Supporting Information for

Air-Stable Secondary Phosphine Oxide as Preligand for Palladium-Catalyzed Intramolecular α-Arylations with Chloroarenes

Lutz Ackermann,* Rubén Vicente, Nora Hofmann

Institut für Organische und Biomolekulare Chemie

Georg-August-Universitaet

Tammannstrasse 2, 37077Goettingen (Germany)

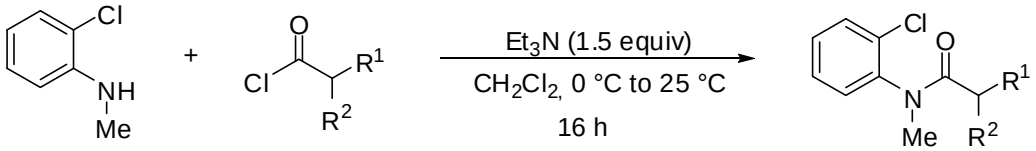
Fax: (+49)551-39-6777 E-mail: Lutz.Ackermann@chemie.uni-goettingen.de

General remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. PhMe, THF and 1,4-dioxane were dried over sodium and CH_2Cl_2 was dried over calcium hydride. The following compounds were prepared according to previously described methods: preligands **3a**,[1] **3b**,[2] **3c**,[3] **3d**,[4] 2-chloro-*N*-methylaniline[5] and *N*-(2-chlorophenyl)-*N*-methylisobutyramide (**1a**).[6] The 2-chloroanilines and sodium *tert*-butoxide 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. Flash chromatography: Macherey-Nagel silica gel 60 (70-230 mesh). NMR: Spectra were recorded on a Varian-NMR 300 instrument in the solvent indicated; chemical shifts (δ) are given in ppm.

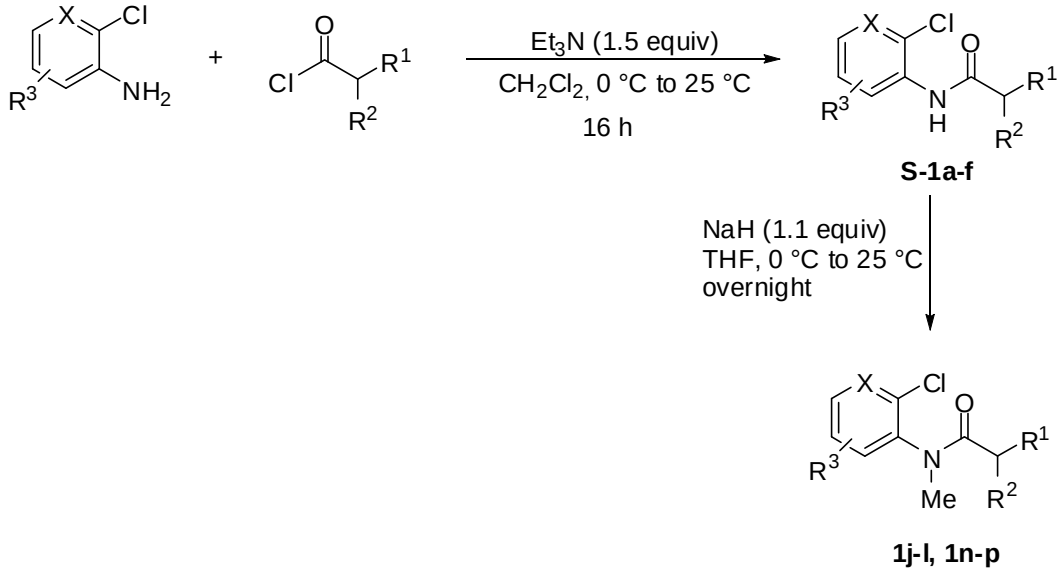
Preparation of *N*-(2-chloroaryl)amides 1a-p.

Route A (unsubstituted 2-chloroanilines)



1a-i, 1m

Route B (substituted 2-chloroanilines)



1j-l, 1n-p

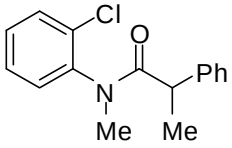
Route A (unsubstituted 2-chloroanilines):[6] To a solution of 2-chloro-*N*-methylaniline (1.0 equiv) and Et_3N (1.5 equiv) in CH_2Cl_2 was added the corresponding acyl chloride dropwise at 0 °C, and the resulting mixture was stirred overnight at ambient temperature. H_2O (100 mL) and Et_2O (100 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed successively with H_2O (50 mL), aq. NH_3 (50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield the corresponding *N*-(2-chlorophenyl)-*N*-methylamide **1**.

Route B (substituted 2-chloroanilines):[6] To a solution of the corresponding substituted 2-chloroaniline (1.0 equiv) and Et_3N (1.5 equiv) in CH_2Cl_2 was added the corresponding acyl chloride dropwise at 0 °C, and the resulting mixture was stirred overnight at ambient temperature. H_2O (100 mL) and Et_2O (100 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed successively with H_2O (50 mL), aq. NH_3 (50 mL) and brine (50

mL), dried over Na_2SO_4 and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield the corresponding *N*-(2-chloroaryl)amide.

To a solution of *N*-(2-chloroaryl)amide (1.0 equiv) in THF, NaH (1.1 equiv) was added in small portions at 0 °C, and the resulting mixture was stirred for 0.5 h at ambient temperature. Then, MeI (1.2 equiv) was added dropwise at 0 °C, and the resulting mixture was stirred overnight at ambient temperature. H_2O (100 mL) and Et_2O (100 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed successively with H_2O (50 mL), aq. NH_3 (50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield the corresponding *N*-(2-chloroaryl)amide **1**.

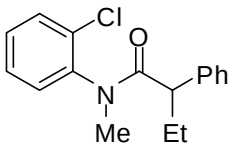
***N*-(2-Chlorophenyl)-*N*-methyl-2-phenylpropanoic acid amide (1b)** (Route A):



1b

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 2:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): *δ* = 7.51 (dd, *J* = 8.0, 1.4 Hz, 1H, *M*), 7.38–7.22 (m, 3H, *M*+*m*), 7.21–7.04 (m, 4.7H, *M*+*m*), 6.96–6.93 (m, 2.7H, *M*+*m*), 6.70 (dd, *J* = 7.8, 1.6 Hz, 1H, *M*), 3.53 (q, *J* = 6.9 Hz, 1H, *m*), 3.34 (q, *J* = 6.9 Hz, 1H, *M*), 3.16 (s, 3H, *m*), 3.15 (s, 3H, *M*), 1.40 (d, *J* = 6.9 Hz, 3H, *M*), 1.39 (d, *J* = 6.9 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): *δ* = 174.0 (C_q, *m*) 173.9 (C_q, *M*), 141.7 (C_q, *M*), 140.9 (C_q, *m*), 140.7 (C_q, *M*), 140.6 (C_q, *m*), 133.9 (C_q, *m*), 133.1 (C_q, *M*), 130.7 (CH, *M*), 130.3 (CH, *M*), 130.1 (CH, *m*), 129.5 (CH, *m*), 129.4 (CH, *M*), 128.5 (CH, *M*), 128.2 (CH, *m*), 127.9 (CH, *m*), 127.8 (CH, *m*), 127.7 (CH, *M*), 127.4 (CH, *M*), 126.7 (CH, *m*), 126.6 (CH, *M*), 43.8 (CH, *M*), 43.3 (CH, *m*), 36.2 (CH_3, *M*), 36.0 (CH_3, *m*), 20.5 (CH_3, *M*), 20.0 (CH_3, *m*). IR (NaCl): 3062, 3028, 2973, 2931, 1667, 1481, 1378, 1280, 1248, 1130, 1056, 765, 732, 699 cm^{-1}. MS (EI) *m/z* (relative intensity) 287 (1) [M^+], 238 (40), 168 (19), 140 (21), 105 (100), 77 (71), 51 (11). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClNO$ 274.0993, found 274.0999. The spectral data are in accordance with those reported in the literature.[7]

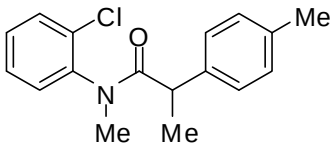
***N*-(2-Chlorophenyl)-*N*-methyl-2-phenylbutanoic acid amide (1c)** (Route A):



1c

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 2.8:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 7.52 (dd, *J* = 8.0, 1.5 Hz, 1H, *M*), 7.38–7.26 (m, 2.8H, *M*+*m*), 7.19–7.13 (m, 3.7H, *M*+*m*), 7.10 (dt, *J* = 7.6, 1.5 Hz, 1H, *M*), 6.95–6.89 (m, 2.5H, *M*+*m*), 6.62 (dd, *J* = 7.9, 1.6 Hz, 1H, *M*), 3.24 (t, *J* = Hz, 1H, *m*), 3.17 (s, 3H, *m*), 3.15 (s, 3H, *M*), 3.01 (dd, *J* = 8.0, 6.8 Hz, 1H, *M*), 2.13–2.02 (m, 1.5H, *M*+*m*), 1.74–1.60 (m, 1.5H, *M*+*m*), 0.79 (t, *J* = 7.4 Hz, 3H, *M*), 0.76 (t, *J* = 7.4 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 173.3 (C_q, *m*) 173.2 (C_q, *M*), 140.9 (C_q, *m*), 140.7 (C_q, *M*), 140.2 (C_q, *M*), 139.1 (C_q, *m*), 134.1 (C_q, *m*), 132.9 (C_q, *M*), 131.1 (CH, *M*), 130.7 (CH, *m*), 130.4 (CH, *m*), 130.3 (CH, *M*), 129.5 (CH, *M*), 129.4 (CH, *m*), 128.3 (CH, *M*), 128.2 (CH, *m*), 128.1 (CH, *m*), 127.9 (CH, *M*), 127.8 (CH, *m*), 127.6 (CH, *M*), 126.7 (CH, *m*), 126.6 (CH, *M*), 51.8 (CH, *M*), 51.0 (CH, *m*), 36.0 (CH_3, *M*), 35.9 (CH_3, *m*), 28.4 (CH_2, *M*), 28.0 (CH_2, *m*), 12.5 (CH_3, *M*), 12.3 (CH_3, *m*). IR (NaCl): 2964, 2930, 1663, 1586, 1482, 1376, 1288, 1245, 1131, 1059, 764, 732, 700 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 287 (2) [M^+], 252 (100), 230 (3), 168 (24), 141 (27), 119 (31), 91 (96), 77 (26), 51 (5), 41 (11). HR-MS (ESI) ***m/z*** calcd for $C_{17}H_{18}ClNO+H^+$ 288.1149, found 288.1150.

***N*-(2-Chlorophenyl)-*N*-methyl-2-*p*-tolylpropanoic acid amide (1d)** (Route A):

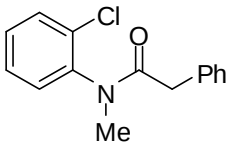


1d

White solid. M.p. = 82–84 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 2.6:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 7.51 (dd, *J* = 8.0, 1.5 Hz, 1H, *M*), 7.36–7.25 (m, 3H, *M*+*m*), 7.13 (td, *J* = 7.7, 1.5 Hz, 1H, *M*), 7.01–6.95 (m, 2.8H, *M*+*m*), 6.68–6.62 (m, 2.8H, *M*+*m*), 6.75 (dd, *J* = 7.8, 1.6 Hz, 1H, *M*), 3.48 (q, *J* = 7.0 Hz, 1H, *m*), 3.30 (q, *J* = 6.9 Hz, 1H, *M*), 3.16 (s, 3H, *m*), 3.15 (s, 3H, *M*), 2.27 (s, 3H, *M*), 2.26 (s, 3H, *m*), 1.38 (t, *J* = 6.9 Hz, 3H, *M*), 1.37 (d, *J* = 7.0 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 174.3 (C_q, *m*) 174.1 (C_q, *M*), 141.0 (C_q, *m*), 140.8 (C_q, *M*), 138.7 (C_q, *M*),

137.6 (C_q, *m*), 136.3 (C_q, *m*), 136.2 (C_q, *M*), 133.8 (C_q, *m*), 133.1 (C_q, *M*), 130.8 (CH, *M*), 130.7 (CH, *m*), 130.3 (CH, *M*), 130.0 (CH, *m*), 129.5 (CH, *m*), 129.4 (CH, *M*), 129.0 (CH, *M*), 128.8 (CH, *m*), 127.9 (CH, *m*), 127.8 (CH, *M*), 127.7 (CH, *m*), 127.3 (CH, *M*), 43.3 (CH, *M*), 42.8 (CH, *m*), 36.1 (CH_3, *M*), 36.0 (CH_3, *m*), 21.0 (CH_3, *M*), 20.5 (CH_3, *M*), 20.0 (CH_3, *m*) (a signal corresponding to a CH_3 of the minor isomer is overlaped). IR (NaCl): 3022, 2987, 2930, 1659, 1481, 1378, 1266, 1129, 1057, 769, 735 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 287 (2) [M^+], 252 (45), 168 (27), 141 (12), 119 (100), 91 (22), 77 (33), 65 (6), 41 (8). HR-MS (ESI) ***m/z*** calcd for $C_{17}H_{18}ClNO+H^+$ 288.1150, found 288.1152.

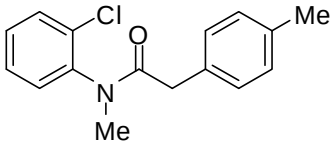
***N*-(2-Chlorophenyl)-*N*-methyl-2-phenylacetic acid amide (1e)** (Route A):



1e

White solid. M.p. = 73–75 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.35–7.22 (m, 2H), 7.25–7.11 (m, 4H), 7.03–6.96 (m, 2H), 3.41 (d, *J* = 14.9 Hz, 1H), 3.31 (d, *J* = 14.9 Hz, 1H), 3.19 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.0 (C_q), 141.0 (C_q), 134.9 (C_q), 133.2 (C_q), 130.6 (CH), 130.2 (CH), 129.6 (CH), 129.1 (CH), 128.2 (CH), 128.1 (CH), 126.6 (CH), 40.9 (CH_2), 36.0 (CH_3). IR (NaCl): 3060, 3030, 1667, 1478, 1408, 1372, 1127, 1064, 766, 731, 704 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 259 (1) [M^+], 224 (80), 168 (13), 141 (36), 91 (100), 77 (35), 65 (32), 51 (11). HR-MS (ESI) ***m/z*** calcd for $C_{15}H_{14}ClNO+H^+$ 260.0837, found 260.0827. The spectral data are in accordance with those reported in the literature.[6]

***N*-(2-Chlorophenyl)-*N*-methyl-2-*p*-tolylacetic acid amide (1f)** (Route A):

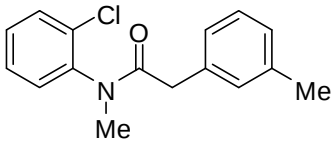


1f

White solid. M.p. = 66–67 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50–7.47 (m, 1H), 7.34–7.23 (m, 2H), 7.14–7.11 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 3.35 (d, *J* = 14.9 Hz, 1H), 3.24 (d, *J* = 14.9 Hz, 1H), 3.18 (s, 3H), 2.26 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.2 (C_q), 141.1 (C_q), 136.1 (C_q),

133.2 (C_q), 131.8 (C_q), 130.6 (CH), 130.3 (CH), 129.6 (CH), 129.0 (CH), 128.9 (CH), 128.1 (CH), 40.4 (CH_2), 36.0 (CH_3), 21.0 (CH_3). IR (NaCl): 3052, 2922, 1662, 1514, 1481, 1374, 1267, 1128, 766, 733 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 273 (4) [M^+], 252 (8), 238 (100), 168 (41), 141 (80), 132 (18), 119 (12), 105 (94), 91 (26), 77 (62), 65 (13), 51 (16). HR-MS (ESI) ***m/z*** calcd for $C_{16}H_{16}ClNO+H^+$ 274.0993, found 274.0995.

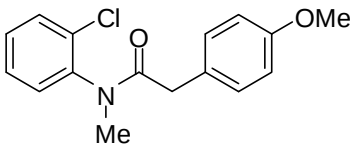
***N*-(2-Chlorophenyl)-*N*-methyl-2-*m*-tolylacetic acid amide (1g)** (Route A):



1g

Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 1H), 7.32–7.23 (m, 2H), 7.14–7.05 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.30 (q, *J* = 8.0 Hz, 2H), 3.19 (s, 3H), 2.23 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.9 (C_q), 140.9 (C_q), 137.7 (C_q), 134.6 (C_q), 133.1 (C_q), 130.5 (CH), 130.2 (CH), 129.8 (CH), 129.5 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.1 (CH), 41.0 (CH_2), 36.1 (CH_3), 21.4 (CH_3). IR (NaCl): 3061, 3025, 2868, 1677, 1587, 1480, 1439, 1282, 1066, 770, cm^{-1}. MS (EI) ***m/z*** (relative intensity) 273 (1) [M^+], 252 (30), 239(96), 168 (35), 141 (100), 127 (80), 105 (63), 91 (25), 77 (50), 65 (27), 43 (12). HR-MS (ESI) ***m/z*** calcd for $C_{16}H_{16}NOCl+Na^+$ 296.0813, found 296.0817.

***N*-(2-Chlorophenyl)-2-(4-methoxyphenyl)-*N*-methylacetic acid amide (1h)** (Route A):

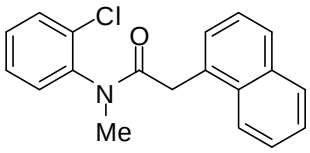


1h

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 1H), 7.34–7.24 (m, 2H), 7.15–7.11 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.33 (d, *J* = 14.9 Hz, 1H), 3.23 (d, *J* = 14.9 Hz, 1H), 3.18 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171 (C_q), 158.2 (C_q), 140.9 (C_q), 133.0 (C_q), 130.5 (CH), 130.1 (CH), 130.0 (CH), 129.5 (CH), 128.0 (CH), 126.9 (C_q), 113.6 (CH), 55.2 (CH_3), 40.0 (CH_2), 36.0 (CH_3). IR (NaCl): 2997, 2935, 2835, 1669, 1586, 1512, 1481, 1375, 1246, 1178, 1128, 1035, 822, 787, 767 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 289 (15) [M^+], 254 (16), 168 (12), 148 (10), 140 (9), 121

(100), 111 (5), 91 (12), 77 (59), 63 (8), 51 (21), 41 (5). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClNO_2$ 290.0942, found 290.0943.

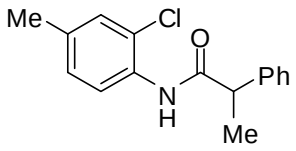
***N*-(2-Chlorophenyl)-*N*-methyl-2-(naphthalen-1-yl)acetic acid amide (1i)** (Route A):



1i

White solid. M.p. = 122–125 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88–7.85 (m, 1H), 7.81–7.76 (m, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.51–7.39 (m, 3H), 7.32–7.16 (m, 4H), 7.04 (d, *J* = 7.0 Hz, 1H), 3.89–3.77 (m, 2H), 3.22 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.8 (C_q), 141.0 (C_q), 133.7 (C_q), 133.1 (C_q), 132.2 (C_q), 131.4 (C_q), 130.7 (CH), 130.0 (CH), 129.6 (CH), 128.5 (CH), 128.2 (CH), 127.6 (CH), 127.5 (CH), 126.0 (CH), 125.5 (CH), 125.2 (CH), 123.9 (CH), 39.0 (CH_2), 36.2 (CH_3). IR (NaCl): 3044, 2914, 1663, 1480, 1368, 1123, 787, 574 cm^{-1}. MS (EI) *m/z* (relative intensity) 309 (51) [M^+], 274 (54), 168 (90), 141 (100), 115 (36), 77 (8). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}NOCl+H^+$ 310.0993, found 310.0995.

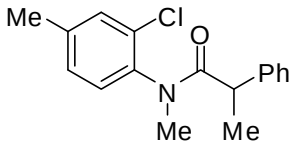
***N*-(2-Chloro-4-methylphenyl)-2-phenylpropanoic acid amide (S-1a)** (Route B):



S-1a

White solid. M.p. = 77–79 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = Hz, 1H), 7.50 (bs, 1H), 7.42–7.34 (m, 3H), 7.33–7.27 (m, 2H), 7.07 (dd, *J* = 1.6, 0.4 Hz, 1H), 7.02 (tdd, *J* = 8.5, 2.0, 0.5 Hz, 1H), 3.76 (q, *J* = 7.2 Hz, 1H), 2.24 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.2 (C_q), 140.4 (C_q), 134.5 (C_q), 132.0 (C_q), 129.2 (CH), 129.1 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 122.5 (C_q), 121.1 (CH), 48.3 (CH), 20.6 (CH_3) 18.1 (CH_3). IR (NaCl): 3029, 2976, 1655, 1609, 1525, 1392, 1285, 1059, 817, 758, 734, 694 cm^{-1}. MS (EI) *m/z* (relative intensity) 273 (67) [M^+], 238 (31), 167 (9), 141 (77), 132 (20), 105 (100), 77 (41). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClNO+H^+$ 274.0993, found 274.0994.

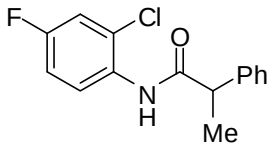
***N*-(2-Chloro-4-methylphenyl)-2-phenylpropanoic acid amide (1j)** (Route B):



1j

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 2.4:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 7.32 (dd, *J* = 1.8, 0.7 Hz, 1H, *M*), 7.22–7.13 (m, 5.3H, *M*+*m*), 7.01–6.96 (m, 2.6H, *M*+*m*), 6.91 (ddd, *J* = 8.0, 1.9, 0.7 Hz, 1H, *M*), 3.54 (q, *J* = 7.0 Hz, 1H, *m*), 3.36 (q, *J* = 6.9 Hz, 1H, *M*), 3.14 (s, 3H, *m*), 3.13 (s, 3H, *M*), 2.37 (s, 3H, *m*), 2.36 (s, 3H, *M*), 1.39 (d, *J* = 6.9 Hz, 3H, *M*), 1.38 (d, *J* = 7.0 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 174.3 (C_q, *m*), 174.2 (C_q, *M*), 141.8 (C_q, *M*), 140.7 (C_q, *m*), 140.0 (C_q, *m*), 139.9 (C_q, *M*), 138.3 (C_q, *m*), 138.1 (C_q, *M*), 133.2 (C_q, *m*), 132.5 (C_q, *M*), 131.1 (CH, *m*), 130.7 (CH, *M*), 130.2 (CH, *M*), 129.5 (CH, *m*), 128.7 (CH, *m*), 128.4 (CH, *M*), 128.3 (CH, *M*), 128.1 (CH, *m*), 127.9 (CH, *m*), 127.5 (CH, *M*), 126.5 (CH, *m*), 126.6 (CH, *M*), 43.6 (CH, *M*), 43.1 (CH, *m*), 36.2 (CH_3, *M*), 36.1 (CH_3, *m*), 21.0 (CH_3, *M*), 20.9 (CH_3, *m*), 20.5 (CH_3, *M*), 19.9 (CH_3, *m*). IR (NaCl): 2972, 2930, 1670, 1498, 1376, 1279, 1131, 1055, 863, 825, 733, 825 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 287 (4) [M^+], 252 (100), 182 (22), 155 (38), 105 (39), 77 (6). HR-MS (ESI) ***m/z*** calcd for $C_{17}H_{18}ClNO+H^+$ 288.1150, found 288.1151.

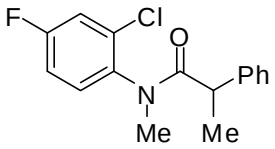
***N*-(2-Chloro-4-fluorophenyl)-2-phenylpropanoic acid amide (S-1b)** (Route B):



S-1b

Pale red solid. M.p. = 99–101 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.28 (dd, *J* = 9.0, 5.7 Hz, 1H), 7.51 (s, 1H), 7.44–7.25 (m, 5H), 7.01–6.89 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.1 (C_q), 158.0 (C_q, $J_{C\text{-}F}$ = 246.4 Hz), 140.1 (C_q), 130.9 (C_q, $J_{C\text{-}F}$ = 3.7 Hz), 130.8 (CH), 129.1 (CH), 127.7 (CH),123.3 (C_q, $J_{C\text{-}F}$ = 10.7 Hz), 122.4 (CH, $J_{C\text{-}F}$ = 8.8 Hz), 116.0 (CH, $J_{C\text{-}F}$ = 26.0 Hz), 114.3 (CH, $J_{C\text{-}F}$ = 21.7 Hz), 48.2 (CH), 18.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -116.49– -116.61 (m). IR (NaCl): 3026, 2978, 1653, 1596, 1522, 1448, 1208, 1075, 959, 868, 761 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 277 (43) [M^+], 242 (11), 202 (6),145 (18), 132 (58, 105 (100), 91 (6), 77 (10). HR-MS (ESI) ***m/z*** calcd for $C_{15}H_{13}NOFCl+H^+$ 278.0743 found 278.0743.

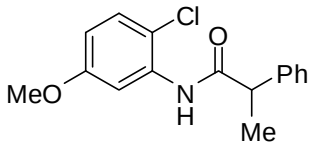
***N*-(2-Chloro-4-fluorophenyl)-*N*-methyl-2-phenylpropanoic acid amide (1k)** (Route B):



1k

Pale red oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 2.4:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 7.35–7.20 (m, 1.8H, *M*+*m*), 7.18–7.10 (m, 4.3H, *M*+*m*), 7.09–7.01 (m, 1H, *M*), 6.96–6.87 (m, 2.8H, *M*+*m*), 6.82–6.73 (m, 1H, *M*), 6.63–6.55 (m, 1H, *M*), 3.47 (q, *J* = 6.9 Hz, 1H, *m*), 3.27 (q, *J* = 6.9 Hz, 1H, *M*), 3.12 (s, 3H, *m*), 3.10 (s, 3H, *M*), 1.37 (d, *J* = 7.3 Hz, 3H, *M*), 1.36 (d, *J* = 7.3 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 173.9 (C_q, *m*), 173.9 (C_q, *M*), 161.7 (C_q, $J_{C\text{-}F}$ = 252.1 Hz, *m*), 161.5 (C_q, $J_{C\text{-}F}$ = 252.1 Hz, *M*), 141.6 (C_q, *M*), 140.4 (C_q, *m*), 137.2 (C_q, $J_{C\text{-}F}$ = 3.8 Hz, *m*), 137.0 (C_q, $J_{C\text{-}F}$ = 3.8 Hz, *M*), 135.1 (C_q, $J_{C\text{-}F}$ = 10.8 Hz, *m*), 134.1 (C_q, $J_{C\text{-}F}$ = 10.9 Hz, *M*), 131.9 (CH, $J_{C\text{-}F}$ = 9.2 Hz, *M*), 131.0 (CH, $J_{C\text{-}F}$ = 9.3 Hz, *m*), 128.5 (CH, *M*), 128.2 (CH, *m*), 127.7 (CH, *m*), 127.3 (CH, *M*), 126.8 (CH, *m*), 126.7 (CH, *M*), 118.1 (CH, $J_{C\text{-}F}$ = 25.5 Hz, *m*), 117.8 (CH, $J_{C\text{-}F}$ = 25.5 Hz, *M*), 115.0 (CH, $J_{C\text{-}F}$ = 22.3 Hz, *m*), 114.9 (CH, $J_{C\text{-}F}$ = 22.2 Hz, *M*), 44.0 (CH, *M*), 43.4 (CH, *m*), 36.3 (CH_3, *M*), 36.1 (CH_3, *m*), 20.5 (CH_3, *M*), 20.1 (CH_3, *m*). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -110.23– -110.36 (m, *M*), -110.38– -110.48 (m, *m*). IR (NaCl): 3062, 2976, 2932, 1673, 1582, 1376, 1256, 1206, 1049, 881,736 cm^{-1}. MS (EI) ***m/z*** (relative intensity) 291 (1) [M^+], 256 (64), 186 (25), 159 (31), 105 (100), 77 (15). HR-MS (ESI) ***m/z*** calcd for $C_{16}H_{15}NOFCl+H^+$ 292.0899, found 292.0901.

