

Electronic Supplementary Information

for

Electrochemical formylation of aryl halides by using DMF as formyl source

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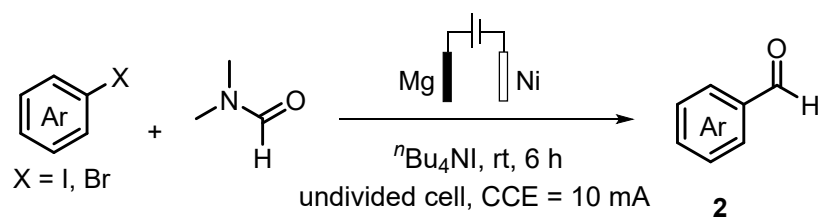
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1 General information

All reagents were obtained from commercial suppliers and used without further purification. The reactions were monitored by TLC (thin layer chromatography). Column chromatography was performed using silica gel (300–400 mesh). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^1H) and 100 MHz (^{13}C) in CDCl_3 or $\text{DMSO-}d_6$ using tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected. The cyclic voltammetry (CV) measurement was conducted using the CHI 601E electrochemical workstation produced by Shanghai Chenhua Company.

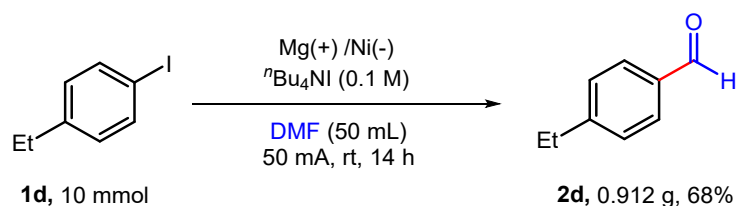
2 Experimental procedures

2.1 General procedure for the formylation of aryl halides



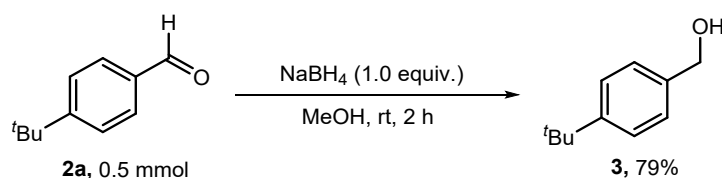
To an undivided three-necked flask (10 mL) were added aryl halide (**1**, 0.5 mmol), DMF (5.0 mL), $^n\text{Bu}_4\text{NI}$ (184.7 mg, 0.5 mmol, 0.1 M). The flask was equipped with Mg as anode and nickel foam as cathode. The reaction mixture was stirred and electrolyzed at a constant current (10 mA) under Ar at room temperature for 6 h. After the reaction was completed, the mixture was diluted with saturated ammonium chloride solution (40 mL) and then extracted by ethyl acetate (20 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in vacuo and the crude product was obtained. The pure product **2** was obtained by silica gel chromatography using petroleum ether/ethyl acetate (100:1-40:1, v/v) as the eluent.

2.2 Gram-scale synthesis of **2d**

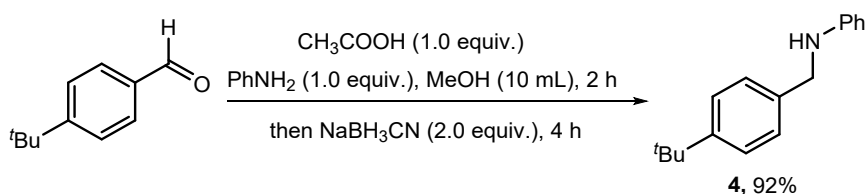


To an undivided three-necked flask (100 mL) were added 1-ethyl-4-iodobenzene (**1d**, 1.46 mL, 10 mmol), $n\text{Bu}_4\text{NI}$ (1.85 g, 5.0 mmol, 0.1 M) and DMF (50 mL). The flask was equipped with Magnesium plate (50 mm \times 20 mm) as anode and nickel foam (50 mm \times 20 mm) as cathode. The reaction mixture was stirred and electrolyzed at a constant current (50 mA) at room temperature for 14 h. After the reaction was completed, the mixture was diluted with saturated ammonium chloride solution (60 mL) and then extracted by ethyl acetate (90 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filter, and vacuum concentrate to obtain the crude product. The pure product **2d** was obtained by silica gel chromatography using petroleum ether/ethyl acetate (100:1, v/v) as the eluent.

2.3 General procedure for the preparation of **3**, **4** and **5**

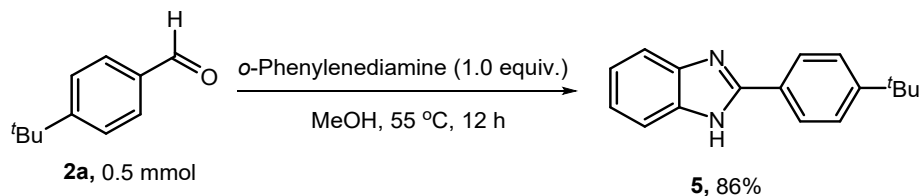


To a dried 25 mL round bottom flask were added the product **2a** (81.1 mg, 0.5 mmol), sodium borohydride (18.9 mg, 0.5 mmol, 1.0 equiv.) and MeOH (10 mL) under air. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with H_2O , extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (50:1, v/v) as the eluent to afford the desired product **3**.



To a dried 25 mL round bottom flask were added the product **2a** (81.1 mg, 0.5 mmol), acetic acid (30.0 mg, 0.5 mmol, 1.0 equiv.), aniline (46.6 mg, 0.5 mmol, 1.0 equiv.) and MeOH (10 mL) under air. The reaction mixture was stirred at room temperature for 2 h. Then sodium cyanide borohydride (2.0 equiv.) was added and stirred for 4 h. The reaction mixture was diluted with H_2O , extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the resulting residue was purified by silica gel

column chromatography using petroleum ether/ethyl acetate (70:1, v/v) as the eluent to afford the desired product **4**.



To a dried 25 mL round bottom flask were added the product **2a** (81.1 mg, 0.5 mmol), *o*-phenylenediamine (54.1 mg, 0.5 mmol, 1.0 equiv.) and MeOH (10 mL) under air. The reaction mixture was stirred at 55 °C for 12 h. The reaction mixture was diluted with H₂O, extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (20:1, v/v) as the eluent to afford the desired product **5**.

3 Mechanism studies

3.1 Cyclic voltammetry studies

Cyclic voltammetry (CV) experiments were performed using three electrodes and glassy carbon as the working electrode (ϕ 3 mm, cylindrical), Pt as counter electrode and saturated calomel electrode as reference electrode (ⁿBu₄NI (0.02 M) in DMF). The working electrode was polished with alumina polishing suspension (0.05 μ m) on the alumina polishing pad, and then rinsed with deionized water and ethanol. The solvent for CV measurement was deoxygenated by bubbling with nitrogen gas. All CV measurements were conducted at room temperature. As shown in Figure S1, a reduction peak of **1a** can be observed at -3.01V vs SCE (blue curve), indicating that aryl halides may be reduced to anions at the cathode.

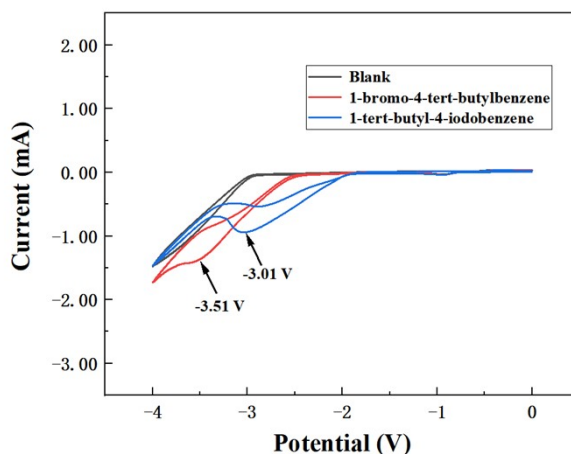
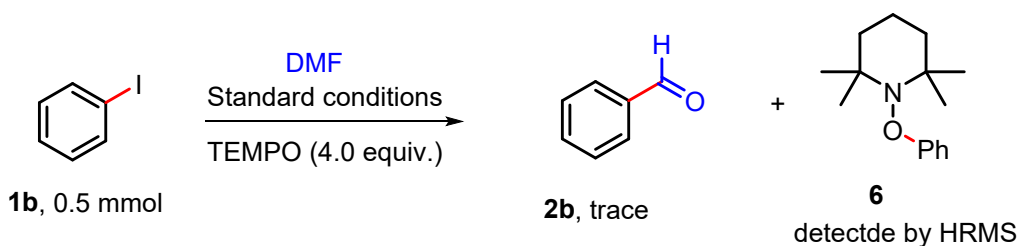


Figure S1. CV scans (scan rate 100 $\text{mv}\cdot\text{s}^{-1}$) of substrates: Blank ($n\text{Bu}_4\text{NI}$ (0.02 M) in DMF, black curve); 1-*tert*-butyl-4-iodobenzene (0.02 M, blue curve); 1-bromo-4-*tert*-butylbenzene (0.02 M, red curve). The CV is plotted by using the IUPAC conversion.

3.2 Radical capture experiment



To an undivided three-necked flask (10 mL) were added aryl halide (**1b**, 0.5 mmol), DMF (5.0 mL), $n\text{Bu}_4\text{NI}$ (184.7 mg, 0.5 mmol, 0.1 M). Then TEMPO (312.5 mg, 2.0 mmol, 4.0 equiv.) was added to the flask. The flask was equipped with Mg as anode and nickel foam as cathode. The reaction mixture was stirred and electrolyzed at a constant current (10 mA) under Ar at room temperature for 6 h. The reaction was obviously suppressed by the addition of TEMPO and trapping products **6** was observed through the HRMS analysis from the reaction solution (Figures S2).

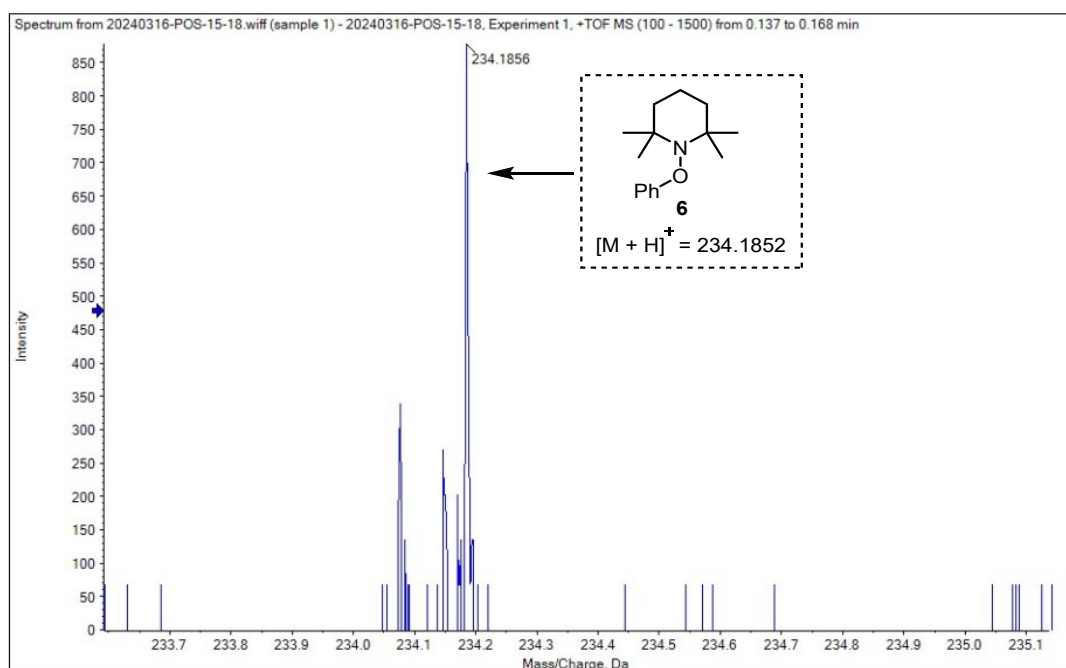
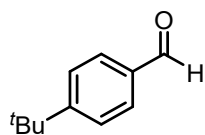
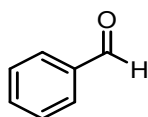


Figure S2. HRMS analysis of the radical-trapping product **6**.

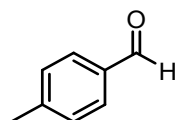
4 Experimental data for the products 2, 3, 4, 5.



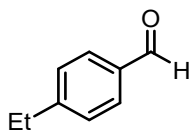
4-(Tert-butyl)benzaldehyde (2a).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (64.06 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.00 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 1.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.1, 158.5, 134.1, 129.7, 126.0, 35.4, 31.1.



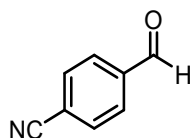
Benzaldehyde (2b).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (37.64 mg, 71% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.03 (s, 1H), 7.92–7.87 (m, 2H), 7.68–7.61 (m, 1H), 7.58–7.51 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.5, 136.4, 134.5, 129.8, 129.0.



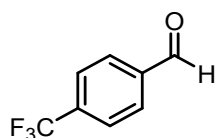
4-Methylbenzaldehyde (2c).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (43.22 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.96 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.1, 145.6, 134.2, 129.9, 129.7, 21.9.



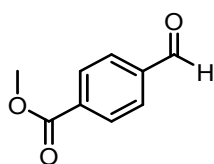
4-Ethylbenzaldehyde (2d).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (50.95 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.00 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.1, 151.7, 134.4, 130.0, 128.6, 29.2, 15.2.



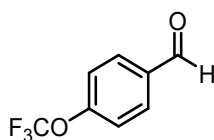
4-Formylbenzonitrile (2e).² The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). White solid (37.35 mg, 57% yield). mp: 99–101 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.11 (s, 1H), 8.05–7.98 (m, 2H), 7.92–7.82 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 190.7, 138.7, 132.9, 129.9, 117.8, 117.6.



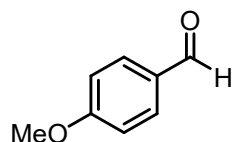
4-(Trifluoromethyl)benzaldehyde (2f).² The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Colorless oil (56.56 mg, 65% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.10 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 191.1, 138.7, 135.6 (q, J = 32.6 Hz), 129.9, 126.1 (q, J = 3.7 Hz), 123.4 (q, J = 271.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -63.226.



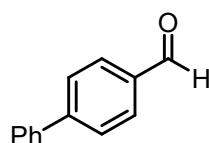
Methyl 4-formylbenzoate (2g).³ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). White solid (63.98 mg, 78% yield). mp: 57–59 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.12 (s, 1H), 8.21 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.3 Hz, 2H), 3.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 191.7, 166.1, 139.1, 135.1, 130.2, 129.6, 52.6.



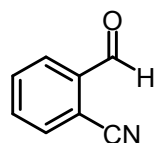
4-(Trifluoromethoxy)benzaldehyde (2h).³ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). Yellow oil (64.61 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.03 (s, 1H), 7.96 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 190.6, 153.5, 134.5, 131.6, 120.2 (q, J = 257.6 Hz), 120.8. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -57.607.



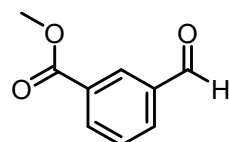
4-Methoxybenzaldehyde (2i).³ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (37.41 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.88 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.



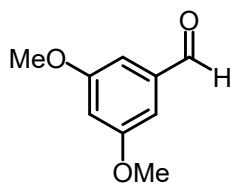
[1,1'-Biphenyl]-4-carbaldehyde (2j).³ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). White solid (58.26 mg, 46% yield). mp: 55–57 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.09 (s, 1H), 8.01–7.95 (m, 2H), 7.81–7.76 (m, 2H), 7.69–7.63 (m, 2H), 7.54–7.42 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.0, 147.2, 139.7, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4.



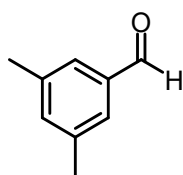
2-Formylbenzonitrile (2k).⁴ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). White solid (33.41 mg, 51% yield). mp: 106–108 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.38 (s, 1H), 8.10–8.02 (m, 1H), 7.87 (dd, J = 7.5, 1.5 Hz, 1H), 7.85–7.75 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 188.6, 136.8, 134.3, 134.1, 133.3, 129.6, 116.0, 113.9.



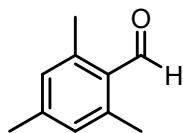
Methyl 3-formylbenzoate (2l).⁵ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). White solid (58.24 mg, 71% yield). mp: 51–53 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.09 (s, 1H), 8.55–8.53 (m, 1H), 8.33–8.29 (m, 1H), 8.11–8.08 (m, 1H), 7.67–7.62 (m, 1H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 191.4, 166.0, 136.6, 135.2, 133.1, 131.3, 131.2, 129.3, 52.5.



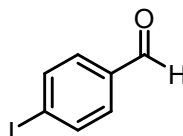
3,5-Dimethoxybenzaldehyde (2m).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (34.87 mg, 42% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.92 (s, 1H), 7.02 (d, J = 2.3 Hz, 2H), 6.72 (t, J = 2.4 Hz, 1H), 3.86 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.0, 161.3, 138.4, 107.2, 107.1, 55.6.



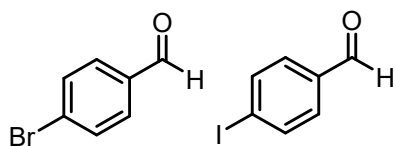
3,5-Dimethylbenzaldehyde (2n).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (52.96 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.95 (s, 1H), 7.49 (s, 2H), 7.27 (s, 1H), 2.40 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.8, 138.8, 136.6, 136.2, 127.6, 21.1.



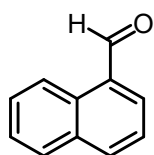
2,4,6-Trimethylbenzaldehyde (2o).⁶ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (47.39 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.58 (s, 1H), 6.92 (s, 2H), 2.60 (s, 6H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 193.0, 143.9, 141.5, 130.5, 130.0, 21.5, 20.5.



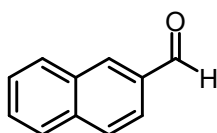
4-Iodobenzaldehyde (2p).⁷ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Yellow solid (90.86 mg, 78% yield). mp: 83–85 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.96 (s, 1H), 7.91 (dd, J = 8.9, 2.0 Hz, 2H), 7.64–7.53 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 191.4, 138.4, 135.6, 130.8, 102.9.



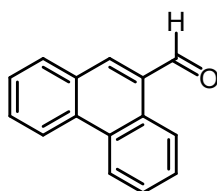
4-Bromobenzaldehyde and 4-Iodobenzaldehyde (2q).^{7, 8} The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Yellow solid (74.52 mg, 77% yield). mp: 75–77 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.99 (s, 1H), 9.97 (s, 0.25H), 7.93–7.91 (m, 0.50H), 7.78–7.75 (m, 2H), 7.71–7.68 (m, 2H), 7.61–7.59 (m, 0.50H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 191.4, 191.1, 138.4, 135.6, 135.1, 132.5, 131.0, 130.8, 129.8, 102.9.



1-Naphthaldehyde (2r).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (54.62 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.43 (s, 1H), 9.29 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.03 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.69–7.61 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 193.6, 136.8, 135.4, 133.8, 131.4, 130.6, 129.1, 128.5, 127.0, 124.9.

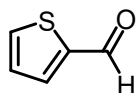


2-Naphthaldehyde (2s).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (57.74 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.18 (s, 1H), 8.36 (d, *J* = 1.4 Hz, 1H), 8.07–7.86 (m, 4H), 7.69–7.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 192.3, 136.5, 134.6, 134.1, 132.7, 129.6, 129.1, 129.1, 128.1, 127.1, 122.8.

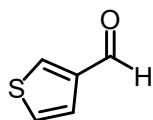


Phenanthrene-9-carbaldehyde (2t).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (70.10 mg, 69%

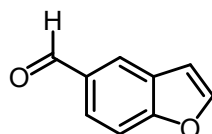
yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.39 (s, 1H), 9.45–9.33 (m, 1H), 8.77–8.66 (m, 2H), 8.26 (s, 1H), 8.05 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.86–7.81 (m, 1H), 7.78–7.73 (m, 2H), 7.72–7.68 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 193.7, 141.4, 133.0, 130.6, 130.5, 130.4, 130.3, 130.1, 128.3, 127.7, 127.3, 126.0, 122.9, 122.8.



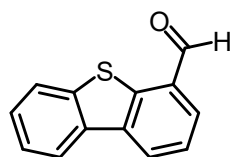
Thiophene-2-carbaldehyde (2u).² The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (47.04 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.93 (s, 1H), 7.77 (dd, $J = 8.9, 4.3$ Hz, 2H), 7.26–7.11 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 183.1, 144.0, 136.5, 135.2, 128.4.



Thiophene-3-carbaldehyde (2v).² The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Yellow oil (47.16 mg, 86% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.93 (s, 1H), 8.13 (dd, $J = 2.9, 1.2$ Hz, 1H), 7.55 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.39–7.37 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 185.0, 143.0, 136.9, 127.5, 125.3.

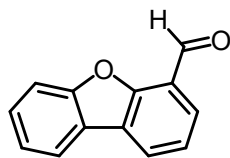


Benzofuran-5-carbaldehyde (2w).⁹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Yellow solid (48.19 mg, 66% yield). mp: 54–56 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.08 (s, 1H), 8.16 (d, $J = 1.7$ Hz, 1H), 7.89 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.74 (d, $J = 2.3$ Hz, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 6.91 (dd, $J = 2.2, 1.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.8, 158.3, 146.8, 132.3, 128.0, 125.8, 124.7, 112.2, 107.3.

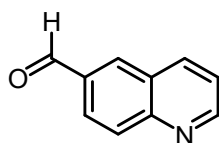


Dibenzo[b,d]thiophene-4-carbaldehyde (2x).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (76.33 mg, 72%

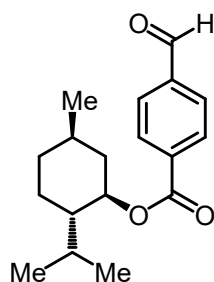
yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.31 (s, 1H), 8.45 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.26–8.23 (m, 1H), 8.04–7.95 (m, 2H), 7.69 (t, $J = 7.6$ Hz, 1H), 7.59–7.49 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.4, 141.7, 138.2, 137.4, 133.6, 133.0, 130.7, 127.5, 127.0, 124.8, 124.4, 123.1, 121.5.



Dibenzo[b,d]furan-4-carbaldehyde (2y).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). Colorless oil (78.42 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.59 (s, 1H), 8.19 (dd, $J = 7.6, 1.3$ Hz, 1H), 8.02–7.91 (m, 2H), 7.72–7.69 (m, 1H), 7.57–7.53 (m, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.45–7.41 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 188.6, 156.6, 155.9, 128.2, 127.6, 126.7, 126.0, 123.6, 123.0, 122.8, 121.2, 120.8, 112.2.

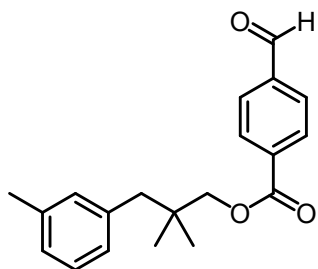


Quinoline-6-carbaldehyde (2z).¹⁰ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). Yellow solid (36.91 mg, 47% yield). mp: 80–82 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.23 (s, 1H), 9.08 (dd, $J = 4.3, 1.7$ Hz, 1H), 8.40–8.33 (m, 2H), 8.27–8.20 (m, 2H), 7.56 (dd, $J = 8.3, 4.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.5, 153.1, 150.8, 137.6, 134.4, 133.7, 130.8, 127.7, 126.8, 122.3.

