Supporting Information

Para-selective Hydroxylation of Alkyl Aryl Ethers

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1. General information

All commercial reagents were purchased from Sigma-Aldrich, Alfa-Aesar, Acros and were used without further purification unless specified. The ligand 1,3-Di-n-butylimidazoliumBromide [bbim]Br was prepared according to the literature[1]. The progress of the reaction was monitored by TLC. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 spectrometers operating respectively at 400 MHz for ^{1}H and 100 MHz for ^{13}C. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. Peak multiplicities are reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet, hept = heptet, dd = doublet of doublets. The high-resolution mass spectra (HRMS) of the new compounds were acquired on a Bruker microTOF-Q III spectrometer. Melting points were determined using X-4 apparatus and not corrected. [Ru-1] = $[RuCl_2(p\text{-cymene})]_2$, [Ru-2] = $[Ru(phen)(p\text{-cymene})]Cl_2$, [Ru-3] = $[Ru(bipy)(p\text{-cymene})]Cl_2$, [Ru-4] = $[Ru(bpym)(p\text{-cymene})]Cl_2$, [Ru-5] = Ru-NHC, [Ru-6] = $[Ru(p\text{-cymene})(O_2CMes)_2]$.

2. Procedures for the preparation of catalysts

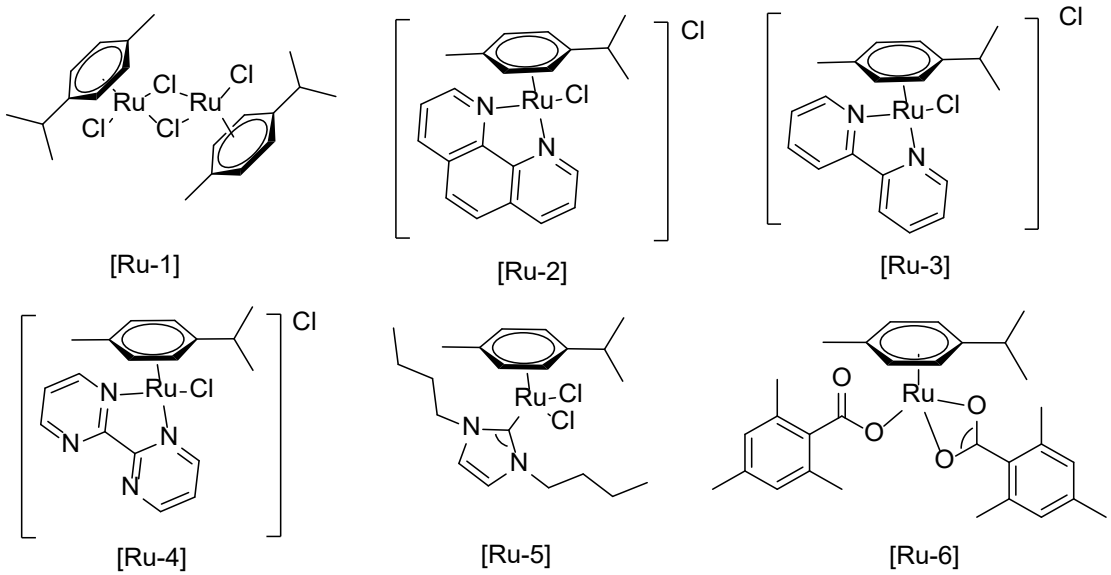


Figure S1. Corresponding structures of the [Ru 1-6] catalysts.

2.1 Preparation of [Ru-1]

A mixture of $RuCl_3$ (103.7 mg, 0.5 mmol), α-phellandrene (1 mL) in dry methanol (8 mL) was refluxed at 70 °C in oil bath for 12 h under nitrogen atmosphere. After completion of the reaction, the volume of the crude mixture is reduced by half and stored at -20 °C overnight. During this period, separate and dry under vacuum to afford Ru-1 as a deep red solid. Synthesis process refer to literature partially[2]. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.47 (d, *J* = 5.8 Hz, 2H), 5.34 (d, *J* = 5.8 Hz, 2H), 2.92 (hept, *J* = 7.0 Hz, 1H), 2.15 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 101.2, 96.7, 81.3, 80.5, 30.6, 22.2, 18.9.

2.2 Preparation of [Ru-2]

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (61.2 mg, 0.1 mmol), 1,10-phenanthroline (36 mg, 0.2 mmol) in dry methanol (5 mL) was refluxed at 90 °C in oil bath for 4 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered. The methanol was removed in vacuo, then dichloromethane was added to the residue and filtered to afford Ru-2 as a yellow solid. Synthesis process refer to literature partially[3]. **^{1}H NMR (400 MHz, Methanol-d_4)** δ 9.84 (dd, *J* = 5.4, 1.4 Hz, 2H), 8.84

(dd, *J* = 8.2, 1.4 Hz, 2H), 8.21 (s, 2H), 8.11 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.23 (d, *J* = 6.4 Hz, 2H), 6.00 (d, *J* = 6.4 Hz, 2H), 2.65 (hept, *J* = 7.0 Hz, 1H), 2.26 (s, 3H), 0.98 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Methanol-*d*$_4$)** δ 155.6, 145.7, 138.6, 130.7, 127.3, 126.2, 104.8, 103.4, 86.1, 84.0, 30.9, 20.9, 17.5.

2.3 Preparation of [Ru-3]

A mixture of [$RuCl_2$(*p*-cymene)]$_2$ (61.2 mg, 0.1 mmol), 2,2'-Bipyridine (31.2 mg, 0.2 mmol) in dry methanol (10 mL) was stirred at room temperature for 3 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered. The methanol was removed in vacuo, then dichloromethane was added to the residue and filtered to afford Ru-3 as a yellow solid. Synthesis process refer to literature partially[4]. **^{1}H NMR (400 MHz, Methanol-*d*$_4$)** δ 9.48 (d, *J* = 6.4 Hz, 2H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.23 (t, *J* = 8.0 Hz, 2H), 7.76 (ddd, *J* = 7.4, 5.8, 1.4 Hz, 2H), 6.12 (d, *J* = 6.2 Hz, 2H), 5.86 (d, *J* = 6.2 Hz, 2H), 2.63 (hept, *J* = 7.0 Hz, 1H), 2.27 (s, 3H), 1.04 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Methanol-*d*$_4$)** δ 155.5, 154.9, 139.8, 127.5, 123.6, 104.6, 104.4, 86.8, 84.1, 31.0, 20.9, 17.6.

2.4 Preparation of [Ru-4]

A mixture of [$RuCl_2$(*p*-cymene)]$_2$ (61.2 mg, 0.1 mmol), 2,2'-Bipyrimidine (31.6 mg, 0.2 mmol) in dry methanol (10 mL) was stirred at room temperature for 3 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered. The methanol was removed in vacuo, and then dichloromethane was added to the residue and filtered to afford Ru-4 as an orange-brown solid. Synthesis process refer to literature partially[5]. **^{1}H NMR (400 MHz, Methanol-*d*$_4$)** δ 9.82 (dd, *J* = 5.8, 2.0 Hz, 2H), 9.27 (dd, *J* = 4.8, 2.0 Hz, 2H), 7.96 (dd, *J* = 5.8, 4.8 Hz, 2H), 6.24 (d, *J* = 6.4 Hz, 2H), 6.03 (d, *J* = 6.4 Hz, 2H), 2.80 (hept, *J* = 7.0 Hz, 1H), 2.24 (s, 3H), 1.16 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Methanol-*d*$_4$)** δ 163.0, 160.2, 160.0, 124.6, 107.1, 103.3, 86.1, 84.8, 31.1, 21.1, 17.4.

2.5 Preparation of [Ru-5]

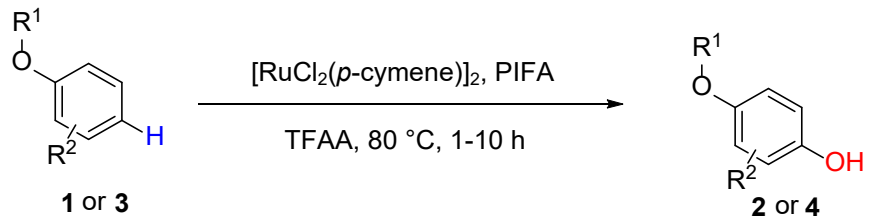
To a solution of [bbim]Br (60 mg, 0.23 mmol) in dry dichloromethane (5 mL) was added Ag_2O (39.3 mg, 0.17 mmol). The mixture was stirred at room temperature for 2

h under nitrogen atmosphere, protected from light. The reaction mixture was filtered through Celite and $[RuCl_2(p\text{-cymene})]_2$ (61.2 mg, 0.1 mmol) was added. The reaction solution is stirred at room temperature and protected from light for 20 hours and then concentrated to dryness. The crude mixture is purified by flash chromatography (2% dichloromethane/acetone) to afford Ru-5 as an orange solid. Synthesis process refer to literature partially[6]. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.06 (s, 2H), 5.38 (d, *J* = 6.0 Hz, 2H), 5.08 (d, *J* = 5.8 Hz, 2H), 4.58 (br, 2H), 3.98 (br, 2H), 2.90 (sept, *J* = 7.0 Hz, 1H), 2.04 (s, 3H), 1.95 (br, 2H), 1.67 (br, 2H), 1.42 (br, *J* = 4.2 Hz, 4H), 1.25 (d, *J* = 7.0 Hz, 6H), 0.96 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 173.1, 121.7, 107.8, 99.3, 85.1, 82.8, 51.3, 33.9, 30.7, 22.6, 20.2, 18.7, 14.0.

2.6 Preparation of [Ru-6]

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (61.2 mg, 0.1 mmol), 2,4,6-Trimethylbenzoic acid (65.7 mg, 0.4 mmol) and K_2CO_3 (138.2 mg, 1 mmol) in toluene (10 mL) was stirred at room temperature for 2 h under nitrogen atmosphere. After completion of the reaction, the toluene was removed in vacuo, then dichloromethane (10 mL) was added to the residue. The resulting suspension was filtered through Celite and concentrated to obtain Ru-6 as an orange-brown solid. Synthesis process refer to literature partially[7]. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.68 (s, 4H), 5.98 (s, 2H), 5.77 (s, 2H), 2.96 (hept, *J* = 7.0 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 6H), 2.16 (s, 12H), 1.42 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 183.1, 137.4, 135.2, 134.5, 127.9, 98.1, 79.0, 78.1, 31.6, 22.7, 21.1, 19.9, 19.0.

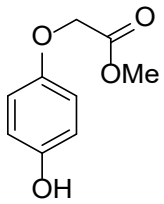
3. General procedures for preparation 2 and 4



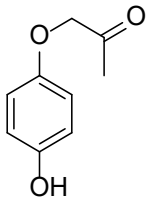
1 or **3** **2** or **4**

To a solution of substrate **1** or **3** (0.30 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (2.75 mg, 1.5 mol %) in TFAA (1.5 mL) was added PIFA (129 mg, 0.30 mmol). The mixture was stirred at 80 °C in oil bath for 1-10 h in a 10 mL of sealed tube. After completion of the reaction, saturated aqueous $NaHCO_3$ solution (10 mL) was added at ambient temperature, then extracted with ethyl acetate 3 times (3×20 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by flash chromatography to afford product **2** or **4**.

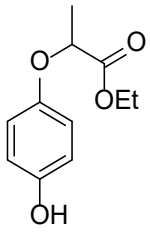
4. Characterization data of products 2 and 4



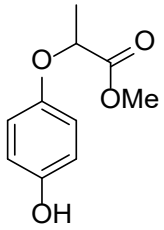
methyl 2-(4-hydroxyphenoxy)acetate (2a): The general procedure was followed using methyl 2-phenoxyacetate **1a** (50.0 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **2a** (32 mg, 60%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 6.83 – 6.73 (m, 4H), 5.14 (brs, 1H), 4.59 (s, 2H), 3.81 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 169.9, 151.9, 150.5, 116.2, 116.0, 66.2, 52.3. Spectra data are consistent with those reported in the literature: *Bioorg. Med. Chem.* **2015**, *23*, 132-140.



1-(4-hydroxyphenoxy)propan-2-one (2b): The general procedure was followed using 1-phenoxypropan-2-one **1b** (45.0 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **2b** (23.9 mg, 48%) as a white solid. **^{1}H NMR (400 MHz, Methanol-d$_4$)** δ 6.78 – 6.74 (m, 2H), 6.72 – 6.68 (m, 2H), 4.58 (s, 2H), 2.19 (s, 3H); **^{13}C NMR (100 MHz, Methanol-d$_4$)** δ 206.5, 151.6, 151.3, 115.5, 115.4, 73.3, 24.9; **HRMS (ESI)**: m/z $[M - H]^-$ calcd for $C_9H_9O_3$: 165.0552; found: 165.0548. Melt point: 104 – 106°C.

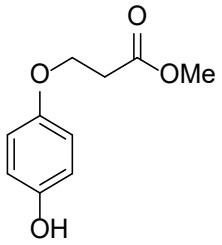


ethyl 2-(4-hydroxyphenoxy)propanoate (2c): The general procedure was followed using ethyl 2-phenoxypropanoate **1c** (58.2 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **2c** (41.6 mg, 66%) as a pale brown oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 6.79 – 6.70 (m, 4H), 4.83 (brs, 1H), 4.64 (q, J = 6.8 Hz, 1H), 4.21 (q, J = 7.6, 7.2 Hz, 2H), 1.59 (d, J = 6.8 Hz, 3H), 1.25 (t, J = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 173.1, 151.4, 150.5, 116.6, 116.1, 73.6, 61.5, 18.6, 14.1; **HRMS (ESI)**: m/z $[M + Na]^+$ calcd for $C_{11}H_{14}NaO_4$: 233.0790; found: 233.0778.

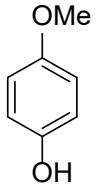


methyl 2-(4-hydroxyphenoxy)propanoate (2d): The general procedure was followed using methyl 2-phenoxypropanoate **1d** (54.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl

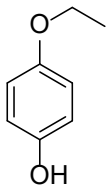
acetate = 3/1) to afford **2d** (37.7 mg, 64%) as a pale brown oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 6.81 – 6.69 (m, 4H), 4.67 (q, J = 6.8 Hz, 1H), 3.76 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 173.5, 151.4, 150.6, 116.6, 116.2, 73.6, 52.5, 18.7; **HRMS (ESI)**: m/z $[M + Na]^+$ calcd for $C_{10}H_{12}NaO_4$: 219.0633; found: 219.0626.



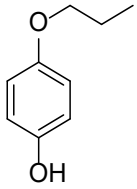
methyl 3-(4-hydroxyphenoxy)propanoate (2e): The general procedure was followed using methyl 3-phenoxypropanoate **1e** (54.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **2e** (36.5 mg, 62%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 6.74 (s, 4H), 5.59 (brs, 1H), 4.17 (t, J = 6.4 Hz, 2H), 3.73 (s, 3H), 2.78 (t, J = 6.4 Hz, 2H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 172.2, 152.4, 150.1, 116.1, 115.9, 64.2, 52.1, 34.6; **HRMS (ESI)**: m/z $[M - H]^-$ calcd for $C_{10}H_{11}O_4$: 195.0657; found: 195.0665. Melt point: 72 – 74°C.



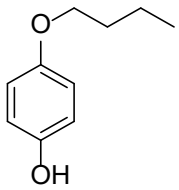
4-methoxyphenol (2f): The general procedure was followed using anisole **1f** (32.4 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2f** (28.2 mg, 75%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.81 – 6.75 (m, 4H), 4.86 (brs, 1H), 3.76 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.7, 149.5, 116.1, 114.9, 55.8. Spectra data are consistent with those reported in the literature: *J. Org. Chem.* **2012**, *77*, 7052-7060.



4-ethoxyphenol (2g): The general procedure was followed using ethoxybenzene **1g** (36.6 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2g** (29.4 mg, 71%) as a beige solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.80 – 6.74 (m, 4H), 4.53 (brs, 1H), 3.98 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.9, 149.5, 116.1, 115.7, 115.7, 64.3, 14.9. Spectra data are consistent with those reported in the literature: *Org. Lett.* **2018**, *20*, 361-364.

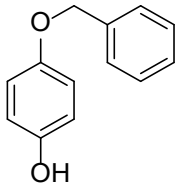


4-propoxyphenol (2h): The general procedure was followed using propoxybenzene **1h** (40.8 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2h** (32.0 mg, 70%) as a beige solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.81 – 6.74 (m, 4H), 4.71 (brs, 1H), 3.86 (t, *J* = 6.6 Hz, 2H), 1.78 (h, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.2, 149.4, 116.1, 115.7, 70.4, 22.7, 10.5. Spectra data are consistent with those reported in the literature: *Tetrahedron Lett.* **2014**, *55*, 86-89.

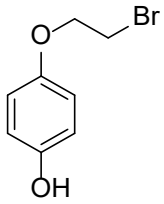


4-butoxyphenol (2i): The general procedure was followed using butoxybenzene **1i** (45 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2i** (42.3 mg, 85%) as a pale brown solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.80 – 6.73 (m, 4H), 4.36 (brs, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.69 (m, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* =

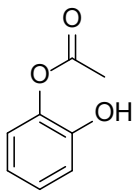
7.4 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.3, 149.4, 116.0, 115.7, 68.5, 31.4, 19.3, 13.9. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **2019**, *141*, 3541-3549.



4-(benzyloxy)phenol (2j): The general procedure was followed using (benzyloxy)benzene **1j** (55.3 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2j** (39.0 mg, 65%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.29 (m, 5H), 6.88 – 6.83 (m, 2H), 6.79 – 6.73 (m, 2H), 5.01 (s, 2H), 4.53 (brs, 1H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.0, 149.7, 137.2, 128.6, 128.0, 127.6, 116.1, 70.8. Spectra data are consistent with those reported in the literature: *Green Chem.* **2021**, *23*, 2308-2316.

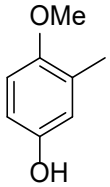


4-(2-bromoethoxy)phenol (2k): The general procedure was followed using (2-bromoethoxy)benzene **1k** (60.3 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **2k** (45.6 mg, 70%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.85 – 6.73 (m, 4H), 4.67 (brs, 1H), 4.23 (t, *J* = 6.4 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.2, 150.1, 116.3, 116.2, 68.9, 29.4. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **2017**, *139*, 3122-3133.

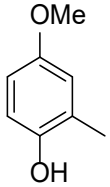


2-hydroxyphenyl acetate (2l): The general procedure was followed using phenyl

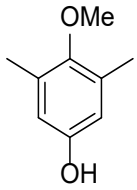
acetate **1l** (40.8 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **2l** (19.6 mg, 43%) as a pale yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.14 – 7.09 (m, 1H), 7.08 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.92 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 1H), 5.04 (brs, 1H), 2.34 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 147.2, 138.5, 127.1, 122.5, 120.9, 117.7, 20.9. Spectra data are consistent with those reported in the literature: *Org. Biomol. Chem.* **2017**, *15*, 6909-6912.



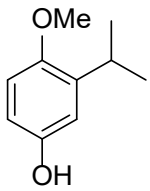
4-methoxy-3-methylphenol (4a): The general procedure was followed using 1-methoxy-2-methylbenzene **3a** (36.6 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4a** (25.3 mg, 61%) as a colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.70 (d, *J* = 8.6 Hz, 1H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.62 (dd, *J* = 8.6, 3.0 Hz, 1H), 3.78 (s, 3H), 2.18 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.0, 149.1, 128.1, 118.0, 112.5, 111.3, 56.0, 16.3. Spectra data are consistent with those reported in the literature: *Org. Lett.* **2017**, *19*, 429-431.



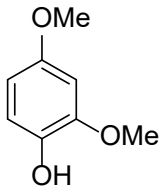
4-methoxy-2-methylphenol (4b): The general procedure was followed using 1-methoxy-3-methylbenzene **3b** (36.6 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4b** (25.0 mg, 60%) as an off-white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.70 (dd, *J* = 5.8, 2.8 Hz, 2H), 6.63 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.53 (brs, 1H), 3.75 (s, 3H), 2.24 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.6, 147.8, 124.9, 116.6, 115.5, 111.8, 55.8, 16.1. Spectra data are consistent with those reported in the literature: *Org. Biomol. Chem.* **2016**, *14*, 5520-5524.



4-methoxy-3,5-dimethylphenol (4c): The general procedure was followed using 2-methoxy-1,3-dimethylbenzene **3c** (40.8 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4c** (28.8 mg, 63%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.47 (s, 2H), 4.71 (brs, 1H), 3.67 (s, 3H), 2.23 (s, 6H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.3, 150.5, 131.9, 115.1, 60.0, 16.2. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **2014**, *53*, 11056-11059.

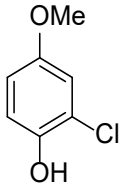


3-isopropyl-4-methoxyphenol (4d): The general procedure was followed using 1-isopropyl-2-methoxybenzene **3d** (45.0 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4d** (31.9 mg, 64%) as a pale yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.72 (dd, *J* = 6.0, 2.8 Hz, 2H), 6.61 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.58 (brs, 1H), 3.78 (s, 3H), 3.28 (hept, *J* = 7.0 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.0, 149.5, 138.7, 113.6, 112.4, 111.9, 56.3, 26.7, 22.7. Spectra data are consistent with those reported in the literature: *J. Med. Chem.* **2016**, *59*, 4790-4799.

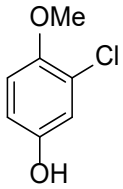


2,4-dimethoxyphenol (4e): The general procedure was followed using 1,3-dimethoxybenzene **3e** (41.4 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to

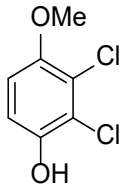
afford **4e** (28.0 mg, 60%) as a colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.83 (d, *J* = 8.6 Hz, 1H), 6.49 (d, *J* = 2.8 Hz, 1H), 6.39 (dd, *J* = 8.6, 2.8 Hz, 1H), 5.24 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.5, 147.1, 139.8, 114.1, 104.2, 99.4, 55.9, 55.8. Spectra data are consistent with those reported in the literature: *J. Org. Chem.* **2020**, *85*, 2040-2047.



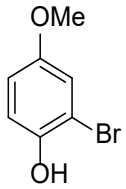
2-chloro-4-methoxyphenol (4f): The general procedure was followed using 1-chloro-3-methoxybenzene **3f** (42.7 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4f** (20.0 mg, 42%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.94 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 6.75 (dd, *J* = 8.8, 3.0 Hz, 1H), 5.19 (s, 1H), 3.75 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.6, 145.5, 119.9, 116.6, 114.5, 114.1, 55.9. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **2009**, *58*, 9547-9550.



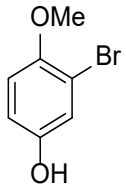
3-chloro-4-methoxyphenol (4g): The general procedure was followed using 1-chloro-2-methoxybenzene **3g** (42.7 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4g** (24.7 mg, 52%) as a yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.91 (dd, *J* = 3.0, 0.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.27 (brs, 1H), 3.84 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 149.7, 149.4, 122.9, 117.7, 114.3, 113.5, 56.9. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **2020**, *59*, 3184-3189.



2,3-dichloro-4-methoxyphenol (4h): The general procedure was followed using 1,2-dichloro-3-methoxybenzene **3h** (53.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 10 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4h** (23.2 mg, 40%) as a beige solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.93 (d, *J* = 9.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 5.31 (brs, 1H), 3.87 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.1, 146.4, 121.4, 120.2, 113.6, 111.5, 57.0. Spectra data are consistent with those reported in the literature: *Org. Biomol. Chem.* **2014**, *12*, 2854-2858.

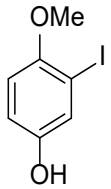


2-bromo-4-methoxyphenol (4i): The general procedure was followed using 1-bromo-3-methoxybenzene **3i** (56.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4i** (33.0 mg, 54%) as a red oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.01 (d, *J* = 2.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.15 (s, 1H), 3.75 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.8, 146.5, 116.8, 116.3, 115.3, 109.9, 56.0. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **2021**, *60*, 685-689.

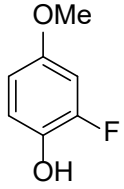


3-bromo-4-methoxyphenol (4j): The general procedure was followed using 1-bromo-2-methoxybenzene **3j** (56.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1 to afford **4j** (34.1 mg, 56%) as a white powder. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.08 (d,

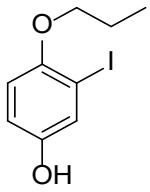
J = 2.6 Hz, 1H), 6.81 – 6.73 (m, 2H), 4.34 (brs, 1H), 3.83 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.2, 150.1, 120.6, 115.1, 113.2, 111.9, 56.9. Spectra data are consistent with those reported in the literature: *ChemComm* **2017**, *53*, 5291-5293.



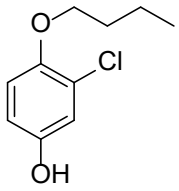
3-iodo-4-methoxyphenol (4k): The general procedure was followed using 1-iodo-2-methoxybenzene **3k** (70.2 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4k** (39.0 mg, 52%) as a yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 (d, *J* = 2.8 Hz, 1H), 6.81 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 4.57 (brs, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.8, 150.1, 126.3, 116.0, 111.8, 86.0, 57.0. Spectra data are consistent with those reported in the literature: *J. Med. Chem.* **2016**, *59*, 4790-4799.



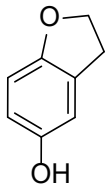
2-fluoro-4-methoxyphenol (4l): The general procedure was followed using 1-fluoro-3-methoxybenzene **3l** (37.8 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4l** (16.0 mg, 37%) as an orange oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.95 – 6.88 (m, 1H), 6.68 (dd, *J* = 12.0, 2.8 Hz, 1H), 6.59 (ddd, *J* = 8.8, 2.8, 1.4 Hz, 1H), 4.97 (brs, 1H), 3.75 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.6 (d, 9.2), 151.1 (d, 237.6), 137.3 (d, 14.4), 117.4 (d, 3.2), 109.8 (d, 3.4), 102.3 (d, 21.6), 55.9. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **2002**, *124*, 5294-5303.



3-iodo-4-propoxyphenol (4m): The general procedure was followed using 1-iodo-2-propoxybenzene **3m** (78.6 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4m** (44.2 mg, 53%) as a yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 (d, *J* = 2.8 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 4.75 (brs, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.3, 150.0, 126.1, 116.0, 113.4, 87.0, 71.8, 22.7, 10.8; **HRMS (ESI)**: m/z [M - H]$^-$ calcd for $C_9H_{10}IO_2$: 276.9725; found: 276.9726.

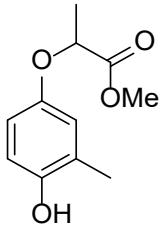


4-butoxy-3-chlorophenol (4n): The general procedure was followed using 1-butoxy-2-chlorobenzene **3n** (55.3 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4n** (33.1 mg, 55%) as a yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.89 (d, *J* = 3.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.56 – 1.45 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR (100 MHz, Chloroform-*d*)** δ 149.7, 148.9, 123.8, 117.5, 115.4, 114.3, 70.1, 31.3, 19.2, 13.9; **HRMS (ESI)**: m/z [M - H]$^-$ calcd for $C_{10}H_{12}ClO_2$: 199.0526; found: 199.0522.

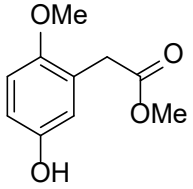


2,3-dihydrobenzofuran-5-ol (4o): The general procedure was followed using 2,3-dihydrobenzofuran **3o** (36.0 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 8/1) to afford **4o** (14.3 mg, 35%) as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.72

(d, *J* = 2.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.56 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.18 (brs, 1H), 4.53 (t, *J* = 8.6 Hz, 2H), 3.15 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.9, 149.6, 128.2, 114.2, 112.4, 109.3, 71.3, 30.2. Spectra data are consistent with those reported in the literature: *Z NATURFORSCH B* **2008**, *63*, 90-94.



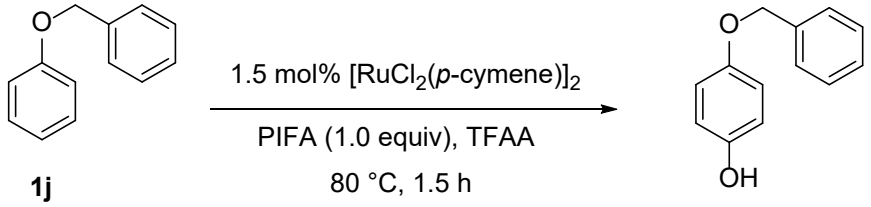
methyl 2-(4-hydroxy-3-methylphenoxy)propanoate (4p): The general procedure was followed methyl 2-(m-tolyloxy)propanoate **3p** (58.2 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 6 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **4p** (39.1 mg, 62%) as a colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.70 (d, *J* = 3.4 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.58 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.74 (brs, 1H), 4.66 (q, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 2.20 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 173.4, 151.3, 148.8, 125.3, 118.5, 115.5, 113.4, 73.5, 52.4, 18.7, 16.1; **HRMS (ESI)**: m/z $[M + Na]^+$ calcd for $C_{11}H_{14}NaO_4$: 233.0790; found: 233.0779.



methyl 2-(5-hydroxy-2-methoxyphenyl)acetate (4q): The general procedure was followed methyl 2-(2-methoxyphenyl)acetate **3q** (54.1 mg, 0.3 mmol). The reaction mixture was stirred at 80 °C for 1.5 h. Isolation by flash chromatography (petroleum ether/ethyl acetate = 3/1) to afford **4q** (44.1 mg, 75%) as a yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.75 – 6.68 (m, 3H), 4.96 (brs, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 3.59 (s, 2H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 173.2, 151.5, 149.6, 123.6, 118.2, 114.8, 111.9, 56.1, 52.2, 35.7; **HRMS (ESI)**: m/z $[M - H]^-$ calcd for $C_{10}H_{11}O_4$: 195.0657; found: 195.0658.

