

Boron-Catalyzed O-H Bond Insertion of α -Aryl α -Diazoesters in Water

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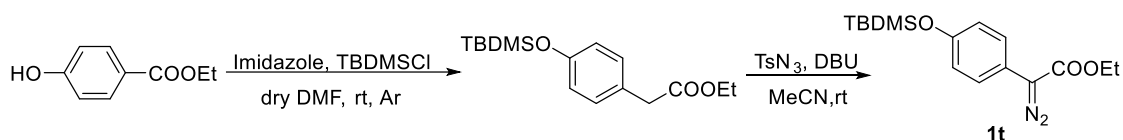
1. General Remarks: ^1H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 400-MR spectrometer in CDCl_3 with tetramethylsilane (TMS) as the internal standard; Chemical shifts (δ) are expressed in ppm and J -values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . The solvents and chemicals were purchased and used as received. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

2. General Procedure for Synthesis of **1**.¹



To a mixture of esters (1.0 equiv) and *p*-toluenesulfonyl azide (TsN₃) (1.2 equiv) in anhydrous acetonitrile (3 mL/mmol), DBU (1.4 equiv) was added. The reaction mixture was stirred at room temperature for overnight. Upon the complete consumption of the starting materials, the reaction mixture was diluted with appropriate water, followed by extraction with ethyl acetate. After washing with 10% NH₄Cl solution and brine, the combined organic extracts were dried over Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 100/1 to 50/1) to give **1**.

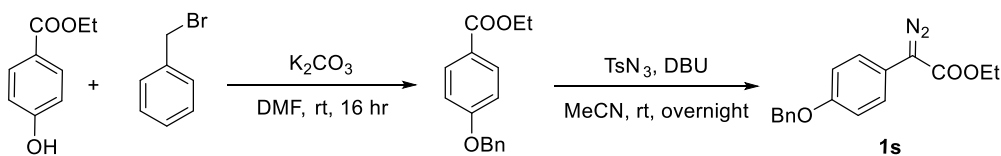
General Procedure for Synthesis of **1i**



The mixture of phenol derivative, ethyl 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)acetate (1.1 equiv) and imidazole (2.0 equiv) in dry DMF (10 mL) was stirred under argon atmosphere until the complete conversion. The mixture was then added into 1M NaOH solution and extracted with ethyl acetate and the organic layer was collected and washed consecutively with H₂O, brine and the combined organic extracts were dried over Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to get the protected phenol in 80% yield.⁴

The next step was followed by the general procedure for synthesis of **1**.

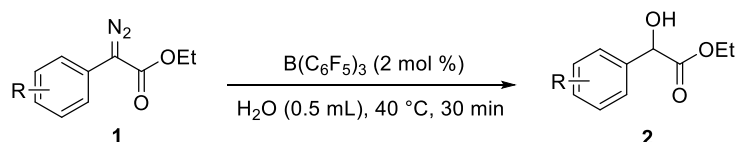
General Procedure for Synthesis of **1h**



A mixture of phenol derivative (1.0 equiv), K₂CO₃ (2.0 equiv) and BnBr (1.1 equiv) was stirred in DMF (10 mL) solvent at room temperature for 16 hr. Then the reaction was diluted with water and extracted with ethyl acetate. After washing with brine solution, the combined organic extracts were dried over Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford the protected intermediate as a clear oily liquid (78%) yield.⁵

The next step was followed by the general procedure for synthesis of **1**.¹

3. General procedure for Synthesis of α -hydroxyesters **2**.

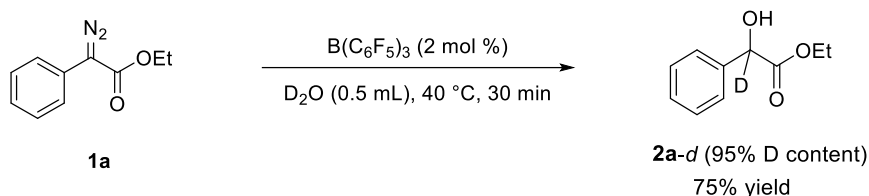


Diazo compound (0.2 mmol) was added into an oven-dried Schlenk tube, followed by the addition of water (0.5 mL), then $(\text{C}_6\text{F}_5)_3\text{B}$ (2 mg, 0.004 mmol) was added to the above mixture and the reaction tube was sealed by a Teflon screw cap. The reaction mixture was heated to 40 °C for indicated time. After completion (checked by TLC), the mixture was extracted with ethyl acetate, the combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation and the residue was purified by flash chromatography (PE/EA = 20:1 to 10:1) to get desired product **2**.

4. General Procedure for the 1 mmol Scale Synthesis of α - hydroxyester **2a**.

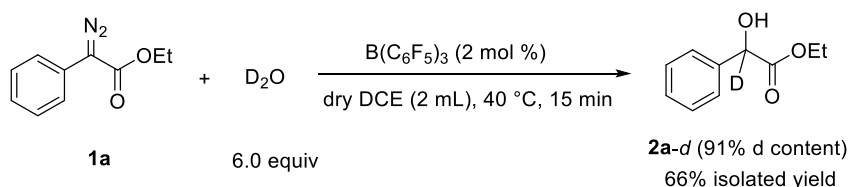
A 25 mL reaction tube equipped with a magnetic stir bar was charged diazo compound (190.2 mg, 1 mmol) and water (5 mL). Then $(\text{C}_6\text{F}_5)_3\text{B}$ (10.2 mg, 0.02 mmol) was added and the reaction tube was sealed by a Teflon screw cap was heated to 40 °C for 2:30 h. After completion (checked by TLC), and followed by extraction with ethyl acetate, the combined organic extract were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (PE/EA = 20:1 to 10:1) to get desired product (134 mg, 74%) **2a**.

5. General procedure for deuterium labeling experiments



To an oven-dried Schlenk tube were added diazo compound **1a** (38.0 mg, 0.2 mmol), and D_2O (0.5 ml). Then $(\text{C}_6\text{F}_5)_3\text{B}$ (2 mg, 0.004 mmol) was added and the reaction tube was sealed by a Teflon screw cap. The reaction mixture was heated to 40 °C for 30 min. After completion (checked by TLC), followed by extraction with ethyl acetate, the combined organic extract were dried over Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by flash chromatography (PE/EA = 20:1 to 10:1) to get desired product **2a-d** (27.0 mg, 75% yield).

Ethyl 2- hydroxy -2- phenyl acetate-d, (D contain = 95%), Colorless oil; 27.0 mg, 75% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.32 (m, 5H), 5.16 (d, J = 5.6 Hz, 0.05H), 4.28-4.13 (m, 2H), 3.47 (s, 1H), 1.23 (t, J = 7.2 Hz, 3H).



Ethyl 2- hydroxy -2- phenyl acetate-*d*, (D contain = 91%), Colorless oil; 24.0 mg, 66% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.30 (m, 5H), 5.15 (d, *J* = 5.6 Hz, 0.09H), 4.30-4.12 (m, 2H), 3.51(s, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).



6. Control NMR experiments

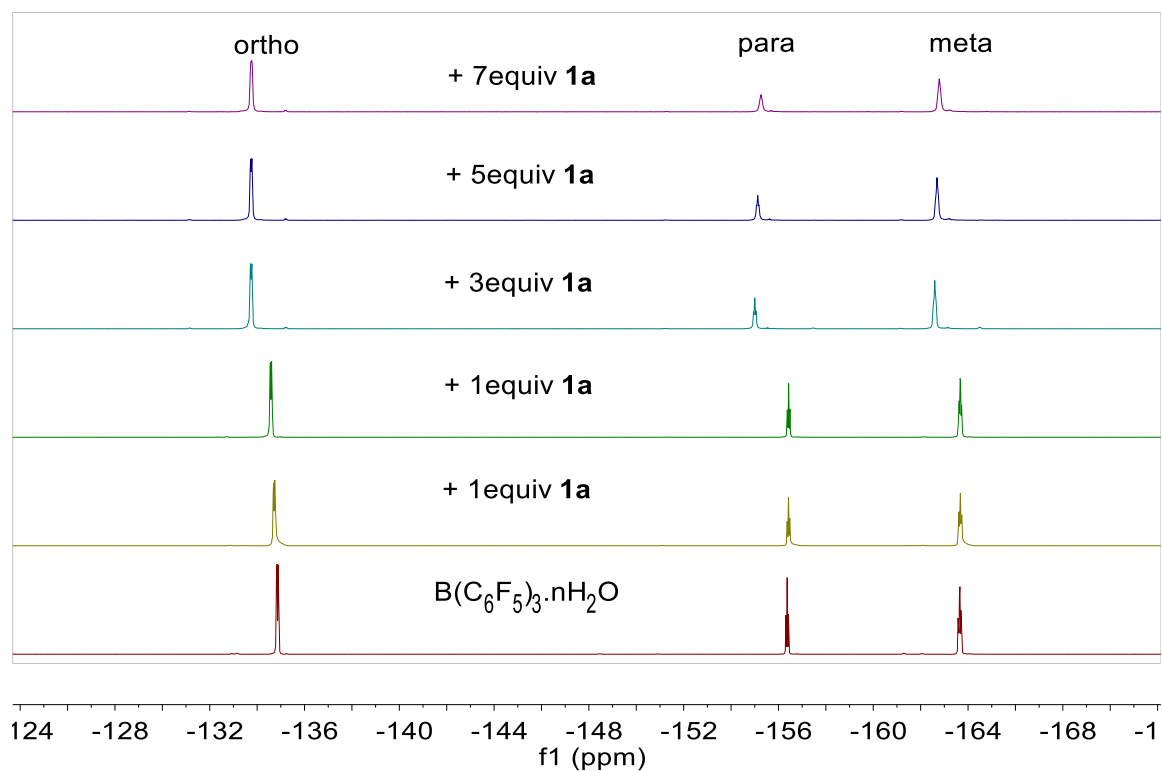


Figure S1 ^{19}F -NMR titration experiments of **1a** with $\text{B}(\text{C}_6\text{F}_5)_3 \cdot n\text{H}_2\text{O}$ in toluene- d_8

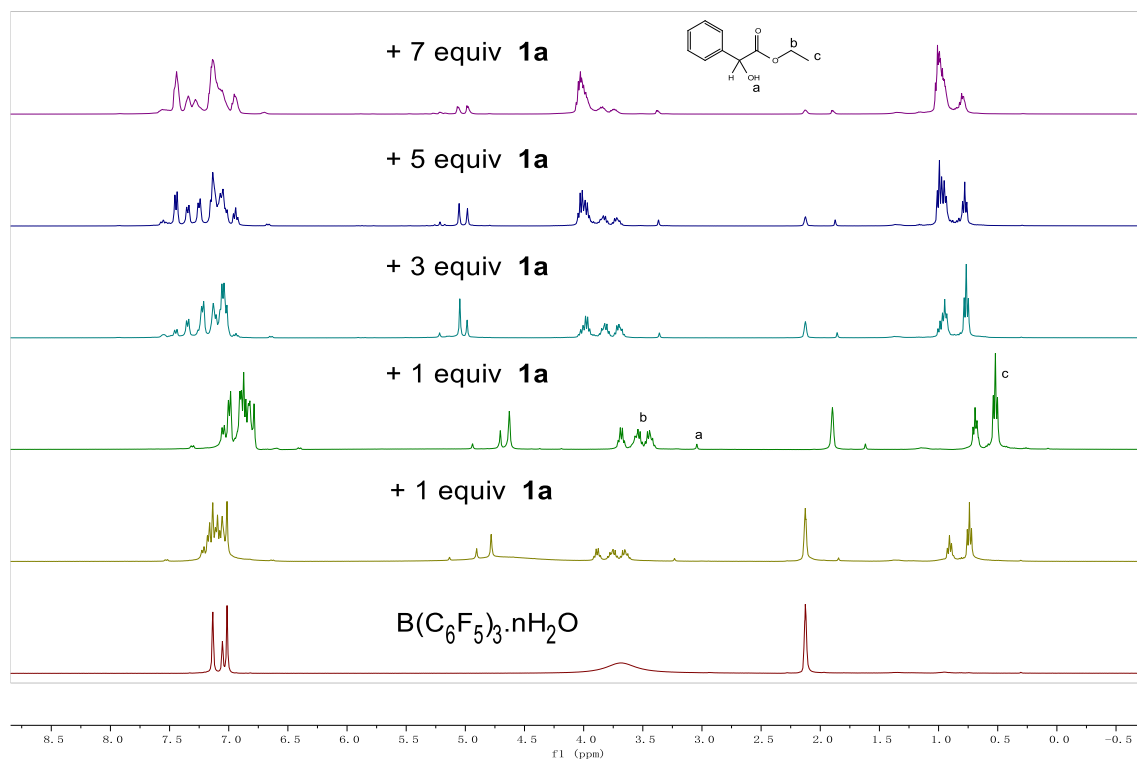


Figure S2 ^1H -NMR titration experiments of **1a** with $\text{B}(\text{C}_6\text{F}_5)_3 \cdot n\text{H}_2\text{O}$ in toluene- d_8

^{19}F NMR of the mixture of $\text{B}(\text{C}_6\text{F}_5)_3 \cdot n\text{H}_2\text{O}$ + compound **1f**

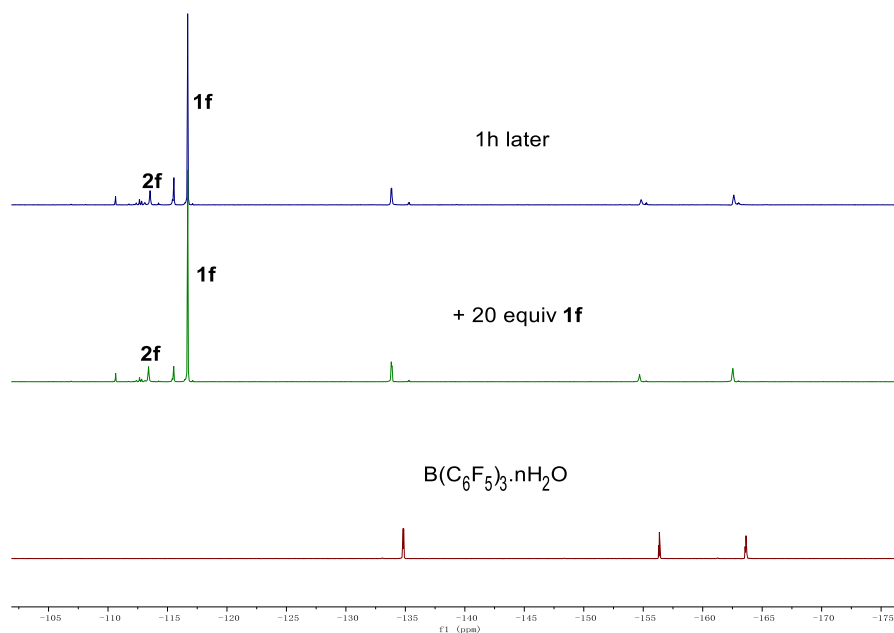


Figure S3 ^{19}F -NMR titration experiments of **1f** with $\text{B}(\text{C}_6\text{F}_5)_3 \cdot n\text{H}_2\text{O}$ in toluene- d_8

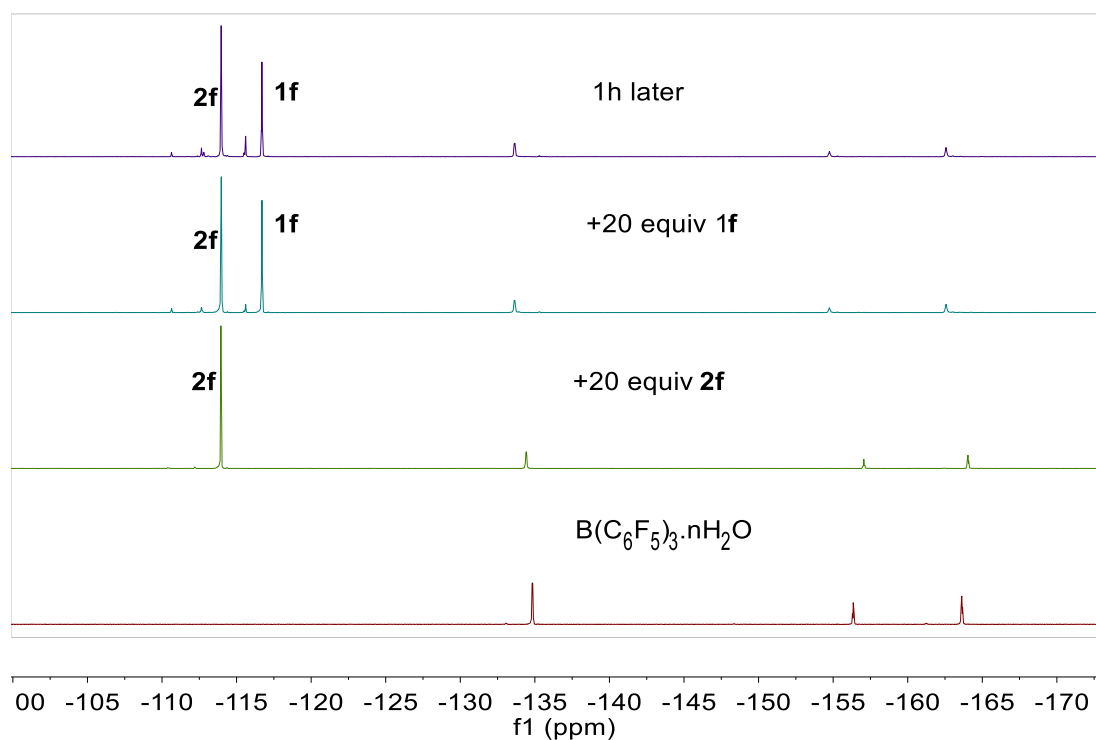


Figure S4 ^{19}F -NMR titration experiments of **2f** and **1f** with $\text{B}(\text{C}_6\text{F}_5)_3 \cdot n\text{H}_2\text{O}$ in toluene- d_8

