Electronic Supplementary Information for Dalton Transactions

Supporting Information

$PdCl_2$-promoted reactions of diaryl-substituted methylenecyclopropanes

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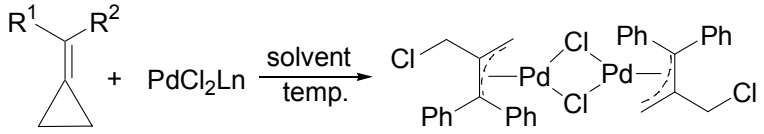
CONTENTS

General Remarks. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Mercury vx-300/400 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument. Satisfactory CHN microanalyses were measured with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. Organic solvents used were dried by standard methods when necessary. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Table SI-1 Optimization for the reaction of MCP **1a** with Pd source



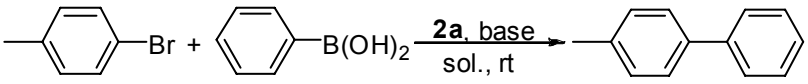
1a: $R^1 = R^2 = Ph$ **2a**

Entry[a]	Ln	Solvent	Temp.	Time/h	Yield/%[b]
1	none	toluene	rt	24	40
2	none	DMSO	rt	35	N.R.
3	none	CH_2Cl_2	rt	40	41
4	none	THF	rt	24	58
5	none	CH_3CN	rt	48	30
6	none	benzene	rt	40	47
7	none	DCE	rt	40	39
8	none	H_2O	rt	24	N.R.
9	none	THF	50 ^oC	24	74
10	none	THF	reflux	24	74
11	none	dioxane	50 ^oC	24	70
12	$(CH_3CN)_2$	THF	50 ^oC	24	57
13	$(PhCN)_2$	THF	50 ^oC	24	52
14	$(PPh_3)_2$	THF	50 ^oC	24	N.R.
15	dppe	THF	50 ^oC	24	28

[a] All reactions were carried out using MCP **1a** (0.3 mmol), Pd source (0.33 mmol) and solvent (1.0 mL) at the listed temperature.
[b] Isolated yields.

The catalytic studies of complex **2a** in Suzuki-Miyaura coupling reaction were also carried out and the two tables below showed the results:

Table SI-2 Suzuki-Miyaura Coupling Reaction Using 2a as Catalyst.

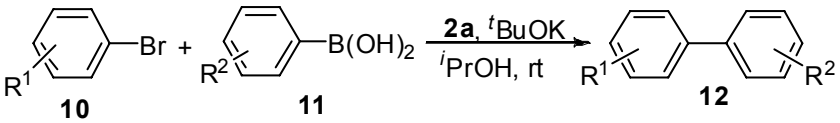


10a **11a** **12a**

entry[a]	base	sol.	yields/%[b]
1	BuOK	BuOH	17
2	BuOK	THF	19
3	BuOK	DCE	N.R.
4	BuOK	CH_3CN	N.R.
5	BuOK	PrOH	81
6	KF	PrOH	68
7	Cs_2CO_3	PrOH	40
8	KOH	PrOH	61
9	K_2CO_3	PrOH	43
10	$K_3PO_4{\cdot}3H_2O$	PrOH	63

[a] Reaction conditions: **10a** (0.5 mmol), **11a** (0.6 mmol), **2a** [10 mg ([Pd]: 2.5 mol%)], base (1.2 mmol), sol. (2.0 mL), rt , 24 h.
[b] Isolated yields.

Table SI-3 Suzuki-Miyaura Coupling Reactions of Arylbromides with Arylboronic Acids Using 2a as Catalyst.



10 **11** **12**

entry[a]	**10** (R^1)	**11** (R^2)	yields/%[b]
1	**10b** (H)	**11b** (4-Me)	**12a**, 75
2	**10b**	**11c** (3,5-Me_2)	**12b**, 88
3	**10a** (4-Me)	**11c**	**12c**, 96
4	**10c** (2-Me)	**11a** (H)	**12d**, 61
5	**10d** (3,5-Me_2)	**11a**	**12b**, 60
6	**10c**	**11c**	**12e**, 68
7	**10e** (4-Cl)	**11c**	**12f**, 92

[a] Reaction conditions: **10** (0.5 mmol), **11** (0.6 mmol), **2a** [10 mg ([Pd]: 2.5 mol%)], ^{t}BuOK (1.2 mmol), ^{i}PrOH (2.0 mL), rt, 24 h.
[b] Isolated yields.

General procedure for the reaction of MCPs 1 with $PdCl_2$ in THF. Under an argon atmosphere, a mixture of MCPs **1** (0.30 mmol) and $PdCl_2$ (0.33 mmol) was stirred in anhydrous THF (1.0 mL) at 50 ^oC for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **2**.

Procedure for the reaction of MCP 1a with $PdBr_2$ in THF. Under an argon atmosphere, a mixture of MCP **1a** (0.30 mmol) and $PdBr_2$ (0.33 mmol) was stirred in anhydrous THF (1.0 mL) at 60 ^oC for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **3a**.

General procedure for the reaction of MCPs 1 with $PdCl_2$ in DMAc. Under an argon atmosphere, a mixture of MCPs **1** (0.30 mmol) and $PdCl_2$ (0.33 mmol) was stirred in anhydrous DMAc (1.0 mL) at 50 ^oC for 24 h. The reaction solution was diluted with EtOAc, washed with saturated brine, dried over anhydrous Na_2SO_4, and then purified by flash column chromatography on silica gel to give complexes **2** and **4**.

Procedure for the reaction of MCP 1e with $PdCl_2$ in THF in the presence of NaBr. A mixture of MCP **1e** (0.30 mmol), $PdCl_2$ (0.33 mmol) and NaBr (0.9 mmol) was stirred in anhydrous THF (1.0 mL) at 50 ^oC for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to give complex **3b**.

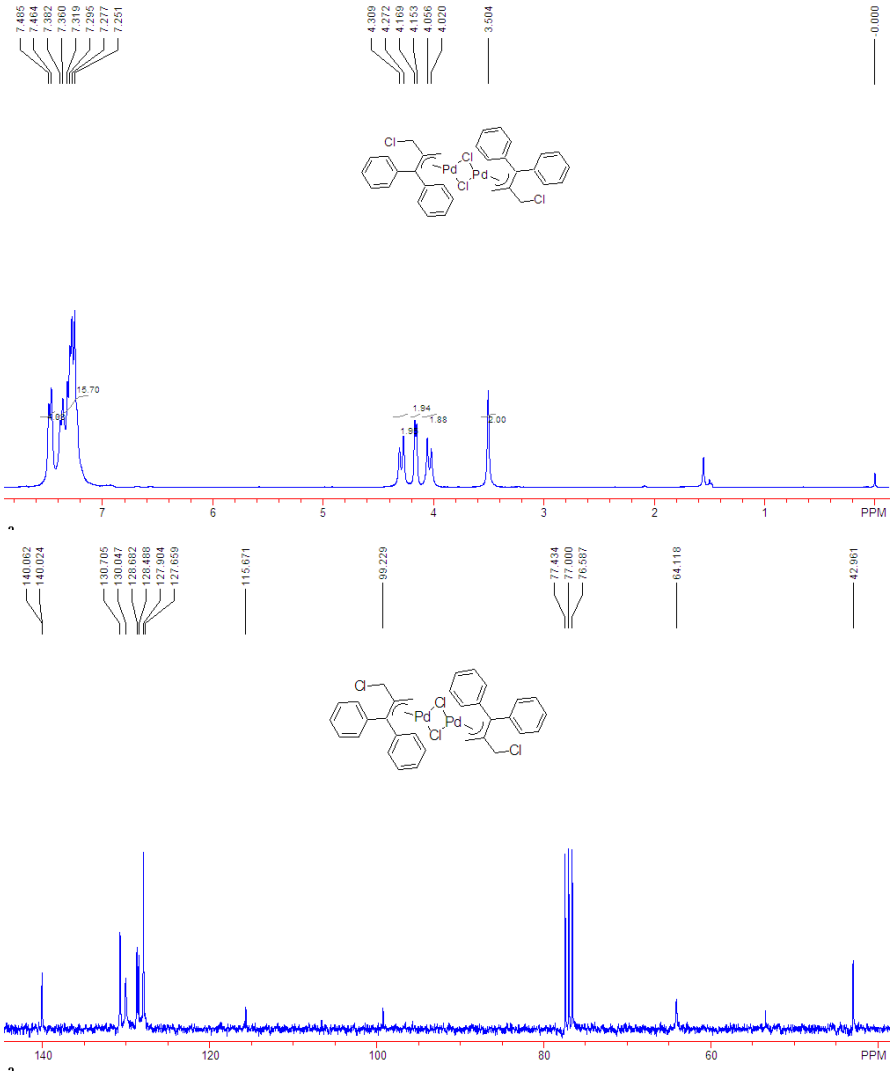
Procedure for the reaction of MCP 1a with $PdCl_2$ in DMF in the presence of H_2O. Under an argon atmosphere, a mixture of MCP **1a** (0.30 mmol), $PdCl_2$ (0.33 mmol) and H_2O (0.6 mmol to 3 mmol) was stirred in anhydrous DMF (1.0 mL) at room temperature for 24 h. The reaction solution was diluted with EtOAc, washed with saturated brine, dried over anhydrous Na_2SO_4, and then purified by flash column chromatography on silica gel to give complexes **2** and/or **5** and/or **6**.

Procedure for the formation of complex 7. Under an argon atmosphere, a mixture of complex **2a** (0.05 mmol), IPr·HCl (0.11 mmol) and ^{t}BuOK (0.25 mmol) was stirred in anhydrous THF (1.0 mL) at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give complex **7**.

