Supporting Information

Ruthenium-Catalyzed C–H Bond Oxygenations with Weakly-Coordinating Ketones

Vedhagiri S. Thirunavukkarasu and Lutz Ackermann,*

Institut für Organische und Bimolekulare Chemie, Georg-August-Universität,

Tammannstrasse 2, 37077 Göttingen, Germany

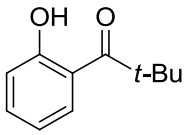
Lutz.Ackermann@chemie.uni-goettingen.de

General Remarks

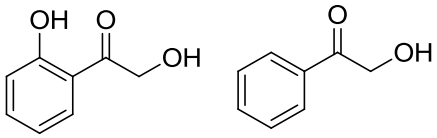
Catalytic reactions were carried out using pre-dried glassware. The following starting materials were synthesized according to previously described methods: **1f–1j**[1] and **1k–1r**.[2] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR and GC. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.040–0.063 mm, 70–230 mesh ASTM). All IR spectra were recorded on a BRUKER ALPHA-P spectrometer. MS: EI-MS: Finnigan MAT 95, 70 eV; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HR-MS): APEX IV 7T FTICR, Bruker Daltonic. M.p.: Stuart® Melting Point Apparatus SMP3 melting point apparatus, values are uncorrected. ^{1}H-, ^{13}C-, and ^{19}F- NMR-spectra were recorded at 300 (^{1}H), 75.5 {^{13}C, APT (Attached Proton Test)} and 283 MHz (^{19}F), respectively, on Varian Unity-300 and AMX 300 instruments in $CDCl_3$ solutions, if not otherwise specified, chemical shifts (δ) are given in ppm.

General Procedure: Ruthenium-Catalyzed Hydroxylation of Ketones 1

In a 20 mL pre-dried screw-capped sealed tube, ketone (**1**) (1.00 mmol), [Ru(O_2CMes)$_2$(*p*-cymene)] (1.0− 5.0 mol %) in TFA/TFAA (2.5 mL, 3:2) was stirred at 120 °C for 30 h. At ambient temperature, the reaction mixture was diluted with H_2O (75 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel to yield product **2**.

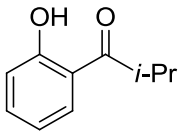


1-(2-Hydroxyphenyl)-2,2-dimethylpropan-1-one (2a): The representative procedure was followed using 2,2-dimethyl-1-phenylpropan-1-one (**1a**) (162 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2a** (151 mg, 85%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.69 (s, 1H), 8.02 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.41 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.84 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 1.45 (s, 9H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 212.1 (C_q), 163.6 (C_q), 135.3 (CH), 130.8 (CH), 119.2 (CH), 117.7 (CH), 117.4 (C_q), 44.5 (C_q), 28.7 (CH_3). IR (neat): 2975, 1627, 1443, 835 cm^{-1}. MS (EI) *m/z* (relative intensity): 178 ([M^+] 10), 121 (100), 77 (5). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}O_2^+$ 178.0994, found 178.0991.

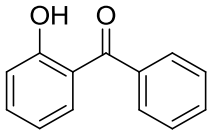


2b **2b'**

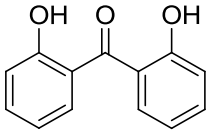
2-Hydroxy-1-(2'-hydroxyphenyl)ethanone (2b) and 2-Hydroxy-1-phenylethanone (2b'): The representative procedure was followed using acetophenone (**1b**) (120 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 9/1) yielded **2b** (3 mg, 2%) as a colorless solid and **2b'** (5 mg, 4%) as a colorless solid. **2b:** M.p. = 63–65 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 11.49 (s, 1H), 7.62 – 7.47 (m, 2H), 7.04 (ddd, *J* = 8.3, 1.2, 0.7 Hz, 1H), 6.93 (dd, *J* = 7.5, 3.0 Hz, 1H), 4.91 (d, *J* = 4.8 Hz, 2H), 3.38 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 202.7 (C_q), 161.9 (C_q), 137.2 (CH), 128.1 (CH), 119.5 (CH), 118.7 (CH), 116.6 (C_q), 64.5 (CH_2). IR (neat): 3419, 2915, 1686, 1612, 1581, 1406, 872 cm^{-1}. MS (ESI) *m/z* (relative intensity): 152 ([M^+] 20), 121 (100), 105 (50), 77 (40). HR-MS (EI) *m/z* calcd for $C_8H_8O_3^+$ 152.0473, found 152.0470. The spectral data are in accordance with those reported in the literature.[4] **2b':** M.p. = 73–75 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.72 – 7.58 (m, 1H), 7.51 (dd, *J* = 8.3, 7.2 Hz, 2H), 4.88 (s, 2H), 3.51 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 198.3 (C_q), 134.2 (CH), 133.4 (C_q), 128.9 (CH), 127.6 (CH), 65.4 (CH_2). IR (neat): 3071, 2935, 1616, 1591, 1406, 866 cm^{-1}. MS (EI) *m/z* (relative intensity): 136 ([M^+] 2), 121 (30), 105 (100), 77 (70). HR-MS (EI) *m/z* calcd for $C_8H_8O_2^+$ 136.0524, found 136.0525. The spectral data are in accordance with those reported in the literature.[3]



1-(2'-Hydroxyphenyl)-2-methylpropan-1-one (2c): The representative procedure was followed using 2-methyl-1-phenylpropan-1-one (**1c**) (148 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 98/2) yielded **2c** (21 mg, 13%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.52 (s, 1H), 7.79 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.94 – 6.84 (m, 1H), 3.62 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 210.8 (C_q), 163.1 (C_q), 136.1 (CH), 129.8 (CH), 118.8 (CH), 118.7 (CH), 118.1 (C_q), 34.9 (CH), 19.3 (CH_3). IR (neat): 2975, 1634, 1580, 1486, 820 cm^{-1}. MS (ESI) *m/z* (relative intensity): 187 ([M+Na$^+$] 90), 140 (15), 115 (25). HR-MS (ESI) *m/z* calcd for $C_{10}H_{12}O_2$+Na$^+$ 187.0735, found 187.0730. The spectral data are in accordance with those reported in the literature.[5]



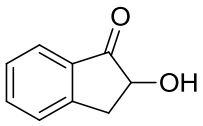
2d



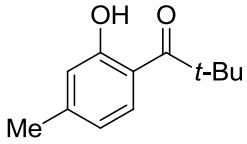
2d'

(2-Hydroxyphenyl)(phenyl)methanone (2d) and Bis(2-hydroxyphenyl)methanone (2d'): The representative procedure was followed using benzophenone (**1d**) (182 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2d** (53 mg, 28%) as a yellow viscous liquid and **2d'** (121 mg, 57%) as a pale yellow viscous liquid. **2d:** ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.06 (s, 1H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.55 – 7.44 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 201.5 (C_q), 163.1 (C_q), 137.8 (C_q), 136.3 (CH), 133.5 (CH), 131.6 (CH), 129.1 (CH), 128.3 (CH), 119.0 (C_q), 118.6 (CH), 118.3 (CH). IR (neat): 3059, 1624, 1598, 824 cm^{-1}. MS (EI) *m/z* (relative intensity): 198 ([M$^+$] 70), 197 ([M-H$^+$] 100), 121 (60), 77 (45). HR-MS (EI) *m/z* calcd for $C_{13}H_{10}O_2$ [M–H$^+$] 197.0603, found 197.0608. The spectral data are in accordance with those reported in the literature.[6] **2d':** ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 10.59 (s, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.52 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.94 (ddd, *J* = 7.4, 6.9, 1.6 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 202.3 (C_q), 161.7 (C_q), 135.9 (CH), 133.0 (CH), 119.8 (C_q), 118.8 (CH), 118.6 (CH). IR (neat): 3060, 1612, 1585, 1226, 840 cm^{-1}.

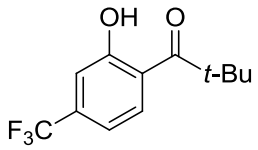
MS (EI) *m/z* (relative intensity): 214 ([M^+] 55), 213 ([M–H^+] 45), 121 (100). HR-MS (EI) *m/z* calcd for $C_{13}H_{10}O_3$ [M− H^+] 213.0552, found 213.0550.



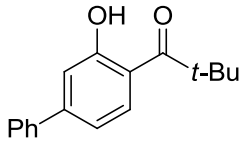
2-Hydroxy-2,3-dihydro-1*H*-inden-1-one (2e): The representative procedure was followed using 2,3-dihydro-1*H*-inden-1-one (**1e**) (132 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 7/3) yielded **2e** (101 mg, 68%) as a yellow viscous liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.50 – 7.40 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 4.56 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.58 (dd, *J* = 16.7, 8.0 Hz, 1H), 3.49 (s, 1H), 3.02 (dd, *J* = 16.6, 5.1 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 206.6 (C_q), 150.9 (C_q), 135.8 (CH), 134.0 (C_q), 128.0 (CH), 126.7 (CH), 124.4 (CH), 74.2 (CH), 35.1 (CH_2). IR (neat): 3400, 1702, 1606, 1466, 991 cm^{-1}. MS (EI) *m/z* (relative intensity): 148 ([M^+] 100), 119 (65), 65 (30). HR-MS (ESI) *m/z* calcd for $C_9H_8O_2$+Na^+ 171.0422, found 171.0419. The spectral data are in accordance with those reported in the literature.[7]



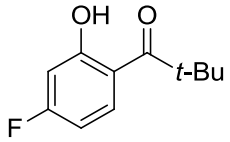
1-(2'-Hydroxy-4'-methylphenyl)-2,2-dimethylpropan-1-one (2f): The representative procedure was followed using 2,2-dimethyl-1-(*p*-tolyl)propan-1-one (**1f**) (171 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 98/2) yielded **2f** (154 mg, 80%) as a yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.79 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 6.81 (s, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 2.33 (s, 3H), 1.44 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.5 (C_q), 163.9 (C_q), 146.7 (C_q), 130.7 (CH), 119.2 (CH), 119.0 (CH), 115.1 (C_q), 44.4 (C_q), 28.7 (CH_3), 21.7 (CH_3). IR (neat): 2973, 1629, 1568, 867 cm^{-1}. MS (EI) *m/z* (relative intensity): 192 ([M^+] 10), 135 (100). HR-MS (EI) *m/z* calcd for $C_{12}H_{16}O_2^+$ 192.1150, found 192.1143.



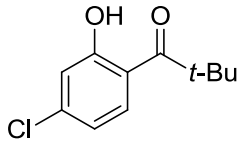
1-{2'-Hydroxy-4'-(trifluoromethyl)phenyl}-2,2-dimethylpropan-1-one (2g): The representative procedure was followed using 2,2-dimethyl-1-{4'-(trifluoromethyl)phenyl}propan-1-one (**1g**) (115 mg, 0.50 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2g** (78 mg, 63%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.63 (s, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.26 (dd, J = 1.3, 0.6 Hz, 1H), 7.06 (ddd, J = 8.6, 1.9, 0.6 Hz, 1H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.9 (C_q), 163.4 (C_q), 136.2 (C_q, $J_{C\text{-}F}$ = 32.8 Hz), 131.5 (CH), 121.2 (C_q), 125.0 (C_q, $J_{C\text{-}F}$ = 259.9 Hz), 119.5 (C_q), 116.7 (CH, $J_{C\text{-}F}$ = 3.9 Hz), 114.1 (CH, $J_{C\text{-}F}$ = 3.6 Hz), 44.9 (C_q), 28.5 (CH_3). ^{19}F-NMR (283 MHz, $CDCl_3$) δ = -64.1 (s). IR (neat): 2979, 1642, 1574, 882 cm^{-1}. MS (EI) *m/z* (relative intensity): 246 ([M^+] 5), 189 (35), 98 (20), 57 (100). HR-MS (EI) *m/z* calcd for $C_{12}H_{13}F_3O_2$ [M–H^+] 245.0789, found 245.0795.



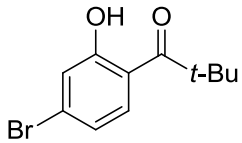
1-(3-Hydroxy-[1,1'-biphenyl]-4-yl)-2,2-dimethylpropan-1-one (2h): The representative procedure was followed using 1-([1,1'-biphenyl]-4-yl)-2,2-dimethylpropan-1-one (**1h**) (119 mg, 0.50 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2h** (72 mg, 57%) as a colorless solid. M.p. = 72–74 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.89 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.64 (d, J = 6.6 Hz, 2H), 7.56 – 7.38 (m, 3H), 7.26 (s, 1H), 7.11 (dd, J = 8.6, 2.0 Hz, 1H), 1.49 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.7 (C_q), 164.0 (C_q), 147.8 (C_q), 139.3 (C_q), 131.3 (CH), 128.9 (CH), 128.5 (CH), 127.1 (CH), 117.2 (CH), 116.7 (CH), 116.2 (C_q), 44.6 (C_q), 28.7 (CH_3). IR (neat): 2974, 1627, 1597, 1476, 867 cm^{-1}. MS (EI) *m/z* (relative intensity): 254 ([M^+] 10), 197 (100) 139 (15), 57 (5). HR-MS (ESI) *m/z* calcd for $C_{17}H_{18}O_2$ [M–H^+] 253.1229, found 253.1225.



1-(4'-Fluoro-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2i): The representative procedure was followed using 1-(4'-fluorophenyl)-2,2-dimethylpropan-1-one (**1i**) (180 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 96/4) yielded **2i** (158 mg, 81%) as a yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 13.08 (s, 1H), 8.03 (ddd, J = 9.2, 6.6, 1.2 Hz, 1H), 6.66 (ddd, J = 10.3, 2.7, 1.3 Hz, 1H), 6.61 – 6.49 (m, 1H), 1.43 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.0 (C_q), 166.5 (C_q, $J_{C\text{-}F}$ = 13.9 Hz), 164.6 (C_q, $J_{C\text{-}F}$ = 256.0 Hz), 133.2 (CH, $J_{C\text{-}F}$ = 11.3 Hz), 114.4 (C_q, $J_{C\text{-}F}$ = 2.3 Hz), 106.0 (CH, $J_{C\text{-}F}$ = 22.2 Hz), 105.5 (CH, $J_{C\text{-}F}$ = 23.2 Hz), 44.6 (C_q), 28.7 (CH_3). ^{19}F-NMR (283 MHz, $CDCl_3$) δ = - (100.8-100.9) (m). IR (neat): 2977, 1632, 1593, 850 cm^{-1}. MS (EI) *m/z* (relative intensity): 196 ([M^+] 10), 167 (25), 139 (100). HR-MS (EI) *m/z* calcd for $C_{11}H_{13}FO_2^+$ 196.0900, found 196.0903.

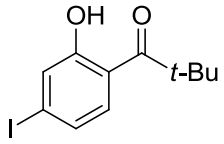


1-(4'-Chloro-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2j): The representative procedure was followed using 1-(4'-chlorophenyl)-2,2-dimethylpropan-1-one (**1j**) (196 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2j** (177 mg, 83%) as a pale yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.82 (s, 1H), 7.91 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 2.2 Hz, 1H), 6.80 (dd, J = 8.8, 2.2 Hz, 1H), 1.41 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.4 (C_q), 164.5 (C_q), 140.9 (C_q), 131.8 (CH), 119.2 (CH), 118.4 (CH), 115.9 (C_q), 44.6 (C_q), 28.9 (CH_3). IR (neat): 2977, 1625, 1596, 860 cm^{-1}. MS (EI) *m/z* (relative intensity): 212 ([M^+] 50), 155 (100), 57 (22). MS (EI) *m/z* (relative intensity): HR-MS (EI) *m/z* calcd for $C_{11}H_{13}ClO_2^+$ 212.0604, found 212.0599.

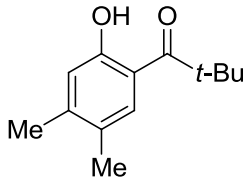


1-(4'-Bromo-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2k): The representative procedure was followed using 1-(4'-bromophenyl)-2,2-dimethylpropan-1-one (**1k**) (241 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2k** (178 mg, 69%) as a colorless solid.

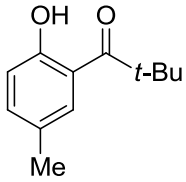
M.p. = 66–68 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.82 (s, 1H), 7.86 (dd, J = 8.8, 0.8 Hz, 1H), 7.20 (dd, J = 2.1, 1.0 Hz, 1H), 6.98 (ddd, J = 8.8, 2.1, 0.9 Hz, 1H), 1.43 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.6 (C_q), 164.3 (C_q), 131.7 (CH), 129.5 (C_q), 122.4 (CH), 121.3 (CH), 116.2 (C_q), 44.6 (C_q), 28.6 (CH_3). IR (neat): 2977, 1715, 1626, 1588, 862 cm^{-1}. MS (EI) *m/z* (relative intensity): 256 ([M^+] 10), 199 (100), 144 (10), 57 (45). HR-MS (ESI) *m/z* calcd for $C_{11}H_{13}BrO_2^+$ 256.0099, found 256.0093.



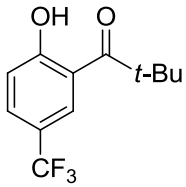
1-(4'-Iodo-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2l): The representative procedure was followed using 1-(4'-iodophenyl)-2,2-dimethylpropan-1-one (**1l**) (144 mg, 0.50 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2l** (118 mg, 78%) as a colorless solid. M.p. = 78–80 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.72 (s, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.19 (dd, J = 8.6, 1.8 Hz, 1H), 1.43 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.9 (C_q), 163.6 (C_q), 131.4 (CH), 128.6 (CH), 127.1 (CH), 116.7 (C_q), 102.5 (C_q), 44.7 (C_q), 28.6 (CH_3). IR (neat): 3134, 2976, 1673, 1579, 860 cm^{-1}. MS (EI) *m/z* (relative intensity): 304 ([M+H^+] 10), 246 (100), 120 (15), 57 (15). HR-MS (EI) *m/z* calcd for $C_{11}H_{13}IO_2^+$ 303.9960, found 303.9967.



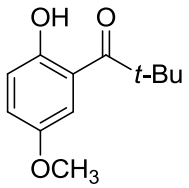
1-(2'-Hydroxy-4',5'-dimethylphenyl)-2,2-dimethylpropan-1-one (2m): The representative procedure was followed using 1-(3',4'-dimethylphenyl)-2,2-dimethylpropan-1-one (**1m**) (196 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2m** (138 mg, 67%) as a yellow solid. M.p. = 61–63 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.61 (s, 1H), 7.75 (s, 1H), 6.80 (s, 1H), 2.24 (s, 3H), 2.22 (s, 3H), 1.44 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.4 (C_q), 162.0 (C_q), 145.6 (C_q), 130.9 (CH), 125.8 (C_q), 119.6 (CH), 115.3 (C_q), 44.4 (C_q), 28.8 (CH_3), 20.2 (CH_3), 19.1 (CH_3). IR (neat): 2954, 1632, 1599, 854 cm^{-1}. MS (EI) *m/z* (relative intensity): 206 ([M^+] 10), 149 (90), 57 (25). HR-MS (ESI) *m/z* calcd for $C_{13}H_{18}O_2^+$ 206.1307, found 206.1304.



