Supporting information

Design and development of POCN-pincer palladium catalysts for C−H bond arylation of azoles with aryl iodides

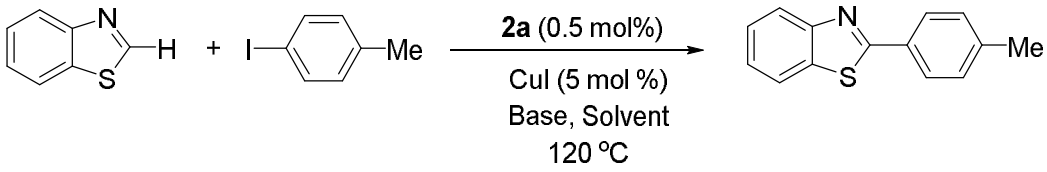
Shrikant M. Khake,[a] Vineeta Soni,[a] Rajesh G. Gonnade[b] and Benudhar Punji*[a]

[a]*Organometallic Synthesis and Catalysis Group, Chemical Engineering Division, CSIR–National Chemical Laboratory (CSIR–NCL), Dr. Homi Bhabha Road, Pune – 411 008, Maharashtra, INDIA. Phone: + 91-20-2590 2733, Fax: + 91-20-2590 2621, E-mail: b.punji@ncl.res.in*

[b]*Centre for Material Characterization, CSIR–National Chemical Laboratory (CSIR–NCL), Dr. Homi Bhabha Road, Pune – 411 008, Maharashtra, INDIA*

Contents

1. Table S1. Optimization of catalytic reaction conditions.

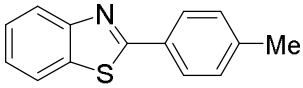


Entry	Base	Solvent	Yield (%)[a]
1	Na_2CO_3	DMF	< 5[b]
2	K_2CO_3	DMF	34
3	K_3PO_4	DMF	88
4	Cs_2CO_3	DMF	97
5	CsOAc	DMF	11
6	Cs_2CO_3	DMSO	47
7	Cs_2CO_3	DMAc	11
8	Cs_2CO_3	dioxane	14
9	Cs_2CO_3	toluene	< 5[b]
10[c]	Cs_2CO_3	DMF	65
11[d]	Cs_2CO_3	DMF	21
12[e]	Cs_2CO_3	DMF	< 2 [b]
13[f]	Cs_2CO_3	DMF	47

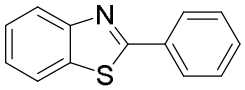
Conditions: Benzothiazole (0.5 mmol), 4-iodotoluene (0.75 mmol), base (0.75 mmol), solvent (1.0 mL). [a]Isolated yields, [b]NMR yields, [c]0.1 mol % of **2a** after 48 h, [d]without CuI, [e]without catalyst **2a**, [f]employing **2b** catalyst.

2. Characterization data for 2-arylated azoles

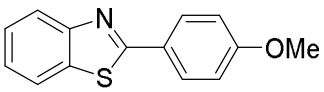
2.1. Characterization data for compounds 8



2-(p-Tolyl)benzo[*d*]thiazole (8aa):[S1] M. p. = 85–87 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.99 (d, *J* = 8.2 Hz, 2H, Ar–H), 7.89 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.49 (vt, *J* = 8.1 Hz, 1H, Ar–H), 7.37 (vt, *J* = 7.9 Hz, 1H, Ar–H), 7.30 (d, *J* = 8.2 Hz, 2H, Ar–H), 2.43 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.5 (C_q), 154.2 (C_q), 141.7 (C_q), 135.0 (C_q), 131.0 (C_q), 129.9 (2C, CH), 127.7 (2C, CH), 126.5 (CH), 125.2 (CH), 123.2 (CH), 121.8 (CH), 21.7 (CH_3). IR (neat): ν_{max}/cm^{-1} 2961, 2918, 2851, 1478, 1428, 1257, 1224, 1084, 1013, 958, 793. HR-MS (ESI) *m/z* calcd for $C_{14}H_{11}NS+H^+$ [M+H$^+$] 226.0690, found 226.0685.

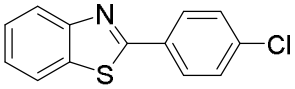


2-Phenylbenzo[*d*]thiazole (8ab):[S1] The representative procedure was followed, using **6a** (0.068 g, 0.5 mmol) and iodobenzene **7b** (0.153 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 25/1) yielded **8ab** (0.099 g, 94%) as a white solid. M. p. = 117–118 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.13-8.08 (m, 3H, Ar–H), 7.91 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.53-7.48 (m, 4H, Ar–H), 7.39 (dvt, *J* = 8.0, 1.0 Hz, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.3 (C_q), 154.2 (C_q), 135.2 (C_q), 133.7 (C_q), 131.2 (CH), 129.2 (2C, CH), 127.7 (2C, CH), 126.5 (CH), 125.4 (CH), 123.4 (CH), 121.8 (CH). IR (neat): ν_{max}/cm^{-1} 2922, 2850, 1472, 1426, 1218, 956, 756, 680. HR-MS (ESI) *m/z* calcd for $C_{13}H_{10}NS+H^+$ [M+H$^+$] 212.0534, found 212.0527.

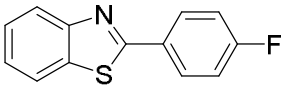


2-(4-Methoxyphenyl)benzo[*d*]thiazole (8ac):[S1] The representative procedure was followed, using **6a** (0.067 g, 0.5 mmol) and 4-iodoanisole **7c** (0.176 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 → 10/1) yielded **8ac** (0.103 g,

86%) as a white solid. M. p. = 125–126 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.04-8.01 (m, 3H, Ar–H), 7.87 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.47 (dvt, *J* = 7.1, 1.4 Hz, 1H, Ar–H), 7.35 (dvt, *J* = 7.8, 1.4 Hz, 1H, Ar–H), 6.99 (d, *J* = 8.7 Hz, 2H, Ar–H), 3.87 (s, 3H, OCH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.0 (C_q), 162.1 (C_q), 154.4 (C_q), 135.0 (C_q), 129.3 (2C, CH), 126.6 (C_q), 126.4 (CH), 124.9 (CH), 122.9 (CH), 121.7 (CH), 114.5 (2C, CH), 55.6 (CH_3). IR (neat): ν_{max}/cm^{-1} 2996, 2936, 2836, 1591, 1521, 1466, 1412, 1286. HR-MS (ESI) *m/z* calcd for $C_{14}H_{11}NOS+H^+$ [M+H$^+$] 242.0640, found 242.0636.

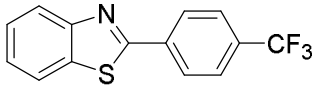


2-(4-Chlorophenyl)benzo[*d*]thiazole (8ad):[S2] The representative procedure was followed, using **6a** (0.065 g, 0.481 mmol) and 1-chloro-4-iodobenzene **7d** (0.18 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 20/1) yielded **8ad** (0.109 g, 92%) as a white solid. M. p. = 118–119 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.7 Hz, 1H, Ar–H), 8.02 (d, *J* = 8.7 Hz, 2H, Ar–H), 7.90 (d, *J* = 7.3 Hz, 1H, Ar–H), 7.50 (dvt, *J* = 7.2, 1.4 Hz, 1H, Ar–H), 7.46 (d, *J* = 8.2 Hz, 2H, Ar–H), 7.40 (dvt, *J* = 7.6, 1.4 Hz, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.2 (C_q), 137.2 (C_q), 135.2 (C_q), 132.3 (C_q), 129.4 (2C, CH), 128.9 (2C, CH), 126.7 (CH), 125.6 (CH), 123.5 (CH), 121.8 (CH). IR (neat): ν_{max}/cm^{-1} 2960, 2922, 2849, 1469, 1429, 1256, 1081, 1012, 797, 755. HR-MS (ESI) *m/z* calcd for $C_{13}H_8ClNS+H^+$ [M+H$^+$] 246.0144, found 246.0141.

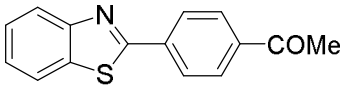


2-(4-Fluorophenyl)benzo[*d*]thiazole (8ae):[S2] The representative procedure was followed, using **6a** (0.072 g, 0.533 mmol) and 1-fluoro-4-iodobenzene **7e** (0.167 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 25/1) yielded **8ae** (0.090 g, 74%) as a white solid. M. p. = 102–103 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.10-8.05 (m, 3H, Ar–H), 7.90 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.50 (vt, *J* = 7.3 Hz, 1H, Ar–H), 7.39 (vt, *J* = 7.7 Hz, 1H, Ar–H), 7.19 (vt, *J* = 8.5 Hz, 2H, Ar–H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.9 (C_q), 164.6 (d, $^1J_{C–F}$ = 251.8 Hz, C_q), 154.3 (C_q), 135.2 (C_q), 130.1 (d, $^4J_{C–F}$ = 2.9 Hz, C_q), 129.7

(d, $^{3}J_{C–F}$ = 8.6 Hz, 2C, CH), 126.6 (CH), 125.4 (CH), 123.4 (CH), 121.8 (CH), 116.3 (d, $^{2}J_{C–F}$ = 21.9 Hz, 2C, CH). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = −108.8 (s). IR (neat): ν_{max}/cm^{-1} 3055, 2924, 2853, 1605, 1483, 1435, 1233, 969, 837, 756. HR-MS (ESI) *m/z* calcd for $C_{13}H_8FNS+H^+$ [M+H$^+$] 230.0440, found 230.0434.

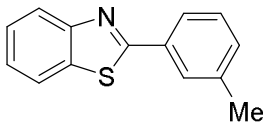


2-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazole (8af):[S1] The representative procedure was followed, using **6a** (0.065 g, 0.481 mmol) and 1-iodo-4-(trifluoromethyl)benzene **7f** (0.20 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 25/1) yielded **8af** (0.078 g, 58%) as a white solid. M. p. = 157–158 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.1 Hz, 2H, Ar–H), 8.11 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.93 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.75 (d, *J* = 8.3 Hz, 2H, Ar–H), 7.53 (dvt, *J* = 8.0, 1.2 Hz, 1H, Ar–H), 7.43 (dvt, *J* = 8.1, 1.0 Hz, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.2 (C_q), 154.2 (C_q), 136.9 (C_q), 135.4 (C_q), 132.7 (q, $^{2}J_{C–F}$ = 32.4 Hz, C_q), 127.9 (2C, CH), 126.9 (CH), 126.2 (q, $^{3}J_{C–F}$ = 3.8 Hz, 2C, CH), 125.9 (CH), 124.0 (q, $^{1}J_{C–F}$ = 272.8 Hz, CF_3), 123.8 (CH), 121.9 (CH). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = −62.9 (s). IR (neat): ν_{max}/cm^{-1} 3058, 2995, 2917, 1594, 1485, 1408, 1231. HR-MS (ESI) *m/z* calcd for $C_{14}H_8F_3NS+H^+$ [M+H$^+$] 280.0408, found 280.0415.

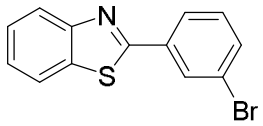


1-(4-(Benzo[*d*]thiazol-2-yl)phenyl)ethan-1-one (8ag): The representative procedure was followed, using **6a** (0.071 g, 0.525 mmol) and 4-iodoacetophenone **7g** (0.184 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1 → 5/1) yielded **8ag** (0.026 g, 20%) as a white solid. M. p. = 185–186 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.6 Hz, 2H, Ar–H), 8.12 (d, *J* = 8.3 Hz, 1H, Ar–H), 8.08 (d, *J* = 8.6 Hz, 2H, Ar–H), 7.94 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.53 (dvt, *J* = 8.3, 1.2 Hz, 1H, Ar–H), 7.43 (dvt, *J* = 7.8, 0.7 Hz, 1H, Ar–H), 2.66 (s, 3H, $COCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.6 (C_q), 166.7 (C_q), 154.2 (C_q), 138.8 (C_q), 137.6 (C_q), 135.4 (C_q), 129.2 (2C, CH), 127.9 (2C, CH), 126.9 (CH), 126.0 (CH), 123.8 (CH), 121.9 (CH), 27.0 (CH_3). IR (neat): ν_{max}/cm^{-1} 2923, 2852, 1676, 1554, 1260,

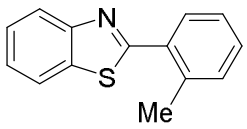
1106, 964, 823, 763. HR-MS (ESI) *m/z* calcd for $C_{15}H_{11}NOS+H^+$ [M+H$^+$] 254.0640, found 254.0643.



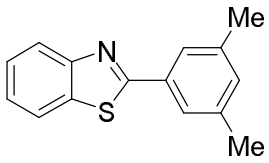
2-(*m*-Tolyl)benzo[*d*]thiazole (8ah): The representative procedure was followed, using **6a** (0.072 g, 0.533 mmol) and 3-iodotoluene **7h** (0.164 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 25/1) yielded **8ah** (0.113 g, 94%) as a white solid. M. p. = 76–78 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.95 (s, 1H, Ar–H), 7.91-7.86 (m, 2H, Ar–H), 7.50 (vt, *J* = 7.3 Hz, 1H, Ar–H), 7.38 (vt, *J* = 7.5 Hz, 2H, Ar–H), 7.30 (d, *J* = 7.6 Hz, 1H, Ar–H), 2.46 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.5 (C_q), 154.3 (C_q), 139.0 (C_q), 135.2 (C_q), 133.7 (C_q), 132.0 (CH), 129.1 (CH), 128.2 (CH), 126.5 (CH), 125.3 (CH), 125.0 (CH), 123.3 (CH), 121.8 (CH), 21.5 (CH_3). IR (neat): ν_{max}/cm^{-1} 3056, 2923, 2854, 1610, 1503, 1433, 1290, 887, 791. HR-MS (ESI) *m/z* calcd for $C_{14}H_{11}NS+H^+$ [M+H$^+$] 226.0690, found 226.0686.



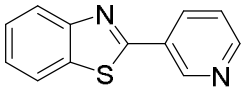
2-(3-Bromophenyl)benzo[*d*]thiazole (8ai): The representative procedure was followed, using **6a** (0.063 g, 0.466 mmol) and 3-bromo-4-iodobenzene **7i** (0.212 g, 0.75 mmol) and reaction was heated for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 20/1) yielded **8ai** (0.055 g, 41%) as a light yellow solid. M. p. = 91–93 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.28 (t, *J* = 1.7 Hz, 1H, Ar–H), 8.09 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.99 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.91 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.61 (dd, *J* = 8.1, 1.0 Hz, 1H, Ar–H), 7.51 (dvt, *J* = 8.3, 1.2 Hz, 1H, Ar–H), 7.41 (dvt, *J* = 8.1, 1.0 Hz, 1H, Ar–H), 7.36 (t, *J* = 7.8 Hz, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.3 (C_q), 154.1 (C_q), 135.6 (C_q), 135.3 (C_q), 134.0 (CH), 130.7 (CH), 130.4 (CH), 126.7 (CH), 126.3 (CH), 125.8 (CH), 123.6 (CH), 123.4 (C_q), 121.9 (CH). IR (neat): ν_{max}/cm^{-1} 2959, 2922, 2851, 1458, 1421, 1216, 970, 788, 749. HR-MS (ESI) *m/z* calcd for $C_{13}H_9BrNS+H^+$ [M+H$^+$] 289.9639, found 289.9644; [M+2+H$^+$] 291.9619, found 291.9625.



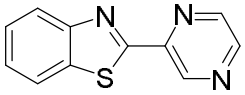
2-(*o*-Tolyl)benzo[*d*]thiazole (8aj): The representative procedure was followed, using **6a** (0.067 g, 0.50 mmol) and 2-iodotoluene **7j** (0.164 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 25/1) yielded **8aj** (0.107 g, 95%) as white solid. M. p. = 58–59 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.2 Hz, 1H, Ar–H), 7.94 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.77 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.52 (dvt, *J* = 7.8, 1.4 Hz, 1H, Ar–H), 7.44-7.30 (m, 4H), 2.67 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.2 (C_q), 153.9 (C_q), 137.4 (C_q), 135.7 (C_q), 133.2 (C_q), 131.7 (CH), 130.7 (CH), 130.2 (CH), 126.3 (CH), 126.2 (CH), 125.3 (CH), 123.5 (CH), 121.5 (CH), 21.5 (CH_3). IR (neat): ν_{max}/cm^{-1} 2923, 2859, 1476, 1452, 1428, 1238, 1041, 951, 756. HR-MS (ESI) *m/z* calcd for $C_{14}H_{11}NS+H^+$ [M+H$^+$] 226.0690, found 226.0687.



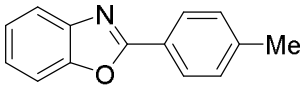
2-(3,5-Dimethylphenyl)benzo[*d*]thiazole (8ak): The representative procedure was followed, using **6a** (0.070 g, 0.518 mmol) and 1-iodo-3,5-dimethylbenzene **7k** (0.174 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 30/1 → 25/1) yielded **8ak** (0.123 g, 99%) as white solid. M. p. = 76–77 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.90 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.73 (s, 2H, Ar–H), 7.49 (vt, *J* = 7.6 Hz, 1H, Ar–H), 7.38 (vt, *J* = 7.6 Hz, 1H, Ar–H), 7.14 (s, 1H, Ar–H), 2.42 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8 (C_q), 154.2 (C_q), 138.9 (2C, C_q), 135.1 (C_q), 133.5 (C_q), 133.0 (CH), 126.4 (CH), 125.5 (2C, CH), 125.3 (CH), 123.3 (CH), 121.8 (CH), 21.4 (2C, CH_3). IR (neat): ν_{max}/cm^{-1} 3055, 2915, 2854, 1599, 1432, 1310, 1163, 842, 772. HR-MS (ESI) *m/z* calcd for $C_{15}H_{13}NS+H^+$ [M+H$^+$] 240.0847, found 240.0843.



2-(Pyridin-3-yl)benzo[*d*]thiazole (8al):[S1] The representative procedure was followed, using **6a** (0.069 g, 0.510 mmol) and 3-iodopyridine **7l** (0.154 g, 0.75 mmol) and reaction was heated for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc/Et_3N: 5/1/0.5 → 3/1/0.5) yielded **8al** (0.076 g, 70%) as white solid. M. p. = 131–133 ^oC. ^1H-NMR (400 MHz, $CDCl_3$): δ = 9.31 (br s, 1H, Ar–H), 8.73 (br s, 1H, Ar–H), 8.41 (d, *J* = 7.8 Hz, 1H, Ar–H), 8.11 (d, *J* = 8.3 Hz, 1H, Ar–H), 7.94 (d, *J* = 7.8 Hz, 1H, Ar–H), 7.54 (vt, *J* = 7.7 Hz, 1H, Ar–H), 7.48-7.43 (m, 2H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.5 (C_q), 154.0 (C_q), 151.5 (CH), 148.5 (CH), 135.0 (C_q), 134.7 (CH), 129.8 (C_q), 126.7 (CH), 125.8 (CH), 123.9 (CH), 123.5 (CH), 121.8 (CH). IR (neat): ν_{max}/cm^{-1} 2959, 2922, 2851, 1419, 1259, 1091, 1015, 954, 802. HR-MS (ESI) *m/z* calcd for $C_{12}H_8N_2S+H^+$ [$M+H^+$] 213.0486, found 213.0491.

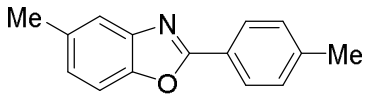


2-(Pyrazin-2-yl)benzo[*d*]thiazole (8am): The representative procedure was followed, using **6a** (0.063 g, 0.466 mmol) and 2-iodopyrazine **7m** (0.154 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc/Et_3N: 5/1/0.5 → 3/1/0.5) yielded **8am** (0.047 g, 47%) as white solid. M. p. = 183–184 ^oC. ^1H-NMR (400 MHz, $CDCl_3$): δ = 9.61 (s, 1H, Ar–H), 8.66 (d, *J* = 9.8 Hz, 2H, Ar–H), 8.14 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.98 (d, *J* = 8.1 Hz, 1H, Ar–H), 7.54 (vt, *J* = 7.6 Hz, 1H, Ar–H), 7.46 (vt, *J* = 7.6 Hz, 1H, Ar–H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6 (C_q), 154.4 (C_q), 147.2 (C_q), 146.0 (CH), 144.3 (CH), 142.6 (CH), 136.2 (C_q), 126.8 (CH), 126.4 (CH), 124.2 (CH), 122.2 (CH). IR (neat): ν_{max}/cm^{-1} 2957, 2921, 2850, 1501, 1392, 1259, 1010, 970, 758. HR-MS (ESI) *m/z* calcd for $C_{11}H_7N_3S+H^+$ [$M+H^+$] 214.0439, found 214.0440.



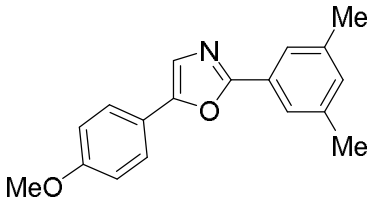
2-(p-Tolyl)benzo[*d*]oxazole (8ba): The representative procedure was followed, using **6b** (0.063 g, 0.528 mmol) and 4-iodotoluene **7a** (0.164 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 40/1) yielded **8ba** (0.094 g, 85%) as a white

solid. M. p. = 115–116 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.2 Hz, 2H, Ar–H), 7.79-7.75 (m, 1H, Ar–H), 7.59-7.55 (m, 1H, Ar–H), 7.37-7.32 (m, 4H, Ar–H), 2.44 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.5 (C_q), 150.8 (C_q), 142.3 (C_q), 142.2 (C_q), 129.8 (2C, CH), 127.8 (2C, CH), 125.1 (CH), 124.7 (CH), 124.5 (C_q), 120.0 (CH), 110.7 (CH), 21.8 (CH_3). IR (neat): ν_{max}/cm^{-1} 3058, 2923, 2856, 1548, 1445, 1240, 1047, 806, 687. HR-MS (ESI) *m/z* calcd for $C_{14}H_{11}NO+H^+$ [M+H$^+$] 210.0919, found 210.0913.



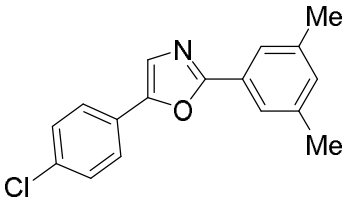
5-Methyl-2-(p-tolyl)benzo[*d*]oxazole (8ca): The representative procedure was followed, using **6c** (0.066 g, 0.50 mmol) and 4-iodotoluene **7a** (0.164 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1 → 30/1) yielded **8ca** (0.102 g, 91%) as a white solid. M. p. = 139–140 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.1 Hz, 2H, Ar–H), 7.54 (s, 1H, Ar–H), 7.43 (d, J = 8.2 Hz, 1H, Ar–H), 7.32 (d, J = 8.1 Hz, 2H, Ar–H), 7.14 (d, J = 8.2 Hz, 1H, Ar–H), 2.48 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.6 (C_q), 149.1 (C_q), 142.5 (C_q), 142.1 (C_q), 134.4 (C_q), 129.8 (2C, CH), 127.7 (2C, CH), 126.1 (CH), 124.7 (C_q), 119.9 (CH), 110.0 (CH), 21.8 (CH_3), 21.7 (CH_3). IR (neat): ν_{max}/cm^{-1} 3031, 2922, 2863, 1564, 1489, 1264, 1185, 1053, 801. HR-MS (ESI) *m/z* calcd for $C_{15}H_{13}NO+H^+$ [M+H$^+$] 224.1075, found 224.1071.

2.2. Characterization data for compounds 10

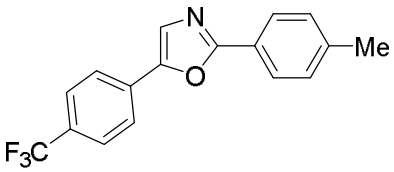


2-(3,5-Dimethylphenyl)-5-(4-methoxyphenyl)oxazole (10ak): The representative procedure was followed, using **9a** (0.088 g, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene **7k** (0.174 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1 → 5/1) yielded **10ak** (0.110 g, 79%) as a white solid. M. p. = 80–82 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.72 (s, 2H, Ar–H), 7.66 (d, J = 8.5 Hz, 2H, Ar–H), 7.31 (s, 1H, Ar–H), 7.08

(s, 1H, Ar–H), 6.97 (d, J = 8.5 Hz, 2H, Ar–H), 3.85 (s, 3H, OCH_3), 2.39 (s, 6H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.1 (C_q), 159.9 (C_q), 151.3 (C_q), 138.6 (2C, C_q), 132.1 (CH), 127.5 (C_q), 125.9 (2C, CH), 124.1 (2C, CH), 121.9 (CH), 121.1 (C_q), 114.6 (2C, CH), 55.5 (OCH_3), 21.4 (2C, CH_3). IR (neat): ν_{max}/cm^{-1} 2958, 2916, 2836, 1607, 1497, 1457, 1244, 1176, 1026, 813, 728. HR-MS (ESI) *m/z* calcd for $C_{18}H_{17}NO_2$+H^+ [M+H^+] 280.1338, found 280.1329.

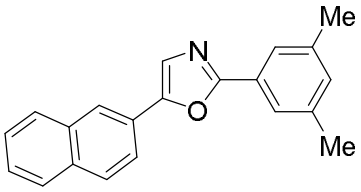


5-(4-Chlorophenyl)-2-(3,5-dimethylphenyl)oxazole (10bk): The representative procedure was followed, using **9b** (0.090 g, 0.50 mmol) and 1-iodo-3,5-dimethylbenzene **7k** (0.174 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 → 10/1) yielded **10bk** (0.125 g, 88%) as a white solid. M. p. = 129–131 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 2H, Ar–H), 7.65 (d, J = 8.7 Hz, 2H, Ar–H), 7.43-4.40 (m, 3H, Ar–H), 7.10 (s, 1H, Ar–H), 2.40 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.9 (C_q), 150.2 (C_q), 138.7 (2C, C_q), 134.2 (C_q), 132.5 (CH), 129.3 (2C, CH), 127.1 (C_q), 126.7 (C_q), 125.5 (2C, CH), 124.3 (2C, CH), 123.9 (CH), 21.4 (2C, CH_3). IR (neat): ν_{max}/cm^{-1} 2959, 2915, 2851, 1531, 1478, 1259, 1085, 1011, 816, 728. HR-MS (ESI) *m/z* calcd for $C_{17}H_{14}ClNO$+H^+ [M+H^+] 284.0842, found 284.0837.

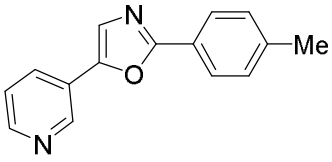


2-(*p*-Tolyl)-5-(4-(trifluoromethyl)phenyl)oxazole (10ca): The representative procedure was followed, using **9c** (0.106 g, 0.50 mmol) and 4-iodo toluene **7a** (0.164 g, 0.75 mmol) and the reaction was continued for 24 h. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1 → 5/1) yielded **10ca** (0.135 g, 89%) as a white solid. M. p. = 157–158 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.8 Hz, 2H, Ar–H), 7.80 (d, J = 8.1 Hz, 2H, Ar–H), 7.68 (d, J = 8.3 Hz, 2H, Ar–H), 7.53 (s, 1H, Ar–H), 7.30 (d, J = 7.8 Hz, 2H, Ar–H), 2.42

(s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.7 (C_q), 141.4 (2C, C_q), 131.5 (C_q), 130.1 (q, $^2J_{C–F}$ = 33.1 Hz, C_q), 129.8 (2C, CH), 126.6 (2C, CH), 126.1 (q, $^3J_{C–F}$ = 3.9 Hz, 2C, CH), 125.3 (CH), 124.5 (C_q), 124.3 (2C, CH), 124.1 (q, $^1J_{C–F}$ = 272.0 Hz, CF_3), 21.8 (CH_3). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = −62.7 (s). IR (neat): ν_{max}/cm^{-1} 3047, 2925, 2862, 1613, 1489, 1326, 1121, 834, 730. HR-MS (ESI) *m/z* calcd for $C_{17}H_{12}F_3NO+H^+$ [M+H$^+$] 304.0949, found 304.0943.

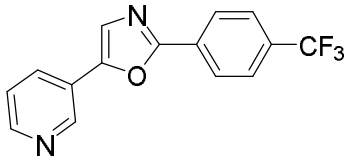


2-(3,5-Dimethylphenyl)-5-(naphthalen-2-yl)oxazole (10dk): The representative procedure was followed, using **9d** (0.098 g, 0.502 mmol) and 1-iodo-3,5-dimethylbenzene **7k** (0.174 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 → 10/1) yielded **10dk** (0.106 g, 71%) as a white solid. M. p. = 134–136 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H, Ar–H), 7.93-7.89 (m, 2H, Ar–H), 7.86-7.84 (m, 1H, Ar–H), 7.79-7.77 (m, 3H, Ar–H), 7.55-7.48 (m, 3H, Ar–H), 7.12 (s, 1H, Ar–H), 2.43 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.9 (C_q), 151.4 (C_q), 138.7 (2C, C_q), 133.6 (C_q), 133.2 (C_q), 132.4 (CH), 128.9 (CH), 128.4 (CH), 128.0 (CH), 127.3 (C_q), 127.0 (CH), 126.7 (CH), 125.5 (C_q), 124.3 (2C, CH), 124.0 (CH), 123.0 (CH), 122.3 (CH), 21.5 (2C, CH_3). IR (neat): ν_{max}/cm^{-1} 2920, 2851, 1561, 1532, 1501, 1261, 1096, 1044, 812, 740. HR-MS (ESI) *m/z* calcd for $C_{21}H_{17}NO+H^+$ [M+H$^+$] 300.1388, found 300.1383.



5-(Pyridine-3-yl)-2-(*p*-tolyl)oxazole (10ea): The representative procedure was followed, using **9e** (0.073 g, 0.5 mmol) and 4-iodo toluene **7a** (0.164 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc/Et_3N: 5/1/0.05 → 2/1/0.05 → 1/1/0.05) yielded **10ea** (0.102 g, 86%) as a white solid. M. p. = 81–83 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 1H, Ar–H), 8.57 (s, 1H, Ar–H), 8.00-7.96 (m, 3H, Ar–H), 7.51 (s, 1H, Ar–H), 7.39-7.28 (m, 3H, Ar–H), 2.41 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.4 (C_q), 149.2

(CH), 148.2 (C_q), 145.6 (CH), 141.3 (C_q), 131.3 (CH), 129.8 (2C, CH), 126.6 (2C, CH), 124.8 (CH), 124.6 (C_q), 124.5 (C_q), 123.9 (CH), 21.7 (CH_3). IR (neat): ν_{max}/cm^{-1} 2920, 2854, 1493, 1423, 1327, 1136, 1020, 951, 823, 730. HR-MS (ESI) *m/z* calcd for $C_{15}H_{12}N_2O+H^+$ [M+H$^+$] 237.1028, found 237.1024.



5-(Pyridine-3-yl)-2-(4-(trifluoromethyl)phenyl)oxazole (10ef): The representative procedure was followed, using **9e** (0.074 g, 0.506 mmol) and 1-iodo-4-(trifluoromethyl)benzene **7f** (0.20 g, 0.75 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc/Et_3N: 5/1/0.05 → 2/1/0.05 → 1/1/0.05) yielded **10ef** (0.115 g, 78%) as a white solid. M. p. = 128–129 ^{o}C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.01 (s, 1H, Ar–H), 8.61 (s, 1H, Ar–H), 8.22 (d, *J* = 8.2 Hz, 2H, Ar–H), 8.01 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.75 (d, *J* = 7.9 Hz, 2H, Ar–H), 7.58 (s, 1H, Ar–H), 7.42-7.40 (m, 1H, Ar–H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 160.7 (C_q), 149.7 (CH), 149.4 (C_q), 145.8 (CH), 132.5 (q, $^2J_{C–F}$ = 32.4 Hz, C_q), 131.7 (CH), 130.3 (C_q), 126.8 (2C, CH), 126.1 (q, $^3J_{C–F}$ = 3.8 Hz, 2C, CH), 125.3 (CH), 124.2 (C_q), 124.0 (CH), 123.9 (q, $^1J_{C–F}$ = 272.8 Hz, CF_3). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = −62.9 (s). IR (neat): ν_{max}/cm^{-1} 3061, 2924, 1563, 1482, 1413, 1328, 1119, 862, 701. HR-MS (ESI) *m/z* calcd for $C_{15}H_9F_3N_2O+H^+$ [M+H$^+$] 291.0745, found 291.0739.

