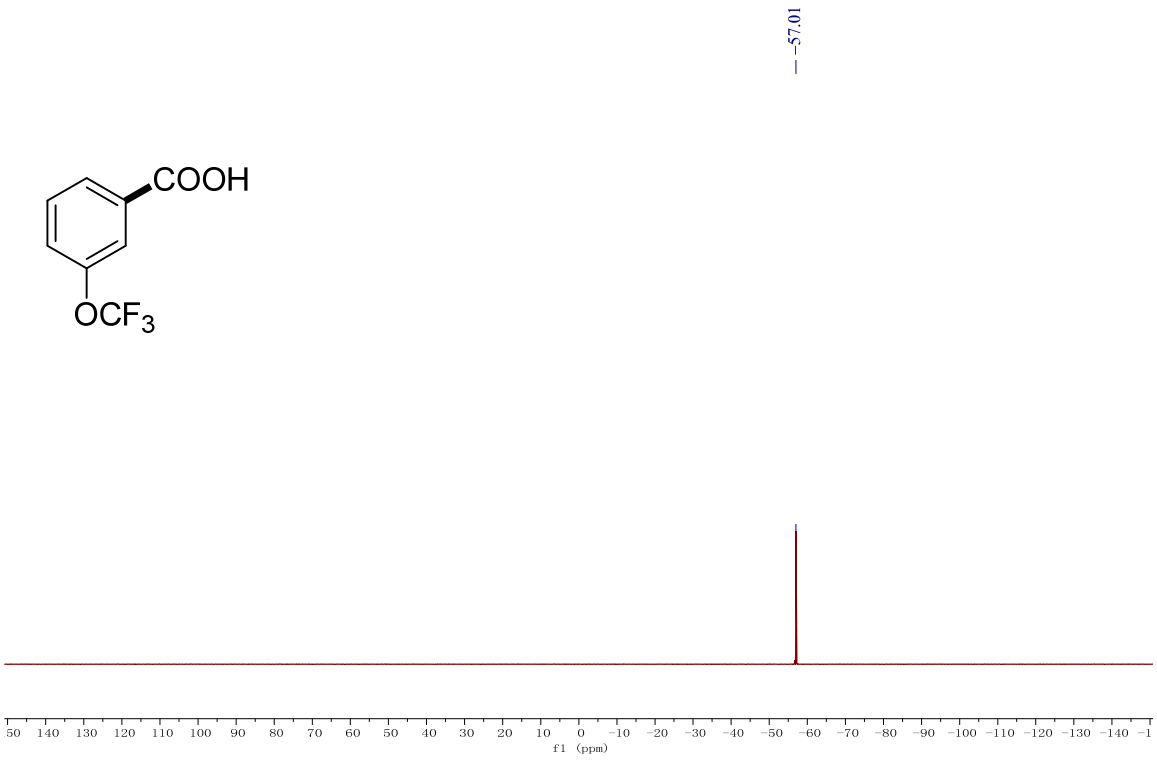
^{1}H NMR spectrum of **13**



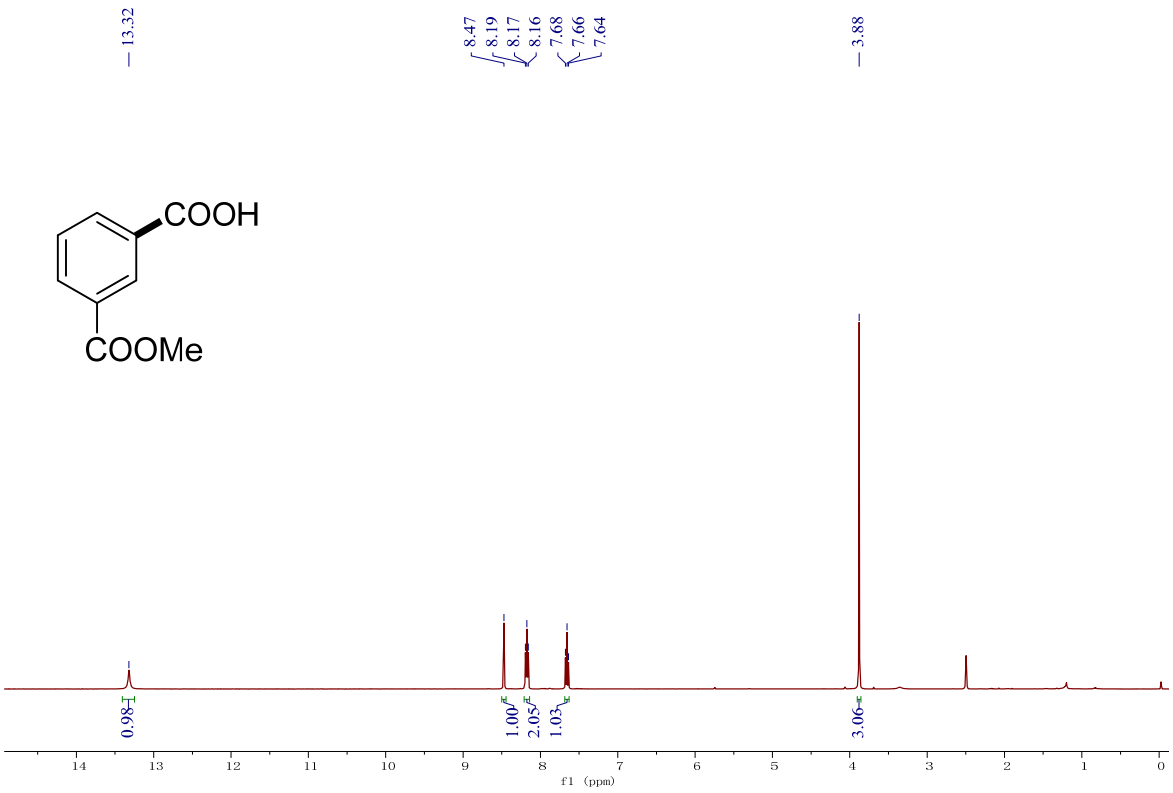
^{13}C NMR spectrum of **13**



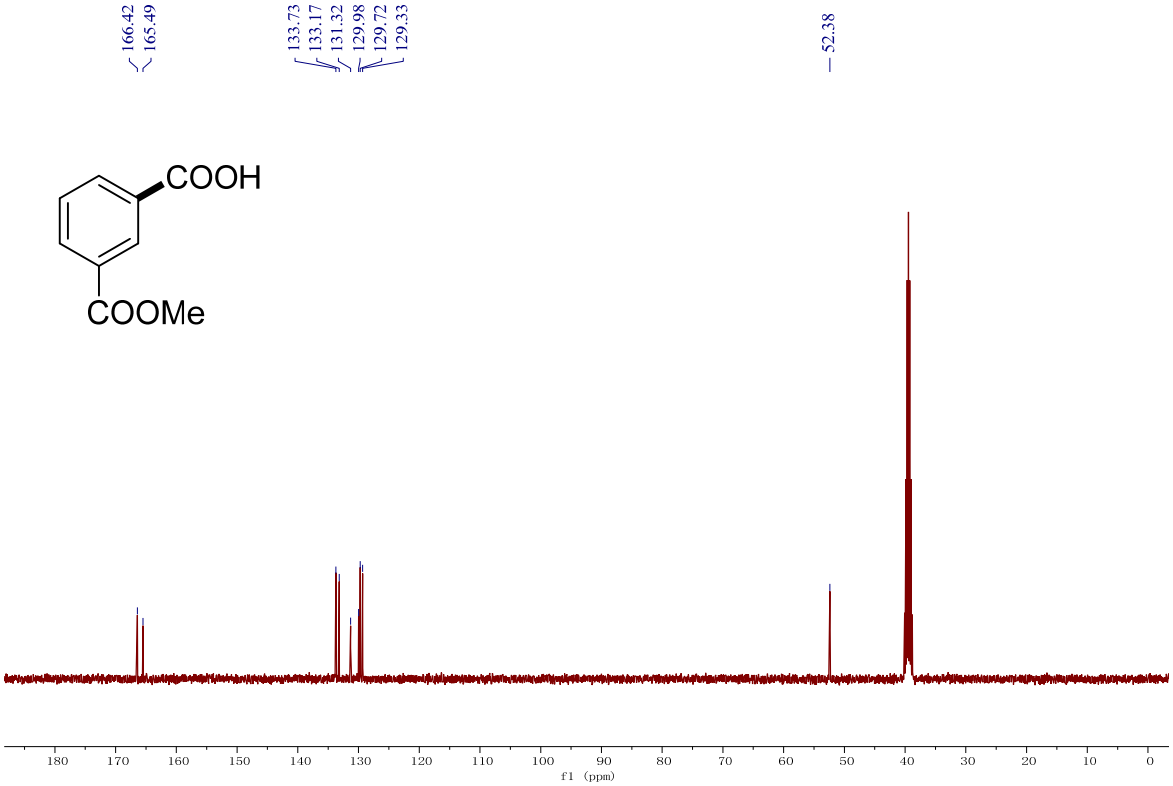
^{19}F NMR spectrum of **13**



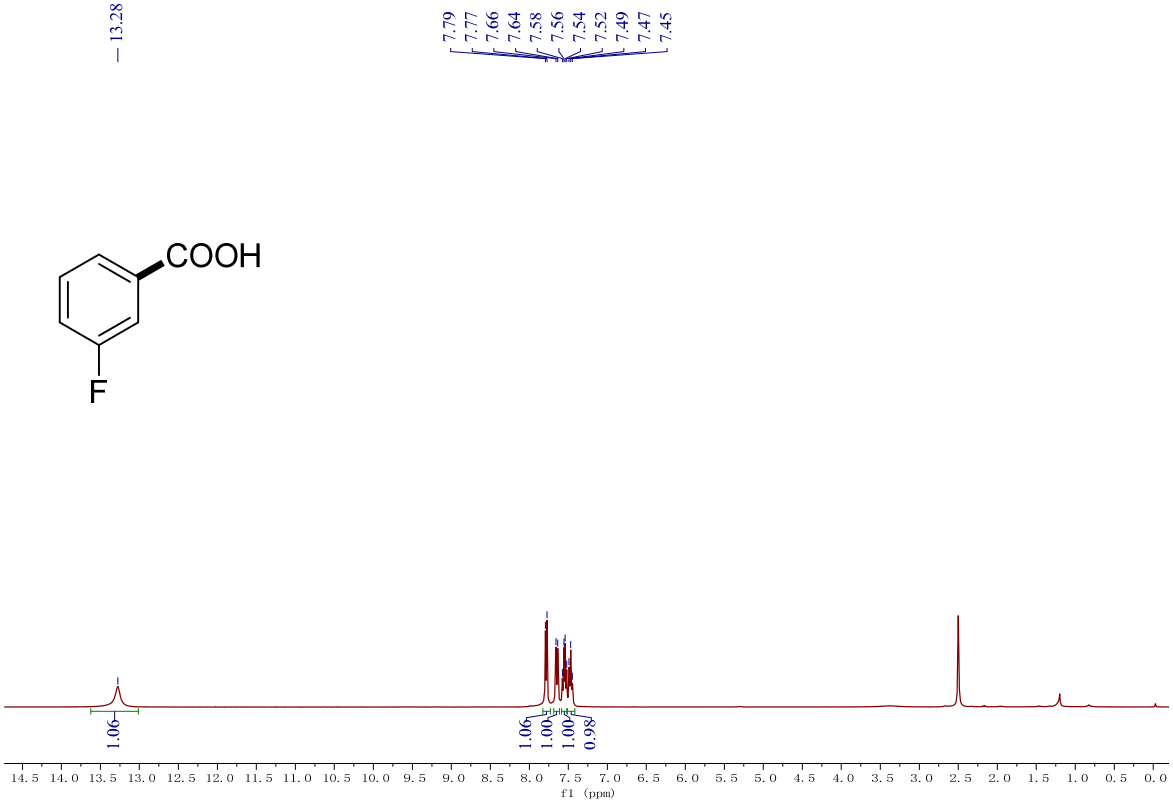
^{1}H NMR spectrum of **14**



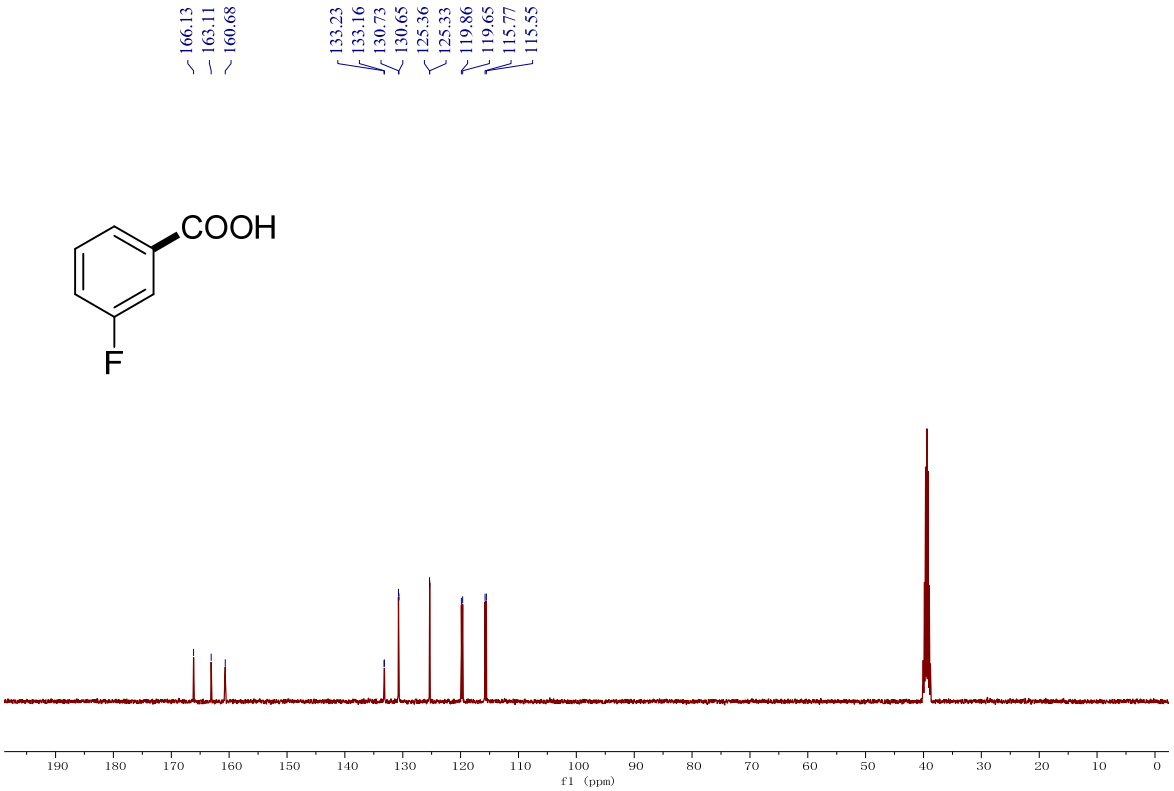
^{13}C NMR spectrum of **14**



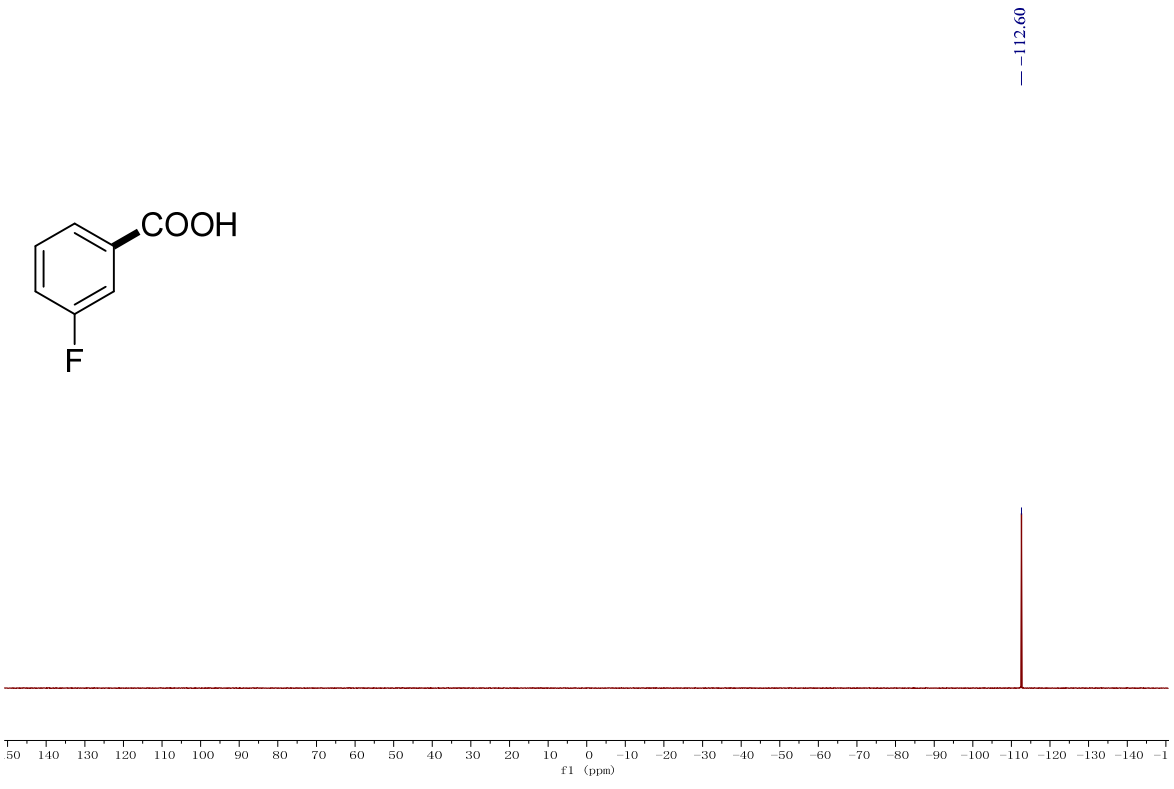
^{1}H NMR spectrum of **15**



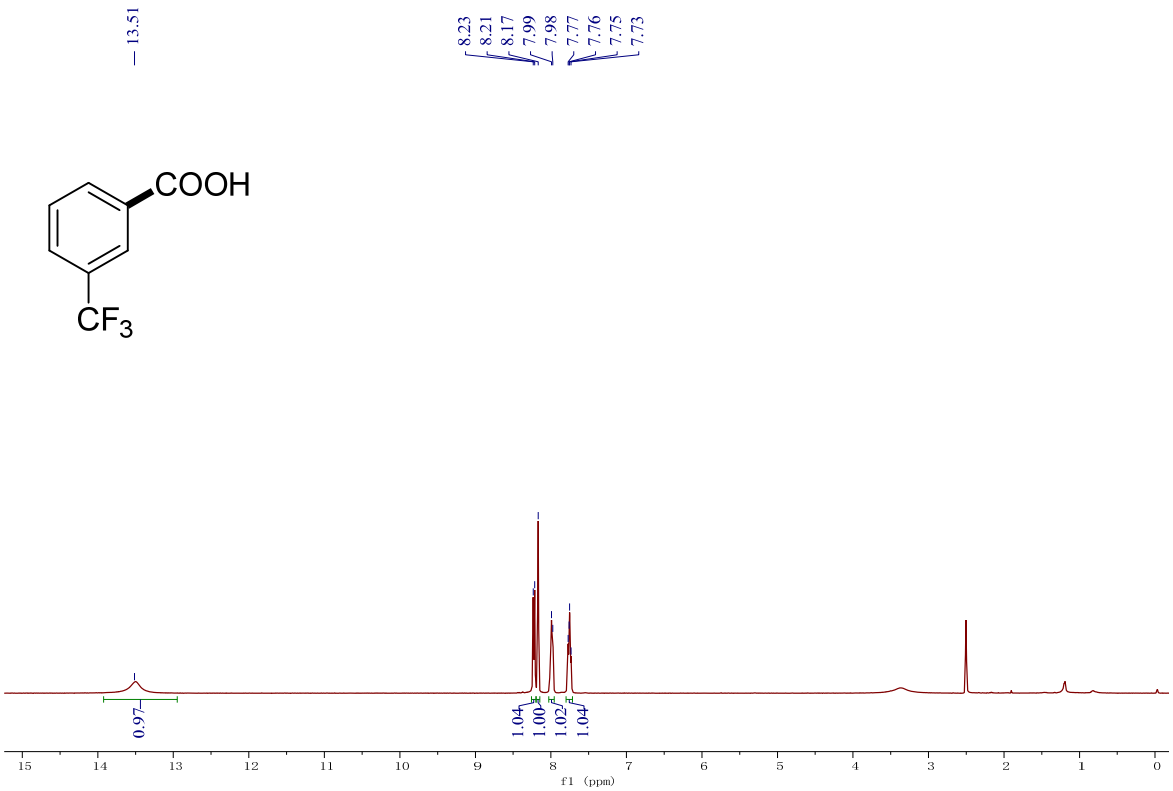
