Supporting Information

Benzyloxycalix[8]arene : new valuable support for NHC palladium complexes in C-C Suzuki-Miyaura couplings

Ibrahim Abdellah,[a] Pauline Kasongo,[a] Axel Labattut,[a] Régis Guillot,[a] Emmanuelle Schulz,[a] Cyril Martini,[a,b]* Vincent Huc[a]*

Table of Contents

a Dr. I. Abdellah, P. Kasongo, A. Labattut, Dr. R. Guillot, Dr. E. Schulz, Dr. C. Martini, Dr. V. Huc
Institut de Chimie Moléculaire et des Matériaux d'Orsay
CNRS UMR 8182, Univ. Paris-Sud, Université Paris-Saclay
Bâtiment 420, 91405 Orsay, France
vincent.huc@u-psud.fr

b Dr. C. Martini
Novecal, www.novecal.com
cyril.martini@novecal.com

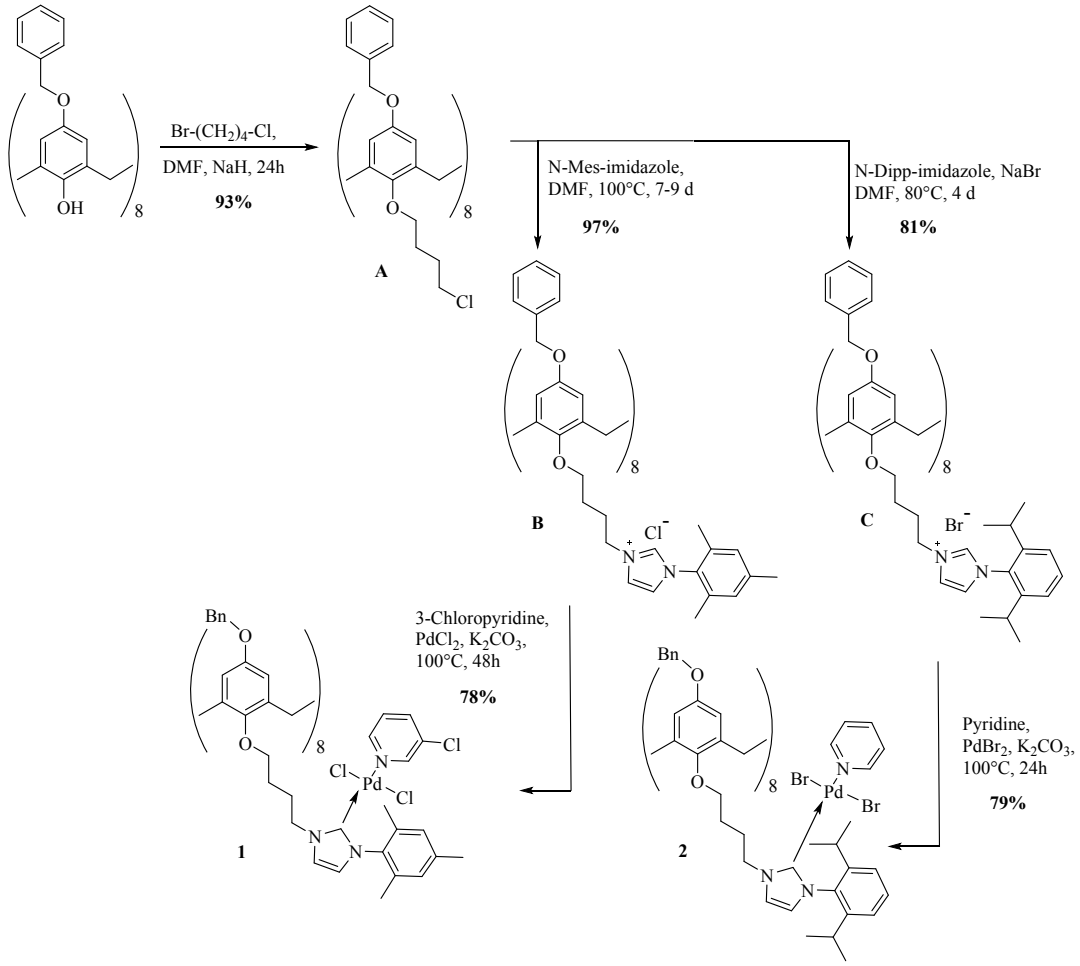
I. General remarks

All reactions were carried out under argon atmosphere and all glassware was flamed before use. THF was distilled over sodium/benzophenone, CH_3CN was distilled over CaH_2 and Methanol (MeOH) was distilled over magnesium. Extra dry Dimethyformamide (DMF), Toluene, Ethanol (EtOH), *n*-Propanol (nPrOH), *n*-Butanol (nBuOH), *iso*-propanol (iPrOH), *tert*-Butanol (tBuOH) were purchased from ACROS and Alfa Aesar. Sodium hydride (NaH), potassium carbonate (K_2CO_3), potassium phosphate (K_3PO_4), sodium acetate (NaOAc), potassium hydroxide (KOH), sodium bromide (NaBr), palladium chloride, palladium bromide, pyridine, 3-choloropyridine and 1-bromo-4-chlorobutane were purchased from Aldrich, Alfa Aesar, VWR, TCI and Strem. tBuCalix[8]arene was purchased from Aldrich. All commercially available reagents were used as received. Benzyloxy[8]calixarene was purchased from NOVECAL; 1-mesityl-1H-imidazole and 1-(2,6-diisopropylphenyl)-1H-imidazole were prepared by previously reported procedures.[1] Complexes **4** and **5** were prepared by previously reported procedures.[2] ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on either a Bruker DPX 250, Brucker 300 MHz, Brucker Avance 360 MHz, Brucker 400 (400 MHz) or Bruker DRX 400 (400 MHz) instrument and data are reported in ppm with the solvent signal as reference. The HRMS analyses were performed with a MicroTOFq (quadrupole coupled with TOF analyzer). Gas chromatography (GC) analyses were performed on a Varian 430-GC gas chromatograph and GC-MS analyses were performed on a DSQ (Thermo Scientific). Elemental analyses were performed by the microanalysis service of the Institut de Chimie des Substances Naturelles in Gif-Sur-Yvette. ICP-MS analyses were performed by IRAMIS (CEA-Saclay).

[1] (a) A. Koch, S. Krieck, H. Görls, M. Wsterhause, *Organometallics*, 2017, **36**, 994-1000. (b) Z. Wang, Y. Yu, Y. X. Zhang, S. Z. Li, H. Qian, Z. Y. Li*, Green. Chem*. 2015, **17**, 413-420.

[2] C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ*, Chem. Eur., J.* 2006, **12**, 4743-4748.

II. Synthetic procedure for catalysts 1, 2 and 3



Compound A

A dry and argon flushed 500 mL schlenk flask, equipped with a magnetic stirring bar, was charged with benzyloxycalix[8]arene (60 g, 35.3 mmol), 1-bromo-4-cholorobutane (520 mL, 300 mmol) and anhydrous DMF (90 mL). The mixture was heated at 40°C and sodium hydride (60% in oil) (22.6 g, 565 mmol) was added in three portions with intervals of 90 min between each addition. The mixture was stirred overnight at 30°C. 350 mL of DCM were added and the suspension was filtered on a Celite pad. The filtrate was evaporated to dryness. 2 L of methanol were added and the resulting mixture was stirred at room temperature over 24 h. The solid was filtered and dried under vacuum to afford the desired product as a white solid (80 g, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.13-7.25 (m, 40H), 6.52 (s, 16H), 4.67 (s, 16H), 3.93 (s, 16H), 3.61 (t, *J*= 5.6 Hz, 16H), 3.41 (t, *J*= 6.3 Hz, 16H), 1.80-1.87 (m, 16H), 1.71-1.78 (m, 16H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ=154.8, 149.2, 137.1, 134.8, 128.4, 127.8, 127.6, 115.0, 72.8, 69.9, 45.1, 30.4, 29.5, 27.7.

HRMS (ESI, positive mode): calcd (m/z) for $C_{144}H_{152}NaCl_8O_{16}$ [M+Na] 2439.8481. Found 2439.8421.

Compound B

In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **A** (10.1 g, 4.2 mmol) and 1-mesityl-1H-imidazole (25 g, 134.2 mmol) were dissolved in dry DMF (200 mL). The reaction mixture was stirred at 100°C under argon for 7 days. After evaporation of DMF, the residue was dissolved in DCM (200 mL) and precipitated with Et_2O (300mL). The solid was filtrated and washed with Et_2O affording a brown solid (15.5 g, 97%).

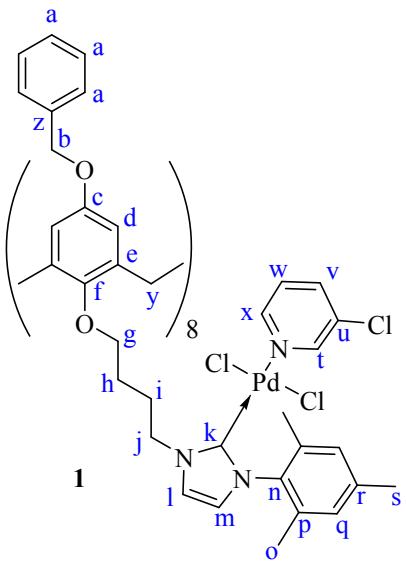
^{1}H NMR (400 MHz, DMSO-d_6): δ=10.12 (bs, 8H), 8.25 (bs, 8H), 7.97 (s, 8H), 7.07 (s, 56H), 6.50 (bs, 16H), 4.61 (bs, 16H), 4.41 (bs, 16H), 3.91 (bs, 16H), 3.72 (bs, 16H), 2.29 (s, 24H), 1.95-2.07 (m, 64H), 1.67 (bs, 16H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ=154.0, 148.2, 140.1, 137.6, 136.7, 134.7, 134.0, 131.0, 129.2, 128.0, 127.5, 127.3, 123.8, 123.0, 114.3, 72.5, 68.8, 48.6, 29.4, 26.1, 25.9, 20.5, 16.8.
HRMS (ESI, positive mode): calcd (m/z) for $C_{240}H_{264}Cl_6N_{16}O_{16}$ $[M-2Cl]^{2+}/2$ 1917.9228. Found 1917.9127

Compound C

In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **A** (3 g, 1.24 mmol), 1-(2,6-diisopropylphenyl)-1H-imidazole (4.24 g, 18.57 mmol) and sodium bromide (12.65 g, 124 mmol) were introduced and dry DMF (30 mL) was added under argon. The reaction mixture was stirred at 80°C under argon for 4 days. 20 mL of DCM was added and the mixture was filtrated on a Celite pad. The mixture was evaporated under vacuum and the residue was dissolved in DCM and precipitated with Et_2O. The solid was filtrated and washed with Et_2O affording a white solid (4.62 g, 81 %).

