Supporting Information

Air-Stable Secondary Phosphine Oxide or Chloride (Pre)Ligands for Cross-Couplings of Unactivated Alkyl Chlorides

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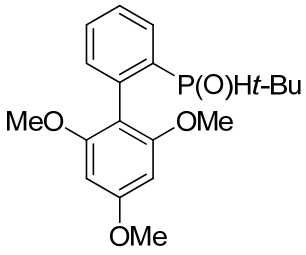
General remarks

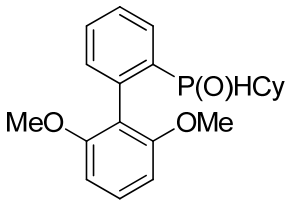
Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. Aryl bromides and iodides were obtained from commercial sources, and were used without further purification. Grignard reagents unless specified were brought from commercial sources. THF was freshly distilled from sodium/benzophenone under N_2. NMP was distilled from CaH_2 and stored under N_2. Starting materials 6-chlorohexanenitrile,[1] 6-chlorohexanoic acid methyl ester,[2] 6-chloro-1-phenyl-1-hexanone,[3] 2-bromo-2',6'-dimethoxybiphenyl,[4] 2-bromo-2',4',6'-trimethoxybiphenyl,[4] *N*-phenylindole,[5] *N*-methyl-2-(2′-bromophenyl)indole[6] and *P*-*tert*-butyl-*P*-(2',6'-dimethoxy-biphen-2-yl)phosphine oxide[7] (**4e**) were prepared according to literature procedure. 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.

Synthesis and characterization of air-stable secondary phosphine oxides (4f-4i), chlorides (5a-5c) and tertiary phosphines (6a-6b):



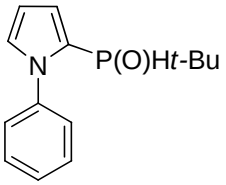
4f

***P*-*tert*-Butyl-*P*-(2',4',6'-trimethoxy-biphen-2-yl)phosphine oxide 4f:** To a solution of 2-bromo-2',4',6'-trimethoxybiphenyl (1.20 g, 3.70 mmol) in THF (20 mL) was added *n*-BuLi (3.10 mL, 1.60 M solution in hexanes, 5.20 mmol) and the reaction was stirred at -78 °C for 3 h. Then, a solution of *t*-$BuPCl_2$ (0.64 g, 4.00 mmol) in THF (5.0 mL) was added dropwise and the mixture was heated to 110 °C for 12 h. After the mixture was cooled to ambient temperature, H_2O (10 mL) was added and the mixture was stirred for 3 d at ambient temperature, extracted with CH_2Cl_2 (2 x 20 mL) and dried over anhydrous $MgSO_4$. The solvents were removed and the remaining residue was subjected to column chromatography (EtOAc/MeOH: 95/5) to yield **4f** (730 mg, 57%) as colourless crystals. m.p: 170–171 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.85 (m, 1H), 7.56–7.45 (m, 1H), 7.44–7.37 (m, 1H), 7.22–7.13 (m, 1H), 6.64 (d, J = 475.0 Hz, 1H), 6.15 (d, J = 3.0 Hz, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 0.93 (d, J = 15.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (C_q), 158.3 (C_q), 157.3 (C_q), 137.0 ($^2J_{C\text{-}P}$ = 18 Hz, C_q), 132.4 (CH), 131.8 (CH), 131.4 (CH), 131.3 (CH), 129.5 ($^1J_{C\text{-}P}$ = 91 Hz, C_q), 126.8 ($^3J_{C\text{-}P}$ = 10 Hz, CH), 109.4 ($^3J_{C\text{-}P}$ = 5 Hz, C_q), 90.4 ($^2J_{C\text{-}P}$ = 58 Hz, CH), 55.8 (CH_3), 55.3 (CH_3), 55.2 (CH_3), 32.0 ($^1J_{C\text{-}P}$ = 67 Hz, C_q), 23.1 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 42.6. IR (KBr): 3016, 2952, 2897, 2181, 1663, 1462, 1284, 1163, 1030, 780 cm^{-1}. MS (EI) *m/z* (relative intensity) 348 (10) [M^+], 317 (100), 291 (10), 276 (20), 261 (30), 243 (10), 217 (5), 101 (20), 59 (30). HRMS (ESI) *m/z* calcd for $C_{19}H_{25}O_4P+H^+$ 349.1563, found 349.1563.



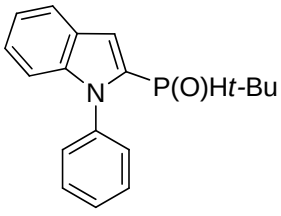
4g

***P*-Cyclohexyl-*P*-(2',6'-dimethoxy-biphen-2-yl)phosphine oxide 4g:** To a solution of 2-bromo-2',6'-dimethoxybiphenyl (0.75 g, 2.50 mmol) in THF (20 mL) was added *n*-BuLi (1.50 mL, 1.60 M solution in hexanes, 3.50 mmol) and the reaction was stirred at -78 °C for 3 h. Then, a solution of $CyPCl_2$ (0.52 g, 2.80 mmol) in THF (5.0 mL) was added dropwise and the mixture was heated to 110 °C for 12 h. After the mixture was cooled to ambient temperature, H_2O (10 mL) was added and the mixture was stirred for 30 min at ambient temperature, extracted with CH_2Cl_2 (2 x 25 mL) and dried over anhydrous $MgSO_4$. The solvents were removed and the remaining residue was subjected to column chromatography (CH_2Cl_2/MeOH: 1/1) to yield **4g** (660 mg, 75%) as colourless crystals. m.p: 120–122 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.05–7.95 (m, 1H), 7.60–7.45 (m, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.22–7.15 (m, 1H), 6.82 (d, J = 474.2 Hz, 1H), 6.62 (t, J = 8.0 Hz, 2H), 3.70 (s, 6H), 1.79–0.90 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7 (C_q), 157.0 (C_q), 136.6 ($^1J_{C\text{-}P}$ = 11 Hz, C_q), 132.1 ($^3J_{C\text{-}P}$ = 7 Hz, CH), 131.6 ($^2J_{C\text{-}P}$ = 11 Hz, CH), 131.5 (CH), 131.4 (CH), 130.2 (CH), 129.0 ($^3J_{C\text{-}P}$ = 4 Hz, C_q), 127.3 (CH), 115.8 ($^2J_{C\text{-}P}$ = 6 Hz, C_q), 103.5 ($^3J_{C\text{-}P}$ = 6 Hz, CH), 55.7 (CH_3), 55.5 (CH_3), 38.0 (CH), 26.4 (CH_2), 26.1 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 23.5 (CH_2). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 30.8. IR (KBr): 3056, 2958, 2846, 2179, 1931, 1680, 1174, 1109, 1039, 739 cm^{-1}. MS (EI) *m/z* (relative intensity) 344 (10) [M^+], 313 (100), 273 (10), 246 (20), 231 (10), 212 (5), 168 (5), 139 (5). HRMS (ESI) *m/z* calcd for $C_{20}H_{25}O_3P+H^+$ 345.1614, found 345.1616.



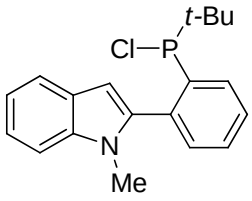
4h

***P*-*tert*-Butyl-*P*-(*N*-phenylpyrrol-2-yl)phosphine oxide 4h:** In a three-necked 100 mL round-bottomed flask equipped with a reflux condenser, *N*-phenylpyrrole (0.50 g, 3.50 mmol) was dissolved in hexane (10 mL). TMEDA (0.60 g, 0.80 mL, 5.20 mmol) was added followed by *n*-BuLi (1.50 mL, 1.60 M in hexane, 3.50 mmol) at ambient temperature. The reaction mixture was refluxed for 3 h. A solution of the *t*-$BuPCl_2$ (0.56 g, 3.50 mmol) in PhMe (5.0 mL) was slowly added through a syringe to the yellow solution. The mixture was heated at 110 °C for 1 h. At ambient temperature, H_2O (15 mL) was added and the mixture was stirred for 10 min. The aqueous layer was extracted with PhMe (2 x 25 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated. Purification by column chromatography (Et_2O/MeOH: 20/1) yielded **4h** (640 mg, 74%) as a colourless solid. Crystals suitable for X-ray analysis were obtained in CH_2Cl_2 as solvent by vapour diffusion method. m.p: 70–72 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.47 (m, 2H), 7.46–7.40 (m, 2H), 7.39–7.32 (m, 1H), 7.09–7.04 (m, 1H), 6.94–6.88 (m, 1H), 6.89 (d, J = 463.0 Hz, 1H), 6.39–6.34 (m, 1H), 0.91 (d, J = 16.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (C_q), 129.4 ($^3J_{C\text{-}P}$ = 6 Hz, CH), 129.3 (CH), 128.1 (CH), 126.2 (CH), 122.3 ($^2J_{C\text{-}P}$ = 15 Hz, CH), 121.8 ($^1J_{C\text{-}P}$ = 104 Hz, C_q), 110.0 ($^3J_{C\text{-}P}$ = 11 Hz, CH), 32.6 ($^1J_{C\text{-}P}$ = 75 Hz, C_q), 23.8 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 33.1. IR (KBr): 3058, 2961, 2897, 1549, 1467, 1172, 1101, 1087, 1029, 765 cm^{-1}. MS (EI) *m/z* (relative intensity) 247 (25) [M^+], 191 (20), 172 (20), 144 (100), 115 (10), 77 (10), 41 (30). HRMS (ESI) *m/z* calcd for $C_{14}H_{18}ONP+H^+$ 248.1198, found 248.1200.



4i

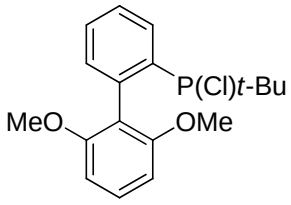
***P*-*tert*-Butyl-*P*-(*N*-phenylindol-2-yl)phosphine oxide 4i:** In a three-necked 100 mL round-bottomed flask equipped with a reflux condenser, *N*-phenylindole (0.92 g, 4.70 mmol) was dissolved in PhMe (10 mL). TMEDA (0.81 g, 1.05 mL, 7.00 mmol) was added, followed by *n*-BuLi (2.00 mL, 1.60 M in hexane, 4.70 mmol) at ambient temperature. The reaction mixture was heated at 110 °C for 3 h. A solution of the *t*-$BuPCl_2$ (0.75 g, 4.70 mmol) in PhMe (5.0 mL) was slowly added through a syringe to the red solution. The mixture was heated at 110 °C for 2 h. At ambient temperature, H_2O (15 mL) was added and the mixture was stirred for 10 min to give a clear solution. The aqueous layer was extracted with PhMe (2 x 25 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to give a yellow viscous liquid. Purification by column chromatography (CH_2Cl_2) yielded **4i** (850 mg, 60%) as colourless solid. m.p. 94–96 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (dt, J = 7.8, 1.6 Hz, 1H), 7.55–7.40 (m, 5H), 7.28 (dd, J = 5.2, 0.6 Hz, 1H), 7.26–7.13 (m, 3H), 6.93 (d, J = 467.1 Hz, 1H), 0.96 (d, J = 17.5 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 ($^3J_{C\text{-}P}$ = 6 Hz, C_q), 137.6 (C_q), 129.5 (2CH), 129.3 ($^1J_{C\text{-}P}$ = 100 Hz, C_q), 128.6 (CH), 128.4 (CH), 126.9 ($^3J_{C\text{-}P}$ = 11 Hz, C_q), 125.0 (CH), 121.9 (CH), 121.2 (CH), 115.2 ($^2J_{C\text{-}P}$ = 14 Hz, CH), 111.1 (CH), 32.5 ($^1J_{C\text{-}P}$ = 78 Hz, C_q), 23.6 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 32.5. IR (KBr): 3054, 2966, 2894, 1654, 1497, 1201, 1172, 1025, 935 cm^{-1}. MS (EI) *m/z* (relative intensity) 297 (90) [M^+], 240 (20), 222 (40), 194 (100), 165 (20), 140 (2). HRMS (ESI) *m/z* calcd for $C_{18}H_{20}ONP+H^+$ 298.1355, found 298.1355.



5a

2-(2-[1-(*tert*-Butyl)-1-chlorophosphino]phenyl)-1-methyl-1*H*-indole 5a: *N*-methyl-2-(2′-bromophenyl)indole (700 mg, 2.40 mmol) was dissolved in THF (10 mL) at ambient temperature. The solution was cooled to -78 ^oC and *n*-BuLi (172 mg, 1.60 M solution in hexanes, 2.60 mmol) was added slowly via syringe. After the reaction was stirred for 30 min at -78 ^oC, *t*-$BuPCl_2$ (413 mg, 2.60 mmol) in THF (5.0 mL) was slowly added over a period of 20 min. The reaction was allowed to warm to ambient

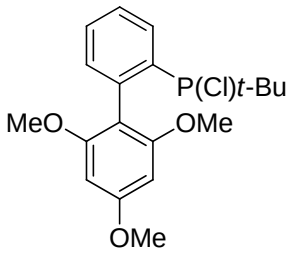
temperature and then stirred overnight. Evaporation of the solvents and diluting the crude material with EtOAc (20 mL) gave **5a** (330 mg, 41%) as a white solid. m.p: 139–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.0 Hz, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.29–7.21 (m, 3H), 7.16 (dt, J = 7.9, 1.0 Hz, 1H), 4.14 (s, 3H), 1.09 (d, J = 14.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9 (C_q), 146.6 ($^{2}J_{C\text{-}P}$ = 13 Hz, C_q), 142.4 (C_q), 136.7 (CH), 131.3 ($^{2}J_{C\text{-}P}$ = 19 Hz, CH), 127.9 (CH), 127.8 ($^{1}J_{C\text{-}P}$ = 14 Hz, C_q), 125.2 ($^{2}J_{C\text{-}P}$ = 8 Hz, CH), 122.0 (CH), 121.1 (CH), 120.2 (CH), 120.0 (CH), 113.7 ($^{3}J_{C\text{-}P}$ = 5 Hz, C_q), 109.7 (CH), 32.2 ($^{1}J_{C\text{-}P}$ = 31 Hz, C_q), 31.6 (CH_3), 27.6 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = -4.20. IR (KBr): 3056, 2989, 2895, 1541, 1463, 1169, 1072, 1032, 791 cm^{-1}. MS (EI) *m/z* (relative intensity) 329 (100) [M^+], 315 (10), 281 (10). HRMS (ESI): m/z calcd $C_{19}H_{21}ClNP+H^+$ 330.1178, found 330.1174.



5b

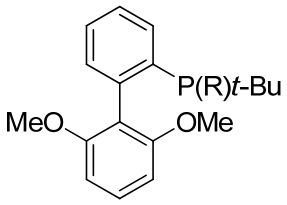
***P*-*tert*-Butyl-*P*-(2',6'-dimethoxy-biphen-2-yl)phosphine chloride 5b:** To a solution of 2-bromo-2',6'-dimethoxybiphenyl (1.00 g, 3.40 mmol) in THF (20 mL) was added *n*-BuLi (2.80 mL, 1.60 M solution in hexanes, 4.70 mmol) and the reaction was stirred at -78 °C for 3 h. Then, a solution of *t*-BuPCl_2 (0.59 g, 3.70 mmol) in THF (5.0 mL) was added dropwise and the mixture was heated at 110 °C for 12 h. At ambient temperature, the solvents were removed and the residue was subjected to column chromatography (*n*-hexane/EtOAc: 5/1) to yield **5b** (0.92 g, 86%) as colourless crystals. Crystals suitable for X-ray analysis were obtained in CH_2Cl_2 as solvent by vapour diffusion method. m.p: 129–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.92–7.89 (m, 1H), 7.45–7.36 (m, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.18–7.14 (m, 1H), 6.58 (dd, J = 8.3, 5.7 Hz, 2H), 3.75 (s, 3H), 3.64 (s, 3H), 0.92 (d, J = 13.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9 (C_q), 157.1 (C_q), 139.7 ($^{2}J_{C\text{–}P}$ = 38 Hz, C_q), 136.3 ($^{1}J_{C\text{-}P}$ = 42 Hz, C_q), 132.2 (CH), 131.0 ($^{3}J_{C\text{-}P}$ = 6 Hz, CH), 129.8 (CH), 129.7 (CH), 129.4 (CH), 126.6 (CH), 117.9 ($^{3}J_{C\text{-}P}$ = 8 Hz, C_q), 103.6 ($^{2}J_{C\text{-}P}$ = 19 Hz, CH), 55.8 (CH_3), 55.2 (CH_3), 34.7 ($^{1}J_{C\text{-}P}$ = 33 Hz, C_q), 25.1 (CH_3). ^{31}P NMR

(121.5 MHz, $CDCl_3$): δ = 107.7. IR (KBr): 2956, 2933, 1609, 1409, 1205, 1158, 1135, 1078, 1014, 787 cm^{-1}. MS (EI) *m/z* (relative intensity) 336 (10) [M^+], 305 (40), 249 (30), 214 (100), 184 (20), 155 (10). HRMS (ESI): m/z calcd $C_{18}H_{22}ClO_2P+H^+$ 337.1124, found 337.1129.



5c

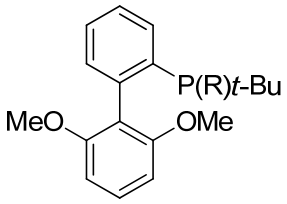
***P*-*tert*-Butyl-*P*-(2',4',6'-trimethoxy-biphen-2-yl)phosphine chloride 5c:** To a solution of 2-bromo-2',4',6'-trimethoxybiphenyl (1.20 g, 3.70 mmol) in THF (20 mL) was added *n*-BuLi (3.10 mL, 1.60 M solution in hexanes, 5.20 mmol) and the reaction was stirred at -78 °C for 3 h. Then, a solution of *t*-$BuPCl_2$ (0.64 g, 4.00 mmol) in THF (5.0 mL) was added dropwise and the mixture was heated at 110 °C for 12 h. At ambient temperature, the solvents were removed and the residue was subjected to column chromatography (*n*-hexane/EtOAc: 5/1) to yield **5c** (1.28 g, 95%) as colourless crystals. Crystals suitable for X-ray analysis were obtained in CH_2Cl_2 as solvent by vapour diffusion method. m.p: 120–122 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.84 (m, 1H), 7.45–7.32 (m, 2H), 7.17–7.10 (m, 1H), 6.18–6.12 (m, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 0.91 (d, J = 15 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.2 (C_q), 158.5 (C_q), 157.0 (C_q), 138.2 ($^2J_{C\text{-}P}$ = 14 Hz, C_q), 133.3 (CH), 133.1 (CH), 133.0 (CH), 132.2 ($^4J_{C\text{-}P}$ = 8 Hz, CH), 127.2 ($^3J_{C\text{-}P}$ = 13 Hz, CH), 109.2 ($^3J_{C\text{-}P}$ = 5 Hz, C_q), 100.5 ($^1J_{C\text{-}P}$ = 18 Hz, C_q), 90.5 ($^2J_{C\text{-}P}$ = 84 Hz, CH), 56.2 (CH_3), 55.4 (CH_3), 55.3 (CH_3), 32.0 ($^1J_{C\text{-}P}$ = 38 Hz, C_q), 22.9 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 109.8. IR (KBr): 3009, 2950, 2898, 2159, 1618, 1416, 1178, 1070, 1047, 777 cm^{-1}. MS (EI) *m/z* (relative intensity) 389 (100) [M+Na^+], 367 (30) [M+H^+], 331 (10), 275 (20). HRMS (ESI) *m/z* calcd for $C_{19}H_{24}O_3PCl+H^+$ 367.1124, found 367.1121.



R = 4-MeOC$_6$H$_4$

6a

***P-tert*-Butyl-*P*-(2',6'-dimethoxy-biphen-2-yl)-P-(4-methoxyphenyl)phosphine 6a:** To a solution of *P-tert*-butyl-*P*-(2',6'-dimethoxy-biphen-2-yl) phosphine chloride (**5b**) (1.14 g, 3.40 mmol) in THF (20 mL) was added $Pd(OAc)_2$ (30 mg, 4.0 mol %, 0.13 mmol). Then, a solution of 4-methoxyphenylmagnesium bromide (5.10 mL, 5.10 mmol 1.00 M in THF) was added dropwise, and the mixture was stirred at 60 ^oC for 12 h. At ambient temperature, the solvents were removed and the residue was subjected to column chromatography (*n*-hexane/EtOAc: 3/1) to yield **6a** (0.72 g, 52%) as colourless crystals. m.p. 148–150 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.59 (m, 1H), 7.46–7.13 (m, 6H), 6.80 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 7.9 Hz, 1H), 6.47 (d, J = 7.9 Hz, 1H), 3.75 (d, 6H), 3.33 (s, 3H), 1.05 (d, J = 12.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (C_q), 157.6 (C_q), 157.4 (C_q), 142.5 ($^1J_{C–P}$ = 34 Hz, C_q), 138.1 ($^2J_{C-P}$ = 19 Hz, C_q), 134.8 ($^2J_{C-P}$ = 19 Hz, CH), 134.3 ($^4J_{C-P}$ = 3 Hz, CH), 131.2 ($^3J_{C-P}$ = 6 Hz, CH), 130.3 ($^1J_{C-P}$ = 20 Hz, C_q), 128.6 (CH), 128.3 (CH), 126.3 (CH), 120.0 ($^3J_{C-P}$ = 8 Hz, C_q), 113.1 ($^3J_{C-P}$ = 7 Hz, CH), 103.4 ($^2J_{C-P}$ = 53 Hz, CH), 55.6 (CH_3), 55.1 (CH_3), 55.0 (CH_3), 30.5 ($^1J_{C-P}$ = 17 Hz, C_q), 28.7 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 7.15. IR (KBr): 3051, 2948, 2895, 2048, 1587, 1442, 1178, 1082, 1034, 910 cm^{-1}. MS (EI) *m/z* (relative intensity) 431 (40) [M+Na^+], 409 (100) [M+H^+], 377 (10). HRMS (ESI): m/z calcd $C_{25}H_{29}O_3P+H^+$ 409.1933, found 409.1928.



R = *n*-hexyl

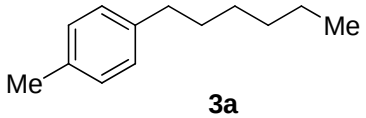
6b

***P-tert*-Butyl-*P*-(2',6'-dimethoxy-biphen-2-yl)-P-(*n*-hexyl)phosphine 6b:** To a solution of *P-tert*-butyl-*P*-(2',6'-dimethoxy-biphen-2-yl) phosphine chloride (**5b**) (0.20 g, 0.58 mmol) in THF (10 mL) was added

n-BuLi (0.75 mL, 1.60 M solution in hexanes, 0.70 mmol) and the reaction was stirred at -78 °C for 2 h. Then, a solution of 1-chlorohexane (0.084 g, 0.70 mmol) in THF (5.0 mL) was added dropwise and the mixture was heated at 110 °C for 12 h. At ambient temperature, H_2O (20 mL) was added and the resulting mixture was stirred for 30 min at ambient temperature, extracted with CH_2Cl_2 (2 x 25 mL), and dried over anhydrous $MgSO_4$. The solvents were removed and purification by column chromatography (*n*-hexane/EtOAc: 9/1) yielded **6b** (182 mg, 81%) as colourless crystals. m.p: 168-170 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 1H), 7.44–7.33 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.19–7.14 (m, 1H), 6.56 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 3.63 (s, 3H), 1.95–1.81 (m, 1H), 1.57–1.43 (m, 1H), 1.39–1.18 (m, 8H), 0.88–0.78 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6 (C_q), 157.2 (C_q), 143.0 ($^1J_{C–P}$ = 33 Hz, C_q), 136.4 ($^2J_{C-P}$ = 25 Hz, C_q), 131.6 ($^4J_{C-P}$ = 4 Hz, CH), 131.0 ($^3J_{C-P}$ = 6 Hz, CH), 128.6 (CH), 128.3 (CH), 126.1 (CH), 120 ($^3J_{C-P}$ = 6 Hz, C_q), 103.2 ($^3J_{C-P}$ = 13 Hz, CH), 55.3 (CH_3), 55.1 (CH_3), 31.7 (CH_2), 31.5 (CH_2), 29.2 ($^1J_{C-P}$ = 14 Hz, C_q), 27.5 (CH_3), 26.4 ($^2J_{C-P}$ = 19 Hz, CH_2), 22.6 (CH_2), 22.2 ($^3J_{C-P}$ = 17 Hz, CH_2), 14.0 (CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = -8.50. IR (KBr): 3051, 2948, 2895, 2048, 1468, 1177, 1071, 1045, 773 cm^{-1}. MS (EI) *m/z* (relative intensity) 386 (10) [M^+], 313 (100), 273 (10), 246 (10), 231 (20), 212 (10), 168 (10), 139 (10). HRMS (ESI): m/z calcd $C_{24}H_{35}O_2P+H^+$ 387.2453, found 387.2451.

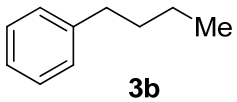
Representative procedure A: Kumada-Corriu cross-coupling of alkyl chlorides (Table 1, entry 12) and characterization data for 3a-3l:

A solution of $Pd(OAc)_2$ (18 mg, 4.0 mol %, 0.08 mmol) and **5b** (26 mg, 4.0 mol %, 0.08 mmol) in NMP (5.0 mL) was stirred for 10 min at ambient temperature under N_2. Then, 1-chloro-*n*-hexane (240 mg, 0.27 mL, 2.00 mmol) was added *via* syringe and the solution was stirred for 5 min at ambient temperature. Thereafter, 4-tolylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) was added dropwise over 3 min to the stirred reaction mixture. The resulting solution was stirred for 20 h at ambient temperature, after which MeOH (1.00 mL) and H_2O (1.00 mL) were added and the resultant solution was concentrated *in vacuo*. Purification of the residue by column chromatography (*n*-hexane) yielded **3a** (281 mg, 80%) as a colourless liquid.



3a

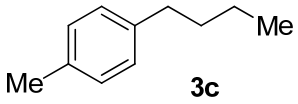
***n*-Hexyl-4-methylbenzene (3a):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (vs, 4H), 2.57 (t, J = 7.7 Hz, 2H), 2.32 (s, 3H), 1.65–1.51 (m, 2H), 1.40–1.21 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (C_q), 134.9 (C_q), 128.8 (CH), 128.2 (CH), 35.5 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 29.0 (CH_2), 22.6 (CH_2), 20.9 (CH_3), 14.1 (CH_3). IR (NaCl): 3089, 2951, 2870, 1799, 1356, 1182, 1103, 1066, 1030, 783 cm^{-1}. MS (EI) *m/z* (relative intensity) 176 (10) [M^+], 165 (5), 119 (5), 105 (100), 91 (10), 79 (5). HRMS (EI) *m/z* calcd for $C_{13}H_{20}$ 176.1565, found 176.1570. The spectral data were in accordance with those reported in the literature.[8]



3b

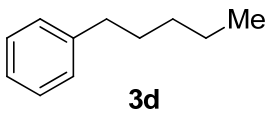
***n*-Butylbenzene (3b):** Representative procedure A was followed, using phenylmagnesium chloride (3.00 mL, 3.00 mmol, 1.00 M in THF) and 1-chloro-*n*-butane (184 mg, 0.21 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3b** (160 mg, 60%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (t, J = 6.7 Hz, 2H), 7.21–7.18 (m, 3H), 2.59 (t, J = 7.6 Hz, 2H), 1.66–1.50

(m, 2H), 1.38–1.21 (m, 2H), 0.86 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7 (C_q), 128.2 (CH), 127.9 (CH), 125.8 (CH), 35.1 (CH_2), 31.2 (CH_2), 22.4 (CH_2), 14.0 (CH_3). IR (NaCl): 2958, 1938, 1786, 1494, 1344, 1032, 785, 726 cm^{-1}. MS (EI) *m/z* (relative intensity) 134 (20) [M^+], 119 (5), 105 (10), 91 (60), 78 (10), 65 (11), 43 (100). HRMS (EI) *m/z* calcd for $C_{10}H_{14}$ 134.1095, found 134.1095. The spectral data were in accordance with those reported in the literature.[9]



3c

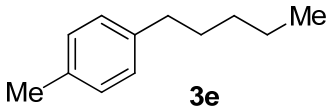
***n*-Butyl-4-methylbenzene (3c):** Representative procedure A was followed, using 4-methylphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) and 1-chloro-*n*-butane (184 mg, 0.21 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3c** (183 mg, 62%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (vs, 4H), 2.60 (t, J = 7.7 Hz, 2H), 2.33 (s, 3H), 1.65–1.53 (m, 2H), 1.44–1.25 (m, 2H), 0.94 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7 (C_q), 134.8 (C_q), 128.8 (CH), 128.2 (CH), 35.2 (CH_2), 33.9 (CH_2), 22.3 (CH_2), 20.9 (CH_3), 13.9 (CH_3). IR (NaCl): 3088, 2961, 1943, 1492, 1345, 1031, 783, 726, 676, 570 cm^{-1}. MS (EI) *m/z* (relative intensity) 148 (20) [M^+], 133 (20), 105 (100), 91 (20), 67 (30), 55 (15), 43 (35). HRMS (EI) *m/z* calcd for $C_{11}H_{16}$ 148.1252, found 148.1252. The spectral data were in accordance with those reported in the literature.[10]



3d

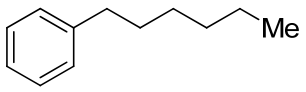
***n*-Pentylbenzene (3d):** Representative procedure A was followed, using phenylmagnesium chloride (1.36 mL, 3.00 mmol, 2.20 M in THF) and 1-chloro-*n*-pentane (212 mg, 0.24 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3d** (192 mg, 65%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (t, J = 6.5 Hz, 2H), 7.20–7.17 (m, 3H), 2.60 (t, J = 7.6 Hz, 2H), 1.65–1.50 (m, 2H), 1.40–1.19 (m, 4H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 142.6 (C_q), 128.4

(CH), 128.2 (CH), 125.8 (CH), 35.5 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3). IR (NaCl): 3081, 2952, 1936, 1795, 1492, 1353, 1033, 787, 726, 698 cm^{-1}. MS (EI) *m/z* (relative intensity) 148 (10) [M^+], 121 (100), 91 (15), 77 (10), 65 (10), 41 (35). HRMS (EI) *m/z* calcd for $C_{11}H_{16}$ 148.1252, found 148.1247. The spectral data were in accordance with those reported in the literature.[9]



3e

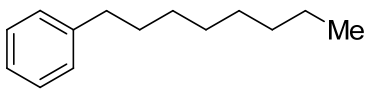
4-Methyl-*n*-pentylbenzene (3e): Representative procedure A was followed, using 4-methylphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) and 1-chloro-*n*-pentane (212 mg, 0.24 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3e** (217 mg, 67%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (vs, 4H), 2.57 (t, J = 7.7 Hz, 2H), 2.34 (s, 3H), 1.67–1.51 (m, 2H), 1.40–1.22 (m, 4H), 0.91 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (C_q), 134.9 (C_q), 128.8 (CH), 128.2 (CH), 35.4 (CH_2), 31.5 (CH_2), 22.5 (CH_2), 22.3 (CH_2), 20.9 (CH_3), 14.0 (CH_3). IR (NaCl): 3086, 2958, 2872, 1799, 1495, 1353, 1031, 783, 726, 696 cm^{-1}. MS (EI) *m/z* (relative intensity) 162 (10) [M^+], 148 (15), 121 (100), 91 (15), 77 (10), 65 (10), 41 (35). HRMS (EI) *m/z* calcd for $C_{12}H_{18}$ 162.1409, found 162.1414. The spectral data were in accordance with those reported in the literature.[11]



3f

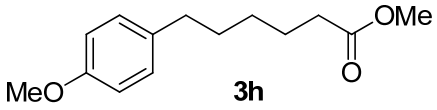
***n*-Hexylbenzene (3f):** Representative procedure A was followed, using phenylmagnesium chloride (1.36 mL, 3.00 mmol, 2.20 M in THF) and 1-chloro-*n*-hexane (240 mg, 0.27 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3f** (226 mg, 70%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (t, J = 6.5 Hz, 2H), 7.17–7.14 (m, 3H), 2.59 (t, J = 7.6 Hz, 2H), 1.67–1.52 (m, 2H), 1.40–1.19 (m, 6H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.9 (C_q), 128.3 (CH), 128.1 (CH), 125.5 (CH), 35.9 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

IR (NaCl): 3080, 2961, 2859, 1793, 1602, 1490, 1353, 1028, 778, 731, 698 cm^{-1}. MS (EI) *m/z* (relative intensity) 162 (10) [M^+], 133 (5), 119 (5), 105 (10), 91 (100), 71 (10), 65 (15), 57 (15), 43 (50). HRMS (EI) *m/z* calcd for $C_{12}H_{18}$ 162.1408, found 162.1415. The spectral data were in accordance with those reported in the literature.[12]



3g

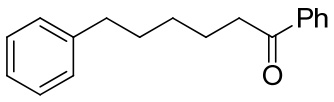
***n*-Octylbenzene (3g):** Representative procedure A was followed, using phenylmagnesium chloride (1.36 mL, 3.00 mmol, 2.20 M in THF) and 1-chloro-*n*-octane (296 mg, 0.34 mL, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane) yielded **3g** (220 mg, 58%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 6.3 Hz, 2H), 7.16–7.13 (m, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.64–1.46 (m, 2H), 1.39–1.19 (m, 10H), 0.86 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (C_q), 128.8 (CH), 128.2 (CH), 125.6 (CH), 35.3 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 29.9 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 22.4 (CH_2), 14.0 (CH_3). IR (NaCl): 3086, 2958, 1939, 1799, 1606, 1495, 1031, 783, 698, 570 cm^{-1}. MS (EI) *m/z* (relative intensity) 190 (20) [M^+], 165 (10), 119 (5), 105 (100), 91 (10), 79 (10), 57 (10), 43 (20). HRMS (EI) *m/z* calcd for $C_{14}H_{22}$ 190.1722, found 190.1728. The spectral data were in accordance with those reported in the literature.[10]



3h

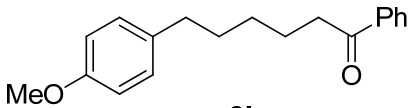
6-(4-Methoxyphenyl)-hexanoic acid methyl ester (3h): Representative procedure A was followed, using 4-methoxyphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) and 6-chloro-1-hexanoic acid methyl ester (328 mg, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane/EtOAc: 10/1) yielded **3h** (240 mg, 51%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.28 (t, *J* = 8.2 Hz, 2H), 1.74–1.49 (m, 4H), 1.45–1.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.1 (C_q),

157.6 (C_q), 134.5 (C_q), 129.2 (CH), 113.6 (CH), 55.2 (CH_3), 51.4 (CH_3), 34.7 (CH_2), 34.0 (CH_2), 31.3 (CH_2), 28.6 (CH_2), 24.7 (CH_2). IR (NaCl): 3015, 2939, 2872, 2365, 1742, 1702, 1610, 1459, 1353, 1179, 1106, 1066, 1025 cm^{-1}. MS (EI) *m/z* (relative intensity) 236 (100) [M^+], 205 (20), 147 (40), 130 (50), 106 (10), 76 (20). HRMS (ESI) *m/z* calcd for $C_{14}H_{20}O_3$+H^+ 237.1491, found 237.1490. The spectral data were in accordance with those reported in the literature.[13]



3i

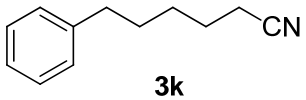
1,6-Diphenyl-1-hexanone (3i): Representative procedure A was followed, using phenylmagnesium chloride (1.36 mL, 3.00 mmol, 2.20 M in THF) and 6-chloro-1-phenyl-1-hexanone (420 mg, 2.00 mmol). After 20 h, purification by chromatography (*n*-hexane/EtOAc: 50/1) yielded **3i** (282 mg, 56%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.20–7.12 (m, 3H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.84–1.60 (m, 4H), 1.49–1.35 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.4 (C_q), 142.5 (C_q), 137.0 (C_q), 132.9 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 125.6 (CH), 38.5 (CH_2), 35.7 (CH_2), 31.3 (CH_2), 29.0 (CH_2), 24.1 (CH_2). IR (NaCl): 3062, 3023, 2959, 1741, 1452, 1291, 1074, 757, 726 cm^{-1}. MS (EI) *m/z* (relative intensity) 252 (100) [M^+], 205 (20), 177 (10), 163 (25), 91 (20), 77 (10). HRMS (EI) *m/z* calcd for $C_{18}H_{20}O$ 252.1514, found 252.1512.



3j

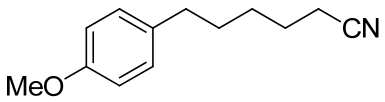
1-Phenyl-6-(4-methoxyphenyl)-1-hexanone (3j): Representative procedure A was followed, using 4-methoxyphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) and 6-chloro-1-phenyl-1-hexanone (420 mg, 2.00 mmol). After 20 h at 60 °C, purification by chromatography (*n*-hexane/EtOAc: 50/1) yielded **3j** (401 mg, 71%) as colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 8.0,

1.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H), 2.95 (t, *J* = 6.9 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.84–1.68 (m, 2H), 1.65–1.55 (m, 2H), 1.51–1.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.4 (C_q), 157.6 (C_q), 137.0 (C_q), 134.6 (C_q), 132.8 (CH), 129.2 (CH), 128.5 (CH), 128.0 (CH), 113.6 (CH), 55.2 (CH_3), 38.5 (CH_2), 34.8 (CH_2), 31.5 (CH_2), 28.9 (CH_2), 24.1 (CH_2). IR (NaCl): 3059, 3009, 2959, 1740, 1588, 1155, 1092, 1074, 757, 726 cm^{-1}. MS (EI) *m/z* (relative intensity) 282 (100) [M^+], 205 (20), 177 (10), 163 (25), 121 (10), 107 (20), 76 (5). HRMS (EI) *m/z* calcd for $C_{19}H_{22}O_2$ 282.1620, found 282.1619.



3k

5-Phenylpentyl cyanide (3k): Representative procedure A was followed, using phenylmagnesium chloride (1.36 mL, 3.00 mmol, 2.20 M in THF) and 5-chloropentyl cyanide (242 mg, 2.00 mmol). After 20 h at 60 °C, purification by chromatography (*n*-hexane/EtOAc: 50/1) yielded **3k** (238 mg, 69%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 7.0 Hz, 2H), 7.19–7.15 (m, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.76–1.58 (m, 4H), 1.54–1.39 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.0 (C_q), 128.3 (CH), 128.3 (CH), 125.8 (CH), 119.7 (C_q), 35.5 (CH_2), 30.6 (CH_2), 28.2 (CH_2), 25.3 (CH_2), 17.0 (CH_2). IR (NaCl): 3062, 2957, 2359, 1701, 1581, 1457, 1259, 1110, 1066, 794 cm^{-1}. MS (EI) *m/z* (relative intensity) 173 (100) [M^+], 147 (10), 119 (5), 105 (10), 91 (40), 79 (10), 57 (10), 43 (20). HRMS (EI) *m/z* calcd for $C_{12}H_{15}N$ 173.1204, found 173.1208. The spectral data were in accordance with those reported in the literature.[14]

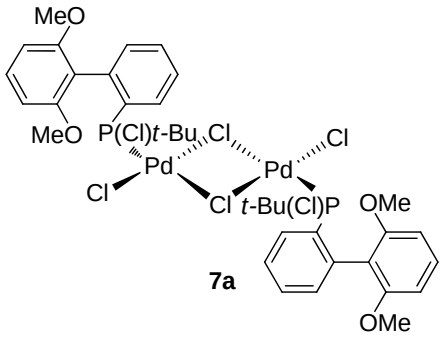


3l

5-(4-Methoxyphenyl)pentyl cyanide (3l): The representative procedure was followed, using 4-methoxyphenylmagnesium bromide (3.00 mL, 3.00 mmol, 1.00 M in THF) and 5-chloropentyl cyanide (242 mg, 2.00 mmol). After 20 h at 60 °C, purification by chromatography (*n*-hexane/EtOAc: 25/1)

yielded **3l** (259 mg, 64%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 2.55 (t, J = 7.6 Hz, 2H), 2.31 (t, J = 7.3 Hz, 2H), 1.76–1.52 (m, 4H), 1.50–1.39 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7 (C_q), 134.0 (C_q), 129.2 (CH), 119.7 (C_q), 113.7 (CH), 55.2 (CH_3), 34.6 (CH_2), 30.8 (CH_2), 28.1 (CH_2), 25.2 (CH_2), 17.0 (CH_2). IR (NaCl): 3059, 2957, 2860, 2359, 1710, 1581, 1254, 1093, 1071, 901 cm^{-1}. MS (EI) *m/z* (relative intensity) 203 (100) [M^+], 177 (10), 163 (25), 121 (5), 107 (15). HRMS (EI) *m/z* calcd for $C_{13}H_{17}ON$ 203.1310, found 203.1312. The spectral data were in accordance with those reported in the literature.[14]

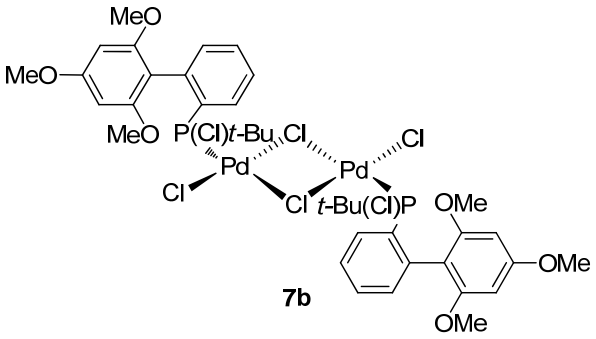
Preparation and characterization data for palladium complex 7a: A suspension of $[PdCl_2(C_6H_5CN)_2]$ (304 mg, 0.79 mmol) and **5b** (268 mg, 0.79 mmol) in PhMe (10 mL) was stirred under N_2 at 90 °C for 3 h and then for 12 h at ambient temperature. The resulting suspension was filtered and washed thoroughly with Et_2O (20 mL). Drying in vacuo yielded **7a** (288 mg, 72%) as an orange-red solid.



7a

m.p. > 210 °C decomposition. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.12–7.94 (m, 2H), 7.61–7.52 (m, 2H), 7.49–7.36 (m, 4H), 7.32–7.24 (m, 2H), 6.76–6.63 (m, 4H), 3.79 (s, 6H), 3.68 (s, 6H), 1.66-1.45 (m, 18H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = 121.2. IR (KBr): 2992, 2861, 2827, 2360, 1601, 1463, 1410, 1336, 1219, 1166, 1125, 1048, 945, 805, 767 cm^{-1}. MS (ESI) *m/z* (relative intensity) 1029 (10) [M+H$^+$], 961 (20), 549 (100), 513 (70). HRMS (ESI) *m/z* calcd for $C_{36}H_{44}O_6P_2Pd_2Cl_6$+H$^+$ 1024.8994, found 1024.8988.

Preparation and characterization data for palladium complex 7b: A suspension of $[PdCl_2(C_6H_5CN)_2]$ (260 mg, 0.68 mmol) and **5c** (250 mg, 0.68 mmol) in PhMe (10 mL) was stirred under N_2 at 90 °C for 3 h and then for 12 h at ambient temperature. The resulting suspension was filtered and washed thoroughly with Et_2O (20 mL). Drying in vacuo yielded **7b** (299 mg, 81%) as an orange solid. Crystals suitable for X-ray analysis were obtained in CH_2Cl_2 (5.0 mL) as solvent by vapour diffusion method.