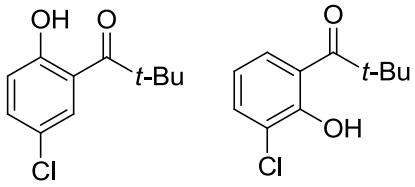
1-(2-Hydroxy-5-methylphenyl)-2,2-dimethylpropan-1-one (2n): The representative procedure was followed using 2,2-dimethyl-1-(*m*-tolyl)propan-1-one (**1n**) (176 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2n** (158 mg, 82%) as a pale yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.50 (s, 1H), 7.79 (d, J = 1.9 Hz, 1H), 7.24 (dd, J = 8.8, 1.9 Hz, 1H), 6.92 (dd, J = 8.5, 1.3 Hz, 1H), 2.31 (s, 3H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 212.0 (C_q), 161.5 (C_q), 136.3 (CH), 130.5 (CH), 126.6 (C_q), 119.0 (CH), 117.2 (C_q), 44.6 (C_q), 28.8 (CH_3), 20.8 (CH_3). IR (neat): 2974, 1632, 1421, 876 cm^{-1}. MS (EI) *m/z* (relative intensity): 192 ([M^+] 10), 135 (100), 107 (10), 77 (15). HR-MS (ESI) *m/z* calcd for $C_{12}H_{16}O_2$+H^+ 193.1229, found 193.1225.



1-{2'-Hydroxy-5'-(trifluoromethyl)phenyl}-2,2-dimethylpropan-1-one (2o): The representative procedure was followed using 2,2-dimethyl-1-{3'-(trifluoromethyl)phenyl}propan-1-one (**1o**) (230 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2o** (97 mg, 39%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.93 (d, J = 0.4 Hz, 1H), 8.27 (dd, J = 2.2, 1.0 Hz, 1H), 7.63 (dd, J = 8.8, 2.3 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.7 (C_q), 166.0 (C_q), 131.7 (CH, $J_{C\text{-}F}$ = 3.4 Hz), 128.3 (CH, $J_{C\text{-}F}$ = 4.1 Hz), 122.0 (C_q, $J_{C\text{-}F}$ = 269.0 Hz), 120.2 (CH), 119.9 (C_q, $J_{C\text{-}F}$ = 33.1 Hz), 116.6 (C_q), 44.8 (C_q), 28.6 (CH_3). ^{19}F-NMR (283 MHz, $CDCl_3$) δ = -61.9 (s). IR (neat): 2980, 1640, 1592, 882 cm^{-1}. MS (EI) *m/z* (relative intensity): 246 ([M^+] 10), 189 (100), 161 (15), 57 (400). HR-MS (EI) *m/z* calcd for $C_{12}H_{13}F_3O_2^+$ 246.0868, found 246.0873.

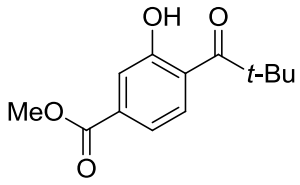


1-(2-Hydroxy-5-methoxyphenyl)-2,2-dimethylpropan-1-one (2p): The representative procedure was followed using 1-(3-methoxyphenyl)-2,2-dimethylpropan-1-one (**1p**) (176 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2p** (158 mg, 76%) as a yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.20 (s, 1H), 7.48 (d, J = 3.0 Hz, 1H), 7.07 (dd, J = 9.1, 3.0 Hz, 1H), 6.94 (d, J = 9.1 Hz, 1H), 3.78 (s, 3H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.5 (C_q), 157.8 (C_q), 150.6 (C_q), 122.7 (CH), 119.8 (CH), 117.0 (C_q), 114.5 (CH), 55.9 (CH_3), 44.6 (C_q), 28.7 (CH_3). IR (neat): 2974, 1636, 1608, 1483, 879 cm^{-1}. MS (EI) *m/z* (relative intensity): 208 ([M^+] 15), 151 (100), 43 (20). HR-MS (ESI) *m/z* calcd for $C_{12}H_{16}O_3^+$ 208.1099, found 208.1101.

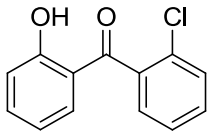


1-(5'-Chloro-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2q') and 1-(3'-Chloro-2'-hydroxyphenyl)-2,2-dimethylpropan-1-one (2q''): The representative procedure was followed using 1-(3'-chlorophenyl)-2,2-dimethylpropan-1-one (**1q**) (196 mg, 1.00 mmol). Purification by thin layer chromatography (*n*-hexane/EtOAc: 97/3) yielded **2q'** (115 mg, 54%) as a colorless liquid and yielded **2q''** (34 mg, 16%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.55 (s, 1H), 7.96 (d, J = 2.5 Hz, 1H), 7.36 (dd, J = 8.9, 2.5 Hz, 1H), 6.96 (d, J = 8.9 Hz, 1H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 211.2 (C_q), 162.1 (C_q), 135.2 (CH), 130.0 (CH), 122.4 (C_q), 120.8 (CH), 117.9 (C_q), 44.7 (C_q), 28.6 (CH_3). IR (neat): 2977, 1625, 1596, 860 cm^{-1}. MS (EI) *m/z* (relative intensity): 212 ([M^+] 20), 155 (100), 57 (22). MS (EI) *m/z* (relative intensity): HR-MS (EI) *m/z* calcd for $C_{11}H_{13}ClO_2^+$ 212.0604, found 212.0603. **2q'':** ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 13.18 (s, 1H), 7.93 (dd, J = 8.3, 1.5 Hz, 1H), 7.51 (dd, J = 7.9, 1.5 Hz, 1H), 6.80 (dd, J = 8.3, 7.9 Hz, 1H), 1.43 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 212.1 (C_q), 159.2 (C_q), 135.3 (CH), 129.2 (CH), 123.6 (C_q), 118.6 (C_q), 117.8 (CH), 44.9 (C_q), 28.7 (CH_3). IR (neat): 2976, 1632, 1602, 860 cm^{-1}. MS (EI) *m/z* (relative intensity): 212

([M^+] 20), 155 (100), 57 (22). MS (EI) *m/z* (relative intensity): HR-MS (EI) *m/z* calcd for $C_{11}H_{13}ClO_2^+$ 212.0604, found 212.0603.

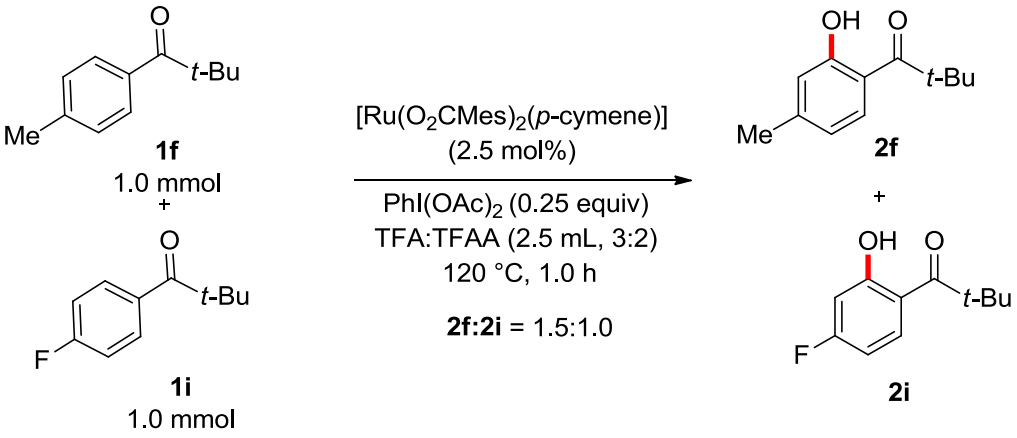


Methyl 3-hydroxy-4-pivaloylbenzoate (2r): The representative procedure was followed using methyl 4-pivaloylbenzoate (**1r**) (220 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 97/3) yielded **2r** (145 mg, 61%) as a colourless solid. M.p. = 73–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 12.46 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 212.0 (C_q), 165.8 (C_q), 163.1 (C_q), 135.5 (C_q), 130.7 (CH), 120.5 (CH), 120.2 (C_q), 118.2, (CH), 52.4 (CH_3), 44.8 (C_q), 28.5 (CH_3). IR (neat): 2981, 1717, 1638, 1562, 1428, 794 cm^{-1}. MS (EI) *m/z* (relative intensity): 236 ([M^+] 7), 179 (100), 136 (10), 57 (30). HR-MS (EI) *m/z* calcd. for $C_{13}H_{16}O_4^+$ 236.1049, found 236.1048.



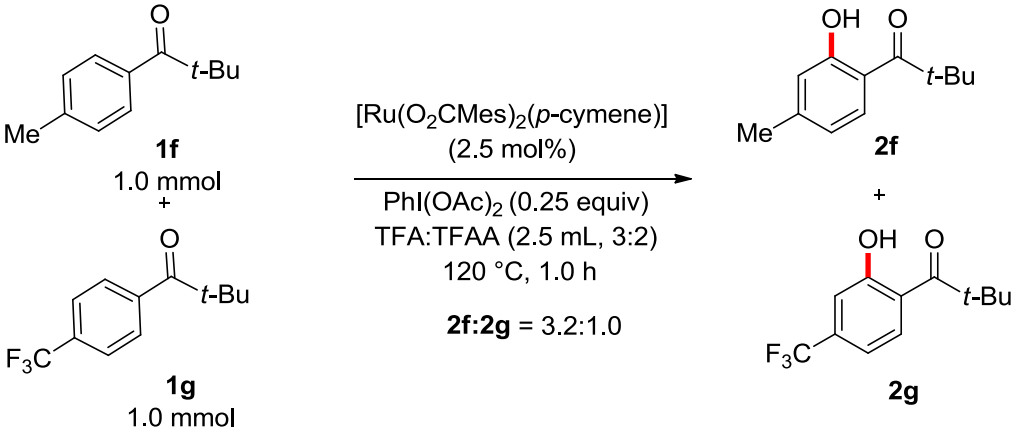
(2-Chlorophenyl)(2-hydroxyphenyl)methanone (2s): The representative procedure was followed using (2-chlorophenyl)(phenyl)methanone (**1s**) (216 mg, 1.00 mmol). Purification by thin layer chromatography (*n*-hexane/EtOAc: 97/3) yielded **2s** (108 mg, 47%) as a yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 11.96 (s, 1H), 7.57 – 7.32 (m, 5H), 7.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.83 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 200.6 (C_q), 163.2 (C_q), 137.3 (C_q), 137.2 (CH), 133.5 (CH), 131.2 (CH), 130.8 (CH), 130.1 (C_q), 128.5 (CH), 126.7 (CH), 119.3 (C_q), 119.1 (CH), 118.3 (CH). IR (neat): 3059, 1624, 1598, 824 cm^{-1}. MS (EI) *m/z* (relative intensity): 198 ([M^+] 70), 197 ([M-H^+] 100), 121 (60), 77 (45). HR-MS (EI) *m/z* calcd for $C_{13}H_9ClO_2$ [M–H^+] 231.0213, found 231.0219.

Intermolecular Competition Experiments between Ketones 1f and 1i



The mixture of 2,2-dimethyl-1-(*p*-tolyl)propan-1-one (**1f**), (176 mg, 1.00 mmol), 1-(4'-fluorophenyl)-2,2-dimethylpropan-1-one (**1i**), (180 mg, 1.00 mmol), [$Ru(O_2CMes)_2$(*p*-cymene)] (14 mg, 2.5 mol %) and $PhI(OAc)_2$ (161 mg, 0.25 equiv) in TFA/TFAA (2.5 mL, 3:2) was stirred at 120 °C under N_2 for 1 h. The reaction mixture was diluted with H_2O (75 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the ratio of products **2f:2i** was found to be 1.5:1.0 by ^{1}H-NMR spectroscopy.

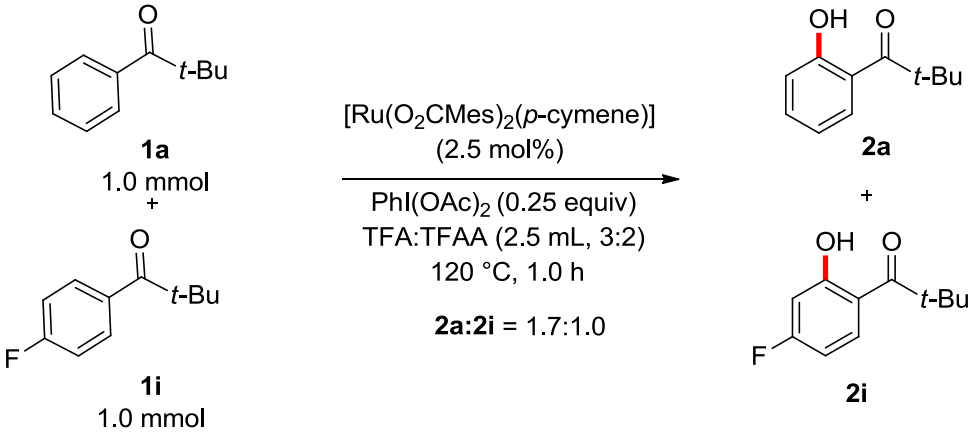
Intermolecular Competition Experiments between Ketones 1f and 1g



The mixture of 2,2-dimethyl-1-(*p*-tolyl)propan-1-one (**1f**), (176 mg, 1.00 mmol), 2,2-dimethyl-1-(4'-(trifluoromethyl)phenyl)propan-1-one (**1g**), (230 mg, 1.00 mmol), [$Ru(O_2CMes)_2$(*p*-cymene)] (14 mg, 2.5 mol %) and $PhI(OAc)_2$ (161 mg, 0.25 equiv) in TFA/TFAA (2.5 mL, 3:2) was stirred at 120 °C

under N_2 for 1 h. The reaction mixture was diluted with H_2O (75 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the ratio of products **2f:2g** was found to be 3.2:1.0 by ^{1}H-NMR spectroscopy.

Intermolecular Competition Experiments between Ketones 1a and 1i



The mixture of 2,2-dimethyl-1-phenylpropan-1-one (**1a**), (162 mg, 1.00 mmol), 1-(4'-fluorophenyl)-2,2-dimethylpropan-1-one (**1i**), (180 mg, 1.00 mmol), [Ru(O_2CMes)$_2$(*p*-cymene)] (14 mg, 2.5 mol %) and PhI(OAc)$_2$ (161 mg, 0.25 equiv) in TFA/TFAA (2.5 mL, 3:2) was stirred at 120 °C under N_2 for 1 h. The reaction mixture was diluted with H_2O (75 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the ratio of products **2a:2i** was found to be 1.7:1.0 by ^{1}H-NMR spectroscopy.

References

1. Ushijima, S.; Dohi, S.; Moriyama, K.; Togo, H. *Tetrahedron* **2012**, *68*, 1436−1442.

2. Fujihara, T.; Semba, K.; Terao, J.; Tsuji, Y. *Angew. Chem. Int. Ed.* **2010**, *49*, 1472–1476.

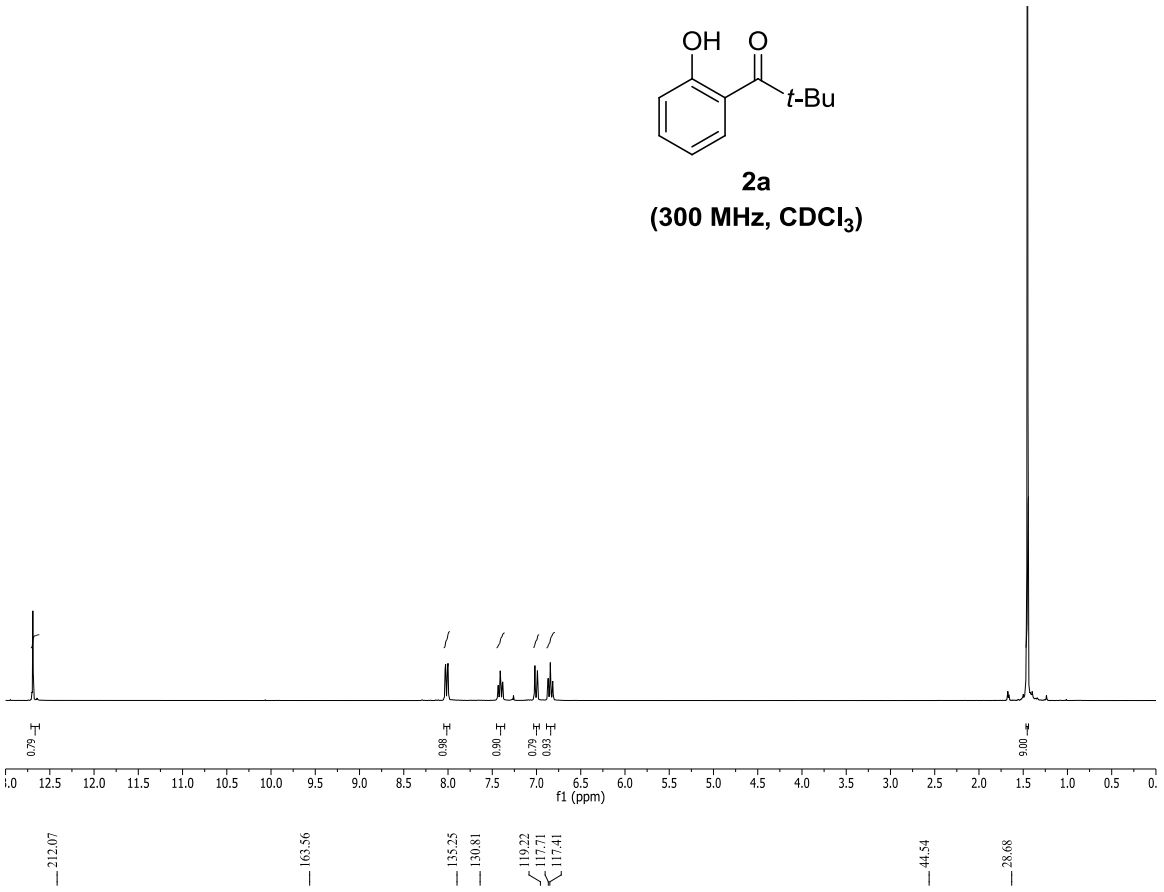
3. Mercier, E. A.; Smith, C. D.; Parvez, M.; Back, T. G. *J. Org. Chem.* **2012**, *77*, 3508−3517.

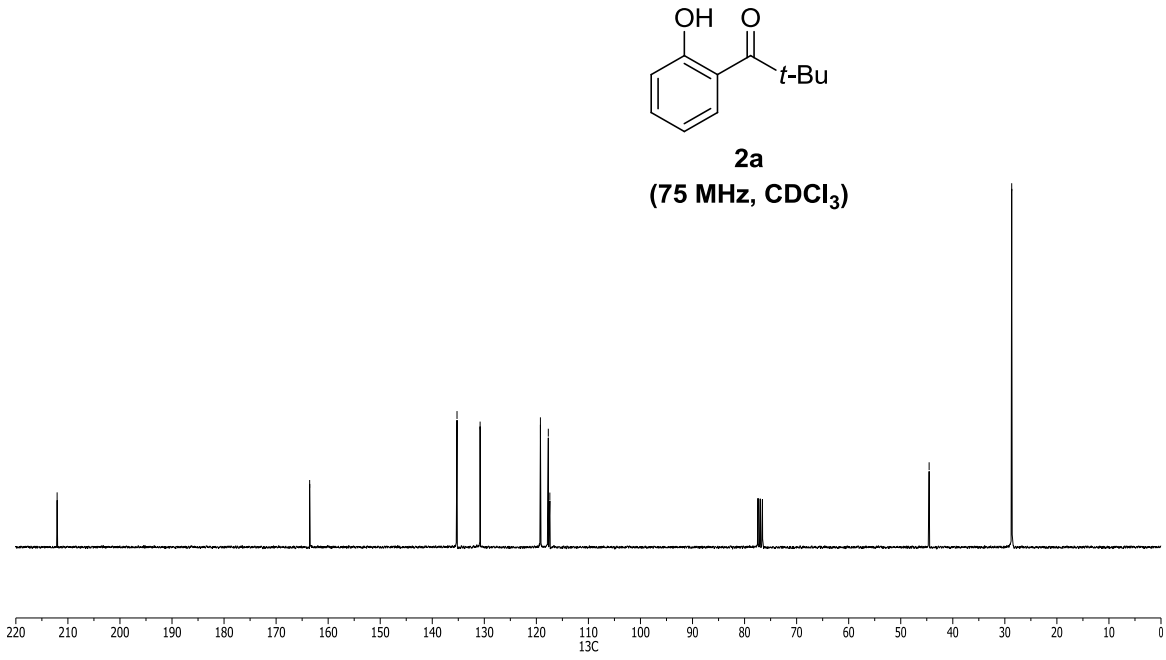
4. Donnelly, J. A.; Kerr, P. A.; O'Boyle, P. *Tetrahedron* **1973**, *29*, 3979−3983.