5. Gram-scale up synthesis of medicine Monobenzone and Pramocaine

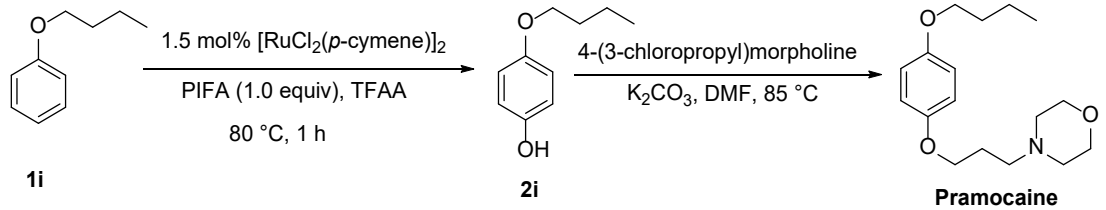
5.1 Gram-scale up synthesis of medicine Monobenzone



1j **2j, Monobenzone**

To a solution of substrate **1j** (1.65 g, 9 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (82.6 mg, 13.5 mol %) in TFAA (32 mL) was added PIFA (3.87 g, 9 mmol). The mixture was stirred at 80 °C in oil bath for 1.5 h in a 75 mL of sealed tube. After completion of the reaction, the reaction mixture was transferred to a round bottom flask, TFAA was recovered by distillation at 70°C, and the residue was transferred to a separatory funnel. A saturated aqueous $NaHCO_3$ solution (60 mL) was added at ambient temperature, and then extracted with ethyl acetate 3 times (3×50 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture is purified by flash chromatography (petroleum ether/ethyl acetate = 8:1) to afford the product **2j (Monobenzone)** as a white solid (1.14 g, 63% yield).

5.2 Gram-scale up synthesis of medicine Pramocaine

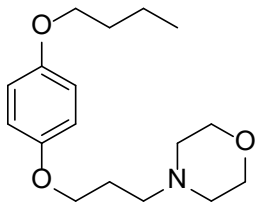


1i **2i** **Pramocaine**

To a solution of substrate **1i** (1.5 g, 10 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (91.8 mg, 15 mol %) in TFAA (32 mL) was added PIFA (4.3 g, 10 mmol). The mixture was stirred at 80 °C in oil bath for 1 h in a 75 mL of sealed tube. After completion of the reaction, the reaction mixture was transferred to a round bottom flask, TFAA was recovered by distillation at 70°C, and the residue was transferred to a separatory funnel. A saturated

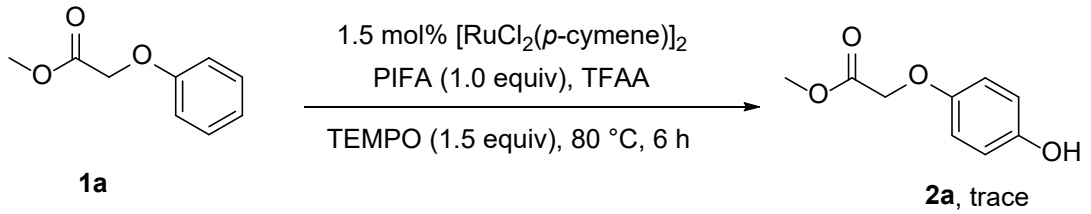
aqueous $NaHCO_3$ solution (60 mL) was added at ambient temperature, and then extracted with ethyl acetate 3 times (3×50 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture is purified by flash chromatography (petroleum ether/ethyl acetate = 8:1) to afford the product **2i** as a pale brown solid (1.41 g, 85% yield).

A mixture of **2i** (1.66 g, 10 mmol), K_2CO_3 (2.07 g, 15 mmol) and 4-(3-chloropropyl)morpholine (2.45 g, 10 mmol) in DMF (15 mL) was stirred at 80 °C in oil bath for 10 h, After completion of the reaction, added 50 mL water to the mixture, and then extracted with ethyl acetate 3 times (3×50 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture is purified by flash chromatography (petroleum ether/ethyl acetate = 3:1) to afford the product **Pramocaine** as a pale yellow oil (2.11 g, 75% yield).



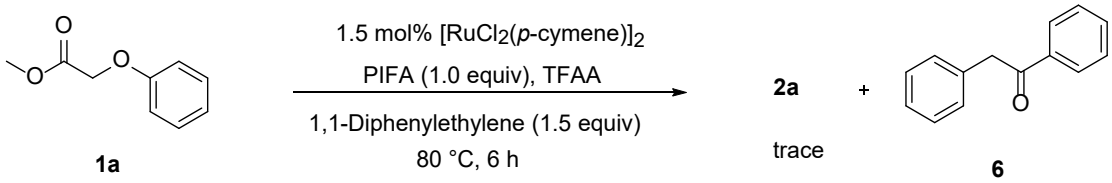
4-(3-(4-butoxyphenoxy)propyl)morpholine (Pramocaine): ^{1}H NMR (400 MHz, Chloroform-d) δ 6.82 (s, 4H), 3.97 (t, J = 6.3 Hz, 2H), 3.90 (t, J = 6.5 Hz, 2H), 3.72 (t, J = 4.7 Hz, 4H), 2.54 – 2.44 (m, 6H), 1.99 – 1.91 (m, 2H), 1.78 – 1.70 (m, 2H), 1.53 – 1.42 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.3, 153.0, 115.4, 115.4, 68.3, 67.0, 66.7, 55.6, 53.8, 31.5, 26.6, 19.3, 13.9.

6. General procedures for TEMPO inhibition experiments

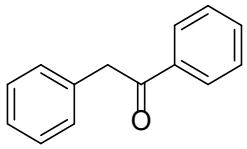


To a solution of substrate **1a** (50.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.75 mg, 1.5 mol %) and TEMPO (70 mg, 0.45 mmol) in TFAA (1.5 mL) was added PIFA (129mg, 0.3 mmol). The mixture was stirred at 80 °C in oil bath for 6 h in a 10 mL of sealed tube. The reaction is inhibited.

7. Radical trapping experiments



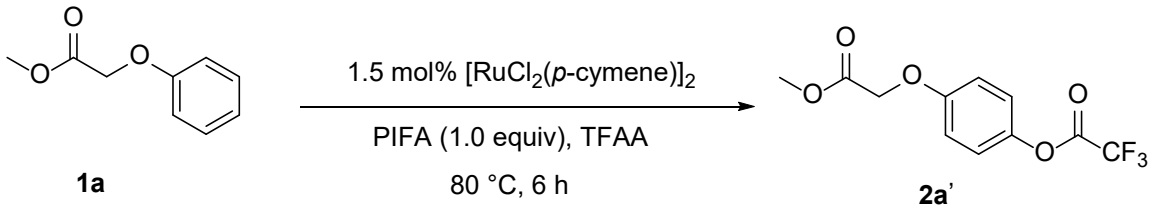
To a solution of substrate **1a** (50.0 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.75 mg, 1.5 mol %) and 1,1-diphenylethylene (81 mg, 0.45 mmol) in TFAA (1.5 mL) was added PIFA (129 mg, 0.3 mmol). The mixture was stirred at 80 °C in oil bath for 6 h in a 10 mL of sealed tube. After completion of the reaction, the mixture was filtered through Celite. The crude mixture is purified by flash chromatography (petroleum ether/ethyl acetate =10:1) to afford the product **6**.



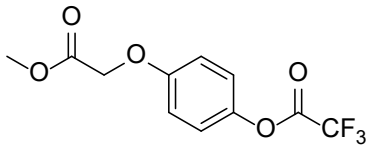
1,2-diphenylethan-1-one (6): Pale yellow solid. Isolated yield: 24mg, 40%. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.02 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 4.29 (s, 2H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 197.7, 136.6, 134.6, 133.2, 129.5, 128.7, 128.7, 128.7, 126.9,

45.5; **HRMS (ESI)**: m/z [M + Na]$^+$ calcd for $C_{14}H_{12}NaO$: 219.0780; found: 219.0779.

8. Capture of trifluoroacetate intermediate



To a solution of substrate **1a** (50 mg, 0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.75 mg, 1.5 mol %) in TFAA (1.5 mL) was added PIFA (129 mg, 0.3 mmol). The mixture was stirred at 80 °C in oil bath for 6 h in a 10 mL of sealed tube. After completion of the reaction, the reaction mixture was transferred to a round bottom flask and concentrated. The crude mixture is purified by flash chromatography (petroleum ether/ethyl acetate = 8:1) to afford the product **2a'**.



4-(2-methoxy-2-oxoethoxy)phenyl 2,2,2-trifluoroacetate (2a'): off-white solid Isolated yield: 45.6 mg, 55%. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.18 – 7.13 (m, 2H), 6.98 – 6.93 (m, 2H), 4.65 (s, 2H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, Chloroform-d)** δ 169.01, 156.41, 155.98 (d, J = 43.3 Hz), 143.57, 121.58, 115.66, 114.58 (d, J = 285.6 Hz), 65.54, 52.33; **^{19}F NMR (376 MHz, Chloroform-d)** δ -74.83. Melt point: 66 – 68°C.

References

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[2] M. Dutta, K. K. Bania and S. Pratihar, *ChemCatChem*, **2019**, 11, 2683-2694.

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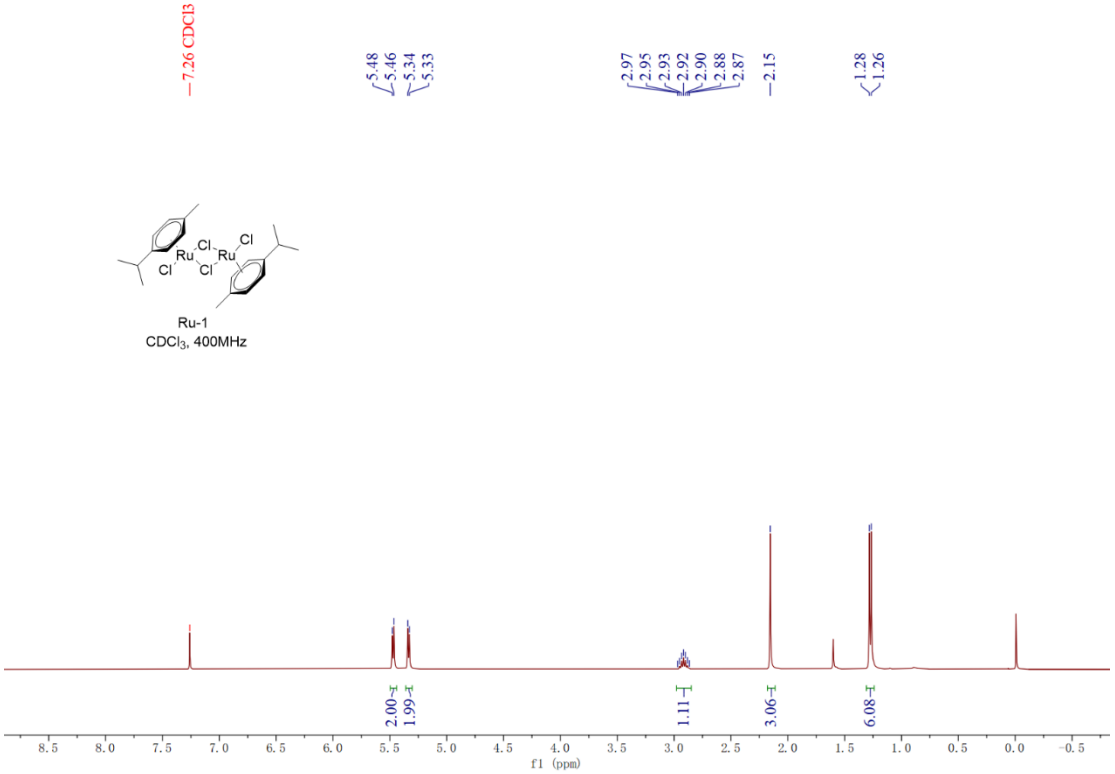
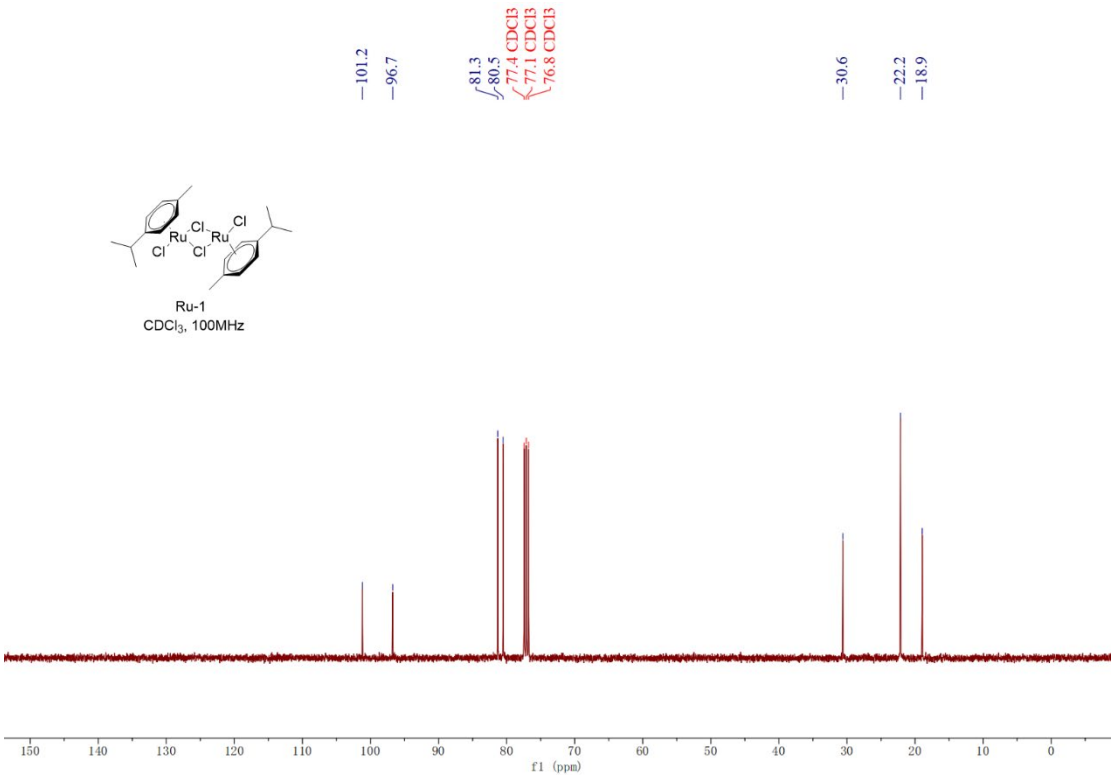
[7] L. Ackermann, R. n. Vicente, H. K. Potukuchi, et al., *Org. Lett.*, **2010**, 12, 5032–5035.

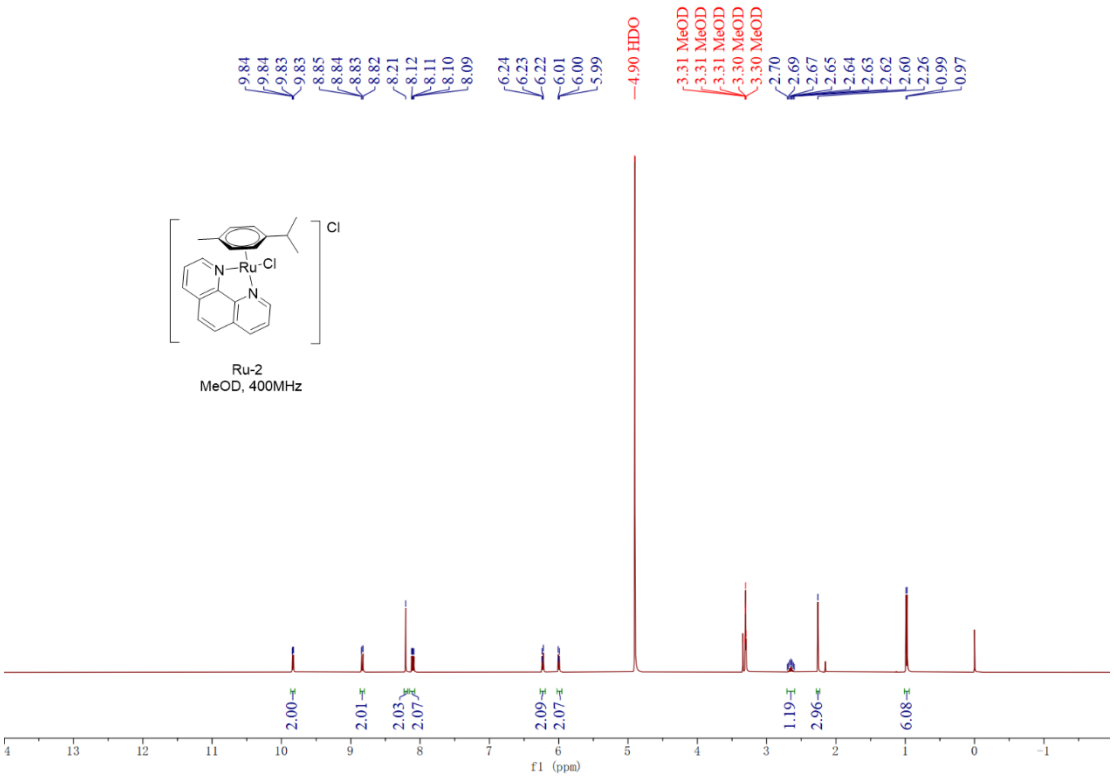
NMR spectra

Ru-1





Ru-2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9.83
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8.82
8.21
8.12
8.11
8.10
8.09
6.24
6.23
6.22
6.01
6.00
5.99
4.90 HDO
3.31 MeOD
3.31 MeOD
3.31 MeOD
3.30 MeOD
3.30 MeOD
2.70
2.69
2.67
2.65
2.64
2.63
2.62
2.60
2.26
0.99
0.97
Cl
N
Ru
Cl
N
Ru-2
MeOD, 400MHz
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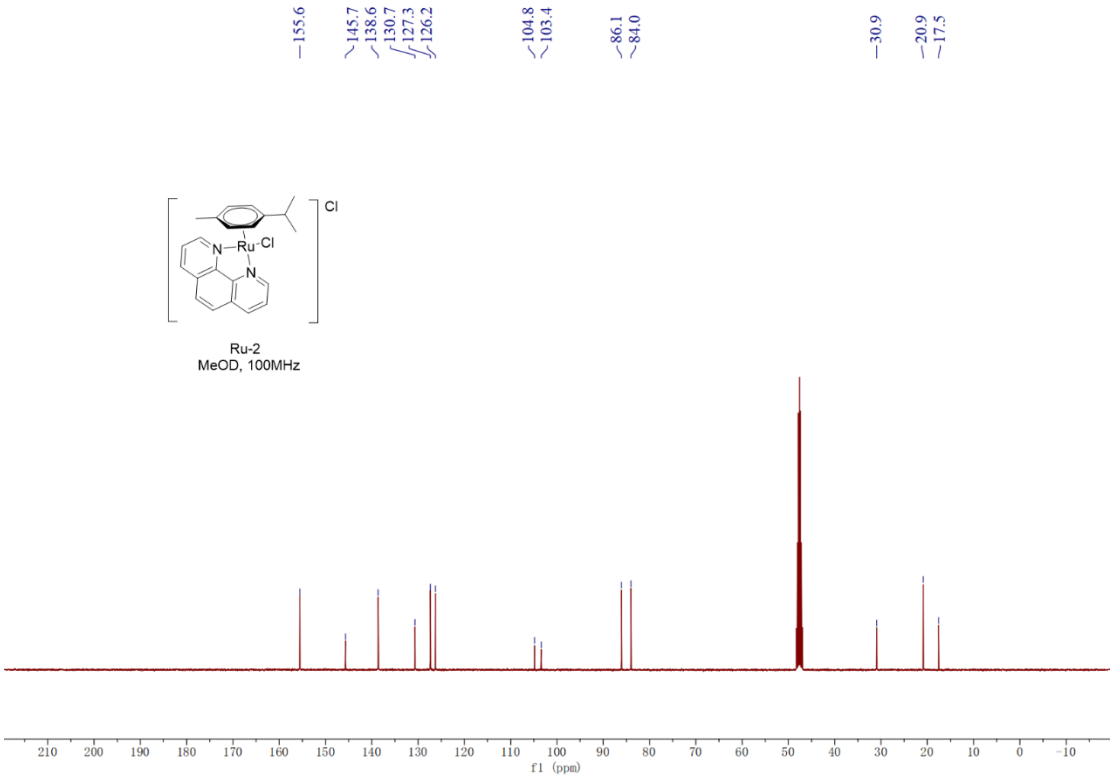
2.01
2.03
2.07
2.09
2.07
1.19
2.96
6.08
f1 (ppm)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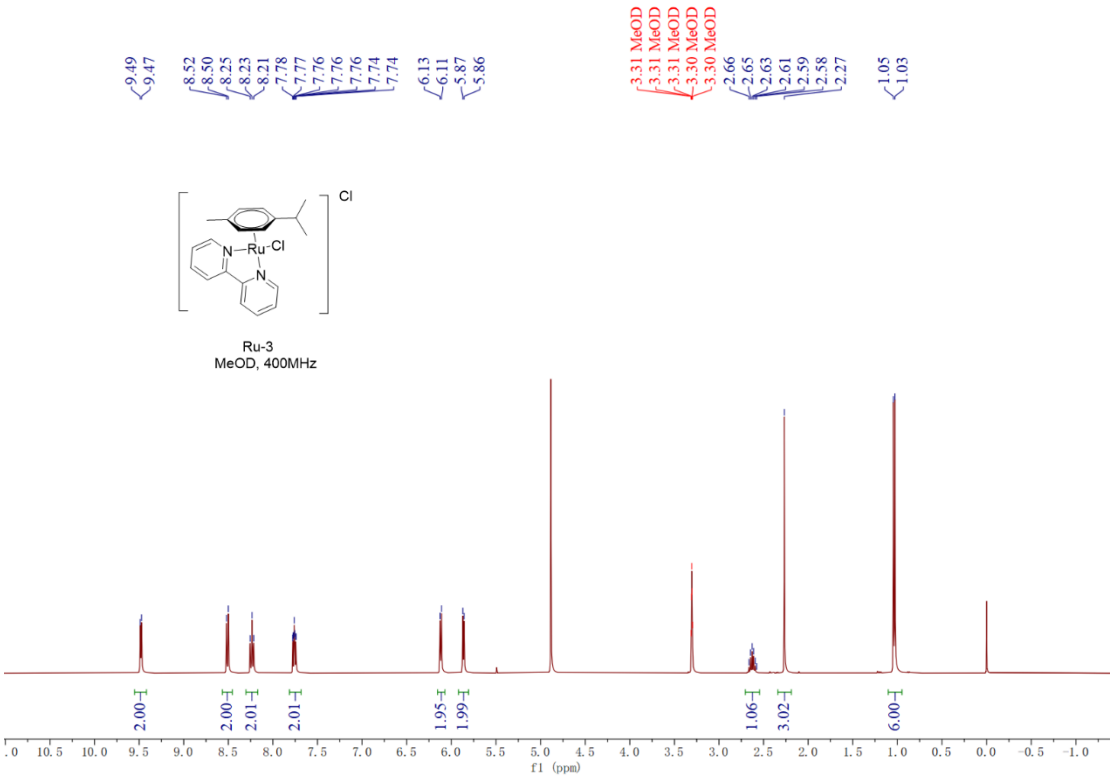
145.7
138.6
130.7
127.3
126.2
104.8
103.4
86.1
84.0
30.9
20.9
17.5
Cl
N
Ru
Cl
N
Ru-2
MeOD, 100MHz
f1 (ppm)

Ru-3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8.21
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7.76
7.76
7.76
7.74
7.74
6.13
6.11
5.87
5.86
3.31 MeOD
3.31 MeOD
3.31 MeOD
3.30 MeOD
3.30 MeOD
2.66
2.65
2.63
2.61
2.59
2.58
2.27
1.05
1.03
Cl
N—Ru—Cl
N
Ru-3
MeOD, 400MHz
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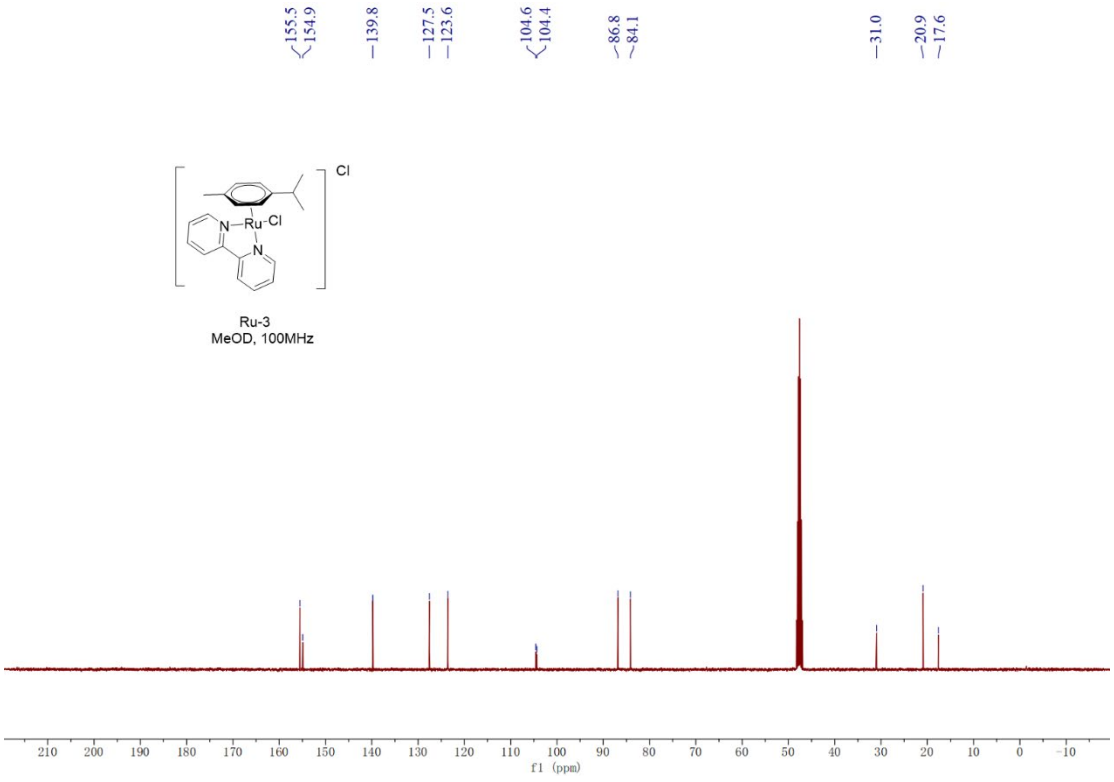
2.00
2.01
2.01
1.95
1.99
1.06
3.02
6.00
f1 (ppm)


155.5
154.9
139.8
127.5
123.6
104.6
104.4
86.8
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31.0
20.9
17.6
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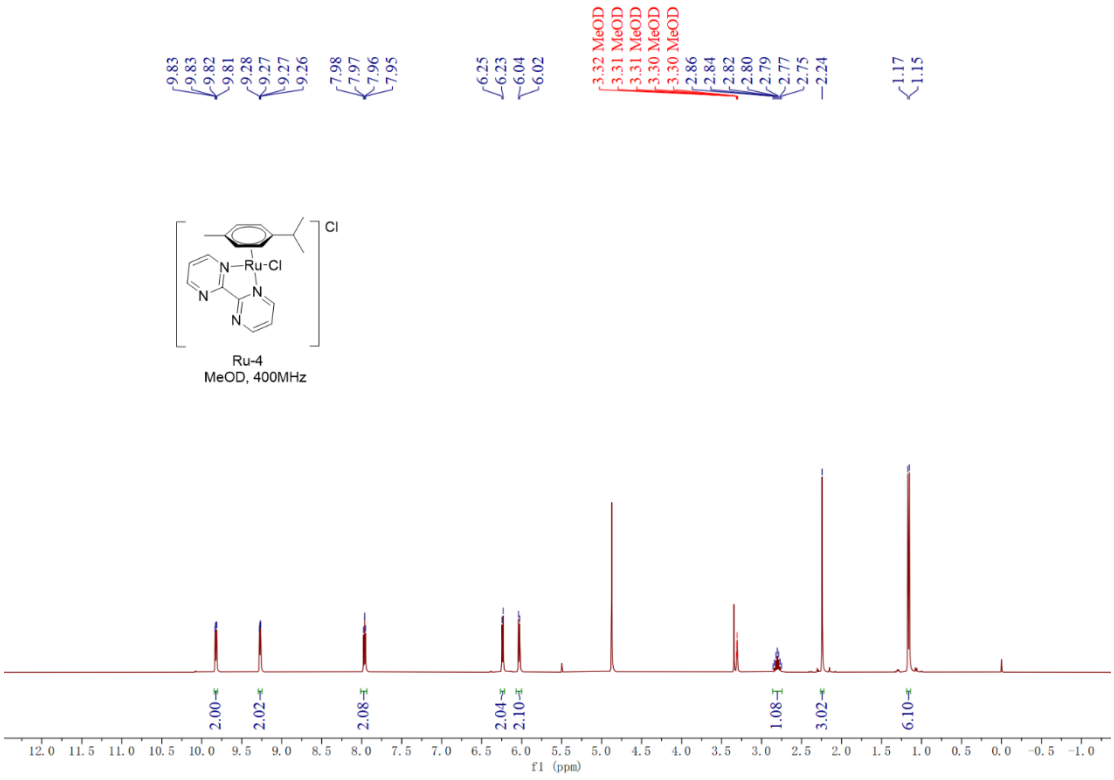
N
Ru-3
MeOD, 100MHz
f1 (ppm)

