Supporting Information

Nickel-Catalyzed Carboxylation of Aryl Iodides with Lithium Formate through Catalytic CO Recycling

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1. General Information

A. Materials:

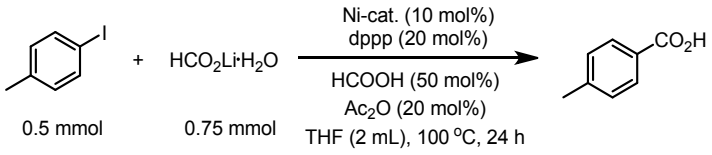
All reactions were conducted in oven-dried Schlenk tubes under argon atmosphere (purity≥99.99%) unless otherwise mentioned. Reagents were purchased from Adamas-beta, TCI and Aldrich, and used as received. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator.

B. Analytical Methods:

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Investigation of the Key Reaction Parameters

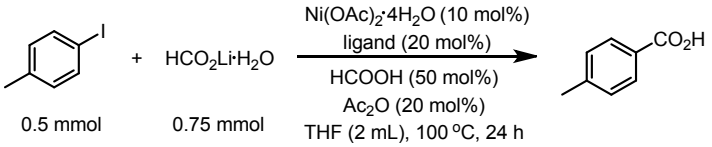
Table S1. Optimization of reaction conditions for nickel catalysts



entry	Ni-cat.	yield
1	$Ni(OAc)_2•4H_2O$	81%
2	$Ni(cod)_2$	64%
3	$Ni(acac)_2$	69%
4	$Ni(PPh_3)_4$	62%
5	$NiCl_2$	66%

Reaction conditions: 4-Iodotoluene (0.5 mmol), $HCO_2Li•H_2O$ (1.5 equiv, 0.75 mmol), HCO_2H (50 mol%), Ni-cat (10 mol%), dppp (20 mol%), Ac_2O (20 mol%), THF (2.0 mL), 100 °C, 24 h. Isolated yields.

Table S2. Optimization of reaction conditions for phosphine ligand



entry	ligand	yield
1	none	0
2	dppe	< 5%
3	dppp	81%
4	dppb	< 5%
5	dppen	< 5%
6	dppbz	< 5%
7	PPh_3	0
8	xantphos	0

Reaction conditions: 4-Iodotoluene (0.5 mmol), $HCO_2Li•H_2O$ (1.5 equiv, 0.75 mmol), HCO_2H (50 mol%), $Ni(OAc)_2•4H_2O$ (10 mol%), ligand (20 mol%), Ac_2O (20 mol%), THF (2.0 mL), 100 °C, 24 h. Isolated yields.

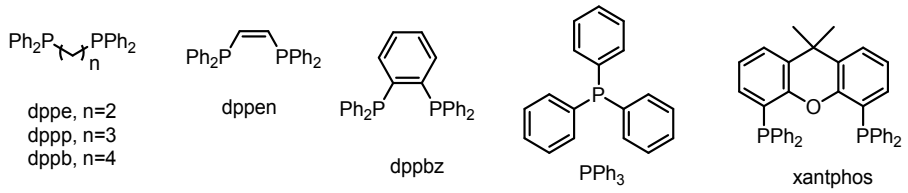
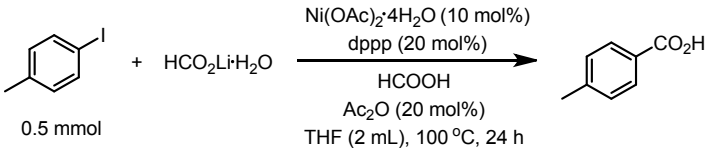


Table S3. Optimization for the addition of formic acid and lithium formate

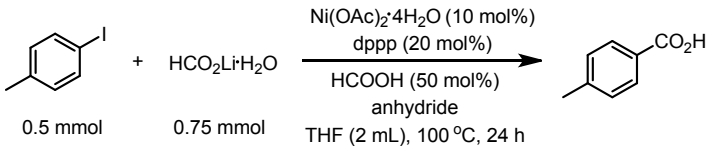


0.5 mmol

entry	$HCO_2Li•H_2O$ (x mmol)	HCOOH (y mmol)	yield
1	1 mmol	0	75%
2	0.75 mmol	0.25 mmol	81%
3	0.5 mmol	0.5 mmol	59%
4	0.25 mmol	0.75 mmol	68%
5	0	1 mmol	33%
6	0	0	0

Reaction conditions: 4-Iodotoluene (0.5 mmol), $HCO_2Li•H_2O$ (x mmol), HCOOH (y mmol), $Ni(OAc)_2•4H_2O$ (10 mol%), dppp (20 mol%), Ac_2O (20 mol%), THF (2.0 mL), 100 °C, 24 h. Isolated yields.

Table S4. Optimization of reaction conditions for anhydride

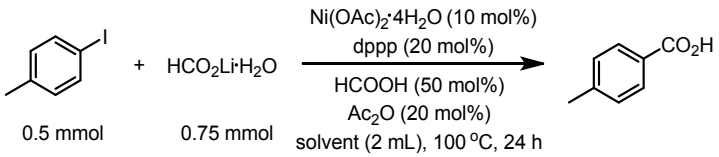


0.5 mmol 0.75 mmol

entry	anhydride (x mol%)	yield
1	none	0
2	Ac_2O (10 mol%)	65%
3	Ac_2O (20 mol%)	81%
4	Ac_2O (50 mol%)	60%
5	Ac_2O (75 mol%)	< 5%
6	Ac_2O (100 mol%)	< 5%
7	Bz_2O (20 mol%)	70%
8	propionic anhydride (20 mol%)	76%
9	trimethylacetic anhydride (20 mol%)	67%

Reaction conditions: 4-Iodotoluene (0.5 mmol), $HCO_2Li•H_2O$ (1.5 equiv, 0.75 mmol), HCO_2H (50 mol%), $Ni(OAc)_2•4H_2O$ (10 mol%), dppp (20 mol%), anhydride (x mol%), THF (2.0 mL), 100 °C, 24 h. Isolated yields.

Table S5. Optimization of reaction conditions for solvents



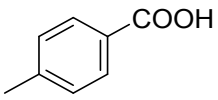
0.5 mmol 0.75 mmol

entry	solvent	yield
1	toluene	46%
2	THF	81%
3	DMF	< 5%
4	MeCN	15%
5	1,4-dioxane	50%

Reaction conditions: 4-Iodotoluene (0.5 mmol), $HCO_2Li•H_2O$ (1.5 equiv), HCO_2H (50 mol%), $Ni(OAc)_2•4H_2O$ (10 mol%), dppp (20 mol%), Ac_2O (20 mol%), solvent (2.0 mL), 100 °C, 24 h. Isolated yields.

3. General Experimental Procedure for Carboxylation Reaction

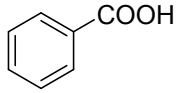
General Procedure: A 10 mL Schlenk tube containing a stirring bar was charged with aryl iodides (0.5 mmol, 1.0 equiv.), $HCO_2Li•H_2O$ (0.75 mmol, 1.5 equiv.), $Ni(OAc)_2•4H_2O$ (10 mol%) and 1,3-Bis(diphenylphosphino)propane (dppp, 20 mol%). The tube was then evacuated and back-filled with argon three times. THF (2.0 mL) was added subsequently, then formic acid (50 mol%, 0.25 mmol) and acetic anhydride (20 mol%, 0.1 mmol) were added under argon atmosphere. The tube was sealed by a plastic screw cap and heated to 100 °C (oil bath). After stirring for 24 h, the reaction mixture was cooled to room temperature, and diluted with EtOAc, concentrated, the residue was purified with silica gel chromatography to give product.



4-methylbenzoic acid (2): Following the general procedure, using 10 mol% $Ni(OAc)_2•4H_2O$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 81% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Org. Lett.* **2014**, *16*, 2876).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H).

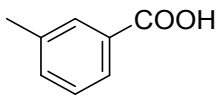
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 144.7, 130.3, 129.2, 126.6, 21.8.



benzoic acid (3): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 71% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2018**, *57*, 7205).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.38 – 7.89 (m, 2H), 7.68 – 7.55 (m, 1H), 7.47 (t, *J* = 11.6, 4.2 Hz, 2H).

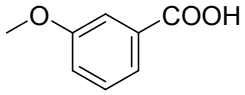
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 133.8, 130.2, 129.3, 128.5.



3-methylbenzoic acid (4): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 78% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2018**, *57*, 10949).

^{1}H NMR (400 MHz, DMSO) δ 8.03 – 7.64 (m, 2H), 7.61 – 7.22 (m, 2H), 2.37 (s, 3H).

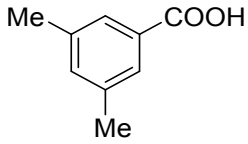
^{13}C NMR (101 MHz, DMSO) δ 167.9, 138.4, 133.9, 131.2, 130.2, 128.9, 126.9, 21.3.



3-methoxybenzoic acid (5): Following the general procedure, using 10 mol% $Ni(cod)_2$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 76% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun.* **2015**, *51*, 4799).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (ddd, J = 7.6, 1.5, 1.0 Hz, 1H), 7.63 (dd, J = 2.6, 1.5 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.16 (ddd, J = 8.3, 2.7, 1.0 Hz, 1H), 3.87 (s, 3H).

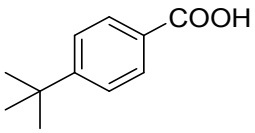
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 159.6, 130.6, 129.6, 122.7, 120.5, 114.4, 55.5.



3,5-dimethylbenzoic acid (6): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 70% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Org. Lett.* **2015**, *17*, 5276).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 7.74 (s, 2H), 7.23 (s, 1H), 2.37 (s, 6H).

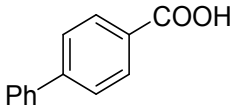
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 138.2, 135.5, 129.2, 127.9, 21.2.



4-(tert-butyl)benzoic acid (7): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 85% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun.* **2012**, *48*, 6292).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H).

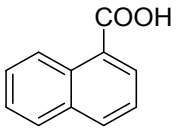
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 157.6, 130.1, 126.6, 125.5, 35.2, 31.1.



[1,1'-biphenyl]-4-carboxylic acid (8): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 80% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Green Chem.* **2013**, *15*, 635).

^{1}H NMR (400 MHz, Acetone) δ 11.25 (s, 1H), 8.21 – 8.08 (m, 2H), 7.84 – 7.79 (m, 2H), 7.77 – 7.72 (m, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.41 (m, 1H).

^{13}C NMR (101 MHz, Acetone) δ 166.6, 145.3, 139.8, 130.2, 129.4, 129.0, 128.2, 127.1, 126.9.

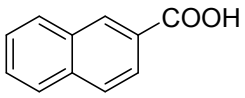


1-naphthoic acid (9): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 35% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1).

The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **2017**, *82*, 3781).

^{1}H NMR (400 MHz, DMSO) δ 13.17 (s, 1H), 8.87 (d, J = 8.6 Hz, 1H), 8.16 (M, 2H), 8.08 – 7.94 (m, 1H), 7.74 – 7.46 (m, 3H).

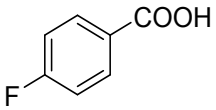
^{13}C NMR (101 MHz, DMSO) δ 169.1, 133.9, 133.4, 131.1, 130.3, 129.1, 128.2, 128.1, 126.7, 126.0, 125.4.



2-naphthoic acid (10): Following the general procedure, using 10 mol% $Ni(acac)_2$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 63% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Green Chem.* **2018**, *20*, 3038).

^{1}H NMR (400 MHz, DMSO) δ 13.11 (s, 1H), 8.63 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05 – 7.97 (m, 3H), 7.70 – 7.55 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 172.67, 140.15, 137.36, 135.82, 134.50, 133.54, 133.39, 133.28, 132.87, 132.02, 130.38.

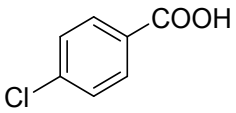


4-fluorobenzoic acid (11): Following the general procedure, using 10 mol% $Ni(OAc)_2•4H_2O$, 20 mol% dppp, 1.5 equiv. $HCO_2Li•H_2O$, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 80% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2018**, *57*, 9896).

^{1}H NMR (400 MHz, Acetone) δ 8.31 – 7.79 (m, 2H), 7.46 – 6.91 (m, 2H).

^{13}C NMR (101 MHz, Acetone) δ 166.9, 166.0 (d, $J_{C\text{-}F}$= 251.3 Hz), 132.4 (d, $J_{C\text{-}F}$ = 9.5 Hz), 127.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.2 Hz).

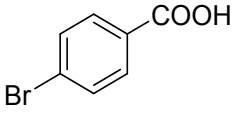
^{19}F NMR (376 MHz, Acetone) δ -107.96.



4-chlorobenzoic acid (12): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 90% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun*. **2013**, *49*, 5213).

^{1}H NMR (400 MHz, DMSO) δ 13.20 (s, 1H), 8.42 – 7.79 (m, 2H), 7.77 – 7.35 (m, 2H).

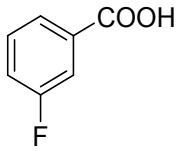
^{13}C NMR (101 MHz, DMSO) δ 171.7, 143.0, 136.3, 134.9, 133.9.



4-bromobenzoic acid (13): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 70% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Green Chem.* **2018**, *20*, 3038).

^{1}H NMR (400 MHz, Acetone) δ 8.28 – 7.84 (m, 2H), 7.81 – 7.60 (m, 2H).

^{13}C NMR (101 MHz, Acetone) δ 166.0, 131.7, 131.4, 129.8, 127.3.



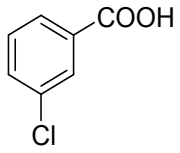
3-fluorobenzoic acid (14): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 81% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun.* **2013**, *49*, 5213).

^{1}H NMR (400 MHz, Acetone) δ 7.89 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 9.5 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.48 – 7.39 (m, 1H).

^{13}C NMR (101 MHz, Acetone) δ 165.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 162.6 (d, $J_{C\text{-}F}$= 245.0 Hz), 133.0 (d, $J_{C\text{-}F}$ = 7.3 Hz), 130.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 125.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 119.8 (d, $J_{C\text{-}F}$

= 21.4 Hz), 116.0 (d, J_{C-F} = 22.9 Hz).

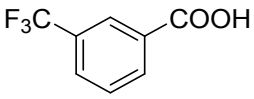
^{19}F NMR (376 MHz, Acetone) δ -114.14.



3-chlorobenzoic acid (15): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 64% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2018**, *57*, 7205).

^{1}H NMR (400 MHz, DMSO) δ 13.36 (s, 1H), 8.36 – 7.76 (m, 2H), 7.71 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.61 – 7.46 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 166.5, 133.8, 133.4, 133.2, 131.1, 129.3, 128.4.

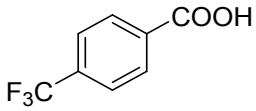


3-(trifluoromethyl)benzoic acid (16): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 73% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chin. J. Chem.* **2017**, *35*, 1761).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 133.4, 131.3 (q, J_{C-F} = 33.1 Hz), 130.4 (q, J_{C-F} = 3.5 Hz), 130.1, 129.3, 127.2 (q, J_{C-F} = 3.9 Hz), 122.2 (q, J_{C-F} = 272.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.87.



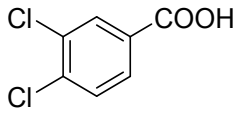
4-(trifluoromethyl)benzoic acid (17): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20

mol% Ac_2O, 2.0 mL THF, obtained in 72% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chin. J. Chem.* **2018**, *36*, 15).

^{1}H NMR (400 MHz, DMSO) δ 13.50 (s, 1H), 8.14 (d, J = 7.9 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 166.7, 135.1, 132.9 (q, $J_{C\text{-}F}$ = 31.9 Hz), 130.6, 126.1 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.3 (q, $J_{C\text{-}F}$ = 272.6 Hz).

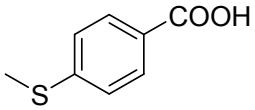
^{19}F NMR (376 MHz, DMSO) δ -61.56.



3,4-dichlorobenzoic acid (18): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 65% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Green Chem*. **2018**, *20*, 3038).

^{1}H NMR (400 MHz, Acetone) δ 8.13 (d, J = 2.0 Hz, 1H), 7.98 (dd, J = 8.4, 2.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H).

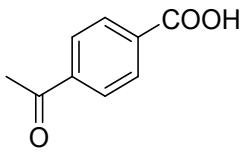
^{13}C NMR (101 MHz, Acetone) δ 164.8, 136.7, 132.2, 131.4, 131.0, 130.9, 129.3.



4-(methylthio)benzoic acid (19): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 81% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Org. Lett.* **2013**, *15*, 1378).

^{1}H NMR (400 MHz, Acetone) δ 8.23 – 7.72 (m, 2H), 7.60 – 7.02 (m, 2H), 2.56 (s, 3H).

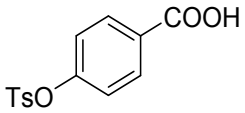
^{13}C NMR (101 MHz, Acetone) δ 166.6, 145.6, 130.0, 126.6, 124.9, 13.7.



4-acetylbenzoic acid (20): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 80% yield as white solid (Eluent: petroleum ether/ethyl acetate = 1/1). The compound data was in agreement with the literature (Ref. *Chem. Commun.* **2018**, *54*, 3701).

^{1}H NMR (400 MHz, DMSO) δ 8.06 (s, 4H), 2.63 (s, 3H).

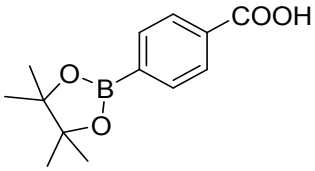
^{13}C NMR (101 MHz, DMSO) δ 198.2, 167.1, 140.3, 135.0, 130.0, 128.8, 27.5.



4-(tosyloxy)benzoic acid (21): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 65% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *J. Am. Chem. Soc*. **2013**, *135*, 2891).

^{1}H NMR (400 MHz, DMSO) δ 13.22 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 2.6 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 2.50 (s, 3H).

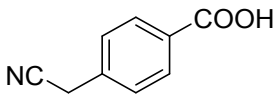
^{13}C NMR (101 MHz, DMSO) δ 166.7, 152.5, 146.6, 131.8, 131.6, 130.8, 130.4, 128.7, 122.7, 21.7.



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (22): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 87% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **2018**, *83*, 1842).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 1.36 (s, 12H).

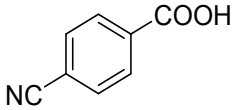
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 134.8, 131.5, 129.2, 84.3, 24.9. (one carbon signal was overlapped)



4-(cyanomethyl)benzoic acid (23): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 70% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Org. Lett*. **2008**, *10*, 2697).

^{1}H NMR (400 MHz, DMSO) δ 13.06 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 4.17 (s, 2H).

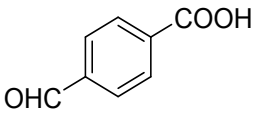
^{13}C NMR (101 MHz, DMSO) δ 167.4, 136.7, 130.6, 130.4, 128.8, 119.3, 22. 9.



4-cyanobenzoic acid (24): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 55% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun*. **2012**, *48*, 6292).

^{1}H NMR (400 MHz, DMSO) δ 13.60 (s, 1H), 8.09 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 166.5, 135.3, 133.2, 130.4, 118.7, 115.5.

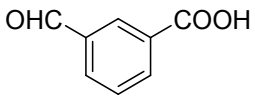


4-formylbenzoic acid (25): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 76% yield as white solid (Eluent: petroleum

ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Chem. Commun*. **2012**, *48*, 6292).

^{1}H NMR (400 MHz, Acetone) δ 11.64 (s, 1H), 10.17 (s, 1H), 8.24 (dd, *J* = 7.4, 3.0 Hz, 2H), 8.06 (dd, *J* = 7.5, 3.1 Hz, 2H).

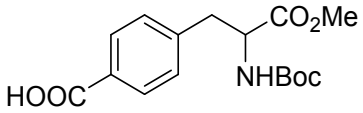
^{13}C NMR (101 MHz, Acetone) δ 191.9, 166.0, 139.6, 135.4, 130.2, 129.4.



3-formylbenzoic acid (26): Following the general procedure, using 10 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 60% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Org. Lett*. **2017**, *19*, 4235).

^{1}H NMR (400 MHz, Acetone) δ 10.16 (s, 1H), 8.56 (t, *J* = 1.5 Hz, 1H), 8.41 – 8.26 (m, 1H), 8.21 – 8.17 (m, 1H), 7.77 (t, *J* = 7.4 Hz, 1H).

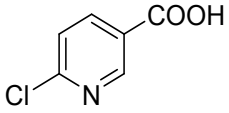
^{13}C NMR (101 MHz, Acetone) δ 191.7, 165.9, 137.0, 134.9, 133.2, 131.6, 130.5, 129.5.



4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (27): Following the general procedure, using 10 mol% $Ni(cod)_2$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 45% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2012**, *51*, 9187).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.04 (d, *J* = 7.9 Hz, 1H), 4.64 (m, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 3.22 (dd, *J* = 13.7, 5.8 Hz, 1H), 3.11 (dd, *J* = 13.3, 5.9 Hz, 1H), 1.42 (s, 9H).

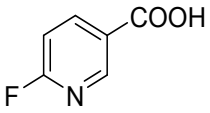
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 171.2, 155.1, 142.4, 130.4, 129.5, 128.2, 80.2, 54.2, 52.4, 38.5, 28.3.



6-chloronicotinic acid (28): Following the general procedure, using 15 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 60% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Tetrahedron Lett*. **2015**, *56*, 5153).

^{1}H NMR (400 MHz, DMSO) δ 13.68 (s, 1H), 8.90 (s, 1H), 8.30 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.67 (dd, *J* = 8.3, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 170.6, 159.3, 156.1, 145.6, 131.4, 129.7.



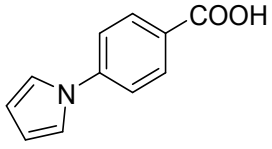
6-fluoronicotinic acid (29): Following the general procedure, using 15 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 63% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *J. Med. Chem.* **1990**, *33*, 1667).

^{1}H NMR (400 MHz, DMSO) δ 13.63 (s, 1H), 8.77 (s, 1H), 8.45 (td, *J* = 8.4, 2.3 Hz, 1H), 7.32 (dd, *J* = 8.3, 2.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 165.75, 165.43 (d, $J_{C\text{-}F}$ = 249.4 Hz), 150.01 (d, $J_{C\text{-}F}$ = 15.9 Hz), 143.70 (d, $J_{C\text{-}F}$ = 7.0 Hz), 126.28, 110.20 (d, $J_{C\text{-}F}$ = 38.0 Hz).

^{19}F NMR (377 MHz, DMSO) δ -63.41.

HRMS (ESI) calcd. for $C_6H_4FNO_2^+$ $[M+H]^+$: 142.0304, found: 142.0299.

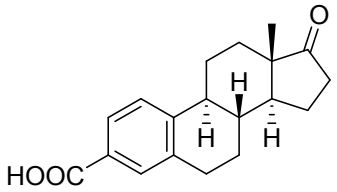


4-(1H-pyrrol-1-yl)benzoic acid (30): Following the general procedure, using 10 mol% $Ni(cod)_2$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 53% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Tetrahedron Lett*. **2011**, *52*, 1924).

^{1}H NMR (400 MHz, DMSO) δ 12.97 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8

Hz, 2H), 7.51 (t, 2H), 6.32 (t, 2H).

^{13}C NMR (101 MHz, DMSO) δ 167.2, 143.5, 131.5, 127.6, 119.5, 119.0, 111.8.



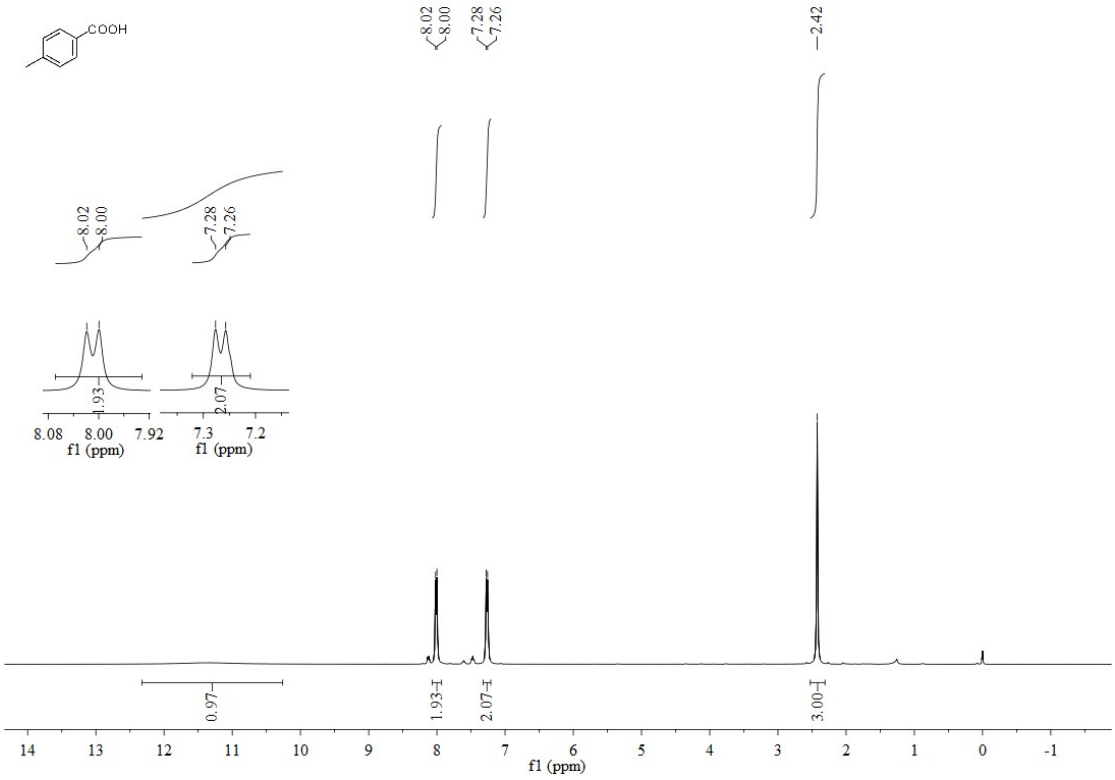
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthrene-3-carboxylic acid (32): Following the general procedure, using 15 mol% $Ni(OAc)_2$•$4H_2O$, 20 mol% dppp, 1.5 equiv. HCO_2Li•H_2O, 50 mol% formic acid , 20 mol% Ac_2O, 2.0 mL THF, obtained in 76% yield as white solid (Eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2017**, *56*, 13426).