3. X-ray structure determinations

X-ray intensity data measurements of compounds **2a** and **2b** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073 Å) radiation at 297 (2) K and 90(2) K, respectively. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 12 frames (total 36 frames). Data were collected with ω scan width of 0.5° at eight different settings of φ and 2θ with a frame time of 10 sec keeping the sample-to-detector distance fixed at 5.00 cm for both compounds. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S3] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[S4] Hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. For compound **2b**, two methyl groups (C15, C16 and C20, C21) of each tert-butyl groups showed large anisotropic displacement parameters (ADP) due to orientational disorder. The two orientations of equal (0.5) occupancies were separated using PART 1 and PART 2 instructions, the C–C bond lengths were restrained using DFIX 1.54 (0.02) instruction to achieve an approximate theoretical geometry. The anisotropic displacement parameters were kept within reasonable limits using DELU (0.01), SIMU (0.04) and ISOR (0.1) instructions in the SHELXL full-matrix least-squares refinement. Crystal data for the structures have been deposited in the Cambridge Crystallographic Data Center with numbers (compound numbers) CCDC-973533 (**2a**), CCDC-973534 (**2b**).

4. Structural data for 2a

4.1. Table S2. Crystal data and structure refinement for 2a.

Identification code	(^{iPr2}POCN^{iPr2})PdCl	
Empirical formula	$C_{19}H_{33}ClNOPPd$	
Formula weight	464.28	
Temperature	297(2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 821.82(2) pm	α= 90°
	b = 1298.77(3) pm	β= 90°
	c = 2023.91(5) pm	γ = 90°
Volume	2.16023(9) nm^3	
Z	4	
Density (calculated)	1.428 Mg/m^3	
Absorption coefficient	1.063 mm^{-1}	
F(000)	960	
Crystal size	0.24 x 0.19 x 0.15 mm^3	
Theta range for data collection	1.86 to 30.00°.	
Index ranges	-11<=h<=9, -14<=k<=18, -28<=l<=26	
Reflections collected	13795	
Independent reflections	6257 [R(int) = 0.0263]	
Completeness to theta = 30.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8569 and 0.7845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6257 / 0 / 225	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0601	
R indices (all data)	R1 = 0.0303, wR2 = 0.0623	
Absolute structure parameter	0.01(2)	
Largest diff. peak and hole	0.495 and -0.270 e.$Å^{-3}$	

4.2. Table S3. Bond lengths [pm] and angles [°] for 2a.

Pd(1)-C(1)	195.6(2)	C(12)-H(12B)	96.00
Pd(1)-P(1)	218.90(6)	C(12)-H(12C)	96.00
Pd(1)-N(1)	222.04(17)	C(8)-C(10)	151.1(5)
Pd(1)-Cl(1)	239.22(6)	C(8)-C(9)	151.9(4)
P(1)-O(1)	164.70(18)	C(8)-H(8)	98.00
P(1)-C(14)	180.3(3)	C(10)-H(10A)	96.00
P(1)-C(17)	181.2(2)	C(10)-H(10B)	96.00
O(1)-C(2)	138.6(3)	C(10)-H(10C)	96.00
C(11)-C(13)	151.7(4)	C(9)-H(9A)	96.00
C(11)-N(1)	152.3(3)	C(9)-H(9B)	96.00
C(11)-C(12)	154.4(4)	C(9)-H(9C)	96.00
C(11)-H(11)	98.00	C(14)-C(15)	151.4(5)
C(2)-C(3)	138.0(4)	C(14)-C(16)	151.8(5)
C(2)-C(1)	138.9(3)	C(14)-H(14)	98.00
C(3)-C(4)	138.8(5)	C(15)-H(15A)	96.00
C(3)-H(3)	93.00	C(15)-H(15B)	96.00
C(4)-C(5)	136.2(4)	C(15)-H(15C)	96.00
C(4)-H(4)	93.00	C(16)-H(16A)	96.00
C(5)-C(6)	139.6(4)	C(16)-H(16B)	96.00
C(5)-H(5)	93.00	C(16)-H(16C)	96.00
C(6)-C(1)	138.1(3)	C(17)-C(19)	151.1(4)
C(6)-C(7)	150.0(4)	C(17)-C(18)	152.7(3)
C(7)-N(1)	151.4(3)	C(17)-H(17)	98.00
C(7)-H(7A)	97.00	C(19)-H(19C)	96.00
C(7)-H(7B)	97.00	C(19)-H(19A)	96.00
N(1)-C(8)	151.8(4)	C(19)-H(19B)	96.00
C(13)-H(13A)	96.00	C(18)-H(18A)	96.00
C(13)-H(13B)	96.00	C(18)-H(18C)	96.00
C(13)-H(13C)	96.00	C(18)-H(18B)	96.00
C(12)-H(12A)	96.00		

C(1)-Pd(1)-P(1)	80.35(7)	C(6)-C(7)-H(7A)	109.2
C(1)-Pd(1)-N(1)	81.84(8)	N(1)-C(7)-H(7A)	109.2
P(1)-Pd(1)-N(1)	162.10(5)	C(6)-C(7)-H(7B)	109.2
C(1)-Pd(1)-Cl(1)	177.32(7)	N(1)-C(7)-H(7B)	109.2
P(1)-Pd(1)-Cl(1)	97.04(2)	H(7A)-C(7)-H(7B)	107.9
N(1)-Pd(1)-Cl(1)	100.79(5)	C(7)-N(1)-C(8)	107.8(2)
O(1)-P(1)-C(14)	101.40(13)	C(7)-N(1)-C(11)	110.01(19)
O(1)-P(1)-C(17)	102.47(11)	C(8)-N(1)-C(11)	111.4(2)
C(14)-P(1)-C(17)	109.34(15)	C(7)-N(1)-Pd(1)	106.63(14)
O(1)-P(1)-Pd(1)	106.99(7)	C(8)-N(1)-Pd(1)	112.24(15)
C(14)-P(1)-Pd(1)	118.50(10)	C(11)-N(1)-Pd(1)	108.68(14)
C(17)-P(1)-Pd(1)	115.78(8)	C(11)-C(13)-H(13A)	109.5
C(2)-O(1)-P(1)	112.56(14)	C(11)-C(13)-H(13B)	109.5
C(13)-C(11)-N(1)	111.3(2)	H(13A)-C(13)-H(13B)	109.5
C(13)-C(11)-C(12)	111.5(3)	C(11)-C(13)-H(13C)	109.5
N(1)-C(11)-C(12)	113.5(3)	H(13A)-C(13)-H(13C)	109.5
C(13)-C(11)-H(11)	106.7	H(13B)-C(13)-H(13C)	109.5
N(1)-C(11)-H(11)	106.7	C(11)-C(12)-H(12A)	109.5
C(12)-C(11)-H(11)	106.7	C(11)-C(12)-H(12B)	109.5
C(3)-C(2)-O(1)	121.0(2)	H(12A)-C(12)-H(12B)	109.5
C(3)-C(2)-C(1)	121.2(3)	C(11)-C(12)-H(12C)	109.5
O(1)-C(2)-C(1)	117.7(2)	H(12A)-C(12)-H(12C)	109.5
C(2)-C(3)-C(4)	118.0(3)	H(12B)-C(12)-H(12C)	109.5
C(2)-C(3)-H(3)	121.0	C(10)-C(8)-N(1)	112.6(3)
C(4)-C(3)-H(3)	121.0	C(10)-C(8)-C(9)	108.8(3)
C(5)-C(4)-C(3)	121.5(2)	N(1)-C(8)-C(9)	111.5(2)
C(5)-C(4)-H(4)	119.2	C(10)-C(8)-H(8)	107.9
C(3)-C(4)-H(4)	119.2	N(1)-C(8)-H(8)	107.9
C(4)-C(5)-C(6)	120.4(3)	C(9)-C(8)-H(8)	107.9
C(4)-C(5)-H(5)	119.8	C(8)-C(10)-H(10A)	109.5
C(6)-C(5)-H(5)	119.8	C(8)-C(10)-H(10B)	109.5
C(1)-C(6)-C(5)	118.9(2)	H(10A)-C(10)-H(10B)	109.5
C(1)-C(6)-C(7)	117.5(2)	C(8)-C(10)-H(10C)	109.5
C(5)-C(6)-C(7)	123.6(2)	H(10A)-C(10)-H(10C)	109.5
C(6)-C(7)-N(1)	112.06(19)	H(10B)-C(10)-H(10C)	109.5
C(8)-C(9)-H(9A)	109.5	H(16A)-C(16)-H(16B)	109.5

C(8)-C(9)-H(9B)	109.5	C(14)-C(16)-H(16C)	109.5
H(9A)-C(9)-H(9B)	109.5	H(16A)-C(16)-H(16C)	109.5
C(8)-C(9)-H(9C)	109.5	H(16B)-C(16)-H(16C)	109.5
H(9A)-C(9)-H(9C)	109.5	C(19)-C(17)-C(18)	111.6(3)
H(9B)-C(9)-H(9C)	109.5	C(19)-C(17)-P(1)	107.86(19)
C(6)-C(1)-C(2)	119.9(2)	C(18)-C(17)-P(1)	113.8(2)
C(6)-C(1)-Pd(1)	118.17(17)	C(19)-C(17)-H(17)	107.8
C(2)-C(1)-Pd(1)	121.86(18)	C(18)-C(17)-H(17)	107.8
C(15)-C(14)-C(16)	112.1(3)	P(1)-C(17)-H(17)	107.8
C(15)-C(14)-P(1)	109.8(3)	C(17)-C(19)-H(19C)	109.5
C(16)-C(14)-P(1)	112.0(2)	C(17)-C(19)-H(19A)	109.5
C(15)-C(14)-H(14)	107.6	H(19C)-C(19)-H(19A)	109.5
C(16)-C(14)-H(14)	107.6	C(17)-C(19)-H(19B)	109.5
P(1)-C(14)-H(14)	107.6	H(19C)-C(19)-H(19B)	109.5
C(14)-C(15)-H(15A)	109.5	H(19A)-C(19)-H(19B)	109.5
C(14)-C(15)-H(15B)	109.5	C(17)-C(18)-H(18A)	109.5
H(15A)-C(15)-H(15B)	109.5	C(17)-C(18)-H(18C)	109.5
C(14)-C(15)-H(15C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(15A)-C(15)-H(15C)	109.5	C(17)-C(18)-H(18B)	109.5
H(15B)-C(15)-H(15C)	109.5	H(18A)-C(18)-H(18B)	109.5
C(14)-C(16)-H(16A)	109.5	H(18C)-C(18)-H(18B)	109.5
C(14)-C(16)-H(16B)	109.5		

Symmetry transformations used to generate equivalent atoms:

5. Structural data for 2b

5.1. Table S4. Crystal data and structure refinement for 2b.

Identification code	(^{tBu2}POCN^{iPr2})PdCl	
Empirical formula	$C_{21}H_{37}ClNOPPd$	
Formula weight	492.34	
Temperature	90(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 1340.29(16) pm	α= 90°
	b = 811.83(10) pm	β= 103.850(8)°
	c = 2122.1(3) pm	γ = 90°
Volume	2.2419(5) nm^3	
Z	4	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	1.029 mm^{-1}	
F(000)	1024	
Crystal size	0.35 x 0.22 x 0.15 mm^3	
Theta range for data collection	1.98 to 27.00°.	
Index ranges	-17<=h<=16, -10<=k<=10, -27<=l<=27	
Reflections collected	21147	
Independent reflections	4822 [R(int) = 0.0837]	
Completeness to theta = 27.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8610 and 0.7148	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4822 / 92 / 285	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.0989	
R indices (all data)	R1 = 0.0672, wR2 = 0.1079	
Largest diff. peak and hole	0.834 and -1.624 e.$Å^{-3}$	

5.2. Table S5. Bond lengths [pm] and angles [°] for 2b.

Pd(1)-C(1)	195.8(4)	C(11)-C(12)	152.5(6)
Pd(1)-P(1)	220.90(11)	C(11)-H(11)	100.00
Pd(1)-N(1)	222.9(3)	C(12)-H(12A)	98.00
Pd(1)-Cl(1)	239.43(11)	C(12)-H(12B)	98.00
P(1)-O(1)	165.3(3)	C(12)-H(12C)	98.00
P(1)-C(14)	183.6(5)	C(13)-H(13A)	98.00
P(1)-C(18)	184.4(5)	C(13)-H(13B)	98.00
O(1)-C(2)	138.8(5)	C(13)-H(13C)	98.00
N(1)-C(7)	150.5(5)	C(14)-C(15)	143.4(10)
N(1)-C(8)	151.2(5)	C(14)-C(16)	149.5(10)
N(1)-C(11)	151.8(6)	C(14)-C(17)	149.7(7)
C(1)-C(6)	139.1(6)	C(14)-C(16')	164.4(9)
C(1)-C(2)	139.3(6)	C(14)-C(15')	166.1(10)
C(2)-C(3)	138.4(6)	C(15)-H(15A)	98.00
C(3)-C(4)	138.8(6)	C(15)-H(15B)	98.00
C(3)-H(3)	95.00	C(15)-H(15C)	98.00
C(4)-C(5)	138.1(6)	C(16)-H(16A)	98.00
C(4)-H(4)	95.00	C(16)-H(16B)	98.00
C(5)-C(6)	139.4(6)	C(16)-H(16C)	98.00
C(5)-H(5)	95.00	C(15')-H(15D)	98.00
C(6)-C(7)	150.3(6)	C(15')-H(15E)	98.00
C(7)-H(7A)	99.00	C(15')-H(15F)	98.00
C(7)-H(7B)	99.00	C(16')-H(16D)	98.00
C(8)-C(9)	152.2(7)	C(16')-H(16E)	98.00
C(8)-C(10)	152.8(6)	C(16')-H(16F)	98.00
C(8)-H(8)	100.00	C(17)-H(17A)	98.00
C(9)-H(9A)	98.00	C(17)-H(17B)	98.00
C(9)-H(9B)	98.00	C(17)-H(17C)	98.00
C(9)-H(9C)	98.00	C(18)-C(21')	141.2(10)
C(10)-H(10A)	98.00	C(18)-C(20)	146.6(10)
C(10)-H(10B)	98.00	C(18)-C(19)	148.6(7)
C(10)-H(10C)	98.00	C(18)-C(20')	170.4(10)
C(11)-C(13)	151.2(6)	C(18)-C(21)	171.7(10)
C(19)-H(19A)	98.00	C(21)-H(21C)	98.00

C(19)-H(19B)	98.00	C(20')-H(20D)	98.00
C(19)-H(19C)	98.00	C(20')-H(20E)	98.00
C(20)-H(20A)	98.00	C(20')-H(20F)	98.00
C(20)-H(20B)	98.00	C(21')-H(21D)	98.00
C(20)-H(20C)	98.00	C(21')-H(21E)	98.00
C(21)-H(21A)	98.00	C(21')-H(21F)	98.00
C(21)-H(21B)	98.00		

C(1)-Pd(1)-P(1)	80.56(12)	C(2)-C(3)-H(3)	121.0
C(1)-Pd(1)-N(1)	81.35(15)	C(4)-C(3)-H(3)	121.0
P(1)-Pd(1)-N(1)	161.65(9)	C(5)-C(4)-C(3)	121.5(4)
C(1)-Pd(1)-Cl(1)	177.93(13)	C(5)-C(4)-H(4)	119.3
P(1)-Pd(1)-Cl(1)	99.18(4)	C(3)-C(4)-H(4)	119.3
N(1)-Pd(1)-Cl(1)	99.00(9)	C(4)-C(5)-C(6)	119.7(4)
O(1)-P(1)-C(14)	100.75(19)	C(4)-C(5)-H(5)	120.2
O(1)-P(1)-C(18)	102.5(2)	C(6)-C(5)-H(5)	120.2
C(14)-P(1)-C(18)	112.9(2)	C(1)-C(6)-C(5)	120.0(4)
O(1)-P(1)-Pd(1)	105.95(11)	C(1)-C(6)-C(7)	116.9(4)
C(14)-P(1)-Pd(1)	115.86(16)	C(5)-C(6)-C(7)	123.0(4)
C(18)-P(1)-Pd(1)	116.31(18)	C(6)-C(7)-N(1)	112.0(3)
C(2)-O(1)-P(1)	114.1(3)	C(6)-C(7)-H(7A)	109.2
C(7)-N(1)-C(8)	111.0(3)	N(1)-C(7)-H(7A)	109.2
C(7)-N(1)-C(11)	107.6(3)	C(6)-C(7)-H(7B)	109.2
C(8)-N(1)-C(11)	111.8(3)	N(1)-C(7)-H(7B)	109.2
C(7)-N(1)-Pd(1)	107.1(2)	H(7A)-C(7)-H(7B)	107.9
C(8)-N(1)-Pd(1)	108.4(2)	N(1)-C(8)-C(9)	111.4(4)
C(11)-N(1)-Pd(1)	110.9(2)	N(1)-C(8)-C(10)	113.9(4)
C(6)-C(1)-C(2)	118.9(4)	C(9)-C(8)-C(10)	109.8(4)
C(6)-C(1)-Pd(1)	118.5(3)	N(1)-C(8)-H(8)	107.1
C(2)-C(1)-Pd(1)	122.6(3)	C(9)-C(8)-H(8)	107.1
C(3)-C(2)-O(1)	121.4(4)	C(10)-C(8)-H(8)	107.1
C(3)-C(2)-C(1)	121.9(4)	C(8)-C(9)-H(9A)	109.5
O(1)-C(2)-C(1)	116.7(4)	C(8)-C(9)-H(9B)	109.5
C(2)-C(3)-C(4)	118.0(4)	H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5	C(15)-C(14)-P(1)	110.5(5)
H(9A)-C(9)-H(9C)	109.5	C(16)-C(14)-P(1)	115.7(5)

H(9B)-C(9)-H(9C)	109.5	C(17)-C(14)-P(1)	115.2(4)
C(8)-C(10)-H(10A)	109.5	C(16')-C(14)-P(1)	103.3(4)
C(8)-C(10)-H(10B)	109.5	C(15')-C(14)-P(1)	99.3(4)
H(10A)-C(10)-H(10B)	109.5	C(14)-C(15)-H(15A)	109.5
C(8)-C(10)-H(10C)	109.5	C(14)-C(15)-H(15B)	109.5
H(10A)-C(10)-H(10C)	109.5	C(14)-C(15)-H(15C)	109.5
H(10B)-C(10)-H(10C)	109.5	C(14)-C(16)-H(16A)	109.5
C(13)-C(11)-N(1)	111.5(4)	C(14)-C(16)-H(16B)	109.5
C(13)-C(11)-C(12)	110.0(4)	C(14)-C(16)-H(16C)	109.5
N(1)-C(11)-C(12)	112.7(3)	C(14)-C(15')-H(15D)	109.5
C(13)-C(11)-H(11)	107.5	C(14)-C(15')-H(15E)	109.5
N(1)-C(11)-H(11)	107.5	H(15D)-C(15')-H(15E)	109.5
C(12)-C(11)-H(11)	107.5	C(14)-C(15')-H(15F)	109.5
C(11)-C(12)-H(12A)	109.5	H(15D)-C(15')-H(15F)	109.5
C(11)-C(12)-H(12B)	109.5	H(15E)-C(15')-H(15F)	109.5
H(12A)-C(12)-H(12B)	109.5	C(14)-C(16')-H(16D)	109.5
C(11)-C(12)-H(12C)	109.5	C(14)-C(16')-H(16E)	109.5
H(12A)-C(12)-H(12C)	109.5	H(16D)-C(16')-H(16E)	109.5
H(12B)-C(12)-H(12C)	109.5	C(14)-C(16')-H(16F)	109.5
C(11)-C(13)-H(13A)	109.5	H(16D)-C(16')-H(16F)	109.5
C(11)-C(13)-H(13B)	109.5	H(16E)-C(16')-H(16F)	109.5
H(13A)-C(13)-H(13B)	109.5	C(14)-C(17)-H(17A)	109.5
C(11)-C(13)-H(13C)	109.5	C(14)-C(17)-H(17B)	109.5
H(13A)-C(13)-H(13C)	109.5	H(17A)-C(17)-H(17B)	109.5
H(13B)-C(13)-H(13C)	109.5	C(14)-C(17)-H(17C)	109.5
C(15)-C(14)-C(16)	62.9(6)	H(17A)-C(17)-H(17C)	109.5
C(15)-C(14)-C(17)	119.6(6)	H(17B)-C(17)-H(17C)	109.5
C(16)-C(14)-C(17)	122.2(5)	C(21')-C(18)-C(20)	58.9(6)
C(15)-C(14)-C(16')	107.4(6)	C(21')-C(18)-C(19)	118.7(6)
C(17)-C(14)-C(16')	98.3(5)	C(20)-C(18)-C(19)	125.0(7)
C(16)-C(14)-C(15')	101.7(7)	C(21')-C(18)-C(20')	104.8(7)
C(17)-C(14)-C(15')	95.3(5)	C(19)-C(18)-C(20')	93.9(6)
C(16')-C(14)-C(15')	145.4(6)	C(20)-C(18)-C(21)	100.4(7)
C(19)-C(18)-C(21)	100.0(5)	C(18)-C(21)-H(21A)	109.5
C(20')-C(18)-C(21)	146.2(7)	C(18)-C(21)-H(21B)	109.5
C(21')-C(18)-P(1)	117.4(6)	C(18)-C(21)-H(21C)	109.5

C(20)-C(18)-P(1)	108.8(5)	C(18)-C(20')-H(20D)	109.5
C(19)-C(18)-P(1)	116.0(4)	C(18)-C(20')-H(20E)	109.5
C(20')-C(18)-P(1)	99.3(4)	H(20D)-C(20')-H(20E)	109.5
C(21)-C(18)-P(1)	101.8(5)	C(18)-C(20')-H(20F)	109.5
C(18)-C(19)-H(19A)	109.5	H(20D)-C(20')-H(20F)	109.5
C(18)-C(19)-H(19B)	109.5	H(20E)-C(20')-H(20F)	109.5
H(19A)-C(19)-H(19B)	109.5	C(18)-C(21')-H(21D)	109.5
C(18)-C(19)-H(19C)	109.5	C(18)-C(21')-H(21E)	109.5
H(19A)-C(19)-H(19C)	109.5	H(21D)-C(21')-H(21E)	109.5
H(19B)-C(19)-H(19C)	109.5	C(18)-C(21')-H(21F)	109.5
C(18)-C(20)-H(20A)	109.5	H(21D)-C(21')-H(21F)	109.5
C(18)-C(20)-H(20B)	109.5	H(21E)-C(21')-H(21F)	109.5
C(18)-C(20)-H(20C)	109.5		

Symmetry transformations used to generate equivalent atoms:

6. References

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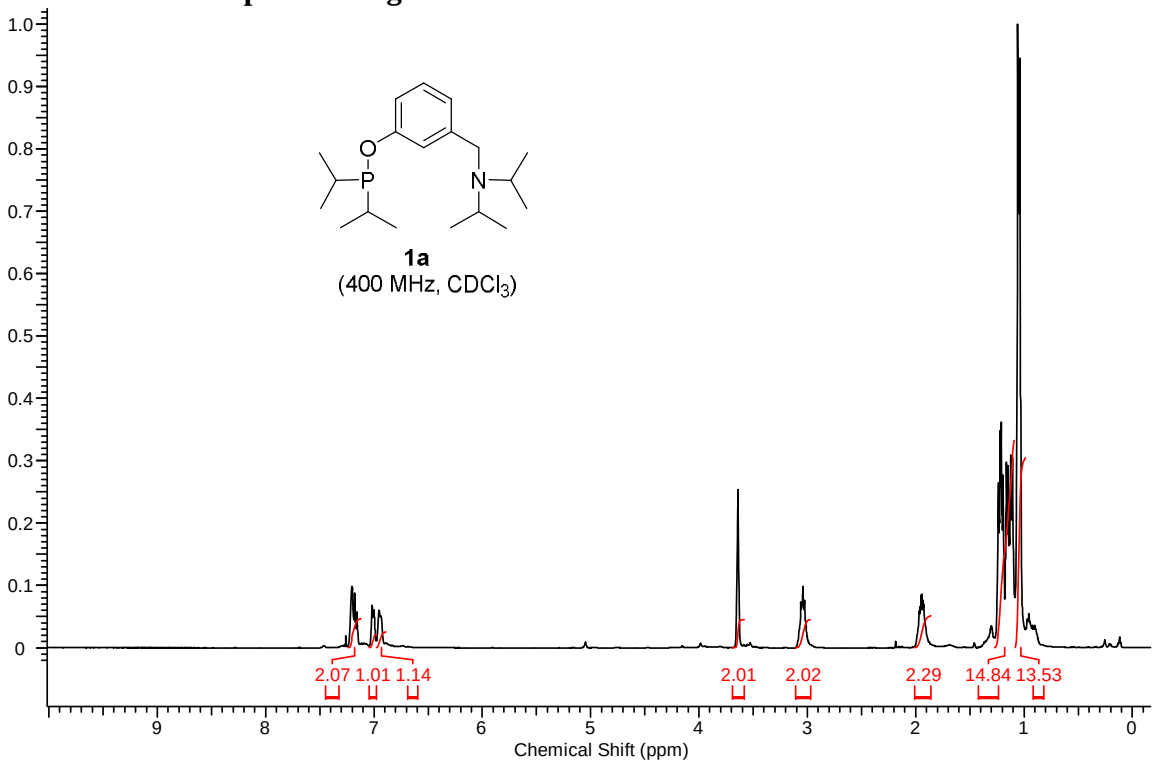
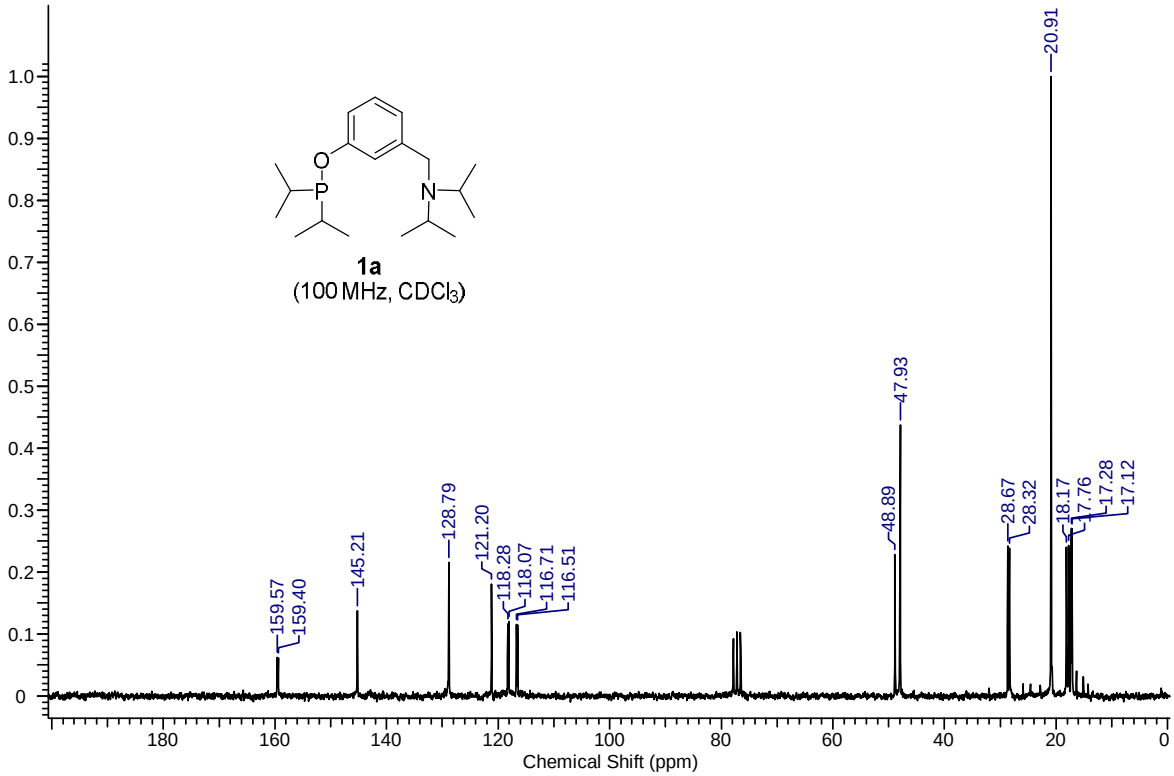
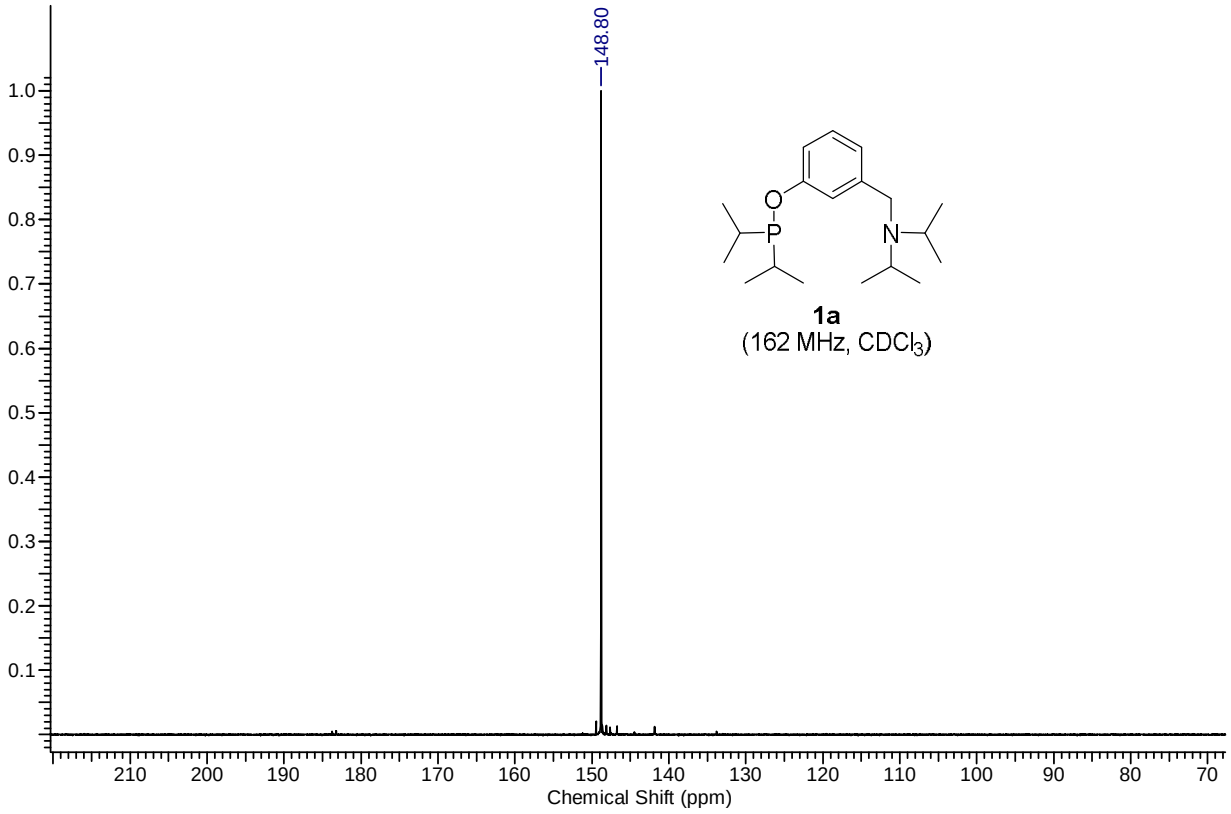
7. NMR spectra of ligands and complexes

