Supplementary Material

Isolation and properties of a palladium PBP pincer complex featuring an ambiphilic boryl site

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General remarks

All manipulations were carried out in an MBraun glove box under an inert argon atmosphere. NMR-experiments were performed in Wilmad® quick pressure valve NMR tubes. ^{1}H, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance II (400.1 MHz, probe: BBO) or a Bruker Avance (400.3 MHz, probe: ATM BBFO) spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent resonances. [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(2,6-lutidine)] **6a** was prepared according to the literature.[1] All deuterated solvents, pyridine, 2,6-lutidine, 3,5-lutidine, iodobenzene and 4-iodobenzotrifluoride were degassed employing the freeze-pump-thaw technique and dried over activated molecular sieves (4 Å). Toluene, diethylether, dichloromethane, tetrahydrofurane, and pentane were dried by an MBraun solvent purification system. Benzene and *n*-hexane were dried over sodium and distilled under argon prior to use. CHN combustion analysis were carried out on an Elementar EL device by Elementar Analysesysteme GmbH. Infrared spectra were recorded on an Avatar 360 FT-IR E.S.P. device by Nicolet. Mass spectra (HRMS) were obtained by a MAT 95 spectrometer (Finnigan).

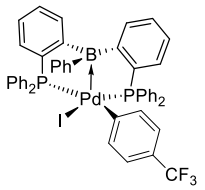
Single Crystal X-ray diffraction

Mo Kα radiation (λ = 0.71073 Å) was produced from an Incoatec I-μS microsource equipped with multilayer optics. Data were collected at 100(2) K on a Bruker D8 goniometer equipped with an Apex CCD detector. Temperature stability during data collection was realized by an Oxford Cryosystems 700 controller. Integration was performed by the SAINT software[2]. The SADABS software[3] was used for multi-scan absorption correction. Using Olex2,[4] the structure was solved with the ShelXS[5] structure solution program employing direct methods. Refinement was performed with the XL[6] refinement package using least squares minimization. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Complex / CCDC	**7d** / 1459014	**8** / 1458013	**17** / 1458010	**18a** / 1458011	**19a** / 1452002
Empirical formula	$C_{66}H_{55}BINO_2P_2Pd$	$C_{36}H_{28}BIP_2Pd$	$C_{32}H_{30}Cl_2I_2NPPd$	$C_{46}H_{45}BINP_2Pd$	$C_{40}H_{40}BP_3Pd$
Formula weight	1200.16	766.63	890.64	917.88	730.84
Temperature/K	100.15	100(2)	100	100(2)	100
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	Fdd2	P-1	$P2_1/c$	$P2_1/c$
a/Å	15.188(3)	18.4700(18)	9.0882(6)	8.8638(12)	10.6783(16)
b/Å	20.733(4)	31.893(3)	10.5044(7)	22.432(3)	18.823(3)
c/Å	18.380(4)	10.3482(10)	16.7224(12)	19.469(3)	17.516(3)
α/°	90	90	82.4700(10)	90	90.00
β/°	109.077(4)	90	80.1740(10)	94.012(2)	97.699(2)
γ/°	90	90	86.8400(10)	90	90.00
Volume/$Å^3$	5469.8(19)	6095.7(10)	1558.56(18)	3861.6(9)	3489.0(9)
Z	4	8	2	4	4
$\rho_{calc}g/cm^3$	1.457	1.671	1.898	1.579	1.391
μ/mm^{-1}	1.009	1.752	2.822	1.398	0.697
F(000)	2432.0	3024.0	860.0	1848.0	1504.0
Crystal size/mm^3	0.28 × 0.18 × 0.11	0.40 × 0.23 × 0.14	0.52 × 0.25 × 0.23	0.40 × 0.07 × 0.07	0.52 × 0.32 × 0.21
2Θ range /°	3.058 to 53.072	4.69 to 59.908	3.92 to 61.72	2.774 to 50.252	4.32 to 61.14
Index ranges	$-19 \le h \le 18$ $-25 \le k \le 25$ $-21 \le l \le 23$	$-25 \le h \le 25$ $-43 \le k \le 44$ $-14 \le l \le 14$	$-13 \le h \le 13$ $-15 \le k \le 14$ $-23 \le l \le 23$	$-10 \le h \le 10$ $-26 \le k \le 26$ $-23 \le l \le 23$	$-15 \le h \le 15$ $-25 \le k \le 26$ $-24 \le l \le 25$
Refls collected	49698	16813	23689	41131	39214
Independent reflections	11278 [R_{int} = 0.1144, R_{sigma} = 0.0975]	4175 [R_{int} = 0.0716, R_{sigma} = 0.0631]	8951 [R_{int} = 0.0575, R_{sigma} = 0.0666]	6885 [R_{int} = 0.0813, R_{sigma} = 0.0888]	10149 [R_{int} = 0.0784, R_{sigma} = 0.0746]
Data/restraints/ parameters	11278/0/668	4175/1/187	8951/0/354	6885/11/426	10149/0/410
GOF	1.013	0.981	1.024	1.091	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.0969	R_1 = 0.0308, wR_2 = 0.0635	R_1 = 0.0324, wR_2 = 0.0799	R_1 = 0.0565, wR_2 = 0.1649	R_1 = 0.0407, wR_2 = 0.0928
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1079	R_1 = 0.0334, wR_2 = 0.0644	R_1 = 0.0374, wR_2 = 0.0825	R_1 = 0.0775, wR_2 = 0.1822	R_1 = 0.0570, wR_2 = 0.1003
Largest diff. peak/ hole / e $Å^{-3}$	0.80/-1.33	0.83/-0.89	1.14/-1.51	3.10/-2.35	1.00/-0.54
Flack parameter	-	-0.020(15)	-	-	-

Experimental Procedures

Synthesis of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$CF_3C_6H_4$)I] **7c**



[{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(2,6-lutidine)] **6a** (50 mg, 60 μmol, 1 equiv.) and 4-iodobenzotrifluoride (16 mg, 60 μmol, 1 equiv.) were solved in benzene (1 mL) and stirred for 1 h. The solvent was reduced *in vacuo*, leading to a yellow precipitate. The solvent was decanted, the residue was washed with pentane (2 x 1 mL) and was dried under reduced pressure, yielding the title compound (42 mg, 43 μmol, 72 %).

^{1}H NMR (400 MHz, THF-d_8): δ = 4.34 (br, 1 H), 5.93 – 6.03 (m, 2 H), 6.05 (br, 1 H), 6.20 – 6.30 (m, 2 H), 6.30 – 6.37 (m, 2 H), 6.67 – 6.75 (m, 3 H), 6.87 (br, 1 H), 6.92 – 7.03 (m, 2 H), 7.24 – 7.30 (m, 5 H), 7.33 – 7.37 (m, 2 H), 7.39 – 7.50 (m, 9 H), 7.53 – 7.64 (m, 2 H), 7.71 (br, 1 H), 8.22 – 8.39 (m, 4 H) ppm.

^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ = 60 (s, $w_{1/2}$ = 3000 ± 1000 Hz) ppm.

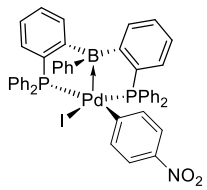
^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 121.04 – 121.49 (br), 124.35 – 124.91 (br), 127.34 (d, J = 8.6 Hz), 127.55, 127.61, 127.66, 128.12 (d, J = 2.0 Hz), 128.52 (d, J = 9.8 Hz), 129.07, 129.25 (d, J = 6.1 Hz), 129.57 (d, J = 11.0 Hz), 129.72 (d, J = 2.8 Hz), 130.00 (d, J = 2.4 Hz), 130.51, 130.55, 131.35 (d, J = 2.3 Hz), 131.91 (d, J = 21.4 Hz), 132.38, 132.59, 132.79 (d, J = 2.4 Hz), 132.88, 133.28, 133.37, 133.60 (d, J = 9.1 Hz), 133.74, 133.81 (d, J = 5.9 Hz), 134.14 (d, J = 2.5 Hz), 134.68 (d, J = 2.5 Hz), 135.47, 135.66, 135.95 (d, J = 2.4 Hz), 137.77 (d, J = 13.6 Hz), 138.05, 138.49, 140.81 (d, J = 11.4 Hz), 144.78 – 145.18 (m), 156.18 – 157.62 (m), 162.90 – 163.24 (m), 164.14 – 164.60 (m) ppm.

^{19}F{^{1}H} NMR (377 MHz, THF-d_8): δ = –62.50 (s) ppm.

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = 17.36 (d, $^2J_{P\text{-}P}$ = 37.3 Hz, 1P), 33.39 (d, $^2J_{P\text{-}P}$ = 37.4 Hz, 1P) ppm.

CHN Found: C, 59.4; H, 3.5. $C_{49}H_{37}BF_3IP_2Pd$ requires C, 59.5; H, 3.8%.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**



[{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(2,6-lutidine)] **6a** (50 mg, 60 μmol, 1 equiv.) and 4-nitroiodobenzene (15 mg, 60 μmol, 1 equiv.) were solved in benzene (1 mL) and stirred for 1 h. The solvent was decanted and the greyish precipitate was washed with pentane (2 x 1 mL). The solid was

dried under reduced pressure, yielding the title compound (48 mg, 50 μmol, 80 %). Single crystals suitable for X-ray diffraction analysis were grown from a concentrated benzene solution.

^{1}H NMR (400 MHz, benzene-d_6): δ = 4.43 – 4.69 (br., 1 H), 6.06 – 6.18 (m, 4 H), 6.21 – 6.28 (m, 2 H), 6.31 – 6.37 (m, 2 H), 6.45 – 6.50 (m, 1 H), 6.54 – 6.64 (m, 2 H), 6.89 – 7.01 (m, 5 H), 7.03 – 7.08 (m, 2 H), 7.10 – 7.25 (m, 9 H), 7.40 – 7.51 (m, 1 H), 7.56 – 7.65 (m, 2 H), 7.77 – 7.92 (br., 1 H), 8.03 – 8.14 (m, 2 H), 8.46 – 8.59 (m, 2 H), 8.63 – 9.10 (br., 1 H) ppm.

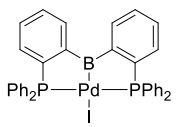
^{11}B{^{1}H} NMR (128 MHz, benzene-d_6): δ = 63 (s, $w_{1/2}$ = 3000 ± 1000 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ = 127.17 (d, J = 8.8 Hz), 127.35, 127.46, 127.52, 128.14 (d, J = 2.1 Hz), 128.49 (d, J = 9.9 Hz), 129.29, 129.35, 129.46, 129.90 (d, J = 2.9 Hz), 130.03, 130.05, 130.54 (d, J = 2.5 Hz), 131.30 – 131.53 (m), 131.60, 132.04, 132.29, 132.34 – 132.66 (m), 132.66 (d, J = 2.5 Hz), 132.84 (d, J = 6.2 Hz), 132.96, 133.07 (d, J = 2.3 Hz), 133.16 (d, J = 9.3 Hz), 133.62 (d, J = 2.2 Hz), 134.21 (d, J = 2.5 Hz), 134.54 (d, J = 2.7 Hz), 135.48, 135.67, 136.87 (d, J = 13.3 Hz), 137.20, 137.65, 140.14 (d, J = 11.5 Hz), 144.02 – 144.28 (m), 144.66, 155.11 – 157.08 (m), 171.09 (d, J = 3.4 Hz), 172.37 (d, J = 3.3 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, benzene-d_6): δ = 19.2 (d, $^{2}J_{P\text{-}P}$ = 37 Hz, 1 P), 34.8 (d, $^{2}J_{P\text{-}P}$ = 37 Hz, 1P) ppm.

CHN Found: C, 62.1; H, 4.7; N, 0.9 $C_{48}H_{37}NBIO_2P_2Pd \cdot C_6H_6$ requires C, 62.1; H, 4.2; N, 1.3%.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2$B}PdI] **8**



[{(*o*-$PPh_2C_6H_4)_2$BPh)}Pd(2,6-lutidine)] **6a** (350 mg, 0.425 mmol, 1.0 equiv.) was solved in benzene (3 mL) and iodobenzene (100 mg, 0.490 mmol, 1.15 equiv.) was added dropwise. The solution was stirred for 24 h, leading to a yellow precipitate. The mother liquor was decanted and the residue was washed with pentane (2 mL) and dichloromethane (2 x 1 mL). The remaining solid was dried *in vacuo*, yielding the title compound as a yellow powder (102 mg, 0.133 mmol, 31 %). Single crystals suitable for X-ray diffraction analysis were grown from a saturated benzene solution.

^{1}H NMR (400 MHz, dichloromethane-d_2): δ = 8.06 – 8.03 (m, 2 H), 7.78 – 7.71 (m, 8 H), 7.71 – 7.65 (m, 2 H), 7.63 – 7.58 (m, 4 H), 7.47 – 7.39 (m, 12 H) ppm.

^{11}B{^{1}H} NMR (128 MHz, dichloromethane-d_2): δ = 97 (s, $w_{1/2}$ = 1250 ± 250 Hz) ppm.

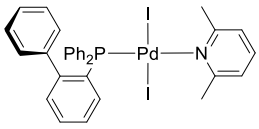
^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ = 128.88, 129.08 (pt, *J* = 5.1 Hz), 131.00, 131.36, 133.04 (pt, *J* = 3.1 Hz), 133.66 (pt, *J* = 21.9 Hz), 133.99, 134.46 (pt, *J* = 7.0 Hz), 135.24 (pt, *J* = 13.3 Hz), 150.97 (pt, *J* = 22.8 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, dichloromethane-d_2): δ = 45.4 (s) ppm.

IR data (KBr disc): $\tilde{\nu}$ = 3051 (w), 1573 (w), 1480 (m), 1433 (s), 1310 (vw), 1256 (m), 1245 (m), 1222 (m), 1182 (w), 1152 (w), 1128 (m), 1095 (m), 1067 (vw), 1028 (vw), 997 (w), 877 (w), 805 (w), 767 (m), 748 (s), 718 (m), 693 (s), 644 (vw), 594 (w), 582 (vw), 512 (s), 505 (vs), 432 (w) cm^{-1}.

CHN Found: C, 56.2; H, 3.7. $C_{36}H_{28}BIP_2Pd$ requires C, 56.4; H, 3.7%.

Synthesis of [*trans*-{(2-biphenyl)diphenylphosphine}Pd(2,6-lutidine)I_2] **17**



The combined mother liquor und washing solutions of pincer **8** synthesis were overlaid with *n*-hexane. Single crystals suitable for single crystal X-ray diffraction analysis formed within 48 h.

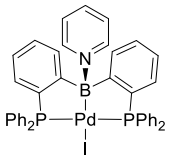
^{1}H NMR (400 MHz, dichloromethane-d_2): δ = 3.10 (s, 6 H), 7.07 – 7.17 (m, 5 H), 7.17 – 7.23 (m, 1 H), 7.27 – 7.35 (m, 5 H), 7.36 – 7.42 (m, 3 H), 7.45 – 7.49 (m, 2 H), 7.54 (m, 1 H), 7.57 (m, 1H), 7.75 – 7.83 (m, 4 H) ppm.

^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ = 28.53, 123.42 (d, *J* = 4.8 Hz), 126.19 (d, *J* = 9.7 Hz), 127.22, 128.07, 128.20 (d, *J* = 2.7 Hz), 130.80 (d, *J* = 2.7 Hz), 130.85, 130.88, 131.41, 132.25 (d, *J* = 6.4 Hz), 133.00 (d, *J* = 8.8 Hz), 136.84 (d, *J* = 10.1 Hz), 138.97, 142.45 (d, *J* = 3.5 Hz), 145.34 (d, *J* = 9.6 Hz), 160.18 (d, *J* = 1.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, dichloromethane-d_2): δ = 21.4 (s) ppm.

IR data (KBr disc): $\tilde{\nu}$ = 3055 (m), 2976 (w), 1606 (w), 1581 (w), 1479 (w), 1463 (s), 1435 (s), 1398 (m), 1372 (m), 1311 (vw), 1258 (m), 1183 (w), 1159 (m), 1124 (vw), 1107 (w), 1093 (m), 1072 (vw), 1027 (w), 998 (w), 916 (w), 839 (vw), 775 (m), 741 (s), 731 (s), 689 (s), 691 (s), 614 (w), 556 (vw), 540 (w), 523 (vs), 504 (s), 459 (w), 438 (w), 425 (w).

Synthesis of [{(*o*-$PPh_2C_6H_4)_2$B(pyridine)}PdI] **18a**



[{(*o*-$PPh_2C_6H_4)_2$B}PdI] **8** (10.0 mg, 13.1 µmol, 1 equiv.) was suspended in *n*-hexane (2 mL) and pyridine (0.1 mL, excess) was added dropwise. After stirring for 2 h, the liquid was decanted, the yellow solid was washed with *n*-pentane and dried *in vacuo*, yielding the title compound (10.4 mg, 12.4 μmol, 95 %). Single crystals suitable for X-ray diffraction analysis were grown by overlaying a saturated dichloromethane solution with *n*-pentane.

^{1}H NMR (400 MHz, dichloromethane-d_2): δ = 6.76 – 6.87 (m, 2 H), 7.14 – 7.35 (m, 19 H), 7.43 – 7.52 (m, 6 H), 7.60 (m, 4 H), 8.13 (m, 2 H) ppm.

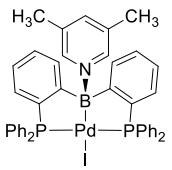
^{11}B{^{1}H} NMR (128 MHz, dichloromethane-d_2): δ = 17 (s, $w_{1/2}$ = 400 ± 100 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ = 125.45, 127.92 (pt, *J* = 3.2 Hz), 128.54 (pt, *J* = 3.5 Hz), 128.85 (pt, *J* = 4.5 Hz), 130.12 (d, *J* = 16.5 Hz), 130.47, 133.09 (pt, *J* = 14.0 Hz), 134.05, 134.34 (pt, *J* = 6.7 Hz), 134.60 (pt, *J* = 6.5 Hz), 136.13, 144.56, 146.84 ppm.

^{31}P{^{1}H} NMR (162 MHz, dichloromethane-d_2): δ = 40.1 (s) ppm.

CHN Found: C, 57.7; H, 4.2; N, 1.3. $C_{41}H_{33}NBIP_2Pd$ requires C, 58.2; H, 4.0; N, 1.7%.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2$B(3,5-lutidine)}PdI] **18b**



[{(*o*-$PPh_2C_6H_4)_2$B}PdI] **8** (10.0 mg, 13.1 μmol, 1 equiv.) was solved in dichloromethane (1 mL) and 3,5-lutidine (0.1 mL, excess) was added dropwise. After stirring for 2 h, the solvent was removed *in vacuo*. The yellow solid was washed with *n*-pentane (2 x 1 mL) and dried *in vacuo*, yielding the title compound (10.4 mg, 11.9 µmol, 91 %).

^{1}H NMR (400 MHz, dichloromethane-d_2): δ = 1.83 (s, 6 H, CH_3), 6.92 (s, 1 H), 7.39 – 7.23 (m, 18 H), 7.60 – 7.51 (m, 6 H), 7.75 – 7.69 (m, 4 H), 7.80 (s, 2 H) ppm.

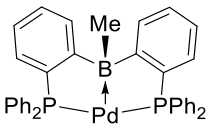
^{11}B{^{1}H} NMR (128 MHz, dichloromethane-d_2): δ = 16 (s, $w_{1/2}$ = 500 ± 100 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ = 18.49 , 127.82 (pt, *J* = 3.0 Hz), 128.49 (pt, *J* = 4.9 Hz), 128.64 (pt, *J* = 4.7 Hz), 130.03, 130.20, 130.36, 133.13 (pt, *J* = 14.1 Hz), 133.94, 134.49 (pt, *J* = 6.8 Hz), 134.59 (pt, *J* = 7.2 Hz), 135.47, 136.11 (pt, *J* = 20.4 Hz), 140.66, 144.49, 144.51 (s + pt, *J* = 21.7 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, dichloromethane-d_2): δ = 40.2 (s) ppm.

CHN Found: C, 59.2; H, 4.3; N, 2.6. $C_{43}H_{37}BINP_2Pd$ requires C, 59.1; H, 4.3; N, 1.60%.

In-situ generation of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd]



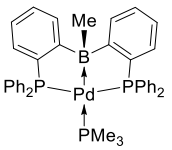
[{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8** (20 mg, 26 µmol, 1 equiv.) was suspended in THF-d_8 (0.6 mL) and a standard solution of Me_2Mg (0.7 mg in 0.1 mL THF-d_8, 13 µmol, 0.5 equiv.) was added. The yellow mixture was stirred for 10 min, during which it became clear orange.

^{1}H NMR (400 MHz, THF-d_8): δ = 0.54 (t, J = 4.9 Hz, 3 H, BMe), 6.97 – 7.03 (m, 2 H), 7.15 – 7.26 (m, 10 H), 7.30 – 7.36 (m, 6 H), 7.52 – 7.60 (m, 4 H), 7.61 – 7.69 (m, 4 H), 7.69 – 7.73 (m, 2 H) ppm.