***N*-(2-Chloro-5-methoxyphenyl)-2-phenylpropanoic acid amide (S1-c)** (Route B):

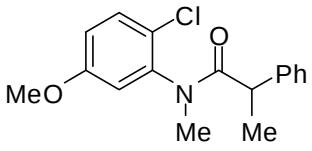


S-1c

Pale yellow solid. M.p. = 88–91 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 3.0 Hz, 1H), 7.62 (s, 1H), 7.36–7.27 (m, 5H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.52 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.76 (q, *J* = 7.1 Hz, 1H), 3.75 (s, 3H), 1.62 (d, *J* = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.3 (C_q), 158.8 (C_q), 140.1 (C_q), 135.1 (C_q), 129.2 (CH), 128.9 (CH), 127.7 (CH), 127.7 (CH), 113.6 (C_q), 111.1 (CH), 105.7 (CH), 55.6 (CH_3), 48.5 (CH), 18.1 (CH_3). IR (NaCl): 2982, 2965, 2929, 1667, 1581, 1468, 1426, 1167, 874, 637, 550 cm^{-1}.

MS (EI) *m/z* (relative intensity) 289 (18) [M^+], 254 (82), 183 (5), 157 (35), 129 (14), 105 (100), 91 (14), 77 (24), 65 (5), 51 (6). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}NO_2Cl+H^+$ 290.0942, found 290.0944.

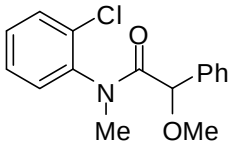
***N*-(2-Chloro-5-methoxyphenyl)-*N*-methyl-2-phenylpropanoic acid amide (1l)** (Route B):



1l

Pale yellow solid. M.p. = 76–78 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 3.6:1 *syn*/*anti* mixture), Major isomer, δ = 7.36 (d, *J* = 8.9 Hz, 1H), 7.21–7.13 (m, 3H), 6.97–6.93 (m, 2H), 6.86–6.80 (m, 1H), 6.11 (d, *J* = 3.0 Hz, 1H), 3.46 (s, 3H), 3.35 (q, *J* = 6.9 Hz, 1H), 3.14 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H); minor isomer, δ = 7.26–7.21 (m, 3H), 7.02–6.99 (m, 2H), 6.88–6.86 (m, 1H), 3.83 (s, 3H), 3.57 (q, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H), the missing resonances overlaped with the major isomer. ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 173.8 (C_q, *m*), 173.5 (C_q, *M*), 158.8 (C_q, *m*), 158.5 (C_q, *M*), 142.1 (C_q, *M*), 141.4 (C_q, *m*), 141.0 (C_q, *M*), 140.5 (C_q, *m*), 130.9 (CH, *m*), 130.4 (CH, *M*), 128.3 (CH, *M*), 128.0 (CH, *m*), 127.8 (CH, *m*), 127.3 (CH, *M*), 126.6 (CH, *m*), 126.5 (CH, *M*), 124.9 (C_q, *m*), 123.9 (C_q, *M*), 116.4 (CH, *M*), 115.4 (CH, *m*), 115.0 (CH, *M*), 114.9 (CH, *m*), 55.8 (CH_3, *m*), 55.4 (CH_3, *M*), 44.1 (CH, *M*), 43.2 (CH, *m*), 36.1 (CH_3, *M*), 36.0 (CH_3, *m*), 20.6 (CH_3, *M*), 20.1 (CH_3, *m*). IR (NaCl): 2973, 2934, 1653, 1521, 1445, 1414, 1131, 809, 774, 650 cm^{-1}. MS (EI) *m/z* (relative intensity) 268 (100) [M^+-Cl], 209 (19), 198 (11), 171 (19), 105 (58), 77 (16), 57 (7), 43 (6). HR-MS (ESI) *m/z* calcd for $C_{17}H_{18}NO_2Cl+Na^+$ 326.0918 found 326.0919.

***N*-(2-Chlorophenyl)-2-methoxy-*N*-methyl-2-phenylacetic acid amide (1m)** (Route A):

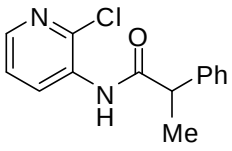


1m

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 3.6:1 *syn*/*anti* mixture, *M* = Major isomer, *m* = minor isomer): δ = 7.53 (dd, *J* = 8.1, 1.5 Hz, 1H, *M*), 7.37–7.17 (m, 8.8H, *M*+*m*), 7.07 (td, *J* = 7.6, 1.5 Hz, 1H, *M*), 7.03–6.96 (m, 3H, *M*+*m*), 6.57 (dd, *J* = 7.9, 1.6 Hz, 1H, *M*), 4.56 (s, 1H, *m*), 4.34 (s, 1H, *M*), 3.34 (s, 3H, *M*), 3.19 (s,

4.8H, *M*+*m*), 3,16 (s, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 169.9 (C_q, *M*), 169.6 (C_q, *m*), 139.9 (C_q, *m*), 139.5 (C_q, *M*), 136.2 (C_q, *M*), 135.4 (C_q, *m*), 134.0 (C_q, *m*), 132.8 (C_q, *M*), 131.2 (CH, *M*), 130.8 (CH, *m*), 130.5 (CH, *M*), 130.4 (CH, *m*), 129.9 (CH, *M*), 129.8 (CH, *m*), 128.7 (CH, *M*), 128.5 (CH, *m*), 128.4 (CH, *M*), 128.3 (CH, *M*), 128.2 (CH, *m*), 128.1 (CH, *m*), 127.9 (CH, *m*), 127.8 (CH, *M*), 81.6 (CH, *M*), 81.1 (CH, *m*), 57.6 (CH_3, *M*), 56.8 (CH_3, *m*), 36.4 (CH_3, *M*), 36.2 (CH_3, *m*). IR (NaCl): 3062, 3030, 2986, 2929, 1683, 1586, 1481, 1380, 1289, 1195, 1103, 975, 759, 699 cm^{-1}. MS (EI) *m/z* (relative intensity) 289 (1) [M^+], 259 (3), 140 (7), 121 (100), 105 (12), 91 (24), 71 (78), 63 (8), 51 (13). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClNO_2$+Na^+ 312.0762, found 312.0762. The spectral data are in accordance with those reported in the literature.[8]

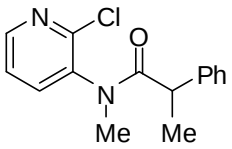
***N*-(2-chloropyridin-3-yl)-2-phenylpropanoic acid amide (S1-d)** (Route B):



S1-d

S1-d was used after work-up for the subsequent methylation without further purification.

***N*-(2-Chloropyridin-3-yl)-*N*-methyl-2-phenylpropanoic acid amide (1n)** (Route B):

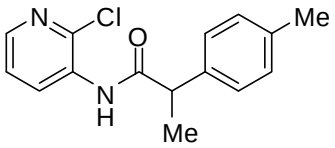


1n

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 2.8:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 8.38 (dd, *J* = 4.7, 1.8 Hz, 1H, *m*), 8.35 (dd, *J* = 4.7, 1.9 Hz, 1H, *M*), 7.69 (dd, *J* = 7.7, 1.8 Hz, 1H, *m*), 7.38–7.33 (m, 1H, *M*), 7.18–7.14 (m, 4H, *M*+*m*), 7.07–7.02 (m, 1.3H, *M*+*m*), 6.92–6.82 (m, 3.7H, *M*+*m*), 3.43 (q, *J* = 6.9 Hz, 1H, *m*), 3.27 (q, *J* = 6.8 Hz, 1H, *M*), 3.16 (s, 3H, *m*), 3.15 (s, 3H, *M*), 1.39 (d, *J* = 6.9 Hz, 3H, *M*), 1.38 (d, *J* = 6.9 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 173.5 (C_q, *m*), 173.4 (C_q, *M*), 151.4 (C_q, *m*), 150.5 (C_q, *M*), 149.0 (CH, *m*), 148.9 (CH, *M*), 141.4 (C_q, *M*), 139.7 (C_q, *m*), 139.3 (CH, *M*), 138.6 (CH, *m*), 137.5 (C_q, *m*), 137.4 (C_q, *M*), 128.6 (CH, *M*), 128.5 (CH, *m*), 127.4 (CH, *m*), 127.2 (CH, *M*), 127.0 (CH, *m*), 126.9 (CH, *M*), 123.1 (CH, *m*), 123.0 (CH, *M*), 44.5 (CH, *M*), 43.7 (CH, *m*), 36.1 (CH_3, *M*), 35.9 (CH_3, *m*), 20.5 (CH_3, *M*), 19.9 (CH_3, *m*). IR (NaCl): 3058, 3027,

2975, 2931, 1666, 1405, 1375, 1143, 1065, 751, 731 cm^{-1}. MS (EI) *m/z* (relative intensity) 274 (1) [M^+], 239 (79), 169 (17), 142 (26), 132 (18), 105 (100), 77 (15). HR-MS (ESI) *m/z* calcd for $C_{15}H_{15}ClNO+Na^+$ 297.0765, found 297.0768.

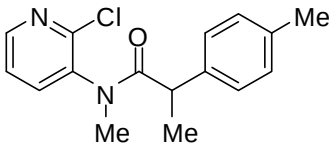
***N*-(2-chloropyridin-3-yl)-2-(4-tolyl)propanoic acid amide (S1-e)** (Route B):



S1-e

S1-e was used after work-up for the subsequent methylation without further purification.

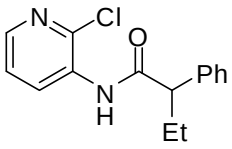
***N*-(2-Chloropyridin-3-yl)-*N*-methyl-2-(4-tolyl)propanoic acid amide (1o)** (Route B):



1o

Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 3.0:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 8.40 (dd, *J* = 4.7, 1.8 Hz, 1H, *m*), 8.36 (dd, *J* = 4.7, 1.8 Hz, 1H, *M*), 7.68 (dd, *J* = 7.7, 1.8 Hz, 1H, *m*), 7.35 (dd, *J* = 7.7, 4.7 Hz, 1H, *m*), 7.08 (dd, *J* = 7.7, 1.8 Hz, 1H, *M*), 7.01–6.94 (m, 3.6H, *M*+*m*), 6.80–6.72 (m, 2.7H, *M*+*m*), 3.40 (q, *J* = 6.8 Hz, 1H, *m*), 3.24 (q, *J* = 6.8 Hz, 1H, *M*), 3.16 (s, 3H, *m*), 3.15 (s, 3H, *M*), 2.27 (s, 3H, *M*), 2.25 (s, 3H, *m*), 1.38 (d, *J* = 6.9 Hz, 3H, *M*), 1.36 (d, *J* = 6.9 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 173.8 (C_q, *m*), 173.6 (C_q, *M*), 150.6 (C_q, *M*), 148.9 (CH, *M*), 139.4 (CH, *M*), 138.6 (CH, *m*), 138.4 (C_q, *M*), 137.7 (C_q, *m*), 137.6 (C_q, *M*), 136.8 (C_q, *m*), 136.7 (C_q, *m*), 136.5 (C_q, *m*), 129.3 (CH, *M*), 129.2 (CH, *m*), 127.4 (CH, *m*), 127.2 (CH, *M*), 123.1 (CH, *m*), 123.0 (CH, *M*), 44.1 (CH, *M*), 43.3 (CH, *m*), 36.1 (CH_3, *M*), 35.9 (CH_3, *m*), 21.0 (CH_3, *M*), 20.5 (CH_3, *M*+*m*), 20.0 (CH_3, *m*) (signals corresponding to one C_q and one CH of the minor isomer are overlaped). IR (NaCl): 2975, 2930, 1678, 1453, 1408, 1374, 1278, 1144, 1069, 819, 751 cm^{-1}. MS (EI) *m/z* (relative intensity) 288 (1) [M^+], 253 (47), 146 (9), 142 (10), 119 (100), 91 (10). HR-MS (ESI) *m/z* calcd for $C_{16}H_{17}ClN_2O+Na^+$ 311.0922, found 311.0923.

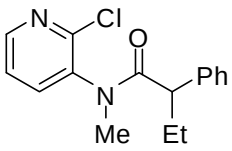
***N*-(2-chloropyridin-3-yl)-2-phenyl-butanoic acid amide (S1-f)** (Route B):



S1-f

S1-f was used after work-up for the subsequent methylation without further purification.

***N*-(2-Chloropyridin-3-yl)-*N*-methyl-2-phenyl-butanoic acid amide (1p)** (Route B):

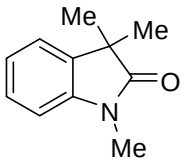


1p

White solid. M. p. = 86–87 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 3.5:1 *syn*/*anti* mixture, *M* = major isomer, *m* = minor isomer): δ = 8.41 (dd, *J* = 4.8, 1.8 Hz, 1H, *m*), 8.37 (dd, *J* = 4.7, 1.9 Hz, 1H, *M*), 7.67 (dd, *J* = 7.7, 1.8 Hz, 1H, *m*), 7.38 (dd, *J* = 7.7, 4.7 Hz, 1H, *m*), 7.34–7.32 (m, 1H, *m*), 7.20–7.15 (m, 3.6H, *M*+*m*), 7.07 (dd, *J* = 7.8, 4.7 Hz, 1H, *M*), 6.89–6.80 (m, 3.4H, *M*+*m*), 3.16 (s, 3H, *m*), 3.15 (s, 3H, *M*), 3.13 (q, *J* = 7.4 Hz, 1H, *m*), 2.95 (dd, *J* = 6.7, 6.7 Hz, 1H, *M*), 2.16–2.01 (m, 1.5H, *M*+ *m*), 1.75–1.54 (m, 1.5H, *M*+*m*), 0.81 (t, *J* = 7.3 Hz, 3H, *M*), 0.75 (t, *J* = 7.4 Hz, 3H, *m*). ^{13}C-NMR (75 MHz, $CDCl_3$, *M* = major isomer, *m* = minor isomer): δ = 172.9 (C_q, *m*), 172.7 (C_q, *M*), 150.5 (C_q, *M*), 149.0 (CH, *M*), 139.9 (C_q, *M*), 139.6 (CH, *M*), 139.0 (CH, *m*), 138.2 (C_q, *m*), 137.7 (C_q, *m*), 137.5 (C_q, *M*), 128.5 (CH, *M*), 128.4 (CH, *m*), 128.0 (CH, *m*), 127.8 (CH, *M*), 127.1 (CH, *m*), 126.9 (CH, *M*), 123.1 (CH, *m*), 112.9 (CH, *M*), 52.4 (CH, *M*), 51.5 (CH, *m*), 35.9 (CH_3, *M*), 35.8 (CH_3, *m*), 28.3 (CH_2, *M*), 27.8 (CH_2, *m*), 12.4 (CH_3, *M*), 12.2 (CH_3, *m*) (signals corresponding to a C_q and a CH of the minor isomer are overlaped). IR (NaCl): 3056, 2966, 2875, 1667, 1560, 1456, 1405, 1289, 1144, 1068, 733 cm^{-1}. MS (EI) *m/z* (relative intensity) 288 (1) [M^+], 253 (90), 213 (4), 169 (9), 146 (16), 142 (25), 119 (55), 107 (6), 91 (100), 78 (9), 51 (4), 41 (8). HR-MS (ESI) *m/z* calcd for $C_{16}H_{17}ClN_2O$+Na^+ 311.0922, found 311.0922.

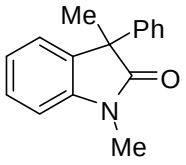
Representative procedure for palladium-catalyzed α-arylation of *N*-(2-chloroaryl)amides (Table 1, entry 5).

A suspension of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5.0 mol %), **3d** (16 mg, 0.050 mmol, 10 mol %), NaO*t*-Bu (106 mg, 1.10 mmol) and **1a** (106 mg, 0.50 mmol) in 1,4-dioxane (2 mL) was stirred under N_2 for 18 h at 100 °C. Et_2O (50 mL) and sat. aq. NH_4Cl (50 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated in vacuum. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 6:1) to yield **2a** as a colorless oil (74 mg, 84 %).



2a

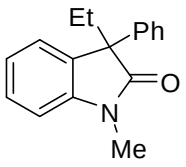
1,3,3-Trimethylindolin-2-one (2a, Table 1, entry 5): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.23 (td, *J* = 7.7, 1.3 Hz, 1H), 7.18 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 3.19 (s, 3H), 1.34 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 181.1 (C_q), 142.4 (C_q), 135.7 (C_q), 127.5 (CH), 122.3 (CH), 122.1 (CH), 107.9 (CH), 44.1 (C_q), 26.2 (CH_3), 24.4 (CH_3). IR (NaCl): 3054, 2963, 2926, 2862, 1695, 1618, 1497, 1475, 1344, 1246, 1129, 1073, 939, 763 cm^{-1}. MS (EI) *m/z* (relative intensity) 175 (56) [M^+], 160 (100), 132 (24), 117 (16), 103 (4), 91 (6), 77 (12), 65 (7), 51 (8), 43 (11). HR-MS (ESI) *m/z* calcd for $C_{11}H_{13}NO+H^+$ 176.1070, found 176.1074. The spectral data are in accordance with those reported in the literature.[9]



2b

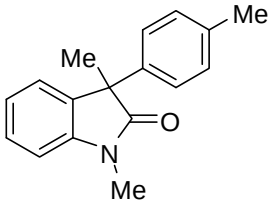
1,3-Dimethyl-3-phenylindolin-2-one (2b, Table 2, entry 1): The representative procedure was followed using **1b** (137 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 6:1) yielded **2b** (106 mg, 89 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34–7.16 (m, 7H), 7.08 (td, *J* =

7.4, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.77 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 179.4 (C_q), 143.2 (C_q), 140.8 (C_q), 134.8 (C_q), 128.5 (CH), 128.1 (CH), 127.2 (CH), 126.6 (CH), 124.2 (CH), 122.7 (CH), 108.2 (CH), 52.1(C_q), 26.4 (CH_3), 23.7 (CH_3). IR (NaCl): 2998, 2912, 2876, 1711, 1612, 1493, 1470, 1373, 1345, 1263, 1100, 753 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (82) [M^+], 222 (100), 208 (8), 194 (18), 178 (5), 165 (10), 152 (5), 134 (17), 105 (18), 77 (19), 51 (7). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}NO+H^+$ 238.1226, found 238.1227. The spectral data are in accordance with those reported in the literature.[6]



2c

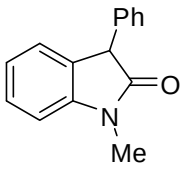
3-Ethyl-1-methyl-3-phenylindolin-2-one (2c, Table 2, entry 2): The representative procedure was followed using **1c** (144 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 6:1) yielded **2c** (114 mg, 91 %) as a white solid. M.p. = 81–84 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.40–7.19 (m, 7H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.49–2.37 (m, 1H), 2.29–2.18 (m, 1H), 0.68 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 178.5 (C_q), 144.0 (C_q), 140.2 (C_q), 132.0 (C_q), 128.4 (CH), 128.0 (CH), 127.1 (CH), 126.9 (CH), 124.7 (CH), 122.5 (CH), 108.1 (CH), 57.2 (C_q), 30.8 (CH_2), 26.2 (CH_3), 9.0 (CH_3). IR (NaCl): 3053, 2963, 2934, 2877, 1732, 1618, 1500, 1381, 1259, 1038, 916, 763 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (35) [M^+], 222 (100), 207 (11), 194 (10), 165 (11), 152 (7). HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}NO+H^+$ 252.1383, found 252.1384. The spectral data are in accordance with those reported in the literature.[10]



2d

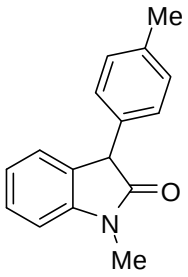
1,3-Dimethyl-3-*p*-tolylindolin-2-one (2d, Table 2, entry 3): The representative procedure was followed using **1d** (143 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 6:1) yielded

2d (114 mg, 91 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31 (td, J = 7.7, 1.4 Hz, 1H), 7.19–7.16 (m, 3H), 7.10–7.05 (m, 3H), 6.90 (d, J = 7.8 Hz, 1H), 3.22 (s, 3H), 2.28 (s, 3H), 1.76 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 179.6 (C_q), 143.2 (C_q), 137.8 (C_q), 136.9 (C_q), 134.9 (C_q), 129.2 (CH), 128.0 (CH), 126.5 (CH), 124.1 (CH), 122.7 (CH), 108.2 (CH), 51.8 (C_q), 26.4 (CH_3), 23.7 (CH_3), 20.9 (CH_3). IR (NaCl): 3053, 2967, 2920,1732, 1697, 1618, 1497, 1360, 1336, 1101, 1027, 762. 738 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (69) [M^+], 236 (100), 221 (10), 228 (14), 193 (8), 178 (5), 165 (9). 91 (6), 77 (4), 43 (8). HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}NO+H^+$ 252.1383, found 252.1384. The spectral data are in accordance with those reported in the literature.[10]



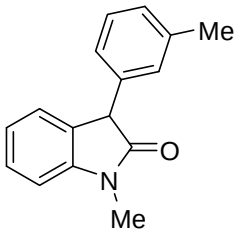
2e

1-Methyl-3-phenylindolin-2-one (2e, Table 2, entry 4): The representative procedure was followed using **1e** (130 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 6:1) yielded **2e** (74 mg, 66 %) as a white solid. M.p. = 120–121 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 4H), 7.21–7.14 (m, 3H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 4.59 (s, 1H), 3.24 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.0 (C_q), 144.4 (C_q), 136.6 (C_q), 128.8 (CH), 128.7 (C_q), 128.4 (2 × CH), 127.5 (CH), 125.0 (CH), 122.7 (CH), 108.1 (CH), 52.0 (CH), 26.4 (CH_3). IR (NaCl): 3052, 3025, 1693, 1609, 1495, 1467, 1346, 1264, 1124, 1086, 751 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (95) [M^+], 194 (75), 179 (10), 165 (18), 152 (10), 141 (29), 115 (8), 91 (100), 77 (41), 65 (37), 51 (31). HR-MS (ESI) *m/z* calcd for $C_{15}H_{13}NO+H^+$ 224.1070, found 224.1076. The spectral data are in accordance with those reported in the literature.[9]



2f

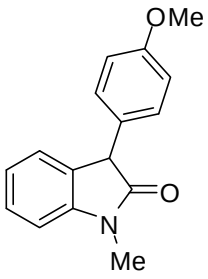
1-Methyl-3-*p*-tolylindolin-2-one (2f, Table 2, entry 6): The representative procedure was followed using **1f** (137 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 6:1) yielded **2f** (77 mg, 65 %) as a white solid. M.p. = 86–87 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31 (dt, J = 7.7, 1.0 Hz, 1H), 7.16–7.01 (m, 6H), 6.88 (d, J = 7.8 Hz, 1H), 4.56 (s, 1H), 3.23 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.2 (C_q), 144.5 (C_q), 137.2 (C_q), 133.5 (C_q), 129.5 (CH), 129.2 (C_q), 128.3 (CH), 128.2 (CH), 125.0 (CH), 122.7 (CH), 108.1 (CH), 51.7 (CH), 26.4 (CH_3), 21.1 (CH_3). IR (NaCl): 3054, 2916, 1693, 1067, 1496, 1342, 1087, 801, 748, 693 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (100) [M^+], 222 (12), 208 (27), 194 (19), 179 (6), 165 (8), 118 (5), 43 (7). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}NO+H^+$ 238.1226, found 238.1228. The spectral data are in accordance with those reported in the literature.[6]



2g

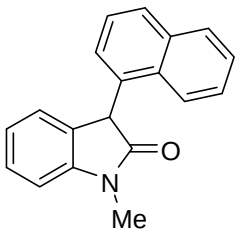
1-Methyl-3-*m*-tolylindolin-2-one (2g, Table 2, entry 7): The representative procedure was followed using **1g** (137 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2g** (71 mg, 60 %) as a pale orange oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 1H), 7.24–7.16 (m, 2H), 7.16–6.97 (m, 4H), 6.89 (d, J = 7.8 Hz, 1H), 4.56 (s, 1H), 3.25 (s, 3H), 2.31 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.9 (C_q), 144.3 (C_q), 138.4 (C_q), 136.4 (C_q), 128.9 (C_q), 128.9 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 125.3 (CH), 124.9 (CH), 122.6 (CH), 108.0 (CH), 52.0 (CH), 26.5 (CH_3), 21.4 (CH_3). IR (NaCl): 3057, 3021, 2949, 1705, 1616, 1496, 1342, 1265, 1177, 1125, 648 cm^{-1}. MS (EI) *m/z* (relative intensity) 237 (100) [M^+], 222 (10), 208 (27), 194 (16), 165 (5), 134 (6), 118 (5), 107 (14). HR-MS (ESI)

m/z calcd for $C_{16}H_{15}NO+H^+$ 238.1226, found 238.1227. The spectral data are in accordance with those reported in the literature.[11]



2h

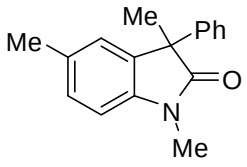
3-(4-Methoxyphenyl)-1-methylindolin-2-one (2h, Table 2, entry 8): The representative procedure was followed using **1h** (145 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2h** (78 mg, 62 %) as an off-white solid. M.p. = 90–91 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.16–7.08 (m, 3H), 7.05 (td, *J* = 7.7, 1.1 Hz, 1H), 6.90–6.81 (m, 3H), 4.54 (s, 1H), 3.76 (s, 3H), 3.22 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.2 (C_q), 159.0 (C_q), 144.4 (C_q), 129.4 (CH), 129.0 (C_q), 128.6 (C_q), 128.3 (CH), 124.9 (CH), 122.6 (CH), 114.2 (CH), 108.0 (CH), 55.2 (CH_3), 51.2 (CH), 26.3 (CH_3). IR (NaCl): 3053, 2957, 2931, 2835, 1711, 1611, 1512, 1469, 1347, 1250, 1032, 736 cm^{-1}. MS (EI) *m/z* (relative intensity) 253 (73) [M^+], 238 (15), 224 (70), 219 (100), 194 (23), 181 (88), 167 (85), 152 (87), 139 (33), 115 (35), 89 (39), 77 (85), 63 (41), 51 (37). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}NO_2+H^+$ 254.1176, found 254.1176. The spectral data are in accordance with those reported in the literature.[12]



2i

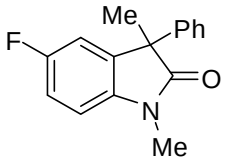
1-Methyl-3-(naphthalen-1-yl)indolin-2-one (2i, Table 2, entry 9): The representative procedure was followed using **1i** (145 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2i** (83 mg, 61 %) as a pale yellow solid. M.p. = 154–156 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.35 (bs, 1H), 7.88 - 6.94 (bs, 10H), 5.45 (bs, 1H), 3.33 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.7 (C_q),

170.8 (C_q), 144.1 (C_q), 134.0 (CH), 129.4 (C_q), 129.2 (CH), 128.6 (2 × CH), 128.1 (CH), 126.2 (CH), 125.6 (CH), 125.3 (CH), 124.6 (C_q), 123.9 (C_q), 123.8 (CH), 122.5 (CH), 108.0 (CH), 36.0 (CH), 26.4 (CH_3). IR (NaCl): 3047, 1695, 1606, 1345, 1086, 797, 753 cm^{-1}. MS (EI) *m/z* (relative intensity) 273 (100) [M^+], 244 (32), 229 (5), 215 (5), 141 (8), 115 (6). HR-MS (ESI) *m/z* calcd for $C_{19}H_{15}NO+H^+$ 274.1226, found 274.1229. The spectral data are in accordance with those reported in the literature.[12]



2j

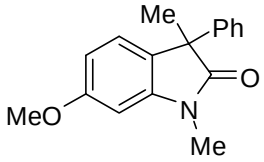
1,3,5-Trimethyl-3-phenylindolin-2-one (2j, Table 2, entry 11): The representative procedure was followed using **1j** (144 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2j** (100 mg, 80 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.33–7.19 (m, 5H), 7.13 (ddd, *J* = 7.9, 1.6, 0.8 Hz, 1H), 7.01 (bs, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 3.24 (s, 3H), 2.35 (s, 3H), 1.79 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 179.4 (C_q), 140.9 (C_q), 140.8 (C_q), 134.9 (C_q), 132.3 (C_q), 128.5 (CH), 128.3 (CH), 127.1 (CH), 126.6 (CH), 124.9 (CH), 108.0 (CH), 52.2 (C_q), 26.4 (CH_3), 23.6 (CH_3), 21.1 (CH_3). IR (NaCl): 3056, 3021, 2968, 2932, 2865, 1731, 1625, 1506, 1373, 1115, 1020, 803, 720, 694 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (95) [M^+], 236 (100), 221 (11), 208 (12), 193 (8), 165 (8), 103 (5), 77 (6). HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}NO+H^+$ 252.1383, found 252.1384.



