Supporting Information

Ortho- and *para*-Selective Ruthenium-Catalyzed C(sp^2)–H Oxygenations of Phenol Derivatives

Weiping Liu and Lutz Ackermann*

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

Tammannstrasse 2, 37077 Göttingen, Germany

Fax: +49/ 551-39-6777

Lutz.Ackermann@chemie.uni-goettingen.de

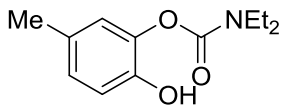
General Remarks	S-2
General Procedure for Oxygenation of Carbamates	S-3
Characterization Data of Products **2**	S-4
Intramolecular Competition Experiment	S-16
Intermolecular Competition Experiments	S-17
Preparation of the Substrate [$\mathbf{D_5}$]-**1n**	S-18
Kinetic Isotope Effect Study	S-19
General Procedure for Oxygenation of Anisoles	S-19
Characterization Data of Products **8**	S-20
References	S-22
^{1}H- and ^{13}C-NMR Spectra	S-23

General Remarks

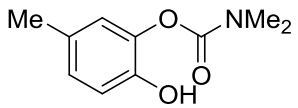
1,2-Dichloroethane (DCE) and 1,4-dioxane were distilled over CaH_2. All aryl carbamates **1** were synthesized according to a previously described procedure.[1] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated 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, 70eV. ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. M. p. Stuart® Melting Point Apparatus SMP3 melting point apparatus, values are uncorrected. ^{1}H, ^{13}C, ^{19}F NMR-spectra were recorded at 300 (^{1}H), 75 {^{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 for Oxygenation of Carbamates:

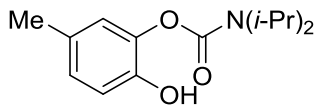
$[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), carbamate **1** (0.50 mmol), $PhI(TFA)_2$ (430 mg, 1.00 mmol) and DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The tube was then placed into an oil bath and the reaction mixture was stirred at 50–80 °C for 3–24 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. The crude products were purified by column chromatography (*n*-hexane/EtOAc) on silica gel to afford the desired products.



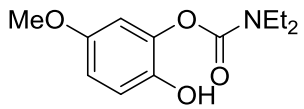
2-Hydroxy-5-methylphenyl diethylcarbamate (2a): The representative procedure was followed using *m*-tolyl diethylcarbamate (**1a**) (103.5 mg, 0.50 mmol), and the reaction mixture was stirred at 50 °C for 24 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2a** (67%) as a colorless solid. M.p. = 80–82 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.92 (s, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.82 (s, 1H), 3.46 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.7 (C_q), 145.3 (C_q), 139.8 (C_q), 130.3 (C_q), 126.9 (CH), 122.3 (CH), 118.9 (CH), 42.5 (CH_2), 42.3 (CH_2), 20.3 (CH_3), 14.1 (CH_3), 13.2 (CH_3). IR (neat): 3333, 2974, 1684, 1163, 783 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (33) [M^{+}], 123 (13), 100 (100), 72 (76), 44 (33). HR-MS (EI) *m/z* calcd for $C_{12}H_{17}NO_3$ [M^{+}] 223.1208, found 223.1206.



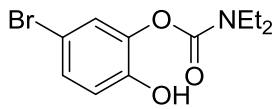
2-Hydroxy-5-methylphenyl dimethylcarbamate (2b): The representative procedure was followed using *m*-tolyl dimethylcarbamate (**1b**) (89.5 mg, 0.50 mmol), and the reaction mixture was stirred at 50 °C for 24 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2b** (63%) as a colorless solid. M.p. = 98–100 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.87–6.81 (m, 4H), 3.10 (s, 3H), 3.00 (s, 3H), 2.24 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 155.1 (C_q), 145.3 (C_q), 139.6 (C_q), 130.4 (C_q), 127.0 (CH), 122.5 (CH), 118.8 (CH), 36.8 (CH_3), 36.6 (CH_3), 20.4 (CH_3). IR (neat): 3262, 2950, 1684, 1295, 1179, 796, 578 cm^{-1}. MS (EI) *m/z* (relative intensity) 195 (25) [M^{+}], 123 (5), 95 (3), 72 (100), 42 (8). HR-MS (EI) *m/z* calcd for $C_{10}H_{13}NO_3$ [M^{+}] 195.0895, found 195.0891.



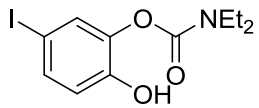
2-Hydroxy-5-methylphenyl di-*iso*propylcarbamate (2c): The representative procedure was followed using *m*-tolyl di-*iso*propylcarbamate (**1c**) (117.5 mg, 0.50 mmol), and the reaction mixture was stirred at 50 °C for 24 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2c** (63%) as a colorless solid. M.p. = 113–115 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.11 (s, 1H), 6.89–6.85 (m, 3H), 4.17–3.94 (m, 2H), 2.27 (s, 3H), 1.36 (d, J = 6.8 Hz, 6H), 1.30 (d, J = 6.8 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.2 (C_q), 145.4 (C_q), 139.8 (C_q), 130.3 (C_q), 126.9 (CH), 122.2 (CH), 119.1 (CH), 47.2 (CH), 46.6 (CH), 21.4 (CH_3), 20.3 (CH_3), 20.2 (CH_3). IR (neat): 3286, 2971, 1665, 1287, 1146, 1110, 813, 611 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (15) [M$^+$], 128 (80), 124 (73), 86 (100), 43 (84). HR-MS (EI) *m/z* calcd for $C_{14}H_{21}NO_3$ [M$^+$] 251.1521, found 251.1520.



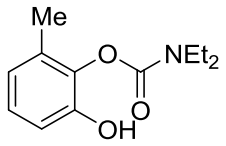
2-Hydroxy-5-methoxyphenyl diethylcarbamate (2d): The representative procedure was followed using 3-methoxyphenyl diethylcarbamate (**1d**) (111.5 mg, 0.50 mmol), and the reaction mixture was stirred at 50 °C for 24 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2d** (46%) as a colorless solid. M.p. = 79–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.89 (d, J = 8.8 Hz, 1H), 6.82 (s, 1H), 6.64 (dd, J = 8.8, 2.8 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 3.73 (s, 3H), 3.46 (q, J = 7.1 Hz, 2H), 3.38 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_q), 153.7 (C_q), 141.6 (C_q), 140.4 (C_q), 119.7 (CH), 111.8 (CH), 107.8 (CH), 55.8 (CH_3), 42.5 (CH_2), 42.3 (CH_2), 14.1 (CH_3), 13.2 (CH_3). IR (neat): 3343, 2981, 1694, 1518, 1274, 1147, 1031, 752 cm^{-1}. MS (EI) *m/z* (relative intensity) 239 (15) [M$^+$], 139 (5), 100 (100), 72 (62), 44 (13). HR-MS (EI) *m/z* calcd for $C_{12}H_{17}NO_4$ [M$^+$] 239.1158, found 239.1161.



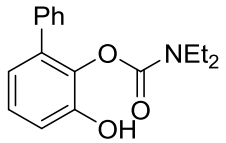
5-Bromo-2-hydroxyphenyl diethylcarbamate (2e): The representative procedure was followed using 3-bromophenyl diethylcarbamate (**1e**) (135.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2e** (66%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.01 (s, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_q), 147.5 (C_q), 140.5 (C_q), 129.3 (CH), 125.2 (CH), 120.3 (CH), 111.4 (C_q), 42.7 (CH_2), 42.4 (CH_2), 14.0 (CH_3), 13.1 (CH_3). IR (neat): 3269, 2976, 1683, 1426, 1274, 1159, 964, 628 cm^{-1}. MS (EI) *m/z* (relative intensity) 287 (5) [M^{+}], 160 (5), 100 (100), 72 (55), 43 (17). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}BrNO_3$ [M^{+}] 287.0157, found 287.0169.



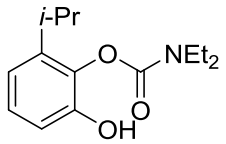
2-Hydroxy-5-iodophenyl diethylcarbamate (2f): The representative procedure was followed using 3-iodophenyl diethylcarbamate (**1f**) (159.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2f** (71%) as a colorless solid. M.p. = 106–108 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.41–7.37 (m, 2 H), 7.34 (d, *J* = 2.1 Hz, 1H), 6.80 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 2H), 3.40 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.22 (t, *J* = 7.1 Hz, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.4 (C_q), 148.4 (C_q), 140.7 (C_q), 135.3 (CH), 130.9 (CH), 120.8 (CH), 80.6 (C_q), 42.6 (CH_2), 42.4 (CH_2), 14.0 (CH_3), 13.2 (CH_3). IR (neat): 3269, 2979, 1700, 1273, 1157, 825, 601 cm^{-1}. MS (EI) *m/z* (relative intensity) 335 (20) [M^{+}], 206 (10), 100 (100), 72 (65), 44 (20). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}INO_3$ [M^{+}] 335.0018, found 335.0018.



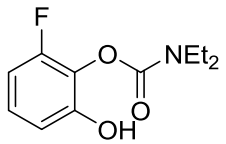
2-Hydroxy-6-methylphenyl diethylcarbamate (2g): The representative procedure was followed using *o*-tolyl diethylcarbamate (**1g**) (103.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2g** (67%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.96 (s, 1H), 6.87 (dd, J = 7.8, 7.8 Hz, 1H), 6.71–6.66 (m, 2H), 3.49 (q, J = 7.1 Hz, 2H), 3.39 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.2 (C_q), 148.2 (C_q), 138.5 (C_q), 130.9 (C_q), 125.7 (CH), 122.1 (CH), 116.0 (CH), 42.4 (CH_2), 42.0 (CH_2), 16.5 (CH_3), 14.0 (CH_3), 13.2 (CH_3). IR (neat): 3304, 2976, 1685, 1424, 1275, 1179, 1159, 769, 726 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (8) [M$^+$], 123 (5), 100 (100), 72 (50), 44 (8). HR-MS (EI) *m/z* calcd for $C_{12}H_{17}NO_3$ [M$^+$] 223.1208, found 223.1208.



3-Hydroxy-[1,1'-biphenyl]-2-yl diethylcarbamate (2h): The representative procedure was followed using [1,1'-biphenyl]-2-yl diethylcarbamate (**1h**) (134.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolated by column chromatography (*n*-hexane/EtOAc: 3/1) yielded **2h** (79%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.43–7.31 (m, 6H), 7.06–7.01 (m, 1H), 6.89–6.84 (m, 2H), 3.32 (q, J = 7.1 Hz, 2H), 3.17 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.6 (C_q), 148.9 (C_q), 138.1 (C_q), 137.2 (C_q), 135.9 (C_q), 128.9 (CH), 127.9 (CH), 127.1 (CH), 126.0 (CH), 121.9 (CH), 117.7 (CH), 42.2 (CH_2), 41.8 (CH_2), 13.5 (CH_3), 13.0 (CH_3). IR (neat): 3282, 2976, 1685, 1424, 1271, 1193, 902, 755, 699 cm^{-1}. MS (EI) *m/z* (relative intensity) 285 (20) [M$^+$], 139 (10), 128 (15), 100 (100), 72 (60), 44 (25). HR-MS (EI) *m/z* calcd for $C_{17}H_{19}NO_3$ [M$^+$] 285.1365, found 285.1362.

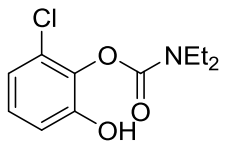


2-Hydroxy-6-isopropylphenyl diethylcarbamate (2i): The representative procedure was followed using 2-isopropylphenyl diethylcarbamate (**1i**) (117.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2i** (76%) as a colorless solid. M.p. = 85–87 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.92 (dd, J = 7.9, 7.9 Hz, 1H), 6.86 (s, 1H), 6.77 (dd, J = 7.9, 1.7 Hz, 1H), 6.64 (dd, J = 7.9, 1.7 Hz, 1H), 3.49 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 3.10 (hept, J = 6.9 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 6.9 Hz, 6H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.6 (C_q), 148.2 (C_q), 141.1 (C_q), 137.6 (C_q), 125.9 (CH), 117.3 (CH), 115.9 (CH), 42.4 (CH_2), 42.0 (CH_2), 27.6 (CH), 22.8 (CH_3), 13.9 (CH_3), 13.2 (CH_3). IR (neat): 3174, 2965, 1685, 1148, 1181, 964, 782, 732 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (5) [M^+], 137 (3), 100 (100), 72 (45), 43 (20). HR-MS (EI) *m/z* calcd for $C_{14}H_{21}NO_3$ [M^+] 251.1521, found 251.1515.

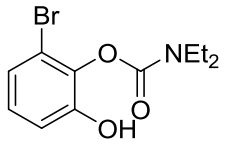


2-Fluoro-6-hydroxyphenyl diethylcarbamate (2j): The representative procedure was followed using 2-fluorophenyl diethylcarbamate (**1j**) (105.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2j** (58%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 6.93–6.85 (m, 1H), 6.66–6.59 (m, 2H), 3.47 (q, J = 7.1 Hz, 2H), 3.38 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 155.1 ($^{1}J_{C–F}$ = 248 Hz, C_q), 154.2 (C_q), 150.1 ($^{3}J_{C–F}$ = 3 Hz, C_q), 128.5 ($^{2}J_{C–F}$ = 13 Hz, C_q), 125.7 ($^{3}J_{C–F}$ = 10 Hz, CH), 113.7 ($^{4}J_{C–F}$ = 3 Hz, CH), 107.6 ($^{2}J_{C–F}$ = 19 Hz, CH), 42.7 (CH_2), 42.5 (CH_2), 13.8 (CH_3), 13.1 (CH_3). ^{19}F-NMR (283 MHz, $CDCl_3$) δ = –(130.1–130.2) (m). IR (neat): 3277, 2979, 1692, 1474, 1013,

768, 562 cm^{-1}. MS (EI) *m/z* (relative intensity) 227 (10) [M^+], 128 (15), 100 (100), 72 (77), 44 (32). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}FNO_3$ [M^+] 227.0958, found 227.0956.

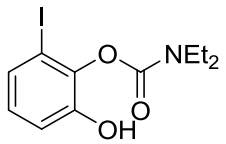


2-Chloro-6-hydroxyphenyl diethylcarbamate (2k): The representative procedure was followed using 2-chlorophenyl diethylcarbamate (**1k**) (113.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2k** (52%) as a colorless solid. M.p. = 75–77 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 6.92–6.80 (m, 2H), 6.68 (dd, J = 7.3, 2.4 Hz, 1H), 3.52 (q, J = 7.1 Hz, 2H), 3.39 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 153.9 (C_q), 150.1 (C_q), 136.5 (C_q), 127.2 (C_q), 126.3 (CH), 121.0 (CH), 116.9 (CH), 42.6 (CH_2), 42.3 (CH_2), 13.9 (CH_3), 13.1 (CH_3). IR (neat): 3298, 2981, 1694, 1425, 1211, 1159, 910, 773, 718 cm^{-1}. MS (EI) *m/z* (relative intensity) 243 (10) [M^+], 144 (15), 100 (100), 72 (75), 44 (33). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}ClNO_3$ [M^+] 243.0662, found 243.0655.

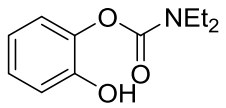


2-Bromo-6-hydroxyphenyl diethylcarbamate (2l): The representative procedure was followed using 2-bromophenyl diethylcarbamate (**1l**) (135.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2l** (57%) as a colorless solid. M.p. = 107–109 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.39 (s, 1H), 7.06 (dd, J = 8.0, 1.7 Hz, 1H), 6.84 (dd, J = 8.0, 8.0 Hz, 1H), 6.77 (dd, J = 8.0, 1.7 Hz, 1H), 3.56 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 153.8 (C_q), 149.9 (C_q), 137.8 (C_q), 127.0 (CH), 124.3 (CH), 118.0 (CH),

116.4 (C_q), 42.6 (CH_2), 42.3 (CH_2), 14.0 (CH_3), 13.1 (CH_3). IR (neat): 3177, 2979, 1690, 1424, 1209, 1162, 885, 751 cm^{-1}. MS (EI) *m/z* (relative intensity) 287 (3) [M^+], 188 (3), 100 (100), 72 (40), 44 (5). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}BrNO_3$ [M^+] 287.0157, found 287.0163.

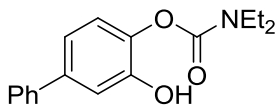


2-Hydroxy-6-iodophenyl diethylcarbamate (2m): The representative procedure was followed using 2-iodophenyl diethylcarbamate (**1m**) (159.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2m** (42%) as a colorless solid. M.p. = 118–120 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.31 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.76 (s, 1H), 6.73 (dd, J = 8.0, 8.0 Hz, 1H), 3.62 (q, J = 7.1 Hz, 2H), 3.42 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 153.7 (C_q), 148.9 (C_q), 140.5 (C_q), 130.5 (CH), 127.9 (CH), 119.1 (CH), 90.6 (C_q), 42.5 (CH_2), 42.4 (CH_2), 14.1 (CH_3), 13.1 (CH_3). IR (neat): 3207, 2978, 1688, 1422, 1207, 1160, 871, 749 cm^{-1}. MS (EI) *m/z* (relative intensity) 335 (6) [M^+], 235 (5), 206 (4), 100 (100), 72 (37). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}INO_3$ [M^+] 335.0018, found 335.0034.

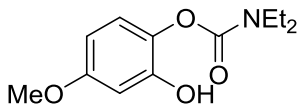


2-Hydroxyphenyl diethylcarbamate (2n): The representative procedure was followed using phenyl diethylcarbamate (**1n**) (96.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2n** (42%) as a colorless solid. M.p. = 69–71 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.31 (s, 1H), 7.07–6.93 (m, 3H), 6.88–6.82 (m, 1H), 3.46 (q, J = 7.2 Hz, 2H), 3.39 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.7 (C_q), 147.9 (C_q), 140.2 (C_q), 126.5

(CH), 122.0 (CH), 120.7 (CH), 119.3 (CH), 42.6 (CH_2), 42.3 (CH_2), 14.1 (CH_3), 13.2 (CH_3). IR (neat): 3289, 2976, 1684, 1278, 1161, 1097, 938, 744 cm^{-1}. MS (EI) *m/z* (relative intensity) 209 (15) [M^+], 110 (15), 100 (100), 72 (80), 44 (36). HR-MS (EI) *m/z* calcd for $C_{11}H_{15}NO_3$ [M^+] 209.1052, found 209.1054. The spectral data are in accordance with those reported in the literature.[2]

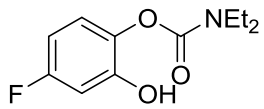


3-Hydroxy-[1,1'-biphenyl]-4-yl diethylcarbamate (2o): The representative procedure was followed using [1,1'-biphenyl]-4-yl diethylcarbamate (**1o**) (134.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1) yielded **2o** (51%) as a colorless solid. M.p. = 81–83 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.51–7.47 (m, 2H), 7.42–7.29 (m, 3H), 7.22 (d, *J* = 1.7 Hz, 1H), 7.11–7.04 (m, 2H), 3.50 (q, *J* = 7.1 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.8 (C_q), 148.0 (C_q), 140.1 (C_q), 139.7 (C_q), 139.5 (C_q), 128.5 (CH), 127.1 (CH), 126.9 (CH), 122.2 (CH), 119.2 (CH), 117.7 (CH), 42.6 (CH_2), 42.3 (CH_2), 14.0 (CH_3), 13.2 (CH_3). IR (neat): 3213, 2978, 1681, 1413, 1240, 1167, 754, 696 cm^{-1}. MS (EI) *m/z* (relative intensity) 285 (10) [M^+], 128 (8), 100 (100), 72 (47), 44 (10). HR-MS (EI) *m/z* calcd for $C_{17}H_{19}NO_3$ [M^+] 285.1365, found 285.1364.

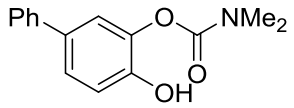


2-Hydroxy-4-methoxyphenyl diethylcarbamate (2p): The representative procedure was followed using 4-methoxyphenyl diethylcarbamate (**1p**) (111.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2p** (46%) as a colorless solid. M.p. = 86–88 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.51 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.47 (d, *J* = 3.0 Hz, 1H), 6.38 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.69 (s, 3H), 3.44 (q, *J* =

7.1 Hz, 2H), 3.37 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 158.0 (C_q), 155.2 (C_q), 148.6 (C_q), 134.1 (C_q), 122.2 (CH), 106.3 (CH), 104.2 (CH), 55.4 (CH_3), 42.6 (CH_2), 42.3 (CH_2), 14.1 (CH_3), 13.2 (CH_3). IR (neat): 3212, 2983, 1671, 1428, 1205, 1166, 1030, 833 cm^{-1}. MS (EI) *m/z* (relative intensity) 239 (15) [M$^+$], 111 (12), 100 (100), 72 (65), 43 (25). HR-MS (EI) *m/z* calcd for $C_{12}H_{17}NO_4$ [M$^+$] 239.1158, found 239.1155.

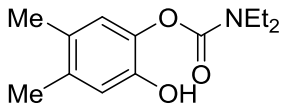


4-Fluoro-2-hydroxyphenyl diethylcarbamate (2q): The representative procedure was followed using 4-fluorophenyl diethylcarbamate (**1q**) (105.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2q** (48%) as a colorless solid. M.p. = 83–85 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 6.94 (dd, J = 8.6, 5.7 Hz, 1H), 6.59–6.51 (m, 2H), 3.46 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 160.5 ($^1J_{C–F}$ = 243 Hz, C_q), 154.9 (C_q), 149.2 ($^3J_{C–F}$ = 13 Hz, C_q), 136.2 ($^4J_{C–F}$ = 3 Hz, C_q), 122.6 ($^3J_{C–F}$ = 13 Hz, CH), 106.8 ($^2J_{C–F}$ = 24 Hz, CH), 106.1 ($^2J_{C–F}$ = 24 Hz, CH), 42.6 (CH_2), 42.3 (CH_2), 14.0 (CH_3), 13.2 (CH_3). ^{19}F-NMR (283 MHz, $CDCl_3$) δ = –(115.8–115.9) (m). IR (neat): 3170, 2984, 1675, 1426, 1227, 1154, 963, 850, 561 cm^{-1}. MS (EI) *m/z* (relative intensity) 227 (8) [M$^+$], 128 (12), 100 (100), 72 (83), 44 (40). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}FNO_3$ [M$^+$] 227.0958, found 227.0957.

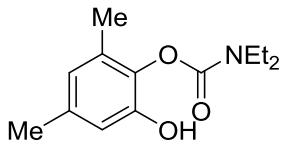


4-Hydroxy-[1,1'-biphenyl]-3-yl dimethylcarbamate (2r): The representative procedure was followed using [1,1'-biphenyl]-3-yl dimethylcarbamate (**1r**) (120.5 mg, 0.50 mmol), and the reaction mixture was stirred at 50 °C for 24 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2r** (75%) as a colorless

solid. M.p. = 127–129 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.52 (d, J = 7.2 Hz, 2H), 7.43–7.38 (m, 2H), 7.33–7.26 (m, 3H), 7.02 (d, J = 8.7 Hz, 1H), 3.16 (s, 3H), 3.06 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 155.2 (C_q), 147.3 (C_q), 140.2 (C_q), 140.1 (C_q), 134.2 (C_q), 128.7 (CH), 126.8 (CH), 126.6 (CH), 125.2 (CH), 120.7 (CH), 119.4 (CH), 36.9 (CH_3), 36.8 (CH_3). IR (neat): 3210, 1682, 1296, 1180, 752, 690 cm^{-1}. MS (EI) *m/z* (relative intensity) 257 (15) [M^+], 157 (8), 128 (10), 72 (100), 42 (6). HR-MS (EI) *m/z* calcd for $C_{15}H_{15}NO_3$ [M^+] 257.1052, found 257.1059.

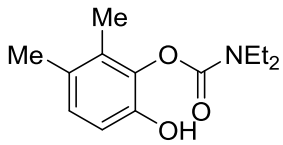


2-Hydroxy-4,5-dimethylphenyl diethylcarbamate (2s): The representative procedure was followed using 3,4-dimethylphenyl diethylcarbamate (**1s**) (110.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2s** (52%) as a colorless solid. M.p. = 82–84 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.08 (s, 1H), 6.78 (s, 1H), 6.74 (s, 1H), 3.46 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 2.14 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.9 (C_q), 145.2 (C_q), 137.6 (C_q), 134.6 (C_q), 128.6 (C_q), 122.6 (CH), 120.2 (CH), 42.5 (CH_2), 42.2 (CH_2), 19.1 (CH_3), 18.7 (CH_3), 14.1 (CH_3), 13.2 (CH_3). IR (neat): 3270, 2977, 1690, 1417, 1305, 1165, 1084, 883, 758 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (25) [M^+], 137 (10), 100 (100), 72 (75), 44 (22). HR-MS (EI) *m/z* calcd for $C_{13}H_{19}NO_3$ [M^+] 237.1365, found 237.1359.