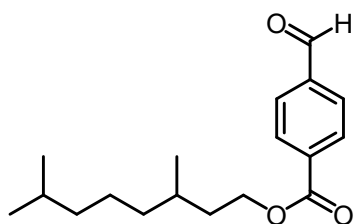


(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-formylbenzoate (2aa).¹¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). Yellow oil (67.72 mg, 47% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.12 (s, 1H), 8.22 (d, $J = 8.2$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 5.02–4.95 (m, 1H), 2.20–2.10 (m, 1H), 2.00–1.92 (m, 1H), 1.79–1.72 (m, 2H), 1.65–1.54 (m, 2H), 1.19–1.11 (m, 2H), 0.95 (dd, $J = 6.8, 4.4$ Hz, 7H), 0.81 (d,

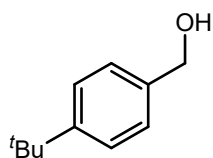
$J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.8, 165.1, 139.0, 135.8, 130.2, 129.5, 75.7, 47.2, 40.9, 34.2, 31.5, 26.5, 23.6, 22.1, 20.8, 16.5.



2,2-Dimethyl-3-(m-tolyl)propyl 4-formylbenzoate (2ab). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). Yellow oil (107.00 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.14 (s, 1H), 8.23 (d, $J = 8.2$ Hz, 2H), 8.00 (d, $J = 8.3$ Hz, 2H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 7.01–6.96 (m, 2H), 4.10 (s, 2H), 2.70 (s, 2H), 2.33 (s, 3H), 1.07 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.7, 165.5, 139.2, 137.9, 137.5, 135.4, 131.3, 130.2, 129.6, 127.9, 127.5, 127.0, 72.8, 45.4, 35.3, 24.6, 21.5. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3^+$, 311.1642; Found 311.1641.

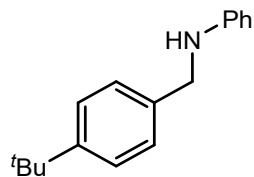


3,7-Dimethyloctyl 4-formylbenzoate (2ac). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). Yellow oil (59.49 mg, 41% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.12 (s, 1H), 8.22 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 4.44–4.38 (m, 2H), 1.87–1.81 (m, 1H), 1.67–1.52 (m, 4H), 1.40–1.35 (m, 2H), 1.22–1.13 (m, 3H), 0.99–0.98 (m, 3H), 0.88 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 191.7, 165.7, 139.1, 135.5, 130.2, 129.5, 64.3, 39.2, 37.1, 35.5, 30.0, 28.0, 24.6, 22.7, 22.6, 19.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_3^+$, 291.1955; Found 291.1953.

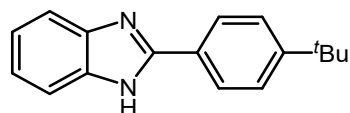


(4-(Tert-butyl)phenyl)methanol (3).¹² The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Colorless oil (64.83 mg, 79%

yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.43 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 4.66 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 150.7, 138.0, 127.0, 125.5, 65.1, 34.6, 31.4.



***N*-(4-(Tert-butyl)benzyl)aniline (4).**¹³ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (70:1, v/v). Yellow oil (110.12 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.46–7.41 (m, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.26–7.22 (m, 2H), 6.79–6.69 (m, 1H), 6.72–6.67 (m, 2H), 4.34 (s, 2H), 4.17–4.04 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 150.3, 148.2, 136.3, 129.3, 127.5, 125.6, 117.6, 112.9, 48.1, 34.6, 31.4.



2-(4-(Tert-butyl)phenyl)-1H-benzo[d]imidazole (5).¹⁴ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). White solid (107.56 mg, 86% yield). mp: 258–260 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm) 12.84 (s, 1H), 8.17–8.02 (m, 2H), 7.70–7.48 (m, 4H), 7.23–7.15 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) 153.0, 151.7, 144.3, 135.4, 127.9, 126.7, 126.2, 122.8, 122.0, 119.2, 111.7, 35.1, 31.5.

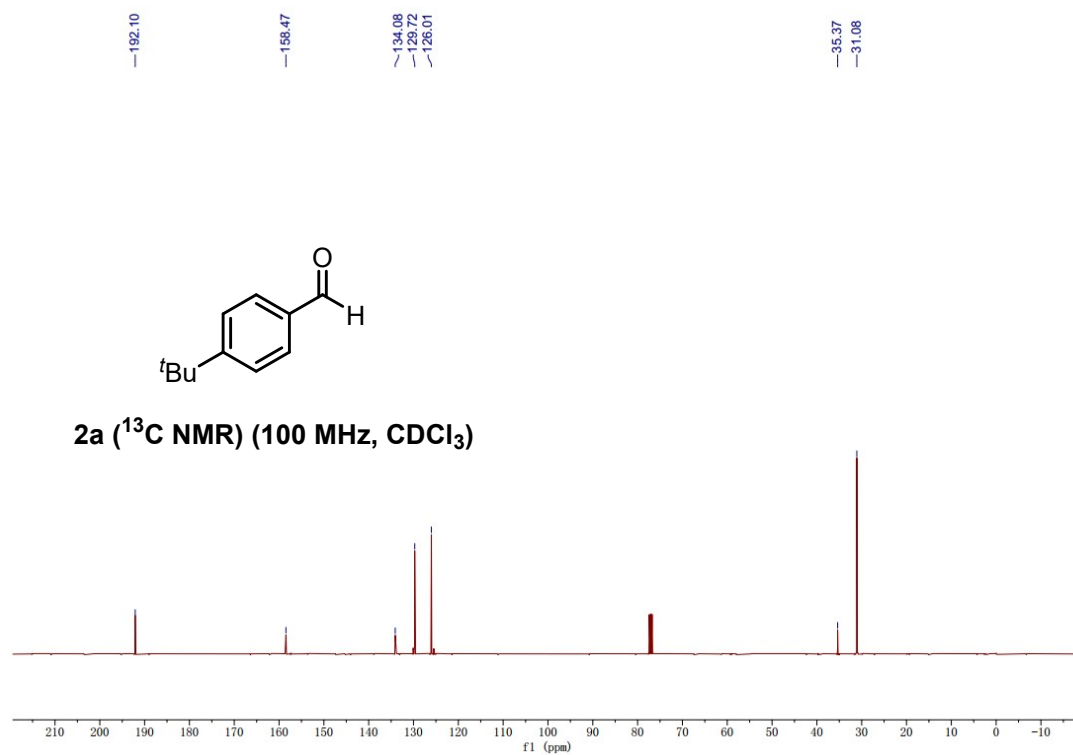
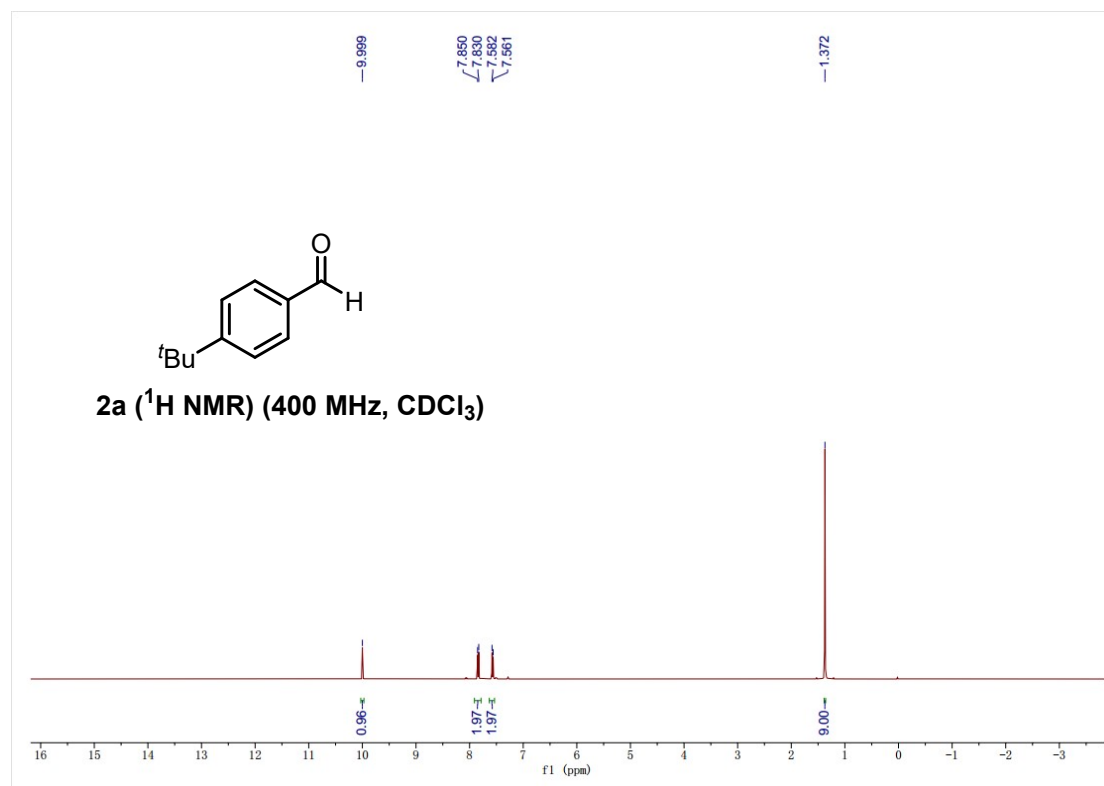
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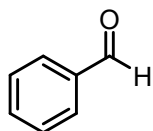
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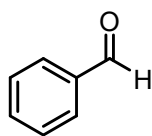
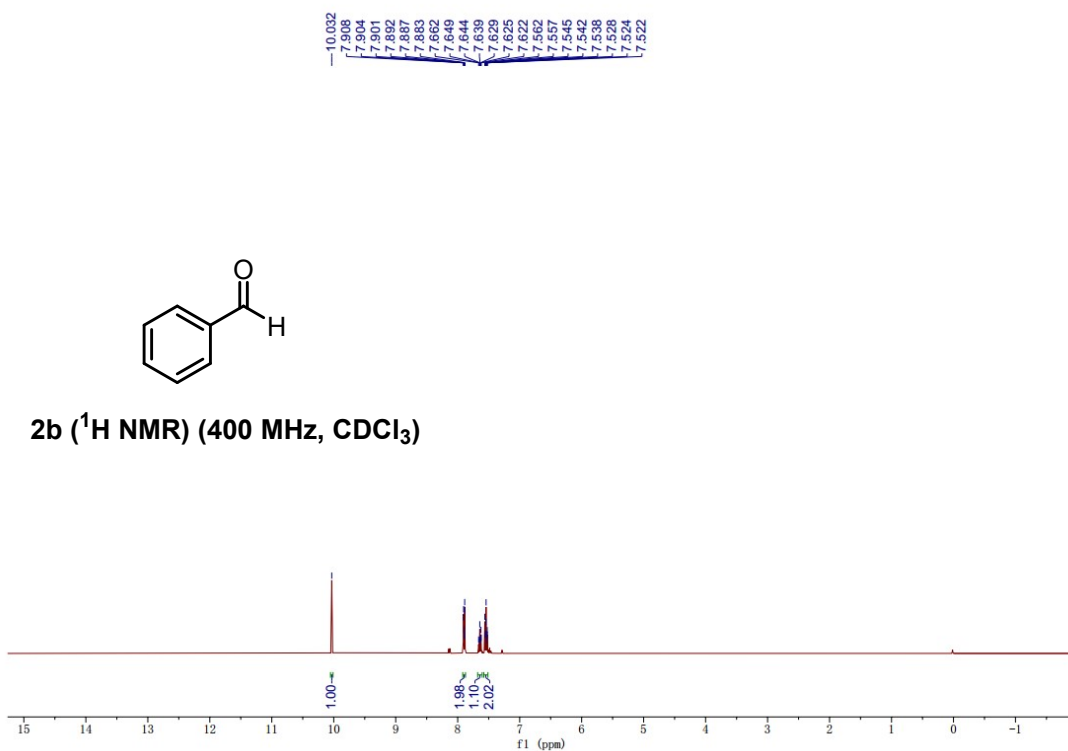
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6 Copies of ^1H and ^{13}C NMR spectra of products 2, 3, 4, 5

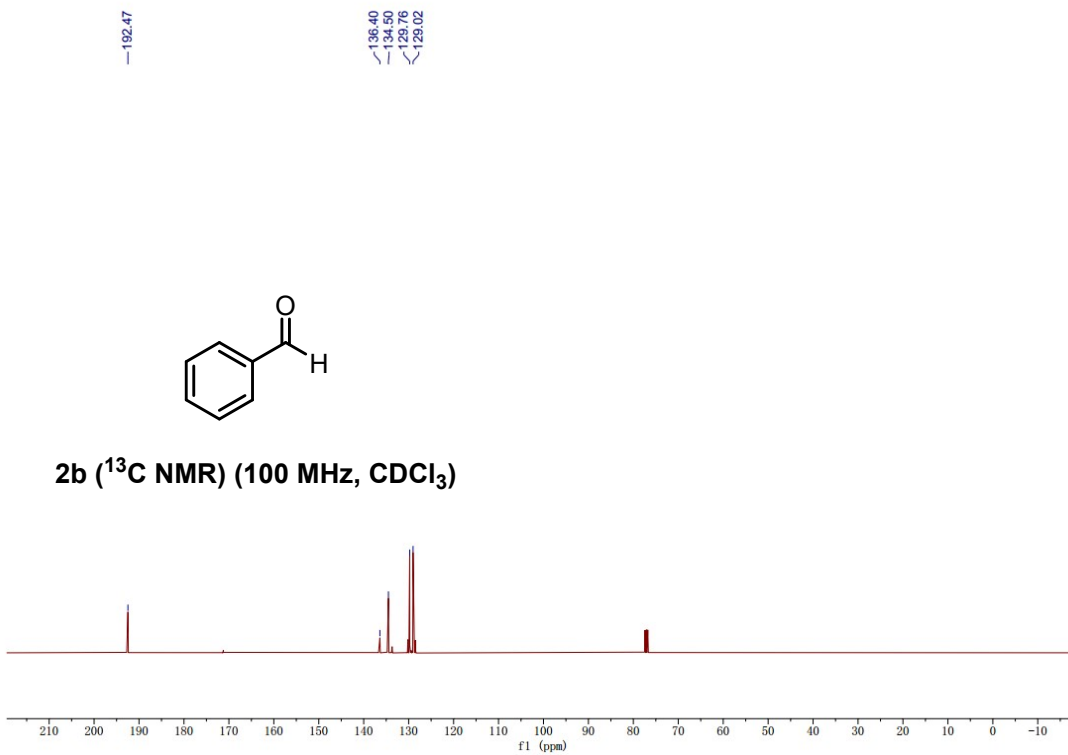


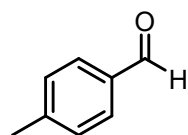


2b (^1H NMR) (400 MHz, CDCl_3)

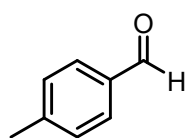
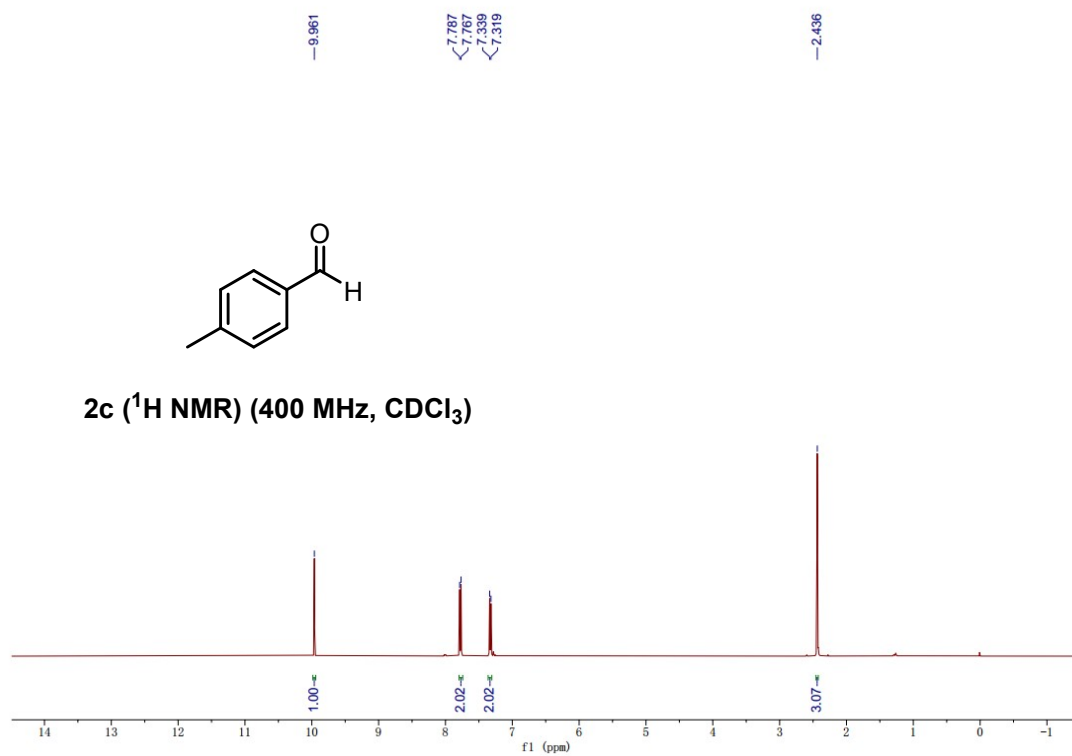


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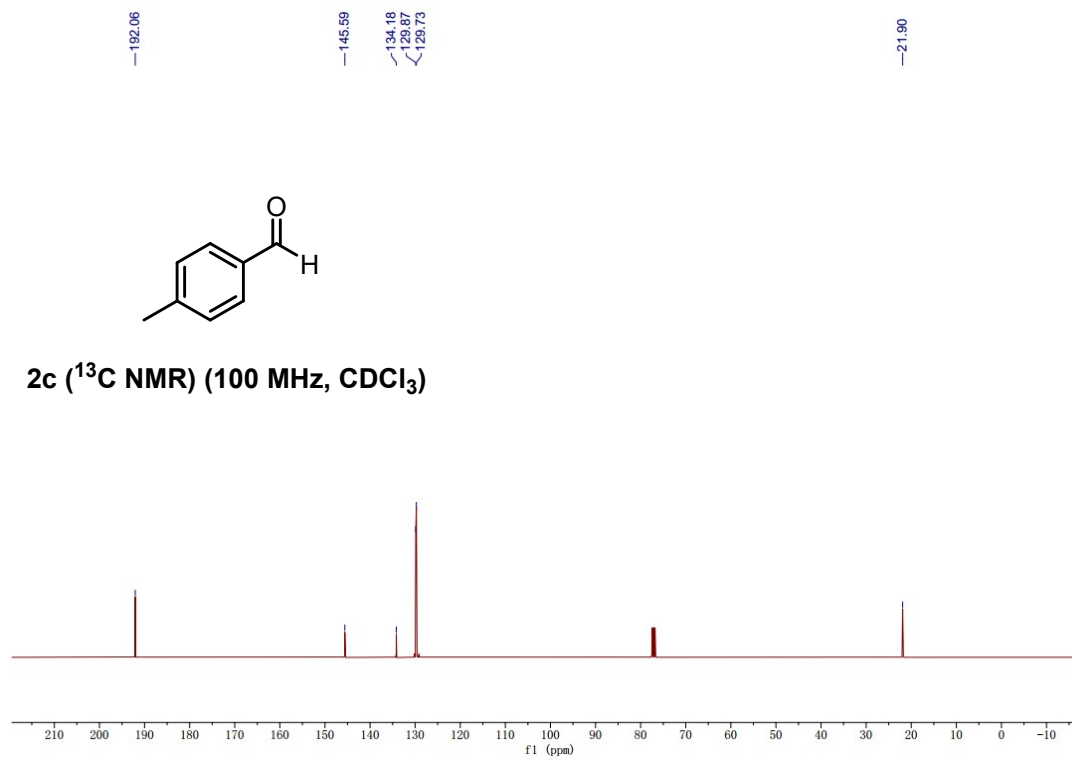


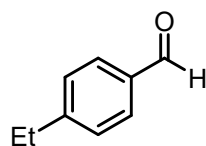


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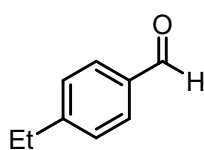
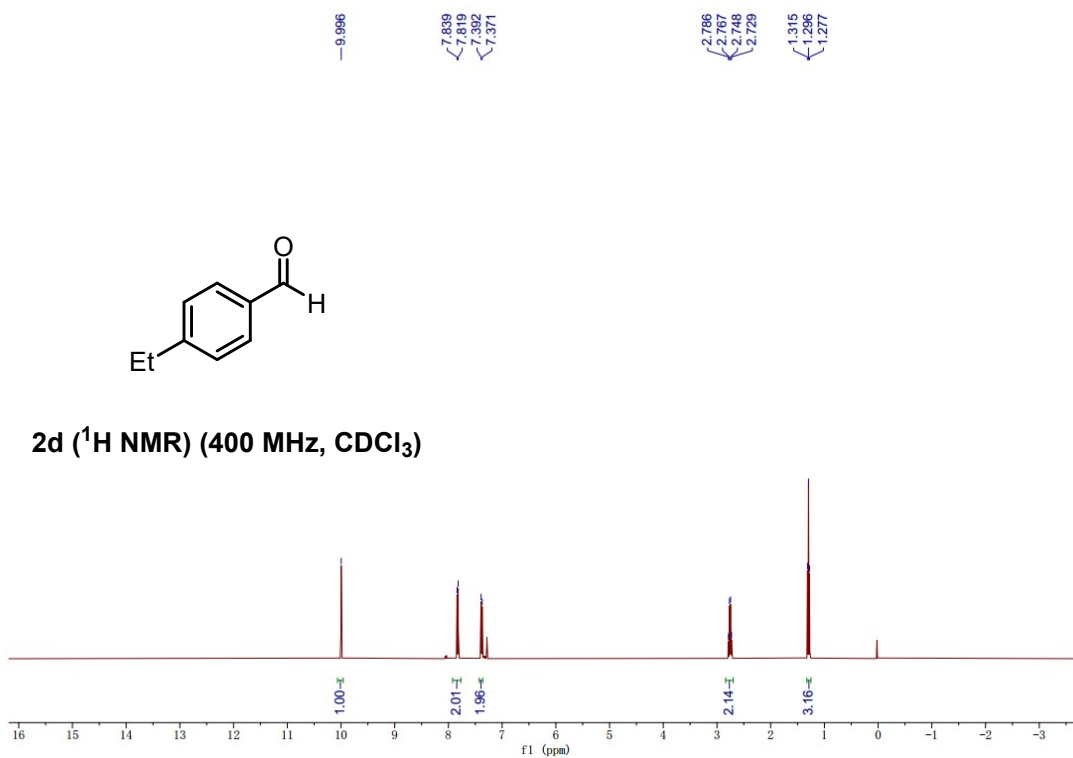