$^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8): δ = 23 (s, $w_{1/2}$ = 500 ± 100 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8): δ = 30.7 (s) ppm.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd(PMe_3)] **19a**



[{(*o*-$PPh_2C_6H_4)_2B$}PdI] (20 mg, 26 μmol, 1 equiv.) was suspended in THF (1 mL) and a standard solution of Me_2Mg (0.7 mg in 0.1 mL THF, 13 μmol, 0.5 equiv.) was added. The yellow mixture was stirred for 10 min, during which it became clear orange. PMe_3 (0.05 mL, 1.0 M in toluene, 50 μmol, 2 equiv.) was added, leading to a white precipitate. The solution was filtered, and the solvent was removed *in vacuo,* yielding the title compound (16 mg, 22 μmol, 85 %). Single crystals suitable for X-ray diffraction analysis were grown by overlaying a saturated benzene solution of **19a** with *n*-hexane.

^{1}H NMR (400 MHz, THF-d_8): δ = 0.65 (pt, J = 7.8 Hz, 3 H, BMe), 0.82 (d, $^{2}J_{P\text{-}H}$ = 4.6 Hz, 9 H, PMe_3), 6.95 – 7.02 (m, 2 H), 7.08 – 7.30 (m, 14 H), 7.32 – 7.36 (m, 6 H), 7.51 – 7.58 (m, 4 H), 7.77 – 7.81 (m, 2 H) ppm.

$^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8): δ = 25 (s, $w_{1/2}$ = 500 ± 100 Hz) ppm.

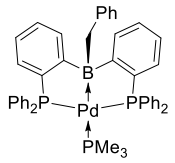
$^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8) δ = 15.43 (br, BMe), 18.58 (d, J = 10.0 Hz, PMe_3), 125.46 (pt, J = 2.9 Hz), 128.72 (pt, J = 4.5 Hz), 129.00 (pt, J = 4.4 Hz), 129.23, 129.32,

129.64, 131.57 (pt, J = 17.1 Hz), 132.58, 133.95 (ptd, J = 7.4, 4.9 Hz), 138.61 (pt, J = 15.7 Hz), 140.71 (pt, J = 16.0 Hz), 142.20 – 142.98 (m), 170.70 (br) ppm.

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = –38.2 (s, 1 P, PMe_3), 38.5 (s, 2 P, $ArPPh_2$) ppm.

CHN Found: C, 65.6; H, 5.8. $C_{40}H_{40}BP_3Pd$ requires C, 65.7; H, 5.5.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2BCH_2Ph$}Pd(PMe_3)] **19b**



[{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8** (10 mg, 13 μmol, 1 equiv.) was suspended in THF (1.0 mL) and $(PhCH_2)_2Mg$ (1.3 mg, 6.5 μmol, 0.5 equiv.) was added, followed by PMe_3 (0.02 mL, 1.0 M in toluene, 20 μmol, 1.5 equiv.). The solution was filtered and the solvent was removed *in vacuo*. The yellow residue was washed with n-pentane and dried under reduced pressure, yielding the title compound (6.9 mg, 8.6 µmol, 66 %).

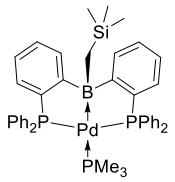
^{1}H NMR (400 MHz, THF-d_8): δ = 0.74 (d, J = 4.5 Hz, 9 H, PMe_3), 2.59 (q, J = 7.6 Hz, 2 H, BCH_2), 6.66 – 6.70 (m, 2 H), 6.74 – 6.80 (m, 2 H), 6.81 – 6.85 (m, 1 H), 6.94 – 7.05 (m, 5 H), 7.12 – 7.17 (m, 5 H), 7.22 – 7.29 (m, 11 H), 7.31 – 7.35 (m, 5 H), 7.80 – 7.84 (m, 2 H) ppm.

^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ = 20 (s, $w_{1/2}$ = 500 ± 100 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 18.46 (d, J = 9.1 Hz, PMe_3), 46.16 (bs, BCH_2, confirmed by HSQC), 122.82, 125.56 (m), 127.75, 128.75 (pt, J = 4.4 Hz), 128.92, 129.05 (pt, J = 4.4 Hz), 129.27, 129.40, 129.71, 129.76, 132.40 (ptd, J =17.1, 3.5 Hz), 132.79, 133.90 (pt, J = 6.9 Hz), 134.23 (pt, J = 7.4 Hz), 138.54 – 138.85 (m), 149.32, 169.51 (br) ppm.

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = –40.6 (br, 1 P, PMe_3), 39.4 (d, $^{2}J_{P\text{-}P}$ = 13 Hz, 2 P, $ArPPh_2$) ppm.

Synthesis of [{(*o*-$PPh_2C_6H_4)_2BCH_2SiMe_3$}Pd($PMe_3$)] **19c**



[{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8** (10 mg, 13 μmol, 1 equiv.) was suspended in THF (1.0 mL) and $(Me_3SiCH_2)_2Mg$ (1.3 mg, 6.5 μmol, 0.5 equiv.) was added, followed by PMe_3 (0.02 mL, 1.0 M in toluene, 20 μmol, 1.5 equiv.). The solution was filtered and the solvent was removed under reduced pressure. The yellow residue was washed with *n*-pentane and dried *in vacuo*, yielding the title compound (7.8 mg, 9.7 mmol, 75 %).

^{1}H NMR (400 MHz, THF-d_8): δ = –0.24 (s, 9 H, $SiMe_3$), 0.70 (pt, J = 6.3 Hz, 2 H, BCH_2), 0.87 (d, $J_{P\text{-}H}$ = 4.6 Hz, 9 H, PMe_3), 6.97 – 7.05 (m, 6 H), 7.08 – 7.18 (m, 8 H), 7.20 – 7.26 (m, 2 H), 7.28 – 7.34 (m, 6 H), 7.46 – 7.55 (m, 4 H), 7.95 – 7.99 (m, 2 H) ppm.

^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ = 28 (s, $w_{1/2}$ = 500 ± 100 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 2.15 ($SiMe_3$), 13.00 (br, BCH_2), 19.44 (d, J = 10.2 Hz, PMe_3), 45.00 (bs), 125.70 (m), 128.62 (pt, J = 4.4 Hz), 128.72 – 129.00 (m), 129.12 , 129.42 , 131.78 – 132.45 (m), 133.12 , 133.69 (pdt, J = 9.3, 7.5 Hz), 138.69 – 139.24 (m), 141.47 – 142.04 (m), 142.70 (m) ppm.

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ = –37.8 (s, 1 P, PMe_3), 35.3 (s, 2 P, $ArPPh_2$) ppm.

HRMS (EI): *m/z* = $[M - PMe_3]^+$ calculated for $C_{40}H_{39}BP_2PdSi$: 726.1424, found 726.1419 (+ 0.04 ppm).

NMR Spectra

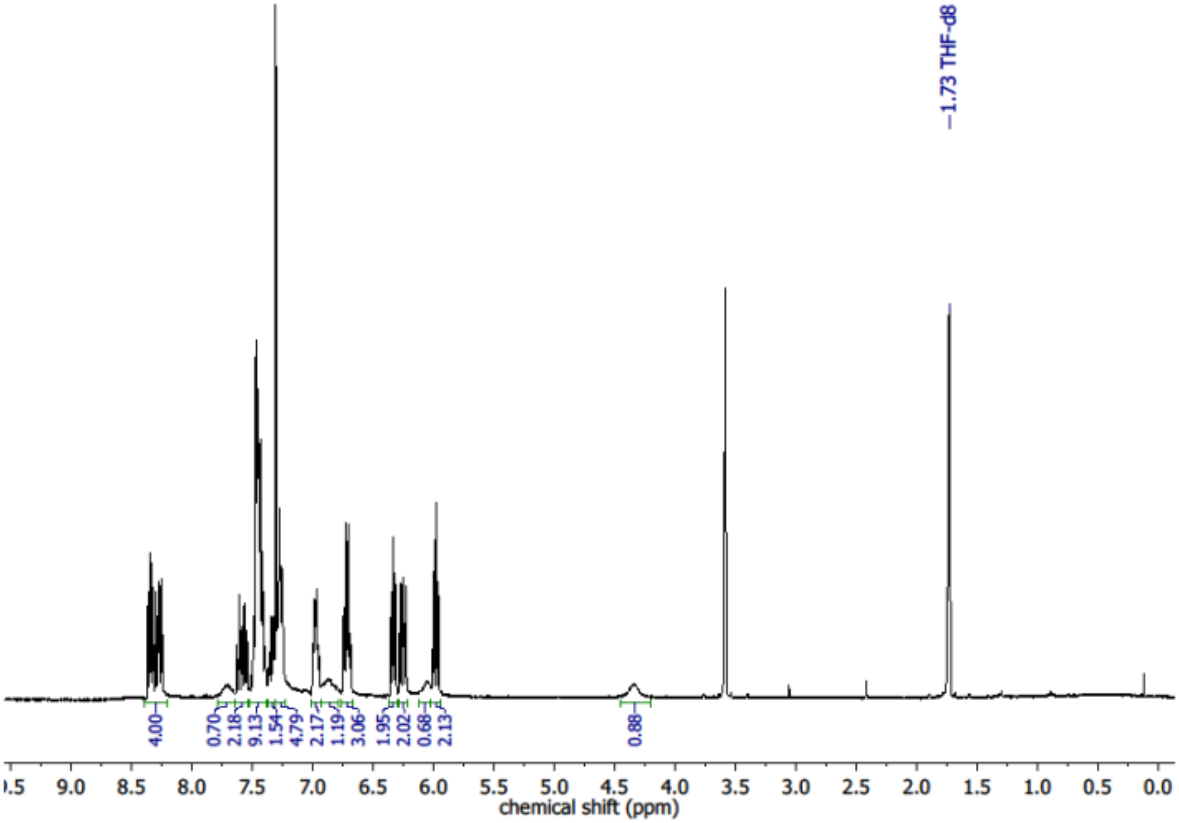


Fig. S1. ^{1}H NMR (400 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$CF_3C_6H_4$)I] **7c**.

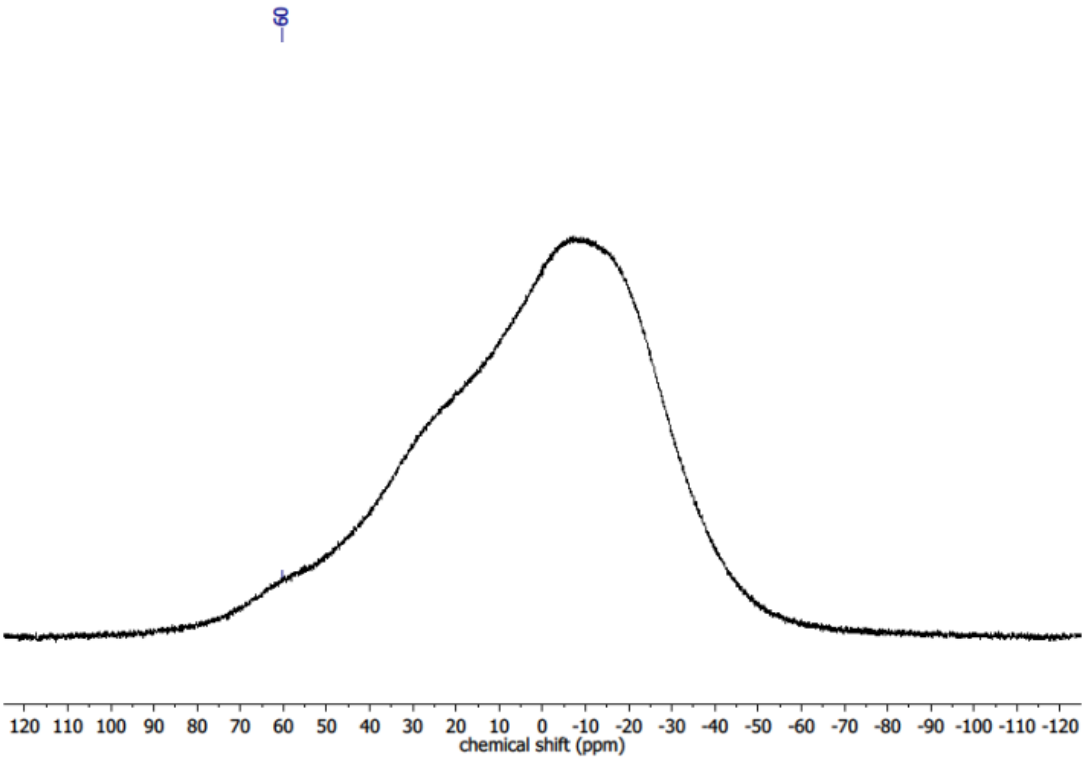


Fig. S2. ^{11}B{^{1}H} NMR (128 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd{*p*-$(CF_3)C_6H_4$}I] **7c**.

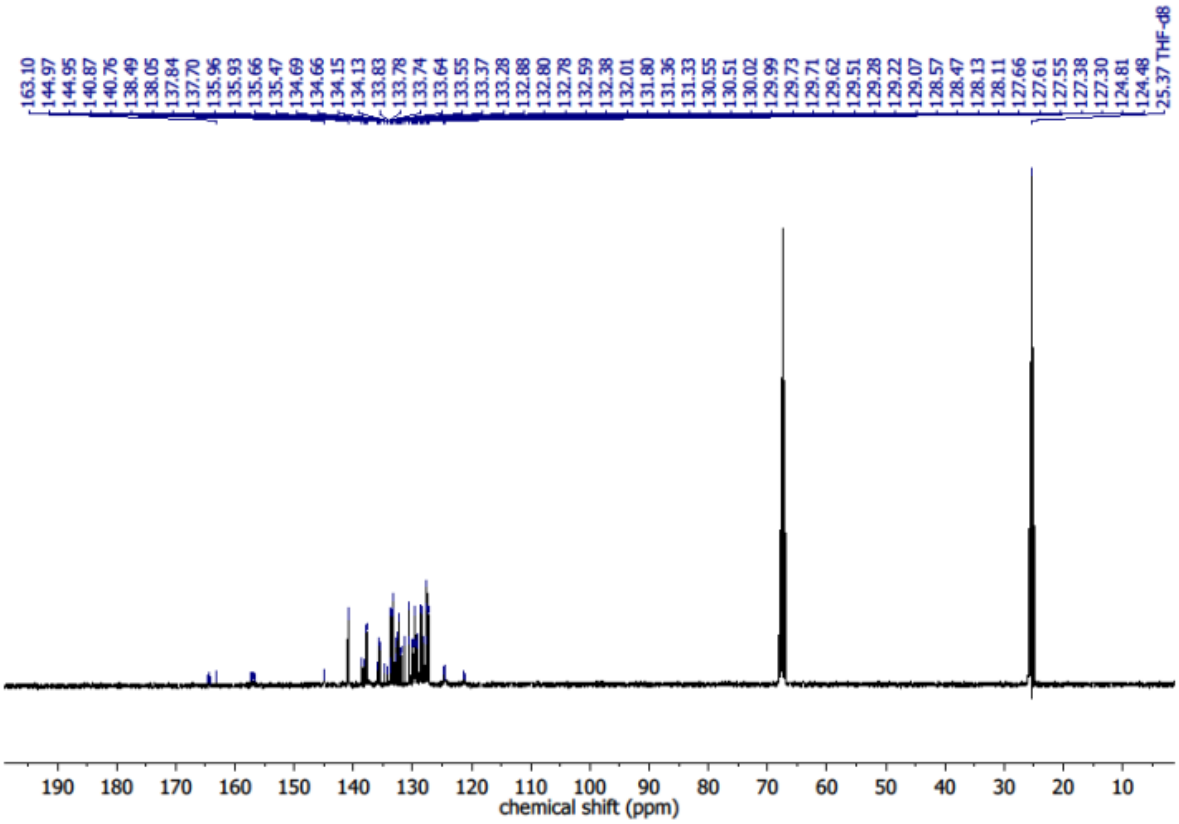


Fig. S3. $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$CF_3C_6H_4$)I] **7c**.

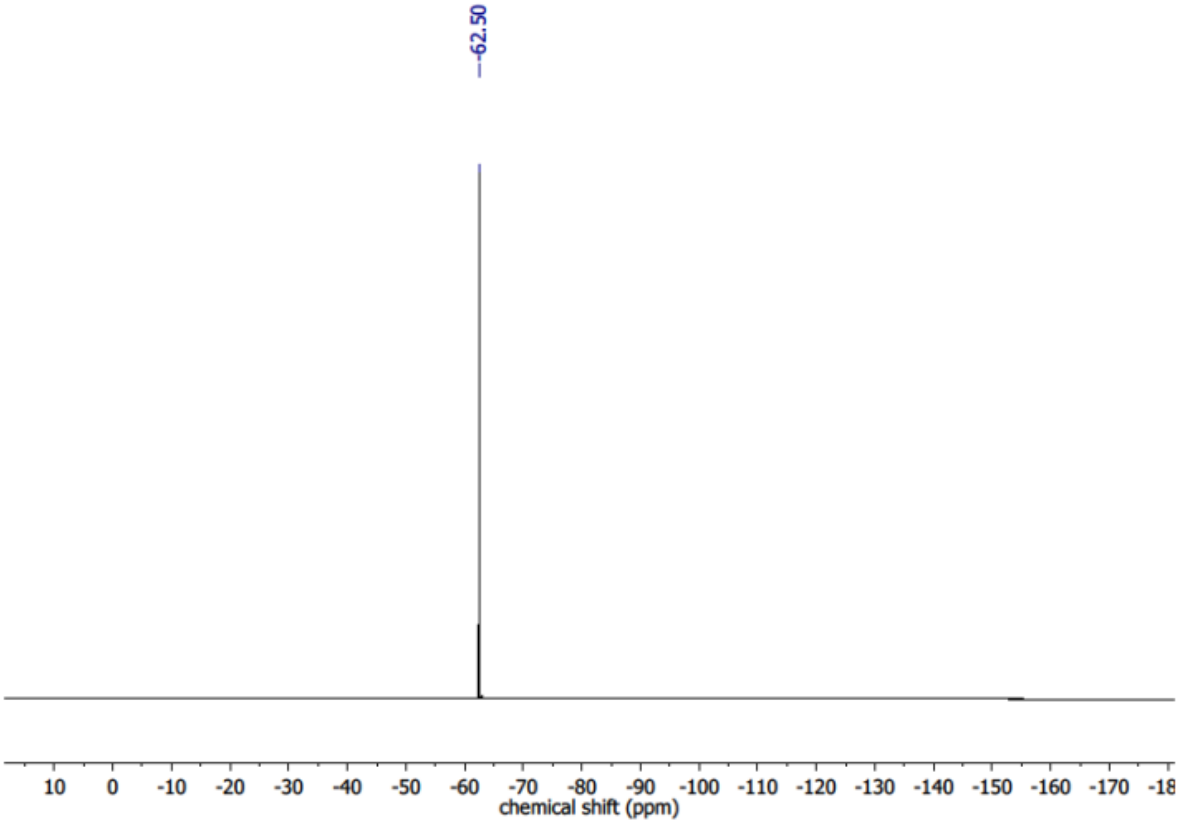


Fig. S4. $^{19}F\{^{1}H\}$ NMR (377 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$CF_3C_6H_4$)I] **7c**.

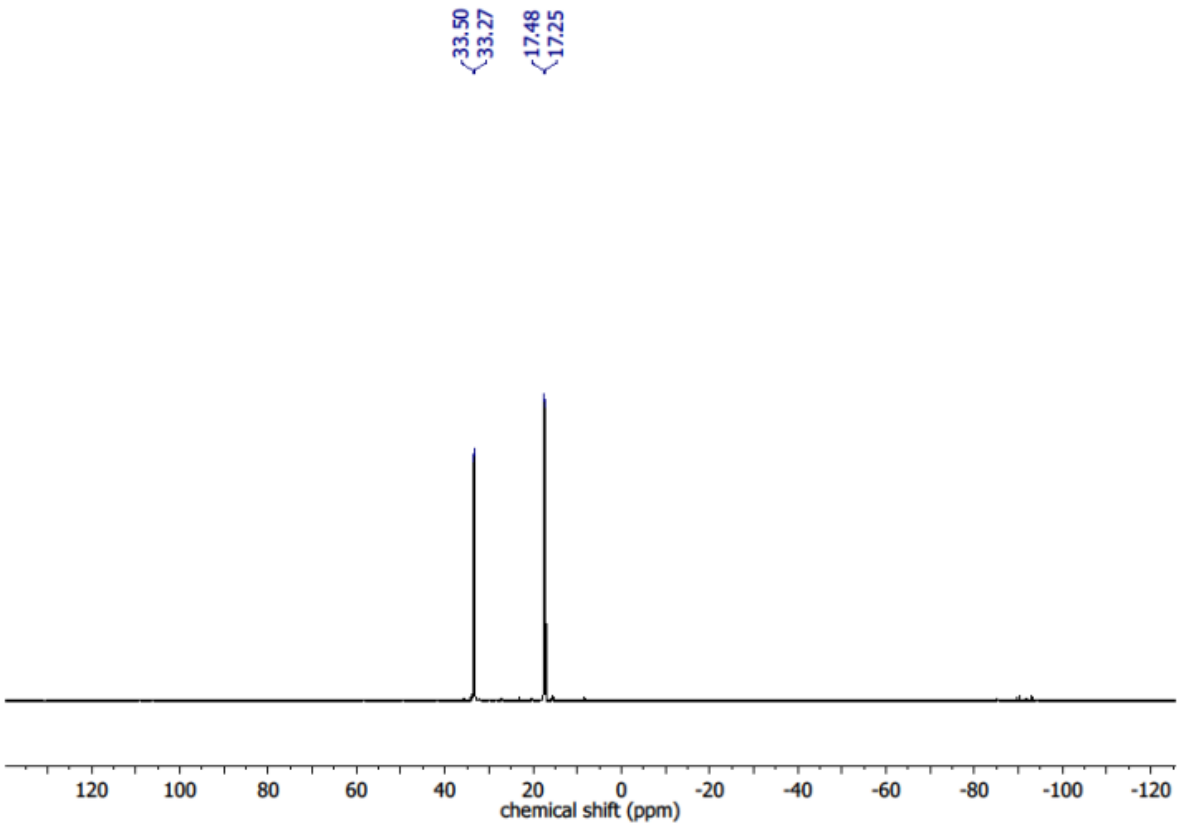


Fig. S5. $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$CF_3C_6H_4$)I] **7c**.