^{1}H NMR (400 MHz, DMSO-d_6): δ=9.95 (bs, 8H), 8.25 (bs, 8H), 8.11(s, 8H), 7.61 (dd, J = 7.8 Hz, 8H), 7.42 (d, J = 7.8 Hz, 16H), 7.03 (bs, 40H), 6.51 (bs, 16H), 4.45-4.58 (m, 32H), 3.78-3.90 (m, 32H), 2.21 (sept, J = 6.6 Hz, 16H), 2.08 (bs, 16H), 1.71 (bs, 16H), 1.07-1.09 (m, 96H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ=154.1, 148.0, 144.9, 137.6, 136.6, 134.9, 131.4, 130.4, 128.1, 128.0, 127.4, 127.2, 125.1, 124.3, 123.3, 114.2, 72.8, 68.8, 54.9, 48.9, 28.0, 26.2, 26.0, 23.7, 23.5.
HRMS (ESI, positive mode): calcd (m/z) for $C_{264}H_{312}Br_5N_{16}O_{16}$ $[M-3Br]^{3+}/3$ 1452.3331. Found 1452.3827.

Complex 1

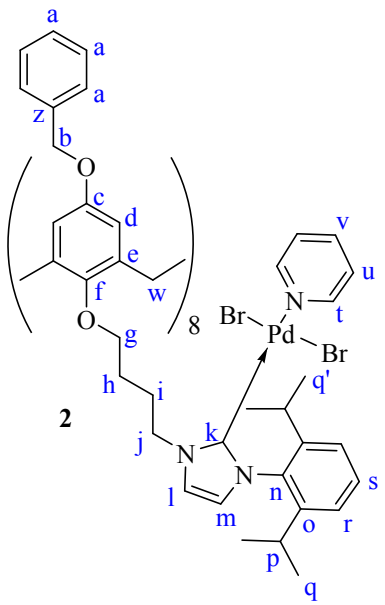


1

In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **B** (3 g, 0.79 mmol), palladium chloride (1.5 g, 8.5 mmol) and potassium carbonate (3 g, 21.7 mmol) were introduced and 3-chloropyridine (25 mL) was added under argon. The reaction mixture was stirred at 100°C under argon for 48 hours. DCM (60 mL) was added and the mixture was centrifuged. The mixture was filtrated and evaporated under vacuum. The residue was dissolved in DCM and precipitated with Et_2O. The solid was filtrated and washed with Et_2O affording a yellowish solid after drying under vacuum (3.61 g, 78 %). Crystals suitable for X-ray analysis could be successfully grown by slow diffusion of Et_2O in DCM/acetonitrile mixture.

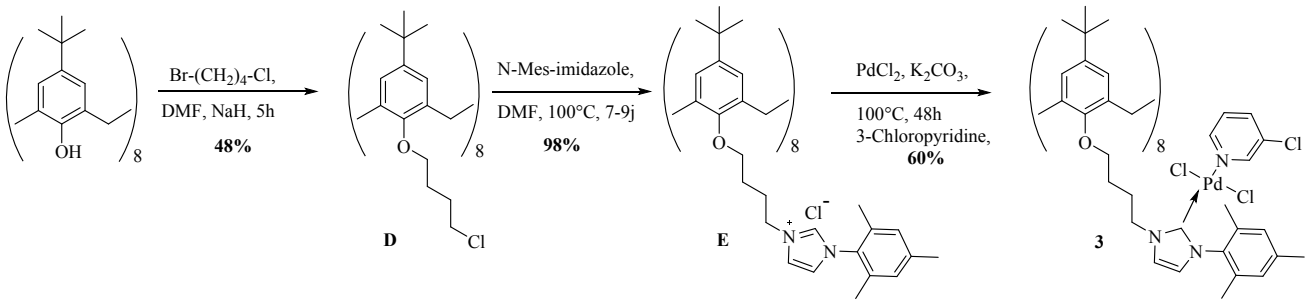
^{1}H NMR (400 MHz, DMSO-d_6): δ=8.58-8.65 (m, 16H, H-t + H-x), 7.94-7.96 (m, 8H, H-w), 7.49 (bs, 8H, H-l), 7.37 (bs, 8H, H-v), 7.24 (s, 8H, H-m), 6.97-7.03 (m, 56H, H-a + H-q), 6.50 (bs, 16H, H-d), 4.65 (bs, 32H, H-b + H-j), 3.86-3.94 (m, 32H, H-g + H-y), 2.23-2.27 (m, 40H, H-i + H-s), 2.10 (s, 48H, H-o), 1.75-1.80 (m, 16H, H-h).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ=154.0 (C-c + C-f), 148.9 (C-t), 148.5 (C-x), 146.7 (C-k), 138.2 (C-r + C-w), 136.8 (C-z + C-e), 135.8 (C-p), 134.8 (C-n), 131.1 (C-u), 128.7 (C-q), 128.0 (C-a), 127.3 (C-a), 125.5 (C-v), 124.6 (C-m), 122.8 (C-l), 114.3 (C-d), 73.1 (C-g), 68.8 (C-b), 50.0 (C-j), 29.6 (C-y), 26.5 (C-h + C-i), 20.5 (C-s), 18.4 (C-o).
Anal. Calcd for $C_{280}H_{288}Cl_{24}N_{24}O_{16}Pd_8$. C, 56.54; H, 4.88; N, 5.65. Found: C, 55.92; H, 4.78; N, 5.73.

Complex 2



In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **C** (0.3 g, 0.065 mmol), palladium bromide (0.15 g, 0.55 mmol) and potassium carbonate (0.36 g, 2.6 mmol) were introduced and pyridine (3 mL) was added under argon. The reaction mixture was stirred at 100°C under argon for 24 hours. DCM (20 mL) was added and the mixture was centrifuged. The mixture was filtrated and evaporated under vacuum. The residue was dissolved in DCM and precipitated with Et_2O. The solid was filtrated and washed with Et_2O affording a yellow solid after drying under vacuum (0.35 g, 79 %).

^{1}H NMR (400 MHz, DMSO-d_6): δ=8.53 (s, 16H, H-t), 7.75 (bs, 8H, H-v), 7.46-7.48 (m, 24H, H-m + H-l + H-s), 7.25-7.32 (m, 32H, H-a), 7.05-7.09 (m, 40H, H-r + H-u), 6.56 (bs, 16H, H-d), 4.59-4.70 (m, 32H, H-b + H-j), 3.93 (bs, 32H, H-g + H-w), 2.86 (bs, 16H, H-p), 2.35 (bs, 16H, H-i), 1.86 (bs, 16H, H-h), 1.26-1.27 (m, 48H, H-q), 0.93-0.94 (m, 48H, H-q').
^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ=154.1 (C-c), 151.7 (C-t), 148.5 (C-k + C-f), 146.4 (C-o), 138.2 (C-v), 136.8 (C-z), 134.9 (C-e), 134.6 (C-n), 129.9 (C-s), 128.0 (C-a), 127.2 (C-a), 126.9 (C-l/m), 124.5 (C-u), 123.6 (C-r), 122.0 (C-l/m), 114.4 (C-d), 73.3 (C-g), 68.8 (C-b), 50.8 (C-j), 29.5 (C-w), 28.0 (C-p), 26.6 (C-h + C-i), 26.0 (C-q), 23.1 (C-q').
Anal. Calcd for $C_{304}H_{344}Br_{16}N_{24}O_{16}Pd_8$. C, 54.33; H, 5.16; N, 5.00. Found: C, 55.01; H, 5.25; N, 4.54.



Compound D

A dry and argon flushed 250 mL schlenk flask, equipped with a magnetic stirring bar, was charged with *tert*-butylcalix[8]arene (5 g, 3.85 mmol), 1-bromo-4-cholorobutane (38.2 mL, 33.1 mmol) and anhydrous DMF (10 mL). The mixture was heated at 40°C and sodium hydride (60% in oil) (2.47 g, 61.7 mmol) was added in three portions with intervals of 60 min between each addition. The mixture was stirred for 5 hours at 30°C. 50 mL of DCM were added and the residue was filtrated on a Celite pad and washed with DCM. The solvent was evaporated at reduced pressure. 200 mL of methanol were added and stirred at room temperature overnight. The solid was filtrated and triturated in ethanol. After drying under vacuum, the desired product was obtained as a white solid (3.3 g, 42 %).

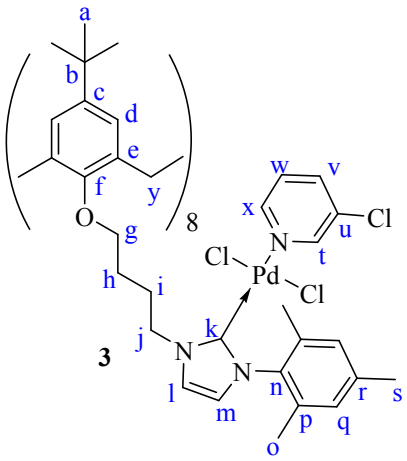
^{1}H NMR (400 MHz, $CDCl_3$): δ=6.94 (s, 16H), 4.03 (s, 16H), 3.53 (s, 16H), 3.43 (t, *J*= 6.4 Hz, 16H), 1.84-1.87 (m, 16H), 1.70 (bs, 16H), 1.09 (s, 72H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ=153.1, 146.0, 132.8, 125.9, 72.1, 44.9, 34.3, 31.5, 29.9, 29.6, 27.8.
HRMS (ESI, positive mode): calcd (m/z) for $C_{120}H_{168}NaCl_8O_8$ $[M+Na]^+$ 2040.0140. Found 2040.0141.

Compound E

In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **D** (1 g, 0.50 mmol) and 1-mesityl-1H-imidazole (2.95 g, 15.8 mmol) were dissolved in dry DMF (10 mL). The reaction mixture was stirred at 100°C under argon for 9 days. At room temperature, the product was precipitated with Et_2O. The precipitate was filtrated and washed with Et_2O affording a white solid (1.7 g, 98 %).

^{1}H NMR (400 MHz, DMSO-d_6): δ=10.23 (s, 8H), 8.38 (s, 8H), 8.06 (s, 8H), 7.11 (s, 16H), 6.89 (bs, 16H), 4.51 (s, 16H), 4.00 (bs, 16H), 3.66 (bs, 16H), 2.32 (s, 24H), 2.12 (bs, 16H), 1.99 (s, 48H), 1,70 (bs, 16H), 0.86-1.25 (m, 72H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ=152.6, 145.1, 140.1, 137.7, 134.1, 132.6, 131.1, 129.2, 125.3, 123.8, 123.1, 72.1, 48.8, 33.8, 33.6, 31.0, 29.0, 26.3, 20.5, 16.9, 15.1.
HRMS (ESI, positive mode): calcd (m/z) for $C_{216}H_{280}Cl_5N_{16}O_8$ $[M-3Cl]^{3+}$/3 1133.6807. Found 1133.6865.