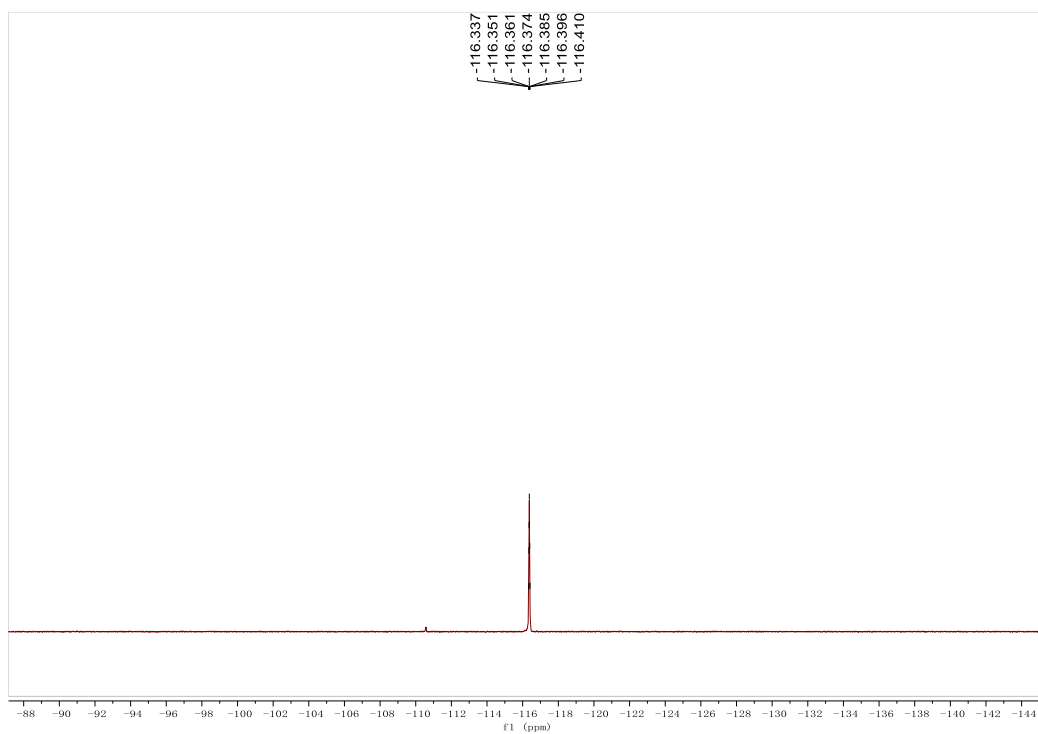


Figure S5 ^{19}F NMR spectra of **1f** in CDCl_3

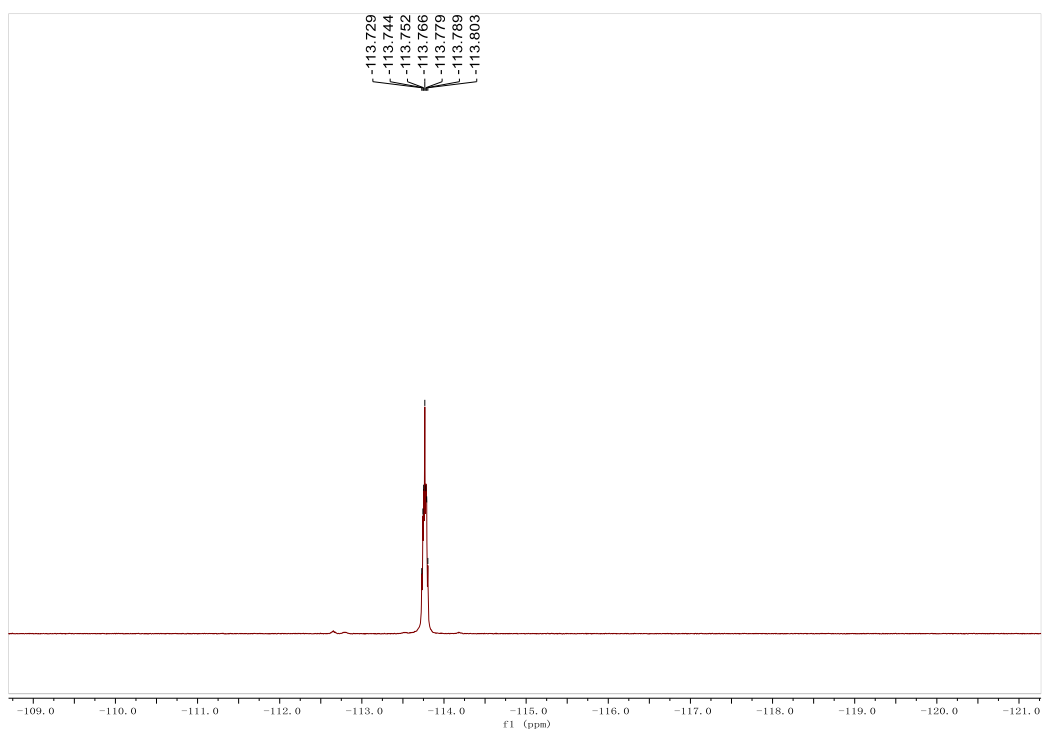
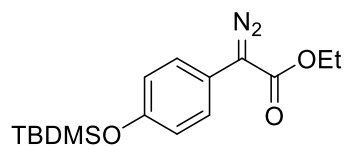
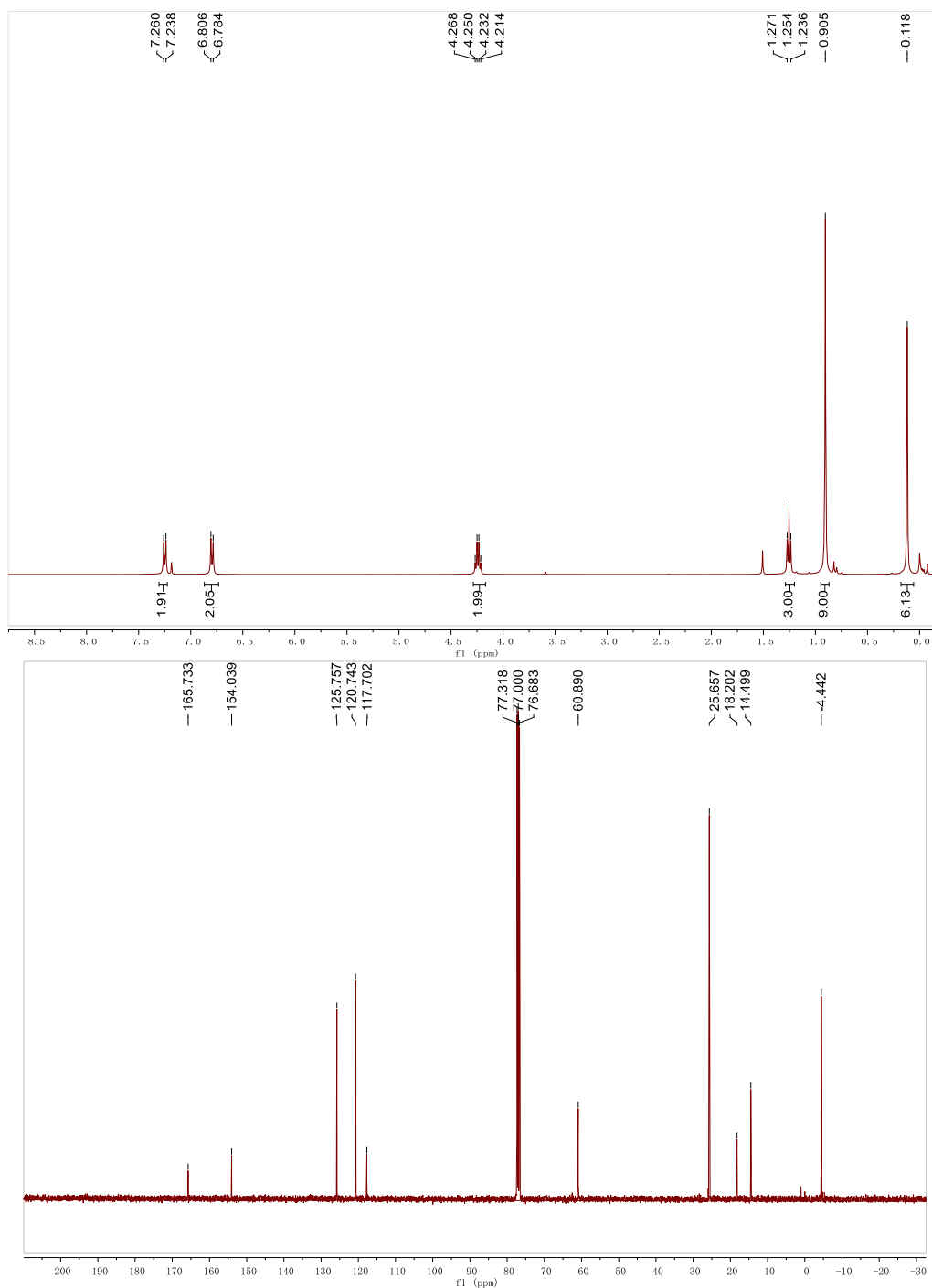


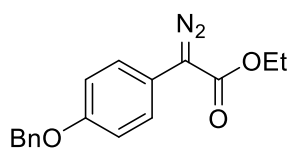
Figure S6 ^{19}F NMR spectra of **2f** in CDCl_3

7. Spectroscopic data

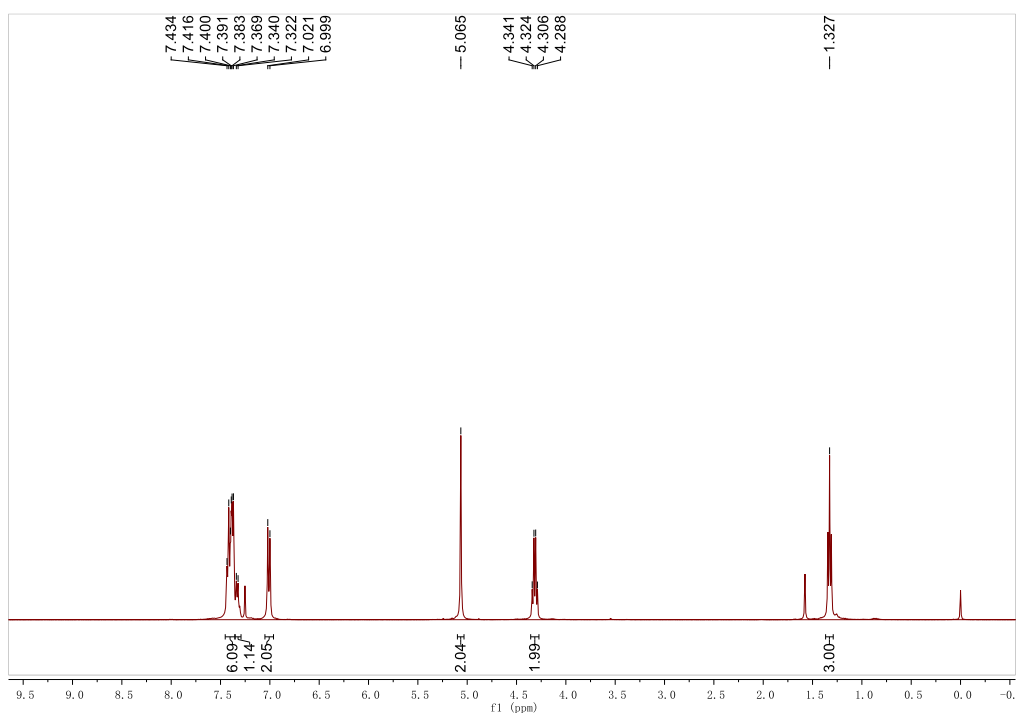


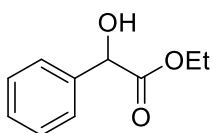
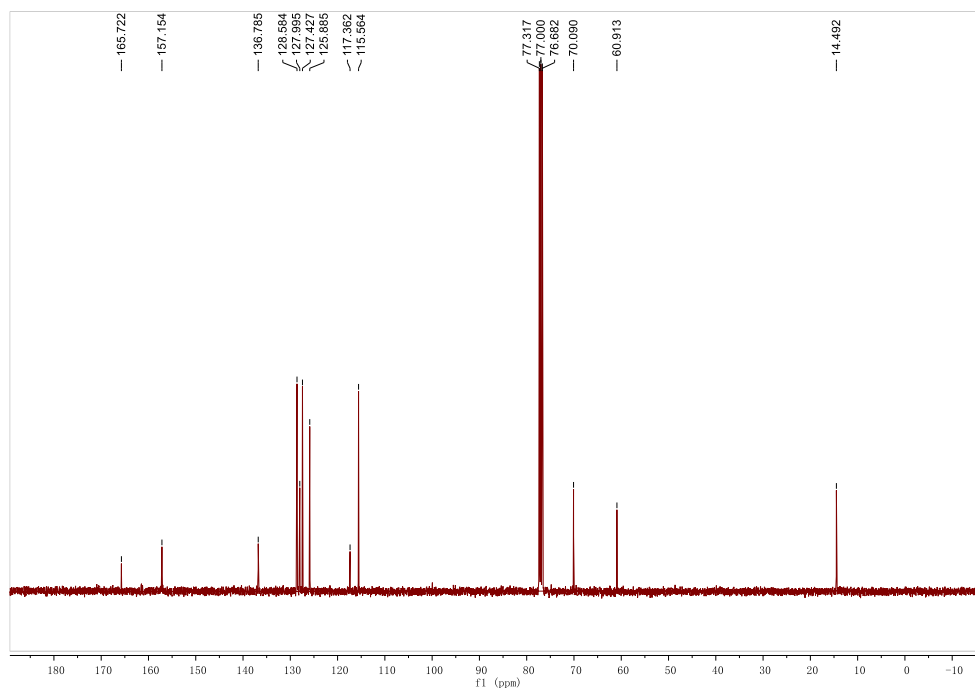
Ethyl 2-diazo-2-(4-(((tert-butyldimethylsilyl)oxy)phenyl)acetate **1i**, unknown compound. Deep orange oil; 452 mg, 71% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.23 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 4.24 (q, $J = 7.2$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.91 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 154.0, 125.8, 120.7, 117.7, 60.9, 25.7, 18.2, 14.5, -4.4. IR (KBr): ν 2957, 2931, 2858, 2082, 1703, 1510, 1260, 1158 cm^{-1} . HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_3\text{SiNa}^+$: 343.1448; found: 343.1449.



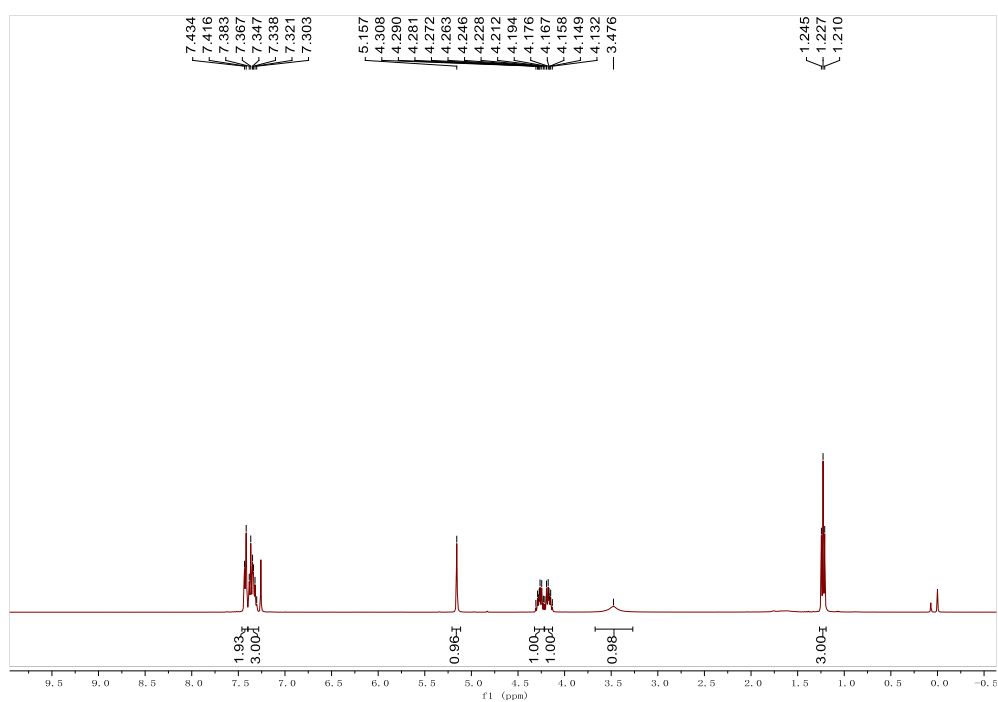


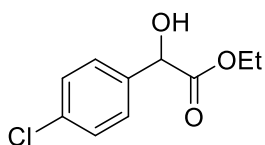
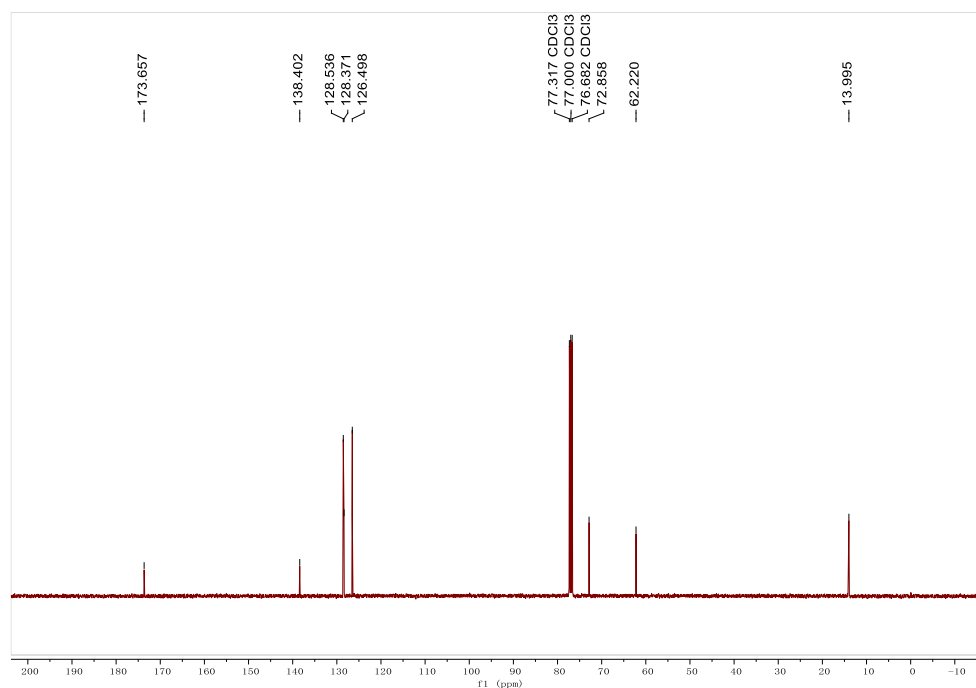
Ethyl 2(4-benzyloxy) phenyl)-2-diazoacetate 1h, unknown compound. Orange oil; 400 mg, 67% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.35 (m, 6H), 7.35-7.29 (m, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 5.06 (s, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 157.2, 136.8, 128.6, 128.0, 127.4, 125.9, 117.4, 115.6, 70.1, 60.9, 14.5. IR (KBr): ν 3453, 3034, 2982, 2094, 1694, 1514, 1246, 1164 cm^{-1} . HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}^+$: 319.1053; found: 319.1054.