^{13}C NMR spectrum of **15**



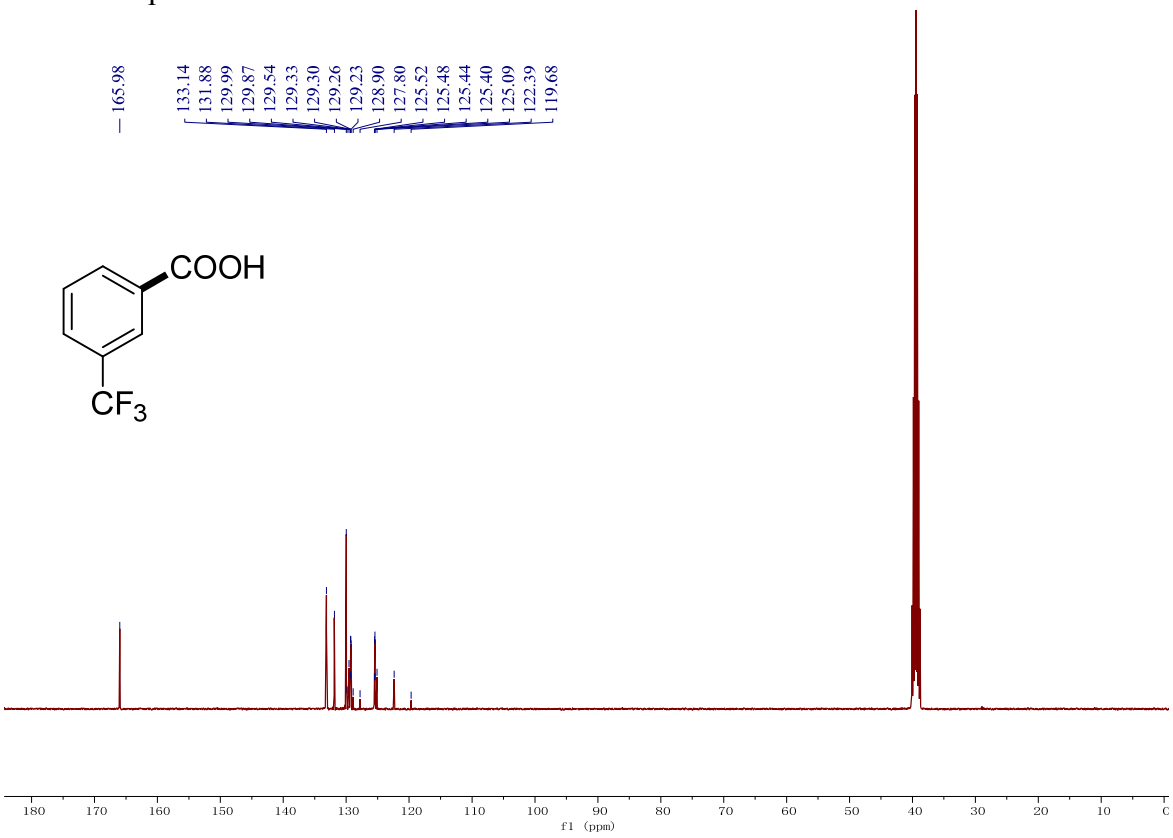
^{19}F NMR spectrum of **15**



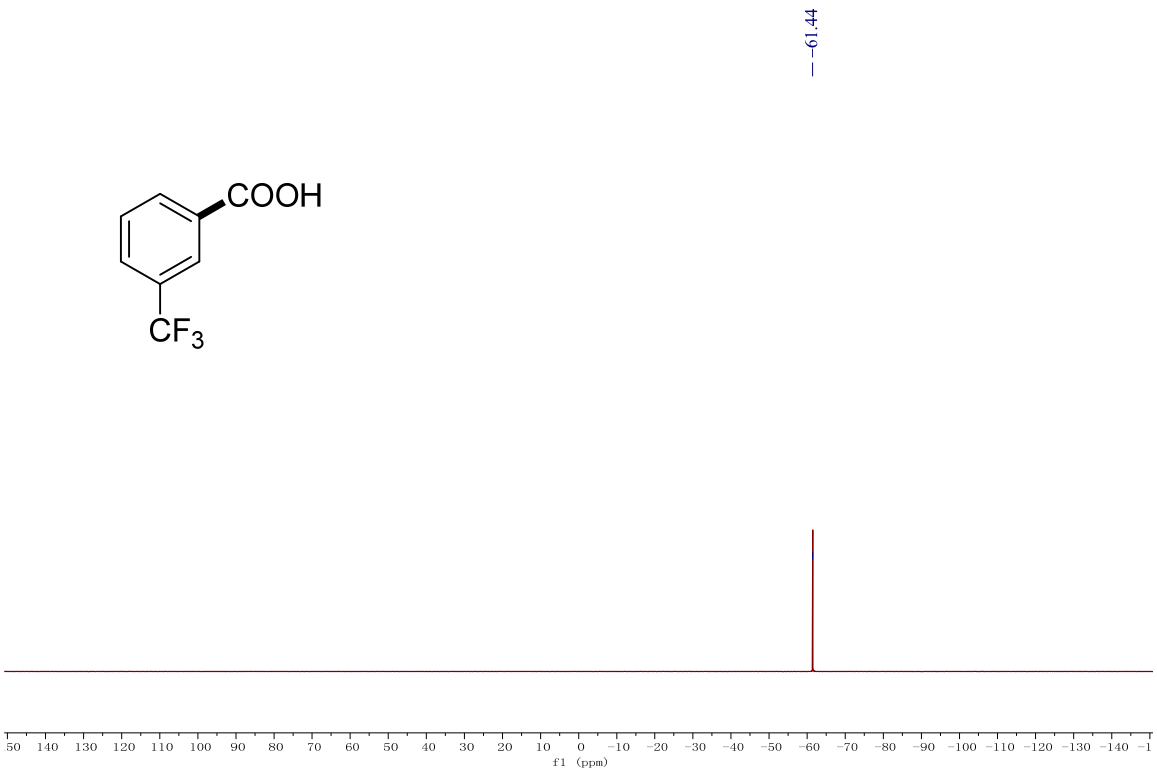
^{1}H NMR spectrum of **16**



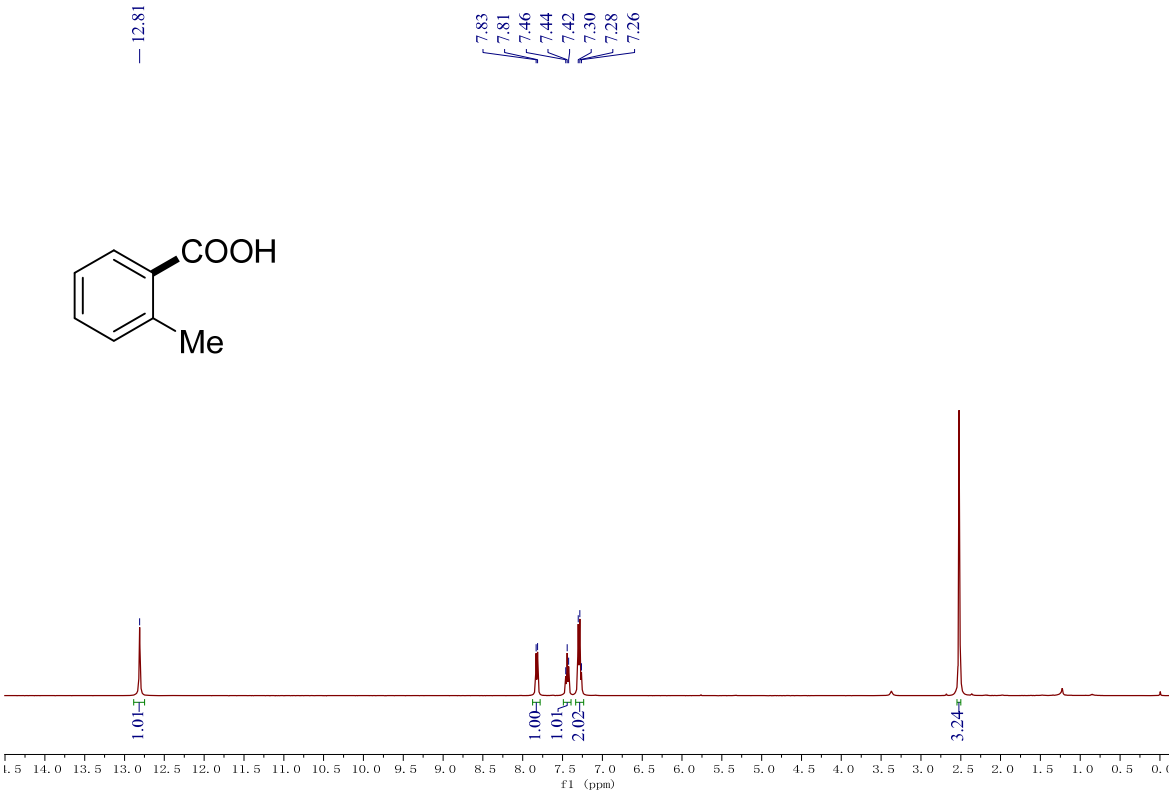
^{13}C NMR spectrum of **16**



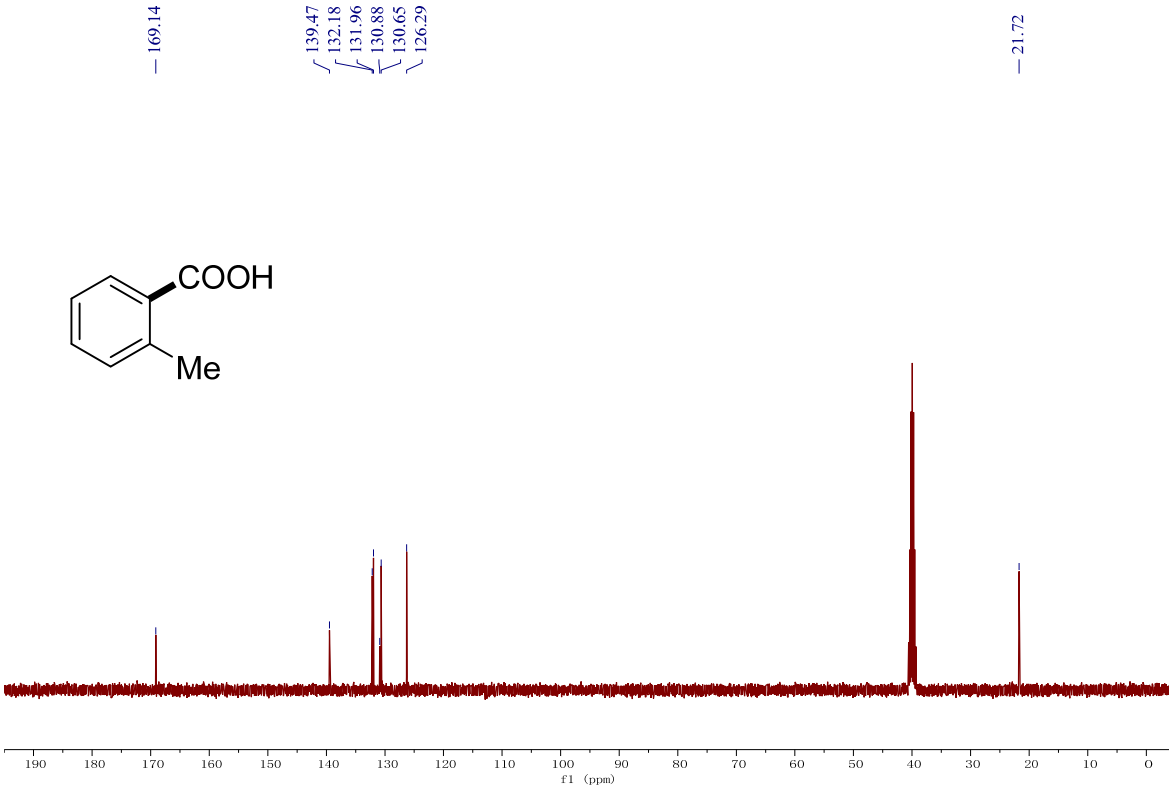
^{19}F NMR spectrum of **16**



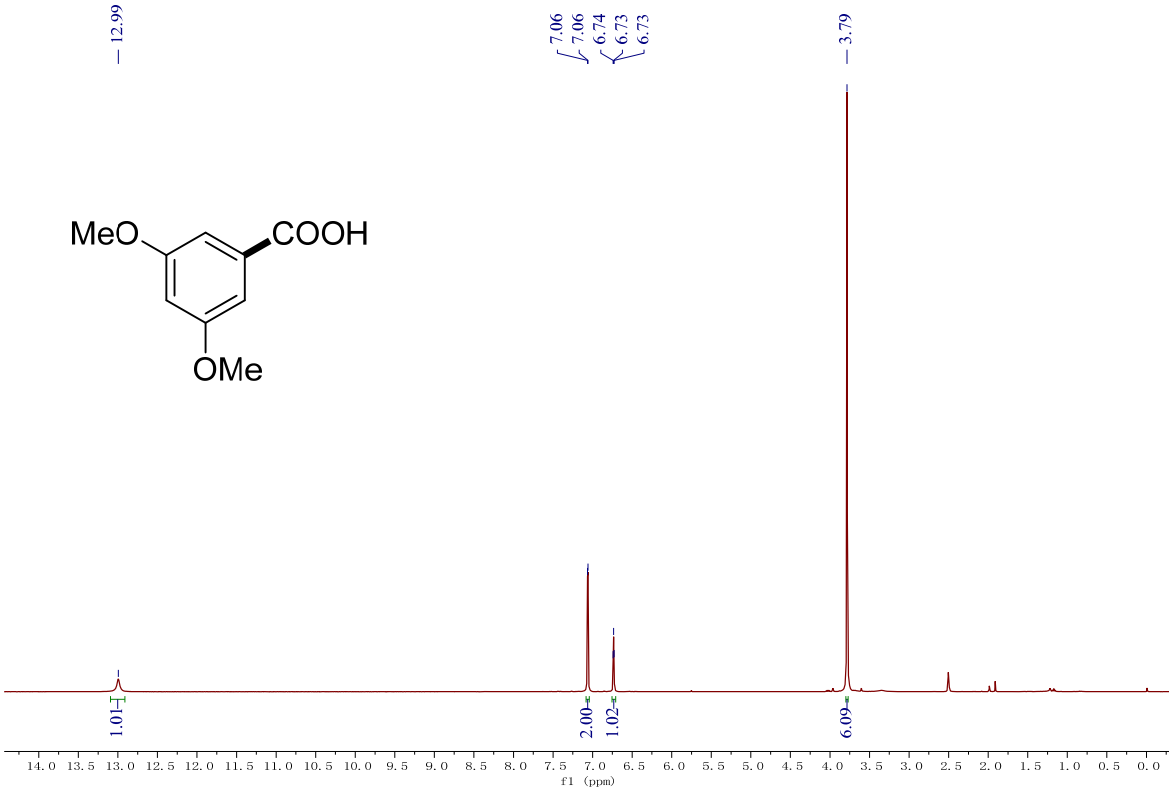
^{1}H NMR spectrum of **17**



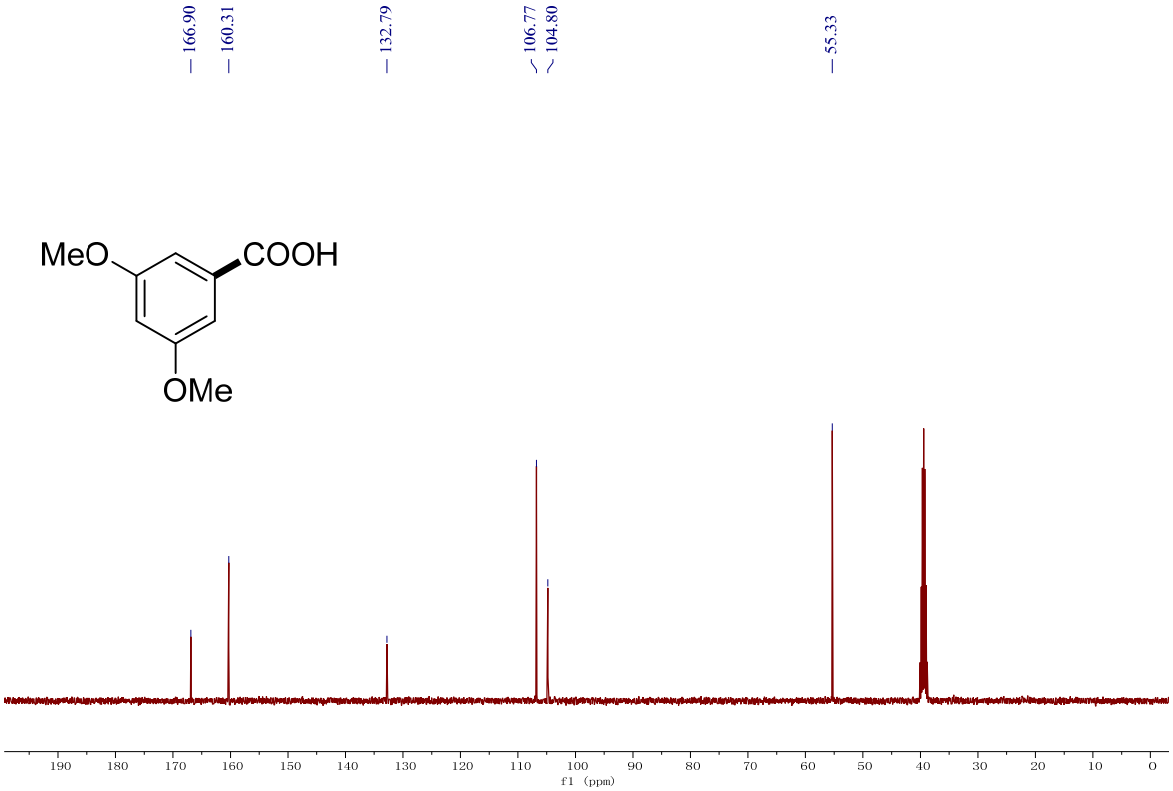
^{13}C NMR spectrum of **17**