2k

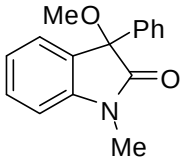
5-Fluoro-1,3-dimethyl-3-phenylindolin-2-one (2k, Table 2, entry 12): The representative procedure was followed using **1k** (146 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2k** (112 mg, 88 %) as a yellow solid. M.p. = 80–82 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31–7.19 (m, 5H), 6.99 (ddd, *J* = 9.1, 8.6, 2.6 Hz, 1H), 6.90 (dd, *J* = 7.9, 2.6 Hz, 1H), 6.80 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.20 (s, 3H), 1.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 178.9 (C_q, $J_{C\text{-}F}$ = 1.0 Hz), 159.1 (C_q, $J_{C\text{-}F}$ =

240.5 Hz), 140.0 (C_q), 139.0 (C_q, $J_{C\text{-}F}$ = 2.2 Hz), 136.3 (C_q, $J_{C\text{-}F}$ = 8.0 Hz), 128.5 (CH), 127.3 (CH), 126.4 (CH), 114.2 (CH, $J_{C\text{-}F}$ = 23.5 Hz,), 112.2 (CH, $J_{C\text{-}F}$ = 24.7 Hz,), 108.7 (CH, $J_{C\text{-}F}$ = 8.3 Hz), 52.7 (C_q), 26.6 (CH_3), 23.6 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -120.08– -120.39 (m). IR (NaCl): 3077, 3056, 2979, 2871, 1701, 1621, 1467, 1354, 1107, 929, 877, 643 cm^{-1}. MS (EI) *m/z* (relative intensity) 255 (100) [M^+], 240 (89), 226 (12), 212 (25), 183 (10). HR-MS (ESI) *m/z* calcd for $C_{16}H_{14}FNO+H^+$ 256.1132, found 256.1133.



2l

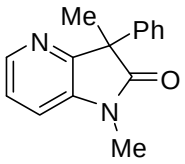
6-Methoxy-1,3-dimethyl-3-phenylindolin-2-one (2l, Table 2, entry 13): The representative procedure was followed using **1l** (152 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 4:1) yielded **2l** (117 mg, 92 %) as a pale yellow solid. M.p. = 79–82 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.29–7.18 (m, 5H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 3.83 (s, 3H), 3.19 (s, 3H), 1.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 179.7 (C_q), 160.0 (C_q), 144.3 (C_q), 141.0 (C_q), 128.3 (CH), 127.0 (CH), 126.6 (C_q), 126.5 (CH), 124.6 (CH), 106.4 (CH), 96.2 (CH), 55.5 (C_q), 51.6 (CH_3), 26.5 (CH_3), 24.0 (CH_3). IR (NaCl): 3052, 2980, 2935, 2834, 1725, 1616, 1452, 1246, 1099, 1075, 937, 784, 515 cm^{-1}. MS (EI) *m/z* (relative intensity) 267 (37) [M^+], 252 (100), 209 (6), 190 (8), 180 (5), 165 (5), 152 (5). HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}NO_2+H^+$ 268.1332, found 268.1334.



2m

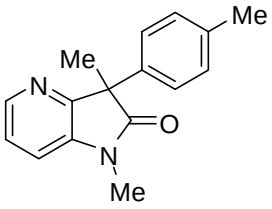
3-Methoxy-1-methyl-3-phenylindolin-2-one (2m, Table 2, entry 14): The representative procedure was followed using **1m** (145 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 5:1) yielded **2m** (57 mg, 45 %) as an off-white solid. M.p. = 77–79 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 3H), 7.29–7.21 (m, 4H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 3H), 3.18

(s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.2 (C_q), 144.5 (C_q), 138.6 (C_q), 130.1 (CH), 128.4 (CH), 128.3 (CH), 127.9 (C_q), 126.3 (CH), 125.7 (CH), 123.2 (CH), 108.5 (CH), 83.9 (C_q), 53.1 (CH_3), 26.3 (CH_3). IR (NaCl): 3065, 3007, 2953, 2824, 1716, 1610, 1465, 1435, 1104, 988, 759 cm^{-1}. MS (EI) *m/z* (relative intensity) 253 (37) [M$^+$], 238 (8), 223 (100), 209 (30), 194 (42), 182 (7), 164 (15), 152 (13), 105 (12), 77 (15). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}NO_2$+Na$^+$ 276.0995, found 276.0996. The spectral data are in accordance with those reported in the literature.[8]



2n

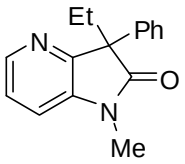
5,7-Dimethyl-7-phenyl-pyrrolo[3,2-*b*]pyridin-6(7*H*)-one (2n, Scheme 2): The representative procedure was followed using **1n** (137 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 2:1) yielded **2n** (71 mg, 60 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.42–7.37 (m, 2H), 7.29–7.13 (m, 4H), 7.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.22 (s, 3H), 1.80 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 177.8 (C_q), 155.0 (C_q), 143.1 (CH), 139.1 (C_q), 138.1 (C_q), 128.5 (CH), 127.3 (CH), 126.6 (CH), 122.6 (CH), 114.3 (CH), 52.1 (C_q), 26.0 (CH_3), 22.7 (CH_3). IR (NaCl): 3065, 2969, 2929, 1737, 1569, 1463, 1319, 1150, 1039, 701 cm^{-1}. MS (EI) *m/z* (relative intensity) 238 (61) [M$^+$], 223 (7), 209 (14), 195 (83), 181 (100), 167 (10), 152 (4), 104 (8), 77 (10). HR-MS (ESI) *m/z* calcd for $C_{15}H_{14}N_2O$+H$^+$ 239.1179, found 239.1179.



2o

5,7-Dimethyl-7-(4-tolyl)-pyrrolo[3,2-*b*]pyridin-6(7*H*)-one (2o, Scheme 2): The representative procedure was followed using **1o** (144 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 3:1) yielded **2o** (95 mg, 75 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.25 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.30 (md, *J* = 8.3 Hz, 2H), 7.15 (dd, *J* = 7.9, 5.1 Hz, 1H), 7.11–7.06 (m, 3H), 3.24 (s, 3H), 2.26 (s,

3H), 1.79 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 178.0 (C_q), 155.3 (C_q), 143.1 (CH), 138.1 (C_q), 137.0 (C_q), 136.2 (C_q), 129.2 (CH), 126.4 (CH), 122.5 (CH), 114.2 (CH), 51.9 (C_q), 26.0 (CH_3), 22.7 (CH_3), 20.9 (CH_3). IR (NaCl): 2970, 2927, 1717, 1603, 1512, 1455, 1370, 1327, 1100, 797 cm^{-1}. MS (EI) *m/z* (relative intensity) 252 (100) [M^+], 237 (35), 223 (13), 209 (70), 195 (94), 180 (5), 167 (6), 118 (9), 91 (7). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}N_2O$+Na^+ 275.1155, found 275.1161.



2p

7-Ethyl-5-methyl-7-phenyl-pyrrolo[3,2-*b*]pyridin-6(7*H*)-one (2p, Scheme 2): The representative procedure was followed using **1p** (144 mg, 0.50 mmol). After 18 h, purification by chromatography (*n*-hexane/EtOAc 3:1) yielded **2o** (111 mg, 88 %) as a white solid. M. p. = 96–98 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.56–7.51 (m, 2H), 7.28–7.12 (m, 4H), 7.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.23 (s, 3H), 2.46–2.32 (m, 2H), 0.66 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 177.0 (C_q), 153.4 (C_q), 143.0 (CH), 139.1 (C_q), 138.7 (C_q), 128.4 (CH), 127.2 (CH), 126.9 (CH), 122.5 (CH), 113.9 (CH), 57.1 (C_q), 31.2 (CH_2), 25.9 (CH_3), 9.0 (CH_3). IR (NaCl): 2968, 1715, 1597, 1446, 1342, 1309, 1078, 1039, 925, 794, 762 cm^{-1}. MS (EI) *m/z* (relative intensity) 252 (63) [M^+], 237 (8), 224 (100), 208 (4), 195 (98), 180 (7), 167 (16), 91 (6), 40 (6). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}N_2O$+Na^+ 275.1155, found 275.1159.

References:

[1] Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277–4280.

[2] Hoffmann, H.; Schellenberg, P. *Chem. Ber.* **1966**, *99*, 1134–1142.

[3] (a) Stewart, A. P.; Trippett, S. J. *J. Chem. Soc. C* **1970**, *9*, 1518–1523. (b) Li, G.-Y. *US Patent*, No. US 6,291,722 B1, **2001**.

[3] Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Zeitschrift für Naturforschung B* **1994**, 801–811.

[5] Barluenga, J; Fañanas, F. J.; Sanz, R.; Fernández, Y. *Chem. Eur. J.* **2002**, *8*, 2034–2046.

[6] Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402–3415.

[7] Würz, S.; Lohre, C.; Fröhlich, R.; Bergander, K.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 8344–8345.

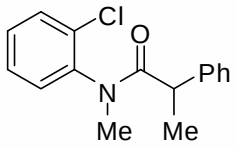
[8] Hillgren, J. M.; Marsden, S. P. *J. Org. Chem.* **2008**, *73*, 6459–6461.

[9] Shaughnessy, K. H.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1998**, *63*, 6546–6553.

[10] (a) Kündig, E. P.; Seidel, T. M.; Jia, Y.-X.; Bernardinell, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8484–8487. (b) Jia, Y.-X.; Kündig, E. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1636–1639.

[11] Trost, B. M.; Frederiksen, M. U. *Angew. Chem., Int. Ed.* **2005**, *44*, 308–310.

[12] Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2007**, *129*, 14548–14549.



1b
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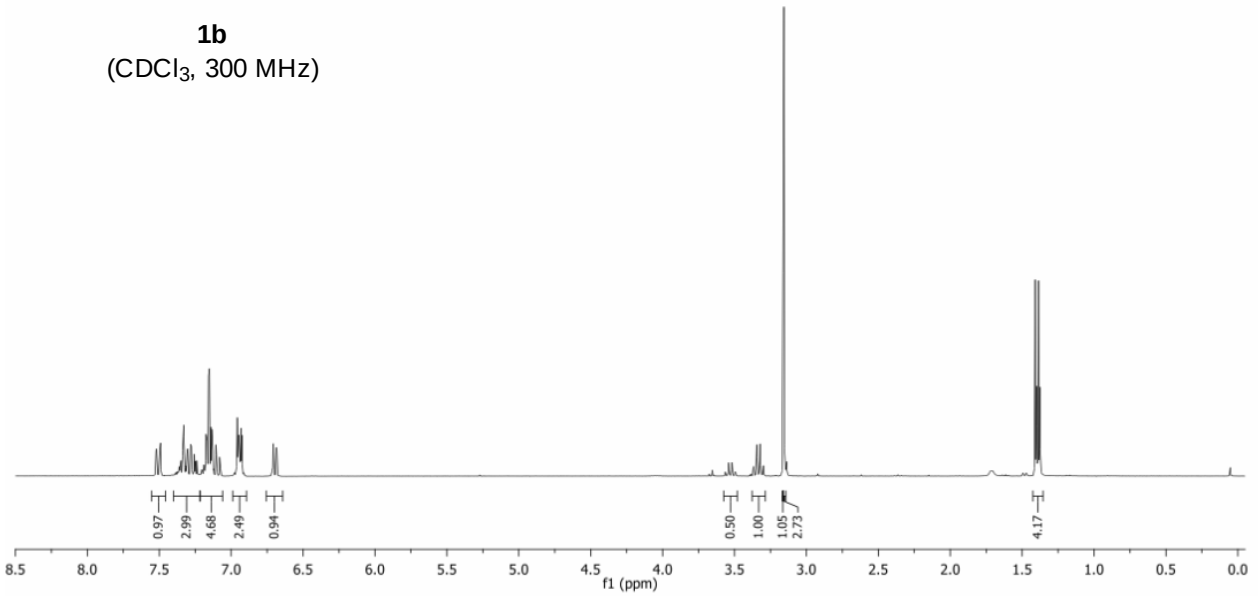

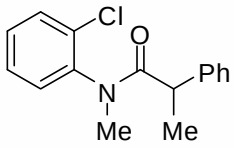

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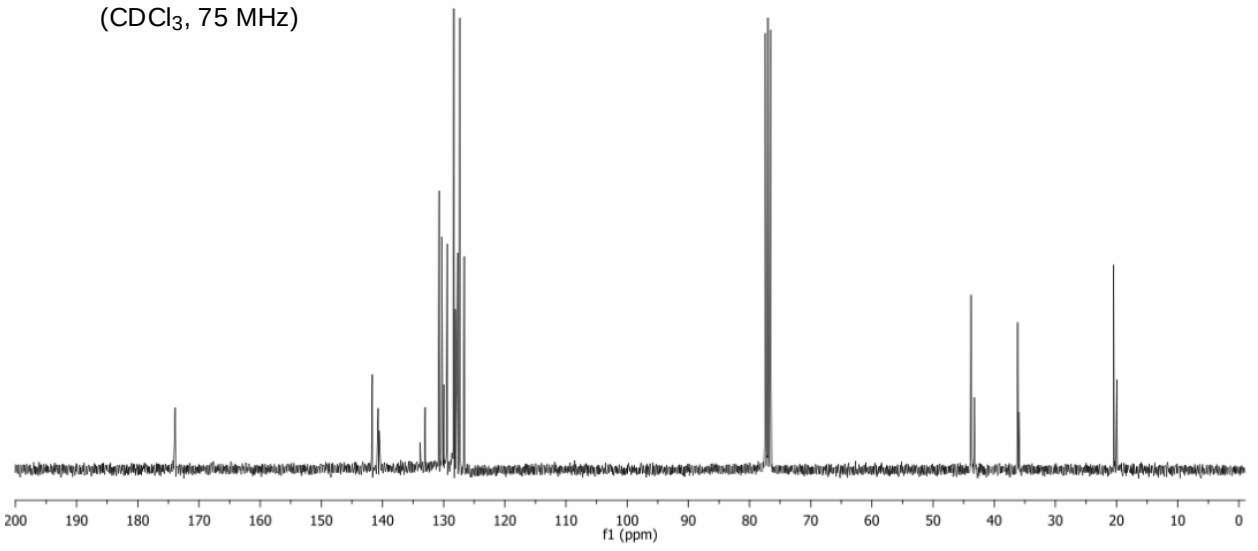

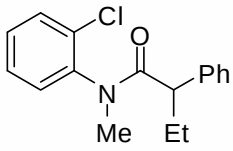

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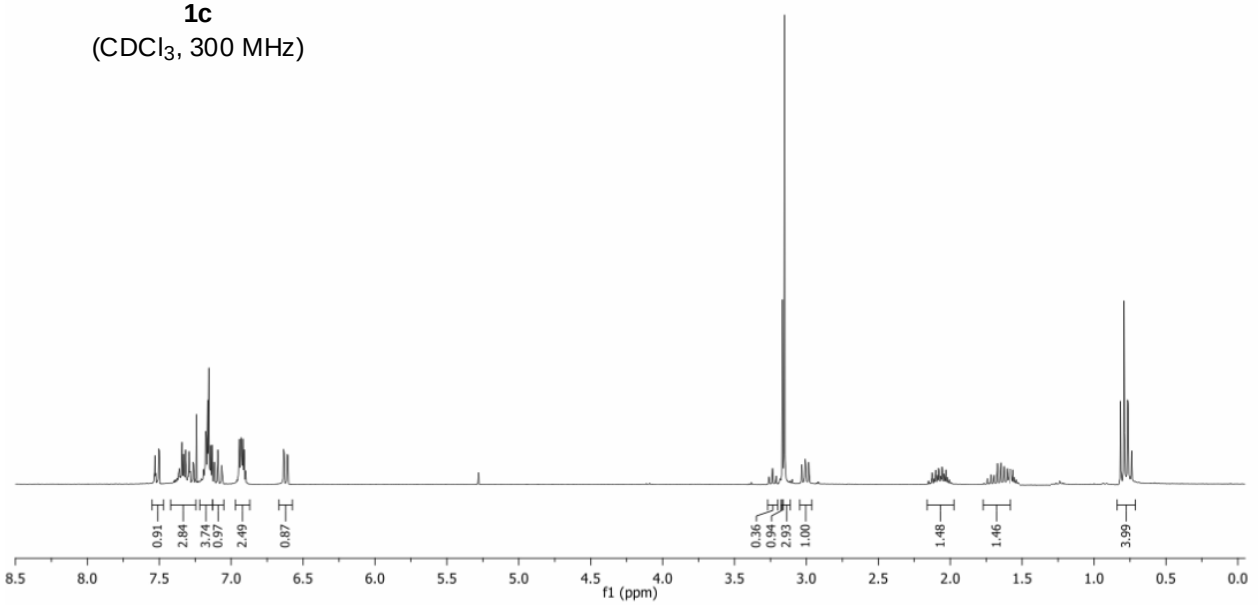

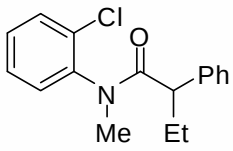

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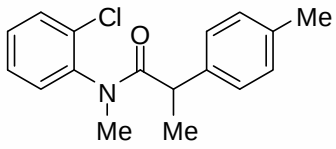

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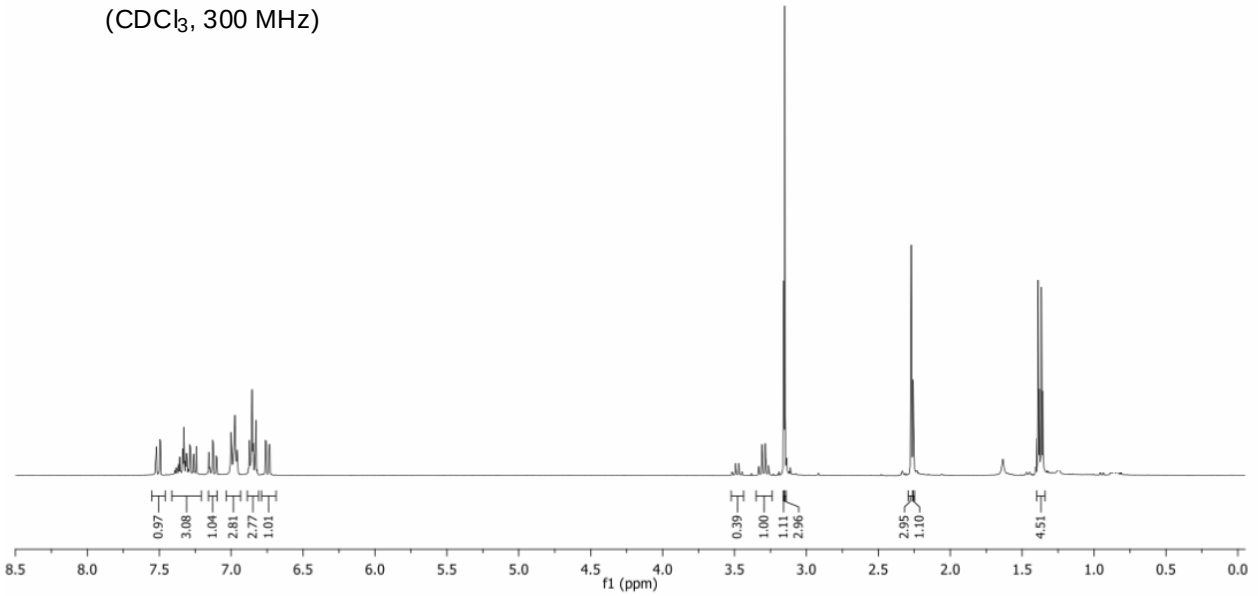

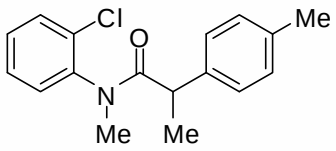

1d
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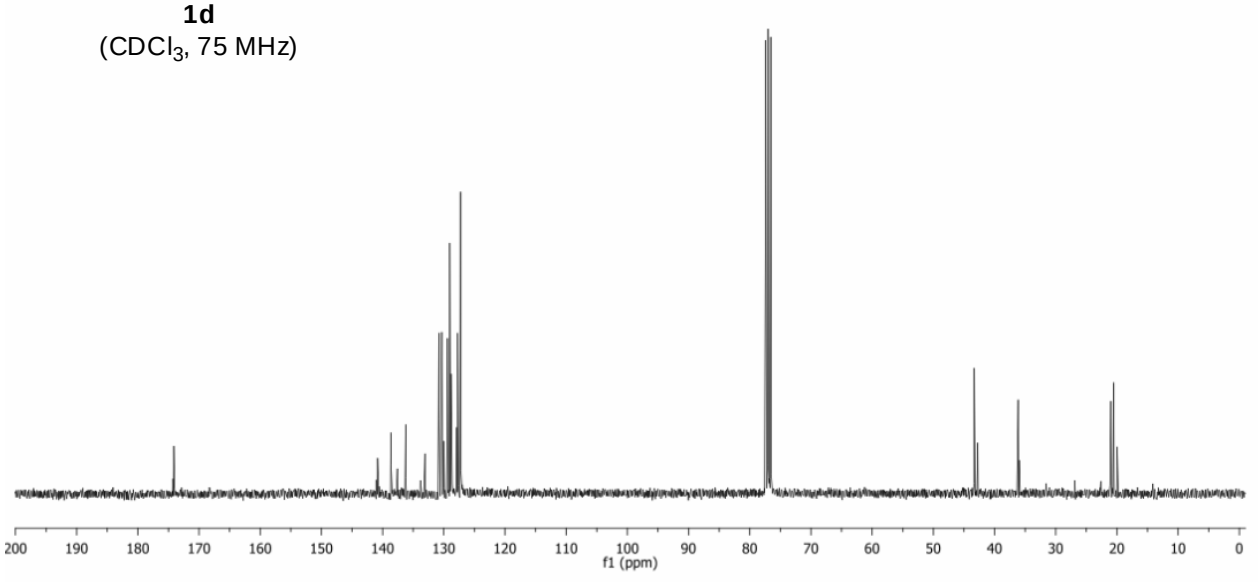

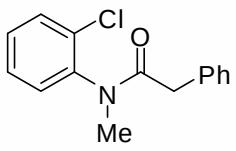

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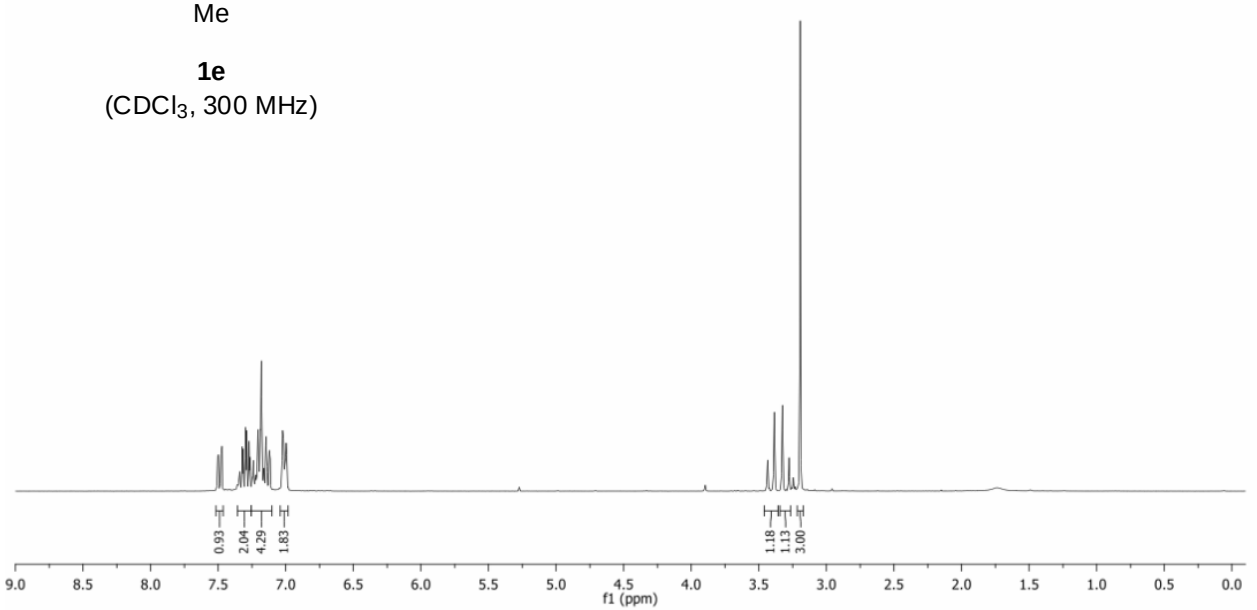

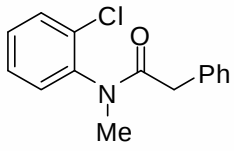

1e
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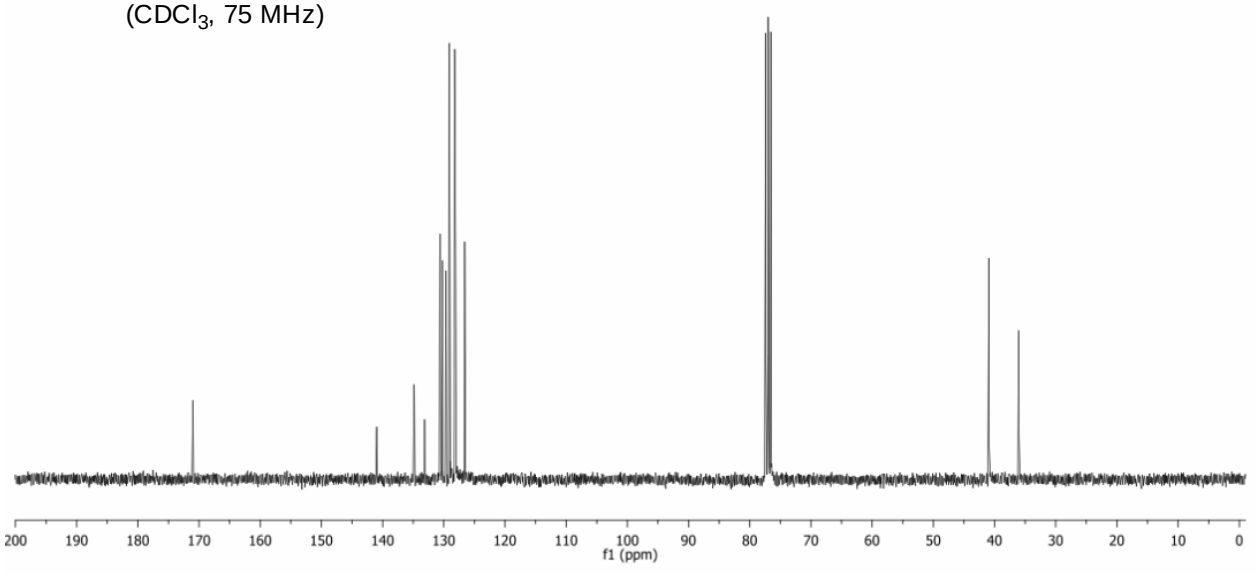
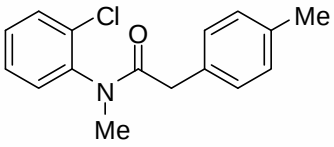
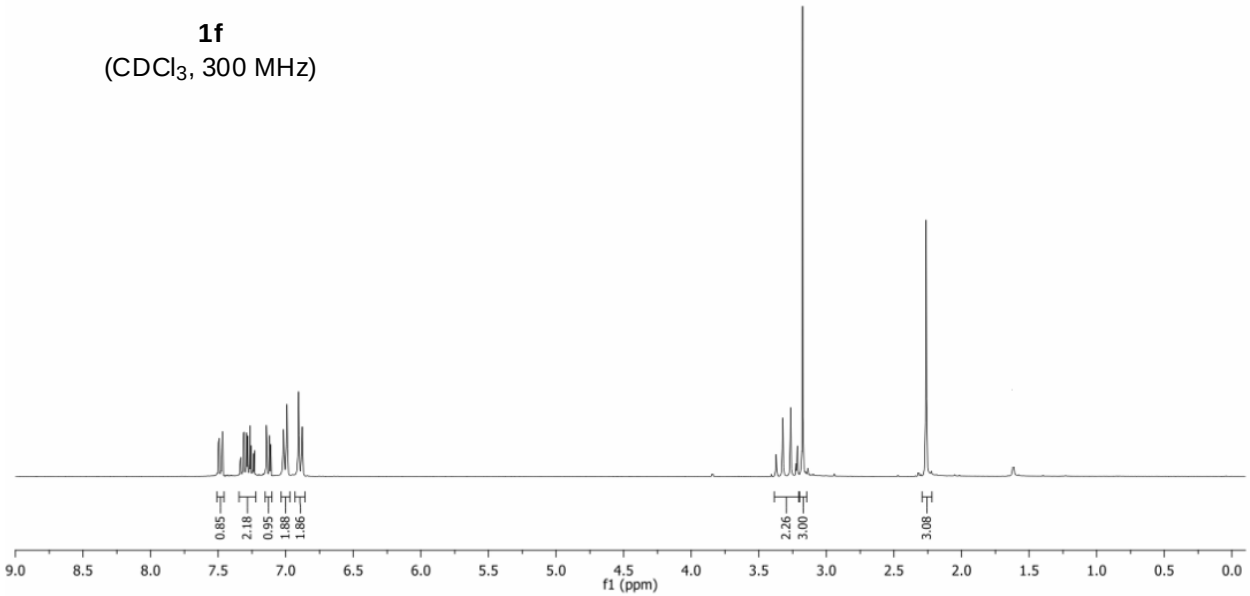
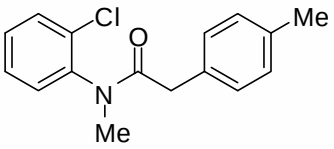