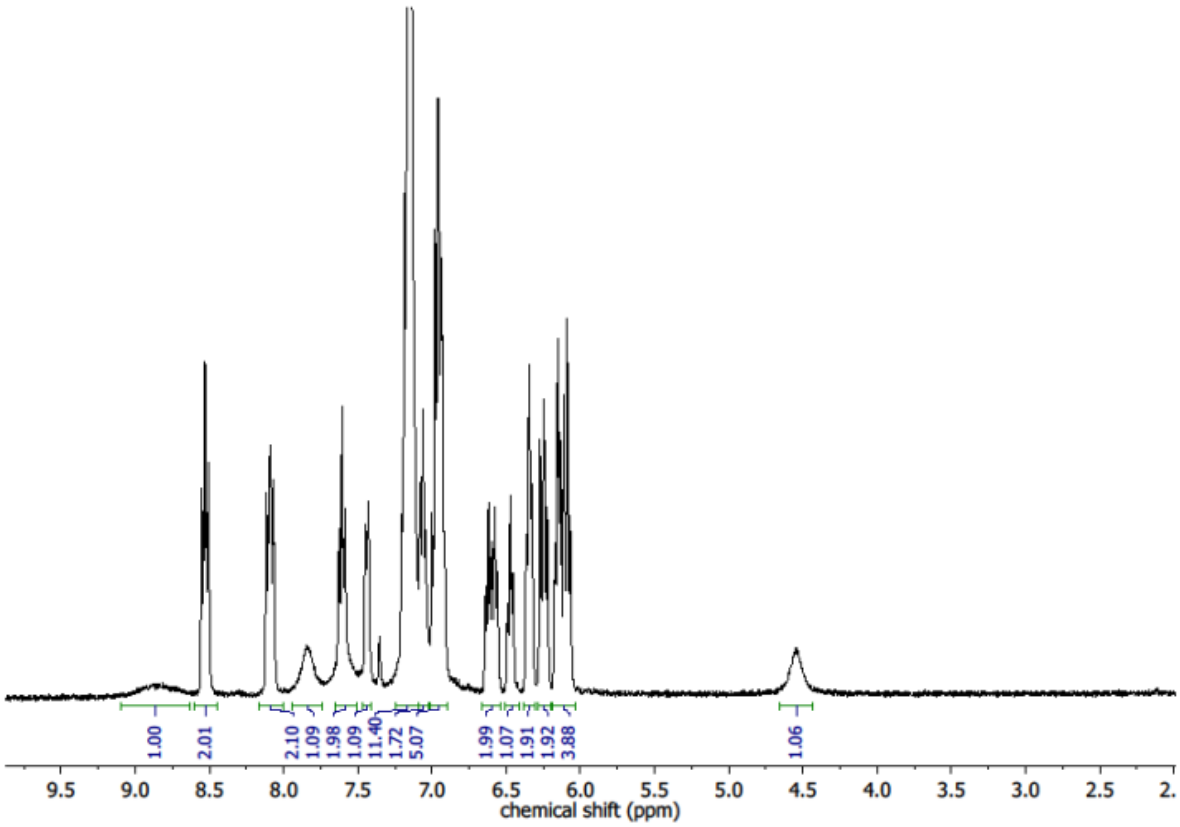


Fig. S6. ^{1}H NMR (400 MHz, benzene-d_6) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

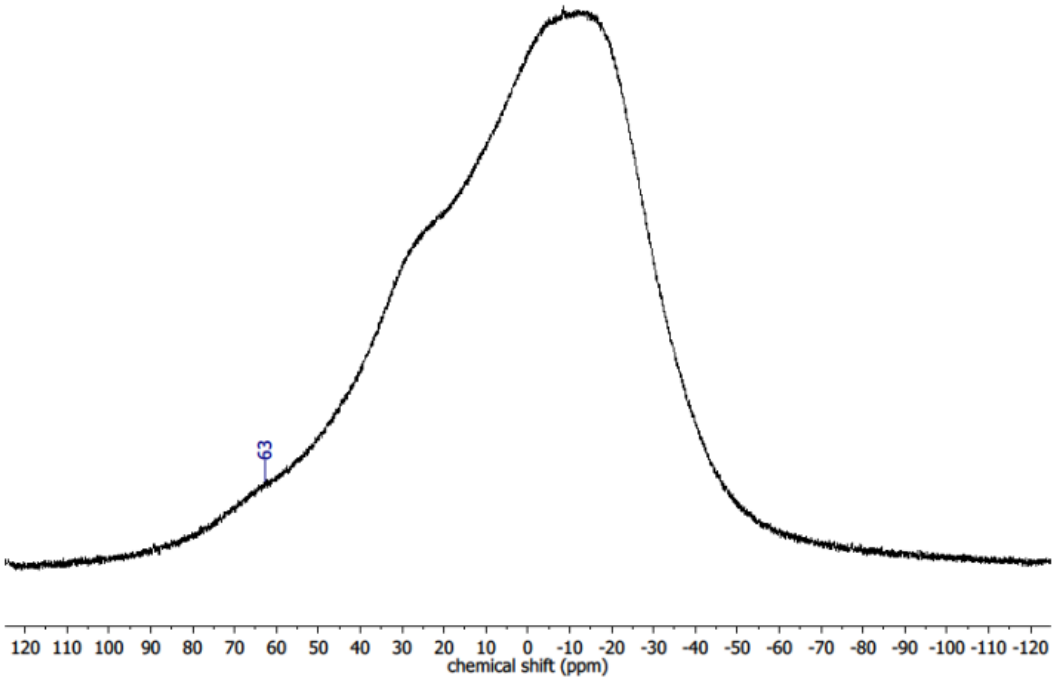


Fig. S7. $^{11}B\{^{1}H\}$ NMR (128 MHz, benzene-d_6) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

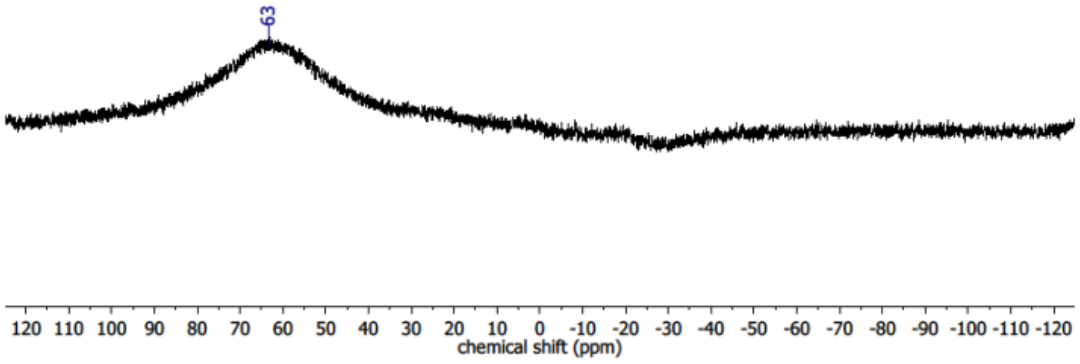


Fig. S8. $^{11}B\{^{1}H\}$ NMR (128 MHz, benzene-d_6) of **7d** after background substraction.

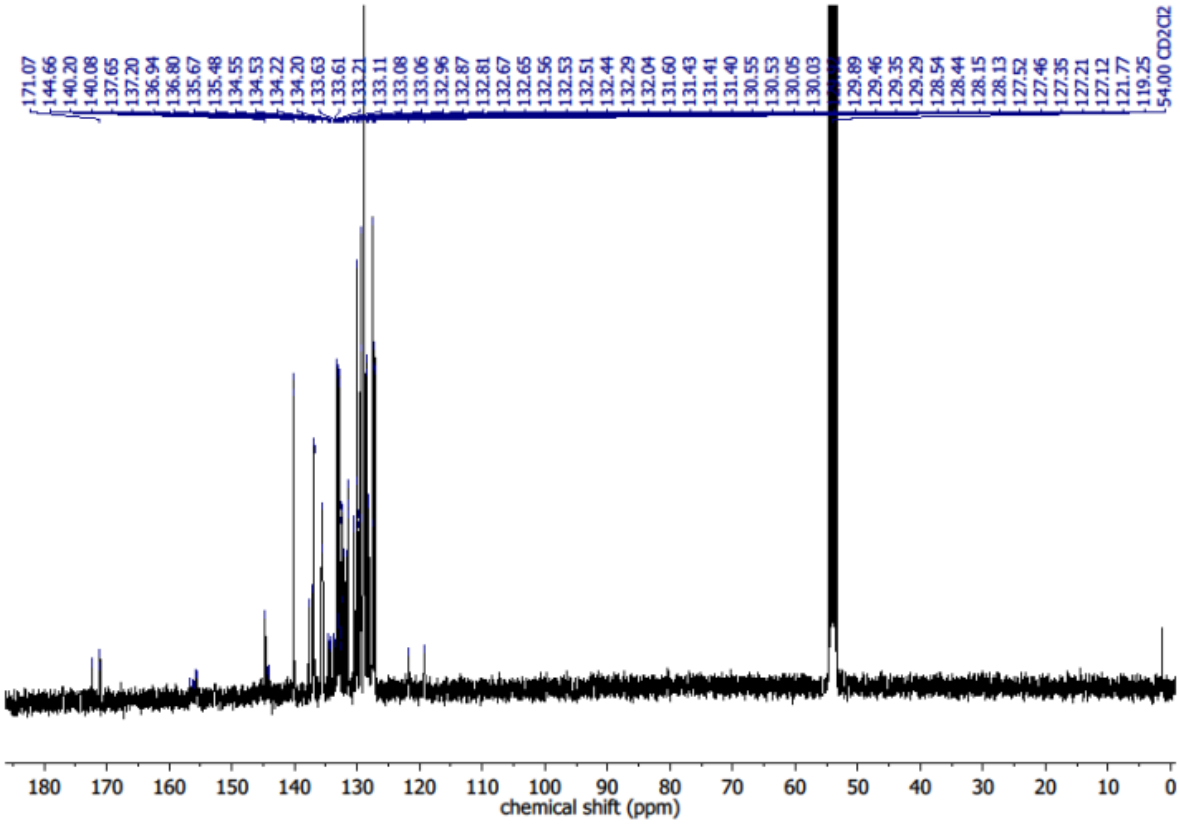


Fig. S9. $^{13}C\{^{1}H\}$ NMR (101 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

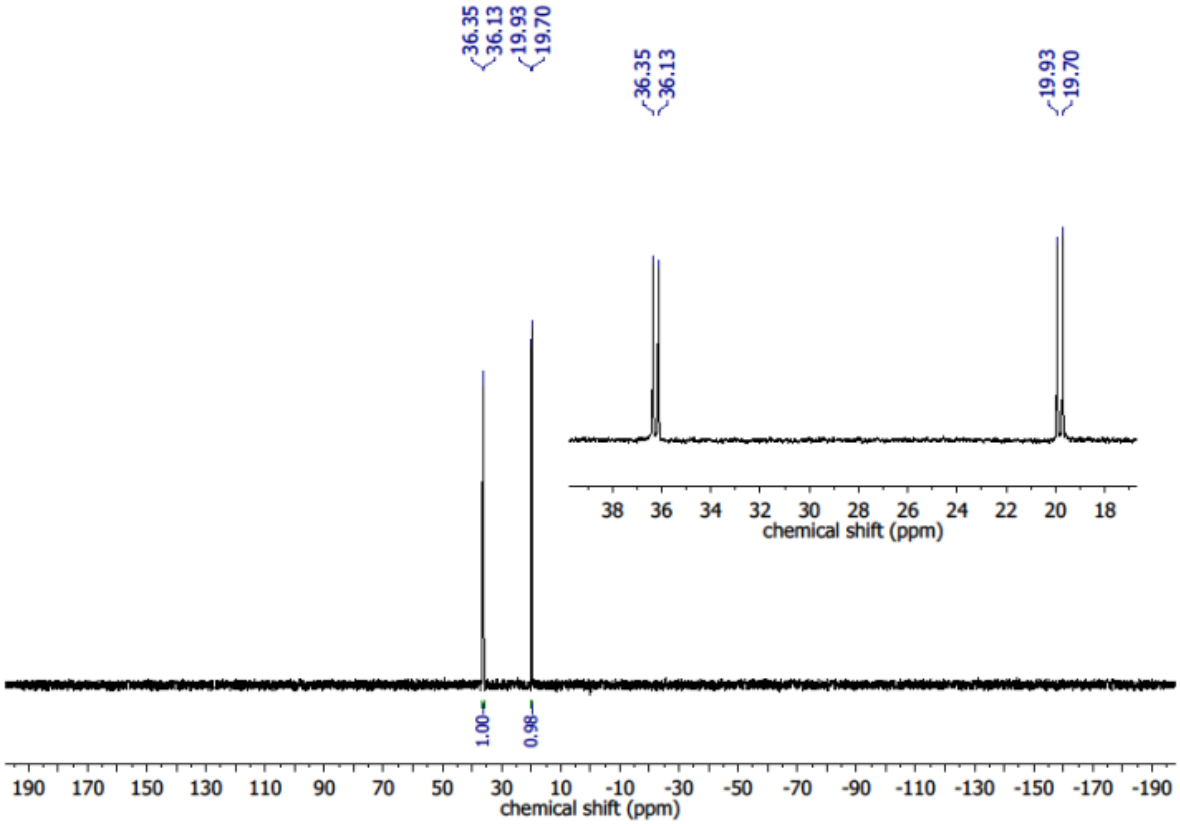


Fig. S10. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

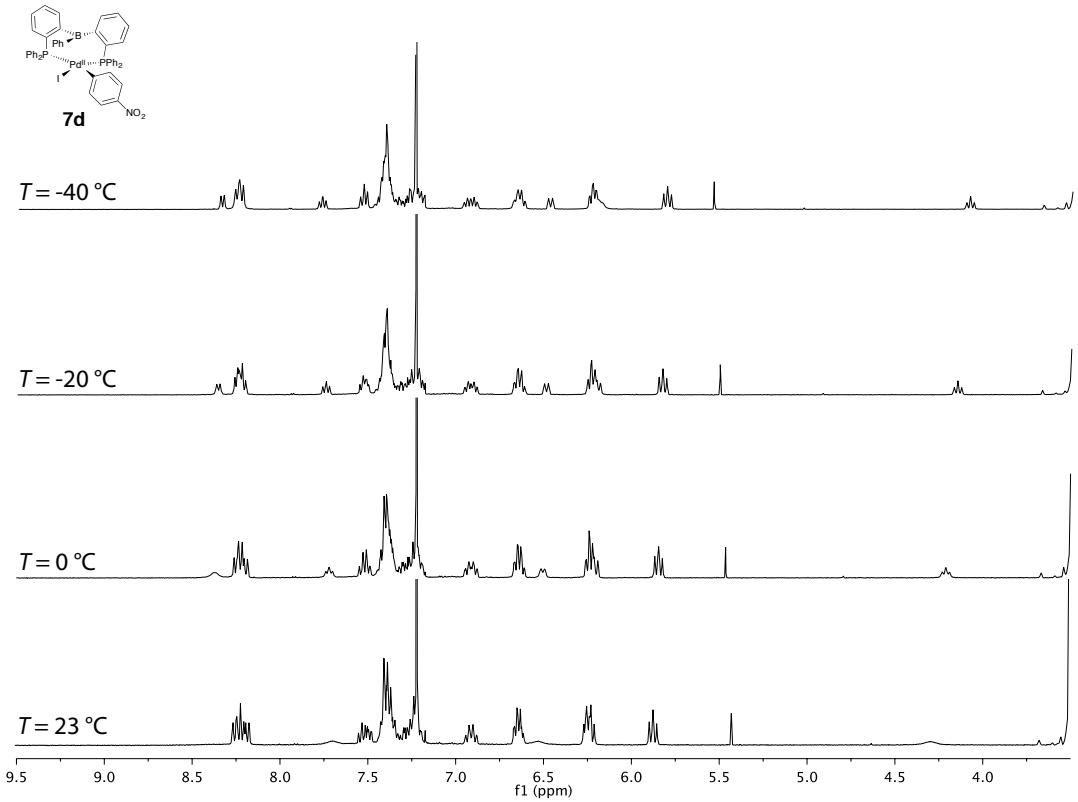


Fig. S11. VT ^{1}H NMR (400 MHz, tetrahydrofurane-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

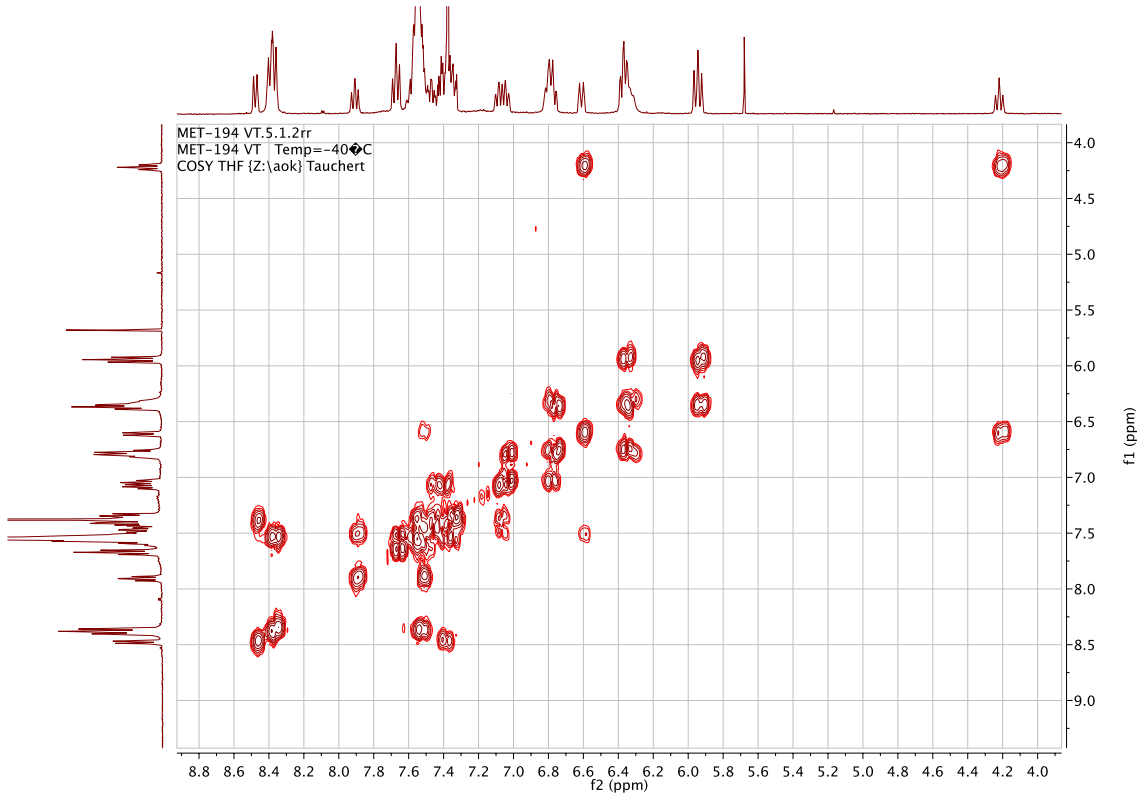


Fig. S12. COSY (400 MHz, -40 °C, tetrahydrofurane-d_8) of [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(*p*-$NO_2C_6H_4$)I] **7d**.

