Supporting Information

Carboxylate-Assisted Ruthenium-Catalyzed Direct Alkylations of Ketimines

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General remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. *m*-Xylene, MeOH, THF and NMP were dried over sodium or magnesium. H_2O was degassed with nitrogen. The following compounds were prepared according to previously described methods: Ketimines **1**[1] and 2-phenylpyridines **1**.[2] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be >95 % pure as determined by ^{1}H-NMR and GC analysis. Flash chromatography: Macherey-Nagel silica gel 60 (70-230 mesh). NMR: Spectra were recorded on a Varian-NMR 300 instrument or on a Varian-NMR 600 in the solvent indicated; chemical shifts (δ) are given in ppm.

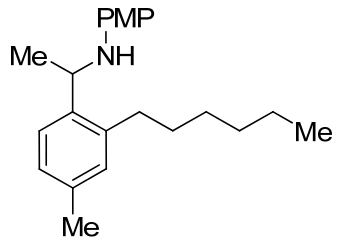
General procedure A: Ruthenium-catalyzed direct alkylations with KOAc as the base

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (0.013 mmol, 2.5 mol %), KOAc (3.20 mmol), **1** (0.50 mmol) and **2** (1.50 mmol) in *m*-xylene (2.0 mL) was stirred under N_2 for 20 h at 120 °C. A solution of $ZnCl_2$ in THF (1.7 M, 0.50 mmol), $NaBH_3CN$ (1.00 mmol) and MeOH (2.0 mL) was added to the cold reaction mixture, and the reaction mixture was stirred for 16 h at ambient temperature. Et_2O (15 mL) and sat. aq. K_2CO_3 (15 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel.

General procedure B: Ruthenium-catalyzed carboxylate-assisted direct alkylations

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (0.013 mmol, 2.5 mol %), 1-$AdCO_2H$ (**4**) (0.15 mmol, 30 mol %), K_2CO_3 (1.60 mmol), **1** (0.50 mmol) and **2** (1.50 mmol) in *m*-xylene (2.0 mL) was stirred under N_2 for 20 h at 120 °C. A solution of $ZnCl_2$ in THF (1.7 M, 0.50 mmol), $NaBH_3CN$ (1.00 mmol) and MeOH (2.0 mL) was added to the cold reaction mixture, and the reaction mixture was stirred for 16 h at ambient temperature. Et_2O (15 mL) and sat. aq. K_2CO_3 (15 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The remaining residue was purified by column chromatography on silica gel.

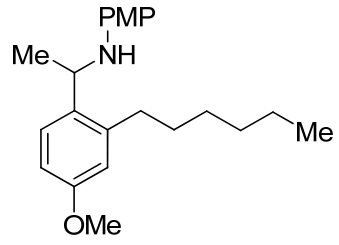
Characterization data for compounds 3



3a

***N*-{1-(2-*n*-Hexyl-4-methylphenyl)ethyl}-4-methoxyaniline (3a):** General procedure **B** was followed using 4-methoxy-*N*-(1-*p*-tolylethyliden)aniline (120 mg, 0.50 mmol) and **2a** (250 mg, 1.52 mmol) in *m*-xylene (2.0 mL). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3a** (126 mg,77 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 7.8 Hz, 1H), 7.04–6.93 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 4.64 (q, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 2.74–2.63 (m, 2H), 2.31 (s, 3H), 1.77–1.58 (m, 2H), 1.52–1.24 (m, 9H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.8 (C_q), 141.6 (C_q), 139.4 (C_q), 139.3 (C_q), 136.0 (C_q), 130.3 (CH), 127.1 (CH), 124.8 (CH), 114.7 (CH), 114.4 (CH), 55.7 (CH_3), 49.8 (CH), 32.2 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 24.0 (CH_3), 22.6 (CH_2), 21.0 (CH_3), 14.1 (CH_3). IR (KBr): 3398, 2927, 2856, 1614, 1464, 1371, 1295, 1153, 1040, 818 cm^{-1}. MS (EI): *m/z* (relative intensity) 325 (36) [M^+], 310 (12), 202 (26), 187 (6), 133 (100), 123 (43), 108 (5). HRMS (ESI): *m/z* calcd for $C_{22}H_{31}NO+H^+$ 326.2478, found 326.2478.

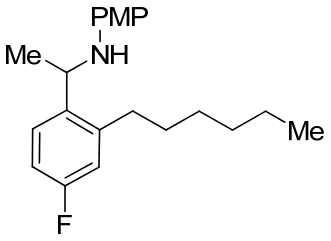
General procedure **A** was followed using (*E*)-4-methoxy-*N*-(1-*p*-tolylethyliden)aniline (119 mg, 0.50 mmol) and **2a** (256 mg, 1.55 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3a** (76 mg, 47 %) as a slightly red oil.



3b

***N*-{1-(2-*n*-Hexyl-4-methoxyphenyl)ethyl}-4-methoxyaniline (3b):** General procedure **A** was followed using (*E*)-4-methoxy-*N*-{1-(4-methoxyphenyl)ethyliden}aniline (121 mg, 0.48 mmol) and **2a** (255 mg, 1.54 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3b** (80 mg, 48 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 1H), 6.77–6.66 (m, 4H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.60 (q, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.75–2.63 (m, 2H), 1.75–1.58 (m, 2H), 1.51–1.23 (m, 9H), 0.90 (t, *J* = 8.8 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 158.2 (C_q), 151.8 (C_q), 141.7 (C_q), 140.9 (C_q), 134.7 (C_q), 126.1 (CH), 115.1 (CH), 114.7 (CH), 114.3 (CH), 111.3 (CH), 55.7 (CH_3), 55.0 (CH_3), 49.6 (CH), 32.3 (CH_2), 31.7 (CH_2), 31.1 (CH_2), 29.5 (CH_2), 24.0 (CH_3), 22.6 (CH_2), 14.1 (CH_3). IR (NaCl): 3389, 2954, 2928, 2855, 1608, 1577, 1511,

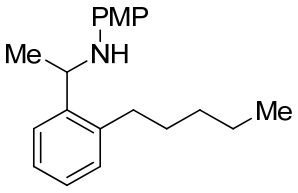
1292, 1236, 1040 cm^{-1}. MS (EI) *m/z* (relative intensity): 341 (19) [M^+], 219 (72), 149 (100), 123 (18), 91 (7), 41 (7). HRMS (ESI): *m/z* calcd for $C_{22}H_{31}NO_2$+Na^+ 364.2247, found 364.2249.



3c

***N*-{1-(4-Fluoro-2-*n*-hexylphenyl)ethyl}-4-methoxyaniline (3c):** General procedure **B** was followed using *N*-{1-(4-fluorophenyl)ethyliden}-4-methoxyaniline (125 mg, 0.52 mmol) and **2a** (249 mg, 1.51 mmol) in *m*-xylene (2 mL). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3c** (128 mg, 76%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.40 (dd, *J* = 8.6, 6.1 Hz, 1H), 6.93–6.77 (m, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 9.0 Hz, 2H), 4.60 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 2.79–2.65 (m, 2H), 1.75–1.59 (m, 2H), 1.49–1.27 (m, 9H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 161.5 (C_q, $^1J_{C\text{-}F}$ = 244 Hz), 151.9 (C_q), 141.6 (C_q, $^3J_{C\text{-}F}$ = 7 Hz), 141.4 (CH), 138.1 (C_q), 126.6 (C_q, $^3J_{C\text{-}F}$ = 8 Hz), 115.7 (CH, $^2J_{C\text{-}F}$ = 21 Hz), 114.7 (CH), 114.3 (CH), 113.0 (CH, $^2J_{C\text{-}F}$ = 22 Hz), 55.6 (CH_3), 49.7 (CH), 31.9 (CH_2), 31.7 (CH_2), 30.8 (CH_2), 29.4 (CH_2), 24.1 (CH_3), 22.6 (CH_2), 14.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -116.9 – -117.0 (m). IR (NaCl): 3388, 2931, 2869, 1612, 1588, 1511, 1373, 1236, 1140, 1040 cm^{-1}. MS (EI): *m/z* (relative intensity) 329 (40) [M^+], 314 (20), 206 (11), 149 (6), 137 (90), 123 (100), 108 (11). HRMS (ESI): *m/z* calcd for $C_{21}H_{28}FNO$+H^+: 330.2228, found 330.2229.

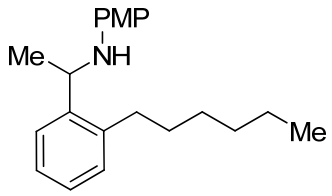
General procedure **A** was followed using *N*-{1-(4-fluorophenyl)ethyliden}-4-methoxyaniline (122 mg, 0.50 mmol) and **2a** (252 mg, 1.52 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3c** (76 mg, 46 %) as a colourless oil.



3d

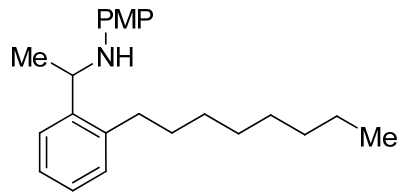
4-Methoxy-*N*-{1-(2-*n*-pentylphenyl)ethyl}aniline (**3d**): General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (113 g, 0.50 mmol) and 1-bromo-*n*-pentane (229 mg, 1.52 mmol) in *m*-xylene (2.0 mL). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3d** (120 mg, 81%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 1H), 7.15–7.12 (m, 3H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 8.8 Hz, 2H), 4.65 (q, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 2.67 (dt, *J* = 9.7, 6.1 Hz, 2H), 1.72–1.61 (m, 2H), 1.48

(d, *J* = 7.0 Hz, 3H), 1.43–1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 152.2 (C_q), 142.3 (C_q), 140.7 (C_q), 139.5 (C_q), 129.5 (CH), 126.8 (CH), 126.4 (CH), 125.0 (CH), 115.0 (CH), 114.7 (CH), 55.7 (CH_3), 50.6 (CH), 32.2 (CH_2), 32.0 (CH_2), 30.9 (CH_2), 23.9 (CH_2), 22.6 (CH_3), 14.0 (CH_3). IR (NaCl): 3403, 3060, 2928, 2915, 2858, 1511, 1404, 1239, 1182, 1053 cm^{-1}. MS (EI): m/z (relative intensity) 297 (100) [M^+], 282 (50), 193 (6), 174 (61), 159 (15), 145 (21), 136 (122), 123 (90), 119 (96), 108 (18), 91 (11), 41 (5). HRMS (ESI): m/z calcd for $C_{20}H_{27}NO+H^+$ 298.2165, found 298.2166.



3e

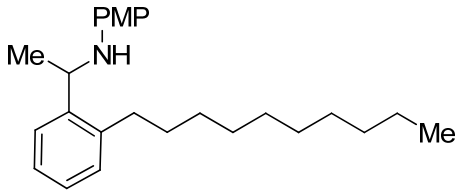
***N*-{1-(2-*n*-Hexylphenyl)ethyl}-4-methoxyaniline (3e):** General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (114 mg, 0.51 mmol) and **2a** (249 mg, 1.51 mmol) in *m*-xylene (2.0 mL) was stirred under N_2 for 20 h at 120 °C. Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3e** (113 mg, 73%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* = 7.48 (m, 1H), 7.22–7.08 (m, 3H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 4.65 (q, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 2.76–2.55 (m, 2H), 1.68–1.52 (m, 2H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.49–1.18 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) *δ* = 151.9 (C_q), 142.5 (C_q), 141.6 (C_q), 139.4 (C_q), 129.5 (CH), 126.7 (CH), 126.4 (CH), 124.9 (CH), 114.8 (CH), 114.4 (CH), 55.7 (CH_3), 50.1 (CH), 32.2 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 29.6 (CH_2), 24.0 (CH_3), 22.6 (CH_2), 14.1 (CH_3). IR (NaCl): 2928, 2856, 2361, 2339, 1512, 1457, 1235, 1040, 818, 757 cm^{-1}. MS (EI): *m/z* (relative intensity) 311 (100) [M^+], 296 (54), 207 (26), 188 (70), 173 (12), 145 (14), 136 (88), 121 (82), 119 (86), 117 (34), 108 (24), 91 (16), 41 (6). HRMS (ESI): *m/z* calcd for $C_{21}H_{29}NO+H^+$: 312.2322, found 312.2321.
Analytical data are in accordance with those reported in the literature. [3]



3f

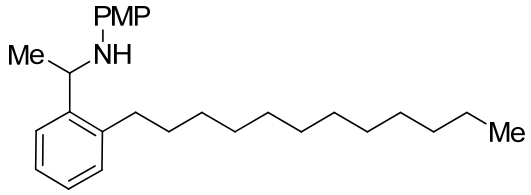
4-Methoxy-*N*-{1-(2-*n*-octylphenyl)ethyl}aniline (3f): General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (113 mg, 0.50 mmol) and 1-bromo-*n*-octane (289 mg, 1.50 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3f** (97 mg, 58%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* = 7.48 (m, 1H), 7.21–7.15 (m, 3H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 4.69 (q, *J* = 6.6 Hz, 1H), 3.71 (s, 3H), 2.78–2.72 (m, 2H), 1.73–1.68 (m, 2H), 1.50–1.25 (m, 14H), 0.91 (t, *J* = 7.8 Hz,

3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.8 (C_q), 142.5 (C_q), 141.6 (C_q), 139.3 (C_q), 129.5 (CH), 126.6 (CH), 126.4 (CH), 124.8 (CH), 114.7 (CH), 114.3 (CH), 55.6 (CH_3), 50.0 (CH), 32.2 (CH_2), 31.8 (CH_2), 31.2 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 24.0 (CH_3), 22.6 (CH_2), 14.1 (CH_3). IR (NaCl): 3402, 2926, 2854, 1685, 1511, 1464, 1372, 1295, 1235, 1179, 1151, 1040, 818, 757, 519 cm^{-1}. MS (EI): *m/z* (relative intensity) 339 (100) [M^+], 324 (44), 216 (46), 145 (13), 131 (14), 123 (88), 119 (99), 108 (19), 91 (14), 91 (14), 77(5), 41 (10). HRMS (ESI): *m/z* calcd for $C_{23}H_{33}NO+H^+$ 340.2635, found 340.2633.



3g

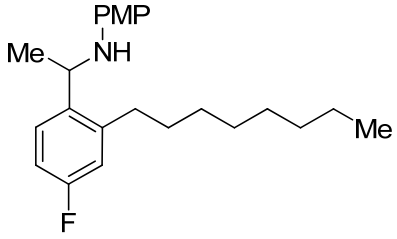
***N*-{1-(2-*n*-Decylphenyl)ethyl}-4-methoxyaniline (3g):** General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (114 mg, 0.51 mmol) and 1-bromo-*n*-decane (341 mg, 1.54 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3g** (135 mg, 73%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.47 (m, 1H), 7.20–7.09 (m, 3H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 2.74–2.61 (m, 2H), 1.72–1.54 (m, 2H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.42–1.08 (m, 14H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.9 (C_q), 142.5 (C_q), 141.6 (C_q), 139.4 (C_q), 129.5 (CH), 126.6 (CH), 126.4 (CH), 124.9 (CH), 114.8 (CH), 114.4 (CH), 55.7 (CH_3), 50.1 (CH), 32.2 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 24.0 (CH_3), 22.7 (CH_2), 14.1 (CH_3). IR (NaCl): 2925, 2853, 2361, 2339, 1463, 1372, 1295, 1236, 1179, 1041 cm^{-1}. MS (EI): *m/z* (relative intensity) 367 (100) [M^+], 353 (50), 263 (43), 244 (63), 229 (6), 150 (6), 145 (17), 136 (94), 132 (25), 123 (74), 119 (70), 117 (34), 108 (16), 91 (14), 41 (8). HRMS (ESI): *m/z* calcd for $C_{25}H_{37}NO+H^+$ 368.2948, found 368.2946.
Analytical data are in accordance with those reported in the literature. [3]



3h

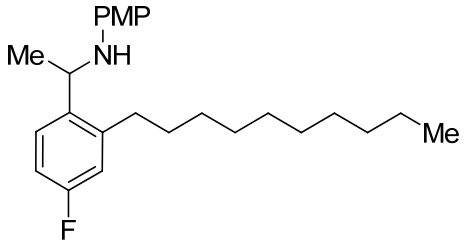
***N*-{1-(2-*n*-Dodecylphenyl)ethyl}-4-methoxyaniline (3h):** General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (112 mg, 0.50 mmol) and 1-bromo-*n*-dodecane (386 mg, 1.55 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3h** (153 mg, 77 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.49 (m, 1H), 7.17–7.14 (m, 3H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 4.65 (q, *J* = 6.6 Hz, 1H), 3.67 (s, 3H), 2.68–2.63 (m, 2H), 1.68–1.53 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H), 1.27–1.22 (m, 19H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 152.7 (C_q), 141.8 (C_q), 139.5 (C_q), 129.5 (CH), 126.8

(CH), 126.4 (CH), 125.1 (CH), 115.4 (C_q), 114.7 (CH), 109.1 (CH), 55.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 23.7 (CH_3), 22.7 (CH_2), 14.1 (CH_3), 14.0 (CH_3). IR (NaCl): 3396, 2924, 2853, 1512, 1485, 1294, 1235, 1180, 1042, 818, 756, 544 cm^{-1}. MS (EI): *m/z* (relative intensity) 395 (100) [M^+], 381 (42), 292 (14), 273 (58), 193 (20), 145 (18), 132 (23), 123 (90), 119 (91), 108 (15), 91 (12). HRMS (ESI): *m/z* calcd for $C_{27}H_{41}NO+H^+$ 396.3261, found 396.3264.



3i

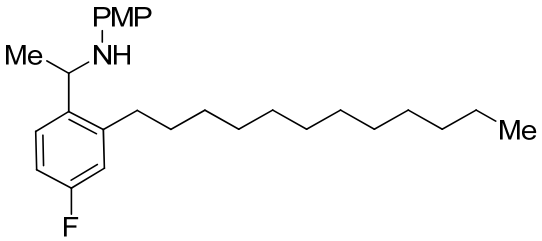
***N*-{1-(4-Fluoro-2-*n*-octylphenyl)ethyl}-4-methoxyaniline (3i):** General procedure **B** was followed using *N*-{1-(4-fluorophenyl)ethyliden}-4-methoxyaniline (122 mg, 0.50 mmol) and 1-bromo-*n*-octane (292 mg, 1.51 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3i** (117 mg, 66%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.44 (dd, *J* = 8.6, 6.0 Hz, 1H), 6.92–6.78 (m, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 4.62 (q, *J* = 6.5 Hz, 1H), 3.69 (s, 3H), 2.69 (td, *J* = 7.5, 4.0 Hz, 2H), 1.72–1.58 (m, 2H), 1.52–1.22 (m, 13H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 161.6 (C_q, $^1J_{C\text{-}F}$ = 246 Hz), 152.3 (C_q), 141.8 (C_q, $^3J_{CF}$ = 6 Hz), 140.7 (C_q), 137.7 (C_q), 126.8 (CH, $^3J_{C\text{-}F}$ = 9 Hz), 115.7 (CH, $^2J_{C\text{-}F}$ = 21 Hz), 114.8 (CH), 114.7 (CH), 113.0 (CH, $^2J_{C\text{-}F}$ = 22 Hz), 55.6 (CH_3), 50.2 (CH), 32.0 (CH_2), 31.9 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 23.9 (CH_3), 22.6 (CH_2), 14.0 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -116.7 (bs). IR (NaCl): 3398, 2954, 2929, 2854, 1612, 1588, 1511, 1465, 1372, 1234, 1179 cm^{-1}. MS (EI): *m/z* (relative intensity) 357 (46) [M^+], 324 (18), 235 (18), 149 (10), 137 (74), 123 (100), 108 (13), 43 (6). HRMS (ESI): *m/z* calcd for $C_{23}H_{32}FNO+H^+$ 358.2541, found 358.2543.



3j

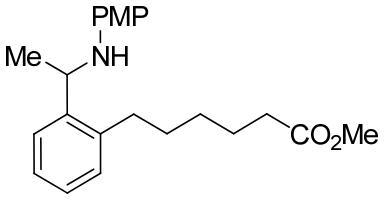
***N*-{1-(2-*n*-Decyl-4-fluorophenyl)ethyl}-4-methoxyaniline (3j):** General procedure **B** was followed using *N*-{1-(4-fluorophenyl)ethyliden}-4-methoxyaniline (126 mg, 0.52 mmol) and 1-bromo-*n*-decane (329 mg, 1.49 mmol) in *m*-xylene (2.0 mL). Reduction and purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **3j** (121 mg, 63%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.43 (dd, *J* = 8.6, 6.1 Hz, 1H), 6.96–6.78 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.64 (q, *J* = 6.6 Hz, 1H), 3.72 (s, 3H), 2.79–2.69 (m, 2H), 1.78–1.61 (m, 2H), 1.51–1.23 (m, 17H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 161.7 (C_q, $^1J_{C\text{-}F}$ = 238 Hz), 151.9

(C_q), 141.6 (C_q, $^3J_{C\text{-}F}$ = 7 Hz), 138.2 (C_q), 141.4 (C_q), 126.6 (CH, $^3J_{C\text{-}F}$ = 8 Hz), 115.7 (CH, $^2J_{C\text{-}F}$ = 21 Hz), 114.7 (CH), 114.4 (CH), 113.0 (CH, $^2J_{C\text{-}F}$ = 21 Hz), 55.6 (CH_3), 49.7 (CH), 31.9 (CH_2), 31.9 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 24.1 (CH_3), 22.6 (CH_2), 14.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ =-117.03 – -116.83 (m). IR (NaCl): 3397, 2953, 2925, 2853, 1618, 1598, 1512, 1465, 1235, 1040, 818, 733 cm^{-1}. MS (EI): *m/z* (relative intensity) 385 (27) [M^+], 370 (13), 263 (30), 149 (7), 136 (100), 123 (74), 108 (10), 55 (7), 43 (8). HRMS (ESI): *m/z* calcd for $C_{25}H_{36}FNO+H^+$ 386.2854, found 386.2855.



3k

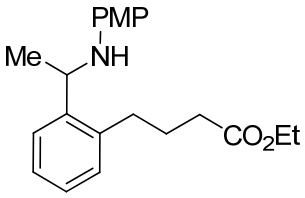
***N*-{1-(2-*n*-Dodecyl-4-fluorophenyl)ethyl}-4-methoxyaniline (3k):** General procedure **B** was followed using *N*-{1-(4-fluorophenyl)ethyliden}-4-methoxyaniline (124 mg, 0.50 mmol) and 1-bromo-*n*-dodecane (384 mg, 1.54 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3k** (143 mg, 69 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.49–7.39 (dd, *J* = 8.6, 6.1 Hz, 1H), 6.97–6.79 (m, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 4.65 (q, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 2.80–2.68 (m, 2H), 1.79–1.61 (m, 4H), 1.43–1.27 (m, 20H), 0.93 (t, *J* = 6.7 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 159.8 (C_q, $^1J_{C\text{-}F}$ = 239 Hz), 150.1 (C_q), 139.6 (C_q, $^3J_{C\text{-}F}$ = 7 Hz), 136.4 (C_q), 136.3 (C_q, 4$JC_{\text{-}F}$ = 3 Hz), 124.8 (CH, $^3J_{C\text{-}F}$ = 7 Hz), 114.0 (CH, $^2J_{C\text{-}F}$ = 19 Hz), 112.9 (CH), 112.9 (CH), 112.5 (CH), 112.5 (CH), 111.2 (CH, $^2J_{C\text{-}F}$ = 20 Hz), 53.8 (CH_3), 47.9 (CH), 30.1 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 27.8 (CH_2), 27.8 (CH_2), 27.7 (CH_2), 27.5 (CH_2), 22.3 (CH_3), 12.3 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -117.01 – -116.81 (m). IR (NaCl): 3396, 2953, 2927, 2853, 1613, 1589, 1465, 1267, 1140, 955 cm^{-1}. MS (EI) *m/z* (relative intensity) 413 (60) [M^+], 398 (18), 290 (7), 150 (10), 137 (62), 123 (100), 108 (6), 43 (8).HRMS (ESI): *m/z* calcd for $C_{27}H_{40}FNO+H^+$ 414.3167, found 414.3168.



3l

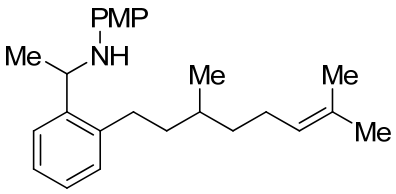
6-[2-{1-(4-Methoxyphenylamino)ethyl}phenyl]hexanoic acid methyl ester (3l): General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (113 mg, 0.50 mmol) and 6-bromo-*n*-hexanoic acid methyl ester (314 mg, 1.50 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3l** (116 mg, 66%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.43 (m, 1H), 7.16–7.12 (m, 3H), 6.83 (bs, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.42 (d, *J* = 8.9 Hz, 2H), 4.63 (q, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 3.65 (s,

3H), 2.72 (dt, *J* = 7.2, 3.2 Hz, 2H), 2.31 (dd, *J* = 7.7, 7.3 Hz, 2H), 1.72–1.62 (m, 4H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.44 (q, *J* = 7.4 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.1 (C_q), 151.9 (C_q), 142.5 (C_q), 141.5 (C_q), 139.0 (C_q), 129.5 (CH), 126.7 (CH), 126.5 (CH), 124.9 (CH), 114.8 (CH), 114.4 (CH), 55.7 (CH_3), 51.4 (CH_3), 50.1 (CH), 34.0 (CH_2), 32.0 (CH_2), 30.8 (CH_2), 29.3 (CH_2), 24.8 (CH_2), 24.0 (CH_3). IR (NaCl): 3399, 2934, 2863, 1733, 1508, 1438, 1234, 1038, 819, 758 cm^{-1}. MS (EI): *m/z* (relative intensity) 355 (12) [M^+], 340 (5), 232 (11), 158 (9), 123 (100), 91 (34), 85 (18), 59 (12), 41 (25). HR-MS (ESI) *m/z* calcd for $C_{22}H_{29}NO_3$+H^+ 356.2220, found 356.2221.



3m

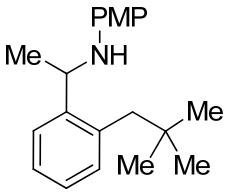
4-[2-{1-(4-Methoxyphenylamino)ethyl}phenyl]butanoic acid ethyl ester (3m): General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (113 mg, 0.50 mmol) and 4-bromobutanoic acid methyl ester (293 mg, 1.50 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3m** (111 mg, 68 %) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45 (m, 1H), 7.18–7.14 (m, 3H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 4.66 (q, *J* = 6.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 2.75 (dd, *J* = 8.2, 7.8 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.04–1.94 (m, 2H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.3 (C_q), 151.9 (C_q), 142.6 (C_q), 141.5 (C_q), 138.1 (C_q), 129.6 (CH), 126.8 (CH), 126.8 (CH), 125.1 (CH), 114.7 (CH), 114.4 (CH), 60.3 (CH_2), 55.7 (CH_3), 50.1 (CH), 34.1 (CH_2), 31.4 (CH_2), 26.2 (CH_2), 23.9 (CH_3), 14.2 (CH_3). IR (NaCl): 3394, 2963, 2831, 1733, 1507, 1456, 1372, 1234, 1037, 819 cm^{-1}. MS (EI): *m/z* (relative intensity) 341 (67) [M^+], 326 (18), 296 (12), 218 (37), 173 (35), 145 (36), 123 (100), 108 (21), 91 (15). HR-MS (ESI) *m/z* calcd for $C_{21}H_{27}NO_3$+H^+ 342.2064, found 342.2066.



