

Supporting Information for

Photo-Induced Deep Aerobic Oxidation of Alkyl Aromatics

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(I) General consideration

1.1 Materials and methods.

All commercial reagents and solvents were used as purchased unless otherwise indicated. CeCl₃ was purchased from 3A Chemicals. 2,2,2-trifluoroethanol were purchased from Adamas. CH₃CN was purchased from Sinopharm Chemical Reagent Co., Ltd. Other reagents were purchased from Aldrich, TCI, Adamas and J&K chemical. ¹H NMR (400 MHz), ¹³C NMR (100 MHz) were registered on Bruker 400 M spectrometers with CDCl₃, DMSO-d₆, D₂O or CD₃OD as solvent and tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. Column chromatography was performed on silica gel 200-300 meshes. HRMS were performed by the Stateauthorized Analytical Center in Fudan University.

1.2 Detailed description of the LED light source and photoreactor.

1.2.1 Detailed description of the 400 nm LED lights.

The LED light with an adjustable power output controller (0-10 W) was purchased from WATTCAS. Water cooling was enforced for effective thermal management to maintain luminous efficiency and life expectancy of LED lights.

The photocatalytic reaction were performed on WATTCAS photoreactor (WP-TEC-1020HSL).

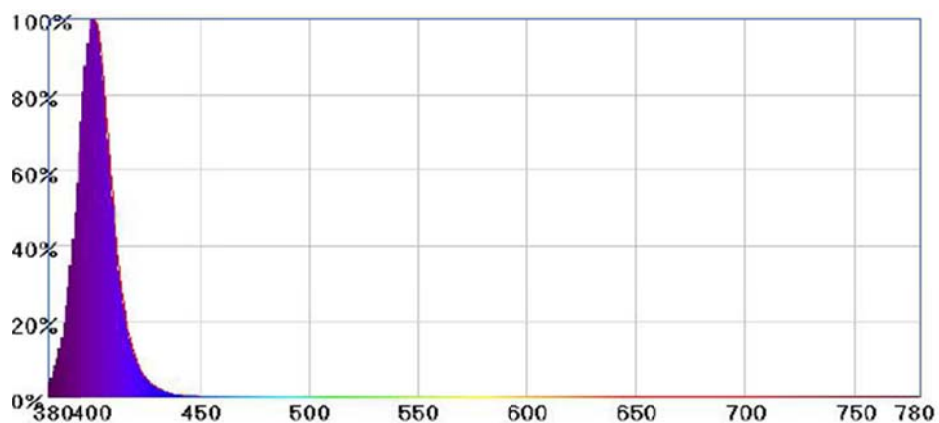


Figure S1. The spectrum of the LED light.



Figure S2. The detailed picture of the photoreactor.

1.2.2 Detailed description of the 390 nm LED lights.

The LED light was purchased from Shanghai Yaosai Instruments Co., Ltd. The reaction vial was then irradiated with a 40 W Kessil PR160L-390 nm.

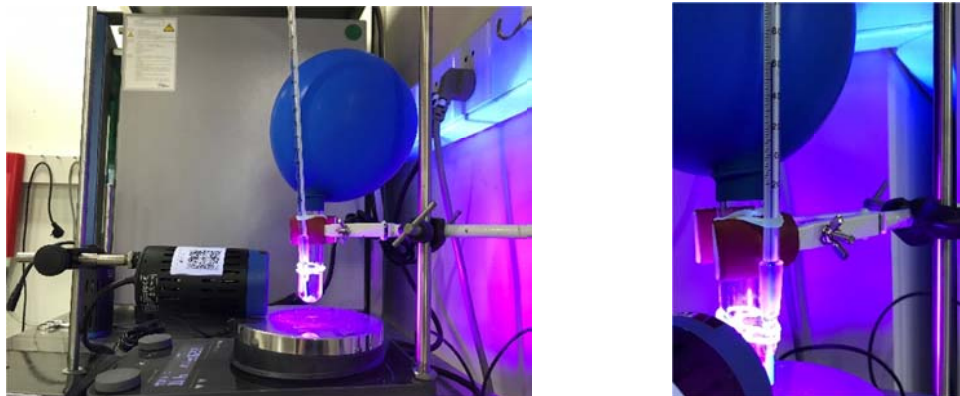
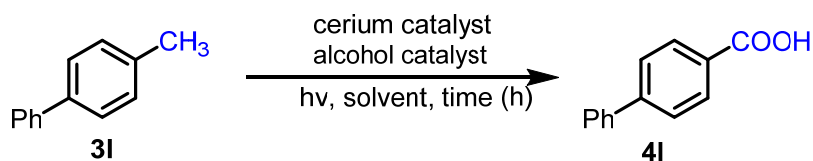


Figure S3. The detailed picture of the photoreactor.

(II) Optimization of the reaction conditions



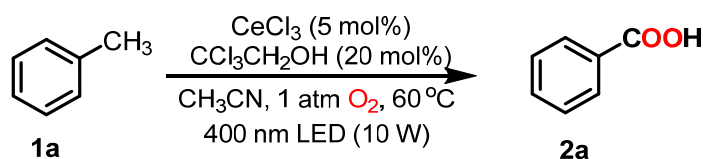
Entry	[Ce]	Alcohol catalyst	T (°C)	Time (h)	Solvent	light	Yield (%) ^b
1	CeCl ₃	EtOH	60	12	CH ₃ CN	400 nm	21
2	Ce(OTf) ₃	EtOH	60	12	CH ₃ CN	400 nm	12
3	Ce(OH) ₄	EtOH	60	12	CH ₃ CN	400 nm	< 5
4	Ce(NH ₄) ₂ (NO ₃) ₆	EtOH	60	12	CH ₃ CN	400 nm	10
5	CeCl ₃	CCl ₃ CH ₂ OH	60	12	CH ₃ CN	400 nm	54
6	CeCl ₃	HFIP	60	12	CH ₃ CN	400 nm	25
7	CeCl ₃	CCl ₃ CH ₂ OH	RT	12	CH ₃ CN	400 nm	22
8	CeCl ₃	CCl ₃ CH ₂ OH	100	12	CH ₃ CN	400 nm	< 5
9	CeCl ₃	CCl ₃ CH ₂ OH	60	24	CH ₃ CN	400 nm	92(88 ^c)
10	CeCl ₃	CCl ₃ CH ₂ OH	60	24	DMSO	400 nm	< 5
11	CeCl ₃	CCl ₃ CH ₂ OH	60	24	H ₂ O	400 nm	N.D.
12	-	CCl ₃ CH ₂ OH	60	24	CH ₃ CN	400 nm	N.D.
13	CeCl ₃	CCl ₃ CH ₂ OH	60	24	CH ₃ CN	dark	N.D.

^a Reaction condition: 1a (0.1 mmol), cerium catalyst (5 mol%), alcohol catalyst (20 mol%), and solvent (2 mL).

^b The yield was determined based on ¹H NMR with CH₂Br₂ as a standard internal compound.

^c Isolated yield.

(III) General procedure

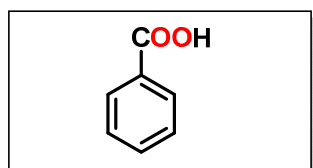


A 25mL quartz glass tube was charged with a stirring bar, and added reagent **1a** (0.1 mmol, 9.2 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (20 mol%, 20 μL (1 M CH_3CN solution)), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

(IV) Synthesis and analytical data for the products

Compound (2a) : benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 24 hours.

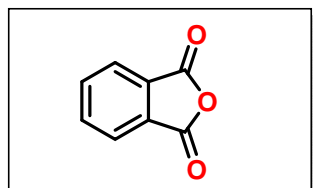


10.3 mg, 84%. ^1H NMR (400 MHz, DMSO-d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (2b) : isobenzofuran-1,3-dione.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1b** (0.1 mmol, 10.6 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (1.0 equiv. 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product.

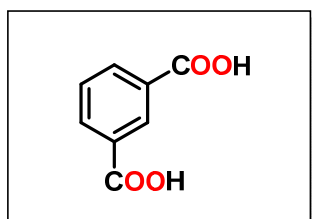


9.6 mg, 65%. ^1H NMR (400 MHz, CDCl_3) δ 8.05-8.03 (m, 2H), 7.93-7.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 136.0, 131.3, 125.7.

The spectroscopic data match a literature report (*Org. Lett.* **2014**, *16*, 1108).

Compound (2c) : isophthalic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1c** (0.1 mmol, 10.6 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

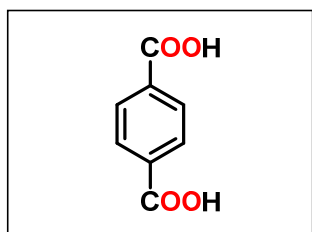


14.1 mg, 85%. ¹H NMR (400 MHz, CD₃OD) δ 8.65 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CD₃OD) δ 167.4, 133.5, 131.1, 130.5, 128.4.

The spectroscopic data match a literature report (*Org. Lett.* **2013**, *15*, 1378).

Compound (2d) : terephthalic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1d** (0.1 mmol, 10.6 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 48 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with ethyl acetate to give the corresponding product.

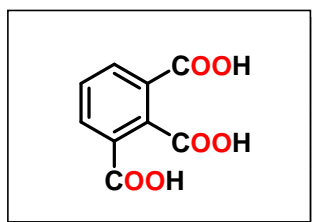


14.2 mg, 86%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.23 (brs, 2H), 8.04 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆) δ 167.2, 135.0, 129.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (2e) : benzene-1,2,3-tricarboxylic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1e** (0.1 mmol, 12.0 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

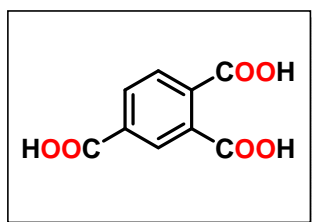


12.4 mg, 59%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.60 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 169.1, 167.3, 137.1, 133.4, 130.4, 129.4.

The spectroscopic data match a literature report (*Org. Lett.* **2014**, *16*, 1108).

Compound (2f) : benzene-1,2,4-tricarboxylic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1f** (0.1 mmol, 12.0 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 $^\circ\text{C}$. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with ethyl acetate and the corresponding product was dissolved in ethyl acetate.

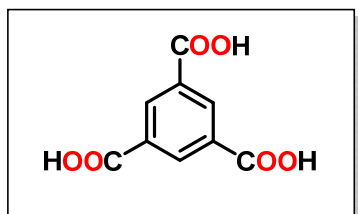


12.5 mg, 60%. ^1H NMR (400 MHz, D_2O) δ 8.38 (s, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 168.8, 168.0, 166.5, 138.0, 132.9, 132.5, 132.2, 130.2, 129.5.

The spectroscopic data match a literature report (*Angew. Chem. Int. Ed.* **2020**, *59*, 1263).

Compound (2g) : benzene-1,3,5-tricarboxylic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1g** (0.1 mmol, 12.0 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 72 hours at 60 $^\circ\text{C}$. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

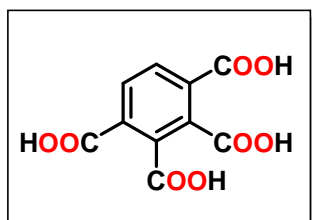


17.7 mg, 84%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.54 (brs, 3H), 8.63 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.3, 134.0, 132.4.

The spectroscopic data match a literature report (*Chem. Commun.* **2018**, *54*, 11574).

Compound (2h) : benzene-1,2,3,4-tetracarboxylic acid

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1h** (0.1 mmol, 13.4 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

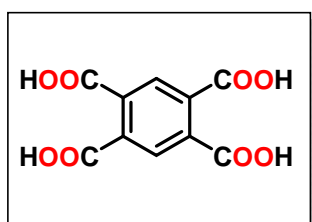


23.4 mg, 75%. ¹H NMR (400 MHz, D₂O) δ 7.98 (s, 2H).
¹³C NMR (100 MHz, DMSO-d₆) δ 168.3, 167.3, 134.4, 133.7, 130.4.

The spectroscopic data match a literature report (*JFE Chemical Corporation - EP2135856*, 2009).

Compound (2i) : benzene-1,2,4,5-tetracarboxylic acid

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1i** (0.1 mmol, 13.4 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

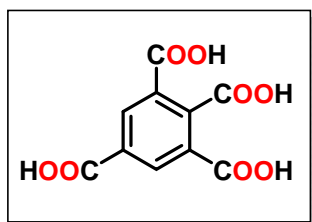


20.1 mg, 79%. ¹H NMR (400 MHz, D₂O) δ 7.97 (s, 2H).
¹³C NMR (100 MHz, D₂O) δ 172.9, 135.9, 128.6.

The spectroscopic data match a literature report (*Green Chem.*, **2017**, *19*, 1663).

Compound (2j) : benzene-1,2,3,5-tetracarboxylic acid

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1j** (0.1 mmol, 13.4 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

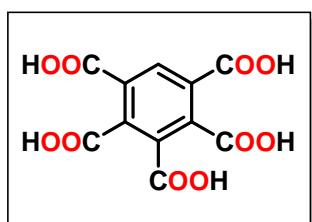


16.5 mg, 65%. ^1H NMR (400 MHz, D_2O) δ 8.69 (s, 2H).
 ^{13}C NMR (100 MHz, D_2O) δ 173.0, 167.7, 167.4, 140.3, 135.4, 131.4, 128.9.

The spectroscopic data match a literature report (*10.1002/hlca.200690260*).

Compound (2k) : benzene-1,2,3,4,5-pentacarboxylic acid

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1k** (0.1 mmol, 14.8 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

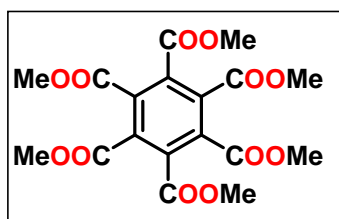


20.6 mg, 69%. ^1H NMR (400 MHz, D_2O) δ 8.62 (s, 1H).
 ^{13}C NMR (100 MHz, D_2O) δ 171.7, 167.4, 138.6, 134.1, 130.0.

The spectroscopic data match a literature report (*Chem. Eu. J.* **2020**, *26*, 11250).

Compound (2l) : hexamethyl benzene-1,2,3,4,5,6-hexacarboxylate.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1l** (0.1 mmol, 16.2 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, added CH_3I and stirred overnight at room temperature. Then, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 10:1) to give the corresponding product.

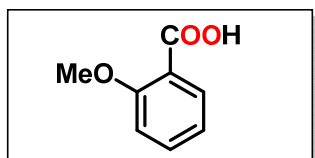


20.8 mg, 49%. ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 133.9, 53.5.

The spectroscopic data match a literature report (*MedChemComm.* **2019**, *10*, 1476).

Compound (4a) : 2-methoxybenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

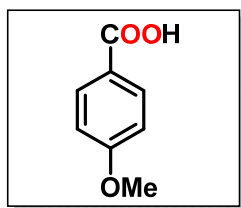


9.9 mg, 65%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.60 (brs, 1H), 7.63 (dd, J = 7.6, 1.6 Hz, 1H), 7.49-7.45 (m, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 158.4, 133.4, 131.0, 121.6, 120.3, 112.7, 56.0.

The spectroscopic data match a literature report (*Org. Lett.* **2013**, *15*, 1378).

Compound (4b) : 4-methoxybenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 24 hours.

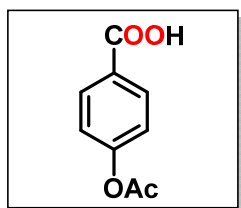


11.9 mg, 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.61 (brs, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.1, 162.9, 131.4, 123.0, 113.9, 55.5.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4c) : 4-acetoxybenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 24 hours.



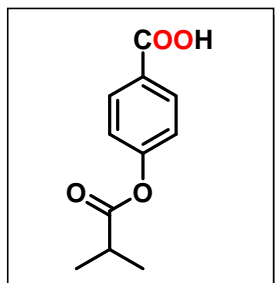
14.5 mg, 80%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.05 (brs, 1H), 7.99 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 169.0, 166.8, 154.1, 131.0, 128.4, 122.2, 21.0.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4d) : 4-(isobutyryloxy)benzoic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **3d** (0.1 mmol, 17.8 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (20 mol%, 20 μL (1M CH_3CN solution)), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular

to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product.

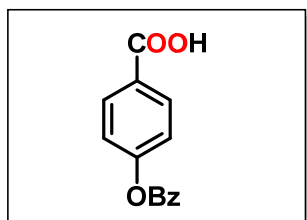


14.9 mg, 72%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.07 (brs, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 2.88-2.81 (m, 1H), 1.24 (dd, *J* = 7.2, 1.2 Hz, 6H). ¹³C NMR (100 MHz, DMSO-d₆) δ 174.8, 166.7, 154.2, 131.0, 128.4, 122.1, 33.5, 18.7.

The spectroscopic data match a literature report (*Green Chem.*, **2018**, *20*, 3038).

Compound (4e) : 4-(benzoyloxy)benzoic acid.

The title compound was synthesized via General Procedure for 24 hours.

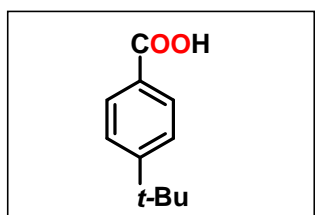


16.5 mg, 68%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.12 (brs, 1H), 8.15 (d, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ 167.0, 164.6, 154.4, 134.6, 131.3, 130.2, 129.4, 128.9, 128.1, 122.6.

The spectroscopic data match a literature report (*J. Phys. Org. Chem.* **2016**, *30*, 3608).

Compound (4f) : 4-(*tert*-butyl)benzoic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **3f** (0.1 mmol, 14.8 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH (20 mol%, 20 μL (1M CH₃CN solution)), CH₃CN (2 mL) under O₂ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product.



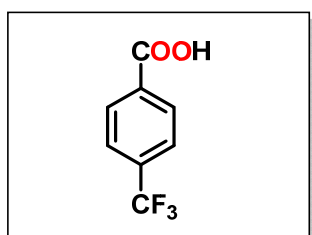
7.2 mg, 40%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.80 (brs, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H),

1.28 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d₆) δ 167.6, 156.1, 129.5, 128.4, 125.7, 35.1, 31.2.

The spectroscopic data match a literature report (*Green Chem.* **2013**, *15*, 635).

Compound (4g) : 4-(trifluoromethyl)benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

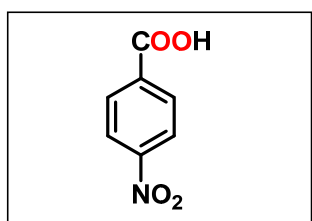


17.1 mg, 90%. ^1H NMR (400 MHz, DMSO-d₆) δ 13.41 (brs, 1H), 8.13 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d₆) δ 166.3, 134.7, 133.1 (q, J = 31.8 Hz), 130.2, 125.7, 125.3 (q, J = 271.0 Hz). ^{19}F NMR (376 MHz, DMSO-d₆) δ -61.7.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4h) : 4-nitrobenzoic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **3h** (0.1 mmol, 13.7 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH (20 mol%, 20 μL (1M CH₃CN solution)), CH₃CN (2 mL) under O₂ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 48 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product.

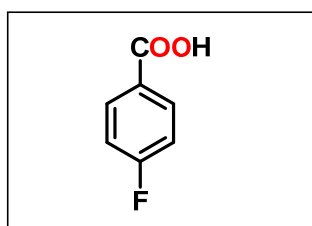


3.8 mg, 21%. ^1H NMR (400 MHz, DMSO-d₆) δ 13.62 (brs, 1H), 8.33 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d₆) δ 166.2, 150.4, 136.7, 131.0, 124.1.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4i) : 4-fluorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.



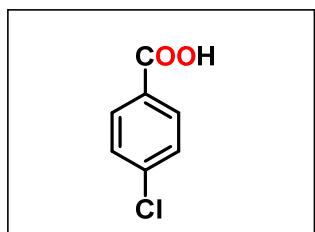
14.9 mg, 81%. ^1H NMR (400 MHz, DMSO-d₆) δ 13.03 (brs, 1H), 8.02-7.98 (m, 2H), 7.33-7.29 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d₆) δ 166.5, 166.3 (d, J = 248.9 Hz),

132.3 (d, $J = 9.0$ Hz), 127.5, 115.8 (d, $J = 22.0$ Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -106.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4j) : 4-chlorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

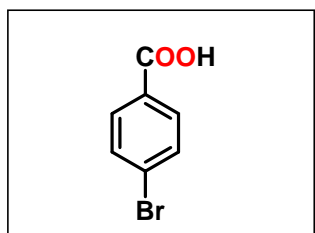


14.5 mg, 88%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.14 (brs, 1H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.56 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.8, 138.1, 131.5, 130.0, 129.1.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4k) : 4-bromobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

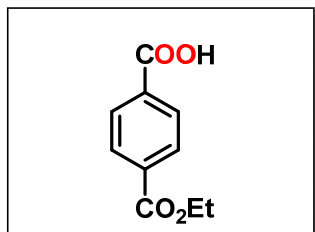


13.3 mg, 66%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.20 (brs, 1H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.7, 131.8, 131.4, 130.1, 127.0.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (4l) : 4-(ethoxycarbonyl)benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 24 hours.

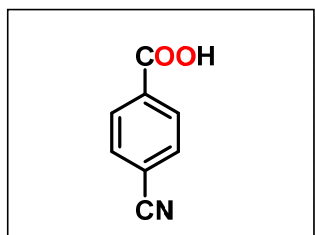


14.0 mg, 72%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.20 (brs, 1H), 8.04 (s, 4H), 4.33 (q, $J = 7.2$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.7, 165.2, 134.9, 133.5, 129.7, 129.4, 61.3, 14.2.

The spectroscopic data match a literature report (*J. Am. Chem. Soc.* **2013**, *135*, 2891).

Compound (4m) : 4-cyanobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

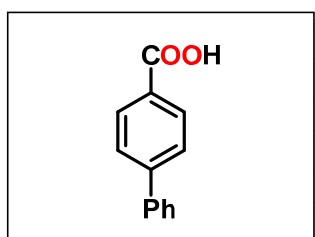


10.6 mg, 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.53 (brs, 1H), 8.08 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.1, 135.0, 132.8, 130.0, 118.3, 115.2.

The spectroscopic data match a literature report (*Green Chem.* **2018**, 20, 3038).

Compound (4n) : [1,1'-biphenyl]-4-carboxylic acid.

Procedure : The title compound was synthesized via General Procedure for 24 hours.

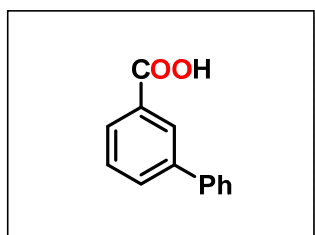


17.5 mg, 88%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.04 (brs, 1H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.44 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.3, 144.4, 139.2, 130.1, 129.7, 129.2, 128.4, 127.1, 126.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, 20, 3038).

Compound (4o) : [1,1'-biphenyl]-3-carboxylic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

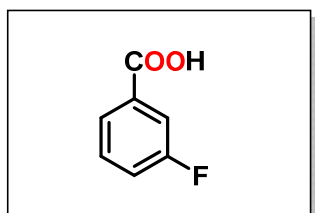


19.5 mg, 92%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.05 (brs, 1H), 8.17 (s, 1H), 7.94-7.89 (m, 2H), 7.68 (d, $J = 7.6$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.4, 140.6, 139.4, 131.6, 131.2, 129.5, 129.2, 128.7, 128.4, 128.0, 127.4, 126.9.

The spectroscopic data match a literature report (*Adv. Synth. Catal.* **2010**, 352, 1075).

Compound (4p) : 3-fluorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.



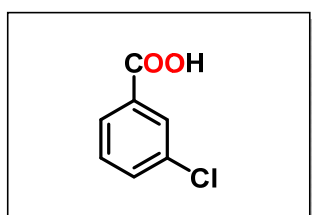
11.6 mg, 83%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.21 (brs, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.66-7.63 (m, 1H), 7.58-7.53 (m, 1H), 7.50-7.46 (m, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.7 (d, $J = 2.8$ Hz), 163.7 (d, $J = 243.0$ Hz),

133.7 (d, $J = 7.2$ Hz), 131.3 (d, $J = 7.9$ Hz), 125.9 (d, $J = 2.8$ Hz), 120.4 (d, $J = 21.0$ Hz), 116.3 (d, $J = 22.5$ Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -112.58, -112.60, -112.61.

The spectroscopic data match a literature report (*Chem. Commun.* **2013**, 49, 5213).

Compound (4q) : 3-chlorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

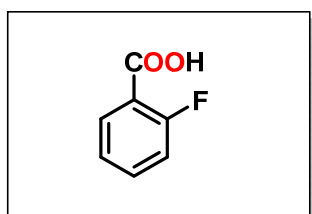


10.9 mg, 70%. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 8.01 (d, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 134.7, 133.9, 131.0, 130.3, 129.9, 128.3.

The spectroscopic data match a literature report (*J. Org. Chem.* **2014**, 79, 6094).

Compound (4r) : 2-fluorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

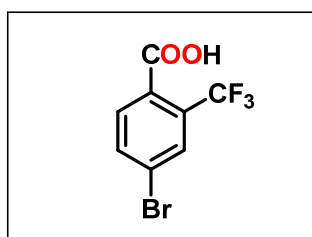


8.5 mg, 61%. ^1H NMR (400 MHz, CDCl_3) δ 11.99 (brs, 1H), 8.03 (t, $J = 7.6$ Hz, 1H), 7.59 (dd, $J = 13.6, 7.2$ Hz, 1H), 7.25-7.16 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.9 (d, $J = 3.1$ Hz), 163.9 (d, $J = 260.6$ Hz), 135.6 (d, $J = 9.3$ Hz), 132.8, 124.1 (d, $J = 3.9$ Hz), 117.5 (d, $J = 8.5$ Hz), 117.3 (d, $J = 22.0$ Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -108.3 - -108.4.

The spectroscopic data match a literature report (*Chem. Eur. J.* **2016**, 22, 3758).

Compound (4s) : 4-bromo-2-(trifluoromethyl)benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

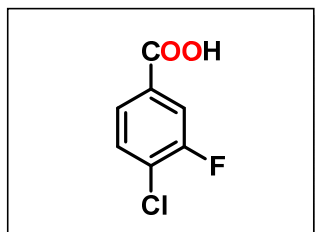


24.1 mg, 87%. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 6.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 135.0, 132.9, 131.4 (q, $J = 33.1$ Hz), 130.5 (q, $J = 5.9$ Hz), 127.6 (q, $J = 5.9$ Hz), 127.0, 123.6 (q, $J = 272.4$ Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -59.72.

The spectroscopic data match a literature report (*Bioorg. Med Chem.* **2007**, *15*, 2198).

Compound (4t) : 4-chloro-3-fluorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

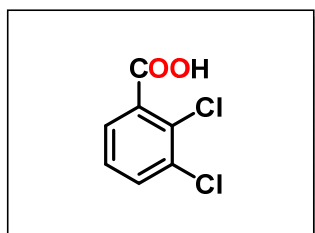


14.7 mg, 84%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.83 (d, J = 10.8 Hz, 1H), 7.79-7.71 (m, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.0, 158.7 (d, J = 246.3 Hz), 132.4 (d, J = 6.6 Hz), 131.6, 127.0 (d, J = 3.6 Hz), 125.0 (d, J = 17.1 Hz), 117.9 (d, J = 21.8 Hz). ^{19}F NMR (376 MHz, DMSO- d_6) δ -115.14, -115.16, -115.16, -115.18.

The spectroscopic data match a literature report (*Bioorg. Med Chem.* **2007**, *15*, 2198).

Compound (4u) : 2,3-dichlorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

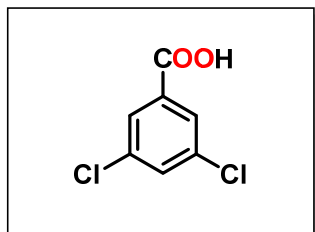


15.8 mg, 82%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.80 (dd, J = 8.0, 1.2 Hz, 1H), 7.70 (dd, J = 7.6, 1.2 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.9, 135.0, 133.3, 133.2, 131.6, 129.3, 129.0.

The spectroscopic data match a literature report (*Magn. Reson. Chem.* **2007**, *45*, 1035).

Compound (4v) : 3,5-dichlorobenzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

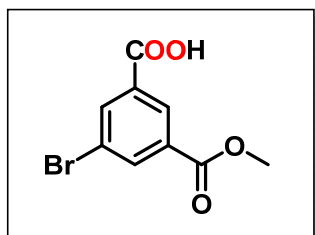


14.9 mg, 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.60 (brs, 1H), 7.92 (s, 1H), 7.87 (s, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 165.4, 135.0, 134.8, 132.7, 128.3.

The spectroscopic data match a literature report (10.1007/s10870-020-00822-9).

Compound (4w) : 3-bromo-5-(methoxycarbonyl)benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

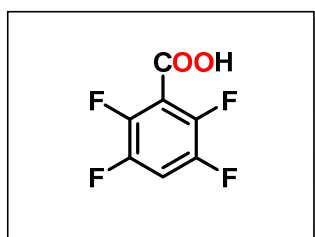


White solid. (21.8 mg, 84%); ^1H NMR (400 MHz, CD_3OD) δ 8.58 (s, 1H), 8.36-8.35 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.6, 164.8, 136.5, 135.9, 134.0, 132.6, 129.0, 122.6, 53.3.

The spectroscopic data match a literature report (*J. Am. Chem. Soc.* **2003**, *125*, 10241).

Compound (4x) : 2,3,5,6-tetrafluorobenzoic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **3x** (0.1 mmol, 16.4 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (20 mol%, 20 μL (1M CH_3CN solution)), CH_3CN (2 mL) under O_2 atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 48 hours at 60 $^\circ\text{C}$. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product.

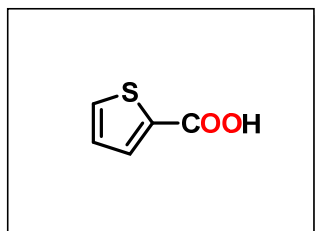


5.1 mg, 27%. ^1H NMR (400 MHz, D_2O) δ 7.29 (tt, J = 10.4, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, D_2O) δ 166.3, 146.7-144.3 (dm, J = 245.5), 143.2-140.7 (J = 247.5), 119.9 (t, J = 22.4 Hz), 105.92 (t, J = 23.1 Hz). ^{19}F NMR (377 MHz, D_2O) δ -139.04 ~ -139.26 (m), -144.85 ~ -145.15 (m).

The spectroscopic data match a literature report (*Organic Electronics*. **2017**, *44*, 85).

Compound (6a) : thiophene-2-carboxylic acid.

Procedure : The title compound was synthesized via General Procedure at 25 $^\circ\text{C}$ for 24 hours.

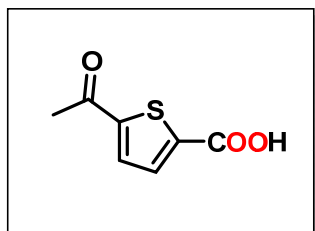


5.6 mg, 44%. ^1H NMR (400 MHz, DMSO-d_6) δ 13.06 (brs, 1H), 7.89 (d, J = 5.2 Hz, 1H), 7.73 (d, J = 3.6 Hz, 1H), 7.19-7.17 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 135.1, 133.8, 133.7, 128.7.

The spectroscopic data match a literature report (*Green Chem.* **2020**, *22*, 4357).

Compound (6b) : 5-acetylthiophene-2-carboxylic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **5b** (0.1 mmol, 14.0 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 30 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

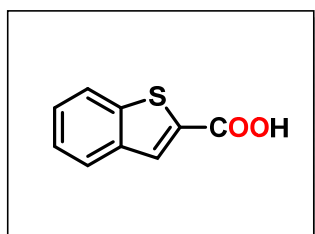


13.9 mg, 81%. ¹H NMR (400 MHz, DMSO-d₆) δ 7.74 (d, *J* = 3.6 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆) δ 192.0, 163.0, 148.7, 141.3, 134.2, 134.1, 27.3.