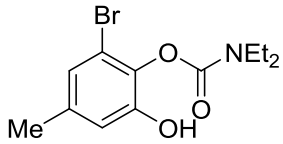


2-Hydroxy-4,6-dimethylphenyl diethylcarbamate (2t): The representative procedure was followed using 2,4-dimethylphenyl diethylcarbamate (**1t**) (110.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2t** (73%) as a colorless solid.

M.p. = 109–111 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.88 (s, 1H), 6.52 (d, J = 2.6 Hz, 1H), 6.52 (d, J = 2.6 Hz, 1H), 3.50 (q, J = 7.1 Hz, 2H), 3.41 (q, J = 7.1 Hz, 2H), 2.18 (s, 3H), 2.17 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.5 (C_q), 147.7 (C_q), 136.4 (C_q), 135.5 (C_q), 130.3 (C_q), 122.9 (CH), 116.7 (CH), 42.4 (CH_2), 42.0 (CH_2), 20.8 (CH_3), 16.5 (CH_3), 14.0 (CH_3), 13.2 (CH_3). IR (neat): 3253, 2981, 1673, 1276, 1157, 831, 569 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (25) [M^{+}], 137 (30), 100 (100), 72 (65), 44 (15). HR-MS (EI) *m/z* calcd for $C_{13}H_{19}NO_3$ [M^{+}] 237.1365, found 237.1364.



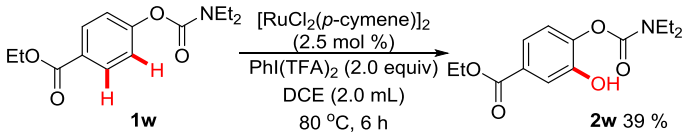
2-Hydroxy-5,6-dimethylphenyl diethylcarbamate (2u): The representative procedure was followed using 2,3-dimethylphenyl diethylcarbamate (**1u**) (110.5 mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 3 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2u** (66%) as a colorless solid. M.p. = 81–83 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.81 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 3.52 (q, J = 7.2 Hz, 2H), 3.41 (q, J = 7.2 Hz, 2H), 2.20 (s, 3H), 2.12 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 154.2 (C_q), 146.0 (C_q), 138.4 (C_q), 129.3 (C_q), 129.0 (C_q), 126.9 (CH), 114.9 (CH), 42.3 (CH_2), 42.0 (CH_2), 19.4 (CH_3), 14.1 (CH_3), 13.2 (CH_3), 12.8 (CH_3). IR (neat): 3337, 2977, 1684, 1423, 1274, 1159, 1025, 729, 654 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (10) [M^{+}], 137 (5), 100 (100), 72 (50), 44 (10). HR-MS (EI) *m/z* calcd for $C_{13}H_{19}NO_3$ [M^{+}] 237.1365, found 237.1372.



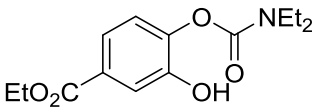
2-Bromo-6-hydroxy-4-methylphenyl diethylcarbamate (2v): The representative procedure was followed using 2-bromo-4-methylphenyl diethylcarbamate (**1v**) (142.5

mg, 0.50 mmol), and the reaction mixture was stirred at 80 °C for 6 h. Isolation by column chromatography (*n*-hexane/EtOAc: 5/1→3/1) yielded **2v** (53%) as a colorless solid. M.p. = 83–85 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 6.87 (d, J = 1.9 Hz, 1H), 6.50 (d, J = 1.9 Hz, 1H), 3.55 (q, J = 7.1 Hz, 2H), 3.41 (q, J = 7.1 Hz, 2H), 2.14 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.1 (C_q), 149.4 (C_q), 137.0 (C_q), 135.4 (C_q), 124.4 (CH), 118.4 (CH), 115.8 (C_q), 42.6 (CH_2), 42.3 (CH_2), 20.6 (CH_3), 14.0 (CH_3), 13.2 (CH_3). IR (neat): 3239, 2976, 1686, 1426, 1305, 1269, 800, 577 cm^{-1}. MS (EI) *m/z* (relative intensity) 301 (3) [M^+], 200 (3), 100 (100), 72 (45), 43 (36). HR-MS (EI) *m/z* calcd for $C_{12}H_{16}BrNO_3$ [M^+] 301.0314, found 301.0304.

Intramolecular Competition Experiment

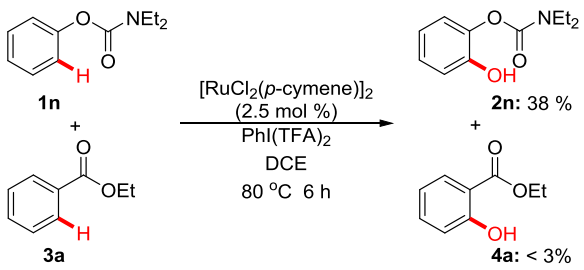


$[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), $PhI(TFA)_2$ (430 mg, 1.0 mmol), **1w** (132.5 mg, 0.5 mmol) and DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The reaction mixture was stirred at 80 °C for 6 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1→3/1) to afford the desired product **2w** (39%) as a colorless oil.

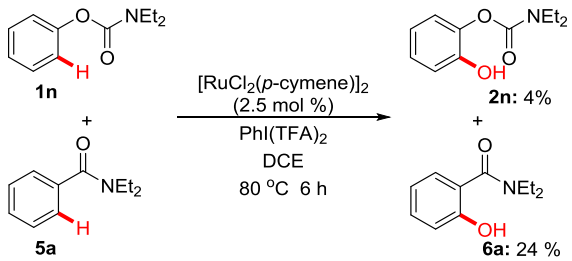


Ethyl 4-{(diethylcarbamoyl)oxy}-3-hydroxybenzoate (2w): ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.64 (d, J = 2.0 Hz, 1H), 7.56 (dd, J = 8.4, 2.0 Hz, 1H), 7.47 (s, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.47 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 165.8 (C_q), 154.1 (C_q), 147.8 (C_q), 143.6 (C_q), 128.5 (C_q), 122.1 (CH), 122.0 (CH), 120.1 (CH), 61.0 (CH_2), 42.7 (CH_2), 42.5 (CH_2), 14.3 (CH_3), 14.1 (CH_3), 13.3 (CH_3). IR (neat): 3274, 2979, 1687, 1427, 1279, 1214, 1094, 759 cm^{-1}. MS (EI) *m/z* (relative intensity) 281 (3) [M$^+$], 236 (5), 100 (100), 72 (50), 44 (10). HR-MS (EI) *m/z* calcd for $C_{14}H_{19}NO_5$ [M$^+$] 281.1263, found 281.1264.

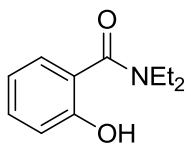
Intermolecular Competition Experiments



$[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), $PhI(TFA)_2$ (430 mg, 1.0 mmol), **1n** (96.5 mg, 0.5 mmol), **3a** (75.0 mg, 0.5 mmol) and DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The reaction mixture was stirred at 80 °C for 6 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure, purified by flash column chromatography on silica gel (*n*-hexane/EtOAc: 5/1→3/1) to afford the desired product **2n** (38%).



$[RuCl_2(p\text{-cymene})]_2$ (7.65 mg, 2.5 mol %), $PhI(TFA)_2$ (430 mg, 1.0 mmol), **1n** (96.5 mg, 0.5 mmol), **5a** (88.5 mg, 0.5 mmol) and DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The reaction mixture was stirred at 80 °C for 6 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure, purified by flash column chromatography on silica gel (*n*-hexane/EtOAc: 5/1→3/1) to afford the desired product **6a** (24%) and **2n** (4%).



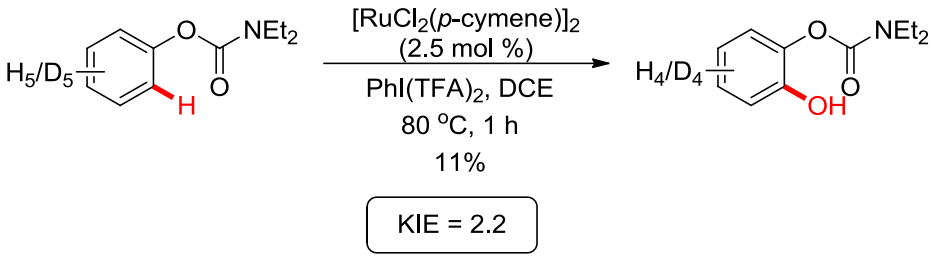
***N,N*-Diethyl-2-hydroxybenzamide (6a):** ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 9.44 (s, 1H), 7.27–7.19 (m, 2H), 6.93 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.82 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 171.2 (C_q), 157.9 (C_q), 131.9 (CH), 127.2 (CH), 118.6 (C_q), 118.5 (CH), 117.7 (CH) 42.0, (CH_2), 13.3 (CH_3). IR (neat): 3165, 2978, 1610, 1582, 1247, 881 cm^{-1}. MS (EI) *m/z* (relative intensity): 193 (35) [M^+], 192 (55), 121 (100). HR-MS (EI) *m/z* calcd for $C_{11}H_{14}NO_2$ [M^+] 193.1103, found 193.1103. The spectral data are in accordance with those reported in the literature.[3]

Preparation of the substrate [D_5]-1n [1, 4]

Seal tube equipped with a magnetic stirring bar was charged with CuI (37.8 mg, 10 mol %) and NaI (59.6 mg, 20 mol %). The tube was evacuated and back-filled with nitrogen. Then by [D_5]-bromobenzene (322.0 mg, 2.0 mmol, 1.0 equiv), DMEDA (88.5 mg, 1.0 mol) and 1,4-dioxane (2.0 mL) were added. The tube was sealed under N_2, and the reaction mixture was stirred at 110 °C. After 6 h, under a stream of N_2 $CsOH{\cdot}H_2O$ (1008 mg, 6.0 mol), and D_2O (2 mL) were added. The tube was sealed under N_2, stirred and heated to 130 °C for 24 h. At ambient temperature, CH_2Cl_2 (10 mL) and HCl (2 mL, 37%) were added. The reaction mixture was stirred for 2 h, then extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was obtained without further purification. The crude product was dissolved in DMF (5.0 mL). Then NaH (125 mg, 60% dispersion, 3.0 mmol) was added, the solution was stirred for 15 min at ambient temperature and diethylcarbamoyl chloride (272 mg, 2.0 mmol) was added. After stirring for 2 h at ambient temperature, the reaction mixture was carefully reacted with ice and extracted with Et_2O (3 x 15 mL). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on

silica gel (*n*-hexane/EtOAc: 10/1) to yield [D_5]-**1n** (95% [D]) (45%) as a colorless oil.

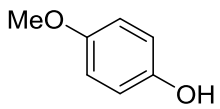
Kinetic Isotope Effect



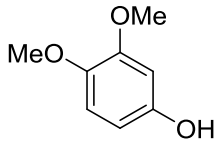
[$RuCl_2$(*p*-cymene)]$_2$ (3.9 mg, 2.5 mol %), PhI(TFA)$_2$ (215 mg, 0.5 mmol), [D_5]-**1n** (50.0 mg, 0.25 mmol), **1n** (48.5 mg, 0.25 mmol), DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The reaction mixture was stirred at 80 °C for 1 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1→3/1) to afford the desired product [D_n]-**2n** (11%). The ratio of **2n**/[D_5]-**2n** was determined to be 50/23 by ^{1}H-NMR spectroscopy.

General Procedure for Oxygenation of Anisoles:

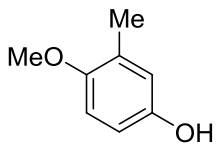
[$RuCl_2$(*p*-cymene)]$_2$ (7.7 mg, 2.5 mol %), **7** (0.5 mmol), PhI(TFA)$_2$ (0.55–1.0 mmol) and DCE (2.0 mL) were placed into a 25 mL schlenk tube equipped with a septum under N_2. The reaction mixture was stirred at 80 °C for 3 h. At ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel to afford the desired product **8**.



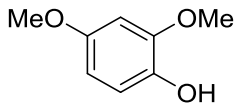
4-Methoxyphenol (8a): The representative procedure was followed using anisole (**7a**) (54.0 mg, 0.50 mmol), $PhI(TFA)_2$ (240 mg, 0.55 mmol). Isolation by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **8a** (71%) as a colorless solid. M.p. = 56–58 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.80 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 5.47 (s_{br}, 1H), 3.77 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 153.6 (C_q), 149.5 (C_q), 116.1 (CH), 114.9 (CH), 55.8 (CH_3). IR (neat): 3401, 2953, 1512, 1277, 1235, 1039, 807, 736 cm^{-1}. MS (EI) *m/z* (relative intensity) 124.1 (90) [M^+], 109.0 (100), 81 (50), 53 (27). HR-MS (EI) *m/z* calcd for $C_7H_8O_2$ [M^+] 124.0524, found 124.0528. The spectral data are in accordance with those reported in the literature.[5]



3,4-Dimethoxyphenol (8b): The representative procedure was followed using 1,2-dimethoxybenzene (**7b**) (69.0 mg, 0.50 mmol), $PhI(TFA)_2$ (240 mg, 0.55 mmol). Isolation by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **8b** (56%) as a colorless solid. M.p. = 79–81 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.70 (d, J = 8.6 Hz, 1H), 6.44 (d, J = 2.8 Hz, 1H), 6.33 (dd, J = 8.6, 2.8 Hz, 1H), 5.48 (s_{br}, 1H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 150.2 (C_q), 149.8 (C_q), 142.9 (C_q), 112.4 (CH), 105.8 (CH), 100.6 (CH), 56.5 (CH_3), 55.7 (CH_3). IR (neat): 3417, 2937, 1509, 1220, 1195, 1024, 952, 765 cm^{-1}. MS (EI) *m/z* (relative intensity) 154 (100) [M^+], 139 (87), 111 (75), 96 (15), 55 (15). HR-MS (EI) *m/z* calcd for $C_8H_{10}O_3$ [M^+] 154.0630, found 154.0634. The spectral data are in accordance with those reported in the literature.[5]



4-Methoxy-3-methylphenol (8c): The representative procedure was followed using 1-methoxy-2-methylbenzene (**7c**) (61.0 mg, 0.50 mmol), $PhI(TFA)_2$ (430 mg, 1.0 mmol). Isolation by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **8c** (47%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.68 (d, J = 8.5 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 6.60 (dd, J = 8.5, 2.9 Hz, 1H), 4.29 (s_{br}, 1H), 3.76 (s, 3H), 2.16 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.9 (C_q), 149.0 (C_q), 128.0 (C_q), 117.9 (CH), 112.5 (CH), 111.3 (CH), 56.0 (CH_3), 16.2 (CH_3). IR (neat): 3382, 2950, 1503, 1465, 1219, 1035, 738 cm^{-1}. MS (EI) *m/z* (relative intensity) 138 (85) [M^+], 123 (100), 95 (15), 77 (15), 67 (17). HR-MS (EI) *m/z* calcd for $C_8H_{10}O_2$ [M^+] 138.0681, found 138.0677. The spectral data are in accordance with those reported in the literature.[6]



2,4-Dimethoxyphenol (8d): The representative procedure was followed using 1,3-dimethoxybenzene (**7d**) (69.0 mg, 0.50 mmol), $PhI(TFA)_2$ (240 mg, 0.55 mmol). Isolation by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **8d** (84%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.82 (d, J = 8.6 Hz, 1H), 6.48 (d, J = 2.8 Hz, 1H), 6.37 (dd, J = 8.6, 2.8 Hz, 1H), 5.32 (s_{br}, 1H), 3.83 (s, 3H), 3.74 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 153.4 (C_q), 147.0 (C_q), 139.7 (C_q), 114.0 (CH), 104.1 (CH), 99.4 (CH), 55.8 (CH_3), 55.7 (CH_3). IR (neat): 3437, 2940, 1506, 1201, 1150, 1026, 789 cm^{-1}. MS (EI) *m/z* (relative intensity) 154 (100) [M^+], 139 (95), 111 (85), 96 (15), 79 (15), 53 (15). HR-MS (EI) *m/z* calcd for $C_8H_{10}O_3$ [M^+] 154.0630, found 154.0629. The spectral data are in accordance with those reported in the literature.[5]

References

[1] Schröder, N.; Wencel-Delord, J.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 8298–8301.

[2] Bracegirdle, S.; Anderson, E. A. *Chem. Commun*. **2010**, *46*, 3454–3456.

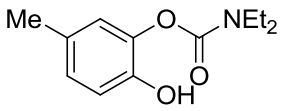
[3] Thirunavukkarasu, V. S.; Hubrich, J.; Ackermann, L. *Org. Lett.* **2012**, *14*, 4210–4213.

[4] Tlili, A.; Xia, N.; Monnier, F.; Taillefer, M. *Angew. Chem. Int. Ed*. **2009**, *48*, 8725–8728.

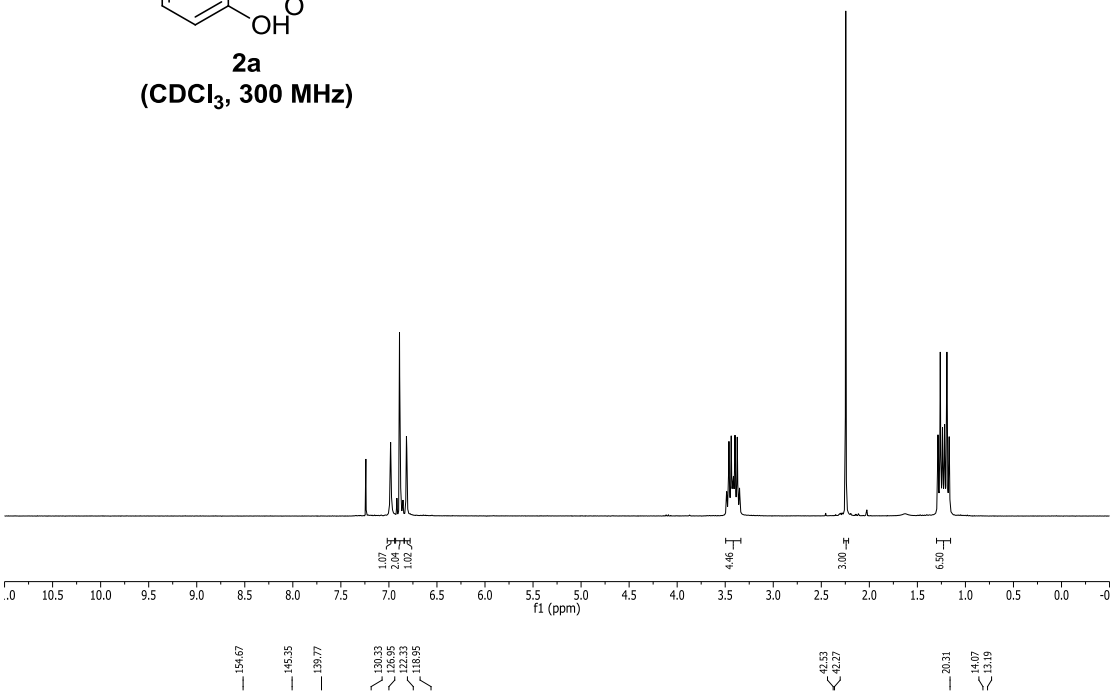
[5] Kamata, K.; Yamaura, T.; Mizuno, N. *Angew. Chem. Int. Ed*. **2012**, *51*, 7275–7278.

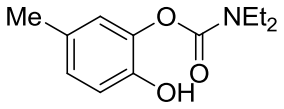
[6] Chuang, K. V.; Navarro, R.; Reisman, S. E. *Chem. Sci.* **2011**, *2*, 1086–1089.

^{1}H- and ^{13}C-NMR Spectra

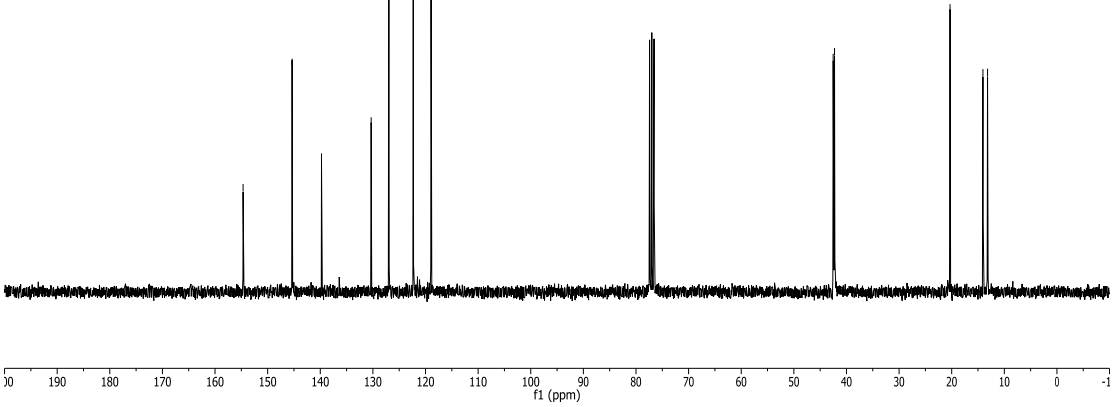


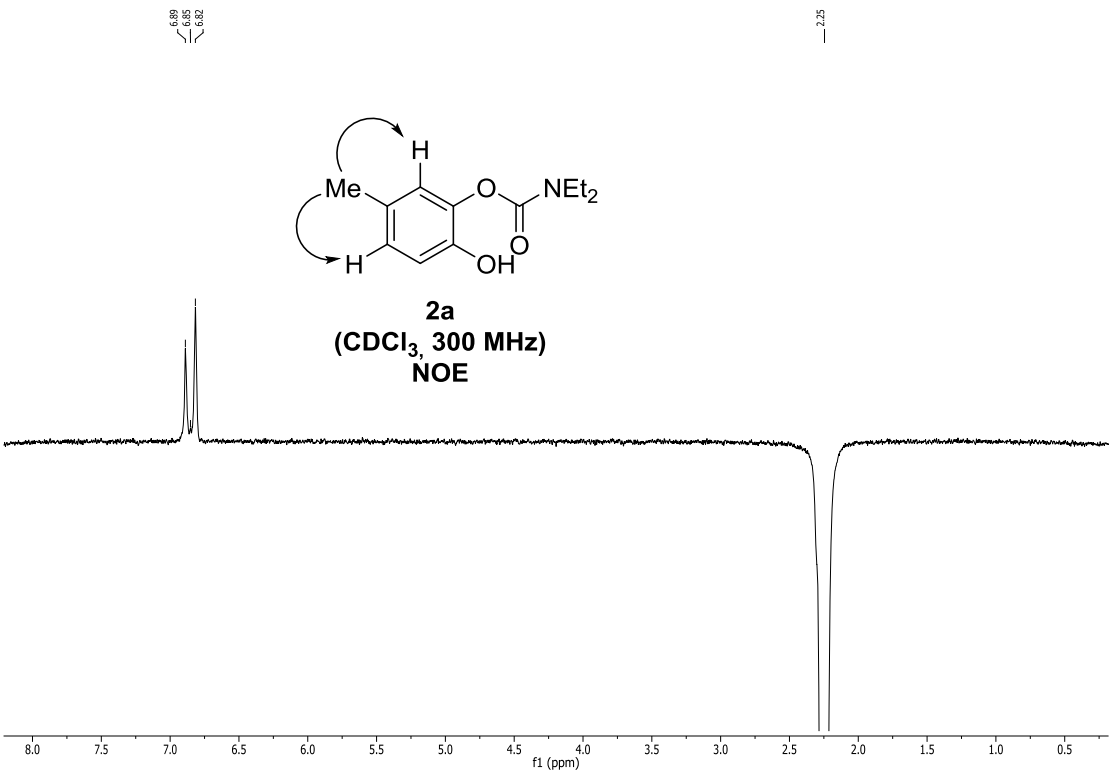
2a
($CDCl_3$, 300 MHz)

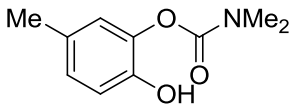




2a
($CDCl_3$, 75 MHz)

