Air-Stable Chiral Primary Phosphines: A Gateway to MOP Ligands with Previously Inaccessible Stereoelectronic Profiles

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1 Experimental Procedures and Analytic Data

1.1 General Considerations

All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques. THF (Na/benzophenone ketyl), toluene (Na) and CH_2Cl_2 (CaH) were dried and distilled prior to use. Flash chromatography was performed on silica gel from Fluorochem (silica gel, 40-63 µm, 60A, LC301) or alumina media from Acros (aluminum oxide, neutral, Brockmann I, 50-200 µm, 60A). Thin-layer chromatography was performed on Merck aluminum-based plates with silica gel and fluorescent indicator 254 nm. ^{1}H, ^{11}B, $^{13}C\{^{1}H\}$, ^{19}F, and $^{31}P\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a JEOL Lambda 500 (^{1}H 500.16 MHz) or JEOL ECS-400 (^{1}H 399.78 MHz) spectrometer at room temperature (21 °C) if not otherwise stated, using the indicated solvent as internal reference. ^{195}Pt chemical shifts are given relative to $\Xi(^{195}Pt)$ = 21.49689 MHz. If necessary, the assignment of signals was done by using two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC). Infrared spectra were recorded on a Varian 800 FT-IR spectrometer. Mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre Swansea. Analytical high-performance liquid chromatography (HPLC) was performed on a Varian Pro Star HPLC or a Shimadzu Prominence HPLC equipped with diode-array detectors. Compounds **1a**,**b**,[1] **2a**,**b**,[2] and *trans*-$[Pt(PEt_3)Cl_2]_2$[3] were synthesised according to literature procedures. All other chemicals were used as purchased without further purification.

Quantum Chemical Calculations: All calculations used density functional theory as implemented in the Spartan 10 software and the B3LYP functional.[4] Full geometry optimisations of the studied compounds were performed using the standard 6-31G* basis set. A vibrational analysis was performed at the same level to characterize calculated structures as minima.

X-ray Diffraction

Table 1: Summary of X-ray crystallographic data for *cis*-**7b**, *trans*-**8b** and *trans*-**9b**.

	cis-**7b**	*trans*-**8b**	*trans*-**9b**
formula	$C_{46}H_{42}Cl_2O_2P_2Pt \cdot 2C_4H_{10}O$	$C_{50}H_{54}Cl_2N_4O_2P_2Pt$	$C_{29}H_{34}Cl_2OP_2Pt$
formula wt	1102.96	1070.90	726.49
cryst syst	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	P1
a, Å; α, deg	11.1244(5); 90	8.3489(4); 90	8.3743(3); 65.118(3)
b, Å; β, deg	20.0436(7); 90	18.6947(8); 90	9.5312(3); 71.277(3)
c, Å; γ, deg	23.8540(12); 90	29.0468(16); 90	10.9589(4); 69.349(3)
V, Å^3	5318.8(4)	4533.6(4)	727.02(5)
Z	4	4	1
ρ_{calc}, g cm^{-3}	1.377	1.569	1.659
μ, mm^{-1}	2.840	3.329	5.139
$F(000)$	2240	2160	358
T_{min}/T_{max}	0.40/0.49	0.44/0.56	0.51/0.63
hkl range	−10 to 13, −21 to 24, −24 to 29	−11 to 10, −25 to 24, −38 to 37	−10 to 11, −12 to 12, −13 to 14
θ range, deg	2.9 to 26.4	3.0 to 28.6	3.0 to 28.6
no. of measd rflns	25923	29323	11181
no. of unique rflns (R_{int})	10440 (0.0403)	9858 (0.0419)	5955 (0.0235)
no. of obsd rflns, $I > 2\sigma(I)$	8558	8759	5953
refined params/restraints	484/360	560/0	320/3
goodness of fit	1.120	1.179	1.034
Abs. structure param.	−0.012(4)	0.006(4)	−0.001(3)
R1/wR2 ($I > 2\sigma(I)$)	0.0569/0.1179	0.0590/0.0971	0.0185/0.0415
R1/wR2 (all data)	0.0757/0.1263	0.0694/0.1010	0.0186/0.0415
resid electron dens, e Å^{-3}	3.11/−1.68	4.26/−3.72	0.78/−0.80

Table 2: Summary of X-ray crystallographic data for *trans*-**11a**, **14b** and **18b**.

	trans-**11a**	**14b**	**18b**
formula	$C_{30}H_{40}Cl_2N_2P_2Pt$	$C_{27}H_{28}ClOPPd\cdot C_4H_{10}O$	$C_{29}H_{34}N_2OPPd^+\cdot C_{32}H_{12}BF_{24}\cdot C_4H_{10}O$
formula wt	756.57	615.43	1501.29
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a, Å; α, deg	7.8976(3); 90	10.5937(4); 90	12.5151(3); 90
b, Å; β, deg	12.9784(4); 90	14.2040(5); 100.385(4)	13.7875(4); 90
c, Å; γ, deg	29.8031(10); 90	18.3113(8); 90	37.1072(15); 90
V, Å^3	3054.76(18)	2710.22(18)	6402.9(4)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.645	1.508	1.557
μ, mm^{-1}	4.895	0.870	0.431
F(000)	1504	1272	3032
T_{min}/T_{max}	0.29/0.32	0.72/0.96	0.5/0.88
hkl range	−10 to 10, −17 to 13, −37 to 38	−14 to 13, −18 to 18, −24 to 19	−16 to 16, −17 to 18, −37 to 50
θ range, deg	2.9 to 28.6	3.1 to 28.6	3.0 to 28.7
no. of measd rflns	15460	26914	34956
no. of unique rflns (R_{int})	6419 (0.0391)	11398 (0.0305)	13681 (0.0295)
no. of obsd rflns, $I > 2\sigma(I)$	6158	10517	12571
refined params/restraints	342/0	591/29	1142/5065
goodness of fit	1.035	1.031	1.092
Abs. structure param.	−0.012(5)	−0.031(13)	−0.012(9)
R1/wR2 ($I > 2\sigma(I)$)	0.0296/0.0506	0.0313/0.0720	0.0419/0.0891
R1/wR2 (all data)	0.0323/0.0520	0.0373/0.0757	0.0477/0.0921
resid electron dens, e Å^{-3}	1.31/−1.08	0.47/−0.37	0.56/−0.59

1.2 (*S*)-[1,1'-Binaphthalen]-2-yldimethylphosphine (**3a**)

PCl_5 (458 mg, 2.20 mmol) was dissolved in toluene (8 mL). **1a** (286 mg, 1.00 mmol) was added and the reaction mixture was stirred for 45 minutes. The volatiles were removed *in vacuo*, THF (8 mL) was added and the resulting solution was cooled to –78 °C. MeMgCl (0.70 mL, 3.0 M in THF, 2.10 mmol) was added and stirred at –78 °C for 30 minutes. The solution was allowed to warm up to ambient temperature and stirred for 1.5 hours. The reaction was slowly quenched with H_2O (10 mL) and extracted with Et_2O (2 × 30 mL). The organic phase was dried over $MgSO_4$ to give the fairly pure crude product as a pale yellow solid. Purification was performed by column chromatography (hexane/EtOAc, 10:1, $R_f = 0.4$) on a silica media (w = 2 cm, h = 10 cm) to yield the intended product as a white solid (238 mg, 0.36 mmol, 76%). **MP** (uncorrected): 112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*4), 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*4'), 7.94 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.91 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.78 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 2.9 Hz, 1H, *H*3), 7.62 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *H*3'), 7.48-7.43 (m, 3H, *H*6/*H*6'/*H*2'), 7.28-7.22 (m, 2H, *H*7'/*H*7), 7.19-7.14 (m, 2H, *H*8/ *H*8'), 1.22 (d, $^2J_{HP}$ = 3.9 Hz, 3H, C*H*$_3$), 1.02 (d, $^2J_{HP}$ = 3.9 Hz, 3H, C*H*$_3$') ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.4 (d, $^{2}J_{CP}$ = 29.7 Hz, *C*1), 138.8 (d, $^{1}J_{CP}$ = 14.4 Hz, *C*2), 137.7 (d, $^{3}J_{CP}$ = 7.8 Hz, *C*1'), 133.5 (*C*10), 133.4 (d, $^{4}J_{CP}$ = 2.4 Hz, *C*9'), 133.3 (*C*10'), 133.1 (d, $^{3}J_{CP}$ = 5.7 Hz, *C*9), 128.7 (d, $^{4}J_{CP}$ = 3.3 Hz, *C*2'), 128.4 (*C*5), 128.2 (*C*4), 128.2 (*C*4'), 127.9 (*C*5'), 127.0 (d, $^{4}J_{CP}$ = 2.3 Hz, *C*8), 126.5 (*C*8'), 126.4 (*C*7'), 126.3 (*C*7), 126.1 (*C*6'), 125.9 (*C*6), 125.7 (d, $^{2}J_{CP}$ = 1.4 Hz, *C*3), 125.3 (*C*3'), 15.0 (d, $^{1}J_{CP}$ = 14.0 Hz, CH_3), 14.4 (d, $^{1}J_{CP}$ = 14.0 Hz, CH_3') ppm. **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ = –54.0 ppm. **IR** (neat): ν = 3052.2 (w), 2893.6 (w), 1591.9 (w), 1501.4 (w), 1428.8 (w), 1360.6 (w), 1154.7 (w), 1013.4 (w), 938.9 (m), 894.3 (m), 869.4 (w), 781.6 (s), 749.5 (s), 708.0 (m), 685.7 (w), 627.5 (w) 578.5 (w) cm^{-1}. **HRMS** (ESI^{+}): Found: m/z = 315.1294. Calculated for $[M + H]^{+}$: m/z = 315.1297. **OR** ($CHCl_3$, c = 1.0 mg/ml): $[\alpha]_D^{20}$ = –44°. **TLC** (silica gel; hexane/EtOAc, 10:1): R_f = 0.4.

1.3 (*R*)-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)dimethylphosphine (**3b**)

The same procedure was followed as for **3a**, except for using **1b** as the substrate. Purification was performed by column chromatography (hexane/EtOAc, 10:1, R_f = 0.4) on a silica media (w = 2 cm, h = 10 cm) to yield the intended product as a white solid (125 mg, 0.36 mmol, 73%). **MP** (uncorrected): 128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.03 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, *H*4'), 8.00 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, *H*4), 7.91 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5), 7.87 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5'), 7.81 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HP}$ = 2.9 Hz, 1H, *H*3), 7.45 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, *H*6), 7.45 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, *H*3'), 7.31 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, *H*6'), 7.24 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, *H*7), 7.20 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*8), 7.19 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, *H*7'), 6.93 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*8'), 3.78 (s, 3H, OCH_3), 1.21 (d, $^{2}J_{HP}$ = 3.9 Hz, 3H, CH_3), 1.05 (d, $^{2}J_{HP}$ = 4.0 Hz, 3H, CH_3') ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 154.8 (d, $^{4}J_{CP}$ = 1.9 Hz, *C*2'), 140.1 (d, $^{2}J_{CP}$ = 31.7 Hz, *C*1), 139.1 (d, $^{1}J_{CP}$ = 13.1 Hz, *C*2), 134.4 (d, $^{4}J_{CP}$ = 1.9 Hz, *C*9'), 133.6 (*C*10), 132.9 (d, $^{3}J_{CP}$ = 6.8 Hz, *C*9), 129.9 (*C*4'), 128.9 (*C*10'), 128.1 (C4), 128.0 (*C*5/*C*5'), 126.5 (*C*8/*C*7'), 126.3 (*C*6/*C*7), 125.7 (d, $^{2}J_{CP}$ = 1.9 Hz, *C*3), 125.4 (*C*8'), 123.6 (*C*6'), 122.4 (d, $^{3}J_{CP}$ = 8.7 Hz, *C*1'), 113.3 (*C*3'), 56.4 (OCH_3), 14.7 (d, $^{1}J_{CP}$ = 14.4 Hz, CH_3), 14.6 (d, $^{1}J_{CP}$ = 13.9 Hz, CH_3') ppm. **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ = –54.0 ppm. **IR** (neat): ν = 3060.9 (w), 1620.3 (m), 1592.8 (m), 1505.0 (m), 1457.8 (w), 1428.1 (w), 1344.2 (m), 1251.4 (s), 1178.1 (w), 1147.4 (w), 1119.2 (w), 1077.7 (s), 1051.3 (m), 1020.7 (m), 937.9 (m), 895.5 (m), 870.5 (w), 810.3 (s), 746.9 (s), 709.1 (m), 679.9 (m), 627.9 (w) cm^{-1}. **HRMS** (ESI^{+}): Found: m/z = 345.1404. Calculated for $[M + H]^{+}$: m/z = 345.1403. **OR** ($CHCl_3$, c = 1.0 mg/ml): $[\alpha]_D^{20}$ = –14°. **TLC** (silica gel; hexane/EtOAc, 10:1): R_f = 0.4.

1.4 (*S*)-*N*,*N*,*N*',*N*'-Tetramethyl-1-(1,1'-binaphthalen-2-yl)phosphinediamine (**4a**)

PCl_5 (687 mg, 3.30 mmol) was dissolved in toluene (12 mL). **1a** (429 mg, 1.50 mmol) was added and the reaction mixture was stirred for 45 minutes after which time the volatiles were removed *in vacuo*.

The resulting solid was dissolved in THF (12 mL). NEt_3 (0.92 mL, 6.60 mmol) and $HNMe_2$ (1.60 mL, 2.0 M in THF, 3.15 mmol) were added subsequently and the solution was stirred overnight. The volatiles were removed *in vacuo* and the crude product was filtrated through a small plug of alumina media in a 1:1 mixture of cyclohexane and Et_2O ($R_f = 0.8$). The title product was obtained, after removal of the solvent, as a white solid (519 mg, 0.93 mmol, 93%). **MP** (uncorrected): 105 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 7.97$ (d, $^3J_{HH} = 8.5$ Hz, 1H, *H*4), 7.94 (d, $^3J_{HH} = 8.3$ Hz, 1H, *H*5), 7.93-7.89 (m, 3H, *H*5'/*H*4'/*H*3), 7.60 (dd, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, *H*3'), 7.46-7.42 (m, 2H, *H*6'/*H*6), 7.41 (d, $^3J_{HH} = 7.0$ Hz, 1H, *H*2'), 7.25-7.19 (m, 3H, *H*7'/*H*7/*H*8'), 7.16 (d, $^3J_{HH} = 8.5$ Hz, 1H, *H*8), 2.42 (d, $^3J_{HP} = 9.0$ Hz, 6H, N(CH_3)$_2$), 2.26 (d, $^3J_{HP} = 9.3$ Hz, 6H, N(CH_3)$_2$') ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 141.5$ (d, $^2J_{CP} = 26.0$ Hz, *C*1), 138.8 (d, $^1J_{CP} = 11.0$ Hz, *C*2), 137.5 (d, $^3J_{CP} = 4.7$ Hz, *C*1'), 133.7 (d, $^3J_{CP} = 3.8$ Hz, *C*9), 133.7 (*C*10), 133.5 (*C*10'), 132.6 (d, $^4J_{CP} = 1.4$ Hz, *C*9'), 128.1 (*C*5), 128.0 (*C*2'), 128.0 (*C*3), 127.8 (*C*4'), 127.5 (*C*5'), 127.1 (d, $^3J_{CP} = 1.3$ Hz, *C*4), 127.0 (d, $^5J_{CP} = 1.3$ Hz, *C*7), 126.4 (d, $^4J_{CP} = 2.5$ Hz, *C*8), 126.0 (*C*7), 125.8 (*C*6/*C*6'), 125.6 (*C*8'), 125.4 (*C*7'), 125.2 (*C*3'), 41.0 (d, $^2J_{CP} = 18.0$ Hz, N(CH$_3$)$_2$), 40.9 (d, $^2J_{CP} = 18.6$ Hz, N(CH$_3$)$_2$') ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): $\delta = 99.9$ ppm. **IR** (neat): $\nu = 3059.0$ (w), 2979.2 (w), 2872.0 (w), 2827.9 (w), 2783.3 (w), 1497.3 (w), 1355.6 (w), 1261.8 (w), 1189.7 (m), 1061.4 (w), 1022.2 (w), 949.1 (s), 869.2 (w), 824.0 (m), 804.6 (m), 781.5 (s), 748.2 (s), 667.4 (s), 640.9 (m) cm^{-1}. **HRMS** (ESI$^+$): Found: $m/z = 373.1827$. Calculated for $[M + H]^+$: $m/z = 373.1828$. **OR** ($CHCl_3$, $c = 1.0$ mg/ml): $[\alpha]_D^{20} = -32°$. **TLC** (alumina; cyclohexane/Et_2O, 1:1): $R_f = 0.8$.

1.5 (*R*)-*N*,*N*,*N'*,*N'*-Tetramethyl-1-(2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphinediamine (4b)

The same procedure was followed as for **4a**, except for using **1b** as the substrate. The title product was obtained as a white solid (536 mg, 1.33 mmol, 89%). **MP** (uncorrected): 122 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 7.97$ (d, $^3J_{HH} = 9.1$ Hz, 1H, *H*4'), 7.96 (d, $^{3,4}J_{HP} = 2.0$ Hz, 2H, *H*3/*H*4), 7.92 (d, $^3J_{HH} = 8.2$ Hz, 1H, *H*5), 7.86 (d, $^3J_{HH} = 8.2$ Hz, 1H, *H*5'), 7.47-7.43 (m, 2H, *H*3'/*H*6), 7.29 (ddd, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, *H*6'), 7.21 (ddd, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 6.5$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, *H*7), 7.18-7.14 (m, 2H, *H*8/*H*7'), 6.93 (d, $^3J_{HH} = 8.5$ Hz, 1H, *H*8'), 3.78 (s, 3H, OCH_3), 2.36 (d, $^3J_{HP} = 9.5$ Hz, 6H, N(CH_3)$_2$), 2.21 (d, $^3J_{HP} = 9.2$ Hz, 6H, N(CH_3)$_2$') ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 154.4$ (d, $^4J_{CP} = 1.6$ Hz, *C*2'), 139.1 (d, $^2J_{CP} = 13.9$ Hz, *C*1), 139.0 (d, $^1J_{CP} = 29.0$ Hz, *C*2), 134.0 (d, $^4J_{CP} = 1.9$ Hz, *C*10), 133.7 (*C*9'), 133.4 (d, $^3J_{CP} = 4.8$ Hz, *C*9), 129.2 (*C*4'), 128.9 (*C*10'), 127.9 (*C*5), 127.8 (d, $^2J_{CP} = 4.2$ Hz, *C*3), 127.7 (*C*5'), 126.8 (d, $^3J_{CP} = 1.2$ Hz, *C*4), 126.1 (*C*6), 126.0 (d, $^5J_{CP} = 2.5$ Hz, *C*7), 125.9 (*C*7'), 125.8 (*C*8'), 125.8 (d, $^4J_{CP} = 1.3$ Hz, *C*8), 123.2 (*C*6'), 121.9 (d, $^3J_{CP} = 6.1$ Hz, *C*1'), 113.0 (*C*3'), 56.0 (OCH$_3$), 40.5 (d, $^2J_{CP} = 19.2$ Hz, N(CH$_3$)$_2$), 40.4 (d, $^2J_{CP} = 19.2$ Hz, N(CH$_3$)$_2$') ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): $\delta = 101.0$ ppm. **IR** (neat): $\nu = 3060.3$ (w), 2965.9 (w), 2825.5 (w), 2780.6 (w), 1621.8 (w), 1593.3 (w), 1510.4 (m), 1461.1 (m), 1340.5 (w), 1263.7 (s), 1194.5 (m), 1078.1 (m), 1053.4 (w), 1021.3 (w), 978.2

(m), 955.4 (s), 910.2 (w), 822.3 (w), 802.7 (s), 742.1 (s), 674.2 (m), 638.3 (m) cm^{-1}. **HRMS** (ESI^+): Found: $m/z = 403.1939$. Calculated for $[M + H]^+$: $m/z = 403.1934$. **OR** ($CHCl_3$, $c = 1.0$ mg/ml): $[\alpha]_D^{20} = -60°$. **TLC** (alumina; cyclohexane/Et_2O, 1:1): $R_f = 0.8$.

1.6 Dimethyl [1,1'-binaphthalen]-2-ylphosphonite (**5a**)

PCl_5 (458 mg, 2.20 mmol) was dissolved in toluene (5 mL). **1a** (286 mg, 1.00 mmol) was added and the reaction mixture was stirred for 45 minutes after which time the volatiles were removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2 (5 mL). NEt_3 (0.61 mL, 4.40 mmol) and MeOH (0.09 mL, 2.20 mmol) were added subsequently and the solution was left for 2 hours. The volatiles were removed *in vacuo* and a toluene suspension of the crude product was filtered through a small plug of celite. The title product was obtained after removal of the solvent as a pale yellow oil. **^{1}H NMR** (400 MHz, CD_2Cl_2): $\delta = 8.04$ (dd, $^3J_{HH} = 8.5$ Hz, $^3J_{HP} = 1.9$ Hz, 1H, *H*3), 8.02-8.00 (m, 2H, *H*4/*H*4'), 7.98-7.94 (m, 2H, *H*5/*H*5'), 7.62 (dd, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, *H*3'), 7.52-7.46 (m, 3H, *H*6/*H*6'/*H*2'), 7.29-7.24 (m, 2H, *H*7/*H*7'), 7.19-7.13 (m, 2H, *H*8/*H*8'), 3.45 (d, $^3J_{HP} = 10.8$ Hz, 3H, POCH_3), 3.00 (d, $^3J_{HP} = 11.7$ Hz, 3H, POCH_3') ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): $\delta = 142.8$ (d, $^2J_{CP} = 32.6$ Hz, *C*1), 137.7 (d, $^1J_{CP} = 21.4$ Hz, *C*2), 135.6 (d, $^3J_{CP} = 7.8$ Hz, *C*1'), 134.3 (*C*10), 133.5 (d, $^4J_{CP} = 1.9$ Hz, *C*9'), 133.3 (*C*10'), 132.1 (d, $^3J_{CP} = 5.0$ Hz, *C*9), 129.6 (d, $^4J_{CP} = 3.4$ Hz, *C*2'), 128.4 (*C*5), 128.2 (*C*5'), 128.0 (*C*4'), 127.3 (d, $^3J_{CP} = 1.4$ Hz, *C*4), 127.0 (*C*6'), 126.6 (*C*8'), 126.6 (*C*8), 126.2 (*C*7'), 126.1 (*C*7), 125.9 (*C*6), 125.3 (d, $^2J_{CP} = 3.4$ Hz, *C*3), 125.0 (*C*3'), 53.8 (d, $^2J_{CP} = 15.8$ Hz, POCH_3'), 53.2 (d, $^2J_{CP} = 10.0$ Hz, POCH_3) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): $\delta = 157.5$ ppm. **IR** (neat): $v = 3052.1$ (w), 2933.4 (w), 2831.1 (w), 1591.7 (w), 1557.6 (w), 1505.7 (w), 1454.6 (w), 1361.8 (w), 1231.7 (w), 1163.4 (w), 1037.0 (s), 1015.7 (s), 879.9 (w), 828.9 (m) cm^{-1}. **HRMS** ($APCI^+$): Found: $m/z = 347.1193$. Calculated for $[M + H]^+$: $m/z = 347.1195$. **OR** ($CHCl_3$, $c = 1.0$ mg/ml): $[\alpha]_D^{20} = -44°$.