The spectroscopic data match a literature report (*Chem. 2020*, 6, 2658).

Compound (6c) : benzo[*b*]thiophene-2-carboxylic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **5c** (0.1 mmol, 14.8 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 30 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

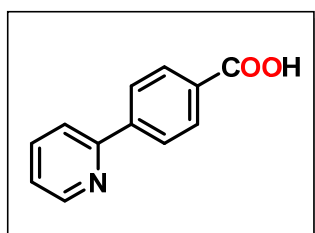


13.1 mg, 74%. ¹H NMR (400 MHz, D₂O) δ 8.31 (dd, *J* = 5.6, 2.8 Hz, 1H), 8.06-8.03 (m, 4H). ¹³C NMR (100 MHz, D₂O) δ 172.8, 139.6, 132.4, 132.3, 131.8, 131.0, 128.7, 127.9.

The spectroscopic data match a literature report (*Chem. Commun. 2014*, 50, 12859).

Compound (6d) : 4-(pyridin-2-yl)benzoic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.



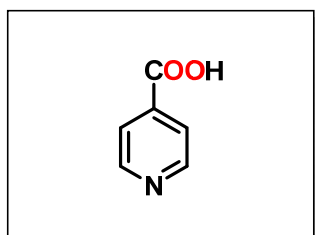
14.1 mg, 71%. ¹H NMR (400 MHz, DMSO-d₆) δ 8.80 (d, *J* = 5.2 Hz, 1H), 8.22-8.20 (m, 4H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 9.2, 4.4 Hz, 1H). ¹³C NMR (100 MHz, DMSO-d₆) δ 167.3, 153.6, 147.6, 141.4, 140.1, 132.4, 130.3, 127.9, 124.9, 123.3.

The spectroscopic data match a literature report (*J. Org.*

Chem. **2018**, 83, 15486).

Compound (6e) : isonicotinic acid.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **5e** (0.1 mmol, 9.3 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 60 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by washing with acetonitrile to give the corresponding product.

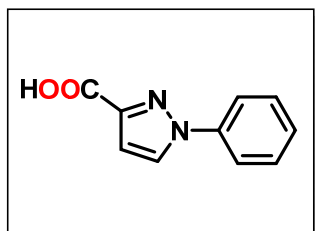


6.6 mg, 54%. ¹H NMR (400 MHz, DMSO-d₆) δ 8.78 (d, *J* = 5.2 Hz, 2H), 7.81 (d, *J* = 6.0 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ 166.7, 151.1, 138.5, 123.2.

The spectroscopic data match a literature report (*Green Chem.* **2018**, 20, 3038).

Compound (6f) : thiophene-2-carboxylic acid.

Procedure : The title compound was synthesized via General Procedure for 48 hours.

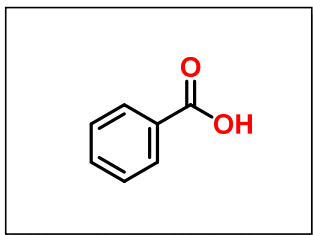


23% (NMR yield). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 1.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 1.2 Hz, 1H).

The spectroscopic data match a literature report (*Green Chem.* **2018**, 20, 3038).

Synthesis of compound 2a from 7a.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **7a** (0.1 mmol, 10.6 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

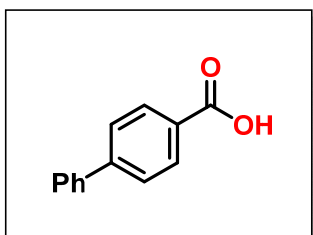


10.1 mg, 83%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 4n from 7b.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **7b** (0.1 mmol, 21.0 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 $^\circ\text{C}$. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

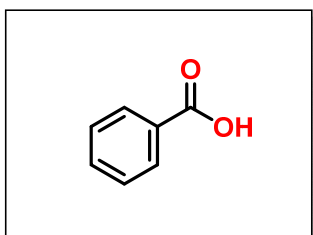


15.0 mg, 76%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.04 (brs, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.3, 144.4, 139.2, 130.1, 129.7, 129.2, 128.4, 127.1, 126.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 9a.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **9a** (0.1 mmol, 12.0 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under O_2 atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 $^\circ\text{C}$. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

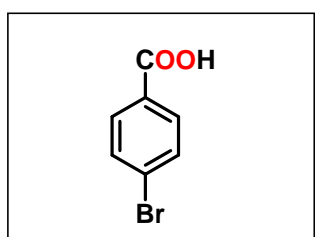


10.3 mg, 84%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 4k from 9b.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **9b** (0.1 mmol, 19.9 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

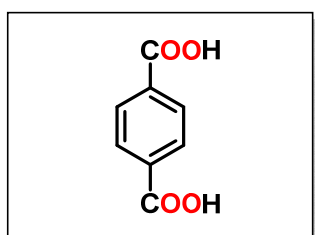


12.0 mg, 60%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.20 (brs, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ 166.7, 131.8, 131.4, 130.1, 127.0.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2d from 9c.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **9c** (0.1 mmol, 16.4 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.



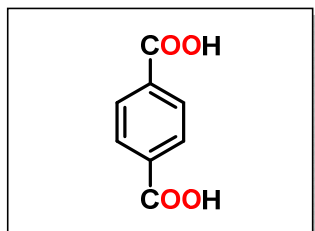
12.7 mg, 77%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.23 (brs, 2H), 8.04 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆) δ 167.2, 135.0, 129.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2d from 9d.

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **9d** (0.1 mmol, 16.2 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH 1.0 equiv, 14.9 mg), CH₃CN (2 mL) under O₂ atmosphere. The mixture was irradiated with a 390 nm LED

lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

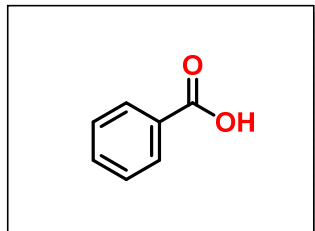


6.8 mg, 41%. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 13.23 (brs, 2H), 8.04 (s, 4H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 167.2, 135.0, 129.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 1a, 7a and 9a (1:1:1 mixture).

Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **1a** (0.1 mmol, 9.2 mg), **7a** (0.1 mmol, 10.6 mg), **9a** (0.1 mmol, 12.0 mg), CeCl_3 (5 mol%, 3.6 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 44.7 mg), CH_3CN (2 mL) under O_2 atmosphere. The mixture was irradiated with a 390 nm LED lights (40 W) for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

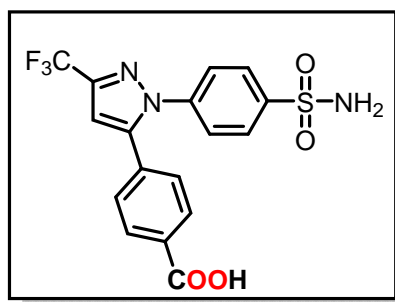


30.0 mg, 82%. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Compound (10) : Celebrex derivative.

Procedure : The title compound was synthesized via General Procedure for 24 hours and the residue was purified directly by flash column chromatography (ethyl acetate) to give the corresponding product.



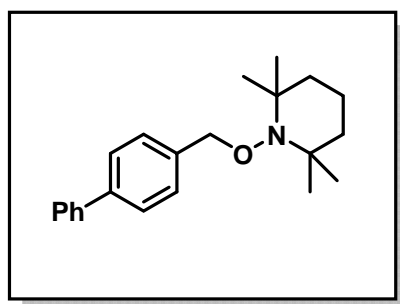
26.2 mg, 65%. $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 12.11 (brs, 1H), 7.94 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 8.8$ Hz, 2H), 7.52 (s, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.35 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 167.0, 144.6, 144.5, 142.5 (q, $J = 10.0$ Hz), 141.2, 132.6, 131.7, 130.0,

129.5, 127.3, 126.4, 120.3 (q, $J = 247.0$ Hz), 107.4. ^{19}F NMR (377 MHz, DMSO- d_6) δ -60.87.

The spectroscopic data match a literature report (10.1016/j.bioorg.2019.103110).

Compound (11) : 1-([1,1'-biphenyl]-4-ylmethoxy)-2,2,6,6-tetramethylpiperidine.

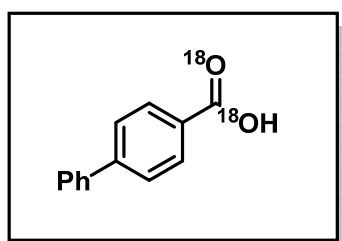
Procedure : A 25mL quartz glass tube was charged with a stirring bar, and added **3n** (0.1 mmol, 16.8 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ 1.0 equiv, 14.9 mg), CH_3CN (2 mL) under N_2 atmosphere. The mixture was irradiated with a 400 nm LED lights (10 W) for 24 hours at 60 °C. After taking out the reaction tube and freezing with liquid nitrogen. Then 3 equivalent TEMPO was added to the system. The mixture was irradiated with a 400 nm LED lights (10 W) for 12 hours at 60 °C under N_2 atmosphere. After completion of reaction as indicated by TLC. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (petroleum ether) to give the corresponding product.



^1H NMR (400 MHz, C_6D_6) δ 7.47-7.44 (m, 4H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 2.0$ Hz, 1H), 4.92 (s, 2H), 1.47 (dd, $J = 12.4, 4.8$ Hz, 3H), 1.31 (s, 9H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ 128.6, 127.8, 127.6, 127.3, 127.0, 126.9, 78.7, 59.7, 39.6, 33.0, 19.9, 17.0.

Compound (4n'): [1,1'-biphenyl]-4-carboxylic acid

Procedure: A 25mL quartz glass tube was charged with a stirring bar, and added **3n** (0.1 mmol, 16.8 mg), CeCl_3 (5 mol%, 1.2 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (20 mol%, 20 μL (1M CH_3CN solution)), CH_3CN (2 mL) under $^{18}\text{O}_2$ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C. After completion of reaction as indicated by TLC. Subsequently, ethyl acetate and water were added to extract for three times. The organic phase was concentrated under reduced pressure to give the corresponding product.

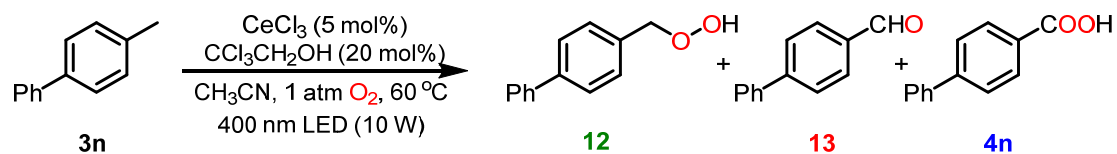


16.6 mg, 82%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.04 (brs, 1H), 8.04 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 7.2$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.3, 144.4, 139.2, 130.1, 129.7, 129.2, 128.4, 127.1,

126.9. HRMS ESI (m/z) calcd for C₁₃H₁₀¹⁸O₂ [M-H] 201.0687, Found: 201.0696.

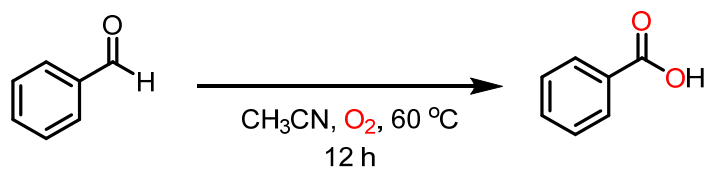
The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Kinetic experiments.



A 25mL quartz glass tube was charged with a stirring bar, and added **3n** (0.1 mmol, 16.8 mg), CeCl₃ (5 mol%, 1.2 mg), CCl₃CH₂OH (20 mol%, 20 μL (1M CH₃CN solution)), CH₃CN (2 mL) under O₂ atmosphere. The tube was perpendicular to a 400 nm LED light (10 W), and the mixture was stirred under the irradiation of blue light for 24 hours at 60 °C and measured the NMRs every 2 h.

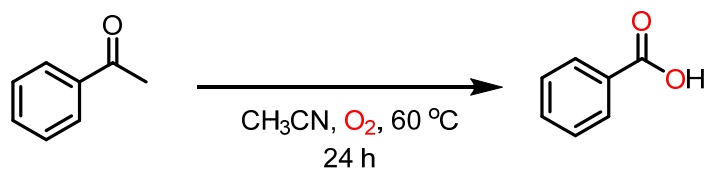
Benzaldehyde oxidation reaction



entry	CeCl ₃	CCl ₃ CH ₂ OH	400 nm	yield (%) ^b
1	5%	20%	✓	92
2	5%	20%	✗	N.R.
3	✗	20%	✓	86
4	5%	✗	✓	88
5	✗	✗	✓	95

^bThe yield was determined based on ¹H NMR with CH₂Br₂ as a standard internal compound.

Acetophenone oxidation reaction

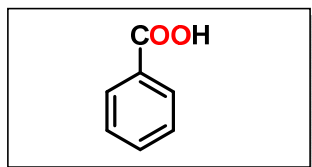


entry	CeCl ₃	CCl ₃ CH ₂ OH	<i>hν</i>	yield (%) ^b
1	5%	20%	✓	85
2	5%	20%	✗	N.R.
3	✗	20%	✓	N.R.
4	5%	✗	✓	N.R.
5	✗	✗	✓	N.R.

^bThe yield was determined based on ¹H NMR with CH₂Br₂ as a standard internal compound.

Synthesis of compound 2a from 14

Procedure : The title compound was synthesized via General Procedure for 24 hours.

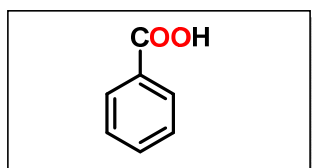


9.5 mg, 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 15

Procedure : The title compound was synthesized via General Procedure for 24 hours.

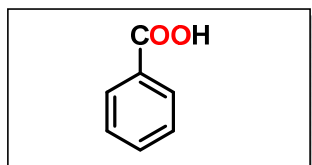


9.3 mg, 76%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 16

Procedure : The title compound was synthesized via General Procedure for 24 hours.

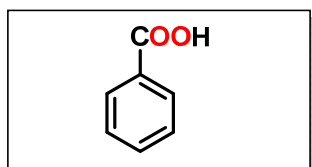


7.4 mg, 61%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 17

Procedure : The title compound was synthesized via General Procedure for 24 hours.

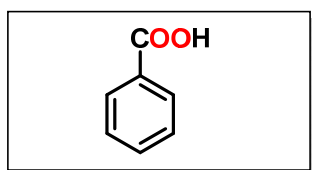


8.8 mg, 72%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

Synthesis of compound 2a from 18

Procedure : The title compound was synthesized via General Procedure for 24 hours.

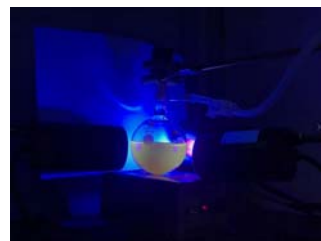
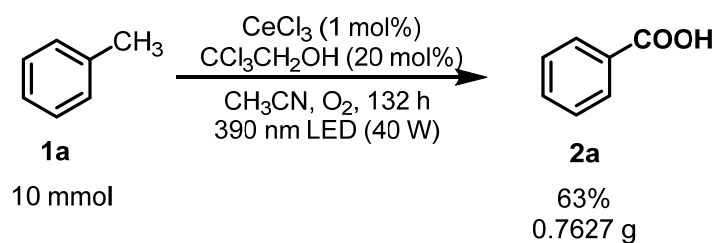


10.0 mg, 82%. ^1H NMR (400 MHz, DMSO- d_6) δ 12.95 (brs, 1H), 7.96-7.93 (m, 2H), 7.64-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9.

The spectroscopic data match a literature report (*Green Chem.* **2018**, *20*, 3038).

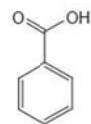
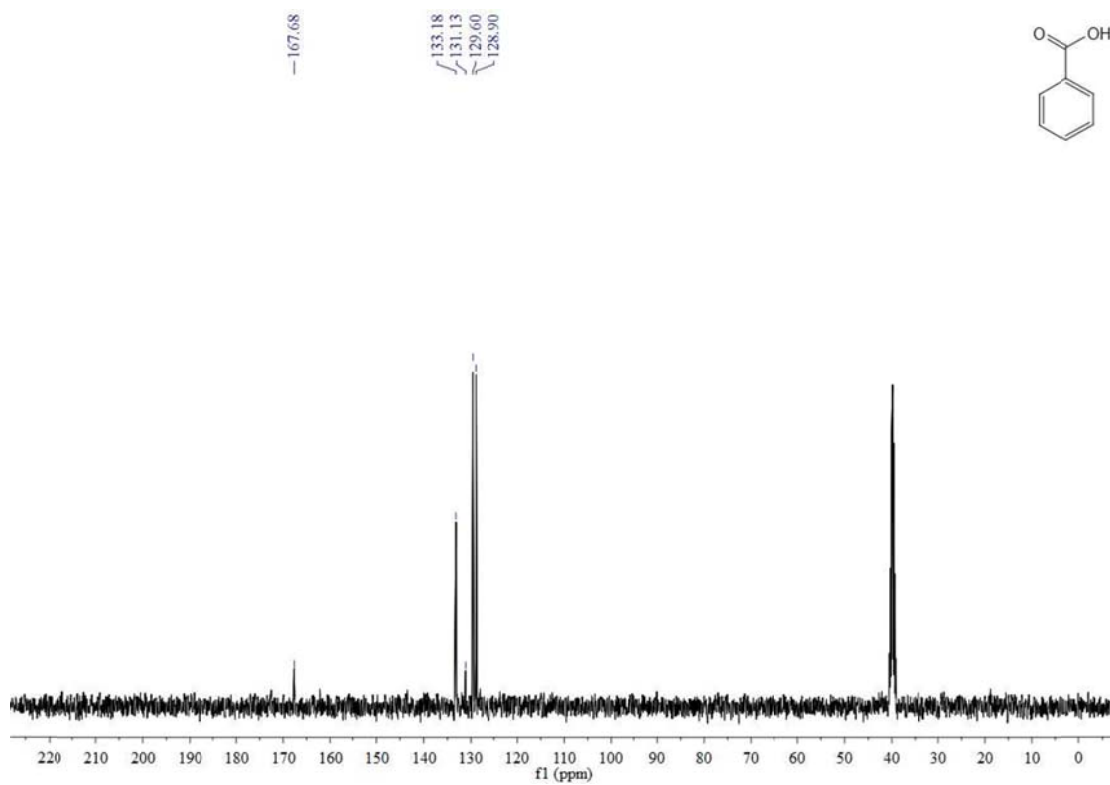
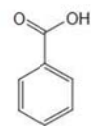
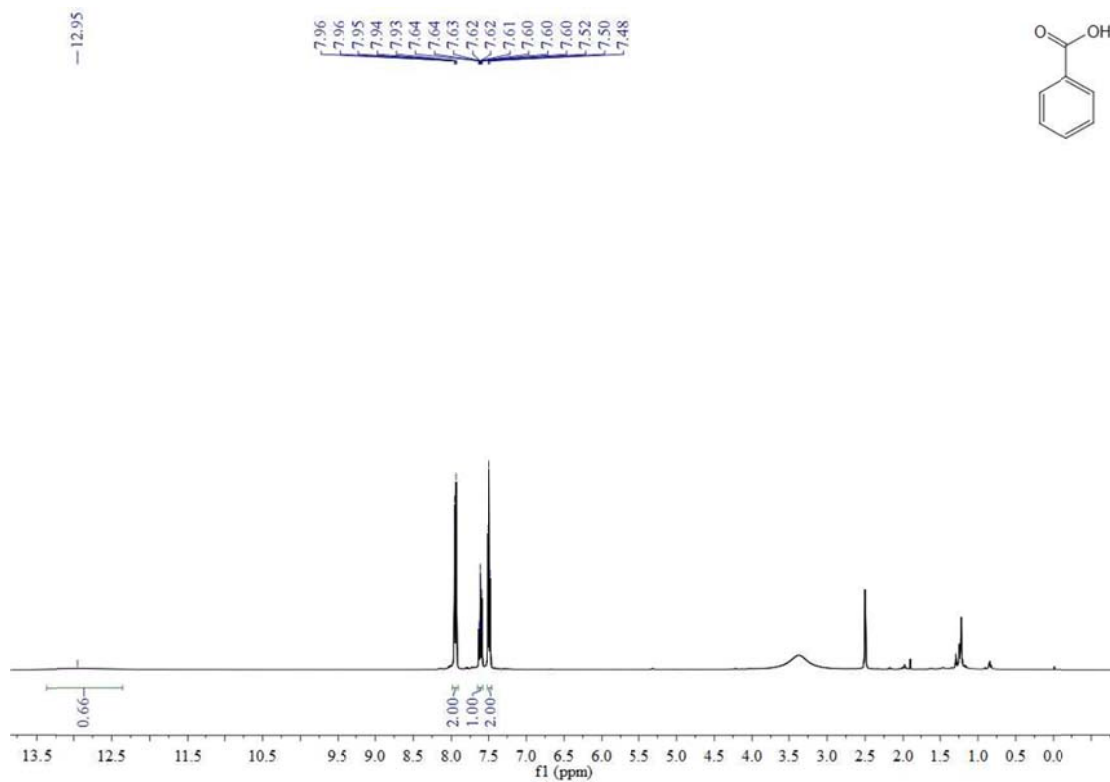
Gram-scale reaction

To evaluate the scalability of the developed protocol, we performed a gram-scale reaction. In a 10 mmol scale reaction, a 250 mL round bottom flask was charged with a stirring bar, and added reagent **1a** (10 mmol, 920 mg), CeCl_3 (1 mol%, 25 mg), $\text{CCl}_3\text{CH}_2\text{OH}$ (20 mol%, 298 mg), CH_3CN (100 mL) under O_2 atmosphere. The mixture was stirred under the irradiation of 390 nm LEDs for 132 hours to obtain the desired product **2a** in 63% isolated yield.



(V) Spectral data for compounds

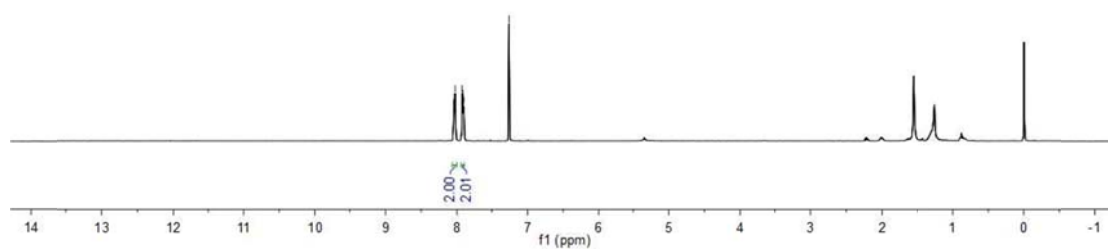
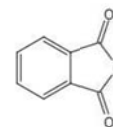
Compound (2a) : benzoic acid.



Compound (2b) : isobenzofuran-1,3-dione.

wcc-44-30
1H

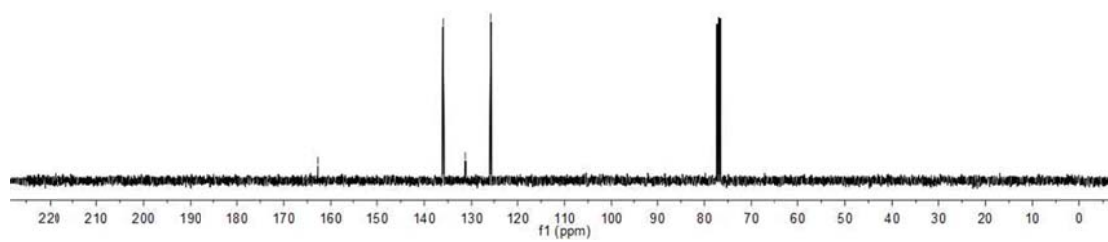
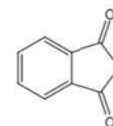
8.05
8.04
8.03
7.93
7.92
7.91
7.26



wcc-4-30-CD-1226
13C

162.75

136.01
131.32
125.70

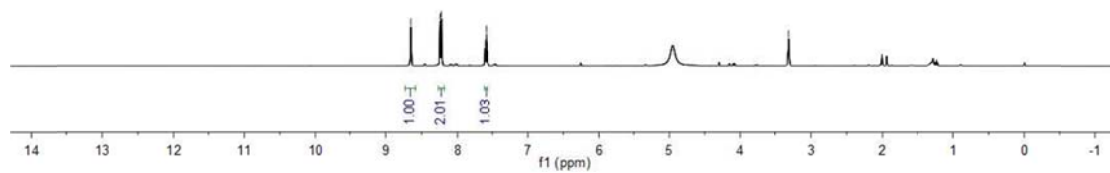
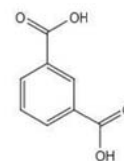


Compound (2c) : isophthalic acid.

2c wcc-6-14-CD3OH
1H

8.65
8.24
8.22
7.61
7.59
7.57

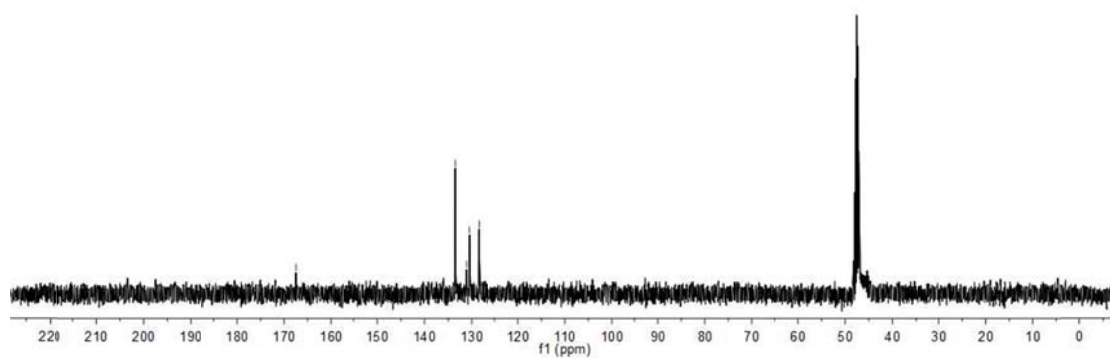
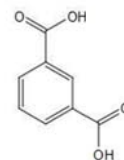
3.31



2c wcc-6-14-CD3OH
13C

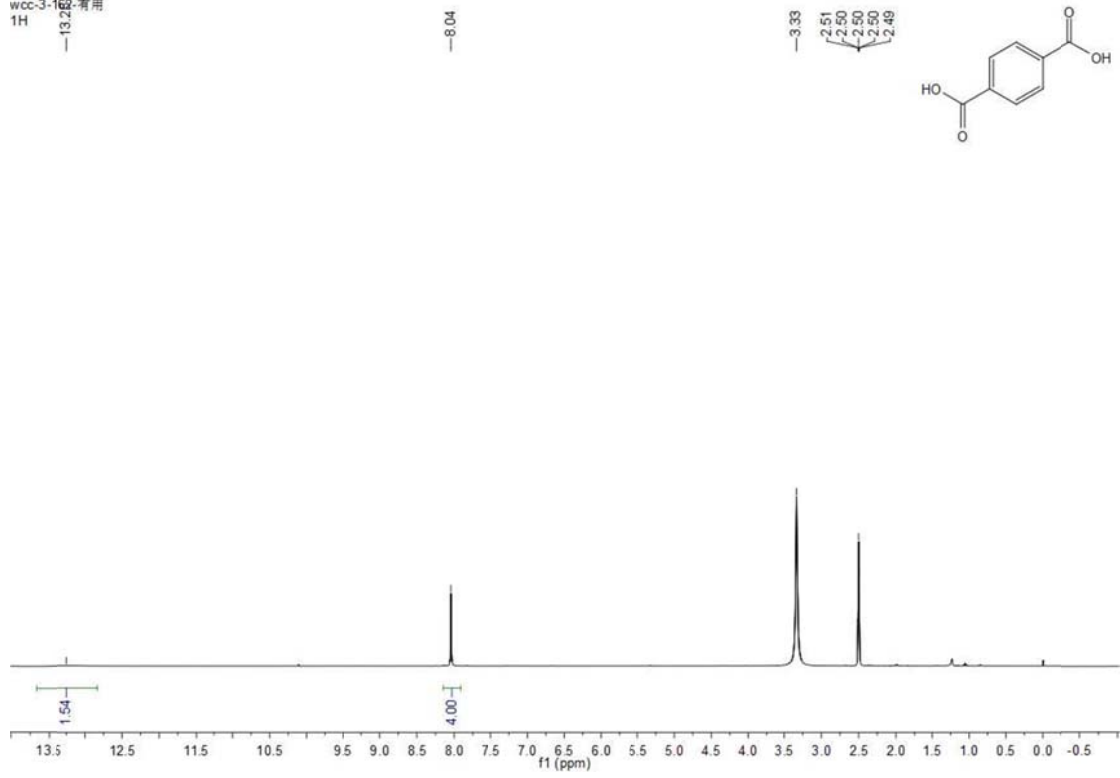
167.43

133.48
131.08
130.49
128.43

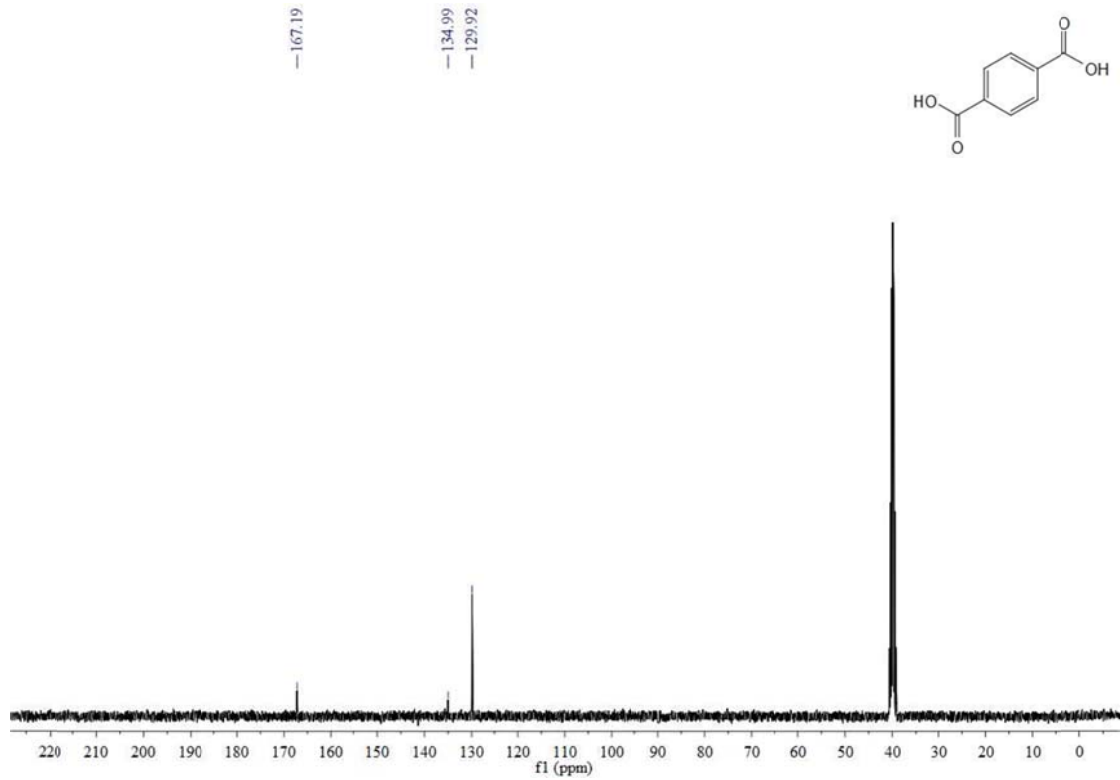


Compound (2d) : terephthalic acid.

