Supporting Information

One-pot Synthesis of 3,5-Disubstituted and Polysubstituted Phenols from Acyclic Precursors

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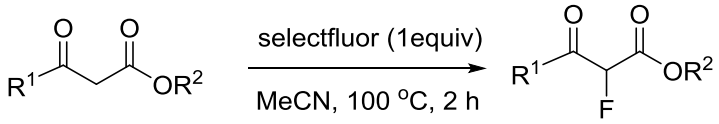
1. General Information

All reactions were run using flame-dried glassware and magnetic stirring. Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, acetone δ 2.09, DMSO δ 2.50), carbon (chloroform δ 77.0, acetone δ 205.87, 30.60, DMSO δ 40.45). GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). For thin-layer chromatography (TLC), Sorbent silica gel XHL TLC plates (130815) were used, and compounds were visualized with a UV light at 254 nm. Melting points were measured on a melting point apparatus and were uncorrected. Mass spectra were recorded on the Waters Q-Tof micro^{TM} (electrospray ionization: ESI).

2. Representative Procedures and Analytical Data

Synthesis of 2-fluoro-3-oxobutanoate



The tert-butyl acetoacetate (1.582 g, 10 mmol) was added to a solution of Selectfluor^{TM} (3.543 g, 10 mmol) in CH_3CN (30 mL). After stirring at 100 ^{o}C for 2 h, the solvents were removed by rotary evaporation to provide raw products. The residue was then chromatographied on silica gel (eluent: cyclohexane/ethyl acetate) to yield corresponding tert-butyl 2-fluoro-3-oxobutanoate (1.602 g, yield 91%). (**1b**, **1c, 9a, 9b** are obtained in the same process.)

Other 2-halogeno-3-oxobutanoates (**1a**, ethyl 2-chloro-3-oxobutanoate and ethyl 2-bromo-3-oxobutanoate) are obtained from commercial suppliers.

Synthesis of chalcone derivatives (2 and **10)**

All products were easily prepared according to the reported procedure.[1]

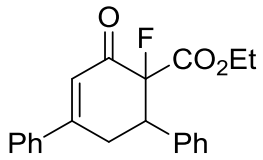
Synthesis of fluoroolefins (6)

All products were easily prepared according to the reported procedure.[2]

Synthesis of intermediate 3a

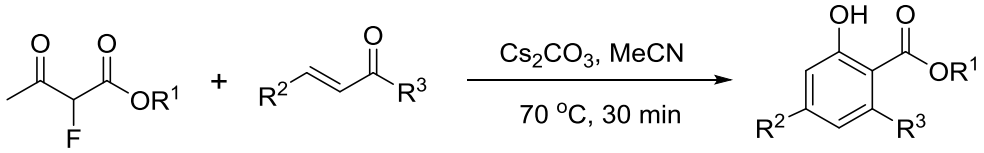
The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at room temperature for 24 h. After completion of the reaction as monitored by TLC, Then the solvent was evaporated and the residual khaki solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (10% ethyl acetate in petroleum ether), affording the desired intermediate **3a** (0.157 g, yield 93%).

Fluorinated cyclohexenone intermediate (3a)



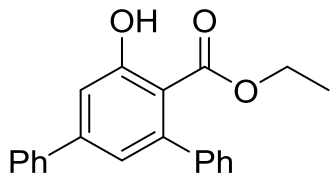
White solid. m.p. 63-65 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.48 – 7.43 (m, 3H), 7.39 – 7.33 (m, 5H), 6.65 – 6.62 (m, 1H), 4.18 – 4.12 (m, 2H), 3.87 – 3.78 (m, 2H), 3.21 – 3.12 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -165.50 (s).
^{c13}C NMR (126 MHz, $CDCl_3$) δ 188.89 (d, *J* = 17.1 Hz), 164.66 (d, *J* = 26.1 Hz), 160.32 (s), 136.50 (s), 135.16 (s), 129.94 (s), 128.01 (s), 127.71 (s), 127.53 (s), 127.38 (s), 125.37 (s), 121.68 (s), 94.07 (d, *J* = 203.3 Hz), 61.33 (s), 47.86 (d, *J* = 20.6 Hz), 31.68 (d, *J* = 6.8 Hz), 12.88 (s). **MS (EI)**: 338.11 (M^+).

General procedure for the synthesis of *o*-phenolic esters (4a-4v)



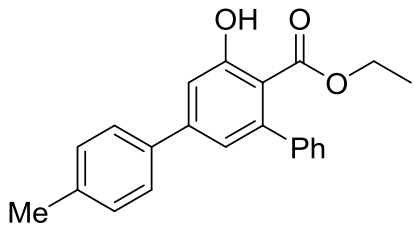
The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^{o}C for half an hour. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual brown solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (10% ethyl acetate in petroleum ether), affording the desired *o*-phenolic esters **4a** (0.142 g, yield 89%).

Ethyl 3,5-diphenyl-phenol-2-carboxylate (4a)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^{o}C for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4a** (0.142 g, 89% yield) as white solid. m.p. 80-82 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.07 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.37 – 7.32 (m, 3H), 7.13 (d, *J* = 1.6 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.99 (s), 161.21 (s), 145.27 (s), 144.60 (s), 142.27 (s), 138.44 (s), 127.96 (s), 127.54 (s), 127.34 (s), 126.69 (s), 126.29 (s), 125.91 (s), 120.54 (s), 113.85 (s), 110.00 (s), 60.08 (s), 12.10 (s). **MS (EI)**: 318.16 (M^+).

Ethyl 3-phenyl-5-(4'-methylphenyl)-phenol-2-carboxylate (4b)

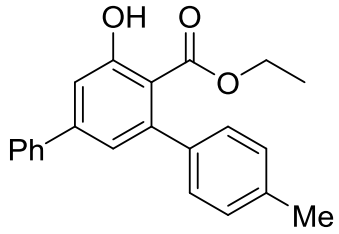


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (0.110 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4b** (0.143 g, 86% yield) as white solid. m.p. 121-124 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (s, 1H), 7.58 – 7.51 (m, 2H), 7.44 – 7.33 (m, 3H), 7.31 – 7.27 (m, 2H), 7.25 (dd, *J* = 4.9, 3.0 Hz, 3H), 7.05 (d, *J* = 1.9 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.98 (s), 161.08 (s), 145.18 (s), 144.47 (s), 142.26 (s), 137.52 (s), 135.46 (s), 128.64 (s), 127.26 (s), 126.61 (s), 126.08 (s), 125.82 (s), 120.34 (s), 113.46 (s), 109.63 (s), 60.00 (s), 20.22 (s), 12.03 (s). **MS (EI)**: 332.20 (M^+).

Ethyl 3-(4'-methylphenyl)-5-phenyl-phenol-2-carboxylate (4c)

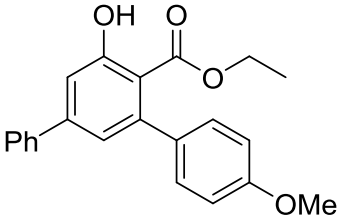


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (0.110 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4c** (0.141 g, 85% yield) as white solid. m.p. 87-89 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.66 – 7.60 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.15 (m, 4H), 7.06 (d, *J* = 1.9 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.04 (s), 160.93 (s), 145.18 (s), 144.55 (s), 139.20 (s), 138.47 (s), 135.56 (s), 127.90 (s), 127.45 (s), 127.29 (s), 127.17 (s), 126.25 (s), 120.62 (s), 113.58 (s), 110.05 (s), 60.08 (s), 20.20 (s), 12.08 (s). **MS (EI)**: 332.21 (M^+).

Ethyl 3-(4'-methoxyphenyl)-5-phenyl-phenol-2-carboxylate (4d)



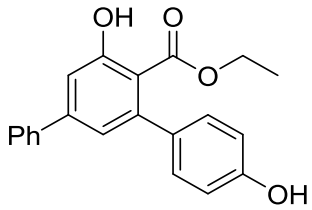
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (0.119 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by

column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4d** (0.143 g, 82% yield) as white solid. m.p. 98-101 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.64 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.25 – 7.18 (m, 3H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.97 – 6.89 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.08 (s), 160.98 (s), 157.88 (s), 145.17 (s), 144.15 (s), 138.48 (s), 134.60 (s), 128.39 (s), 127.90 (s), 127.45 (s), 126.24 (s), 120.71 (s), 113.51 (s), 112.11 (s), 110.10 (s), 60.08 (s), 54.44 (s), 12.29 (s). **MS (EI)**: 348.12 (M^+).

Ethyl 3-(4'-hydroxyphenyl)-5-phenyl-phenol-2-carboxylate (4e)



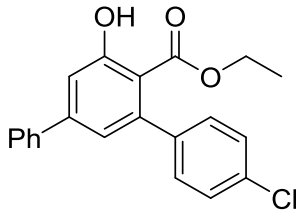
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (0.112 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4e** (0.134 g, 80% yield) as white solid. m.p. 88-91 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 7.22 (d, *J* = 1.1 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 3H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.19 (s), 161.78 (s), 156.55 (s), 145.95 (s), 145.59 (s), 143.19 (s), 131.51 (s), 128.64 (s), 128.27 (s), 127.66 (s), 126.89 (s), 121.27 (s), 115.98 (s), 113.93 (s), 110.29 (s), 61.21 (s), 13.02 (s). **MS (EI)**: 334.18 (M^+).

HRMS (ESI): calculated for $C_{21}H_{18}O_4$ $[M+Na]^+$: 357.1103, found 357.1113.

Ethyl 3-(4'-chlorophenyl)-5-phenyl-phenol-2-carboxylate (4f)



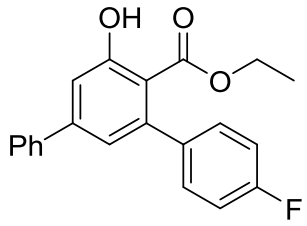
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (0.121 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4f** (0.162 g, 92% yield) as white solid. m.p. 118-120 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.29 (d, *J* = 1.7 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 1.7 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.68 (s), 162.34 (s), 146.41 (s), 144.15 (s), 141.68 (s), 139.19 (s), 132.93 (s), 129.66 (s), 128.96 (s), 128.62 (s), 127.76 (s), 127.23 (s),

121.37 (s), 115.20 (s), 110.67 (s), 61.27 (s), 13.16 (s). **MS (EI)**: 352.06 (M^+).

Ethyl 3-(4'-fluorophenyl)-5-phenyl-phenol-2-carboxylate (4g)

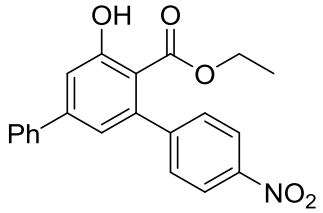


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4g** (0.155 g, 92% yield) as white solid. m.p. 119-121 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.12 – 7.05 (m, 2H), 7.02 (d, *J* = 1.8 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.81 (s), 161.25 (s), 161.16 (d, *J* = 245.4 Hz), 145.34 (s), 143.36 (s), 138.21 (d, *J* = 12.6 Hz), 128.81 (d, *J* = 7.0 Hz), 127.98 (s), 127.58 (s), 126.24 (s), 120.60 (s), 114.04 (s), 113.57 (s), 113.40 (s), 109.84 (s), 60.19 (s), 12.19 (s). **MS (EI)**: 336.12 (M^+).

Ethyl 3-(4'-nitrophenyl)-5-phenyl-phenol-2-carboxylate (4h)

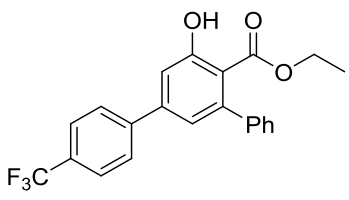


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (0.127 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4h** (0.167 g, 92% yield) as white solid. m.p. 162-164 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.25 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.38 (m, 5H), 7.30 (d, *J* = 1.7 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.80 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.15 (s), 162.65 (s), 150.10 (s), 146.90 (s), 146.73 (s), 142.94 (s), 138.82 (s), 129.27 (s), 129.03 (s), 128.83 (s), 127.20 (s), 122.88 (s), 120.98 (s), 116.02 (s), 110.05 (s), 61.47 (s), 13.16 (s). **MS (EI)**: 363.17 (M^+).

Ethyl 3-phenyl-5-(4'-trifluoromethylphenyl)-phenol-2-carboxylate (4i)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half

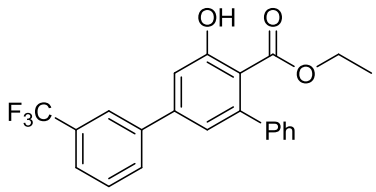
an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4i** (0.180 g, 93% yield) as white solid. m.p. 100-102 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.37 (m, 5H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.49 (s), 162.52 (s), 147.00 (s), 146.56 (s), 143.93 (s), 139.05 (s), 128.98 (s), 128.69 (s), 128.65 (s), 127.21 (s), 125.47 (s), 124.54 (q, *J* = 3.7 Hz), 123.31 (s), 121.13 (s), 115.54 (s), 110.44 (s), 61.26 (s), 12.82 (s). **MS (EI)**: 386.13 (M^+).

HRMS (ESI): calculated for $C_{22}H_{16}O_3F_3$ $[M-H]^-$: 385.1052, found 385.1062.

Ethyl 3-phenyl-5-(3'-trifluoromethylphenyl)-phenol-2-carboxylate (4j)



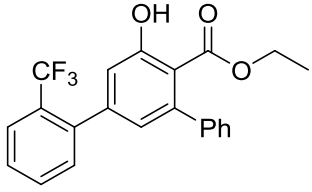
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4j** (0.181 g, 94% yield) as white solid. m.p. 96-98 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.65 (t, *J* = 7.0 Hz, 3H), 7.60 (s, 1H), 7.56 – 7.48 (m, 2H), 7.45 (q, J = 6.8 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 1.6 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.55 (s), 161.63 (s), 145.60 (s), 143.03 (s), 142.79 (s), 138.06 (s), 130.54 (s), 129.46 (s), 129.34 – 127.71 (m), 127.70 (s), 127.17 (s), 126.24 (s), 124.31 (s), 122.57 (s), 122.18 (s), 120.38 (s), 114.58 (s), 109.46 (s), 60.23 (s), 11.89 (s). **MS (EI)**: 386.11 (M^+).

HRMS (ESI): calculated for $C_{22}H_{16}O_3F_3$ $[M-H]^-$: 385.1052, found 385.1060.

Ethyl 3-phenyl-5-(2'-trifluoromethylphenyl)-phenol-2-carboxylate (4k)

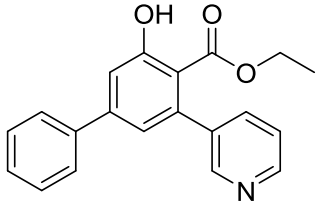


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4k** (0.178 g, 92% yield) as white solid. m.p. 100-101 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.35 (m, 5H), 7.31 (d, *J* = 1.7 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 6.98 (d, *J* = 1.3 Hz, 1H), 4.05 – 3.88 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H).

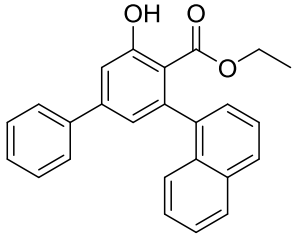
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.46 (s), 161.49 (s), 145.03 (s), 140.89 (s), 140.75 (s), 138.13 (s), 129.83 (s), 129.50 (s), 127.90 (s), 127.58 (s), 126.76 (q, *J* = 30.1 Hz), 126.26 (s), 126.02 (s), 124.48 (s), 124.28 (s), 120.33 (s), 114.64 (s), 109.74 (s), 59.93 (s), 11.87 (s). **MS (EI)**: 386.15 (M^+).
HRMS (ESI): calculated for $C_{22}H_{16}O_3F_3$ $[M-H]^-$: 385.1052, found 385.1062.

Ethyl 3-(3'-Pyridyl)-5-phenyl-phenol-2-carboxylate (4l)



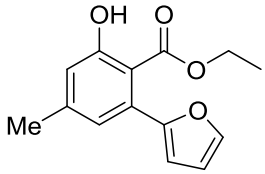
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(pyridin-3-yl)prop-2-en-1-one (0.105 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4l** (0.144 g, 90% yield) as white solid. m.p. 179-181 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.25 (s, 1H), 8.59 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.54 (d, *J* = 1.7 Hz, 1H), 7.66 – 7.58 (m, 3H), 7.48 – 7.42 (m, 2H), 7.42 – 7.37 (m, 1H), 7.35 – 7.30 (m, 1H), 7.30 (d, J = 1.8 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.53 (s), 162.76 (s), 148.94 (s), 147.97 (s), 146.77 (s), 141.53 (s), 139.06 (s), 135.55 (s), 129.07 (s), 128.80 (s), 127.30 (s), 122.66 (s), 121.77 (s), 115.88 (s), 110.67 (s), 61.43 (s), 13.27 (s). **MS (EI)**: 319.14 (M^+).

Ethyl 3-(1'-naphthyl)-5-phenyl-phenol-2-carboxylate (4m)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (0.129 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4m** (0.156 g, 85% yield) as white solid. m.p. 127-128 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (s, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.36 (m, 7H), 7.36 – 7.33 (m, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 3.70 (qd, *J* = 7.1, 1.9 Hz, 2H), 0.19 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.70 (s), 161.52 (s), 145.63 (s), 142.50 (s), 140.18 (s), 138.23 (s), 132.12 (s), 131.50 (s), 127.91 (s), 127.54 (s), 126.97 (s), 126.25 (s), 126.15 (s), 124.99 (s), 124.73 (s), 124.60 (s), 124.21 (s), 124.10 (s), 121.12 (s), 114.20 (s), 110.81 (s), 59.77 (s), 11.29 (s). **MS (EI)**: 368.16 (M^+).

Ethyl 3-(2'-furanyl)-5-methyl-phenol-2-carboxylate (4n)



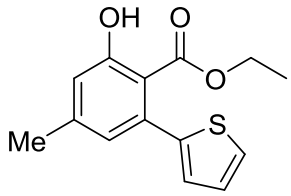
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-(furan-2-yl)but-3-en-2-one (0.068 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4n** (0.107 g, 87% yield) as white solid. m.p. 64-66 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.46 (s, 1H), 6.85 (s, 1H), 6.80 (s, 1H), 6.47 (s, 1H), 6.39 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.55 (s), 160.44 (s), 153.29 (s), 143.89 (s), 140.78 (s), 131.65 (s), 122.54 (s), 117.22 (s), 110.05 (s), 108.65 (s), 106.06 (s), 60.27 (s), 20.58 (s), 12.78 (s). **MS (EI)**: 246.13 (M^+).

HRMS (ESI): calculated for $C_{14}H_{14}O_4$ $[M+Na]^+$: 269.0790, found 269.0796.

Ethyl 3-(2'-thienyl)-5-methyl-phenol-2-carboxylate (4o)



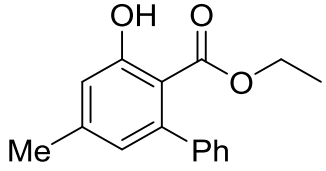
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-(thiophen-2-yl)but-3-en-2-one (0.076 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4o** (0.117 g, 89% yield) as white solid. m.p. 70-73 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.83 (d, *J* = 3.7 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.84 (s, 1H), 6.76 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.72 (s), 160.69 (s), 143.55 (s), 142.82 (s), 135.57 (s), 125.42 (s), 124.77 (s), 124.05 (s), 123.74 (s), 116.89 (s), 109.62 (s), 60.07 (s), 20.56 (s), 12.19 (s). **MS (EI)**: 262.09 (M^+).

HRMS (ESI): calculated for $C_{14}H_{14}O_3S$ $[M+Na]^+$: 285.0561, found 285.0567.

Ethyl 3-phenyl-5-methyl-phenol-2-carboxylate (4p)



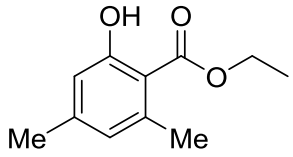
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-phenylbut-3-en-2-one (0.073 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4p** (0.101 g, 79% yield) as yellow solid. m.p. 46-48 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 7.37 – 7.28 (m, 3H), 7.20 (dd, *J* = 7.4,

1.6 Hz, 2H), 6.82 (s, 1H), 6.61 (s, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 0.73 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.00 (s), 160.80 (s), 143.89 (s), 143.72 (s), 142.22 (s), 127.16 (s), 126.50 (s), 125.63 (s), 122.87 (s), 115.87 (s), 108.48 (s), 59.81 (s), 20.66 (s), 11.99 (s). **MS (EI)**: 256.13 (M^+).

Ethyl 3,5-dimethyl-phenol-2-carboxylate (4q)

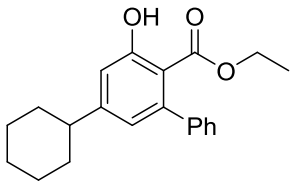


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-pent-3-en-2-one (0.042 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4q** (0.078 g, 80% yield) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.41 (s, 1H), 6.65 (s, 1H), 6.53 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.27 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.80 (s), 163.04 (s), 145.15 (s), 141.10 (s), 124.23 (s), 115.81 (s), 109.72 (s), 61.37 (s), 24.02 (s), 21.51 (s), 14.22 (s). **MS (EI)**: 194.11 (M^+).

Ethyl 3-phenyl-5-cyclohexyl-phenol-2-carboxylate (4r)

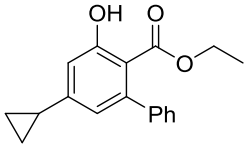


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-cyclohexyl-3-phenylprop-2-en-1-one (0.107 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4r** (0.130 g, 80% yield) as yellow solid. m.p. 77-79 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.14 (d, *J* = 1.4 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 3.51 – 3.43 (m, 1H), 1.95 (d, J = 12.4 Hz, 2H), 1.90 (d, J = 12.6 Hz, 3H), 1.80 (d, *J* = 12.8 Hz, 2H), 1.54 – 1.42 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.55 (s), 160.91 (s), 150.08 (s), 145.48 (s), 139.14 (s), 127.82 (s), 127.22 (s), 126.22 (s), 116.37 (s), 112.52 (s), 110.32 (s), 60.76 (s), 40.61 (s), 33.83 (s), 26.27 (s), 25.33 (s), 13.22 (s). **MS (EI)**: 324.15 (M^+).

Ethyl 3-phenyl-5-cyclopropyl-phenol-2-carboxylate (4s)



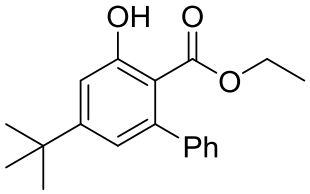
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-cyclopropyl-3-phenylprop-2-en-1-one (0.086 g, 0.5

mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4s** (0.110 g, 78% yield) as white solid. m.p. 72-74 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.01 (s, 1H), 7.36 – 7.32 (m, 3H), 7.26 – 7.19 (m, 2H), 6.68 (s, 1H), 6.51 (s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 1.93 – 1.81 (m, 1H), 1.11 – 0.98 (m, 2H), 0.84 – 0.78 (m, 2H), 0.76 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.94 (s), 161.01 (s), 150.33 (s), 143.97 (s), 142.36 (s), 127.18 (s), 126.49 (s), 125.64 (s), 119.34 (s), 111.77 (s), 108.31 (s), 59.76 (s), 14.73 (s), 12.00 (s), 9.27 (s). **MS (EI)**: 282.11 (M^+).

Ethyl 3-phenyl-5-(tert-Butyl)-phenol-2-carboxylate (4t)



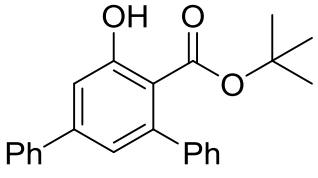
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4,4-dimethyl-1-phenylpent-1-en-3-one (0.094 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4t** (0.112 g, 75% yield) as white solid. m.p. 69-71 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 7.41 – 7.32 (m, 3H), 7.31 – 7.24 (m, 2H), 7.06 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 1.34 (s, 9H), 0.77 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.91 (s), 160.65 (s), 156.78 (s), 143.60 (s), 142.60 (s), 127.34 (s), 126.52 (s), 125.64 (s), 119.33 (s), 112.58 (s), 108.48 (s), 59.80 (s), 34.15 (s), 29.89 (s), 12.02 (s). **MS (EI)**: 298.14 (M^+).

HRMS (ESI): calculated for $C_{19}H_{22}O_3$ $[M+Na]^+$: 321.1467, found 321.1474.

(tert-Butyl) 3,5-diphenylphenol-2-carboxylate (4u)

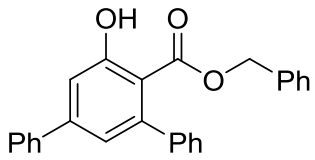


Following the general procedure, tert-butyl 2-fluoro-3-oxobutanoate (0.106 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4u** (0.151 g, 87% yield) as white solid. m.p. 70-72 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.15 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.43 – 7.36 (m, 4H), 7.36 – 7.31 (m, 2H), 7.29 (d, *J* = 1.7 Hz, 1H), 7.06 (d, *J* = 1.7 Hz, 1H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.40 (s), 162.01 (s), 145.79 (s), 145.35 (s), 143.56 (s), 139.57 (s), 128.90 (s), 128.42 (d, *J* = 6.5 Hz), 127.82 (s), 127.26 (s), 126.80 (s), 121.53 (s), 114.74 (s), 112.28 (s), 82.79 (s), 27.46 (s). **MS (EI)**: 346.18 (M^+).

Benzyl 3,5-diphenylphenol-2-carboxylate (4v)

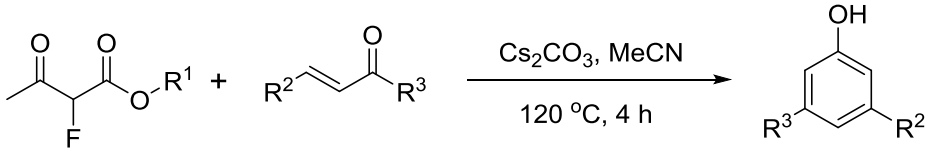


Following the general procedure, benzyl 2-fluoro-3-oxobutanoate (0.126 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **4v** (0.169 g, 89% yield) as white solid. m.p. 97-99 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.32 – 7.18 (m, 9H), 7.05 (d, *J* = 1.7 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 5.03 (s, 2H).

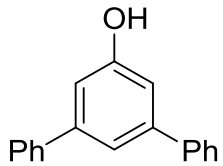
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.82 (s), 162.08 (s), 146.40 (s), 145.42 (s), 142.86 (s), 139.33 (s), 134.41 (s), 128.90 (s), 128.51 (s), 128.28 (s), 128.24 (s), 128.20 (s), 128.11 (s), 127.80 (s), 127.24 (s), 126.98 (s), 121.86 (s), 114.79 (s), 110.72 (s), 67.08 (s). **MS (EI)**: 380.14 (M^+).

General procedure for the synthesis of phenol (5a-5t)



The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual black solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (15% ethyl acetate in petroleum ether), affording the desired phenols **5a** (0.112 g, yield 91%).

3,5-diphenylphenol (5a)

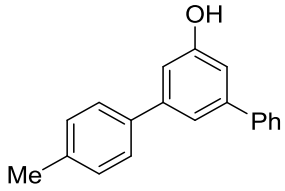


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5a** (0.112 g, 91% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 4H), 7.52 – 7.44 (m, 5H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.11 (s, 2H), 5.63 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.15 (s), 142.51 (s), 139.79 (s), 127.90 (s), 126.73 (s), 126.29 (s), 118.12 (s), 112.24 (s). **MS (EI)**: 246.12 (M^+).

3-phenyl-5-(4'-methylphenyl)-phenol (5b)

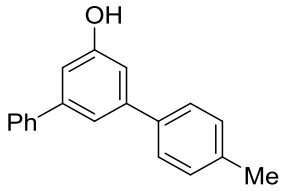


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (0.110 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5b** (0.113 g, 87% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.05 – 7.02 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.19 (s), 142.37 (s), 139.87 (s), 136.88 (s), 136.50 (s), 128.55 (s), 127.81 (s), 126.62 (s), 126.25 (s), 126.06 (s), 117.80 (s), 111.87 (d, *J* = 6.1 Hz), 20.17 (s). **MS (EI)**: 260.10 (M^+).

3-(4'-methylphenyl)-5-phenyl-phenol (5c)

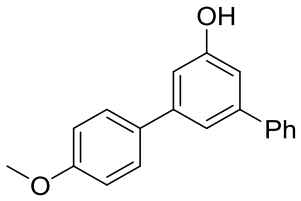


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (0.110 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5c** (0.110 g, 85% yield) as yellow oil.

^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.54 – 7.50 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.05 – 7.02 (m, 2H), 5.14 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 155.20 (s), 142.36 (s), 139.87 (s), 136.88 (s), 136.50 (s), 128.55 (s), 127.81 (s), 126.61 (s), 126.24 (s), 126.06 (s), 117.80 (s), 111.87 (d, J = 6.2 Hz), 20.18 (s). **MS (EI)**: 260.11 (M^+).

3-phenyl-5-(4'-methoxyphenyl)-phenol (5d)

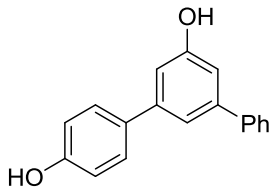


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (0.119 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5d** (0.110 g, 80% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 7.03 (p, *J* = 2.5 Hz, 2H), 7.01 – 6.96 (m, 2H), 5.66 (d, *J* = 5.5 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.33 (s), 155.32 (s),

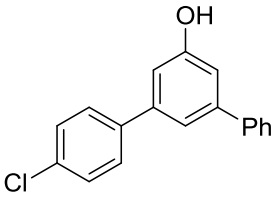
142.38 (s), 141.97 (s), 139.91 (s), 132.38 (s), 127.82 (s), 127.28 (s), 126.61 (s), 126.24 (s), 117.49 (s), 113.29 (s), 111.68 (d, *J* = 14.5 Hz), 54.44 (s). **MS (EI)**: 276.10 (M^+).

3-phenyl-5-(4'-hydroxyphenyl)-phenol (5e)



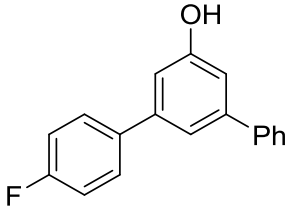
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (0.112 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5e** (0.106 g, 81% yield) as white solid.
^{1}H NMR (500 MHz, DMSO) δ 9.63 (d, *J* = 5.5 Hz, 1H), 9.57 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.23 (s, 1H), 6.96 (d, *J* = 5.4 Hz, 2H), 6.85 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 158.67 (s), 157.69 (s), 142.74 (s), 142.57 (s), 141.01 (s), 131.56 (s), 129.32 (s), 128.33 (s), 127.92 (s), 127.24 (s), 116.16 (s), 112.59 (s), 112.29 (s). **MS (EI)**: 262.14 (M^+).

3-phenyl-5-(4'-chlorophenyl)-phenol (5f)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (0.121 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5f** (0.130 g, 93% yield) as white solid. m.p. 110-112 °C;
^{1}H NMR (500 MHz, DMSO) δ 9.79 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 7.4 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.31 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H).
^{13}C NMR (126 MHz, DMSO) δ 158.85 (s), 142.87 (s), 141.37 (s), 140.69 (s), 139.59 (s), 132.89 (s), 129.31 (d, *J* = 8.4 Hz), 129.04 (s), 128.06 (s), 127.30 (s), 116.69 (s), 113.61 (s), 113.17 (s). **MS (EI)**: 280.11 (M^+).

3-phenyl-5-(4'-fluorophenyl)-phenol (5g)



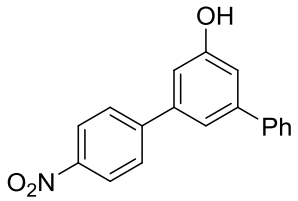
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 %

EtOAc in petroleum ether) to afford the **5g** (0.123 g, 93% yield) as white solid. m.p. 67-69 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.33 (s, 1H), 7.13 (t, *J* = 8.7 Hz, 2H), 7.07 – 7.02 (m, 1H), 7.02 – 6.98 (m, 1H), 5.25 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.65 (d, *J* = 246.7 Hz), 155.27 (s), 142.54 (s), 141.42 (s), 139.67 (s), 135.89 (s), 127.80 (d, *J* = 11.1 Hz), 127.21 (s), 126.73 (s), 126.22 (s), 117.82 (s), 114.78 (s), 114.61 (s), 112.11 (s), 112.00 (s). **MS (EI)**: 264.14 (M^+).

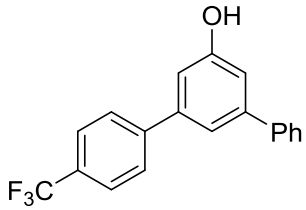
3-phenyl-5-(4'-nitrophenyl)-phenol (5h)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (0.127 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5h** (0.135 g, 93% yield) as yellow solid. m.p. 191-193 °C;

^{1}H NMR (500 MHz, DMSO) δ 9.90 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.30 (m, 4H), 7.12 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 158.96 (s), 147.20 (s), 147.13 (s), 143.06 (s), 140.42 (s), 140.31 (s), 129.35 (s), 128.40 (s), 128.18 (s), 127.32 (s), 124.43 (s), 117.20 (s), 114.75 (s), 113.62 (s). **MS (EI)**: 291.11 (M^+).

3-phenyl-5-(4'-trifluoromethylphenyl)-phenol (5i)



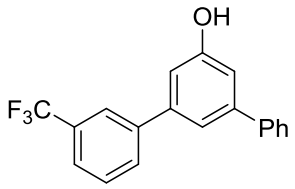
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5i** (0.148 g, 94% yield) as white solid. m.p. 69-71 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.15 (s, 1H), 7.09 (s, 1H), 6.23 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.35 (s), 144.21 (s), 143.78 (s), 141.96 (s), 140.43 (s), 129.67 (q, *J* = 32.6 Hz), 128.94 (s), 127.91 (s), 127.49 (s), 127.20 (s), 125.76 (q, *J* = 3.7 Hz), 125.40 (s), 123.24 (s), 119.05 (s), 114.07 (s), 113.30 (s). **MS (EI)**: 314.13 (M^+).

HRMS (ESI): calculated for $C_{19}H_{12}OF_3$ $[M-H]^-$: 313.0840, found 313.0848.

3-phenyl-5-(3'-trifluoromethylphenyl)-phenol (5j)



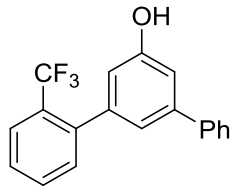
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5j** (0.144 g, 92% yield) as white solid. m.p. 65-67 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.62 (m, 3H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.14 (s, 1H), 7.08 (s, 1H), 5.98 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.40 (s), 142.81 (s), 140.96 (s), 140.58 (s), 139.48 (s), 130.20 (q, *J* = 32.3 Hz), 129.52 (s), 128.33 (s), 127.93 (s), 126.88 (s), 126.24 (s), 123.33 (s), 123.01 (s), 117.96 (s), 112.93 (s), 112.22 (s). **MS (EI)**: 314.15 (M^+).

HRMS (ESI): calculated for $C_{19}H_{12}OF_3$ $[M-H]^-$: 313.0840, found 313.0847.

3-phenyl-5-(2'-trifluoromethylphenyl)-phenol (5k)



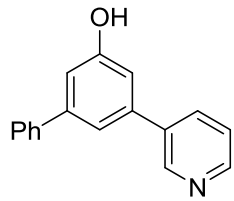
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(2-(trifluoromethyl)-phenyl)prop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5k** (0.141 g, 90% yield) as white solid. m.p. 64-66 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.21 (s, 1H), 7.18 (s, 1H), 6.89 (s, 1H), 6.09 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.29 (s), 141.40 (s), 140.83 (s), 139.87 (s), 139.47 (s), 130.96 (s), 130.69 (d, *J* = 61.6 Hz), 127.87 (s), 126.72 (s), 126.60 (s), 126.25 (s), 125.17 (s), 119.87 (s), 114.21 (s), 112.54 (s). **MS (EI)**: 314.11 (M^+).

HRMS (ESI): calculated for $C_{19}H_{12}OF_3$ $[M-H]^-$: 313.0840, found 313.0849.

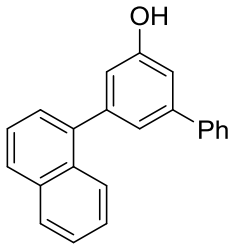
3-phenyl-5-(3'-pyridyl)-phenol (5l)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-phenyl-1-(pyridin-3-yl)-prop-2-en-1-one (0.105 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5l** (0.115 g, 93% yield) as yellow solid. m.p. 228-229 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 2.0 Hz, 1H), 8.60 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.64 – 7.57 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.33 (m, 1H), 7.30 (t, *J* = 1.4 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.21 – 7.17 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.37 (s), 147.63 (s), 147.40 (s), 144.06 (s), 140.81 (s), 139.04 (s), 137.67 (s), 135.61 (s), 128.94 (s), 127.81 (s), 127.30 (s), 124.35 (s), 117.72 (s), 114.99 (s), 113.46 (s). **MS (EI)**: 247.06 (M^+).

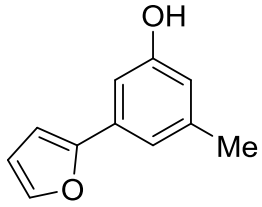
3-phenyl-5-(1'-naphthyl)-phenol (5m)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-3-(naphthalen-2-yl)-1-phenyl-prop-2-en-1-one (0.129 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5m** (0.130 g, 88% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.41 (m, 6H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34 (s, 1H), 7.20 – 7.13 (m, 1H), 6.97 (dd, *J* = 2.1, 1.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.75 (s), 141.82 (s), 139.57 (s), 138.73 (s), 132.81 (s), 130.55 (s), 127.83 (s), 127.31 (s), 126.89 (s), 126.65 (s), 126.22 (s), 125.80 (s), 125.18 (s), 125.03 (s), 124.88 (s), 124.37 (s), 120.80 (s), 114.97 (s), 111.98 (s). **MS (EI)**: 296.08 (M^+).

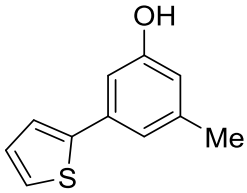
3-methyl-5-(2'-furanyl)-phenol (5n)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-(furan-2-yl)but-3-en-2-one (0.068 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5n** (0.077 g, 89% yield) as Yellow oil.

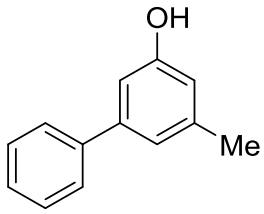
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.11 (s, 1H), 7.01 (s, 1H), 6.67 – 6.55 (m, 2H), 6.47 (s, 1H), 5.82 (s, 1H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.77 (s), 152.73 (s), 141.05 (s), 139.24 (s), 131.13 (s), 116.29 (s), 114.33 (s), 110.67 (s), 106.95 (s), 104.34 (s), 20.44 (s). **MS (EI)**: 174.11 (M^+).
HRMS (ESI): calculated for $C_{11}H_9O_2$ $[M-H]^-$: 173.0603, found 173.0608.

3-methyl-5-(2'-thienyl)-phenol (5o)



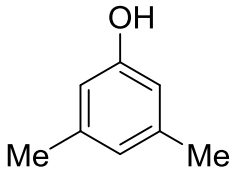
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-(thiophen-2-yl)but-3-en-2-one (0.076 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5o** (0.086 g, 90% yield) as yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.06 (dd, *J* = 4.8, 3.8 Hz, 1H), 7.03 (s, 1H), 6.92 (s, 1H), 6.60 (s, 1H), 5.30 (s, 1H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.87 (s), 143.13 (s), 139.36 (s), 134.71 (s), 126.93 (s), 123.80 (s), 122.26 (s), 118.52 (s), 114.32 (s), 109.07 (s), 20.41 (s). **MS (EI)**: 190.09 (M^+).
HRMS (ESI): calculated for $C_{11}H_9OS$ $[M-H]^-$: 189.0374, found 189.0378.

3-methyl-5-phenyl-phenol (5p)



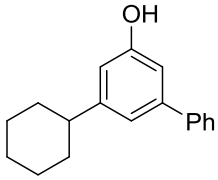
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4-phenylbut-3-en-2-one (0.073 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5p** (0.074 g, 80% yield) as white solid. m.p. 55-57 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.44 – 7.38 (m, 3H), 7.36 – 7.31 (m, 2H), 6.98 (d, *J* = 0.5 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 6.66 (s, 1H), 2.37 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.93 (s), 141.81 (s), 139.94 (s), 139.09 (s), 127.70 (s), 126.39 (s), 126.13 (s), 119.64 (s), 113.98 (s), 110.27 (s), 20.52 (s). **MS (EI)**: 184.07 (M^+).

3,5-dimethylphenol (5q)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-pent-3-en-2-one (0.042 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5q** (0.051 g, 83% yield) as yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.55 (s, 2H), 5.75 (s, 1H), 2.32 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.29 (s), 138.65 (s), 121.71 (s), 112.25 (s), 20.29 (s). **MS (EI)**: 122.09 (M^+).

3-phenyl-5-cyclohexylphenol (5r)

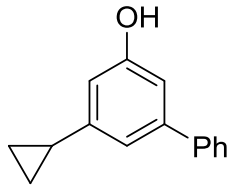


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-cyclohexyl-3-phenylprop-2-en-1-one (0.107 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5r** (0.107 g, 85% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H), 6.90 (s, 1H), 6.71 (s, 1H), 4.97 (s, 1H), 2.59 – 2.49 (m, 1H), 1.94 (d, *J* = 11.4 Hz, 2H), 1.87 (d, *J* = 12.0 Hz, 2H), 1.77 (d, *J* = 13.2 Hz, 1H), 1.53 – 1.34 (m, 4H), 1.33 – 1.24 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.84 (s), 149.54 (s), 141.79 (s), 140.16 (s), 127.68 (s), 126.34 (s), 126.19 (s), 117.65 (s), 111.76 (s), 110.62 (s), 43.68 (s), 33.42 (s), 25.89 (s), 25.18 (s). **MS (EI)**: 252.11 (M^+).

3-phenyl-5-cyclopropylphenol (5s)

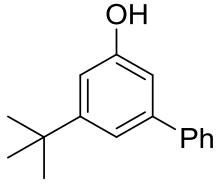


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-1-cyclopropyl-3-phenylprop-2-en-1-one (0.086 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5s** (0.083 g, 79% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.95 (s, 1H), 6.90 (d, *J* = 1.4 Hz, 1H), 6.58 (s, 1H), 5.80 (s, 1H), 2.00 – 1.89 (m, 1H), 1.04 – 0.98 (m, 2H), 0.81 – 0.72 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.01 (s), 145.57 (s), 141.88 (s), 140.05 (s), 127.74 (s), 126.46 (s), 126.20 (s), 116.53 (s), 110.50 (s), 14.56 (s), 8.39 (s). **MS (EI)**: 210.08 (M^+).

3-phenyl-5-tert-Butylphenol (5t)

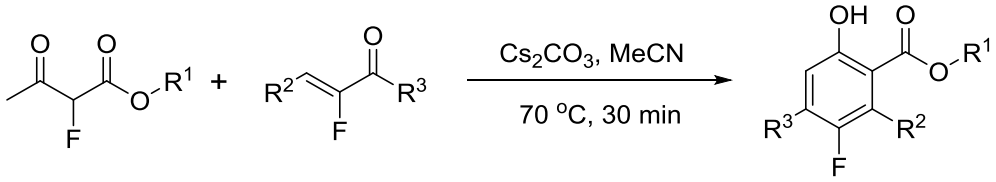


Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*E*)-4,4-dimethyl-1-phenylpent-1-en-3-one (0.094 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **5t** (0.087 g, 77% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 6.92 (s, 2H), 5.38 (s, 1H), 1.38 (s, 9H).

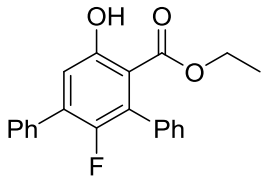
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.72 (s), 152.70 (s), 141.58 (s), 140.48 (s), 127.72 (s), 126.30 (s), 116.13 (s), 110.71 (s), 110.40 (s), 30.37 (s). **MS (EI)**: 226.10 (M^+). **HRMS** (ESI): calculated for $C_{16}H_{17}O$ $[M-H]^-$: 225.1279, found 225.1286.

General procedure for the synthesis of *p*-fluoro-*o*-phenolic esters (7a-7h)



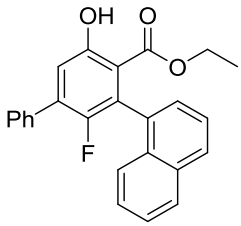
The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 °C for half an hour. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual brown solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (10% ethyl acetate in petroleum ether), affording the desired *o*-phenolic esters **7a** (0.146 g, yield 87%).

Ethyl 3,5-diphenyl-4-fluorophenol-2-carboxylate (7a)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 °C for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7a** (0.146 g, 87% yield) as white solid. m.p. 96-98 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.53 (dd, *J* = 6.8, 1.3 Hz, 2H), 7.41 – 7.30 (m, 6H), 7.23 – 7.18 (m, 2H), 7.06 (d, *J* = 6.5 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 0.66 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -127.86 (s).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.23 (s), 156.63 (s), 149.02 (d, *J* = 238.1 Hz), 134.91 (s), 133.78 (s), 128.06 (s), 127.64 (s), 127.53 (s), 126.72 (s), 126.34 (s), 117.21 (s), 110.76 (s), 60.28 (s), 11.92 (s). **MS (EI)**: 336.10 (M^+).

Ethyl 3-naphthyl-4-fluoro-5-phenylphenol-2-carboxylate (7b)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 °C for half an hour. After

the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7b** (0.160 g, 83% yield) as white solid. m.p. 67-68 °C;

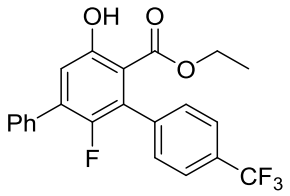
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.17 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.39 (m, 6H), 7.34 (d, *J* = 6.9 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 3.76 – 3.63 (m, 2H), 0.20 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -125.81 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.07 (s), 157.25 (s), 149.49 (d, *J* = 238.2 Hz), 135.10 (d, *J* = 17.2 Hz), 133.73 (s), 132.91 (s), 132.35 (s), 131.57 (s), 128.19 (s), 127.73 (s), 127.58 (s), 127.15 (s), 126.81 (s), 125.32 (s), 125.20 (s), 124.72 (s), 124.31 (s), 124.12 (s), 124.03 (d, *J* = 22.1 Hz), 117.72 (s), 111.36 (s), 60.06 (s), 11.30 (s). **MS (EI)**: 386.09 (M^+).

HRMS (ESI): calculated for $C_{25}H_{19}O_3F$ $[M+Na]^+$: 409.1216, found 409.1225.

Ethyl 3-(4'-trifluoromethylphenyl)-4-fluoro-5-phenylphenol-2-carboxylate (7c)



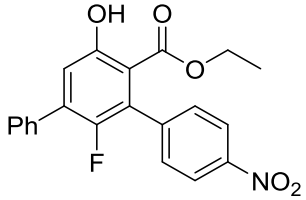
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en -1-one (0.147 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^{o}C for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7c** (0.182 g, 90% yield) as white solid. m.p. 130-132 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 6.8, 1.3 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.17 (d, *J* = 6.6 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 0.71 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.44 (s), -127.57 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.82 (s), 157.11 (s), 148.78 (d, *J* = 238.8 Hz), 138.94 (s), 135.21 (d, *J* = 17.1 Hz), 133.43 (s), 128.54 (s), 128.07 (s), 127.85 (s), 127.61 (s), 123.68 (s), 118.03 (s), 110.13 (s), 60.52 (s), 11.70 (s). **MS (EI)**: 404.12 (M^+).

HRMS (ESI): calculated for $C_{22}H_{15}O_3F_4$ $[M-H]^-$: 403.0957, found 403.0966.