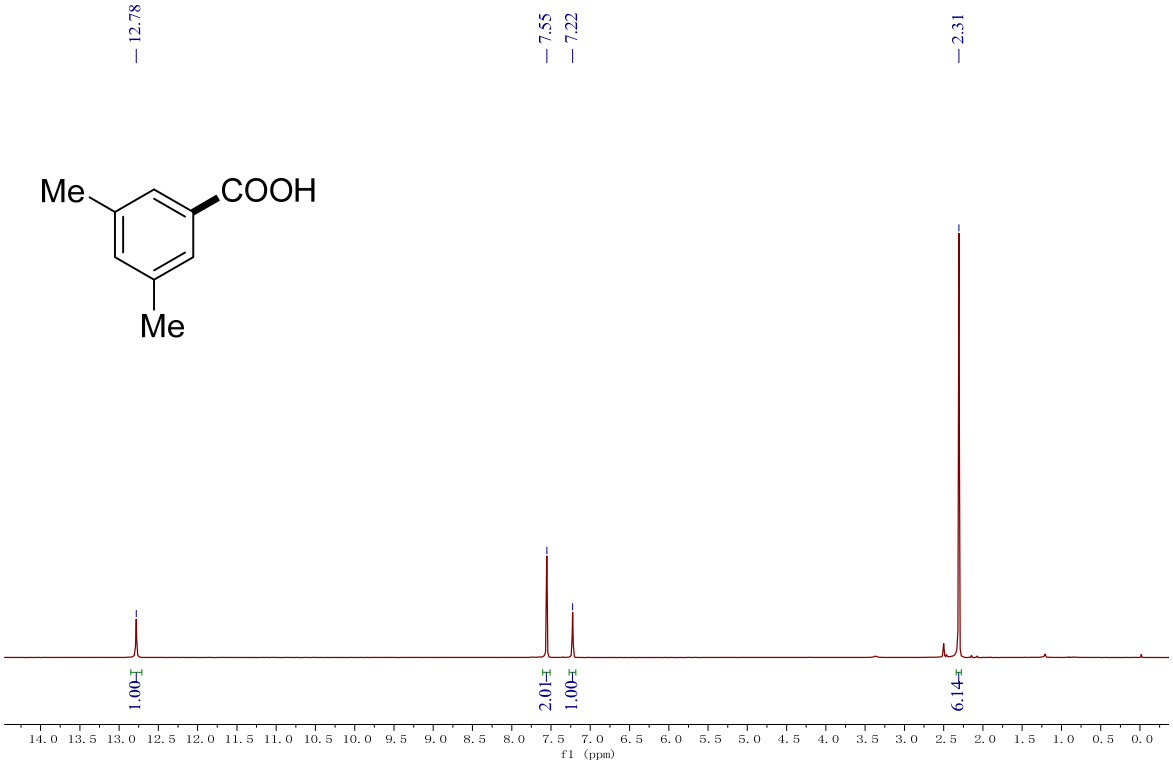
^{1}H NMR spectrum of **18**



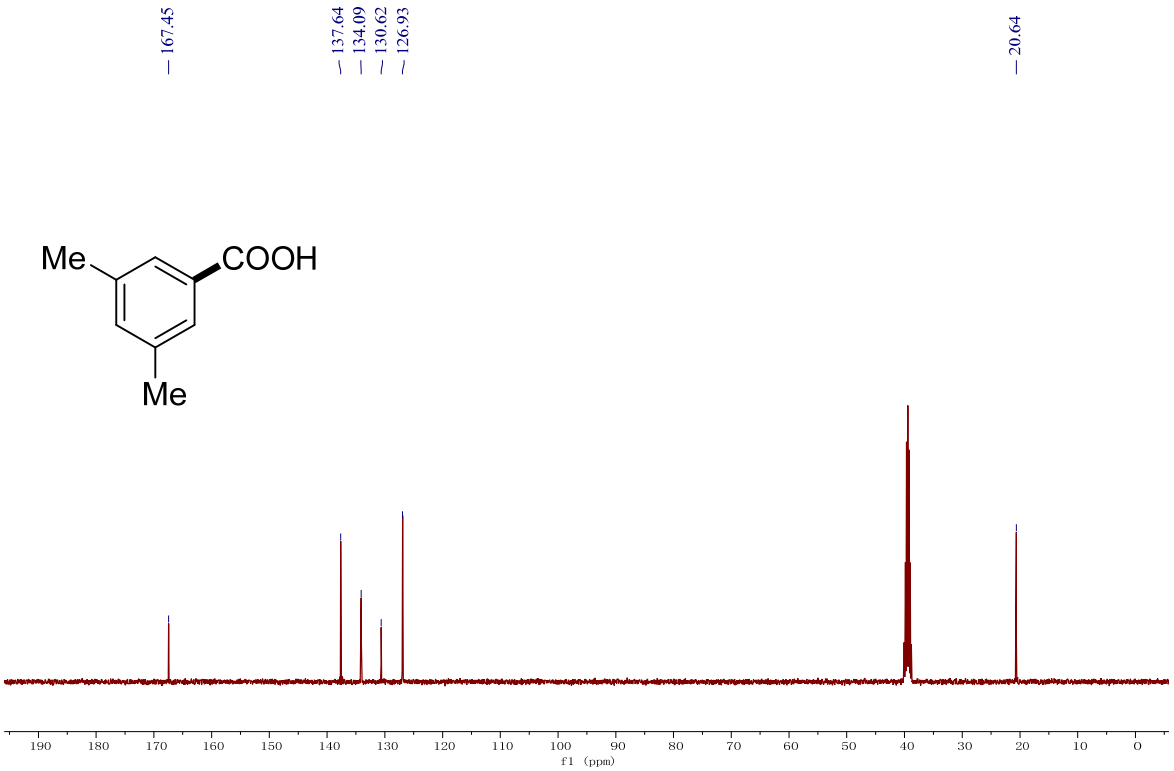
^{13}C NMR spectrum of **18**



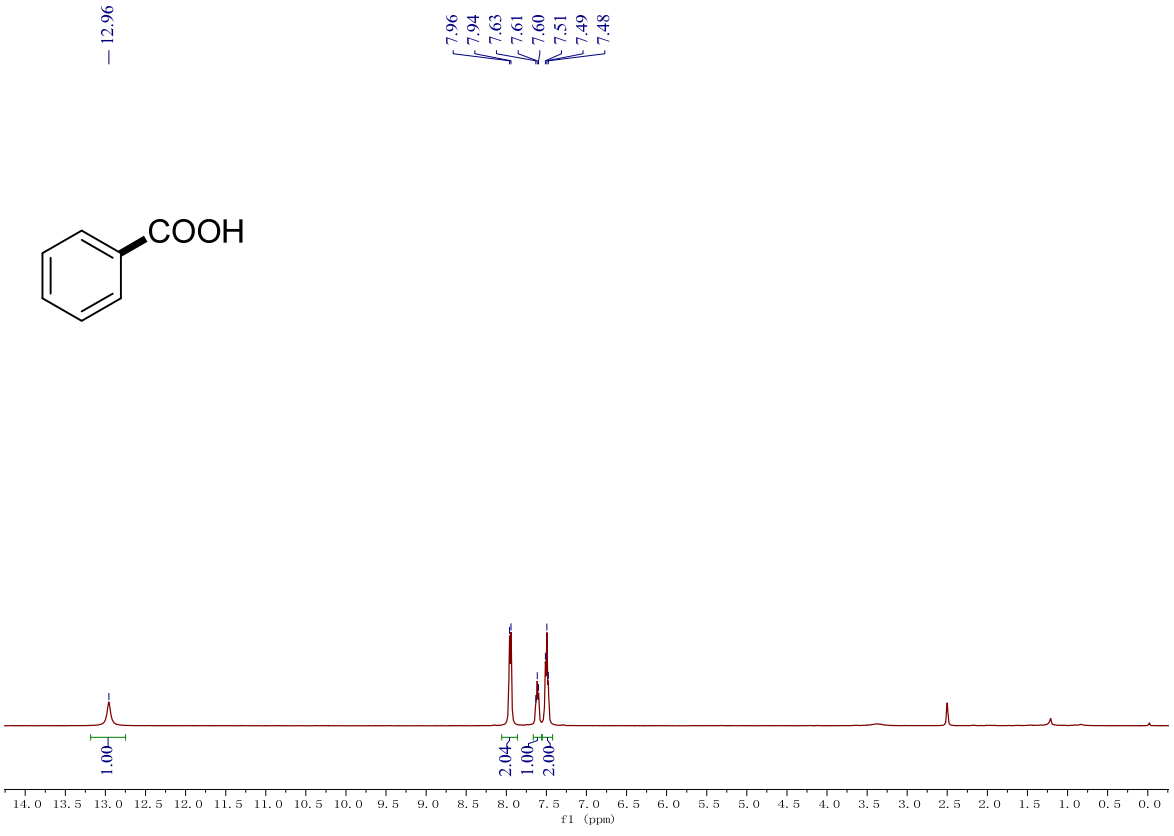
^{1}H NMR spectrum of **19**



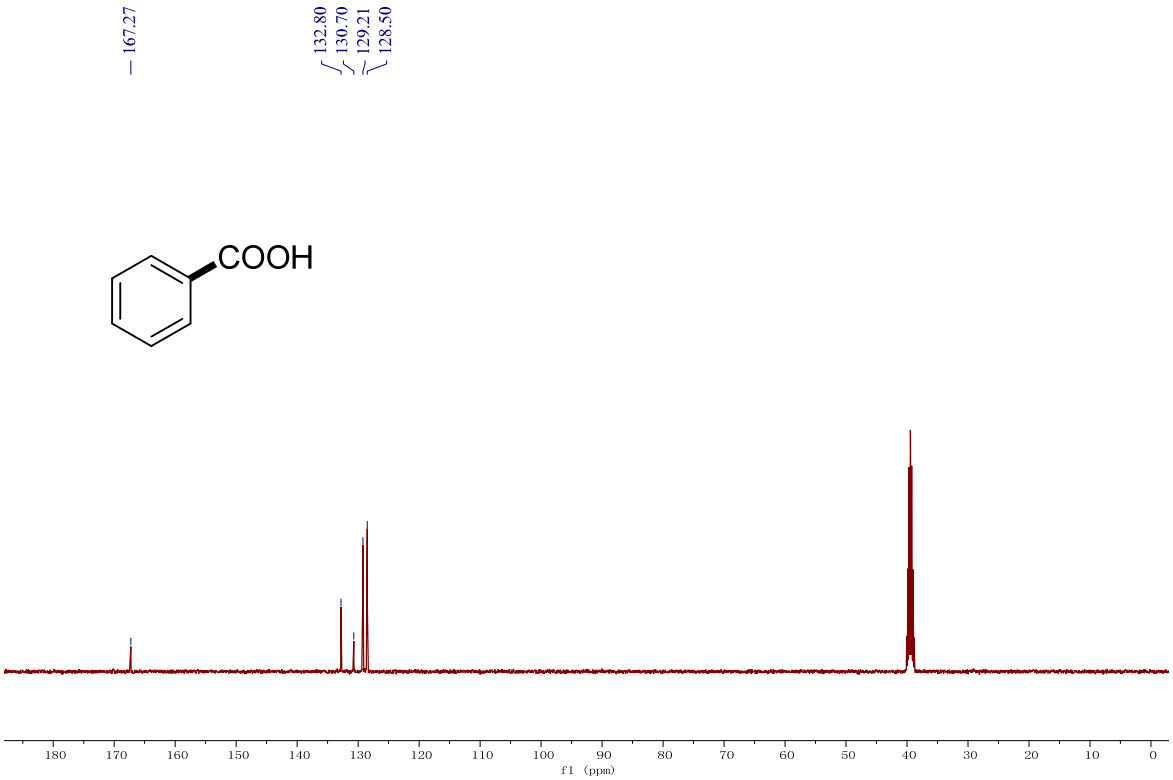
^{13}C NMR spectrum of **19**



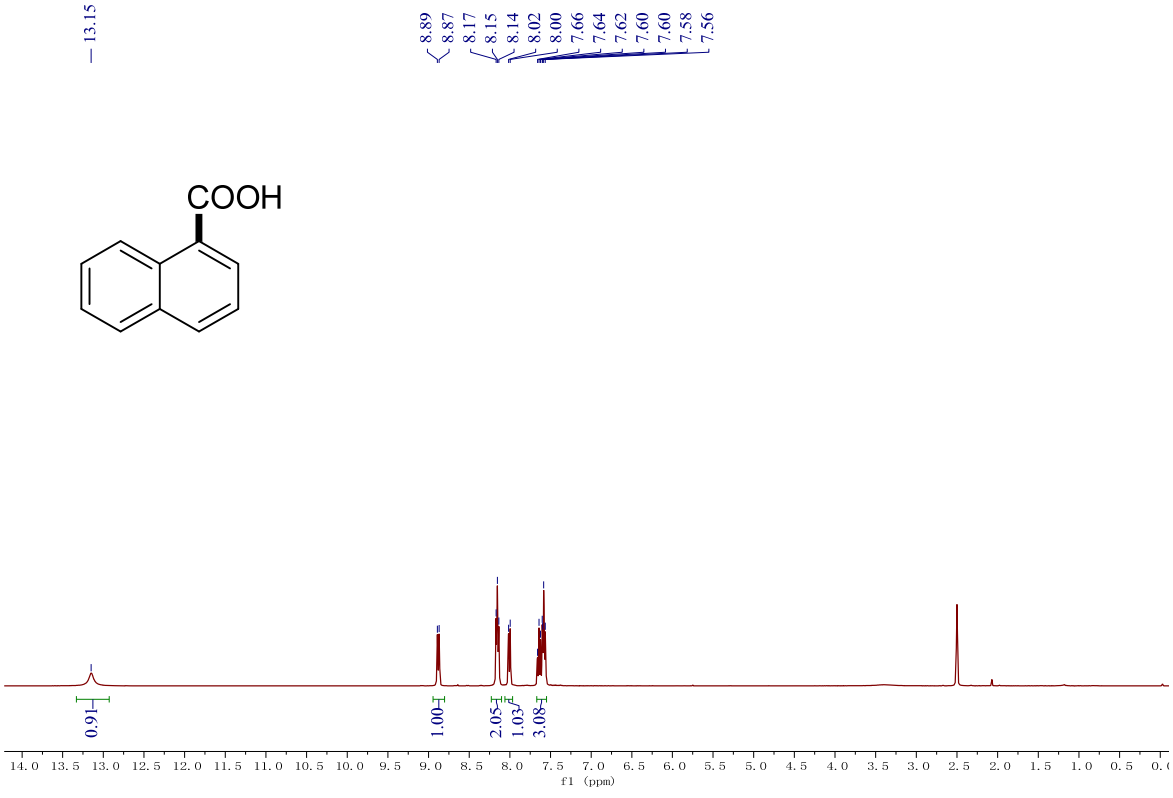
^{1}H NMR spectrum of **20**



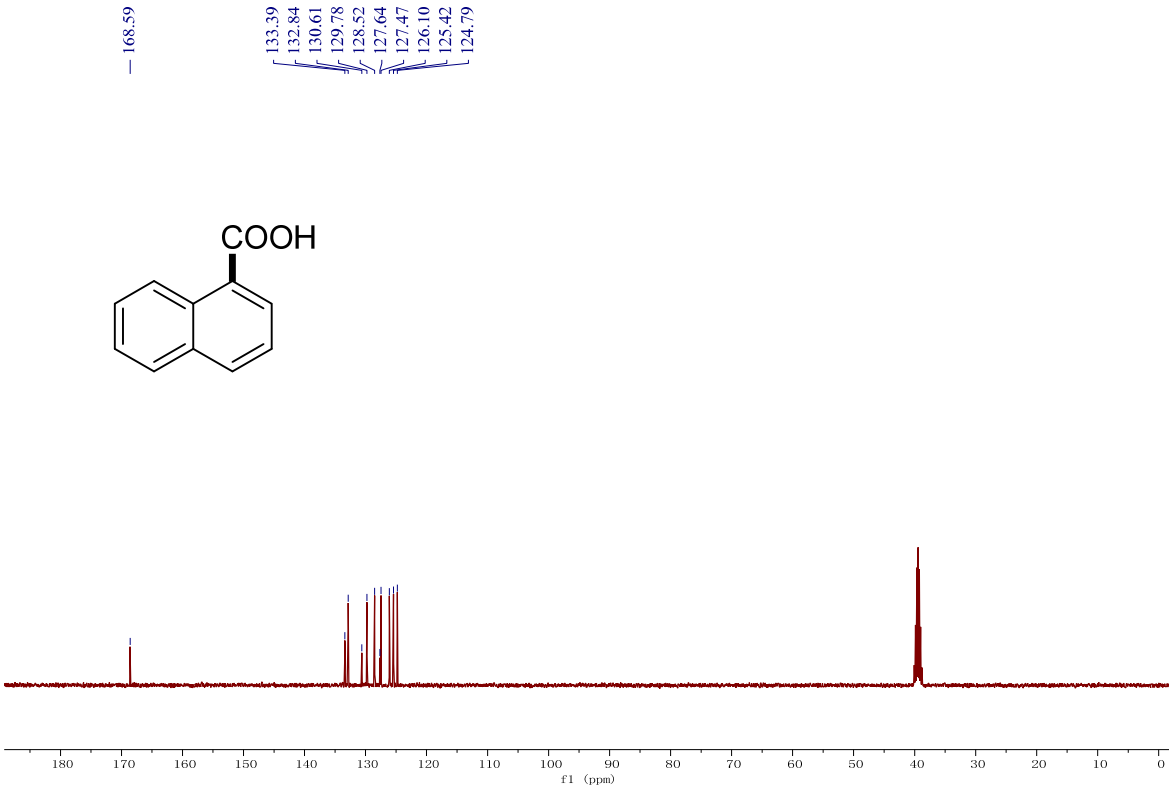
^{13}C NMR spectrum of **20**



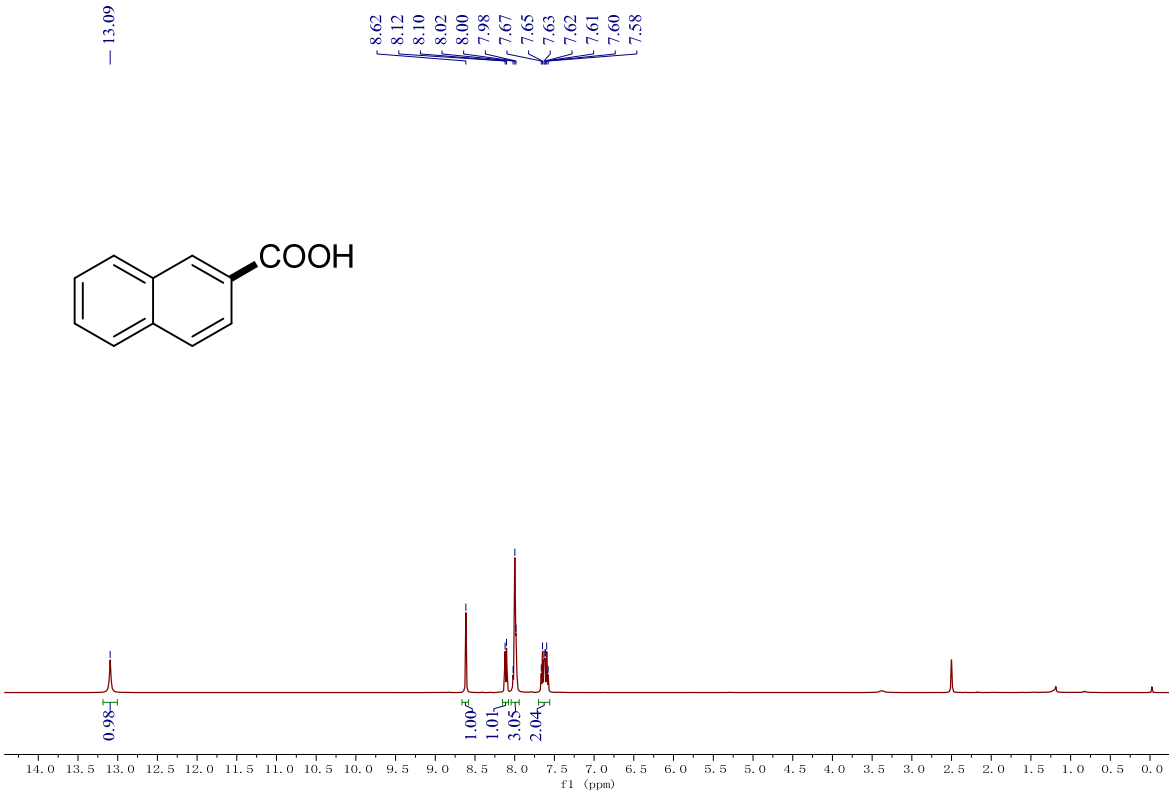