7.1. NMR spectra of ligands 1a and 1b



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Chemical Shift (ppm)
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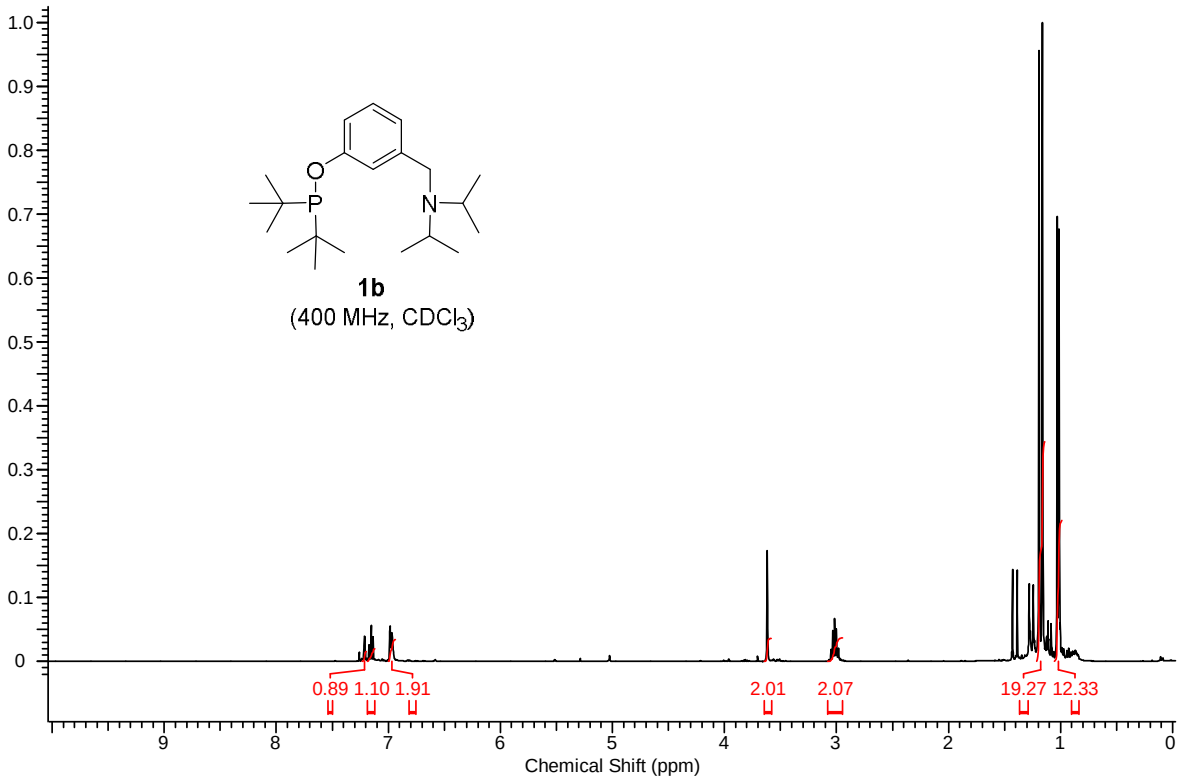
P
N
1a
(162 MHz, CDCl3)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Chemical Shift (ppm)
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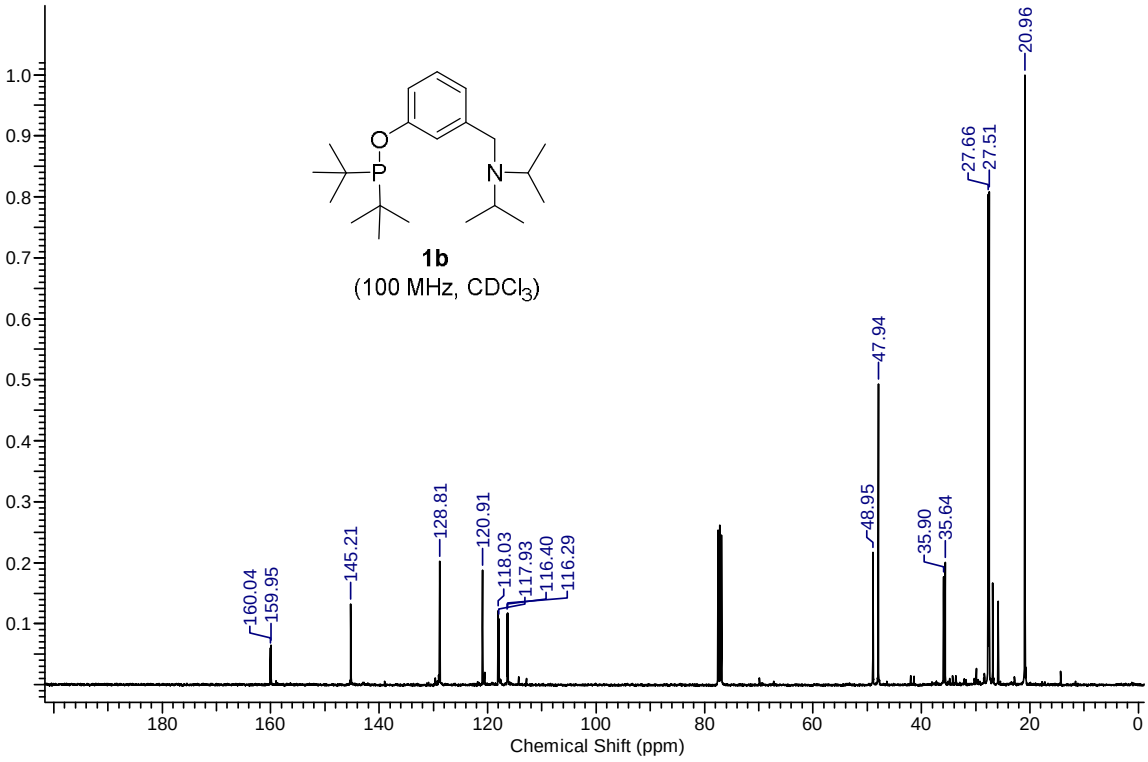
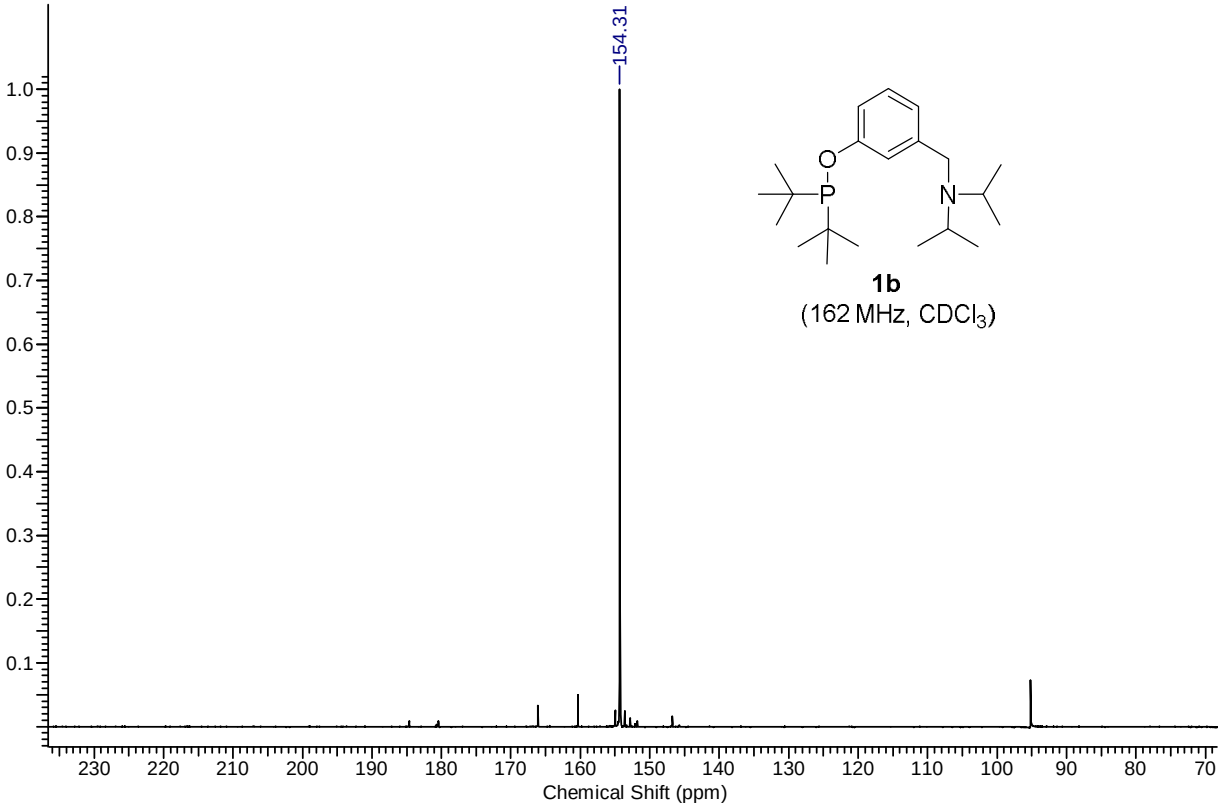
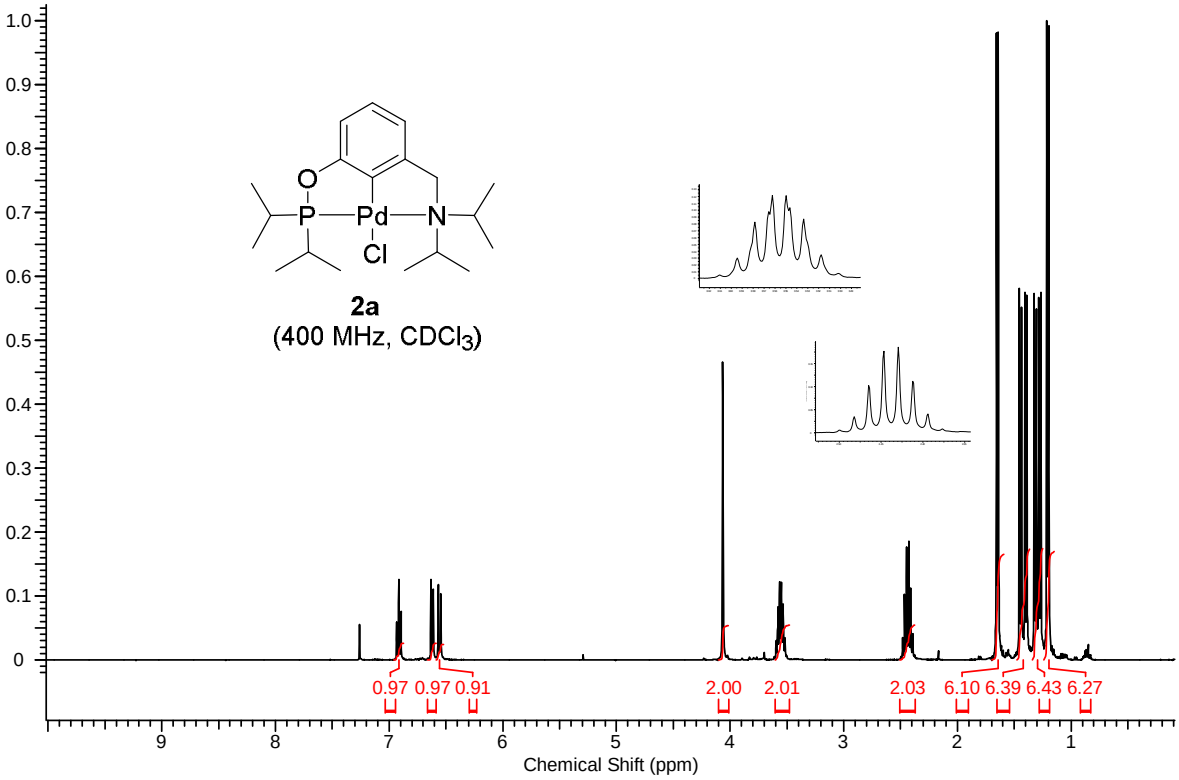
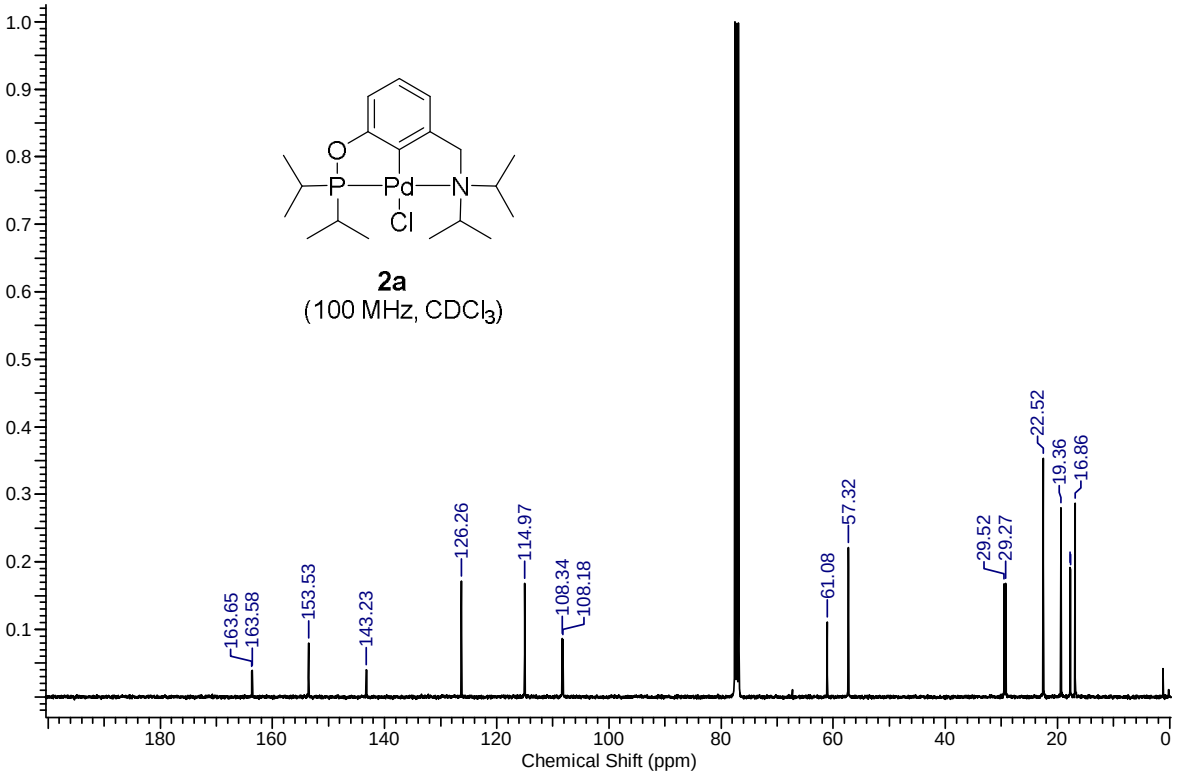
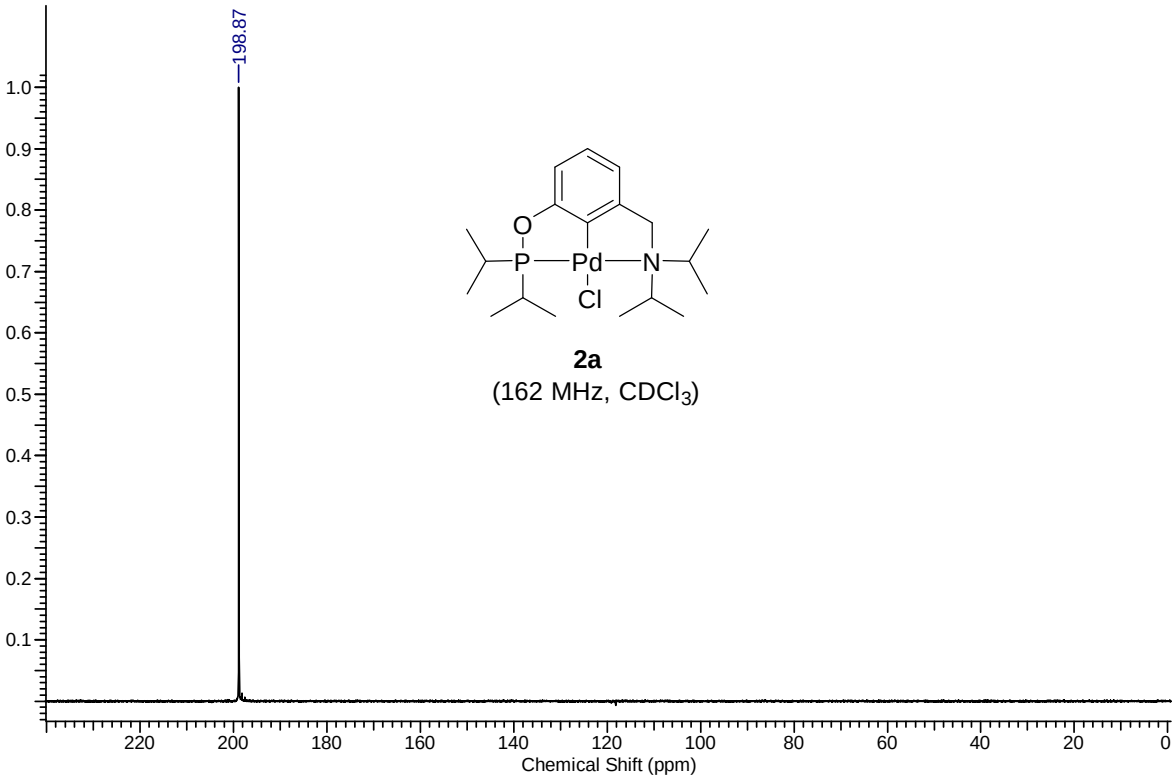

1b
(100 MHz, CDCl3)
160.04
159.95
145.21
128.81
120.91
118.03
117.93
116.40
116.29
48.95
47.94
35.90
35.64
27.66
27.51
20.96
Chemical Shift (ppm)


1b
(162 MHz, CDCl3)
154.31
Chemical Shift (ppm)

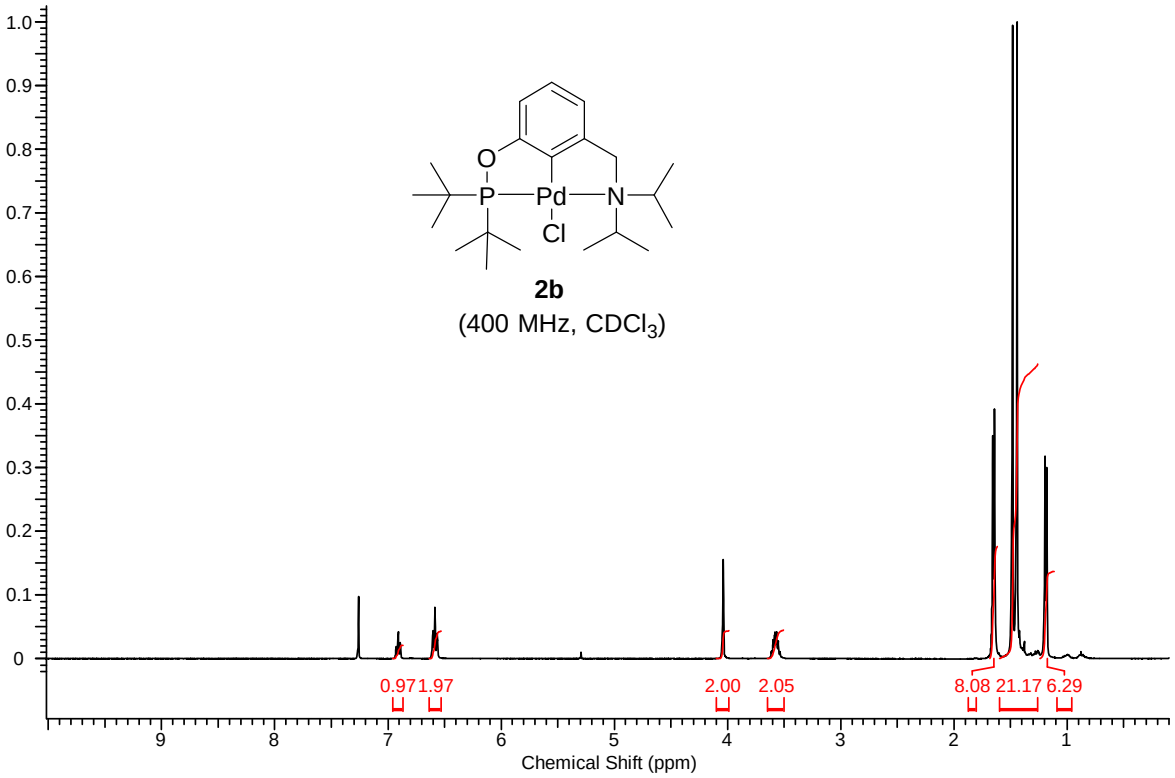
7.2. NMR spectra of complexes 2a-4a



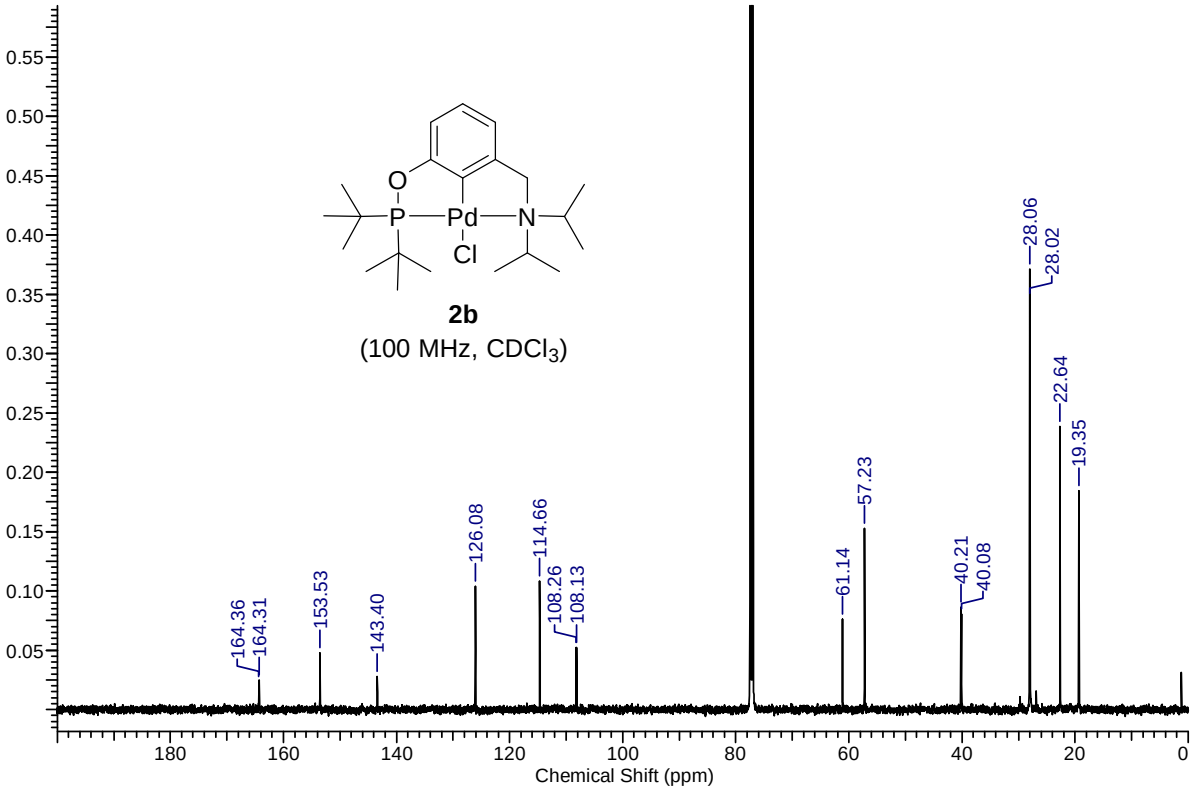


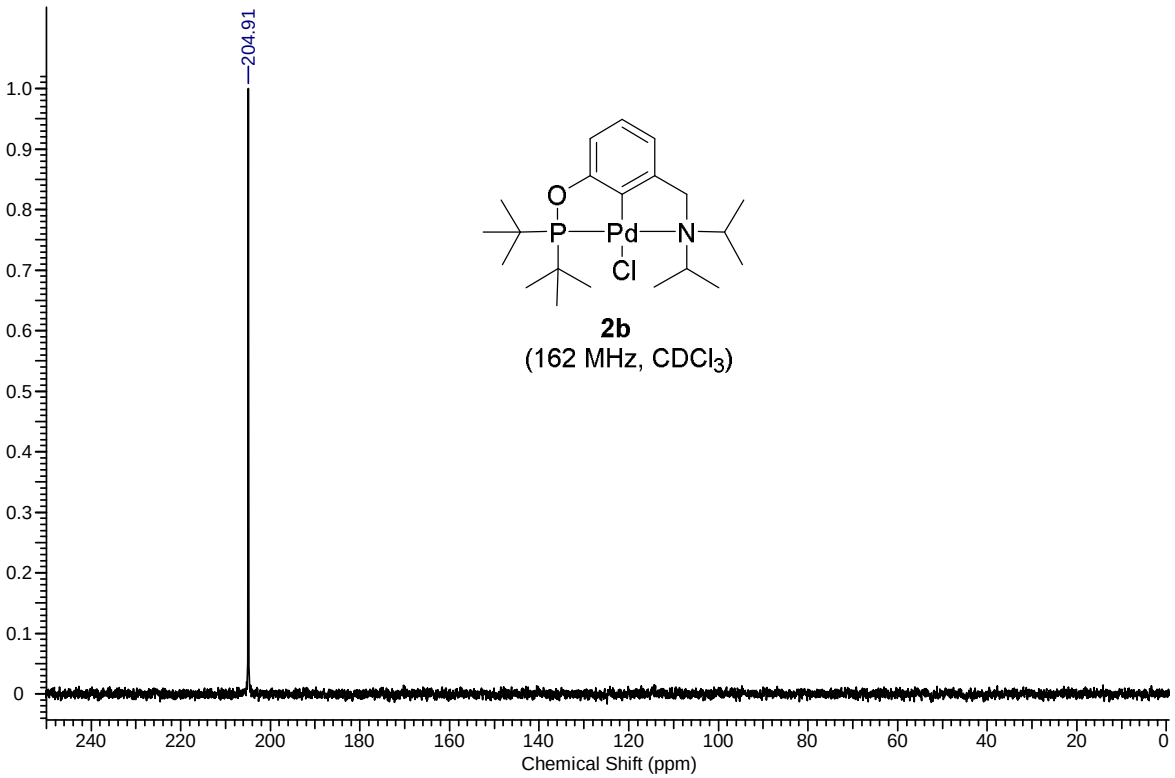


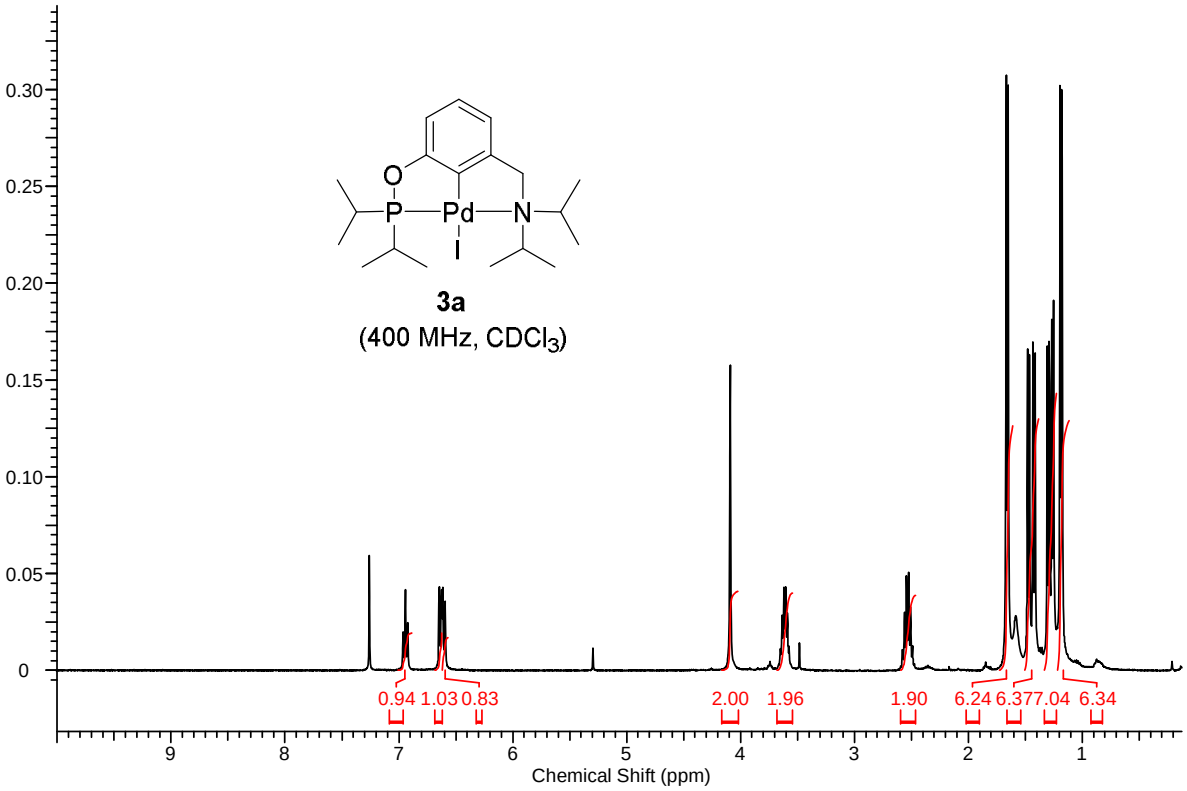
2a
(162 MHz, $CDCl_3$)