1H NMR (400 MHz, DMSO) δ 12.70 (br, 1H), 8.15 – 7.45 (m, 2H), 7.41 (d, J = 8.2 Hz, 1H), 3.05 – 2.76 (m, 2H), 2.39 (dd, J = 28.5, 21.9 Hz, 3H), 2.12 – 1.93 (ddd, 3H), 1.83 – 1.74 (d, 1H), 1.58 –1.38 (m, J = 16.2, 14.3, 3.8 Hz, 6H), 0.84 (s, 3H).

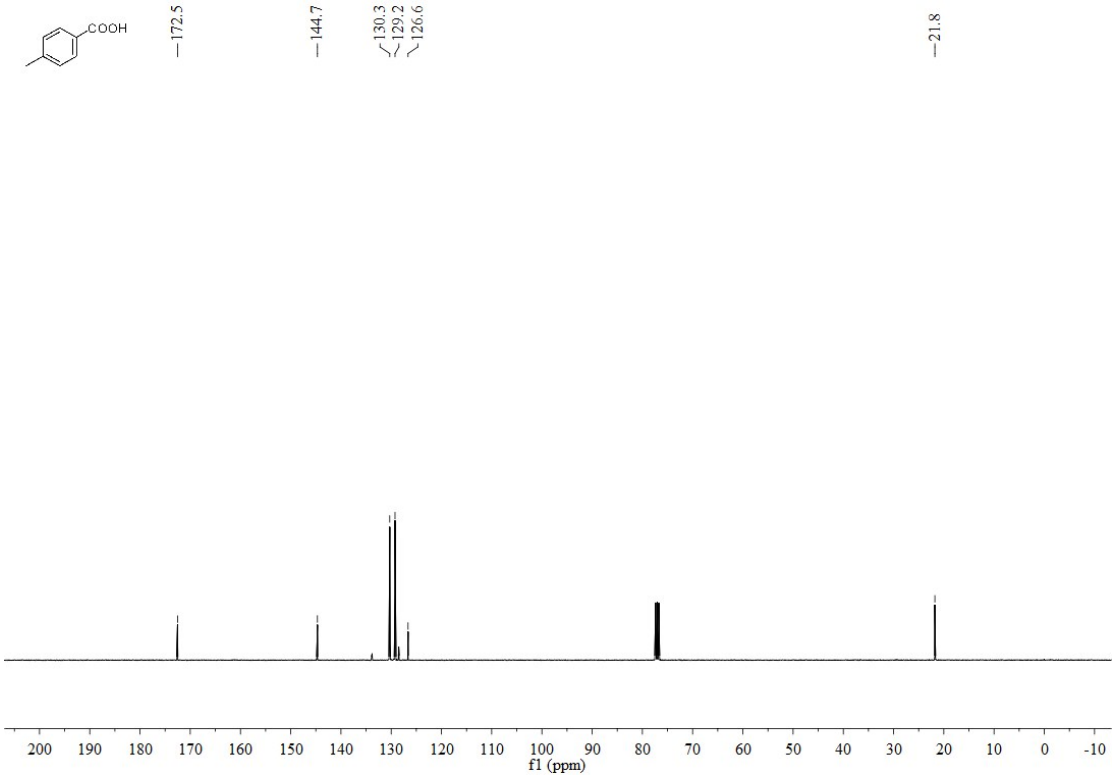
13C NMR (101 MHz, DMSO) δ 220.1, 167.8, 145.3, 137.2, 130.2, 128.5, 127.0, 126.0, 50.1, 47.7, 44.5, 37.7, 35.8, 31.8, 29.2, 26.2, 25.6, 21.6, 13.9.

4. NMR spectra

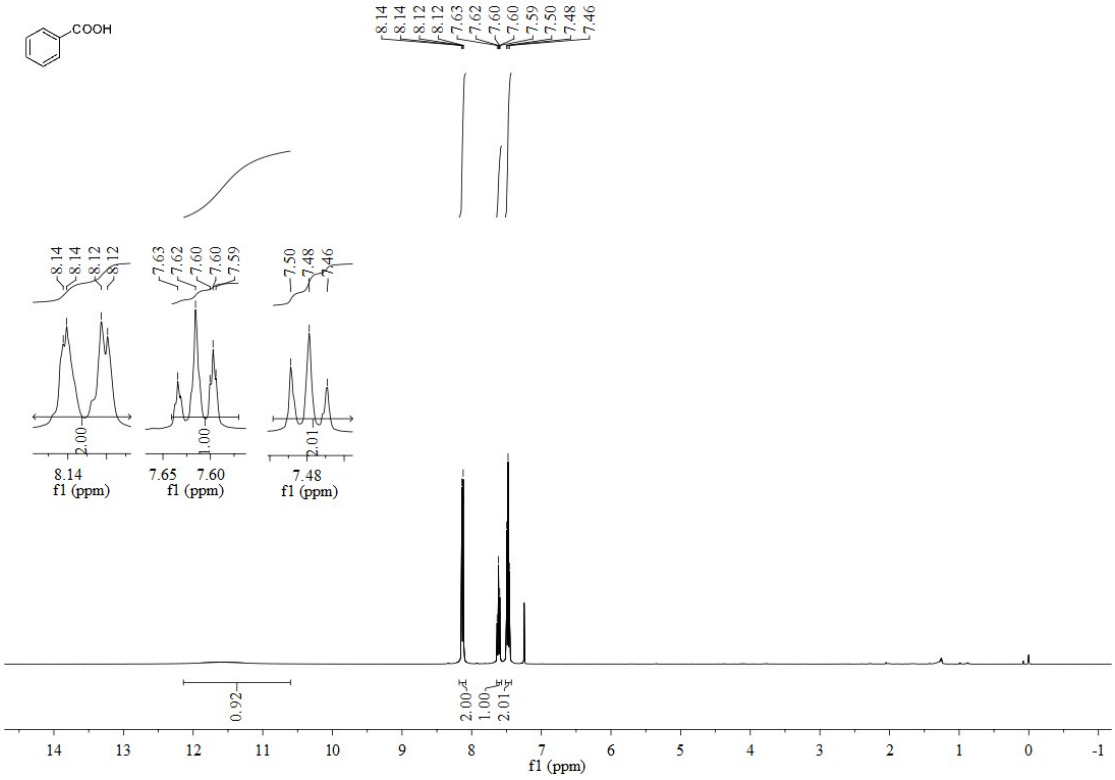
^{1}H NMR spectrum of **4-methylbenzoic acid (2):**



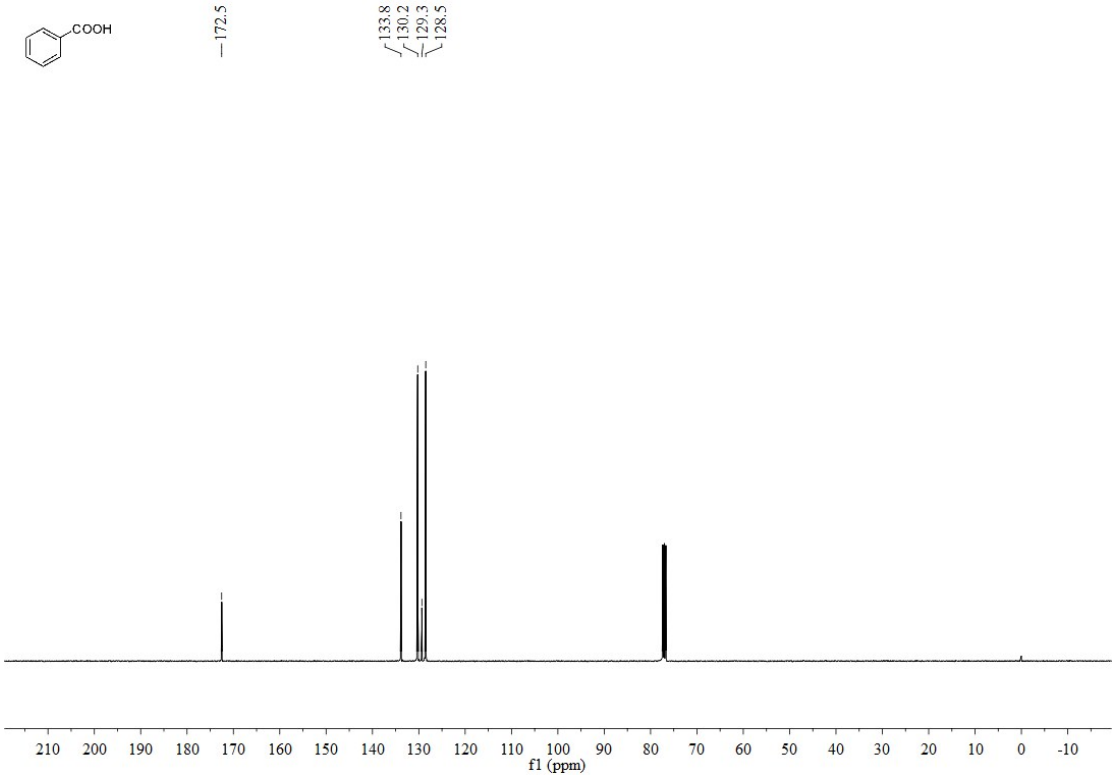
^{13}C NMR spectrum of **4-methylbenzoic acid (2):**



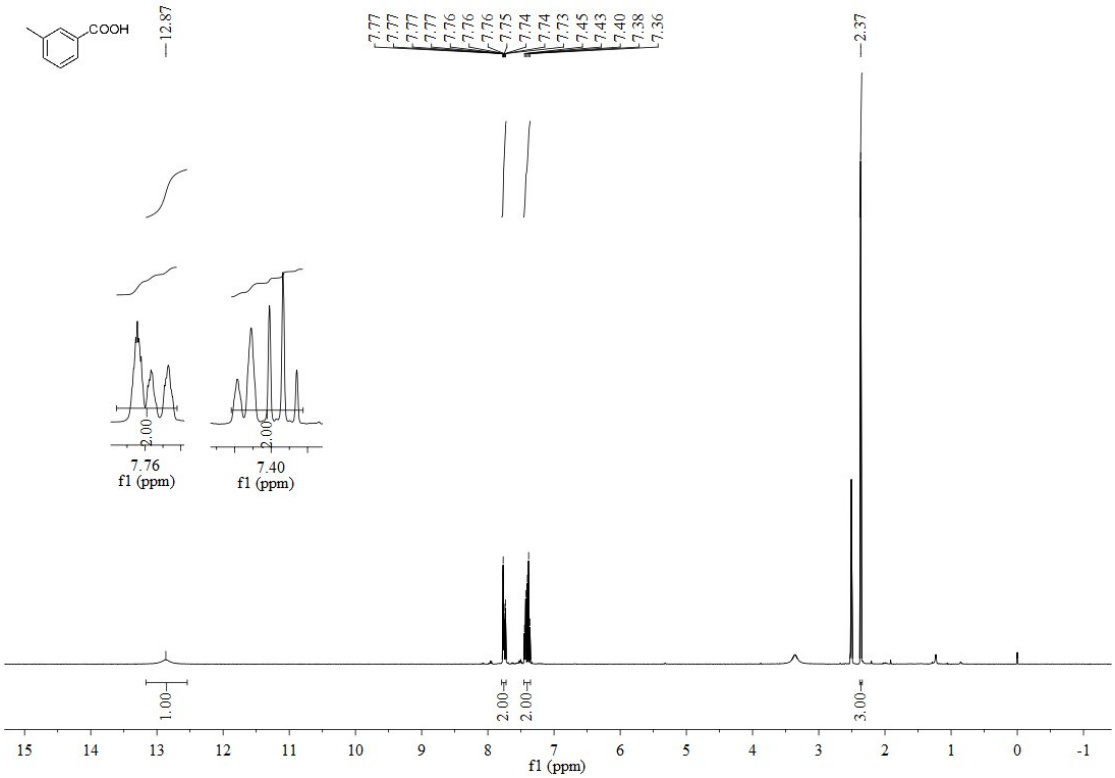
^{1}H NMR spectrum of **benzoic acid (3):**



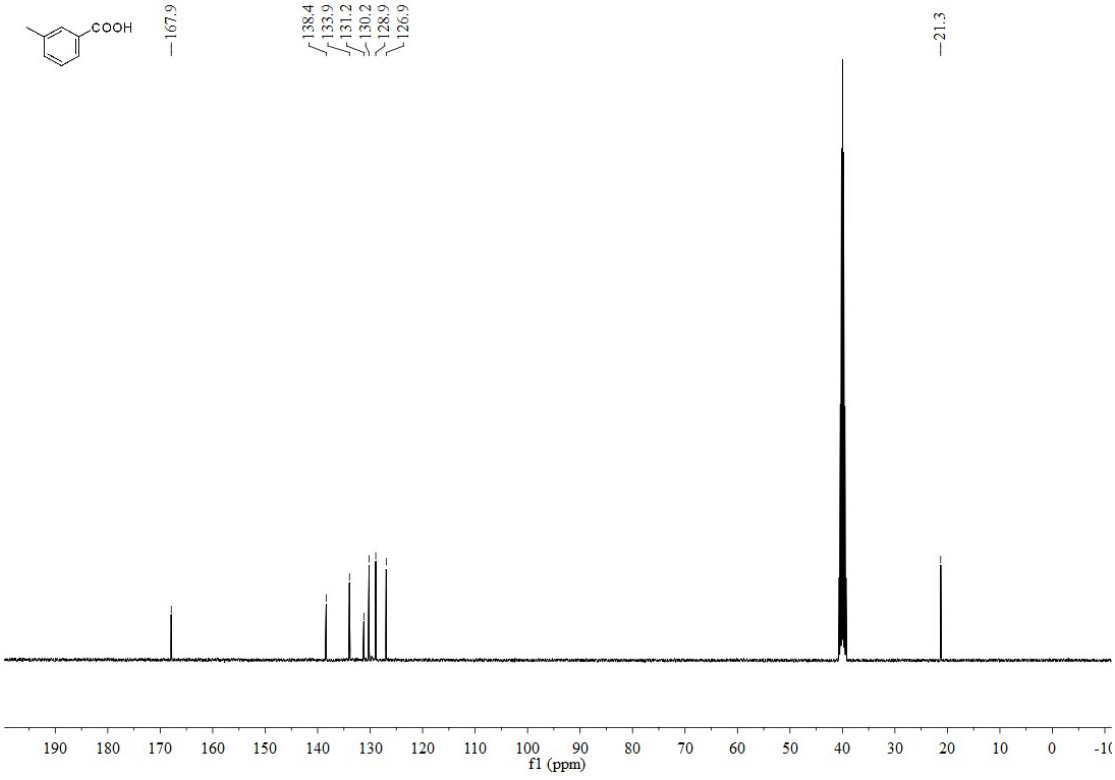
^{13}C NMR spectrum of **benzoic acid (3):**



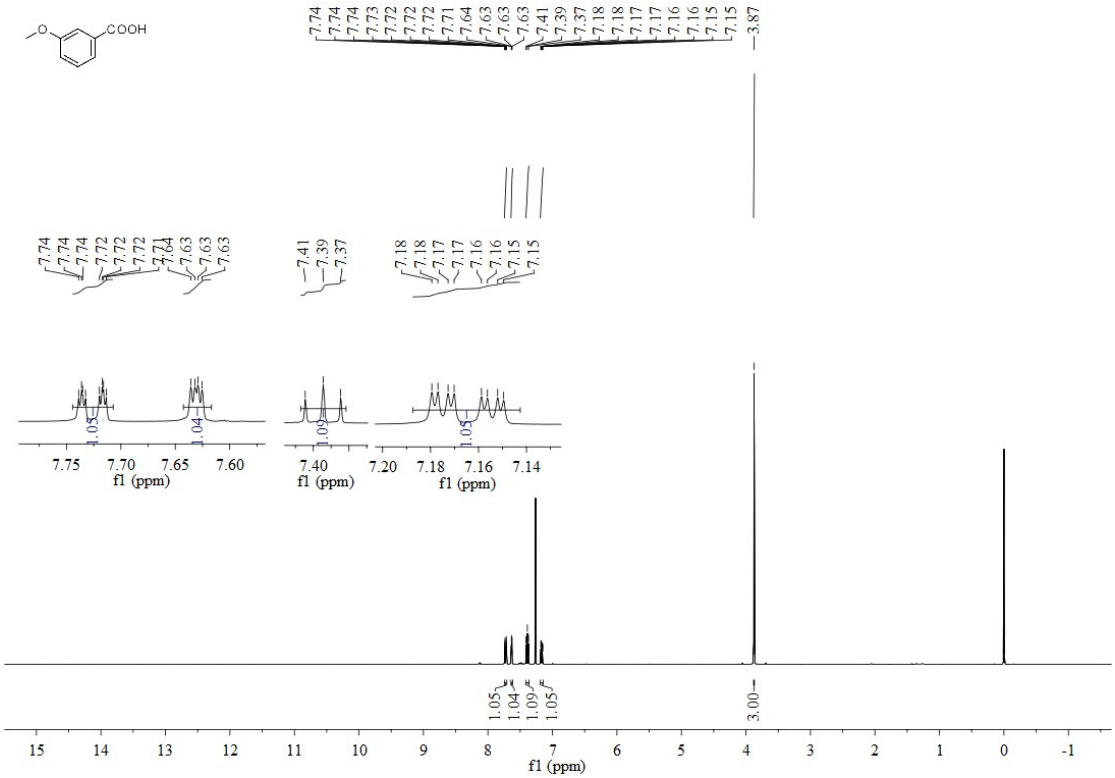
^{1}H NMR spectrum of **3-methylbenzoic acid (4):**



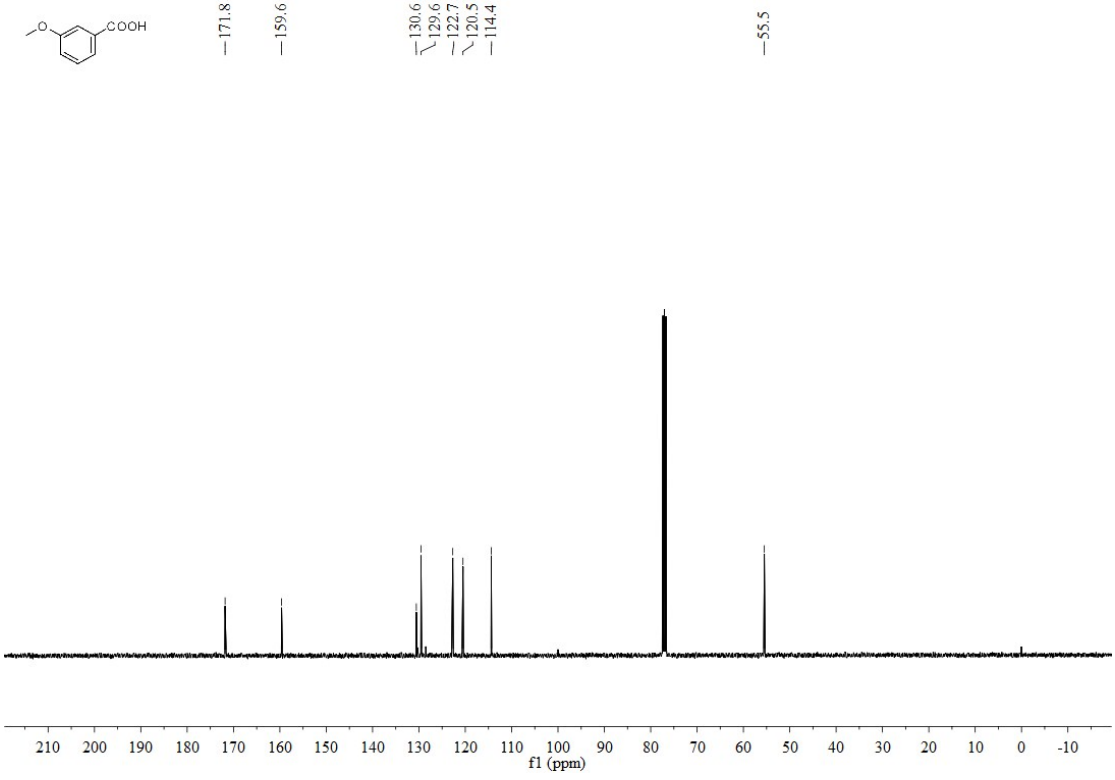
^{13}C NMR spectrum of **3-methylbenzoic acid (4):**



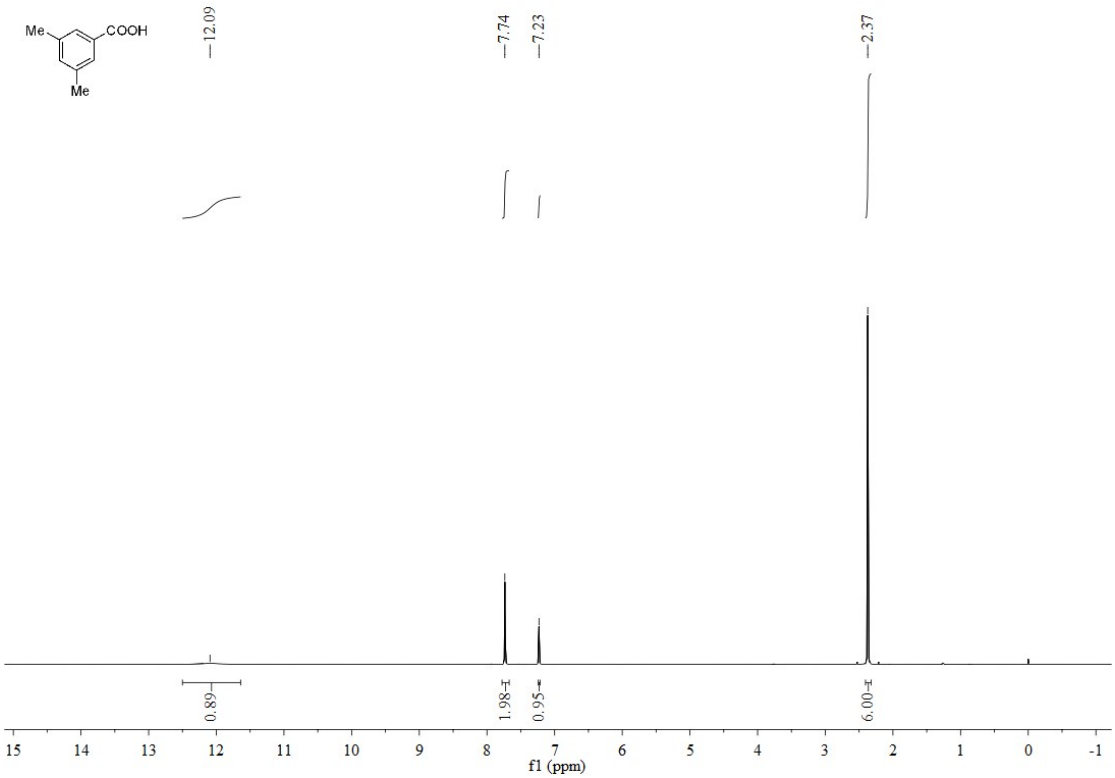
^{1}H NMR spectrum of **3-methoxybenzoic acid (5):**