wcc-3-162-有用
1H



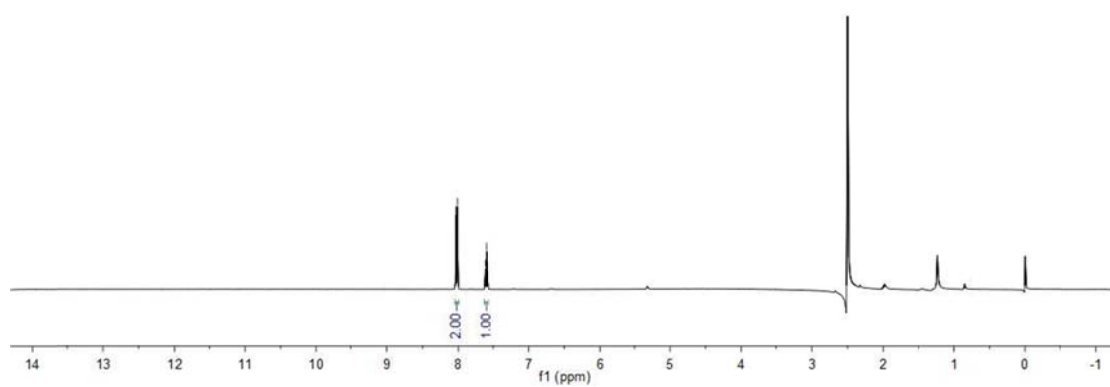
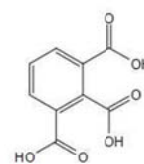
167.19
134.99
129.92



Compound (2e) : benzene-1,2,3-tricarboxylic acid.

wcc-6-11-H
1H

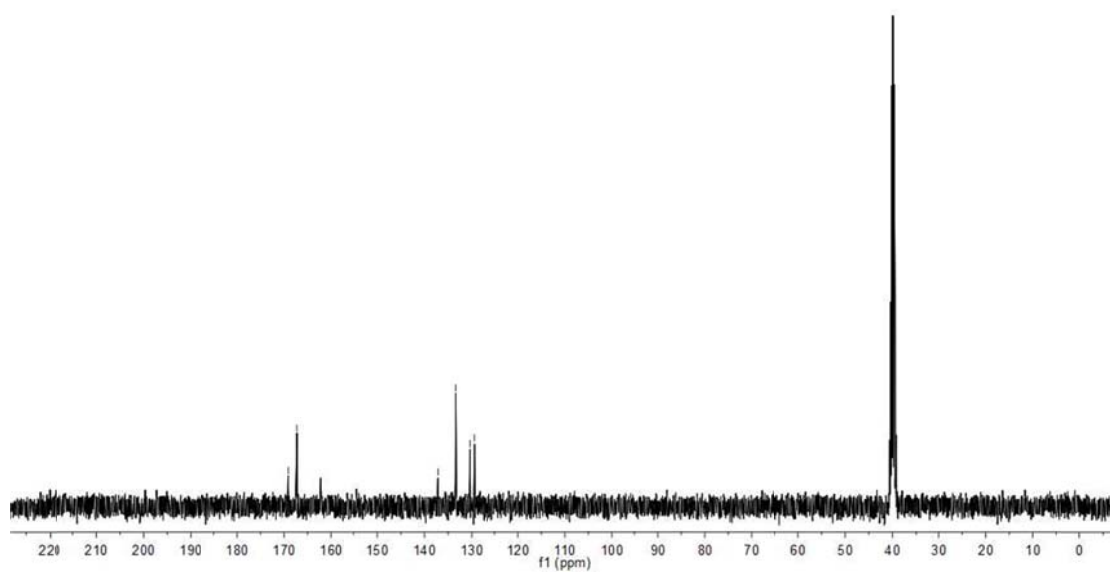
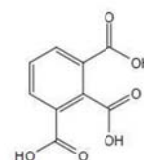
8.03
8.01
7.62
7.58



B6 wcc-6-11-1023
13C

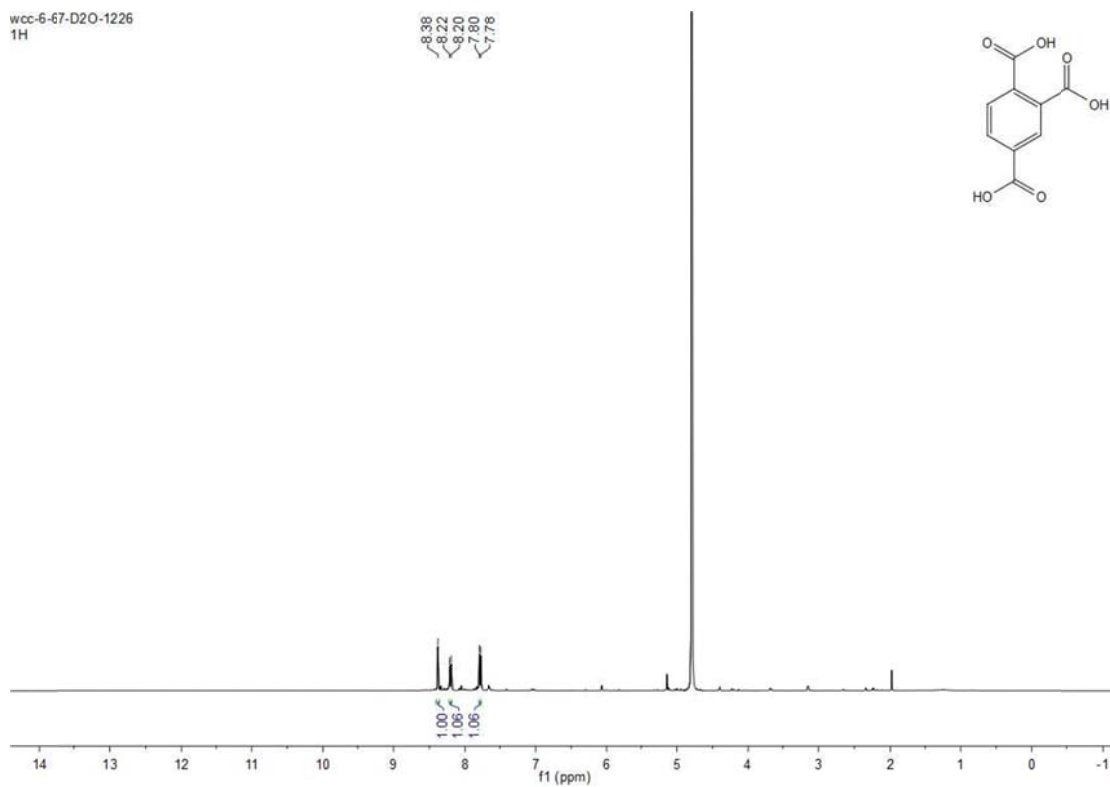
168.11
167.25

137.13
133.39
130.38
129.43

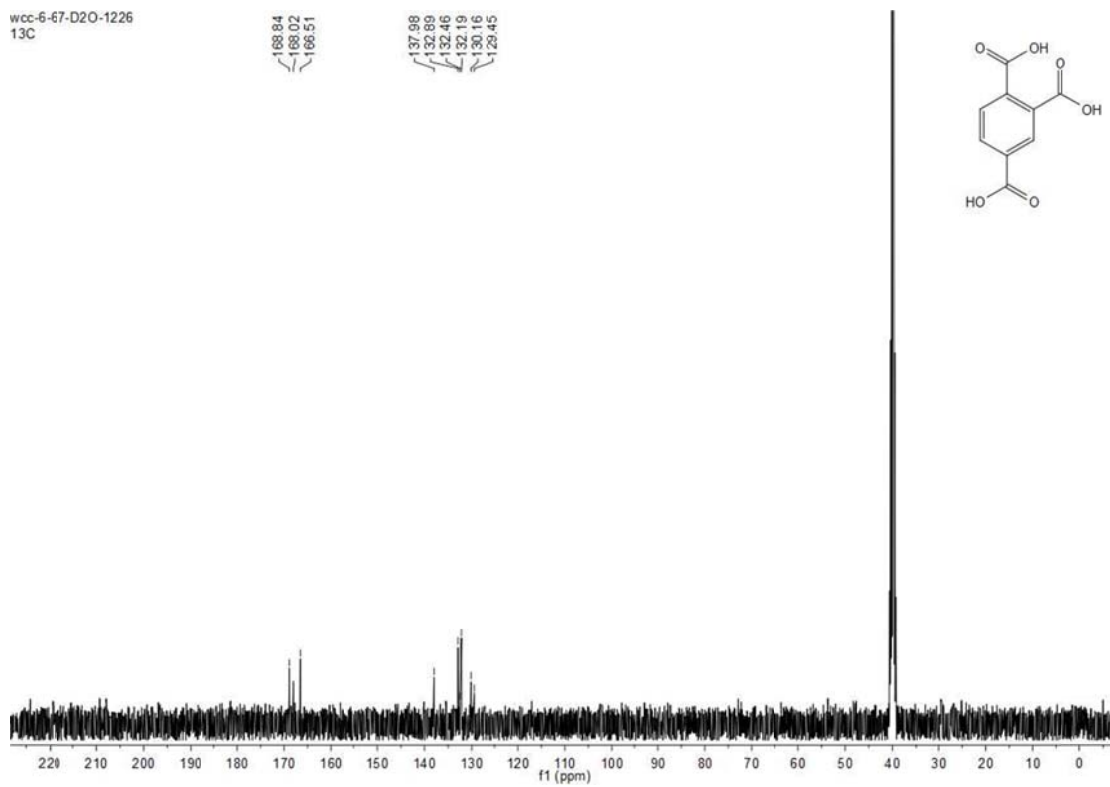


Compound (2f) : benzene-1,2,4-tricarboxylic acid.

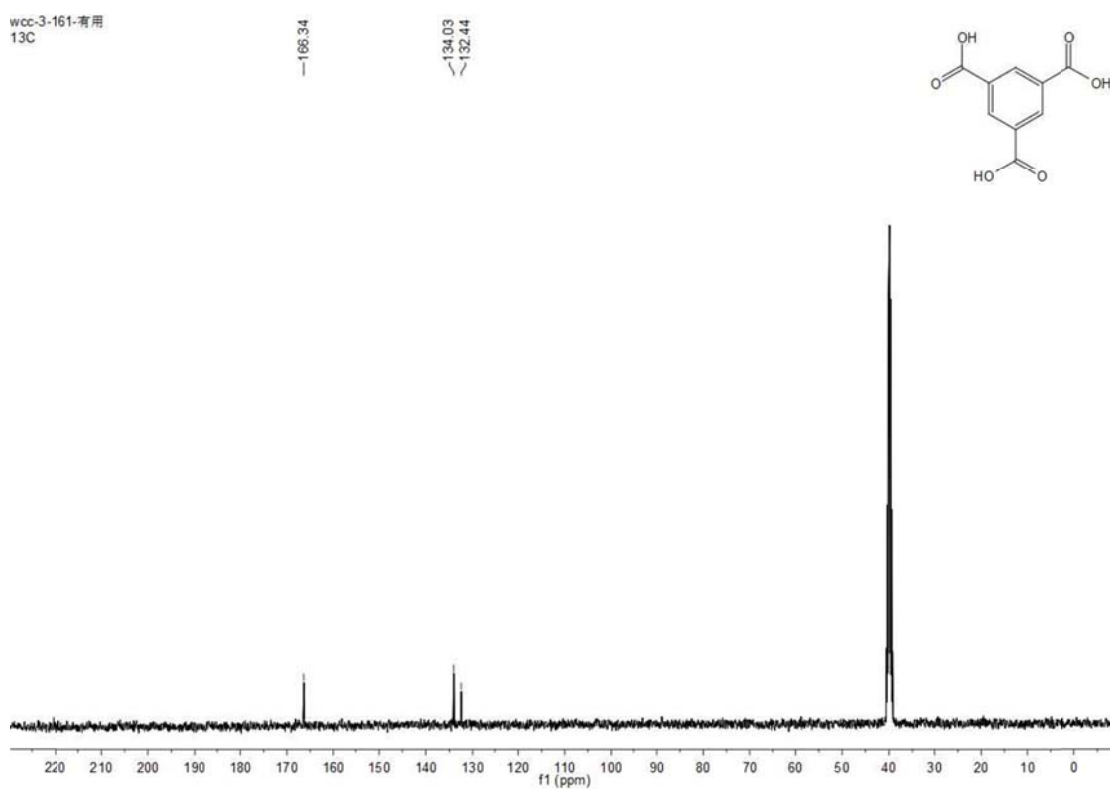
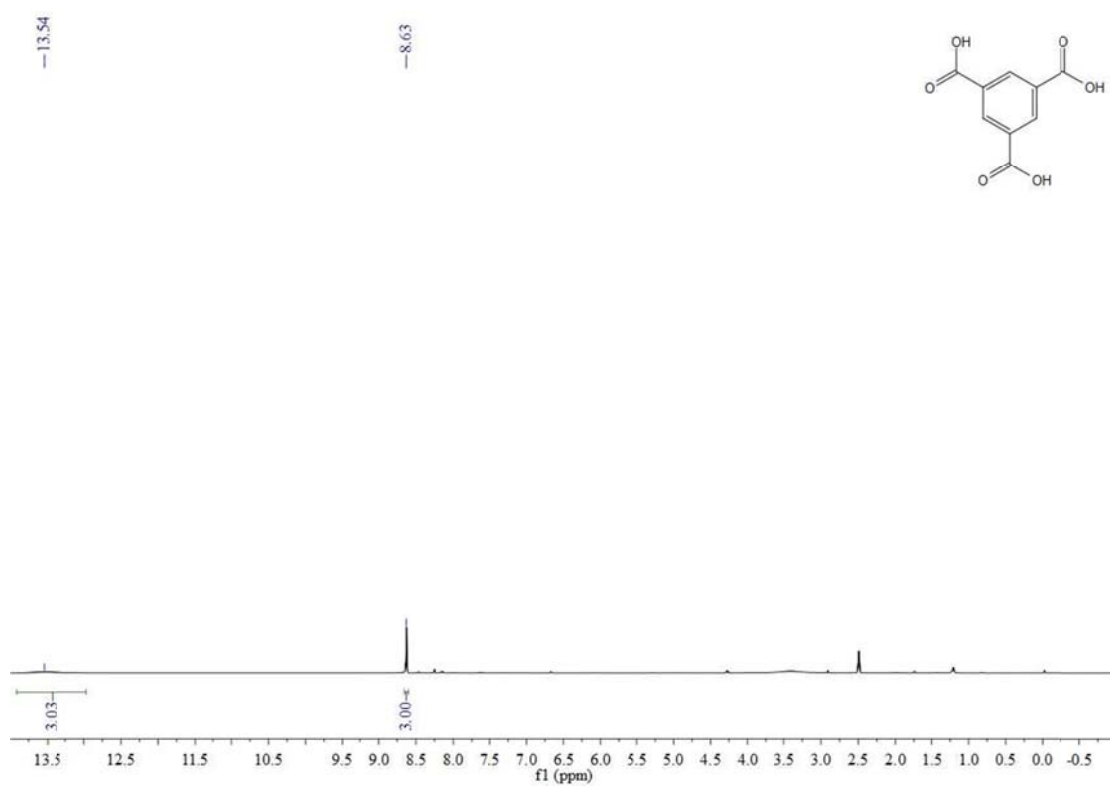
wcc-6-67-D2O-1226
1H



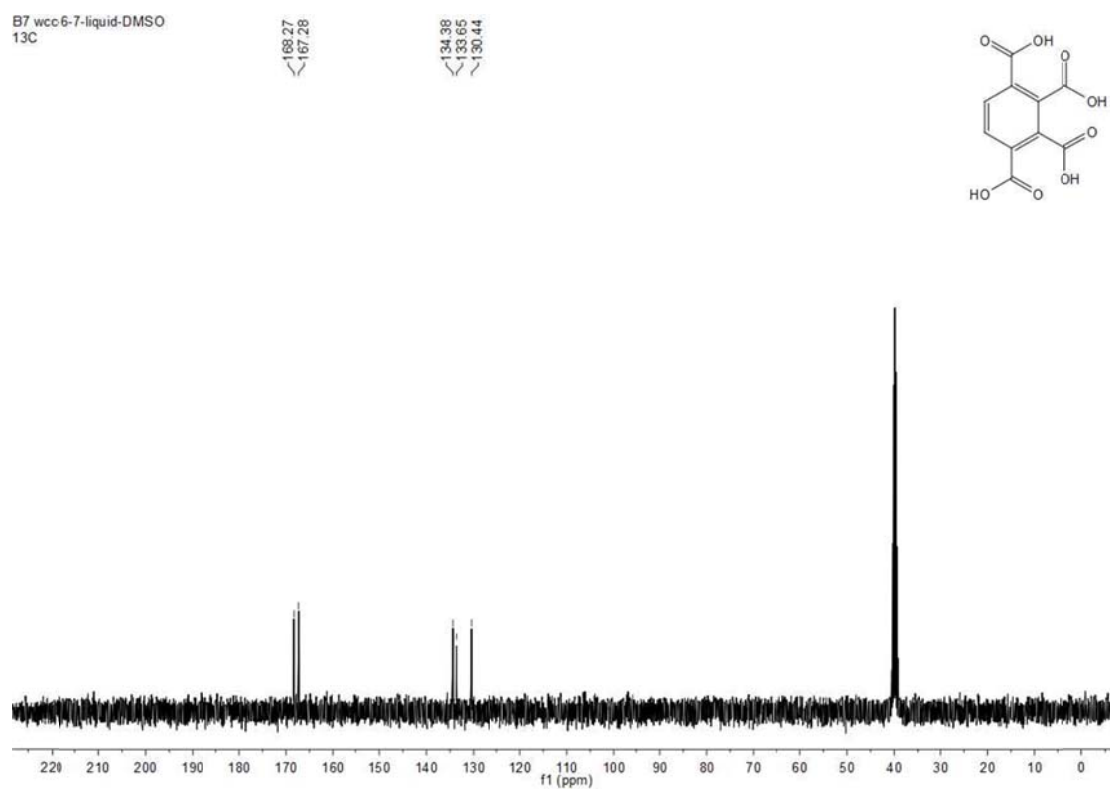
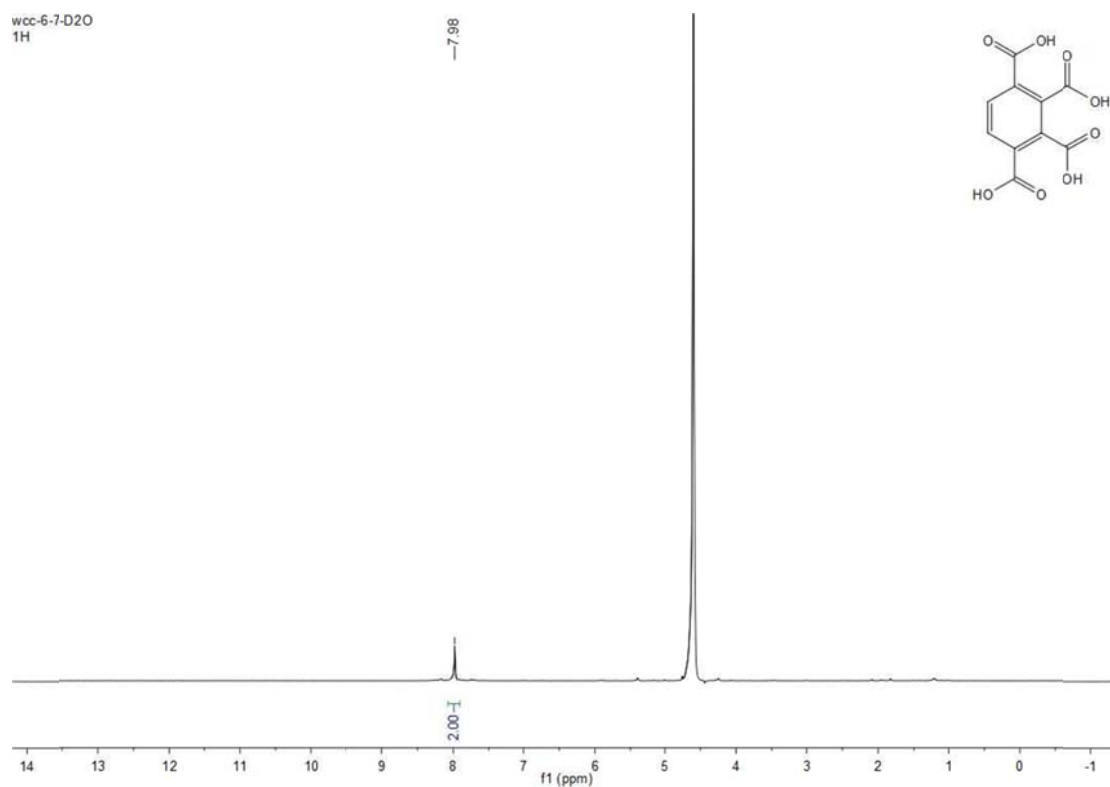
wcc-6-67-D2O-1226
13C



Compound (2g) : benzene-1,3,5-tricarboxylic acid.

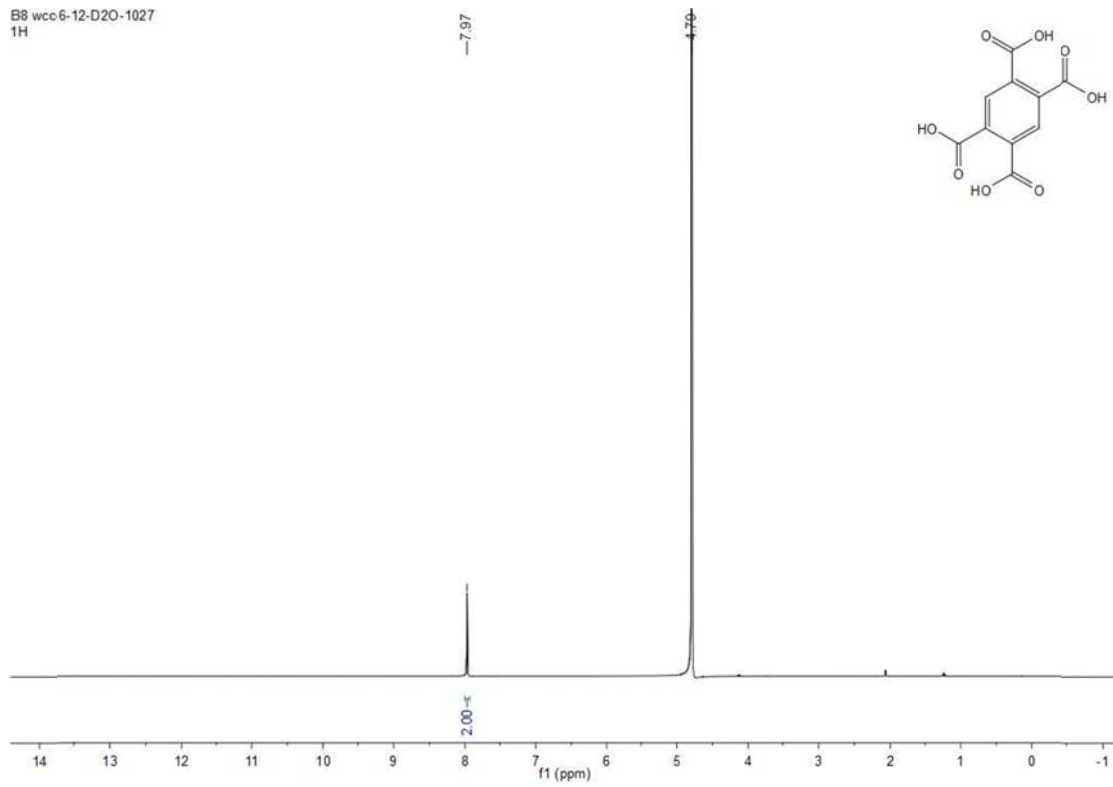


Compound (2h) : benzene-1,2,3,4-tetracarboxylic acid.

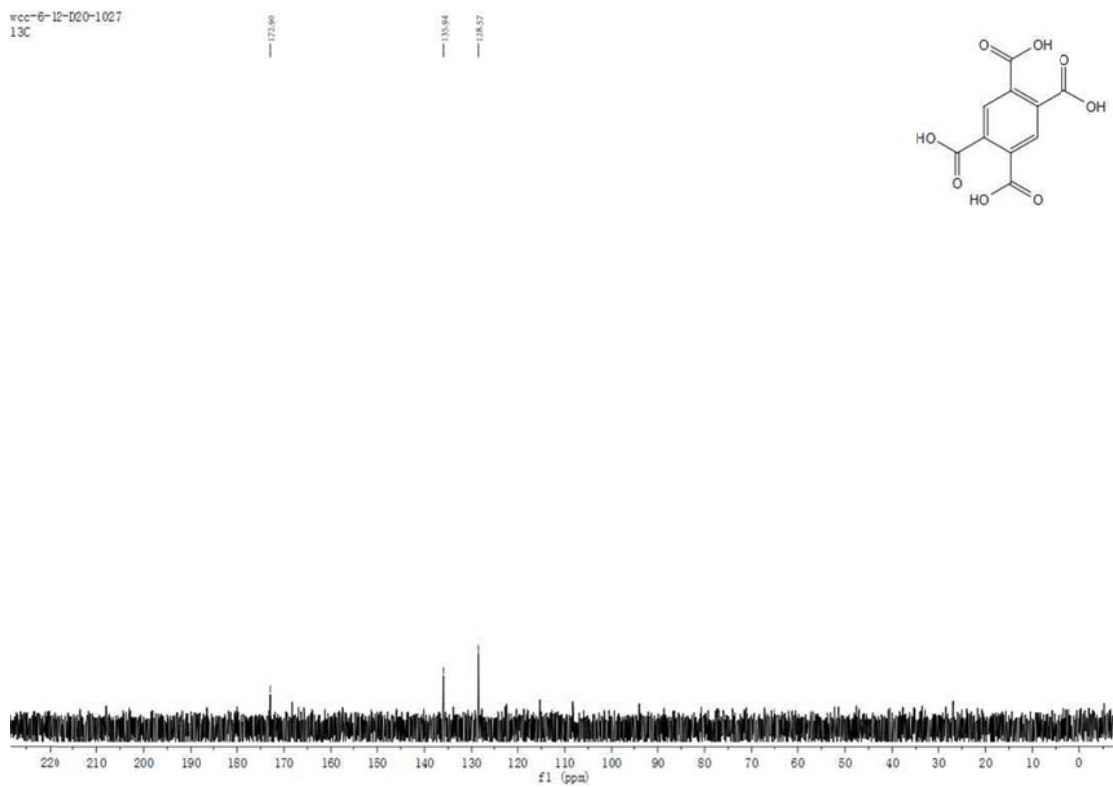


Compound (2i) : benzene-1,2,4,5-tetracarboxylic acid.

