

Supplementary Information

for

**Transition-metal-free C(sp³)-C(sp²) couplings with secondary
alcohols and boronic acids via neighboring group activation**

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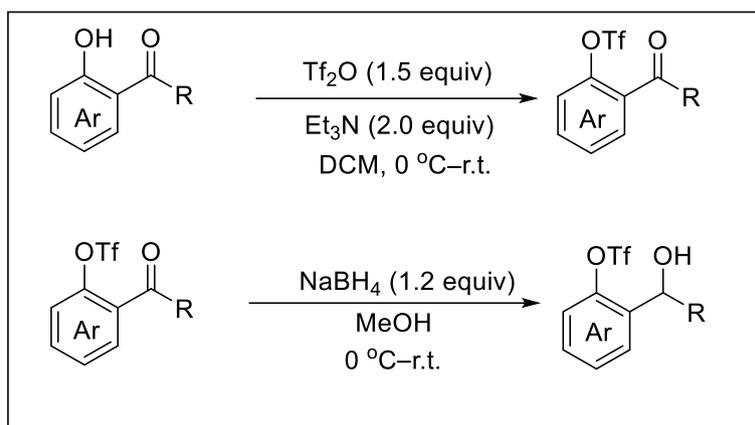
1. General information

Unless otherwise noted, commercialized reagents were used without further purifications. Toluene was purchased from Sigma-Aldrich Chemical Co. and Yonghua Chemical Co. 1,2-Dichloroethane was purchased from Sinopharm Group Co. All other solvents were purified and dried according to standard methods before use. Potassium phosphate was purchased from Shanghai Aladdin Biochemical Technology Co.

^1H NMR, ^{31}P NMR, ^{19}F NMR, and ^{13}C NMR data were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 MHz Agilent spectrometer Bruker AVANCE NEO 600M with CDCl_3 as the solvent. ^1H chemical shifts were referenced to CDCl_3 at 7.26 ppm. ^{13}C chemical shifts were referenced to CDCl_3 at 77.16 ppm and obtained with ^1H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), multiplet (m), and broad (br). HRMS was measured on GCTOF-HRMS, Waters GCT Premier or MALDI-TOF MS, Bruker Ultraflex.

2. General procedures for the synthesis of secondary alcohols

2.1 Preparation of 2-(1-hydroxyethyl)phenyl trifluoromethanesulfonate and its derivatives

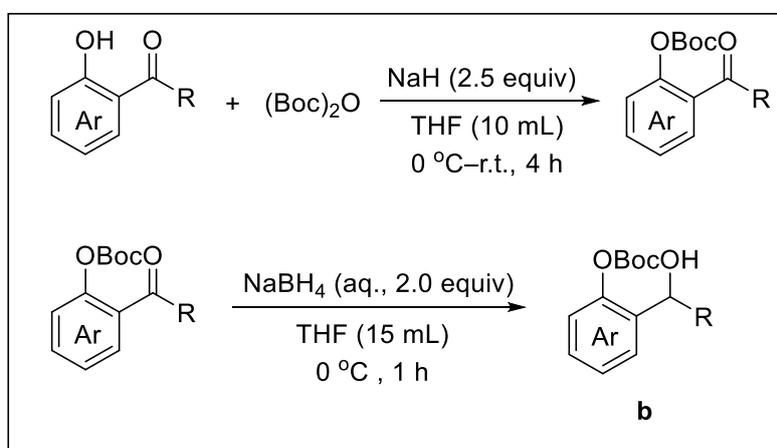


To a solution of ketone (5 mmol, 1.0 equiv) and Et_3N (10 mmol, 2.0 equiv) in DCM (0.1 M) was added Tf_2O (1.5 equiv) dropwise at $0\text{ }^\circ\text{C}$. The reaction mixture was then allowed to stir at room temperature for 8 h. Then the mixture was quenched by H_2O and diluted by DCM . The solution was washed with brine, dried over Na_2SO_4 , filtered, and concentrated in vacuo. The crude residue was purified by flash column

chromatography over silica gel (EtOAc/petroleum ether = 1/40) to provide the desired product.

To a solution of protected ketones (5 mmol, 1.0 equiv) in MeOH (0.1 M) was added NaBH₄ (6 mmol, 1.2 equiv) portion-wise at 0 °C. The reaction mixture was then allowed to stir at room temperature for 0.5 h. Then the mixture was quenched by H₂O and diluted by EtOAc. The solution was washed with 0.5 N HCl, brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography over silica gel (EtOAc/petroleum ether = 1/10) to provide the desired 2-(1-hydroxyethyl)phenyl trifluoromethanesulfonate and its derivatives.

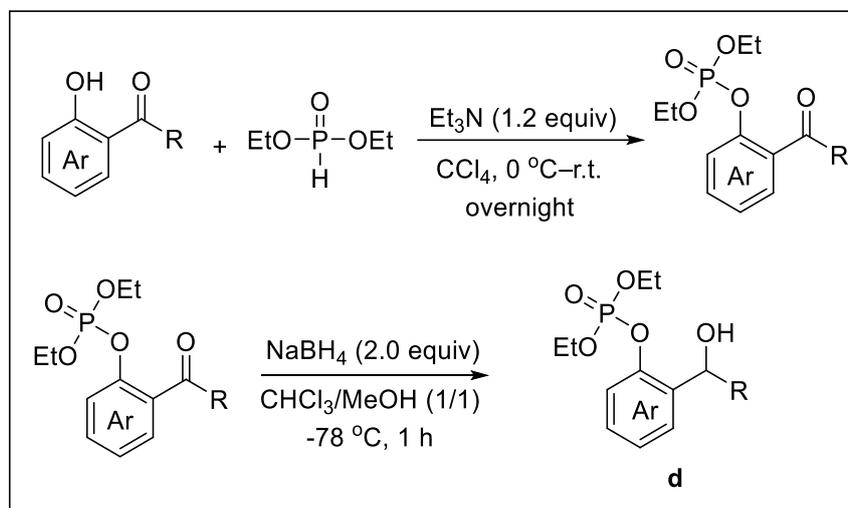
2.2 Preparation of *t*-butyl (2-(1-hydroxyethyl)phenyl) carbonate and its derivatives



To a solution of the phenol (5 mmol, 1 equiv) at 0 °C was added the di-*tert*-butyl dicarbonate (2.73 g, 12.5 mmol, 2.5 equiv) followed by sodium hydride (0.50 g, 12.5 mmol, 60% in oil). The mixture was stirred at room temperature for 4 hours, after which the reaction was quenched by the addition of water, extracted with ethyl acetate, and washed with brine. The organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography with silica gel (EtOAc/petroleum ether = 1/10) to give the Boc-protected ketones.

The Boc-protected ketones (5 mmol, 1 equiv) were dissolved in 15 mL of THF and cooled down to 0 °C. A 15 mL solution of NaBH₄ (0.38 g, 10 mmol, 2 equiv) in water precooled to was then added with stirring. The reaction was then monitored by TLC. After 1 hour the reaction was quenched by 0.5 N HCl and then extracted with ethyl acetate, and washed with brine. The organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash chromatography with silica gel (EtOAc/petroleum ether = 1/5) to give the desired material.

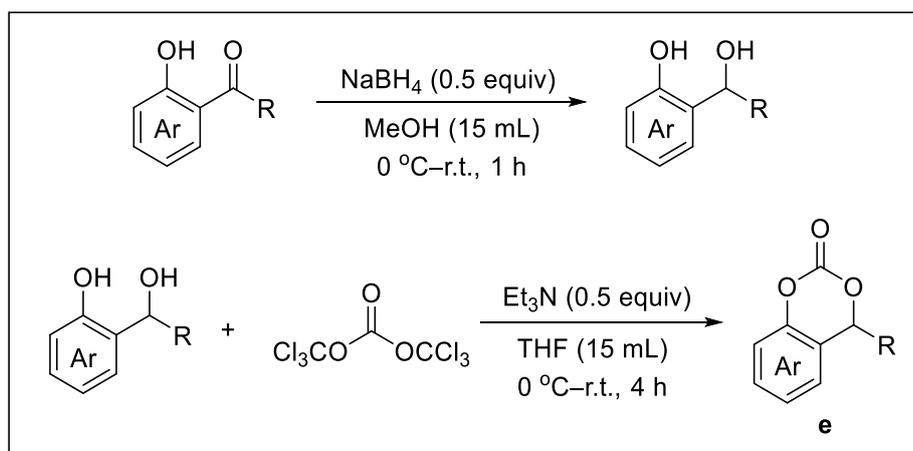
2.3 Preparation of diethyl (2-(1-hydroxyethyl)phenyl) phosphate and its derivatives



Et₃N (0.83 mL, 6.0 mmol, 1.2 equiv) was added dropwise to a solution of the phenol (5.0 mmol, 1 equiv, 1.0 M in CCl₄) at 0 °C, and diethyl phosphite (0.77 mL, 6 mmol, 1.2equiv.) was added very slowly at the same temperature. Then the mixture was moved to room temperature and stirred overnight. After that, the reaction was diluted with water, and the organic layer was washed with 1 N HCl, brine, and distilled water. The organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by chromatography with silica gel (EtOAc/petroleum ether = 1/2) to give the corresponding diethyl phosphate ketones.

The obtained diethyl phosphate material (5.0 mmol, 1 equiv) was suspended in a 30 mL mixture of CHCl₃ and MeOH (v/v 1/1), and the reaction temperature was lowered to -78 °C. After stirring at the same temperature for a few minutes under the N₂ atmosphere, NaBH₄ (378.3 mg, 10 mmol, 2 equiv) was added in portions and the reaction was maintained at -78 °C for 1 hour. After completion, the reaction was diluted with DCM, and quenched by slow addition of 1 N HCl. The organic layer was separated, extracted with saturated NaHCO₃ solution and brine, and then dried over anhydrous Na₂SO₄. The organic layer was concentrated under reduced pressure and the product was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/2).

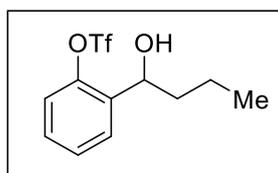
2.4 Preparation of 4-methyl-4*H*-benzo[*d*][1,3]dioxin-2-one and its derivatives



To a stirred solution of the phenol (10 mmol, 1 equiv) dissolved in methanol (15 mL) at 0 °C was added sodium borohydride (5 mmol, 0.5 equiv). After 1h, the mixture was quenched by adding 1 N HCl and then extracted by ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate twice. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product.

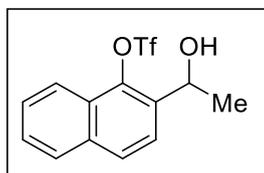
To a solution of secondary alcohol (5 mmol, 1 equiv) and Et₃N (15 mmol, 3 equiv) in THF (15 mL) at 0 °C was added triphosgene (2.5-7.5 mmol, 0.5-1.5 equiv) in toluene dropwise and then stirred at rt. The reaction was then monitored by TLC. After the reaction was completed, the mixture was quenched with water at 0 °C and stirred for 10 minutes. After that, EtOAc was added to the mixture, and the organic phase was separated, the aqueous phase was washed with EtOAc twice. The organic phase was combined, washed with brine, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give the product.

2.5 Analytical data of substrates

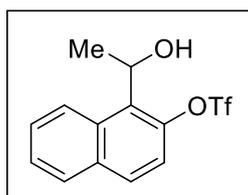


2-(1-hydroxybutyl)phenyl trifluoromethanesulfonate: ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.41 (td, *J* = 7.4, 1.0 Hz, 1H), 7.35 (td, *J* = 8.2, 1.9 Hz, 1H), 7.24 (dd, *J* = 8.2, 0.8 Hz, 1H), 5.05 (m, 1H), 2.12 (s, 1H), 1.84-1.63 (m, 2H), 1.55-1.29 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 137.7,

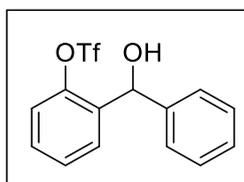
129.1, 128.8, 128.3, 121.1, 118.5 (q, $J = 318.4$ Hz), 67.7, 40.0, 18.9, 13.7; ^{19}F NMR (376 MHz, CDCl_3) δ 73.8; HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{F}_3\text{O}_4\text{S}$ (M^+): 298.0487, found: 298.0495.



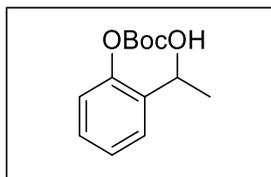
2-(1-hydroxyethyl)naphthalen-1-yl trifluoromethanesulfonate : ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.6$ Hz, 1H), 7.94-7.88 (m, 2H), 7.77 (d, $J = 8.6$ Hz, 1H), 7.65 (t, $J = 6.8$ Hz, 1H), 7.59 (t, $J = 7.0$ Hz, 1H), 5.48-5.45 (m, 1H), 2.23 (d, $J = 2.9$ Hz, 1H), 1.58 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.9, 135.6, 134.3, 129.3, 127.9, 127.2, 126.5, 124.0, 121.6, 118.7 (q, $J = 318.4$ Hz), 63.8, 23.6; ^{19}F NMR (376 MHz, CDCl_3) δ 73.0; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$ (M^+): 320.0330, found: 320.0318.



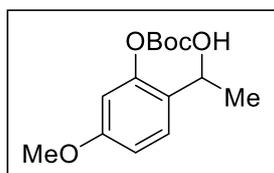
1-(1-hydroxyethyl)naphthalen-2-yl trifluoromethanesulfonate : ^1H NMR (400 MHz, CDCl_3) δ 8.79 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 7.4$ Hz, 1H), 7.84 (d, $J = 9.0$ Hz, 1H), 7.60-7.56 (m, 2H), 7.31 (d, $J = 9.0$ Hz, 1H), 5.78-5.83 (m, 1H), 2.38 (s, 1H), 1.80 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 133.4, 132.4, 131.5, 130.6, 128.9, 127.0, 126.8, 126.6, 119.2, 118.6 (q, $J = 318.5$ Hz), 65.0, 23.0; ^{19}F NMR (376 MHz, CDCl_3) δ 73.6; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$ (M^+): 320.0330, found: 320.0333.



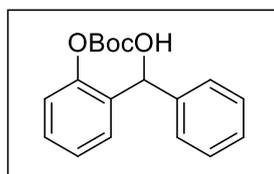
2-(hydroxy(phenyl)methyl)phenyl trifluoromethanesulfonate : ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.60 (m, 1H), 7.40-7.32 (m, 6H), 7.31-7.24 (m, 2H), 6.16 (d, $J = 3.3$ Hz, 1H), 2.46 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 141.6, 136.5, 129.5, 129.1, 128.7, 128.6, 128.1, 126.6, 121.2, 118.5 (q, $J = 318.6$ Hz), 70.2; ^{19}F NMR (376 MHz, CDCl_3) δ 73.7; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$ (M^+): 332.0330, found: 332.0326.



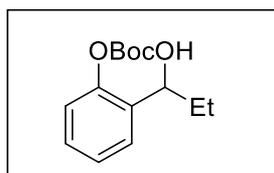
tert-butyl (2-(1-hydroxyethyl)phenyl) carbonate: ^1H NMR (600 MHz, CDCl_3) δ 7.55 (dd, $J = 7.3, 2.1$ Hz, 1H), 7.32-7.26 (m, 2H), 7.10 (dd, $J = 7.7, 1.7$ Hz, 1H), 5.08-5.04 (m, 1H), 2.21 (d, $J = 3.5$ Hz, 1H), 1.56 (s, 9H), 1.49 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 152.3, 147.9, 137.4, 128.4, 126.62, 126.57, 122.1, 83.8, 64.7, 27.7, 23.2; HRMS (ESI) m/z calcd for $[\text{C}_{13}\text{H}_{18}\text{O}_4+\text{Na}]^+$: 261.1097, found: 261.1096.



tert-butyl (2-(1-hydroxyethyl)-5-methoxyphenyl) carbonate: ^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, $J = 8.7$ Hz, 1H), 6.82 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.64 (d, $J = 2.4$ Hz, 1H), 4.97 (q, $J = 6.6$ Hz, 1H), 3.79 (s, 3H), 1.55 (s, 9H), 1.46 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.7, 152.3, 148.7, 129.5, 127.4, 112.5, 107.8, 83.9, 64.2, 55.5, 27.7, 23.0; HRMS (ESI) m/z calcd for $[\text{C}_{14}\text{H}_{20}\text{O}_5+\text{Na}]^+$: 291.1203, found: 291.1202.

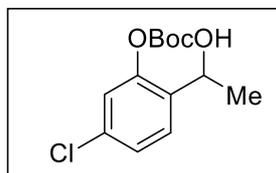


tert-butyl (2-(hydroxy(phenyl)methyl)phenyl) carbonate: ^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.38-7.36 (m, 2H), 7.33-7.29 (m, 3H), 7.25-7.22 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 1H), 6.02 (d, $J = 3.6$ Hz, 1H), 2.59 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 151.9, 148.4, 142.5, 135.9, 128.7, 128.4, 128.3, 127.5, 126.5, 126.4, 122.4, 83.8, 70.8, 27.6; HRMS (ESI) m/z calcd for $[\text{C}_{18}\text{H}_{20}\text{O}_4+\text{Na}]^+$: 323.1254, found: 323.1255.

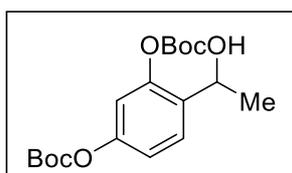


tert-butyl (2-(1-hydroxypropyl)phenyl) carbonate: ^1H NMR (600 MHz, CDCl_3) δ 7.49 (dd, $J = 7.5, 2.0$ Hz, 1H), 7.30-7.22 (m, 2H), 7.08 (dd, $J = 7.8, 1.6$ Hz, 1H), 4.77-

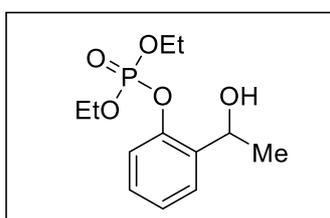
4.75 (m, 1H), 2.39 (d, $J = 3.7$ Hz, 1H), 1.83-1.72 (m, 2H), 1.54 (s, 9H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.3, 148.1, 136.5, 128.3, 127.2, 126.4, 122.1, 83.7, 70.0, 30.3, 27.7, 10.2; HRMS (ESI) m/z calcd for $[\text{C}_{14}\text{H}_{20}\text{O}_4+\text{Na}]^+$: 275.1254, found: 275.1252.



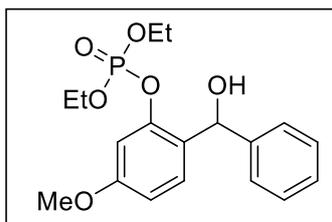
tert-butyl (5-chloro-2-(1-hydroxyethyl)phenyl) carbonate: ^1H NMR (600 MHz, CDCl_3) δ 7.46 (d, $J = 8.4$ Hz, 1H), 7.23 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.12 (d, $J = 2.1$ Hz, 1H), 4.99 (q, $J = 6.5$ Hz, 1H), 2.37 (s, 1H), 1.55 (s, 9H), 1.44 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.8, 148.1, 136.2, 133.4, 127.7, 126.8, 122.6, 84.4, 64.3, 27.6, 23.3; HRMS (ESI) m/z calcd for $[\text{C}_{13}\text{H}_{17}\text{ClO}_4+\text{Na}]^+$: 295.0708, found: 295.0709.