Ru-4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9.83
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9.28
9.27
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9.26
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7.97
7.96
7.95
6.25
6.23
6.04
6.02
3.32 MeOD
3.31 MeOD
3.31 MeOD
3.30 MeOD
3.30 MeOD
2.86
2.84
2.82
2.80
2.79
2.77
2.75
2.24
1.17
1.15
Cl
Ru-Cl
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1.08
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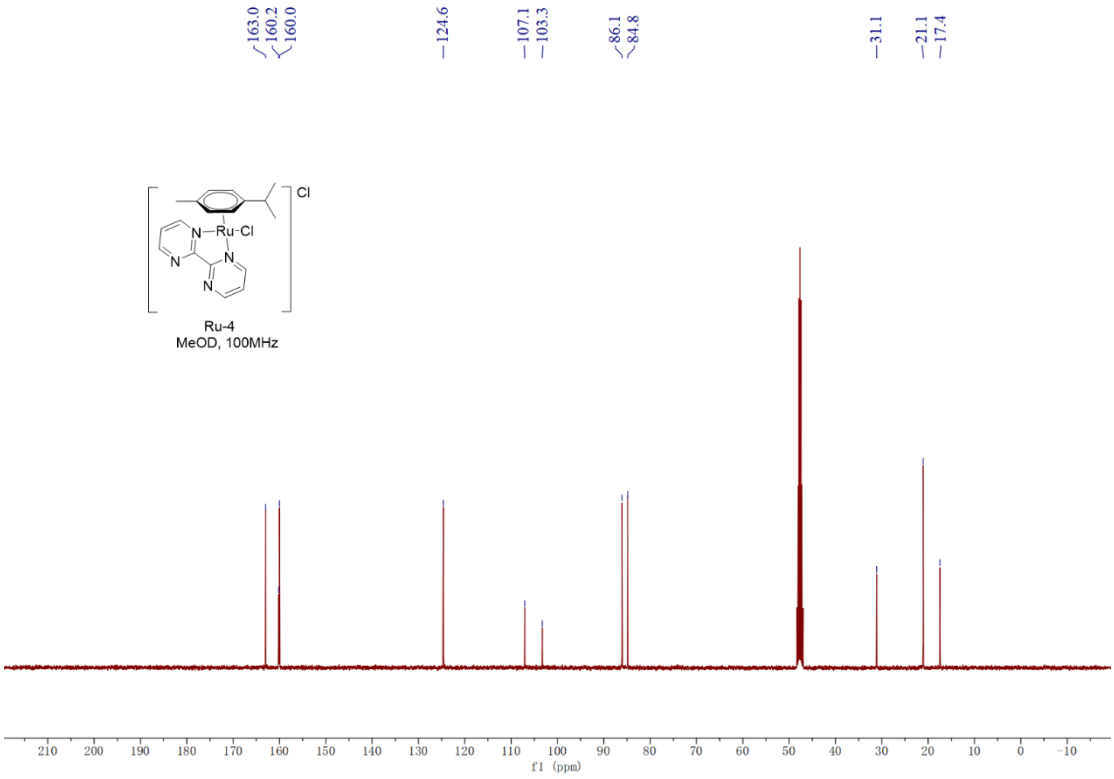
f1 (ppm)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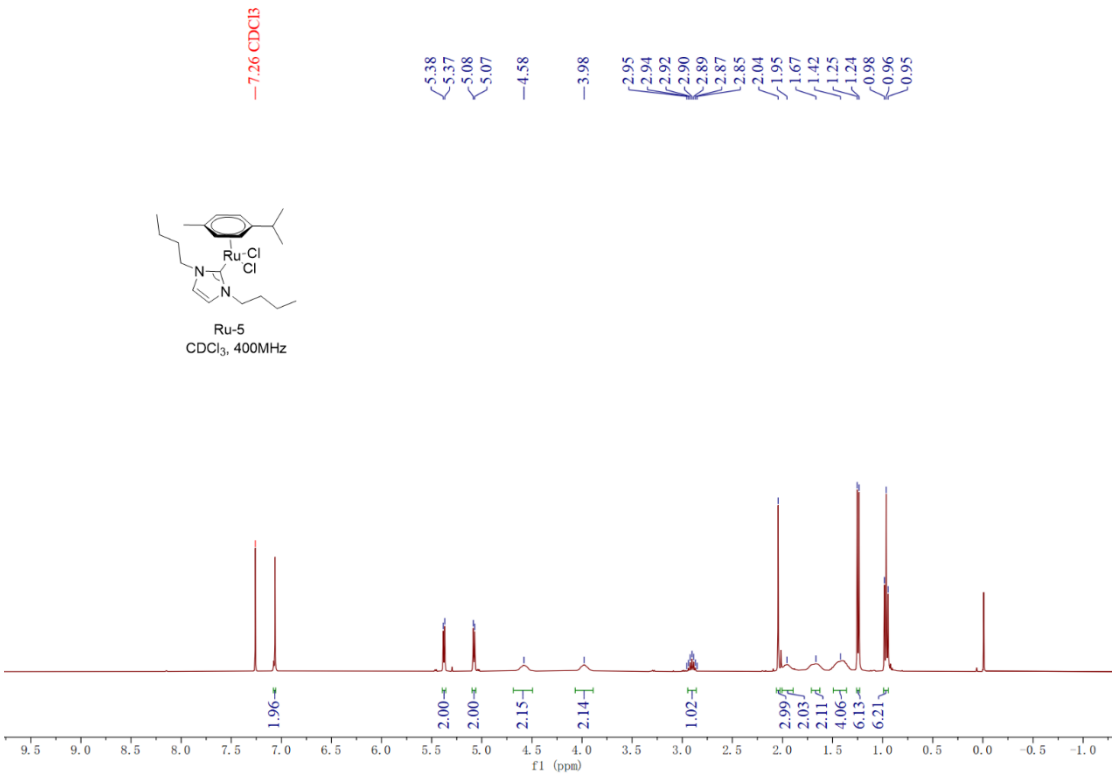
21.1
17.4
Cl
Ru-Cl
Ru-4
MeOD, 100MHz
f1 (ppm)

Ru-5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2.89
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2.85
2.04
1.95
1.67
1.42
1.25
1.24
0.98
0.96
0.95
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Cl
N
N
Ru-5
CDCl3, 400MHz
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2.99
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4.06
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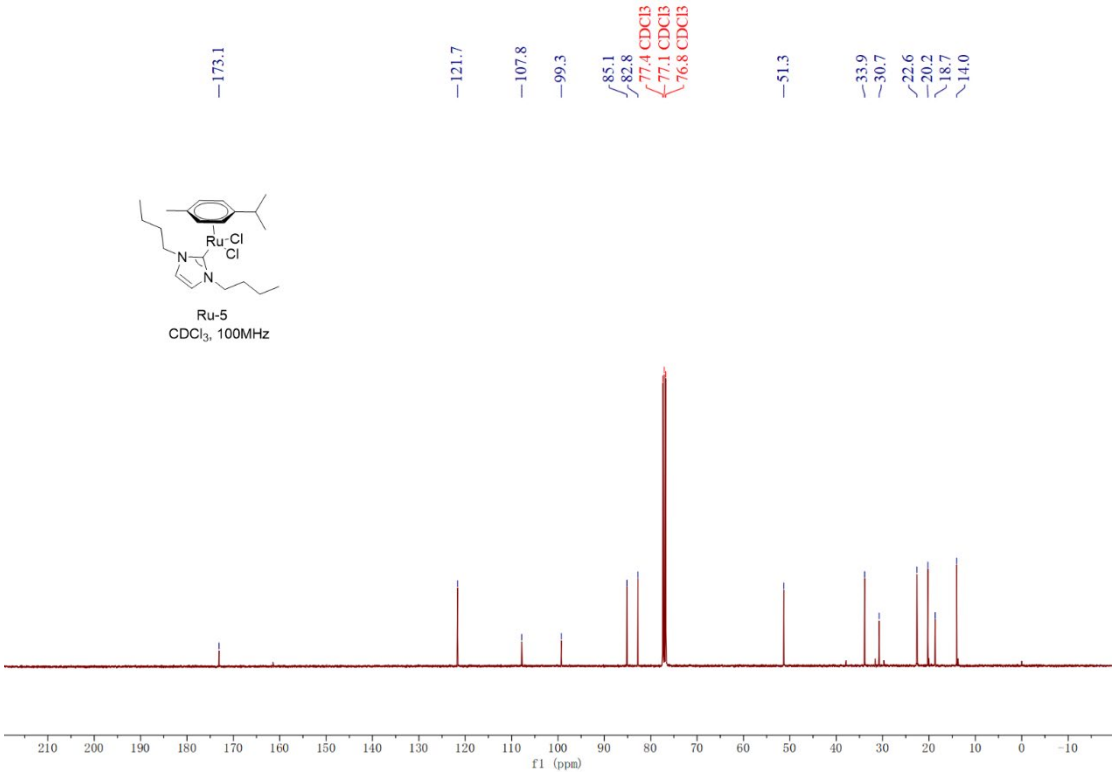
6.21
f1 (ppm)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77.1 CDCl3
76.8 CDCl3
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30.7
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14.0
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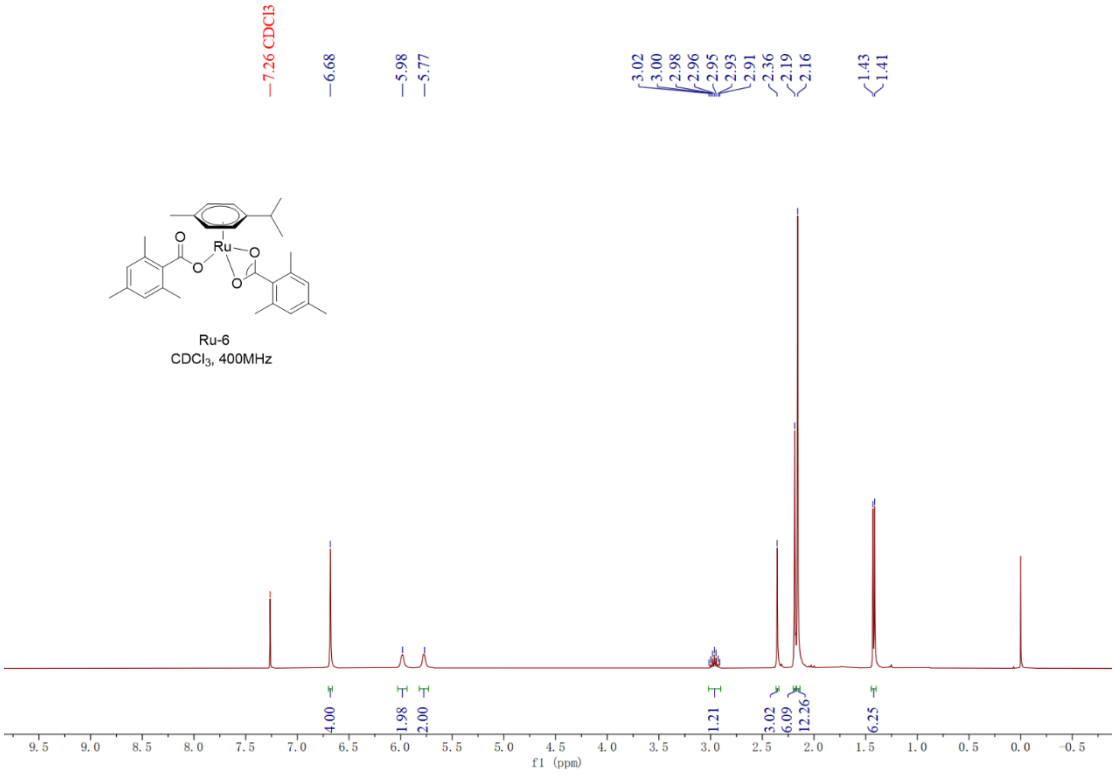
Cl
N
N
Ru-5
CDCl3, 100MHz
f1 (ppm)

Ru-6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Ru
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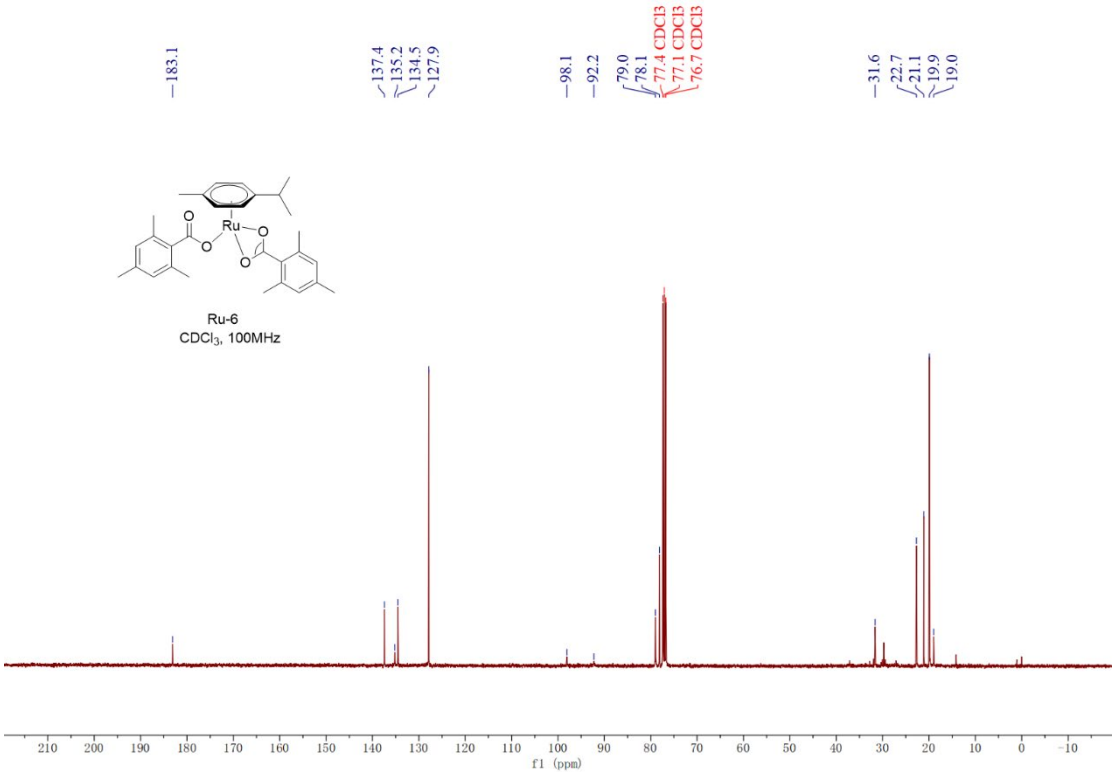
f1 (ppm)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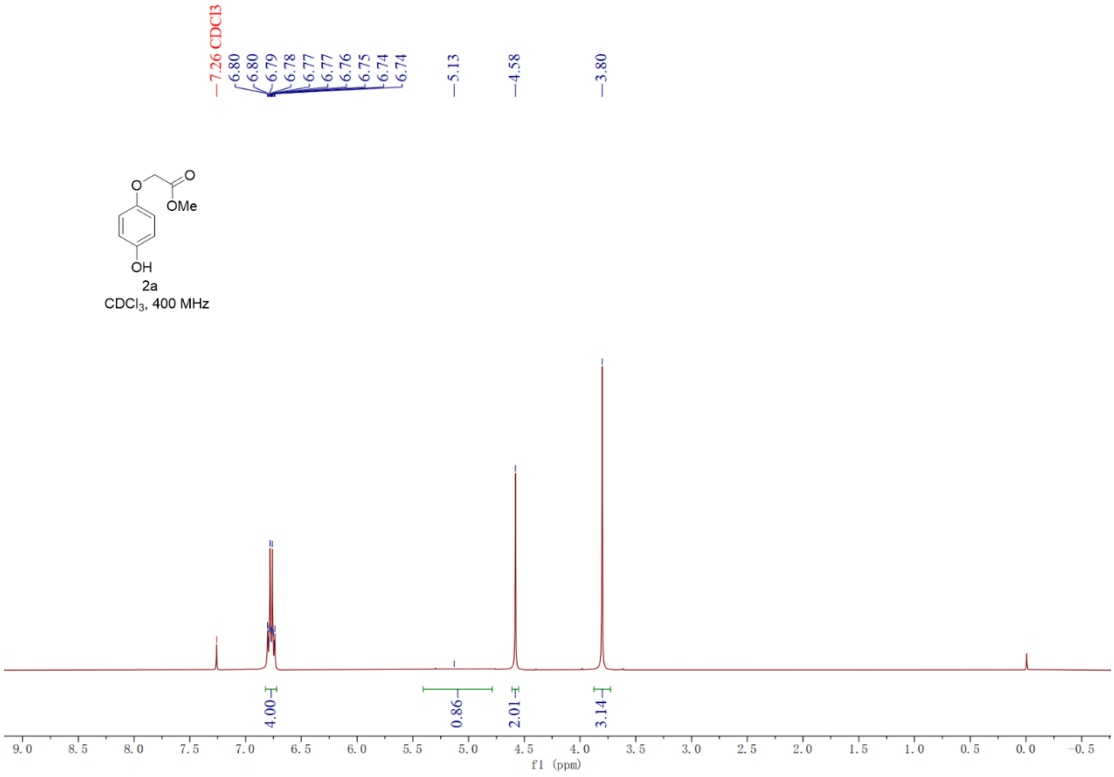
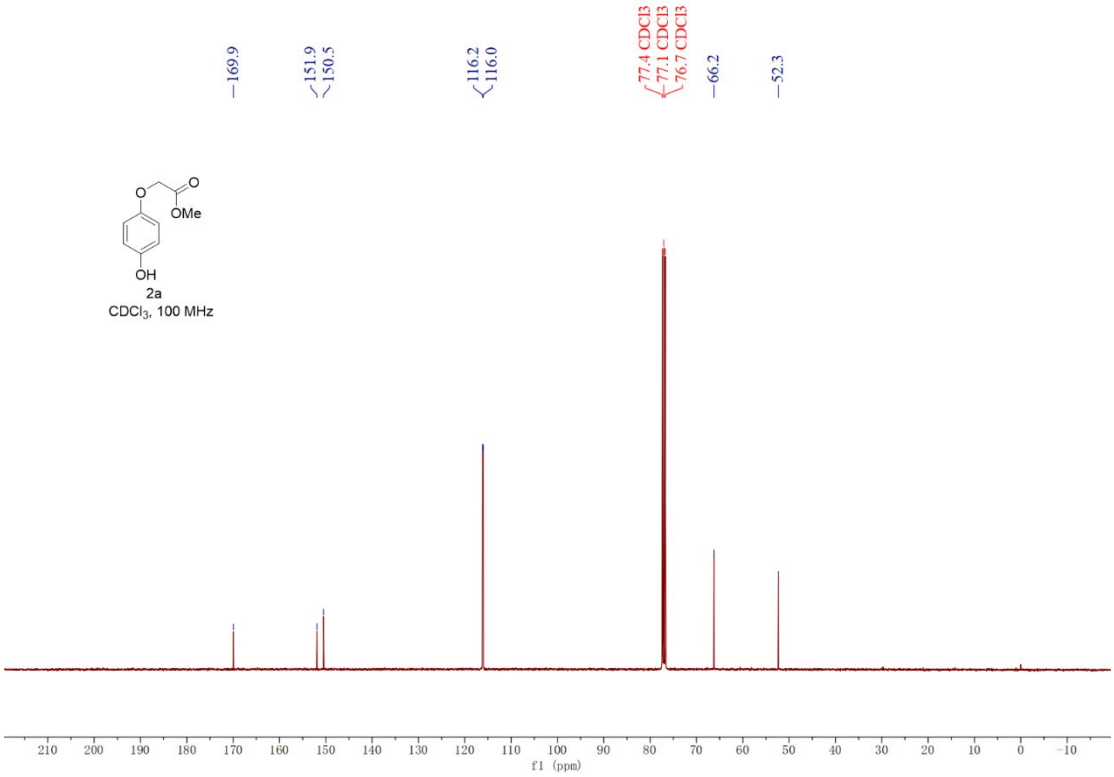
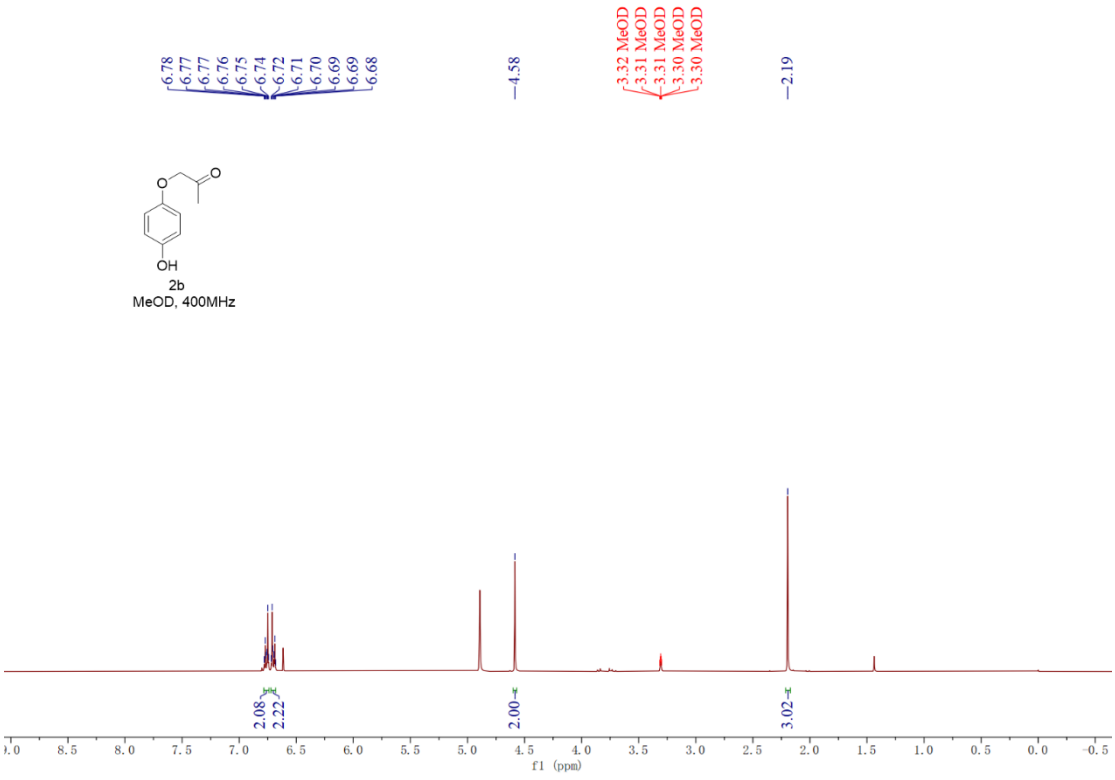
77.1 CDCl3
76.7 CDCl3
31.6
22.7
21.1
19.9
19.0
Ru
O
Ru-6
CDCl3, 100MHz
f1 (ppm)

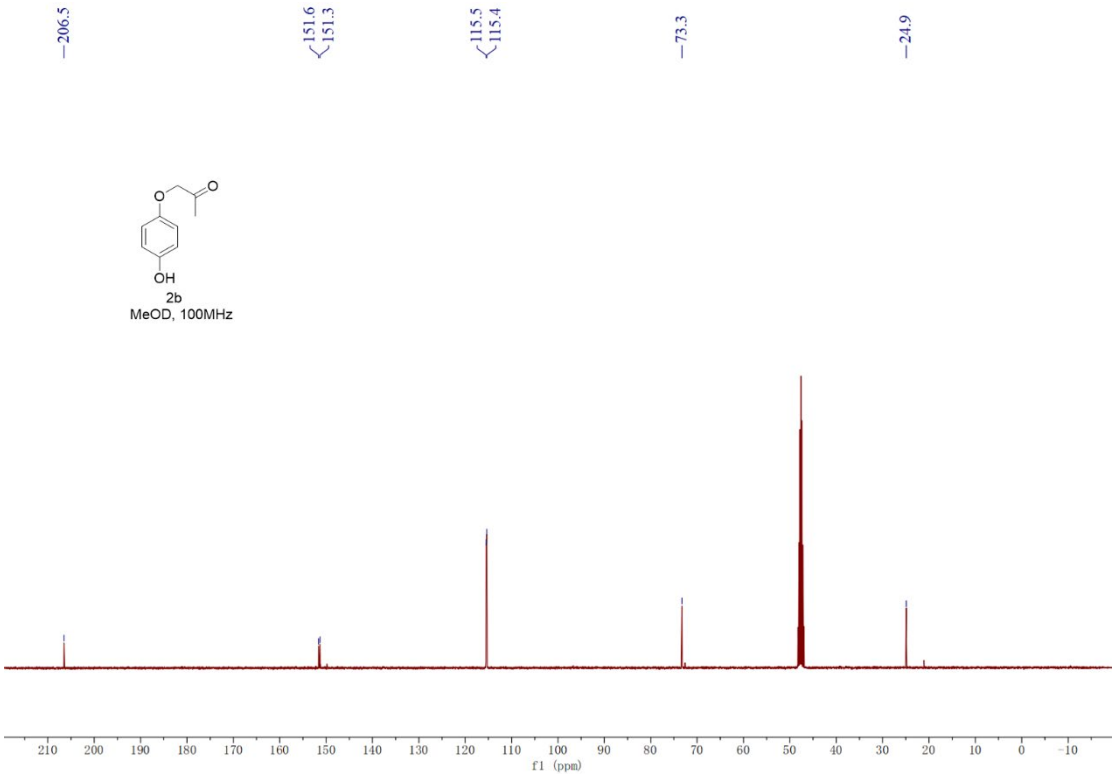
methyl 2-(4-hydroxyphenoxy)acetate



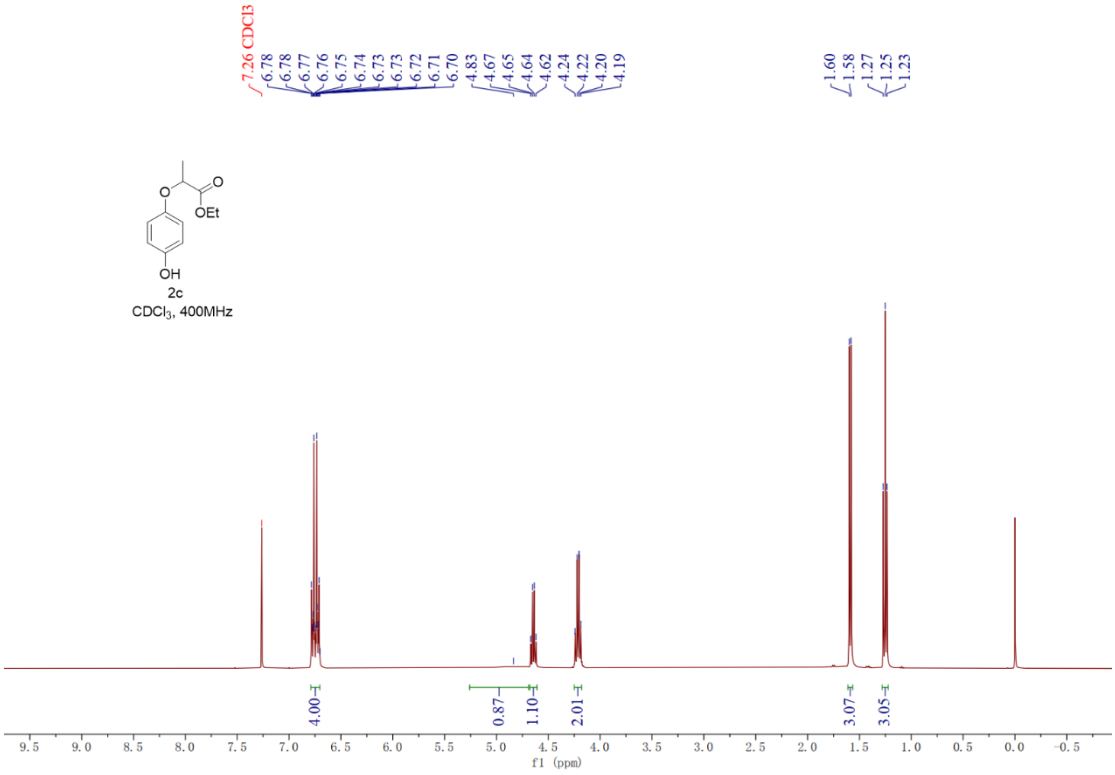


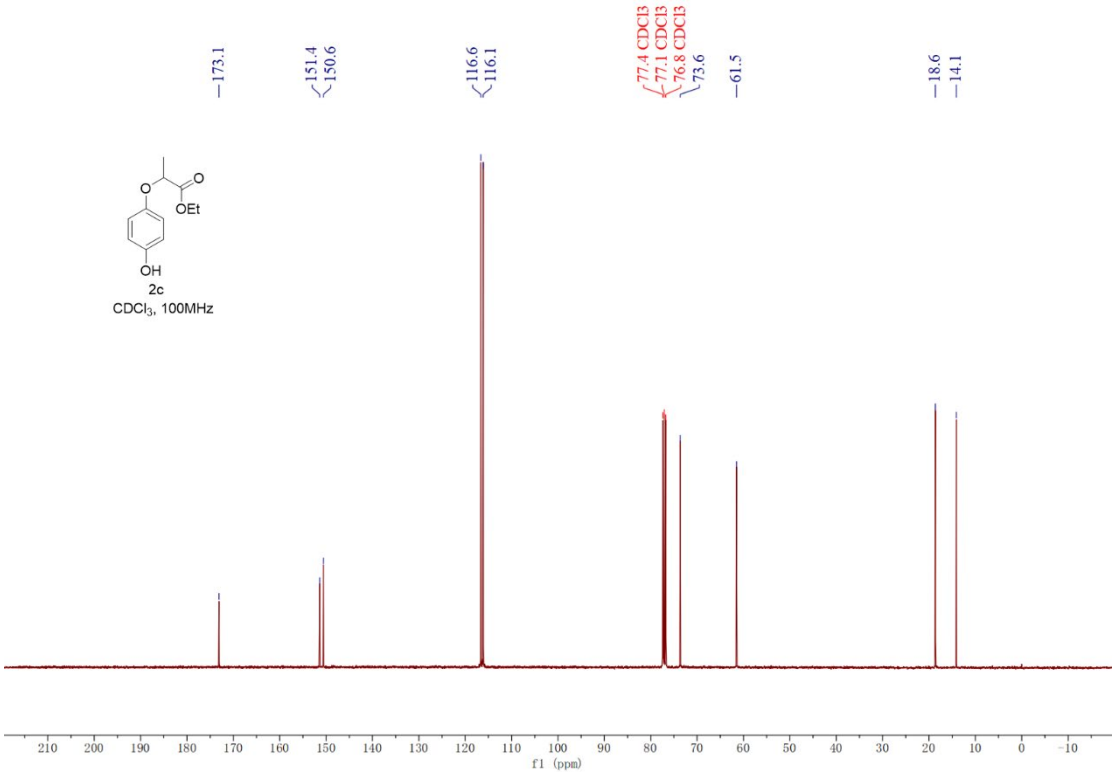
1-(4-hydroxyphenoxy)propan-2-one





ethyl 2-(4-hydroxyphenoxy)propanoate





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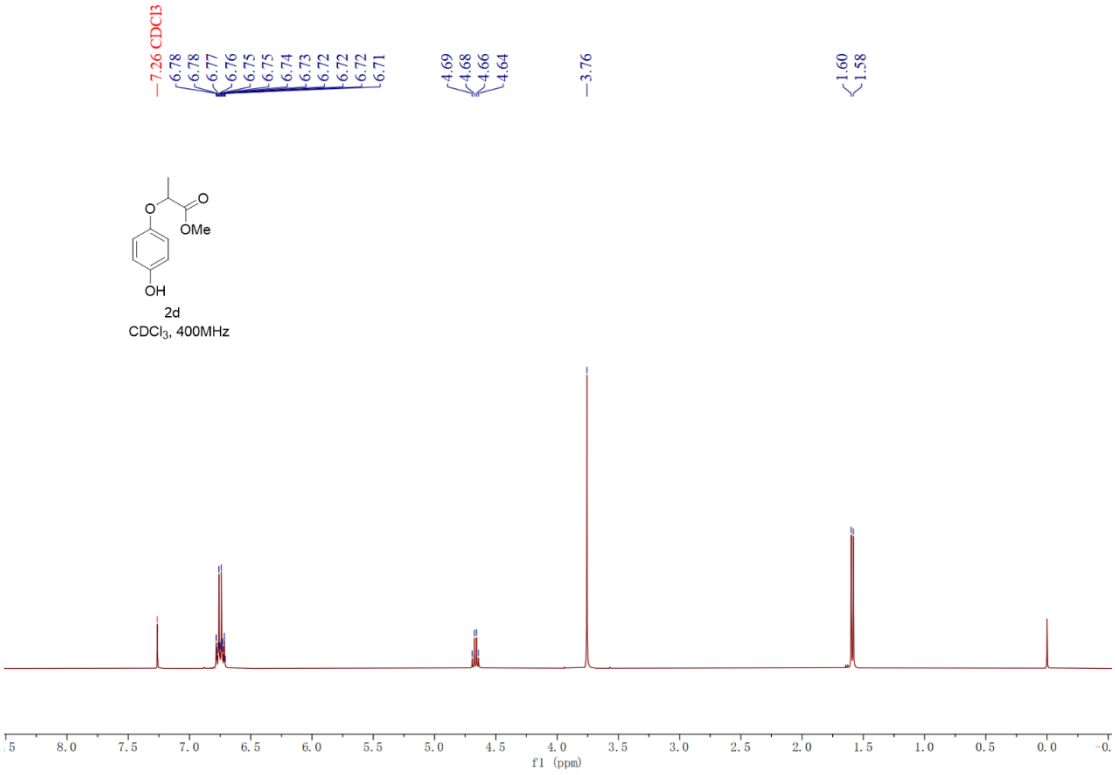