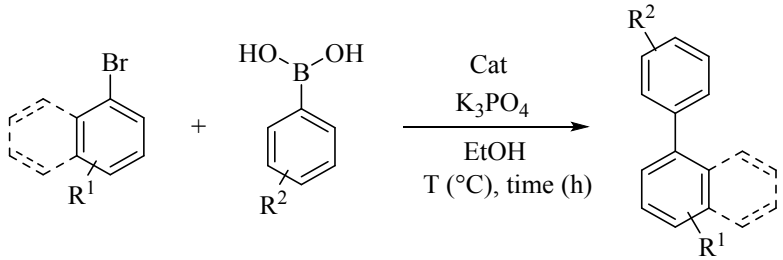
Complex 3



In a schlenk flask equipped with a magnetic stirring bar and flushed with argon, compound **E** (0.5 g, 0.14 mmol), palladium chloride (0.261 g, 1.5 mmol) and potassium carbonate (0.586 g, 4.24 mmol) were introduce and 3-chloropyridine (3 mL) was then added under argon. The reaction mixture was stirred at 100°C under argon for 36 hours. DCM (10 mL) was added and the mixture was centrifuged. The mixture was filtrated and evaporated under vacuum. The residue was dissolved in DCM and precipitated with Et_2O and pentane. The solid was filtrated and washed with Et_2O affording a yellowish solid after drying under vacuum (0.469 g, 60 %).

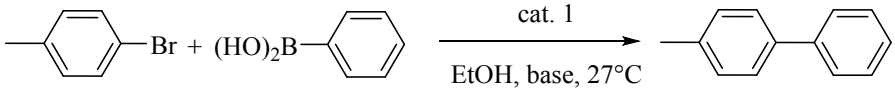
^{1}H NMR (400 MHz, DMSO-d_6): δ=8.58-8.62 (m, 16H, H-t + H-x), 7.99 (bs, 8H, H-w), 7.53 (s, 8H, H-l), 7.30-7.53 (m, 16H, H-m + H-v), 6.91-6.98 (m, 32H, H-d + H-q), 4.69 (bs, 16H, H-j), 3.80-4.02 (m, 32H, H-g + H-y), 2.28-2.40 (m, 40H, H-I + H-s), 2.10 (s, 48H, H-o), 1.81 (bs, 16H, H-h), 0.96 (s, 72H, H-a).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ=152.6 (C-f), 149.0 (C-t + C-x), 148.5 (C-k), 146.8 (C-c), 145.0 (C-r), 138.6 (C-w), 138.2 (C-d), 135.8 (C-n), 134.8 (C-p), 132.8 (C-u), 131.1 (C-e), 128.7 (C-q), 125.6 (C-v), 124.7 (C-m), 122.7 (C-l), 72.3 (C-g), 50.0 (C-j), 33.6 (C-b), 31.0 (C-a), 29.5 (C-y), 26.6 (C-h + C-i), 20.6 (C-s), 18.4 (C-o).
Anal. Calcd for $C_{256}H_{304}Cl_{24}N_{24}O_8Pd_8$. C, 55.43; H, 5.52; N, 6.06. Found: C, 55.56; H, 5.70; N, 5.85.

III. General procedure to perform the catalytic Suzuki-Miyaura couplings



A Schlenk tube equipped with a magnetic stirring, was charged with arylhalide (1 mmol), boronic acid (1.5 mmol), K_3PO_4 (2 mmol) and catalyst (Pd content, x mol%). The flask was evacuated and backfilled with argon three times. The reaction mixture was stirred at 27°C or 80°C for two (or more) hours. The mixture was then filtrated and the solutions was evaporated under reduce pressure. The residue was washed with water and extracted with DCM. The organic layer was dried over $MgSO_4$ and concentrated under reduce pressure. The crude product was purified by column chromatography on silica gel, with (EtOAc/n-pentane) as eluent to afford the targeted bisarenes.

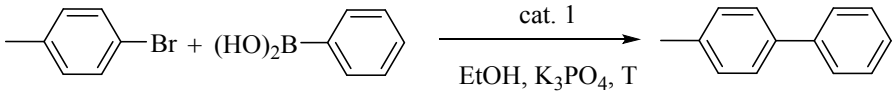
Table S1. Optimization of reaction conditions; nature of the base, substrate concentration



Entry	Base	t (h)	[Substrate] (Mol.l^{-1})	Conv (%)[a,b]
1	K_3PO_4	2	0.25	98
2	K_2CO_3	24	0.25	92
3	AcONa	23	0.25	29
4	KOH	23	0.25	64
5	K_3PO_4	2	0.17	93
6	K_3PO_4	2	0.5	99 (93)[c]

[a] Bromotoluene (1 equiv.), phenylboronic acid (1.5 equiv.), base (2 equiv.), cat **1** (0.5 mol%), at 27°C in ethanol, under argon atmosphere. [b] Conversion determined by GC analysis (see SI). [c] Isolated yield.

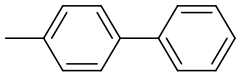
Table S2. Optimization of reaction conditions; catalyst loading



Entry	Pd (mol%)	T (°C)	Conv (%)[a,b]	Yield[c] (%)
1	0.1	27	98	90
2	0.05	27	92	81
3	0.05	40	97	85
4	0.01	27	70	nd
5	0.01	40	91	87
6	0.005	40	81	nd
7	0.005	80	92	84
8	0.001	80	93	71

[a] Bromotoluene (1 equiv., 0.50 M), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.), cat **1** in ethanol for 2 h, under argon atmosphere. [b] Conversion determined by GC analysis (see SI). [c] Isolated yield, nd = not determined.

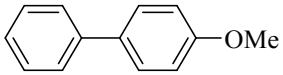
IV. Description of Suzuki-Miyaura coupling products



4-methyl-1,1'-biphenyl:[3] 90 % (151 mg, 0.90 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 1-bromo-4-methylbenzene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.1 mol% Pd) in EtOH (0.5M) at RT.

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.60-7.62 (m, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.43-7.45 (m, 2H), 7.33-7.38 (m, 1H), 7.27-7.29 (m, 2H), 2.43 (s, 3H).

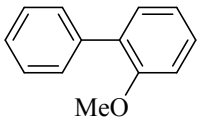
MS (IE): 168.



4-methoxy-1,1'-biphenyl:[4] 84 % (155 mg, 0.84 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 1-bromo-4-methoxybenzene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.05 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.57 (m, 4H), 7.42 (t, *J* = 7.5, 2H), 7.27-7.7.28 (m, 1H), 6.98 (d, *J* = 8.8, 2H), 3.86 (s, 3H).

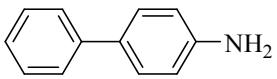
MS (IE): 184.0.



2-methoxy-1,1'-biphenyl:[4] 87 % (161 mg, 0.87 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 1-bromo-2-methoxybenzene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (1 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.54-7.58 (m, 2H), 7.41-7.47 (m, 2H), 7.37 – 7.28 (m, 3H), 7.08 (dd, *J* = 1.0, 7.4 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{13}H_{12}NaO$ 207.0780 $[M+Na]^+$. Found 207.0779.

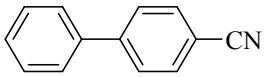


[3] S. Santra, P. K. Hota, R. Bhattacharyya, P. Bera, P. Ghosh, S. K. Mandal, *ACS. Catal.,* 2013, **3**, 2776-2789.
[4] X. Li, C. Liu, L. Wang, Q. Ye, Z. Jin, *ChemistrySelect*, 2017, **2**, 4061-4020.

1,1'-biphenyl-4-amine:[5] 89 % (150 mg, 0.89 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/1), obtained from 4-bromoaniline (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.01 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 7.50 (d, *J* = 7.7 Hz, 2H), 7.31-7.37 (m, 4H), 7.18 (t, *J* = 7.2, 1H), 6.61 (d, J = 8.5 Hz, 2H), 5.22 (s, 3H).

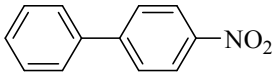
HRMS (ESI, positive mode): calcd (m/z) for $C_{12}H_{12}N$ 170.0964 $[M+H]^+$. Found 170.0966.



1,1'-biphenyl-4-carbonitrile:[3] 93 % (166 mg, 0.93 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 2:8), obtained from 4-bromobenzonitrile (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.05 mol% Pd) in EtOH (0.5M) at RT.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.6, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.61 (m, 2H), 7.39-7.52 (m, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{13}H_{10}N$ 180.0808 $[M+H]^+$. Found 180.0807.

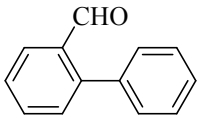


4-nitro-1,1'-biphenyl:[3] 99 % (198 mg, 0.80 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 2:8), obtained from 4-bromobenzonitrile (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.01 mol% Pd) in EtOH (0.5M) at 40°C.

80 % (166 mg, 0.80 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 2:8), obtained from 4-chlorobenzonitrile (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.5 mol% Pd) in *n*-BuOH (0.5M) at 100°C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.9, Hz, 2H), 7.74 (d, *J* = 8.9, Hz, 2H), 7.61-7.64 (m, 2H), 7.42 – 7.53 (m, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{12}H_9NNaO_2$ 222.0525 $[M+Na]^+$. Found 222.0535.

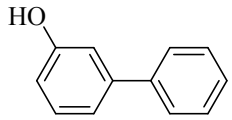


1,1'-biphenyl-2-carbaldehyde:[5] 87 % (159 mg, 0.87 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 2-bromobenzaldehyde (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (0.5 mol% Pd) in EtOH (0.5M) at 80°C.

[5] X. Cheng, W. Li, R. Nie, X. Ma, R. Sang, L. Guo, Y. Wu, *Adv. Synth. Catal.,* 2017, **359**, 454-466.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 8.03 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.65 (td, *J* = 1.4, 7.5 Hz, 1H), 7.44 – 7.52 (m, 5H), 7.37 – 7.40 (m, 2H).

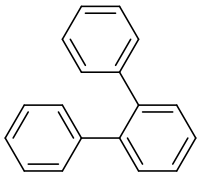
HRMS (ESI, positive mode): calcd (m/z) for $C_{13}H_{11}O$ 183.0804 $[M+H]^+$. Found 183.0805.



Biphenyl-3-ol:[5] 88 % (149 mg, 0.88 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 3-bromophenol (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (0.5 mol % Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.55-7.58 (m, 2H), 7.41-7.45 (m, 2H), 7.31-7.37 (m, 2H), 7.17 (d, *J* = 7.8, 1H), 7.06-7.07 (m, 1H), 6.82 (ddd, *J* = 0.9, 2.5, 7.9 Hz, 1H), 4.73 (s, 1H).

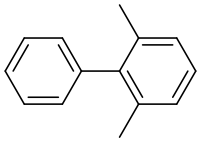
HRMS (ESI, positive mode): calcd (m/z) for $C_{12}H_{11}O$ [M+H] 171.0804. Found 171.0801.