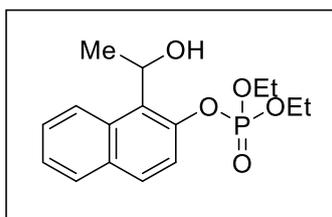
di-tert-butyl (4-(1-hydroxyethyl)-1,3-phenylene) bis(carbonate): ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, $J = 8.6$ Hz, 1H), 7.08 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.99 (d, $J = 2.4$ Hz, 1H), 5.00 (qd, $J = 6.5, 2.4$ Hz, 1H), 2.41 (d, $J = 3.2$ Hz, 1H), 1.53 (s, 9H), 1.52 (s, 9H), 1.43 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.8, 151.4, 150.4, 147.9, 135.0, 127.1, 119.3, 115.4, 84.1, 83.8, 64.3, 27.7, 27.6, 23.3; HRMS (ESI) m/z calcd for $[\text{C}_{18}\text{H}_{26}\text{O}_7+\text{Na}]^+$: 377.1571, found: 377.1573.



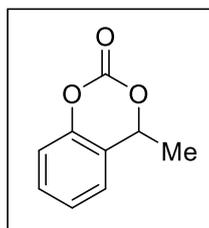
diethyl (2-(1-hydroxyethyl)phenyl) phosphate: ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, $J = 7.3$ Hz, 1H), 7.22-7.19 (m, 2H), 7.18-7.15 (m, 1H), 5.19 (q, $J = 6.6$ Hz, 1H), 4.26-4.09 (m, 4H), 3.60 (s, 1H), 1.46 (d, $J = 6.6$ Hz, 3H), 1.34 (td, $J = 7.1, 1.1$ Hz, 3H), 1.29 (td, $J = 7.1, 1.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.4 (d, $J = 7.1$ Hz), 137.0 (d, $J = 5.9$ Hz), 128.3, 126.9, 125.7, 120.1 (d, $J = 2.6$ Hz), 64.9 (dd, $J = 13.4, 6.1$ Hz), 63.5, 22.7, 16.1 (dd, $J = 6.6, 2.6$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ -5.68; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_5\text{P}$ (M^+): 274.0970, found: 274.0967.



diethyl (2-(hydroxy(phenyl)methyl)-5-methoxyphenyl) phosphate: ^1H NMR (600 MHz, CDCl_3) δ 7.40-7.38 (m, 2H), 7.32-7.29 (m, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.15 (d, $J = 8.6$ Hz, 1H), 6.84-6.80 (m, 1H), 6.68 (dd, $J = 8.6, 2.2$ Hz, 1H), 6.11 (s, 1H), 4.25-4.05 (m, 4H), 4.05-4.02 (m, 1H), 3.76 (s, 3H), 1.35 (td, $J = 7.1, 1.1$ Hz, 3H), 1.28 (td, $J = 7.1, 1.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 148.7 (d, $J = 7.2$ Hz), 143.0 (d, $J = 1.9$ Hz), 130.1, 128.2 (d, $J = 5.7$ Hz), 128.1, 127.0, 126.5, 111.3, 106.5 (d, $J = 2.5$ Hz), 69.4, 65.0 (dd, $J = 9.3, 6.1$ Hz), 55.5, 16.1 (dd, $J = 6.7, 4.3$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ -5.53; HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{O}_6\text{P}$ (M^+): 366.1232, found: 366.1226.

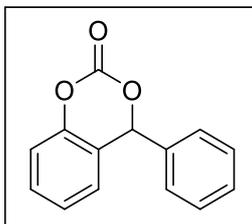


diethyl (1-(1-hydroxyethyl)naphthalen-2-yl) phosphate: ^1H NMR (600 MHz, CDCl_3) δ 8.63 (d, $J = 8.6$ Hz, 1H), 7.83-7.77 (m, 1H), 7.71 (d, $J = 9.0$ Hz, 1H), 7.50-7.47 (m, 1H), 7.44-7.41 (m, 1H), 7.40-7.38 (m, 1H), 5.83 (d, $J = 7.1$ Hz, 1H), 4.29-4.10 (m, 4H), 3.45 (s, 1H), 1.74 (d, $J = 6.9$ Hz, 3H), 1.35 (td, $J = 7.1, 1.2$ Hz, 3H), 1.30 (td, $J = 7.1, 1.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.0 (d, $J = 7.3$ Hz), 132.1, 131.8, 129.9 (d, $J = 6.5$ Hz), 129.5, 128.6, 126.3, 125.8, 125.2, 119.9 (d, $J = 2.0$ Hz), 64.9 (t, $J = 6.1$ Hz), 22.9, 16.1 (dd, $J = 6.2, 5.3$ Hz); ^{31}P NMR (243 MHz, CDCl_3) δ -5.66; HRMS (ESI) m/z calcd for $[\text{C}_{16}\text{H}_{21}\text{O}_5\text{P}+\text{Na}]^+$: 347.1019, found: 347.1020.

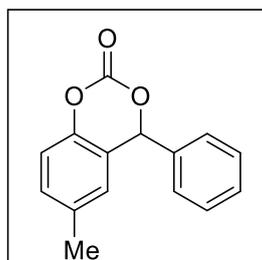


4-methyl-4H-benzo[d][1,3]dioxin-2-one: ^1H NMR (600 MHz, CDCl_3) δ 7.39-7.34 (m, 1H), 7.24-7.20 (m, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 8.2$ Hz, 1H), 5.61 (q, $J = 6.6$ Hz, 1H), 1.74 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.8, 147.0,

129.9, 125.4, 123.8, 122.7, 116.2, 76.2, 20.9; HRMS (ESI) m/z calcd for $[C_9H_8O_3+Na]^+$: 187.0366, found: 187.0365.



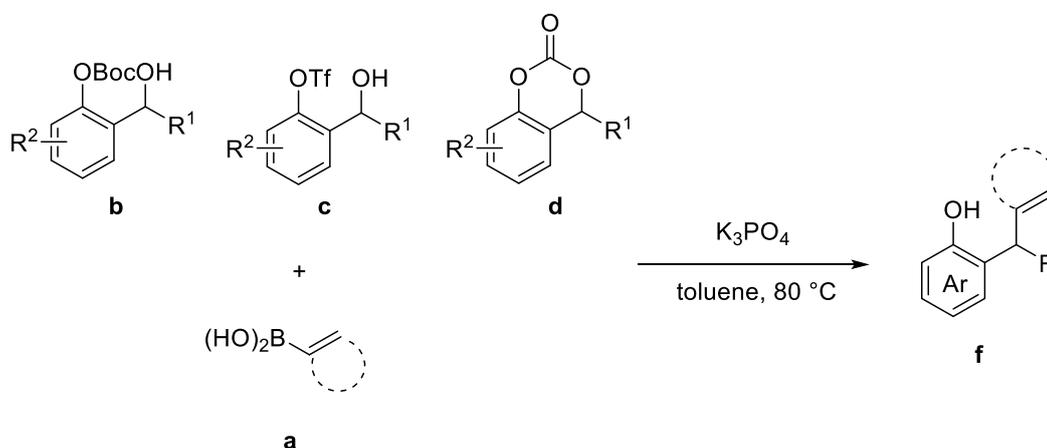
4-phenyl-4H-benzo[d][1,3]dioxin-2-one: 1H NMR (600 MHz, $CDCl_3$) δ 7.47-7.37 (m, 4H), 7.36-7.31 (m, 2H), 7.21-7.13 (m, 2H), 6.97-6.90 (m, 1H), 6.45 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 146.6, 136.3, 130.3, 129.8, 129.1, 127.8, 125.8, 125.3, 121.1, 116.3, 81.5; HRMS (ESI) m/z calcd for $[C_{14}H_{10}O_3+Na]^+$: 249.0522, found: 249.0521.



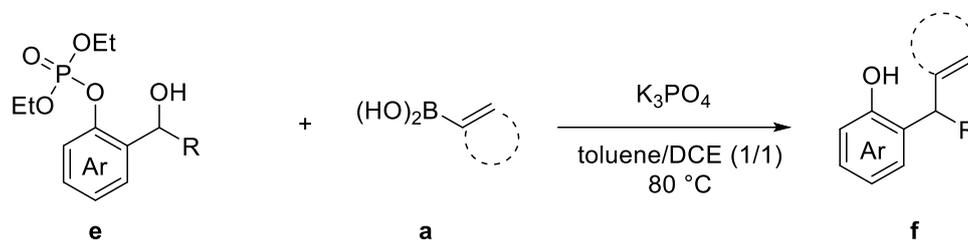
6-methyl-4-phenyl-4H-benzo[d][1,3]dioxin-2-one: 1H NMR (600 MHz, $CDCl_3$) δ 7.44-7.40 (m, 3H), 7.36-7.32 (m, 2H), 7.18 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 1H), 6.72 (d, $J = 2.1$ Hz, 1H), 6.40 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 146.8, 136.6, 135.2, 130.8, 129.8, 129.1, 127.8, 126.0, 120.7, 115.9, 81.6, 20.8; HRMS (ESI) m/z calcd for $[C_{15}H_{12}O_3+Na]^+$: 263.0679, found: 263.0680.

3. Metal-free couplings between secondary alcohols and boronic acids

3.1 General procedures

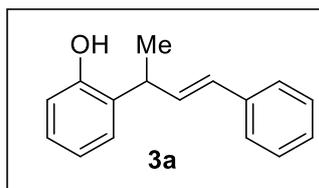


A mixture of boronic acid (0.3 mmol, 1.5 equiv) and potassium phosphate (0.4 mmol, 2 equiv) was charged with degassed toluene (2 mL). Then substrate (0.2 mmol, 1.0 equiv) was added. The resulting mixture was stirred at $80\text{ }^\circ\text{C}$ for 4 h. The mixture was directly purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10) to provide the coupling product.

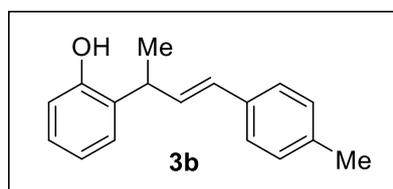


A mixture of boronic acid (0.3 mmol, 1.5 equiv) and potassium phosphate (0.4 mmol, 2 equiv) was charged degassed toluene with DCE as cosolvent (v/v = 1/1, 2 mL). Then substrate (0.2 mmol, 1.0 equiv) was added. The resulting mixture was stirred at $80\text{ }^\circ\text{C}$ for 4 h. The mixture was directly purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10) to provide the coupling product.

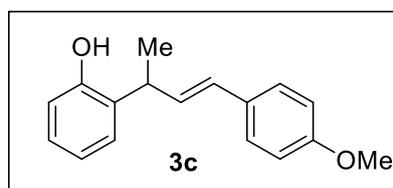
3.2 Analytical data of coupling products



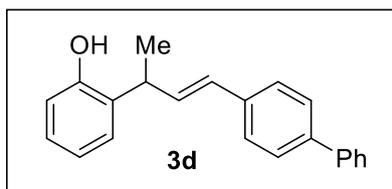
(E)-2-(4-phenylbut-3-en-2-yl)phenol (3a): ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.33 (m, 2H), 7.32-7.25 (m, 2H), 7.23-7.17 (m, 2H), 7.16-7.09 (m, 1H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.43 (dd, $J = 16.0, 5.9$ Hz, 1H), 4.99 (s, 1H), 3.94-3.85 (m, 1H), 1.49 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 137.1, 133.9, 130.7, 129.4, 128.5, 127.9, 127.6, 127.3, 126.2, 121.0, 116.1, 36.8, 19.5; HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}$ (M^+): 224.1201, found: 224.1205.



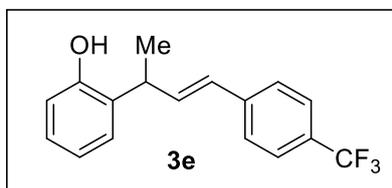
(E)-2-(4-(p-tolyl)but-3-en-2-yl)phenol (3b): ^1H NMR (500 MHz, CDCl_3) δ 7.29-7.26 (d, $J = 8.8$ Hz, 2H), 7.22 (dd, $J = 7.6$ Hz, 1.3 Hz, 1H), 7.17-7.11 (m, 3H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 7.5$ Hz, 1H), 6.51 (d, $J = 16.1$ Hz, 1H), 6.40 (dd, $J = 16.1, 6.3$ Hz, 1H), 5.13 (br s, 1H), 3.92-3.86 (m, 1H), 2.34 (s, 3H), 1.51 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 137.1, 134.2, 132.8, 130.8, 129.3, 129.2, 128.0, 127.6, 126.1, 121.0, 116.1, 36.8, 21.2, 19.5; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ (M^+): 238.1358, found: 238.1352.



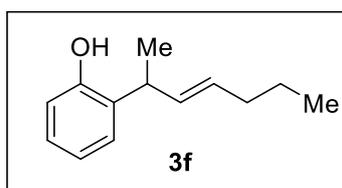
(E)-2-(4-(4-methoxyphenyl)but-3-en-2-yl)phenol (3c): ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.29 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.11 (m, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.88-6.79 (m, 3H), 6.48 (d, $J = 16.1$ Hz, 1H), 6.31 (dd, $J = 16.1, 6.4$ Hz, 1H), 5.16 (s, 1H), 3.91-3.84 (m, 1H), 3.81 (s, 3H), 1.50 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 153.6, 131.7, 130.9, 129.8, 128.9, 127.9, 127.6, 127.4, 121.0, 116.1, 113.9, 55.3, 36.8, 19.6; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ (M^+): 254.1307, found: 254.1304.



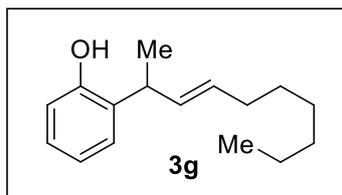
(E)-2-(4-([1,1'-biphenyl]-4-yl)but-3-en-2-yl)phenol (3d) : ^1H NMR (500 MHz, CDCl_3) δ 7.61-7.58 (m, 2H), 7.56-7.54 (m, 2H), 7.46-7.42 (m, 4H), 7.34 (t, $J = 7.4$, 1.2 Hz, 1H), 7.23 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.15 (td, $J = 7.8$, 1.7 Hz, 1H), 6.95 (td, $J = 7.6$, 1.2 Hz, 1H), 6.83 (dd, $J = 8.0$, 1.2 Hz, 1H), 6.47-6.57 (m, 2H), 3.97-3.90 (m, 1H), 1.59 (br s, 1H), 1.52 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 140.7, 140.1, 136.1, 134.1, 130.7, 128.9, 128.7, 128.0, 127.6, 127.22, 127.20, 126.9, 126.6, 121.1, 116.0, 36.8, 19.5; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$ (M^+): 300.1514, found: 300.1522.



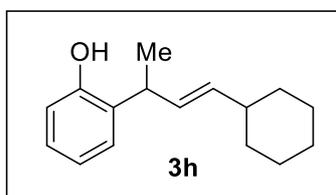
(E)-2-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)phenol (3e) : ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.22 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.15 (td, $J = 7.7$, 1.6 Hz, 1H), 6.96 (td, $J = 7.5$, 1.0 Hz, 1H), 6.81 (dd, $J = 8.0$, 1.0 Hz, 1H), 6.49-6.59 (m, 2H), 4.96 (s, 1H), 4.02-3.94 (m, 1H), 1.51 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 140.8, 136.9, 130.6, 128.9 (q, $J = 32.2$ Hz), 128.0, 127.8, 127.6, 126.3, 125.4 (q, $J = 3.8$ Hz), 124.2 (q, $J = 270.4$ Hz), 121.1, 115.9, 36.4, 19.4; ^{19}F NMR (376 MHz, CDCl_3) δ -62.37; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}$ (M^+): 292.1075, found: 292.1077.



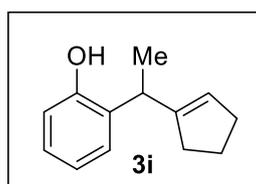
(E)-2-(hept-3-en-2-yl)phenol (3f): ^1H NMR (400 MHz, CDCl_3) δ 7.16-7.12 (m, 2H), 6.91 (td, $J = 7.6$, 1.2 Hz, 1H), 6.84-6.81 (m, 1H), 5.72-5.62 (m, 2H), 5.32 (br s, 1H), 3.64-3.58 (m, 1H), 2.07-2.02 (m, 2H), 1.46-1.37 (m, 5H), 0.91 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 134.1, 131.1, 130.6, 127.8, 127.6, 120.9, 116.3, 37.3, 34.6, 22.5, 19.4, 13.7; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ (M^+): 190.1358, found: 190.1365.



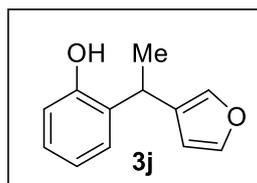
(E)-2-(dec-3-en-2-yl)phenol (3g): ^1H NMR (500 MHz, CDCl_3) δ 7.15-7.12 (m, 2H), 6.91 (td, $J = 7.6, 1.2$ Hz, 1H), 6.83-6.82 (m, 1H), 5.70-5.63 (m, 2H), 5.29 (br s, 1H), 3.63-3.58 (m, 1H), 2.08-2.04 (m, 2H), 1.40-1.35 (m, 5H), 1.34-1.23 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 133.7, 131.3, 130.6, 127.8, 127.6, 120.8, 116.3, 37.3, 32.5, 31.7, 29.3, 28.8, 22.6, 19.4, 14.1; HRMS (ESI) m/z calcd for $[\text{C}_{16}\text{H}_{24}\text{O}-\text{H}]$: 231.1754, found: 231.1752.



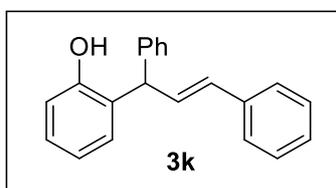
(E)-2-(4-cyclohexylbut-3-en-2-yl)phenol (3h): ^1H NMR (500 MHz, CDCl_3) δ 7.15-7.12 (m, 2H), 6.90 (td, $J = 7.5, 1.2$ Hz, 1H), 6.83-6.81 (m, 1H), 5.67-5.60 (m, 2H), 5.36 (br s, 1H), 3.58-3.56 (m, 1H), 2.20-1.97 (m, 1H), 1.74-1.71 (m, 4H), 1.66-1.64 (m, 1H), 1.38 (d, $J = 7.1$ Hz, 3H), 1.31-1.23 (m, 2H), 1.20-1.05 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 137.3, 131.3, 130.5, 127.8, 127.6, 120.7, 116.4, 40.6, 37.6, 33.0, 26.1, 26.0, 19.3; HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{22}\text{O}$ (M^+): 230.1671, found: 230.1666.



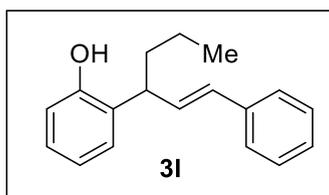
2-(1-(cyclopent-1-en-1-yl)ethyl)phenol (3i): ^1H NMR (500 MHz, CDCl_3) δ 7.16-7.01 (m, 2H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 5.70 (s, 1H), 5.49 (br s, 1H), 3.64-3.61 (m, 1H), 2.42-2.39 (m, 2H), 2.22-2.12 (m, 2H), 1.92-1.86 (m, 2H), 1.47 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.4, 148.7, 129.8, 128.6, 127.6, 125.6, 120.7, 116.3, 37.6, 33.9, 32.4, 23.4, 18.7; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (M^+): 188.1201, found: 188.1198.