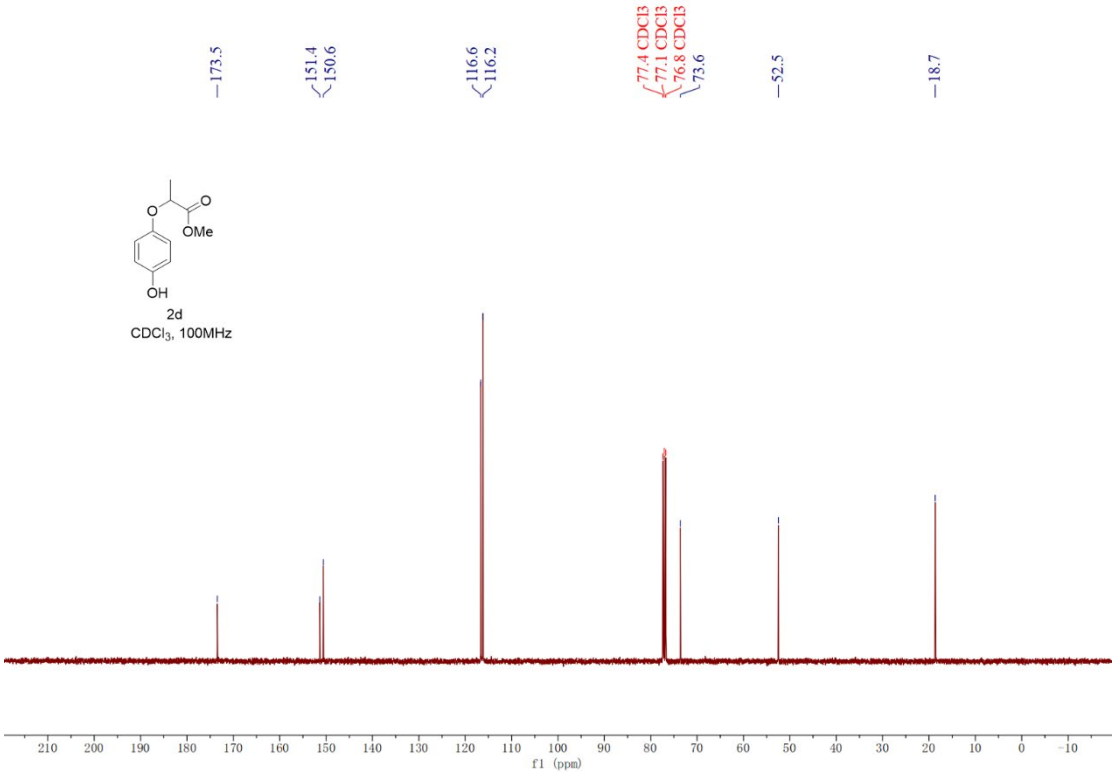

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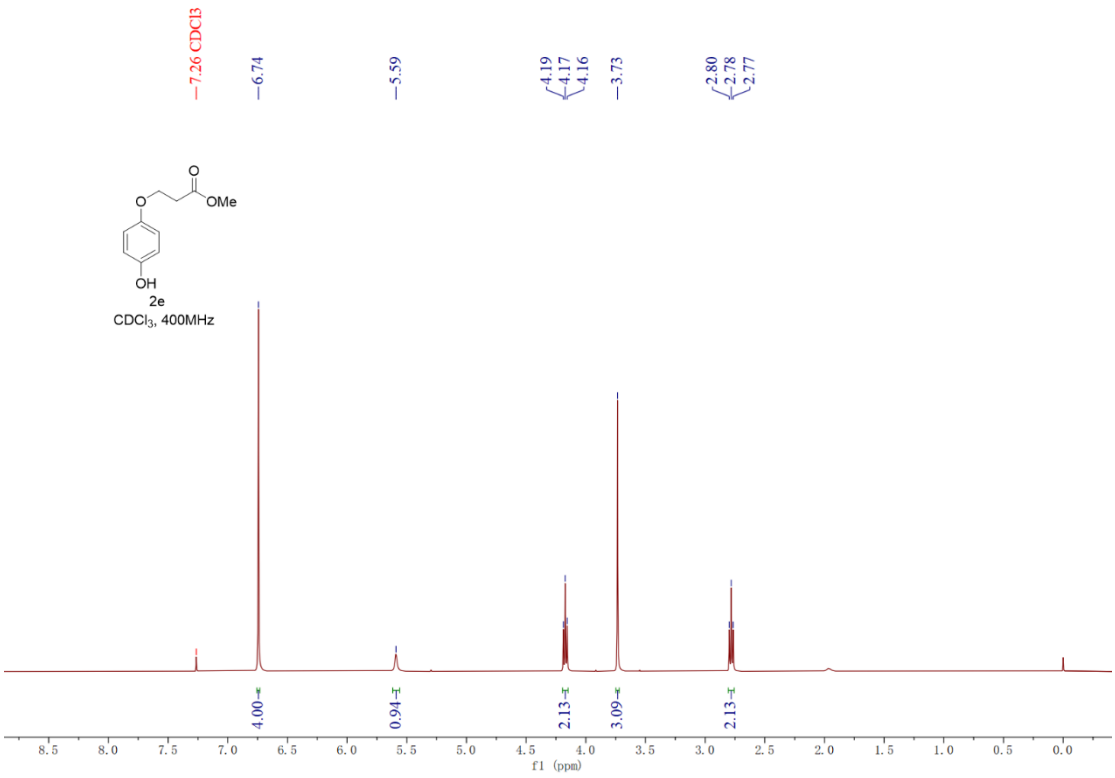
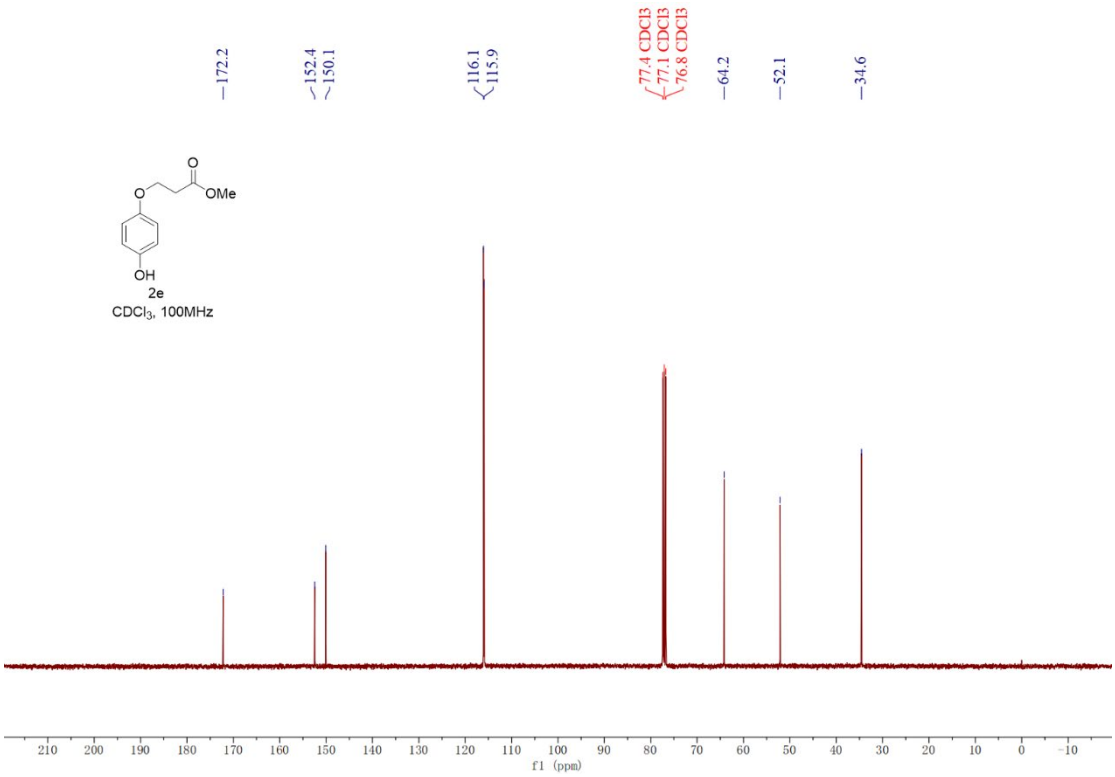
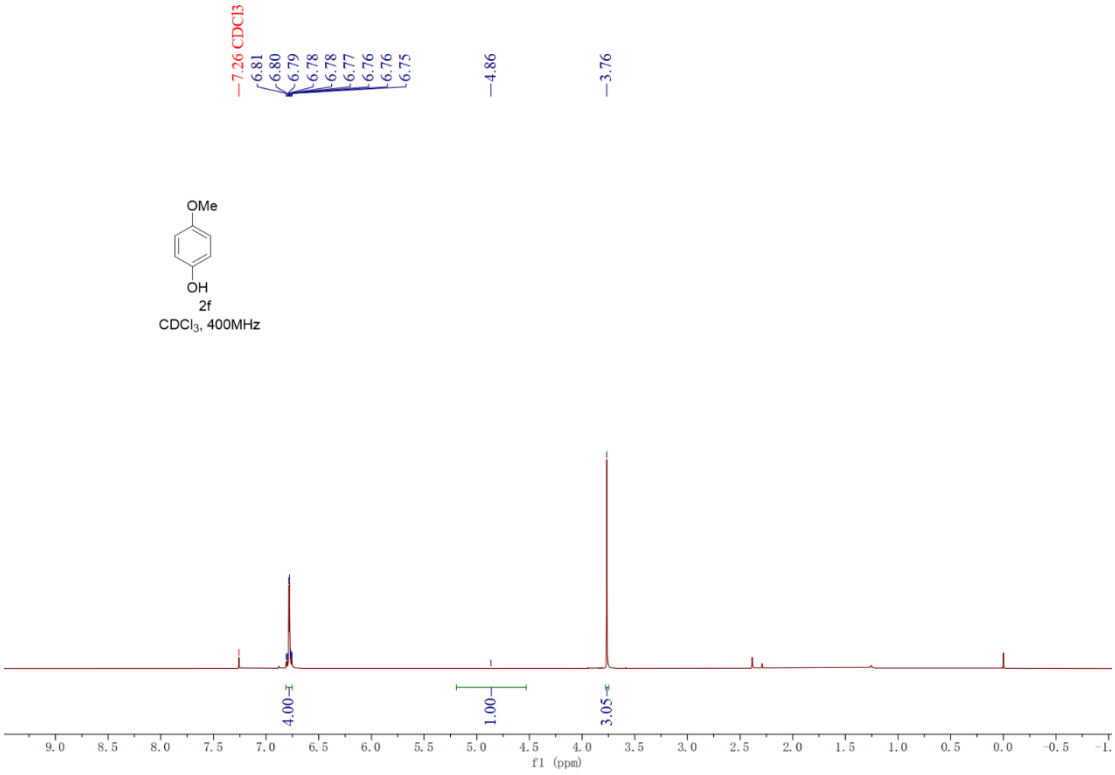
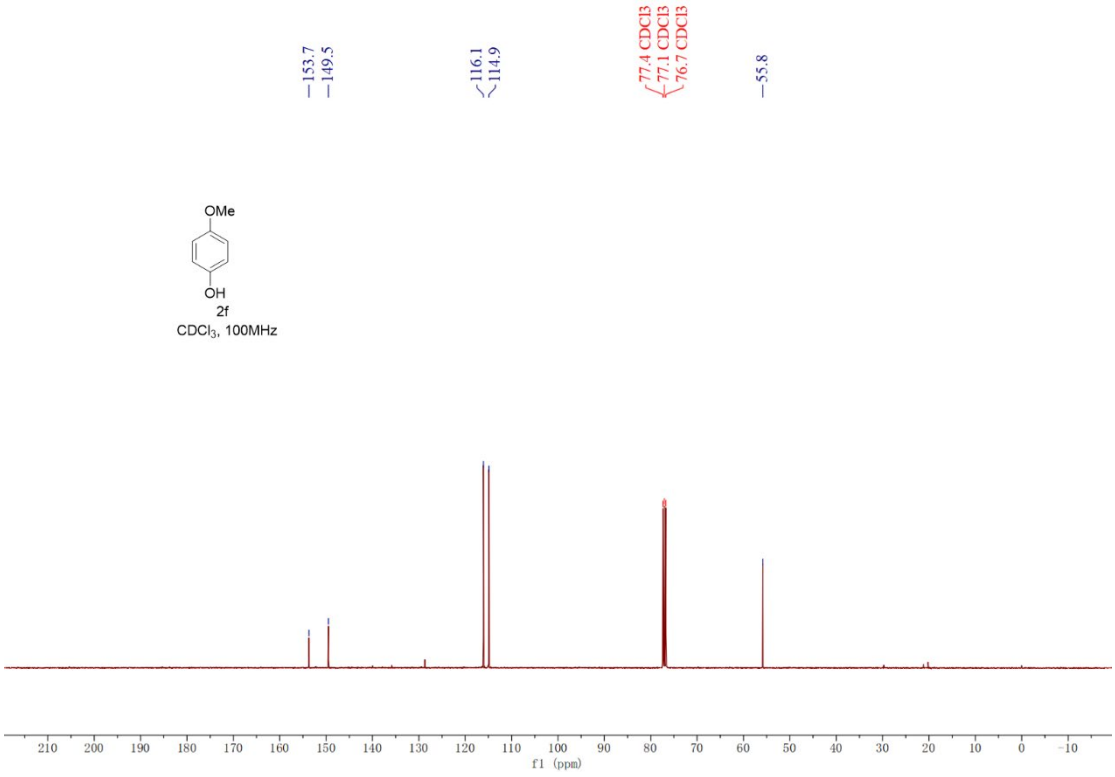