B8 wcc6-12-D2O-1027
1H

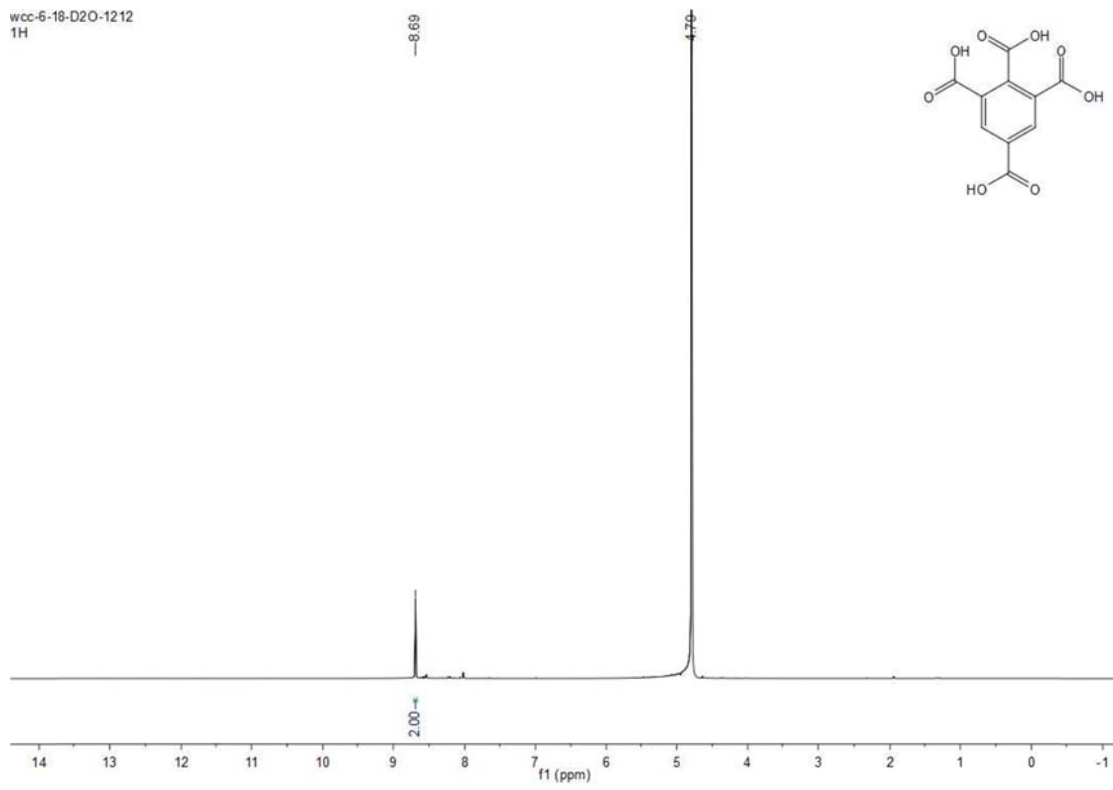


wcc-6-12-D2O-1027
13C

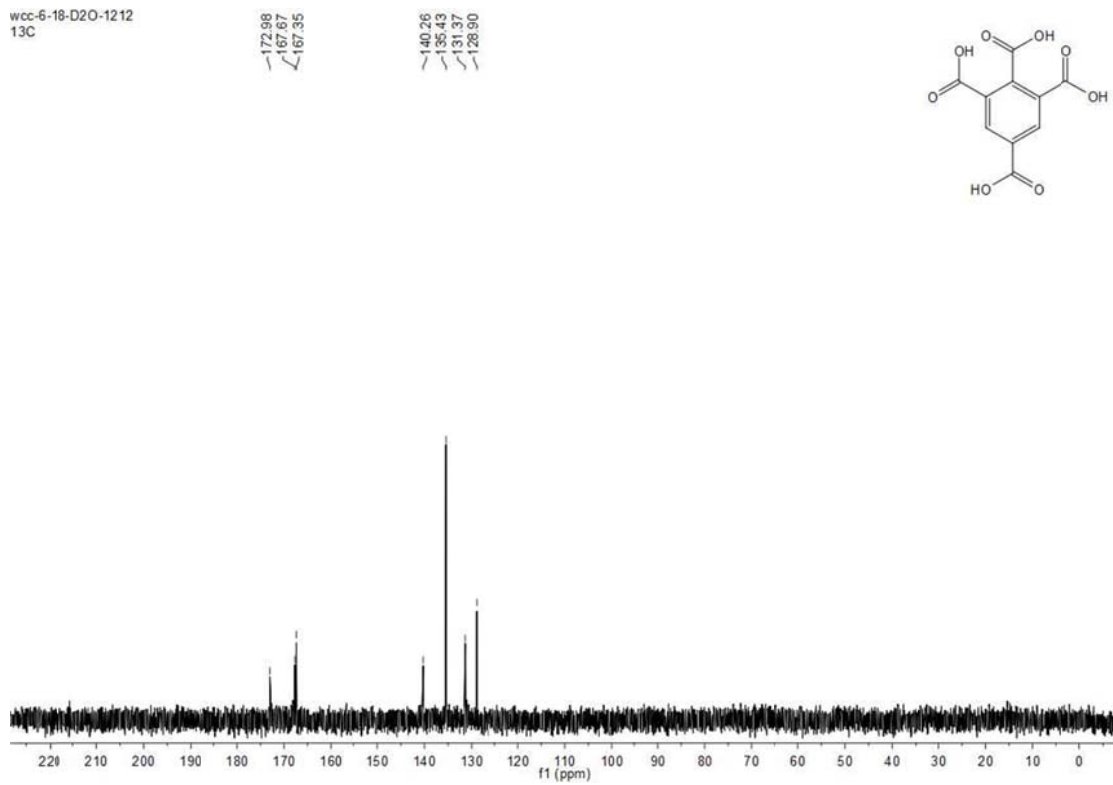


Compound (2j) : benzene-1,2,3,5-tetracarboxylic acid.

wcc-6-18-D2O-1212
1H

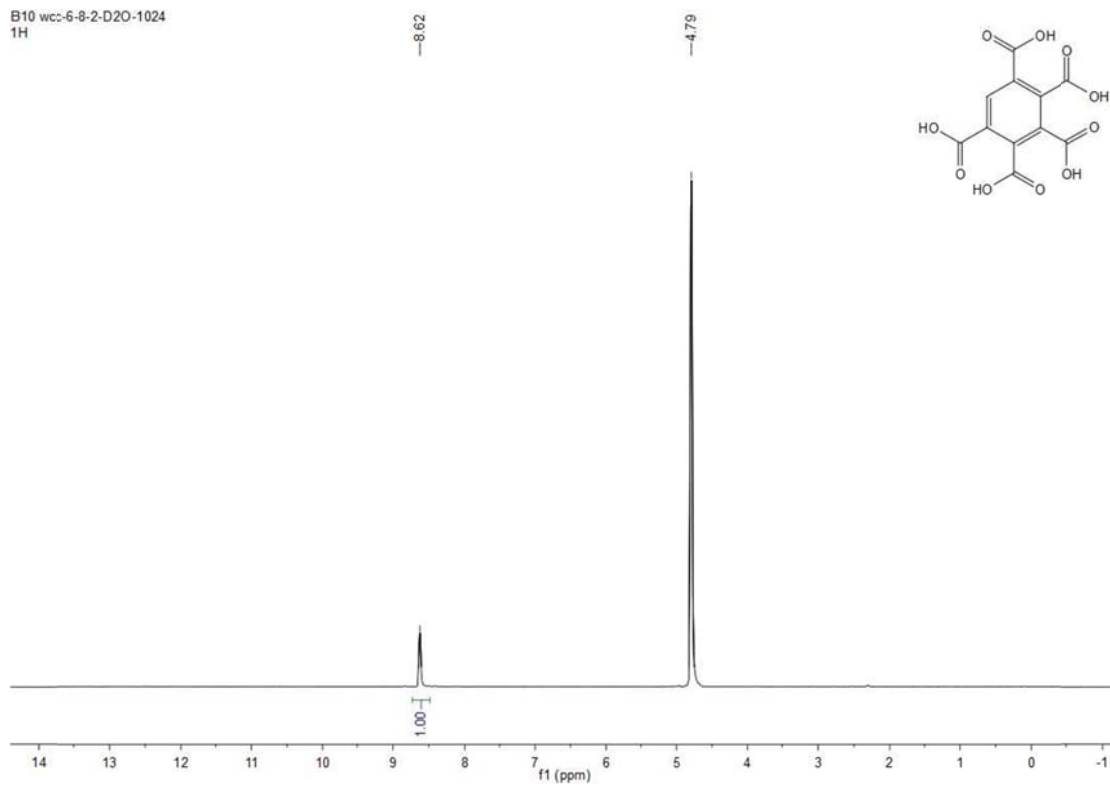


wcc-6-18-D2O-1212
13C

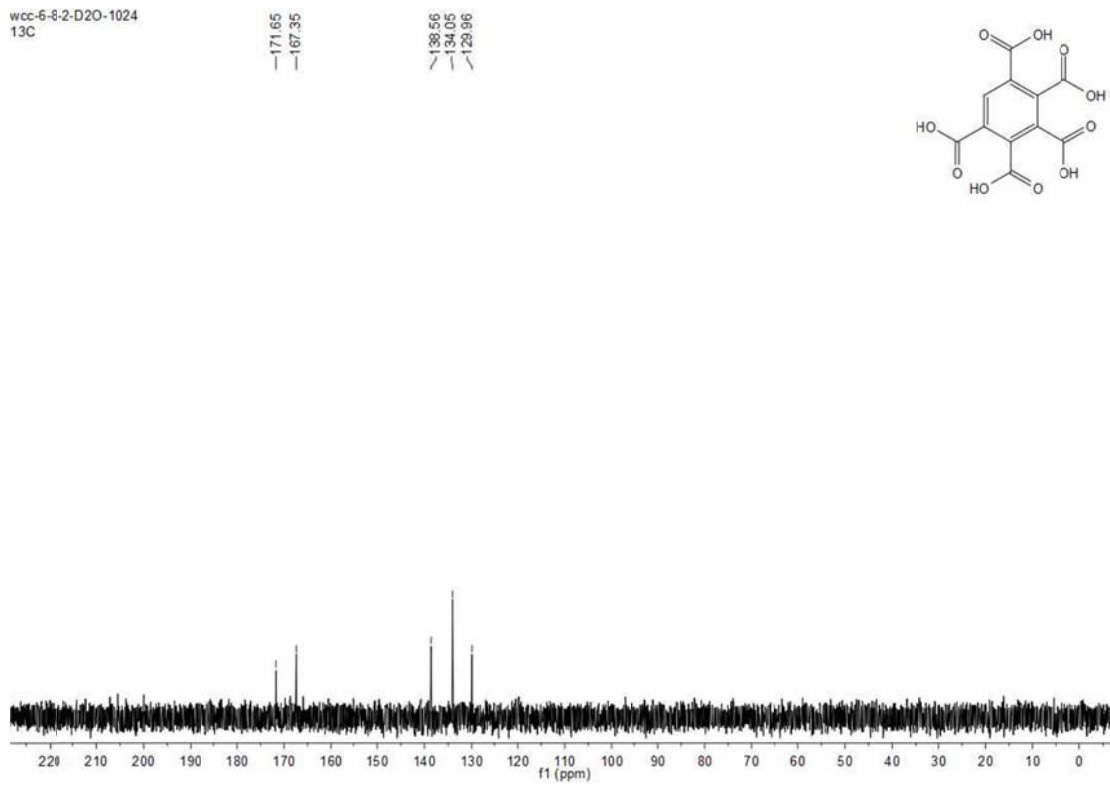


Compound (2k) : benzene-1,2,3,4,5-pentacarboxylic acid.

B10 wcc-6-8-2-D20-1024
1H

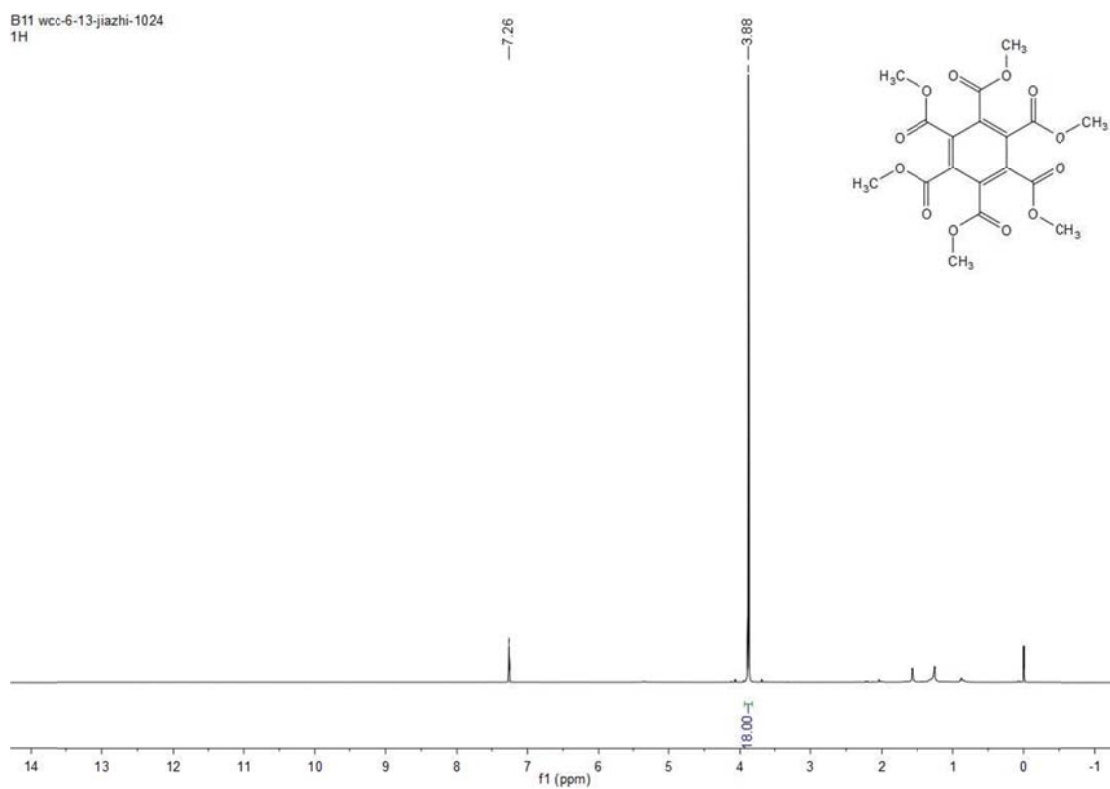


wcc-6-8-2-D20-1024
13C

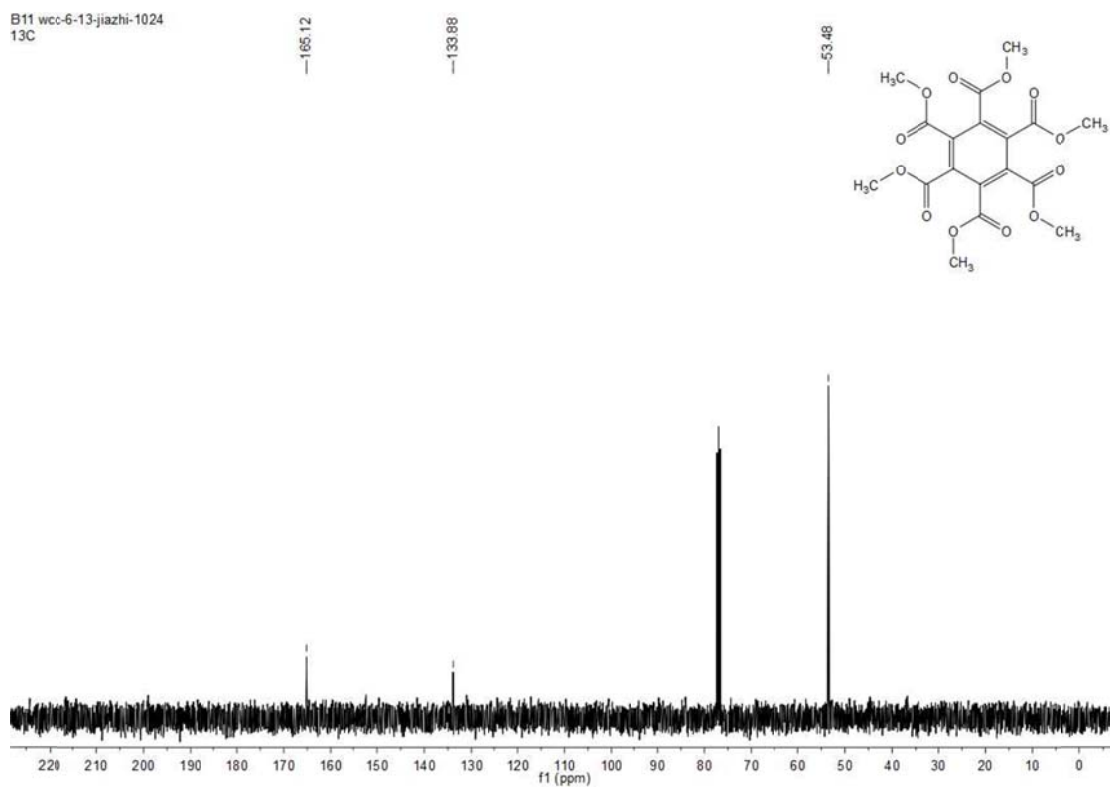


Compound (2l) : benzene-1,2,3,4,5,6-hexacarboxylic acid.

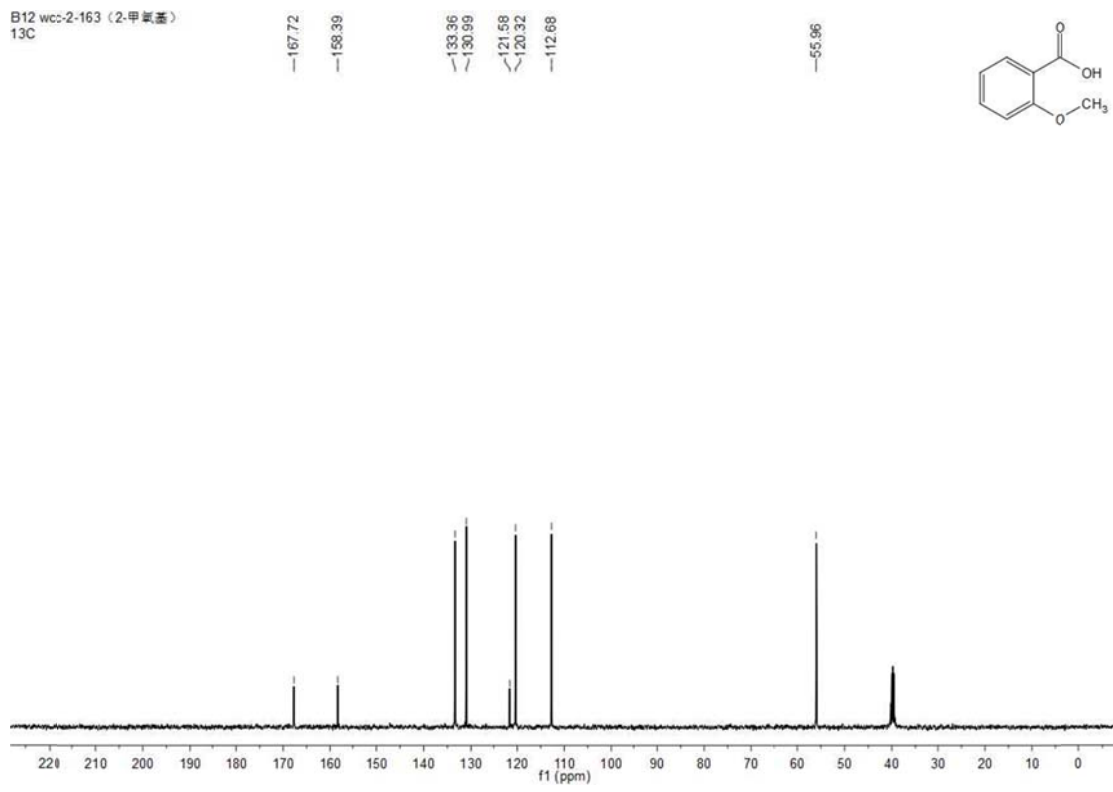
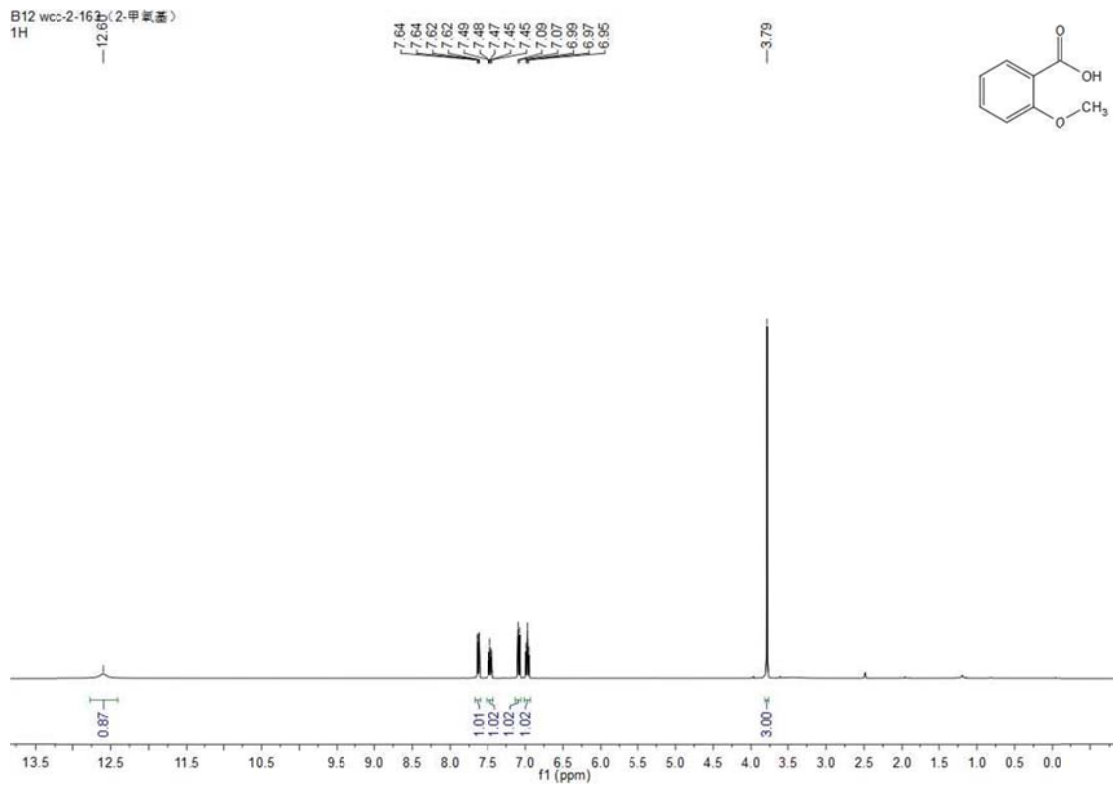
B11 wcc-6-13-jiazhi-1024
1H



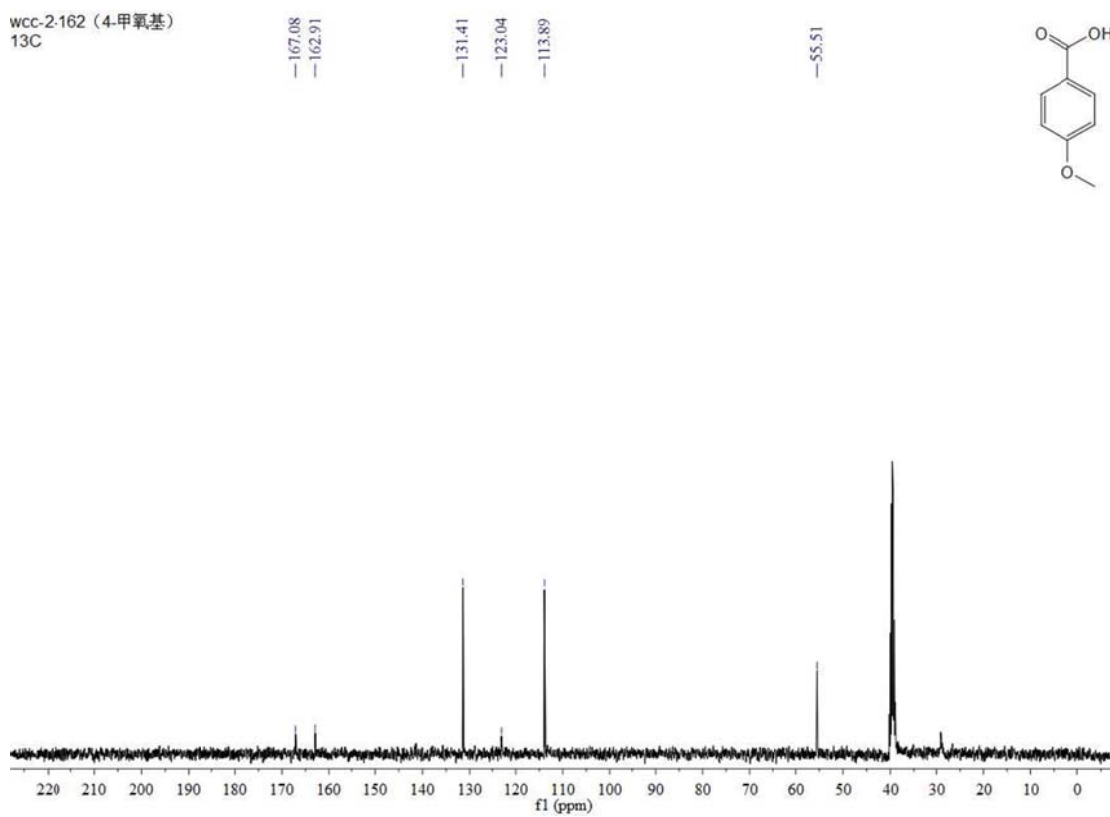
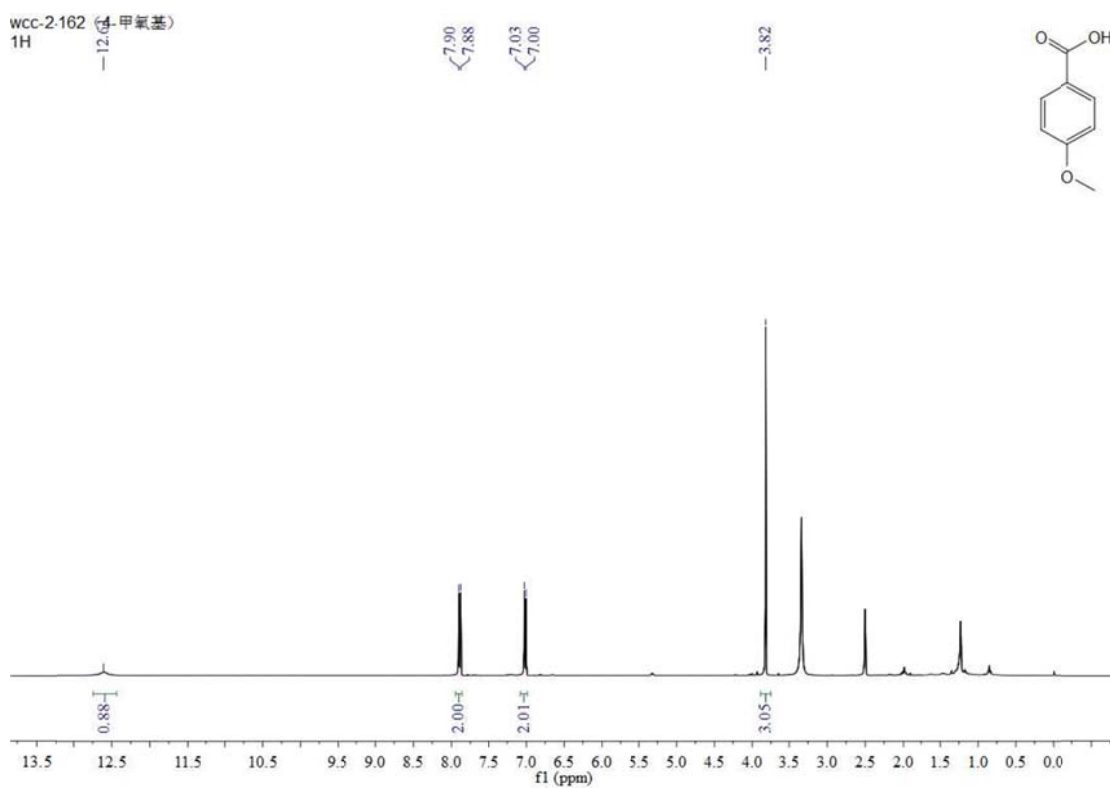
B11 wcc-6-13-jiazhi-1024
13C



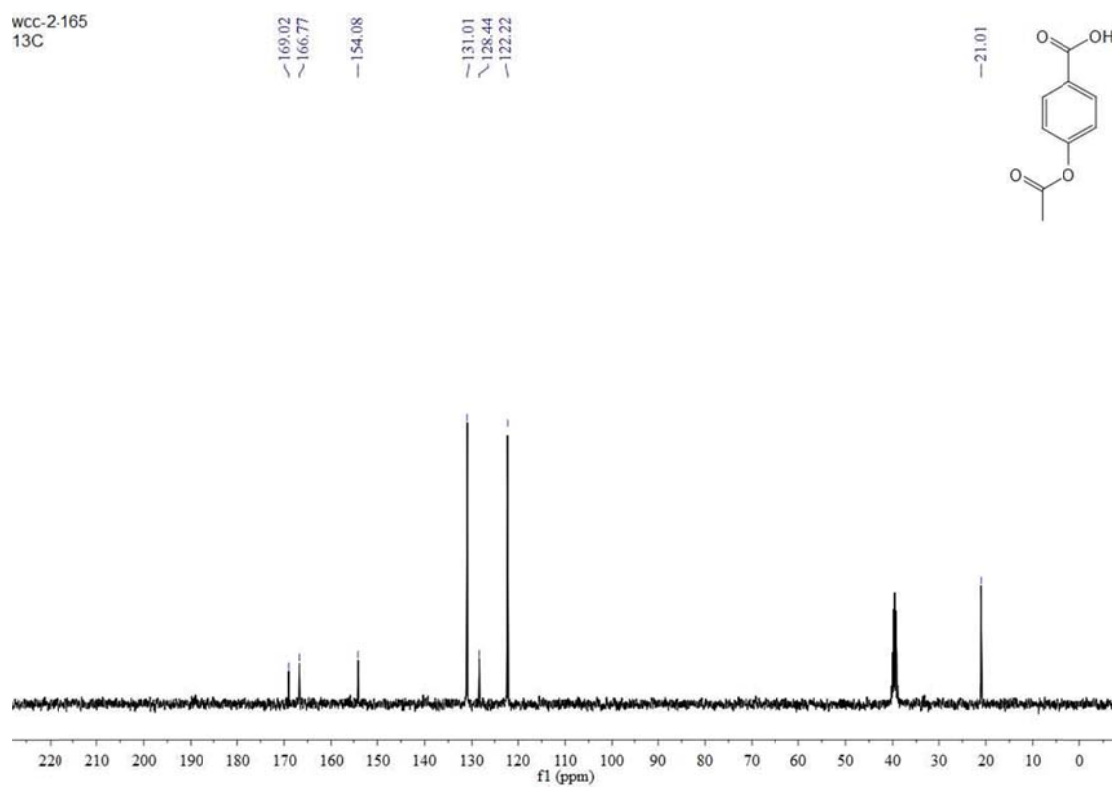
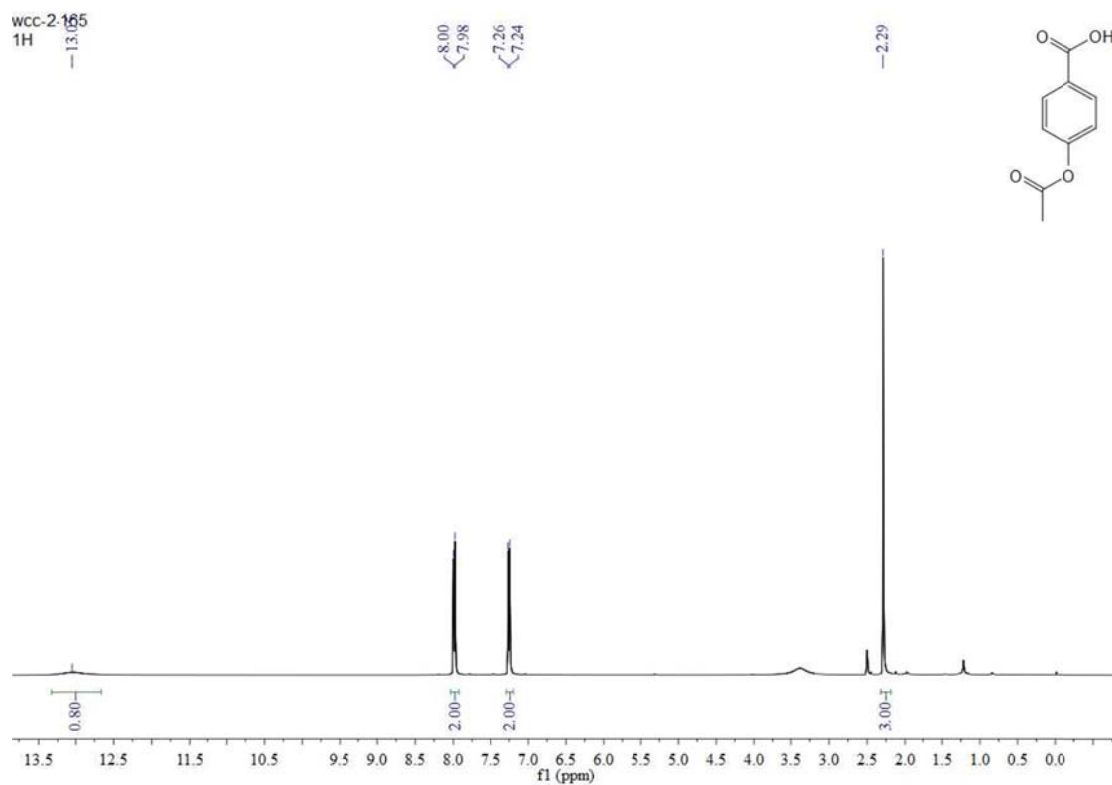
Compound (4a) : 2-methoxybenzoic acid.