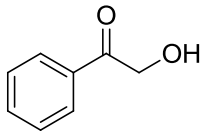
5. Cimarelli, C.; Palmieri, G. *Tetrahedron* **1998**, *54*, 15711−15720.

6. Rao, H.; Li, C.-J. *Angew.Chem. Int. Ed.* **2011**, *50*, 8936−8939.

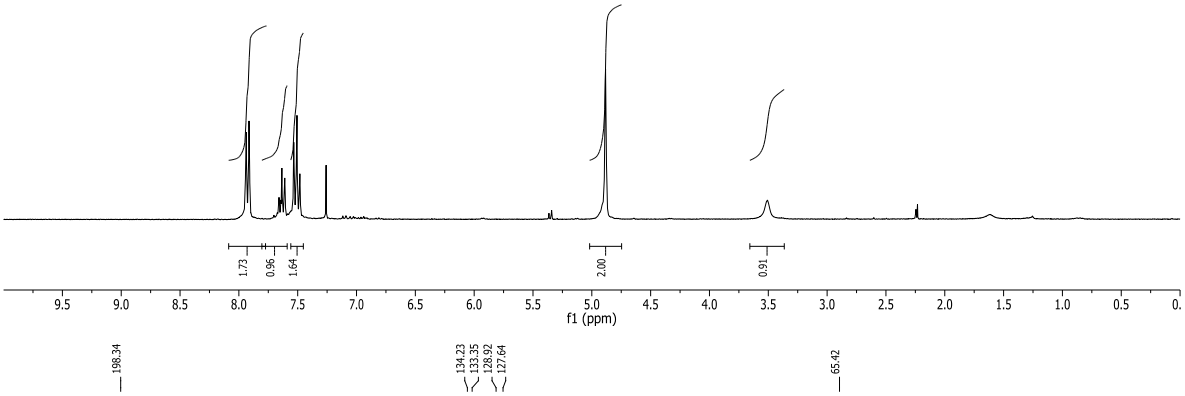
7. Chen, C.; Feng, X.; Zhang, G.; Zhao, Q.; Huang, G. *Synthesis* **2008**, 3205–3208.

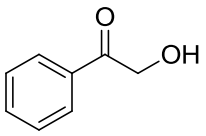

OH
O
t-Bu
2a
(300 MHz, CDCl3)
0.79
0.98
0.90
0.79
0.93
9.00
f1 (ppm)
212.07
163.56
135.25
130.81
119.22
117.71
117.41
44.54
28.68


OH
O
t-Bu
2a
(75 MHz, CDCl3)
13C

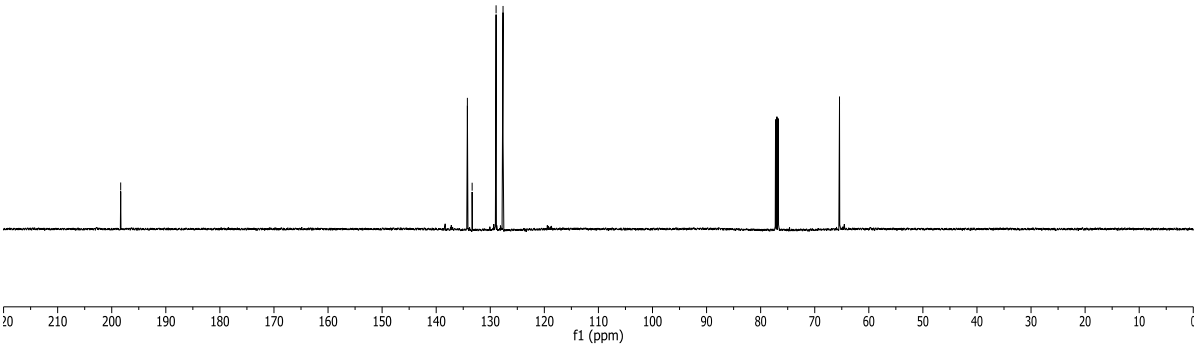


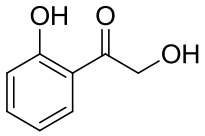
2b'
(300 MHz, $CDCl_3$)





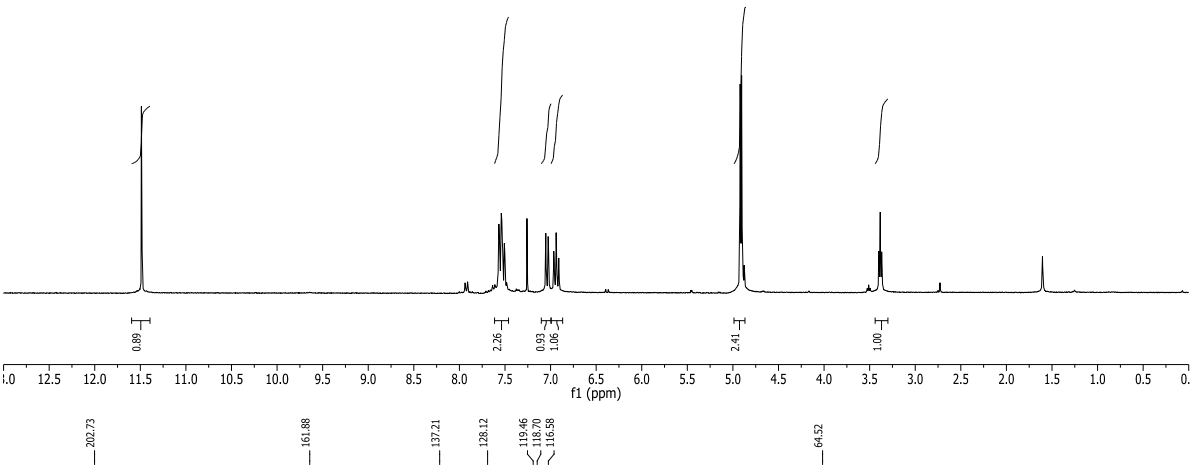
2b'
(75 MHz, $CDCl_3$)

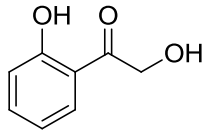




2b

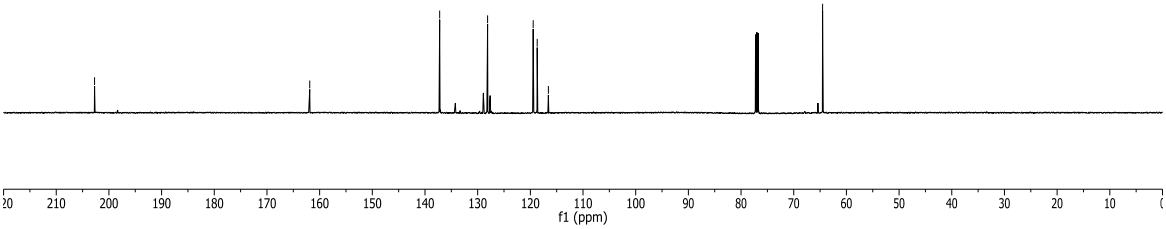
(300 MHz, $CDCl_3$)

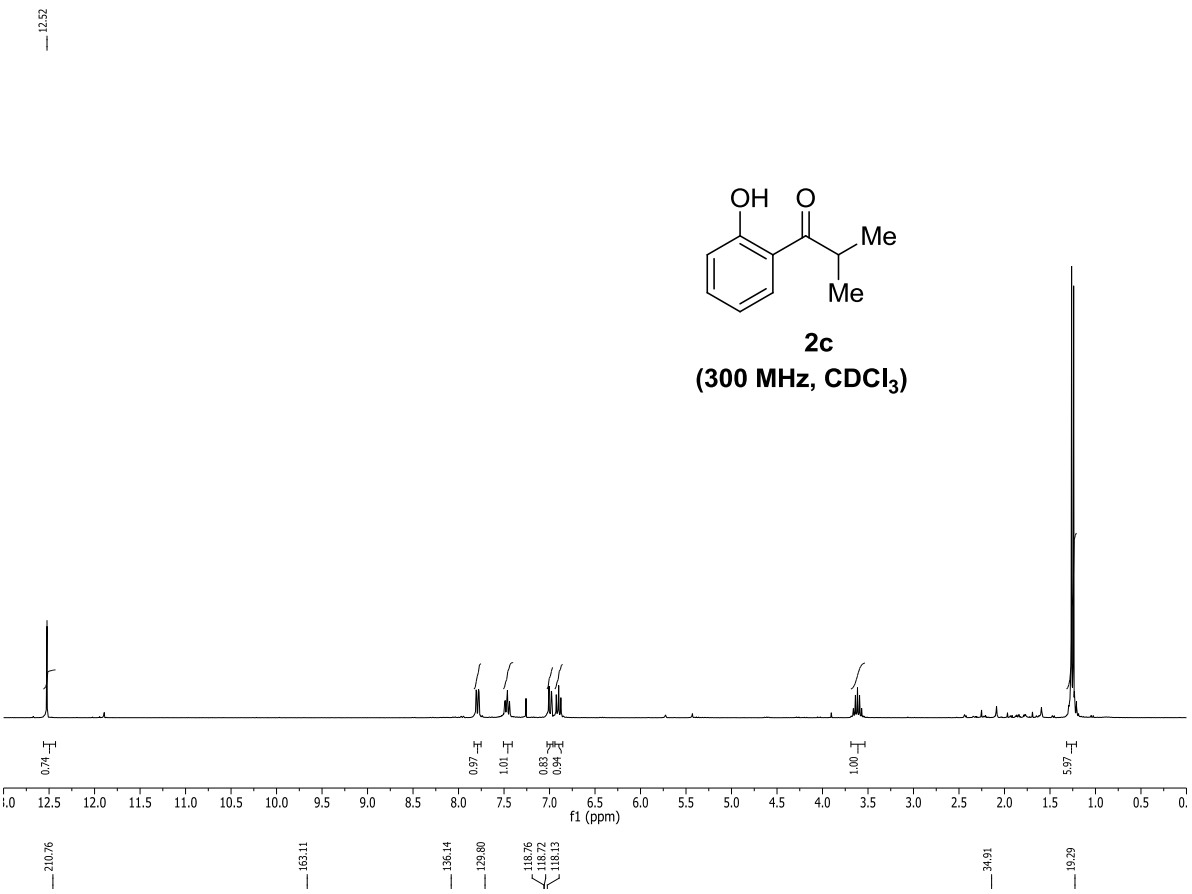




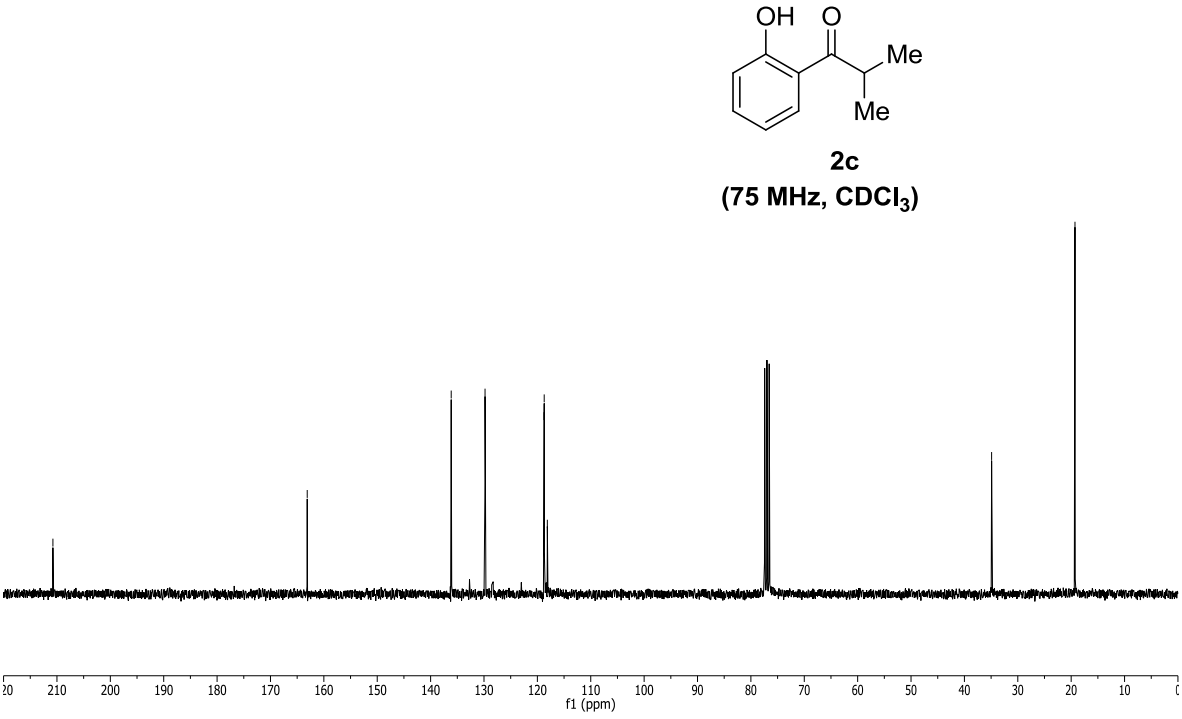
2b

(75 MHz, $CDCl_3$)

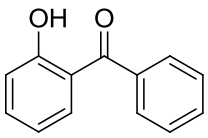




2c
(300 MHz, $CDCl_3$)

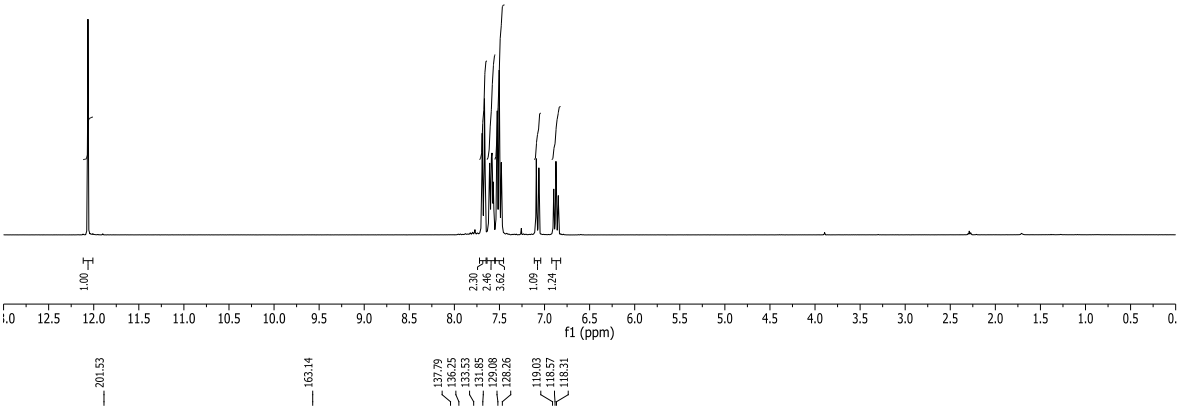


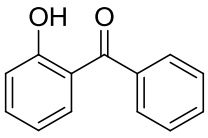
2c
(75 MHz, $CDCl_3$)



2d

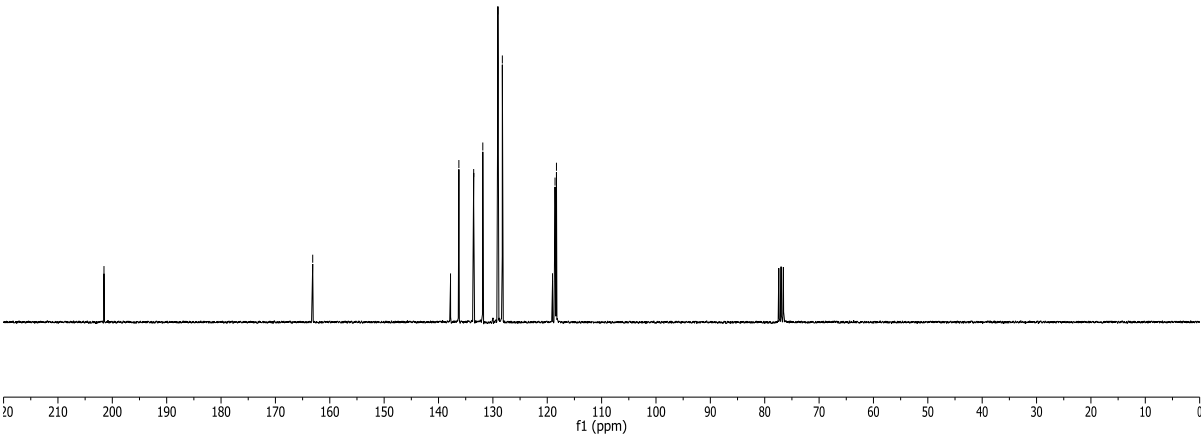
(300 MHz, $CDCl_3$)

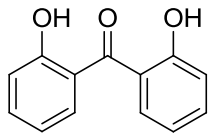




2d

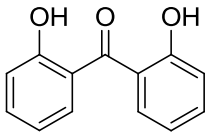
(75 MHz, $CDCl_3$)





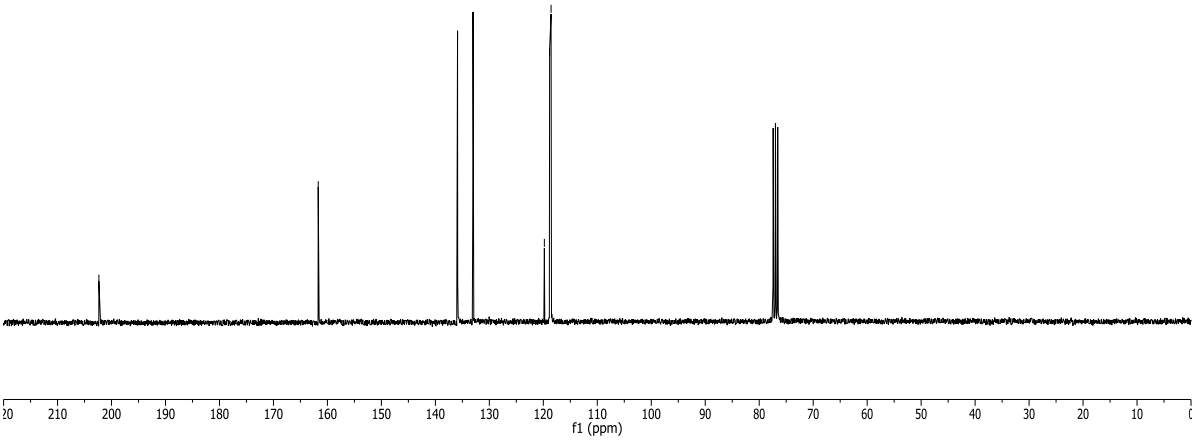
2d'