1.7 Dimethyl (2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphonite (**5b**)

The same procedure was followed as for **5a**, except for using **1b** as the substrate. The title product was obtained as a pale yellow oil. **^{1}H NMR** (500 MHz, CD_2Cl_2): $\delta = 8.05$ (d, $^3J_{HH} = 9.1$ Hz, 1H, *H*4'), 8.04 (d, $^3J_{HH} = 8.5$ Hz, $^3J_{HP} = 1.9$ Hz, 1H, *H*3), 7.99 (d, $^3J_{HH} = 8.5$ Hz, 1H, *H*4), 7.95 (d, $^3J_{HH} = 8.1$ Hz, 1H, *H*5), 7.89 (d, $^3J_{HH} = 8.2$ Hz, 1H, *H*5'), 7.51 (ddd, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, *H*6), 7.47 (d, $^3J_{HH} = 9.1$ Hz, 1H, *H*3'), 7.32 (ddd, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 1.2$ Hz, 1H, *H*6'), 7.28-7.18 (m, 3H, *H*7/*H*7'/*H*8), 6.91 (d, $^3J_{HH} = 8.5$ Hz, 1H, *H*8'), 3.79 (s, 3H, OCH_3), 3.43 (d, $^3J_{HP} = 10.3$ Hz, 3H, POCH_3), 3.32 (d, $^3J_{HP} = 11.5$ Hz, 3H, POCH_3') ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): $\delta = 155.6$ (d, $^4J_{CP} = 2.0$ Hz, *C*2'), 139.6 (d, $^2J_{CP} = 33.8$ Hz, *C*1), 137.8 (d, $^1J_{CP} = 21.7$ Hz, *C*2), 134.6 (*C*9'), 134.5 (d, $^4J_{CP} = 2.2$ Hz, *C*10), 132.9 (d, $^3J_{CP} = 5.2$ Hz, *C*9), 130.2 (*C*4'), 128.6 (*C*10'), 128.1 (*C*5), 127.9 (*C*5'), 127.1 (*C*4), 127.0 (*C*6), 126.5 (*C*7'), 126.2 (*C*7), 126.0 (d, $^4J_{CP} = 2.4$ Hz, *C*8), 125.7 (d, $^{2}J_{CP}$ = 3.3 Hz, *C*3), 125.3 (*C*8'), 123.5 (*C*6'), 119.9 (d, $^{3}J_{CP}$ = 8.1 Hz, *C*1'), 112.9 (*C*3'), 56.1 (O*C*H_3), 53.6 (d, $^{2}J_{CP}$ = 15.1 Hz, PO*C*H_3'), 52.6 (d, $^{2}J_{CP}$ = 8.5 Hz, PO*C*H_3) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 155.8 ppm. **IR** (neat): ν = 3053.8 (w), 2933.5 (w), 2828.0 (w), 1621.2 (w), 1592.6 (w), 1507.8 (m), 1461.7 (w), 1332.7 (w), 1268.9 (s), 1248.9 (s), 1147.3 (w), 1079.4 (m), 1035.7 (s), 1011.6 (s), 907.8 (w), 868.1 (w) cm^{-1}. **HRMS** (APCI^{+}): Found: *m*/*z* = 376.1218. Calculated for [M]$^{+}$: *m*/*z* = 376.1223. **OR** ($CHCl_3$, *c* = 1.0 mg/ml): $[\alpha]_D^{20}$ = –20°.

1.8 *cis*-[Pt(**3b**)$_2$Cl$_2$] (*cis*-**7b**)

[Pt(cod)Cl_2] (6.7 mg, 17.5 µmol) and **3b** (11.0 mg, 35.0 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred at room temperature for 15 minutes. The volatiles were removed *in vacuo* to give the intended product as a colorless solid (quantitative conversion). Slow diffusion of Et_2O into the reaction mixture yielded colorless crystals overnight which were suitable for X-ray diffraction analysis. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.66 (dd, $^{3}J_{HP}$ = 13.9 Hz, $^{3}J_{HH}$ = 8.7 Hz, 2H, *H*3), 7.98 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H, *H*4'), 7.87-7.81 (m, 6H, *H*5/*H*4/*H*5'), 7.48 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, *H*6), 7.35-7.28 (m, 4H, *H*3'/*H*6'), 7.20 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, *H*7), 7.03 (ddd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, *H*7'), 6.96 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*8), 6.72 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*8'), 3.57 (s, 6H, OC*H*$_3$), 1.26 (d, $^{2}J_{HP}$ = 10.6 Hz, 6H, PC*H*$_3$), 1.11 (d, $^{2}J_{HP}$ = 10.6 Hz, 6H, PC*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 154.9 (*C*2'), 138.5 (*C*1), 134.5 (*C*10), 134.5 (*C*9'), 133.2 (*C*9), 132.3 (m, *C*3), 131.2 (*C*4'), 128.8 (*C*5'), 128.7 (*C*10'), 128.1 (*C*4), 128.1 (*C*5), 127.8 (*C*6), 127.3 (*C*7'), 127.1 (*C*7), 126.5 (*C*8), 125.7 (*C*8'), 124.1 (*C*6'), 119.6 (*C*1'), 112.8 (*C*3'), 55.8 (s, O*C*H_3), 7.8 (d, $^{1}J_{CP}$ = 44.6 Hz, *C*H_3), 7.2 (d, $^{1}J_{CP}$ = 43.1 Hz, *C*H_3) ppm. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = –6.1 (s with ^{195}Pt satellites, $^{1}J_{PtP}$ = 3647 Hz) ppm. **^{195}Pt{^{1}H} NMR** (108 MHz, CD_2Cl_2): δ = –4362 (t, $^{1}J_{PtP}$ = 3647 Hz) ppm. **HRMS** (ESI^{+}, MeOH): Found: *m*/*z* = 917.1960. Calculated for [M – Cl]$^{+}$: *m*/*z* = 917.1975.

1.9 *trans*-[Pt(**4b**)$_2$Cl$_2$] (*trans*-**8b**)

[Pt(cod)Cl_2] (6.7 mg, 17.5 µmol) and **4b** (11.0 mg, 35.0 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred at room temperature for 15 minutes. The volatiles were removed *in vacuo* to give the intended product as a colorless solid (quantitative conversion). Slow diffusion of Et_2O into the reaction mixture yielded colorless crystals overnight which were suitable for X-ray diffraction analysis. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 8.02 (m, $^{3}J_{HH}$ = 8.8 Hz, $^{3}J_{HP}$ ≈ 12.9 Hz, 2H, *H*3), 7.96 (d, $^{3}J_{HH}$ = 9.1 Hz, 2H, *H*4'), 7.85 (m, 6H, *H*5'/*H*5/*H*4), 7.44 (d, $^{3}J_{HH}$ = 9.1 Hz, 2H, *H*3'), 7.41 (ddd, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, *H*6), 7.39 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *H*8'), 7.27 (ddd, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, *H*6'), 7.11 (ddd, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, *H*7), 7.05 (ddd, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, *H*7'), 6.79 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *H*8) 3.72 (s, 6H, OC*H*$_3$), 2.77 (pt, $^{3}J_{HP}$ ≈ 9.3 Hz, 12H, N(C*H*$_3$)$_2$), 1.84 (pt, $^{3}J_{HP}$ ≈ 10.0 Hz, 12H, N(C*H*$_3$)$_2$') ppm.

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 154.2 (*C*2'), 137.6 (pt, $^{2}J_{CP}+^{4}J_{CP} \approx 6.3$ Hz, *C*1), 134.6 (*C*9'), 134.3 (pt, $^{1}J_{CP}+^{3}J_{CP} \approx 74.0$ Hz, *C*2), 133.9 (*C*10), 133.2 (pt, $^{3}J_{CP} \approx 9.3$ Hz, *C*9), 131.9 (pt, $^{2}J_{CP}+^{4}J_{CP} \approx 20.8$ Hz, *C*3), 129.0 (*C*4'), 128.9 (*C*10'), 127.7 (*C*5), 127.4 (*C*5'), 126.9 (*C*6), 126.7 (*C*8'), 126.4 (*C*7'), 126.3 (*C*8), 125.8 (*C*7), 125.0 (pt, $^{3}J_{CP}+^{5}J_{CP} \approx 13.7$ Hz, *C*4), 123.6 (*C*6'), 122.0 (*C*1'), 112.5 (*C*3'), 55.7 (O*C*H_3), 41.8 (pt, $^{2}J_{CP}+^{4}J_{CP} \approx 6.7$ Hz, N(*C*H_3)$_2$), 39.6 (pt, $^{2}J_{CP}+^{4}J_{CP} \approx 8.6$ Hz, N(*C*H_3)$_2$') ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = 87.8 (s with ^{195}Pt satellites, $^{1}J_{PtP}$ = 2955 Hz) ppm. **^{195}Pt{^{1}H} NMR** (108 MHz, CD_2Cl_2): δ = –3747 (t, $^{1}J_{PtP}$ = 2955 Hz) ppm. **HRMS** (ESI^{+}, MeOH): Found: *m*/*z* = 1093.2626. Calculated for [M + Na]$^{+}$: *m*/*z* = 1093.2636.

1.10 General Procedure for the Preparation of L_P(Se)

The phosphorus ligand (L_P, 50.0 µmol) and KSeCN (14.4 mg, 100 µmol) were dissolved in THF (1 mL) and heated to 50 °C for 2 hours. The solvent was removed and the residue dissolved in $CDCl_3$. After filtration through celite the product was analysed by ^{31}P {^{1}H} NMR. **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ = **3a**(Se): 19.6 ($^{1}J_{PSe}$ = 685 Hz); **3b**(Se): 22.0 ($^{1}J_{PSe}$ = 683 Hz); **4a**(Se): 80.1 ($^{1}J_{PSe}$ = 770 Hz); **4b**(Se): 79.8 ($^{1}J_{PSe}$ = 765 Hz); **5a**(Se): 95.8 ($^{1}J_{PSe}$ = 858 Hz); **5b**(Se): 97.4 ($^{1}J_{PSe}$ = 860 Hz) ppm.

1.11 General Procedure for the Preparation of *trans*-[Rh(L_P)$_2$(CO)Cl]

[Rh(CO)$_2$Cl]$_2$ (1.2 mg, 3.125 µmol) and the phosphorus ligand (L_P, 12.5 µmol) were dissolved in CH_2Cl_2 (0.5 mL) and left to react for 10 minutes. The solvent was removed *in vacuo* and the product analysed by IR spectroscopy. **IR** (CH_2Cl_2): *v* [Rh(**2a**)$_2$(CO)Cl]: 1983; [Rh(**2b**)$_2$(CO)Cl]: 1985; [Rh(**3a**)$_2$(CO)Cl]: 1965; [Rh(**3b**)$_2$(CO)Cl]: 1963; [Rh(**4a**)$_2$(CO)Cl]: 1972; [Rh(**4b**)$_2$(CO)Cl]: 1969; [Rh(**5a**)$_2$(CO)Cl]: 1999; [Rh(**5b**)$_2$(CO)Cl]: 1996 cm^{-1}.

1.11.1 General Procedure for the Preparation of *trans*-[Pt(L_P)(PEt_3)Cl_2]

[Pt(PEt_3)Cl_2]$_2$ (19.2 mg, 25.0 µmol) and the phosphorus ligand (L_P, 50.0 µmol) were dissolved in CD_2Cl_2 (0.55 mL) and left to react for 30 minutes. The products were analysed by ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectroscopy. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = **9a** (*trans*, 51%): 15.5 ($^{1}J_{PPt}$ = 2871 Hz, $^{2}J_{PP}$ = 573 Hz, PEt_3), –149.6 ($^{1}J_{PPt}$ = 2570 Hz, $^{2}J_{PP}$ = 573 Hz, **2a**); (*cis*, 49%): 10.4 ($^{1}J_{PPt}$ = 3281 Hz, $^{2}J_{PP}$ = 23 Hz, PEt_3), –144.1 ($^{1}J_{PPt}$ = 4381 Hz, $^{2}J_{PP}$ = 23 Hz, **2a**); **9b** (*trans*, 65%): 13.8 ($^{1}J_{PPt}$ = 2886 Hz, $^{2}J_{PP}$ = 575 Hz, PEt_3), –151.9 ($^{1}J_{PPt}$ = 2566 Hz, $^{2}J_{PP}$ = 575 Hz, **2b**); (*cis*, 35%): 9.8 ($^{1}J_{PPt}$ = 3282 Hz, $^{2}J_{PP}$ = 24 Hz, PEt_3), –144.1 ($^{1}J_{PPt}$ = 4377 Hz, $^{2}J_{PP}$ = 24 Hz, **2b**); **10a** (*trans*, 32%): 12.5 ($^{1}J_{PPt}$ = 2479 Hz, $^{2}J_{PP}$ = 484 Hz, PEt_3), –4.5 ($^{1}J_{PPt}$ = 2364 Hz, $^{2}J_{PP}$ = 484 Hz, **3a**); (*cis*, 68%): 7.1 ($^{1}J_{PPt}$ = 3412 Hz, $^{2}J_{PP}$ = 18 Hz, PEt_3), –5.1 ($^{1}J_{PPt}$ = 3725 Hz, $^{2}J_{PP}$ = 18 Hz, **3a**); **10b** (*trans*, 36%): 12.0 ($^{1}J_{PPt}$ = 2464 Hz, $^{2}J_{PP}$ = 482 Hz, PEt_3), –1.3 ($^{1}J_{PPt}$ = 2402 Hz, $^{2}J_{PP}$ = 482 Hz, **3b**); (*cis*, 64%): 7.2 ($^{1}J_{PPt}$ = 3404 Hz, $^{2}J_{PP}$ = 18 Hz, PEt_3), –2.9 ($^{1}J_{PPt}$ = 3737 Hz, $^{2}J_{PP}$ = 18 Hz, **3b**); **11a** (*trans*, 100%): 90.4 ($^{1}J_{PPt}$ = 3030 Hz, $^{2}J_{PP}$ = 545 Hz, **4a**), 10.7 ($^{1}J_{PPt}$ = 2365 Hz, $^{2}J_{PP}$ = 545 Hz, PEt_3); **11b** (*trans*, 100%):

90.4 ($^1J_{PPt}$ = 3049 Hz, $^2J_{PP}$ = 543 Hz, **4b**), 10.4 ($^1J_{PPt}$ = 2332 Hz, $^2J_{PP}$ = 543 Hz, PEt_3); **12a** (*trans*, 100%): 119.8 ($^1J_{PPt}$ = 3428 Hz, $^2J_{PP}$ = 604 Hz, **5a**), 10.4 ($^1J_{PPt}$ = 2402 Hz, $^2J_{PP}$ = 604 Hz, PEt_3); **12b** (*trans*, 100%): 117.3 ($^1J_{PPt}$ = 3454 Hz, $^2J_{PP}$ = 604 Hz, **5b**), 8.9 ($^1J_{PPt}$ = 2407 Hz, $^2J_{PP}$ = 604 Hz, PEt_3) ppm. **^{195}Pt{^{1}H} NMR** (108 MHz, CD_2Cl_2): δ = **9a**: –3941 (dd, $^1J_{PtP}$ = 2871 Hz, $^1J_{PtP}$ = 2570 Hz, *trans*), –4493 (dd, $^1J_{PtP}$ = 4381 Hz, $^1J_{PtP}$ = 3281 Hz, *cis*); **9b**: –3921 (dd, $^1J_{PtP}$ = 2886 Hz, $^1J_{PtP}$ = 2566 Hz, *trans*), –4501 (dd, $^1J_{PtP}$ = 4377 Hz, $^1J_{PtP}$ = 3282 Hz, *cis*); **10a**: –3914 (dd, $^1J_{PtP}$ = 2479 Hz, $^1J_{PtP}$ = 2364 Hz, *trans*), –4401 (dd, $^1J_{PtP}$ = 3412 Hz, $^1J_{PtP}$ = 3725 Hz, *cis*); **10b**: –3917 (dd, $^1J_{PtP}$ = 2464 Hz, $^1J_{PtP}$ = 2402 Hz, *trans*), –4412 (dd, $^1J_{PtP}$ = 3404 Hz, $^1J_{PtP}$ = 3737 Hz, *cis*); **11a**: –3869 (dd, $^1J_{PtP}$ = 3030 Hz, $^1J_{PtP}$ = 2365 Hz, *trans*); **11b**: –3839 (dd, $^1J_{PtP}$ = 3049 Hz, $^1J_{PtP}$ = 2332 Hz, *trans*); **12a**: –3881 (dd, $^1J_{PtP}$ = 3428 Hz, $^1J_{PtP}$ = 2402 Hz, *trans*); **12b**: –3859 (dd, $^1J_{PtP}$ = 3454 Hz, $^1J_{PtP}$ = 2407 Hz, *trans*).

1.12 [Pd(**2b**)(η^3-C_4H_7)Cl] (**13b**)

[Pd(η^3-C_4H_7)Cl]$_2$ (19.7 mg, 50 µmol) and **2b** (34.2 mg, 100 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The intended complex was formed quantitatively. **^{1}H NMR** (500 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 8.14-8.10 (m, 2H, $H4'^B/H4'^A$), 7.99-7.92 (m, 5H, $H4^A/H4^B/H5^{AB}/H5'^B$), 7.92-7.86 (m, 2H, $H5'^A/H3^A$), 7.84 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 8.5 Hz, 1H, $H3^B$), 7.56-7.49 (m, 4H, $H3'^{AB}/H6^{AB}$), 7.33-7.23 (m, 5H, $H6'^{AB}/H7^{AB}/H7'^A$), 7.19-7.09 (m, 3H, $H7'^B/H8^A/H8^B$), 6.98 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8'^A$), 6.83 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8'^B$), 4.19 (dd, $^3J_{HP}$ = 7.4 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, allyl-$Ht_{syn}{}^B$), 4.12 (dd, $^3J_{HP}$ = 7.4 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, allyl-$Ht_{syn}{}^A$), 3.83 (s, 3H, $OCH_3{}^B$), 3.82 (s, 3H, $OCH_3{}^A$), 3.14 (s, 1H, allyl-$Hc_{syn}{}^B$), 2.90 (d, $^3J_{HP}$ = 12.8 Hz, 1H, allyl-$Ht_{anti}{}^B$), 2.47 (s, 1H, allyl-$Hc_{syn}{}^A$), 2.75 (d, $^3J_{HP}$ = 12.8 Hz, 1H, allyl-$Ht_{anti}{}^A$), 2.14 (s, 1H, allyl-$Hc_{anti}{}^B$), 1.71 (s, 3H, allyl-$CH_3{}^B$), 1.61 (s, 3H, allyl-$CH_3{}^A$), 1.59 (s, 1H, allyl-$Hc_{anti}{}^A$), 1.55-1.05 (m, 8H, $P(CH_2CH_2)^{AB}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 154.7 ($C2'^B$), 154.6 ($C2'^A$), 140.8 (d, $^2J_{CP}$ = 10.9 Hz, $C1^{AB}$), 134.1 ($C9'^B$), 134.0 ($C9'^A$), 133.6, 133.5, 132.6-132.4 (m), 132.0-131.7, (m) 131.4 (d, J_{CP} = 5.9 Hz), 130.9 ($C4'^B$), 130.8 ($C4'^A$), 130.2 (d, $^2J_{CP}$ = 10.2 Hz, $C3^A$), 129.7 (d, $^2J_{CP}$ = 11.1 Hz, $C3^B$), 129.0 ($C10'^B$), 128.9 ($C10'^A$), 128.4 ($C5^B$), 128.3 ($C5^A$), 128.3 ($C5'^B$), 128.3 ($C5'^A$), 128.2 (d, $^3J_{CP}$ = 9.0 Hz, $C4^B$), 128.0 (d, $^3J_{CP}$ = 8.5 Hz, $C4^A$), 127.6 ($C7'^A$), 127.5 ($C6^{AB}$), 127.2 ($C7^B$), 127.1 ($C7^A$), 127.0 ($C7'^B$), 126.2 ($C8^B$), 126.1 ($C8^A$), 125.6 ($C8'^A$), 125.2 ($C8'^B$), 124.0 ($C6'^B$), 123.8 ($C6'^A$), 119.9 (m, $C1'^{AB}$), 113.2 ($C3'^B$), 113.0 ($C3'^A$), 75.9 (d, $^2J_{CP}$ = 40.6 Hz, allyl-Ct^B), 75.6 (d, $^2J_{CP}$ = 40.6 Hz, allyl-Ct^A), 57.7 (allyl-Cc^A), 57.6 (allyl-Cc^B), 56.2 ($OCH_3{}^B$), 56.0 ($OCH_3{}^A$), 23.3 (allyl-$CH_3{}^B$), 23.2 (allyl-$CH_3{}^A$), 18.5 (d, $^1J_{CP}$ = 17.5 Hz, $P(CH_2CH_2)^B$), 7.7 (d, $^1J_{CP}$ = 16.5 Hz, $P(CH_2CH_2)^A$), 7.6 (d, $^1J_{CP}$ = 16.5 Hz, $P(CH_2CH_2)^B$), 7.4 (d, $^1J_{CP}$ = 17.1 Hz, $P(CH_2CH_2)^A$) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** (63%) –164.9; isomer **B** (37%) –165.8 ppm. **HRMS** (ESI$^+$): Found: m/z = 503.0744. Calculated for $[M – Cl]^+$: m/z = 503.0751.

1.13 [Pd(**3b**)(η^3-C_4H_7)Cl] (**14b**)

[Pd(η^3-C_4H_7)Cl]$_2$ (19.7 mg, 50 µmol) and **3b** (34.4 mg, 100 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The intended complex was formed quantitatively. Slow diffusion of Et_2O into the reaction mixture yielded colorless crystals overnight, which were suitable for X-ray diffraction analysis. **^{1}H NMR** (500 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 8.07-8.03 (m, 4H, $H4'^{A}/H4^{A}/H4^{B}/H4'^{B}$), 7.96-7.93 (m, 2H, $H5^{AB}$), 7.91 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HP}$ = 8.8 Hz, 1H, $H3^{B}$), 7.85 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H5'^{B}$), 7.83 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HP}$ = 8.8 Hz, 1H, $H3^{A}$), 7.81 (d, $^3J_{HH}$ = 8.1 Hz, 1H, $H5'^{A}$), 7.52-7.48 (m, 3H, $H3'^{B}/H6^{AB}$), 7.47 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H3'^{A}$), 7.29-7.18 (m, 5H, $H6'^{A}/H7^{AB}/H6'^{B}/H7'^{A}$), 7.15 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H7'^{B}$), 7.12 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8'^{A}$), 7.03-6.99 (m, 2H, $H8^{AB}$), 6.79 (d, $^3J_{HH}$ = 8.3 Hz, 1H, $H8'^{B}$), 3.92 (dd, $^3J_{HP}$ = 7.1 Hz, $^4J_{HH}$ = 2.9 Hz, 1H, allyl-$Ht_{syn}{}^{B}$), 3.88 (s, 3H, $OCH_3{}^{B}$), 3.82 (dd, $^3J_{HP}$ = 7.1 Hz, $^4J_{HH}$ = 2.6 Hz, 1H, allyl-$Ht_{syn}{}^{A}$), 3.79 (s, 3H, $OCH_3{}^{A}$), 2.61 (m, 1H, allyl-$Hc_{syn}{}^{B}$), 2.47 (m, 1H, allyl-$Hc_{syn}{}^{A}$), 2.14 (d, $^3J_{HP}$ = 10.6 Hz, 1H, allyl-$Ht_{anti}{}^{B}$), 2.03 (d, $^3J_{HP}$ = 10.4 Hz, 1H, allyl-$Ht_{anti}{}^{A}$), 1.72 (d, $^2J_{HP}$ = 8.7 Hz, 3H, $PCH_3{}^{A}$), 1.65 (s, 3H, allyl-$CH_3{}^{A}$), 1.63 (s, 3H, allyl-$CH_3{}^{B}$), 1.53 (d, $^2J_{HP}$ = 7.7 Hz, 3H, $PCH_3{}^{B}$), 1.50 (d, $^2J_{HP}$ = 9.6 Hz, 3H, $PCH_3{}^{B}$), 1.26 (d, $^2J_{HP}$ = 9.1 Hz, 3H, $PCH_3{}^{A}$), 0.91 (s, 1H, allyl-$Hc_{anti}{}^{B}$), 0.53 (s, 1H, allyl-$Hc_{anti}{}^{A}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 155.5 ($C2'^{B}$), 155.1 ($C2'^{A}$), 139.5 (d, $^2J_{CP}$ = 14.5 Hz, $C1^{B}$), 138.7 (d, $^2J_{CP}$ = 11.3 Hz, $C1^{A}$), 134.4, 134.0, 133.8, 133.8, 133.1 (d, $^1J_{CP}$ = 56.2 Hz, $C2^{B}$), 133.0 (d, J_{CP} = 8.4 Hz), 132.8 (d, J_{CP} = 8.4 Hz), 132.6 (d, $^1J_{CP}$ = 56.2 Hz, $C2^{A}$), 131.9 (d, $^2J_{CP}$ = 5.4 Hz, allyl-C^{B}), 131.2 (d, $^2J_{CP}$ = 5.4 Hz, allyl-C^{A}), 130.9, 129.9, 128.8, 128.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.7, 127.7, 127.5, 127.3 ($C6^{AB}$), 127.2, 127.1, 127.0 ($C3^{A}$), 126.9 ($C3^{B}$), 126.9 ($C8'^{B}$), 126.8 ($C7^{AB}$), 126.7 ($C7'^{B}$), 125.7 ($C8^{A}$), 123.4 ($C8'^{A}$), 119.8 (d, $^3J_{CP}$ = 5.7 Hz, $C1'^{A}$), 119.5 (d, $^3J_{CP}$ = 6.7 Hz, $C1'^{B}$), 113.8 ($C3'^{B}$), 112.6 ($C3'^{A}$), 76.8 (d, $^2J_{CP}$ = 35.4 Hz, allyl-Ct^{B}), 75.1 (d, $^2J_{CP}$ = 35.1 Hz, allyl-Ct^{A}), 55.8 ($OCH_3{}^{A}$), 55.8 ($OCH_3{}^{B}$), 55.1 (allyl-Cc^{B}), 53.6 (d, $^2J_{CP}$ = 1.8 Hz, allyl-Cc^{A}), 23.6 (allyl-$CH_3{}^{B}$), 23.6 (allyl-$CH_3{}^{A}$), 17.6 (d, $^1J_{CP}$ = 26.2 Hz, $PCH_3{}^{B}$), 16.3 (d, $^1J_{CP}$ = 25.8 Hz, $PCH_3{}^{A}$), 15.4 (d, $^1J_{CP}$ = 26.4 Hz, $PCH_3{}^{B}$), 14.4 (d, $^1J_{CP}$ = 28.7 Hz, $PCH_3{}^{A}$) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** (67%) –6.1; isomer **B** (33%) –8.7 ppm. **HRMS** (NSI$^+$, MeOH): Found: *m*/*z* = 505.0906. Calculated for $[M – Cl]^+$: *m*/*z* = 505.0918.