Ethyl 3-(4'-nitrophenyl)-4-fluoro-5-phenylphenol-2-carboxylate (7d)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (0.136 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^{o}C for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7d** (0.170 g, 89% yield) as yellow solid. m.p. 154-156 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.28 (d, *J* = 8.7 Hz, 2H), 7.61 – 7.52 (m,

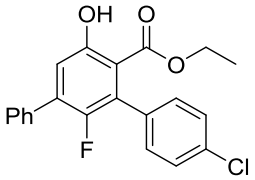
2H), 7.48 – 7.38 (m, 5H), 7.17 (d, *J* = 6.6 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 0.74 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -127.25 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.49 (s), 157.27 (s), 148.53 (d, *J* = 239.7 Hz), 146.28 (s), 142.16 (s), 135.47 (d, *J* = 17.2 Hz), 133.18 (s), 129.22 (s), 128.03 (s), 127.66 (s), 121.96 (s), 118.57 (s), 109.62 (s), 60.71 (s), 12.07 (s). **MS (EI)**: 381.06 (M^+).

HRMS (ESI): calculated for $C_{21}H_{15}NO_5F$ [M-H]$^-$: 380.0934, found 380.0944.

Ethyl 3-(4'-chlorophenyl)-4-fluoro-5-phenylphenol-2-carboxylate (7e)



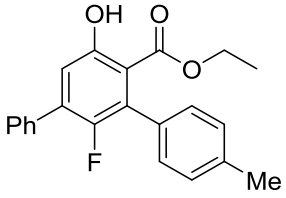
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-3-(4-chlorophenyl)-2-fluoro-1-phenylprop-2-en-1-one (0.130 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7e** (0.159 g, 86% yield) as white solid. m.p. 150-152 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.62 – 7.55 (m, 2H), 7.50 – 7.38 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -127.70 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.98 (s), 156.86 (s), 148.91 (d, *J* = 238.4 Hz), 135.00 (d, *J* = 17.5 Hz), 133.57 (s), 133.40 (s), 132.43 (s), 129.47 (s), 128.07 (s), 127.75 (s), 127.57 (s), 126.94 (s), 117.67 (s), 60.51 (s), 12.02 (s). **MS (EI)**: 370.10 (M^+).

HRMS (ESI): calculated for $C_{21}H_{15}O_3ClF$ [M-H]$^-$: 369.0694, found 369.0703.

Ethyl 3-(4'-methylphenyl)-4-fluoro-5-phenylphenol-2-carboxylate (7f)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-3-(4-methyl)-2-fluoro-1-phenylprop-2-en-1-one (0.120 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7f** (0.144 g, 82% yield) as white solid.

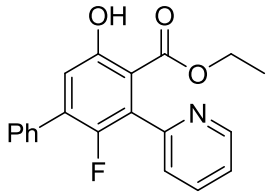
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.56 – 7.49 (m, 2H), 7.41 – 7.30 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 6.5 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 0.69 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -128.06 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.29 (s), 156.49 (s), 149.11 (d, *J* = 237.5 Hz), 136.04 (s), 134.66 (d, *J* = 17.7 Hz), 133.85 (s), 131.82 (s), 130.26 (d, *J* = 20.2 Hz), 128.11 (s), 127.93 (s), 127.58 (s), 127.51 (s), 127.40 (s), 117.00 (s), 110.97 (s), 60.29

(s), 20.28 (s), 11.93 (s). **MS (EI)**: 350.15 (M^+).

Ethyl 3-(2'-pyridyl)-4-fluoro-5-phenylphenol-2-carboxylate (7g)



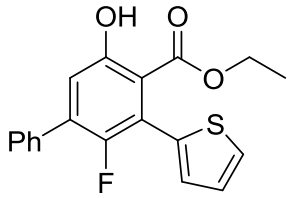
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one (0.114 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7g** (0.143 g, 85% yield) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s,1H), 8.66 (d, *J* = 3.9 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.38 (m, 4H), 7.38 – 7.25 (m, 2H), 7.21 – 7.09 (m, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -129.72 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.06 (s), 160.33 (s), 156.83 (s), 153.88 (s), 149.30 (s), 147.76 (s), 144.28 (s), 135.25 (s), 134.86 (s), 133.57 (s), 128.78 (s), 127.98 (d, *J* = 23.6 Hz), 127.62 (d, *J* = 19.9 Hz), 126.26 (s), 123.64 (s), 122.13 (s), 121.28 (s), 120.87 (s), 119.91 (s), 118.27 (s), 114.85 (s), 110.05 (s), 60.18 (d, *J* = 29.5 Hz), 12.17 (d, *J* = 8.5 Hz). **MS (EI)**: 337.13 (M^+).

Ethyl 3-(2'-thienyl)-4-fluoro-5-phenylphenol-2-carboxylate (7h)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (0.116 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **7h** (0.149 g, 87% yield) as white solid. m.p. 90-92 °C;

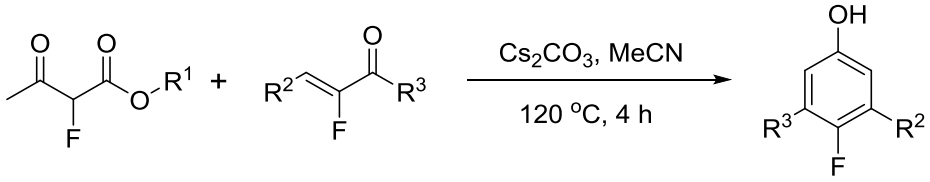
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.19 (d, *J* = 6.5 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -125.08 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.99 (s), 156.51 (s), 149.85 (d, *J* = 240.3 Hz), 134.67 (d, *J* = 18.0 Hz), 134.40 (s), 133.55 (s), 128.11 (s), 127.77 (s), 127.60 (s), 126.67 (s), 126.24 (s), 125.63 (s), 125.13 (s), 118.34 (s), 111.95 (s), 60.56 (s), 12.15 (s). **MS (EI)**: 342.09 (M^+).

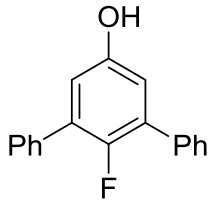
HRMS (ESI): calculated for $C_{19}H_{14}O_3SF$ $[M-H]^-$: 341.0648, found 341.0656.

General procedure for the synthesis of *p*-fluoro-phenol (8a-8h)



The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual black solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (15% ethyl acetate in petroleum ether), affording the desired phenols **8a** (0.119 g, yield 90%).

3,5-Diphenyl-4-fluorophenol (8a)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8a** (0.119 g, 90% yield) as yellow oil.

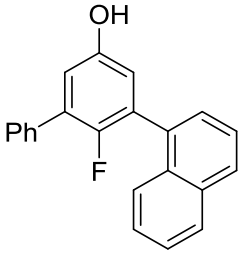
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 2H), 6.82 (d, *J* = 5.6 Hz, 2H), 5.07 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -133.65 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.39 (s), 150.09 (d, *J* = 242.5 Hz), 134.80 (s), 129.64 (d, *J* = 16.6 Hz), 128.14 (s), 127.46 (s), 126.89 (s), 115.22 (s). **MS (EI)**: 264.14 (M^+).

HRMS (ESI): calculated for $C_{18}H_{12}OF$ $[M-H]^-$: 263.0872, found 263.0880.

3-Naphthyl-4-fluoro-5-phenylphenol (8b)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (0.138 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8b** (0.127 g, 81% yield) as yellow solid. m.p. 77-79 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 3.0 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H),

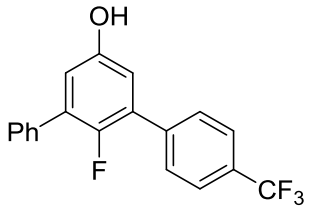
7.61 (d, *J* = 7.7 Hz, 2H), 7.53 (dt, *J* = 14.8, 7.4 Hz, 2H), 7.46 (dd, *J* = 14.9, 7.3 Hz, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.01 (dd, *J* = 5.7, 3.2 Hz, 1H), 6.83 (dd, *J* = 5.0, 3.3 Hz, 1H), 5.33 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -129.33 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.49 (d, *J* = 241.5 Hz), 150.28 (s), 134.73 (s), 132.88 (s), 132.60 (s), 130.75 (s), 129.53 (d, *J* = 38.4 Hz), 128.57 (d, *J* = 19.9 Hz), 128.17 (s), 127.52 (s), 127.34 (s), 126.94 (s), 126.63 (s), 125.38 (s), 124.96 (d, *J* = 7.5 Hz), 124.32 (s), 116.75 (s), 115.61 (s). **MS (EI)**: 314.09 (M^+).

HRMS (ESI): calculated for $C_{22}H_{14}OF$ $[M-H]^-$: 313.1029, found 313.1036.

3-(4'-Trifluoromethylphenyl)-4-fluoro-5-phenylphenol (8c)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (0.147 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8c** (0.154 g, 93% yield) as white solid. m.p. 79-83 °C;

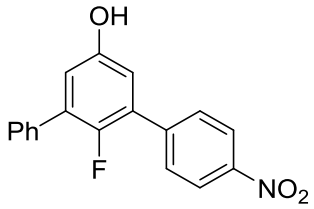
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (q, *J* = 8.4 Hz, 4H), 7.61 – 7.54 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28 (dd, *J* = 7.8, 2.3 Hz, 1H), 7.17 (dd, *J* = 6.6, 2.3 Hz, 1H), 5.50 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.54 (s), -148.41 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.93 (d, *J* = 240.0 Hz), 143.32 (d, *J* = 15.0 Hz), 138.78 (s), 137.99 (s), 137.40 (s), 129.09 (q, *J* = 32.3 Hz), 128.33 (s), 128.13 (d, *J* = 50.5 Hz), 127.29 (d, *J* = 10.8 Hz), 126.76 (s), 126.06 (s), 124.51 (s), 119.42 (s), 114.81 (s). **MS (EI)**: 332.10 (M^+).

HRMS (ESI): calculated for $C_{19}H_{11}OF_4$ $[M-H]^-$: 331.0746, found 331.0752.

3-(4'-Nitrophenyl)-4-fluoro-5-phenylphenol (8d)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (0.136 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8d** (0.139 g, 90% yield) as yellow solid. m.p. 221-222 °C;

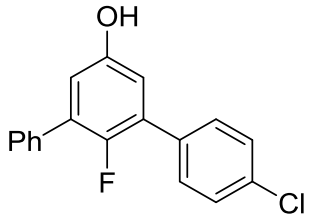
^{1}H NMR (500 MHz, Acetone) δ 8.67 (s, 1H), 8.38 – 8.29 (m, 2H), 7.88 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.63 – 7.54 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.00 (dq, *J* = 6.2, 3.0 Hz, 2H).

^{19}F NMR (470 MHz, Acetone) δ -136.02 (s).

^{13}C NMR (126 MHz, Acetone) δ 152.75 (s), 149.10 (d, *J* = 240.8 Hz), 146.40 (s), 141.71 (s), 134.68 (s), 129.77 (d, *J* = 16.3 Hz), 129.23 (s), 128.02 (s), 127.50 (s), 127.14 (d, *J* = 16.2 Hz), 126.96 (s), 122.50 (s), 116.57 (s), 114.95 (s). **MS (EI)**: 309.10 (M^+).

HRMS (ESI): calculated for $C_{18}H_{11}NO_3F$ [M-H]$^-$: 308.0723, found 308.0730.

3-(4'-Chlorophenyl)-4-fluoro-5-phenylphenol (8e)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-3-(4-chlorophenyl)-2-fluoro-1-phenylprop-2-en-1-one (0.130 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8e** (0.133 g, 89% yield) as white solid. m.p. 78-80 °C;

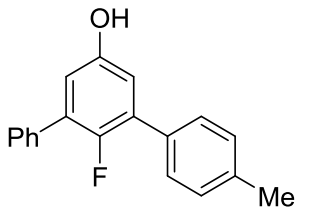
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.53 – 7.38 (m, 7H), 6.90 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.85 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.94 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -133.47 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.44 (s), 150.00 (d, *J* = 242.4 Hz), 134.58 (s), 133.18 (s), 132.98 (s), 129.83 (d, *J* = 17.2 Hz), 129.40 (s), 128.43 (d, *J* = 16.8 Hz), 128.09 (s), 127.67 (s), 127.49 (s), 126.99 (s), 115.56 (s), 114.92 (s). **MS (EI)**: 298.10 (M^+).

HRMS (ESI): calculated for $C_{18}H_{11}OClF$ [M-H]$^-$: 297.0482, found 297.0490.

3-(4'-Methylphenyl)-4-fluoro-5-phenylphenol (8f)



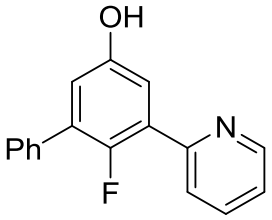
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-3-(4-methyl)-2-fluoro-1-phenylprop-2-en-1-one (0.120 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8f** (0.117 g, 84% yield) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.80 (dd, *J* = 5.7, 3.4 Hz, 2H), 2.35 (s, 3H)

^{19}F NMR (470 MHz, $CDCl_3$) δ -133.64 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.37 (s), 150.12 (d, *J* = 241.9 Hz), 136.76 (s), 134.88 (s), 131.86 (s), 129.59 (d, *J* = 16.7 Hz), 128.58 (s), 128.18 (d, *J* = 5.4 Hz), 127.99 (s), 127.45 (s), 126.85 (s), 125.97 (s), 115.12 (s), 114.95 (s), 20.27 (s). **MS (EI)**: 278.09 (M^+).

3-(2'-Pyridyl)-4-fluoro-5-phenylphenol (8g)



Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one (0.114 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8g** (0.123 g, 93% yield) as yellow solid. m.p. 148-151 °C;

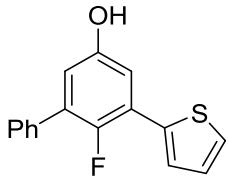
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.2 Hz, 1H), 7.76 (s, 2H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.38 (dt, *J* = 14.0, 7.3 Hz, 4H), 7.28 (d, *J* = 6.2 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -134.97 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.62 (s), 152.01 (s), 149.96 (d, *J* = 243.0 Hz), 148.04 (s), 136.20 (s), 134.75 (s), 129.74 (d, *J* = 16.1 Hz), 128.15 (s), 127.37 (s), 126.76 (s), 126.64 (s), 124.47 (s), 121.92 (s), 117.94 (s), 115.62 (s). **MS (EI)**: 265.11 (M^+).

HRMS (ESI): calculated for $C_{17}H_{13}NOF$ $[M+H]^+$: 266.0981, found 266.0985.

3-(2'-Thienyl)-4-fluoro-5-phenylphenol (8h)



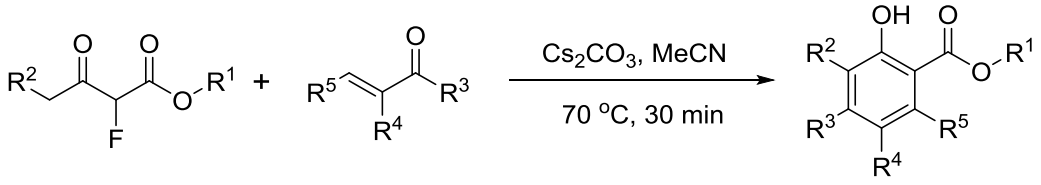
Following the general procedure, ethyl 2-fluoro-3-oxobutanoate (0.089 g, 0.6 mmol), (*Z*)-2-fluoro-1-phenyl-3-(thiophen-2-yl)-prop-2-en-1-one (0.116 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **8h** (0.123 g, 91% yield) as yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.41 (dd, *J* = 14.8, 6.1 Hz, 2H), 7.17 – 7.09 (m, 2H), 6.84 (dd, *J* = 4.6, 2.9 Hz, 1H), 5.47 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -129.03 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.34 (s), 149.65 (d, *J* = 244.4 Hz), 136.01 (s), 134.57 (s), 130.03 (d, *J* = 16.5 Hz), 128.11 (s), 127.51 (s), 127.03 (s), 126.71 (s), 125.79 (d, *J* = 4.9 Hz), 125.14 (s), 122.57 (d, *J* = 15.9 Hz), 115.19 (s), 113.09 (s). **MS (EI)**: 270.09 (M^+).

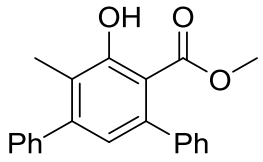
HRMS (ESI): calculated for $C_{16}H_{10}OSF$ $[M-H]^-$: 269.0436, found 269.0442.

General procedure for the synthesis of polysubstituted phenol esters (11a-11c)



The reaction mixture of methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual brown solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (10% ethyl acetate in petroleum ether), affording the desired *o*-phenolic esters **11a** (0.100 g, yield 63%).

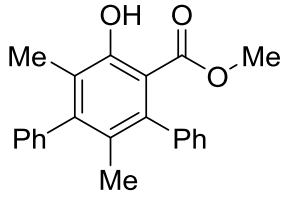
Methyl 3,5-diphenol-6-methyl-2-carboxylate (11a)



Following the general procedure, methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **11a** (0.100 g, 63% yield) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.17 (s, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.37 (m, 5H), 7.31 – 7.29 (m, 3H), 6.81 (s, 1H), 3.55 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.92 (s), 160.09 (s), 147.10 (s), 142.84 (s), 141.48 (s), 140.78 (s), 128.98 (s), 128.23 (s), 128.14 (s), 127.56 (s), 127.43 (s), 126.66 (s), 123.83 (s), 123.29 (s), 110.00 (s), 51.65 (s), 13.23 (s). **MS (EI)**: 318.10 (M^+).

Methyl 3,5-diphenol-4,6-dimethyl-2-carboxylate (11b)



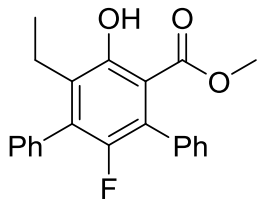
Following the general procedure, methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), (*E*)-2-methyl-1,3-diphenylprop-2-en-1-one (0.111 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **11b** (0.068 g, 41% yield) as white solid. m.p. 146-148 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 3H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.19 – 7.10 (m, 4H), 3.39 (s, 3H), 1.99 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.98 (s), 157.40 (s), 148.37 (s), 142.54 (s), 140.98 (s), 129.89 (s), 128.63 (s), 128.51 (s), 128.51 (s), 127.65 (s), 126.95 (s), 126.22 (s), 125.80 (s), 124.24 (s), 111.48 (s), 51.67 (s), 18.56 (s), 13.70 (s). **MS (EI)**: 332.16 (M^+).

HRMS (ESI): calculated for $C_{22}H_{19}O_3$ $[M-H]^-$: 331.1334, found 331.1344.

Methyl 3,5-diphenol-4-fluoro-6-ethyl-2-carboxylate (11c)



Following the general procedure, methyl 2-fluoro-3-oxohexanoate (0.097 g, 0.6 mmol), (*E*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.163 g, 0.5 mmol) and CH_3CN (1.5 mL) was stirred at 70 ^oC for half an hour. After the work-up, the residue was purified by column chromatography on silicagel (10 % EtOAc in petroleum ether) to afford the **11c** (0.046 g, 26% yield) as white solid. m.p. 124-126 °C;

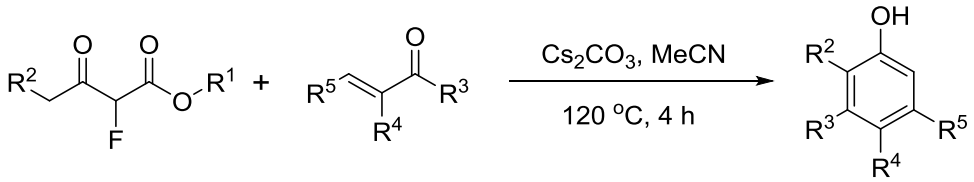
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 5.6 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 3.46 (s, 3H), 2.56 (q, *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -124.09 (s).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.25 (s), 155.85 (s), 149.98 (d, *J* = 234.5 Hz), 135.92 (d, *J* = 20.3 Hz), 135.76 (s), 132.34 (s), 129.32 (s), 129.14 (s), 128.17 (s), 127.87 (s), 127.58 (s), 127.20 (s), 127.11 (s), 127.04 (s), 111.21 (s), 51.88 (s), 20.77 (s), 13.92 (s). **MS (EI)**: 350.10 (M^+).

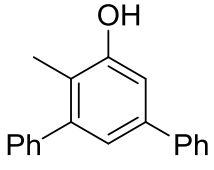
HRMS (ESI): calculated for $C_{22}H_{18}O_3F$ $[M-H]^-$: 349.1240, found 349.1249.

General procedure for the synthesis of polysubstituted phenol (12a-12c)



The reaction mixture of methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual black solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (15% ethyl acetate in petroleum ether), affording the desired phenols **12a** (0.121 g, yield 93%).

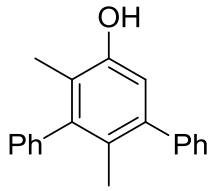
3,5-phenyl-6-methylphenol (12a)



Following the general procedure, methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), chalcone (0.104 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **12a** (0.121 g, 93% yield) as colorless solid. m.p. 94-96 °C;

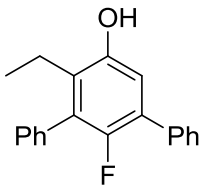
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.57 – 7.38 (m, 8H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.15 (d, *J* = 1.6 Hz, 1H), 5.50 (s, 1H), 2.31 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.48 (s), 144.14 (s), 141.74 (s), 140.61 (s), 139.48 (s), 129.39 (s), 128.82 (s), 128.19 (s), 127.37 (s), 127.06 (s), 127.02 (s), 121.40 (s), 121.01 (s), 112.58 (s), 13.03 (s). **MS (EI)**: 260.10 (M^+).

3,5-phenyl-4,6-methylphenol (12b)



Following the general procedure, methyl 2-fluoro-3-oxopentanoate (0.089 g, 0.6 mmol), (*E*)-2-methyl-1,3-diphenylprop-2-en-1-one (0.111 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **12b** (0.112 g, 82% yield) as colorless oil. m.p. 103-105 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 9H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.75 (s, 1H), 5.03 – 4.86 (m, 1H), 1.97 (s, 3H), 1.83 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.41 (s), 144.05 (s), 142.34 (s), 141.65 (s), 140.65 (s), 129.45 (s), 129.28 (s), 128.56 (s), 128.13 (s), 127.49 (s), 126.79 (s), 125.78 (s), 121.60 (s), 115.53 (s), 18.34 (s), 13.52 (s). **MS (EI)**: 274.16 (M^+).
HRMS (ESI): calculated for $C_{20}H_{17}O$ $[M-H]^-$: 273.1279, found 273.1286.

3,5-diphenyl-4-fluoro-6-ethylphenol (12c)



Following the general procedure, methyl 2-fluoro-3-oxohexanoate (0.097 g, 0.6 mmol), (*E*)-2-fluoro-1,3-diphenylprop-2-en-1-one (0.113 g, 0.5 mmol), cesium carbonate (0.326 g, 1 mmol) and CH_3CN (1.5 mL) was stirred at 120 ^oC for 4 hours. After the work-up, the residue was purified by column chromatography on silicagel (15 % EtOAc in petroleum ether) to afford the **12c** (0.112 g, 77% yield) as yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.49 – 7.37 (m, 5H), 7.37 – 7.29 (m, 3H), 6.88 (d, *J* = 6.5 Hz, 1H), 4.82 (s, 1H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H).
^{19}F NMR (470 MHz, $CDCl_3$) δ -127.92 (s).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.31 (d, *J* = 238.8 Hz), 149.60 (s), 135.91 (s), 135.07 (s), 130.98 (d, *J* = 18.9 Hz), 129.92 (s), 129.80 (s), 129.08 (s), 128.46 (s), 128.24 (s), 127.63 (s), 126.83 (d, *J* = 16.7 Hz), 115.68 (s), 20.65 (s), 14.26 (s). **MS (EI)**: 292.11 (M^+).
HRMS (ESI): calculated for $C_{20}H_{16}OF$ $[M-H]^-$: 291.1185, found 291.1193.

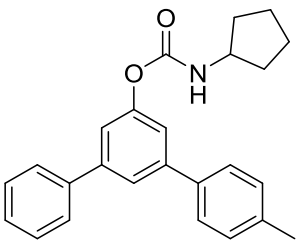
The synthesis of CD40 function inhibitor
The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (1.777 g, 12 mmol), 1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (2.091 g, 10 mmol), cesium carbonate

(3.258 g, 10mmol) and CH_3CN (30 mL) was stirred at 70 ^oC for half an hour. After completion of the reaction as monitored by TLC, the pH of reaction mixture was adjusted to 4-5 by using diluted hydrochloric acid (18%). Then the solvent was evaporated and the residual brown solid was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (10% ethyl acetate in petroleum ether), affording the desired *o*-phenolic esters (CD40 function inhibitor) in 90 % yield (2.872 g).

One-pot synthesis of LH-receptor antagonists (LUF5771)

The reaction mixture of ethyl 2-fluoro-3-oxobutanoate (1.777g, 12 mmol), (*E*)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one (2.221 g, 10 mmol), cesium carbonate (7.085 g, 20 mmol) and CH_3CN (30 mL) was stirred at 120 ^oC for 4 hours. After completion of the reaction as monitored by TLC, then the reaction mixture was cooled to room temperature. Isocyanatocyclopentane (1.111 g, 10 mmol) and triethylamine (1.518 g, 15 mmol) were added to the mixture and stirred at room temperature for 24 hours. After the completion of the reaction, the solvent was evaporated and the residual black residue was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated under reduced pressure and was purified through silica gel column chromatography (5% ethyl acetate in petroleum ether), affording the desired LH-receptor antagonists in the 76 % yield (2.821 g).

LH-receptor antagonists (LUF5771)



White solid. m.p. 157-158 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 3H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.25 (m, 2H), 5.18 (d, *J* = 7.3 Hz, 1H), 4.13 (q, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 2.06 (dd, *J* = 12.4, 5.7 Hz, 2H), 1.73 (dt, *J* = 9.0, 6.2 Hz, 2H), 1.65 (ddd, *J* = 11.4, 8.7, 3.3 Hz, 2H), 1.58 – 1.48 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.11 (s), 150.87 (s), 141.94 (s), 139.58 (s), 136.59 (s), 136.54 (s), 128.57 (s), 127.83 (s), 126.67 (s), 126.35 (s), 126.16 (s), 121.79 (s), 118.12 (s), 52.11 (s), 32.20 (s), 22.63 (s), 20.18 (s). **MS (EI)**: 371.11 (M^+).

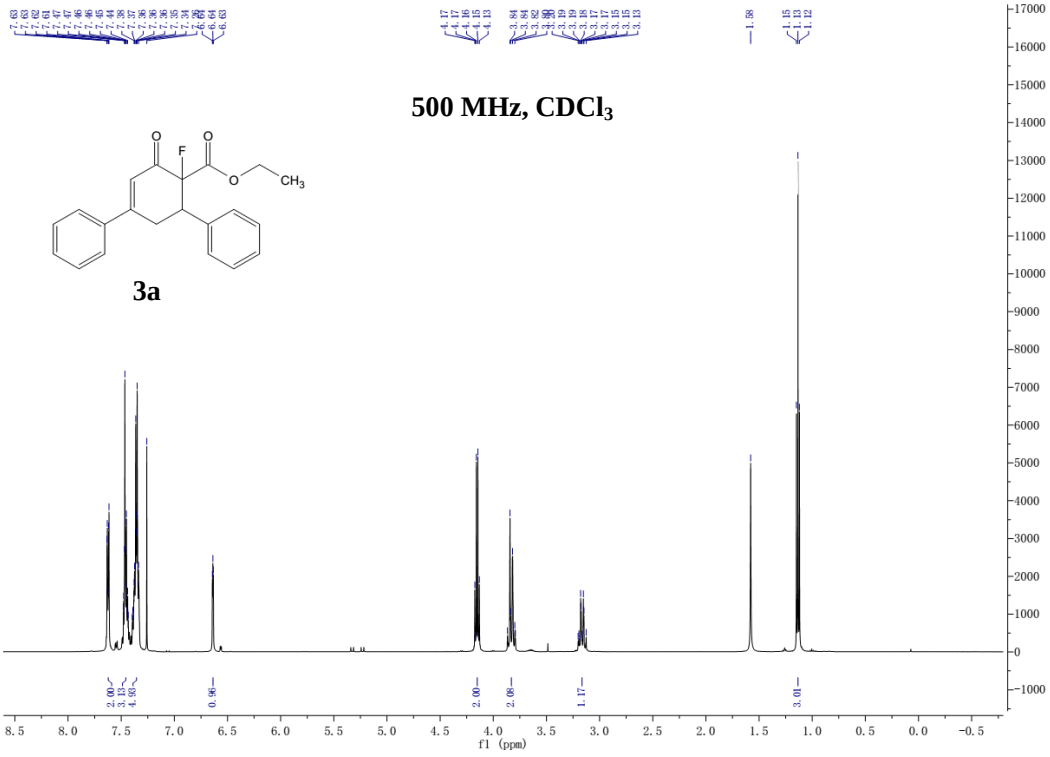
The **ALL** known compounds and their spectral data matched those reported.[3,4,5]

Reference

(1) Chang, M. Y.; Chen, Y. C.; Chan. C. K. *Tetrahedron* **2014**, *70*, 2257.
(2) He, Y.; Zhang, X. Y.; Shen, N. N.; Fan. X. S. *J. Fluorine Chem.* **2013**, *156*, 9.
(3) Teo, W. T.; Rao, W.; Ng, C. J. H.; Koh, S. W. Y., Chan, P. W. H. *Org. Lett.* **2014**, 16, 1248.
(4) Katritzky, A. R.; Belyakov, S. A.; Henderson, S. A. *J. Org. Chem.* **1997**, 62, 8215.
(5) Luo, Q. L.; Tan, J. P.; Li,Z. F.; Nan,W. H.; Xiao, D. R. *J. Org. Chem.* **2012**, 77, 8332.

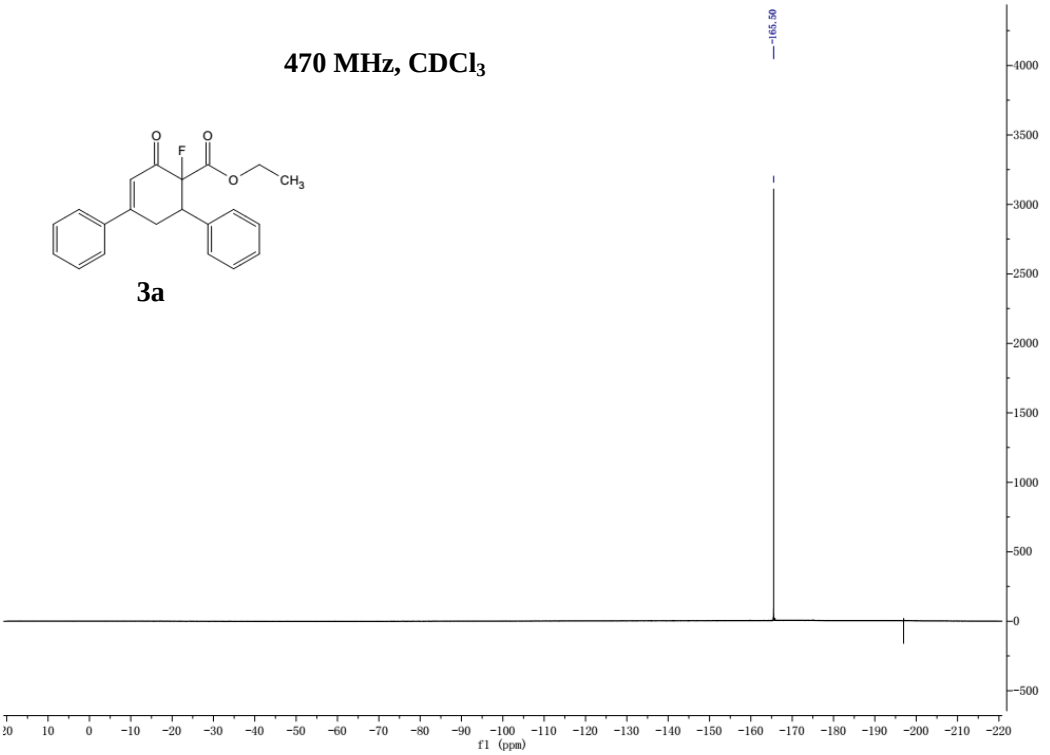
3. NMR Spectra

500 MHz, $CDCl_3$

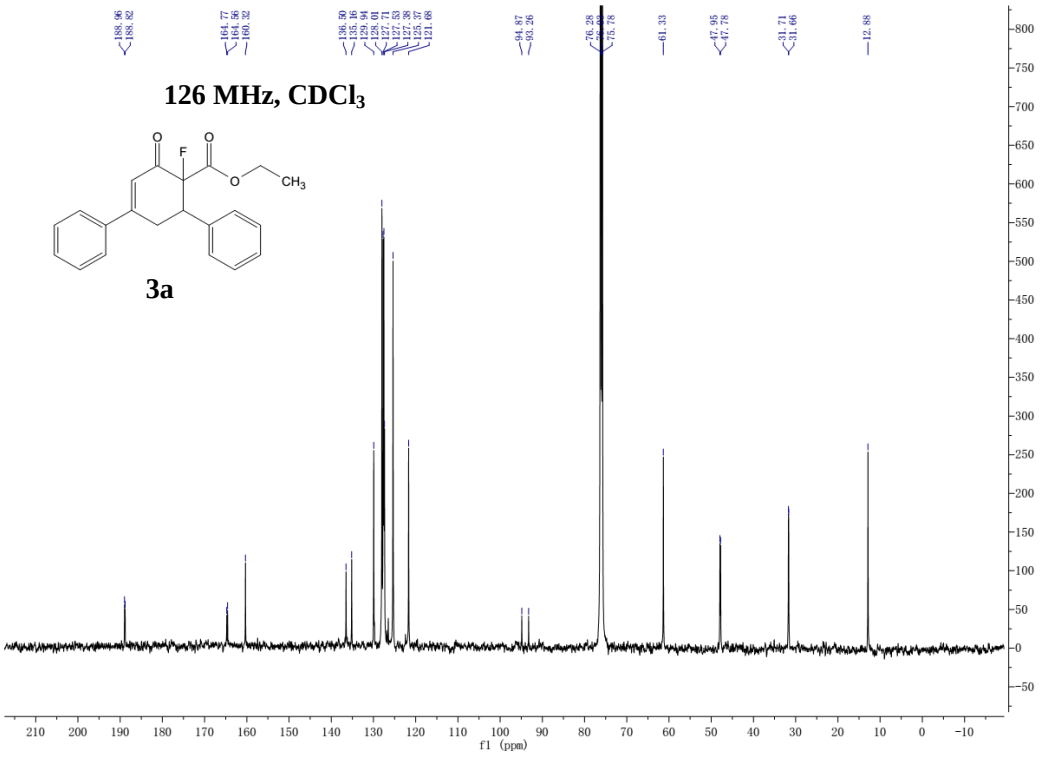


3a

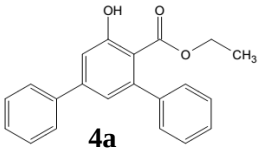
470 MHz, $CDCl_3$



3a

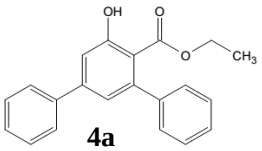

188.96
188.82
164.77
164.58
160.32
136.80
135.16
129.94
129.61
127.71
127.53
127.38
125.57
121.68
94.87
93.26
76.28
75.78
61.33
47.95
47.78
31.71
31.66
12.88
126 MHz, CDCl3
F
O
O
O
CH3
3a
f1 (ppm)