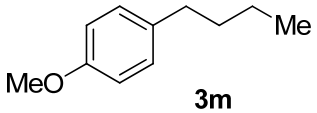


7b

m.p. > 200 ^{o}C decomposition. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82–7.70 (m, 2H), 7.58–7.34 (m, 4H), 6.74 (m, 2H), 6.11–5.93 (m, 4H), 4.05 (s, 6H), 3.74 (s, 12H), 1.44 (d, J = 20 Hz, 18H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = 125.9. IR (KBr): 2989, 2854, 2827, 1648, 1602, 1463, 1409, 1336, 1219, 1166, 1125, 1048, 945, 805, 767 cm^{-1}. MS (ESI) *m/z* (relative intensity) 1111 (10) [M+Na^{+}], 1089 (30) [M+H^{+}], 1055 (10), 993 (10), 549 (20), 505 (100). HRMS (ESI) *m/z* calcd for $C_{38}H_{48}O_6P_2Pd_2Cl_6$+H^{+} 1084.9205, found 1084.9201.

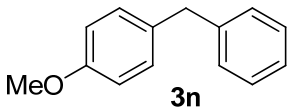
Representative procedure B: Kumada-Corriu cross-coupling of aryl bromide with alkyl-substituted Grignard reagents (Table 3, entry 1) and characterization data for 3m-3r:

A solution of **7a** (20 mg, 2.0 mol %, 0.02 mmol) in THF (1.00 mL) was stirred for 10 min at ambient temperature under N_2. 4-Bromoanisole (187 mg, 0.125 mL, 1.00 mmol) was then added *via* syringe and the solution stirred for 5 min. Then, *n*-butylmagnesium chloride (0.75 mL, 1.50 mmol, 2.00 M in THF) was added dropwise over 3 min to the mixture. The resulting solution was stirred for 24 h at 60 °C, after which H_2O (5.0 mL) was added at ambient temperature. The aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic phases were concentrated in vacuo and purification by column chromatography (*n*-hexane/EtOAc: 200/1) yielded **3m** (150 mg, 92%) as a colourless liquid.



3m

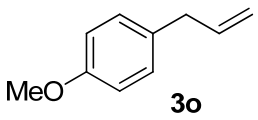
***n*-Butyl-4-methoxybenzene (3m):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 3.74 (s, 3H), 2.53 (t, J = 7.6 Hz, 2H), 1.56–1.41 (m, 2H), 1.32–1.15 (m, 2H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9 (C_q), 135.1 (C_q), 129.6 (CH), 113.2 (CH), 55.4 (CH_3), 35.2 (CH_2), 31.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3). IR (NaCl): 3097, 2956, 1486, 1363, 1110, 1082, 1052, 783, 726, 698 cm^{-1}. MS (EI) *m/z* (relative intensity) 164 (20) [M^+], 149 (30), 134 (10), 119 (10), 105 (100), 91 (10), 65 (15), 43 (100). HRMS (EI) *m/z* calcd for $C_{11}H_{16}O$ 164.1201, found 164.1198. The spectral data were in accordance with those reported in the literature.[15]



3n

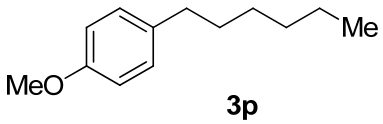
1-Benzyl-4-methoxybenzene (3n): Representative procedure B was followed, using benzylmagnesium chloride (0.75 mL, 1.50 mmol, 2.00 M in ether) and 4-bromoanisole (187 mg, 1.00 mmol). After 24 h at 60 ^{o}C, purification by chromatography (*n*-hexane:EtOAc 100:1) yielded **3n** (172 mg, 87%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.4 Hz, 2H), 7.21–7.14 (m, 3H), 7.11 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.92 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9 (C_q),

141.6 (C_q), 133.3 (C_q), 129.8 (CH), 128.8 (CH), 128.4 (CH), 126.0 (CH), 113.9 (CH), 55.2 (CH_3), 41.0 (CH_2). IR (NaCl): 2962, 2905, 1948, 1610, 1508, 1447, 1408, 1258, 1093, 1076, 796, 695 cm^{-1}. MS (ESI) *m/z* (relative intensity) 221 (100) [M+Na^+]. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}O$+Na^+ 221.0940, found 221.0937. The spectral data were in accordance with those reported in the literature.[15]



3o

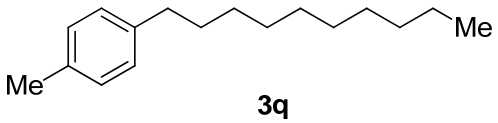
1-Allyl-4-methoxybenzene (3o): Representative procedure B was followed, using allylmagnesium chloride (1.50 mL, 1.50 mmol, 1.00 M in ether) and 4-bromoanisole (187 mg, 1.00 mmol). After 24 h at 60 ^oC, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3o** (121 mg, 82%) as a colourless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.94 (ddt, *J* = 16.5, 10.2, 7.0 Hz, 1H), 5.05 (d, *J* = 16.5 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 3.31 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9 (C_q), 137.9 (CH), 132.1 (C_q), 129.5 (CH), 115.4 (CH), 113.8 (CH), 55.2 (CH_3), 39.3 (CH_2). IR (NaCl): 2999, 2899, 2828, 1646, 1503, 1245, 1177, 1042, 987, 911 cm^{-1}. MS (EI) *m/z* (relative intensity) 148 (100) [M^+], 133 (10), 121 (30), 105 (20), 91 (10), 77 (15). HRMS (EI) *m/z* calcd for $C_{10}H_{12}O$ 148.0888, found 148.0887. The spectral data were in accordance with those reported in the literature.[16]



3p

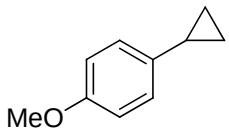
***n*-Hexyl-4-methoxybenzene (3p):** Representative procedure B was followed, using *n*-hexylmagnesium bromide[17] (1.50 mL, 1.50 mmol, 1.00 M in THF) and 4-bromoanisole (187 mg, 1.00 mmol). After 24 h at 60 ^oC, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3p** (163 mg, 85%) as a colourless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 3.76 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.61–1.48 (m, 2H), 1.35–1.16 (m, 6H), 0.86 (t, *J* = 6.5 Hz, 3H). ^{13}C

NMR (75 MHz, $CDCl_3$): δ = 157.5 (C_q), 135.0 (C_q), 129.2 (CH), 113.6 (CH), 55.2 (CH_3), 35.0 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 28.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3). IR (NaCl): 3094, 2956, 1799, 1495, 1108, 1070, 1050, 1031, 783 cm^{-1}. MS (EI) *m/z* (relative intensity) 192 (5) [M^+], 178 (15), 147 (5), 121 (100), 91 (10), 77 (5), 65 (5), 41 (10). HRMS (EI) *m/z* calcd for $C_{13}H_{20}O$ 192.1514, found 192.1514. The spectral data were in accordance with those reported in the literature.[18]



3q

***n*-Decyl-4-methylbenzene (3q):** Representative procedure B was followed, using *n*-decylmagnesium bromide[17] (1.50 mL, 1.50 mmol, 1.00 M in THF) and 4-bromotoluene (171 mg, 1.00 mmol). After 24 h at 60 °C, purification by chromatography (*n*-hexane) yielded **3q** (183 mg, 79%) as a colourless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.04 (vs, 4H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.67–1.51 (m, 2H), 1.40–1.18 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9 (C_q), 134.9 (C_q), 128.9 (CH), 128.2 (CH), 35.5 (CH_2), 31.9 (CH_2), 31.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 21.0 (CH_3), 14.1 (CH_2). IR (NaCl): 3011, 2958, 2872, 1643, 1512, 1457, 1373, 1114, 1034, 805, 723 cm^{-1}. MS (EI) *m/z* (relative intensity) 232 (100) [M^+], 217 (20), 147 (10), 133 (10), 105 (20), 92 (40), 43 (40). HRMS (EI) *m/z* calcd for $C_{17}H_{28}$ 232.2191, found 232.2188.



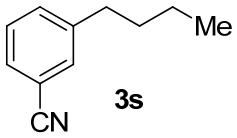
3r

Cyclopropyl-4-methoxybenzene (3r): Representative procedure B was followed, using cyclopropylmagnesium bromide (1.50 mL, 1.50 mmol, 1.00 M in THF) and 4-bromoanisole (187 mg, 1.00 mmol). After 24 h at 60 °C, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3r** (124 mg, 84%) as a colourless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.00 (d, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 3H), 1.93–1.79 (m, 1H), 0.95–0.84 (m, 2H), 0.66–0.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6 (C_q), 135.8 (C_q), 126.8 (CH), 113.7 (CH), 55.3 (CH_3), 14.6 (CH), 8.5 (CH_2). IR

(NaCl): 3003, 1701, 1644, 1619, 1513, 1461, 1297, 1247, 1176, 1033, 819 cm^{-1}. MS (EI) *m/z* (relative intensity) 148 (100) [M^+], 133 (85), 117 (90), 105 (70), 91 (80), 77 (65), 65 (50), 51 (70). HRMS (EI) *m/z* calcd for $C_{10}H_{12}O$ 148.0888, found 148.0888.

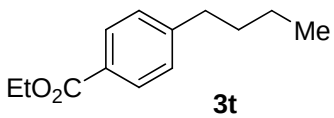
Representative procedure C: Negishi cross-coupling of aryl iodides with alkyl zinc reagents (Table 3, entry 9) and characterization data for 3s-3x:

To a solution of $ZnCl_2$ (1.60 mL, 1.60 mmol, 1.00 M in THF) was added dropwise *n*-butylmagnesium chloride (0.75 mL, 1.50 mmol, 2.00 M in THF) over 3 min at 0 °C. The solution was stirred at 0 °C for 1 h. In a second dry N_2-flushed Schlenk flask, a solution of **7a** (20 mg, 2.00 mol %, 0.02 mmol) and 3-iodobenzonitrile (229 mg, 1.00 mmol) in THF (2.00 mL) was stirred for 5 min at ambient temperature and the organozinc reagent was added. The reaction mixture was then stirred at 60 °C for 24 h. At ambient temperature, H_2O (5.0 mL) was added. The aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic phases were concentrated in vacuo. Purification by column chromatography (*n*-hexane/EtOAc: 100/1) yielded **3s** (111 mg, 70%) as a colourless liquid.



3s

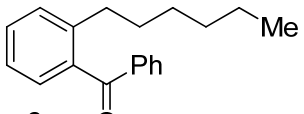
3-*n*-Butyl benzonitrile (3s): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.42 (m, 2H), 7.41–7.31 (m, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.65–1.51 (m, 2H), 1.41–1.18 (m, 2H), 0.91 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.2 (C_q), 133.1 (CH), 131.9 (CH), 129.4 (CH), 129.0 (CH), 119.1 (C_q), 112.2 (C_q), 35.2 (CH_2), 33.2 (CH_2), 22.1 (CH_2), 13.8 (CH_3). IR (NaCl): 3059, 2956, 2359, 2229, 1590, 1468, 1105, 1073, 794 cm^{-1}. MS (ESI) *m/z* (relative intensity) 182 (100) [M+Na$^+$]. HRMS (ESI) *m/z* calcd for $C_{11}H_{13}N$+Na$^+$ 182.0940, found 182.0946. The spectral data were in accordance with those reported in the literature.[19]



3t

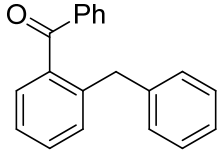
4-*n*-Butylbenzoic acid ethyl ester (3t): Representative procedure C was followed, using *n*-butylzinc chloride (1.50 mmol, 1.00 M in THF) and 4-iodobenzoic acid ethyl ester (276 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3t** (161 mg, 84%) as a colourless

liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.34 (q, J = 7.0 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 1.67–1.49 (m, 2H), 1.44–1.12 (m, 5H), 0.91 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 148.3 (C_q), 129.5 (CH), 128.4 (CH), 127.9 (C_q), 60.7 (CH_2), 35.7 (CH_2), 33.3 (CH_2), 22.3 (CH_2), 14.3 (CH_3), 13.9 (CH_3). IR (NaCl): 2958, 2866, 2360, 1718, 1419, 1176, 1109, 1023, 761, 701 cm^{-1}. MS (EI) *m/z* (relative intensity) 192 (30) [M^+], 178 (25), 161 (100), 149 (10), 136 (20), 118 (10), 107 (20), 91 (60), 77 (10), 65 (5), 51 (5). HRMS (EI) *m/z* calcd for $C_{12}H_{18}O_2$ 192.1150, found 192.1147. The spectral data were in accordance with those reported in the literature.[20]



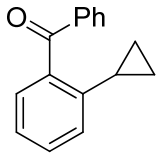
3u

2-Hexylbenzophenone (3u): Representative procedure C was followed, using *n*-hexylzinc chloride (1.50 mmol, 1.00 M in THF) and 2-iodobenzophenone (308 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3u** (231 mg, 87%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (dd, J = 7.8, 1.9 Hz, 2H), 7.60–7.53 (m, 1H), 7.49–7.42 (m, 2H), 7.42–7.36 (m, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.27–7.17 (m, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.58–1.44 (m, 2H), 1.32–1.10 (m, 6H), 0.80 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.7 (C_q), 141.7 (C_q), 138.5 (C_q), 137.9 (C_q), 133.1 (CH), 130.1 (CH), 130.0 (CH), 129.9 (CH), 128.3 (CH), 128.2 (CH), 125.0 (CH), 33.2 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 29.0 (CH_2), 22.5 (CH_2), 14.0 (CH_3). IR (NaCl): 3062, 3023, 2959, 2858, 1741, 1452, 1161, 1074, 757 cm^{-1}. MS (EI) *m/z* (relative intensity) 266 (35) [M^+], 237 (75), 223 (90), 194 (100), 178 (30), 165 (50), 145 (20), 131 (60), 115 (30), 91 (85). HRMS (ESI) *m/z* calcd for $C_{19}H_{22}O+H^+$ 267.1743, found 267.1745.



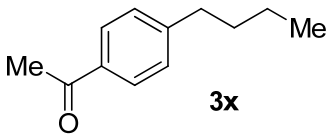
3v

2-Benzylbenzophenone (3v): Representative procedure C was followed, using benzylzinc chloride (1.50 mmol, 1.00 M in THF) and 2-iodobenzophenone (308 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3v** (252 mg, 93%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, J = 7.8, 1.9 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.45–7.37 (m, 3H), 7.35–7.24 (m, 3H), 7.22–7.13 (m, 2H), 7.11–7.07 (m, 3H), 4.07 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.5 (C_q), 140.4 (C_q), 140.0 (C_q), 138.6 (C_q), 137.6 (C_q), 133.0 (CH), 130.8 (CH), 130.2 (CH), 130.1 (CH), 129.1 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 126.0 (CH), 125.5 (CH), 38.8 (CH_2). IR (NaCl): 3061, 3027, 2915, 1731, 1489, 1154, 1076, 1031, 736, 701 cm^{-1}. MS (EI) *m/z* (relative intensity) 272 (30) [M^+], 194 (90), 165 (30), 105 (100), 77 (60), 65 (10), 51 (20). HRMS (ESI) *m/z* calcd for $C_{20}H_{16}O+H^+$ 273.1273, found 273.1275.



3w

2-Cyclopropylbenzophenone (3w): Representative procedure C was followed, using cyclopropylzinc chloride (1.50 mmol, 1.00 M in THF) and 2-iodobenzophenone (308 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3w** (159 mg, 72%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (dd, J = 8.1, 1.8 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 8.1 Hz, 2H), 7.40–7.33 (m, 1H), 7.27 (dt, J = 7.8, 1.9 Hz, 1H), 7.24–7.17 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 1.98–1.84 (m, 1H), 0.85–0.73 (m, 2H), 0.67–0.58 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.9 (C_q), 141.9 (C_q), 139.8 (C_q), 137.8 (C_q), 133.1 (CH), 130.2 (CH), 130.1 (CH), 128.4 (CH), 127.8 (CH), 125.1 (CH), 125.0 (CH), 13.6 (CH), 9.0 (CH_2). IR (NaCl): 3069, 3011, 1740, 1589, 1489, 1152, 1061, 1029, 895, 757 cm^{-1}. MS (EI) *m/z* (relative intensity) 222 (10) [M^+], 207 (10), 194 (100), 178 (10), 165 (30), 115 (20), 105 (10), 91 (5), 77 (10). HRMS (ESI) *m/z* calcd for $C_{16}H_{14}O+H^+$ 223.1174, found 223.1118.



3x

4-*n*-Butylacetophenone (3x): Representative procedure C was followed, using *n*-butylzinc chloride (1.50 mmol, 1.00 M in THF) and 4-iodoacetophenone (246 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-hexane/EtOAc: 100/1) yielded **3x** (159 mg, 88%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.59 (s, 3H), 1.68–1.55 (m, 2H), 1.43–1.28 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.9 (C_q), 148.8 (C_q), 137.9 (C_q), 128.6 (CH), 128.4 (CH), 35.7 (CH_2), 33.2 (CH_2), 26.5 (CH_3), 22.3 (CH_2), 13.9 (CH_3). IR (NaCl): 3002, 2962, 1710, 1606, 1498, 1178, 1070, 1021, 961, 839 cm^{-1}. MS (EI) *m/z* (relative intensity) 176 (20) [M^+], 161 (100), 133 (10), 118 (10), 105 (10), 91 77 (10), (25), 65 (15). HRMS (ESI) *m/z* calcd for $C_{12}H_{16}O$+Na^+ 199.1093, found 199.1094. The spectral data were in accordance with those reported in the literature.[19]

References:

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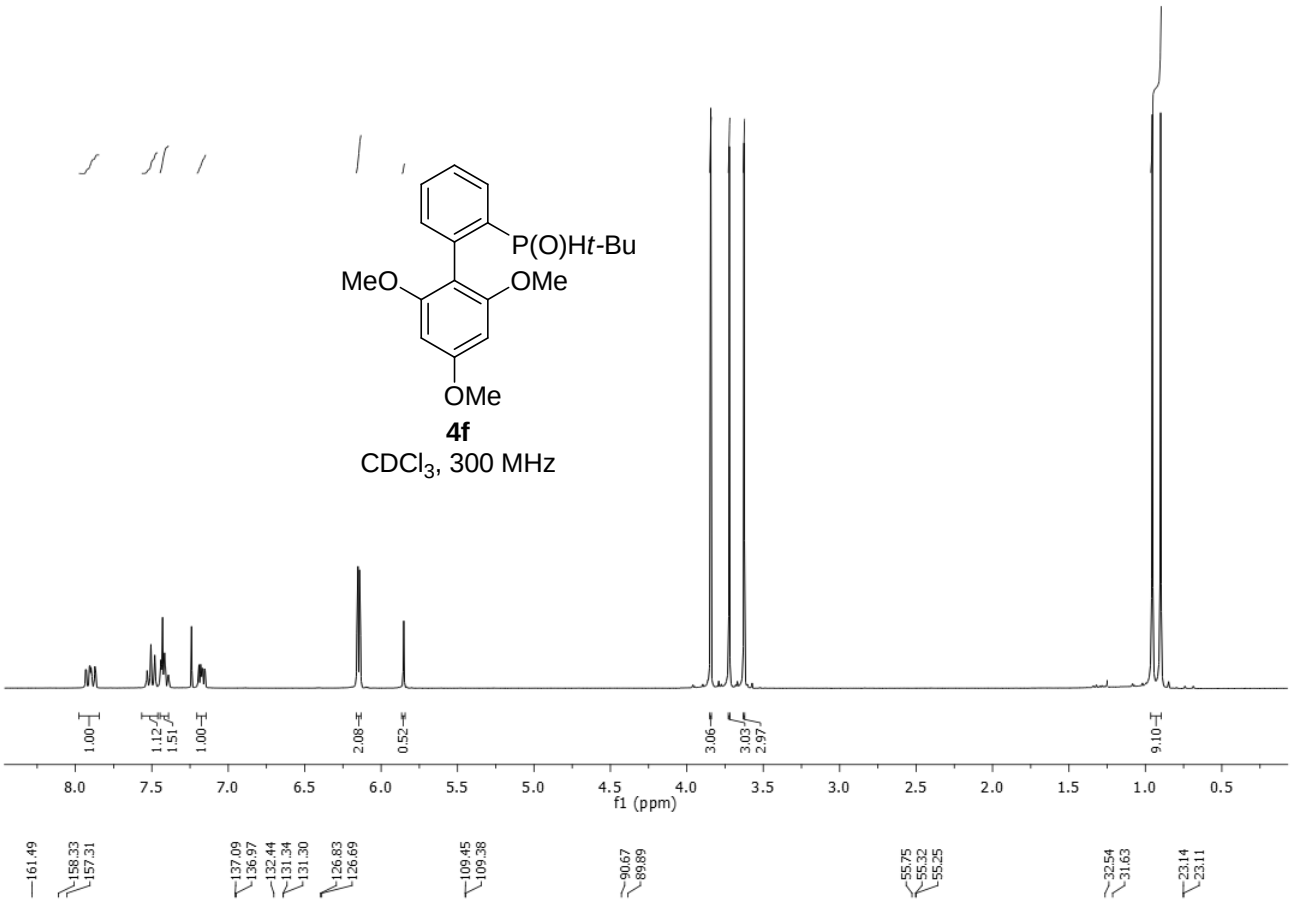
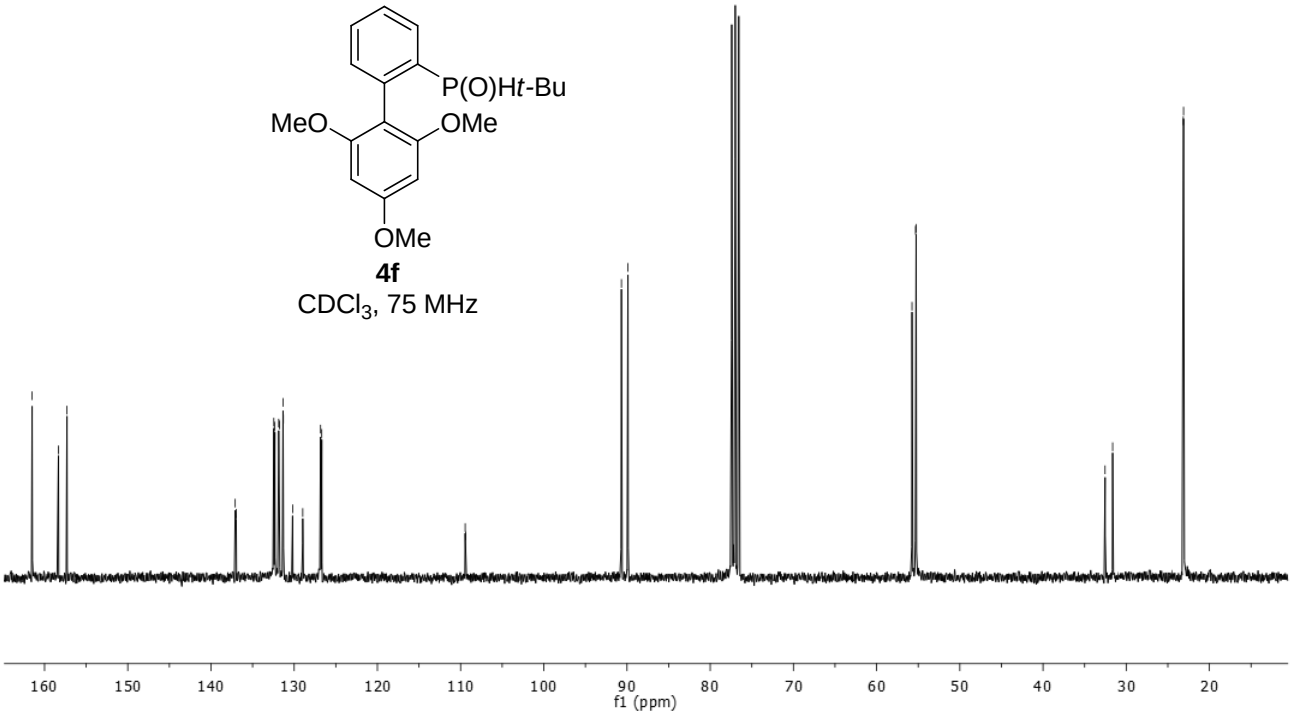
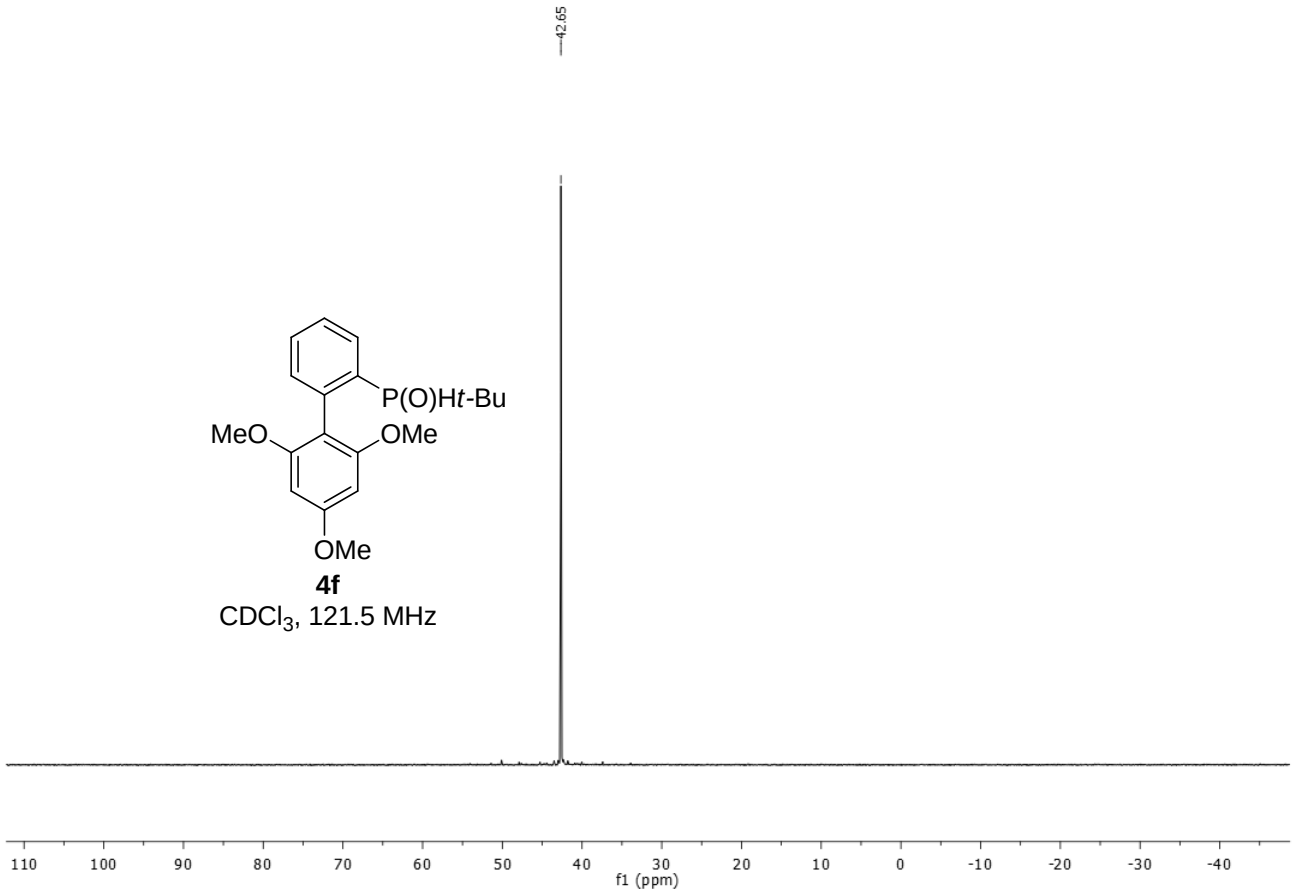
^{1}H-, ^{13}C-NMR, spectras for 3a-3x, 4f-4i, 5a-5c, 6a-6b, complexes 7a and 7b.

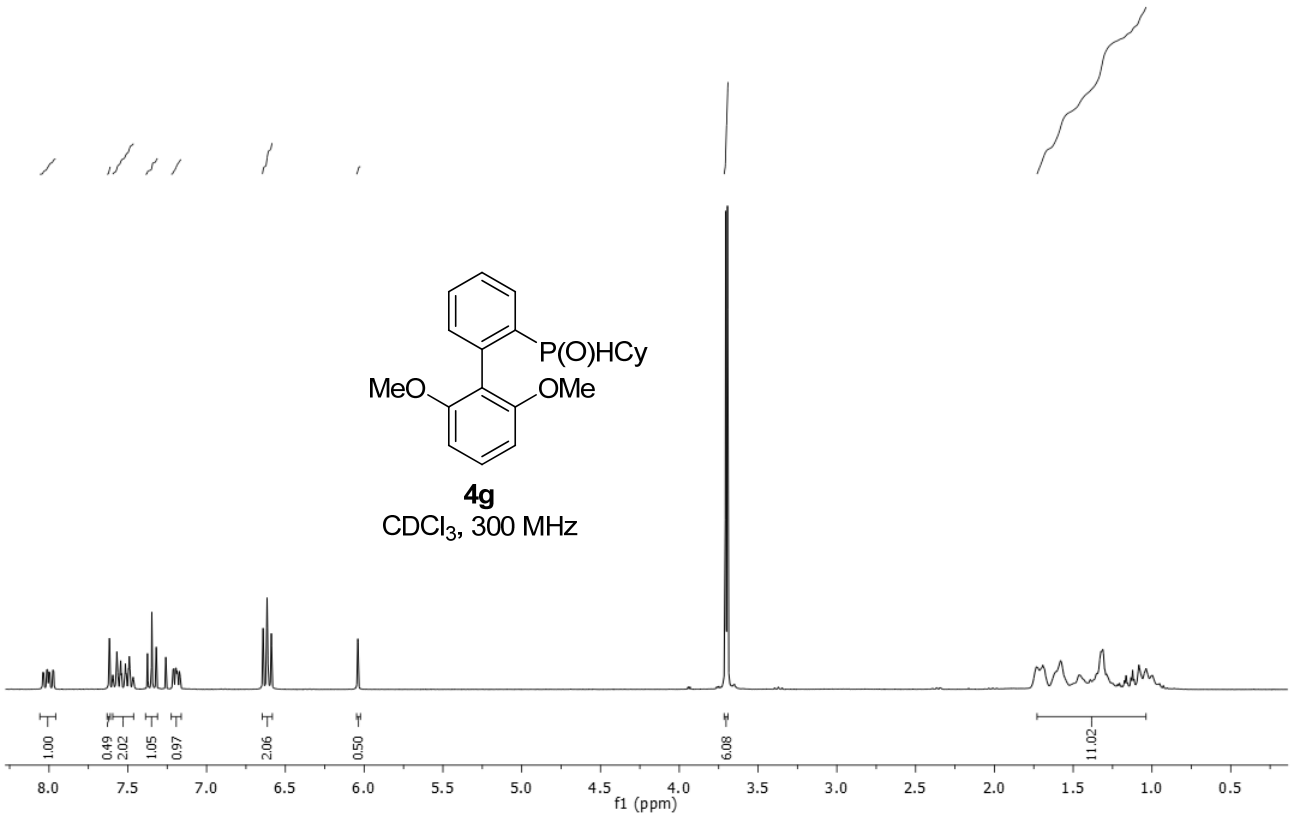






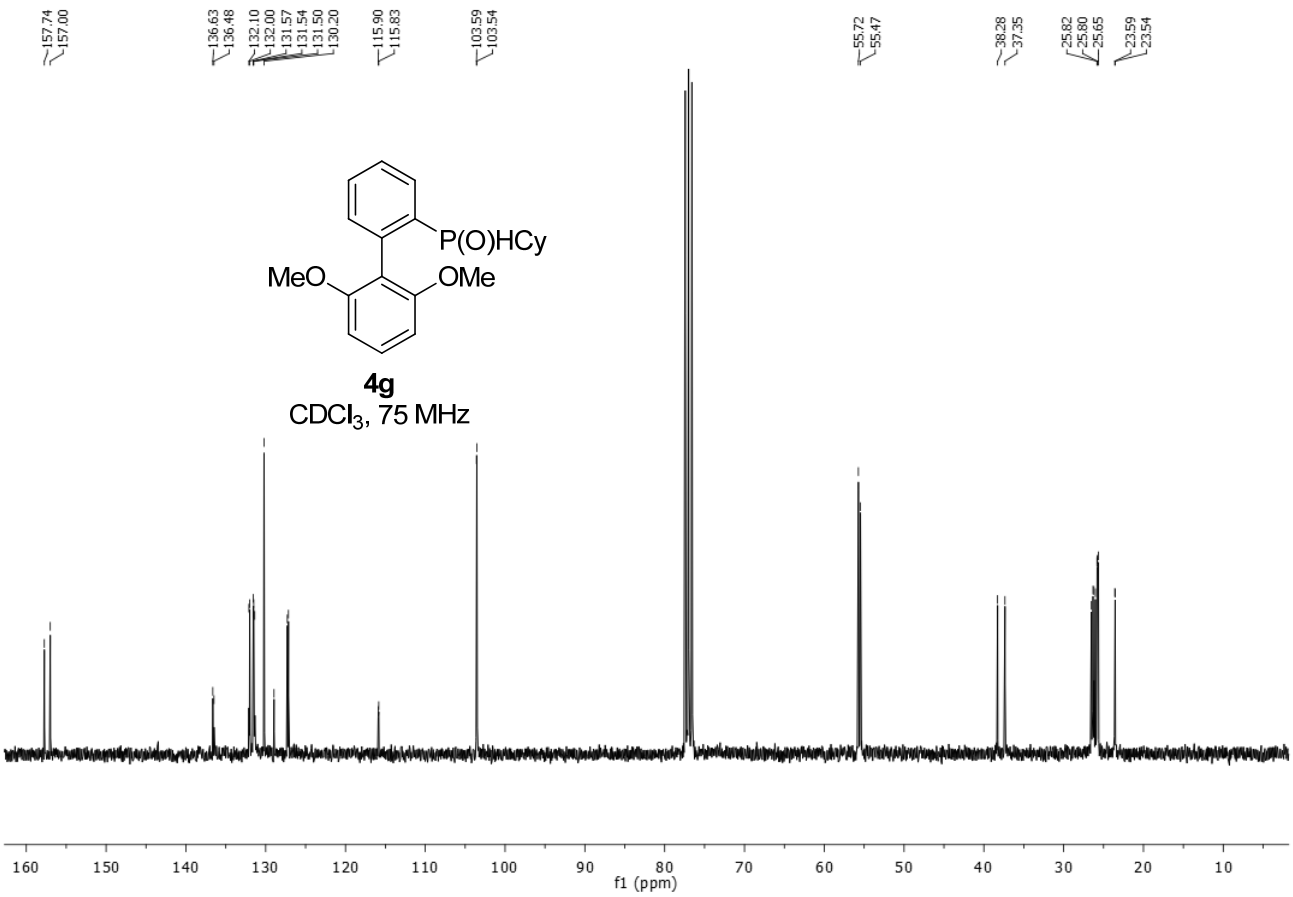
4f

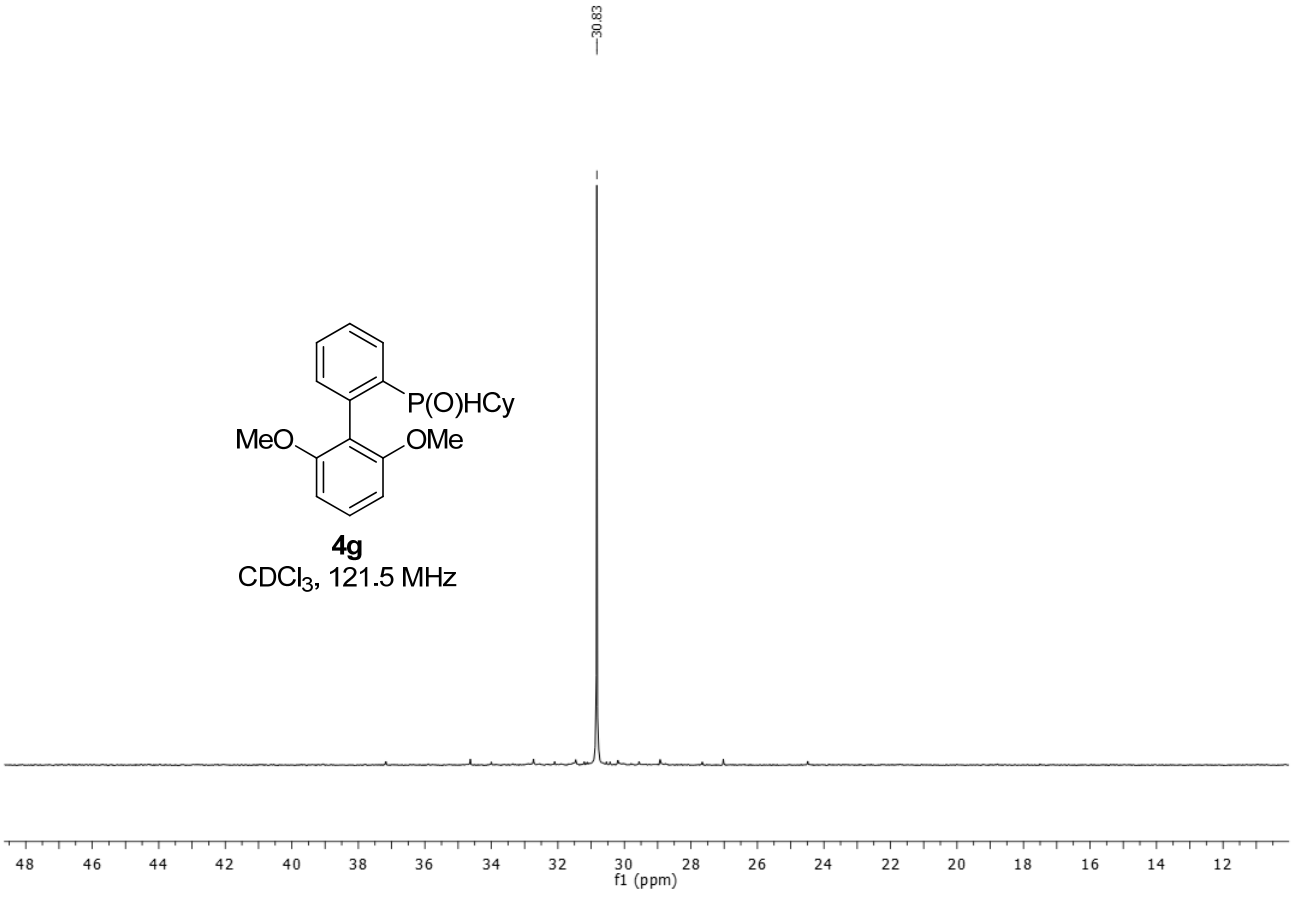
$CDCl_3$, 121.5 MHz

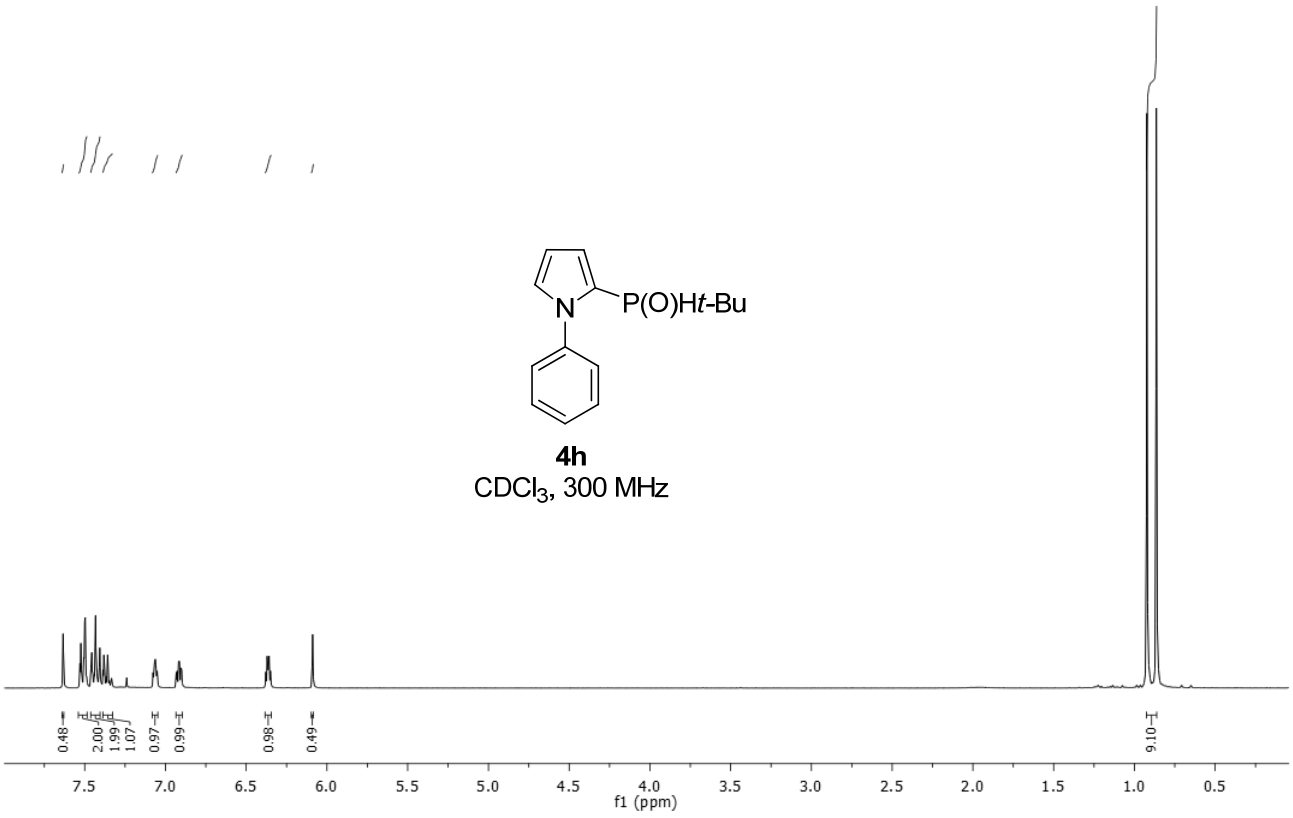


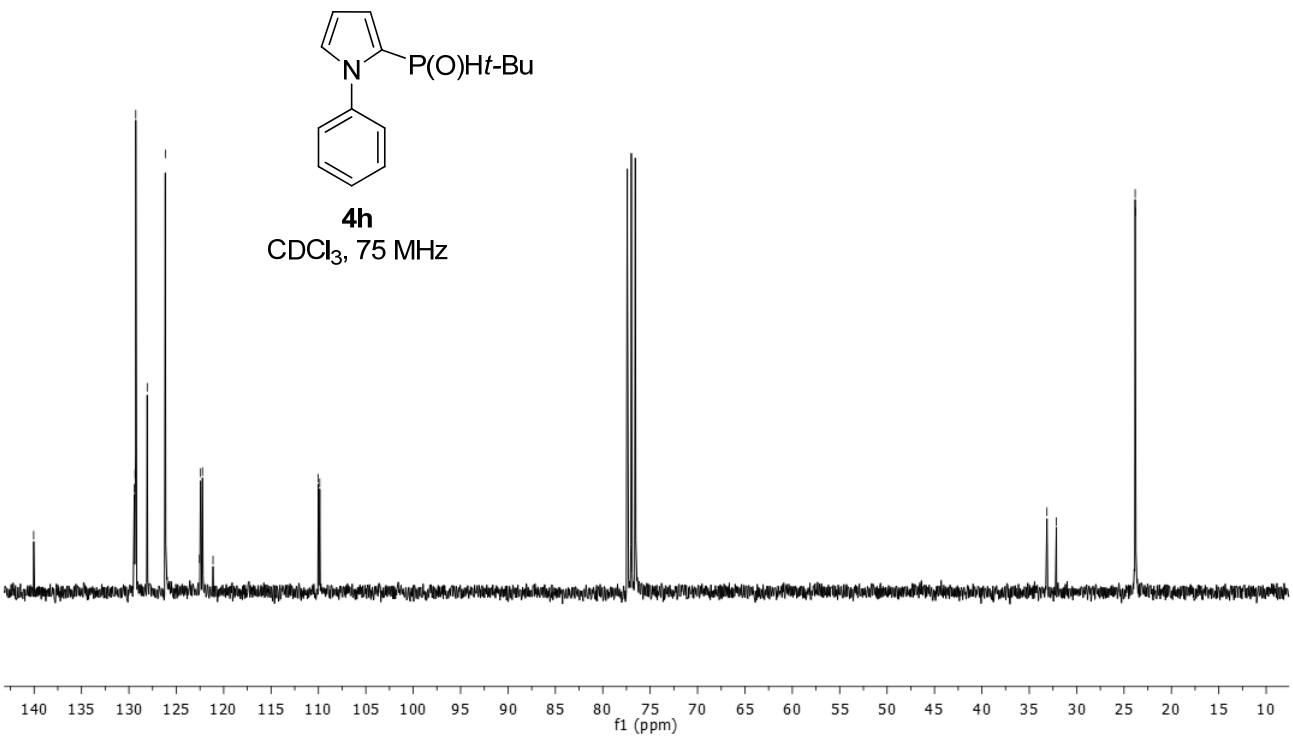
4g

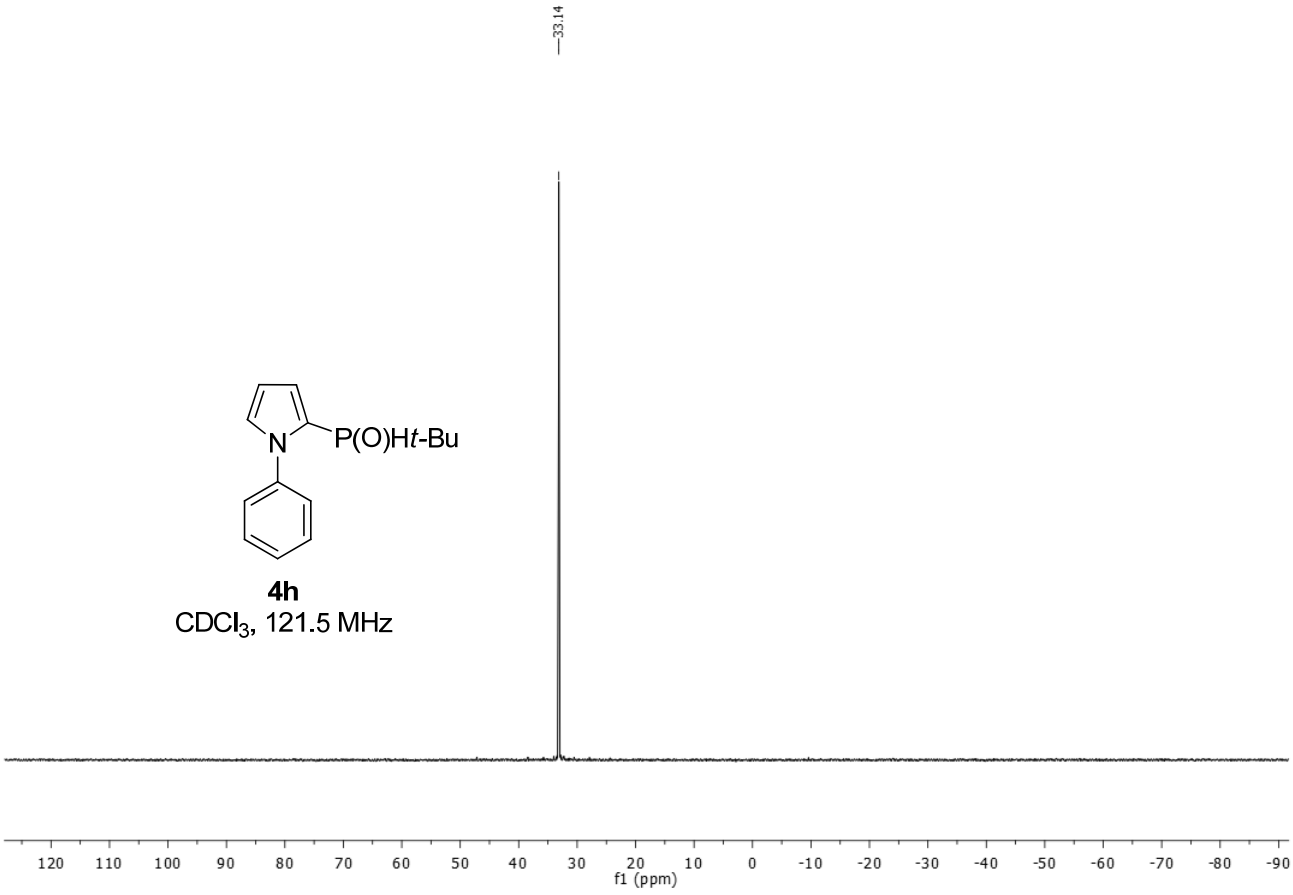
$CDCl_3$, 300 MHz


157.74
157.00
136.63
136.48
132.10
132.00
131.57
131.54
131.50
130.20
115.90
115.83
103.59
103.54
55.72
55.47
38.28
37.35
25.82
25.80
25.65
23.59
23.54
P(O)HCy
MeO
OMe
4g
CDCl3, 75 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