1, 2-diphenylbenzene:[6] 83 % (192 mg, 0.83 mmol) isolated yield, after purification by silica gel column chromatography (cyclohexane 100%), obtained from 1,2-dibromobenzene (1 equiv.), phenylboronic acid (2.5 equiv.), K_3PO_4 (3 equiv.) and complex **2** (2 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 0.7 Hz, 4H), 7.18-7.22 (m, 6H), 7.13-7.15 (m, 4H).

MS (IE): 230.0.

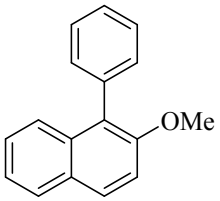


2,6-dimethylbiphenyl:[6] 76 % (138 mg, 0.76 mmol) isolated yield, after purification by silica gel column chromatography (cyclohexane 100%), obtained from 2,6-dimethybromobenzene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (2 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.40-7.45 (m, 2H), 7.31-7.36 (m, 1H), 7.10-7.19 (m, 5H), 2.03 (s, 6H).

MS (IE): 182.0.

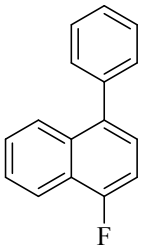
[6] Y. Ramakrishna, N. D. Reddy, *Dalton trans.* 2017, **46**, 8598-8610.



2-methoxy-1-phenylnaphthalene:[7] 95 % (222 mg, 0.95 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 2/8), obtained from 1-bromo-2-methoxynaphthalene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (1 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, CDCl3): δ = 7.87 (d, *J* = 8.6 Hz, 1H), 7.80-7.83 (m, 1H), 7.46-7.51 (m, 3H), 7.30-7.40 (m, 6H), 3.82 (s, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{17}H_{14}NaO$ $[M+Na]^+$ 257.0936. Found 257.0935.



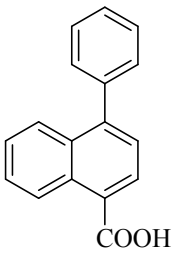
1-fluoro-4-phenylnaphthalene: 94 % (209 mg, 0.94 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane, 1/9), obtained from 1-bromo-4-fluoronaphthalene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.05 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.54-7.58 (m, 1H), 7.41 – 7.52 (m, 6H), 7.35 (dd, *J* = 4.4, 7.9, Hz, 1H), 7.20 (dd, *J* = 6.0, 10.2 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.5, 157.0, 140.1, 136.3 (d, *J* = 3.9 Hz), 132.9 (d, *J* = 4.4 Hz), 130.1, 128.3, 127.3, 126.9, 126.5 (d, *J* = 8.4 Hz), 126.0, 123.8 (d, *J* = 16.3 Hz), 120.7 (d, *J* = 5.8 Hz), 108.9 (d, *J* = 19.9 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ = -124.1.

MS (IE): 222.0.



4-phenyl-1-naphthoic acid: 95 % (235 mg, 0.95 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 2/8 and 0.2% AcOH), obtained from 4-

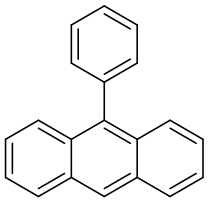
[7] M. Lukeman, H. Simon, P. Wan, Y. H. Wang, *J. Org. Chem*., 2015, **80**, 11281-11293.

bromo-1-naphthoic acid (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.5 mol % Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.01 (s, 1H), 9.17 (d, *J* = 8.7 Hz, 1H), 8.43 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.65-7.69 (m, 1H), 7.48 – 7.53 (m, 8H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 173.4, 146.9, 140.2, 132.4, 132.2, 131.4, 130.0, 128.5, 128.1, 128.0, 127.1, 126.5, 126.2, 125.9, 125.1.

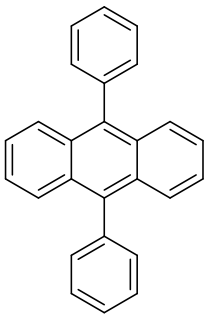
HRMS (ESI, negative mode): calcd (m/z) for $C_{17}H_{11}O_2$ 247.0765 $[M-H]^-$. Found 247.0769.



9-phenylanthracene:[8] 95 % (242 mg, 0.95 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 1/9), obtained from 9-bromoanthracene (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **2** (0.1 mol% Pd) in EtOH (0.25M) at 80°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.04 (d , *J* = 8.5 Hz, 2H) , 7.67 (dd , *J* = 1.0, 2.0 Hz, 2H), 7.64 (dd , *J* = 1.0, 2.0 Hz, 2H), 7.52-7.61 (m, 3H), 7.41-7.46 (m, 4H), 7.31-7.37 (m, 2H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{20}H_{15}$ 254.1168 $[M+H]^+$. Found 255.1150.

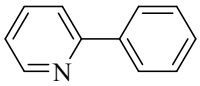


9,10-diphenylanthracene:[9] 97 % (319 mg, 0.97 mmol) isolated yield, after purification by silica gel column chromatography (*n*-pentane 100%), obtained from 9,10-dibromoanthracene (1 equiv.), phenylboronic acid (2.5 equiv.), K_3PO_4 (3 equiv.) and complex **2** (0.2 mol% Pd) in EtOH (0.25M) at 80°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 3.2, 6.8 Hz, 4H), 7.55-7.64 (m, 6H), 7.47-7.51 (m, 4H), 7.33 (dd, *J* = 3.2, 6.8 Hz, 2H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{26}H_{19}$ 331.1481 $[M+H]^+$. Found 331.1464.

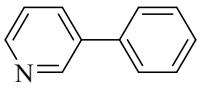
[8] S. Ando, H. Matsunaga, T. Ishizuka, *J. Org. Chem*., 2017, **82**, 1266-1272.
[9] S. Mattiello, M. Rooney, A. Sanzone, P. Brazzo, M. Sassi, L. Beverina, *Org. Lett*. 2017, **19**, 654-657.



2-phenylpyridine:[4] 72 % (112 mg, 0.72 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 2/8 and 4% of Et_3N), obtained from 2-bromopyridine (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (2 mol% Pd) in EtOH (0.25M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.7 Hz, 1H), 7.98 – 8.00 (m, 2H), 7.72 – 7.78 (m, 2H), 7.39 – 7.50 (m, 3H), 7.21-7.25 (m, 1H).

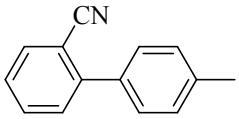
HRMS (ESI, positive mode): calcd (m/z) for $C_{11}H_{10}N$ 156.0808 $[M+H]^+$. Found 156.0811.



3-phenylpyridine:[3] 69 % (107 mg, 0.69 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 2/8 and 4% of Et_3N), obtained from 3-bromopyridine (1 equiv.), phenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (2 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 1.9 Hz, 1H), 8.60 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.86-7.91 (m, 1H), 7.56 – 7.61 (m, 2H), 7.34 – 7.61 (m, 4H).

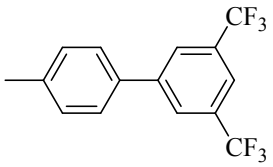
HRMS (ESI, positive mode): calcd (m/z) for $C_{11}H_{10}N$ 156.0807 $[M+H]^+$. Found 156.0814.



4'-methyl-[1,1'-biphenyl]-2-carbonitrile:[4] 95 % (183 mg, 0.95 mmol) isolated yield, after purification by silica gel column chromatography (DCM/*n*-pentane 1/9), obtained from 2-bromobenzonitrile (1 equiv.), 4-methylphenylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.5 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.63 (dt, *J* = 1.3, 7.7 Hz, 1H), 7.39-7.51 (m, 4H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{14}H_{11}NNa$ 216.0783 $[M+H]^+$. Found 216.0794.



4'-methyl-3,5-bis(trifluoromethyl)-1,1'-biphenyl:[10] 77 % (183 mg, 0.77 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 1/9), obtained from 1-bromo-4-methylbenzene (1 equiv.), 3,5-bis(trifluoromethyl)phenyl boronic acid (1.5

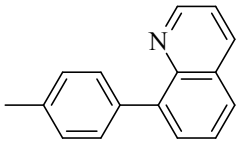
[10] S. K. Gurung, S. Thapa, A. Kafle, D. A. Dickie, R. Giri, *Org. Lett*. 2014, **16**, 1264-1267.

equiv.), K_3PO_4 (2 equiv.) and complex **1** (0.5 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (250MHz, $CDCl_3$): δ = 7.99 (s, 2H), 7.82 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).

^{19}F NMR (235 MHz, $CDCl_3$) δ = - 62.81.

MS (IE): 304.0.



8-(p-tolyl)quinoline:[11] 82 % (179 mg, 0.82 mmol) isolated yield, after purification by silica gel column chromatography (EtOAc/*n*-pentane 1/9), obtained from 1-bromo-4-methylbenzene (1 equiv.), quinolin-8-ylboronic acid (1.5 equiv.), K_3PO_4 (2 equiv.) and complex **1** (2 mol% Pd) in EtOH (0.5M) at 80°C.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.95 (dd, *J* = 1.8, 4.1 Hz, 1H), 8.19 (dd, *J* = 1.8, 8.2 Hz, 1H), 7.81 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.72 (dd, *J* = 1.5, 7.1 Hz, 1H), 7.57 – 7.61 (m, 3H), 7.40 (dd, *J* = 4.1, 8.2 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

HRMS (ESI, positive mode): calcd (m/z) for $C_{16}H_{14}N$ [M+H] 220.1120. Found 220.1123.

V. Preparation of samples for ICP-MS analyses

After a Suzuki-Miyaura reaction, the mixture was filtrated on a Whatman 5 filter; the ethanol solution was then evaporated under reduced pressure. Water was added (10 mL) and the residue was extracted with Et_2O (3x10 mL).The organic layer was finally dried over $MgSO_4$ and concentrated under reduced pressure. The solid was heated under high vacuum at 200°C for 1 h and the residue was mineralized in nitric acid (69%) at 120°C for 2 h.

VI. General procedure for heterogeneous tests

A first Schlenk tube, equipped with a magnetic stirring, was charged with catalyst **1** (0.05 mol%) and ethanol (20 mL), the solution was degassed three times and heated under argon at 80°C for 10min. A second schlenk equipped with a magnetic stirring was charged with 4-bromotoluene, phenylboronic acid and K_3PO_4; this schlenk was evacuated and backfilled with argon three times. The hot solution of the first schlenk was filtrated with a syringe filter (0.2 μm) to the second schlenk under argon. The resulting mixture was heated at 80°C. After 24 hours, no reaction was observed.

[11] J. Kawak, M. Kim, S. Chang, *J. Am. Chem. Soc*., 2011, **133**, 3780-3783.