General procedure for Suzuki-Miyaura coupling reaction. Under an argon atmosphere, boronic acid **11** (0.6 mmol), ^{t}BuOK (1.2 mmol), complex **2a** (10 mg, 2.5 mol%), ^{i}PrOH (2.0

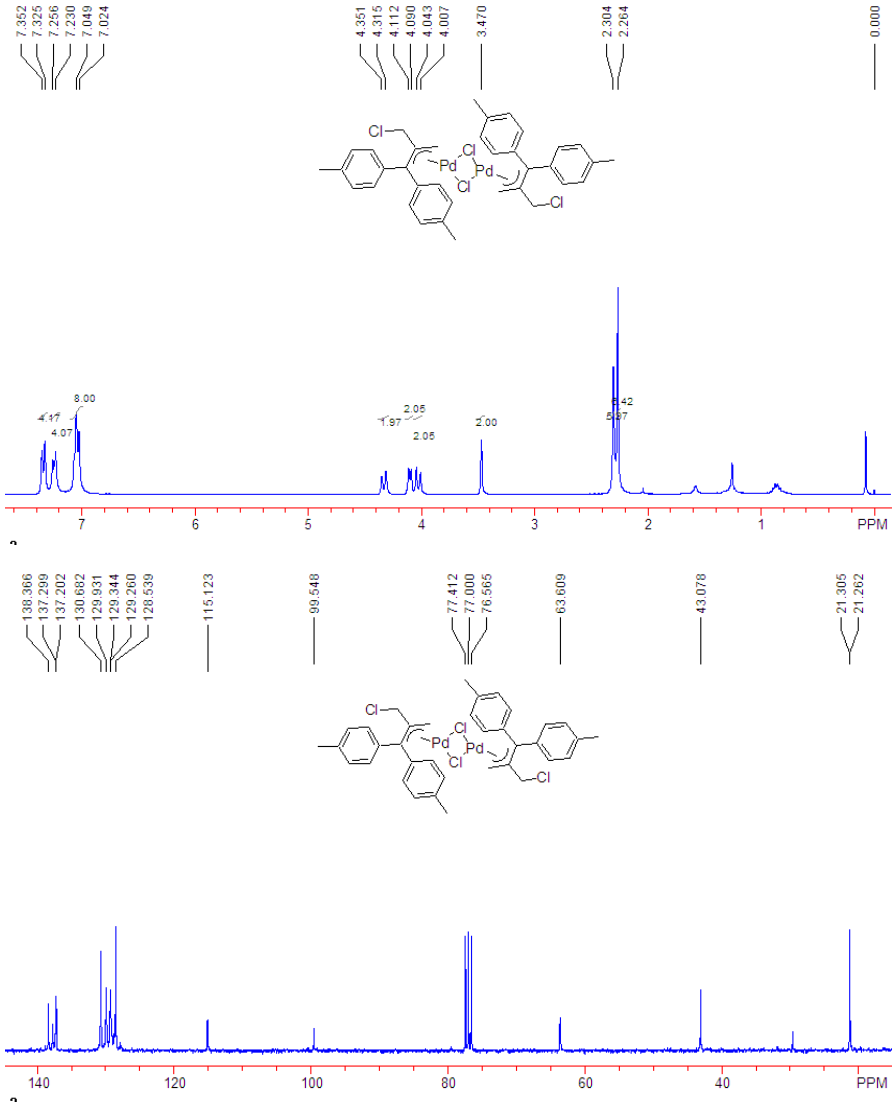
mL) and bromide **10** (0.5 mmol) was successively added into a Schlenk reaction tube. The mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give products **12**.

Product **2a**. A yellow solid. Mp: 220 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.51 (s, 2H), 4.04 (d, 2H, *J* = 11.1 Hz), 4.16 (d, 2H, *J* = 4.5 Hz), 4.29 (d, 2H, *J* = 11.1 Hz), 7.23-7.39 (m, 16H, Ar), 7.48 (d, 4H, *J* = 7.2 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.0, 64.1, 99.2, 115.7, 127.7, 127.9, 128.5, 128.7, 130.0, 130.7, 140.0, 140.1. IR (CH_2Cl_2): ν 3056, 2925, 1490, 1443, 1260, 1077, 760 cm^{-1}. MS (MALDI) *m/z*: 654 (M^{+}-^{102}Pd). Anal. Calcd. For $C_{32}H_{28}Cl_4Pd_2$ requires: C, 50.10 %; H, 3.68%; Found: C, 49.97 %; H, 3.84%.

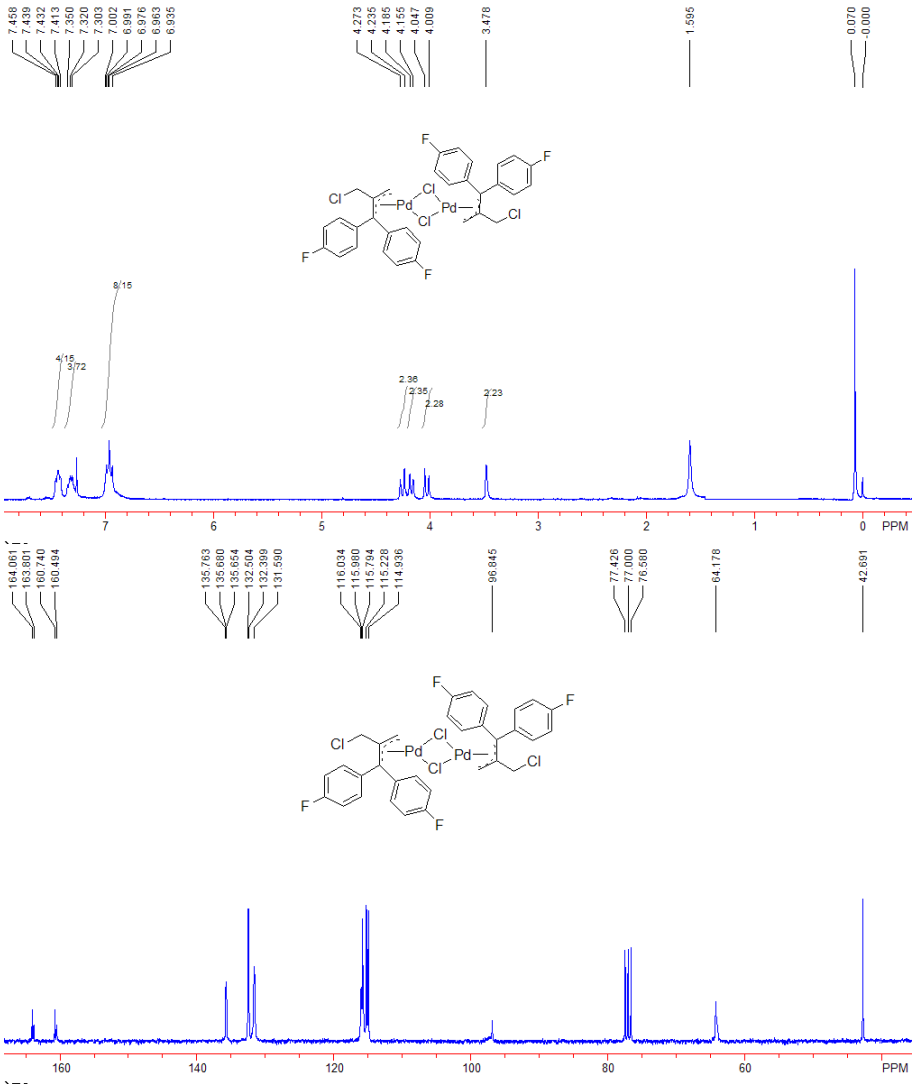


Product **2b**. A yellow solid. Mp: 196 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.26 (s, 6H), 2.30 (s, 6H), 3.47 (s, 2H), 4.03 (d, 2H, *J* = 10.8 Hz), 4.10 (d, 2H, *J* = 6.6 Hz), 4.33 (d, 2H, *J* = 10.8 Hz), 7.04 (d, 8H, *J* = 7.5 Hz, Ar), 7.24 (d, 4H, *J* = 7.8 Hz, Ar), 7.34 (d, 4H, *J* = 8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.26, 21.31, 43.1, 63.6, 99.5, 115.1, 128.5, 129.26, 129.34, 129.9, 130.7, 137.2, 137.3, 138.4. IR (CH_2Cl_2): ν 3015, 2922, 2844, 1609,

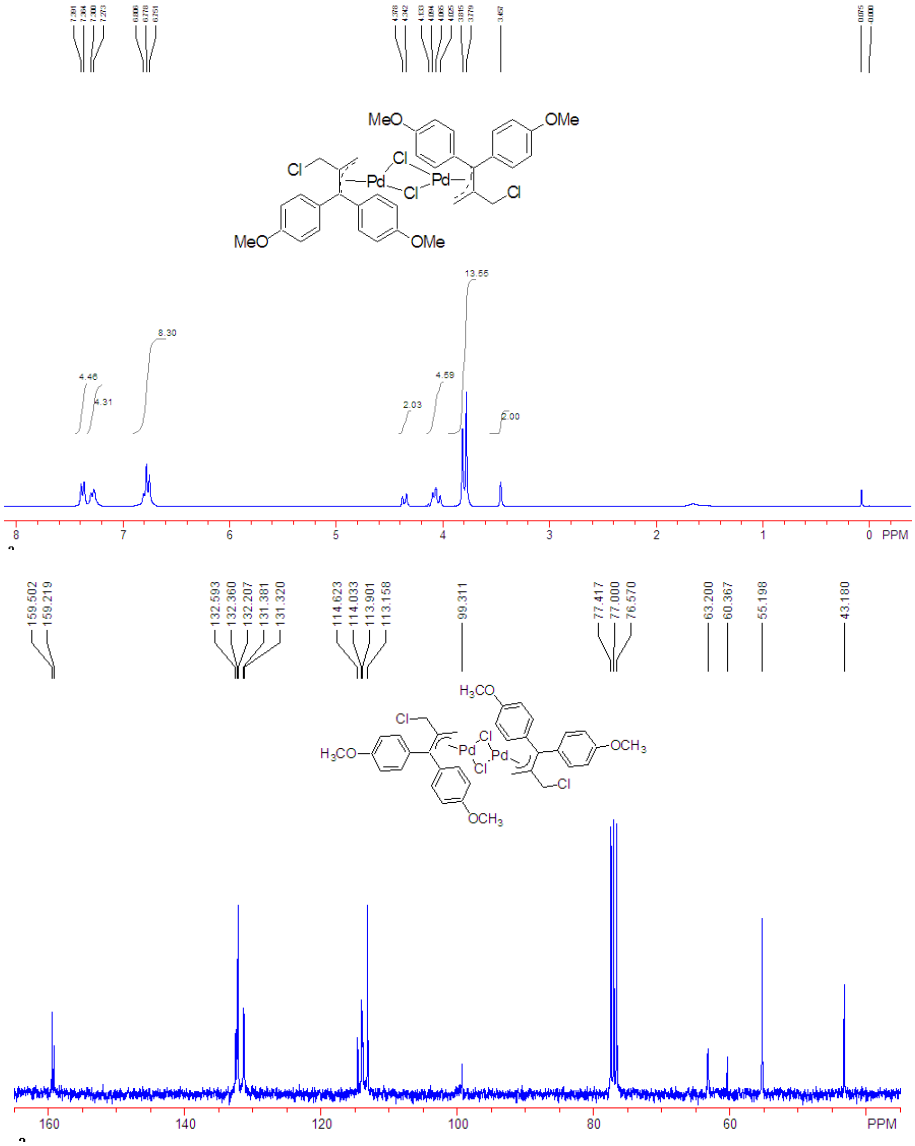
1508, 1442, 1260, 1185, 1021, 818 cm^{-1}. MS (MALDI) *m/z*: 710 (M^{+}-^{102}Pd). Anal. Calcd. For $C_{36}H_{36}Cl_4Pd_2$ requires: C, 52.52 %; H, 4.41%; Found: C, 52.82 %; H, 4.51%.