3n

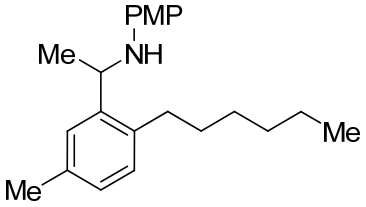
***N*-[1-{2-(3,7-dimethyl-*n*-oct-6-enyl)phenyl}ethyl]-4-methoxyaniline (3n)**: General procedure **B** was followed 4-methoxy-*N*-(1-phenylethylidene)aniline (113 mg, 0.50 mmol) and citronellyl bromide (329 mg, 1.50 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3n** (94 mg, 51%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of diastereoisomers 1:1): δ = 7.44 (m, 1H), 7.19–7.13 (m, 3H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.14–5.08 (m, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 2.76–2.68 (m, 2H), 2.03–1.96 (m, 2H), 1.65–1.34 (m, 3H), 1.69 (s, 3H, overlapped with a broad multiplet), 1.61 (s, 3H,

overlapped with a broad multiplet), 1.48 (d, *J* = 6.6 Hz, 3H, overlapped with a broad multiplet), 1.27–1.15 (m, 2H), 0.98 (d, *J* = 6.4, Hz, 1.5H, diastereomeric CH_3), 0.97 (d, *J* = 6.4, Hz, 1.5H, diastereomeric CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 151.9 (C_q), 142.4 (C_q), 141.5 (C_q), 139.7 (C_q), 131.2 (C_q), 129.6 (CH), 126.7 (CH), 126.4 (CH), 124.9 (CH), 124.8 (CH), 114.8 (CH), 114.4 (CH), 55.7 (CH_3), 50.1 (CH), 38.8 (diastereoismeric CH_2), 38.7 (diastereoismeric CH_2), 37.0 (diastereoismeric CH_2), 36.9 (diastereoismeric CH_2), 32.8 (CH), 29.8 (diastereoismeric CH_2), 29.7 (diastereoismeric CH_2), 25.7 (CH_3), 25.6 (diastereoismeric CH_2), 25.5 (diastereoismeric CH_2), 24.0 (CH_3), 19.6 (CH_3), 17.6 (CH_3). IR (NaCl): 3402, 2923, 1507, 1456, 1374, 1234, 1179, 1040, 817, 757 cm^{-1}. MS (EI): *m/z* (relative intensity) 365 (27) [M^+], 350, (9), 199 (10), 173 (13), 131 (10), 123 (100), 108 (14), 69 (23). HR-MS (ESI) *m/z* calcd for $C_{25}H_{35}NO+H^+$ 366.2791, found 366.2798.



3o

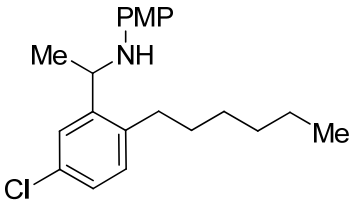
4-Methoxy-*N*-{1-(2-neopentylphenyl)ethyl}aniline (3o): General procedure **B** was followed using 4-methoxy-*N*-(1-phenylethylidene)aniline (114 mg, 0.50 mmol) and *neo*-pentyl bromide (235 mg, 1.55 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3o** (88 mg, 59%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 7.1 Hz, 1H), 7.27–7.17 (m, 3H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 4.80 (q, *J* = 6.4 Hz, 1H), 3.74 (s, 3H), 2.71 (d, *J* = 13.8 Hz, 2H), 2.65 (d, *J* = 13.8 Hz, 2H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.01 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 152.1 (C_q), 143.5 (C_q), 141.4 (C_q), 136.8 (C_q), 132.1 (CH), 126.6 (CH), 126.0 (CH), 125.1 (CH), 115.0 (CH), 114.8 (CH), 55.7 (CH_3), 50.2 (CH), 44.7 (CH_2), 32.7 (C_q), 30.0 (CH_3), 22.7 (CH_3). IR (NaCl): 3383, 3024, 2964, 2866, 1519, 1476, 1363, 1251, 1129, 765 cm^{-1}. MS (EI): *m/z* (relative intensity) 297 (100) [M^+], 282 (46), 261 (14), 174 (27), 159 (65), 133 (10), 123 (97), 119 (63), 108 (16), 91 (10), 69 (6), 57 (24), 41 (15). HRMS (ESI): *m/z* calcd for $C_{20}H_{27}NO+H^+$ 298.2165, found 298.2166.



3p

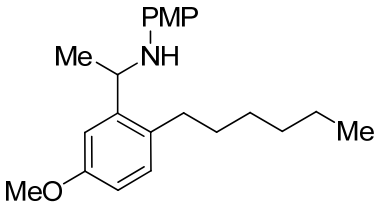
***N*-{1-(2-*n*-Hexyl-5-methylphenyl)ethyl}-4-methoxyaniline (3p):** General procedure **B** was followed using 4-methoxy-*N*-(1-*m*-tolylethyliden)aniline **(1a)** (130 mg, 0.54 mmol) and **2a** (246 mg, 1.49 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3p** (85 mg, 52%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 1.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.70 (d, *J*

= 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 4.63 (q, *J* = 6.4 Hz, 1H), 3.69 (s, 3H), 2.73–2.62 (m, 2H), 2.26 (s, 3H), 1.72–1.54 (m, 2H), 1.50–1.22 (m, 9H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.7 (C_q), 142.2 (C_q), 141.6 (C_q), 136.2 (C_q), 135.6 (C_q), 129.4 (CH), 127.4 (CH), 125.4 (CH), 114.7 (CH), 114.4 (CH), 55.8 (CH_3), 50.2 (CH), 32.0 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 24.1 (CH_3), 22.7 (CH_2), 21.3 (CH_3), 14.2 (CH_3). IR (NaCl): 3395, 2955, 2928, 2856, 1511, 1464, 1305, 1236, 1168, 1039, 909, 818, 733, 647 cm^{-1}. MS (EI): *m/z* (relative intensity) 325 (41) [M^+], 310 (26), 202 (57), 173 (6), 159 (19), 134 (9), 133 (100), 123 (62), 108 (12), 91 (7), 41 (5). HRMS (ESI): *m/z* calcd for $C_{22}H_{31}NO+H^+$ 326.2478, found 326.2478.



3q

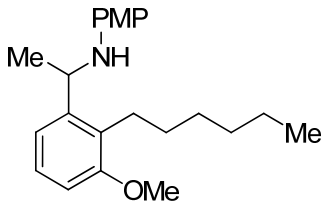
***N*-{1-(5-Chloro-2-*n*-hexylphenyl)ethyl}-4-methoxyaniline (3q):** General procedure **B** was followed using 4-methoxy-*N*-{1-(3-chlorophenyl)ethyliden}aniline **(1b)** (128 mg, 0.51 mmol) and **2a** (243 mg, 1.47 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3q** (119 mg, 68%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 1.2 Hz, 1H), 7.14–7.10 (m, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 9.0 Hz, 2H), 4.58 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 2.75–2.59 (m, 2H), 1.77–1.54 (m, 2H), 1.49–1.19 (m, 9H), 0.92–0.81 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 152.2 (C_q), 144.5 (C_q), 140.9 (C_q), 137.7 (C_q), 132.2 (C_q), 130.9 (CH), 126.8 (CH), 125.2 (CH), 114.8 (CH), 114.7 (CH), 55.6 (CH_3), 50.5 (CH), 31.7 (CH_2), 31.6 (CH_2), 31.0 (CH_2), 29.4 (CH_2), 24.0 (CH_2), 22.6 (CH_2), 14.1. IR (ATR): 3401, 2954, 2927, 2856, 1592, 1509, 1464, 1374, 1233, 1120, 1038, 815, 757, 663, 518 cm^{-1}. MS (EI): *m/z* (relative intensity) 345 (60) [M^+], 330 (59), 222 (33), 179 (22), 153 (65), 123 (100), 108 (53), 91 (12), 43 (20). HRMS (ESI): *m/z* calcd for $C_{21}H_{28}NOCl^+$ 346.1859, found 345.1860.



3r

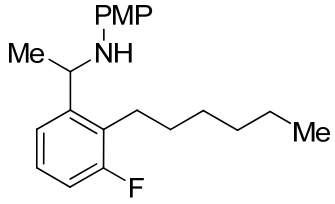
***N*-{1-(2-*n*-Hexyl-5-methoxyphenyl)ethyl}-4-methoxyaniline (3r) and *N*-{1-(2-*n*-Hexyl-3-methoxyphenyl)ethyl}-4-methoxyaniline (3s):** General procedure **B** was followed using 4-methoxy-*N*-{1-(3-methoxyphenyl)-ethyliden}aniline **(1c)** (117 mg, 0.46 mmol) and **2a** (248 mg, 1.50 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3r** (60 mg, 38%) and **3s** (31 mg, 20%) as colourless oils.

(3q): ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.09 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 2H), 4.60 (q, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.66 (dt, *J* = 8.7, 4.2 Hz, 2H), 1.71–1.56 (m, 2H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.43–1.23 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 158.1 (C_q), 151.7 (C_q), 144.0 (C_q), 141.5 (C_q), 131.3 (C_q), 130.4 (CH), 114.7 (CH), 114.3 (CH), 111.6 (CH), 110.6 (CH), 55.7 (CH_3), 55.1 (CH_3), 50.3 (CH), 31.8 (CH_2), 31.5 (CH_2), 31.5 (CH_2), 29.5 (CH_2), 24.2 (CH_3), 22.7 (CH_2), 14.2 (CH_3). IR (NaCl): 2985, 2940, 2899, 1741, 1514, 1456, 1373, 1241, 1097, 1047, 847 cm^{-1}. MS (EI): *m/z* (relative intensity) 341 (50) [M^+], 326 (21), 284 (6), 227 (14), 218 (100), 175 (38), 149 (78), 123 (39), 105 (17), 77 (8). HRMS (ESI): *m/z* calcd for $C_{22}H_{31}NO_2$+H^+ 342.2428, found 342.2426.



3s

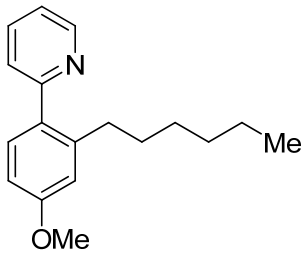
(3s): ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.12 (dd, *J* = 8.0, 7.7 Hz, 1H), 7.08 (dd, *J* =8.0, 1.5 Hz, 1H), 6.75 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 6.47 (d, *J* = 9.0 Hz, 2H), 4.67 (q, *J* = 6.6 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 2.89–2.52 (m, 2H), 1.69–1.52 (m, 2H), 1.51–1.22 (m, 9H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 157.6 (C_q), 151.8 (C_q), 143.8 (C_q), 141.5 (C_q), 128.4 (C_q), 126.8 (CH), 117.1 (CH), 114.7 (CH), 114.5 (CH), 108.7 (CH), 55.7 (CH_3), 55.4 (CH_3), 50.4 (CH), 31.7 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 25.4 (CH_2), 24.2(CH_3), 22.6 (CH_2), 14.1 (CH_3). IR (ATR): 3396, 2954, 2926, 2856, 1581, 1465, 1372, 1231, 1177 cm^{-1}. MS (EI): *m/z* (relative intensity) 341 (55) [M^+], 326 (41), 218 (80), 157 (34), 149 (100), 123 (72), 108 (24), 91 (21). HRMS (ESI): *m/z* calcd for $C_{22}H_{31}NO_2^+$ 341.2355, found 341.2363.



3t

***N*-{1-(3-Fluoro-2-*n*-hexylphenyl)ethyl}-4-methoxyaniline (3t):** General procedure **B** was followed using **1d** (122 mg, 0.50 mmol) and **2a** (244 mg, 1.48 mmol). Reduction and purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **3t** (121 mg, 74%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 7.7 Hz, 1H), 7.11 (dt, *J* = 8.3, 6.1 Hz, 1H), 6.90 (dt, *J* = 8.3, 1.7 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 4.64 (q, *J* = 6.6 Hz, 1H), 3.71 (s, 3H), 2.87–2.64 (m, 2H), 1.74–1.55 (m, 2H), 1.53–1.23 (m, 9H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 161.3 (C_q, $^{1}J_{C\text{-}F}$ = 243 Hz), 151.9 (C_q), 145.0 (C_q), 141.2 (C_q), 127.2 (CH, $^{3}J_{C\text{-}F}$ = 8 Hz), 126.8 (C_q, $^{2}J_{C\text{-}F}$ = 16 Hz), 120.4 (CH), 114.7 (CH), 114.4 (CH), 113.4 (CH, $^{2}J_{C\text{-}F}$ = 22 Hz), 55.7 (CH_3), 50.2 (CH), 31.7 (CH_2), 30.4 (CH_2), 29.7 (CH_2), 24.9 (CH_2), 24.3 (CH_3), 22.7 (CH_2), 14.1 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -

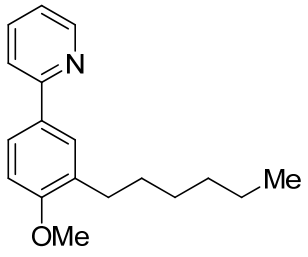
117.75 – -117.54 (m). IR (NaCl): 3403, 2960, 2930, 2871, 2859, 2244, 1579, 1512, 1464, 1238, 1180, 1040, 910, 819, 793, 739, 649 cm^{-1}. MS (EI): *m/z* (relative intensity) 329 (17) [M^+], 314 (18), 206 (9), 163 (6), 150 (12), 136 (47), 123 (100), 108 (25), 95 (8), 41 (5). HRMS (ESI): *m/z* calcd for $C_{21}H_{28}FNO+H^+$ 330.2228, found 330.2227.



3v

2-(2-*n*-hexyl-4-methoxyphenyl)pyridine (3v) and 2-(3-*n*-hexyl-4-methoxyphenyl)pyridine (3w): General procedure **B** was followed using $MesCO_2H$ (24 mg, 0.15 mmol, 29 mol %), K_2CO_3 (138 mg, 1.00 mmol), **1f** (94 mg, 0.51 mmol) and **2a** (236 mg, 1.43 mmol) in H_2O (2.0 mL). Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3v** (62 mg, 45%) and **3w** (9 mg, 7%) as colourless oils.

(3v): ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.63 (d, J = 4.7 Hz, 1H), 7.68 (td, *J* = 7.7, 1.9 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.20–7.15 (m, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.82 (s, 3H), 2.75–2.62 (m, 2H), 1.49–1.34 (m, 2H), 1.22–1.07 (m, 6H), 0.79 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) *δ* = 160.0 (C_q), 159.4 (C_q), 149.0 (CH), 142.4 (C_q), 135.9 (CH), 133.1 (C_q), 131.0 (CH), 124.1 (CH), 121.2 (CH), 115.2 (CH), 110.9 (CH), 55.2 (CH_3), 33.1 (CH_2), 31.4 (CH_2), 31.1 (CH_2), 29.0 (CH_2), 22.4 (CH_2), 14.0 (CH_3). IR (NaCl): 2927, 2855, 1587, 1505, 1465, 1427, 1280, 1236, 1162, 1045 cm^{-1}. MS (EI): *m/z* (relative intensity) 269 (33) [M^+], 226 (9), 212 (100), 197 (18), 154 (10). HR-MS (ESI) *m/z* calcd for $C_{18}H_{23}NO+H^+$ 270.1858, found 270.1852.
Analytical data are in accordance with those reported in the literature. [3]



3w

(3w): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.6 Hz, 1H), 7.83–7.74 (m, 2H), 7.60–7.47 (m, 2H), 7.10 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 2.72–2.59 (m, 2H), 1.65–1.54 (m, 2H), 1.41–1.25 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) *δ* = 158.4 (C_q) , 157.4 (C_q), 149.4 (CH), 136.6 (CH), 131.7 (C_q), 131.5 (C_q), 128.4 (CH), 125.4 (CH), 121.2 (CH), 119.9 (CH), 110.3 (CH), 55.4 (CH_3), 31.8 (CH_2), 30.4 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3). IR (ATR): 3176, 3003, 2954, 1606, 1587, 1426, 1279, 1149, 1129, 1019 cm^{-1}. MS (EI): *m/z*

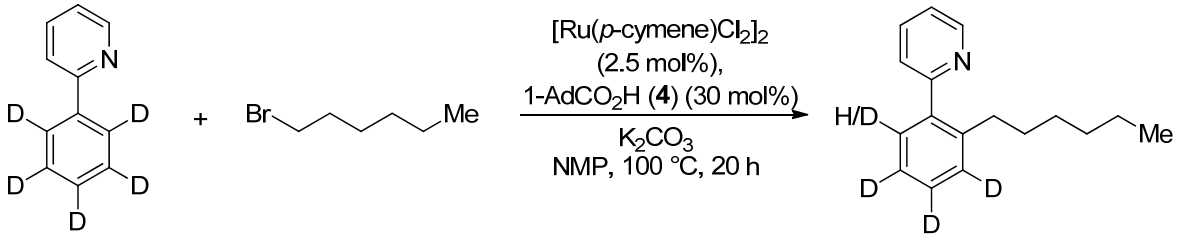
(relative intensity) 269 (77) [M^+], 238 (13), 226 (16), 198 (100), 168 (65), 154 (19), 43 (15). HRMS (ESI): *m/z* calcd for $C_{18}H_{23}NO^+$ 269.1780, found 269.1780.

Competition experiments

a) A suspension of $[RuCl_2(p\text{-cymene})]_2$ (15.4 mg, 0.025 mmol, 3.9 mol %), (1-Ad)CO_2H (**4**) (27.6 mg, 0.15 mmol, 24 mol %), K_2CO_3 (225 mg, 1.62 mmol), **1a** (254 mg, 0.98 mmol), **1b** (224 mg, 0.94 mmol) and **2a** (106 mg, 0.64 mmol) in *m*-xylene (3.0 mL) was stirred under N_2 for 20 h at 120 °C. A solution of $ZnCl_2$ in THF (0.65 mL, 1.10 mmol, 1.7 M), $NaBH_3CN$ (126 mg, 2.00 mmol) and MeOH (4.0 mL) was added to the cooled reaction mixture and the resulting mixture was stirred at ambient temperature. Analysis by GC showed that **3q** and **3p** were formed in a ratio of 4.4/1.0. Et_2O (30 mL) and sat. aq. K_2CO_3 (30 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 40 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 9:1) yielded **3q** (88 mg, 40%) as a colourless oil.

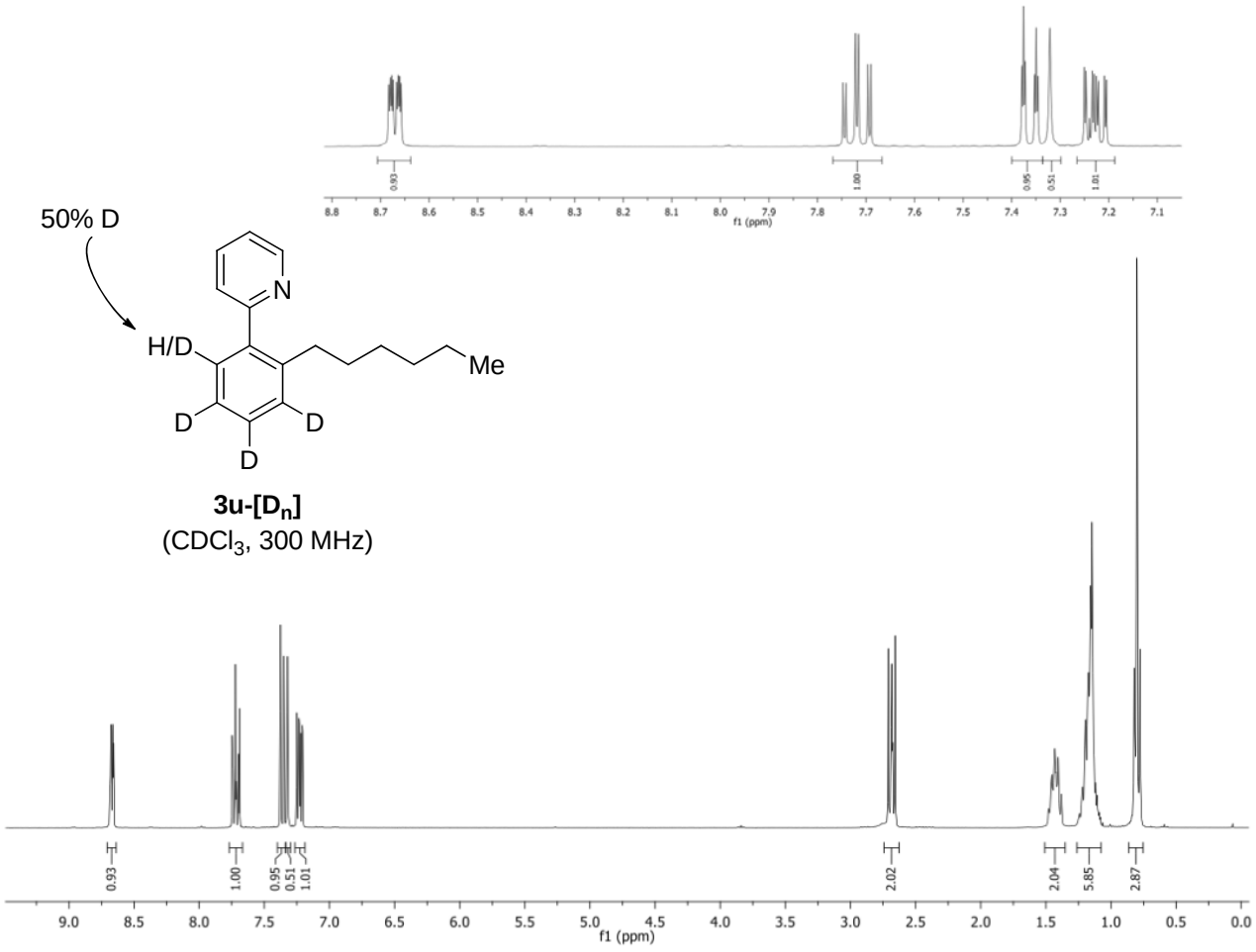
b) A suspension of $[RuCl_2(p\text{-cymene})]_2$ (15.0 mg, 0.025 mmol, 5.0 mol %), (1-Ad)CO_2H (**4**) (26.3 mg, 0.15 mmol, 30 mol %), K_2CO_3 (226 mg, 1.64 mmol), **1d** (244 mg, 1.00 mmol), **1b** (252 mg, 0.97 mmol) and **2a** (97 mg, 0.59 mmol) in *m*-xylene (3.0 mL) was stirred under N_2 for 20 h at 120 °C. A solution of $ZnCl_2$ in THF (0.65 mL, 1.10 mmol, 1.7 M), $NaBH_3CN$ (126 mg, 2.00 mmol) and MeOH (4.0 mL) was added to the cooled reaction mixture and the resulting mixture was stirred at ambient temperature. Analysis by GC showed that **3t** and **3q** were formed in a ratio of 3.2/1.0. Et_2O (30 mL) and sat. aq. K_2CO_3 (30 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 40 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **3t** (107 mg, 56%) and **3q** (42 mg, 20%) as colourless oils.

Direct alkylation of 1e-[D_5]

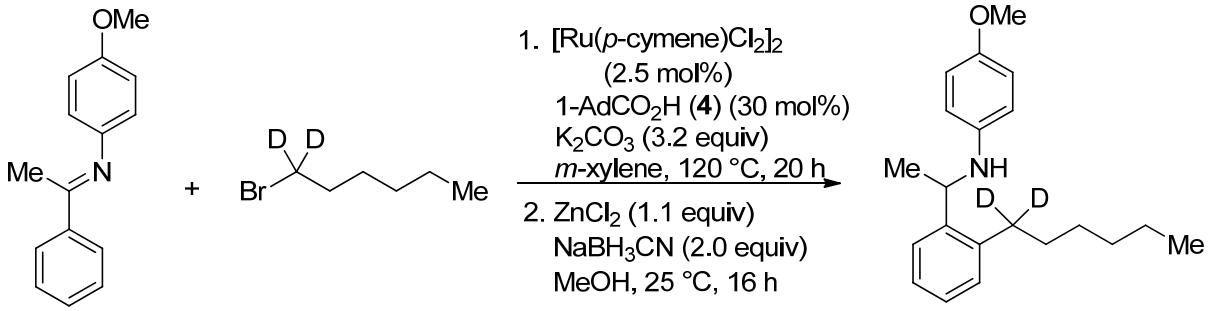


1e-[D_5] **2a** **3u-[D_n]**

A suspension of [Ru(*p*-cymene)Cl_2]$_2$ (7.7 mg, 0.0125 mmol, 2.5 mol %), **1e-[D_5]** (80 mg, 0.50 mmol), **2a** (248 mg, 1.50 mmol), **4** (27 mg, 0.15 mmol, 30 mol %) and K_2CO_3 (138 mg, 2.00 mmol) in NMP (2.0 mL) was stirred under N_2 for 20 h at 100 °C. *t*-BuOMe (25 mL) and H_2O (25 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with *t*-BuOMe (2 x 25 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 residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 15:1) to yield **3u-[D_n]** (55 mg, 45 %, 50 % D estimated by ^{1}H-NMR) as colourless oil.