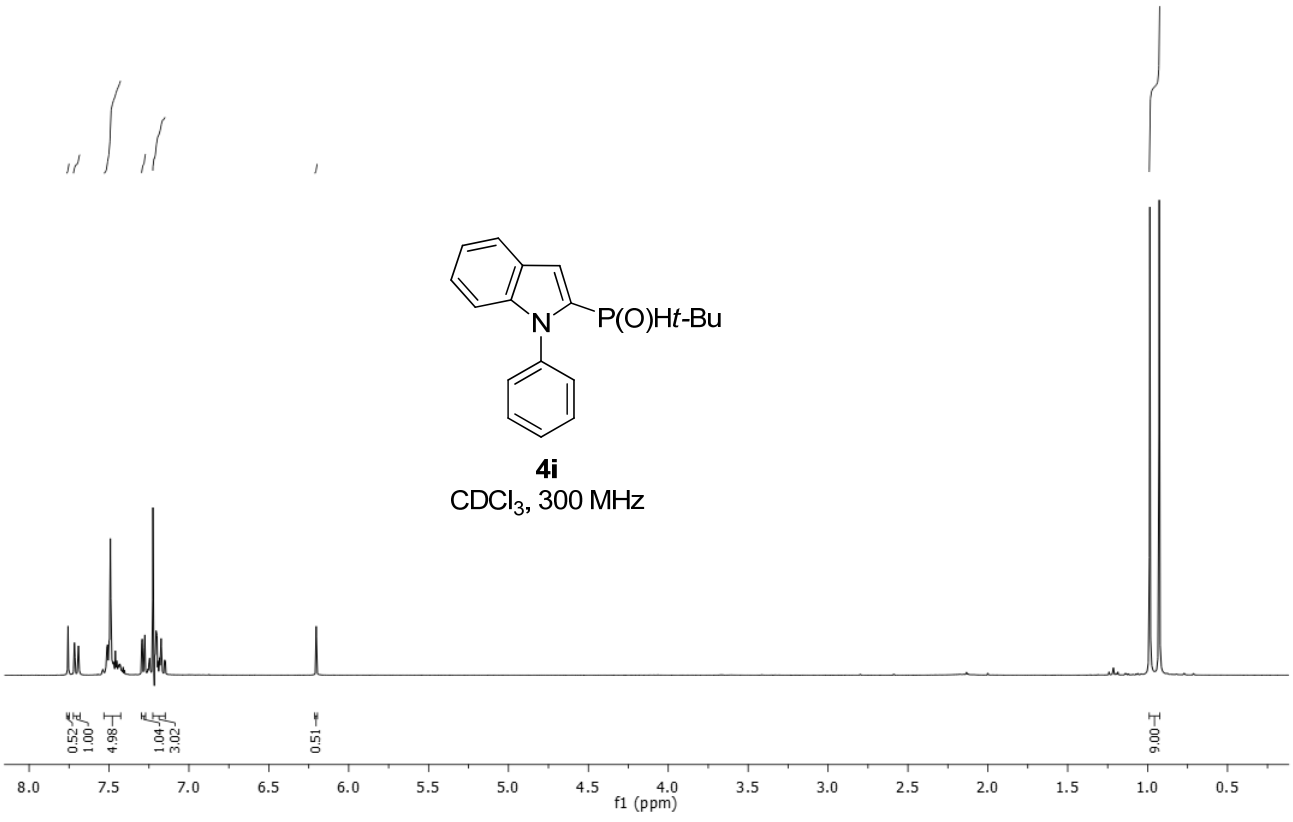

30.83
P(O)HCy
MeO
OMe
4g
CDCl3, 121.5 MHz
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
f1 (ppm)


P(O)H*t*-Bu
4h
$CDCl_3$, 300 MHz
0.48
2.00
1.99
1.07
0.97
0.99
0.98
0.49
9.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

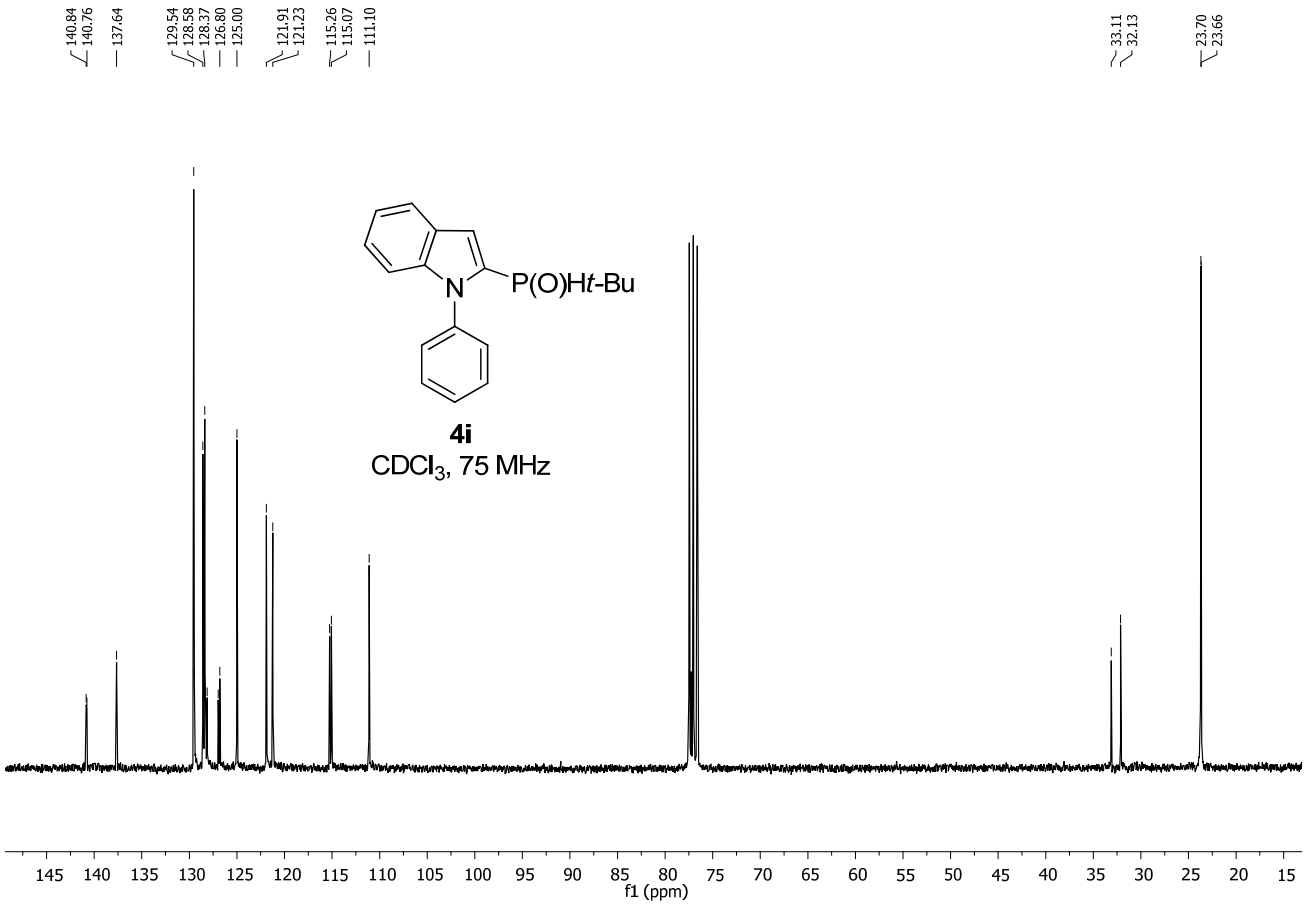

140.05
129.43
129.35
129.28
128.07
126.16
122.55
122.44
122.24
121.12
110.02
109.87
33.13
32.14
23.82
23.79
P(O)H*t*-Bu
4h
$CDCl_3$, 75 MHz
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

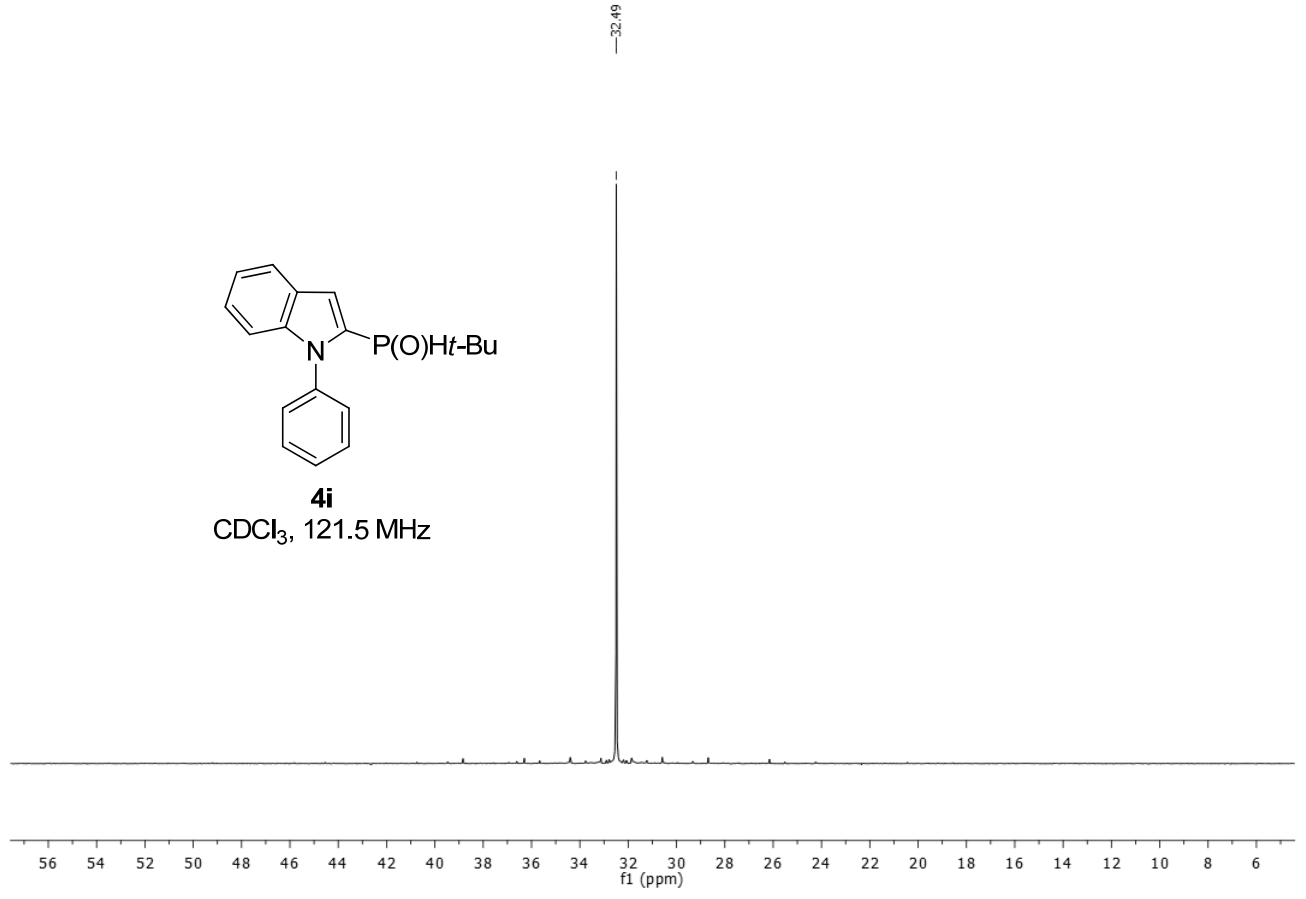


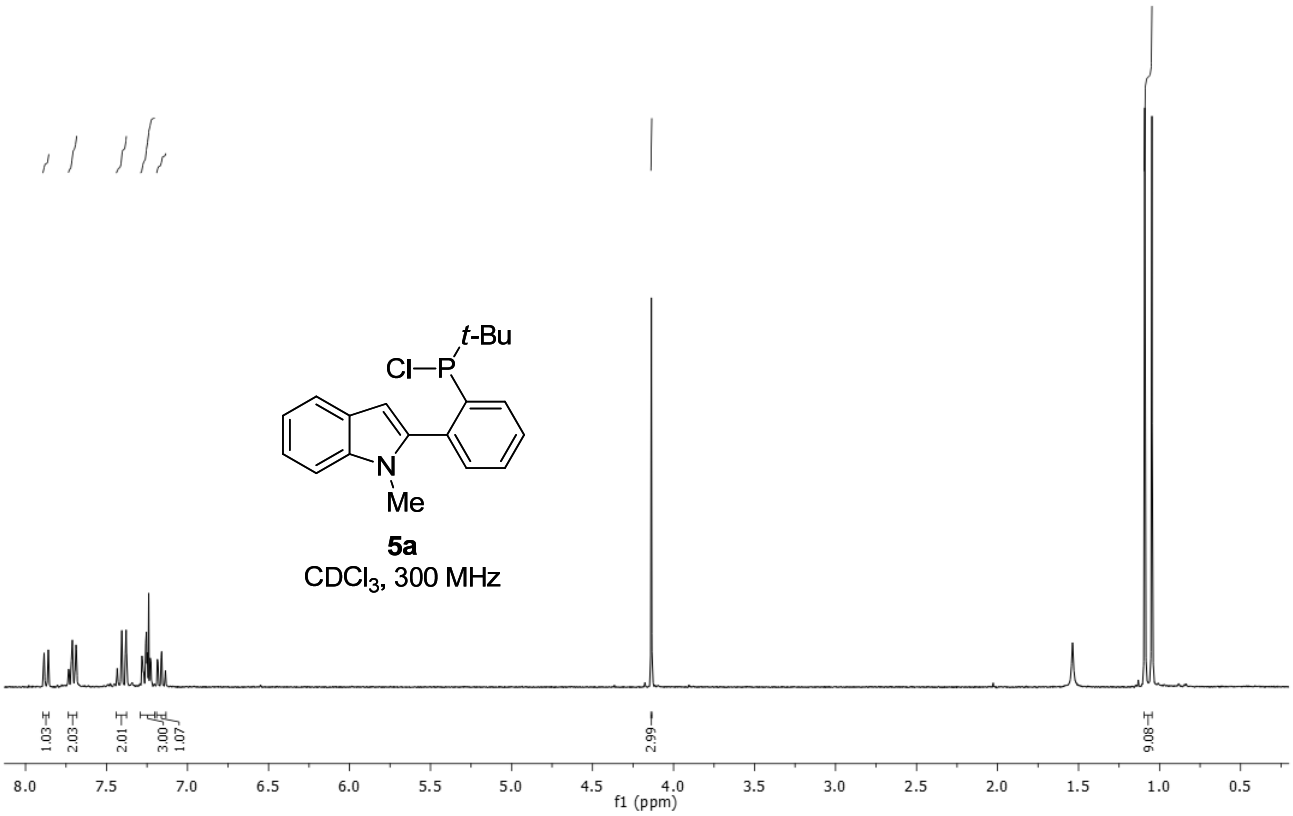
4h
$CDCl_3$, 121.5 MHz



4i
$CDCl_3$, 300 MHz

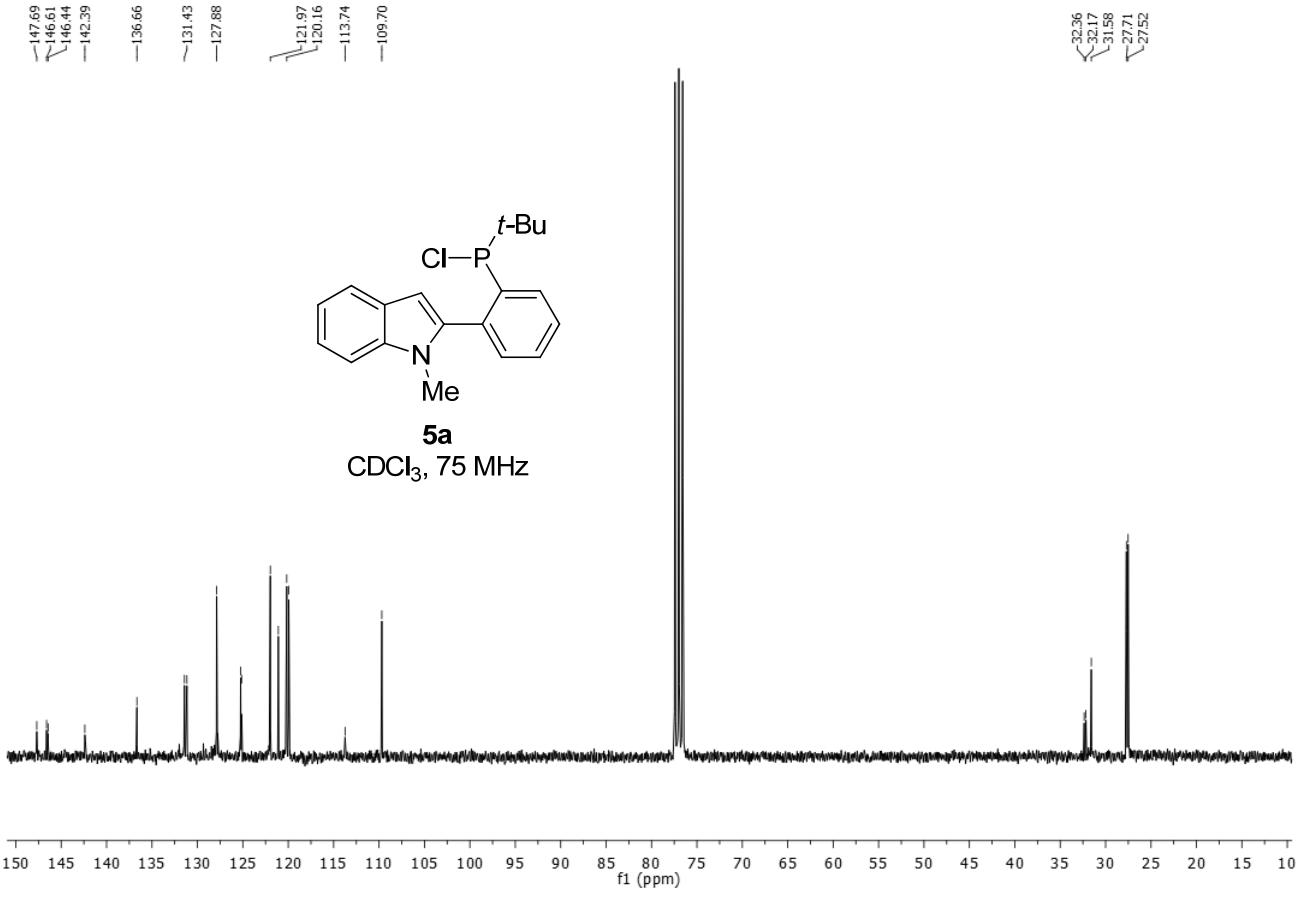

140.84
140.76
137.64
129.54
128.58
128.37
126.80
125.00
121.91
121.23
115.26
115.07
111.10
33.11
32.13
23.70
23.66
P(O)H*t*-Bu
4i
$CDCl_3$, 75 MHz
f1 (ppm)


32.49
P(O)H*t*-Bu
4i
$CDCl_3$, 121.5 MHz
f1 (ppm)



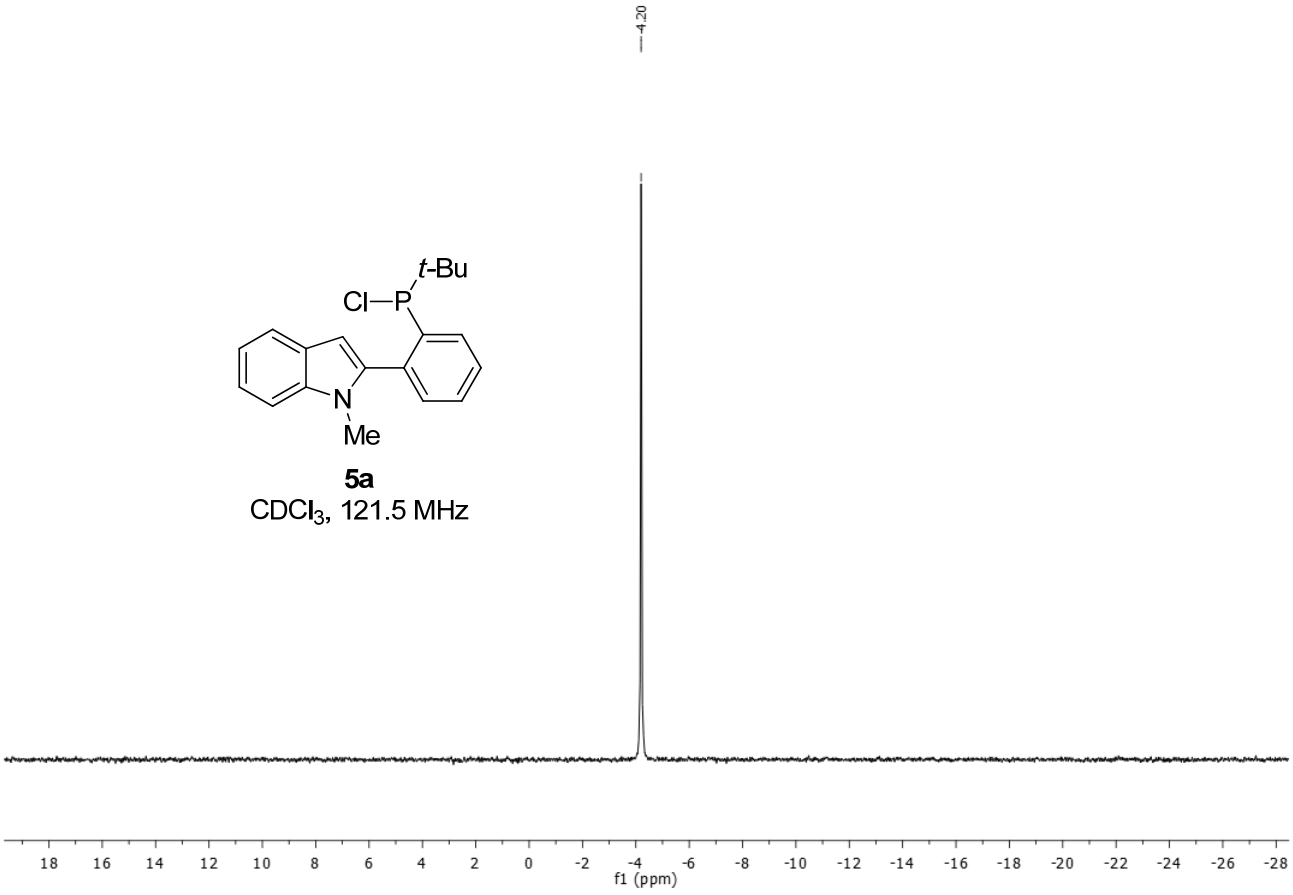
5a

$CDCl_3$, 300 MHz

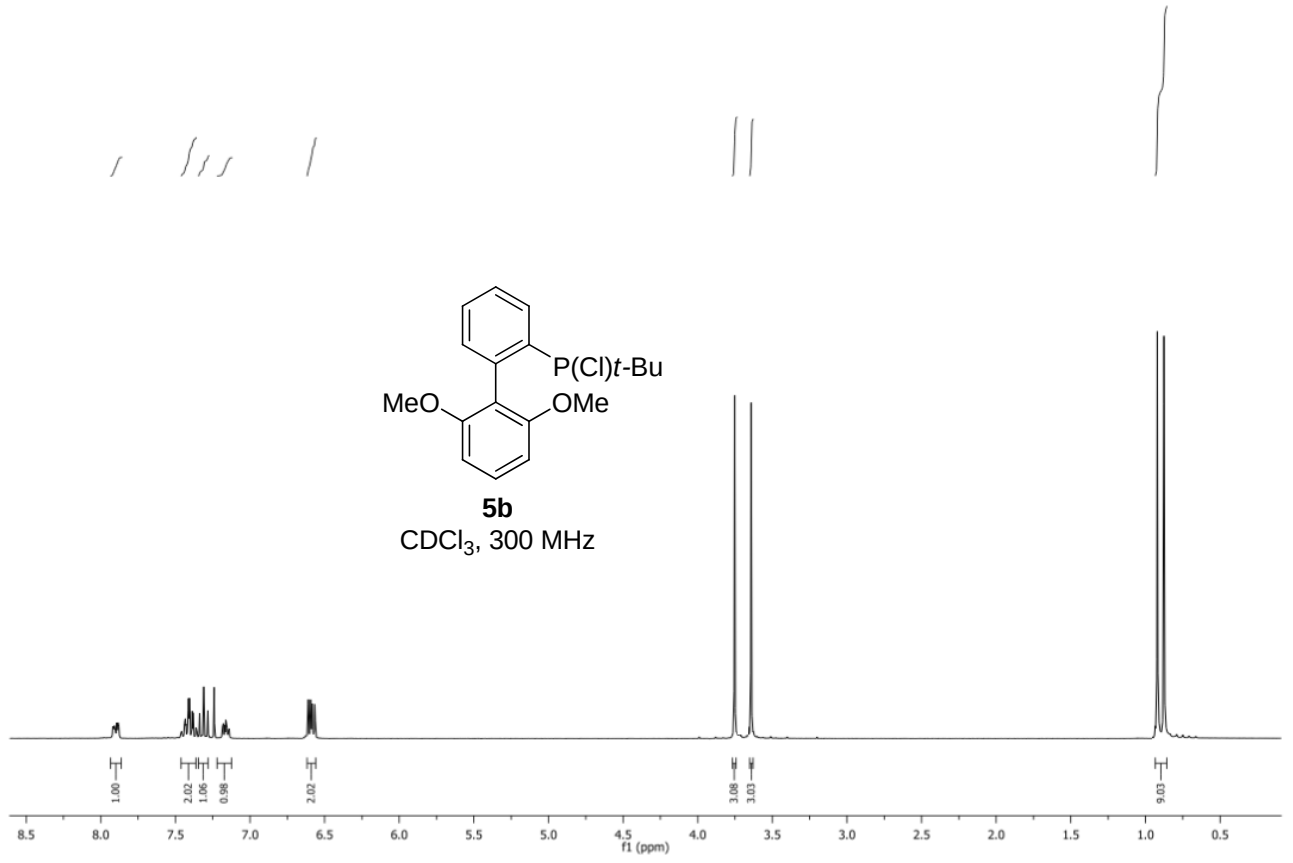


5a

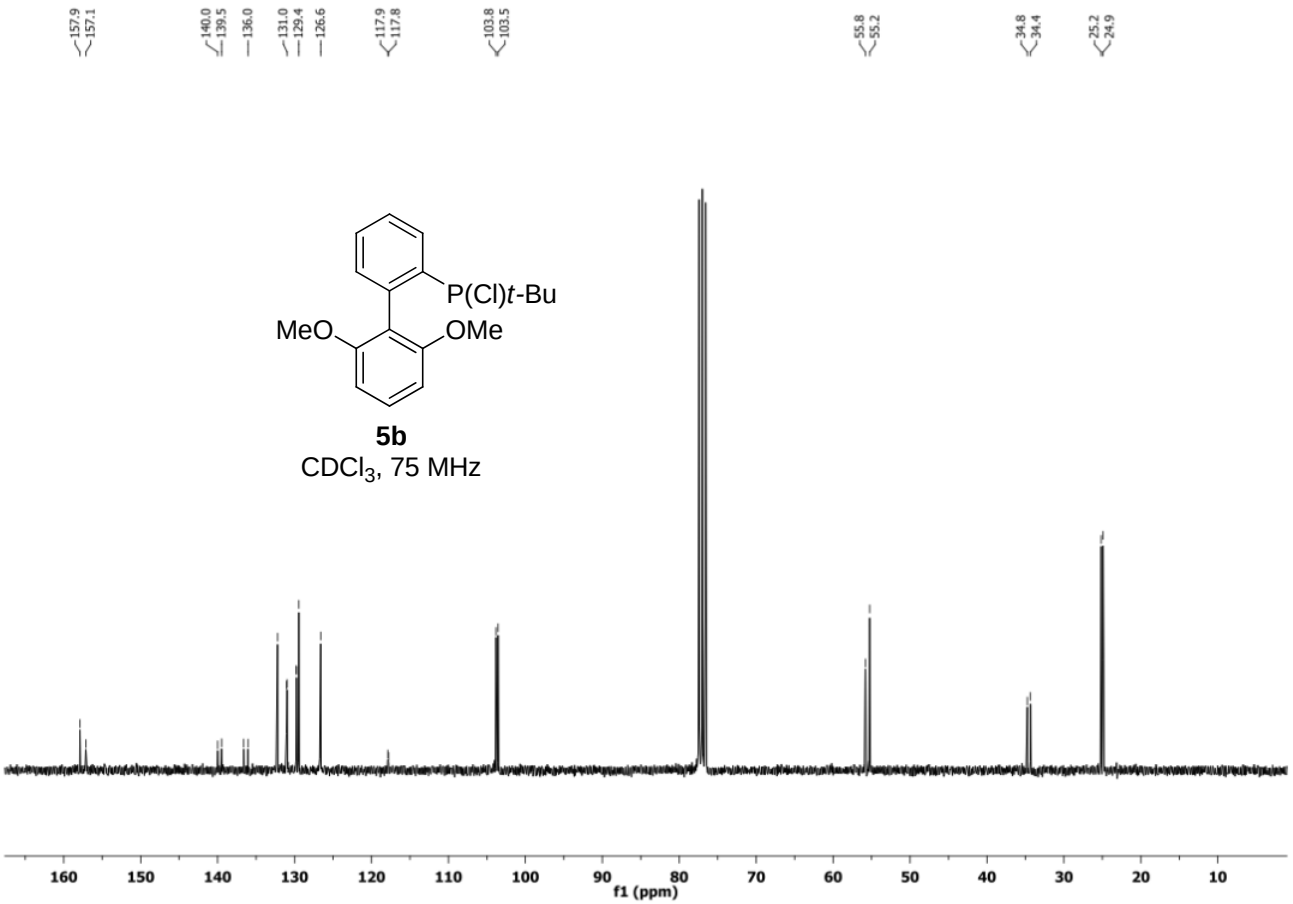
$CDCl_3$, 75 MHz



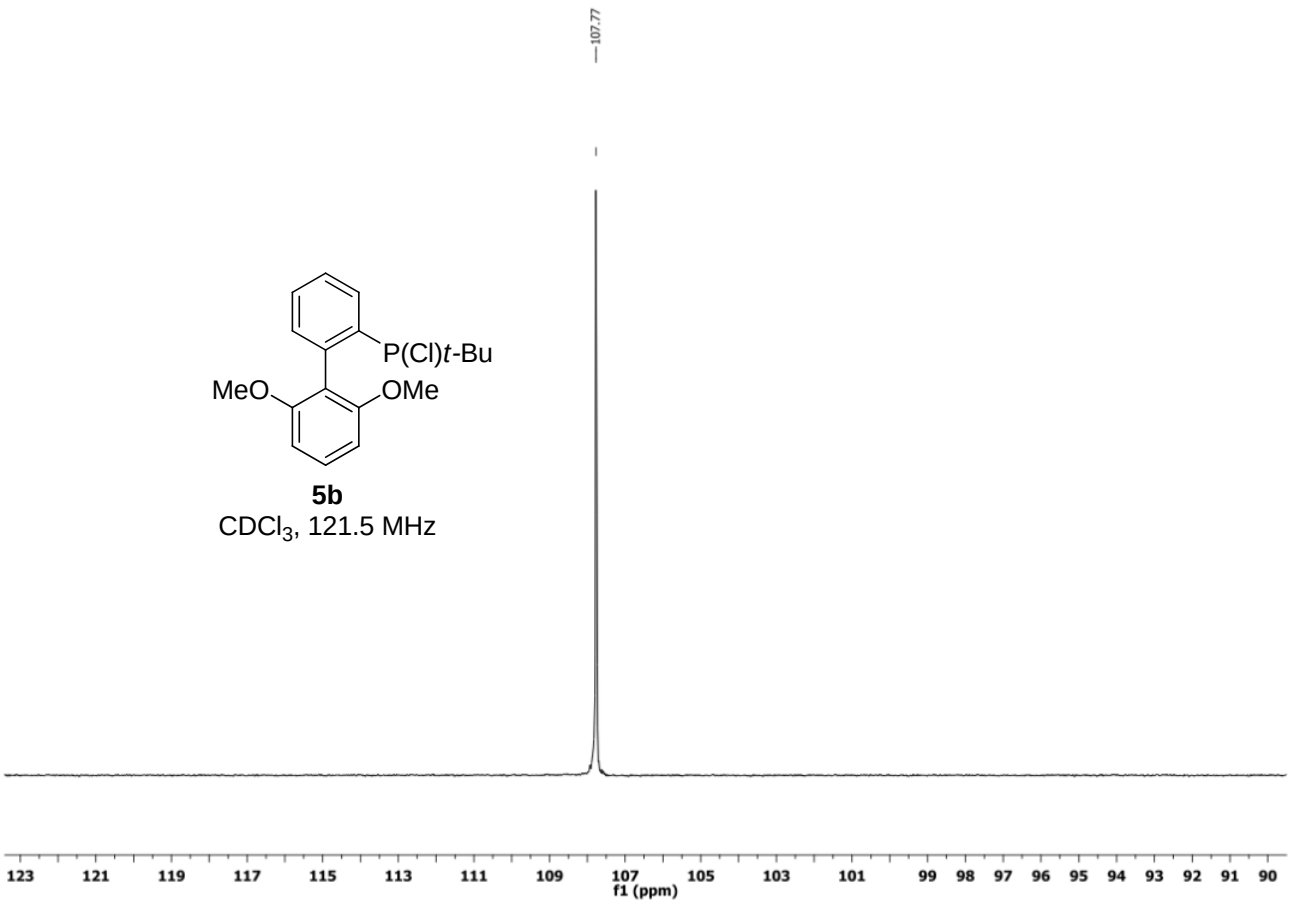
5a
$CDCl_3$, 121.5 MHz



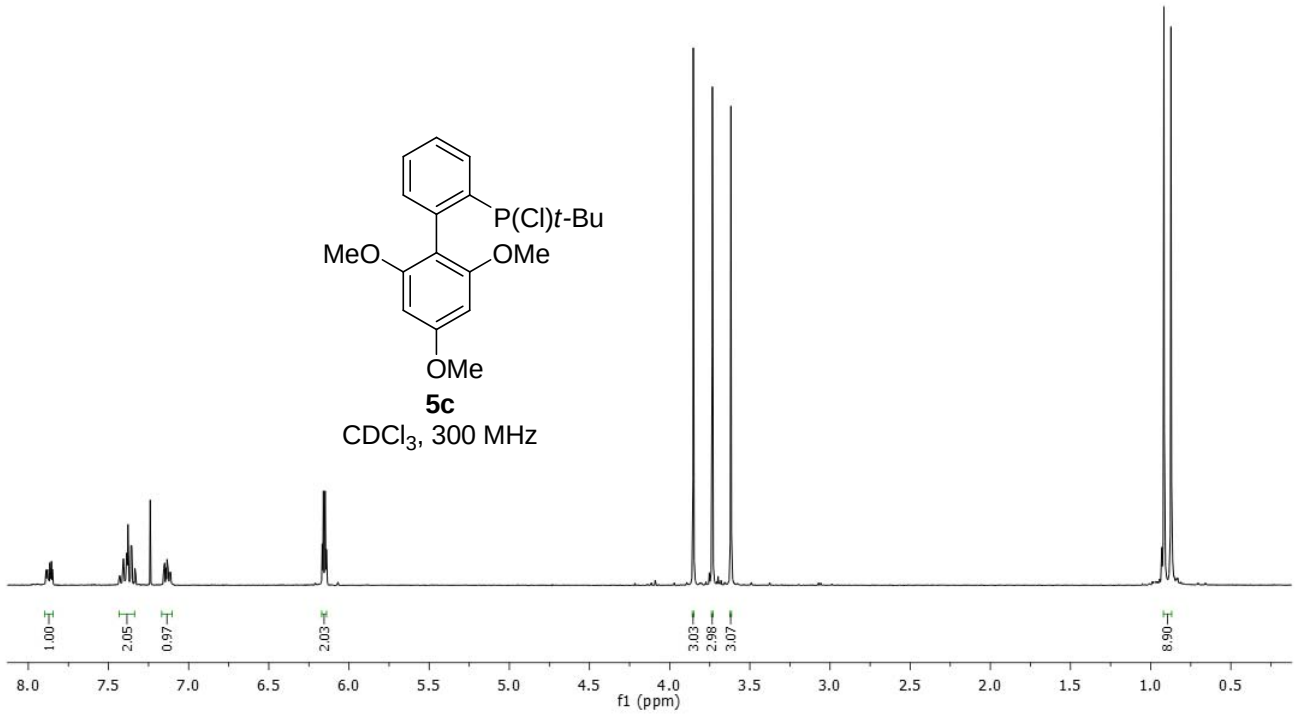
5b
$CDCl_3$, 300 MHz

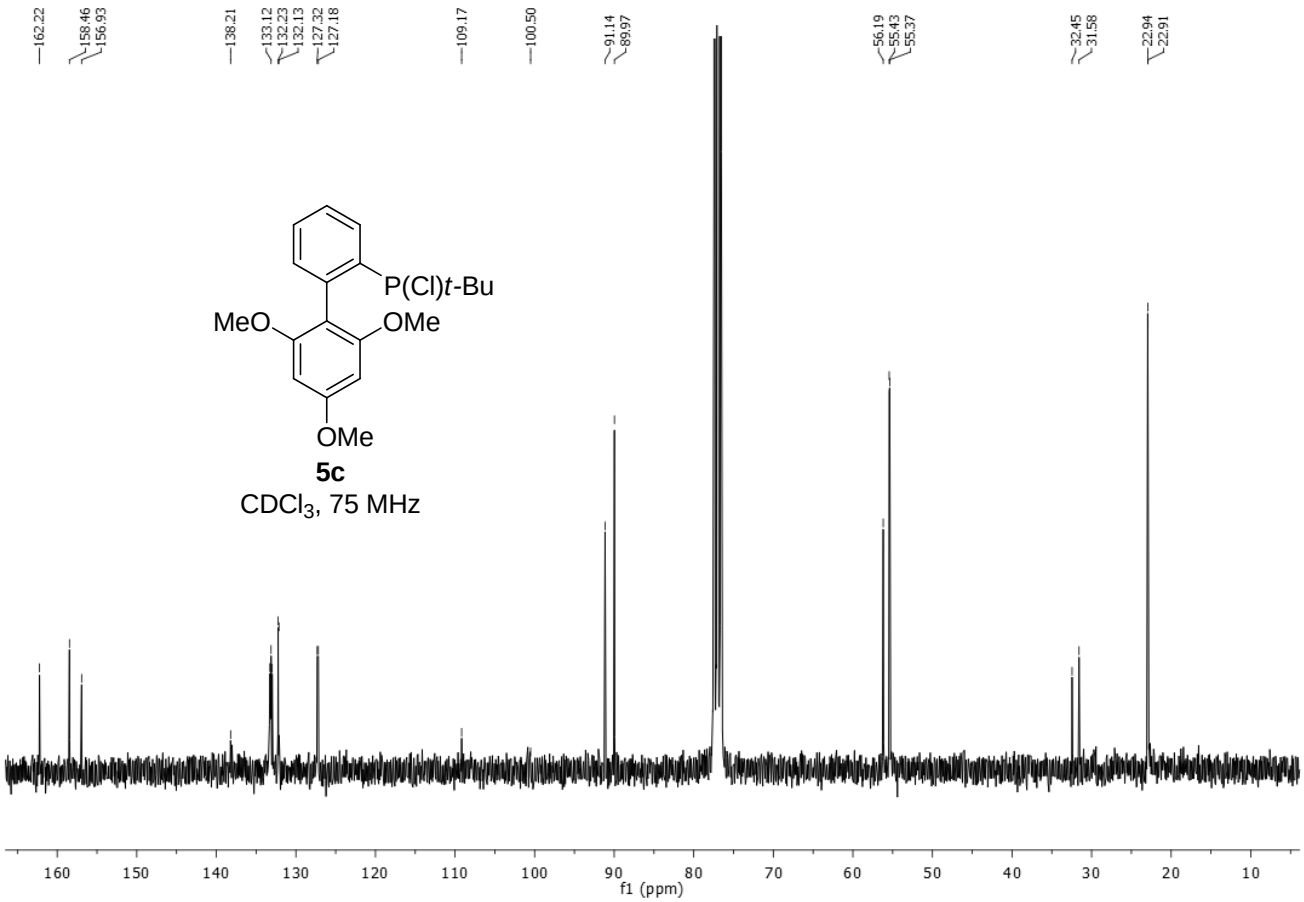


5b
$CDCl_3$, 75 MHz



5b
$CDCl_3$, 121.5 MHz


P(Cl)t-Bu
MeO
OMe
OMe
5c
CDCl3, 300 MHz
1.00
2.05
0.97
2.03
3.03
2.98
3.07
8.90
f1 (ppm)