500 MHz, $CDCl_3$



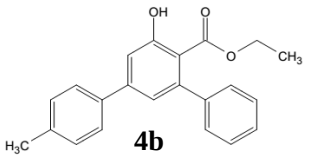
4a

126 MHz, $CDCl_3$



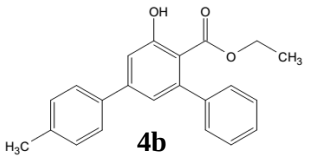
4a

500 MHz, $CDCl_3$



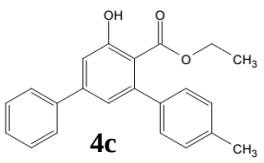
4b

126 MHz, $CDCl_3$



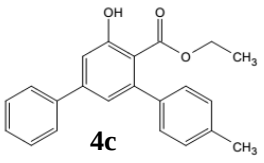
4b

500 MHz, $CDCl_3$

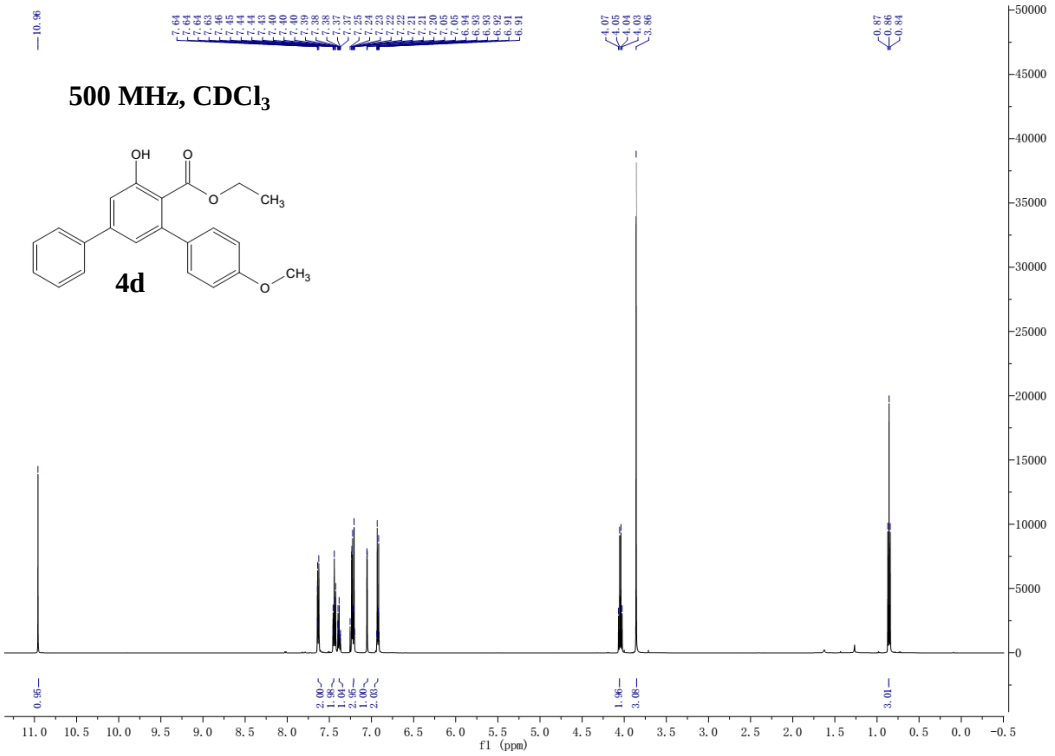


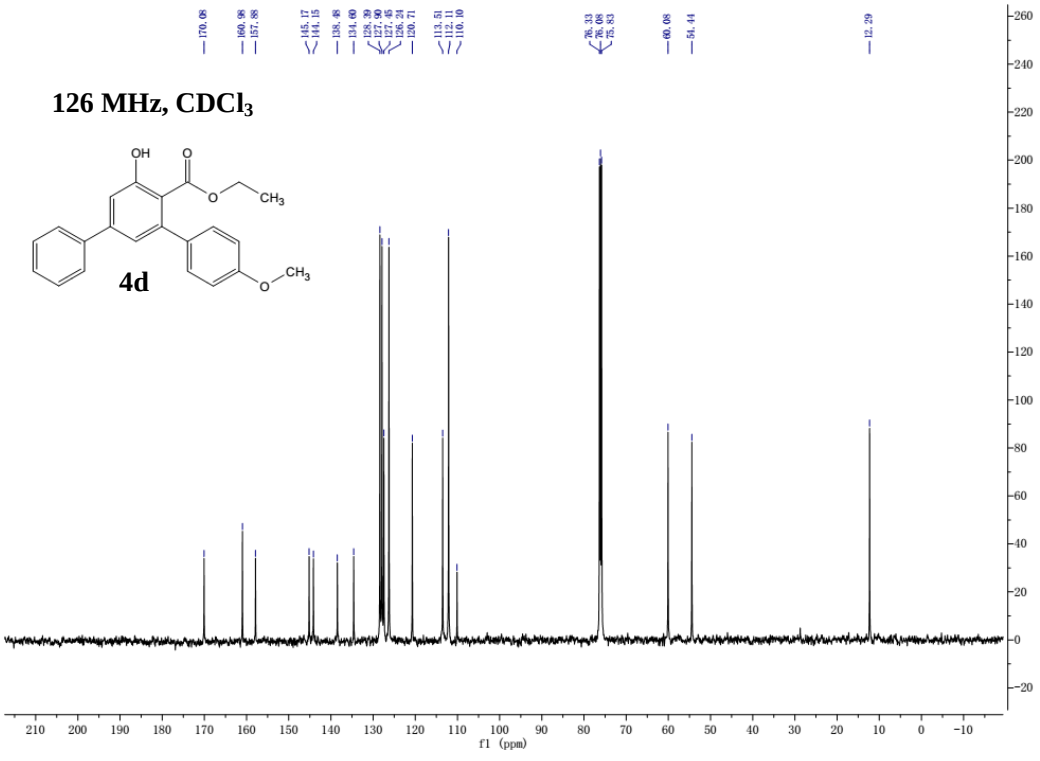
4c

126 MHz, $CDCl_3$

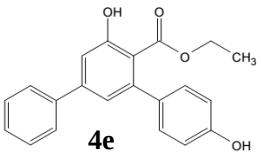


4c


500 MHz, CDCl3
OH
O
CH3
O
CH3
4d
f1 (ppm)

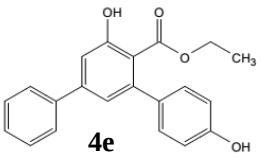

126 MHz, CDCl3
OH
O
CH3
O
CH3
4d
f1 (ppm)

500 MHz, $CDCl_3$



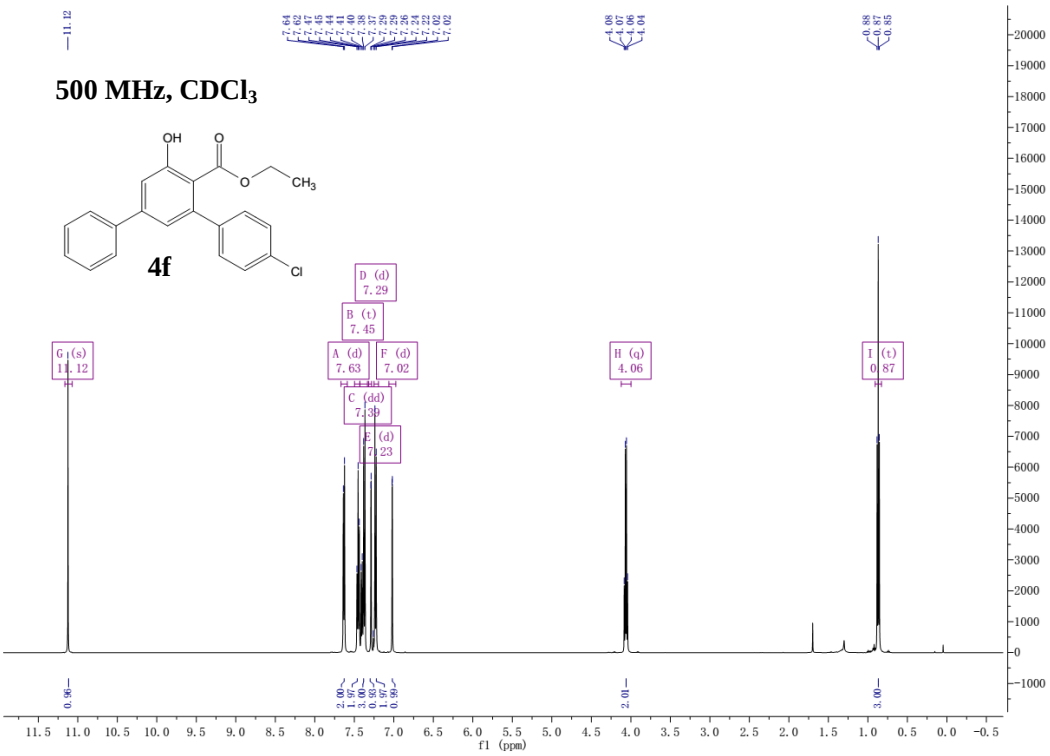
4e

126 MHz, $CDCl_3$

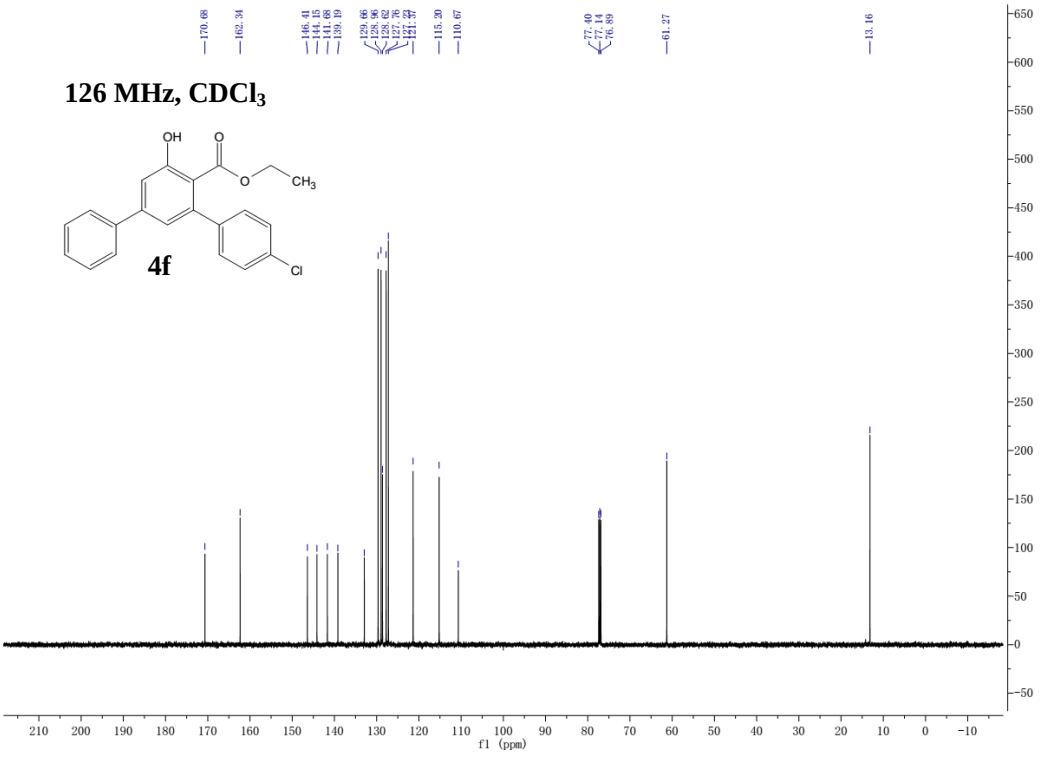


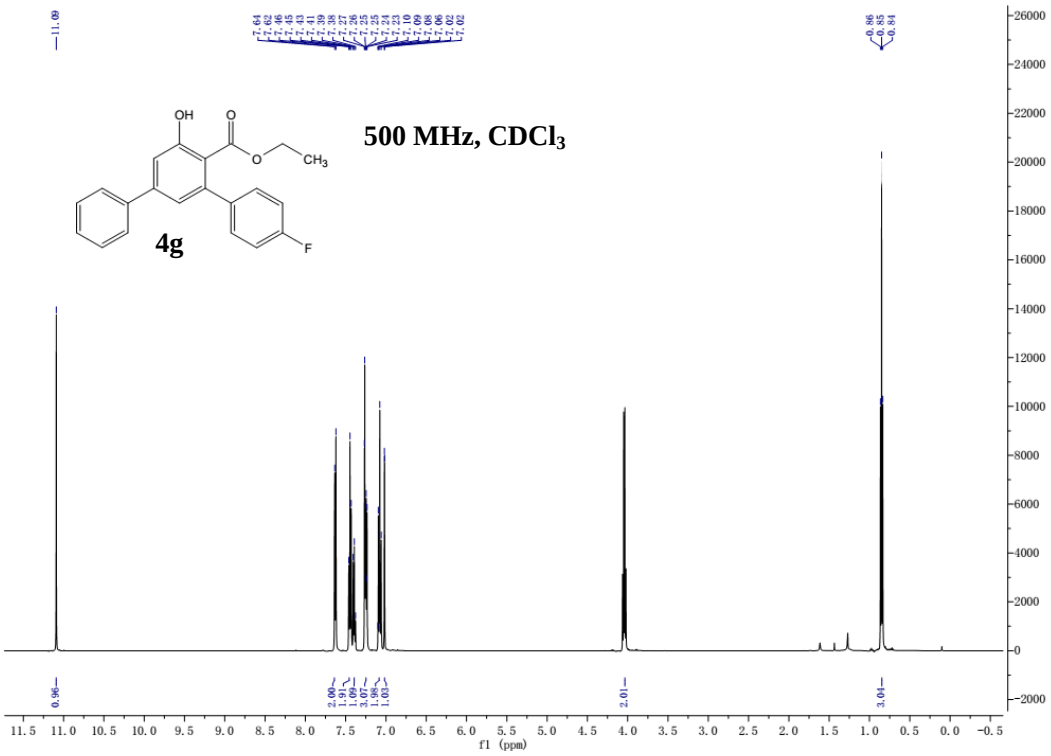
4e

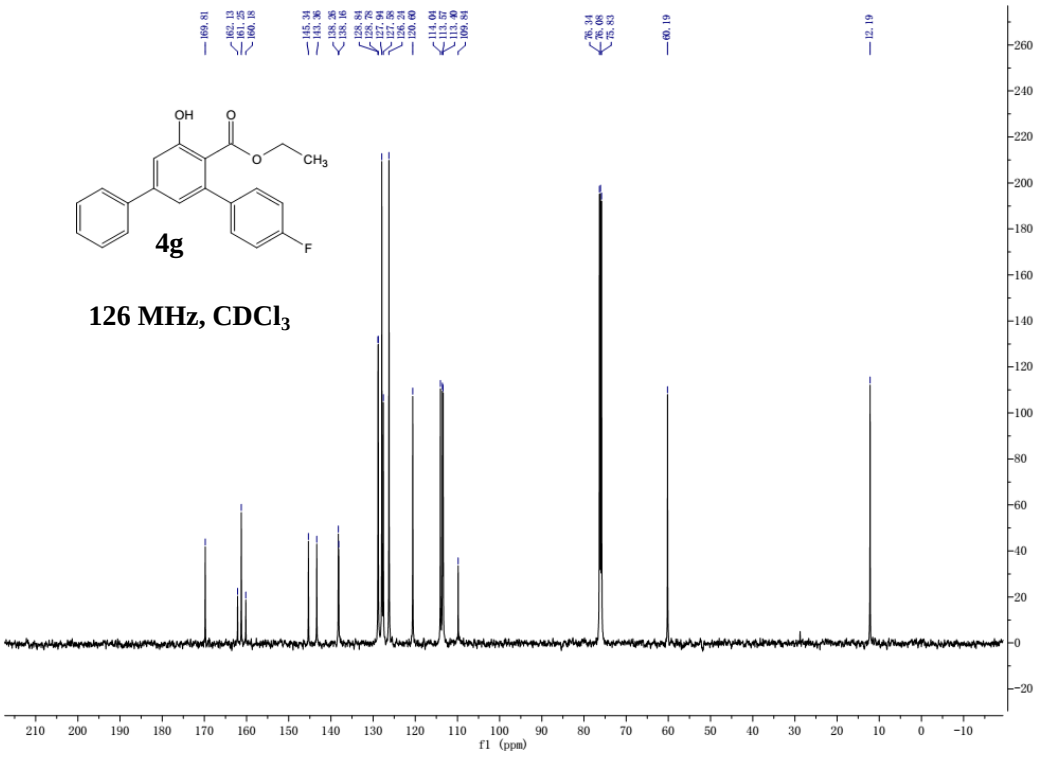
500 MHz, $CDCl_3$

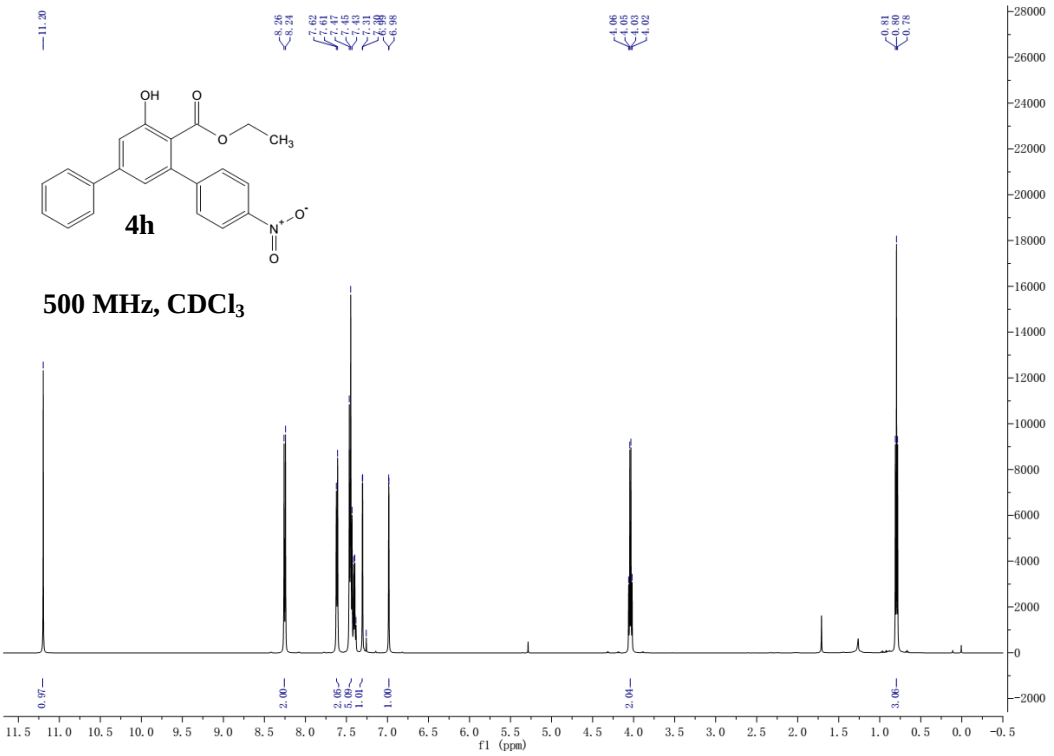


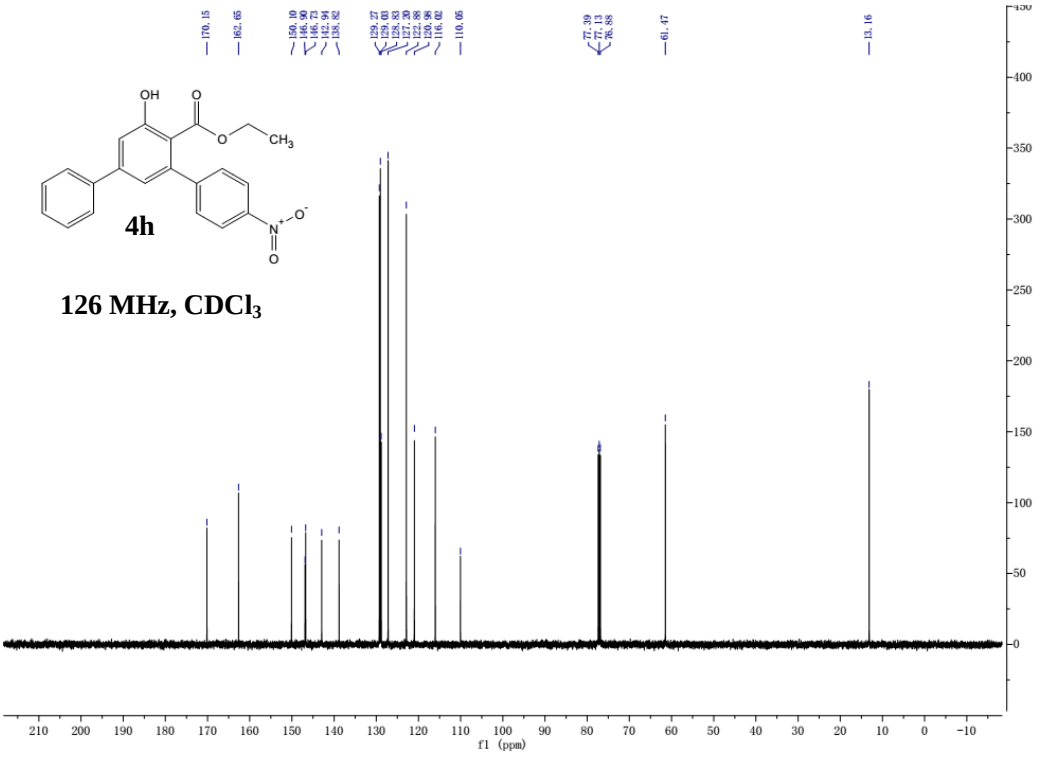
126 MHz, $CDCl_3$

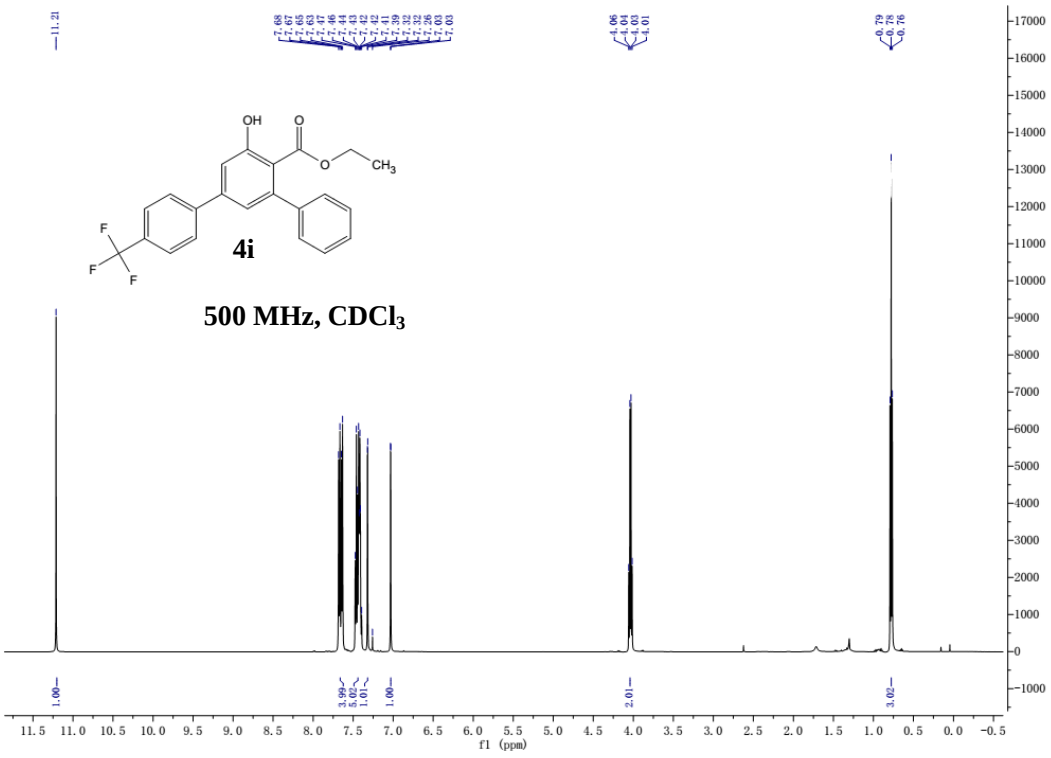



500 MHz, CDCl3
4g
f1 (ppm)


126 MHz, CDCl3
4g
f1 (ppm)

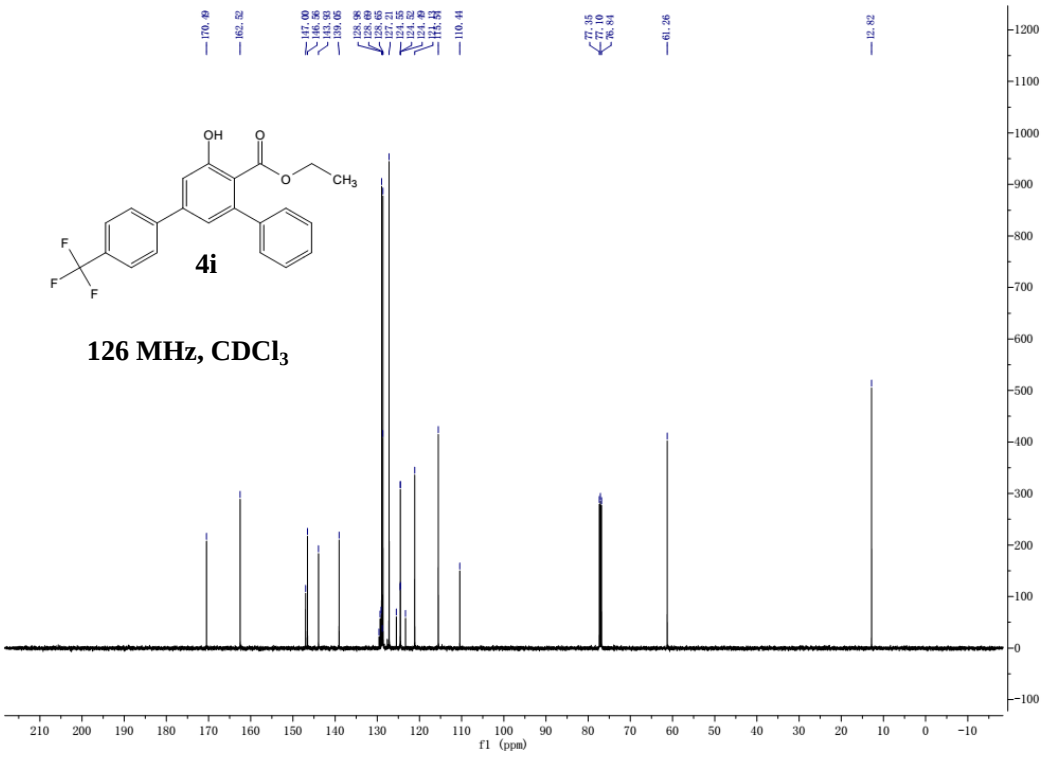

4h
500 MHz, CDCl3
f1 (ppm)


4h
126 MHz, CDCl3
f1 (ppm)



4i

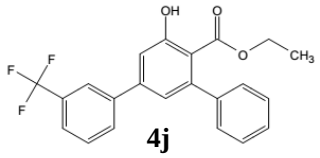
500 MHz, $CDCl_3$



4i

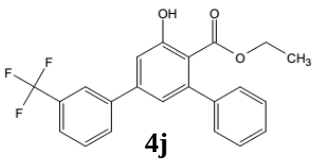
126 MHz, $CDCl_3$

500 MHz, $CDCl_3$



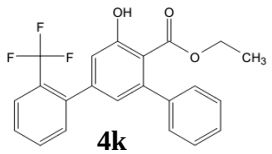
4j

126 MHz, $CDCl_3$



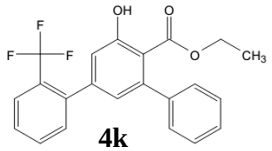
4j

500 MHz, $CDCl_3$

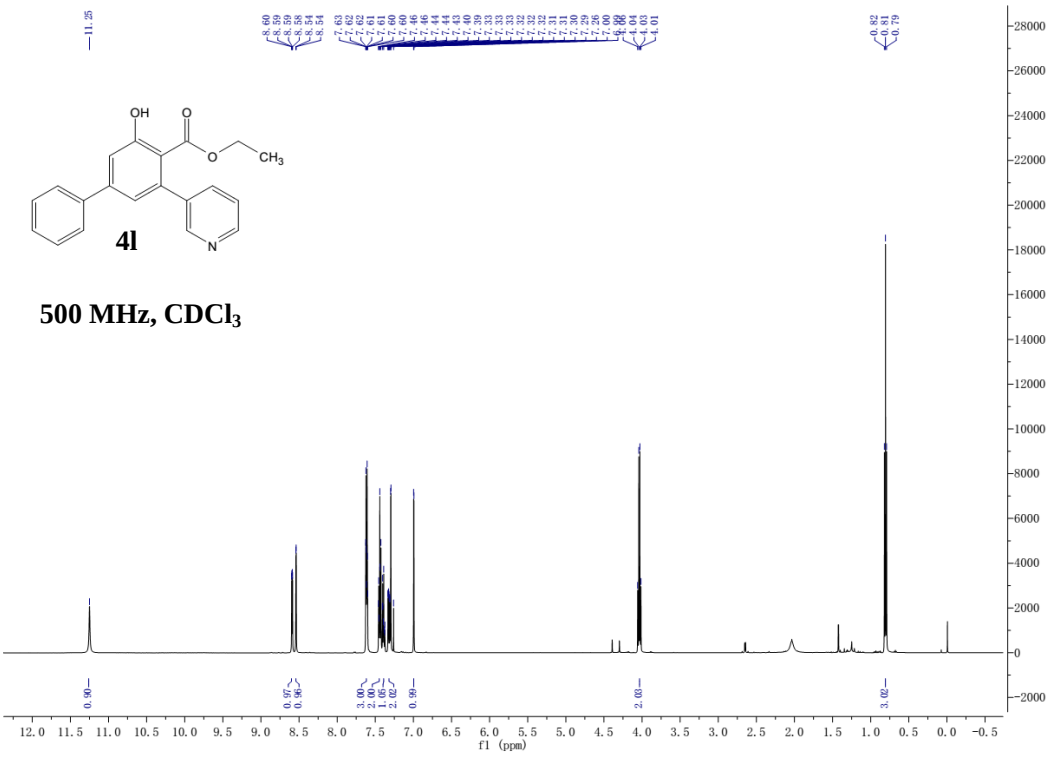


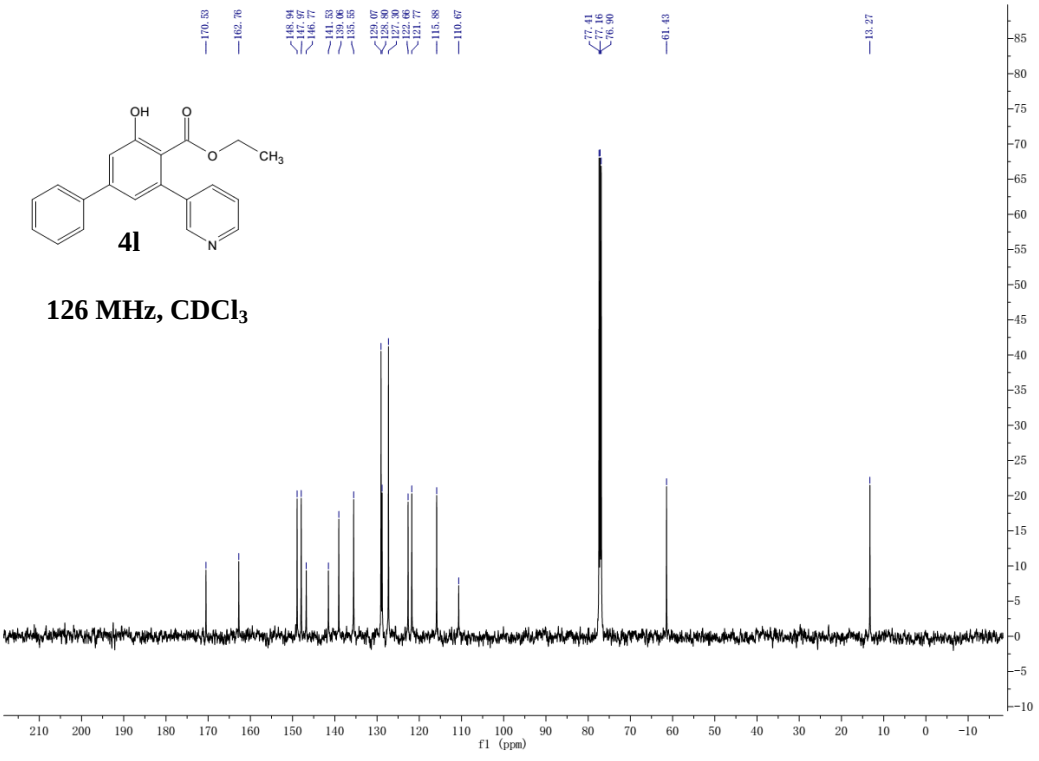
4k

126 MHz, $CDCl_3$

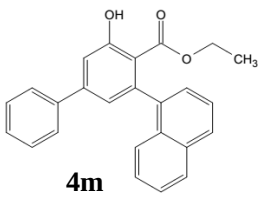


4k


OH
O
O
CH3
N
4l
500 MHz, CDCl3
f1 (ppm)

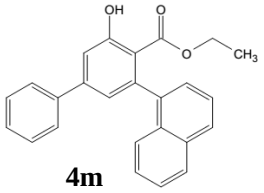

OH
O
O
CH3
N
4l
126 MHz, CDCl3
f1 (ppm)

500 MHz, $CDCl_3$



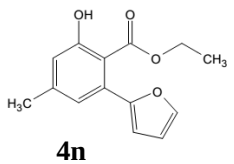
4m

126 MHz, $CDCl_3$



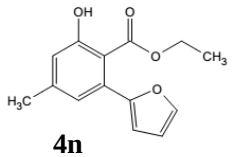
4m

500 MHz, $CDCl_3$



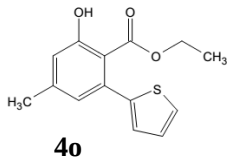
4n

126 MHz, $CDCl_3$



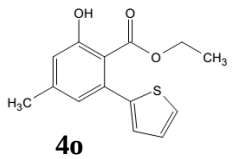
4n

500 MHz, $CDCl_3$



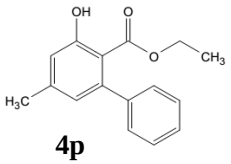
4o

126 MHz, $CDCl_3$



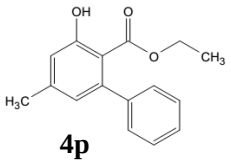
4o

500 MHz, $CDCl_3$



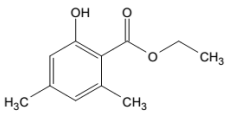
4p

126 MHz, $CDCl_3$



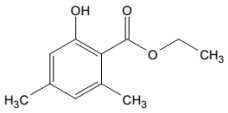
4p

500 MHz, $CDCl_3$



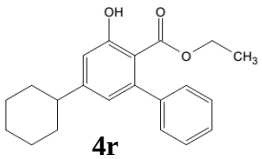
4q

126 MHz, $CDCl_3$



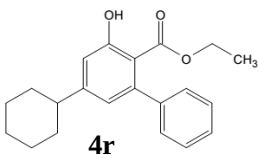
4q

500 MHz, $CDCl_3$



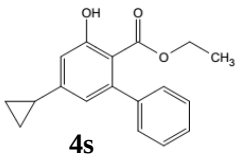
4r

126 MHz, $CDCl_3$



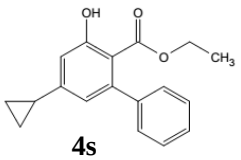
4r

500 MHz, $CDCl_3$



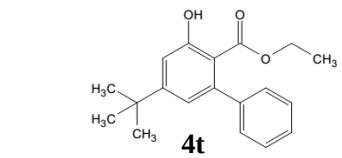
4s

126 MHz, $CDCl_3$



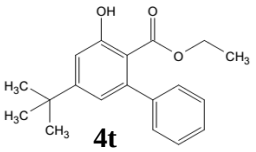
4s

500 MHz, $CDCl_3$



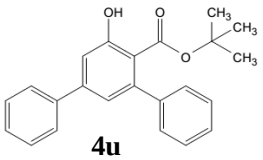
4t

126 MHz, $CDCl_3$



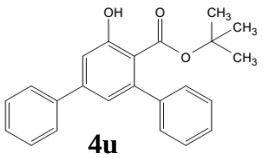
4t

500 MHz, $CDCl_3$

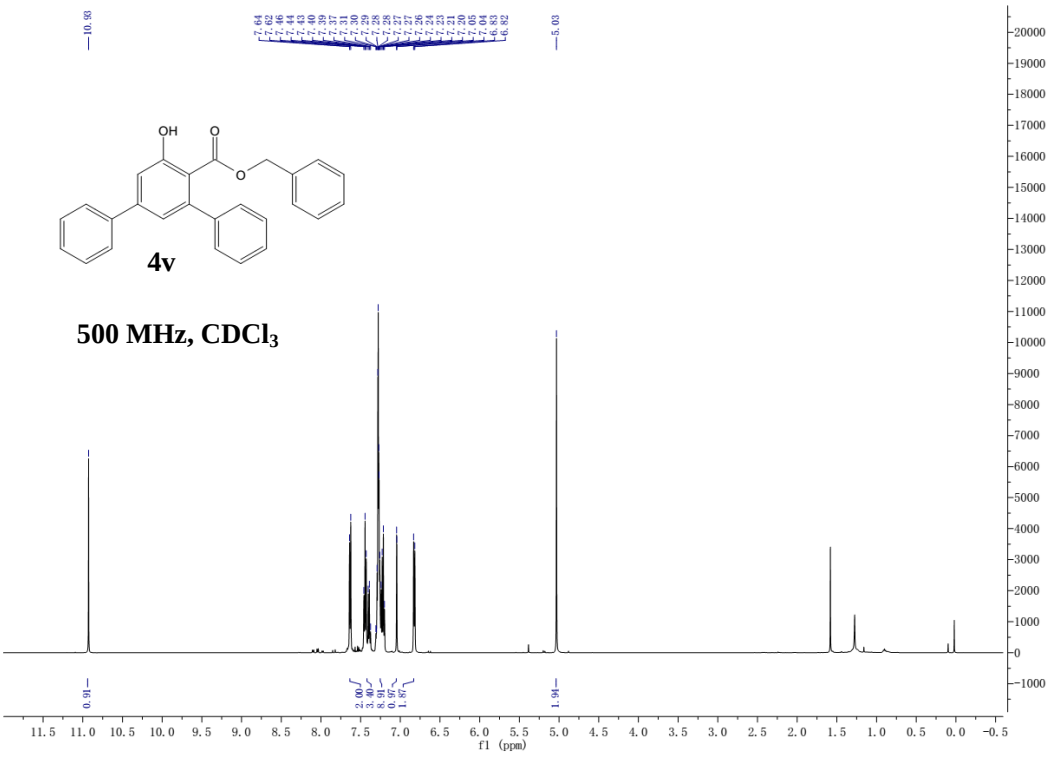


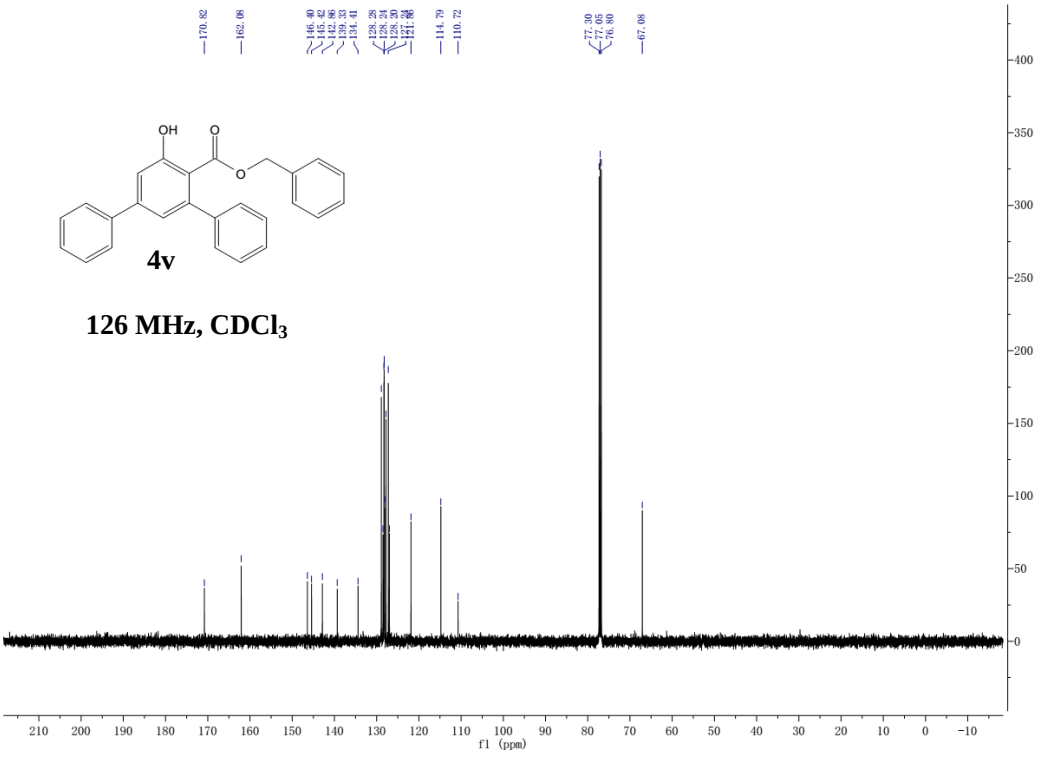
4u

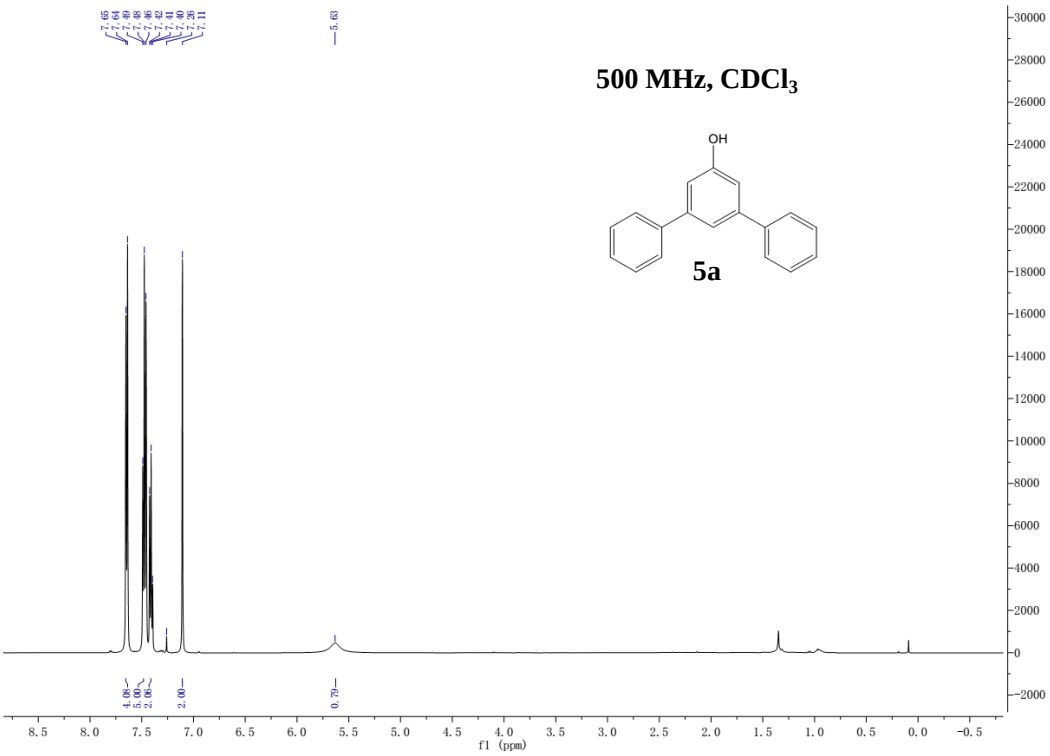
126 MHz, $CDCl_3$

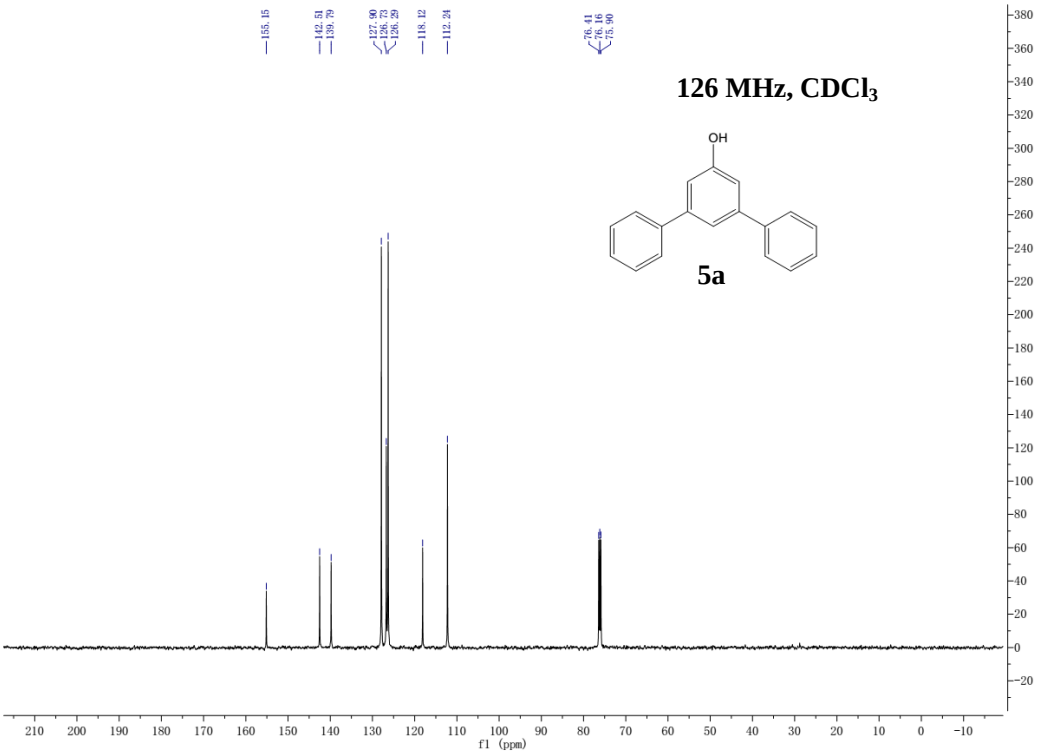


4u

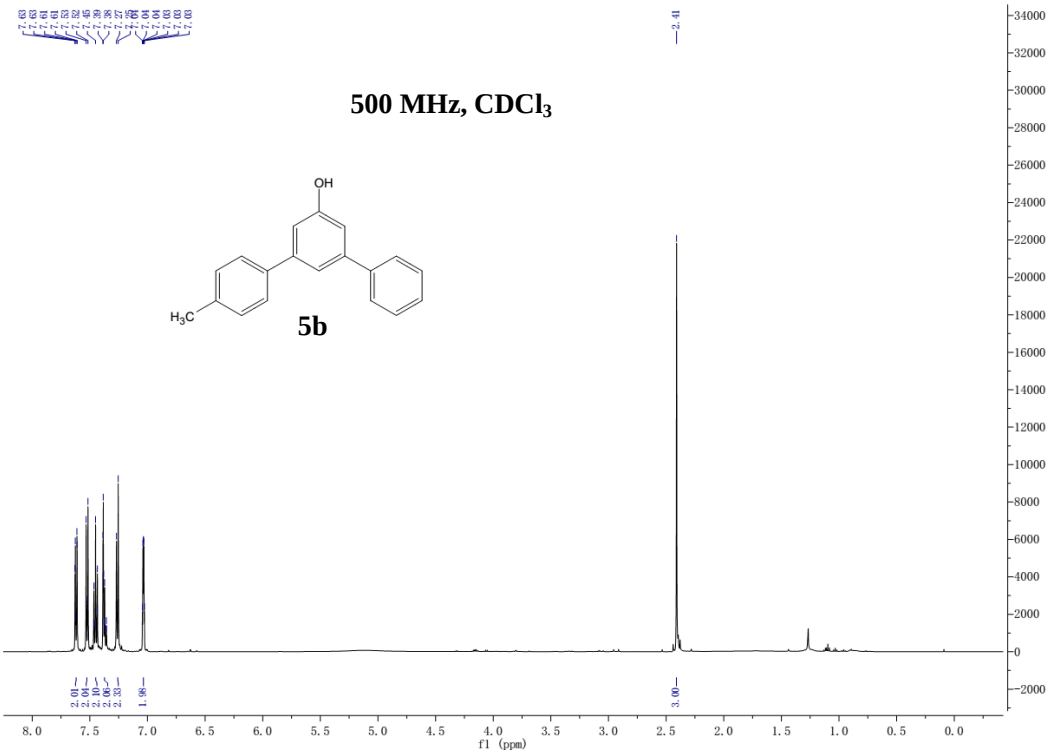

OH
O
O
4v
500 MHz, CDCl3
f1 (ppm)


OH
O
O
4v
126 MHz, CDCl3
f1 (ppm)

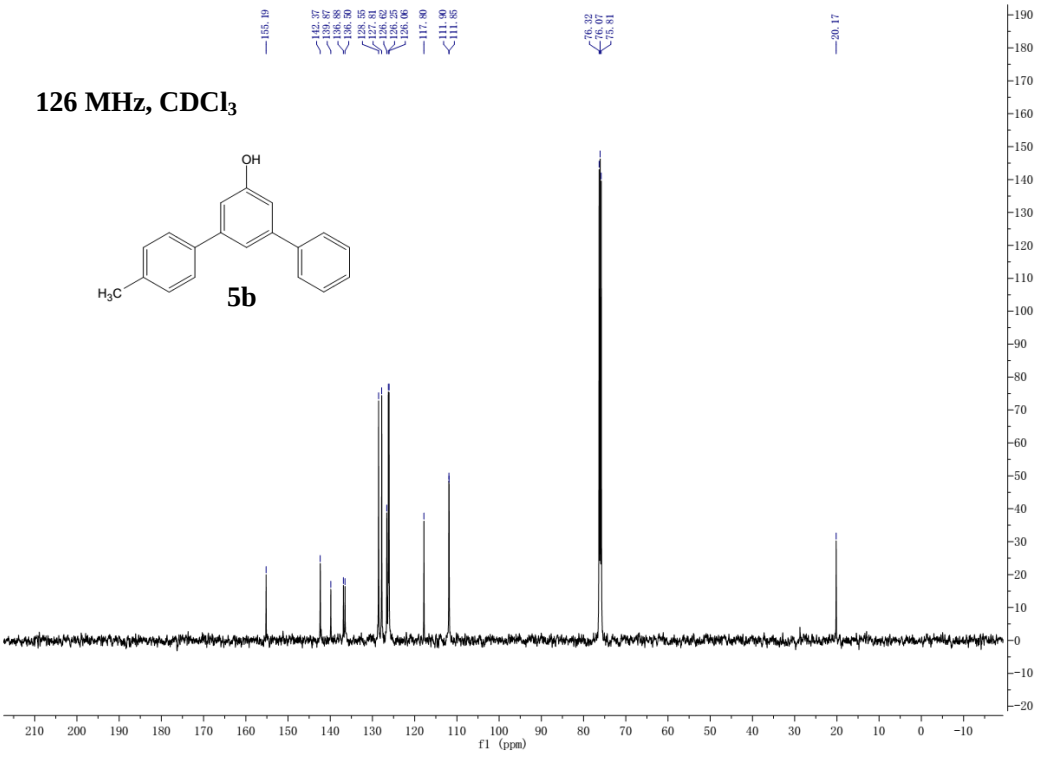

7.65
7.64
7.49
7.48
7.46
7.42
7.41
7.40
7.36
7.11
5.63
500 MHz, CDCl3
OH
5a
4.08
5.00
2.06
2.00
0.79
f1 (ppm)

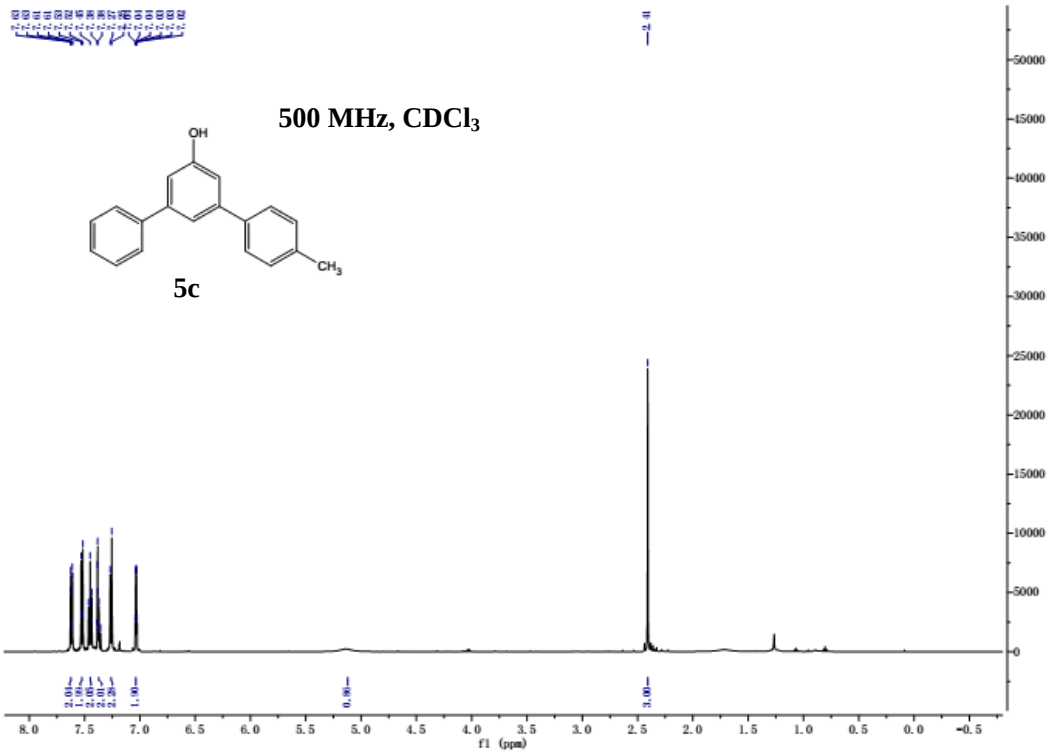

155.15
142.51
139.79
127.90
126.73
126.29
118.12
112.24
76.41
76.16
75.90
126 MHz, CDCl3
OH
5a
f1 (ppm)