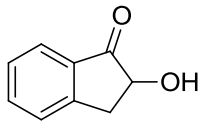
(300 MHz, $CDCl_3$)



2d'

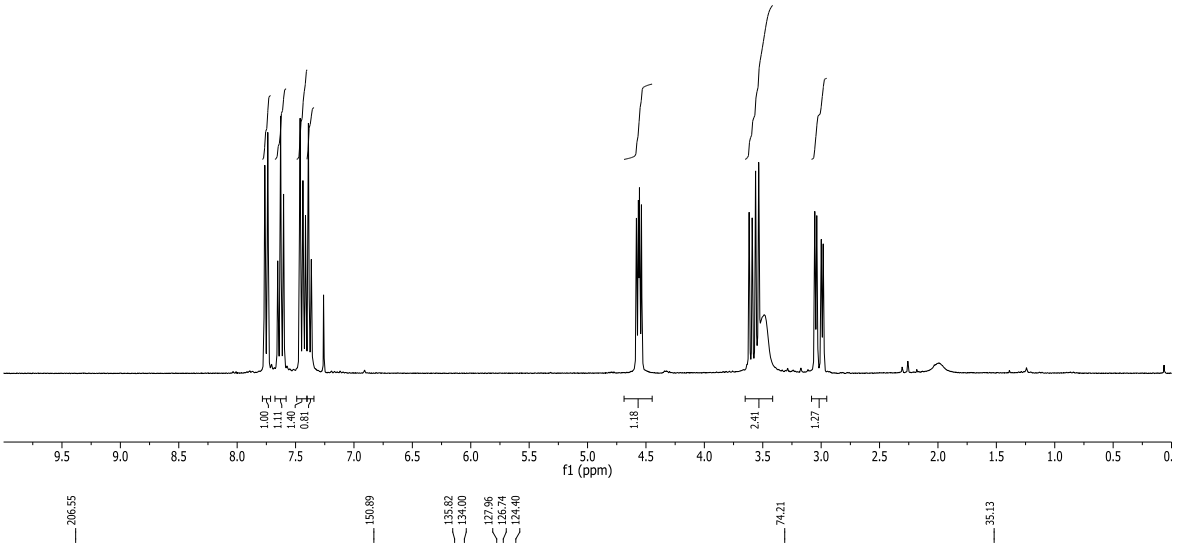
(75 MHz, $CDCl_3$)

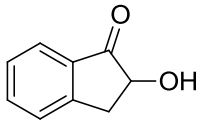




2e

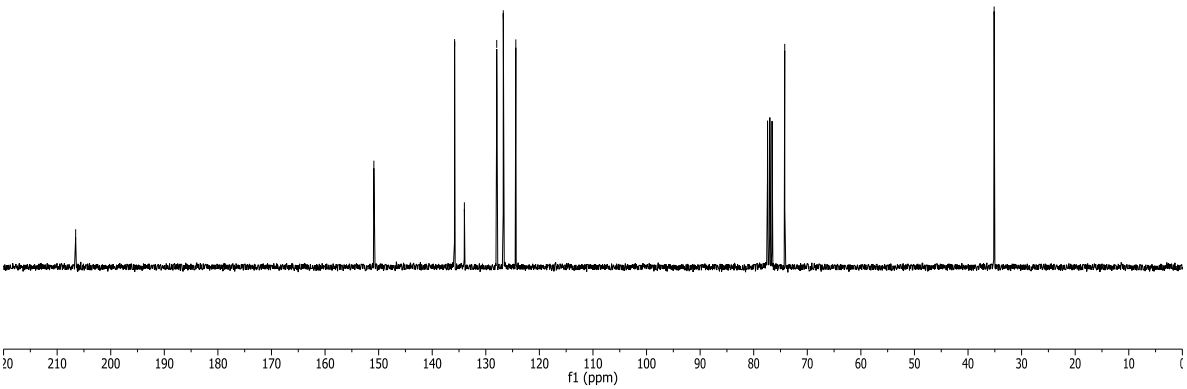
(300 MHz, $CDCl_3$)

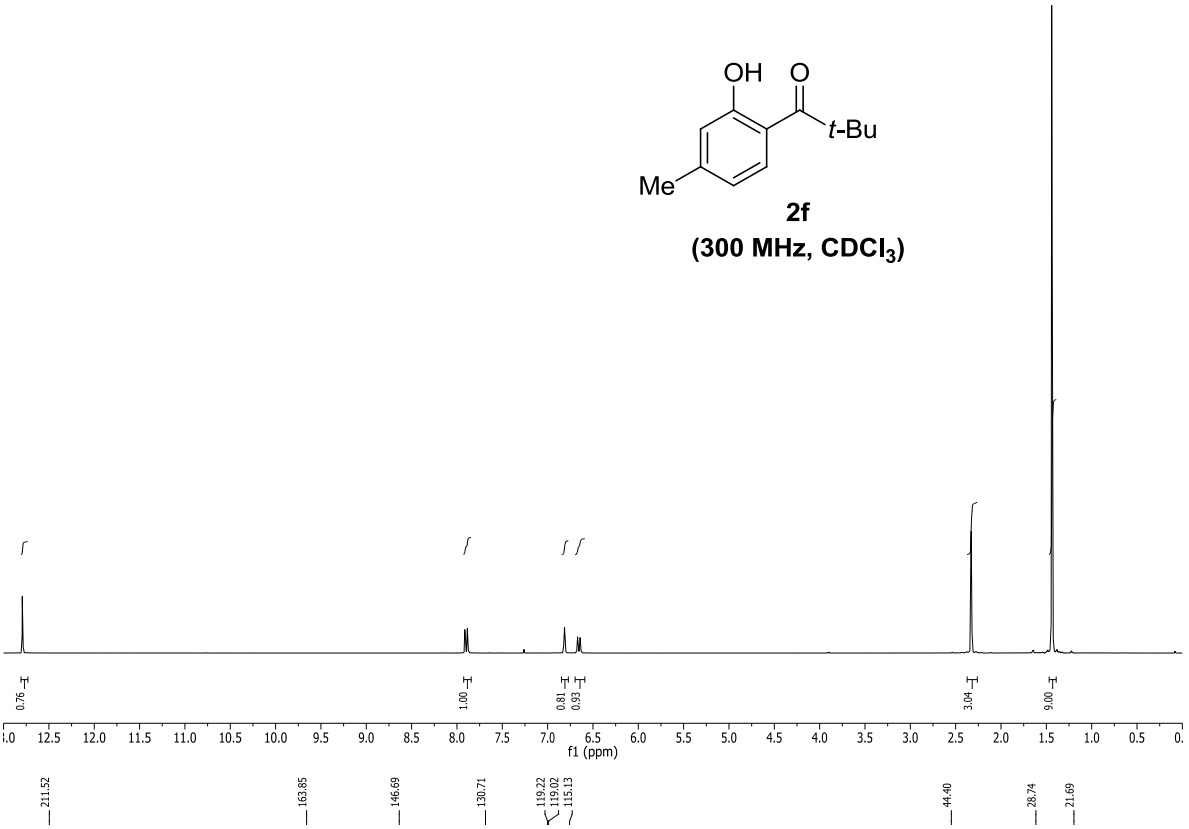




2e

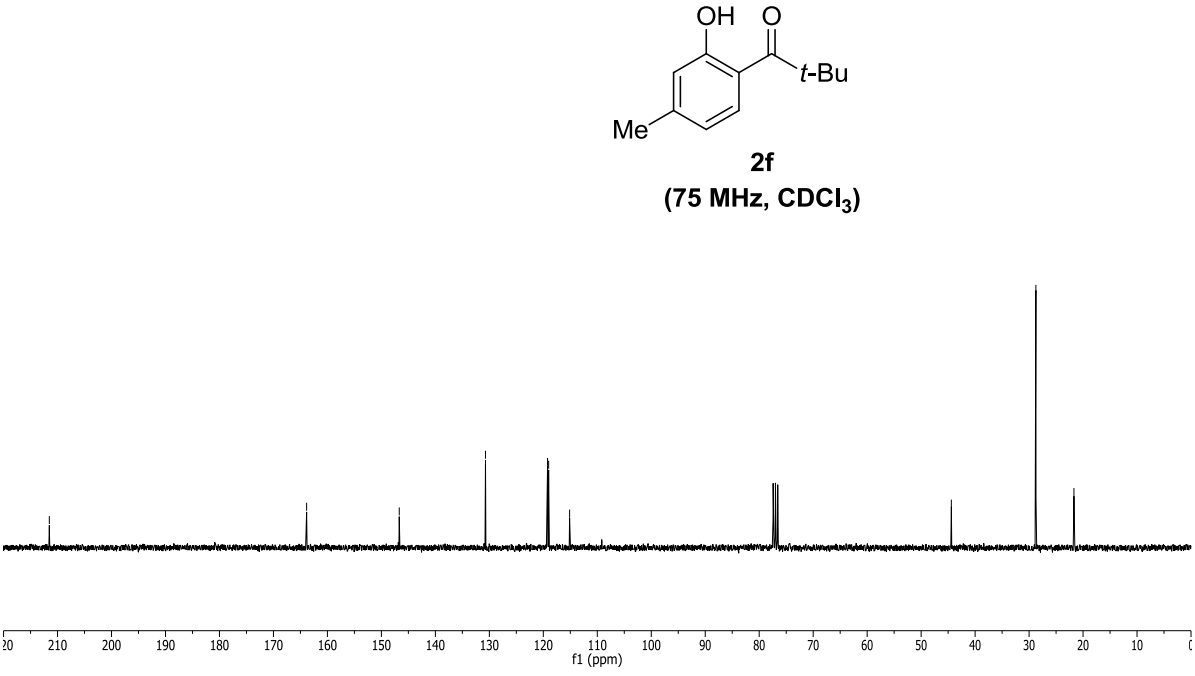
(75 MHz, $CDCl_3$)





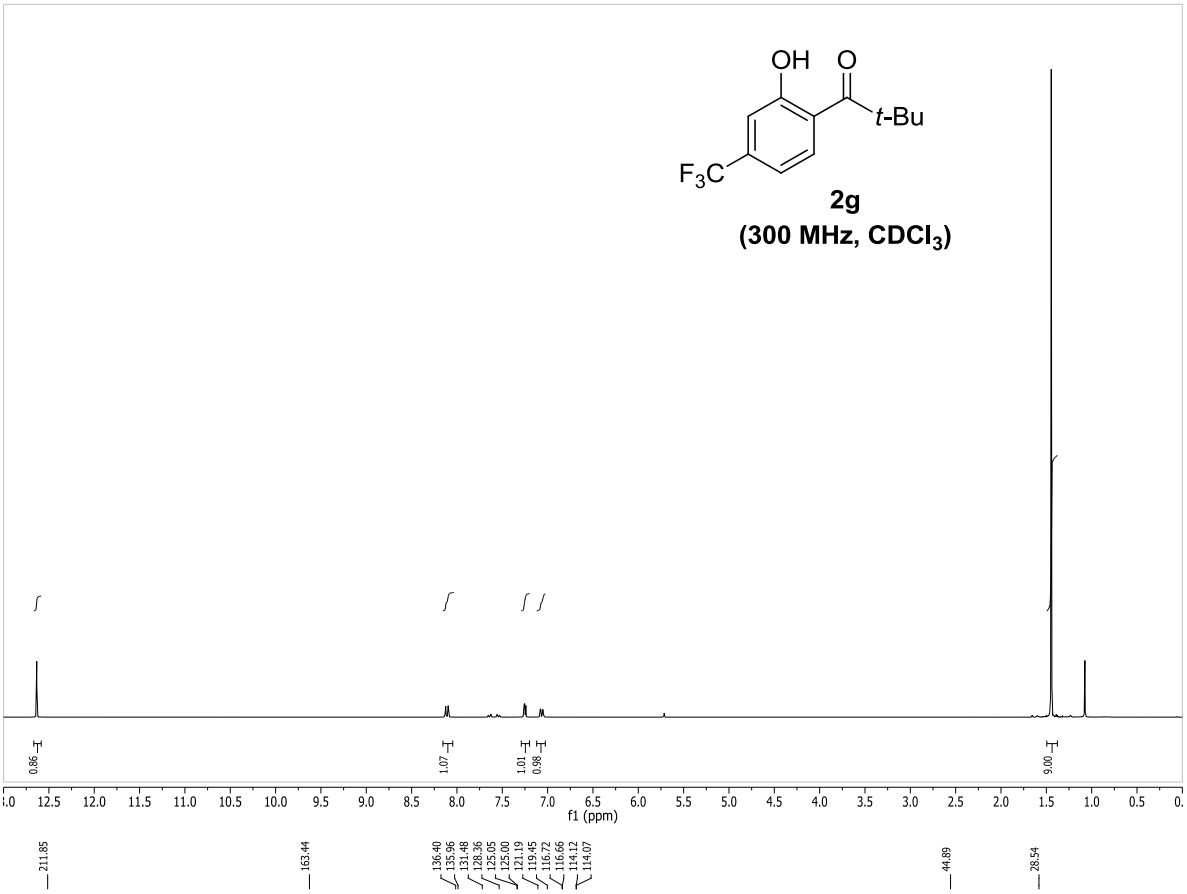
2f

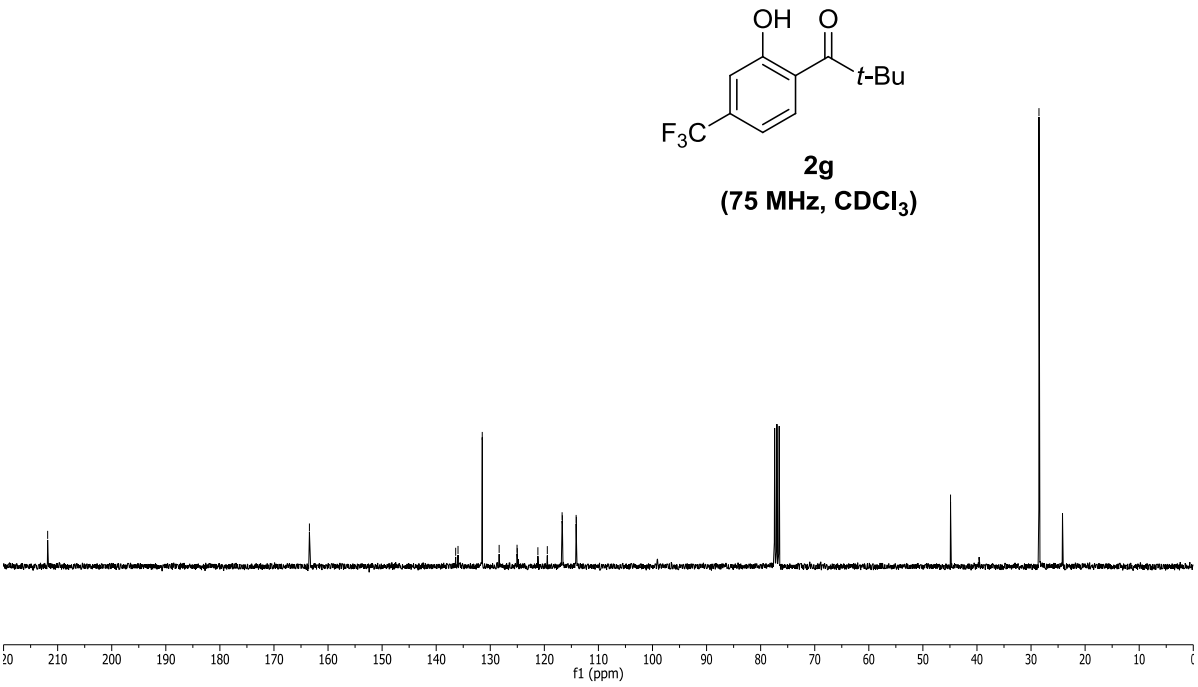
(300 MHz, $CDCl_3$)

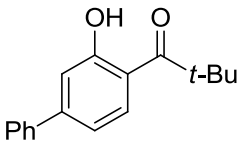


2f

(75 MHz, $CDCl_3$)

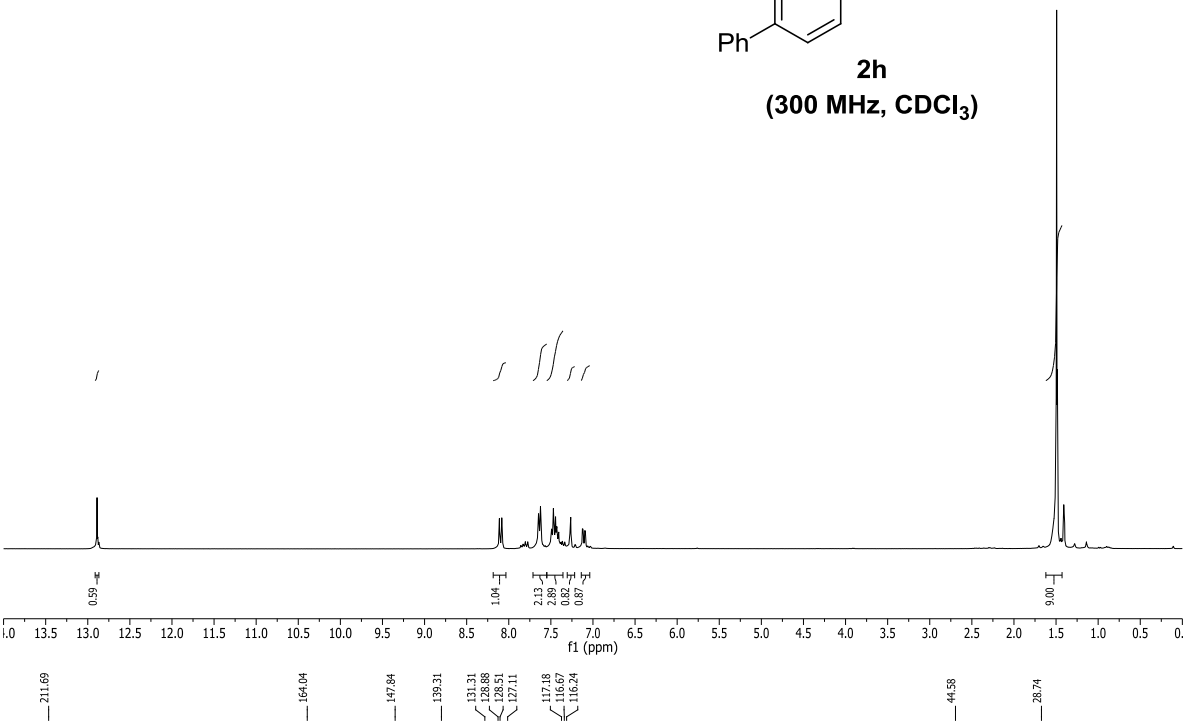

OH
O
t-Bu
F3C
2g
(300 MHz, CDCl3)
0.86
1.07
1.01
0.98
9.00
f1 (ppm)
211.85
163.44
136.40
135.96
131.48
128.36
125.05
125.00
121.19
119.45
116.72
116.66
114.12
114.07
44.89
28.54

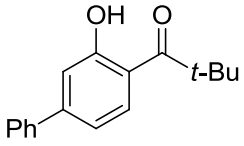

OH
O
t-Bu
F3C
2g
(75 MHz, CDCl3)
f1 (ppm)