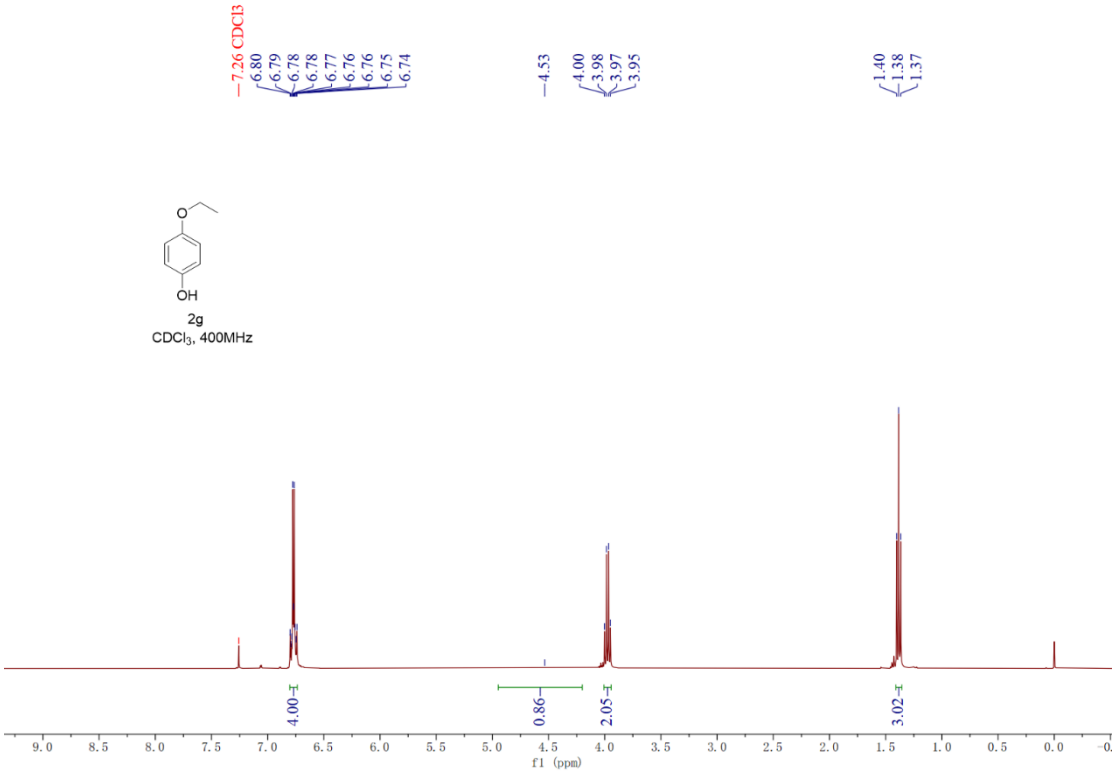


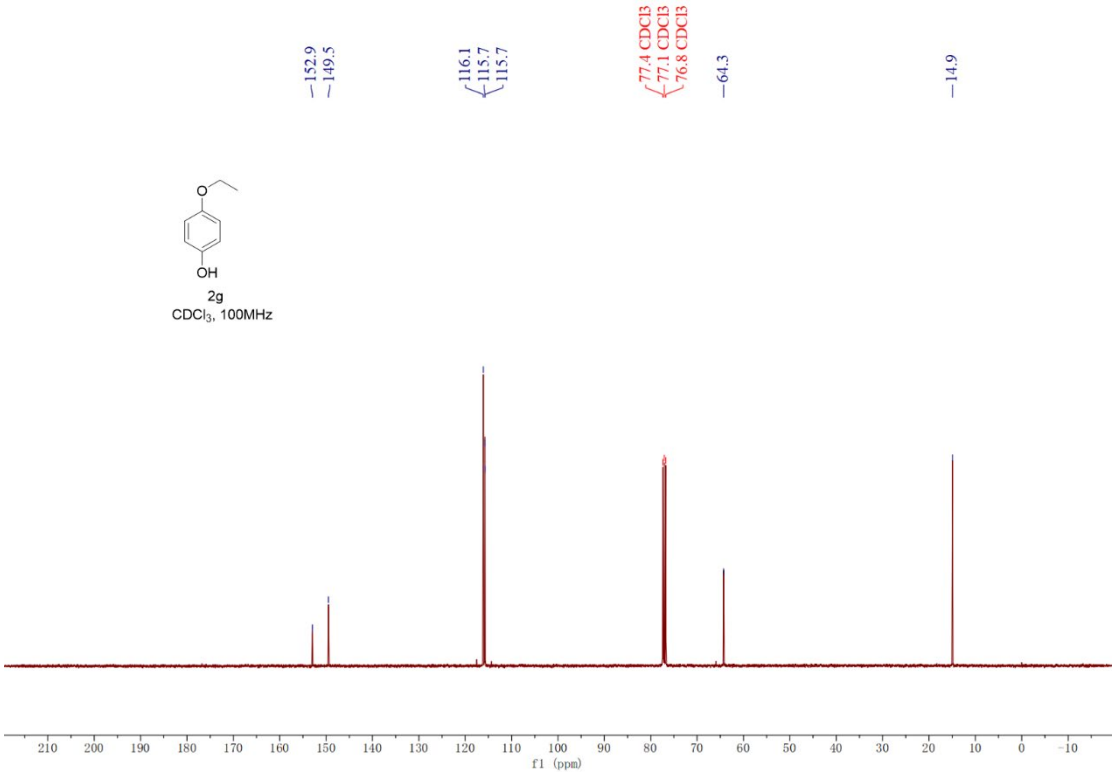
4-methoxyphenol



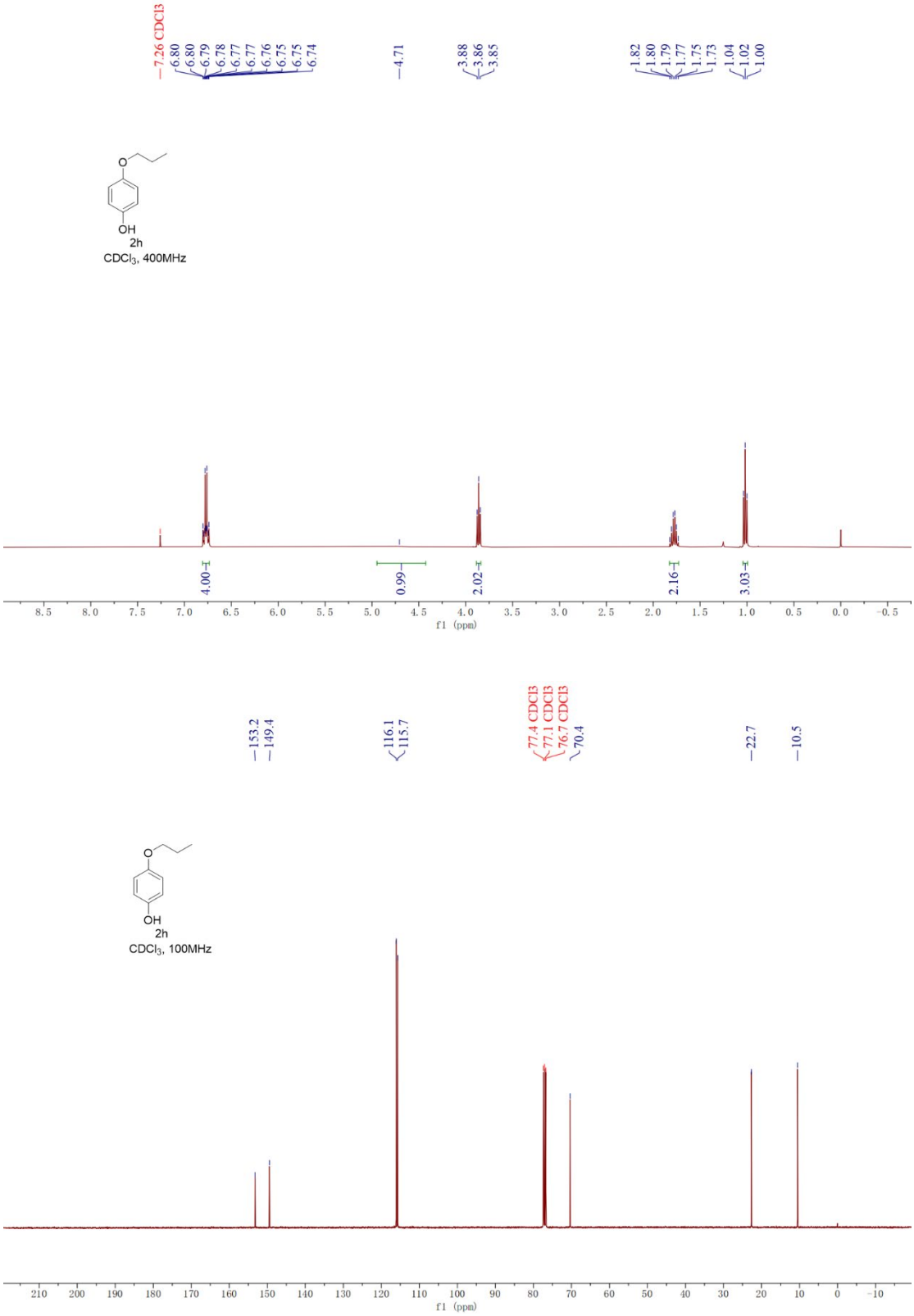


4-ethoxyphenol

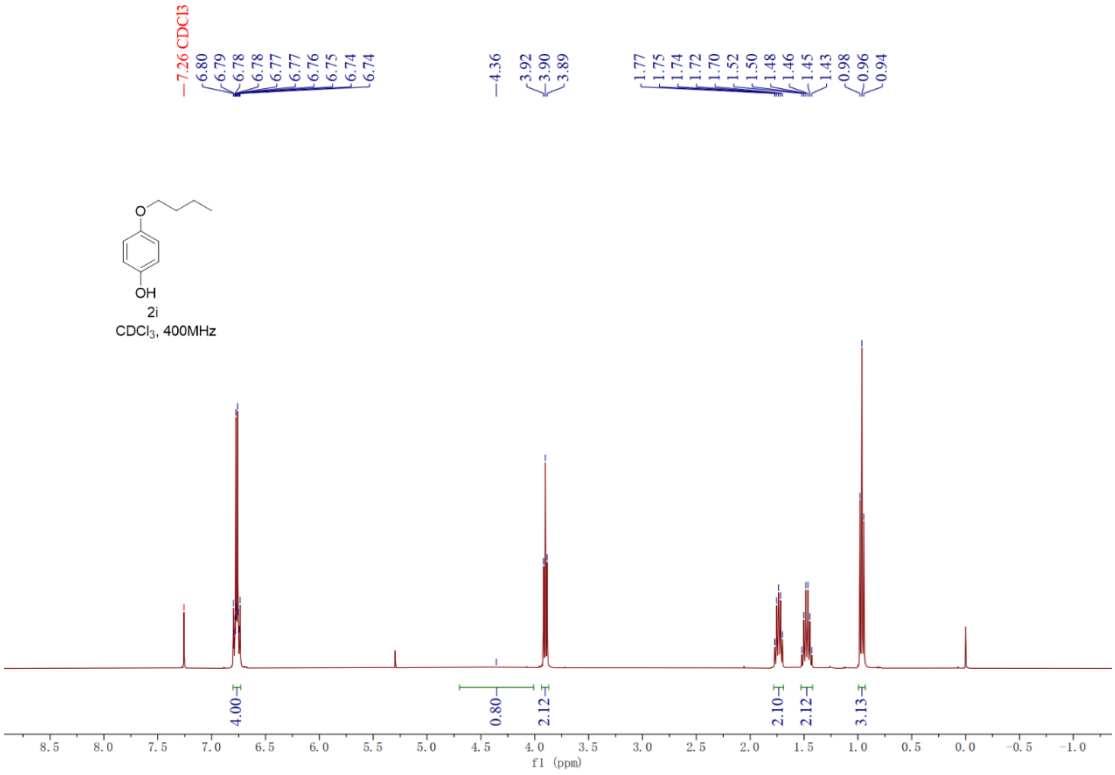


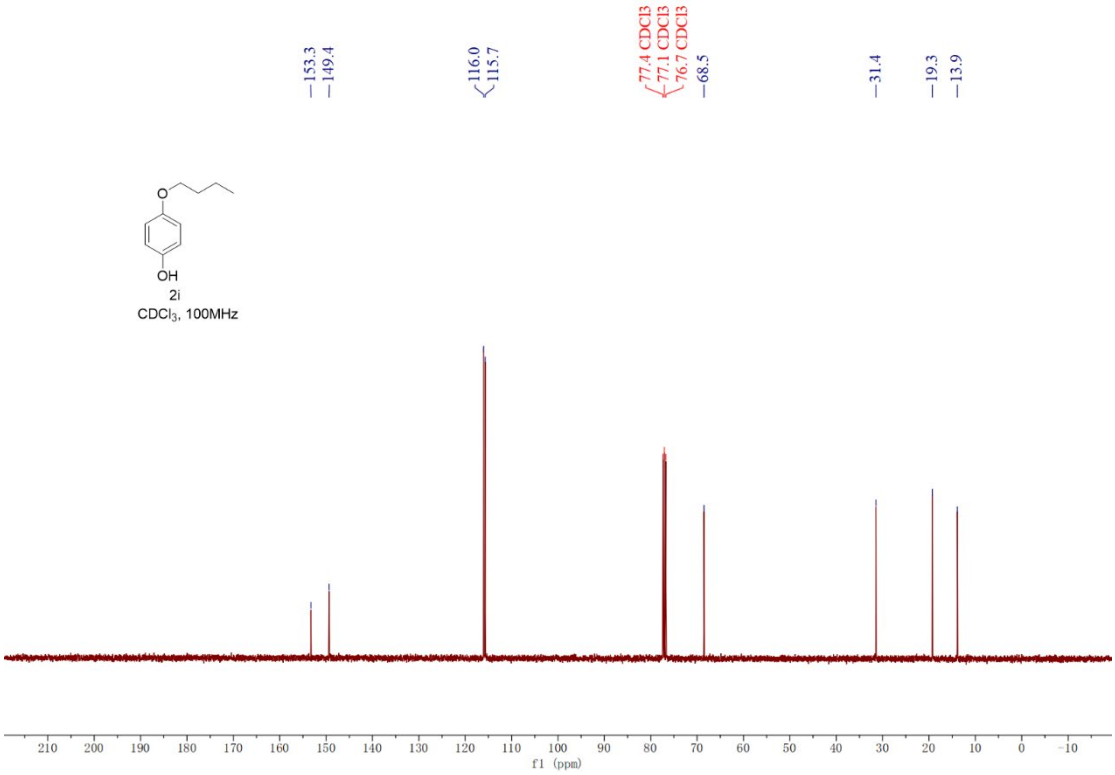


4-propoxyphenol

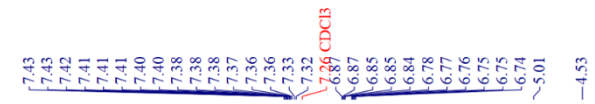


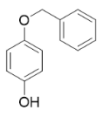
4-butoxyphenol





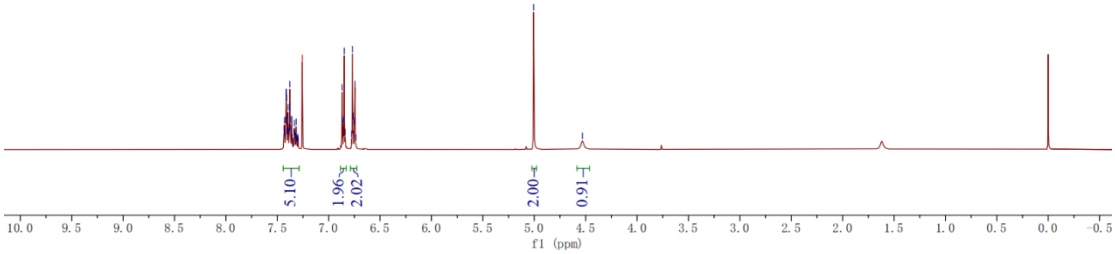
4-(benzyloxy)phenol

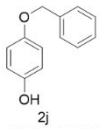




2j

$CDCl_3$, 400MHz

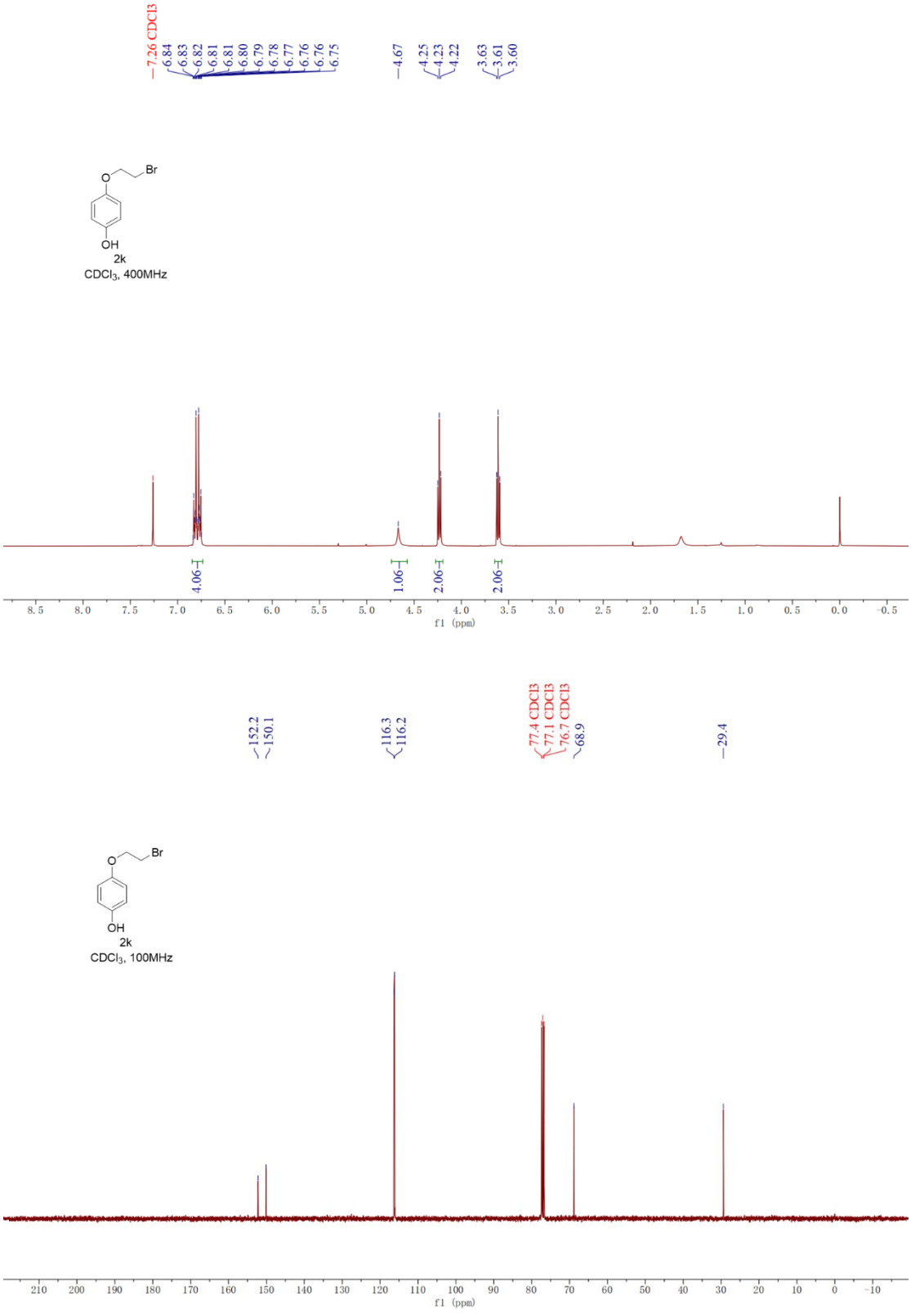




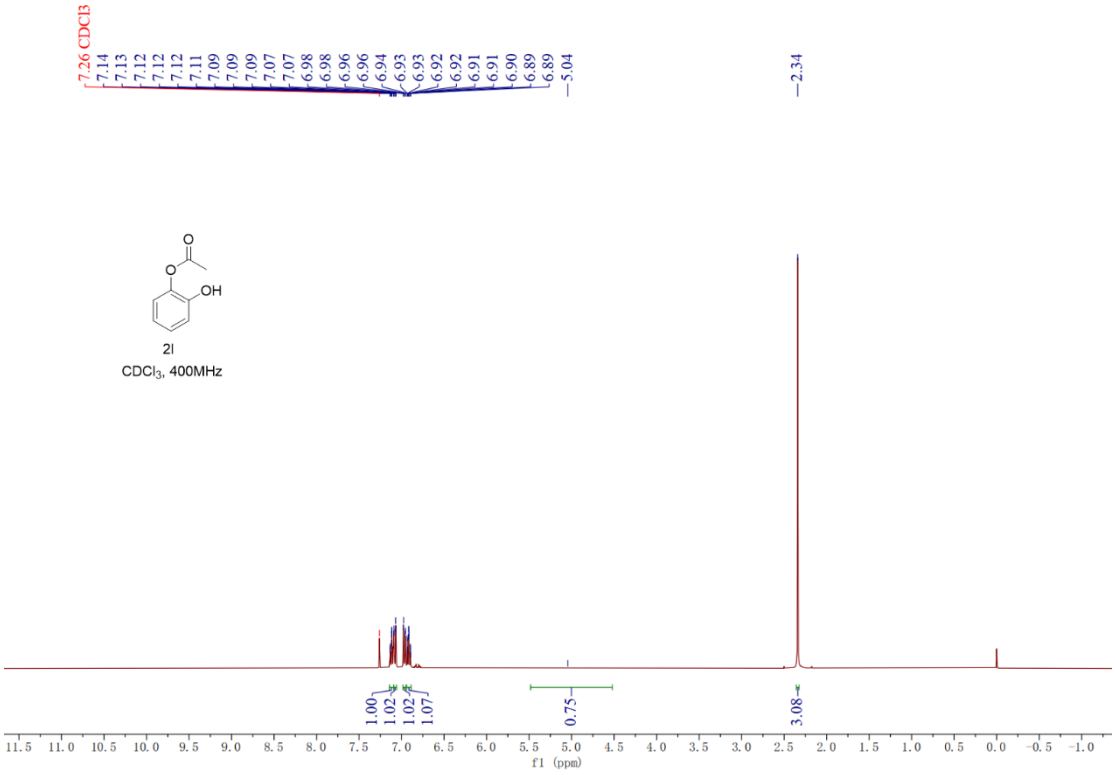
2j

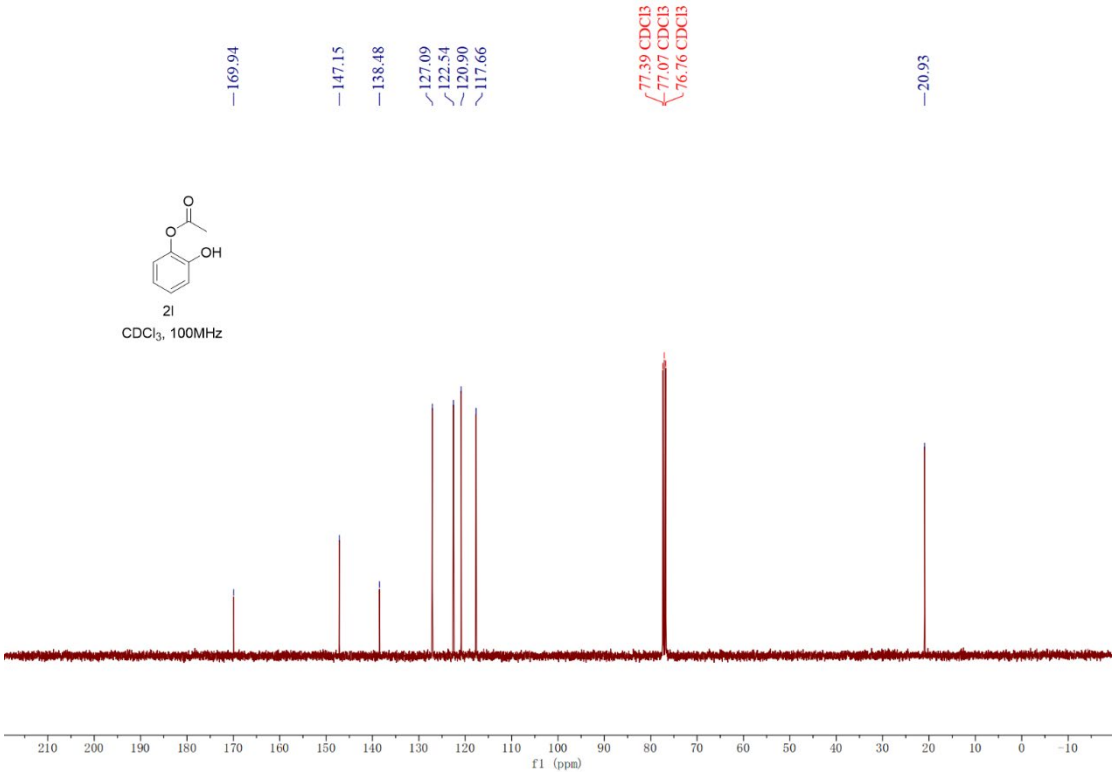
$CDCl_3$, 100MHz

4-(2-bromoethoxy)phenol

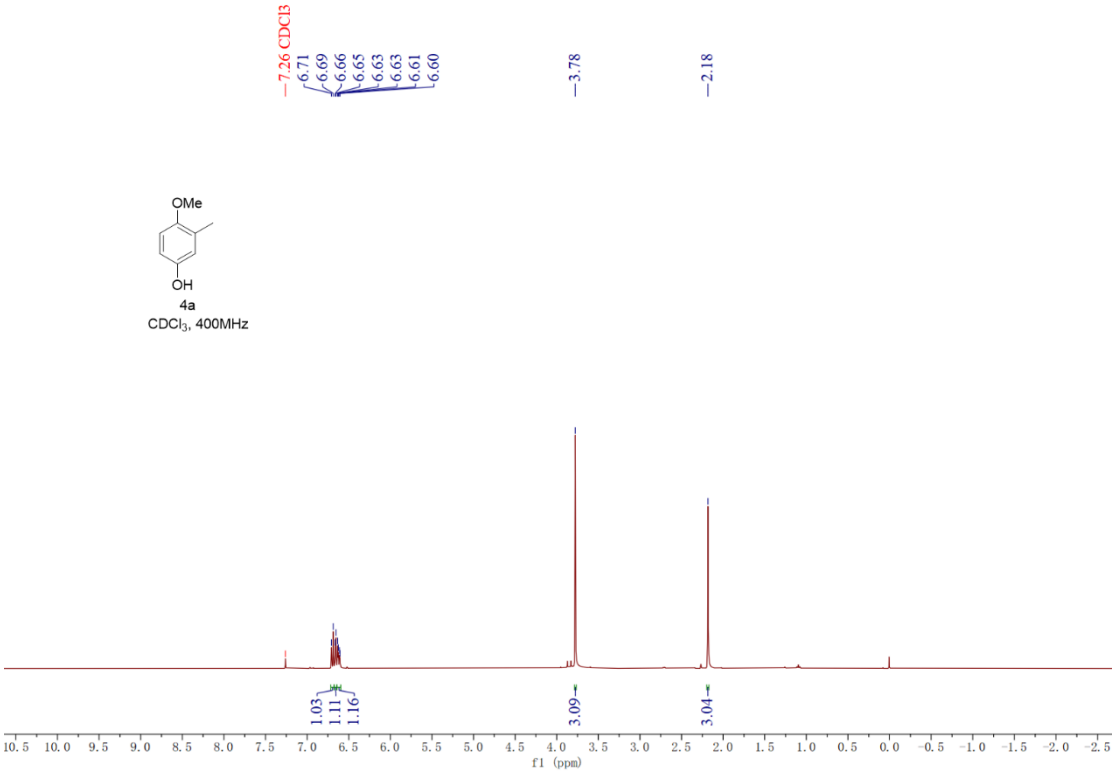


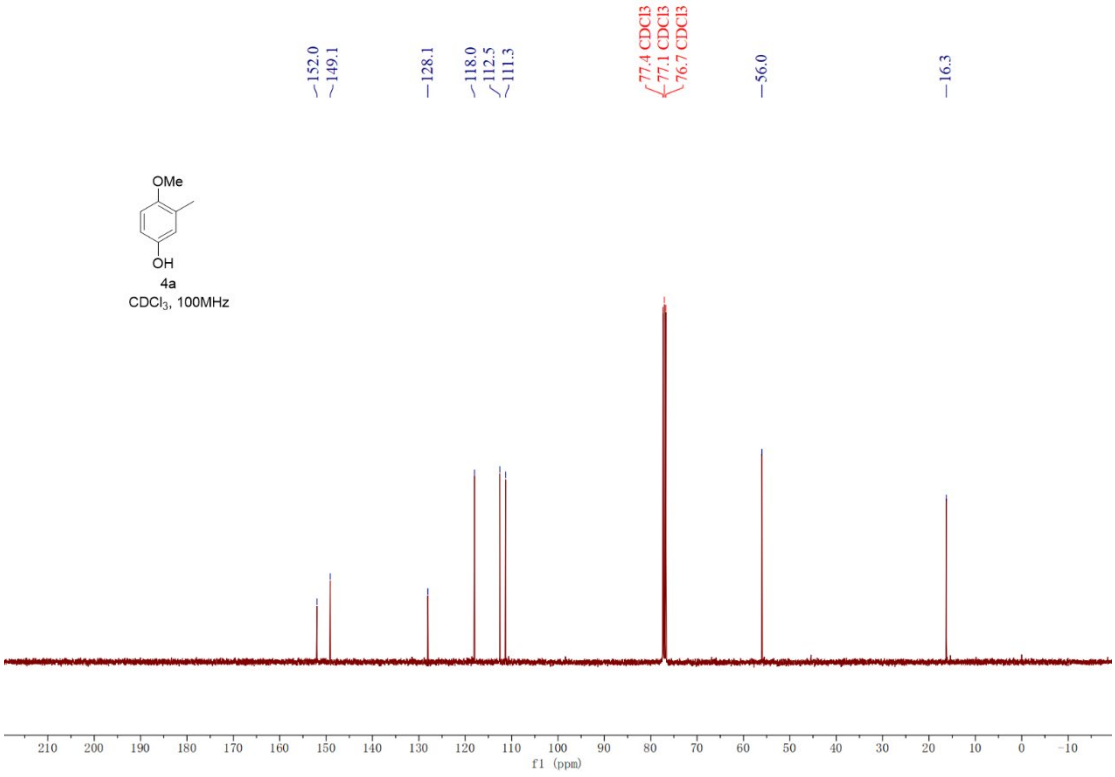
2-hydroxyphenyl acetate



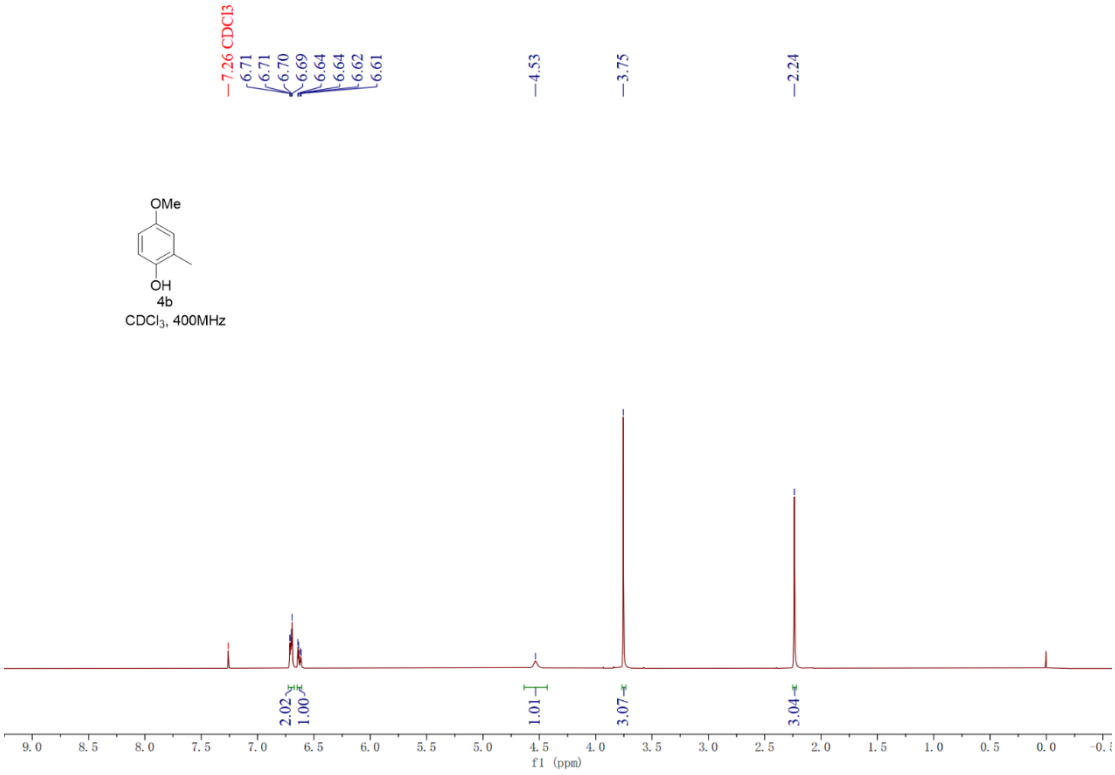


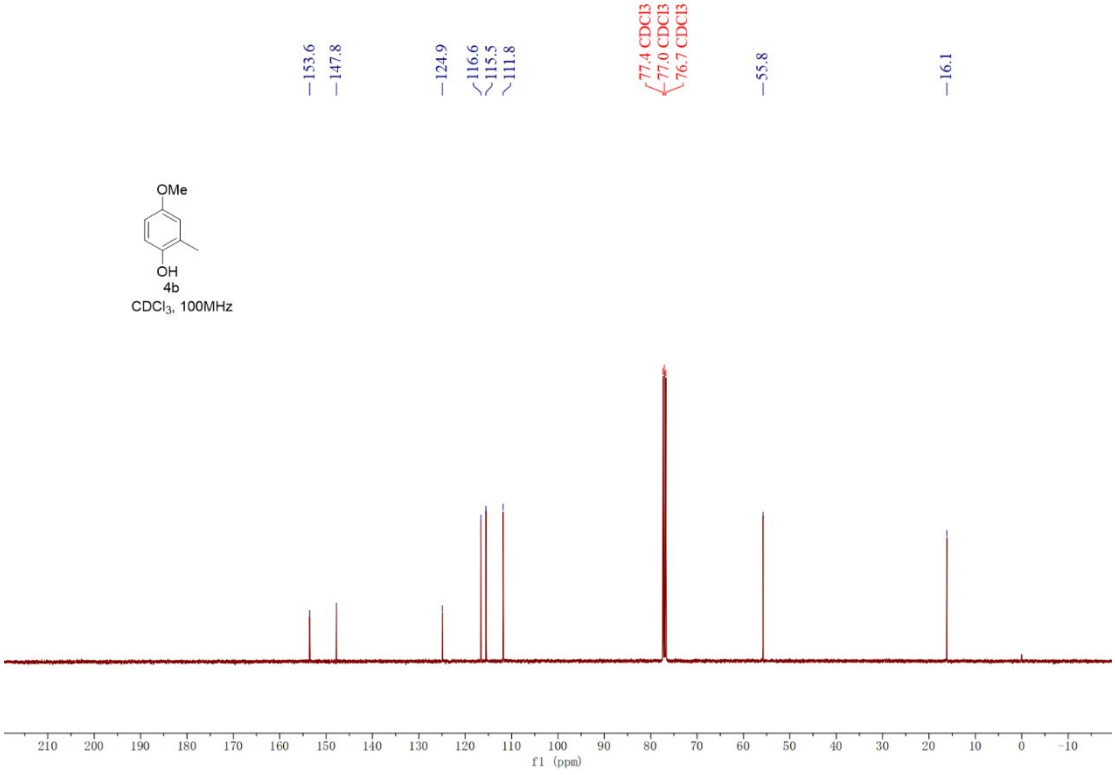