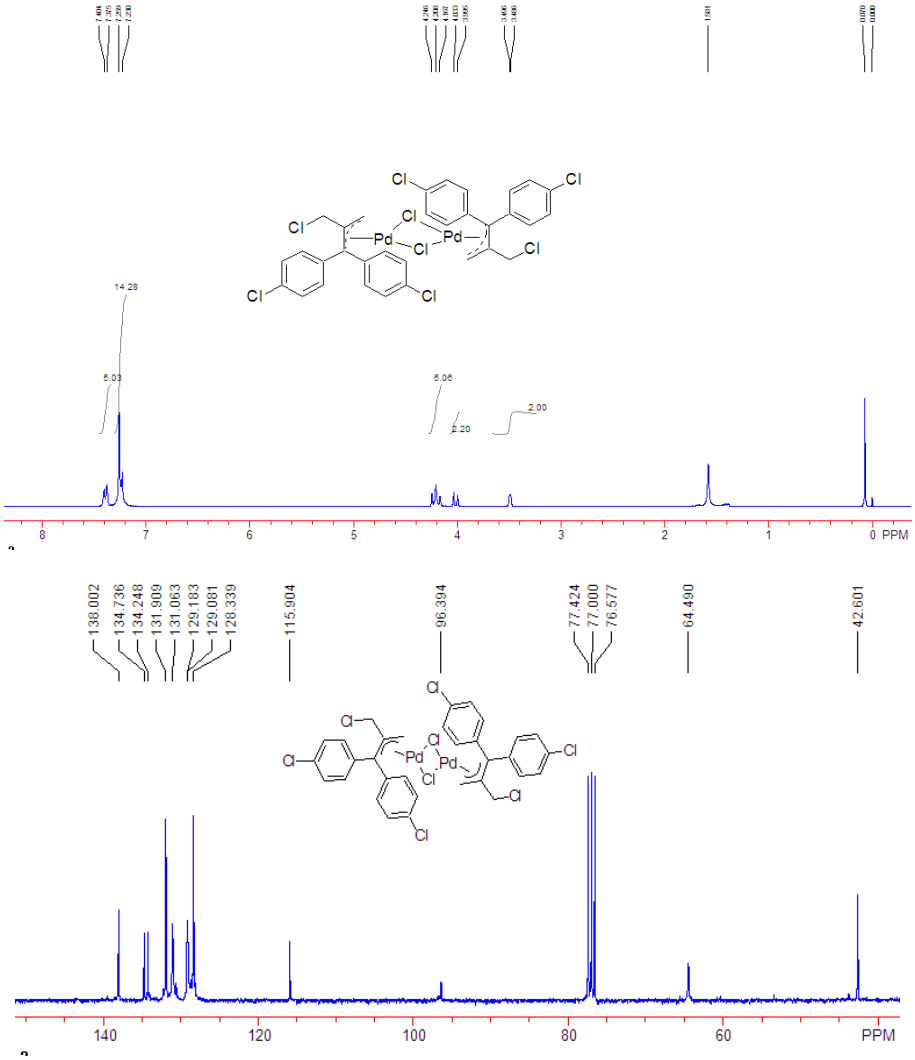
Product **2c**. A yellow solid. Mp: 202 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.48 (s, 2H), 4.03 (d, 2H, *J* = 11.4 Hz), 4.17 (d, 2H, *J* = 9.0 Hz), 4.25 (d, 2H, *J* = 11.4 Hz), 6.94-7.00 (m, 8H, Ar), 7.30-7.35 (m, 4H, Ar), 7.41-7.46 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.7, 64.2, 96.8, 115.1 (d, J_{C-F} = 21.9 Hz), 115.9 (d, J_{C-F} = 18.0 Hz), 116.0, 131.6, 132.5 (d, J_{C-F} = 7.9 Hz), 135.68, 135.71 (d, J_{C-F} = 8.2 Hz), 162.1 (d, J_{C-F} = 248.0 Hz), 162.4 (d, J_{C-F} = 249.1 Hz). IR (CH_2Cl_2): ν 2950, 2926, 1601, 1505, 1235, 1160, 1099, 1015, 837 cm^{-1}. MS (MALDI) *m/z*: 726 (M^{+}-^{102}Pd). HRMS (MALDI) Calcd. For $C_{32}H_{24}F_4Cl_4{}^{102}Pd^{+1}$ requires: 725.9619; Found: 725.9599.



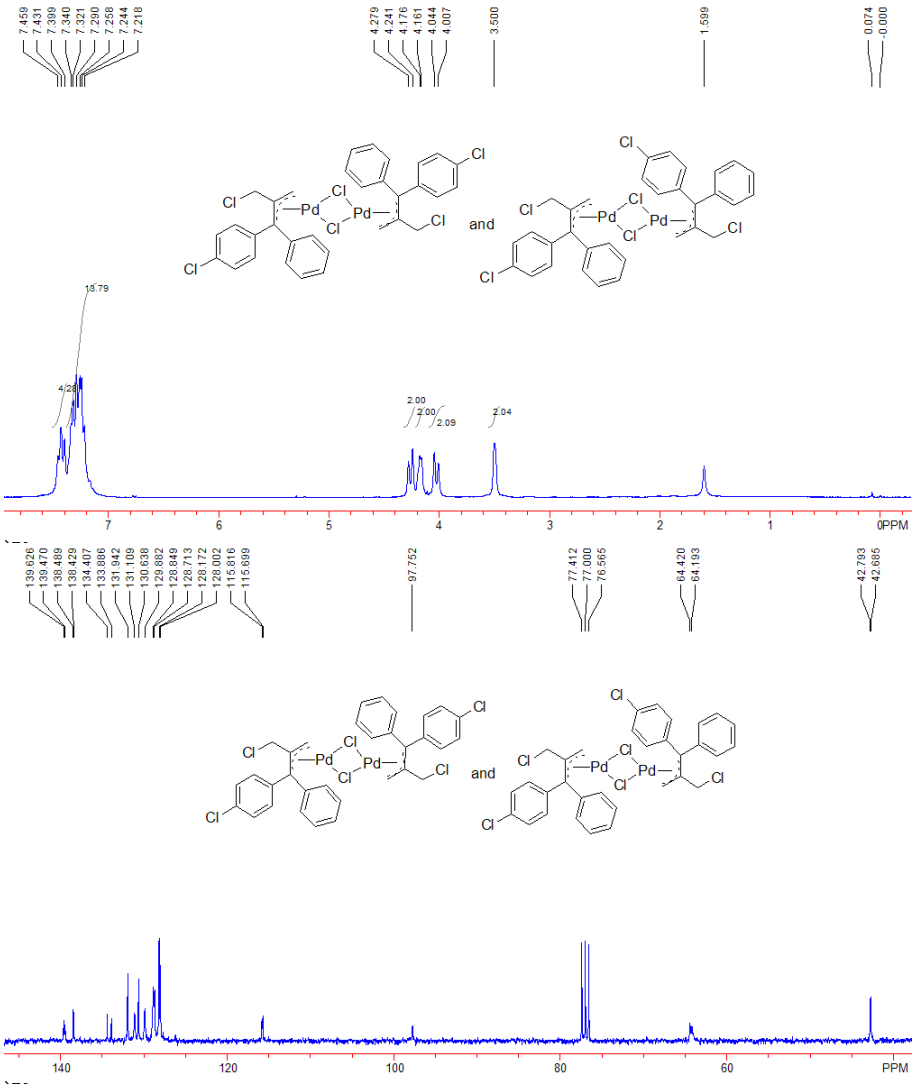
Product **2d**. A yellow solid. Mp: 156-158 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.46 (s, 2H), 3.78 (s, 6H, OMe), 3.82 (s, 6H, OMe), 4.05 (d, 2H, J = 12.3 Hz), 4.11 (d, 2H, J = 11.7 Hz), 4.36 (d, 2H, J = 10.8 Hz), 6.76 (d, 4H, J = 8.1 Hz, Ar), 6.79 (d, 4H, J = 8.1 Hz, Ar), 7.29 (d, 4H, J = 8.1 Hz, Ar), 7.38 (d, 4H, J = 8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.2, 55.2, 60.4, 63.2, 99.3, 113.2, 113.9, 114.0, 114.6, 131.3, 131.4, 132.2, 132.4, 132.6, 159.2, 159.5. IR (CH_2Cl_2): ν 3002, 2950, 2929, 2387, 1604, 1508, 1295, 1252, 1176, 1034, 833 cm^{-1}. MS (MALDI) *m/z*: 774 (M^{+}-^{102}Pd). HRMS (MALDI) Calcd. For $C_{36}H_{36}O_4Cl_4{}^{102}Pd^{+1}$ requires: 774.0418; Found: 774.0425.