2h

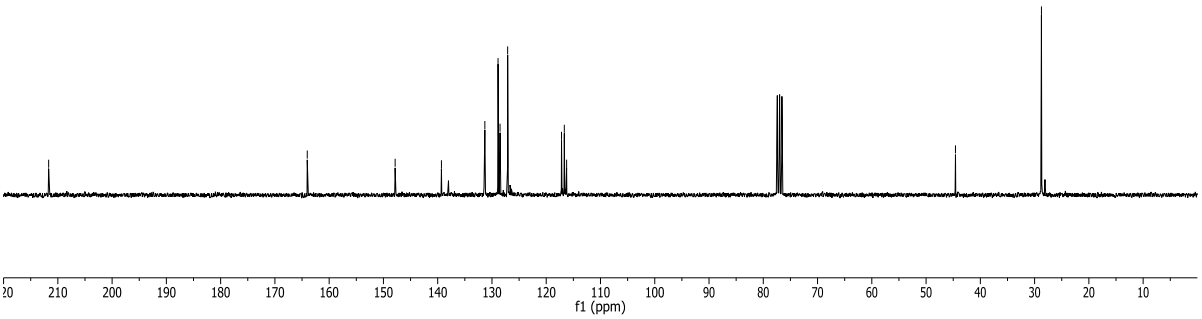
(300 MHz, $CDCl_3$)

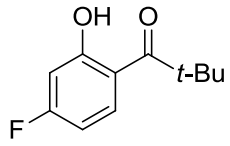




2h

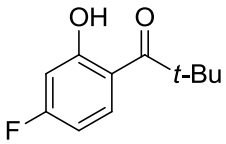
(75 MHz, $CDCl_3$)





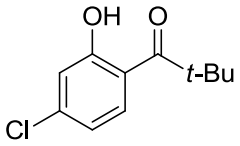
2i

(300 MHz, $CDCl_3$)



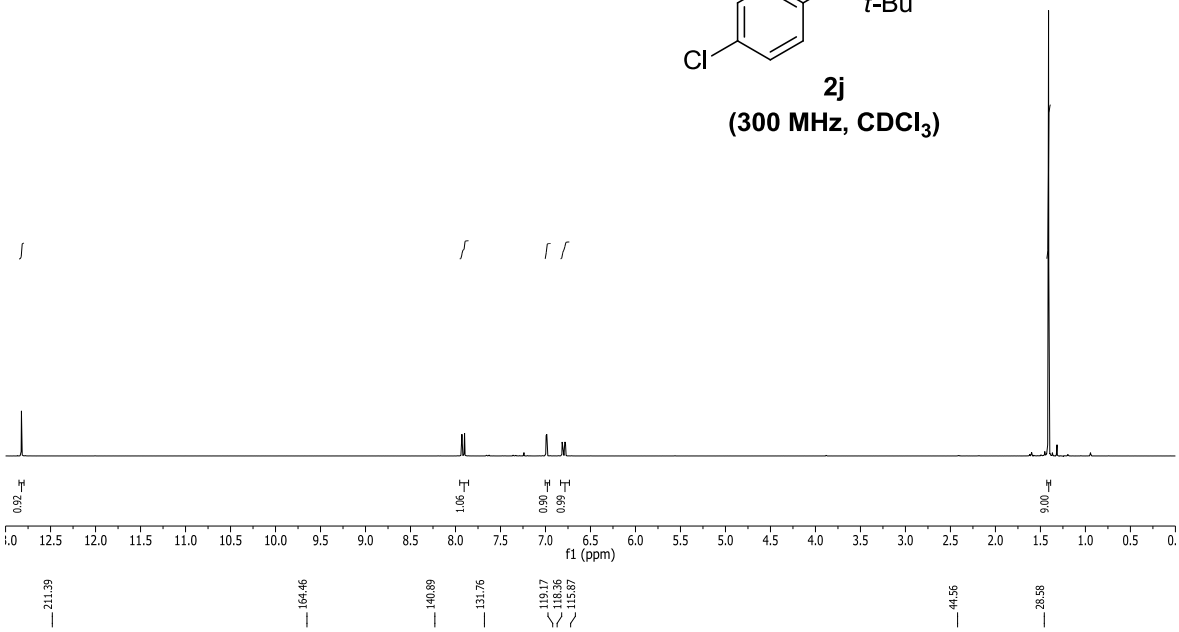
2i

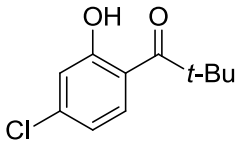
(75 MHz, $CDCl_3$)



2j

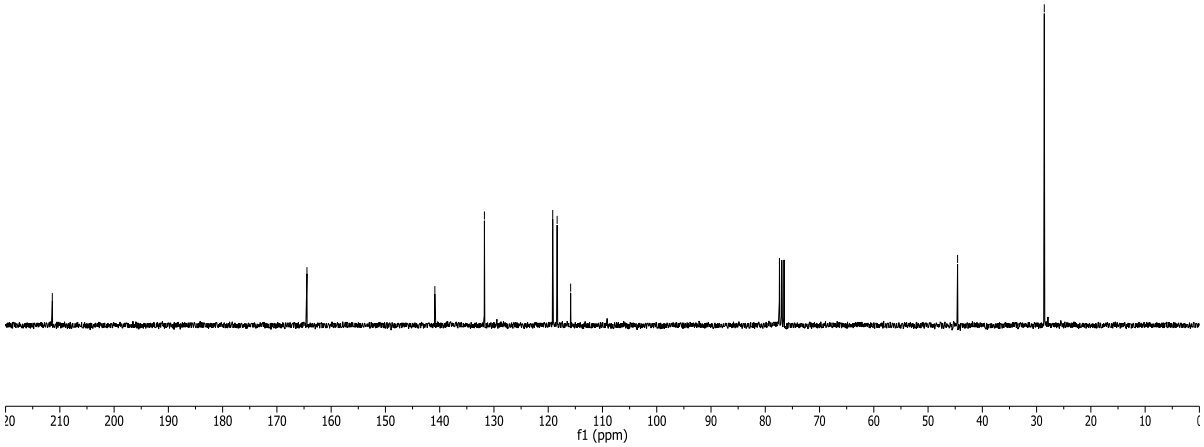
(300 MHz, $CDCl_3$)

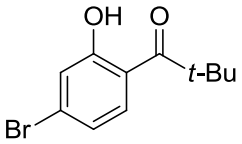




2j

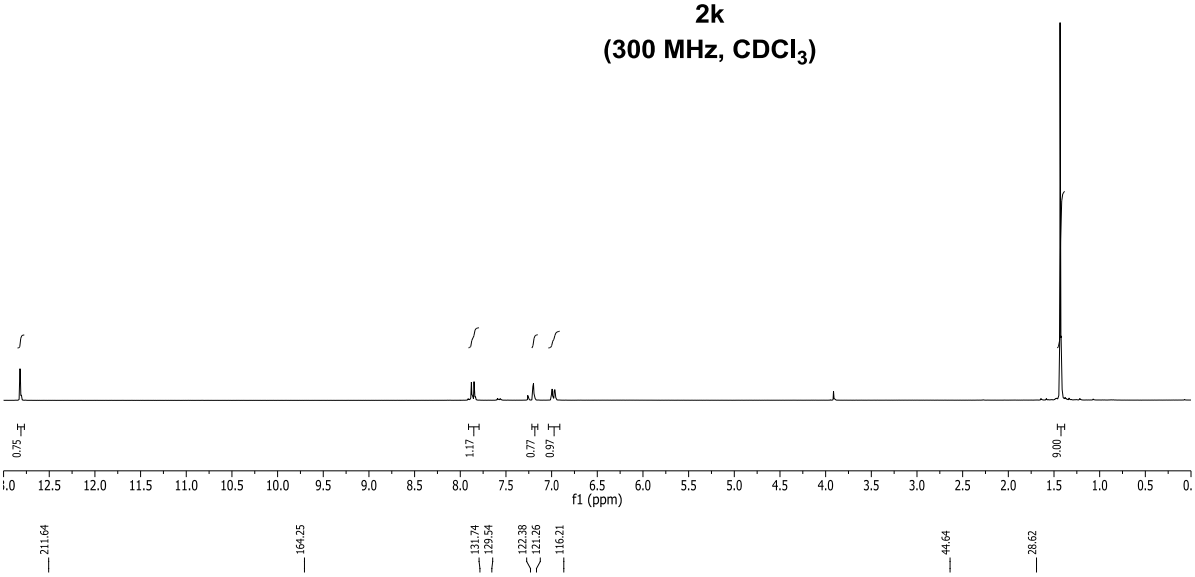
(75 MHz, $CDCl_3$)

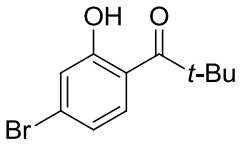




2k

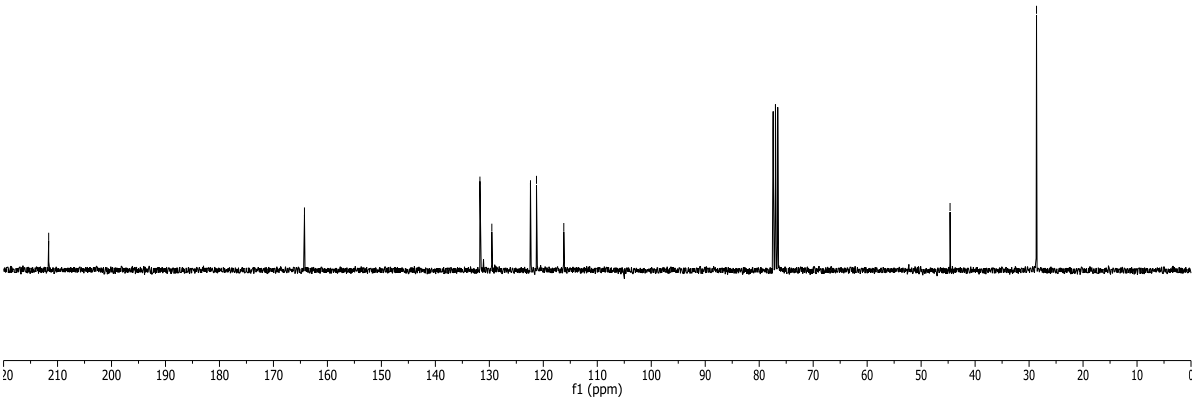
(300 MHz, $CDCl_3$)

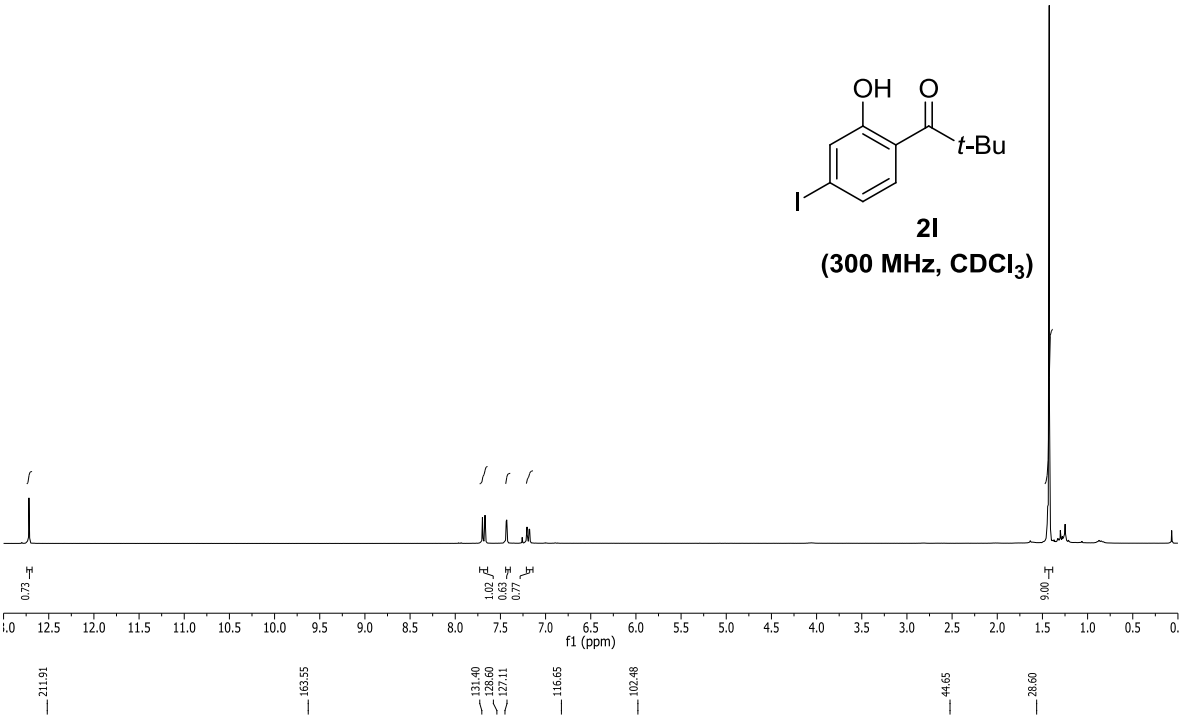




2k

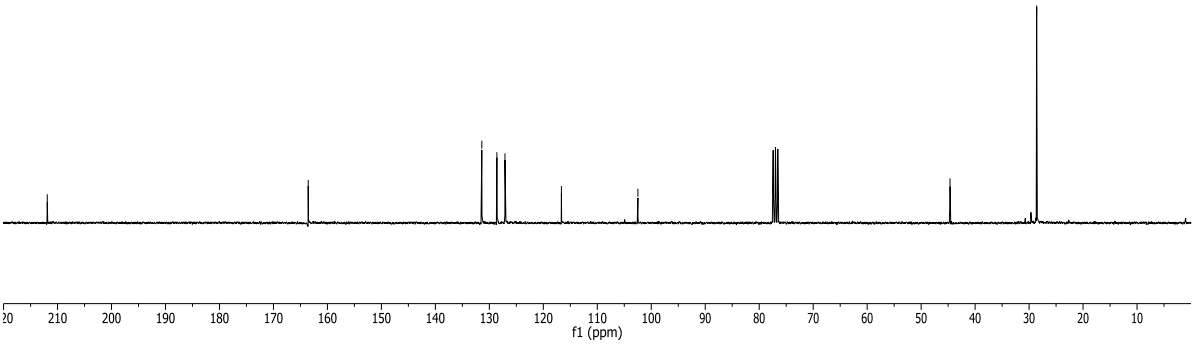
(75 MHz, $CDCl_3$)





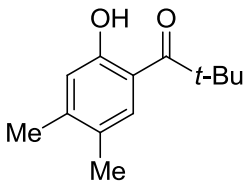
2l

(300 MHz, $CDCl_3$)



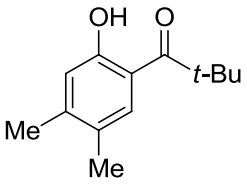
2l

(75 MHz, $CDCl_3$)



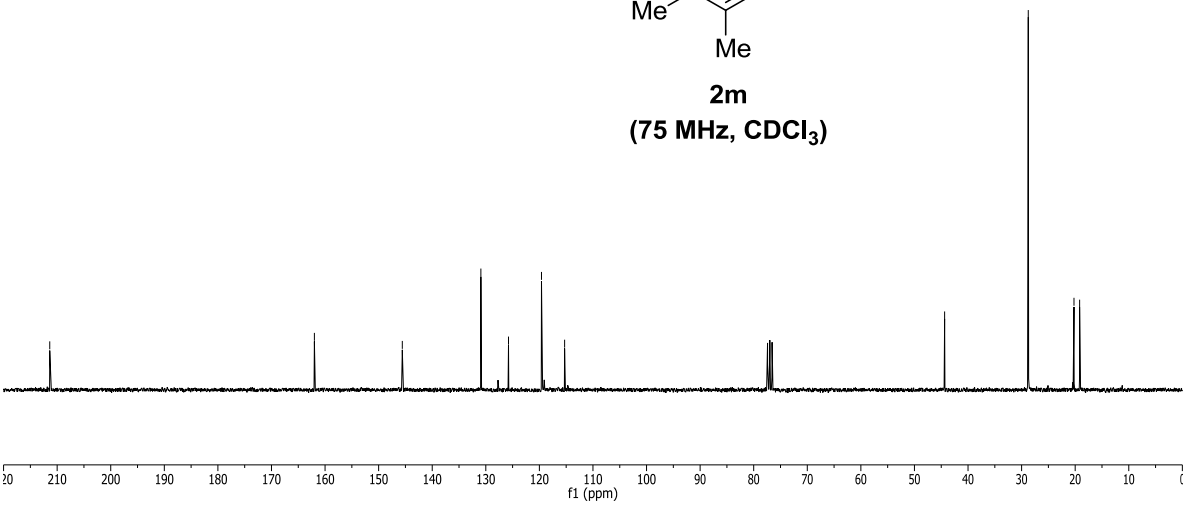
2m

(300 MHz, $CDCl_3$)