4-methoxy-3-methylphenol



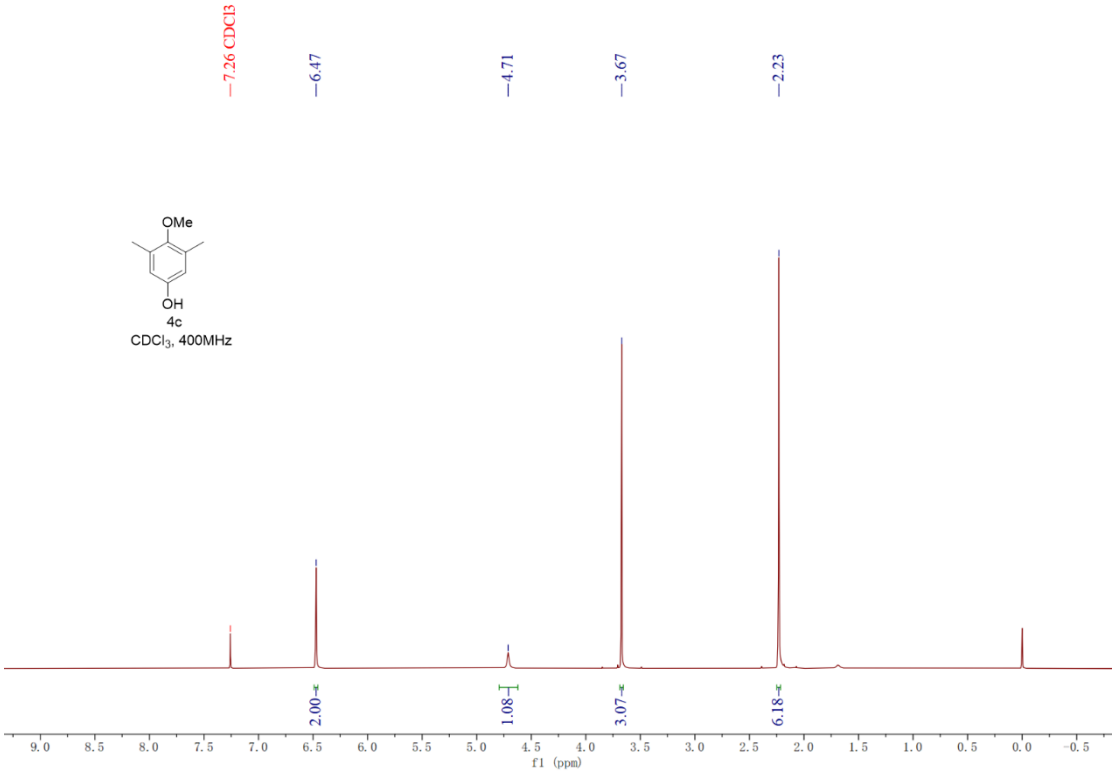


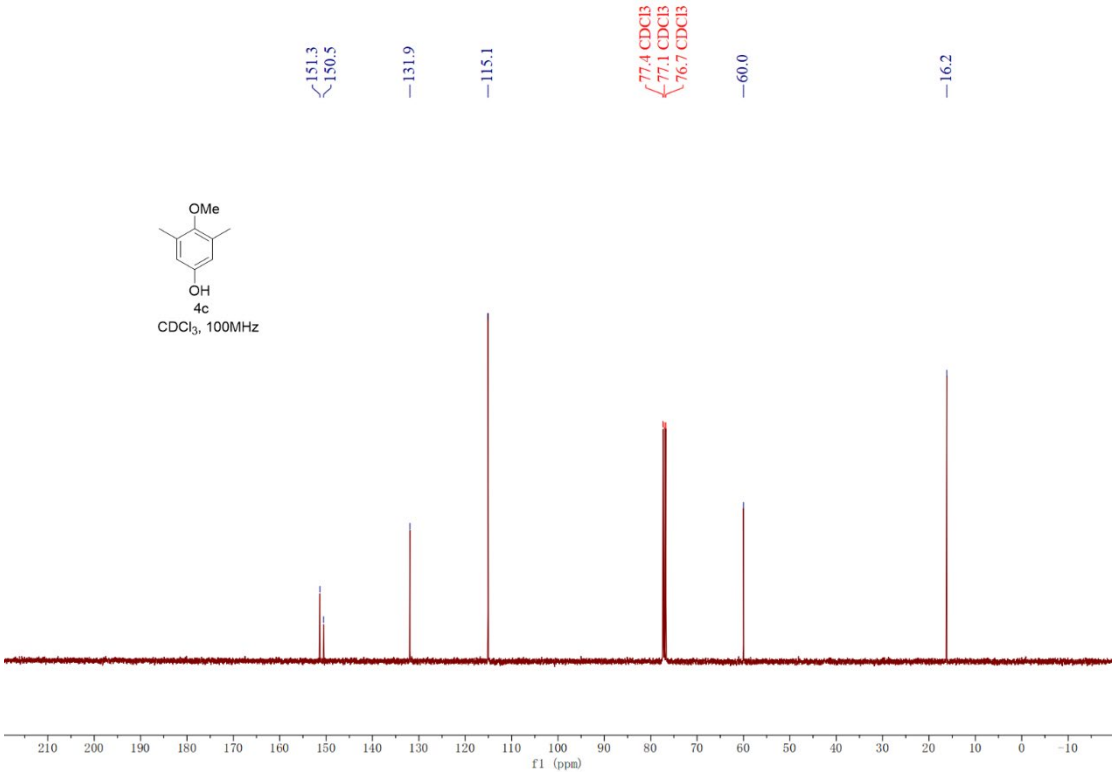
4-methoxy-2-methylphenol



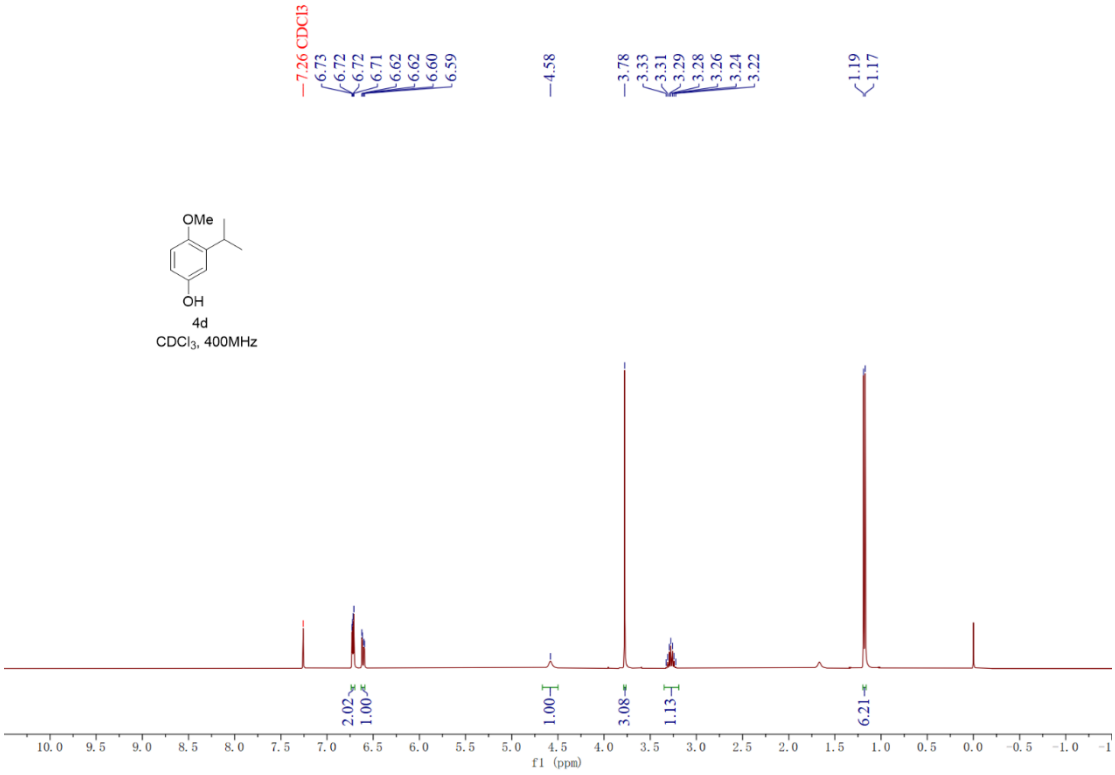


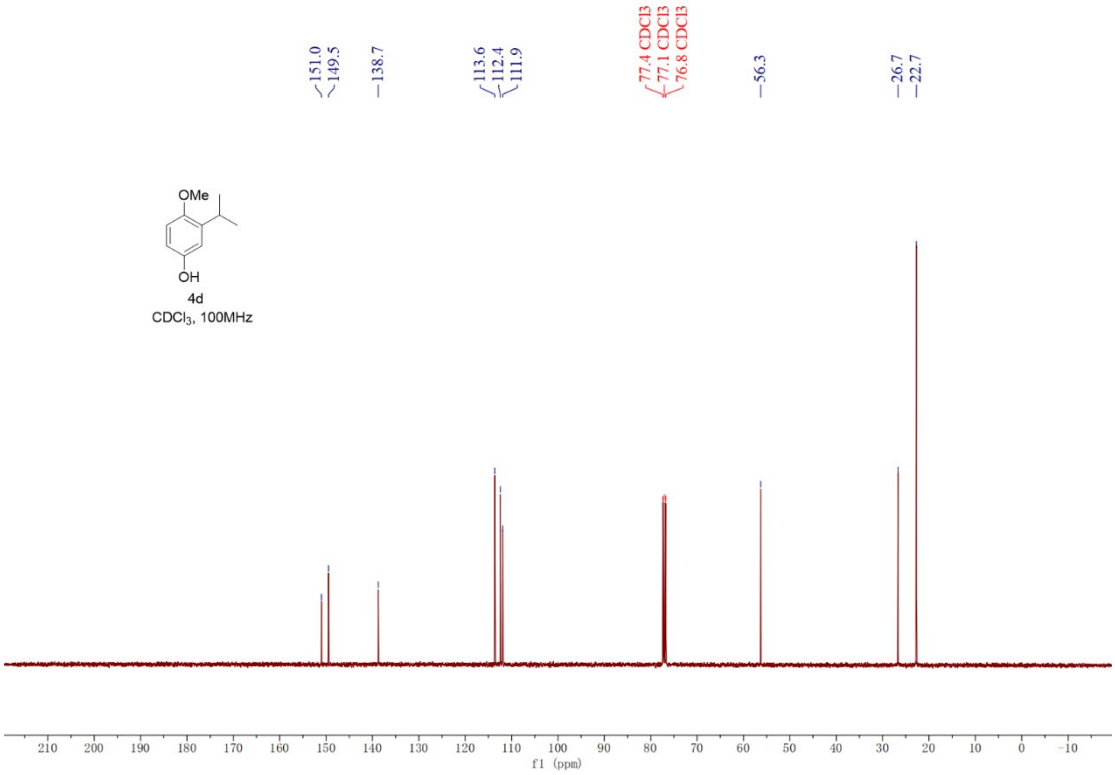
4-methoxy-3,5-dimethylphenol



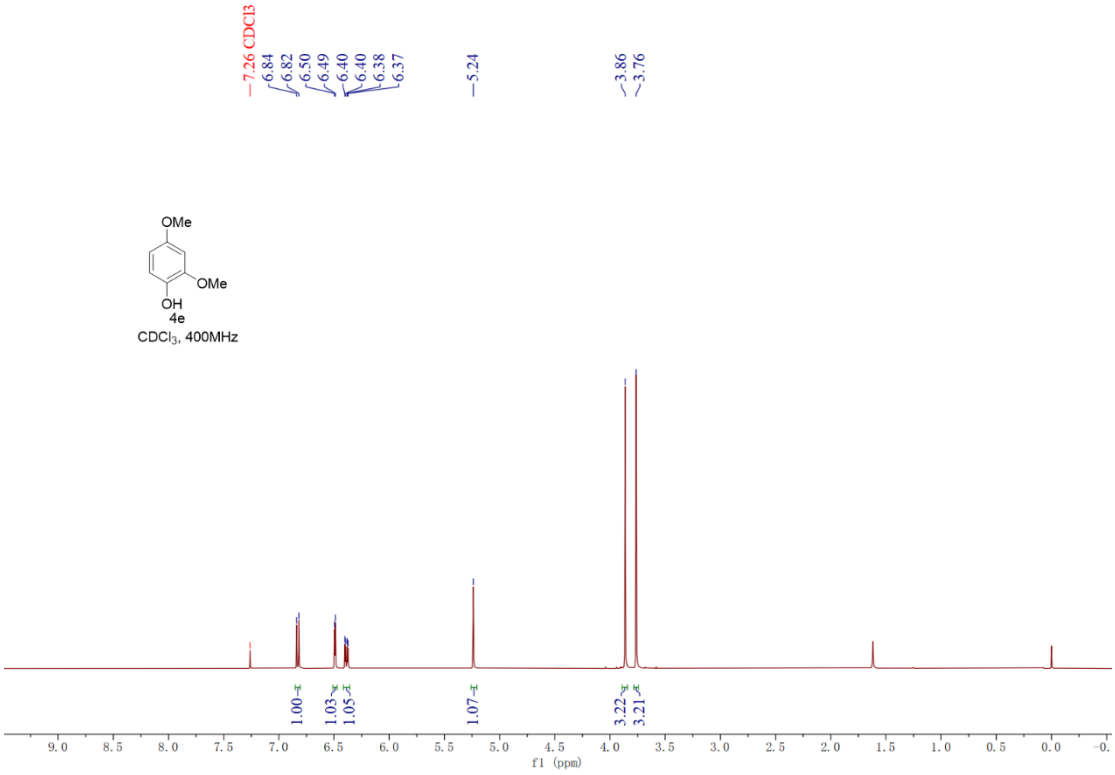


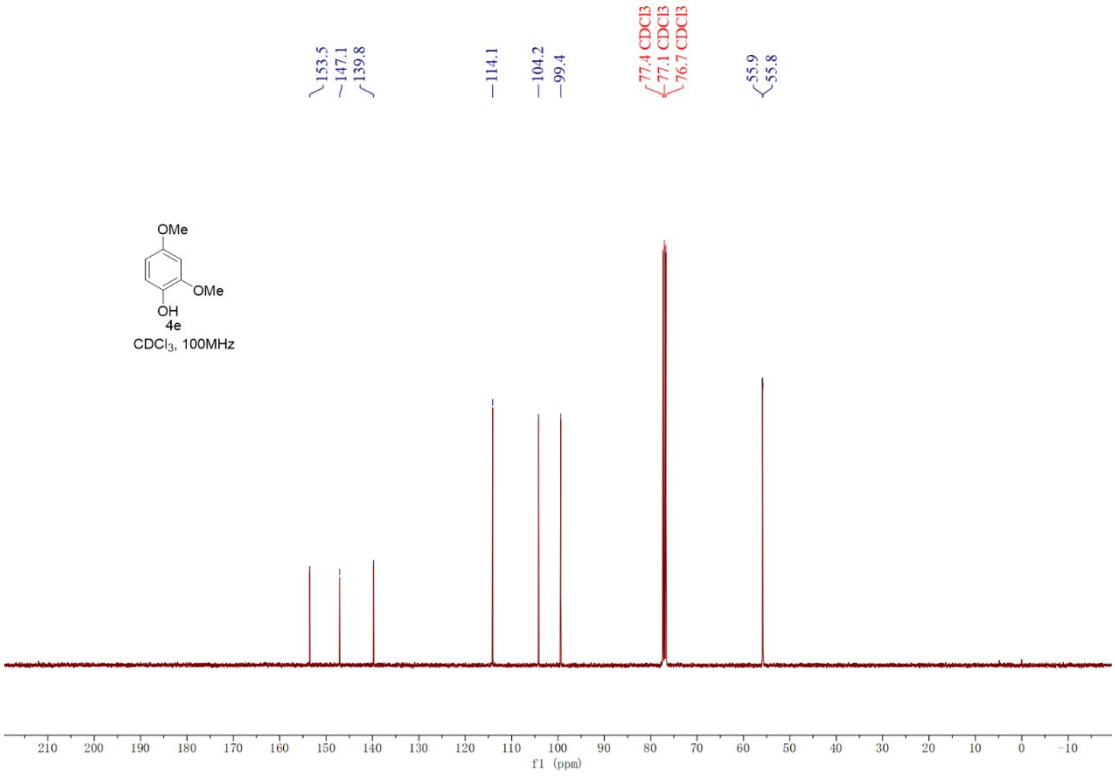
3-isopropyl-4-methoxyphenol



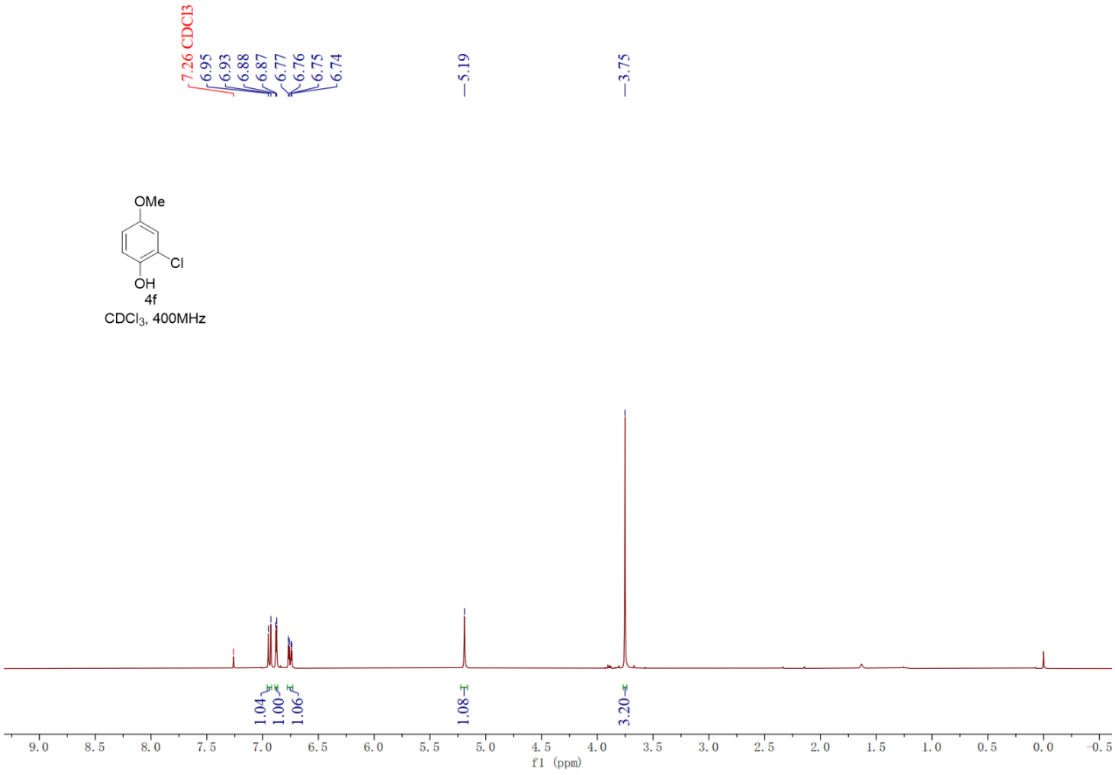


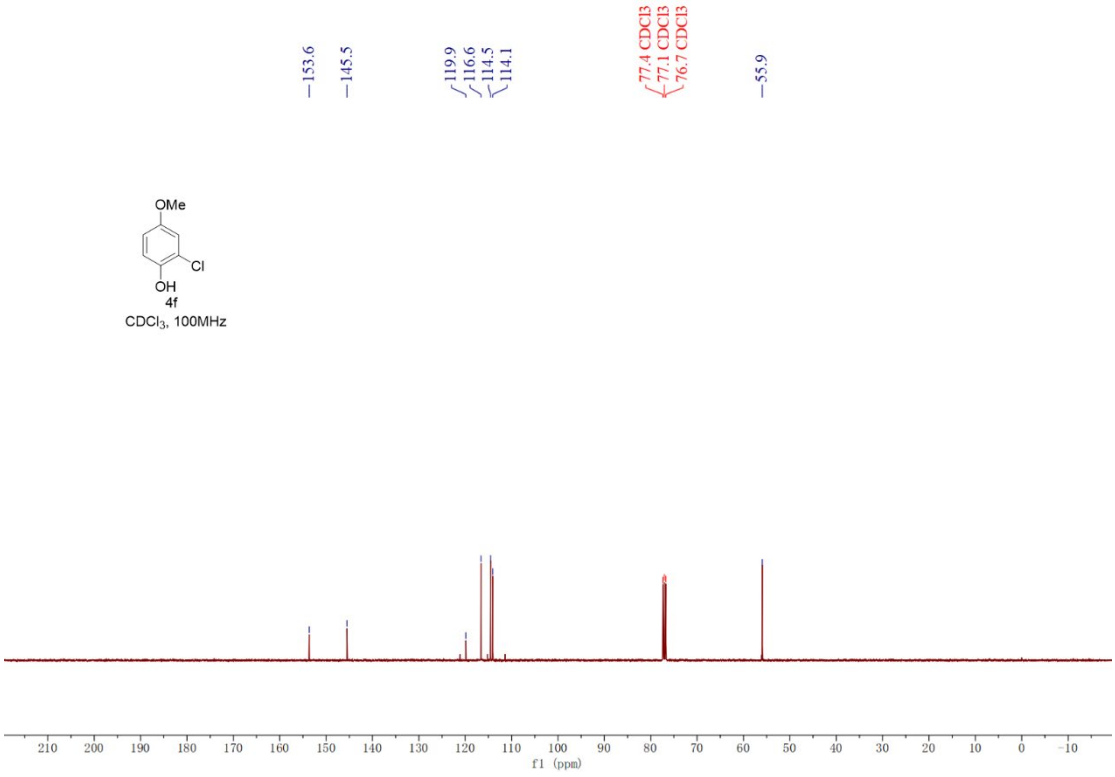
2,4-dimethoxyphenol



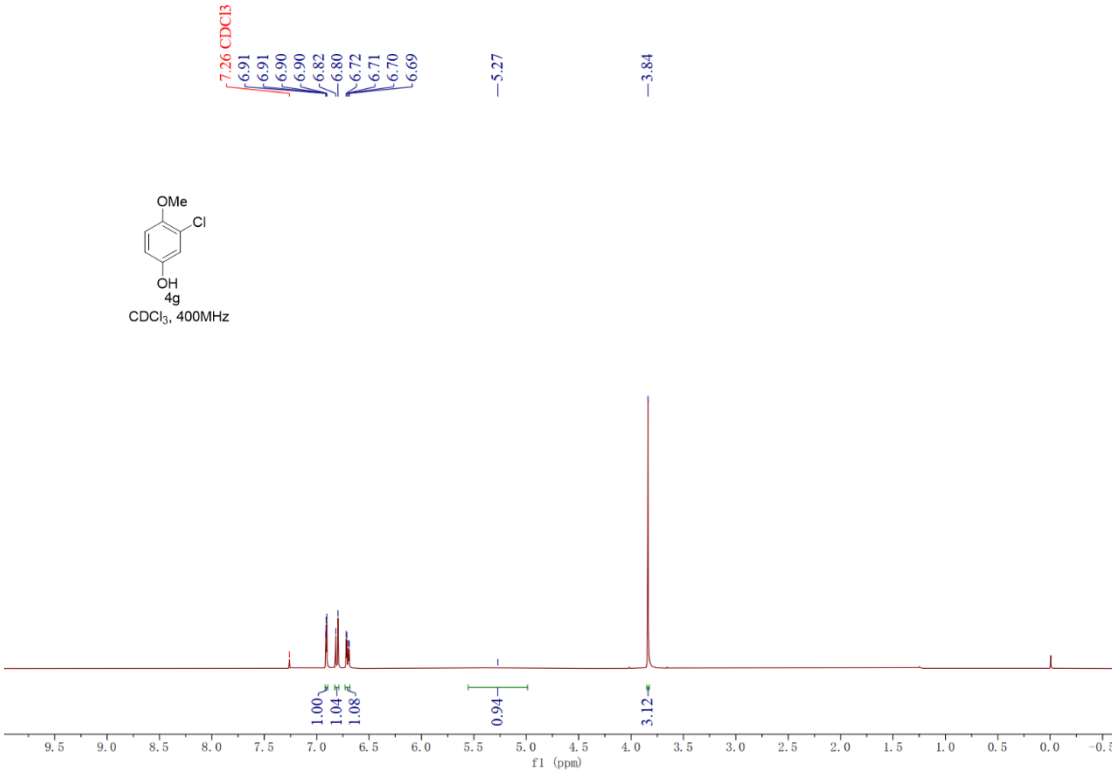


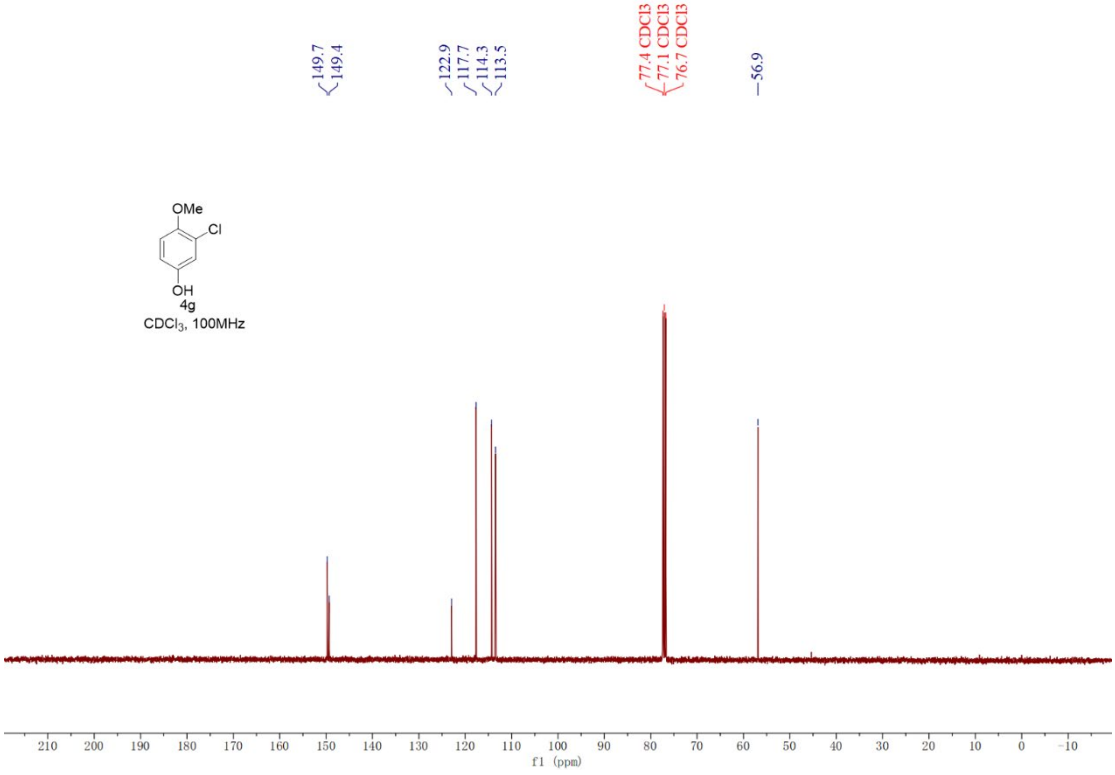
2-chloro-4-methoxyphenol



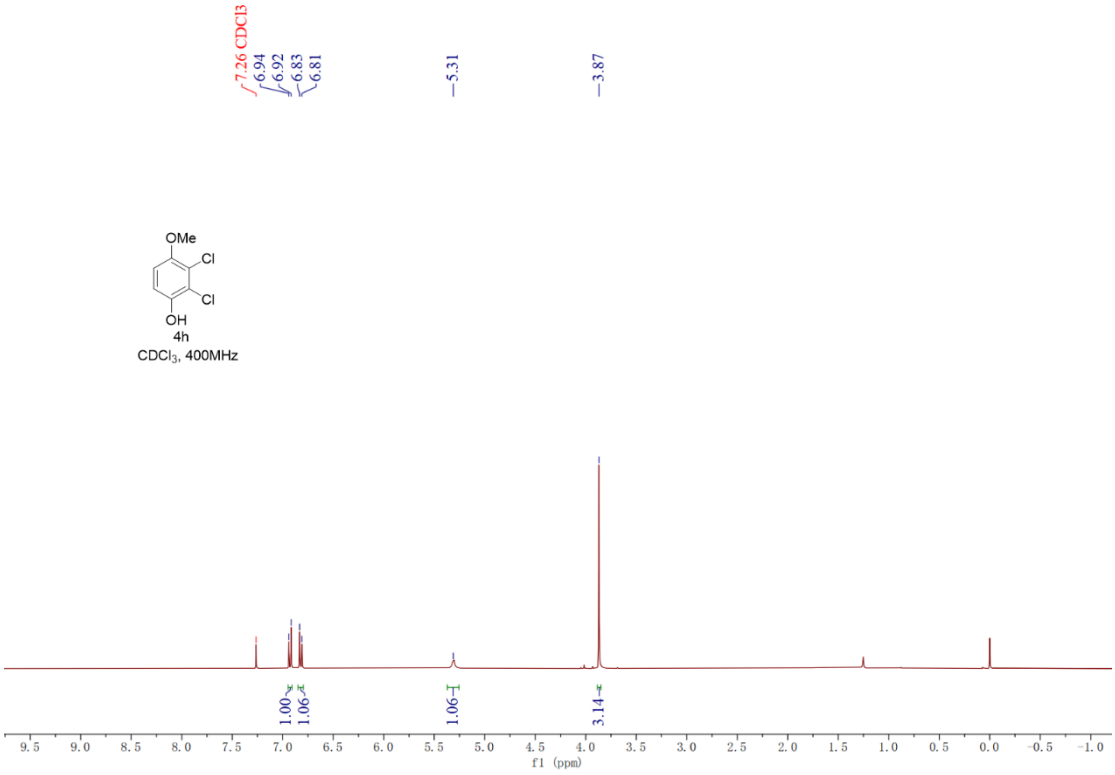


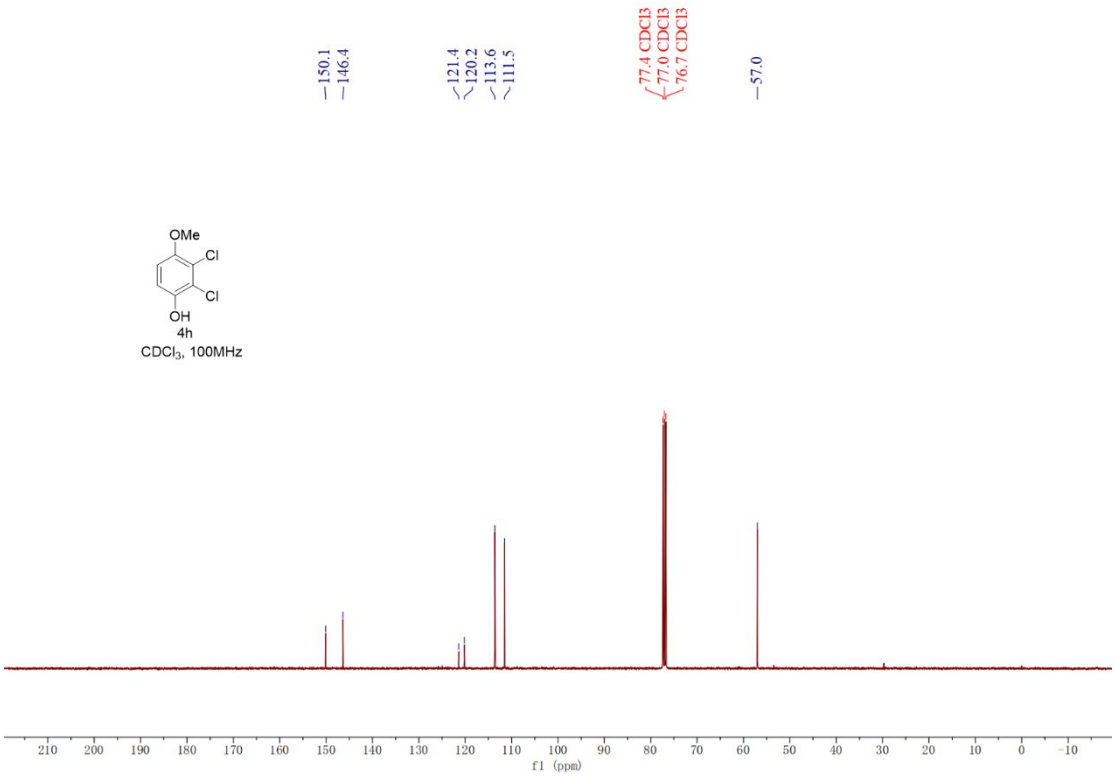
3-chloro-4-methoxyphenol



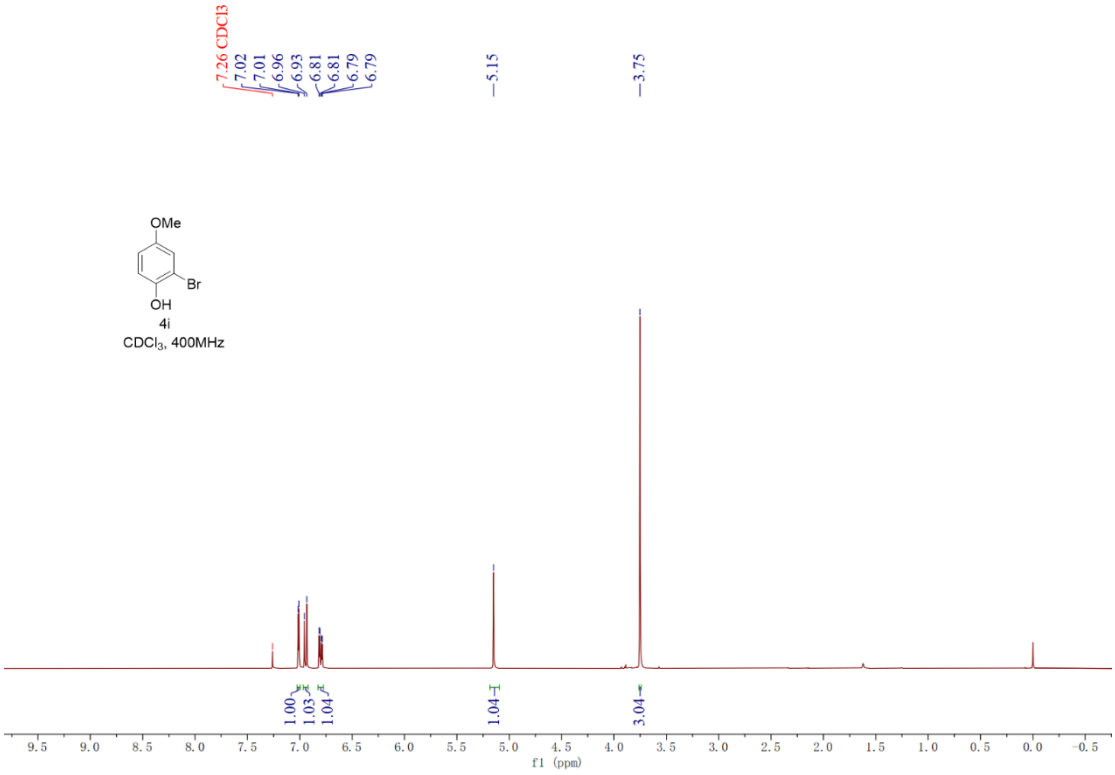


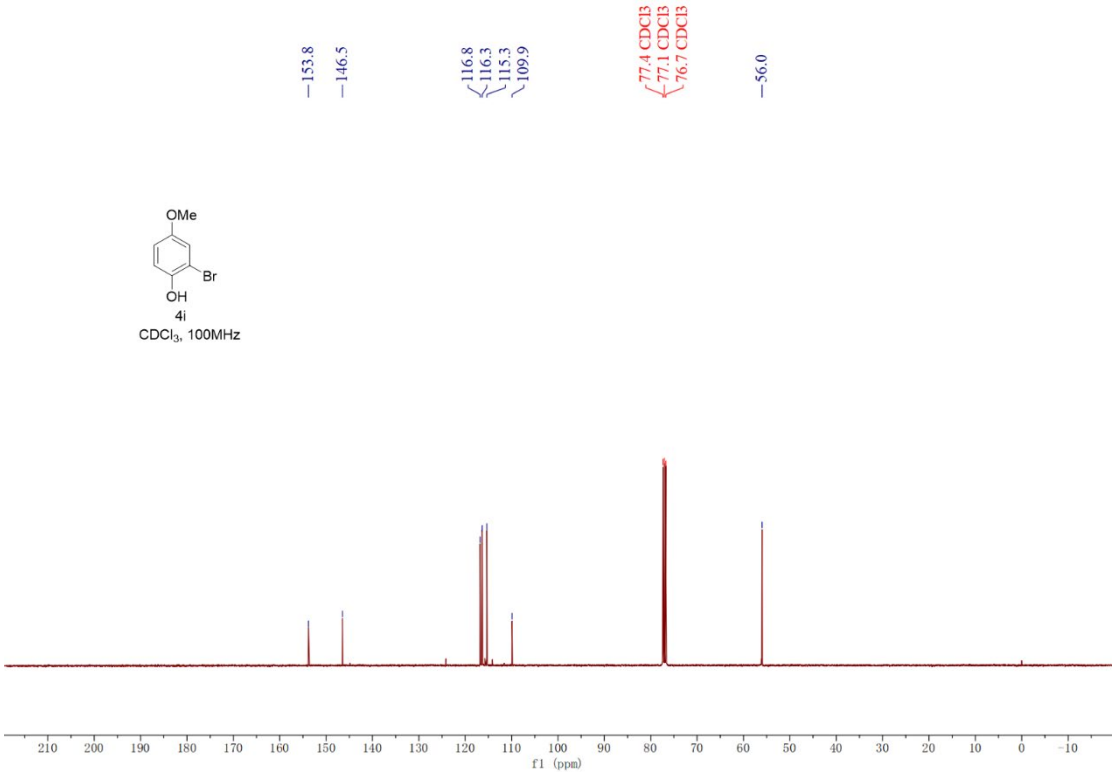
2,3-dichloro-4-methoxyphenol