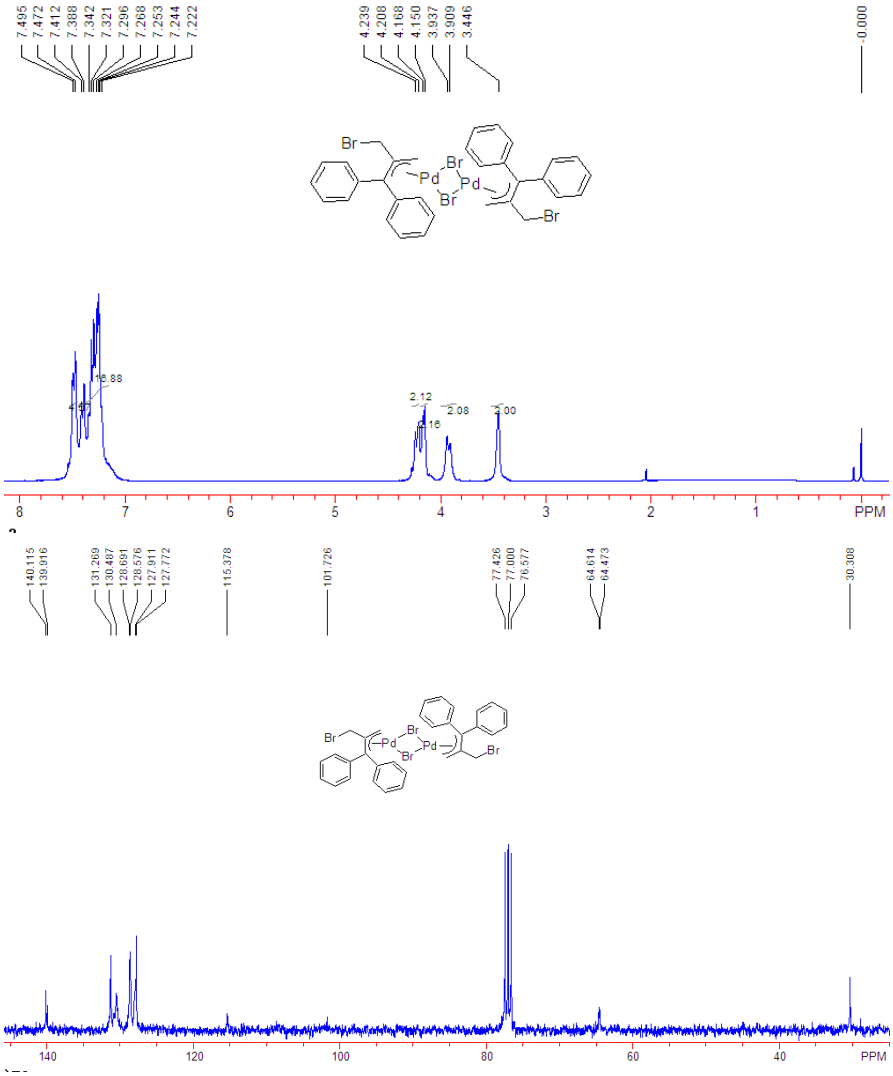
Product **2e**. A yellow solid. Mp: 212 ^{o}C (decomposed).^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.50 (s, 2H), 4.01 (d, 2H, J = 11.1 Hz), 4.19 (d, 2H, J = 12.3 Hz), 4.23 (d, 2H, J = 11.4 Hz), 7.23-7.27 (m, 12H), 7.39 (d, 4H, J = 8.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.6, 64.5, 96.4, 115.9, 128.3, 129.1, 129.2, 131.1, 131.9, 134.2, 134.7, 138.0. IR (CH_2Cl_2): ν 2950, 2925, 2854, 1718, 1588, 1488, 1398, 1259, 1092, 1014, 829 cm^{-1}. MS (MALDI) *m/z*: 790 (M^{+}-^{102}Pd). HRMS (MALDI) Calcd. For $C_{32}H_{24}Cl_8{}^{102}Pd^{+1}$ requires: 789.8437; Found: 789.8445.



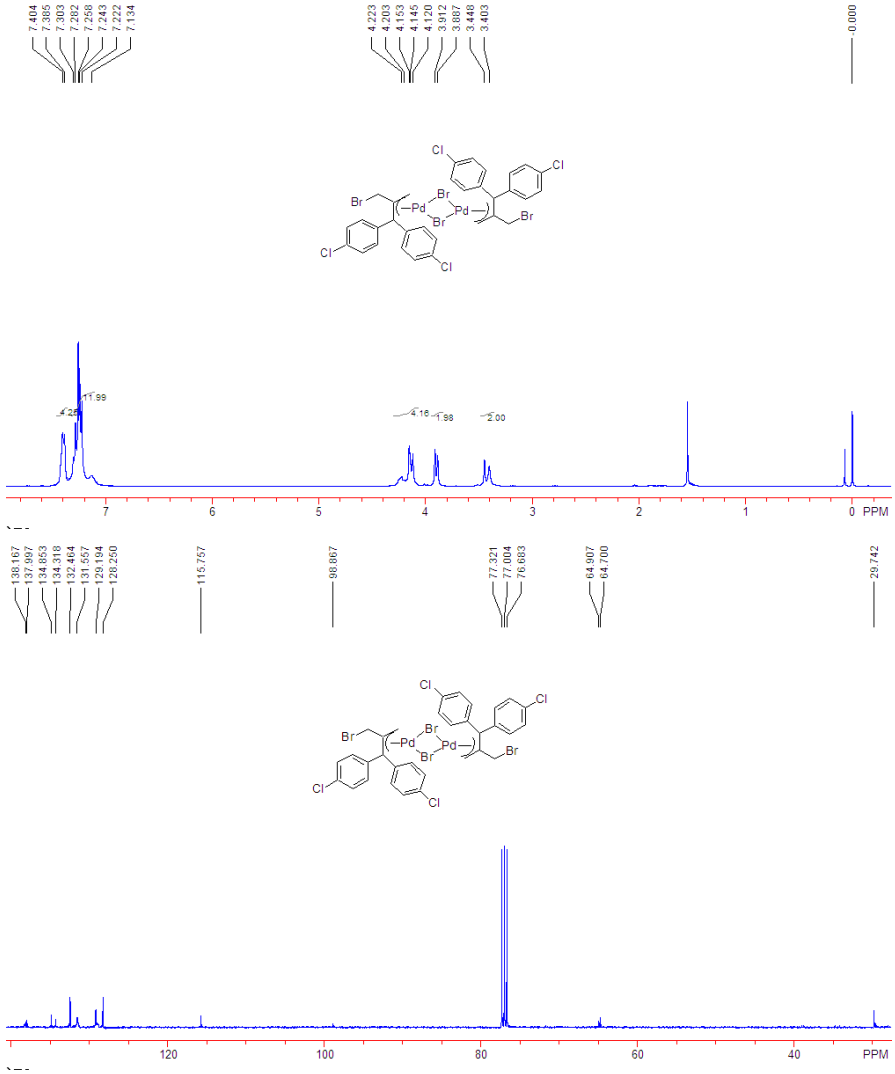
Product **2f**. A yellow solid. Mp: 197 ^{o}C (decomposed). (*Z*, *Z*- or *Z*, *E*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.50 (s, 2H), 4.03 (d, 2H, *J* = 11.1 Hz), 4.17 (d, 2H, *J* = 4.5 Hz), 4.26 (d, 2H, *J* = 11.1 Hz), 7.22-7.34 (m, 14H, Ar), 7.40-7.46 (m, 4H, Ar). (*Z*, *E*- or *Z*, *Z*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.50 (s, 2H), 4.03 (d, 2H, *J* = 11.1 Hz), 4.17 (d, 2H, *J* = 4.5 Hz), 4.26 (d, 2H, *J* = 11.1 Hz), 7.22-7.34 (m, 14H, Ar), 7.40-7.46 (m, 4H, Ar). (*Z*, *Z*- or *Z*, *E*-isomer) ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.7, 64.2, 97.8, 115.7, 128.0, 128.7, 129.9, 131.1, 133.9, 134.4, 138.4, 139.5. (*Z*, *E*- or *Z*, *Z*-isomer) ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.8, 64.4, 97.8, 115.8, 128.2, 128.8, 130.6, 131.9, 133.9, 134.4, 138.5, 139.6. IR (CH_2Cl_2): ν 3058, 3006, 2950, 2926, 2854, 1908, 1782, 1589, 1487, 1445, 1260, 1216, 1092, 1014, 828 cm^{-1}. MS (MALDI) *m/z*: 722 (M^{+}-^{102}Pd). HRMS (MALDI) Calcd. For $C_{32}H_{26}Cl_6{}^{102}Pd^{+1}$ requires: 721.9216; Found: 721.9219.



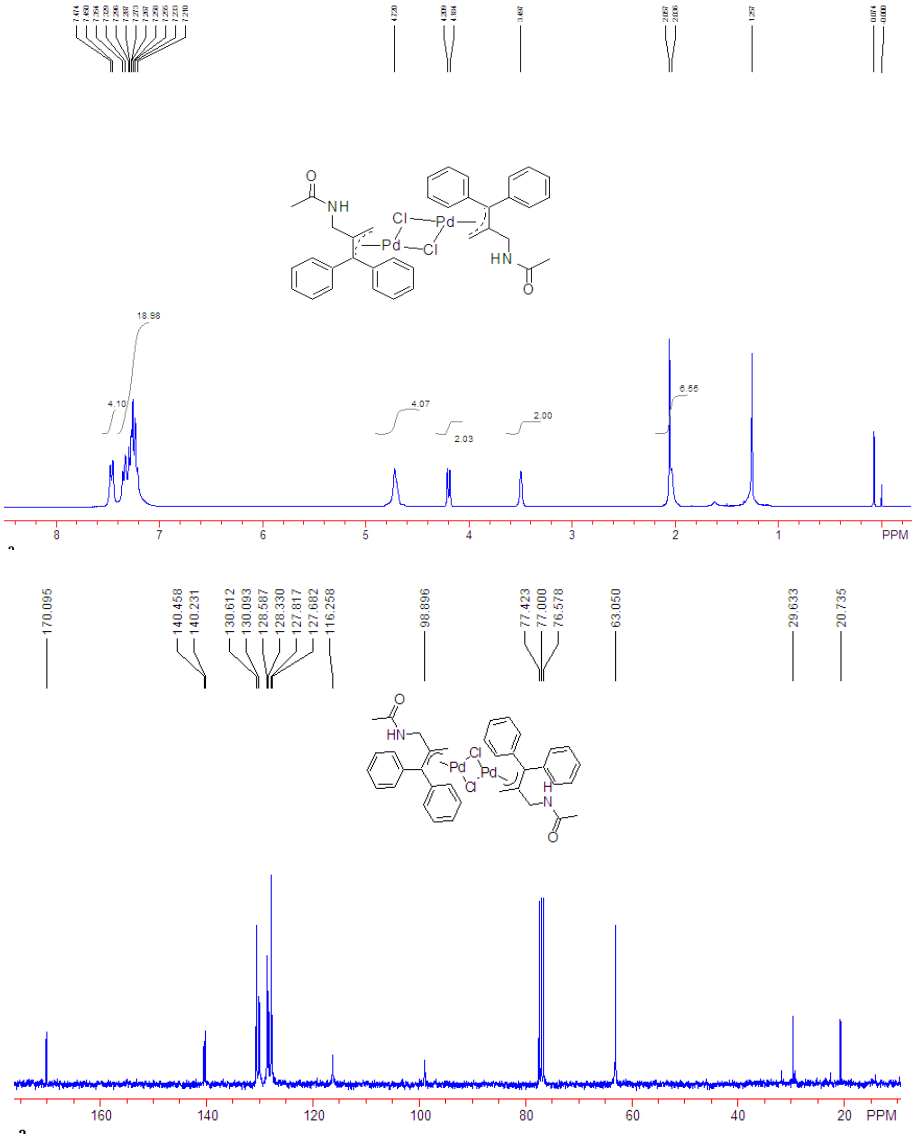
Product **3a**. A yellow solid. Mp: 186 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.45 (s, 2H), 3.92 (d, 2H, J = 8.4 Hz), 4.16 (d, 2H, J = 5.4 Hz), 4.22 (d, 2H, J = 9.3 Hz), 7.22-7.41 (m, 16H, Ar), 7.48 (d, 4H, J = 6.9 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.3, 64.5, 64.6, 101.7, 115.4, 127.8, 127.9, 128.6, 128.7, 130.5, 131.3, 139.9, 140.1. IR (CH_2Cl_2): ν 3054, 2954, 2925, 2853, 1737, 1489, 1443, 1338, 1213, 761 cm^{-1}. MS (MALDI) *m/z*: 834 (M^{+}-^{106}Pd).