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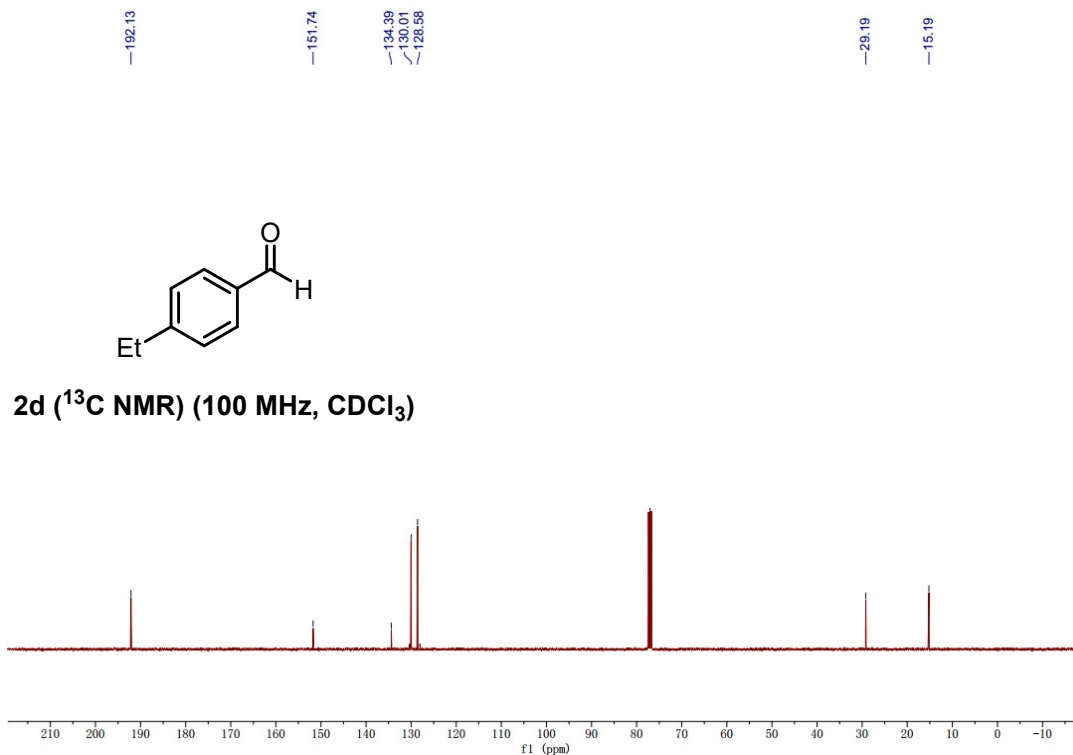


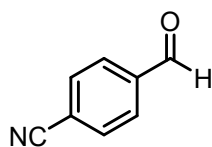


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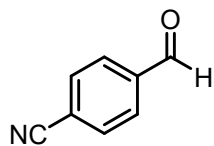
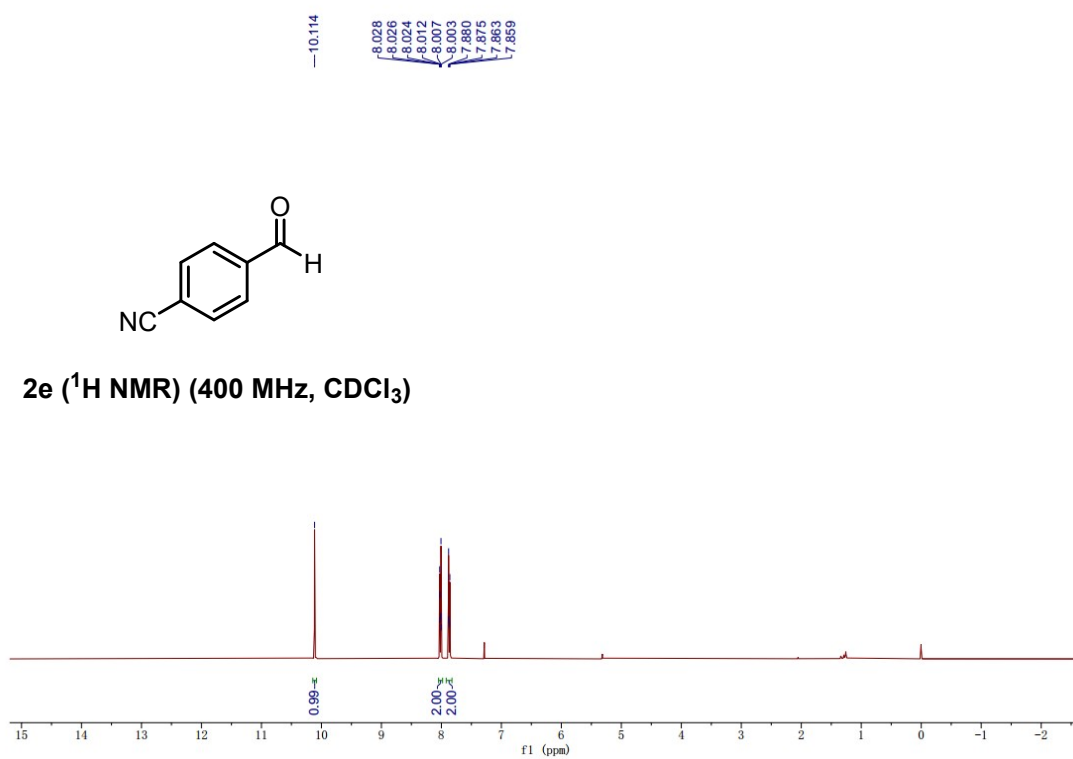


2d (¹³C NMR) (100 MHz, CDCl₃)

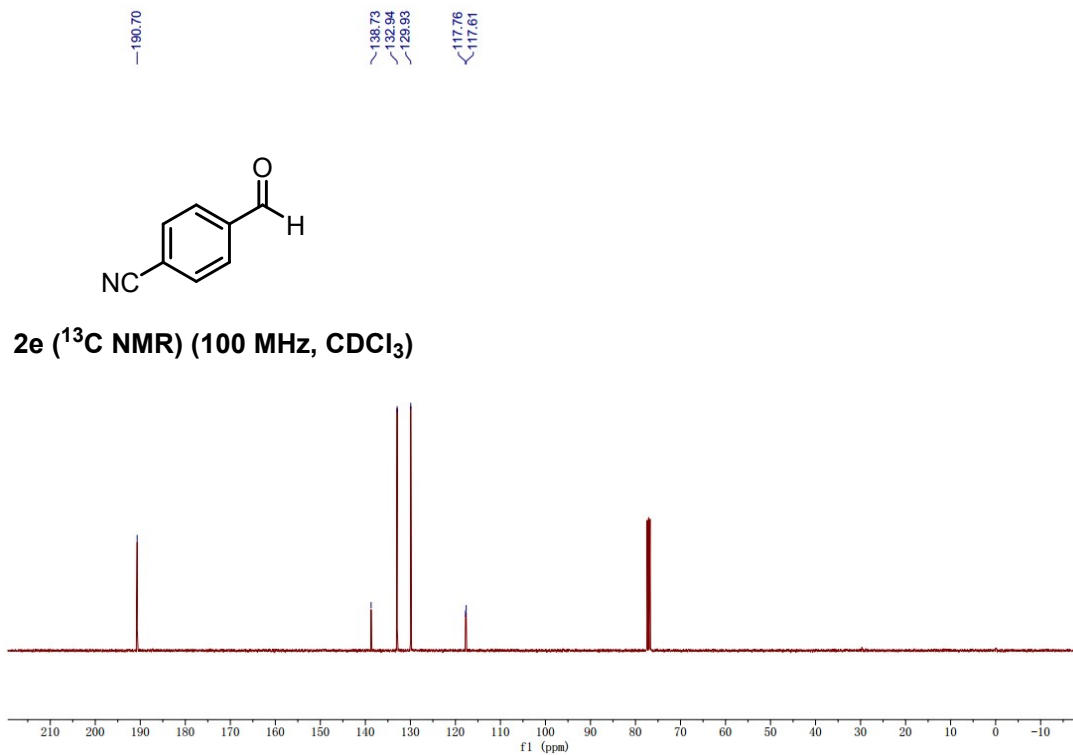


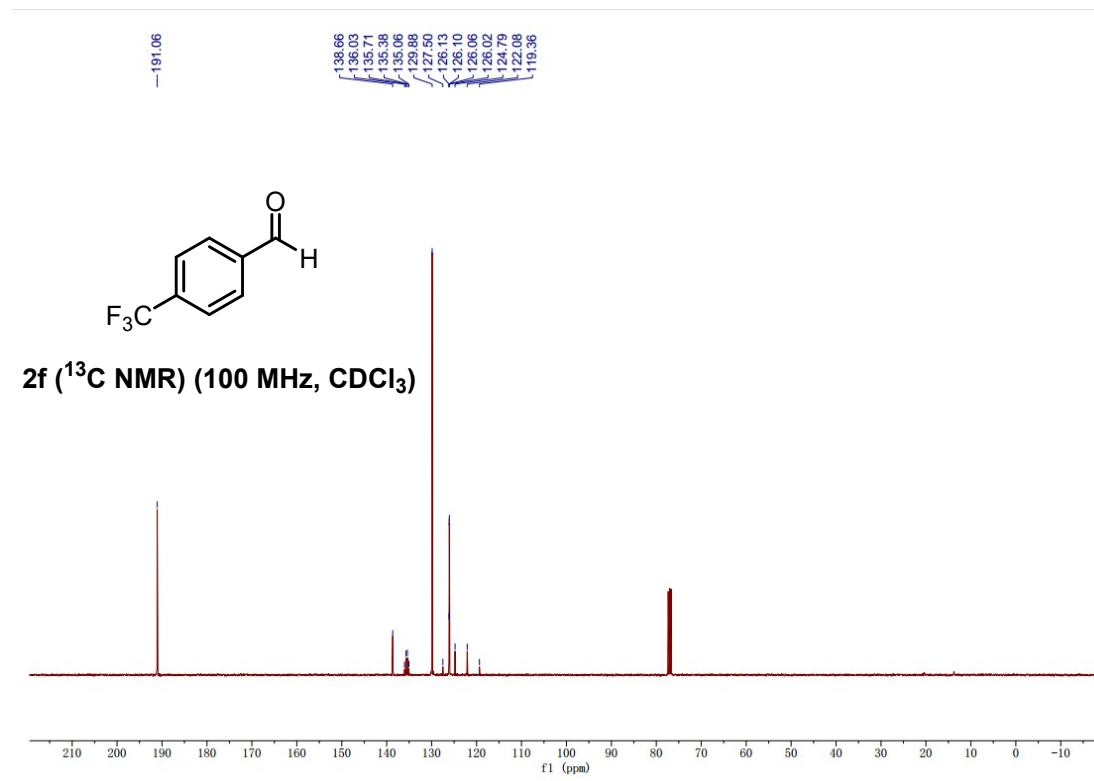
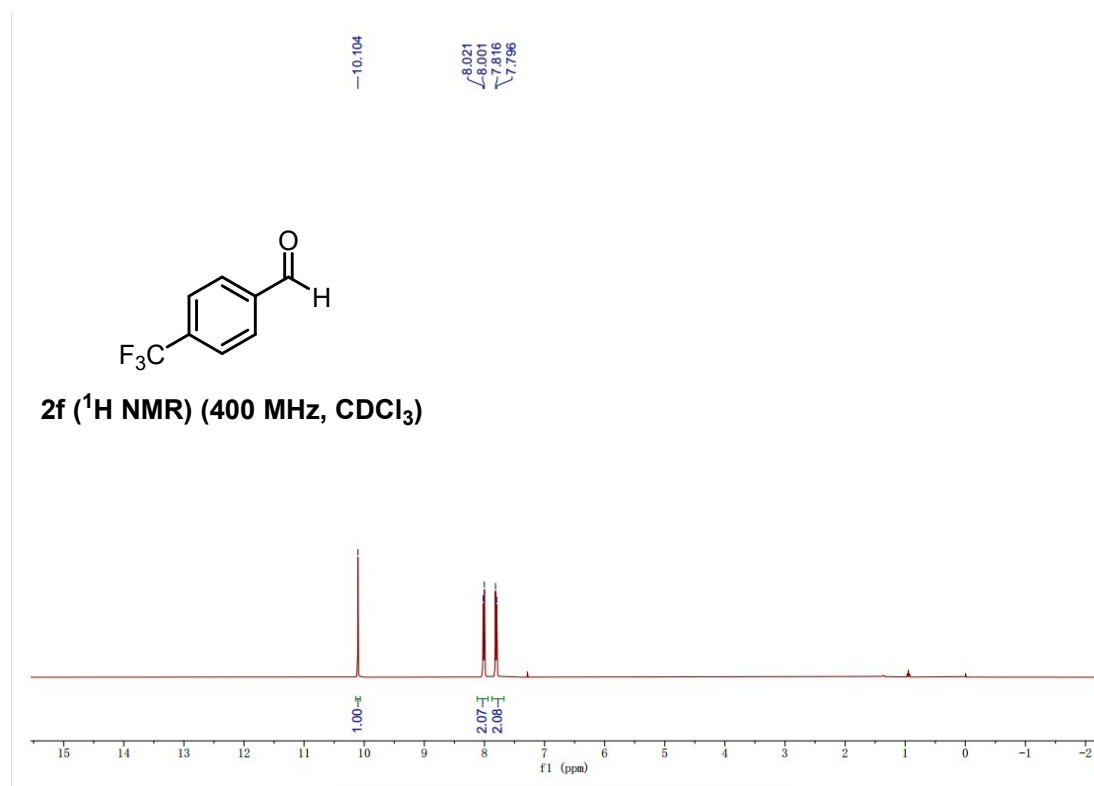


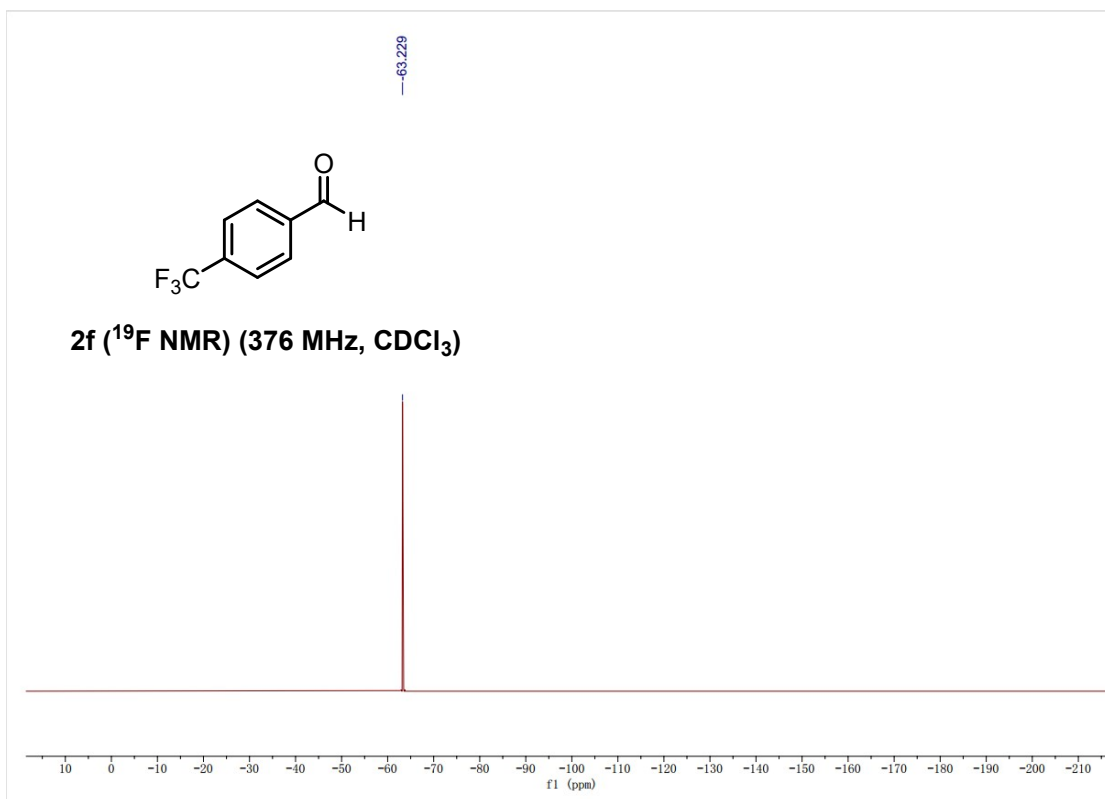
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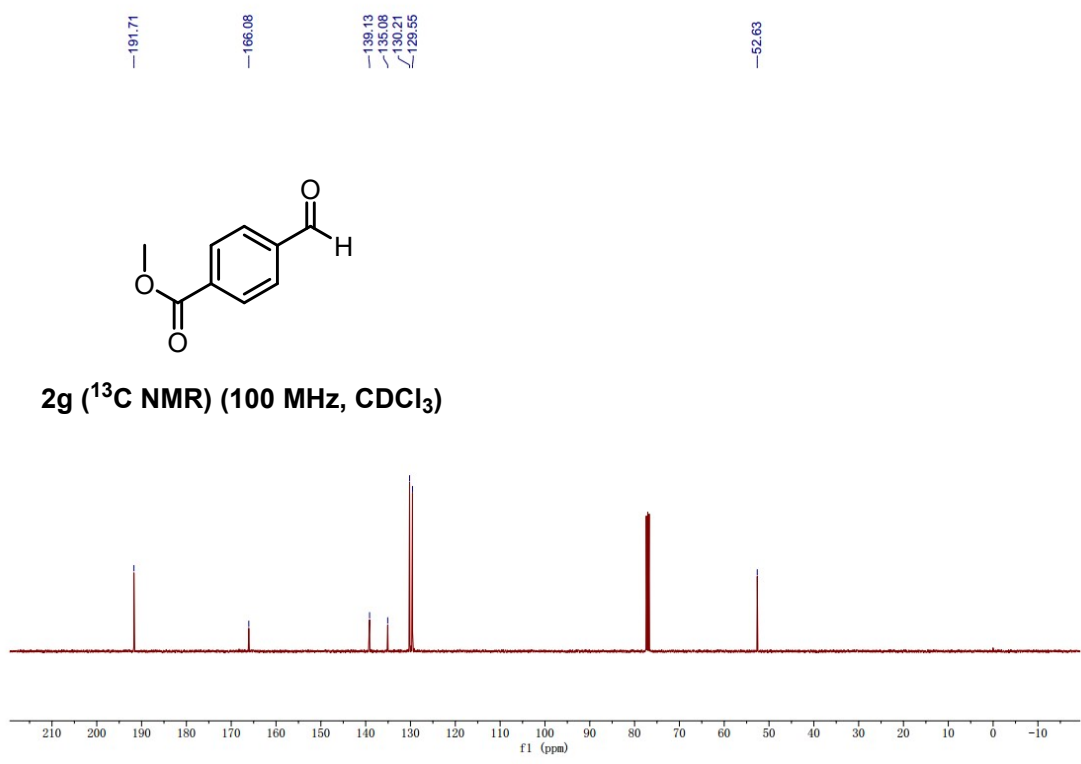
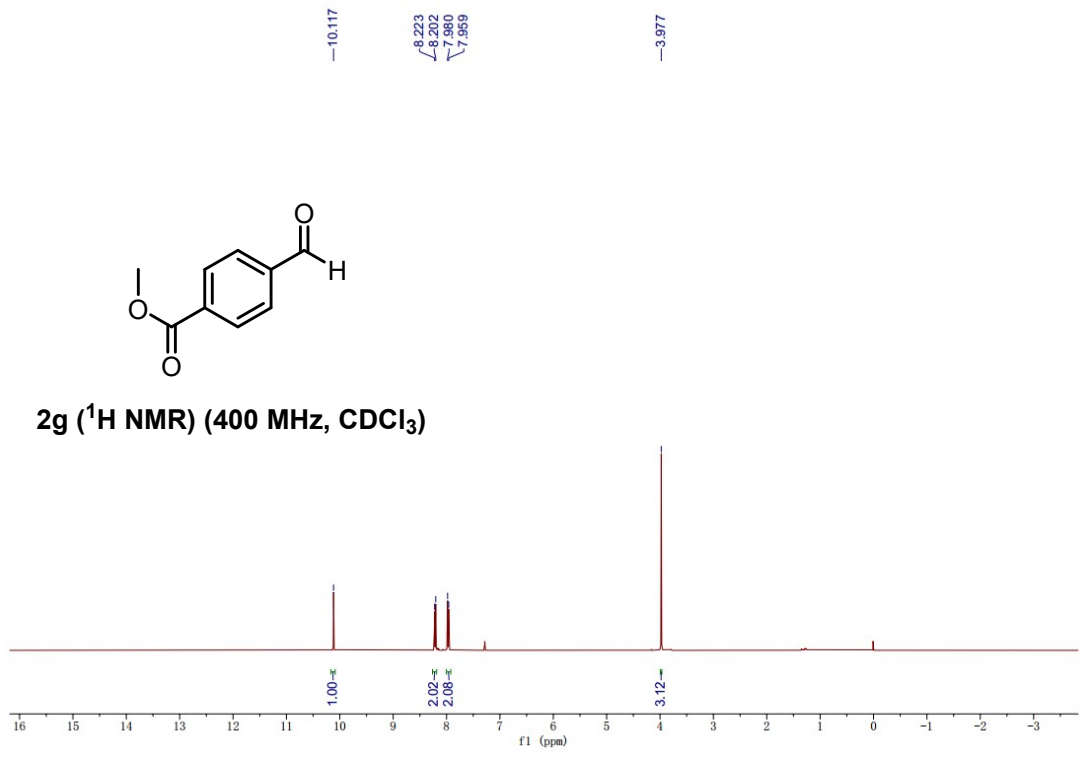


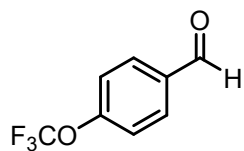
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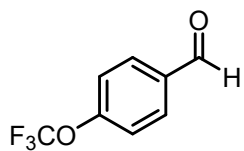
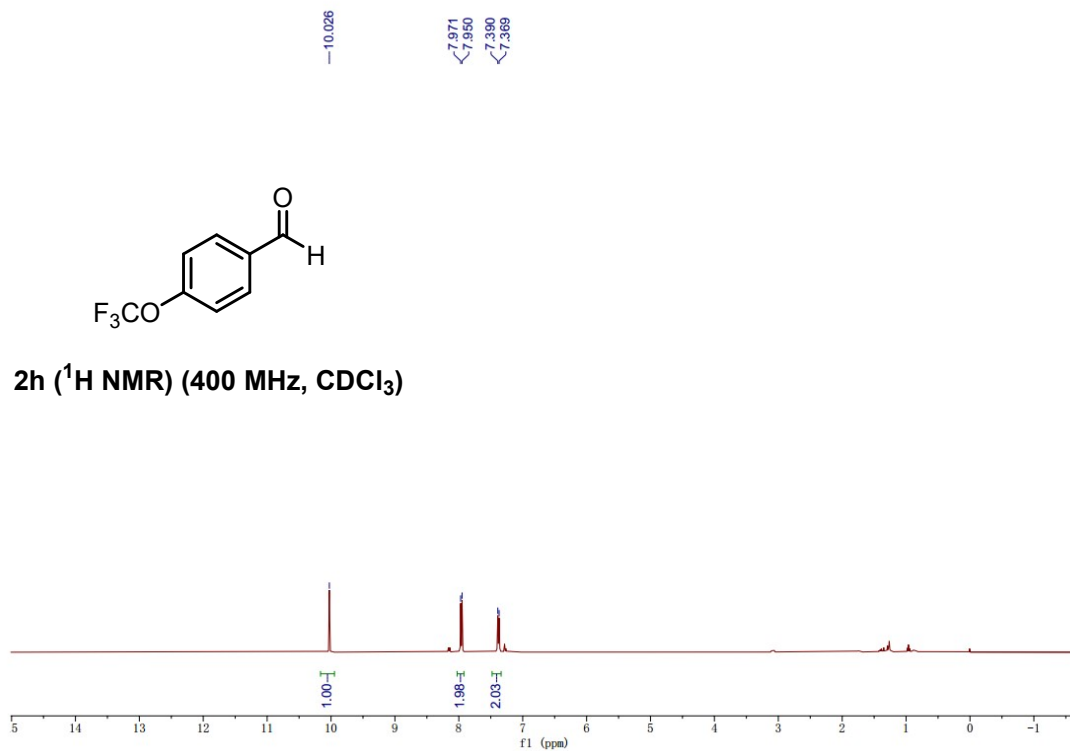