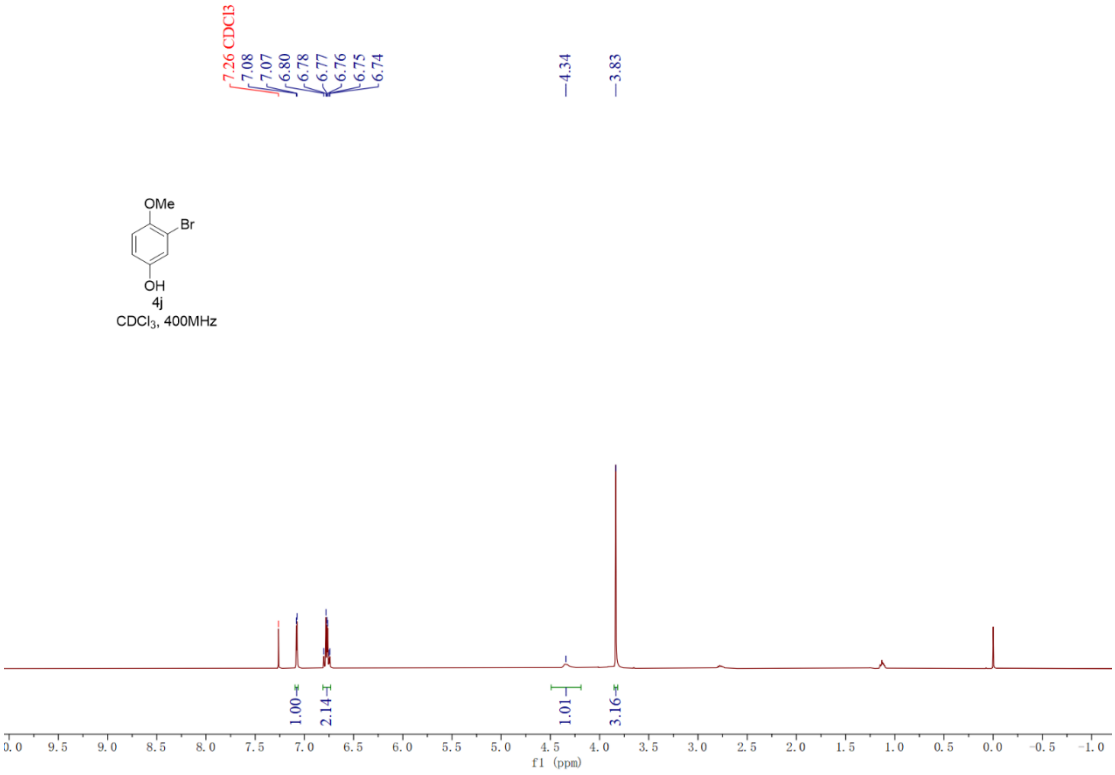


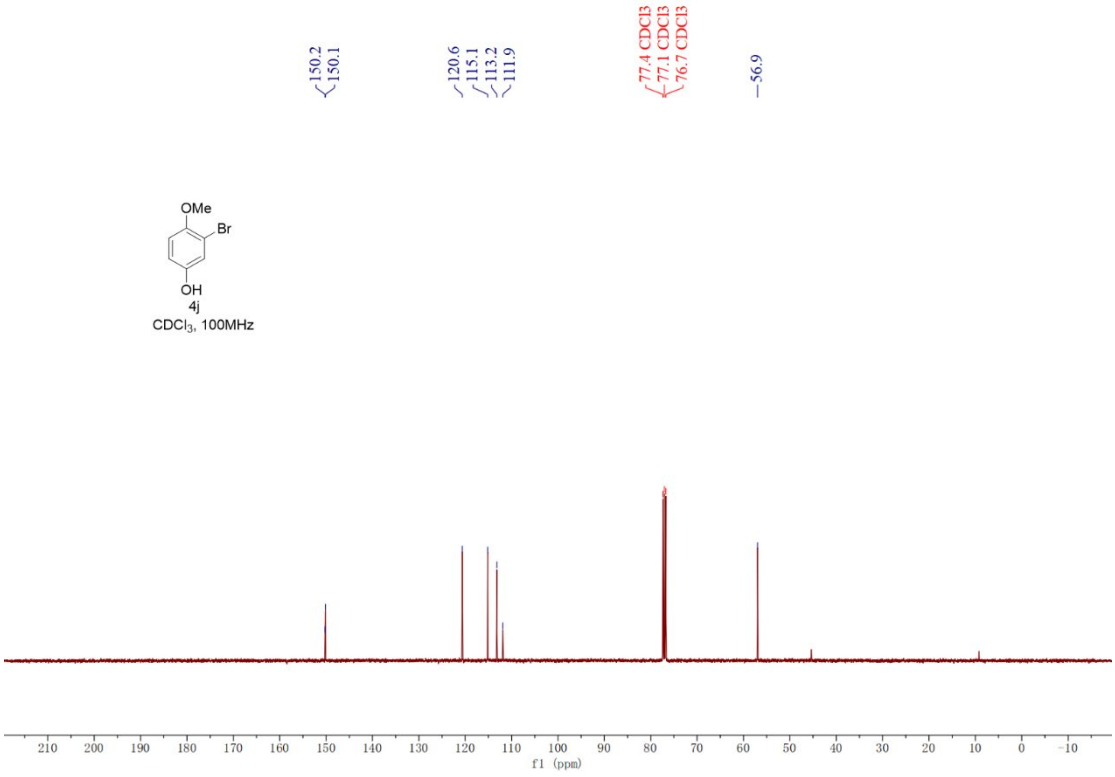
2-bromo-4-methoxyphenol



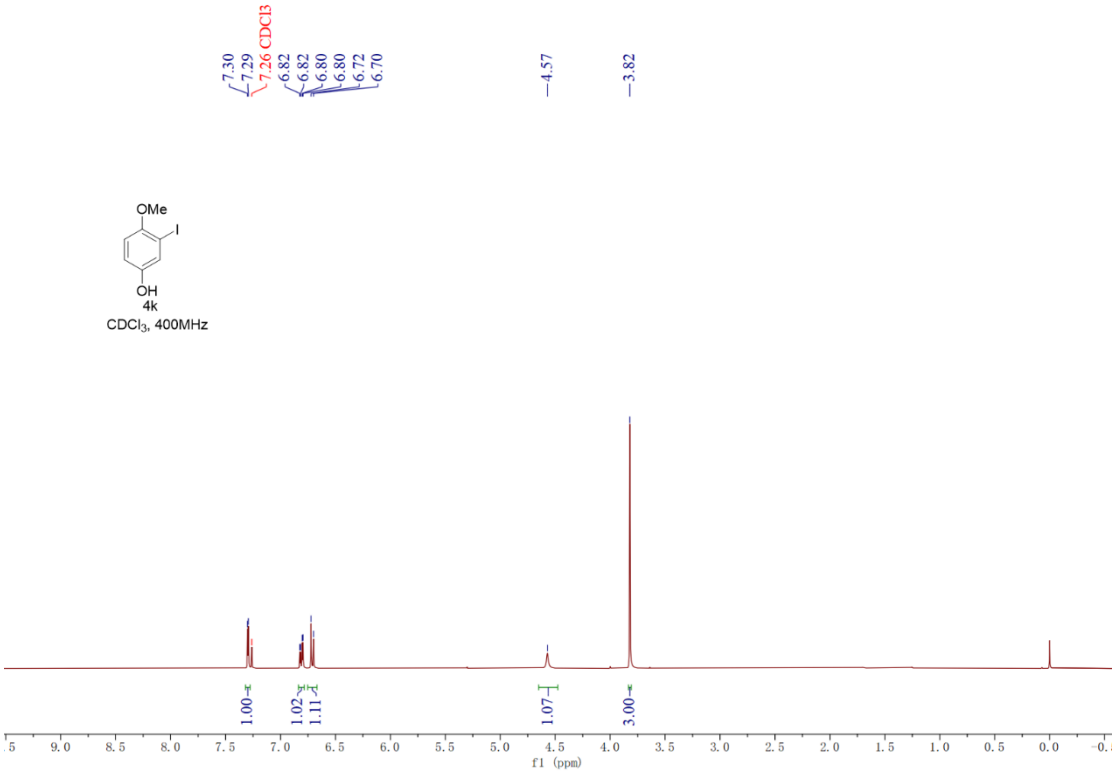


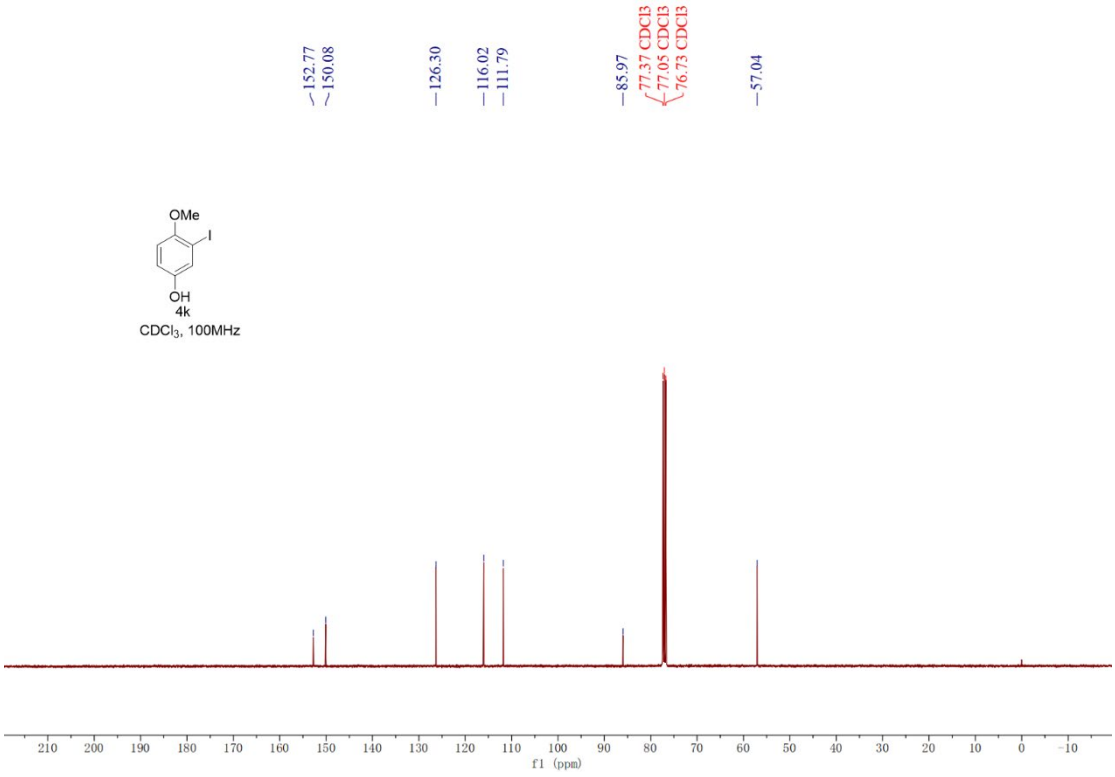
3-bromo-4-methoxyphenol



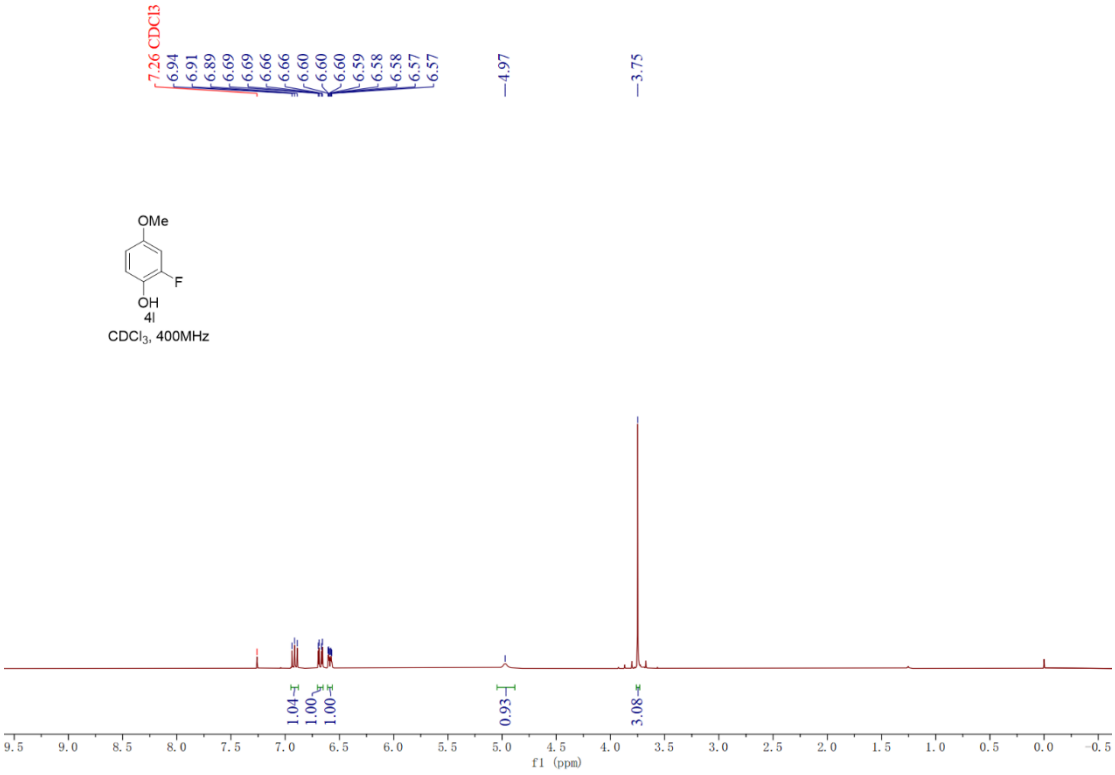


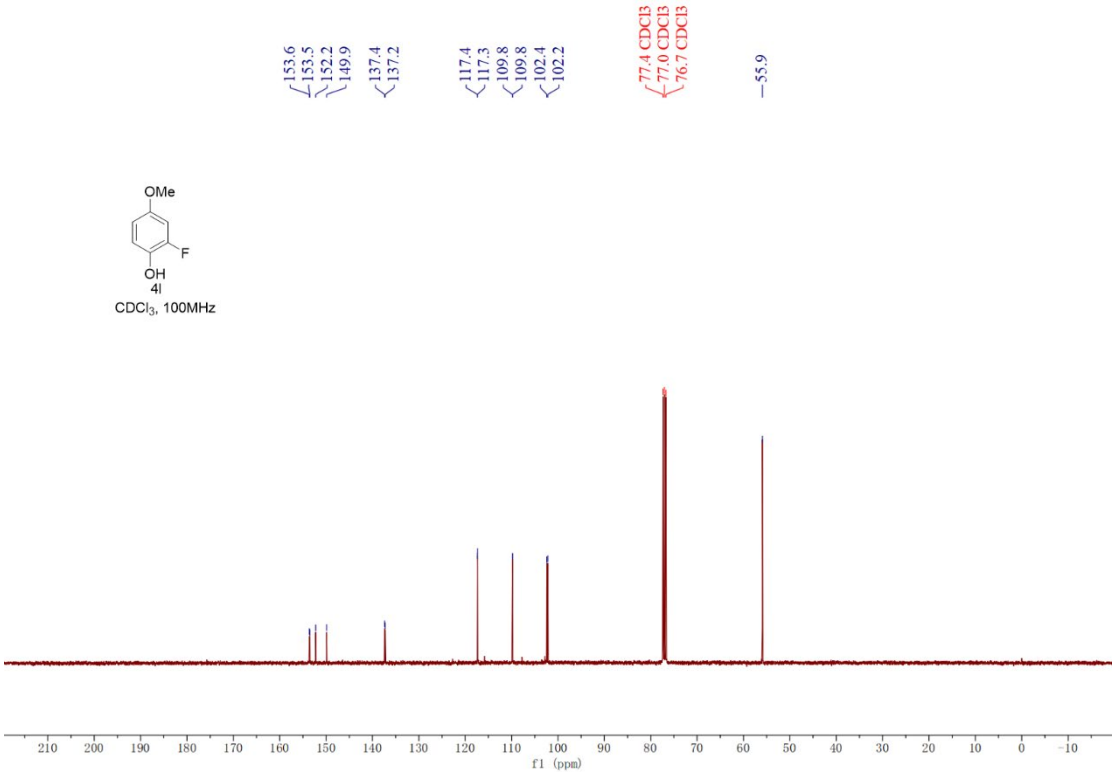
3-iodo-4-methoxyphenol



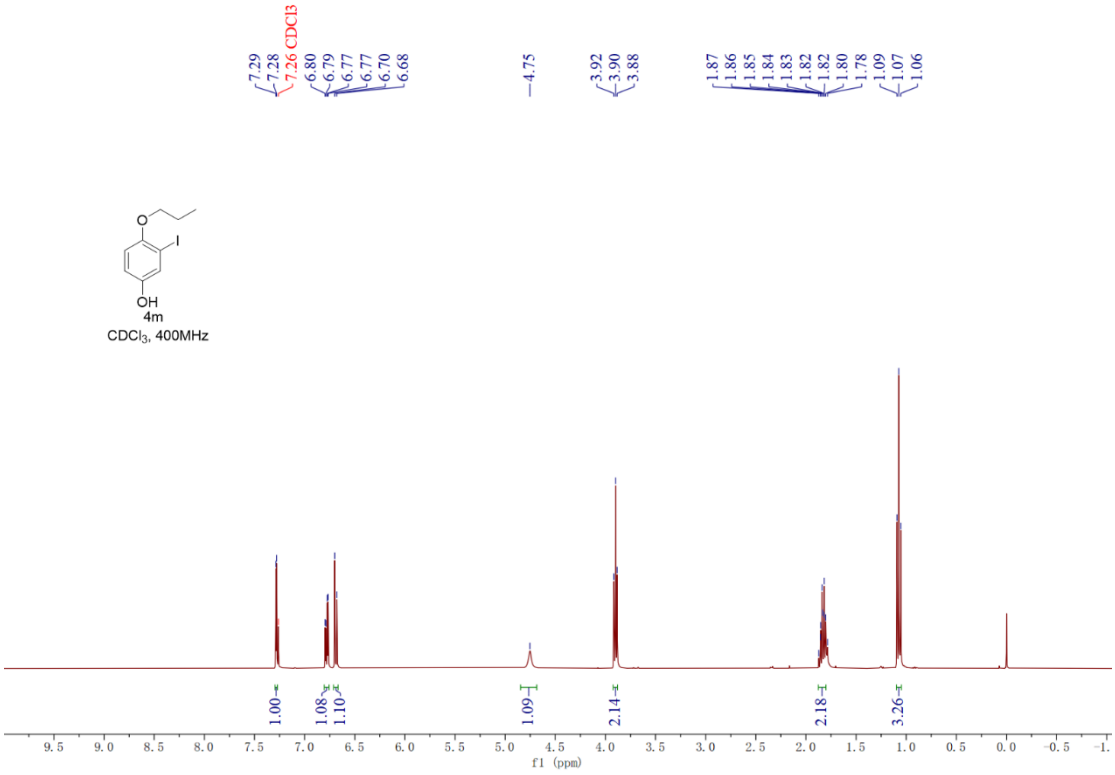


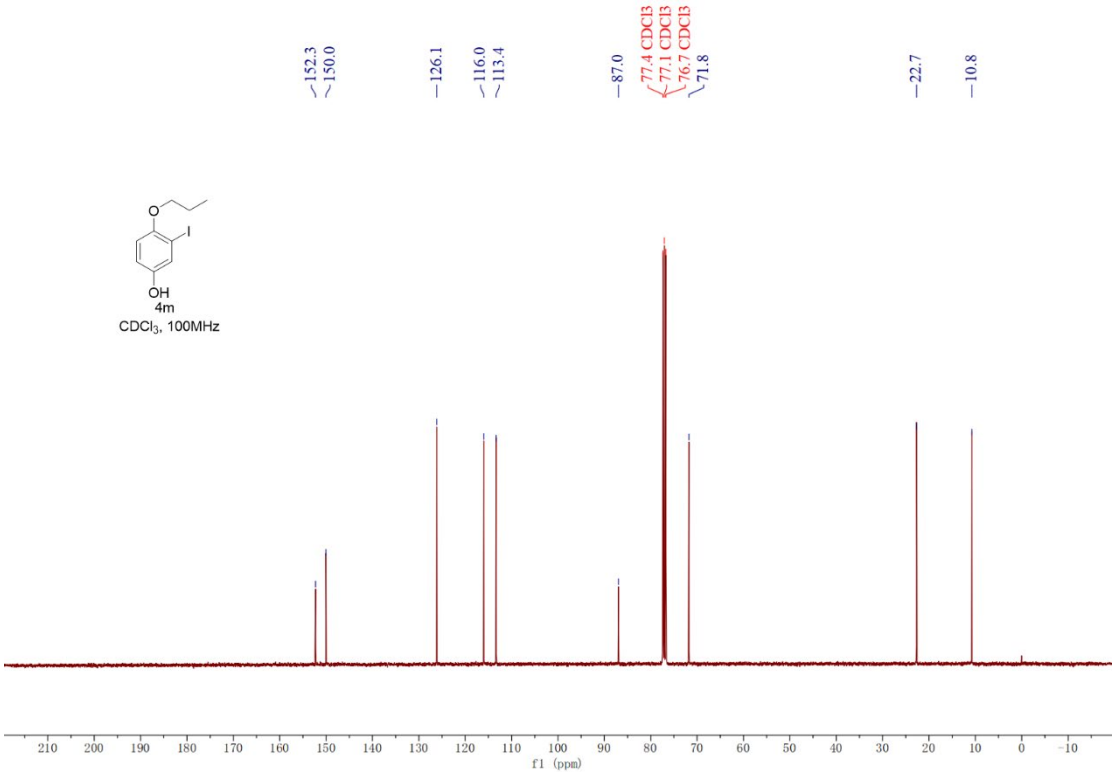
2-fluoro-4-methoxyphenol



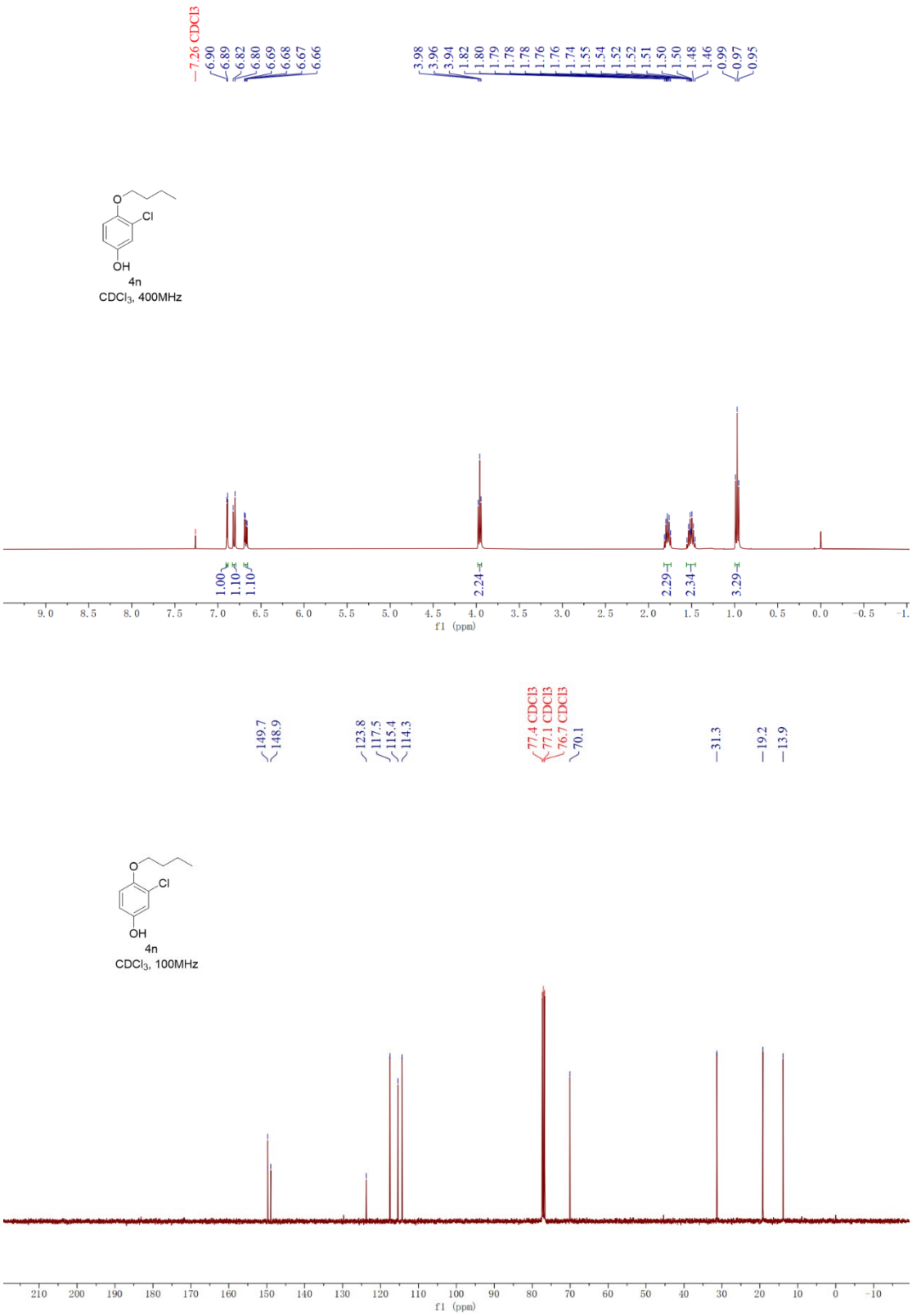


3-iodo-4-propoxyphenol

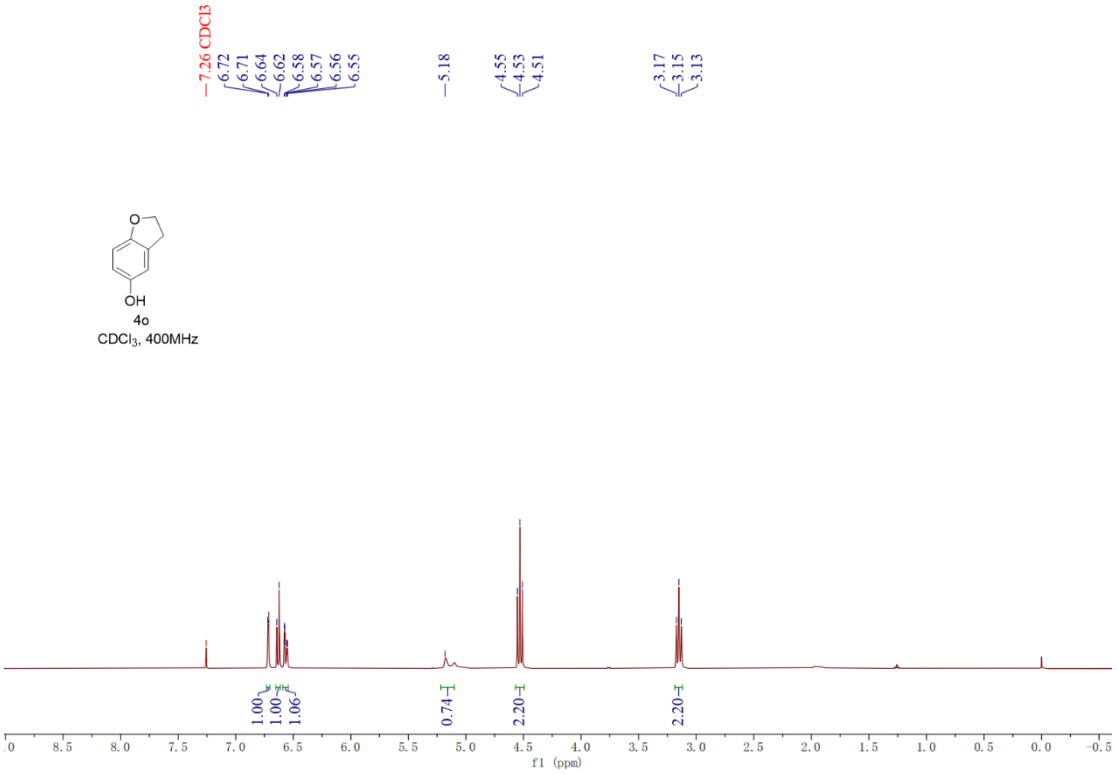


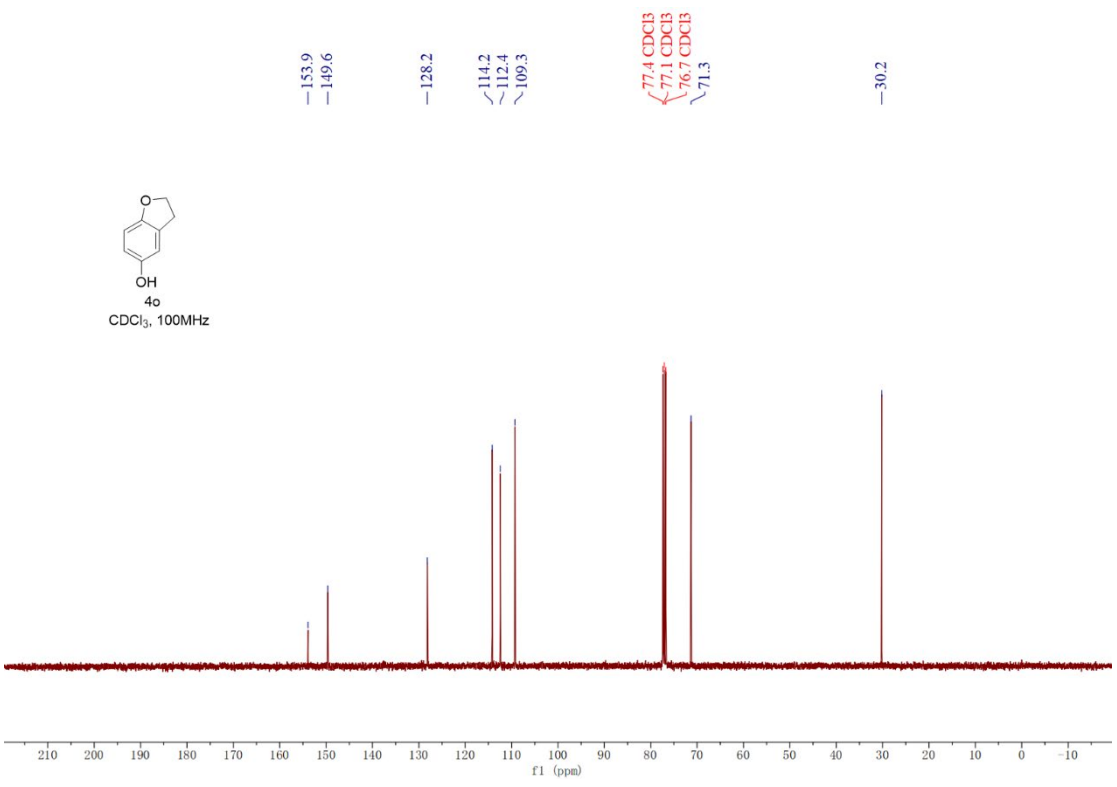


4-butoxy-3-chlorophenol

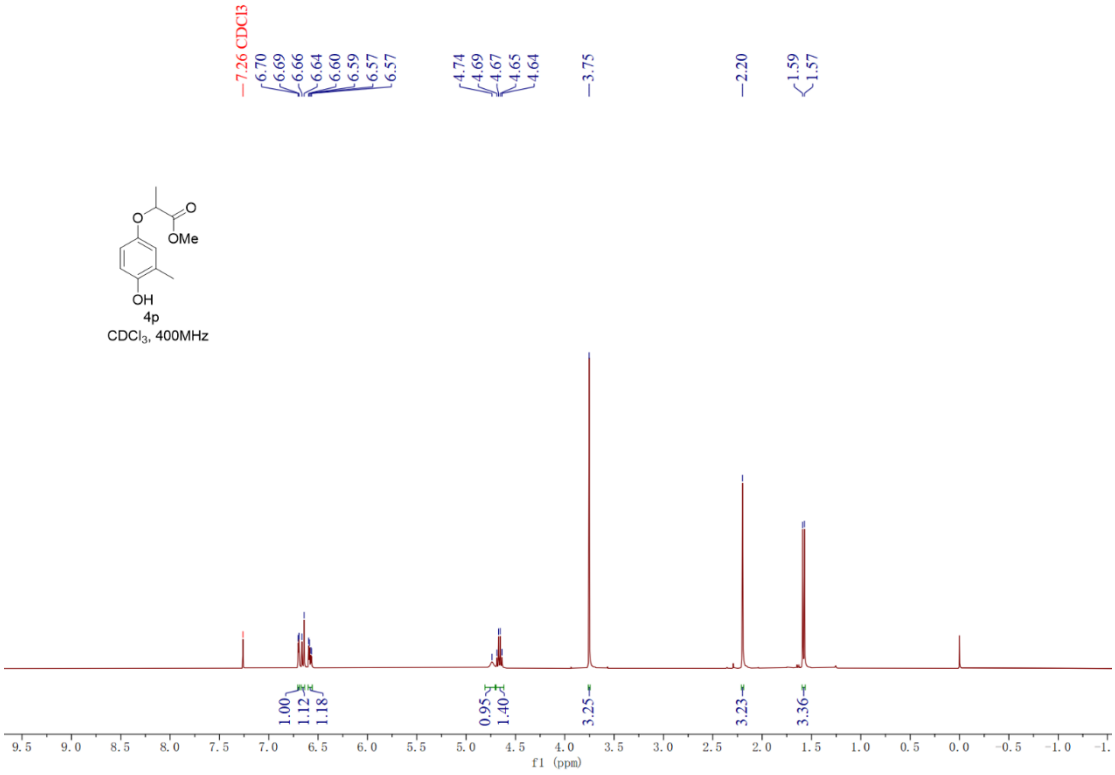


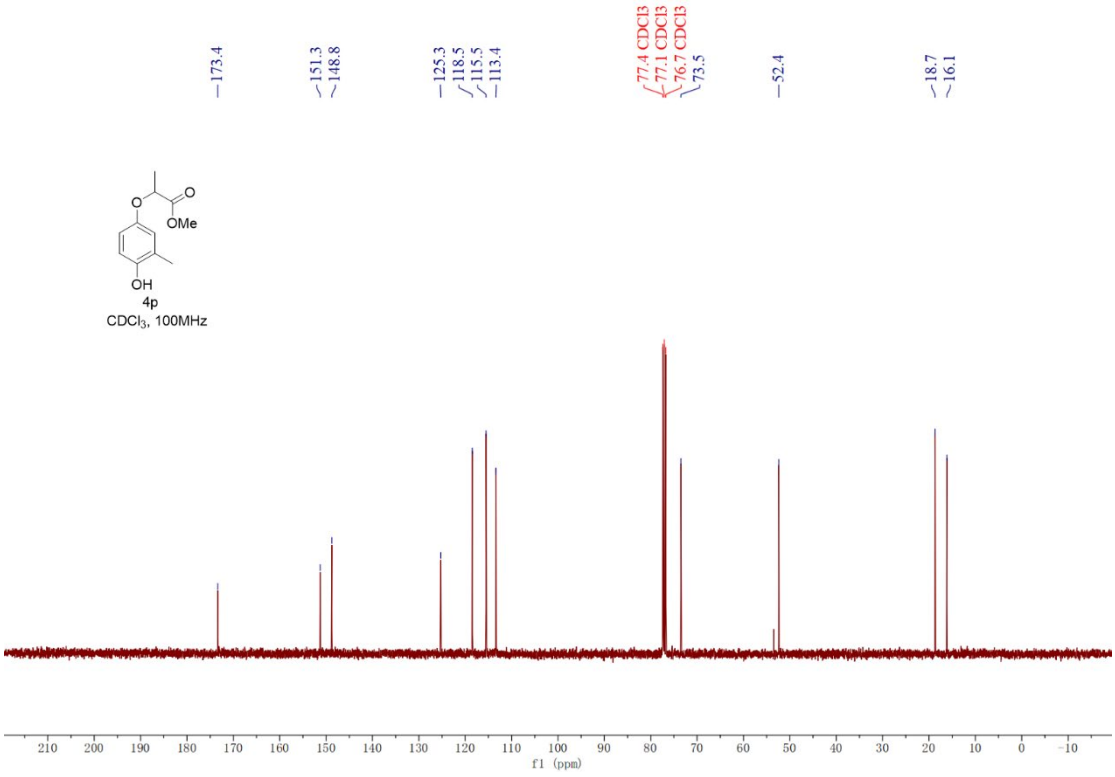
2,3-dihydrobenzofuran-5-ol



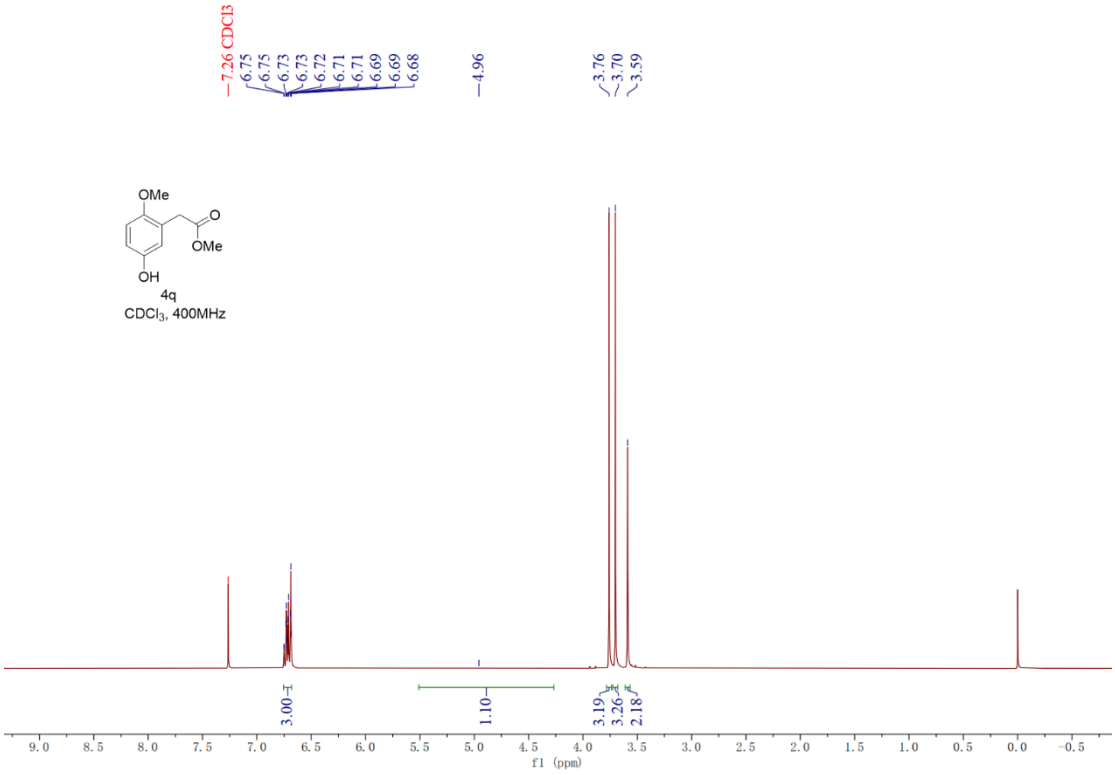


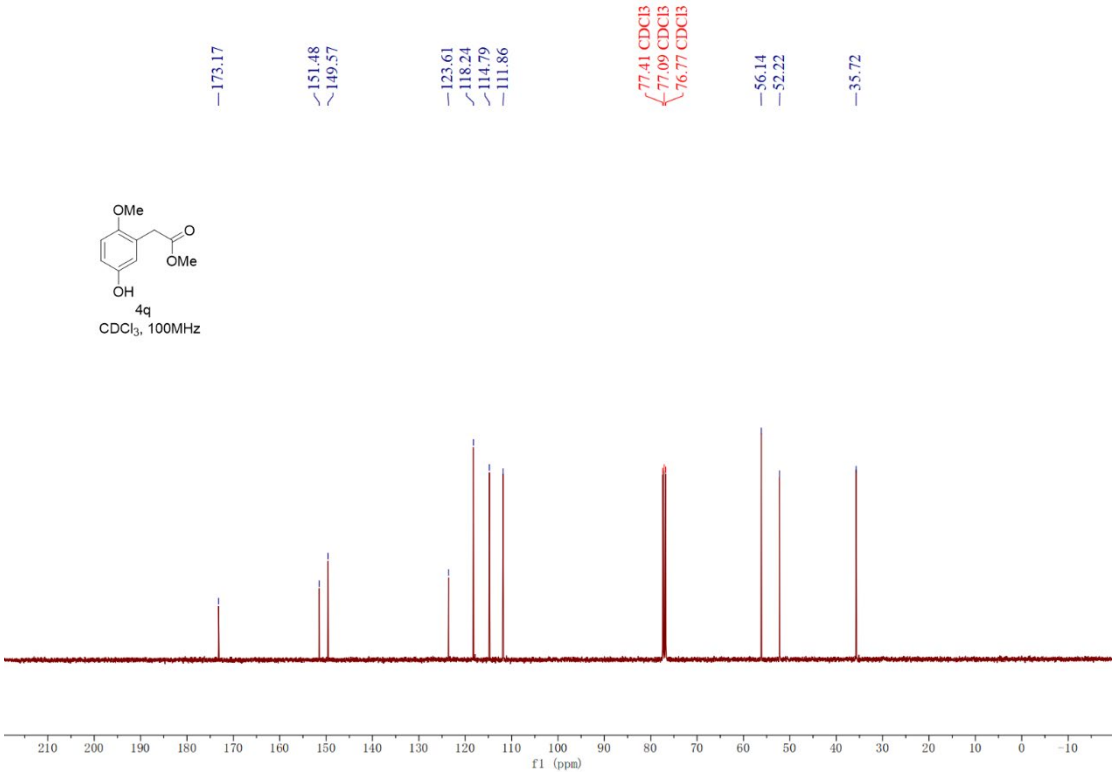
methyl 2-(4-hydroxy-3-methylphenoxy)propanoate