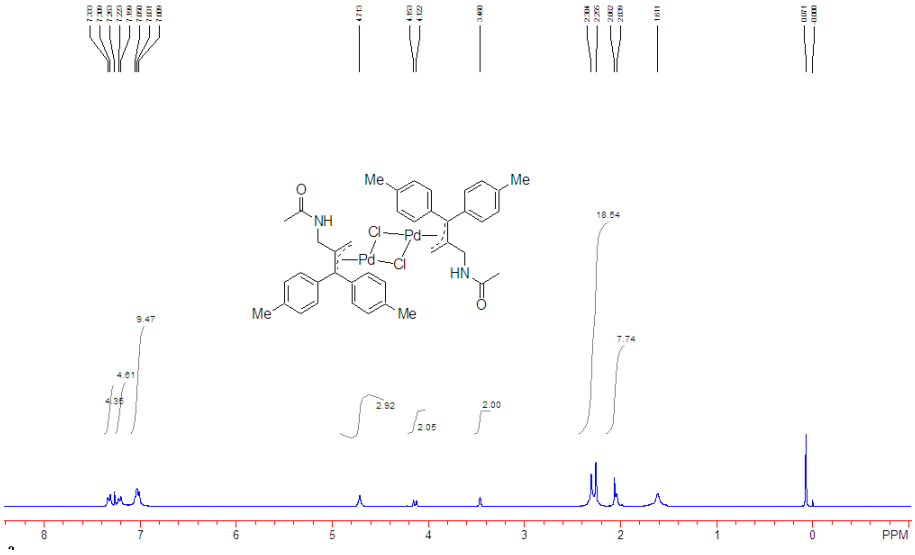
Product **3b**. A yellow solid. Mp: 194 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.43 (d, 2H, J = 18.0 Hz), 3.90 (d, 2H, J = 10.0 Hz), 4.12-4.22 (m, 4H), 7.13-7.30 (m, 12H, Ar), 7.39 (d, 4H, J = 7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 64.7, 64.9, 98.9, 115.8, 128.2, 129.2, 131.6, 132.5, 134.3, 134.9, 138.0, 138.2. IR (CH_2Cl_2): ν 3048, 1908, 1588, 1488, 1398, 1275, 1262, 1213, 1093, 1013, 828 cm^{-1}. MS (ESI) *m/z*: 1076 (M^++H). HRMS (ESI) Calcd. For $C_{32}H_{25}Br_4Cl_4Pd_2$ requires: 1076.5514; Found: 1076.4431.



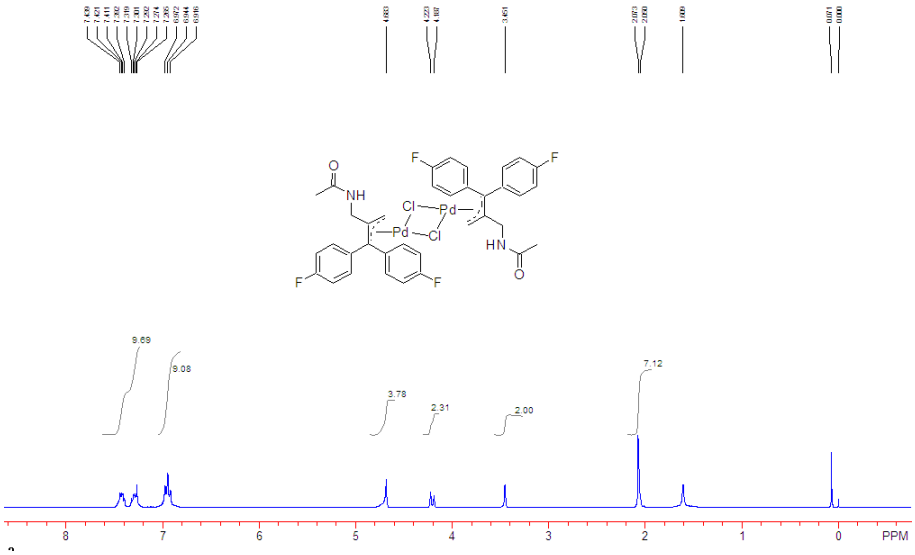
Product **4a**. A yellow solid. Mp: 213 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.04 (s, 3H), 2.06 (s, 3H), 3.50 (s, 2H), 4.20 (d, 2H, J = 7.5 Hz), 4.72 (s, 4H), 7.21-7.36 (m, 16H, Ar), 7.46 (d, 4H, J = 7.2 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 29.6, 63.1, 98.9, 116.3, 127.7, 127.8, 128.3, 128.6, 130.1, 130.6, 140.2, 140.5, 170.1. IR (CH_2Cl_2): ν 3056, 3022, 2926, 1745, 1677, 1597, 1490, 1444, 1371, 1222, 1033, 760 cm^{-1}. MS (ESI) *m/z*: 833 $(M+Na)^+$. HRMS (ESI) Calcd. For $C_{36}H_{36}N_2O_2NaCl_2Pd_2$ $(M+Na)^+$ requires: 833.0121; Found: 833.0180.



Product **4b**. A yellow solid. Mp: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.04 (s, 3H), 2.06 (s, 3H), 2.26 (s, 6H), 2.30 (s, 6H), 3.46 (s, 2H), 4.14 (d, 2H, J = 9.3 Hz), 4.71 (s, 4H), 7.02 (d, 4H, J = 6.9 Hz, Ar), 7.05 (d, 4H, J = 7.8 Hz, Ar), 7.21 (d, 4H, J = 6.9 Hz, Ar), 7.32 (d, 4H, J = 7.8 Hz, Ar). IR (CH_2Cl_2): ν 2949, 2925, 2855, 1745, 1459, 1376, 1222, 1028, 818, 772 cm^{-1}. MS (ESI) *m/z*: 889 (M^++Na). HRMS (ESI) Calcd. For $C_{40}H_{44}N_2O_2NaCl_2Pd_2$ (M^++ Na) requires: 889.0747; Found: 889.0803.

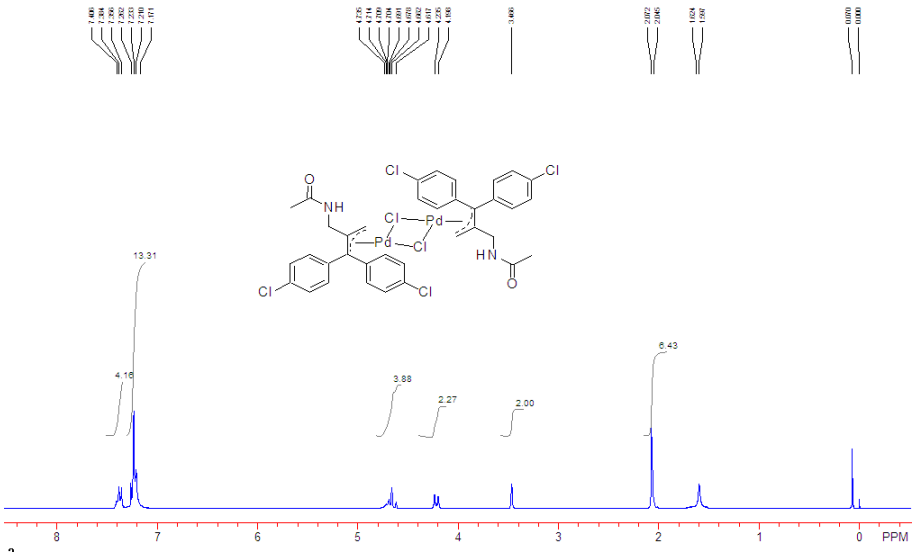


Product **4c**. A yellow solid. Mp: 135-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.06 (s, 3H), 2.07 (s, 3H), 3.45 (s, 2H), 4.21 (d, 2H, J = 11.7 Hz), 4.68 (s, 4H), 6.92-6.97 (m, 8H, Ar), 7.27-7.44 (m, 8H, Ar). IR (CH_2Cl_2): ν 2919, 1738, 1494, 1364, 1217, 1094, 829 cm^{-1}. MS (ESI) *m/z*: 905 (M^++Na). HRMS (ESI) Calcd. For $C_{36}H_{32}N_2O_2NaF_4Cl_2Pd_2$ (M^++Na) requires: 904.9744; Found: 904.9763.