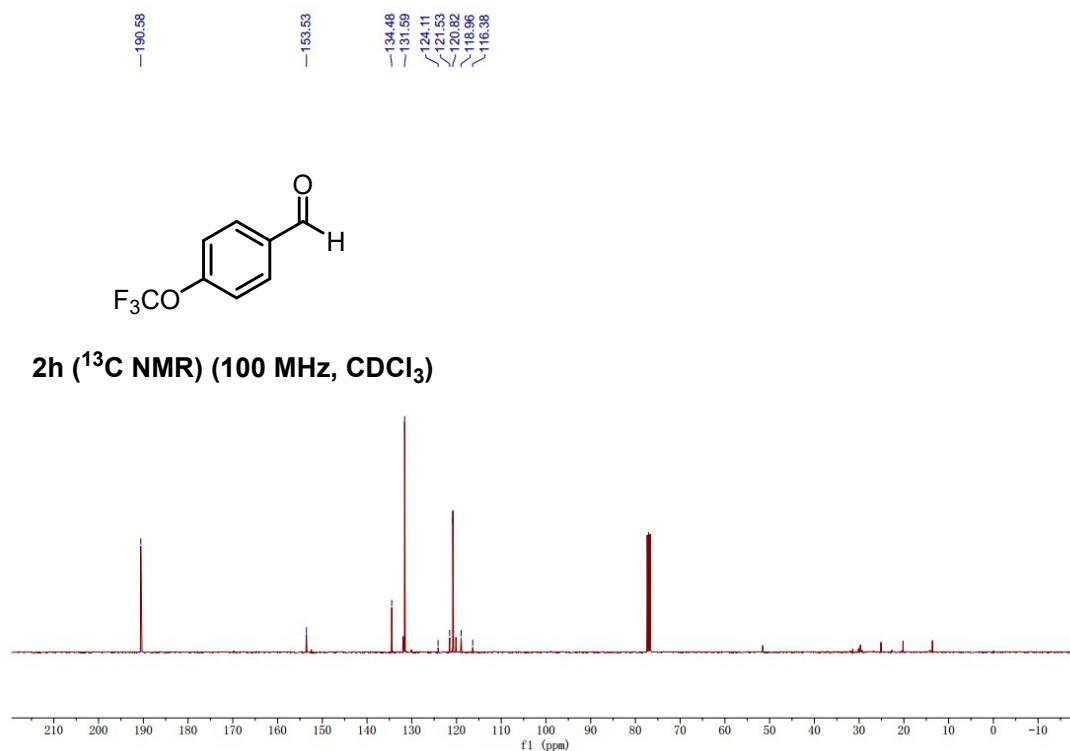


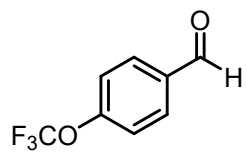


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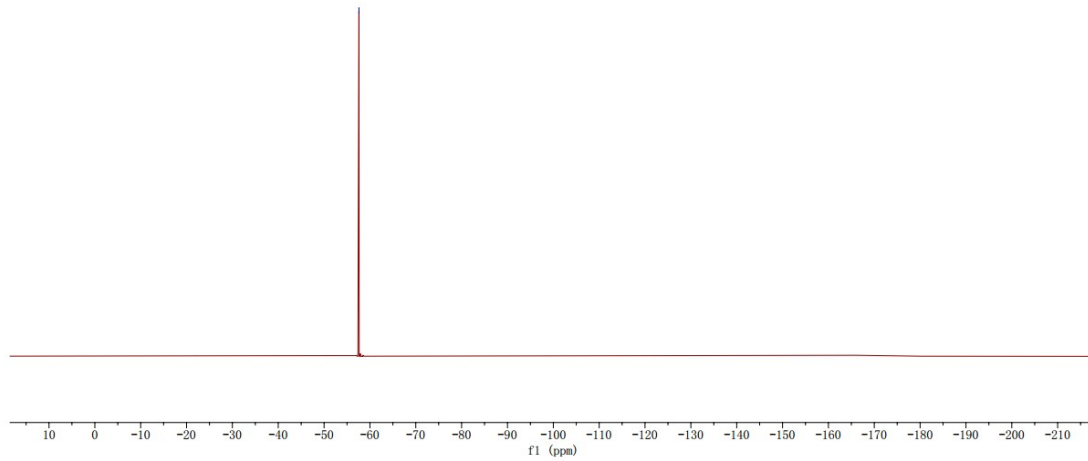
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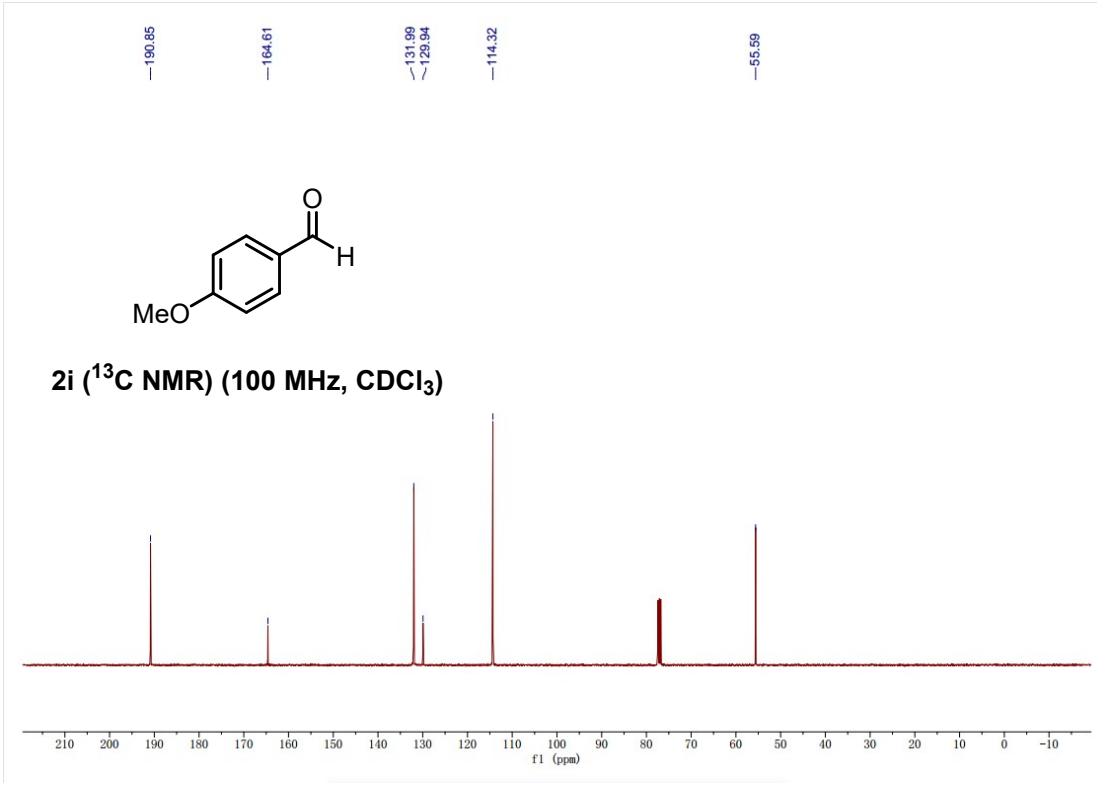
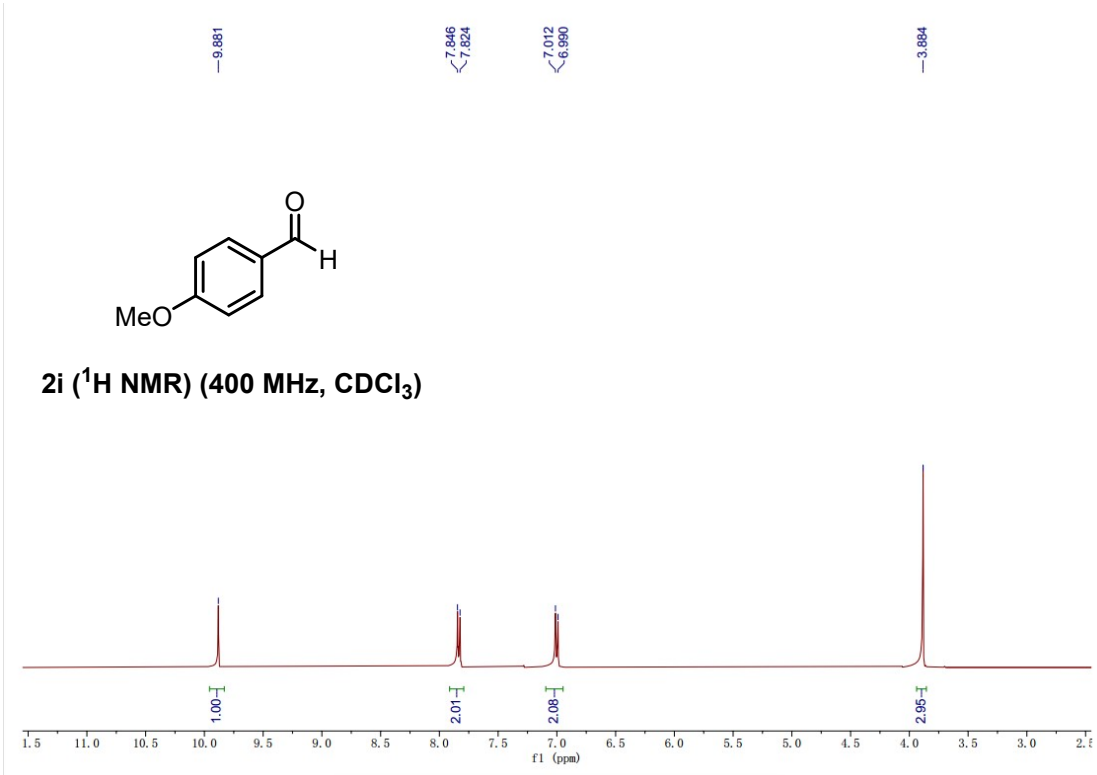


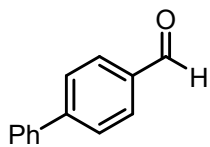


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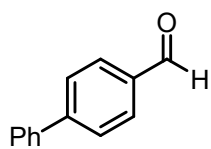
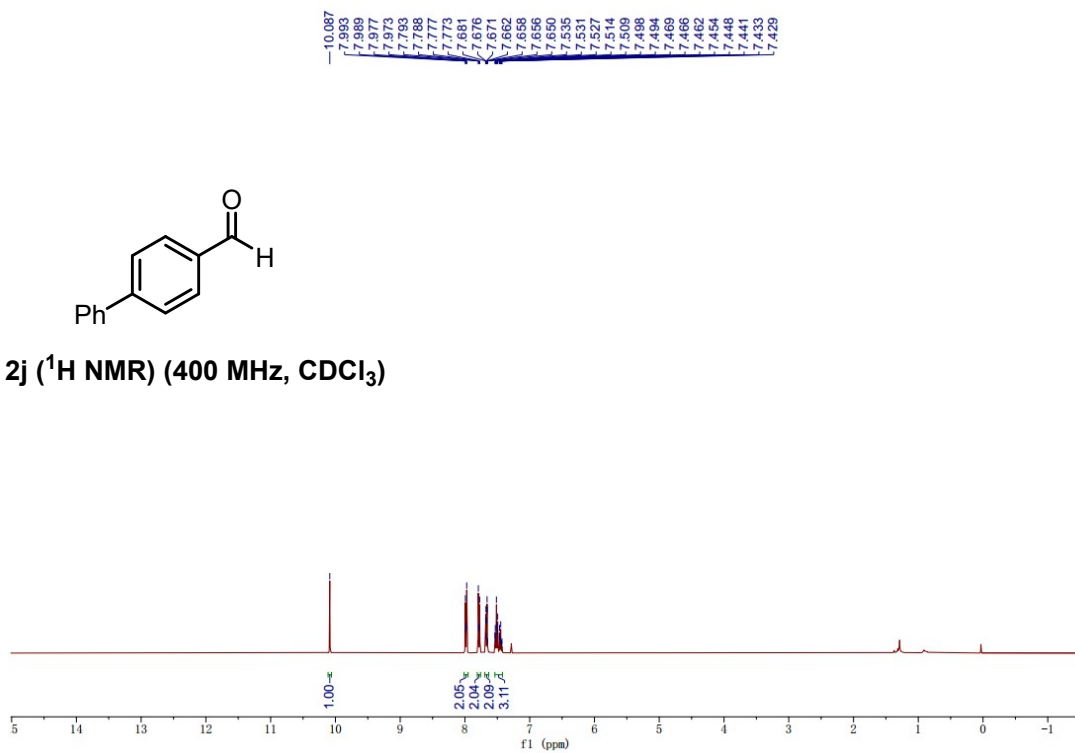
2h (^{19}F NMR) (376 MHz, CDCl_3)



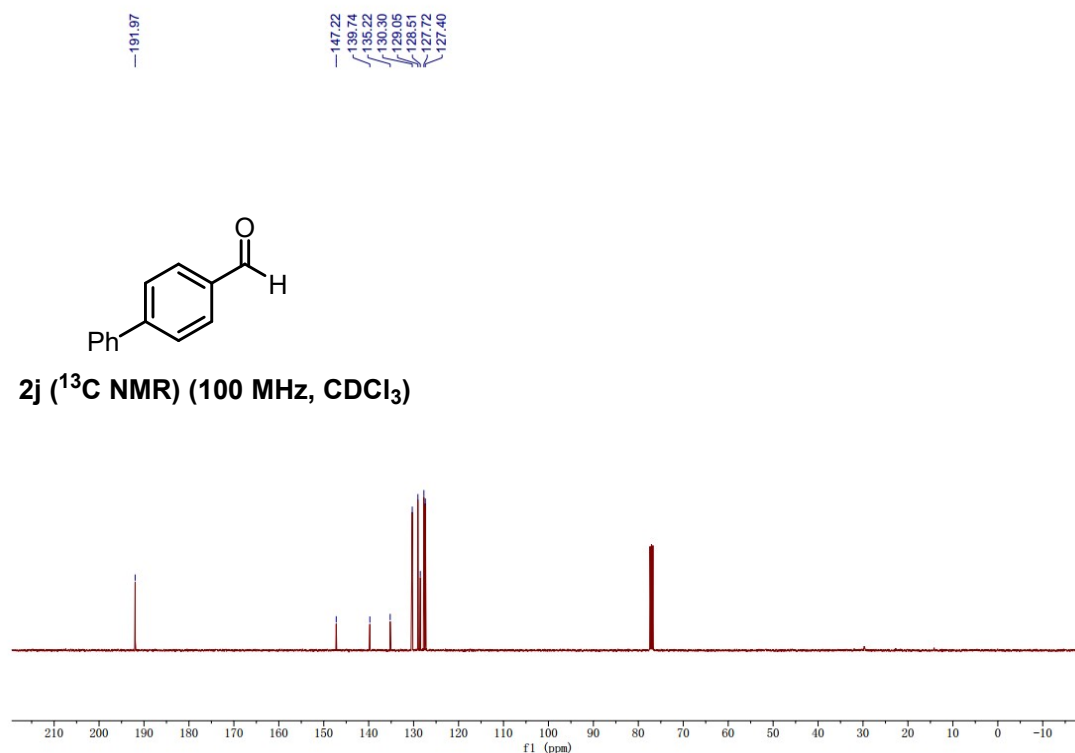


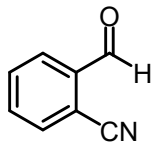


2j (¹H NMR) (400 MHz, CDCl₃)

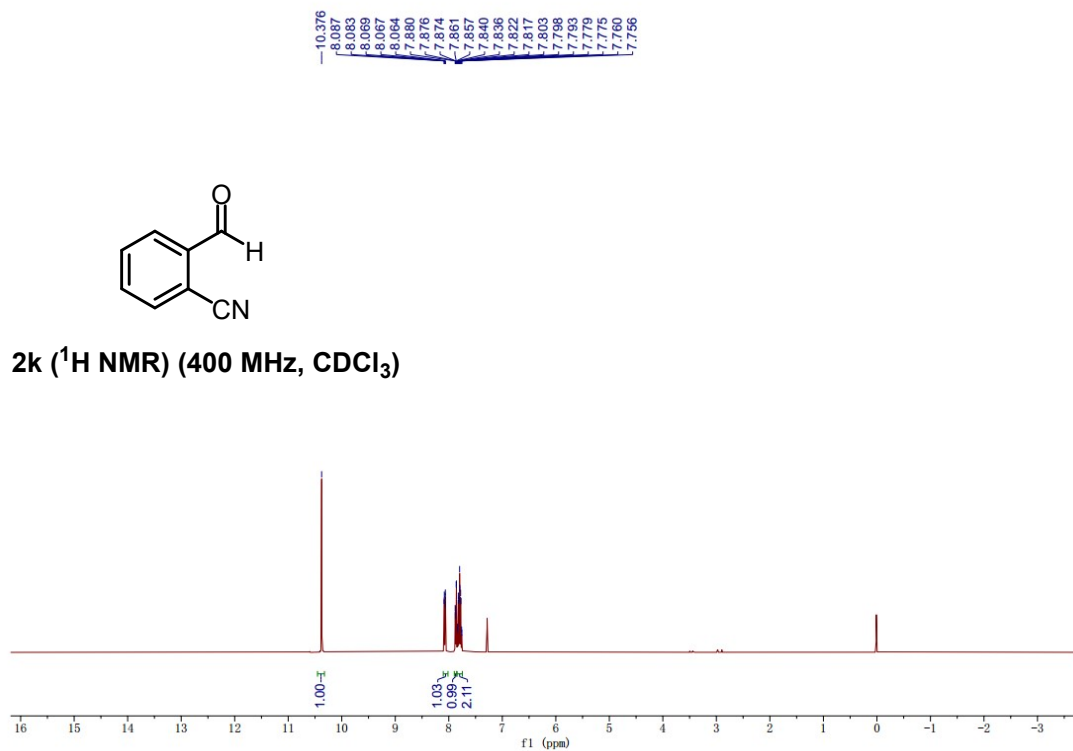


2j (¹³C NMR) (100 MHz, CDCl₃)

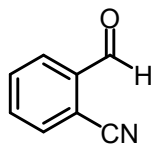




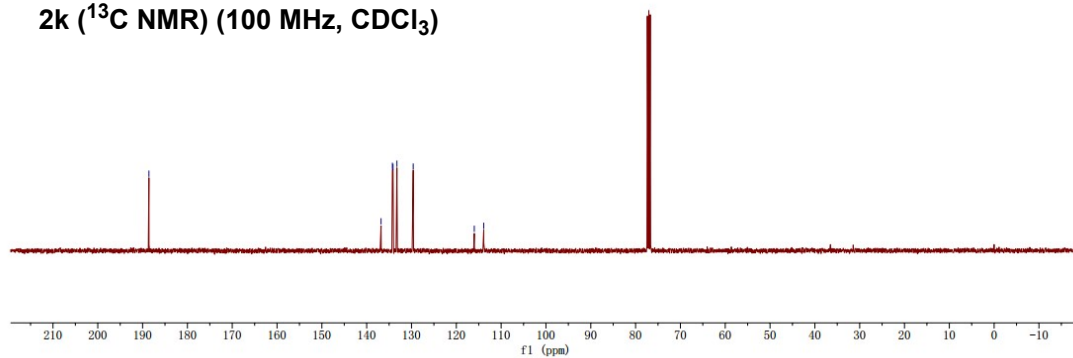
2k (¹H NMR) (400 MHz, CDCl₃)

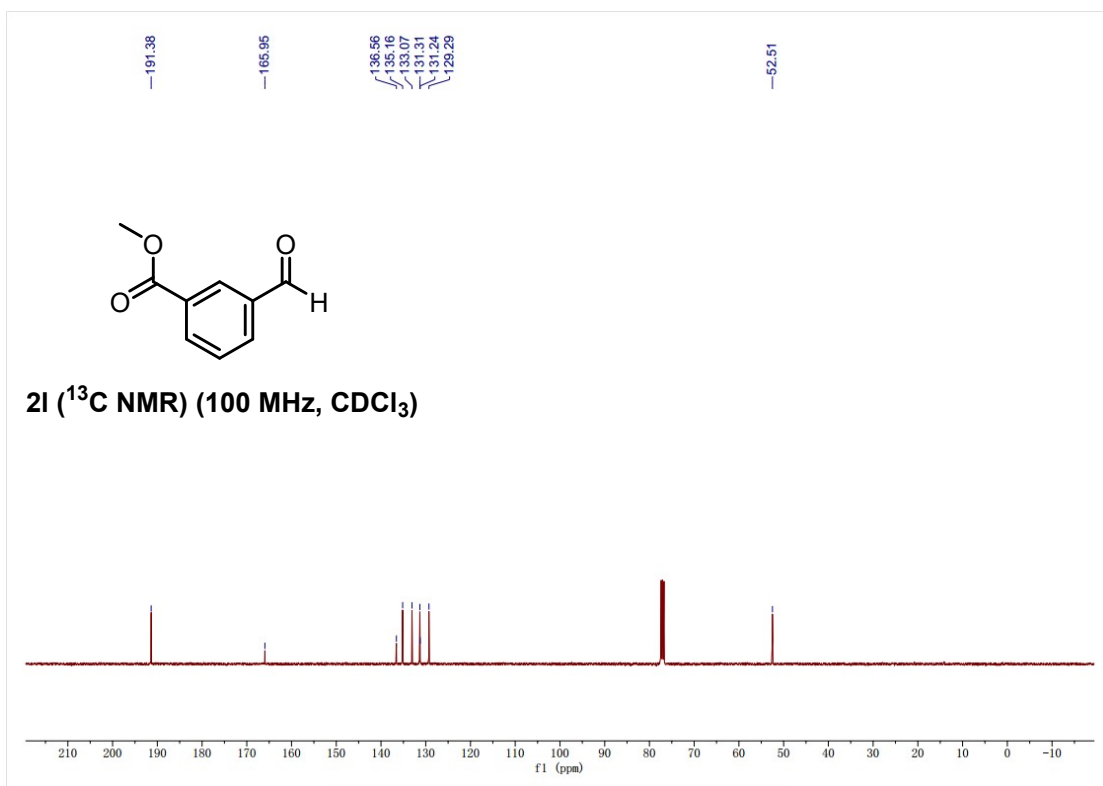
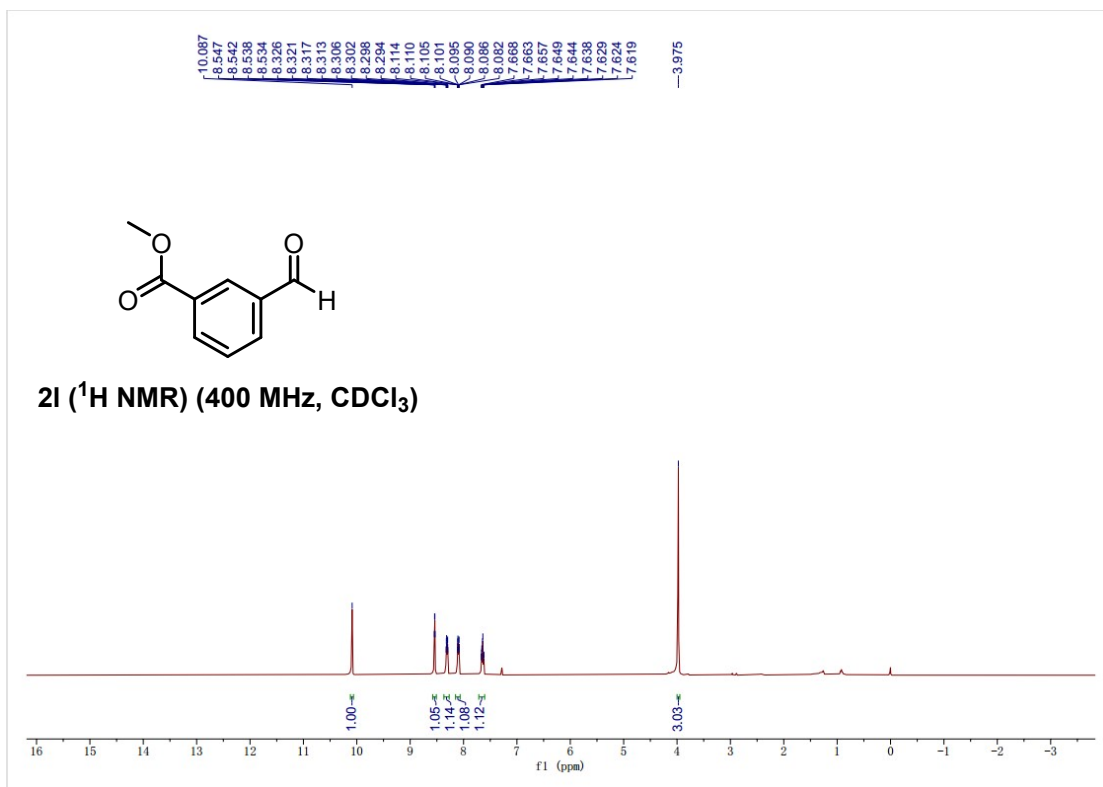