1.14 [Pd(**4b**)(η^3-C_4H_7)Cl] (**15b**)

[Pd(η^3-C_4H_7)Cl]$_2$ (19.7 mg, 50 µmol) and **4b** (34.4 mg, 100 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The intended complex was formed quantitatively. **^{1}H NMR** (500 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 7.99-7.95 (m, 4H, $H4'^{AB}/H4^{AB}$), 7.90-7.87 (m, 4H, $H5^{AB}/H5'^{AB}$), 7.68 (dd, $^3J_{HP}$ = 12.9 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, $H3^{B}$), 7.68 (dd, $^3J_{HP}$ = 12.6 Hz, $^3J_{HH}$ = 8.8 Hz, 1H, $H3^{A}$), 7.50-7.45 (m, 4H, $H3'^{AB}/H6^{AB}$), 7.31-7.26 (m, 2H, $H6'^{AB}$), 7.20-7.15 (m, 4H, $H7^{AB}/H7'^{AB}$), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 1H, $H8'^{B}$), 6.99 (d, $^3J_{HH}$ = 8.4 Hz, 1H, $H8'^{A}$), 6.91 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8^{B}$), 6.88 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8^{A}$), 4.20 (dd, $^3J_{HP}$ = 8.1 Hz, $^4J_{HH}$ = 3.2 Hz, 1H, allyl-$Ht_{syn}{}^{B}$), 4.18 (dd,

$^{3}J_{HP}$ = 8.0 Hz, $^{4}J_{HH}$ = 3.1 Hz, 1H, allyl-Ht$_{syn}^{A}$), 3.76 (s, 3H, OCH_3^{B}), 3.74 (s, 3H, OCH_3^{A}), 3.32 (d, $^{3}J_{HP}$ = 11.2 Hz, 1H, allyl-Ht$_{anti}^{B}$), 3.30 (d, $^{3}J_{HP}$ = 11.2 Hz, 1H, allyl-Ht$_{anti}^{A}$), 2.78 (s, 1H, allyl-Hc$_{syn}^{B}$), 2.59 (s, 1H, allyl-Hc$_{syn}^{A}$), 2.49 (d, $^{3}J_{HP}$ = 9.4 Hz, 6H, N(CH_3)$_2^{A}$), 2.44 (s, 2H, allyl-Hc$_{anti}^{AB}$), 2.30 (d, $^{3}J_{HP}$ = 9.4 Hz, 6H, N(CH_3)$_2^{B}$), 2.16 (d, $^{3}J_{HP}$ = 10.0 Hz, 6H, N(CH_3)$_2^{B}$), 2.04 (d, $^{3}J_{HP}$ = 9.4 Hz, 6H, N(CH_3)$_2^{A}$), 1.88 (s, 3H, allyl-CH_3^{B}), 1.85 (s, 3H, allyl-CH_3^{A}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, –25 °C): δ = isomer **A**,**B** 153.9 ($C2'^{A}$), 153.9 ($C2'^{B}$), 138.6 (d, $^{1}J_{CP}$ = 20.3 Hz, $C2^{A}$), 138.3 (d, $^{1}J_{CP}$ = 22.3 Hz, $C2^{B}$), 135.6 (d, $^{2}J_{CP}$ = 6.6 Hz, $C1^{A}$), 135.5 (d, $^{2}J_{CP}$ = 6.2 Hz, $C1^{B}$), 134.0 ($C9'^{B}$), 133.9 ($C9'^{A}$), 133.5 (d, $^{4}J_{CP}$ = 1.5 Hz, $C10^{A}$), 133.5 (d, $^{4}J_{CP}$ = 1.5 Hz, $C10^{B}$), 133.0 (d, $^{3}J_{CP}$ = 8.1 Hz, $C9^{A}$), 132.9 (d, $^{3}J_{CP}$ = 8.1 Hz, $C9^{B}$), 132.7 (d, $^{2}J_{CP}$ = 5.7 Hz, allyl-C^{A}), 132.6 (d, $^{2}J_{CP}$ = 5.7 Hz, allyl-C^{B}), 129.6 (d, $^{2}J_{CP}$ = 23.0 Hz, $C3^{B}$), 129.5 (d, $^{2}J_{CP}$ = 21.9 Hz, $C3^{A}$), 129.2 ($C4'^{B}$), 129.2 ($C4'^{A}$), 128.9 ($C10'^{B}$), 128.8 ($C10'^{A}$), 128.2 ($C5'^{A}$), 128.2 ($C5'^{B}$), 128.0 ($C5^{AB}$), 127.7 (d, $^{3}J_{CP}$ = 12.6 Hz, $C4^{B}$), 127.7 (d, $^{3}J_{CP}$ = 12.1 Hz, $C4^{A}$), 127.1 ($C6^{B}$), 127.1 ($C6^{A}$), 126.7 ($C7^{AB}$), 126.7 ($C7'^{A}$), 126.6 ($C7'^{B}$), 126.5 ($C8^{A}$), 126.5 ($C8^{B}$), 125.2, 123.6 ($C6'^{B}$), 123.5 ($C6'^{A}$), 121.0 ($C1'^{B}$), 120.8 ($C1'^{A}$), 112.9 ($C3'^{B}$), 112.6 ($C3'^{A}$), 77.8 (d, $^{2}J_{CP}$ = 38.7 Hz, allyl-Ct^{B}), 77.4 (d, $^{2}J_{CP}$ = 38.7 Hz, allyl-Ct^{A}), 59.9 (allyl-Cc^{A}), 59.5 (allyl-Cc^{B}), 56.0 (OCH$_3^{B}$), 55.7 (OCH$_3^{A}$), 41.3 (d, $^{2}J_{CP}$ = 7.4 Hz, N(CH$_3$)$_2^{A}$), 40.7 (d, $^{2}J_{CP}$ = 7.9 Hz, N(CH$_3$)$_2^{B}$), 40.3 (d, $^{2}J_{CP}$ = 7.9 Hz, N(CH$_3$)$_2^{B}$), 40.2 (d, $^{2}J_{CP}$ = 7.9 Hz, N(CH$_3$)$_2^{A}$), 23.2 (allyl-CH$_3$), 23.2 (allyl-CH$_3$) ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** (61%) 105.0; isomer **B** (39%) 105.4 ppm. **HRMS** (ESI$^+$): Found: m/z = 563.1446. Calculated for [M – Cl]$^+$: m/z = 563.1449.

1.15 [Pd(**5b**)(η^3-C_4H_7)Cl] (**16b**)

[Pd(η^3-C_4H_7)Cl]$_2$ (9.8 mg, 25 µmol) and **5b** (18.8 mg, 50 µmol) were dissolved in CD_2Cl_2 (0.7 mL) and stirred for 15 minutes. The intended complex was formed quantitatively. **^{1}H NMR** (500 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** 8.15 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 5.6 Hz, 1H, $H$3), 8.07 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, $H$4), 7.99-7.97 (m, 2H), 7.77 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.54 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, $H$6), 7.45 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, $H$3'), 7.30-7.21 (m, 3H, $H$6'/$H$7/$H$7'), 7.18 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, $H$8'), 7.05 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, $H$8), 3.78 (d, $^{3}J_{HP}$ = 14.2 Hz, 3H, POCH_3), 3.78 (s, 3H, OCH_3), 3.77 (m, 1H, allyl-Ht$_{syn}$), 3.35 (d, $^{3}J_{HP}$ = 11.2 Hz, 3H, POCH_3), 2.73 (s, 1H, allyl-Hc$_{syn}$), 1.58 (d, $^{3}J_{HP}$ = 11.2 Hz, 1H, allyl-Ht$_{anti}$), 0.46 (s, 1H, allyl-Hc$_{anti}$), 1.65 (s, 3H, allyl-CH_3) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** 156.1 ($C$2'), 140.1 (d, $^{2}J_{CP}$ = 22.4 Hz, $C$1), 133.9 ($C$10), 133.0 (d, $^{1}J_{CP}$ = 10.6 Hz, $C$2), 132.5 (d, $^{3}J_{CP}$ = 8.4 Hz, $C$9), 131.5 (d, allyl-C), 130.6 ($C$4'), 128.3 ($C$8'), 128.3 ($C$5), 127.5 ($C$4), 127.9 ($C$6), 127.7 ($C$7'), 127.3 ($C$5'), 127.0 (d, $^{2}J_{CP}$ = 3.9 Hz, $C$3), 126.8 ($C$7), 126.1 ($C$8), 123.9 ($C$6'), 118.3 (d, $^{3}J_{CP}$ = 7.7 Hz, $C$1'), 112.6 ($C$3'), 76.6 (d, $^{2}J_{CP}$ = 43.5 Hz, allyl-Ct), 56.0 (d, $^{2}J_{CP}$ = 5.8 Hz, POCH$_3$), 55.7 (OCH$_3$), 54.5 (d, $^{2}J_{CP}$ = 5.2 Hz, allyl-Cc), 52.3 (d, $^{2}J_{CP}$ = 13.0 Hz, POCH$_3$), 23.4 (allyl-CH$_3$) ppm; resonances for $C$9' and $C$10' are obscured. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2, –25 °C): δ = isomer **A** (89%) 148.9; isomer **B** (11%) 147.2 ppm. **HRMS** (NSI$^+$): Found: m/z = 533.0824. Calculated for [M – Cl]$^+$: m/z = 533.0827.

1.16 [Pd(**3b**)(η^3-C_4H_7)]BArF (**17b**)

NaBArF (44.3 mg, 50.0 µmol) and **14b** (27.1 mg, 50.0 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The reaction mixture was filtered through a layer of celite and the solvent removed *in vacuo*; the intended product was obtained as a pale yellow solid. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = isomer **A**,**B** 8.17-8.11 (m, 4H, *H*4/*H*4'), 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 8.03 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.96 (m, 2H, *H*5), 7.91 (d, $^3J_{HH}$ = 9.3 Hz, 1H, *H*3'^{A}), 7.84 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*3'^{B}), 7.76 (m, 2H, *H*3), 7.75 (s, 16H, *o*-BArF), 7.58 (s, 8H, *p*-BArF), 7.54-7.49 (m, 4H, *H*6'/*H*6), 7.43 (m, 1H, *H*7'), 7.35 (m, 1H, *H*7'), 7.19-7.14 (m, 2H, *H*7), 7.00 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*8'), 6.89 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*8'), 5.83 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8), 5.78 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8), 3.90 (s, 3H, OCH_3^A), 3.82 (s, 3H, OCH_3^B), 3.58 (d, $^3J_{HP}$ = 9.5 Hz, 1H, allyl-*H*t$_{anti}$), 3.44 (s, 1H, allyl-*H*c$_{syn}$), 3.23 (s, 1H, allyl-*H*c$_{syn}$), 2.71 (d, $^3J_{HP}$ = 9.5 Hz, 1H, allyl-*H*t$_{anti}$), 2.61 (s, 1H, allyl-*H*c$_{anti}$), 2.55 (dd, $^3J_{HP}$ = 5.8 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, allyl-*H*t$_{syn}$), 2.47 (s, 1H, allyl-*H*c$_{anti}$), 2.06 (dd, $^3J_{HP}$ = 6.3 Hz, $^4J_{HH}$ = 3.1 Hz, 1H, allyl-*H*t$_{syn}$), 1.95 (d, $^2J_{HP}$ = 10.2 Hz, 3H, PCH_3), 1.93 (d, $^2J_{HP}$ = 10.0 Hz, 3H, PCH_3), 1.83 (s, 3H, allyl-CH_3), 1.80 (d, $^2J_{HP}$ = 10.3 Hz, 3H, PCH_3), 1.72 (d, $^2J_{HP}$ = 10.3 Hz, 3H, PCH_3), 1.10 (s, 3H, allyl-CH_3) ppm; in some cases the distinct assignment of resonances to the respective isomer was unavailable. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –7.6 ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = isomer **A**,**B** 161.8 (q, $^1J_{CB}$ = 49.9 Hz, *ipso*-BArF), 155.6 (*C*2'^{A}), 154.0 (*C*2'^{B}), 140.6 (d, $^2J_{CP}$ = 27.0 Hz, *C*1), 137.0 (d, $^2J_{CP}$ = 27.0 Hz, allyl-*C*^{A}), 136.4 (d, $^2J_{CP}$ = 27.0 Hz, allyl-*C*^{B}), 136.1 (d, $^1J_{CP}$ = 30.7 Hz, *C*2), 135.8, 135.7 (d, $^1J_{CP}$ = 30.7 Hz, *C*2), 134.9 (*o*-BArF), 134.2 (*C*4'^{A}), 133.9 (*C*4'^{B}), 132.3 (*C*9'^{B}), 131.9 (d, $^3J_{CP}$ = 3.9 Hz, *C*9), 131.8 (d, $^3J_{CP}$ = 3.7 Hz, *C*9), 131.5 (*C*4), 131.4 (*C*4), 131.2 (*C*9'^{A}), 129.9 (*C*10'^{B}), 129.7 (*C*5'), 129.5 (*C*5'), 129.3, 129.0 (qq, $^2J_{CF}$ = 31.2 Hz, $^4J_{CF}$ = 2.9 Hz, *m*-BArF), 128.6 (*C*5), 128.5 (*C*6), 128.3 (*C*7), 128.3 (*C*7), 126.4 (*C*6'^{B}), 126.3 (*C*6'^{A}), 124.7 (q, $^1J_{CF}$ = 272.3 Hz, CF_3), 124.7 (*C*8), 124.5 (*C*8), 124.0, 122.6 (*C*8'^{A}), 122.0 (*C*8'^{B}), 117.5 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-BArF), 115.5 (*C*3'^{B}), 115.0 (*C*3'^{A}), 105.2 (*C*1'^{B}), 104.6 (*C*1'^{A}), 98.2 (d, $^2J_{CP}$ = 30.4 Hz, allyl-*C*t), 97.6 (d, $^2J_{CP}$ = 30.7 Hz, allyl-*C*t), 57.2 (OCH_3^A), 57.0 (OCH_3^B), 52.7 (d, $^2J_{CP}$ = 2.7 Hz, allyl-*C*c^B), 52.5 (d, $^2J_{CP}$ = 2.7 Hz, allyl-*C*c^A), 22.9 (allyl-CH_3^B), 21.7 (allyl-CH_3^A), 16.2 (d, $^1J_{CP}$ = 28.9 Hz, PCH_3), 16.2 (d, $^1J_{CP}$ = 29.3 Hz, PCH_3), 15.4 (d, $^1J_{CP}$ = 28.3 Hz, PCH_3), 15.0 (d, $^1J_{CP}$ = 29.3 Hz, PCH_3) ppm; in some cases the distinct assignment of resonances to the respective isomer was unavailable. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –62.7 ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = isomer **A** (50%) 9.4; isomer **B** (50%) 8.7 ppm. **HRMS** (ESI$^+$): Found: *m*/*z* = 501.0925. Calculated for [M – BArF]$^+$: *m*/*z* = 501.0934.

1.17 [Pd(**4b**)(η^3-C_4H_7)]BArF (**18b**)

NaBArF (44.3 mg, 50.0 µmol) and **15b** (30.0 mg, 50.0 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The reaction mixture was filtered through a layer of celite and the solvent removed *in vacuo*; the intended product was obtained as a pale yellow solid. Slow evaporation of a

CH_2Cl_2 solution gave crystals which were suitable for X-ray analysis. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = isomer **A**,**B** 8.12 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H, *H*4'), 8.10 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *H*4), 8.05 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5'), 8.03 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5'), 7.94 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*5), 7.93 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, *H*3'), 7.85 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, *H*3'), 7.81 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HP}$ = 6.5 Hz, 2H, *H*3), 7.75 (s, 16H, *o*-BArF), 7.58 (s, 8H, *p*-BArF), 7.55-7.47 (m, 4H, *H*6'/*H*6), 7.44 (m, 1H, *H*7'), 7.36 (m, 1H, *H*7'), 7.15-7.10 (m, 2H, *H*7), 7.07 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*8'), 6.95 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*8'), 5.67 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*8), 5.66 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*8), 3.87 (s, 3H, OCH_3), 3.82 (d, $^{3}J_{HP}$ = 10.6 Hz, 1H, allyl-Ht_{anti}), 3.78 (s, 3H, OCH_3), 3.63 (m, 1H, allyl-Hc_{syn}), 3.33 (m, 1H, allyl-Hc_{syn}), 2.70 (d, $^{3}J_{HP}$ = 14.4 Hz, 3H, NCH_3), 2.69 (d, $^{3}J_{HP}$ = 14.4 Hz, 3H, NCH_3), 2.68 (m, 1H, allyl-Ht_{anti}), 2.61 (d, $^{3}J_{HP}$ = 12.2 Hz, 6H, NCH_3), 2.58 (m, 1H, allyl-Hc_{anti}), 2.45 (dd, $^{3}J_{HP}$ = 7.4 Hz, $^{4}J_{HH}$ = 2.8 Hz, 1H, allyl-Ht_{syn}), 2.37 (s, 1H, allyl-Hc_{anti}), 1.90-1.84 (m, 4H, allyl-Ht_{syn}/allyl-CH_3), 1.08 (s, 3H, allyl-CH_3) ppm; in some cases the distinct assignment of resonances to the respective isomer was unavailable. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –7.5 ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = isomer **A**,**B** 161.8 (q, $^{1}J_{CB}$ = 50.2 Hz, *ipso*-BArF), 156.2 (*C*2'), 154.5 (*C*2'), 140.7 (d, $^{1}J_{CP}$ = 35.3 Hz, *C*2), 140.6 (d, $^{1}J_{CP}$ = 35.1 Hz, *C*2), 140.5 (d, $^{2}J_{CP}$ = 18.2 Hz, *C*1), 140.0 (d, $^{2}J_{CP}$ = 18.5 Hz, *C*1), 136.1 (m, *C*9), 135.7 (d, $^{2}J_{CP}$ = 7.8 Hz, allyl-*C*), 135.2 (d, $^{2}J_{CP}$ = 8.0 Hz, allyl-*C*), 134.8 (*o*-BArF), 134.4 (*C*4'), 134.2 (*C*4'), 133.2 (*C*9'), 132.2 (*C*9'), 132.0 (m, *C*9), 131.9 (m, *C*10), 130.6 (d, $^{3}J_{CP}$ = 3.4 Hz, *C*4), 130.5 (d, $^{3}J_{CP}$ = 3.4 Hz, *C*4), 130.1 (*C*7'), 129.8 (*C*7'), 129.5 (*C*5'), 129.3 (*C*5'), 129.2 (d, $^{5}J_{CP}$ = 0.9 Hz, *C*10'), 128.9 (d, $^{5}J_{CP}$ = 0.9 Hz, *C*10'), 128.9 (qq, $^{2}J_{CF}$ = 31.2 Hz, $^{4}J_{CF}$ = 2.9 Hz, *m*-BArF), 128.5 (*C*5/*C*6), 128.1 (*C*7), 126.6 (*C*6'), 126.3 (*C*6'), 124.7 (q, $^{1}J_{CF}$ = 272.3 Hz, CF_3), 124.5-124.3 (m, *C*3/*C*8'/*C*8), 117.5 (septet, $^{3}J_{CF}$ = 4.0 Hz, *p*-BArF), 115.6 (*C*3'), 115.1 (*C*3'), 102.5 (*C*1'), 102.4 (*C*1'), 101.0 (d, $^{2}J_{CP}$ = 34.8 Hz, allyl-*C*t), 100.1 (d, $^{2}J_{CP}$ = 34.4 Hz, allyl-*C*t), 57.0 (OCH_3), 56.8 (OCH_3), 46.0 (d, $^{2}J_{CP}$ = 5.5 Hz, allyl-*C*c), 45.7 (d, $^{2}J_{CP}$ = 5.7 Hz, allyl-*C*c), 38.1 (d, $^{2}J_{CP}$ = 9.1 Hz, NCH_3), 38.0 (d, $^{2}J_{CP}$ = 8.7 Hz, NCH_3), 37.9 (d, $^{2}J_{CP}$ = 9.1 Hz, NCH_3), 37.8 (d, $^{2}J_{CP}$ = 8.7 Hz, NCH_3), 22.9 (allyl-CH_3), 21.6 (allyl-CH_3) ppm; in some cases the distinct assignment of resonances to the respective isomer was unavailable. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –62.7 ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = isomer **A** (50%) 120.5; isomer **B** (50%) 120.5 ppm. **HRMS** (ESI^{+}): Found: *m*/*z* = 562.1448. Calculated for [M – BArF]$^{+}$: *m*/*z* = 562.1460.