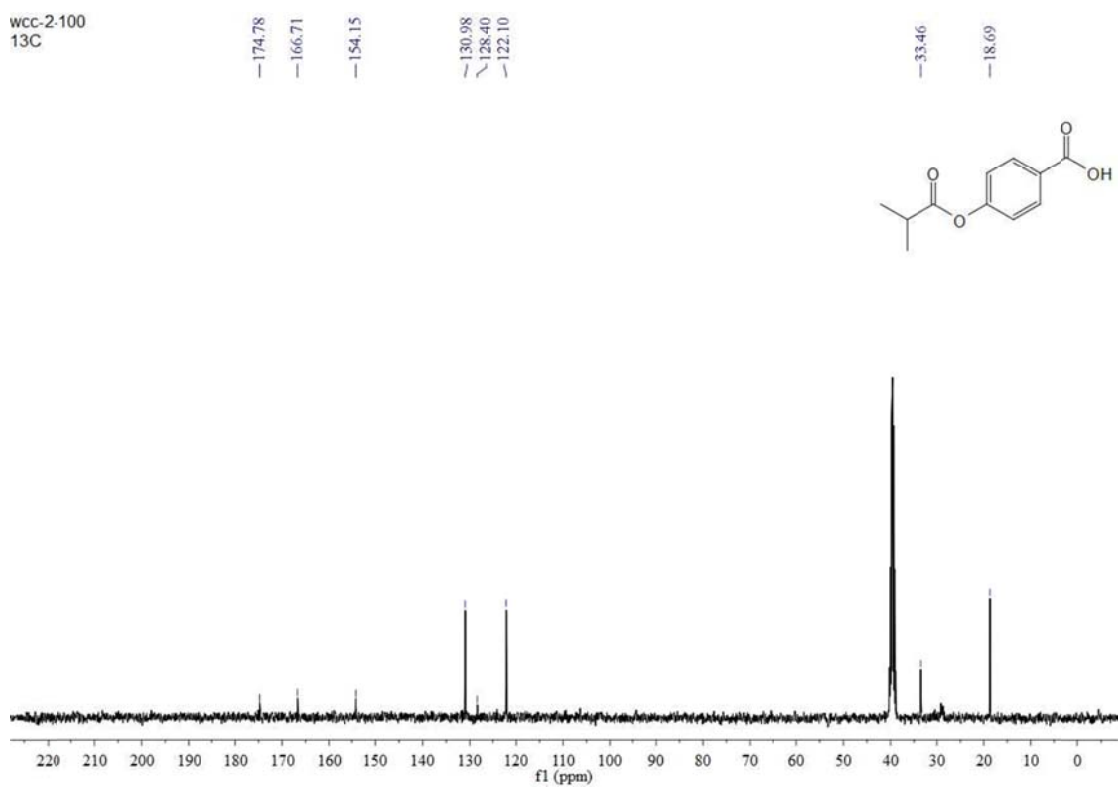
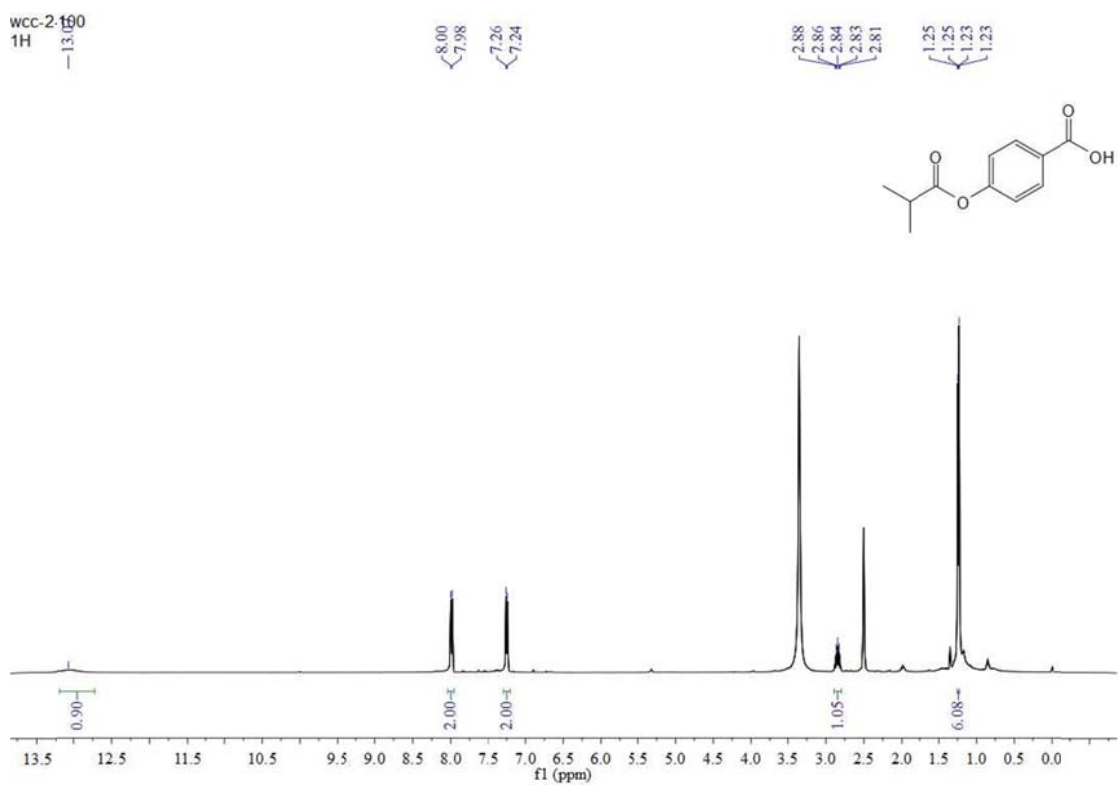
Compound (4b) : 4-methoxybenzoic acid.



Compound (4c) : 4-acetoxybenzoic acid.



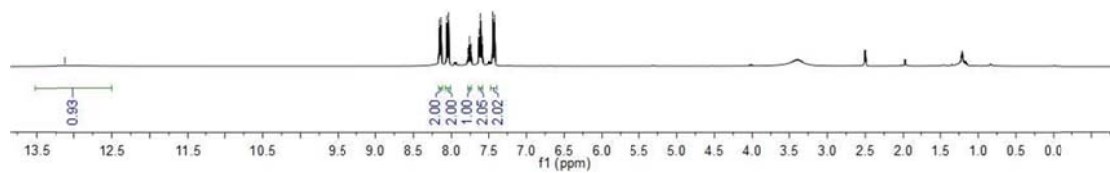
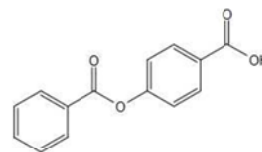
Compound (4d) : 4-(isobutyryloxy)benzoic acid.



Compound (4e) : 4-(benzoyloxy)benzoic acid.

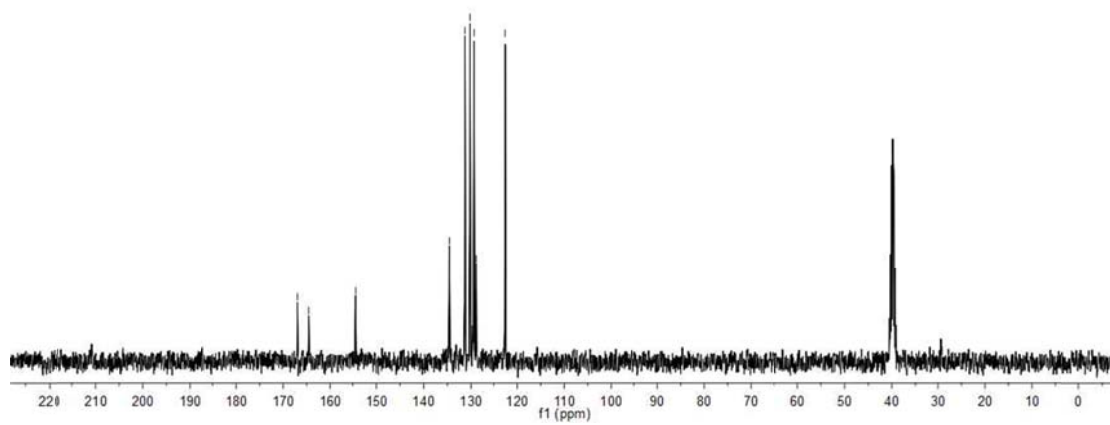
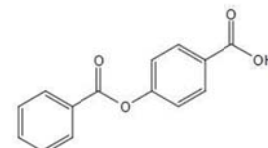
2f wcc-2-169
1H

8.16
8.14
8.06
8.04
7.78
7.76
7.74
7.64
7.62
7.44
7.42

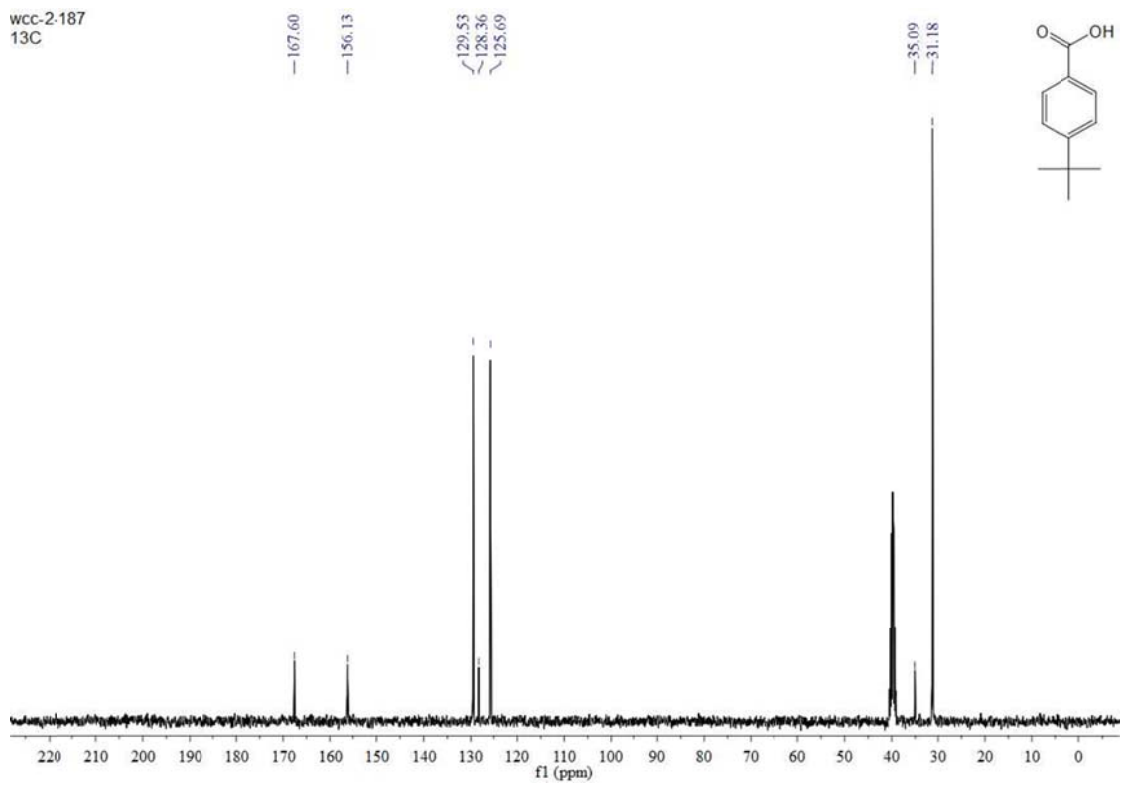
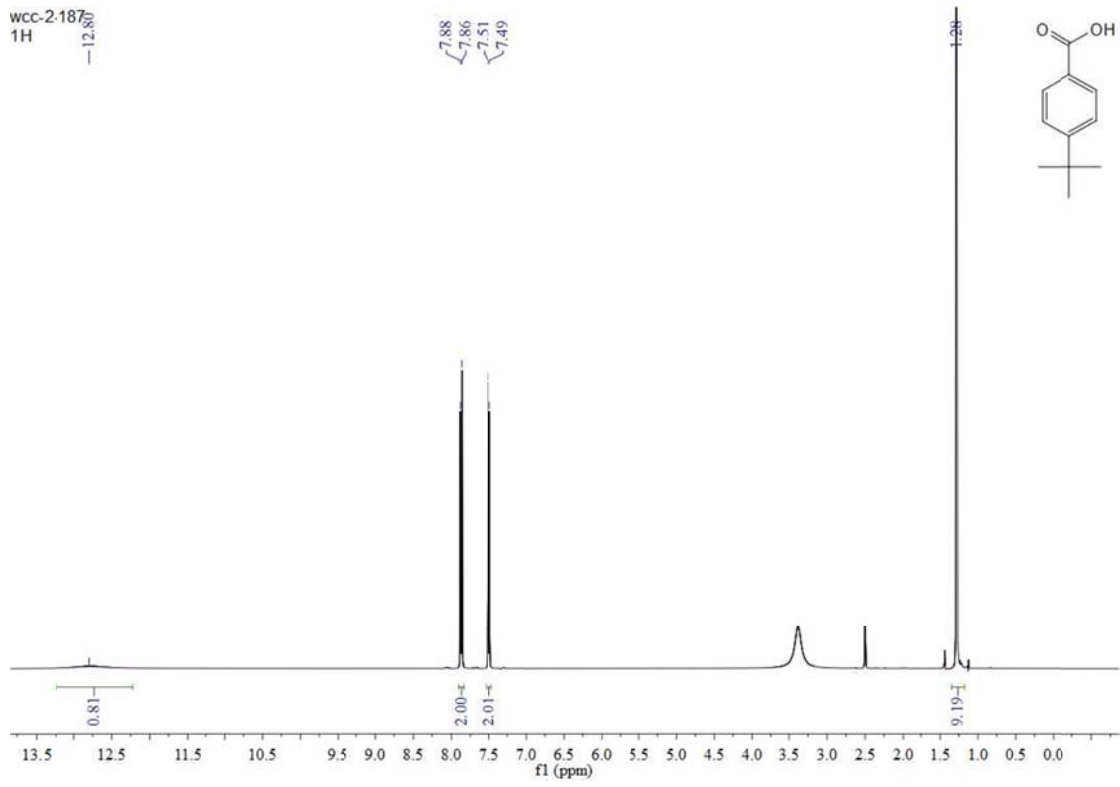


2f wcc-2-169
13C

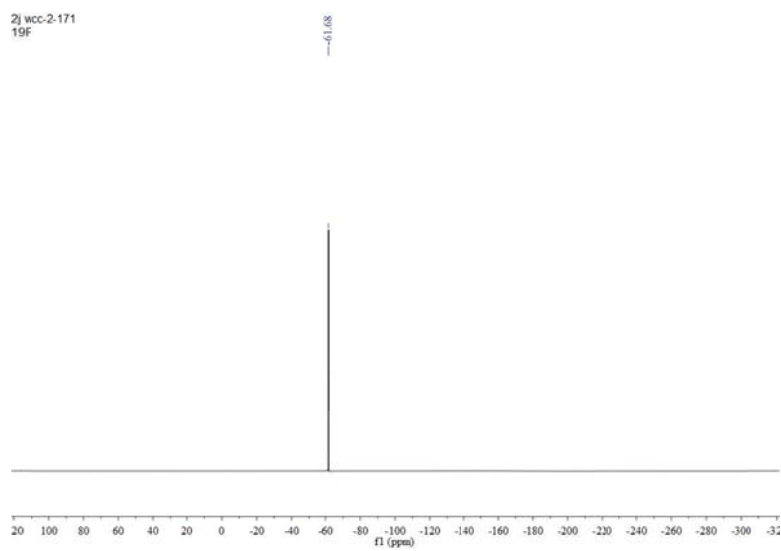
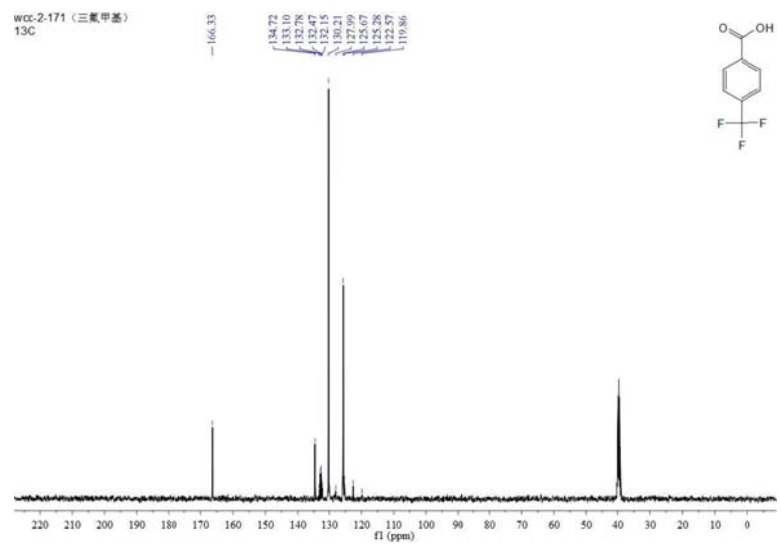
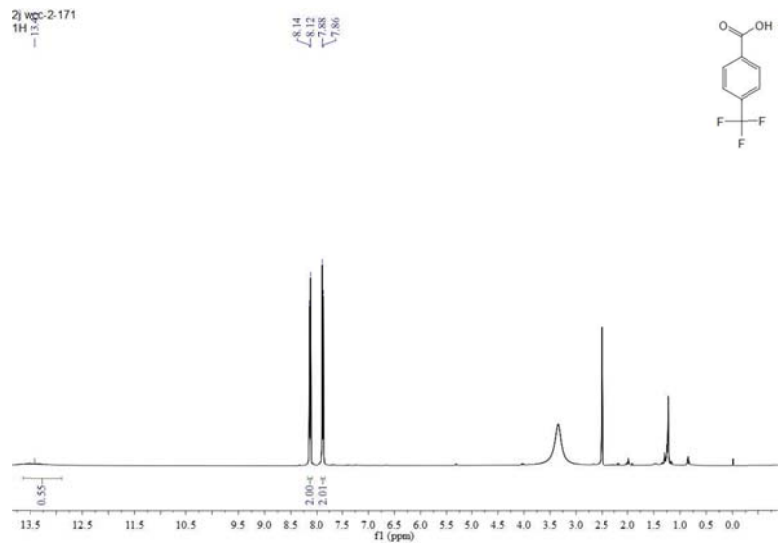
166.98
164.57
154.41
134.59
131.29
130.23
129.37
128.90
122.56



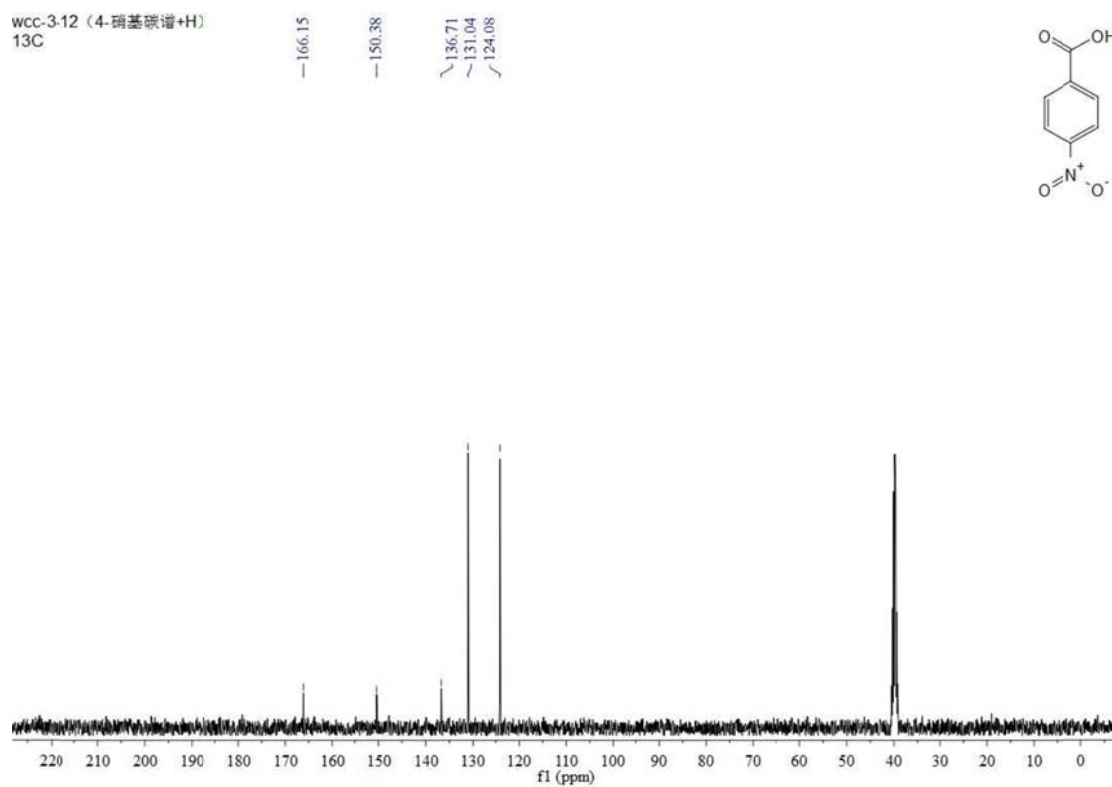
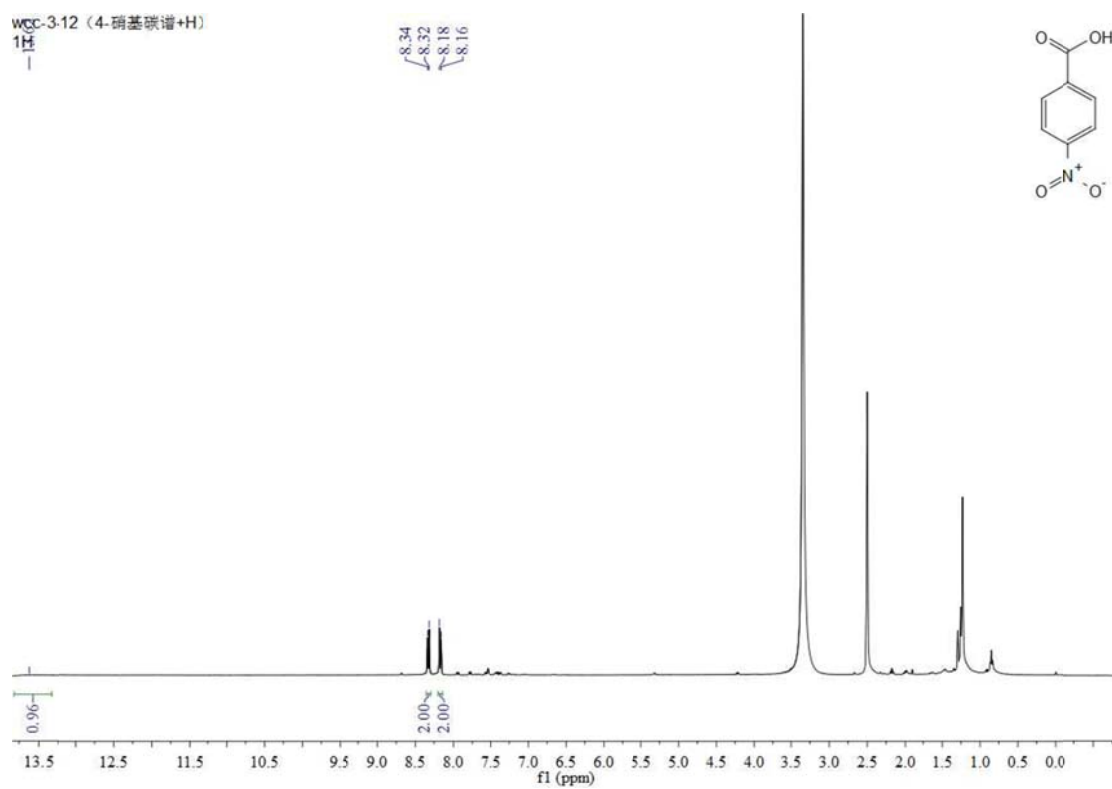
Compound (4f) : 4-(*tert*-butyl)benzoic acid.



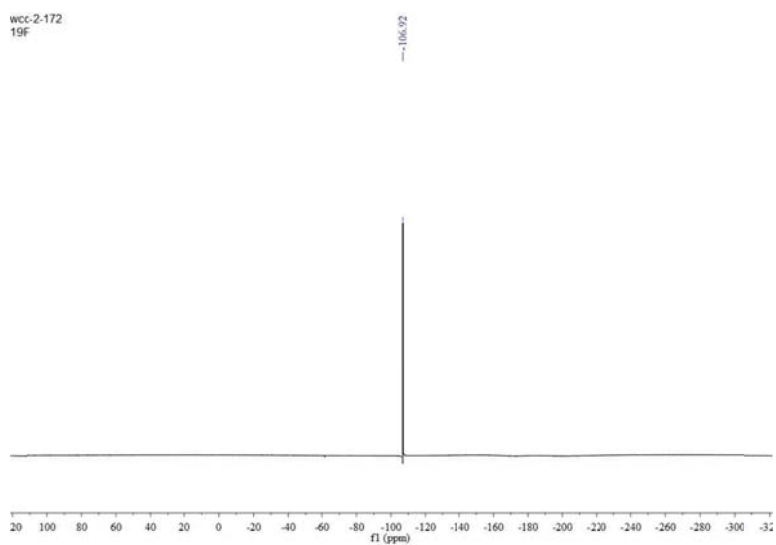
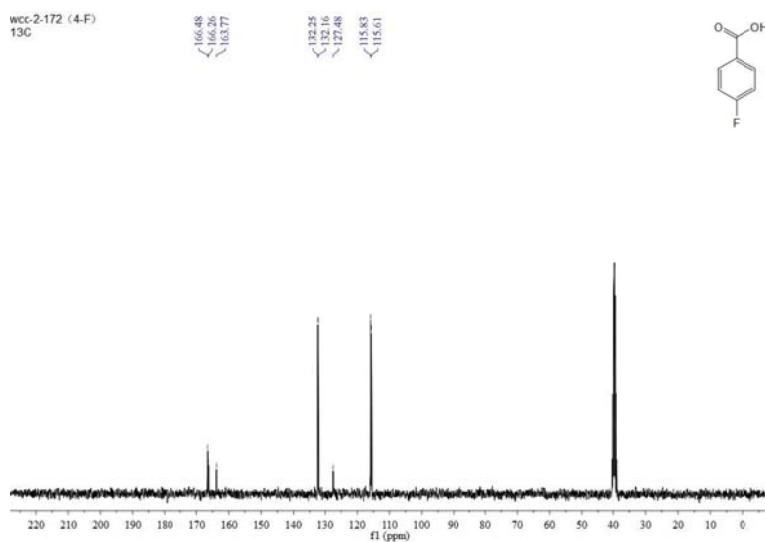
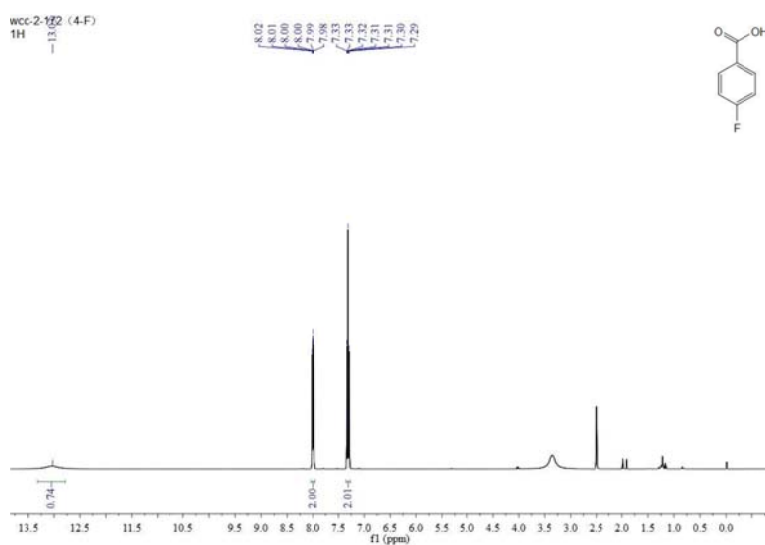
Compound (4g) : 4-(trifluoromethyl)benzoic acid.



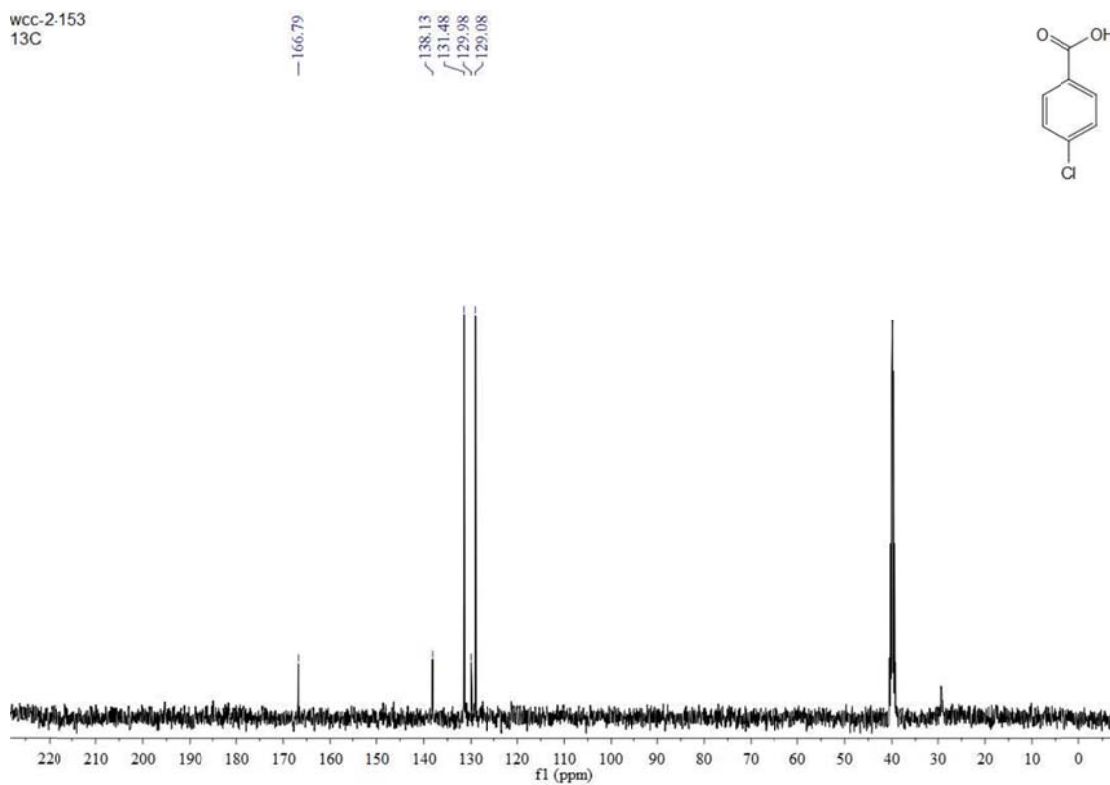
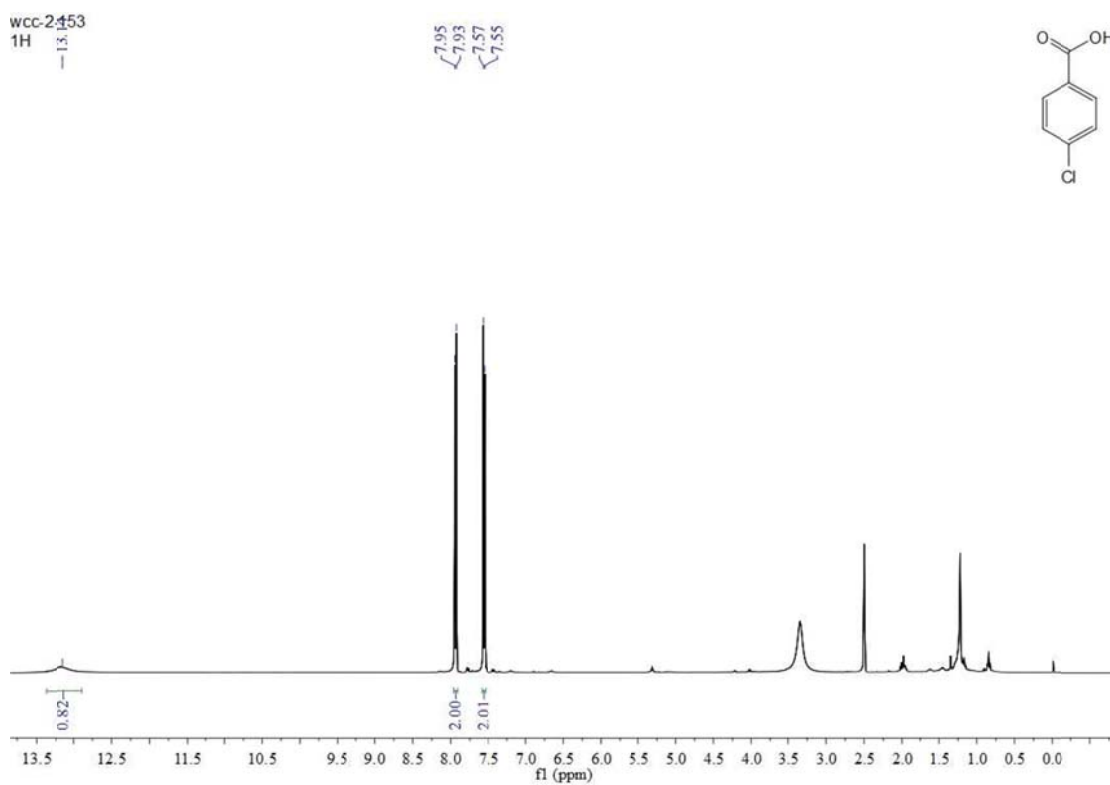
Compound (4h) : 4-nitrobenzoic acid.