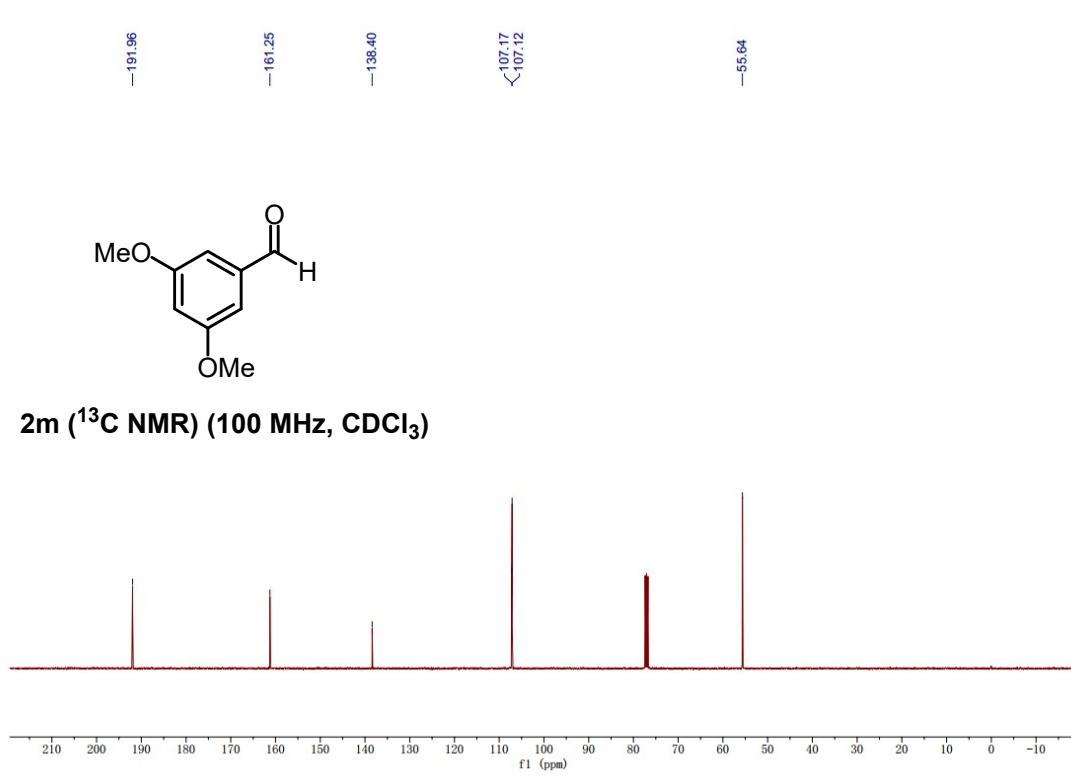
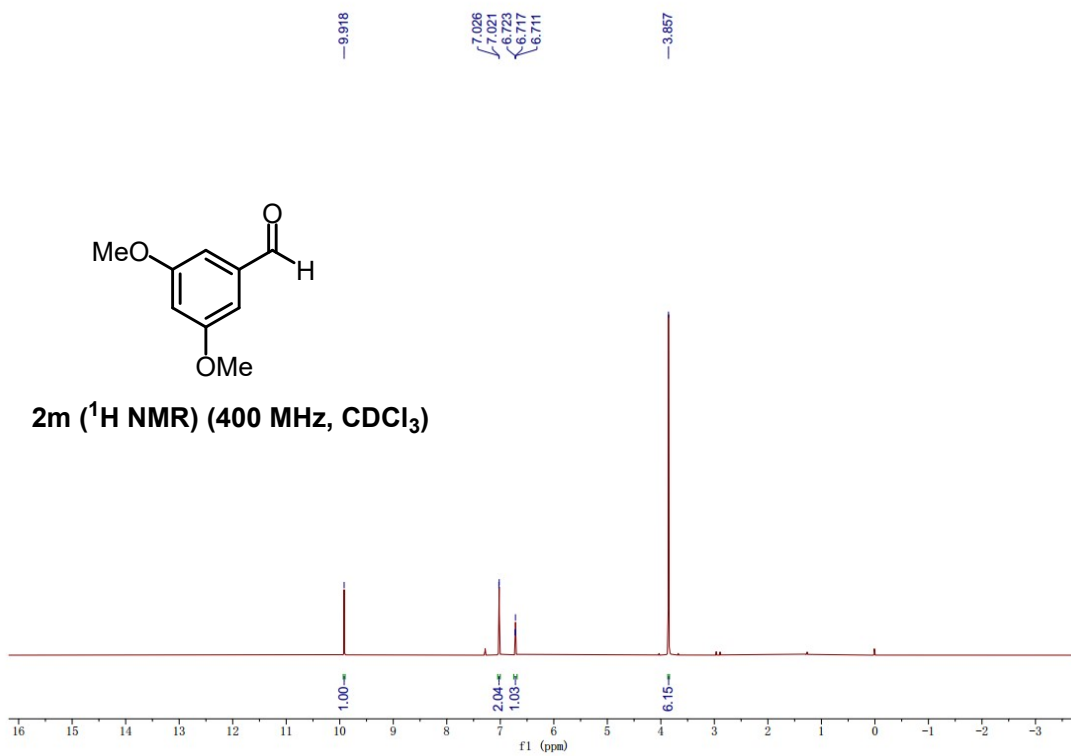
Chemical shift values (ppm): 186.59, 136.79, 134.26, 134.12, 133.25, 129.62, 115.99, 113.88.

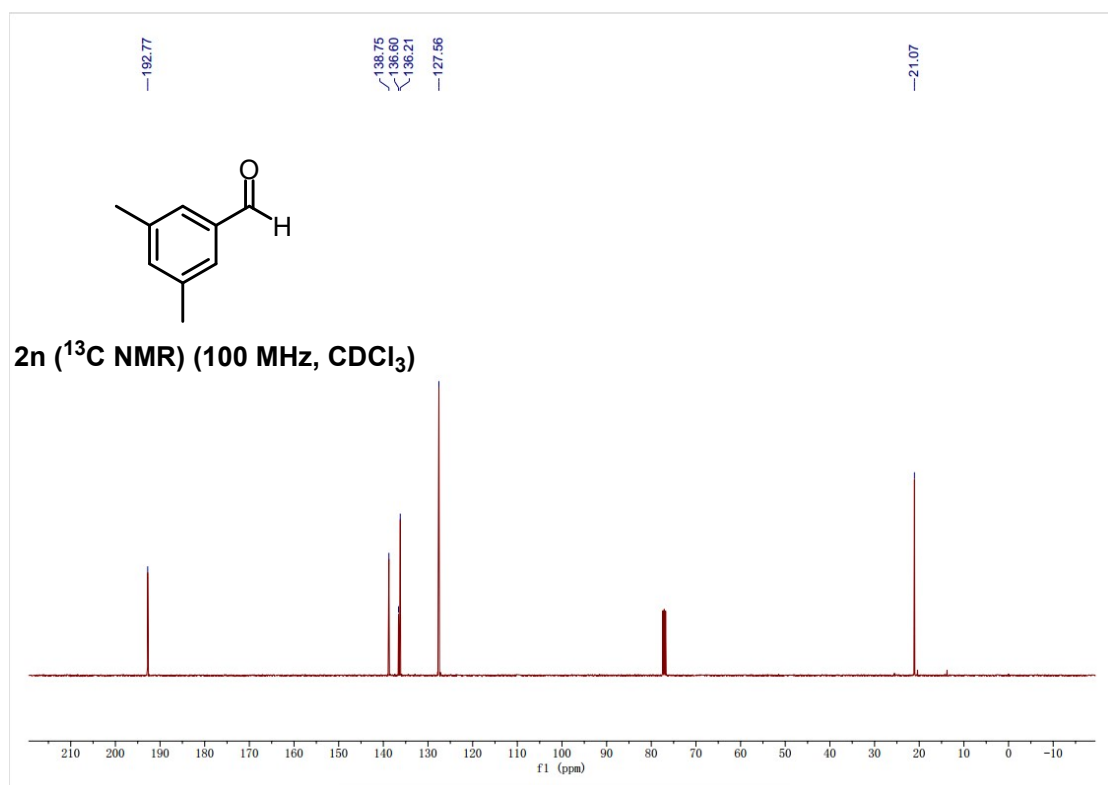
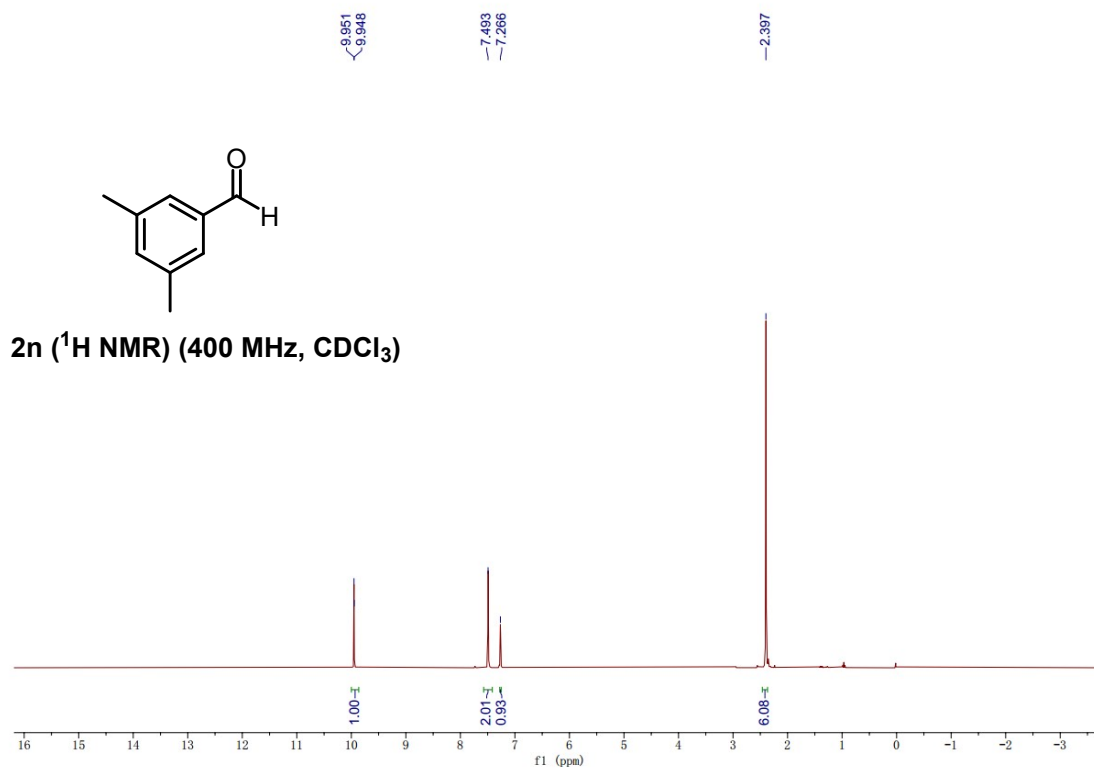


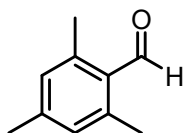
2k (¹³C NMR) (100 MHz, CDCl₃)



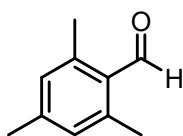
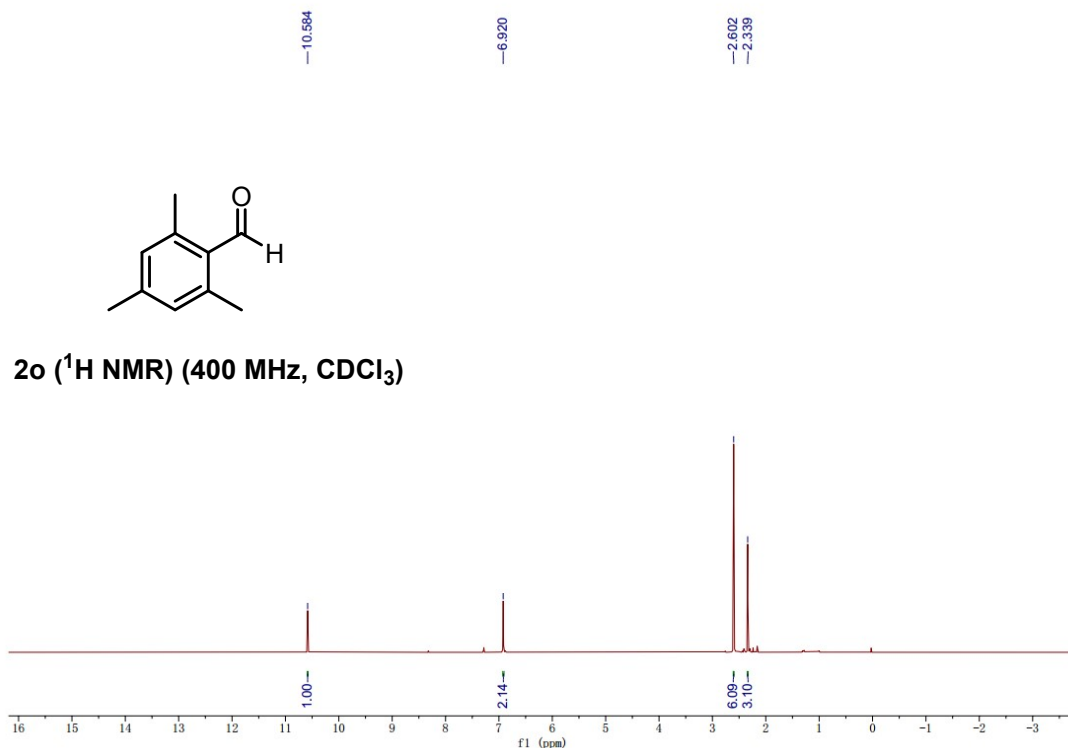




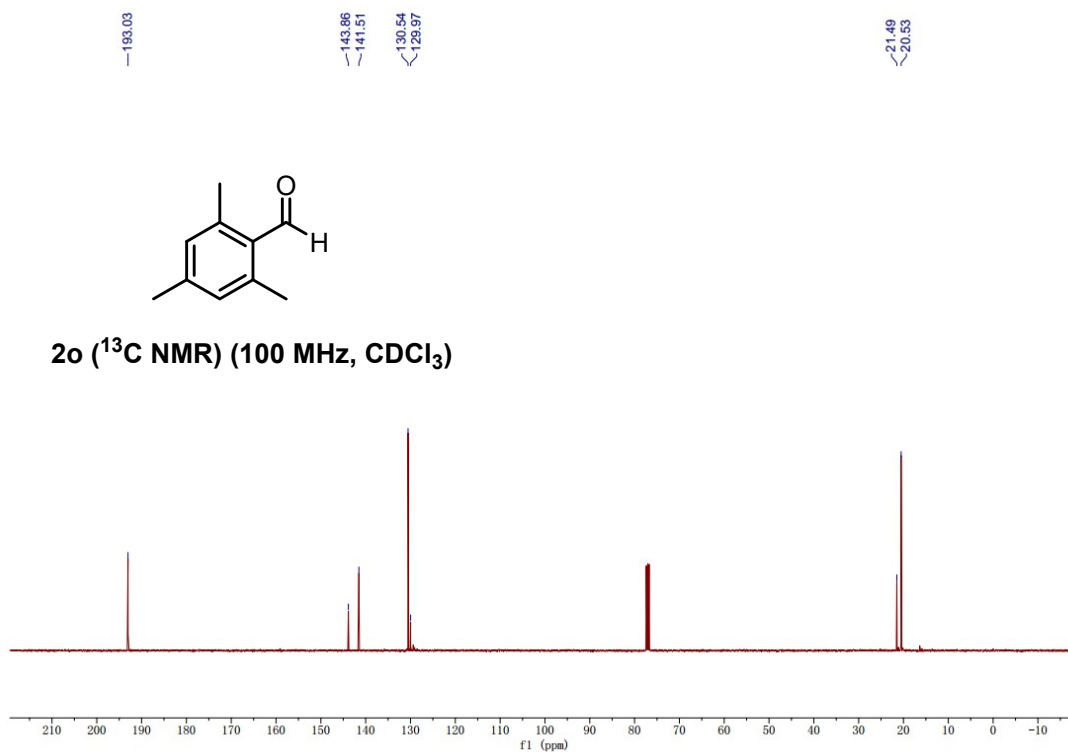


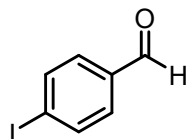


2o (¹H NMR) (400 MHz, CDCl₃)

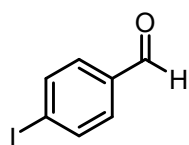
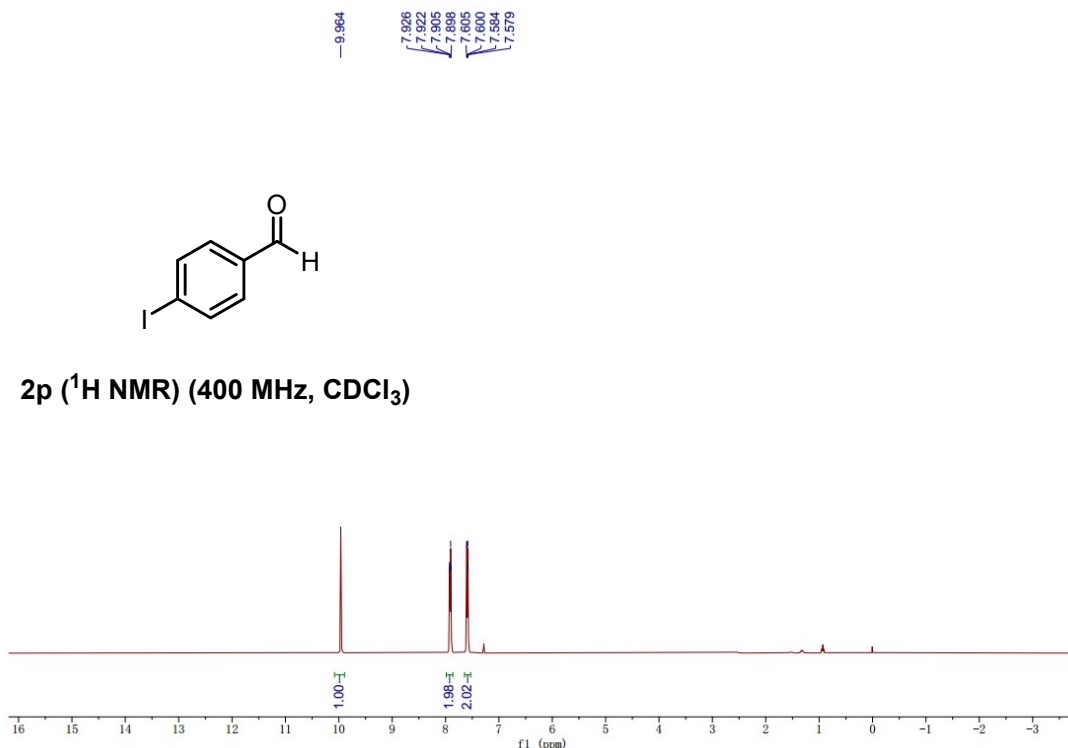


2o (¹³C NMR) (100 MHz, CDCl₃)

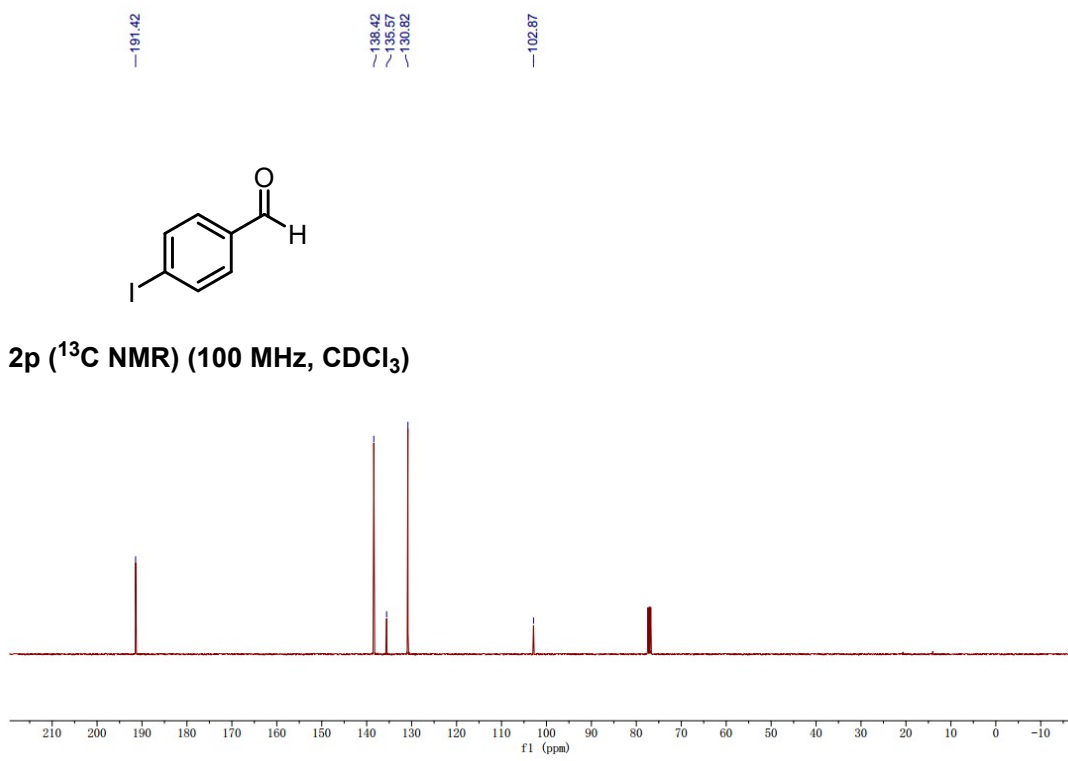




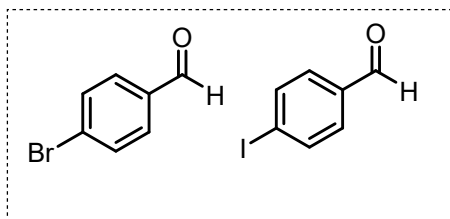
2p (^1H NMR) (400 MHz, CDCl_3)