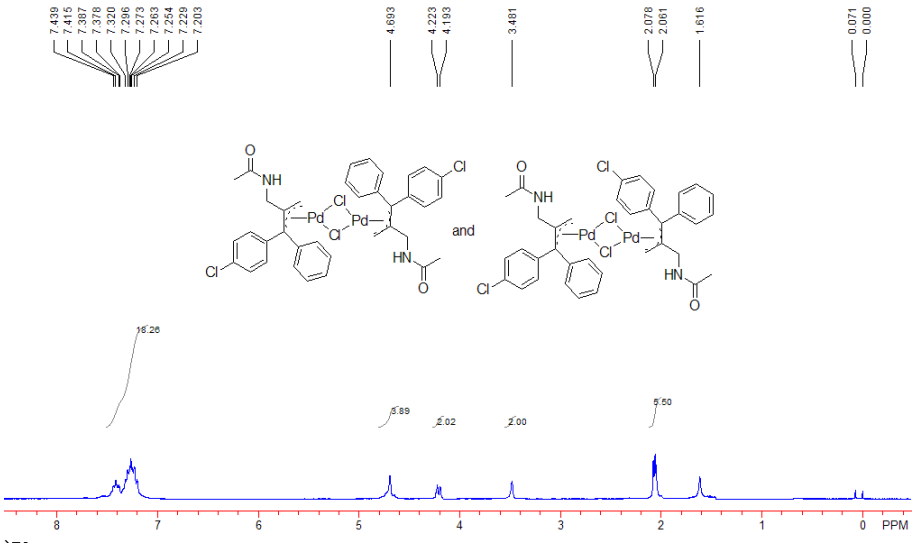


Product **4d**. A yellow solid. Mp: 85-87 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.05 (s, 3H), 2.07 (s, 3H), 3.47 (s, 2H), 4.22 (d, 2H, J = 11.4 Hz), 4.62-4.74 (m, 4H), 7.17-7.26 (m, 12H, Ar), 7.37 (d, 2H, J = 8.4 Hz, Ar), 7.40 (d, 2H, J = 6.6 Hz, Ar). IR (CH_2Cl_2): ν 2950, 2926, 1744, 1589, 1490, 1376, 1221, 1092, 1015, 828 cm^{-1}. MS (ESI) *m/z*: 969 (M^++Na). HRMS

(ESI) Calcd. For $C_{36}H_{32}N_2O_2NaCl_6Pd_2$ (M^++ Na) requires: 968.8562; Found: 968.8572.

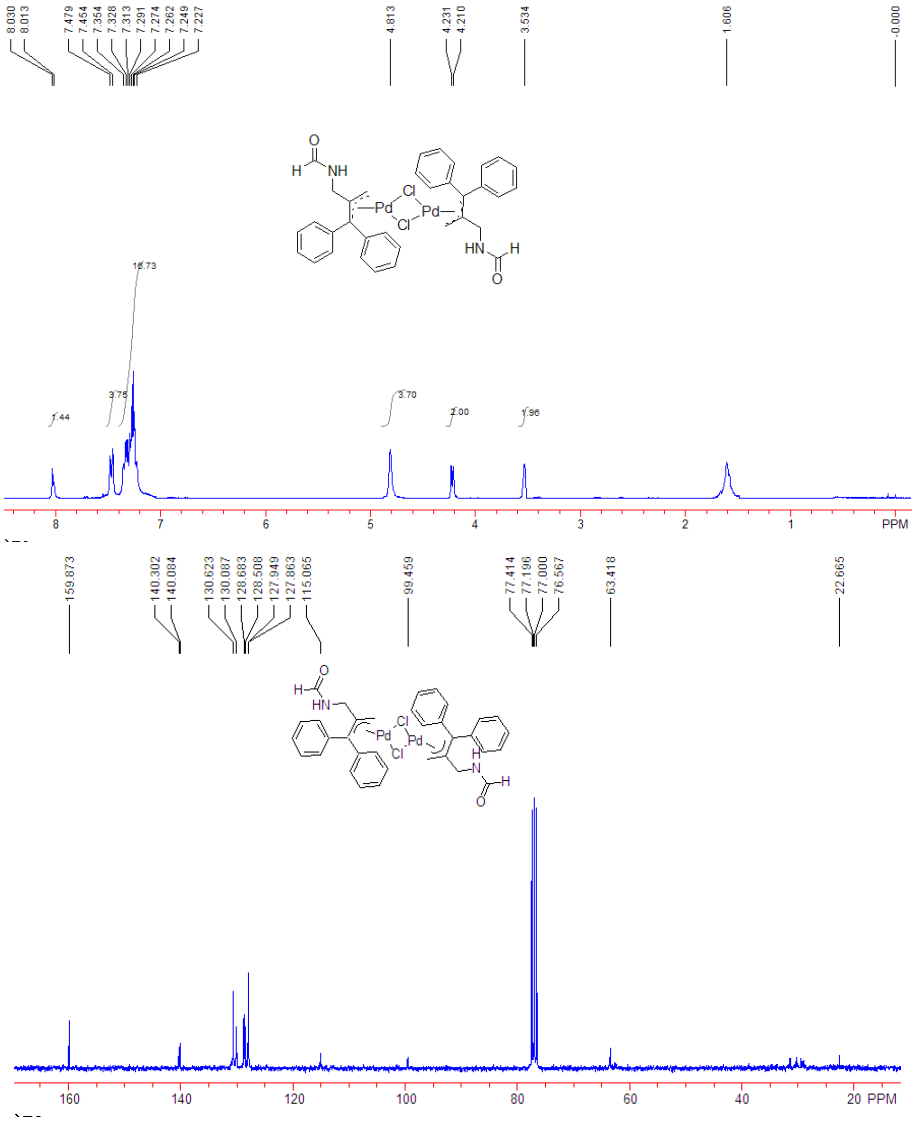


Product **4e**. A yellow solid. Mp: 83-85 ^oC. (*Z*, *Z*- or *Z*, *E*-isomer) ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.06 (s, 3H), 2.08 (s, 3H), 3.48 (s, 2H), 4.21 (d, 2H, *J* = 9.0 Hz), 4.69 (s, 4H), 7.20-7.44 (m, 18H, Ar). (*Z*, *E*- or *Z*, *Z*-isomer) ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.06 (s, 3H), 2.08 (s, 3H), 3.48 (s, 2H), 4.21 (d, 2H, *J* = 9.0 Hz), 4.69 (s, 4H), 7.20-7.44 (m, 18H, Ar).. IR (CH_2Cl_2): ν 2950, 2926, 2841, 1745, 1488, 1371, 1221, 1092, 829, 760 cm^{-1}. MS (ESI) *m/z*: 901 (M^++Na). HRMS (ESI) Calcd. For $C_{36}H_{34}N_2O_2NaCl_4Pd_2$ (M^++Na) requires: 900.9342; Found: 900.9438.

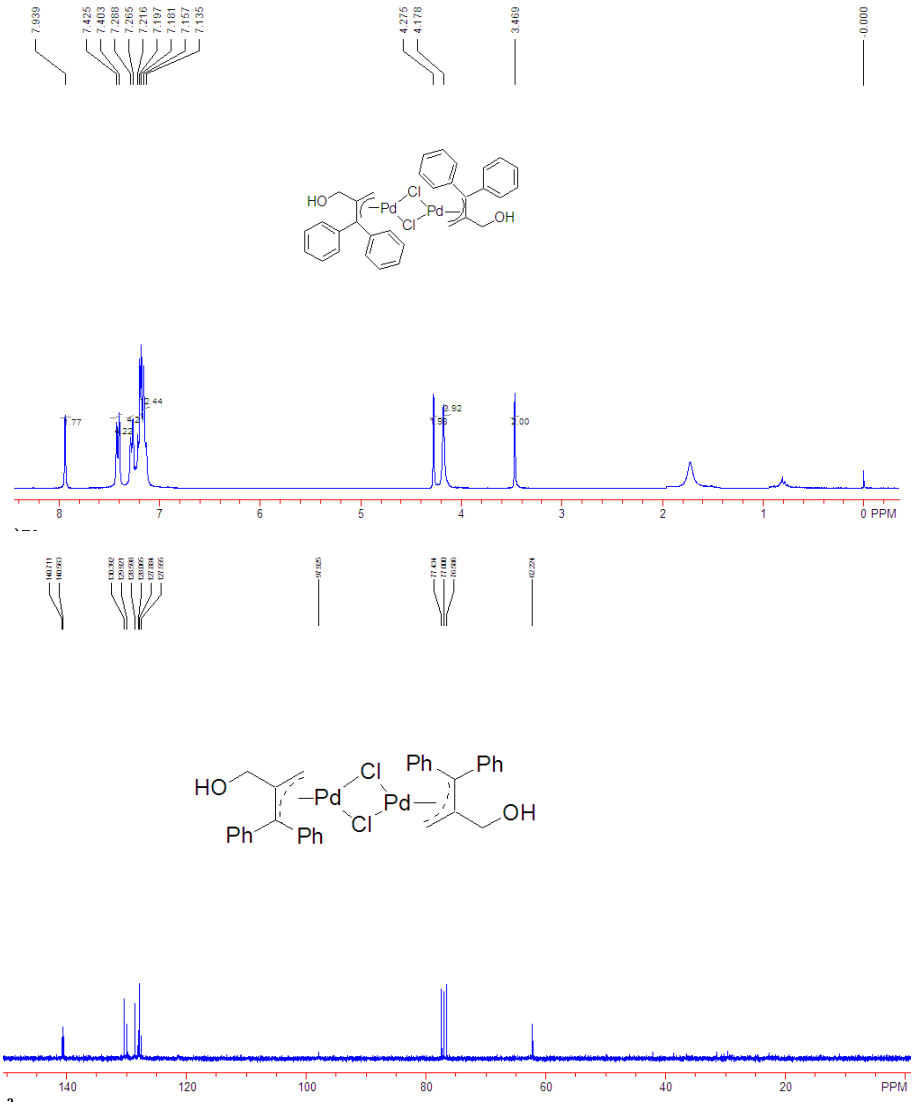


Product **5**. A yellow solid. Mp: 169-171 ^oC. ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.53 (s, 2H), 4.22 (d, 2H, *J* = 6.3 Hz), 4.81 (s, 4H), 7.23-7.35 (m, 16H, Ar), 7.47 (d, 4H, *J* = 7.5 Hz, Ar),