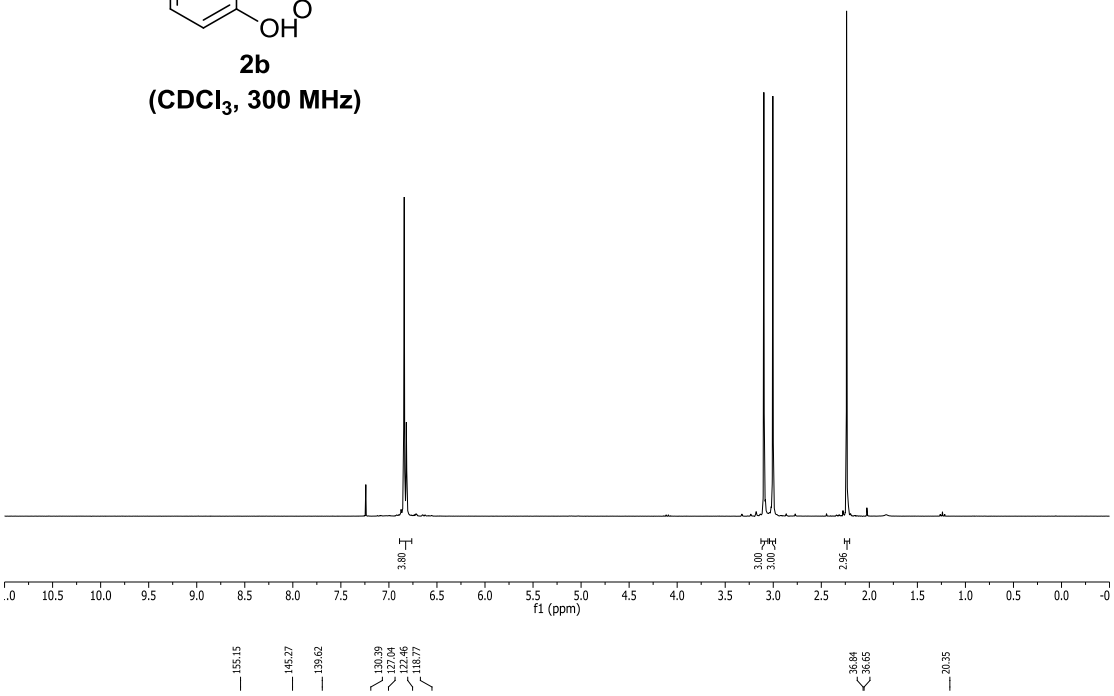


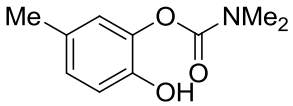

6.89
6.85
6.82
2.25
H
Me
O
NEt2
O
H
OH
2a
(CDCl3, 300 MHz)
NOE
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



2b

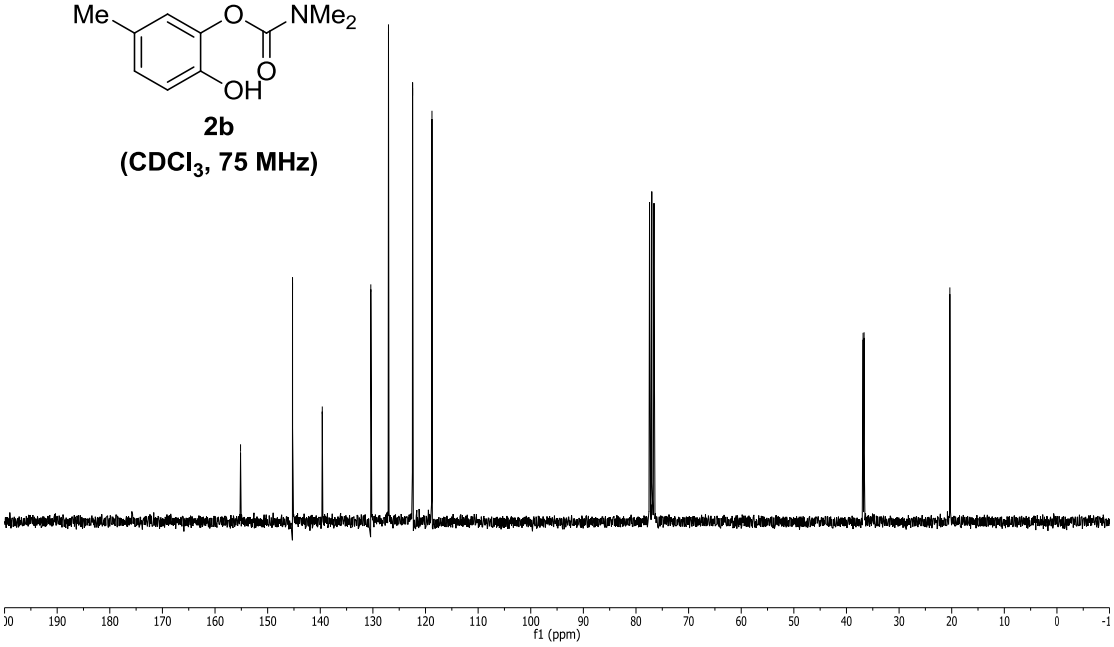
($CDCl_3$, 300 MHz)

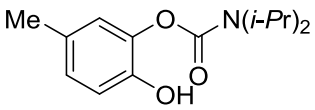




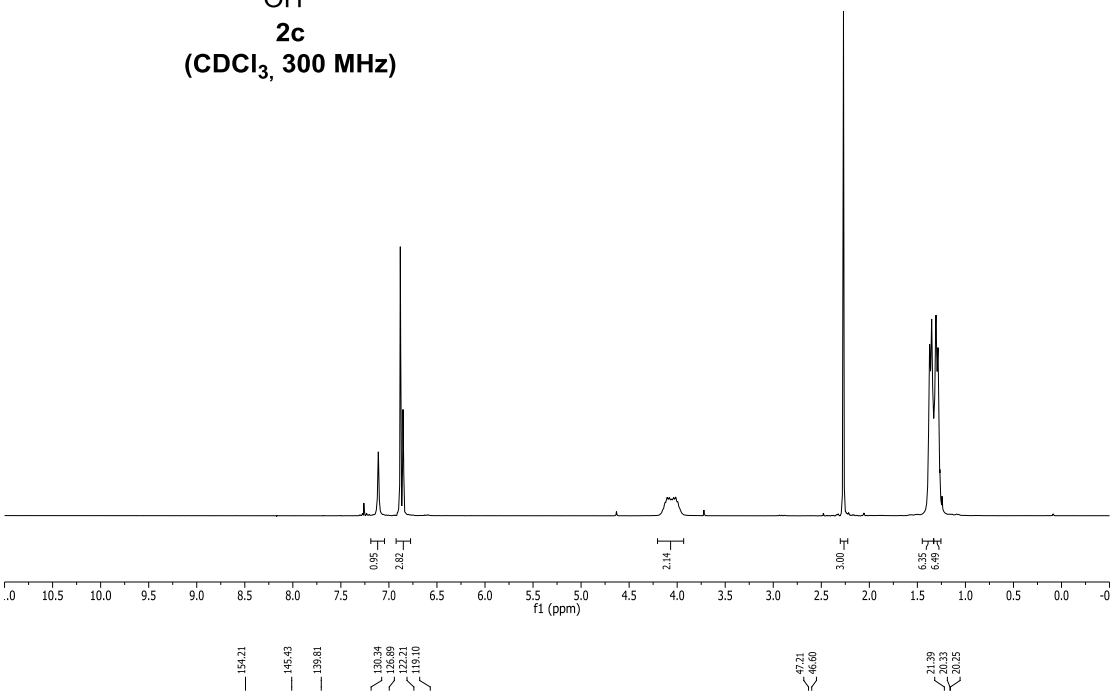
2b

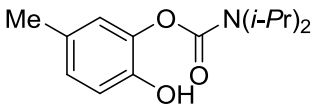
($CDCl_3$, 75 MHz)



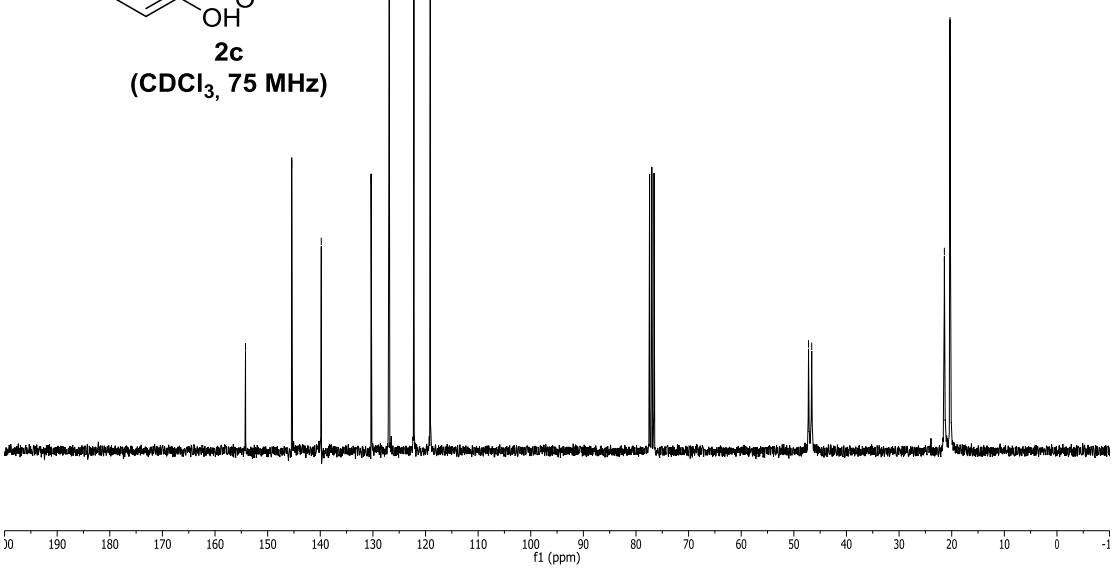


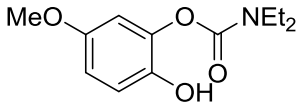
2c
($CDCl_3$, 300 MHz)



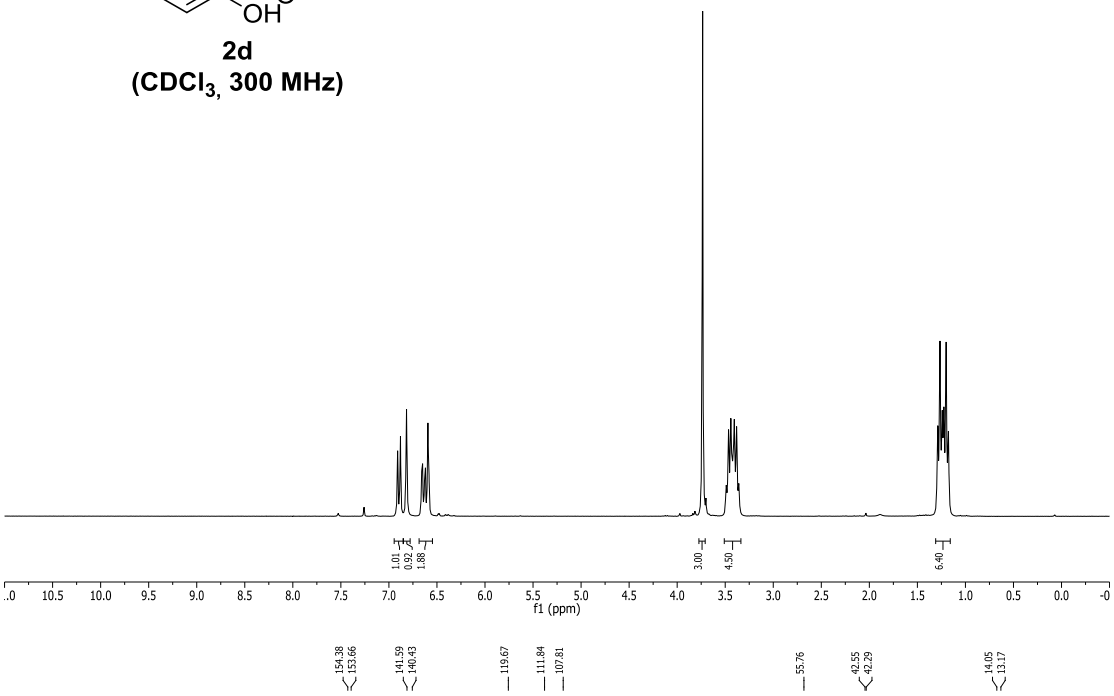


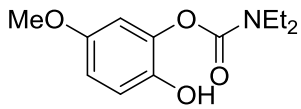
2c
($CDCl_3$, 75 MHz)



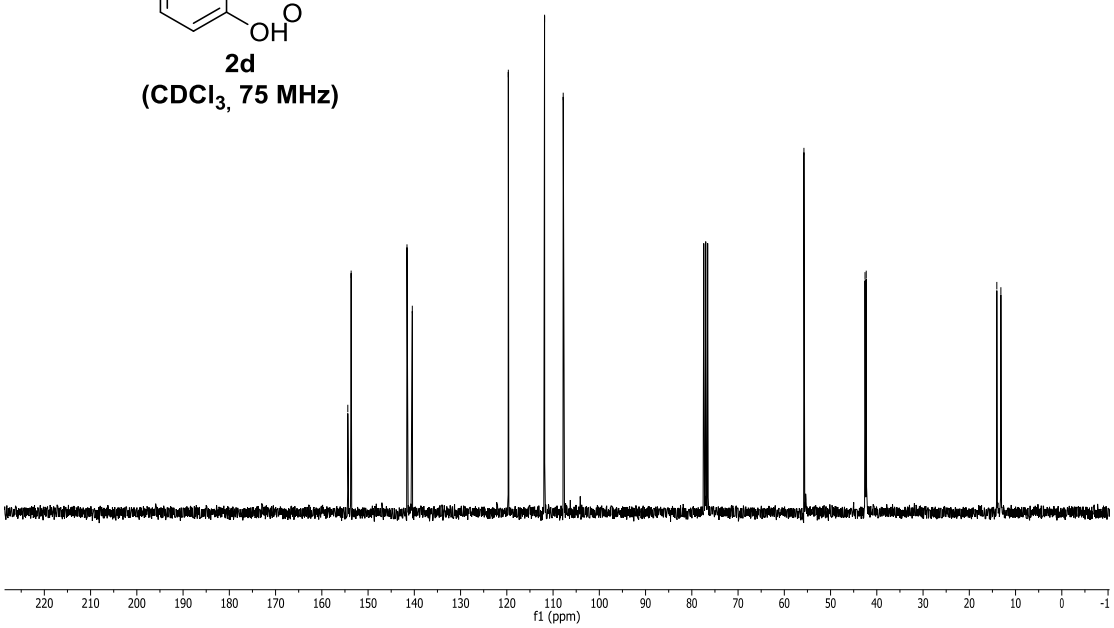


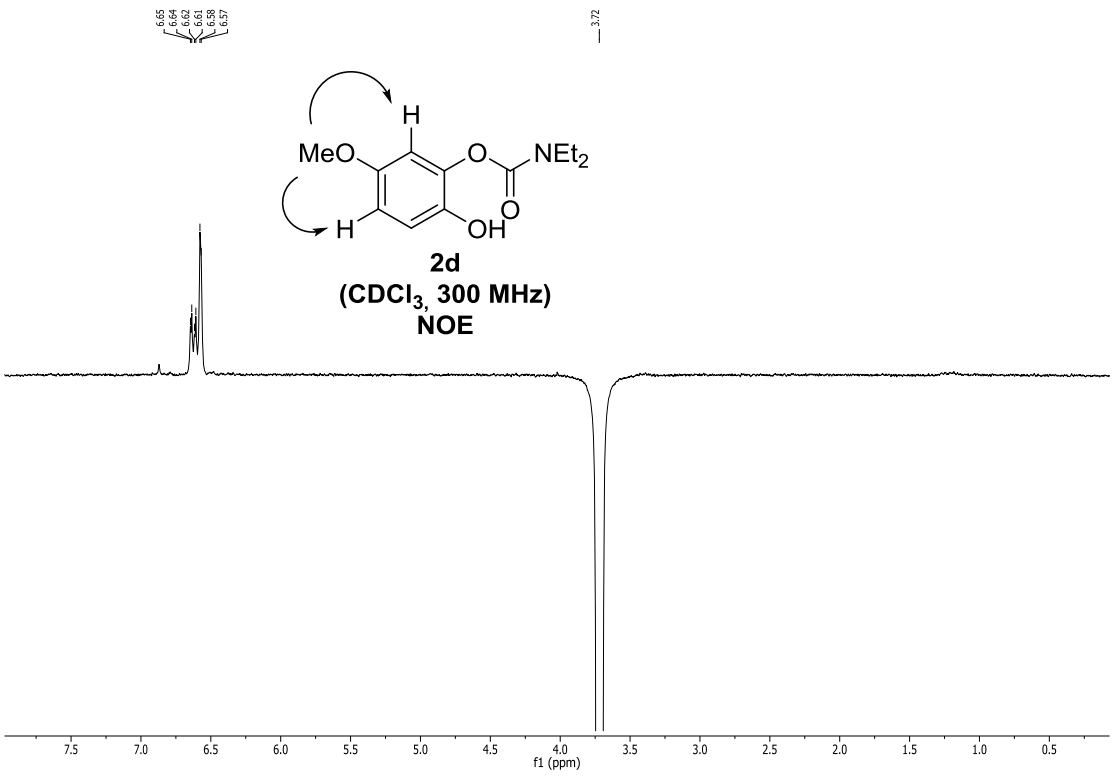
2d
($CDCl_3$, 300 MHz)

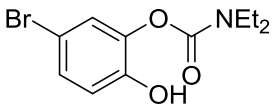




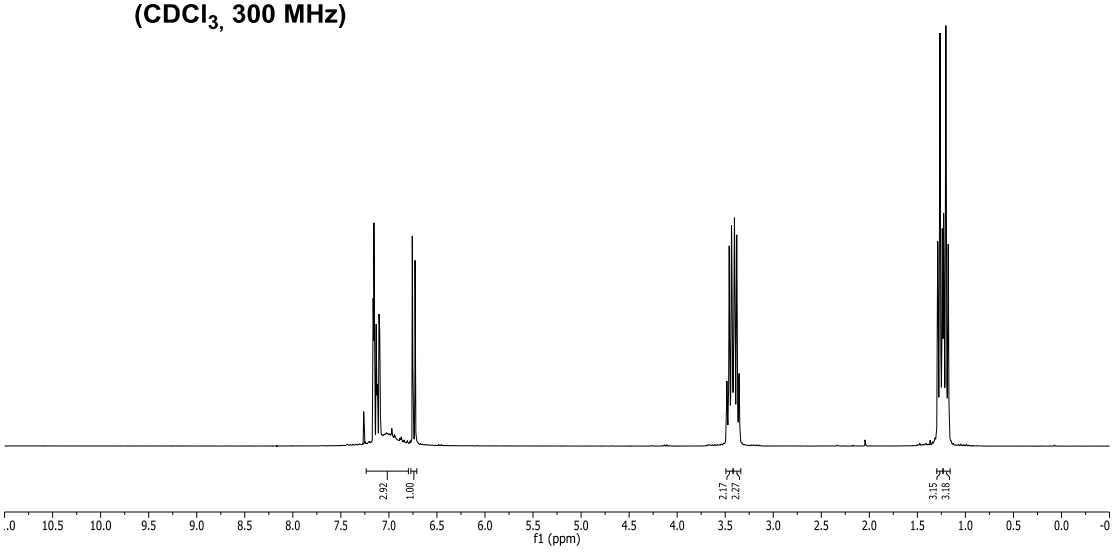
2d
($CDCl_3$, 75 MHz)



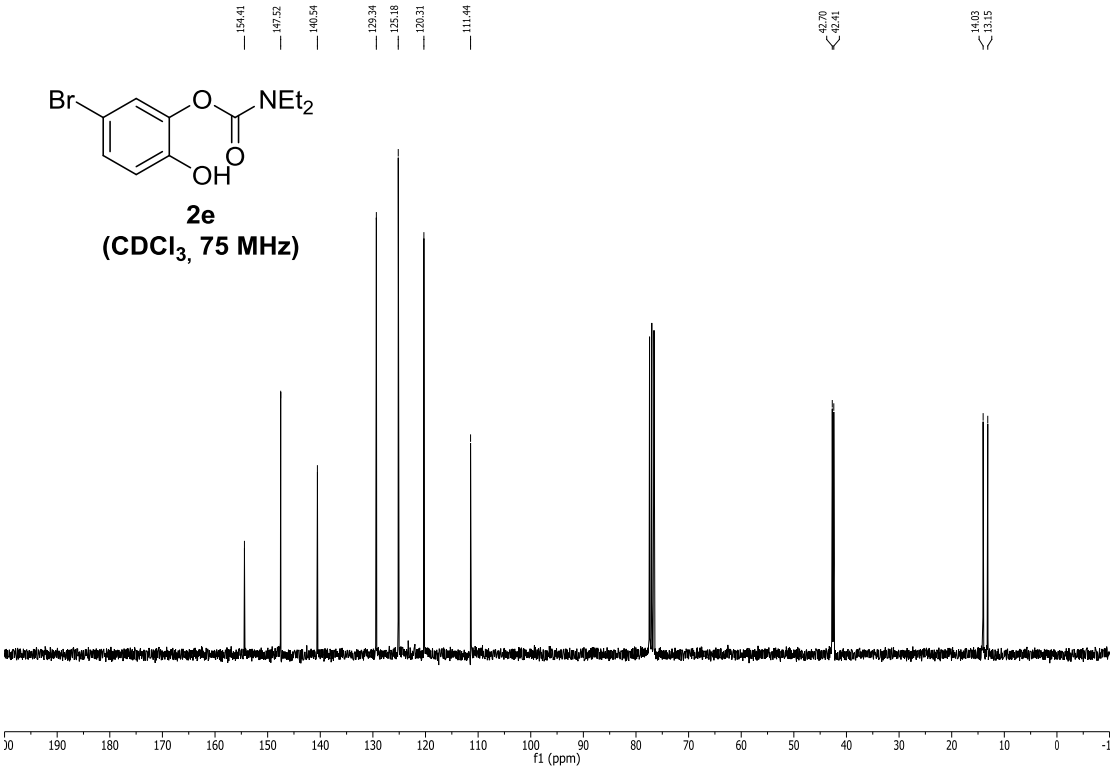

6.65
6.64
6.62
6.61
6.59
6.57
3.72
H
MeO
O
NEt2
O
H
OH
2d
(CDCl3, 300 MHz)
NOE
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

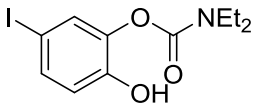


2e
($CDCl_3$, 300 MHz)

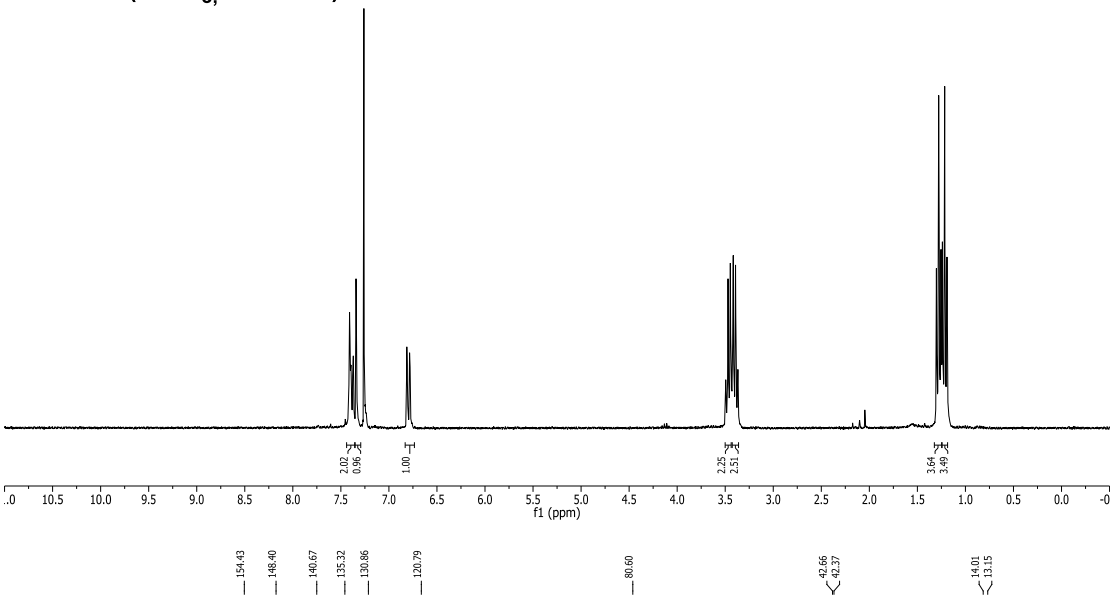


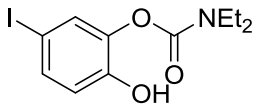
2e
($CDCl_3$, 75 MHz)