1f

($CDCl_3$, 300 MHz)





1f

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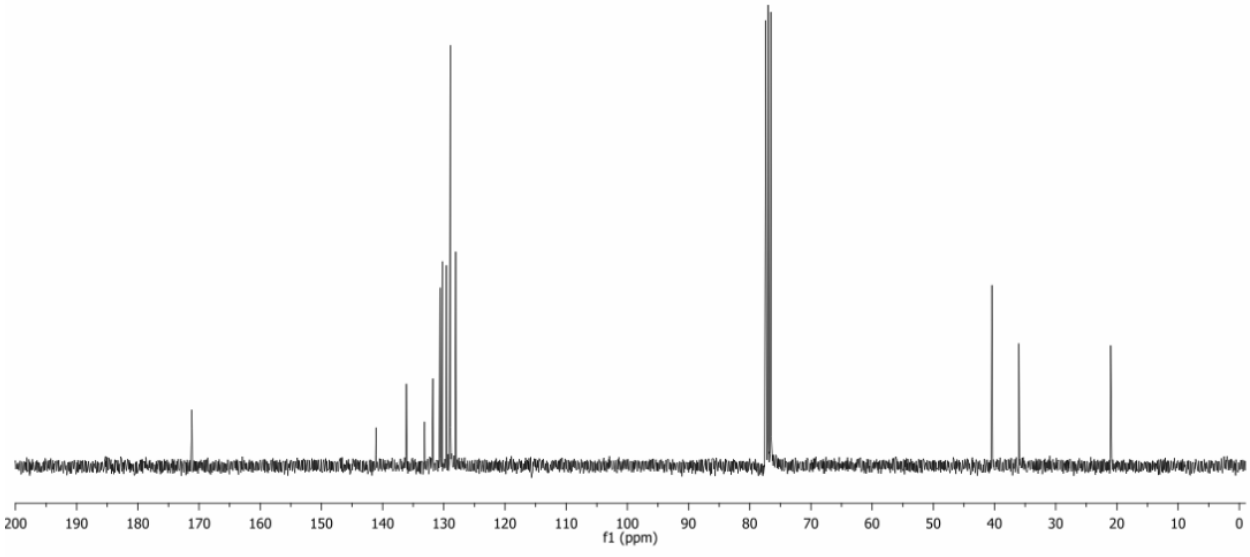

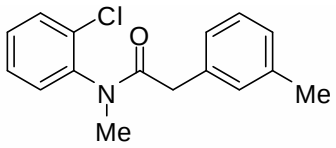

1g
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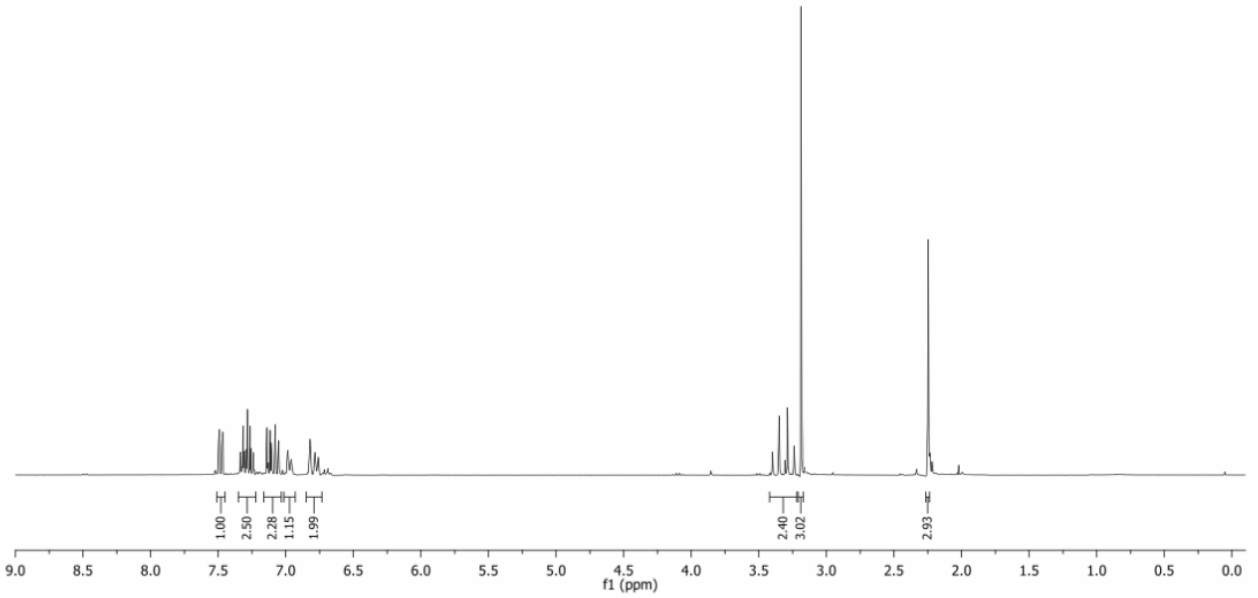

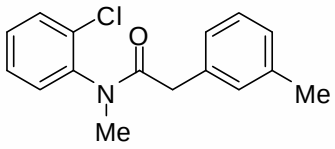

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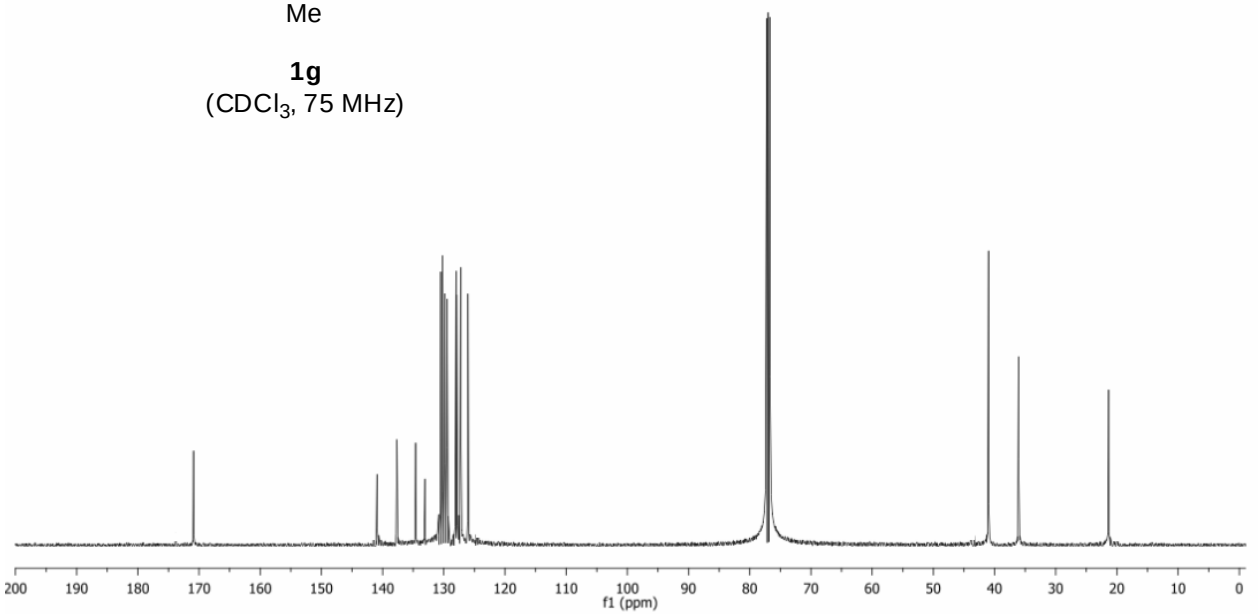

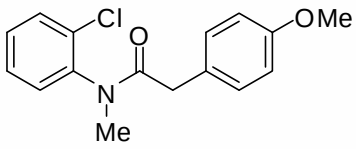

1h
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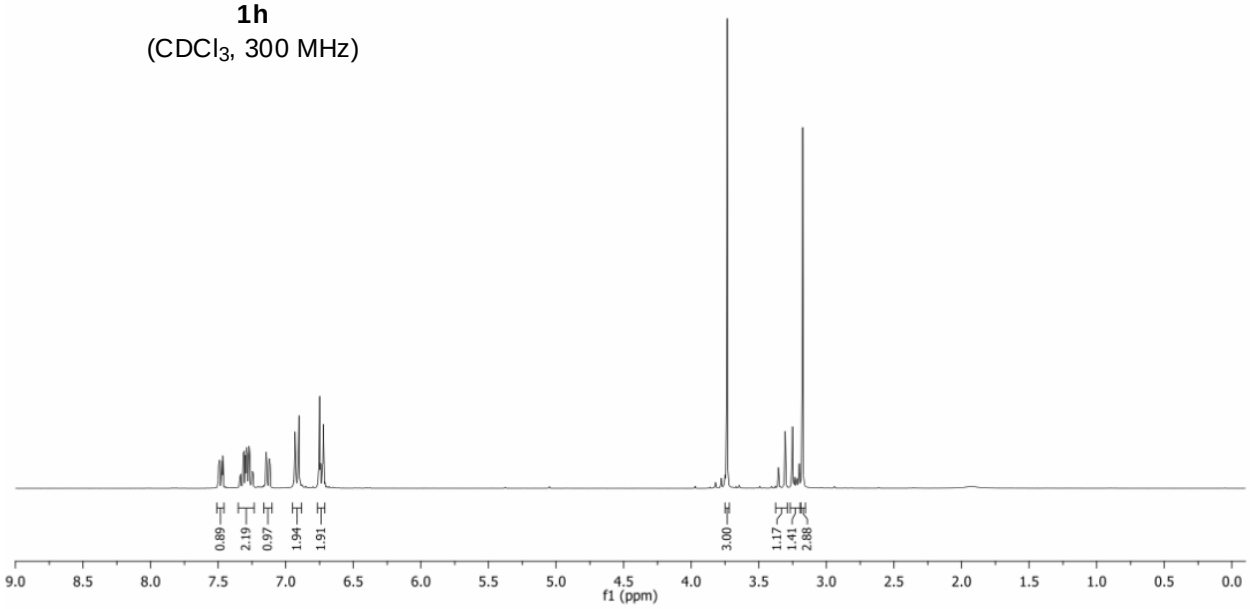

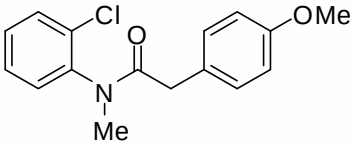

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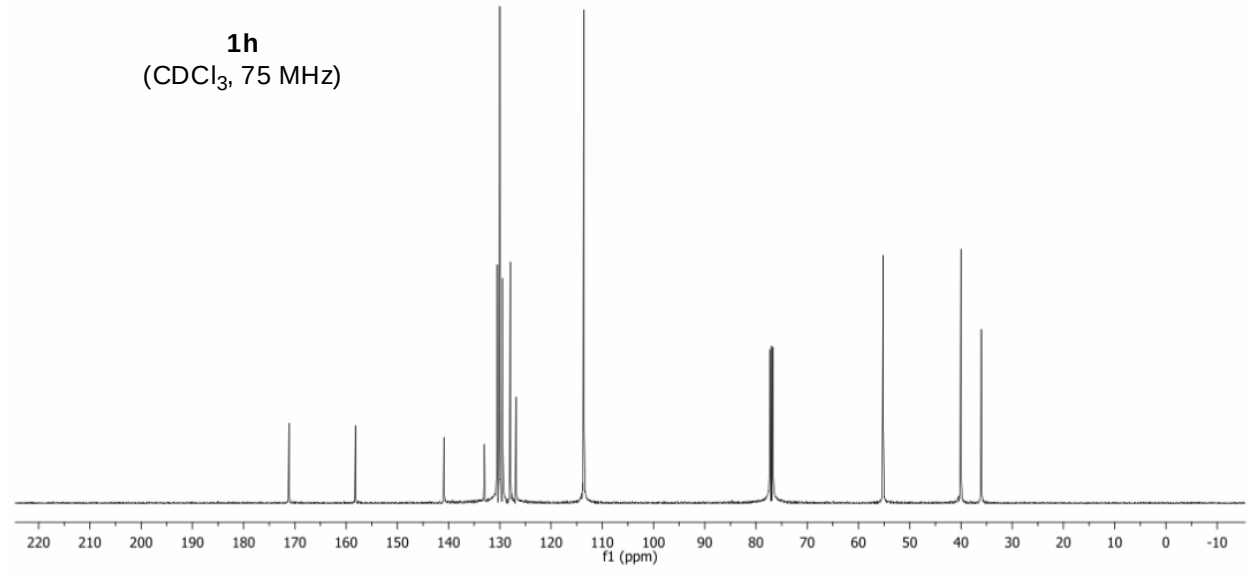

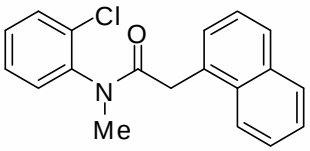

1i
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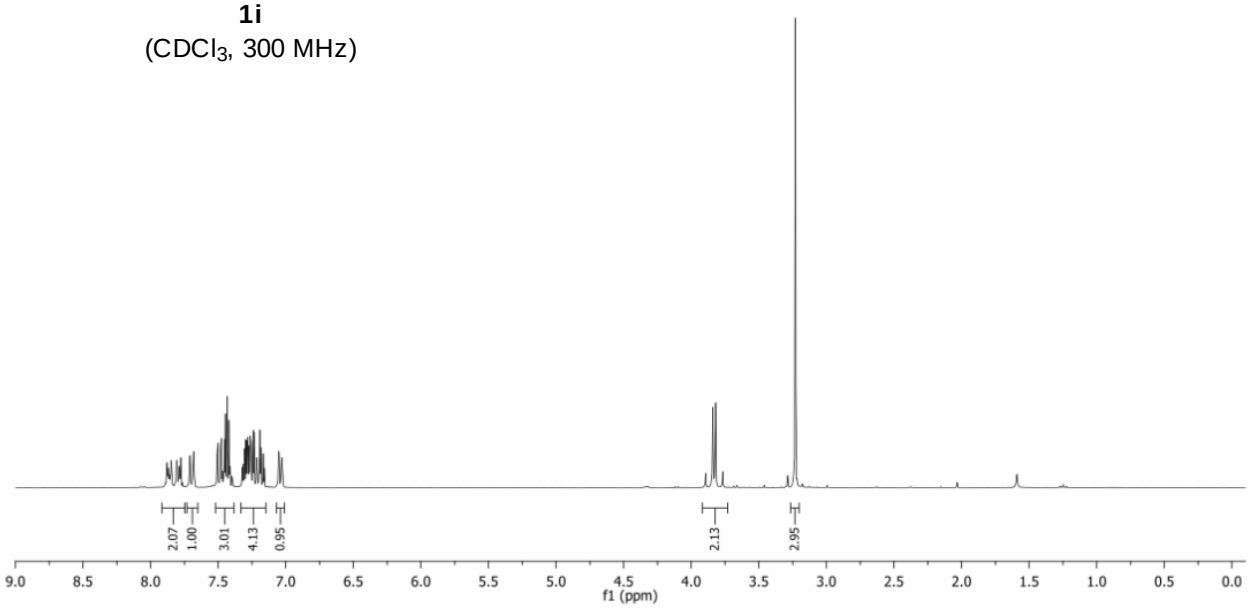

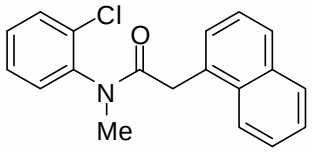

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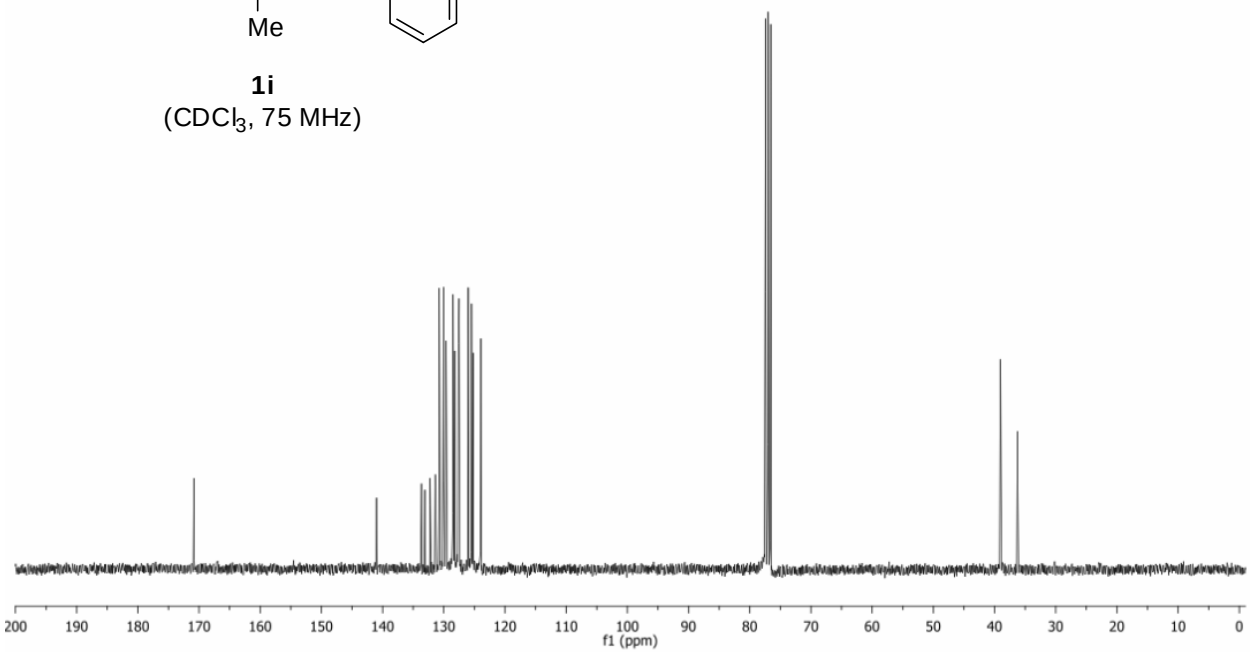
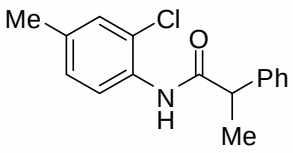
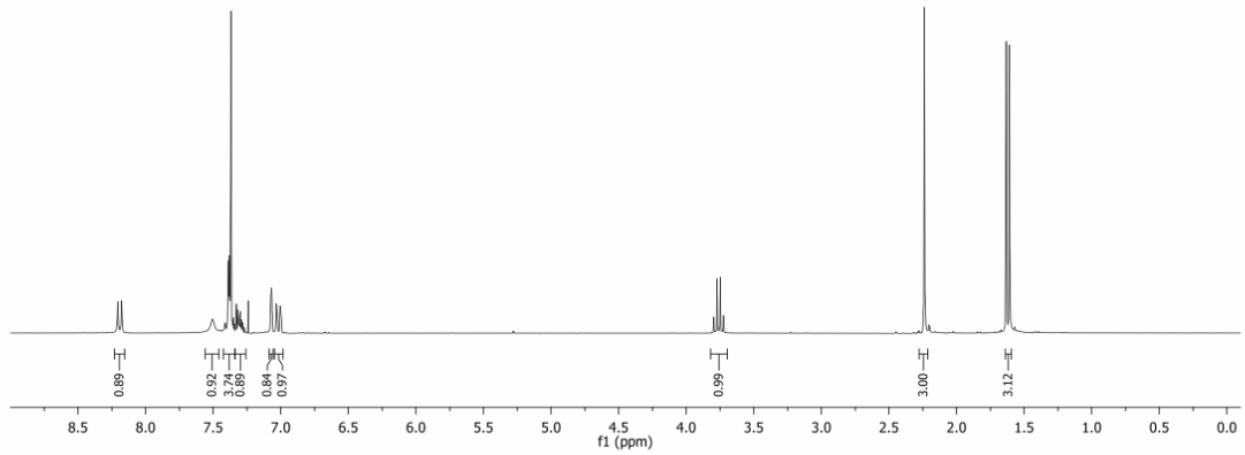
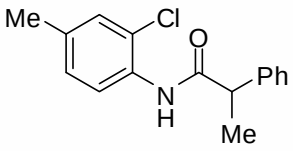


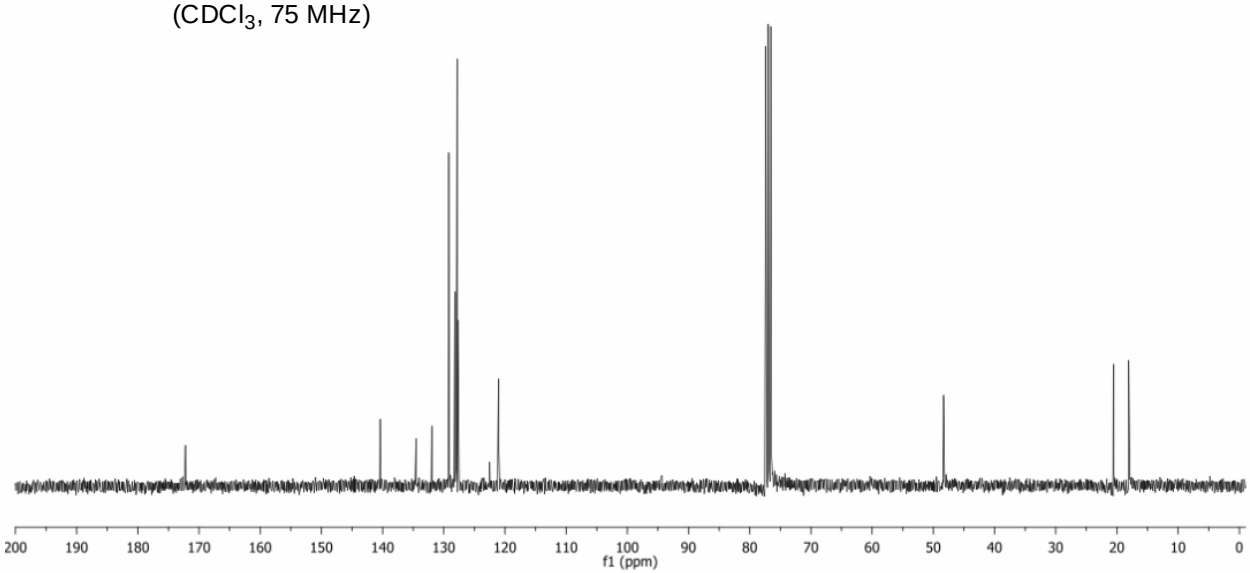


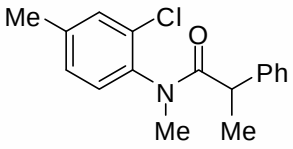
S-1a
($CDCl_3$, 300 MHz)



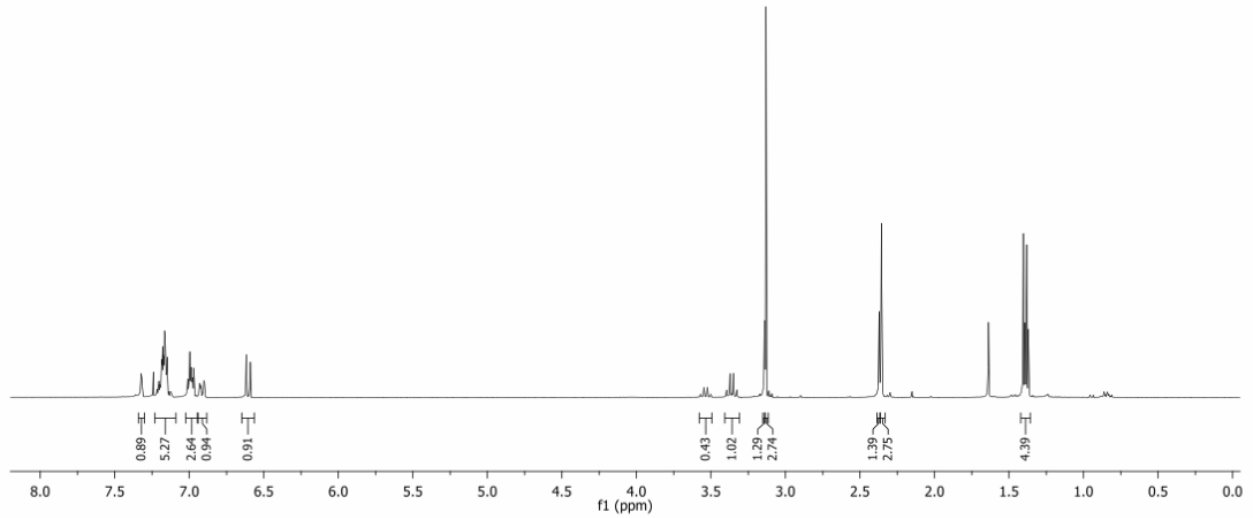


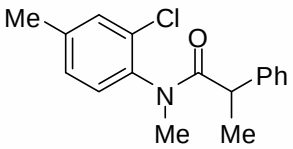
S-1a
($CDCl_3$, 75 MHz)



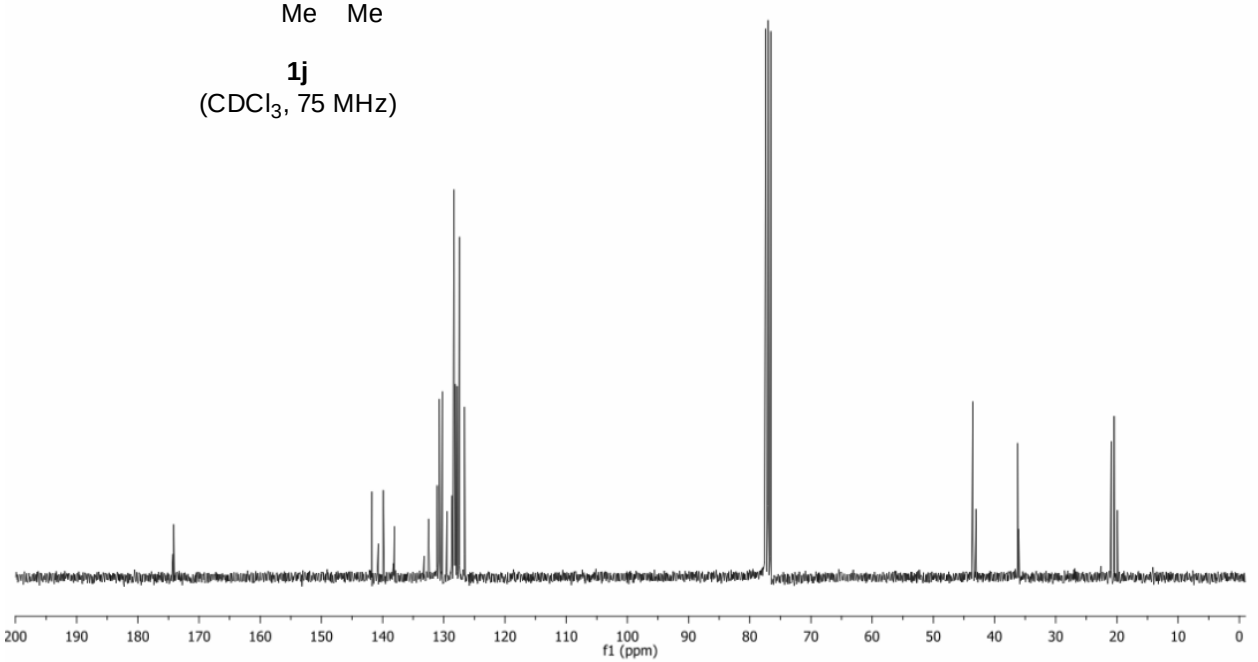


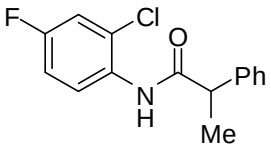
1j
($CDCl_3$, 300 MHz)