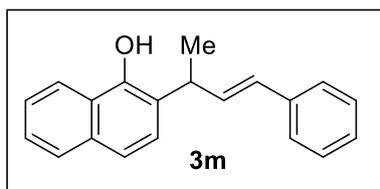
2-(1-(furan-3-yl)ethyl)phenol (3j): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 (d, $J = 1.2$ Hz, 1H), 7.14-7.08 (m, 2H), 6.90 (td, $J = 7.5, 1.0$ Hz, 1H), 6.80 (dd, $J = 8.0, 1.0$ Hz, 1H), 6.32 (dd, $J = 3.2, 1.9$ Hz, 1H), 6.13 (d, $J = 3.2$ Hz, 1H), 5.00 (s, 1H), 4.44-4.40 (m, 1H), 1.61 (d, $J = 1.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.1, 153.1, 141.6, 129.9, 128.2, 127.8, 121.1, 116.2, 110.0, 105.2, 33.3, 18.6; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (M^+): 188.0837, found: 188.0838.



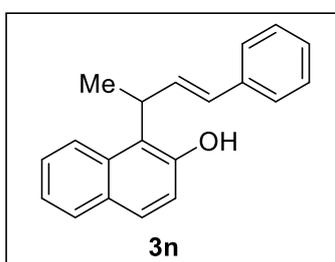
(E)-2-(1,3-diphenylallyl)phenol (3k): $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.38-7.36 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.19 (m, 6H), 7.18-7.12 (m, 2H), 6.92 (td, $J = 7.5, 1.3$ Hz, 1H), 6.80 (dd, $J = 8.4, 1.3$ Hz, 1H), 6.70 (dd, $J = 15.9, 7.2$ Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 5.14 (d, $J = 7.2$ Hz, 1H), 4.95 (s, 1H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 153.5, 142.2, 137.1, 131.9, 131.3, 129.8, 129.5, 128.74, 128.70, 128.6, 128.1, 127.5, 126.8, 126.4, 121.1, 116.4, 48.4; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{O}$ (M^+): 286.1358, found: 286.1350.



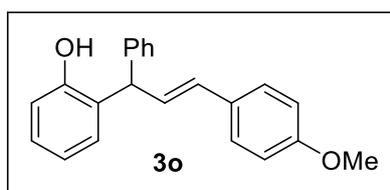
(E)-2-(1-phenylhex-1-en-3-yl)phenol (3l): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.22 (m, 2H), 7.13 (td, $J = 7.7, 1.6$ Hz, 1H), 6.95 (td, $J = 7.5, 1.0$ Hz, 1H), 6.81 (dd, $J = 8.0, 1.0$ Hz, 1H), 6.37-6.52 (m, 2H), 4.97 (s, 1H), 3.76-3.74 (m, 1H), 1.85 (q, $J = 7.6$ Hz, 2H), 1.29-1.50 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.5, 137.2, 133.2, 129.97, 129.90, 128.5, 128.4, 127.4, 127.2, 126.2, 121.0, 116.1, 42.5, 36.3, 20.8, 14.1; HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ (M^+): 252.1514, found: 252.1510.



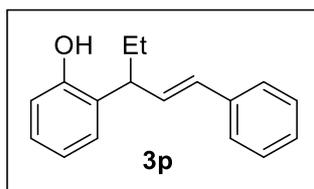
(E)-2-(4-phenylbut-3-en-2-yl)naphthalen-1-ol (3m): ^1H NMR (600 MHz, CDCl_3) δ 8.16-8.09 (m, 1H), 7.79-7.72 (m, 1H), 7.45-7.41 (m, 3H), 7.35-7.25 (m, 5H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.57 (dd, $J = 16.1, 1.8$ Hz, 1H), 6.48 (dd, $J = 16.1, 5.8$ Hz, 1H), 5.67 (s, 1H), 3.97-3.90 (m, 1H), 1.55 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.9, 136.8, 133.6, 130.1, 128.7, 127.7, 127.6, 126.4, 126.1, 125.9, 125.4, 125.1, 123.5, 121.5, 120.7, 37.7, 19.5; HRMS (ESI) m/z calcd for $[\text{C}_{20}\text{H}_{18}\text{O}-\text{H}]$: 273.1285, found: 273.1285.



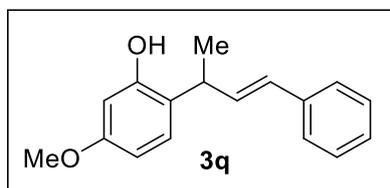
(E)-1-(4-phenylbut-3-en-2-yl)naphthalen-2-ol (3n): ^1H NMR (600 MHz, CDCl_3) δ 8.04 (d, $J = 8.7$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.7$ Hz, 1H), 7.50-7.46 (m, 1H), 7.41-7.37 (m, 2H), 7.36-7.28 (m, 3H), 7.26-7.21 (m, 1H), 7.07 (d, $J = 8.8$ Hz, 1H), 6.79-6.70 (m, 2H), 5.90 (s, 1H), 4.66-4.61 (m, 1H), 1.63 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.3, 136.7, 133.6, 132.5, 130.5, 129.7, 128.9, 128.8, 128.7, 127.7, 126.6, 126.4, 123.1, 122.5, 121.3, 119.3, 33.5, 17.3; HRMS (ESI) m/z calcd for $[\text{C}_{20}\text{H}_{18}\text{O}-\text{H}]$: 273.1285, found: 273.1285.



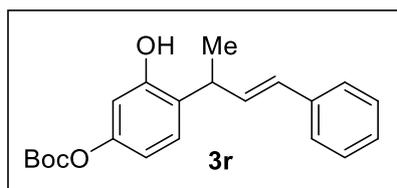
(E)-2-(3-(4-methoxyphenyl)-1-phenylallyl)phenol (3o): ^1H NMR (600 MHz, CDCl_3) δ 7.36-7.30 (m, 4H), 7.30-7.24 (m, 3H), 7.19-7.12 (m, 2H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.87-6.83 (m, 3H), 6.56 (dd, $J = 15.9, 7.1$ Hz, 1H), 6.32 (d, $J = 15.9$ Hz, 1H), 5.11 (d, $J = 7.1$ Hz, 1H), 4.93 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 153.5, 142.2, 131.3, 129.9, 129.8, 129.6, 129.0, 128.74, 128.70, 128.0, 127.6, 126.8, 121.0, 116.4, 114.0, 55.3, 48.5; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2$ (M^+): 316.1463, found: 316.1455.



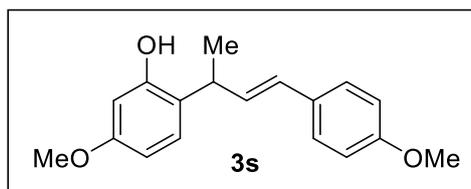
(E)-2-(1-phenylpent-1-en-3-yl)phenol (3p): ^1H NMR (600 MHz, CDCl_3) δ 7.38-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.19 (m, 2H), 7.13 (td, $J = 7.7, 1.7$ Hz, 1H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.81 (dd, $J = 8.0, 1.3$ Hz, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.39 (dd, $J = 16.0, 7.3$ Hz, 1H), 5.02 (s, 1H), 3.64 (q, $J = 7.4$ Hz, 1H), 1.93-1.88 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.6, 137.3, 133.0, 130.1, 129.9, 128.52, 128.47, 127.4, 127.2, 126.2, 121.0, 116.1, 44.6, 27.1, 12.3; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ (M^+): 238.1358, found: 238.1353.



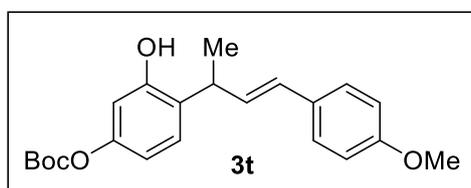
(E)-5-methoxy-2-(4-phenylbut-3-en-2-yl)phenol (3q): ^1H NMR (600 MHz, CDCl_3) δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 6.52-6.48 (m, 2H), 6.44-6.39 (m, 2H), 5.25-5.08 (m, 1H), 3.83-3.79 (m, 1H), 3.78 (s, 3H), 1.47 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.4, 154.6, 137.1, 134.3, 129.3, 128.6, 128.5, 127.3, 126.3, 123.0, 106.4, 102.3, 55.3, 36.4, 19.6; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ (M^+): 254.1307, found: 254.1310.



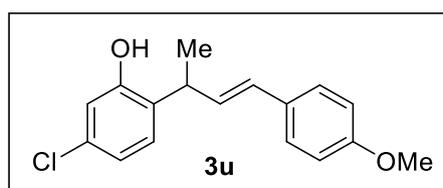
(E)-tert-butyl (3-hydroxy-4-(4-phenylbut-3-en-2-yl)phenyl) carbonate (3r): ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 6.75-6.69 (m, 1H), 6.64 (d, $J = 1.9$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.38 (dd, $J = 16.0, 6.3$ Hz, 1H), 5.51 (s, 1H), 3.87-3.82 (m, 1H), 1.55 (s, 9H), 1.44 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.2, 152.1, 150.1, 137.1, 133.8, 129.4, 128.7, 128.5, 128.4, 127.3, 126.3, 113.5, 109.3, 83.7, 36.2, 27.7, 19.5; HRMS (ESI) m/z calcd for $[\text{C}_{21}\text{H}_{24}\text{O}_4 + \text{Na}]^+$: 353.1567, found: 353.1567.



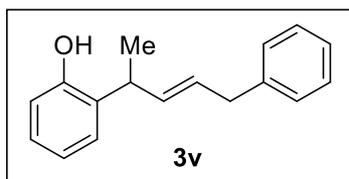
(E)-5-methoxy-2-(4-(4-methoxyphenyl)but-3-en-2-yl)phenol (3s): ^1H NMR (600 MHz, CDCl_3) δ 7.32-7.27 (m, 2H), 7.09 (d, $J = 8.5$ Hz, 1H), 6.86-6.82 (m, 2H), 6.50 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.46 (dd, $J = 16.0, 1.6$ Hz, 1H), 6.42 (d, $J = 2.6$ Hz, 1H), 6.27 (dd, $J = 16.0, 6.3$ Hz, 1H), 5.27-5.23 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.76 (t, $J = 7.0$ Hz, 1H), 1.46 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 159.1, 154.7, 132.1, 129.9, 128.8, 128.5, 127.4, 123.1, 114.0, 106.4, 102.3, 55.3, 36.5, 19.7; HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ (M^+): 284.1412, found: 284.1408.



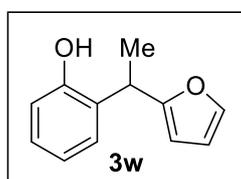
(E)-tert-butyl (3-hydroxy-4-(4-methoxyphenyl)but-3-en-2-yl)phenyl carbonate (3t): ^1H NMR (600 MHz, CDCl_3) δ 7.28-7.26 (m, 2H), 7.15 (d, $J = 8.4$ Hz, 1H), 6.83-6.81 (m, 2H), 6.74-6.68 (m, 1H), 6.64 (d, $J = 1.8$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.24 (dd, $J = 16.0, 6.4$ Hz, 1H), 5.57 (s, 1H), 3.83-3.80 (m, 1H), 3.79 (s, 3H), 1.55 (s, 9H), 1.43 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.1, 154.3, 152.1, 150.1, 131.5, 129.9, 129.0, 128.8, 128.3, 127.4, 114.0, 113.4, 109.4, 83.6, 55.3, 36.4, 27.7, 19.6; HRMS (ESI) m/z calcd for $[\text{C}_{22}\text{H}_{26}\text{O}_5 + \text{Na}]^+$: 393.1672, found: 393.1673.



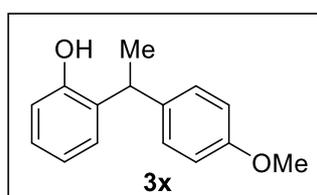
(E)-5-chloro-2-(4-(4-methoxyphenyl)but-3-en-2-yl)phenol (3u): ^1H NMR (600 MHz, CDCl_3) δ 7.30-7.28 (m, 2H), 7.11 (d, $J = 8.2$ Hz, 1H), 6.91 (dd, $J = 8.2, 2.1$ Hz, 1H), 6.85-6.84 (m, 2H), 6.83 (d, $J = 2.1$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.24 (dd, $J = 16.0, 6.4$ Hz, 1H), 5.35 (s, 1H), 3.82-3.78 (m, 1H), 3.81 (s, 3H), 1.46 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 154.4, 132.6, 131.0, 129.7, 129.6, 129.3, 128.9, 127.4, 121.1, 116.5, 114.0, 55.3, 36.5, 19.5; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{ClO}_2$ (M^+): 288.0917, found: 288.0912.



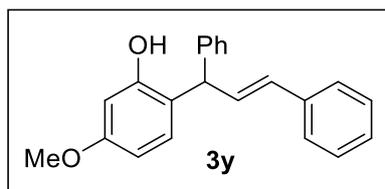
(E)-2-(5-phenylpent-3-en-2-yl)phenol (3v): ^1H NMR (400 MHz, CDCl_3) δ 7.29 (m, 2H), 7.21-7.09 (m, 5H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 5.82-5.72 (m, 2H), 5.09 (s, 1H), 3.75-3.71 (m, 1H), 3.43-3.34 (m, 2H), 1.38 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 140.3, 135.4, 130.7, 129.4, 128.5 (2C), 127.9, 127.6, 126.1, 120.9, 116.2, 38.9, 36.8, 19.5; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ (M^+): 238.1358, found: 238.1362.



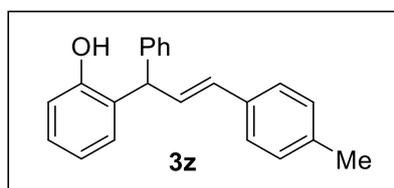
2-(1-(furan-2-yl)ethyl)phenol (3w): ^1H NMR (600 MHz, CDCl_3) δ 7.33 (s, 1H), 7.13-7.07 (m, 2H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.31 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.12 (d, $J = 3.2$ Hz, 1H), 5.09 (s, 1H), 4.45-4.41 (m, 1H), 1.61 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.2, 153.2, 141.6, 130.0, 128.3, 127.8, 121.1, 116.2, 110.1, 105.2, 33.3, 18.6; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (M^+): 188.0837, found: 188.0835.



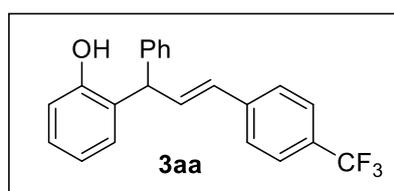
2-(1-(4-methoxyphenyl)ethyl)phenol (3x): ^1H NMR (600 MHz, CDCl_3) δ 7.24 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.17 (d, $J = 8.7$ Hz, 2H), 7.12 (td, $J = 7.6, 1.6$ Hz, 1H), 6.94 (td, $J = 7.5, 1.3$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.76 (dd, $J = 7.9, 1.3$ Hz, 1H), 4.70 (s, 1H), 4.31 (q, $J = 7.2$ Hz, 1H), 3.78 (s, 3H), 1.61 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.2, 153.4, 137.2, 132.1, 128.5, 127.8, 127.5, 120.9, 116.1, 114.2, 55.3, 38.1, 21.2. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ (M^+): 228.115, found: 228.1147.



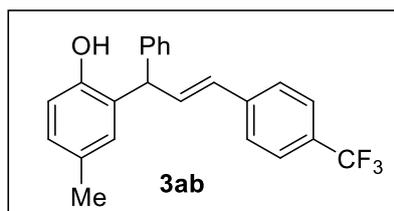
(E)-2-(1,3-diphenylallyl)-5-methoxyphenol (3y): ^1H NMR (600 MHz, CDCl_3) δ 7.37-7.20 (m, 10H), 7.00 (d, $J = 8.5$ Hz, 1H), 6.66 (dd, $J = 15.9, 7.0$ Hz, 1H), 6.47 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.40 (d, $J = 2.6$ Hz, 1H), 6.34 (d, $J = 15.9$ Hz, 1H), 5.03 (d, $J = 7.0$ Hz, 1H), 4.95 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.7, 154.5, 142.2, 137.1, 131.7, 131.5, 130.4, 128.7, 128.61, 128.57, 127.5, 126.8, 126.4, 121.7, 106.4, 102.5, 55.3, 48.0; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2$ (M^+): 316.1463, found: 316.1460.



(E)-2-(1-phenyl-3-(p-tolyl)allyl)phenol (3z): ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.31 (m, 2H), 7.29-7.23 (m, 5H), 7.16-7.09 (m, 4H), 6.94-6.89 (m, 1H), 6.81 (dd, $J = 7.9, 1.3$ Hz, 1H), 6.63 (dd, $J = 15.9, 7.2$ Hz, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 5.11 (d, $J = 7.2$ Hz, 1H), 4.87 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 153.5, 142.1, 137.3, 134.3, 131.8, 130.1, 129.8, 129.5, 129.2, 128.70, 128.66, 128.0, 126.8, 126.3, 121.0, 116.4, 48.5, 21.2; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$ (M^+): 300.1514, found: 300.1509.



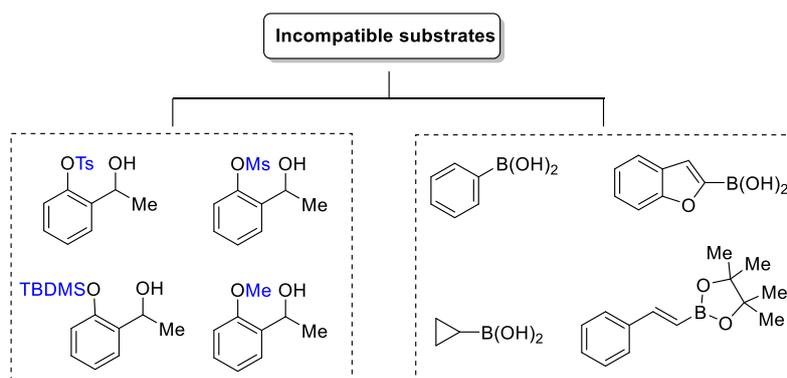
(E)-2-(1-phenyl-3-(4-(trifluoromethyl)phenyl)allyl)phenol (3aa): ^1H NMR (600 MHz, CDCl_3) δ 7.55-7.50 (m, 2H), 7.46-7.42 (m, 2H), 7.35-7.30 (m, 2H), 7.27-7.22 (m, 3H), 7.18-7.12 (m, 2H), 6.95-6.90 (m, 1H), 6.83-6.75 (m, 2H), 6.35 (d, $J = 15.9$ Hz, 1H), 5.17 (d, $J = 7.1$ Hz, 1H), 4.76 (s, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 153.3, 141.7, 140.6, 134.2, 130.5, 129.7, 129.2 (q, $J = 32.2$ Hz), 129.1, 128.7, 128.6, 128.2, 126.9, 126.5, 125.5 (q, $J = 3.9$ Hz), 124.2 (q, $J = 271.2$ Hz), 121.1, 116.3, 48.2; ^{19}F NMR (565 MHz, CDCl_3) δ -62.46; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{F}_3\text{O}$ (M^+): 354.1231, found: 354.1229.