^{1}H NMR spectrum of **21**



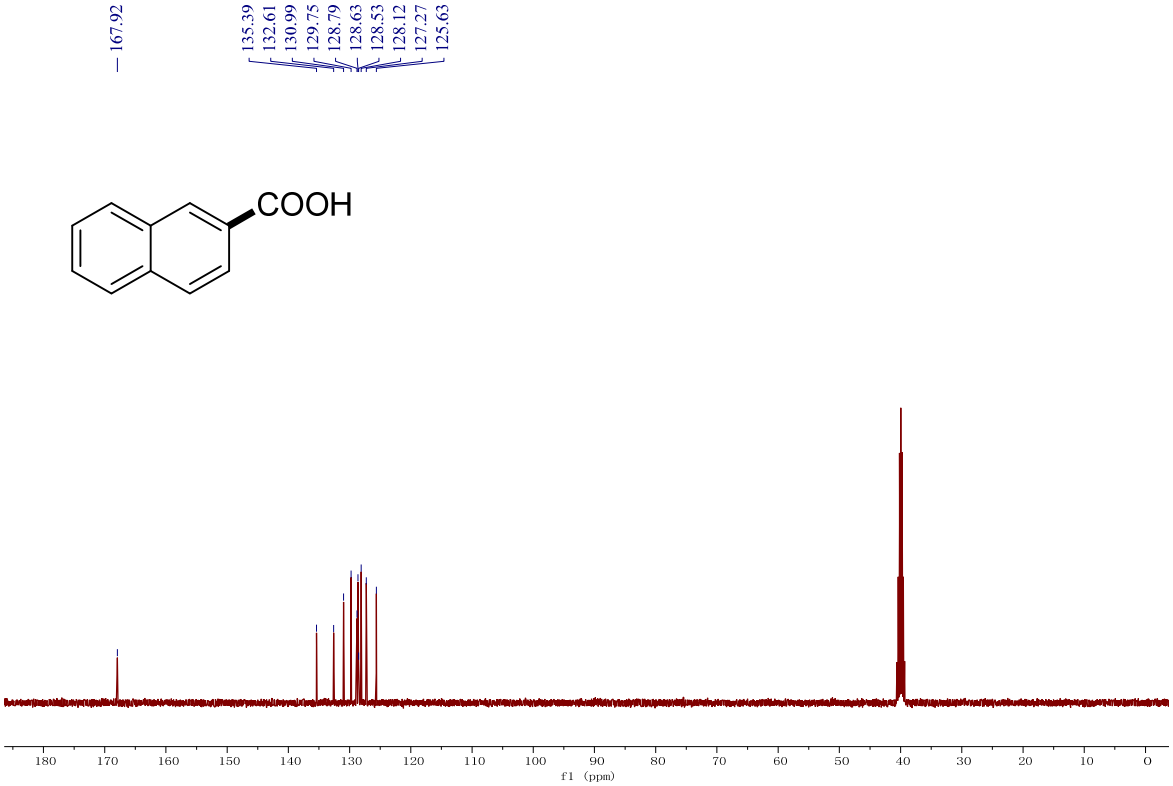
^{13}C NMR spectrum of **21**



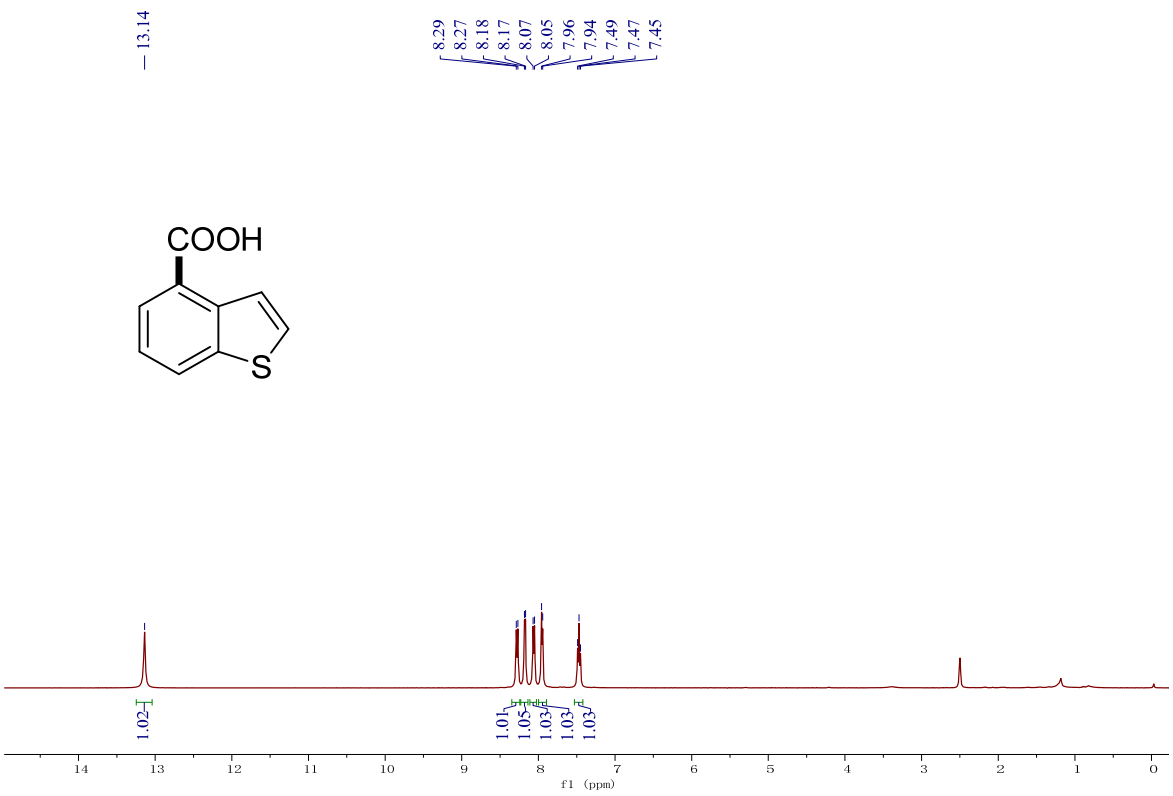
^{1}H NMR spectrum of **22**



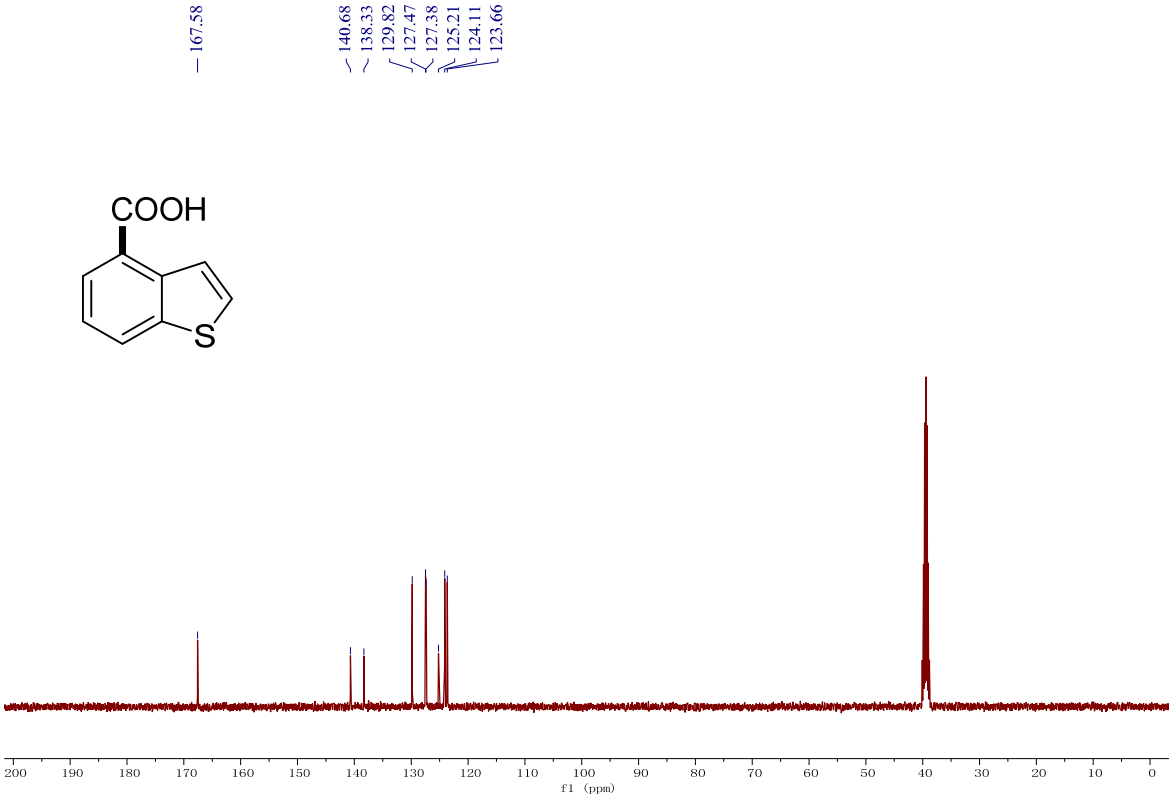
^{13}C NMR spectrum of **22**



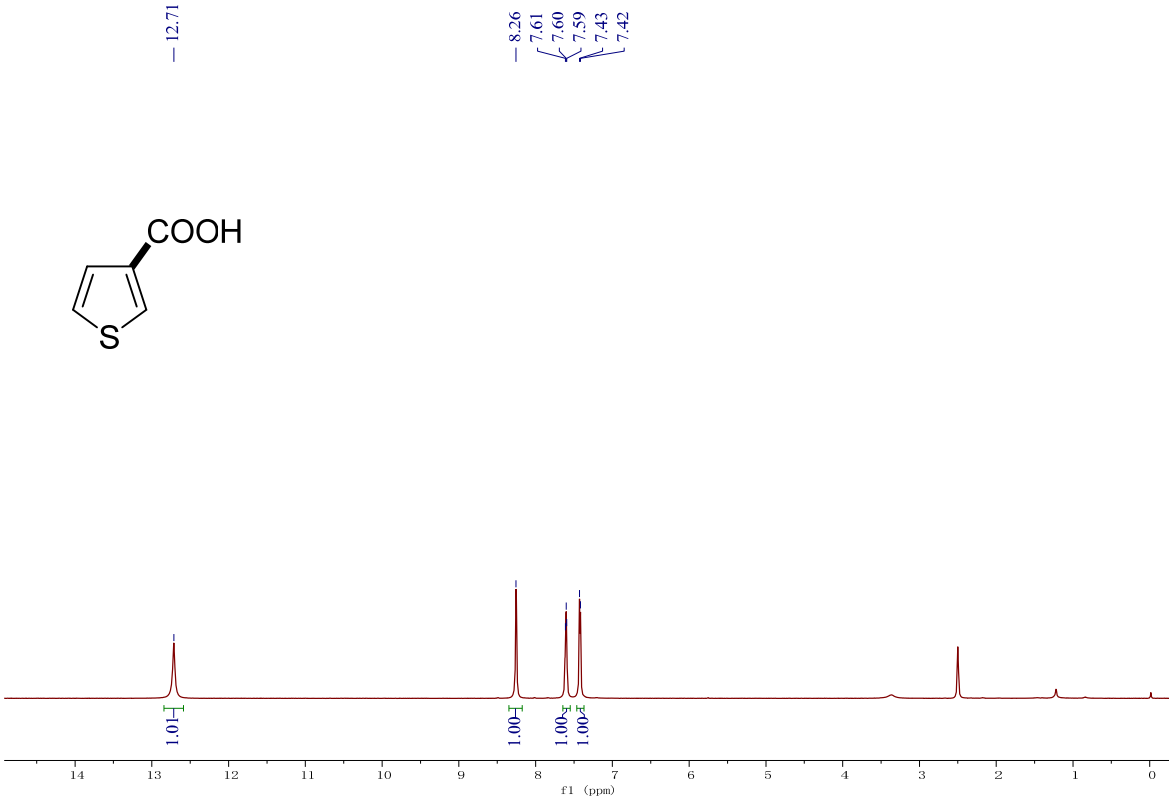
^{1}H NMR spectrum of **23**



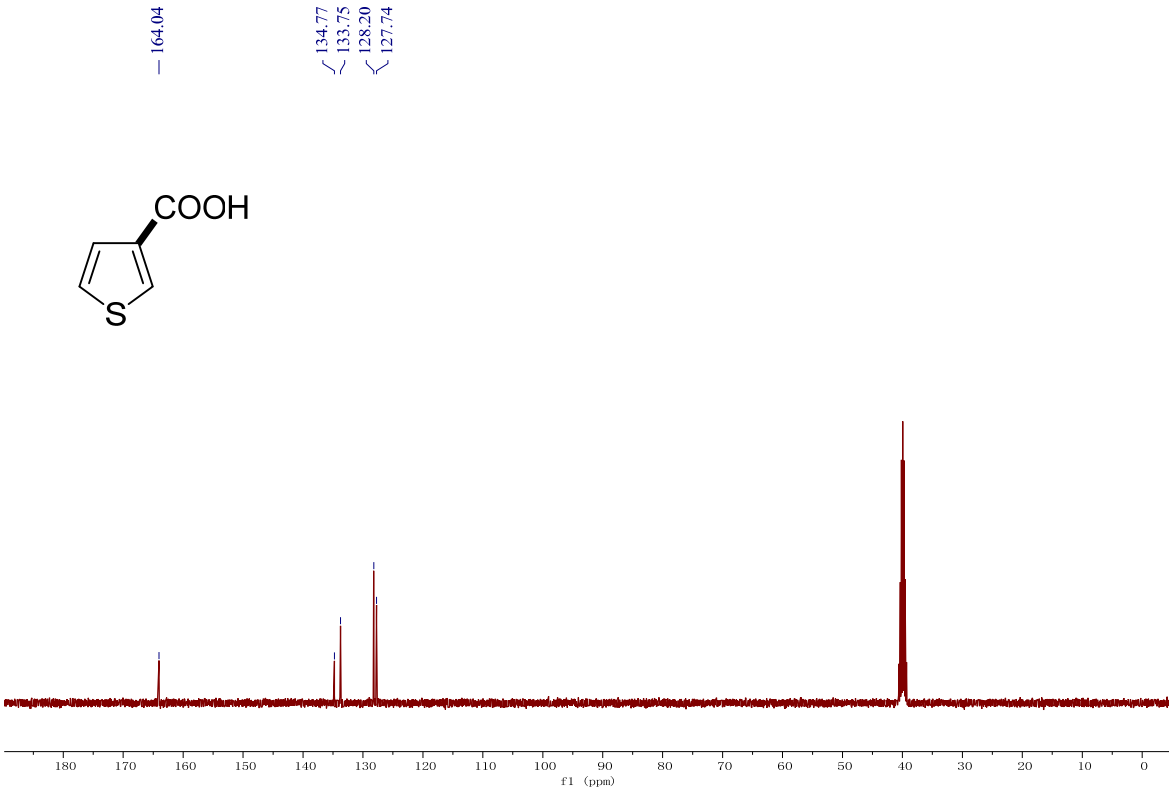
^{13}C NMR spectrum of **23**



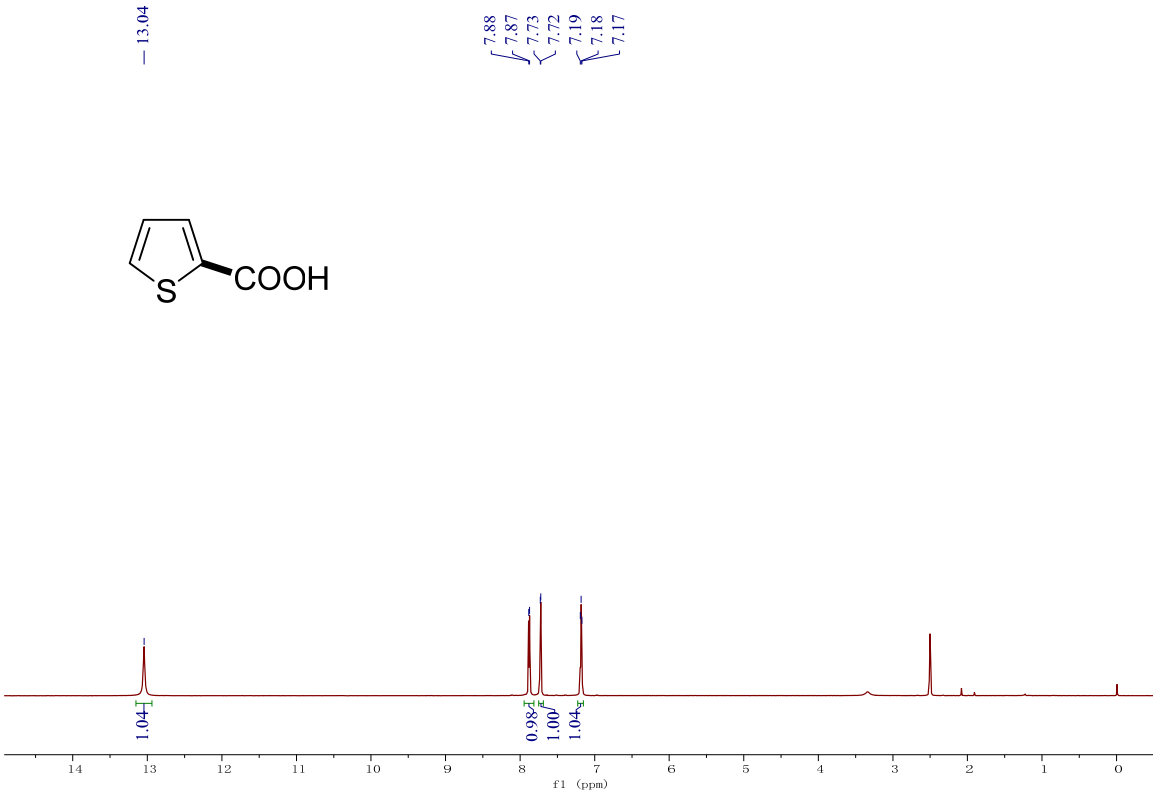
^{1}H NMR spectrum of **24**



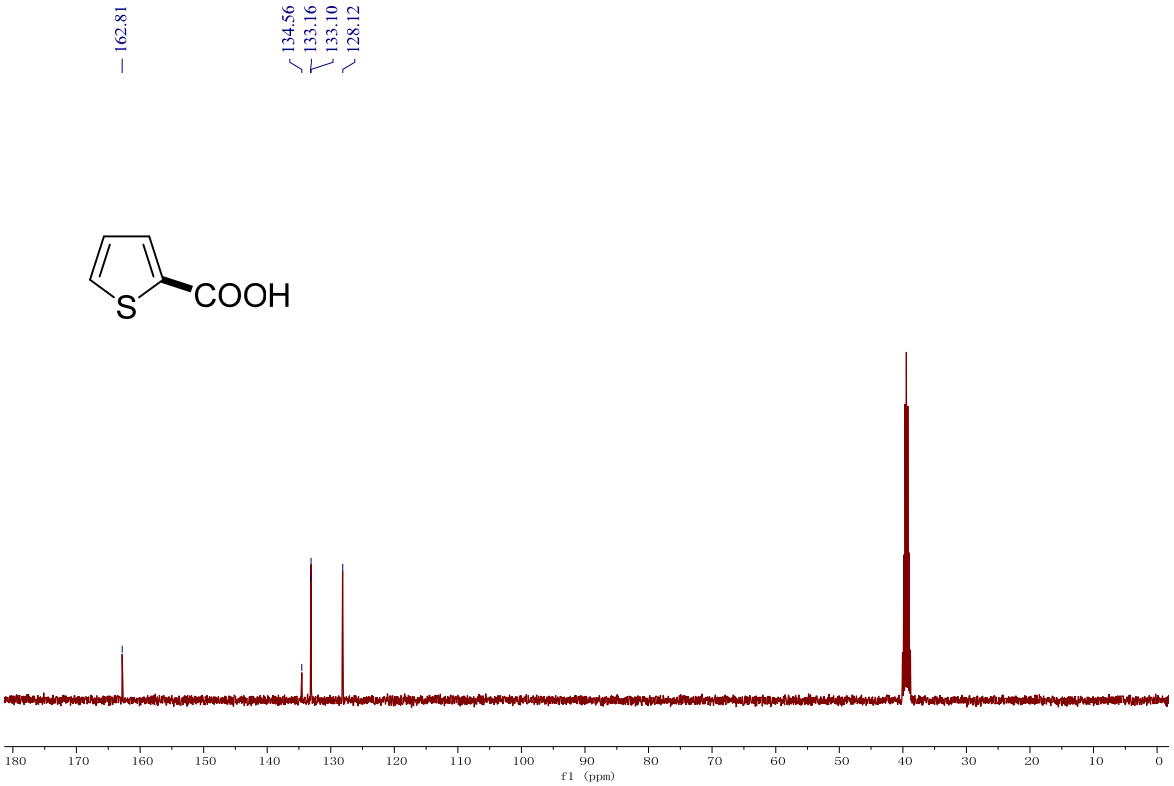