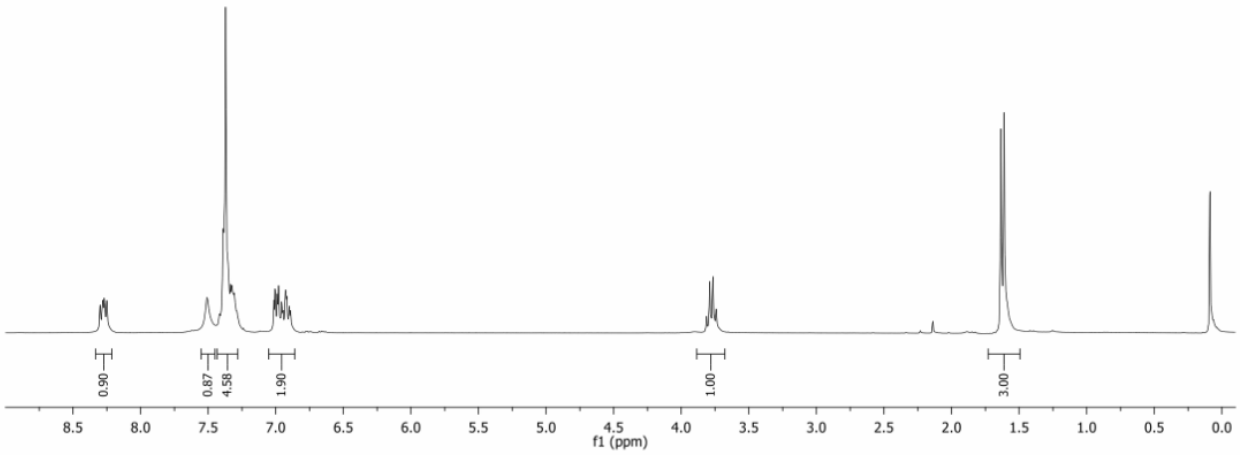


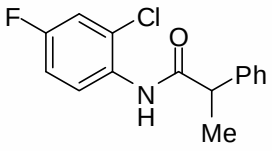
1j
($CDCl_3$, 75 MHz)



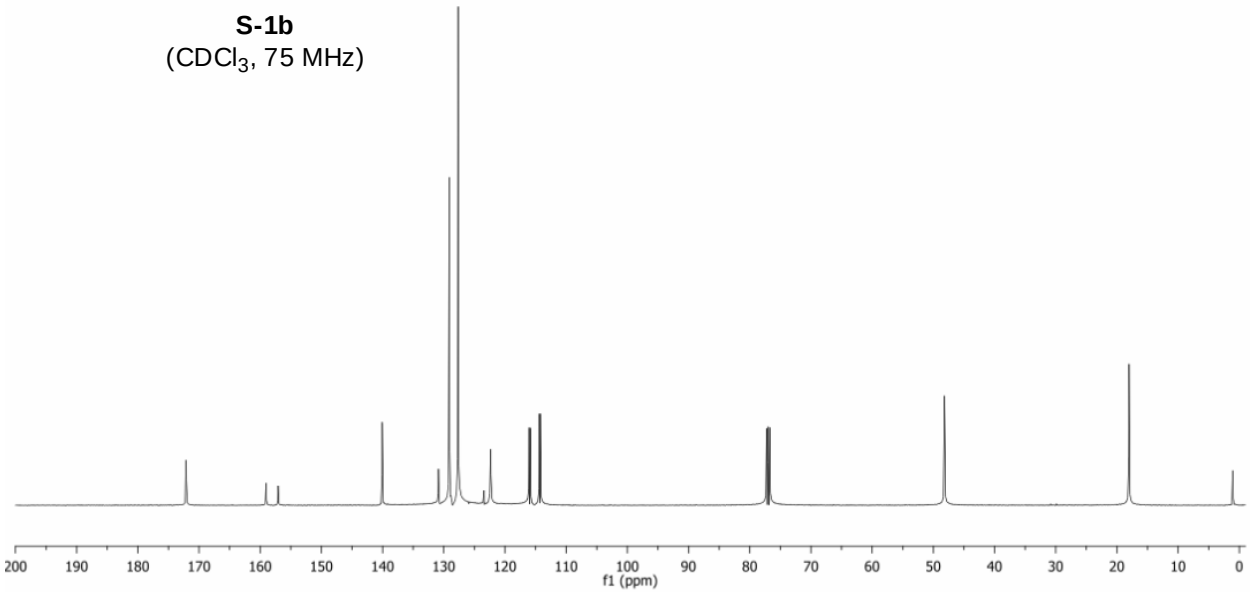


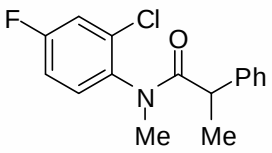
S1-b
($CDCl_3$, 300 MHz)



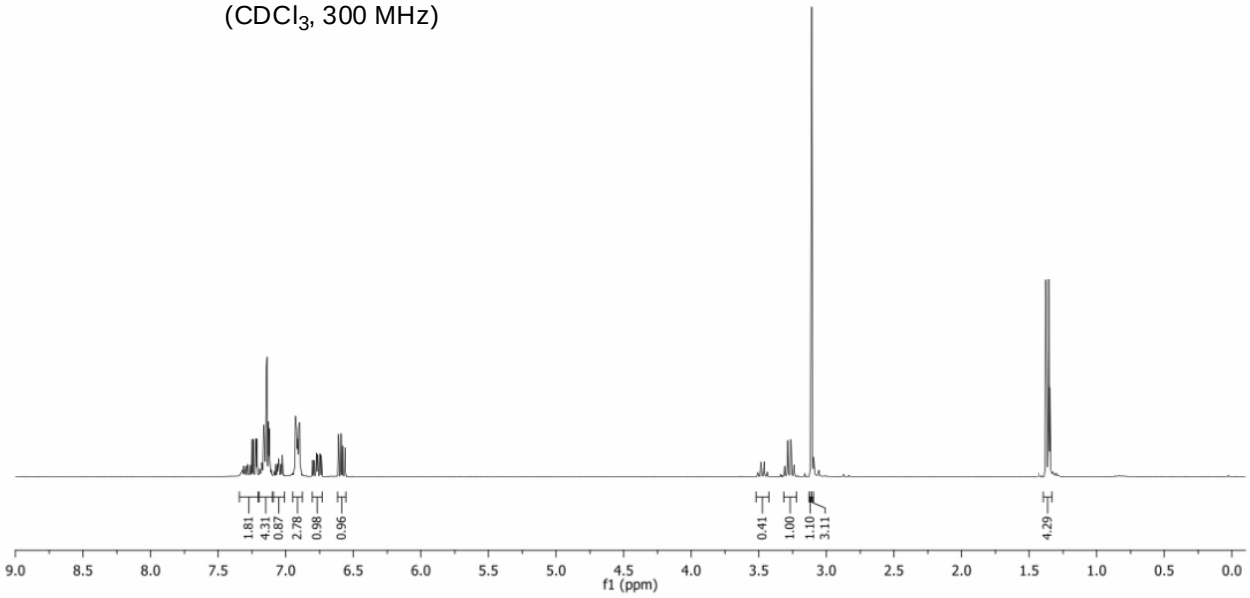


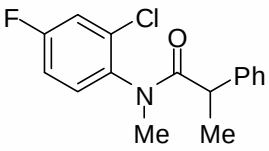
S-1b
($CDCl_3$, 75 MHz)



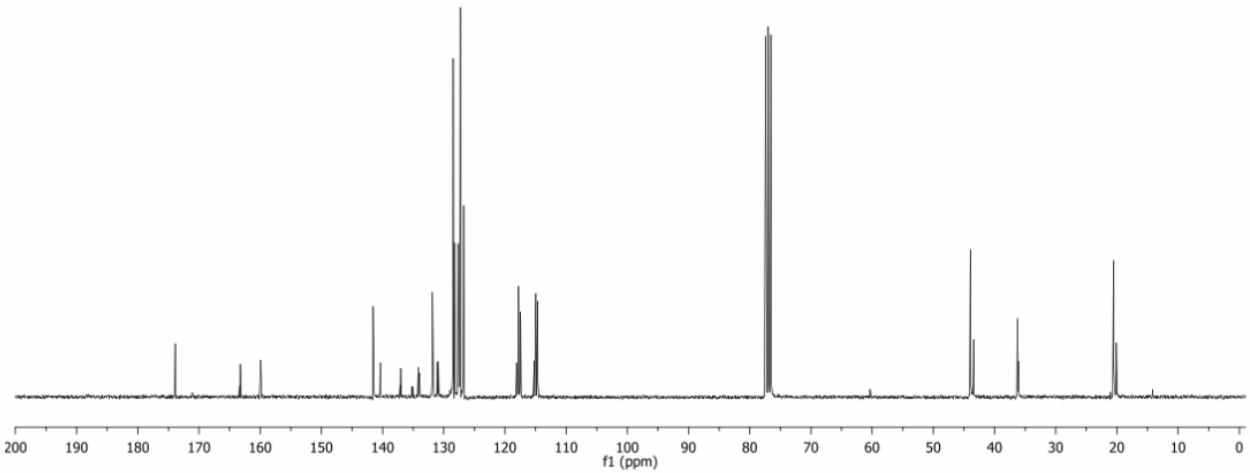


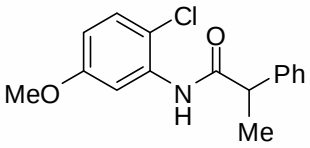
1k
($CDCl_3$, 300 MHz)



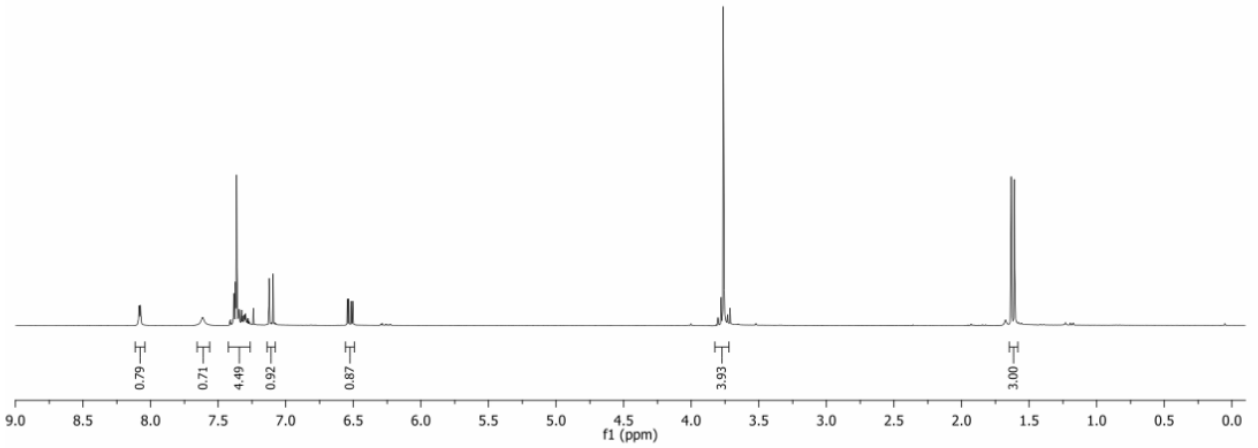


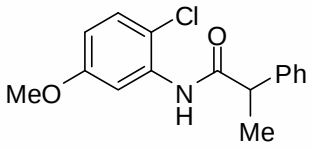
1k
($CDCl_3$, 75 MHz)



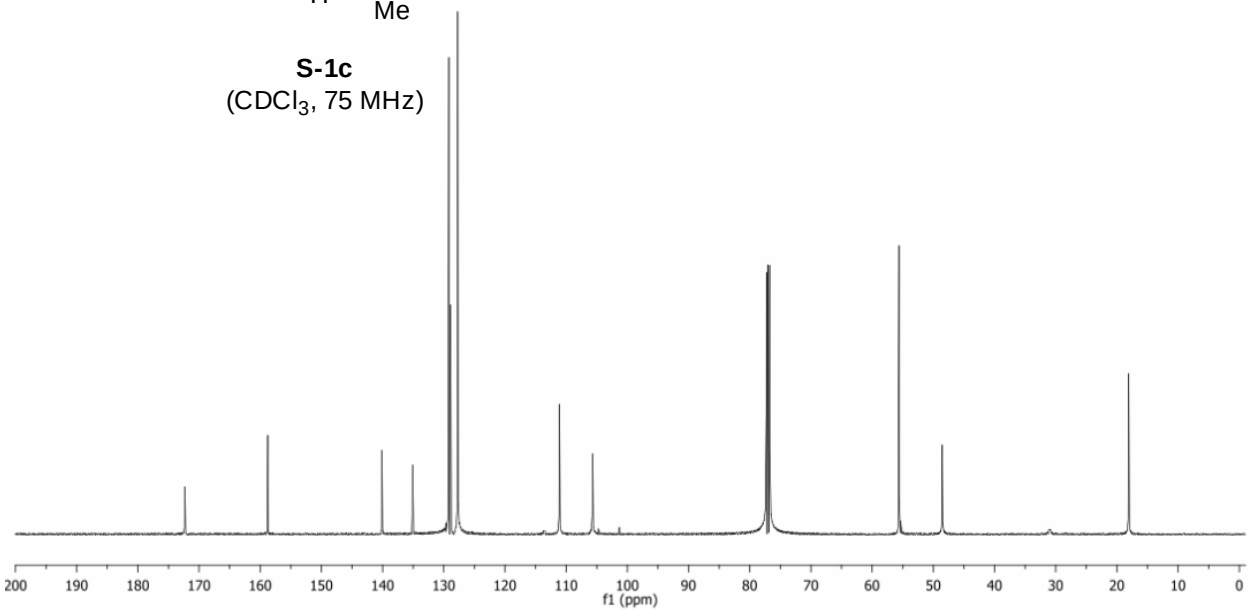


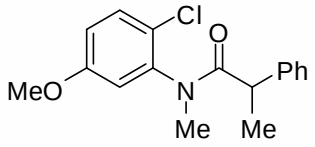
S-1c
($CDCl_3$, 300 MHz)



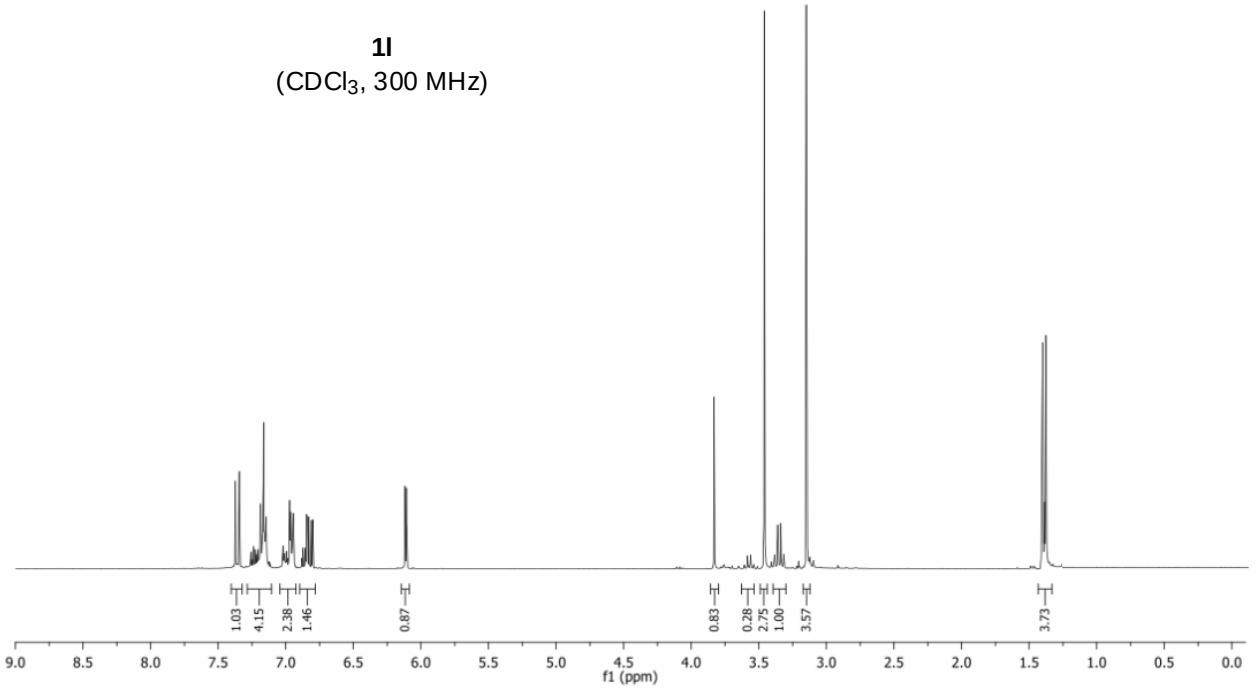


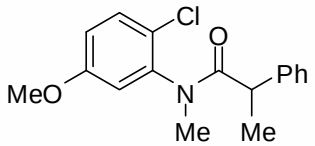
S-1c
($CDCl_3$, 75 MHz)



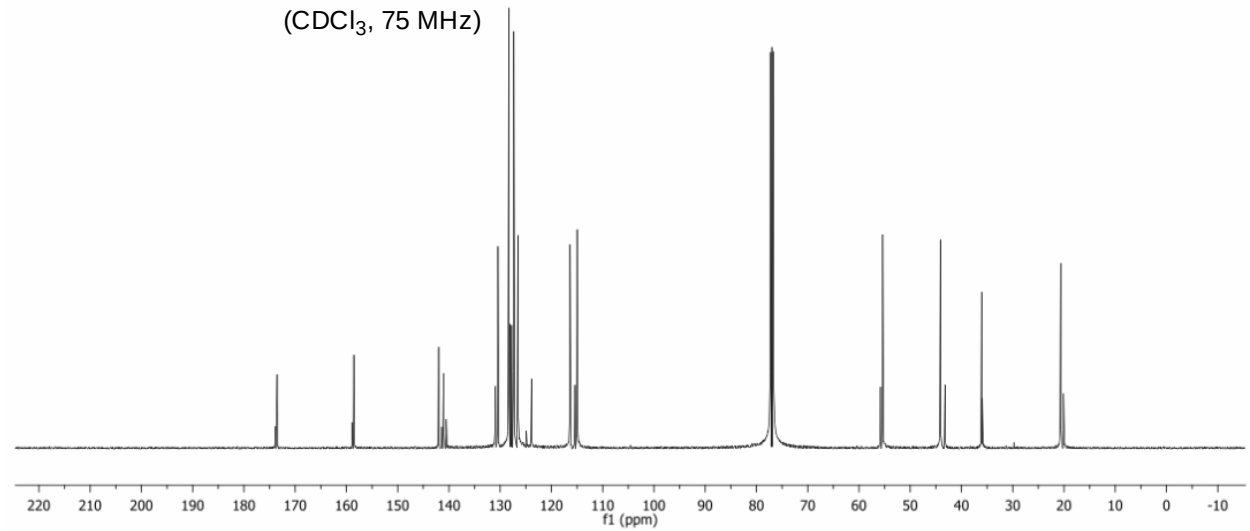


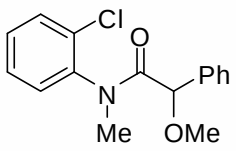
1l
($CDCl_3$, 300 MHz)



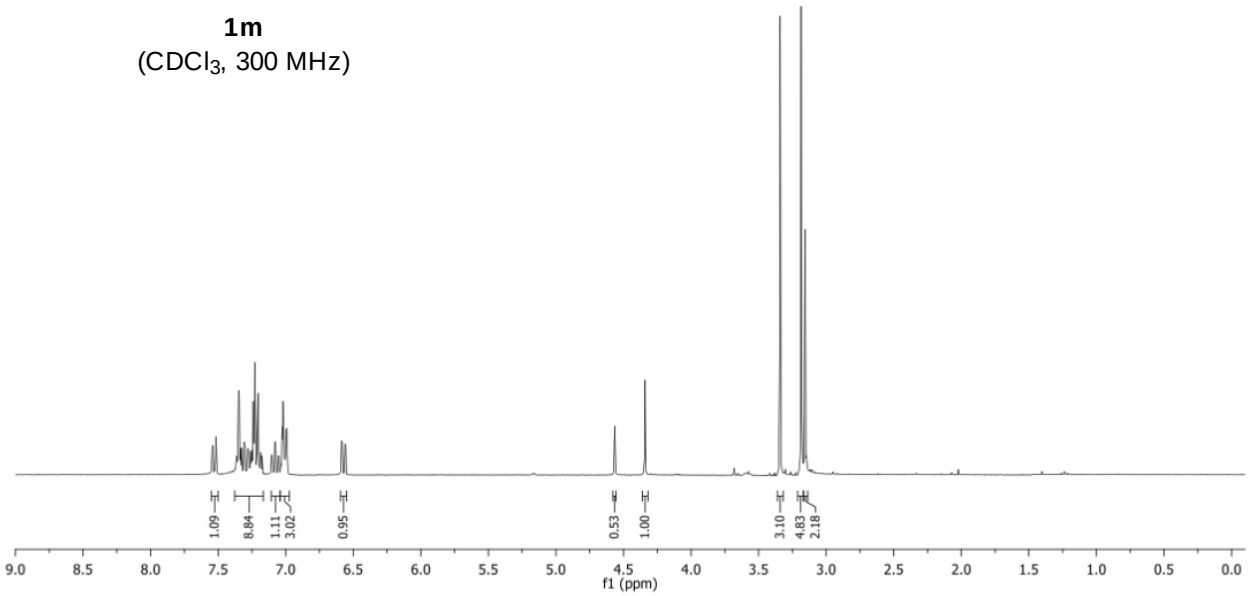


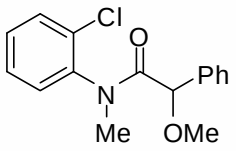
1l
($CDCl_3$, 75 MHz)



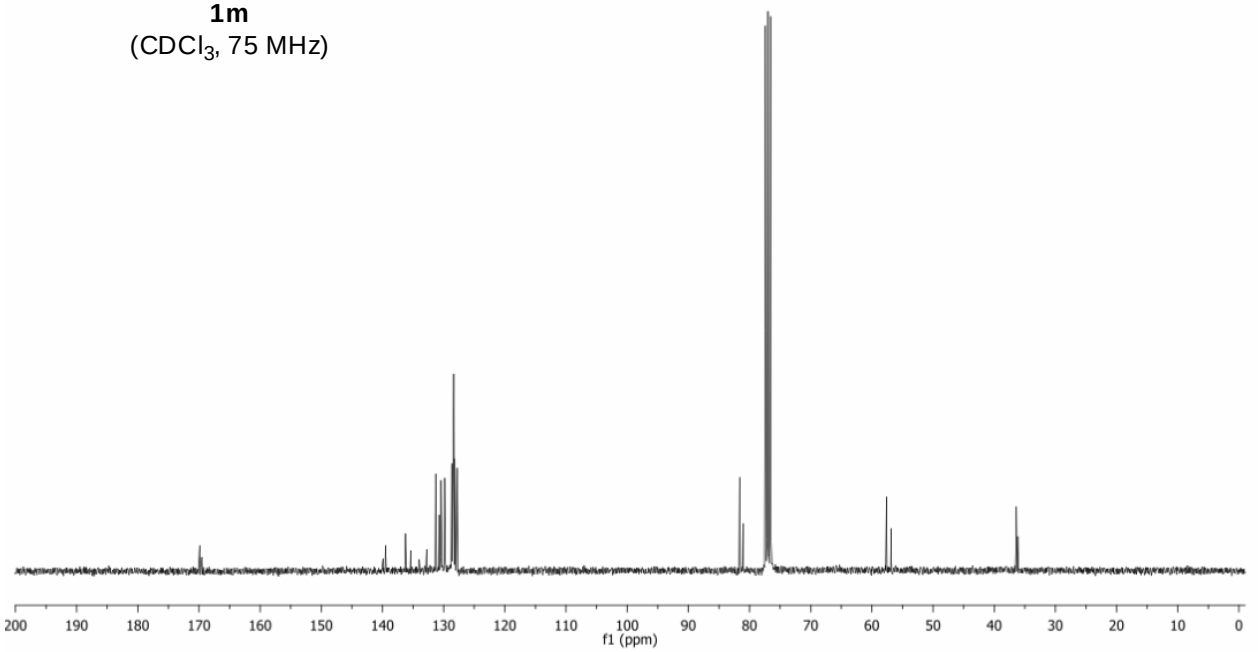


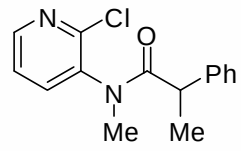
1m
($CDCl_3$, 300 MHz)



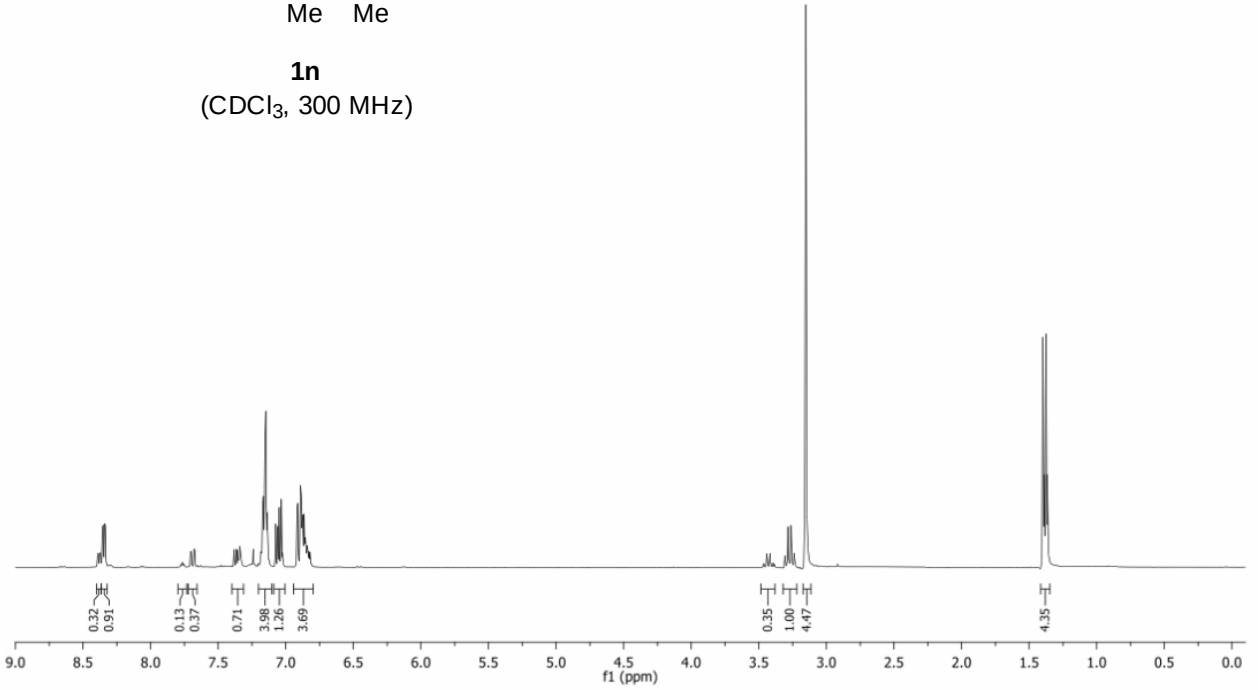


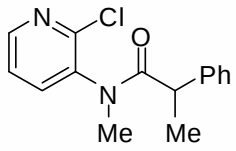
1m
($CDCl_3$, 75 MHz)