(E)-4-methyl-2-(1-phenyl-3-(4-(trifluoromethyl)phenyl)allyl)phenol (3ab): ^1H NMR (600 MHz, CDCl_3) δ 7.56-7.51 (m, 2H), 7.48-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.27-7.24 (m, 3H), 6.98-6.90 (m, 2H), 6.83-6.77 (m, 1H), 6.72-6.68 (m, 1H), 6.36 (dd, $J = 15.9, 3.2$ Hz, 1H), 5.15-5.10 (m, 1H), 4.57 (d, $J = 2.9$ Hz, 1H), 2.26 (d, $J = 3.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.1, 141.8, 140.7, 134.3, 130.4, 130.3, 130.2, 128.8, 129.2 (q, $J = 31.8$ Hz), 128.7, 128.6, 128.5, 126.9, 126.5, 125.5 (q, $J = 3.74$ Hz), 124.2 (q, $J = 271.4$ Hz), 116.2, 48.4, 20.7; ^{19}F NMR (565 MHz, CDCl_3) δ -62.41; HRMS (EI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{O}$ (M^+): 368.1388, found: 368.1388.

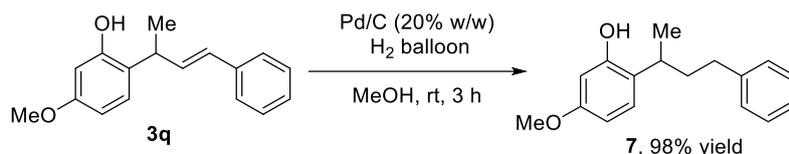
3.3 Incompatible substrate

In addition to the results we presented, we also tested other functional groups on the phenolic hydroxyl group, including *p*-toluenesulfonyl (Ts), mesyl (Ms), *tert*-butyldimethylsilyl (TBDMS), and a simple methyl group. These compounds were inert in our metal-free coupling reaction. Furthermore, aryl boronic acids, such as phenylboronic acid and benzofuran-2-boronic acid, exhibited low reactivity. Cyclopropylboronic acid, as well as phenylstyrylboronic ester, were also not tolerated in our reaction. The list of incompatible substrates is provided below.



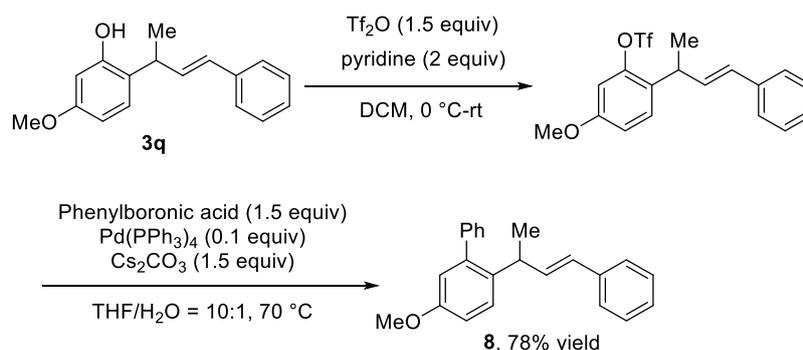
4. Product transformations

4.1 Hydrogenation



To a solution of compound **3q** (0.2 mmol, 50.8 mg) in MeOH (2 mL) was added Pd/C (20% w/w). The mixture was degassed and charged with a hydrogen balloon, followed by stirring at room temperature for 2 h. After the consumption of **7**, the reaction was filtered, concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to deliver alkylphenol **g** (50.2 mg, 98% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.22-7.16 (m, 2H), 7.12-7.06 (m, 3H), 7.00 (d, $J = 8.5$ Hz, 1H), 6.42 (dd, $J = 8.5, 2.4$ Hz, 1H), 6.28 (d, $J = 2.4$ Hz, 1H), 4.61 (s, 1H), 3.69 (s, 3H), 2.87 (q, $J = 7.0$ Hz, 1H), 2.54-2.42 (m, 2H), 1.94-1.74 (m, 2H), 1.18 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.6, 153.8, 142.6, 128.4, 128.4, 127.7, 125.7, 125.0, 106.3, 101.8, 55.3, 38.9, 33.9, 31.4, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ (M^-): 256.1463, found: 255.1389.

4.2 Triflation/Suzuki-Miyaura coupling

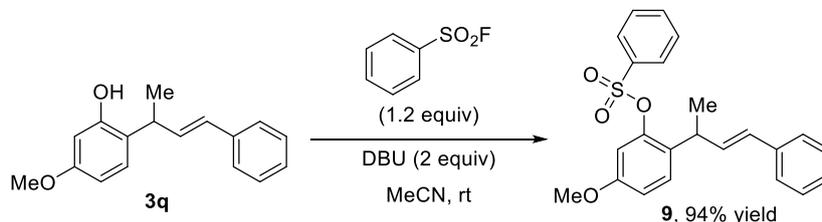


To a solution of compound **3q** (0.2 mmol, 50.8 mg) and pyridine (2 equiv, 0.4 mmol, 67 μL) in DCM (5 mL) was stirred at 0 °C, and Tf_2O was added (1.5 equiv, 0.3 mmol, 32 μL) dropwise. The mixture was moved to room temperature and stirred for 0.5 h. The reaction was quenched with water and diluted with ethyl acetate. After extraction, the combined organic layer was dried and concentrated to crude triflate. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) and used for the next coupling reaction.

To an oven-dried Schlenk tube equipped with a stir bar was added triflate product and phenylboronic acid (1.5 equiv, 0.3 mmol, 36 mg), $\text{Pd}(\text{PPh}_3)_4$ (0.1 equiv, 0.02 mmol, 22 mg), Cs_2CO_3 (1.5 equiv, 0.3 mmol, 98 mg) in THF/ H_2O (10/1, 2 mL). The tube was evacuated and backfilled with nitrogen three times. The resulting mixture was heated to 70 °C for 12 h. After completion, the mixture was filtered through celite and concentrated. The crude residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to give coupling product **8** (49 mg, 78% yield) of two steps. ^1H NMR (600 MHz, CDCl_3) δ 7.36-7.32 (m, 2H), 7.31-7.25 (m, 3H), 7.24-7.16 (m, 5H), 7.12-7.08 (m, 1H), 6.85 (dd, $J = 8.6, 2.8$ Hz, 1H), 6.70 (d, $J = 2.8$ Hz, 1H), 6.26 (dd, $J = 16.0, 6.0$ Hz, 1H), 6.09 (dd, $J = 16.0, 1.7$ Hz, 1H), 3.73 (s, 3H), 3.66-3.59

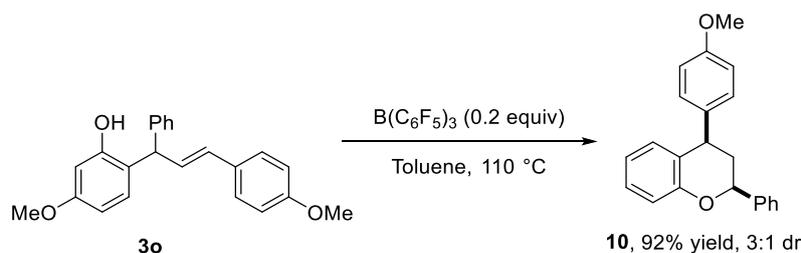
(m, 1H), 1.25 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 157.3, 142.6, 141.7, 137.7, 136.0, 135.2, 129.3, 128.5, 128.3, 128.1, 128.1, 127.0, 126.9, 126.1, 115.0, 113.8, 55.3, 37.3, 21.8. HRMS (EI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{O}$ (M^+): 314.1671, found: 314.1657.

4.3 SuFEx reaction



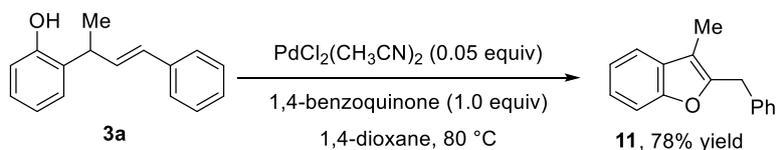
To a solution of compound **3q** (0.2 mmol, 50.8 mg) in MeCN was added phenylsulfonyl fluoride (1.2 equiv, 0.24 mmol, 29 μL) and DBU (2 equiv, 0.4 mmol, 60 μL). The mixture was stirred at room temperature for overnight. After completion, the resulting mixture was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give the product **9** (74 mg, 94% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 7.6$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 4.3$ Hz, 4H), 7.11 (q, $J = 4.3$ Hz, 1H), 7.05 (d, $J = 8.7$ Hz, 1H), 6.71 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.58 (d, $J = 2.5$ Hz, 1H), 6.17-6.11 (m, 1H), 5.99 (dd, $J = 16.0, 6.0$ Hz, 1H), 3.66 (q, $J = 7.0$ Hz, 1H), 3.63 (s, 3H), 1.14 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 158.4, 147.5, 137.4, 136.0, 134.3, 133.8, 130.4, 129.3, 129.0, 128.55, 128.53, 128.49, 127.11, 126.15, 113.69, 107.65, 55.50, 34.38, 20.40. ^{13}C NMR (151 MHz, CDCl_3) δ 158.40, 147.53, 137.42, 136.00, 134.28, 133.80, 130.44, 129.29, 128.99, 128.6, 128.5, 128.5, 127.1, 126.1, 113.7, 107.6, 55.5, 34.4, 20.4. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{O}_4\text{SNa}$ (M^+): 417.1131, found: 417.1132.

4.4 Intramolecular cyclization



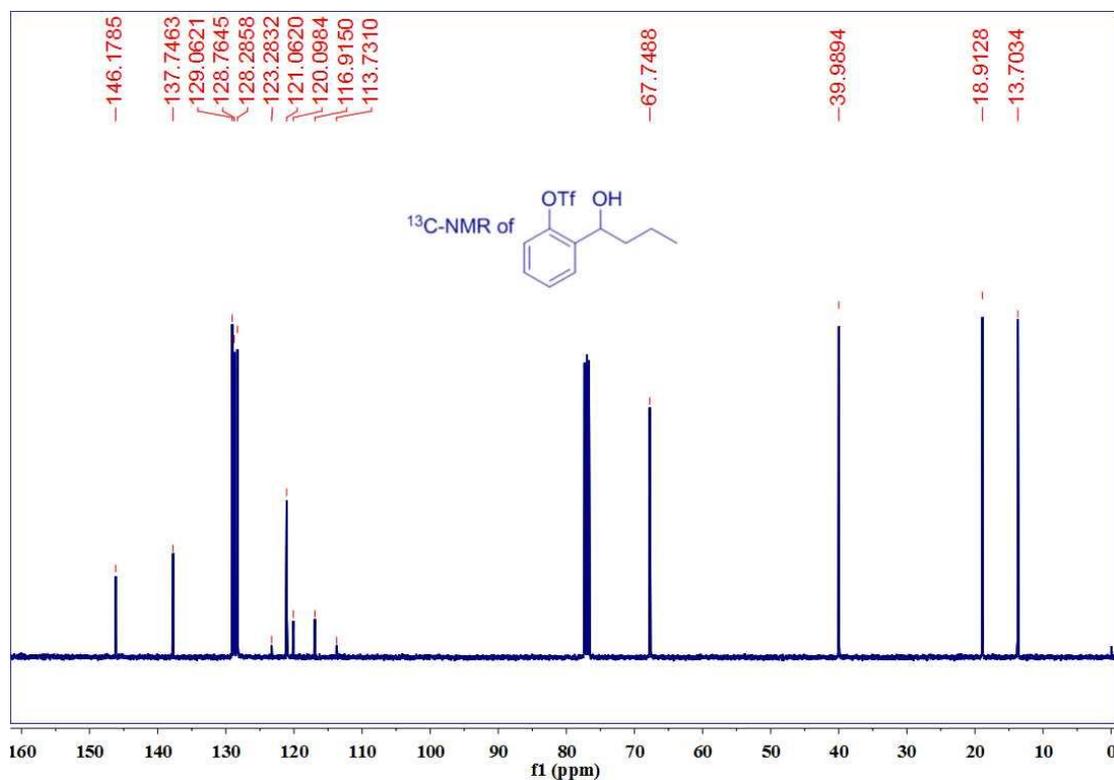
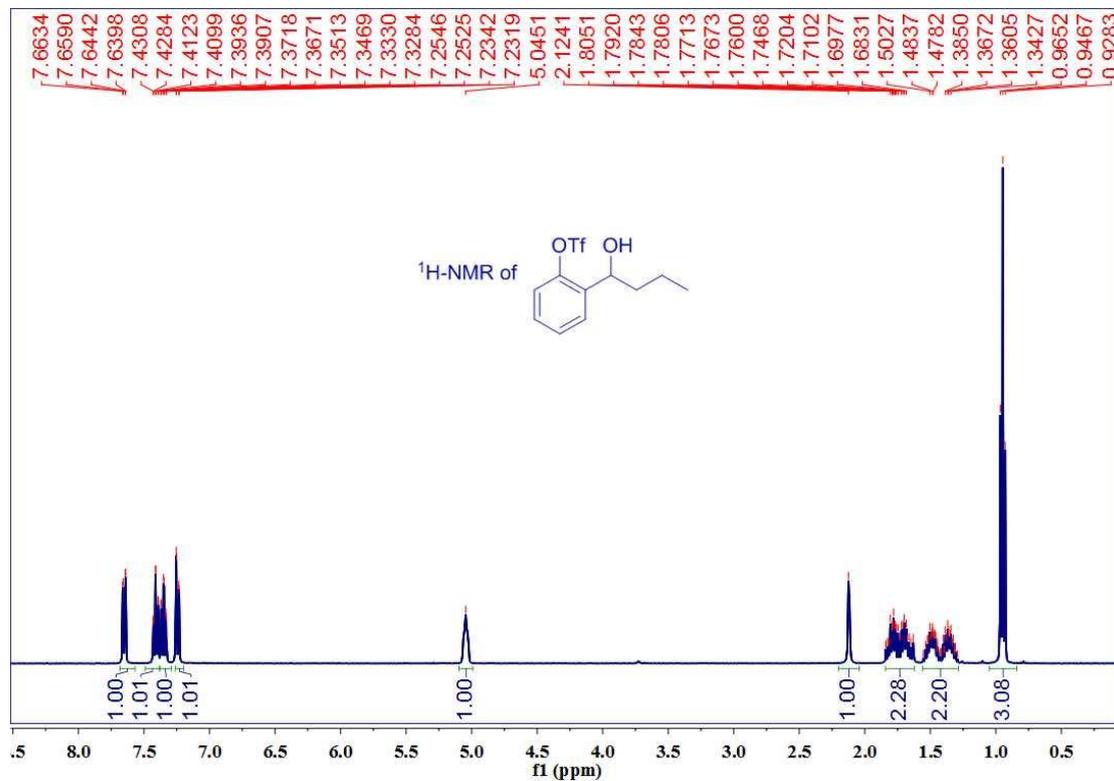
To a solution of compound **3o** (0.2 mmol, 63.2 mg) in toluene (2 mL) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (0.2 equiv, 0.04 mmol, 10.2 mg) and was heated at 110 $^\circ\text{C}$ for 8 h. The resulting mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to give chroman **10** (58 mg, 92% yield) with a 3:1 diastereomer ratio. ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.30 (m, 2H), 7.27-7.21 (m, 2H), 7.20-7.13 (m, 4H), 6.87-6.83 (m, 3H), 6.74-6.67 (m, 2H), 5.08 (dd, $J = 11.8, 1.9$ Hz, 1H), 4.27 (dd, $J = 12.2, 5.9$ Hz, 1H), 3.74 (s, 3H), 2.30 (ddd, $J = 13.7, 5.9, 1.9$ Hz, 1H), 2.21 (dt, $J = 13.7, 11.8$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.5, 155.6, 144.6, 133.3, 129.8, 128.7, 128.6, 127.8, 127.5, 126.8, 125.7, 120.5, 117.0, 114.0, 77.8, 55.4, 43.6, 40.4. HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2$ (M^+): 316.1463, found: 316.1453.