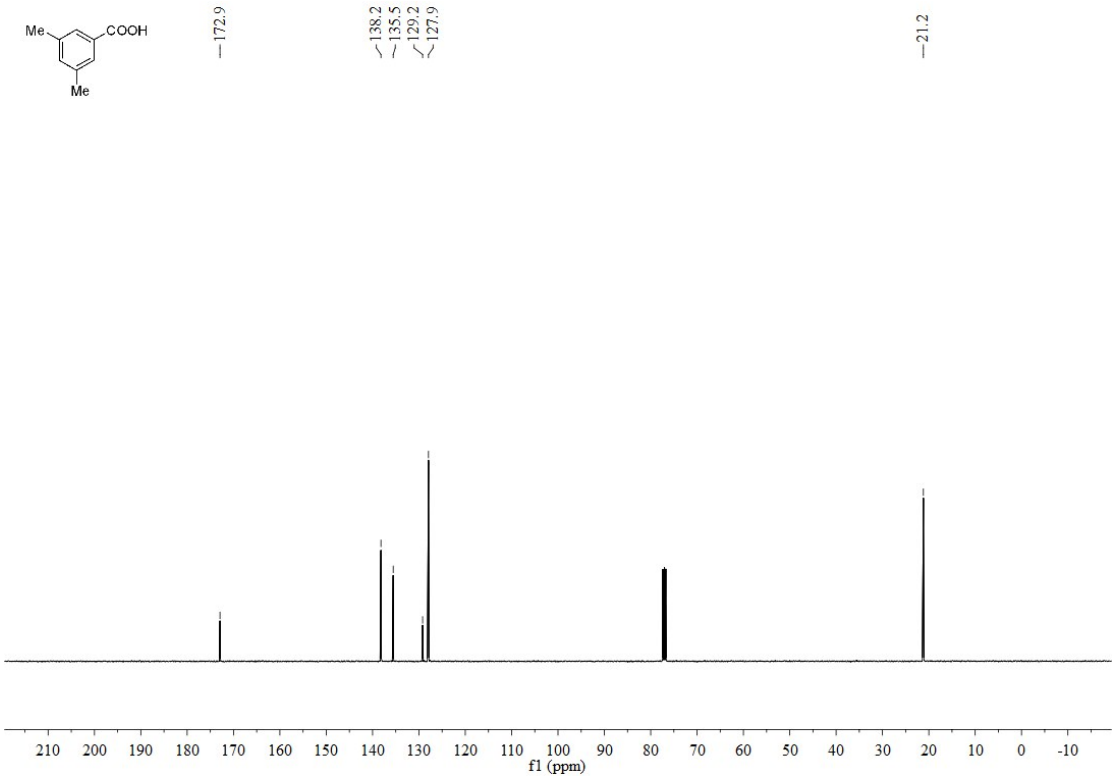
^{13}C NMR spectrum of **3-methoxybenzoic acid (5):**



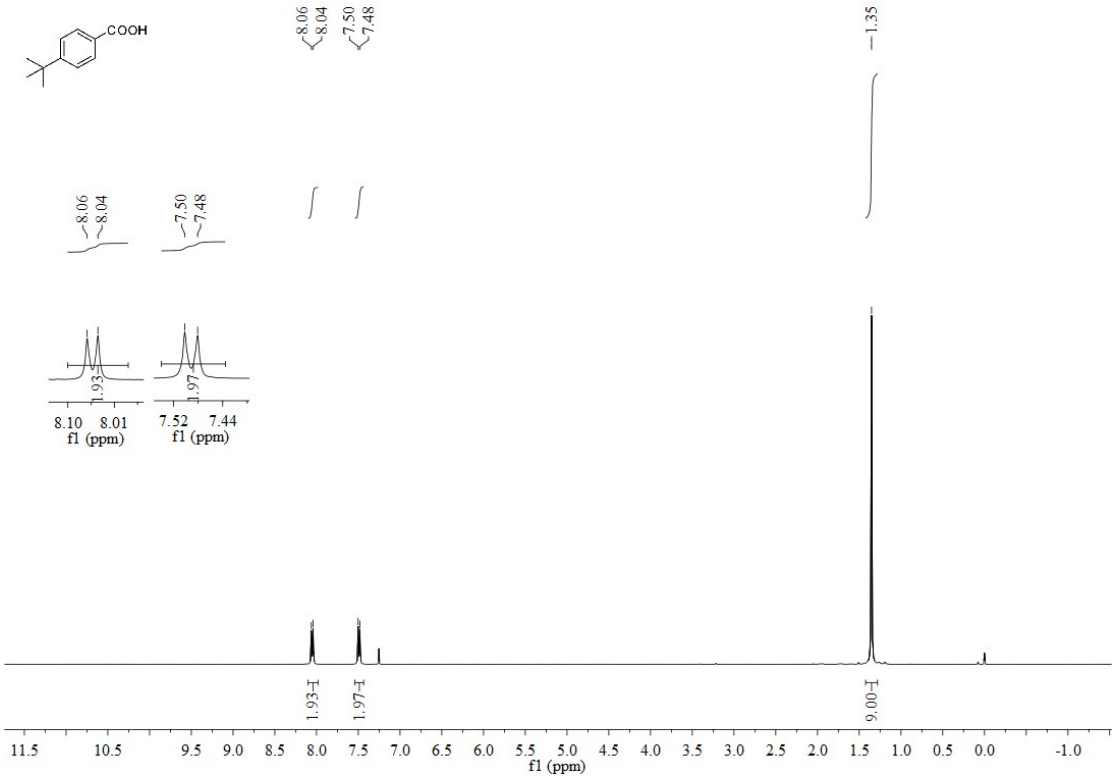
^{1}H NMR spectrum of **3,5-dimethylbenzoic acid (6):**



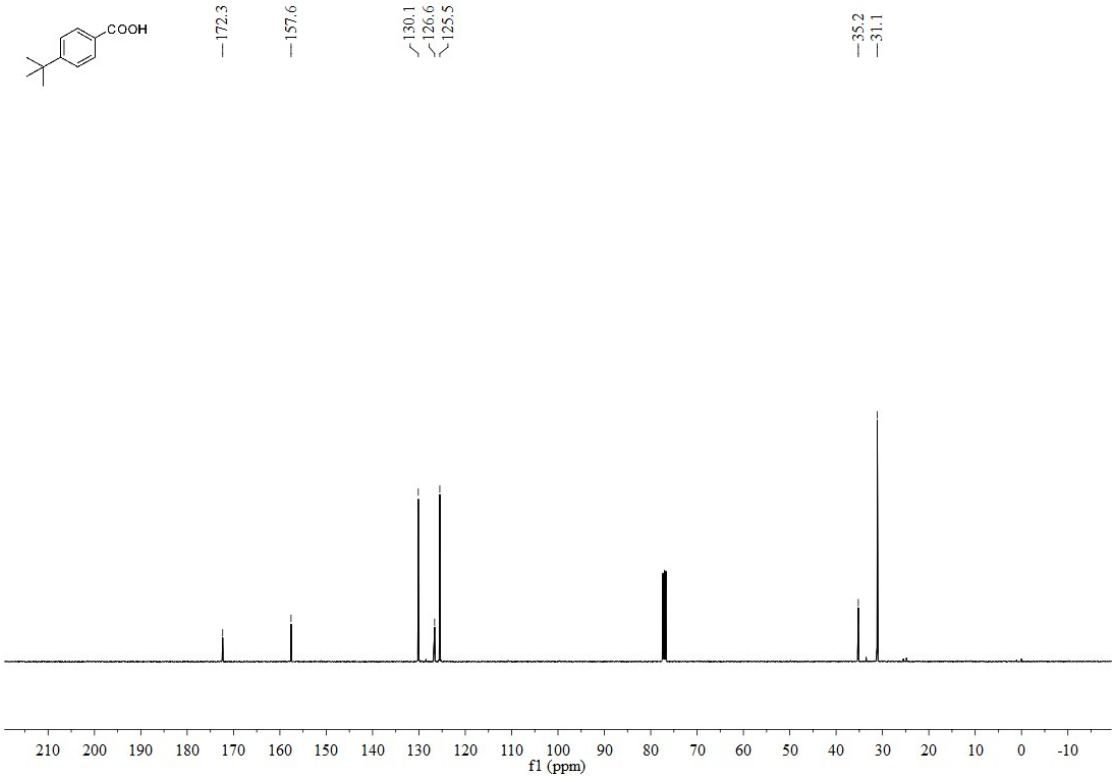
^{13}C NMR spectrum of **3,5-dimethylbenzoic acid (6):**



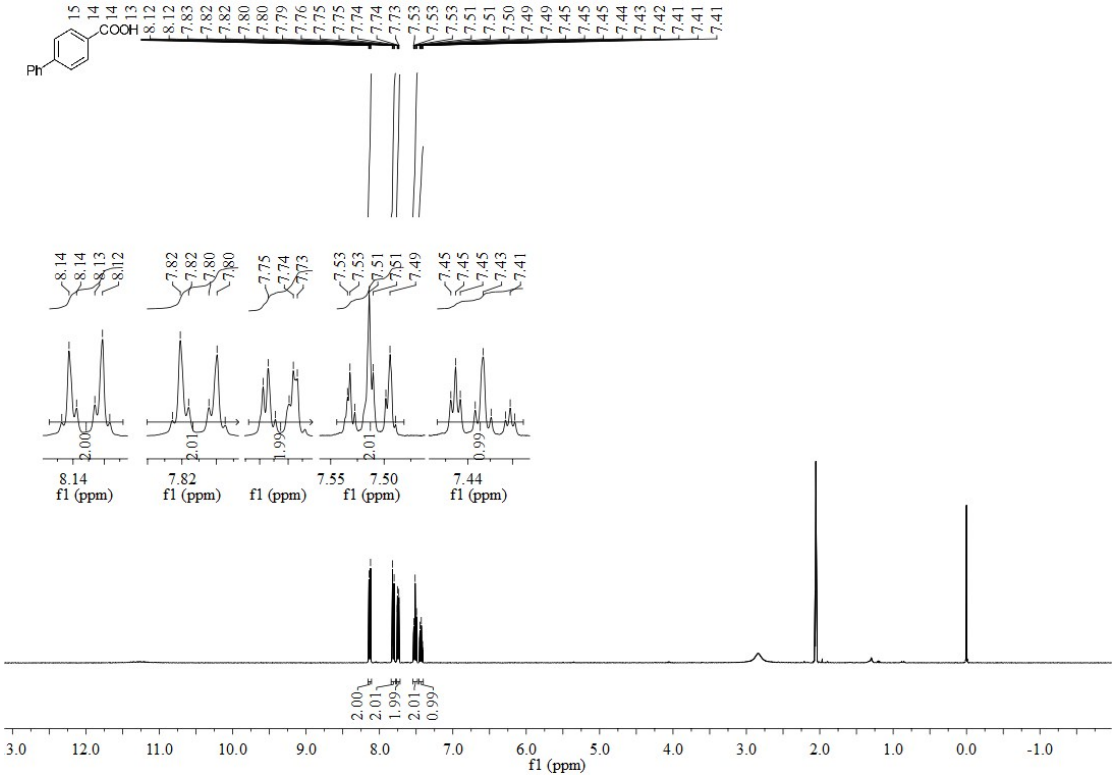
^{1}H NMR spectrum of **4-(tert-butyl)benzoic acid (7):**



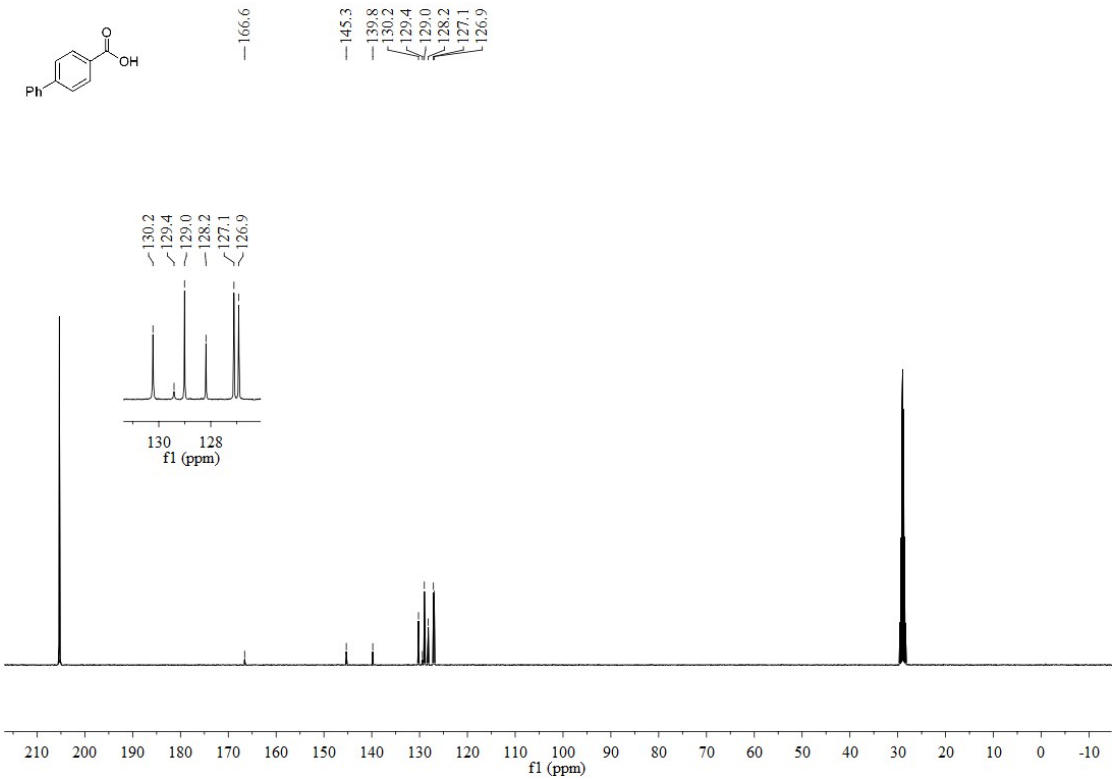
^{13}C NMR spectrum of **4-(tert-butyl)benzoic acid (7):**



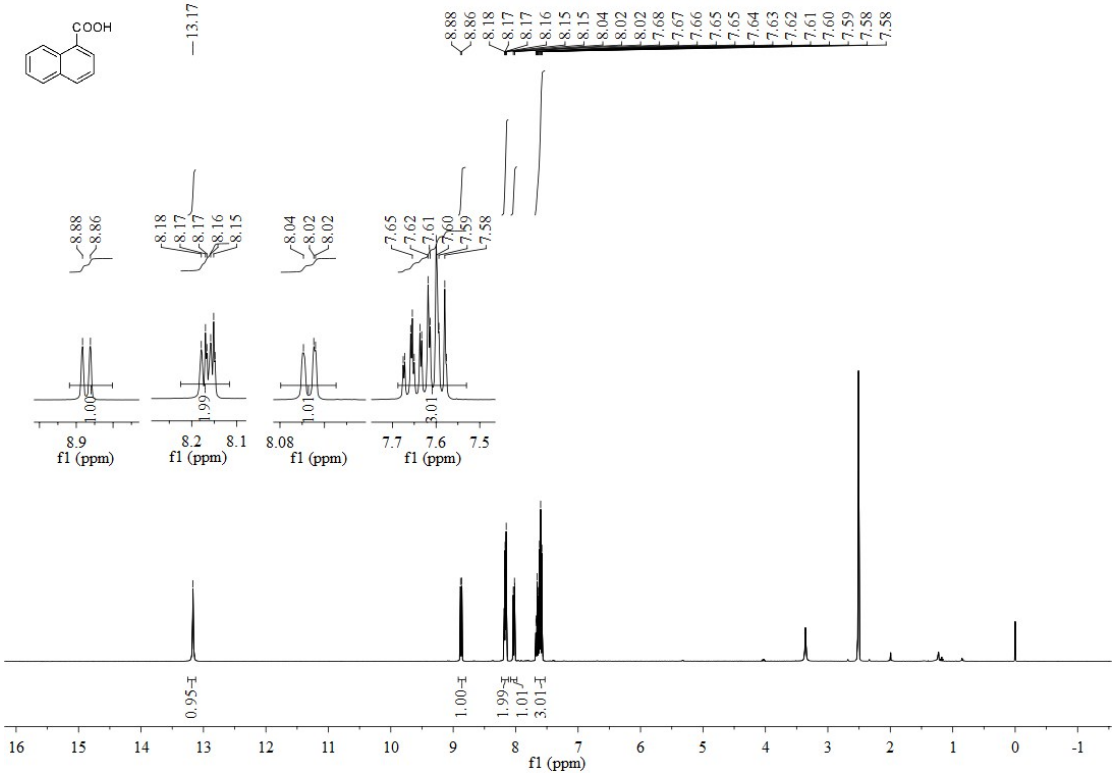
^{1}H NMR spectrum of **[1,1'-biphenyl]-4-carboxylic acid (8):**



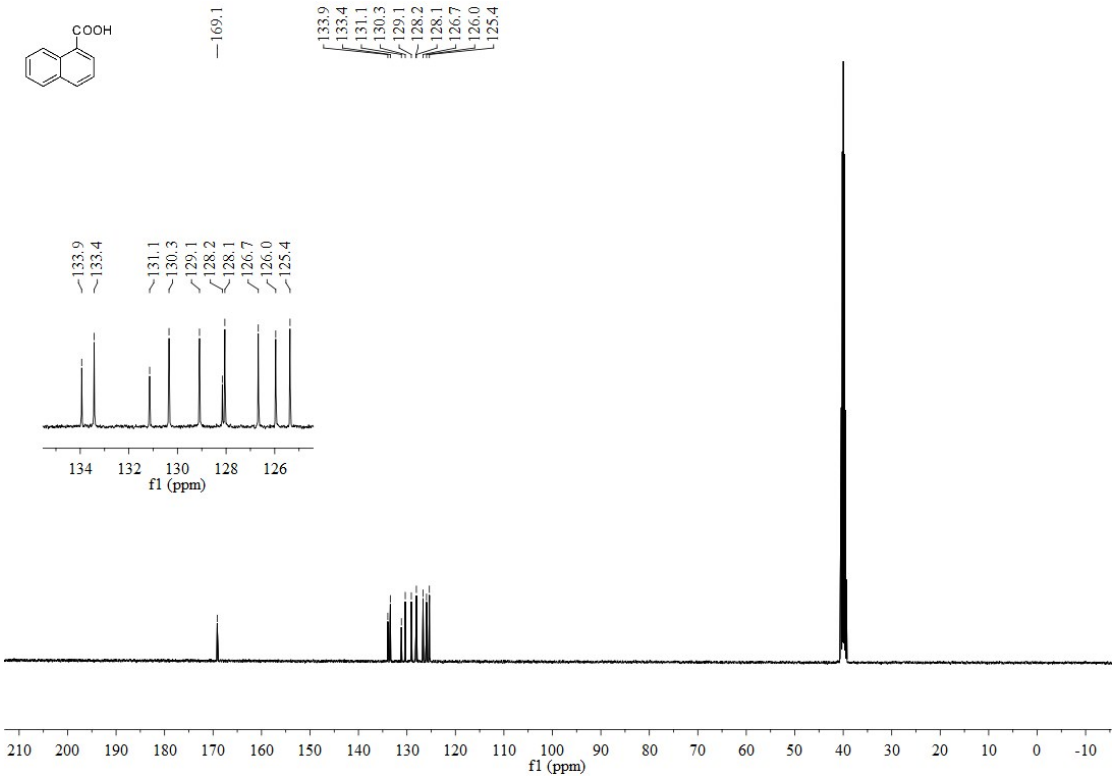
^{13}C NMR spectrum of **[1,1'-biphenyl]-4-carboxylic acid (8):**



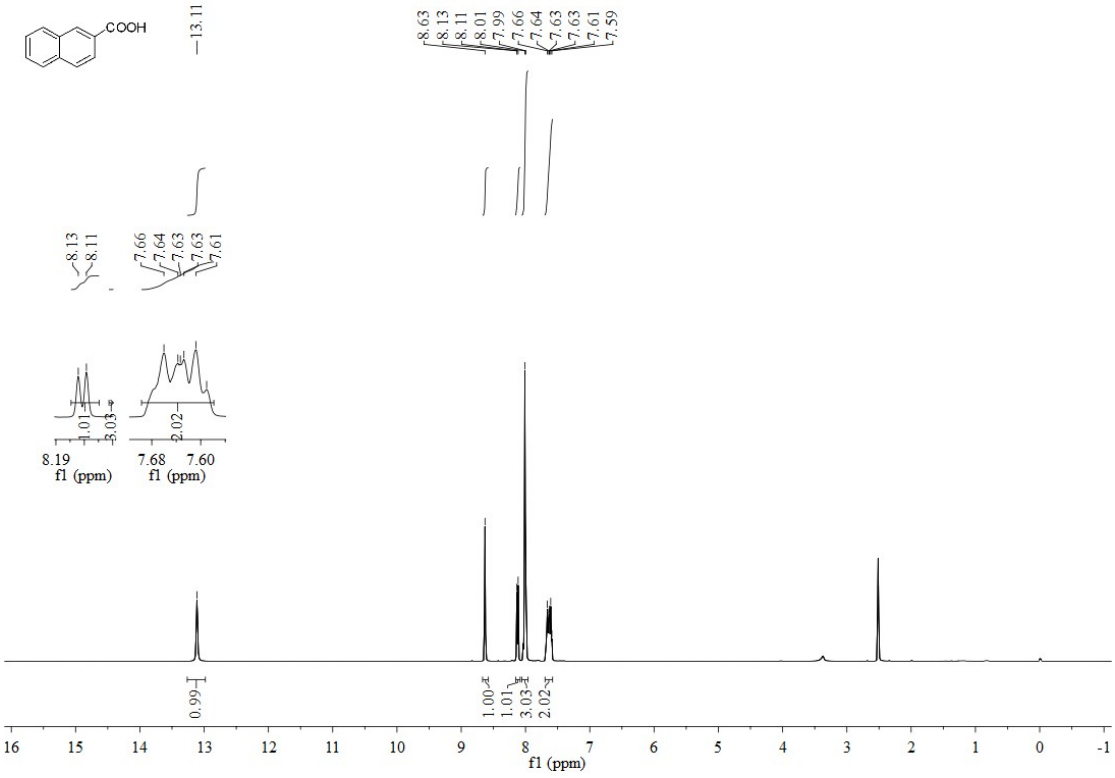
^{1}H NMR spectrum of **1-naphthoic acid (9):**



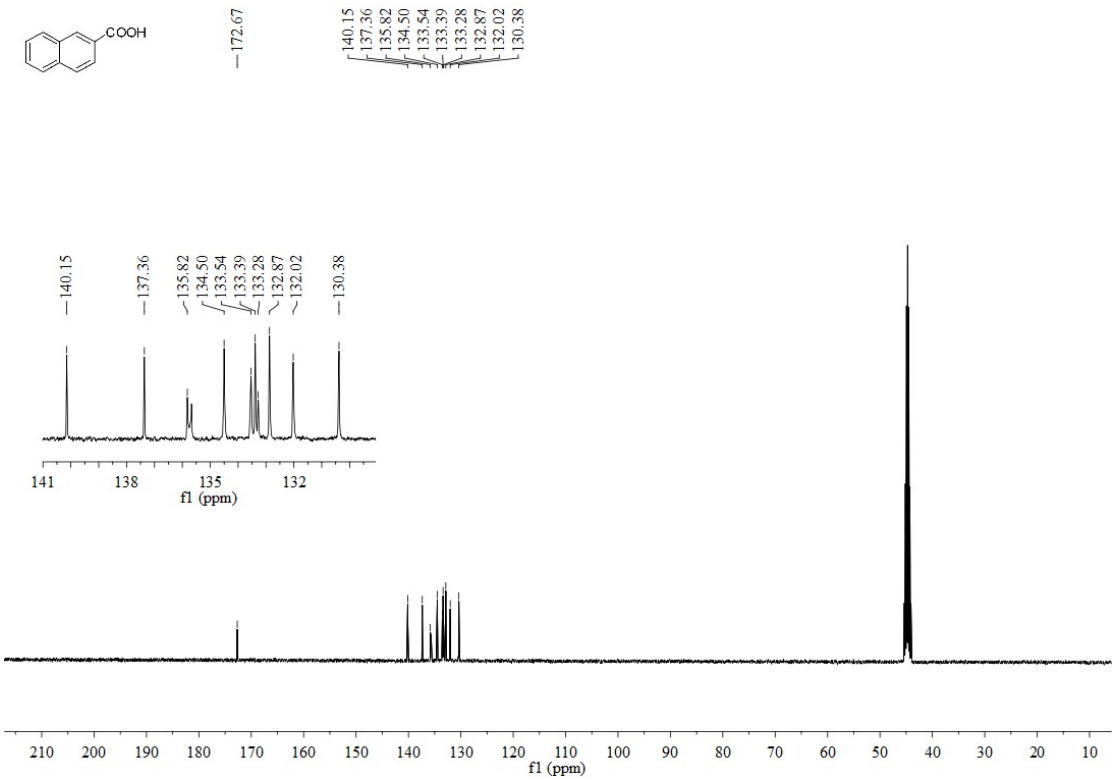
^{13}C NMR spectrum of **1-naphthoic acid (9):**



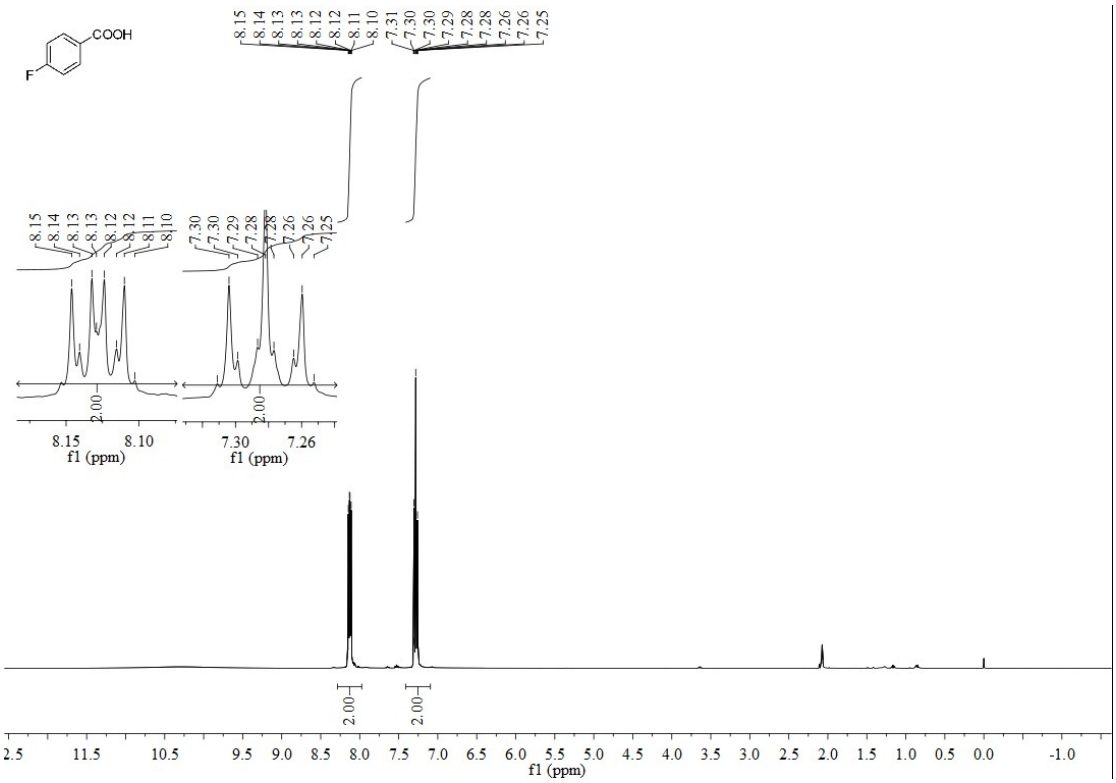
^{1}H NMR spectrum of **2-naphthoic acid (10):**