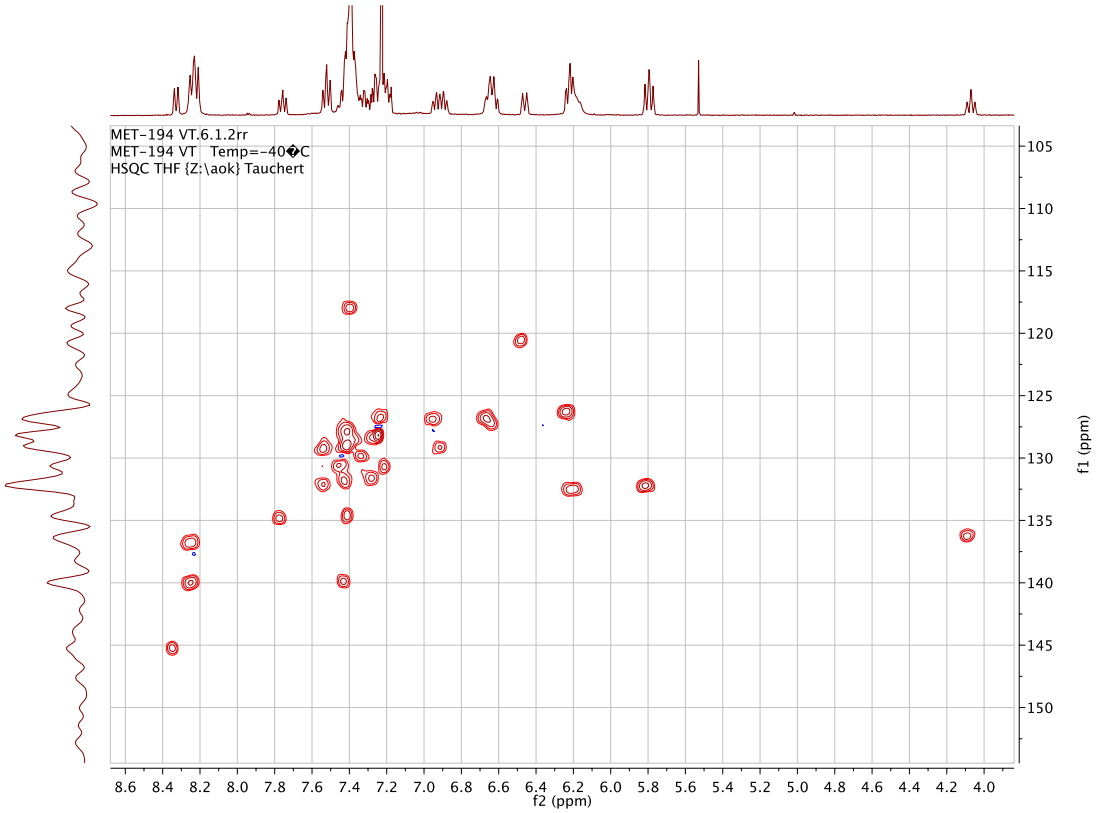


Fig. S13. HSQC (400 MHz, -40 °C, tetrahydrofurane-d_8) of [{(o-$PPh_2C_6H_4$)$_2$BPh}Pd(p-$NO_2C_6H_4$)I] **7d**.

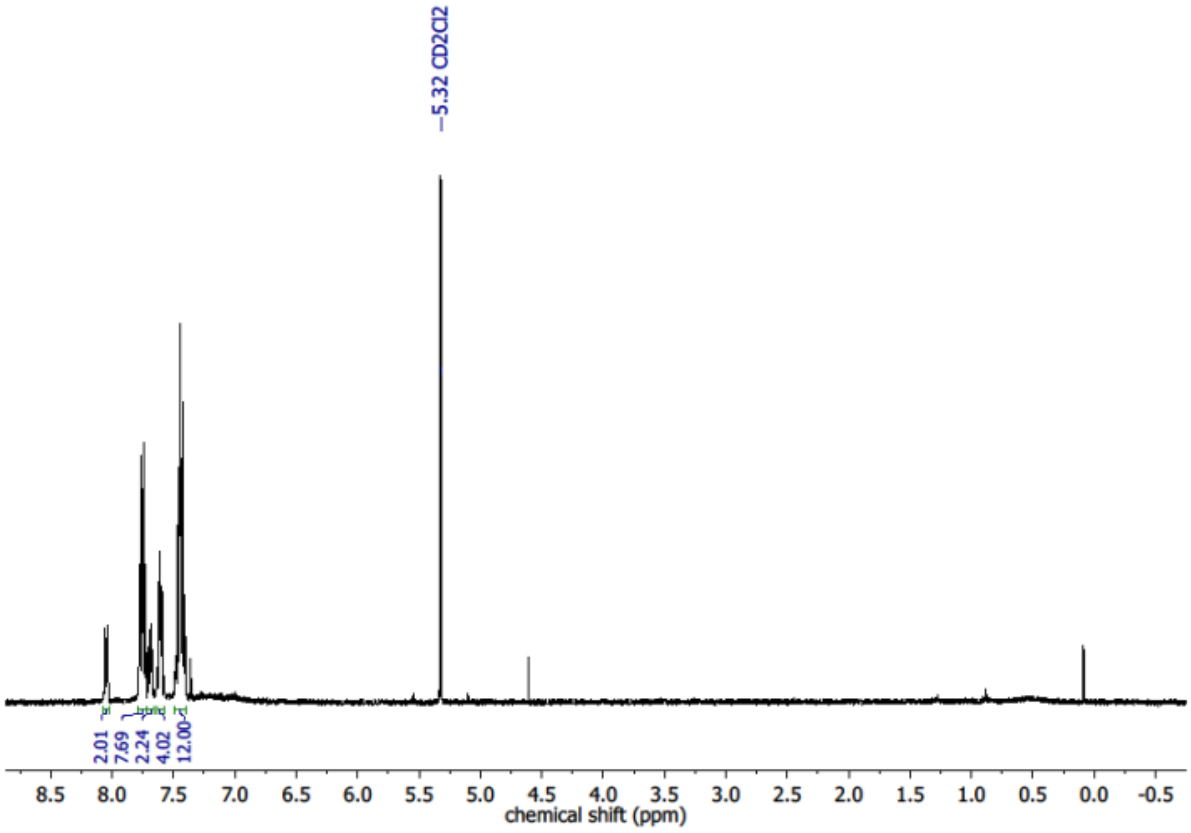


Fig. S14. ^{1}H NMR (400 MHz, dichloromethane-d_2) of [{(o-$PPh_2C_6H_4$)$_2$B}PdI] **8**

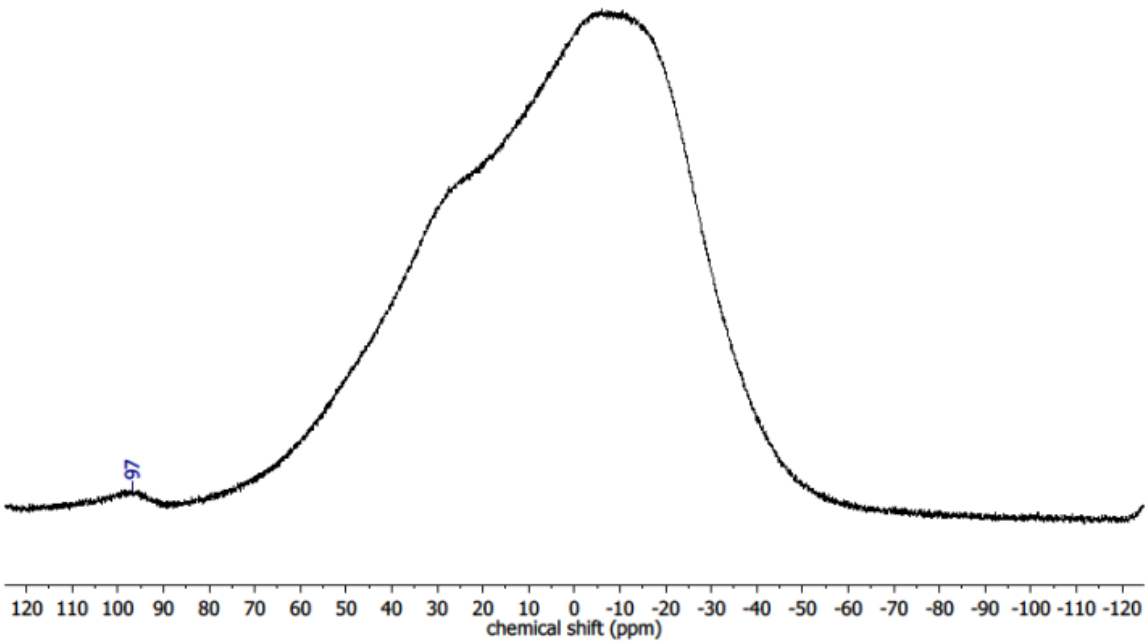


Fig. S15. $^{11}B\{^{1}H\}$ NMR (128 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8**

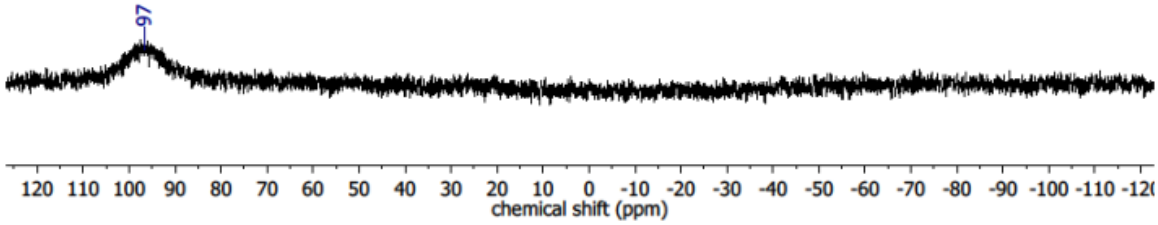


Fig. S16. $^{11}B\{^{1}H\}$ NMR (128 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8** after background subtraction.

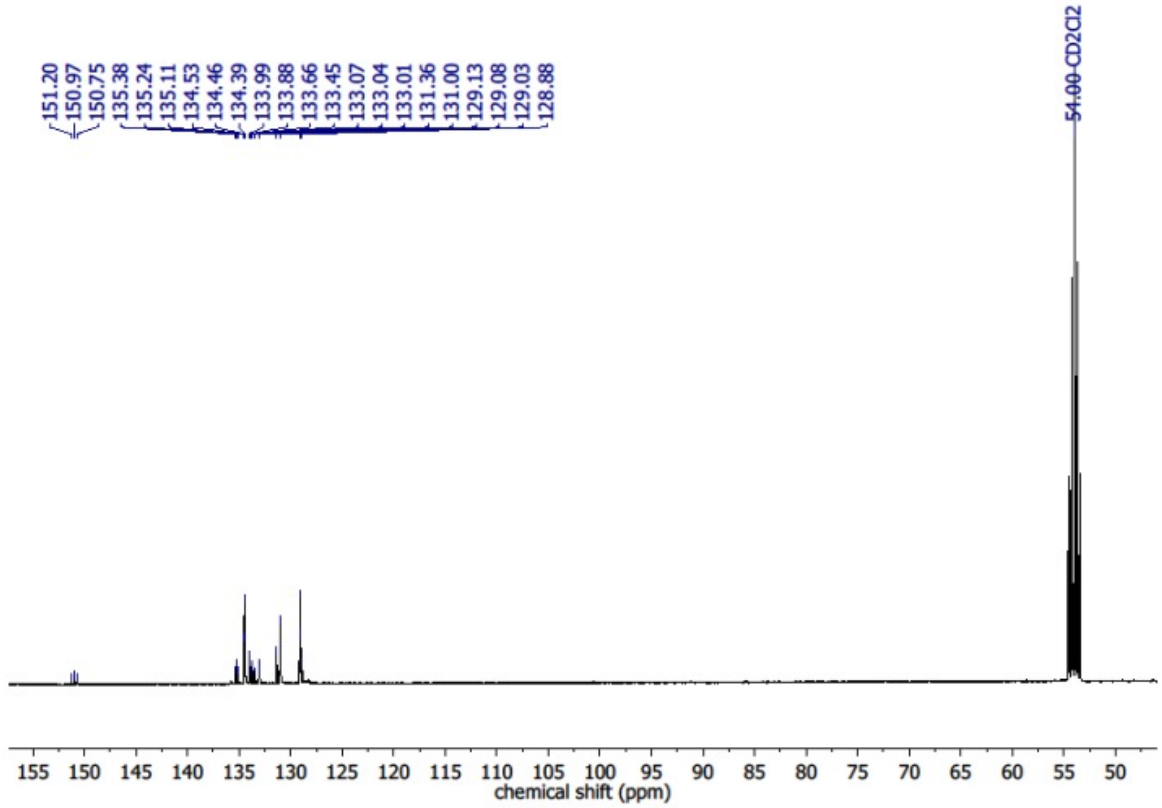


Fig. S17. $^{13}C\{^{1}H\}$ NMR (101 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8**

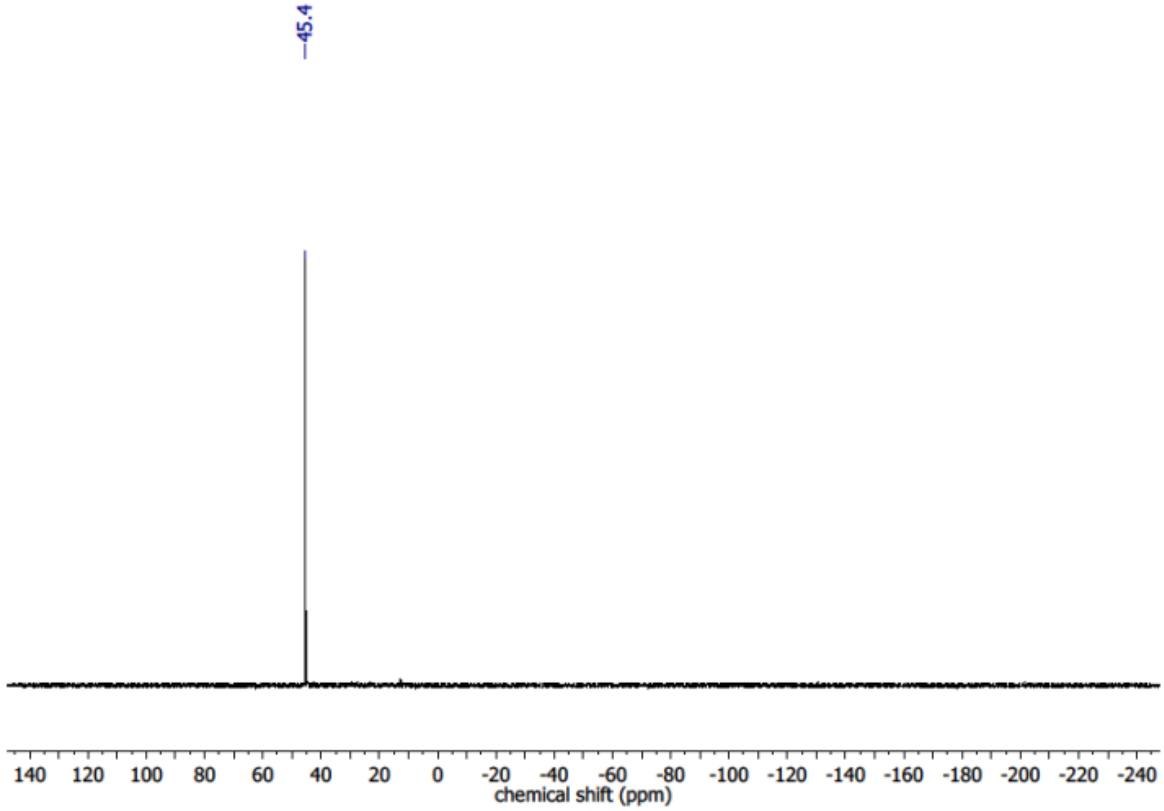


Fig. S18. $^{31}P\{^{1}H\}$ NMR (162 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$}PdI] **8**

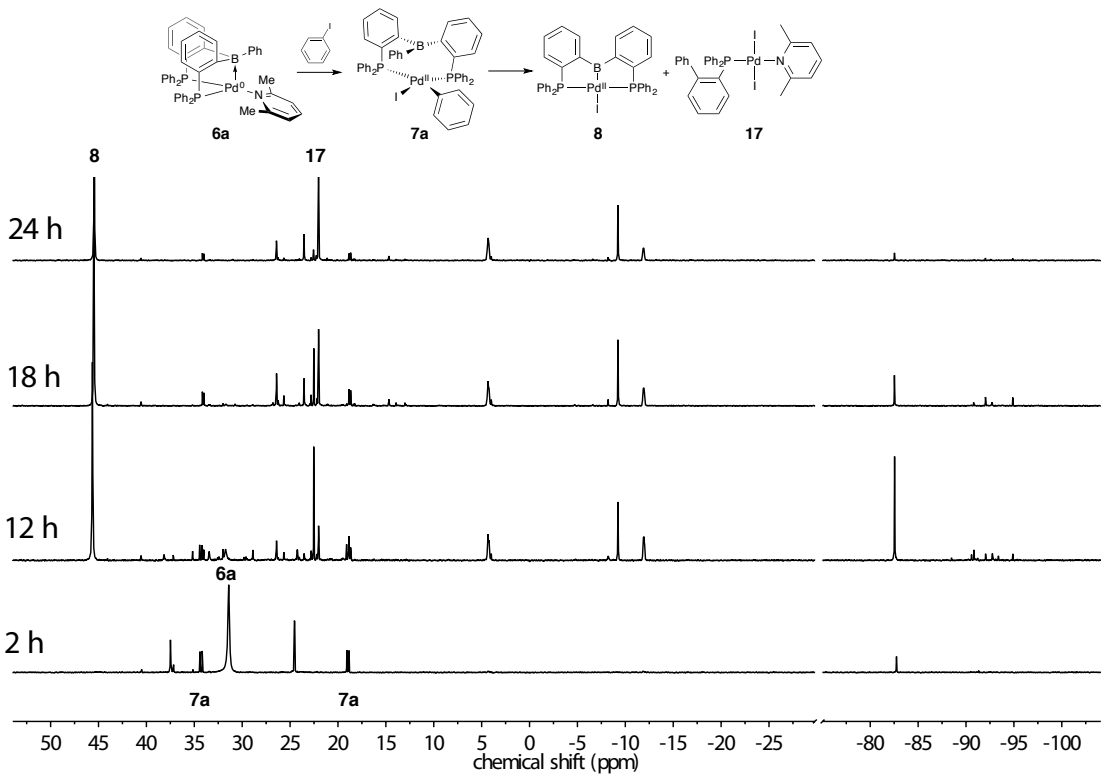


Fig. S19. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6) monitoring of the reaction [{(*o*-$PPh_2C_6H_4)_2BPh$}Pd(2,6-lutidine)] **6** and 1.5 equiv PhI at r.t..

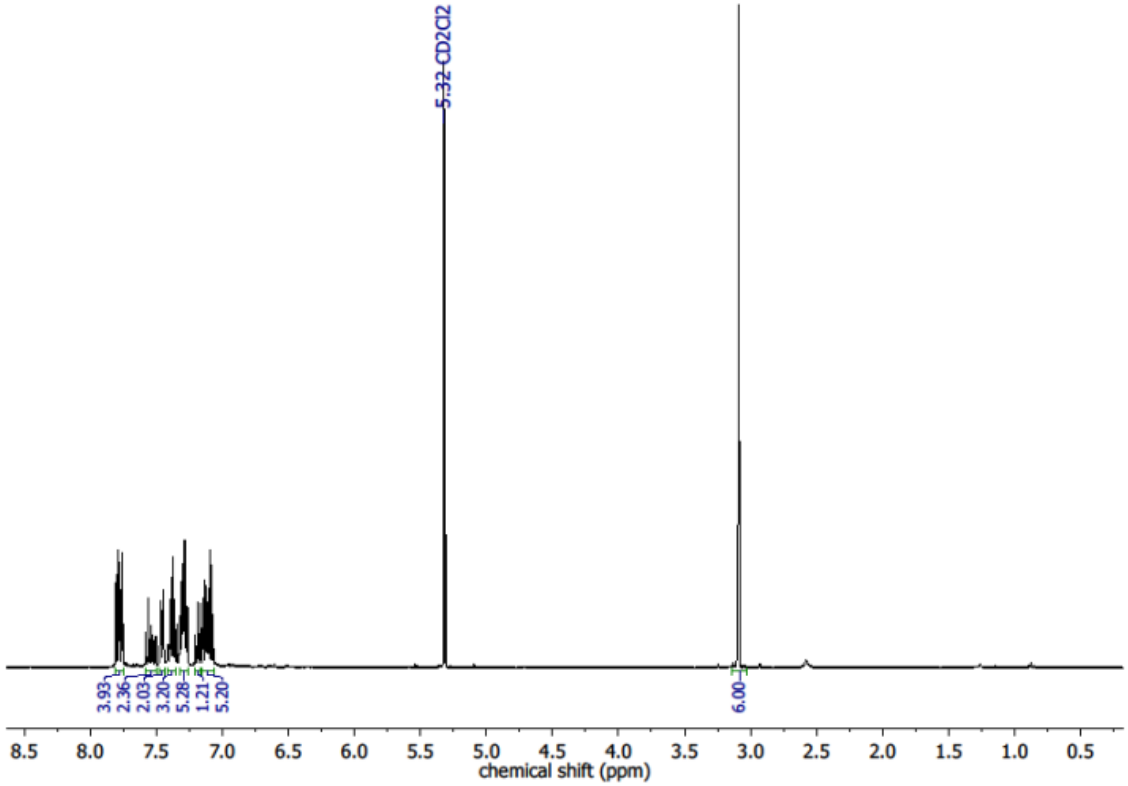


Fig. S20. ^{1}H NMR (400 MHz, dichloromethane-d_2) spectrum of [*trans*-{(2-bi–phenyl)–di–phenyl–phosphine}Pd(2,6-lutidine)I_2] **17**.