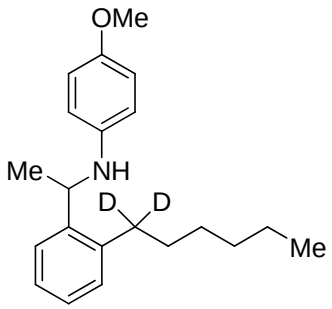
Direct alkylation of 2a-[D_2]



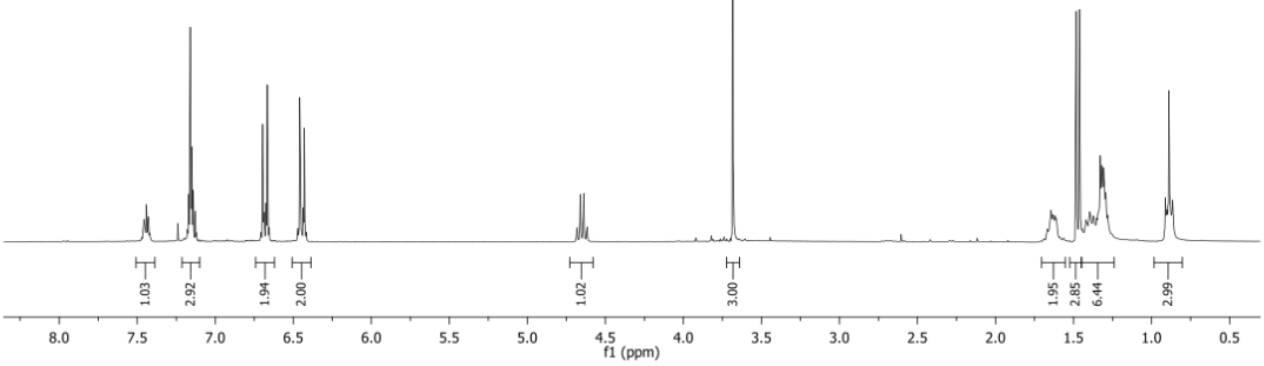
1 **2a-[D_2]** **3e-[D_2]**

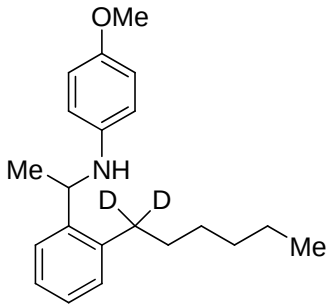
A suspension of [Ru(*p*-cymene)Cl_2]$_2$ (4.6 mg, 0.013 mmol, 2.5 mol %), 4-methoxy-*N*-(1-phenyl-ethylidene)aniline (68 mg, 0.30 mmol), **2a-[D_2]** (150 mg, 0.90 mmol), **4** (20 mg, 0.09 mmol, 30 mol %) and K_2CO_3 (132 mg, 0.96 mmol) in *m*-xylene (1.2 mL) was stirred under N_2 for 20 h at 120 °C. A solution of $ZnCl_2$ in THF (0.33 mL, 0.56 mmol, 1.7 M), $NaBH_3CN$ (63 mg, 1.00 mmol) and MeOH (2.0 mL) was added to the cooled reaction mixture and the resulting mixture, was stirred at ambient temperature. After 16 h sat. aq. K_2CO_3 (60 mL) was added and the separated aqueous phase was extracted with *t*-BuOMe (3 x 60 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuum. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 9:1) to yield **3e-[D_2]** (47 mg, 50%, >95% D as estimated by ESI analysis and ^{1}H-NMR) as a yellow oil.

***N*-[1-{2-(1,1-Dideutero-*n*-hexyl)phenyl}ethyl]-4-methoxyaniline (3e-[D_2])**: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 1H), 7.17–7.13 (m, 3H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 4.65 (q, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 1.65-1.61 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 3H), 1.40-1.27 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 151.9 (C_q), 142.5 (C_q), 141.6 (C_q), 139.4 (C_q), 129.5 (CH), 126.7 (CH), 126.4 (CH), 124.9 (CH), 114.8 (CH), 114.4 (CH), 55.7 (CH_3), 50.1 (CH), 31.6 (CH_2), 31.5 (m, CD_2) 31.0 (CH_2), 29.4 (CH_2), 24.0 (CH_3), 22.6 (CH_2), 14.1 (CH_3) . IR (NaCl): 2928, 2856, 2361, 2339, 1512, 1457, 1235, 1040, 818, 757 cm^{-1}. MS (EI): *m/z* (relative intensity) 313 (16) [M^+], 298 (11), 209 (21), 189 (16), 138 (100), 123 (45), 108 (15), 40 (22). HR-MS (ESI) *m/z* calcd for $[C_{21}H_{27}D_2NO+H]^+$ 314.2447, found 314.2446.

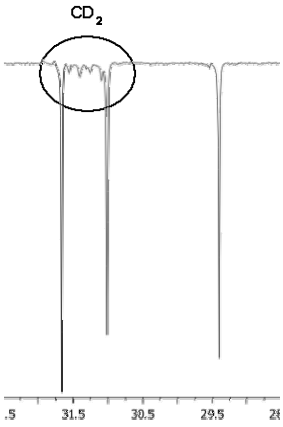


3e-[D_2]
($CDCl_3$, 300 MHz)





3e-[D_2]
($CDCl_3$, 75 MHz)



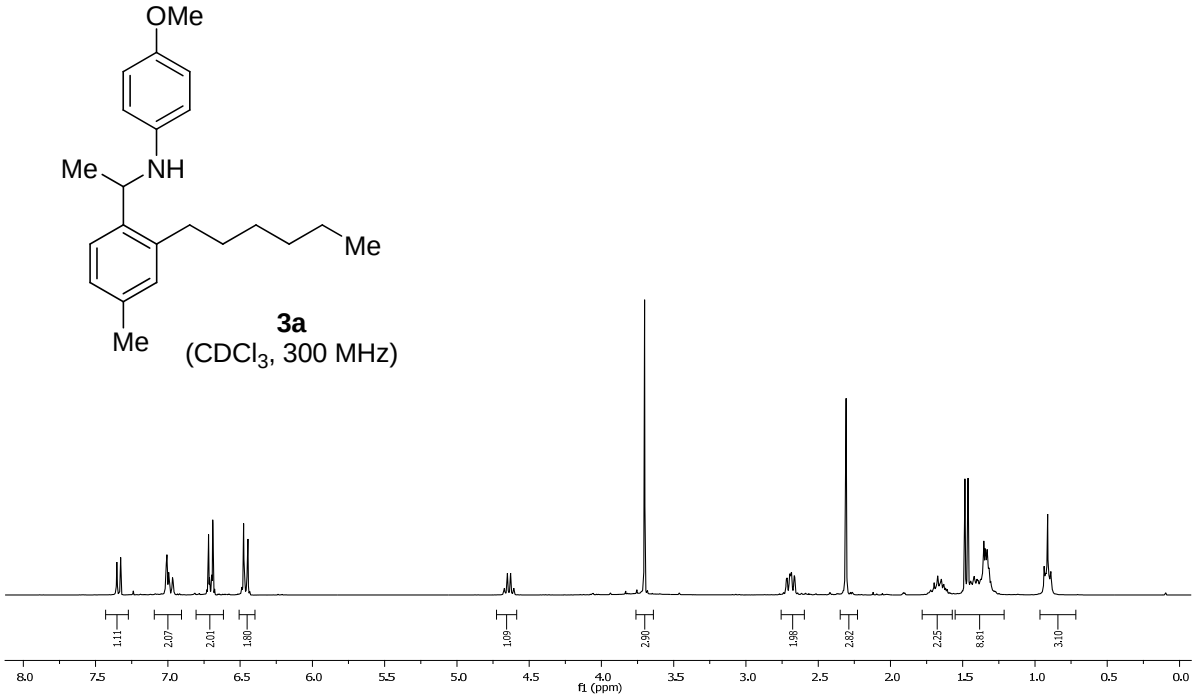
References

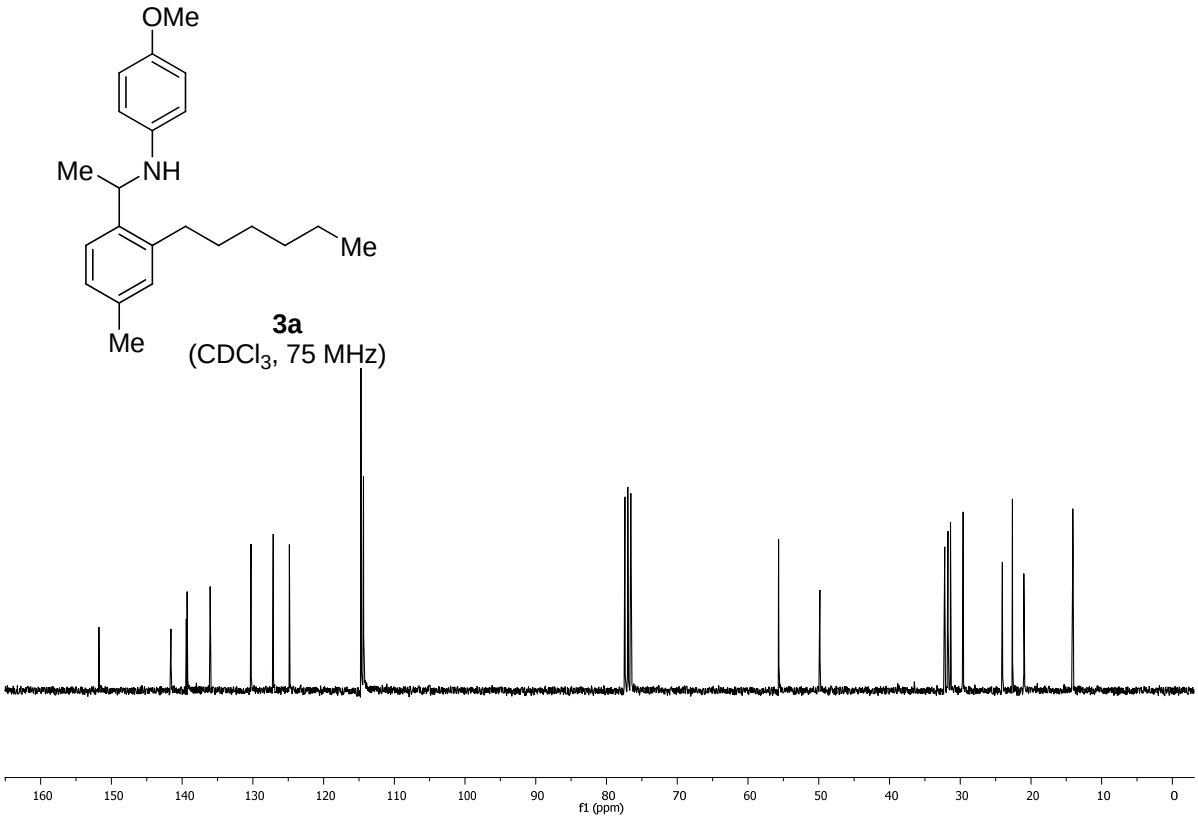
[1](a) Periasamy, M.; Srinivas, G.; Bharathi, P. *J. Org. Chem* **1999**, *64*, 4204–4205. (b) Mršić, N.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *J. Am. Chem. Soc.* **2009**, *131*, 8358-8359.

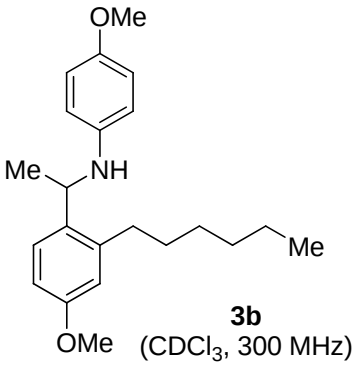
[2] Böhm, V. P. W .; Weskamp, T.; Gstöttmayr, C. W. K .; Herrmann W.A. *Angew. Chem., Int. Ed*. **2000**, *39*, 1602–1604.

[3] Ackermann, L.; Novák, P.; Vicente, R.; Hofmann, N. *Angew. Chem., Int. Ed.* **2009***, 48*, 6045–6048.

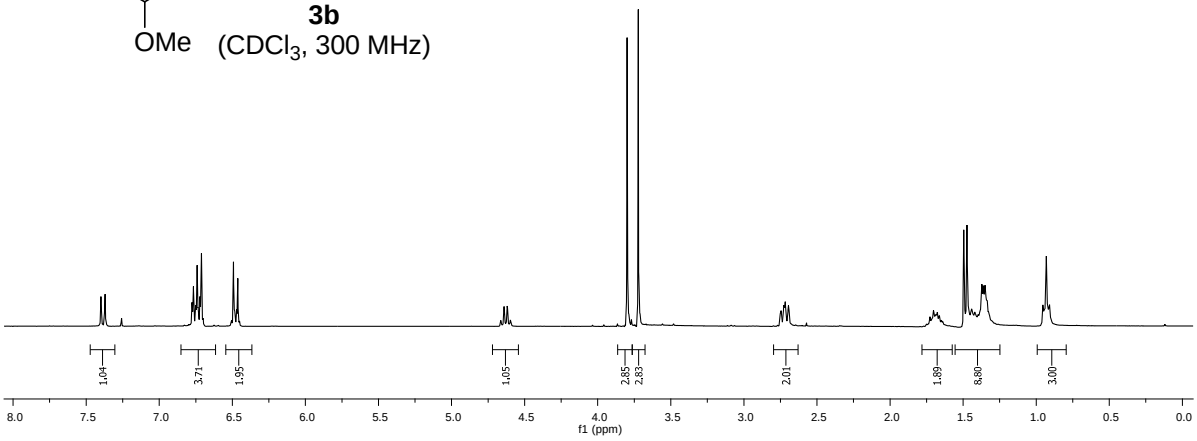
^{1}H-, ^{13}C-NMR spectra for compounds 3a–g

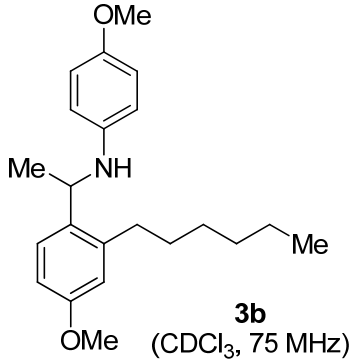




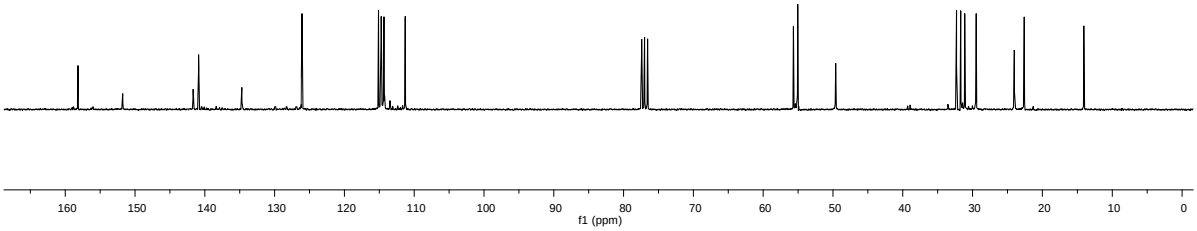


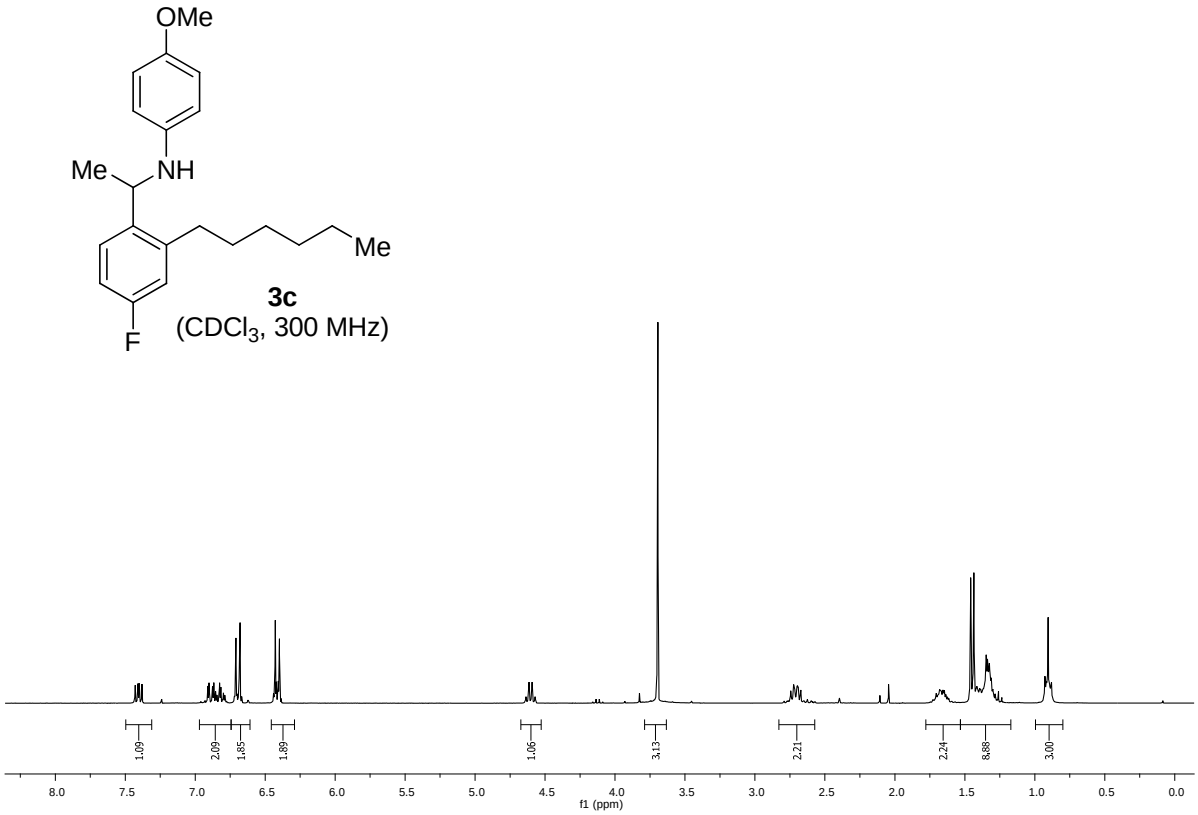
3b
($CDCl_3$, 300 MHz)





3b
($CDCl_3$, 75 MHz)




OMe
Me
NH
Me
F
3c
(CDCl3, 300 MHz)
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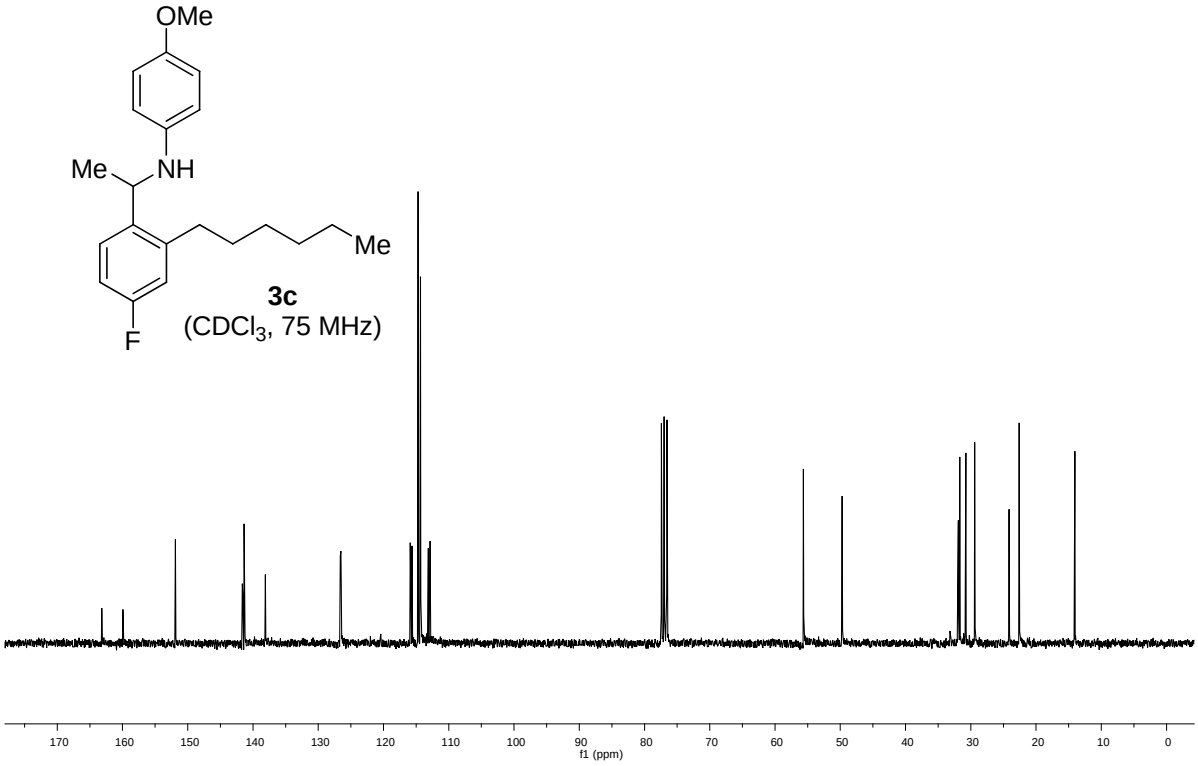
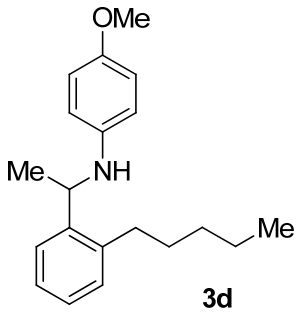
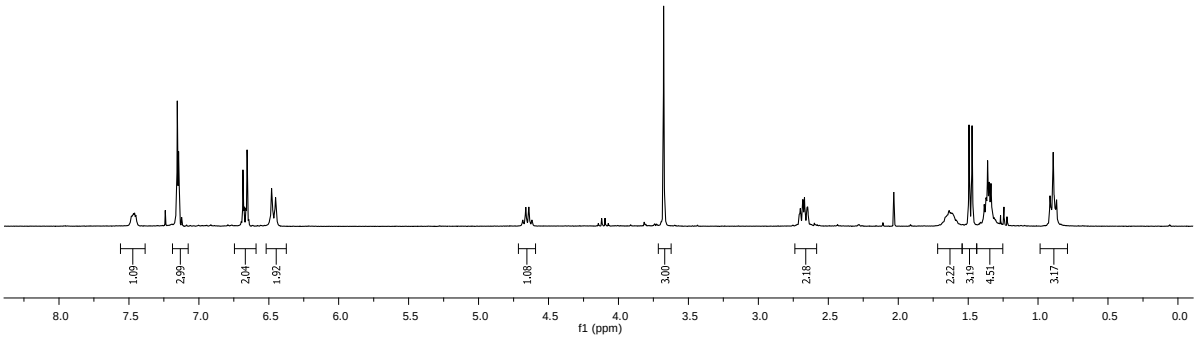
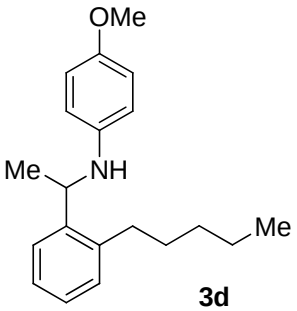
2.09
1.85
1.89
1.06
3.13
2.21
2.24
8.88
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
Me
NH
Me
F
3c
(CDCl3, 75 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

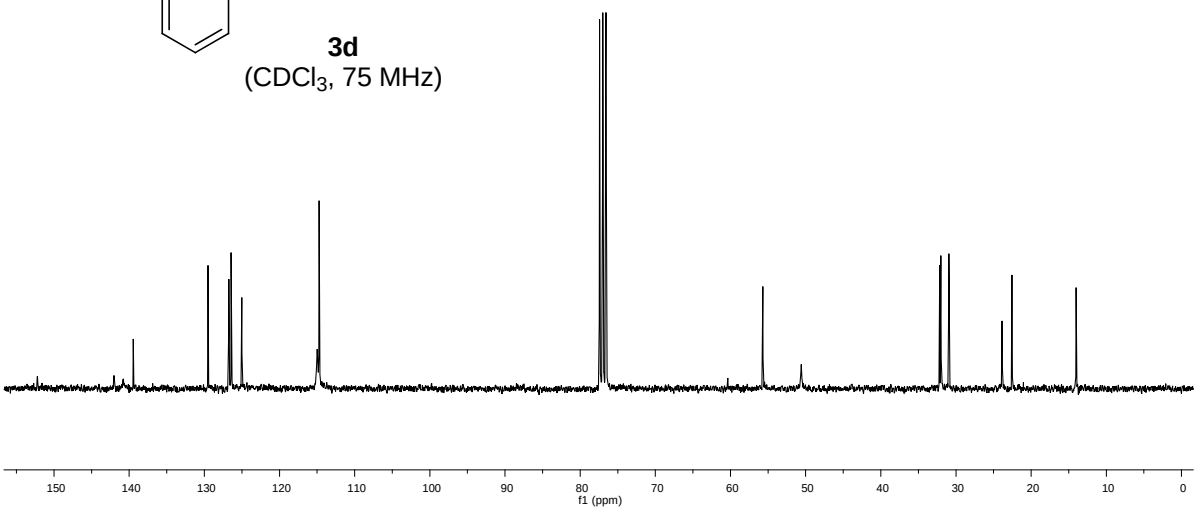


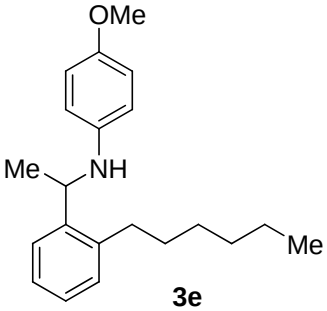
3d
($CDCl_3$, 300 MHz)





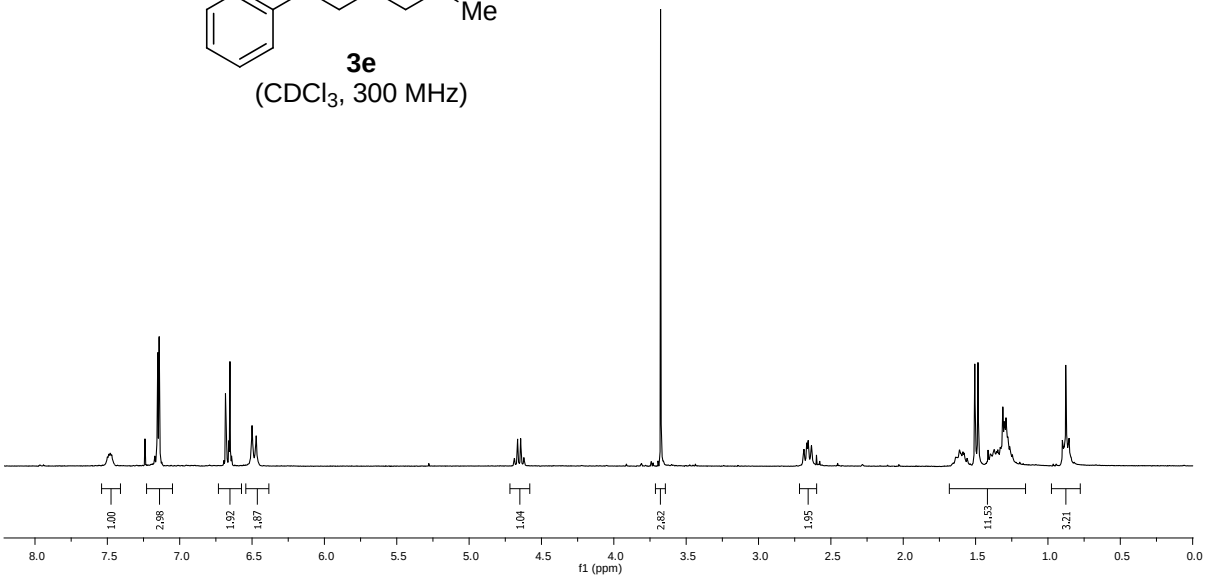
3d
($CDCl_3$, 75 MHz)