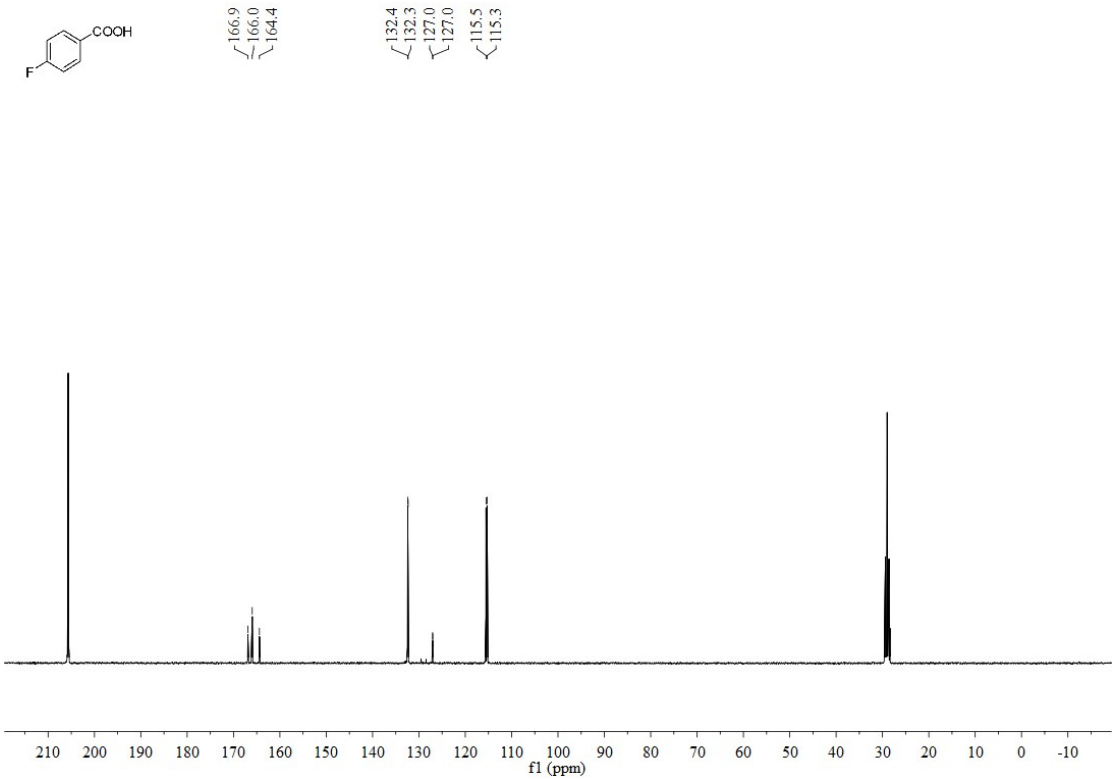
^{13}C NMR spectrum of **2-naphthoic acid (10):**



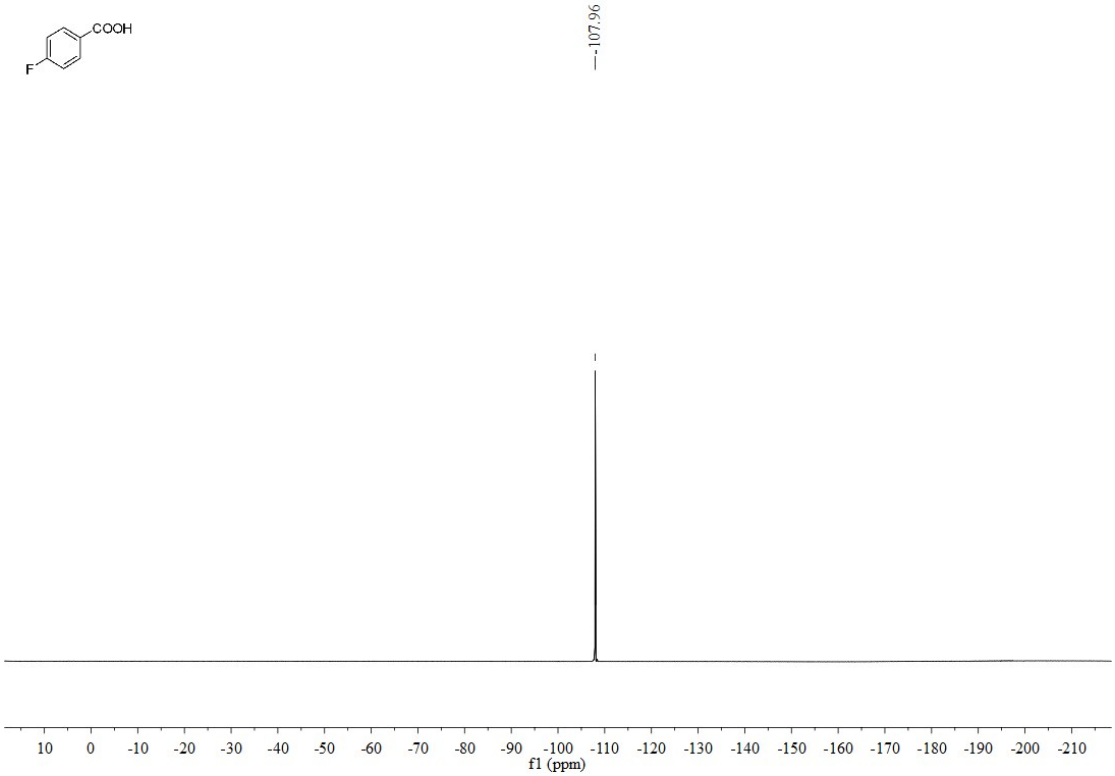
^{1}H NMR spectrum of **4-fluorobenzoic acid (11):**



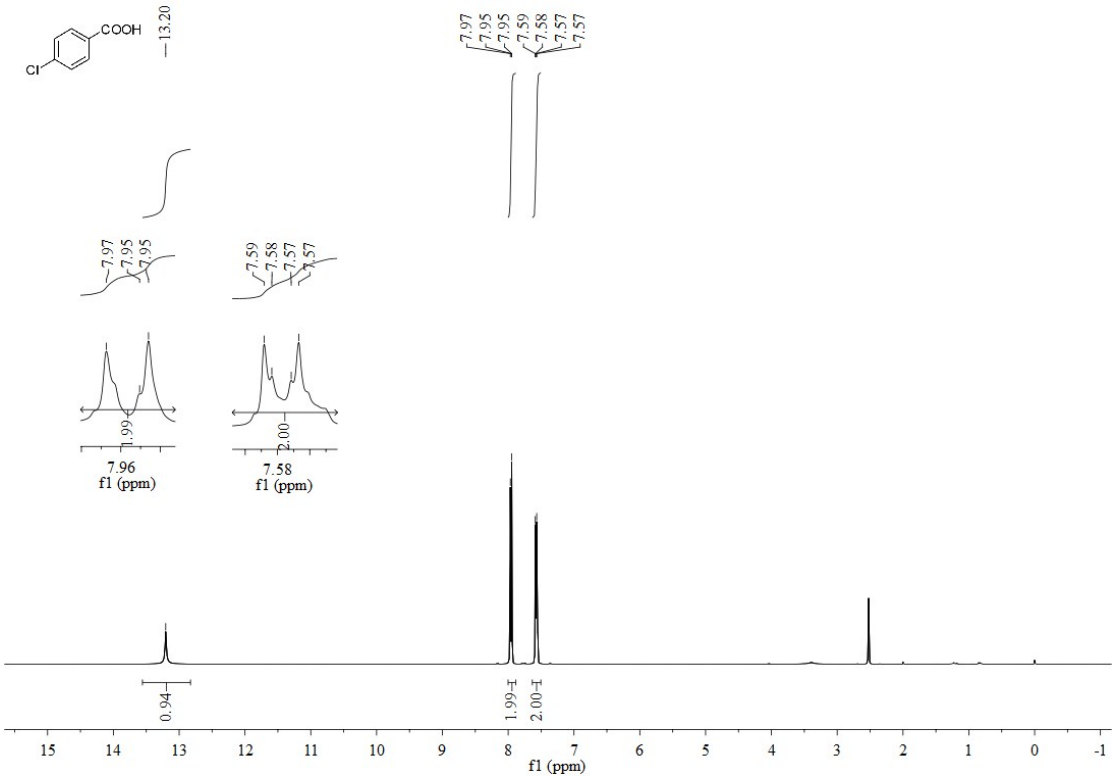
^{13}C NMR spectrum of **4-fluorobenzoic acid (11):**



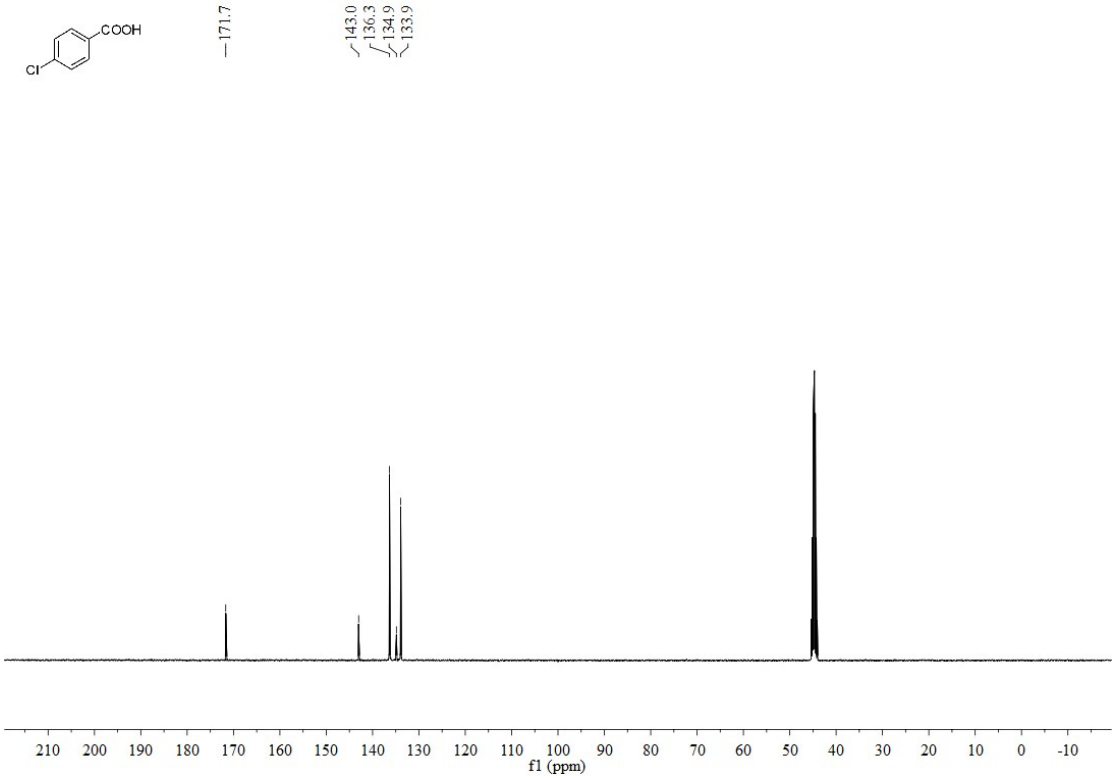
^{19}F NMR spectrum of **4-fluorobenzoic acid (11):**



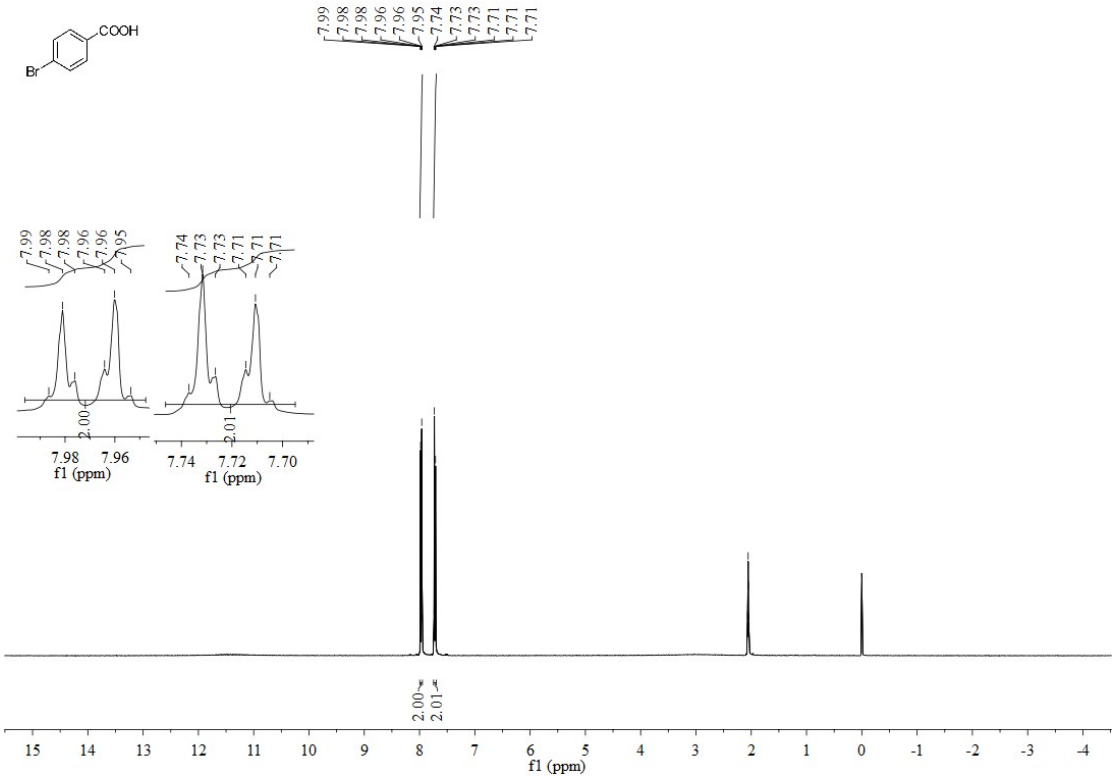
^{1}H NMR spectrum of **4-chlorobenzoic acid (12):**



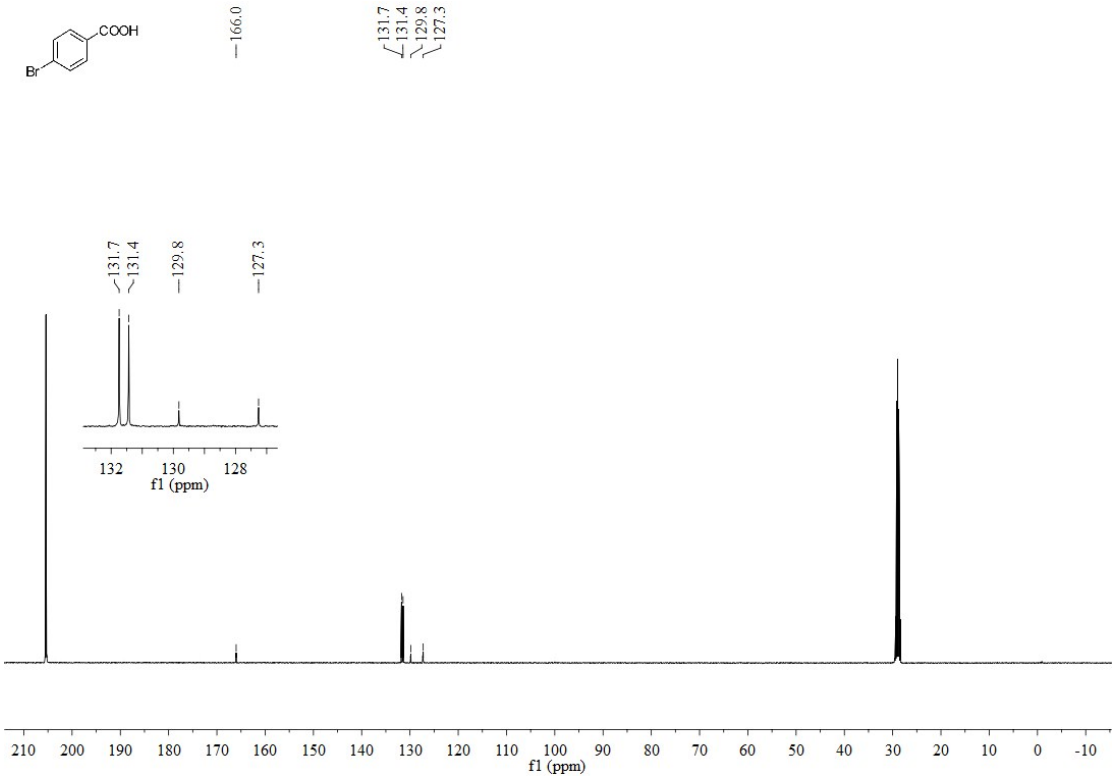
^{13}C NMR spectrum of **4-chlorobenzoic acid (12):**



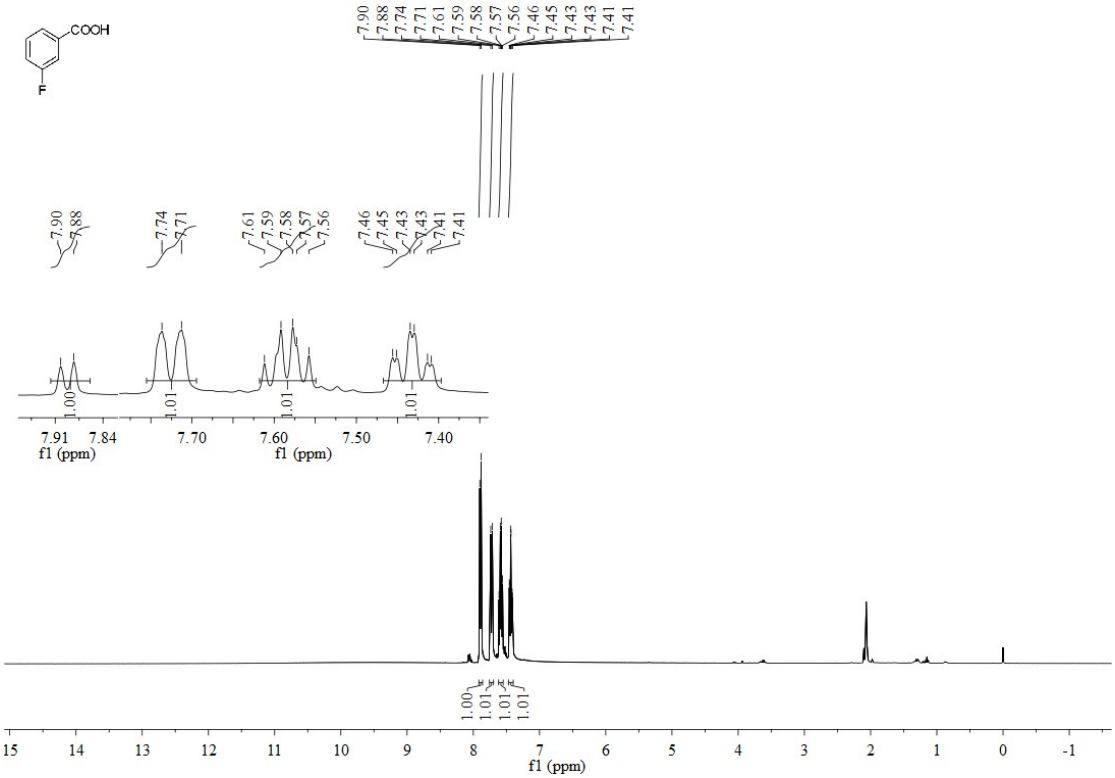
^{1}H NMR spectrum of **4-bromobenzoic acid (13):**



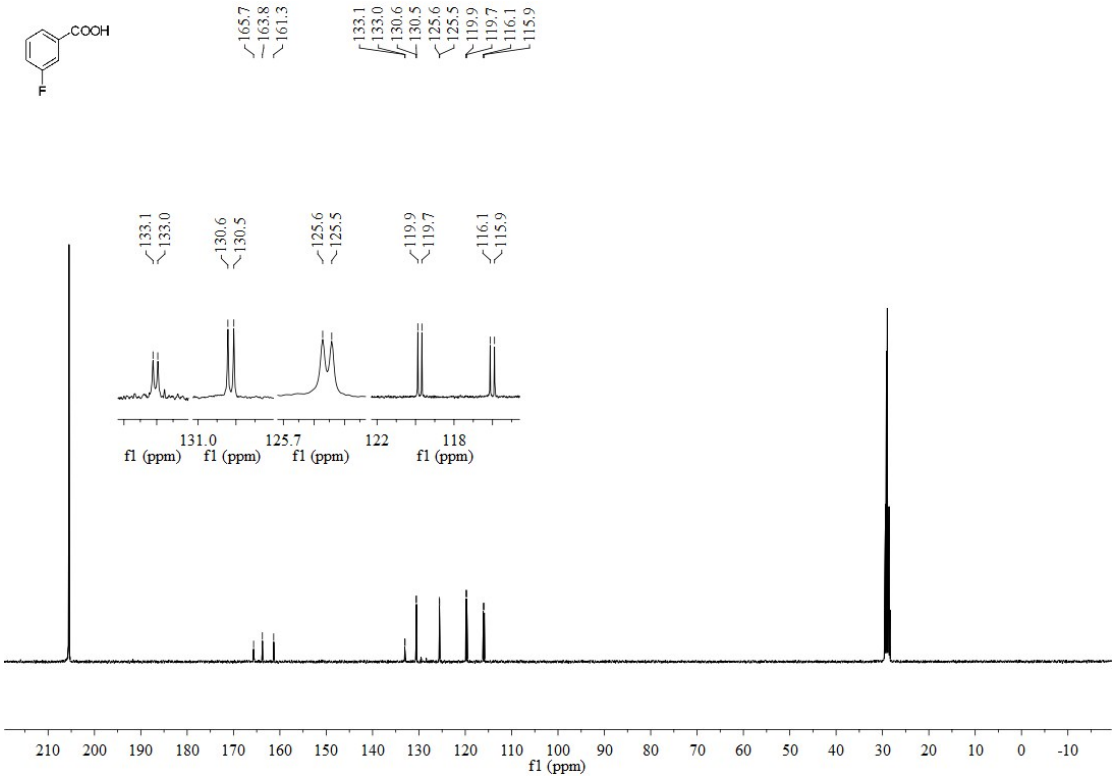
^{13}C NMR spectrum of **4-bromobenzoic acid (13):**



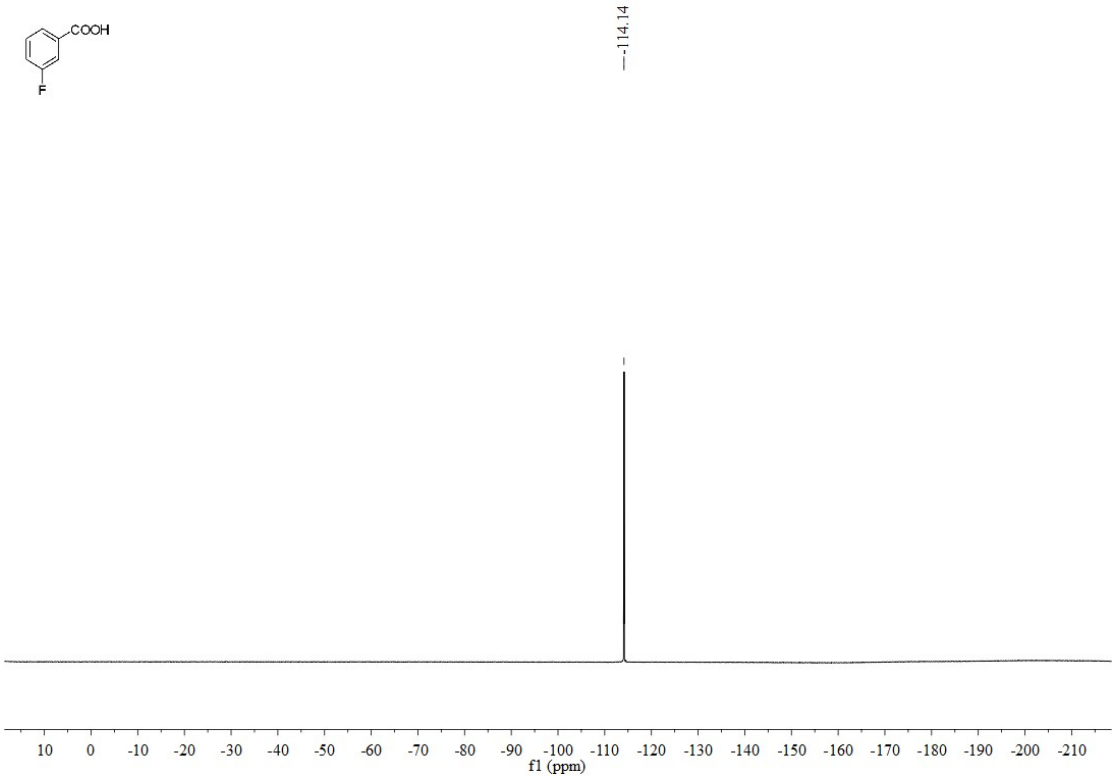
^{1}H NMR spectrum of **3-fluorobenzoic acid (14):**