VII. X-ray analysis of complex 1

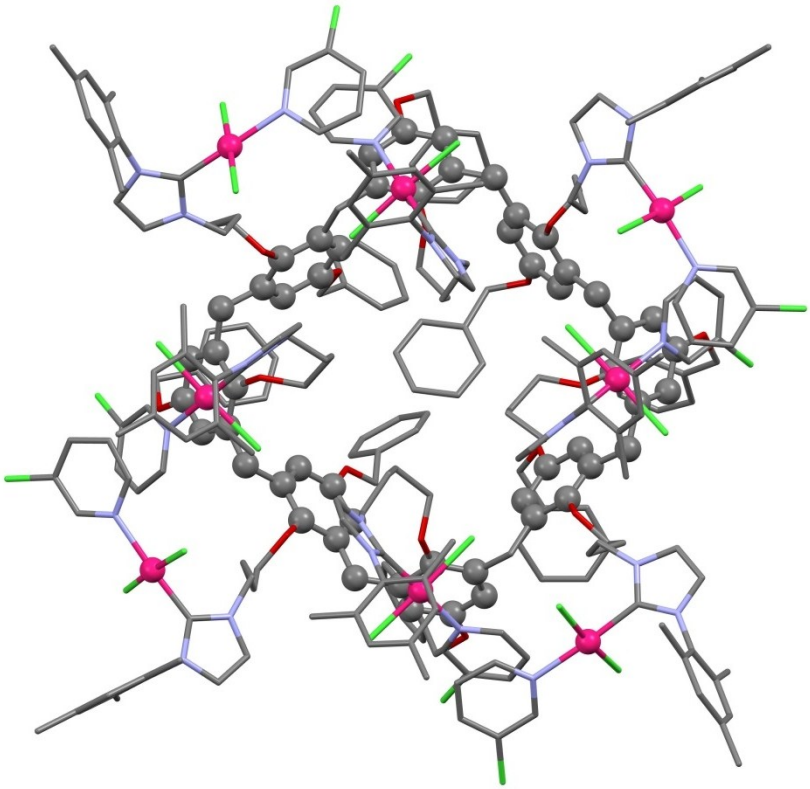


Fig. 1. Compound **1**. Disorder, H atoms and solvent are omitted for clarity.

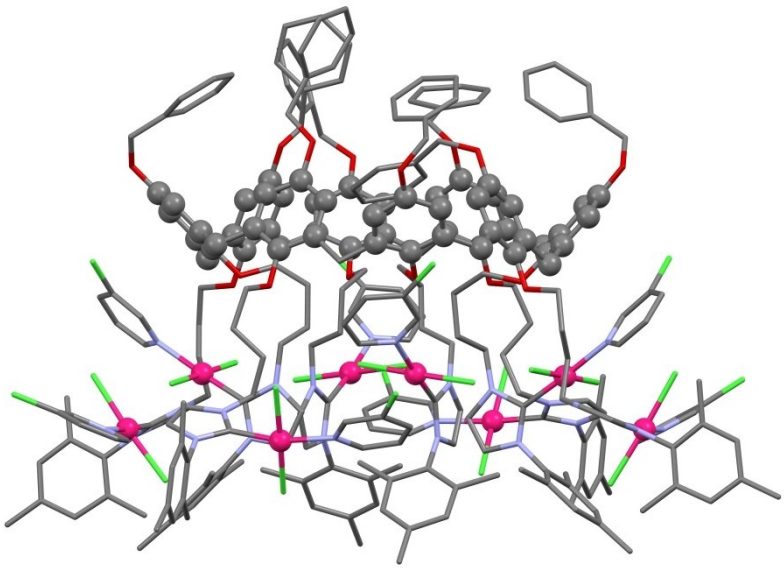


Fig. 2. Compound **1**. Disorder, H atoms and solvent are omitted for clarity.

A suitable crystal was obtained by vapour diffusion of diethyl ether into a dichloromethane/ acetonitrile solution of **1**.

X-ray diffraction data for compound **1** was collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IμS source CuKα radiation. Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value (100K) by means of a N-Helix cooling device to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[12] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2013[13] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[14]

The crystal data collection and refinement parameters are given in Table X1.

CCDC 1541128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

The asymmetric unit of the compound contains one calix[8]arene, diethyl ether and water solvents molecules. Two benzyl groups of the calix[8]arene were disordered on two positions with occupancy factors 0.4791/0.5209. Two diethyl ether and one water molecules were disordered.

The calix[8]arene structure adopts a cone conformation with the benzyloxy substituents interestingly covering the cavity, on the upper side. The stabilization of the cone conformation is due to eight π-π intramolecular interactions between the chloropyridine together with CH-π intramolecular interactions between the 3-chloropyridine and the mesityl rings (cf. Fig 3).

Table X1. Crystallographic data and structure refinement details.

Compound	**1**
Empirical Formula	$C_{294}H_{293}Cl_{24}N_{24}O_{25}Pd_8$
M_r	6264.45
Crystal size, mm^3	0.08 x 0.06 x 0.01
Crystal system	monoclinic
Space group	$P\ 2_1/c$
a, Å	28.057(2)
b, Å	37.109(3)
c, Å	28.306(2)
α, °	90
β, °	90.656(2)

[12] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.
[13] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
[14] L. J. Farrugia, *J. Appl. Cryst*., 1999, **32**, 837-838.

γ, °	90
Cell volume, Å^3	29470(4)
Z ; Z'	4; 1
T, K	100(1)
Radiation type ; wavelength Å	MoKα ; 0.71073
F_{000}	12 804
μ, mm^{-1}	0.760
θ range, °	2.187 - 26.837
Reflection collected	652 167
Reflections unique	61 188
GOF	1.036
Refl. obs. (I>2σ(I))	26 376
Parameters	2 898
wR_2 (all data)	0.2790
R value (I>2σ(I))	0.1004
Largest diff. peak and hole (e-.Å^{-3})	2.903; -1.596

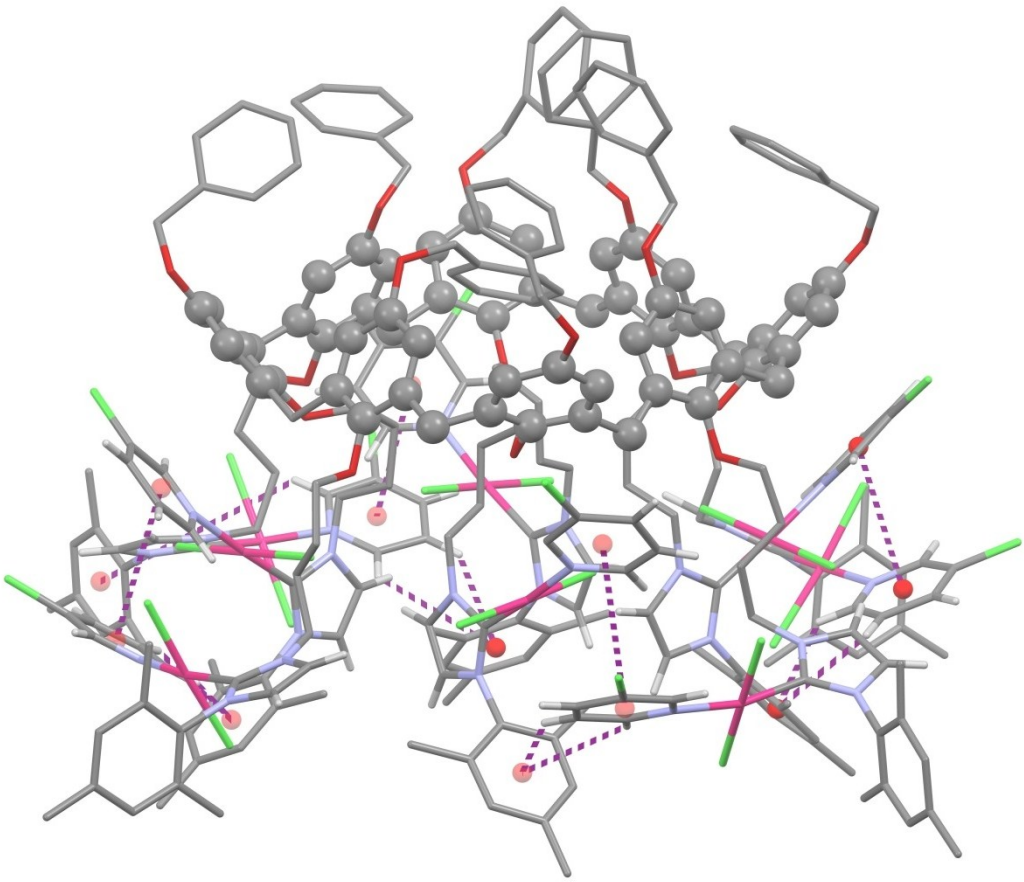
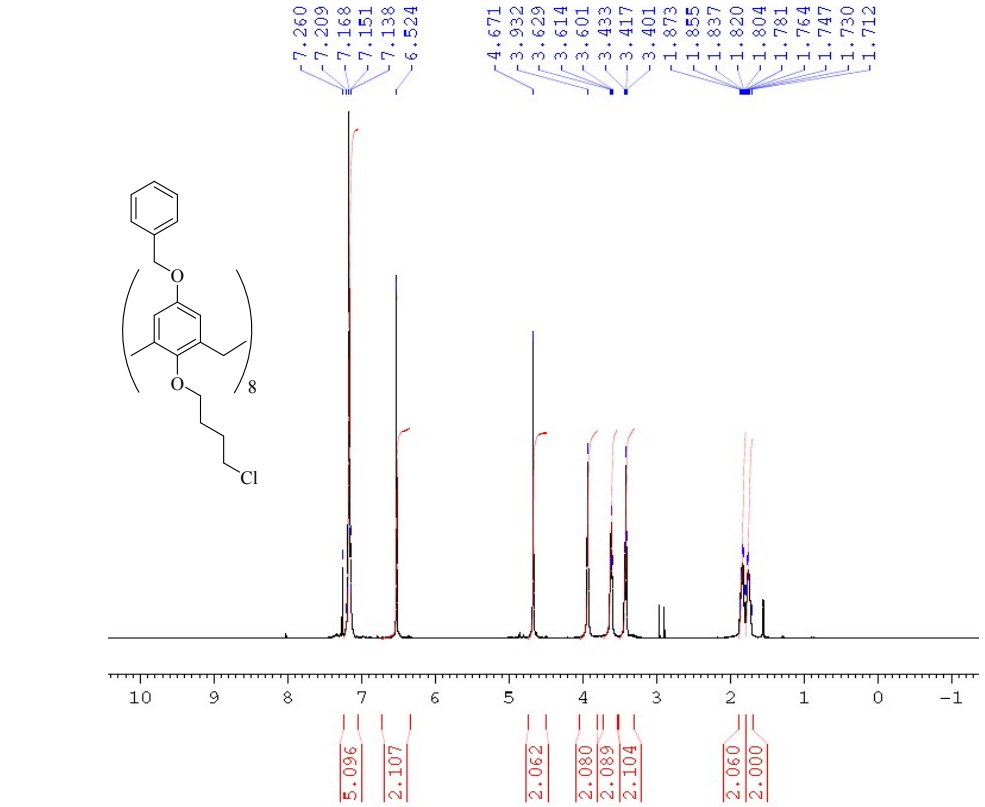
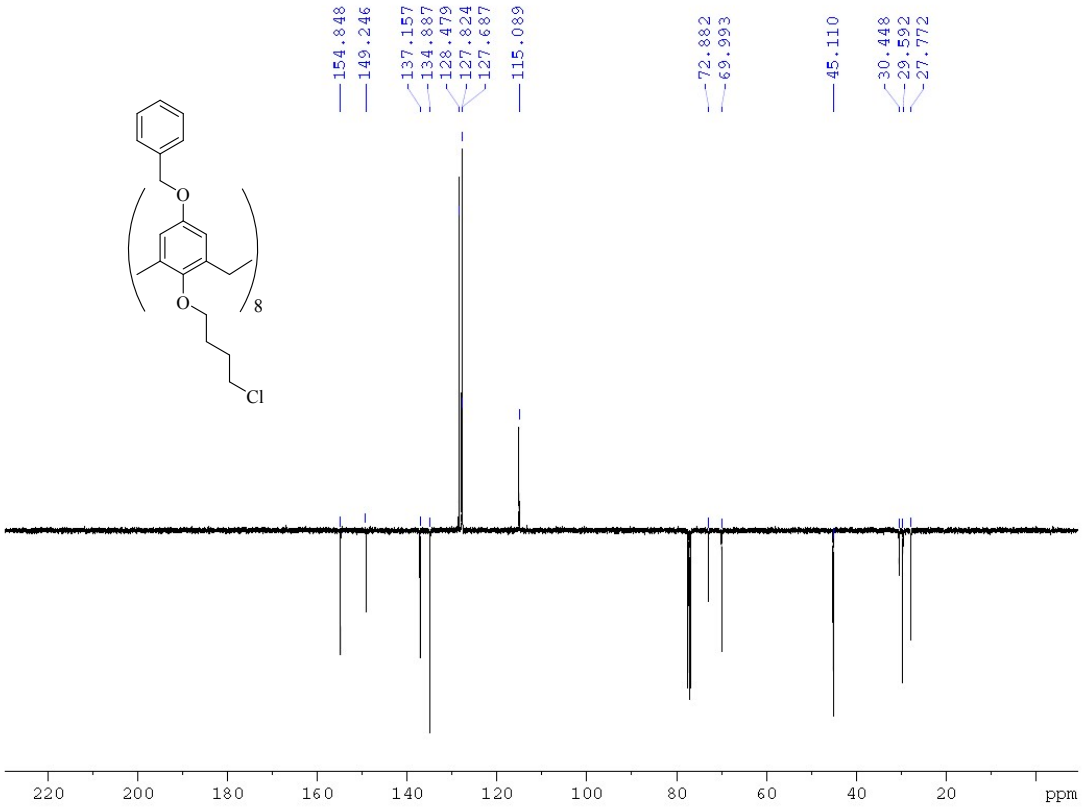