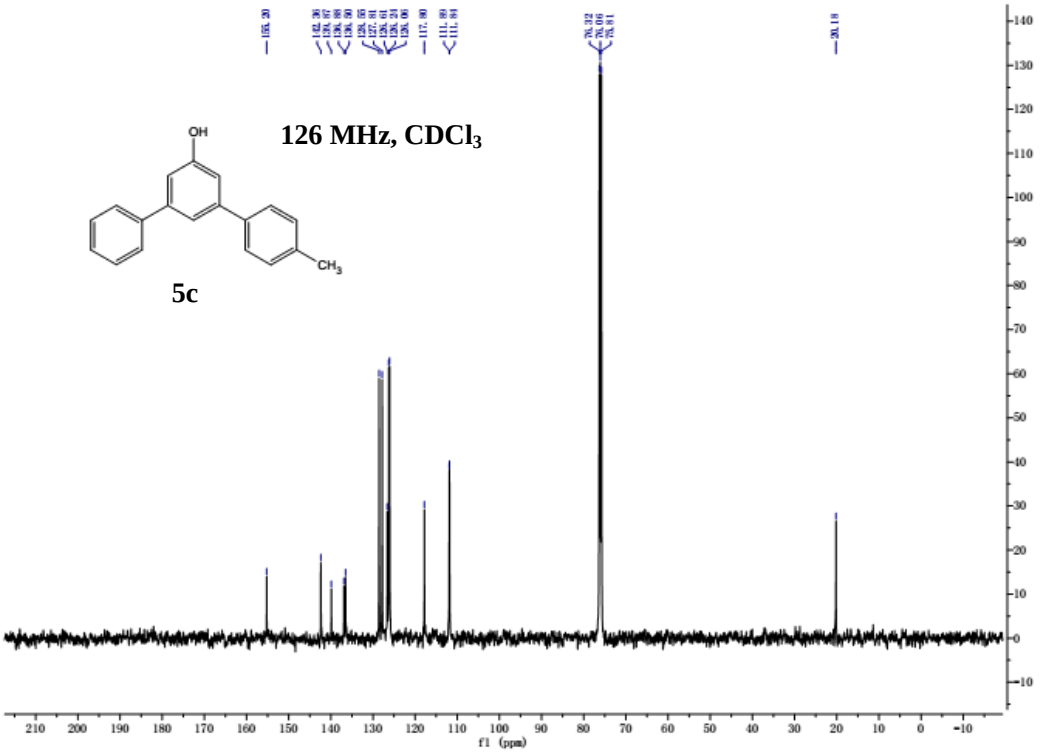
500 MHz, $CDCl_3$

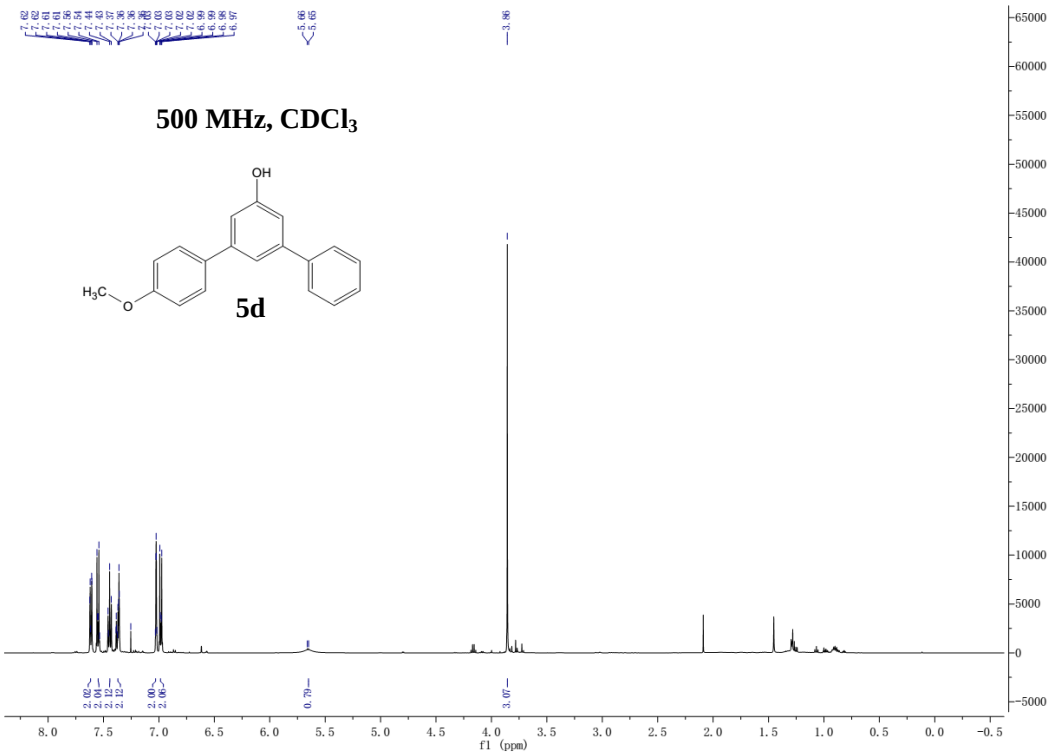


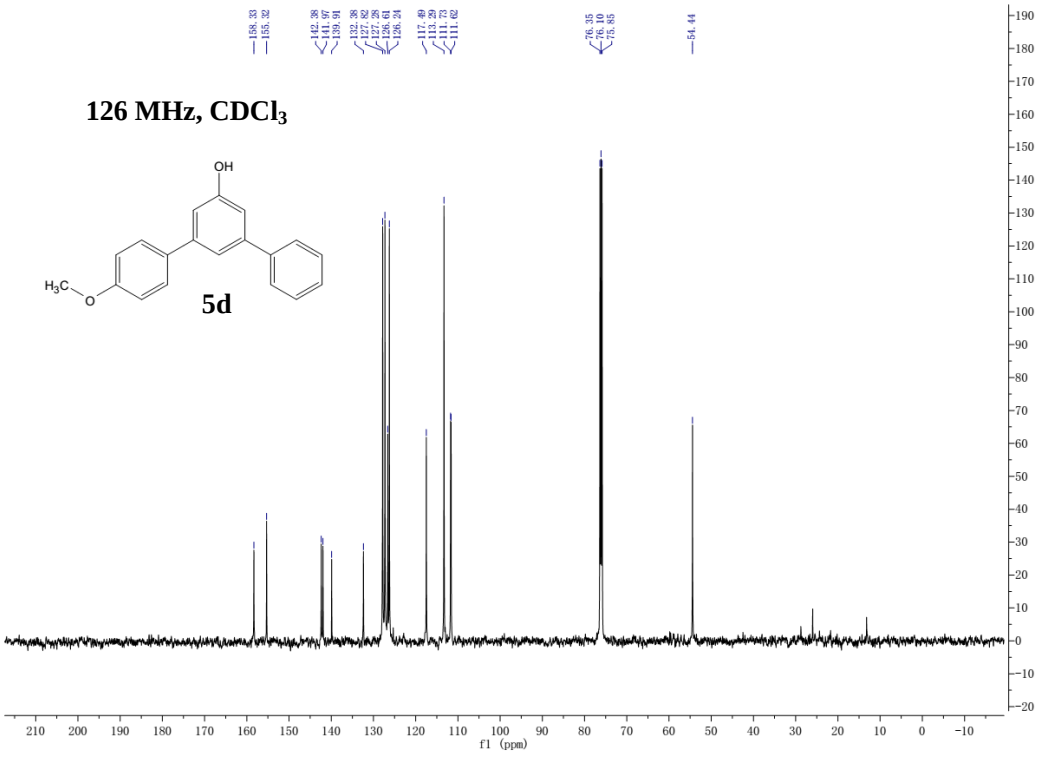
126 MHz, $CDCl_3$



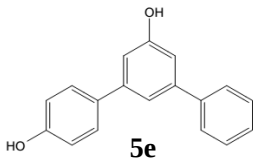

500 MHz, CDCl3
OH
CH3
5c
f1 (ppm)


126 MHz, CDCl3
OH
CH3
5c
f1 (ppm)


500 MHz, CDCl3
OH
H3C
O
5d
f1 (ppm)

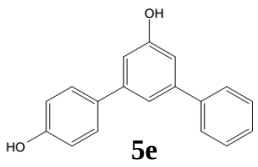

126 MHz, CDCl3
OH
H3C
O
5d
f1 (ppm)

500 MHz, DMSO

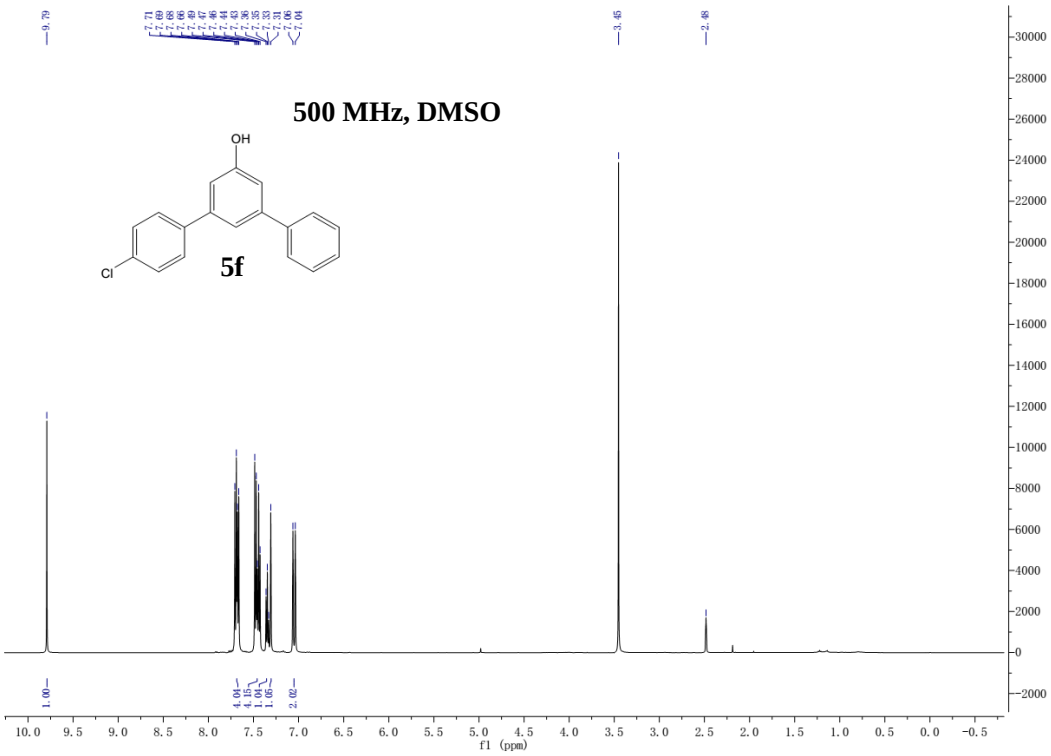


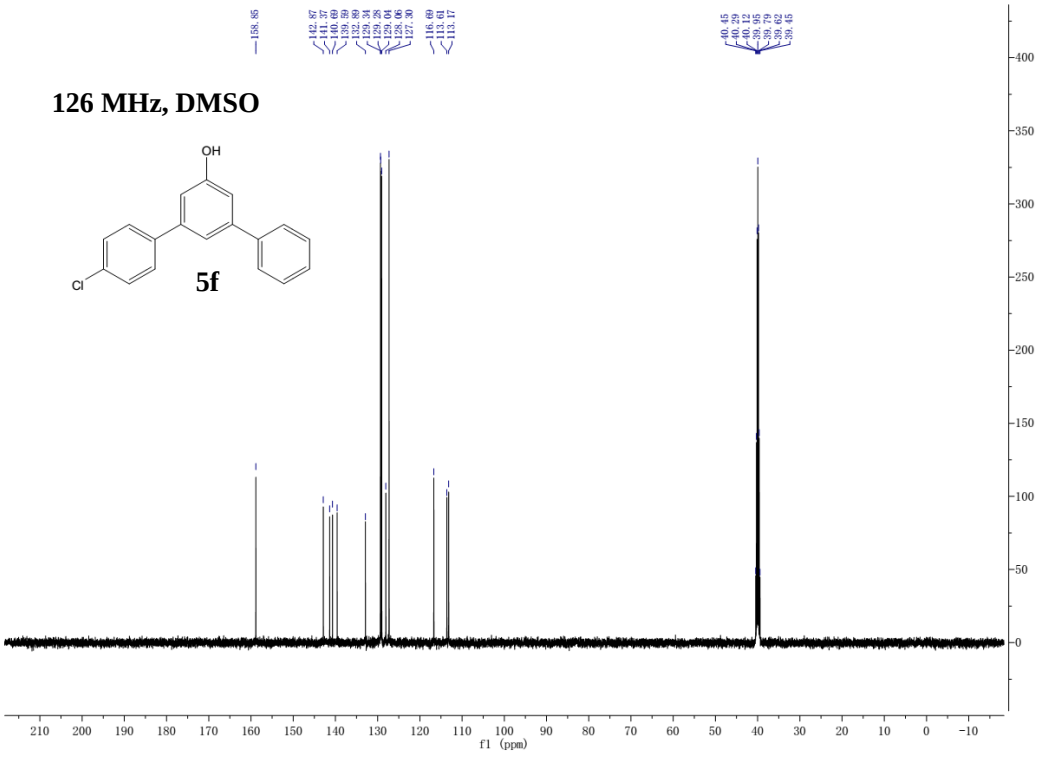
5e

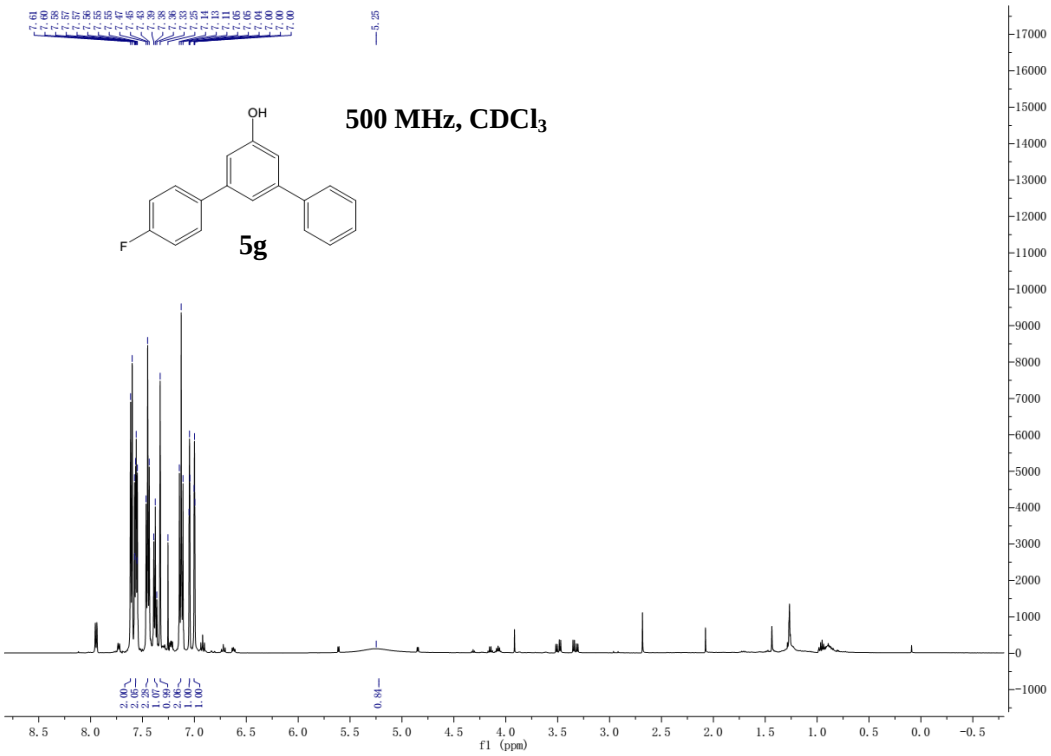
126 MHz, DMSO

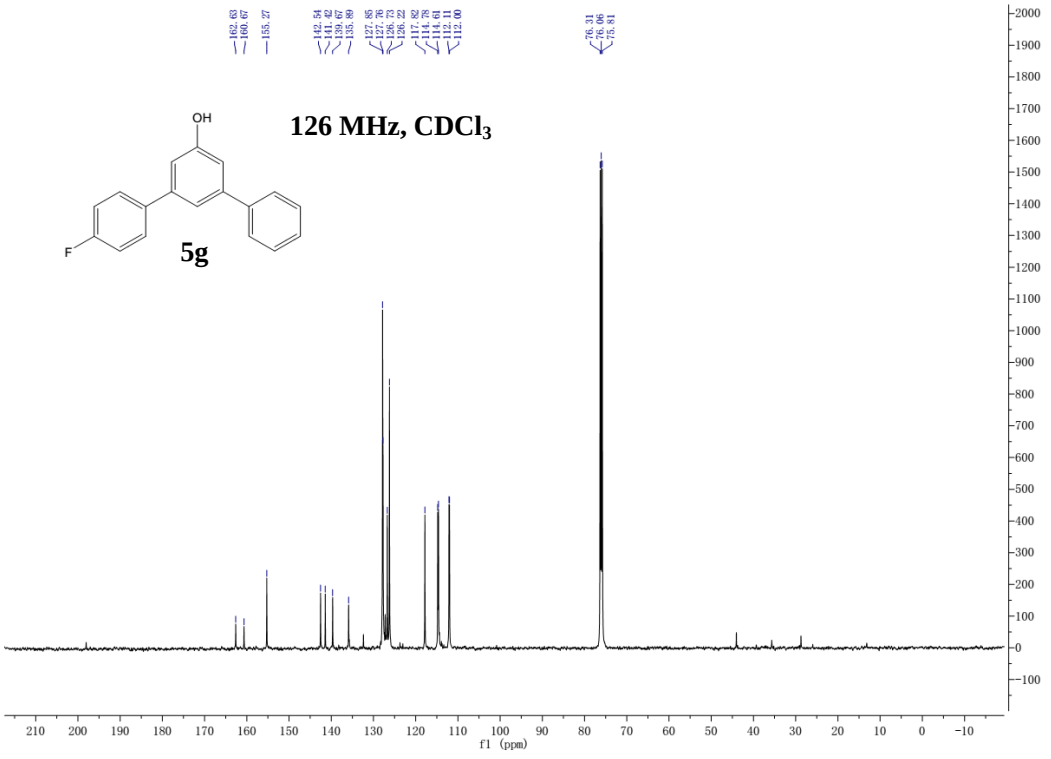


5e

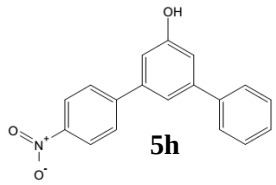

9.79
7.71
7.69
7.68
7.66
7.49
7.47
7.46
7.44
7.43
7.36
7.35
7.33
7.31
7.06
7.04
3.45
2.48
500 MHz, DMSO
OH
Cl
5f
1.00
4.04
4.15
1.04
1.05
2.02
f1 (ppm)


158.85
142.87
141.37
140.69
139.59
132.89
129.34
129.28
129.04
128.06
127.30
116.69
113.61
113.17
40.45
40.29
40.12
39.95
39.79
39.62
39.45
126 MHz, DMSO
OH
Cl
5f
f1 (ppm)


500 MHz, CDCl3
OH
F
5g
f1 (ppm)

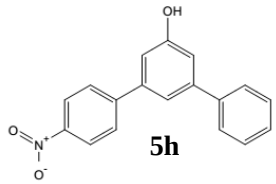

126 MHz, CDCl3
OH
F
5g
f1 (ppm)

500 MHz, DMSO

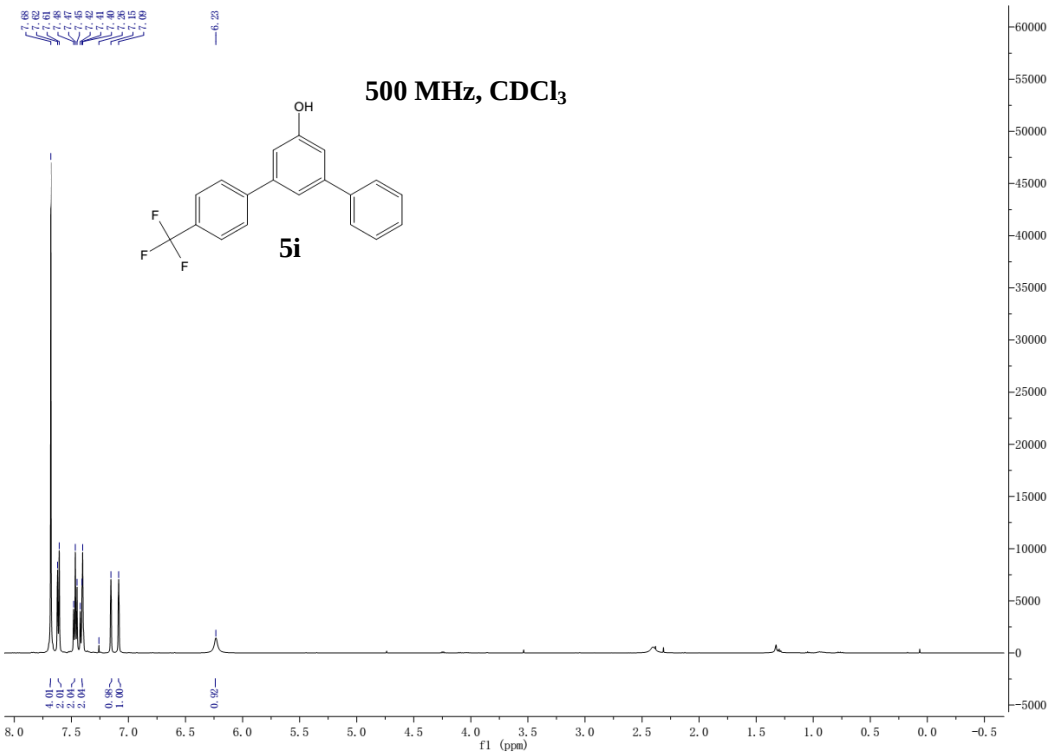


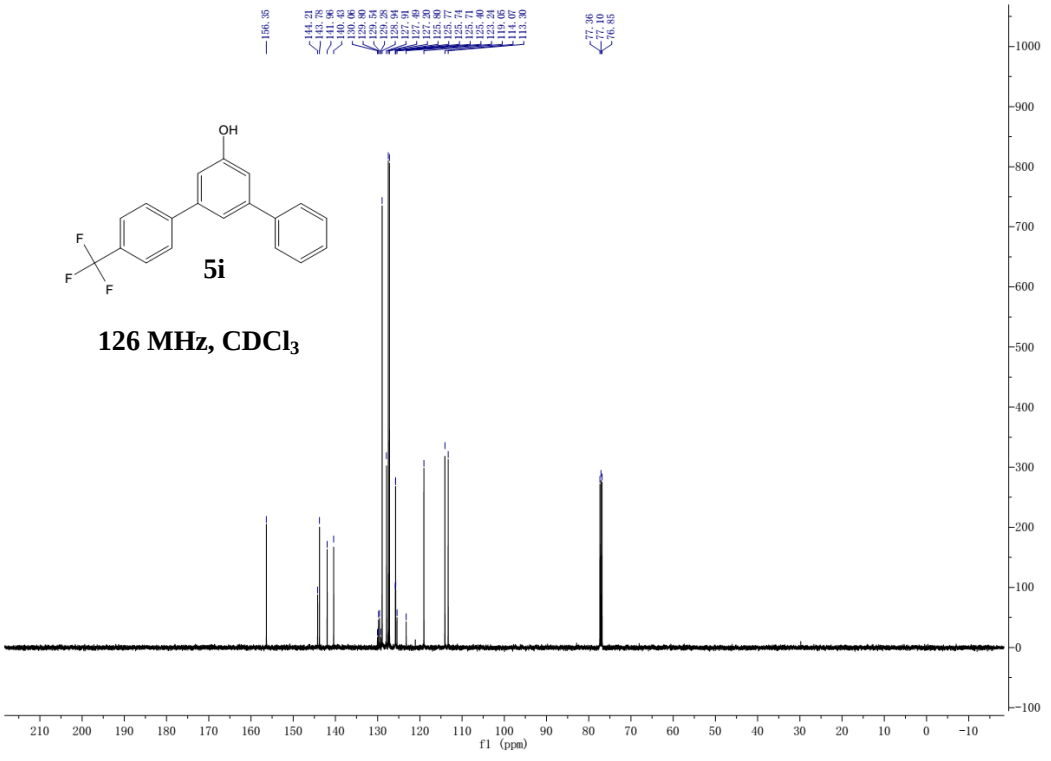
5h

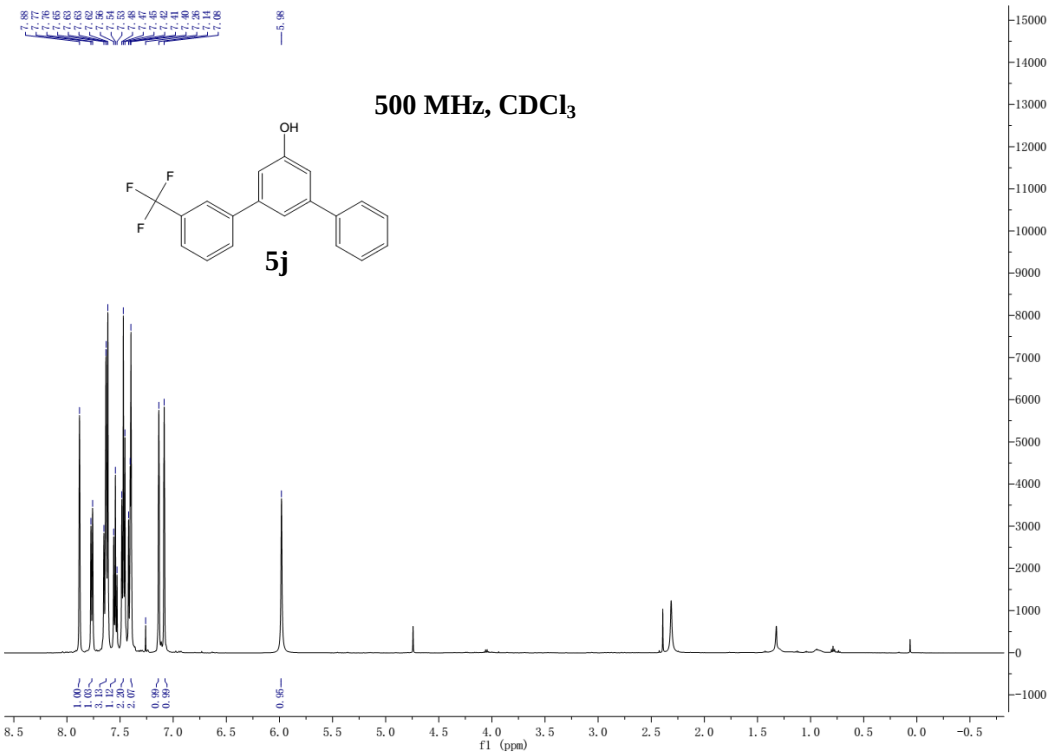
126 MHz, DMSO

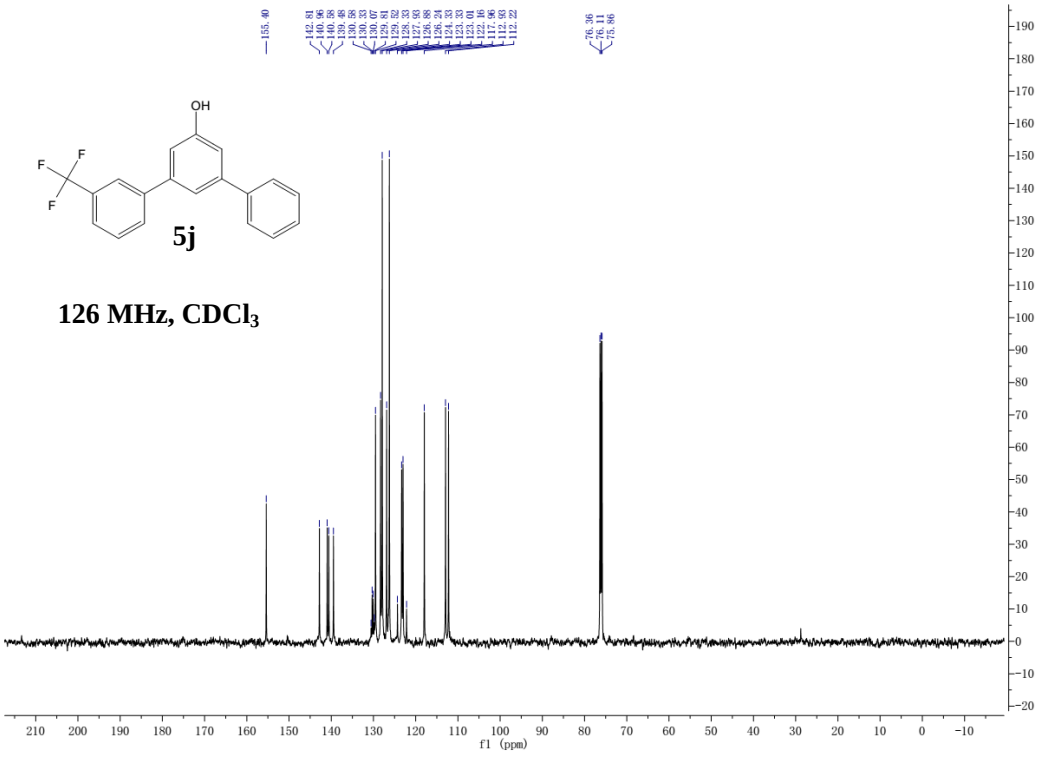


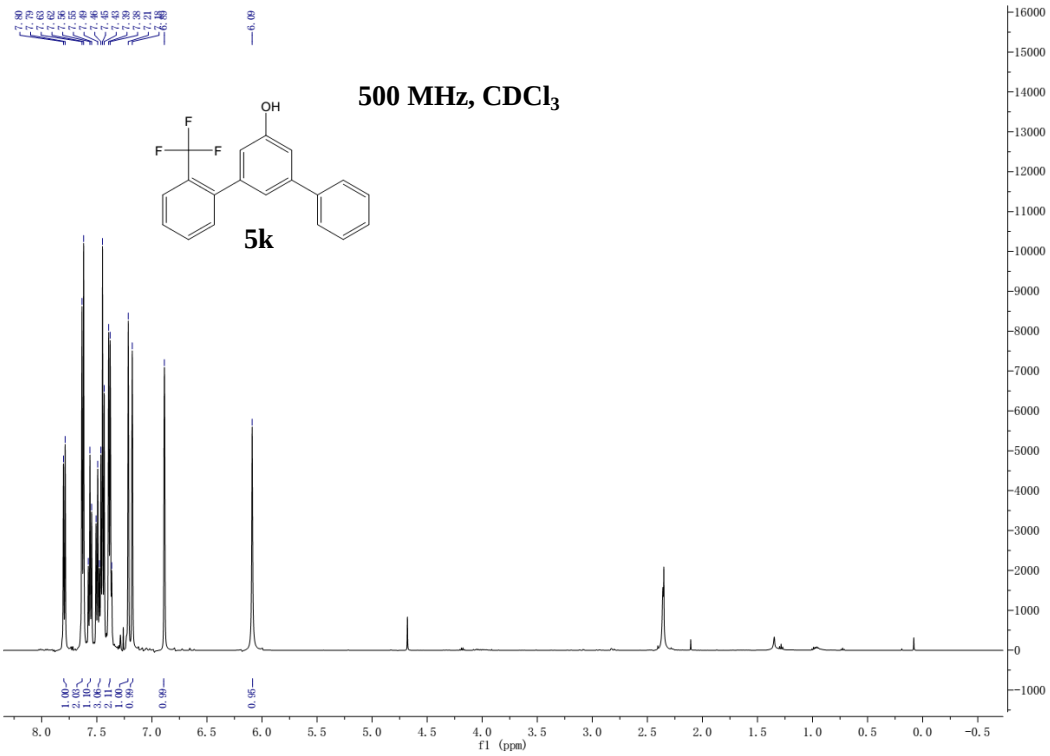
5h

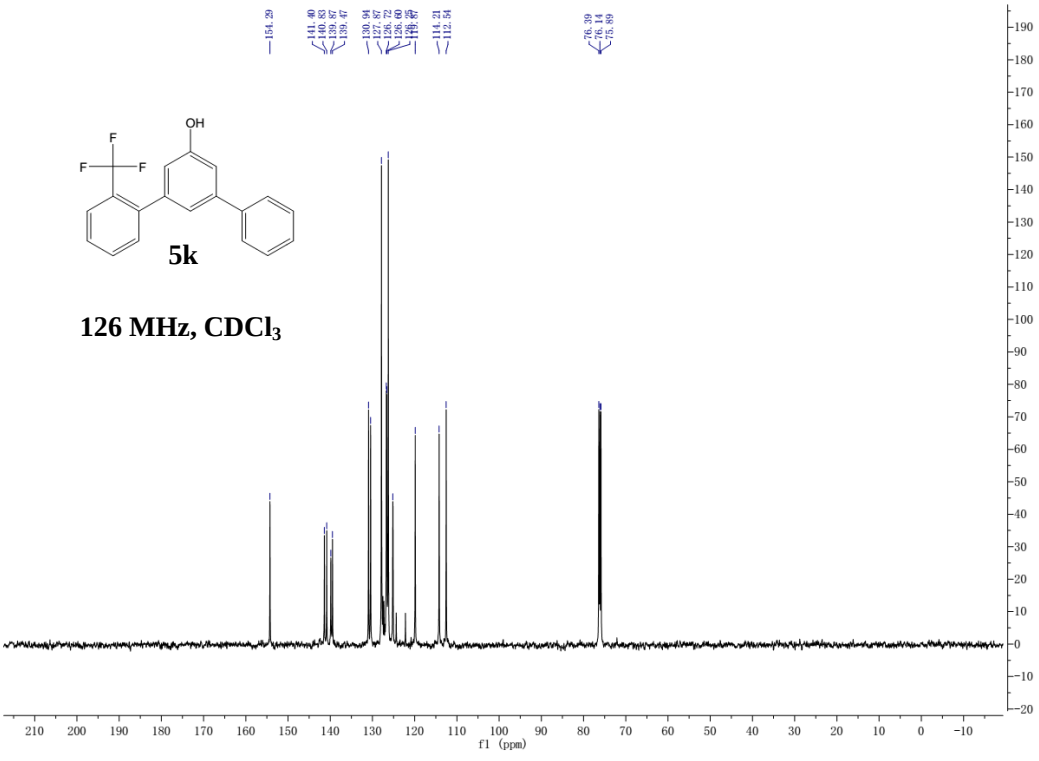

500 MHz, CDCl3
OH
F
F
F
5i
f1 (ppm)

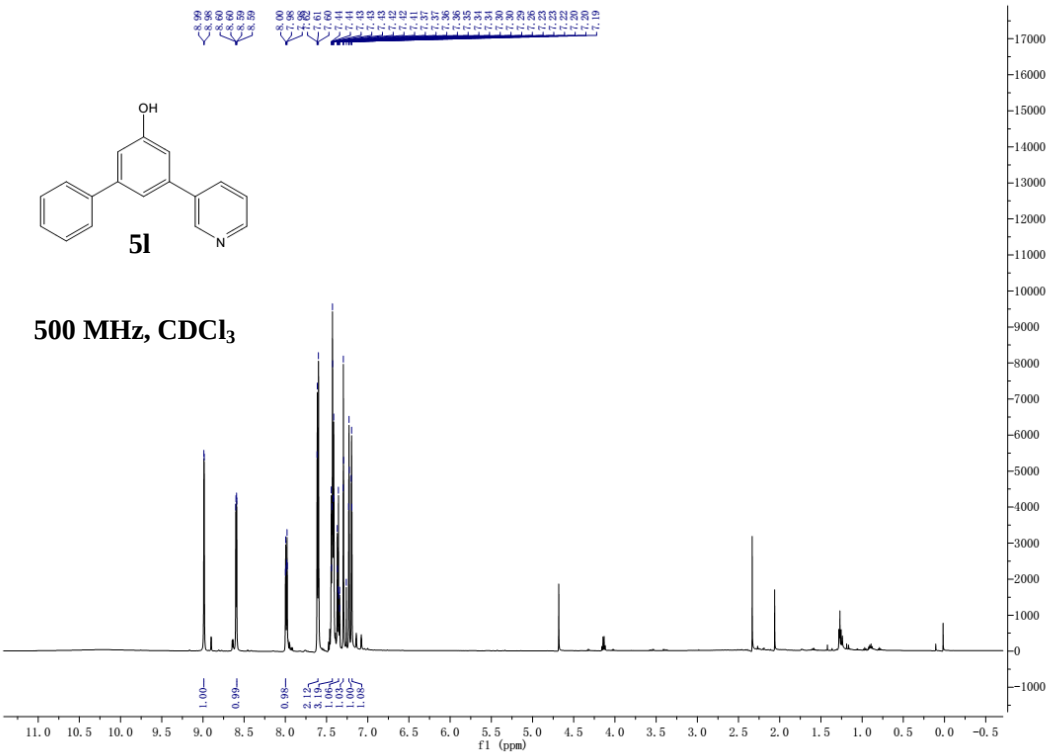

OH
F
F
F
5i
126 MHz, CDCl3
f1 (ppm)

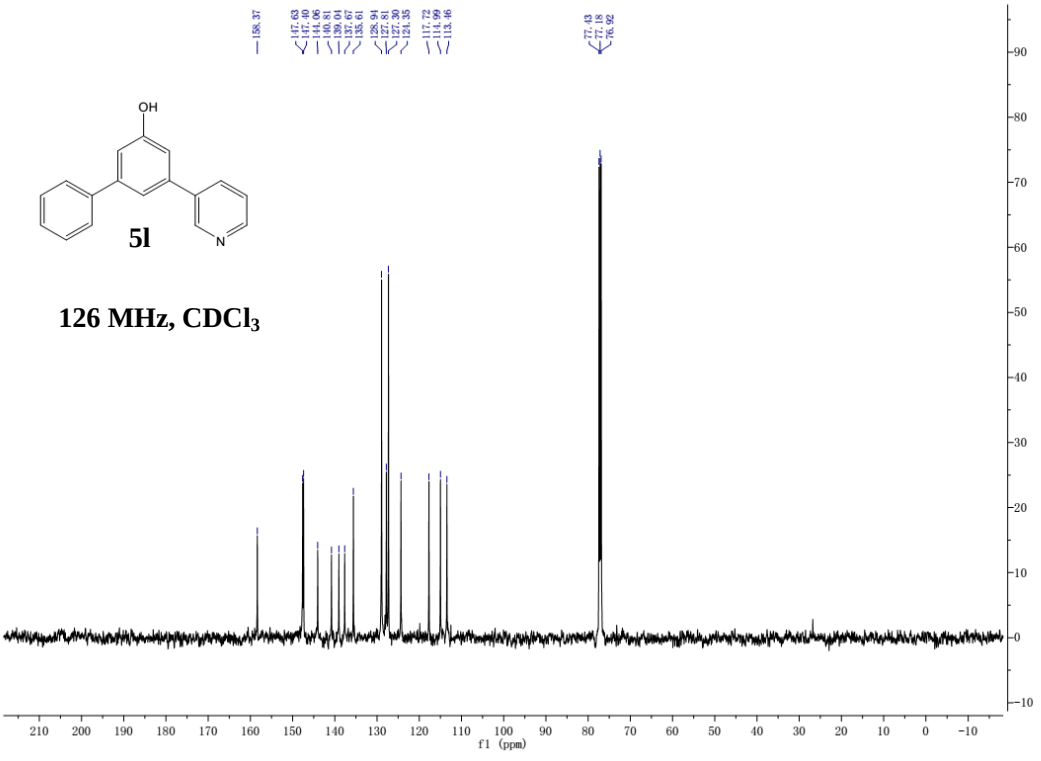

500 MHz, CDCl3
OH
F
F
F
5j
f1 (ppm)

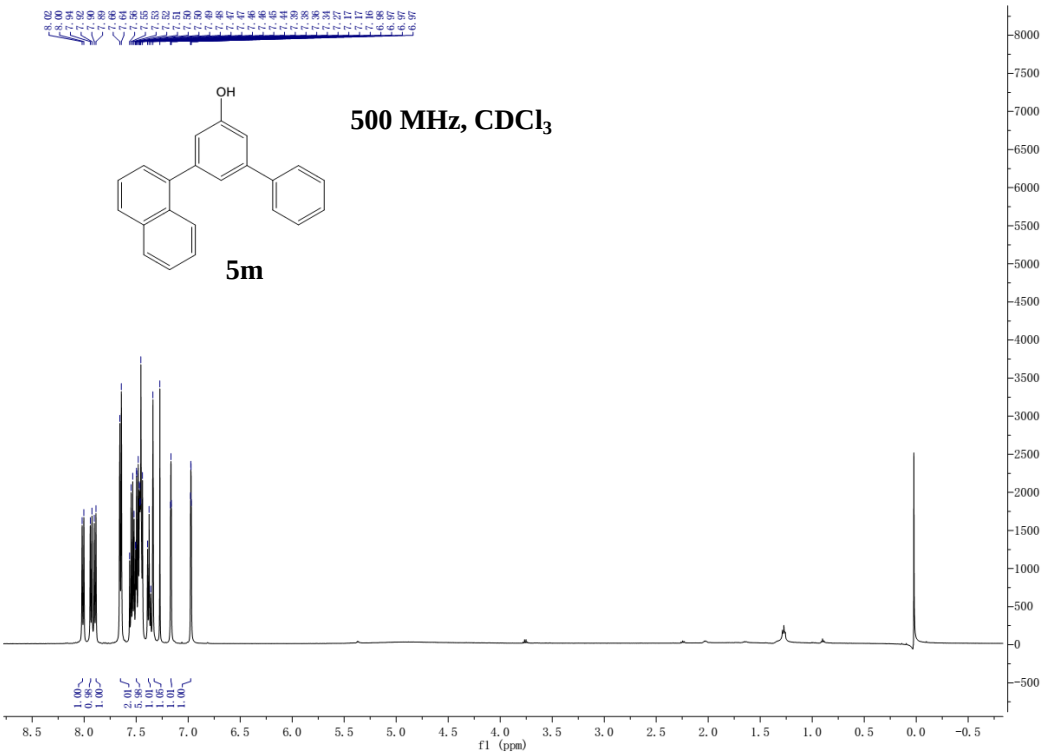

OH
F
F
F
5j
126 MHz, CDCl3
f1 (ppm)

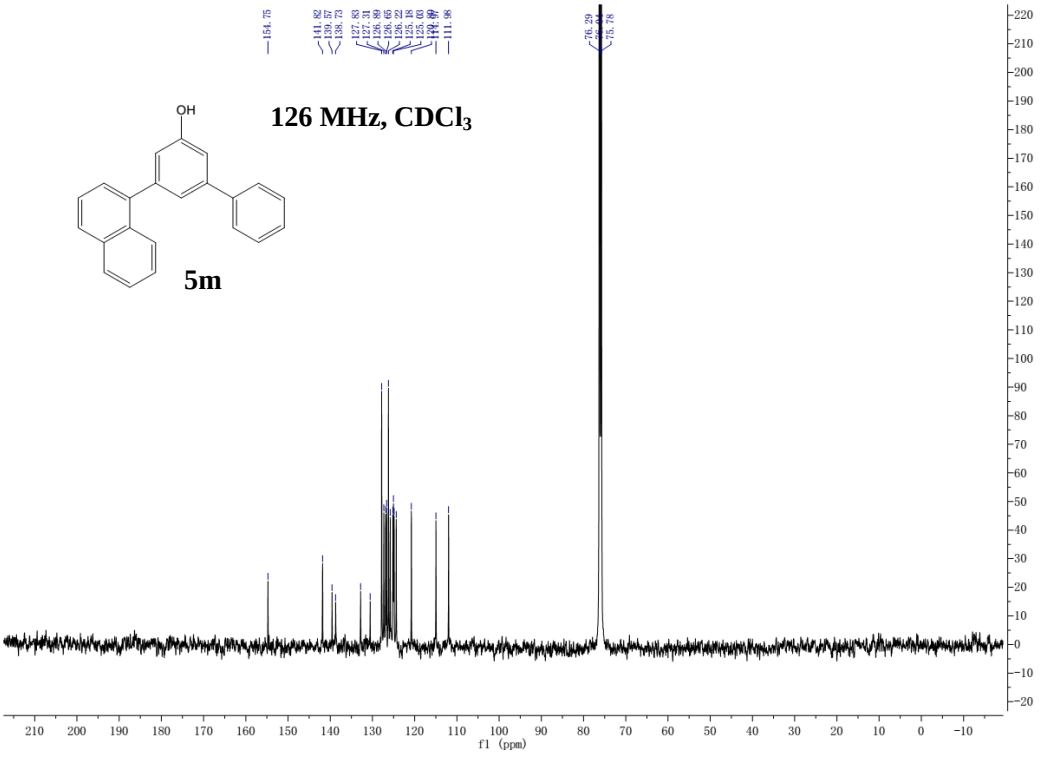

500 MHz, CDCl3
OH
F
F
F
5k
f1 (ppm)

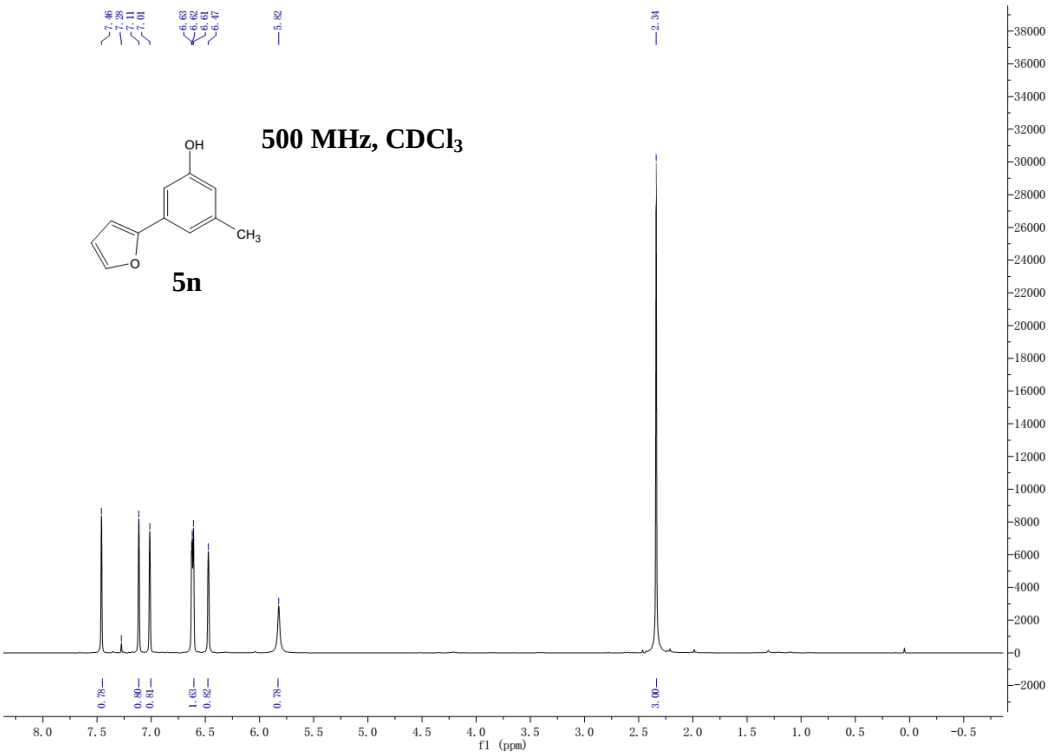

OH
F
F
F
5k
126 MHz, CDCl3
f1 (ppm)

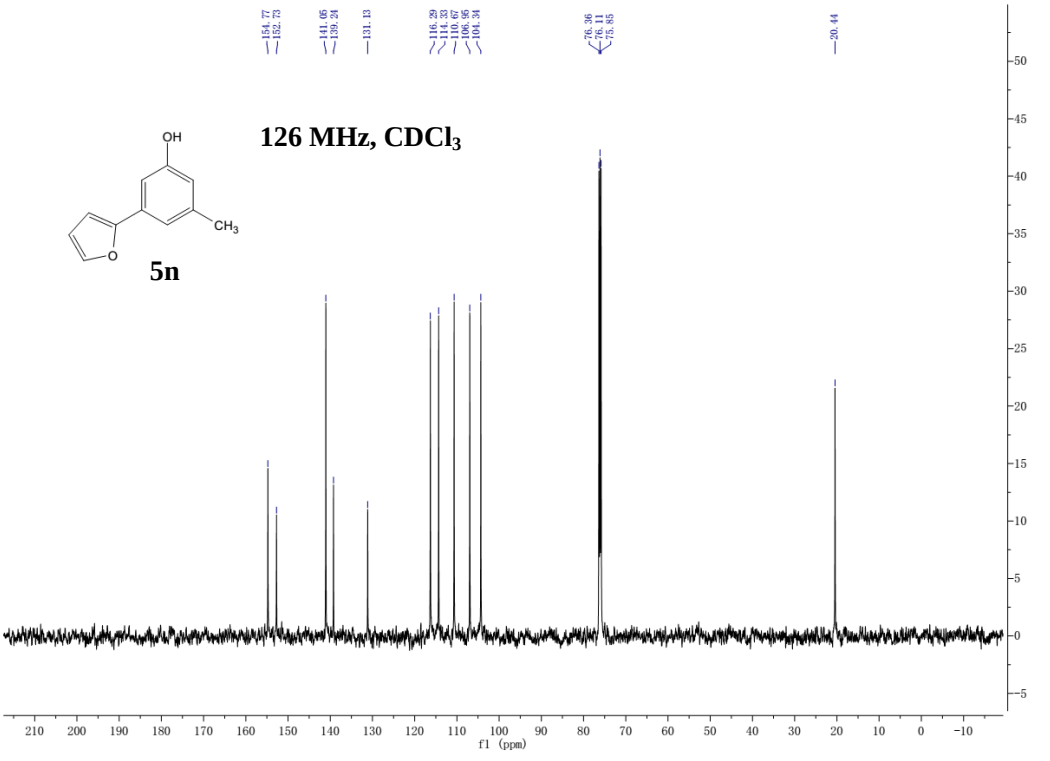

OH
N
5l
500 MHz, CDCl3
f1 (ppm)

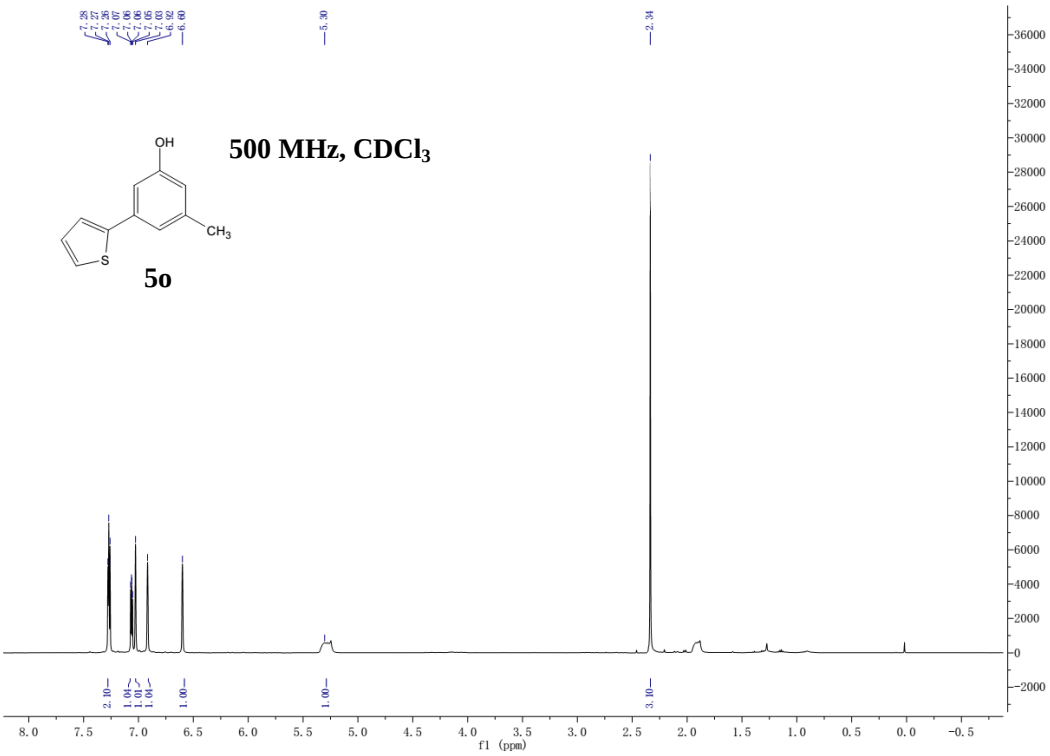

OH
N
5l
126 MHz, CDCl3
f1 (ppm)

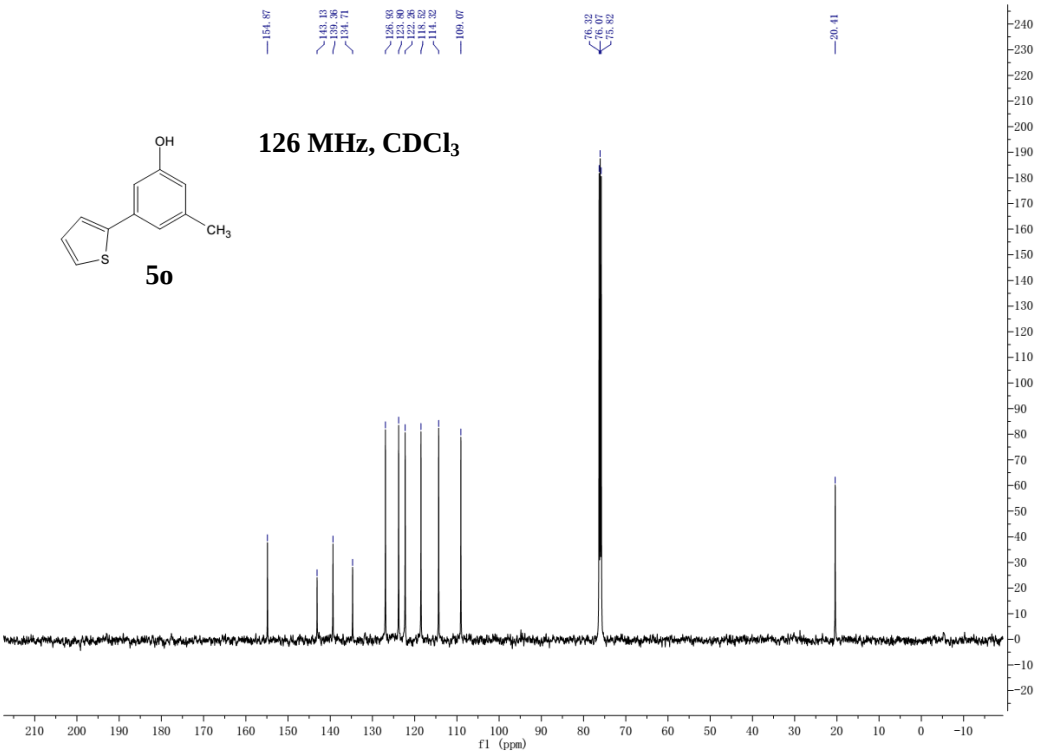

OH
500 MHz, CDCl3
5m
f1 (ppm)