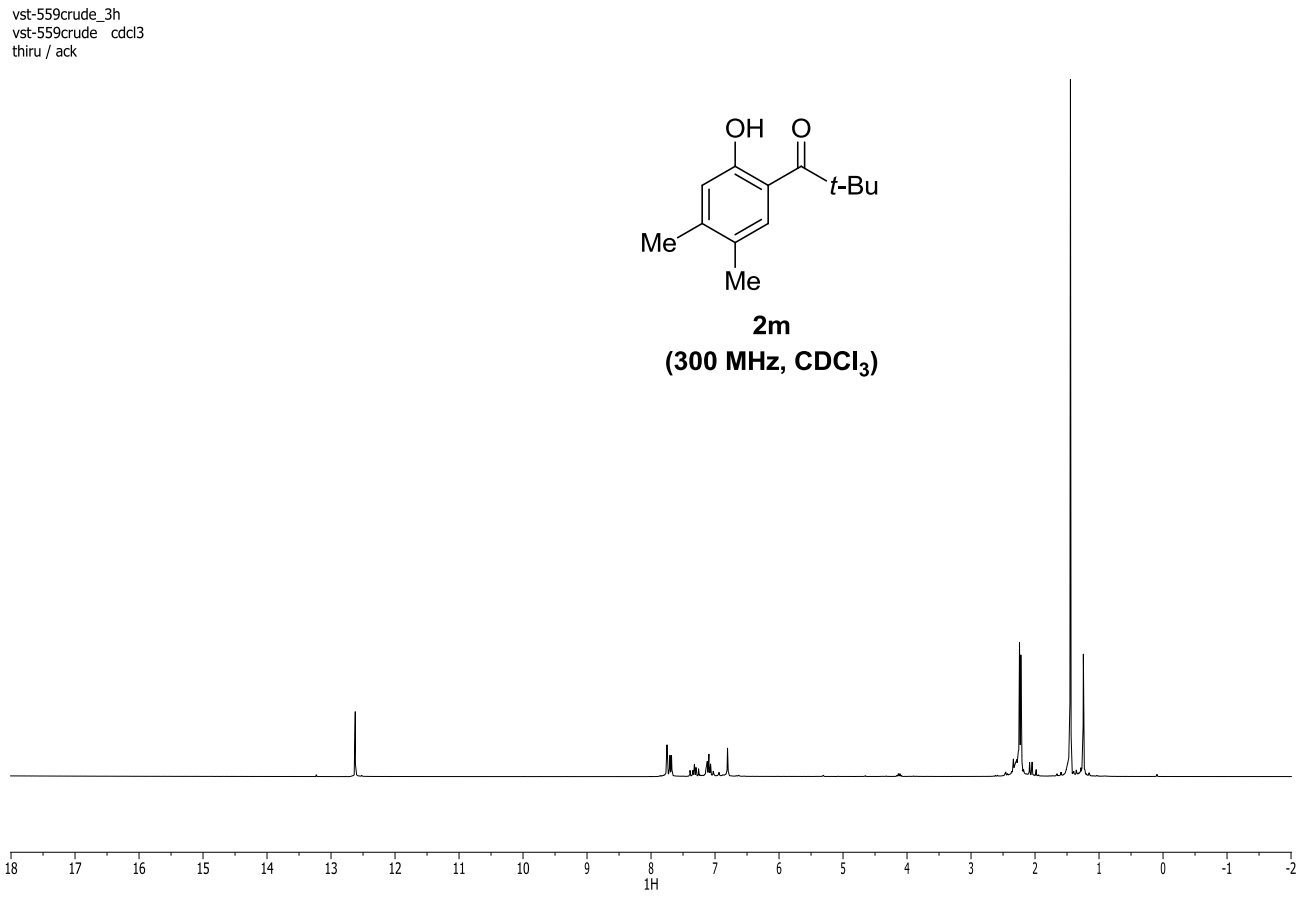


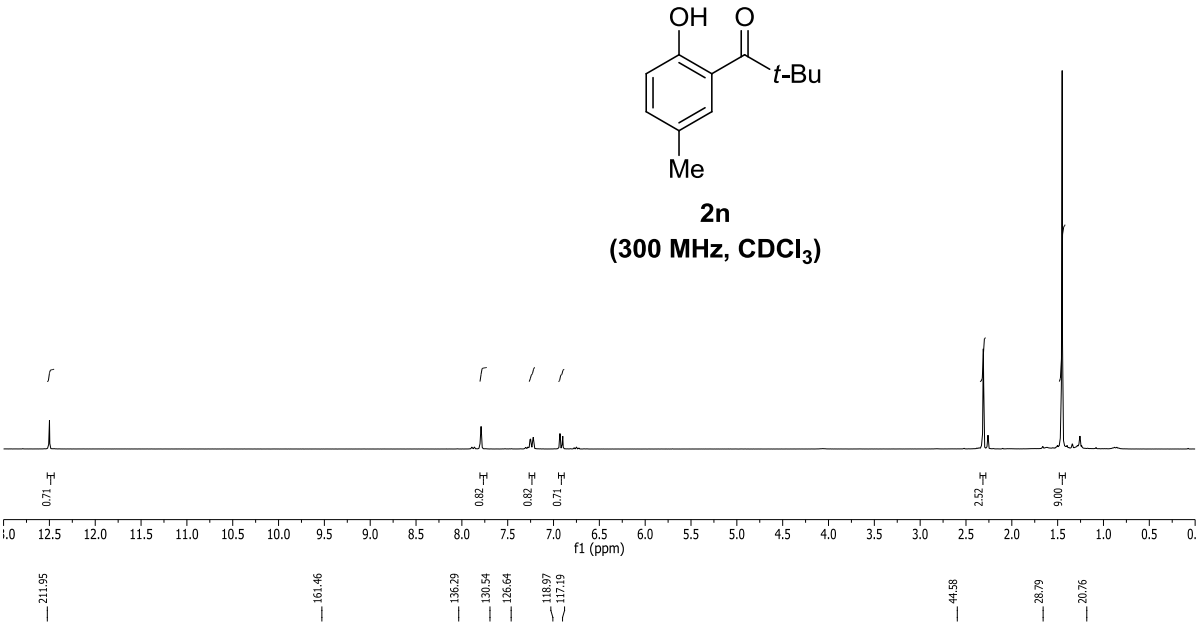
2m

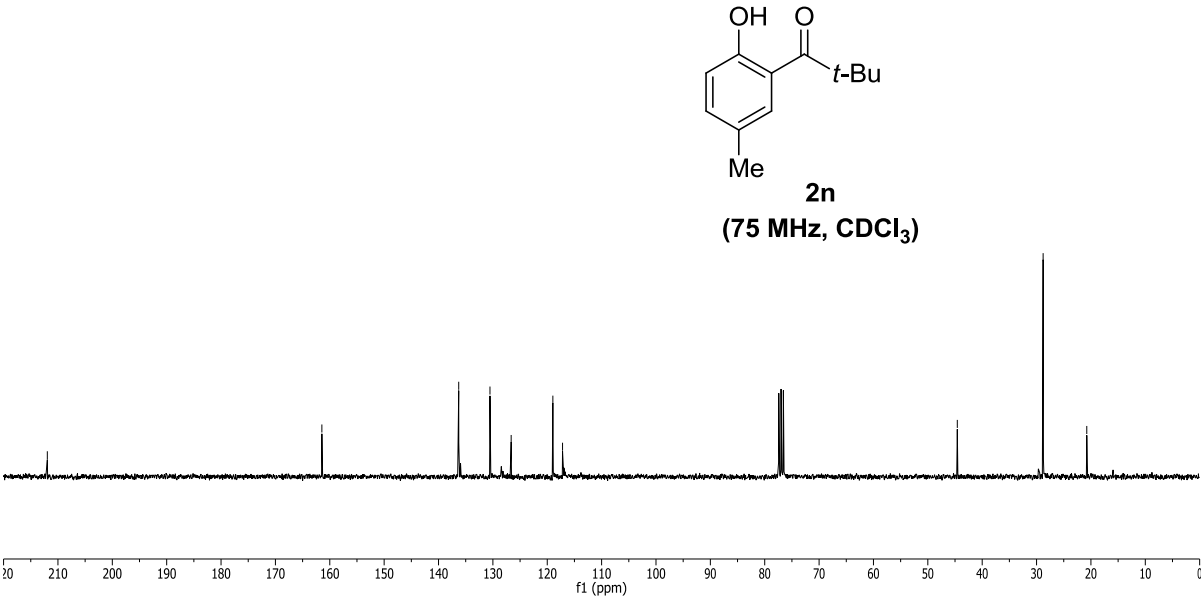
(75 MHz, $CDCl_3$)



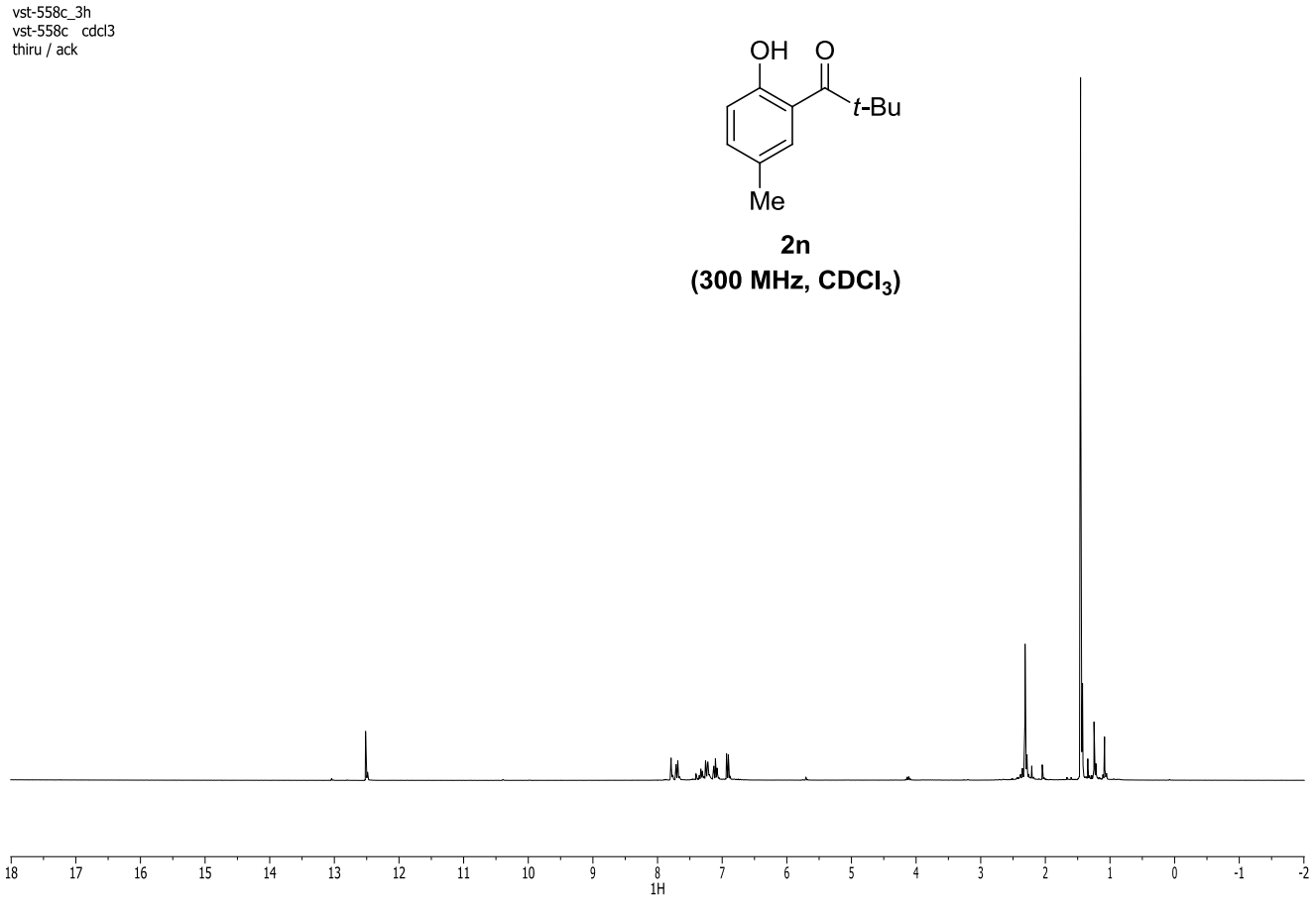
Crude spectra of **2m**

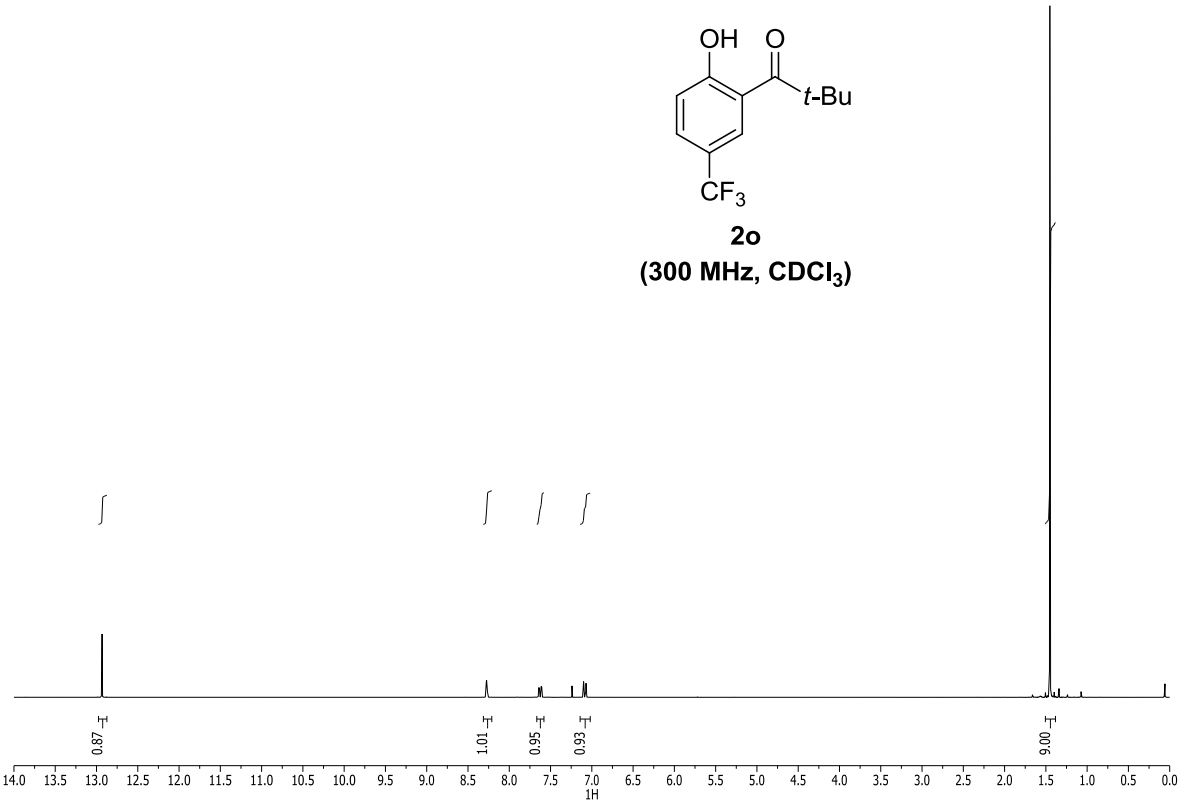



OH
O
t-Bu
Me
2n
(300 MHz, CDCl3)
0.71
0.82
0.82
0.71
2.52
9.00
f1 (ppm)
211.95
161.46
136.29
130.54
126.64
118.97
117.19
44.58
28.79
20.76


OH
O
t-Bu
Me
2n
(75 MHz, CDCl3)
f1 (ppm)

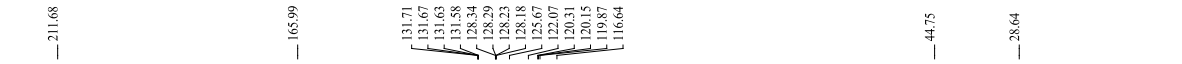
Crude spectra of **2n**





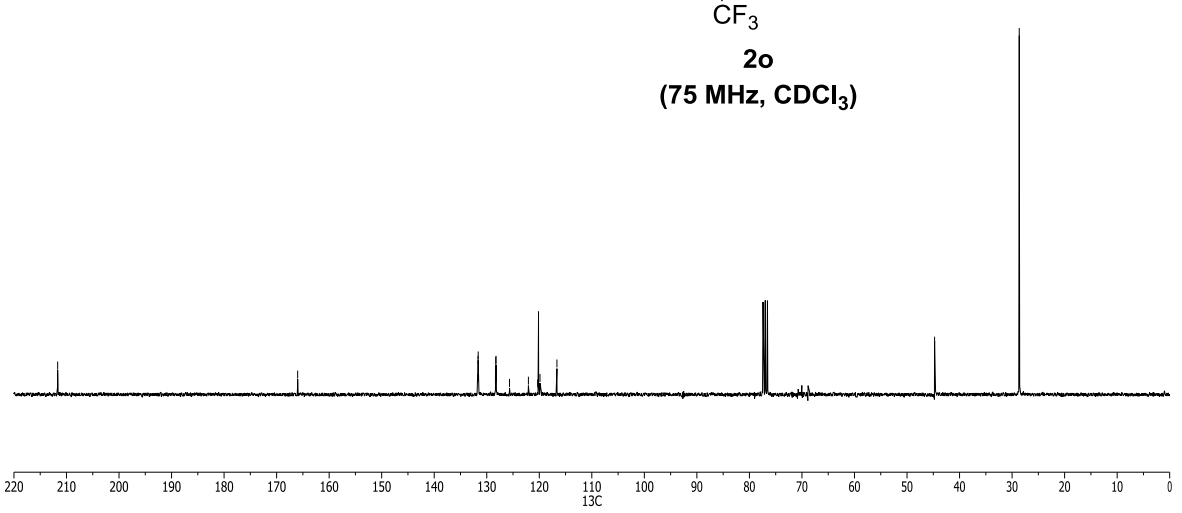
2o

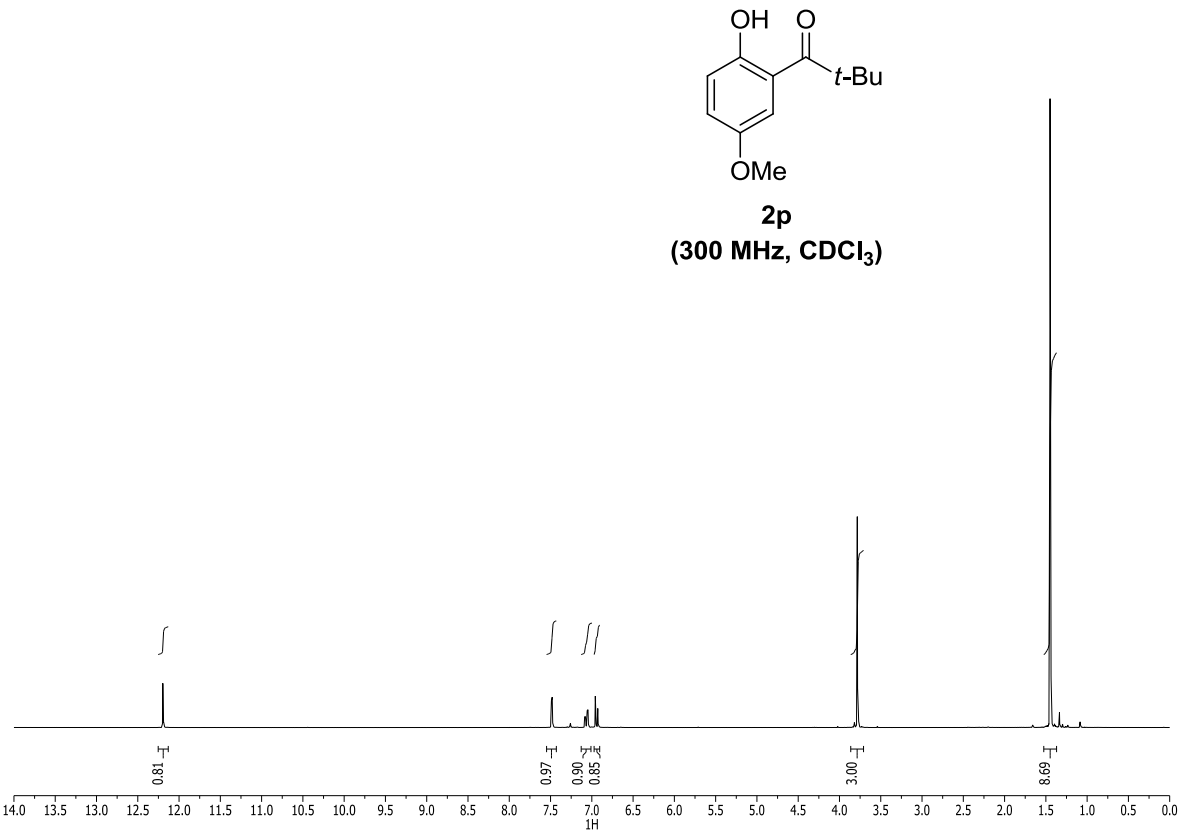
(300 MHz, $CDCl_3$)