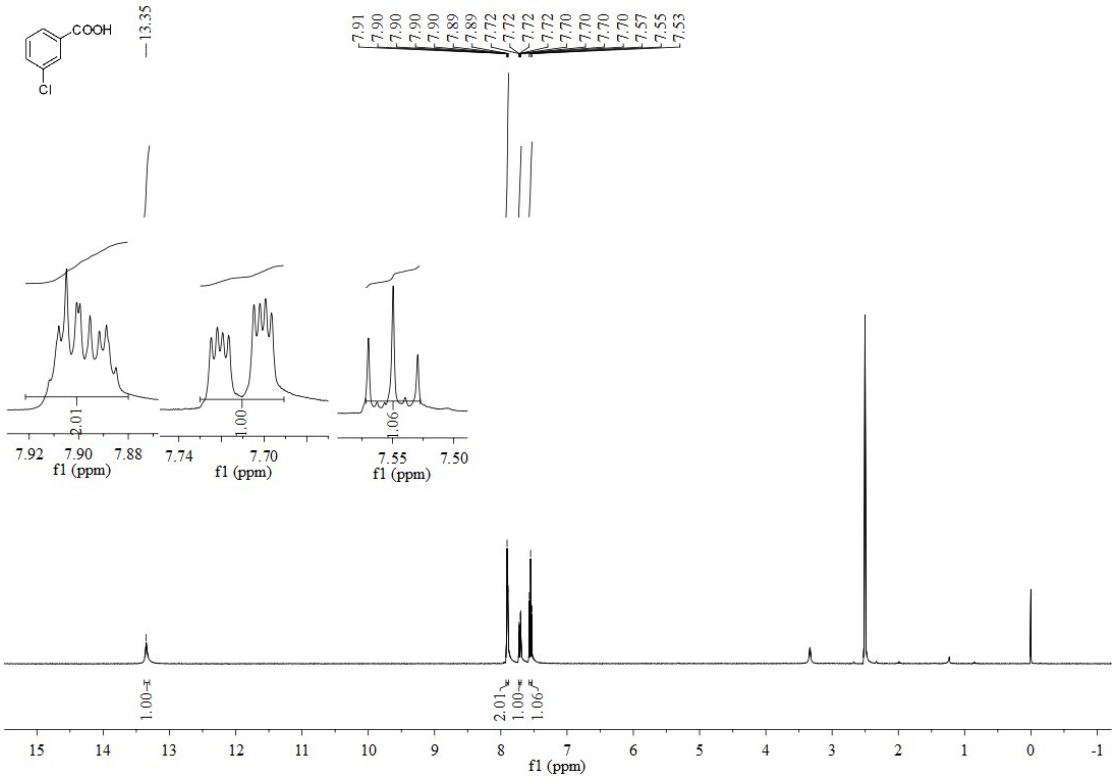
^{13}C NMR spectrum of **3-fluorobenzoic acid (14):**



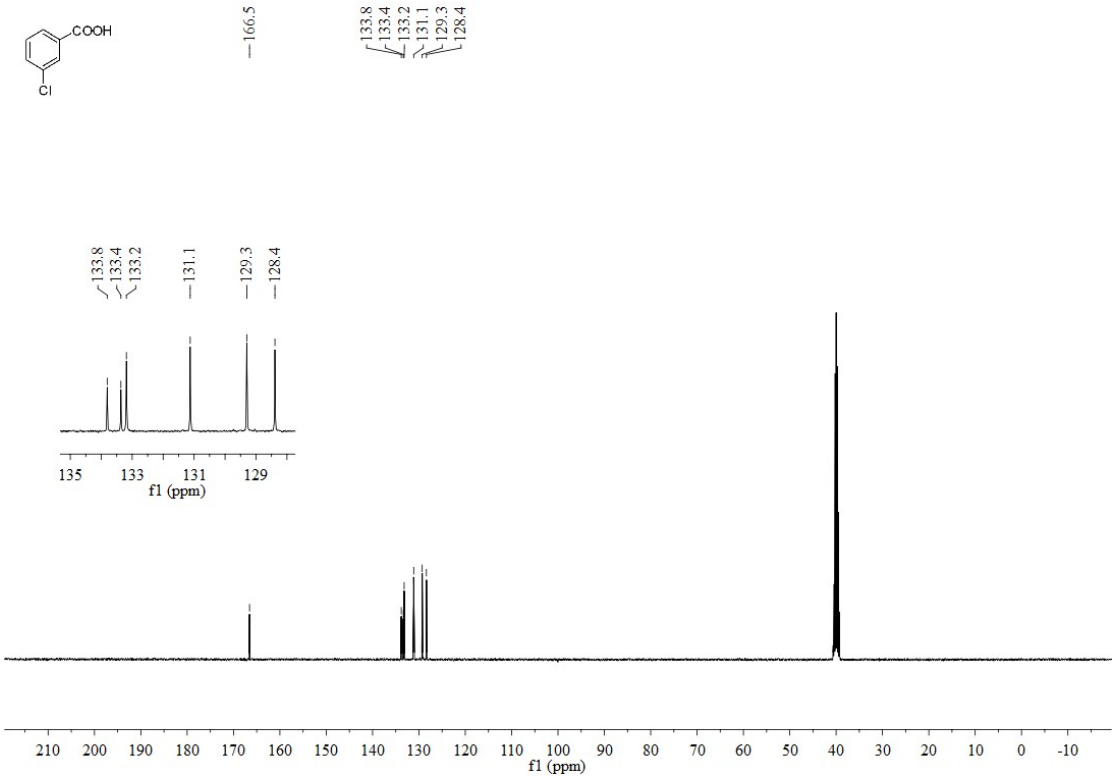
^{19}F NMR spectrum of **3-fluorobenzoic acid (14):**



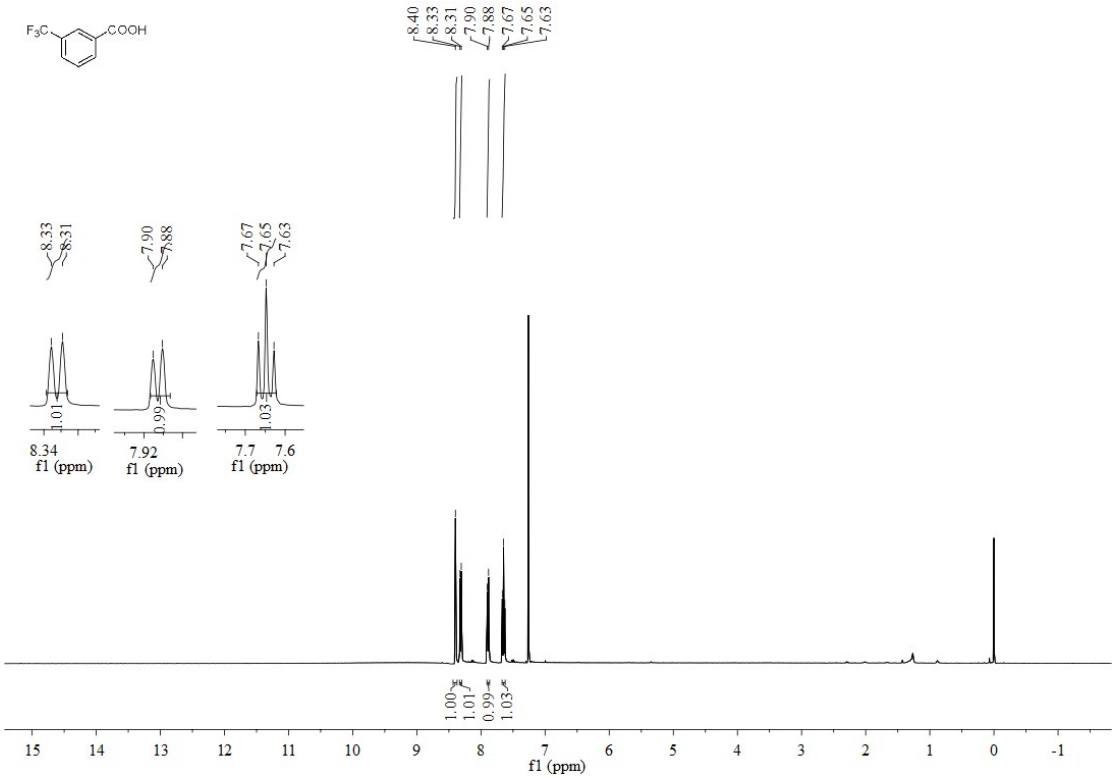
^{1}H NMR spectrum of **3-chlorobenzoic acid (15):**



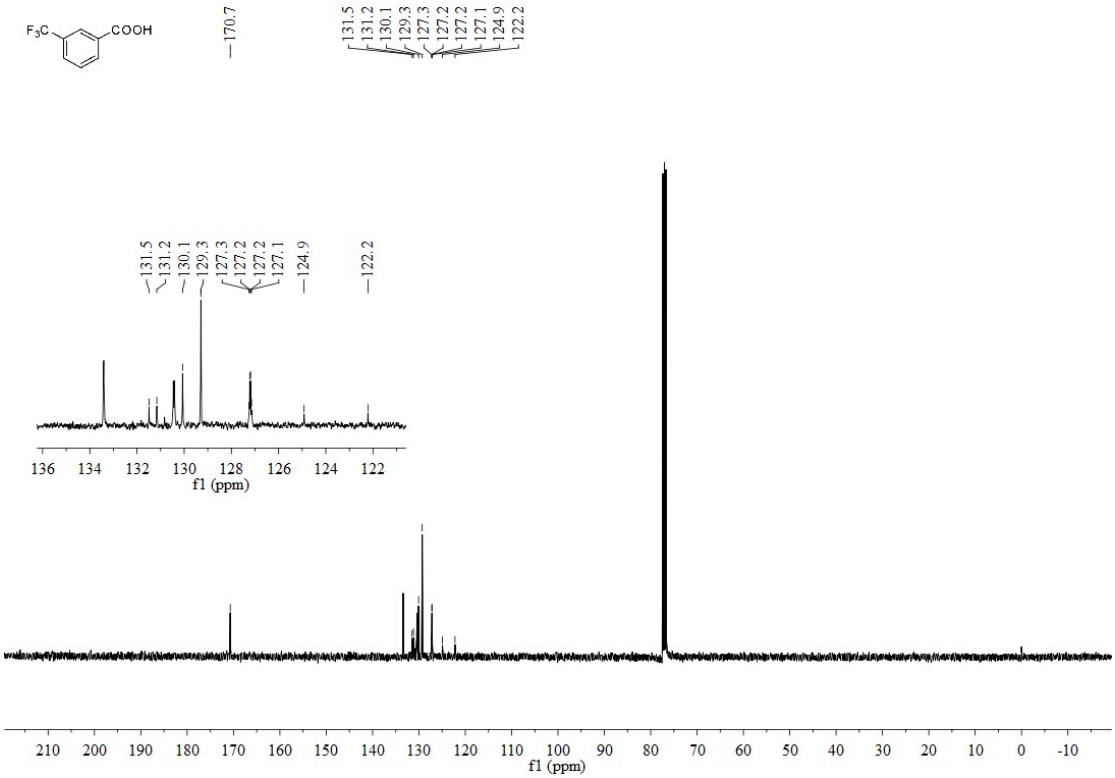
^{13}C NMR spectrum of **3-chlorobenzoic acid (15):**



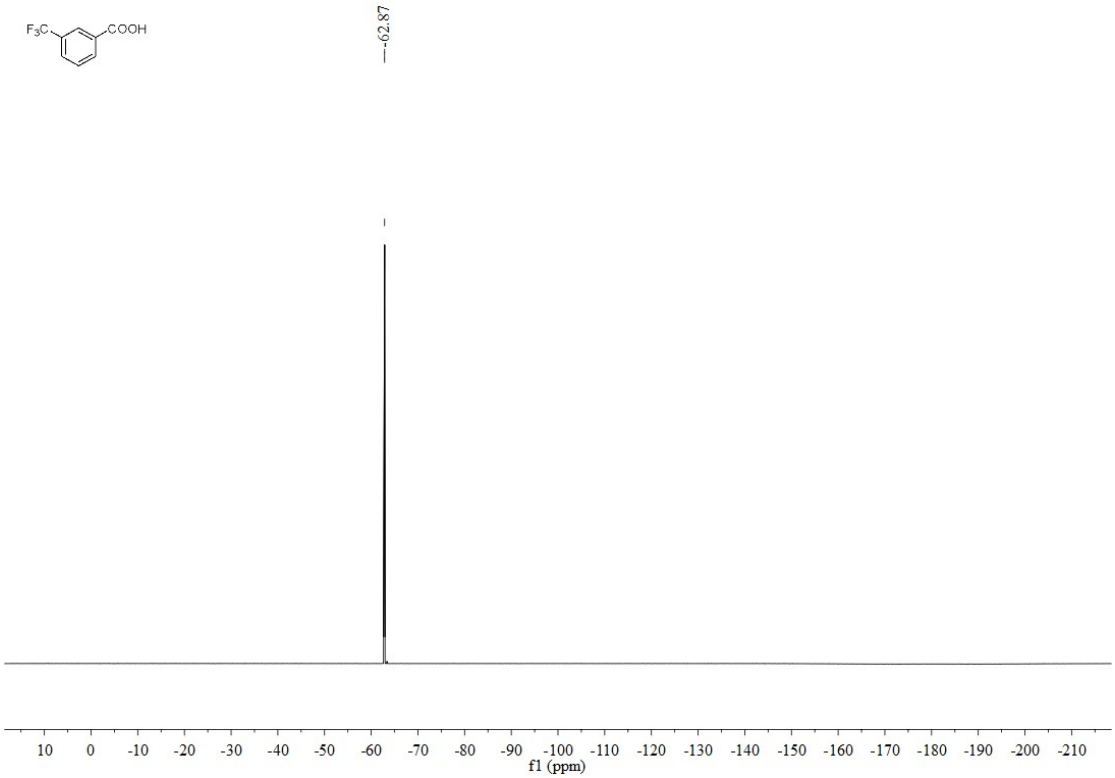
^{1}H NMR spectrum of **3-(trifluoromethyl)benzoic acid (16):**



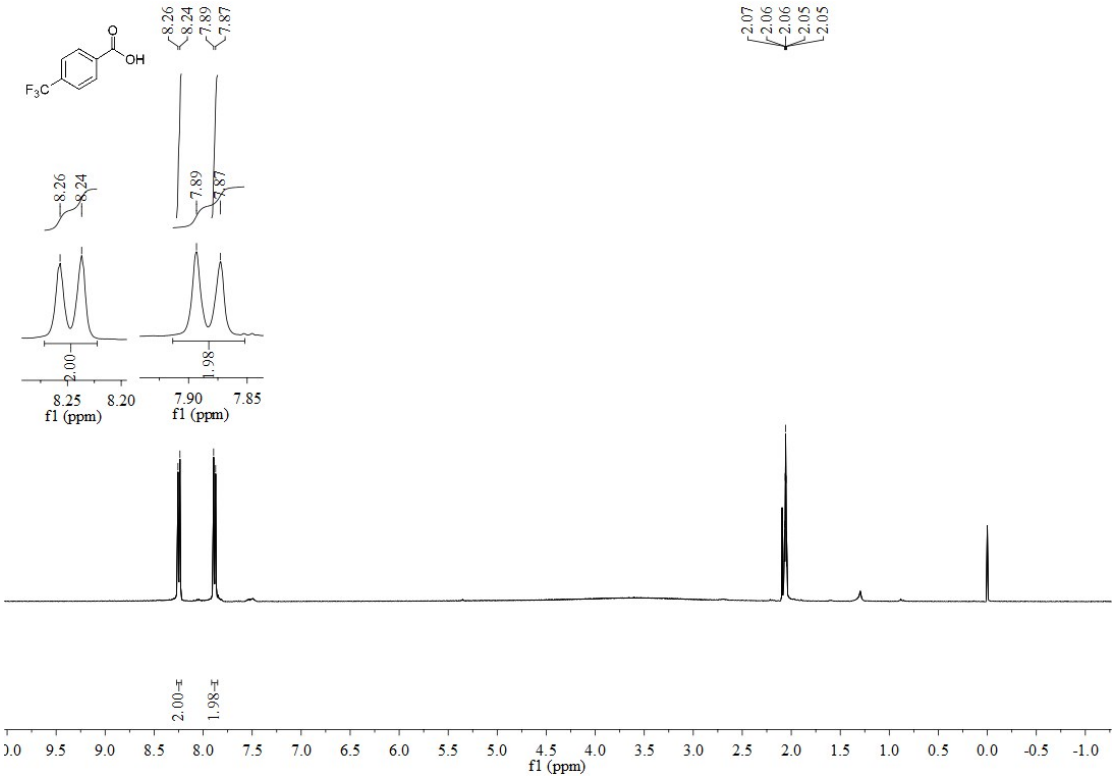
^{13}C NMR spectrum of **3-(trifluoromethyl)benzoic acid (16):**



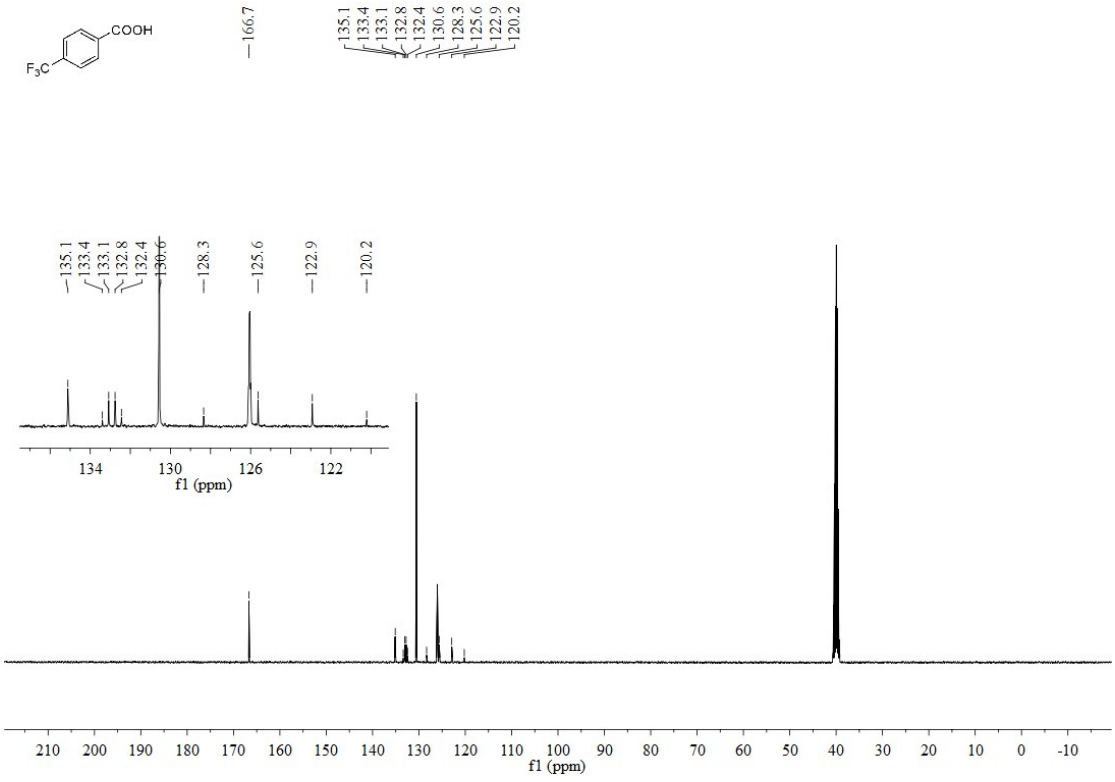
^{19}F NMR spectrum of **3-(trifluoromethyl)benzoic acid (16):**



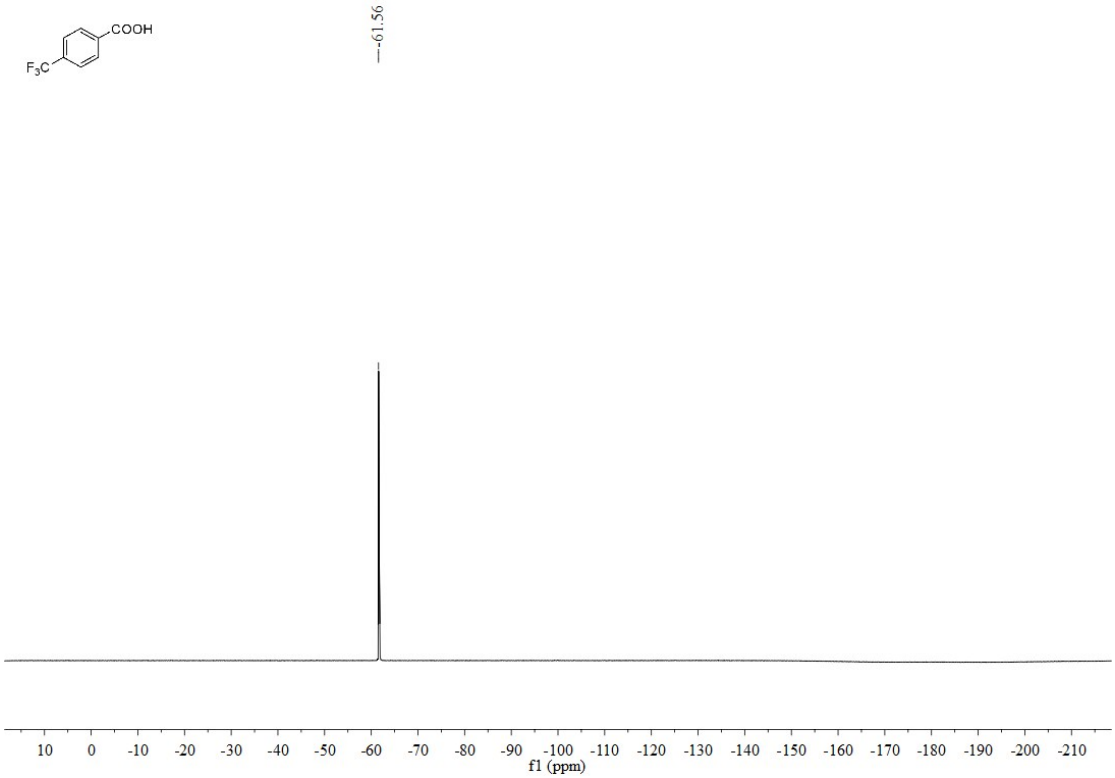
^{1}H NMR spectrum of **4-(trifluoromethyl)benzoic acid (17):**



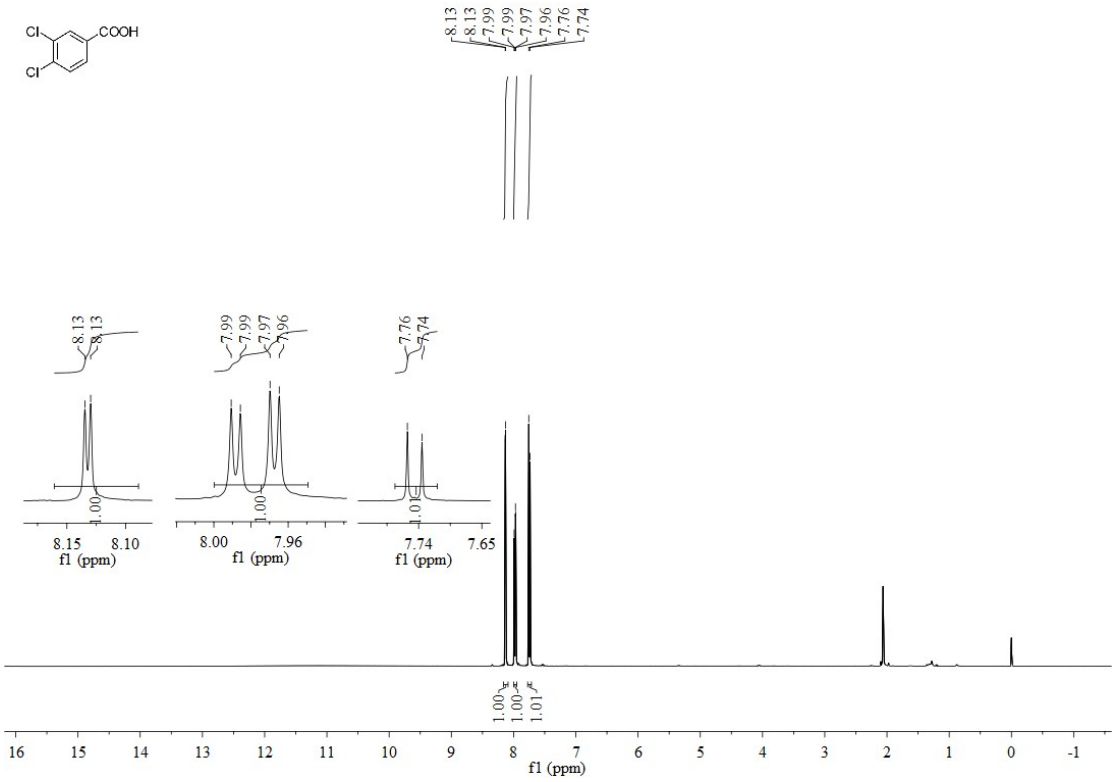
^{13}C NMR spectrum of **4-(trifluoromethyl)benzoic acid (17):**