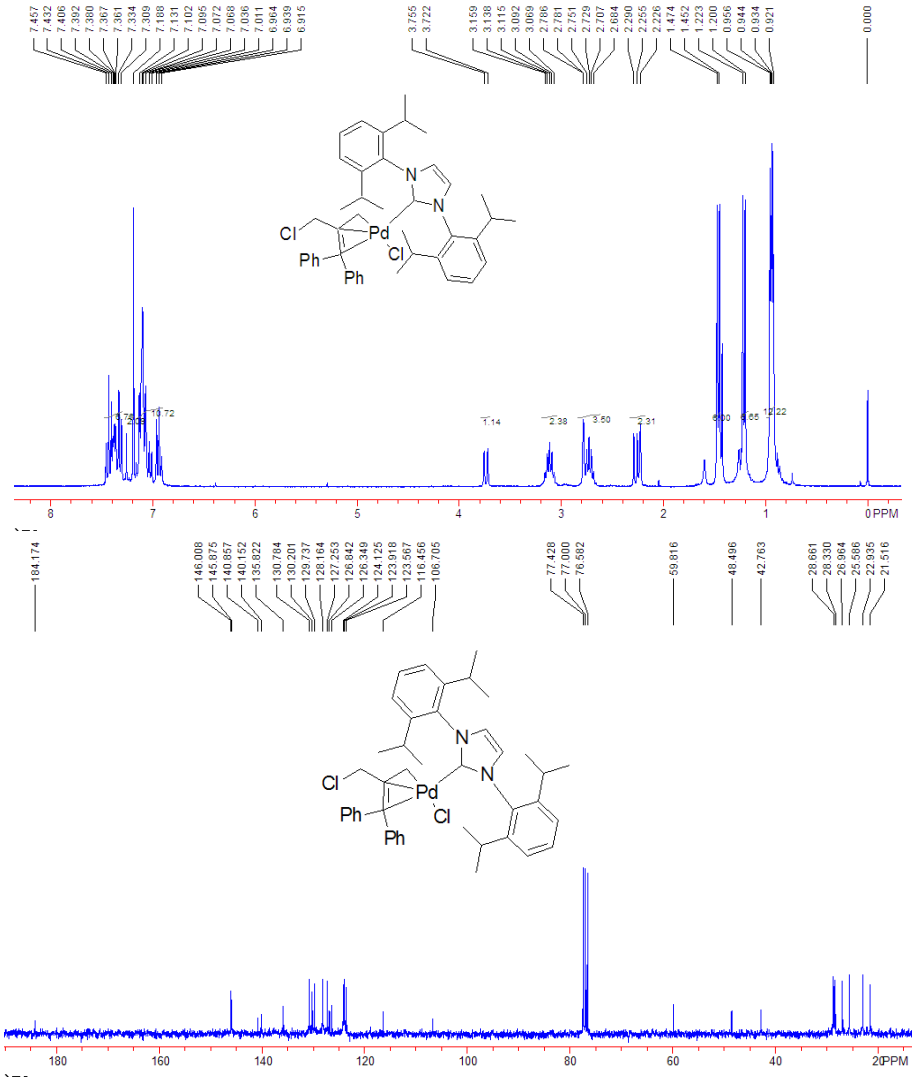
8.01 (s, 1H), 8.03 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.7, 63.4, 99.5, 115.1, 127.9, 128.0, 128.5, 128.7, 130.1, 130.6, 140.1, 140.3, 159.9. IR (CH_2Cl_2): ν 3052, 2926, 2854, 1727, 1491, 1443, 1147, 925, 759 cm^{-1}. MS (ESI) *m/z*: 805 (M^++Na). HRMS (ESI) Calcd. For $C_{34}H_{32}N_2O_2NaCl_2Pd_2$ (M^++Na) requires: 804.9808; Found: 804.9826.



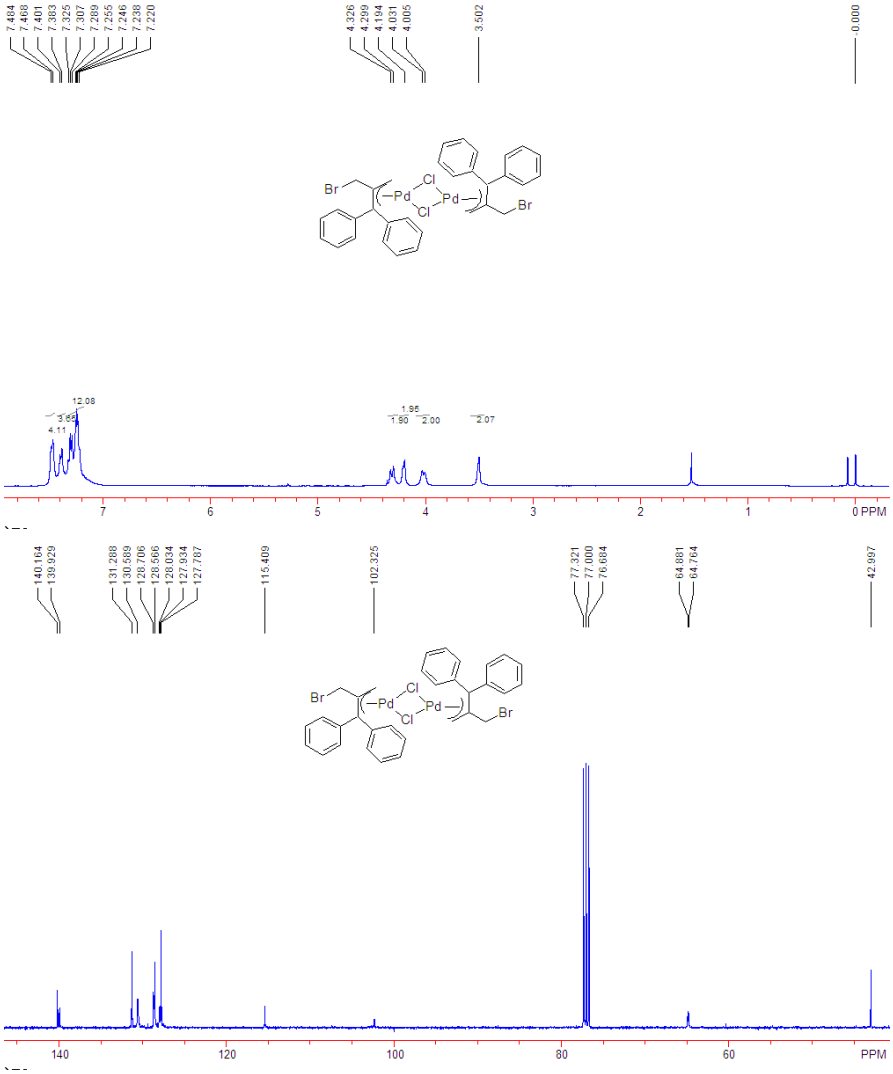
Product **6**. A yellow solid. Mp: 169 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.47 (s, 2H), 4.18 (s, 4H), 4.28 (s, 2H), 7.14-7.22 (m, 12H, Ar), 7.28 (d, 4H, *J* = 6.9 Hz, Ar), 7.41 (d, 4H, *J* = 6.6 Hz, Ar), 7.94 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 62.2, 97.9, 127.6, 127.9, 128.1, 128.6, 129.9, 130.3, 140.6, 140.7. IR (CH_2Cl_2): ν 3446, 2924, 1705, 1490, 1443, 1362, 1220, 1077, 1015, 974, 763 cm^{-1}. MS (ESI) *m/z*:701 (M^+-Cl). HRMS (ESI) Calcd. For $C_{32}H_{30}O_2Cl^{110}Pd_2$ (M^+-Cl) requires: 701.0037; Found: 701.0062.



Product **7**. A yellow solid. Mp: 230 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.93 (d, 6H, J = 3.9 Hz), 0.95 (d, 6H, J = 3.9 Hz), 1.21 (d, 6H, J = 6.6 Hz), 1.46 (d, 6H, J = 6.6 Hz), 2.23 (s, 1H), 2.27 (d, 1H, J = 10.5 Hz), 2.68-2.78 (m, 2H), 2.79 (s, 1H), 3.07-3.16 (m, 2H), 3.74 (d, 1H, J = 9.9 Hz), 6.92-7.13 (m, 10H, Ar), 7.19 (s, 2H), 7.31-7.46 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 22.9, 25.6, 27.0, 28.3, 28.7, 42.8, 48.5, 59.8, 106.7, 116.5, 123.6, 123.9, 124.1, 126.3, 126.8, 127.3, 128.2, 129.7, 130.2, 130.8, 135.8, 140.2, 140.9, 145.9, 146.0, 184.2. IR (CH_2Cl_2): ν 3056, 2964, 2928, 2868, 1596, 1464, 1444, 1404, 1333, 1264, 944, 801 cm^{-1}. MS (ESI) *m/z*: 735 (M^+). HRMS (ESI) Calcd. For $C_{43}H_{50}N_2{}^{37}Cl^{104}Pd$ requires: 735.2673; Found: 735.2679.

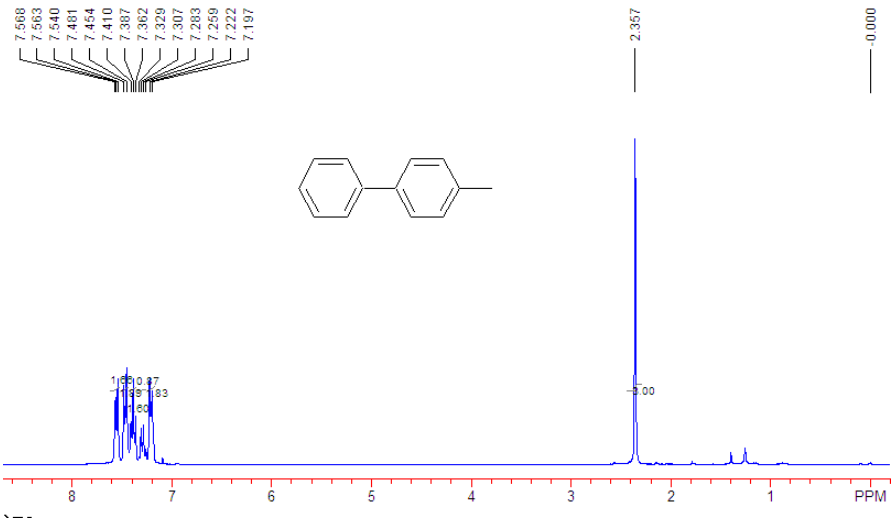


Product **9**. A yellow solid. Mp: 196 ^{o}C (decomposed). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.50 (s, 2H), 4.02 (d, 2H, *J* = 10.4 Hz), 4.20 (s, 2H), 4.31 (d, 2H, *J* = 10.8 Hz), 7.22-7.33 (m, 12H, Ar), 7.39 (d, 4H, *J* = 7.2 Hz, Ar), 7.48 (d, 4H, *J* = 6.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.0, 64.8, 64.9, 102.3, 115.4, 127.8, 127.9, 128.0, 128.6, 128.7, 130.6, 131.3, 139.9, 140.2. IR (CH_2Cl_2): ν 3055, 2926, 1948, 1893, 1673, 1596, 1489, 1443, 1339, 1262, 1158, 1078, 1033, 1019, 923 cm^{-1}. MS (ESI) *m/z*: 818 (M^+-Cl+H). HRMS (ESI) Calcd. For $C_{32}H_{29}Br_2ClPd_2$ requires: 817.8394; Found: 817.9464.