Fig. 3. Schematic representation of the intramolecular interaction (dashed lines) involving the chloropyridine. Centroids of the ring are shown in red balls.

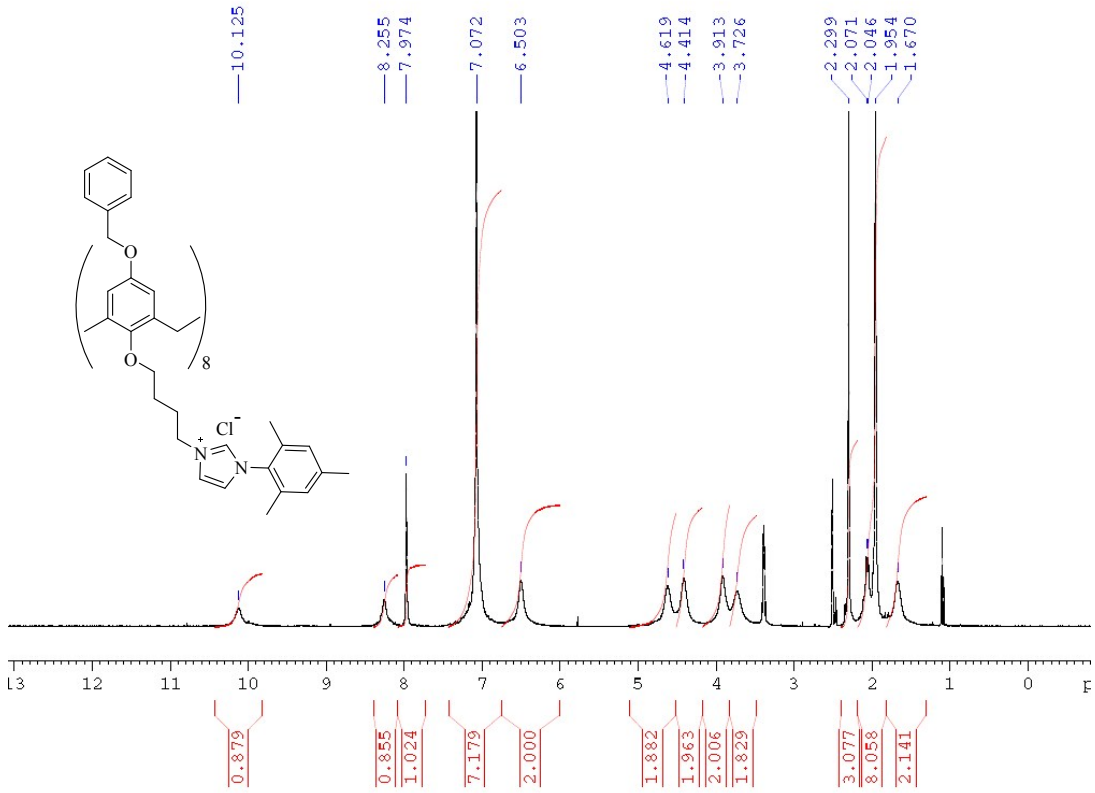
VIII. NMR Spectra

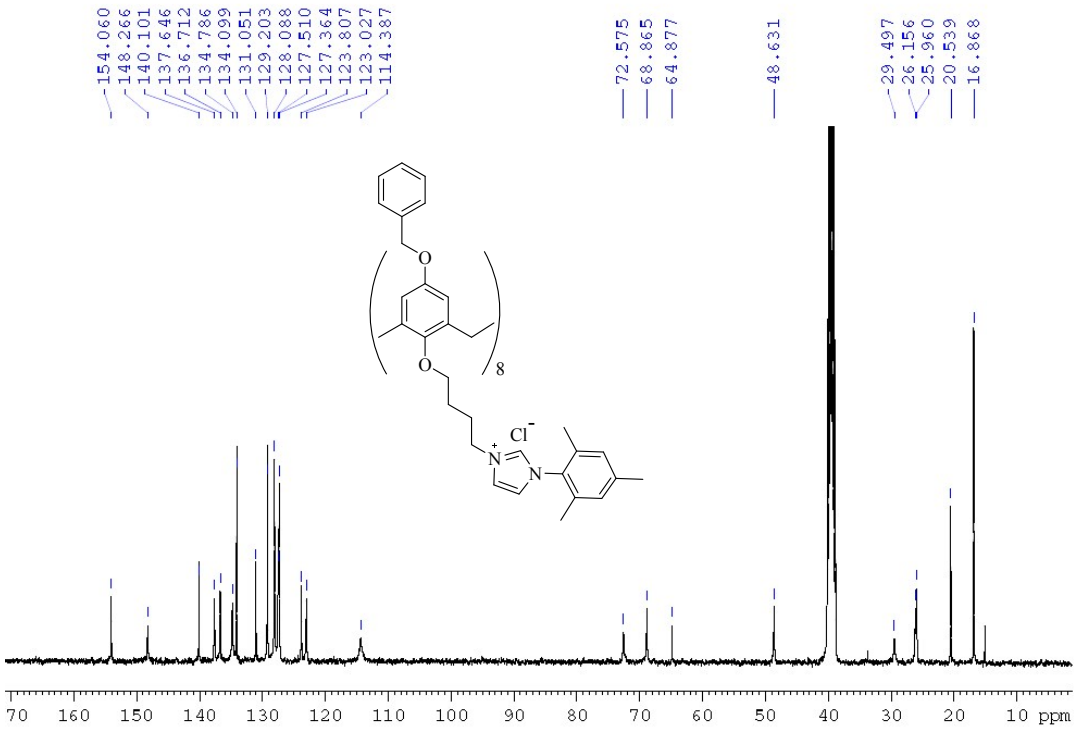
Compound A



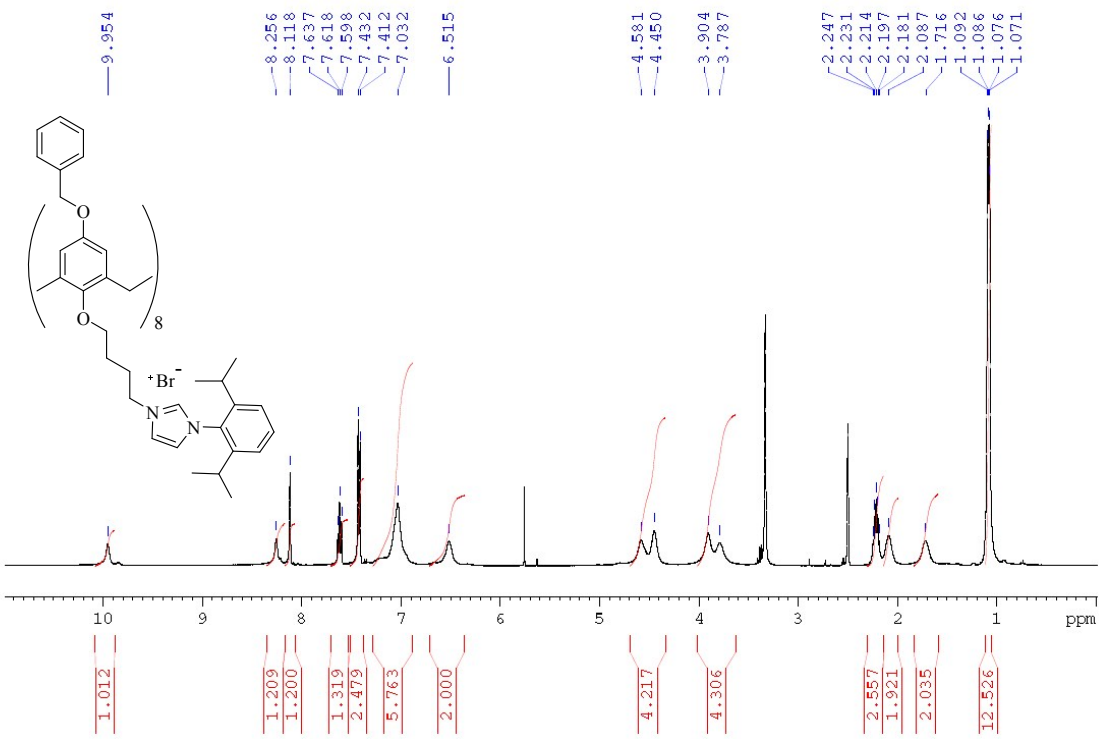


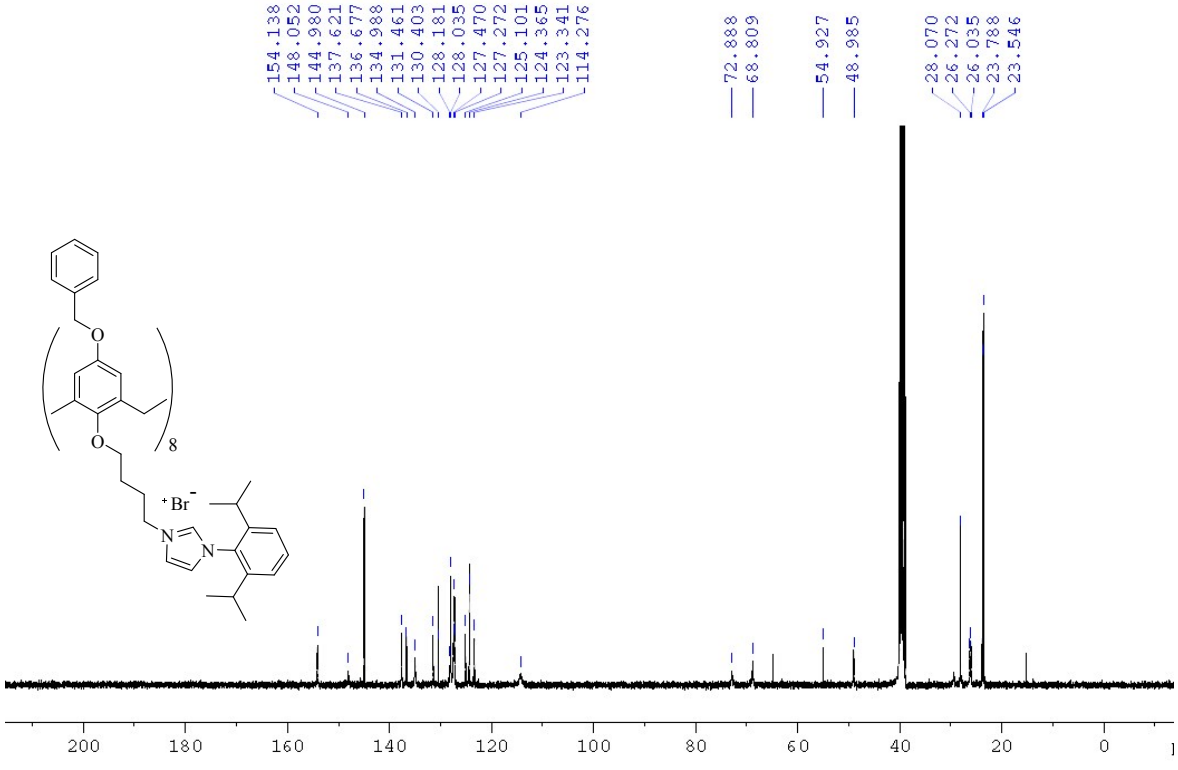
Compound B


10.125
8.255
7.974
7.072
6.503
4.619
4.414
3.913
3.726
2.299
2.071
2.046
1.954
1.670
0.879
0.855
1.024
7.179
2.000
1.882
1.963
2.006
1.829
3.077
8.058