Compound (4i) : 4-fluorobenzoic acid.



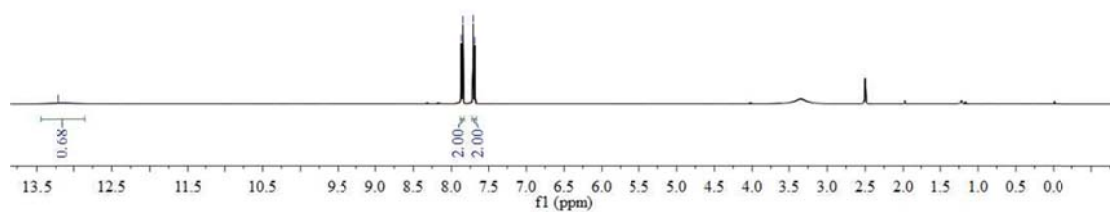
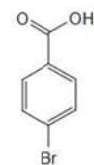
Compound (4j) : 4-chlorobenzoic acid.



Compound (4k) : 4-bromobenzoic acid.

wcc-2160 (4-溴)
1H

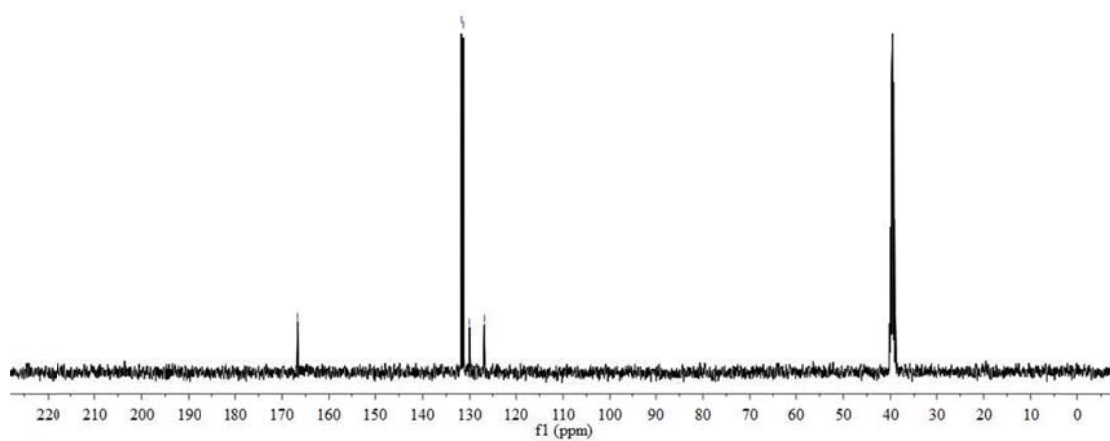
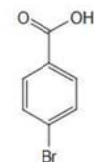
7.87
7.85
7.71
7.69



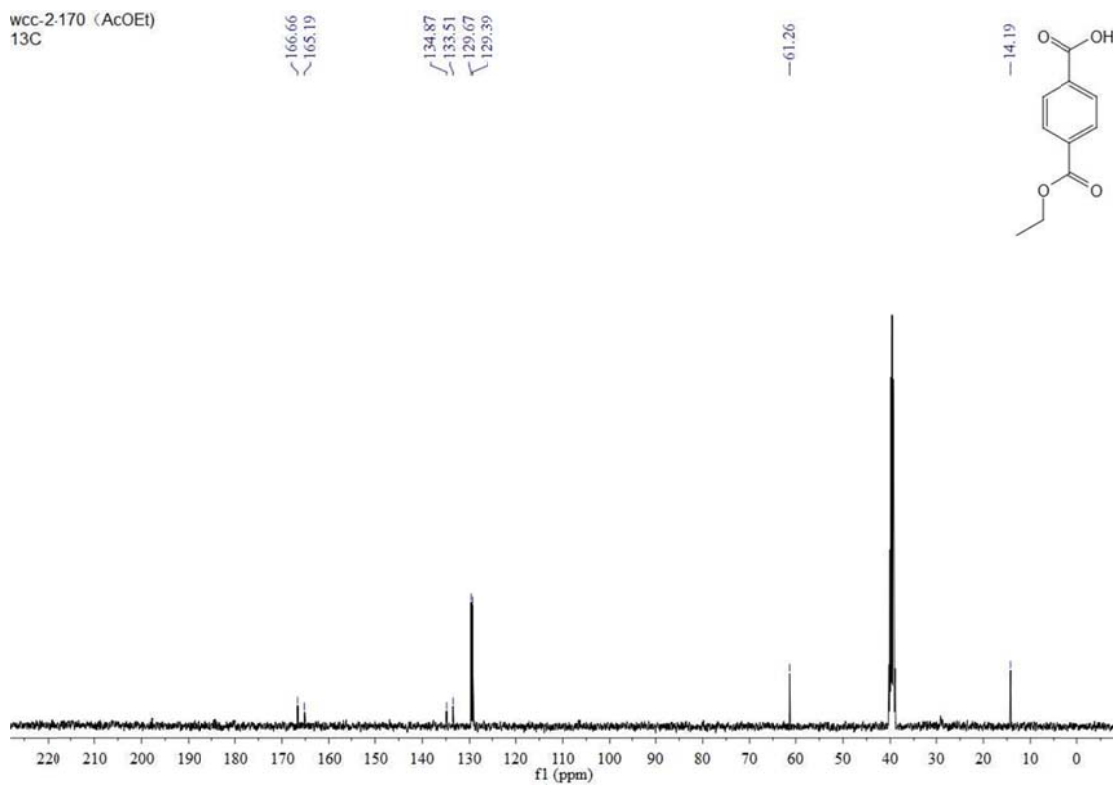
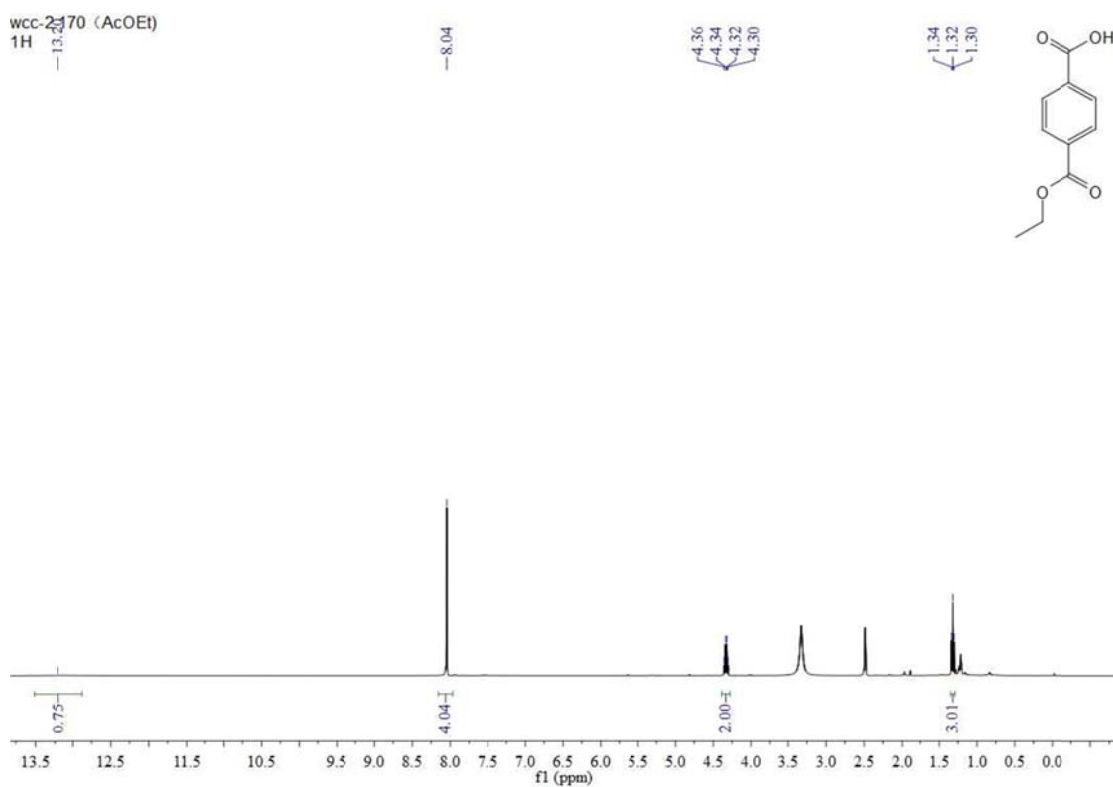
wcc-2160 (4-溴)
13C

166.69

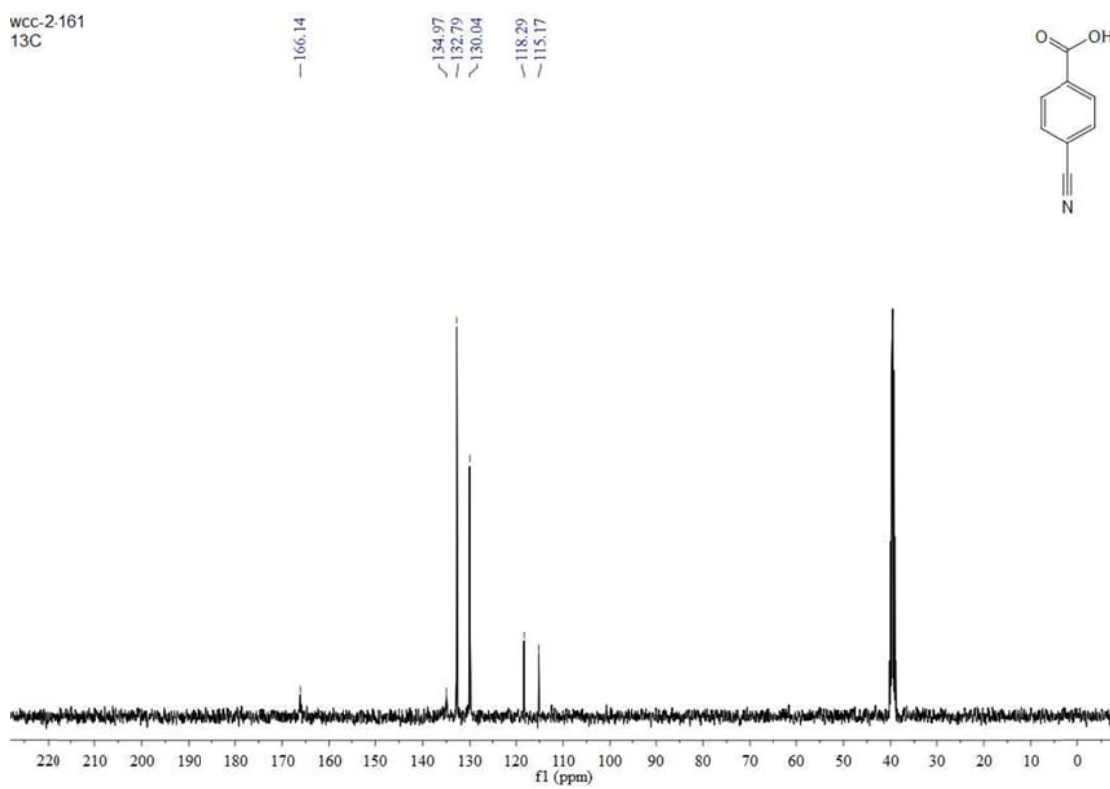
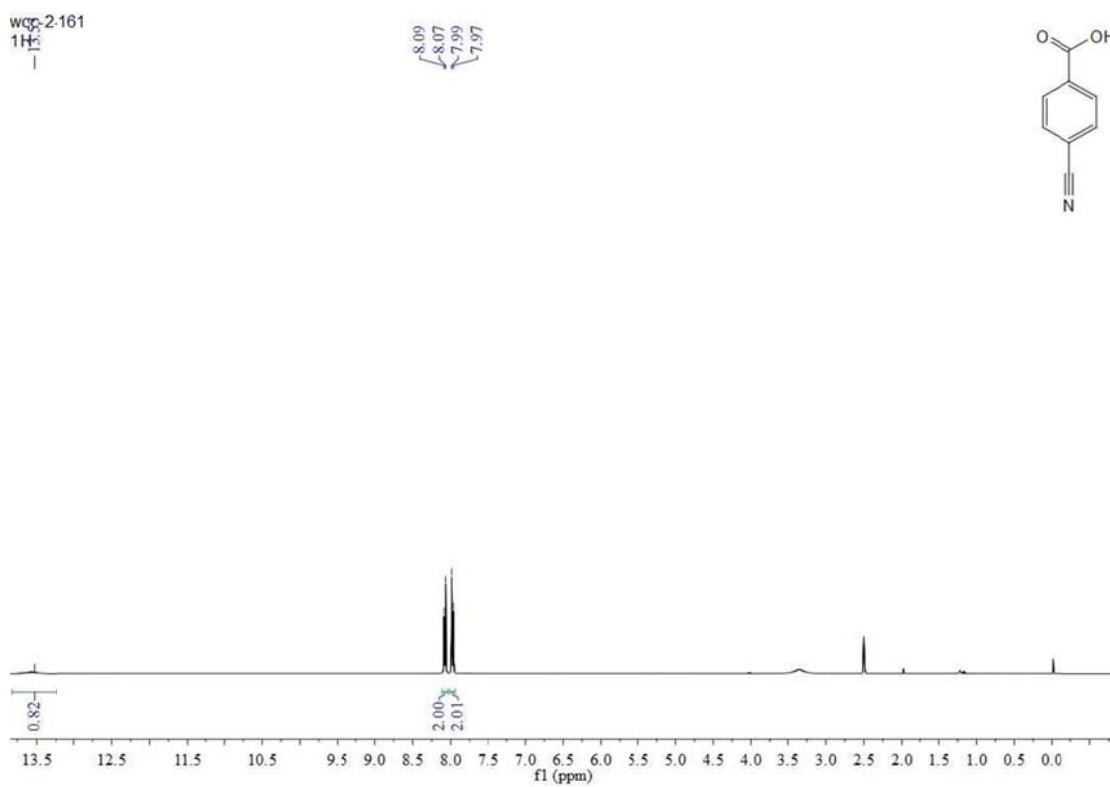
131.78
131.36
130.10
126.95



Compound (4I) : 4-(ethoxycarbonyl)benzoic acid.



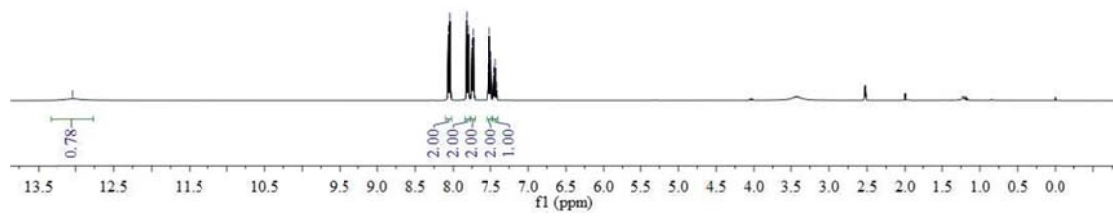
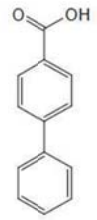
Compound (4m) : 4-cyanobenzoic acid.



Compound (4n) : [1,1'-biphenyl]-4-carboxylic acid.

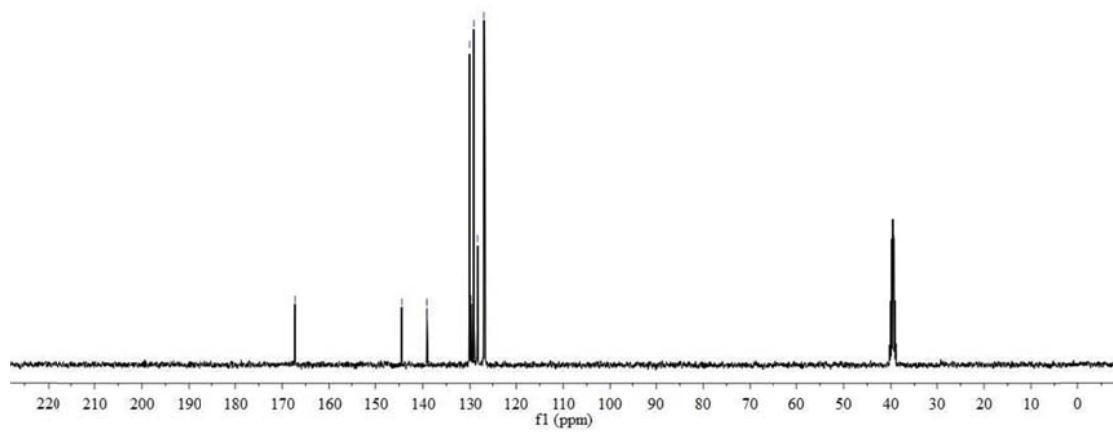
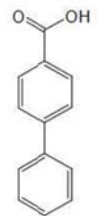
wcc-299
1H
-13.0

8.06
8.04
7.82
7.80
7.75
7.74
7.53
7.52
7.50
7.45
7.44
7.42

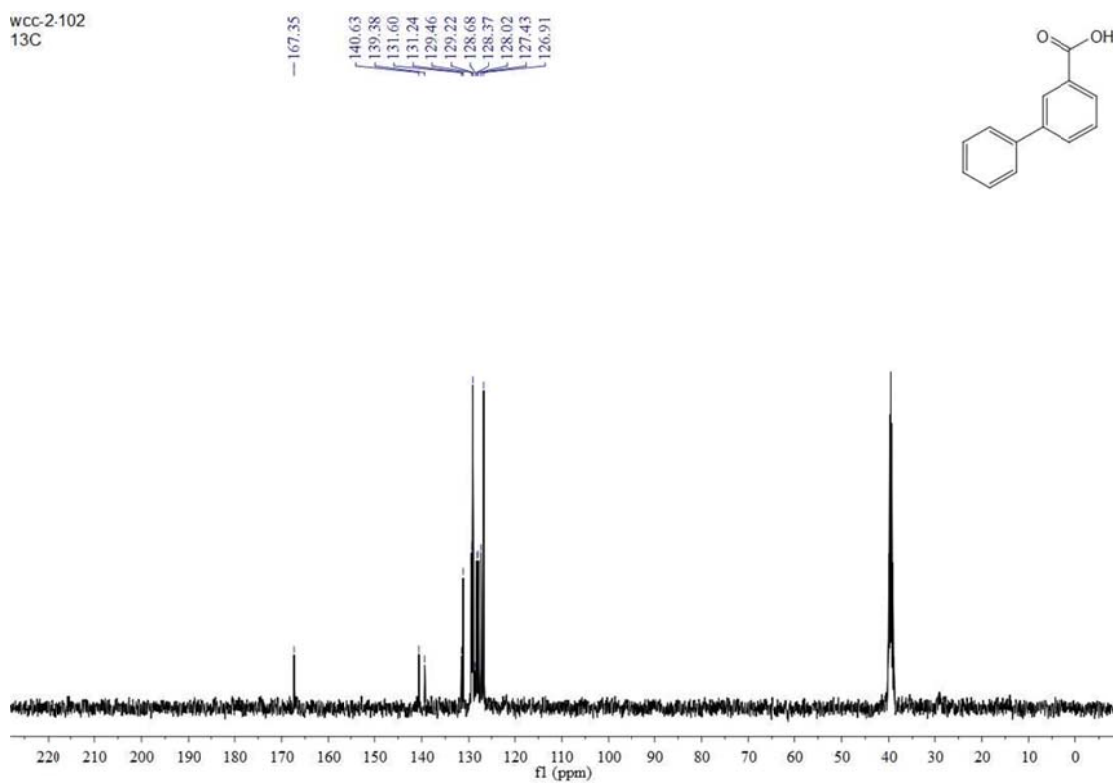
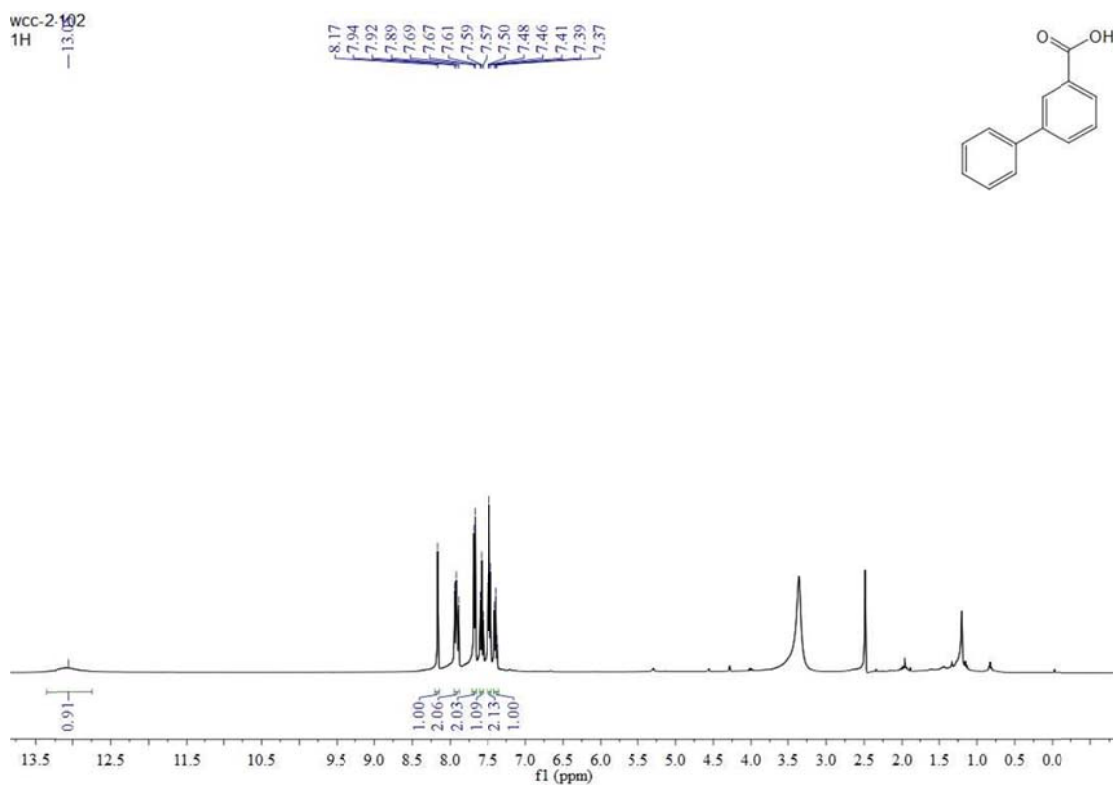


wcc-290
13C

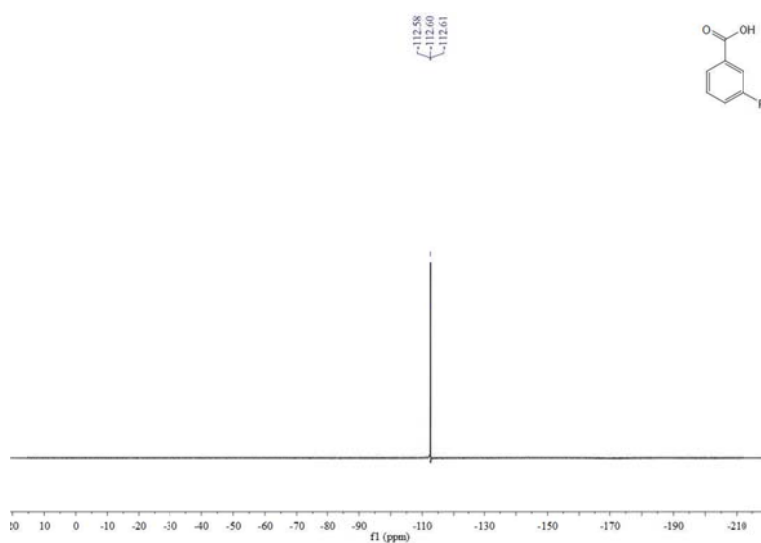
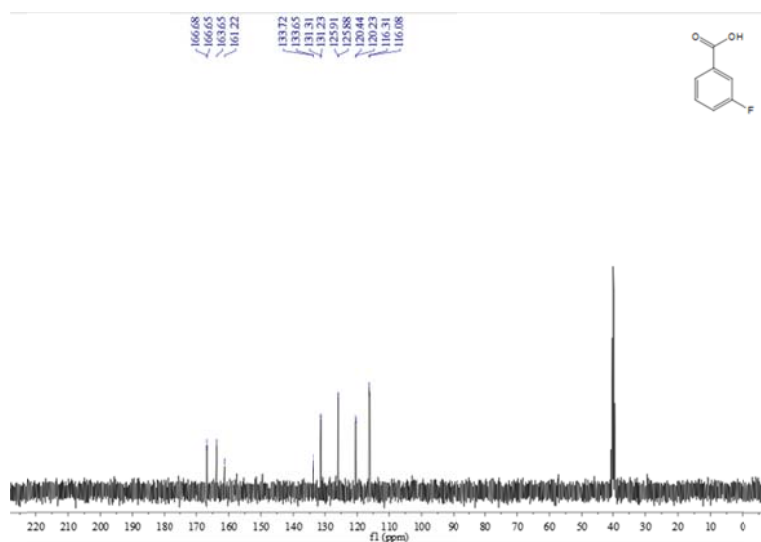
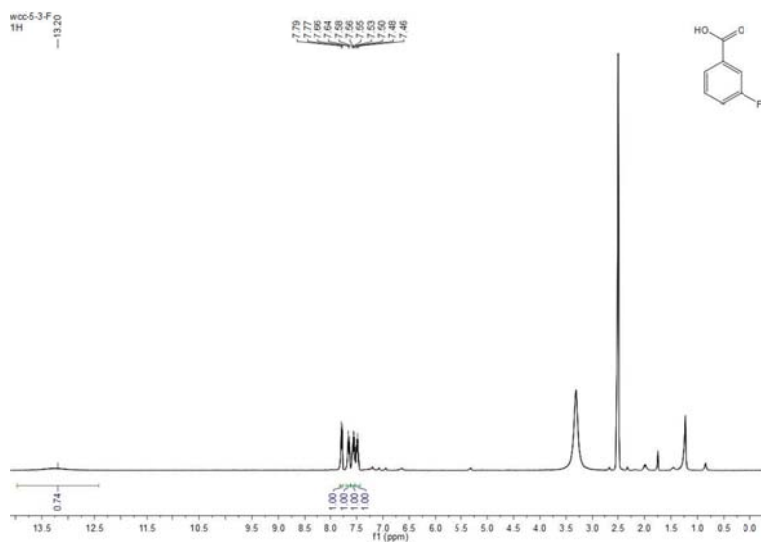
167.29
144.44
139.15
130.10
129.74
129.20
128.41
127.09
126.94



Compound (4o) : [1,1'-biphenyl]-3-carboxylic acid.



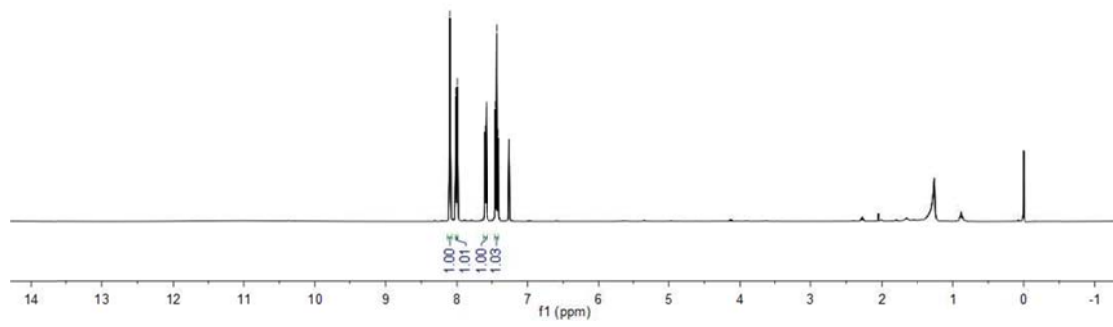
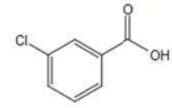
Compound (4p) : 3-fluorobenzoic acid.