1.18 [Pd(**3b**)$_2$(η^3-C_4H_7)]BArF (**19b**)

3b (17.2 mg, 50.0 µmol) and **17b** (68.5 mg, 50.0 µmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 minutes. The solvent was removed *in vacuo* and the intended product was obtained as a yellow solid. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 8.09 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, $H4'^{B}$), 8.09 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, $H4'^{A}$), 8.04 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, $H4^{A}$), 7.96 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, $H5^{A}$), 7.93-7.88 (m, 4H, $H5'^{B}$/$H4^{B}$/$H5^{B}$/$H5'^{A}$), 7.78 (s, 8H, *o*-BArF), 7.64 (dd, $^{3}J_{HP}$ = 11.5 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1H, $H3^{A}$), 7.60 (s, 4H, *p*-BArF), 7.58-7.54 (m, 2H, $H6^{A}$/$H6^{B}$), 7.49 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, $H3'^{A}$), 7.49 (dd, $^{3}J_{HP}$ = 13.9 Hz, $^{3}J_{HH}$ = 8.7 Hz, 1H, $H3^{B}$), 7.46 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, $H3'^{B}$), 7.37 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 6.8 Hz,

$^4J_{HH}$ = 1.1 Hz, 1H, $H6'^{B}$), 7.33-7.24 (m, 3H, $H7^{B}$/$H6'^{A}$/$H7^{A}$), 7.22 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H7'^{B}$), 7.05 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H8^{B}$), 7.05 (ddd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $H7'^{A}$), 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H8^{A}$), 6.76 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8'^{B}$), 6.73 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H8'^{A}$), 3.79 (s, 3H, OCH_3^{B}), 3.76 (s, 3H, OCH_3^{A}), 3.65 (s, 1H, allyl-H_{syn}), 3.57 (s, 1H, allyl-H_{syn}), 1.78 (d, $^3J_{HP}$ = 10.1 Hz, 1H, allyl-H_{anti}), 1.74 (s, 3H, allyl-CH_3), 1.64 (d, $^3J_{HP}$ = 10.1 Hz, 1H, allyl-H_{anti}), 1.40 (d, $^2J_{HP}$ = 8.5 Hz, 3H, PCH_3^{A}), 1.21 (d, $^2J_{HP}$ = 9.5 Hz, 3H, PC$H_3'^{A}$), 1.10 (d, $^2J_{HP}$ = 9.0 Hz, 3H, PCH_3^{B}), 1.08 (d, $^2J_{HP}$ = 8.9 Hz, 3H, PC$H_3'^{B}$) ppm; only one isomer was observed; labelled as A,B to distinguish between the resonances of the two ligands. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ = –7.5 ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 161.9 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-BArF), 155.4 ($C2'^{A}$), 155.1 ($C2'^{B}$), 139.5 (d, $^2J_{CP}$ = 7.6 Hz, $C1^{A}$), 139.3 (d, $^2J_{CP}$ = 3.4 Hz, $C1^{B}$), 137.3 (pt, $^2J_{CP}$ = 5.4 Hz, allyl-*C*), 134.9 (*o*-BArF), 134.4 (d, $^4J_{CP}$ = 2.0 Hz, $C10^{A}$), 134.3 (d, $^4J_{CP}$ = 2.0 Hz, $C10^{B}$), 134.3 ($C9'^{A}$), 134.2 ($C9'^{B}$), 133.4 (d, $^3J_{CP}$ = 1.6 Hz, $C9^{A}$), 133.3 (d, $^3J_{CP}$ = 2.4 Hz, $C9^{B}$), 131.5 ($C4'^{A}$), 131.4 ($C4'^{B}$), 130.5 (d, $^1J_{CP}$ = 41.6 Hz, $C2^{A}$), 129.9 (d, $^1J_{CP}$ = 41.8 Hz, $C2^{B}$), 129.4 (d, $^2J_{CP}$ = 24.3 Hz, $C3^{B}$), 129.1 ($C10'^{B}$), 129.0 (qq, $^2J_{CF}$ = 31.2 Hz, $^4J_{CF}$ = 2.9 Hz, *m*-BArF), 128.9 ($C10'^{A}$), 128.7 ($C4^{A}$/$C5'^{A}$), 128.5 ($C4^{B}$/$C5^{B}$), 128.2 ($C5^{A}$), 128.2 ($C6^{A}$/$C6^{B}$), 128.1 ($C5'^{B}$), 127.6 ($C7^{A}$), 127.6 ($C7^{B}$), 127.3 ($C7'^{B}$), 127.1 (d, $^2J_{CP}$ = 12.6 Hz, $C3^{A}$), 127.1 ($C7'^{A}$), 126.2 ($C8^{B}$), 126.1 ($C8^{A}$), 124.7 (q, $^1J_{CF}$ = 272.3 Hz, CF_3), 125.0 ($C8'^{B}$), 124.5 ($C6'^{B}$), 124.3 ($C8'^{A}$), 124.1 ($C6'^{A}$), 120.1 ($C1'^{B}$), 119.7 ($C1'^{A}$), 117.6 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-BArF), 113.4 ($C3'^{A}$), 113.3 ($C3'^{B}$), 70.6 (d, $^2J_{CP}$ = 30.5 Hz, allyl-CH_2), 69.8 (d, $^2J_{CP}$ = 30.8 Hz, allyl-CH_2'), 56.3 (OCH_3^{B}), 55.9 (OCH_3^{A}), 23.6 (allyl-CH_3), 17.7 (dd, $^1J_{CP}$ = 27.2 Hz, $^3J_{CP}$ = 2.4 Hz, P$CH_3'^{A}$), 17.5 (dd, $^1J_{CP}$ = 26.9 Hz, $^3J_{CP}$ = 2.4 Hz, PCH_3^{B}), 16.3 (m, PCH_3^{A}/P$CH_3'^{B}$) ppm; only one isomer was observed; labelled as A,B to distinguish between the resonances of the two ligands. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ = –62.7 ppm. **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = –2.1 (d, $^2J_{PP}$ = 43 Hz, P^{A}), –7.6 (d, $^2J_{PP}$ = 43 Hz, P^{B}) ppm; only one isomer was observed; labelled as A,B to distinguish between the resonances of the two ligands. **HRMS** (ESI$^+$): Found: *m*/*z* = 845.2245. Calculated for [M – BArF]$^+$: *m*/*z* = 845.2258.

1.19 General Procedure for the Palladium-Catalysed Hydrosilylation of Styrene

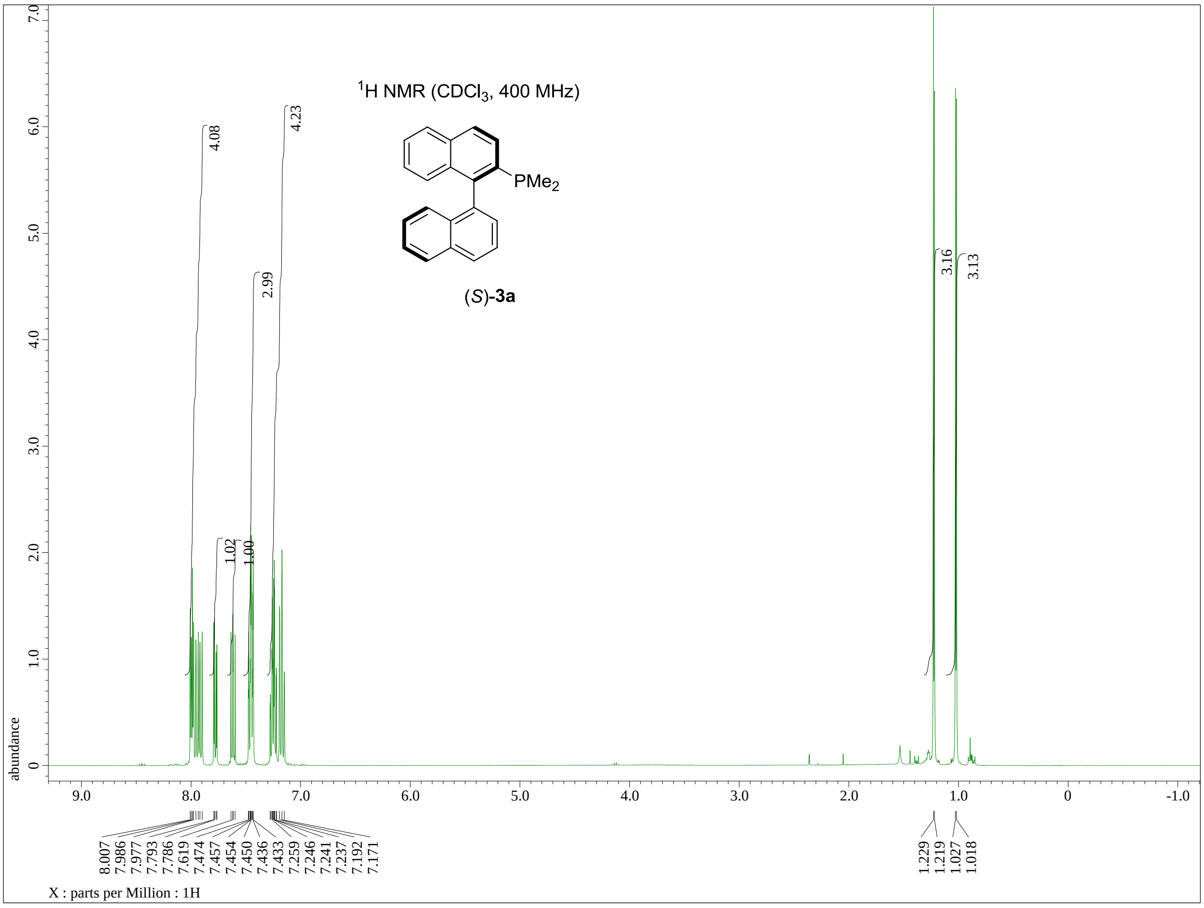
[Pd(η^3-C_3H_5)Cl]$_2$ (4.6 mg, 0.0125 mmol), the ligand (0.025 or 0.050 mmol) and styrene (1.2 mL, 1.0 g, 10.0 mmol) were stirred at room temperature for 20 minutes. $HSiCl_3$ (1.2 mL, 1.6 g, 12.0 mmol) was added and the reaction was stirred at room temperature for the appropriate time. The conversion of the reaction was followed by ^{1}H NMR spectroscopy. The product was purified by Kugelrohr distillation (reduced pressure, 150 °C).

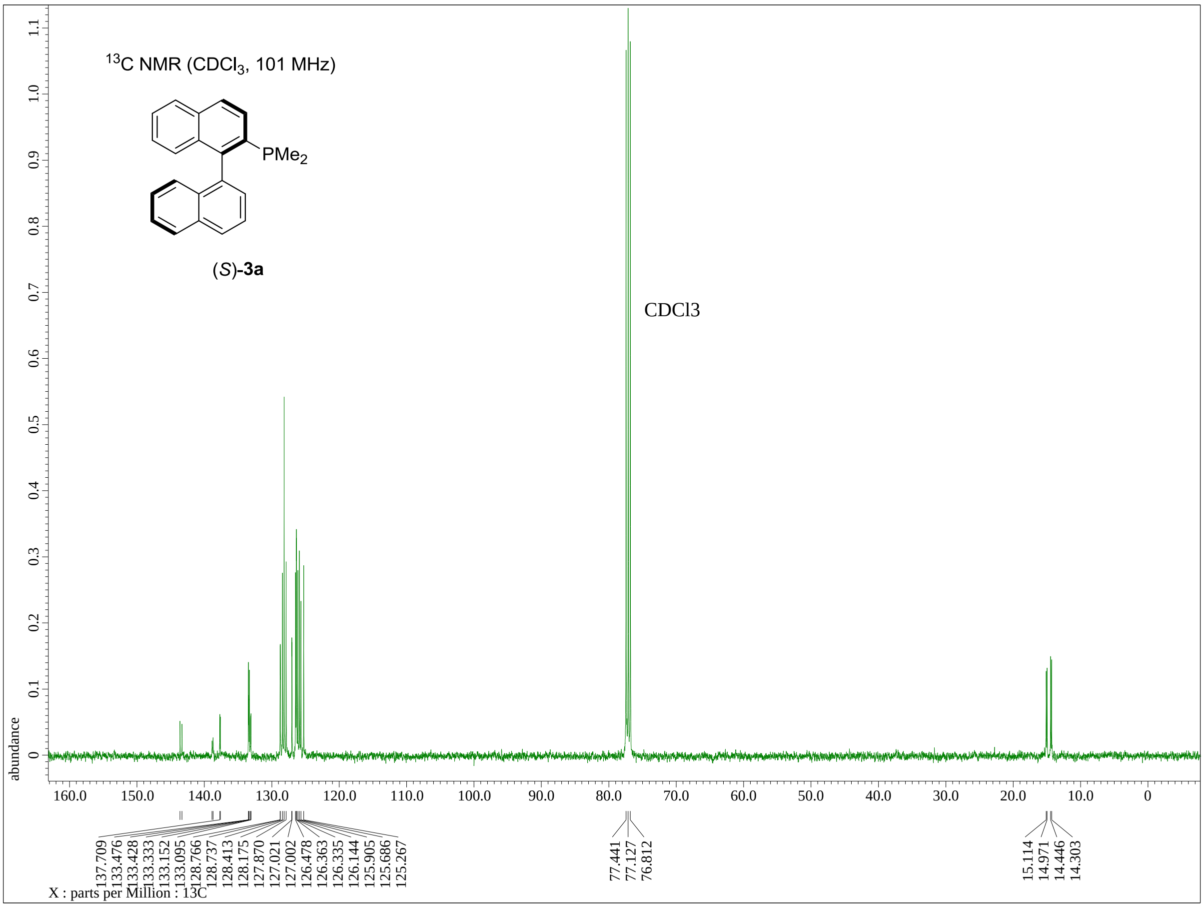
Trichloro(1-phenylethyl)silane (400 mg, 1.67 mmol) was dissolved in MeOH (30 mL) and THF (30 mL). K_2CO_3 (1.40 g, 10.1 mmol), KF (600 mg, 10.3 mmol) and 35% H_2O_2 (1.8mL) were added subsequently and the mixture was stirred overnight. After filtration, H_2O was added and the product was extracted with Et_2O (3×). The combined organic washings were dried over $MgSO_4$. The crude product was purified by column chromatography (hexane/EtOAc, 4:1, R_f = 0.20) on silica media to obtain the desired product. The enantiomeric excess was measured by chiral HPLC (Lux 5u Cellulose-1 Column, 250 × 4.6 mm; flow rate: 1.0 mL/min; hexane/2-propanol, 95:5; retention times: (*R*) t_1 = 8.9 min, (*S*) t_2 = 10.2 min). The absolute assignment was made according to literature data.[5]

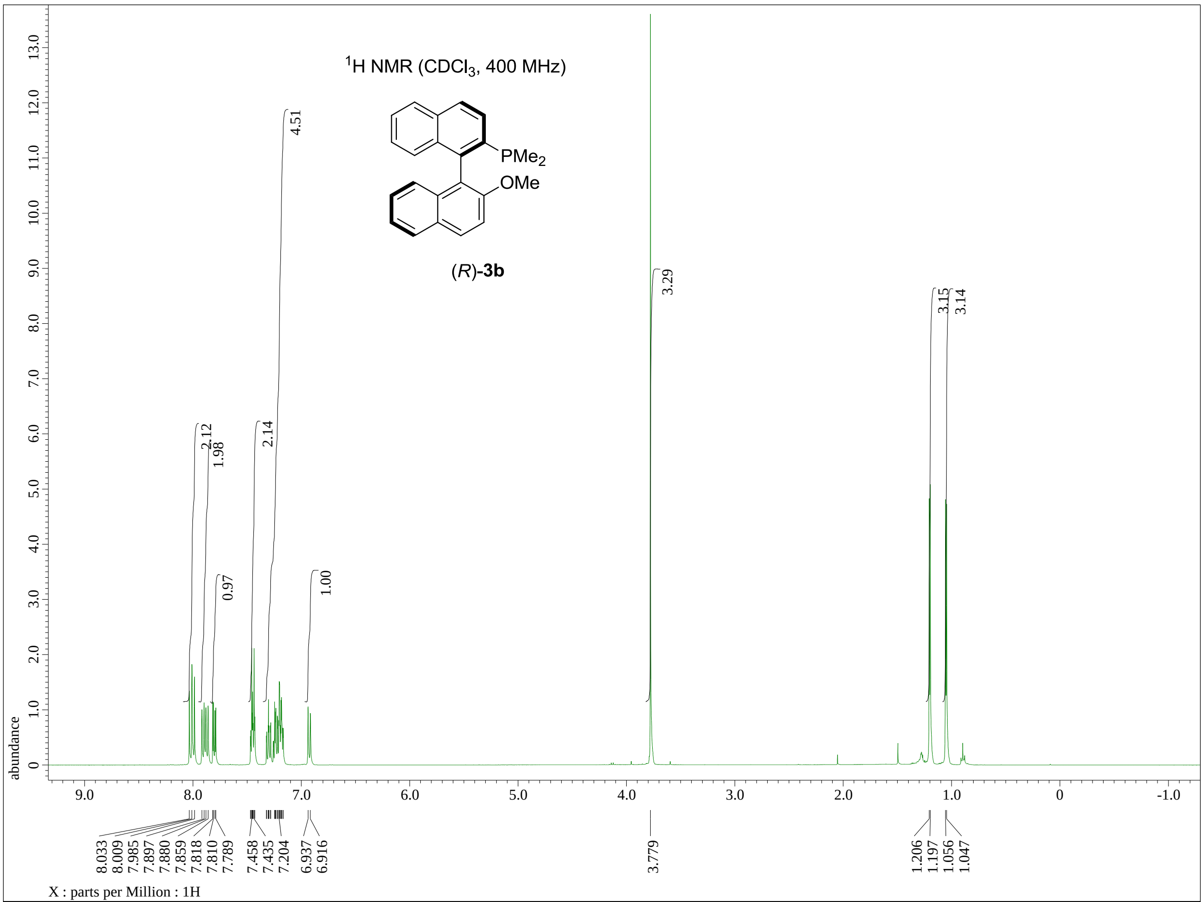
1.20 General Procedure for the Palladium-Catalysed Asymmetric Allylic Alkylation of (*rac*)-(*E*)-1,3-Diphenylallyl Acetate

$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.01 mmol) and the ligand (0.02 or 0.04 mmol) were dissolved in CH_2Cl_2 (3ml) and stirred for 20 minutes. Subsequently the reaction was treated with a solution of (*rac*)-(*E*)-1,3-diphenylallyl acetate (126 mg, 0.5 mmol) in CH_2Cl_2 (3 mL), KOAc (5 mg, 0.05 mmol), dimethyl malonate (0.11 mL, 1.0 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (0.25 mL, 1.0 mmol). The reaction mixture was stirred at room temperature and the conversion was monitored by TLC analysis. After the appropriate reaction time the solution was diluted with Et_2O (20 ml) and washed with saturated aqueous NH_4Cl (3 × 20 ml). The organic phase was dried over $MgSO_4$. The product was purified by column chromatography (hexane/EtOAc, 3:1, R_f = 0.50) on silica media (h = 13 cm, d = 2 cm) to give a colorless oil (in some cases the oil became a white solid after a few hours). The enantiomeric excess was measured by chiral HPLC (Column Daicel Chiralcel AD-H; flow rate: 1.0 mL/min; hexane/2-propanol, 90:10; retention times: (*R*) t_1 = 10.0 min, (*S*) t_2 = 13.4 min). The absolute assignment was made according to literature data.[6]

2 NMR Spectra


1H NMR (CDCl3, 400 MHz)
PMe2
(S)-3a
abundance
X : parts per Million : 1H
4.08
2.99
4.23
1.02
1.00
3.16
3.13
8.007 7.986 7.977 7.793 7.786 7.619 7.474 7.457 7.454 7.450 7.436 7.433 7.259 7.246 7.241 7.237 7.192 7.171
1.229 1.219 1.027 1.018


13C NMR (CDCl3, 101 MHz)
PMe2
(S)-3a
CDCl3
abundance
X : parts per Million : 13C
137.709 133.476 133.428 133.333 133.152 133.095 128.766 128.737 128.413 128.175 127.870 127.021 127.002 126.478 126.363 126.335 126.144 125.905 125.686 125.267
77.441 77.127 76.812
15.114 14.971 14.446 14.303



1H NMR (CDCl3, 400 MHz)
PMe2
OMe
(R)-3b
abundance
X : parts per Million : 1H
2.12
1.98
0.97
2.14
4.51
1.00
3.29
3.15
3.14
8.033
8.009
7.985
7.897
7.880
7.859
7.818
7.810
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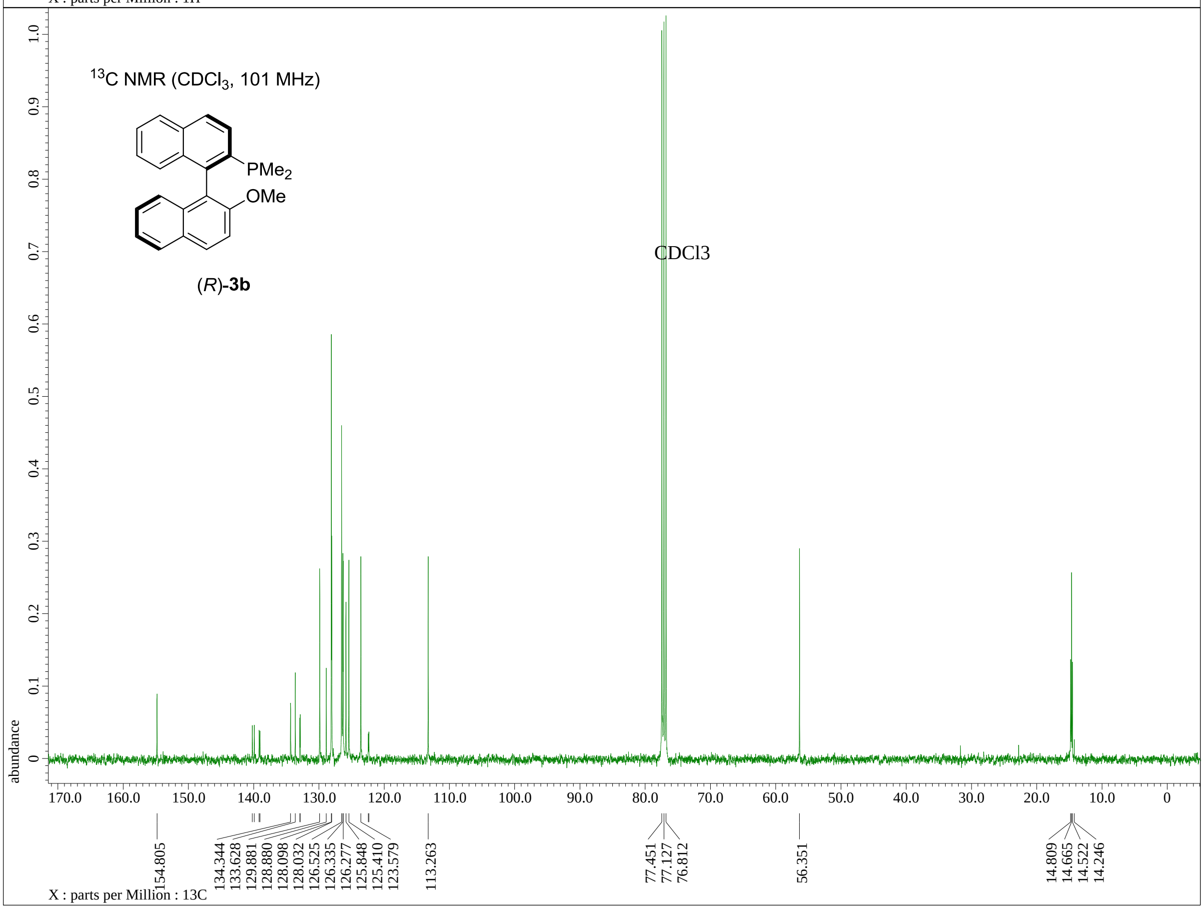
1.197
1.056
1.047