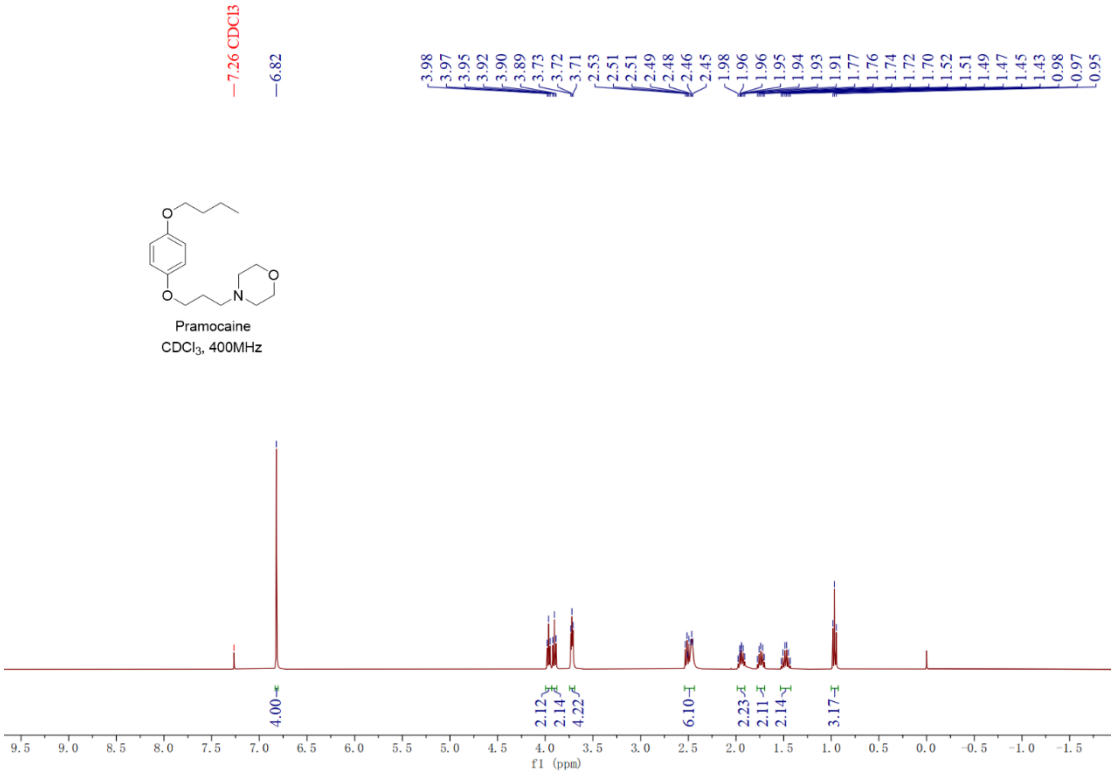


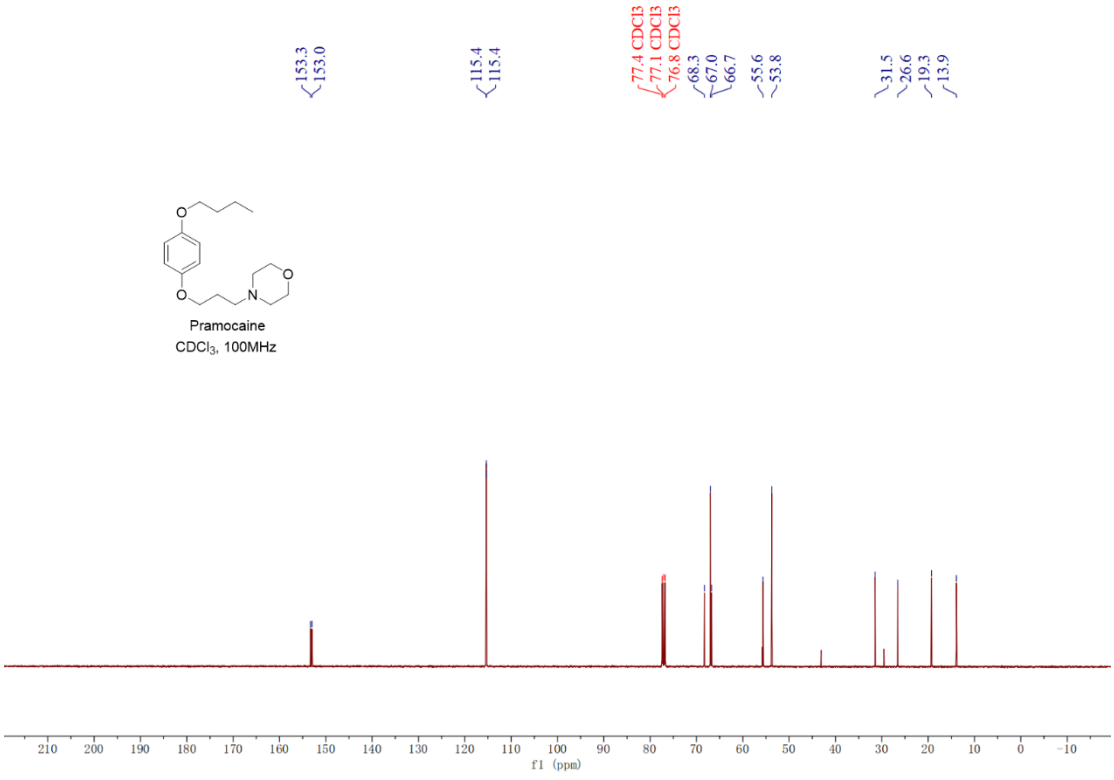
methyl 2-(5-hydroxy-2-methoxyphenyl)acetate



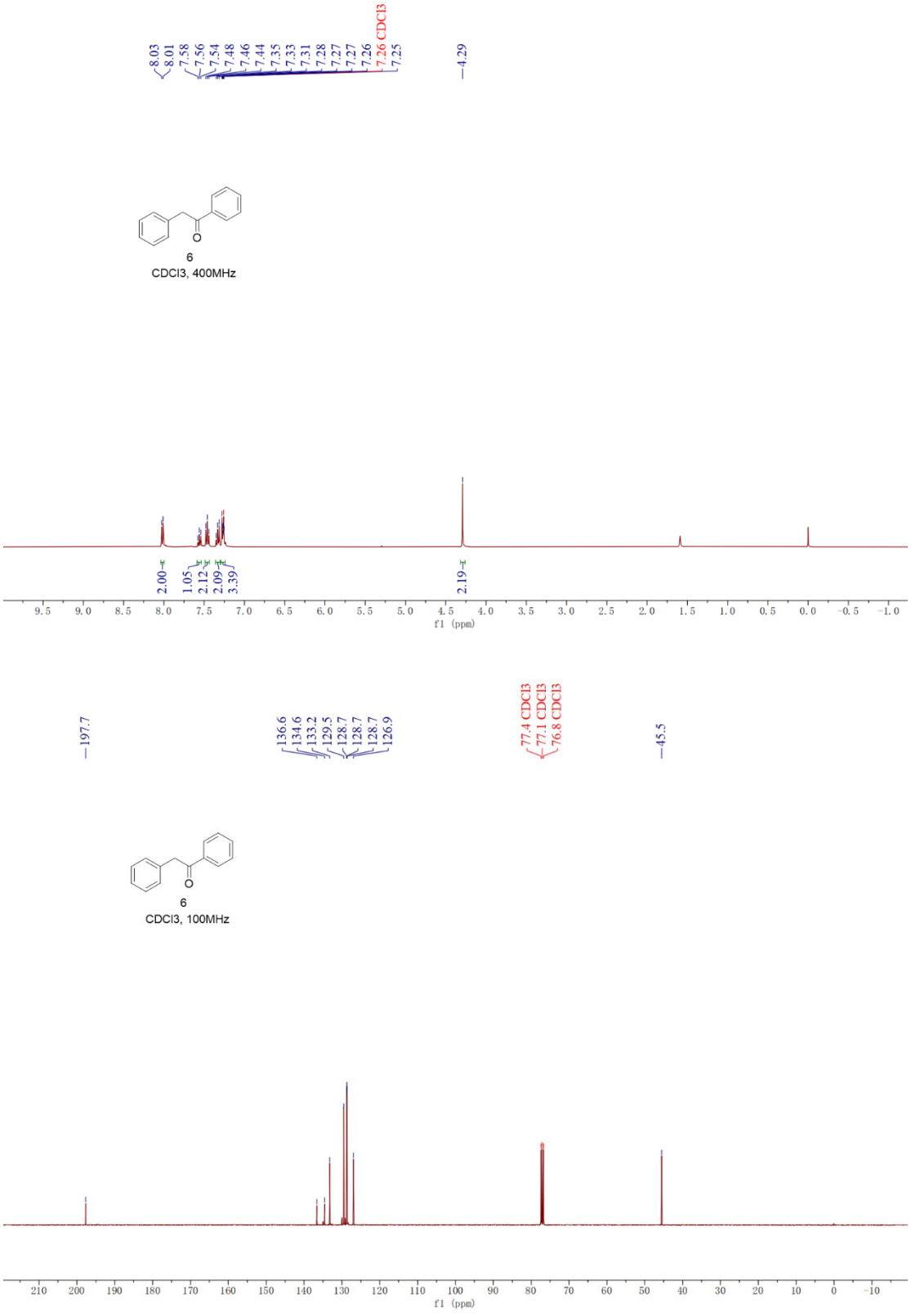


Pramocaine

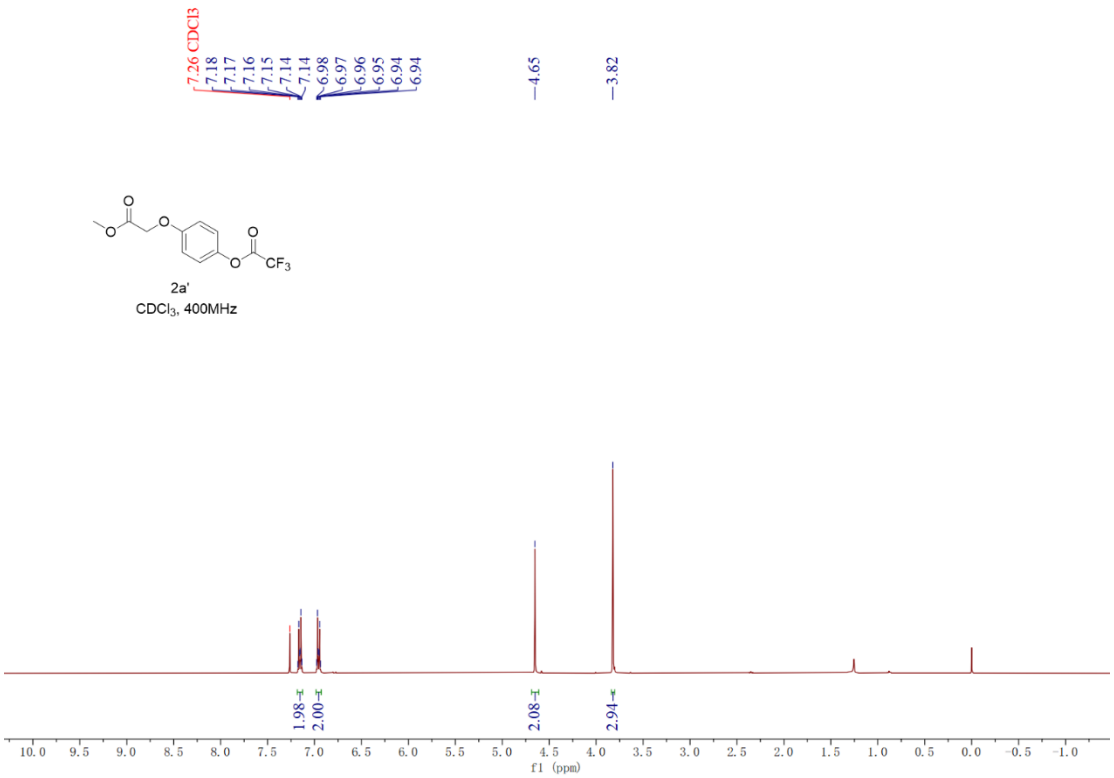

7.26 CDCl3
6.82
3.98
3.97
3.95
3.92
3.90
3.89
3.73
3.72
3.71
2.53
2.51
2.51
2.49
2.48
2.46
2.45
1.98
1.96
1.96
1.95
1.94
1.93
1.91
1.77
1.76
1.74
1.72
1.70
1.52
1.51
1.49
1.47
1.45
1.43
0.98
0.97
0.95
Pramocaine
CDCl3, 400MHz
4.00
2.12
2.14
4.22
6.10
2.23
2.11
2.14
3.17
f1 (ppm)

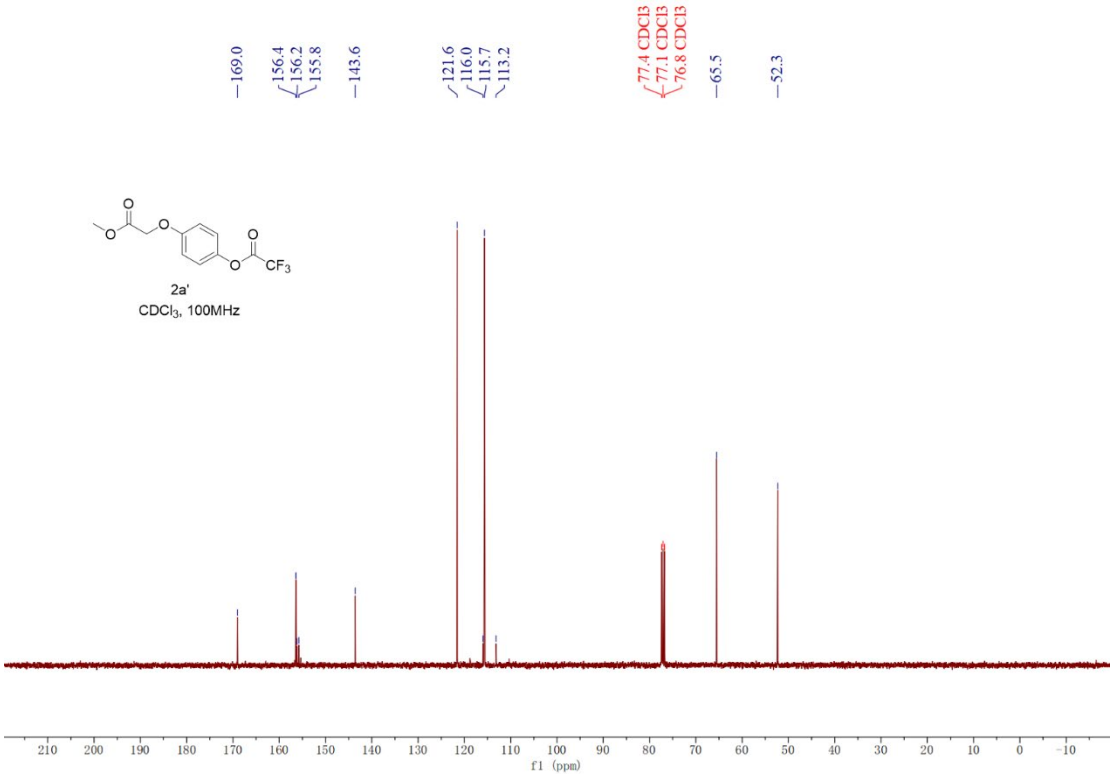

153.3
153.0
115.4
115.4
77.4 CDCl3
77.1 CDCl3
76.8 CDCl3
68.3
67.0
66.7
55.6
53.8
31.5
26.6
19.3
13.9
Pramocaine
CDCl3, 100MHz
f1 (ppm)

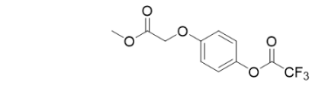
1,2-diphenylethan-1-one



4-(2-methoxy-2-oxoethoxy)phenyl 2,2,2-trifluoroacetate







2a'

$CDCl_3$, 376MHz