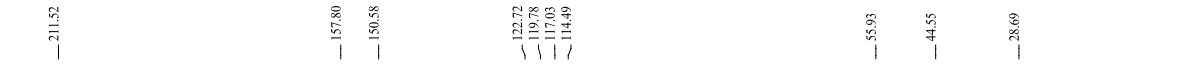
2o

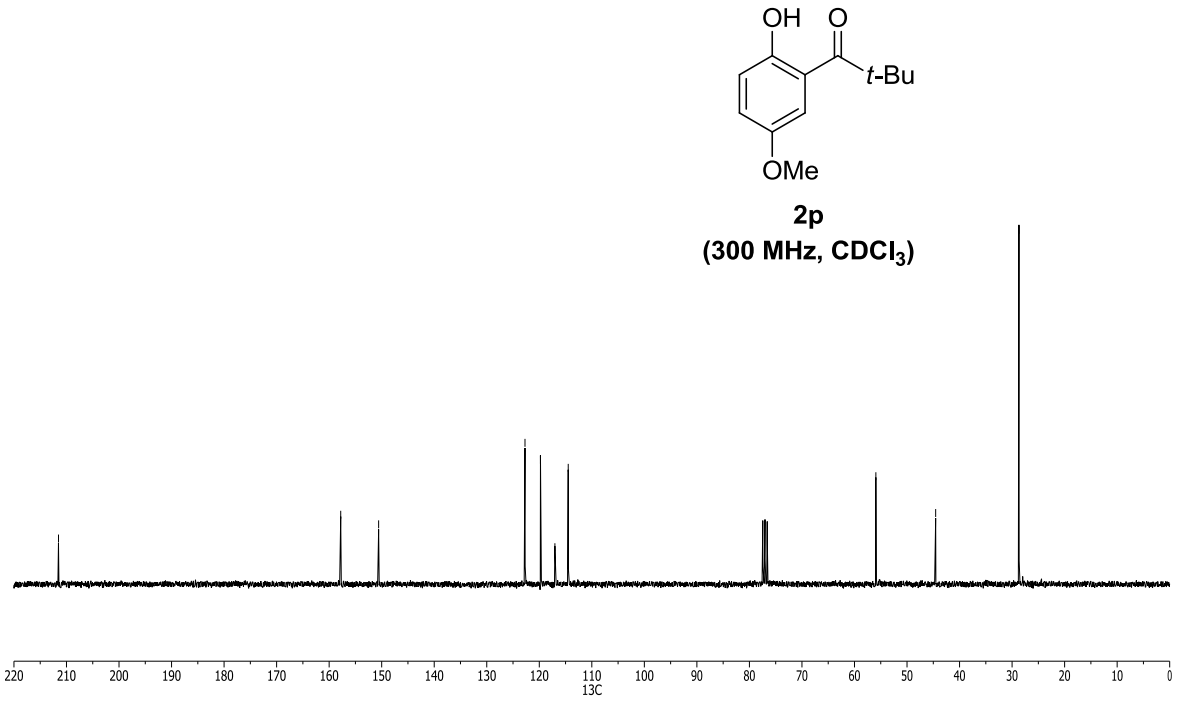
(75 MHz, $CDCl_3$)



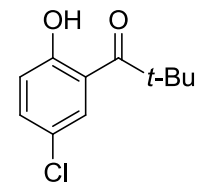


2p
(300 MHz, $CDCl_3$)

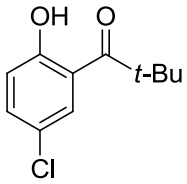




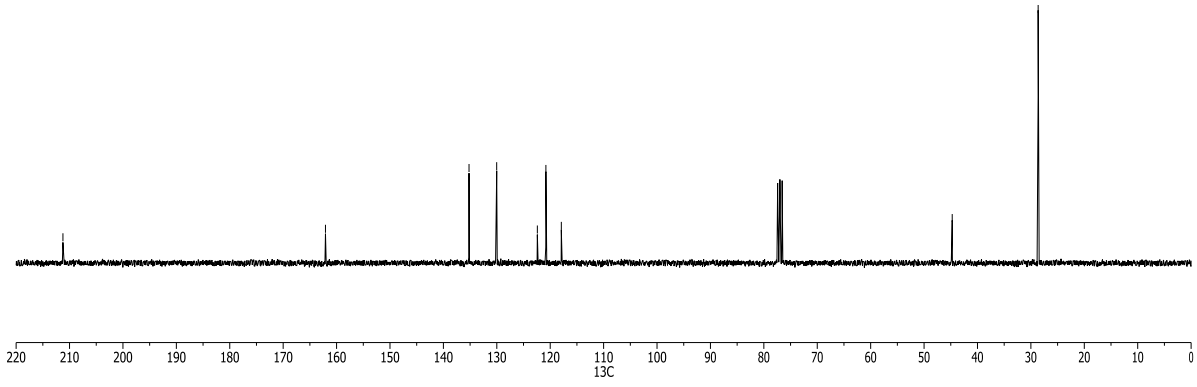
2p
(300 MHz, $CDCl_3$)

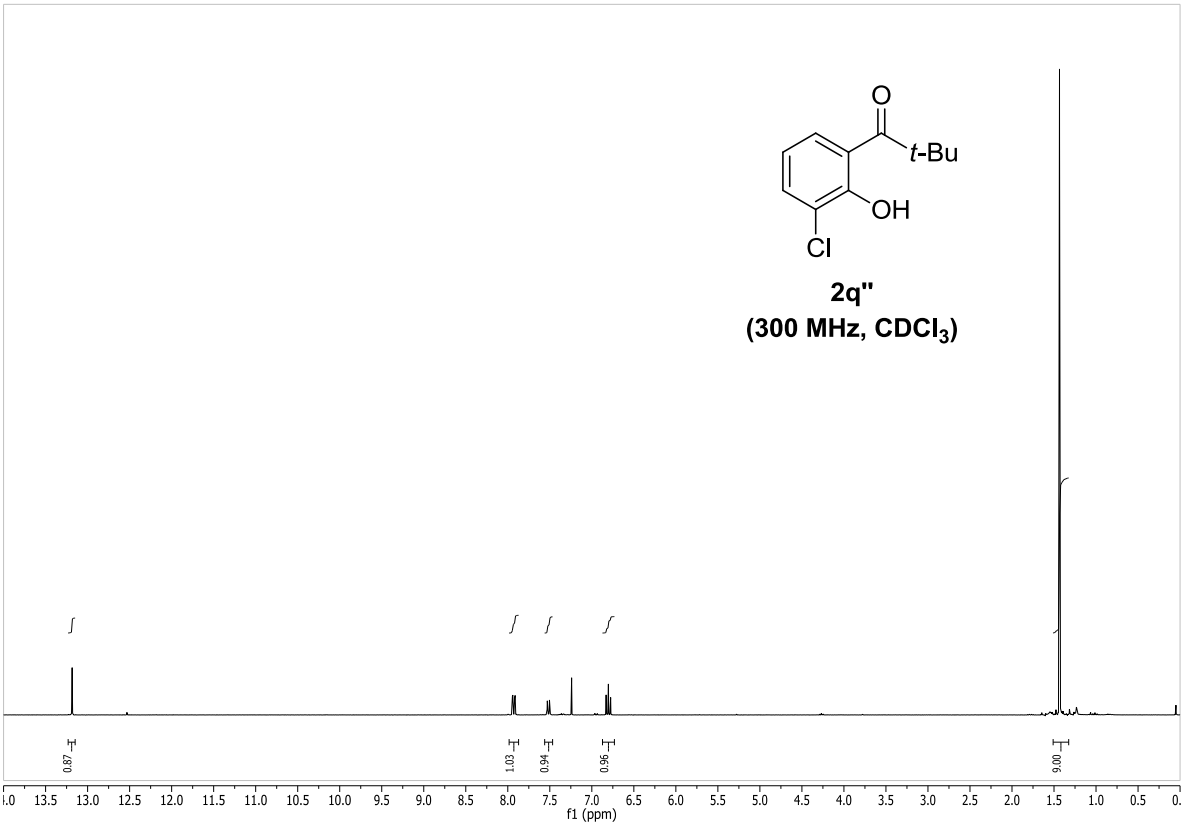


2q'
(300 MHz, $CDCl_3$)

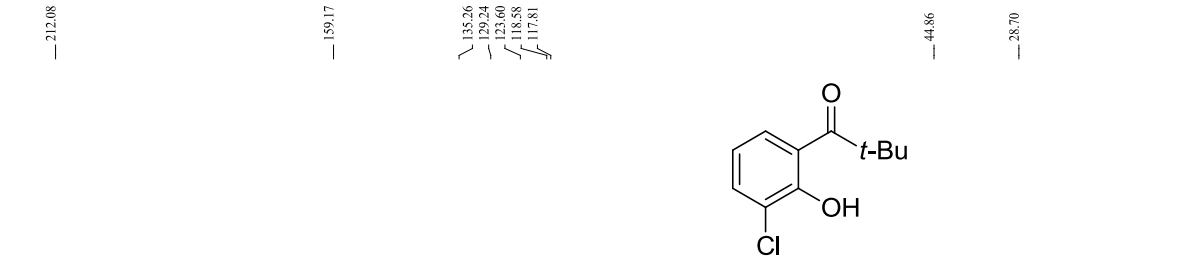


2q''
(75 MHz, $CDCl_3$)

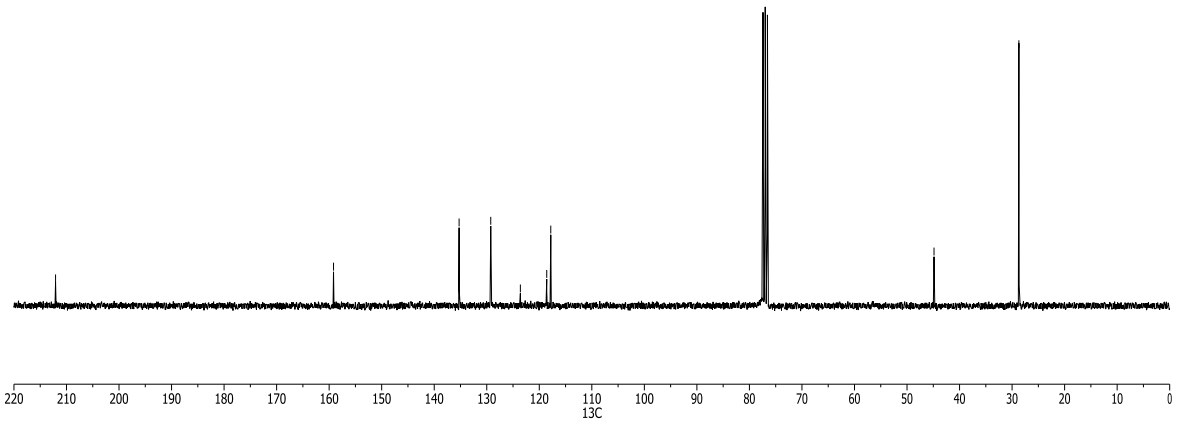


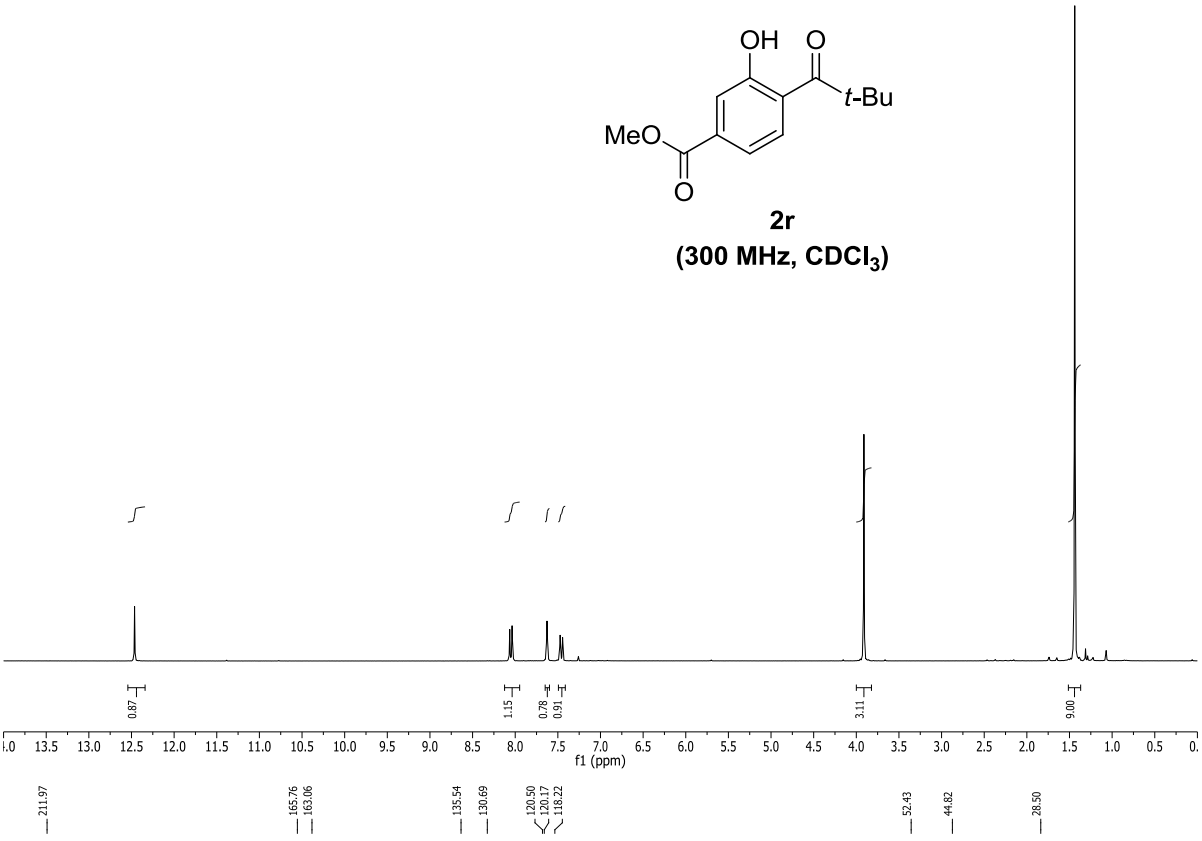


2q"
(300 MHz, $CDCl_3$)



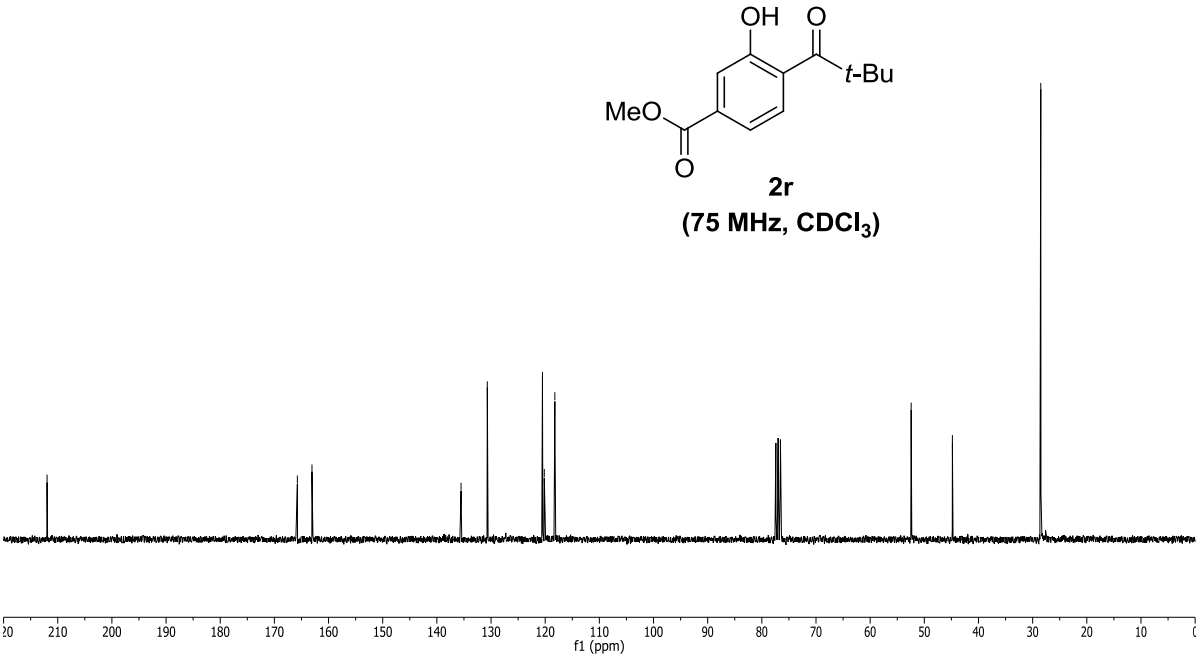
2q"
(300 MHz, $CDCl_3$)





2r

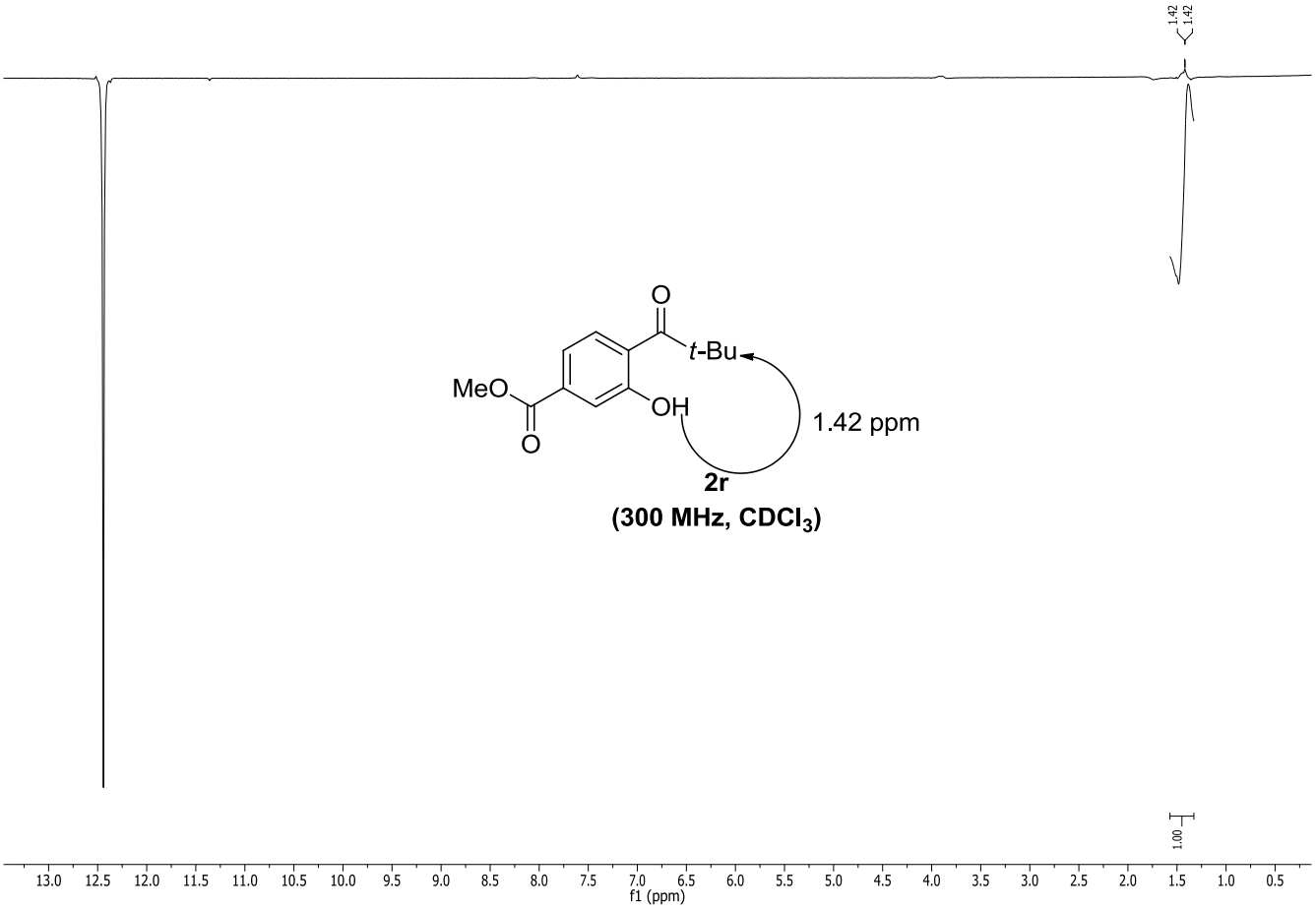
(300 MHz, $CDCl_3$)