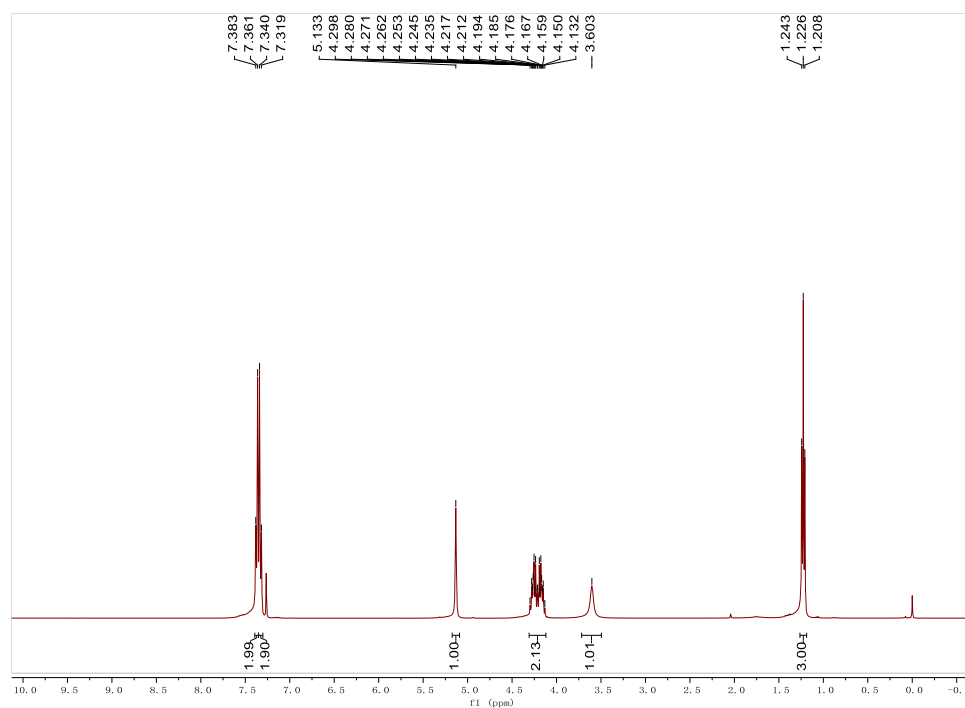


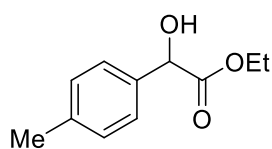
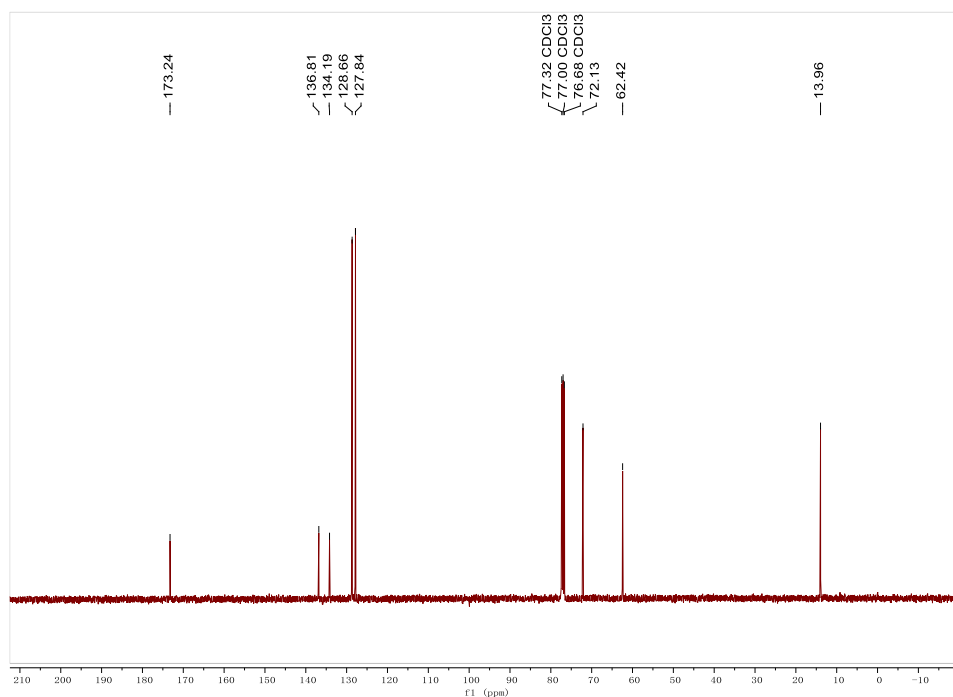
Ethyl 2-hydroxy-2-phenylacetate 2a, known compound.² Colorless oil; 29.0 mg, 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.30 (m, 5H), 5.16 (s, 1H), 4.35-4.13 (m, 2H), 3.48 (s, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 138.4, 128.5, 128.4, 126.5, 72.9, 62.2, 14.0.



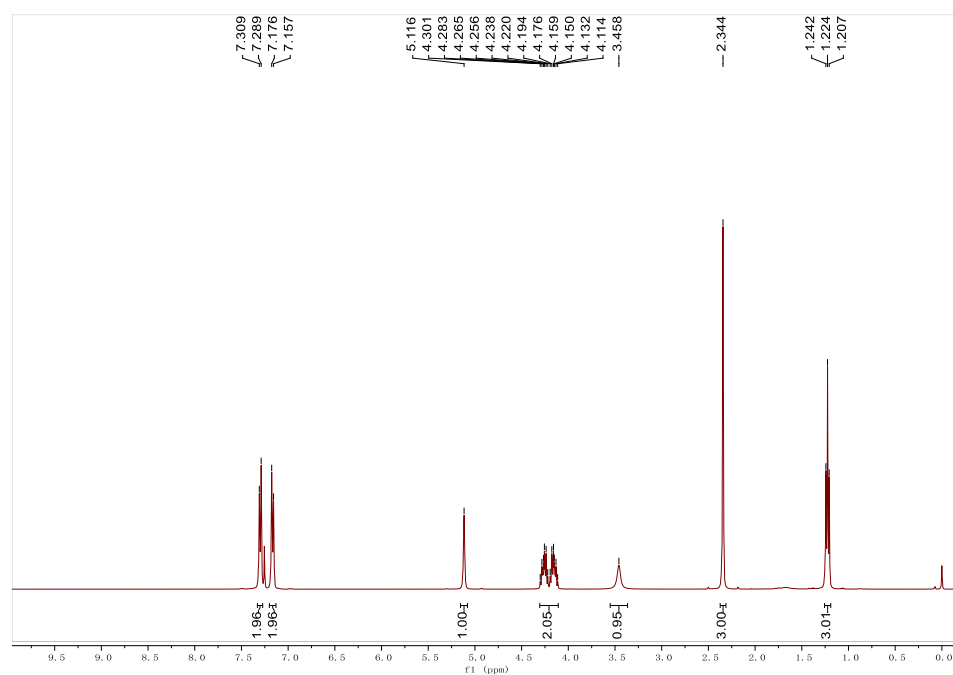


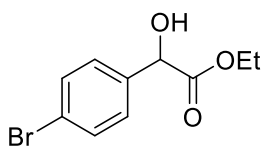
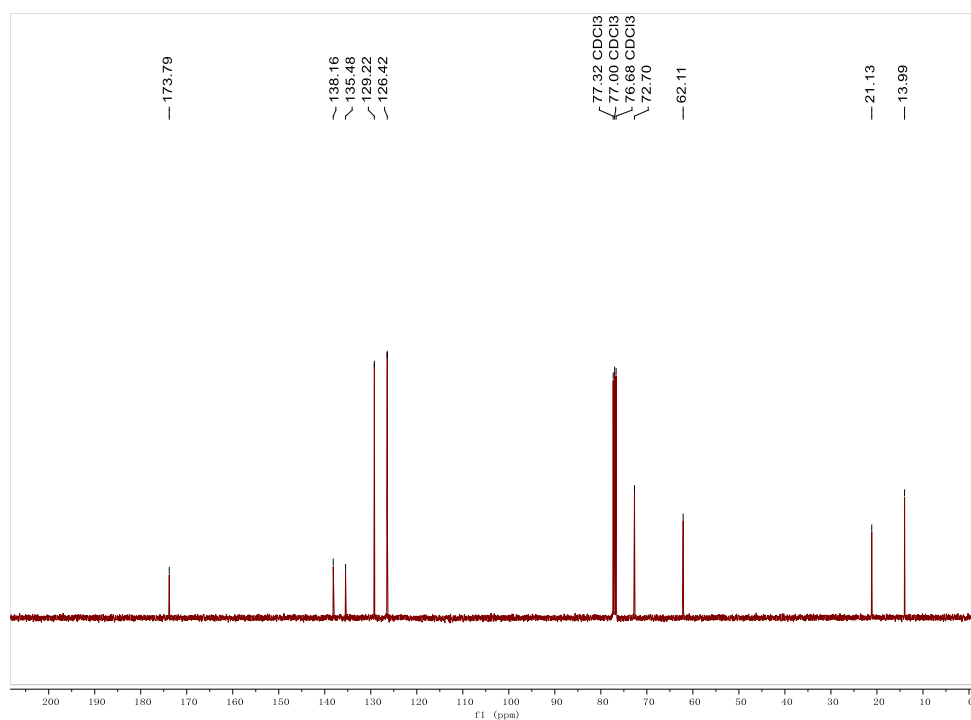
Ethyl 2-(4-chlorophenyl)-2-hydroxyacetate 2b, known compound.³ white solid; 34.0 mg, 79% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 5.13 (s, 1H), 4.30-4.13 (m, 2H), 3.60 (s, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.2, 136.8, 134.2, 128.7, 127.8, 72.1, 62.4, 14.0.



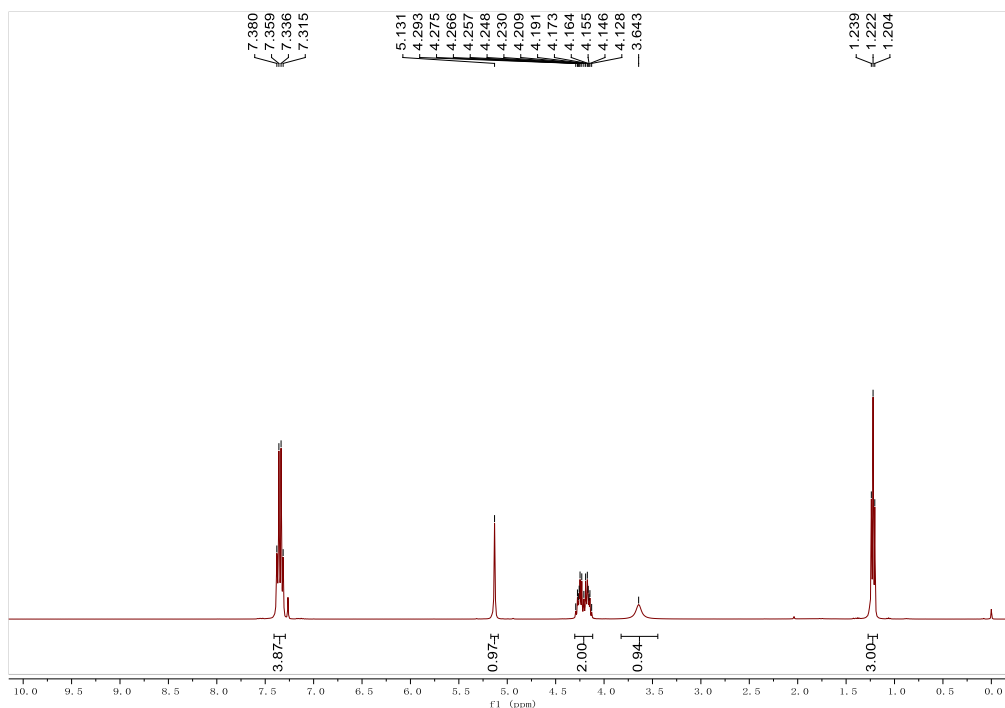


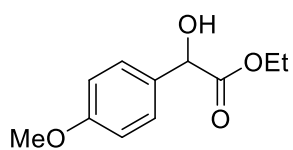
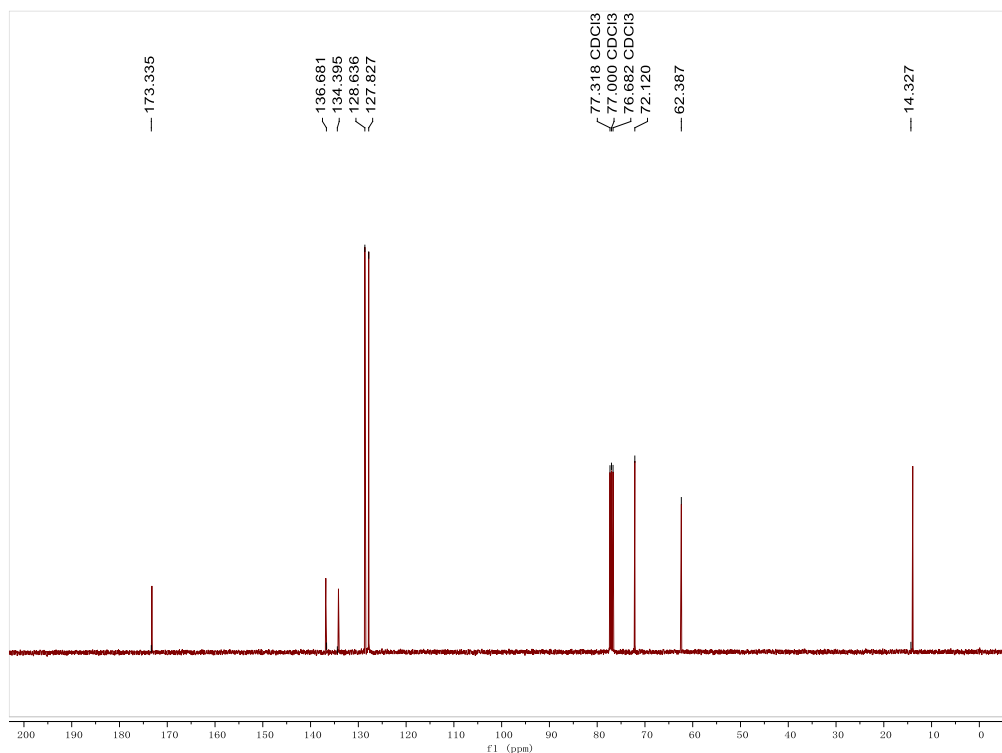
Ethyl 2-hydroxy-2-*p*-tolylacetate 2c, known compound.² Colorless semi-solid; 30.2 mg, 78% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 4.30-4.11 (m, 2H), 3.46 (s, 1H), 2.34 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.8, 138.2, 135.5, 129.2, 126.4, 72.7, 62.1, 21.1, 14.0.



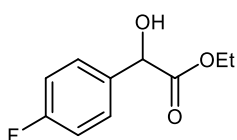
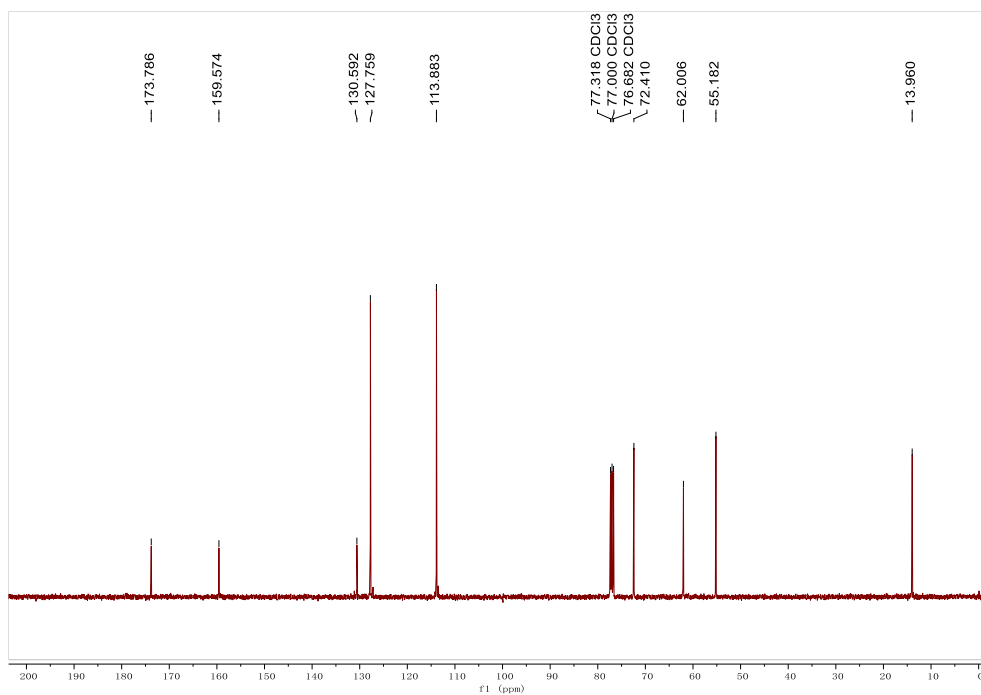
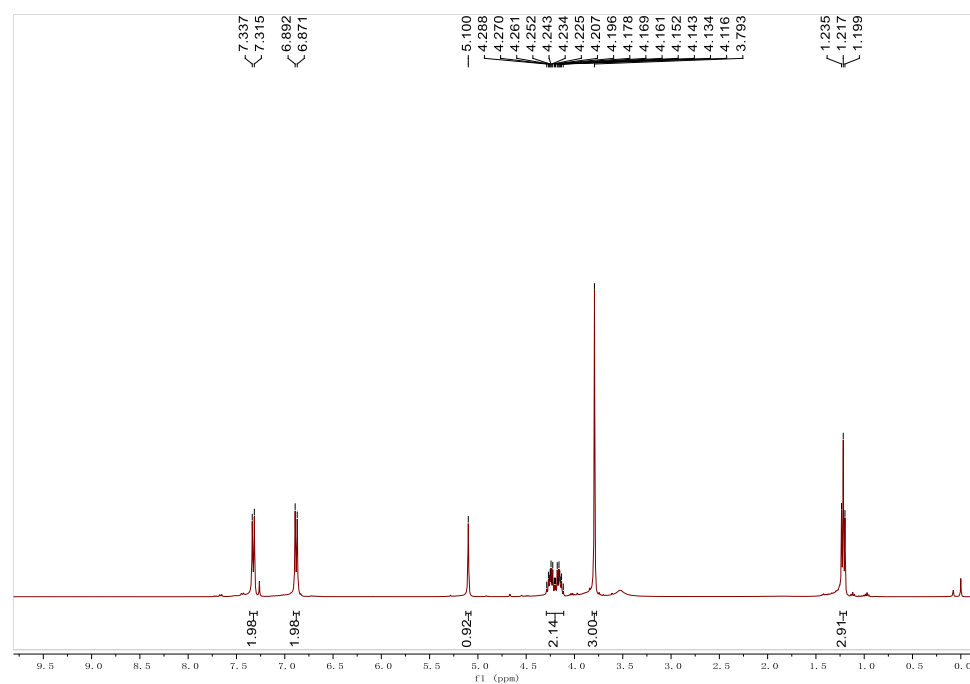


Ethyl 2-(4-bromophenyl)-2-hydroxyacetate **2d**, known compound.³ white solid; 41.2 mg, 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 1H), 4.29-4.12 (m, 2H), 3.64 (s, 1H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.3, 136.7, 134.4, 128.6, 127.8, 72.1, 62.4, 14.3.