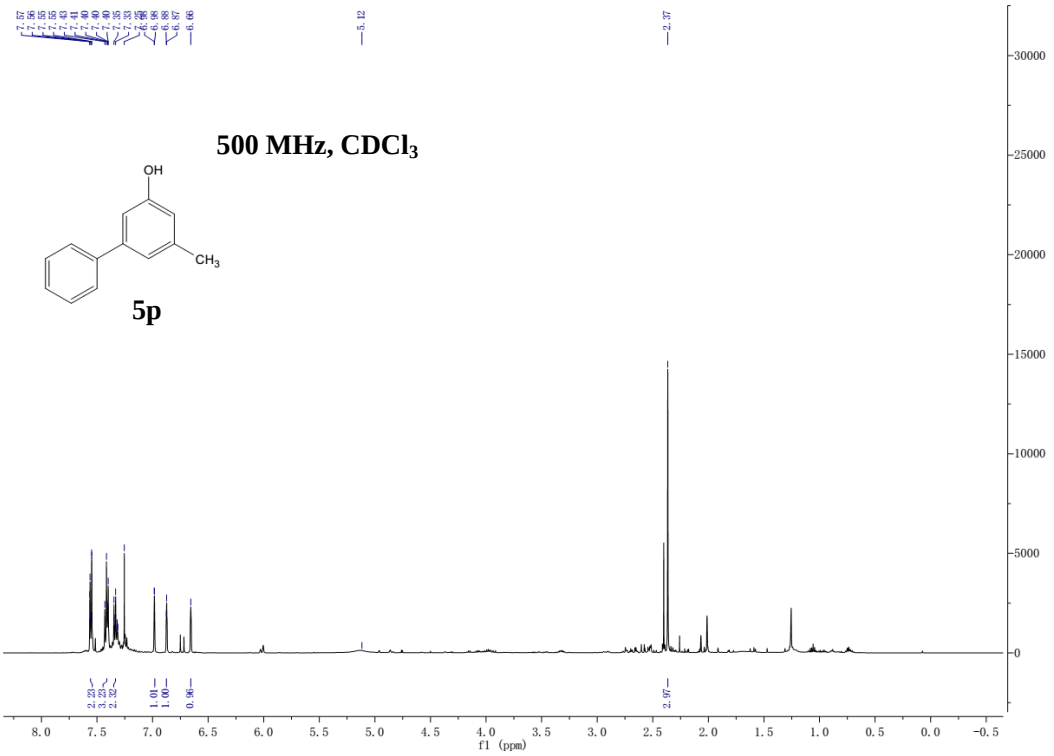

OH
126 MHz, CDCl3
5m
f1 (ppm)

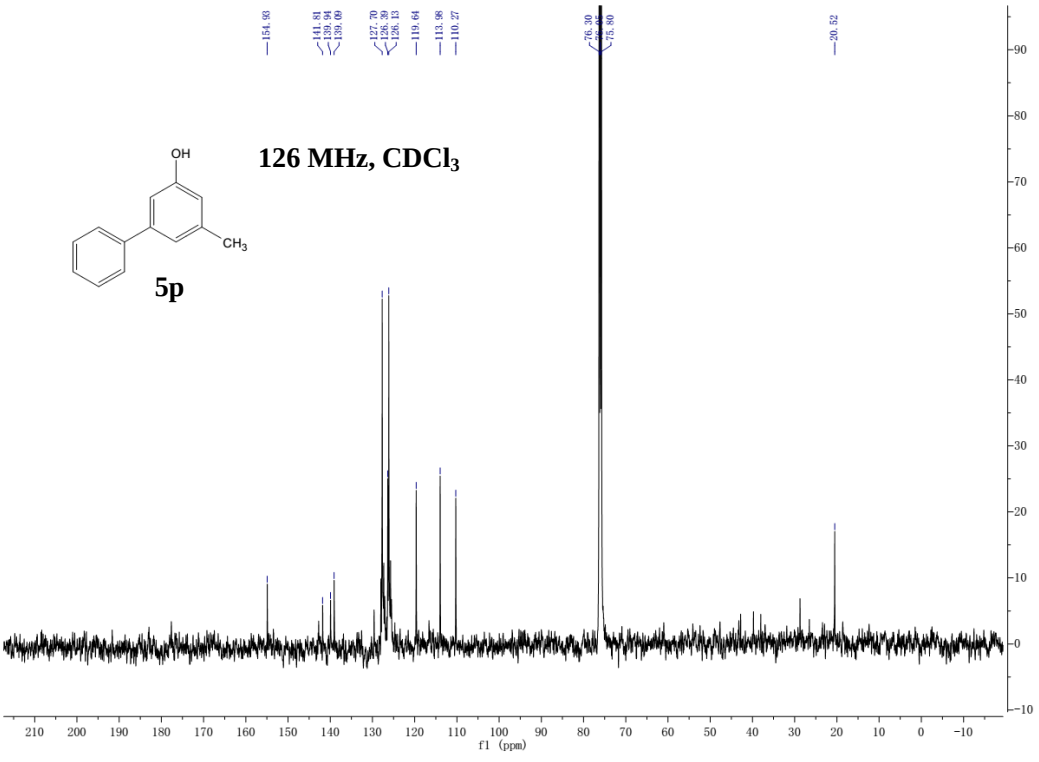

7.46
7.28
7.11
7.01
6.63
6.62
6.61
6.47
5.82
2.34
500 MHz, CDCl3
OH
CH3
O
5n
0.78
0.80
0.81
1.63
0.82
0.78
3.00
f1 (ppm)


154.77
152.73
141.05
139.24
131.13
116.29
114.33
110.67
106.95
104.34
76.36
76.11
75.85
20.44
126 MHz, CDCl3
OH
CH3
O
5n
f1 (ppm)

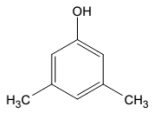

7.28
7.27
7.26
7.25
7.07
7.06
7.05
7.05
7.03
6.92
6.60
5.30
2.34
OH
CH3
S
500 MHz, CDCl3
5o
2.10
1.04
1.01
1.04
1.00
1.00
3.10
f1 (ppm)


154.87
143.13
139.36
134.71
126.93
123.80
122.26
118.32
114.32
109.07
76.32
76.07
75.82
20.41
OH
CH3
S
126 MHz, CDCl3
5o
f1 (ppm)


500 MHz, CDCl3
OH
CH3
5p
f1 (ppm)

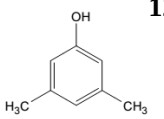

126 MHz, CDCl3
OH
CH3
5p
f1 (ppm)

500 MHz, $CDCl_3$

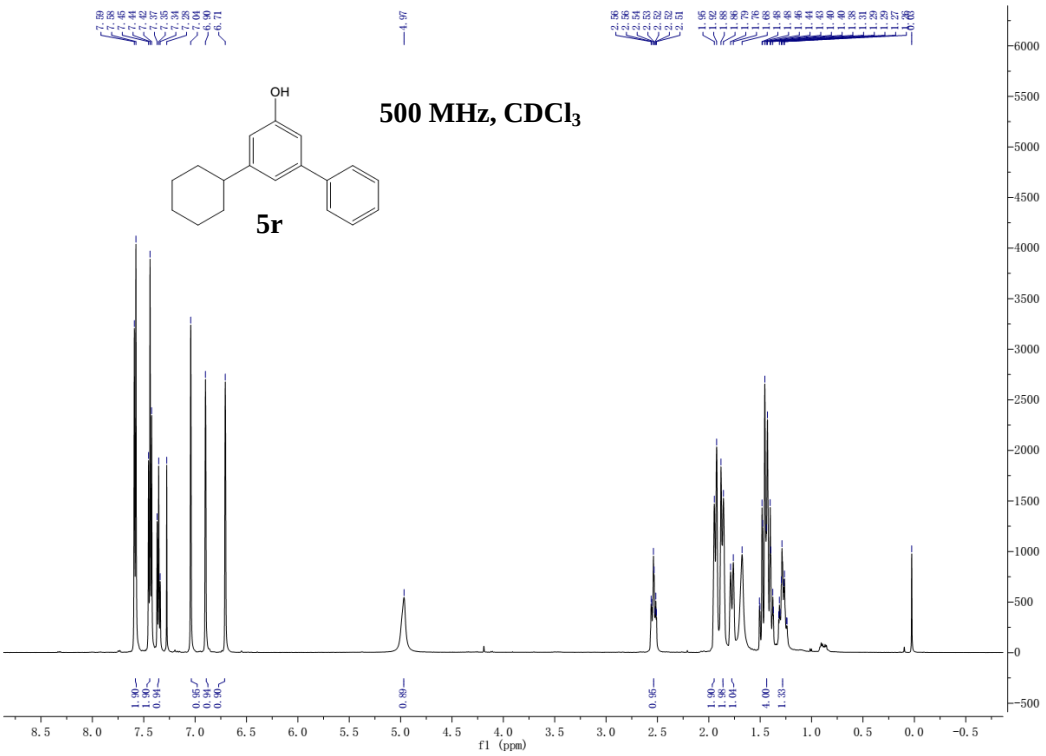


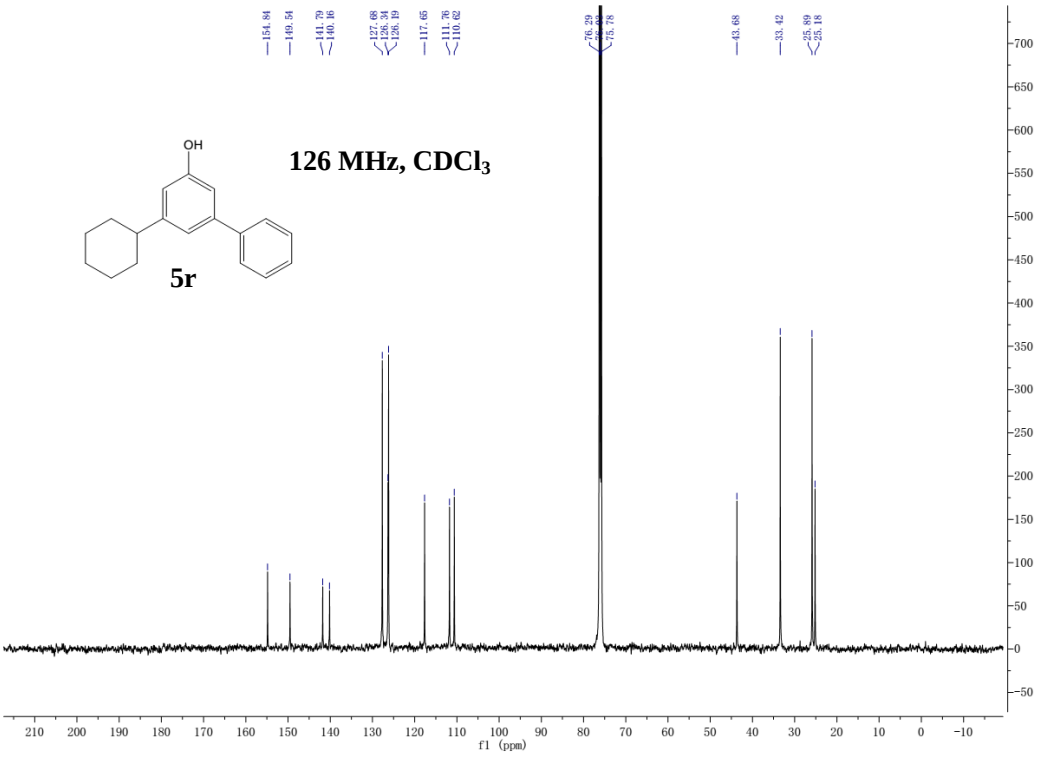
5q

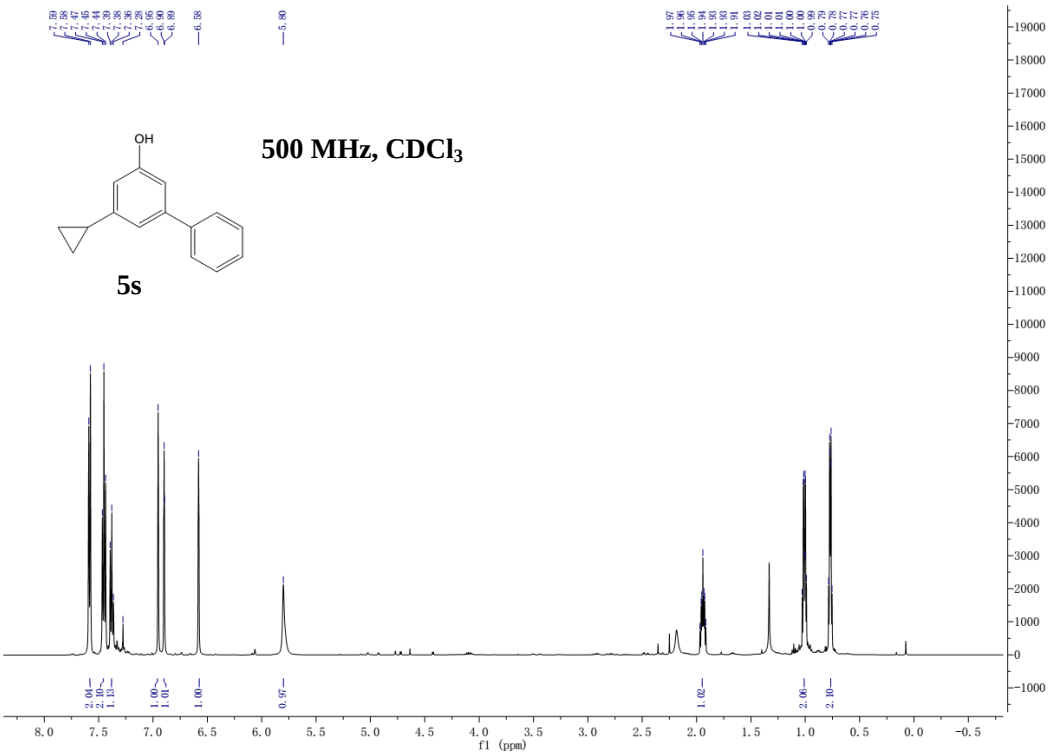
126 MHz, $CDCl_3$

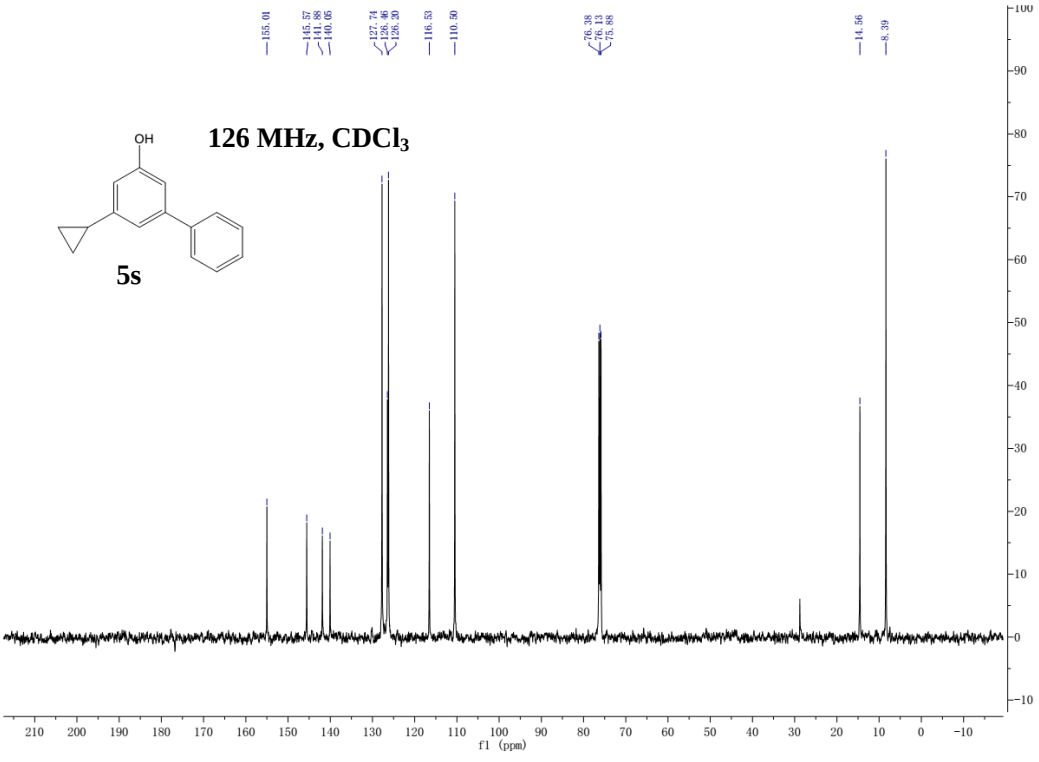


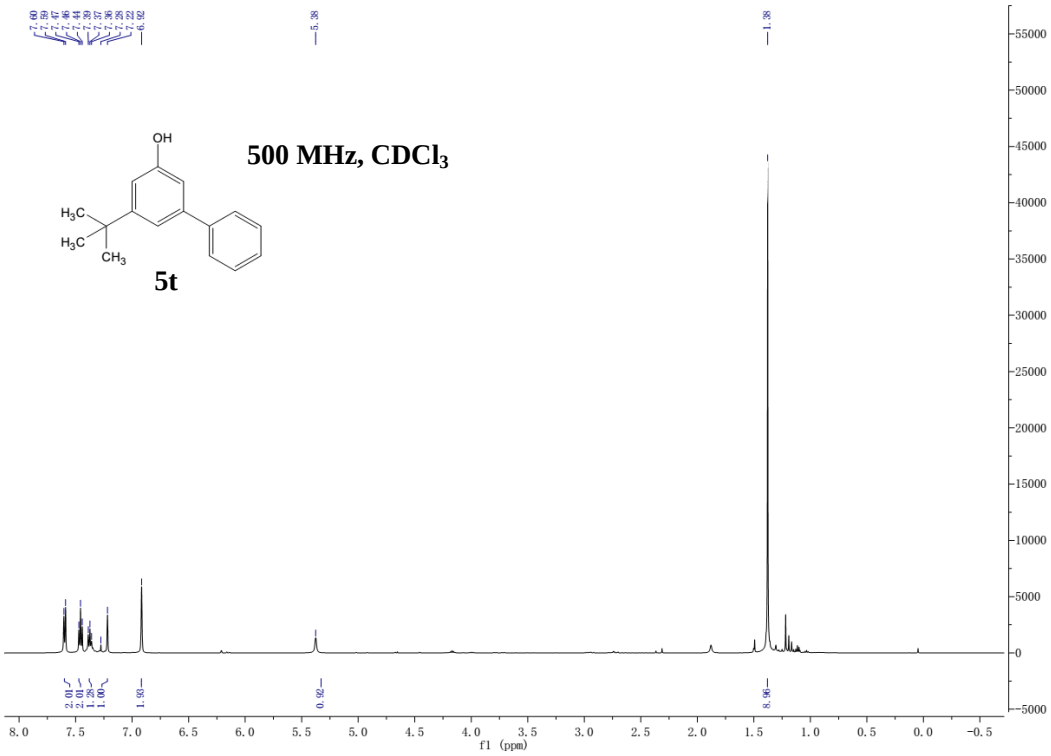
5q

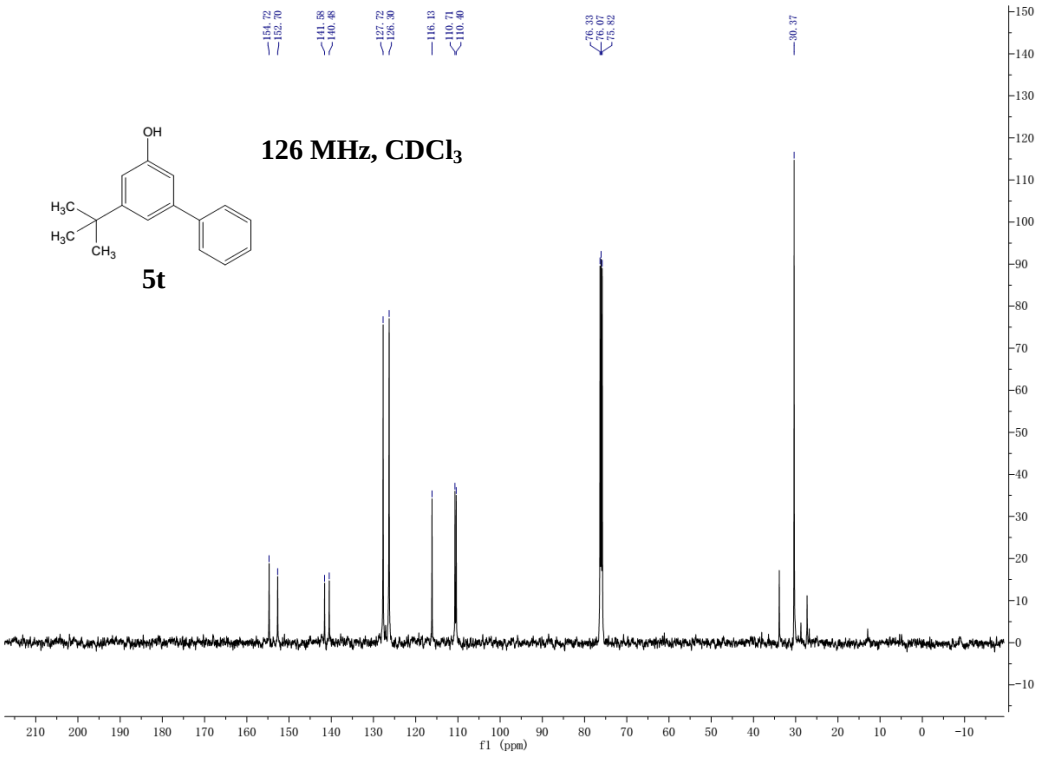

500 MHz, CDCl3
OH
5r
f1 (ppm)

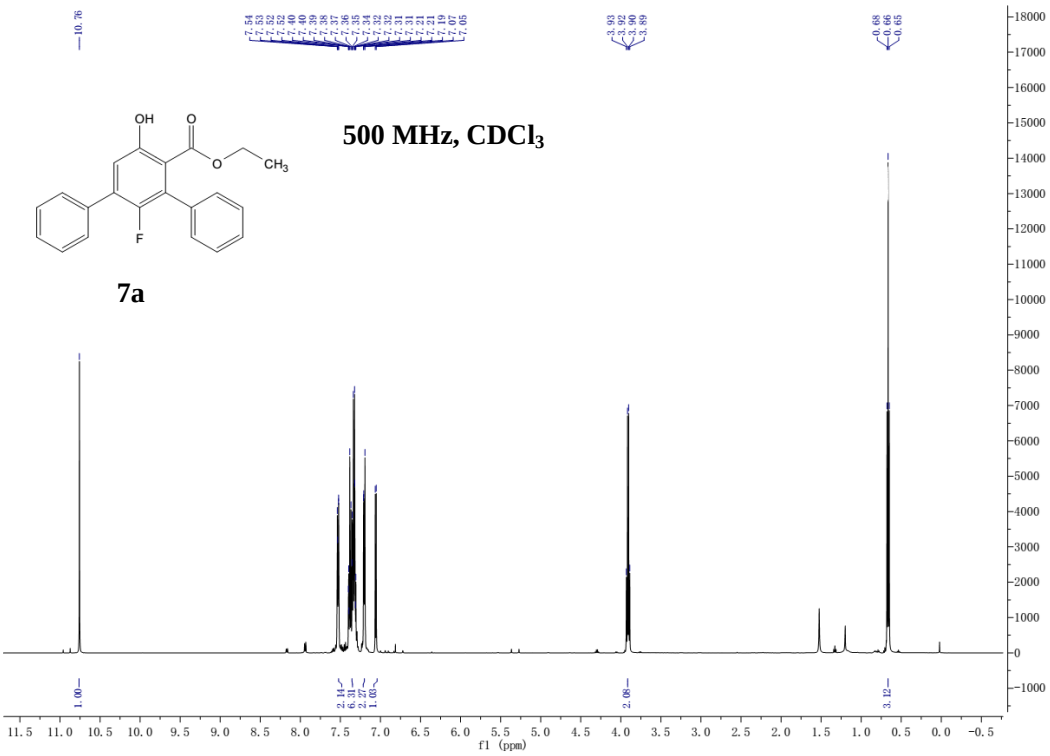

126 MHz, CDCl3
OH
5r
f1 (ppm)

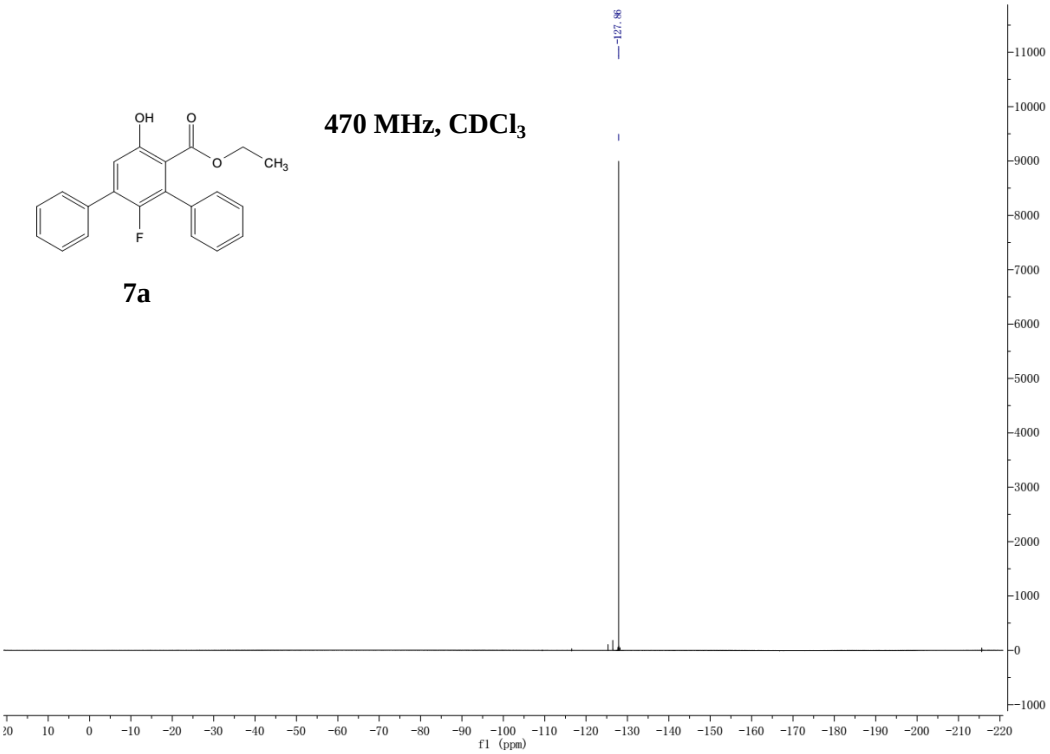

OH
500 MHz, CDCl3
5s
f1 (ppm)

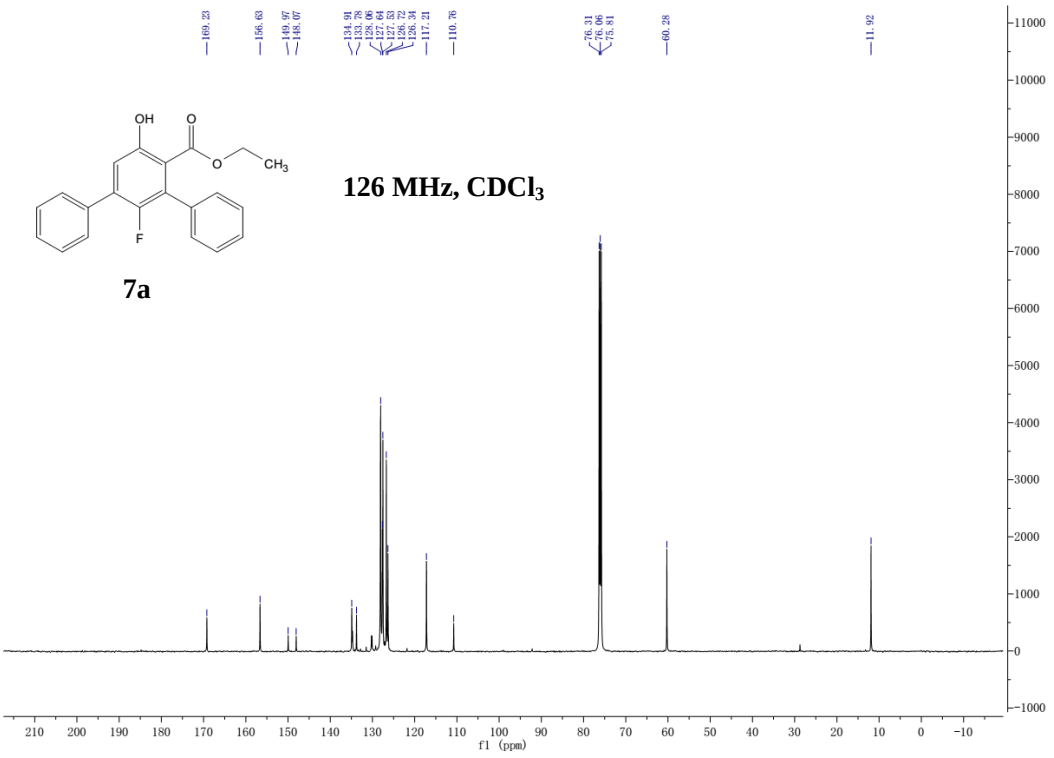

OH
126 MHz, CDCl3
5s
f1 (ppm)


500 MHz, CDCl3
OH
H3C
H3C
CH3
5t
f1 (ppm)

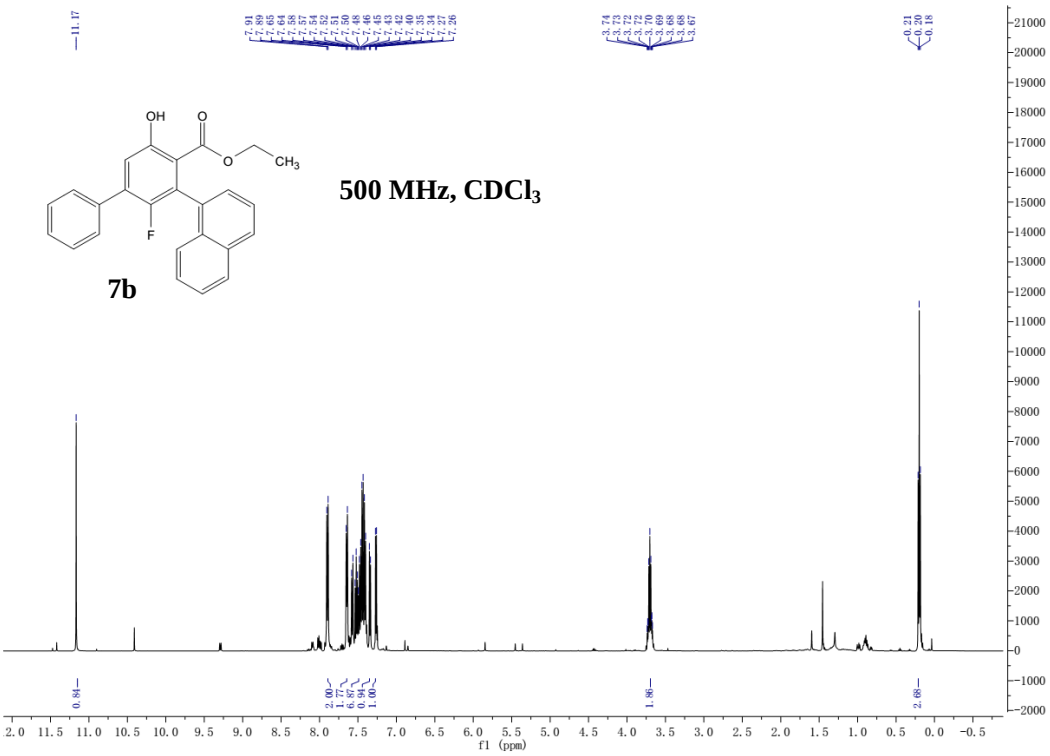

126 MHz, CDCl3
OH
H3C
H3C
CH3
5t
f1 (ppm)

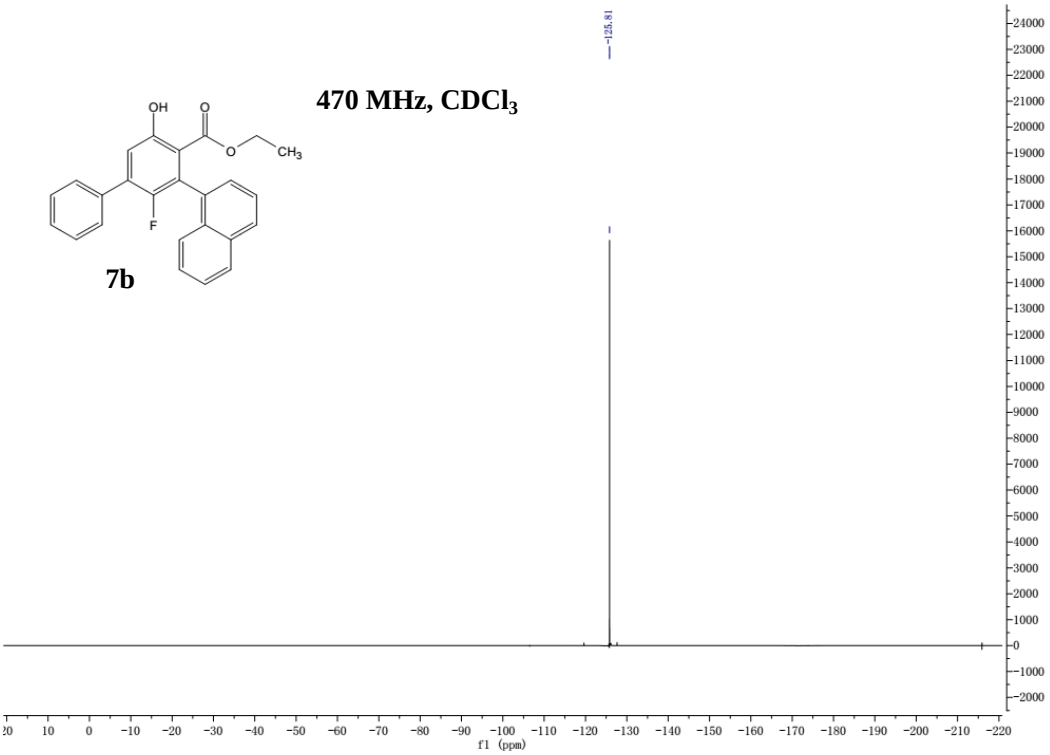

500 MHz, CDCl3
7a
f1 (ppm)

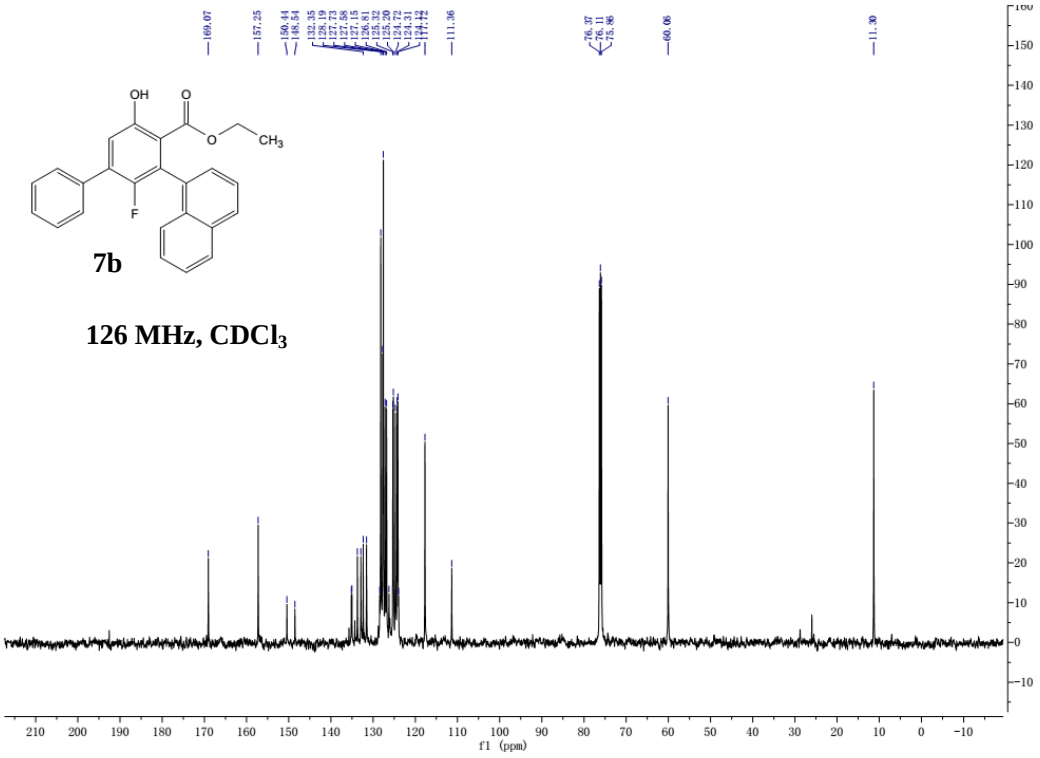

470 MHz, CDCl3
7a
f1 (ppm)

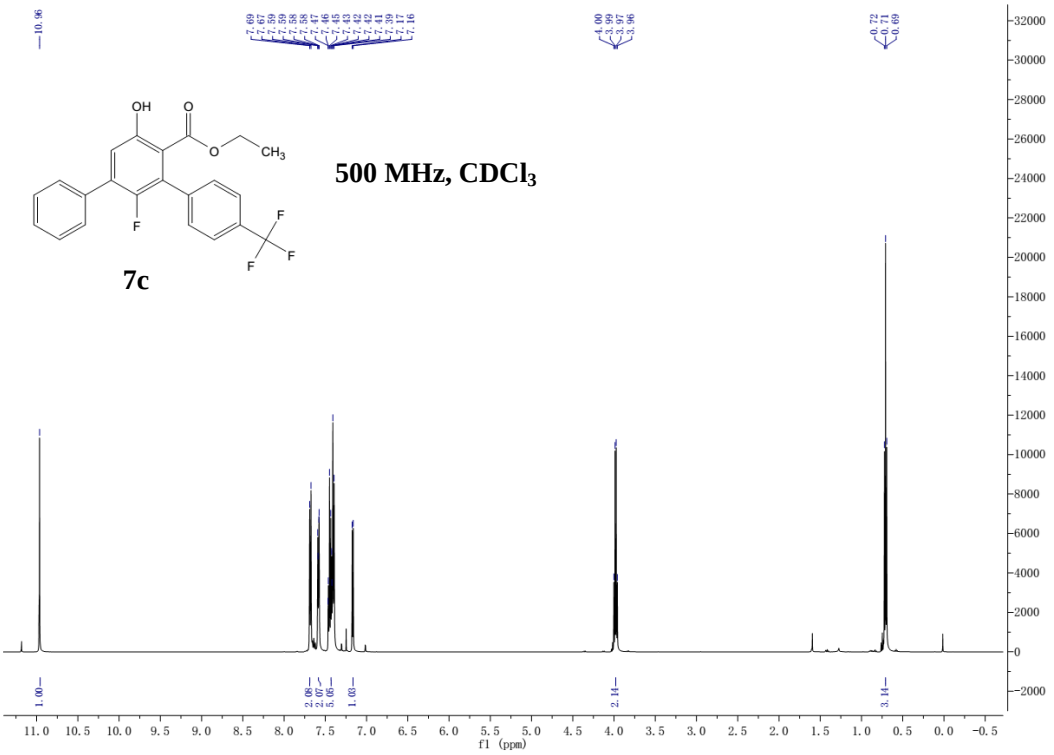

169.23
156.63
149.97
148.07
134.91
133.78
128.06
127.64
127.53
127.22
126.34
117.21
110.76
76.31
76.06
75.81
60.28
11.92
OH
O
O
CH3
F
126 MHz, CDCl3
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7a


OH
O
O
CH3
F
7b
500 MHz, CDCl3
f1 (ppm)

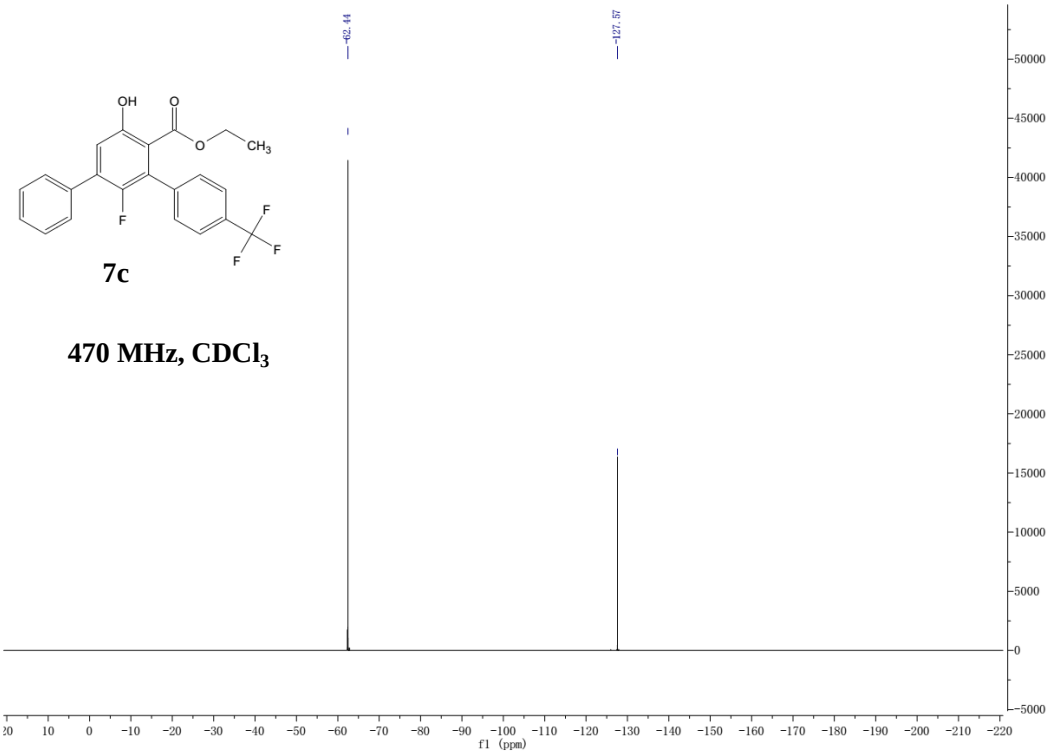

OH
O
O
CH3
F
7b
470 MHz, CDCl3
-125.81
f1 (ppm)


OH
O
O
CH3
F
7b
126 MHz, CDCl3
169.07
157.25
150.44
146.54
132.35
129.19
127.73
127.58
127.15
126.81
125.32
125.29
124.72
124.31
111.36
76.37
76.11
75.86
60.06
11.30
f1 (ppm)