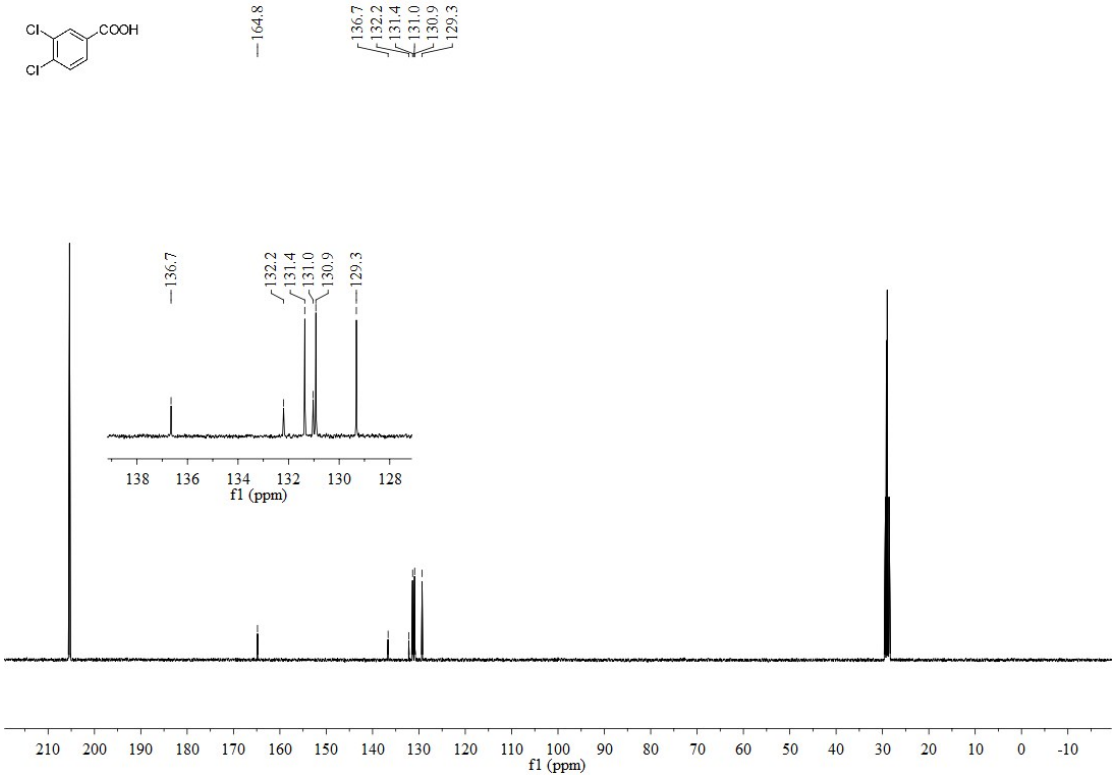
^{19}F NMR spectrum of **4-(trifluoromethyl)benzoic acid (17):**



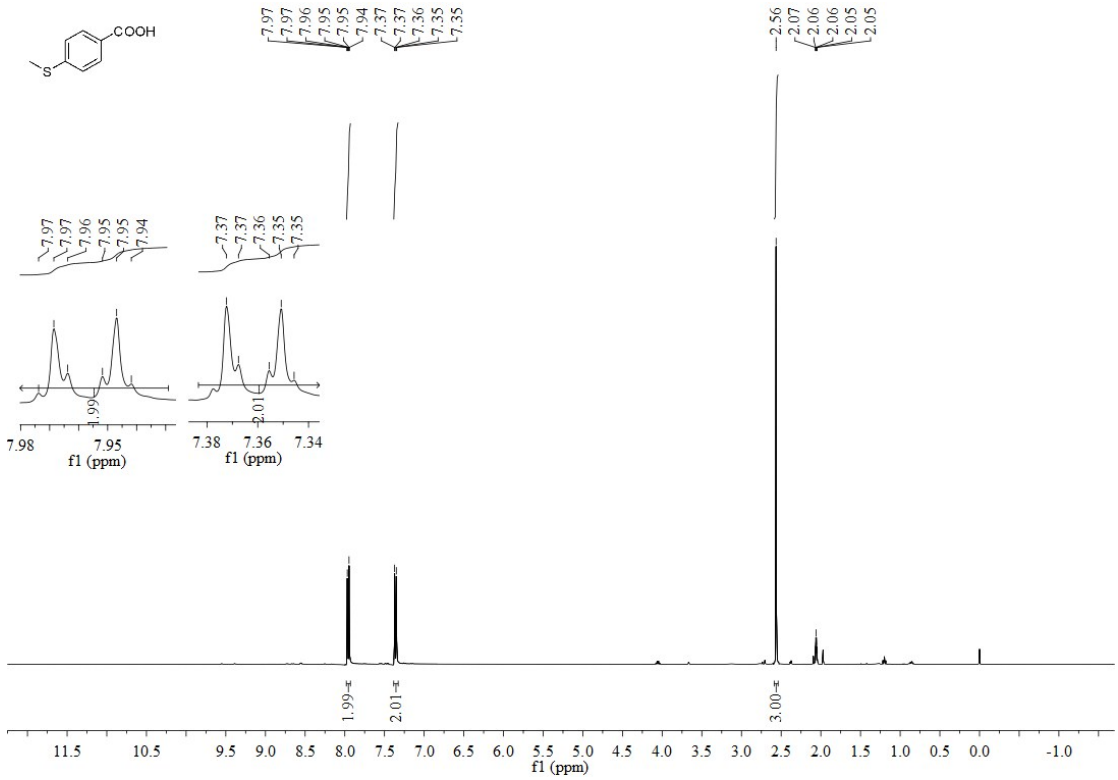
^{1}H NMR spectrum of **3,4-dichlorobenzoic acid (18):**



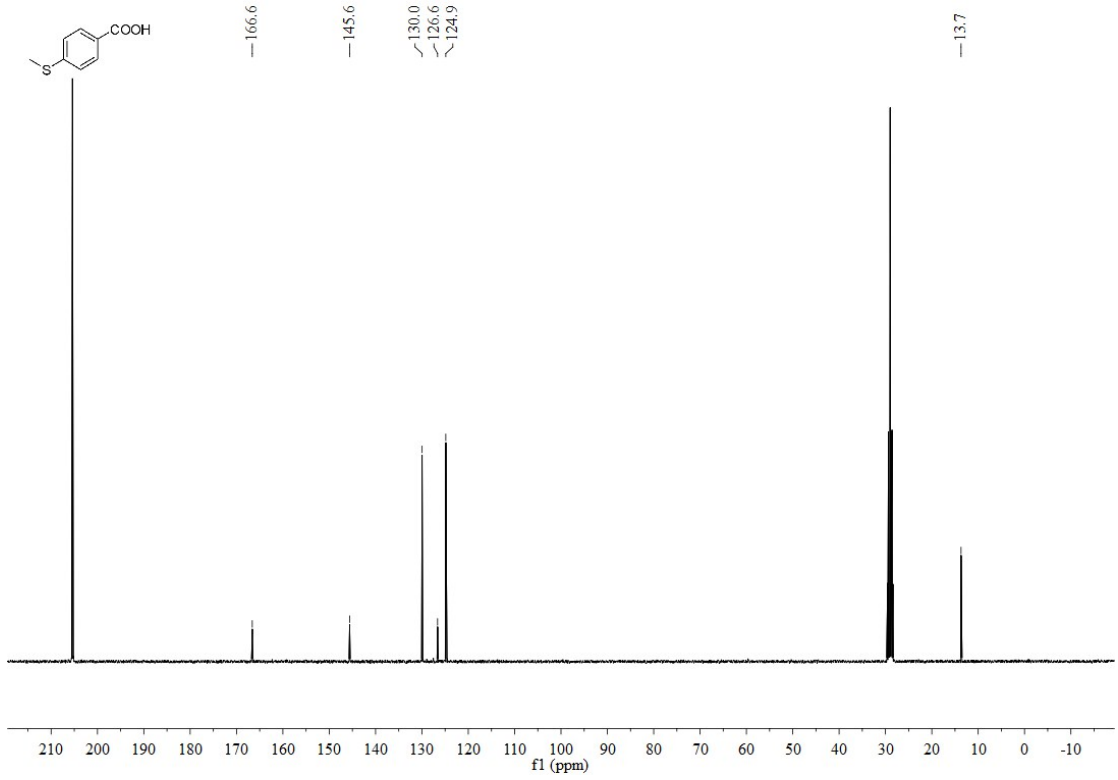
^{13}C NMR spectrum of **3,4-dichlorobenzoic acid (18):**



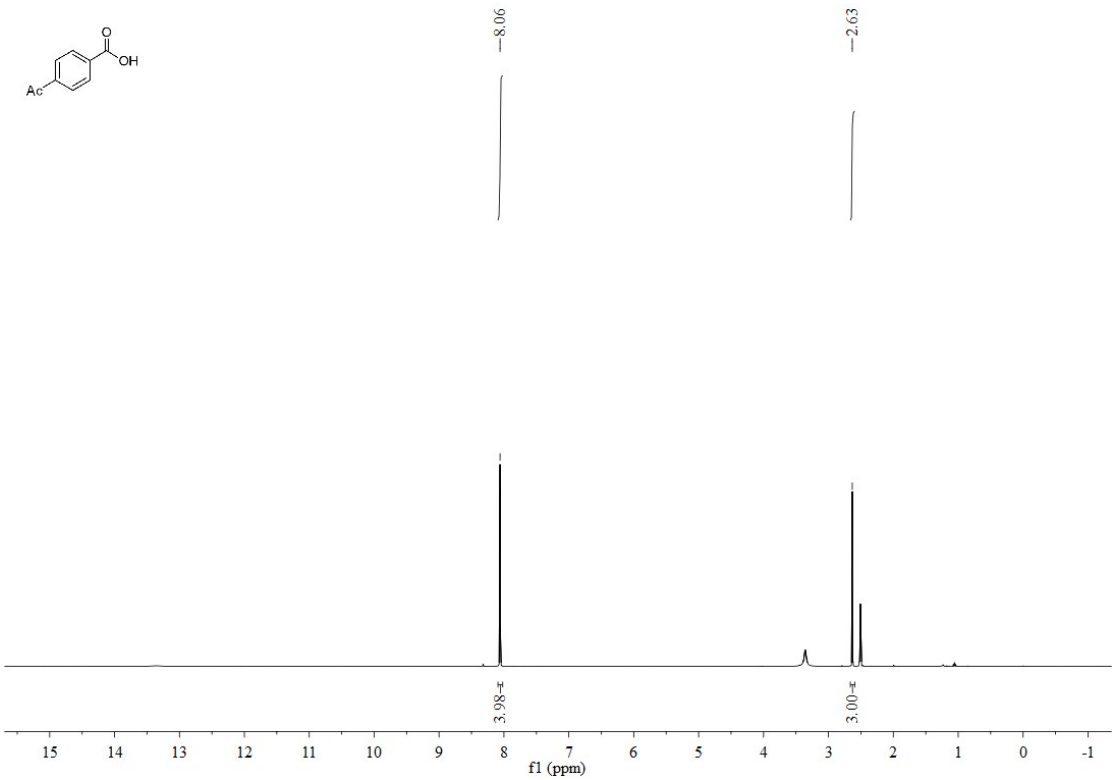
^{1}H NMR spectrum of **4-(methylthio)benzoic acid (19):**



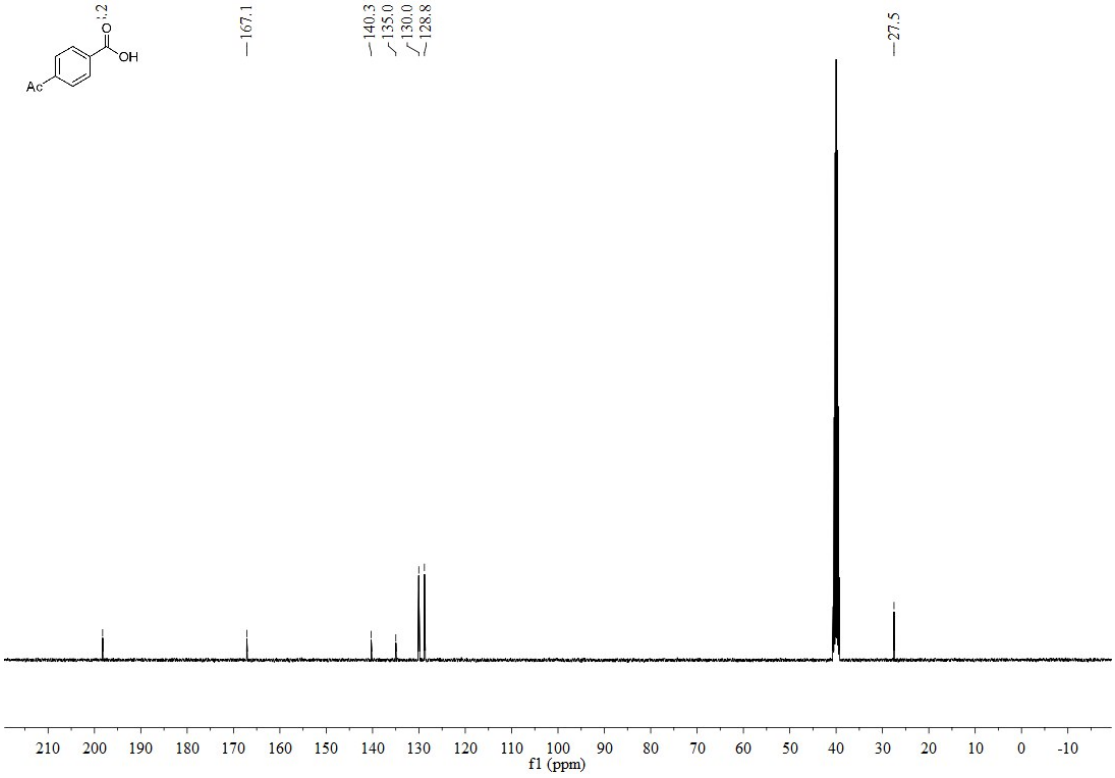
^{13}C NMR spectrum of **4-(methylthio)benzoic acid (19):**



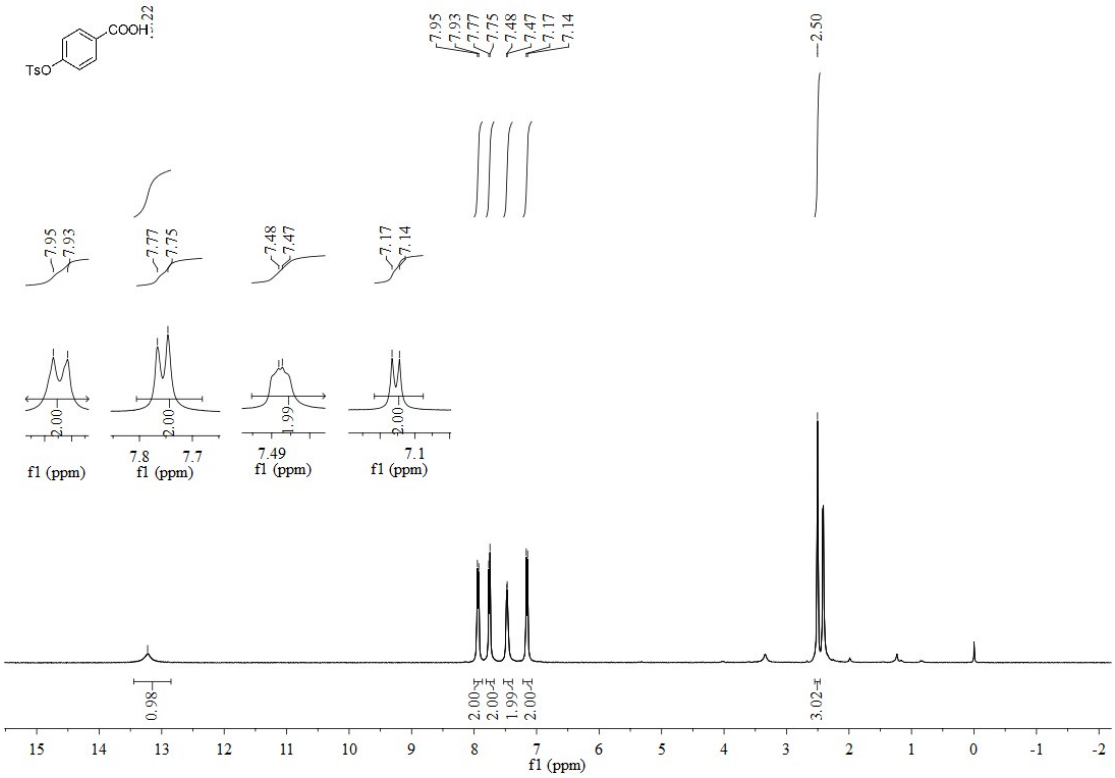
^{1}H NMR spectrum of **4-acetylbenzoic acid (20):**



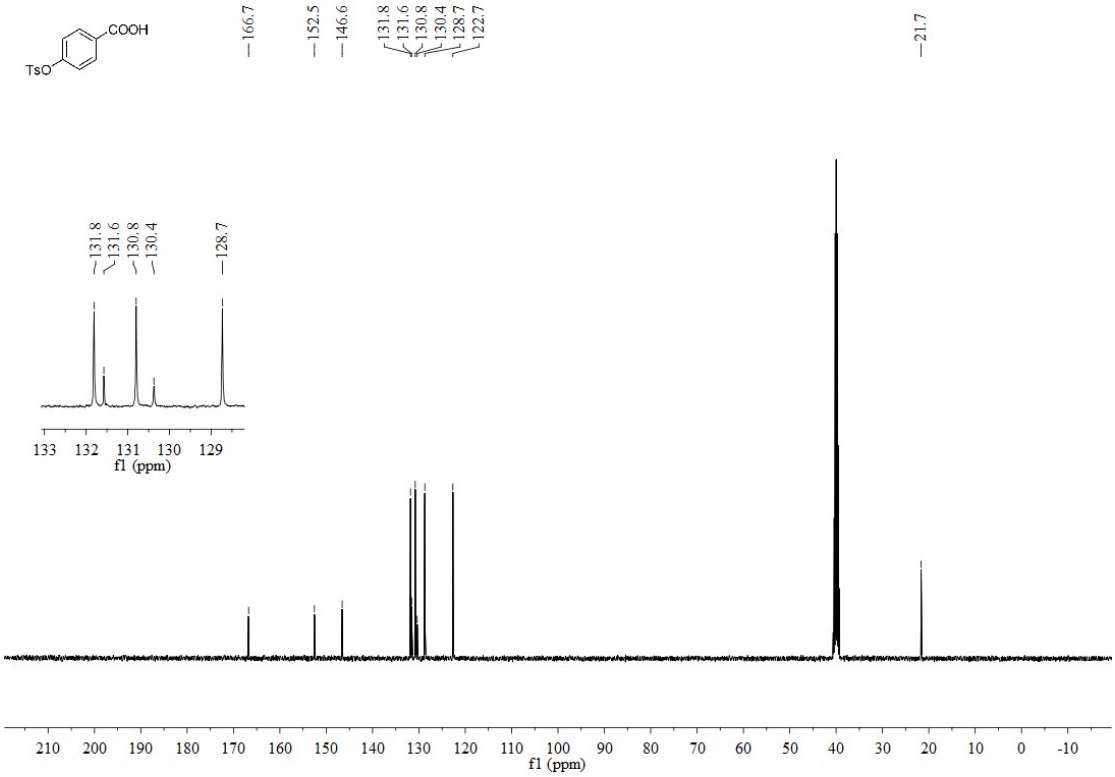
^{13}C NMR spectrum of **4-acetylbenzoic acid (20):**



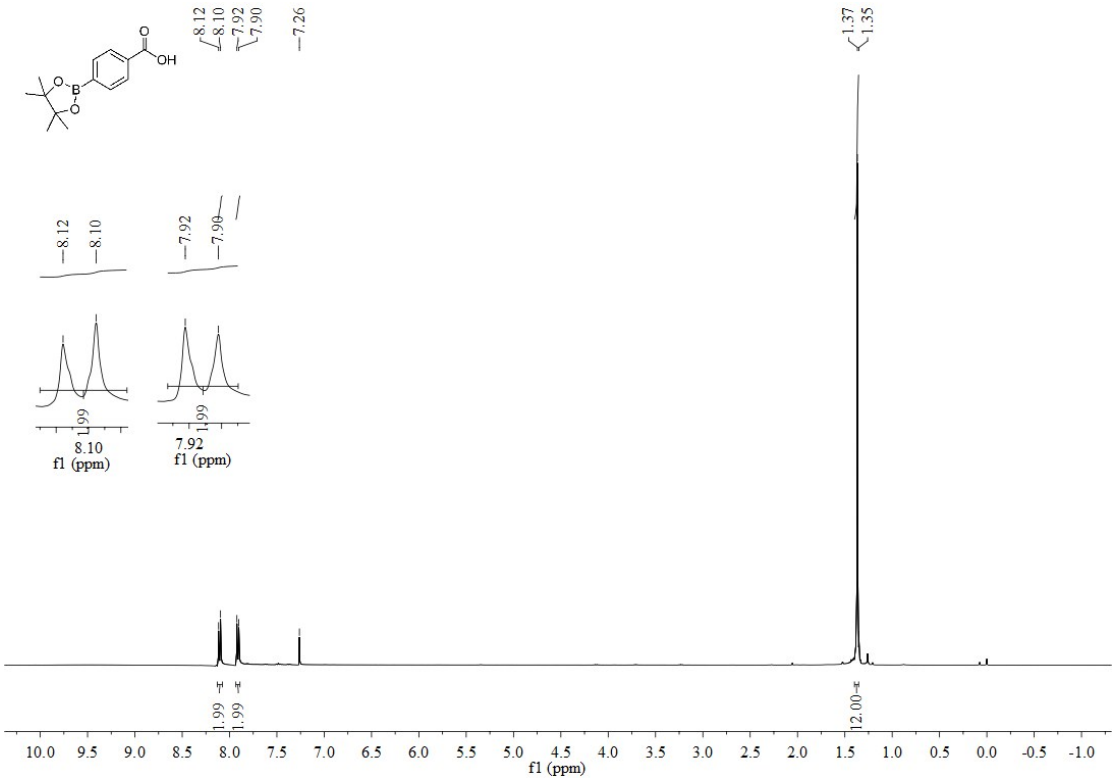
^{1}H NMR spectrum of **4-(tosyloxy)benzoic acid (21):**



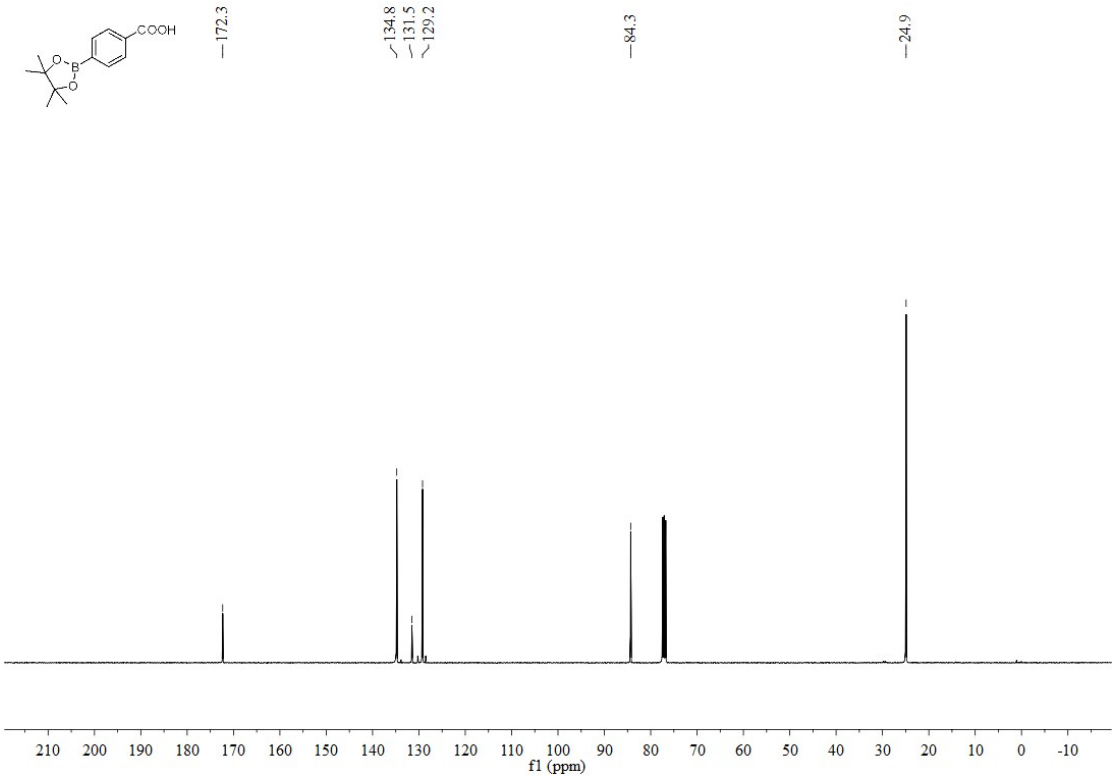
^{13}C NMR spectrum of **4-(tosyloxy)benzoic acid (21):**