Compound (4q) : 3-chlorobenzoic acid.

wcc-6-89-CD
1H

8.10
8.02
8.00
7.61
7.59
7.45
7.43
7.41

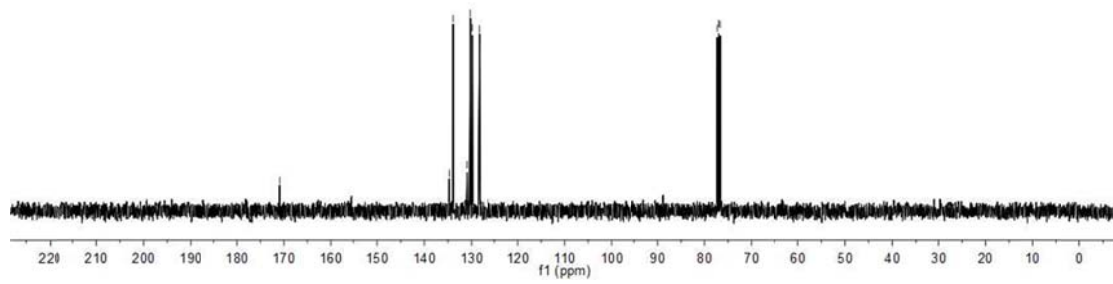
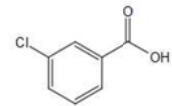


wcc-6-89-CD
13C

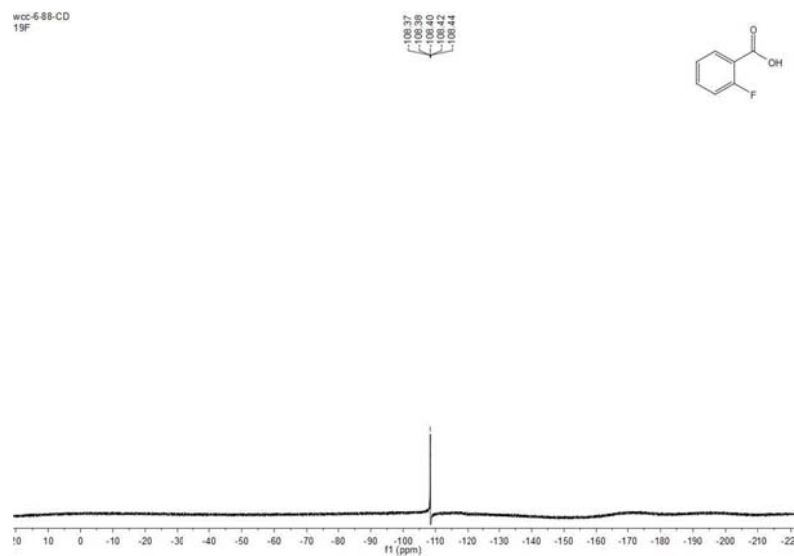
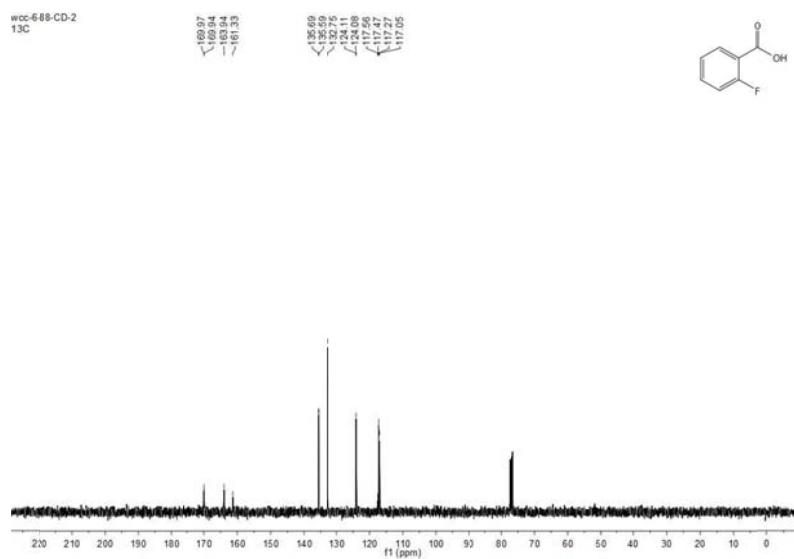
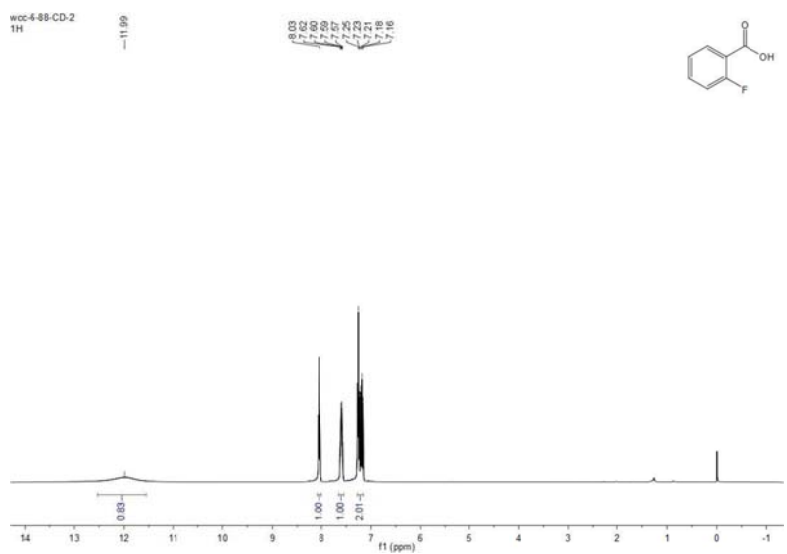
170.87

134.72
133.91
130.95
130.27
128.95
128.32

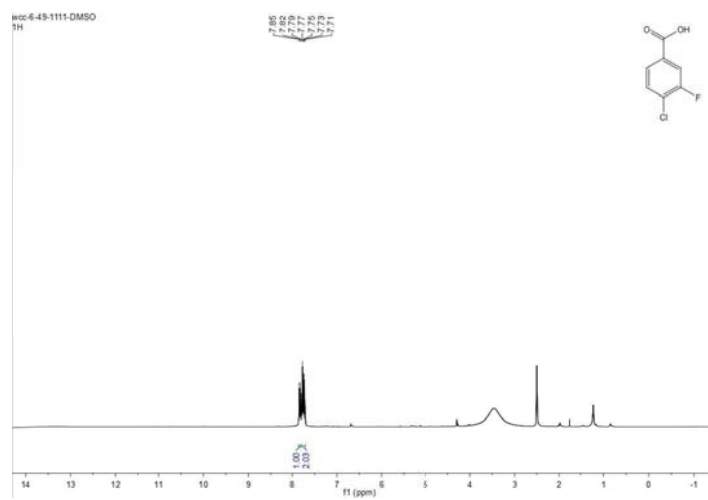
77.32
77.00
76.68



Compound (4r) : 2-fluorobenzoic acid.



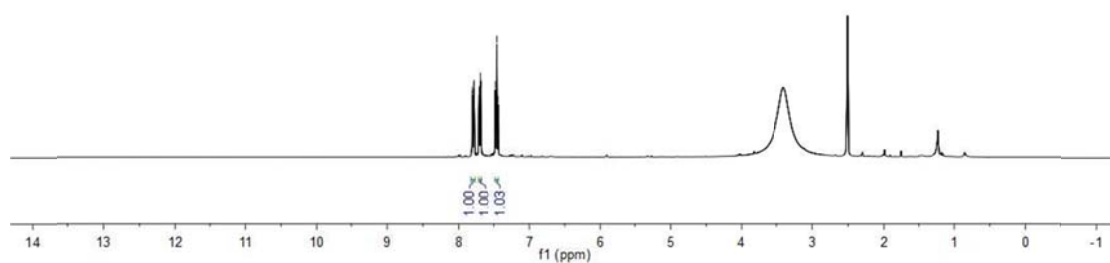
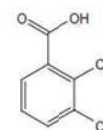
Compound (4t) : 4-chloro-3-fluorobenzoic acid.



Compound (4u) : 2,3-dichlorobenzoic acid.

wcc-6-53-DMSO
1H

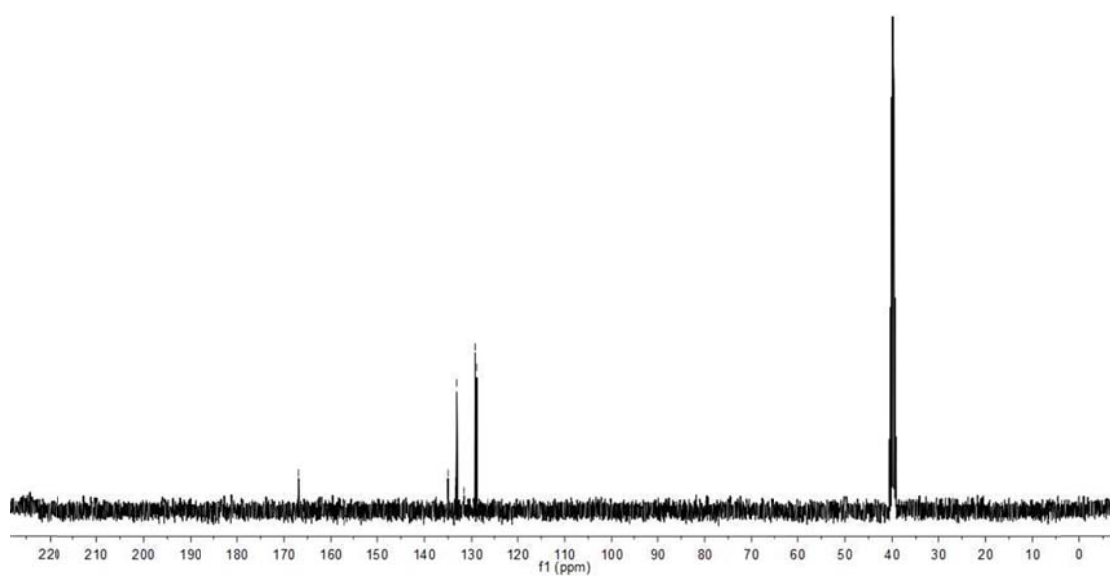
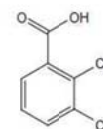
7.81
7.81
7.79
7.79
7.77
7.77
7.70
7.69
7.48
7.46
7.44



wcc-6-53-DMSO
13C

166.87

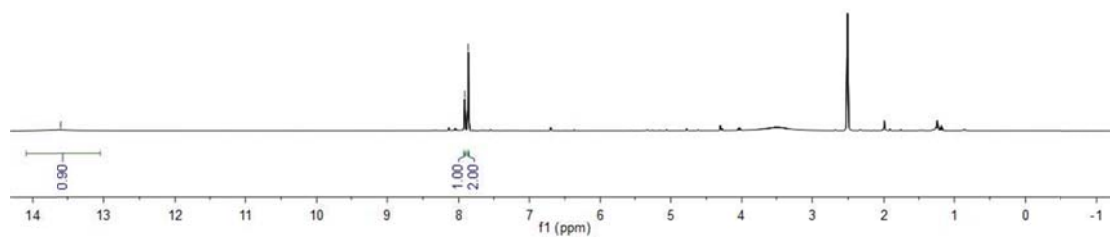
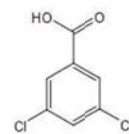
135.00
133.30
133.16
131.61
129.27
128.95



Compound (4v) : 3,5-dichlorobenzoic acid.

wcc-6-48
1H

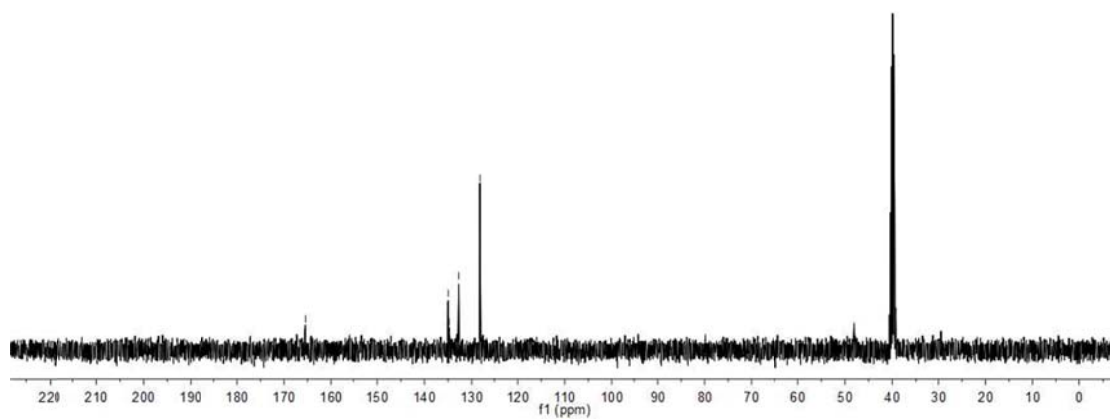
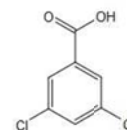
7.92
7.87



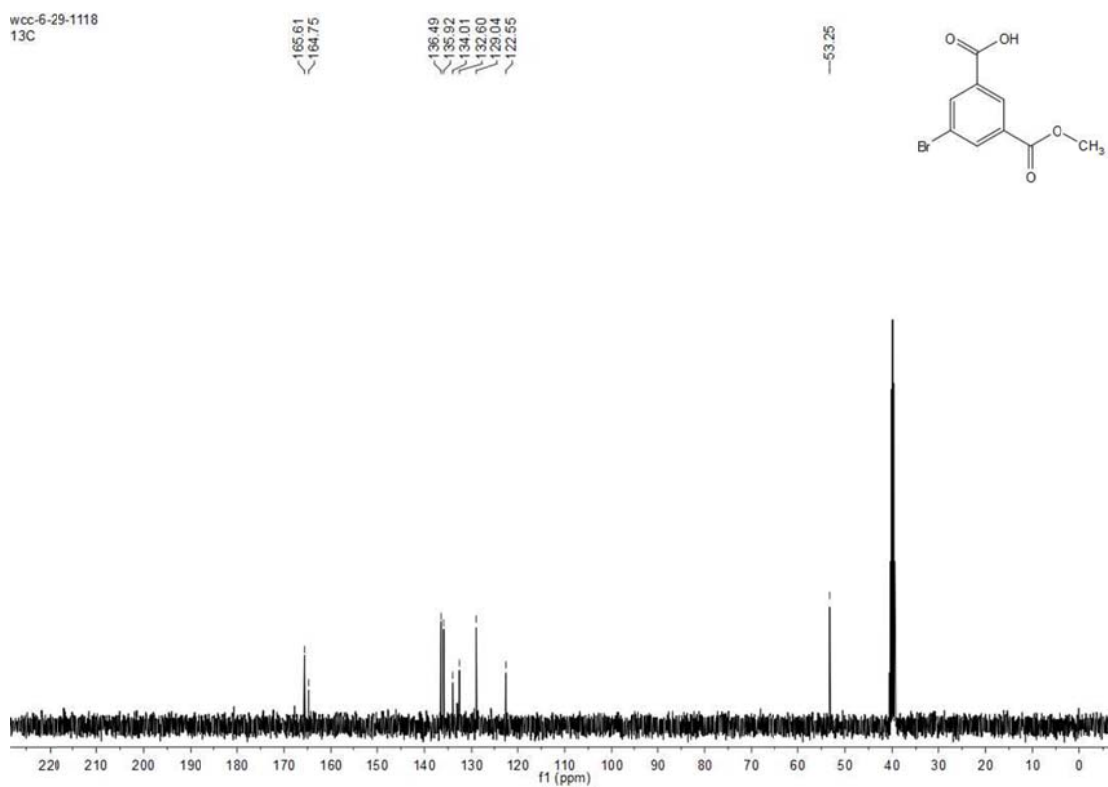
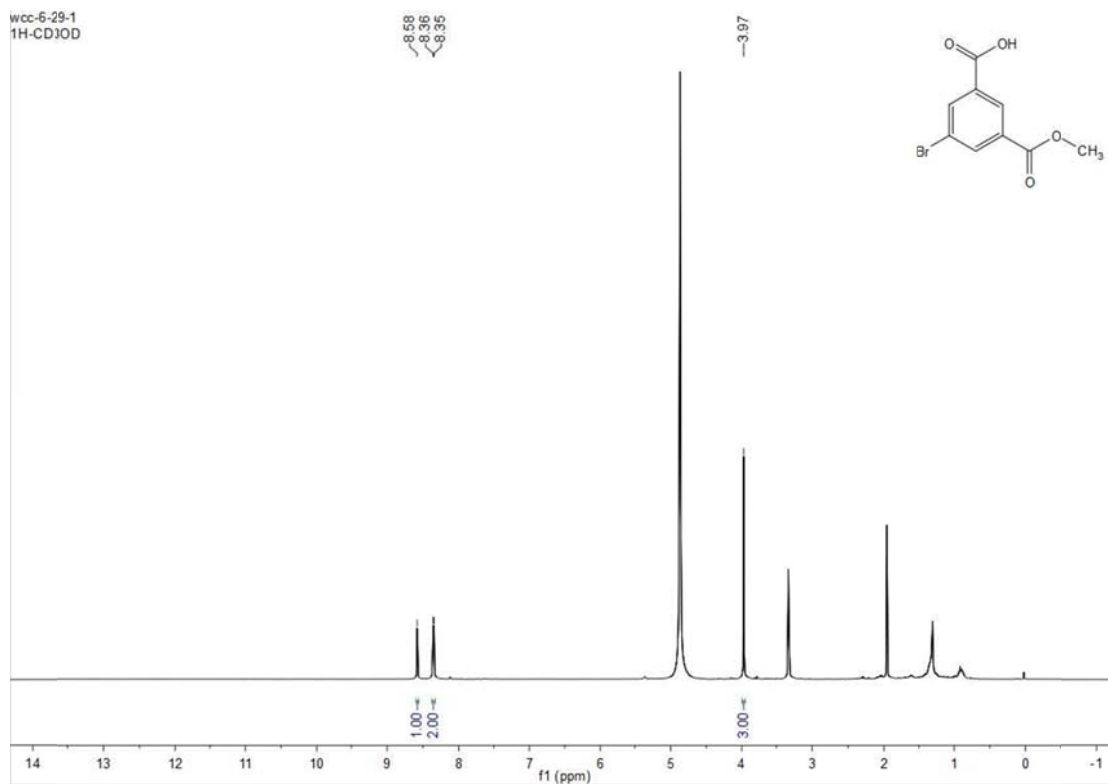
wcc-6-48-1112-DMSO
13C

165.41

134.97
134.76
132.72
128.26



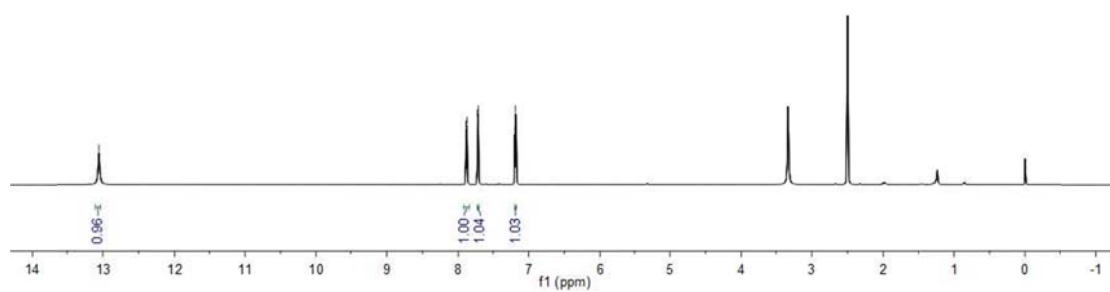
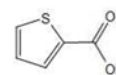
Compound (4w) : 3-bromo-5-(methoxycarbonyl)benzoic acid.



Compound (6a) :thiophene-2-carboxylic acid.

45 wcc-6-saizuo-DMSO
1H

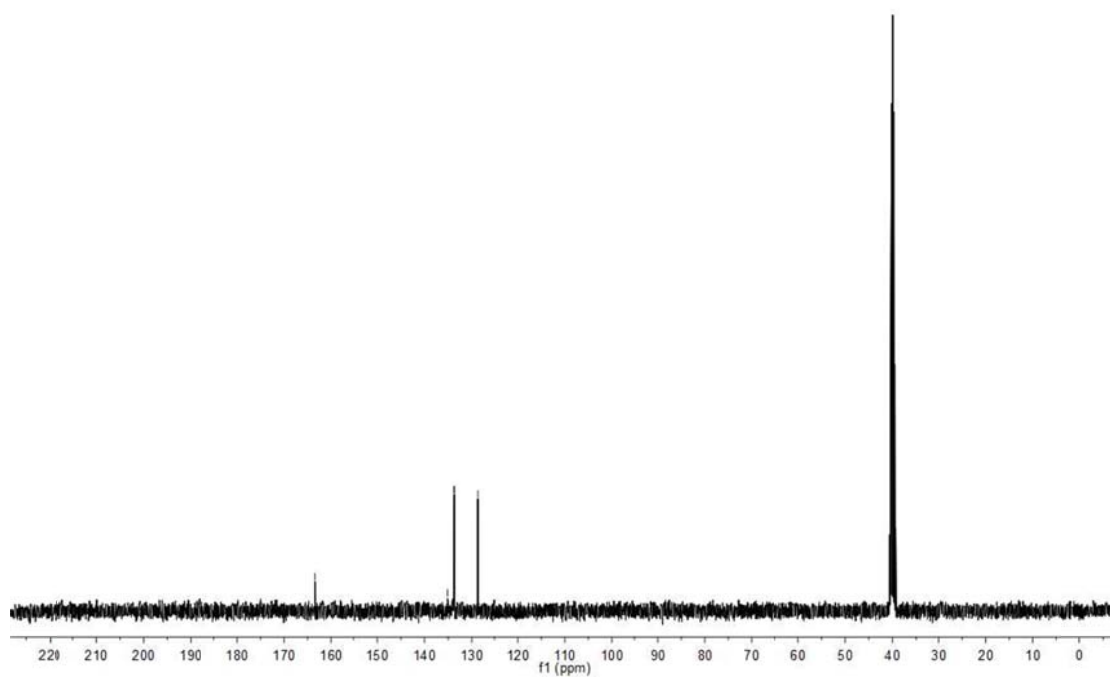
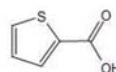
7.89
7.88
7.73
7.72
7.19
7.17



45 wcc-6-saizuo-DMSO
13C

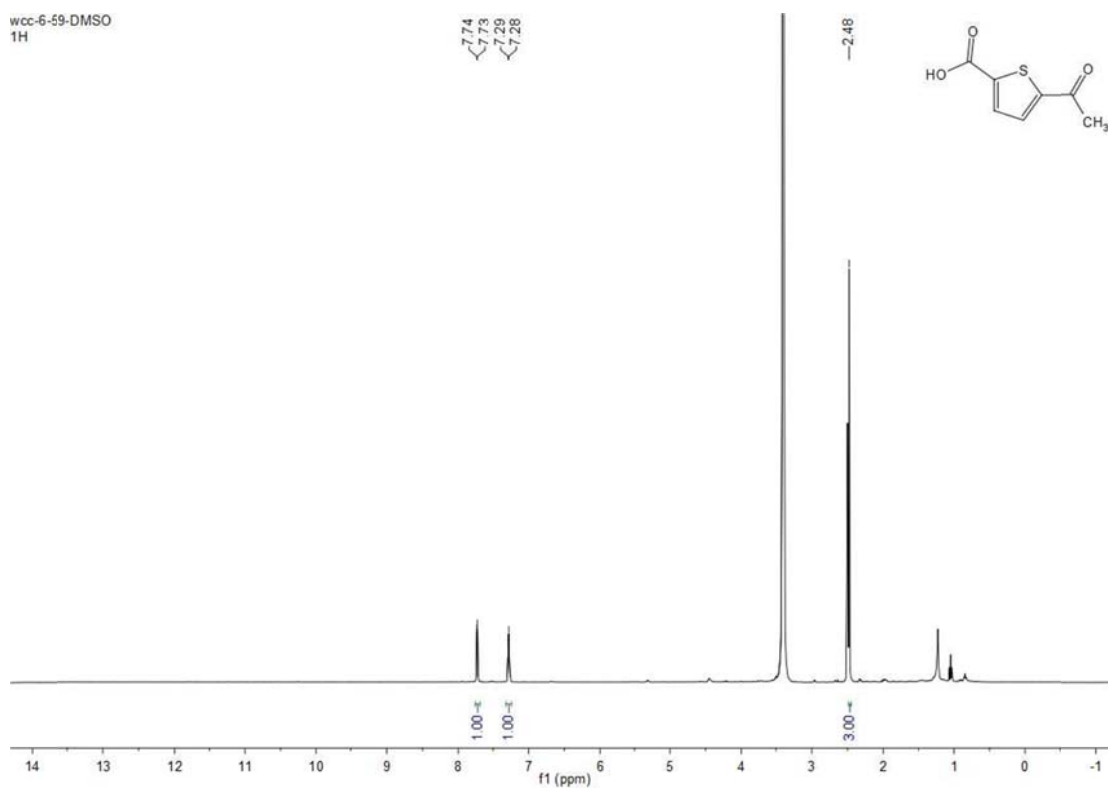
163.39

135.12
133.76
133.68
128.70

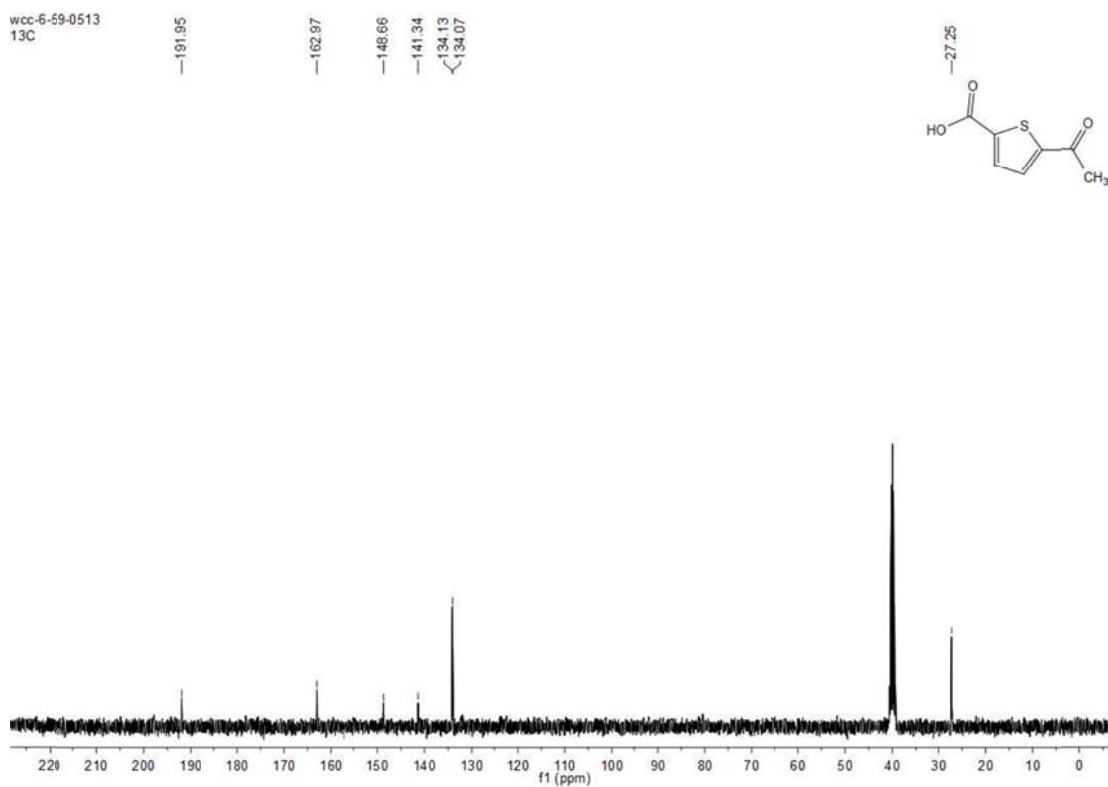


Compound (6b) : 5-acetylthiophene-2-carboxylic acid.

wcc-6-59-DMSO
1H

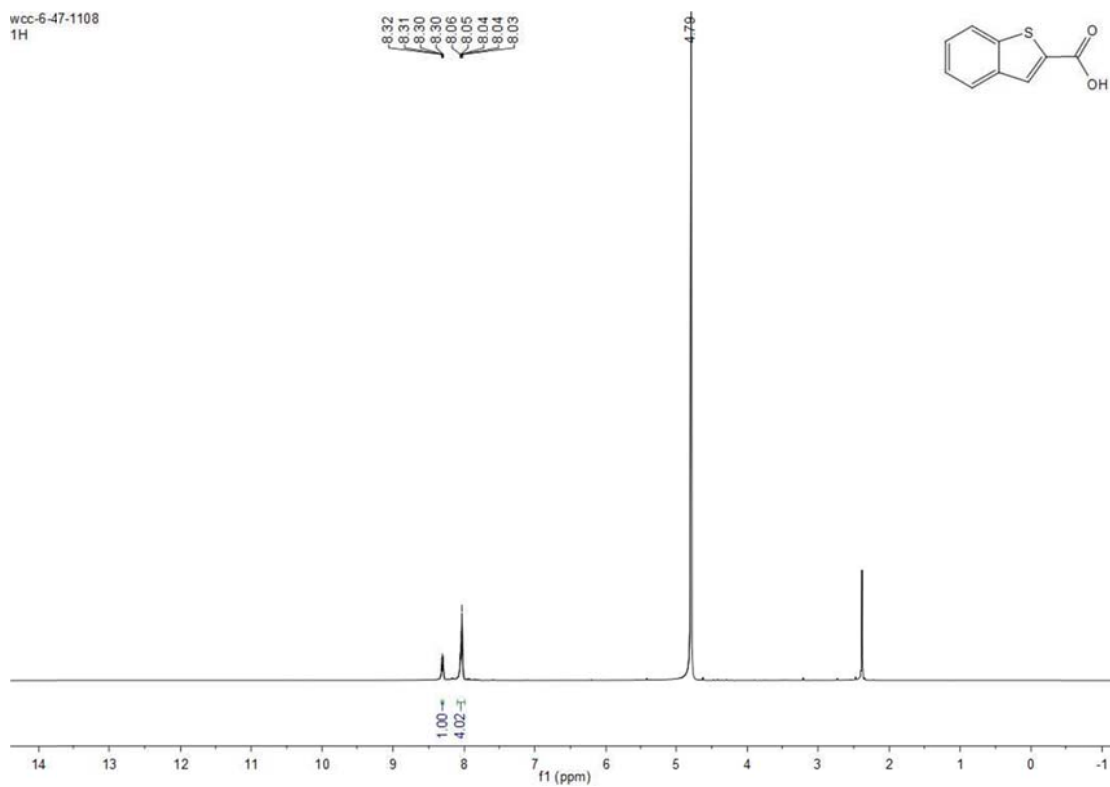


wcc-6-59-0513
13C

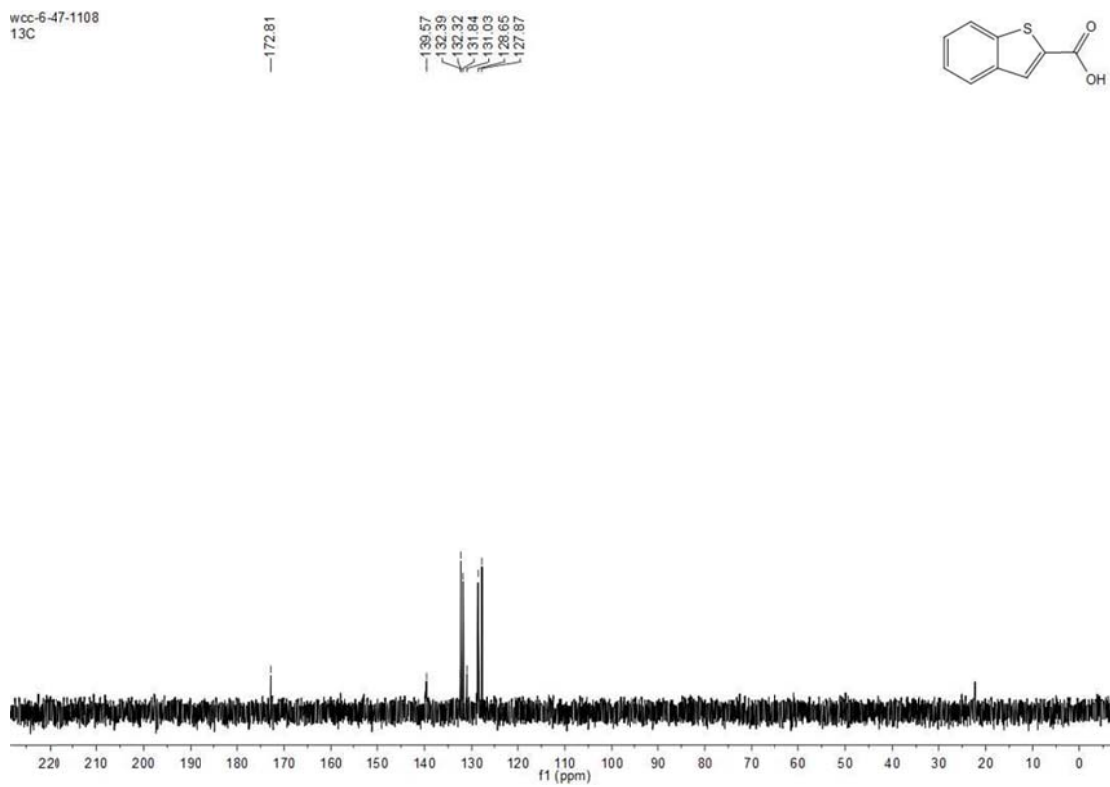


Compound (6c) : benzo[*b*]thiophene-2-carboxylic acid.

wcc-6-47-1108
1H



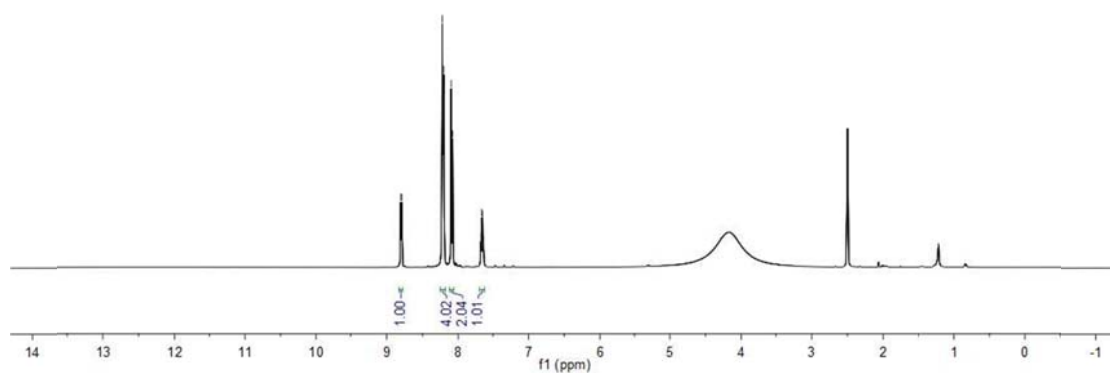
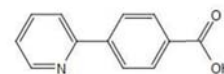
wcc-6-47-1108
13C



Compound (6d) : 4-(pyridin-2-yl)benzoic acid.