162.22
158.46
156.93
138.21
133.12
132.23
132.13
127.32
127.18
109.17
100.50
91.14
89.97
56.19
55.43
55.37
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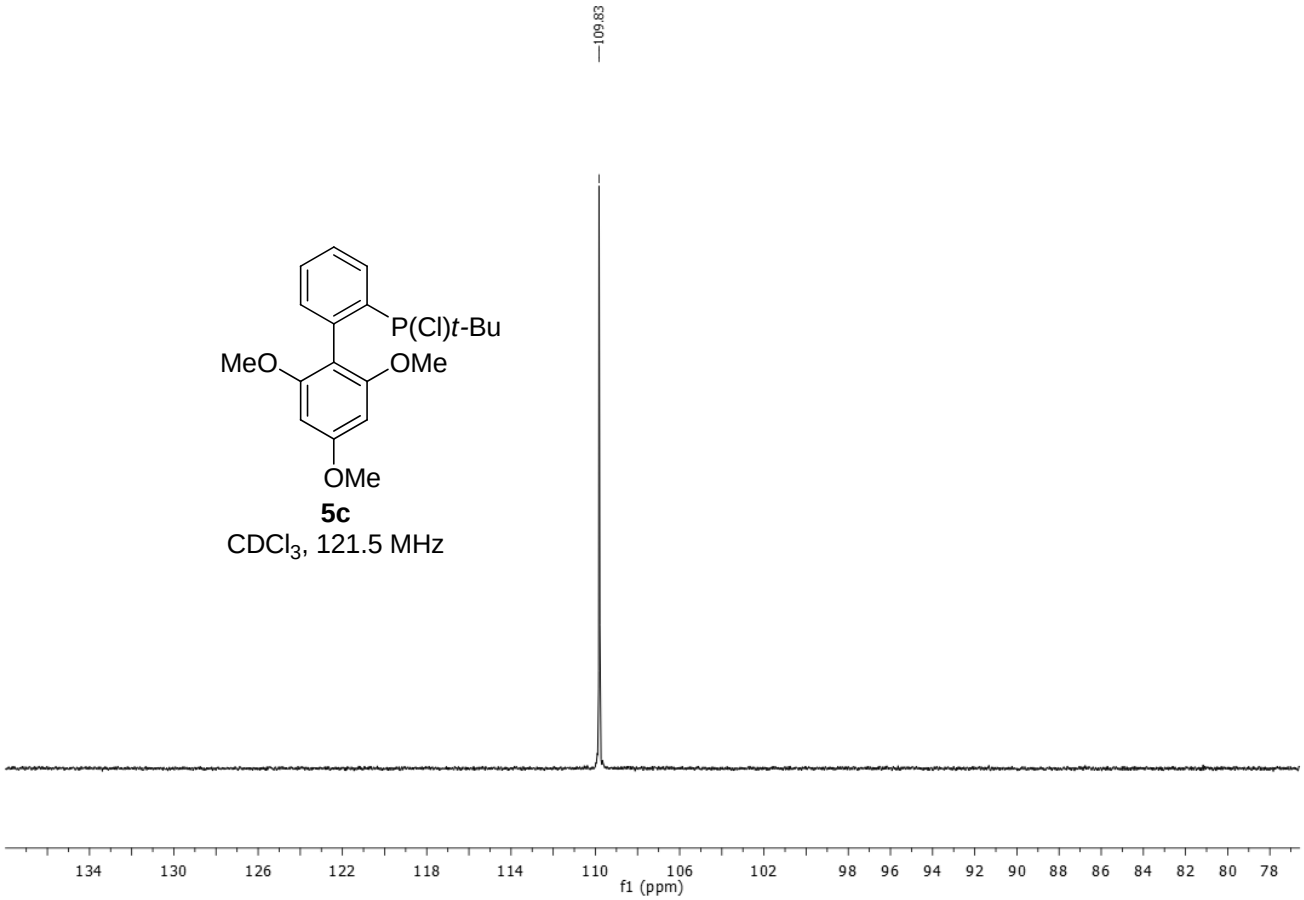
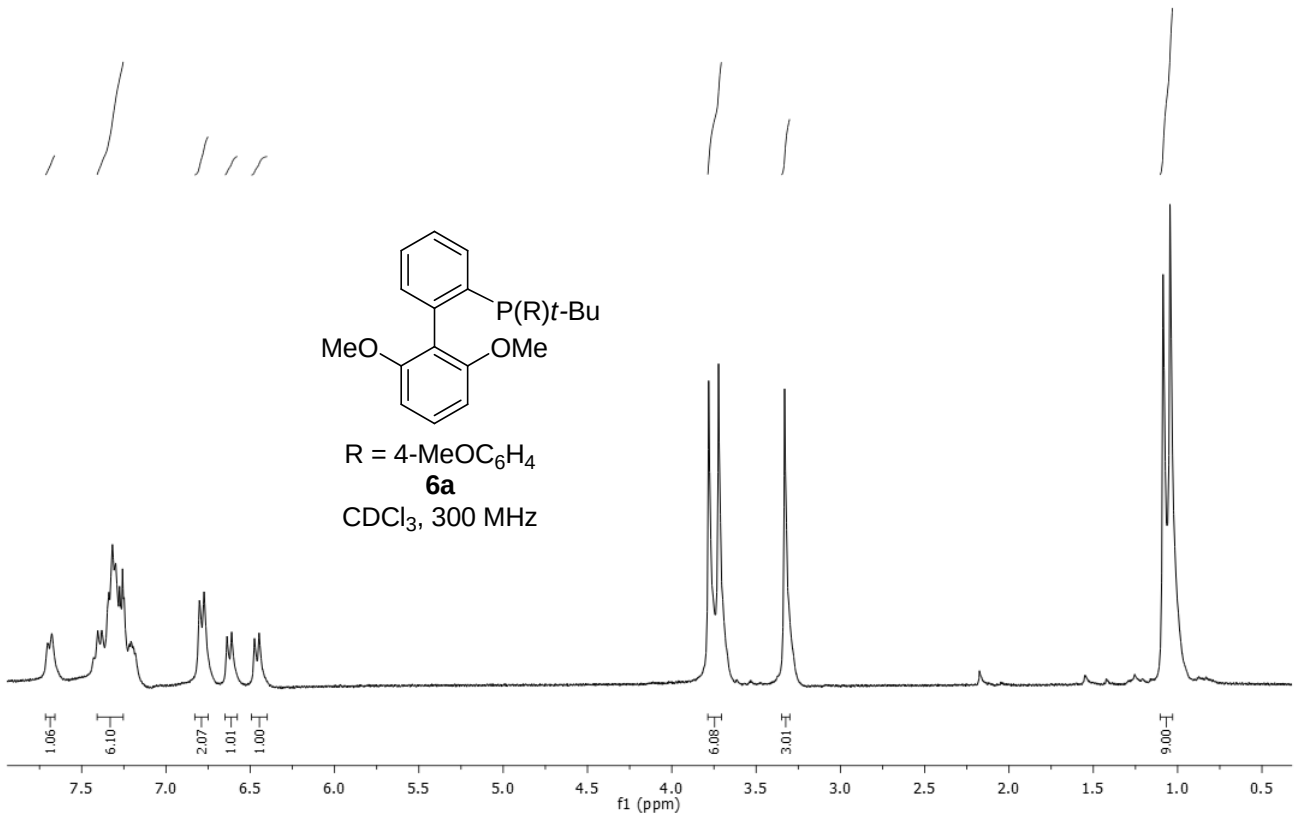
22.94
22.91
P(Cl)t-Bu
MeO
OMe
OMe
5c
CDCl3, 75 MHz
f1 (ppm)



5c

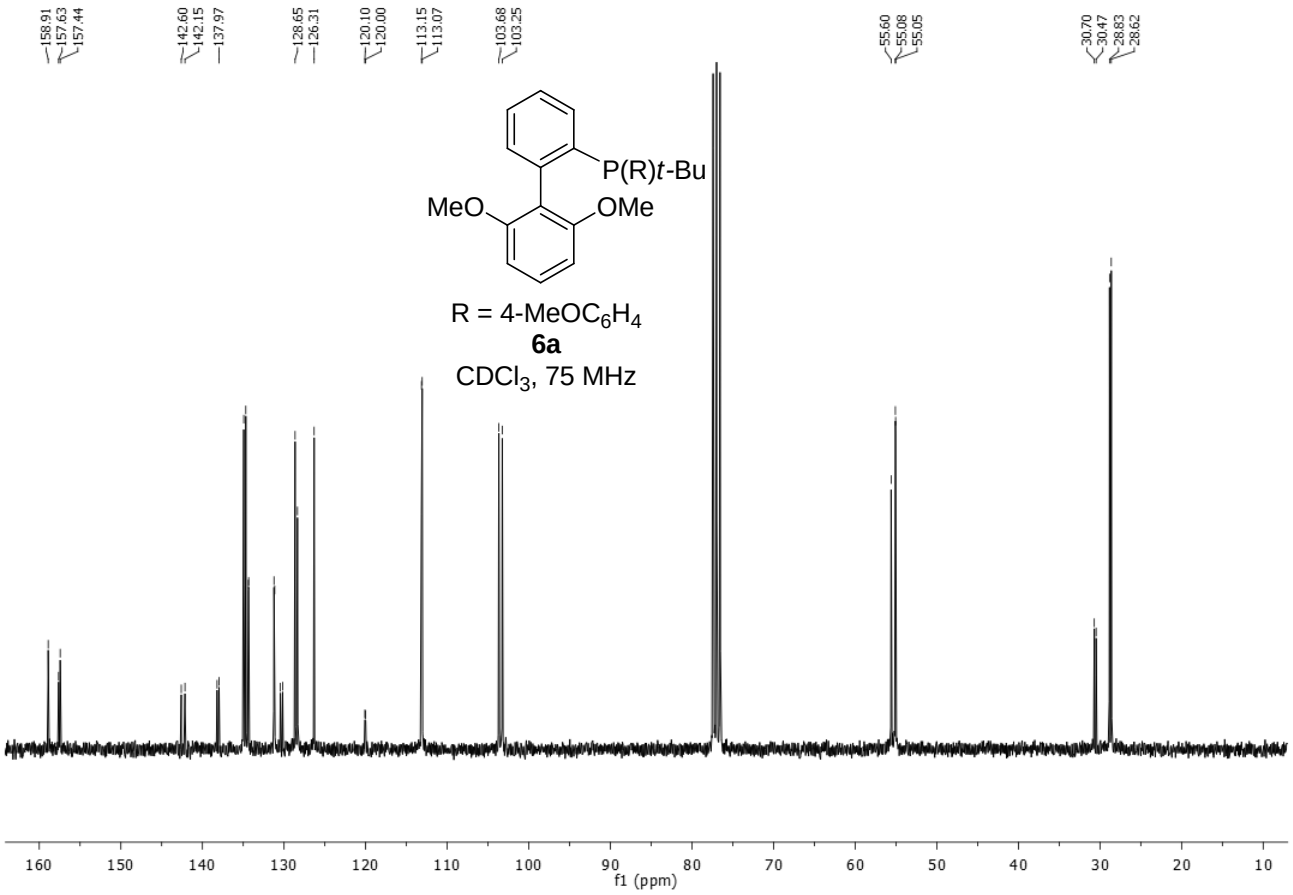
$CDCl_3$, 121.5 MHz

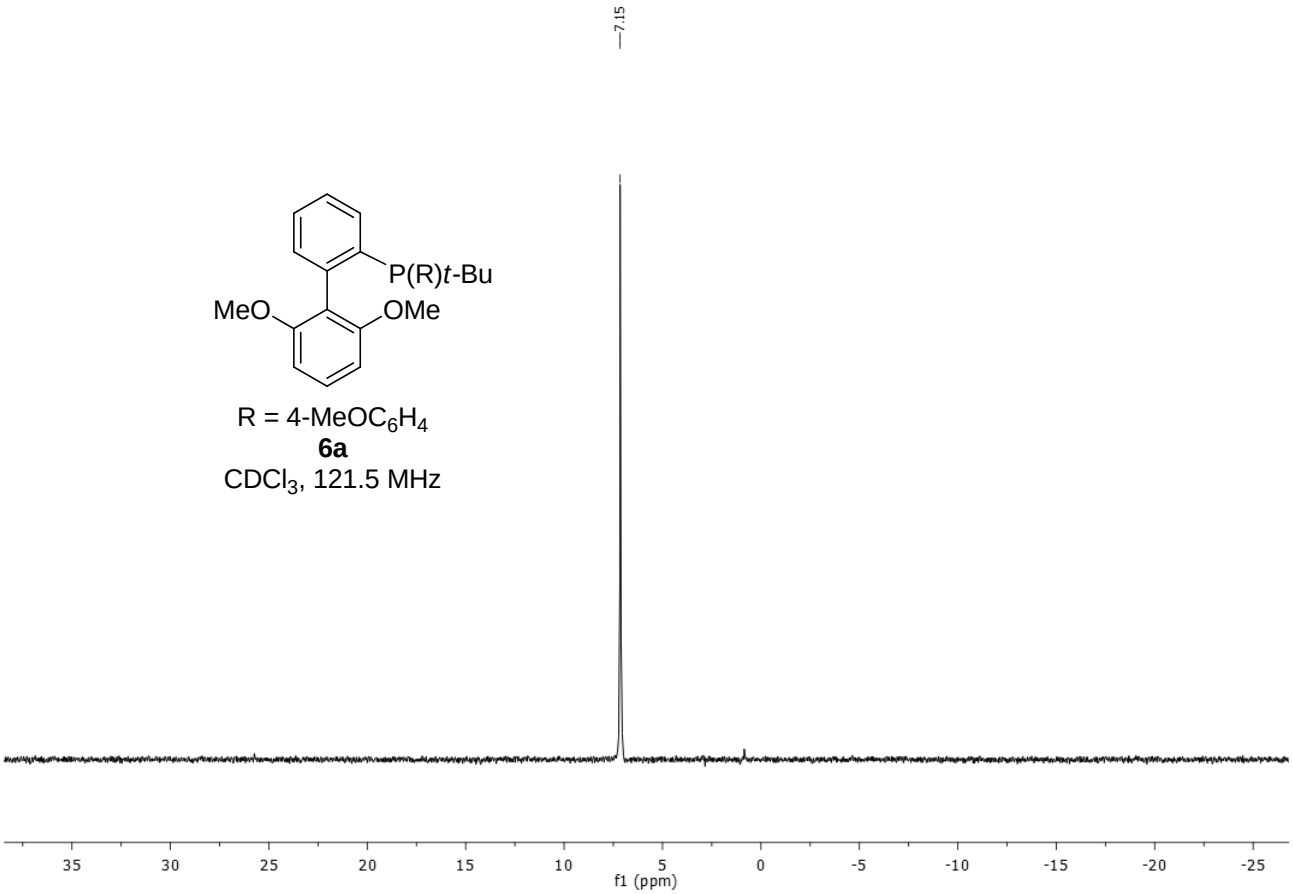


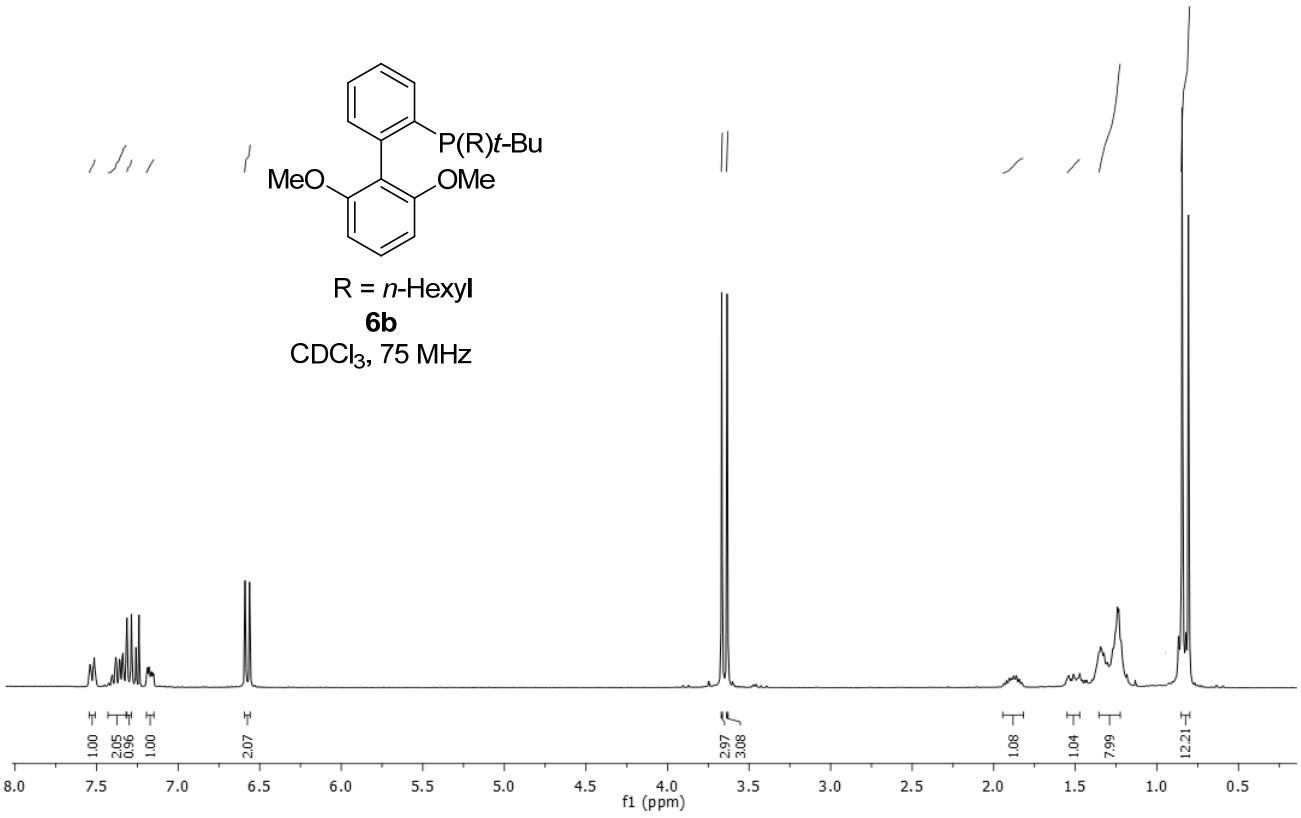
R = 4-$MeOC_6H_4$

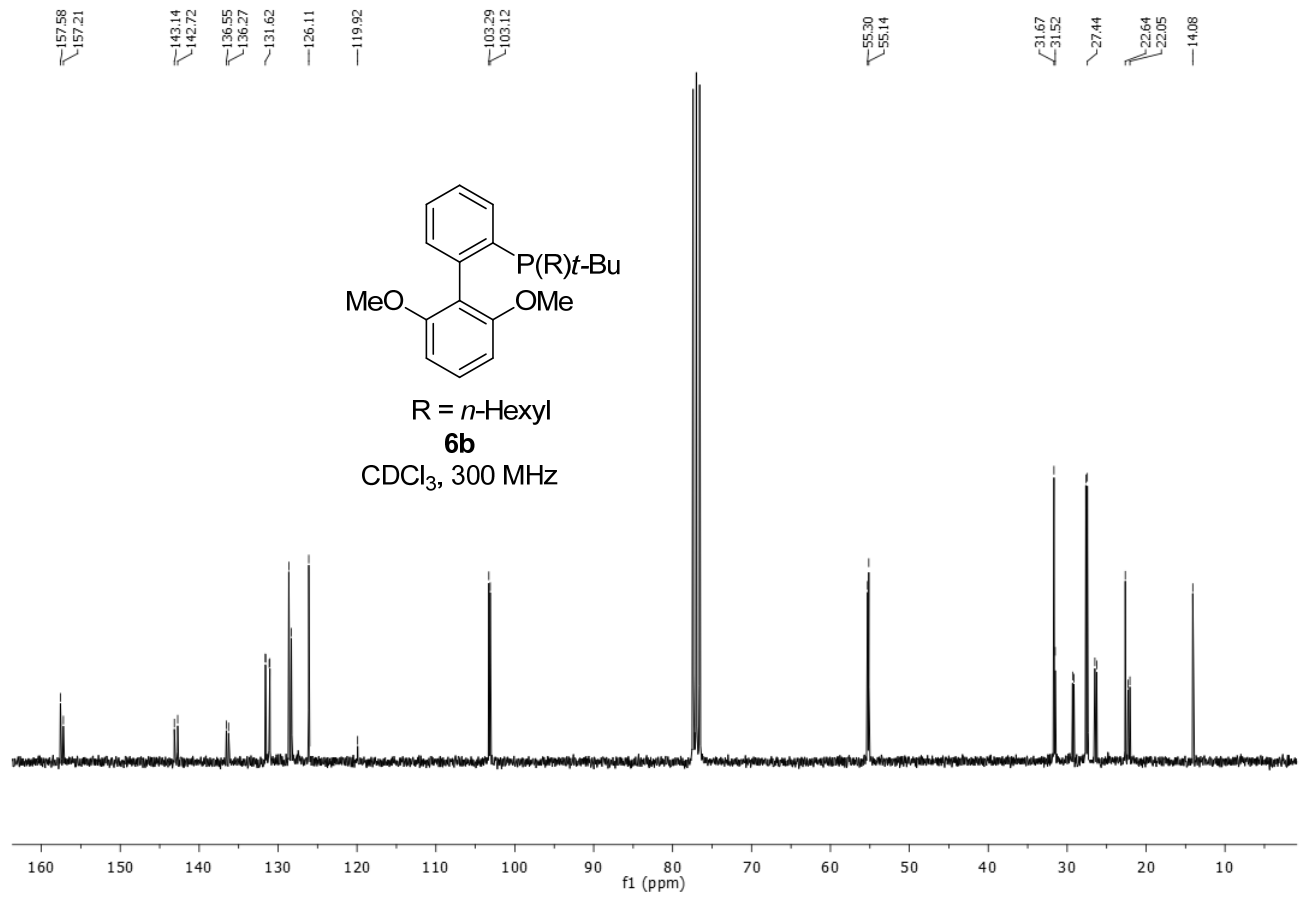
6a

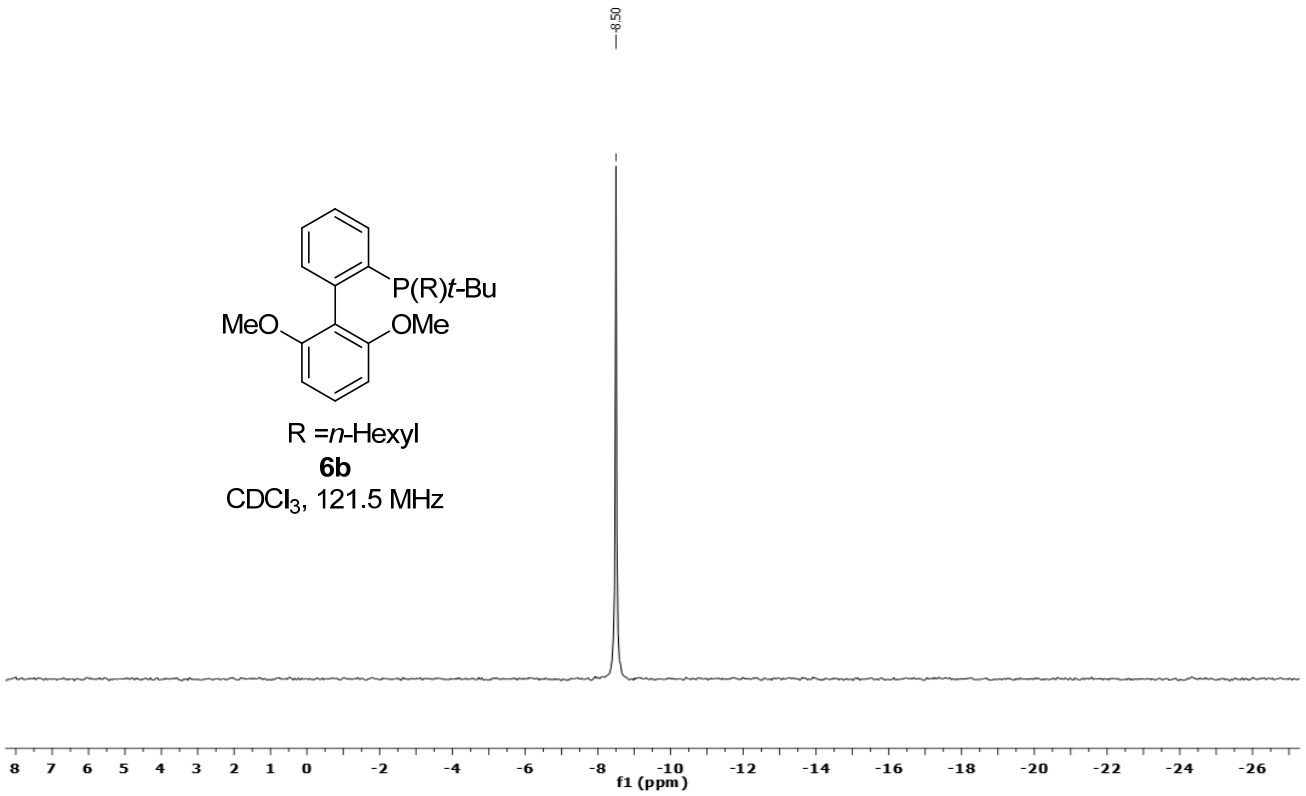
$CDCl_3$, 300 MHz

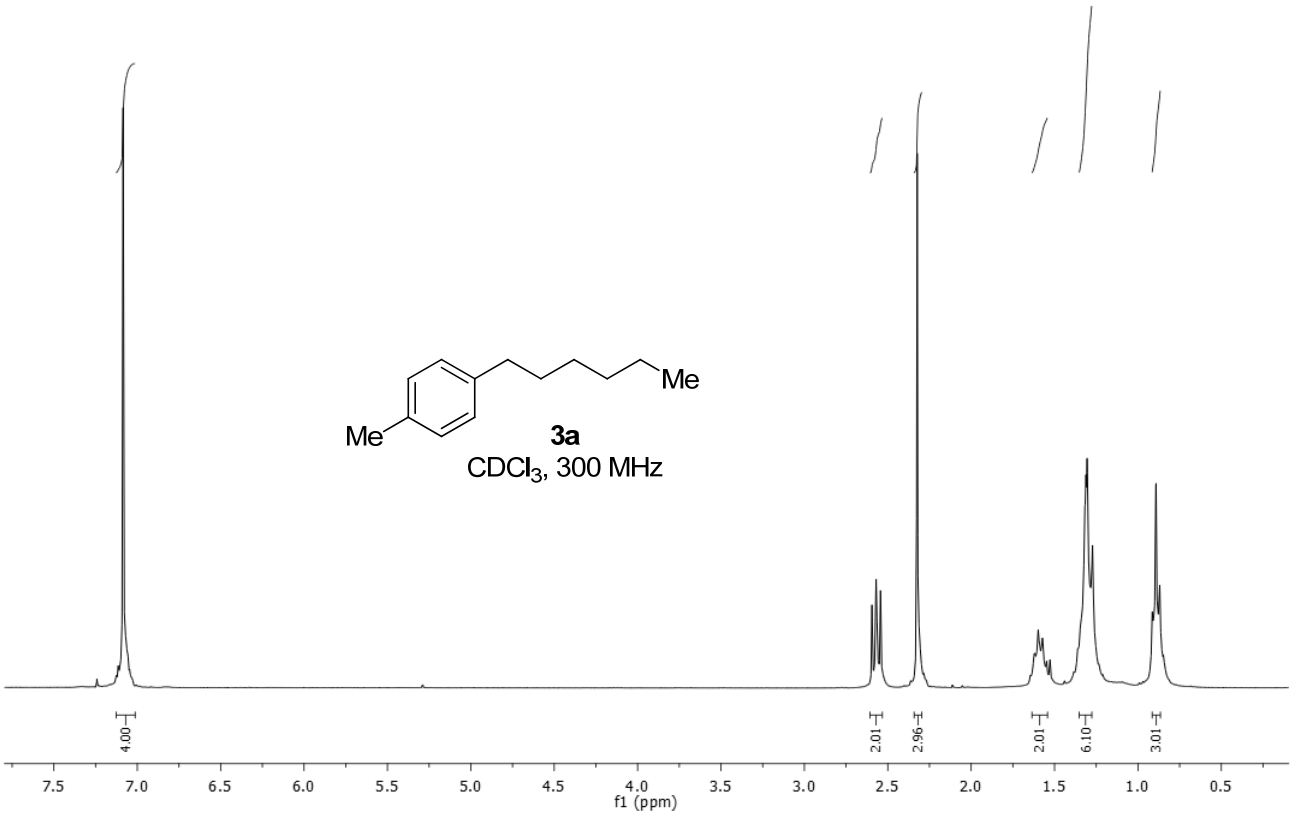

158.91
157.63
157.44
142.60
142.15
137.97
128.65
126.31
120.10
120.00
113.15
113.07
103.68
103.25
55.60
55.08
55.05
30.70
30.47
28.83
28.62
P(R)t-Bu
MeO
OMe
R = 4-MeOC6H4
6a
CDCl3, 75 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

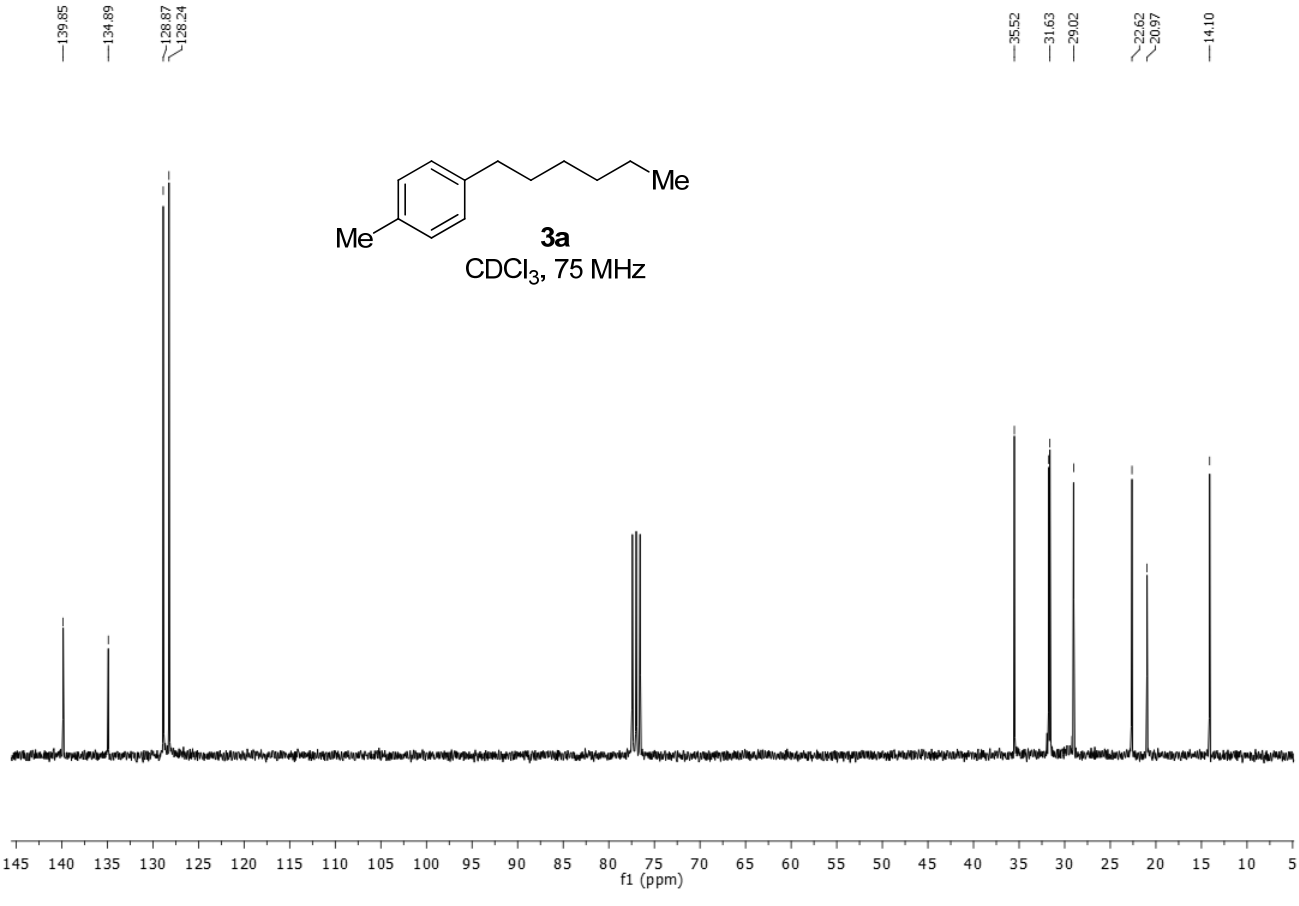

7.15
P(R)t-Bu
MeO
OMe
R = 4-MeOC6H4
6a
CDCl3, 121.5 MHz
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

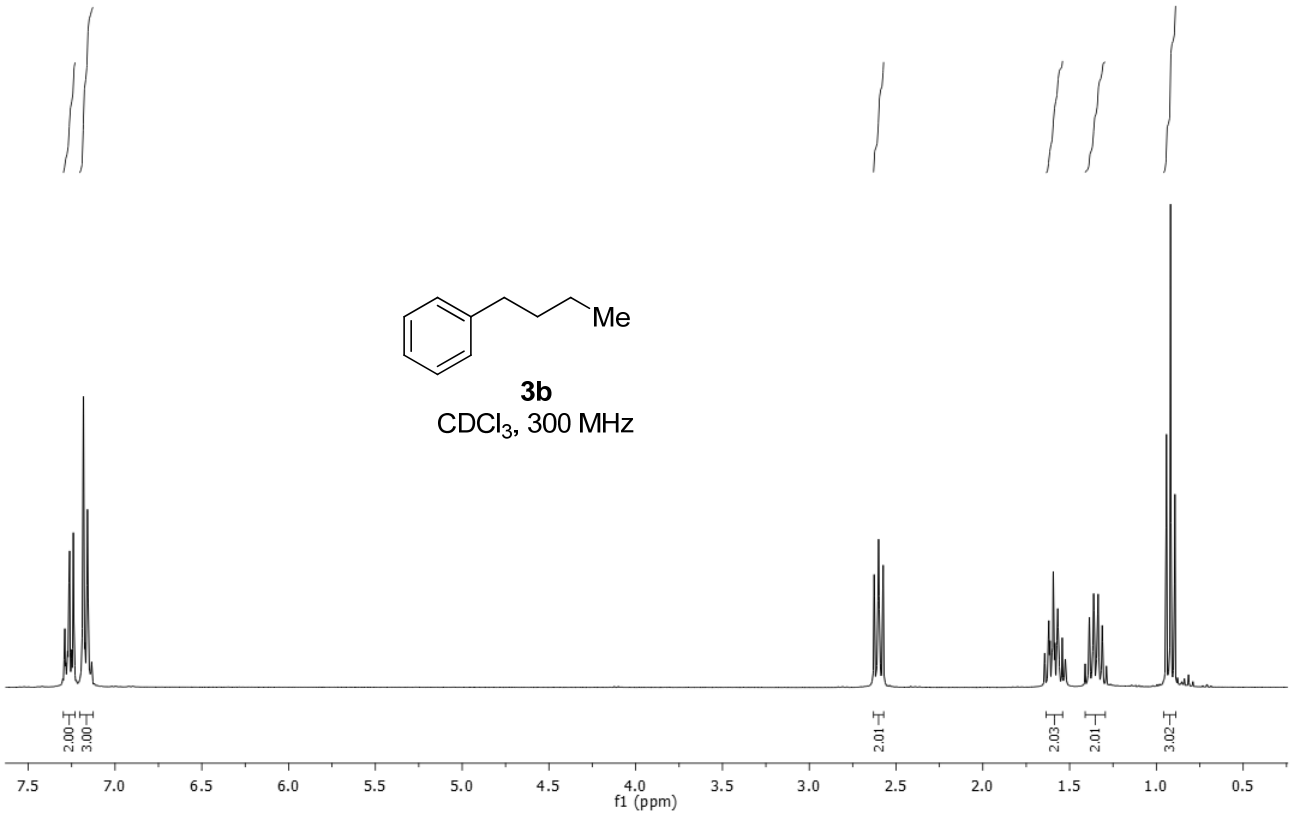

P(R)t-Bu
MeO
OMe
R = n-Hexyl
6b
CDCl3, 75 MHz
1.00
2.05
0.96
1.00
2.07
2.97
3.08
1.08
1.04
7.99
12.21
f1 (ppm)


157.58
157.21
143.14
142.72
136.55
136.27
131.62
126.11
119.92
103.29
103.12
55.30
55.14
31.67
31.52
27.44
22.64
22.05
14.08
P(R)t-Bu
MeO
OMe
R = n-Hexyl
6b
CDCl3, 300 MHz
f1 (ppm)


8.50
P(R)t-Bu
MeO
OMe
R =n-Hexyl
6b
CDCl3, 121.5 MHz
8 7 6 5 4 3 2 1 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26
f1 (ppm)

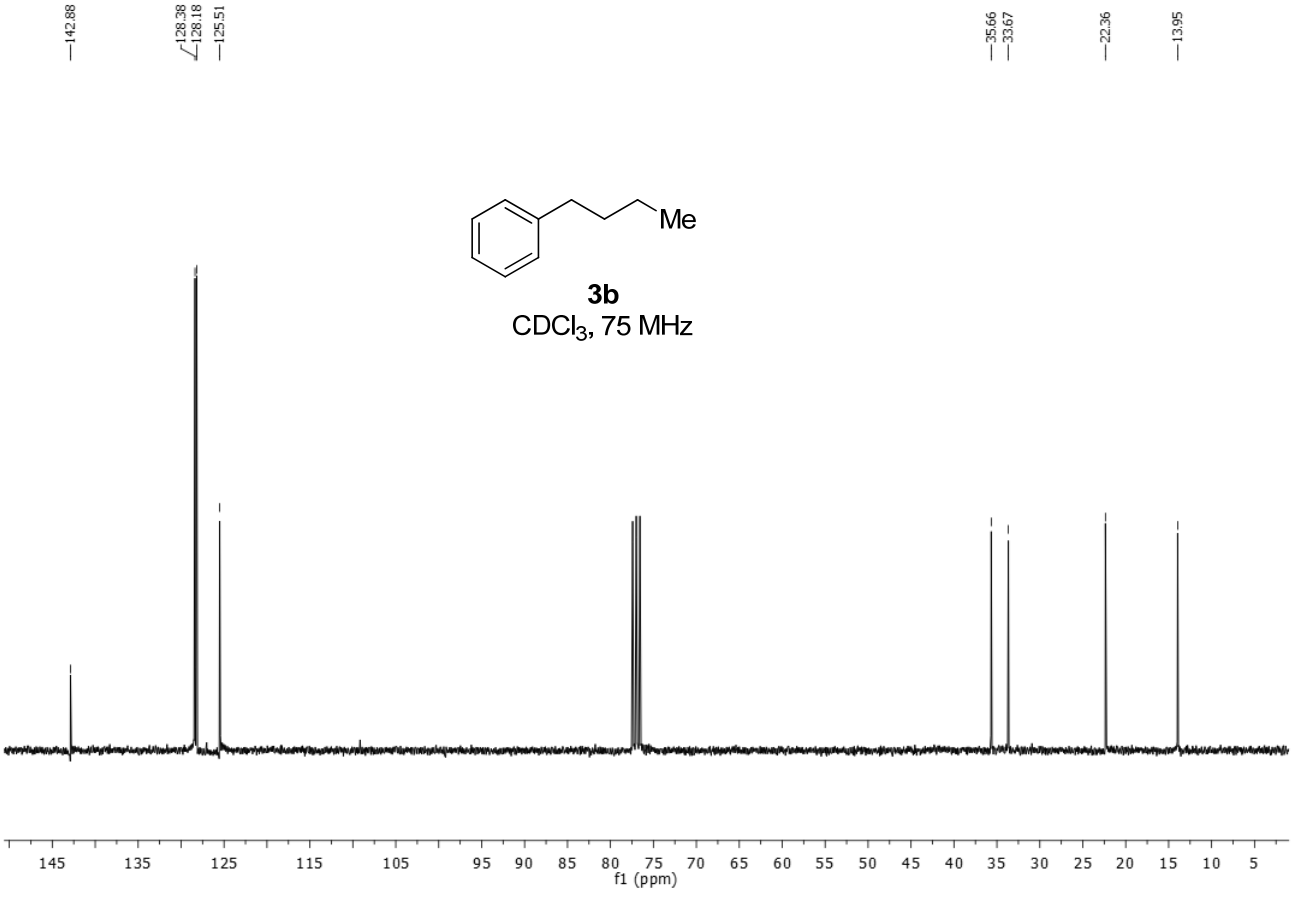

Me
Me
3a
CDCl3, 300 MHz
4.00
2.01
2.96
2.01
6.10
3.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


139.85
134.89
128.87
128.24
35.52
31.63
29.02
22.62
20.97
14.10
Me
Me
3a
CDCl3, 75 MHz
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)