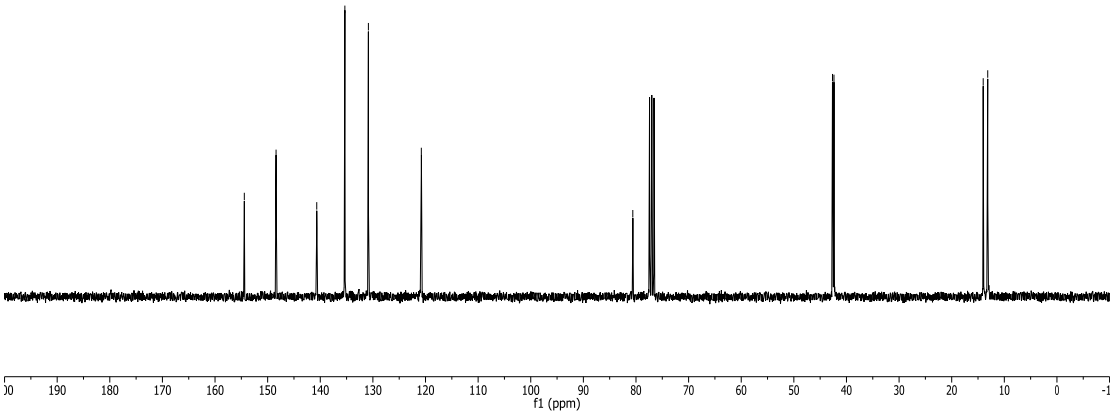


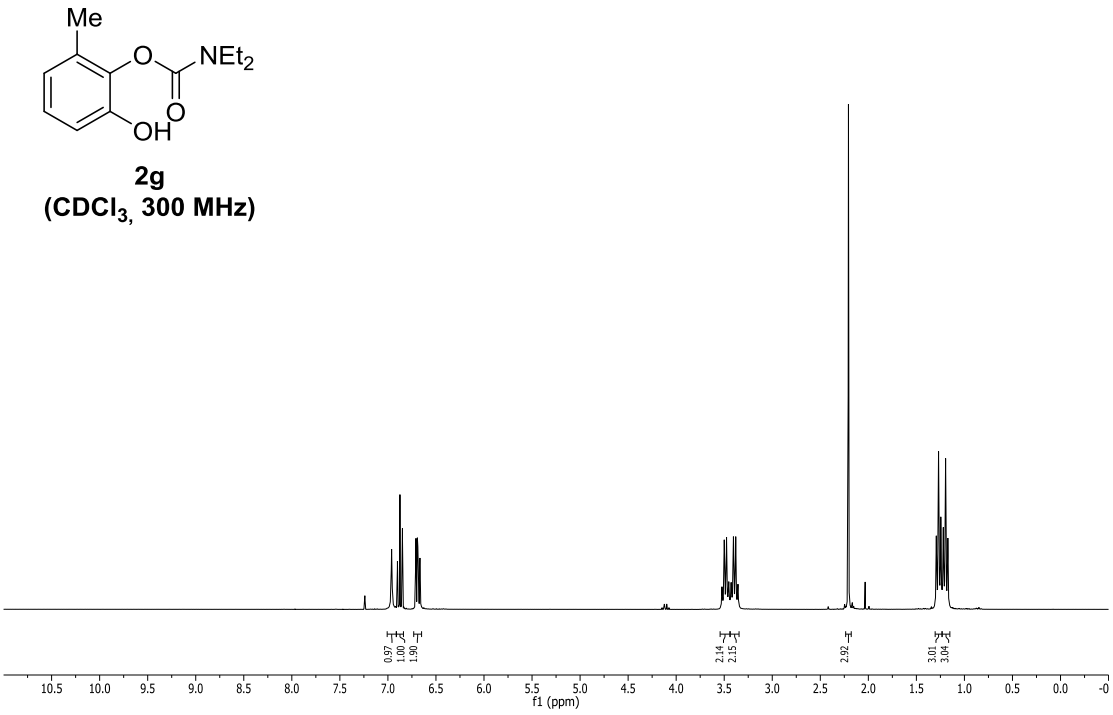
2f
($CDCl_3$, 300 MHz)

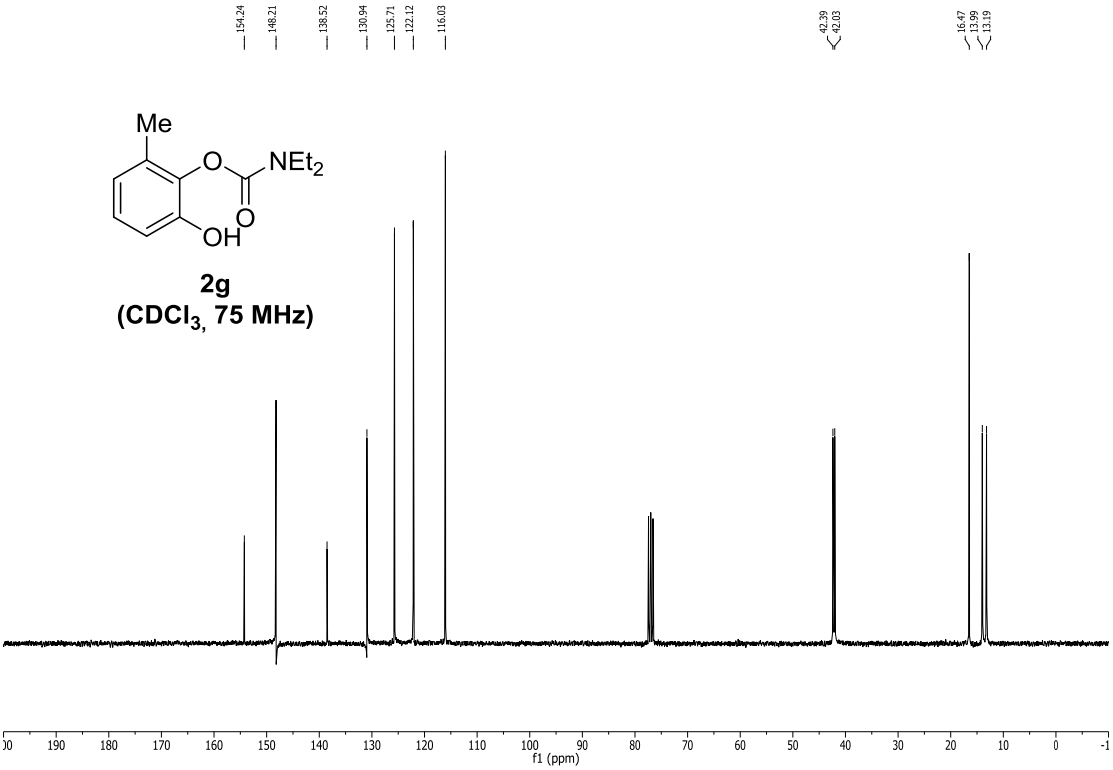


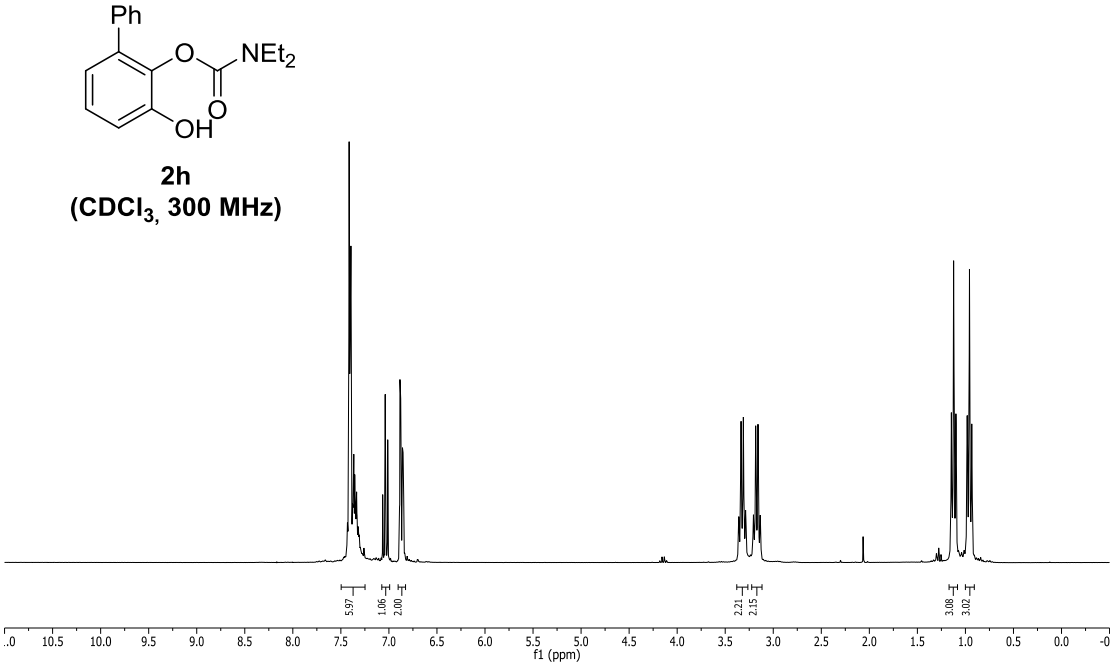


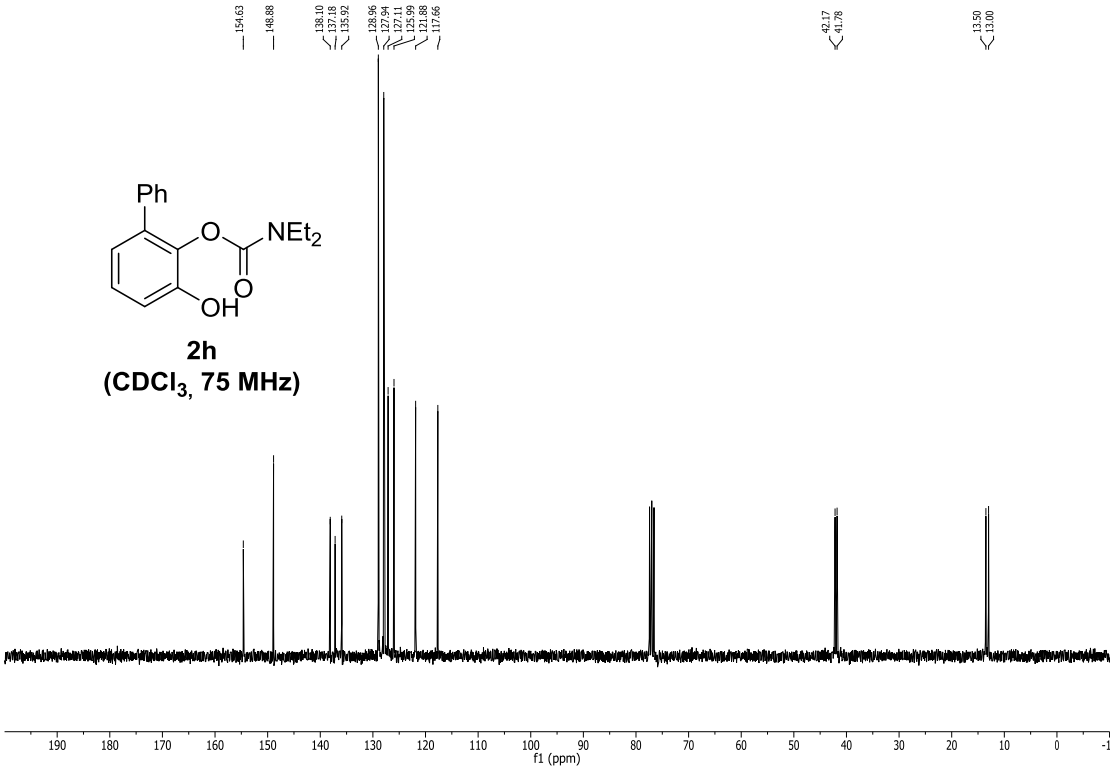
2f
($CDCl_3$, 75 MHz)

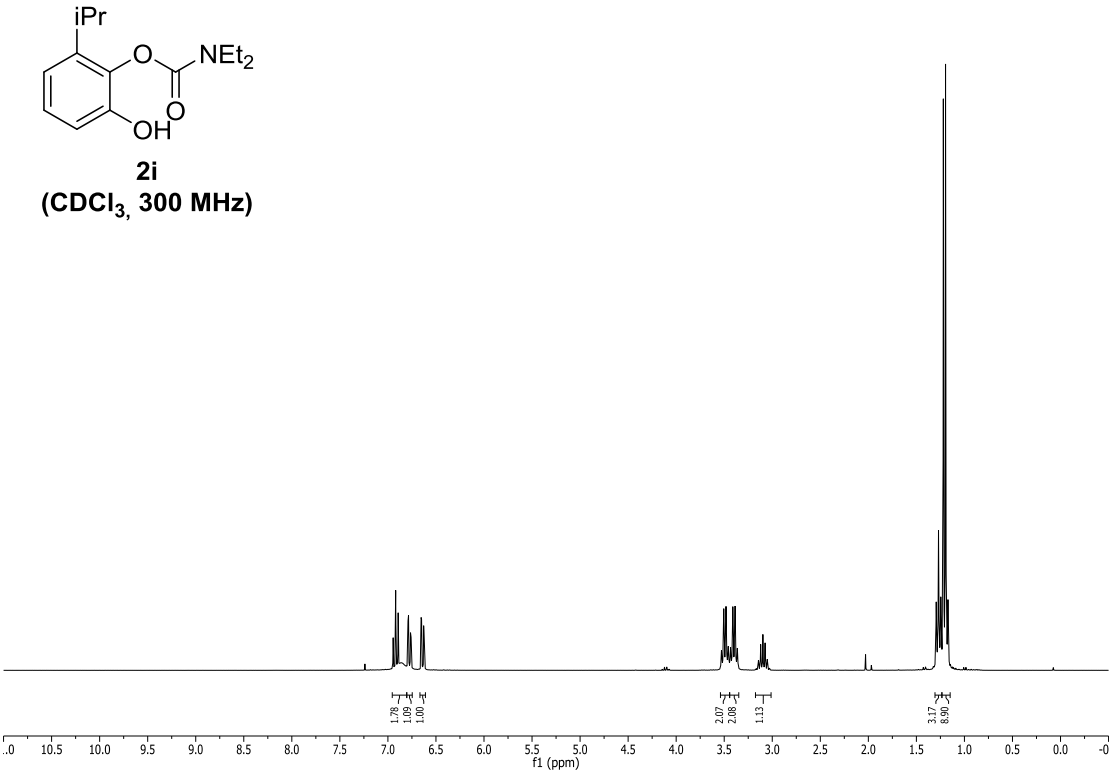


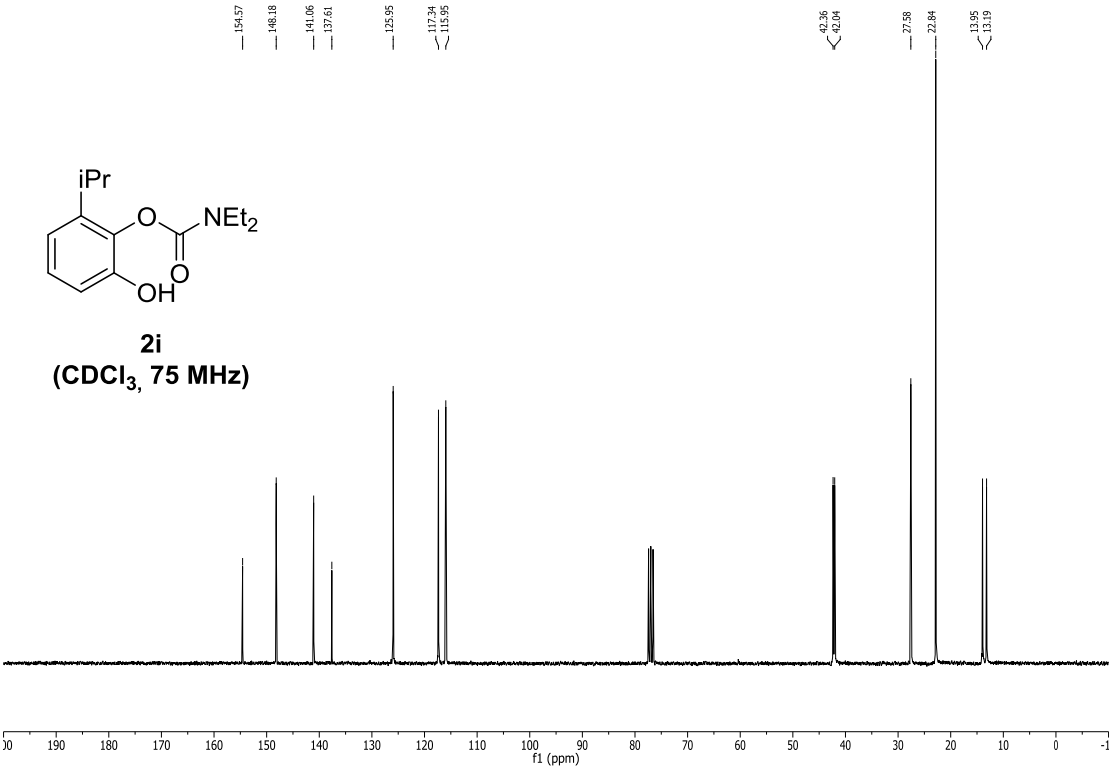

Me
O
NEt2
O
OH
2g
(CDCl3, 300 MHz)
0.97
1.00
1.90
2.14
2.15
2.92
3.01
3.04
f1 (ppm)

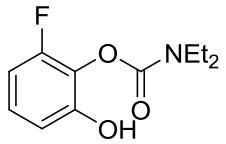

Me
O
NEt2
O
OH
2g
(CDCl3, 75 MHz)
154.24
148.21
138.52
130.94
125.71
122.12
116.03
42.39
42.03
16.47
13.99
13.19
f1 (ppm)


Ph
O
NEt2
O
OH
2h
(CDCl3, 300 MHz)
5.97
1.06
2.00
2.21
2.15
3.08
3.02
f1 (ppm)

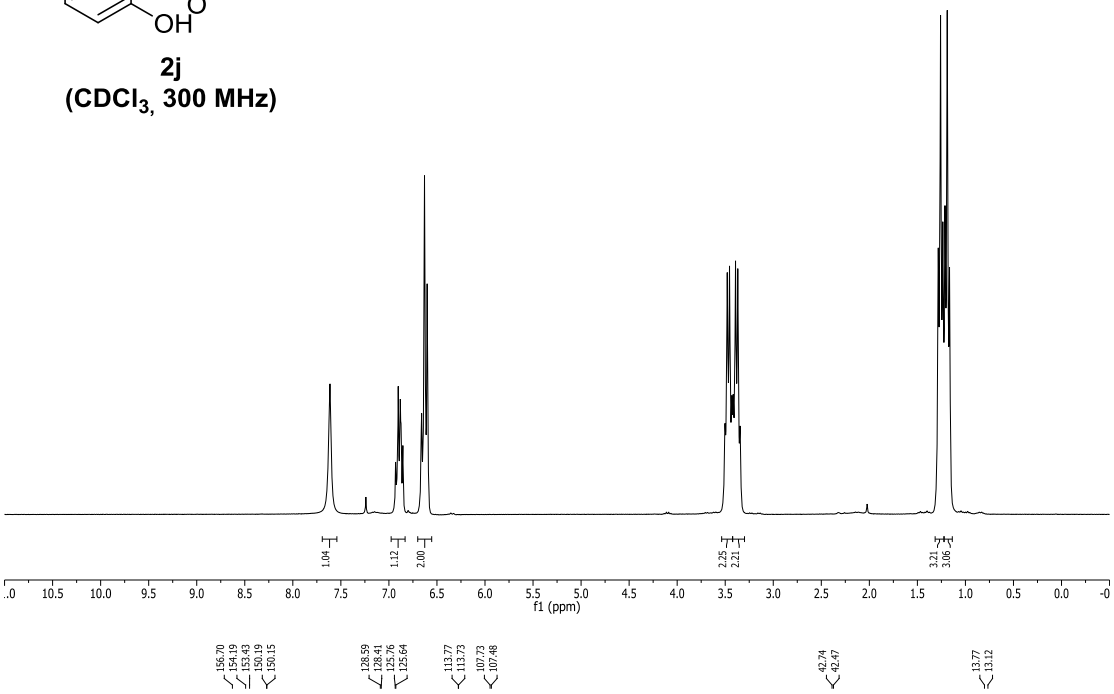

154.63
148.88
138.10
137.18
135.92
128.96
127.94
127.11
125.99
121.88
117.66
42.17
41.78
13.50
13.00
Ph
O
NEt2
O
OH
2h
(CDCl3, 75 MHz)
f1 (ppm)

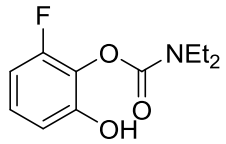

iPr
O
NEt2
O
OH
2i
(CDCl3, 300 MHz)
1.78
1.09
1.00
2.07
2.08
1.13
3.17
6.90
f1 (ppm)


154.57
148.18
141.06
137.61
125.95
117.34
115.95
42.36
42.04
27.58
22.84
13.95
13.19
iPr
O
NEt2
O
OH
2i
(CDCl3, 75 MHz)
f1 (ppm)

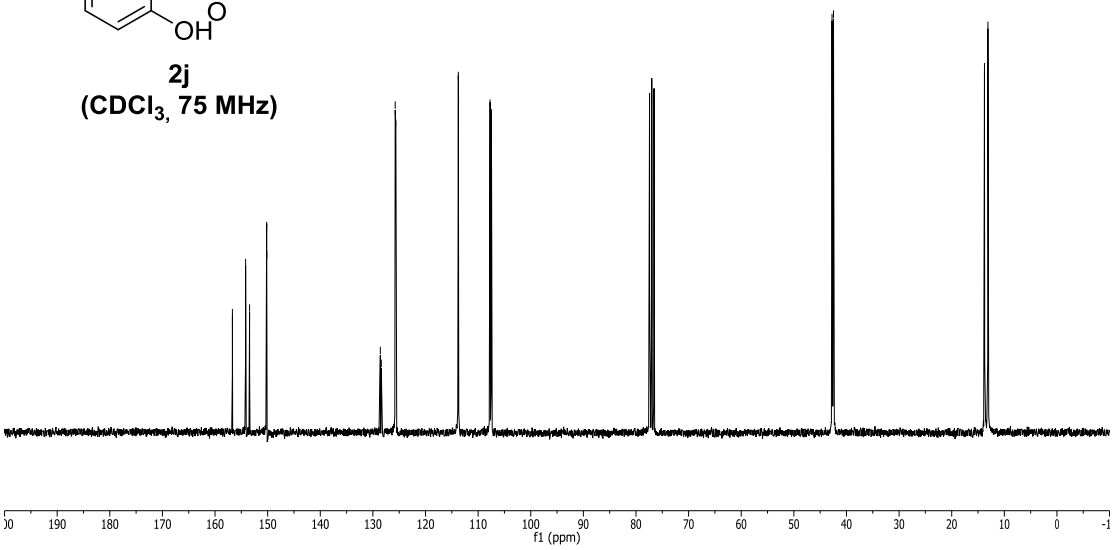


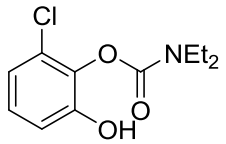
2j
($CDCl_3$, 300 MHz)



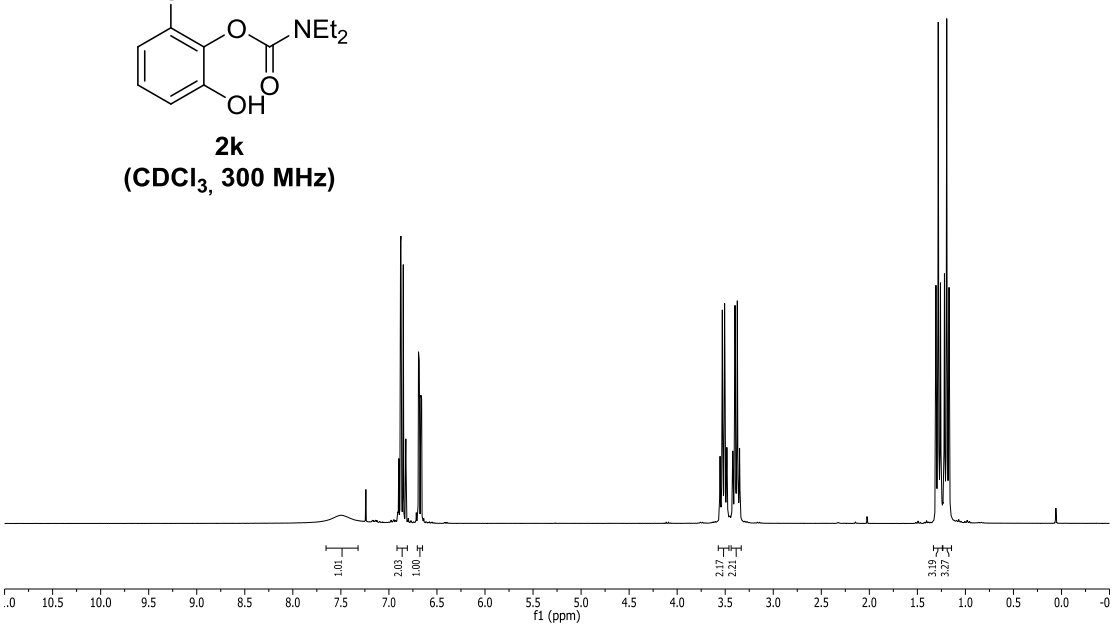


2j
($CDCl_3$, 75 MHz)