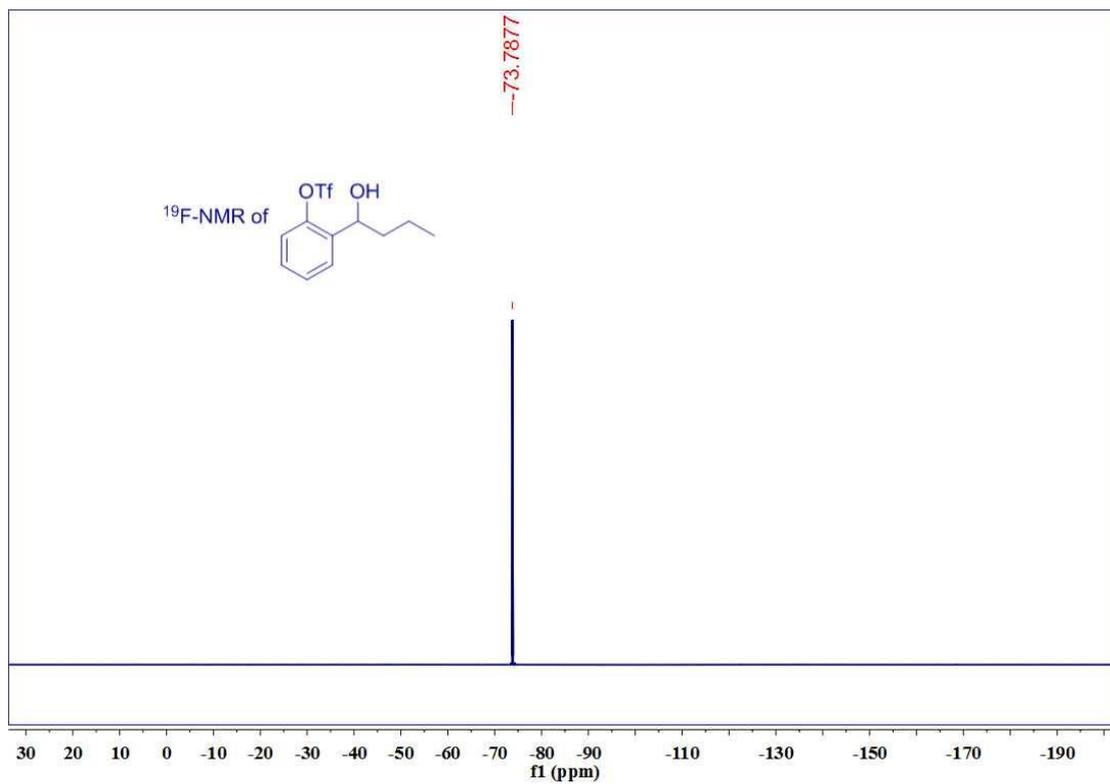
4.5 Oxidation cyclization

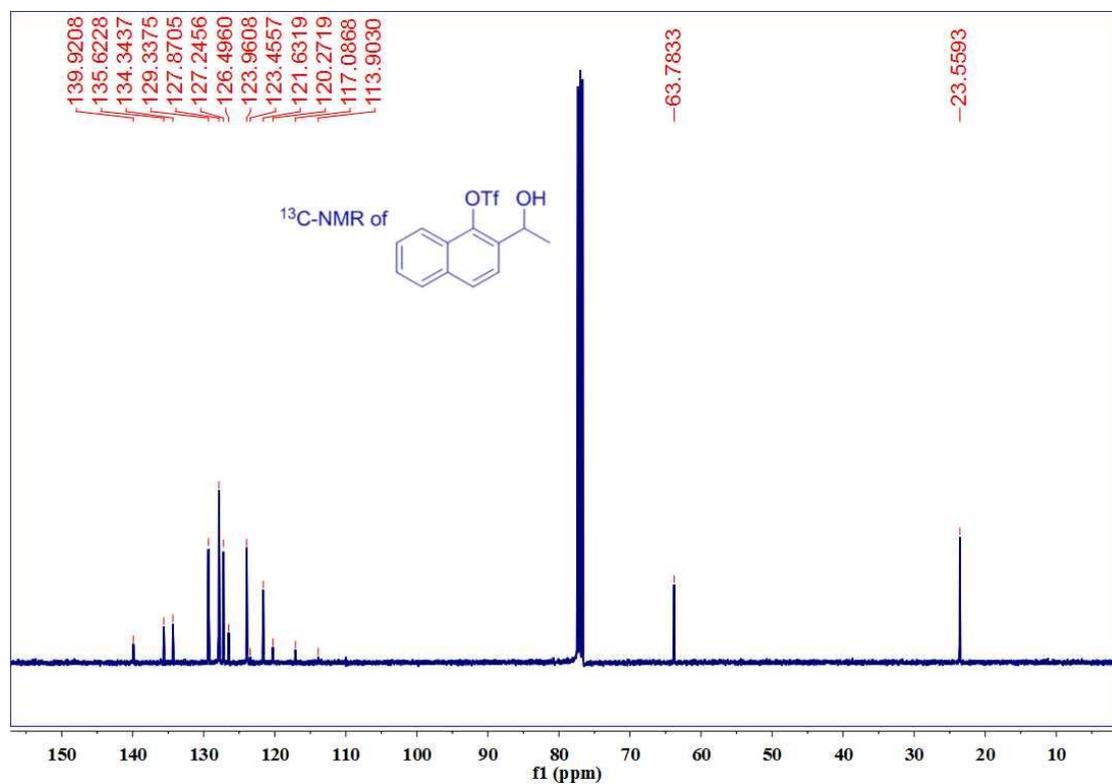
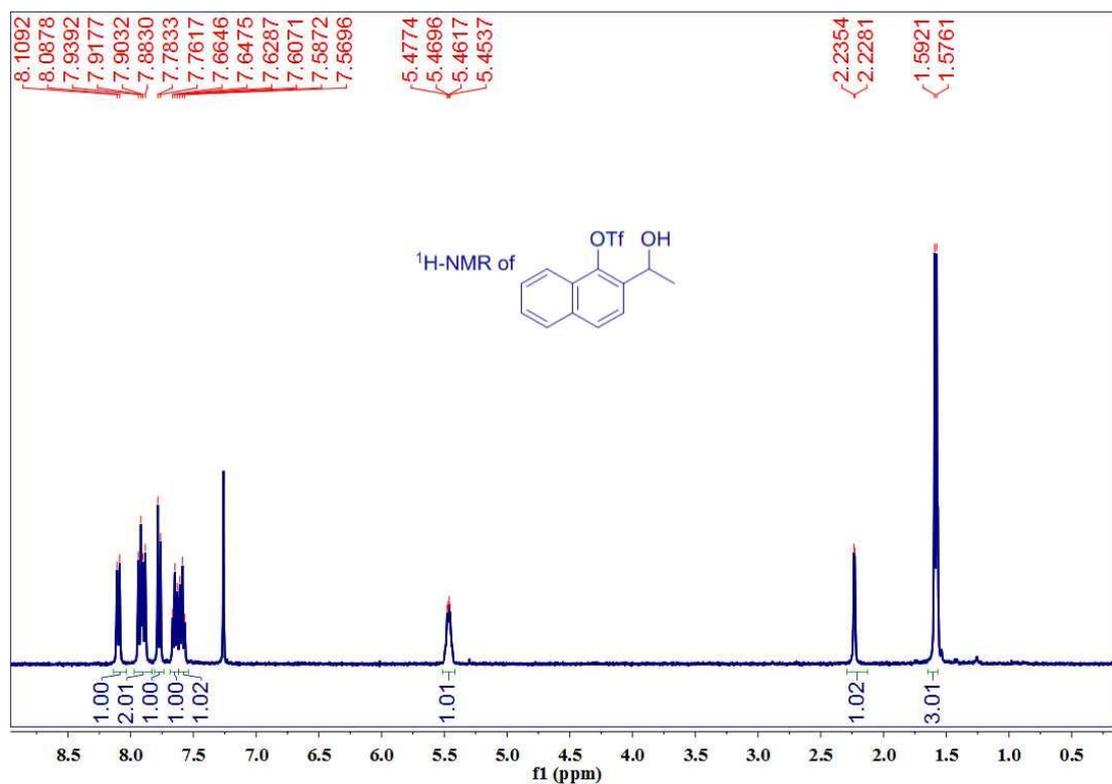


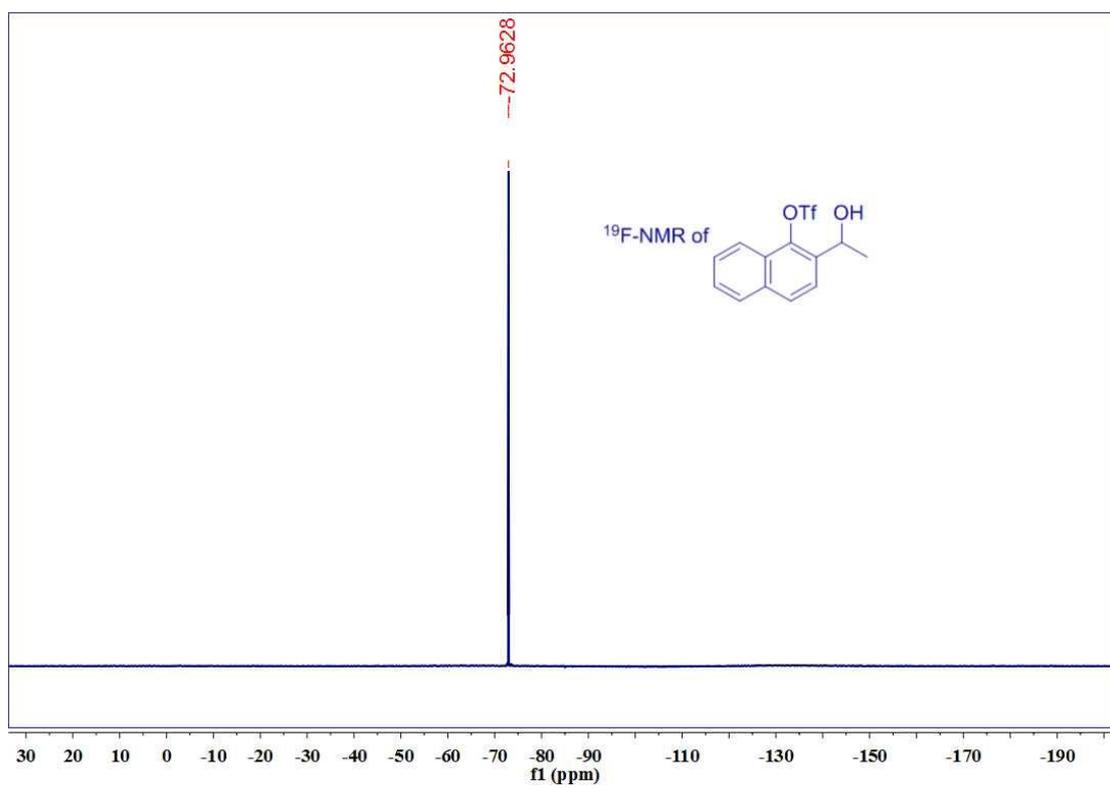
To a solution of compound **3a** (0.13 mmol, 29.0 mg) in 1,4-dioxane (1 mL) was added $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.05 equiv, 0.0065 mmol, 1.7 mg) and 1,4-benzoquinone (1.0 equiv, 0.13 mmol, 14 mg). The mixture was heated at 80 °C and stirred at room temperature for 2 h. After completion, the dark solution was filtered by celite and the filtrate was concentrated. The residue was directly purified by flash chromatography on silica gel (DCM/petroleum ether = 1/100) to afford benzofuran **11** (58 mg, 82% yield). ^1H NMR (600 MHz, CDCl_3) δ ppm 7.40-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.16-7.10 (m, 3H), 4.02 (s, 2H), 2.15 (d, J = 1.7 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ ppm 154.1, 152.2, 138.0, 130.3, 128.6, 128.5, 126.5, 123.5, 122.1, 118.9, 110.8, 110.8, 32.6, 8.1. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ (M^+): 222.1045, found: 222.1034.

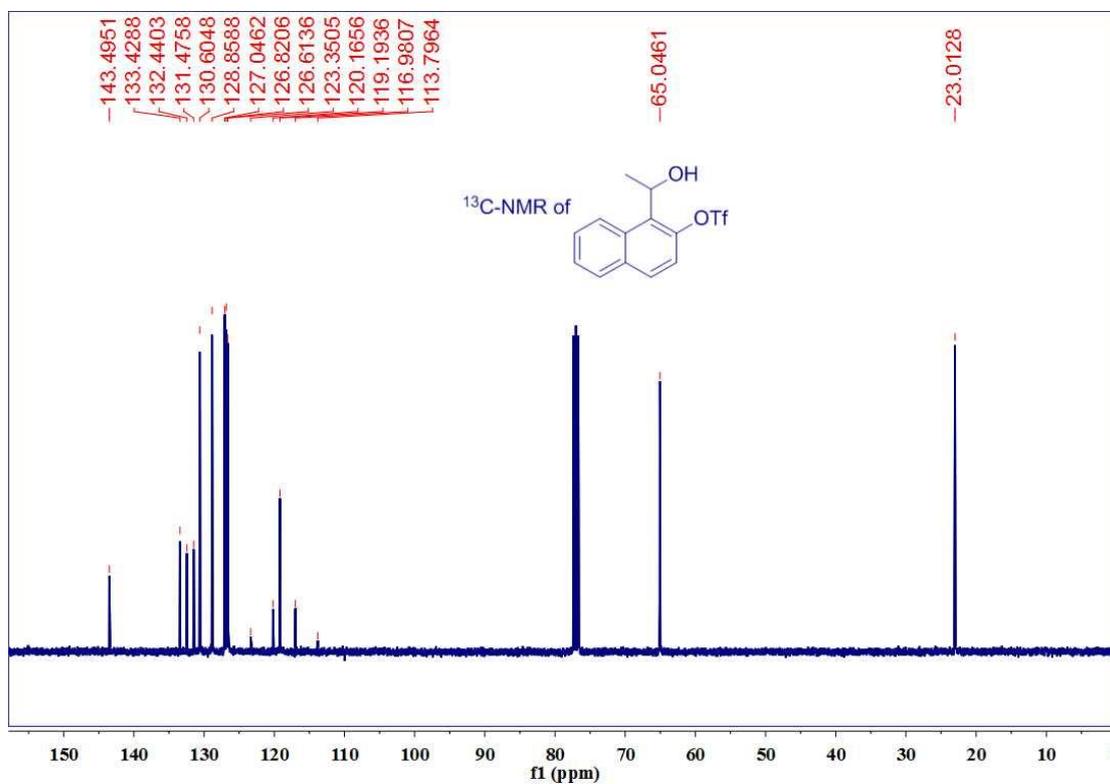
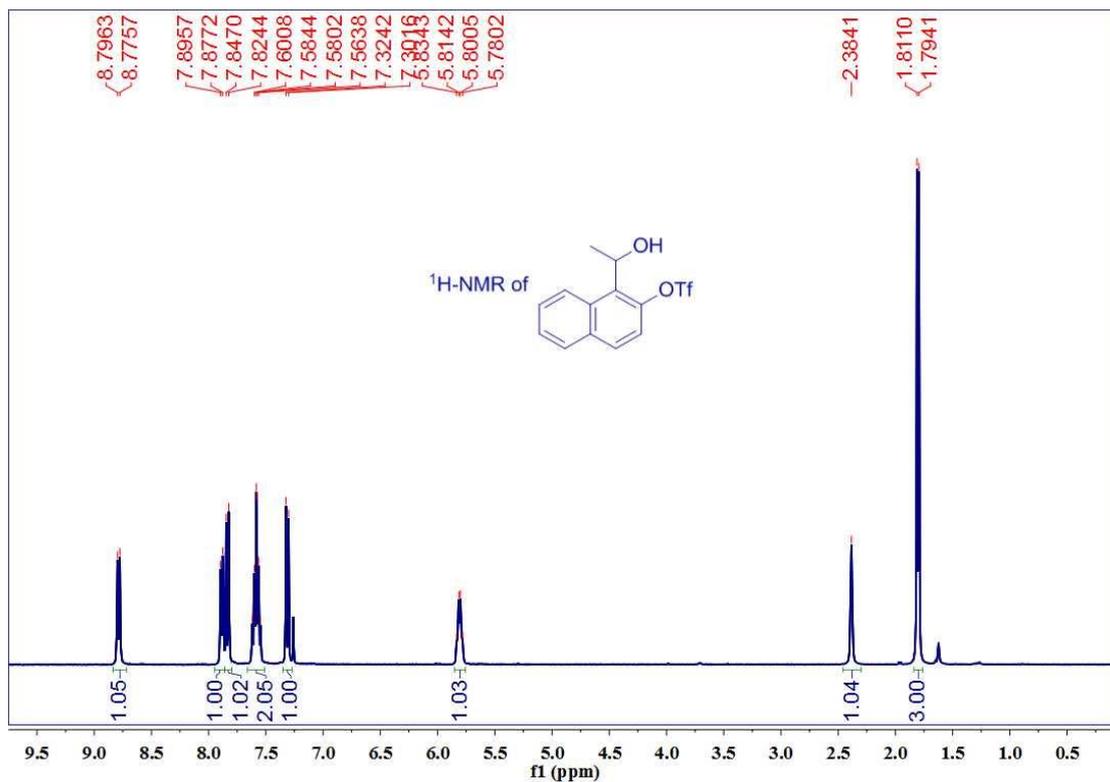
5. NMR spectra

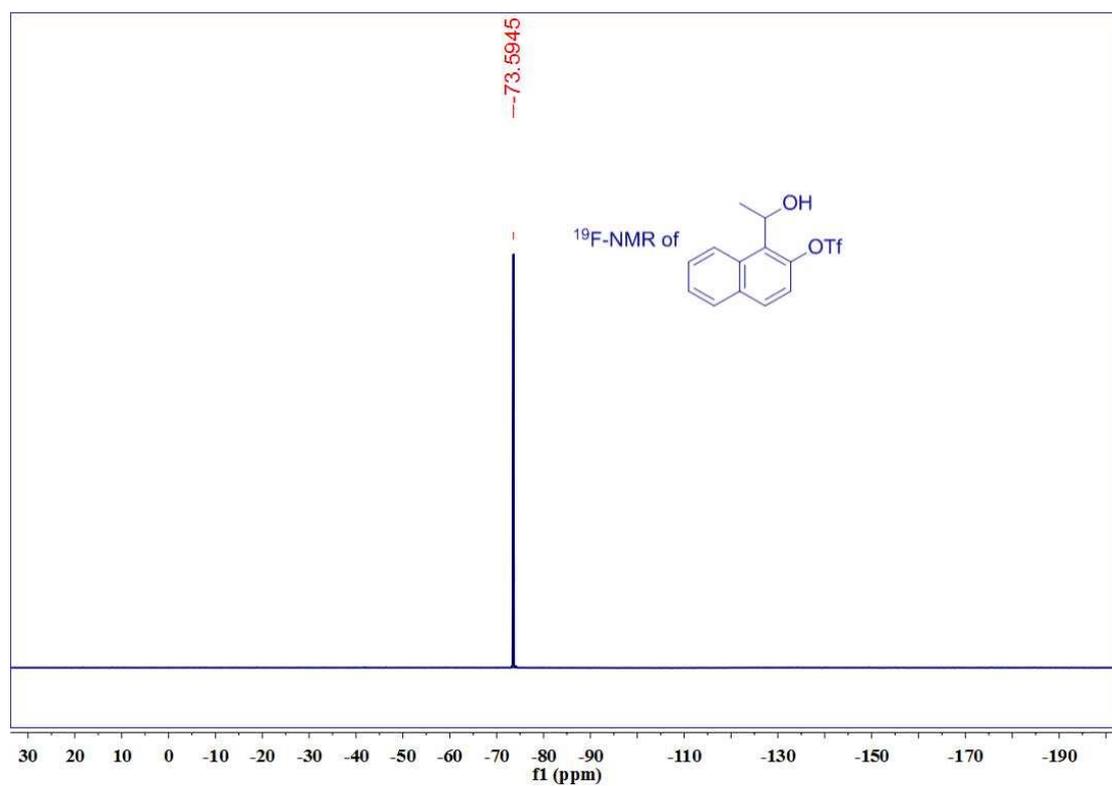


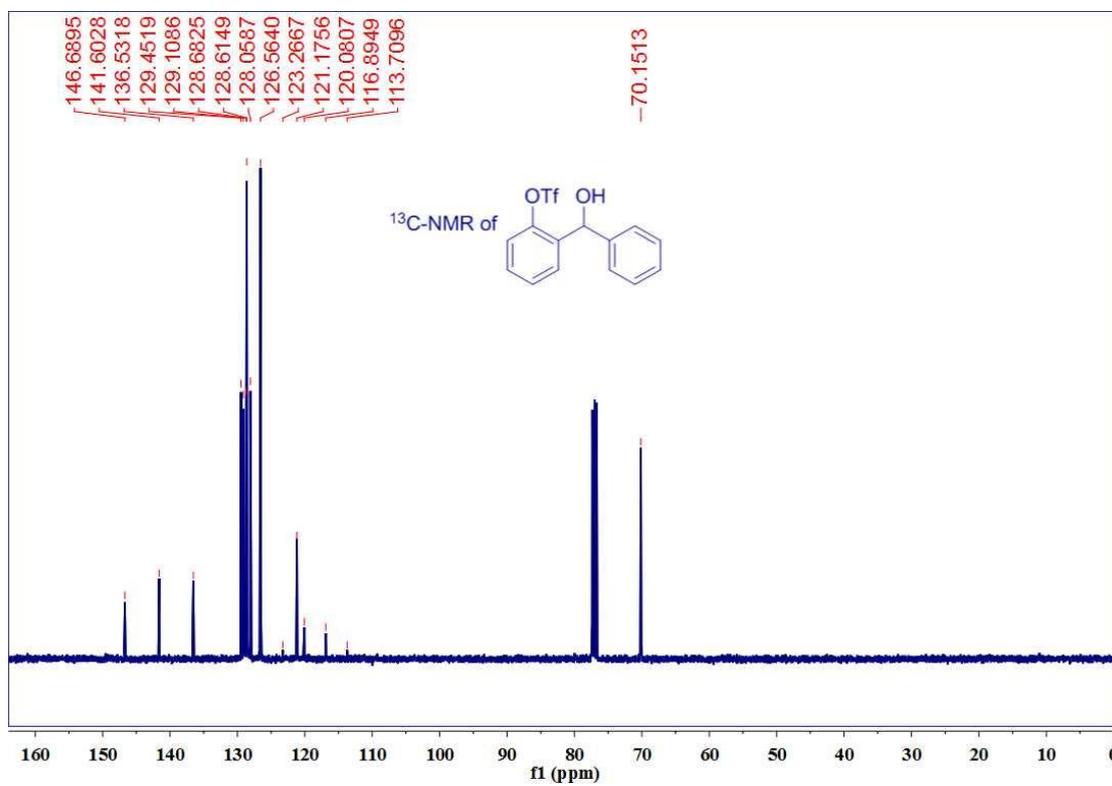
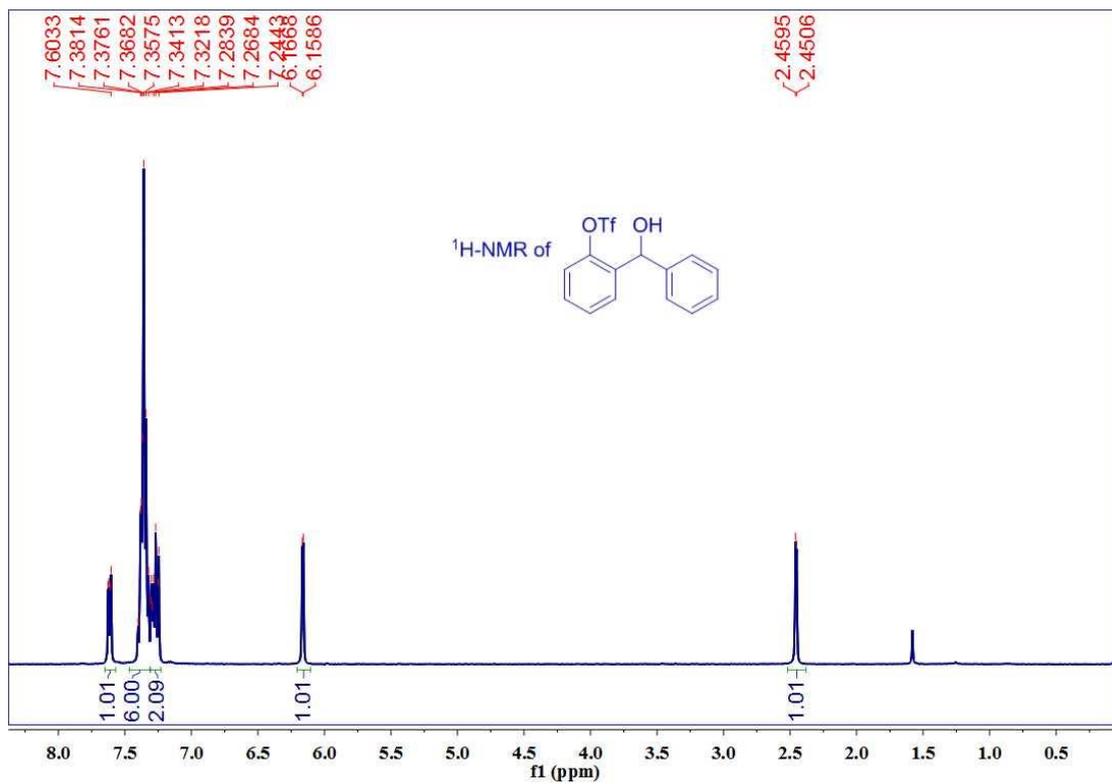