13C NMR (CDCl3, 101 MHz)
PMe2
OMe
(R)-3b
CDCl3
abundance
X : parts per Million : 13C
154.805
134.344
133.628
129.881
128.880
128.098
128.032
126.525
126.335
126.277
125.848
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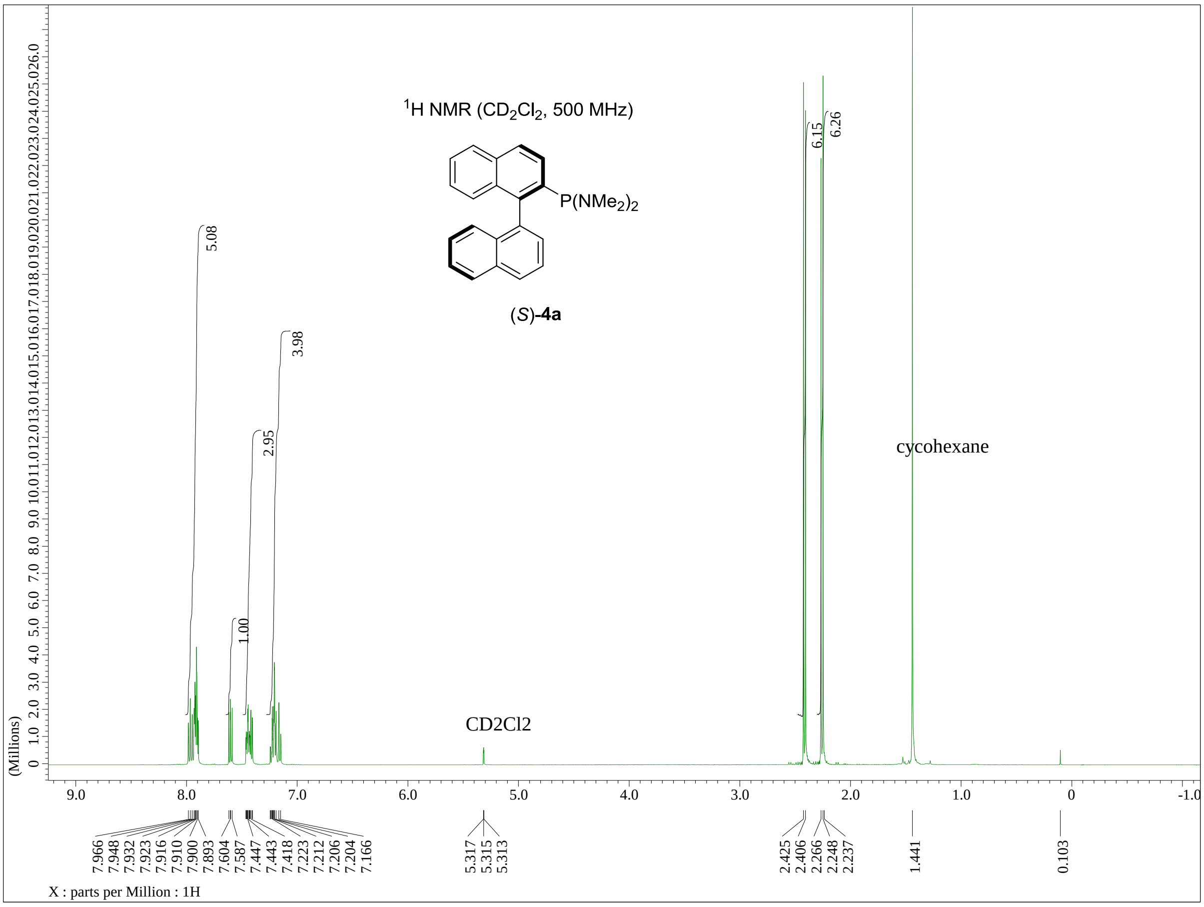
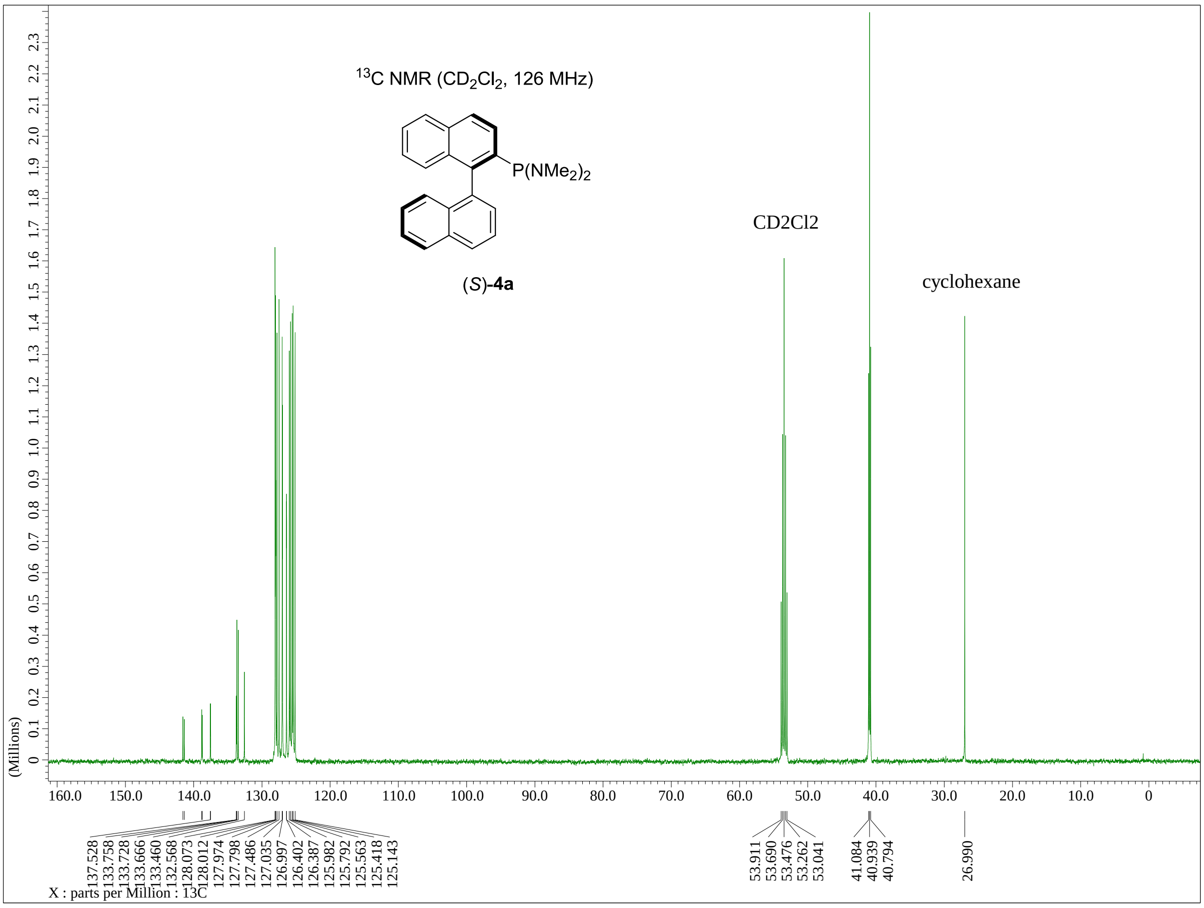
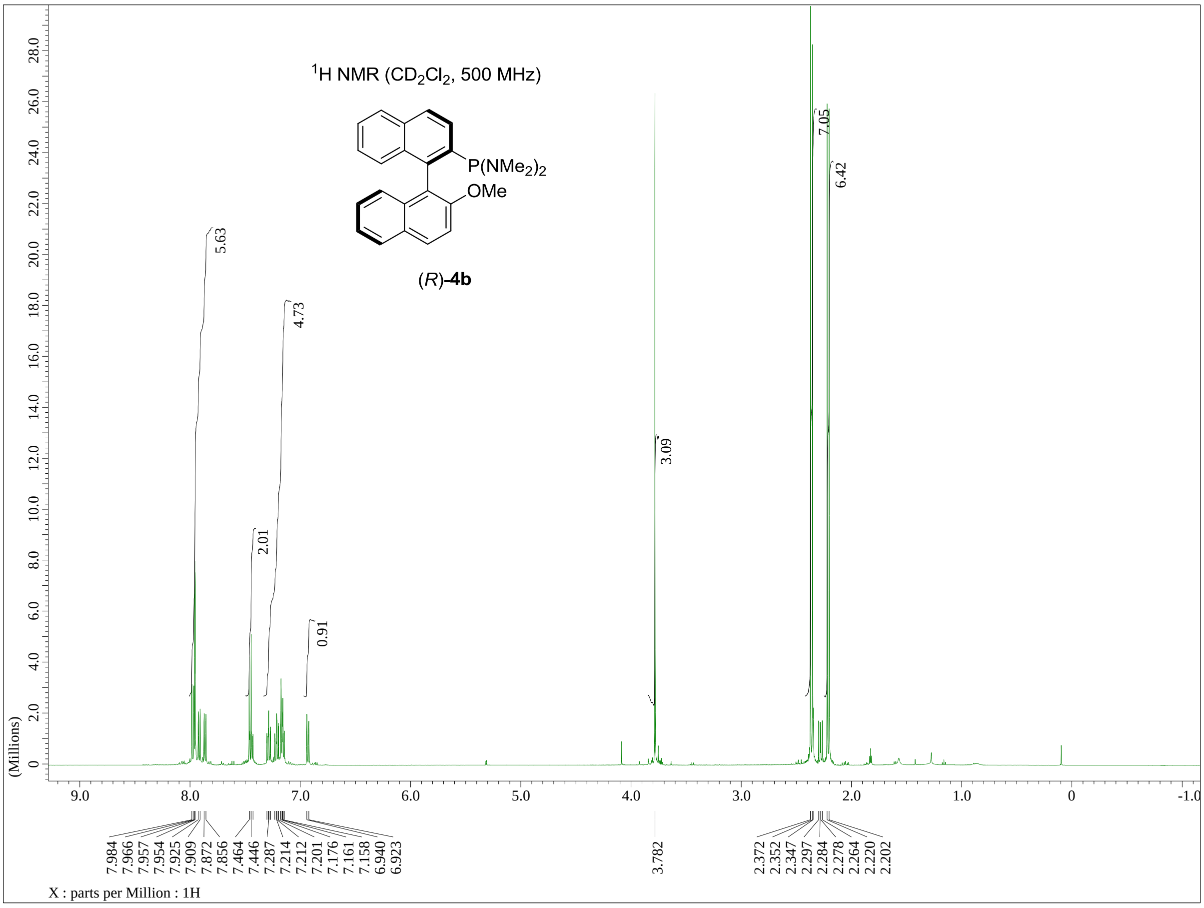
14.665
14.522
14.246



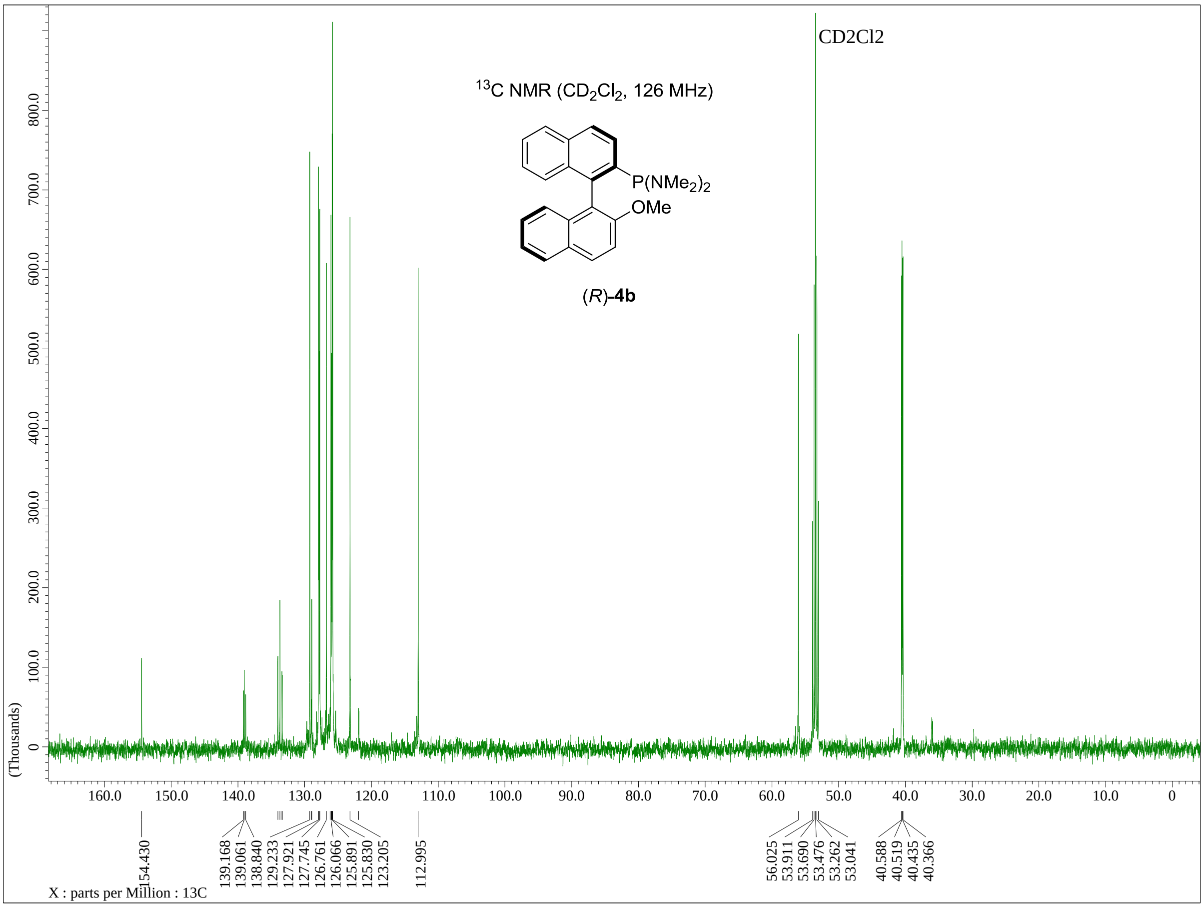
¹H NMR (CD₂Cl₂, 500 MHz)
P(NMe₂)₂
(S)-4a
5.08
3.98
2.95
1.00
6.15
6.26
cycohexane
CD2Cl2
7.966 7.948 7.932 7.923 7.916 7.910 7.900 7.893 7.604 7.587 7.447 7.443 7.418 7.223 7.212 7.206 7.204 7.166
5.317 5.315 5.313
2.425 2.406 2.266 2.248 2.237
1.441
0.103
X : parts per Million : 1H
(Millions)



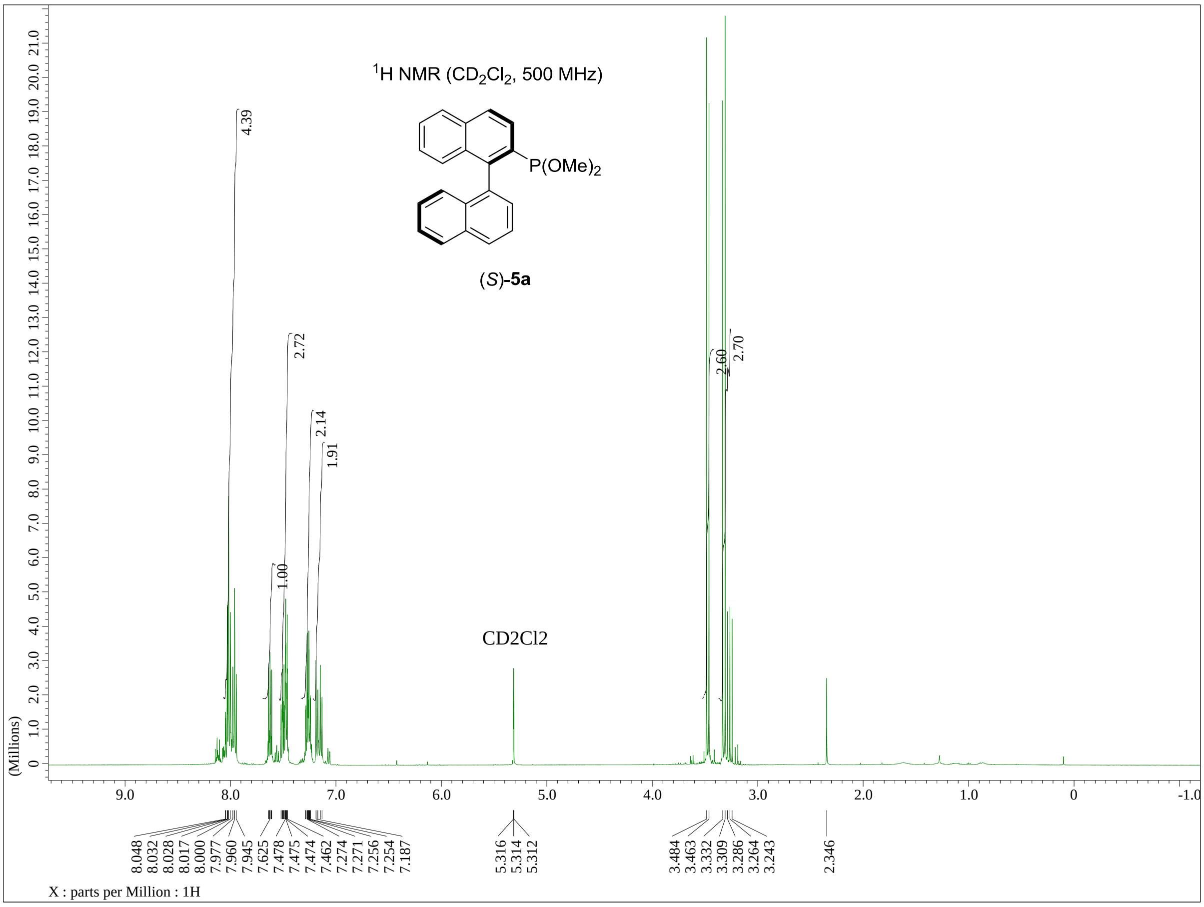
¹³C NMR (CD₂Cl₂, 126 MHz)
P(NMe₂)₂
(S)-4a
CD2Cl2
cyclohexane
137.528 133.758 133.728 133.666 133.460 132.568 128.073 128.012 127.974 127.798 127.486 127.035 126.997 126.402 126.387 125.982 125.792 125.563 125.418 125.143
53.911 53.690 53.476 53.262 53.041
41.084 40.939 40.794
26.990
X : parts per Million : 13C
(Millions)



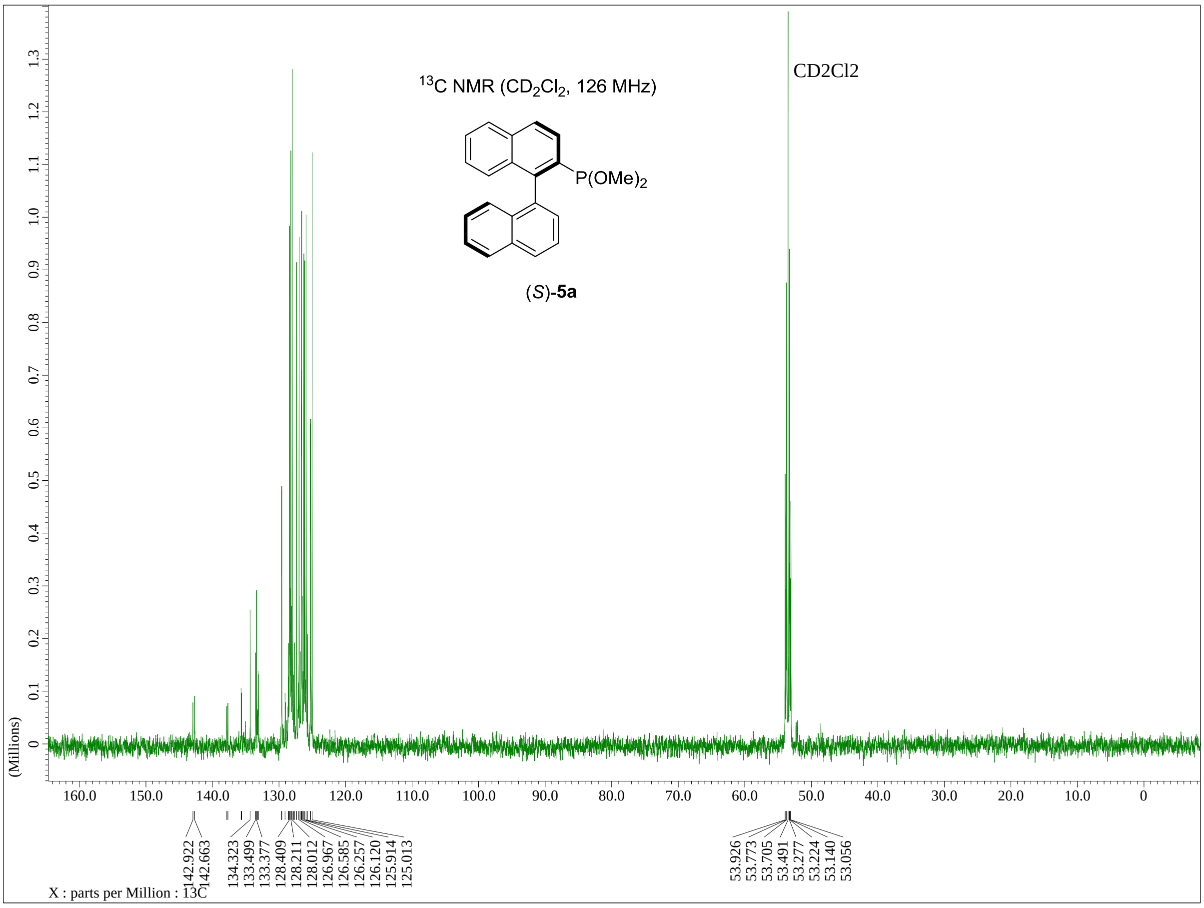
^{1}H NMR (CD_2Cl_2, 500 MHz)
P(NMe$_2$)$_2$
OMe
(R)-4b
X : parts per Million : 1H
(Millions)



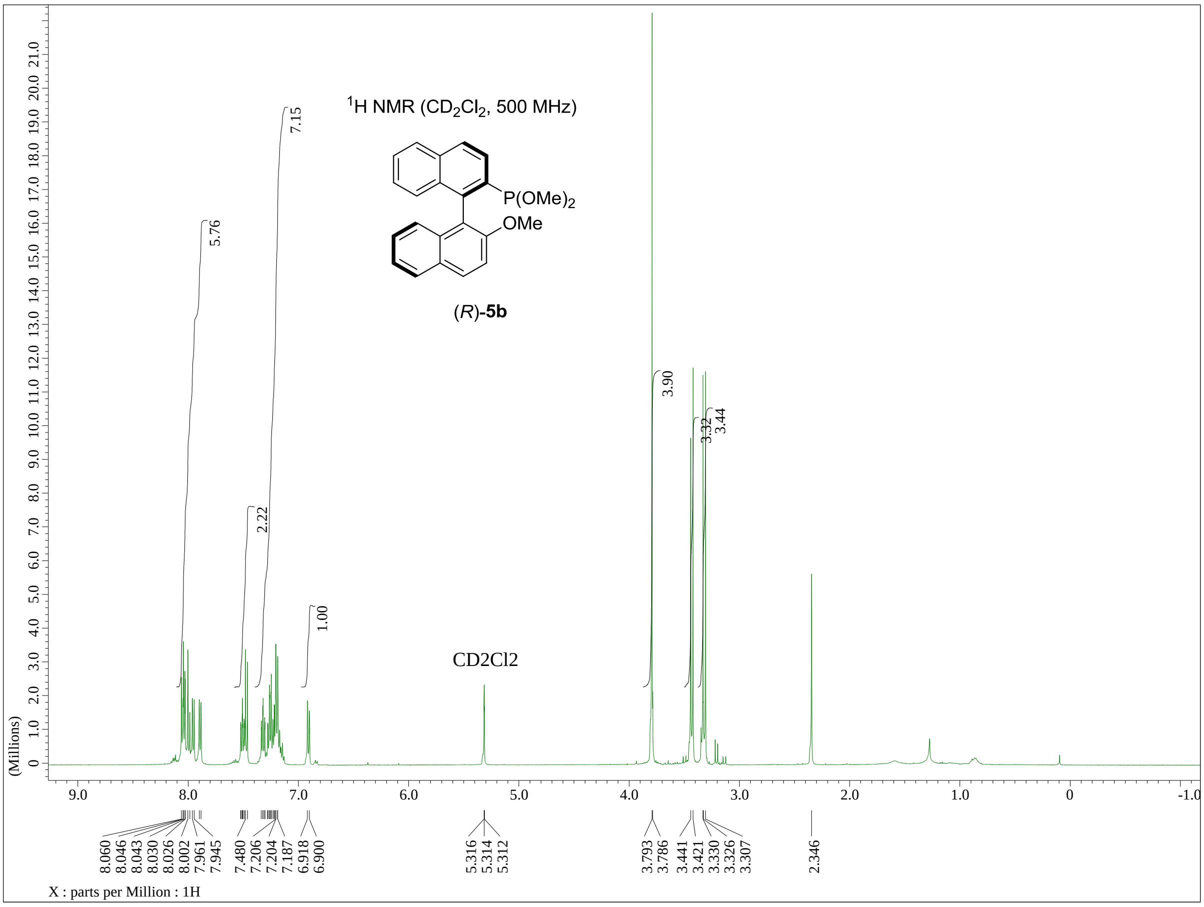
^{13}C NMR (CD_2Cl_2, 126 MHz)
CD2Cl2
P(NMe$_2$)$_2$
OMe
(R)-4b
X : parts per Million : 13C
(Thousands)