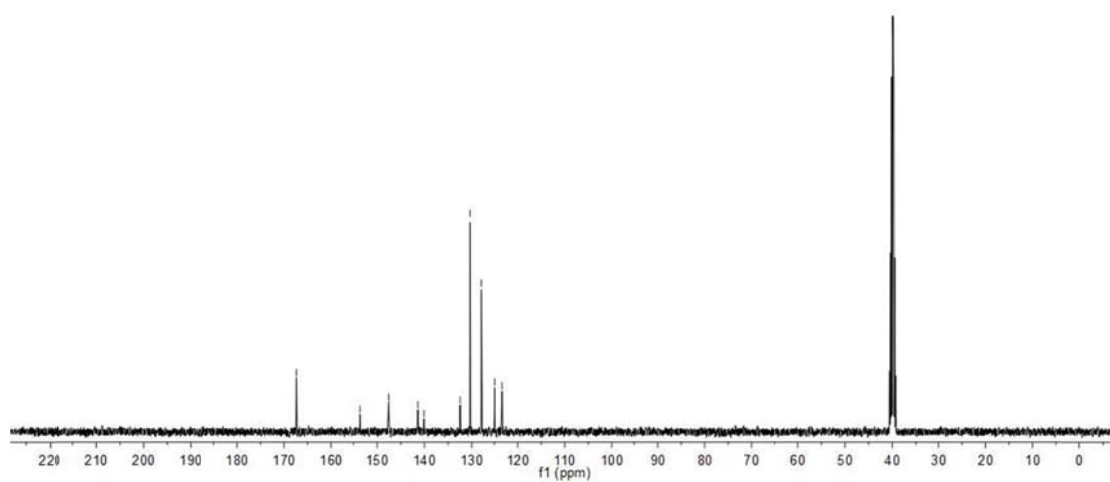
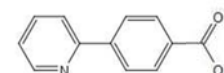
wcc-4-166-2
1H

8.80
8.79
8.22
8.21
8.20
8.20
8.00
7.69
7.66
7.65



wcc-4-166-2
13C

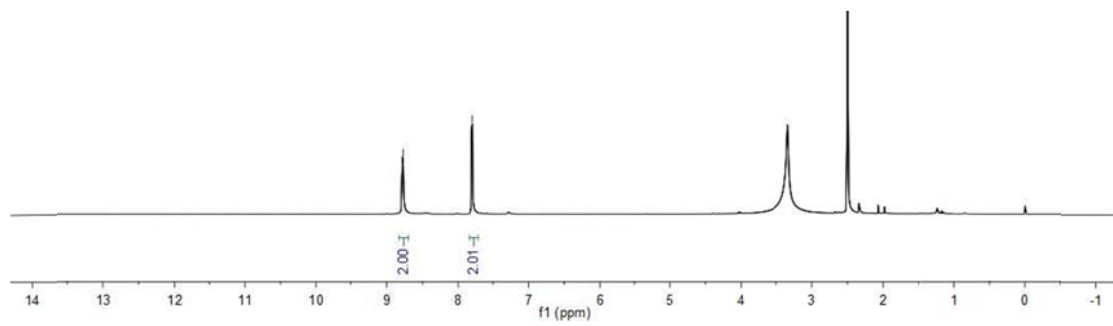
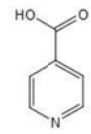
167.32
153.59
147.56
141.36
140.06
132.44
130.32
127.94
124.93
123.33



Compound (6e) : isonicotinic acid.

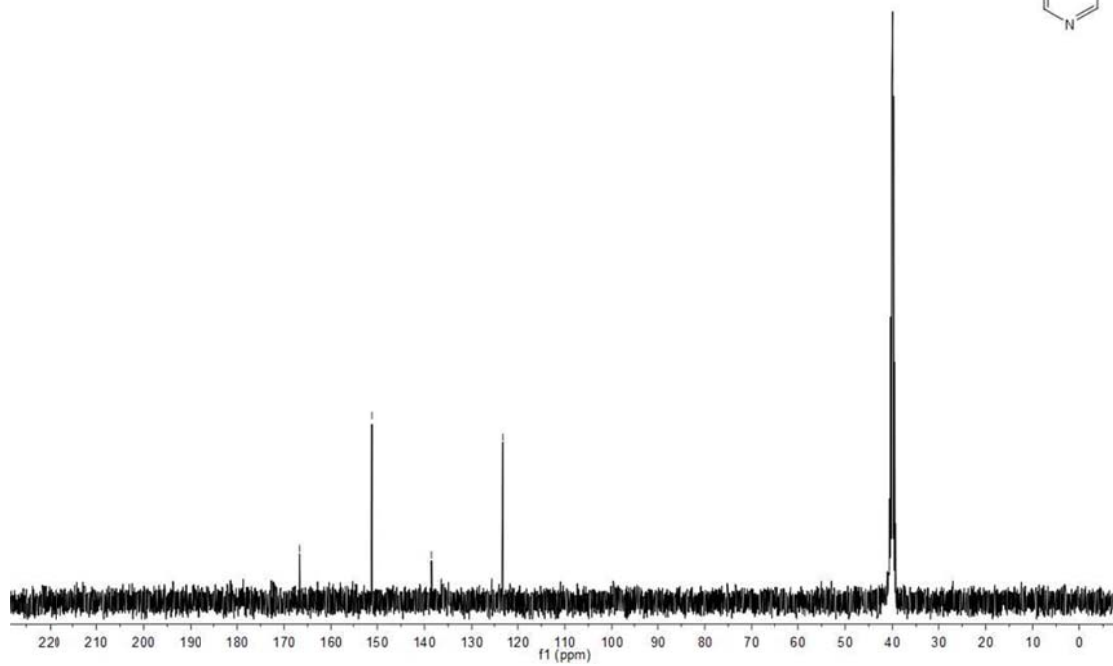
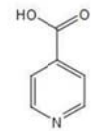
wcc-4-107-4 甲基吡啶
1H

8.78
8.77
7.82
7.80

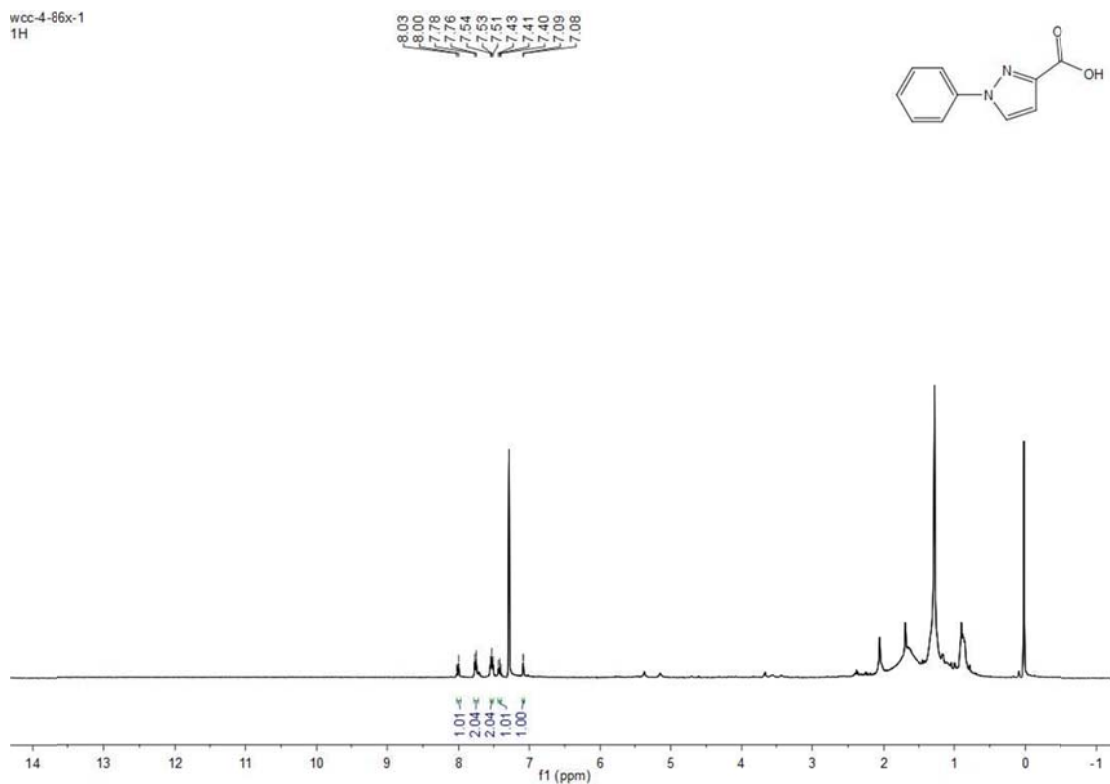


wcc-4-107-4 甲基吡啶
13C

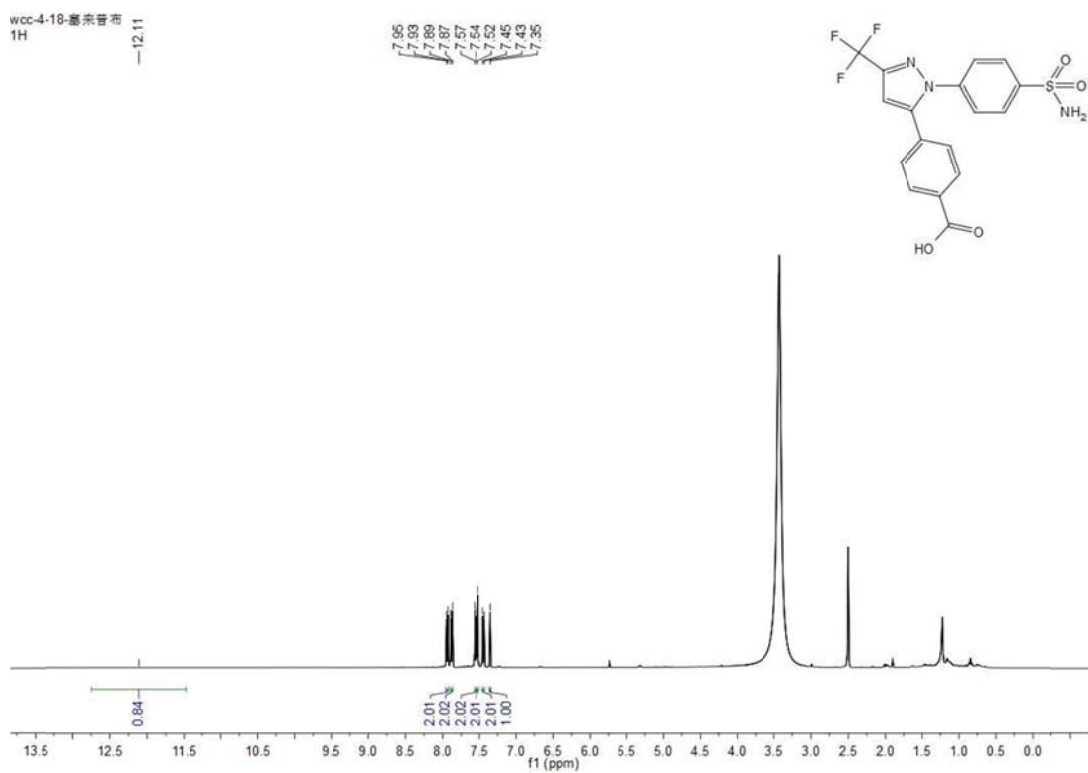
166.66
151.11
138.52
123.22



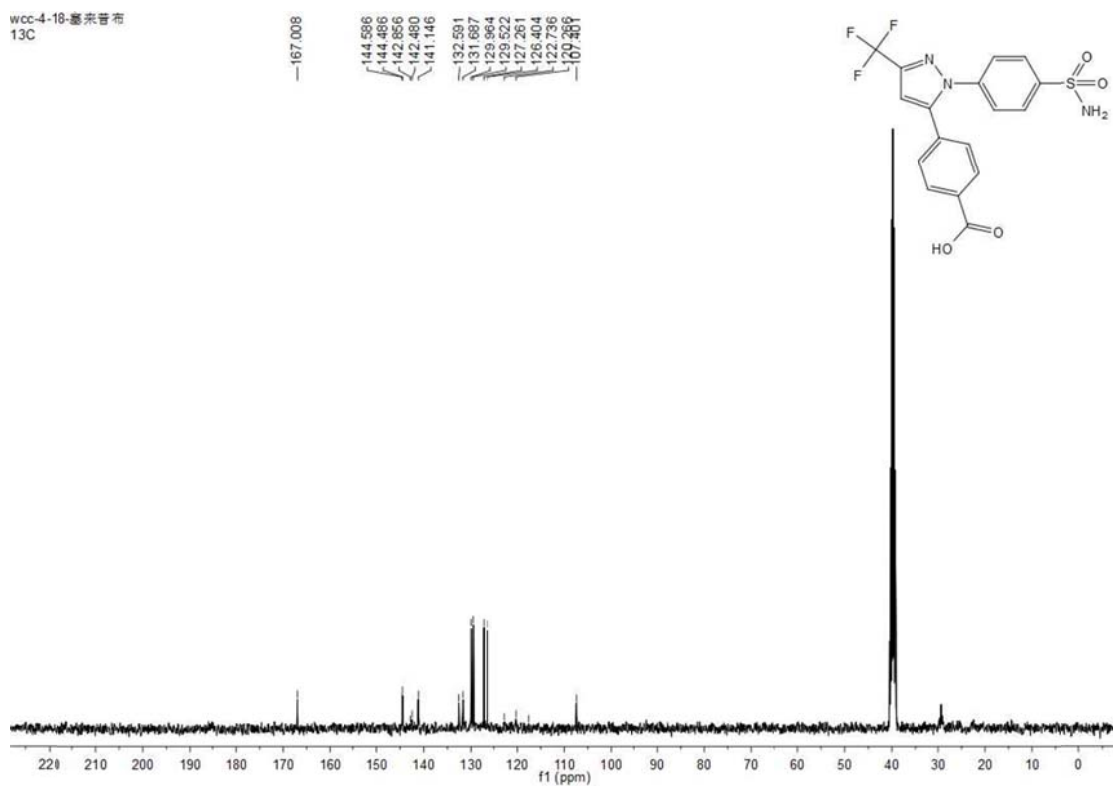
Compound (6f) : thiophene-2-carboxylic acid.



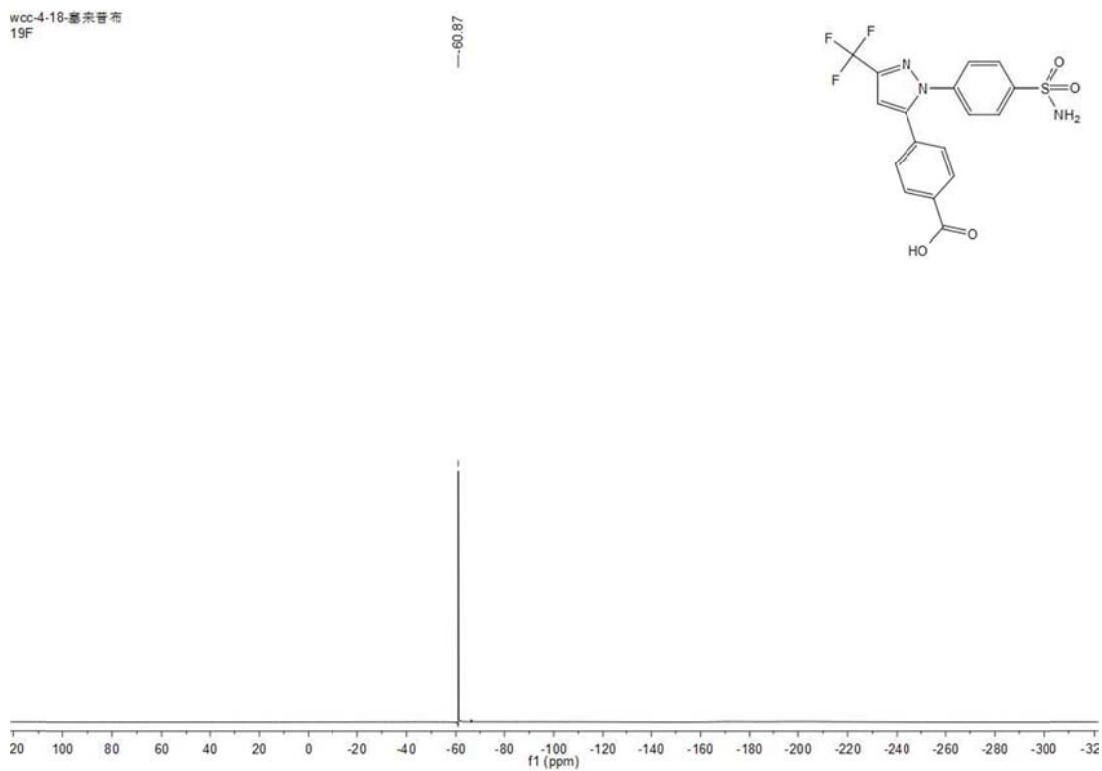
Compound (10) : Celebrex derivative.



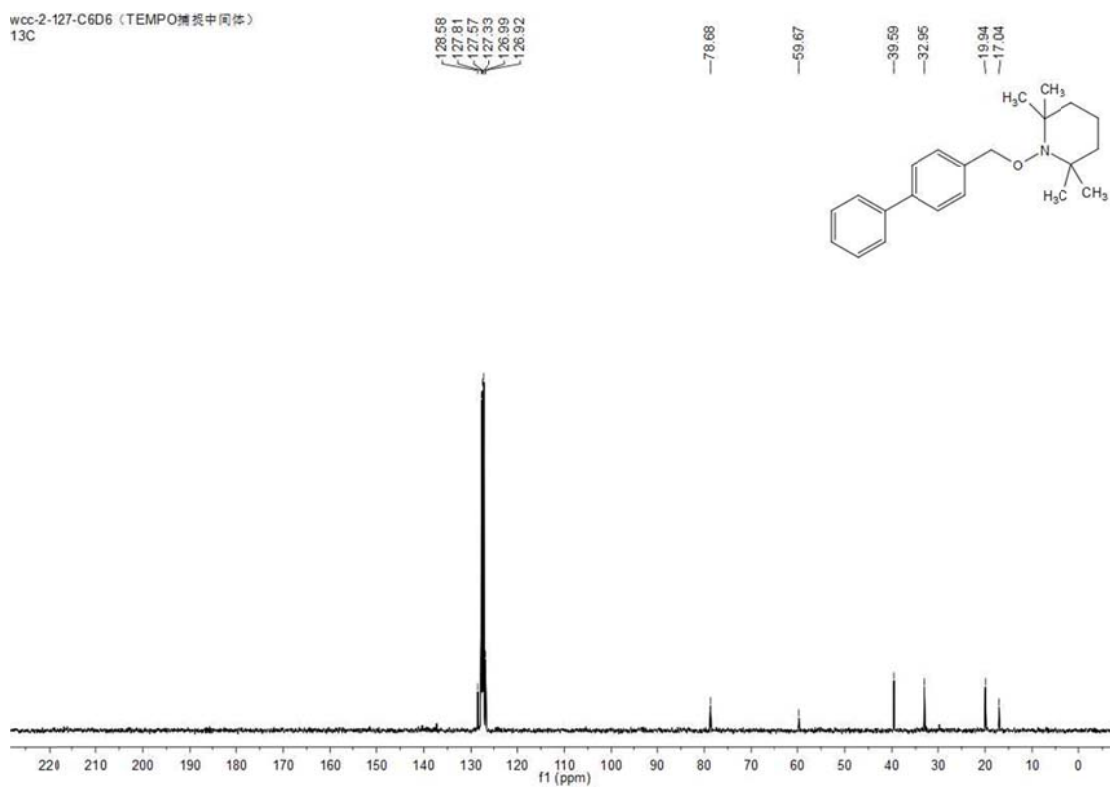
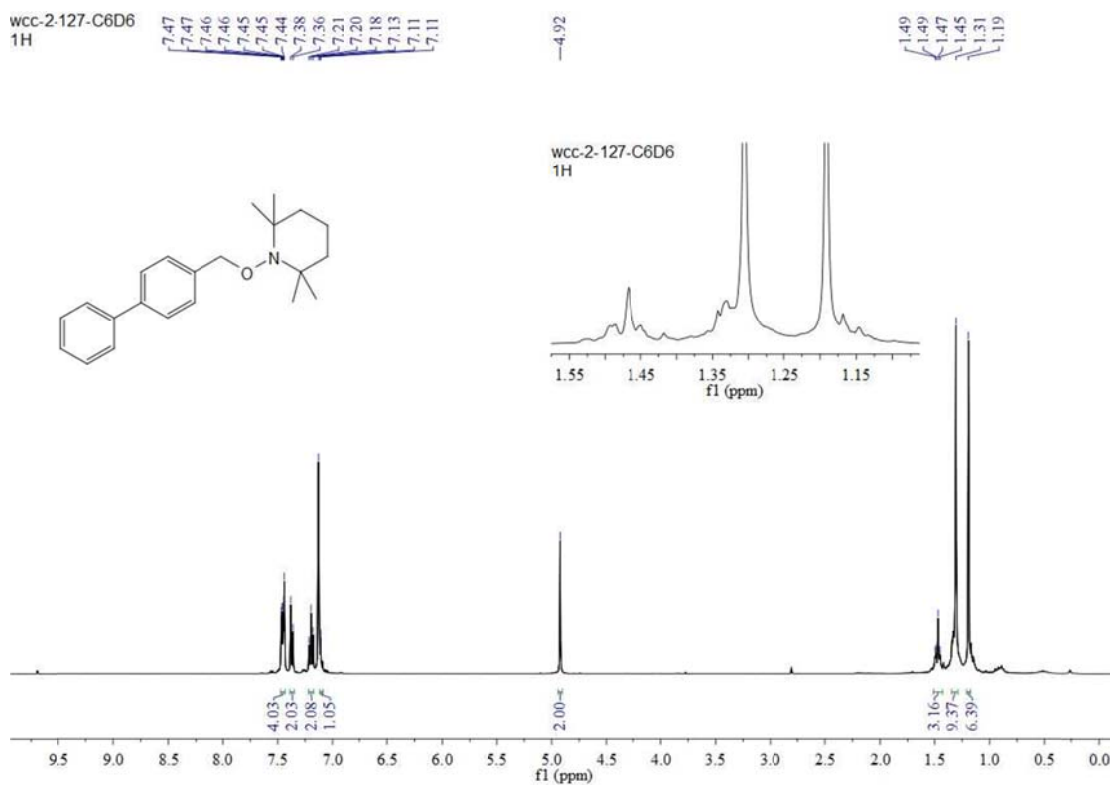
wcc-4-18-羧基普布
13C



wcc-4-18-羧基普布
19F



Compound (11) : 1-([1,1'-biphenyl]-4-ylmethoxy)-2,2,6,6-tetramethylpiperidine.



Compound (4n'): [1,1'-biphenyl]-4-carboxylic acid

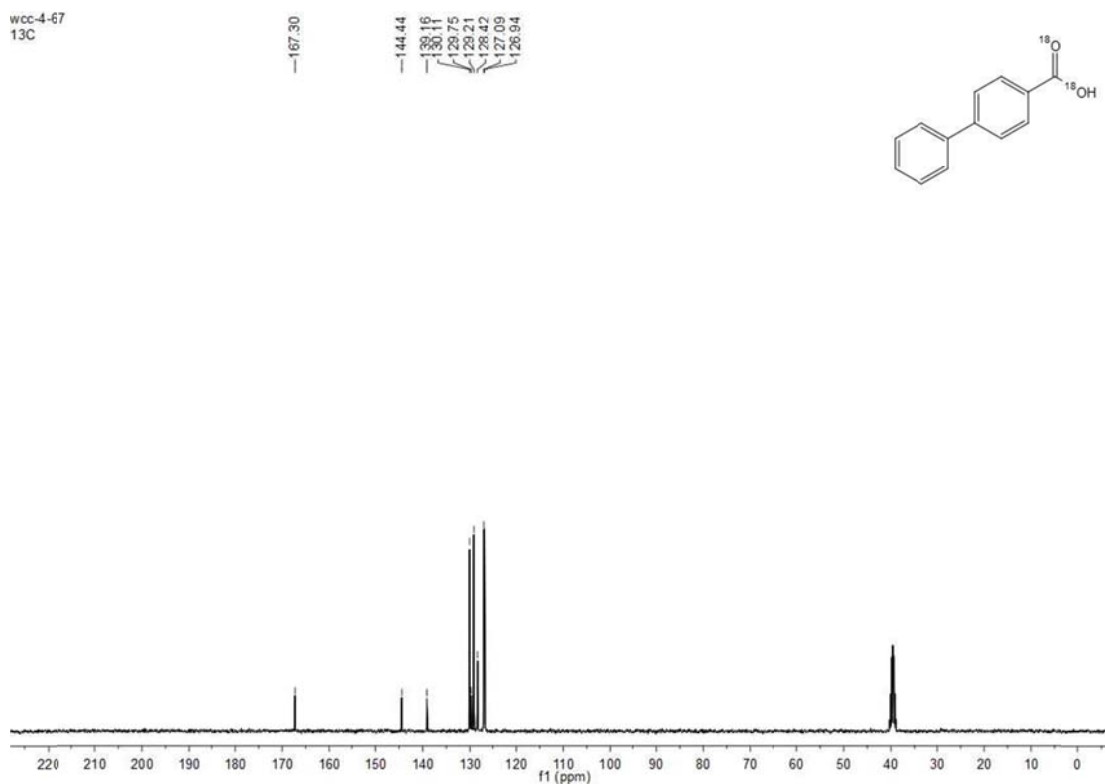
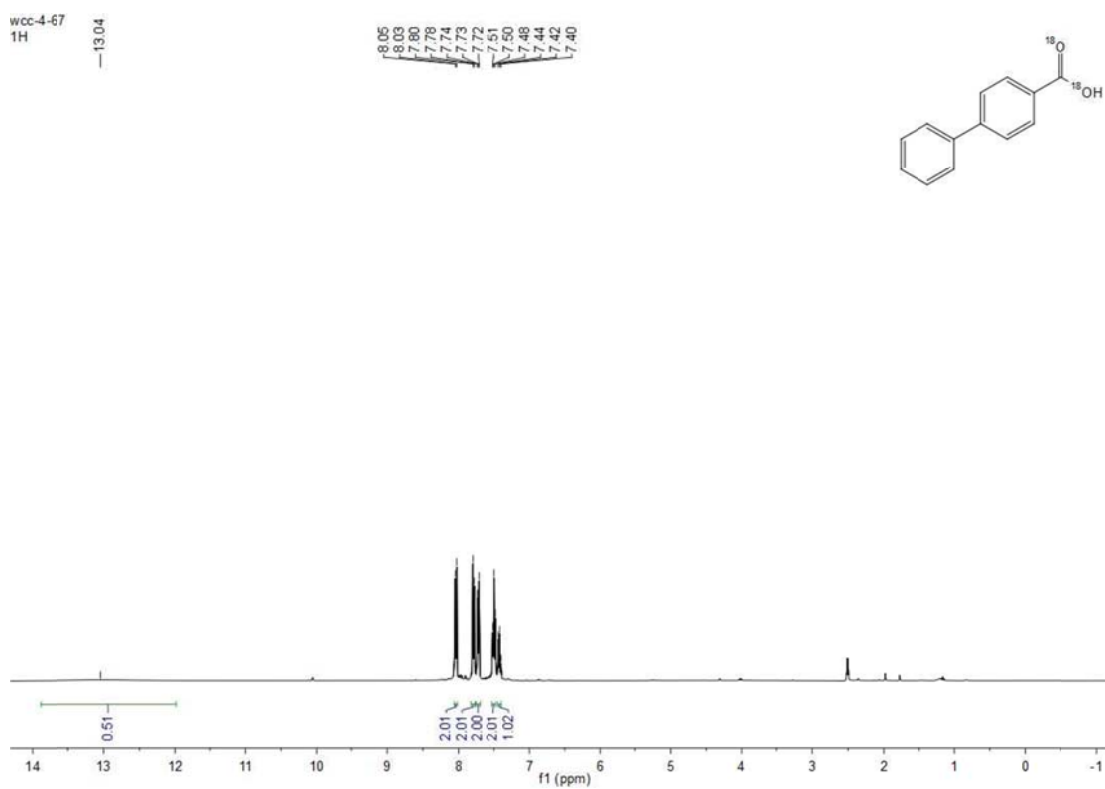
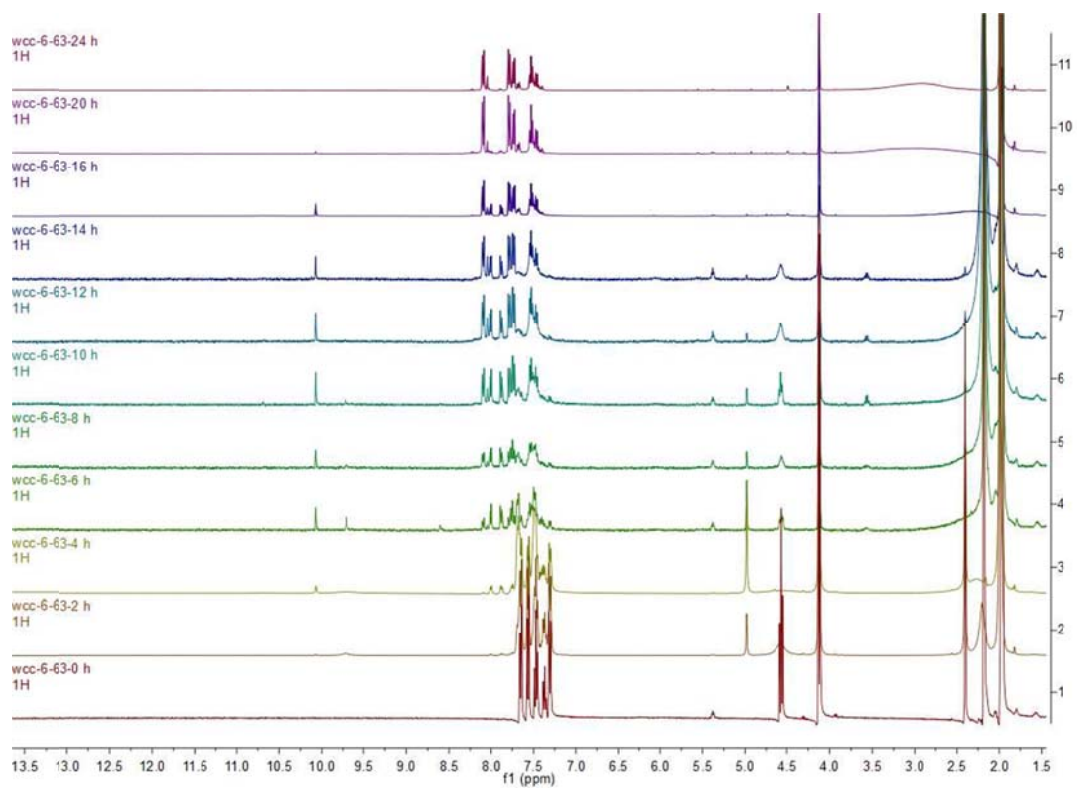


Figure 4b Kinetic experiments



4n' HRMS