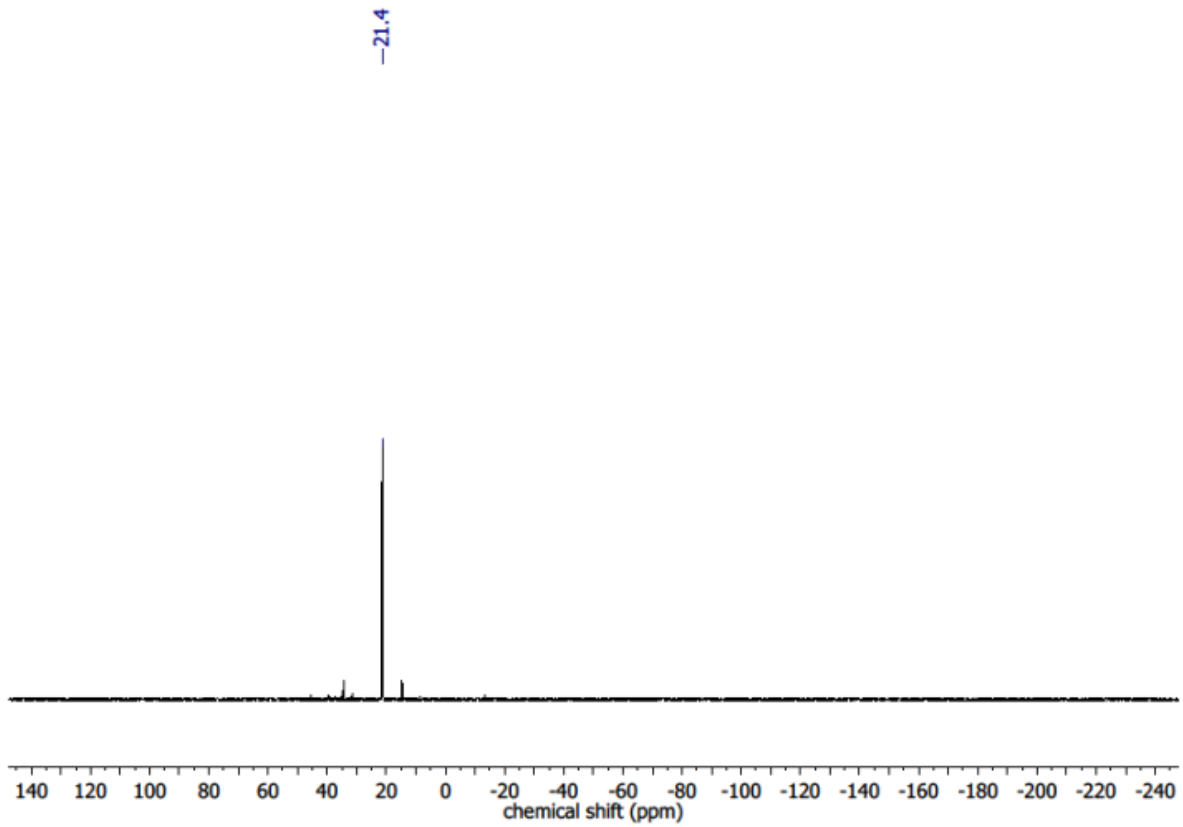


Fig. S21. $^{31}P\{^{1}H\}$ NMR (162 MHz, dichloromethane-d_2) of [*trans*-{(2-biphenyl)diphenylphosphine}Pd(2,6-lutidine)I_2] **17**.

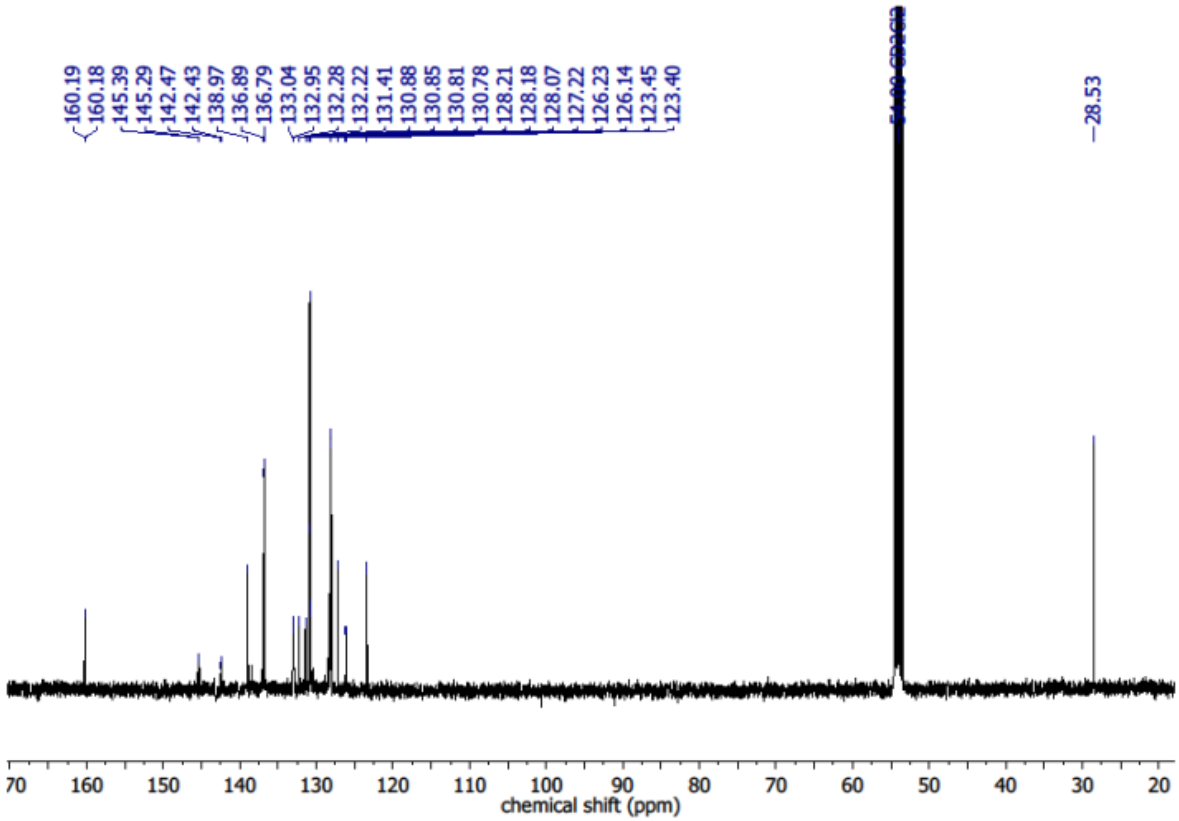


Fig. S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, dichloromethane-d_2) of [trans-{(2-biphenyl)diphenylphosphine}Pd(2,6-lutidine)I_2] **17**.

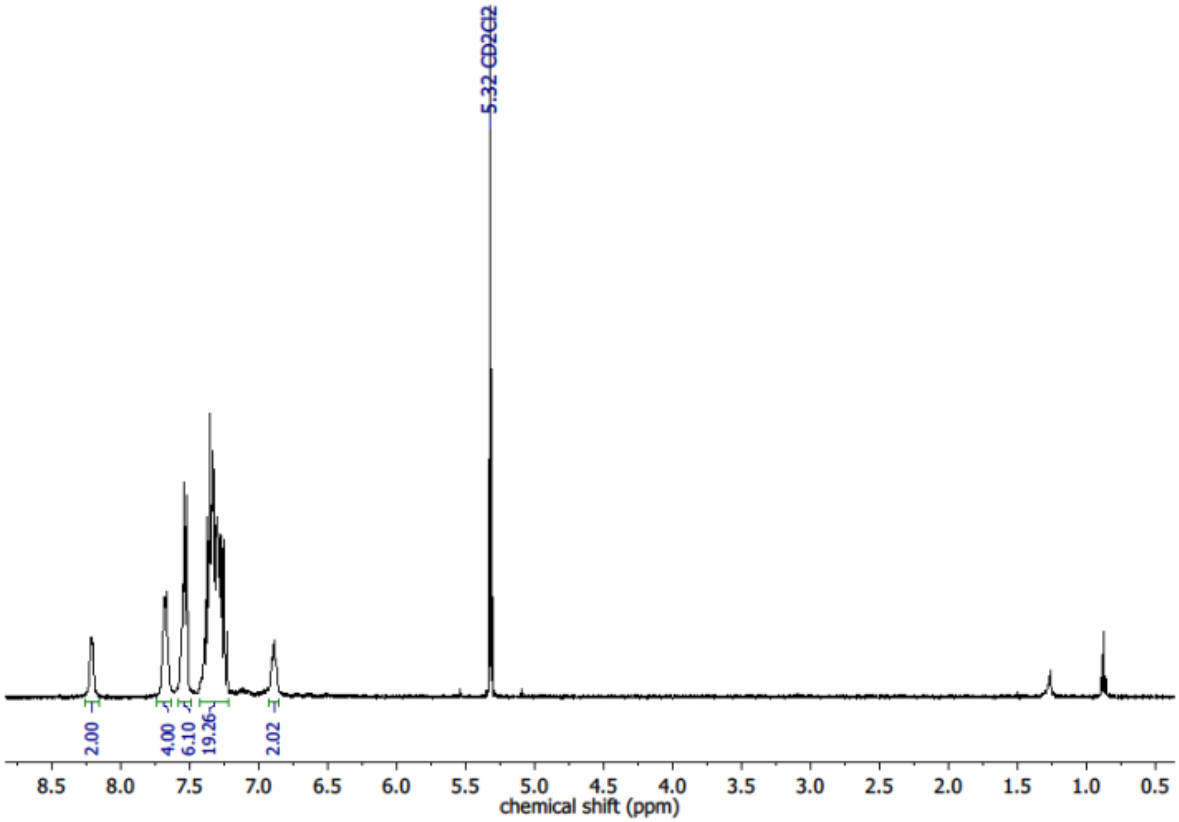


Fig. S23. ^{1}H NMR (400 MHz, dichloromethane-d_2) spectrum of [{(*o*-$PPh_2C_6H_4)_2$B(pyridine)}PdI] **18a**.

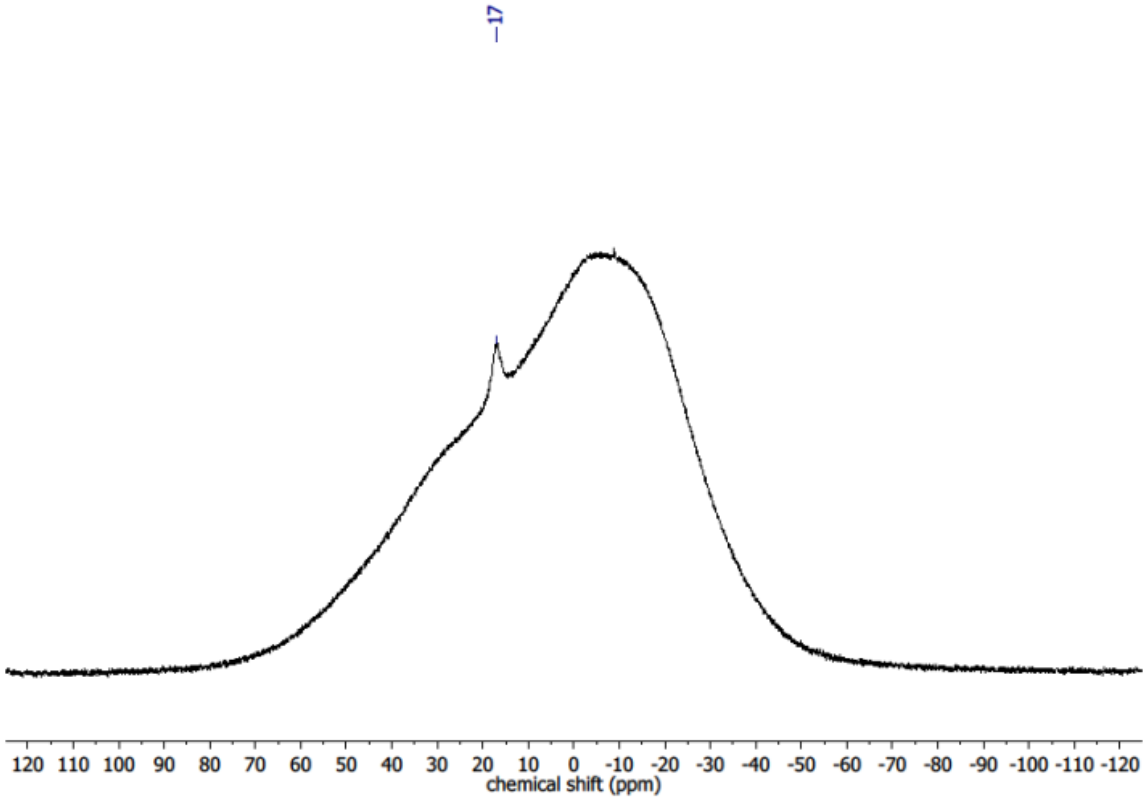


Fig. S24. ^{11}B{^{1}H} NMR (128 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2$B(pyridine)}PdI] **18a**.

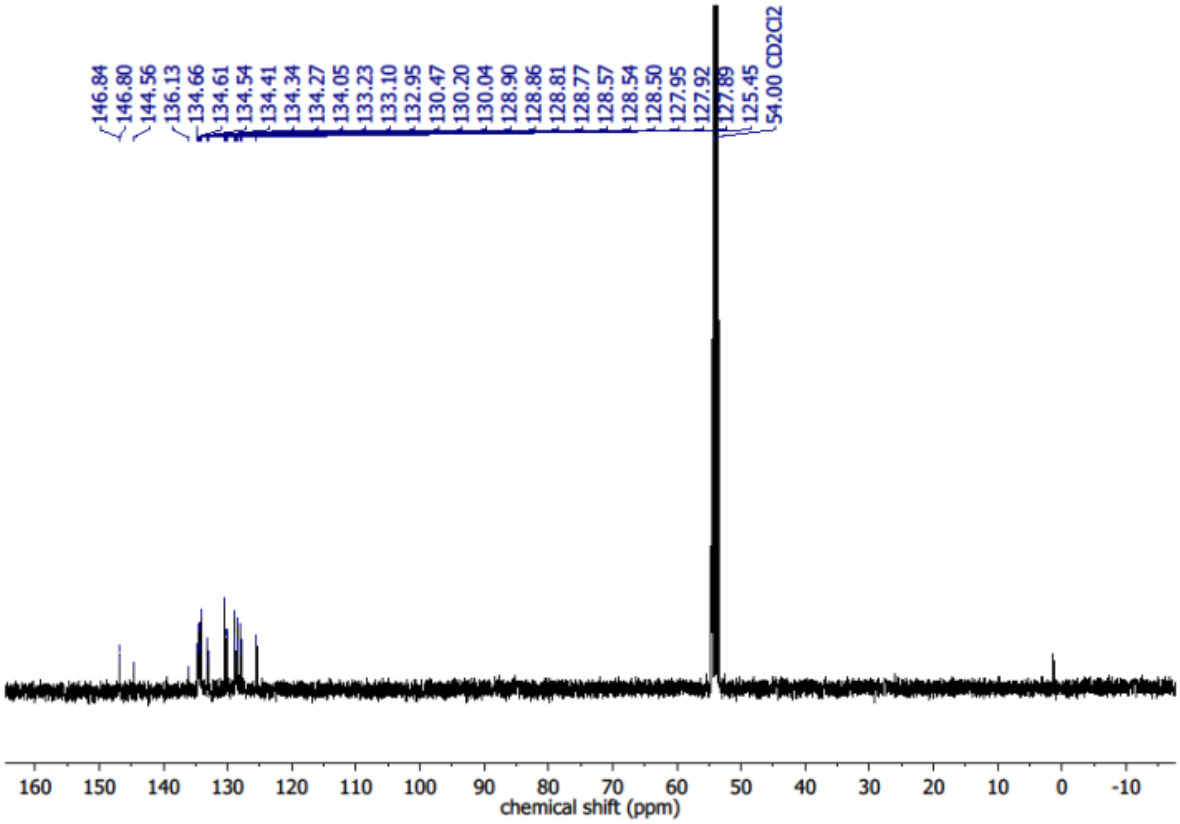


Fig. S25. $^{13}C\{^{1}H\}$ NMR (101 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$(pyridine)}PdI] **18a**.

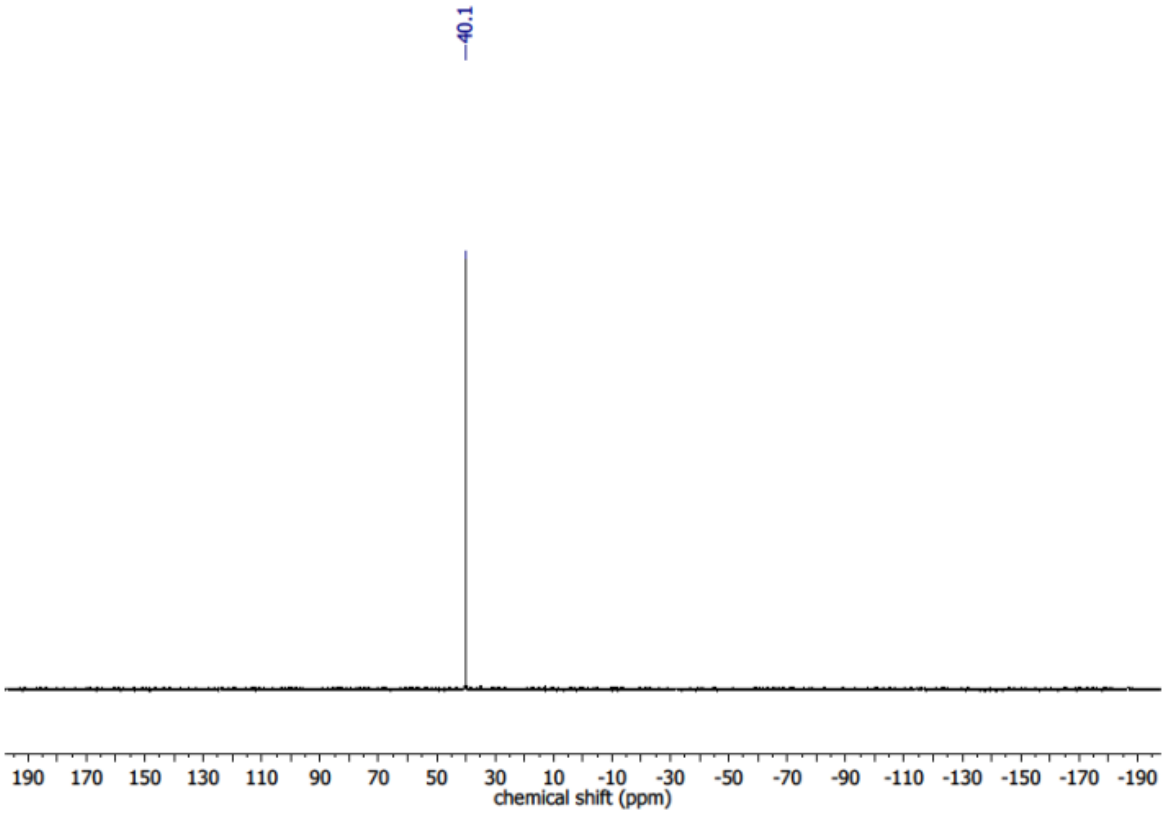


Fig. S26. $^{31}P\{^{1}H\}$ NMR (162 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$(pyridine)}PdI] **18a**.

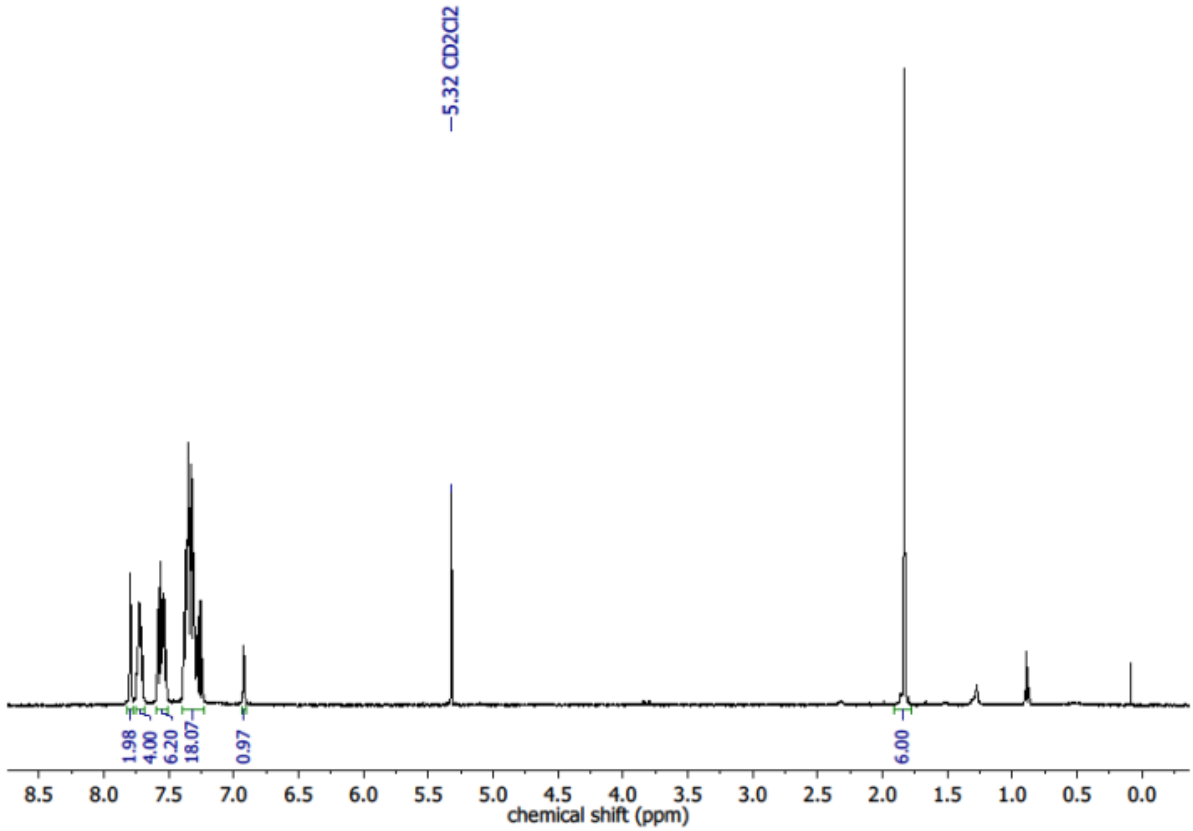


Fig. S27. ^{1}H NMR (400 MHz, dichloromethane-d_2) of [{(o-$PPh_2C_6H_4$)$_2$B(3,5-lutidine)}PdI] **18b**.