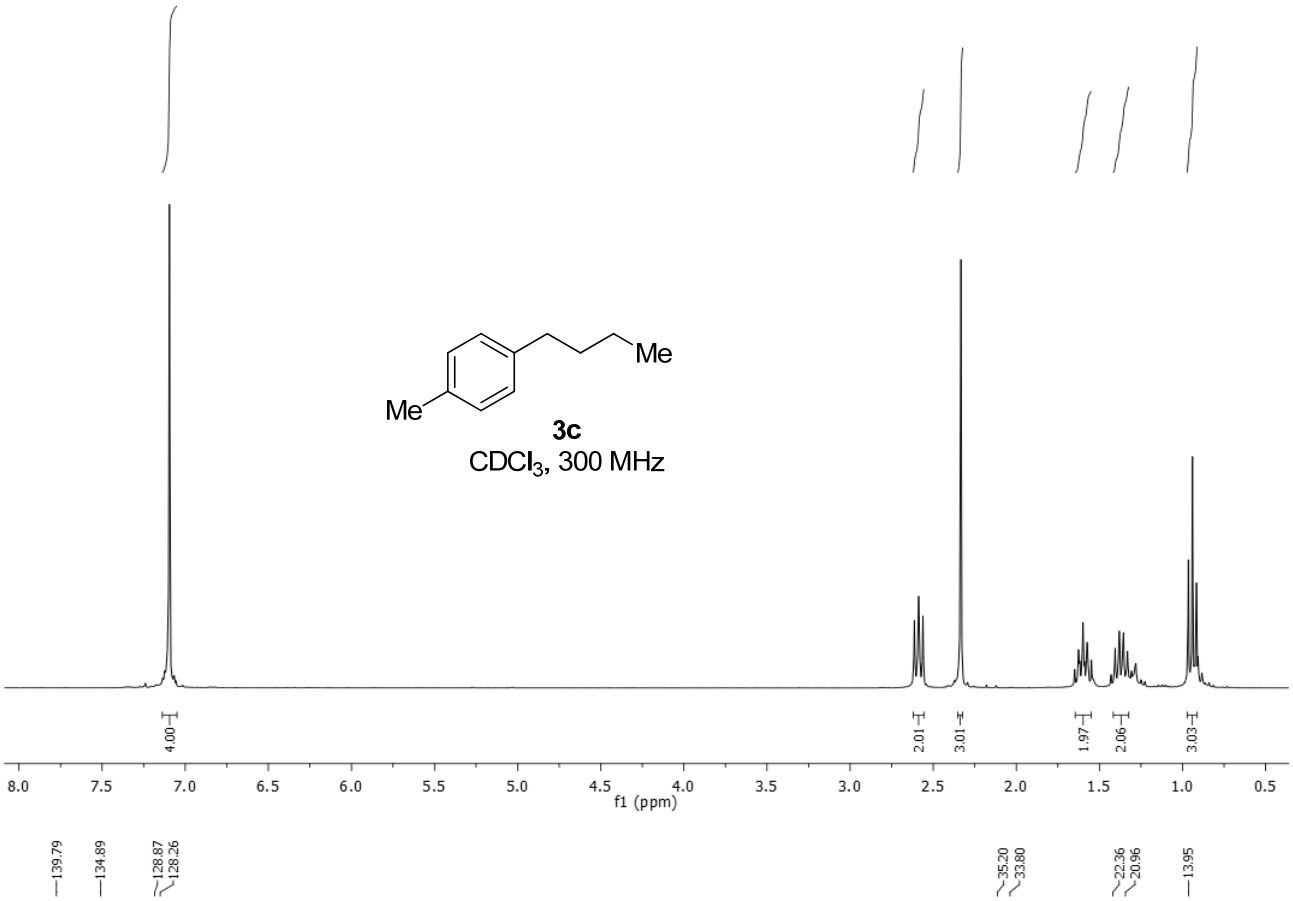
3b

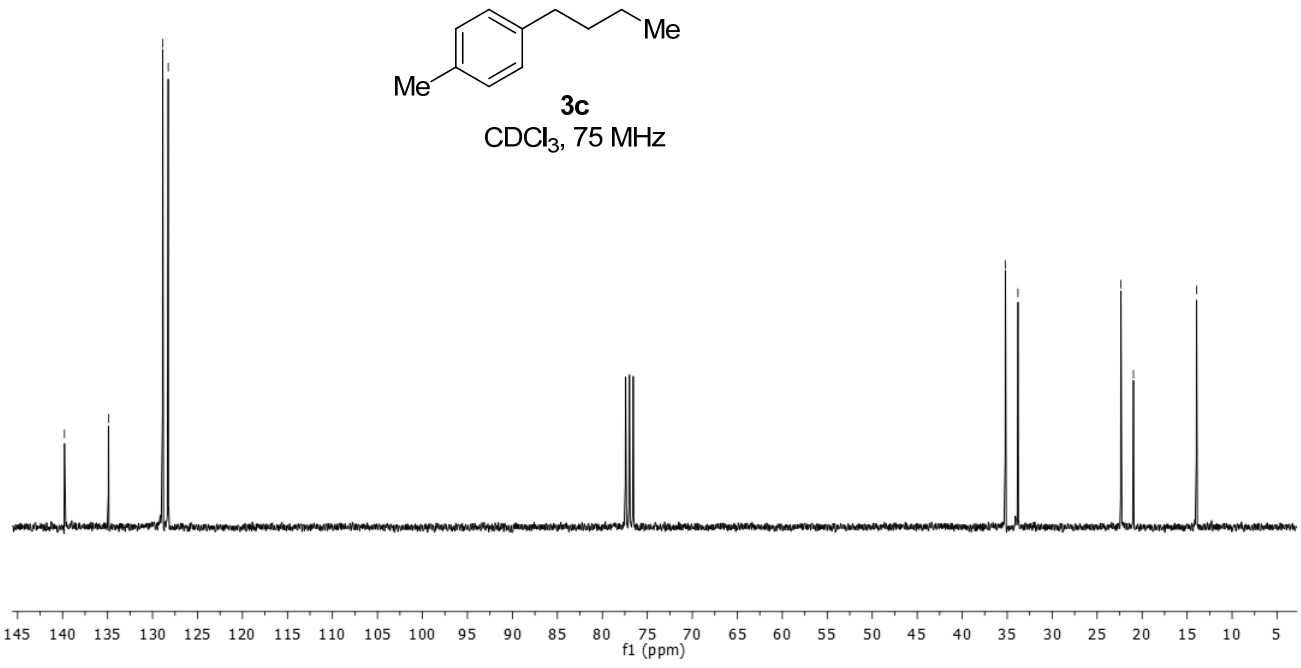
$CDCl_3$, 300 MHz

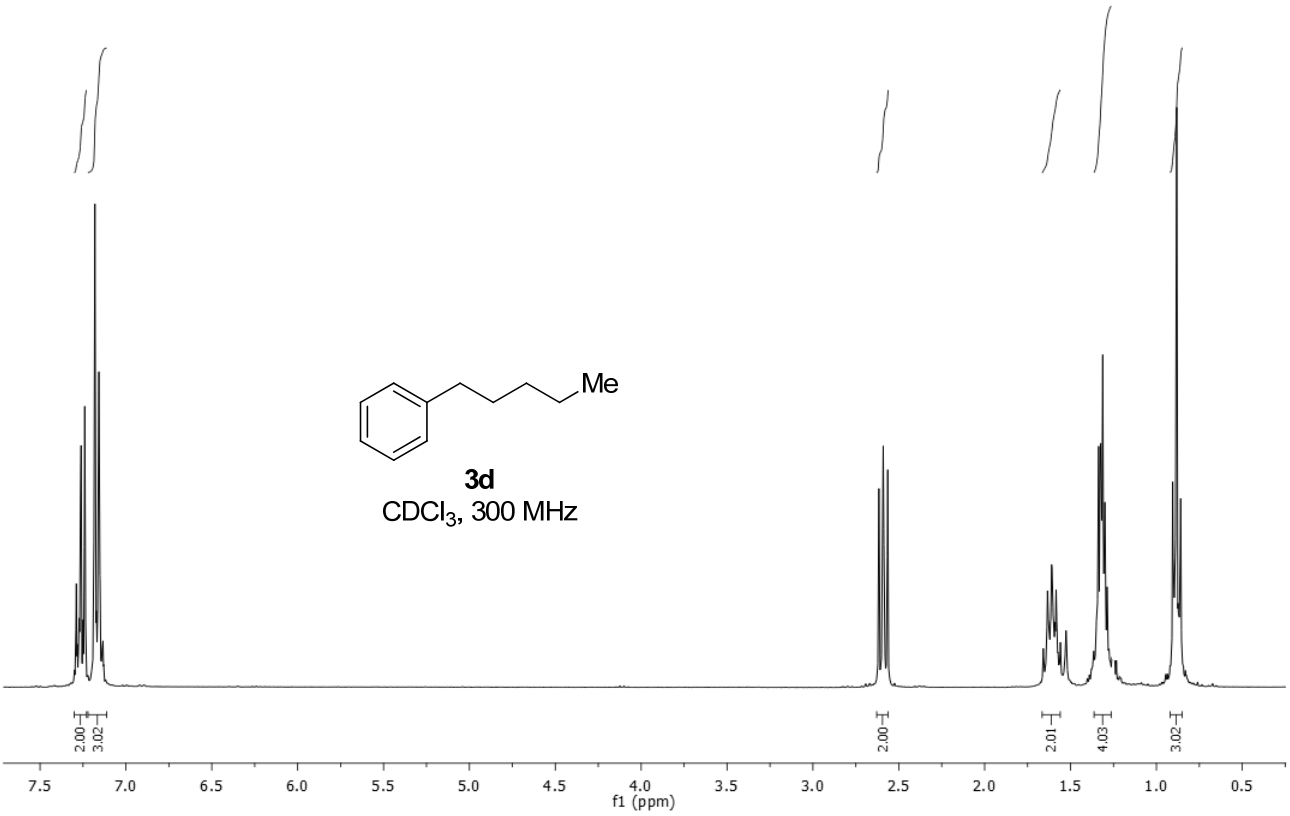


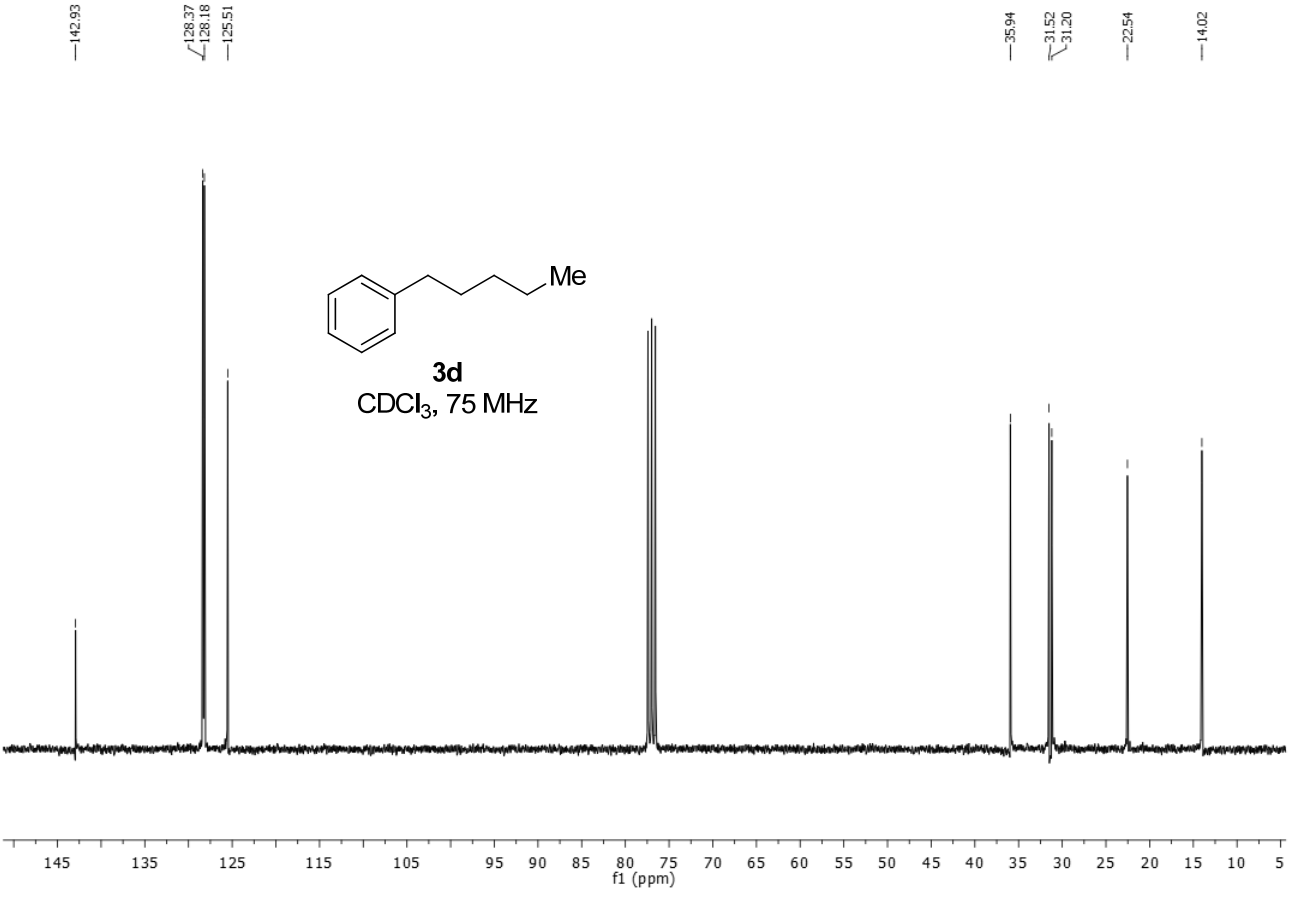
3b

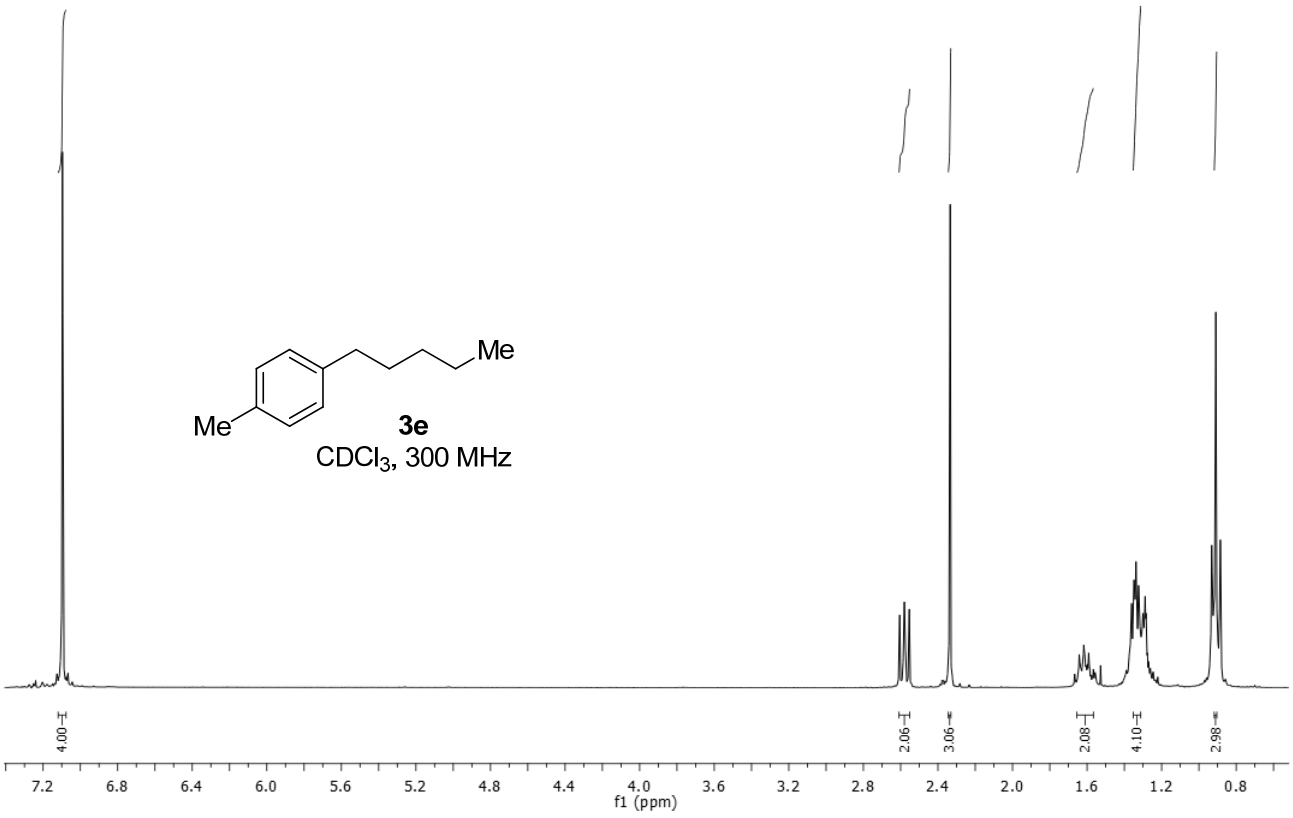
$CDCl_3$, 75 MHz

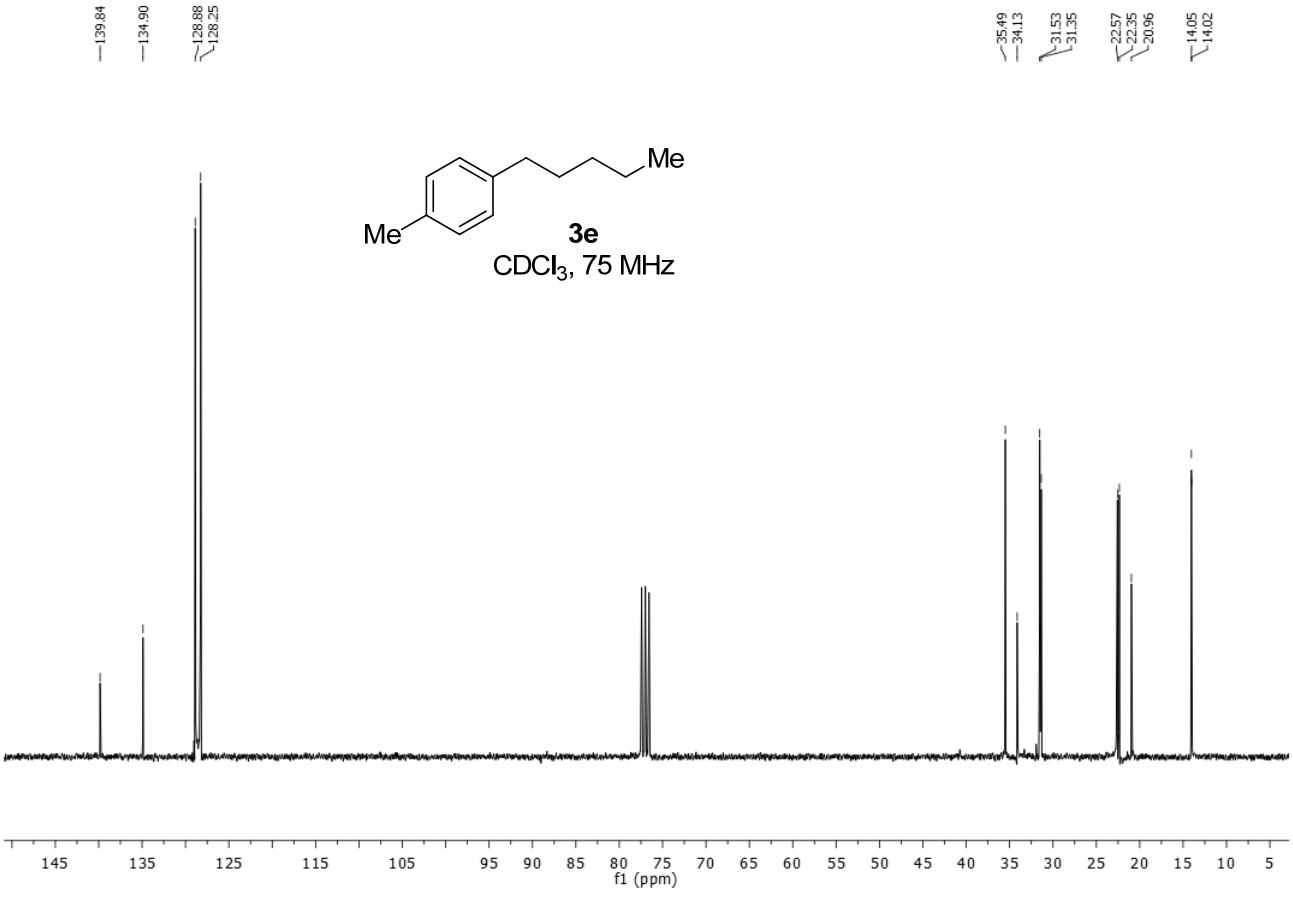

Me
Me
3c
CDCl3, 300 MHz
4.00
2.01
3.01
1.97
2.06
3.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
139.79
134.89
128.87
128.26
35.20
33.80
22.36
20.96
13.95

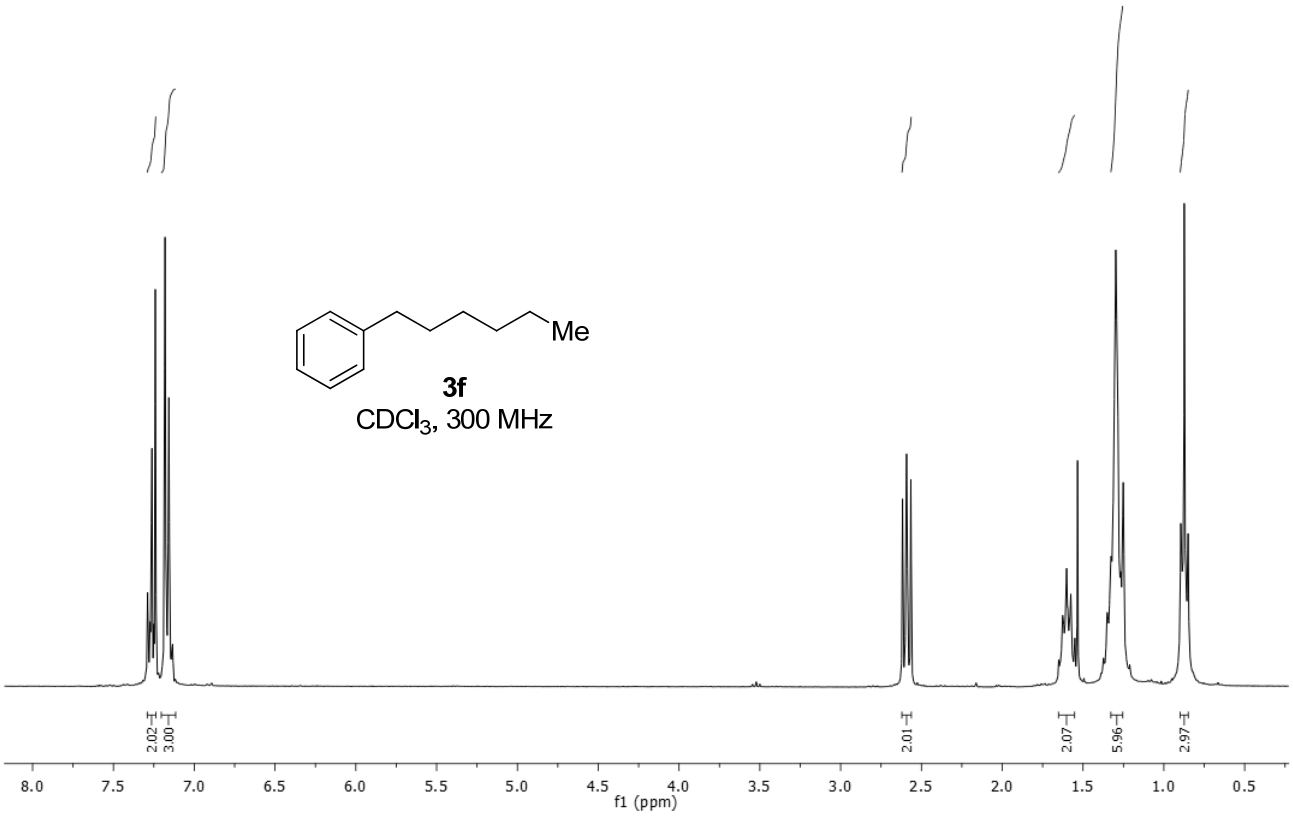

Me
Me
3c
CDCl3, 75 MHz
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

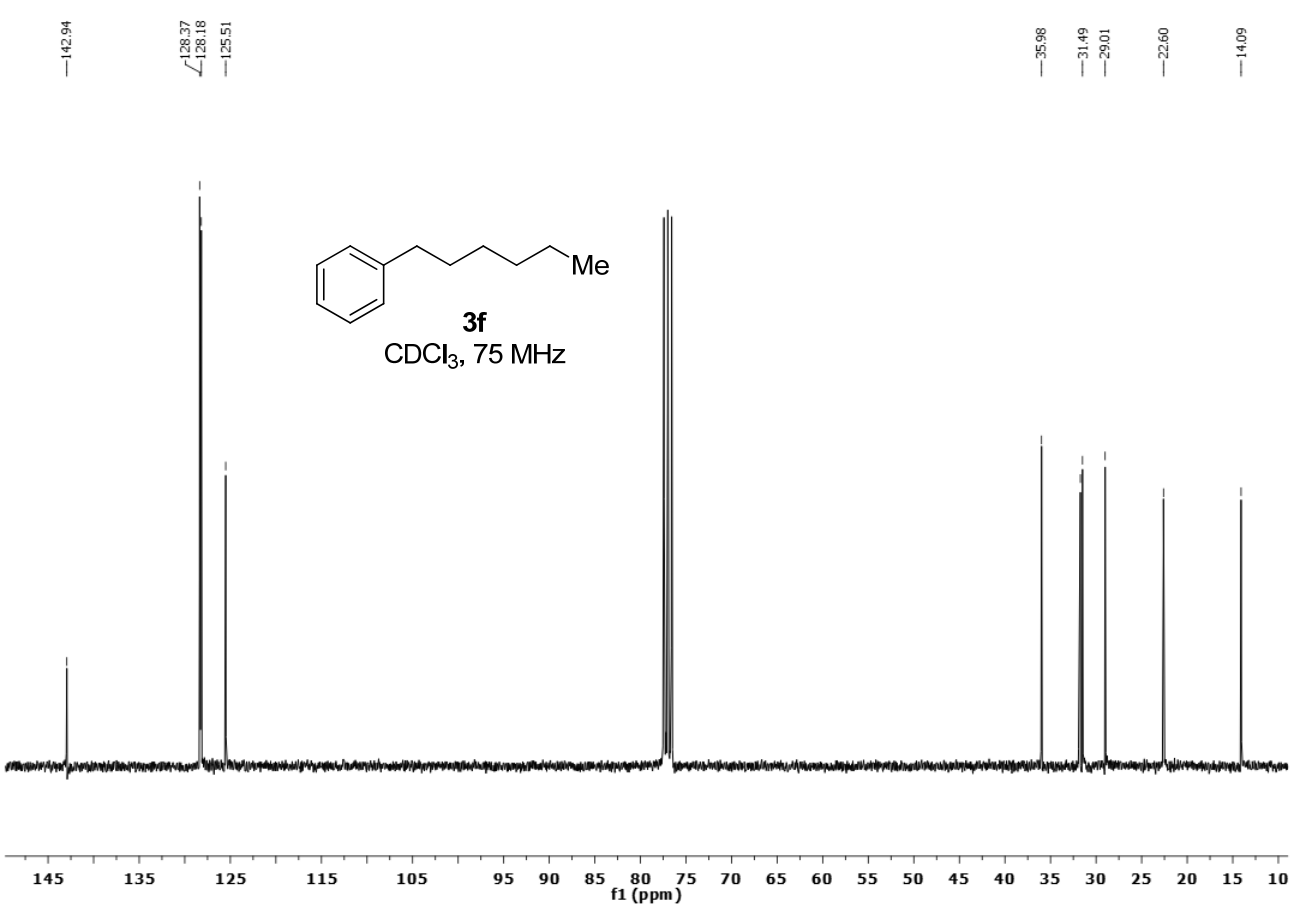

Me
3d
CDCl3, 300 MHz
2.00
3.02
2.00
2.01
4.03
3.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

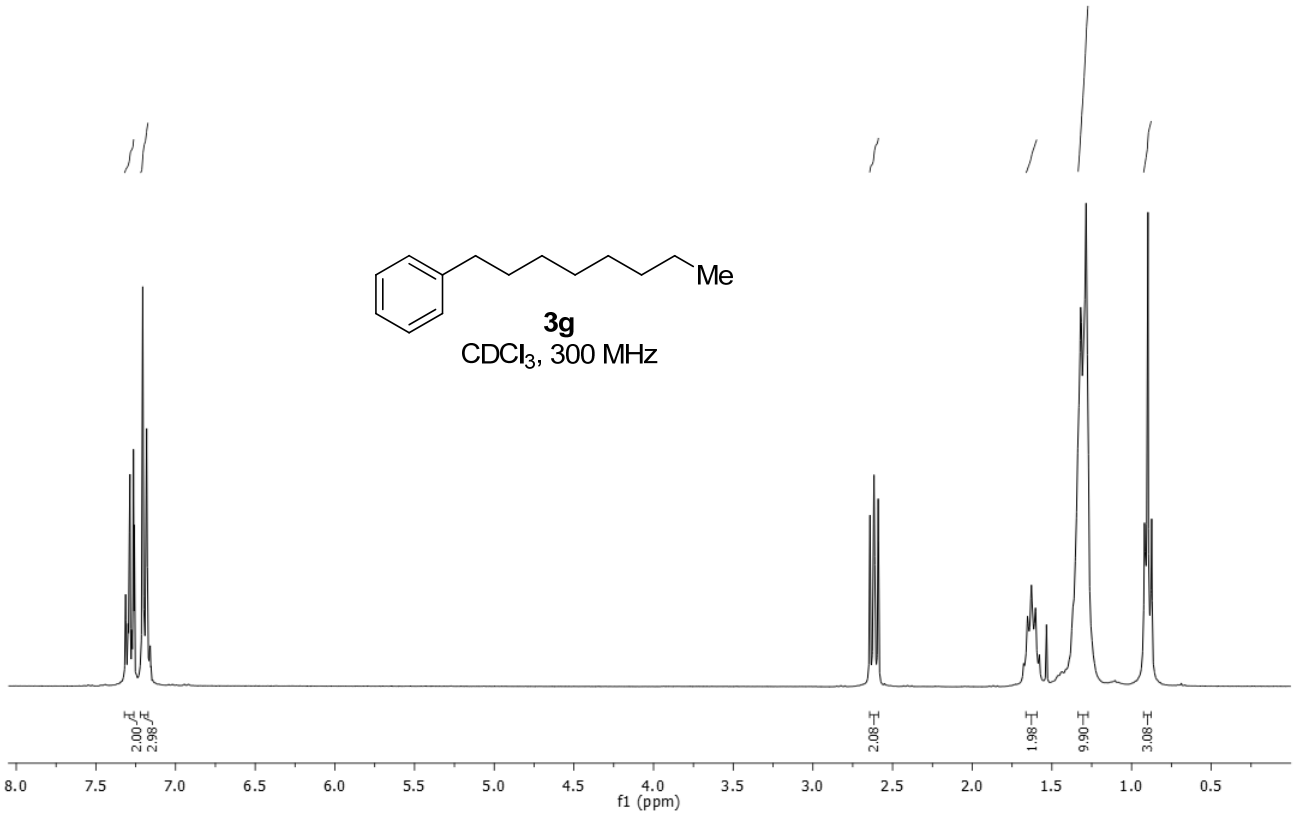

142.93
128.37
128.18
125.51
35.94
31.52
31.20
22.54
14.02
Me
3d
CDCl3, 75 MHz
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

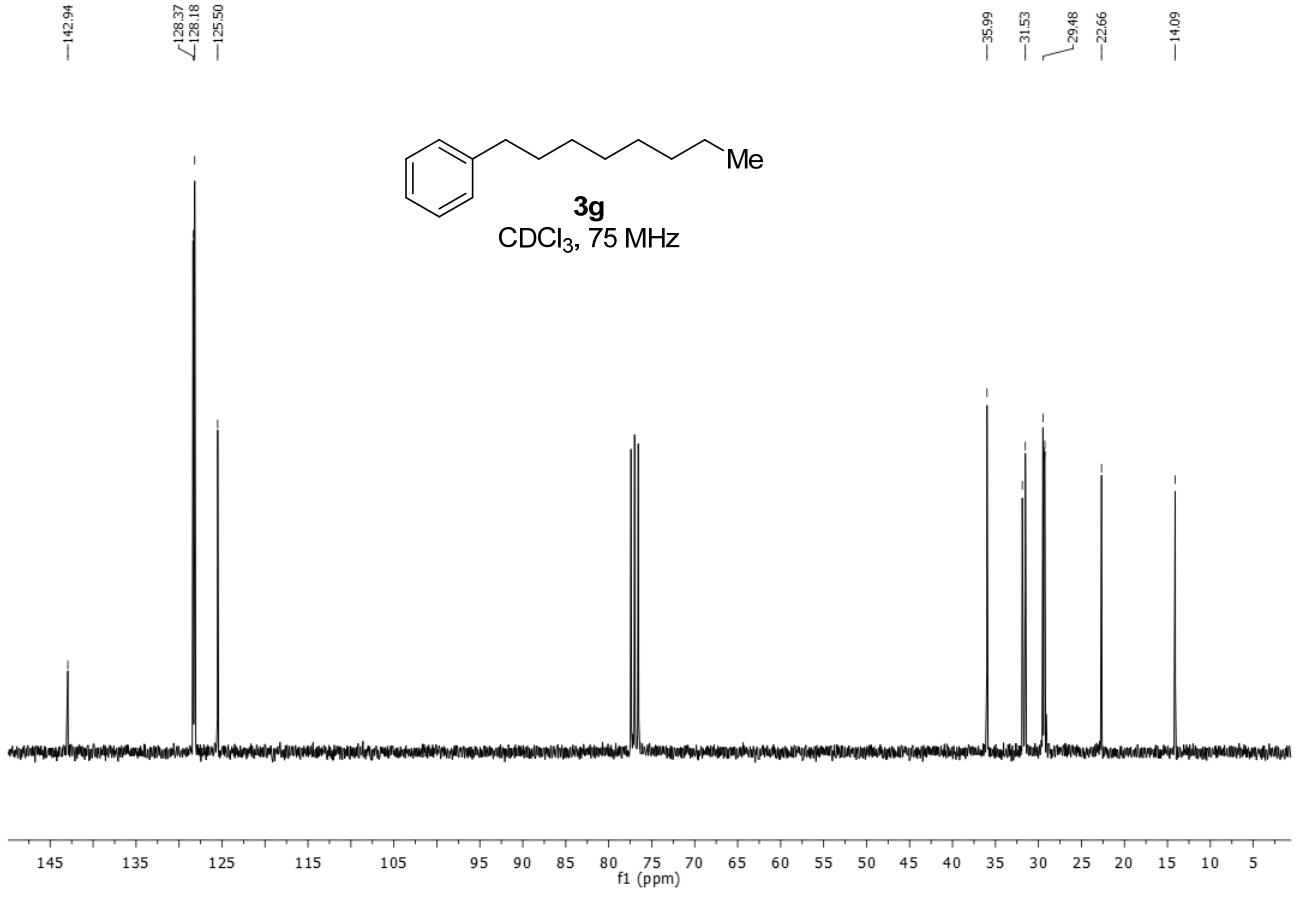

Me
Me
3e
CDCl3, 300 MHz
4.00
2.06
3.06
2.08
4.10
2.98
7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8
f1 (ppm)

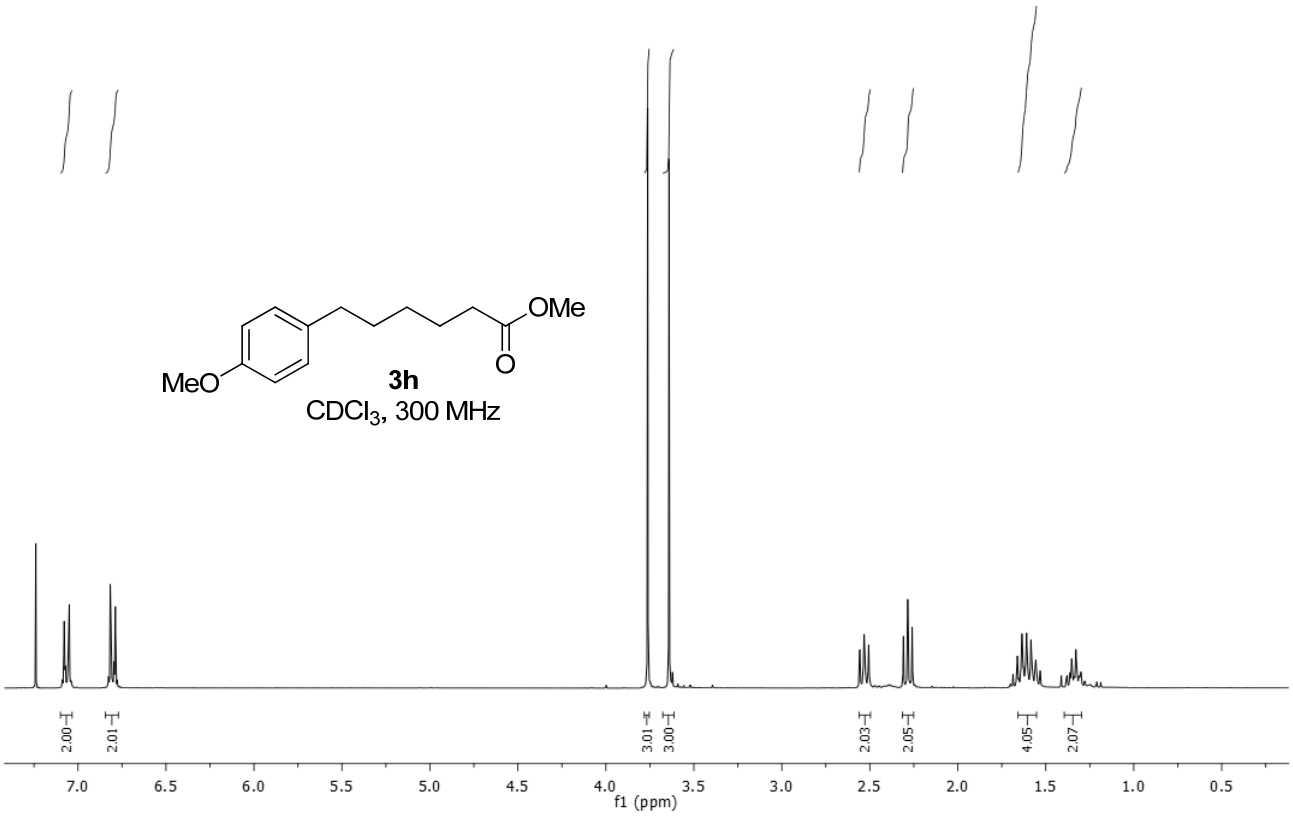

139.84
134.90
128.88
128.25
35.49
34.13
31.53
31.35
22.57
22.35
20.96
14.05
14.02
Me
Me
3e
CDCl3, 75 MHz
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

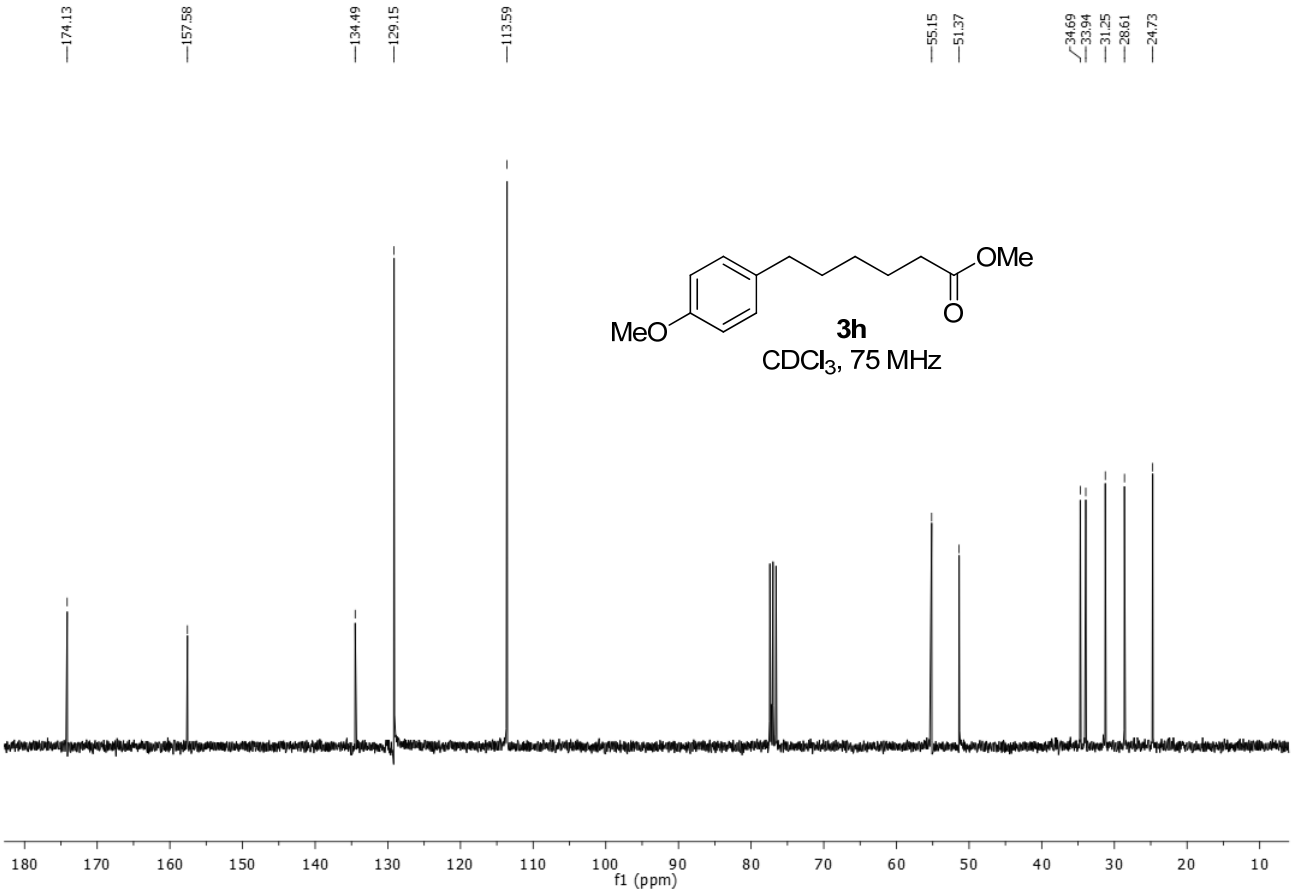

Me
3f
CDCl3, 300 MHz
2.02
3.00
2.01
2.07
5.96
2.97
f1 (ppm)