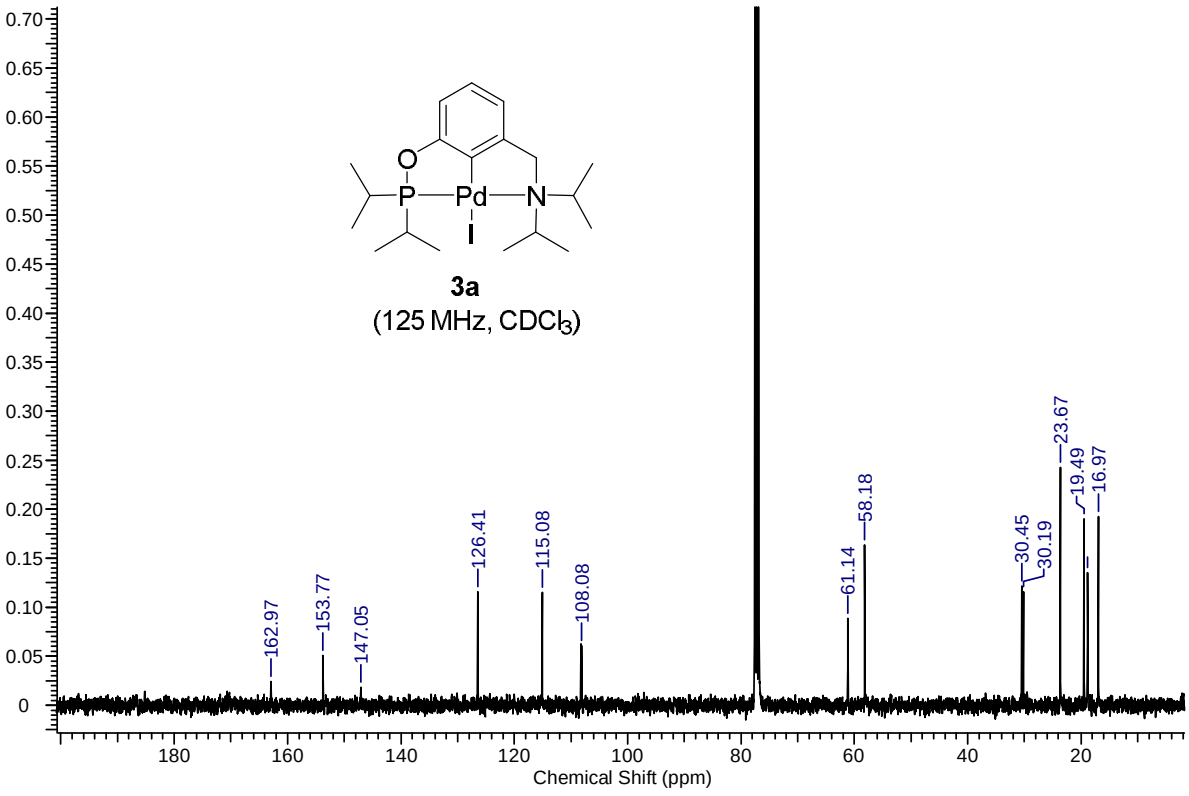


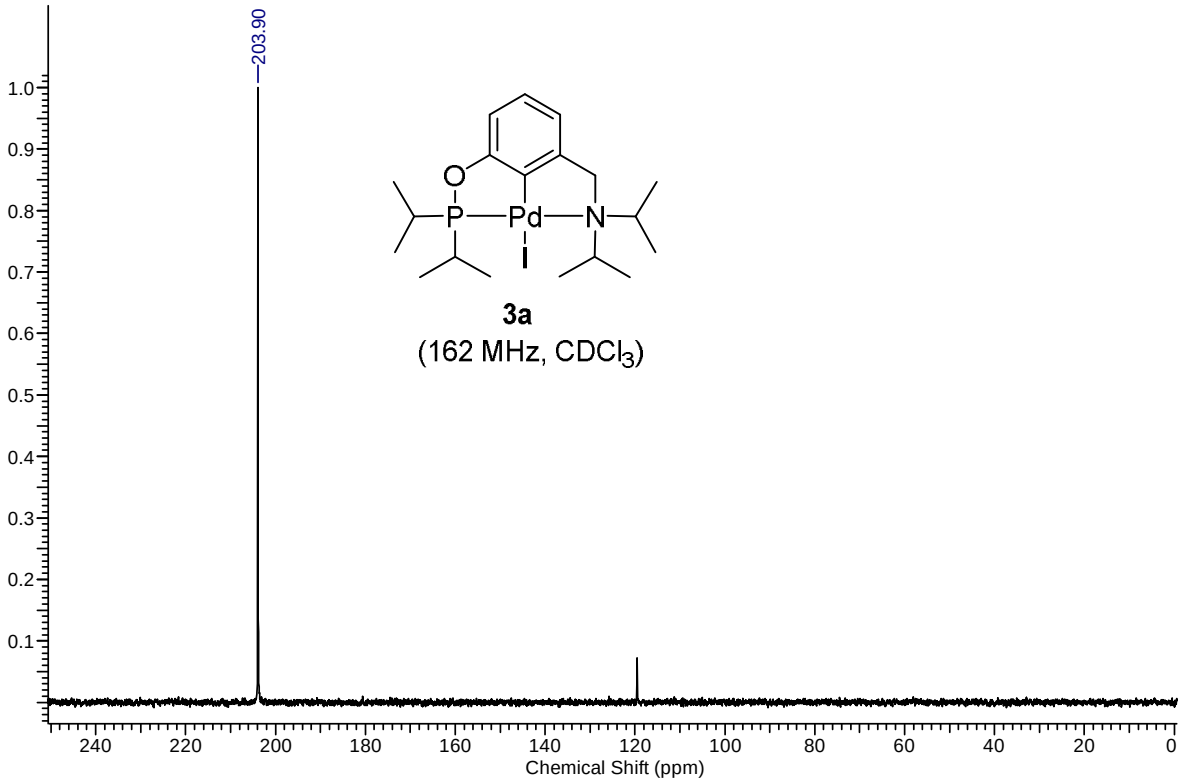
2b
(400 MHz, $CDCl_3$)

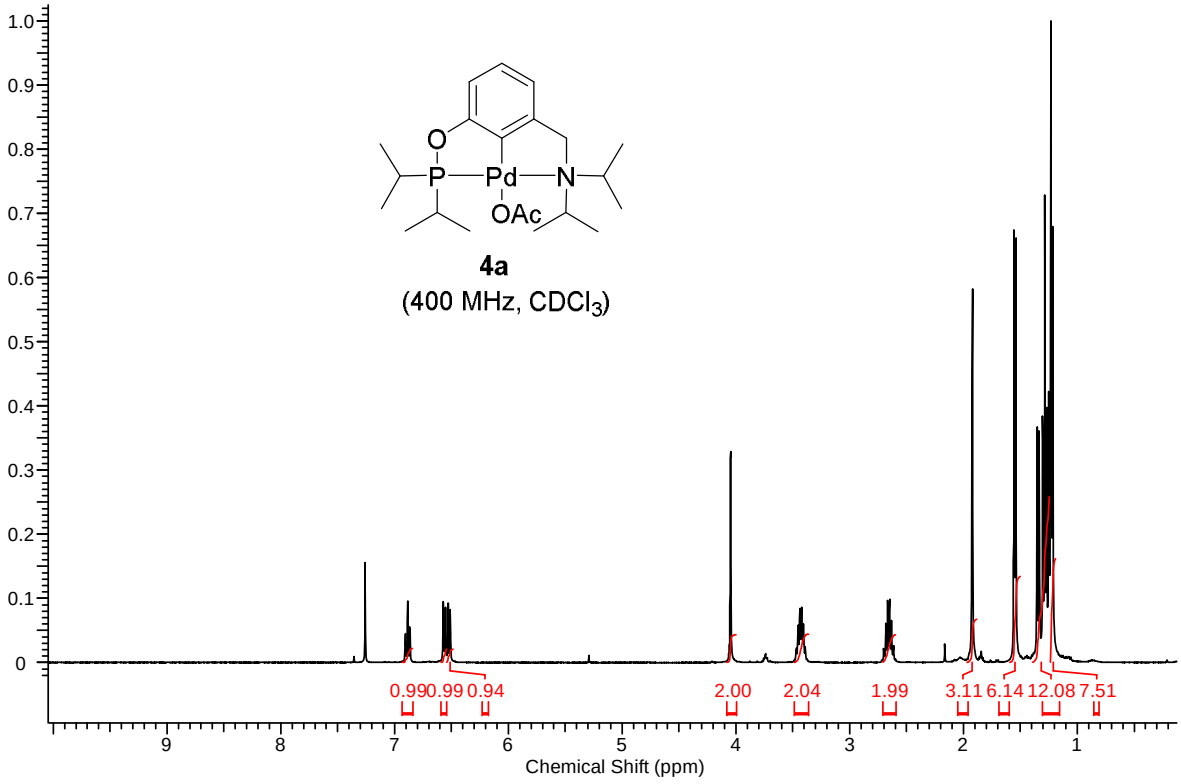

O
P
Pd
N
Cl
2b
(100 MHz, CDCl3)
164.36
164.31
153.53
143.40
126.08
114.66
108.26
108.13
61.14
57.23
40.21
40.08
28.06
28.02
22.64
19.35
Chemical Shift (ppm)

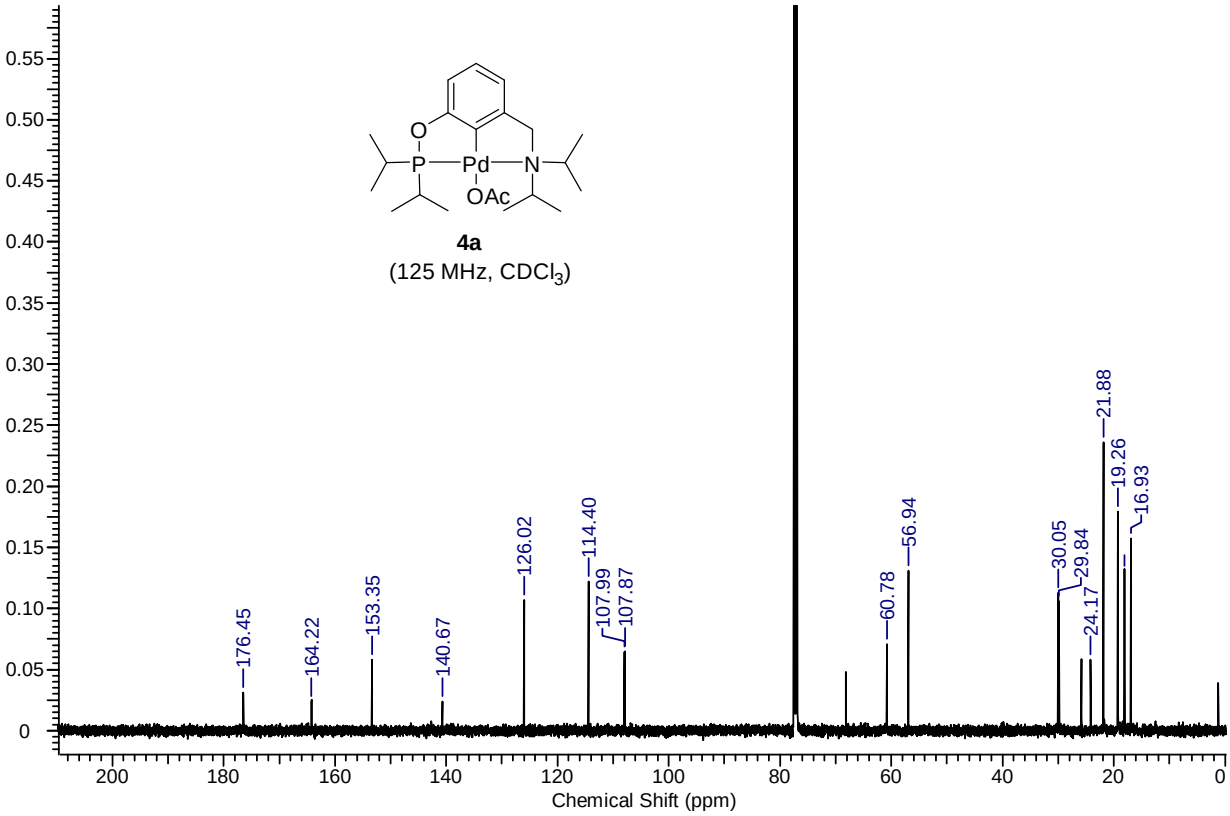

204.91
O
P
Pd
N
Cl
2b
(162 MHz, CDCl3)
Chemical Shift (ppm)

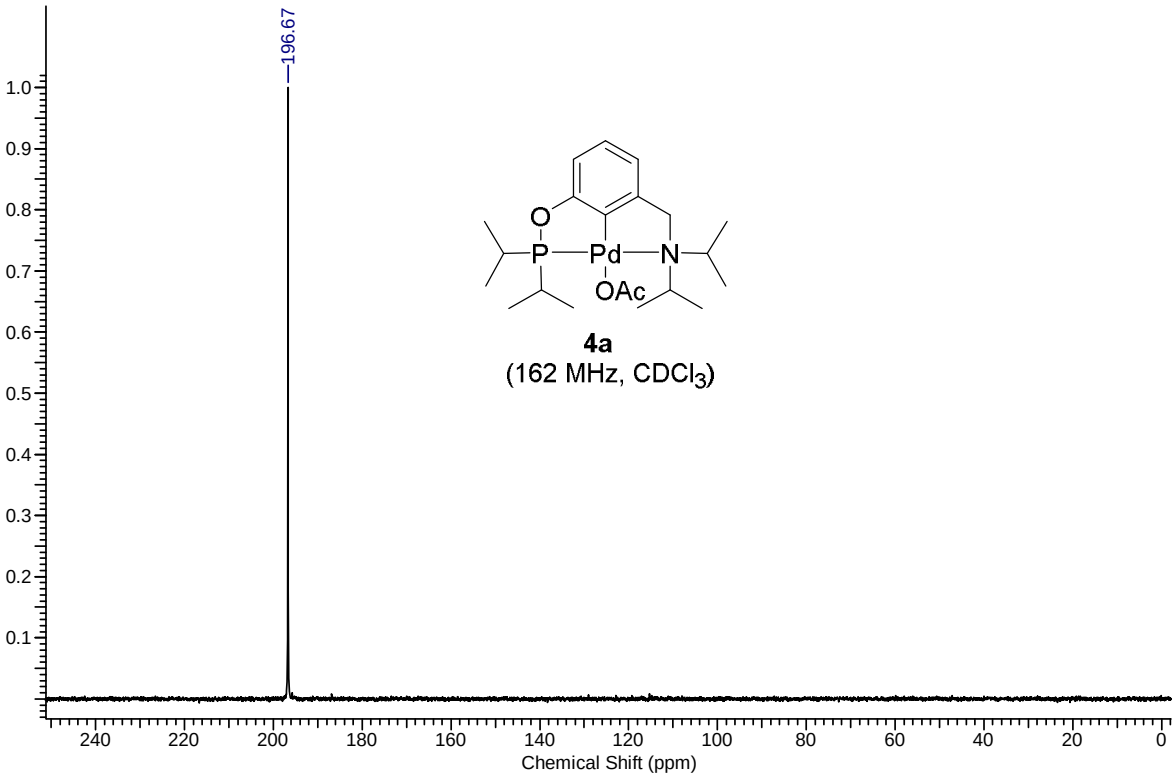

O
P
Pd
N
I
3a
(400 MHz, CDCl3)
0.94 1.03 0.83
2.00
1.96
1.90
6.24 6.37 7.04
6.34
Chemical Shift (ppm)

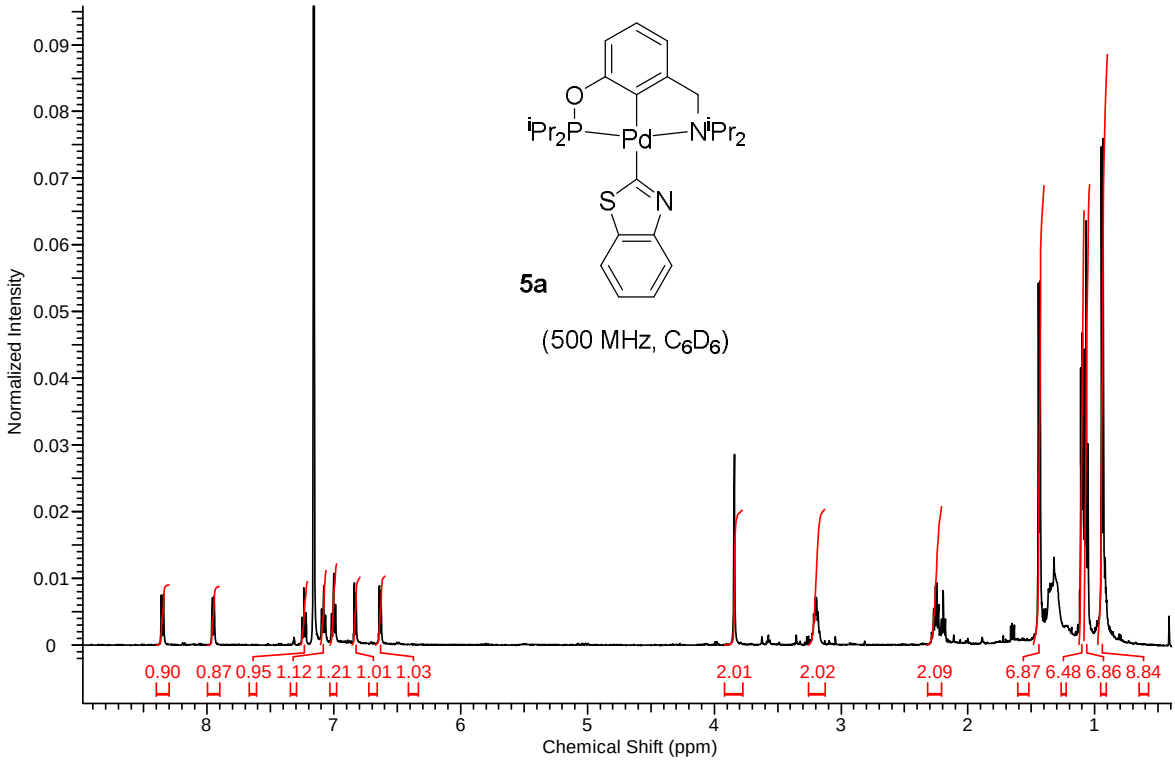

O
P
Pd
N
I
3a
(125 MHz, CDCl3)
162.97
153.77
147.05
126.41
115.08
108.08
61.14
58.18
30.45
30.19
23.67
19.49
16.97
Chemical Shift (ppm)

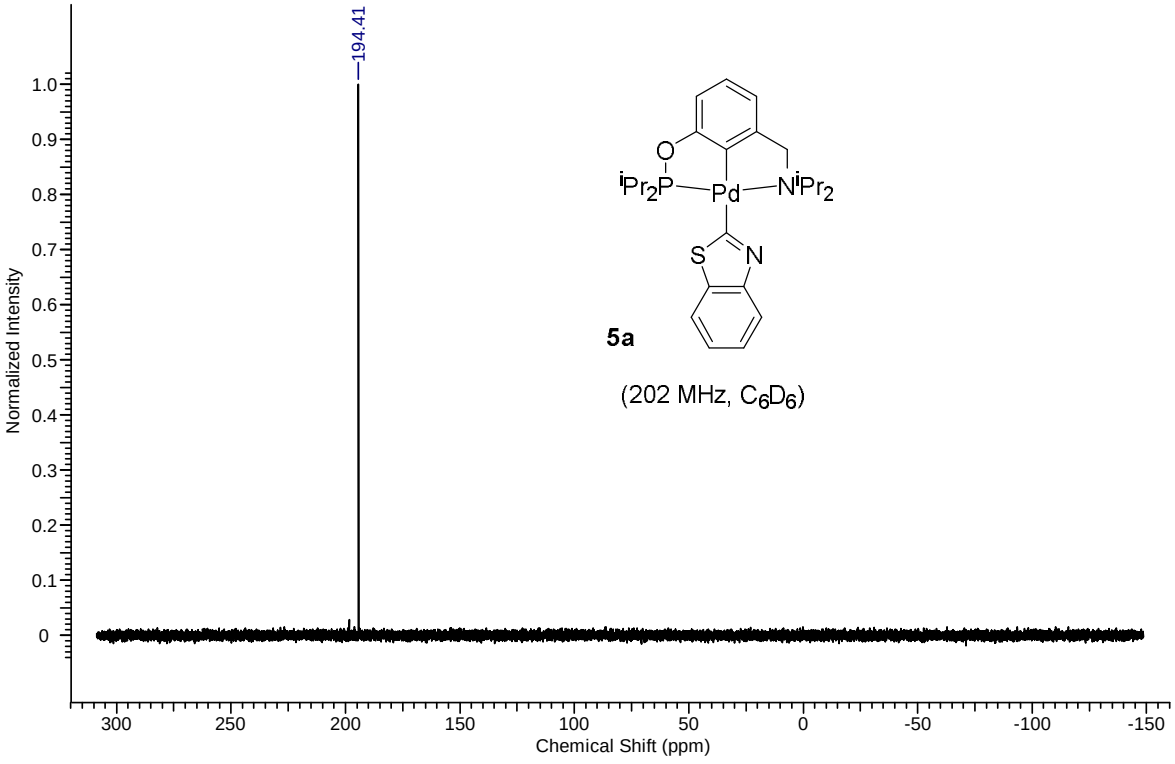

203.90
O
P
Pd
N
I
3a
(162 MHz, CDCl3)
Chemical Shift (ppm)


O
P
Pd
N
OAc
4a
(400 MHz, CDCl3)
0.99 0.99 0.94
2.00
2.04
1.99
3.11 6.14 12.08 7.51
Chemical Shift (ppm)


O
P
Pd
N
OAc
4a
(125 MHz, CDCl3)
176.45
164.22
153.35
140.67
126.02
114.40
107.99
107.87
60.78
56.94
30.05
29.84
24.17
21.88
19.26
16.93
Chemical Shift (ppm)

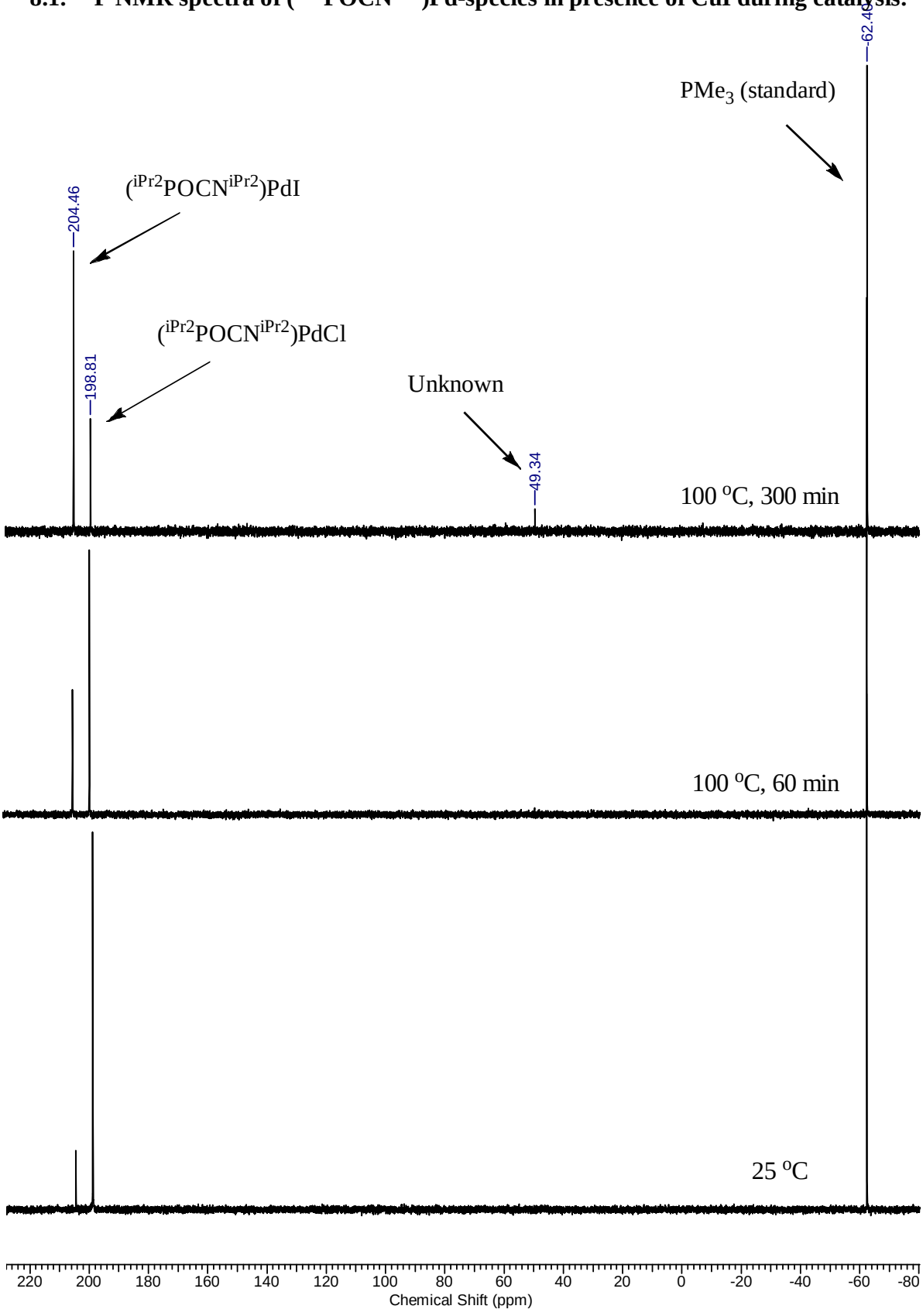

196.67
O
P
Pd
N
OAc
4a
(162 MHz, CDCl3)
Chemical Shift (ppm)


Normalized Intensity
Chemical Shift (ppm)
0.90 0.87 0.95 1.12 1.21 1.01 1.03
2.01 2.02 2.09 6.87 6.48 6.86 8.84
O
iPr2P
Pd
NiPr2
S
N
5a
(500 MHz, C6D6)

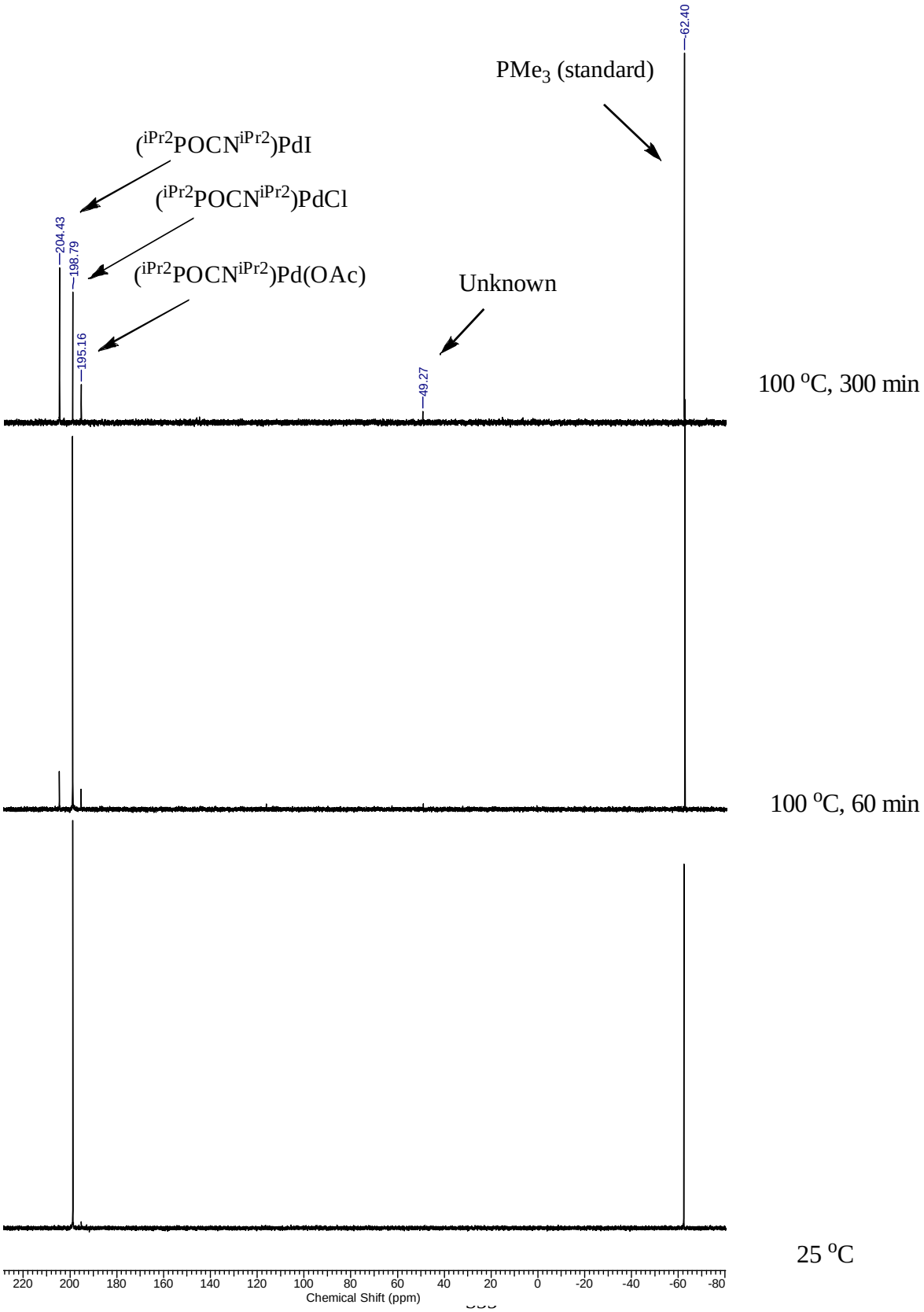

194.41
Normalized Intensity
Chemical Shift (ppm)
O
iPr2P
Pd
NiPr2
S
N
5a
(202 MHz, C6D6)

8. ^{31}P NMR spectra of (^{iPr2}POCN^{iPr2})Pd-species during resting state study.

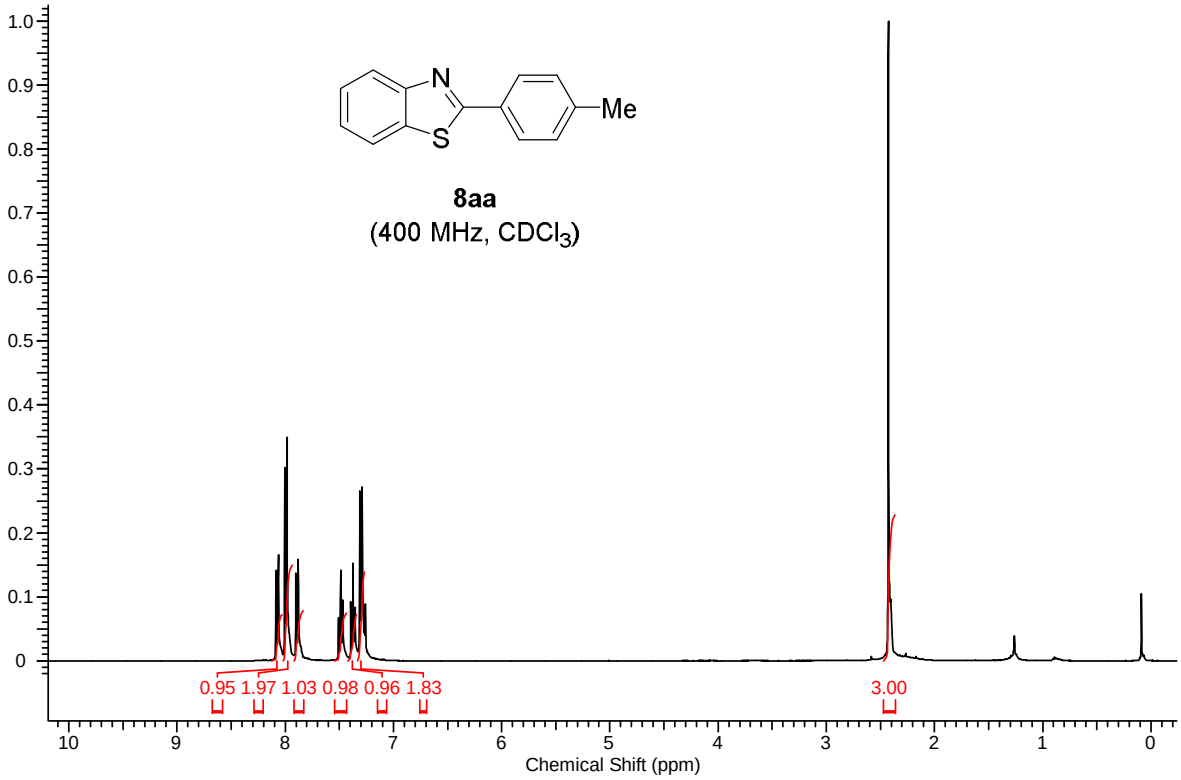
8.1. ^{31}P NMR spectra of (^{iPr2}POCN^{iPr2})Pd-species in presence of CuI during catalysis.