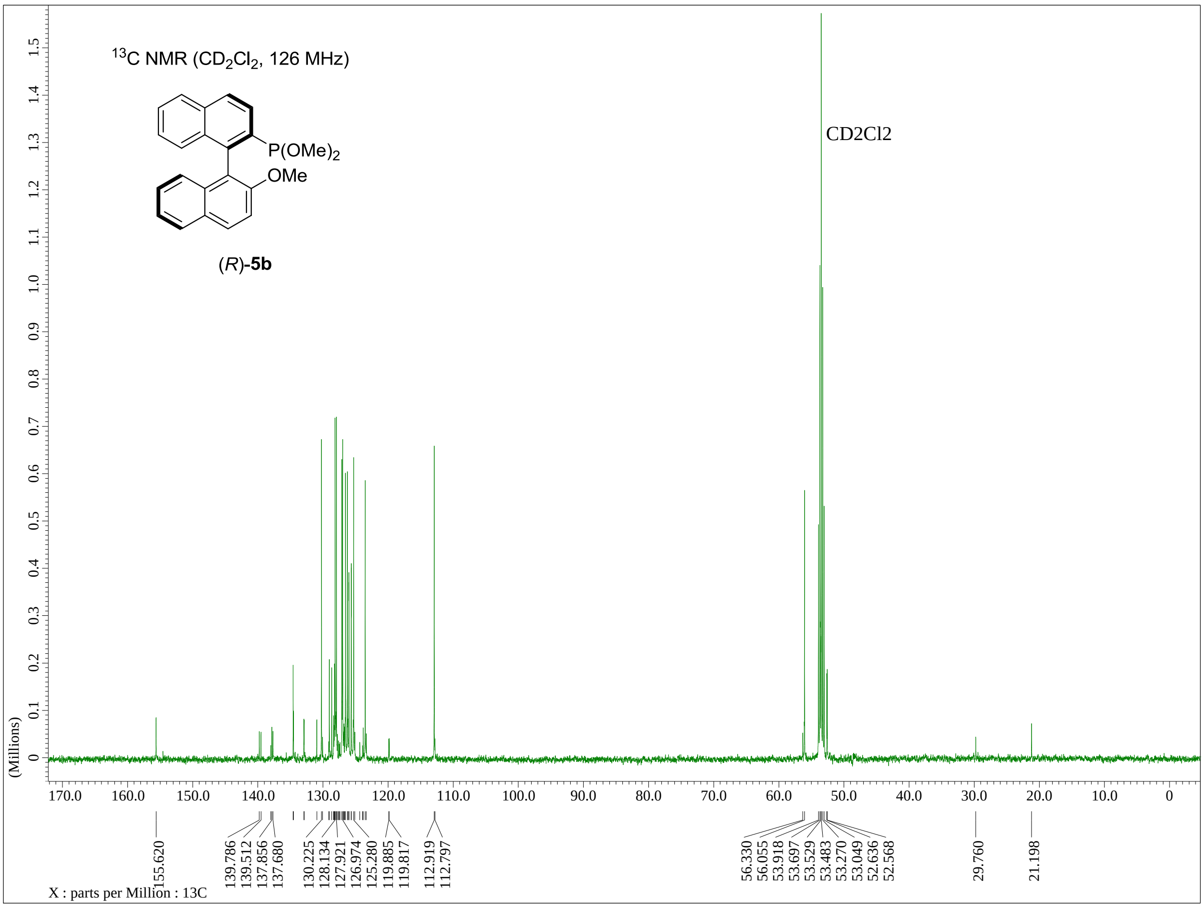
^{1}H NMR (CD$_2$Cl$_2$, 500 MHz)
P(OMe)$_2$
(S)-5a
CD2Cl2
4.39
2.72
2.14
1.91
1.00
2.60
2.70
8.048 8.032 8.028 8.017 8.000 7.977 7.960 7.945 7.625 7.478 7.475 7.474 7.462 7.274 7.271 7.256 7.254 7.187
5.316 5.314 5.312
3.484 3.463 3.332 3.309 3.286 3.264 3.243
2.346
(Millions)
X : parts per Million : 1H



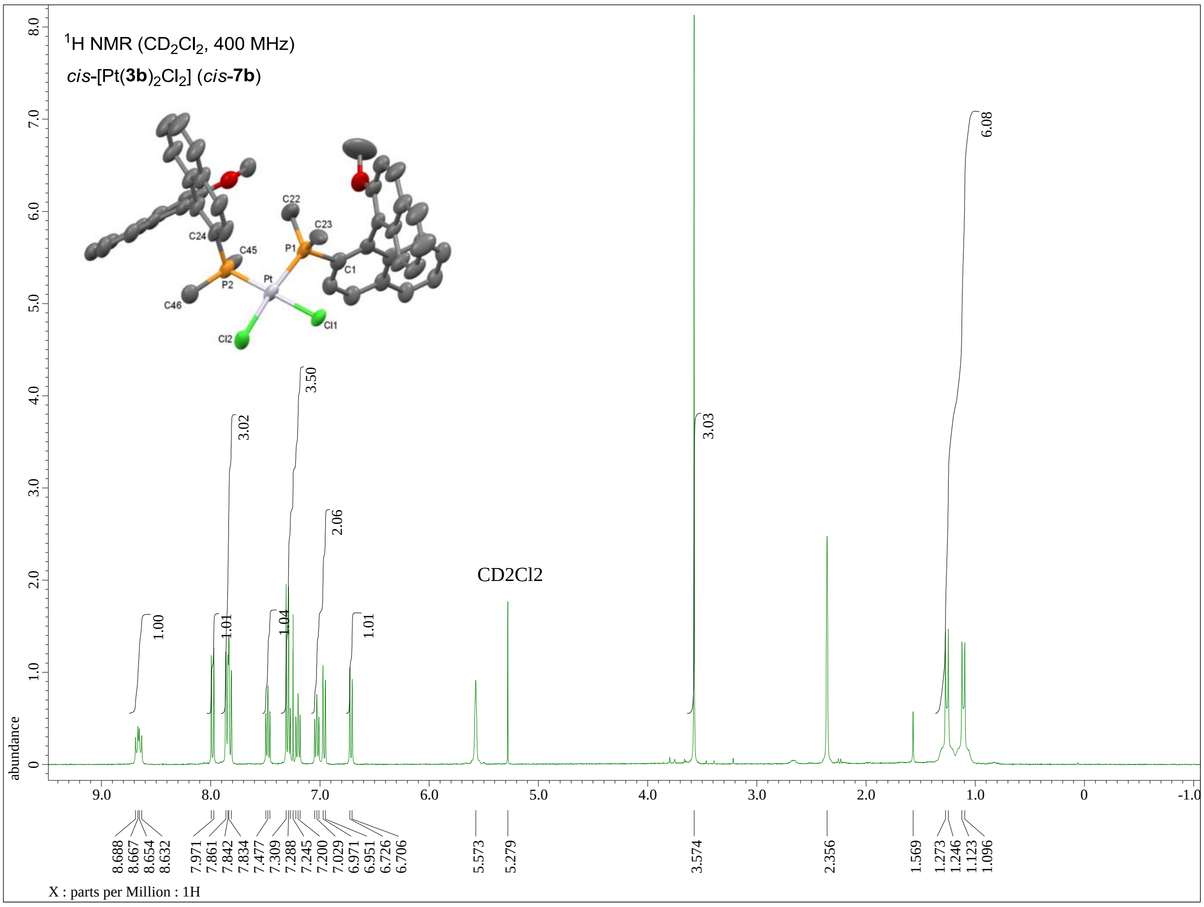
^{13}C NMR (CD$_2$Cl$_2$, 126 MHz)
P(OMe)$_2$
(S)-5a
CD2Cl2
142.922 142.663 134.323 133.499 133.377 128.409 128.211 128.012 126.967 126.585 126.257 126.120 125.914 125.013
53.926 53.773 53.705 53.491 53.277 53.224 53.140 53.056
(Millions)
X : parts per Million : 13C



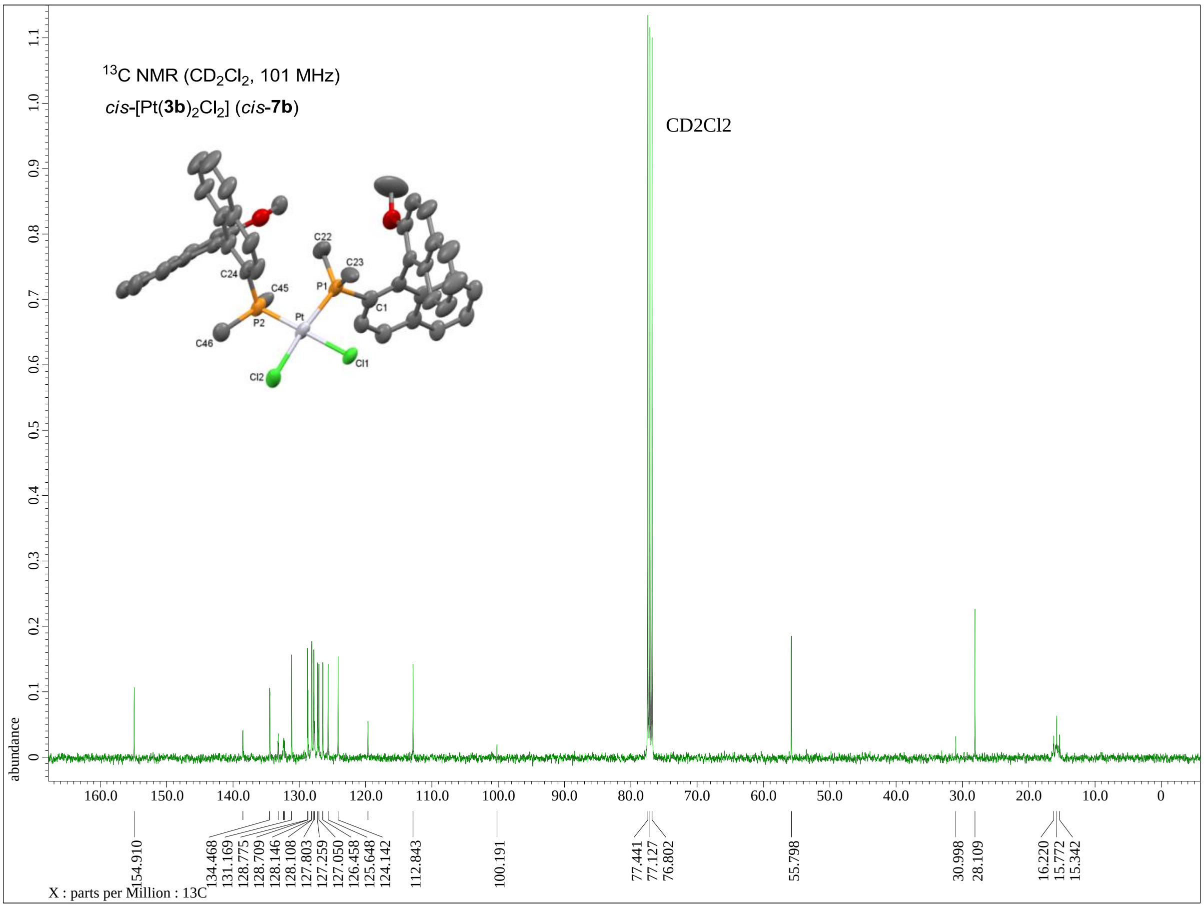
^{1}H NMR (CD_2Cl_2, 500 MHz)
P(OMe)$_2$
OMe
(R)-**5b**
CD2Cl2
5.76
7.15
2.22
1.00
3.90
3.32
3.44
8.060
8.046
8.043
8.030
8.026
8.002
7.961
7.945
7.480
7.206
7.204
7.187
6.918
6.900
5.316
5.314
5.312
3.793
3.786
3.441
3.421
3.330
3.326
3.307
2.346
(Millions)
X : parts per Million : 1H



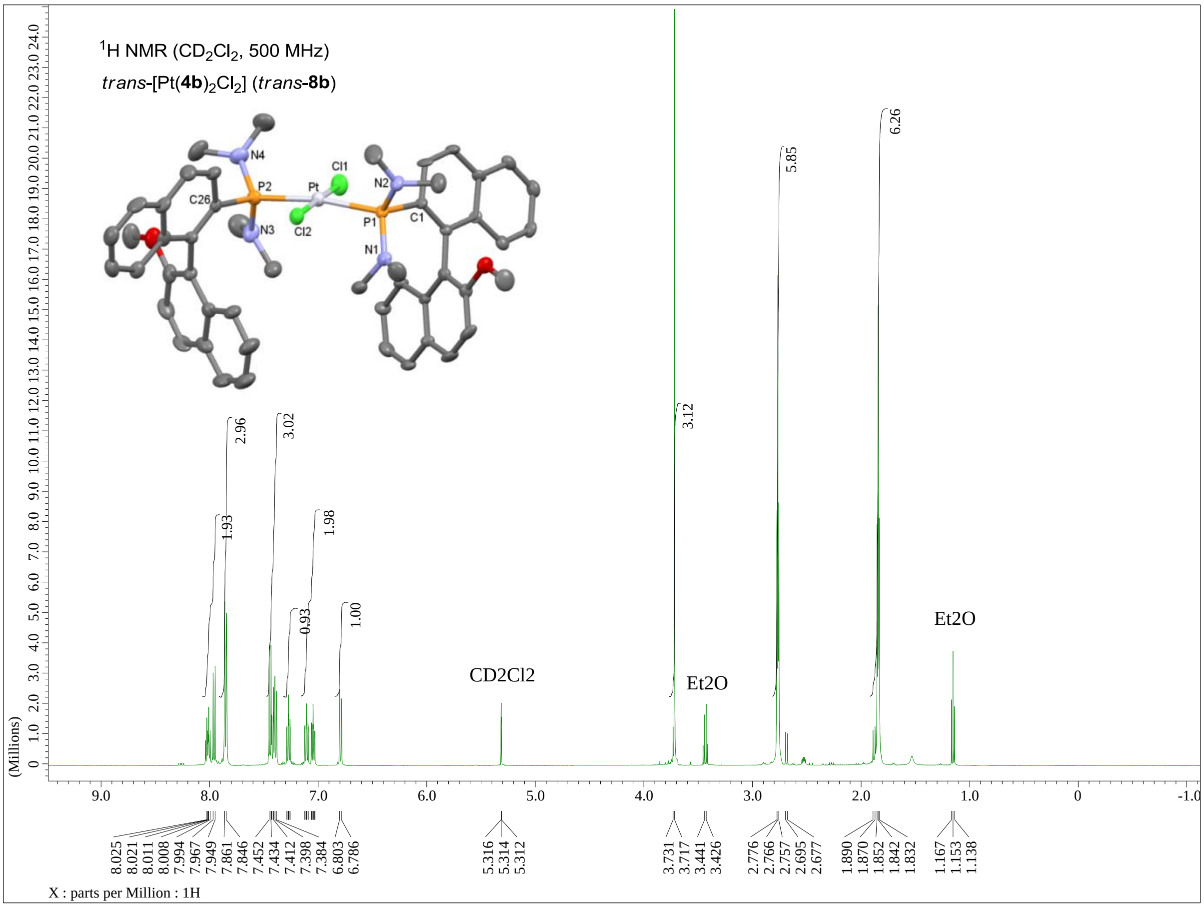
^{13}C NMR (CD_2Cl_2, 126 MHz)
P(OMe)$_2$
OMe
(R)-**5b**
CD2Cl2
155.620
139.786
139.512
137.856
137.680
130.225
128.134
127.921
126.974
125.280
119.885
119.817
112.919
112.797
56.330
56.055
53.918
53.697
53.529
53.483
53.270
53.049
52.636
52.568
29.760
21.198
(Millions)
X : parts per Million : 13C



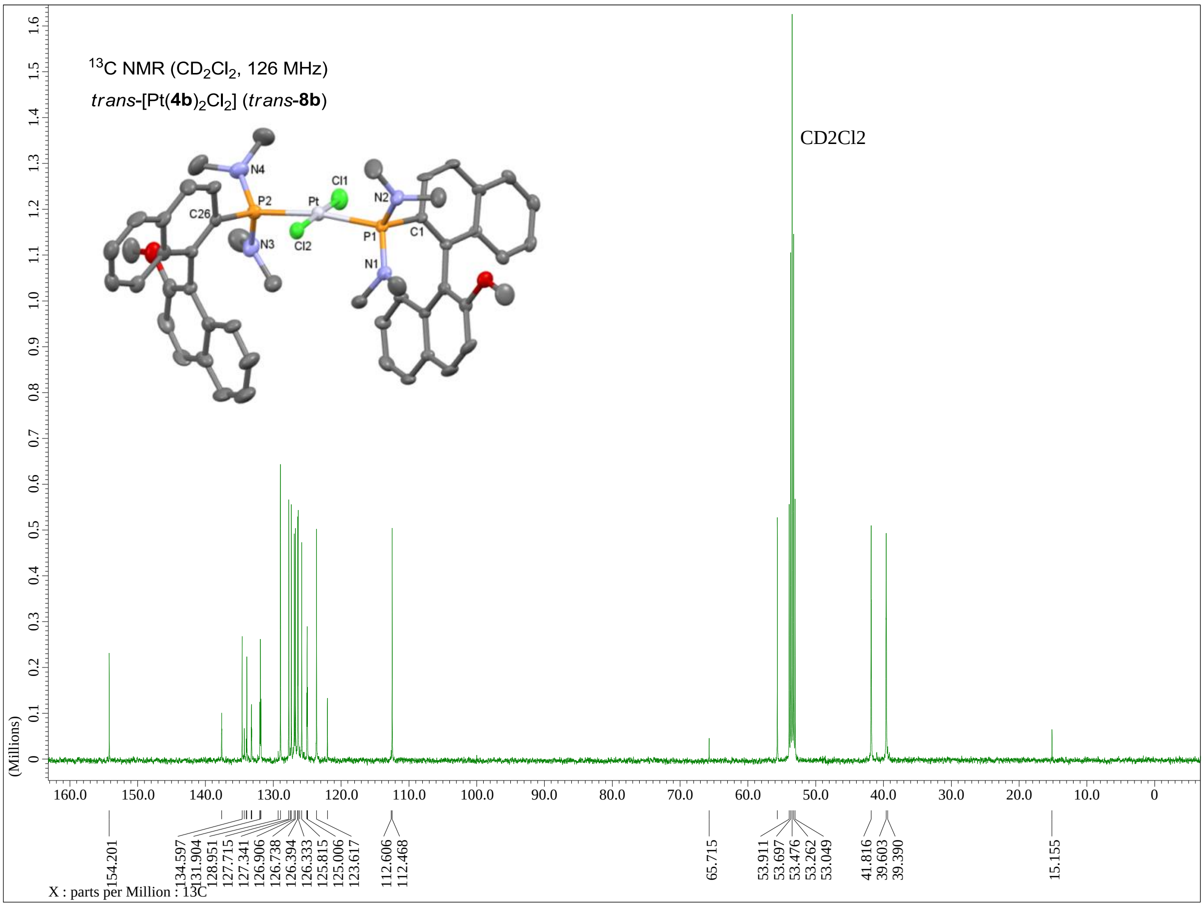
1H NMR (CD2Cl2, 400 MHz)
cis-[Pt(3b)2Cl2] (cis-7b)
C22
C23
P1
C1
C24
C45
Pt
P2
C46
Cl1
Cl2
CD2Cl2
1.00
1.01
3.02
1.04
3.50
2.06
1.01
3.03
6.08
8.688
8.667
8.654
8.632
7.971
7.861
7.842
7.834
7.477
7.309
7.288
7.245
7.200
7.029
6.971
6.951
6.726
6.706
5.573
5.279
3.574
2.356
1.569
1.273
1.246
1.123
1.096
abundance
X : parts per Million : 1H



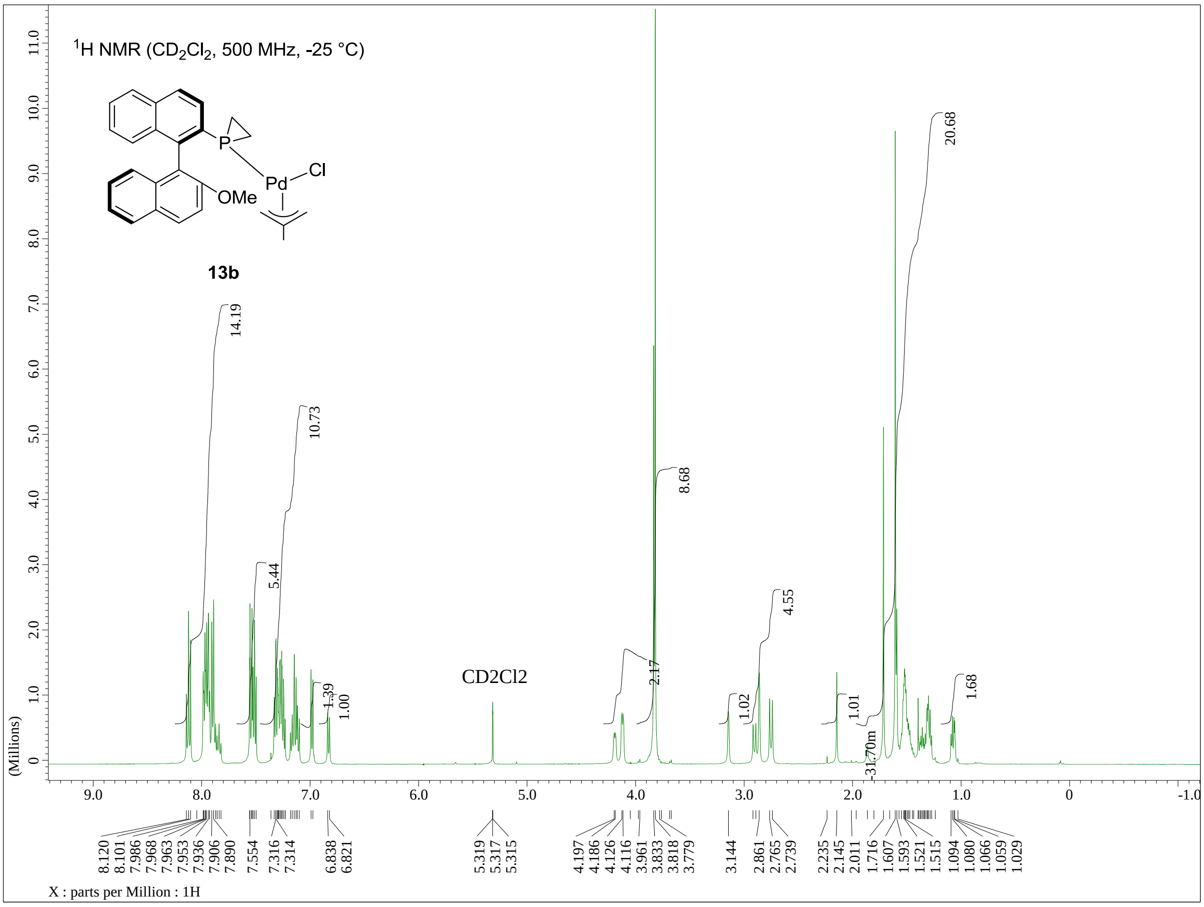
13C NMR (CD2Cl2, 101 MHz)
cis-[Pt(3b)2Cl2] (cis-7b)
C22
C23
P1
C1
C24
C45
Pt
P2
C46
Cl1
Cl2
CD2Cl2
154.910
134.468
131.169
128.775
128.709
128.146
128.108
127.803
127.259
127.050
126.458
125.648
124.142
112.843
100.191
77.441
77.127
76.802
55.798
30.998
28.109
16.220
15.772
15.342
abundance
X : parts per Million : 13C



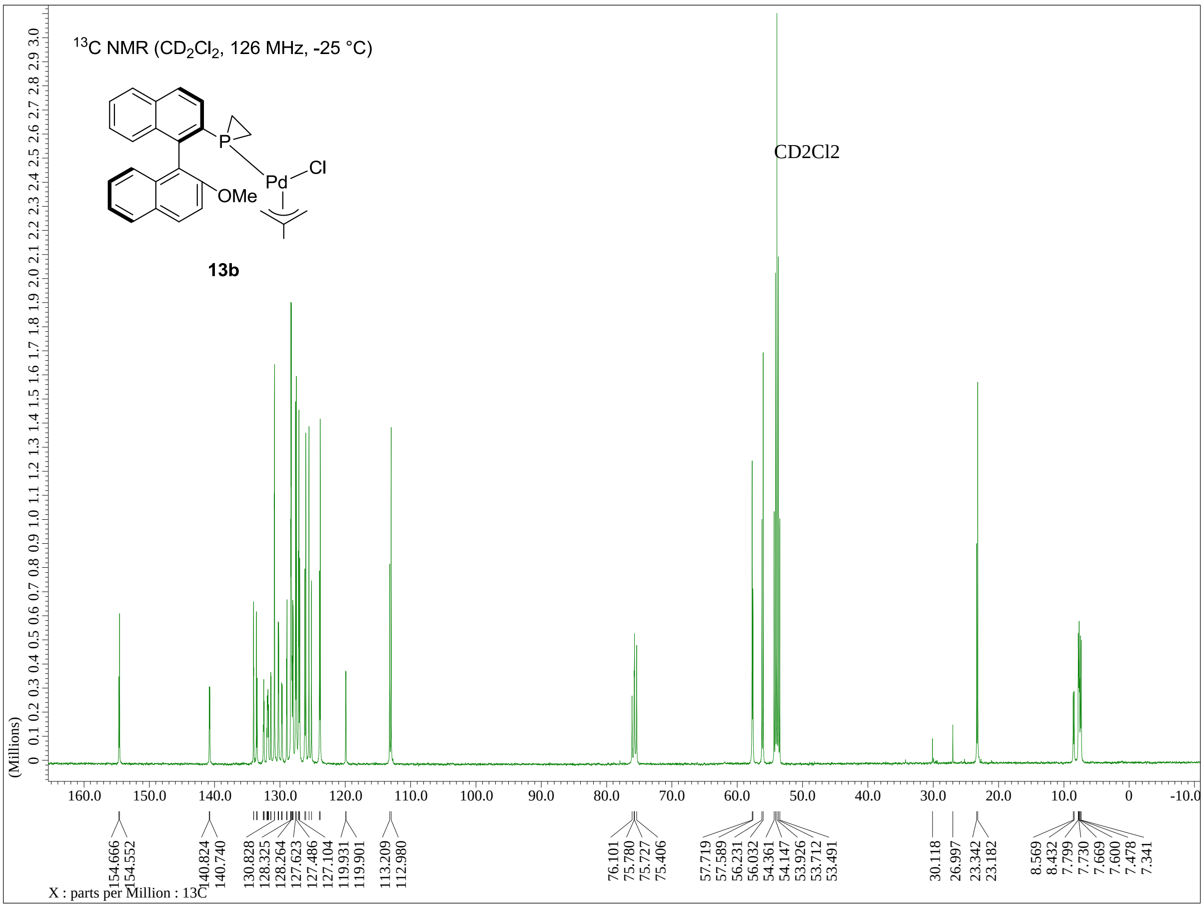
^{1}H NMR (CD_2Cl_2, 500 MHz)
trans-[Pt(**4b**)$_2$Cl$_2$] (*trans*-**8b**)
CD2Cl2
Et2O
Et2O
X : parts per Million : 1H