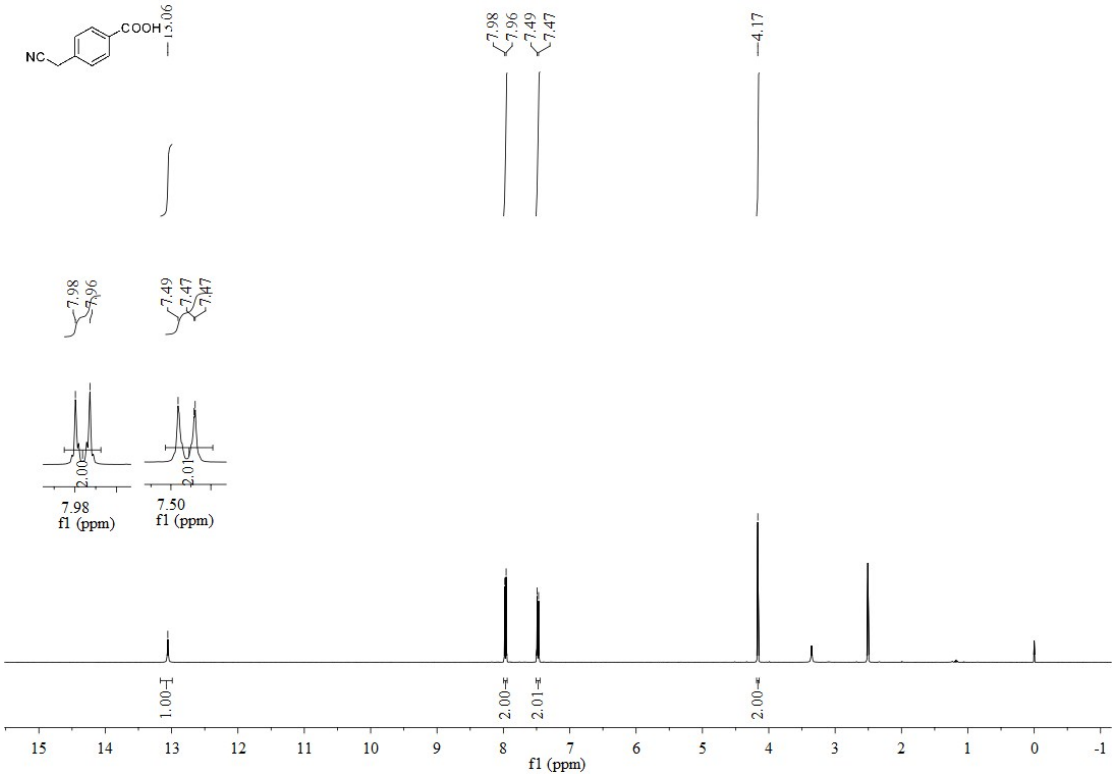
^{1}H NMR spectrum of **4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (22):**



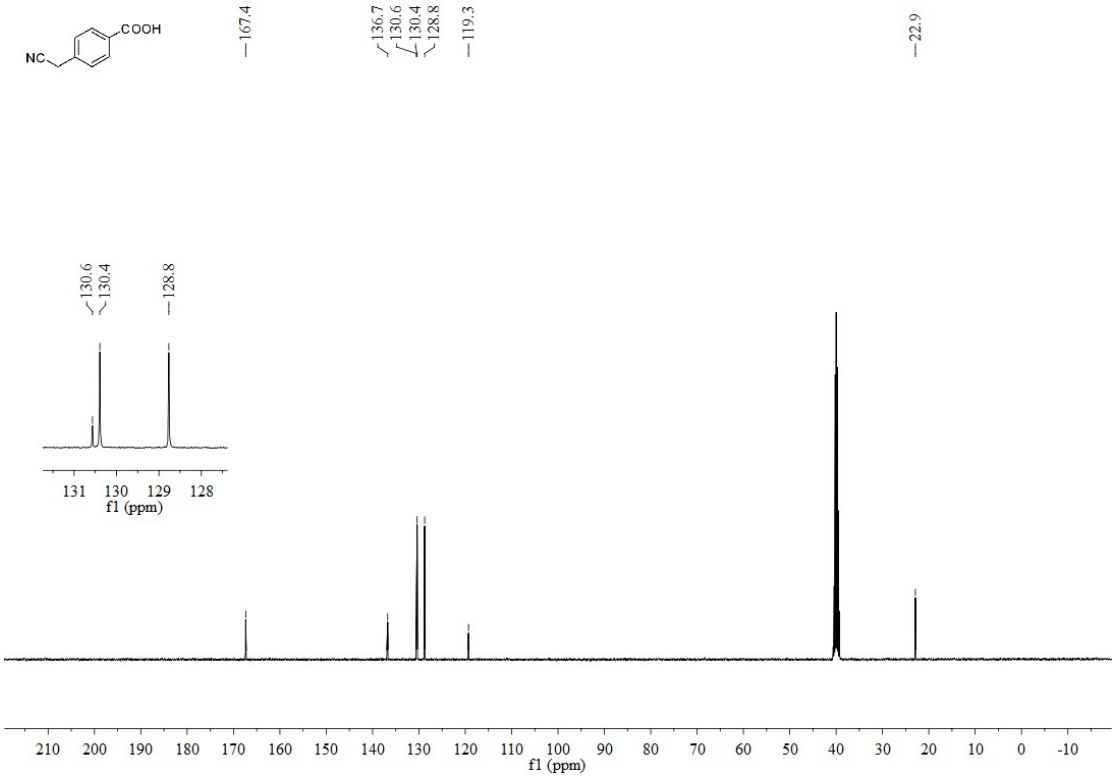
^{13}C NMR spectrum of **4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (22):**



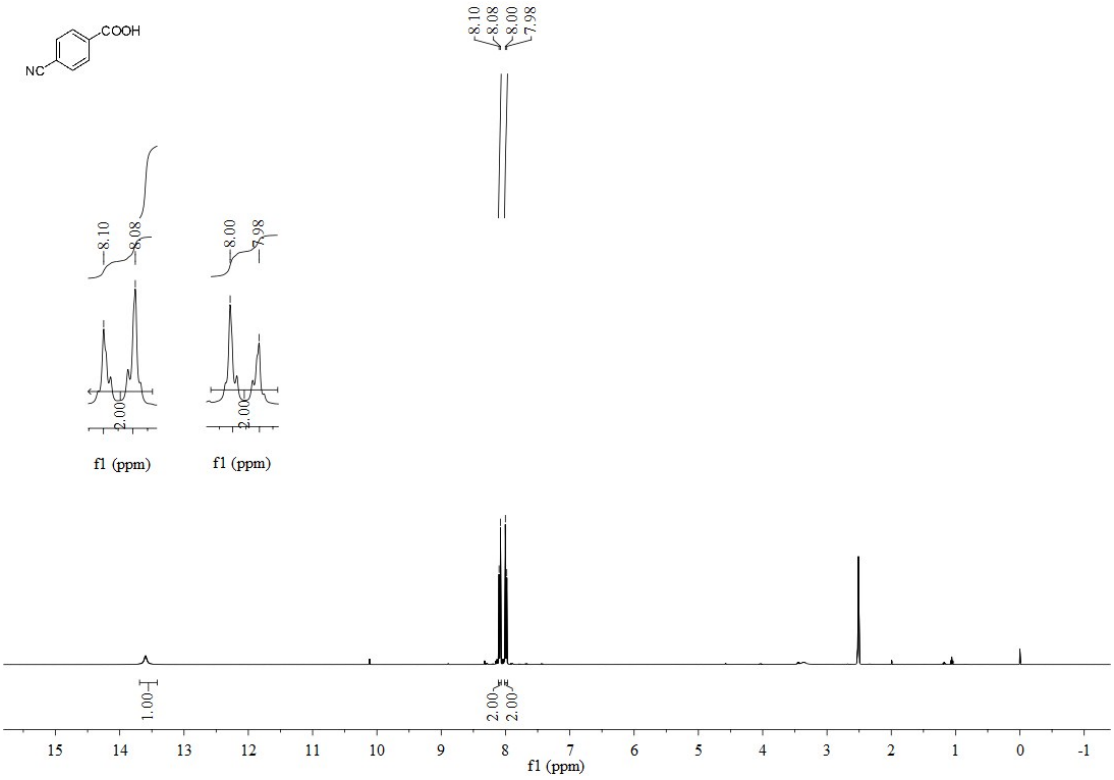
^{1}H NMR spectrum of **4-(cyanomethyl)benzoic acid (23):**



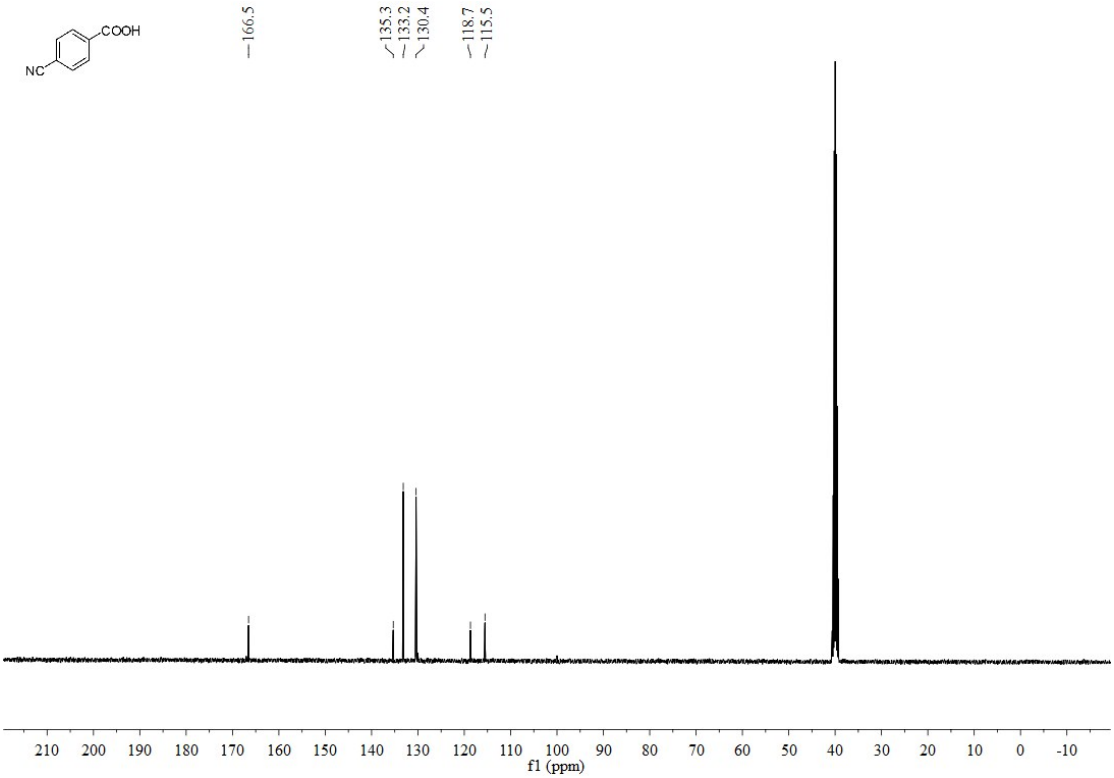
^{13}C NMR spectrum of **4-(cyanomethyl)benzoic acid (23):**



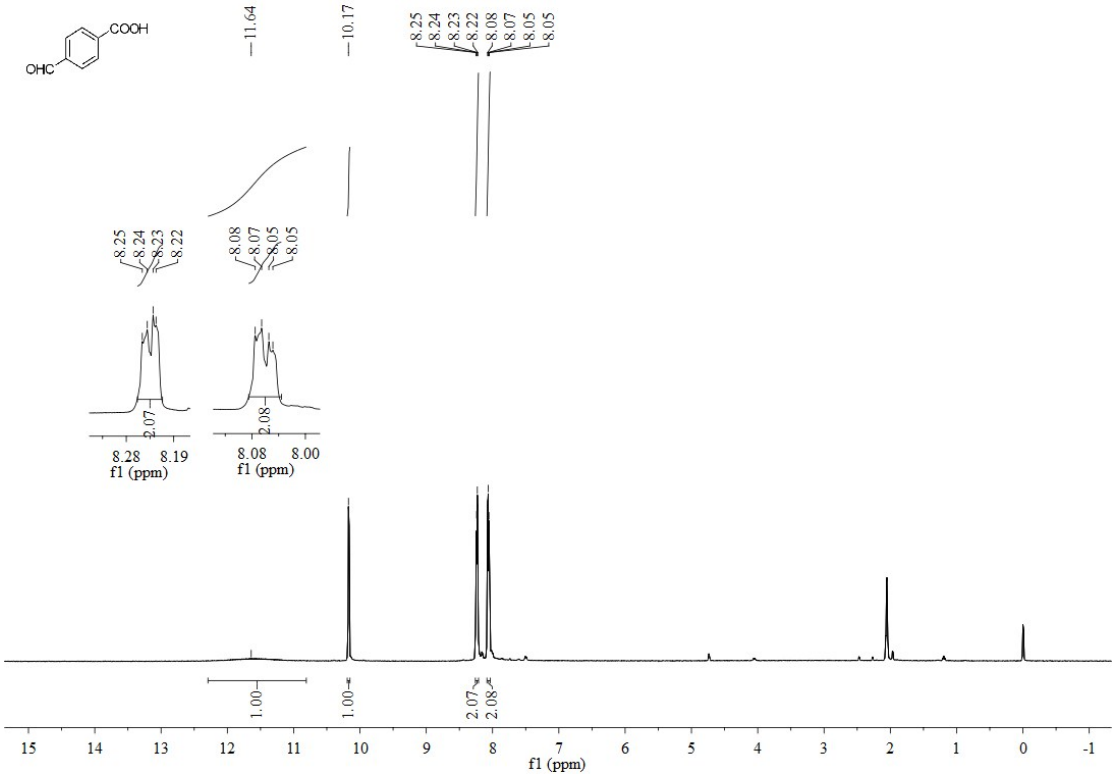
^{1}H NMR spectrum of **4-cyanobenzoic acid (24):**



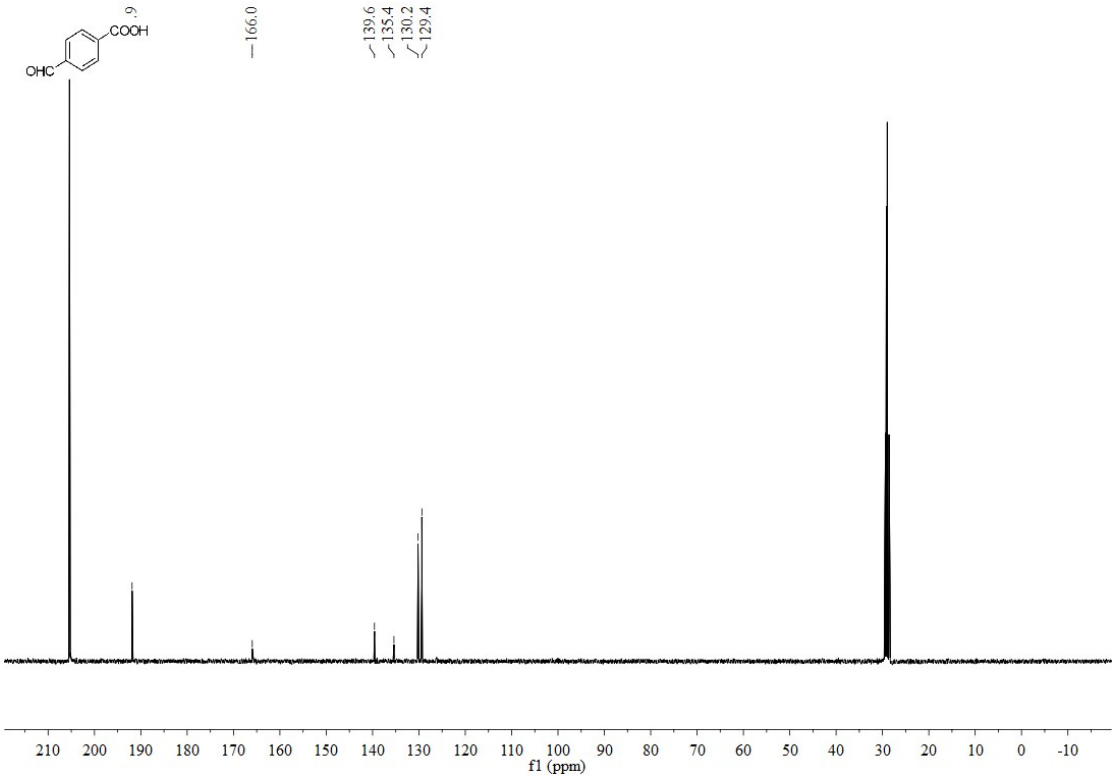
^{13}C NMR spectrum of **4-cyanobenzoic acid (24):**



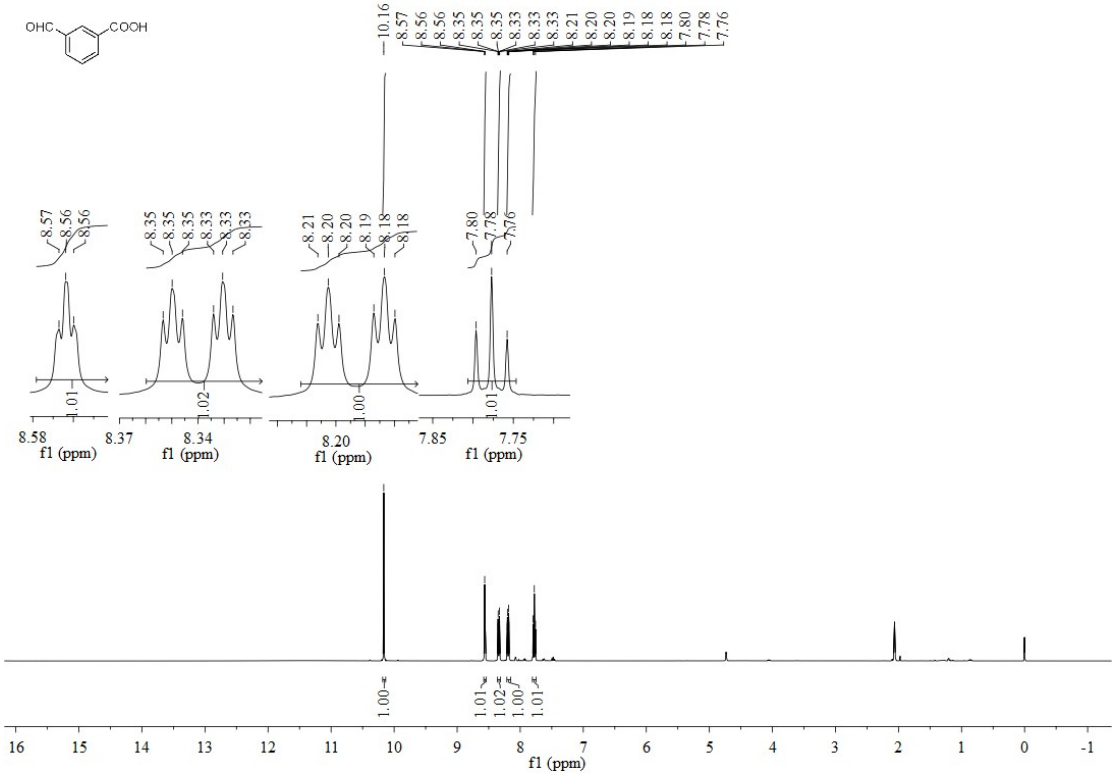
^{1}H NMR spectrum of **4-formylbenzoic acid (25):**



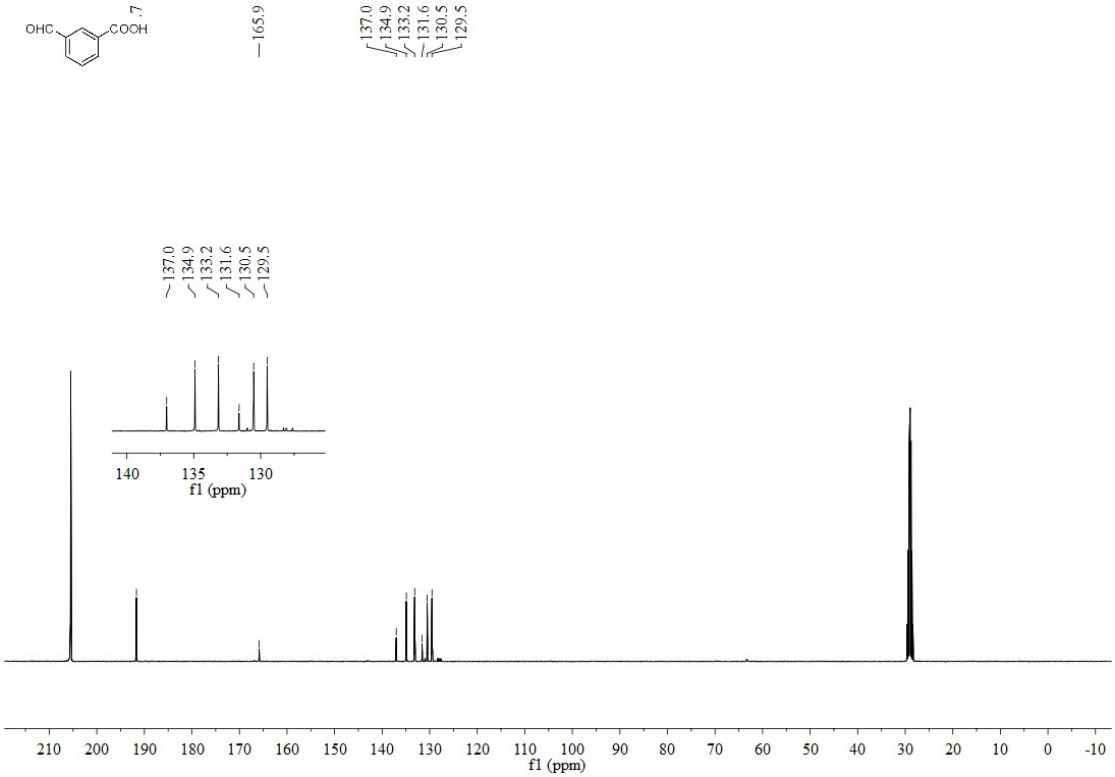
^{13}C NMR spectrum of **4-formylbenzoic acid (25):**



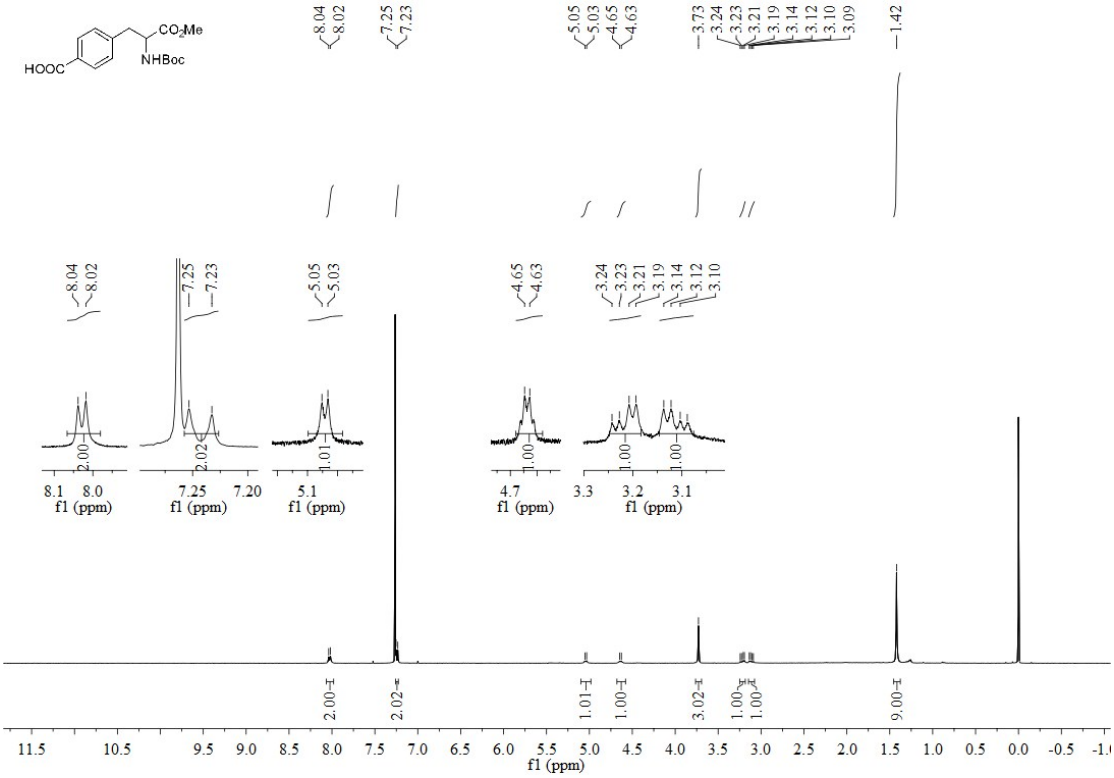
^{1}H NMR spectrum of **3-formylbenzoic acid (26):**