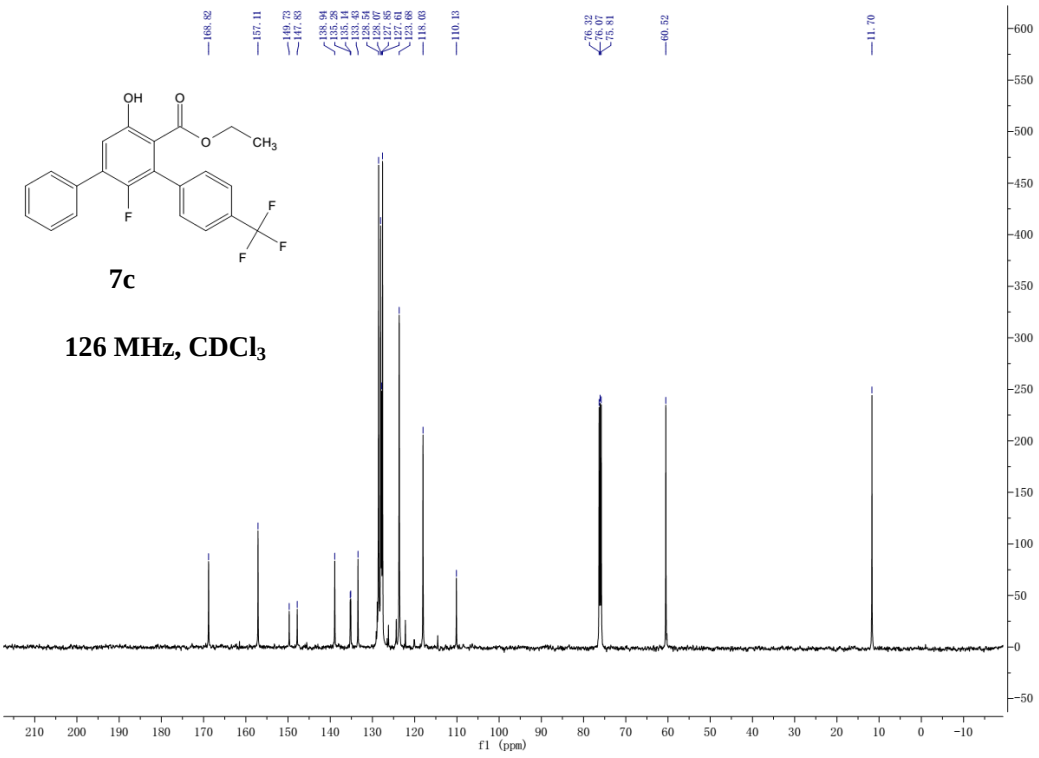
7c

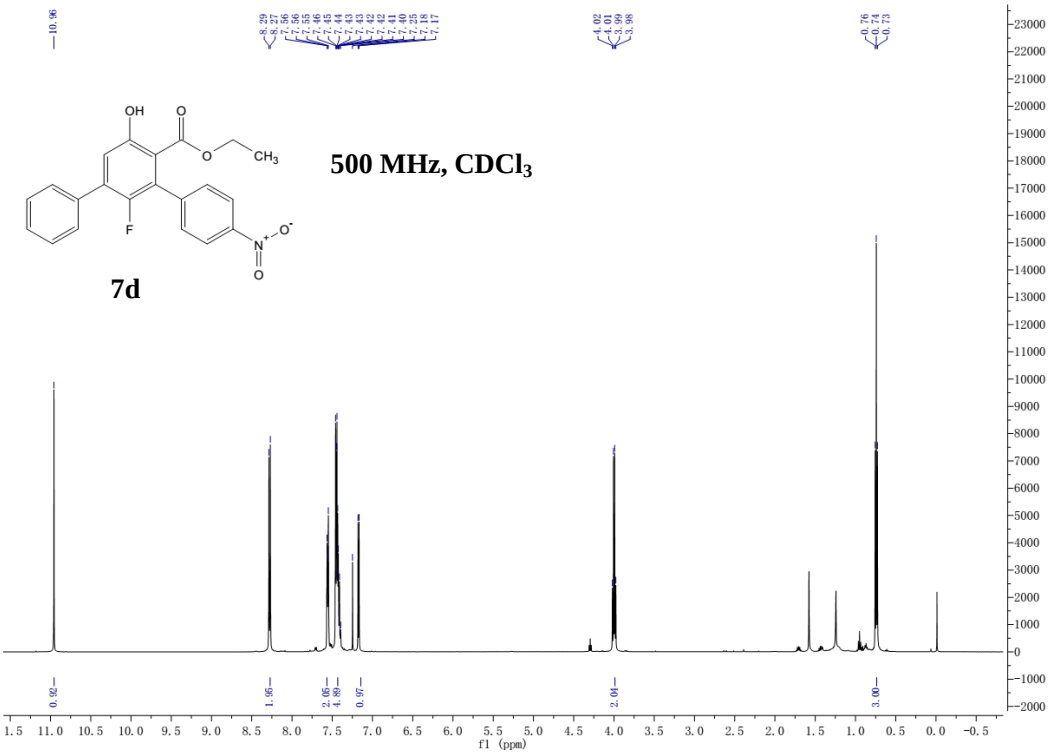
500 MHz, $CDCl_3$



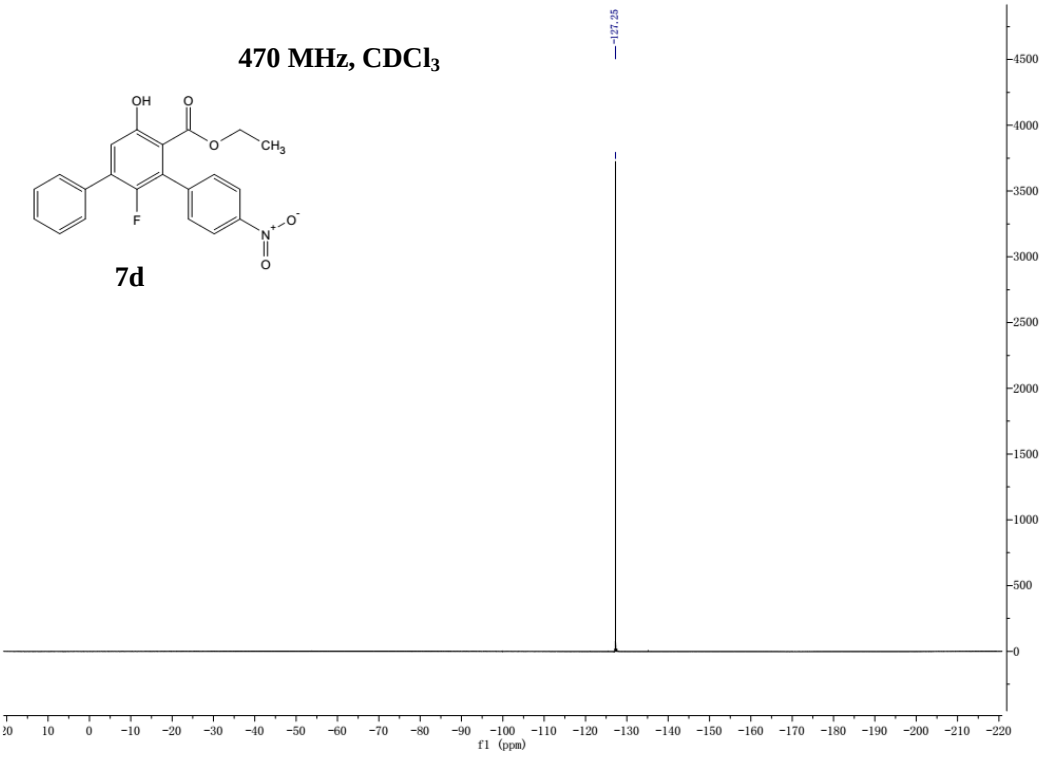
7c

470 MHz, $CDCl_3$

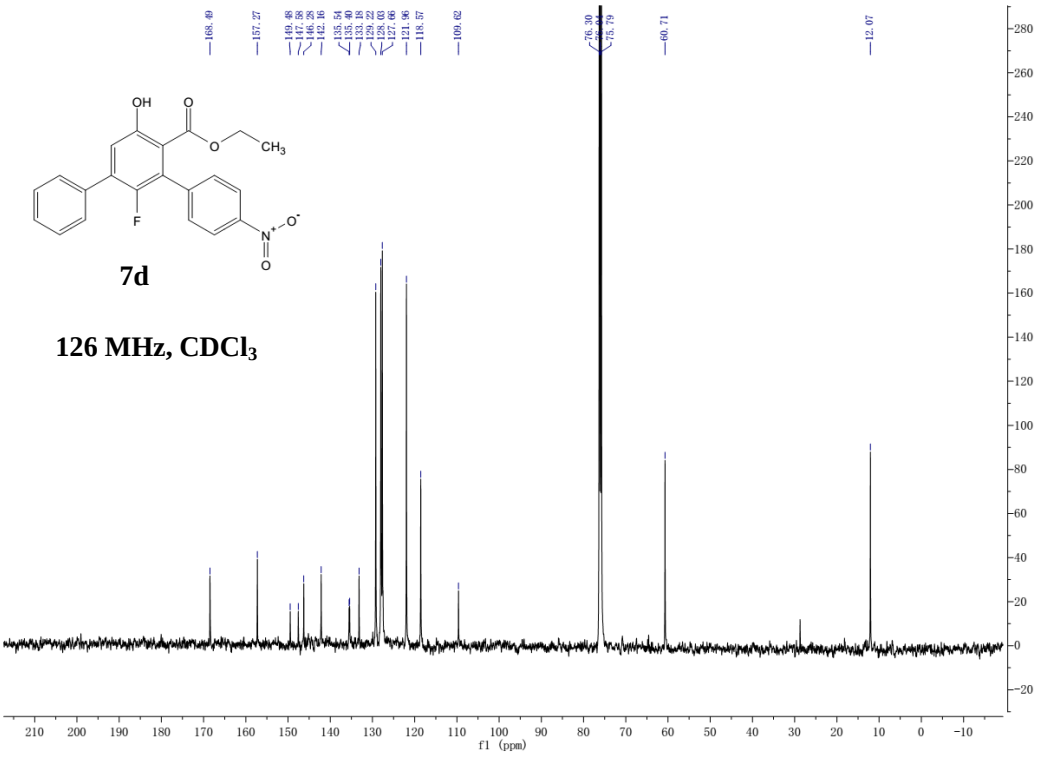

168.82
157.11
149.73
147.83
138.94
135.28
133.14
133.43
128.54
128.07
127.95
127.61
123.68
118.03
110.13
76.32
76.07
75.81
60.52
11.70
OH
O
O
CH3
F
F
F
F
7c
126 MHz, CDCl3
f1 (ppm)

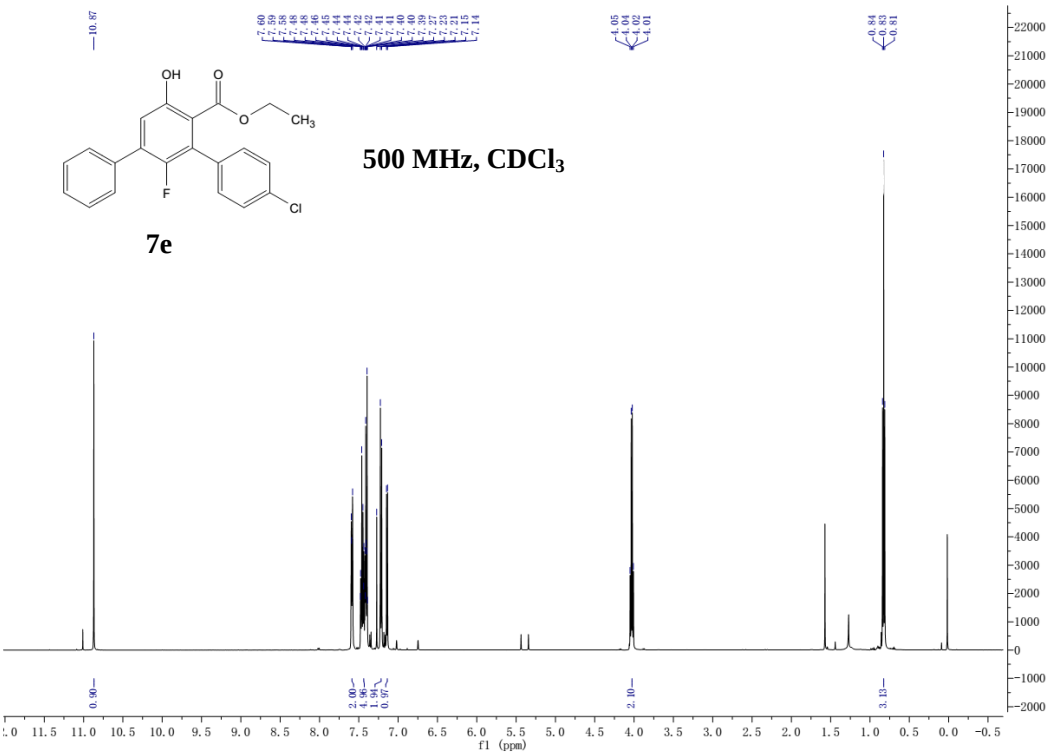

10.96
8.29
8.27
7.56
7.56
7.55
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.25
7.18
7.17
4.02
4.01
3.99
3.98
0.76
0.74
0.73
OH
O
O
CH3
F
N+
O-
O
500 MHz, CDCl3
0.92
1.95
2.05
4.89
0.97
2.04
3.00
f1 (ppm)

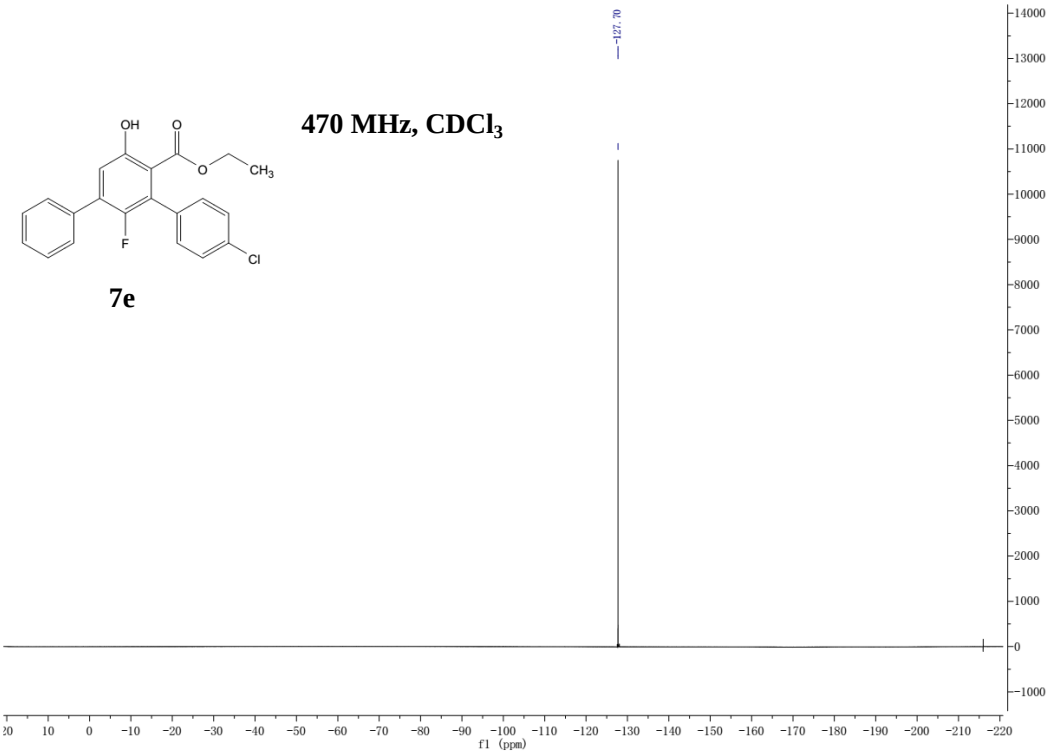
7d

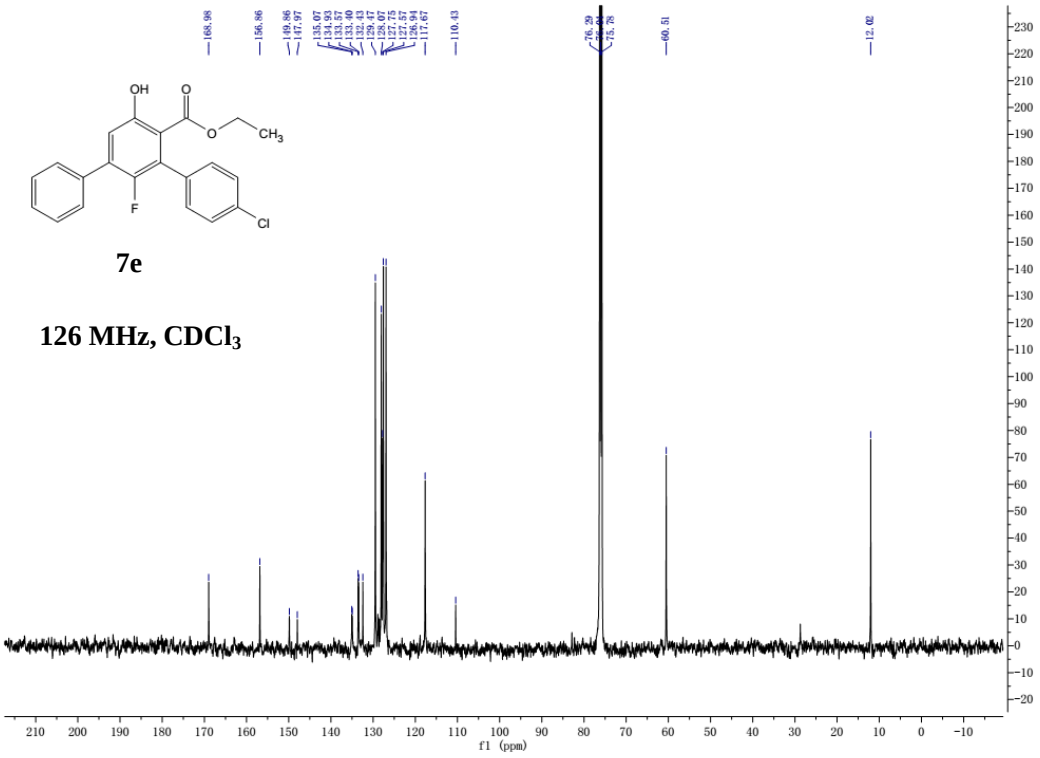

-127.25
470 MHz, CDCl3
OH
O
O
CH3
F
N+
O-
O
f1 (ppm)

7d


168.49
157.27
149.48
147.38
146.28
142.16
135.54
135.40
133.35
129.22
128.03
127.66
121.96
118.57
109.62
76.30
77.04
75.79
60.71
12.07
OH
O
O
CH3
F
N+
O-
O
7d
126 MHz, CDCl3
f1 (ppm)

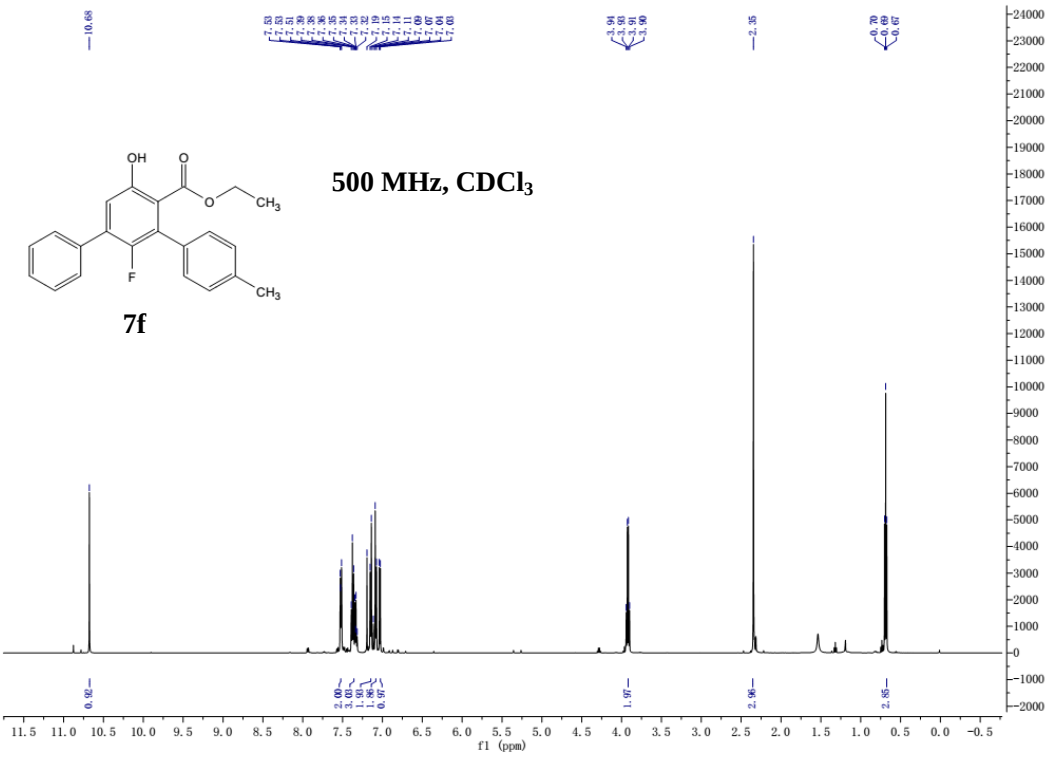

OH
O
O
CH3
F
Cl
500 MHz, CDCl3
7e
f1 (ppm)

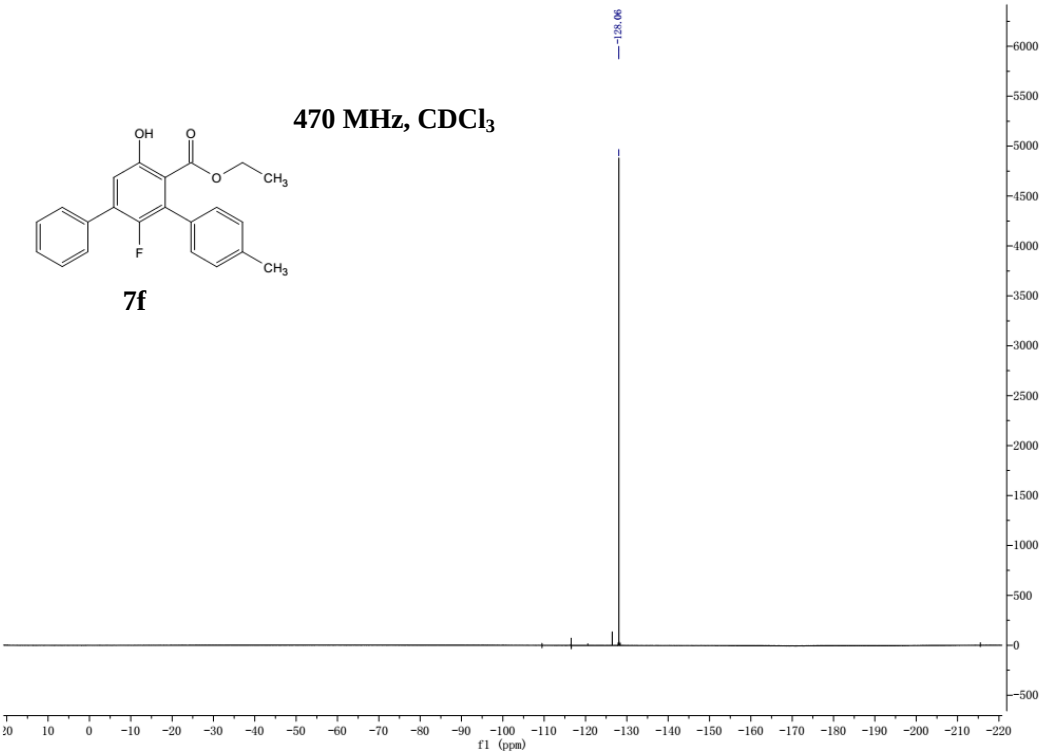

OH
O
O
CH3
F
Cl
470 MHz, CDCl3
7e
f1 (ppm)

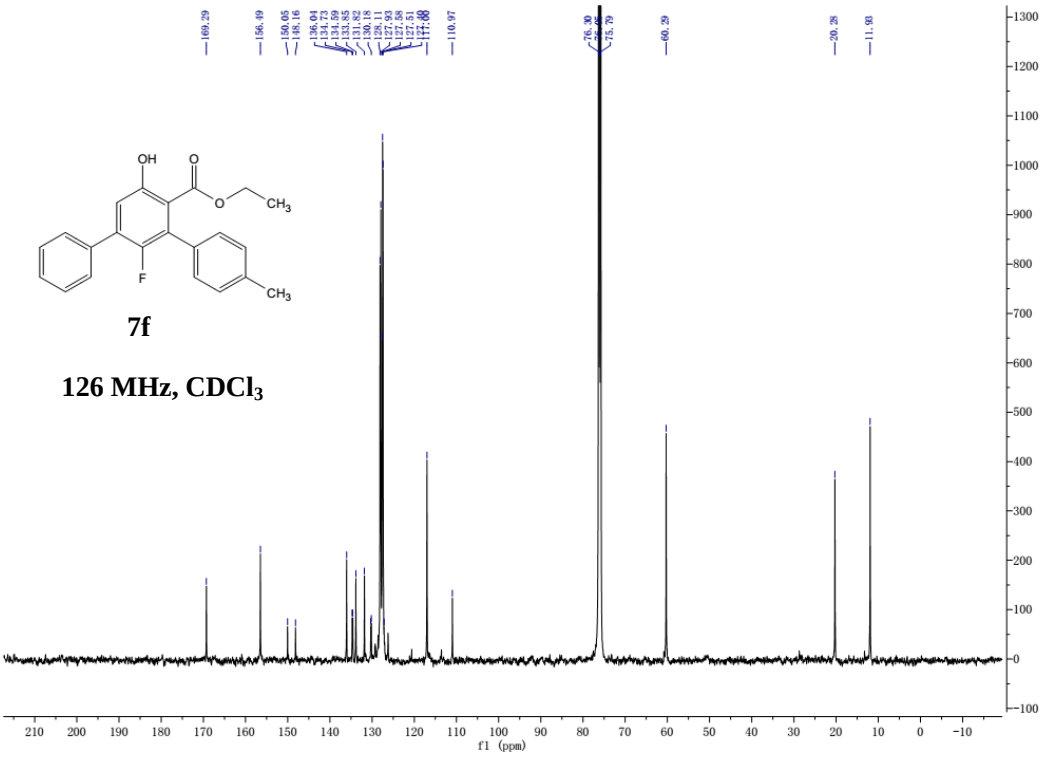


7e

126 MHz, $CDCl_3$

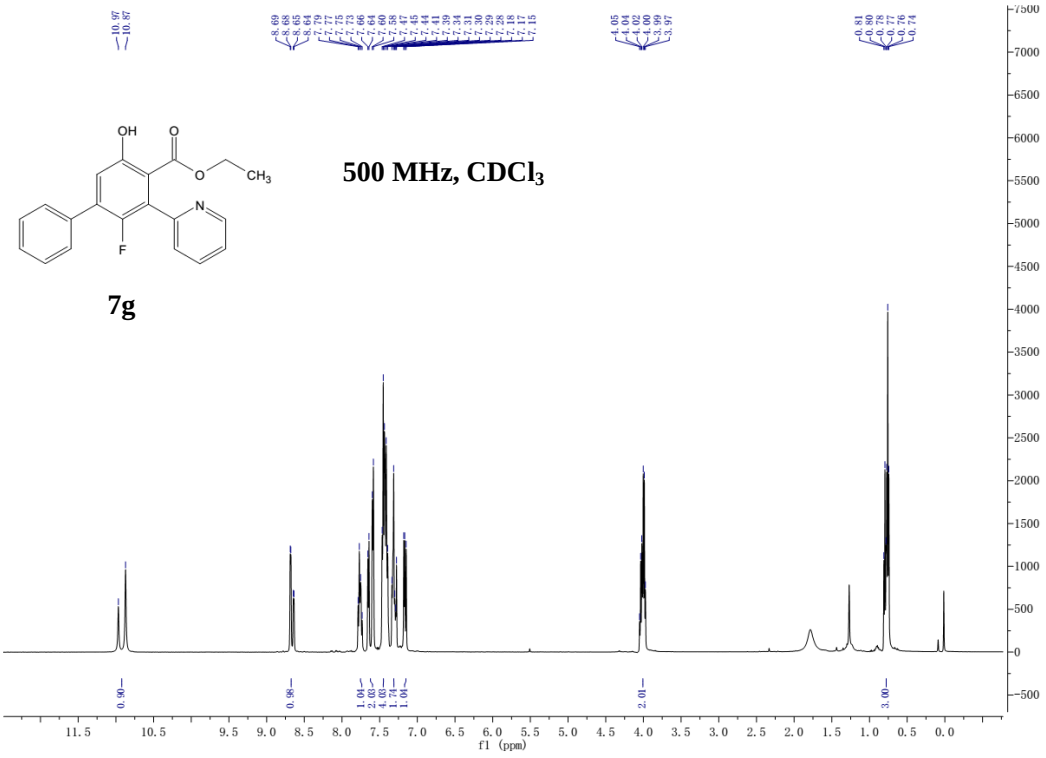

500 MHz, CDCl3
7f
f1 (ppm)


470 MHz, CDCl3
7f
f1 (ppm)



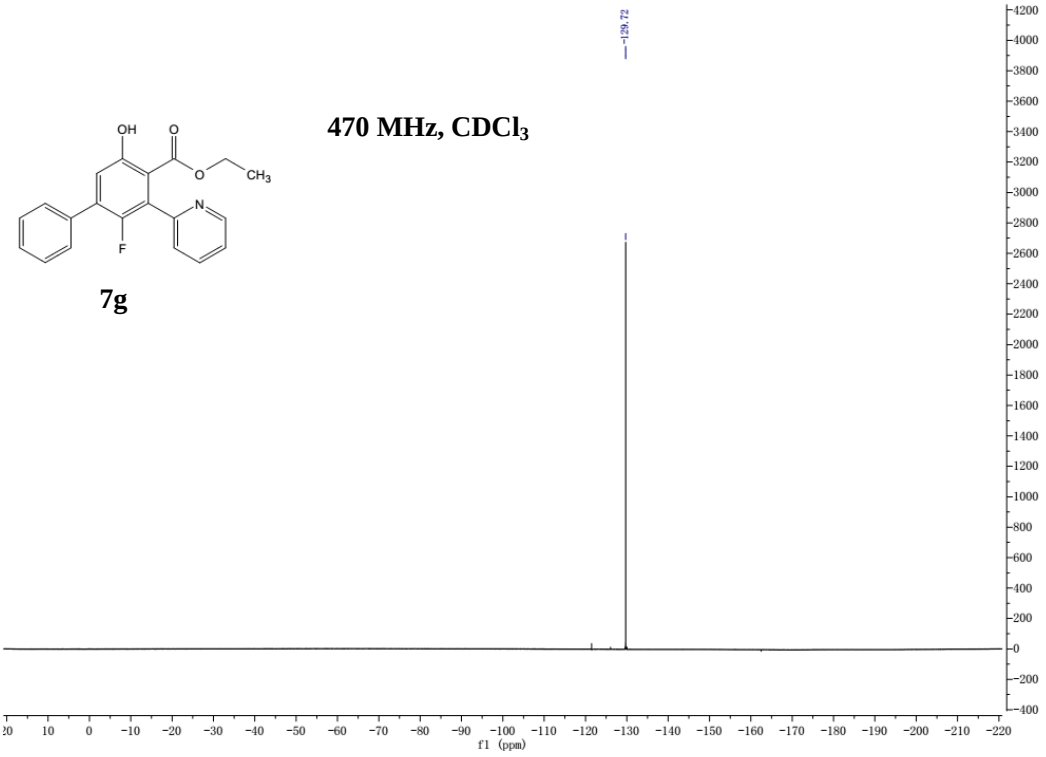
7f

126 MHz, $CDCl_3$



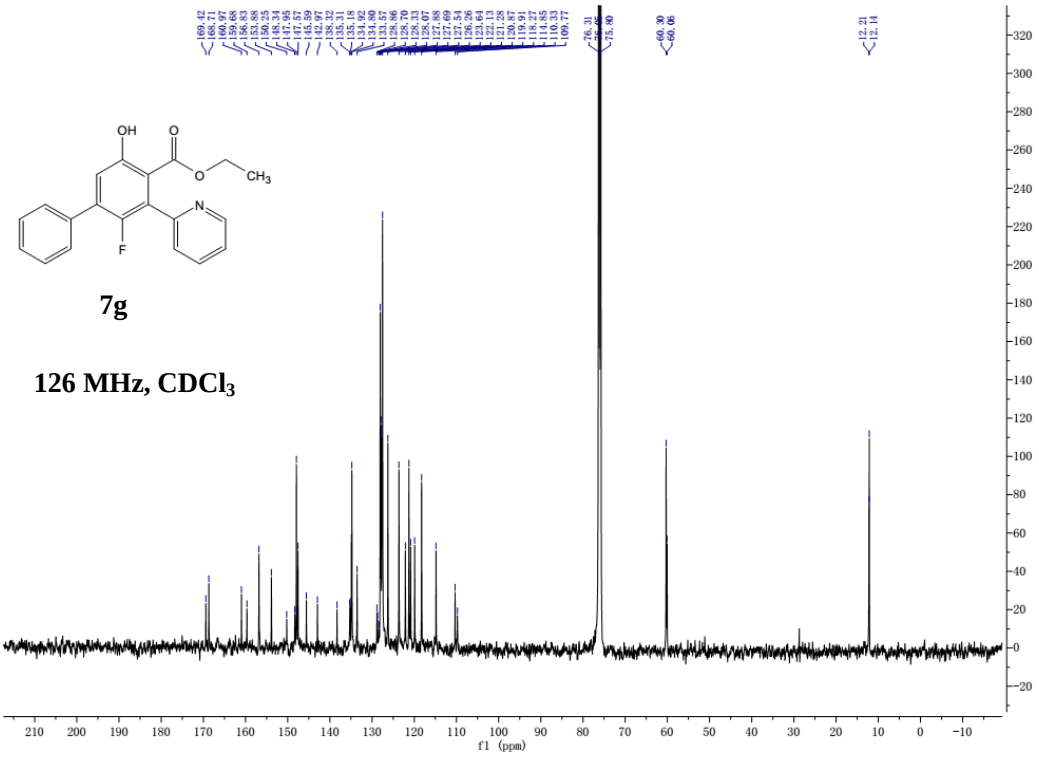
500 MHz, $CDCl_3$

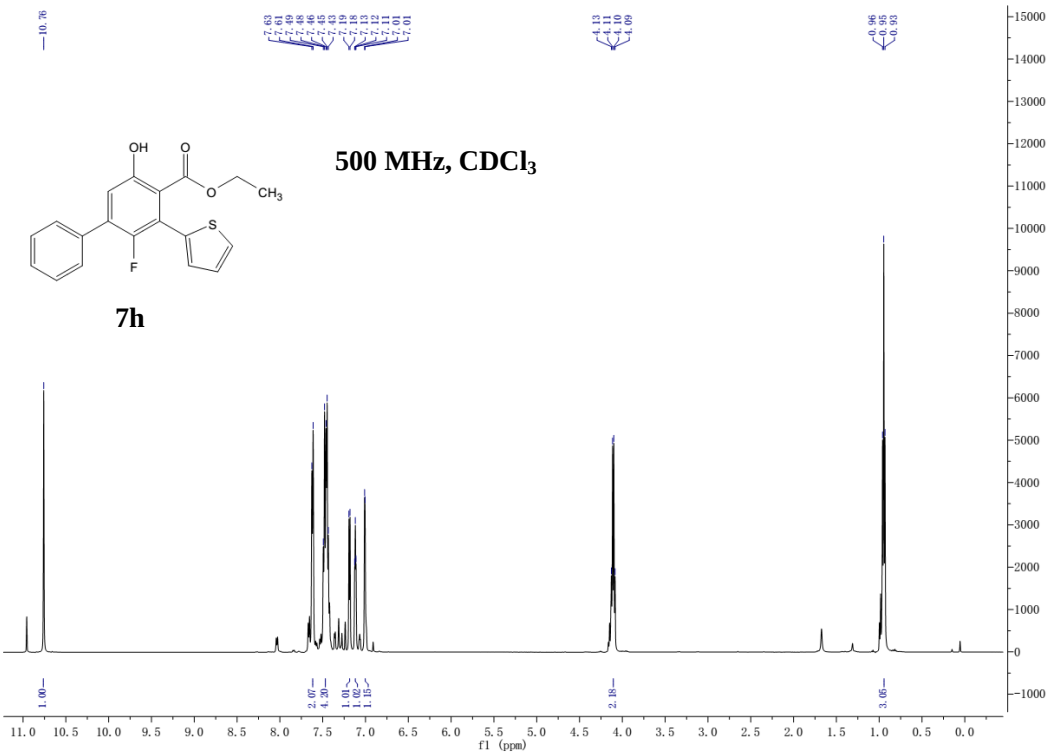
7g



470 MHz, $CDCl_3$

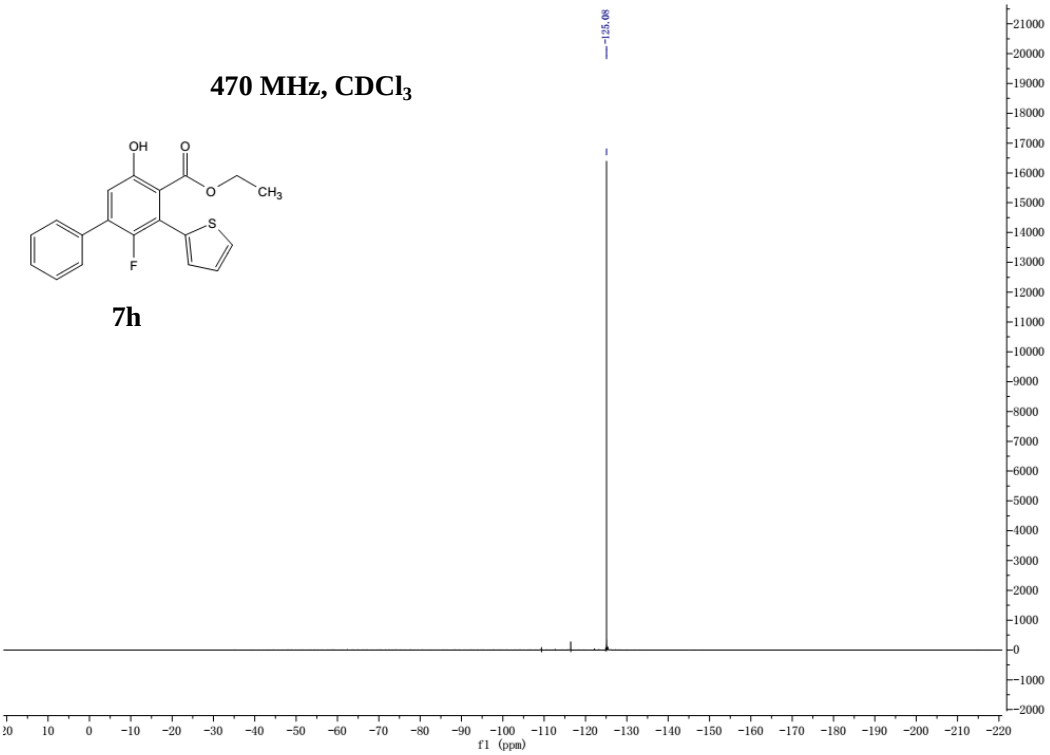
7g


OH
O
O
CH3
N
F
7g
126 MHz, CDCl3
f1 (ppm)



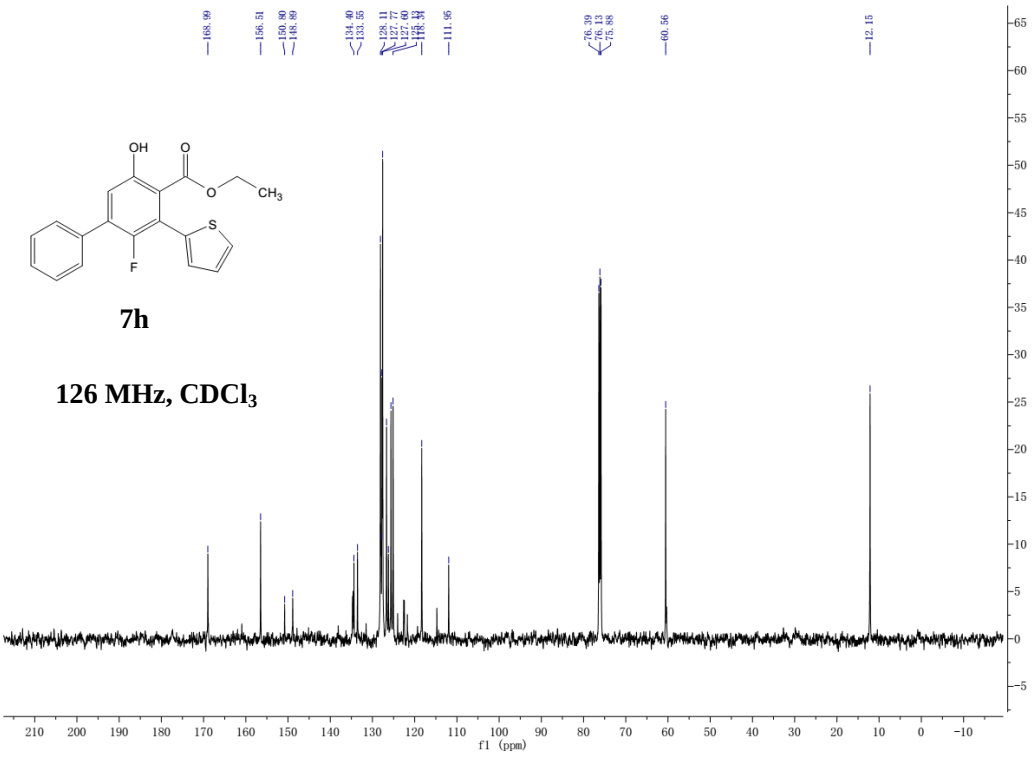
500 MHz, $CDCl_3$

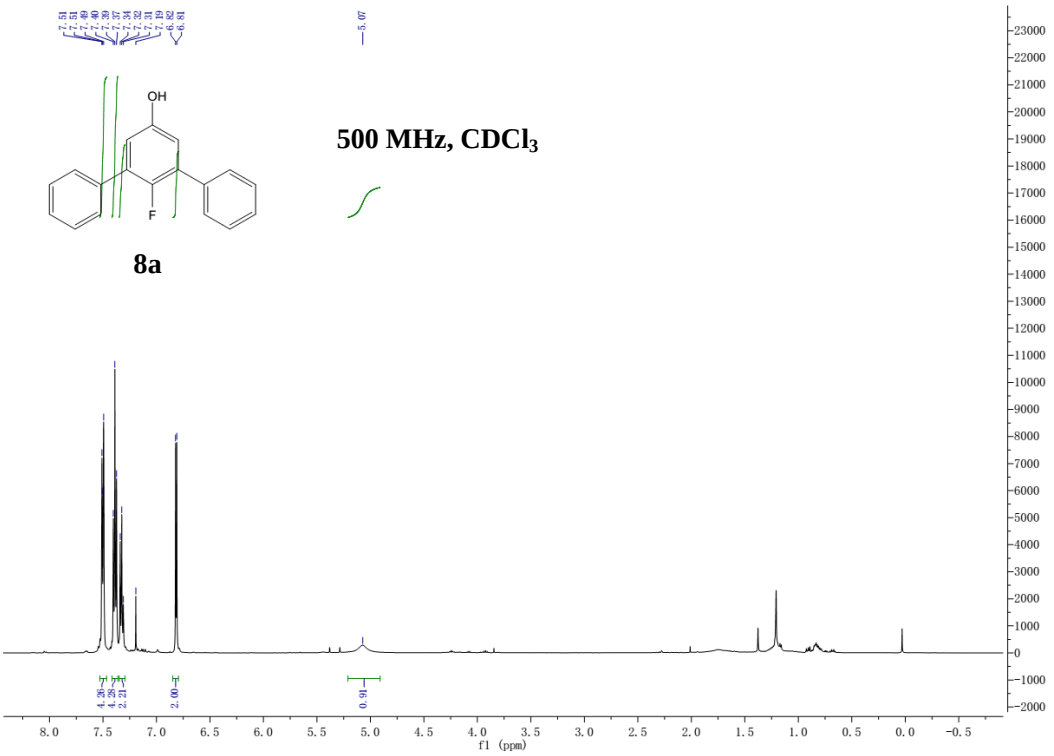
7h



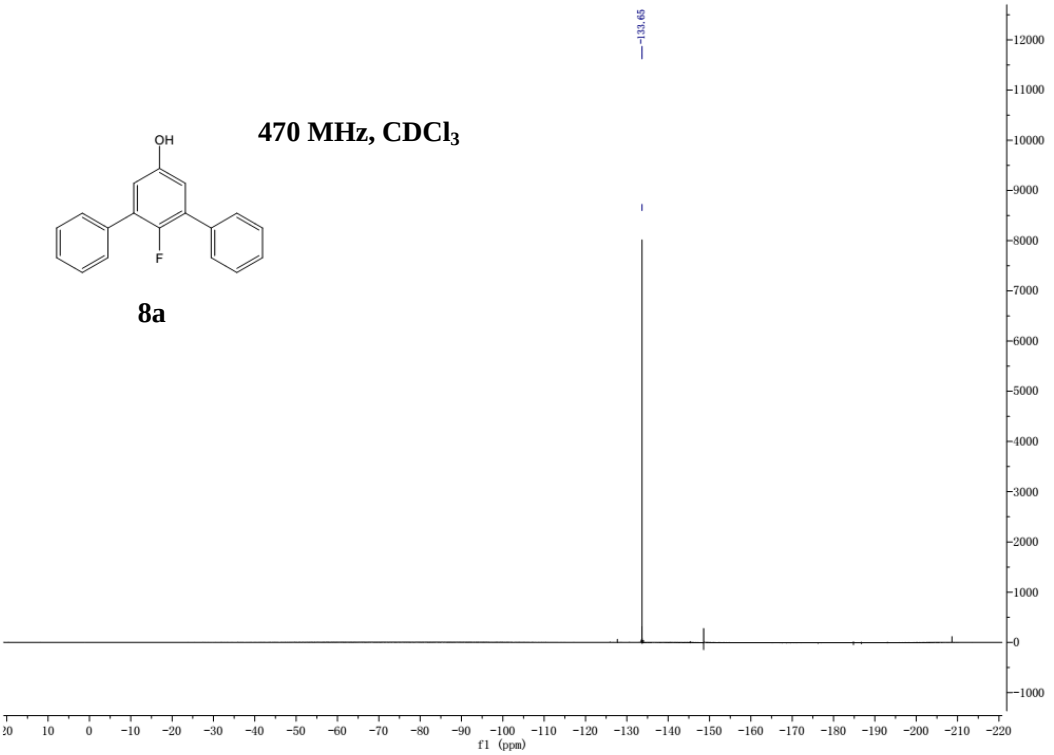
470 MHz, $CDCl_3$

7h

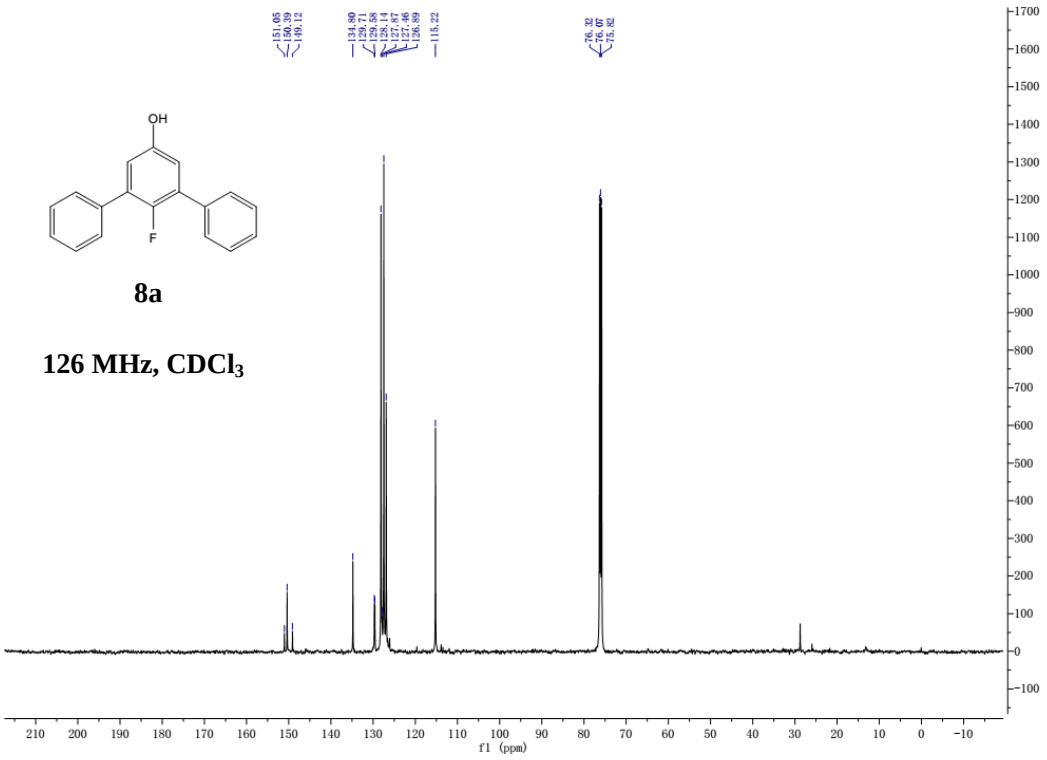

168.89
156.51
150.80
148.89
134.40
133.85
128.11
127.77
127.60
118.34
111.95
76.39
76.13
75.88
60.56
12.15
OH
O
O
CH3
S
F
7h
126 MHz, CDCl3
f1 (ppm)

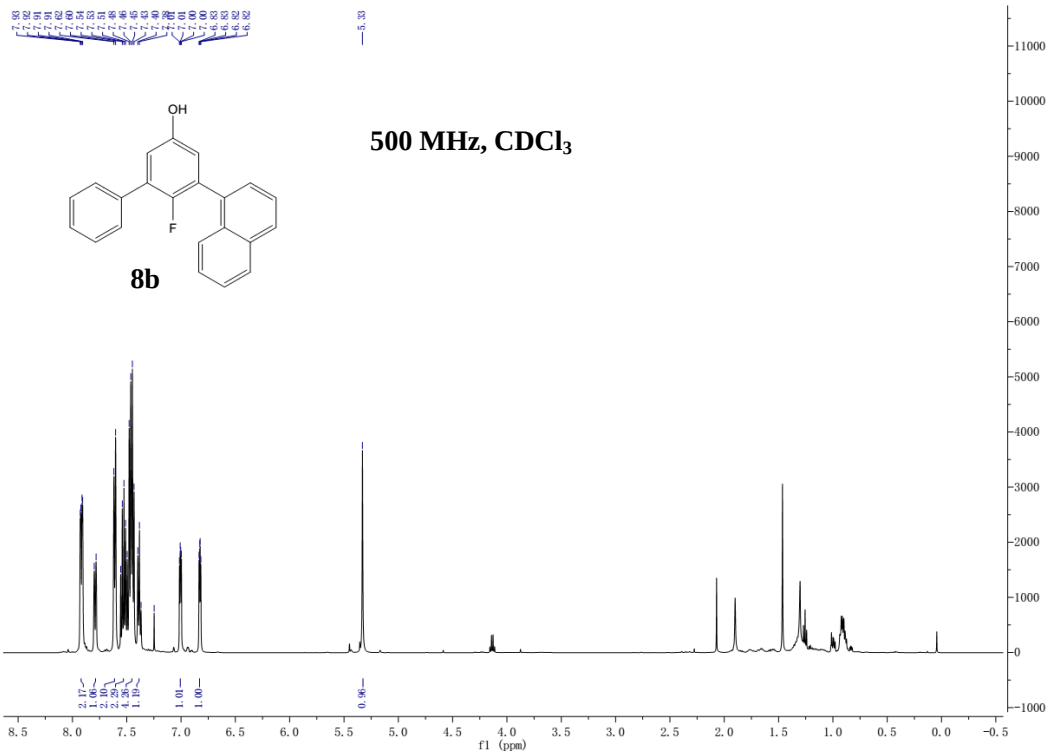

7.51
7.51
7.49
7.49
7.39
7.39
7.37
7.34
7.32
7.32
7.31
7.19
6.82
6.81
5.07
OH
F
500 MHz, CDCl3
4.26
4.25
2.21
2.00
0.91
f1 (ppm)