^{13}C NMR spectrum of **24**



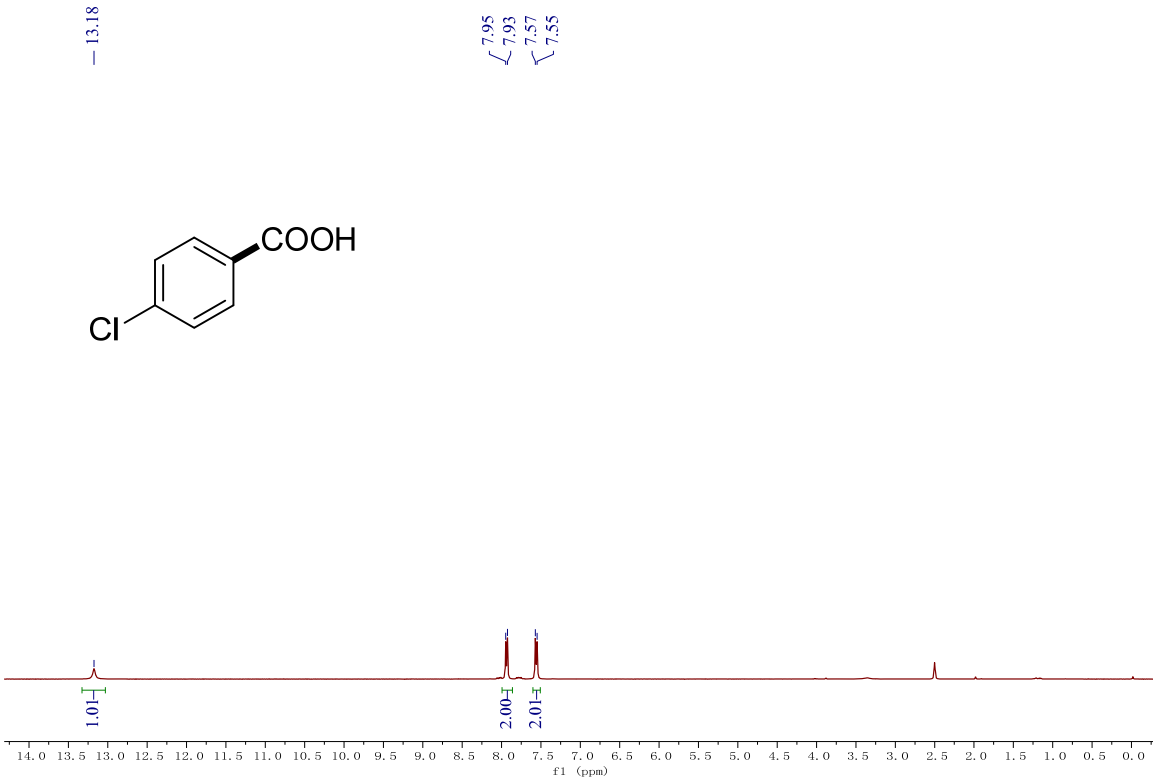
^{1}H NMR spectrum of **25**



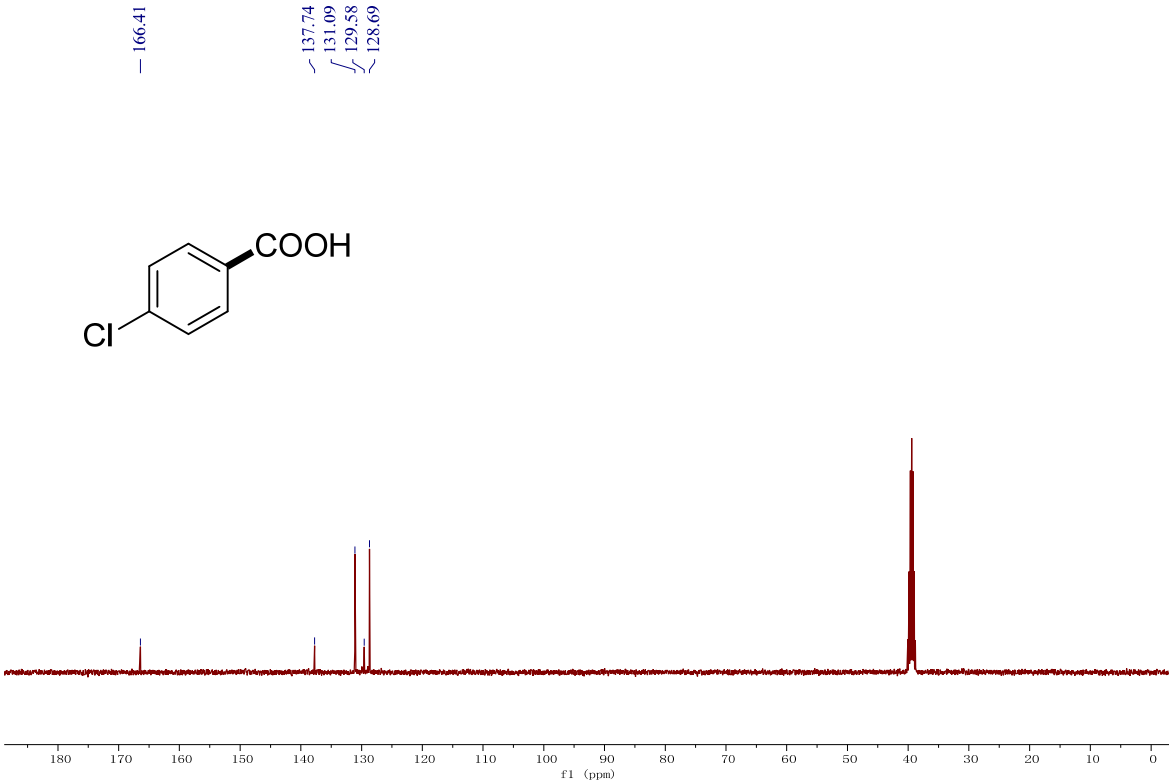
^{13}C NMR spectrum of **25**



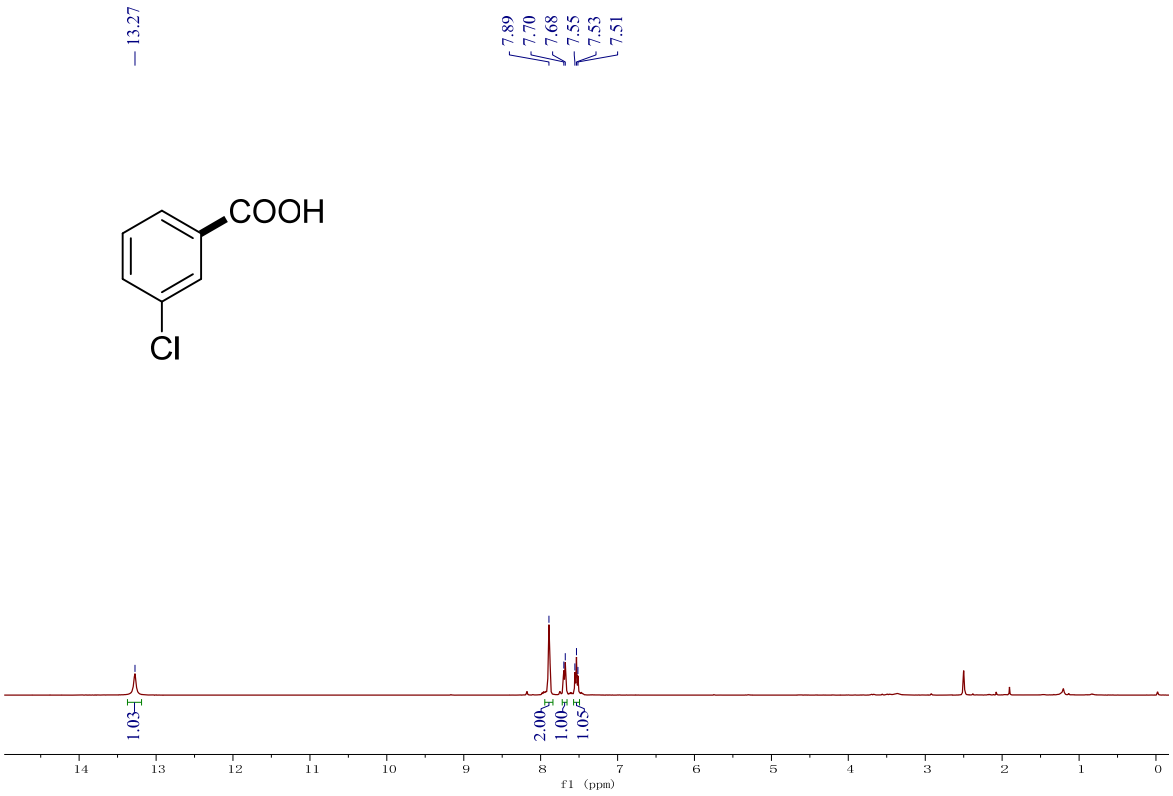
^{1}H NMR spectrum of **26**



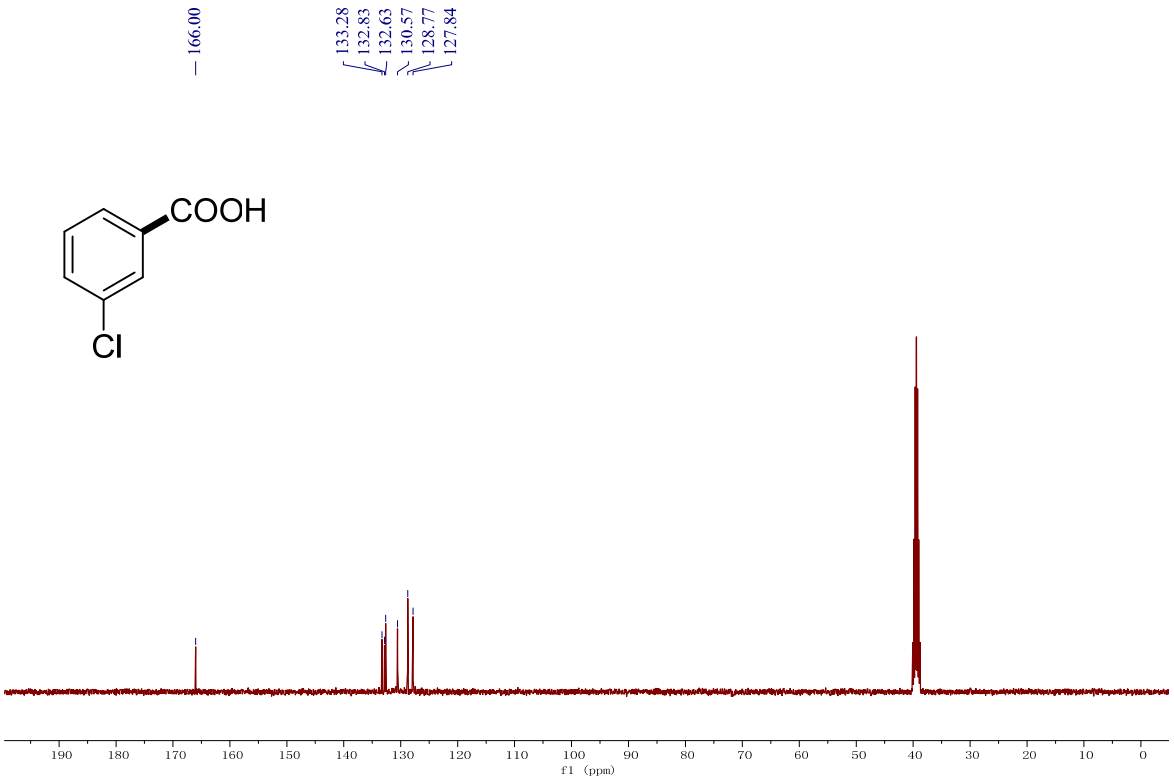
^{13}C NMR spectrum of **26**



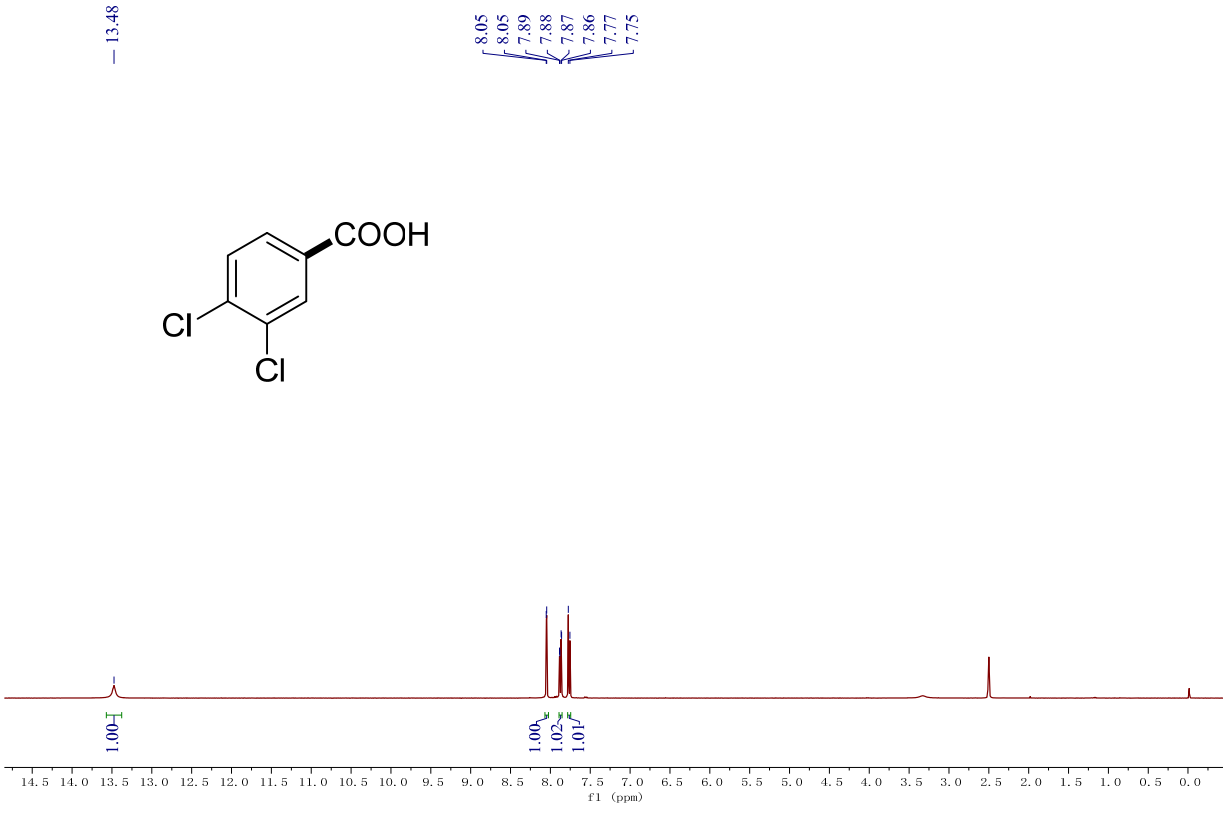
^{1}H NMR spectrum of **27**



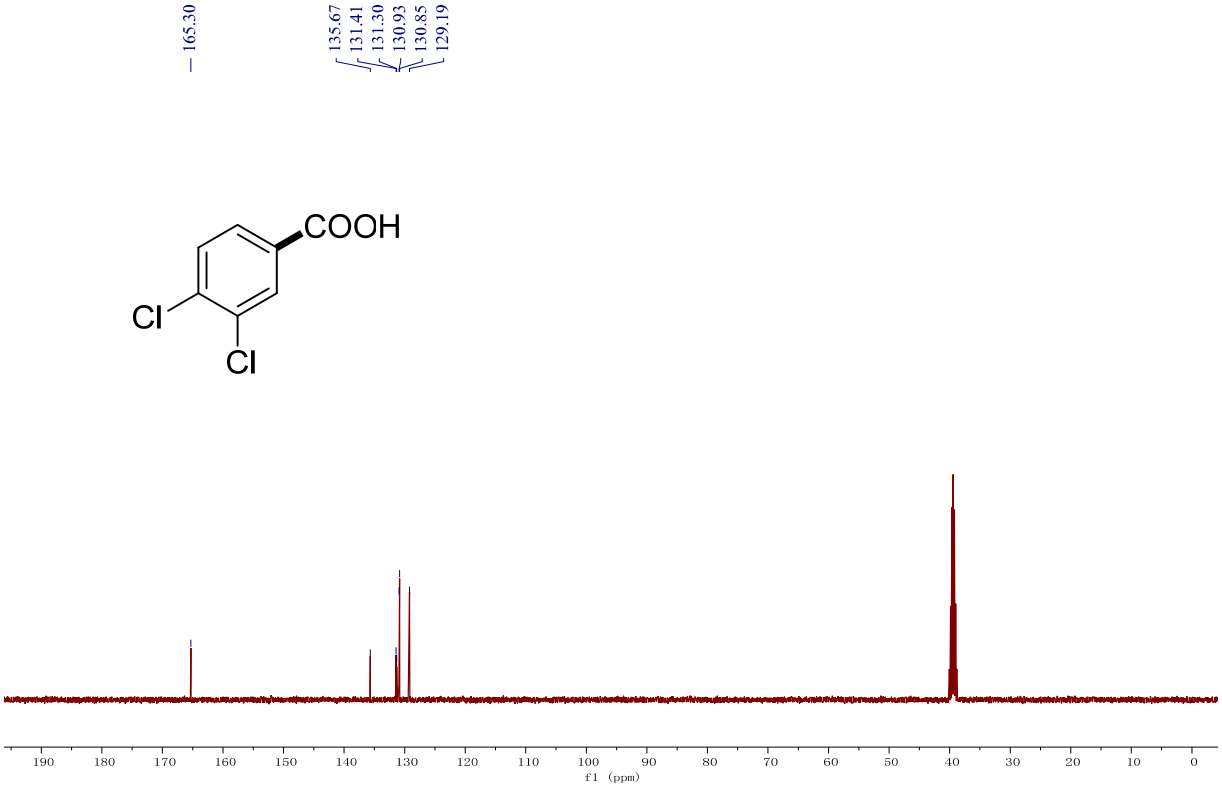
^{13}C NMR spectrum of **27**