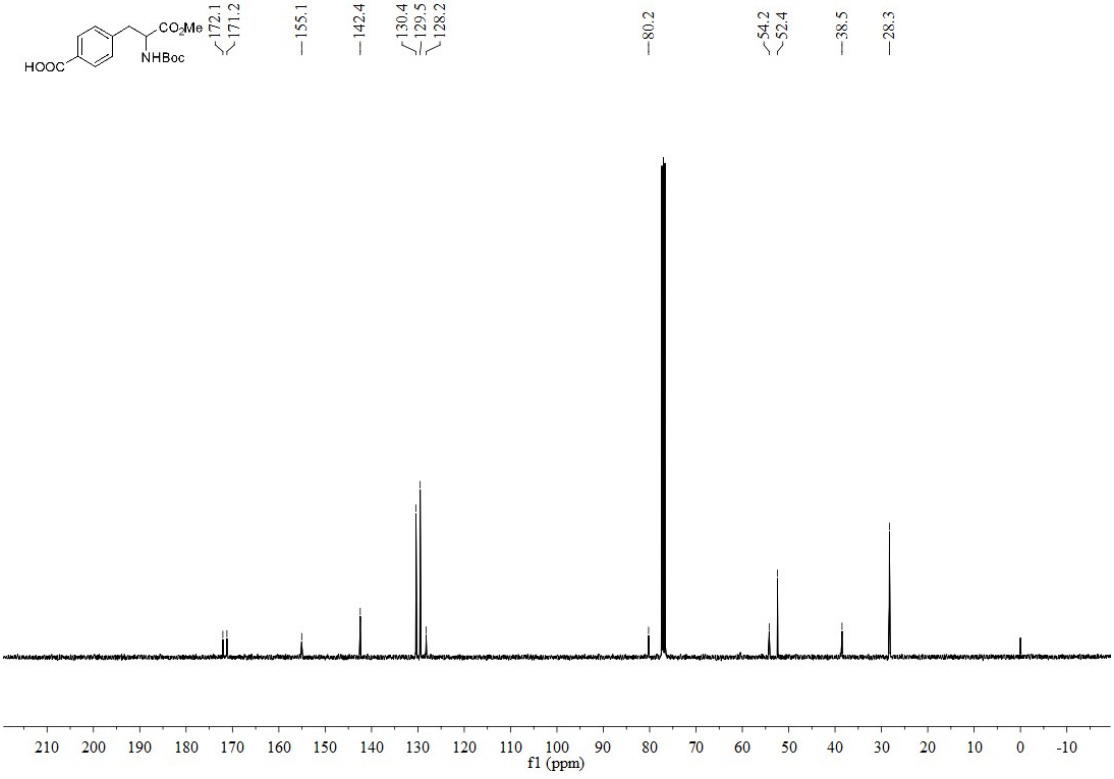
^{13}C NMR spectrum of **3-formylbenzoic acid (26):**



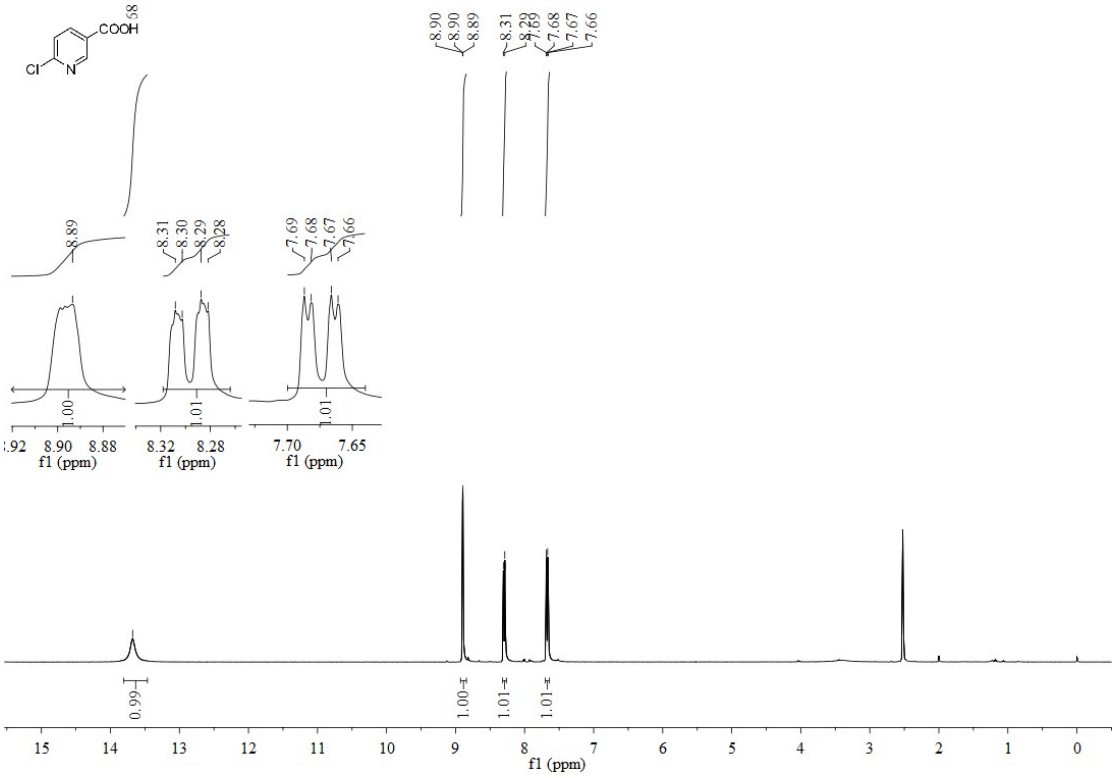
^{1}H NMR spectrum of **4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (27):**



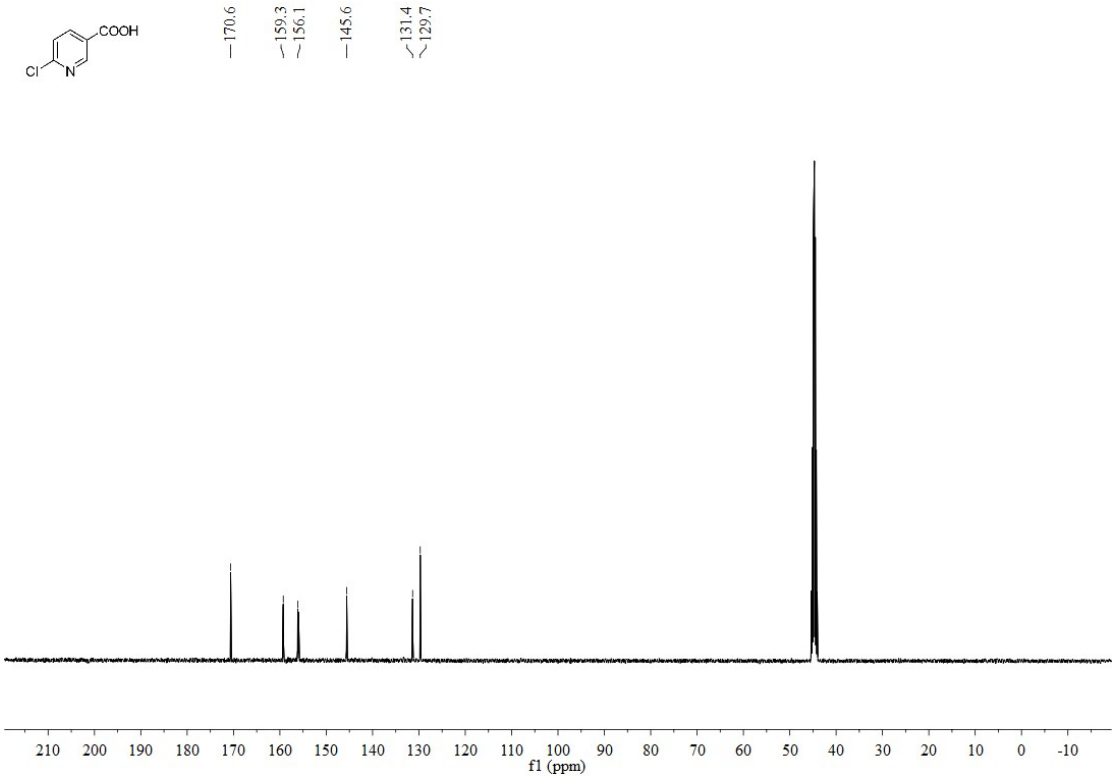
^{13}C NMR spectrum of **4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (27):**



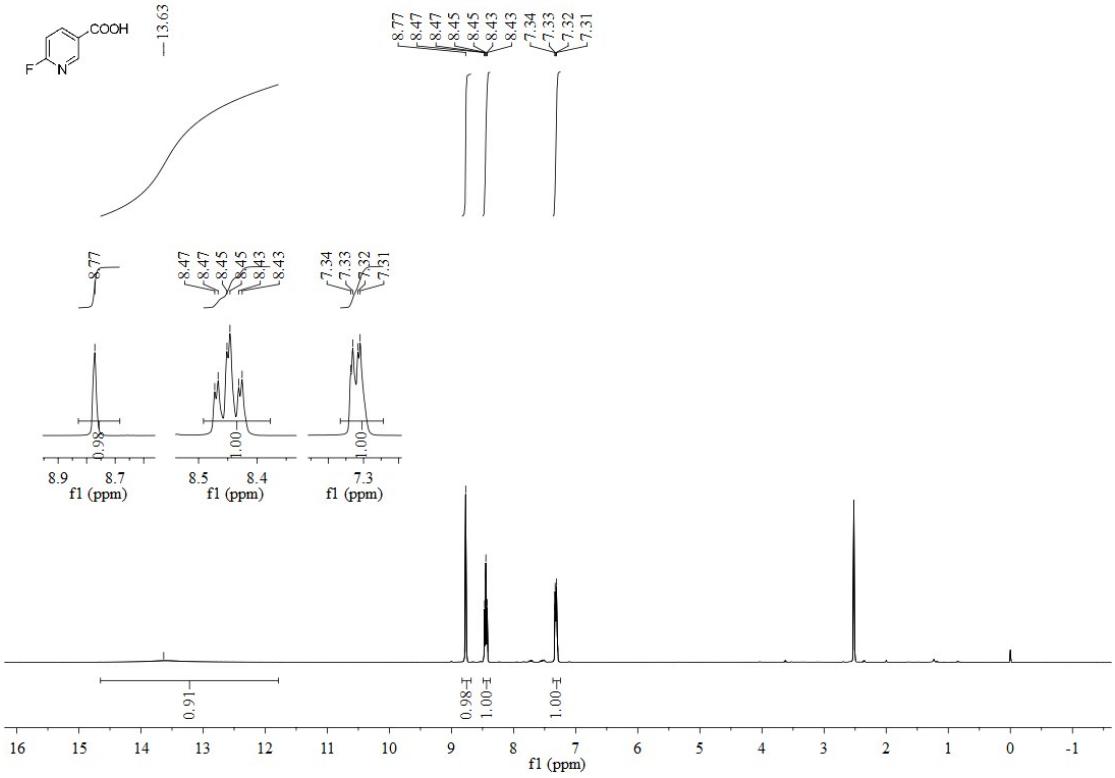
^{1}H NMR spectrum of **6-chloronicotinic acid (28):**



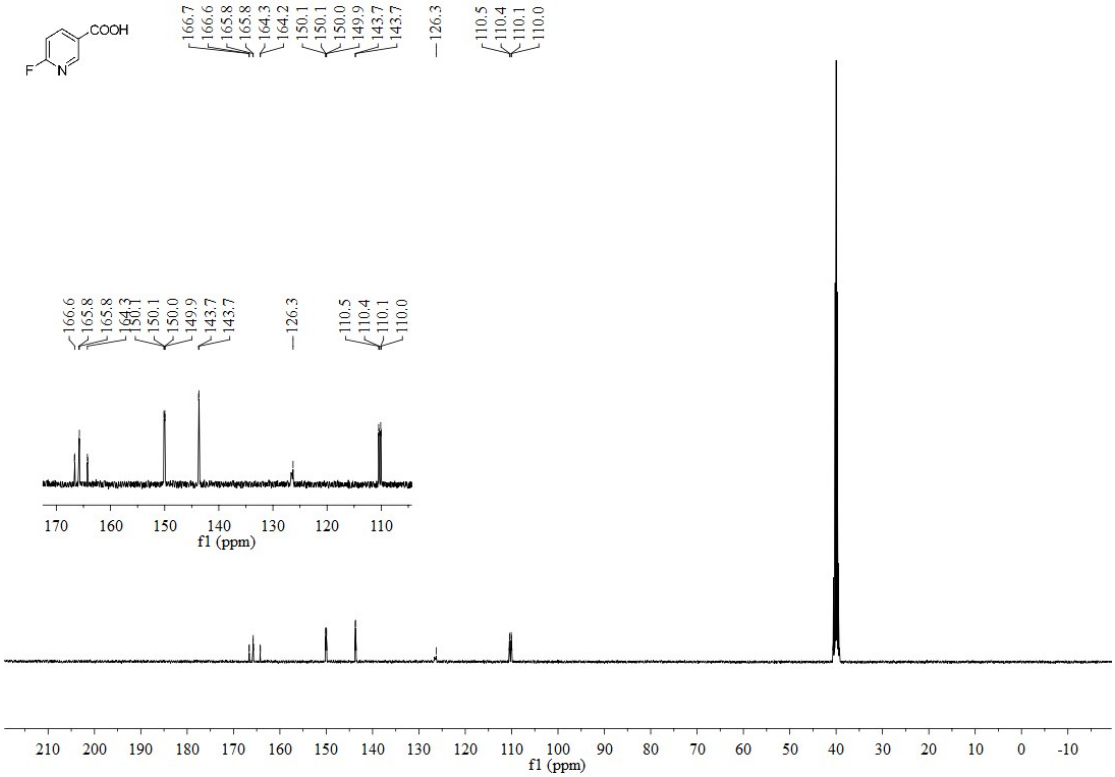
^{13}C NMR spectrum of **6-chloronicotinic acid (28):**



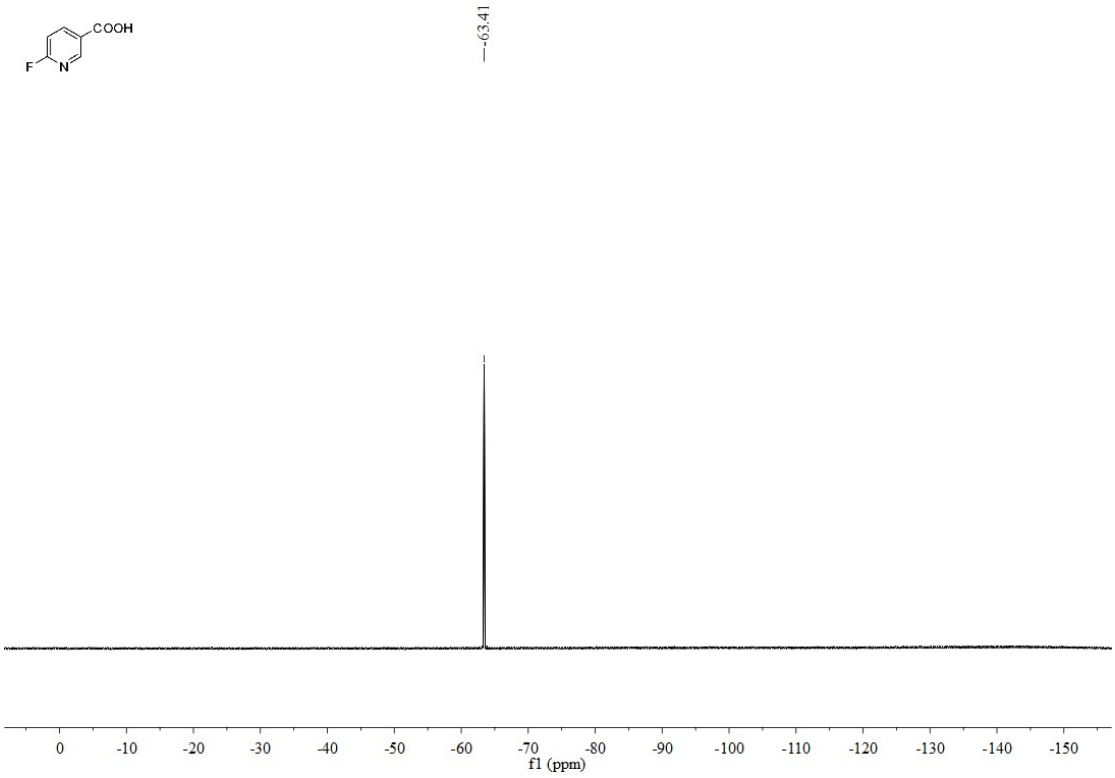
^{1}H NMR spectrum of **6-fluoronicotinic acid (29):**



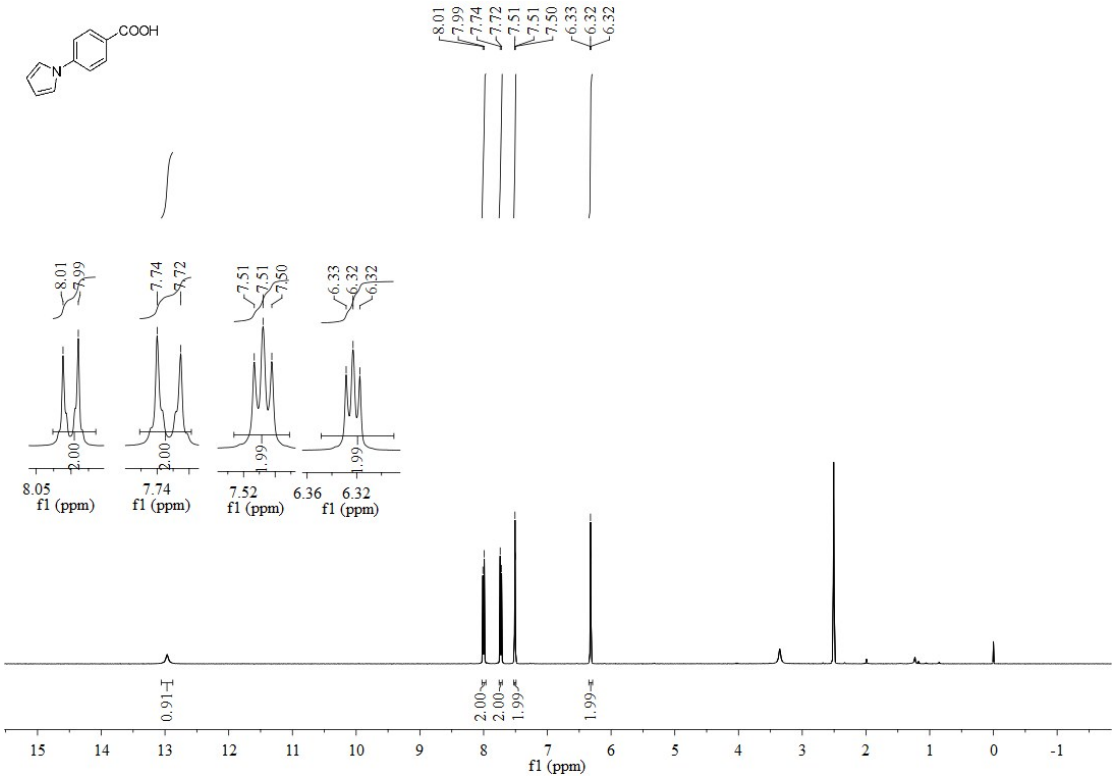
^{13}C NMR spectrum of **6-fluoronicotinic acid (29):**



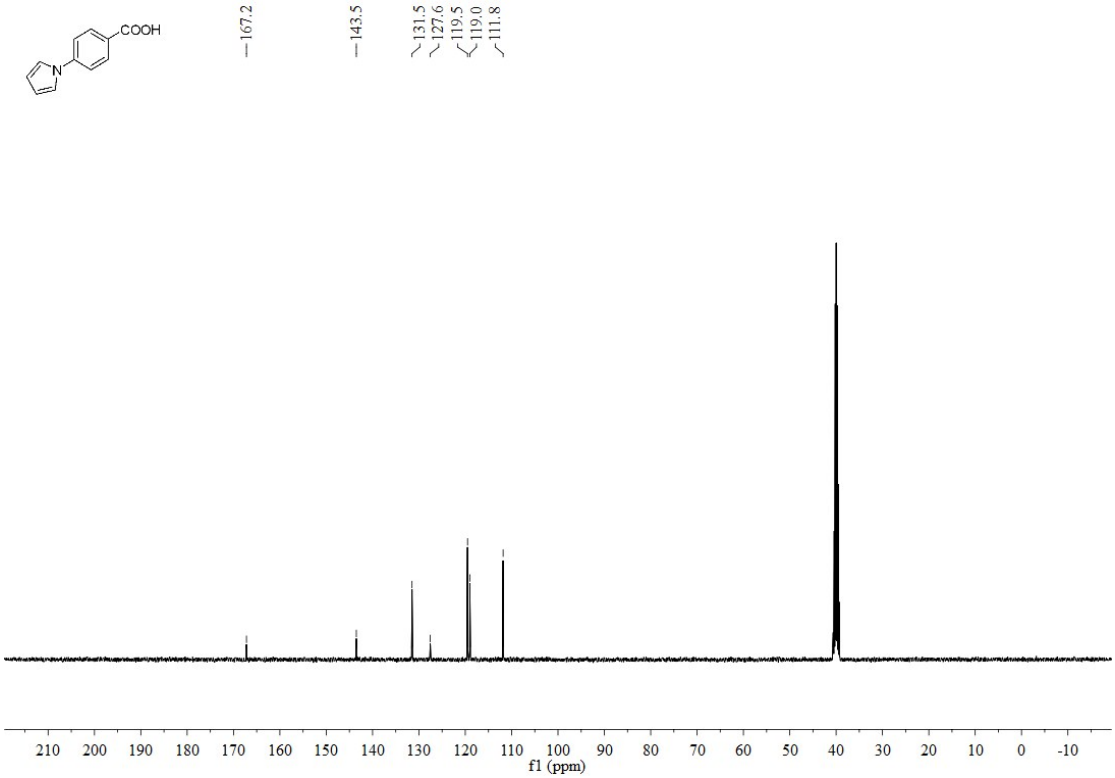
^{19}F NMR spectrum of **6-fluoronicotinic acid (29):**



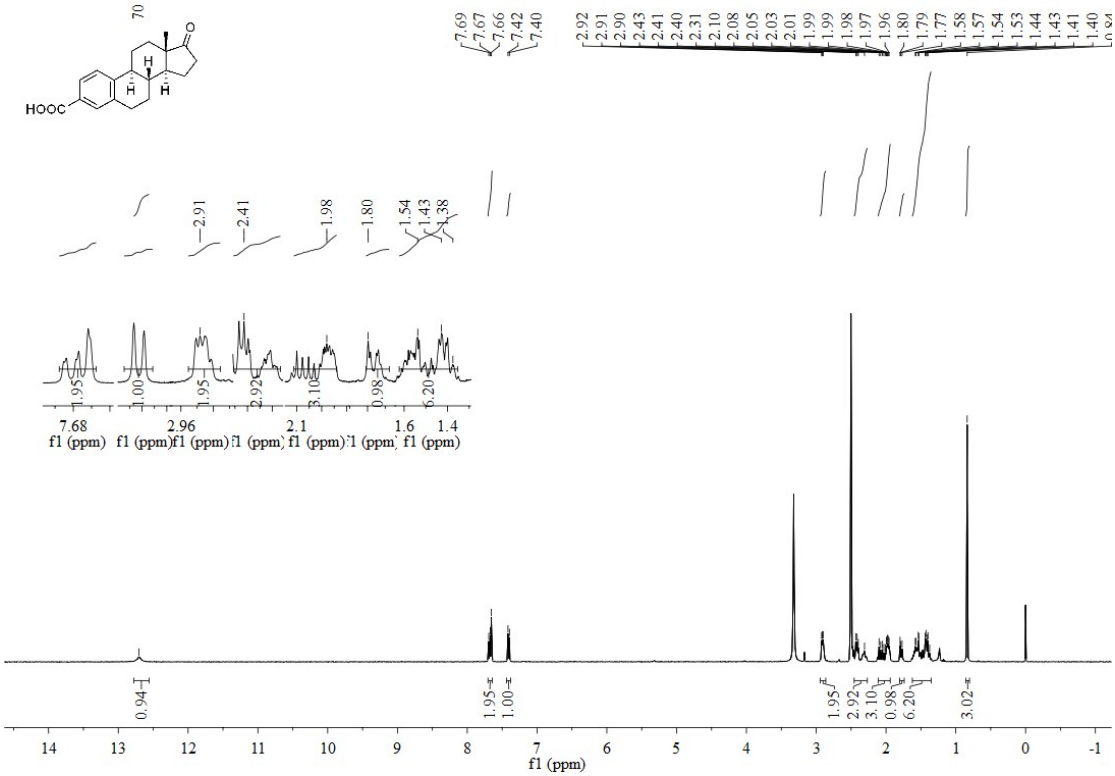
^{1}H NMR spectrum of **4-(1H-pyrrol-1-yl)benzoic acid (30):**



^{13}C NMR spectrum of **4-(1H-pyrrol-1-yl)benzoic acid (30):**



^{1}H NMR spectrum of **(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthrene-3-carboxylic acid (32):**



^{13}C NMR spectrum of **(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthrene-3-carboxylic acid (32):**