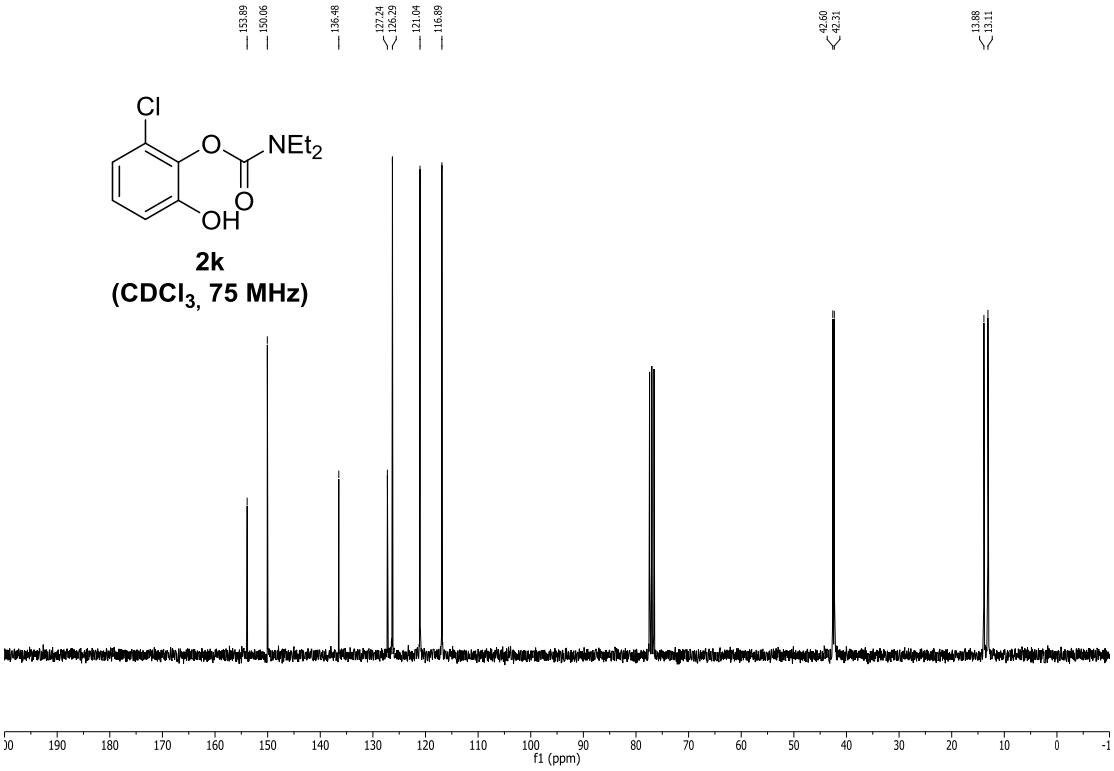


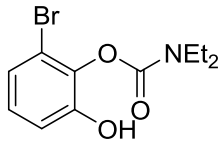


2k
($CDCl_3$, 300 MHz)

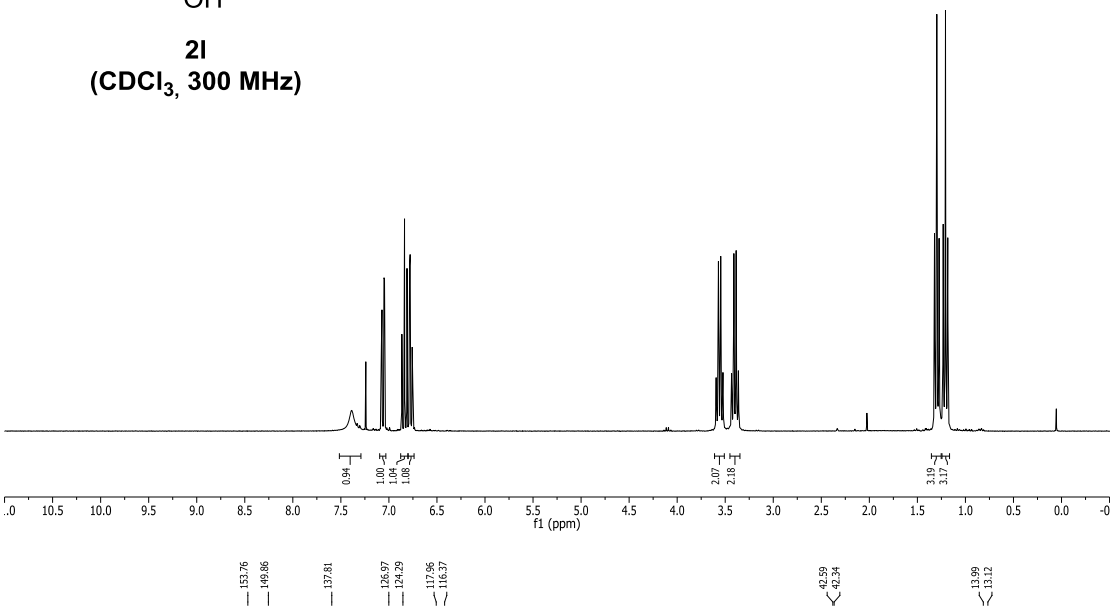


2k
($CDCl_3$, 75 MHz)

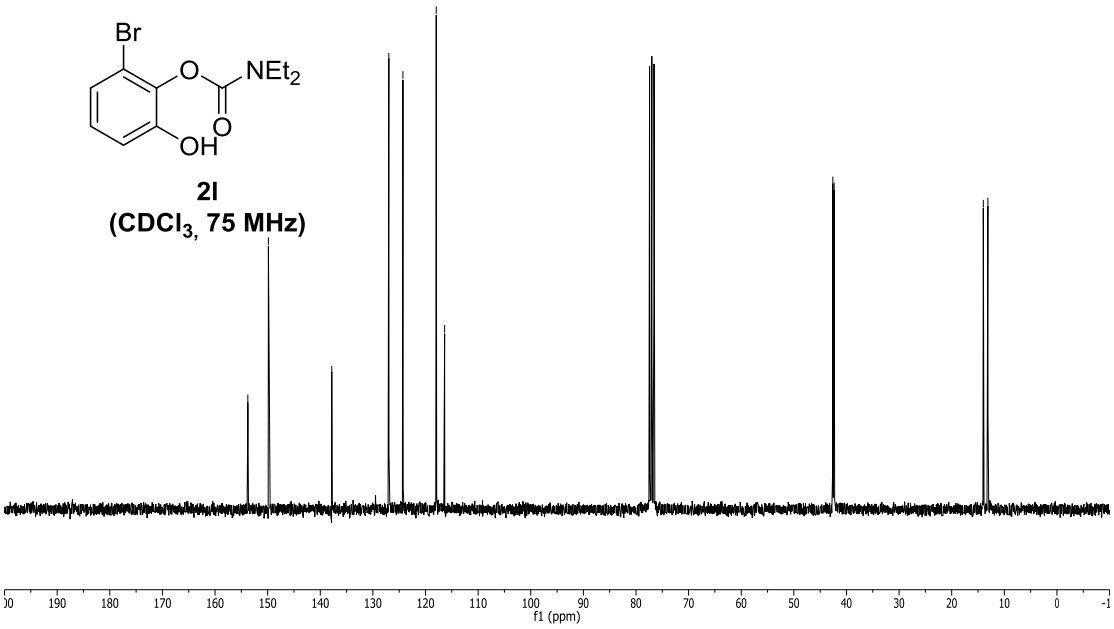




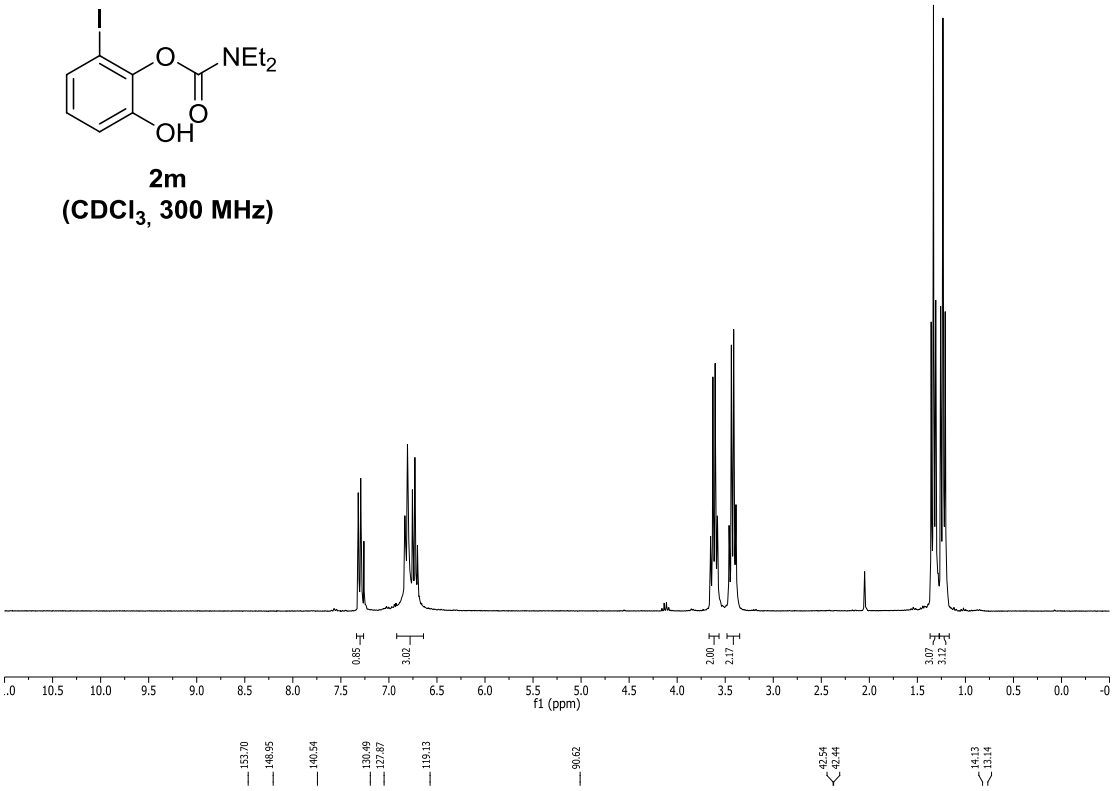
2l
($CDCl_3$, 300 MHz)

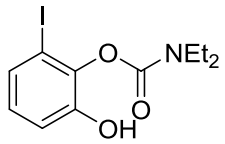


2l
($CDCl_3$, 75 MHz)

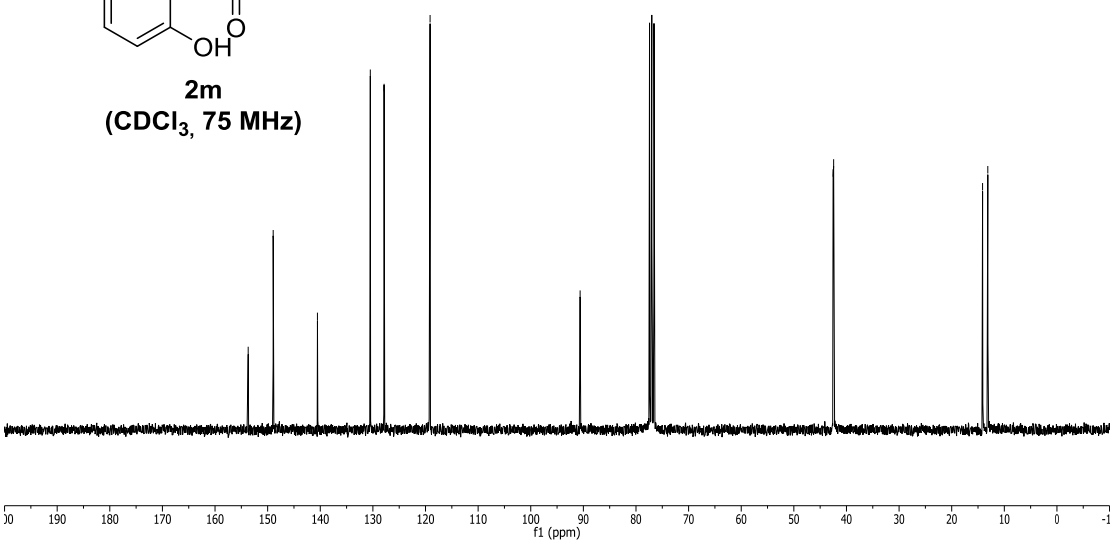


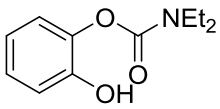
2m
($CDCl_3$, 300 MHz)



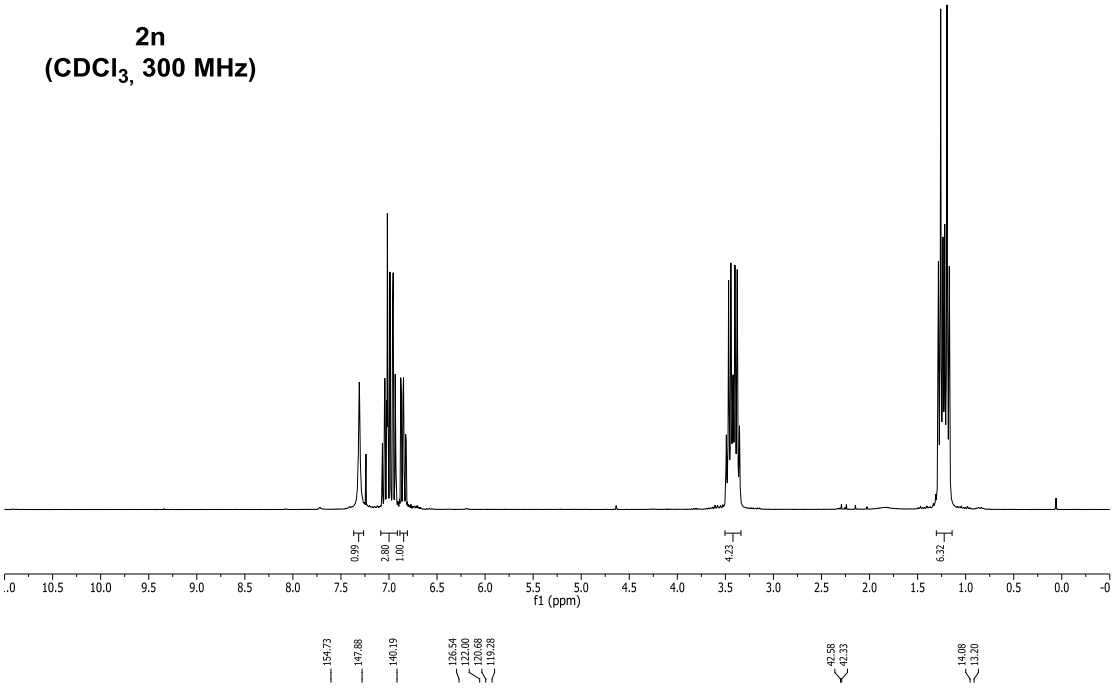


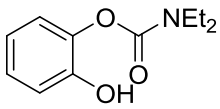
2m
($CDCl_3$, 75 MHz)



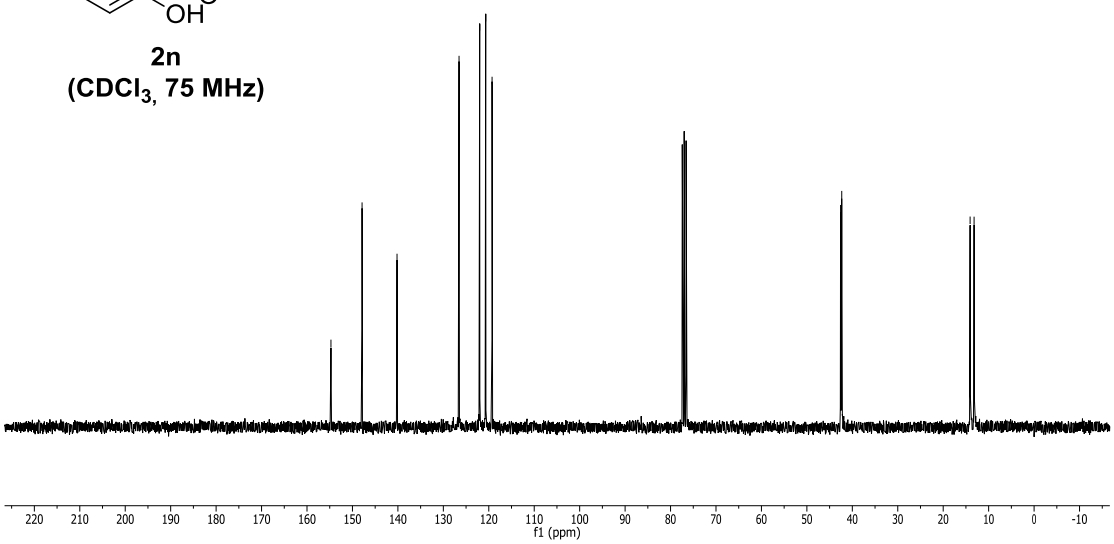


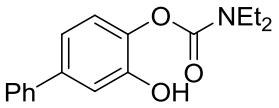
2n
($CDCl_3$, 300 MHz)



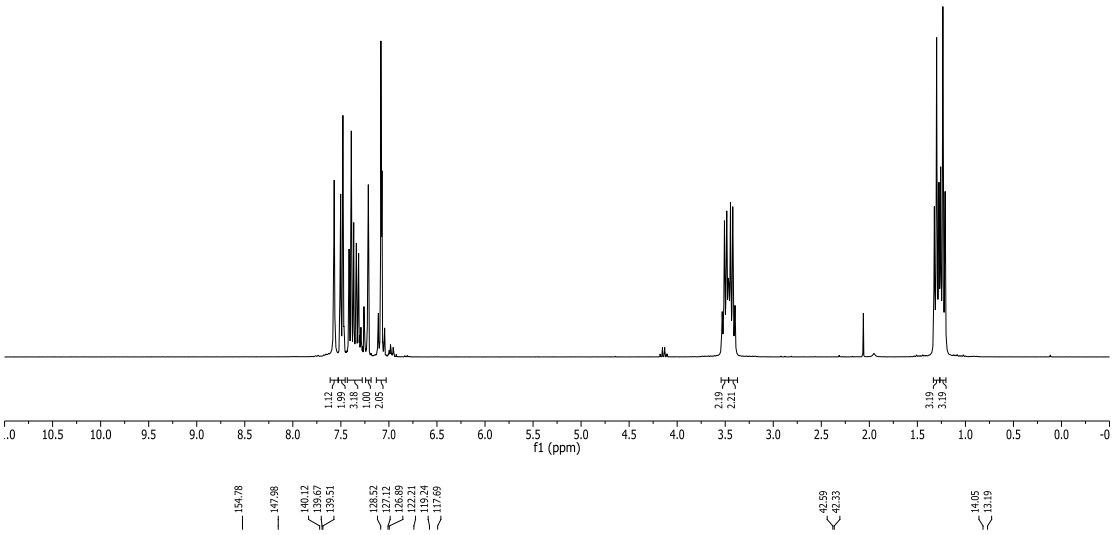


2n
($CDCl_3$, 75 MHz)

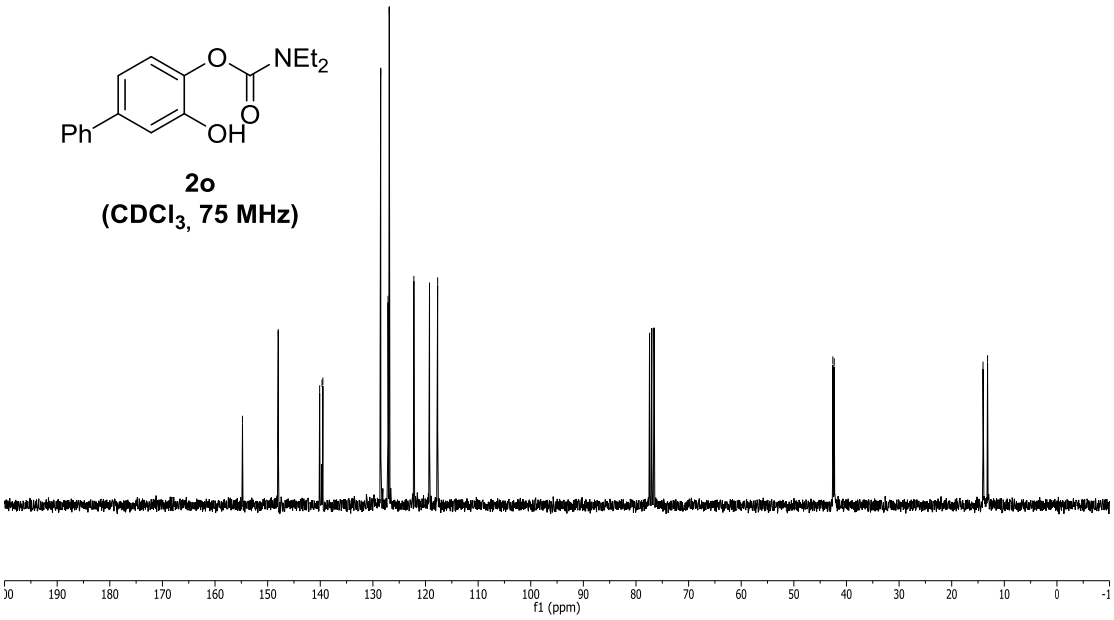


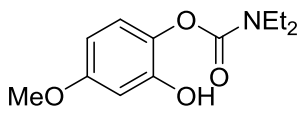


2o
($CDCl_3$, 300 MHz)

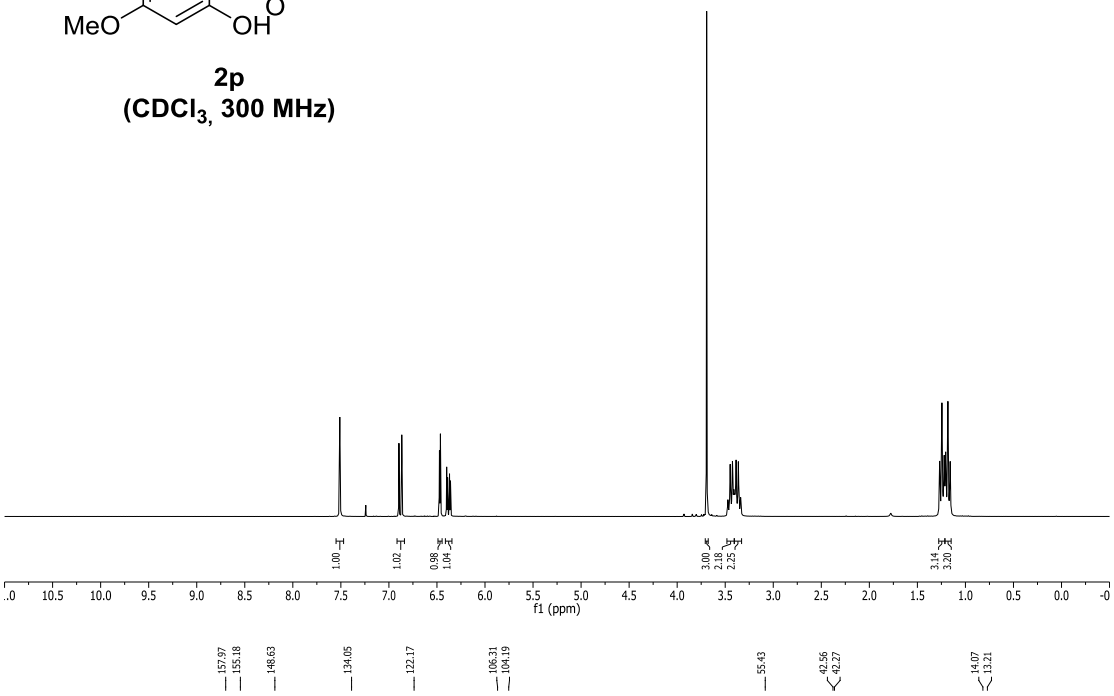


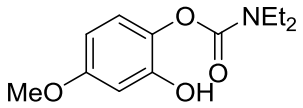
2o
($CDCl_3$, 75 MHz)