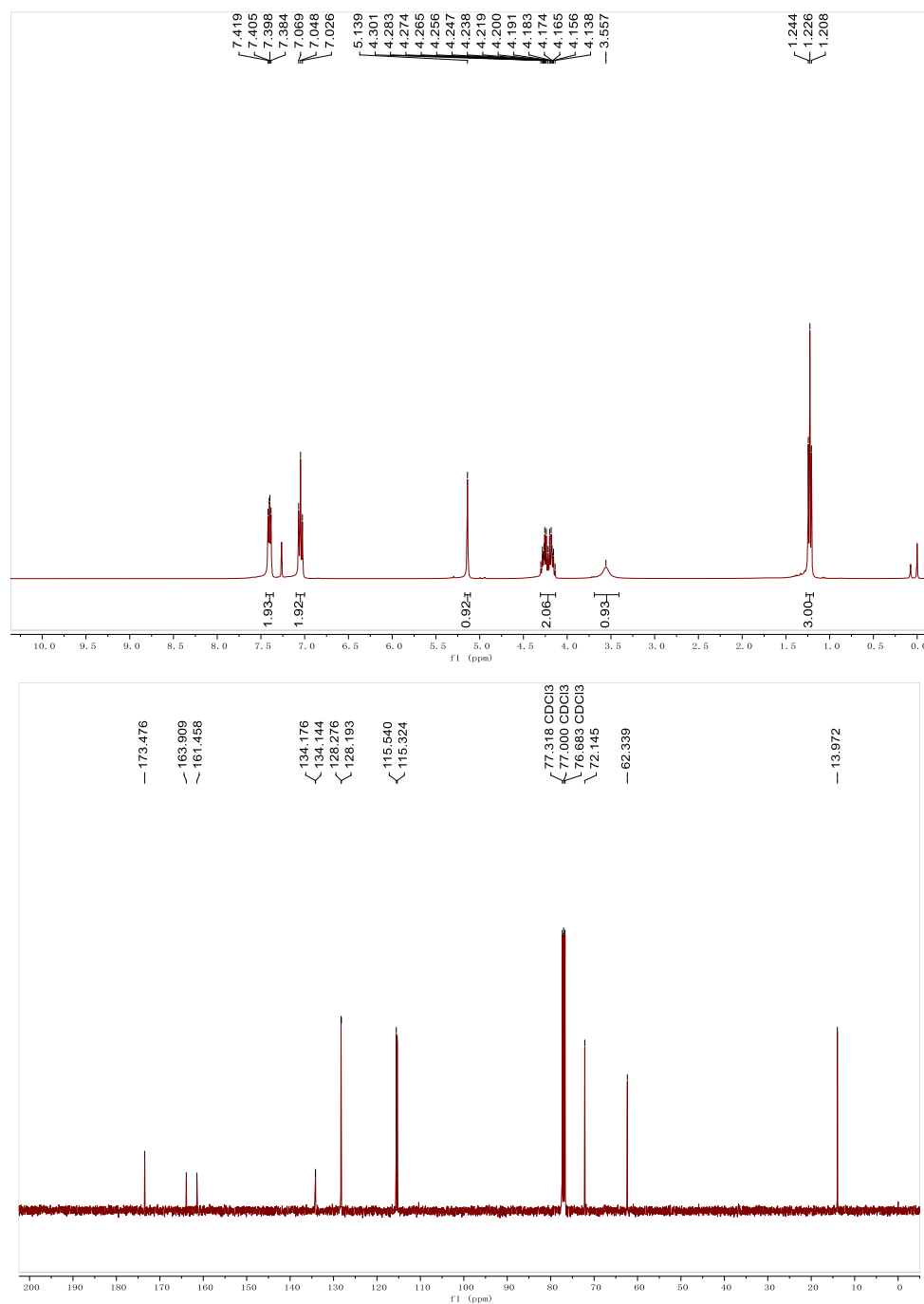


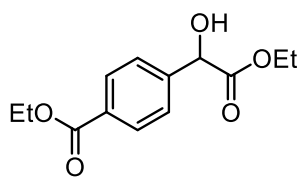
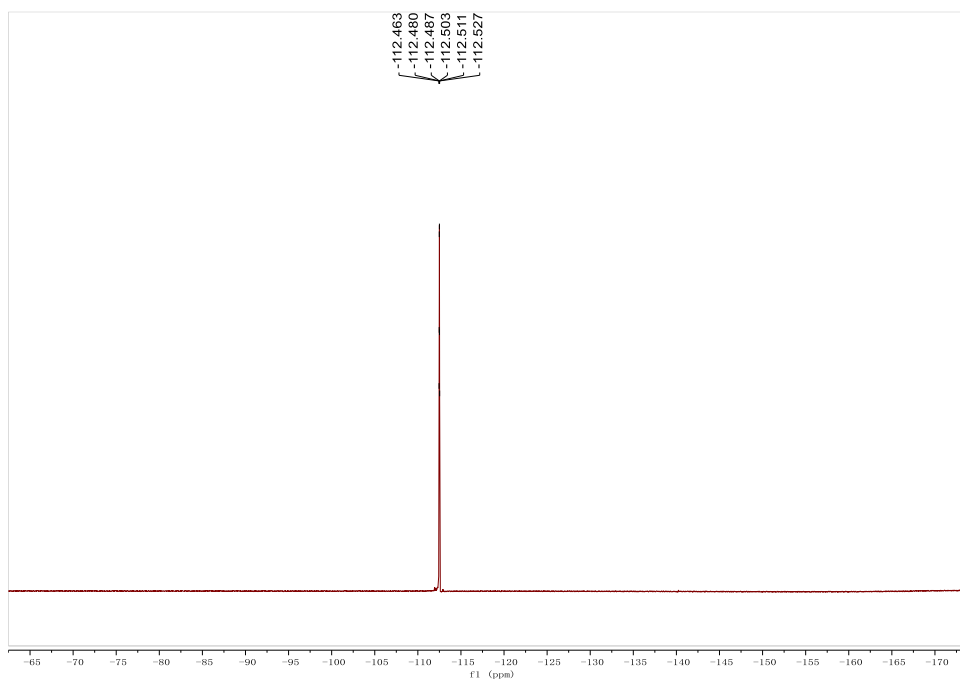
Ethyl 2-hydroxy-2-(4-methoxyphenyl) acetate 2e, known compound.⁴ White solid; 34.3 mg, 82% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 1H), 4.29-4.11 (m, 2H), q3.79 (s, 1H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.8, 159.6, 130.6, 127.8, 113.9, 72.4, 62.0, 55.2, 14.0.



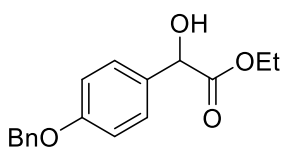
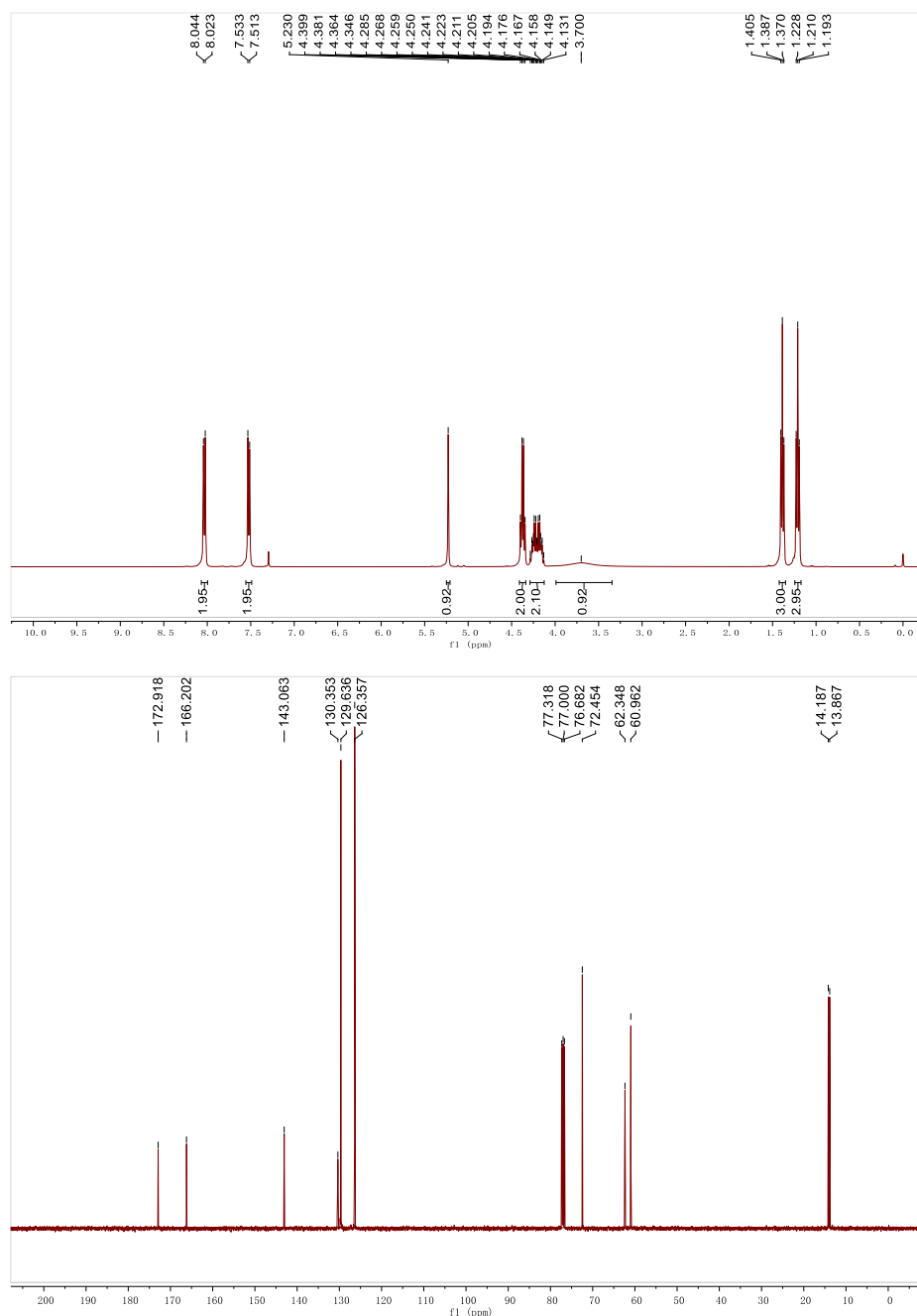
Ethyl 2-(4-chlorophenyl)-2-hydroxyacetate **2f**, known compound.³ White solid; 29.4 mg, 74% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.40 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.07-7.02 (m, 2H), 5.14 (s, 1H), 4.30-4.13 (m, 2H), 3.56 (s, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -

112.46 ~ -112.53 (m). ^{13}C NMR (100 MHz, CDCl_3): δ 173.5, 162.7 (d, $J = 245.1$ Hz), 134.2 (d, $J = 3.2$ Hz), 128.2 (d, $J = 8.3$ Hz), 115.4 (d, $J = 21.6$ Hz), 72.1, 62.3, 14.0.



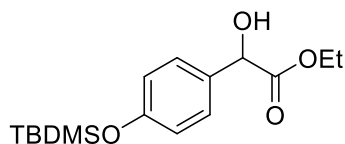
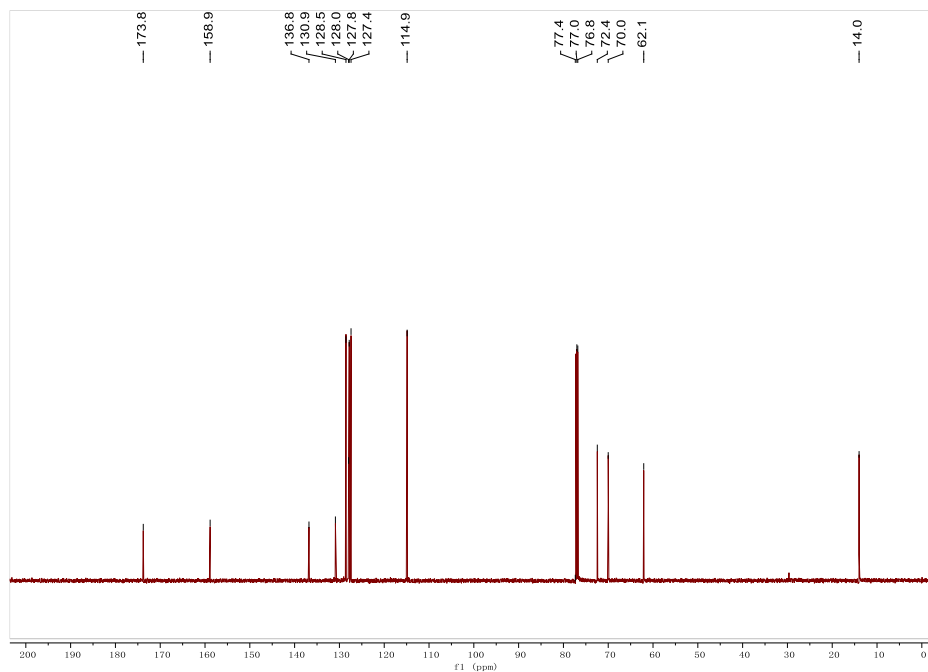
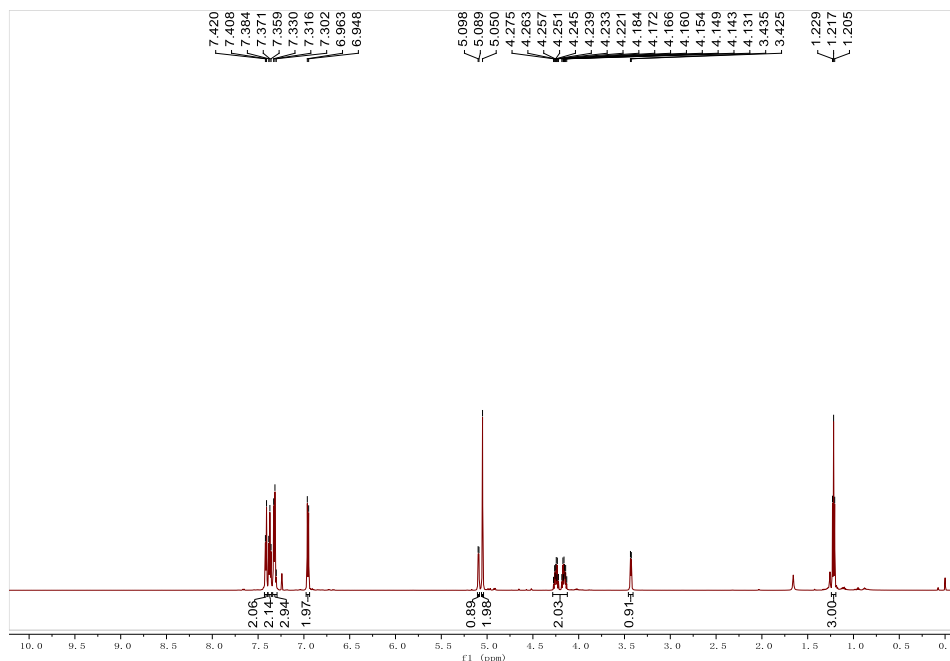


Ethyl 4-(2-ethoxy-1-hydroxy-2-oxoethyl) 2g, a known compound.² Colorless liquid; 30.0 mg, 60% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 8.4, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 5.23 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.29-4.13 (m, 2H), 3.70 (s, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.0, 166.2, 143.1, 130.4, 129.6, 126.4, 72.5, 62.4, 61.0, 14.2, 13.9.



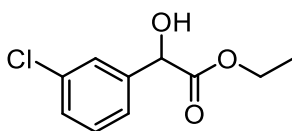
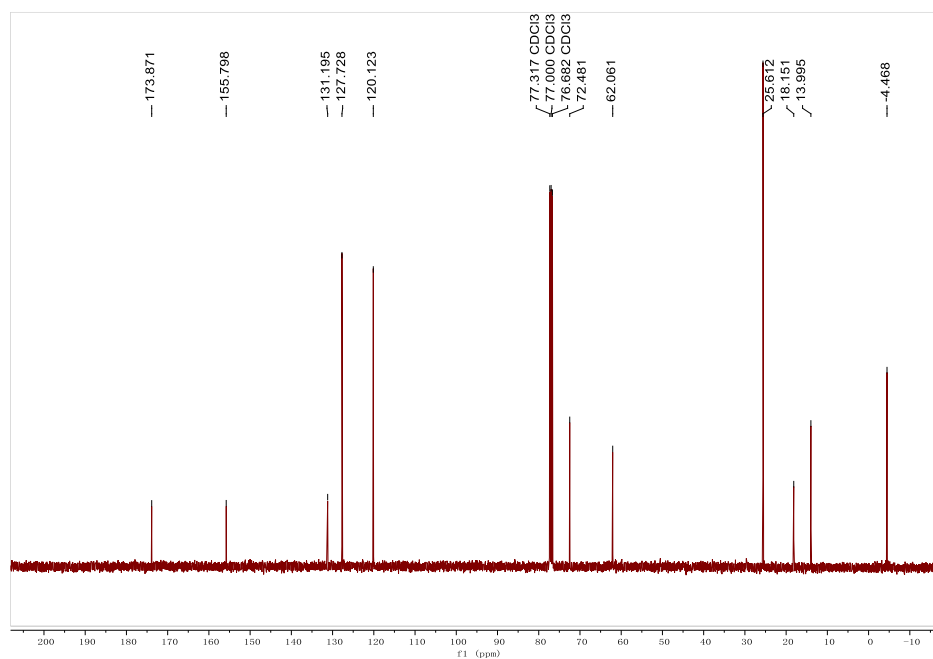
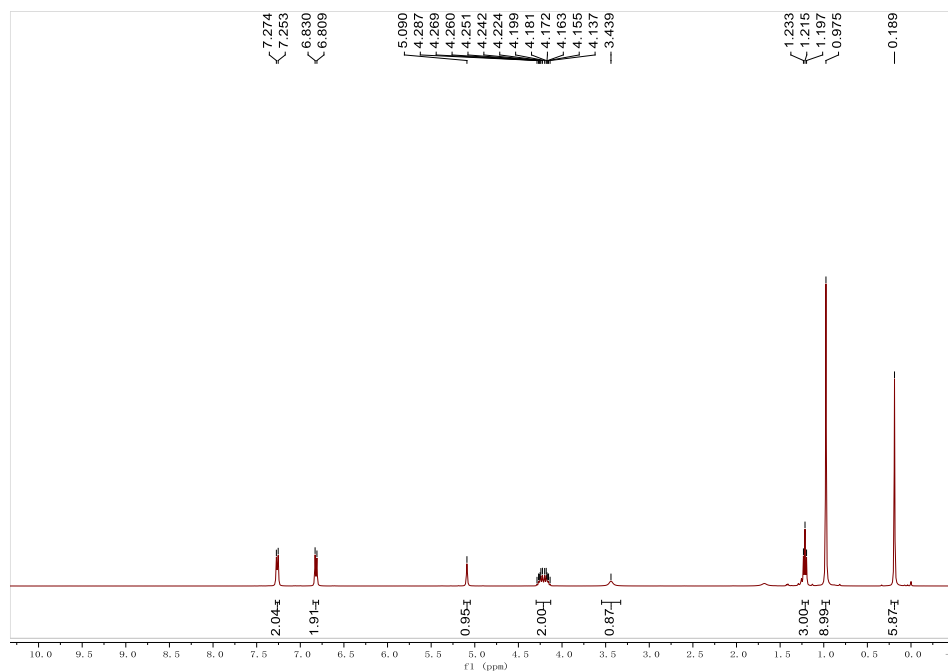
Ethyl 2-(4-(benzyloxy) phenyl)-2-hydroxy acetate 2h, unknown compound. White solid; 48.0 mg, 85% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 8.7 Hz, 3H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.09 (d, *J* = 5.4 Hz, 1H), 5.05 (s, 2H), 4.28-4.13 (m, 2H), 3.43 (d, *J* = 5.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.9, 158.9, 136.8, 130.9, 128.5, 128.0, 127.8, 127.4, 114.9, 72.4, 70.0, 62.1, 14.0. IR (KBr): ν 3449,

3040, 2982, 2906, 2862, 1732, 1202, 1079 cm^{-1} . HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{Na}^+$: 309.1103, found: 309.1097.