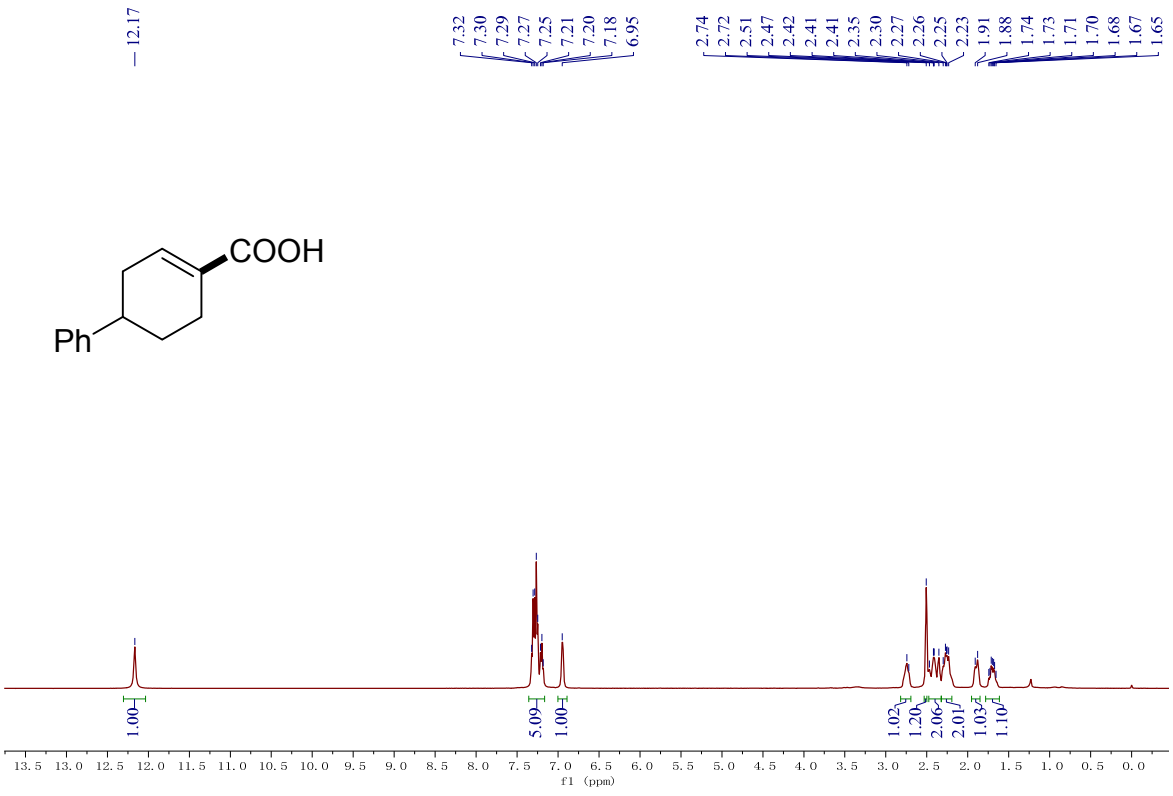
^{1}H NMR spectrum of **28**



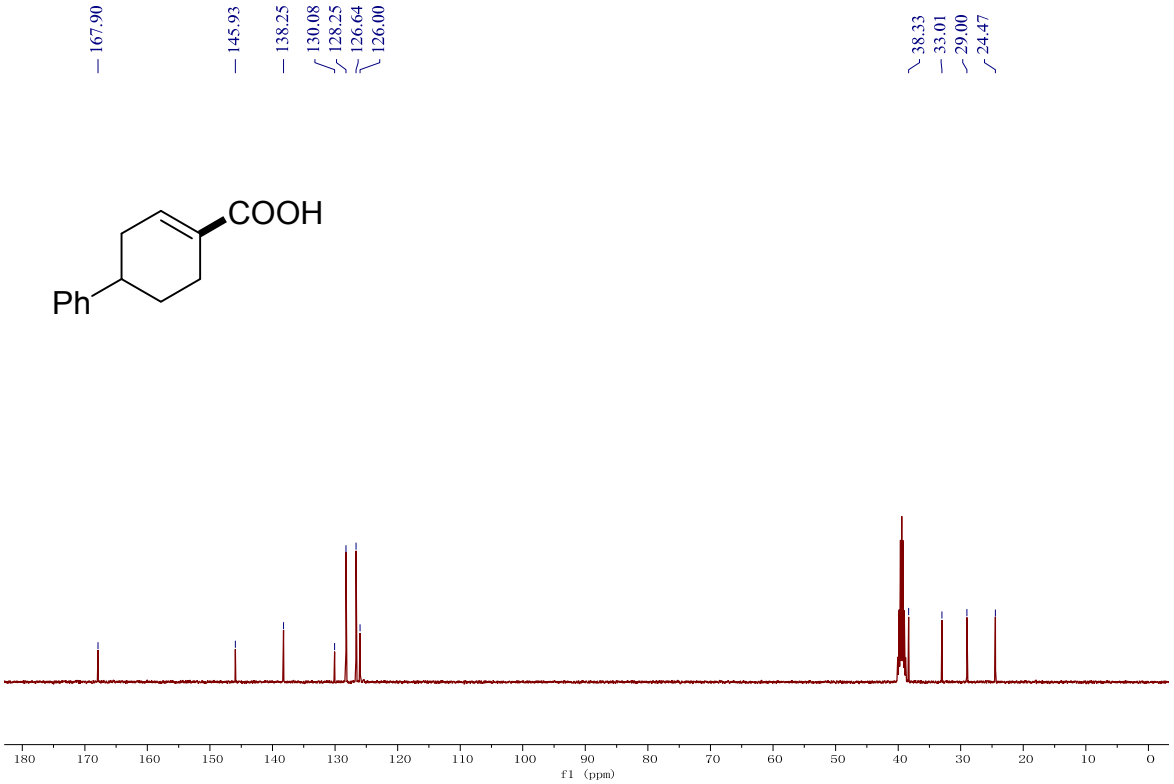
^{13}C NMR spectrum of **28**



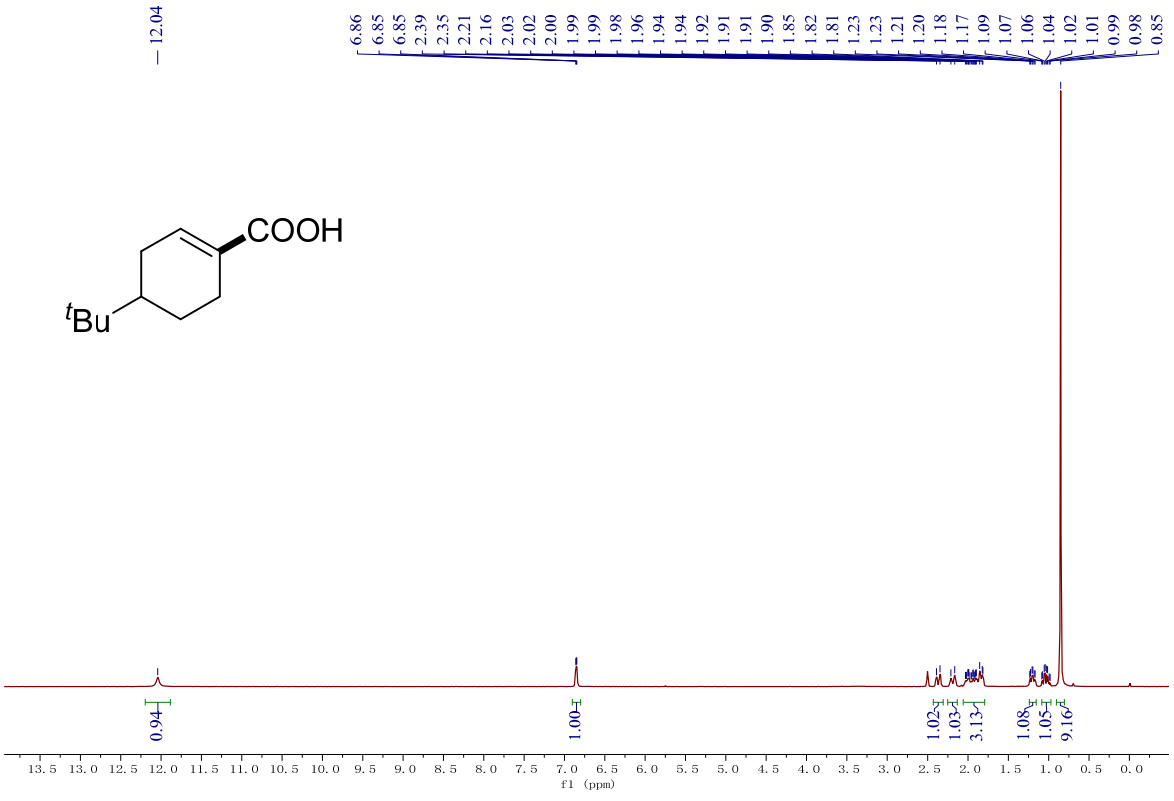
^{1}H NMR spectrum of **29**



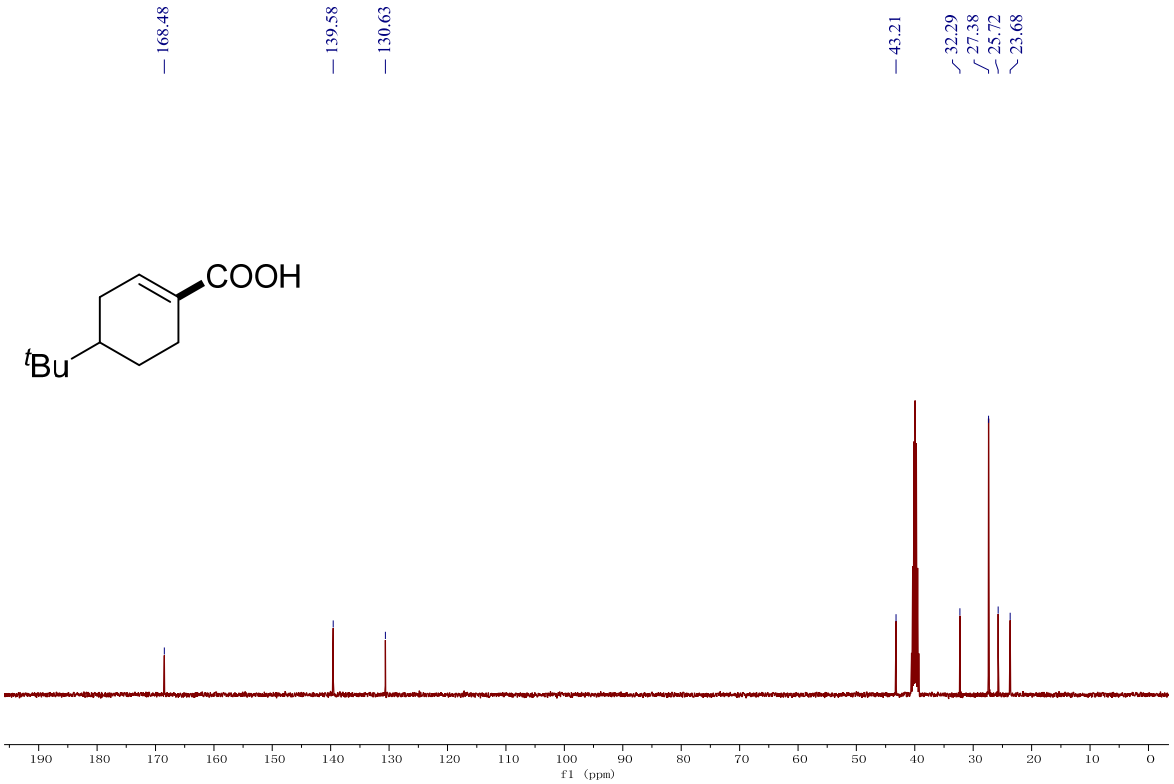
^{13}C NMR spectrum of **29**



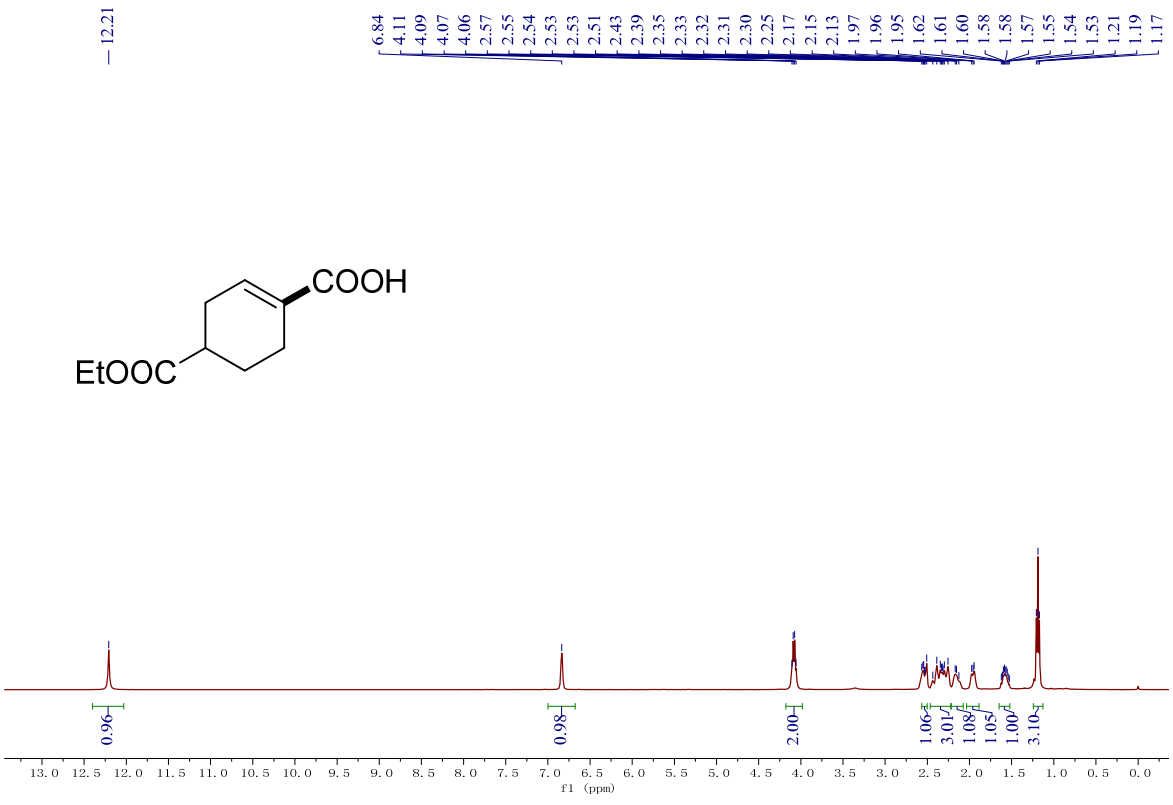
^{1}H NMR spectrum of **30**



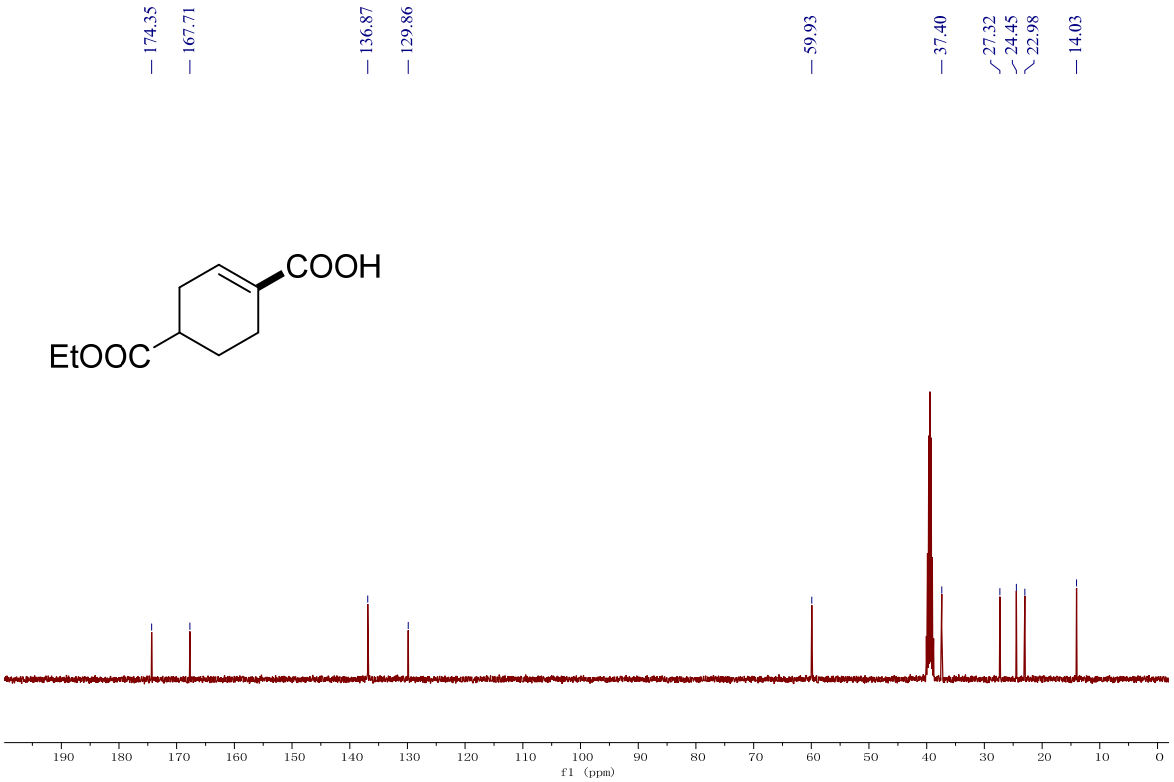
^{13}C NMR spectrum of **30**



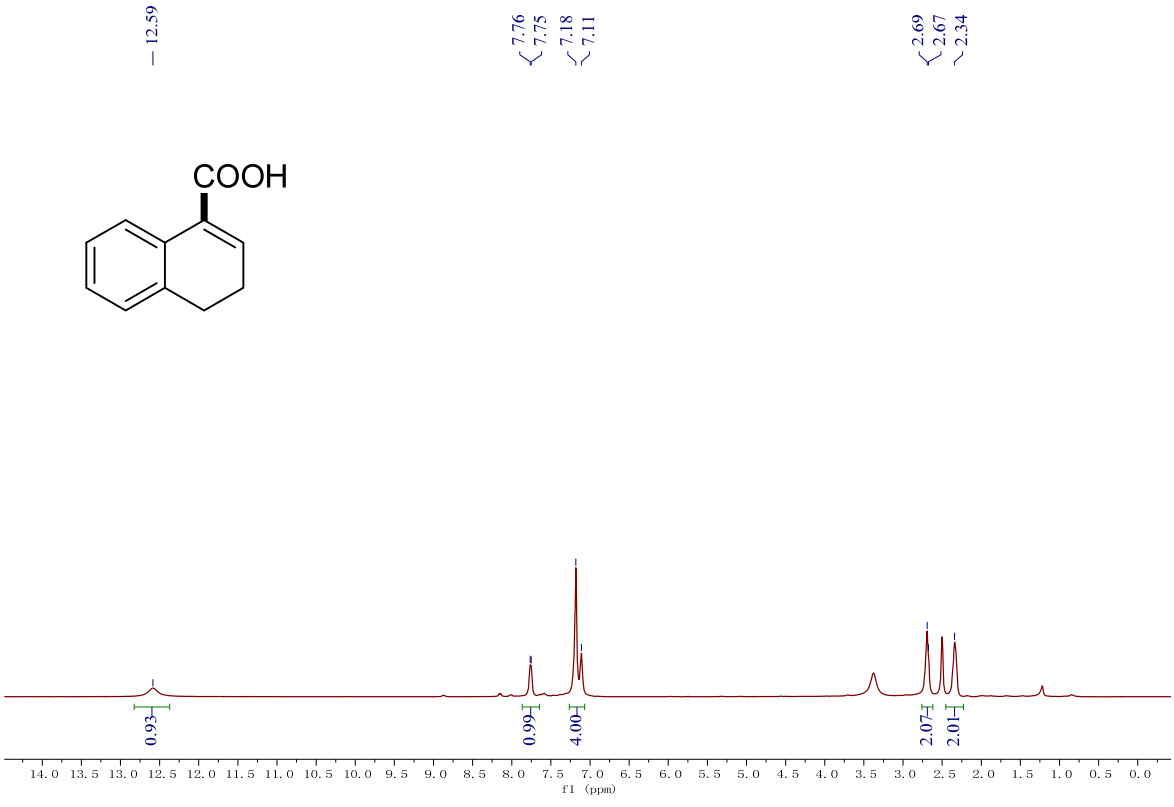