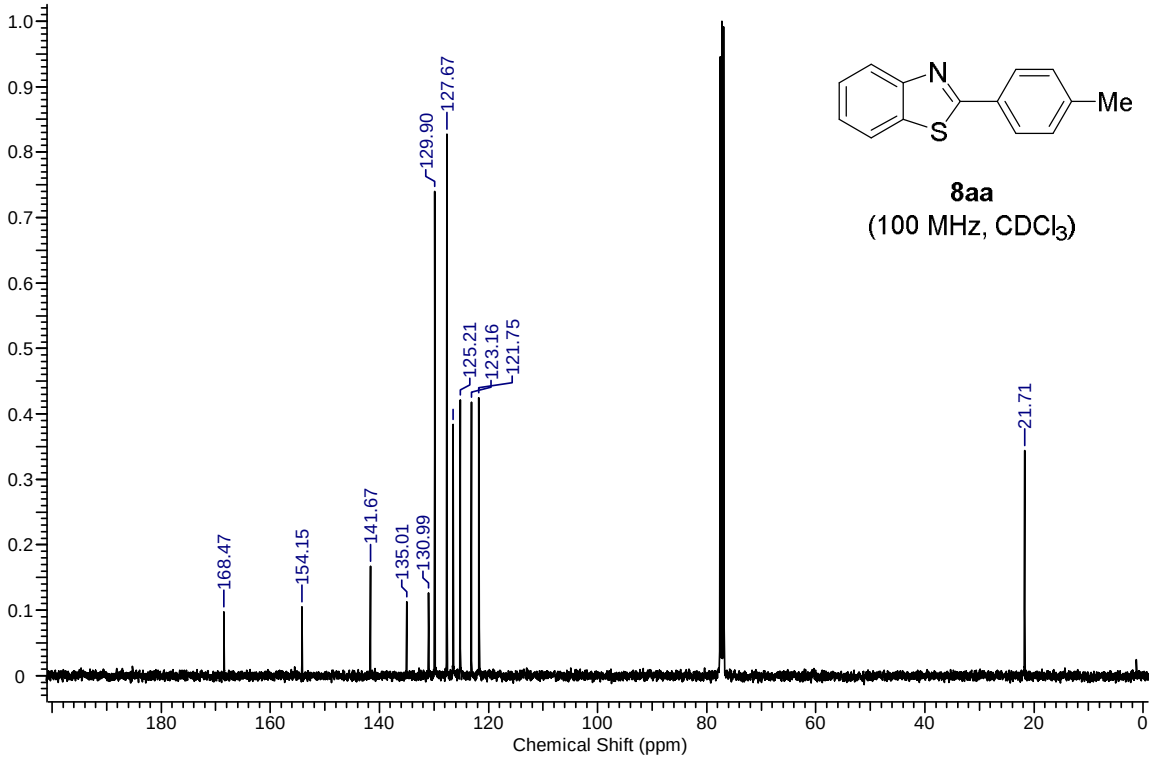


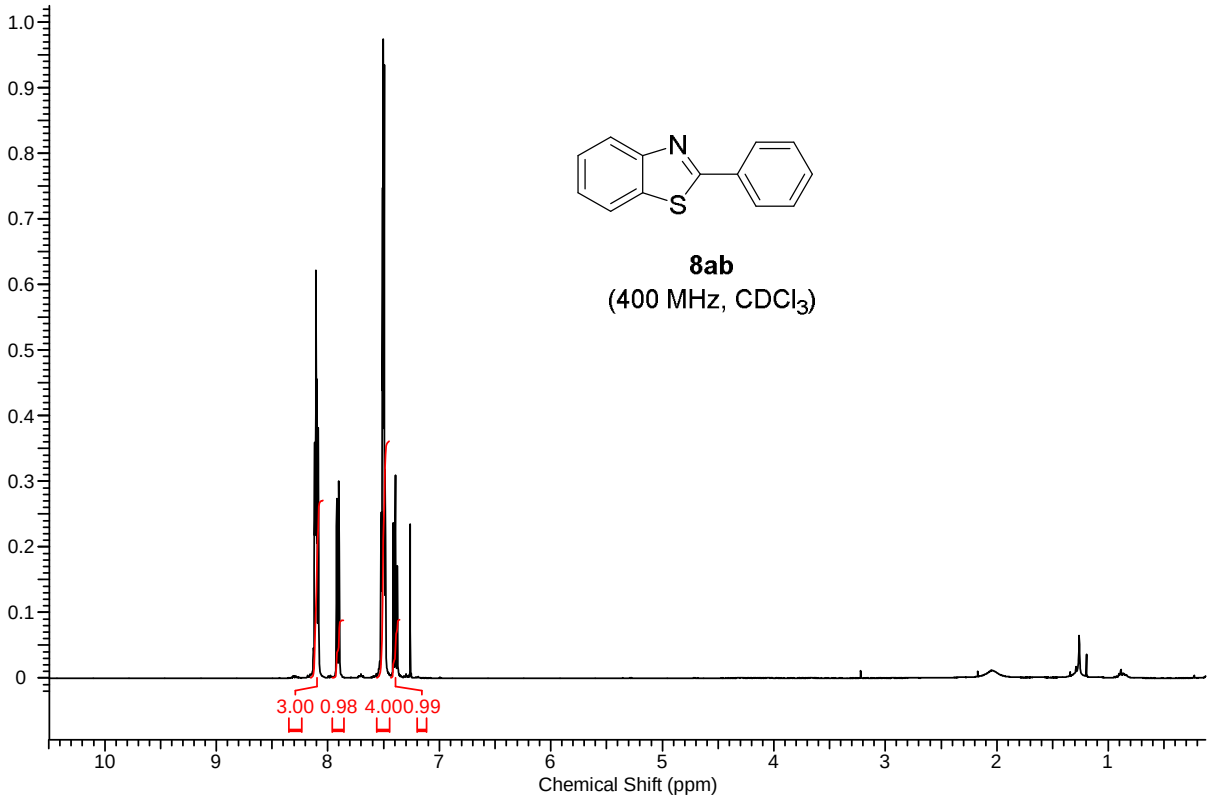
8.2. ^{31}P NMR spectra of (^{iPr2}POCN^{iPr2})Pd-species in presence of CuOAc during catalysis.

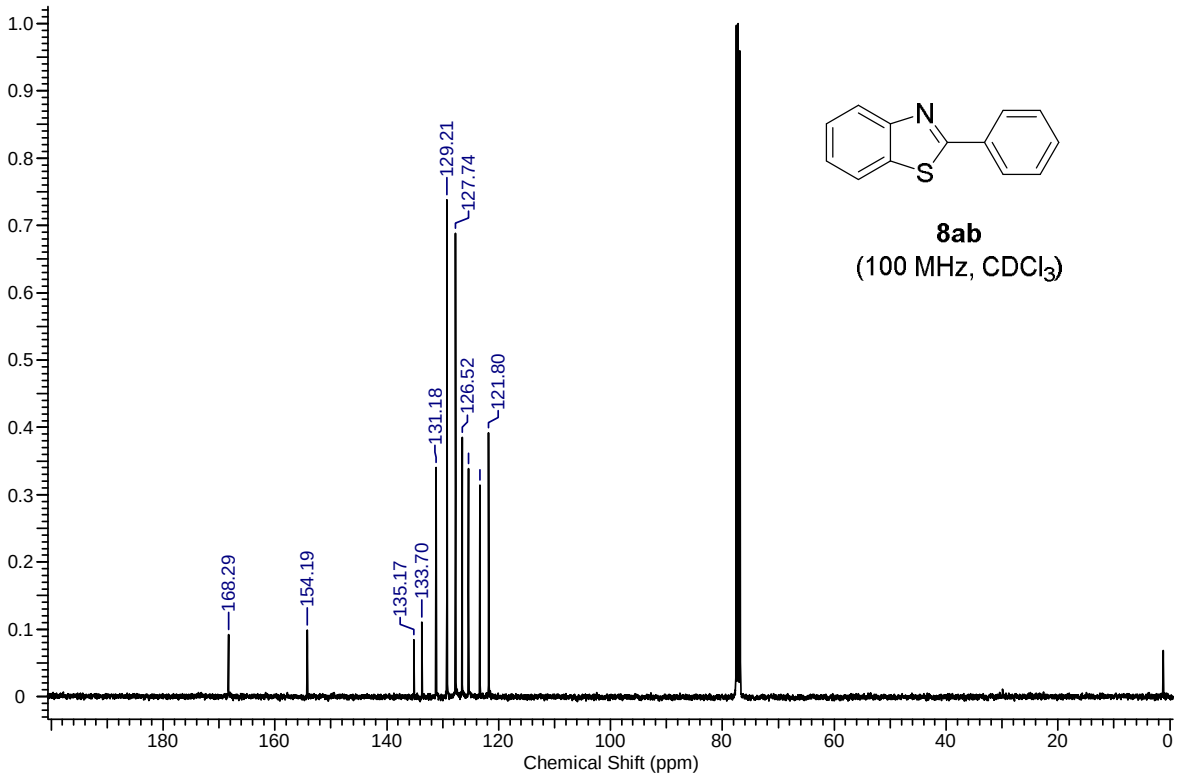


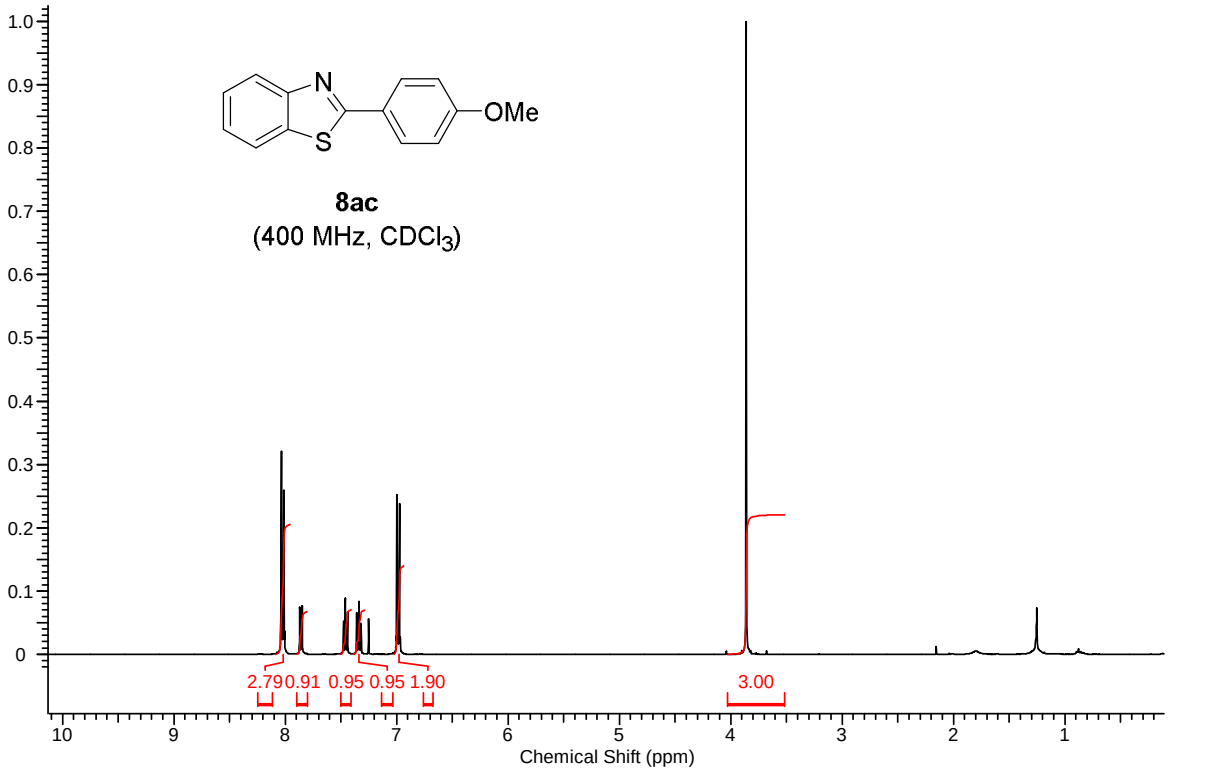
9. ^{1}H and ^{13}C NMR spectra of compounds 8

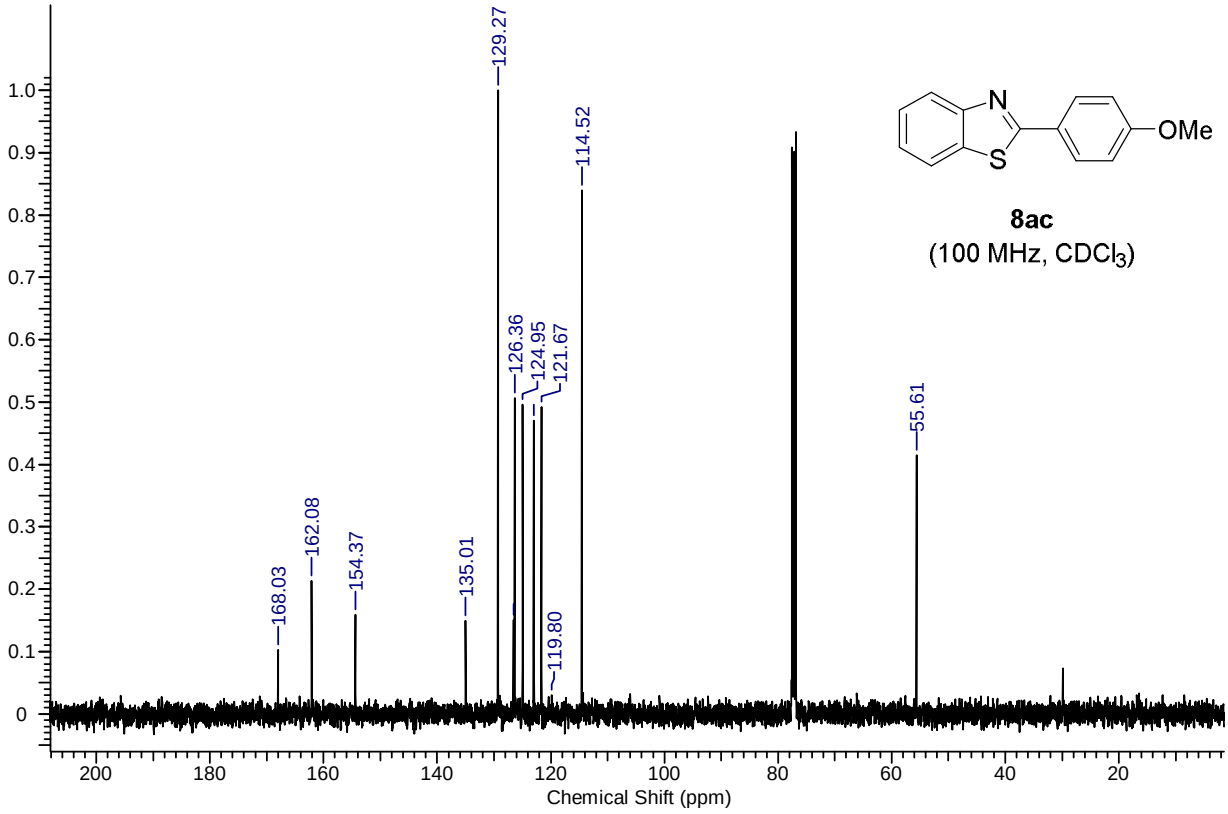


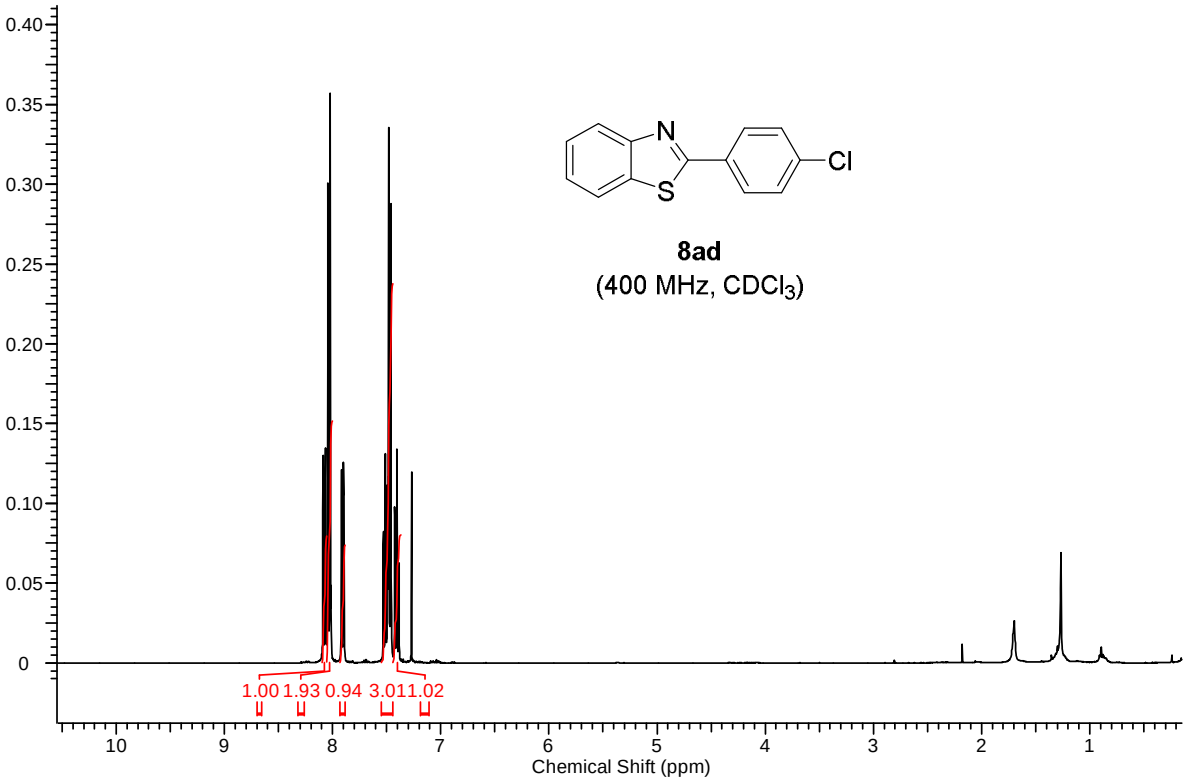


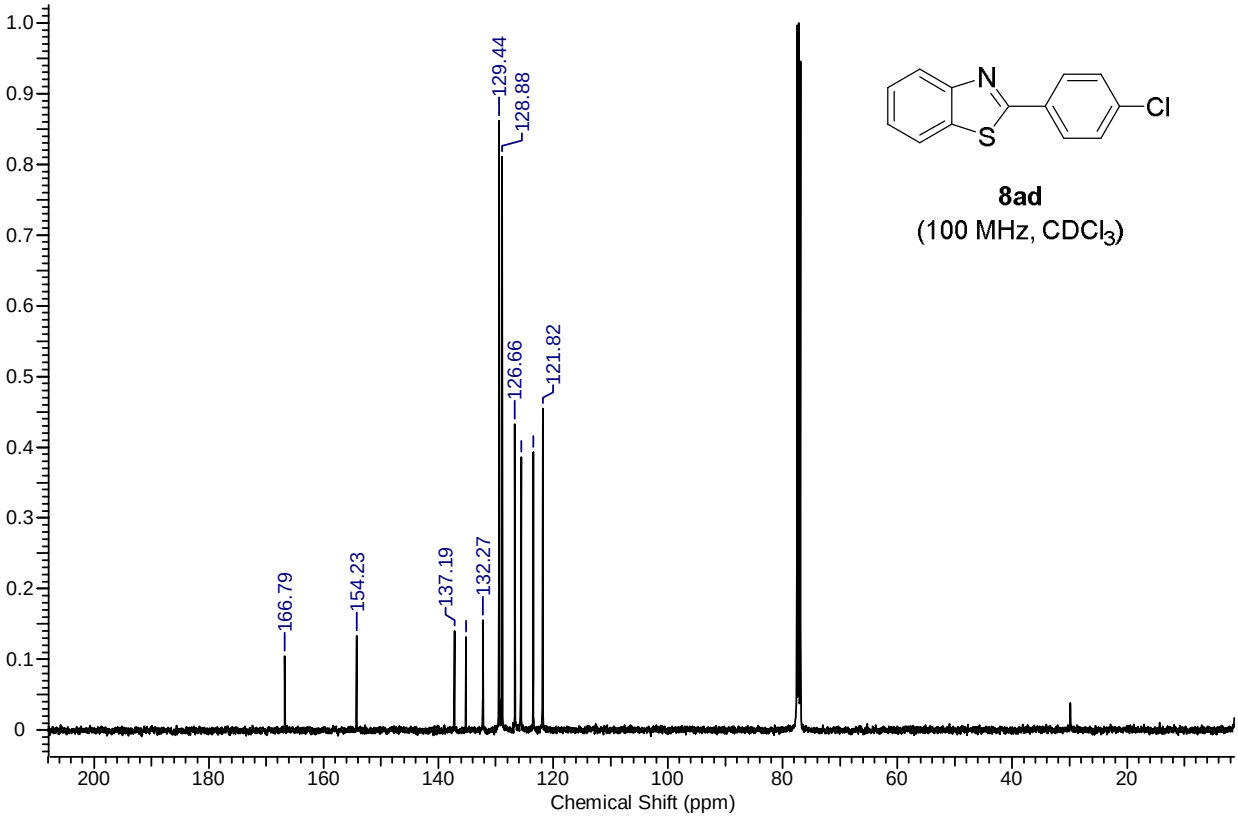

N
S
8ab
(400 MHz, CDCl3)
3.00 0.98 4.000.99
Chemical Shift (ppm)

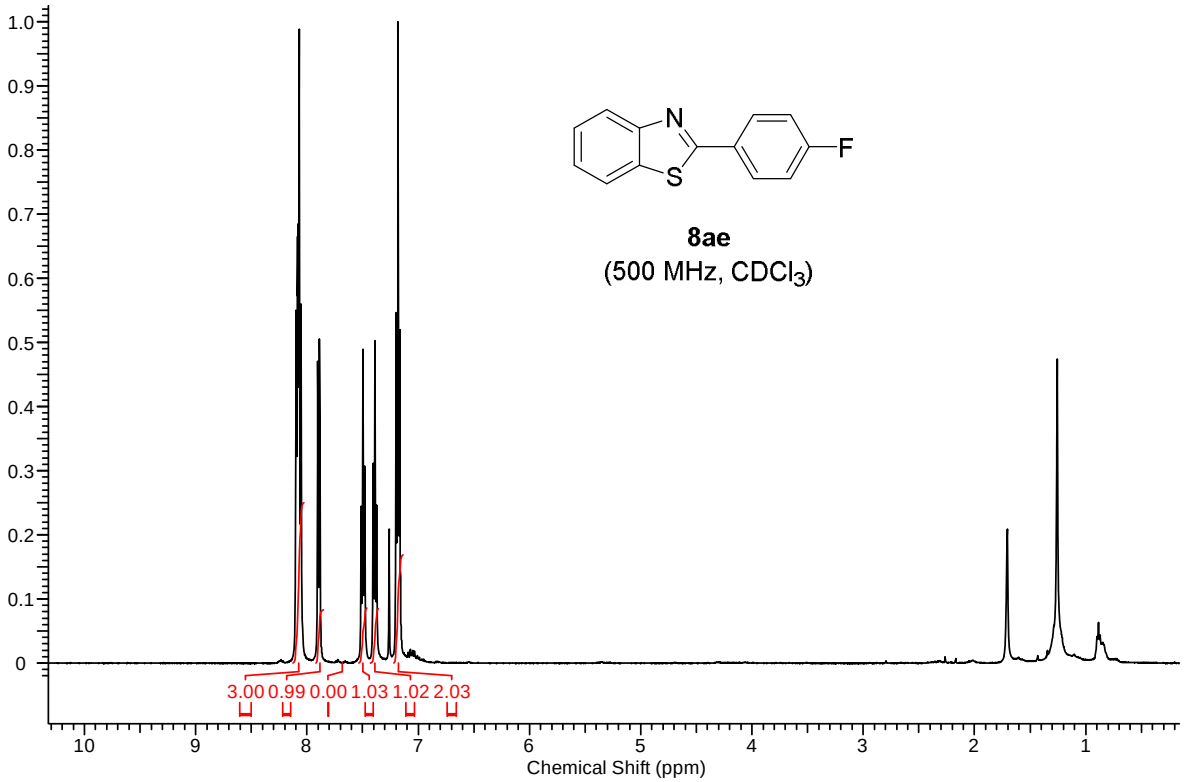

N
S
8ab
(100 MHz, CDCl3)
168.29
154.19
135.17
133.70
131.18
129.21
127.74
126.52
121.80
Chemical Shift (ppm)

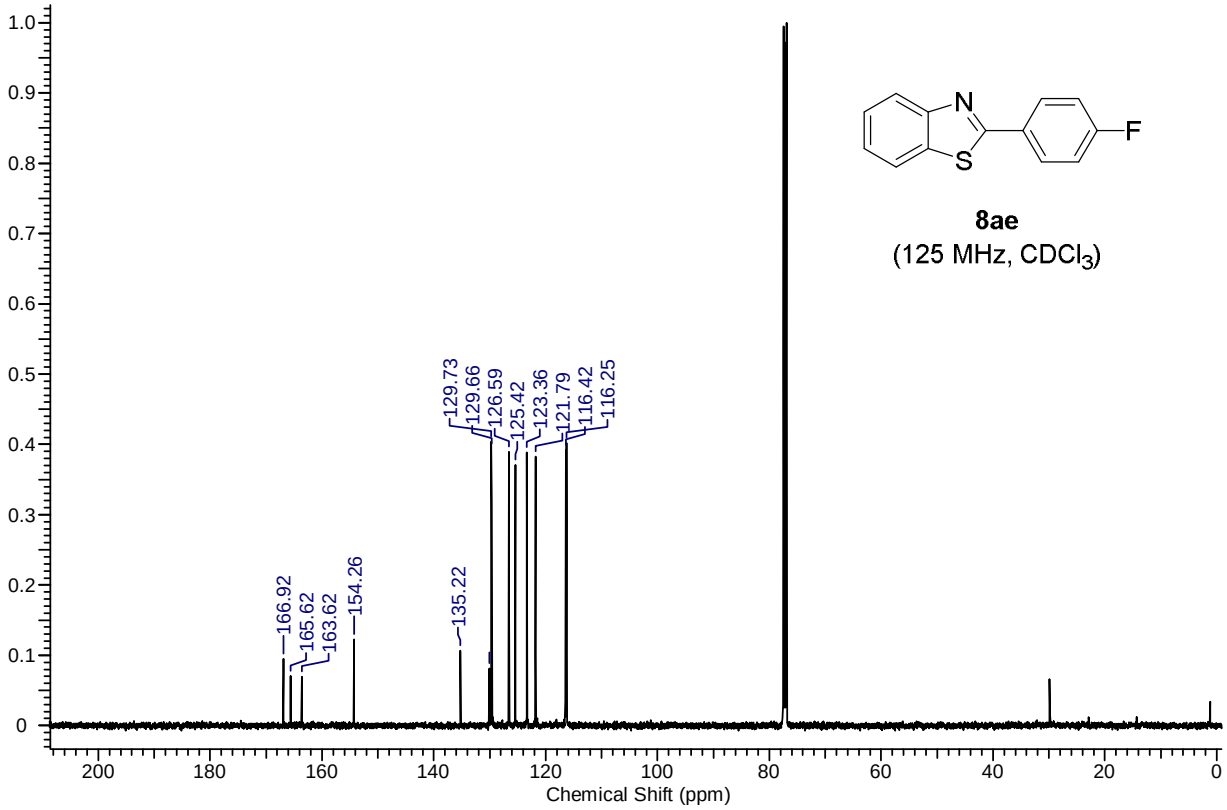

N
S
OMe
8ac
(400 MHz, CDCl3)
2.79
0.91
0.95
0.95
1.90
3.00
Chemical Shift (ppm)

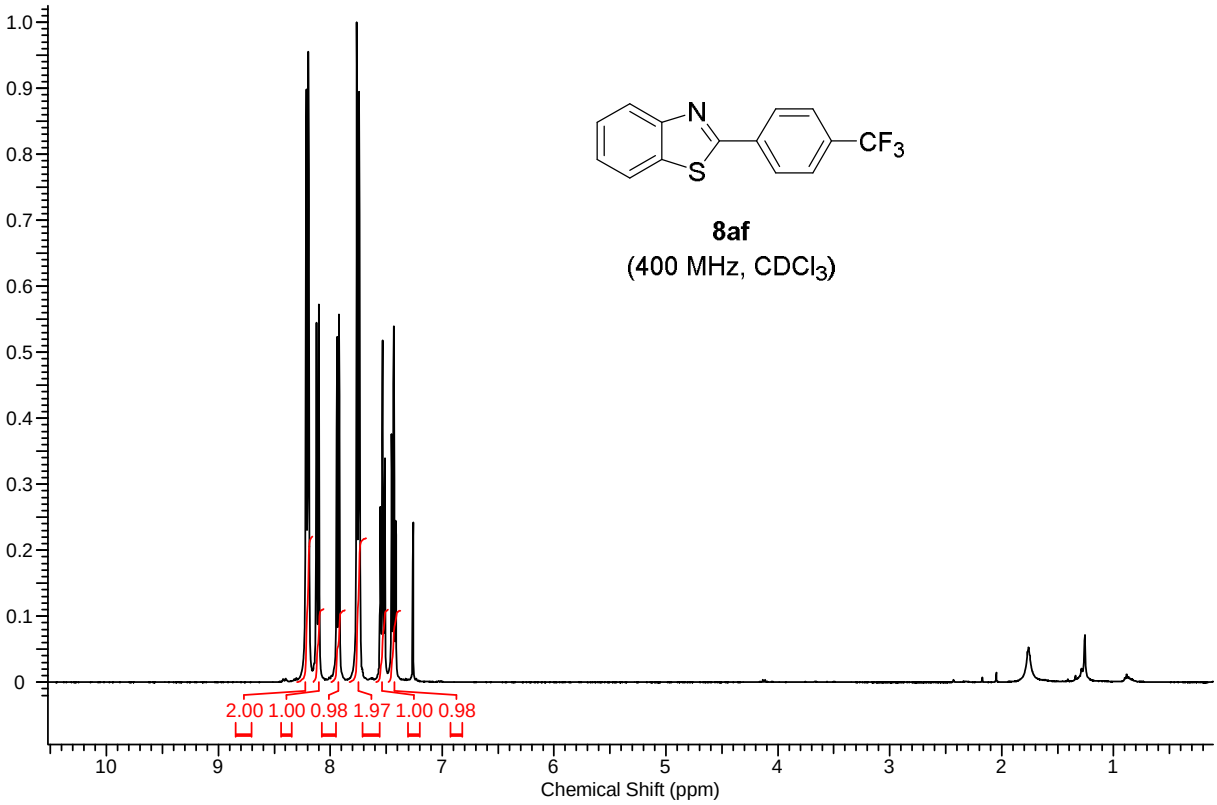

129.27
114.52
126.36
124.95
121.67
55.61
168.03
162.08
154.37
135.01
119.80
N
S
OMe
8ac
(100 MHz, CDCl3)
Chemical Shift (ppm)

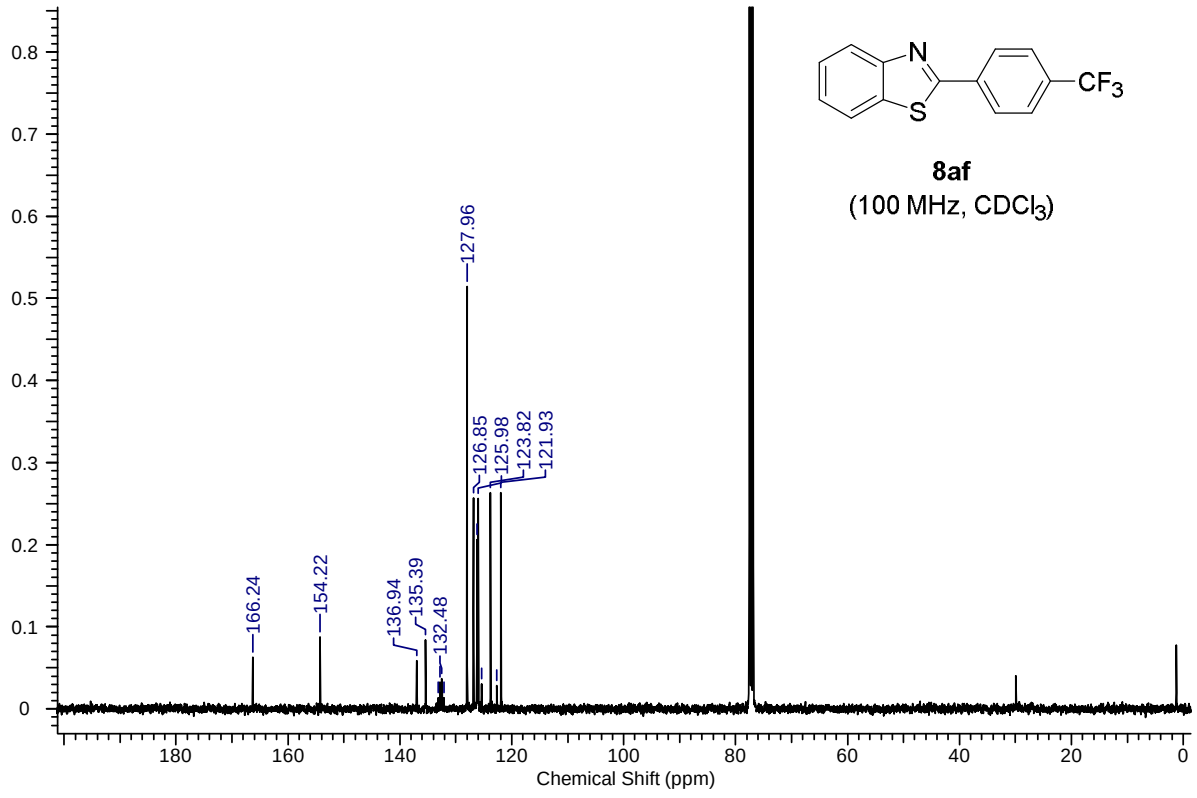

N
S
Cl
8ad
(400 MHz, CDCl3)
1.00 1.93 0.94 3.01 1.02
Chemical Shift (ppm)