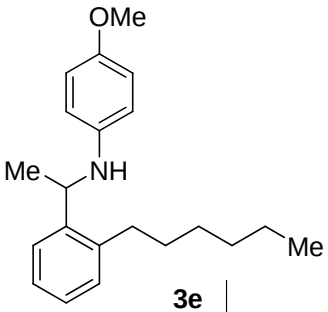




3e

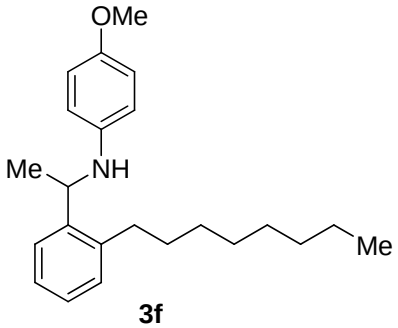
($CDCl_3$, 300 MHz)





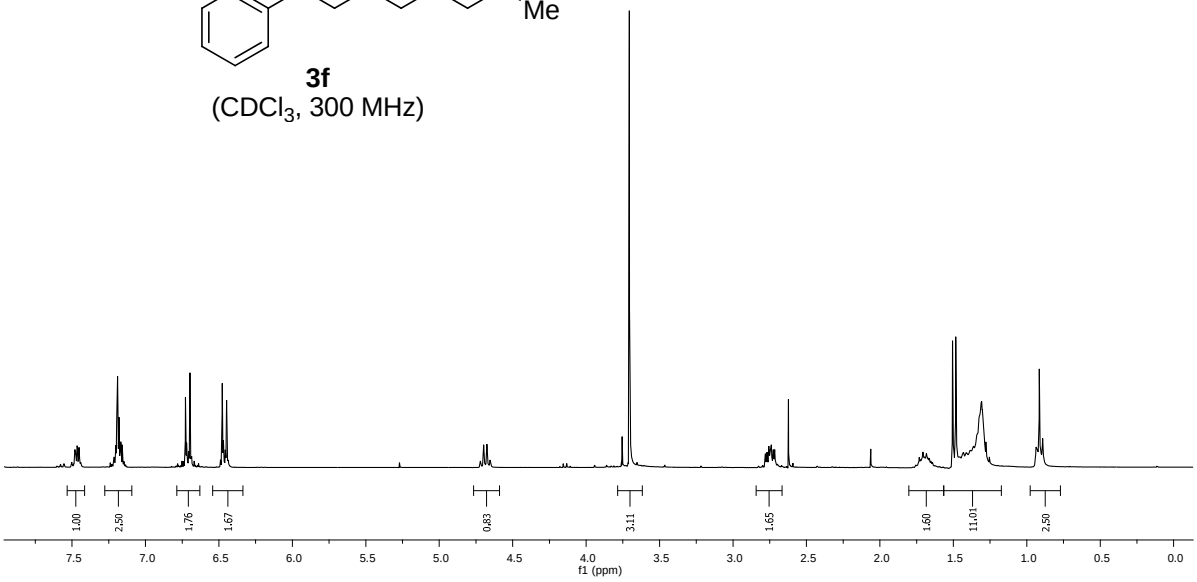
3e

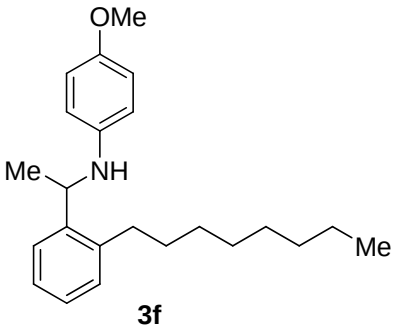
($CDCl_3$, 75 MHz)



3f

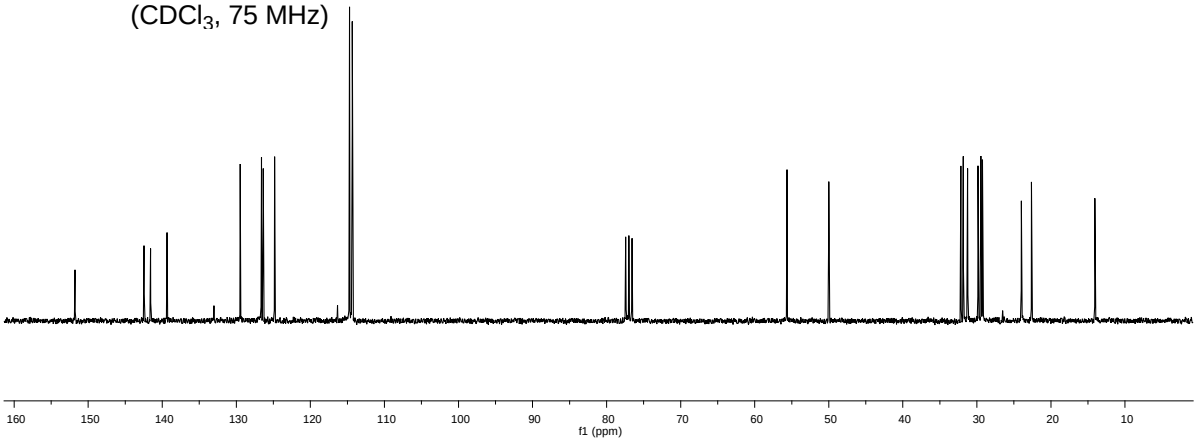
($CDCl_3$, 300 MHz)

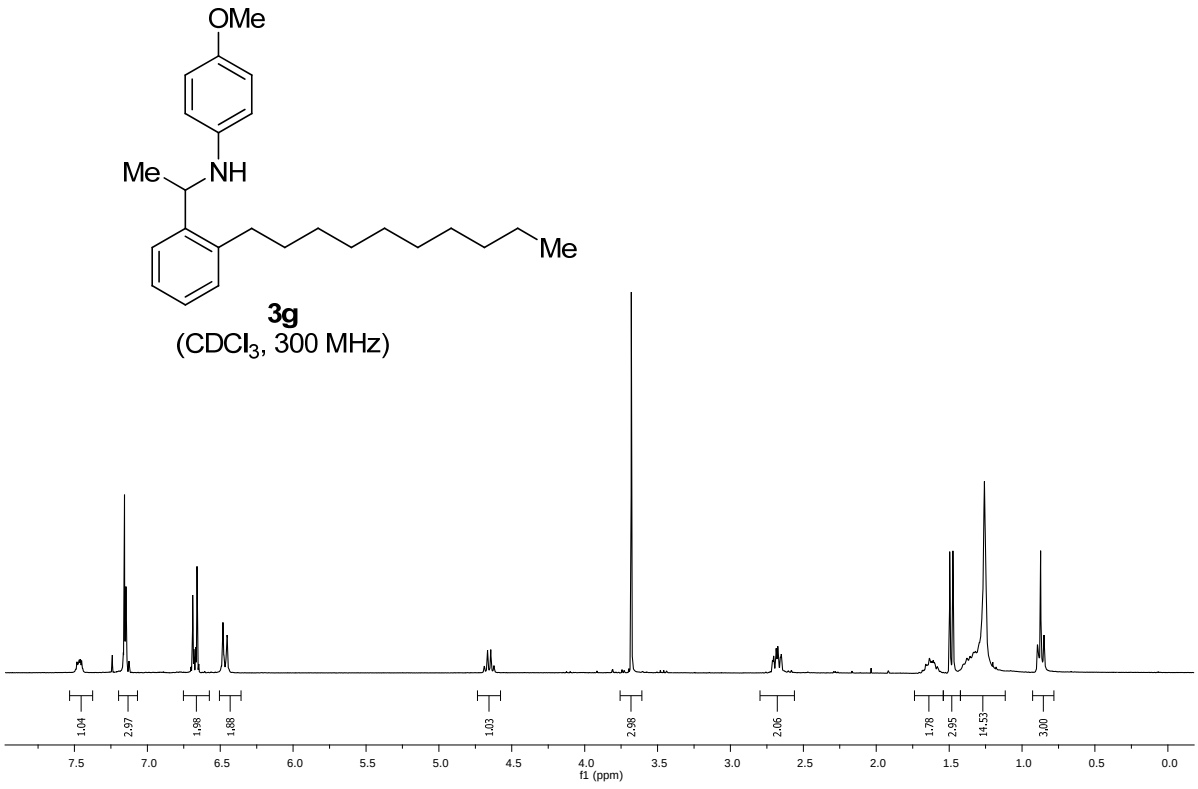


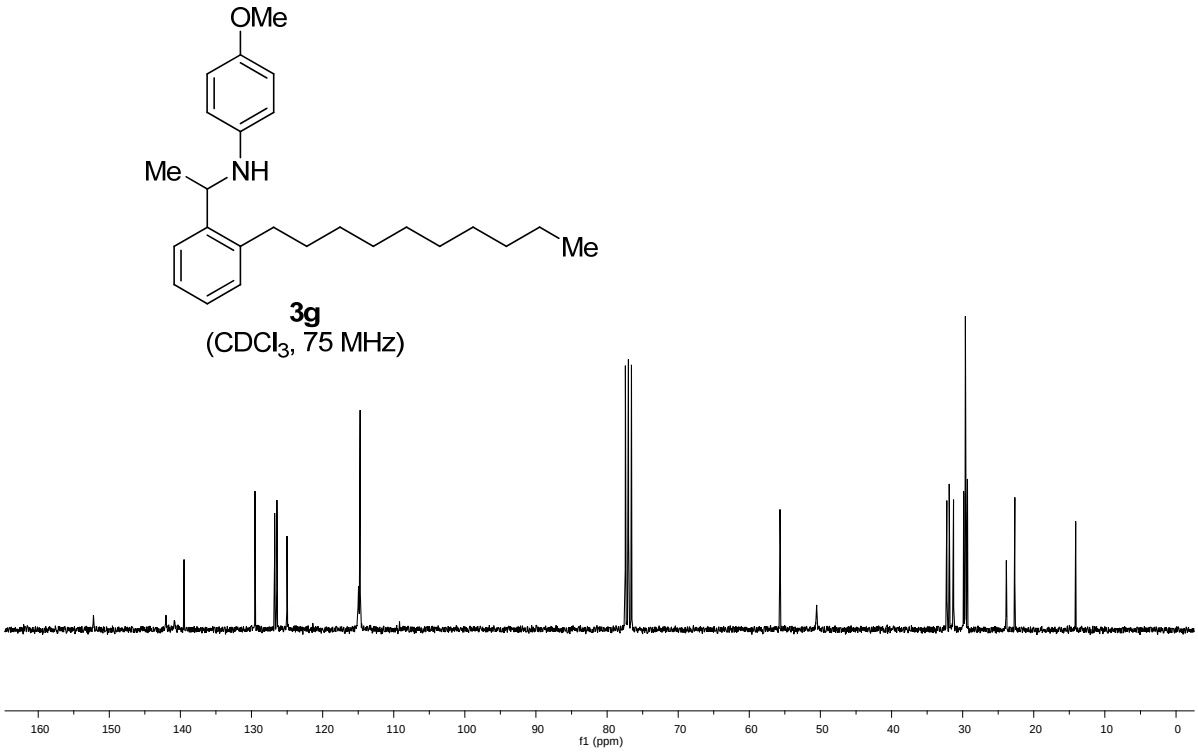


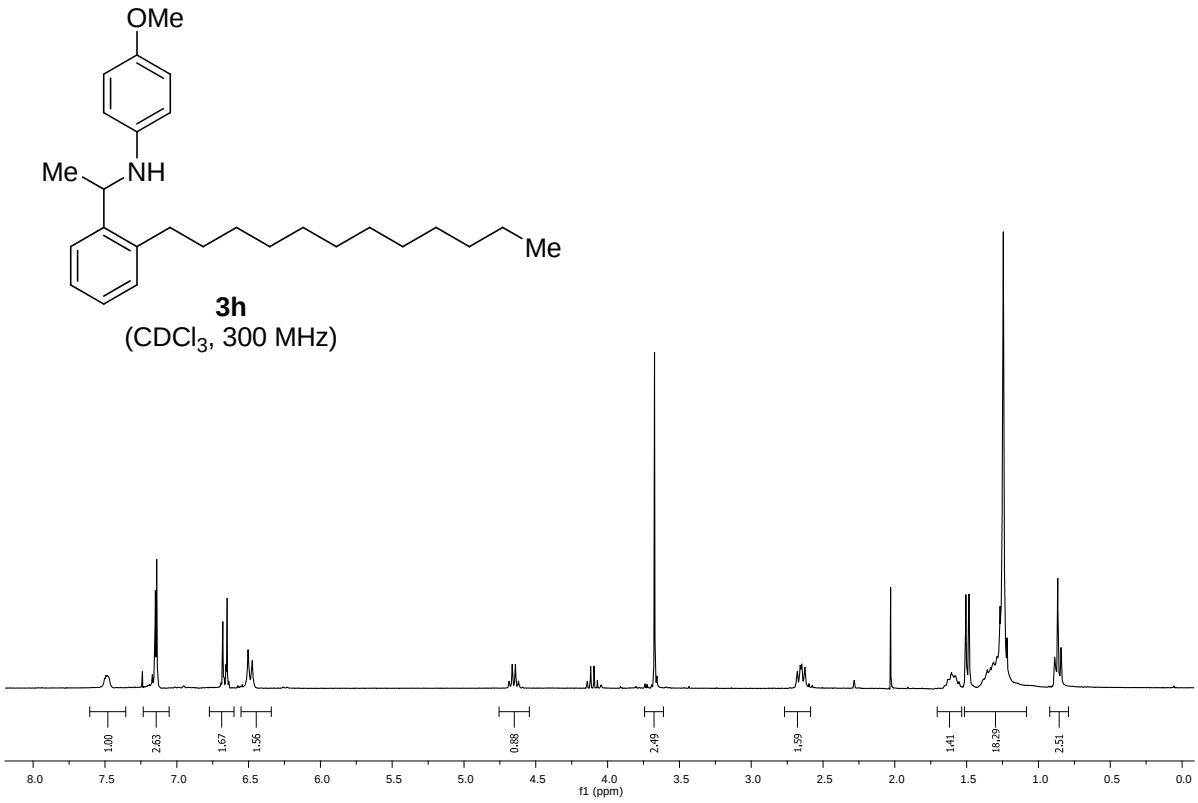
3f

($CDCl_3$, 75 MHz)

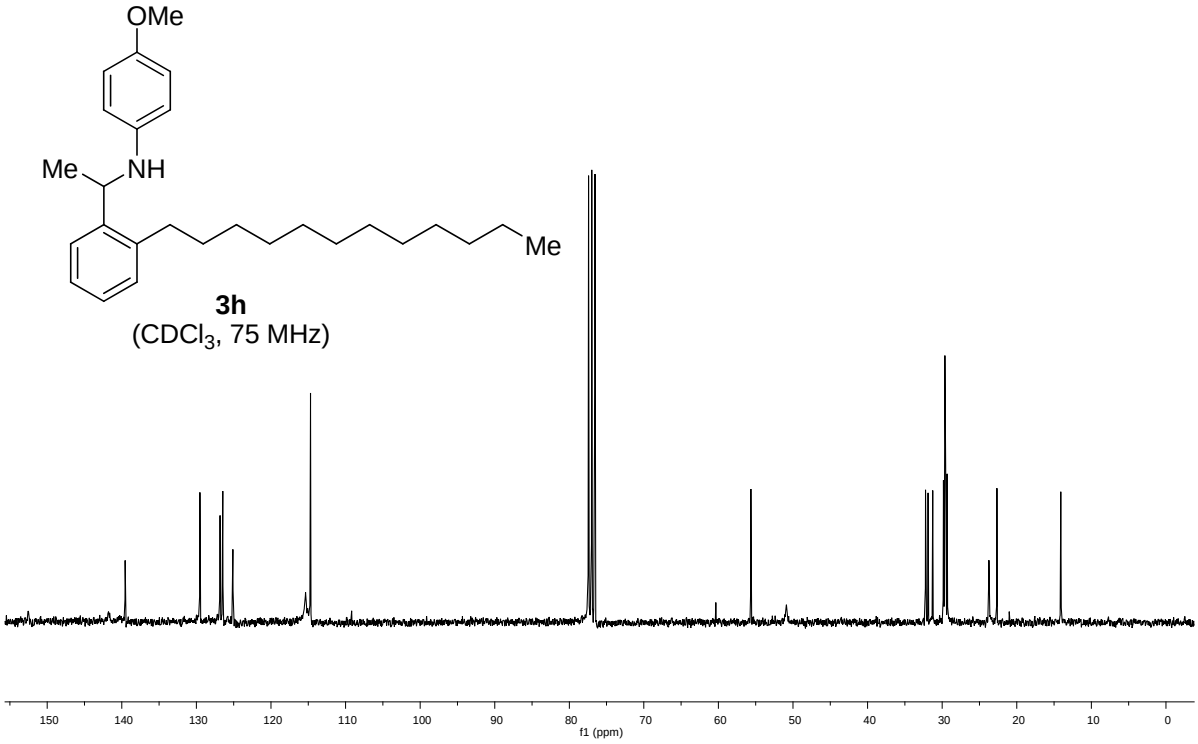



OMe
Me
NH
Me
3g
(CDCl3, 300 MHz)
1.04
2.97
1.98
1.88
1.03
2.98
2.06
1.78
2.95
14.53
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

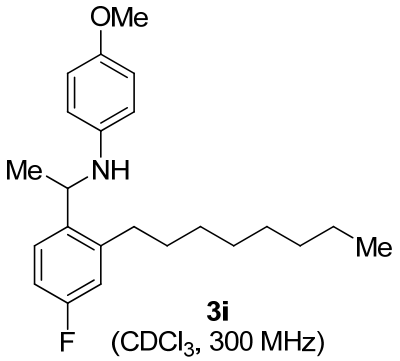

OMe
Me
NH
Me
3g
(CDCl3, 75 MHz)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3h
($CDCl_3$, 300 MHz)

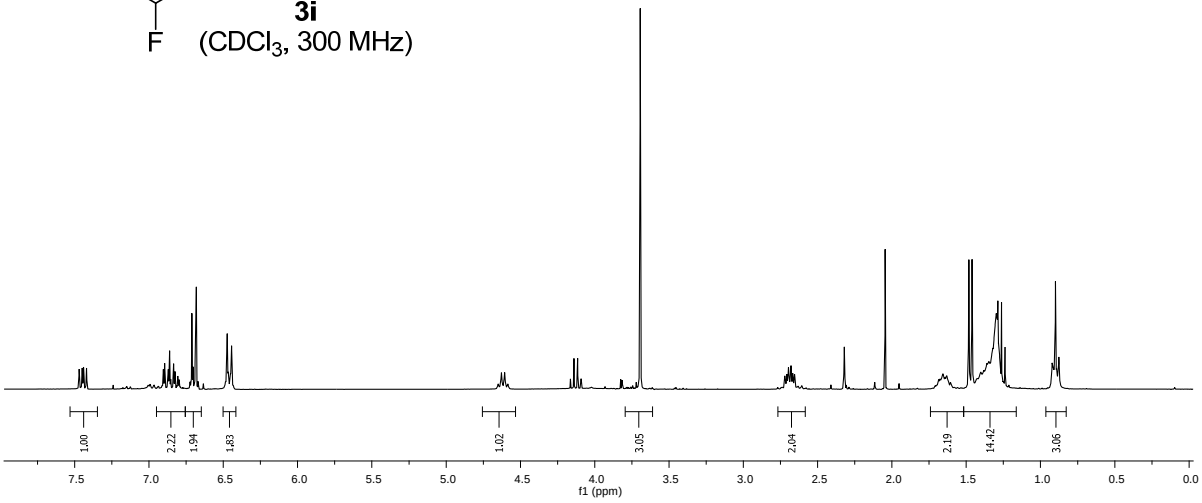


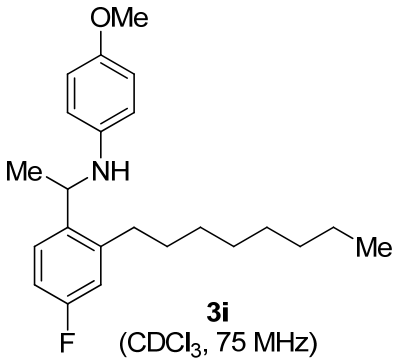
3h
($CDCl_3$, 75 MHz)



3i

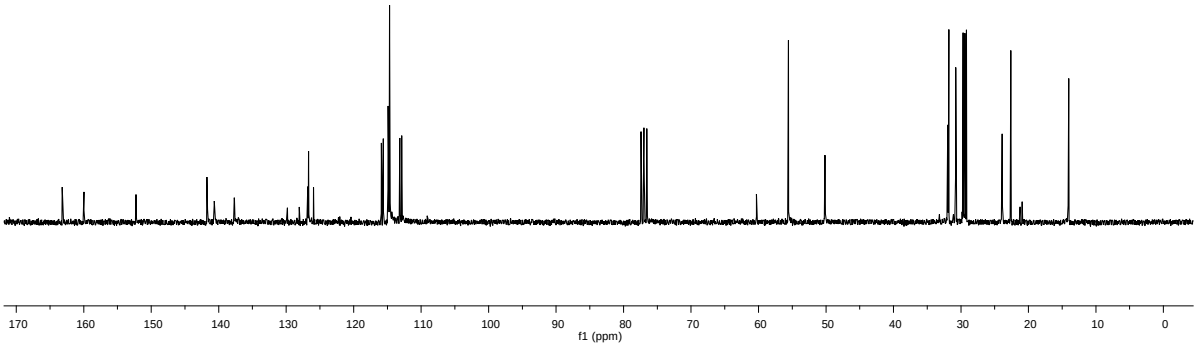
($CDCl_3$, 300 MHz)

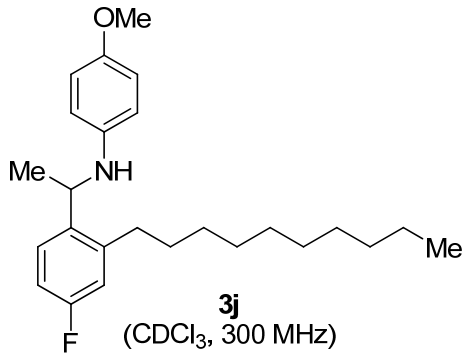




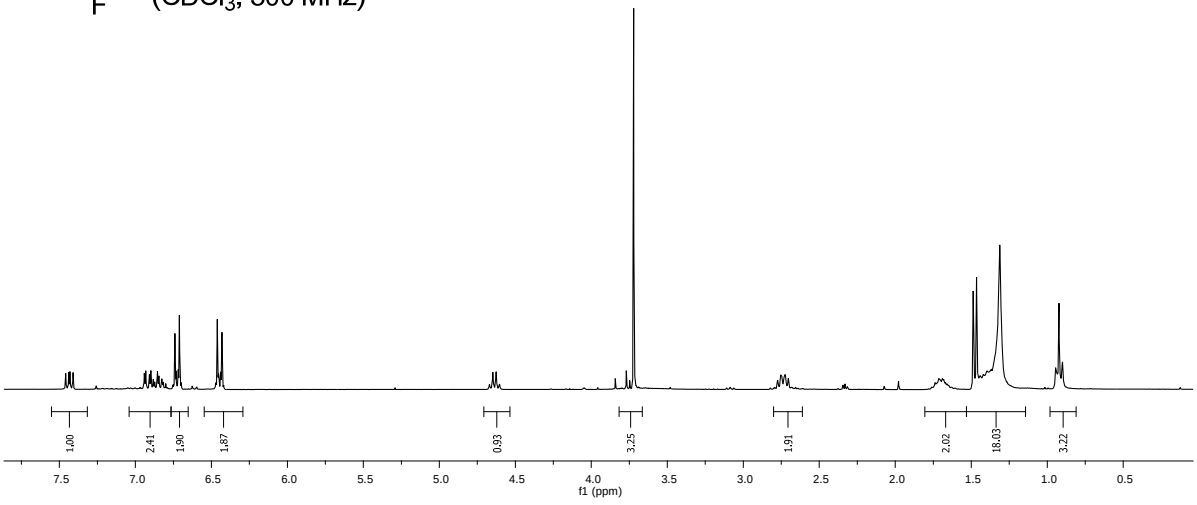
3i

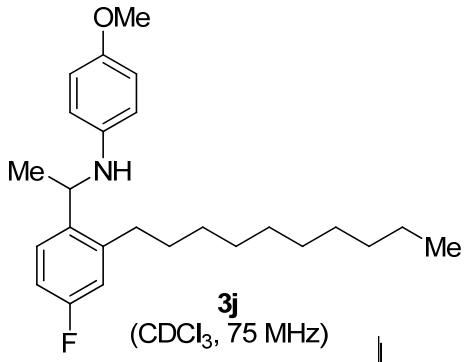
($CDCl_3$, 75 MHz)



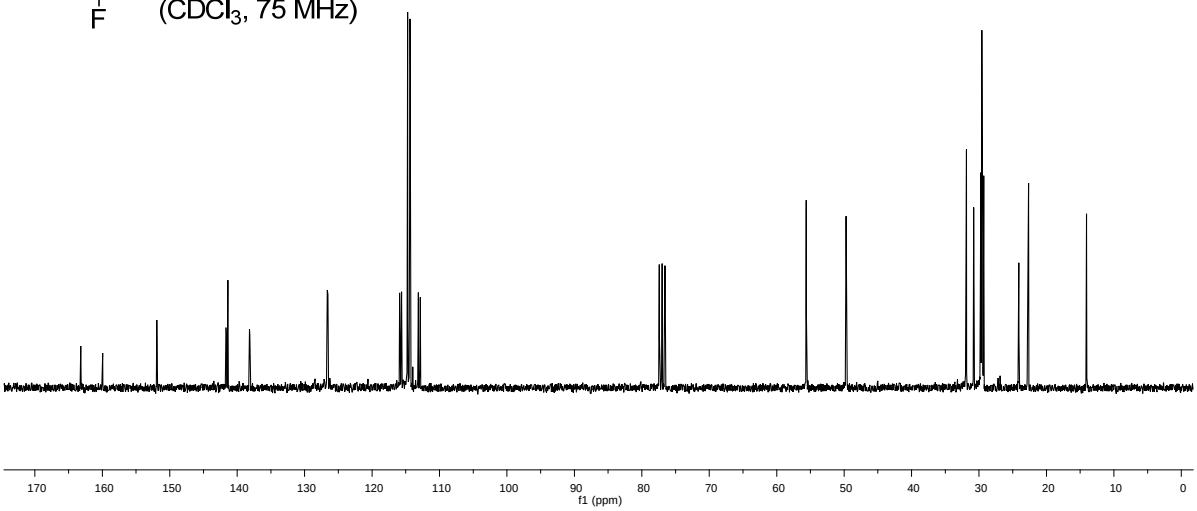


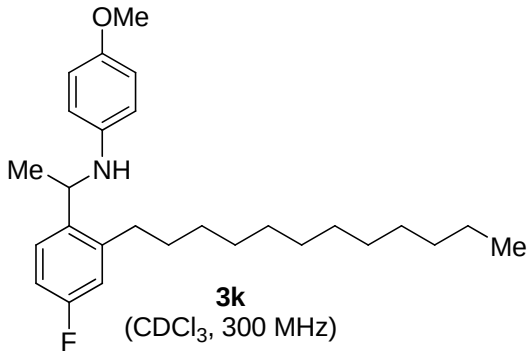
3j
($CDCl_3$, 300 MHz)