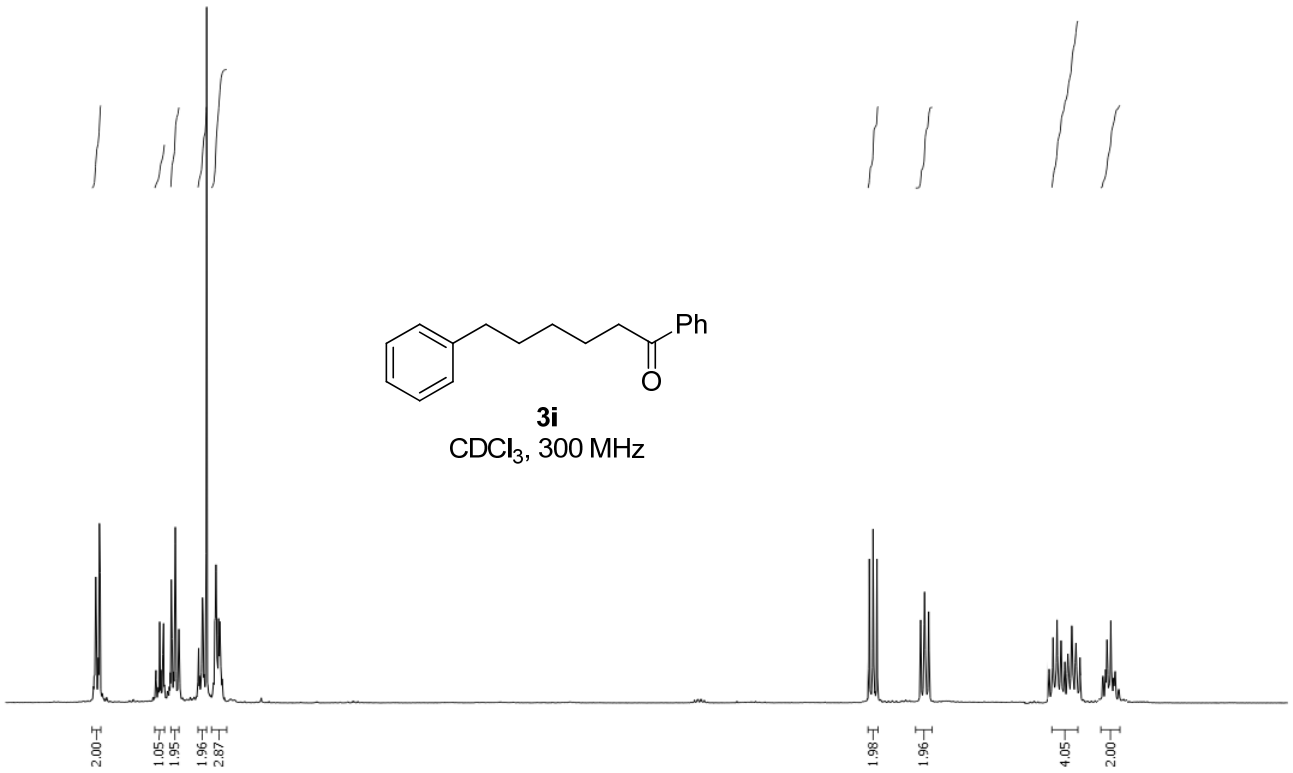

142.94
128.37
128.18
125.51
35.98
31.49
29.01
22.60
14.09
Me
3f
CDCl3, 75 MHz
f1 (ppm)


Me
3g
CDCl3, 300 MHz
2.00
2.98
2.08
1.98
9.90
3.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


142.94
128.37
128.18
125.50
35.99
31.53
29.48
22.66
14.09
Me
3g
CDCl3, 75 MHz
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

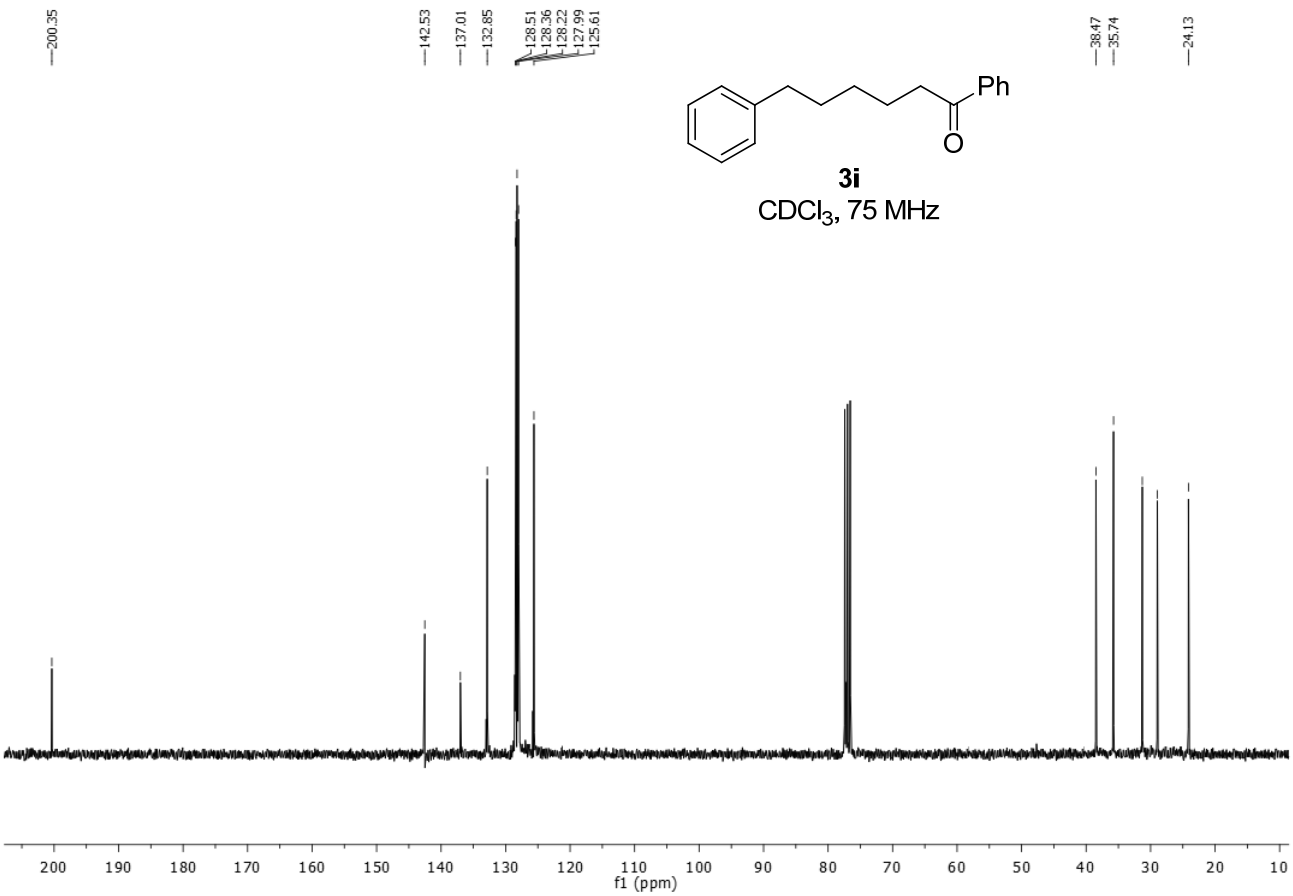

OMe
O
MeO
3h
CDCl3, 300 MHz
2.00
2.01
3.01
3.00
2.03
2.05
4.05
2.07
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


174.13
157.58
134.49
129.15
113.59
55.15
51.37
34.69
33.94
31.25
28.61
24.73
OMe
O
MeO
3h
CDCl3, 75 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



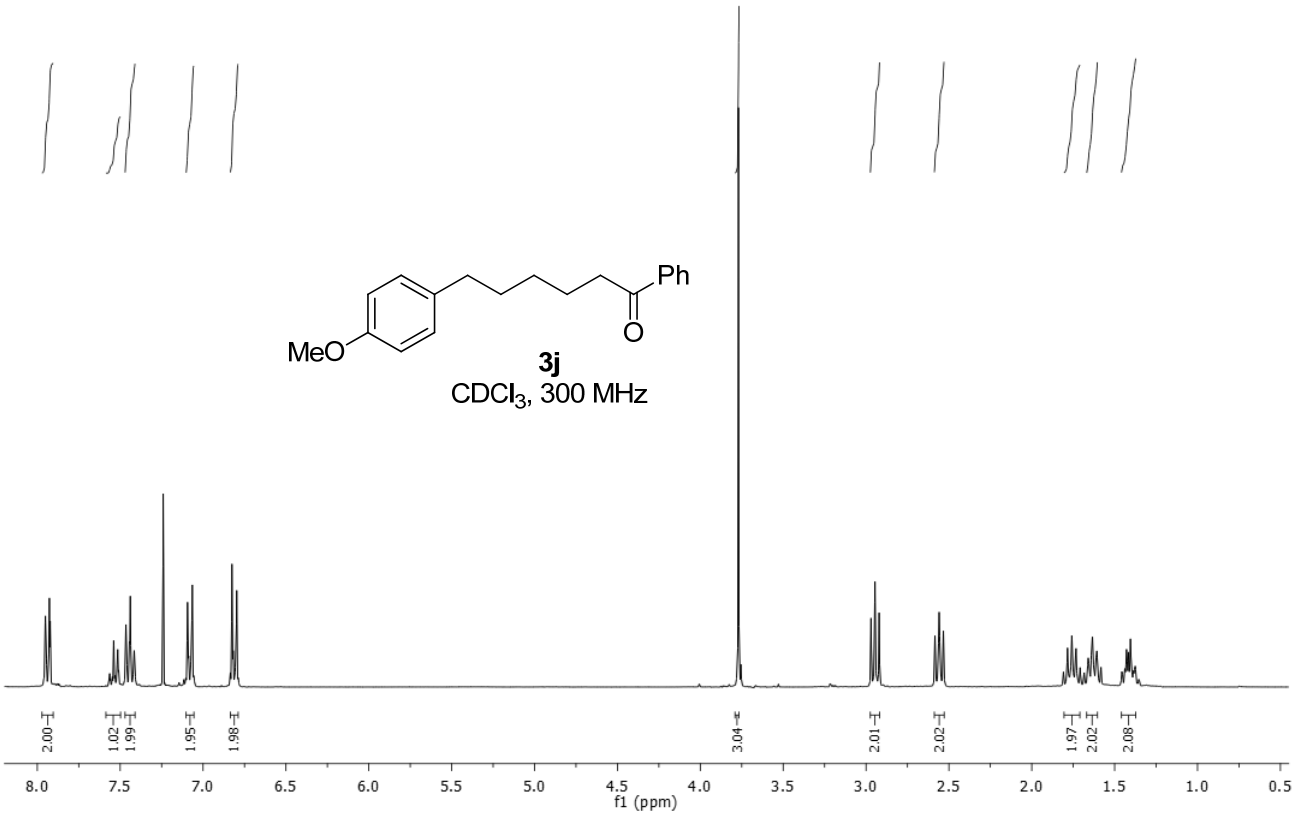
3i

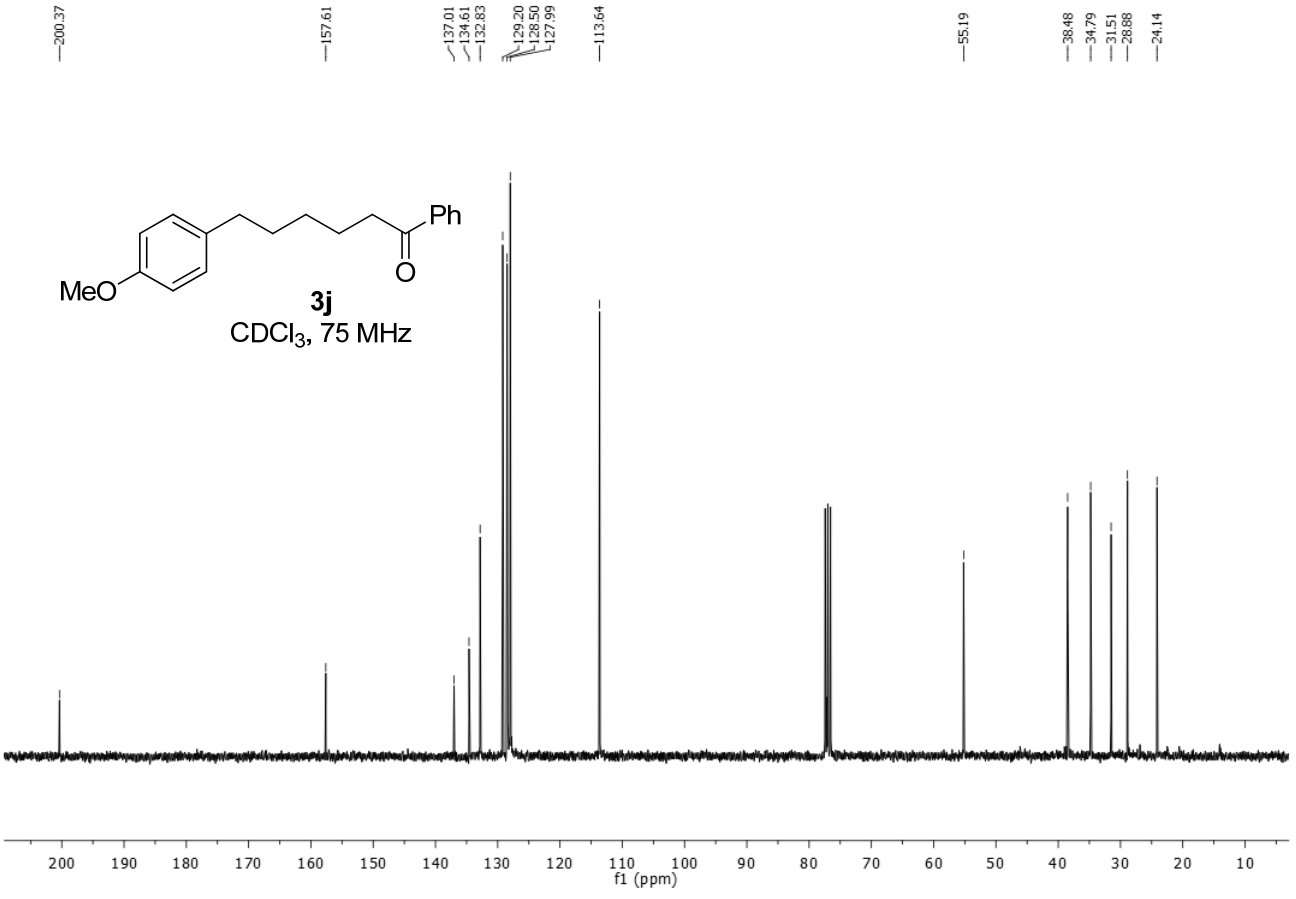
$CDCl_3$, 300 MHz

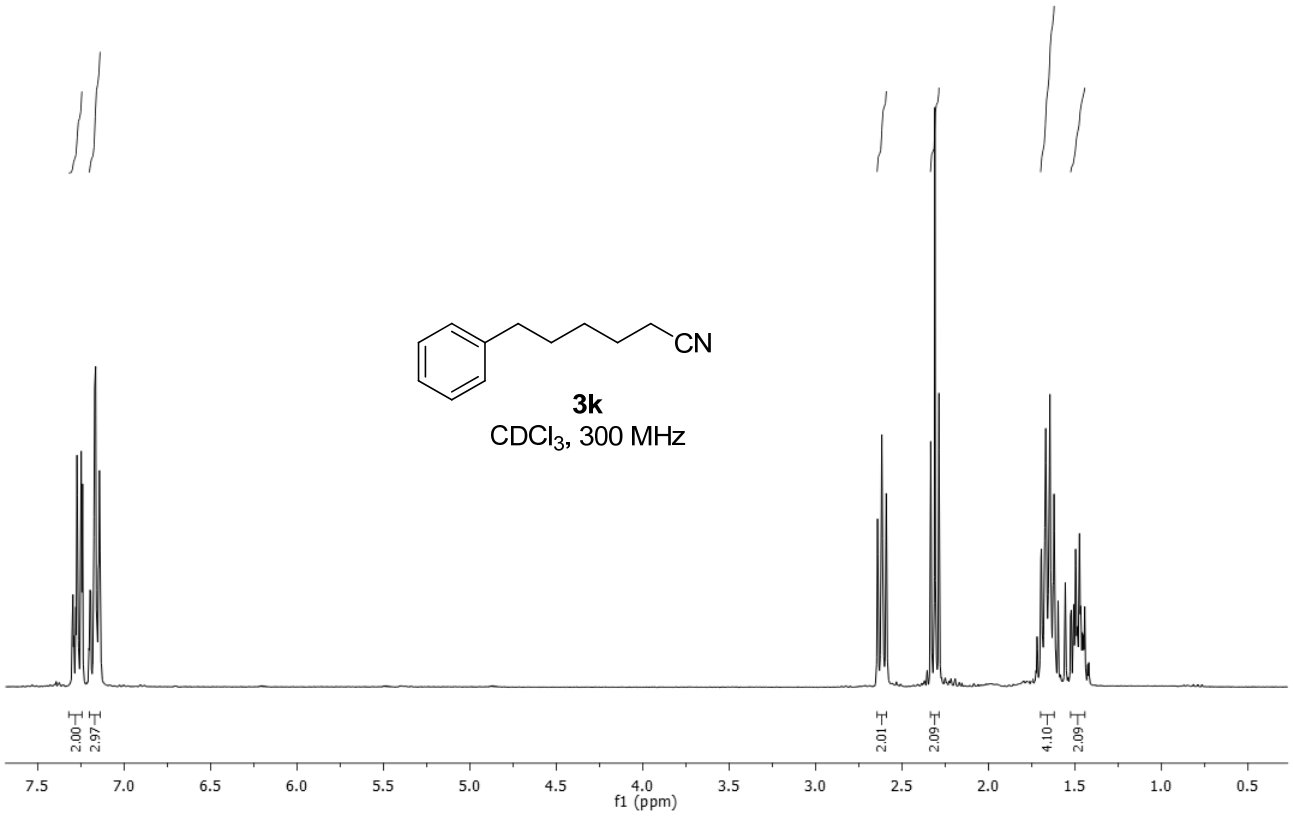


3i

$CDCl_3$, 75 MHz

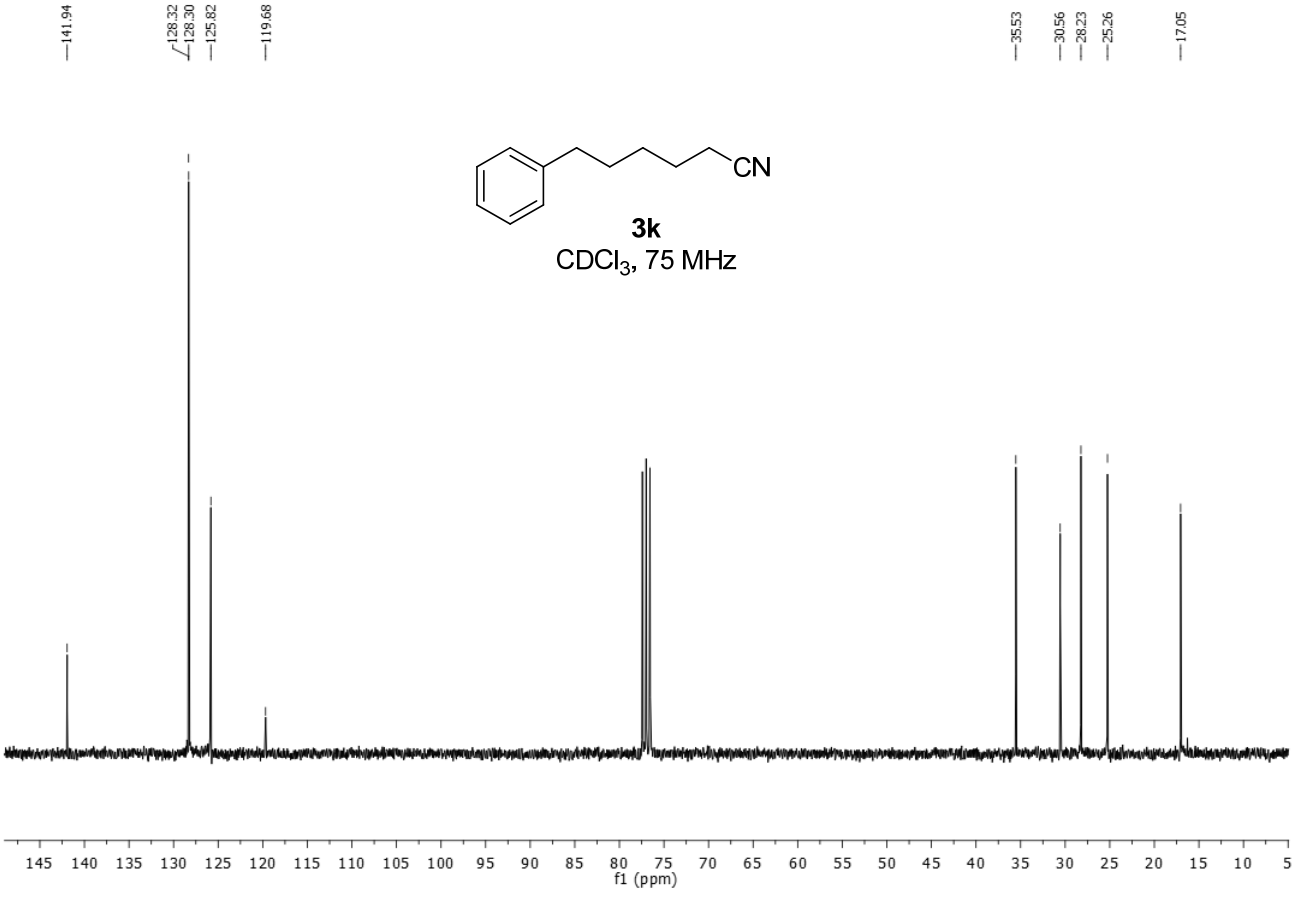

Ph
O
MeO
3j
CDCl3, 300 MHz
2.00
1.02
1.99
1.95
1.98
3.04
2.01
2.02
1.97
2.02
2.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200.37
157.61
137.01
134.61
132.83
129.20
128.50
127.99
113.64
55.19
38.48
34.79
31.51
28.88
24.14
Ph
O
MeO
3j
CDCl3, 75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



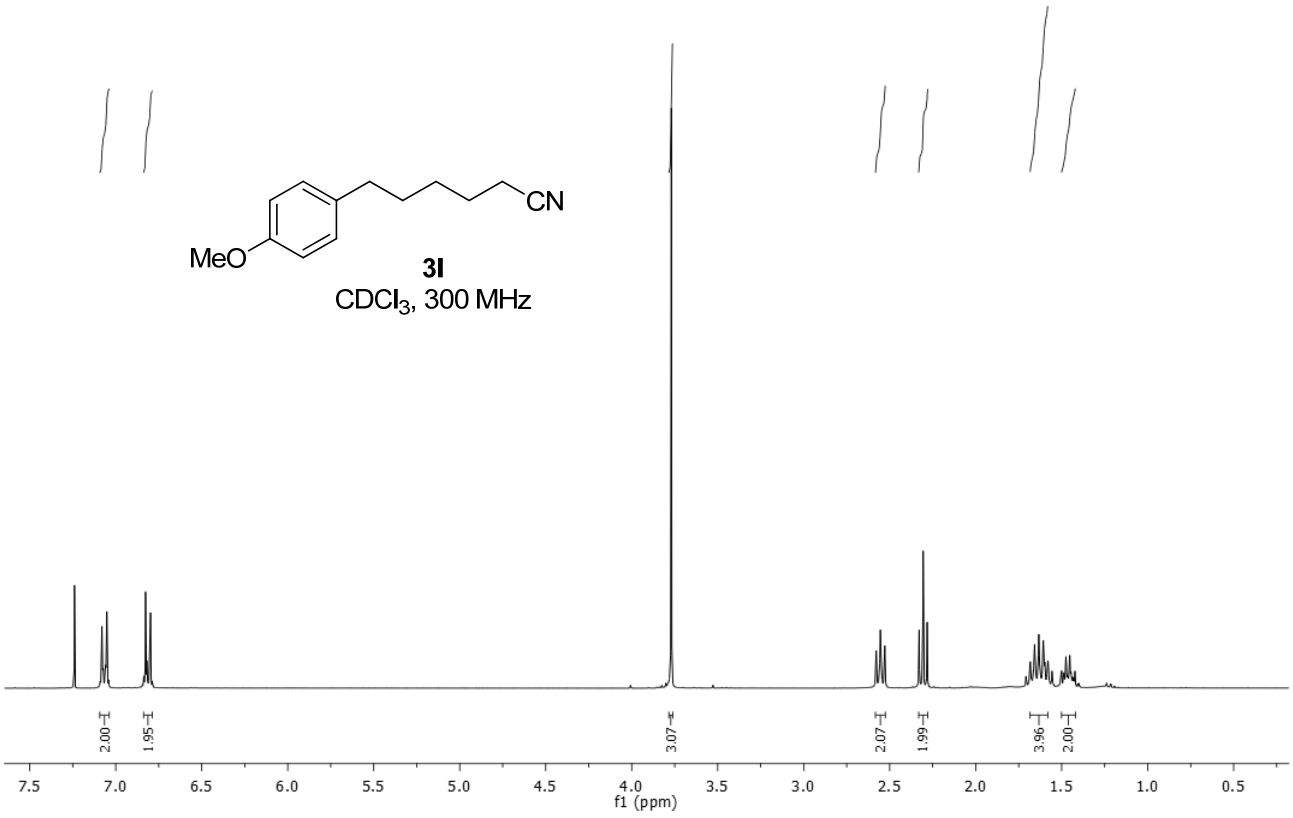
3k

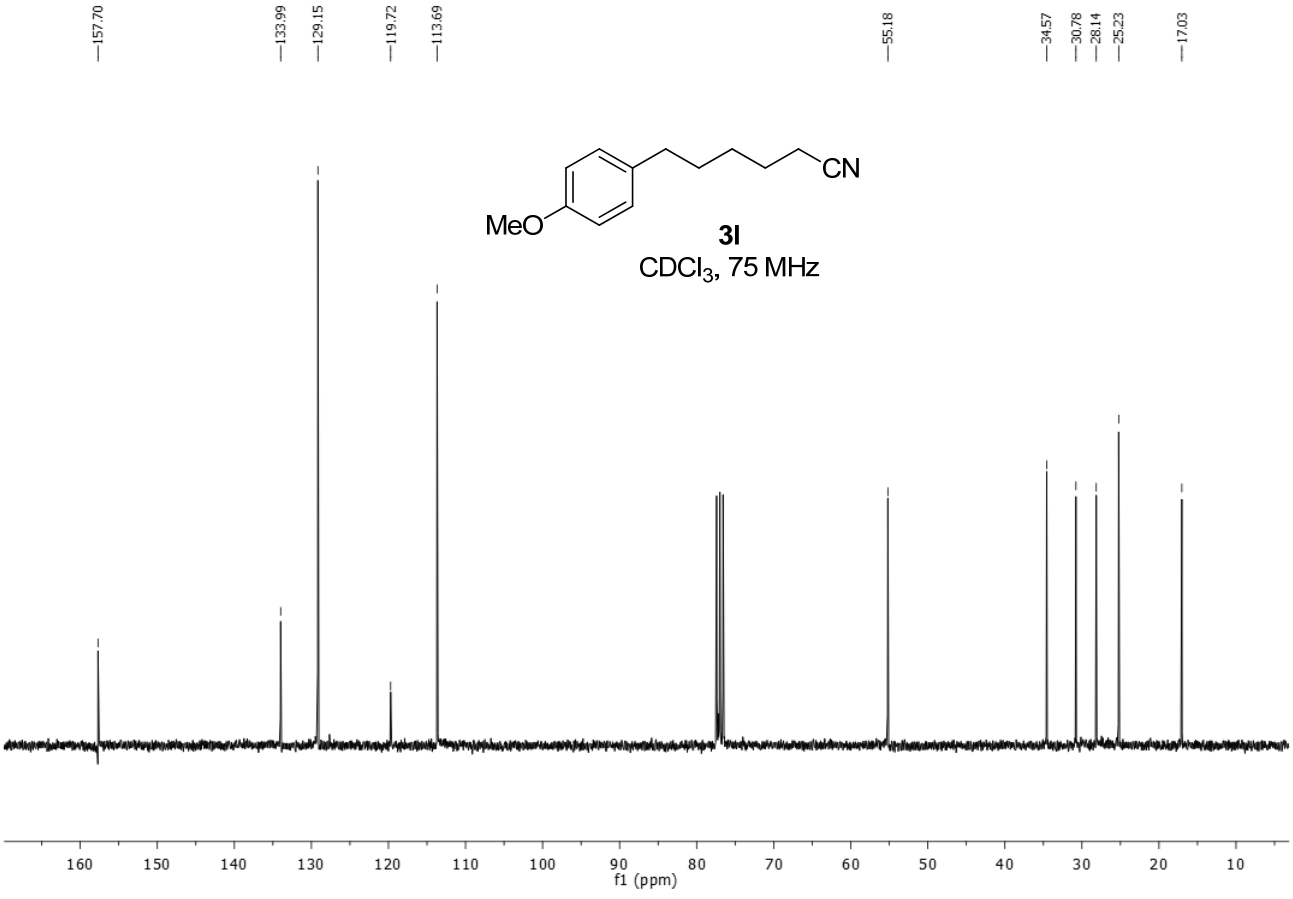
$CDCl_3$, 300 MHz

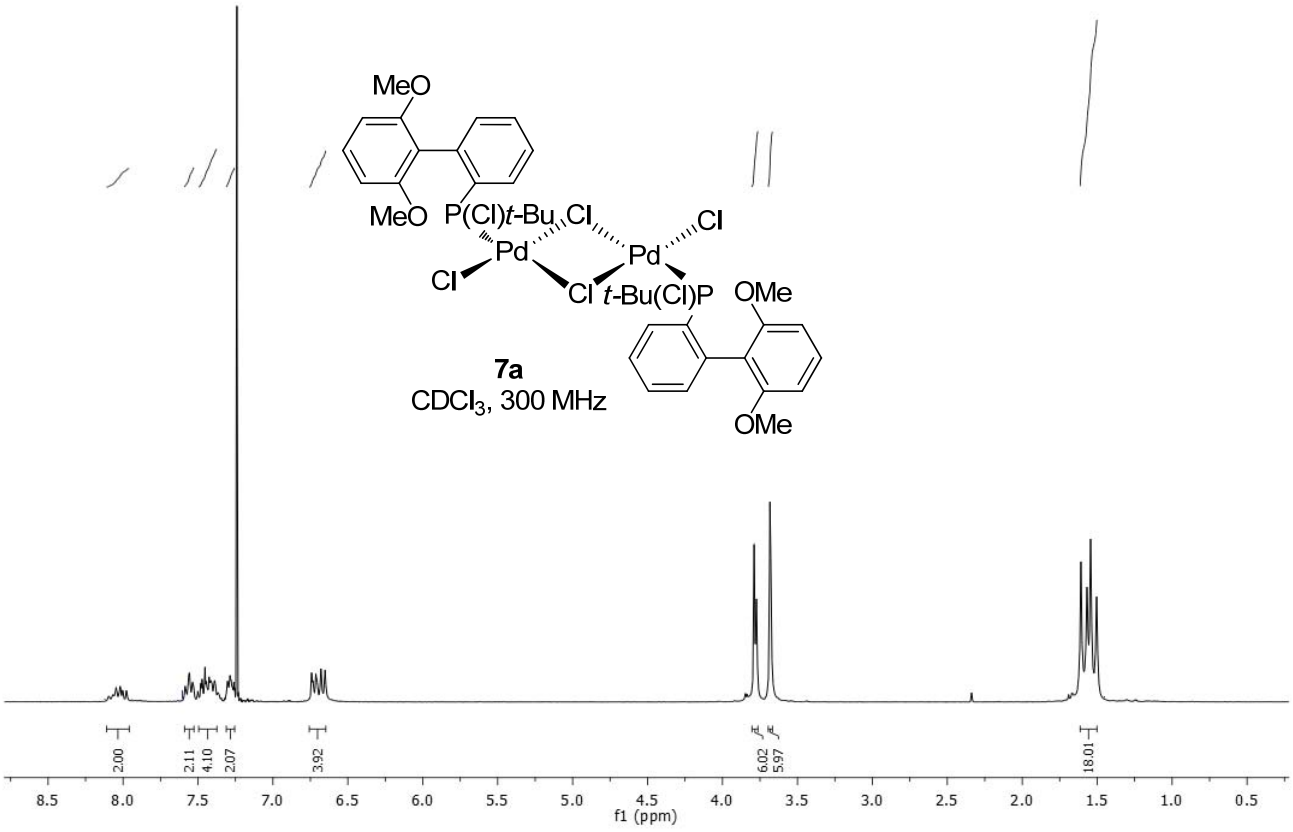


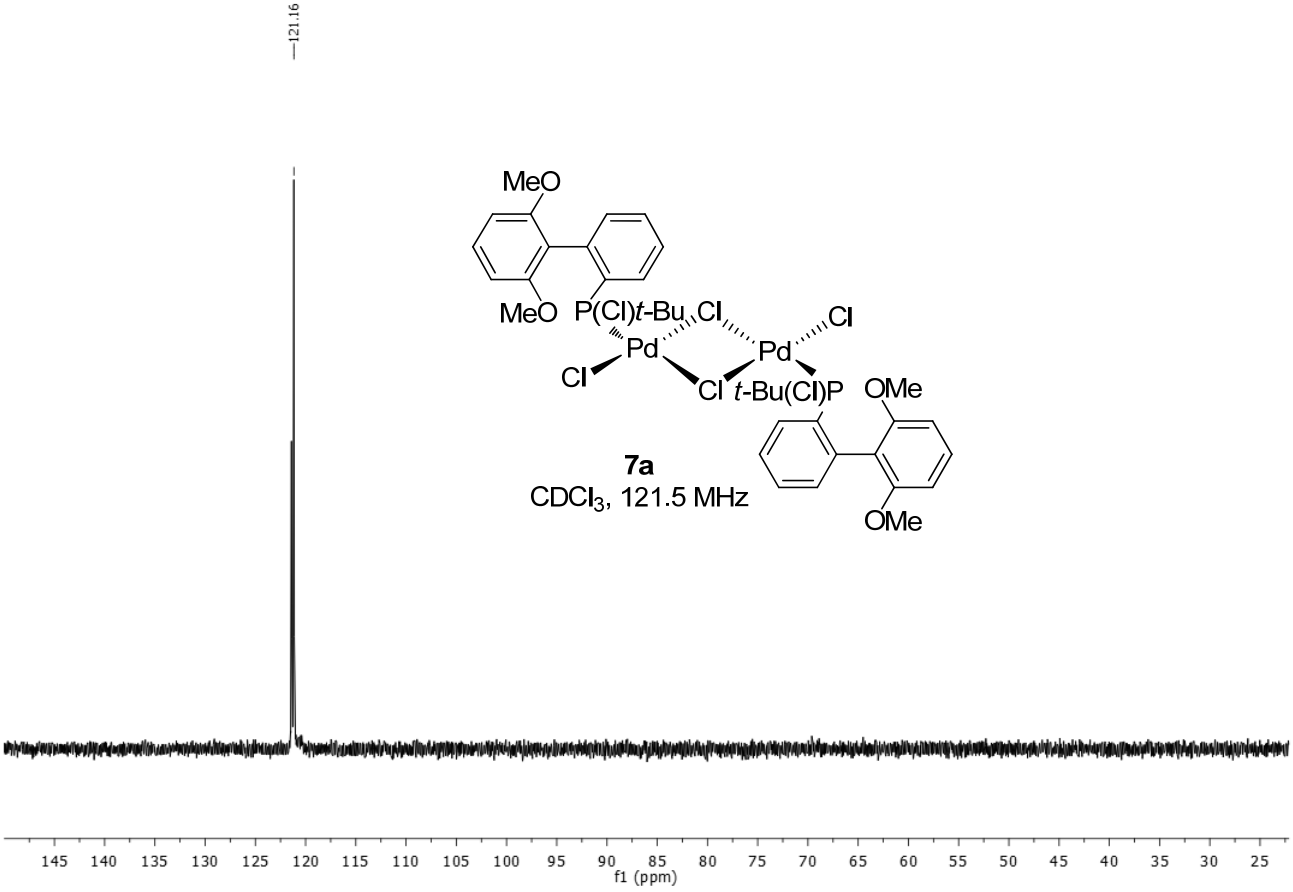
3k

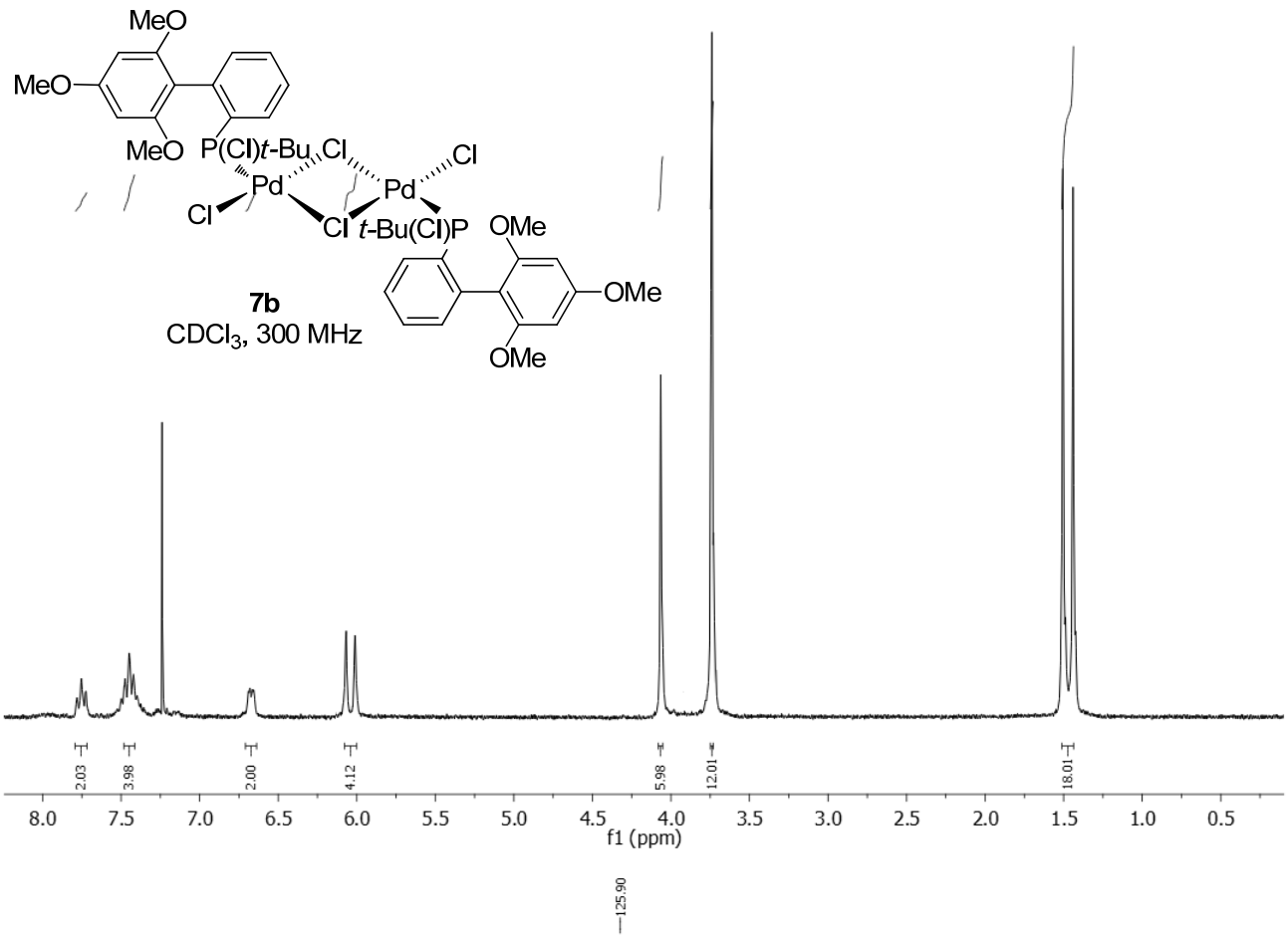
$CDCl_3$, 75 MHz

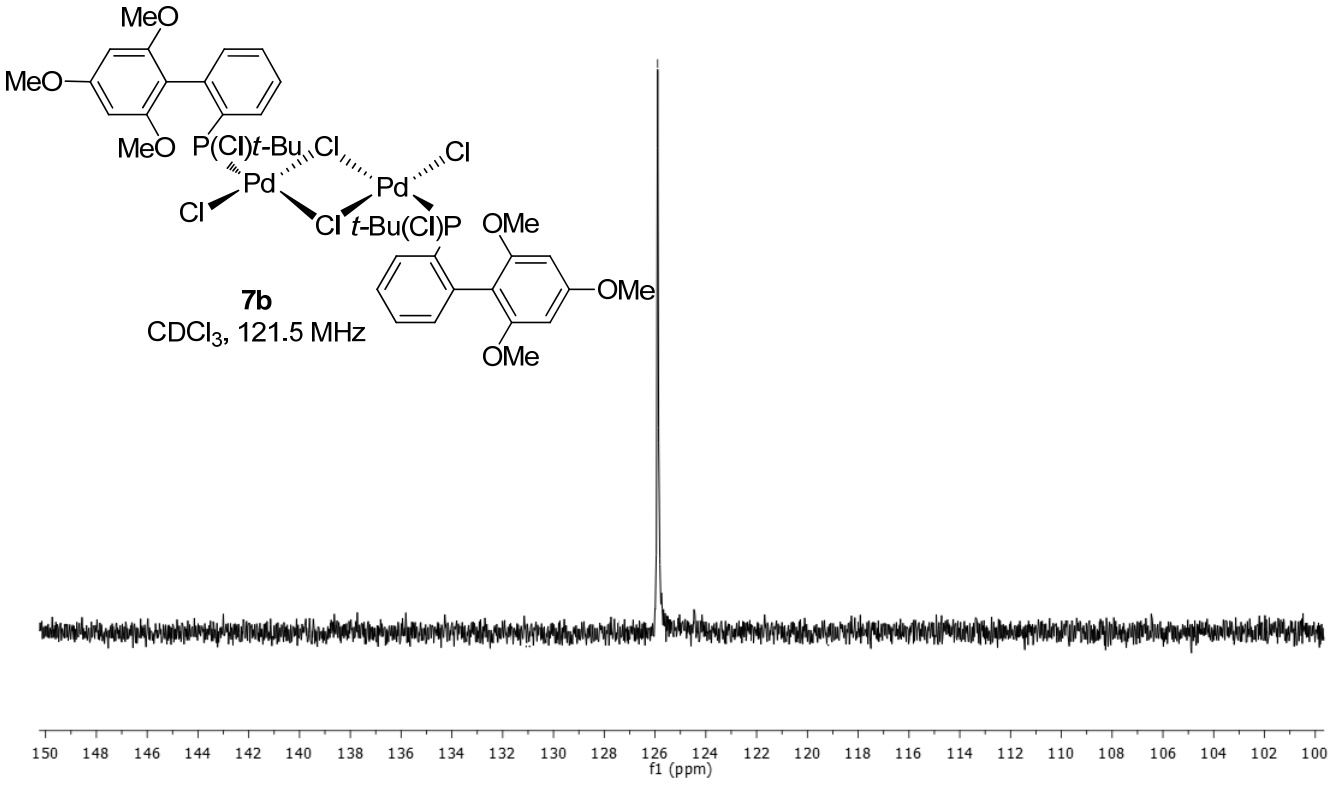

CN
MeO
3l
CDCl3, 300 MHz
2.00
1.95
3.07
2.07
1.99
3.96
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