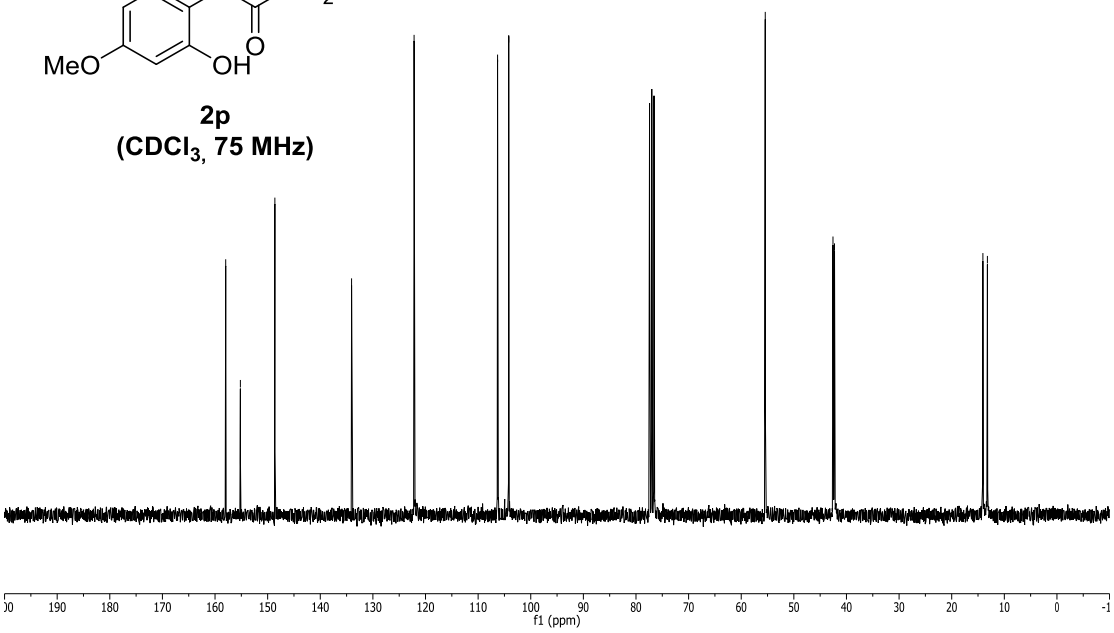


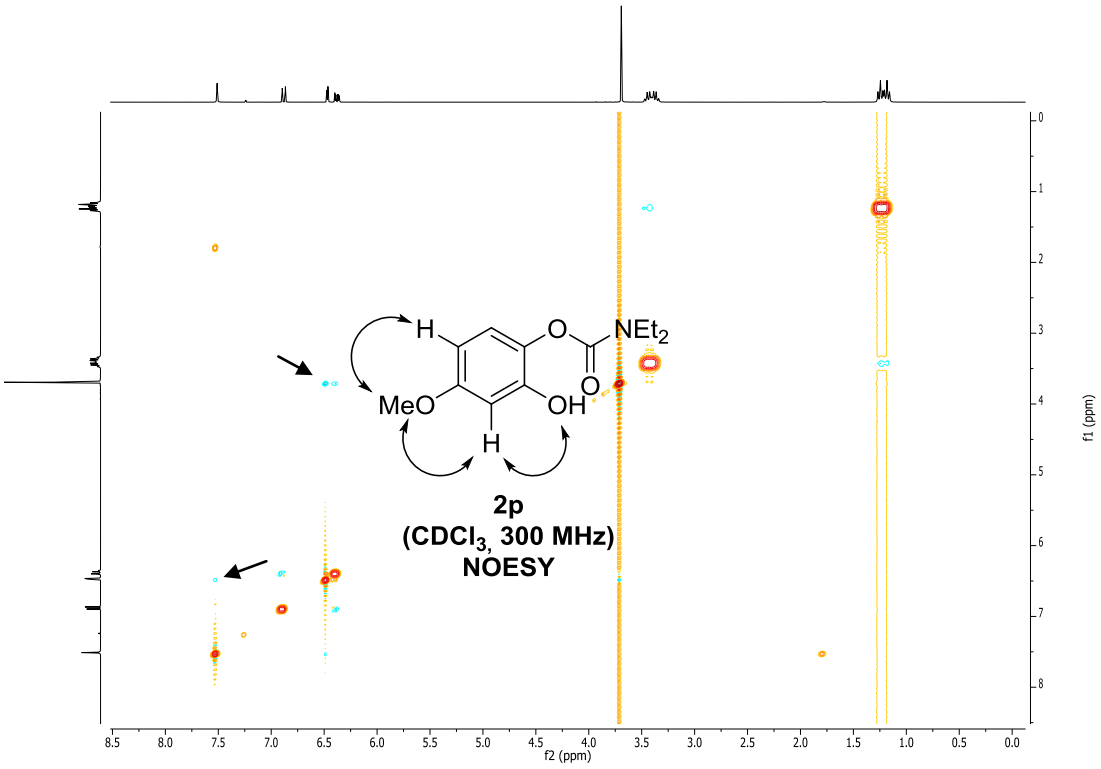
2p
($CDCl_3$, 300 MHz)

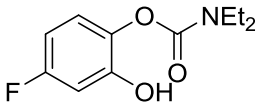




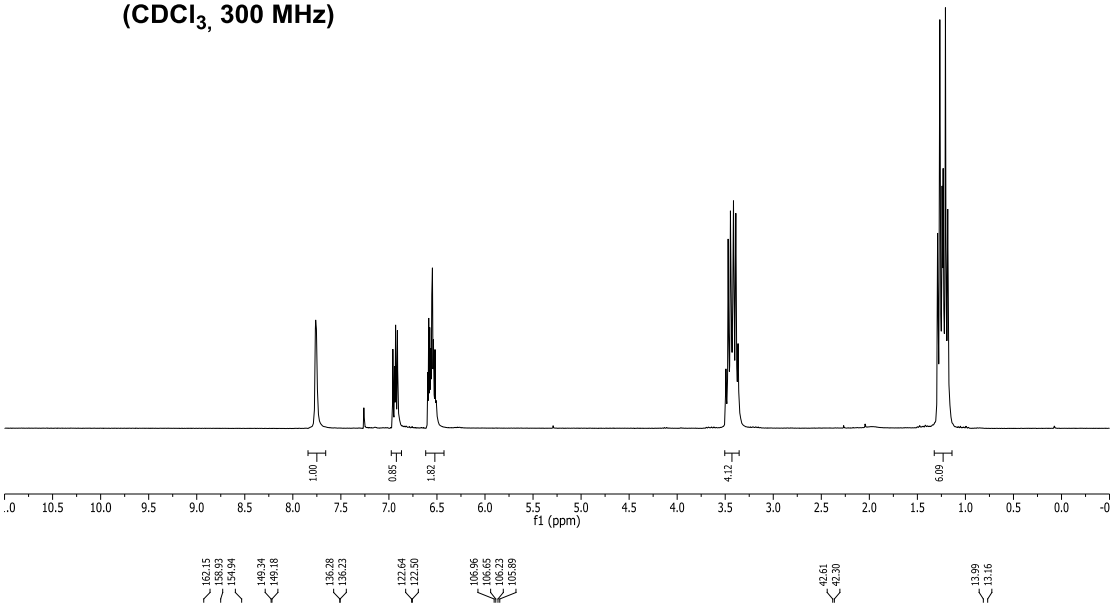
2p
($CDCl_3$, 75 MHz)

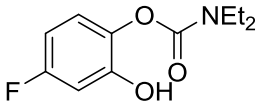



H
O
NEt2
O
MeO
OH
H
2p
(CDCl3, 300 MHz)
NOESY
f2 (ppm)
f1 (ppm)

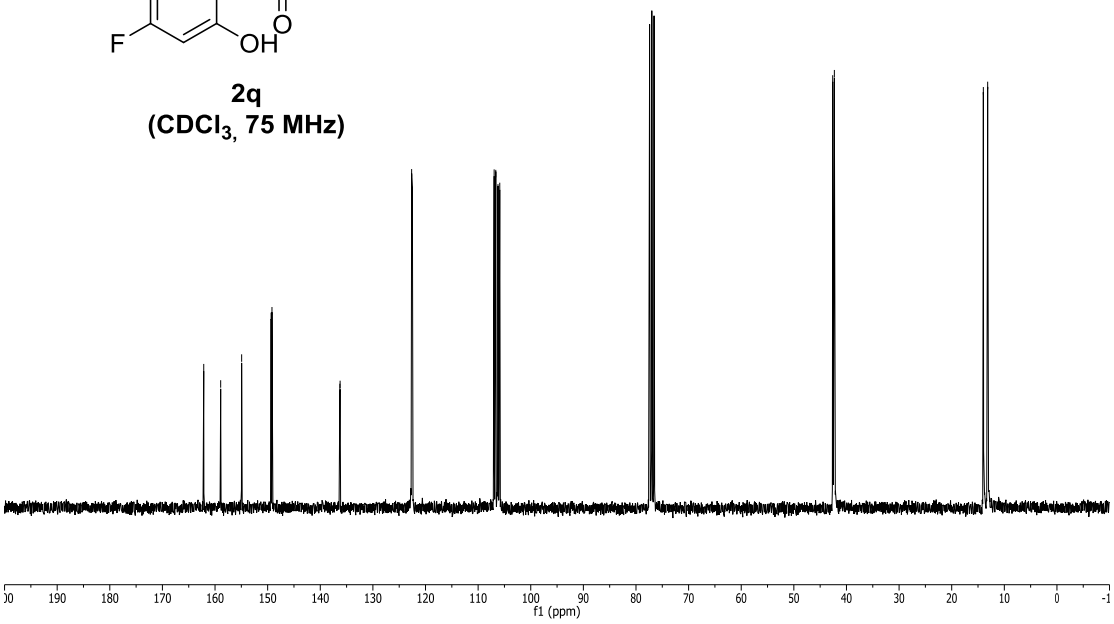


2q
($CDCl_3$, 300 MHz)

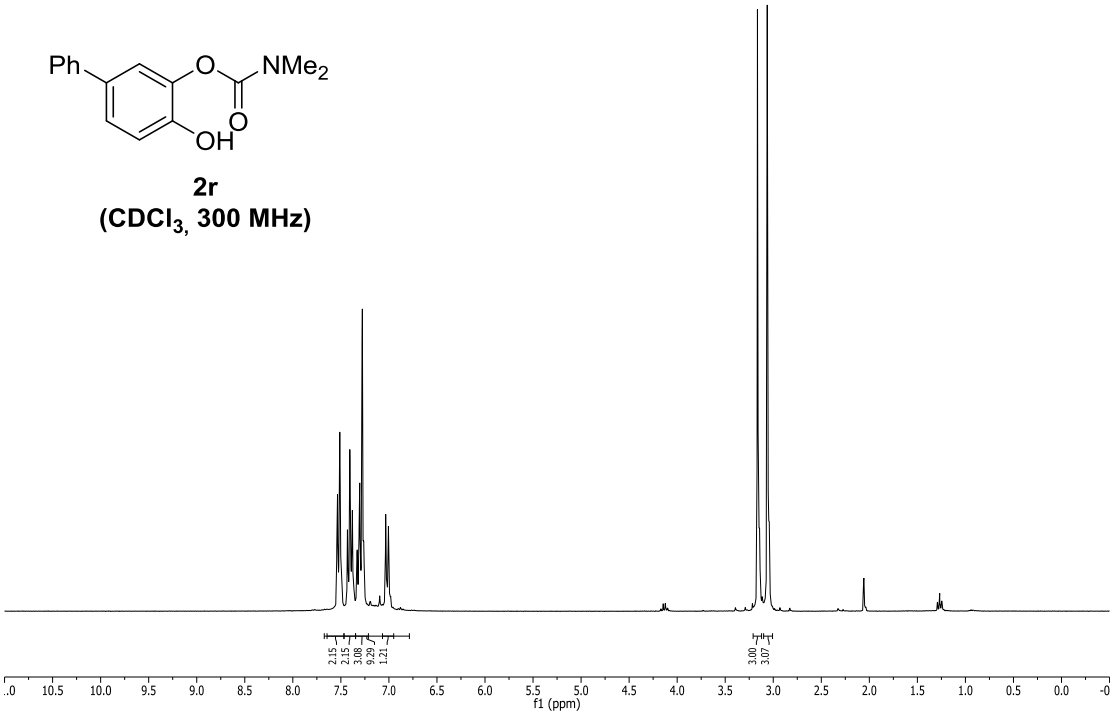




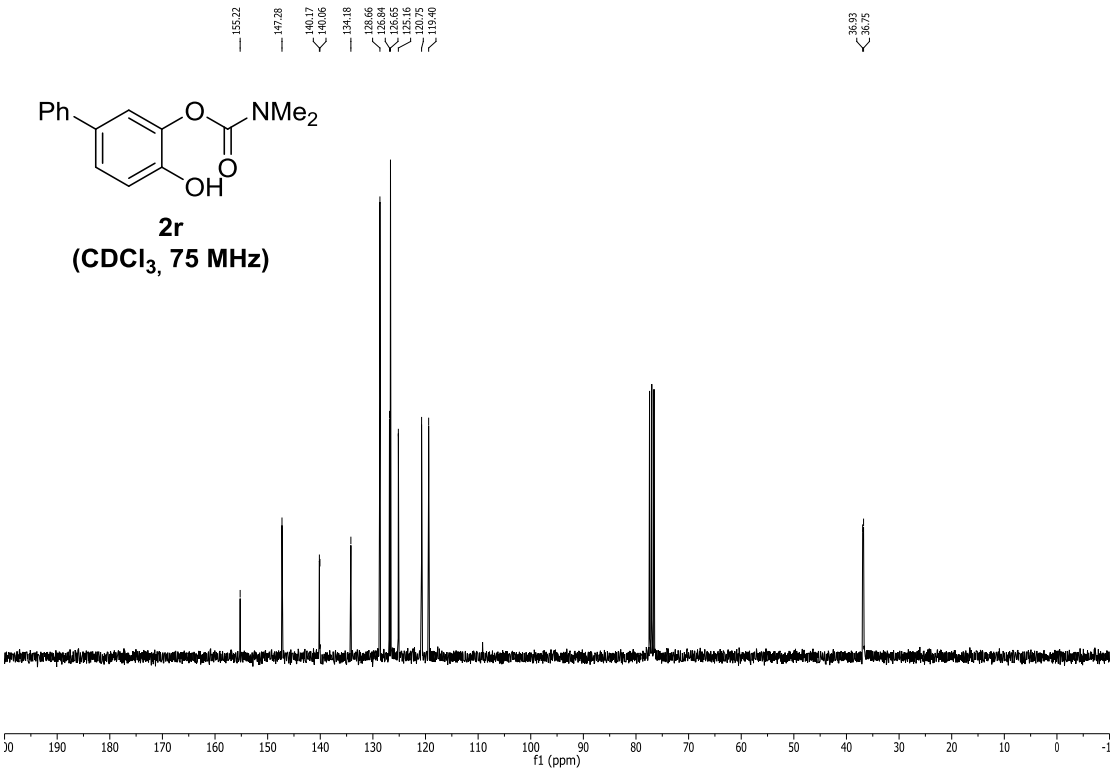
2q
($CDCl_3$, 75 MHz)

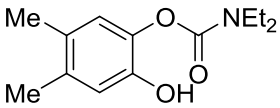


2r
($CDCl_3$, 300 MHz)

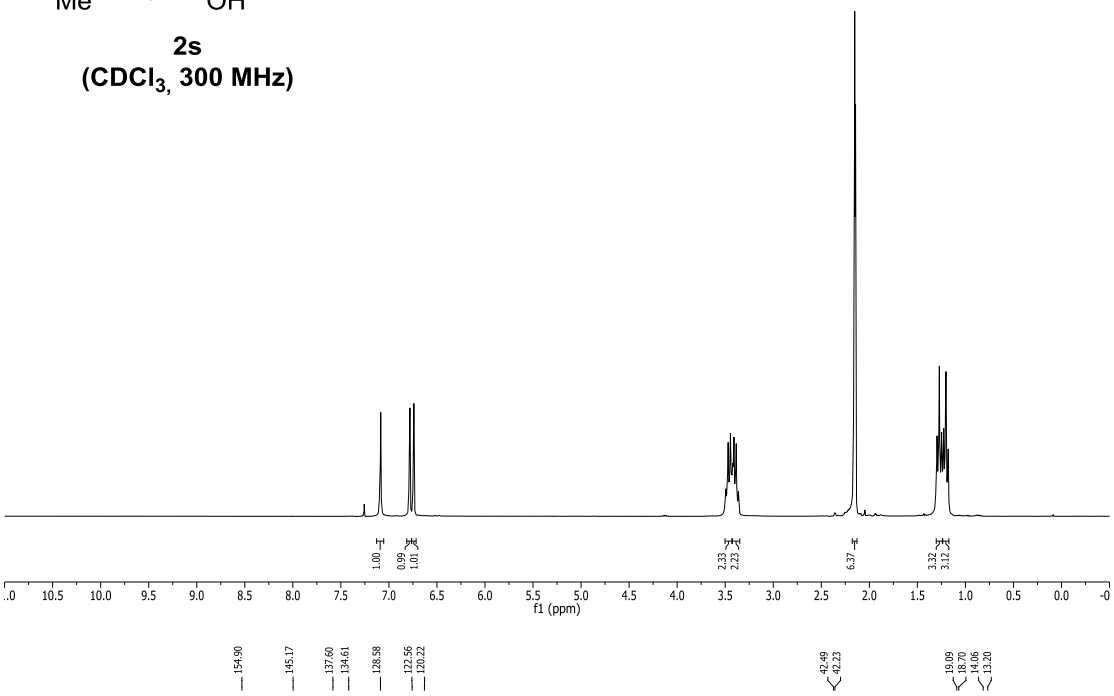


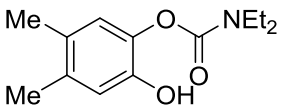
2r
($CDCl_3$, 75 MHz)



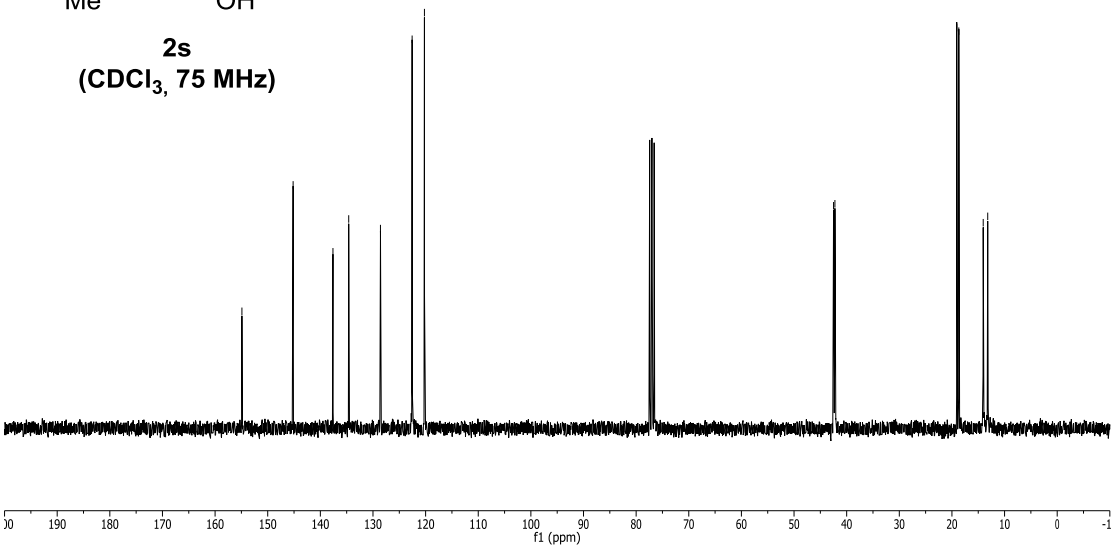


2s
($CDCl_3$, 300 MHz)

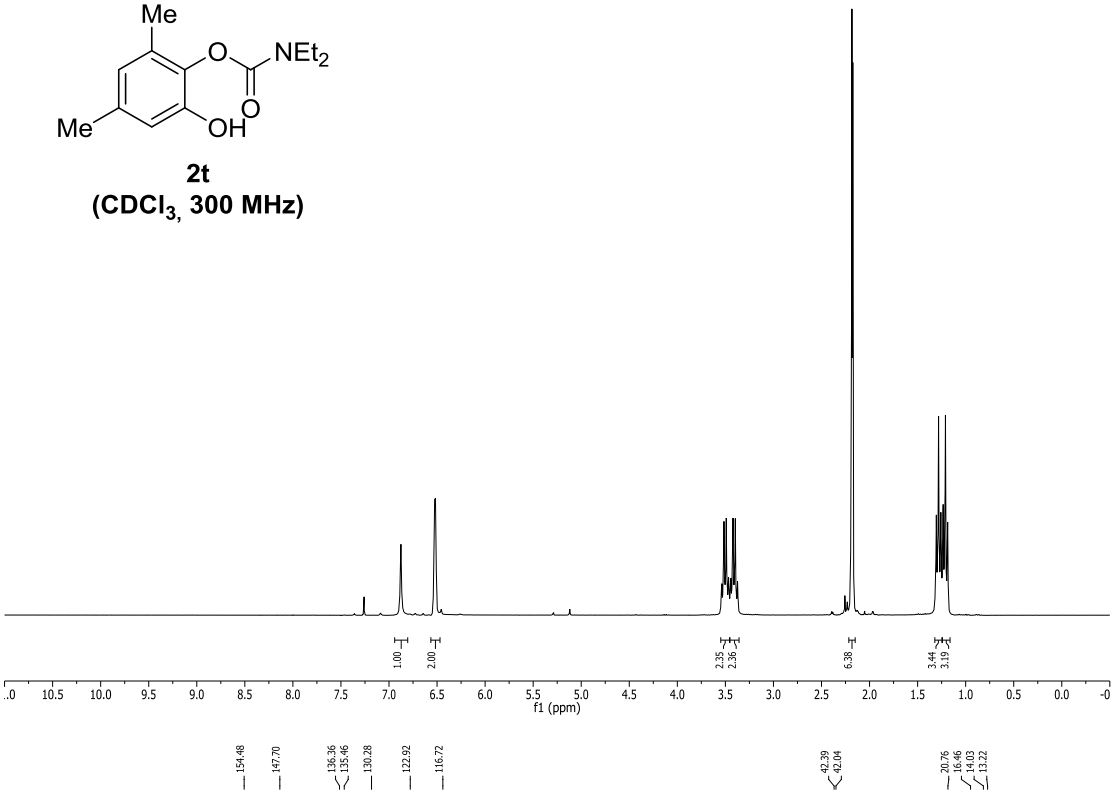


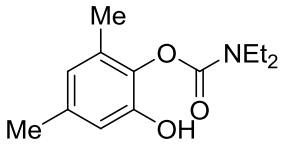


2s
($CDCl_3$, 75 MHz)

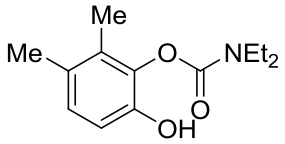


2t
($CDCl_3$, 300 MHz)

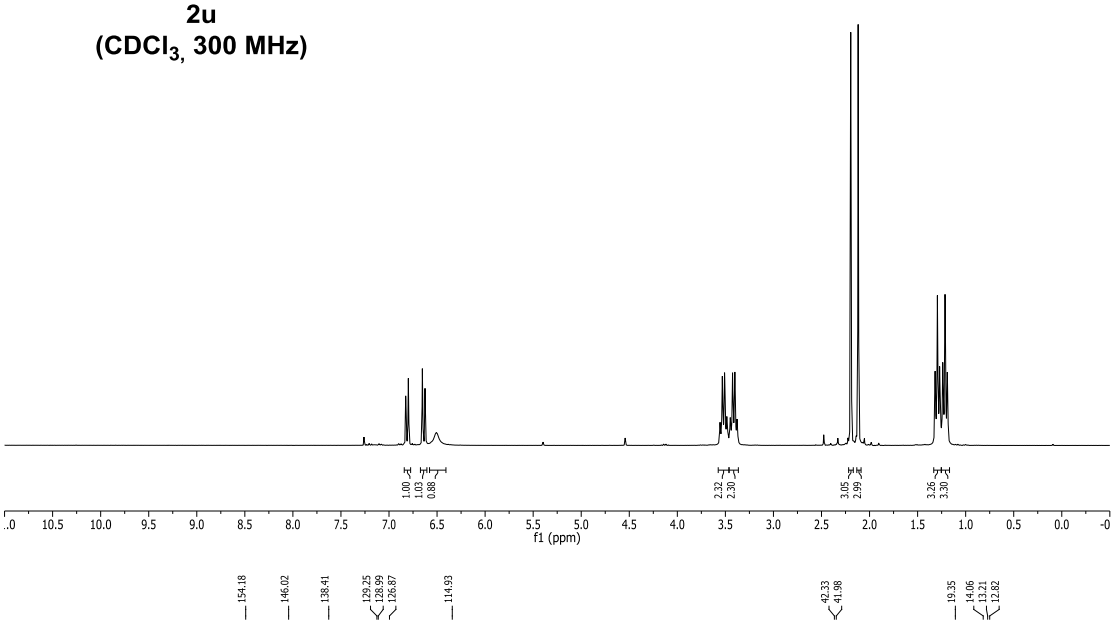


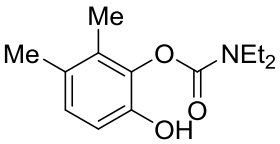


2t
($CDCl_3$, 75 MHz)