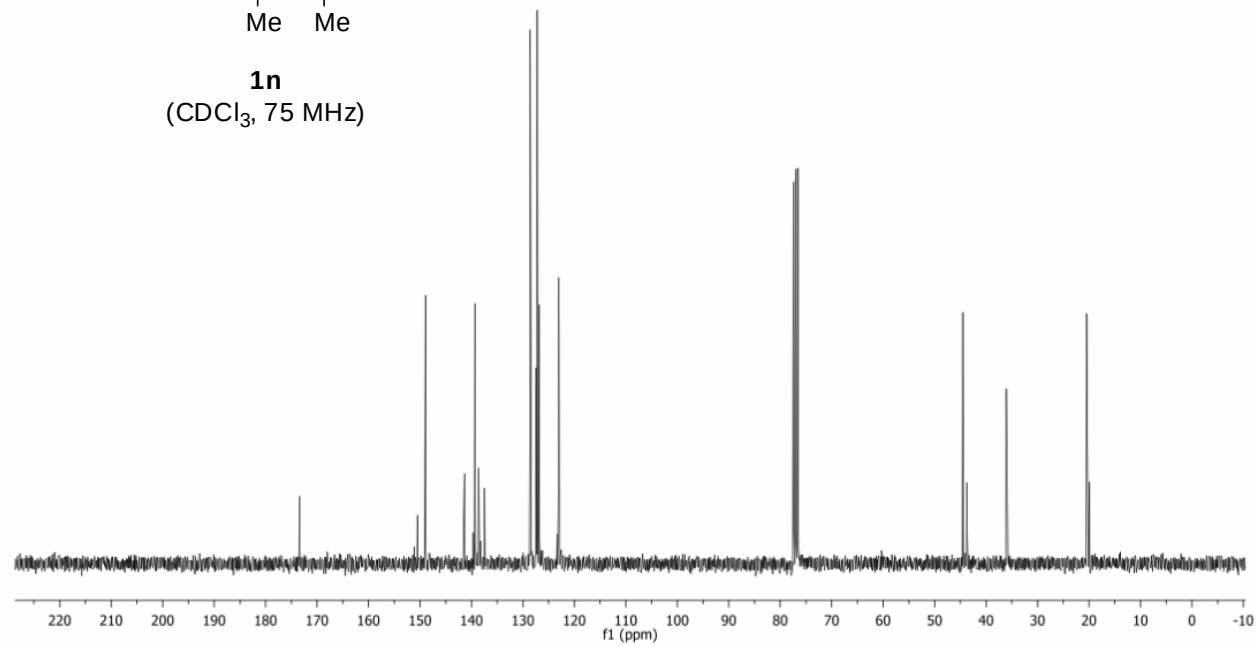


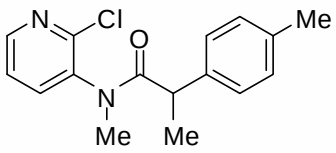
1n
($CDCl_3$, 300 MHz)



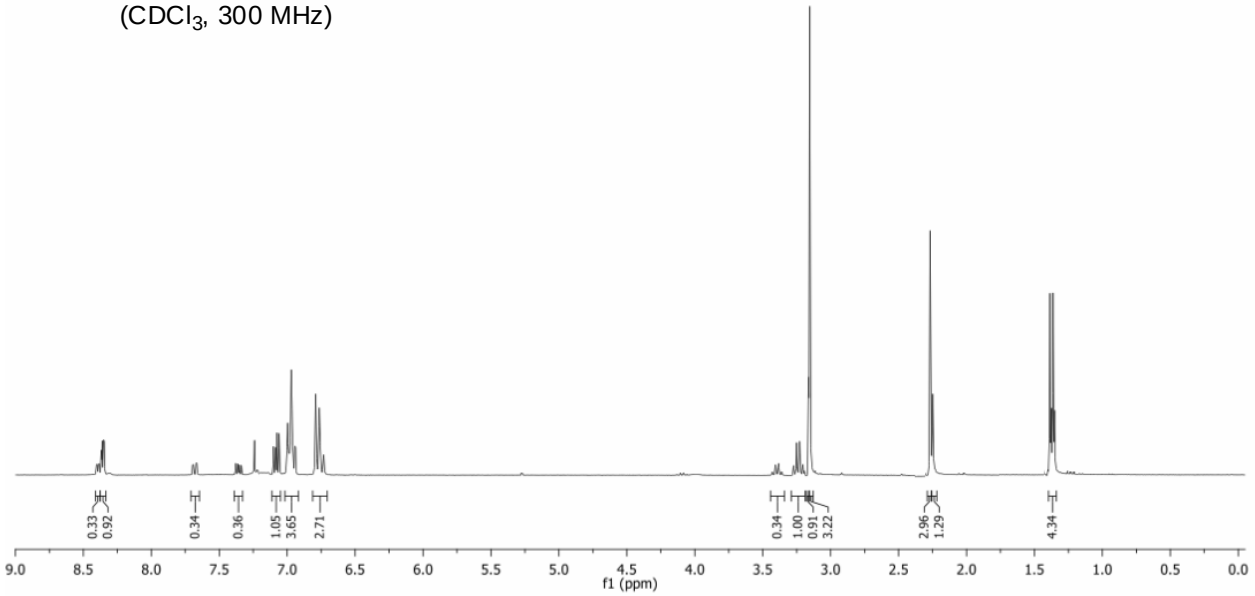


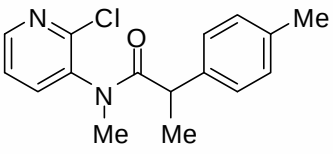
1n
($CDCl_3$, 75 MHz)



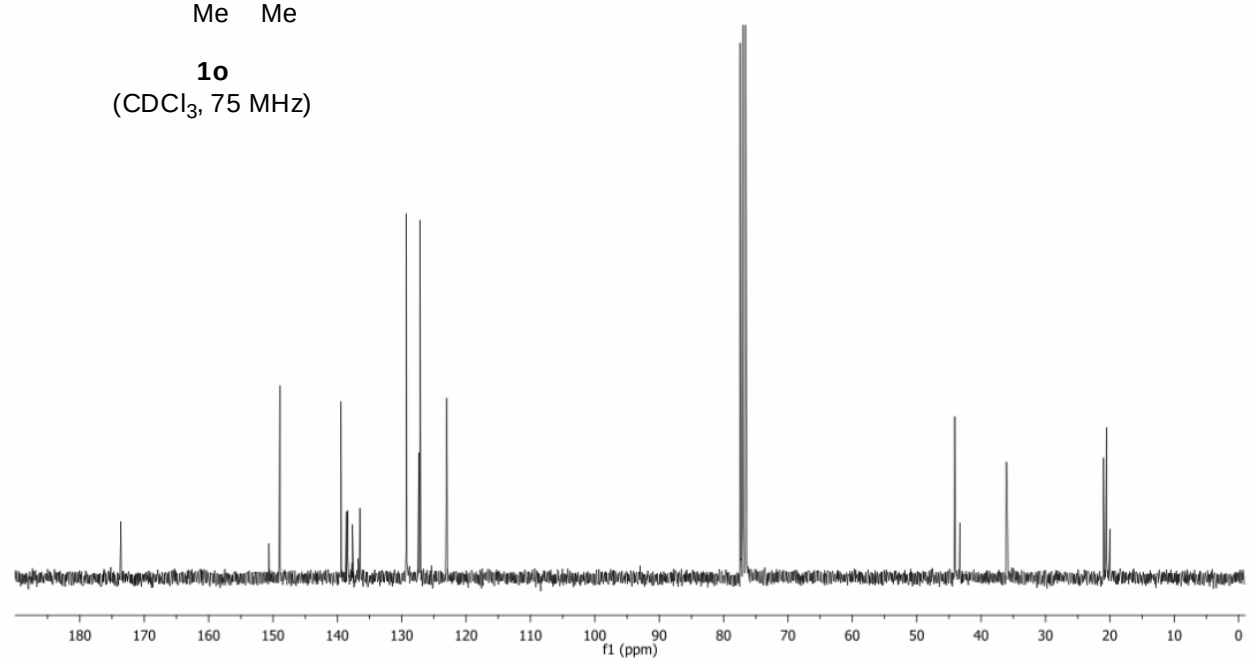


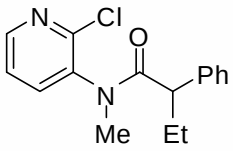
1o
($CDCl_3$, 300 MHz)



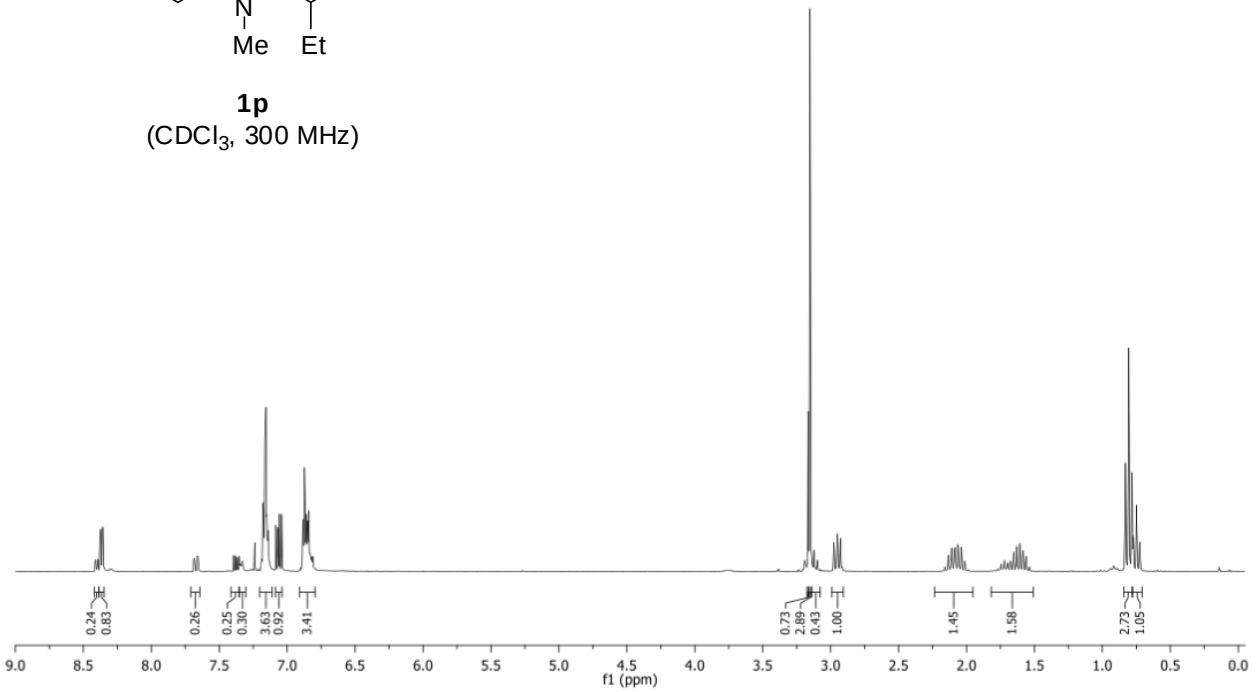


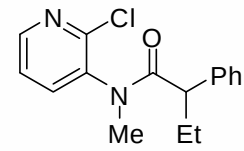
1o
($CDCl_3$, 75 MHz)



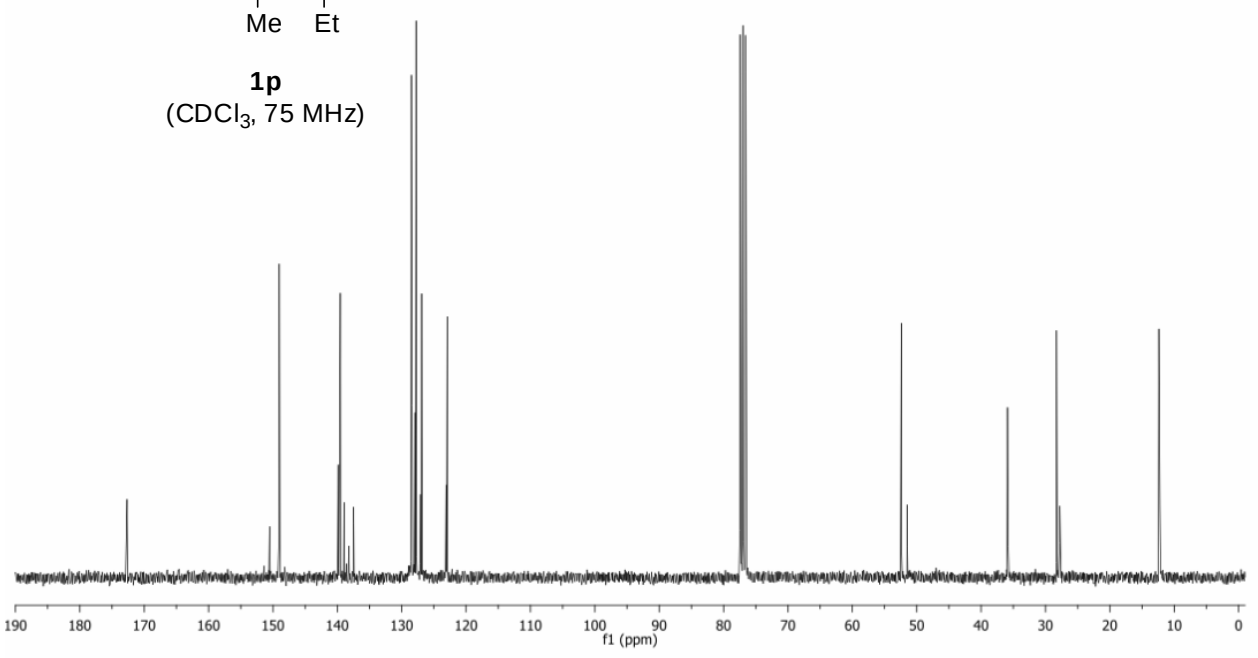


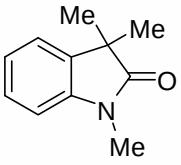
1p
($CDCl_3$, 300 MHz)



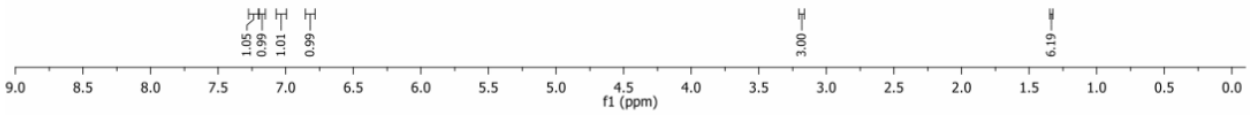


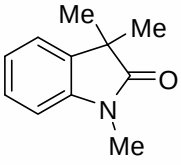
1p
($CDCl_3$, 75 MHz)



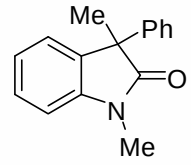


2a
($CDCl_3$, 300 MHz)

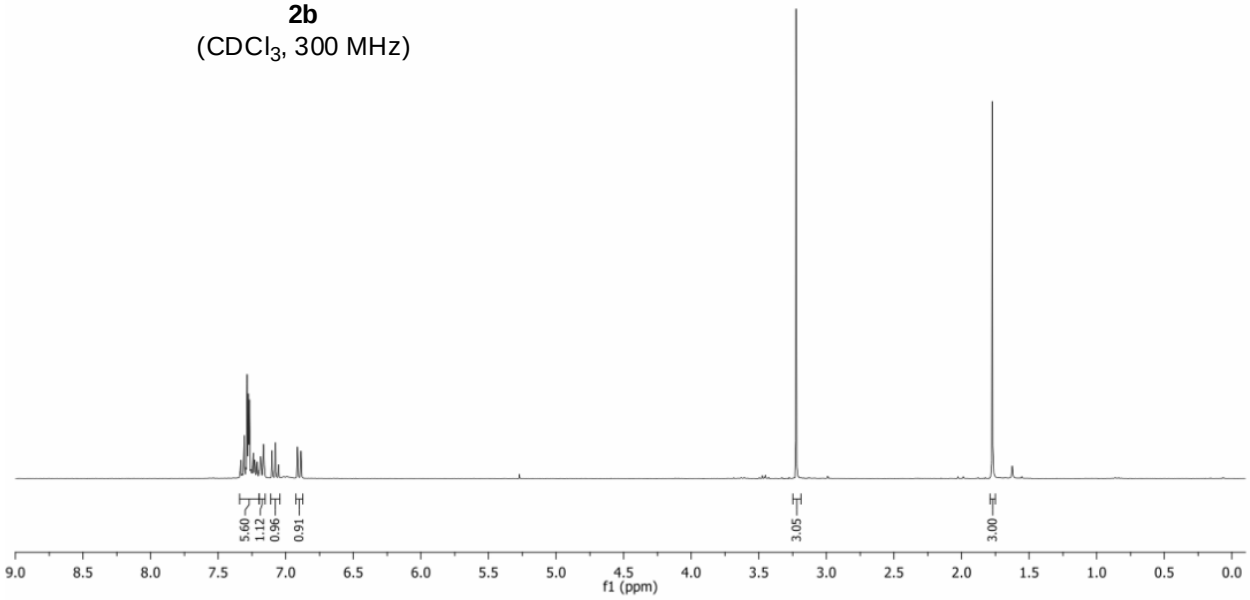


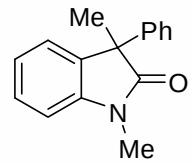


2a
($CDCl_3$, 75 MHz)

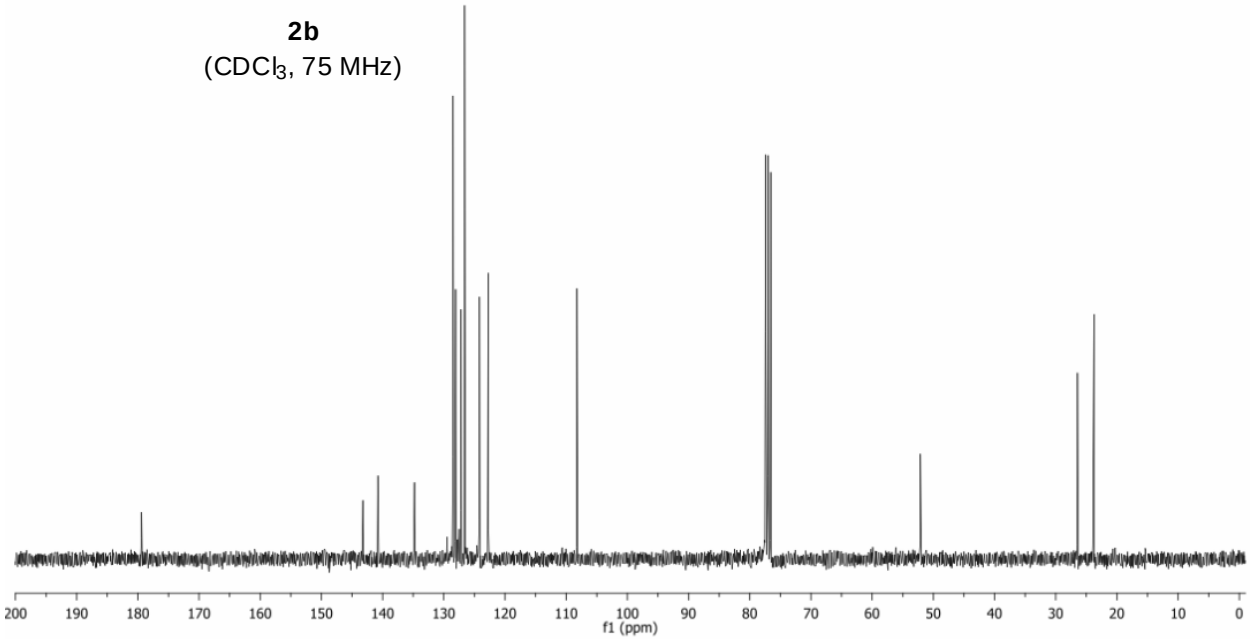


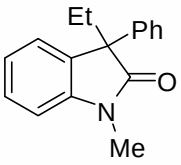
2b
($CDCl_3$, 300 MHz)



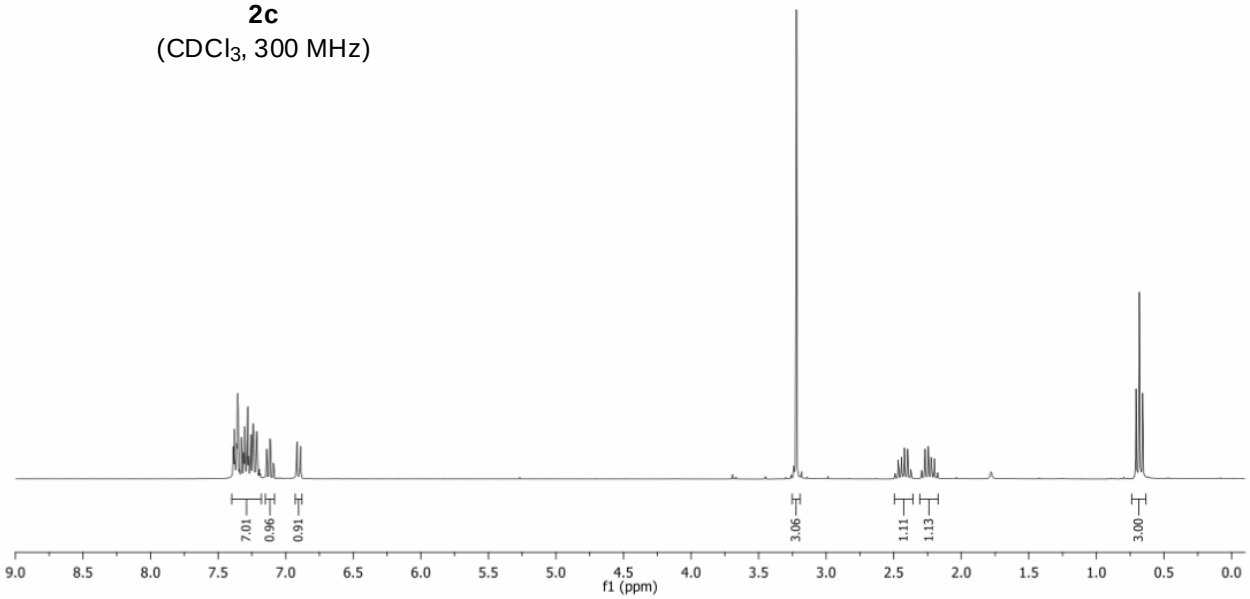


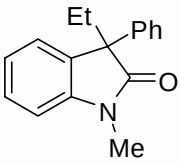
2b
($CDCl_3$, 75 MHz)



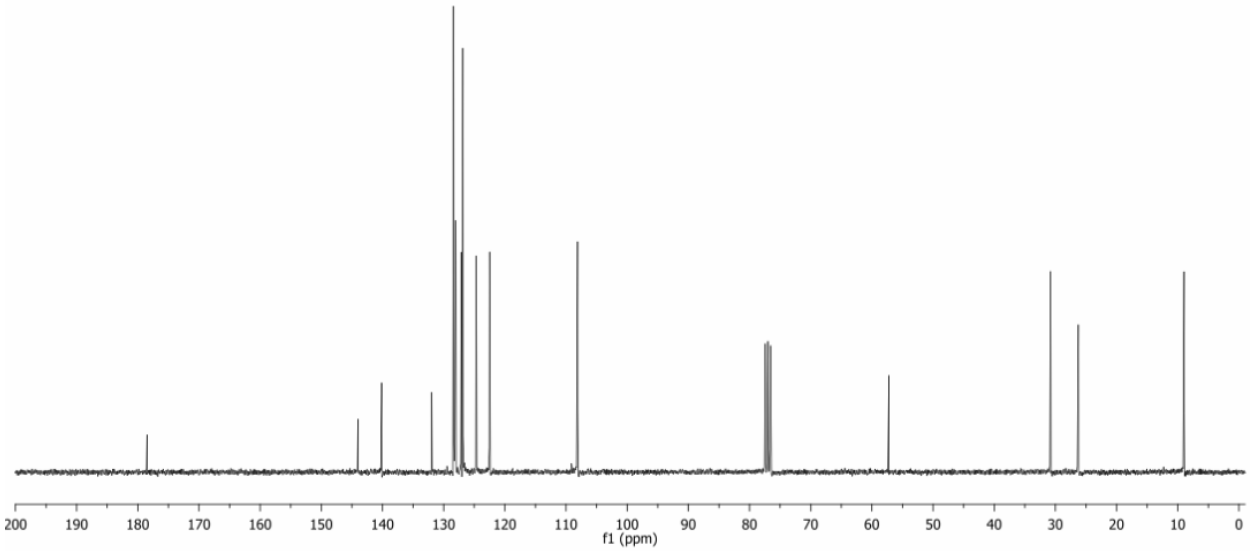


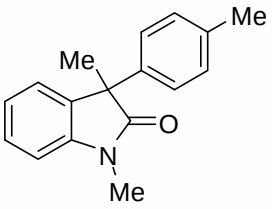
2c
($CDCl_3$, 300 MHz)



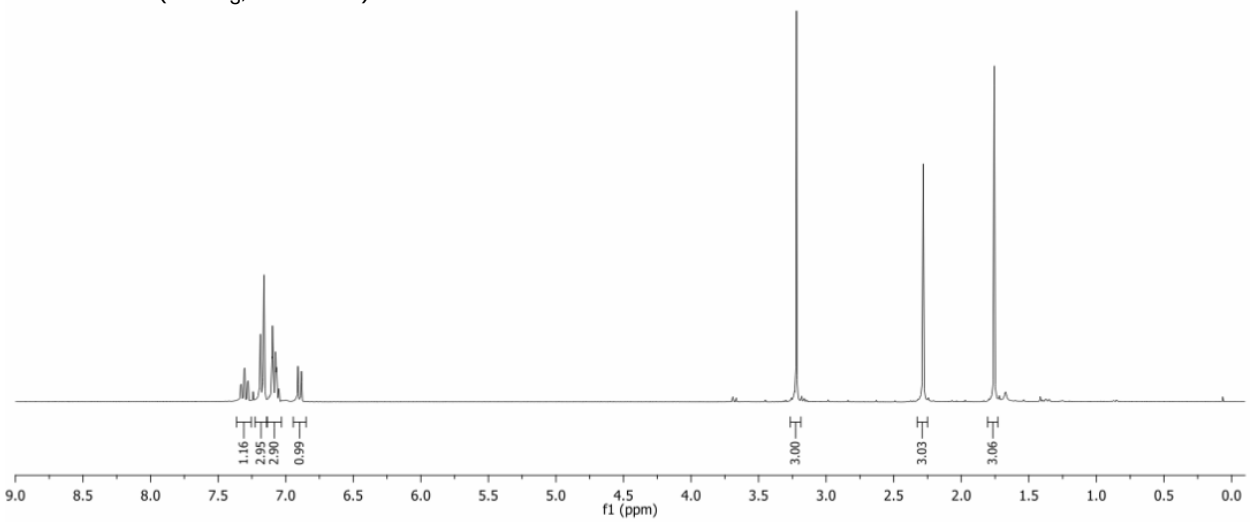


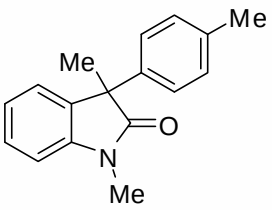
2c
($CDCl_3$, 75 MHz)