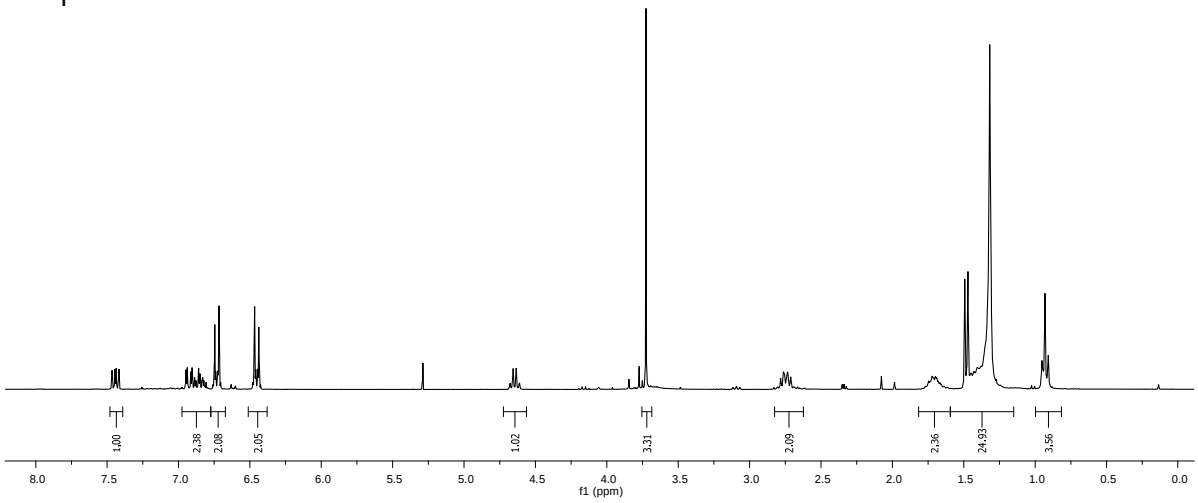


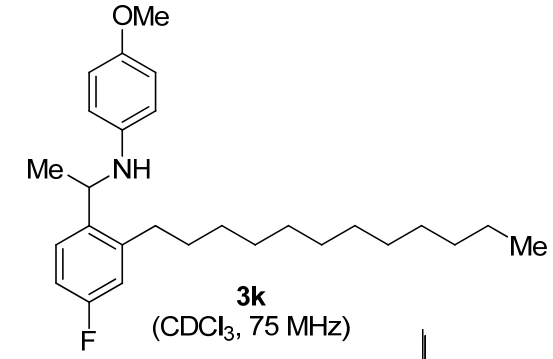
3j
($CDCl_3$, 75 MHz)



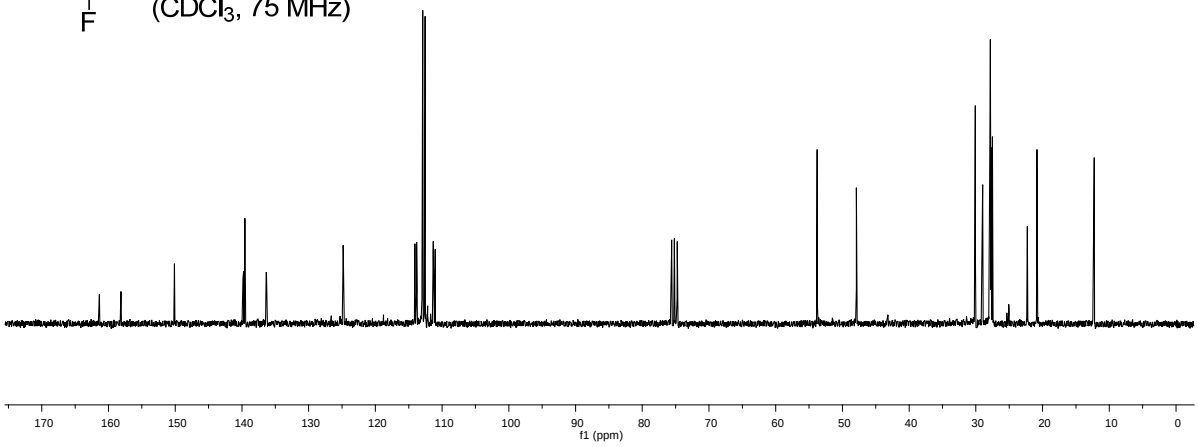


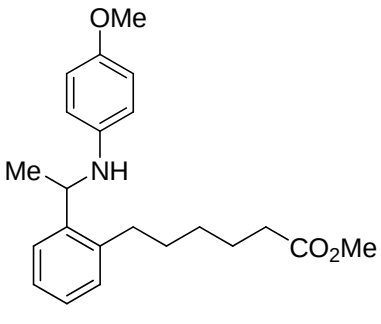
3k
($CDCl_3$, 300 MHz)



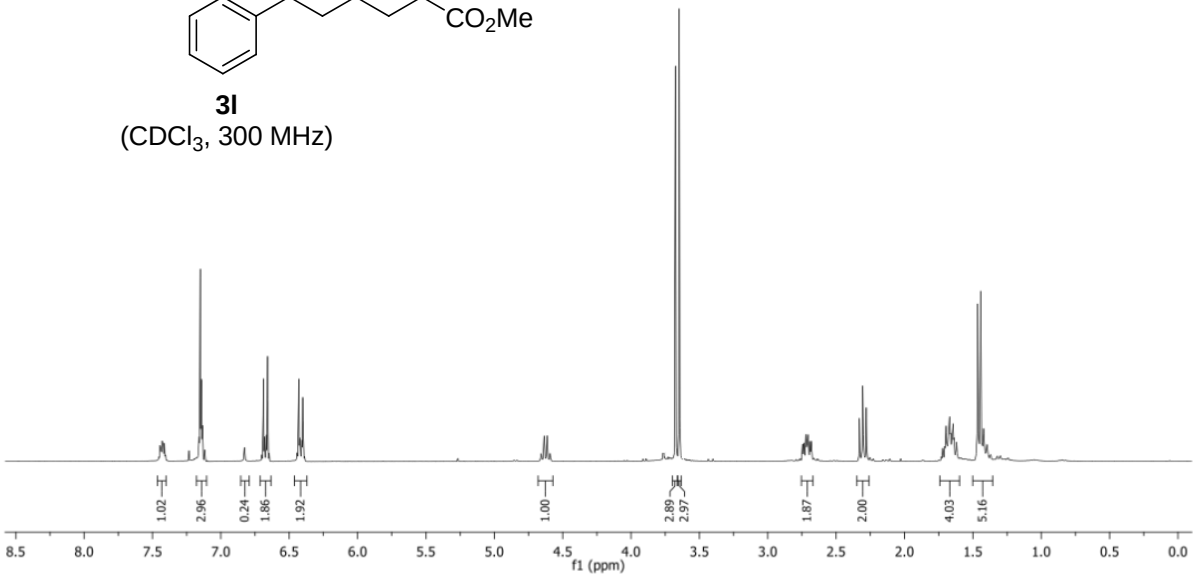


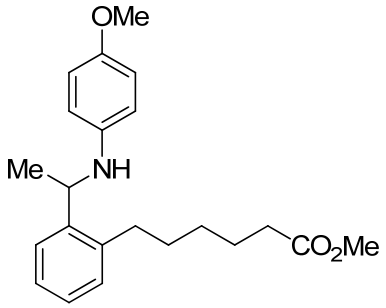
3k
($CDCl_3$, 75 MHz)



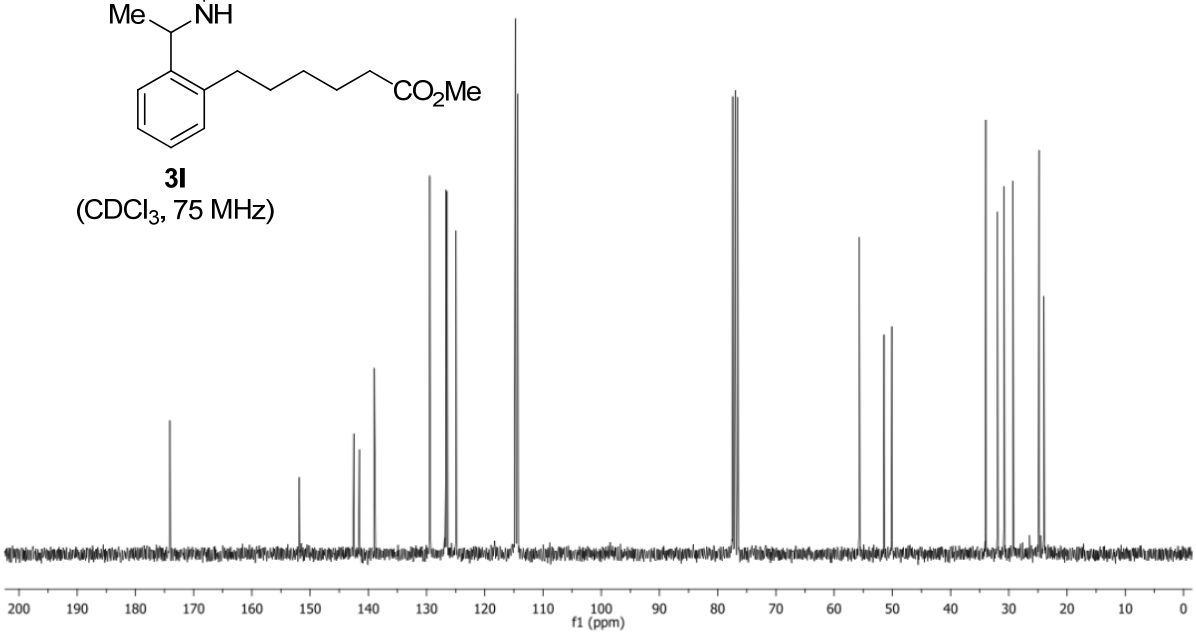


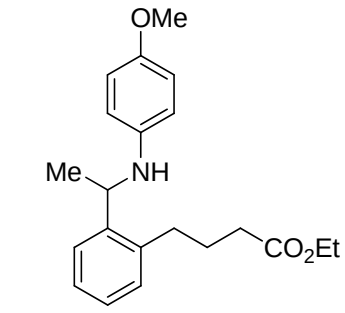
3l
($CDCl_3$, 300 MHz)





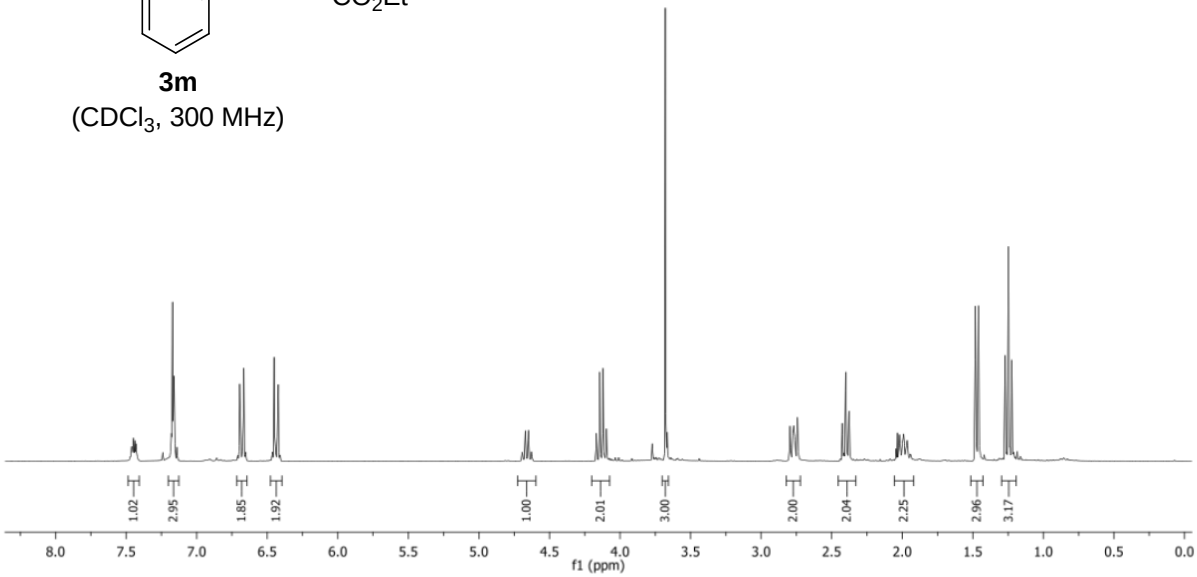
3l
($CDCl_3$, 75 MHz)

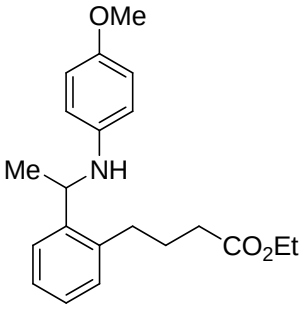




3m

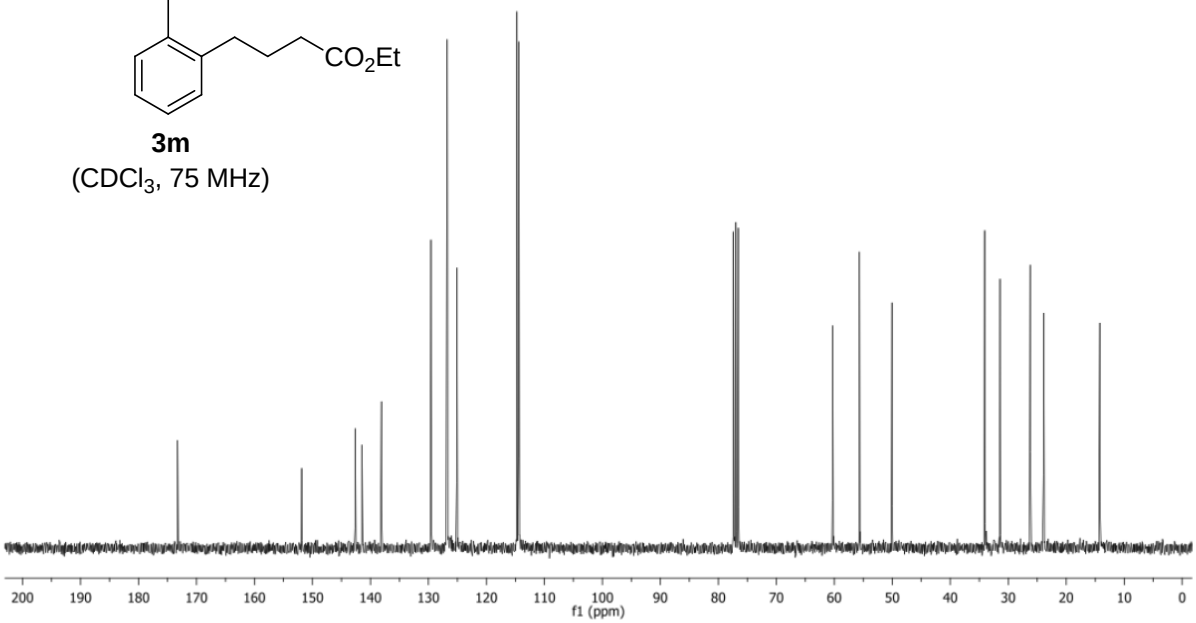
($CDCl_3$, 300 MHz)

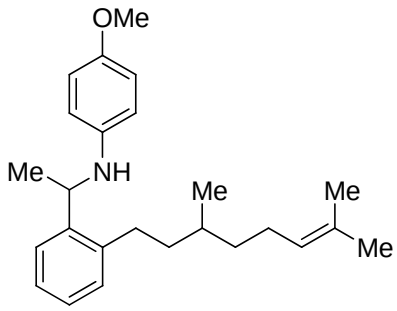




3m

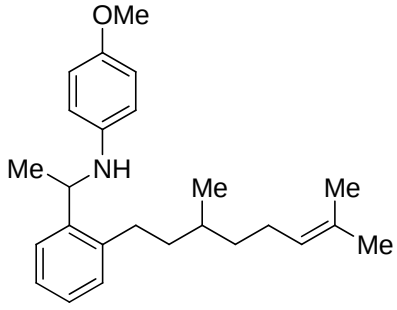
($CDCl_3$, 75 MHz)





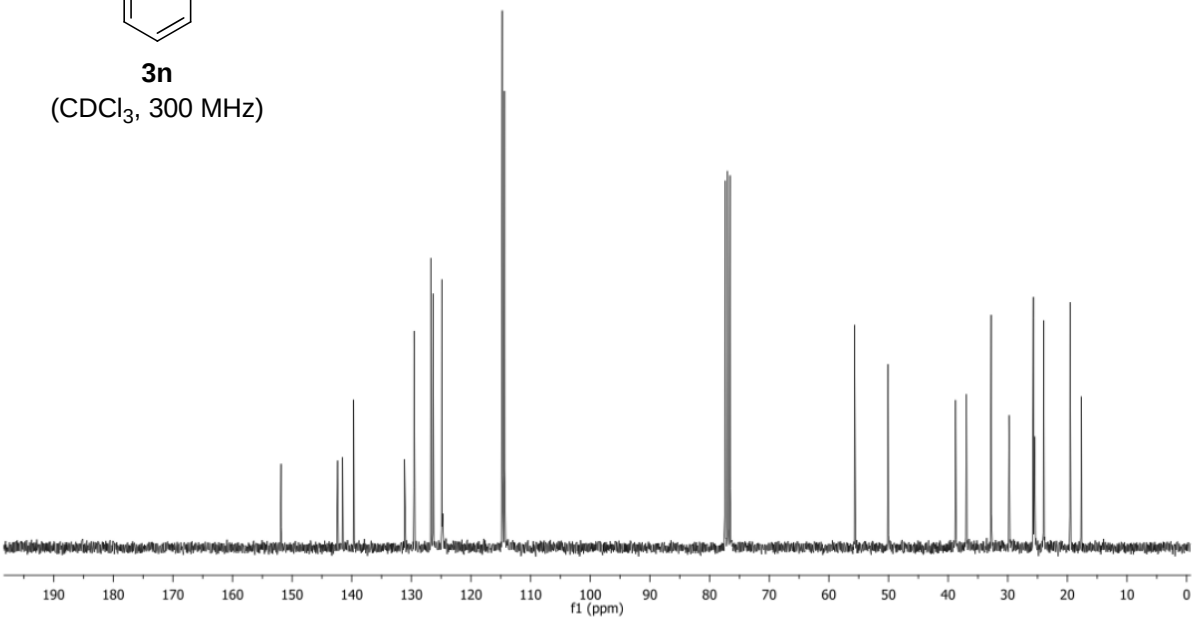
3n

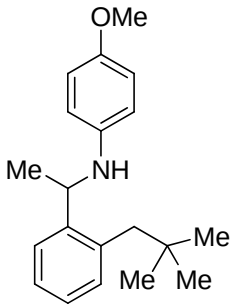
($CDCl_3$, 300 MHz)



3n

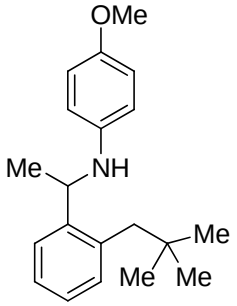
($CDCl_3$, 300 MHz)





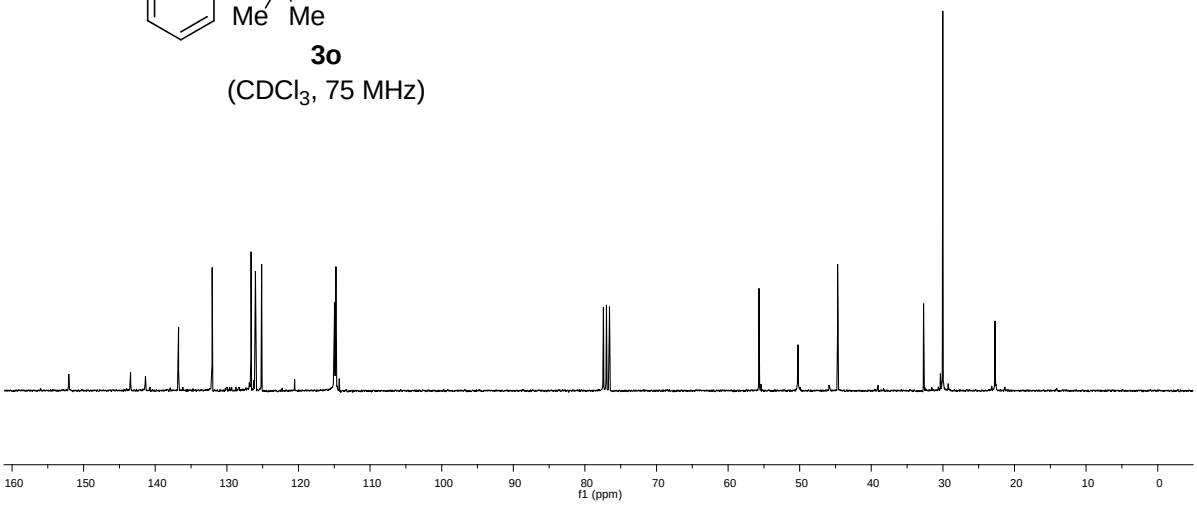
3o

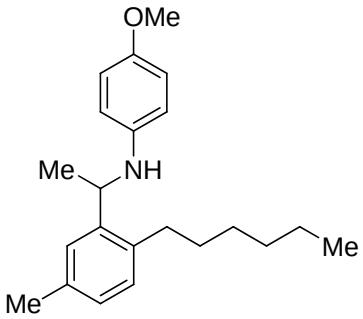
($CDCl_3$, 300 MHz)



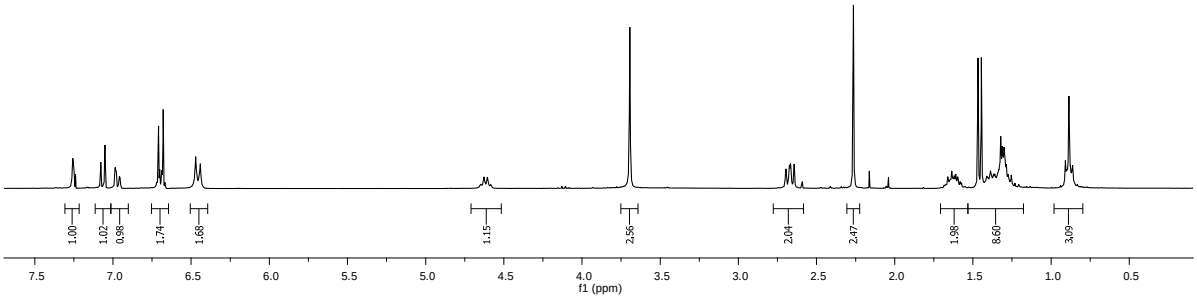
3o

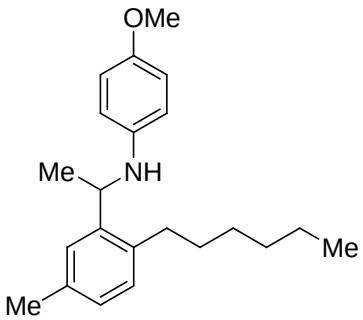
($CDCl_3$, 75 MHz)



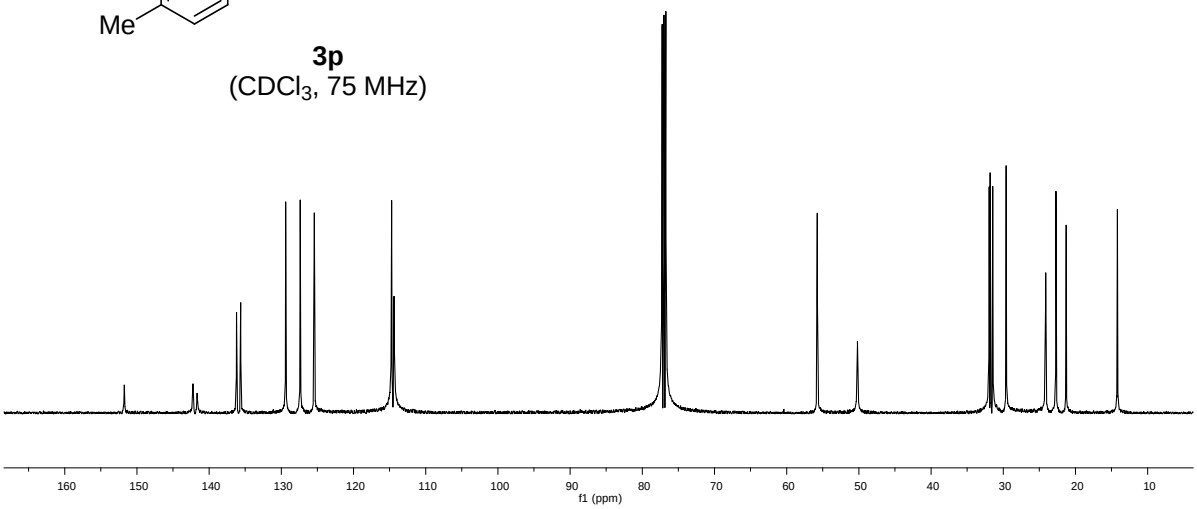


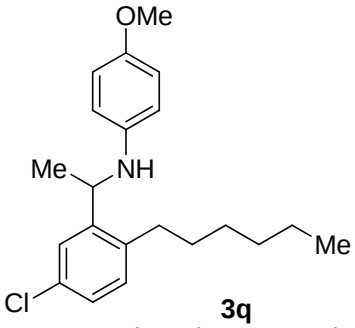
3p
($CDCl_3$, 300 MHz)