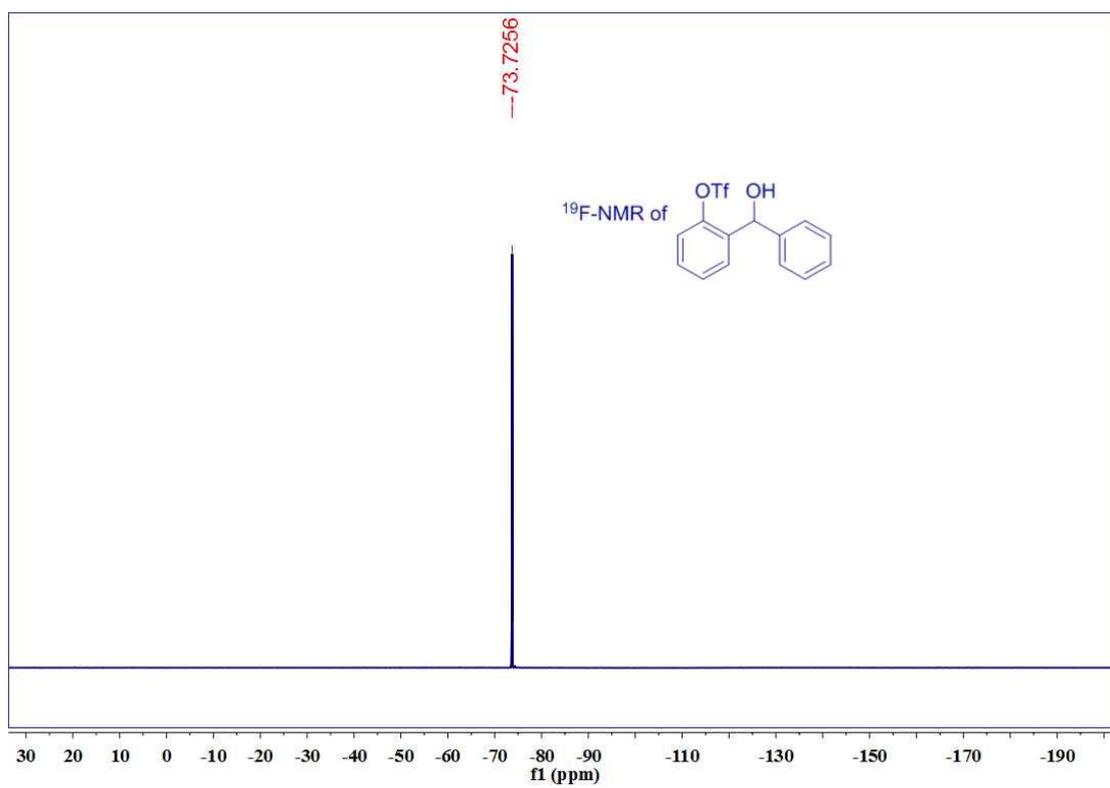


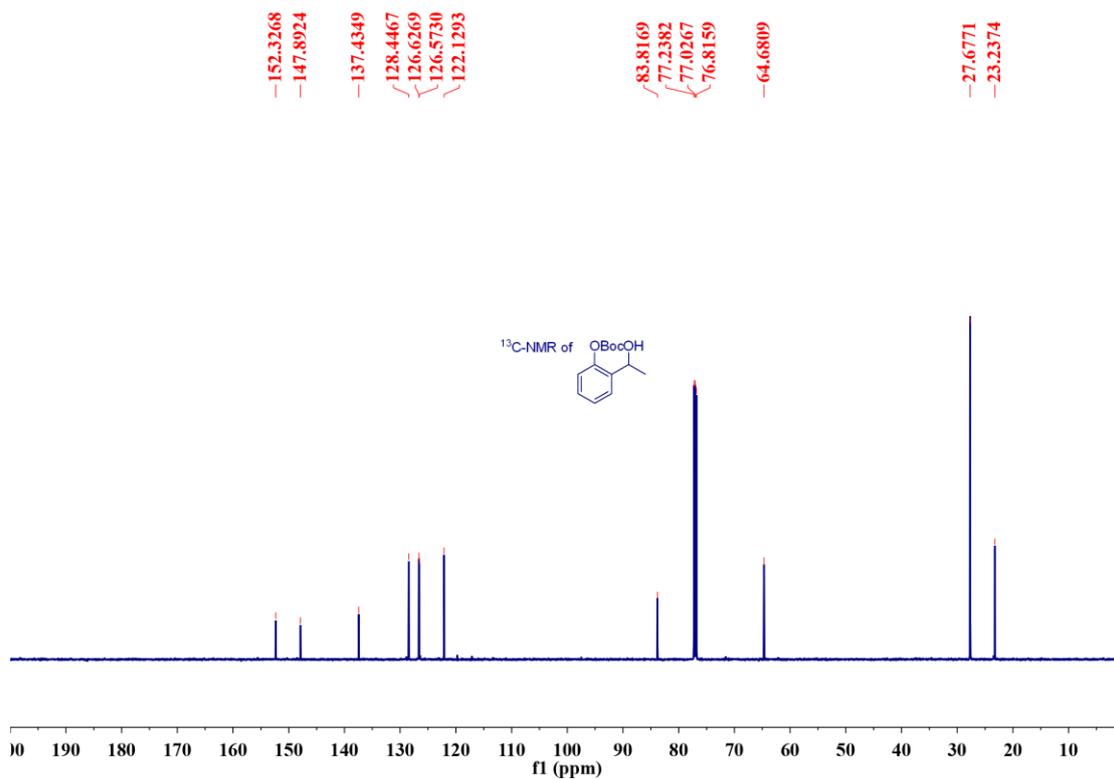
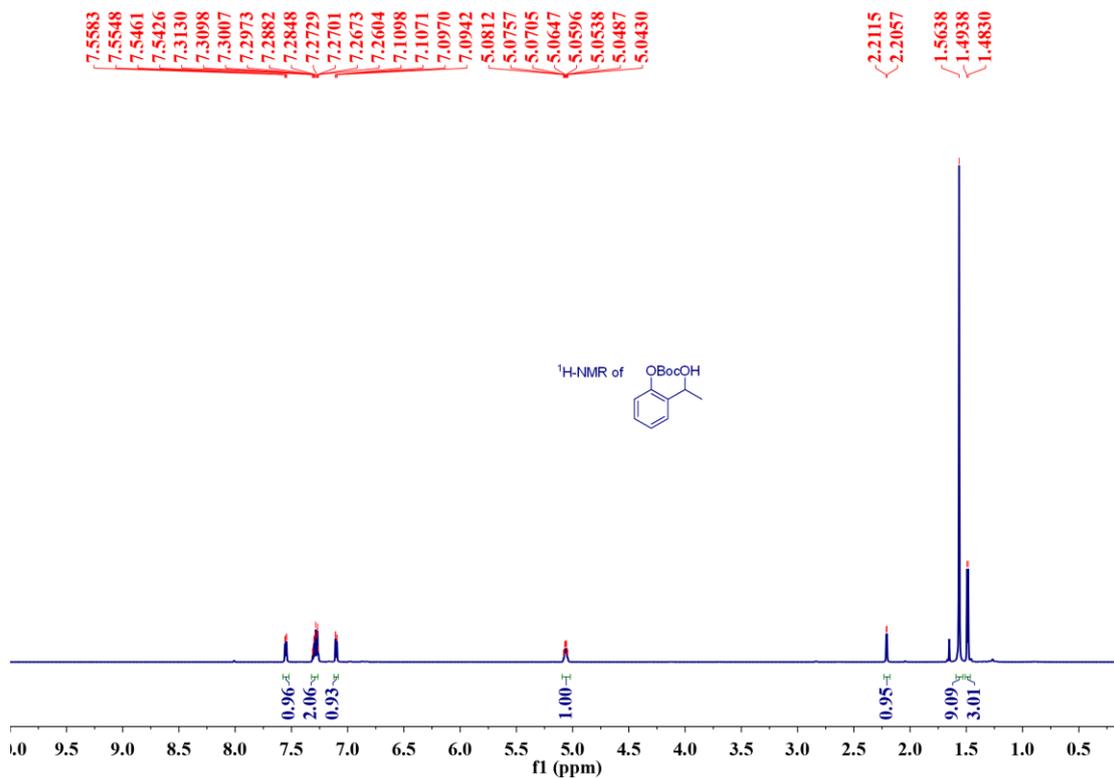


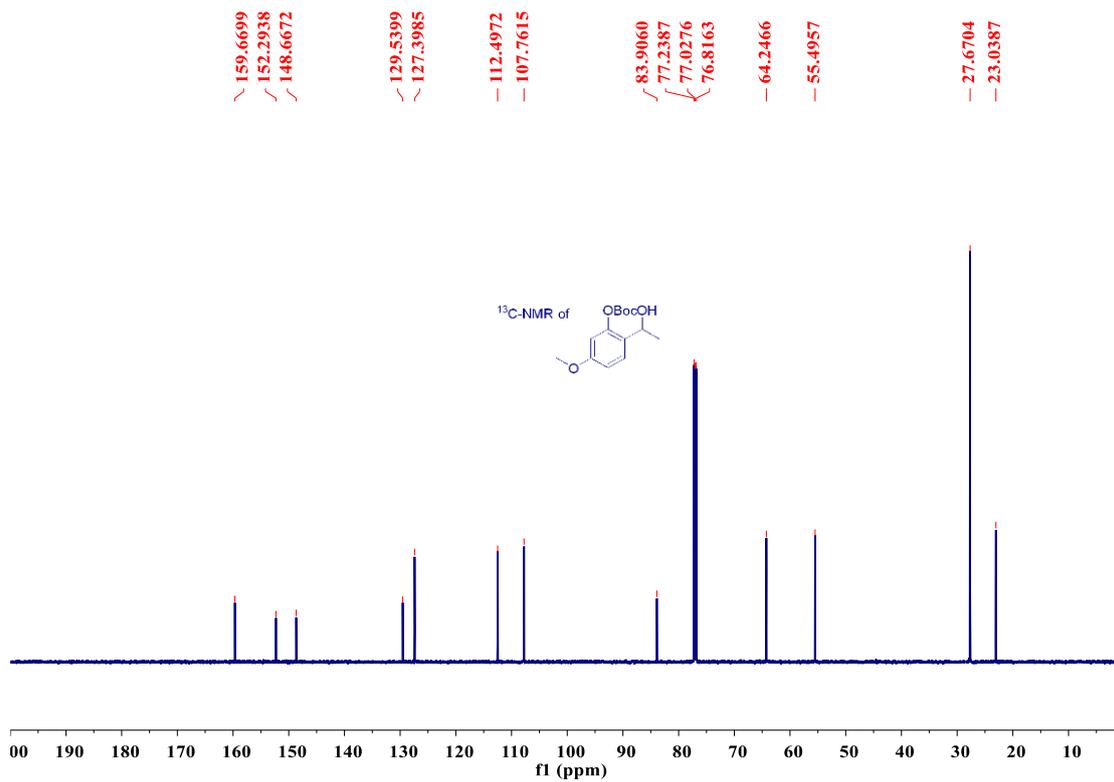
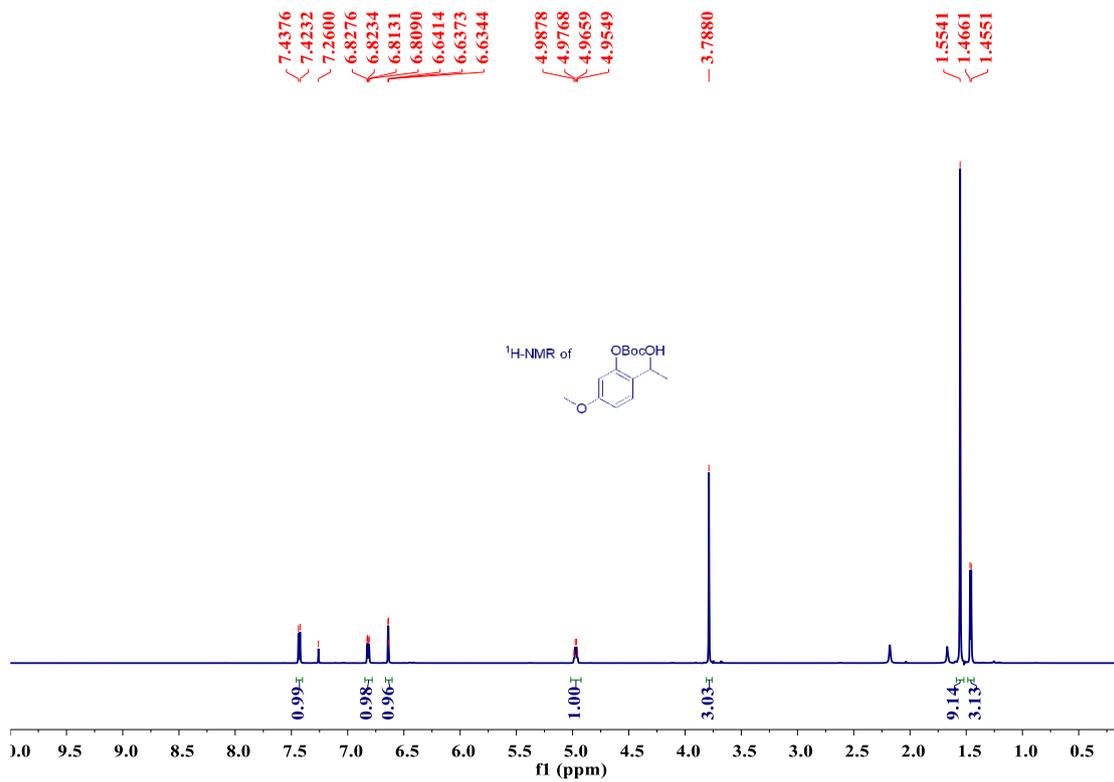


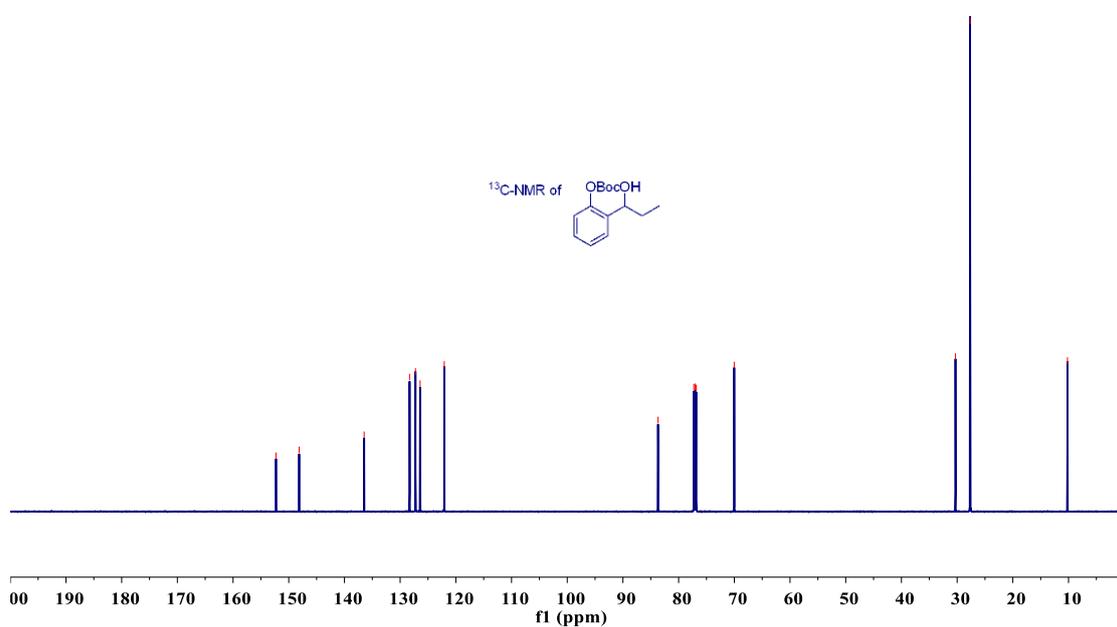
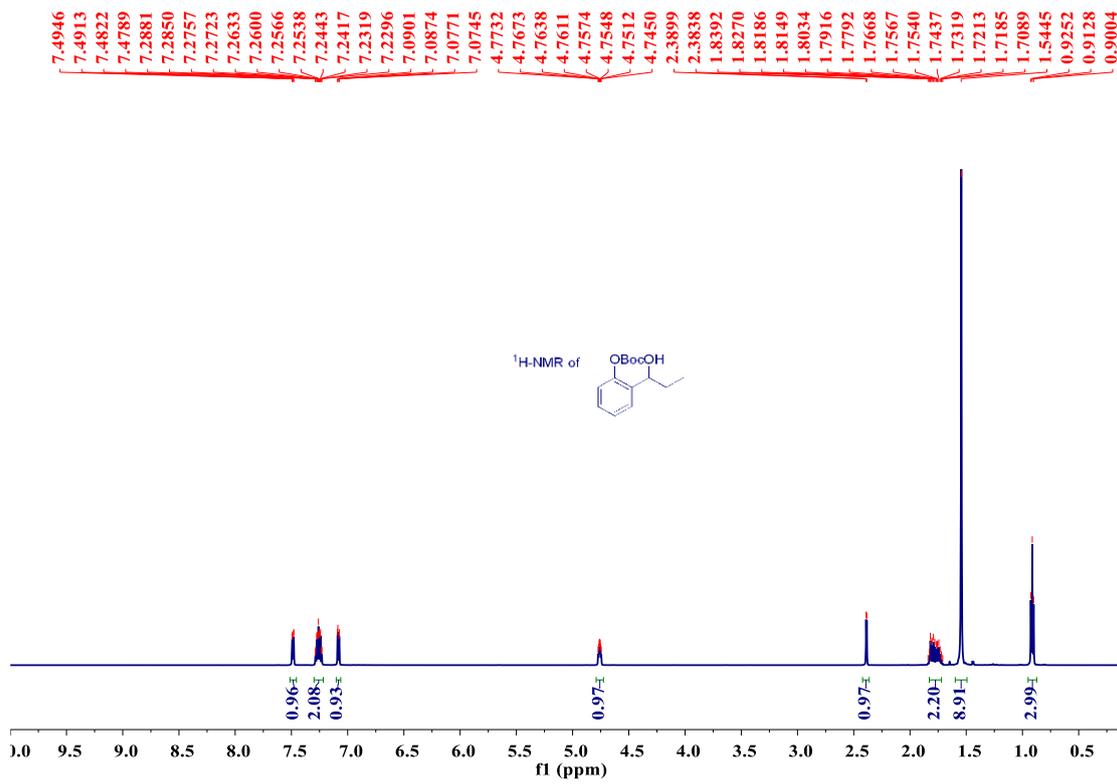