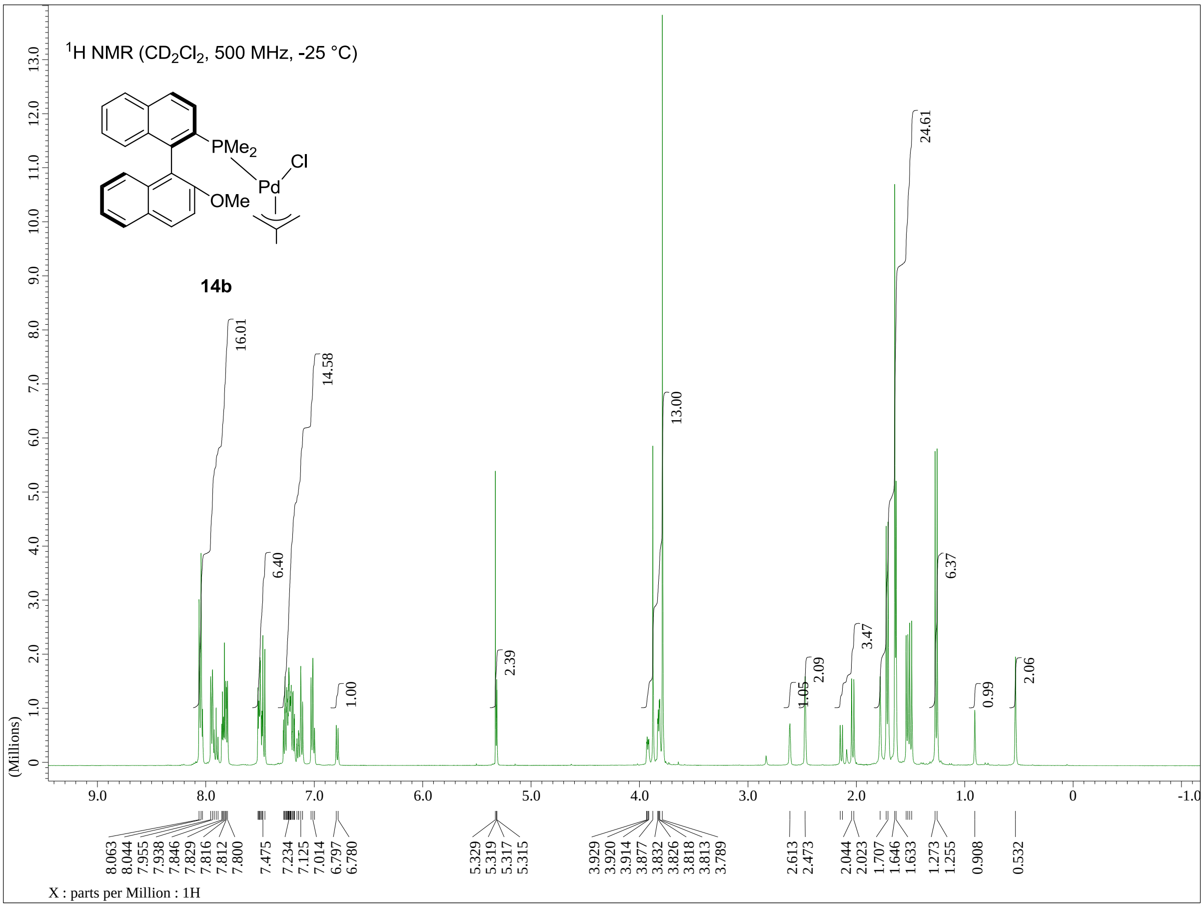
^{13}C NMR (CD_2Cl_2, 126 MHz)
trans-[Pt(**4b**)$_2$Cl$_2$] (*trans*-**8b**)
CD2Cl2
X : parts per Million : 13C



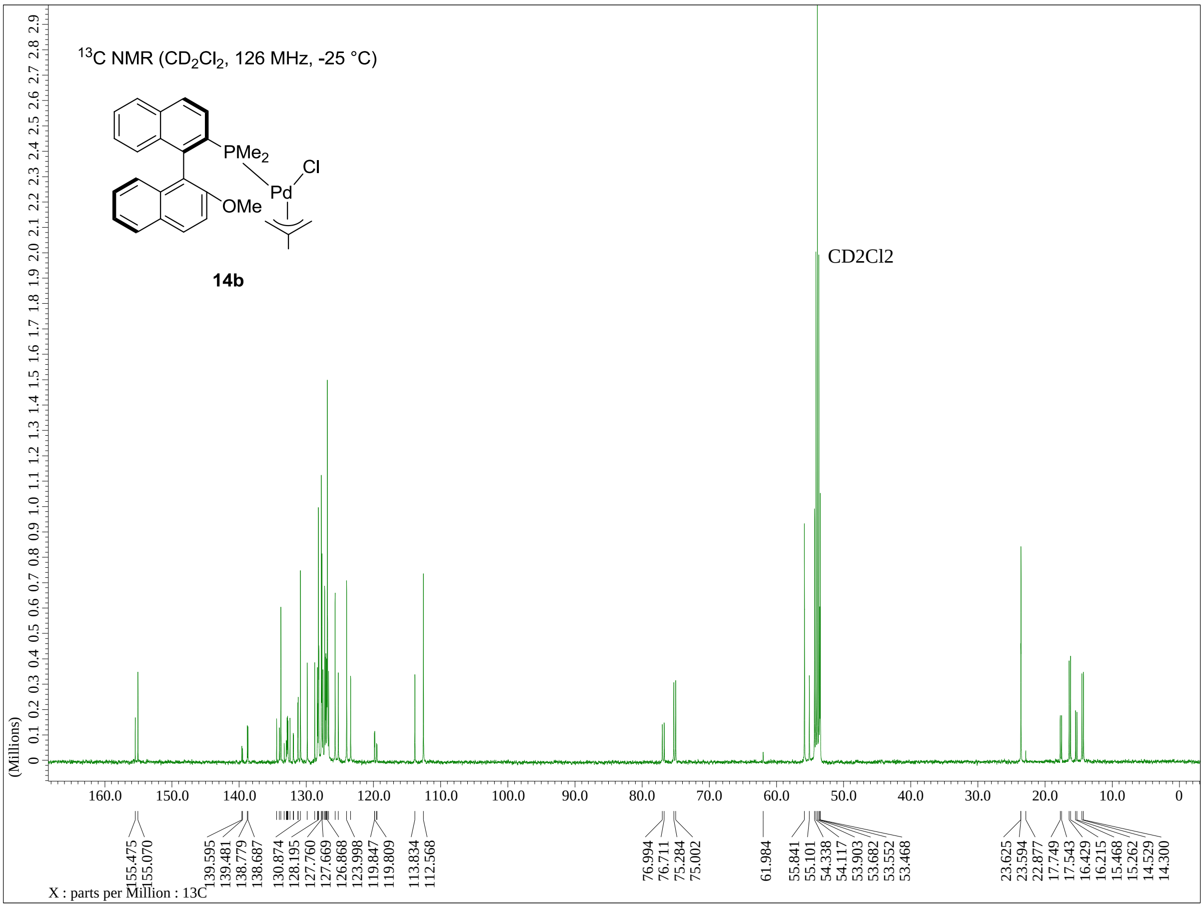
1H NMR (CD2Cl2, 500 MHz, -25 °C)
P
Pd
Cl
OMe
13b
CD2Cl2
14.19
10.73
5.44
8.68
2.17
1.02
4.55
1.01
20.68
1.68
1.39
1.00
(Millions)
8.120 8.101 7.986 7.968 7.963 7.953 7.936 7.906 7.890 7.554 7.316 7.314 6.838 6.821
5.319 5.317 5.315
4.197 4.186 4.126 4.116 3.961 3.833 3.818 3.779
3.144 2.861 2.765 2.739 2.235 2.145 2.011 1.716 1.607 1.593 1.521 1.515 1.094 1.080 1.066 1.059 1.029
X : parts per Million : 1H



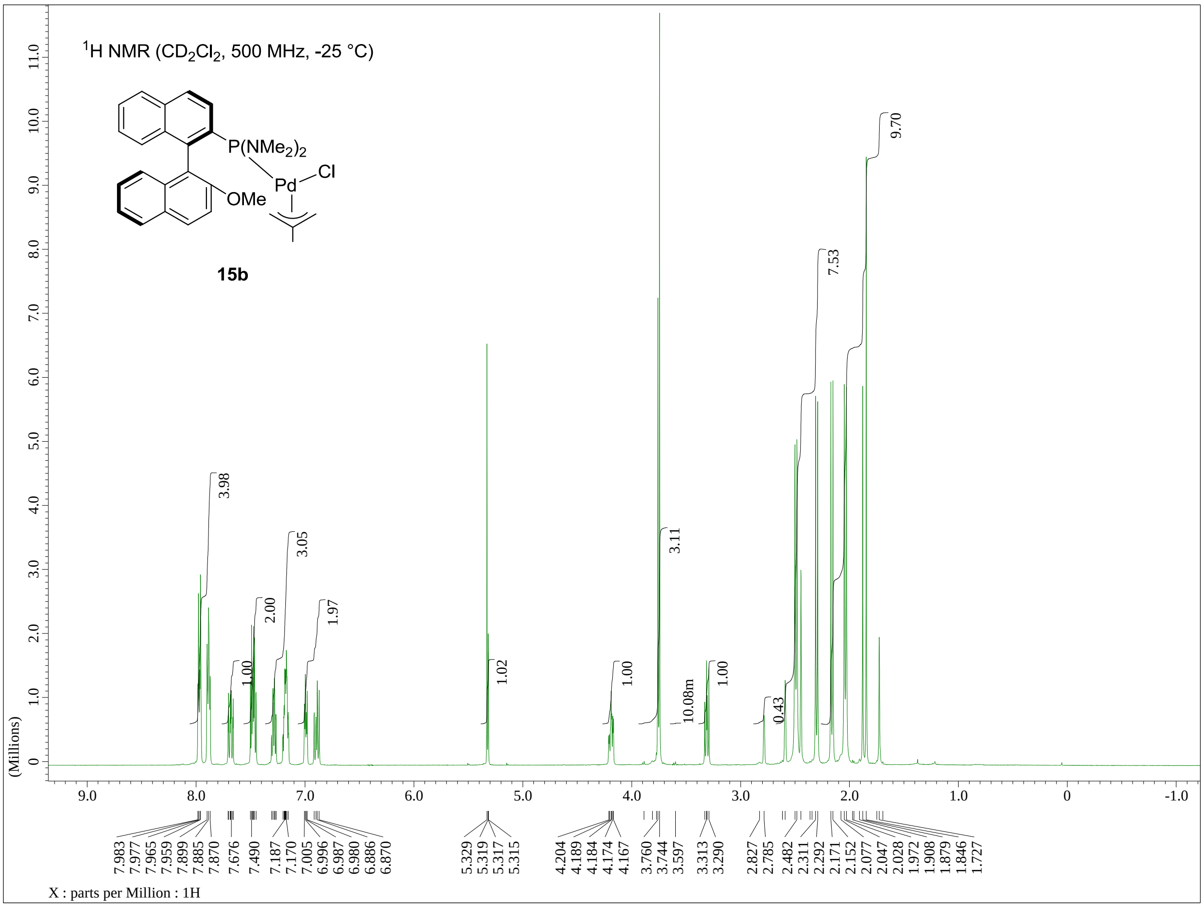
13C NMR (CD2Cl2, 126 MHz, -25 °C)
P
Pd
Cl
OMe
13b
CD2Cl2
(Millions)
154.666 154.552 140.824 140.740 130.828 128.325 128.264 127.623 127.486 127.104 119.931 119.901 113.209 112.980
76.101 75.780 75.727 75.406
57.719 57.589 56.231 56.032 54.361 54.147 53.926 53.712 53.491
30.118 26.997 23.342 23.182
8.569 8.432 7.799 7.730 7.669 7.600 7.478 7.341
X : parts per Million : 13C

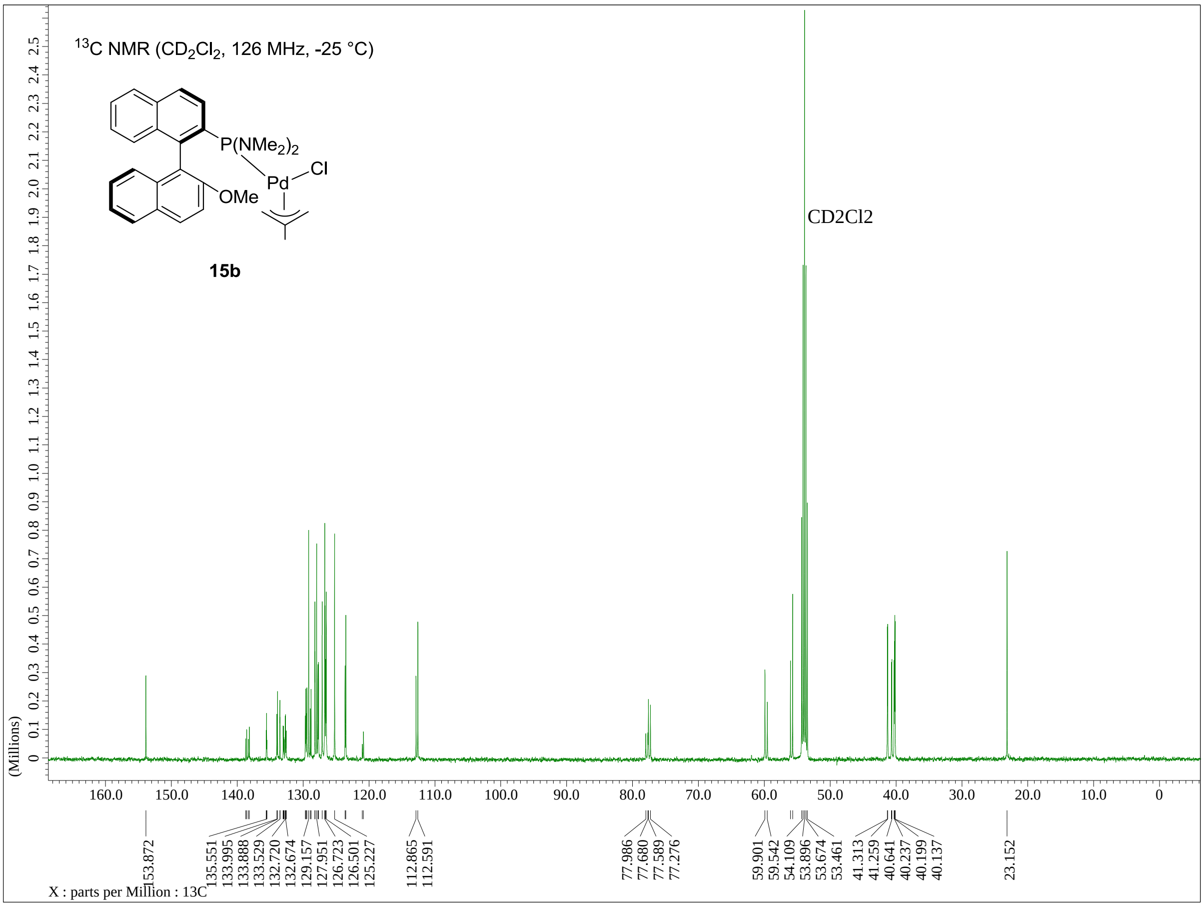


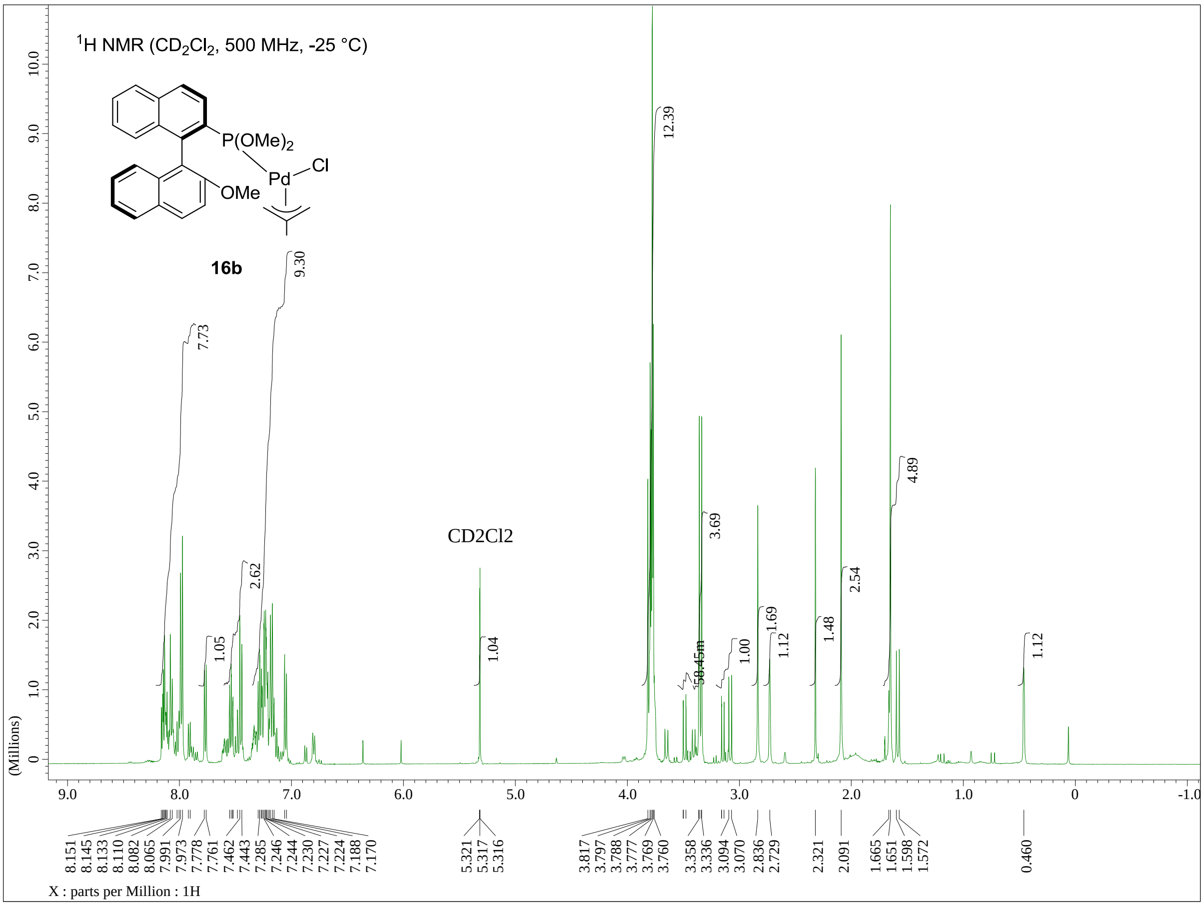
^{1}H NMR (CD_2Cl_2, 500 MHz, -25 °C)
PMe2
Cl
Pd
OMe
14b
16.01
14.58
6.40
1.00
2.39
13.00
1.05
2.09
3.47
24.61
6.37
0.99
2.06
8.063 8.044 7.955 7.938 7.846 7.829 7.816 7.812 7.800
7.475 7.234 7.125 7.014 6.797 6.780
5.329 5.319 5.317 5.315
3.929 3.920 3.914 3.877 3.832 3.826 3.818 3.813 3.789
2.613 2.473
2.044 2.023 1.707 1.646 1.633
1.273 1.255
0.908
0.532
(Millions)
X : parts per Million : 1H



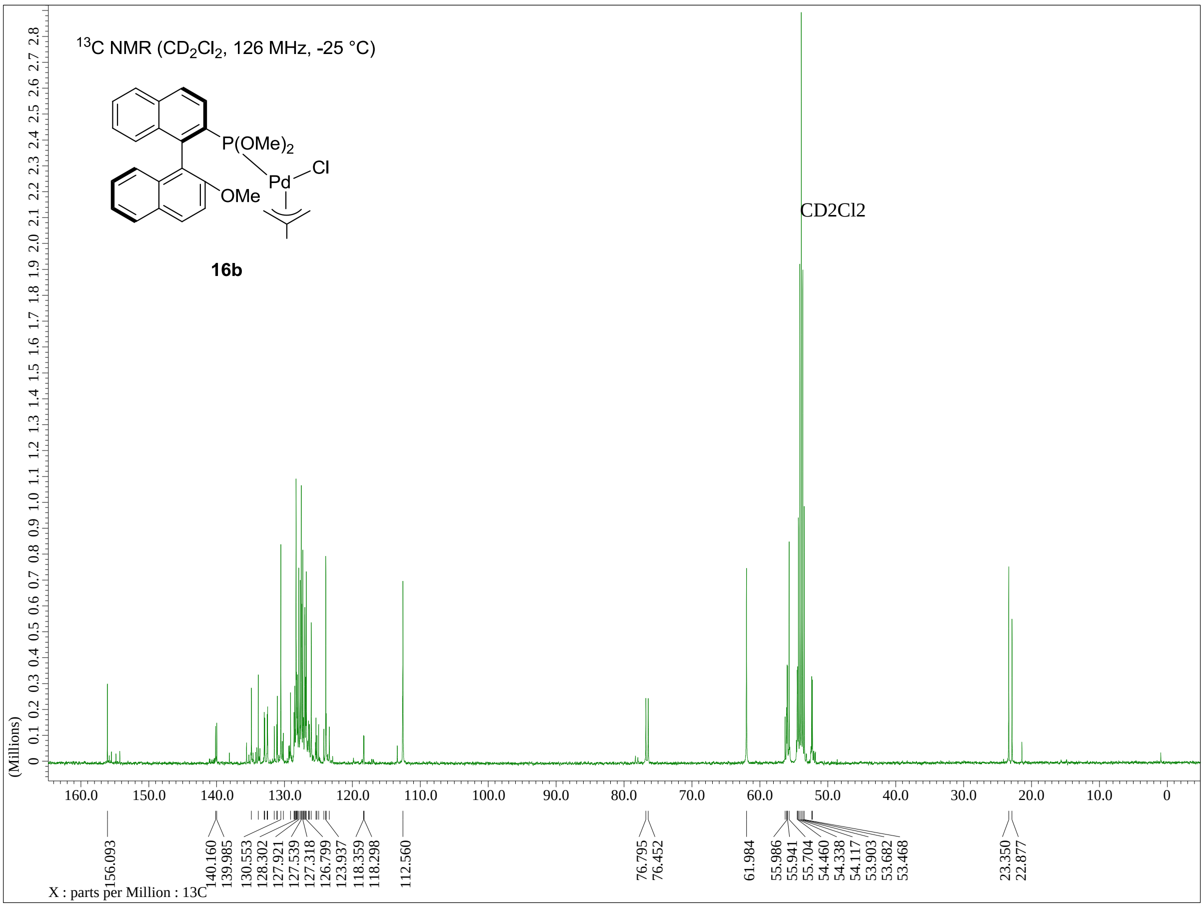
^{13}C NMR (CD_2Cl_2, 126 MHz, -25 °C)
PMe2
Cl
Pd
OMe
14b
CD2Cl2
155.475 155.070
139.595 139.481 138.779 138.687
130.874 128.195 127.760 127.669 126.868 123.998 119.847 119.809
113.834 112.568
76.994 76.711 75.284 75.002
61.984
55.841 55.101 54.338 54.117 53.903 53.682 53.552 53.468
23.625 23.594 22.877 17.749 17.543 16.429 16.215 15.468 15.262 14.529 14.300
(Millions)
X : parts per Million : 13C