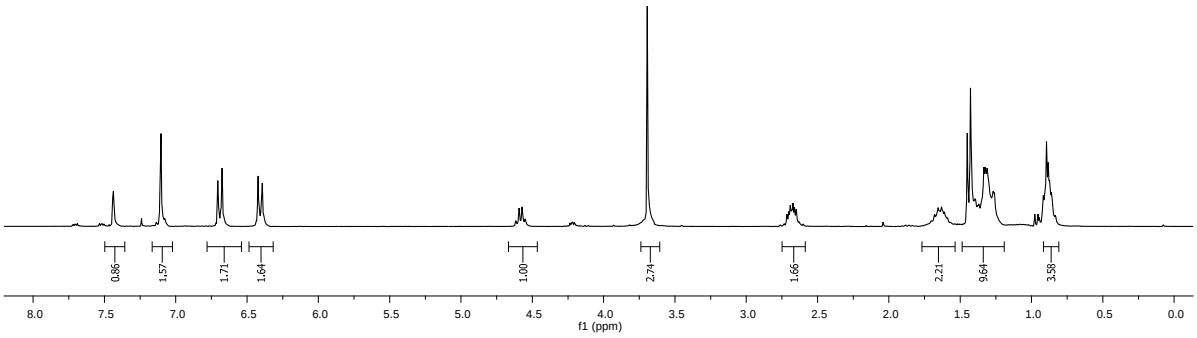


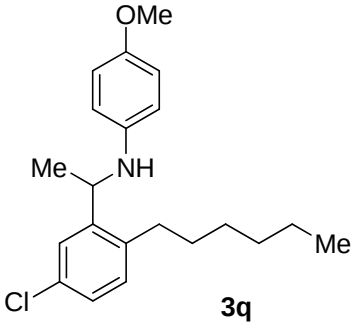
3p
($CDCl_3$, 75 MHz)



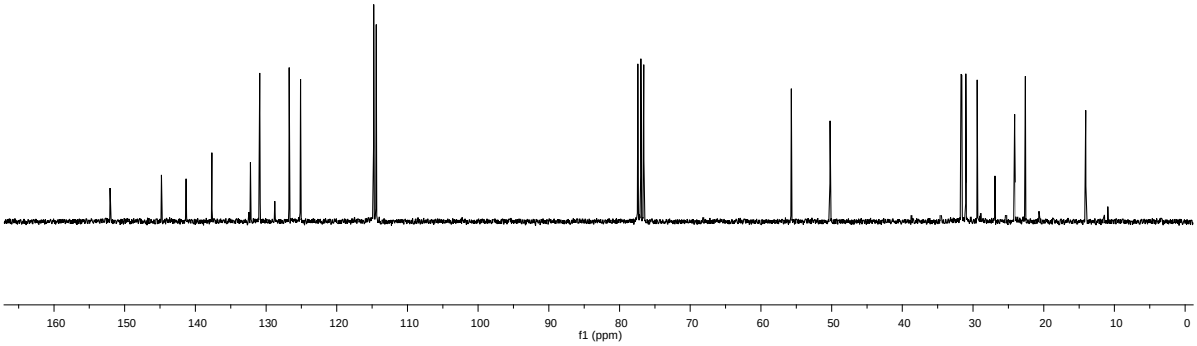


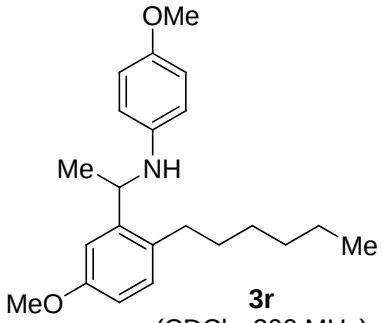
3q
($CDCl_3$, 300 MHz)





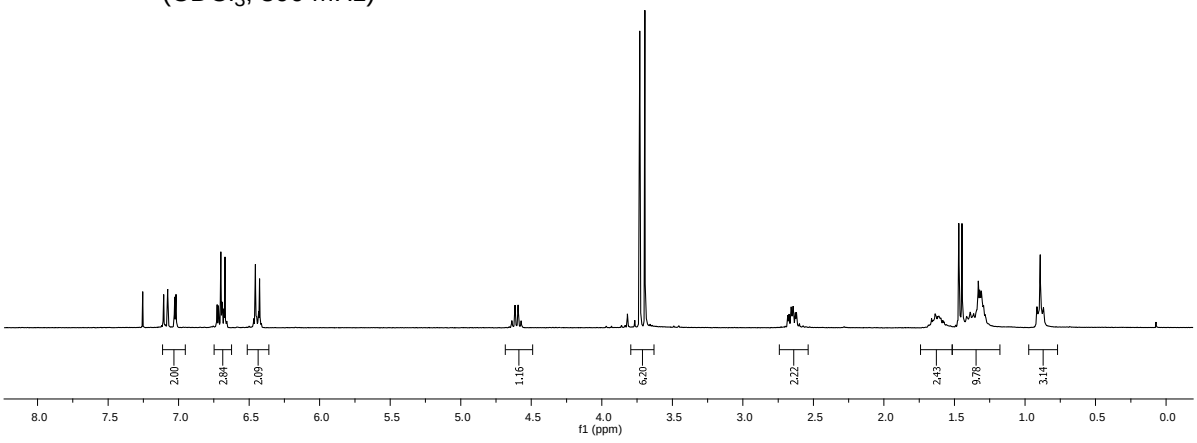
3q
($CDCl_3$, 75 MHz)

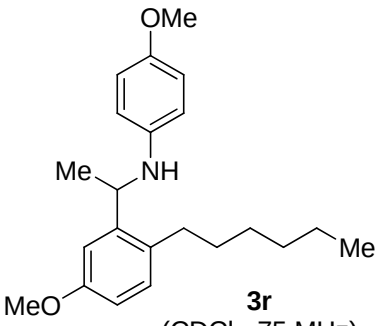




3r

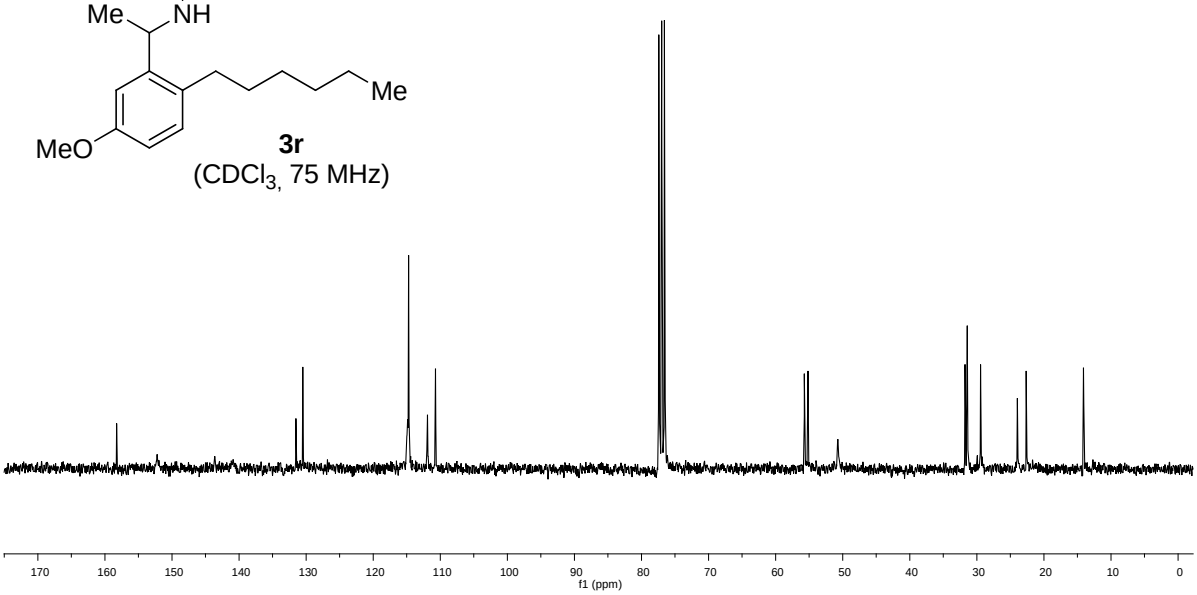
($CDCl_3$, 300 MHz)

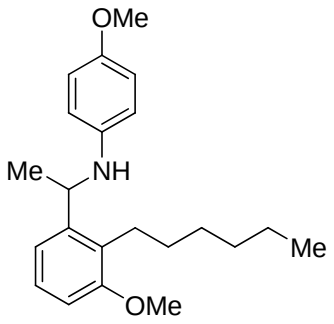




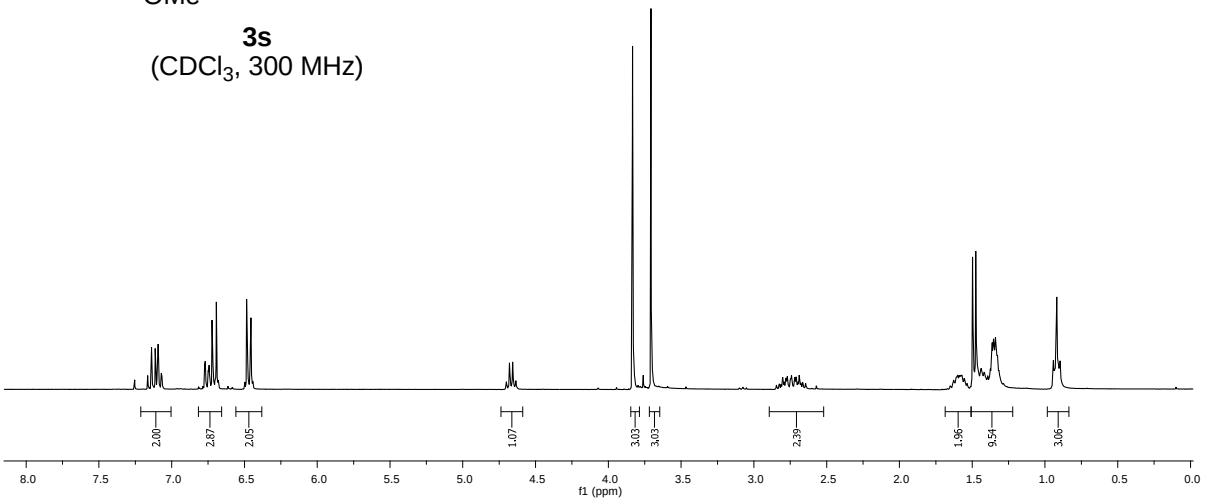
3r

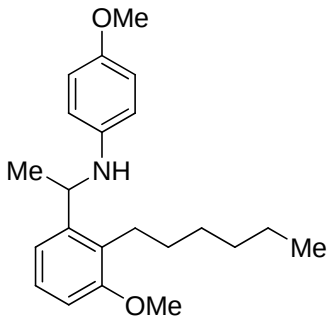
($CDCl_3$, 75 MHz)



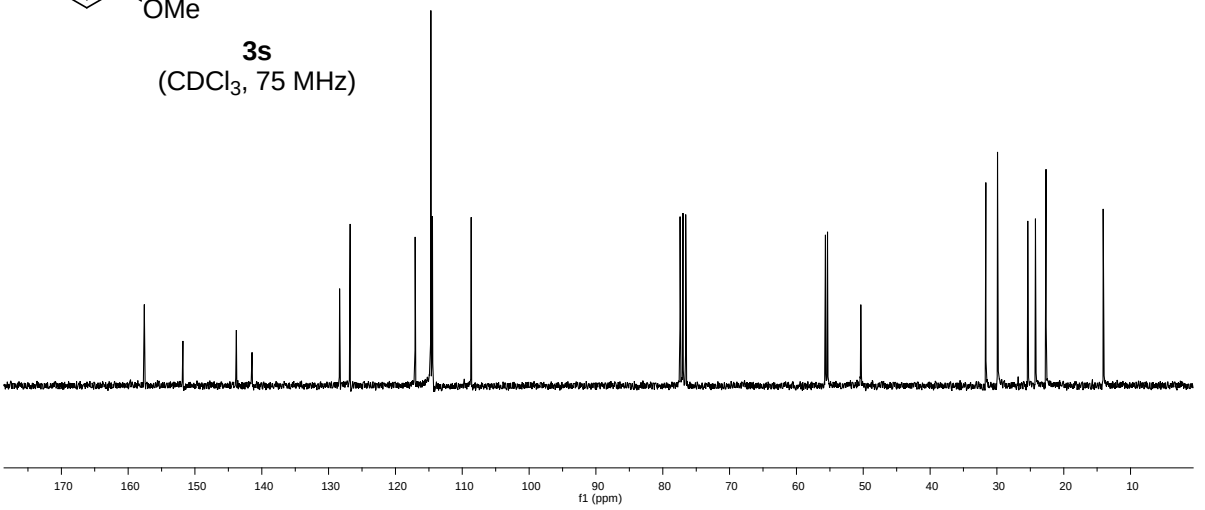


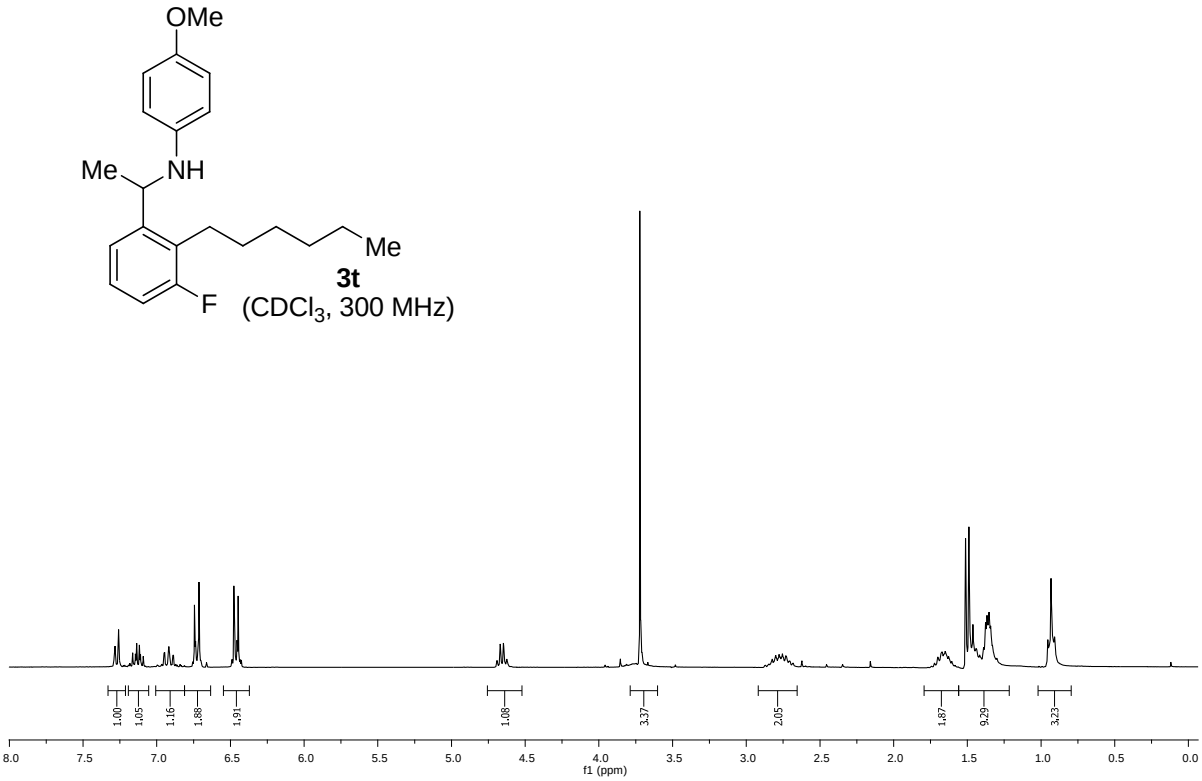
3s
($CDCl_3$, 300 MHz)

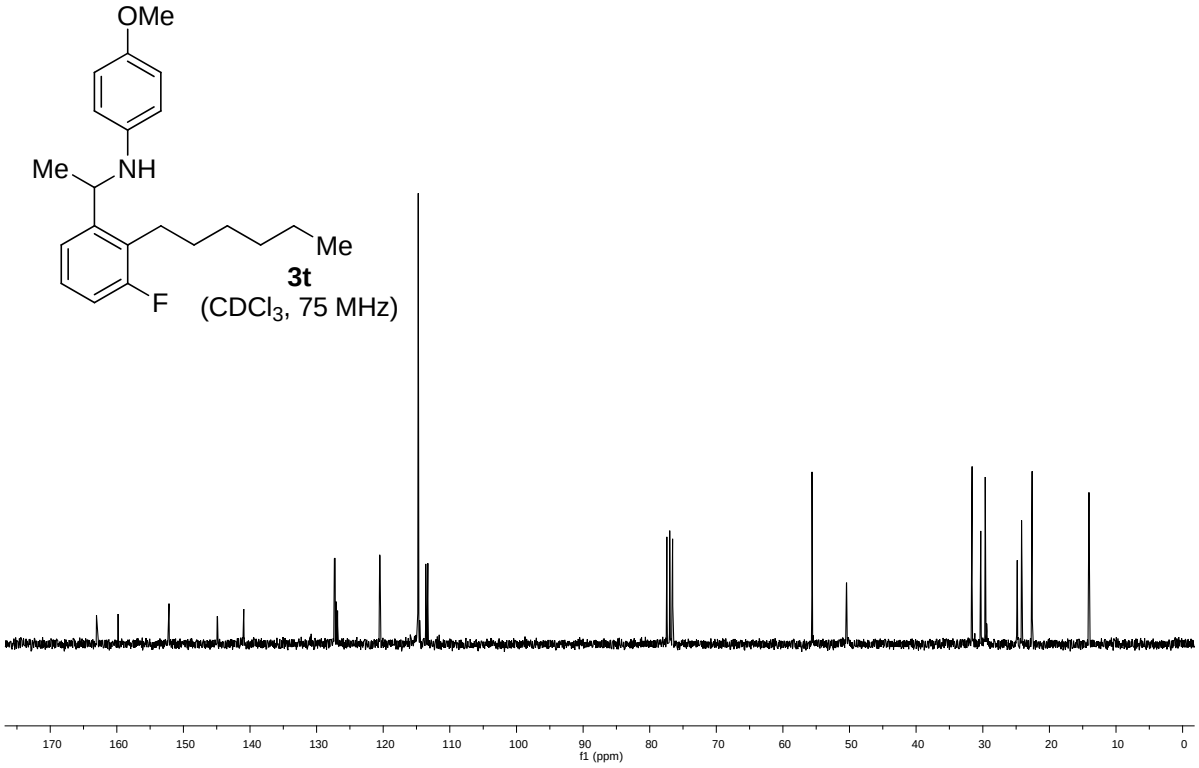


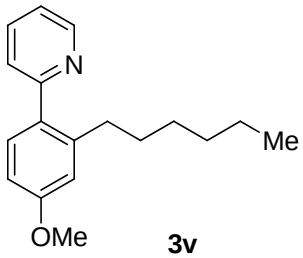


3s
($CDCl_3$, 75 MHz)



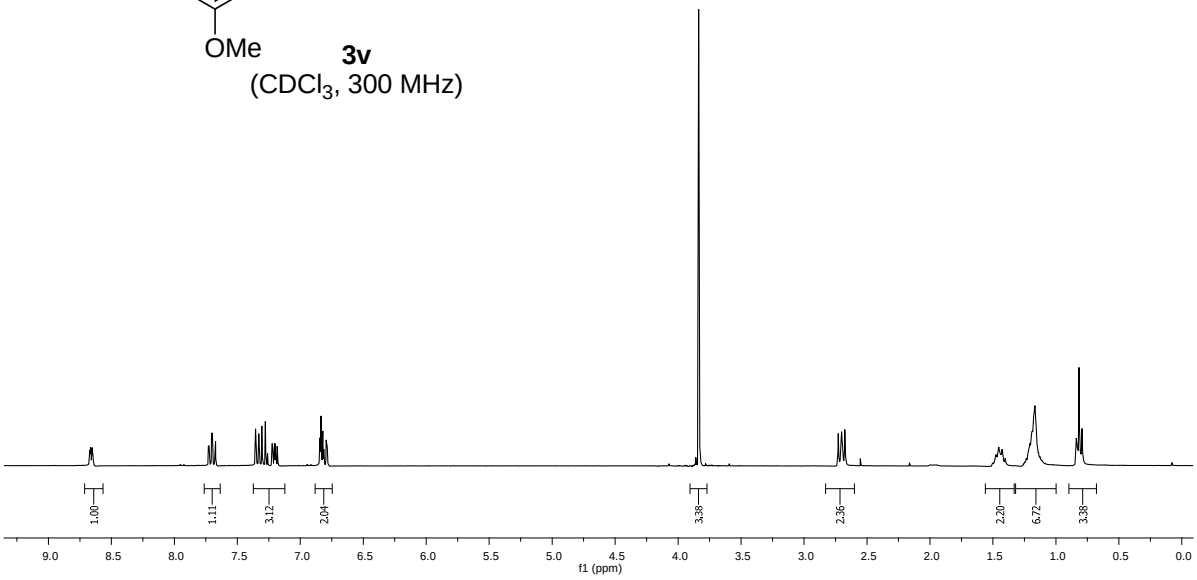

OMe
Me
NH
Me
F
3t
(CDCl3, 300 MHz)
1.00
1.05
1.16
1.88
1.91
1.08
3.37
2.05
1.87
9.29
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

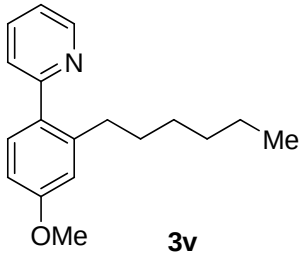

OMe
Me
NH
Me
F
3t
(CDCl3, 75 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3v

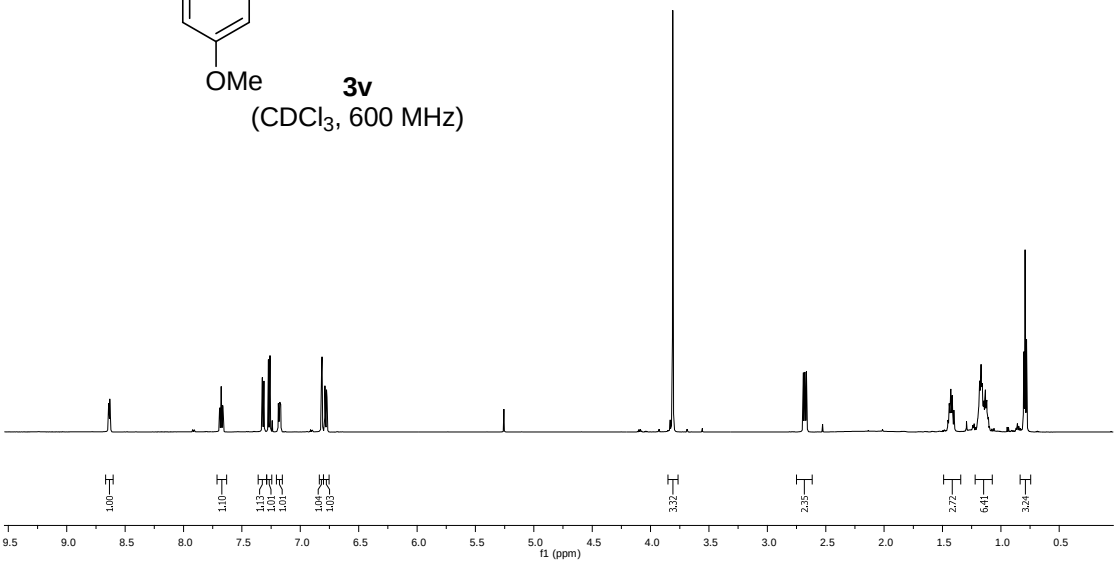
($CDCl_3$, 300 MHz)

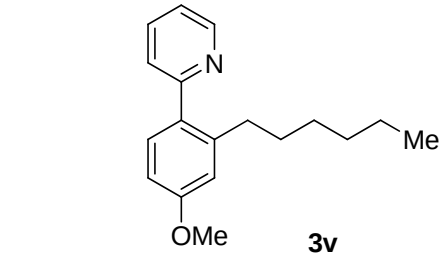




3v

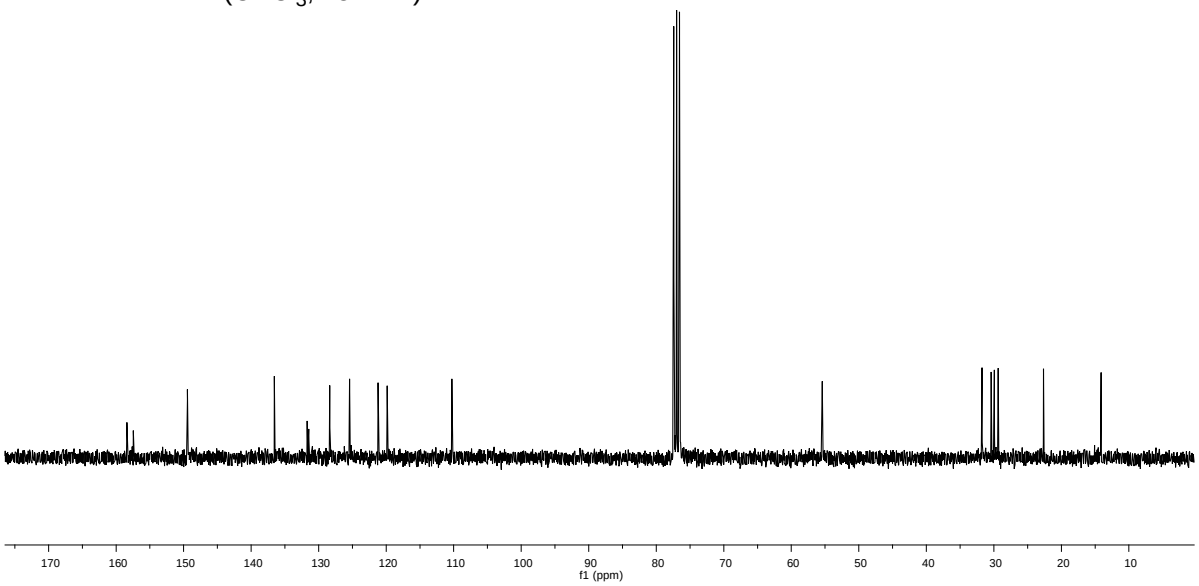
($CDCl_3$, 600 MHz)