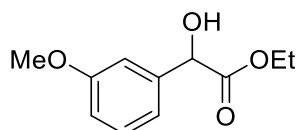
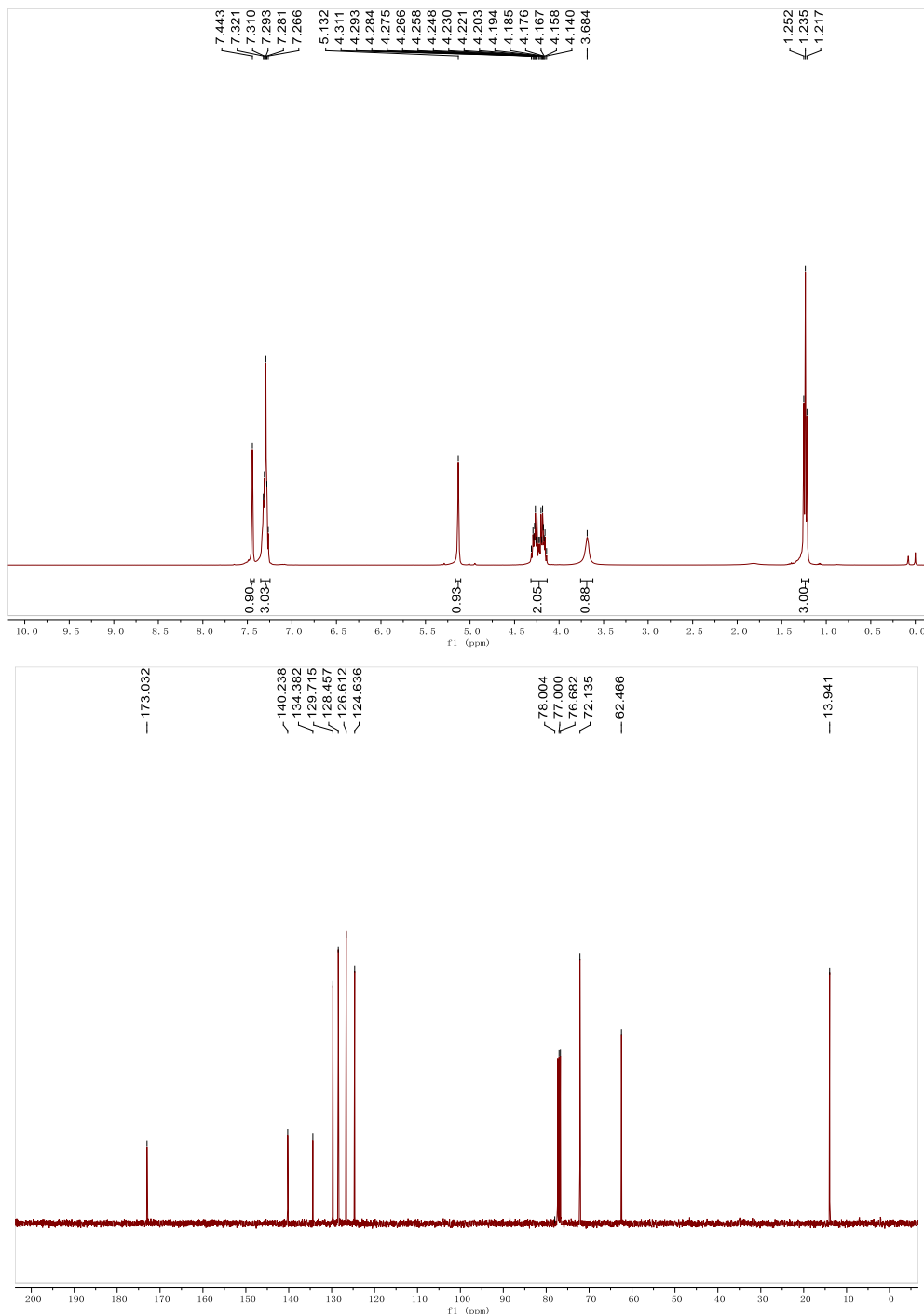


Ethyl 2-(4-(tert-butyl dimethyl silyl)oxy)phenyl-2-hydroxy acetate 2i, unknown compound
 Colorless oil; 45.0 mg, 73% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.26 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 5.09 (s, 1H), 4.29-4.13 (m, 2H), 3.44 (s, 1H), 1.22 (t, $J = 7.2$ Hz, 3H), 0.98 (s, 9H),

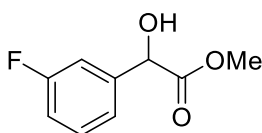
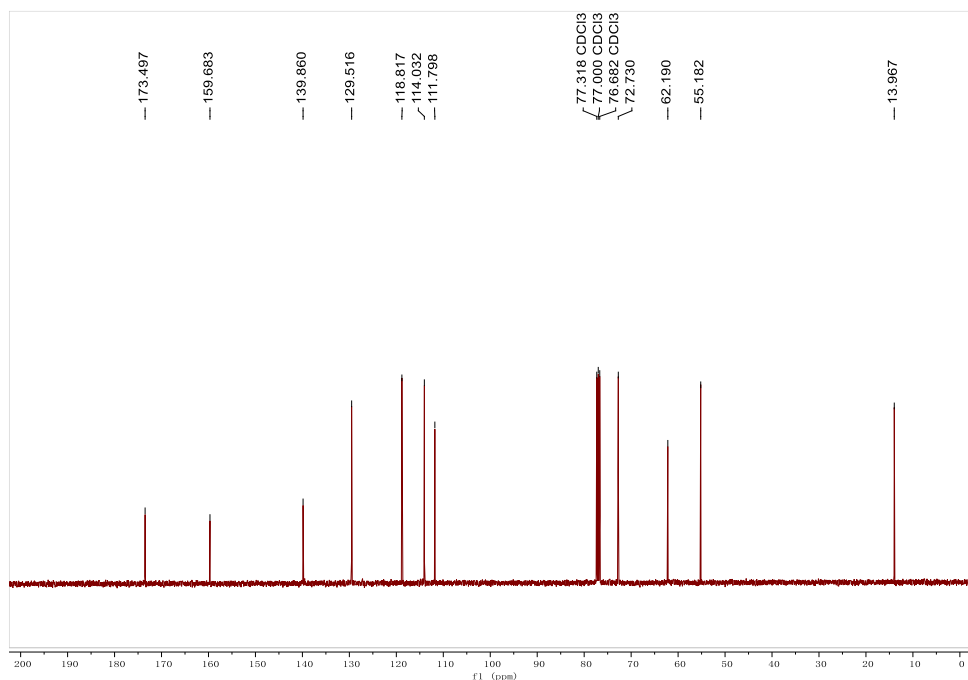
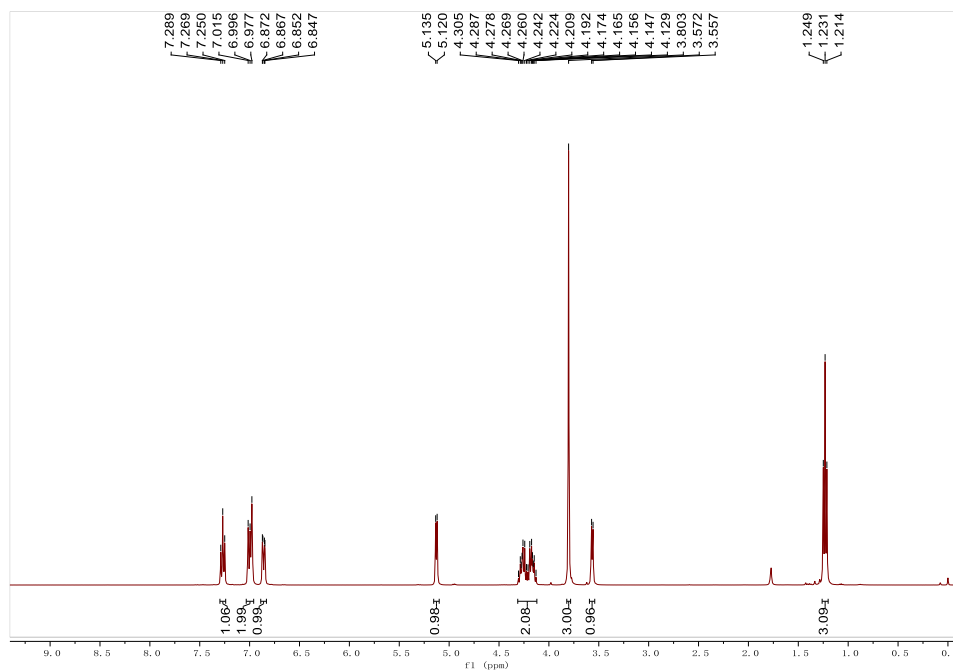
0.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.9, 155.8, 131.2, 127.7, 120.1, 72.5, 62.1, 25.6, 18.2, 14.0, -4.5. IR (KBr): ν 3483, 2955, 2934, 2894, 2859, 1736, 1261, 1082 cm^{-1} . HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4\text{Si Na}^+$: 333.1493, found: 333.1493.



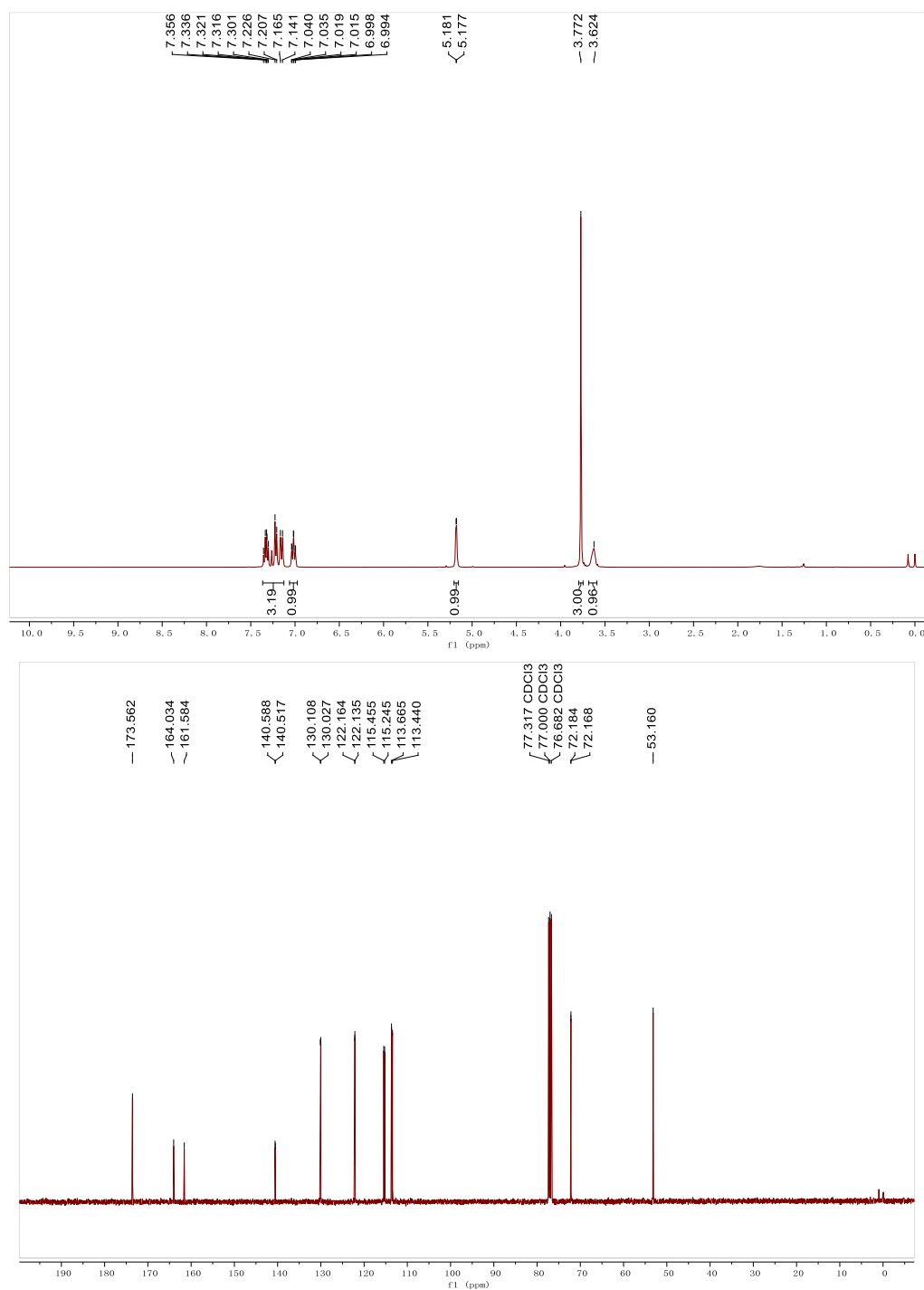
Ethyl 2-(3-chlorophenyl)-2-hydroxyacetate 2j, known compound.² Colorless oil; 31.4 mg, 73% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.44 (s, 1H), 7.32-7.27 (m, 3H), 5.13 (s, 1H), 4.31-4.14 (m, 2H), 3.68 (s, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.0, 140.2, 134.4, 129.7, 128.5, 126.6, 124.6, 72.1, 62.5, 13.9.

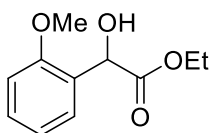
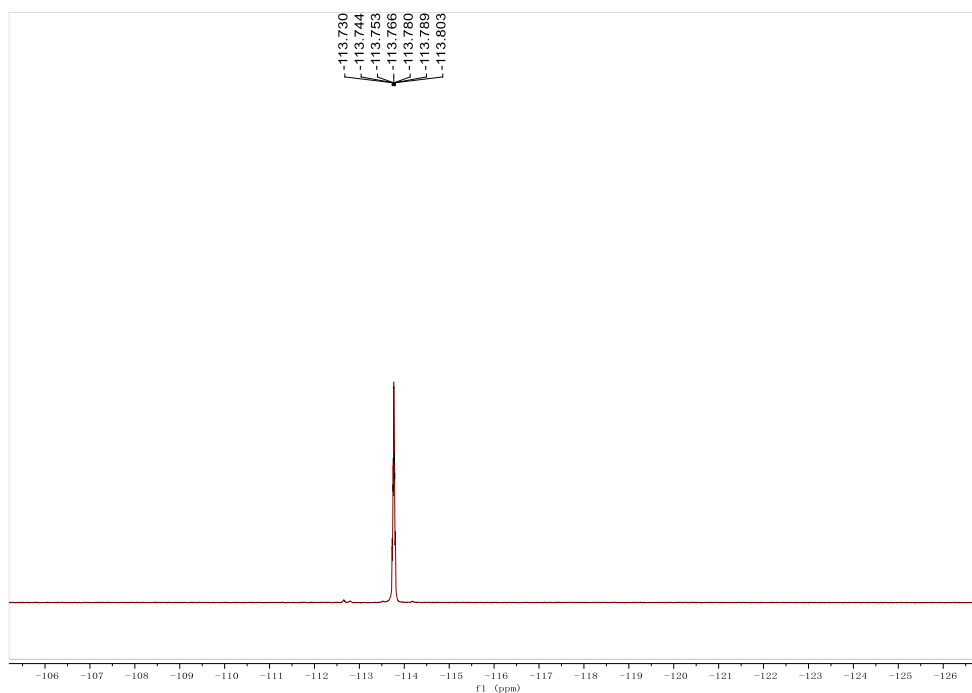


Ethyl 2-hydroxy-2-(3-methoxyphenyl) acetate (2k), known compound.⁴ White solid; 27.0 mg, 64% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.25 (m, 1H), 7.02-6.97 (m, 2H), 6.86 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.13 (d, *J* = 6.0 Hz, 1H), 4.31-4.12 (m, 2H), 3.80 (s, 3H), 3.56 (d, *J* = 6.0 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), ¹³C NMR (100 MHz, CDCl₃): δ 173.5, 159.7, 139.9, 129.5, 118.8, 114.0, 111.8, 72.7, 62.2, 55.2, 14.0.

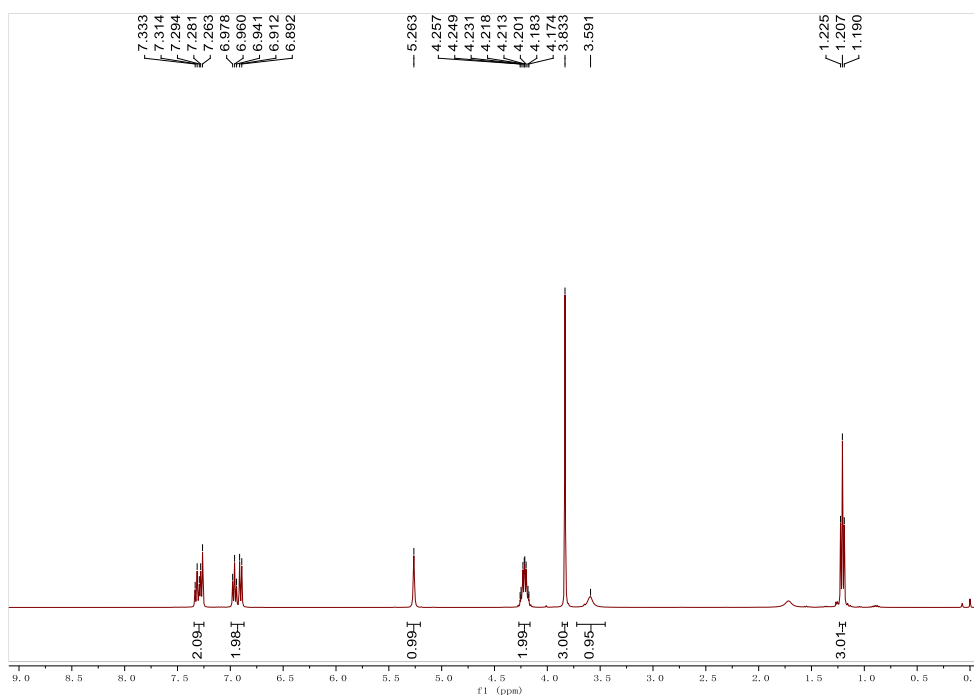


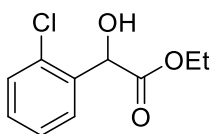
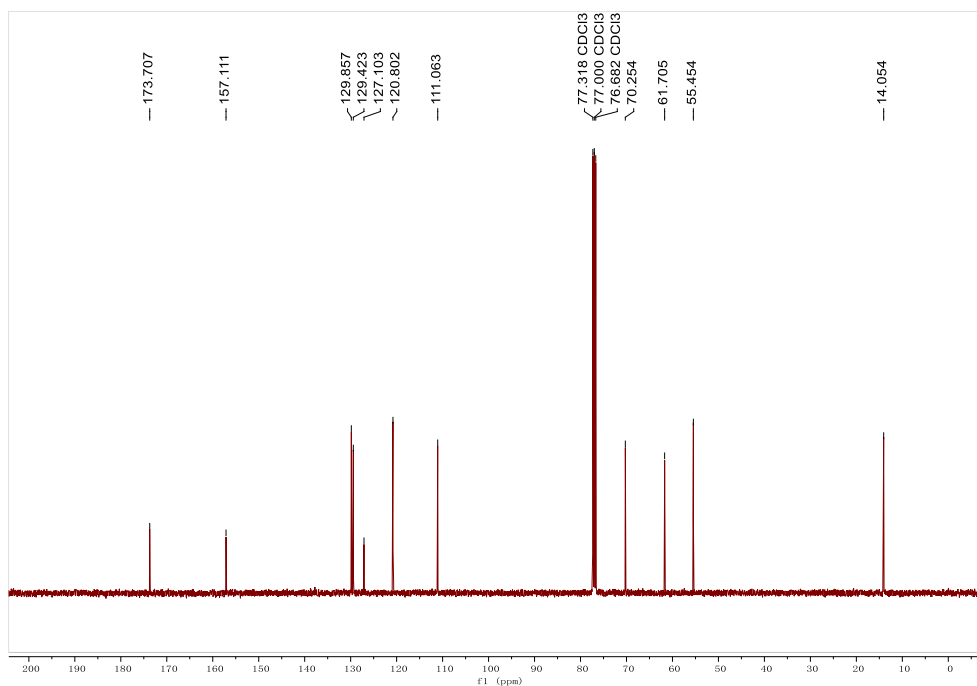
Methyl 2-(3-fluorophenyl)-2-hydroxyacetate **2l**, known compound.³ Colorless oil; 26.0 mg, 70% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.14 (m, 3H), 7.02 (ddd, *J* = 8.4, 8.4, 1.7 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.73 ~ -113.80 (m). ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 162.8 (d, *J* = 245.0 Hz), 140.6 (d, *J* = 7.1 Hz), 130.1(d, *J* = 8.1 Hz), 122.1(d, *J* = 2.9 Hz), 115.4 (d, *J* = 21.0 Hz), 113.6 (d, *J* = 22.5 Hz), 72.2 (d, *J* = 1.6 Hz), 53.2.