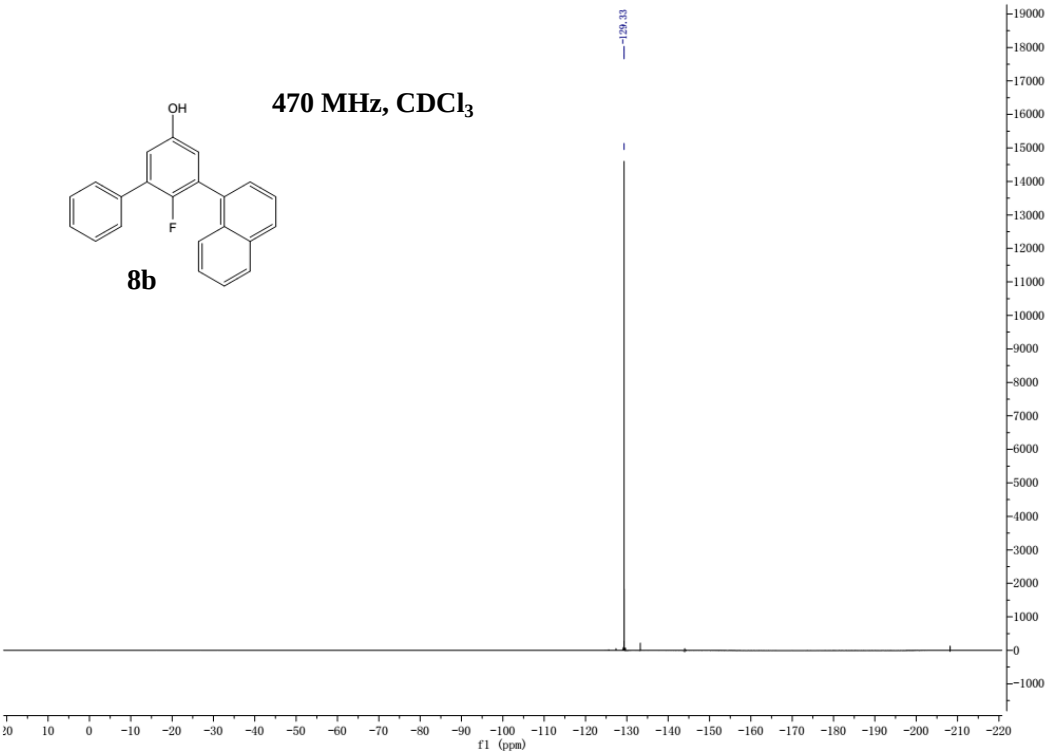
8a

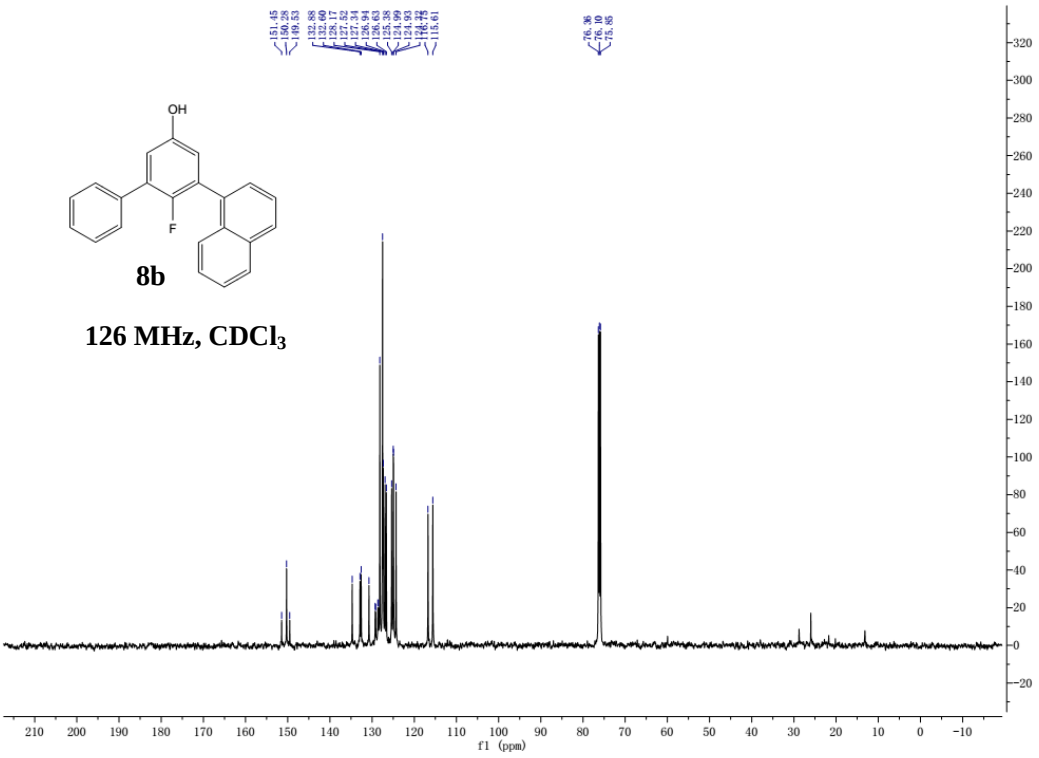

-133.65
OH
F
470 MHz, CDCl3
f1 (ppm)

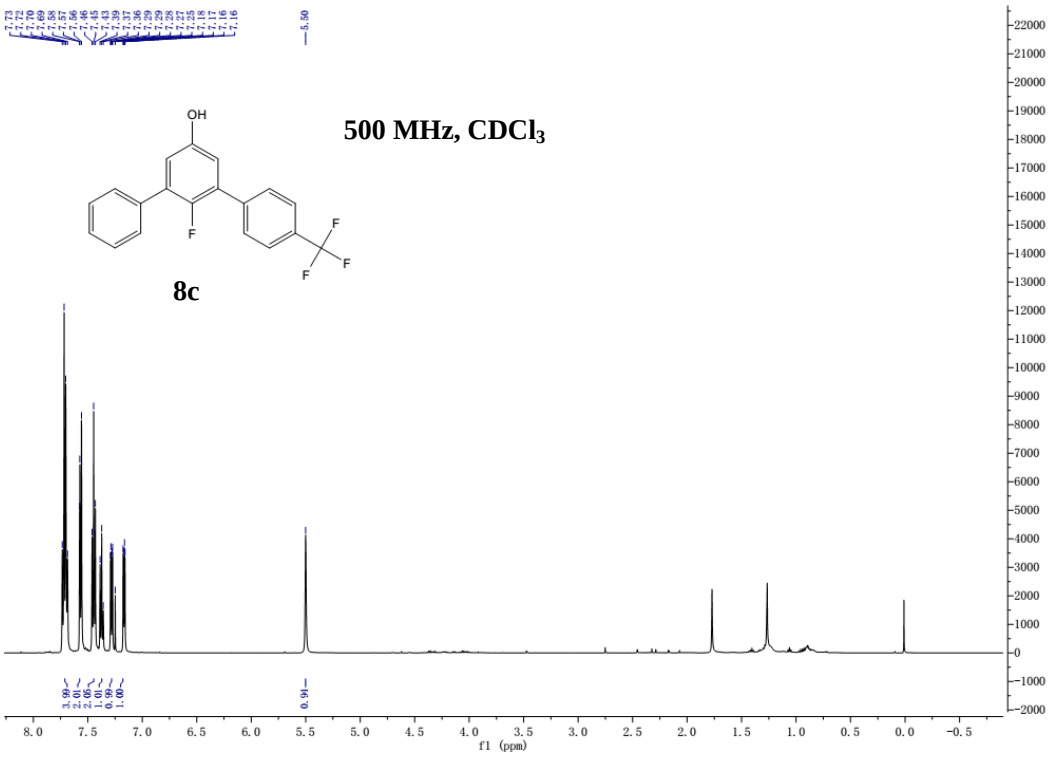
8a

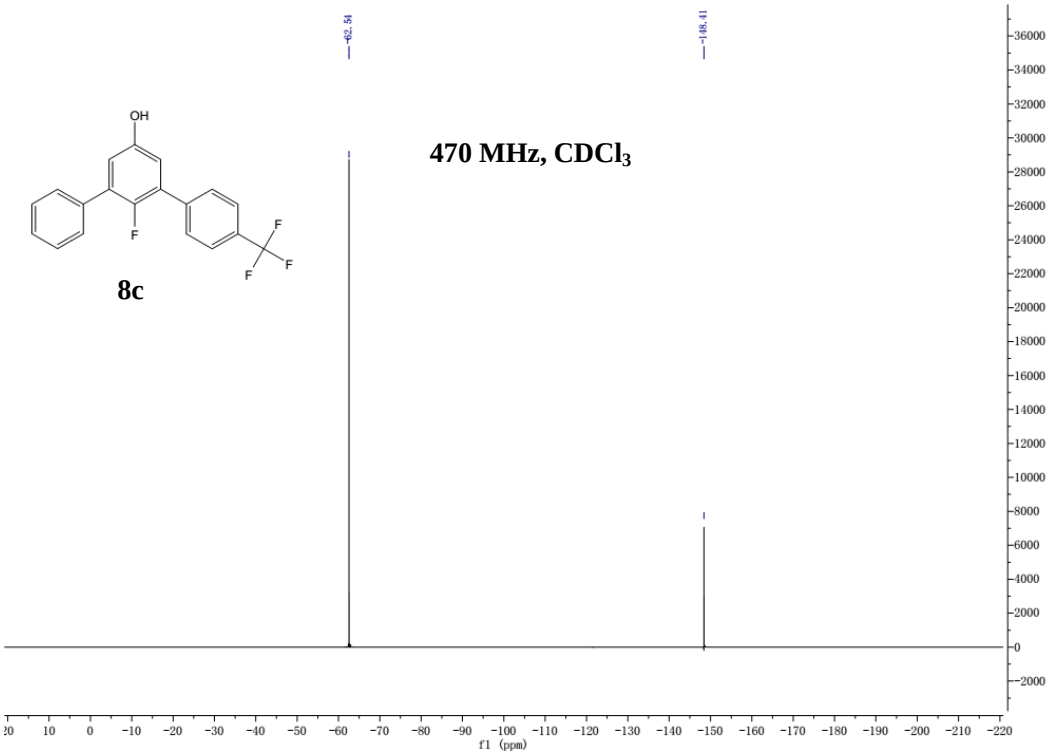

151.05
150.39
149.12
134.80
129.71
129.58
128.14
127.87
127.46
126.89
115.22
76.32
76.05
75.82
OH
F
8a
126 MHz, CDCl3
f1 (ppm)

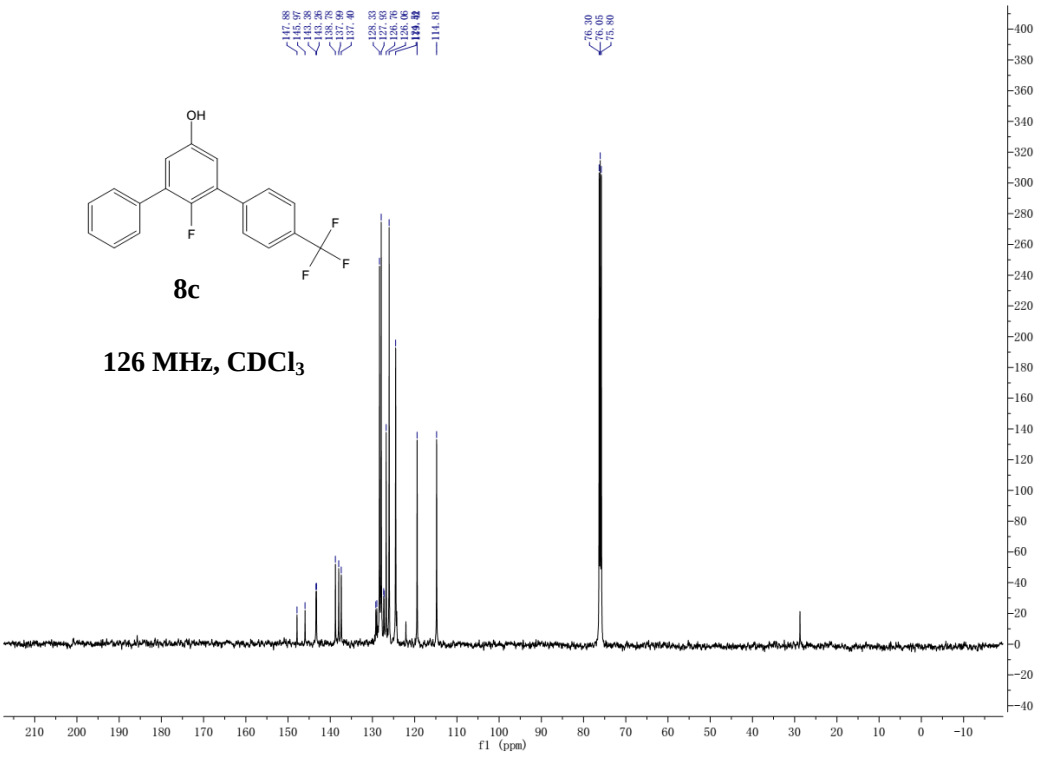

OH
F
8b
500 MHz, CDCl3
f1 (ppm)

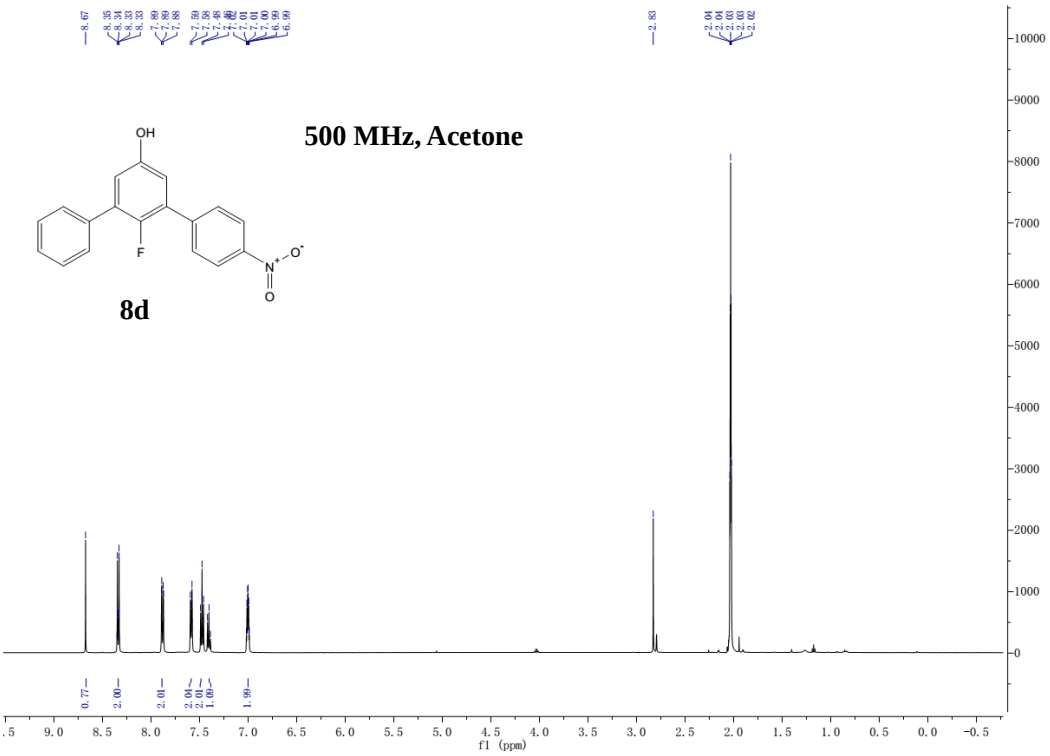

OH
F
8b
470 MHz, CDCl3
f1 (ppm)

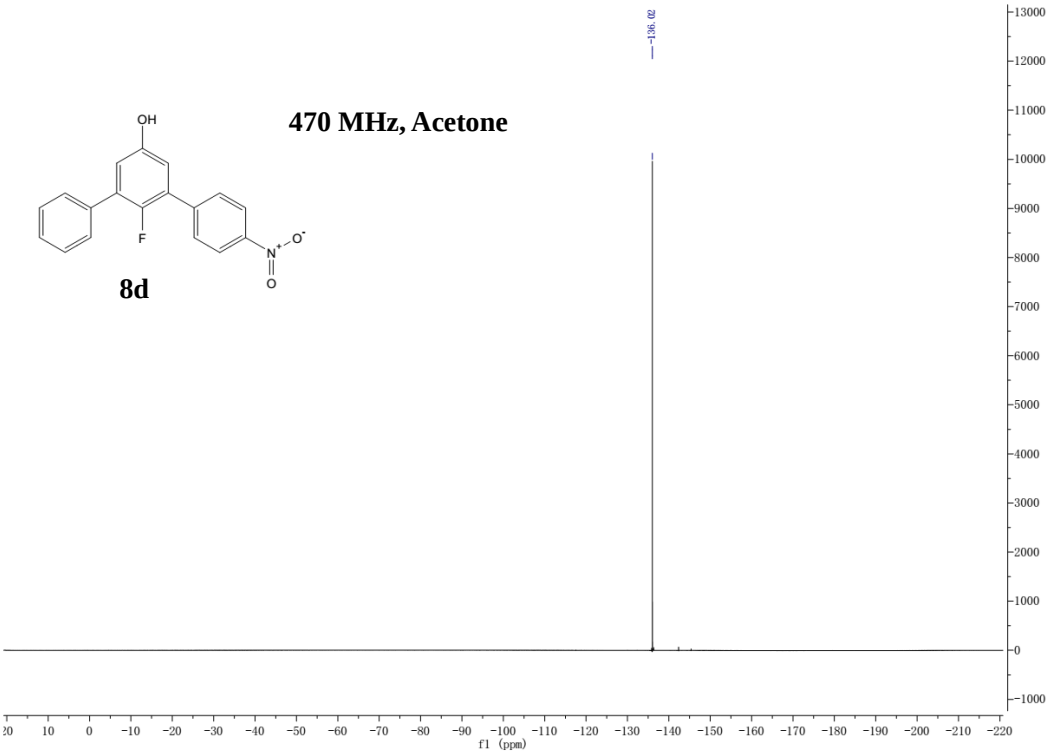

OH
F
8b
126 MHz, CDCl3
f1 (ppm)

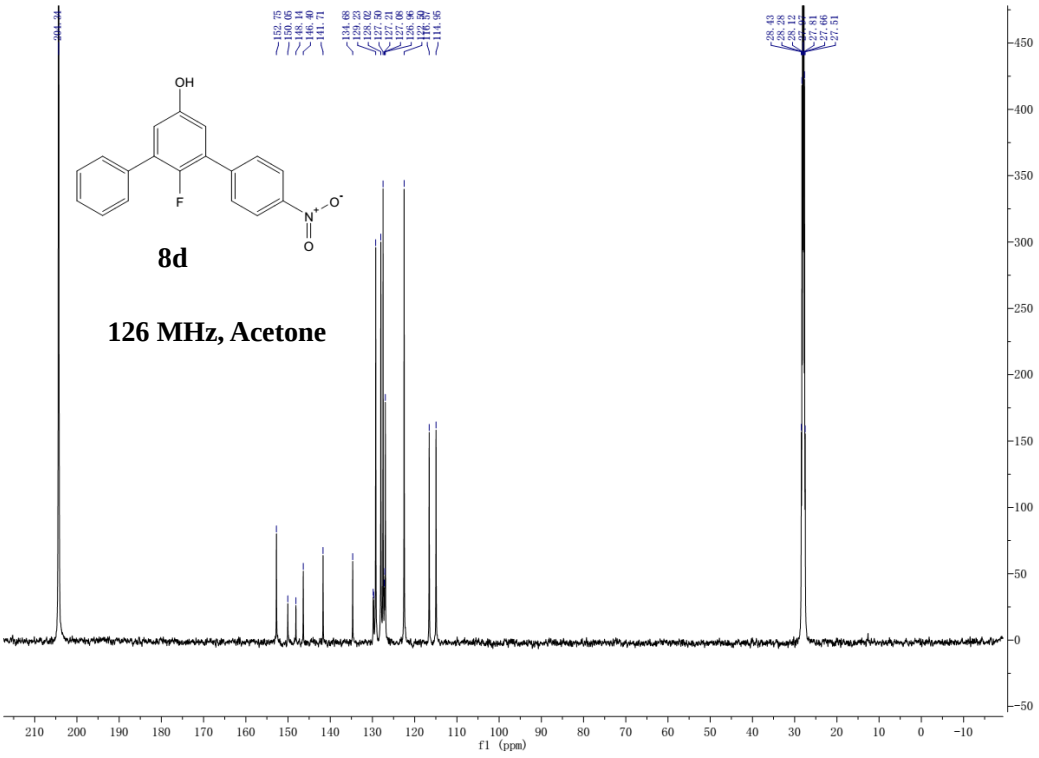

500 MHz, CDCl3
OH
F
F
F
F
8c
f1 (ppm)

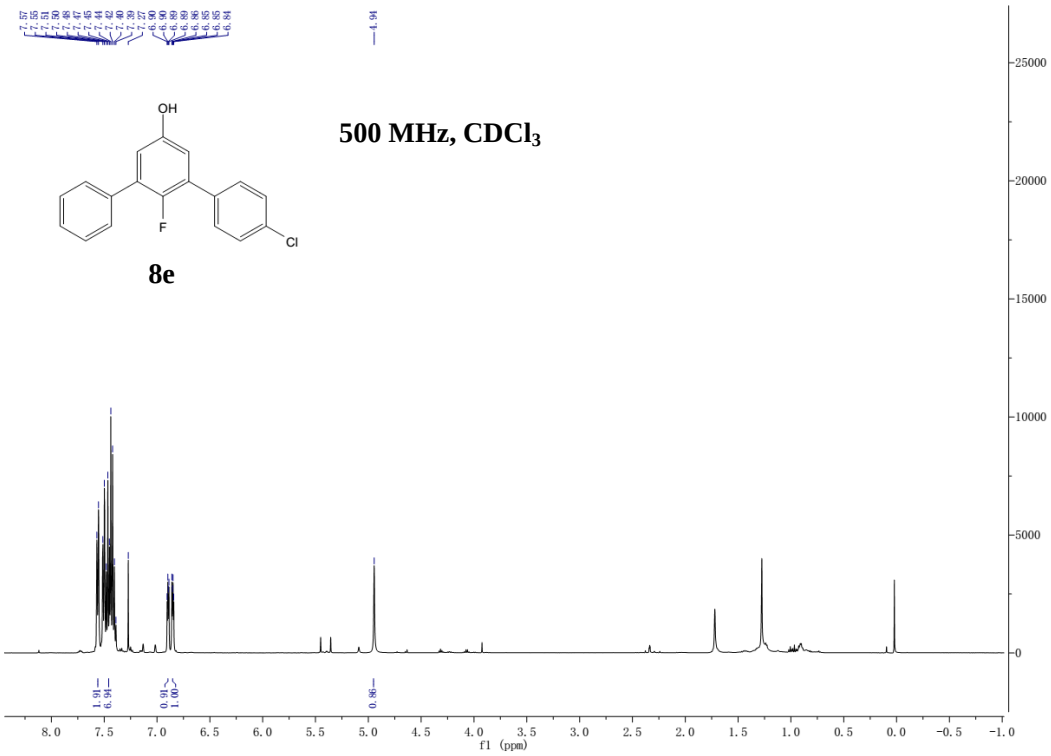

470 MHz, CDCl3
OH
F
F
F
F
8c
f1 (ppm)

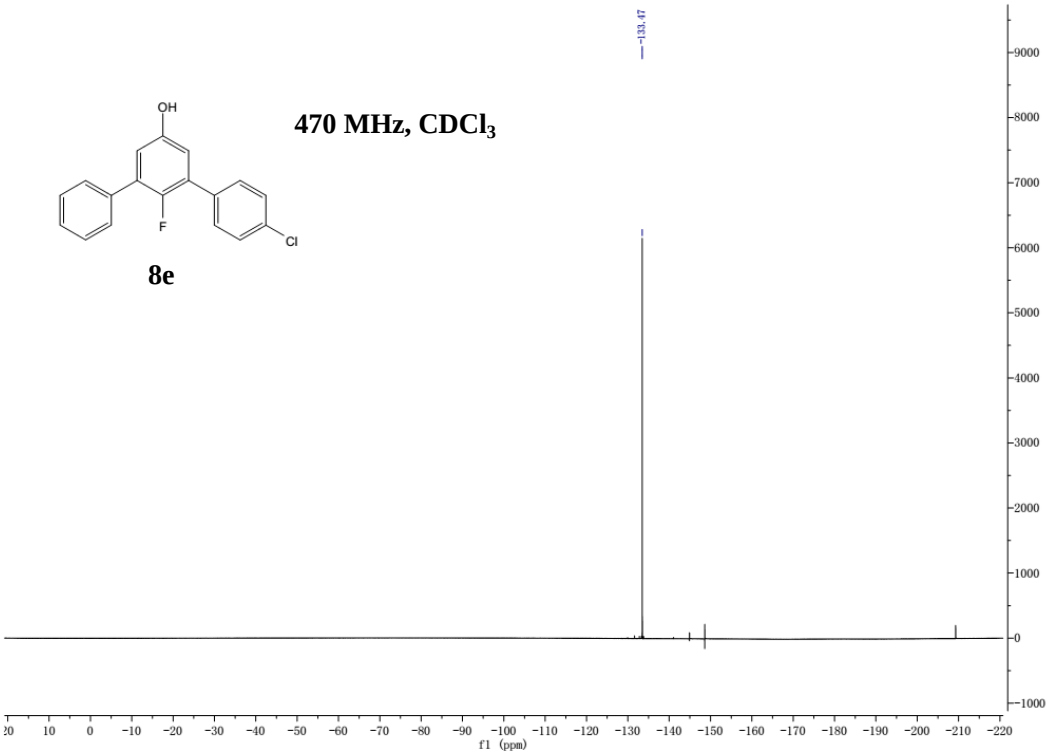

147.88
145.97
143.38
141.28
138.78
137.99
137.40
128.33
127.93
126.76
126.05
120.42
114.81
76.30
76.05
75.80
OH
F
F
F
F
8c
126 MHz, CDCl3
f1 (ppm)

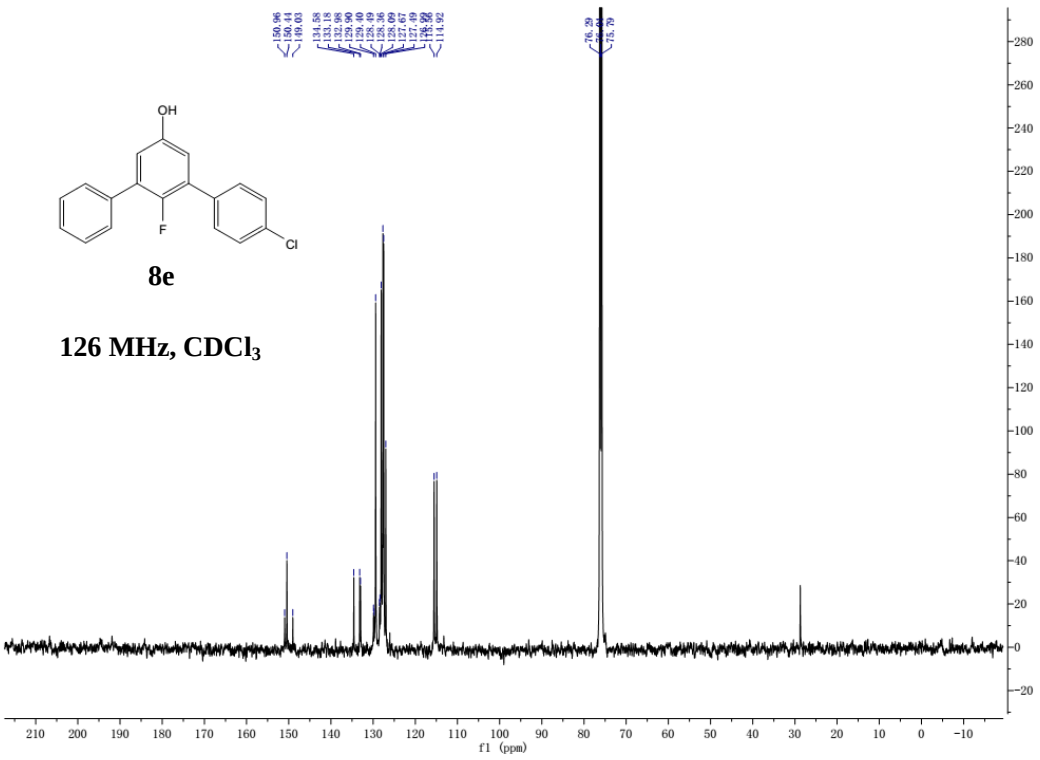

500 MHz, Acetone
OH
F
N+
O-
O
8d
f1 (ppm)

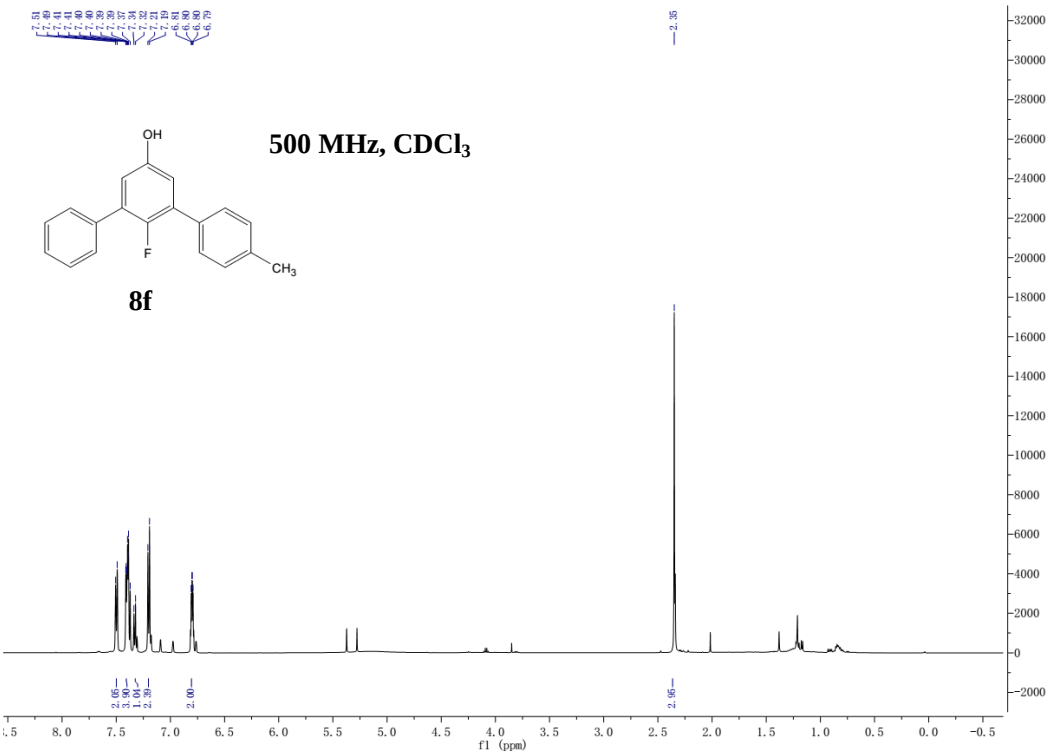

470 MHz, Acetone
OH
F
N+
O-
O
8d
f1 (ppm)


OH
F
N+
O-
O
8d
126 MHz, Acetone
f1 (ppm)


OH
F
Cl
8e
500 MHz, CDCl3
f1 (ppm)

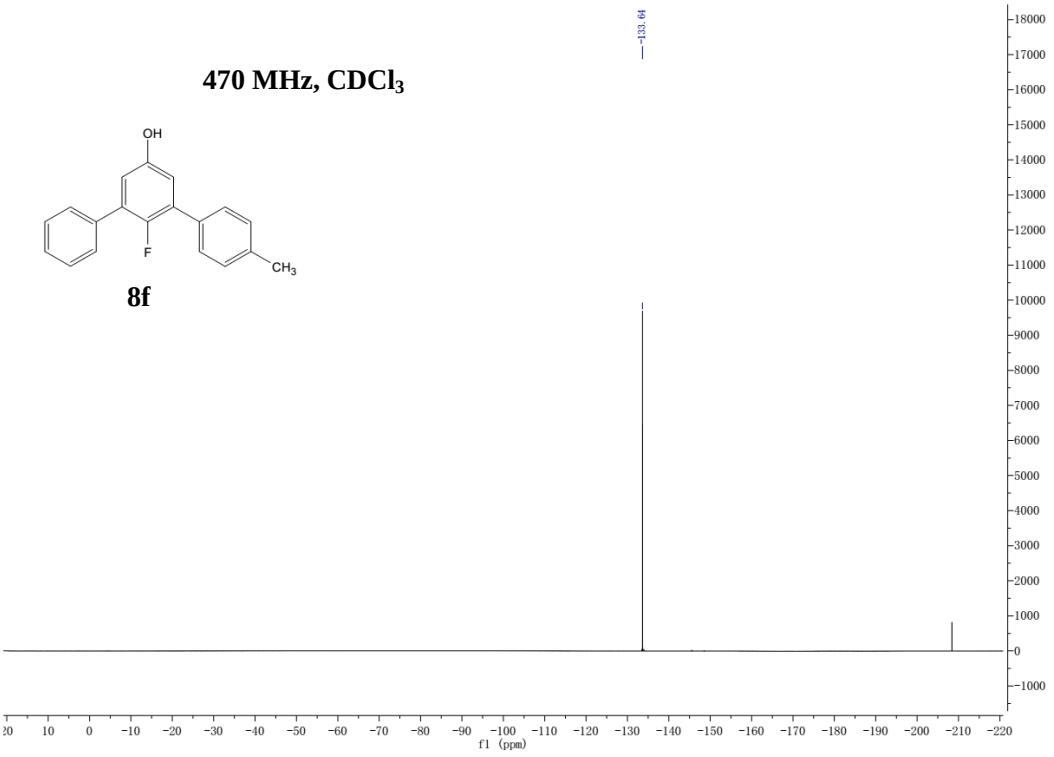

OH
F
Cl
8e
470 MHz, CDCl3
f1 (ppm)


OH
F
Cl
8e
126 MHz, CDCl3
f1 (ppm)



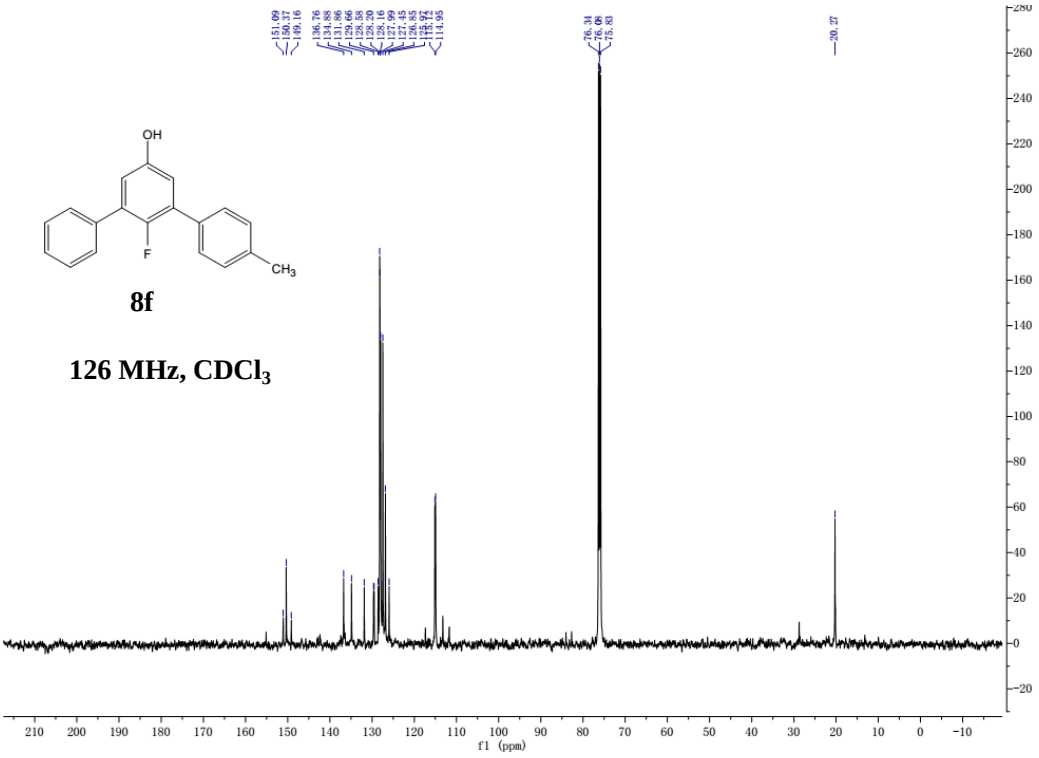
500 MHz, $CDCl_3$

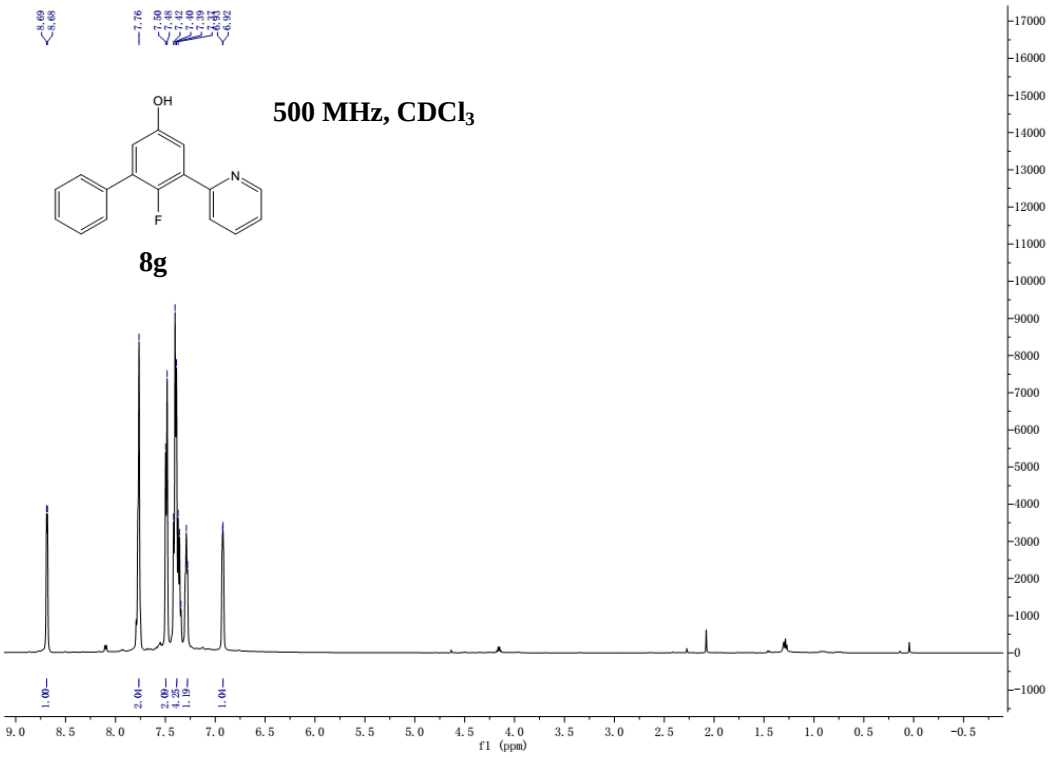
8f

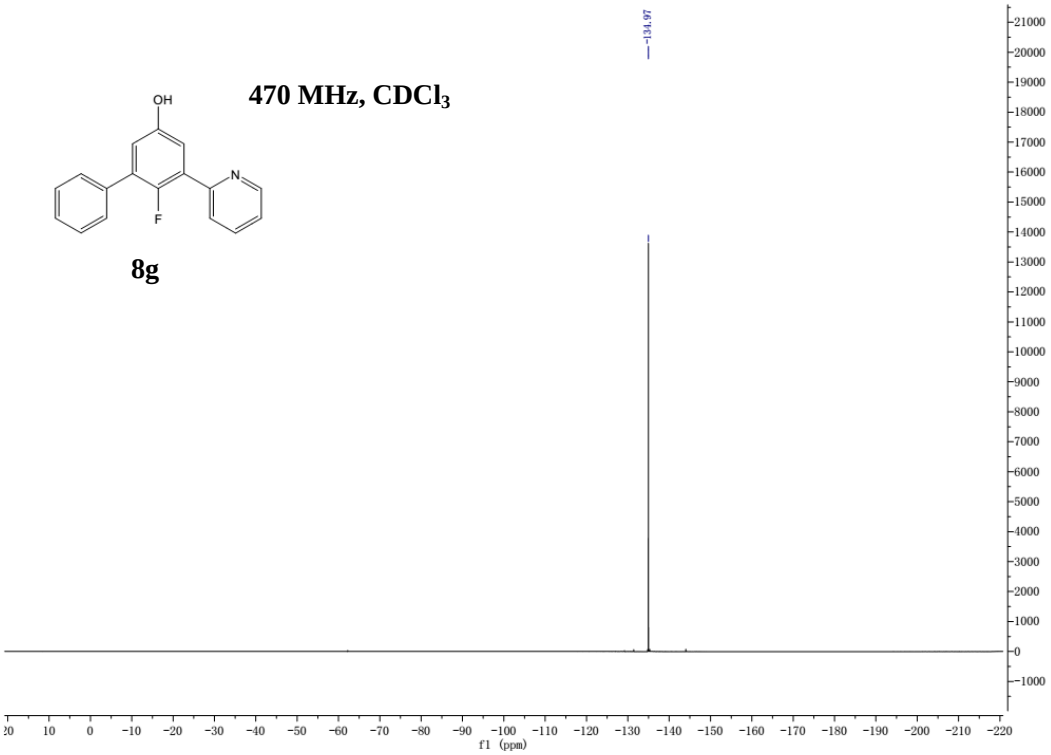


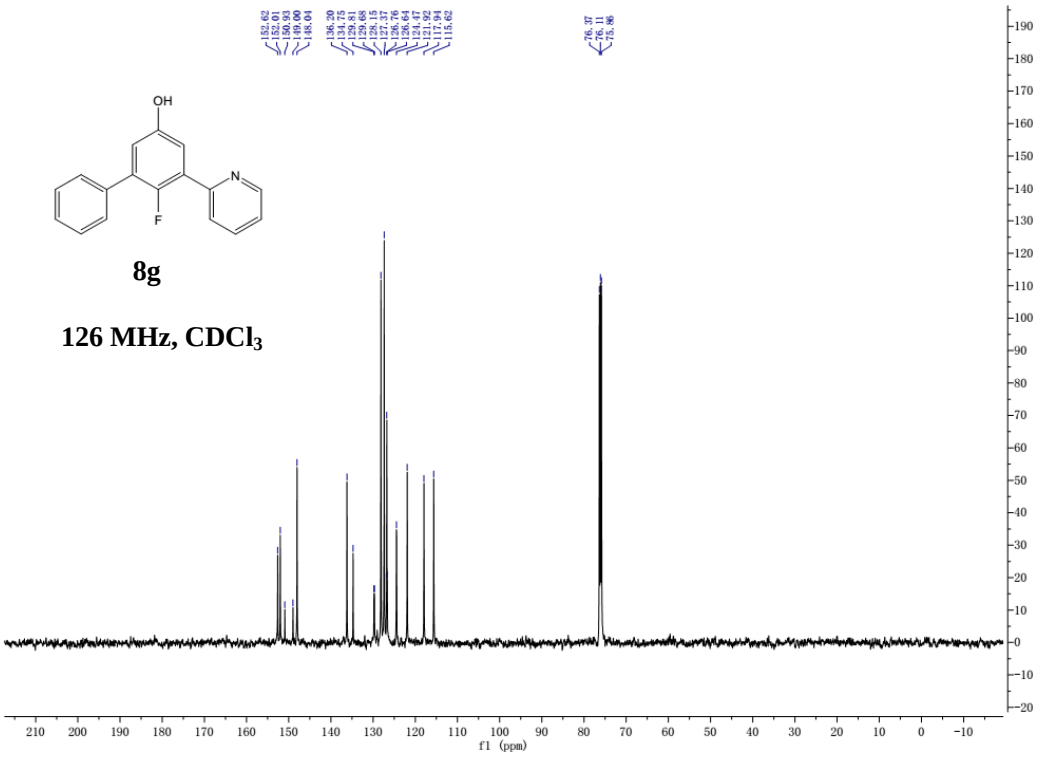
470 MHz, $CDCl_3$

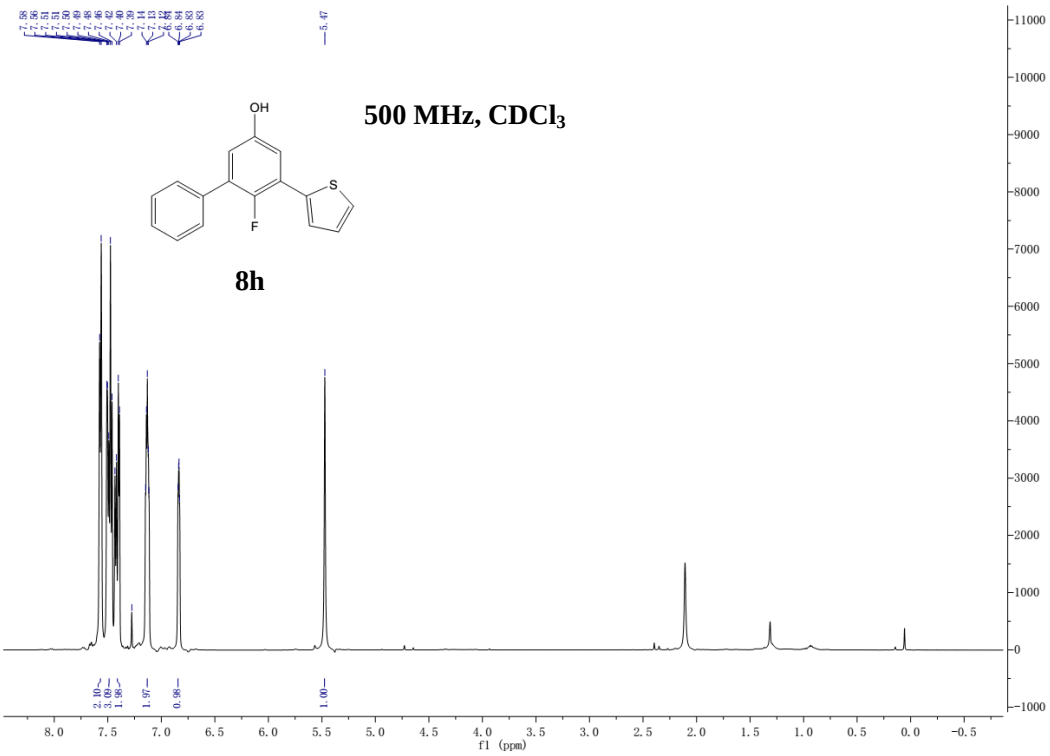
8f

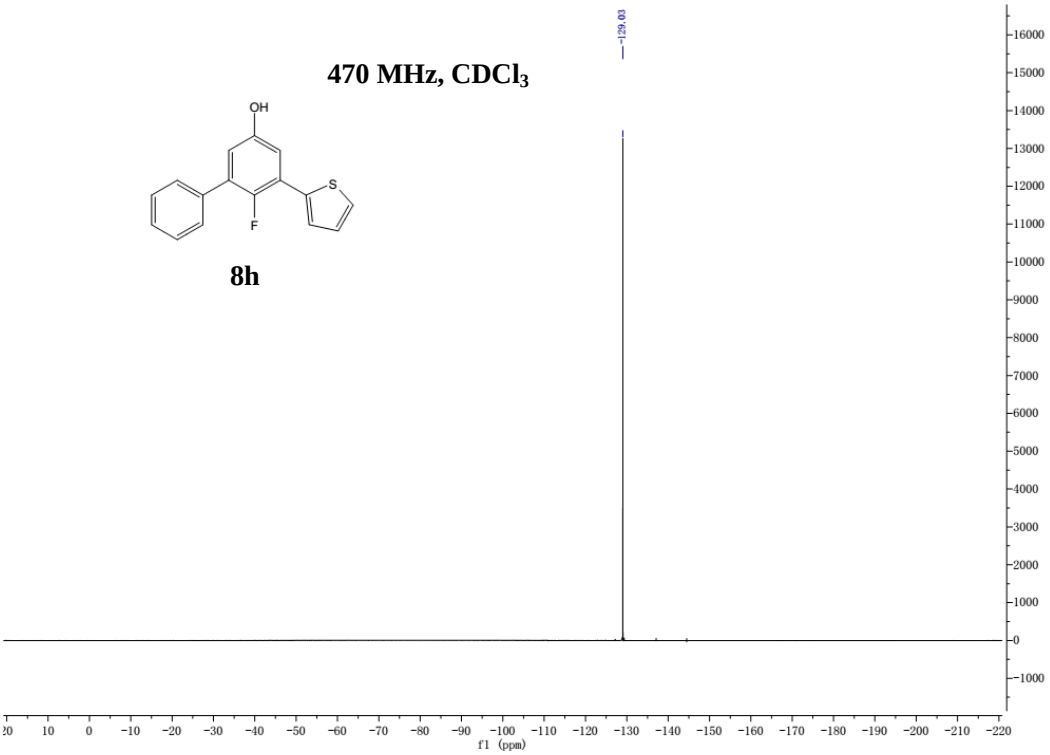

OH
F
CH3
8f
126 MHz, CDCl3
f1 (ppm)