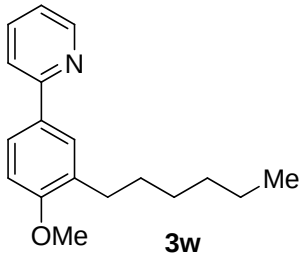




3v

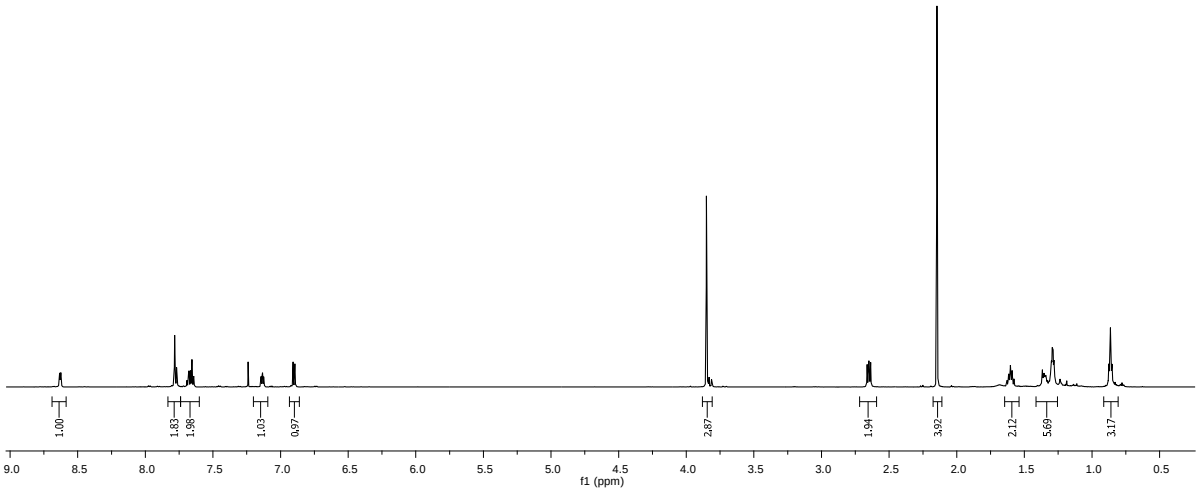
($CDCl_3$, 75 MHz)

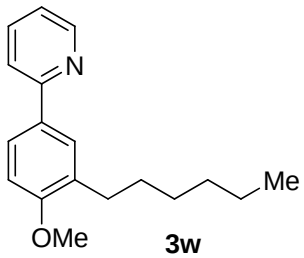




3w

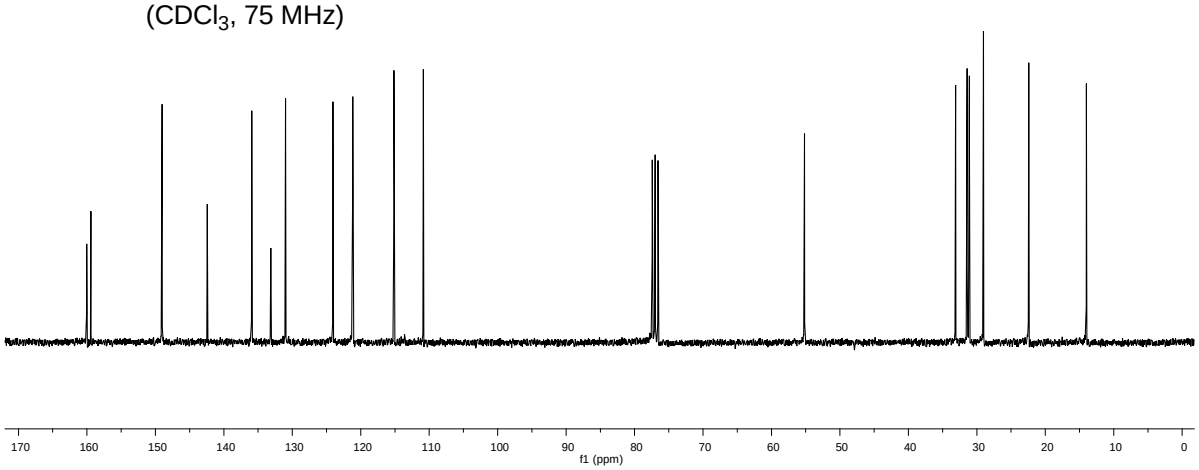
($CDCl_3$, 600 MHz)



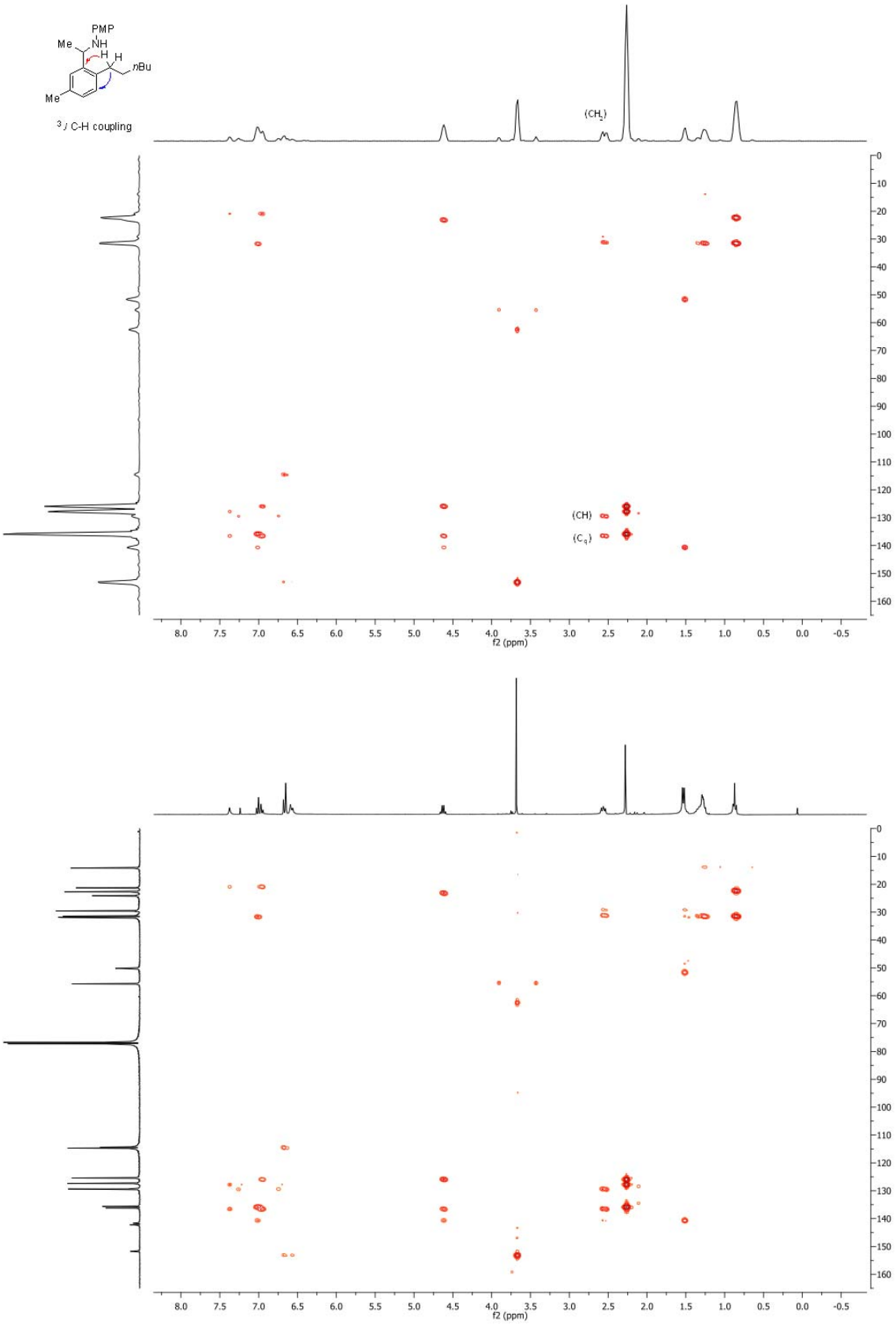


3w

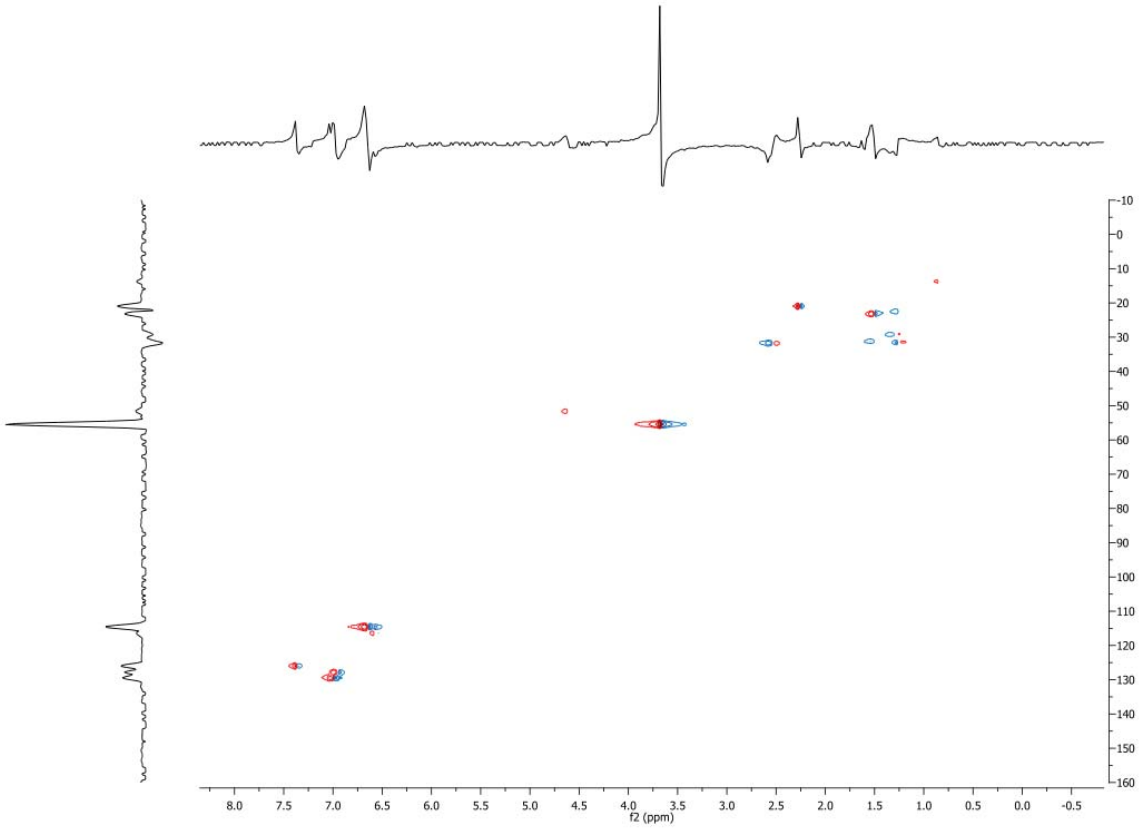
($CDCl_3$, 75 MHz)



HMBC and HSQC spectra of 3p - 3w
3p (HMBC)



3p (HSQC)


-10
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130
140
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160
8.0
7.5
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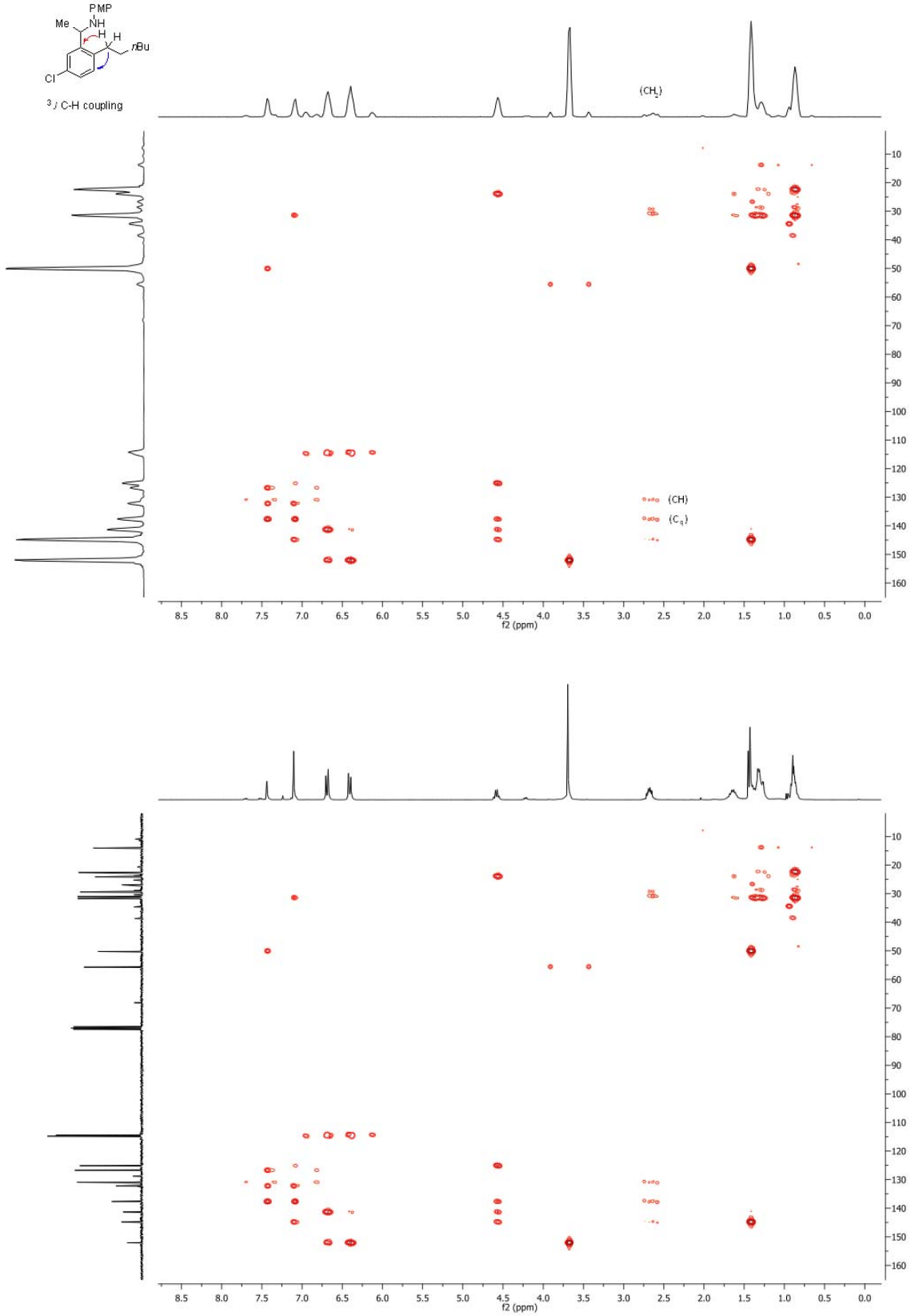
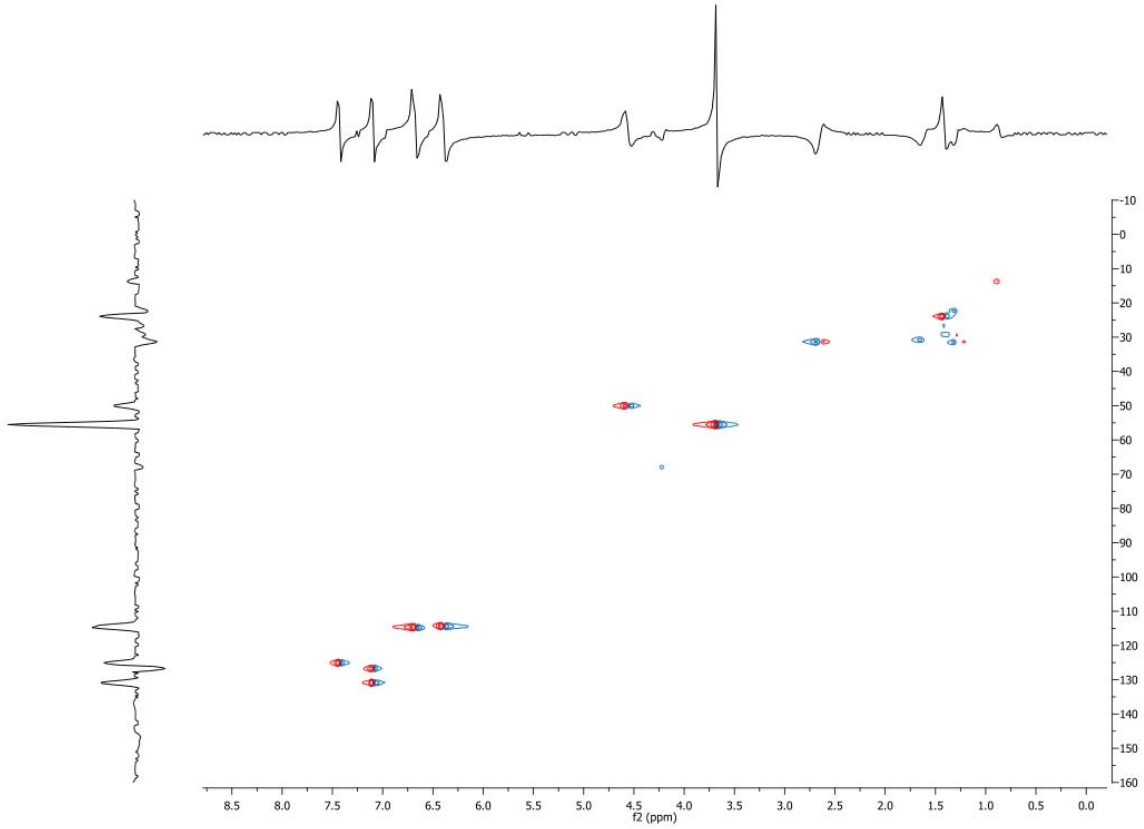
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

3q (HMBC)



3q (HSCQ)


-10
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8.0
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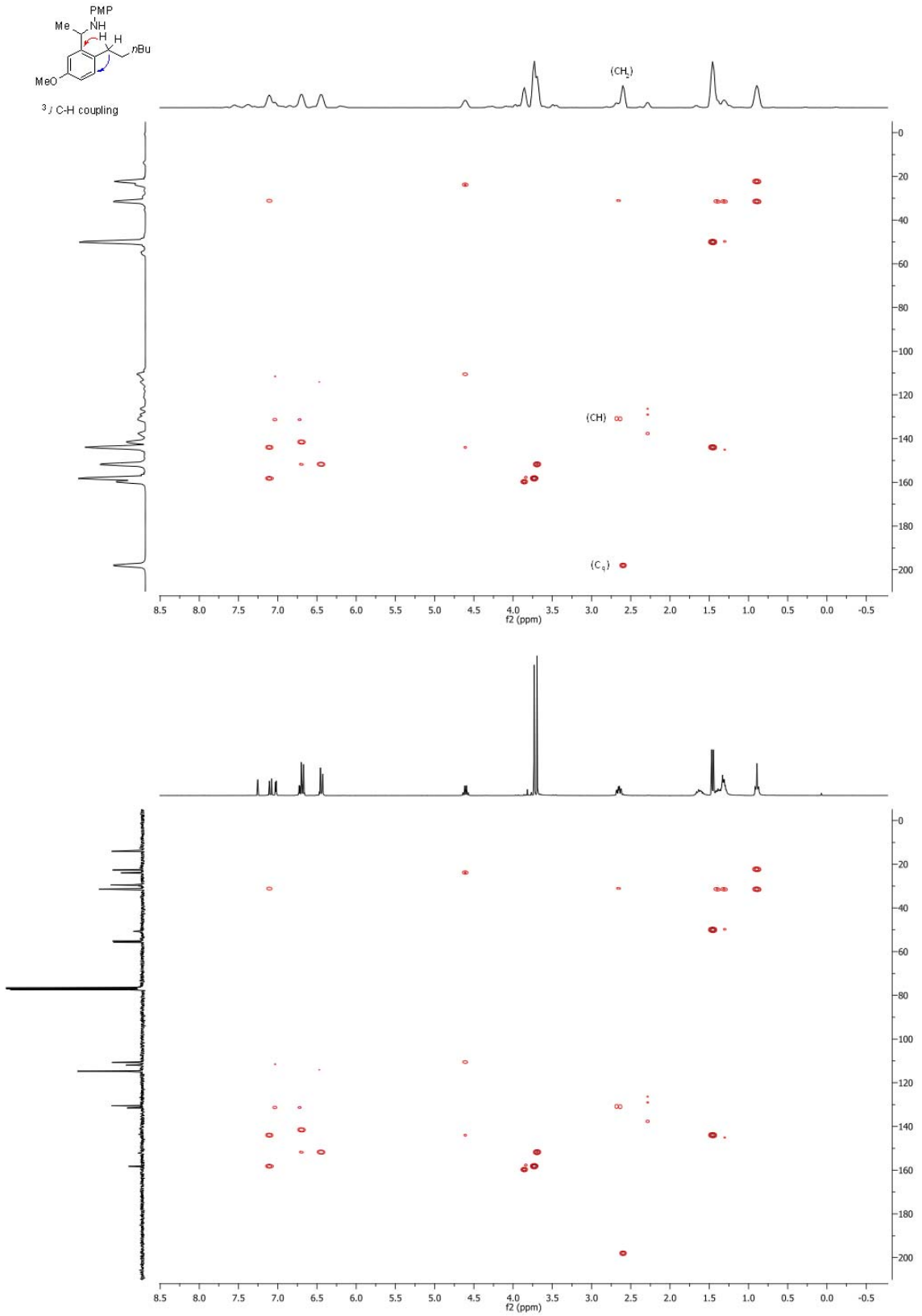
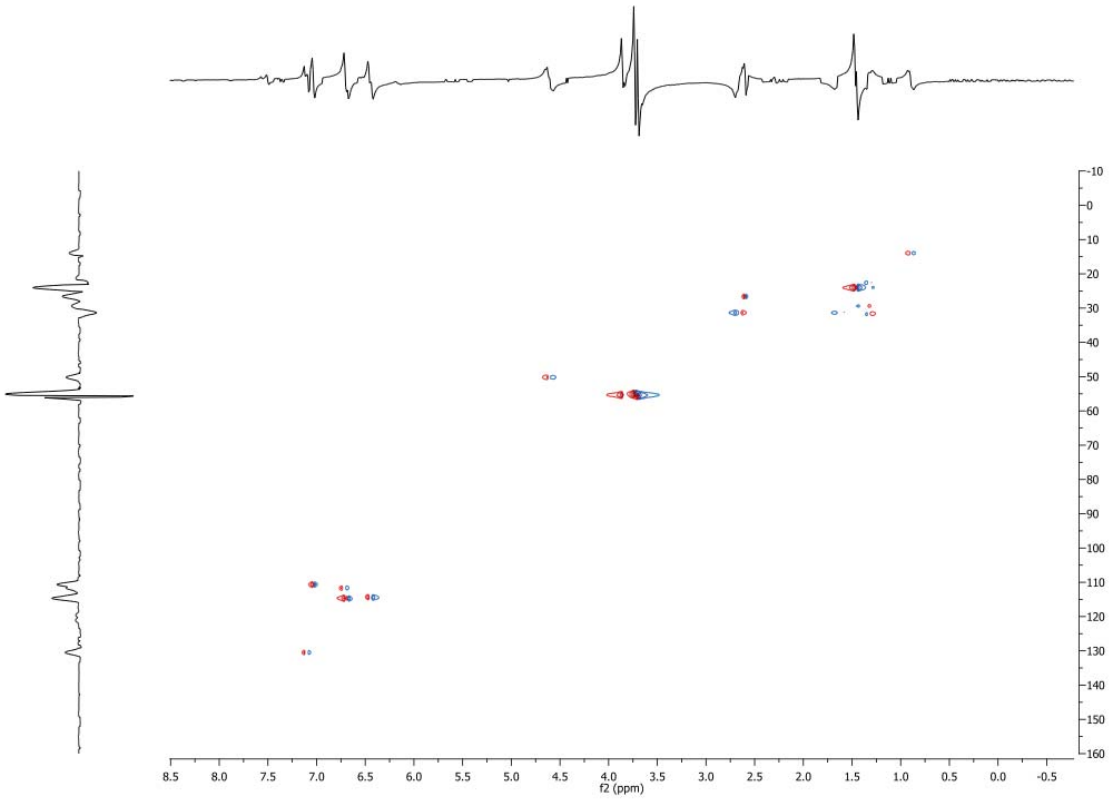
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

3r (HMBC)