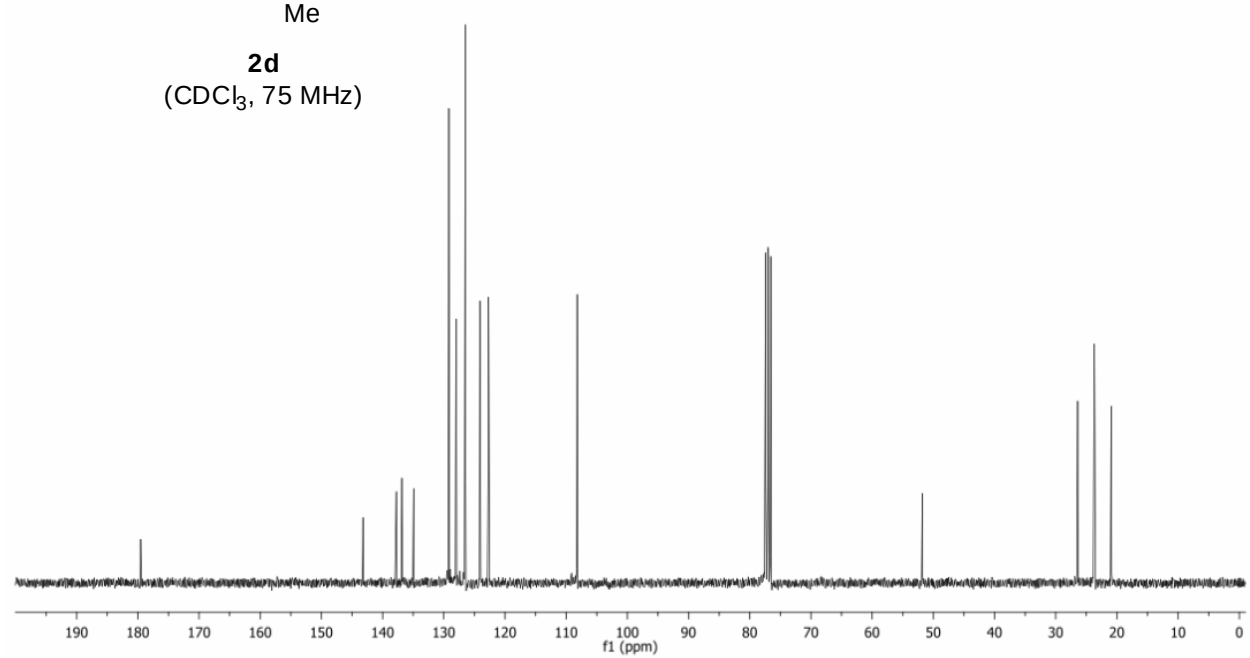


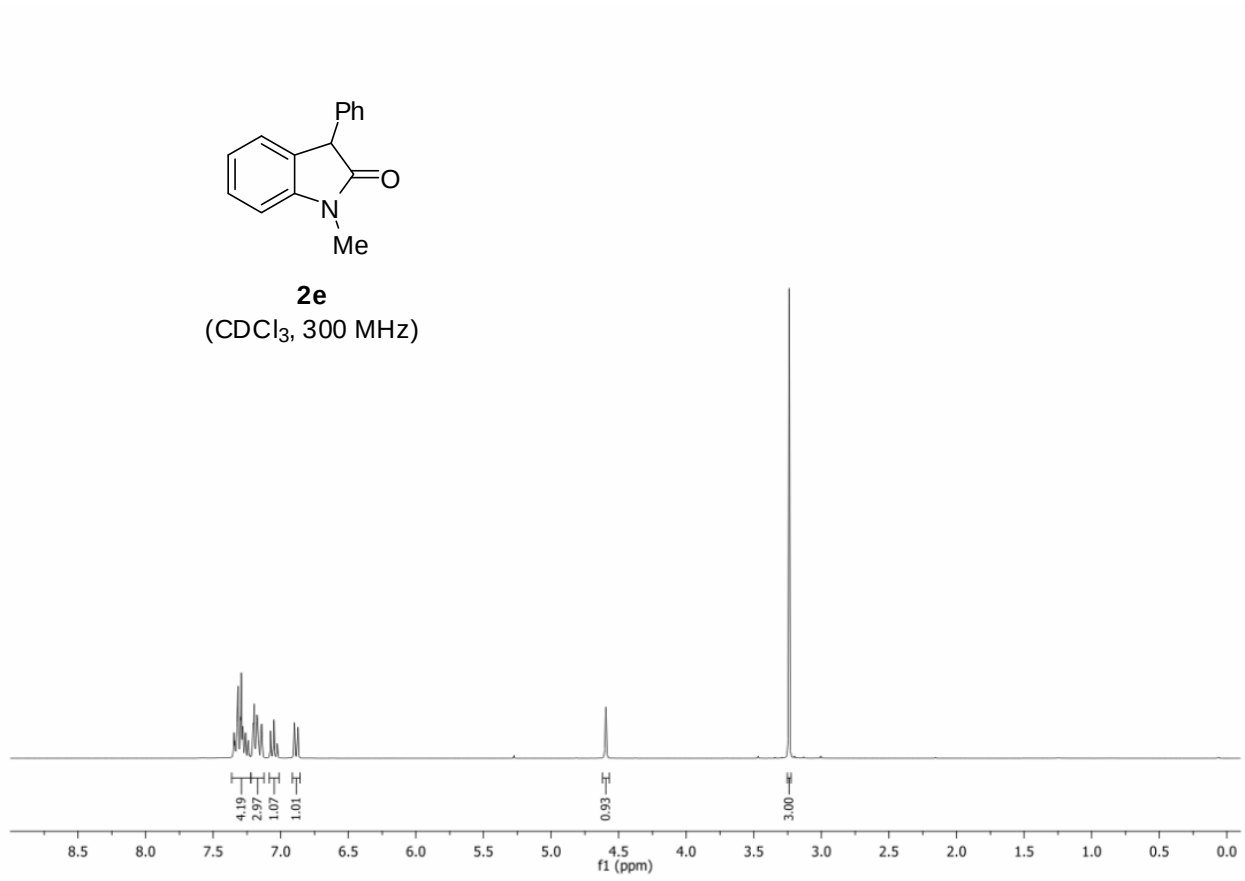
2d
($CDCl_3$, 300 MHz)



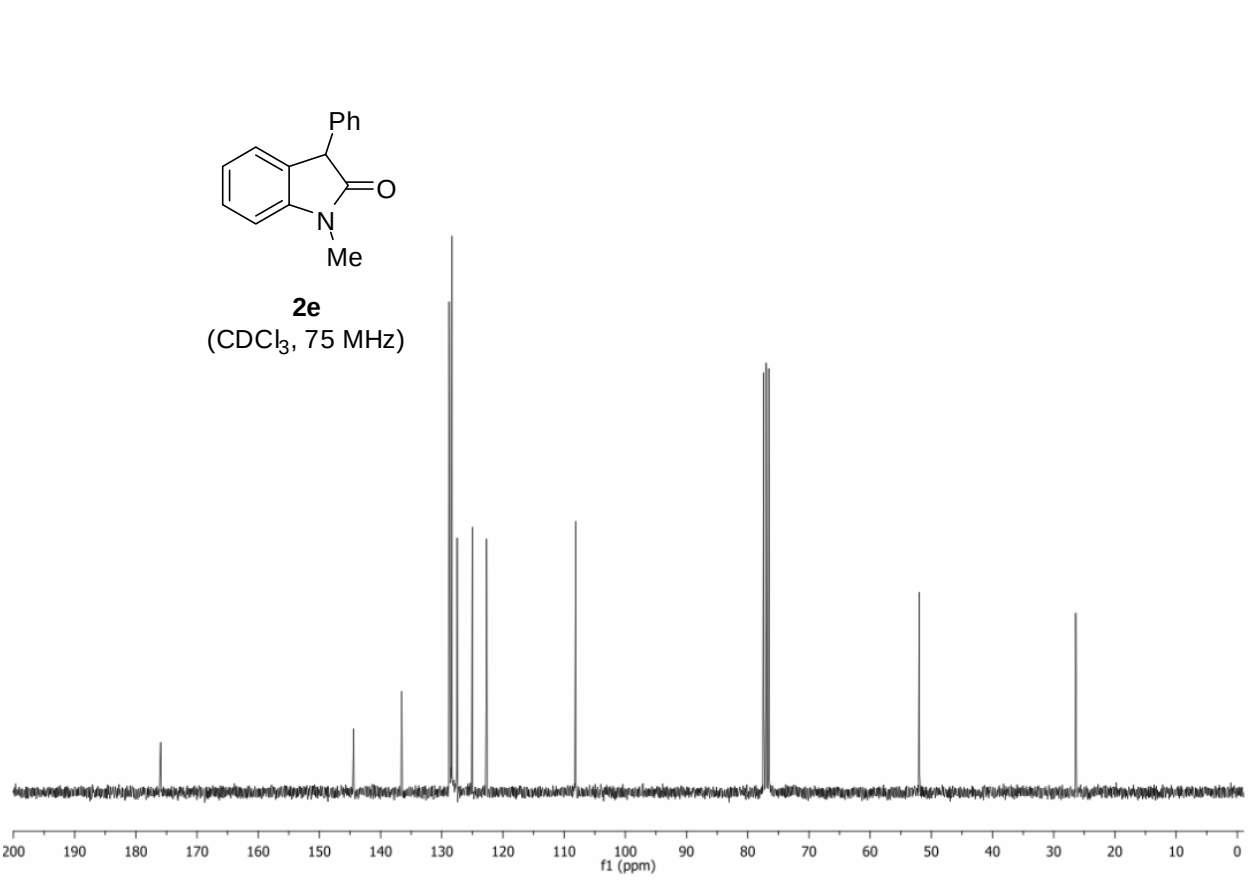


2d
($CDCl_3$, 75 MHz)

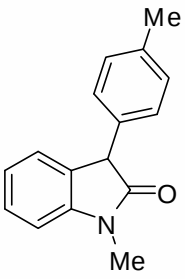




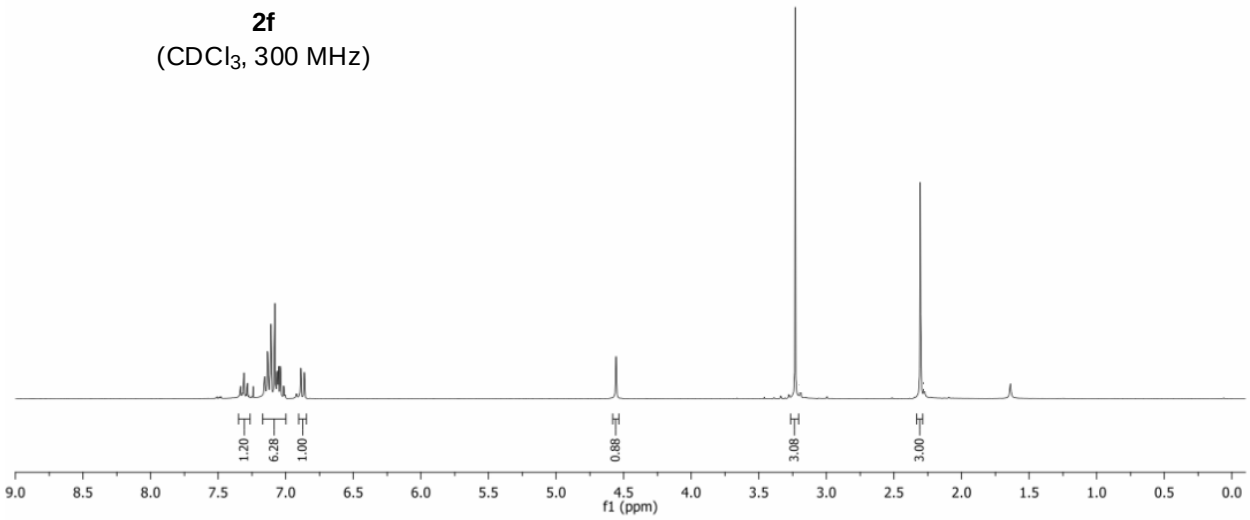
2e
($CDCl_3$, 300 MHz)

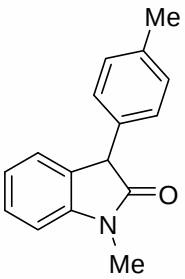


2e
($CDCl_3$, 75 MHz)

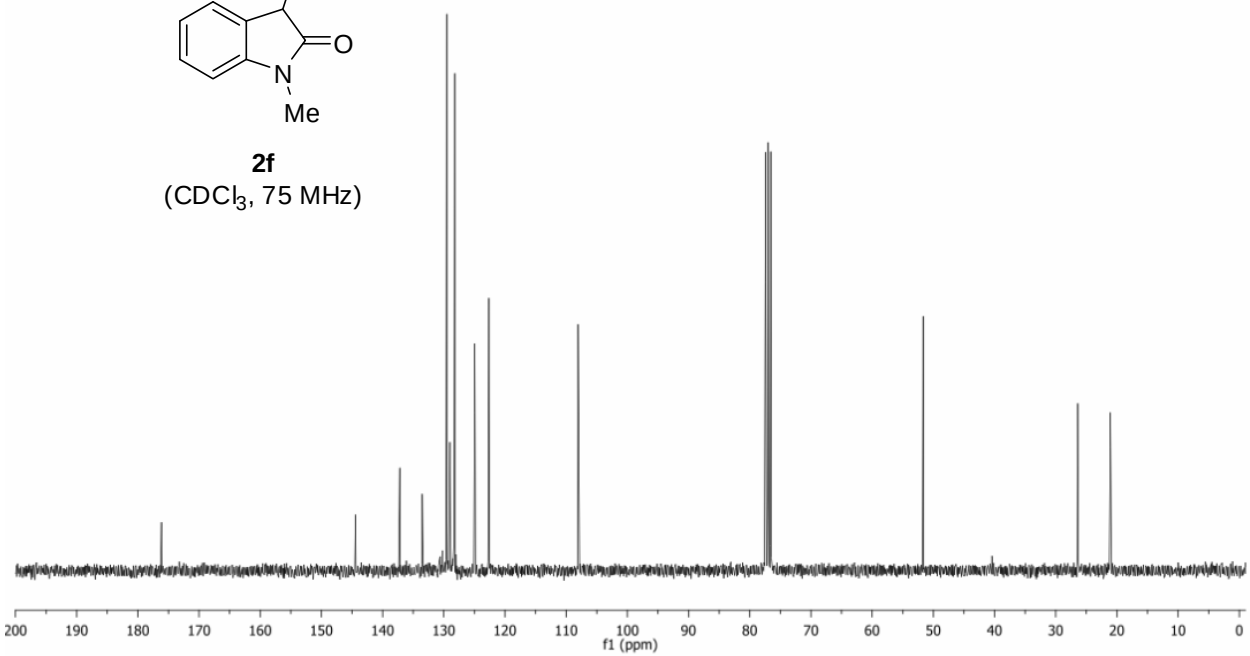


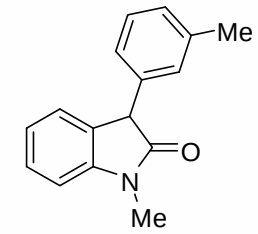
2f
($CDCl_3$, 300 MHz)



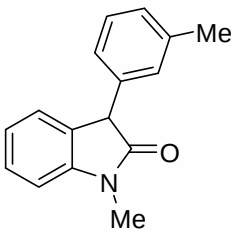


2f
($CDCl_3$, 75 MHz)

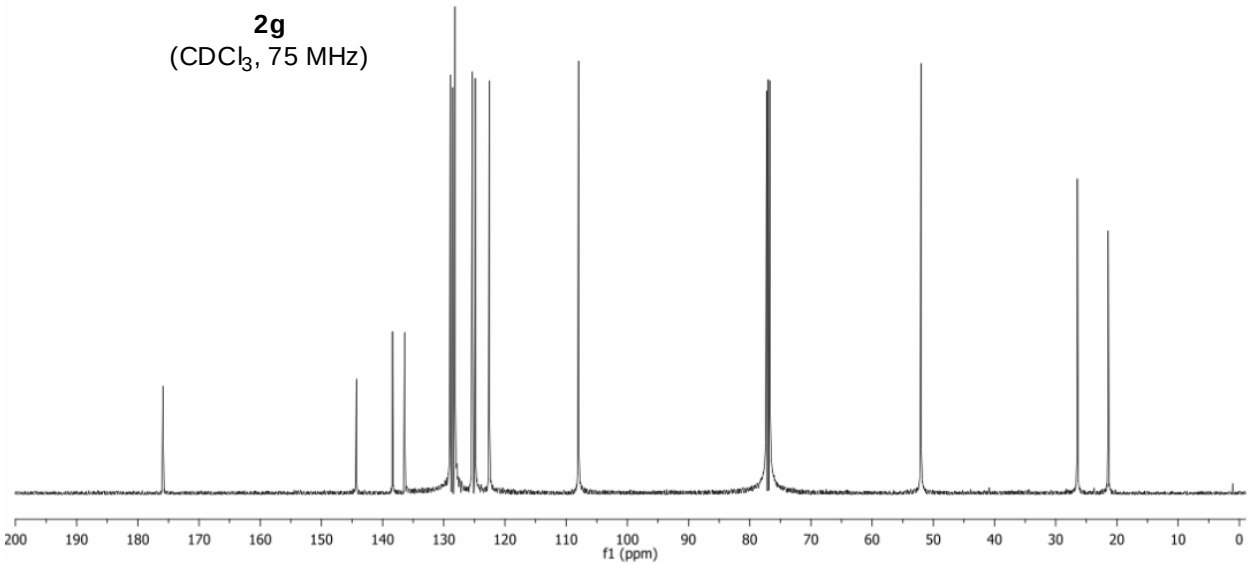


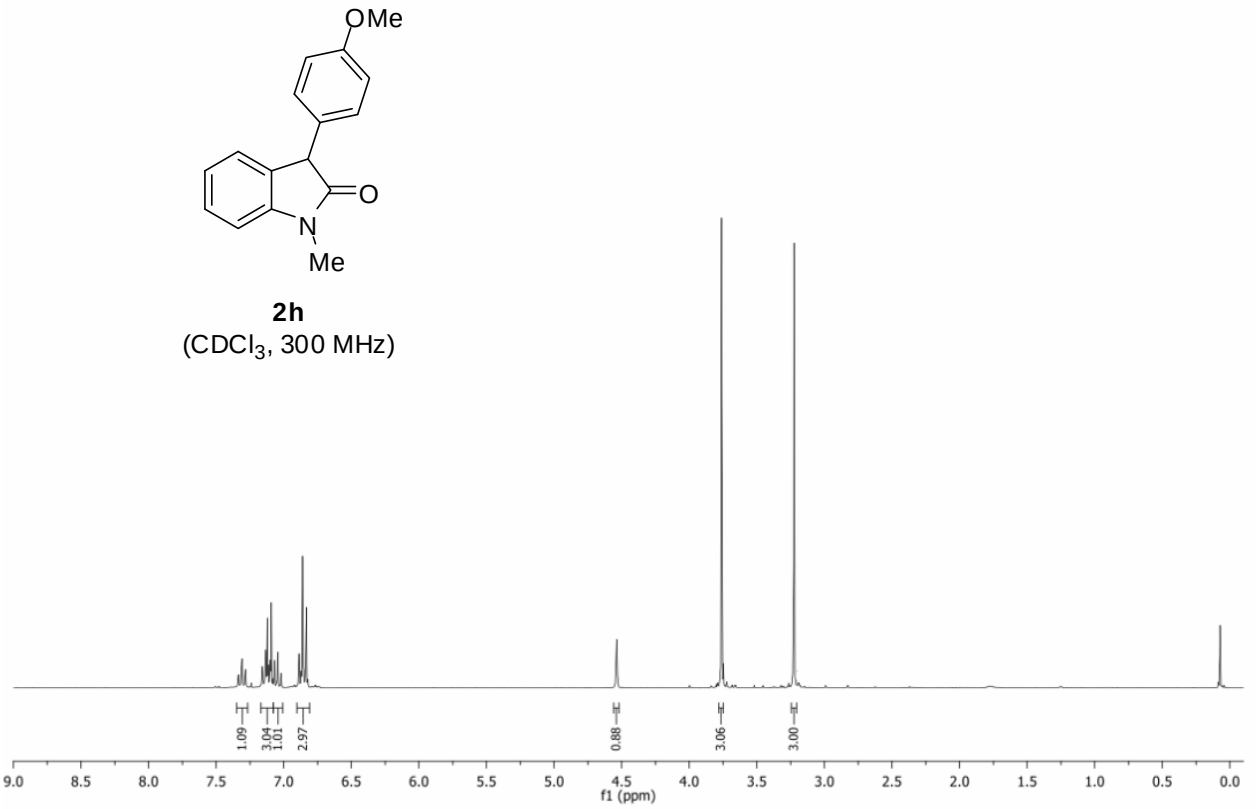


2g
($CDCl_3$, 300 MHz)

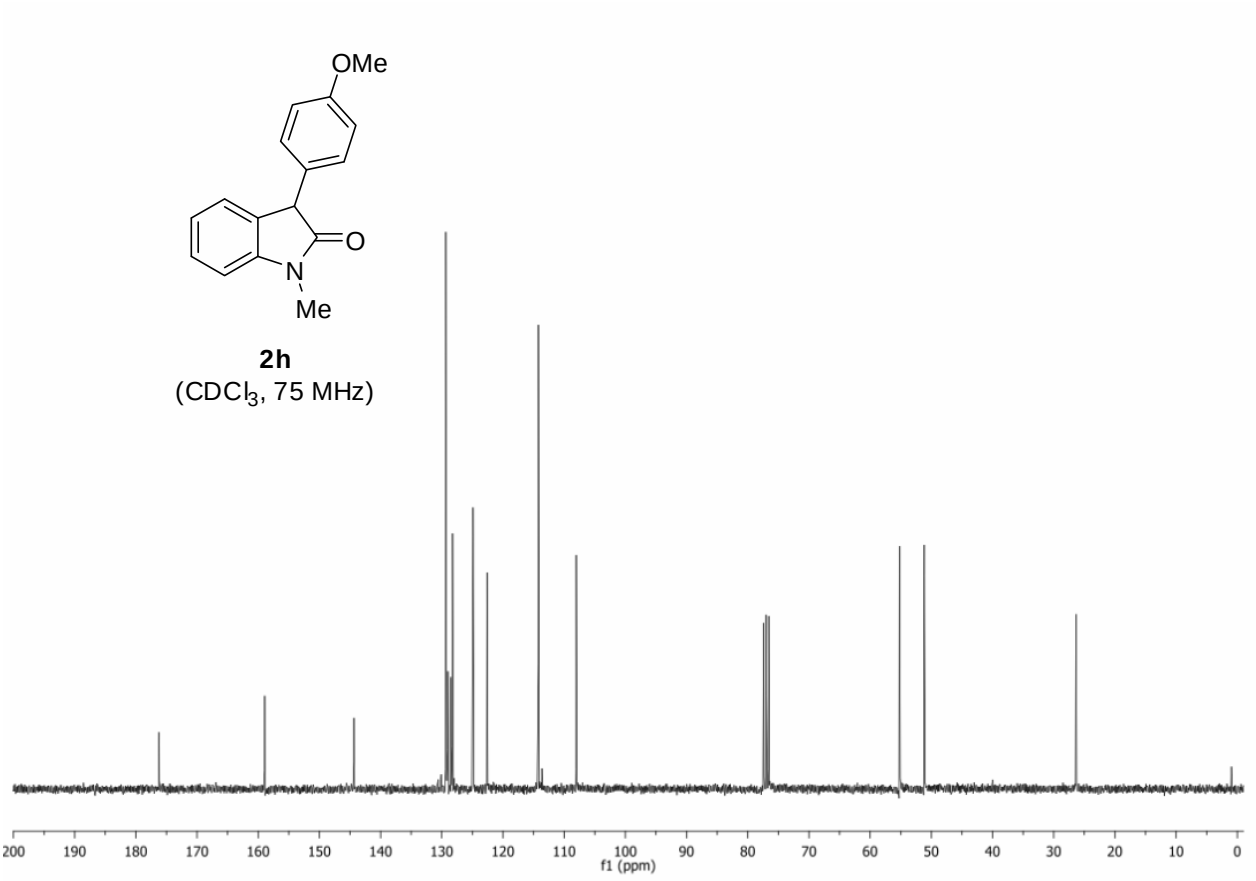


2g
($CDCl_3$, 75 MHz)

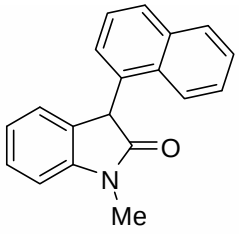




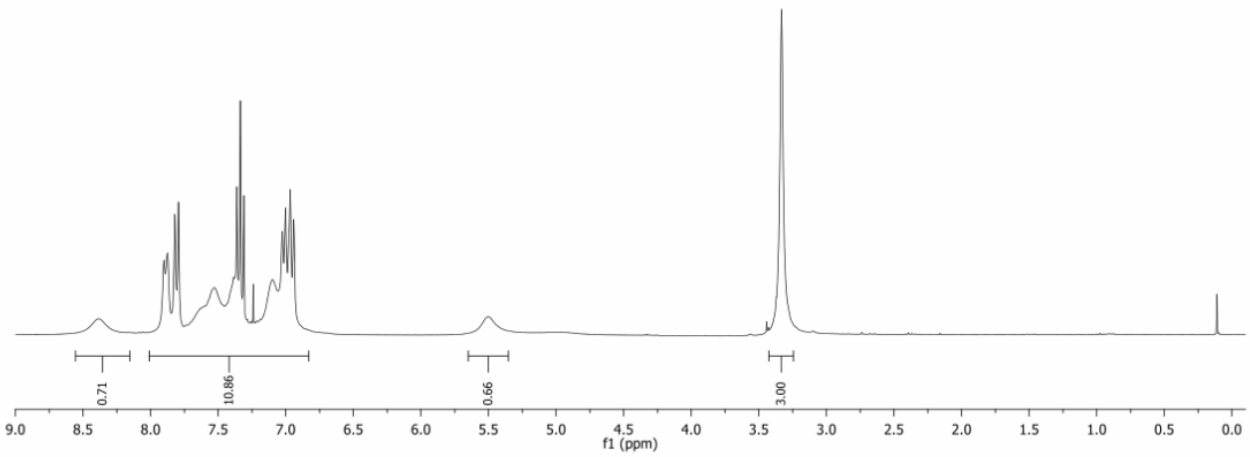
2h
($CDCl_3$, 300 MHz)

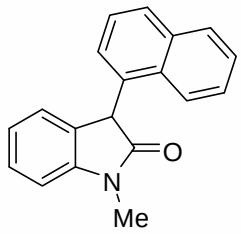


2h
($CDCl_3$, 75 MHz)

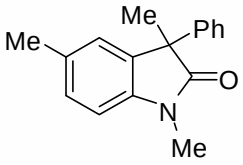


2i
($CDCl_3$, 300 MHz)

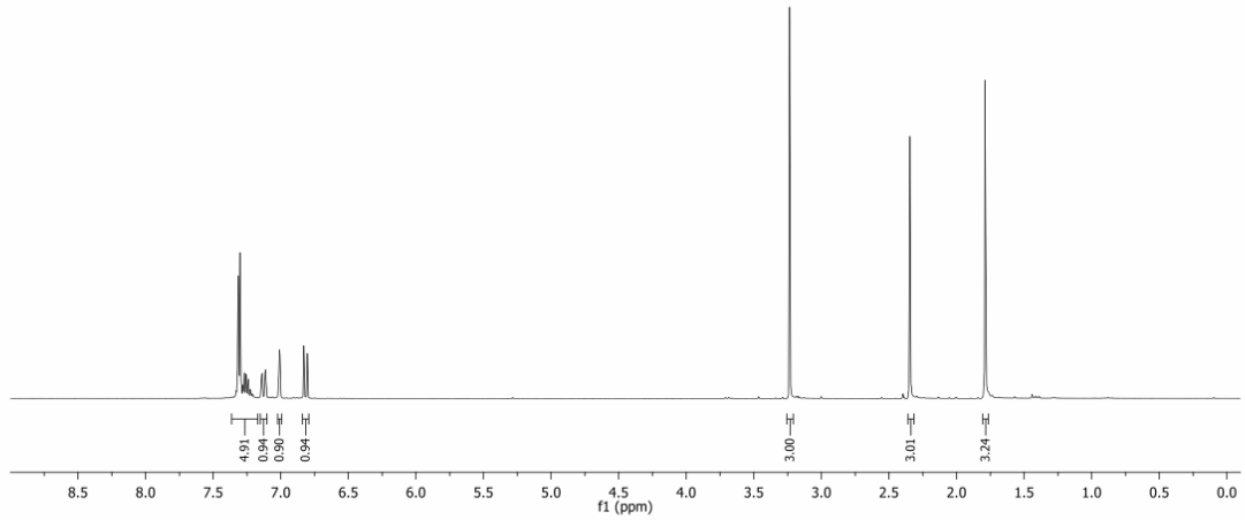


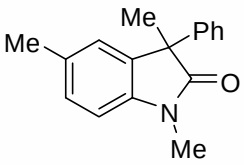


2i
($CDCl_3$, 75 MHz)