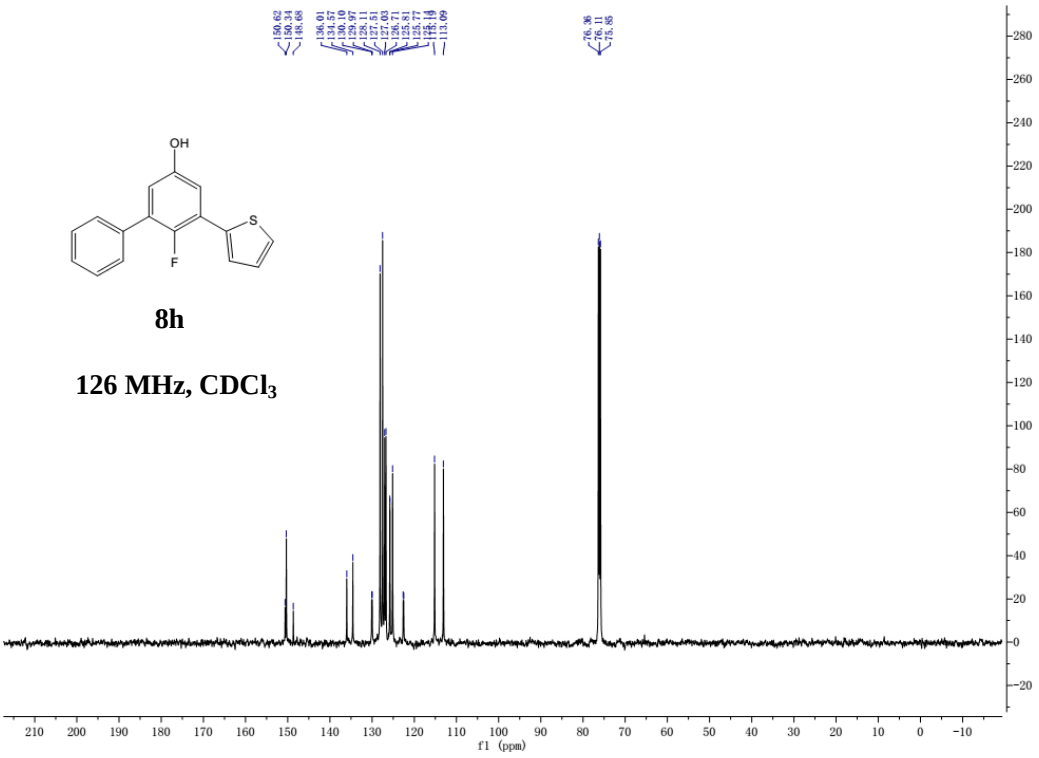

OH
N
F
500 MHz, CDCl3
8g
f1 (ppm)

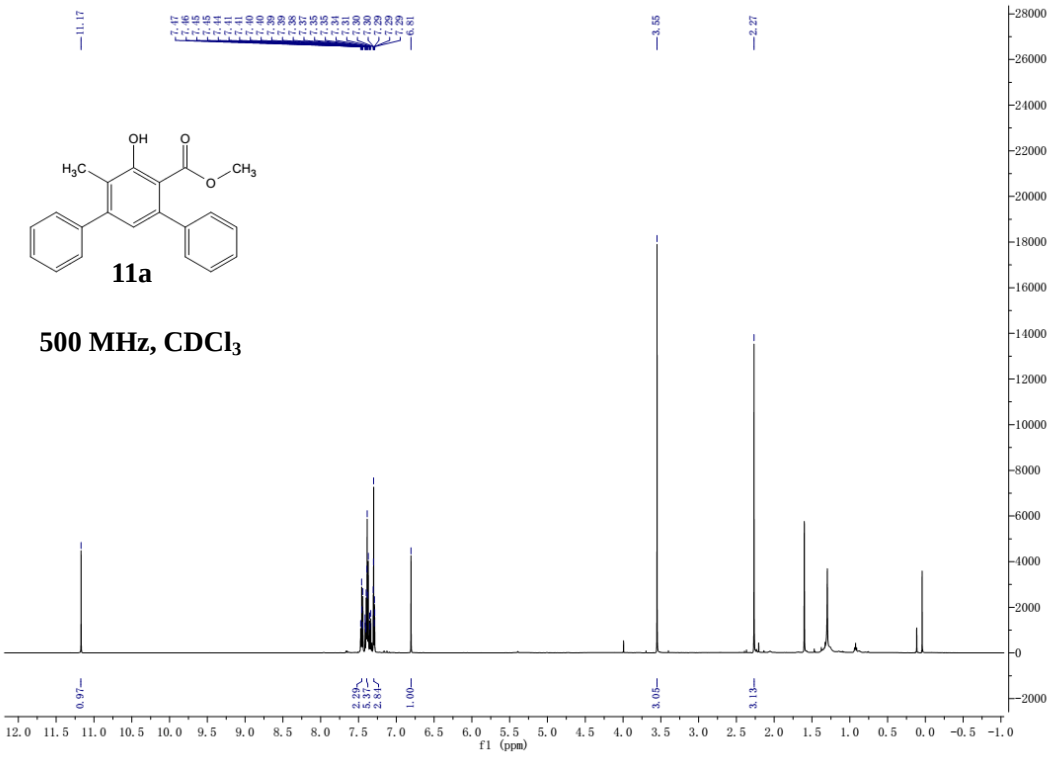

OH
N
F
470 MHz, CDCl3
8g
-134.97
f1 (ppm)


OH
N
F
8g
126 MHz, CDCl3
153.62
152.01
150.93
149.00
148.04
136.29
134.75
129.81
129.68
128.15
127.37
126.76
125.64
124.47
121.92
117.94
115.62
76.37
75.11
74.86
f1 (ppm)


500 MHz, CDCl3
OH
S
F
8h
f1 (ppm)

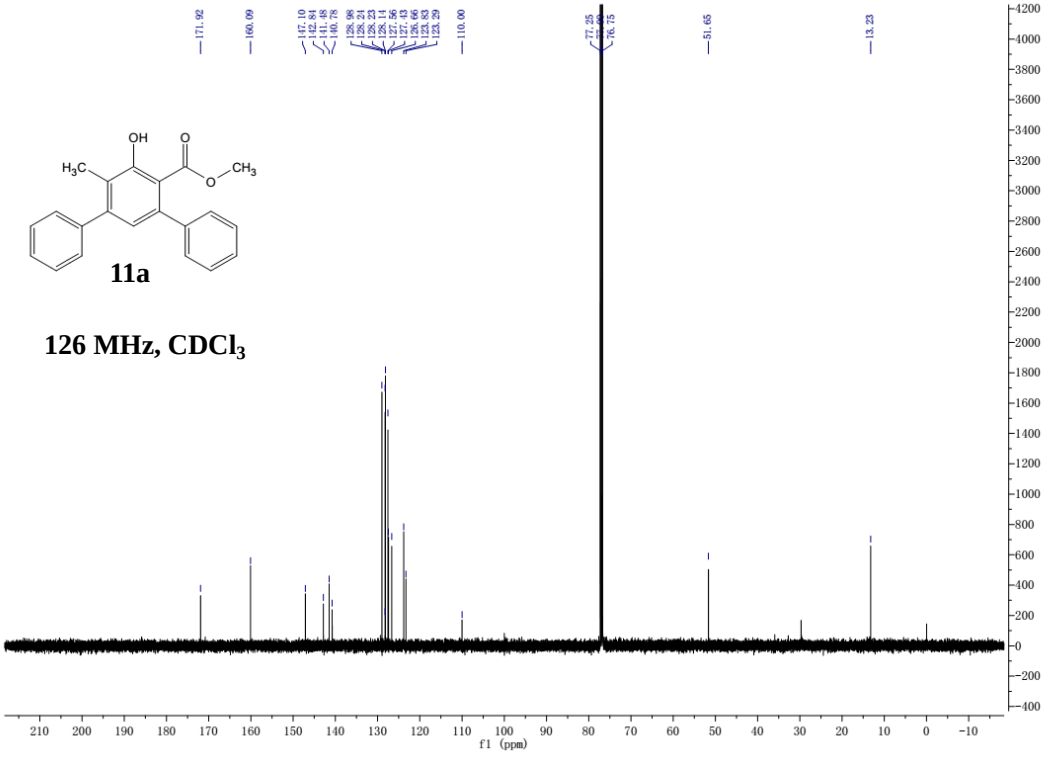

470 MHz, CDCl3
OH
S
F
8h
-129.03
f1 (ppm)


OH
S
F
8h
126 MHz, CDCl3
f1 (ppm)



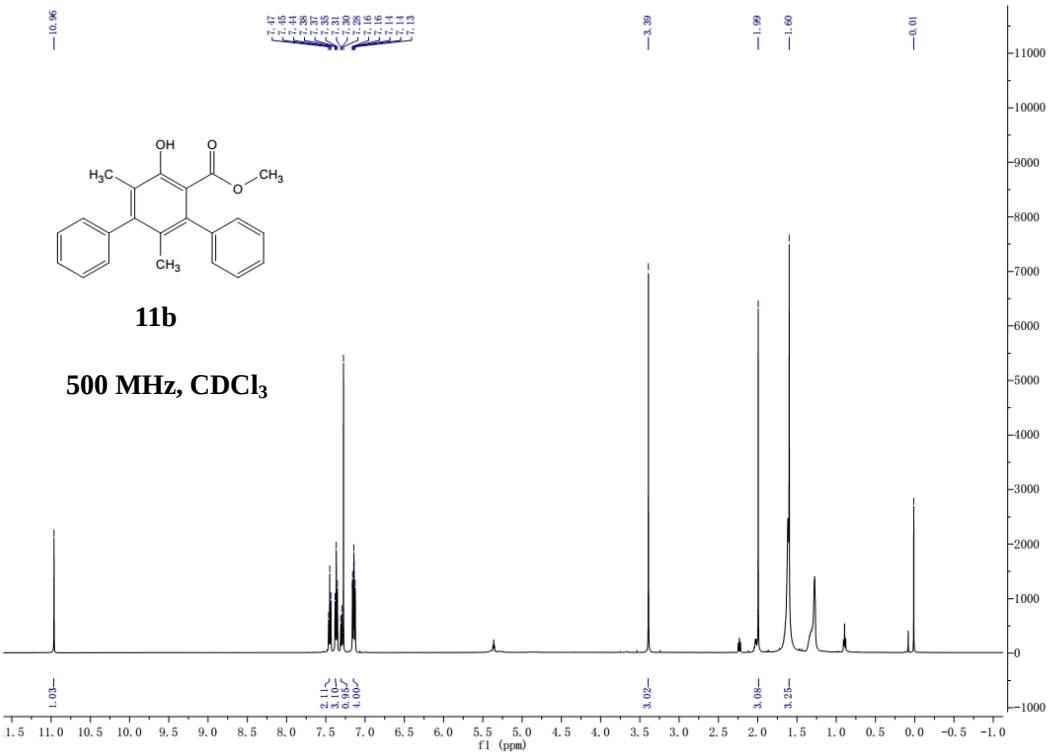
11a

500 MHz, $CDCl_3$



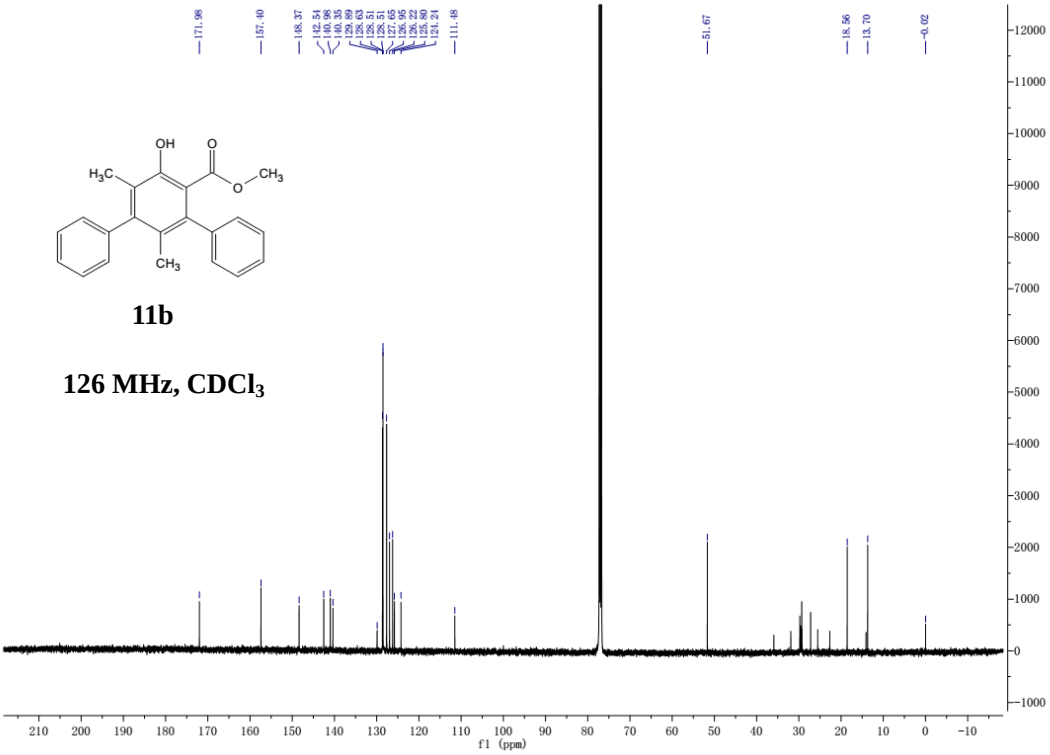
11a

126 MHz, $CDCl_3$



11b

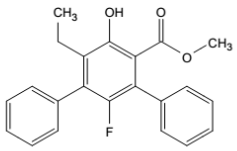
500 MHz, $CDCl_3$



11b

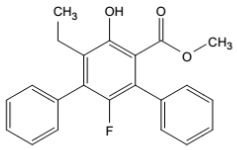
126 MHz, $CDCl_3$

500 MHz, $CDCl_3$

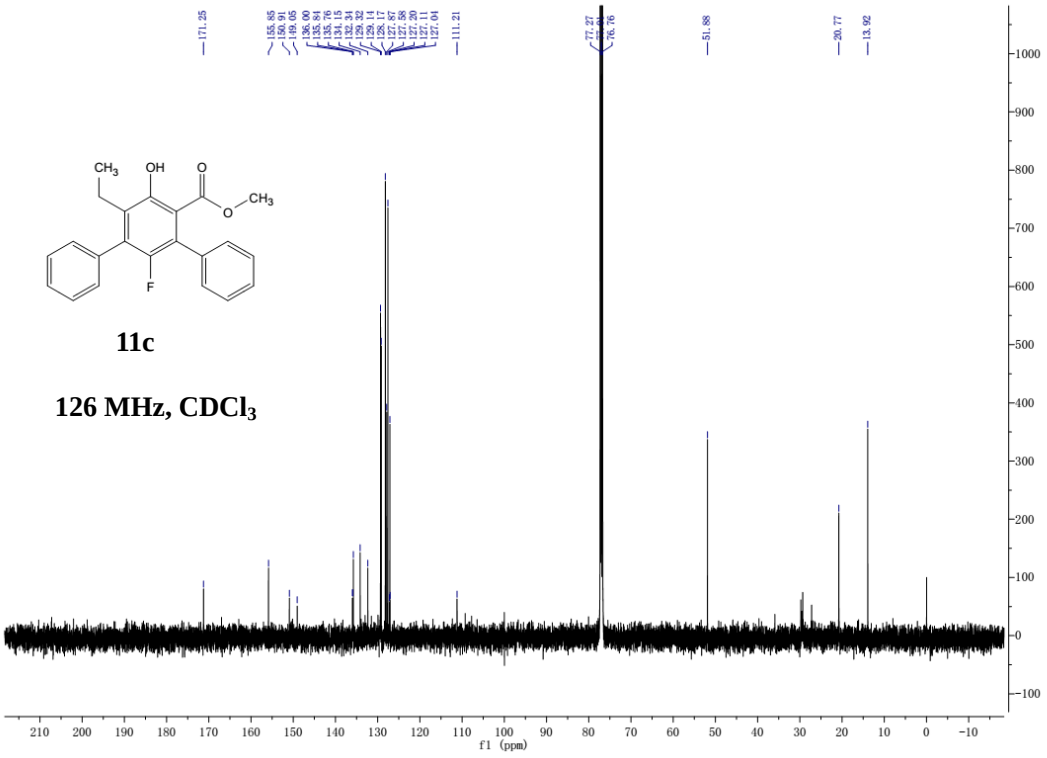


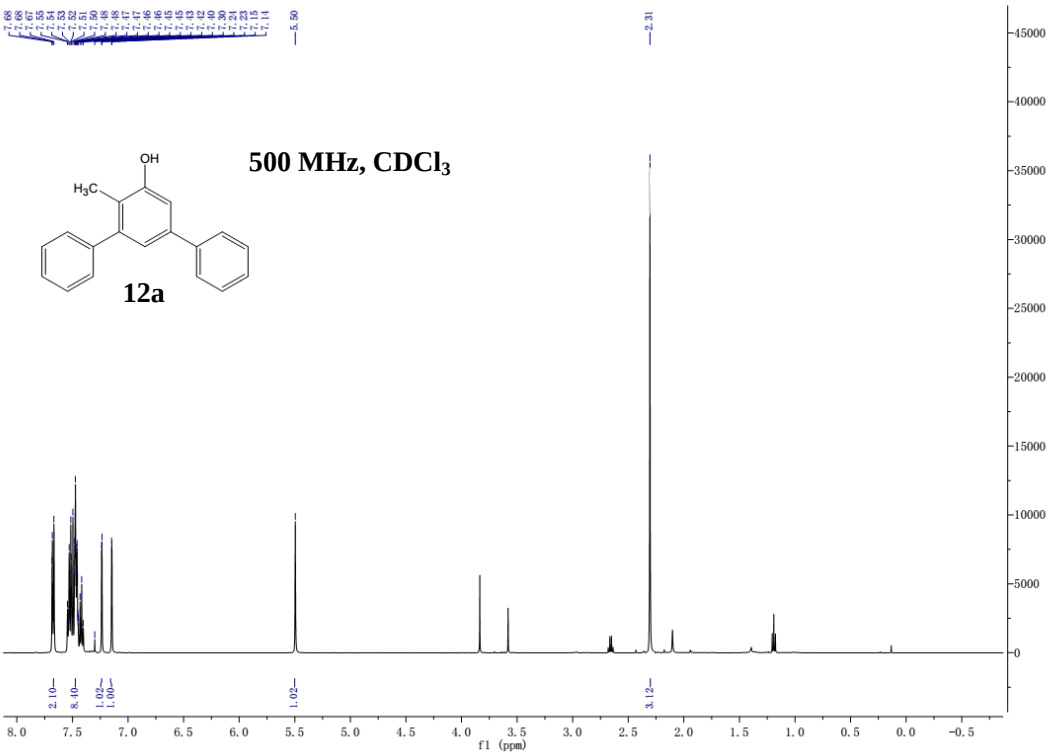
11c

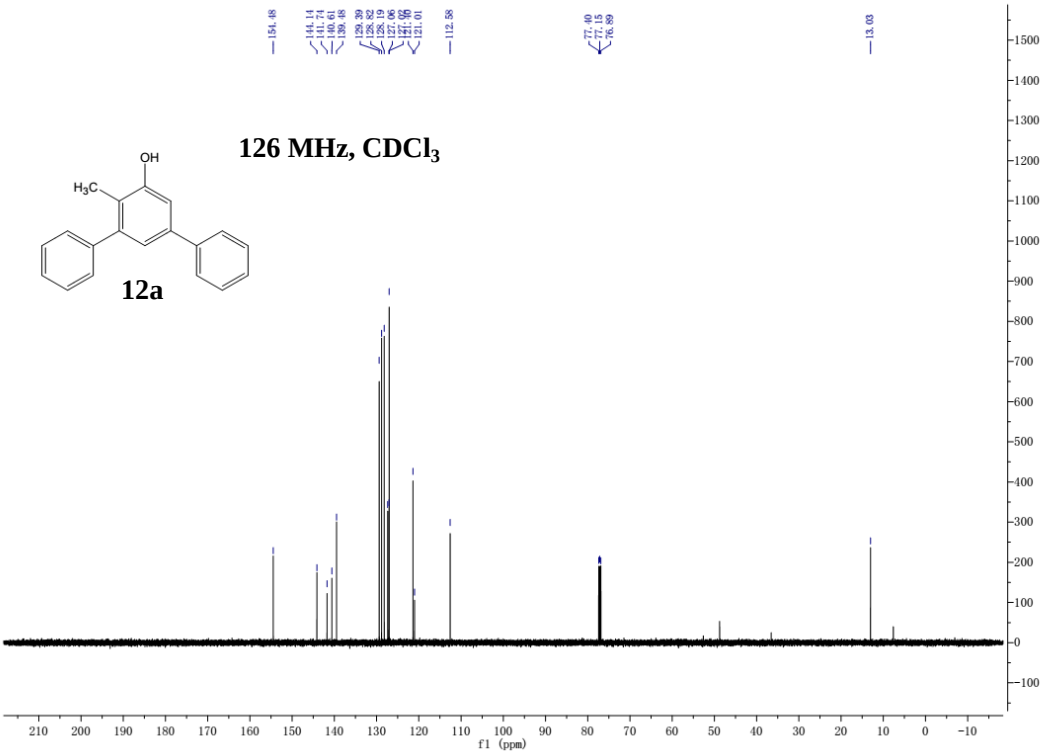
470 MHz, $CDCl_3$

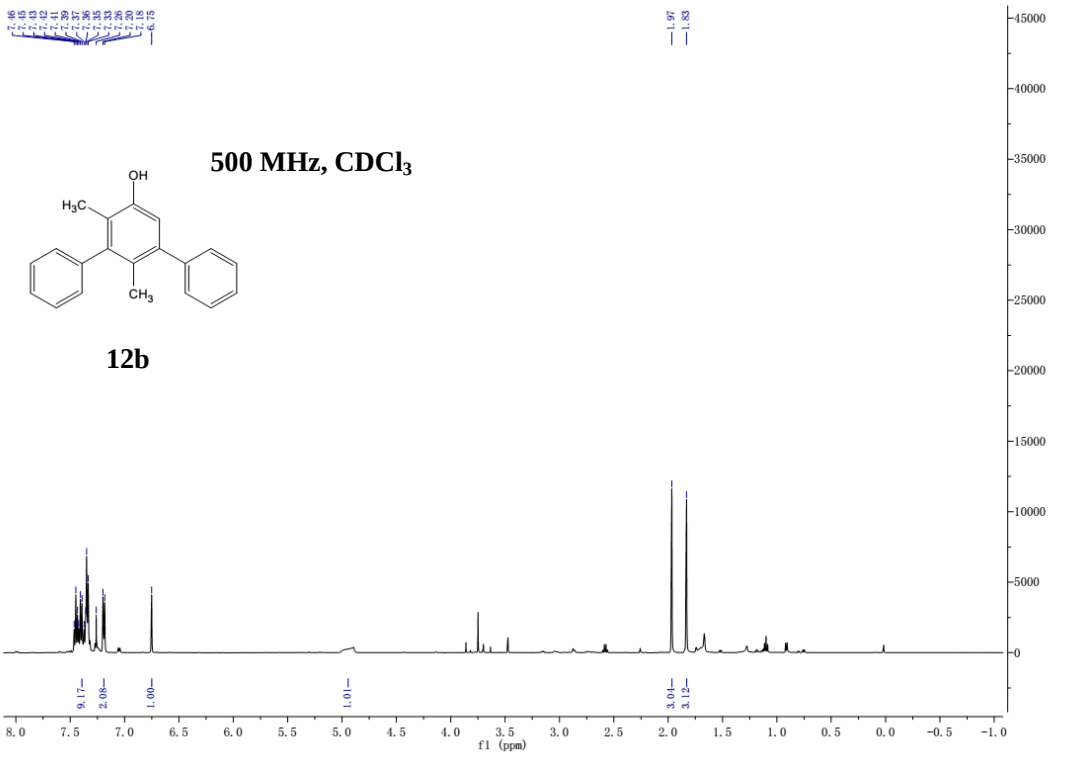


11c


171.25
155.85
150.91
149.05
136.60
135.84
135.76
134.15
132.34
129.32
129.14
128.17
127.87
127.58
127.30
127.11
127.04
111.21
77.27
77.04
76.76
51.88
20.77
13.92
CH3
OH
O
O
CH3
F
11c
126 MHz, CDCl3
f1 (ppm)

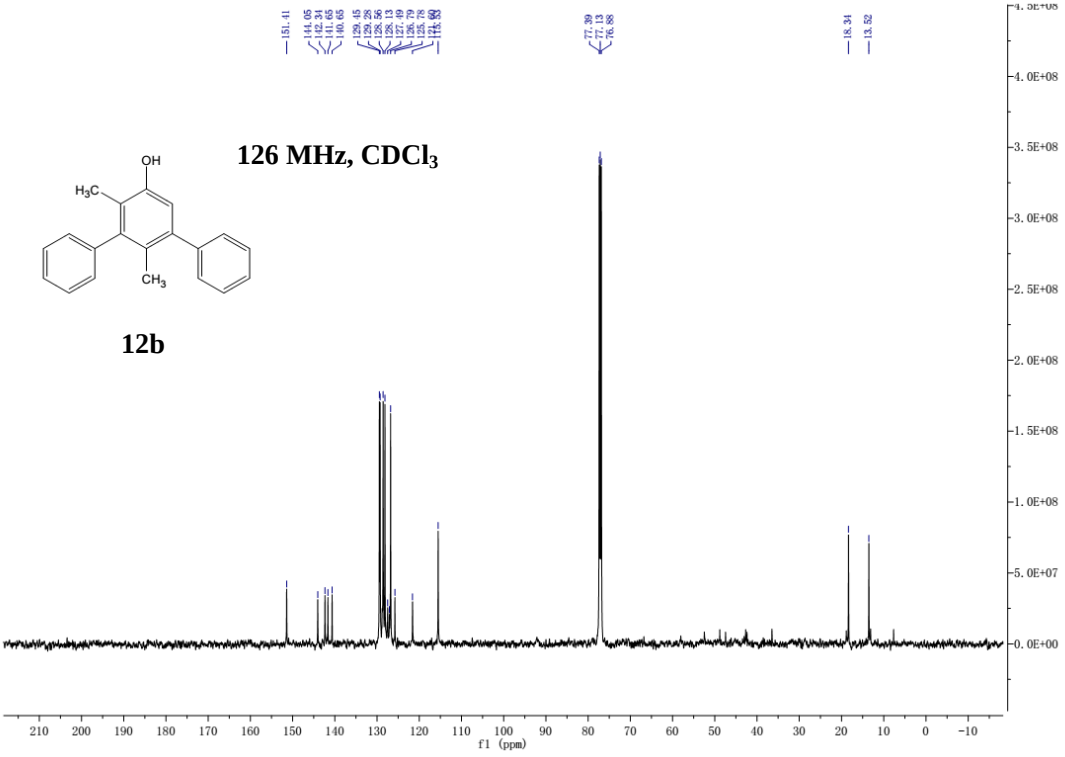

OH
H3C
500 MHz, CDCl3
12a
f1 (ppm)


OH
H3C
126 MHz, CDCl3
12a
f1 (ppm)



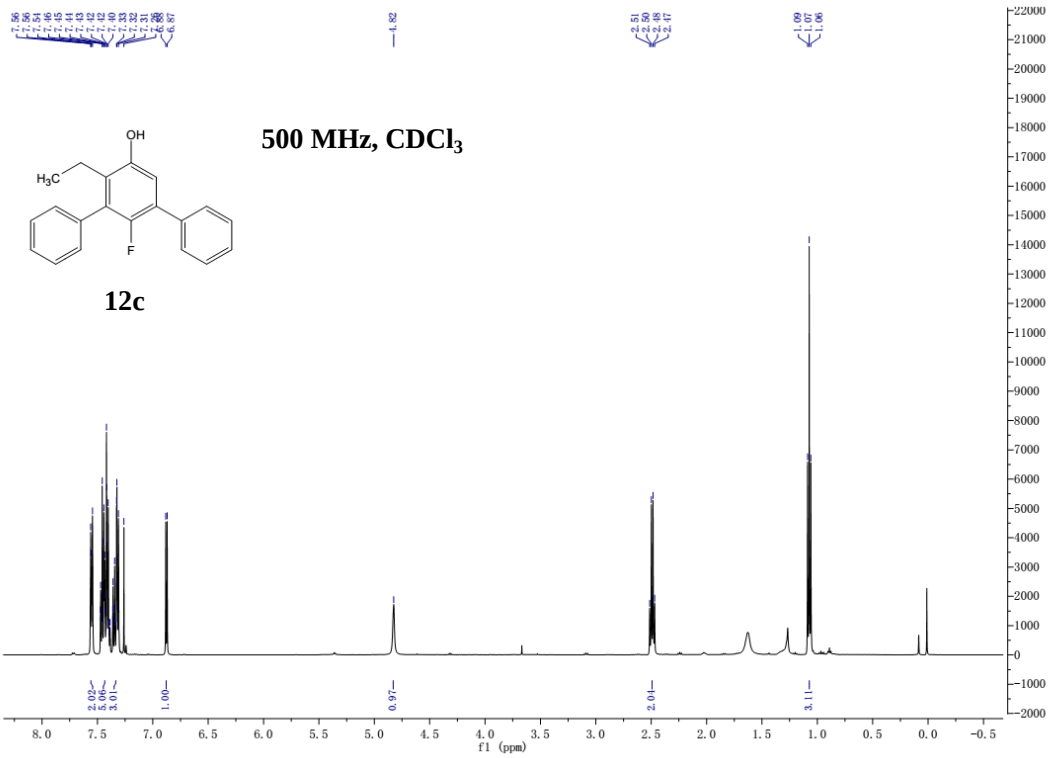
500 MHz, $CDCl_3$

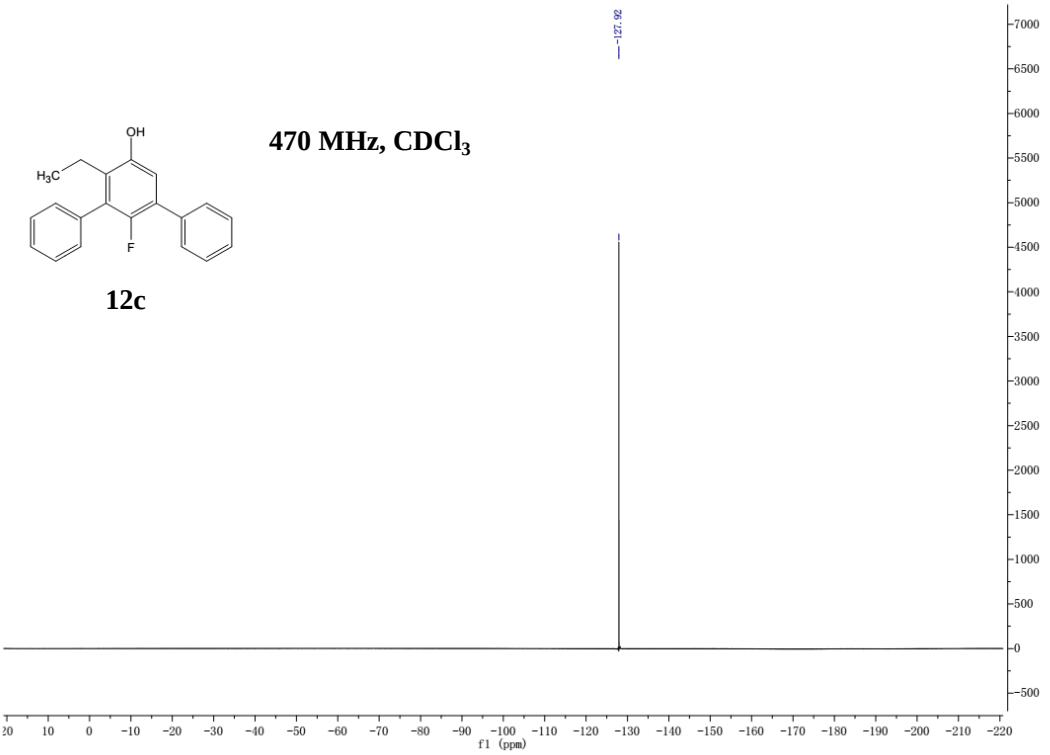
12b

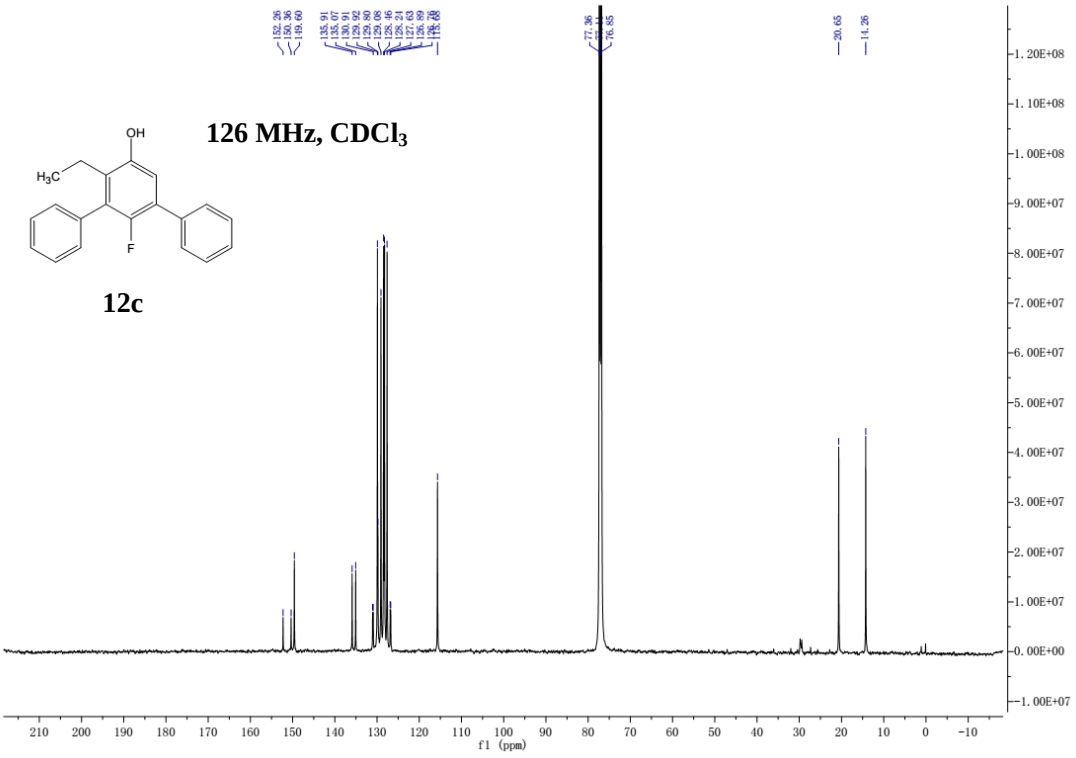


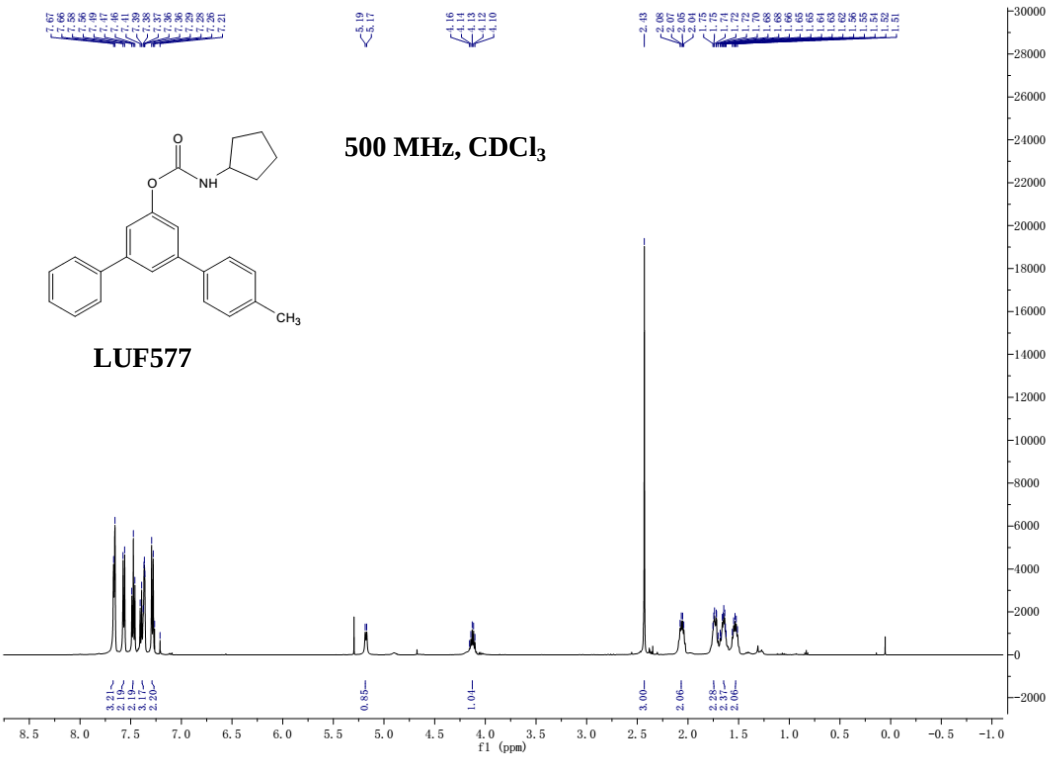
126 MHz, $CDCl_3$

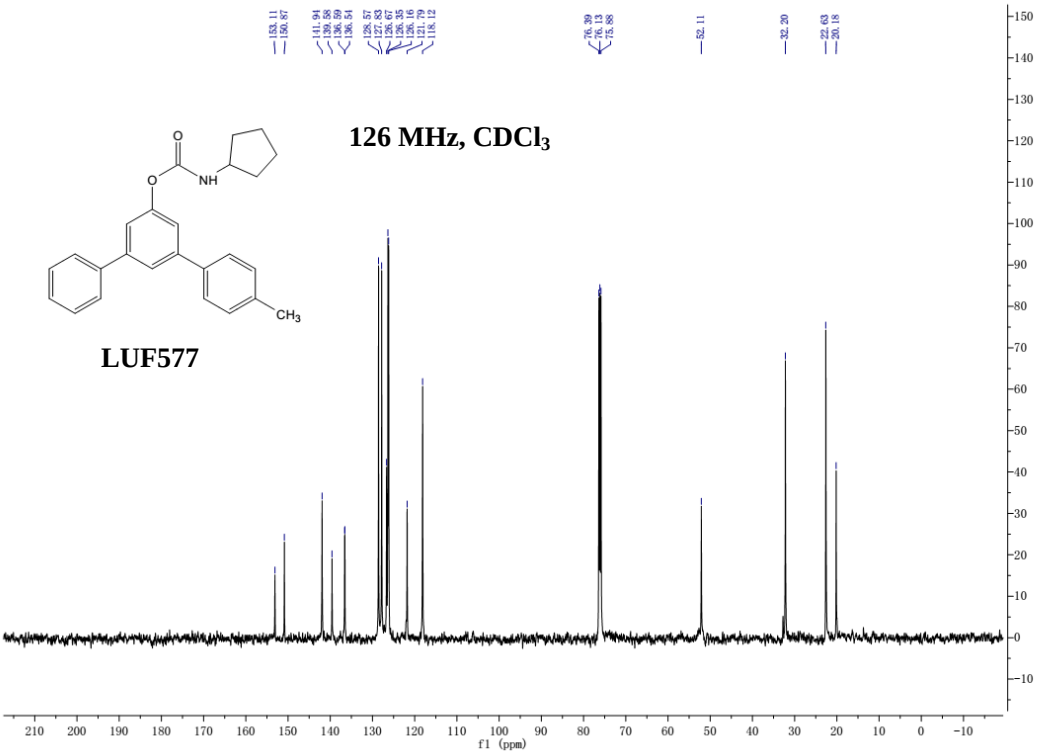
12b


OH
H3C
F
500 MHz, CDCl3
12c
f1 (ppm)


OH
H3C
F
470 MHz, CDCl3
12c
f1 (ppm)


126 MHz, CDCl3
OH
H3C
F
12c
153.26
150.36
149.60
135.91
135.07
130.91
129.92
129.80
129.08
128.45
128.21
127.63
126.89
77.36
77.14
76.85
20.65
14.26
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

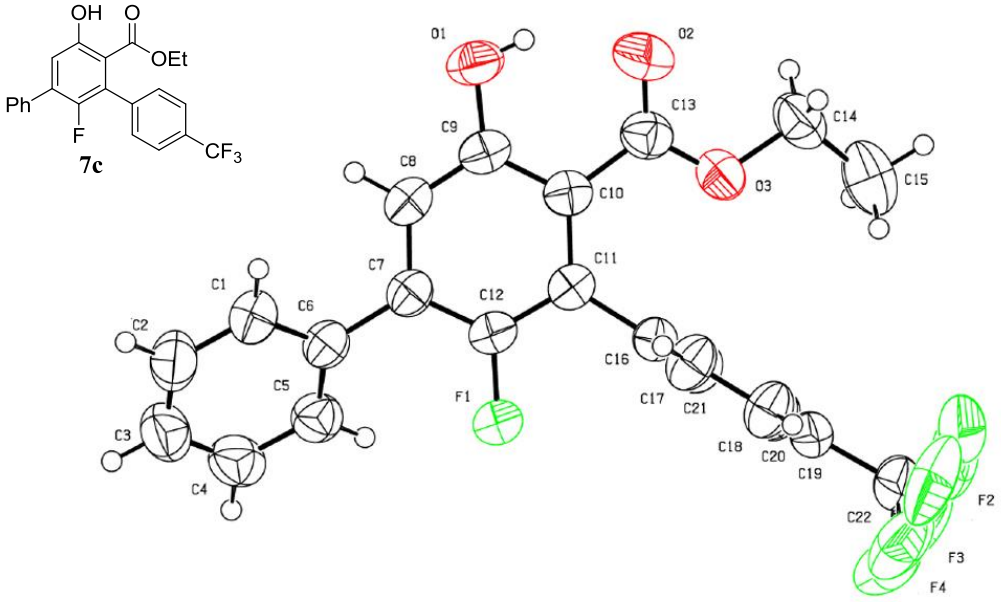

500 MHz, CDCl3
LUF577
f1 (ppm)


126 MHz, CDCl3
LUF577
f1 (ppm)

4. Crystallographic Data

Crystallographic data of complexes was collected at 296 K on a Bruker APEX-II CCD system equipped with graphite-monochromated Mo-Kα radiation (λ = 0.071073 nm) using ω-φ scan technique. Diffraction data were integrated by the SAINT program, which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using SADABS. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package.

X-ray crystal structure of compound **7c**



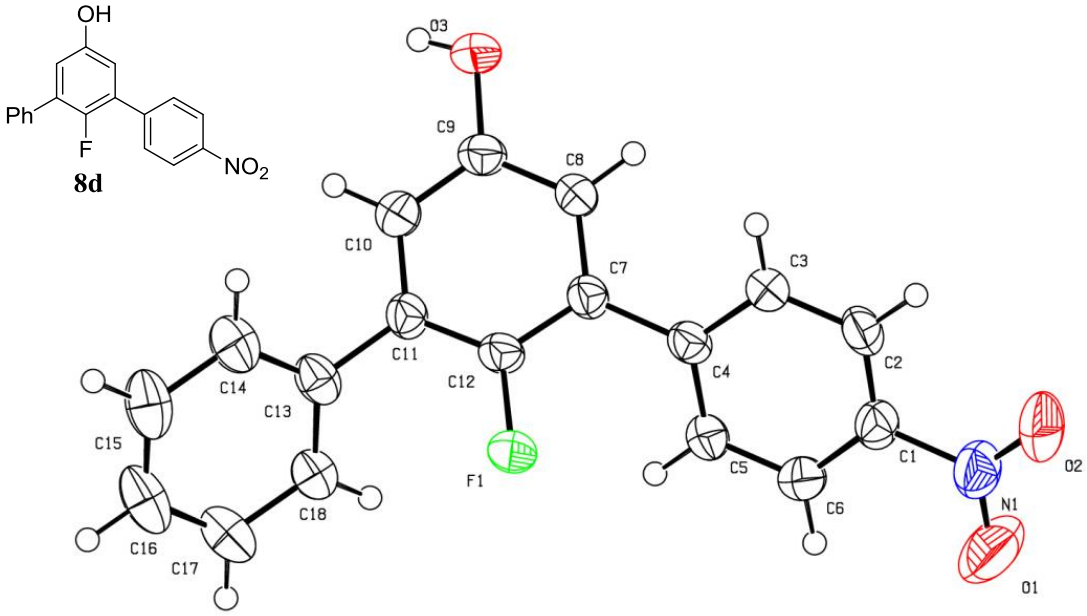
Crystal data and structure refinement for compound **7c**.

complex	**7c**
Formula	$C_{18}H_{12}FNO_3$
Formula weight	309.29
Crystal system	Monoclinic
space group	*P*2(1)/C
a (Å)	3.798(6)
b (Å)	11.416(15)
c (Å)	31.20(4)
α (º)	90.00
β (º)	90.82(2)
γ (º)	90.00
Volume(Å^3)	1353(3)
Z	4
T, (K)	296(2)
μ (mm^{-1})	0.113
D_{calcd} (g/m^3)	1.519
F(000)	640
Reflections collected	2330
Unique reflections	1848
Goof	1.163
R_1[I> 2σ(I)]	0.0868
wR_2[I>2σ(I)]	0.1799[a]

[a]$w=1/[\sigma^2(F_0)^2+(0.0142P)^2 +3.9502P]$, where $P = (F_0^2 + 2F_c^2)/3$

Crystallographic data (excluding structural factors) for compound **7c** also has been deposited at the Cambridge Crystallographic Data Centre under the deposition number **CCDC 993684.**

X-ray crystal structure of compound **8d**.



Crystal data and structure refinement for compound **8d**.

complex	**8d**
Formula	C22H16F4O3
Formula weight	404.35
Crystal system	Triclinic
space group	*P*-1
a (Å)	7.668(3)
b (Å)	11.450(4)
c (Å)	11.497(4)
α (º)	97.960(6)
β (º)	98.584(6)
γ (º)	103.944(6)
Volume(Å^3)	952.6(6)
Z	2
T, (K)	296(2)

μ (mm^{-1})	0.119
D_{calcd} (g/m^3)	1.410
F(000)	416
Reflections collected	3334
Unique reflections	2705
Goof	1.022
R_1[I> 2σ(I)]	0.0400
wR_2[I>2σ(I)]	0.1015[b]

[b] $w = 1/[s^2(F0)^2+(0.0516P)^2 +0.2150P]$, where $P = (F0^2 + 2Fc^2)/3$

Crystallographic data (excluding structural factors) for compound **8d** also has been deposited at the Cambridge Crystallographic Data Centre under the deposition number **CCDC 1009193.**