3r (HSQC)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8.5
8.0
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1.0
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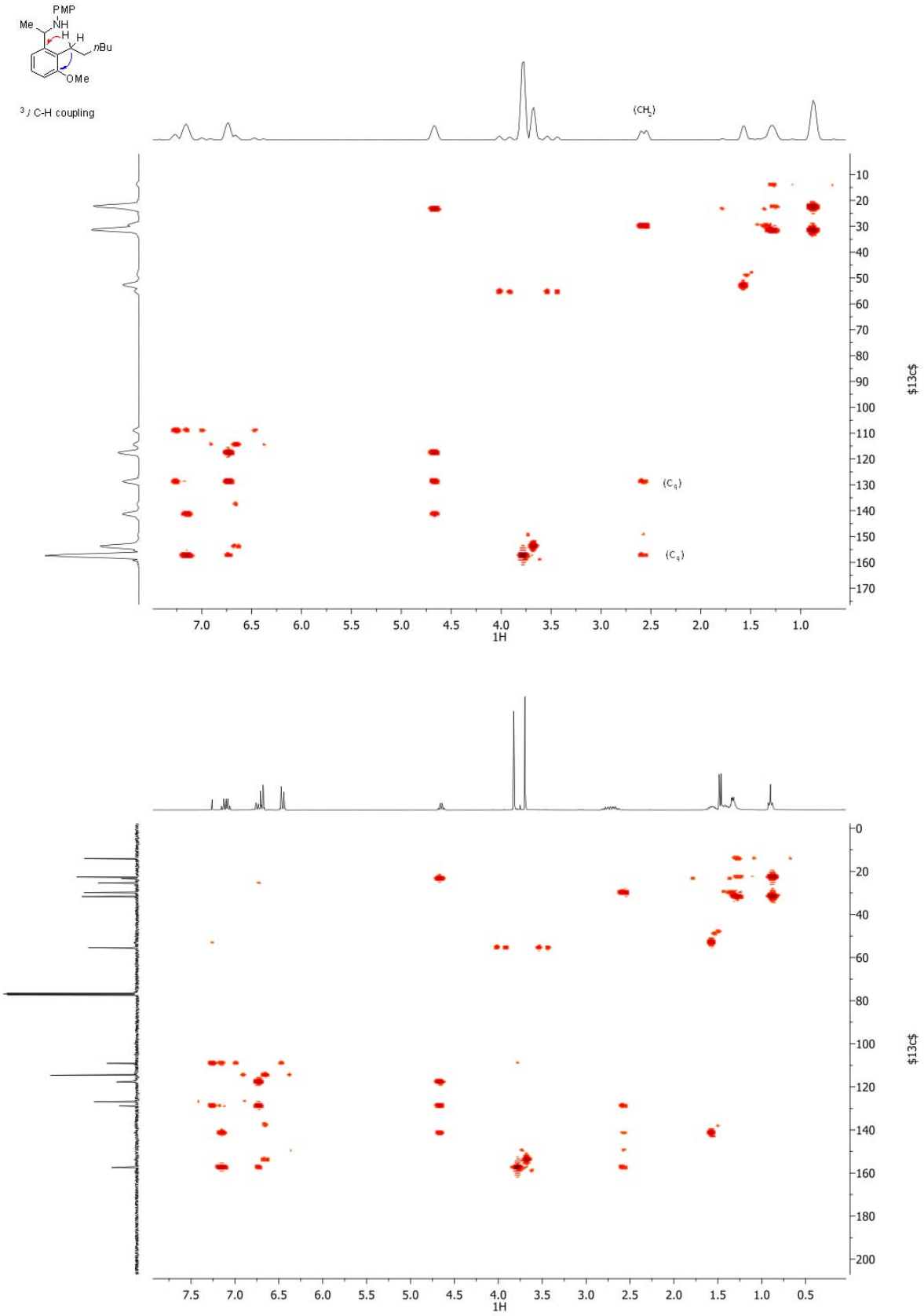
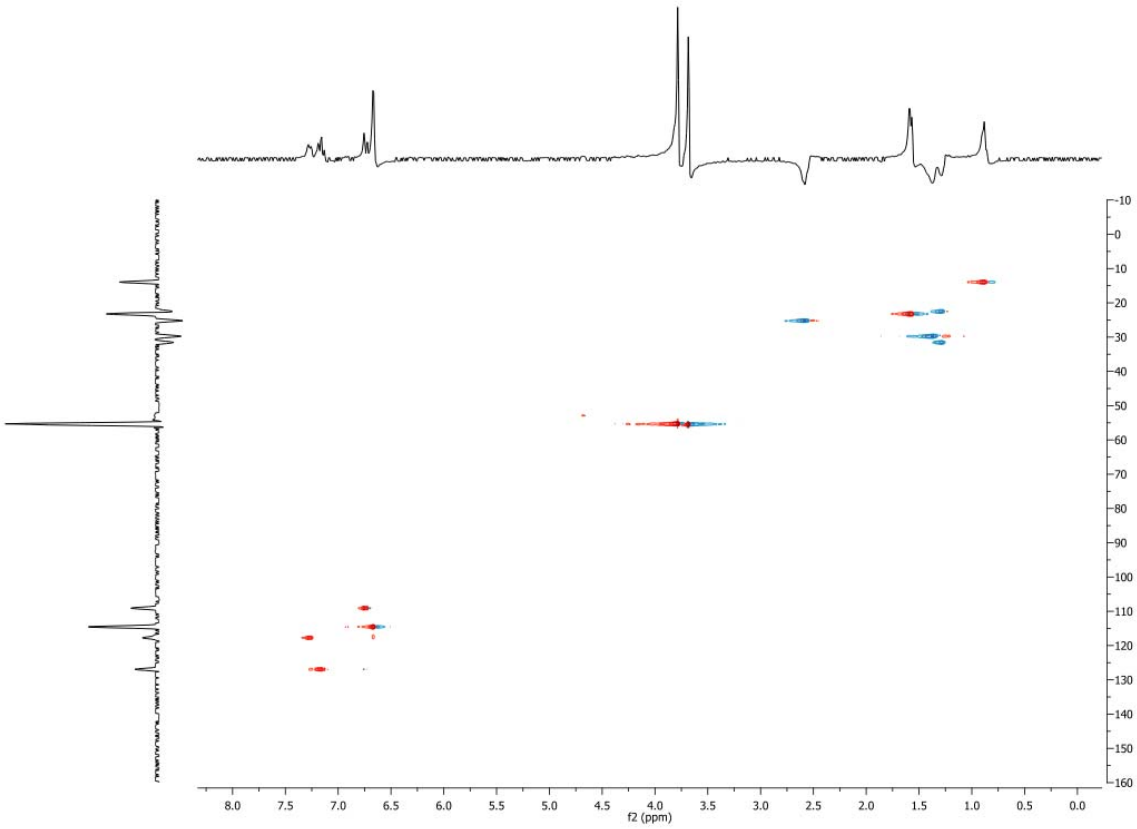
0.0
-0.5
f2 (ppm)

3s (HMBC)



3s (HSQC)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4.5
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3.0
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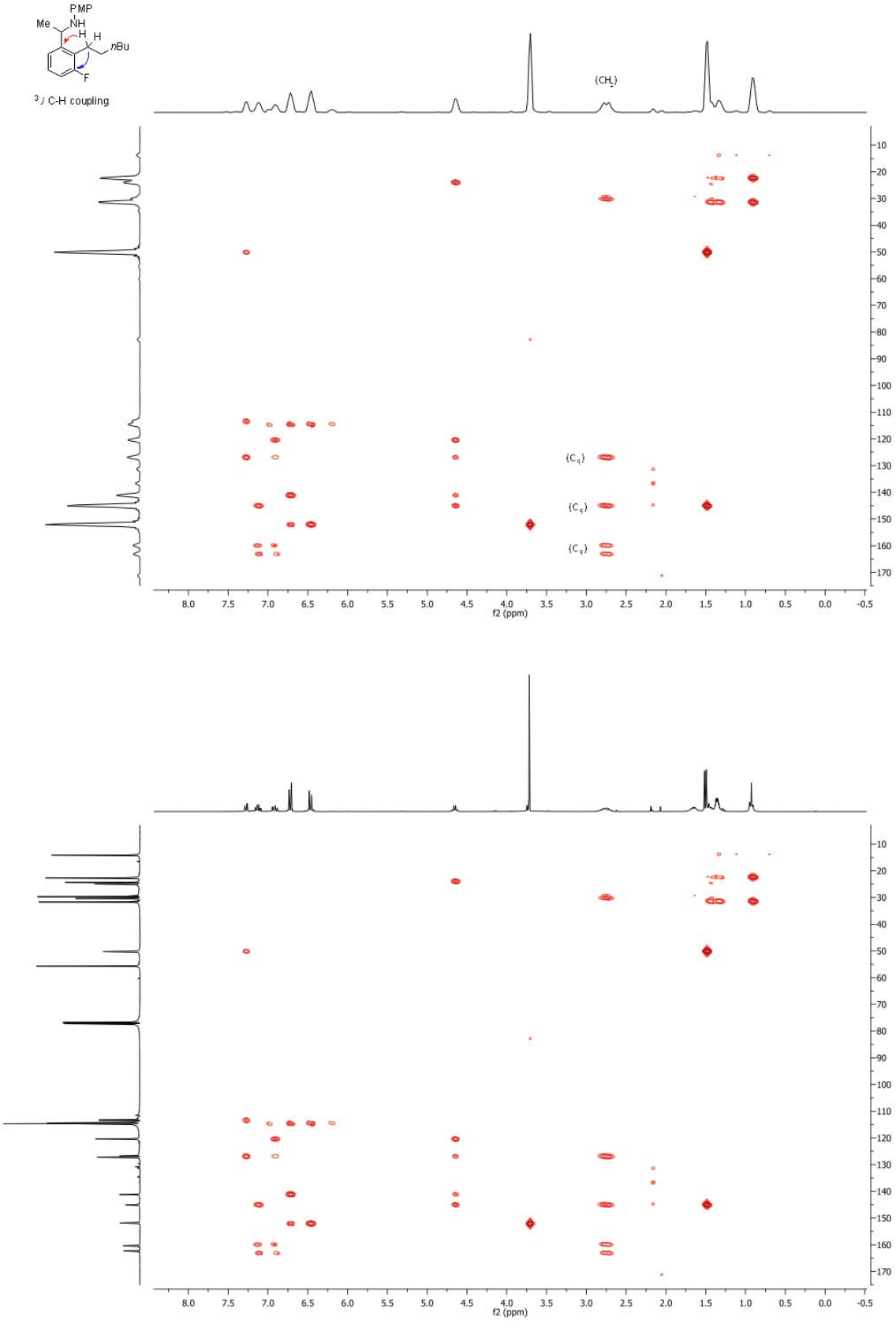
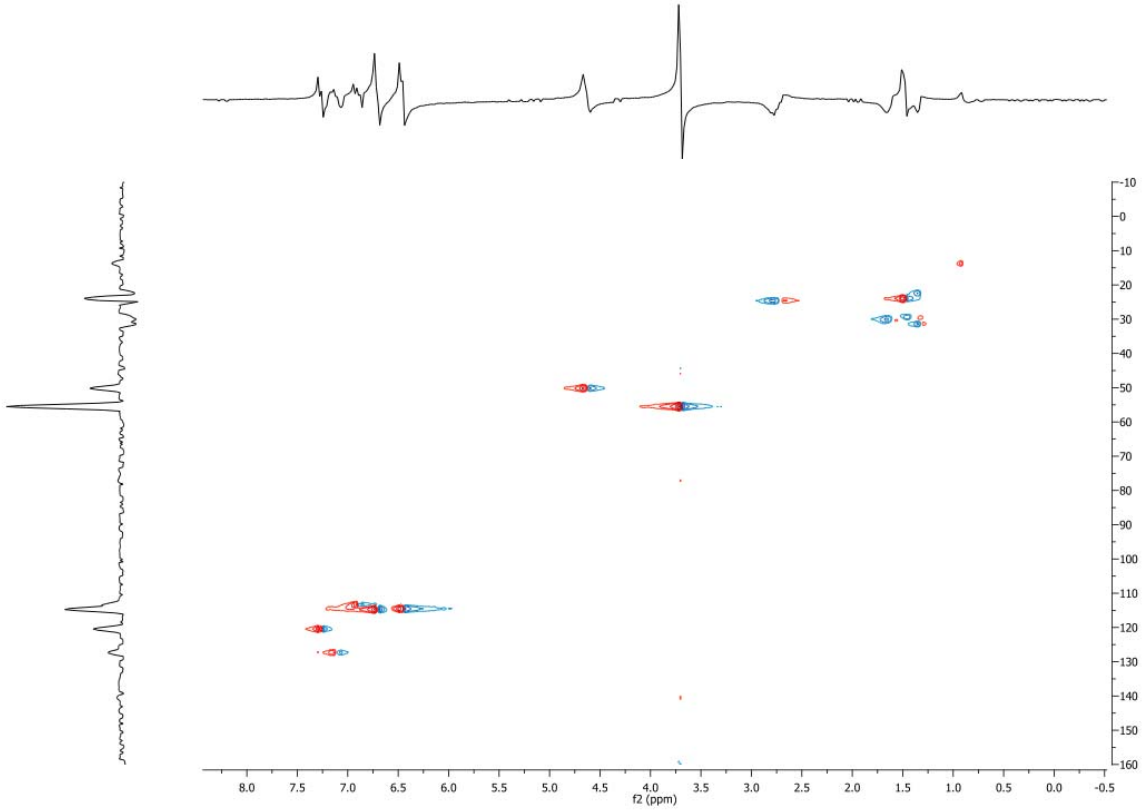
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

3t (HMBC)



3t (HSCQ)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8.0
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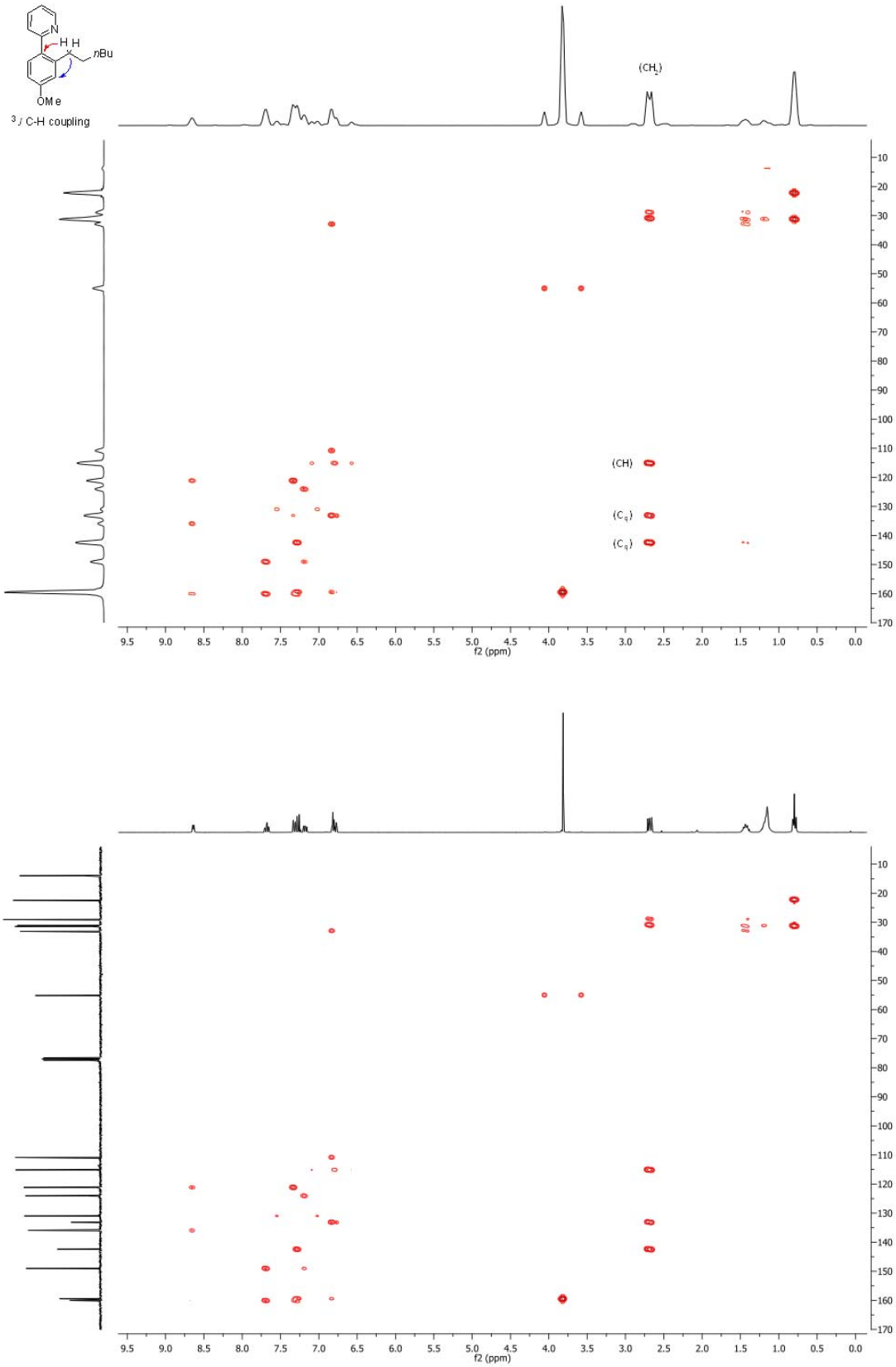
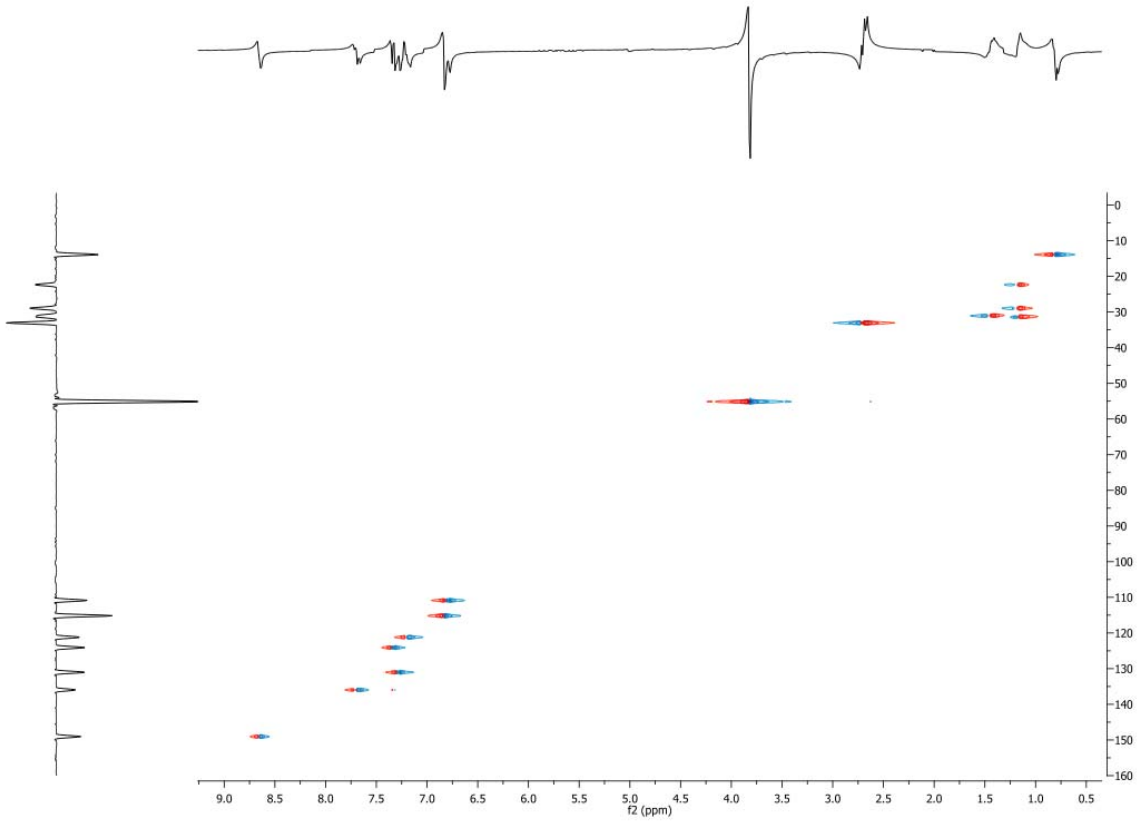
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

3v (HMBC)



3v (HSCQ)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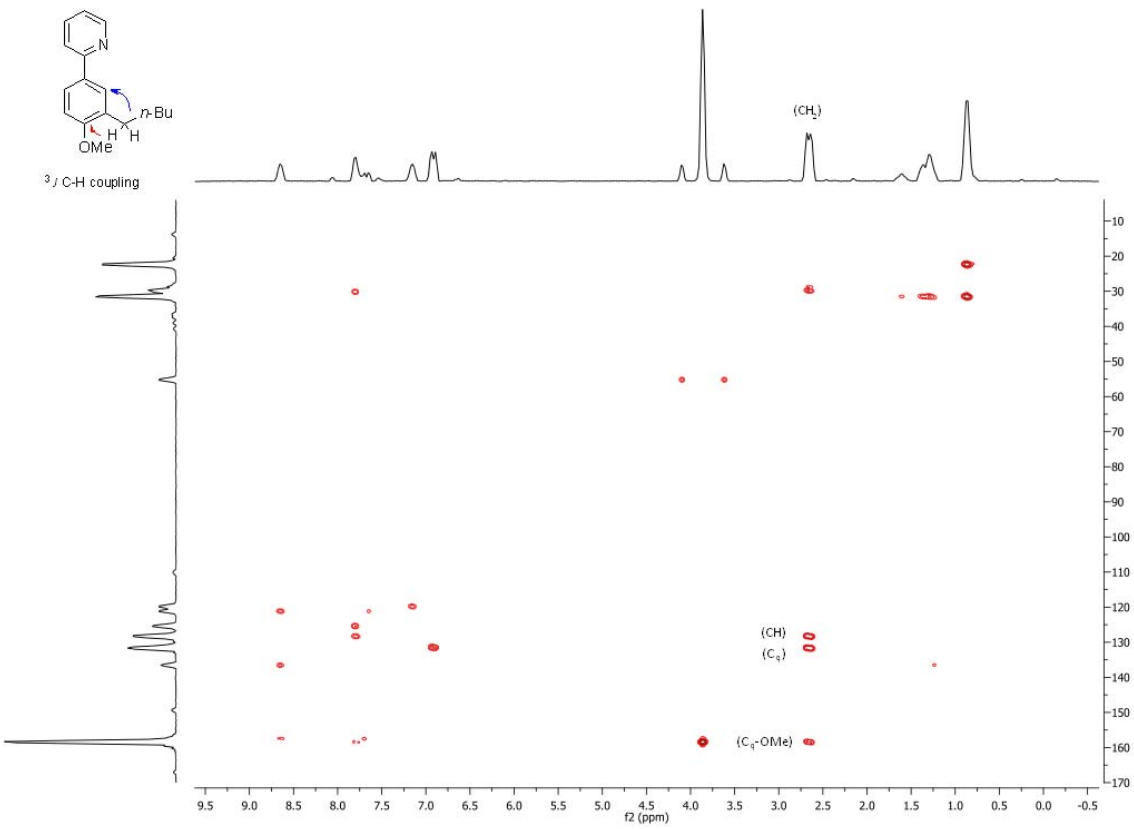
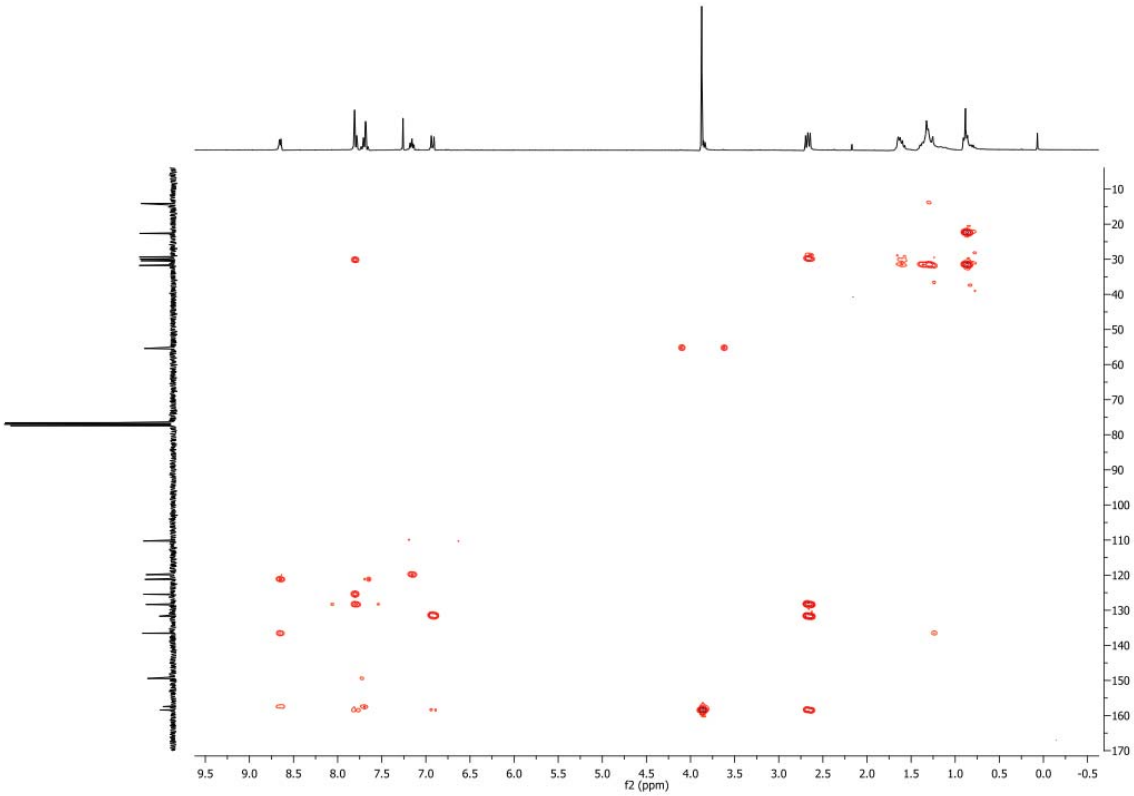
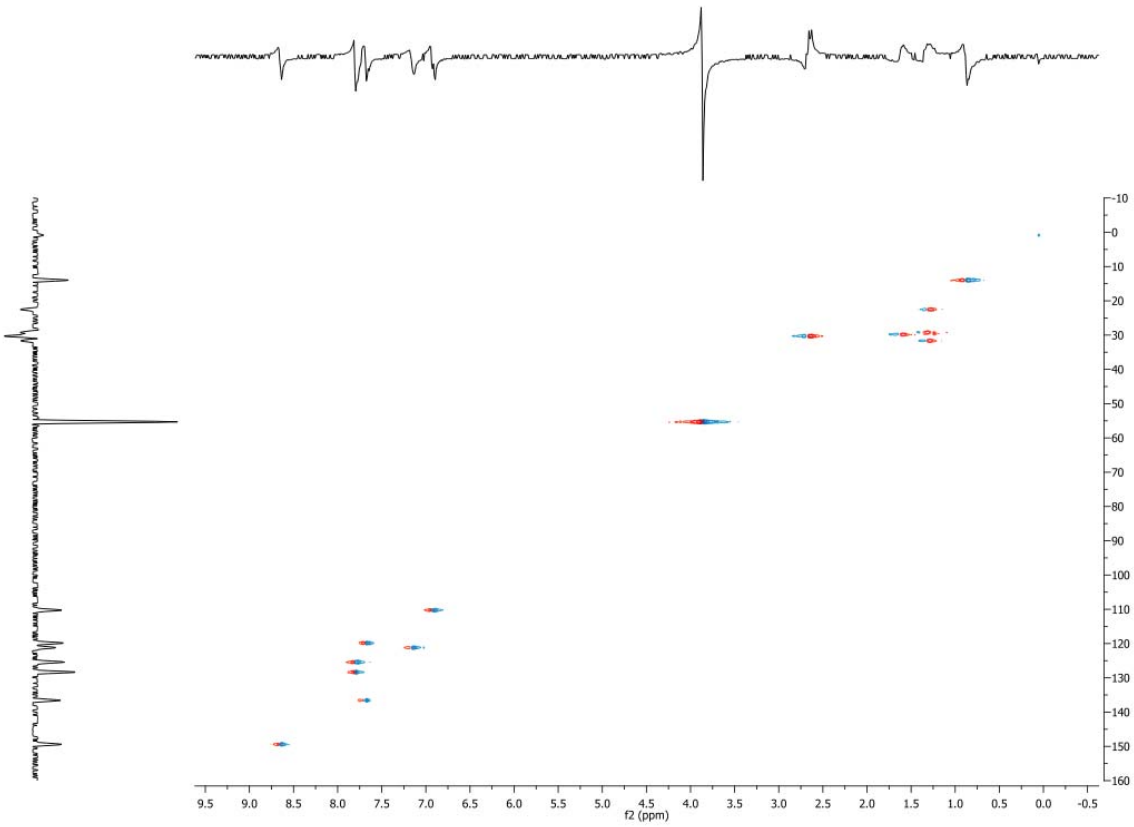
120
130
140
150
160
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

3w (HMBC)





3w (HSQC)


9.5
9.0
8.5
8.0
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160