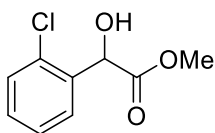
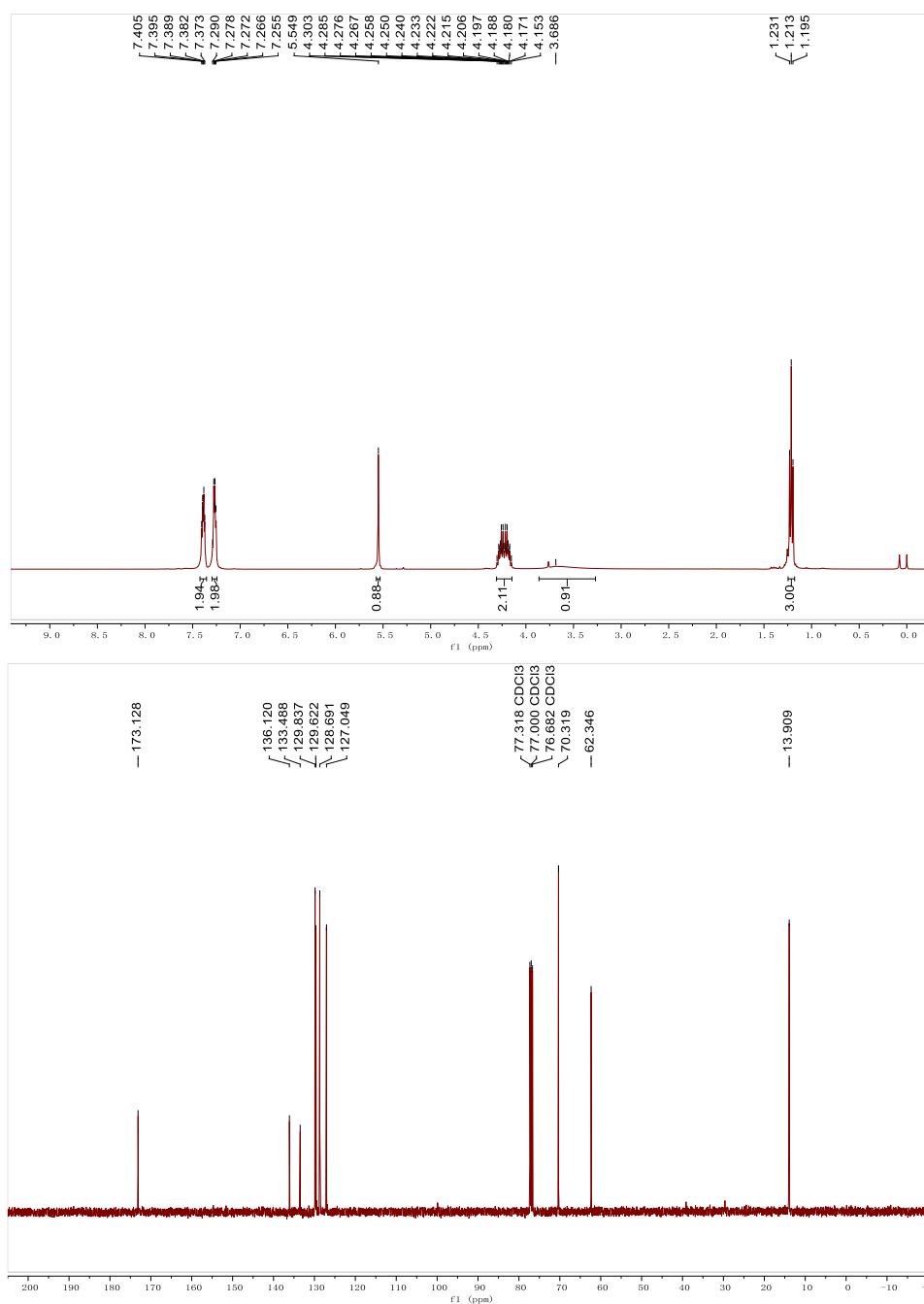


Ethyl 2-hydroxy-2-(2-methoxyphenyl)acetate 2m, known compound.⁴ White solid; 28.0 mg, 66% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.26 (m, 2H), 6.98-6.89 (m, 2H), 5.26 (s, 1H), 4.26-4.17 (m, 2H), 3.83 (s, 3H), 3.59 (s, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 157.1, 129.9, 129.4, 127.1, 120.8, 111.1, 70.3, 61.7, 55.5, 14.1.

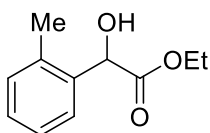
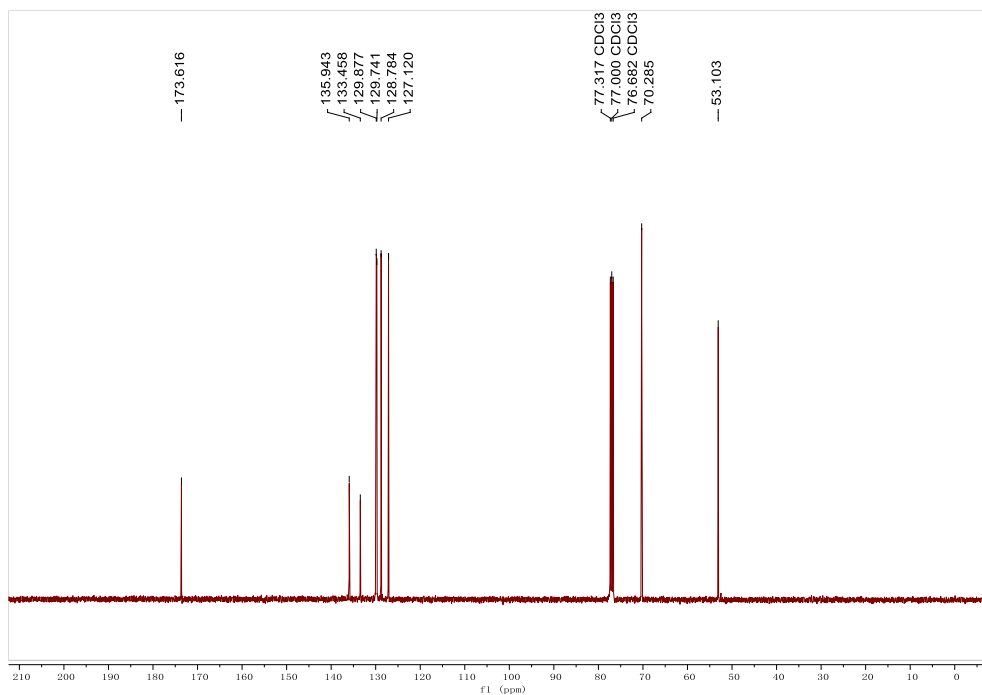
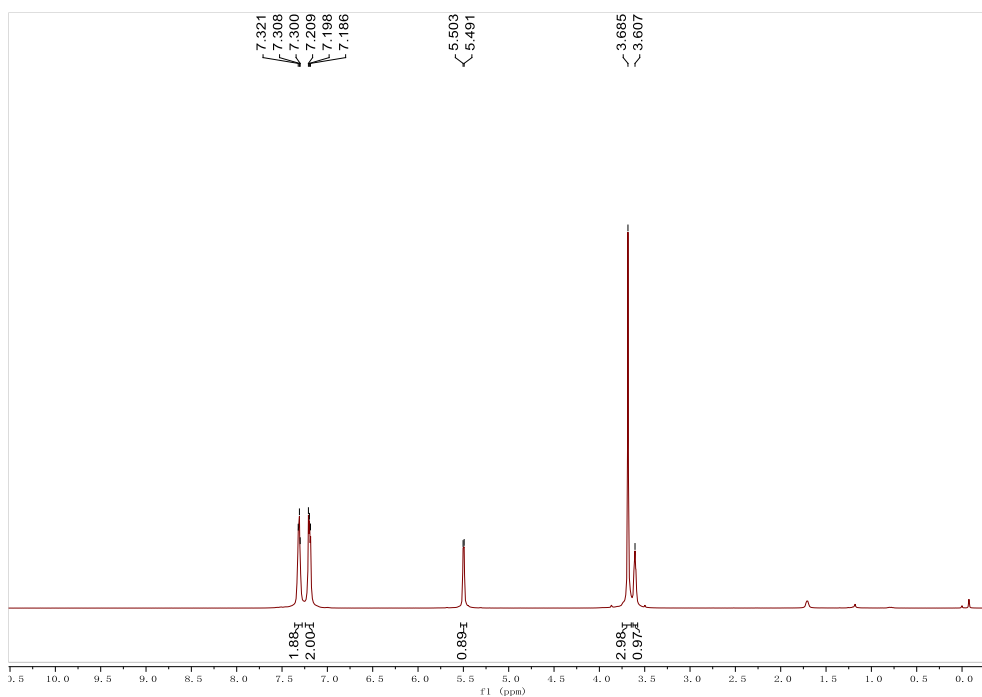




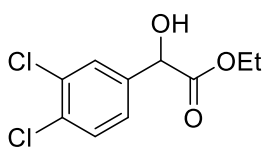
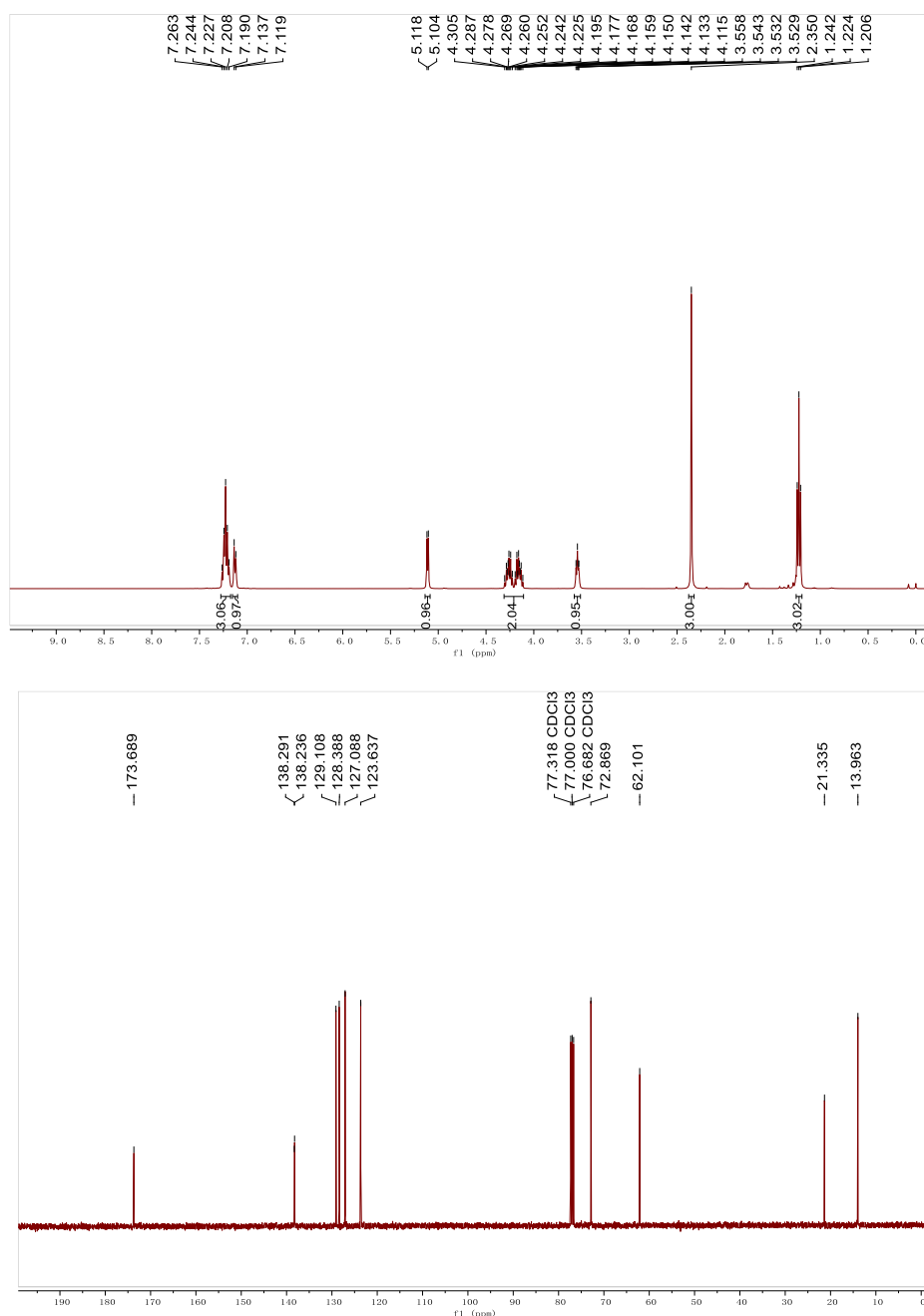
Ethyl 2-(2-chlorophenyl)-2-hydroxyacetate 2n, known compound.² Pale yellow oil; 34.4 mg, 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.37 (m, 2H), 7.29-7.26 (m, 2H), 5.55 (s, 1H), 4.30-4.15 (m, 2H), 3.69 (s, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 136.1, 133.5, 129.8, 129.6, 128.7, 127.1, 70.3, 62.4, 13.9.



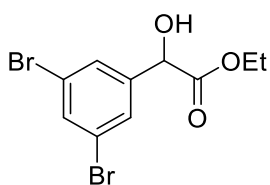
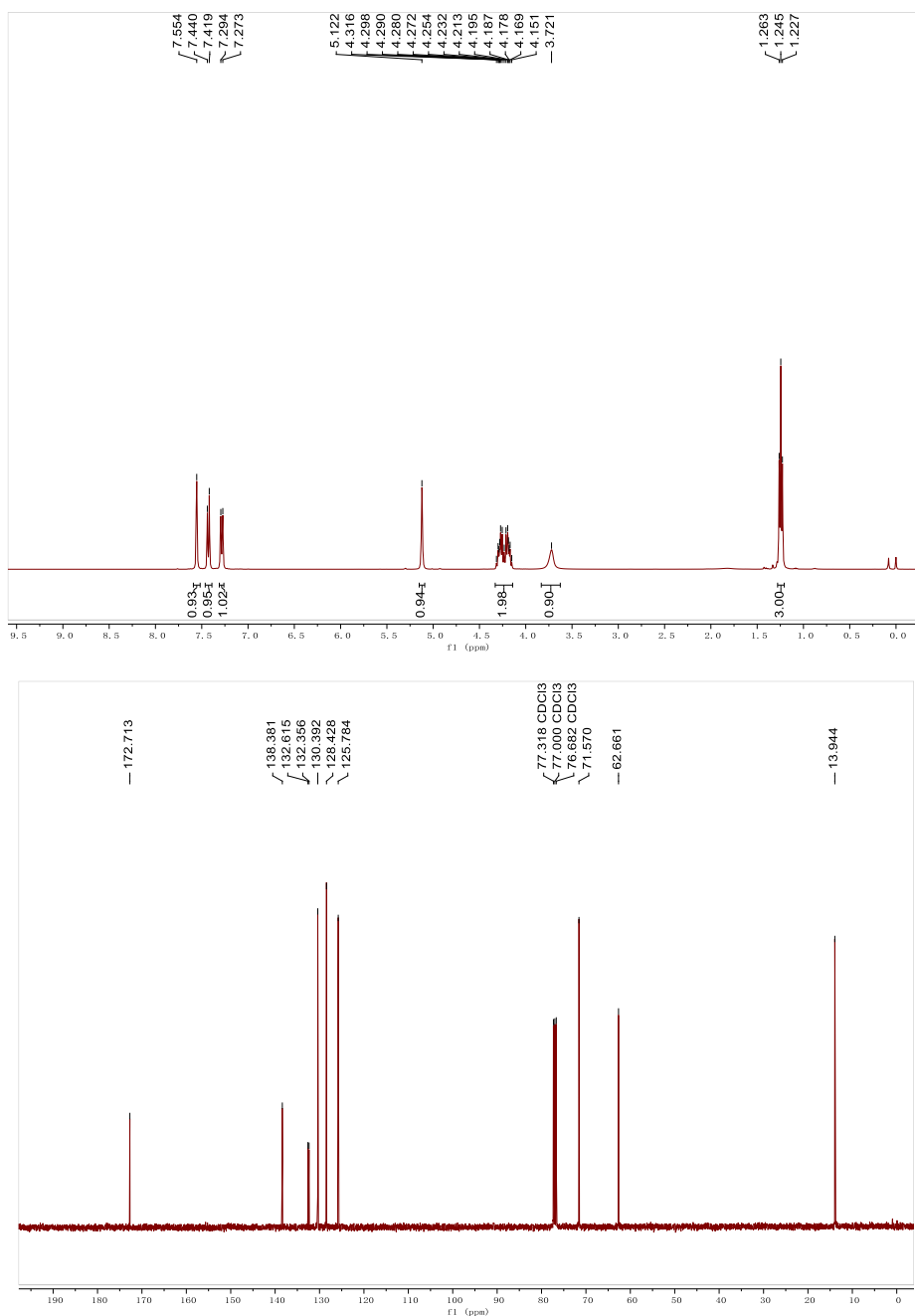
Methyl 2-(2-chlorophenyl)-2-hydroxyacetate **2o**, known compound.² Colorless oil; 28.0 mg, 70% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.30 (m, 2H), 7.21-7.18 (m, 2H), 5.50 (d, *J* = 4.8 Hz, 1H), 3.69 (s, 3H), 3.61 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 135.9, 133.5, 129.9, 129.7, 128.8, 127.1, 70.3, 53.1.