1H NMR (CD2Cl2, 500 MHz, -25 °C)
P(NMe2)2
Pd
Cl
OMe
15b
(Millions)
X : parts per Million : 1H

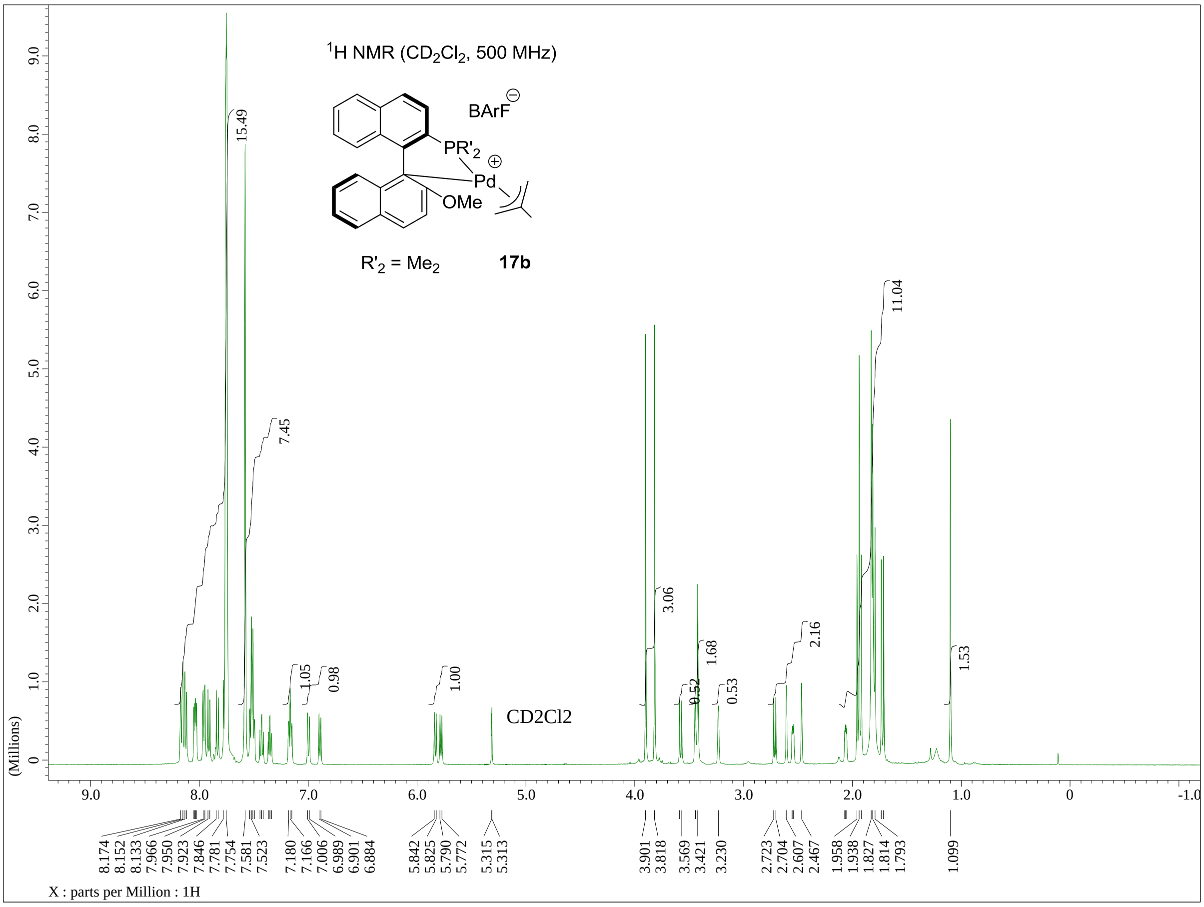

13C NMR (CD2Cl2, 126 MHz, -25 °C)
P(NMe2)2
Pd
Cl
OMe
15b
CD2Cl2
(Millions)
X : parts per Million : 13C



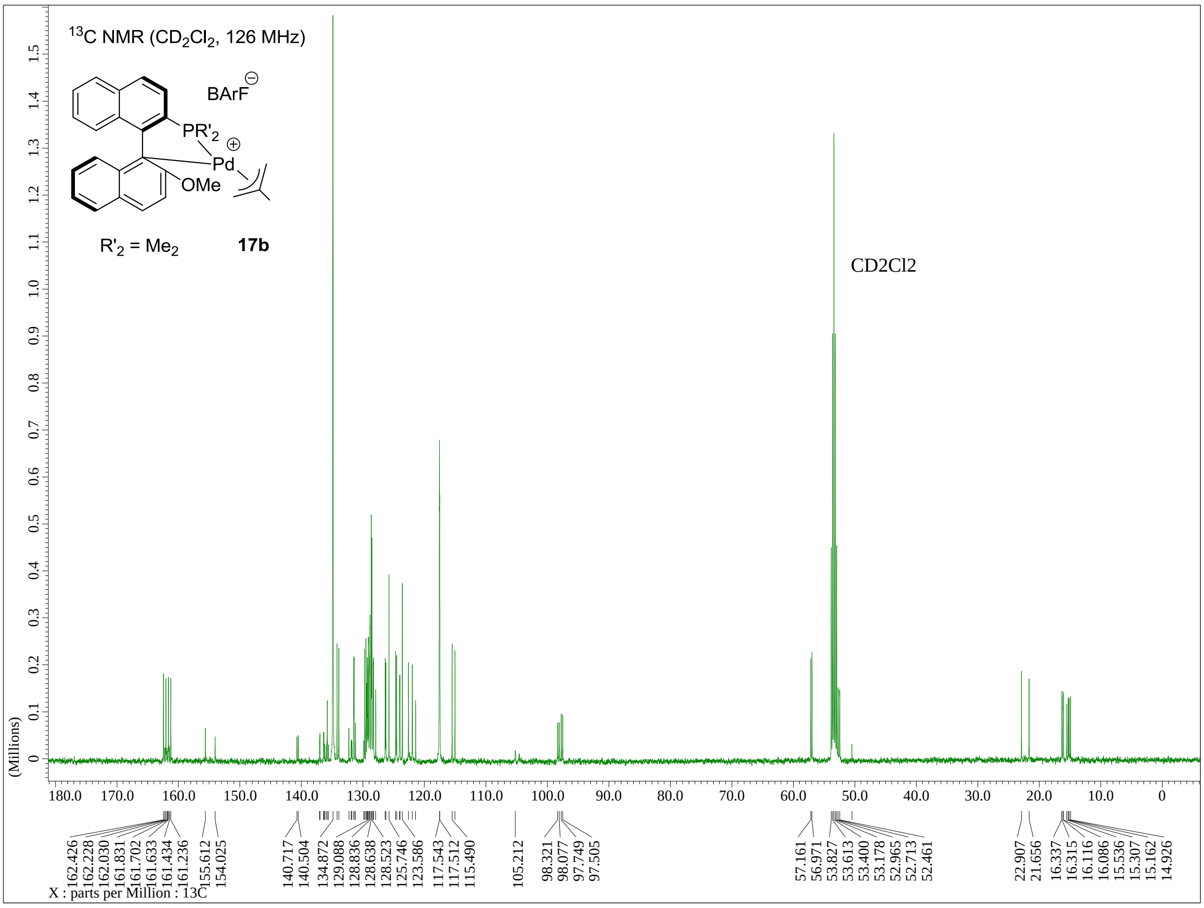
1H NMR (CD2Cl2, 500 MHz, -25 °C)
P(OMe)2
Pd
Cl
OMe
16b
CD2Cl2
7.73
9.30
12.39
1.05
2.62
1.04
3.69
58.45m
1.00
1.69
1.12
1.48
2.54
4.89
1.12
8.151
8.145
8.133
8.110
8.082
8.065
7.991
7.973
7.778
7.761
7.462
7.443
7.285
7.246
7.244
7.230
7.227
7.224
7.188
7.170
5.321
5.317
5.316
3.817
3.797
3.788
3.777
3.769
3.760
3.358
3.336
3.094
3.070
2.836
2.729
2.321
2.091
1.665
1.651
1.598
1.572
0.460
(Millions)
X : parts per Million : 1H



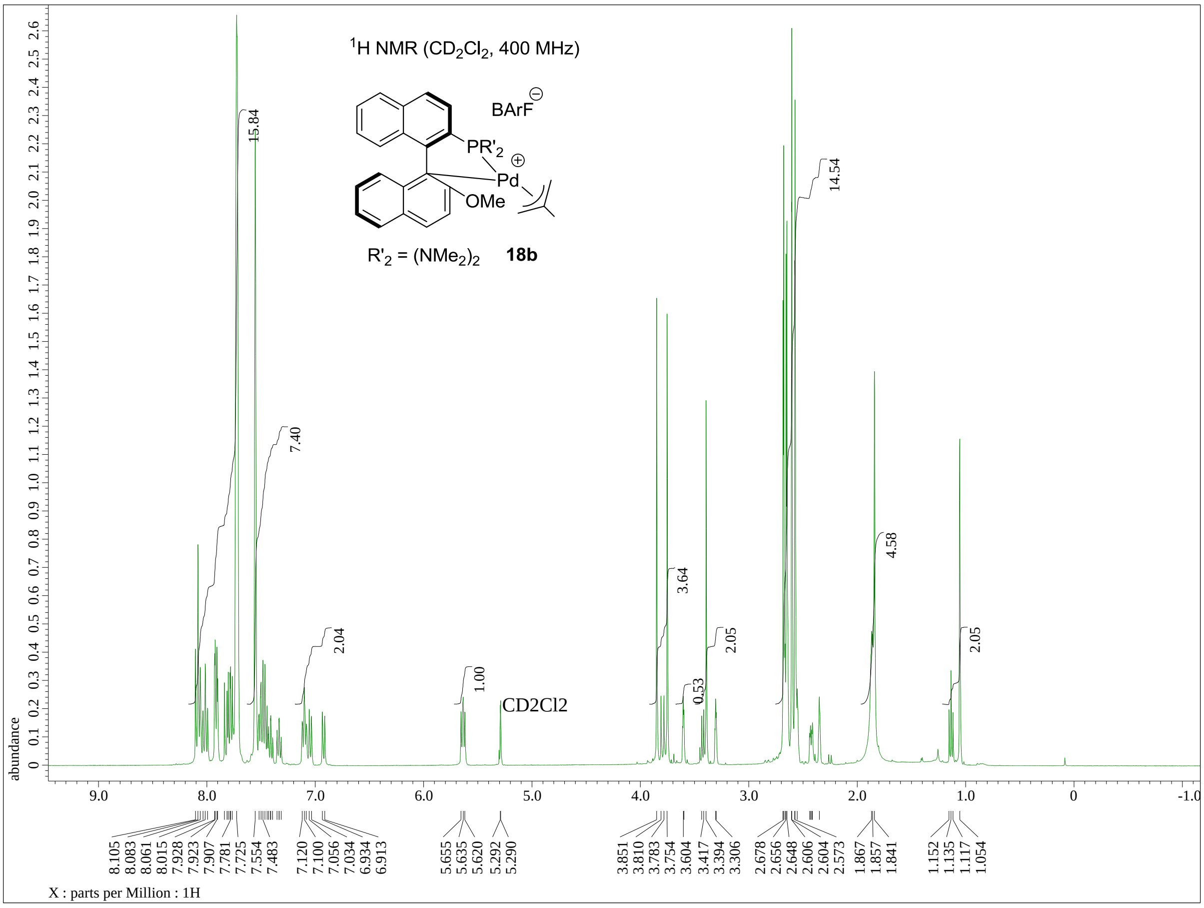
13C NMR (CD2Cl2, 126 MHz, -25 °C)
P(OMe)2
Pd
Cl
OMe
16b
CD2Cl2
156.093
140.160
139.985
130.553
128.302
127.921
127.539
127.318
126.799
123.937
118.359
118.298
112.560
76.795
76.452
61.984
55.986
55.941
55.704
54.460
54.338
54.117
53.903
53.682
53.468
23.350
22.877
(Millions)
X : parts per Million : 13C



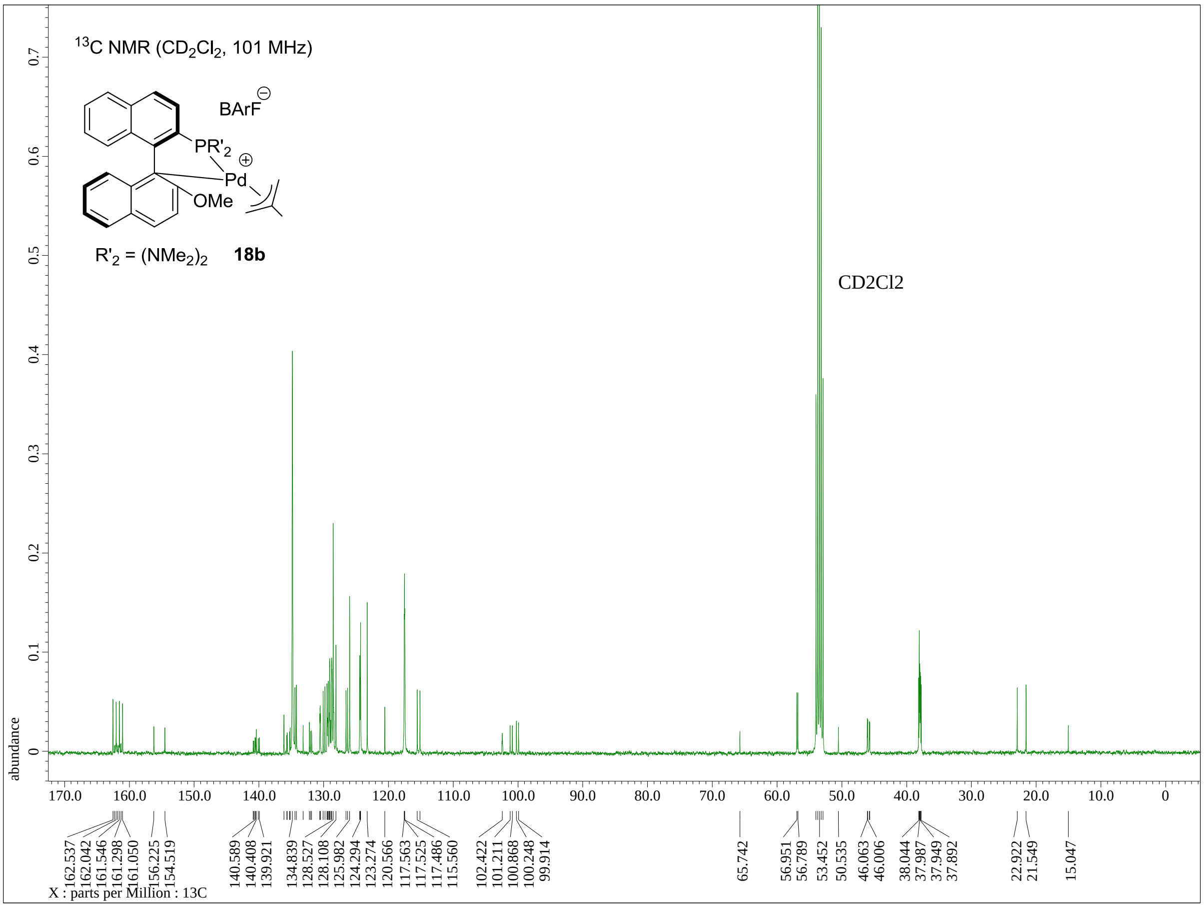
1H NMR (CD2Cl2, 500 MHz)
BArF
PR'2
Pd
OMe
R'2 = Me2
17b
CD2Cl2
X : parts per Million : 1H
(Millions)



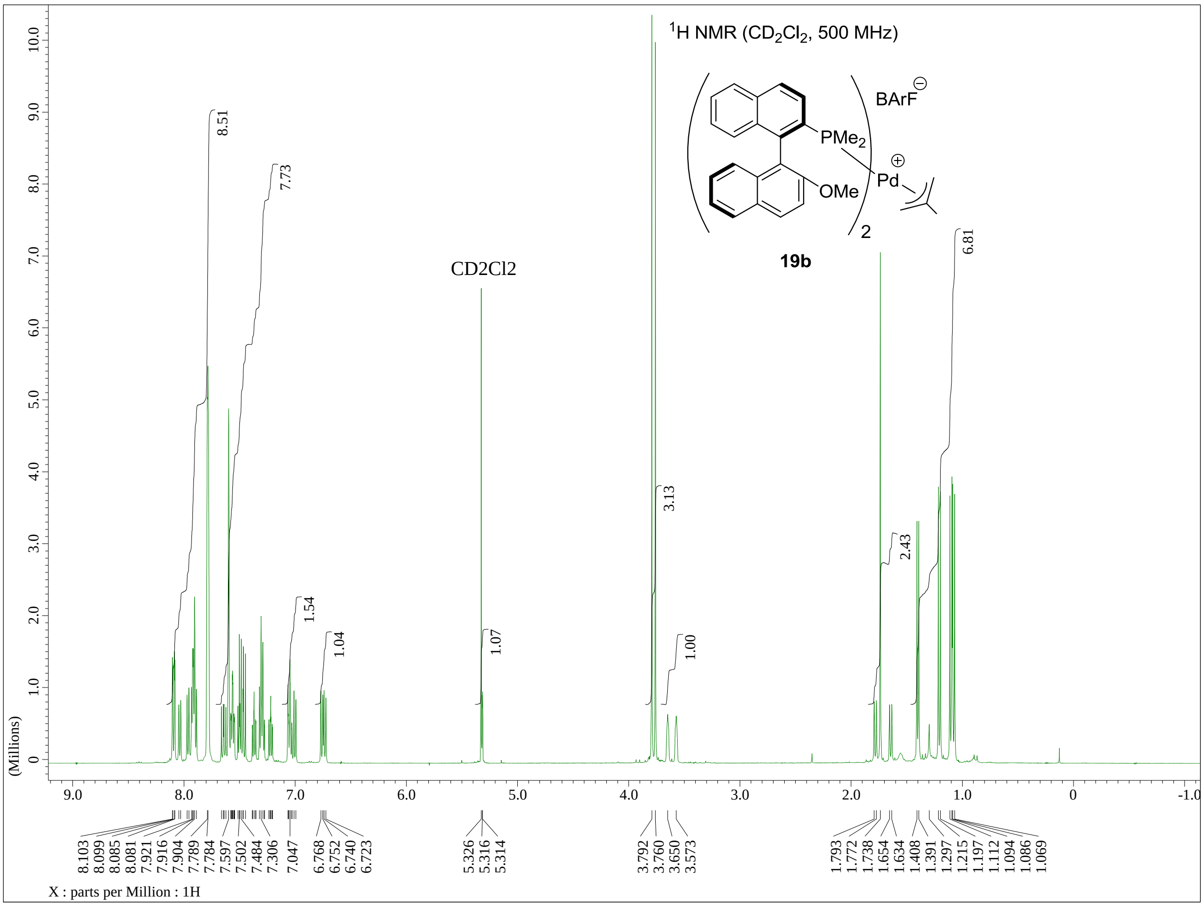
13C NMR (CD2Cl2, 126 MHz)
BArF
PR'2
Pd
OMe
R'2 = Me2
17b
CD2Cl2
X : parts per Million : 13C
(Millions)



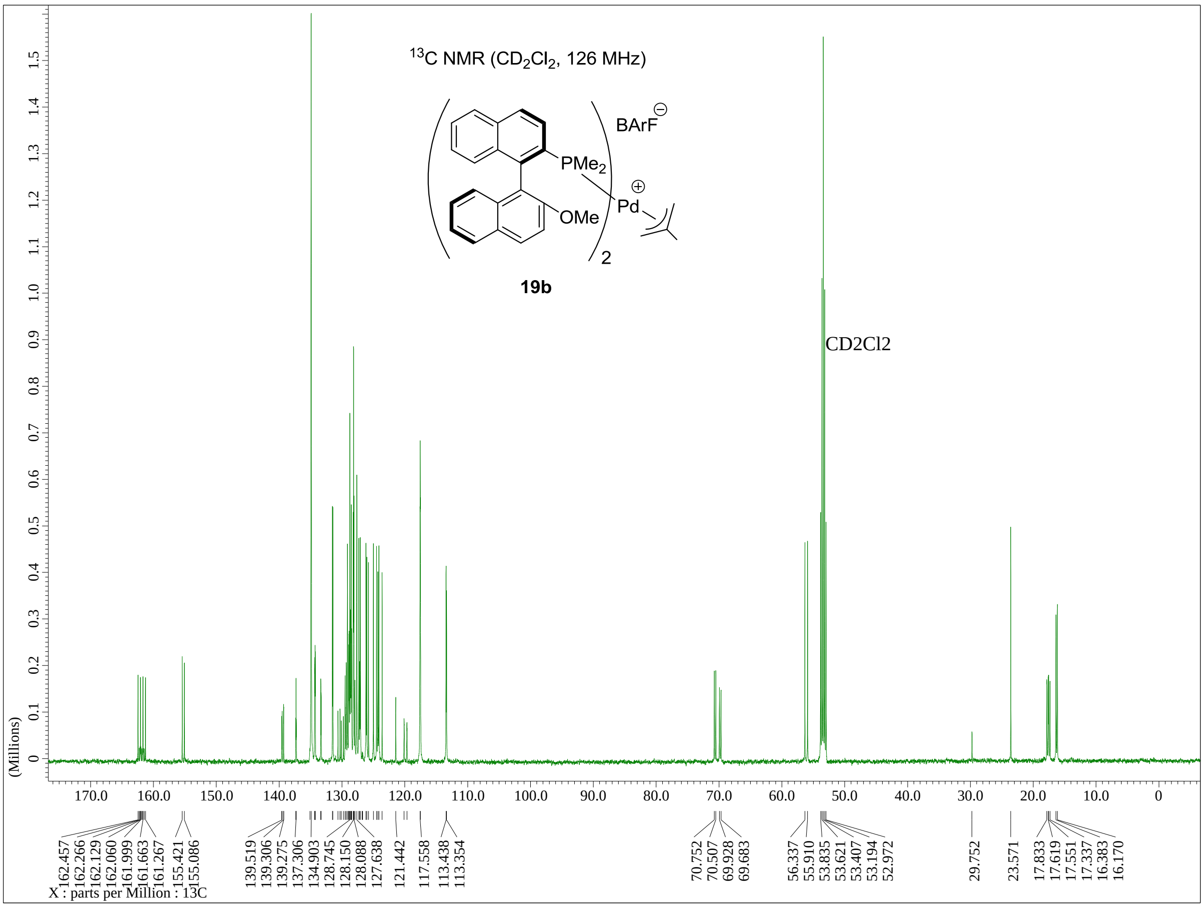
¹H NMR (CD2Cl2, 400 MHz)
BArF
PR'2
Pd
OMe
R'2 = (NMe2)2 18b
CD2Cl2
abundance
X : parts per Million : 1H



¹³C NMR (CD2Cl2, 101 MHz)
BArF
PR'2
Pd
OMe
R'2 = (NMe2)2 18b
CD2Cl2
abundance
X : parts per Million : 13C



^{1}H NMR (CD_2Cl_2, 500 MHz)
BArF
PMe$_2$
Pd
OMe
2
19b
CD2Cl2
8.51
7.73
1.54
1.04
1.07
3.13
1.00
2.43
6.81
(Millions)
8.103 8.099 8.085 8.081 7.921 7.916 7.904 7.789 7.784 7.597 7.502 7.484 7.306 7.047 6.768 6.752 6.740 6.723
5.326 5.316 5.314
3.792 3.760 3.650 3.573
1.793 1.772 1.738 1.654 1.634 1.408 1.391 1.297 1.215 1.197 1.112 1.094 1.086 1.069
X : parts per Million : 1H



^{13}C NMR (CD_2Cl_2, 126 MHz)
BArF
PMe$_2$
Pd
OMe
2
19b
CD2Cl2
(Millions)
162.457 162.266 162.129 162.060 161.999 161.663 161.267 155.421 155.086
139.519 139.306 139.275 137.306 134.903 128.745 128.150 128.088 127.638 121.442 117.558 113.438 113.354
70.752 70.507 69.928 69.683
56.337 55.910 53.835 53.621 53.407 53.194 52.972
29.752 23.571 17.833 17.619 17.551 17.337 16.383 16.170
X : parts per Million : 13C

References

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