2.141

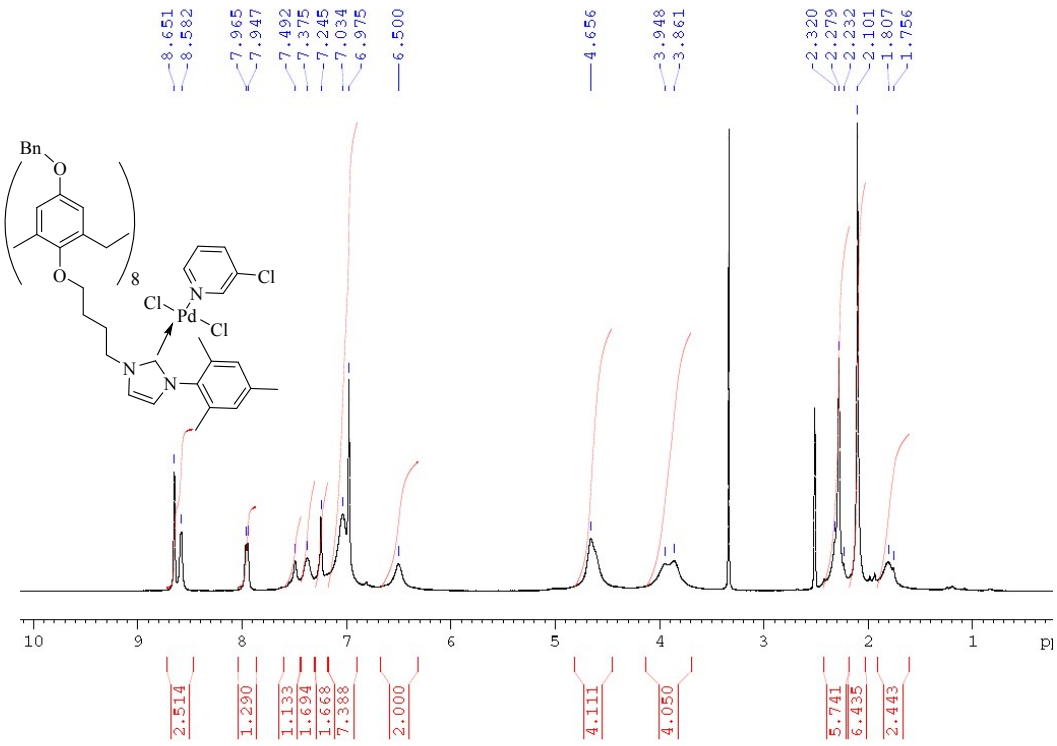

154.060
148.266
140.101
137.646
136.712
134.786
134.099
131.051
129.203
128.088
127.510
127.364
123.807
123.027
114.387
72.575
68.865
64.877
48.631
29.497
26.156
25.960
20.539
16.868

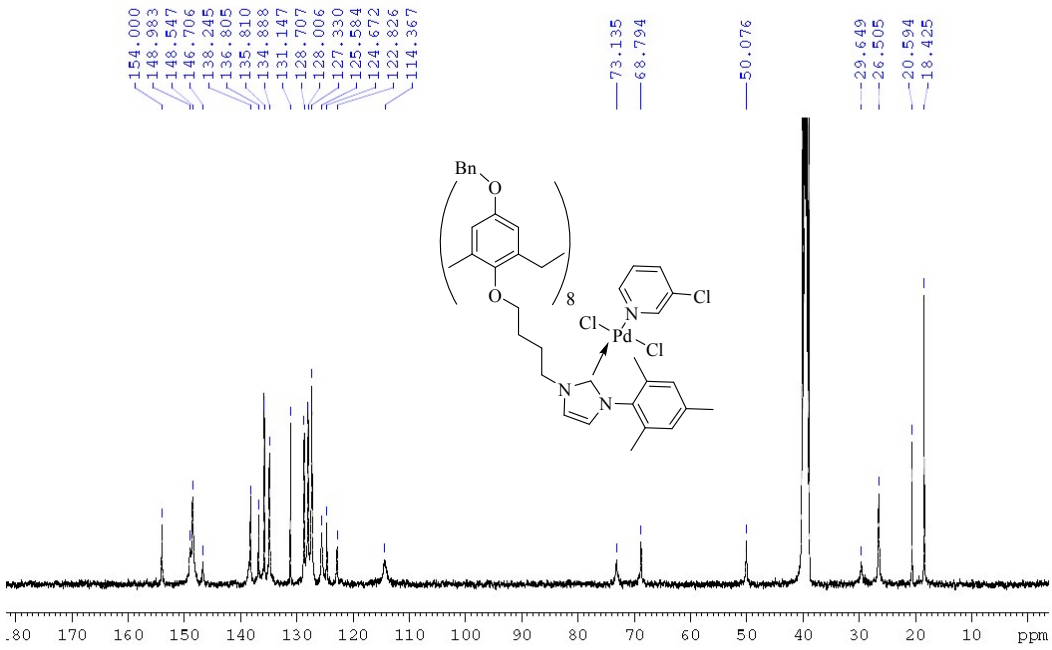
Compound C


9.954
8.256
8.118
7.637
7.618
7.598
7.432
7.412
7.032
6.515
4.581
4.450
3.904
3.787
2.247
2.231
2.214
2.197
2.181
2.087
1.716
1.092
1.086
1.076
1.071
ppm
1.012
1.209
1.200
1.319
2.479
5.763
2.000
4.217
4.306
2.557
1.921
2.035
12.526