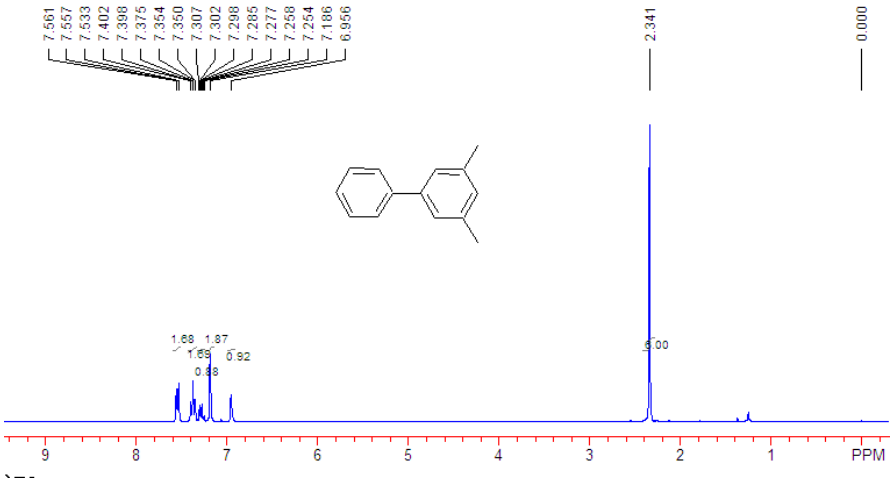


Product **12a**.[1] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.36 (s, 3H), 7.21 (d, 2H, J = 7.8 Hz, Ar), 7.26-7.33 (m, 1H, Ar), 7.39 (t, 2H, J = 7.5 Hz, Ar), 7.47 (d, 2H, J = 7.8 Hz, Ar), 7.54-7.57 (m, 2H, Ar).

(1) Shi, M.; Qian, H.-X. *Tetrahedron* **2005**, *61*, 4949-4955.

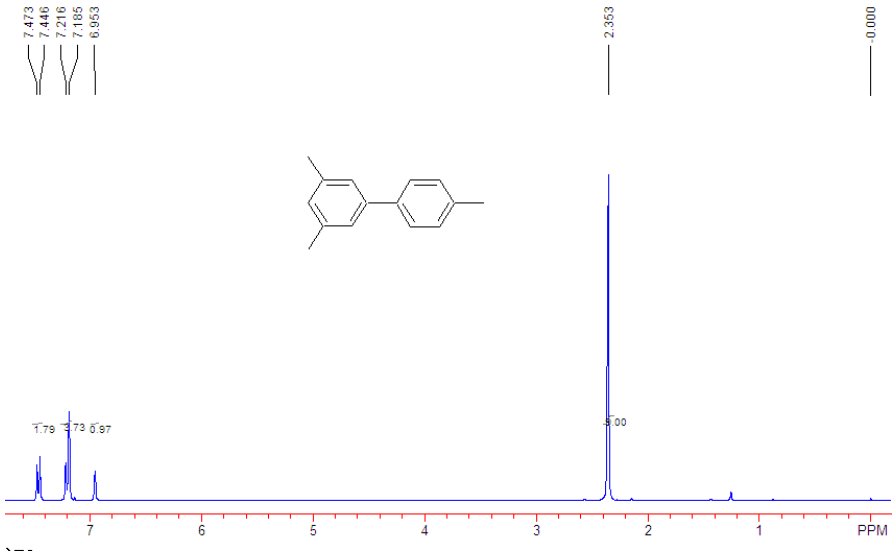


Product **12b**.[1] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (s, 6H), 6.96 (s, 1H, Ar), 7.19 (s, 2H, Ar), 7.25-7.31 (m, 1H, Ar), 7.35-7.40 (m, 2H, Ar), 7.53-7.56 (m, 2H, Ar).

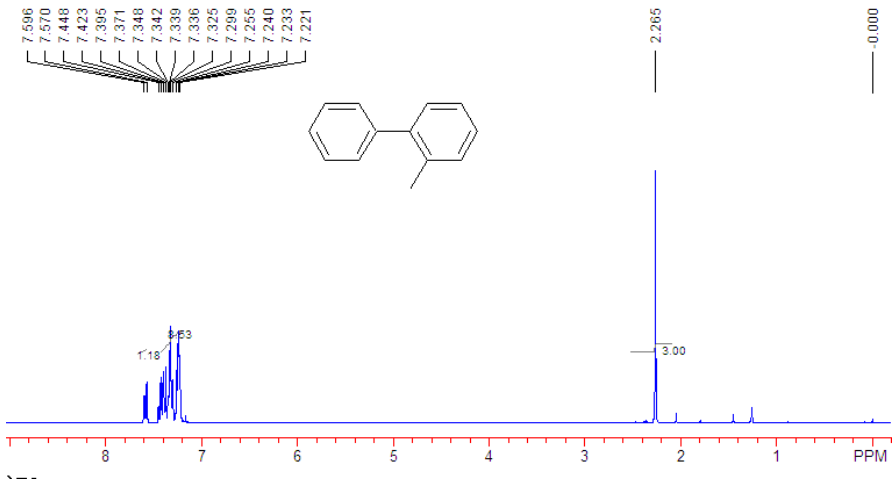


Product **12c**.[2] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.35 (s, 9H), 6.95 (s, 1H, Ar), 7.19-7.22 (m, 4H, Ar), 7.46 (d, 2H, J = 8.1 Hz, Ar).

(2) Voegtle, F.; Steinhagen, G. *Chem. Ber.* **1978**, *111*, 205–212.

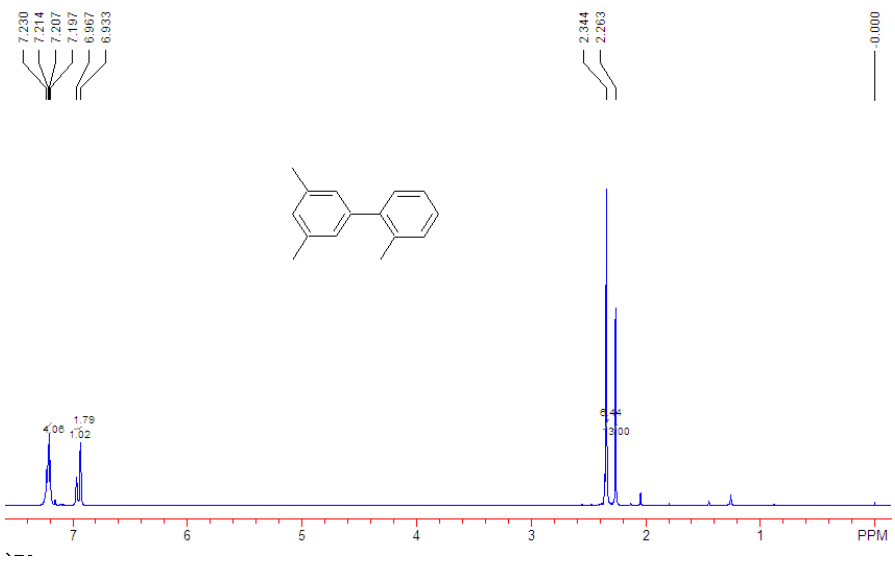


Product **12d**.[1] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.27 (s, 3H), 7.22-7.45 (m, 8H, Ar), 7.58 (d, 1H, J = 7.8 Hz, Ar).

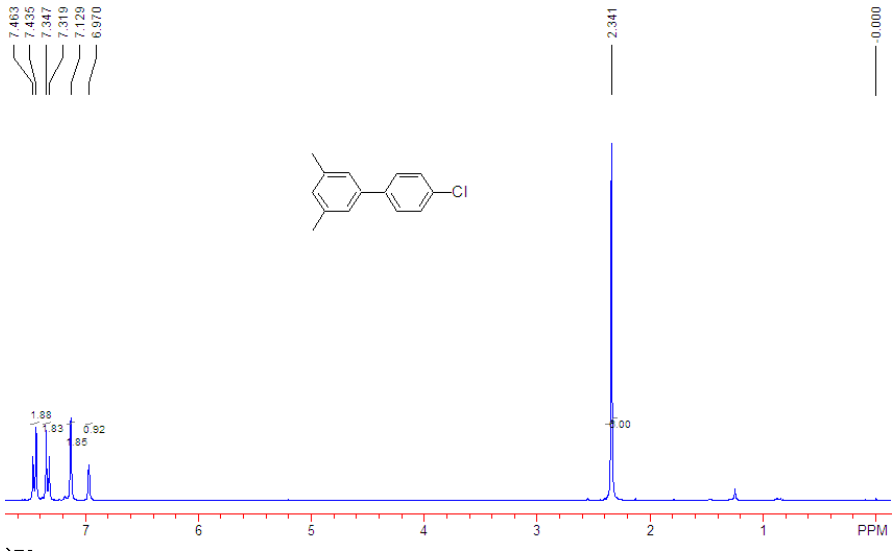


Product **12e**.[3] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.26 (s, 3H), 2.34 (s, 6H), 6.93 (s, 2H, Ar), 6.97 (s, 1H, Ar), 7.20-7.23 (m, 4H, Ar).

(3) So, C.-M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8059-8063.



Product **12f**.[4] A white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (s, 6H), 6.97 (s, 1H, Ar), 7.13 (s, 2H, Ar), 7.33 (d, 2H, J = 8.4 Hz, Ar), 7.45 (d, 2H, J = 8.4 Hz, Ar).



(4) Gregory, N .L. *J .Chem. Soc. B* **1968**, 295-299.