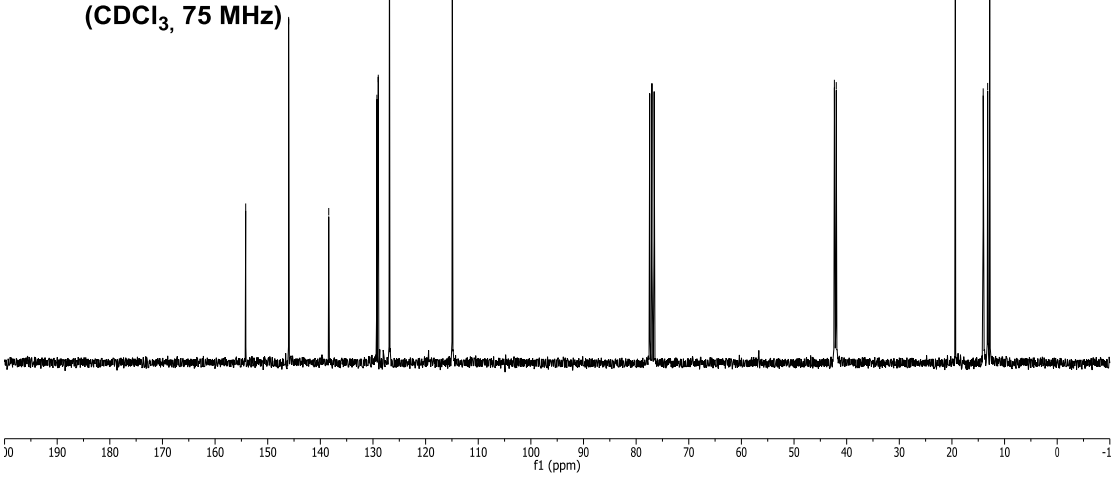


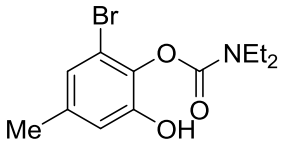
2u
($CDCl_3$, 300 MHz)



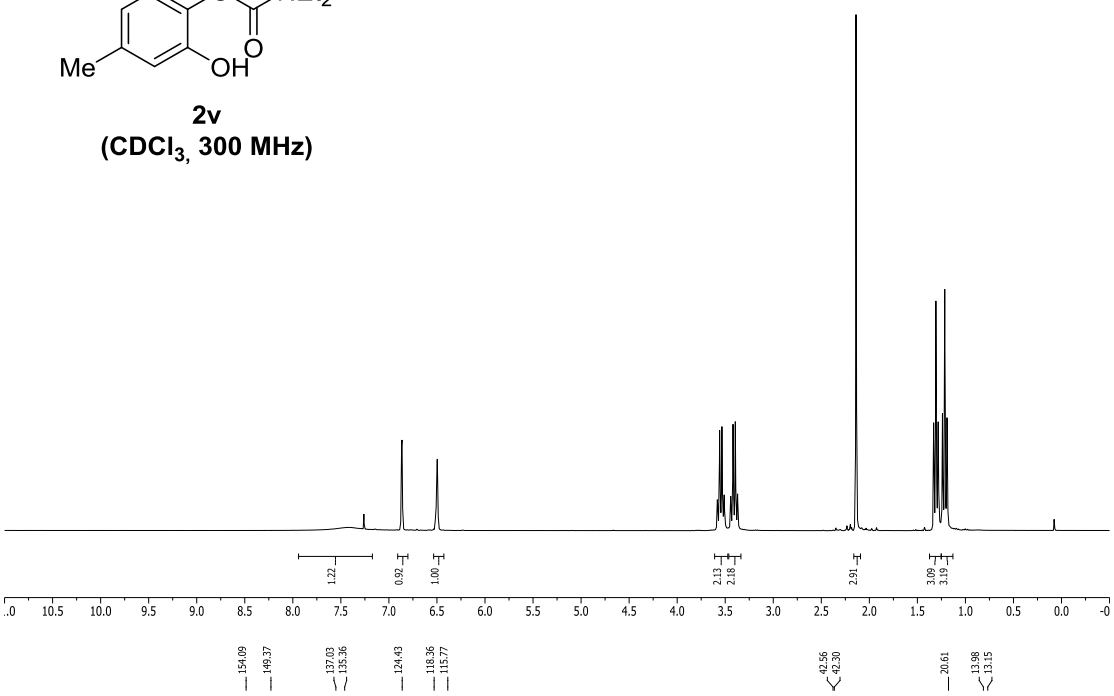


2u
($CDCl_3$, 75 MHz)

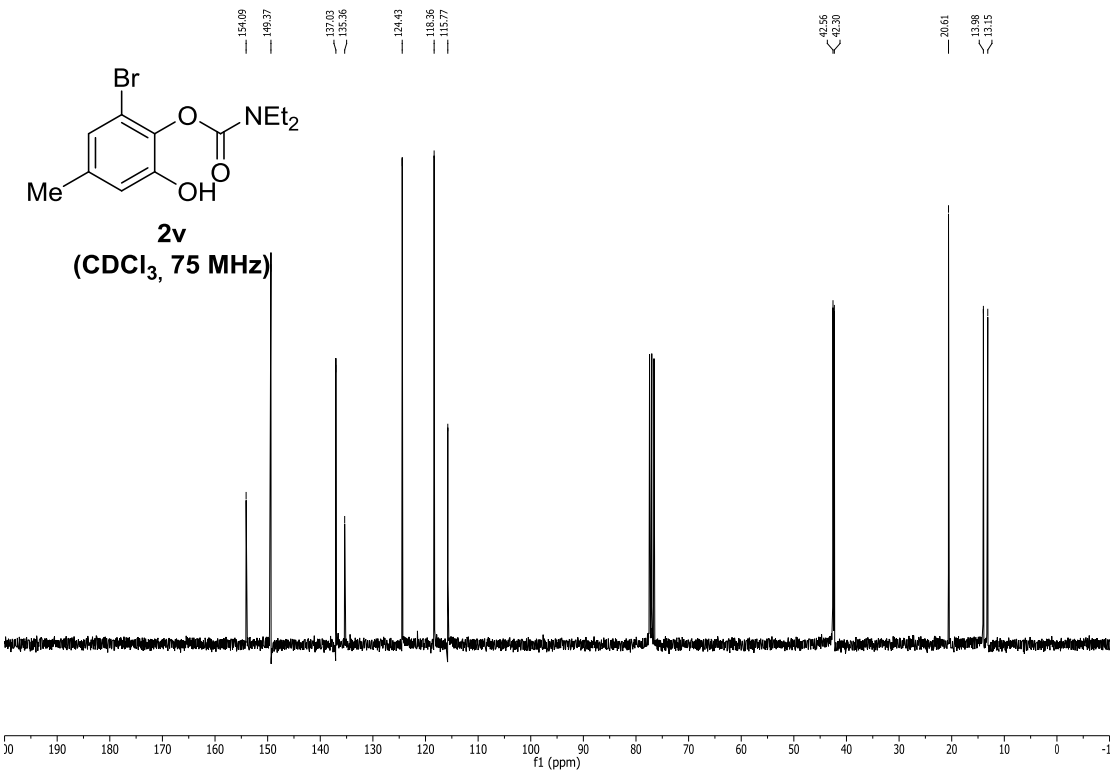


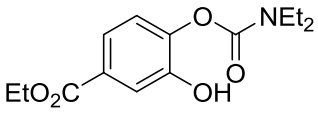


2v
($CDCl_3$, 300 MHz)

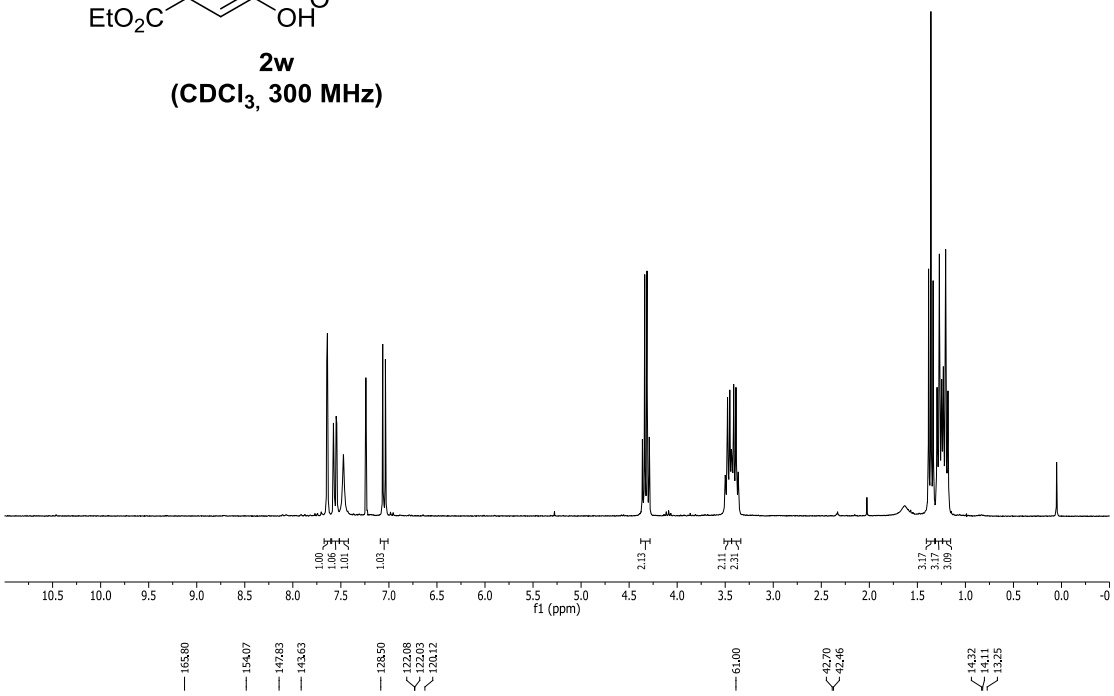


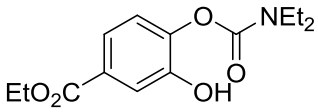
2v
($CDCl_3$, 75 MHz)



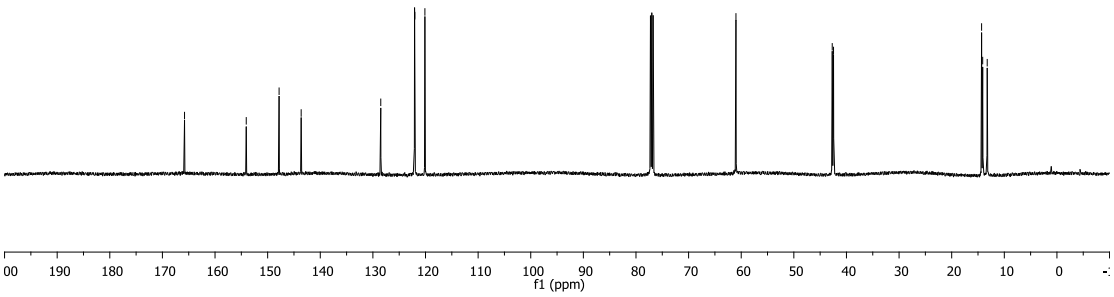


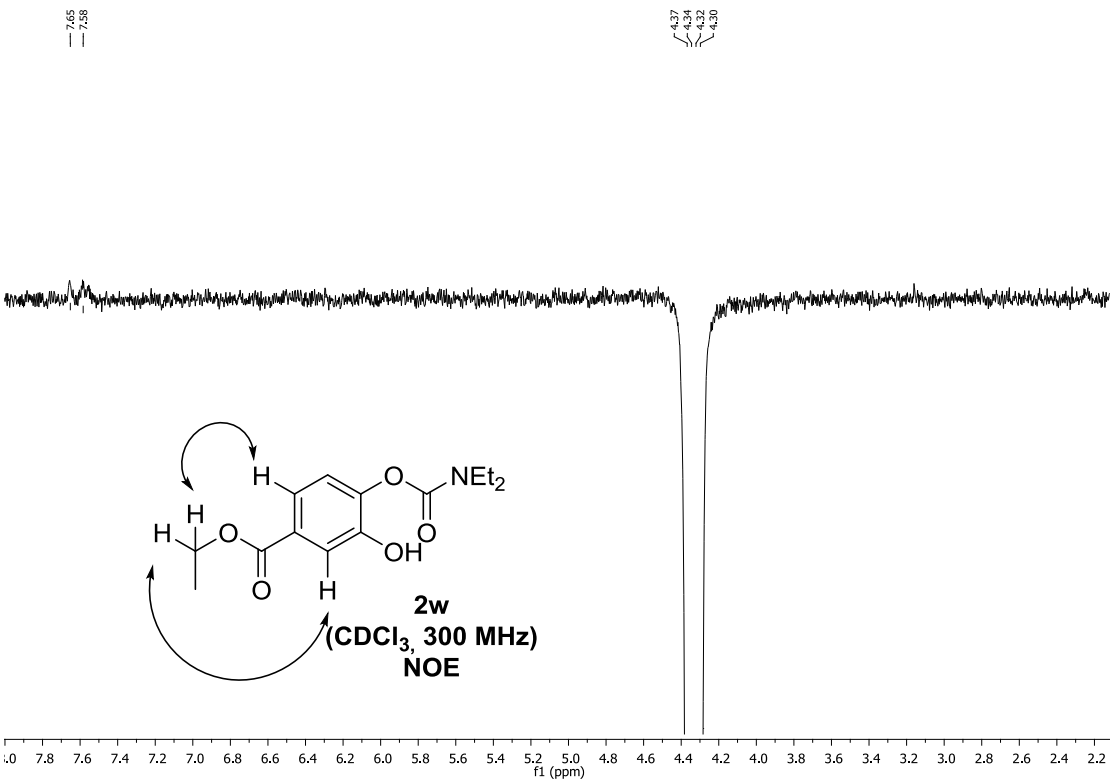
2w
($CDCl_3$, 300 MHz)

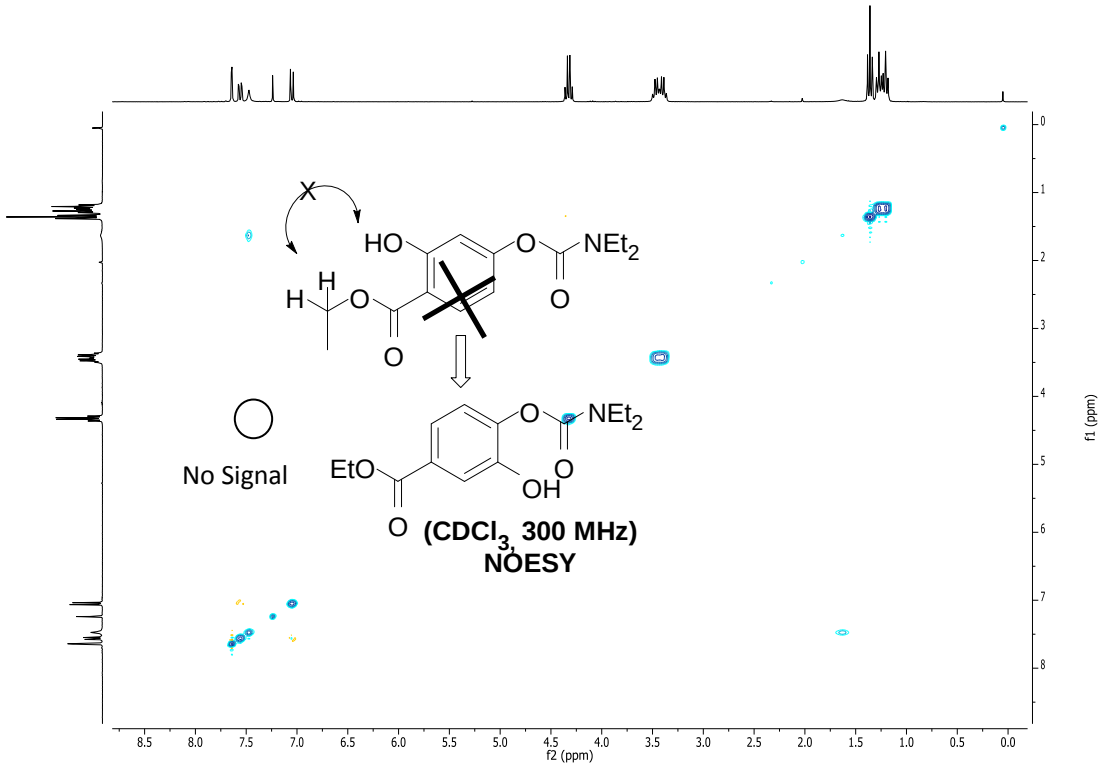


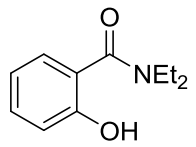


2w
($CDCl_3$, 75 MHz)

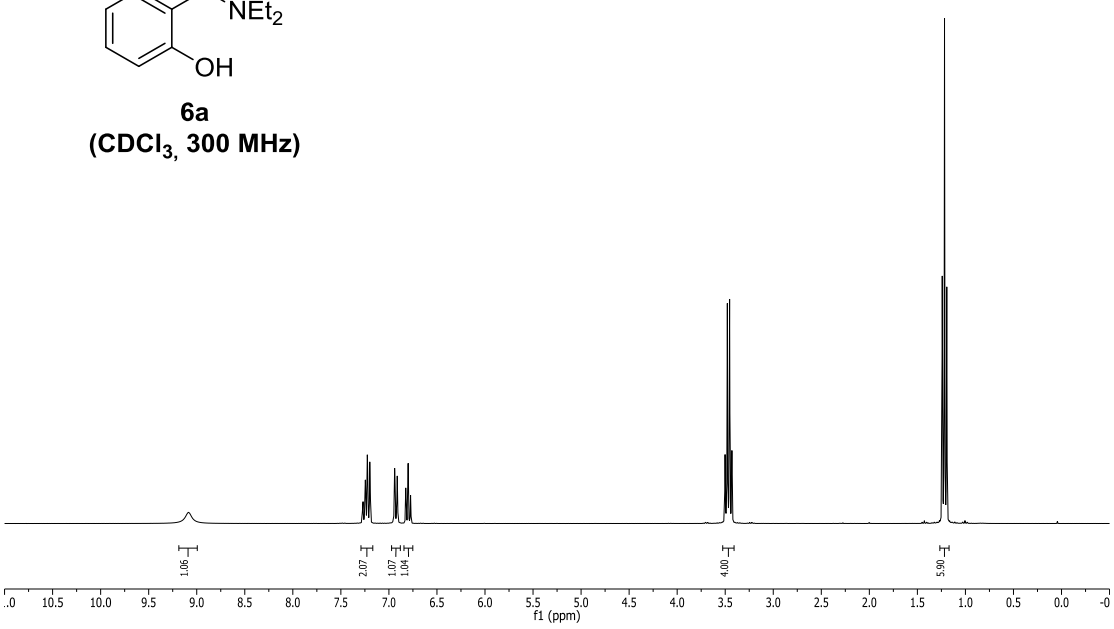


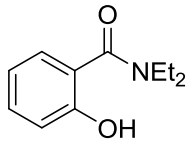

7.65
7.58
4.37
4.34
4.32
4.30
H
O
NEt2
H
H
O
OH
O
O
H
2w
(CDCl3, 300 MHz)
NOE
f1 (ppm)


X
HO
O
NEt2
H
O
O
O
No Signal
O
NEt2
EtO
O
OH
O
(CDCl3, 300 MHz)
NOESY
f2 (ppm)
f1 (ppm)

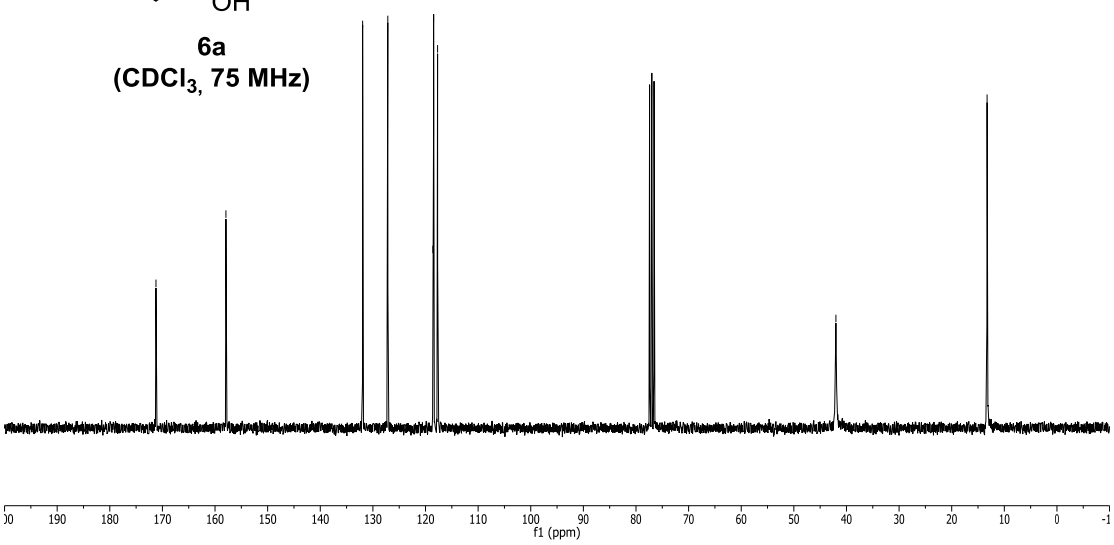


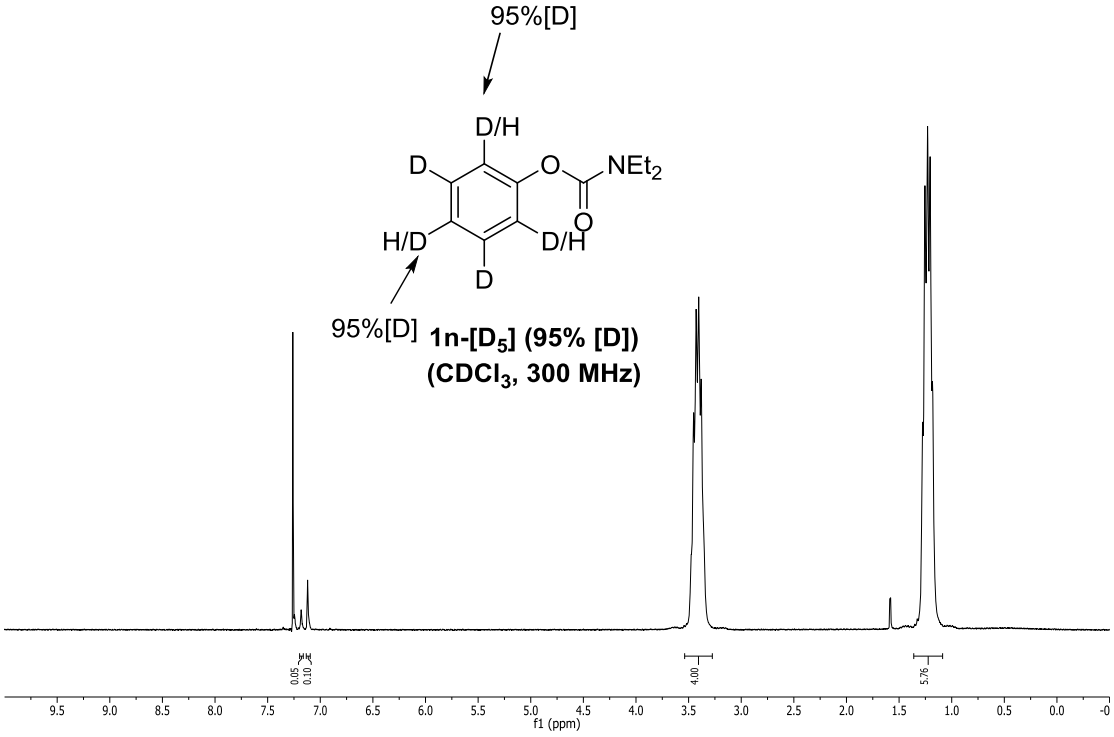
6a
($CDCl_3$, 300 MHz)

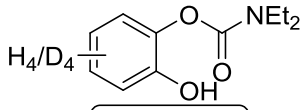




6a
($CDCl_3$, 75 MHz)

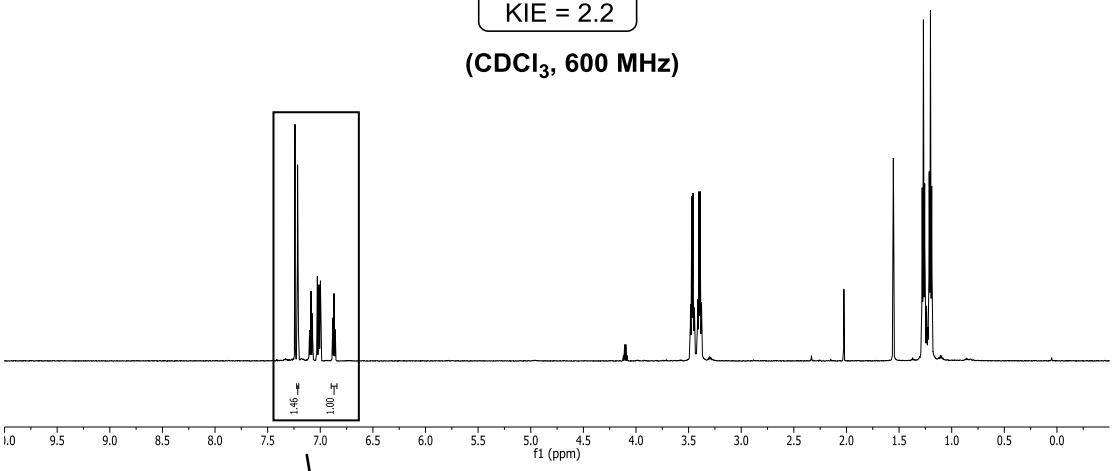


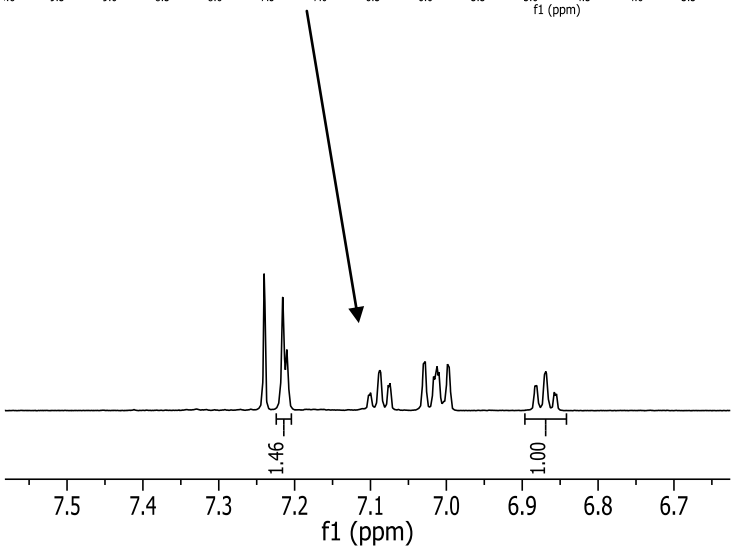

95%[D]
D/H
D
O
NEt2
O
H/D
D/H
D
95%[D]
1n-[D5] (95% [D])
(CDCl3, 300 MHz)
0.05
0.10
4.00
5.76
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