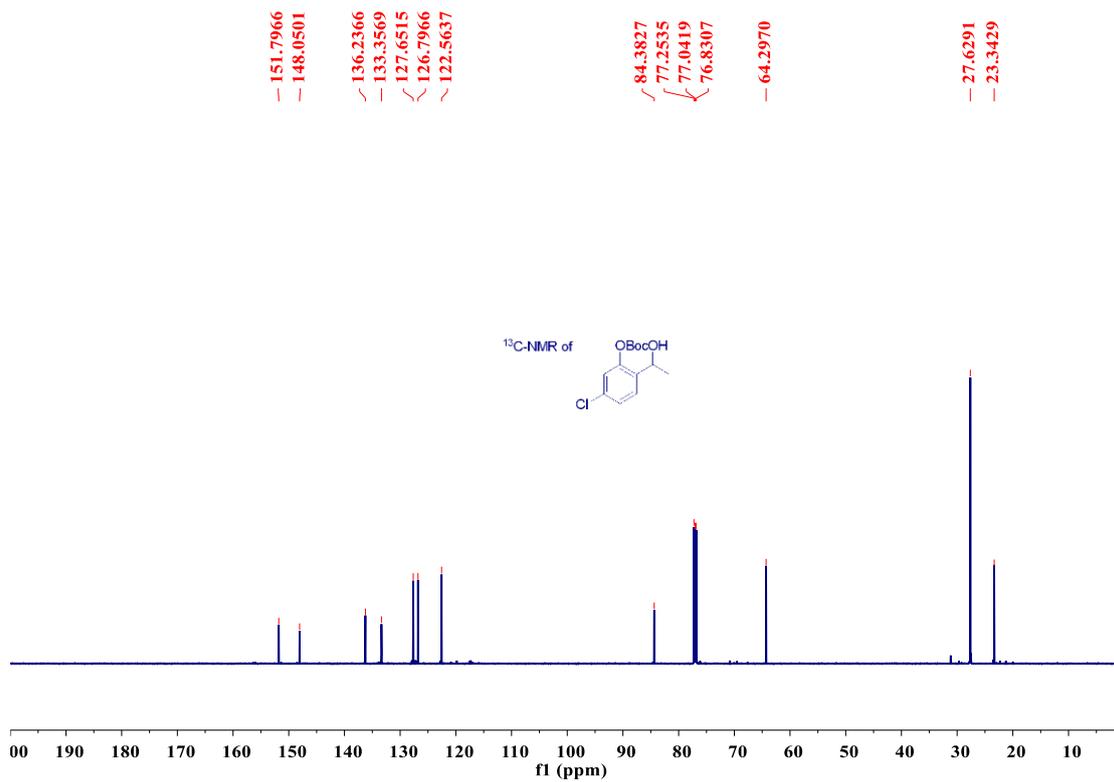
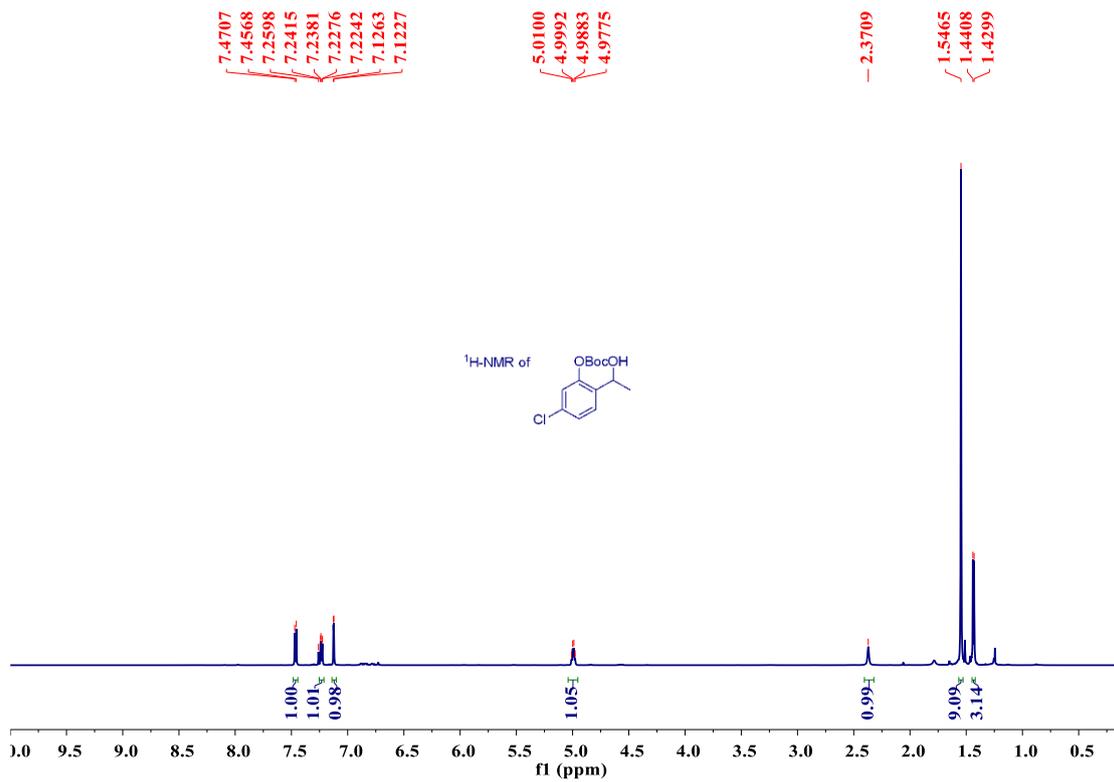


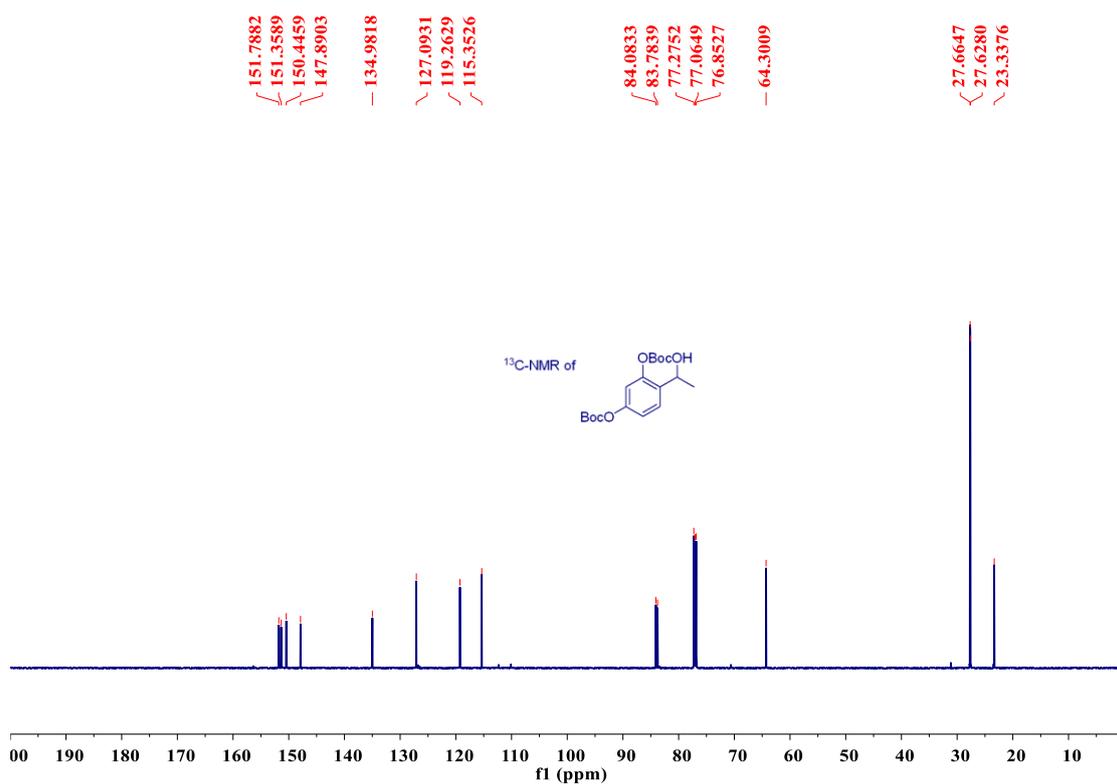
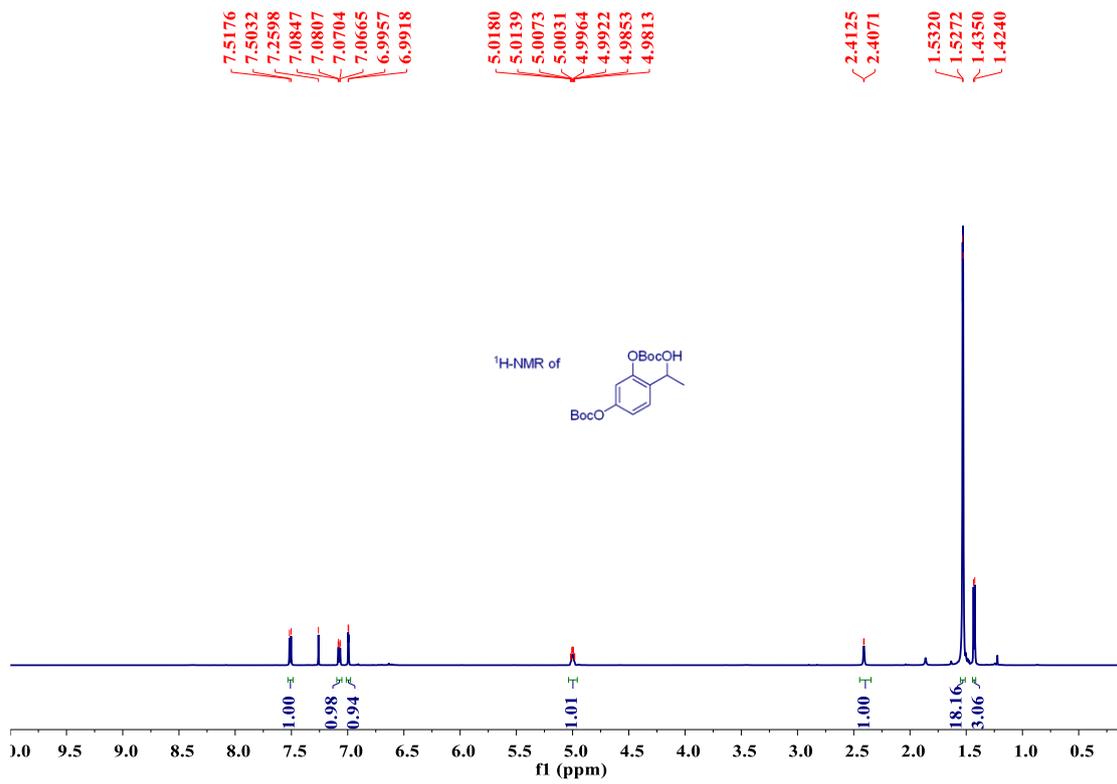


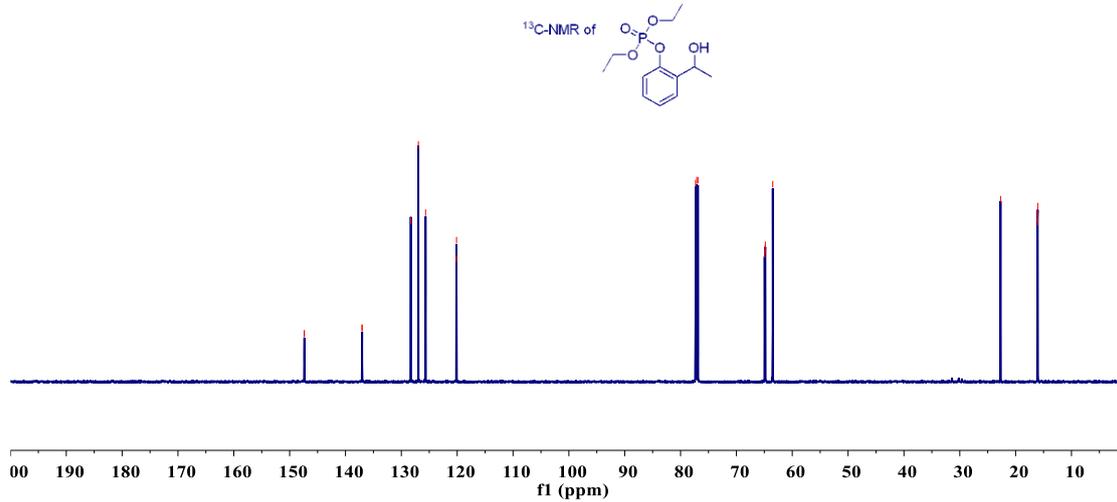
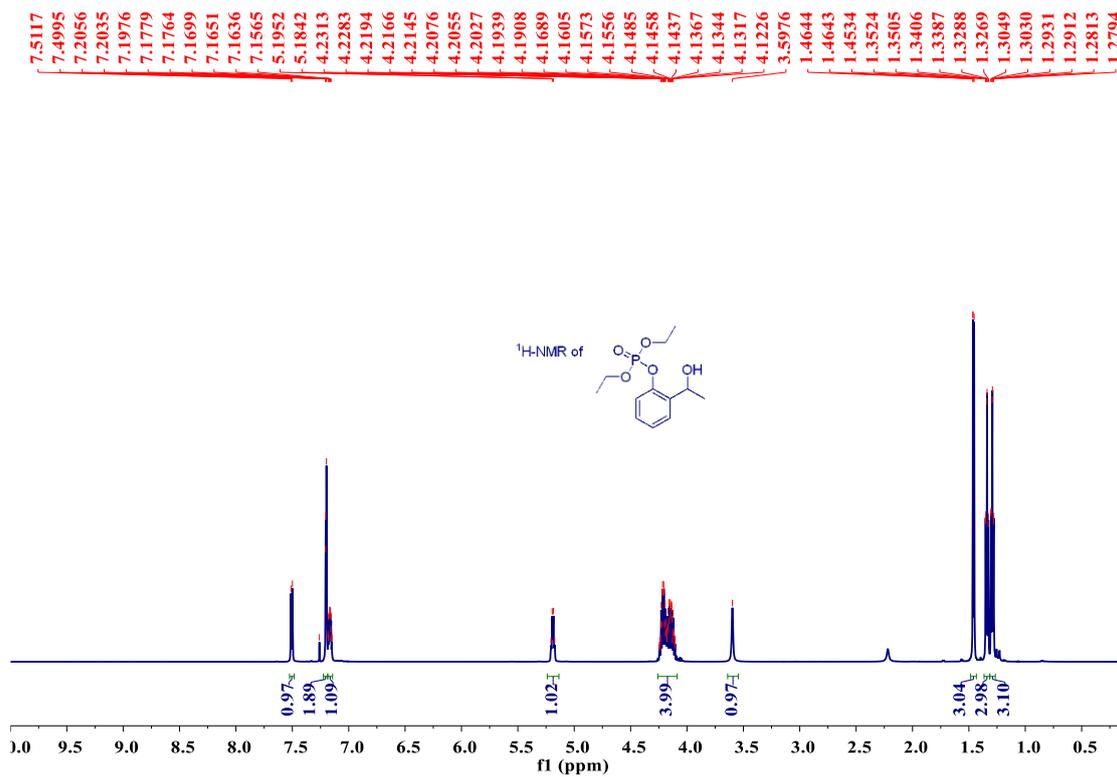