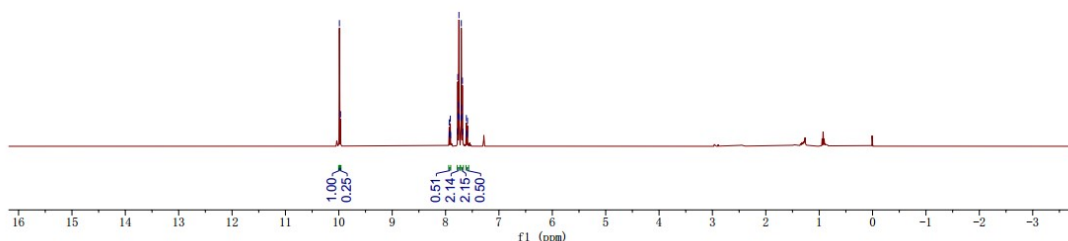
2p (^{13}C NMR) (100 MHz, CDCl_3)



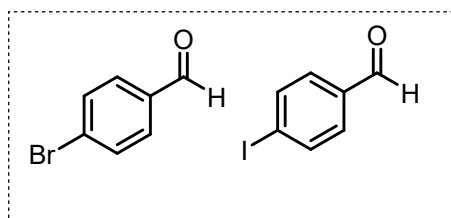
9.989
9.968
7.932
7.928
7.916
7.911
7.906
7.776
7.771
7.768
7.755
7.750
7.745
7.710
7.705
7.700
7.689
7.684
7.679
7.605
7.584
7.589



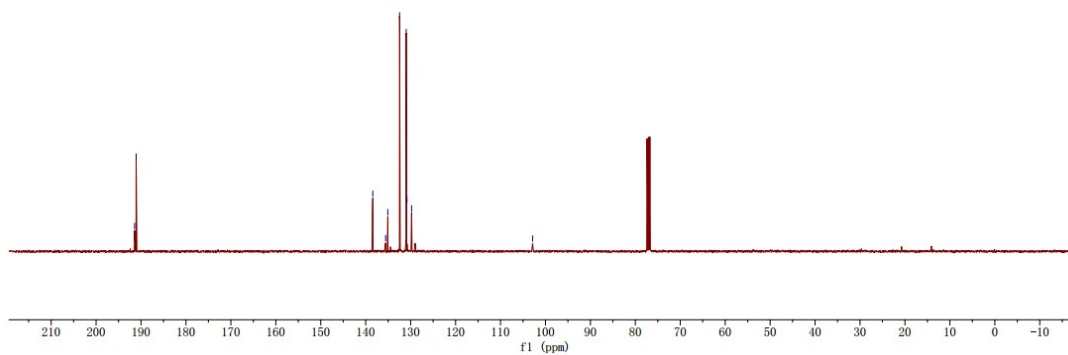
2q (^1H NMR) (400 MHz, CDCl_3)

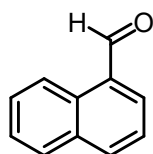


191.43
191.08
138.42
135.57
135.08
132.46
130.99
130.82
129.79
102.85

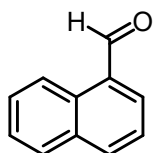
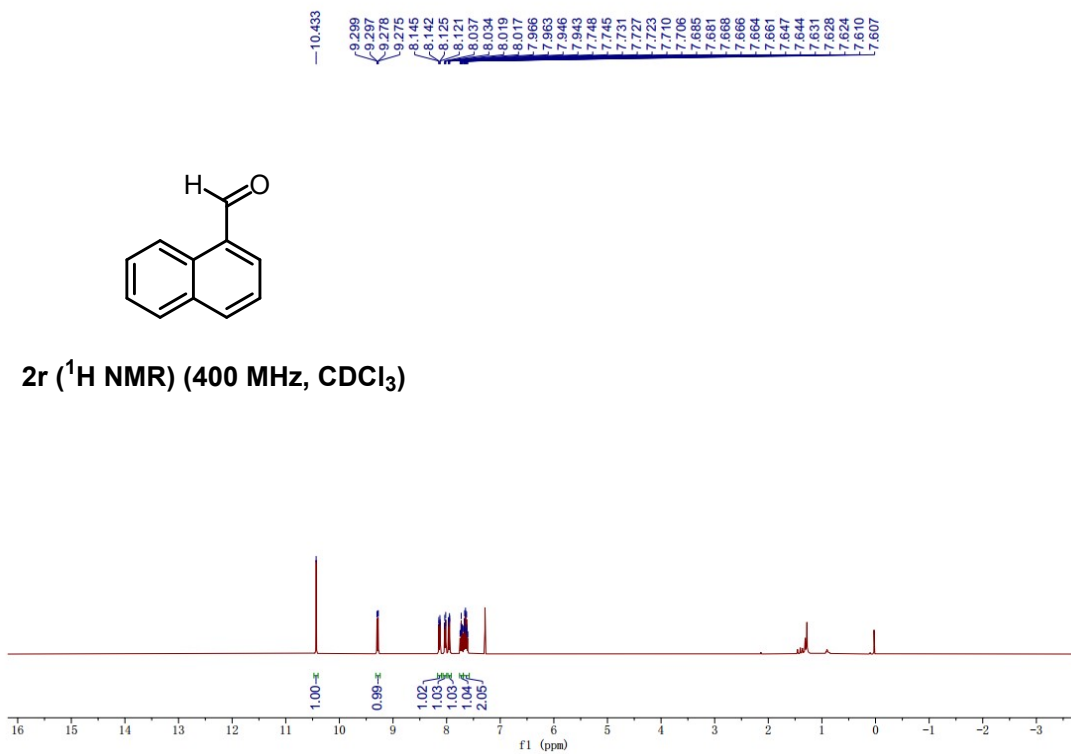


2q (^{13}C NMR) (100 MHz, CDCl_3)

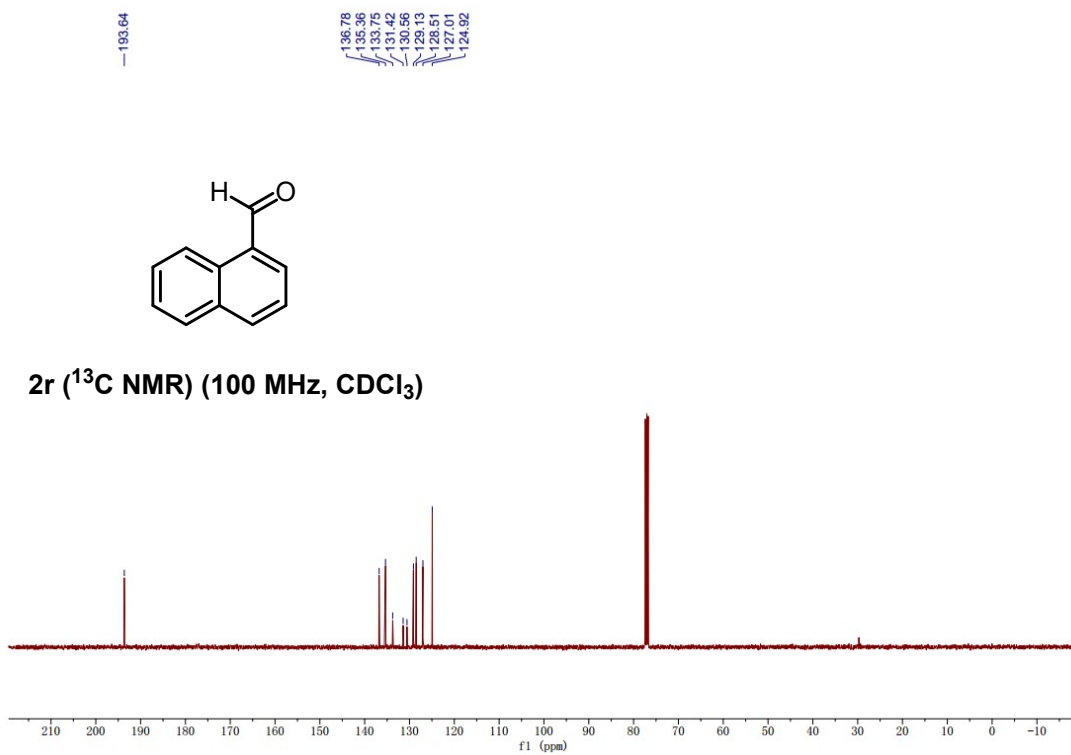


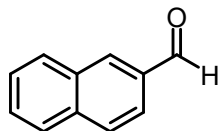


2r (¹H NMR) (400 MHz, CDCl₃)

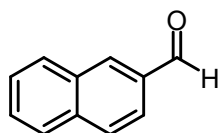
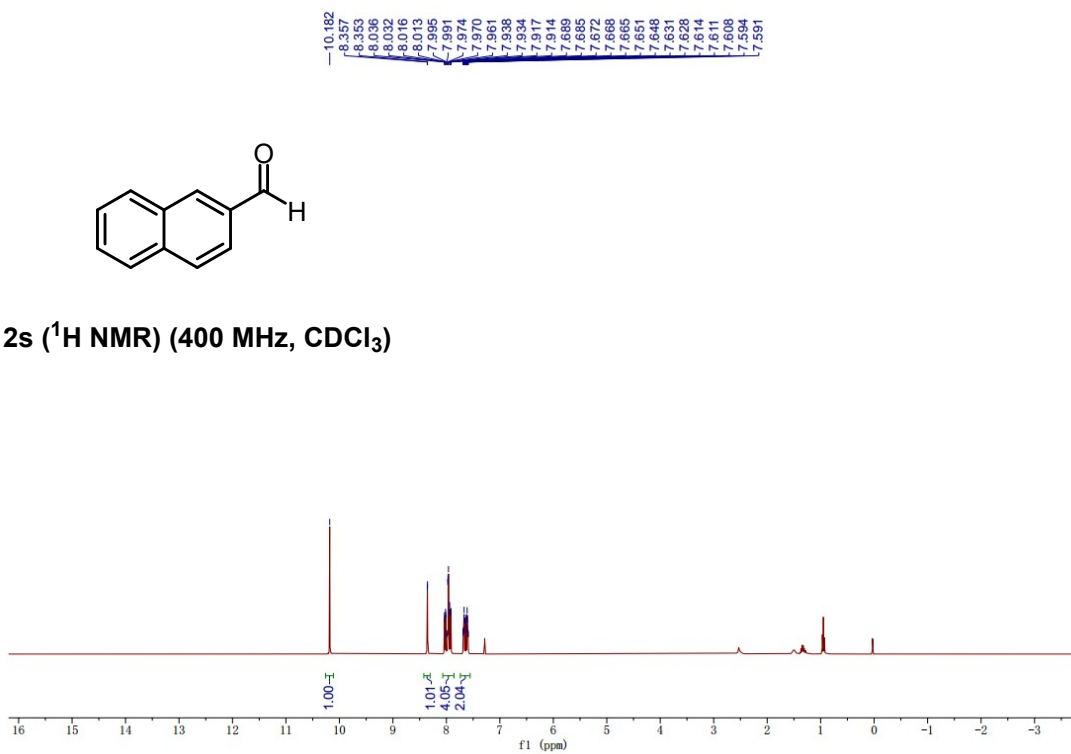


2r (¹³C NMR) (100 MHz, CDCl₃)

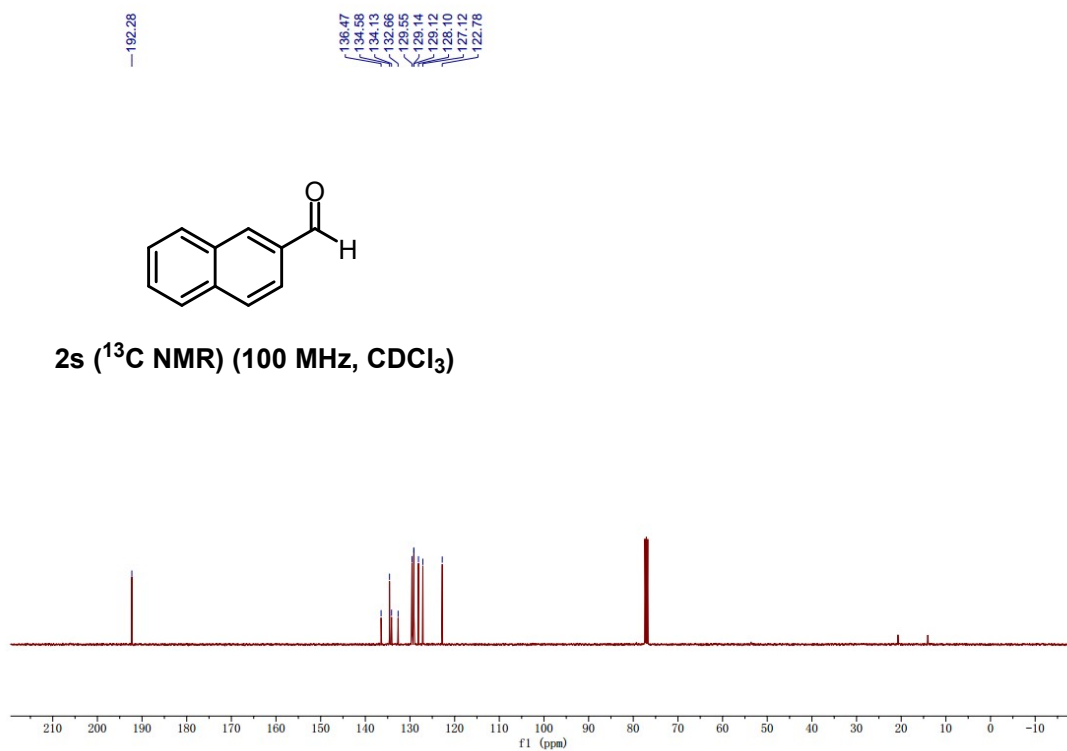


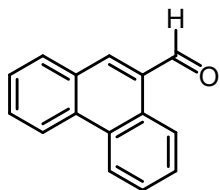


2s (^1H NMR) (400 MHz, CDCl_3)

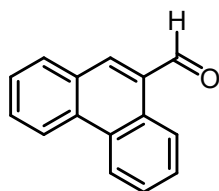
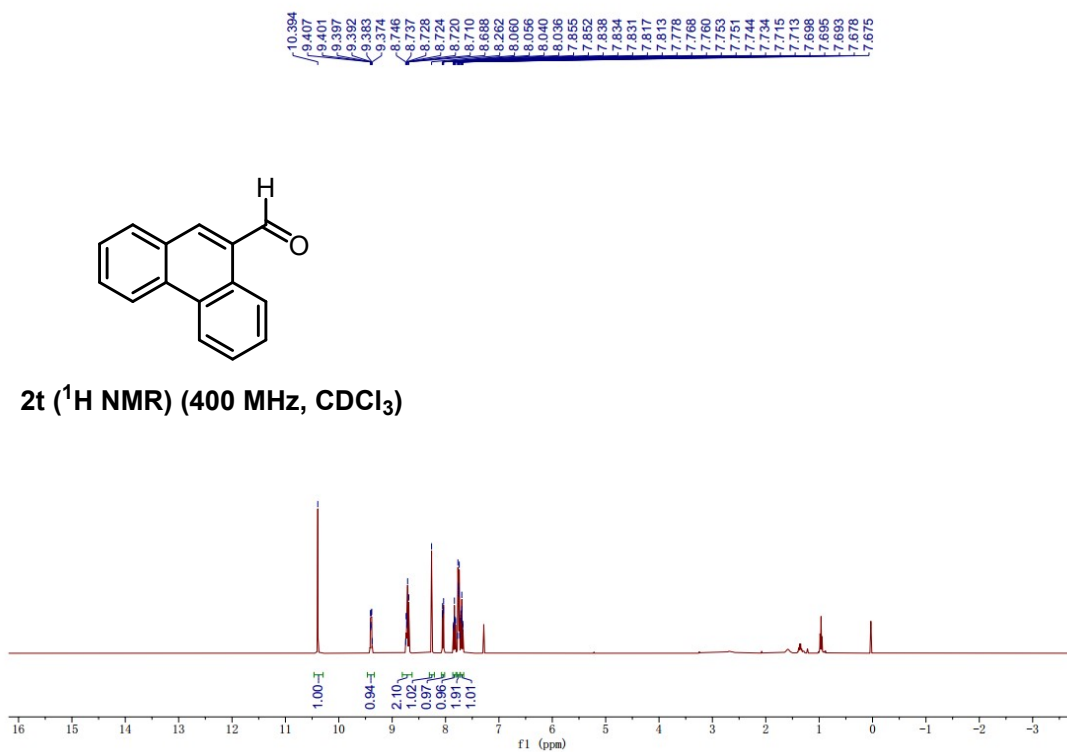


2s (^{13}C NMR) (100 MHz, CDCl_3)

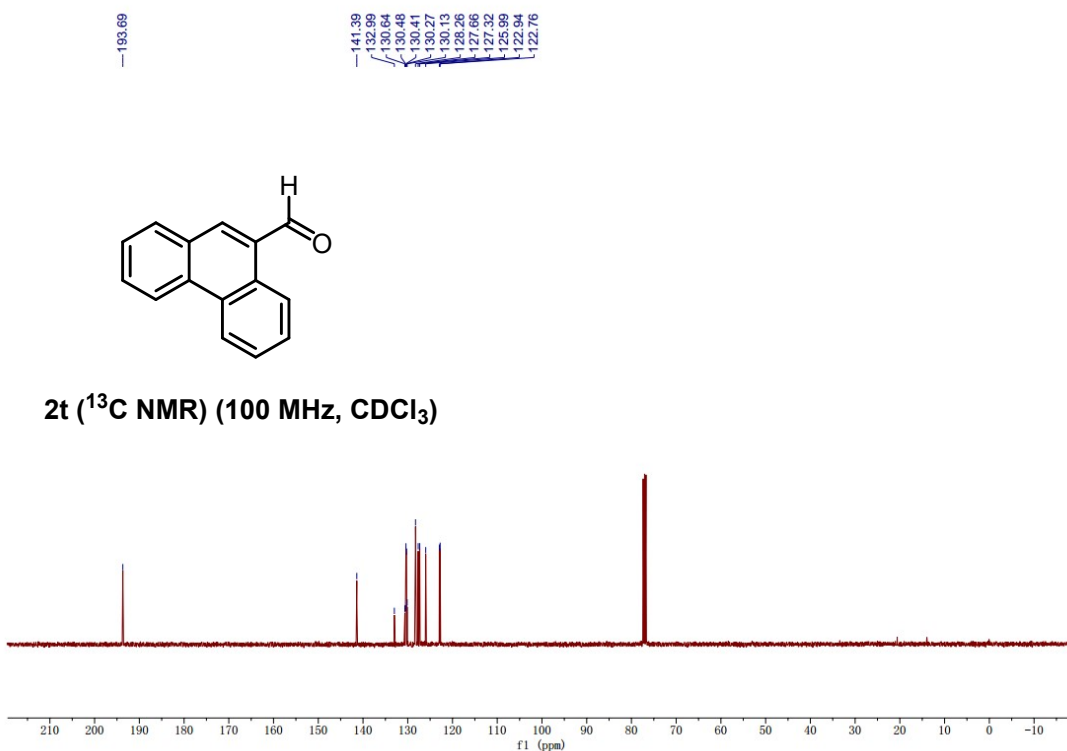




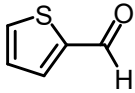
2t (^1H NMR) (400 MHz, CDCl_3)



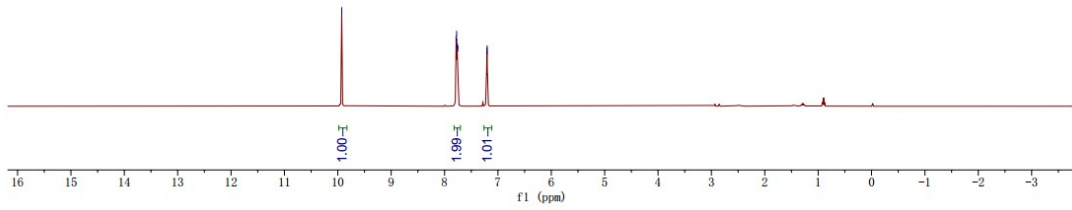
2t (^{13}C NMR) (100 MHz, CDCl_3)



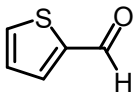
9.926
7.784
7.774
7.763
7.753
7.705
7.202



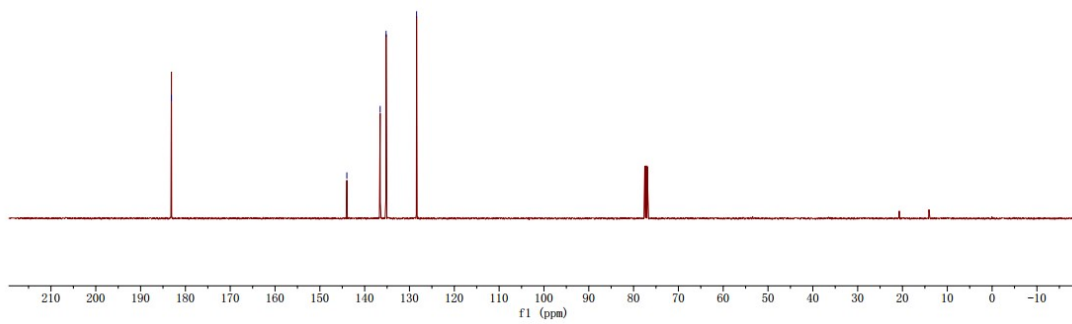
2u (¹H NMR) (400 MHz, CDCl₃)

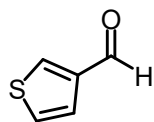


183.13
143.98
136.54
135.22
128.41

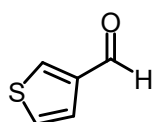
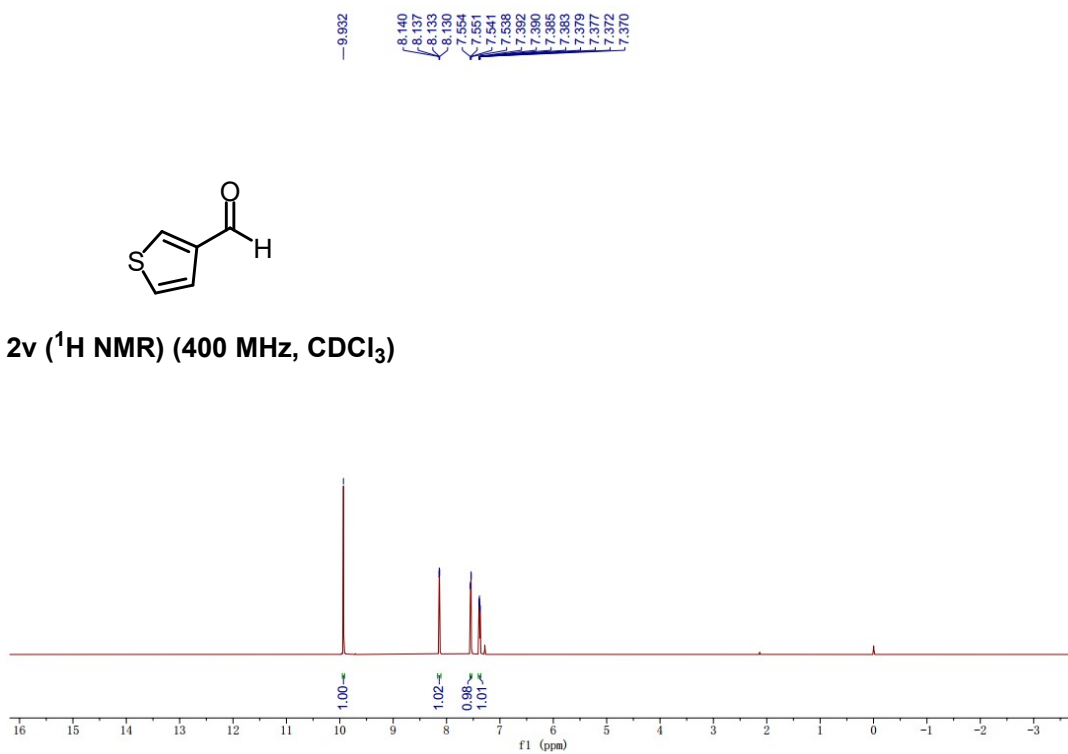