^{1}H NMR spectrum of **31**



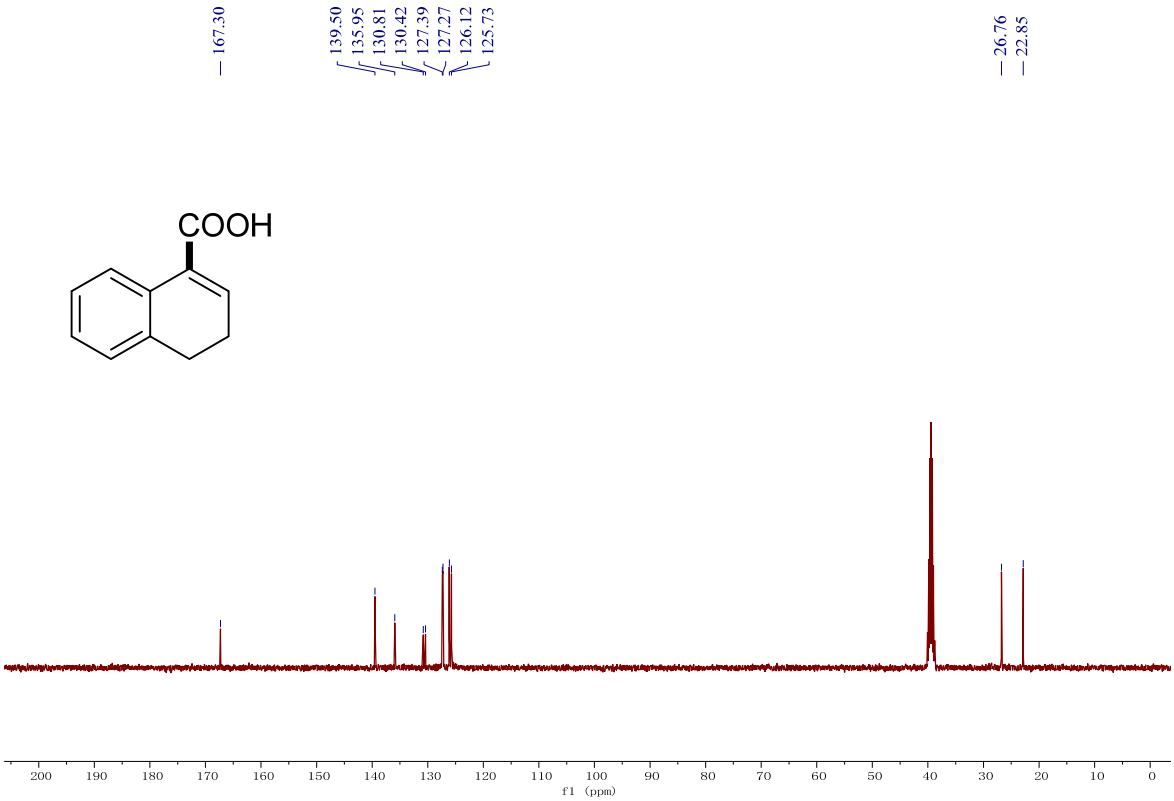
^{13}C NMR spectrum of **31**



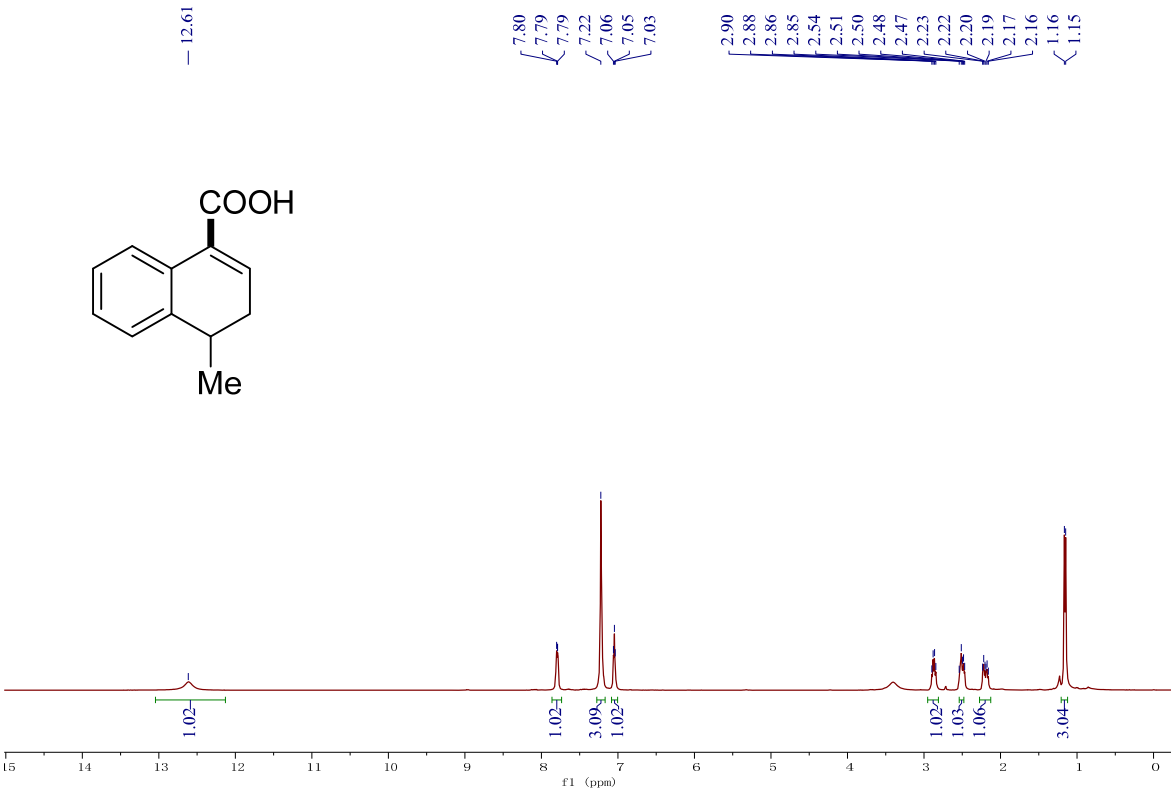
^{1}H NMR spectrum of **32**



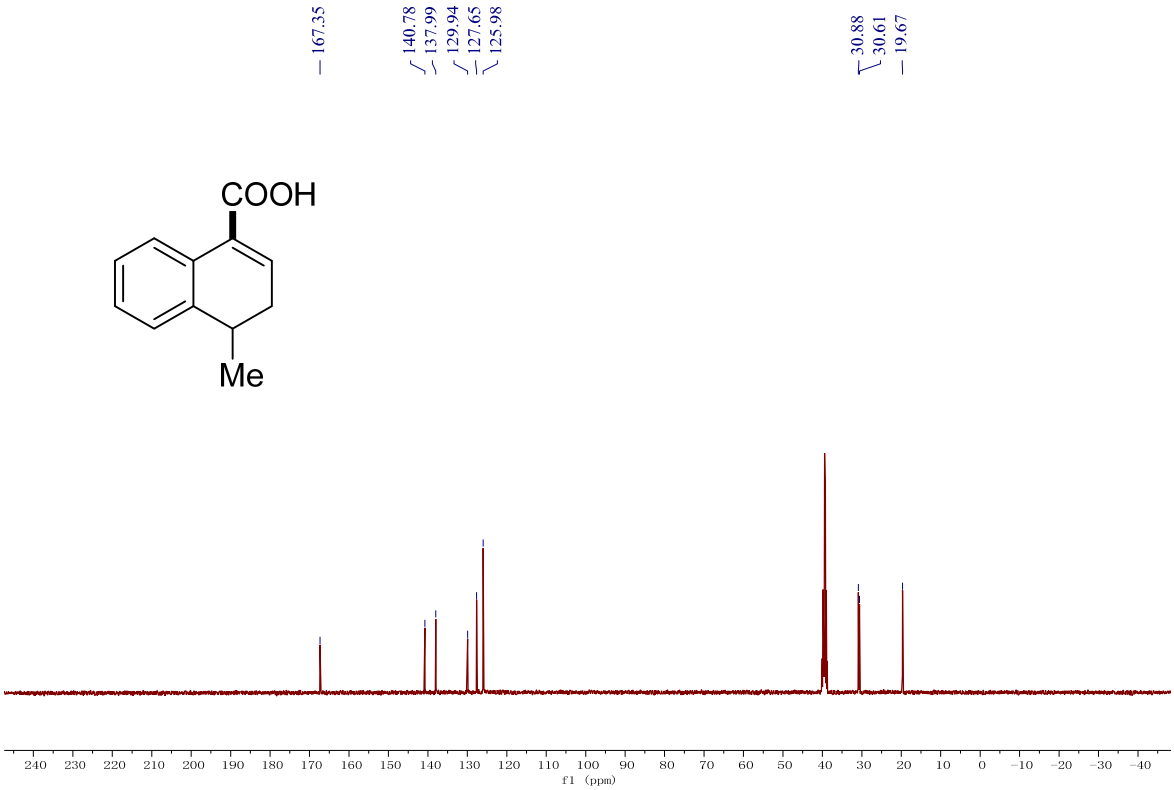
^{13}C NMR spectrum of **32**



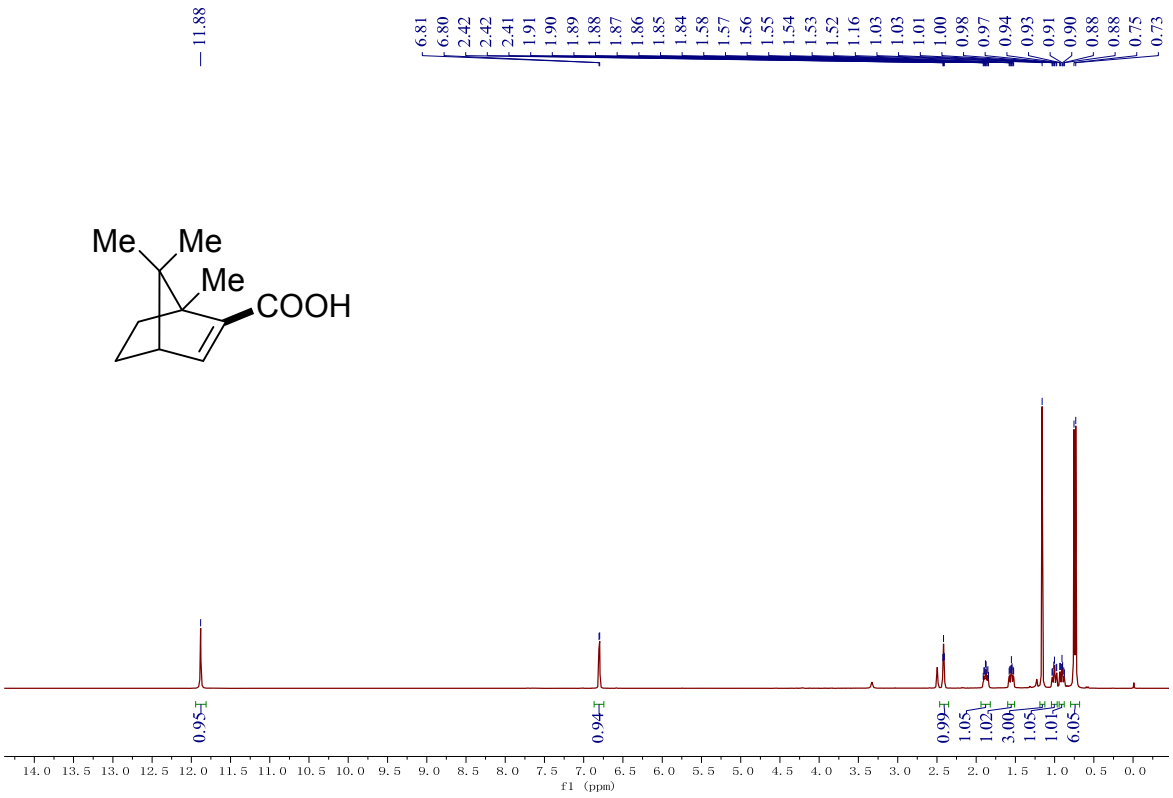
^{1}H NMR spectrum of **33**



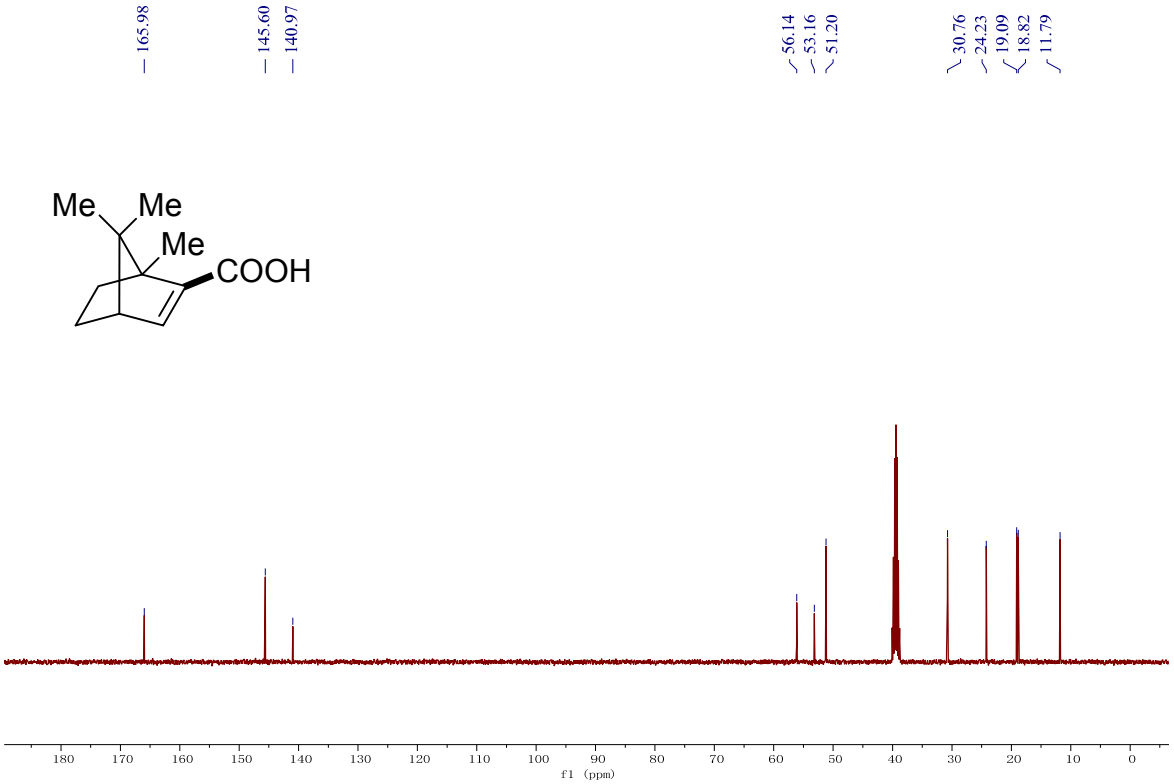
^{13}C NMR spectrum of **33**



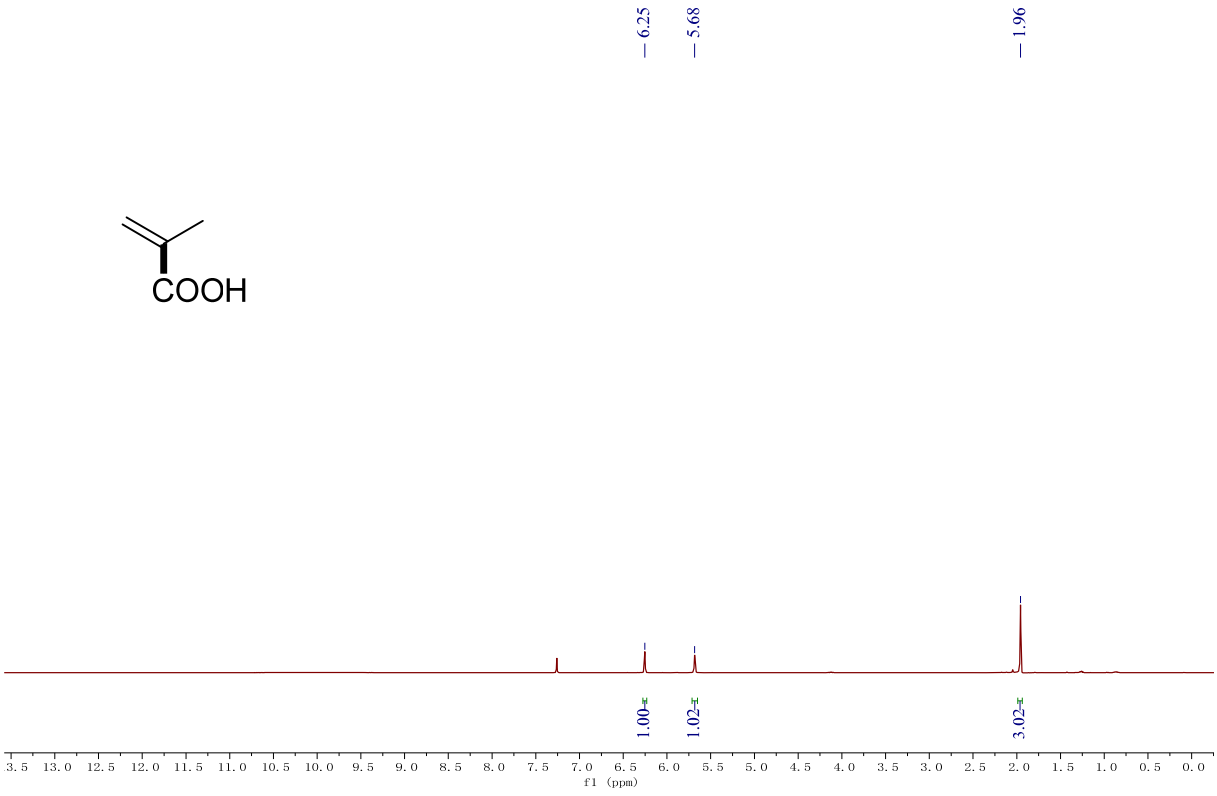
^{1}H NMR spectrum of **34**