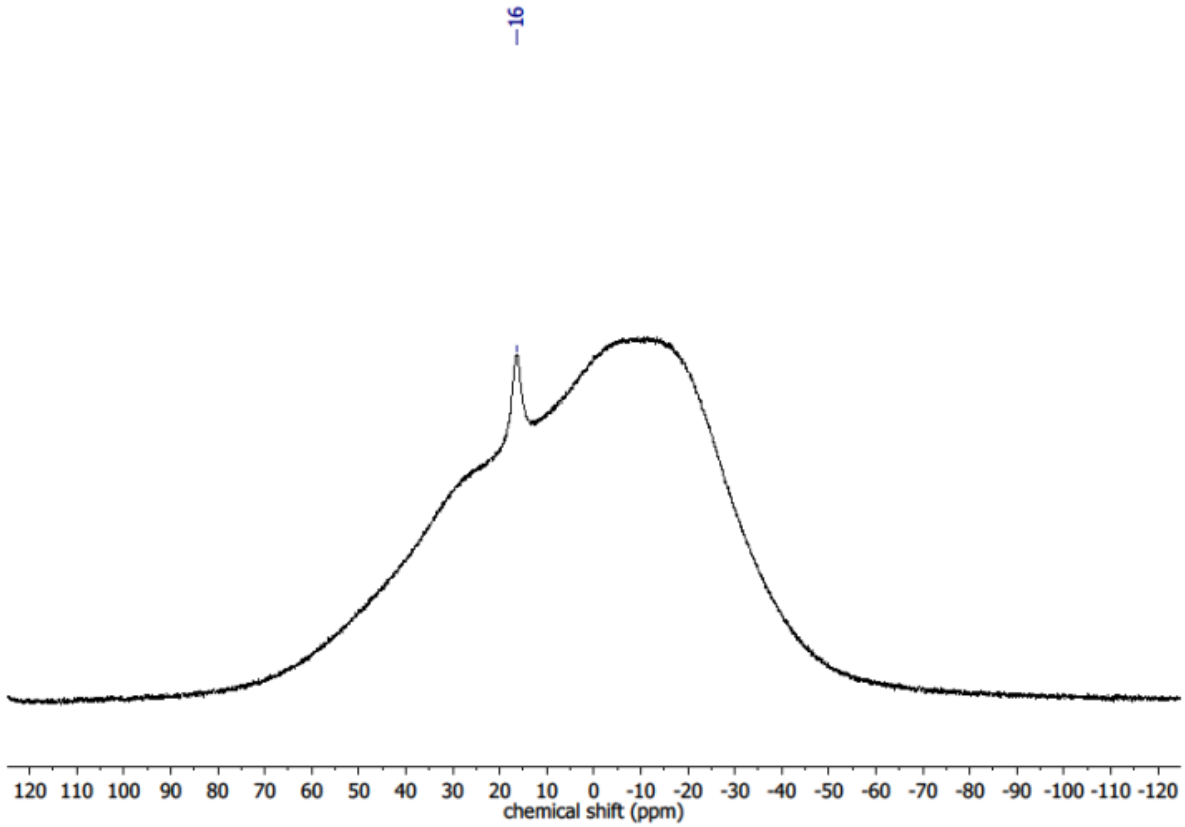


Fig. S28. ^{11}B{^{1}H} NMR (128 MHz, dichloromethane-d_2) of [{(o-$PPh_2C_6H_4$)$_2$B(3,5-lutidine)}PdI] **18b**.

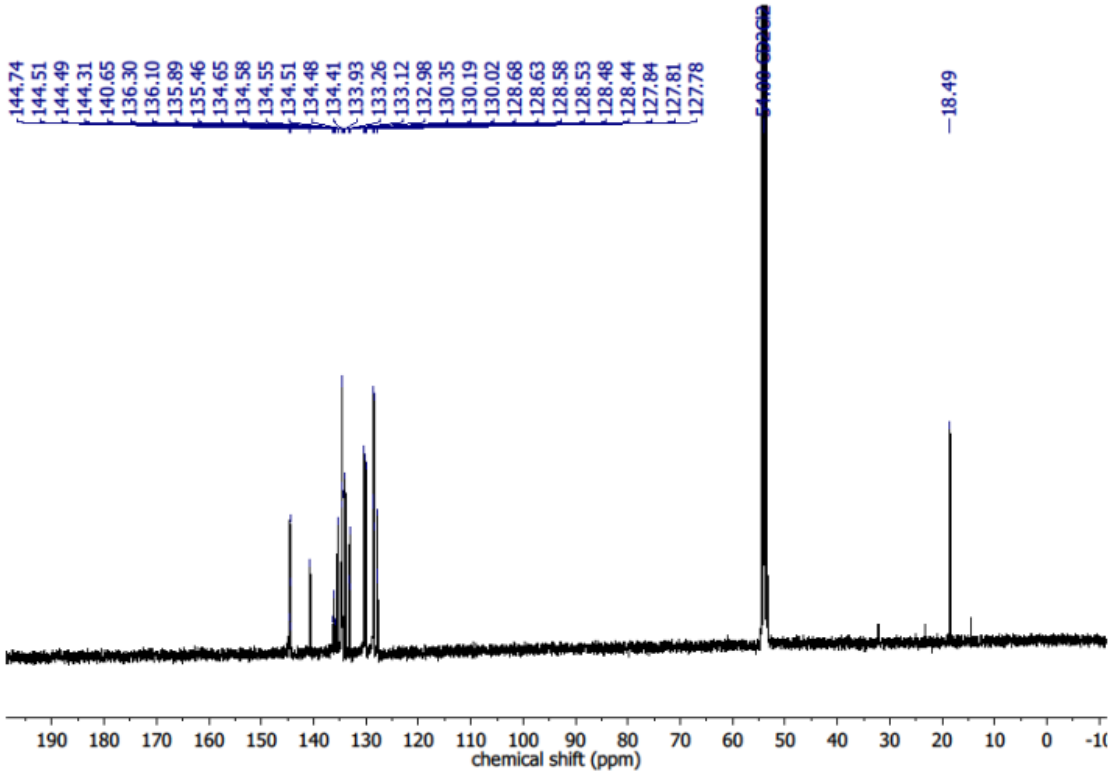


Fig. S29. $^{13}C\{^{1}H\}$ NMR (101 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$(3,5-lutidine)}PdI] **18b**.

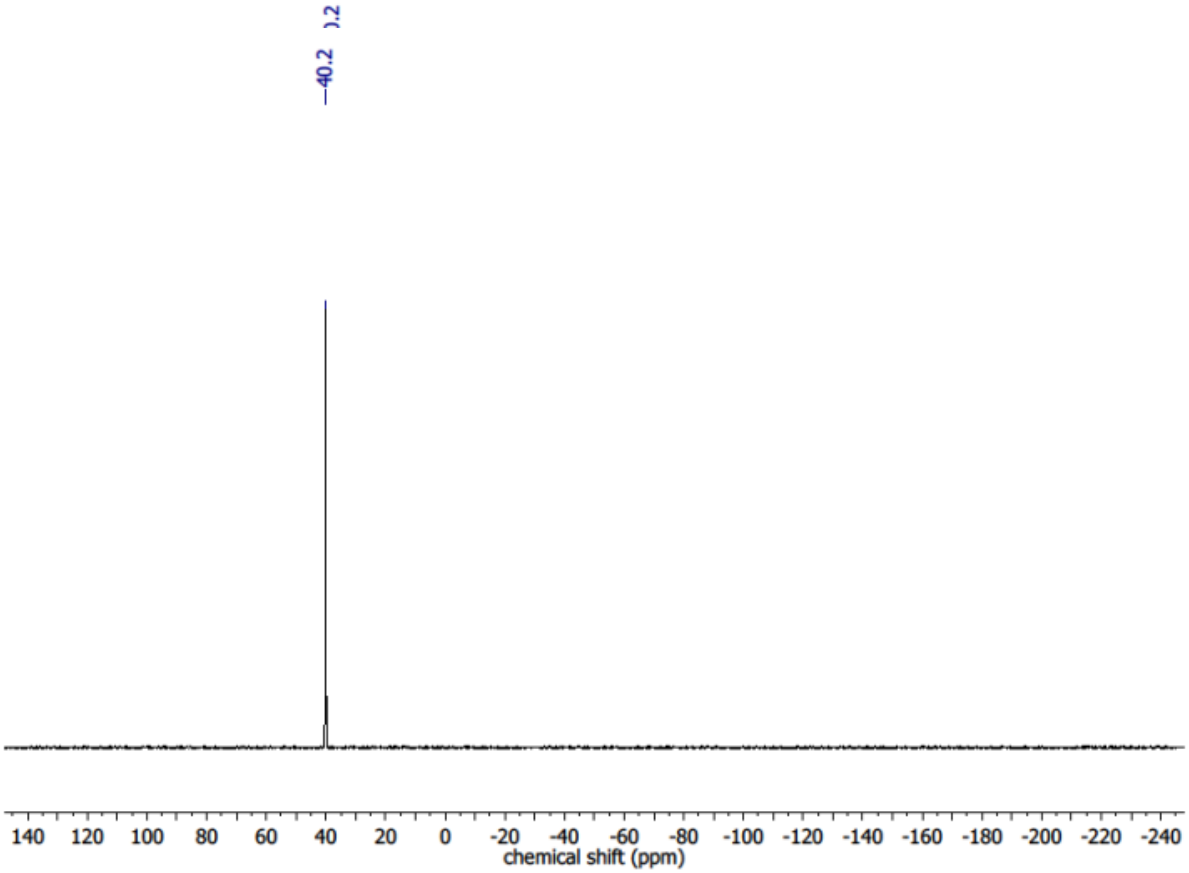


Fig. S30. $^{31}P\{^{1}H\}$ NMR (162 MHz, dichloromethane-d_2) of [{(*o*-$PPh_2C_6H_4)_2B$(3,5-lutidine)}PdI] **18b**.

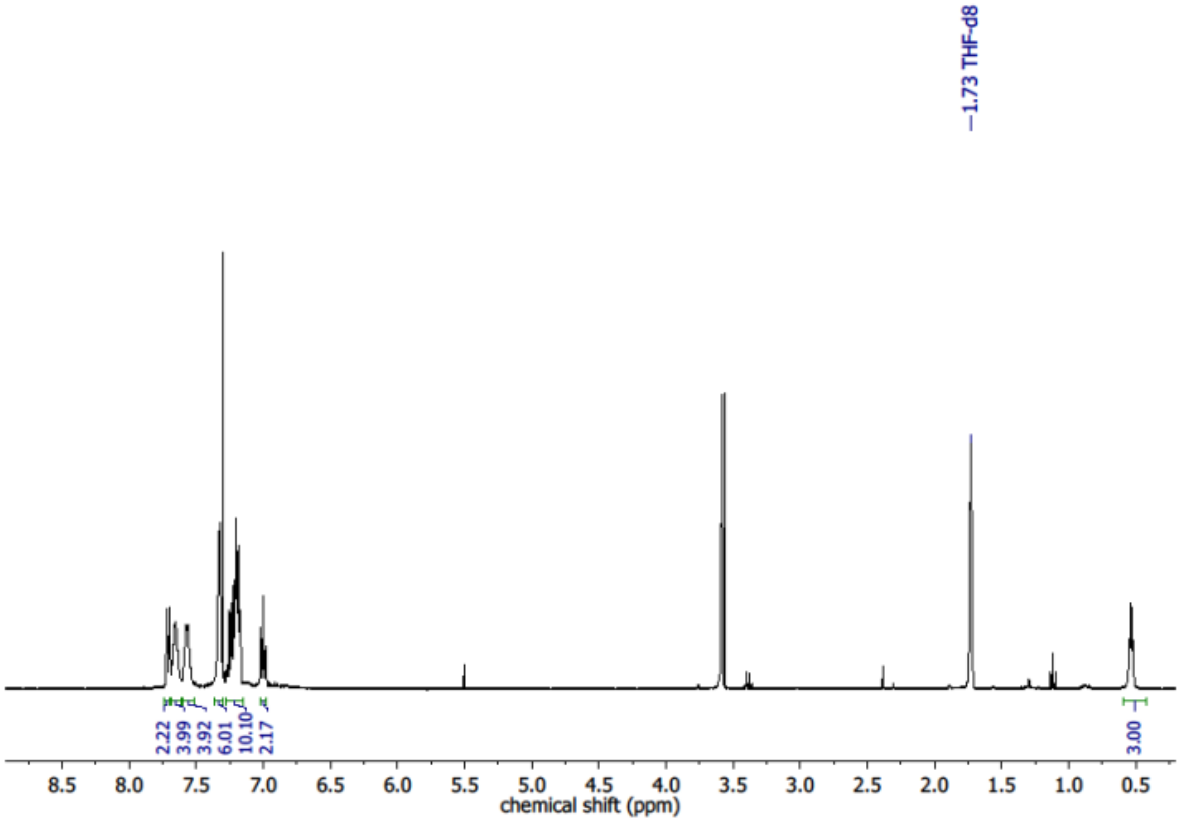


Fig. S31. ^{1}H NMR (400.1 MHz, THF-d_8) spectrum of [{(o-$PPh_2C_6H_4$)$_2$BMe}Pd].

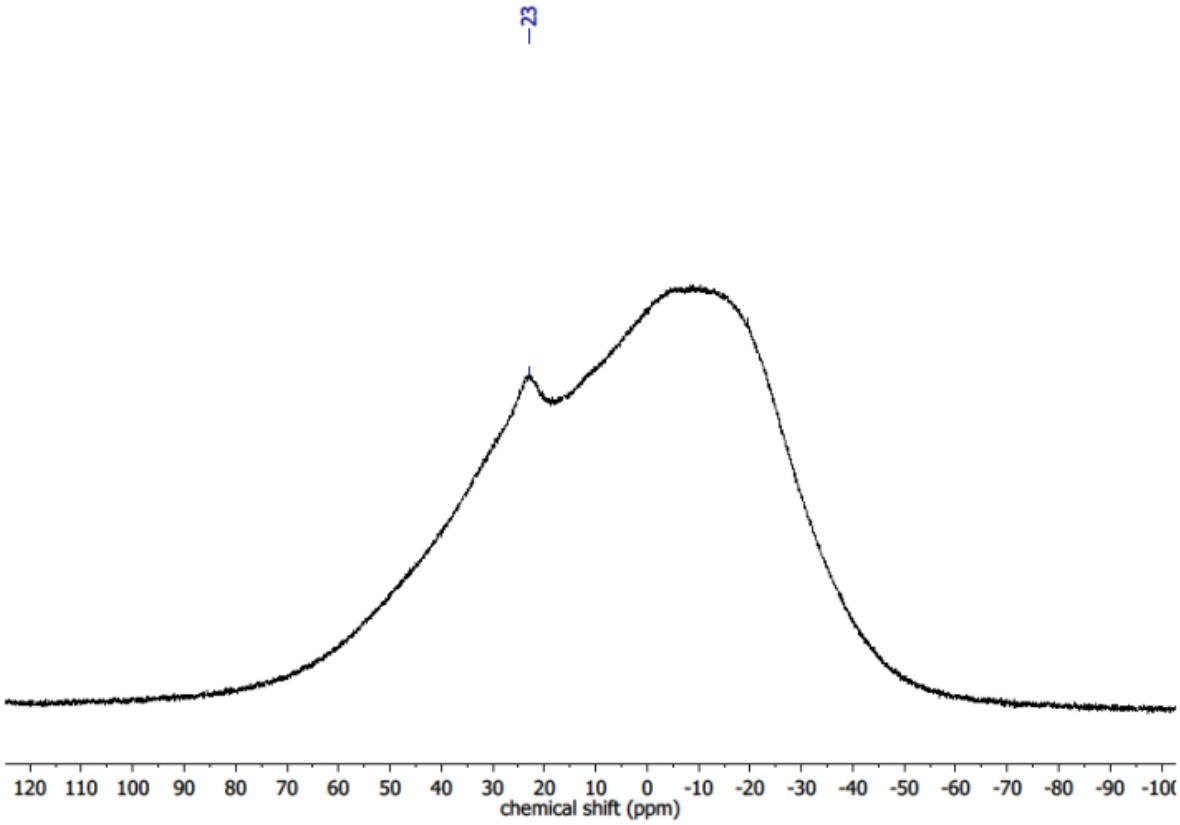


Fig. S32. ^{11}B{^{1}H} NMR (128 MHz, THF-d_8) of [{(o-$PPh_2C_6H_4$)$_2$BMe}Pd].

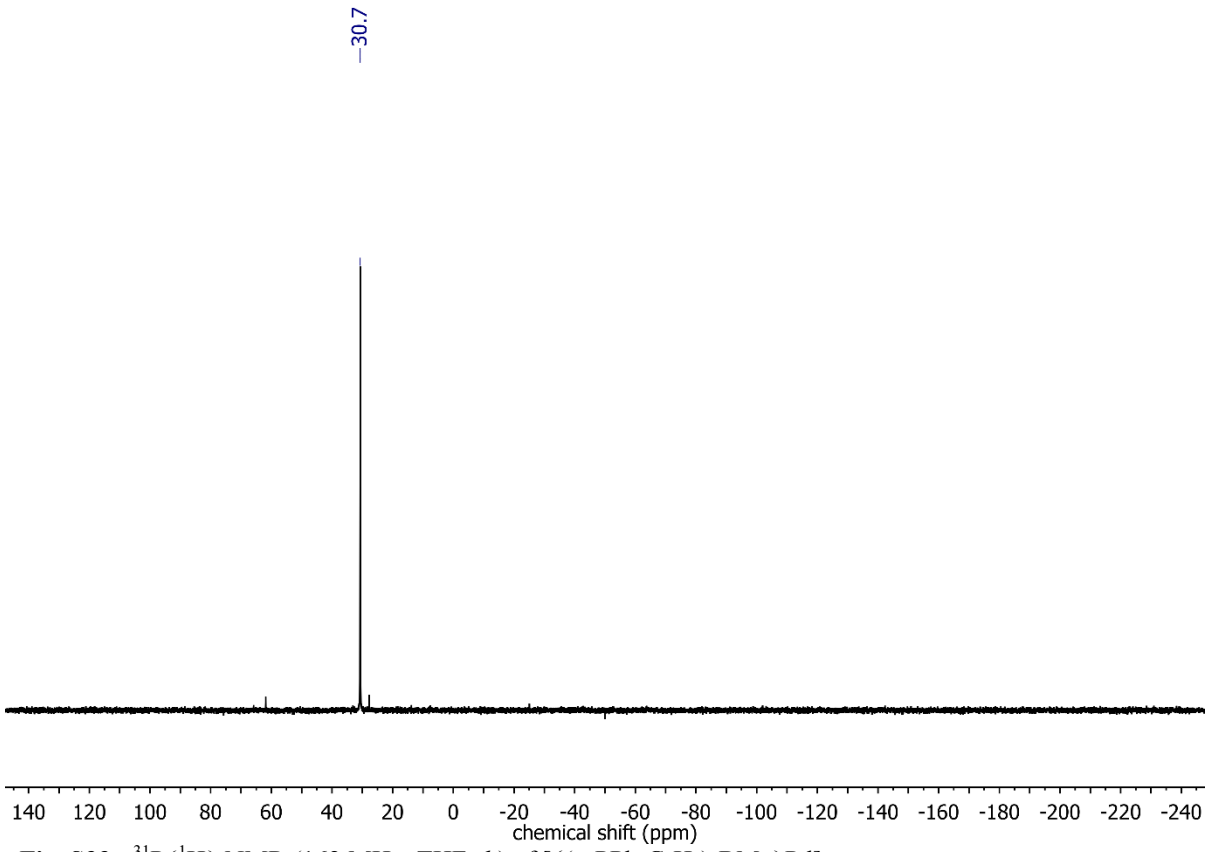


Fig. S33. $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd].