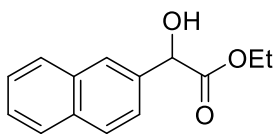
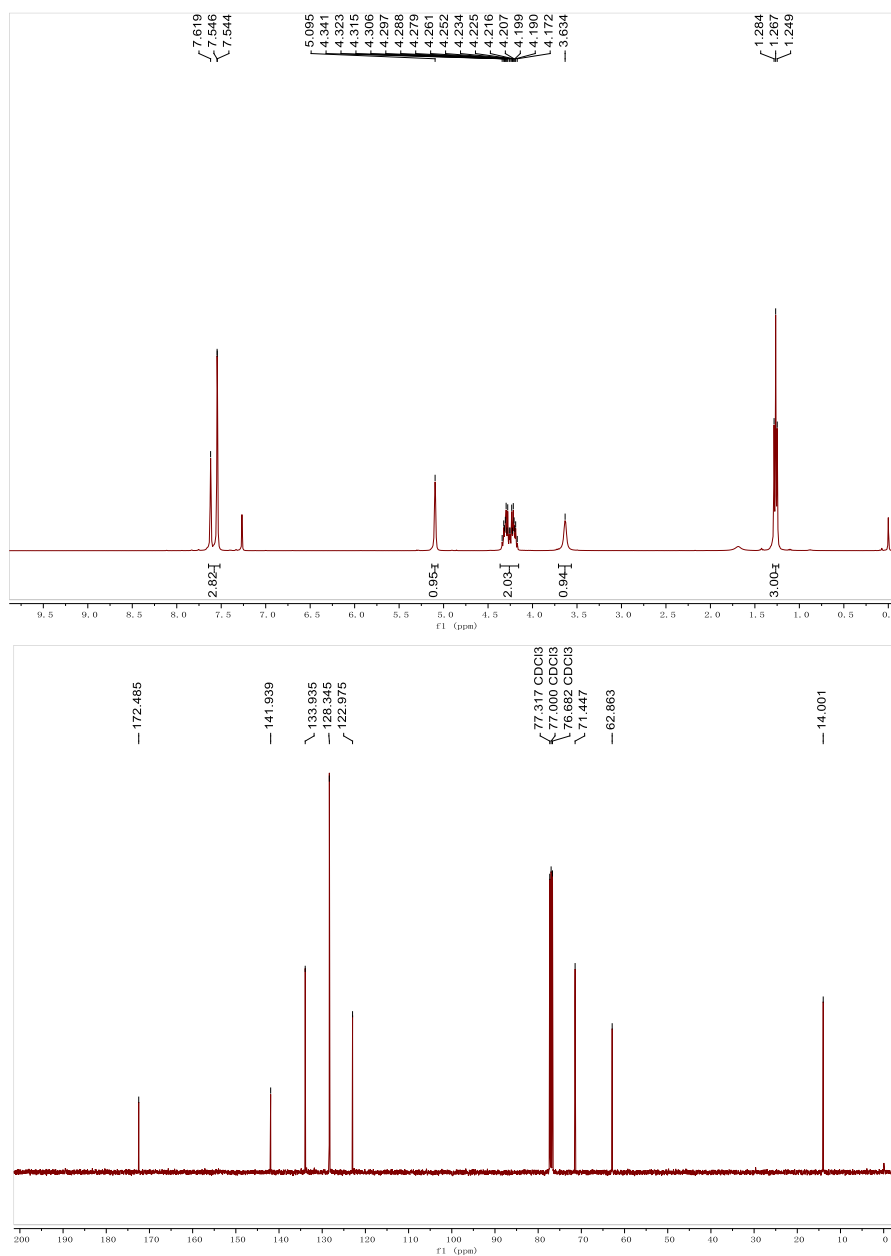
Ethyl 2-hydroxy-2-*o*-tolylacetate 2p, known compound.² Colorless oil; 25.4 mg, 65% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.23 (q, *J* = 7.4 Hz, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 5.11 (d, *J* = 5.8 Hz, 1H), 4.31-4.12 (m, 2H), 3.54 (dd, *J* = 8.1, 3.4 Hz, 1H), 2.35 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 138.3, 138.2, 129.1, 128.4, 127.1, 123.6, 72.9, 62.1, 21.3, 14.0.



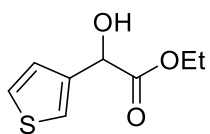
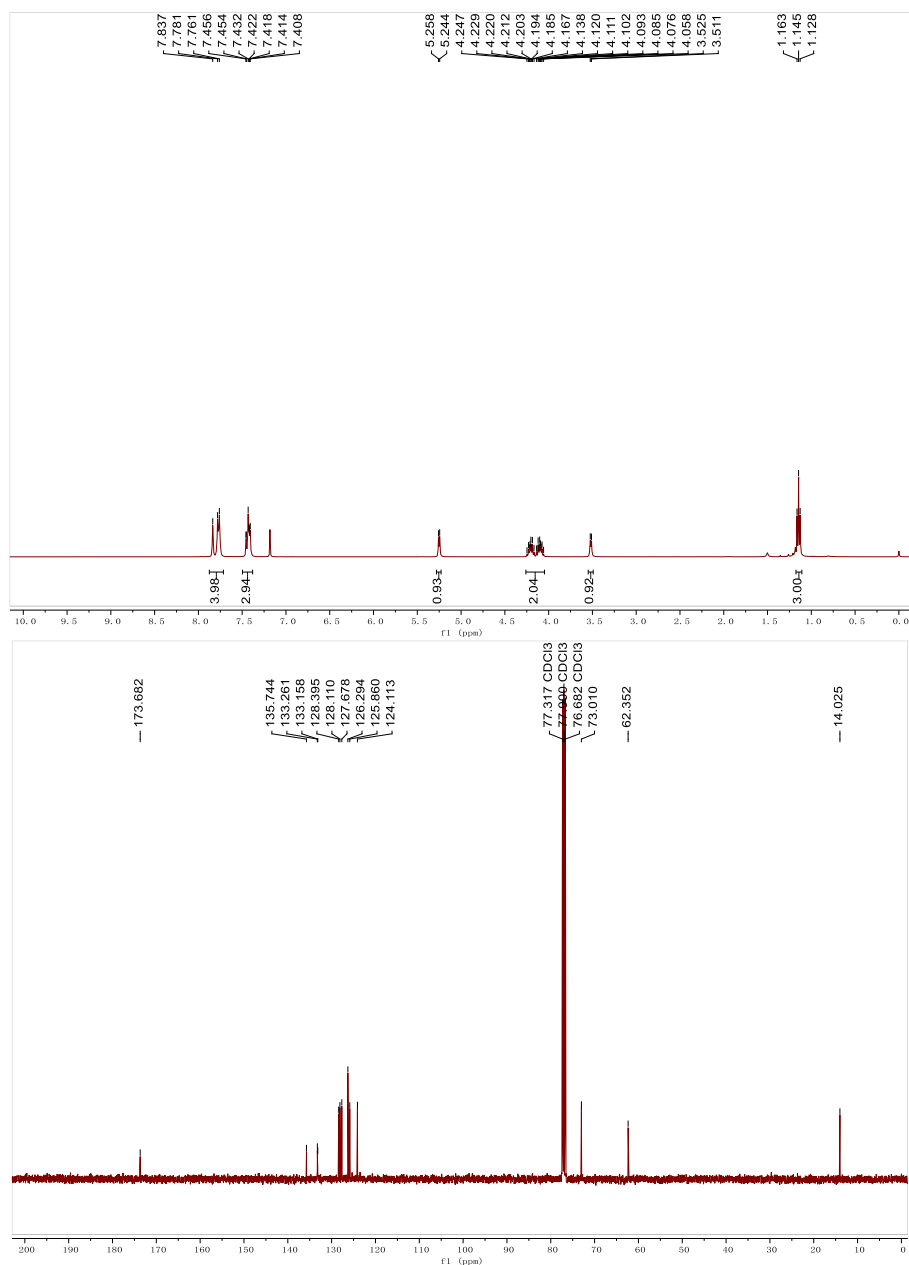
Ethyl 2-(3,4-dichlorophenyl)-2-hydroxyacetate 2q, known compound.² White solid; 39.4 mg, 79% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.12 (s, 1H), 4.32-4.15 (m, 2H), 3.72 (s, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.7, 138.4, 132.6, 132.4, 130.4, 128.4, 125.8, 71.6, 62.7, 13.9.



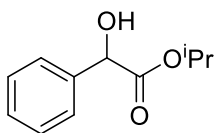
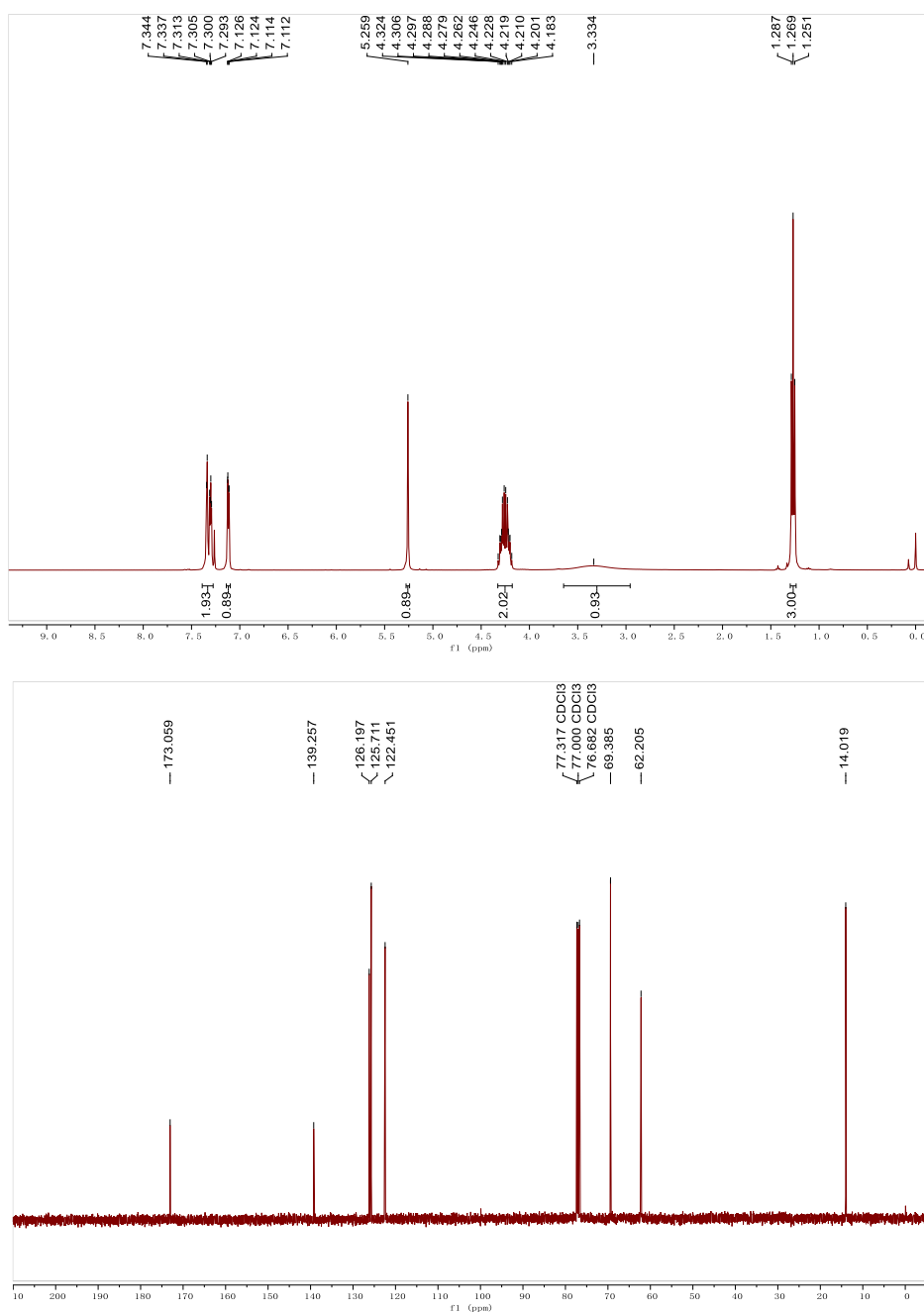
Ethyl 2-(3,5-dibromophenyl)-2-hydroxyacetate 2r, unknown compound. Brown oil liquid; 38.4 mg, 57% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.54 (m, 3H), 5.10 (s, 1H), 4.34-4.17 (m, 2H), 3.63 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 142.0, 134.0, 128.3, 123.0, 71.4, 62.9, 14.0. IR (KBr): ν 3475, 3077, 2983, 2907, 2872, 1739, 1560, 1189 cm⁻¹. HRMS (EI) Calcd for C₁₀H₁₀Br₂O₃Na⁺: 358.8894; found: 358.8888.



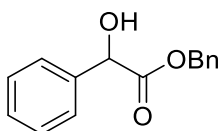
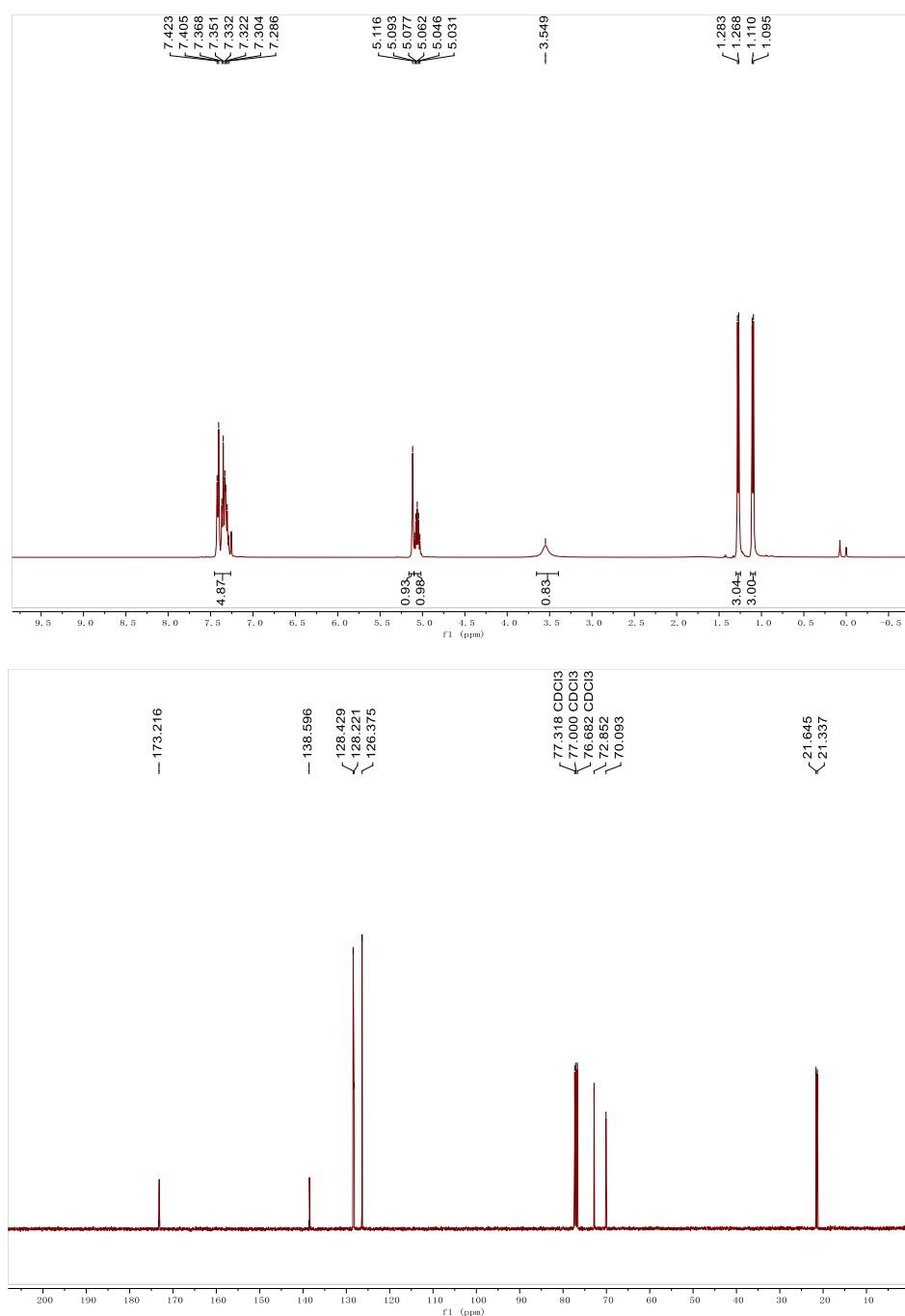
Ethyl 2-hydroxy-2-(naphthalen-2-yl)acetate 2s, known compound.² White solid; 30.0 mg, 65% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.76 (m, 4H), 7.46-7.40 (m, 3H), 5.25 (d, *J* = 5.6 Hz, 1H), 4.25-4.05 (m, 2H), 3.52 (d, *J* = 5.6 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 135.7, 133.3, 133.2, 128.4, 128.1, 127.7, 126.3, 125.9, 124.1, 73.0, 62.4, 14.0.



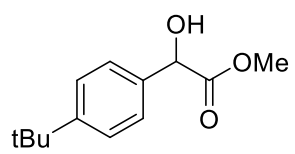
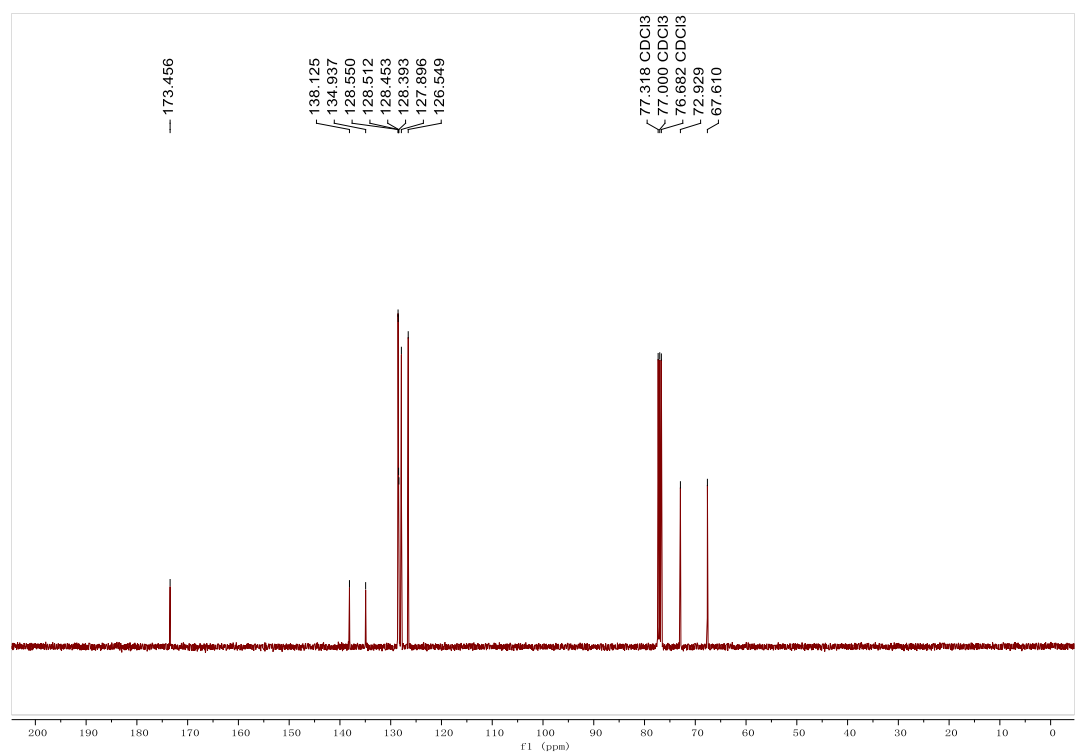
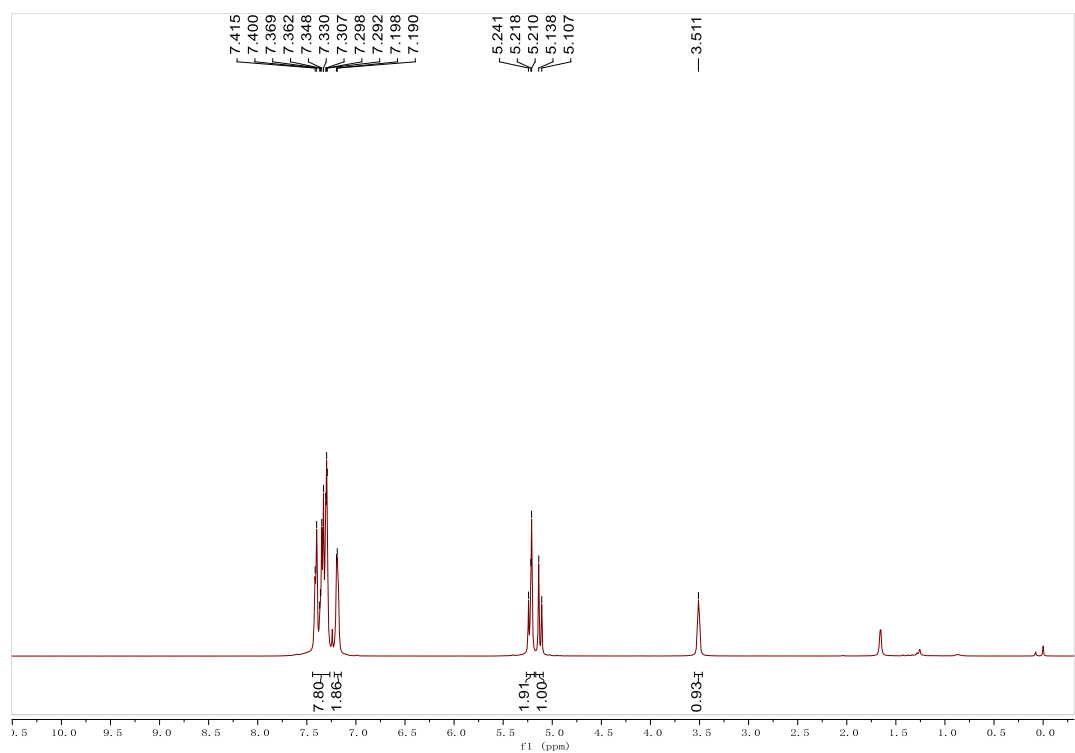
Ethyl 2-hydroxy-2-thiophene-3-ylacetate **2t**, known compound.² Pale yellow oil; 26.4 mg, 71% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.29 (m, 2H), 7.12 (dd, *J* = 4.8 Hz, 1.0 Hz, 1H), 5.26 (s, 1H), 4.32-4.18 (m, 2H), 3.33 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 139.3, 126.2, 125.7, 122.5, 69.4, 62.2, 14.0.