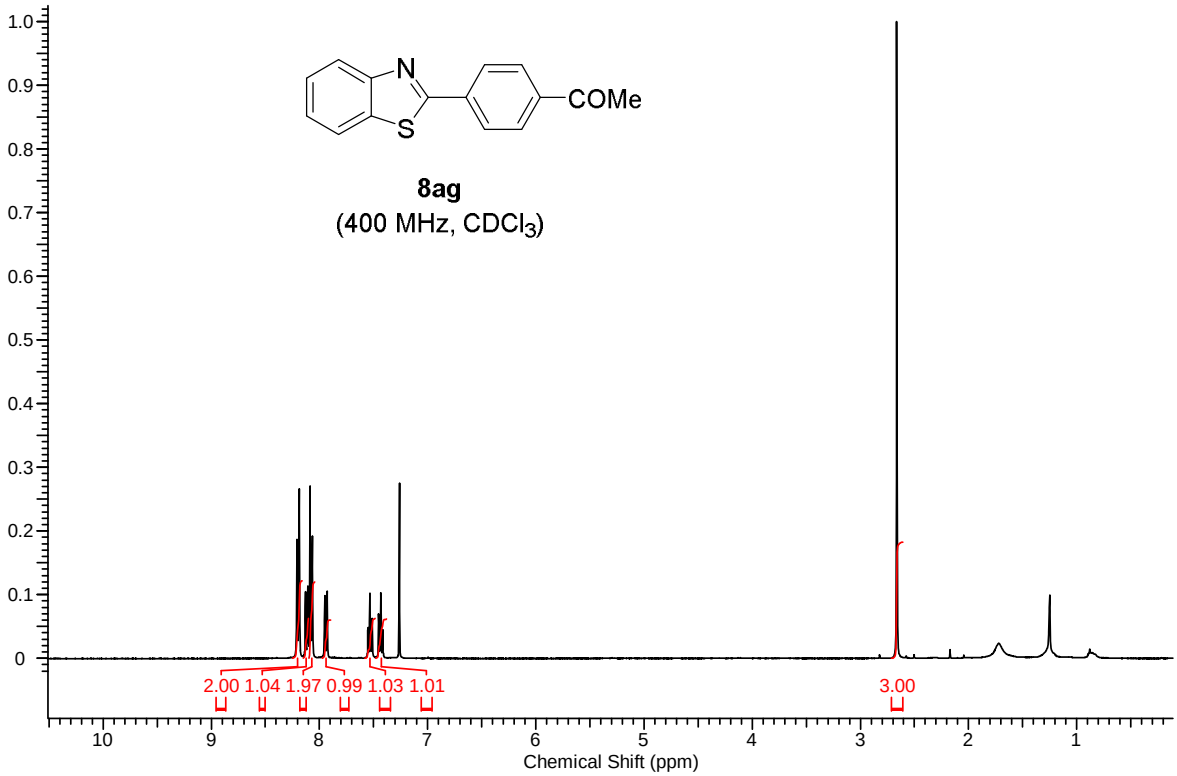

129.44
128.88
126.66
121.82
166.79
154.23
137.19
132.27
N
S
Cl
8ad
(100 MHz, CDCl3)
Chemical Shift (ppm)

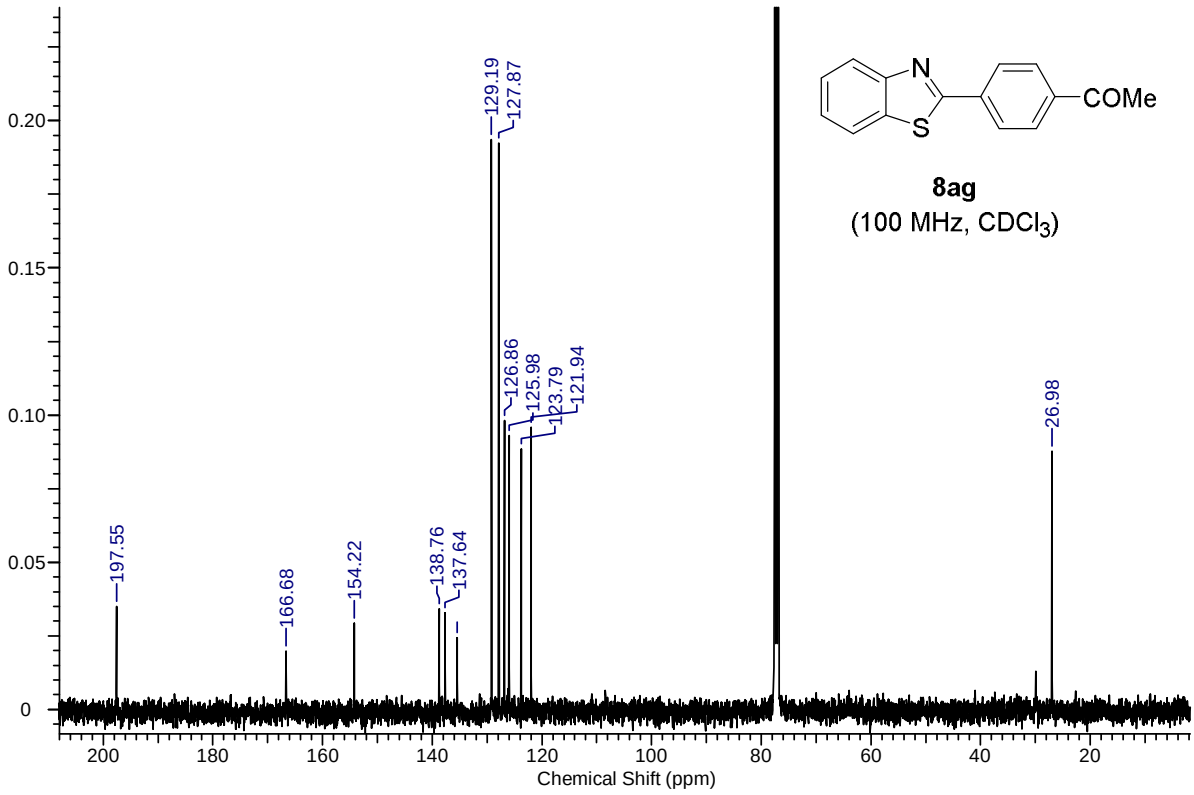

N
S
F
8ae
(500 MHz, CDCl3)
3.00 0.99 0.00 1.03 1.02 2.03
Chemical Shift (ppm)

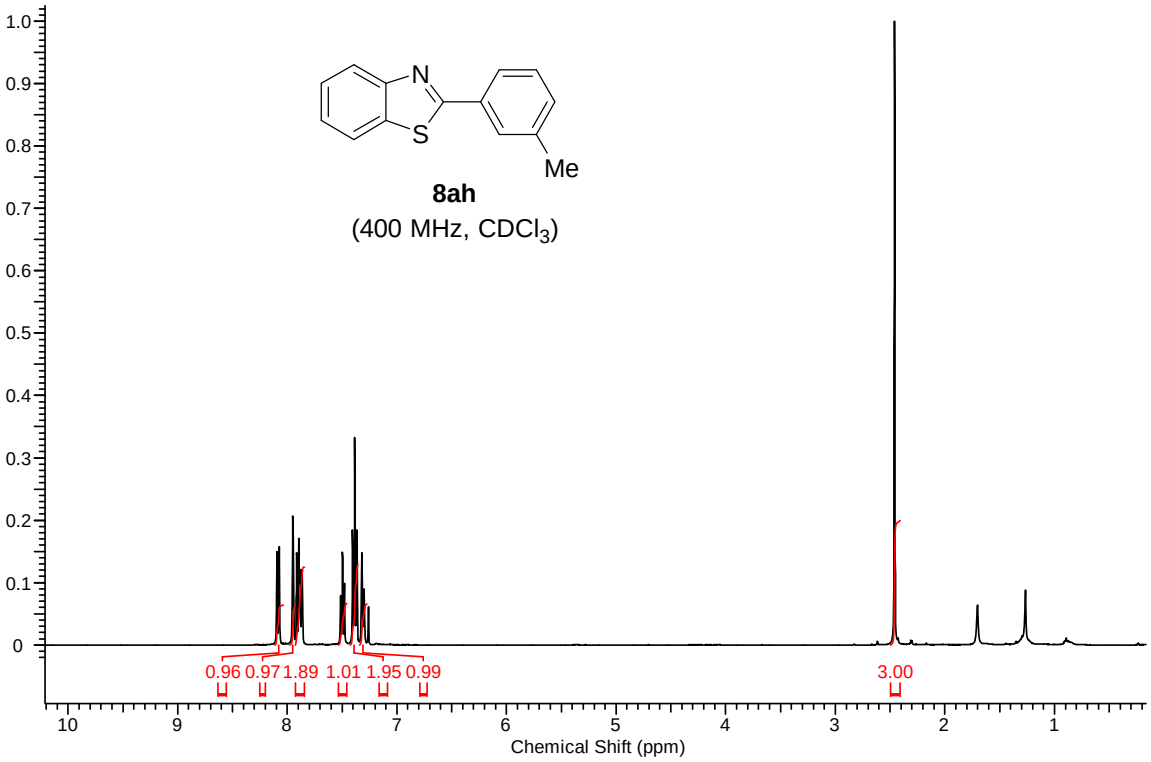

N
S
F
8ae
(125 MHz, CDCl3)
166.92
165.62
163.62
154.26
135.22
129.73
129.66
126.59
125.42
123.36
121.79
116.42
116.25
Chemical Shift (ppm)

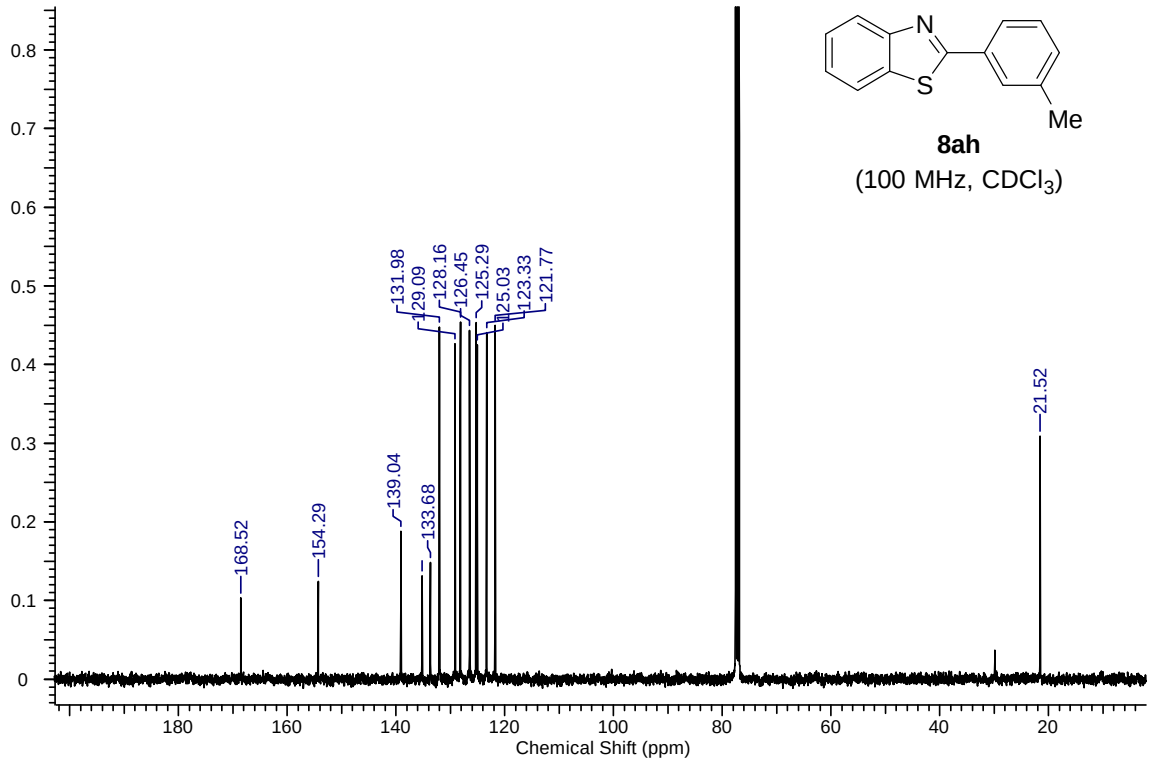

N
S
CF3
8af
(400 MHz, CDCl3)
2.00 1.00 0.98 1.97 1.00 0.98
Chemical Shift (ppm)

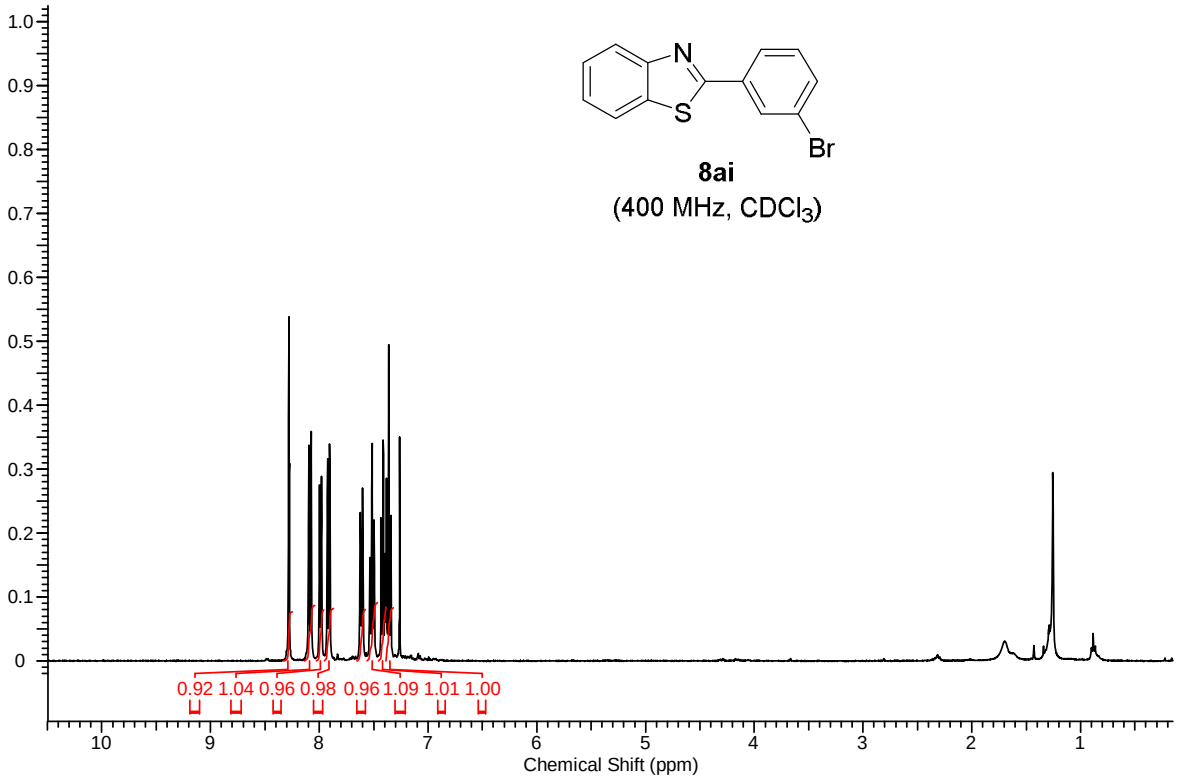

N
S
CF3
8af
(100 MHz, CDCl3)
166.24
154.22
136.94
135.39
132.48
127.96
126.85
125.98
123.82
121.93
Chemical Shift (ppm)

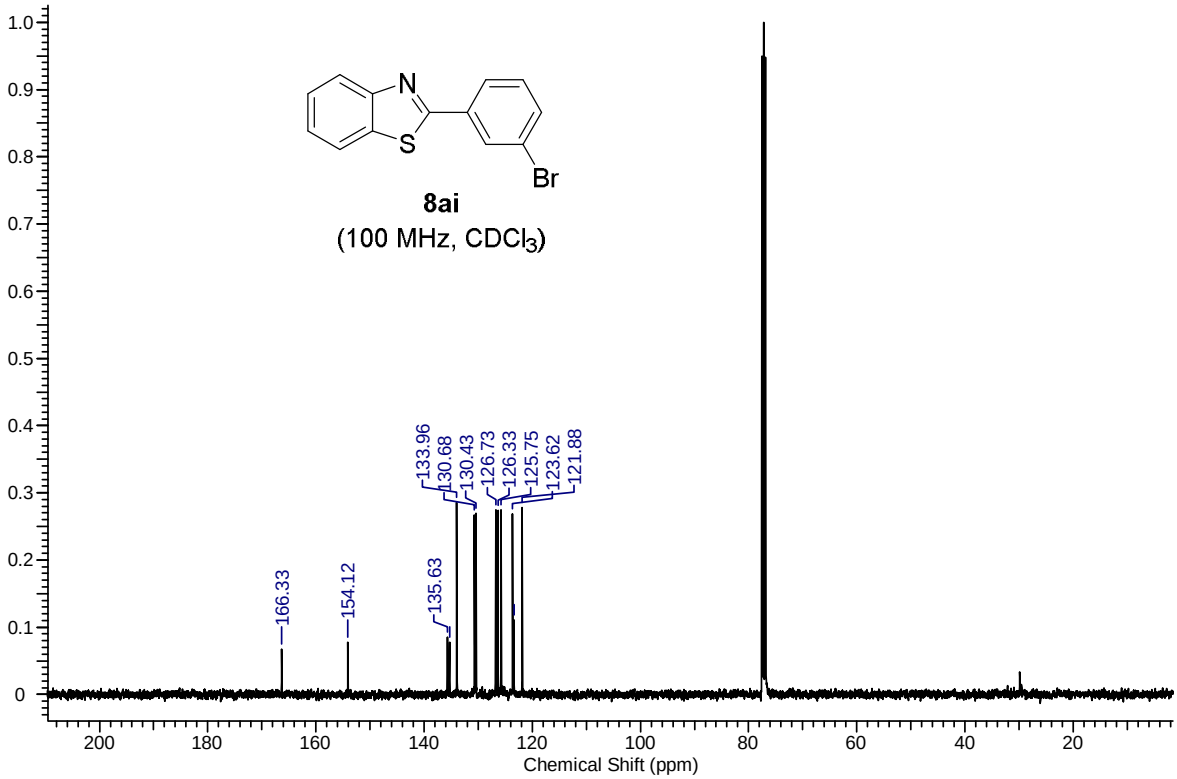

N
S
COMe
8ag
(400 MHz, CDCl3)
2.00 1.04 1.97 0.99 1.03 1.01
3.00
Chemical Shift (ppm)

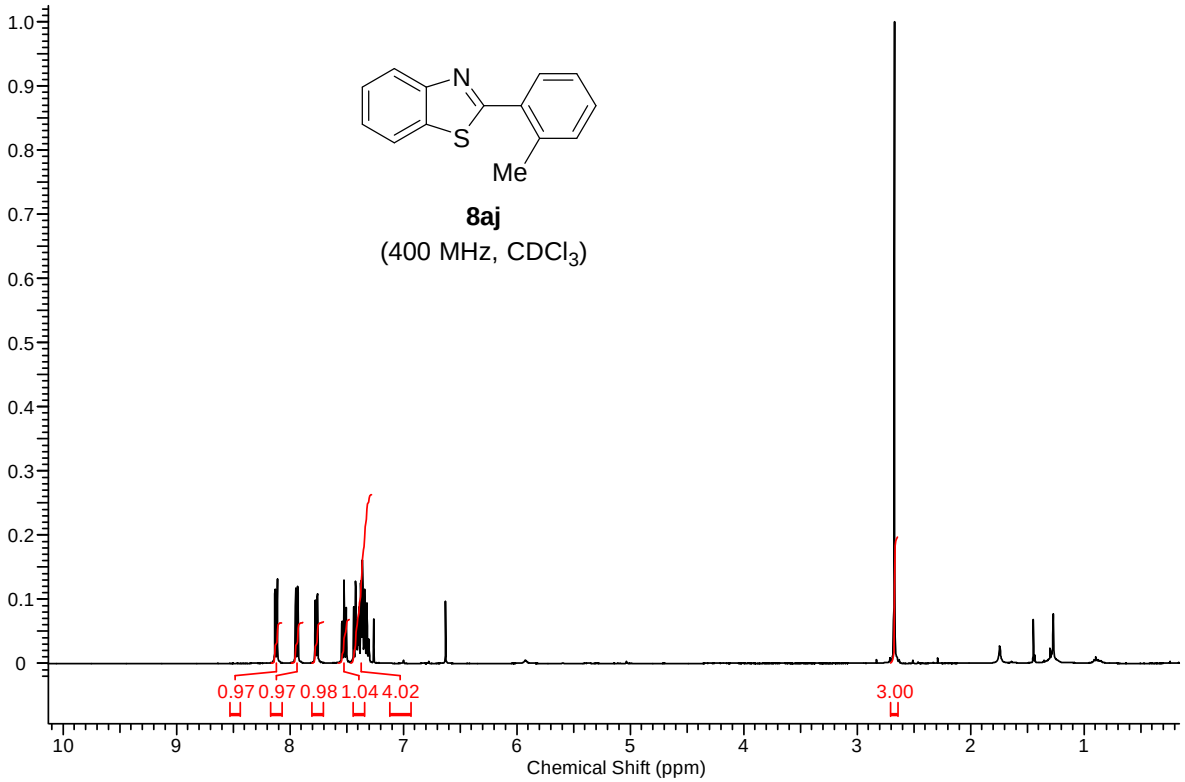

N
S
COMe
8ag
(100 MHz, CDCl3)
197.55
166.68
154.22
138.76
137.64
129.19
127.87
126.86
125.98
123.79
121.94
26.98
Chemical Shift (ppm)

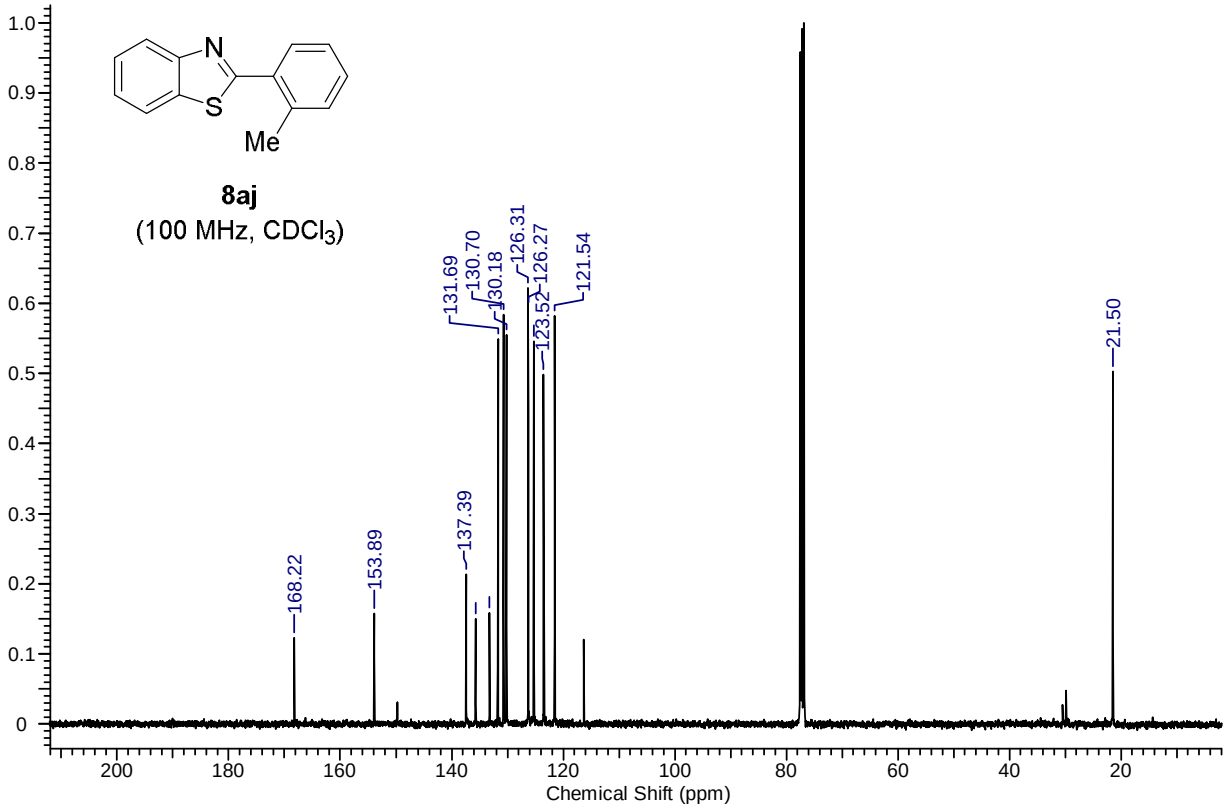

N
S
Me
8ah
(400 MHz, CDCl3)
0.96 0.97 1.89 1.01 1.95 0.99
3.00
Chemical Shift (ppm)

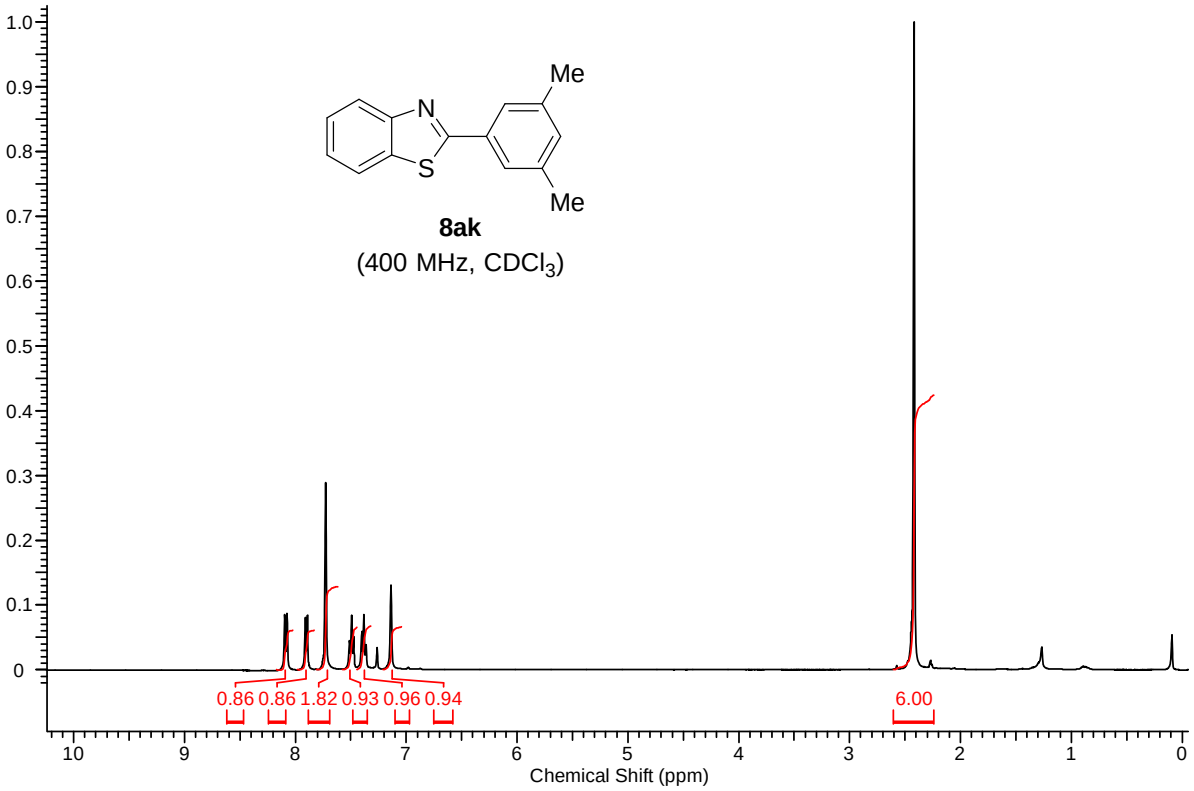

N
S
Me
8ah
(100 MHz, CDCl3)
131.98
129.09
128.16
126.45
125.29
125.03
123.33
121.77
139.04
133.68
168.52
154.29
21.52
Chemical Shift (ppm)

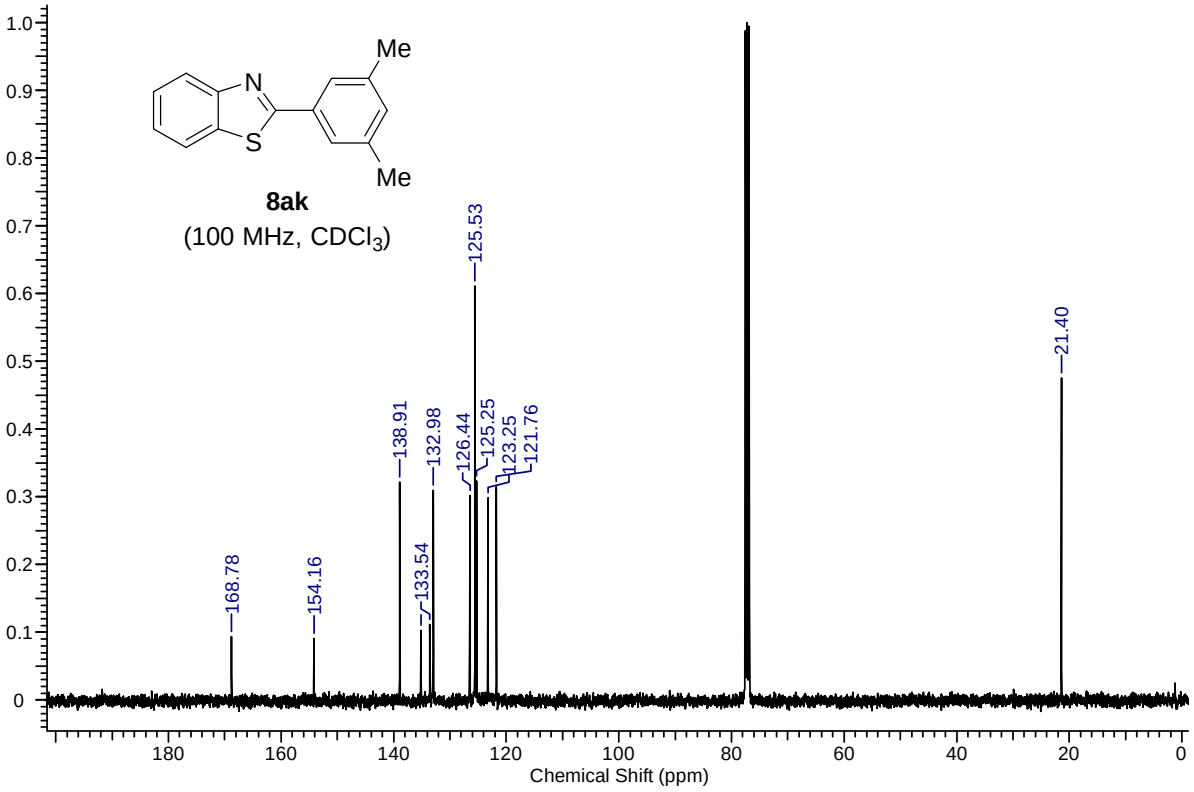

N
S
Br
8ai
(400 MHz, CDCl3)
0.92 1.04 0.96 0.98 0.96 1.09 1.01 1.00
Chemical Shift (ppm)