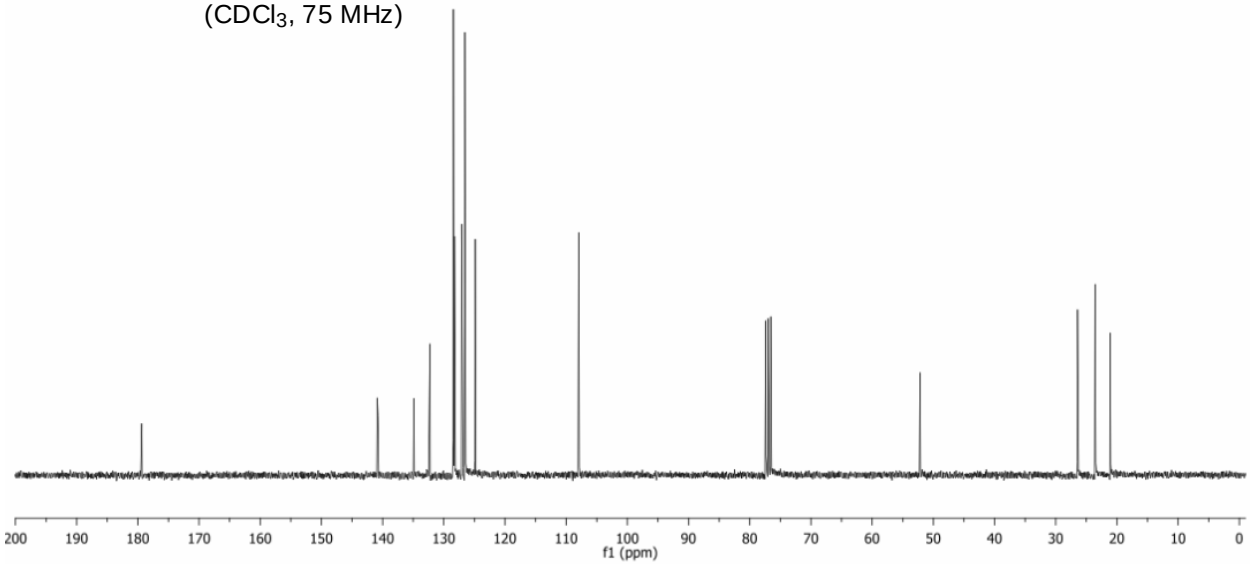


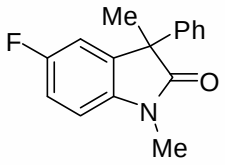
2j
($CDCl_3$, 300 MHz)



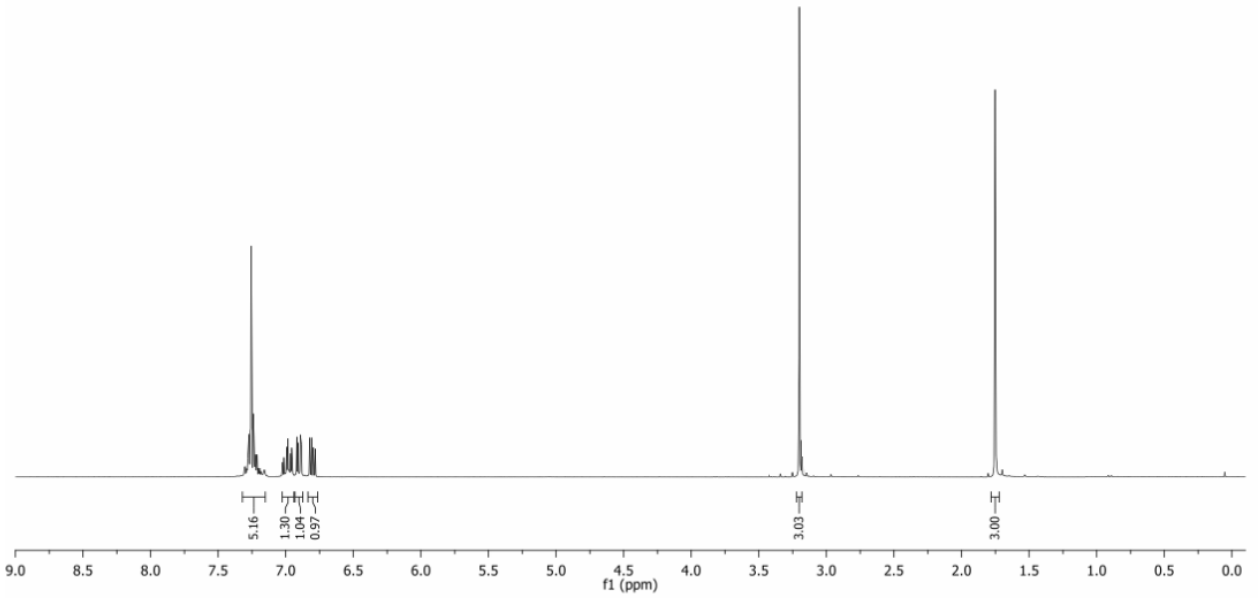


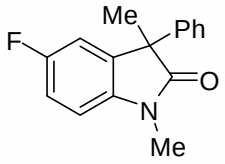
2j
($CDCl_3$, 75 MHz)



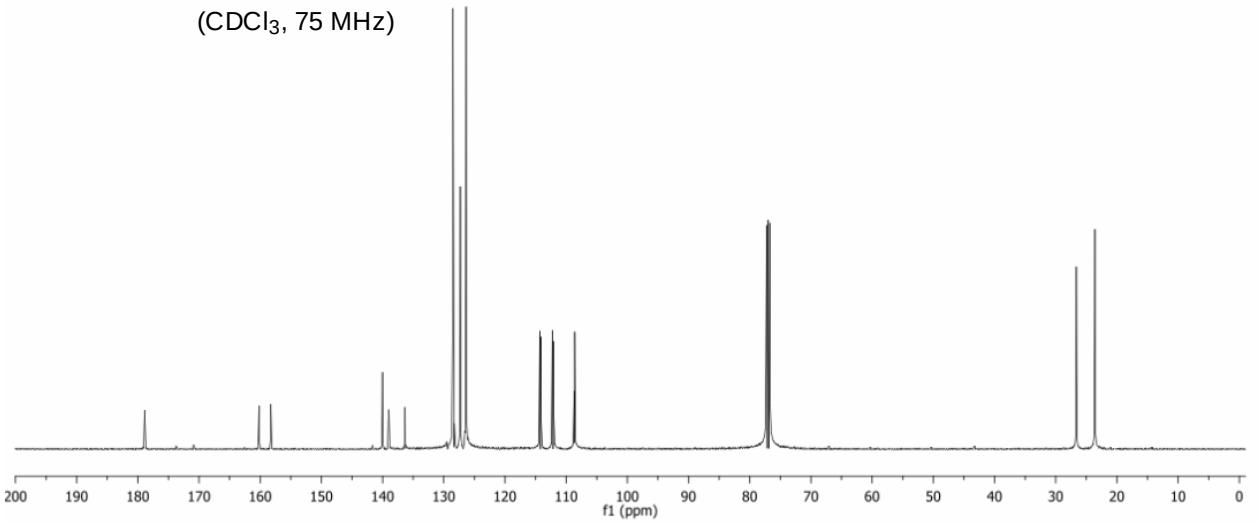


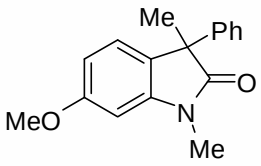
2k
($CDCl_3$, 300 MHz)





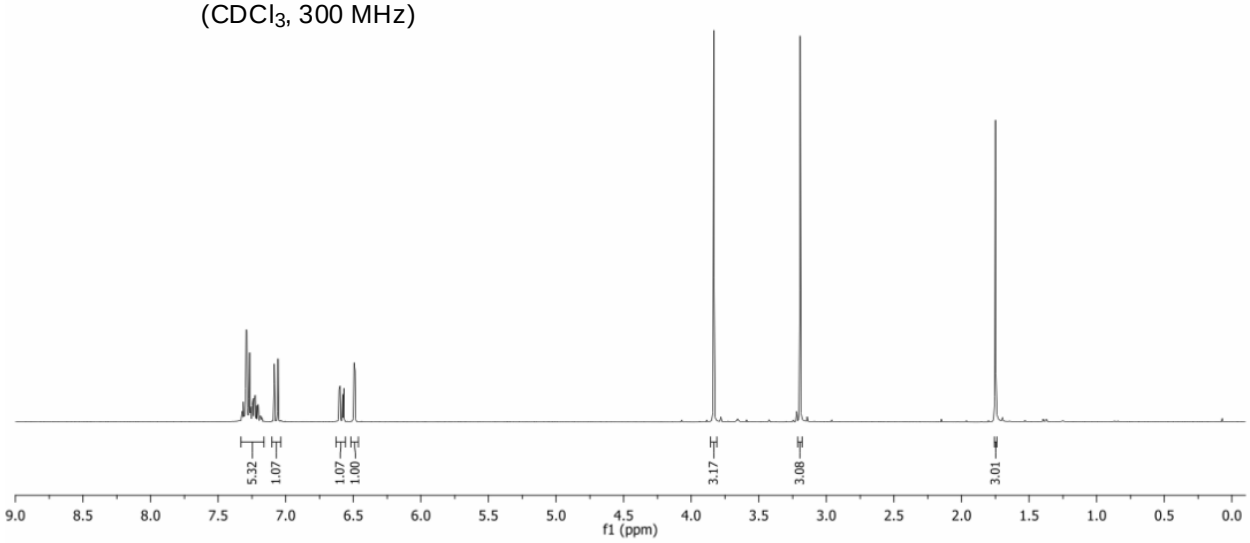
2k
($CDCl_3$, 75 MHz)

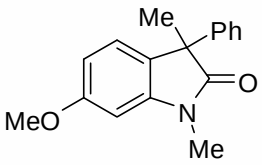




2l

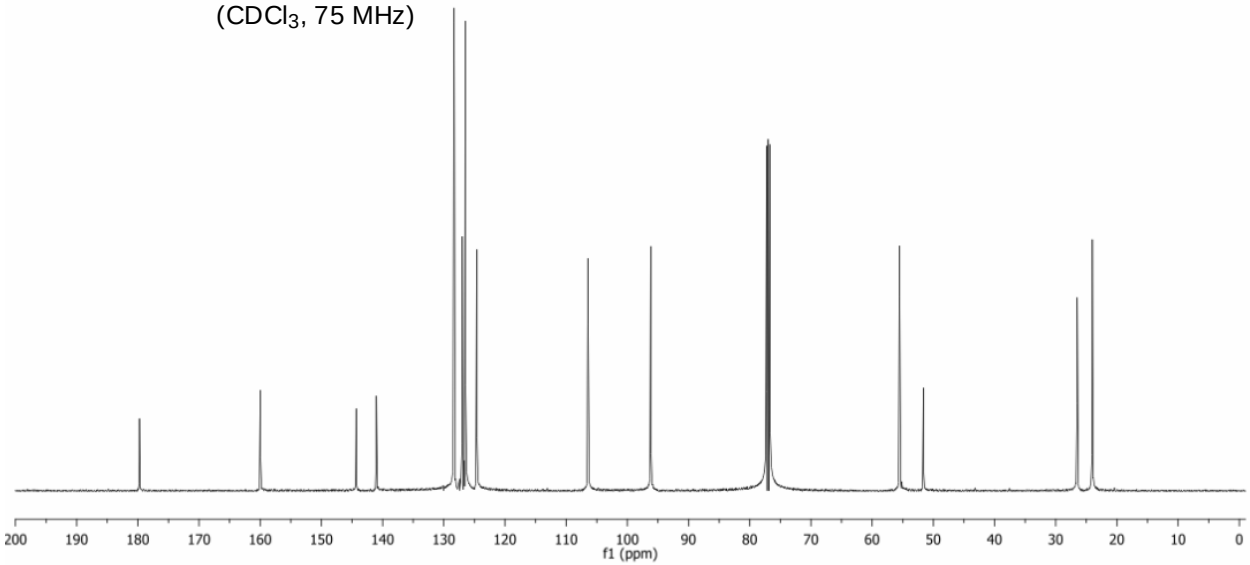
($CDCl_3$, 300 MHz)

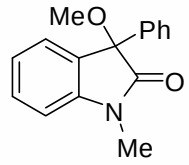




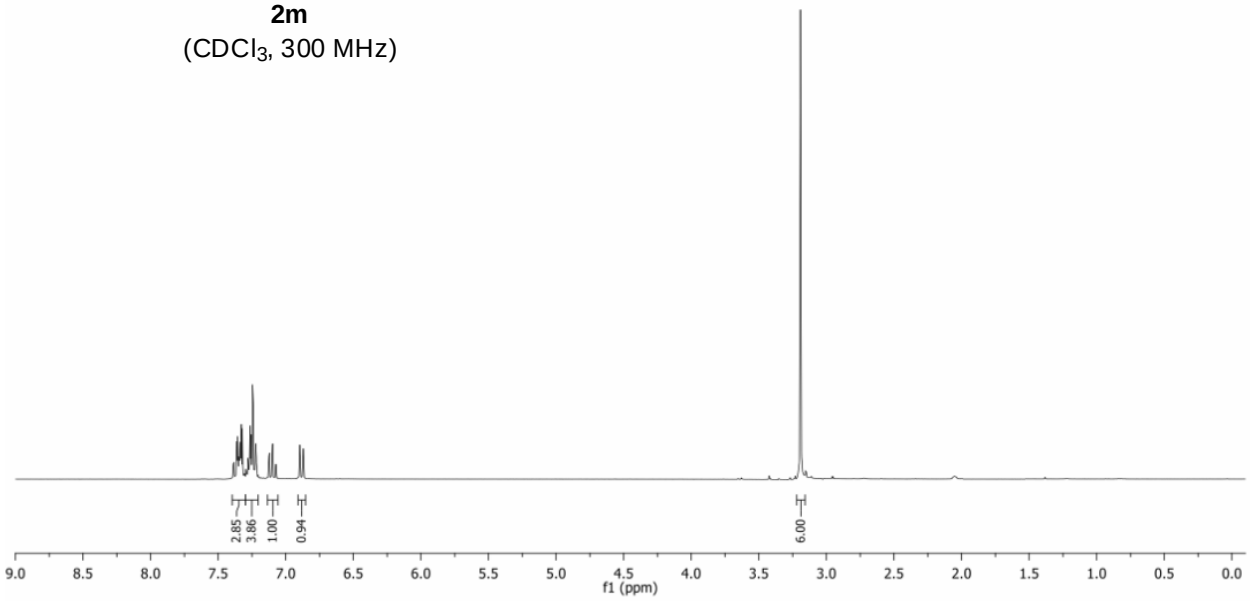
2l

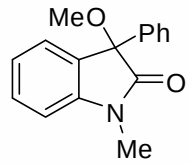
($CDCl_3$, 75 MHz)



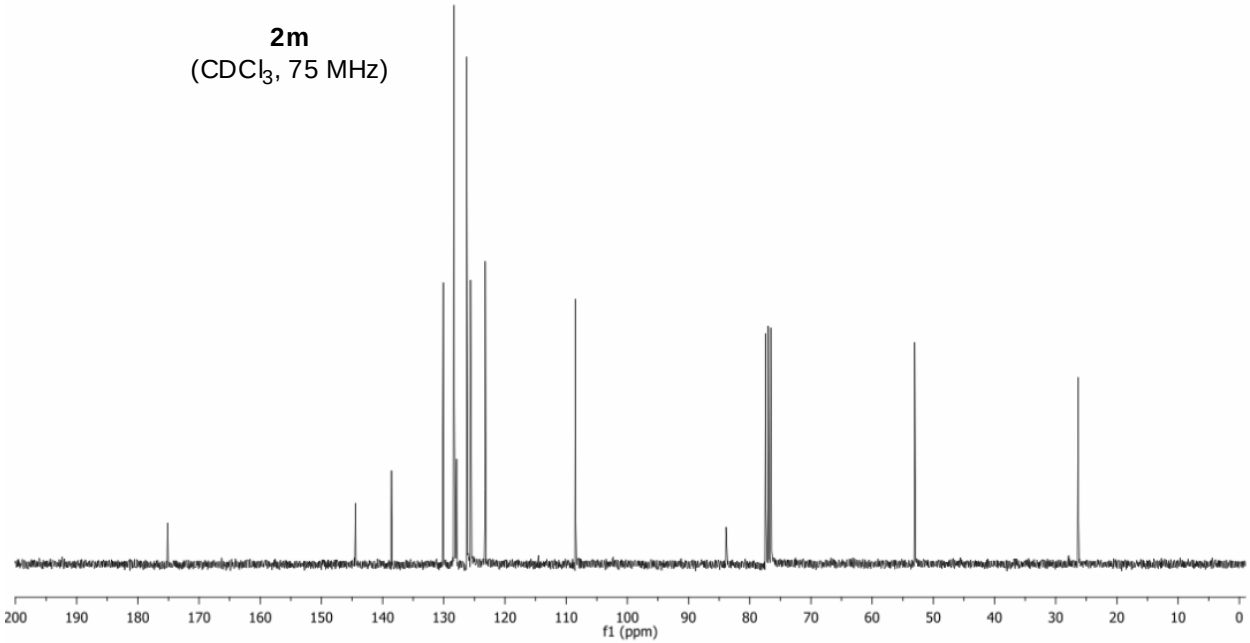


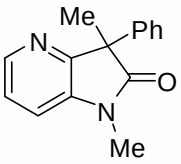
2m
($CDCl_3$, 300 MHz)



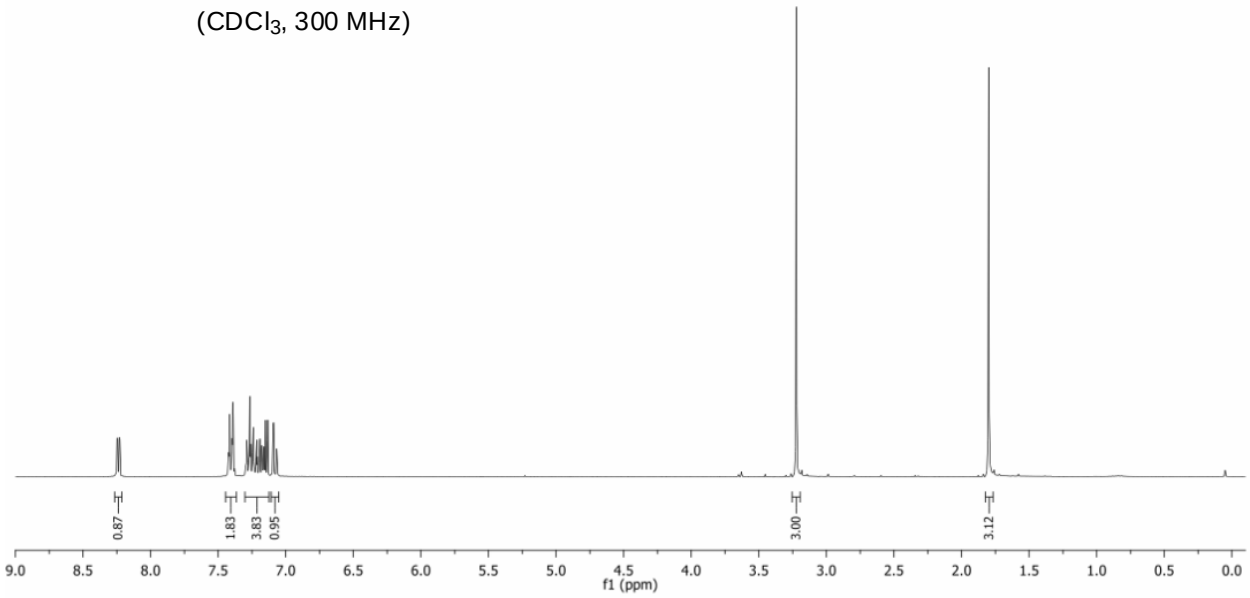


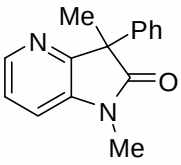
2m
($CDCl_3$, 75 MHz)



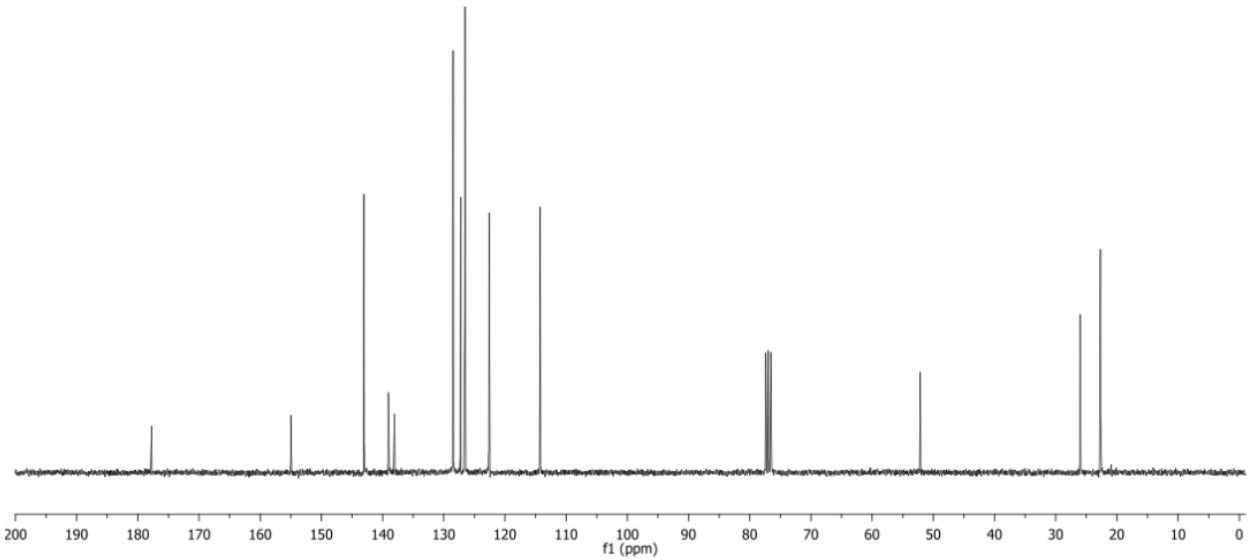


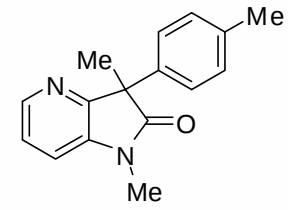
2n
($CDCl_3$, 300 MHz)



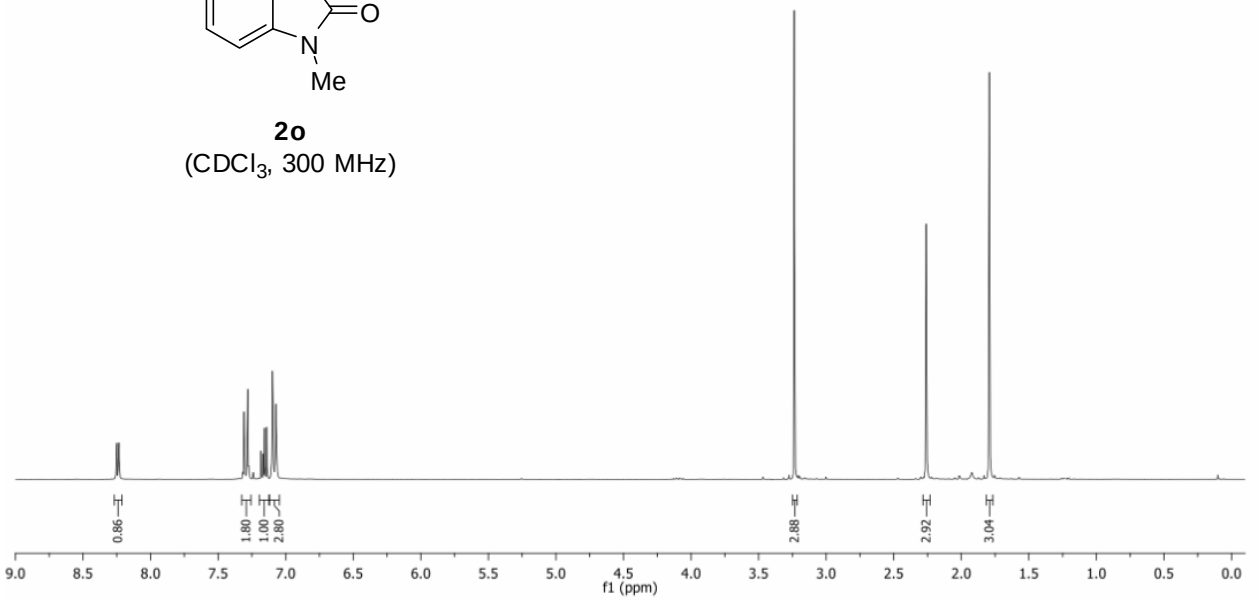


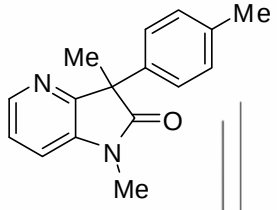
2n
($CDCl_3$, 75 MHz)



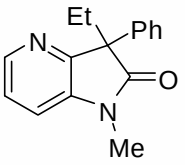


2o
($CDCl_3$, 300 MHz)

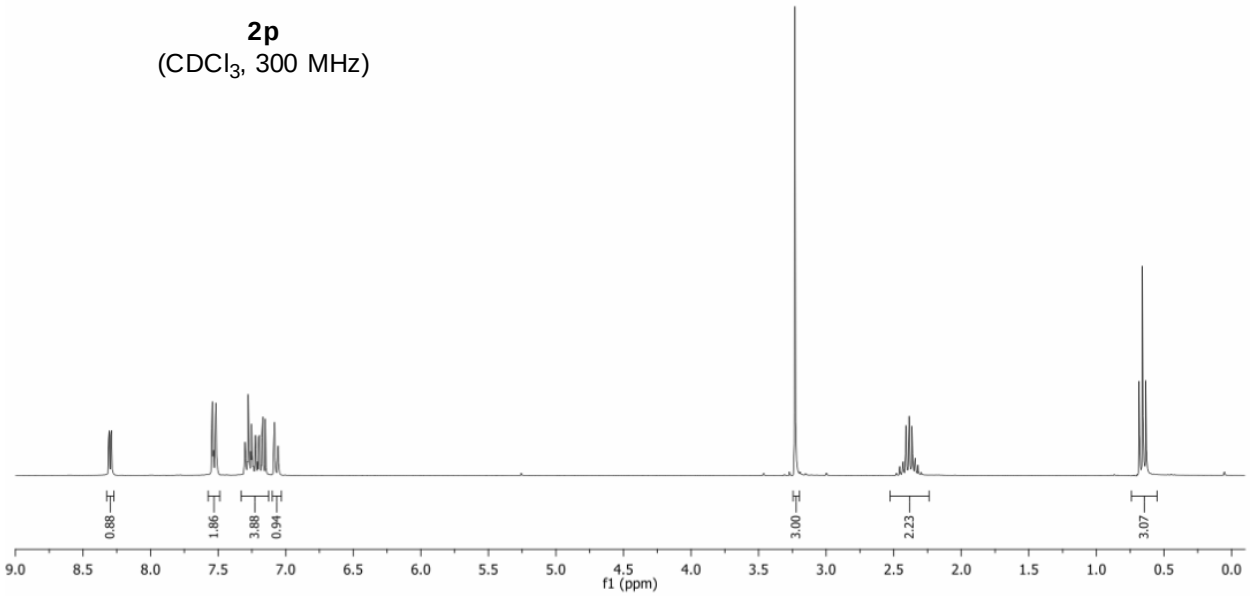


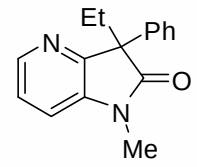


2o
($CDCl_3$, 75 MHz)



2p
($CDCl_3$, 300 MHz)





2p
($CDCl_3$, 75 MHz)