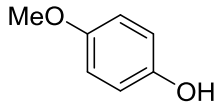


H/D = 50/23
KIE = 2.2

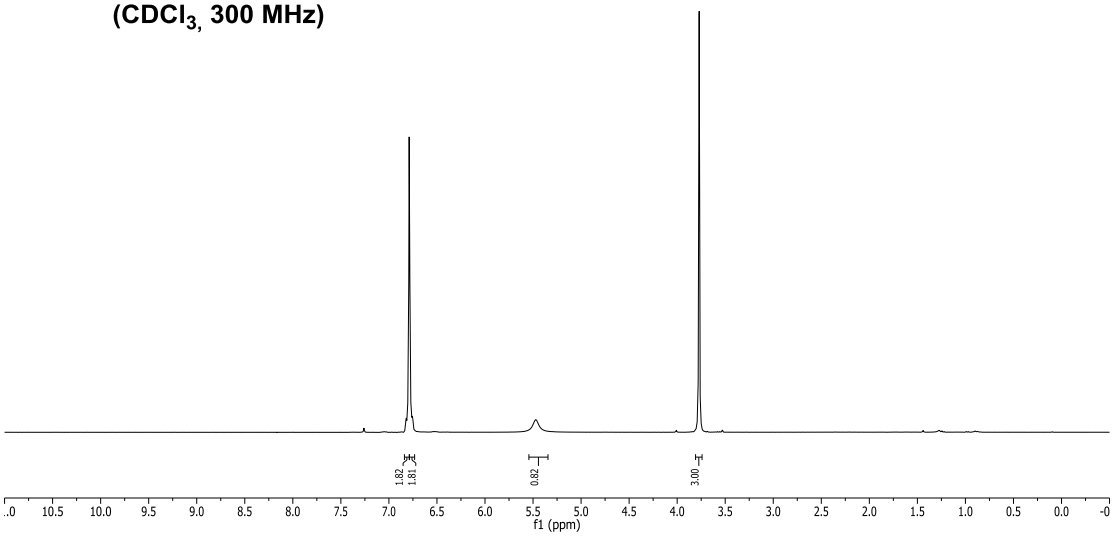
($CDCl_3$, 600 MHz)



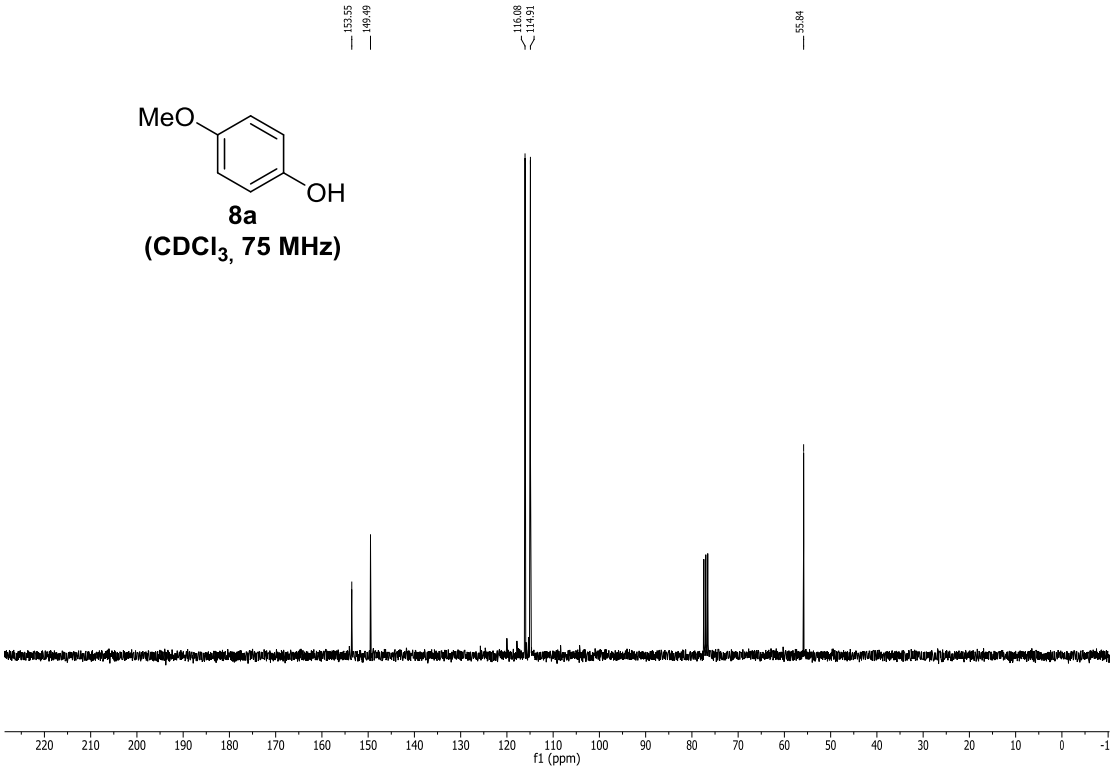




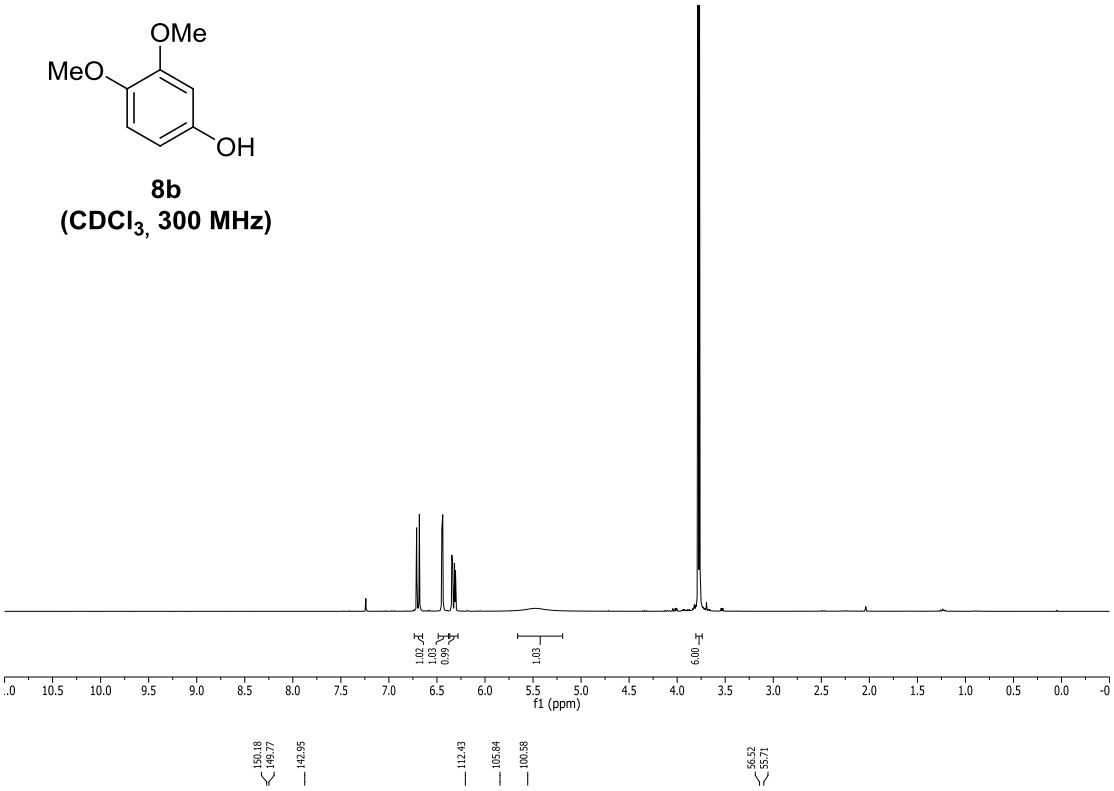
8a
($CDCl_3$, 300 MHz)

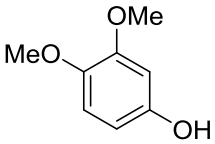


8a
($CDCl_3$, 75 MHz)

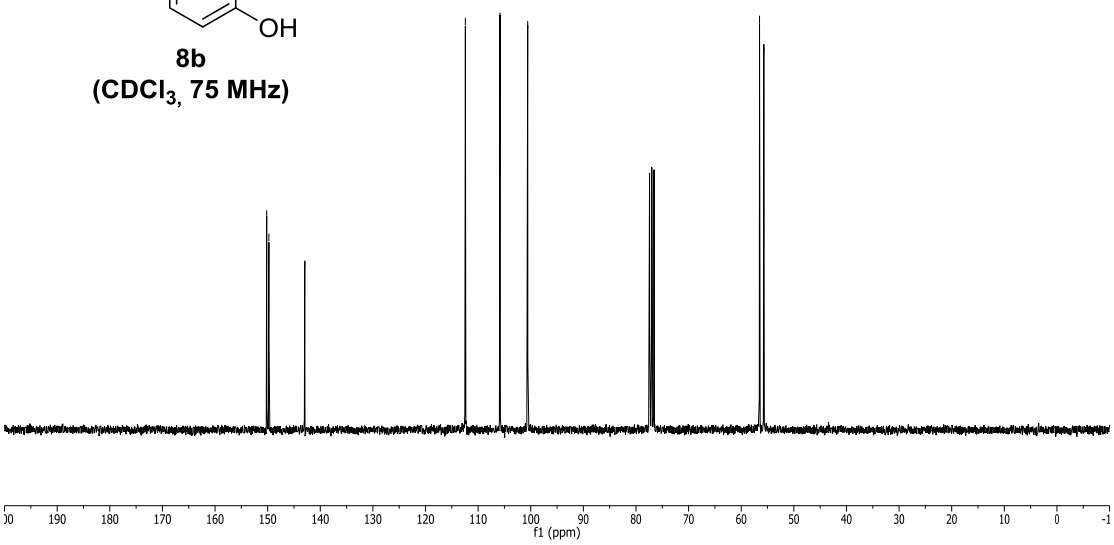


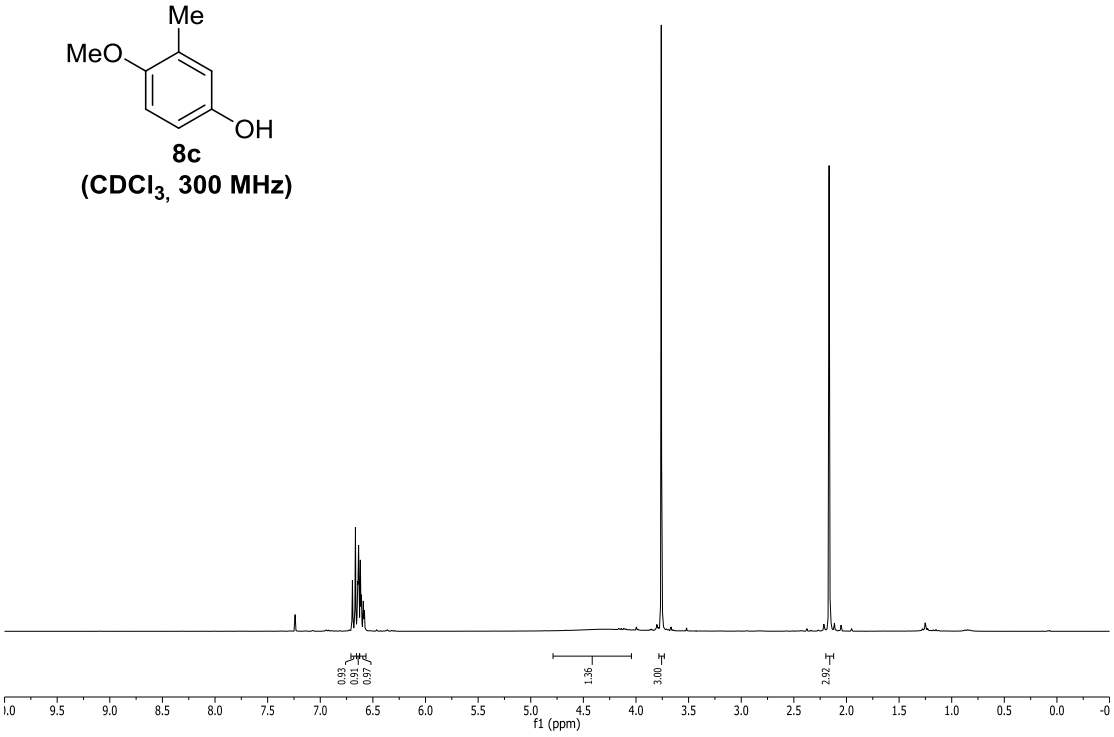
8b
($CDCl_3$, 300 MHz)

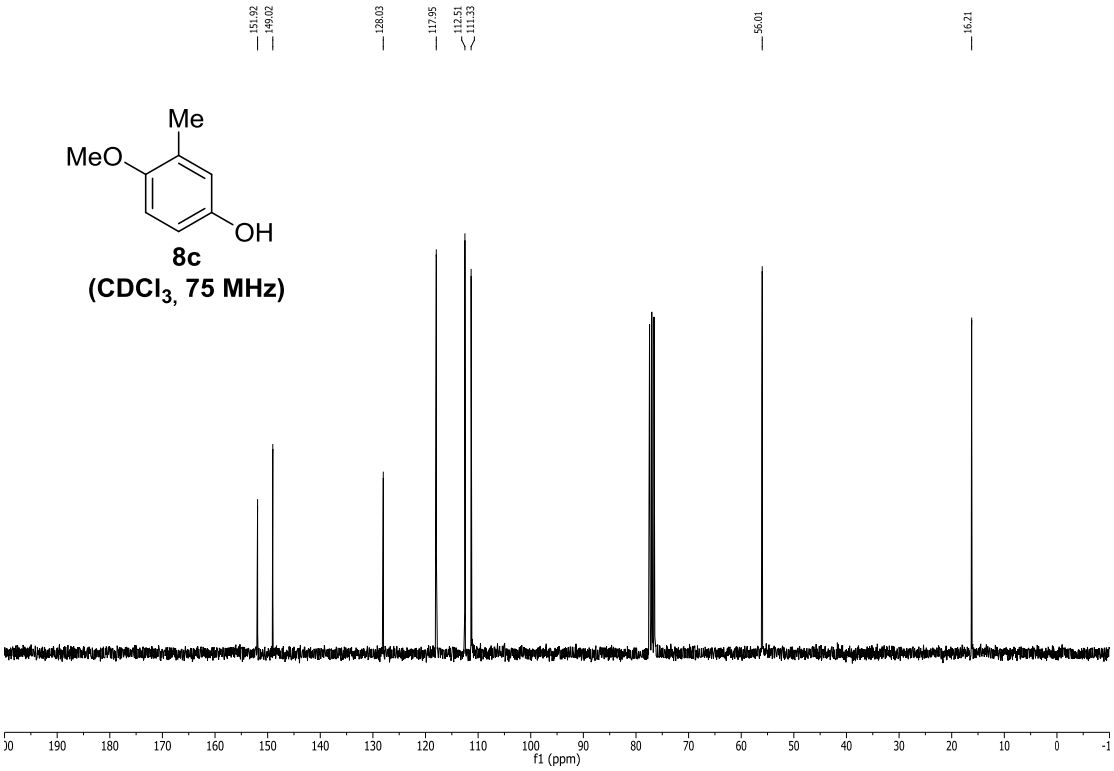


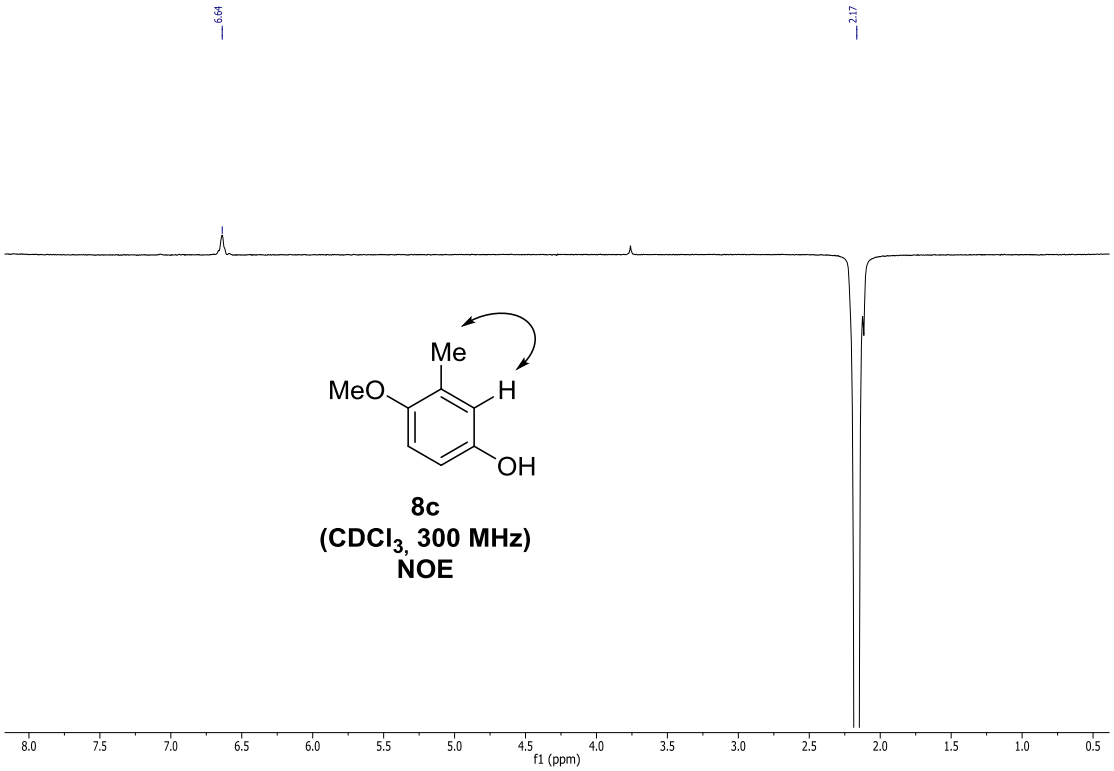


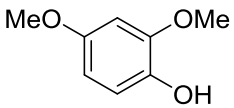
8b
($CDCl_3$, 75 MHz)



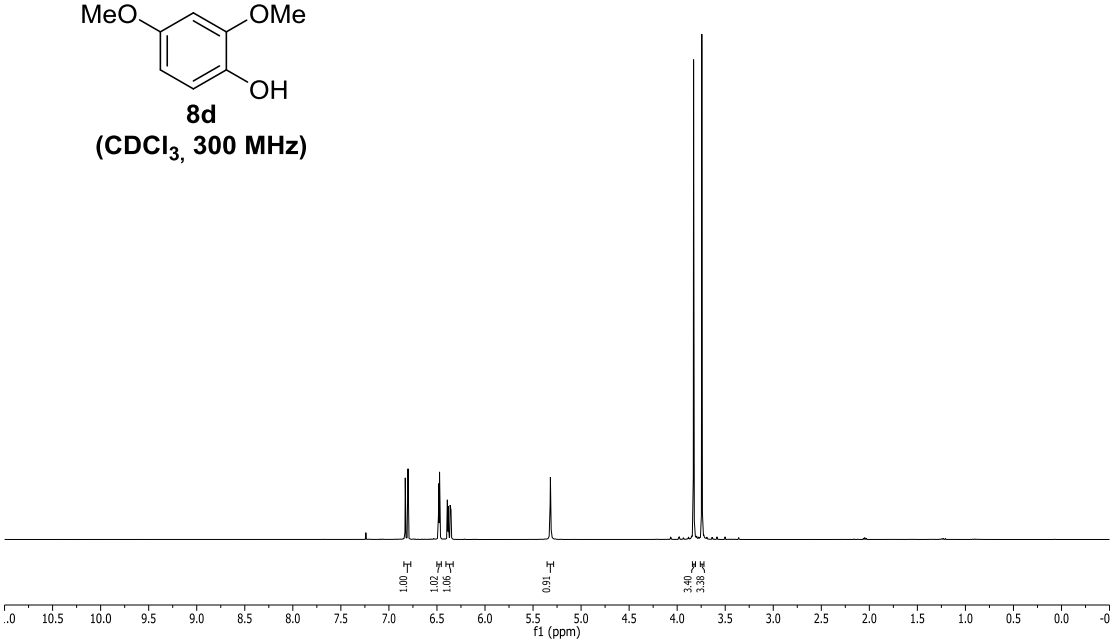
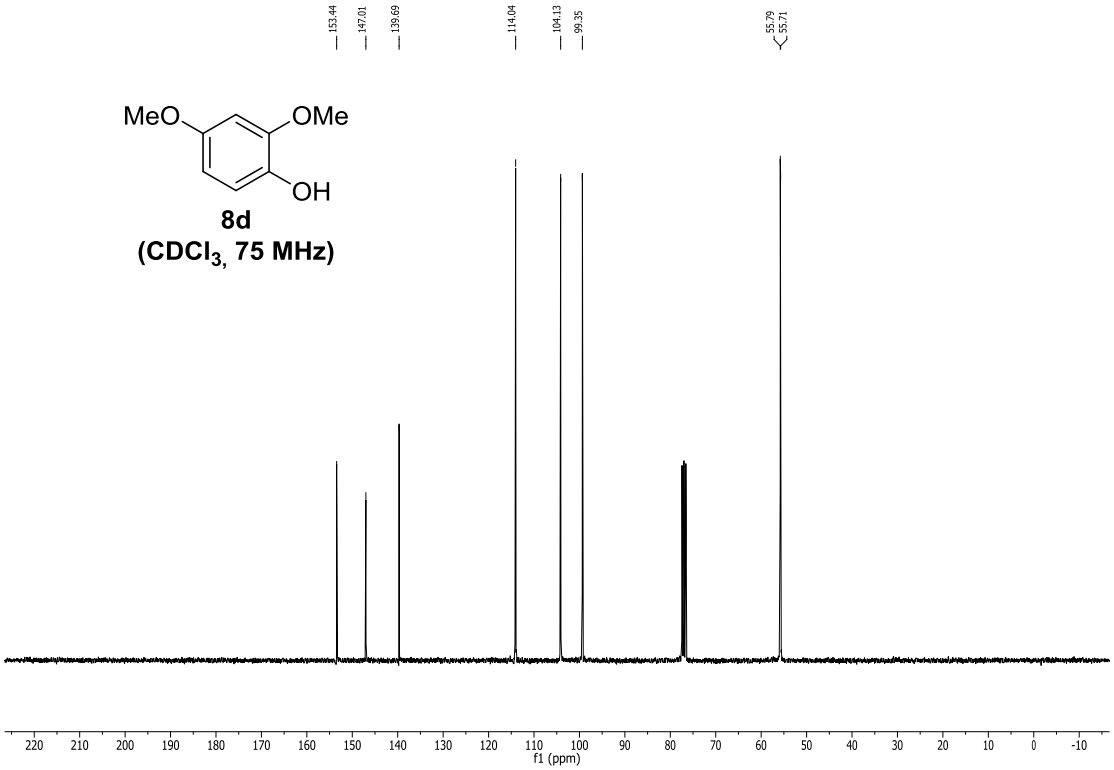

Me
MeO
OH
8c
(CDCl3, 300 MHz)
0.93
0.91
0.97
1.36
3.00
2.92
f1 (ppm)


151.92
149.02
128.03
117.95
112.51
111.33
56.01
16.21
Me
MeO
OH
8c
(CDCl3, 75 MHz)
f1 (ppm)


6.64
2.17
Me
MeO
H
OH
8c
(CDCl3, 300 MHz)
NOE
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



8d
($CDCl_3$, 300 MHz)



8d
($CDCl_3$, 75 MHz)