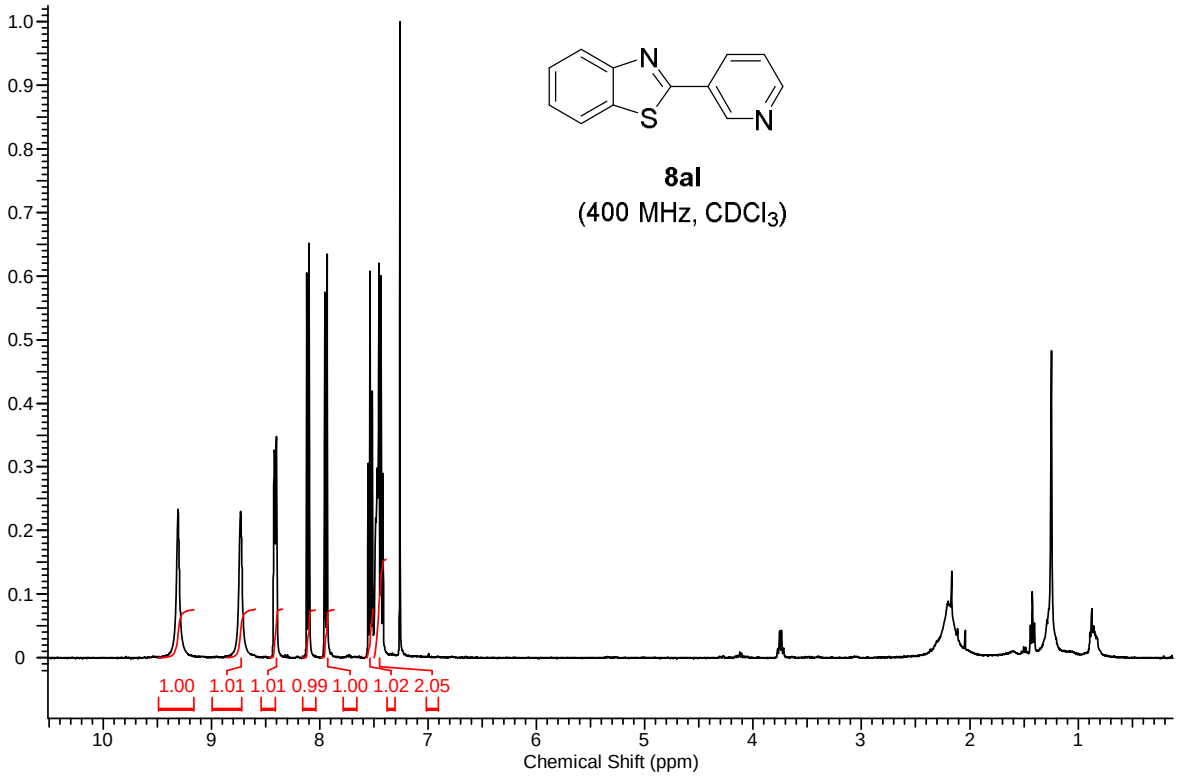

N
S
Br
8ai
(100 MHz, CDCl3)
166.33
154.12
135.63
133.96
130.68
130.43
126.73
126.33
125.75
123.62
121.88
Chemical Shift (ppm)

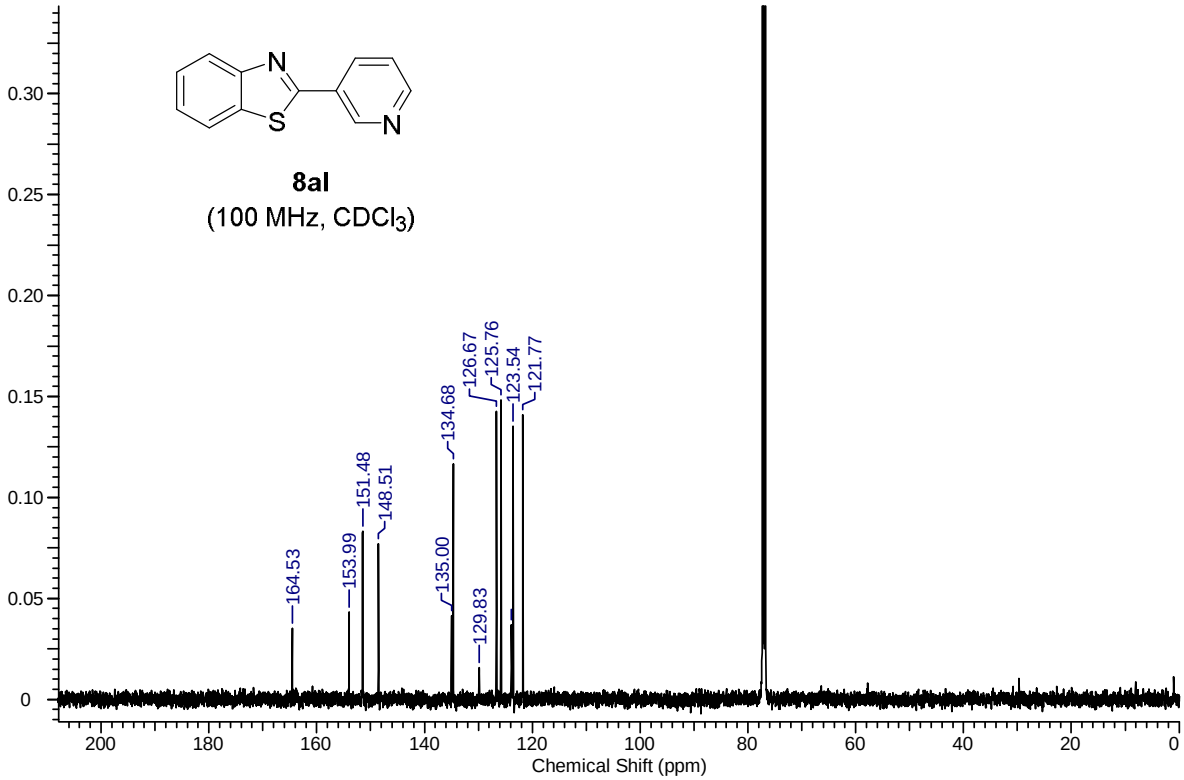

N
S
Me
8aj
(400 MHz, CDCl3)
0.97 0.97 0.98 1.04 4.02
3.00
Chemical Shift (ppm)

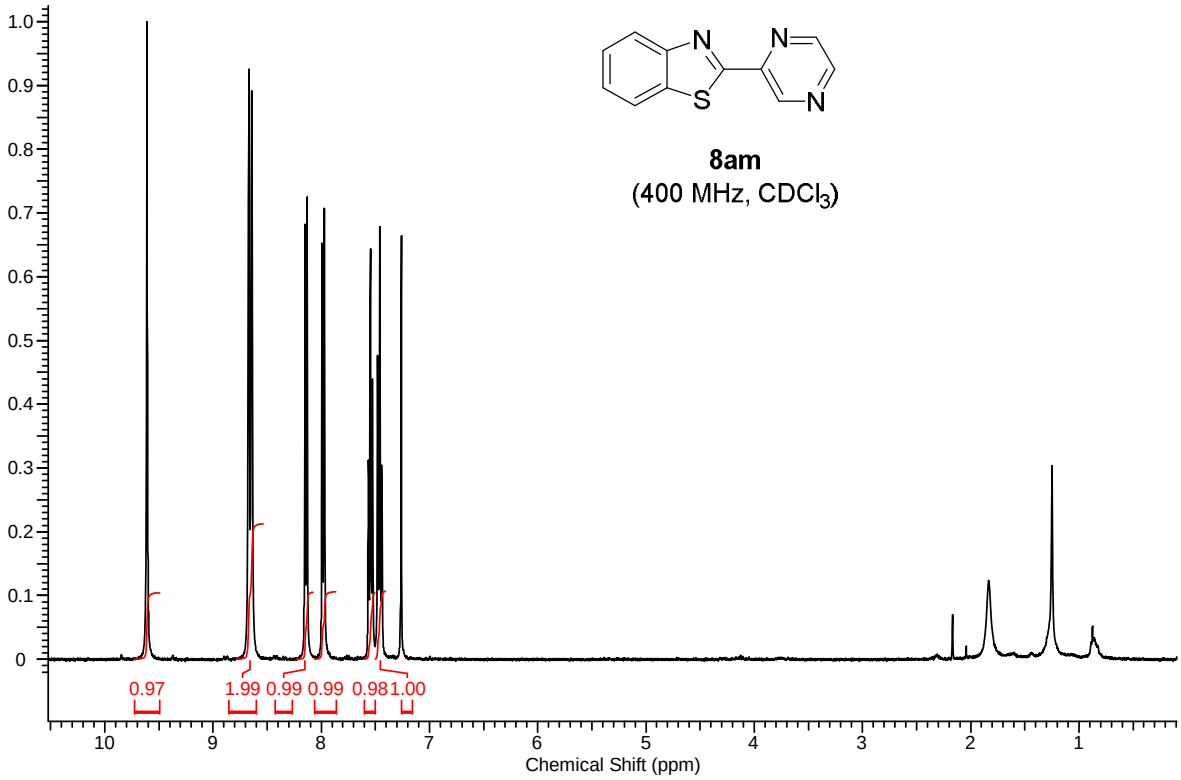

N
S
Me
8aj
(100 MHz, CDCl3)
168.22
153.89
137.39
131.69
130.70
130.18
126.31
126.27
123.52
121.54
21.50
Chemical Shift (ppm)

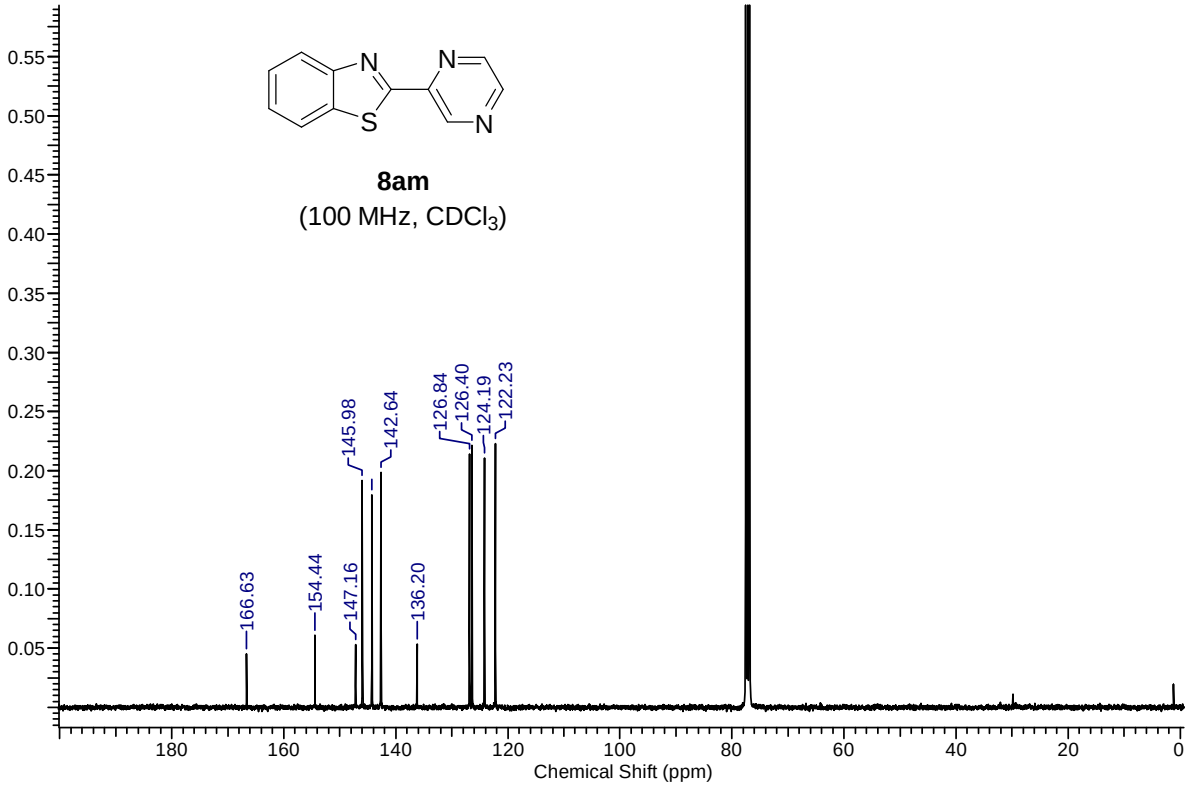

Me
N
S
Me
8ak
(400 MHz, CDCl3)
0.86 0.86 1.82 0.93 0.96 0.94
6.00
Chemical Shift (ppm)

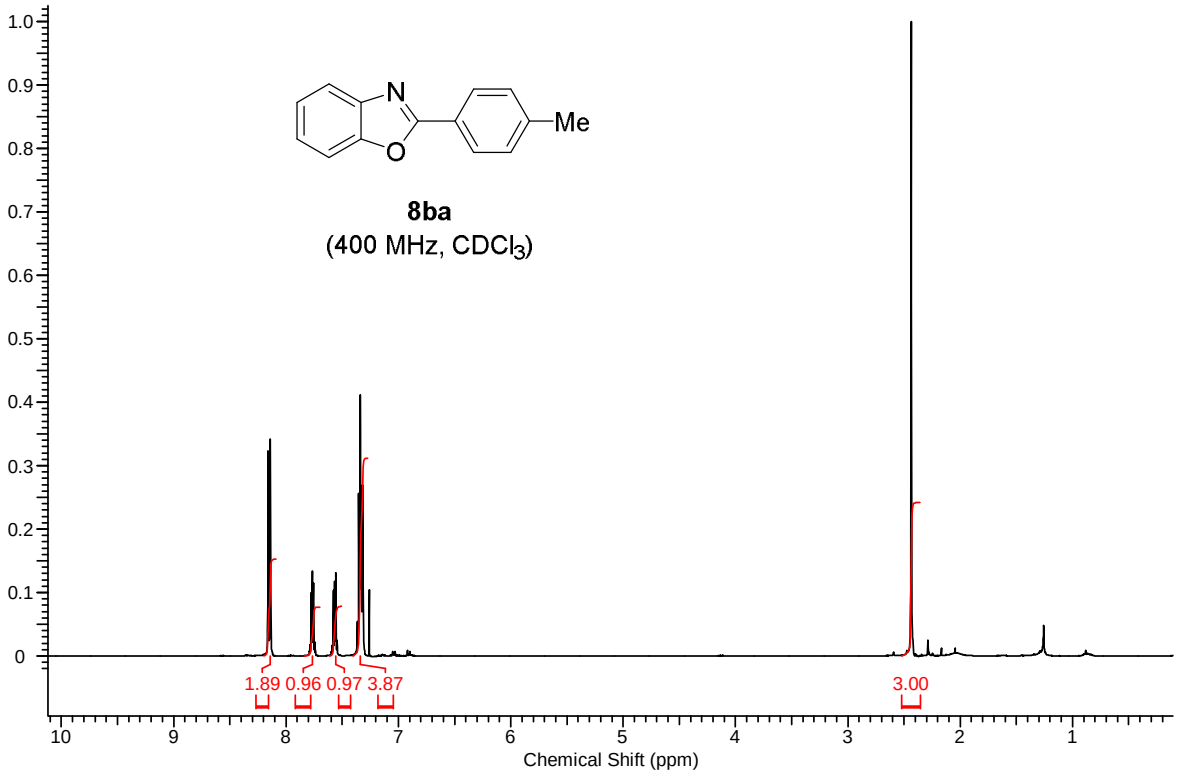

Me
N
S
Me
8ak
(100 MHz, CDCl3)
168.78
154.16
138.91
133.54
132.98
126.44
125.53
125.25
123.25
121.76
21.40
Chemical Shift (ppm)

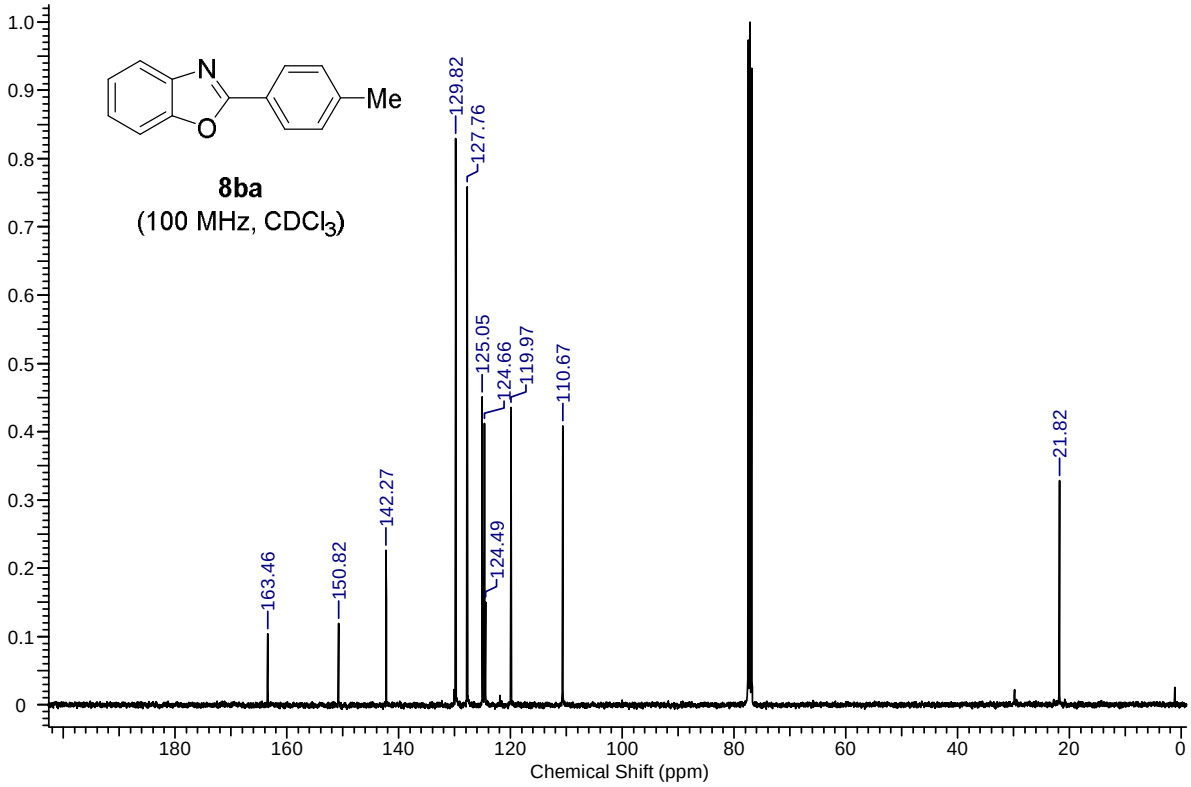

8al
(400 MHz, CDCl3)
1.00 1.01 1.01 0.99 1.00 1.02 2.05
Chemical Shift (ppm)

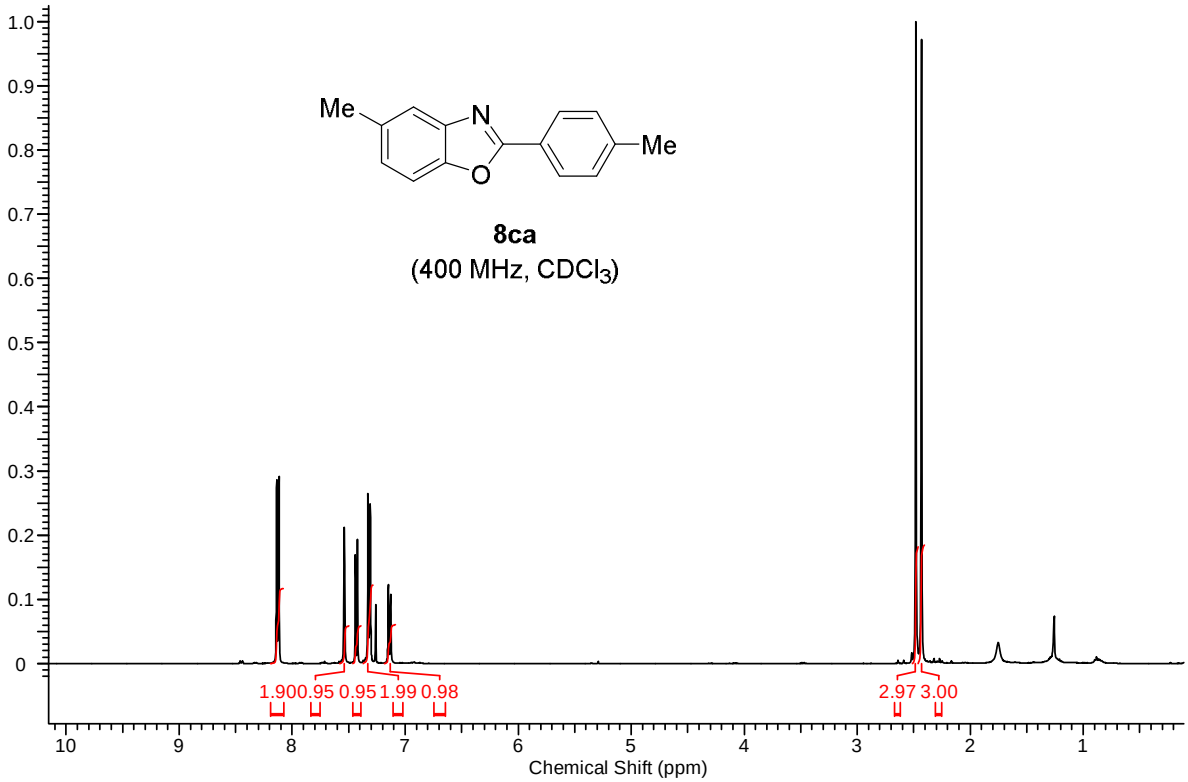

8al
(100 MHz, CDCl3)
164.53
153.99
151.48
148.51
135.00
134.68
129.83
126.67
125.76
123.54
121.77
Chemical Shift (ppm)

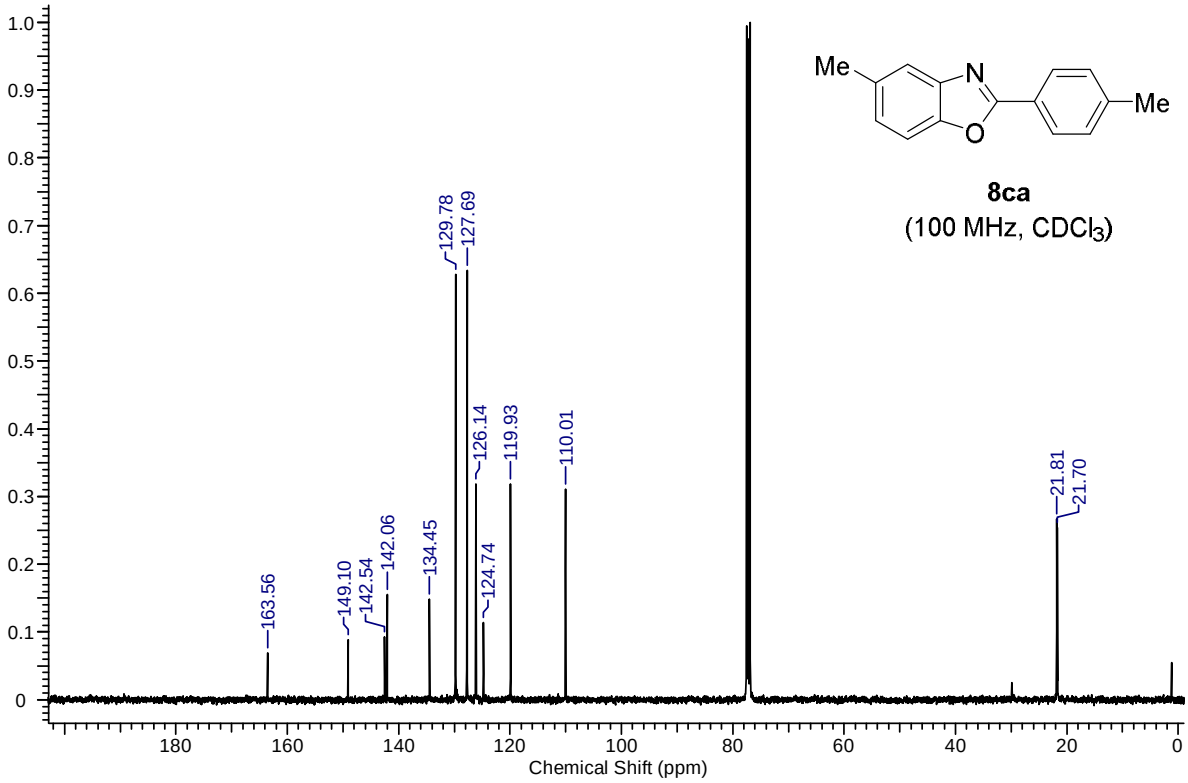

N
N
S
N
8am
(400 MHz, CDCl3)
0.97
1.99
0.99
0.99
0.98
1.00
Chemical Shift (ppm)


N
N
S
N
8am
(100 MHz, CDCl3)
166.63
154.44
147.16
145.98
142.64
136.20
126.84
126.40
124.19
122.23
Chemical Shift (ppm)

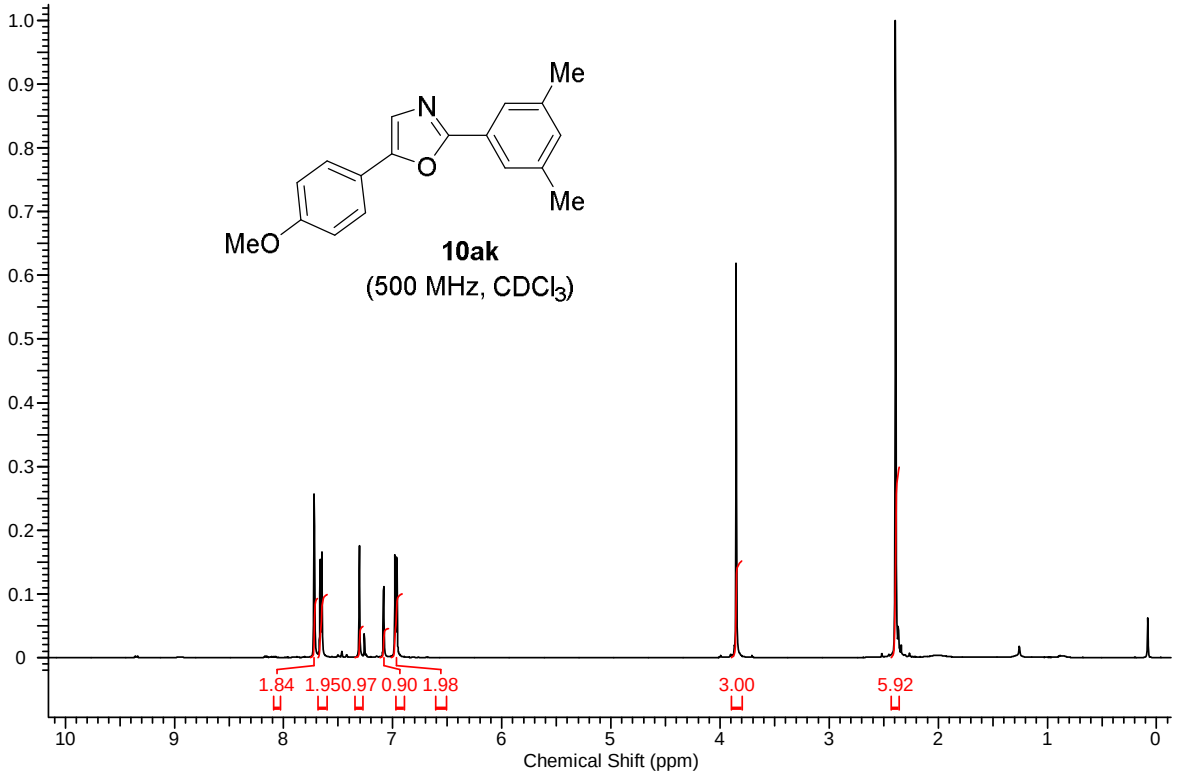

N
O
Me
8ba
(400 MHz, CDCl3)
1.89 0.96 0.97 3.87
3.00
Chemical Shift (ppm)

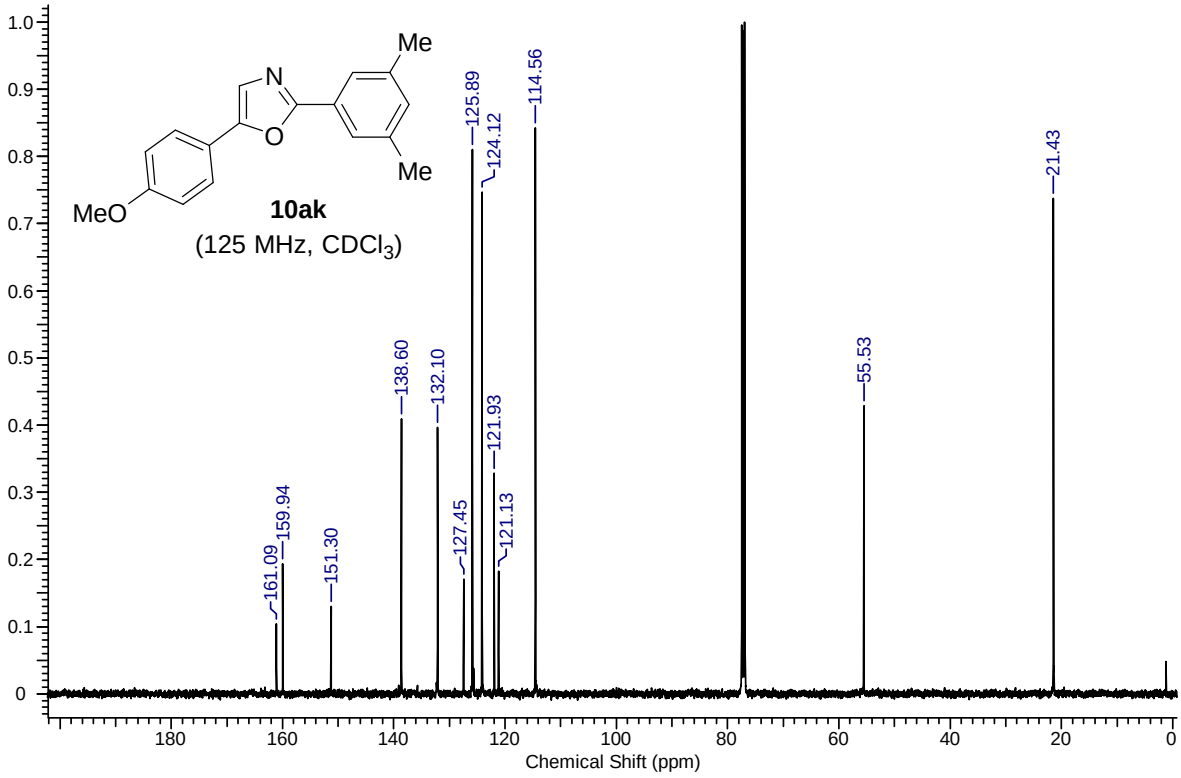

N
O
Me
8ba
(100 MHz, CDCl3)
163.46
150.82
142.27
129.82
127.76
125.05
124.66
124.49
119.97
110.67
21.82
Chemical Shift (ppm)