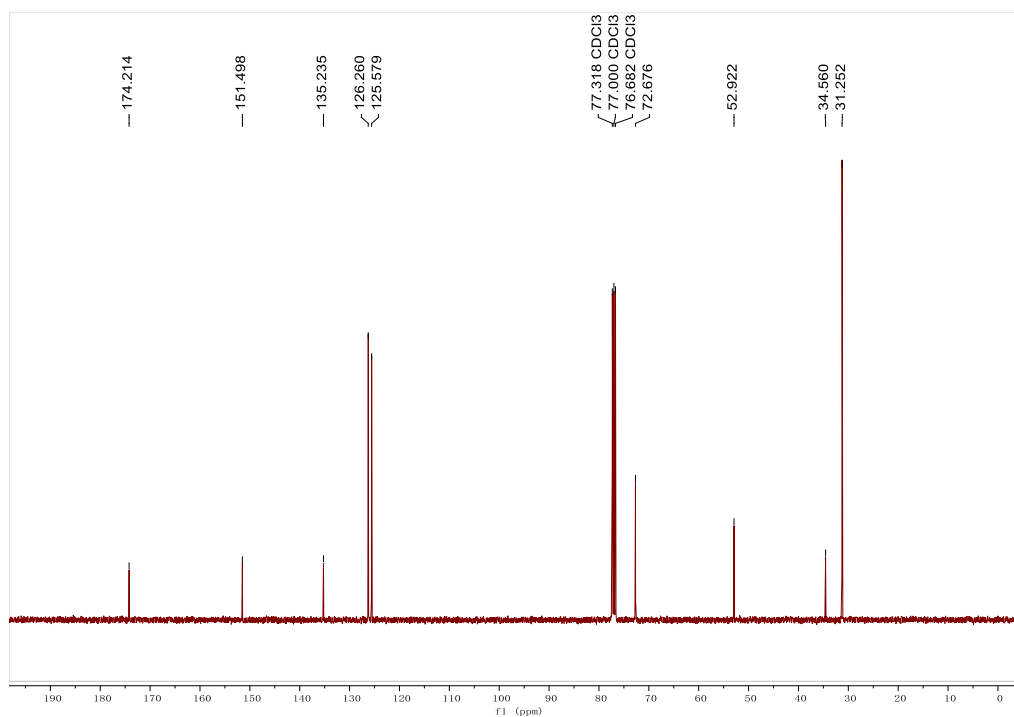
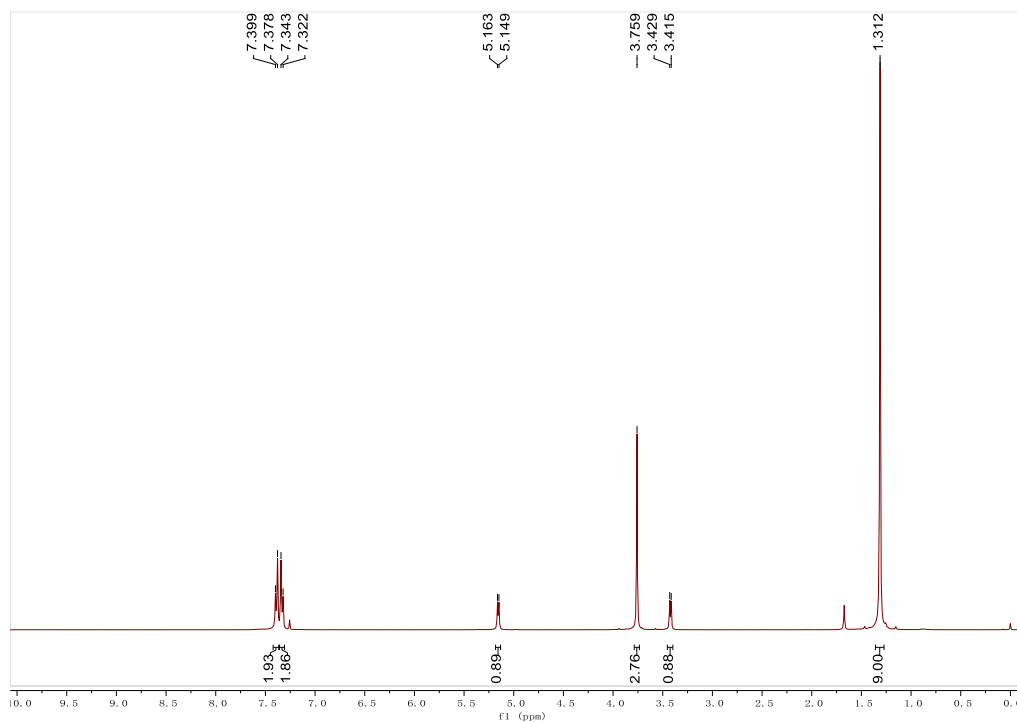
Isopropyl 2-hydroxy-2-phenylacetate 2u, known compound.⁶ Colorless oil; 26.0 mg, 67% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.28 (m, 5H), 5.12 (s, 1H), 5.10-5.03 (m, 1H), 3.55 (s, 1H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.10 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 173.2, 138.6, 128.4, 128.2, 126.4, 72.9, 70.1, 21.6, 21.3.

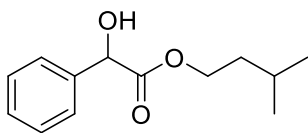


Benzyl 2-hydroxy-2-phenylacetate 2v, known compound.⁶ White solid; 30.0 mg, 62% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.29 (m, 8H), 7.20-7.19 (m, 2H), 5.24-5.21 (m, 2H), 5.12 (d, *J* = 12.4 Hz, 1H), 3.51 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 173.5, 138.1, 134.9, 128.6, 128.5, 128.4, 128.3, 127.9, 126.6, 72.9, 67.6.

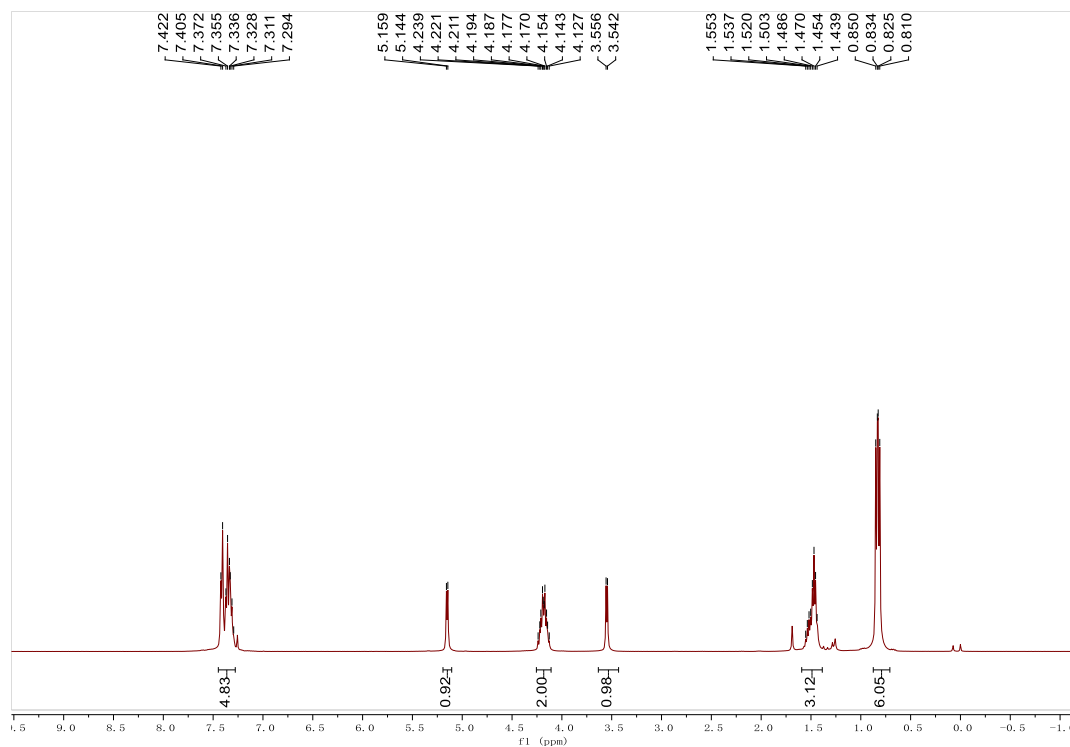


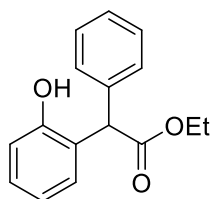
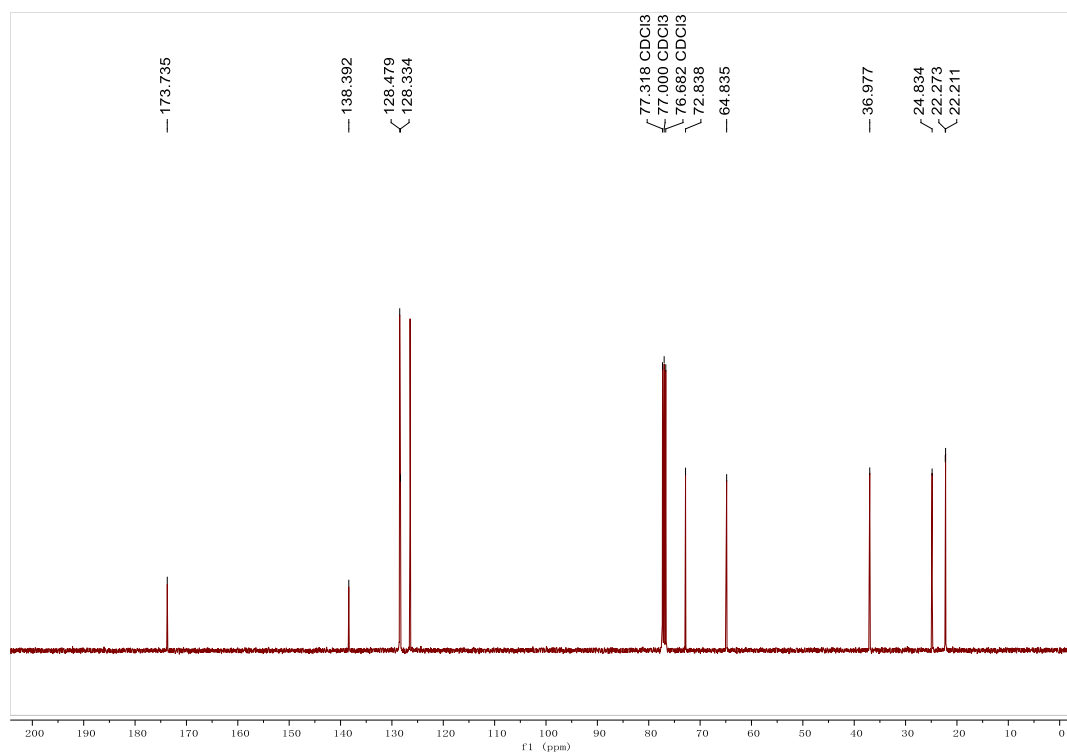
Methyl 2-(4-(tert-butyl) phenyl)-2-hydroxyacetate **2w**, known compound.⁷ Colorless liquid; 24.4 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.16 (d, *J* = 5.6 Hz, 1H), 3.76 (s, 3H), 3.42 (d, *J* = 5.6 Hz, 1H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 174.2, 151.5, 135.2, 126.3, 125.6, 72.7, 52.9, 34.6, 31.3.



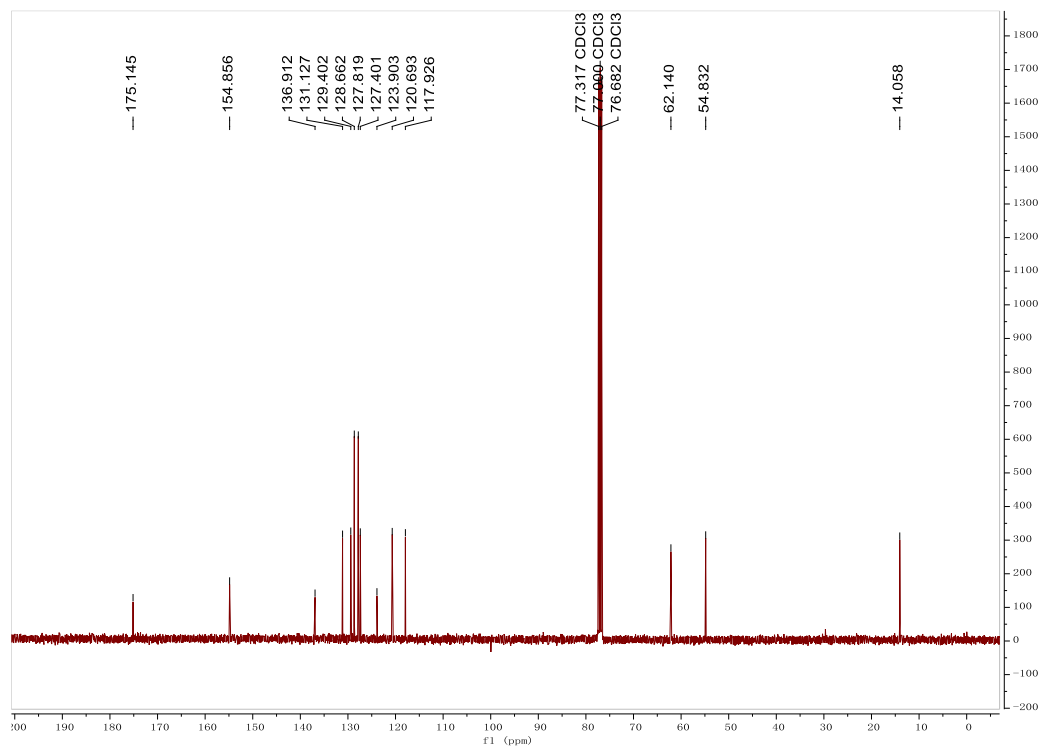
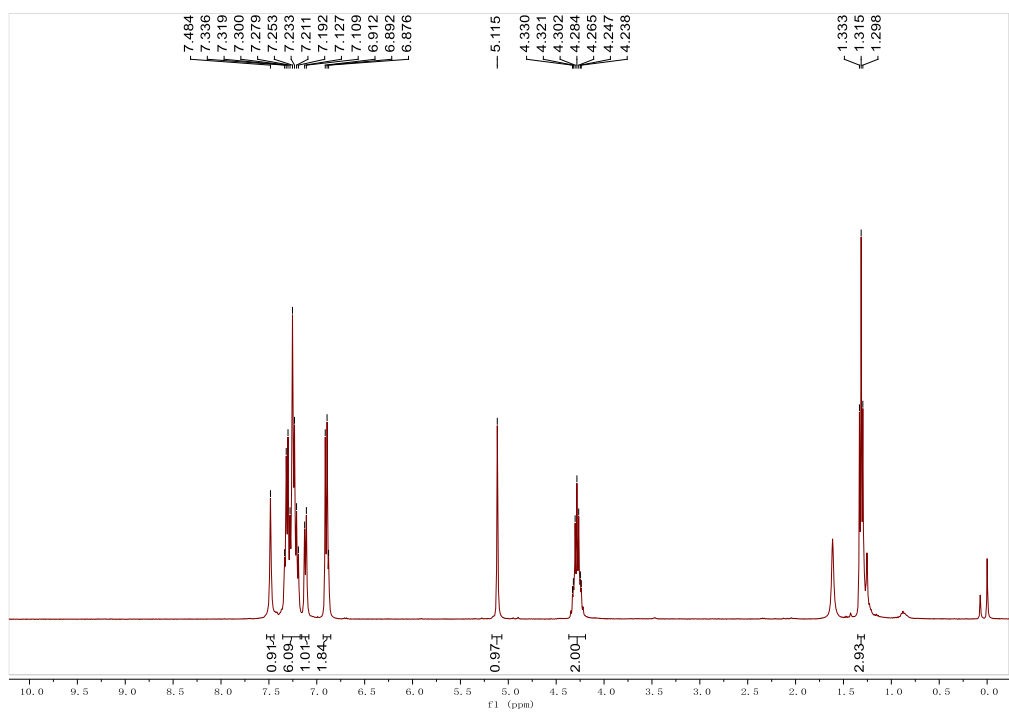


Isopentyl 2-hydroxy-2-phenylacetate **2x**, known compound.⁸ Colorless liquid; 27.0 mg, 61% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.29 (m, 5H), 5.15 (d, *J* = 6.0 Hz, 1H), 4.24-4.12 (m, 2H), 3.55 (d, *J* = 5.6 Hz, 1H), 1.55-1.43 (m, 3H), 0.83 (dd, *J* = 9.8, 6.2 Hz, 6H), ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 138.4, 128.5, 128.3, 72.8, 64.8, 37.0, 24.8, 22.3, 22.2.





Ethyl-2(2-hydroxyphenyl)-2-(phenylacetate) **3a**, known compound,⁹ White solid; 66.6 mg, 65% yield; ¹H NMR (400 MHz, CDCl₃): δ ¹H NMR 7.48 (s, 1H), 7.33-7.19 (m, 6H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.91-6.87 (m, 2H), 5.12 (s, 1H), 4.33- 4.23 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 175.2, 154.9, 136.9, 131.1, 129.4, 128.7, 127.8, 127.4, 123.9, 120.7, 117.9, 62.1, 54.8, 14.1.



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