2u (¹³C NMR) (100 MHz, CDCl₃)

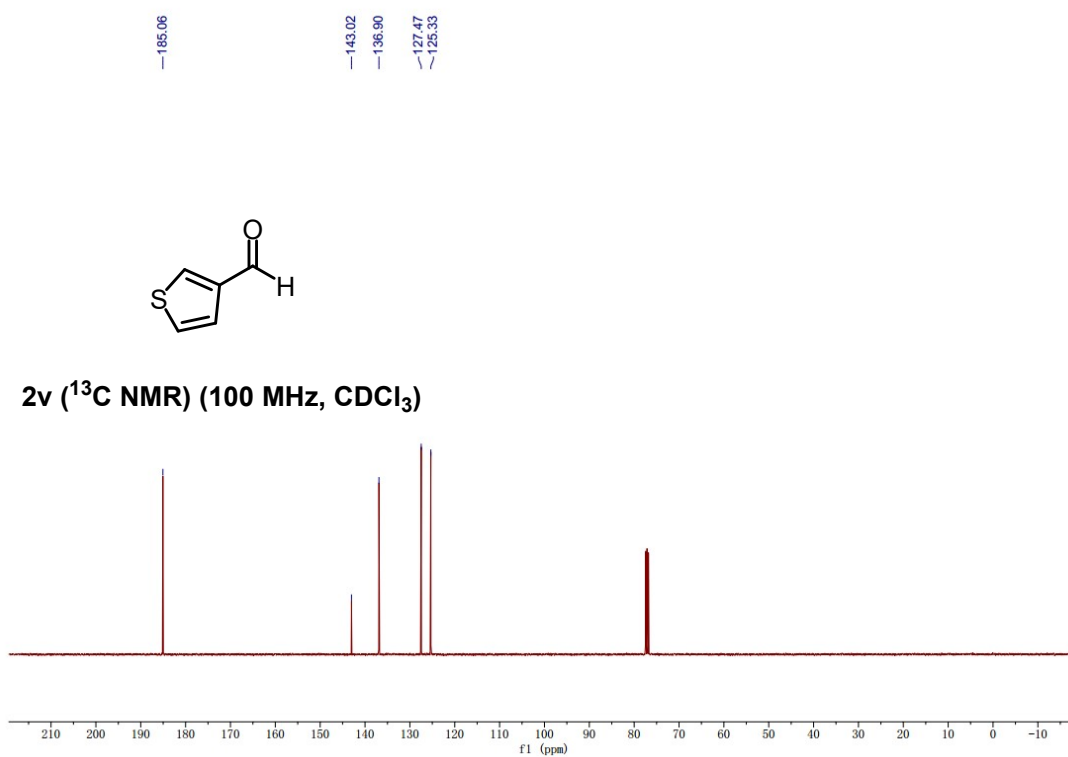


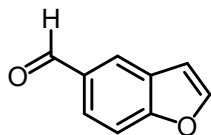


2v (^1H NMR) (400 MHz, CDCl_3)

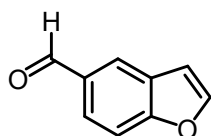
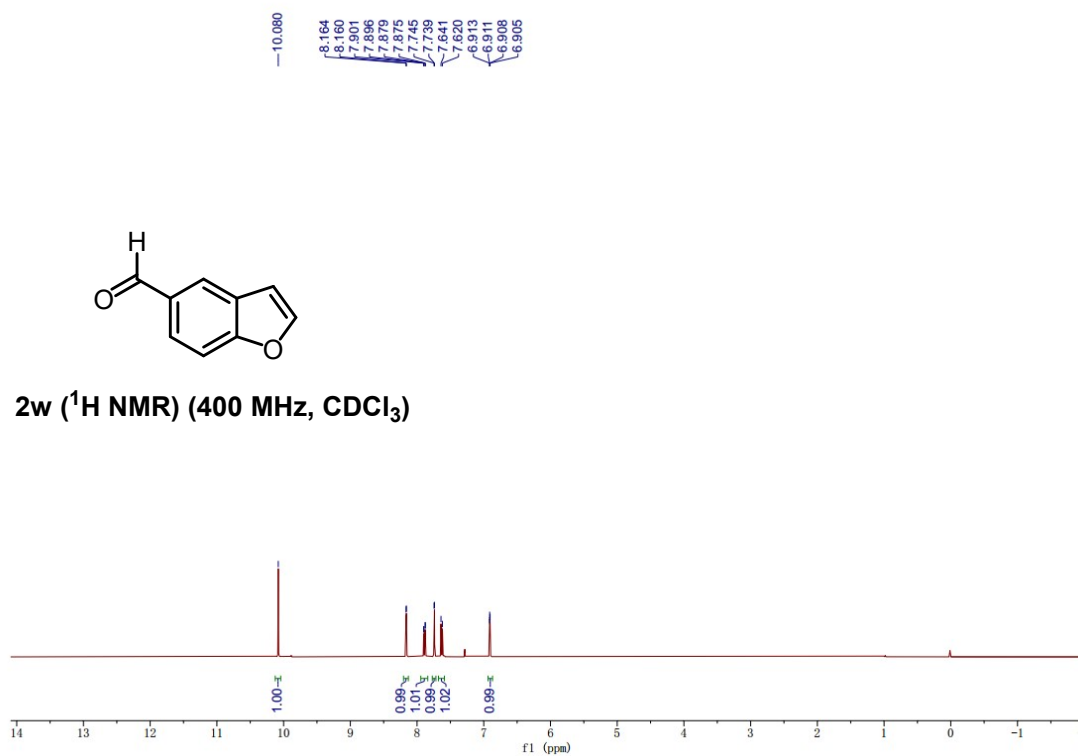


2v (^{13}C NMR) (100 MHz, CDCl_3)

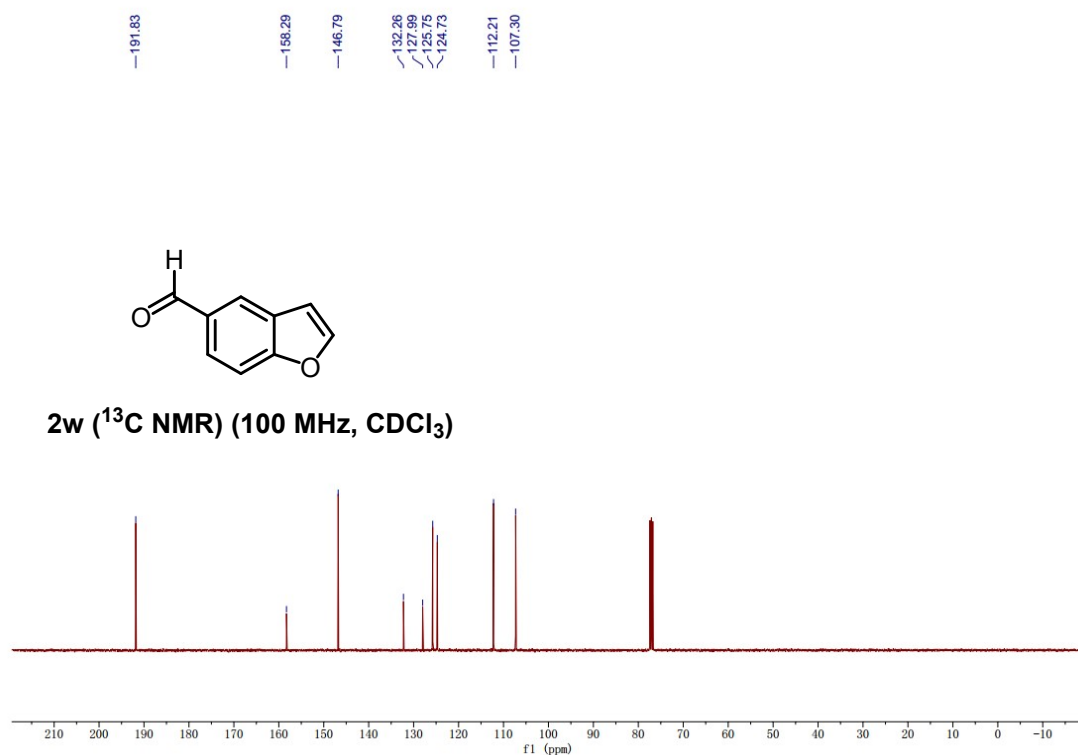


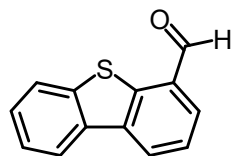


2w (^1H NMR) (400 MHz, CDCl_3)

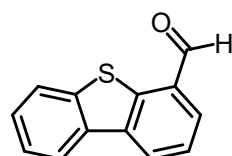
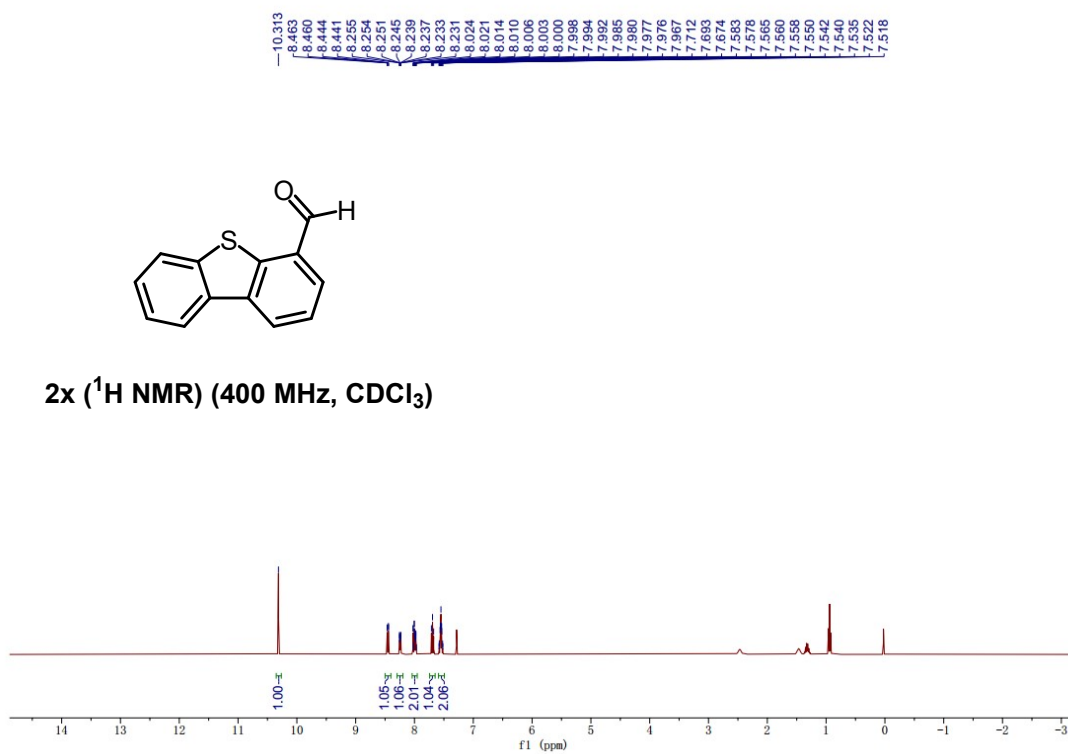


2w (^{13}C NMR) (100 MHz, CDCl_3)

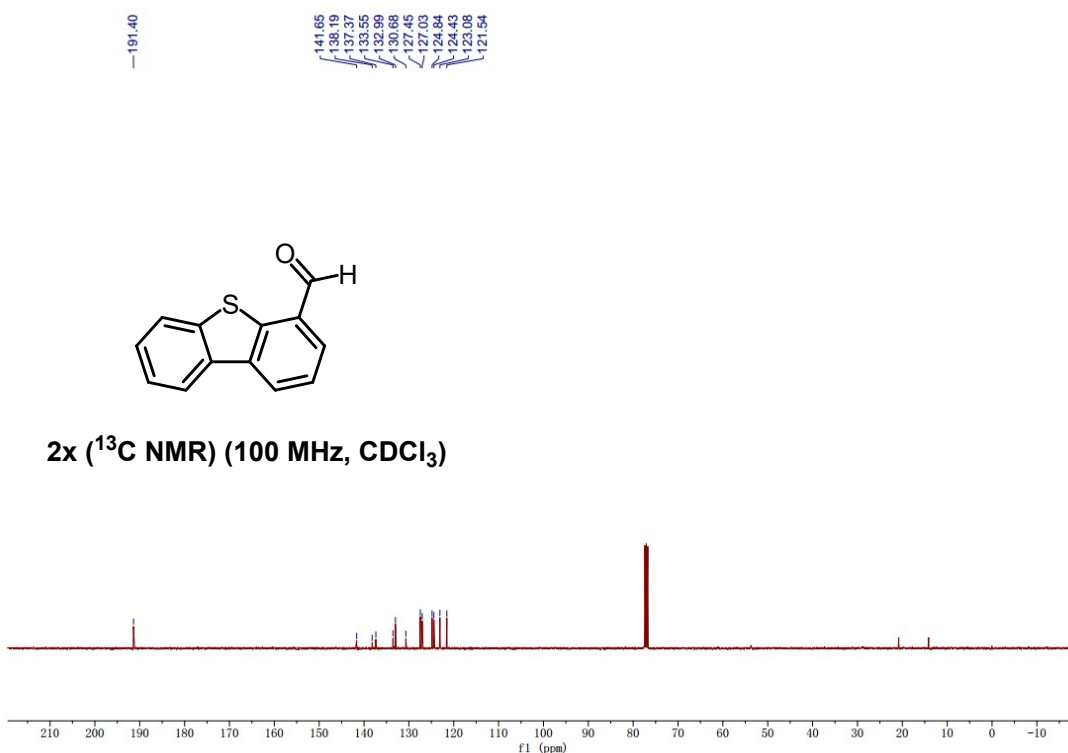


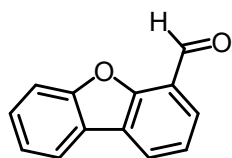


2x (¹H NMR) (400 MHz, CDCl₃)

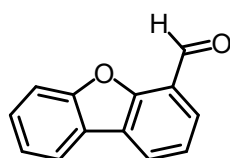
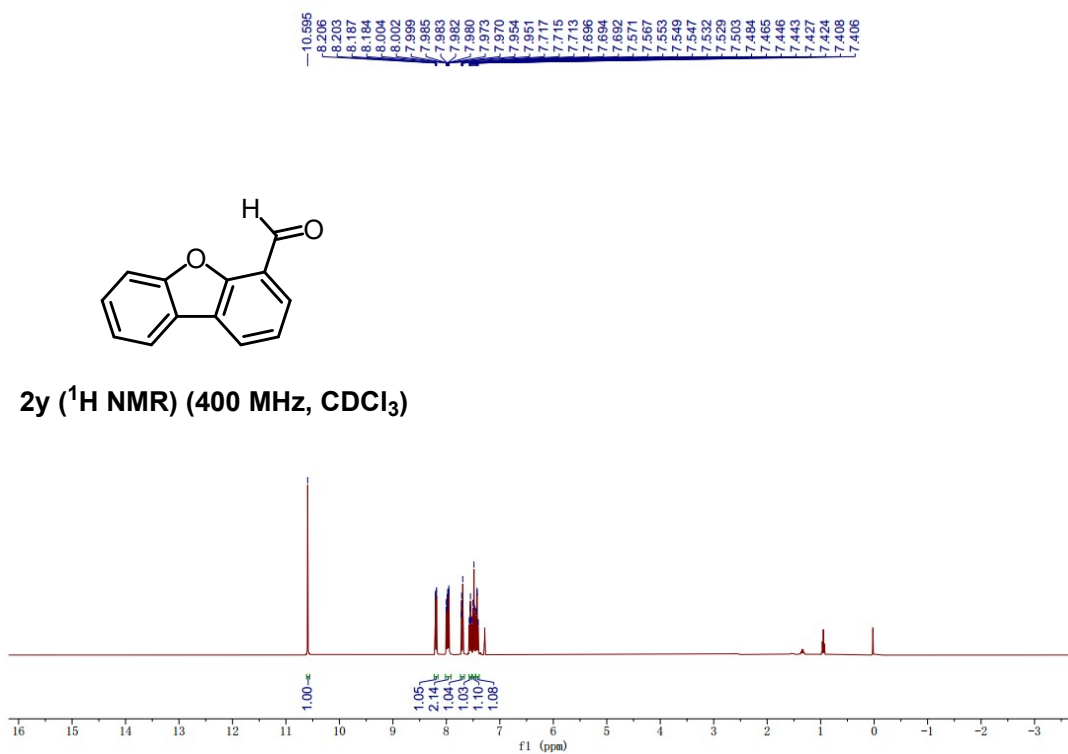


2x (¹³C NMR) (100 MHz, CDCl₃)

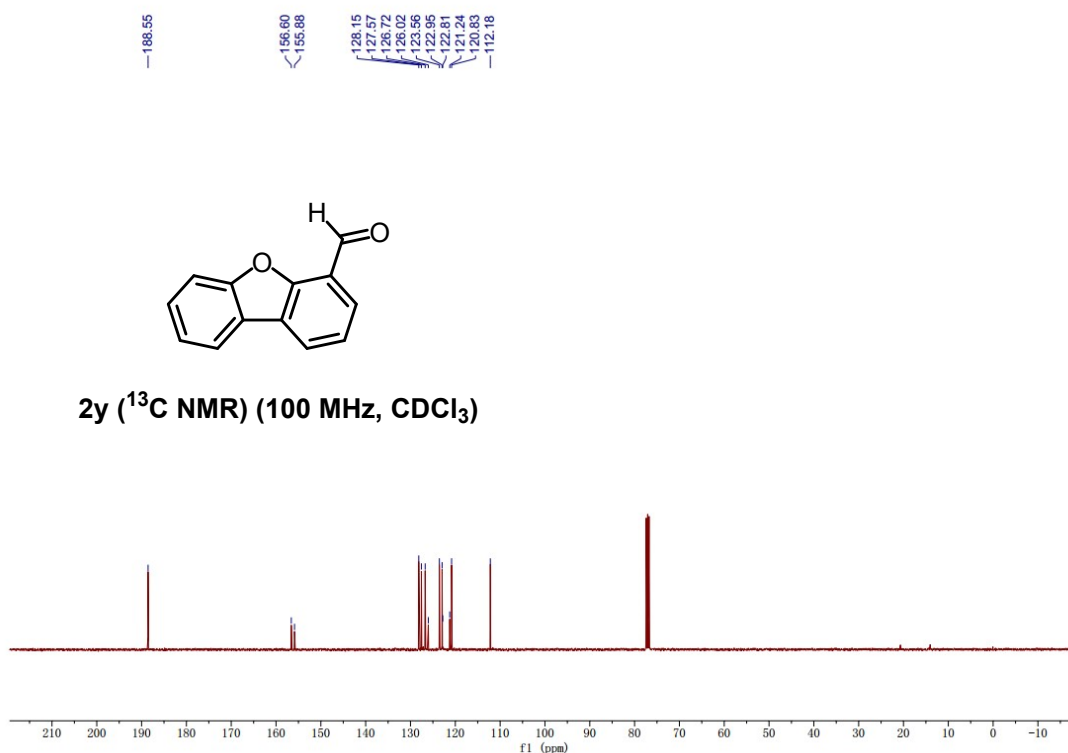


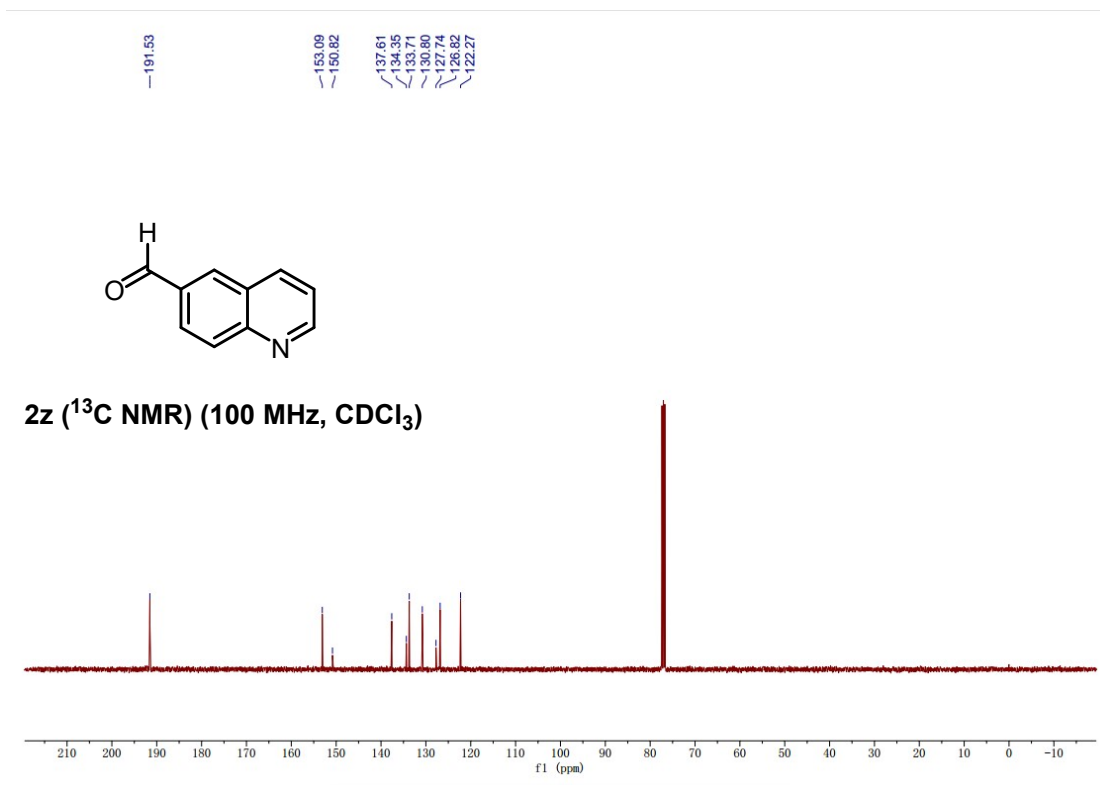
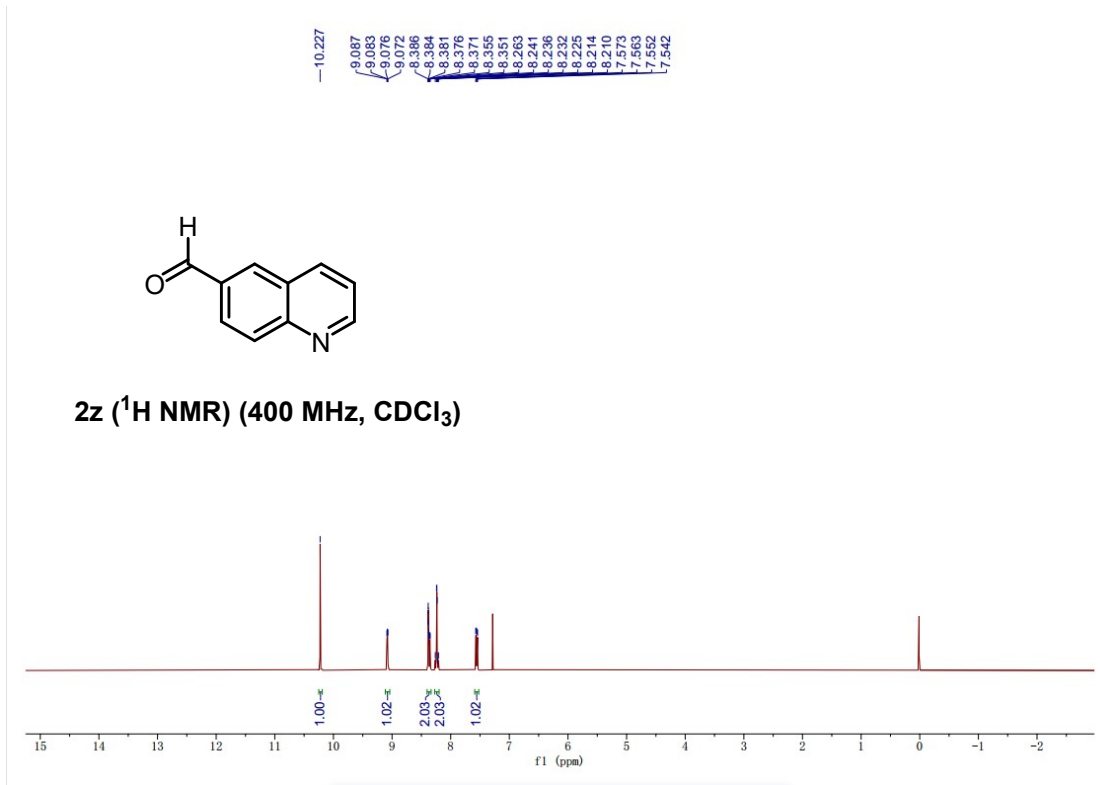