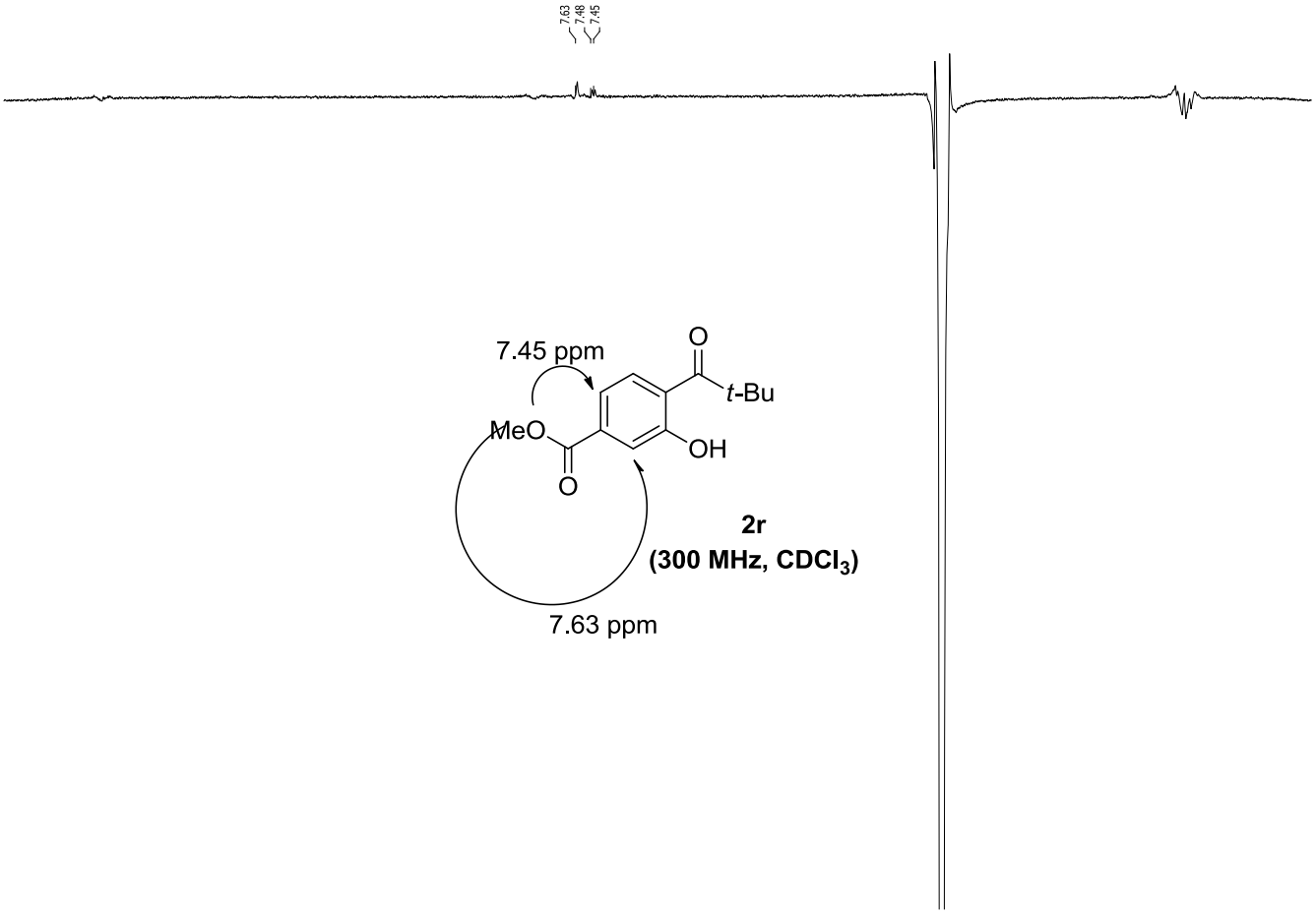
2r

(75 MHz, $CDCl_3$)

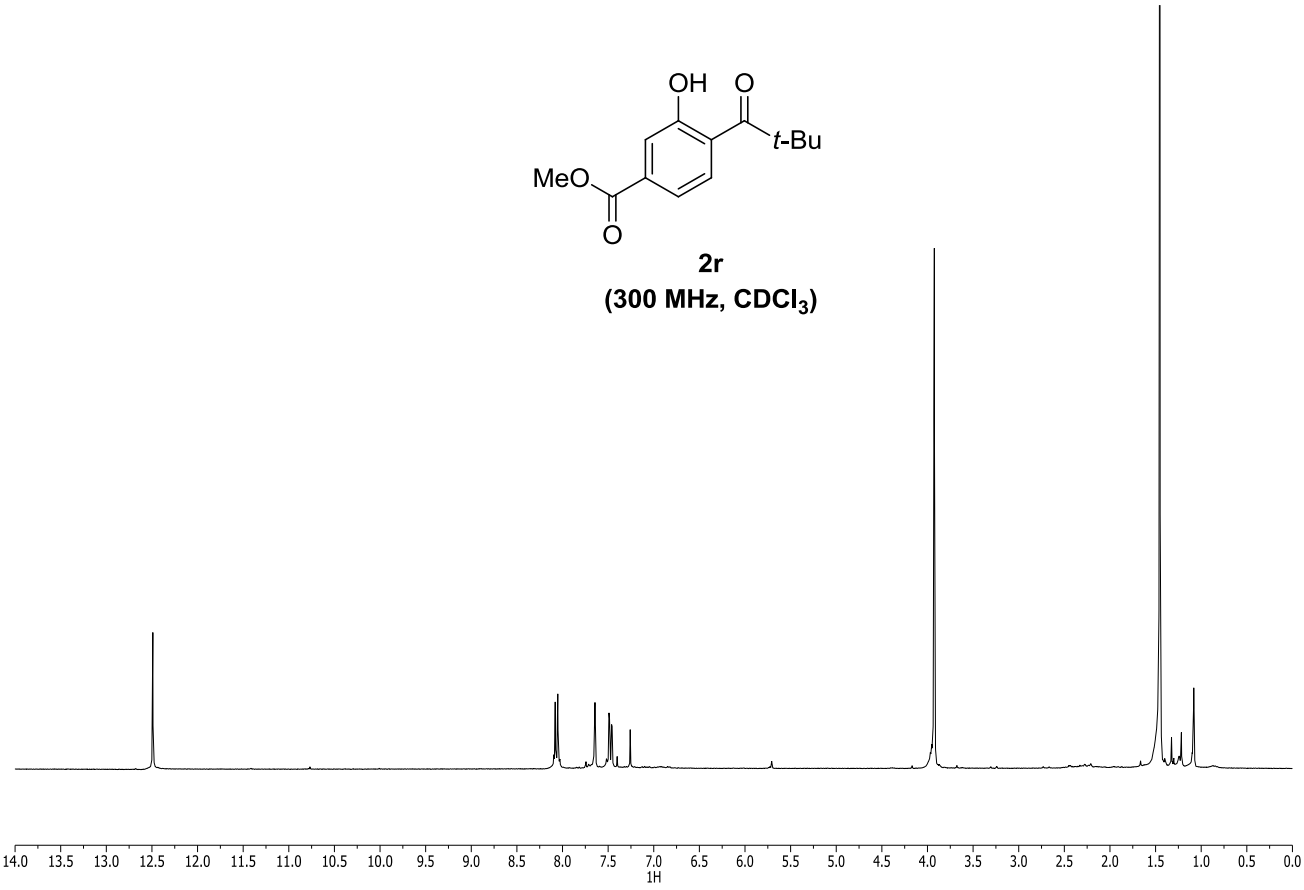
NOE spectra of **2r**

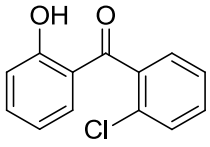


NOE spectra of **2r**

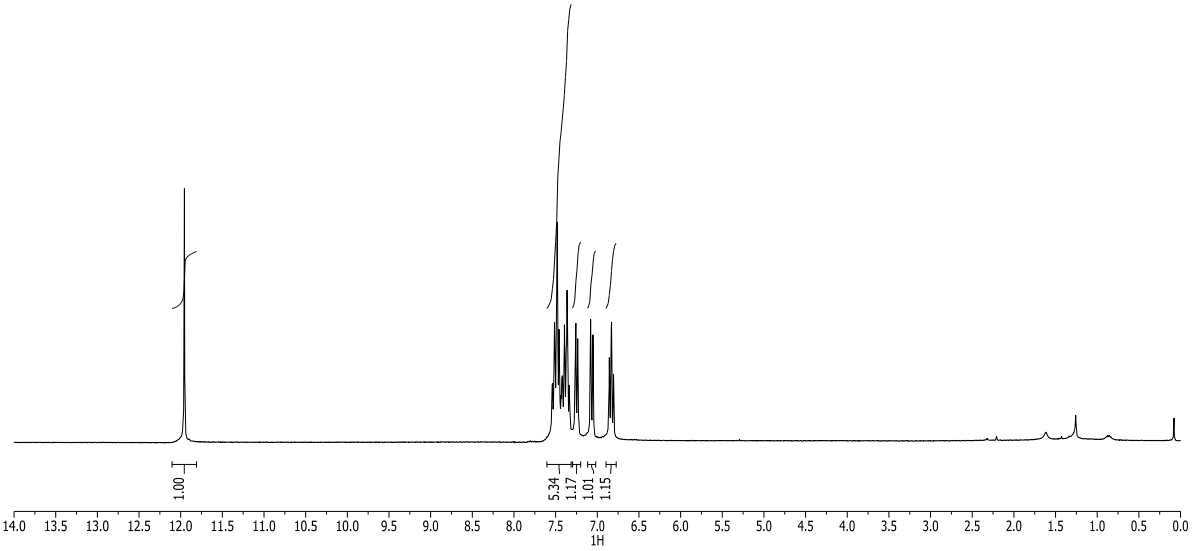


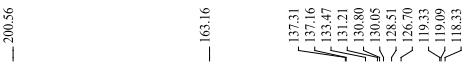
Crude spectra of **2r**

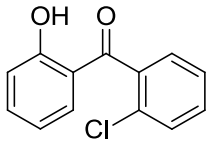




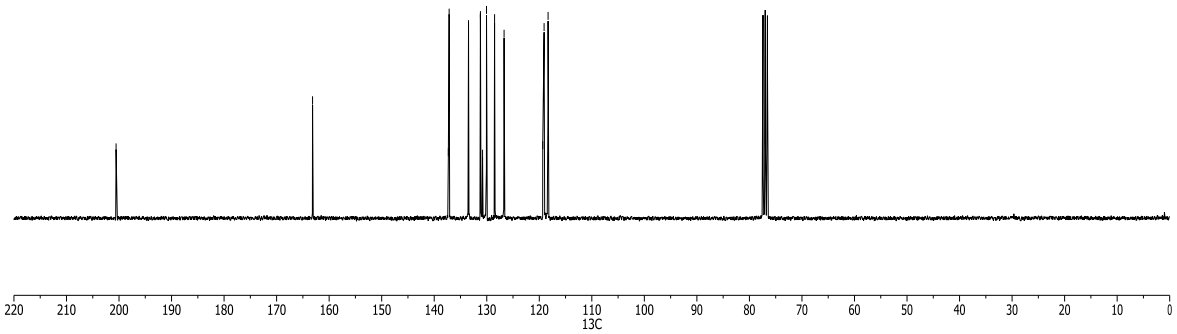
2s
(300 MHz, $CDCl_3$)



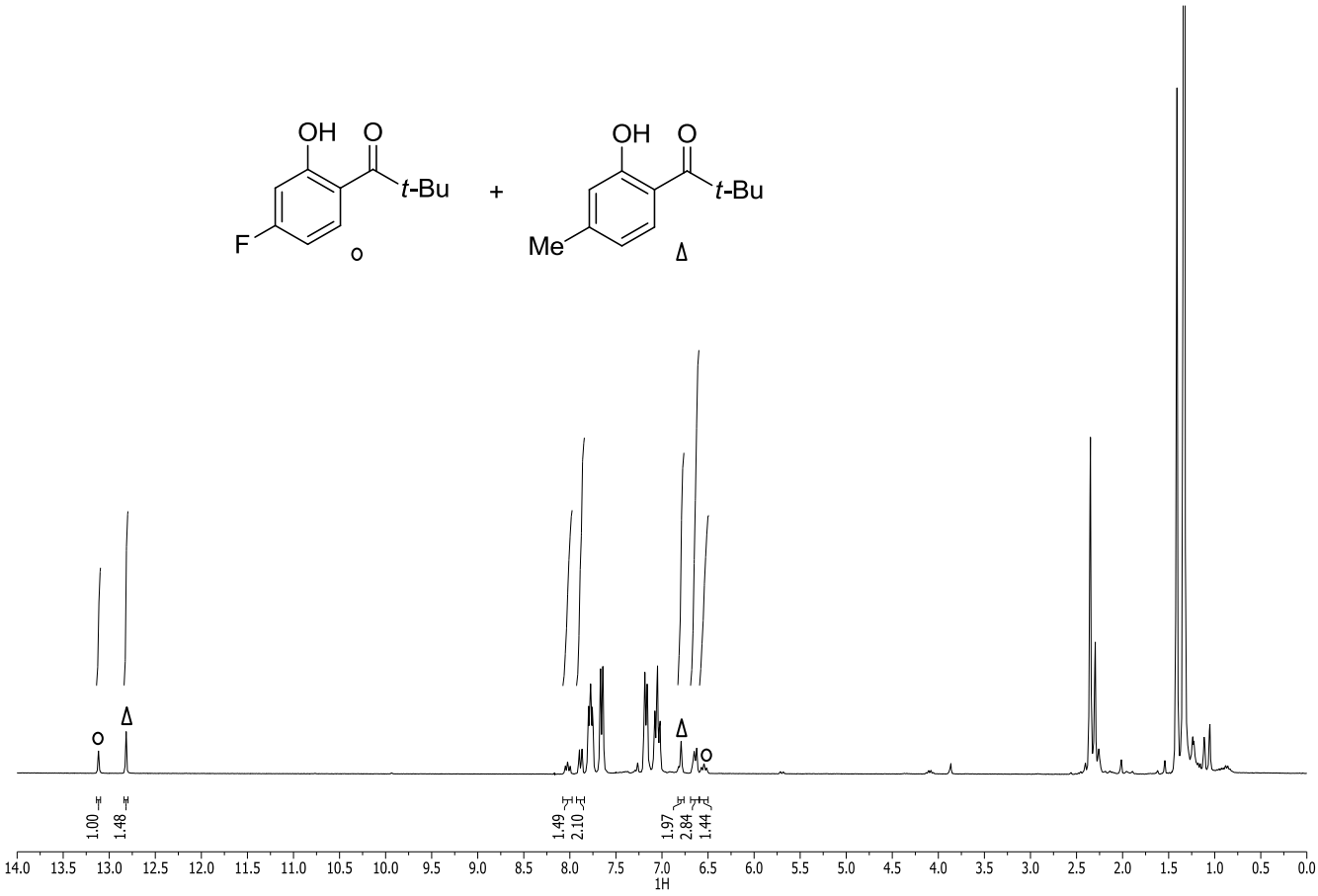




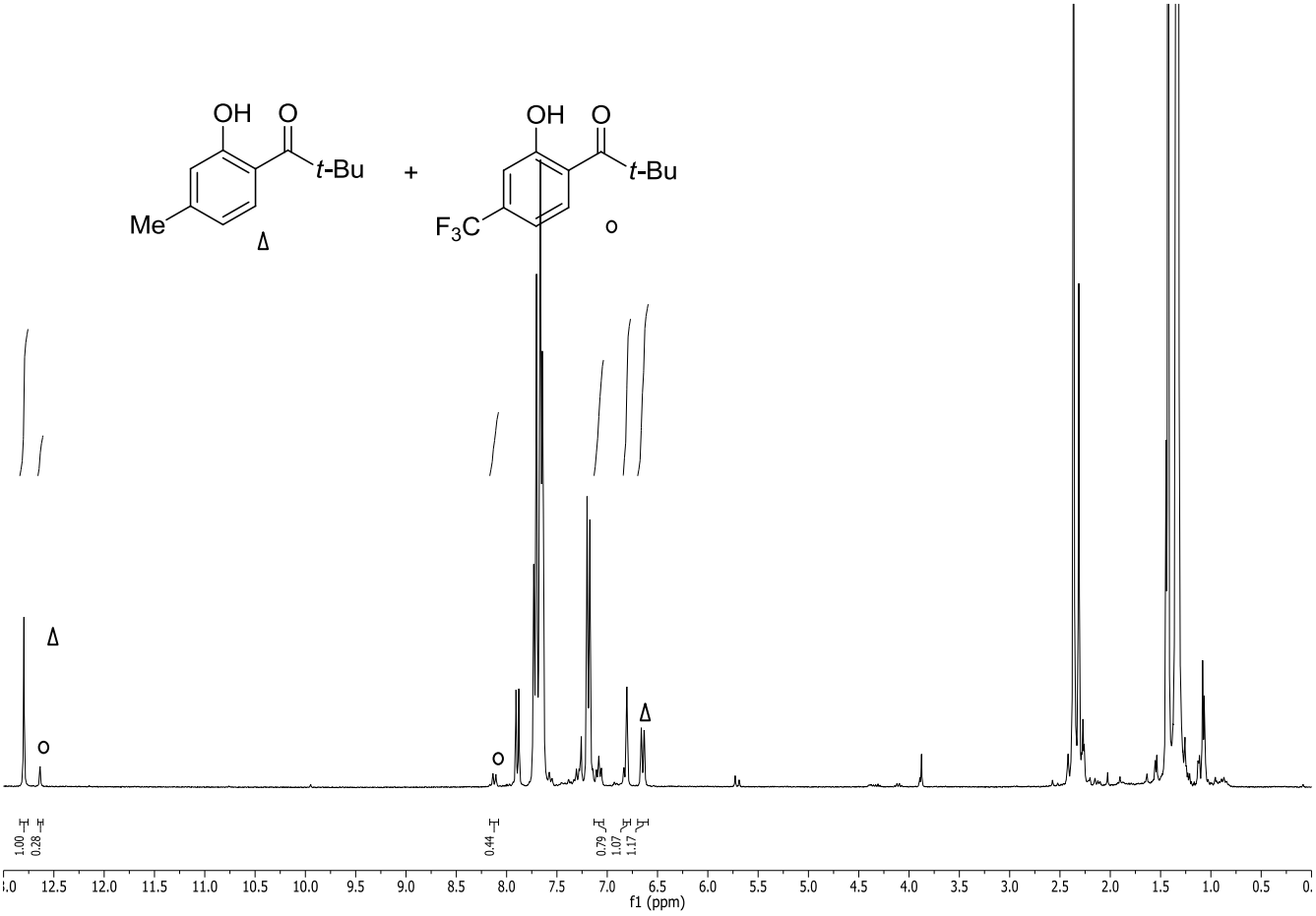
2s
(75 MHz, $CDCl_3$)



The NMR Spectra of Competition Study between **1f** and **1i**



The NMR Spectra of Competition Study between **1f** and **1g**



The NMR Spectra of Competition Study between **1a** and **1i**