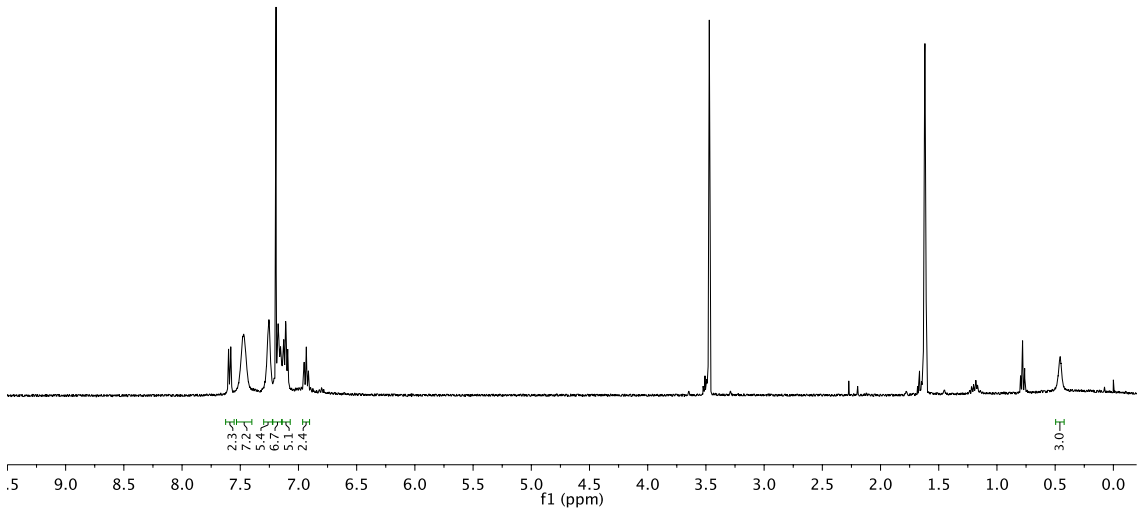


Fig. S34. ^{1}H NMR (400 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd] after 6 d.

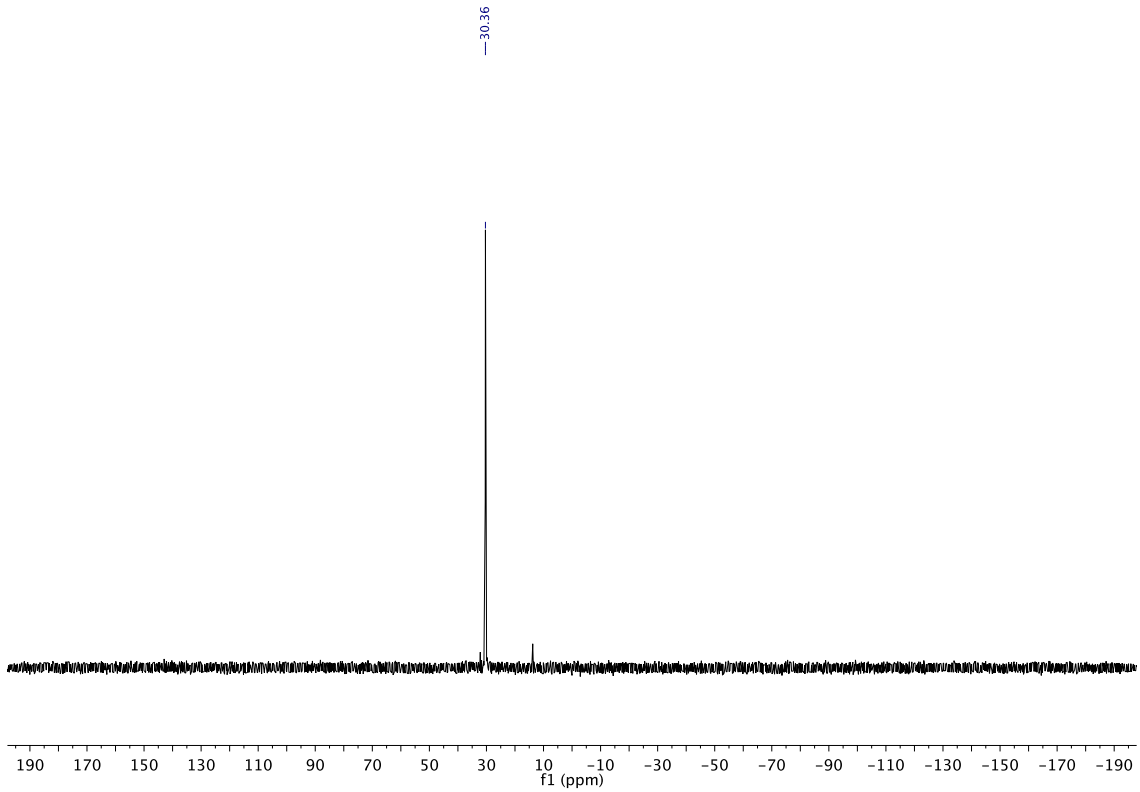


Fig. S35. $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of [{(o-$PPh_2C_6H_4$)$_2$BMe}Pd] after 6 d.

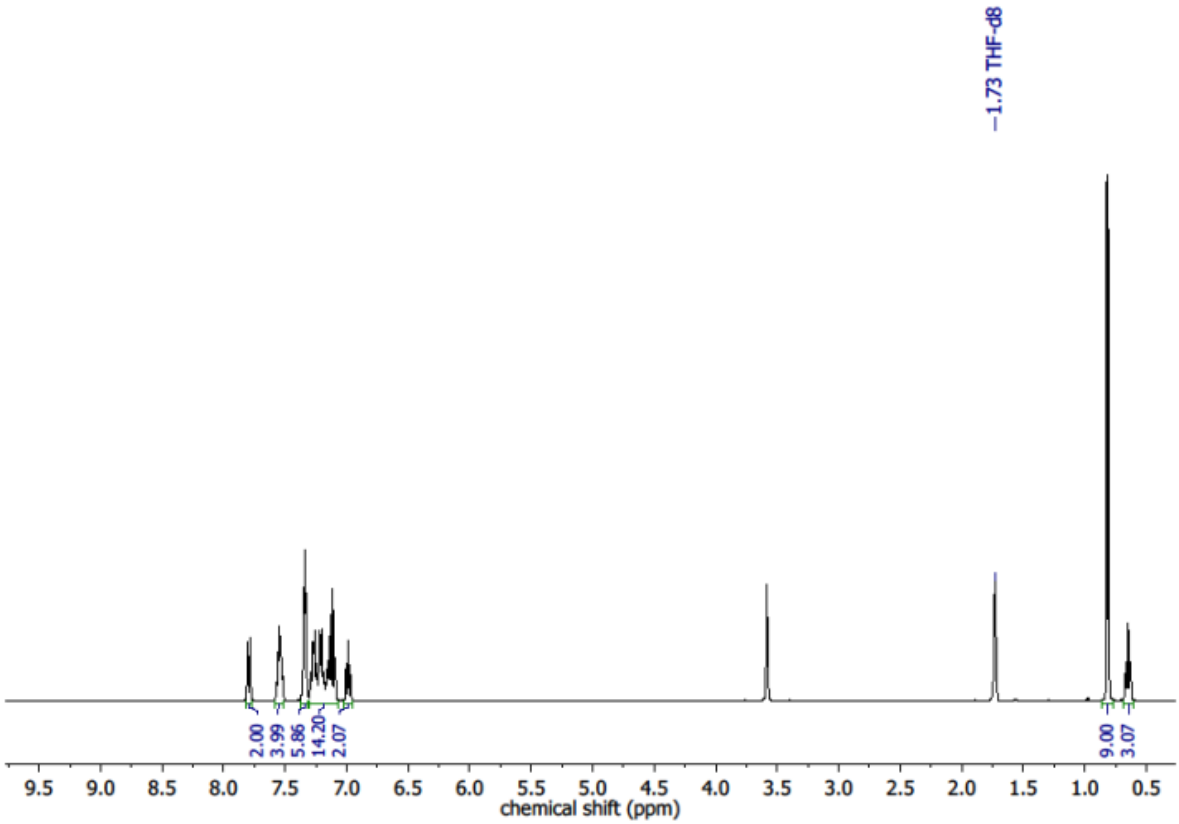


Fig. S36. ^{1}H NMR (400 MHz, THF-d_8) spectrum of [{(o-$PPh_2C_6H_4$)$_2$BMe}Pd(PMe_3)] **19a**.

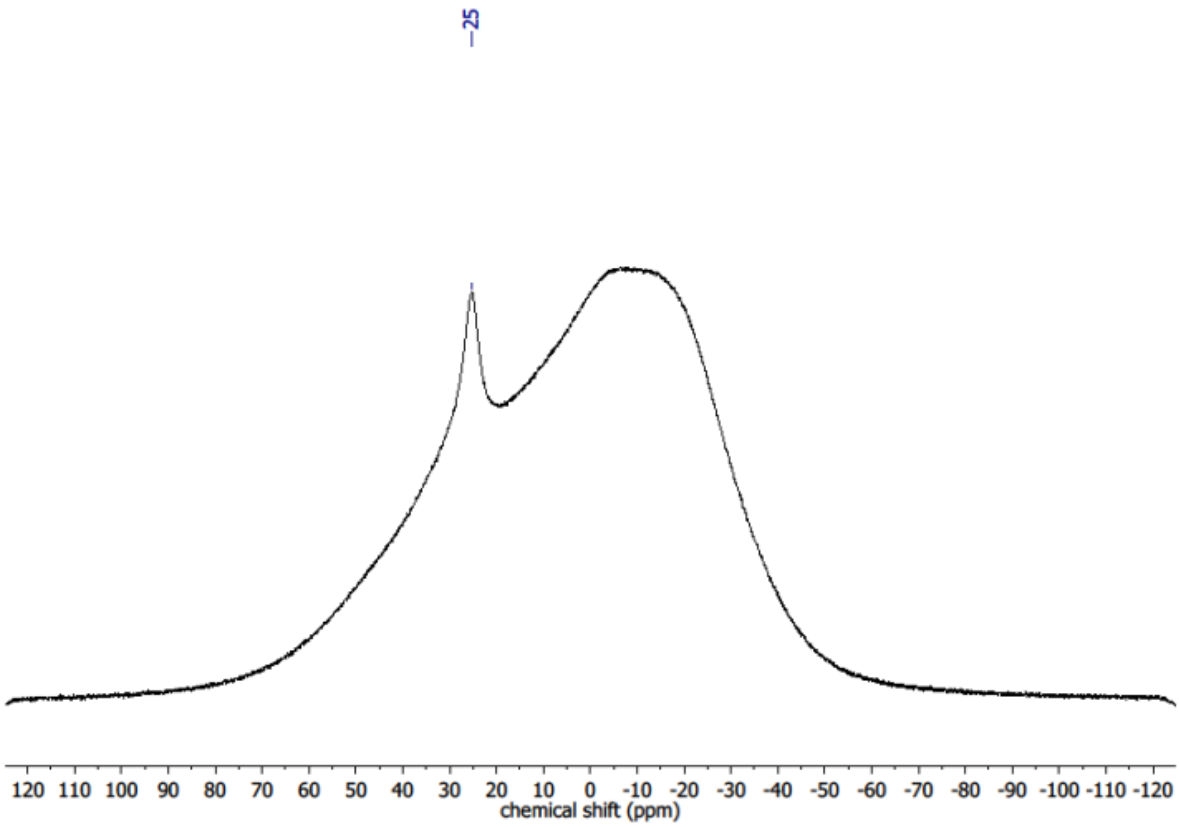


Fig. S37. $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd(PMe_3)] **19a**.

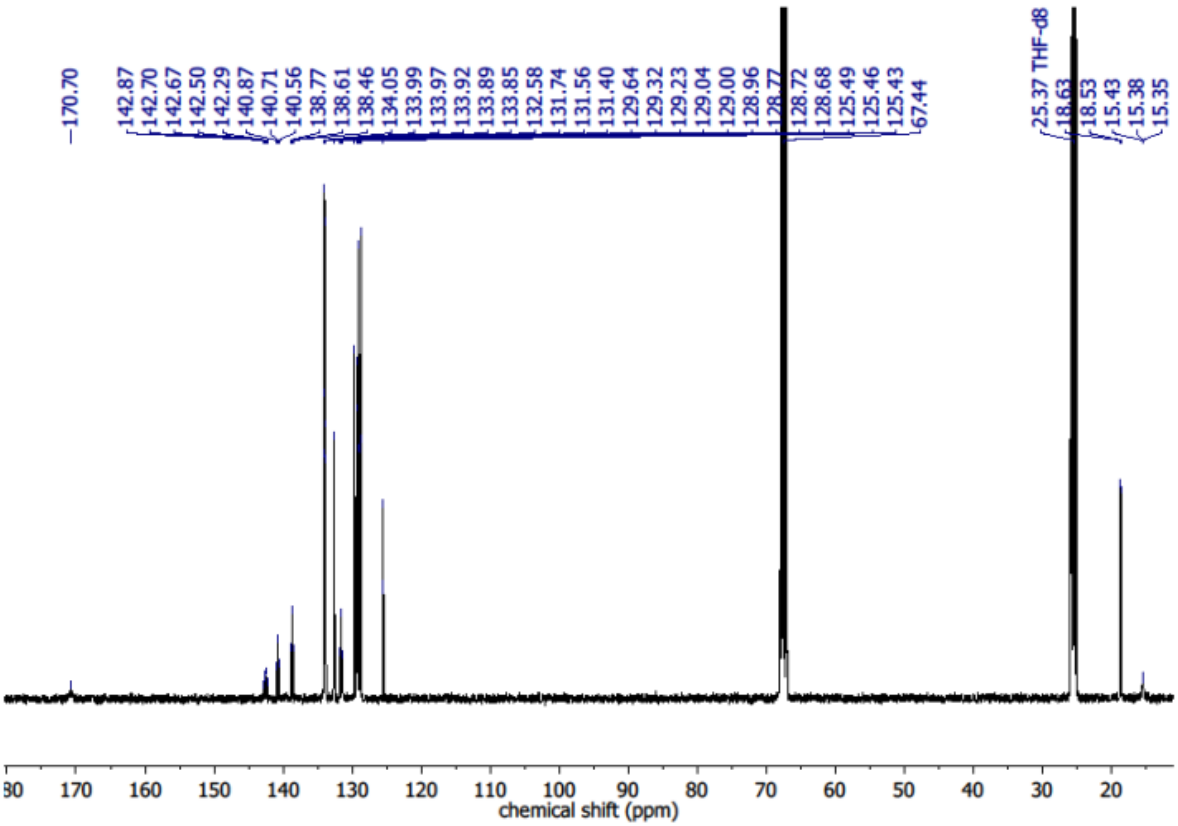


Fig. S38. $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd(PMe_3)] **19a**.

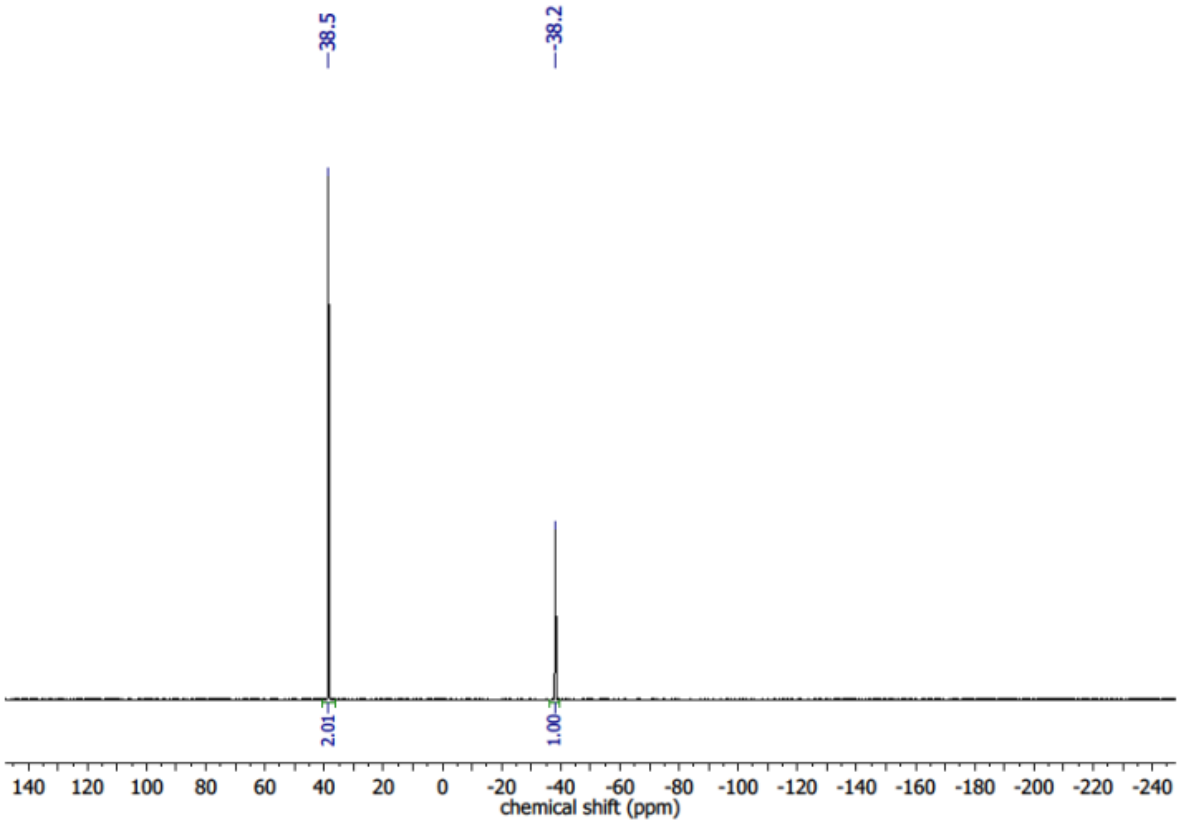


Fig. S39. $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BMe$}Pd(PMe_3)] **19a**.

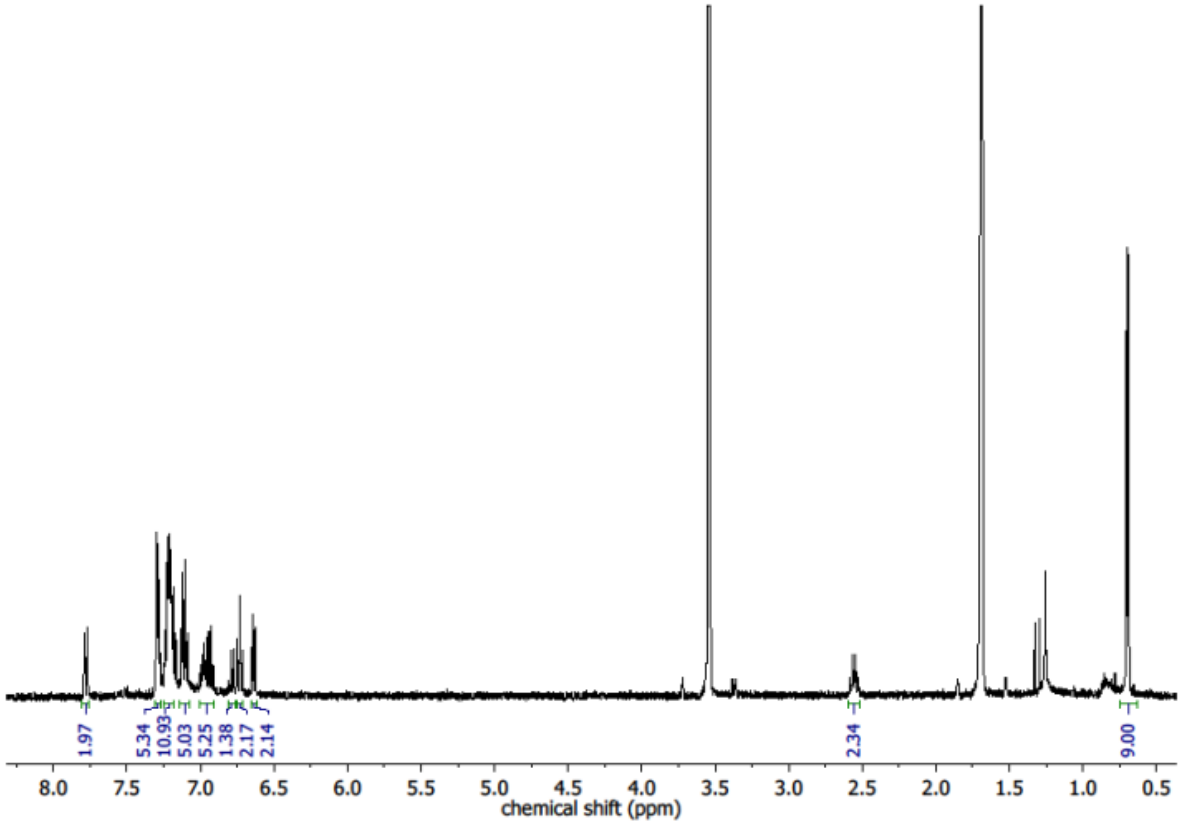


Fig. S40. ^{1}H NMR (400 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2Ph$}Pd(PMe_3)] **19b**.