2y (^1H NMR) (400 MHz, CDCl_3)

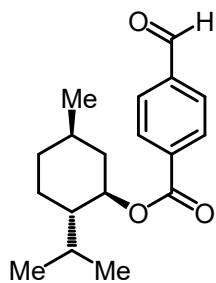


2y (^{13}C NMR) (100 MHz, CDCl_3)

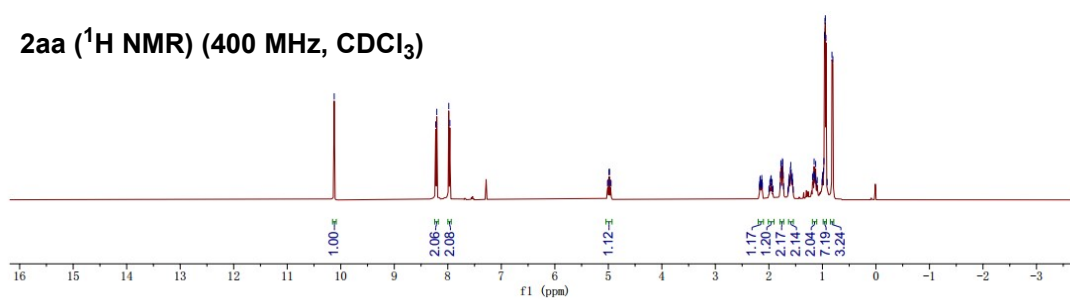




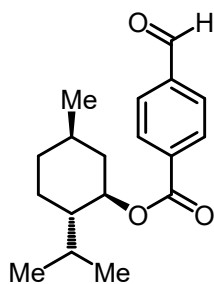
10.122
8.206
7.982
7.961
5.015
5.004
4.988
4.977
4.961
4.950
2.176
2.172
2.167
2.162
2.157
2.153
2.147
2.142
2.133
2.127
2.122
1.992
1.982
1.975
1.965
1.968
1.947
1.840
1.822
1.784
1.776
1.769
1.752
1.746
1.741
1.732
1.725
1.637
1.629
1.621
1.614
1.607
1.602
1.591
1.583
1.571
1.563
1.555
1.185
1.178
1.169
1.155
1.144
1.138
1.134
1.128
1.105
1.097
1.007
1.000
0.997
0.978
0.973
0.962
0.951
0.945
0.934
0.911
-0.822
-0.805



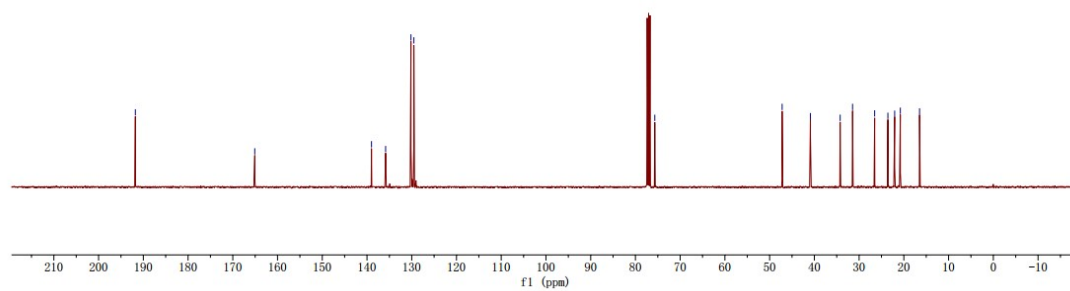
2aa (¹H NMR) (400 MHz, CDCl₃)

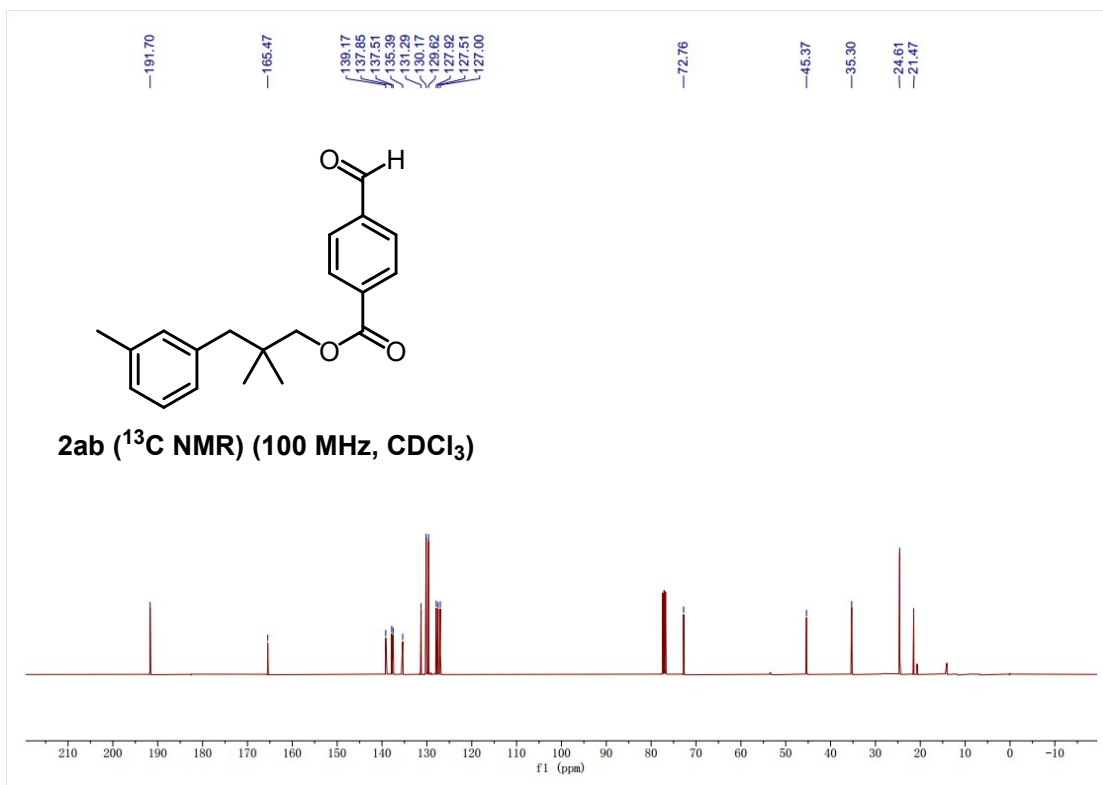
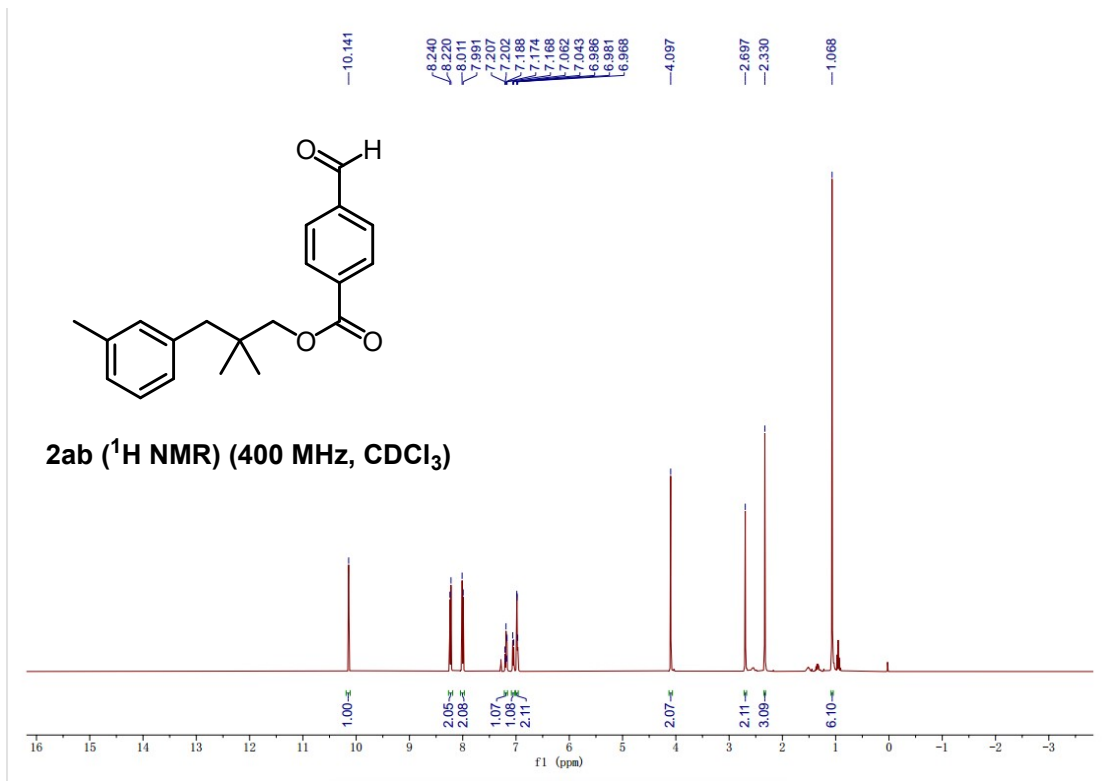


191.76
165.09
135.84
135.84
130.18
129.52
75.67
47.20
40.88
34.24
31.46
23.65
23.67
22.05
20.79
16.49

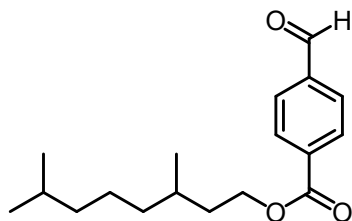


2aa (¹³C NMR) (100 MHz, CDCl₃)

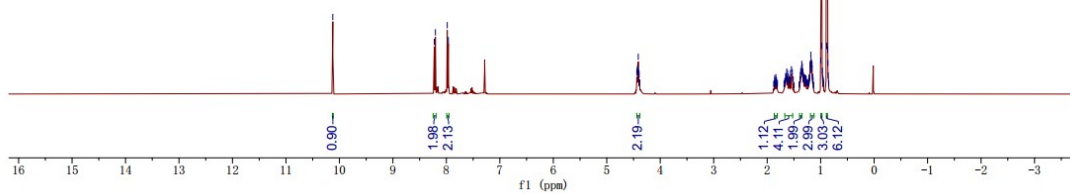




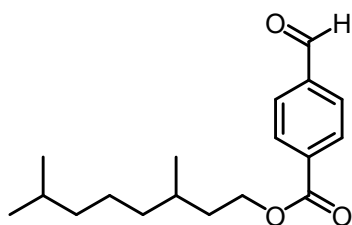
10.1239
8.2256
8.2051
7.9838
7.9630
4.4375
4.4287
4.4224
4.4187
4.4114
4.4044
4.4005
4.3943
4.3880
4.3516
4.3465
1.6412
1.6350
1.6296
1.6194
1.6028
1.5829
1.5791
1.5627
1.5461
1.5295
1.5129
1.3638
1.3606
1.3572
1.3534
1.3587
1.3531
1.3441
1.3387
1.3349
1.3303
1.3226
1.3132
1.3019
1.2967
1.2926
1.2767
1.2729
1.2657
1.2101
1.1983
1.1917
1.1821
1.1781
1.1724
1.1662
1.1623
1.1592
1.1536
1.1489
1.1457
0.9961
0.9854
0.9820
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0.9606
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0.8860
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0.8760
0.8694
0.8655
0.8604



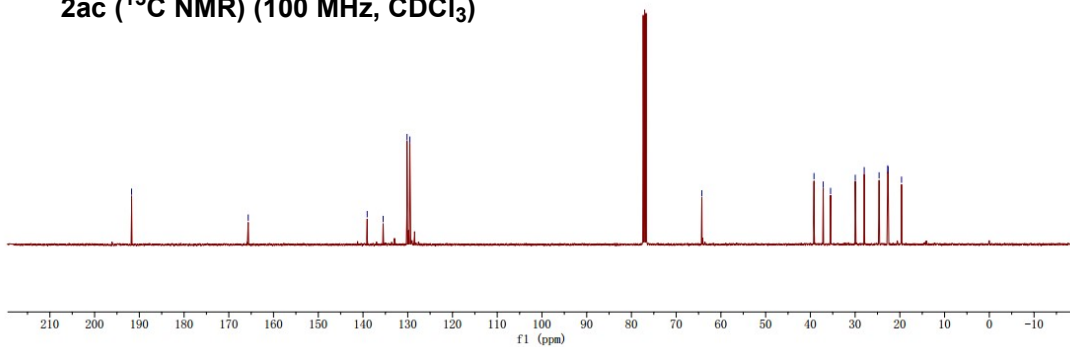
2ac ($^1\text{H NMR}$) (400 MHz, CDCl_3)

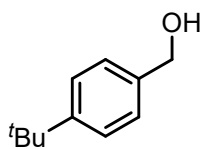


-191.74
-165.66
-139.07
-135.50
-130.16
-129.53
-64.27
39.19
37.13
35.48
29.96
27.97
24.64
22.71
22.62
19.63

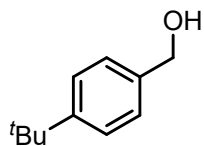
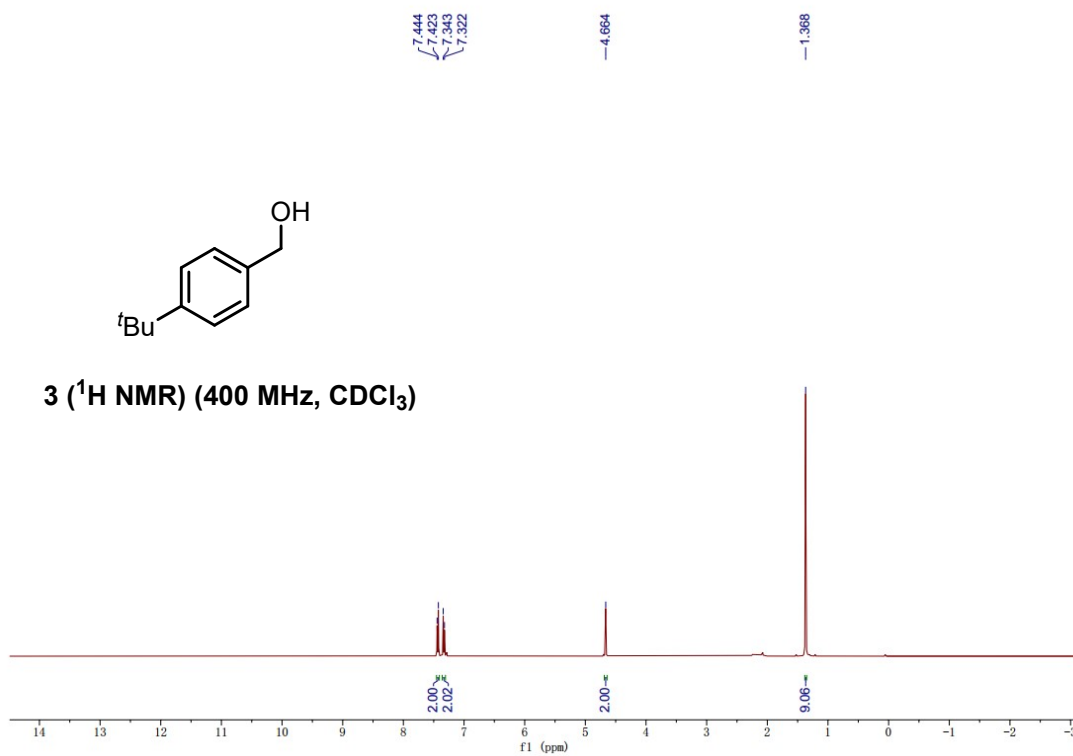


2ac ($^{13}\text{C NMR}$) (100 MHz, CDCl_3)

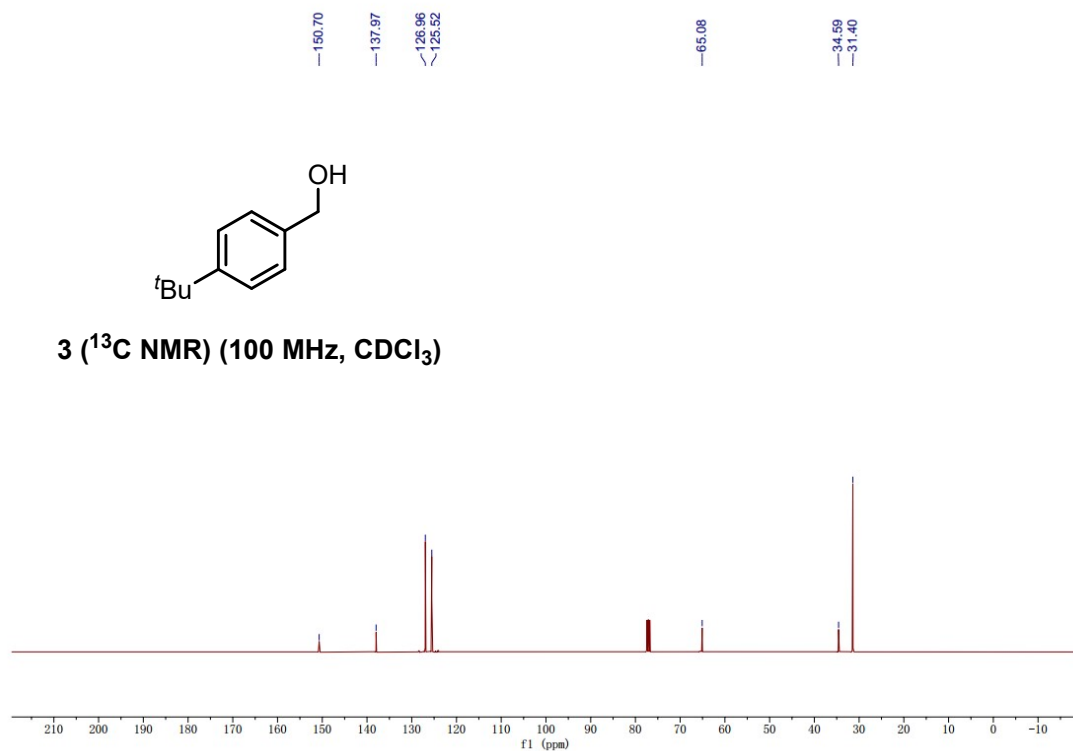


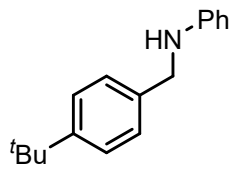


3 (^1H NMR) (400 MHz, CDCl_3)

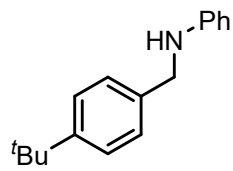
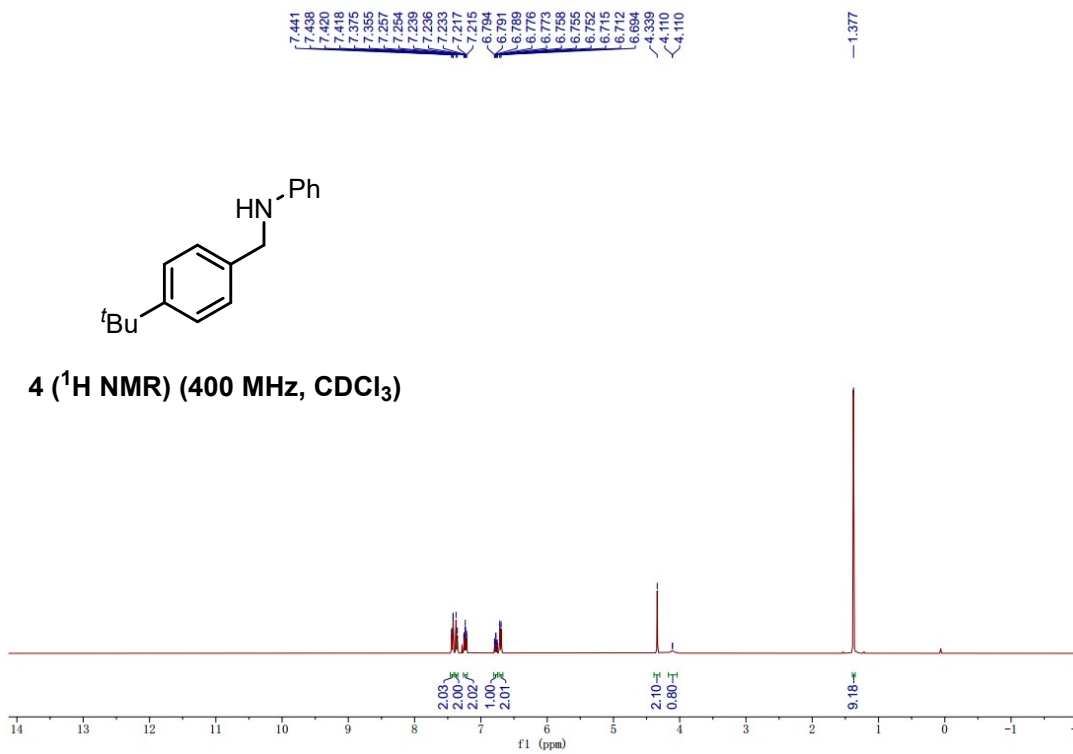


3 (^{13}C NMR) (100 MHz, CDCl_3)





4 (¹H NMR) (400 MHz, CDCl₃)



4 (¹³C NMR) (100 MHz, CDCl₃)