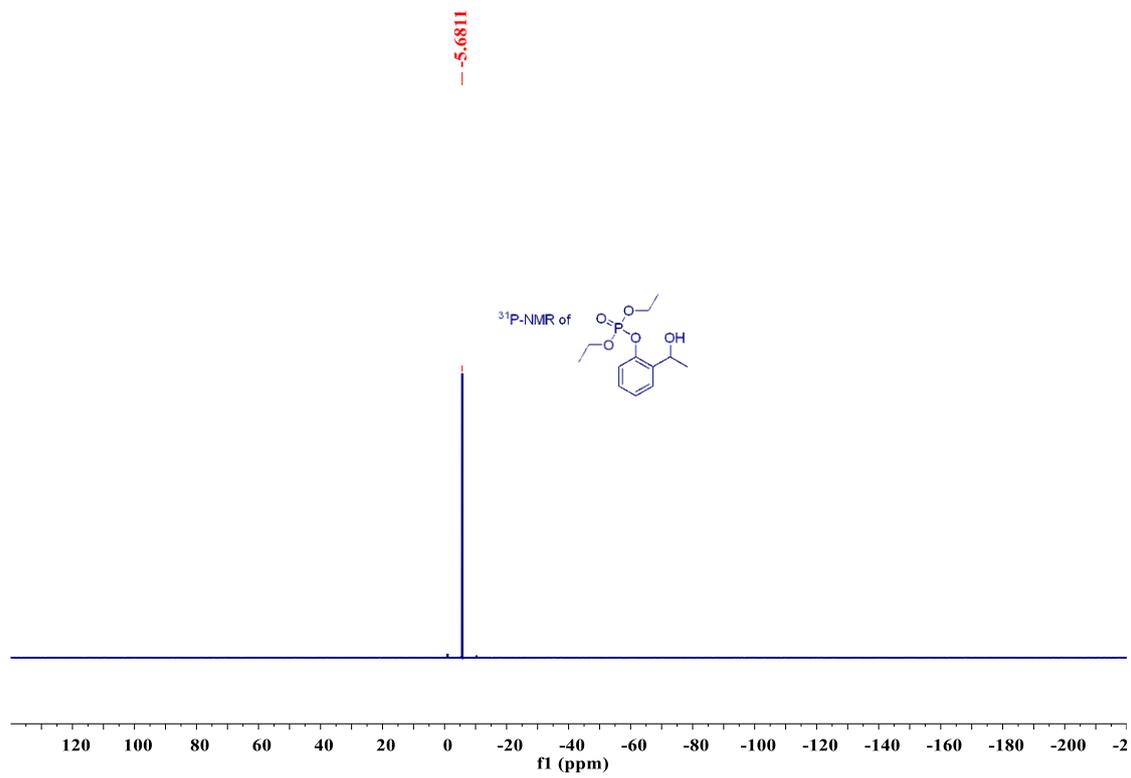


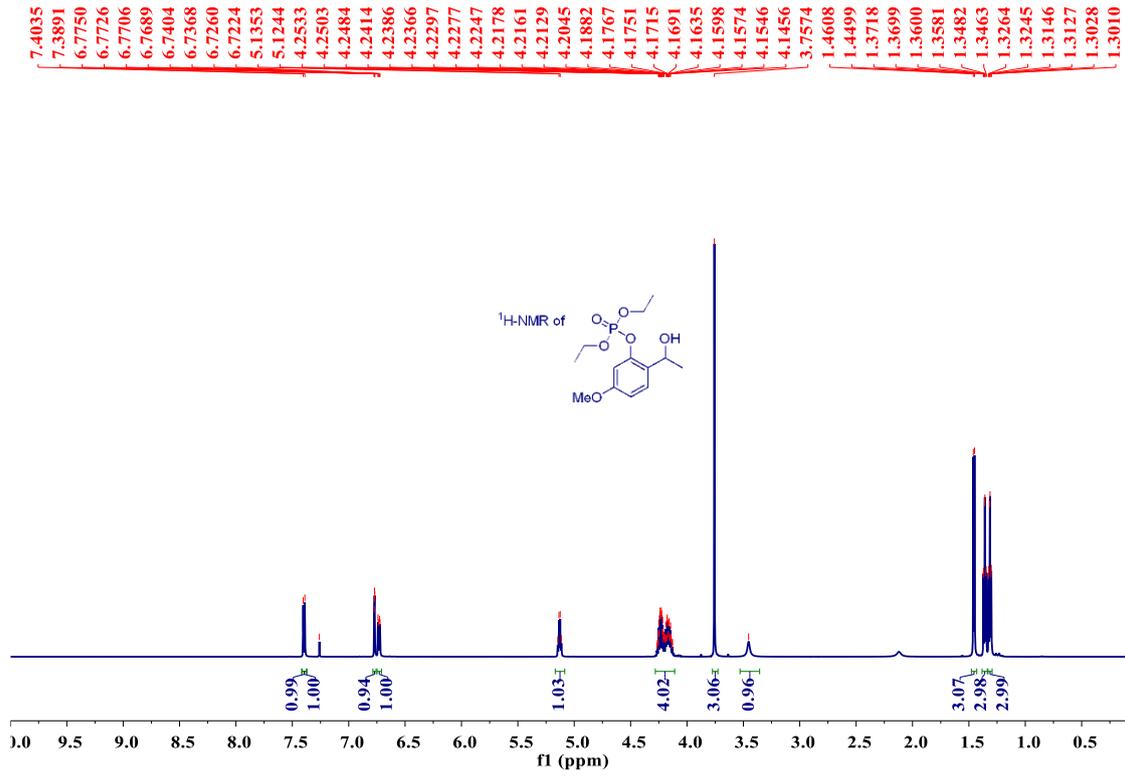




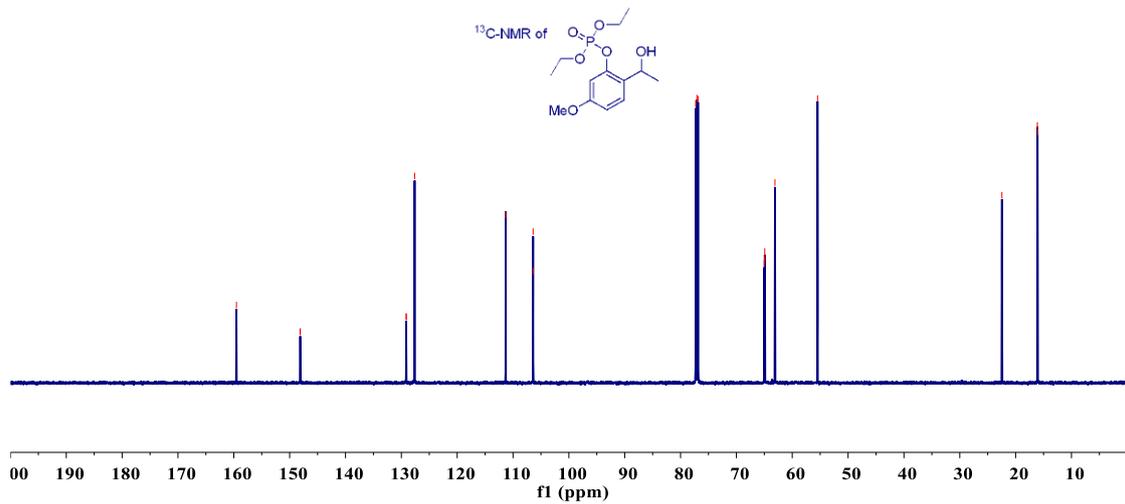




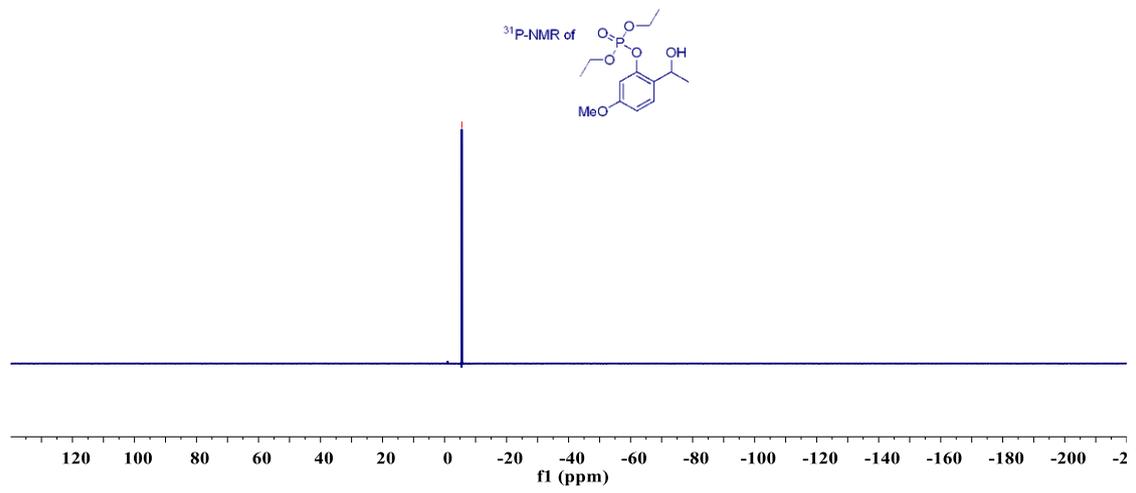


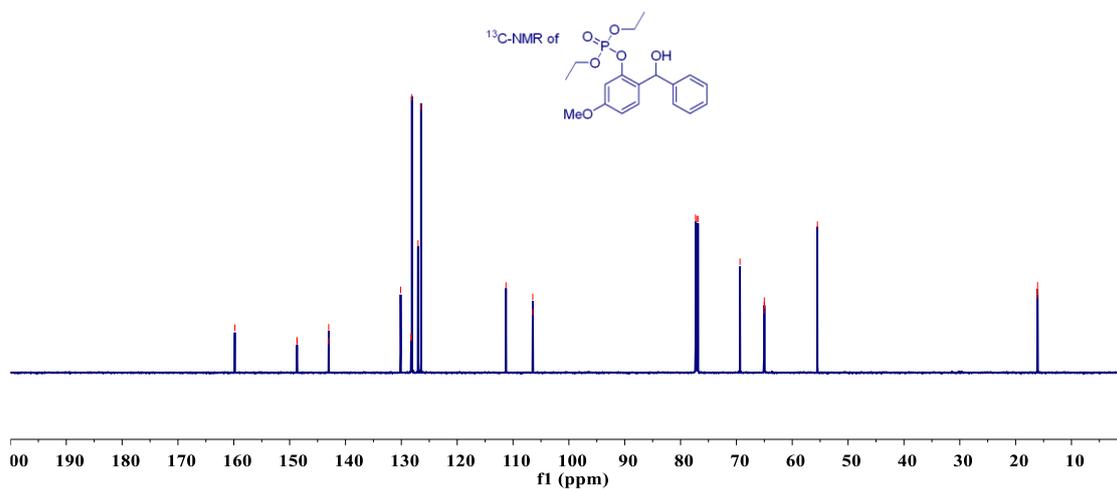
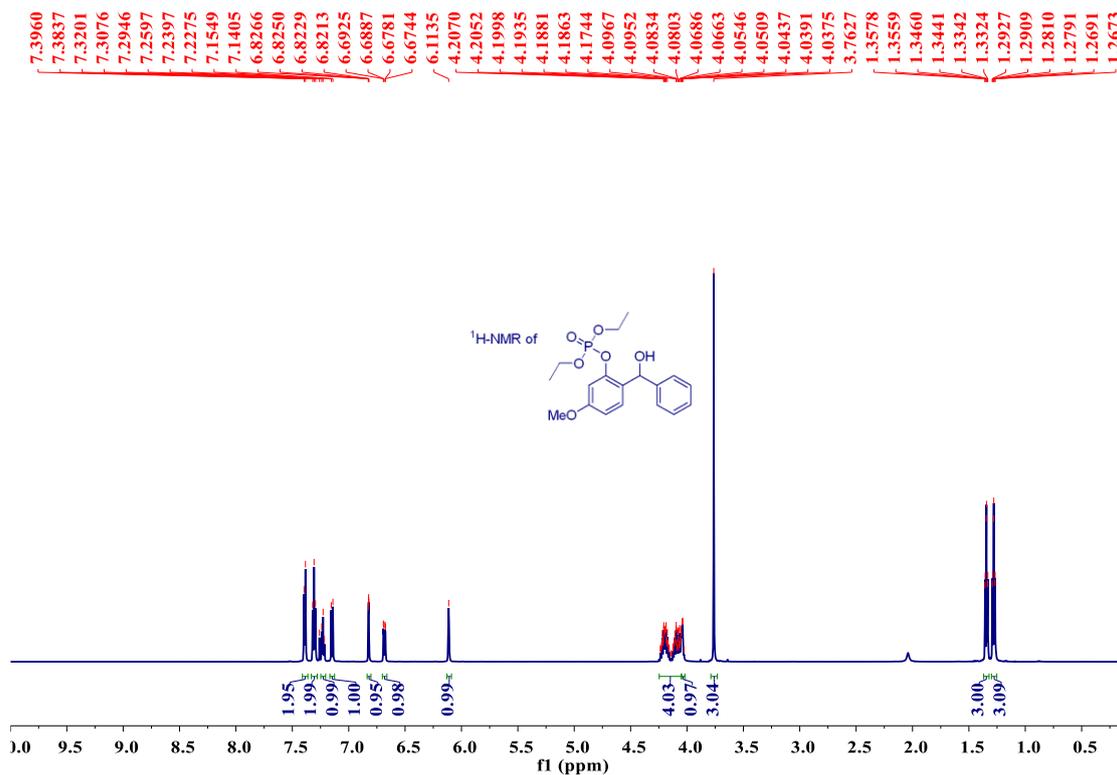


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- 148.0875
- 129.1363
- 129.0999
- 127.6153
- 111.3210
- 106.4180
- 106.4005
- 77.2917
- 77.0795
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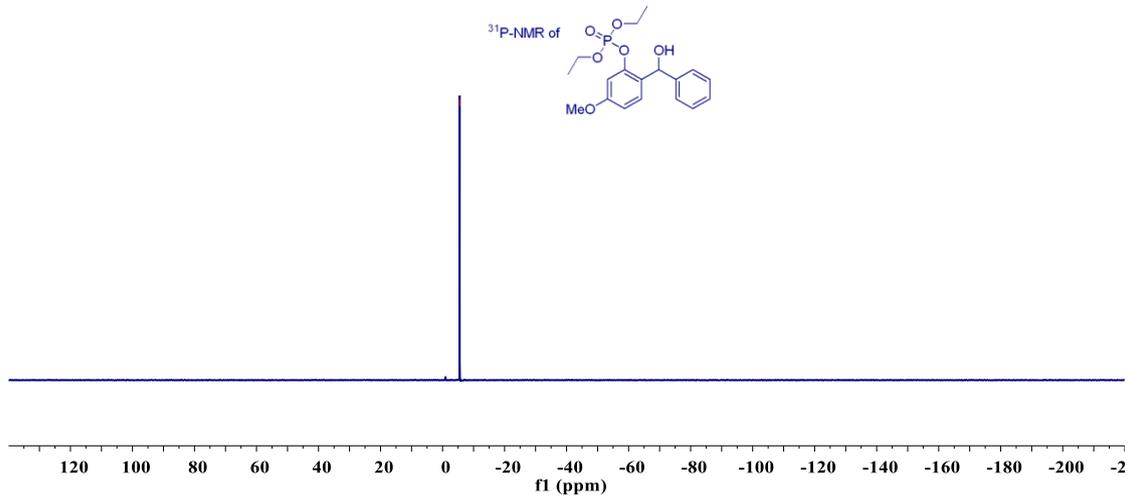


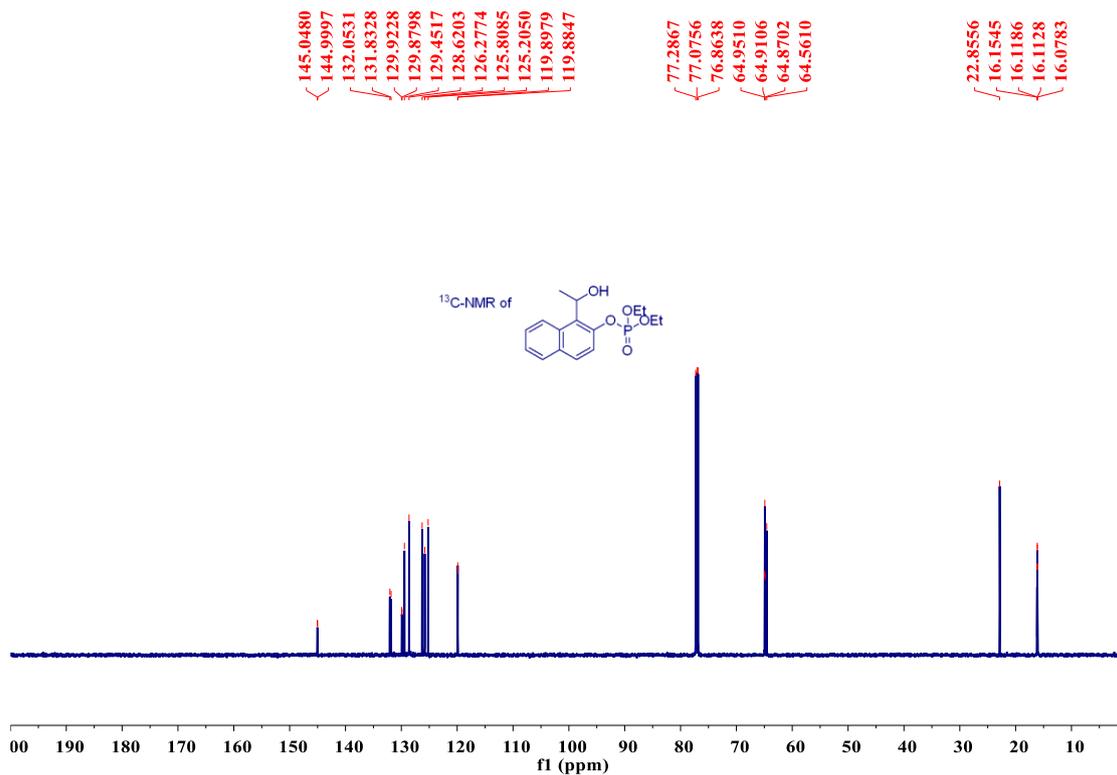
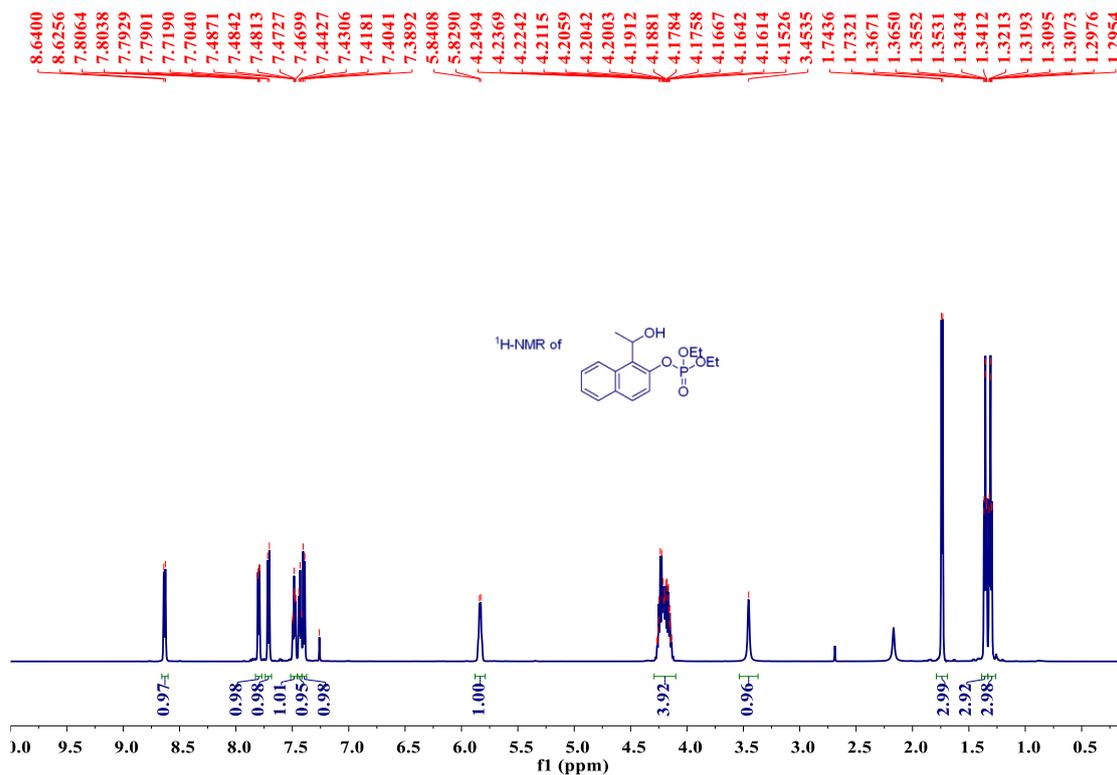
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-5.6571