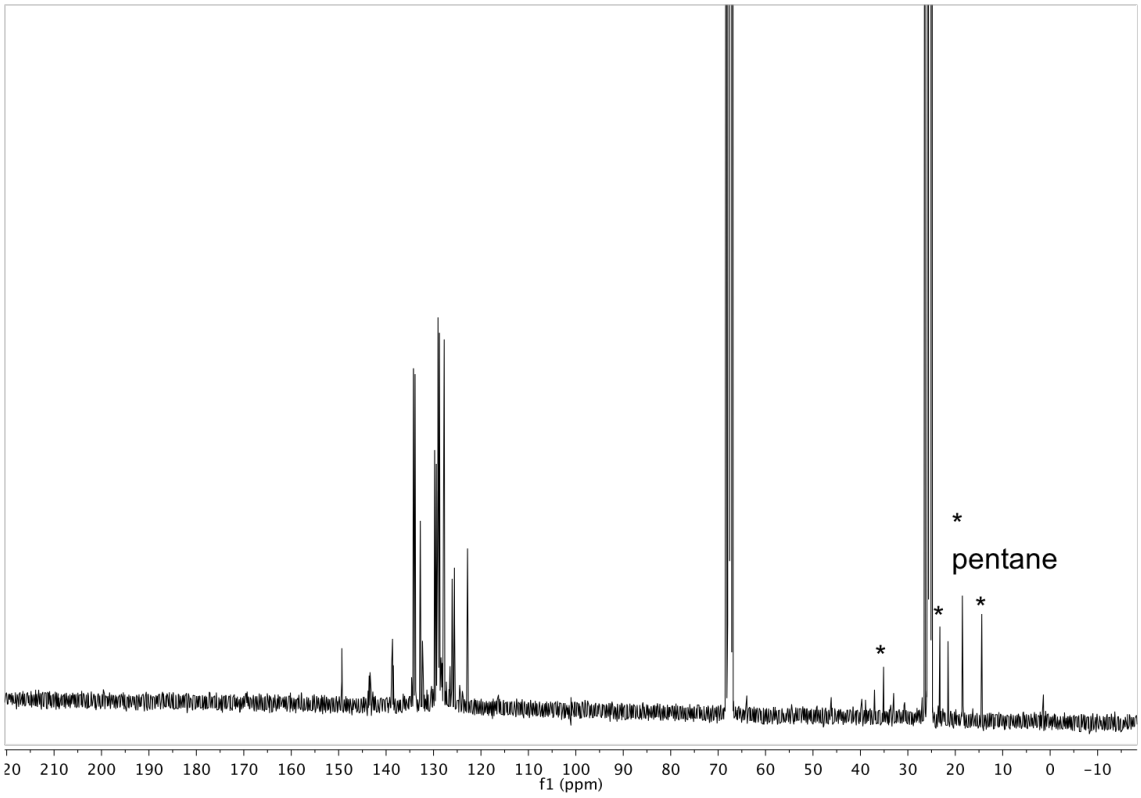


Fig. S41. $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2Ph$}Pd(PMe_3)] **19b**.

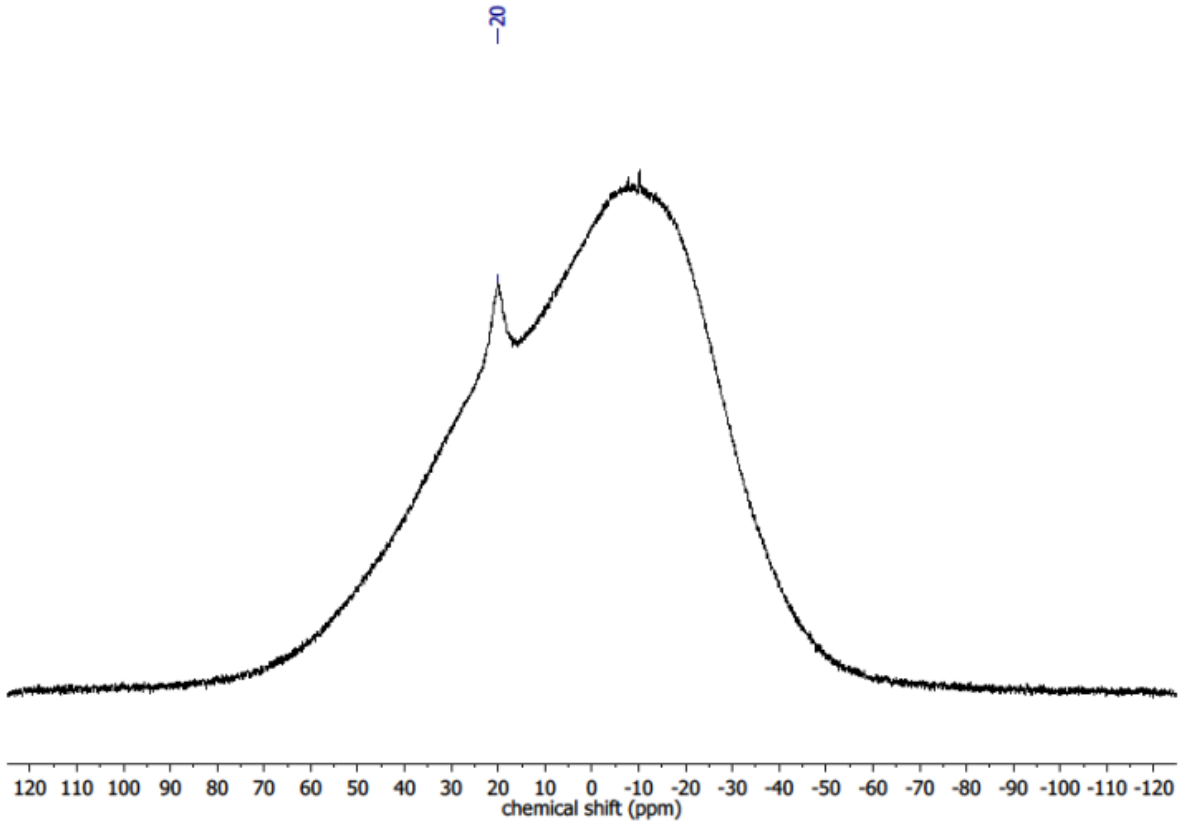


Fig. S42. $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2Ph$}Pd(PMe_3)] **19b**.

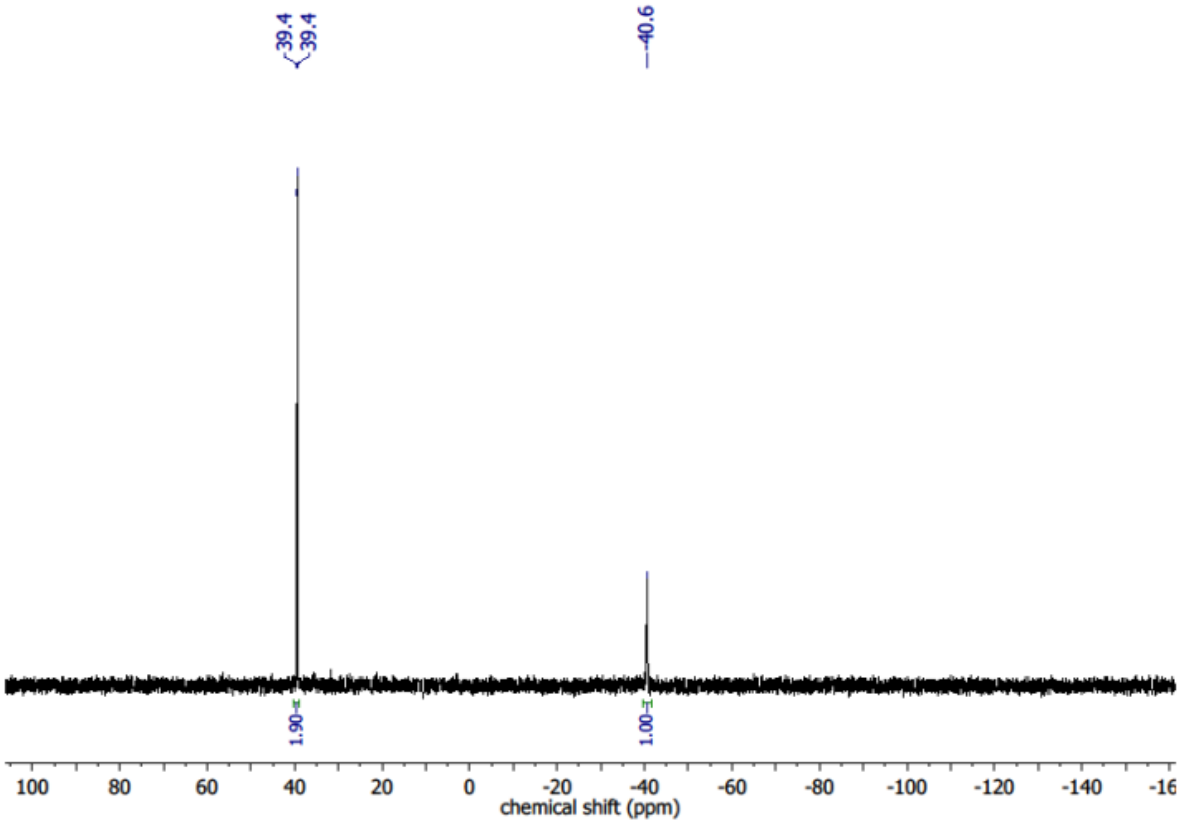


Fig. S43. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2Ph$}Pd(PMe_3)] **19b**.

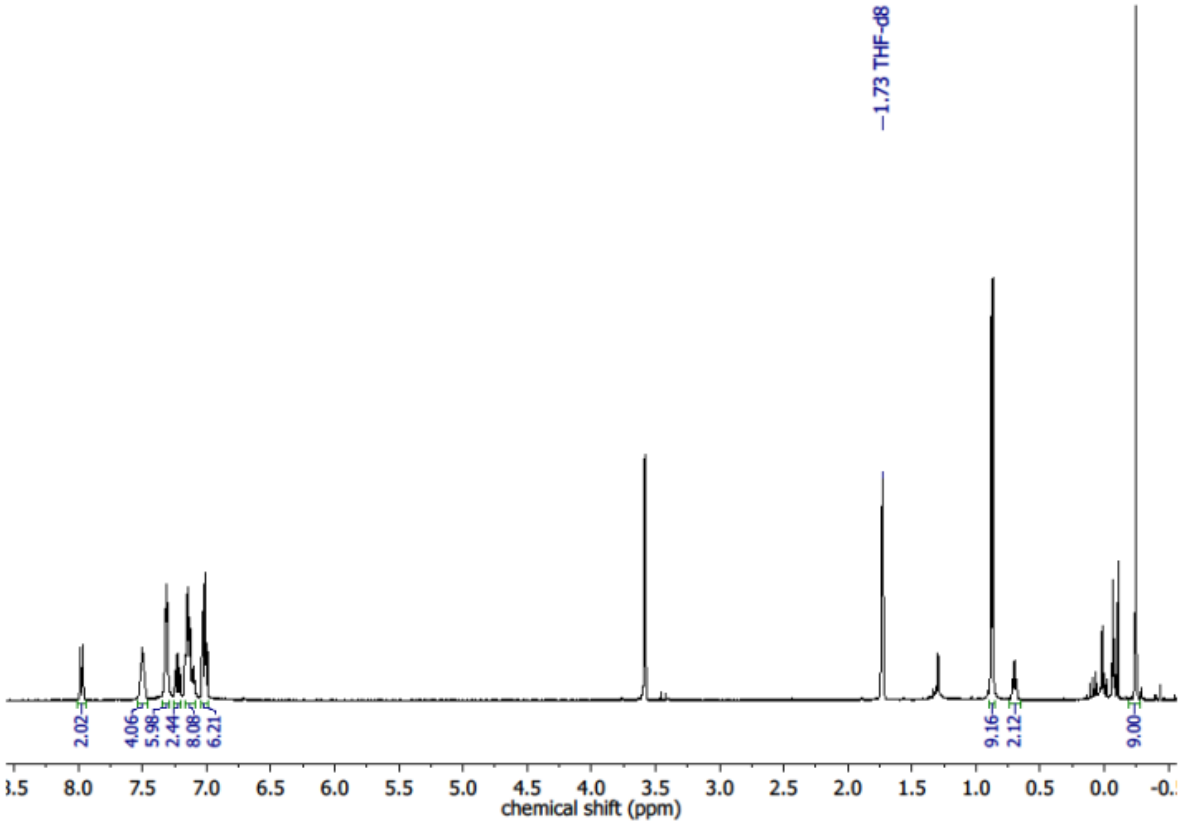


Fig. S44. ^{1}H NMR (400 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2SiMe_3$}Pd($PMe_3$)] **19c**.

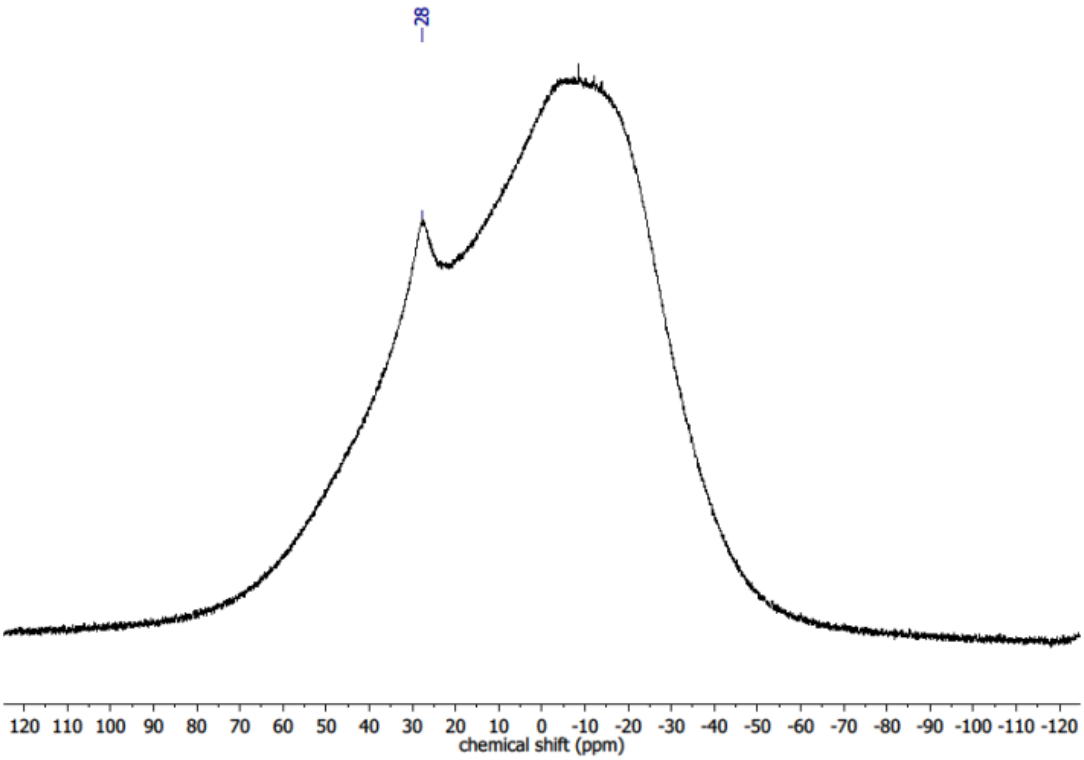


Fig. S45. $^{11}B\{^{1}H\}$ NMR (128 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2SiMe_3$}Pd($PMe_3$)] **19c**.

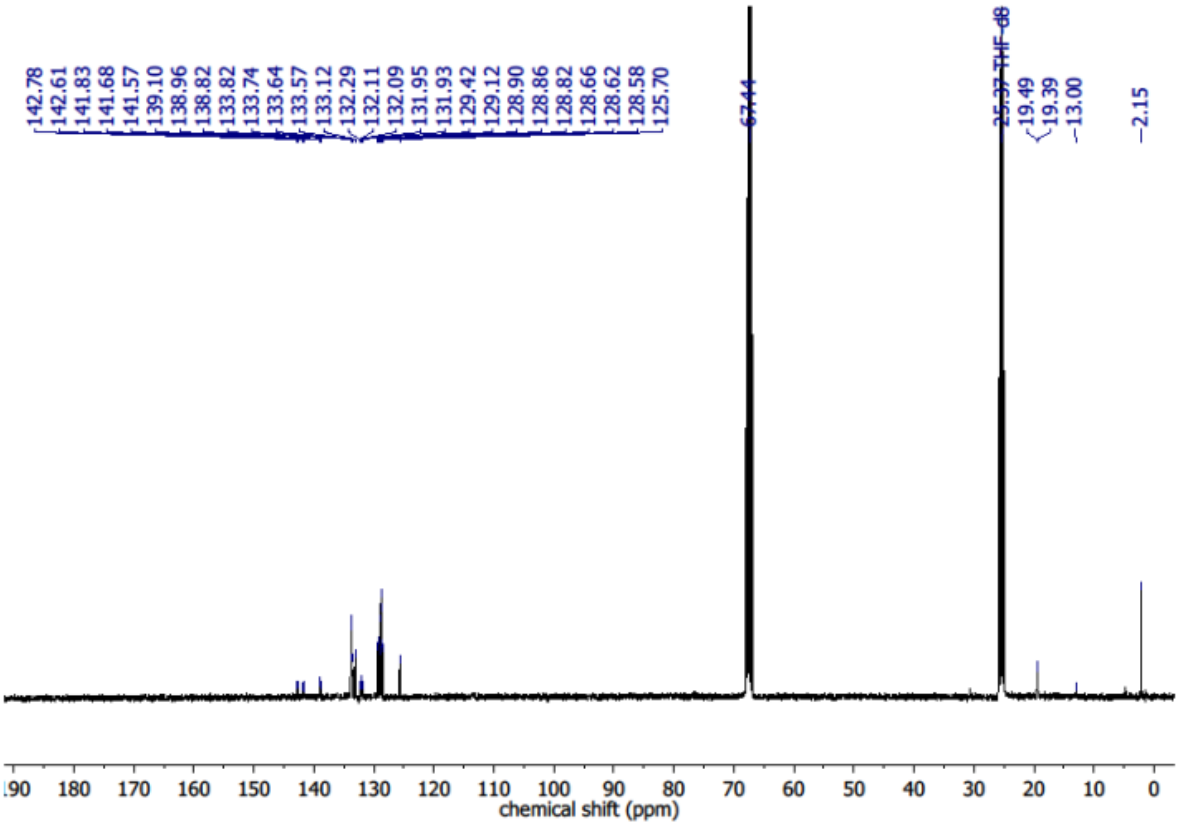


Fig. S46. $^{13}C\{^{1}H\}$ NMR (101 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2SiMe_3$}Pd($PMe_3$)] **19c**.

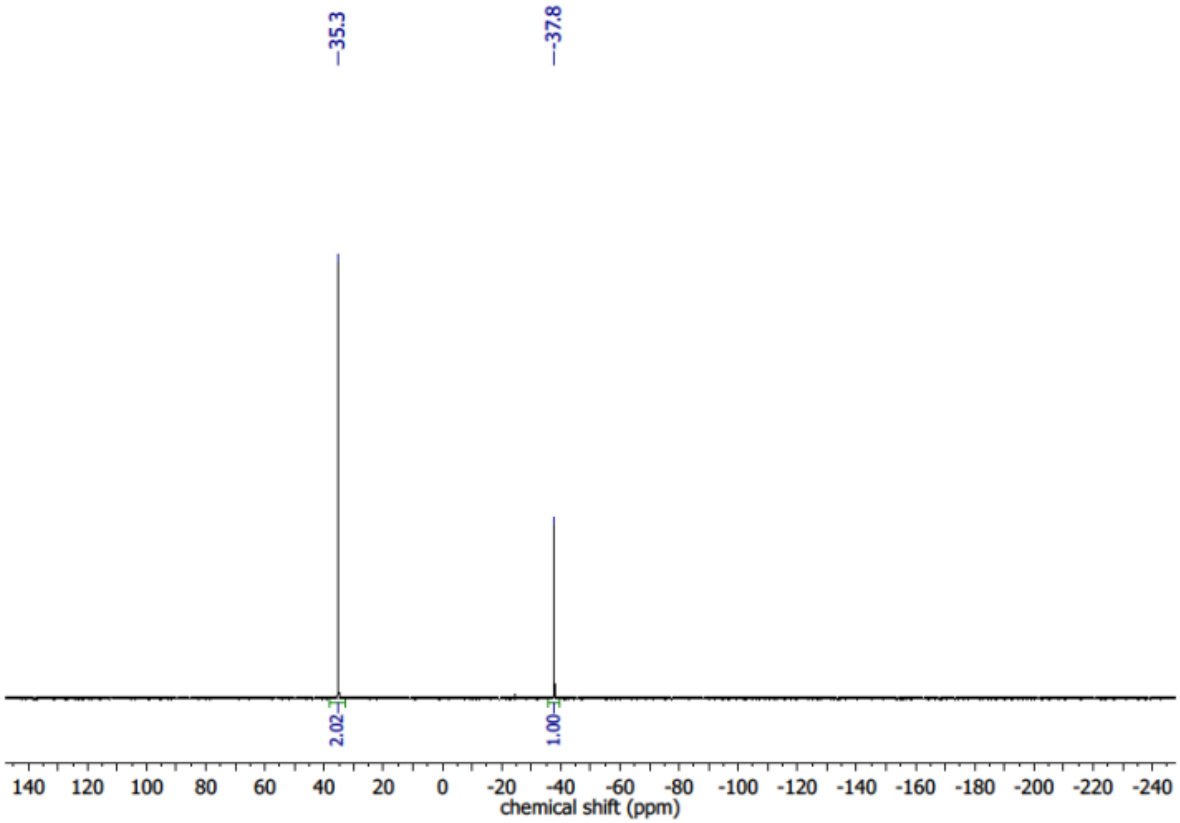


Fig. S47. $^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of [{(*o*-$PPh_2C_6H_4)_2BCH_2SiMe_3$}Pd($PMe_3$)] **19c**.

References

1 T. Schindler, M. Lux, M. Peters, L. T. Scharf, H Osseili, L. Maron and M. E. Tauchert, *Organometallics*, 2015, **34**, 1978.

2 SAINT, Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA, 2003.

3 SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339.

5 G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

6 G. M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3.