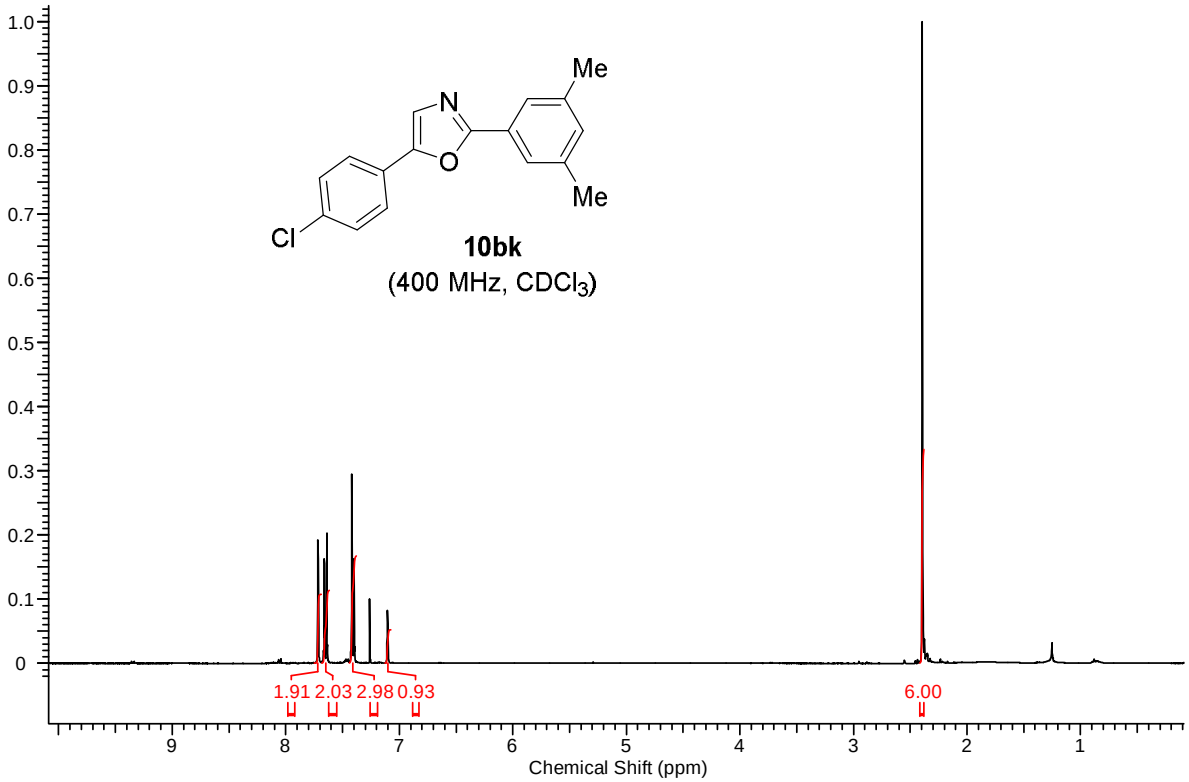

Me
N
O
Me
8ca
(400 MHz, CDCl3)
1.90 0.95 0.95 1.99 0.98
2.97 3.00
Chemical Shift (ppm)

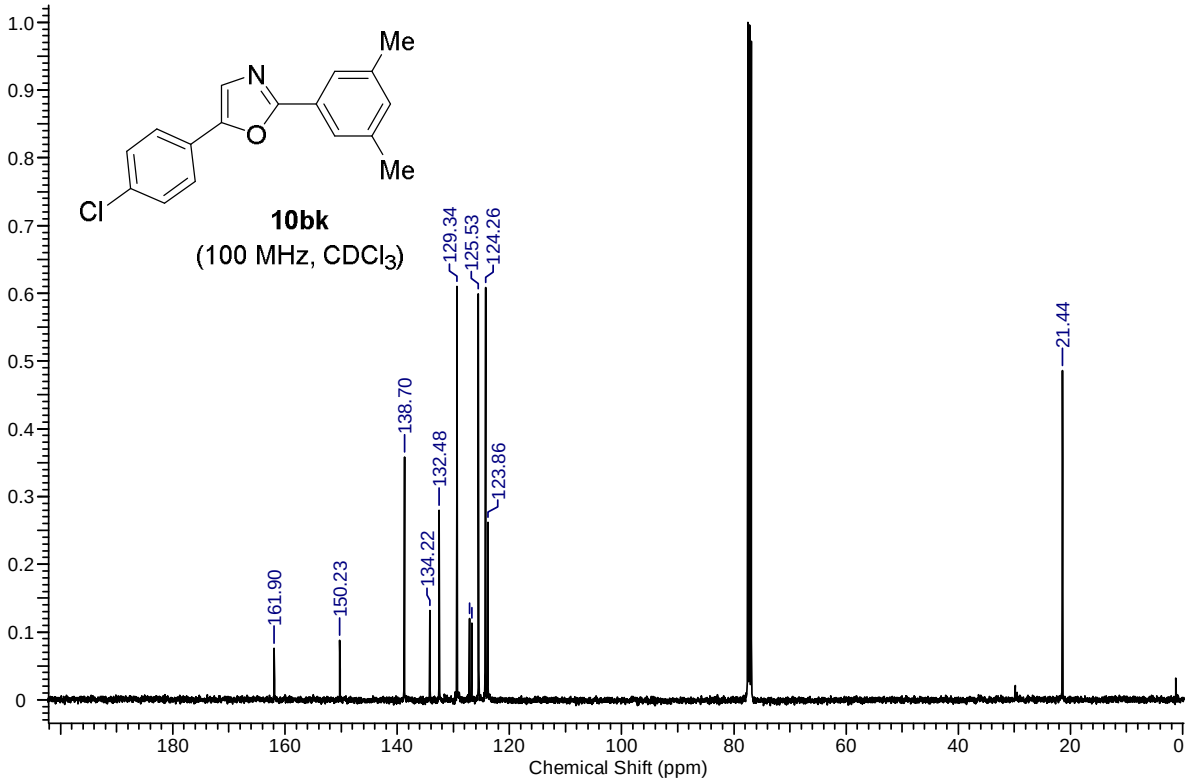

Me
N
O
Me
8ca
(100 MHz, CDCl3)
163.56
149.10
142.54
142.06
134.45
129.78
127.69
126.14
124.74
119.93
110.01
21.81
21.70
Chemical Shift (ppm)

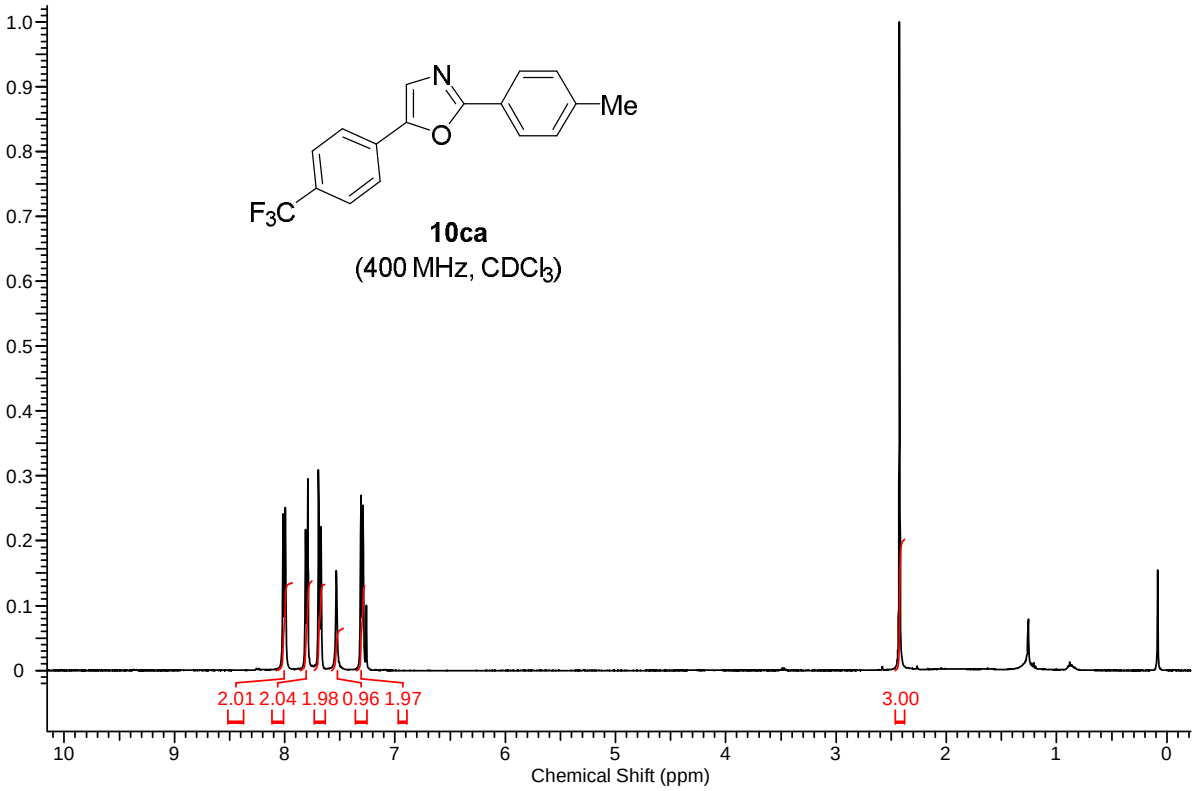
10. ^{1}H and ^{13}C NMR spectra of compounds 10

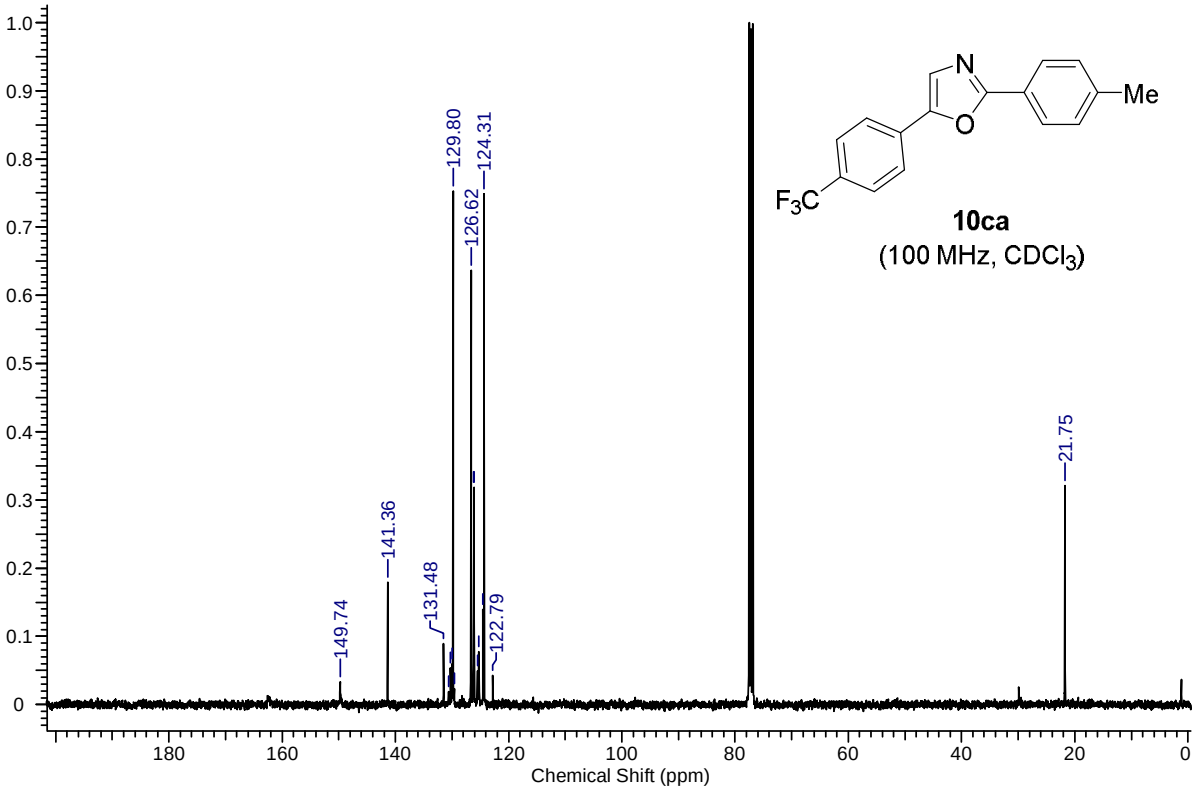


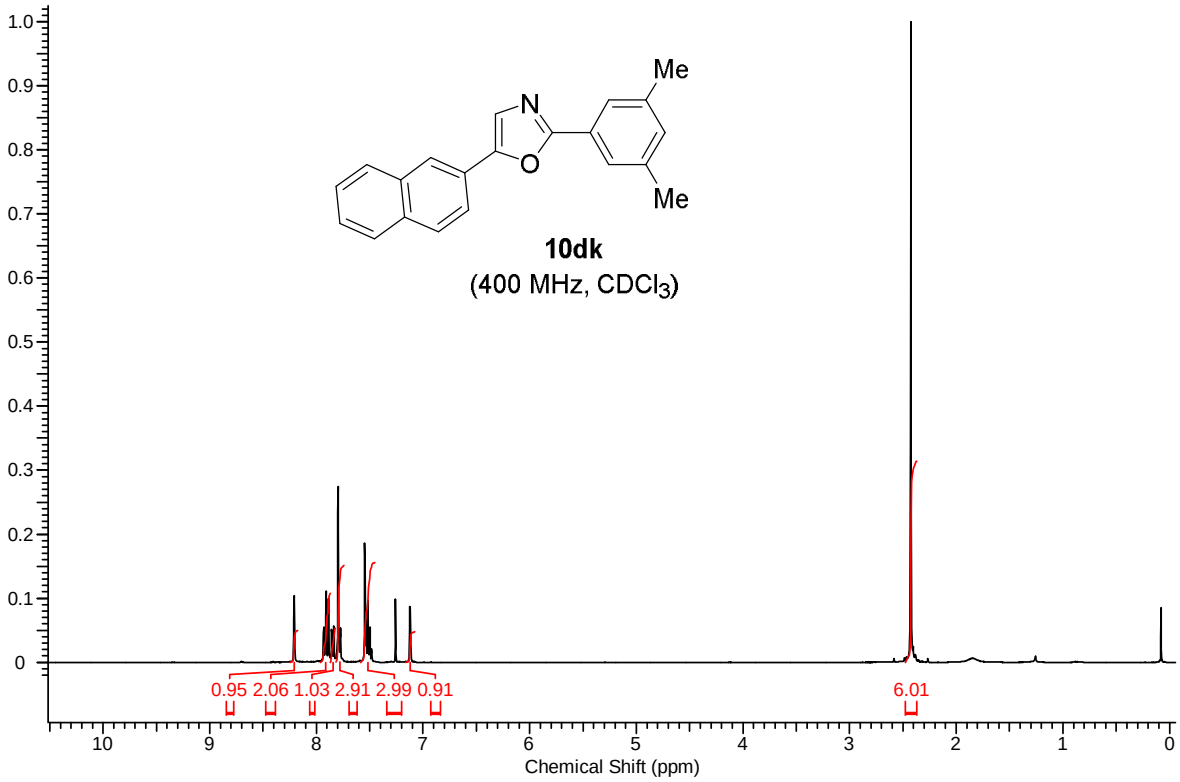


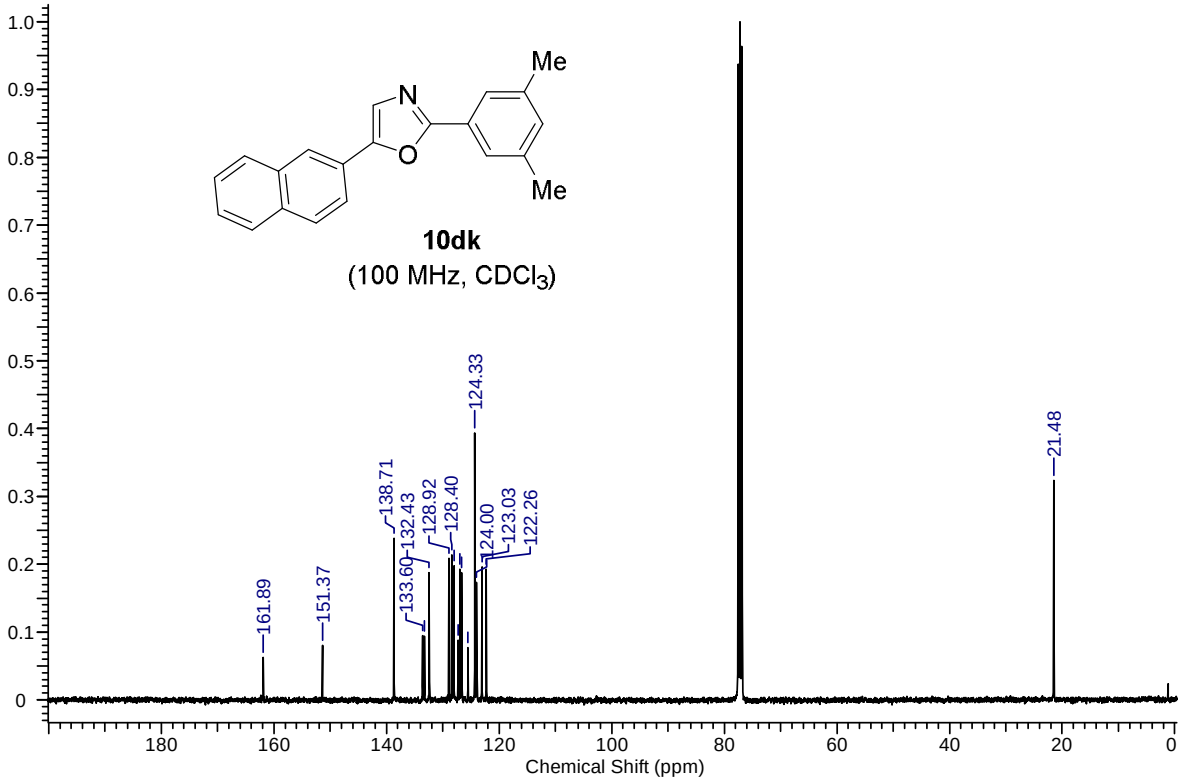

Me
N
O
Me
Cl
10bk
(400 MHz, CDCl3)
1.91
2.03
2.98
0.93
6.00
Chemical Shift (ppm)

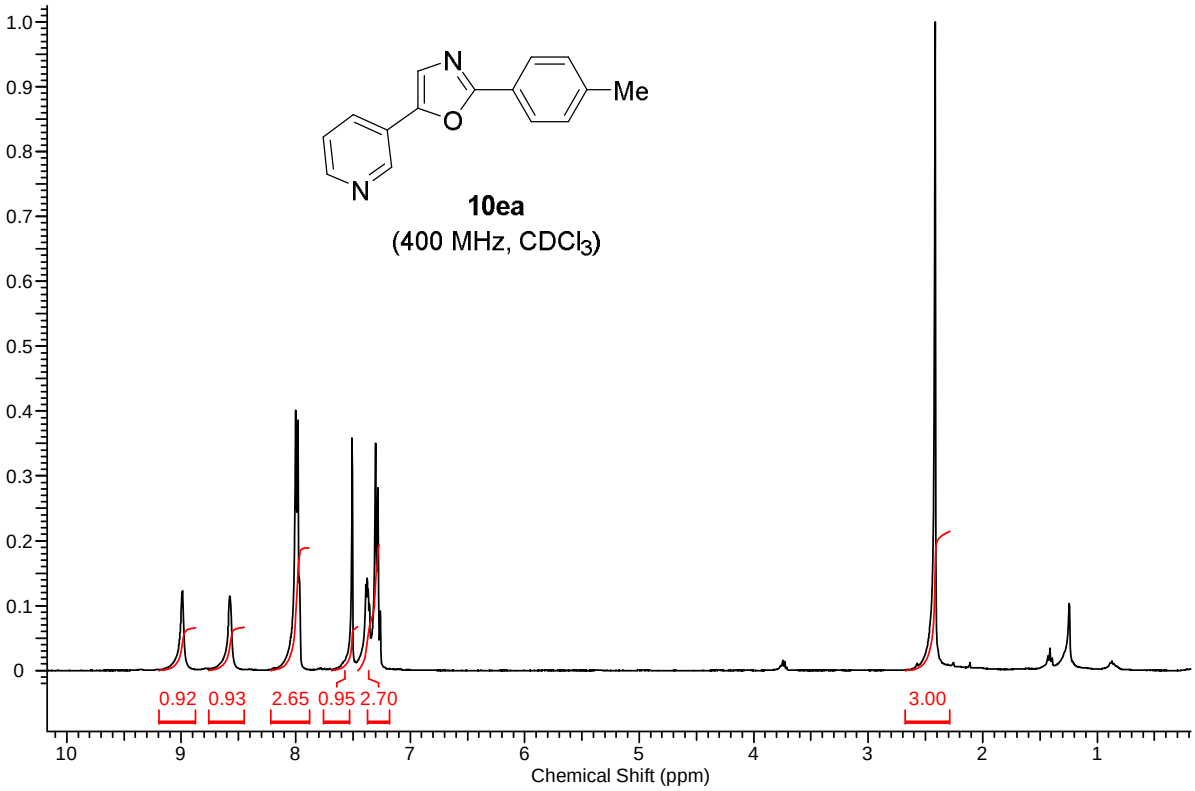

Me
N
O
Me
Cl
10bk
(100 MHz, CDCl3)
161.90
150.23
138.70
134.22
132.48
129.34
125.53
124.26
123.86
21.44
Chemical Shift (ppm)

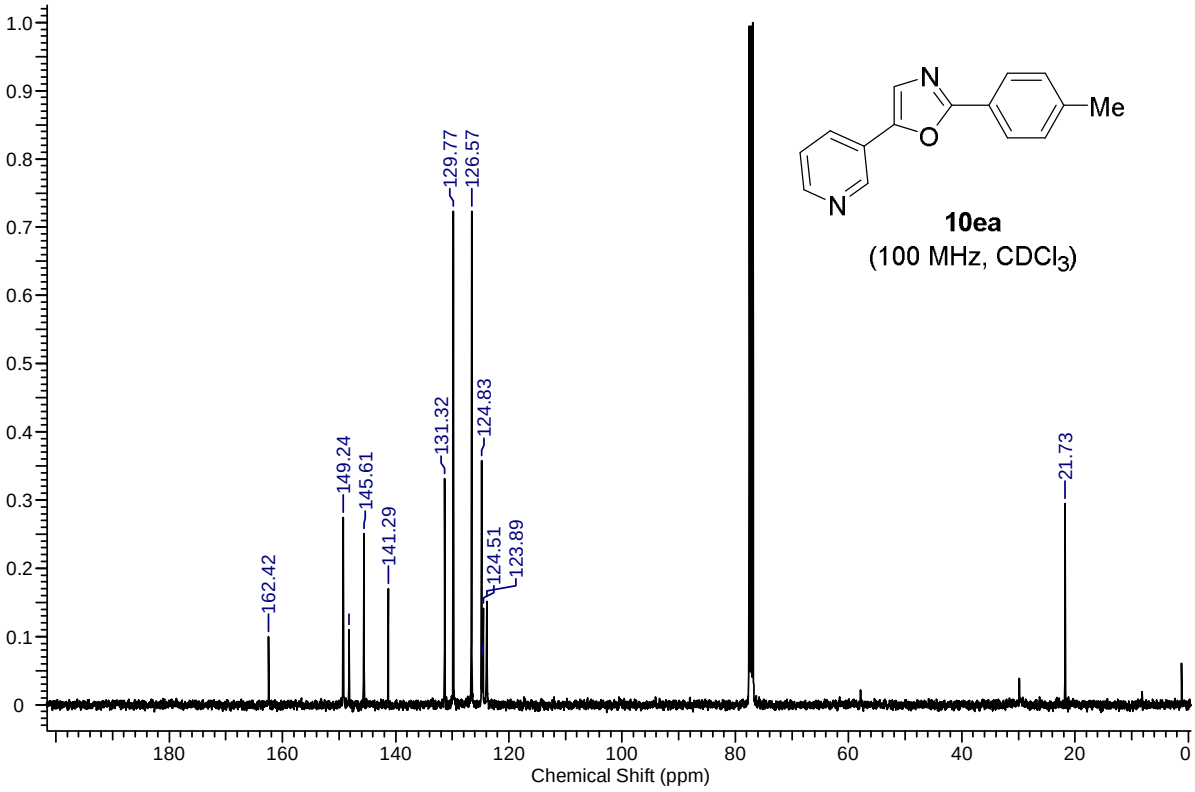

N
O
Me
F3C
10ca
(400 MHz, CDCl3)
2.01 2.04 1.98 0.96 1.97
3.00
Chemical Shift (ppm)

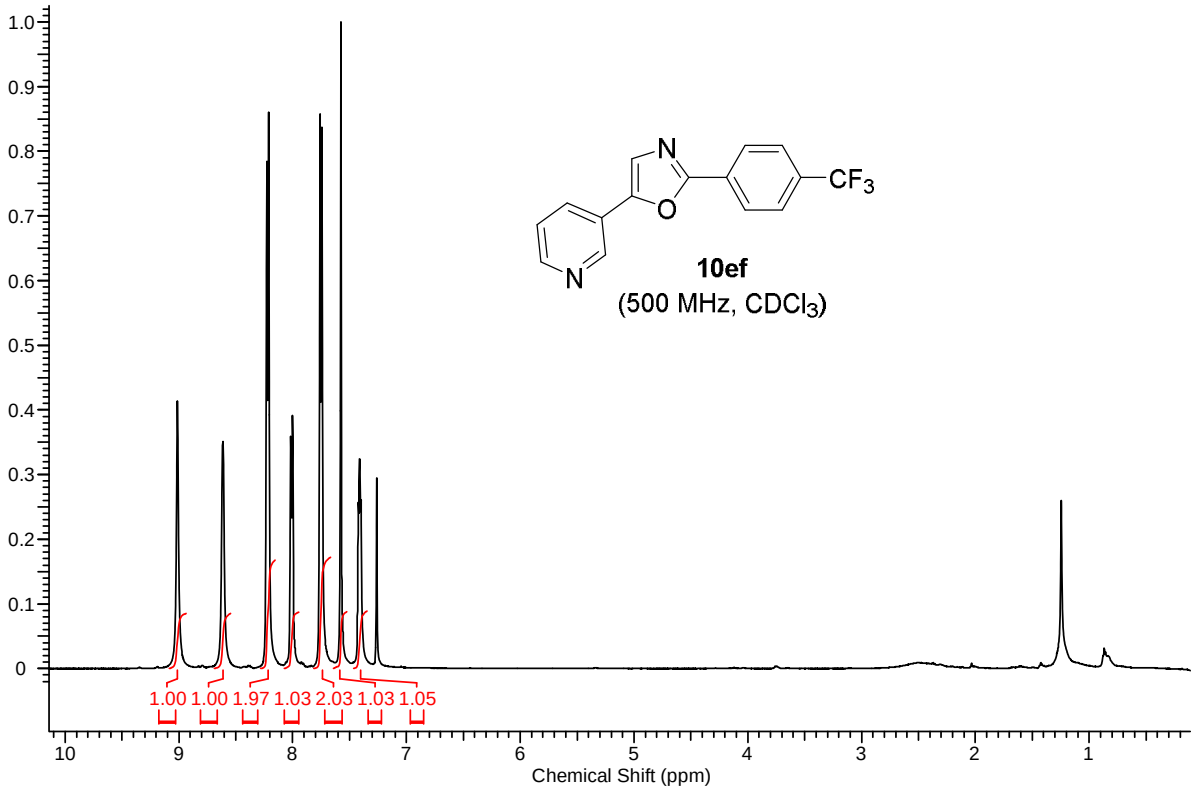

N
O
Me
F3C
10ca
(100 MHz, CDCl3)
129.80
124.31
126.62
141.36
131.48
122.79
149.74
21.75
Chemical Shift (ppm)

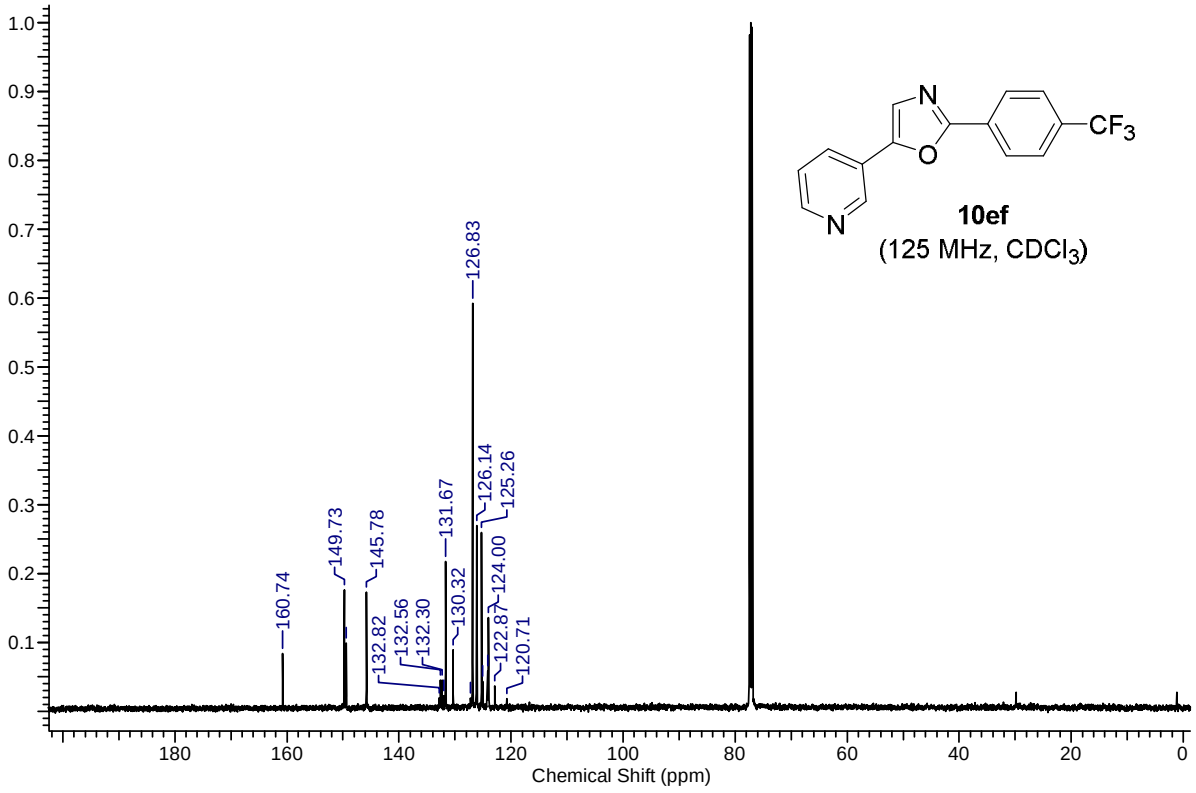

Me
N
O
Me
10dk
(400 MHz, CDCl3)
0.95 2.06 1.03 2.91 2.99 0.91
6.01
Chemical Shift (ppm)


Me
N
O
Me
10dk
(100 MHz, CDCl3)
161.89
151.37
138.71
133.60
132.43
128.92
128.40
124.33
124.00
123.03
122.26
21.48
Chemical Shift (ppm)


N
O
N
Me
10ea
(400 MHz, CDCl3)
0.92
0.93
2.65
0.95
2.70
3.00
Chemical Shift (ppm)


N
O
N
Me
10ea
(100 MHz, CDCl3)
162.42
149.24
145.61
141.29
131.32
129.77
126.57
124.83
124.51
123.89
21.73
Chemical Shift (ppm)


1.00 1.00 1.97 1.03 2.03 1.03 1.05
Chemical Shift (ppm)
10ef
(500 MHz, CDCl3)


160.74
149.73
145.78
132.82
132.56
132.30
131.67
130.32
126.83
126.14
125.26
124.00
122.87
120.71
Chemical Shift (ppm)
10ef
(125 MHz, CDCl3)