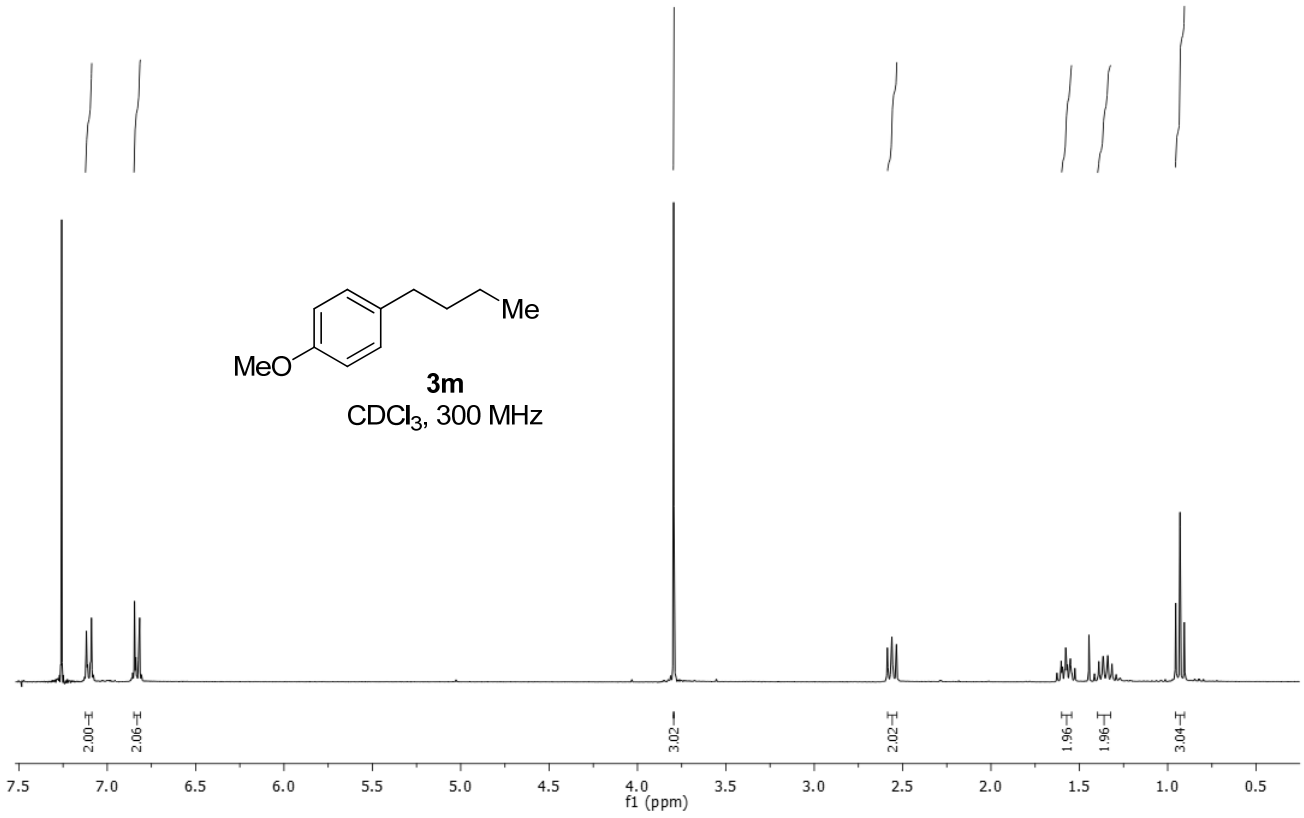

157.70
133.99
129.15
119.72
113.69
55.18
34.57
30.78
28.14
25.23
17.03
CN
MeO
3l
CDCl3, 75 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

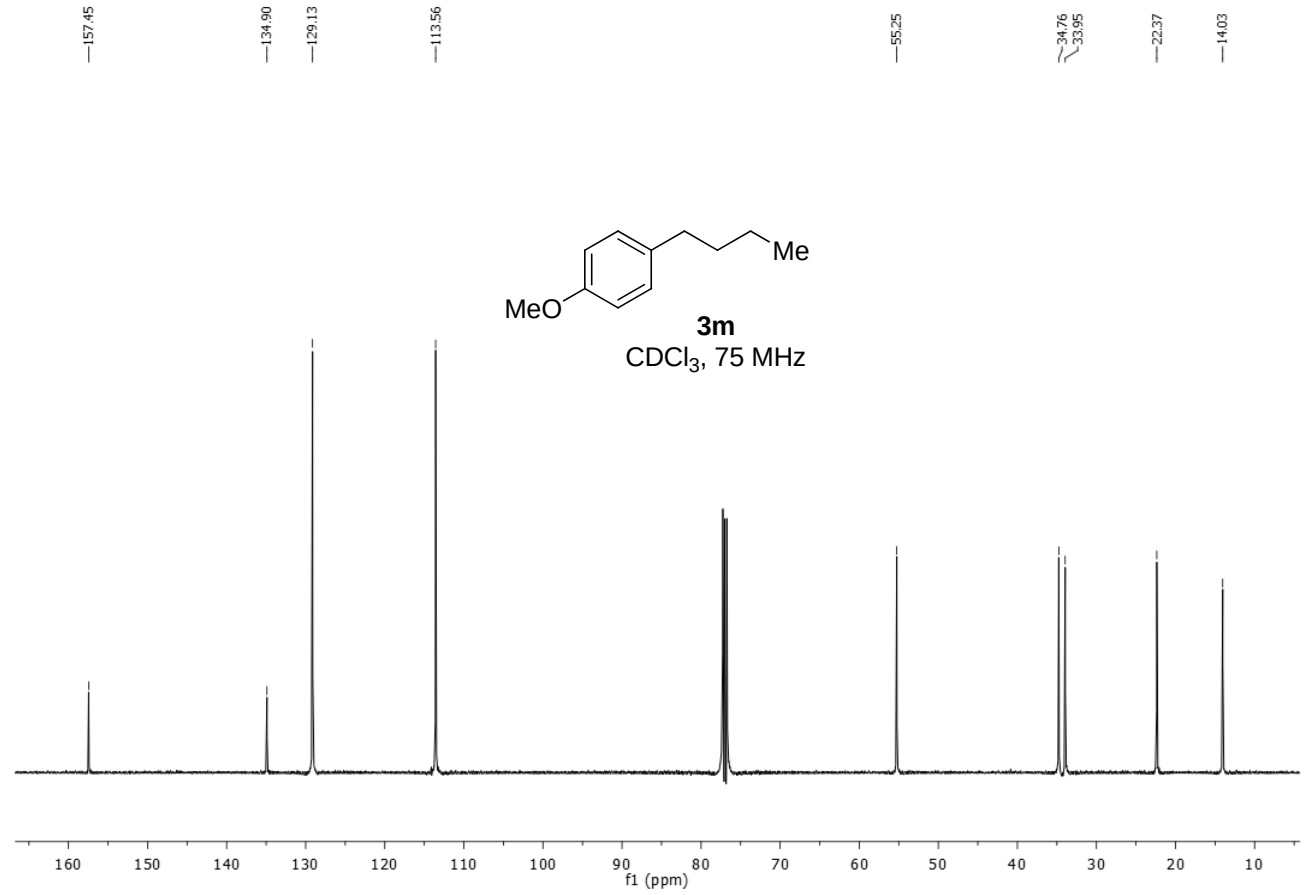

MeO
MeO
P(Cl)t-Bu
Cl
Cl
Pd
Pd
Cl
Cl
t-Bu(Cl)P
OMe
OMe
7a
CDCl3, 300 MHz
2.00
2.11
4.10
2.07
3.92
6.02
5.97
18.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

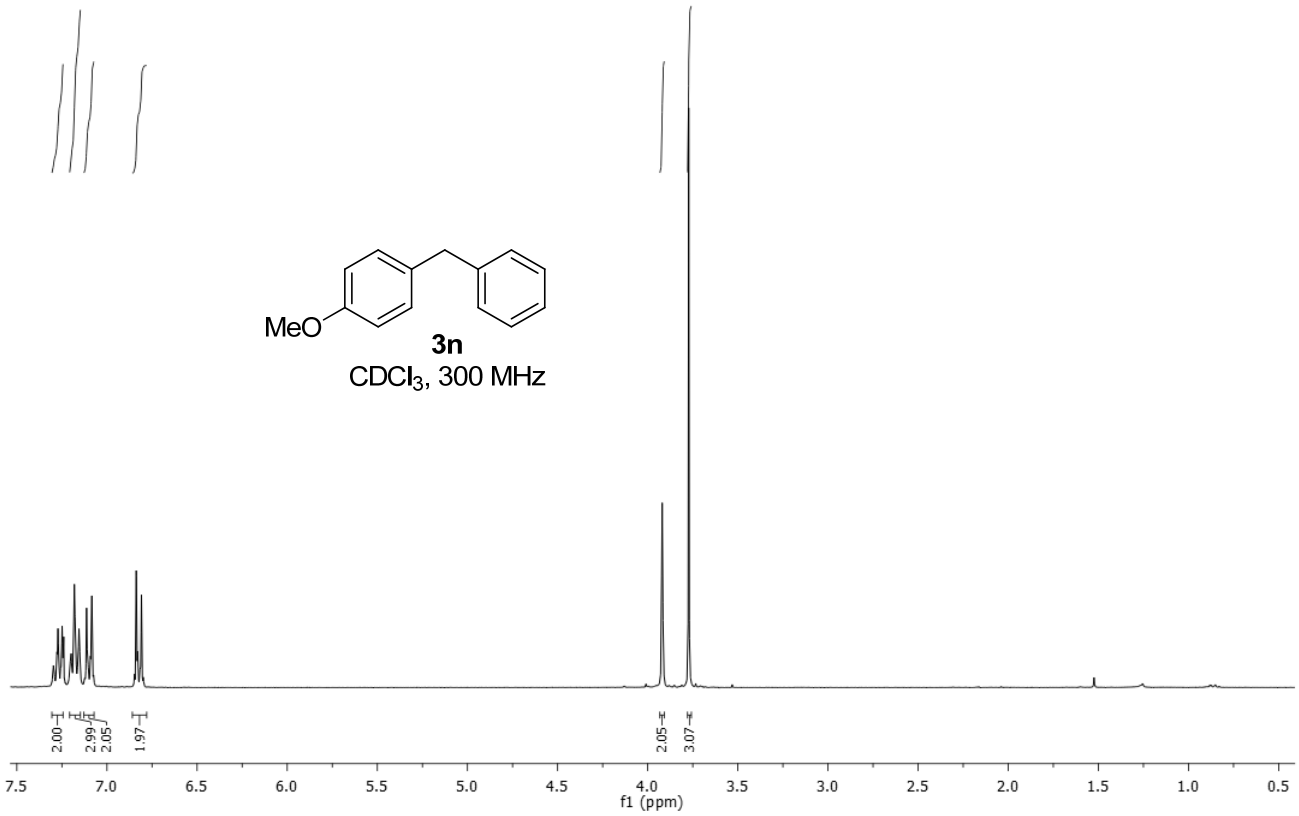

121.16
MeO
MeO
P(Cl)t-Bu
Cl
Cl
Pd
Pd
Cl
Cl
t-Bu(Cl)P
OMe
OMe
7a
CDCl3, 121.5 MHz
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

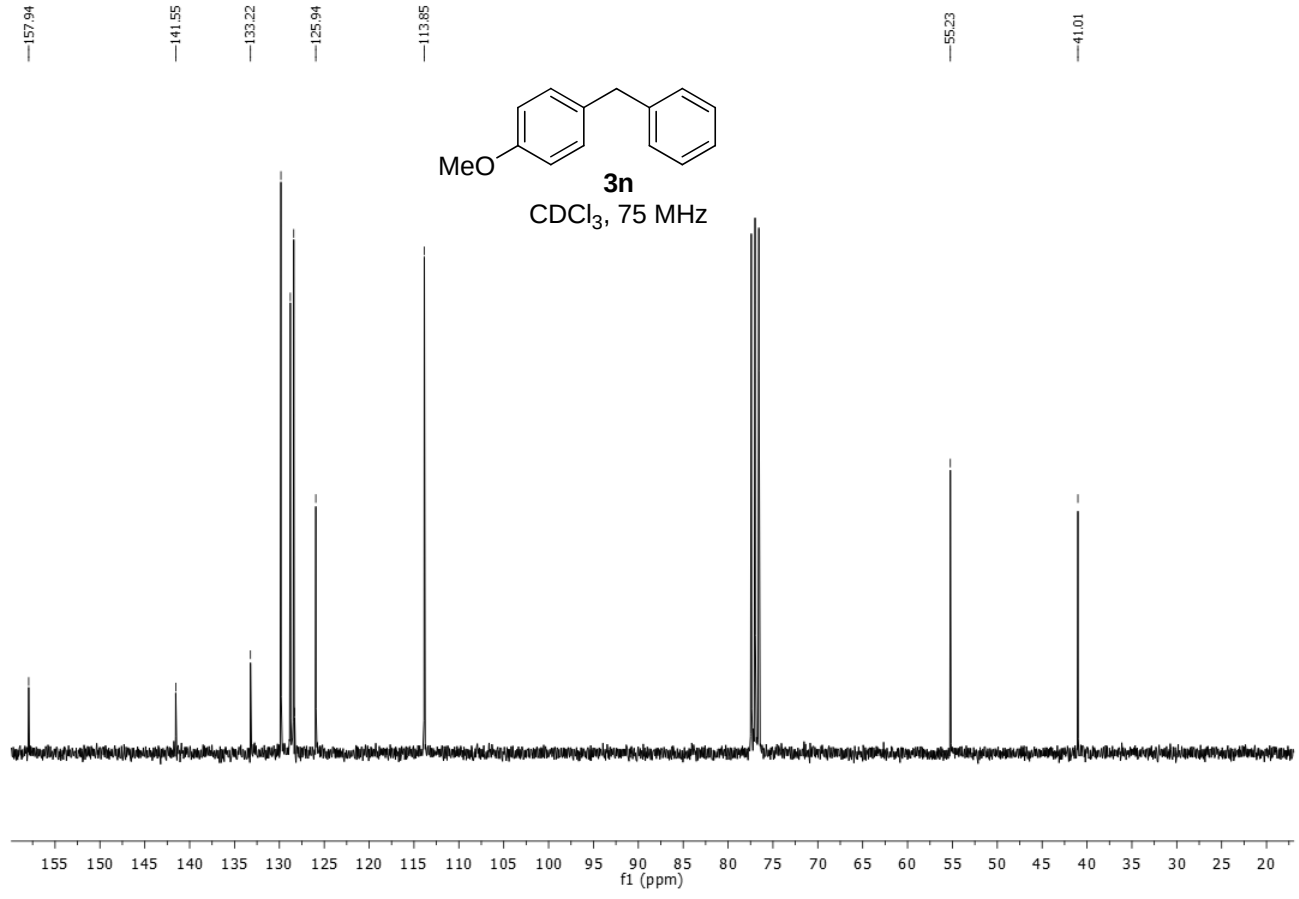

MeO
MeO
MeO
P(Cl)t-Bu
Cl
Pd
Pd
Cl
Cl
Cl
t-Bu(Cl)P
OMe
OMe
OMe
7b
CDCl3, 300 MHz
2.03
3.98
2.00
4.12
5.98
12.01
18.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

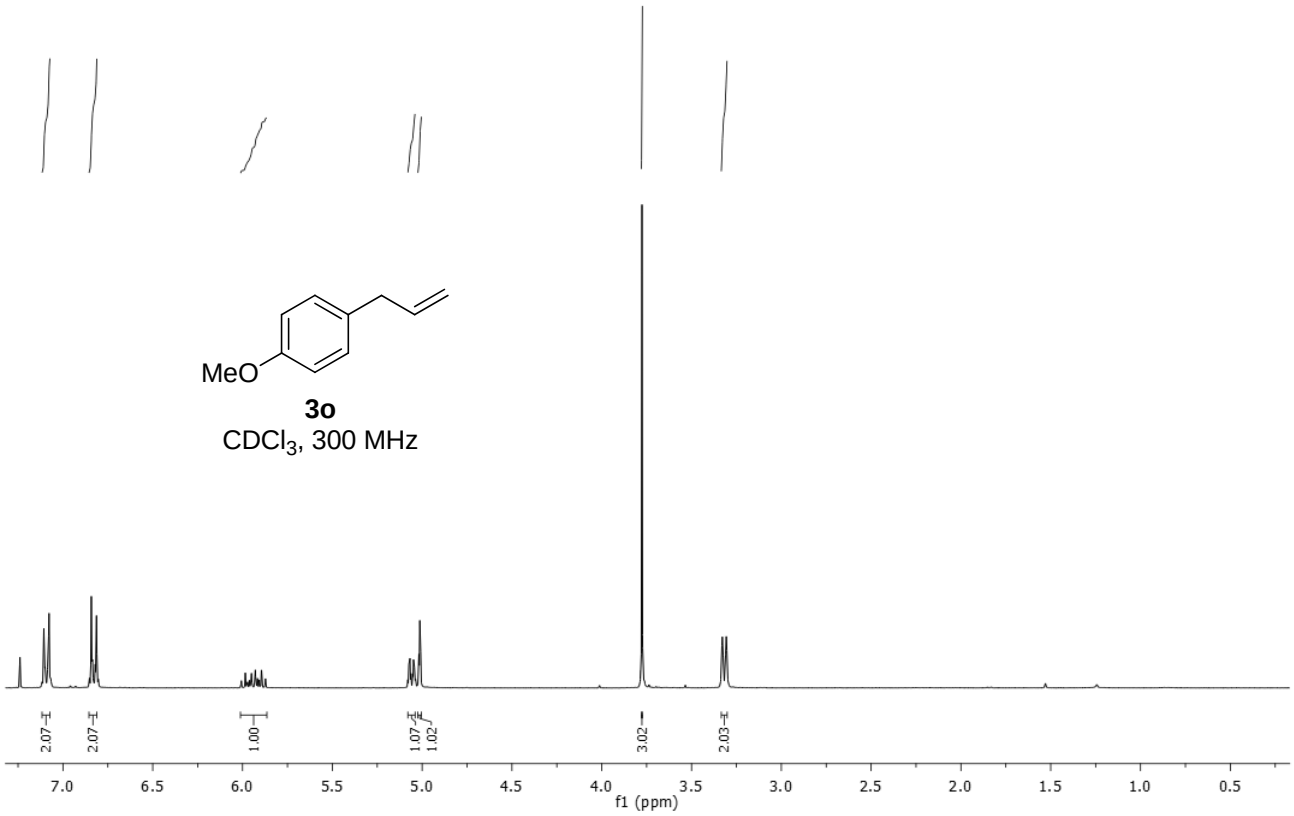

125.90
MeO
MeO
MeO
P(Cl)t-Bu
Cl
Pd
Pd
Cl
Cl
Cl
t-Bu(Cl)P
OMe
OMe
OMe
7b
CDCl3, 121.5 MHz
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
104
102
100
f1 (ppm)


Me
MeO
3m
CDCl3, 300 MHz
2.00
2.06
3.02
2.02
1.96
1.96
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


157.45
134.90
129.13
113.56
55.25
34.76
33.95
22.37
14.03
Me
MeO
3m
CDCl3, 75 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

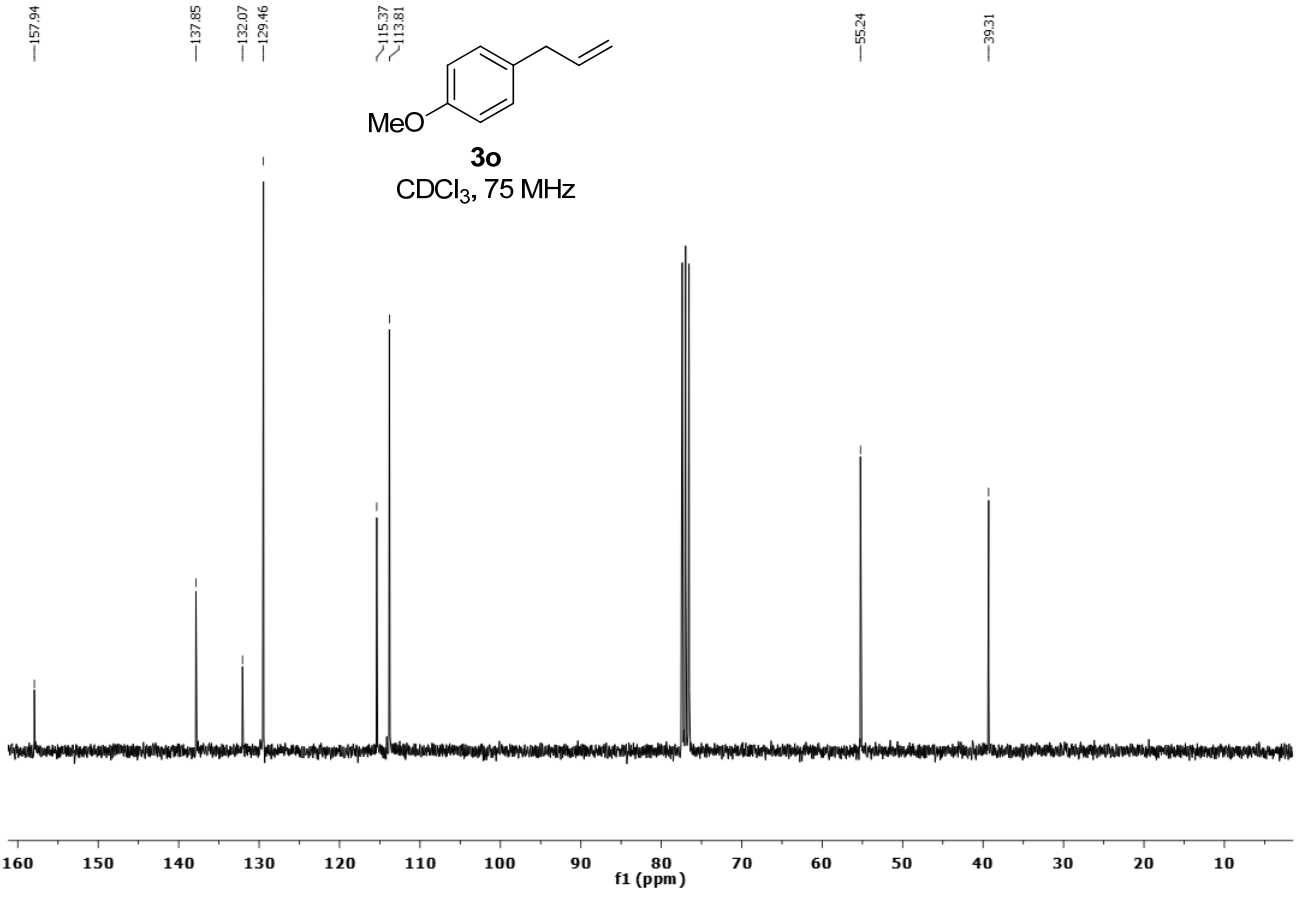

MeO
3n
CDCl3, 300 MHz
2.00
2.99
2.05
1.97
2.05
3.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


157.94
141.55
133.22
125.94
113.85
55.23
41.01
MeO
3n
CDCl3, 75 MHz
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



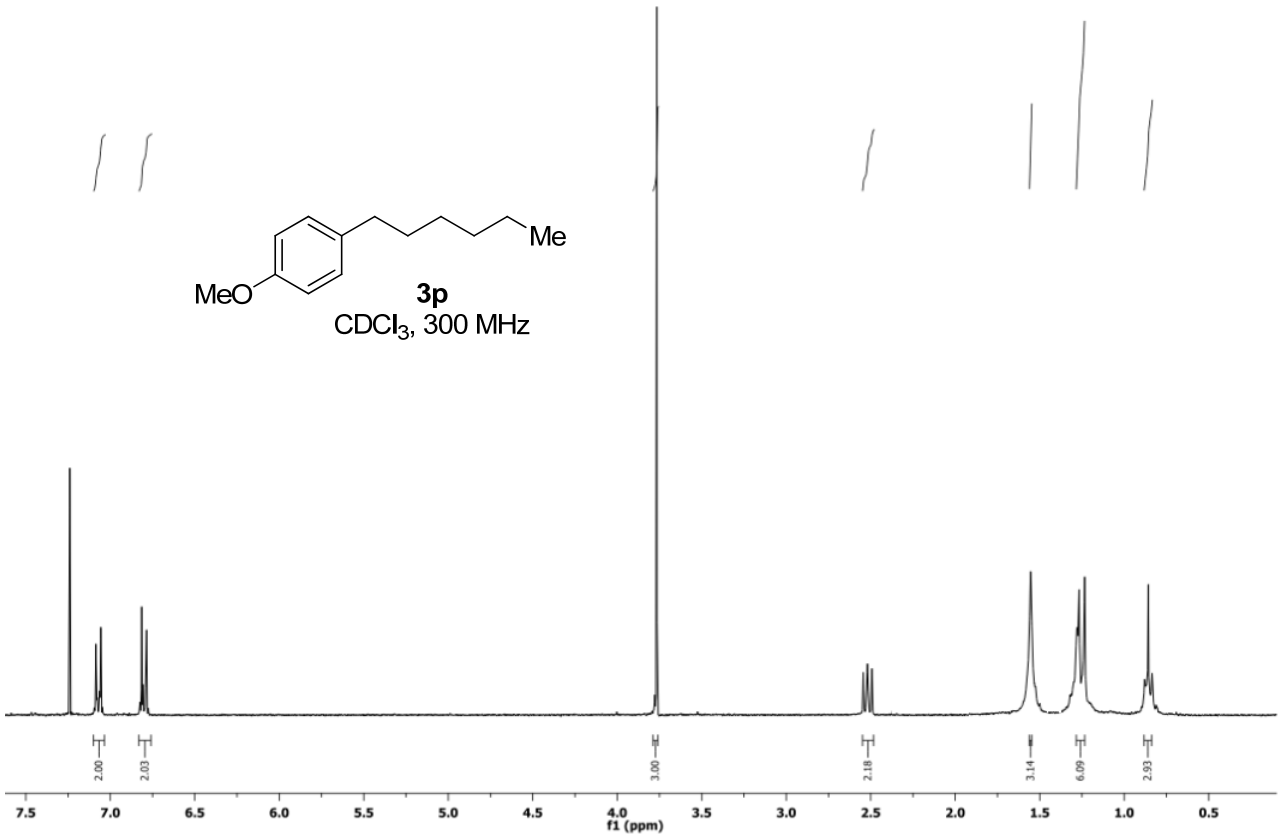
3o

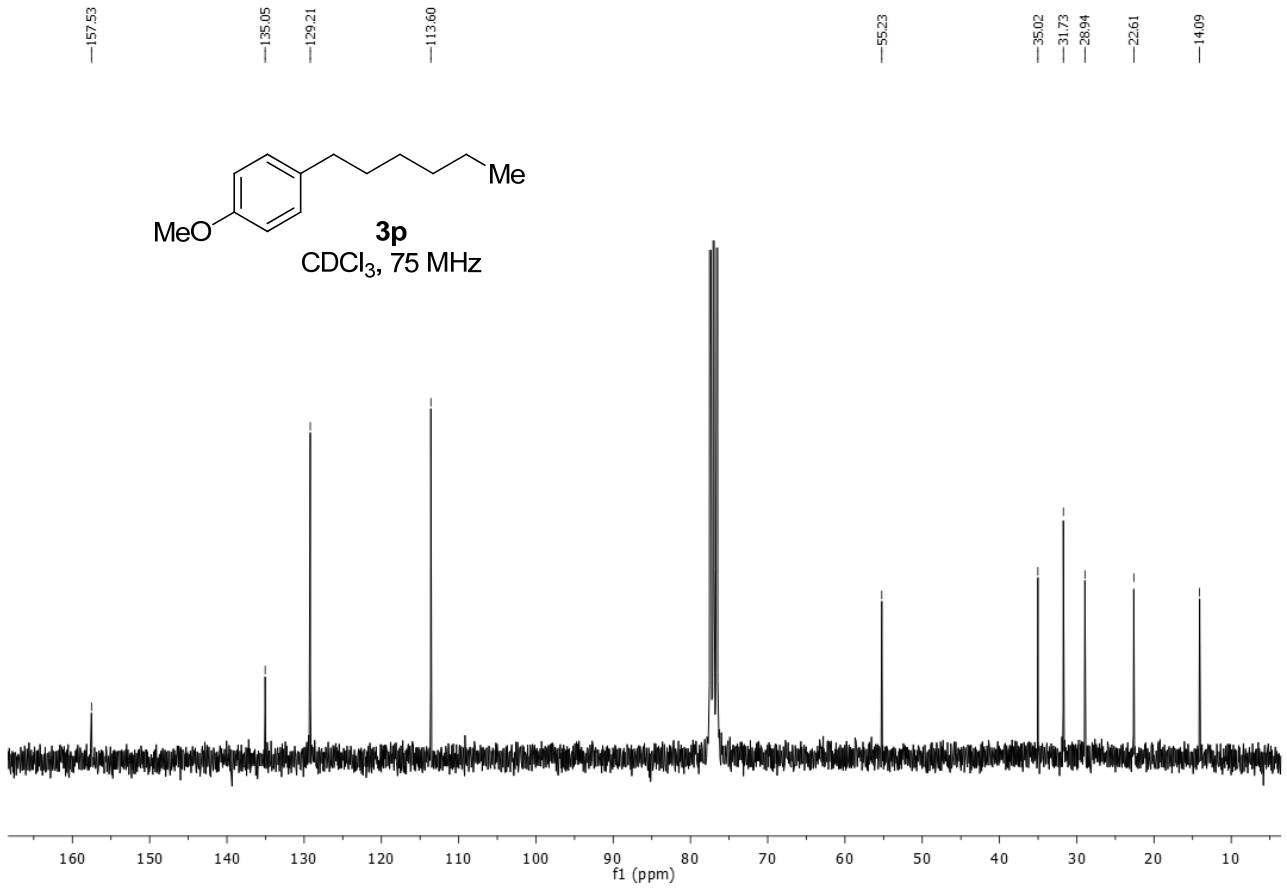
$CDCl_3$, 300 MHz

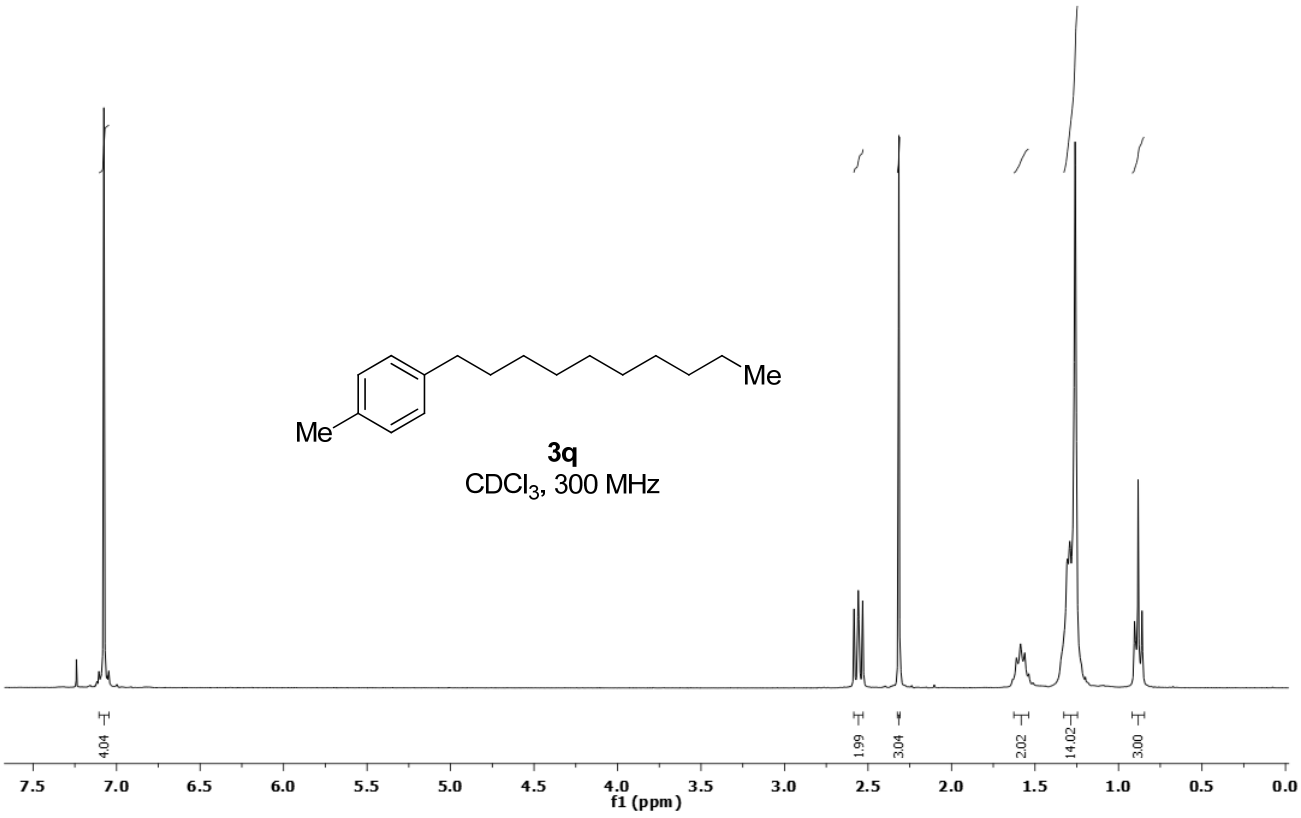


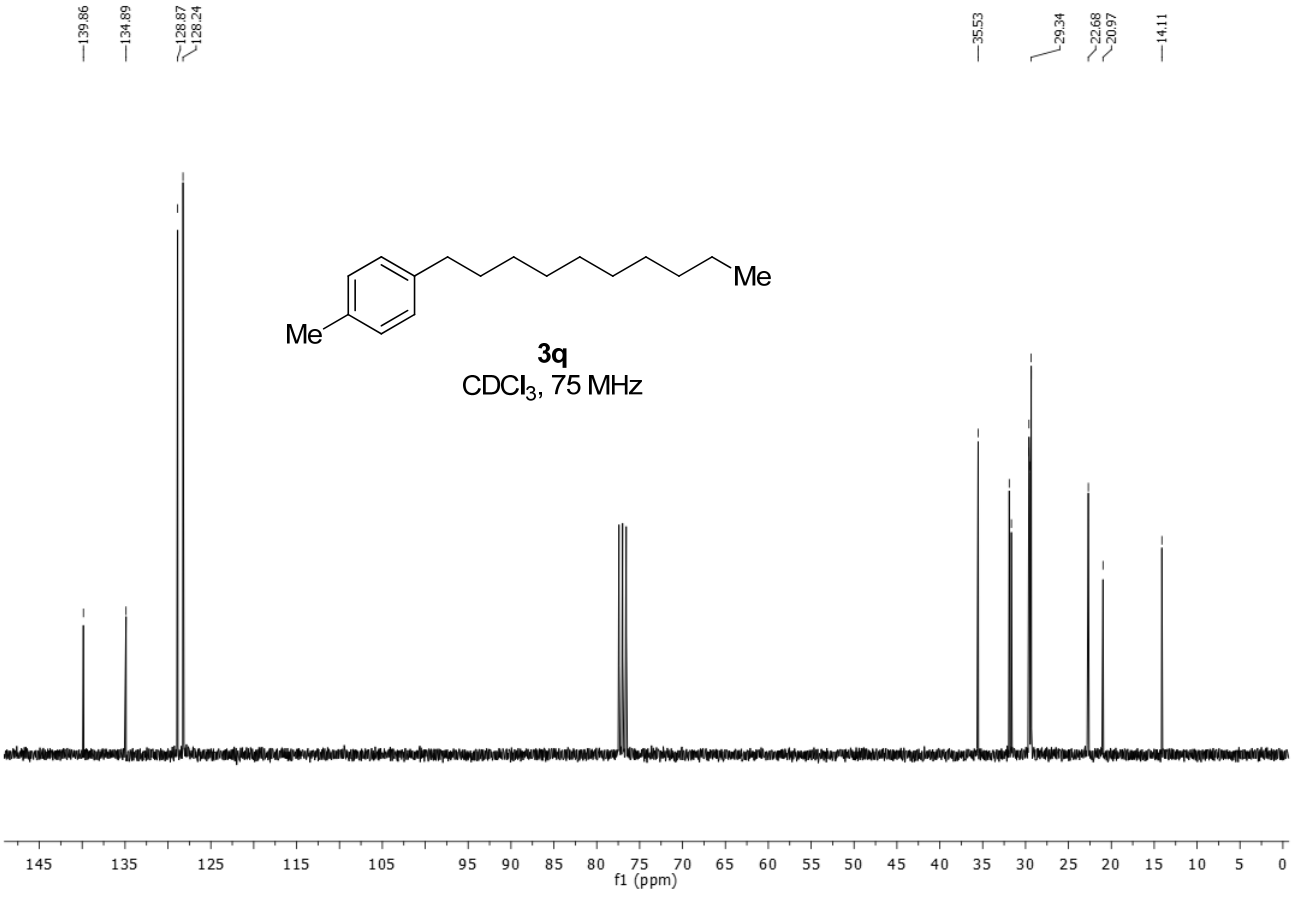
3o

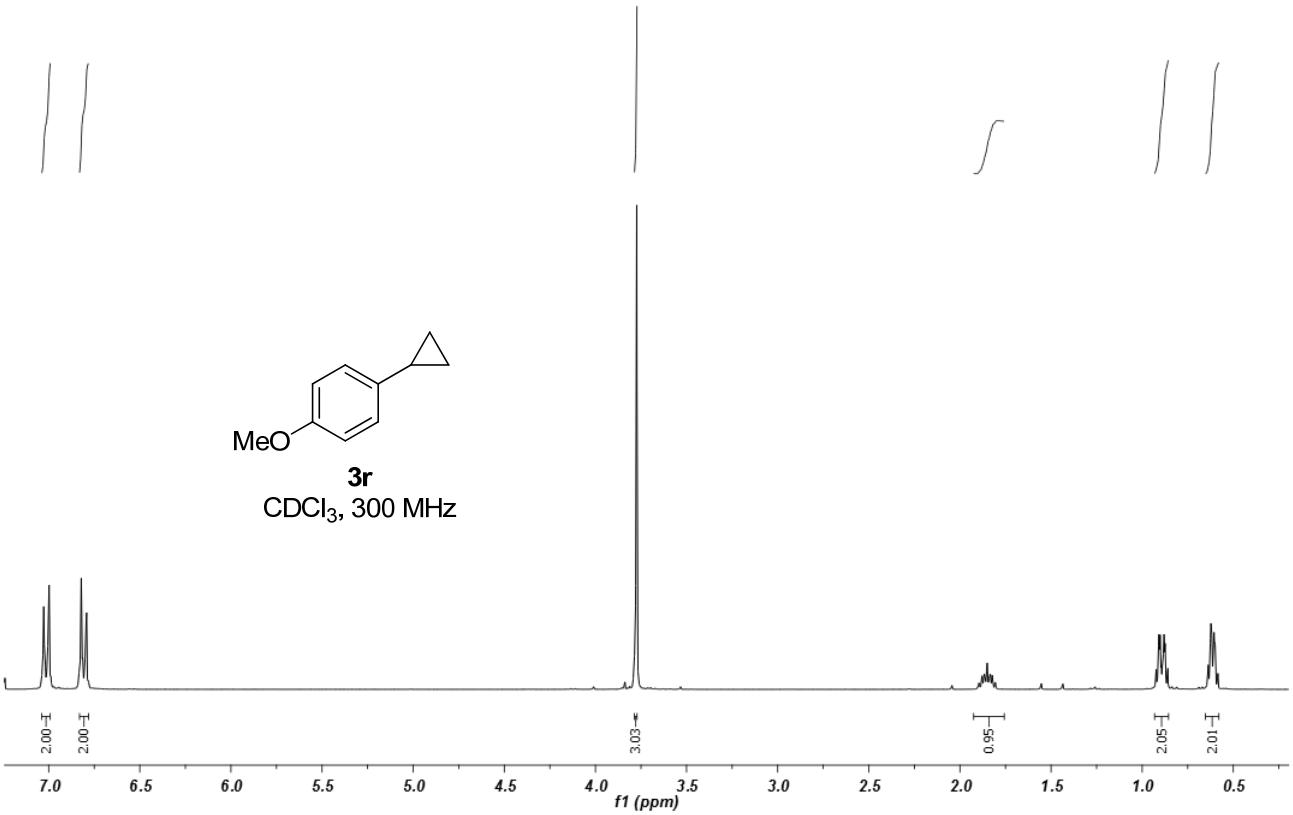
$CDCl_3$, 75 MHz

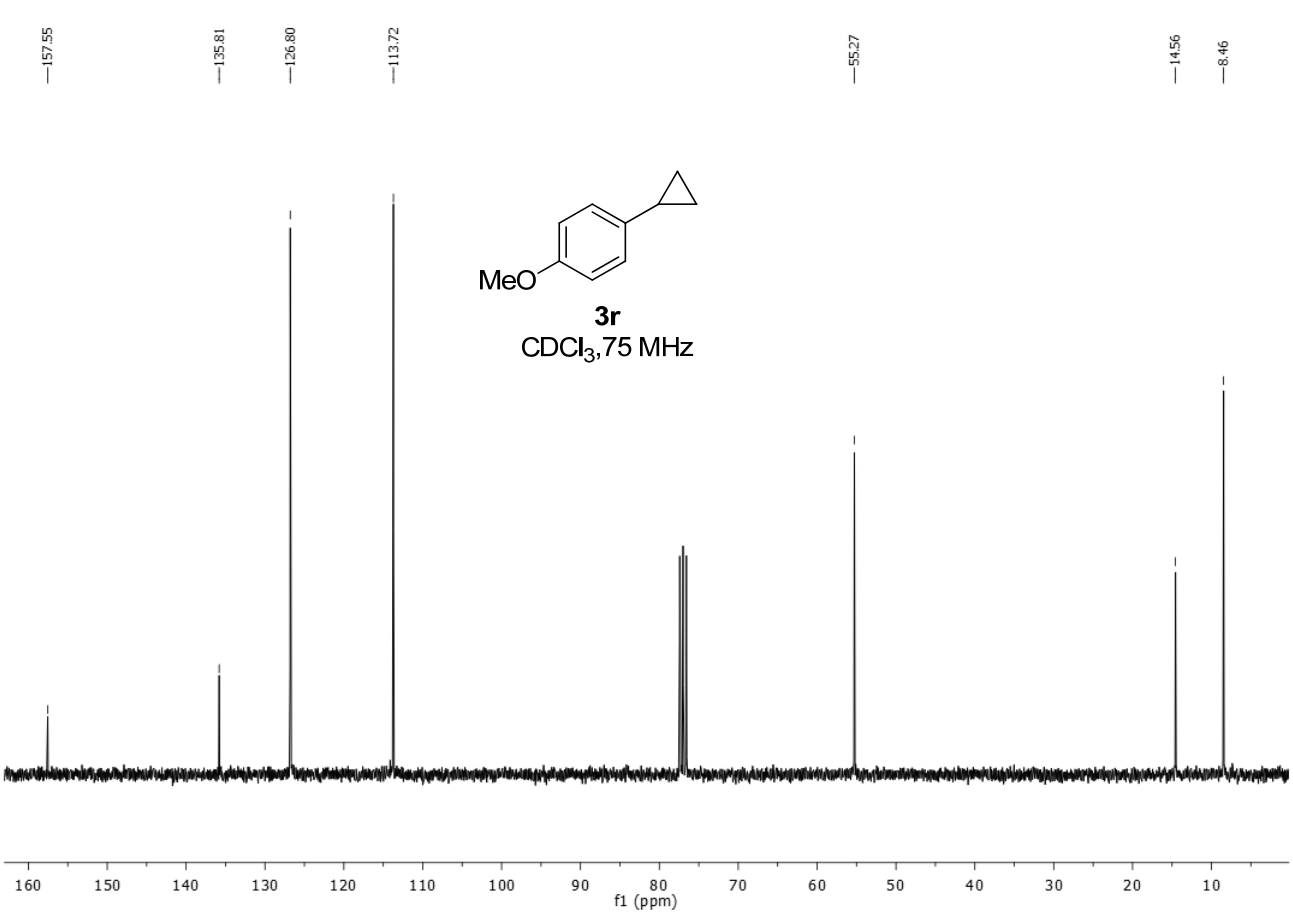

Me
MeO
3p
CDCl3, 300 MHz
2.00
2.03
3.00
2.18
3.14
6.09
2.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