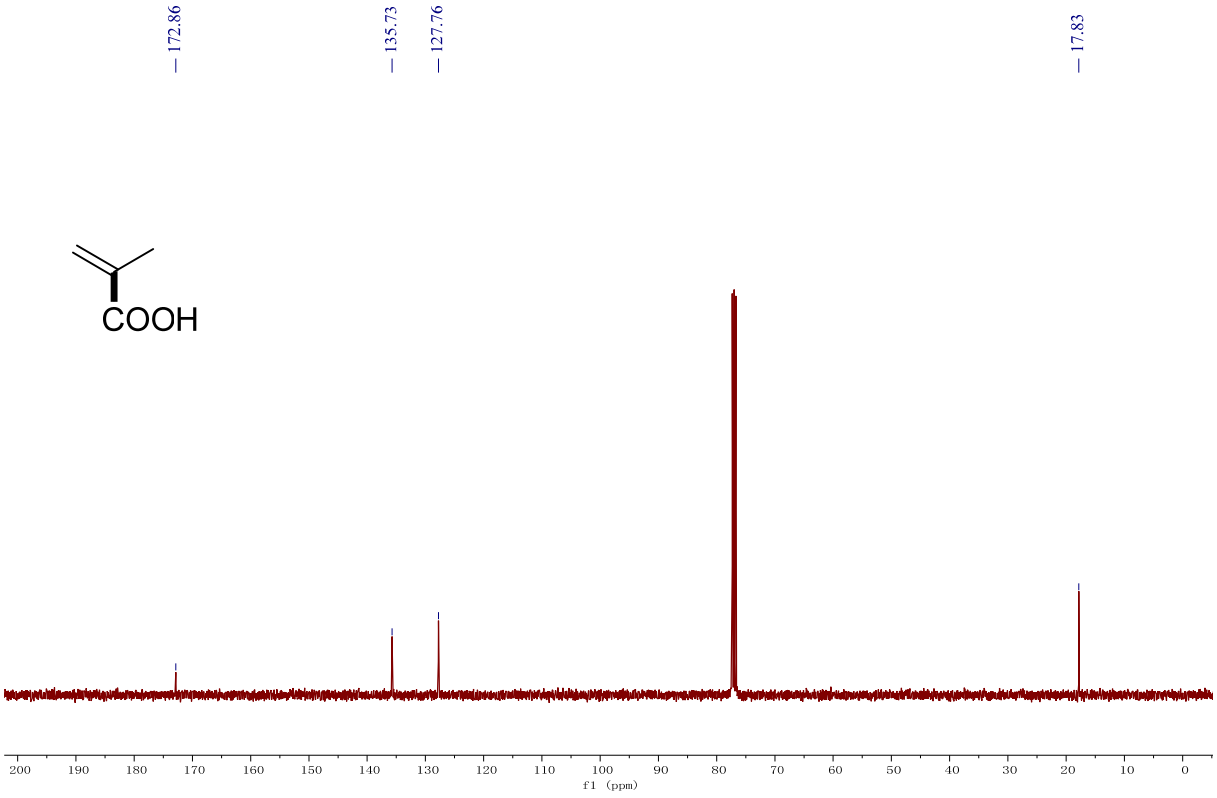
^{13}C NMR spectrum of **34**



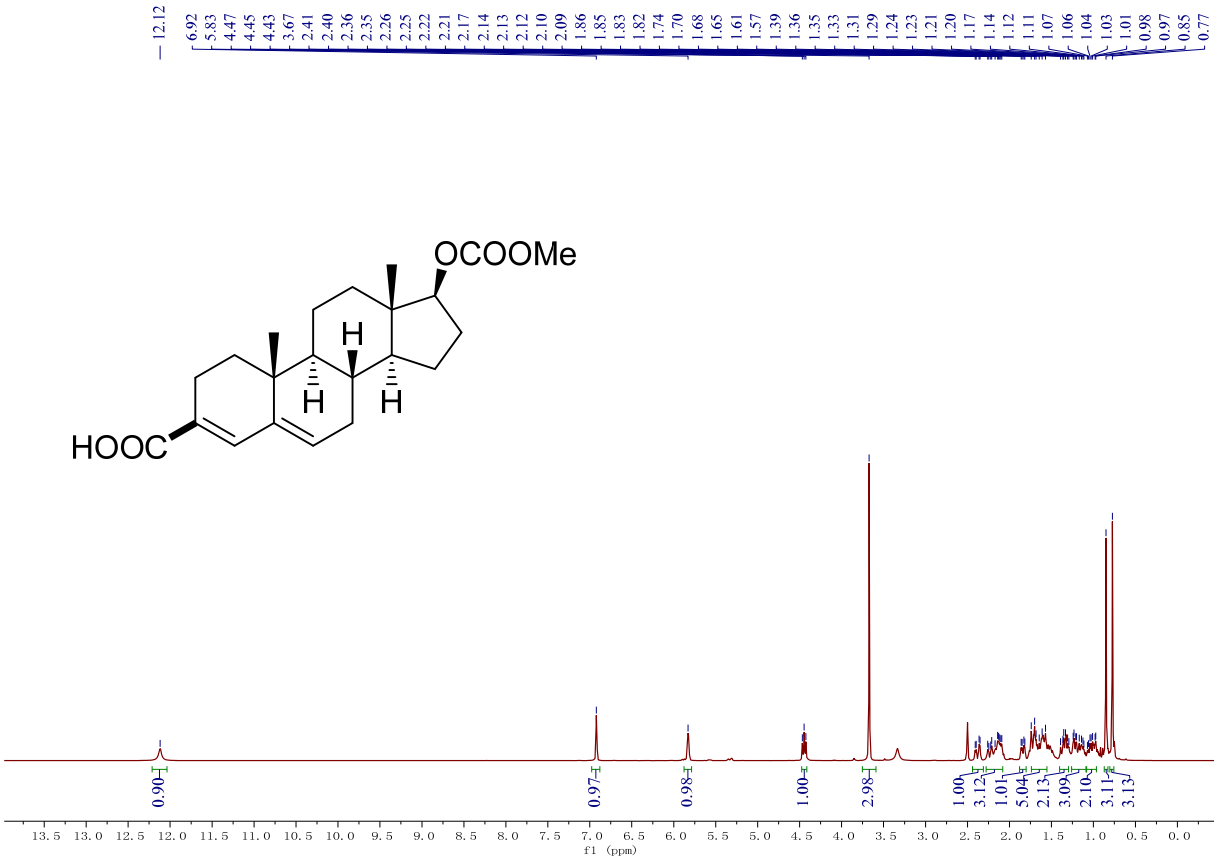
^{1}H NMR spectrum of **35**



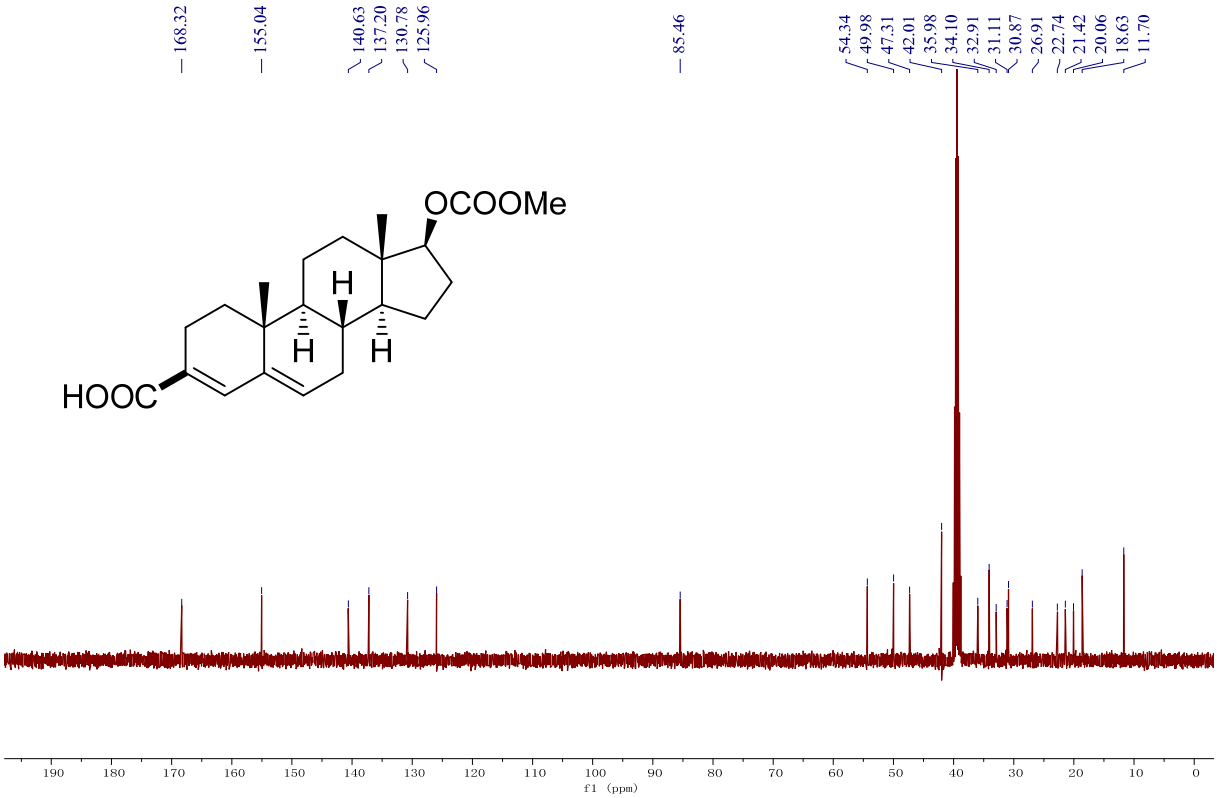
^{13}C NMR spectrum of **35**



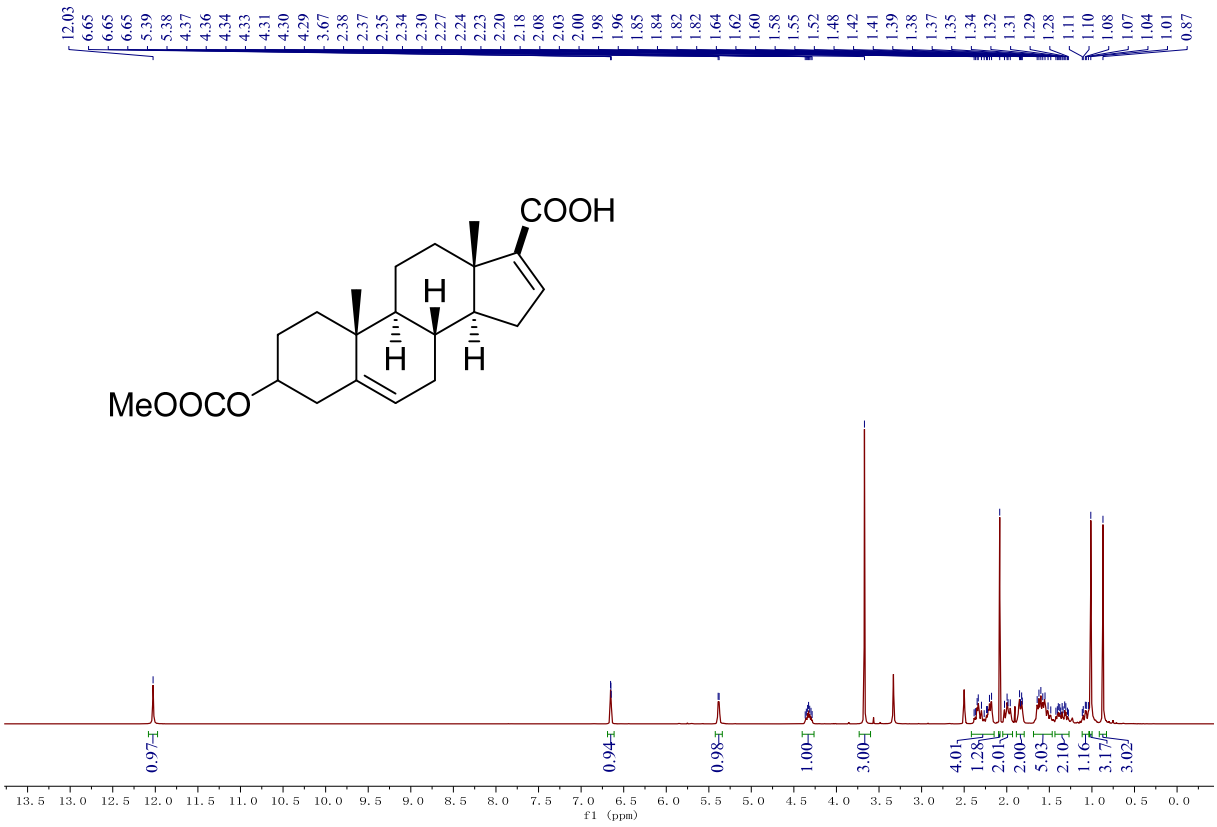
^{1}H NMR spectrum of **36**



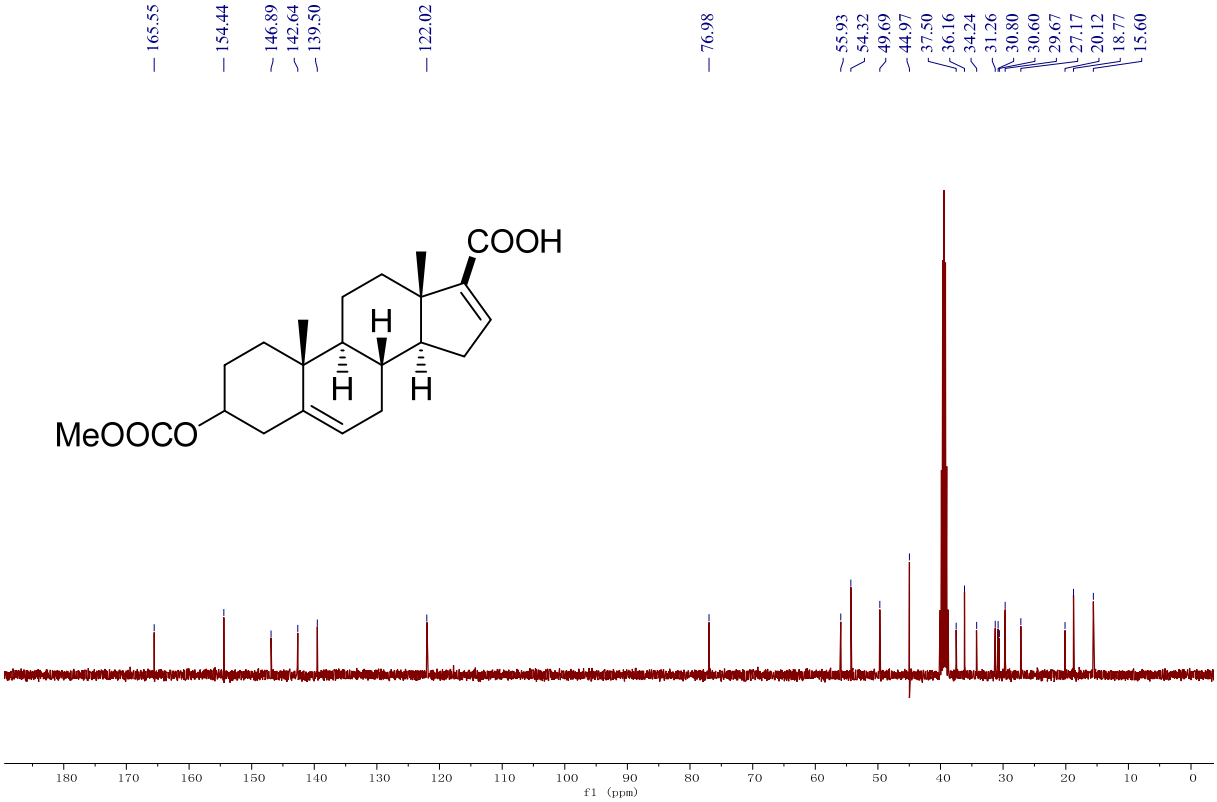
^{13}C NMR spectrum of **36**



^{1}H NMR spectrum of **37**



^{13}C NMR spectrum of **37**



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