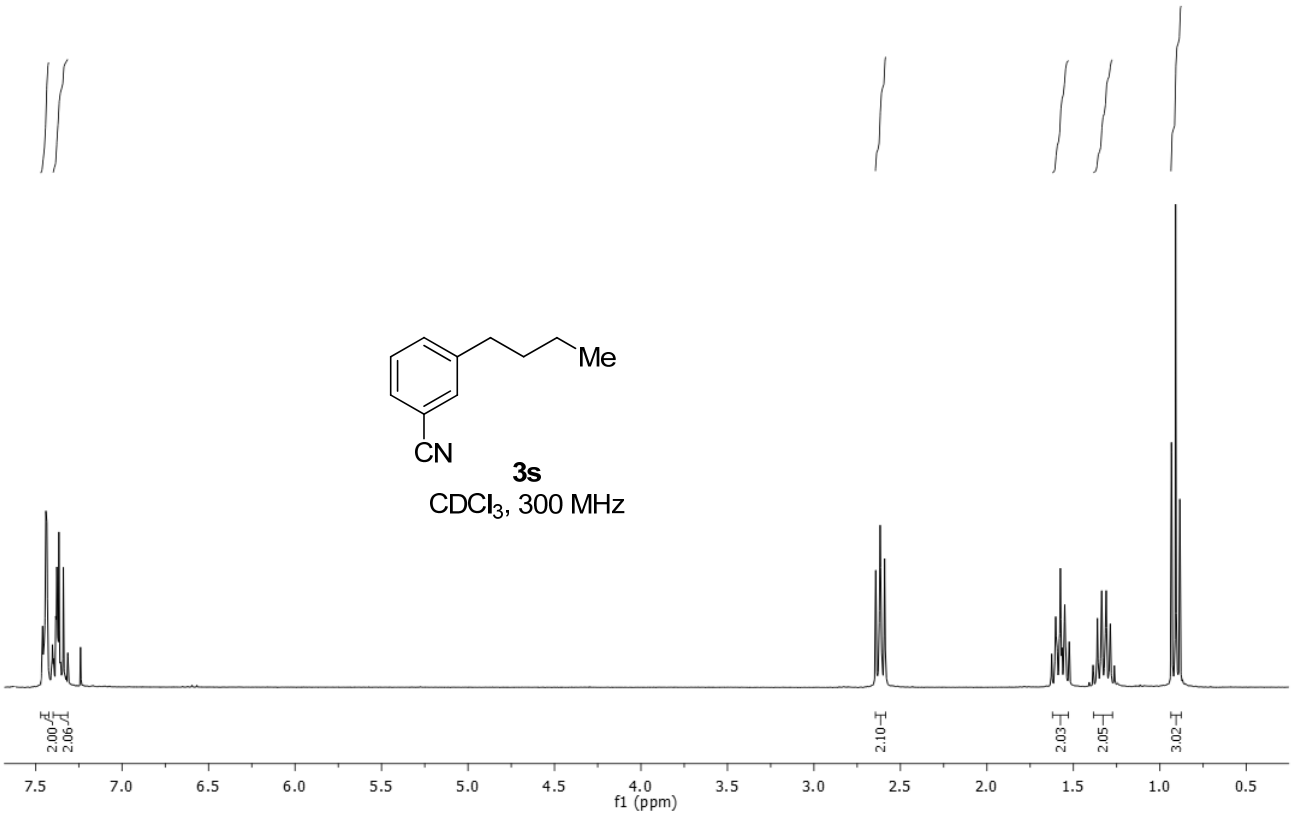

157.53
135.05
129.21
113.60
55.23
35.02
31.73
28.94
22.61
14.09
Me
MeO
3p
CDCl3, 75 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

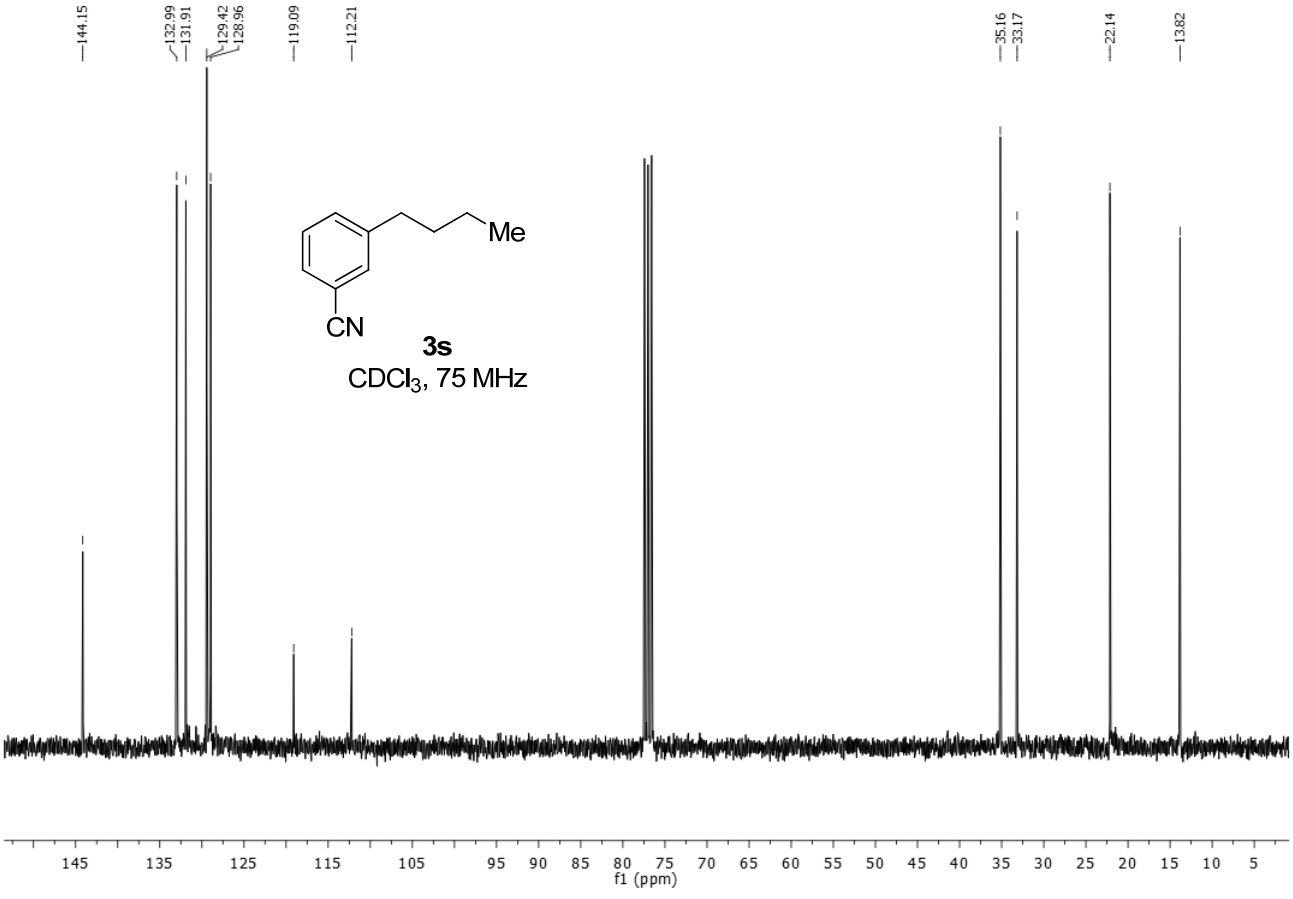

Me
Me
3q
CDCl3, 300 MHz
4.04
1.99
3.04
2.02
14.02
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

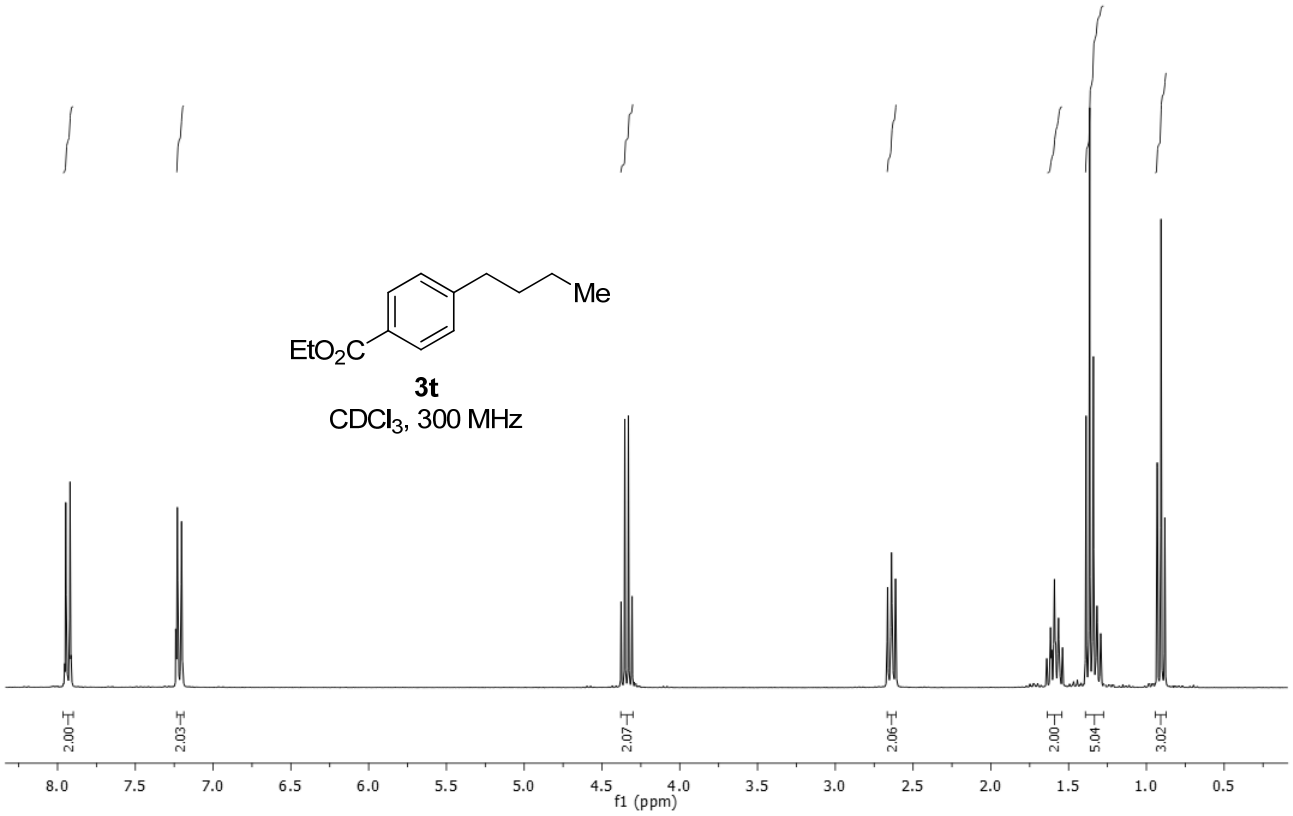

139.86
134.89
128.87
128.24
35.53
29.34
22.68
20.97
14.11
Me
Me
3q
CDCl3, 75 MHz
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

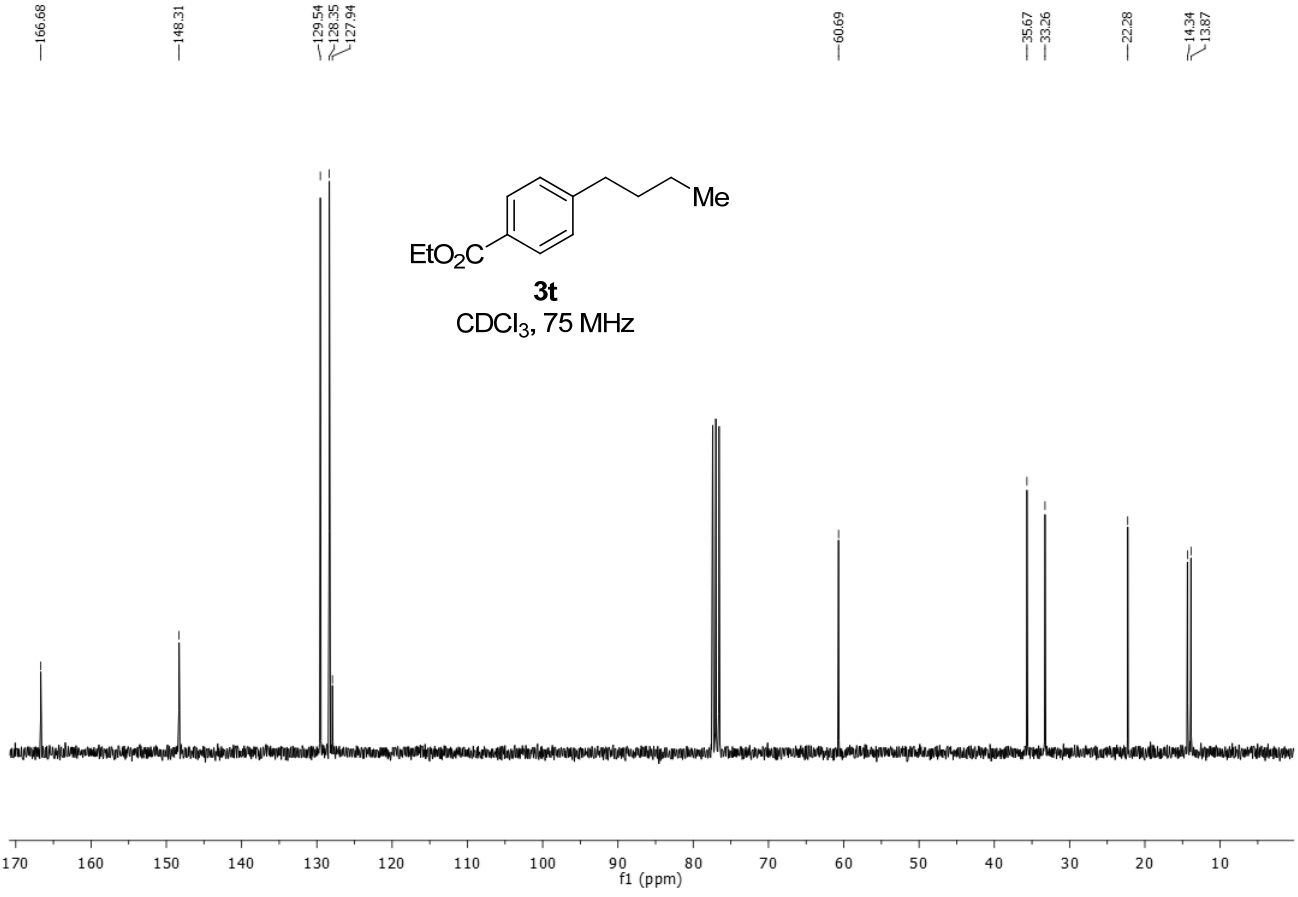

MeO
3r
CDCl3, 300 MHz
2.00
2.00
3.03
0.95
2.05
2.01
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

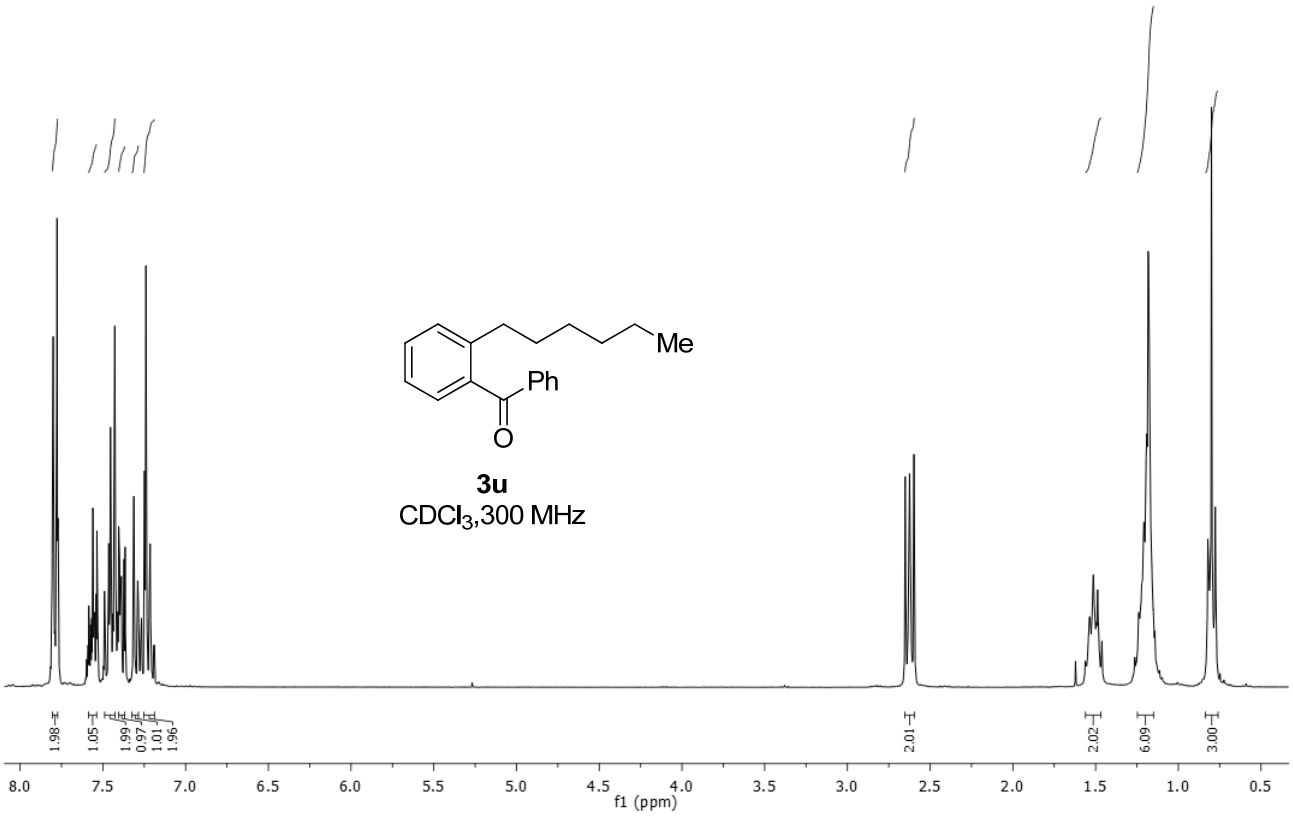

157.55
135.81
126.80
113.72
55.27
14.56
8.46
MeO
3r
CDCl3,75 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
CN
3s
CDCl3, 300 MHz
2.00
2.06
2.10
2.03
2.05
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

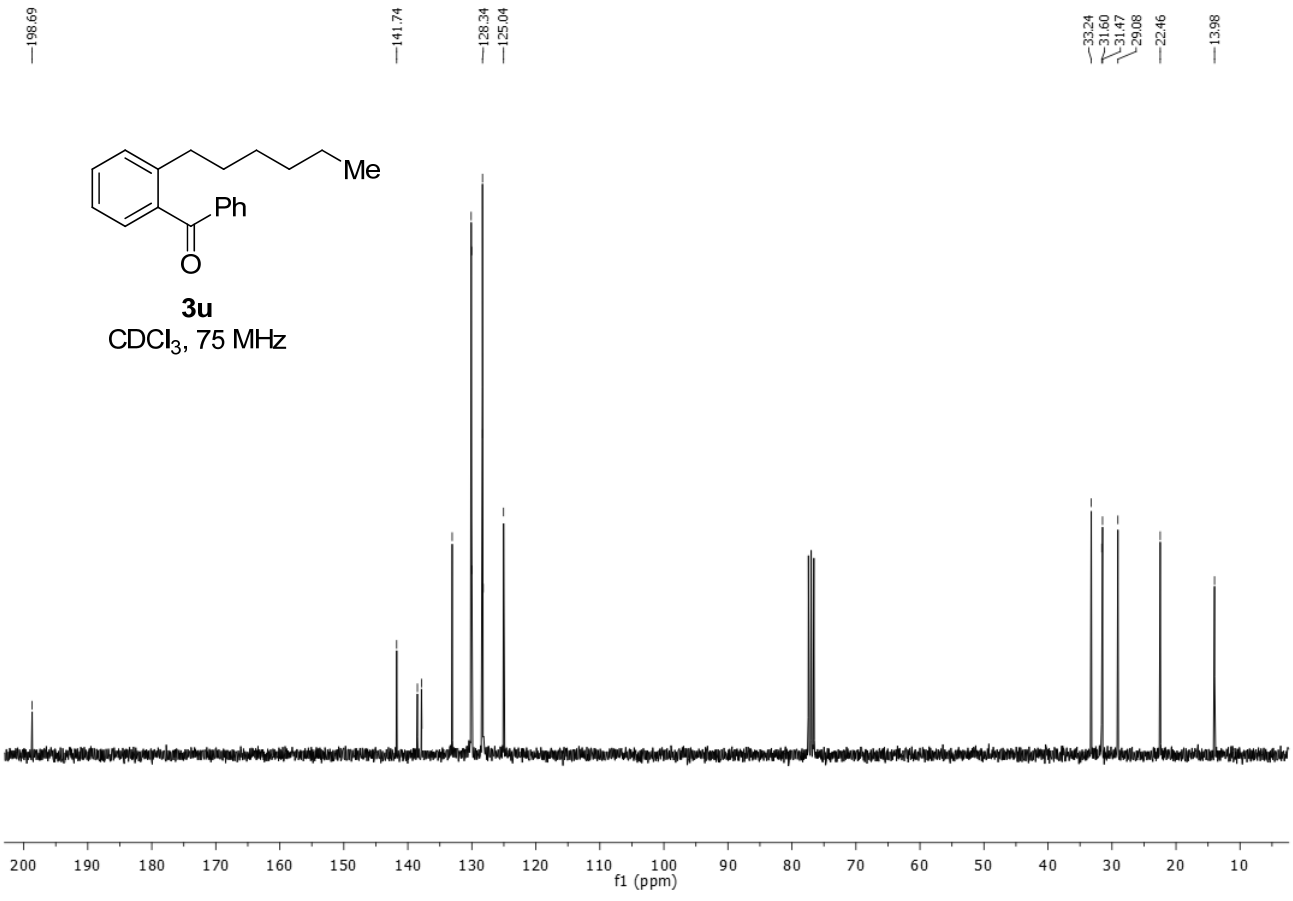

144.15
132.99
131.91
129.42
128.96
119.09
112.21
35.16
33.17
22.14
13.82
Me
CN
3s
CDCl3, 75 MHz
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


Me
EtO2C
3t
CDCl3, 300 MHz
2.00
2.03
2.07
2.06
2.00
5.04
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

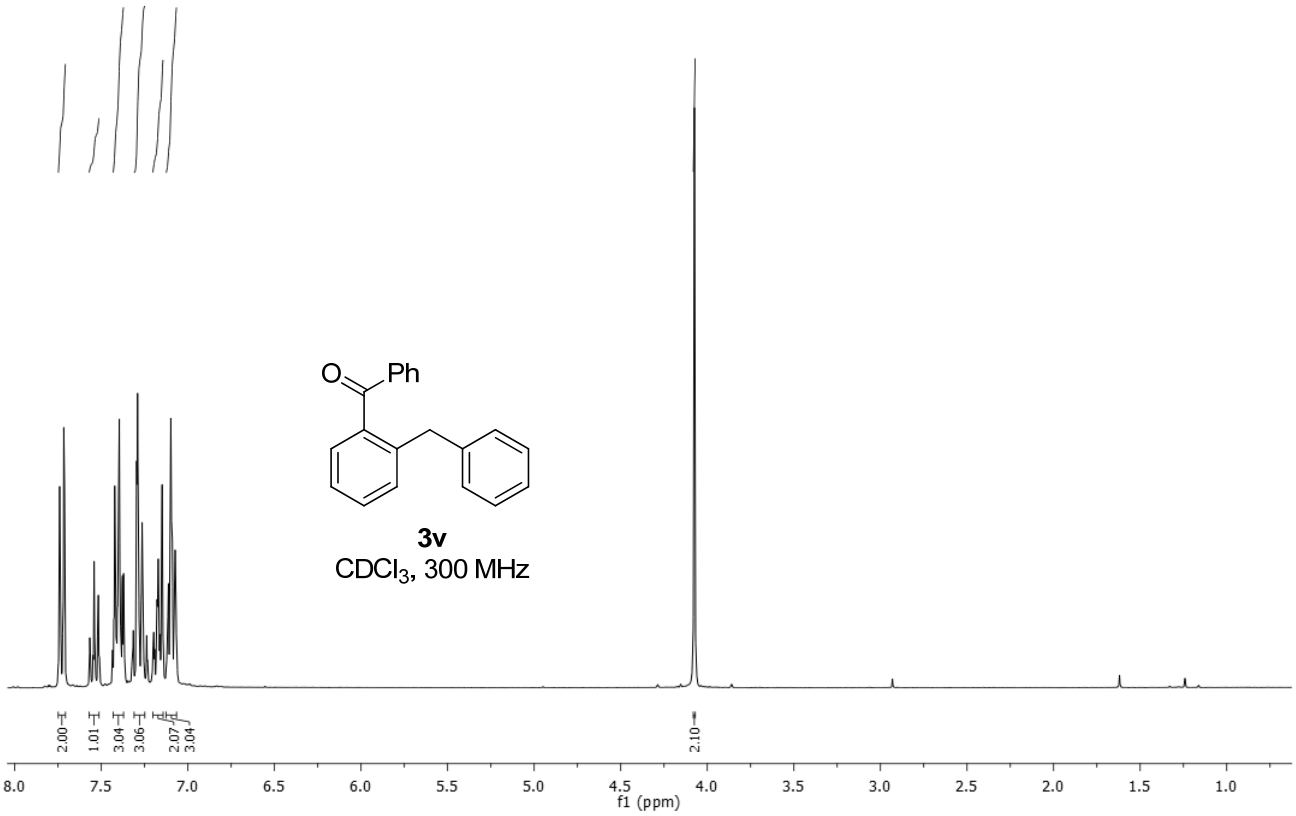

166.68
148.31
129.54
128.35
127.94
60.69
35.67
33.26
22.28
14.34
13.87
Me
EtO2C
3t
CDCl3, 75 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

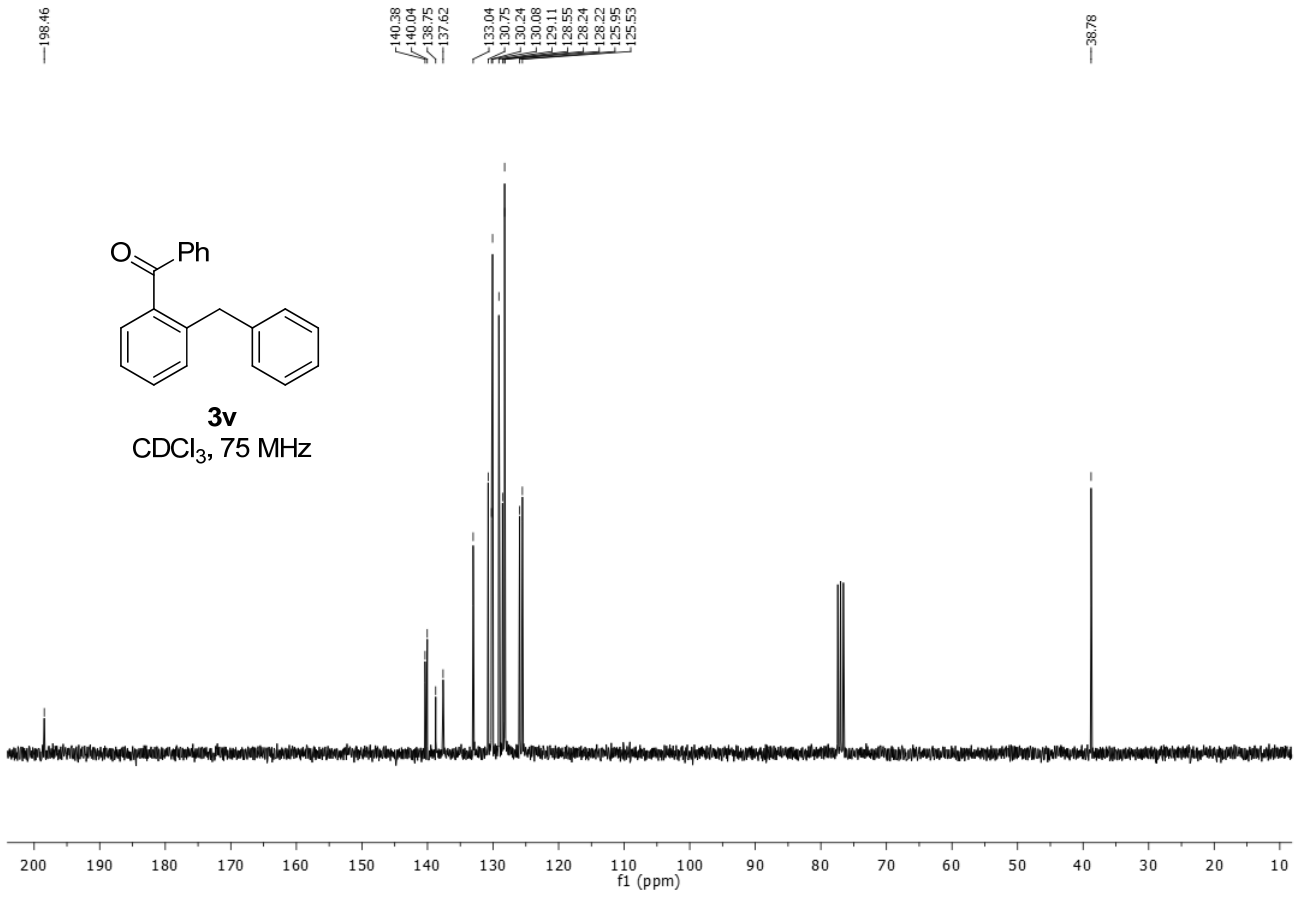


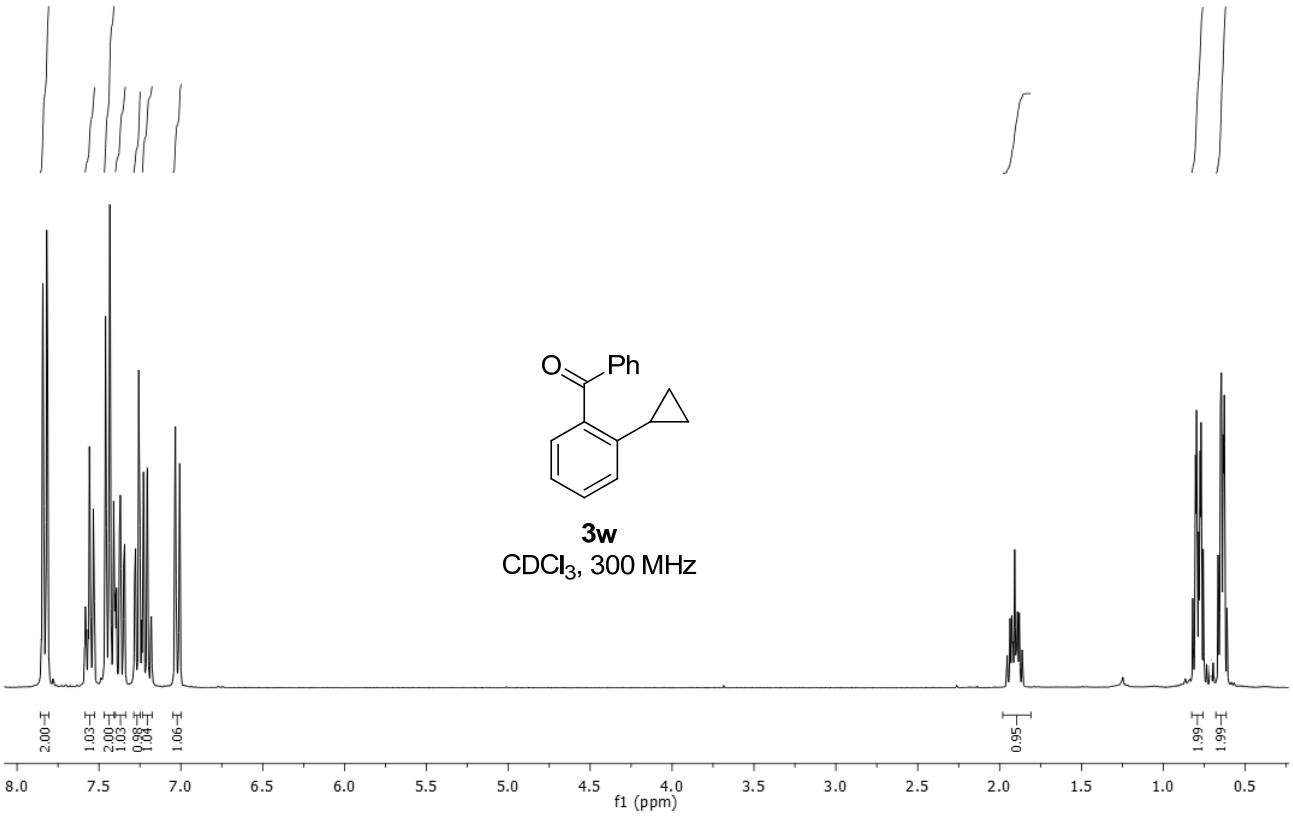
3u
$CDCl_3$,300 MHz



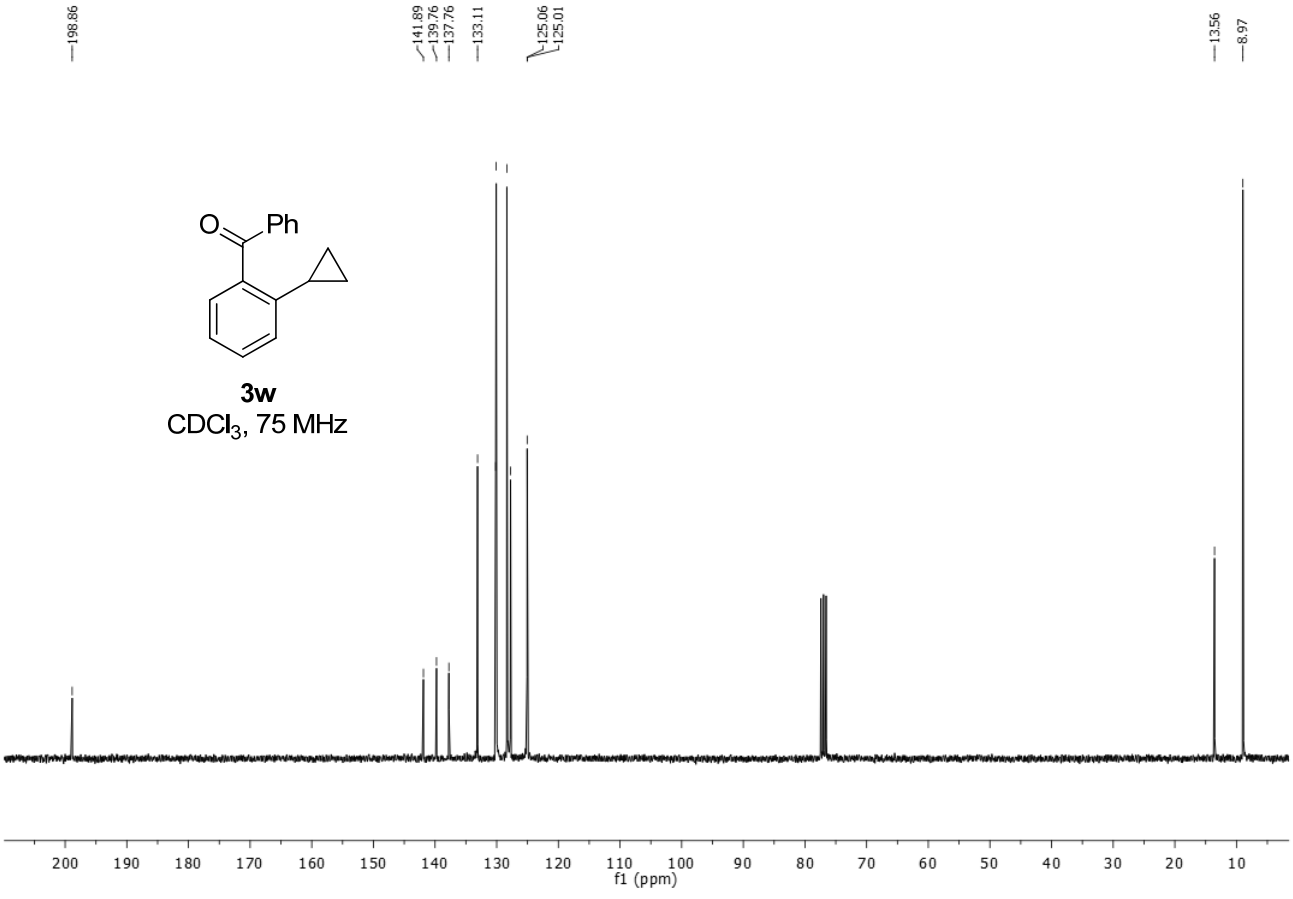
3u
$CDCl_3$, 75 MHz


O
Ph
3v
CDCl3, 300 MHz
2.00
1.01
3.04
3.06
2.07
3.04
2.10
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
f1 (ppm)

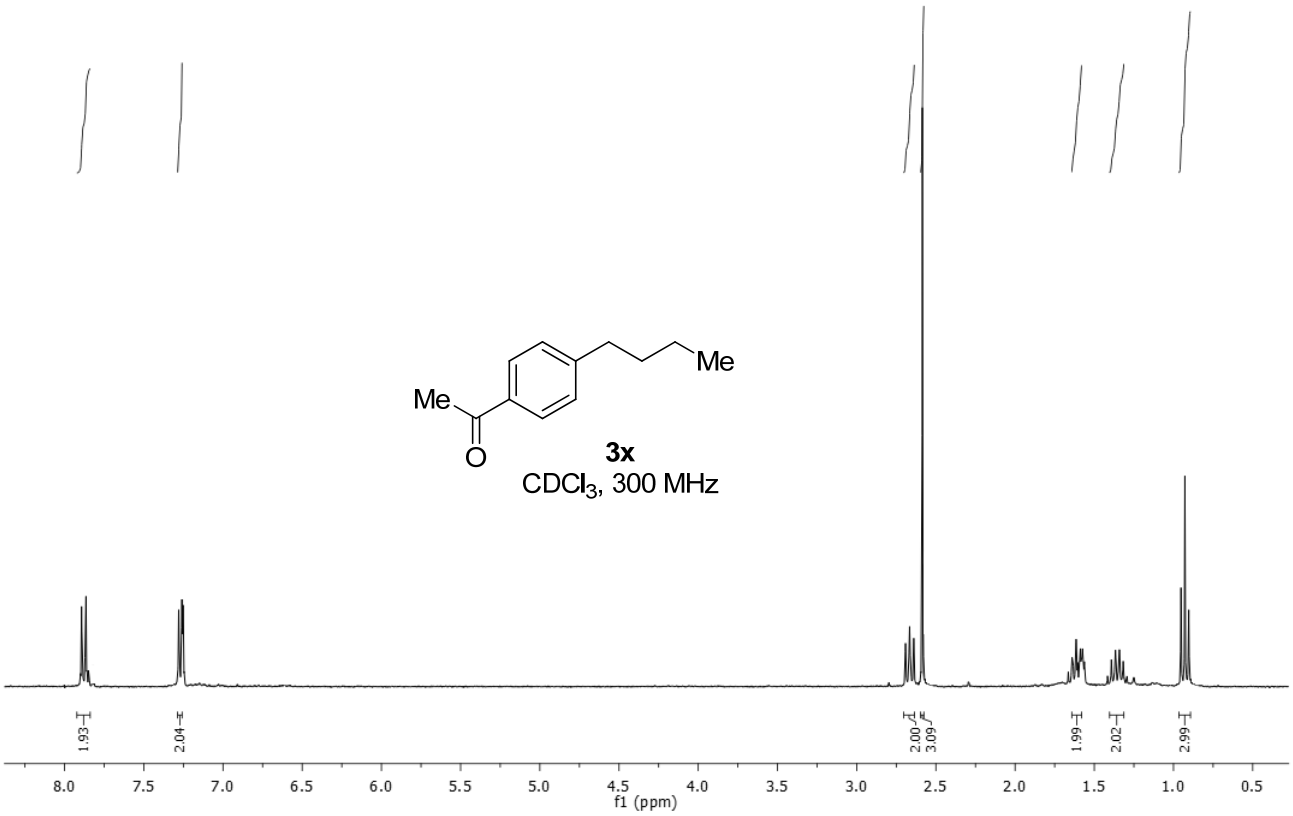

198.46
140.38
140.04
138.75
137.62
133.04
130.75
130.24
130.08
129.11
128.55
128.24
128.22
125.95
125.53
38.78
O
Ph
3v
CDCl3, 75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

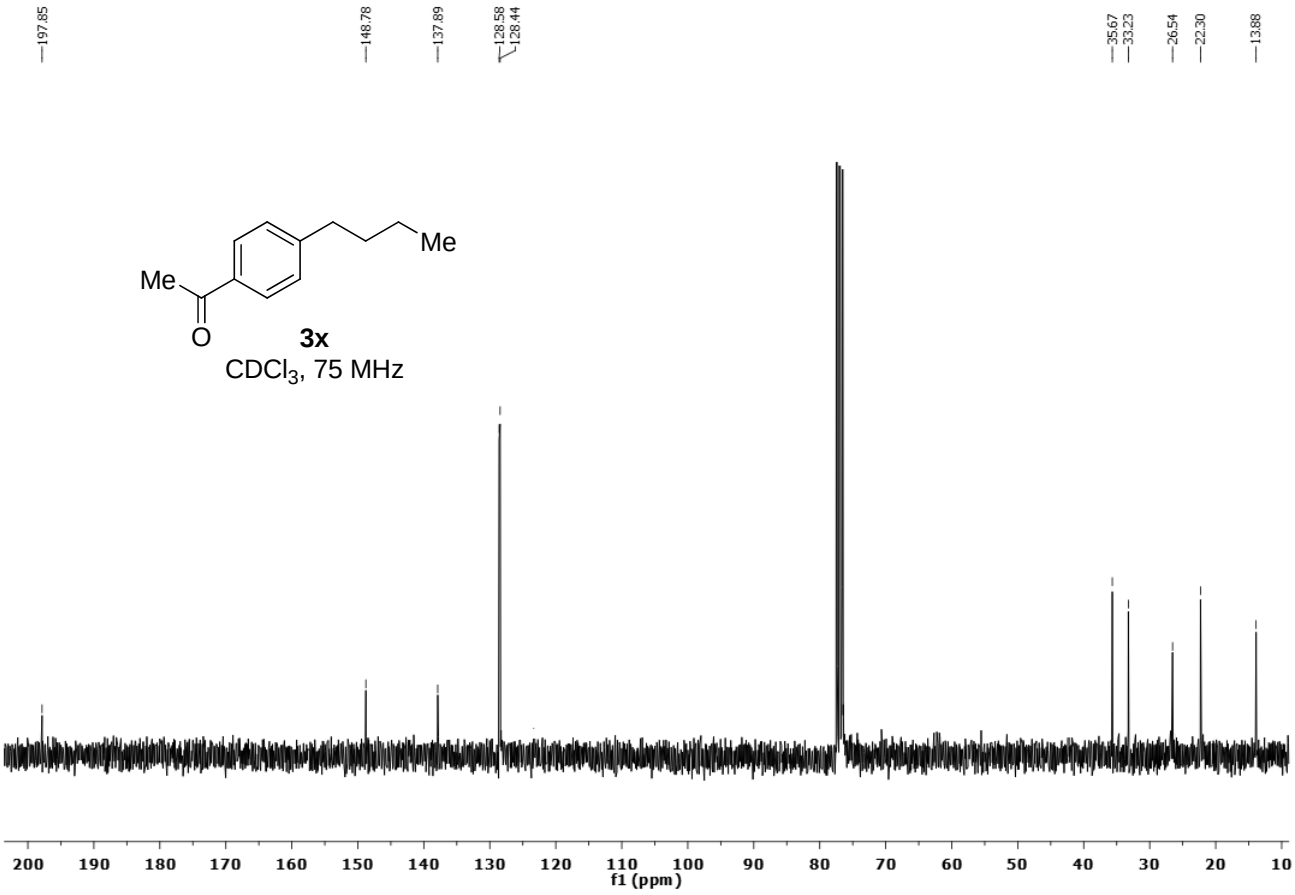


3w
$CDCl_3$, 300 MHz



3w
$CDCl_3$, 75 MHz


Me
Me
O
3x
CDCl3, 300 MHz
1.93
2.04
2.00
3.09
1.99
2.02
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


197.85
148.78
137.89
128.58
128.44
35.67
33.23
26.54
22.30
13.88
Me
Me
O
3x
CDCl3, 75 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)