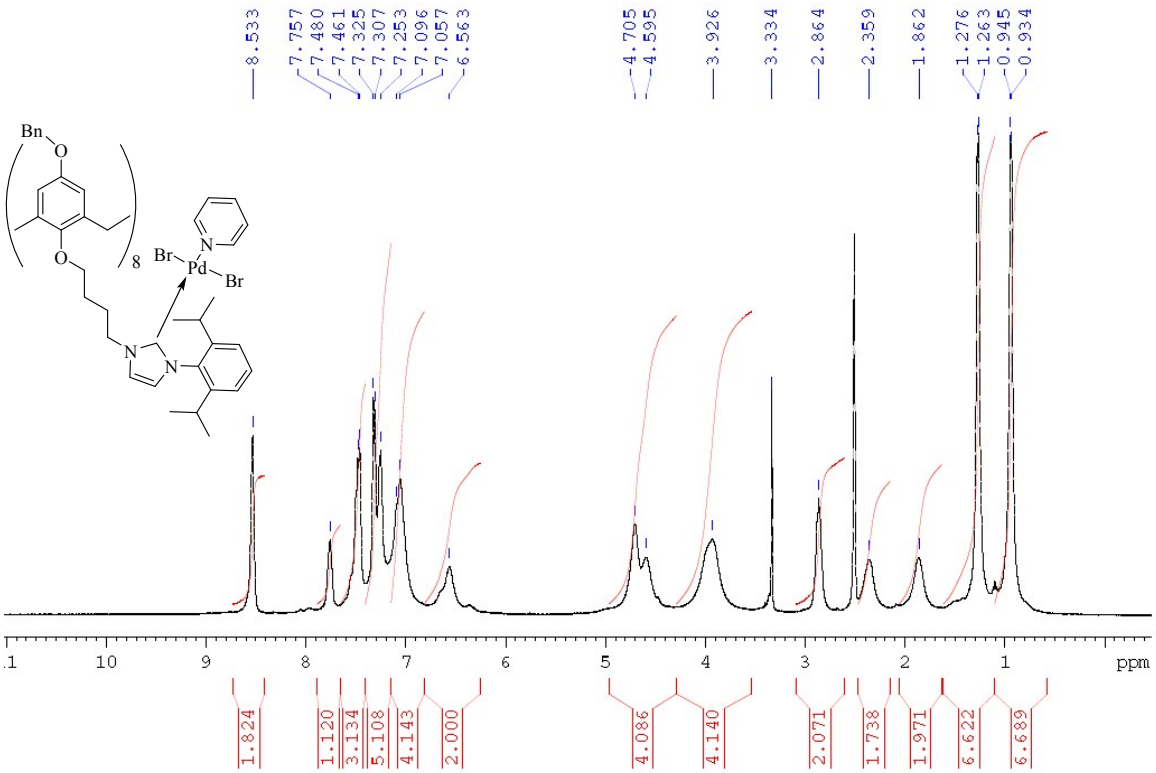

154.138
148.052
144.980
137.621
136.677
134.988
131.461
130.403
128.181
128.035
127.470
127.272
125.101
124.365
123.341
114.276
72.888
68.809
54.927
48.985
28.070
26.272
26.035
23.788
23.546

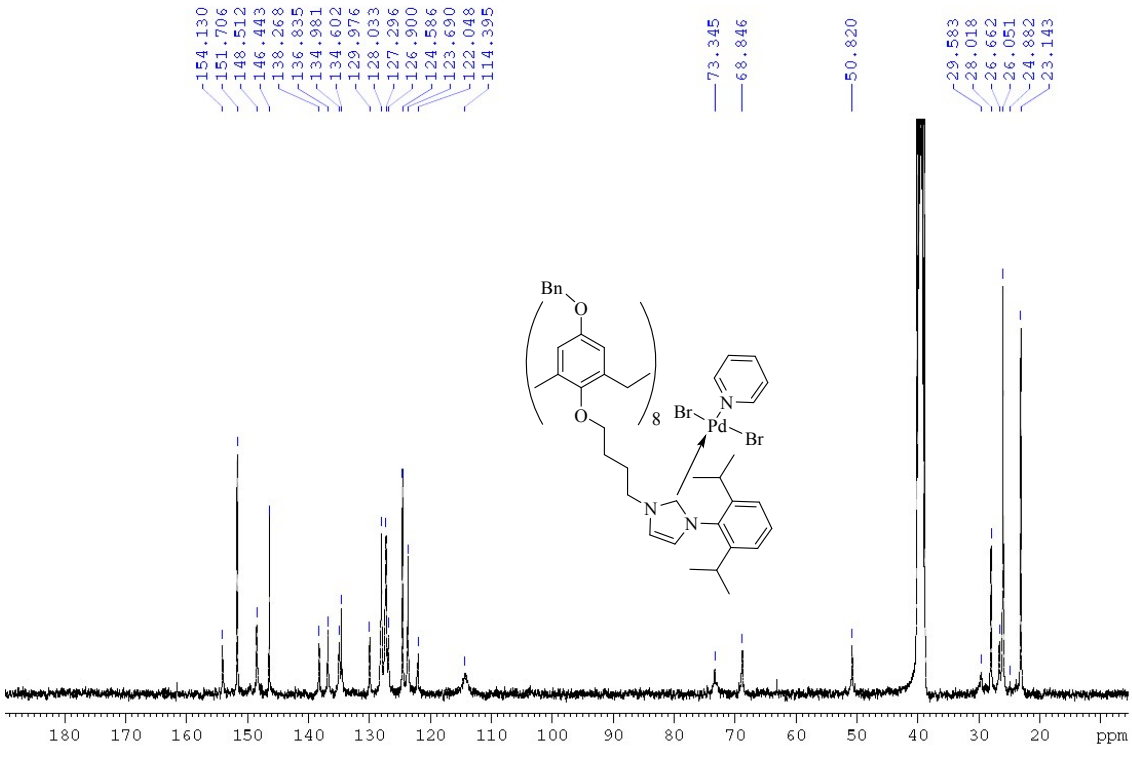
Complex 1


8.651
8.582
7.965
7.947
7.492
7.375
7.245
7.034
6.975
6.500
4.656
3.948
3.861
2.320
2.279
2.232
2.101
1.807
1.756
Bn
O
8
Cl
N
Pd
Cl
2.514
1.290
1.133
1.694
1.668
7.388
2.000
4.111
4.050
5.741
6.435
2.443

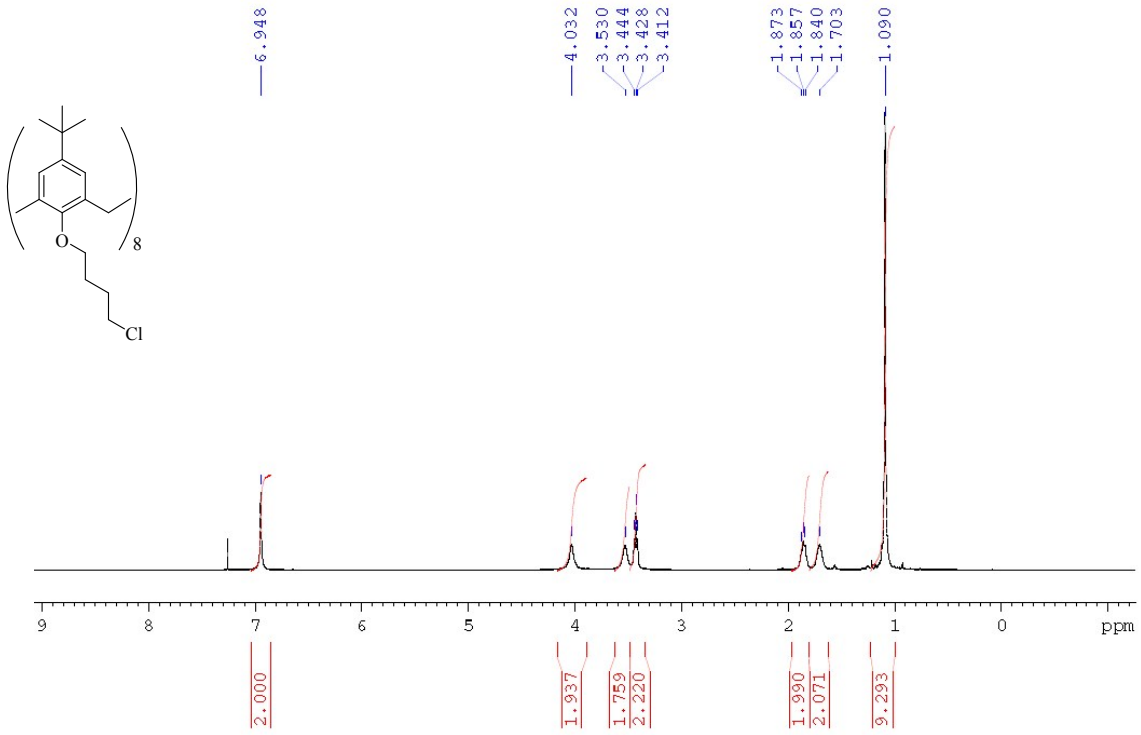

154.000
148.983
148.547
146.706
138.245
136.805
135.810
134.888
131.147
128.707
128.006
127.330
125.584
124.672
122.826
114.367
73.135
68.794
50.076
29.649
26.505
20.594
18.425
Bn
O
8
Cl
N
Pd
Cl
ppm

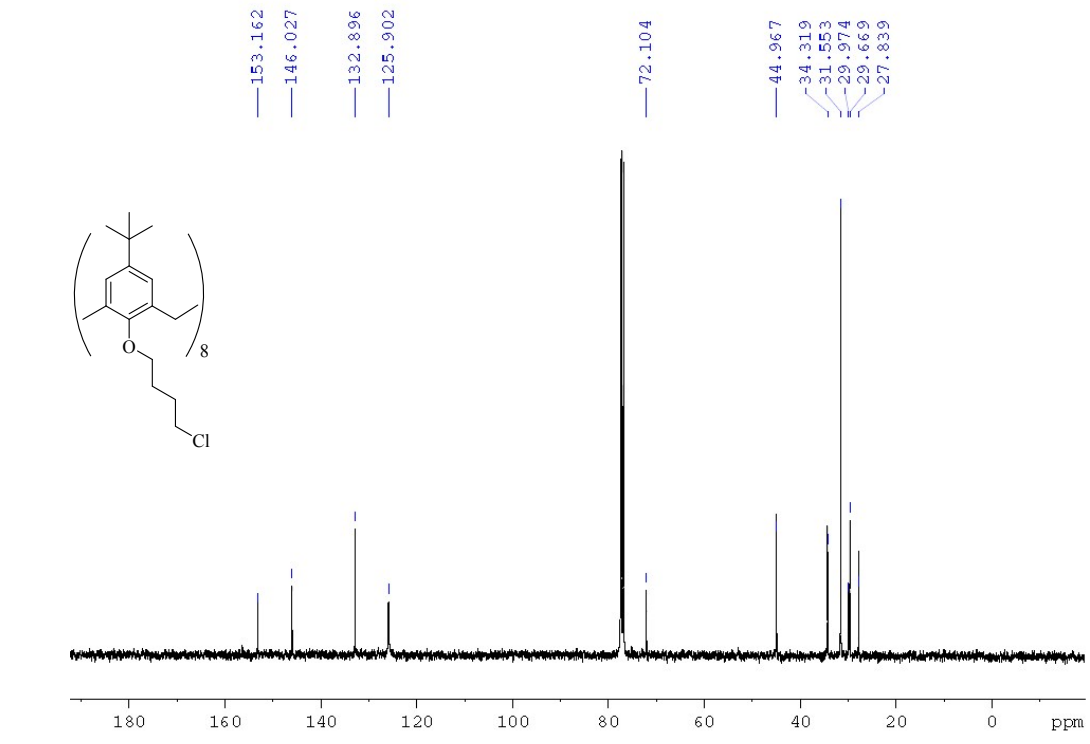
Complex 2


8.533
7.757
7.480
7.461
7.325
7.307
7.253
7.096
7.057
6.563
4.705
4.595
3.926
3.334
2.864
2.359
1.862
1.276
1.263
0.945
0.934
Bn
O
8
Br
Pd
N
ppm
1.824
1.120
3.134
5.108
4.143
2.000
4.086
4.140
2.071
1.738
1.971
6.622
6.689

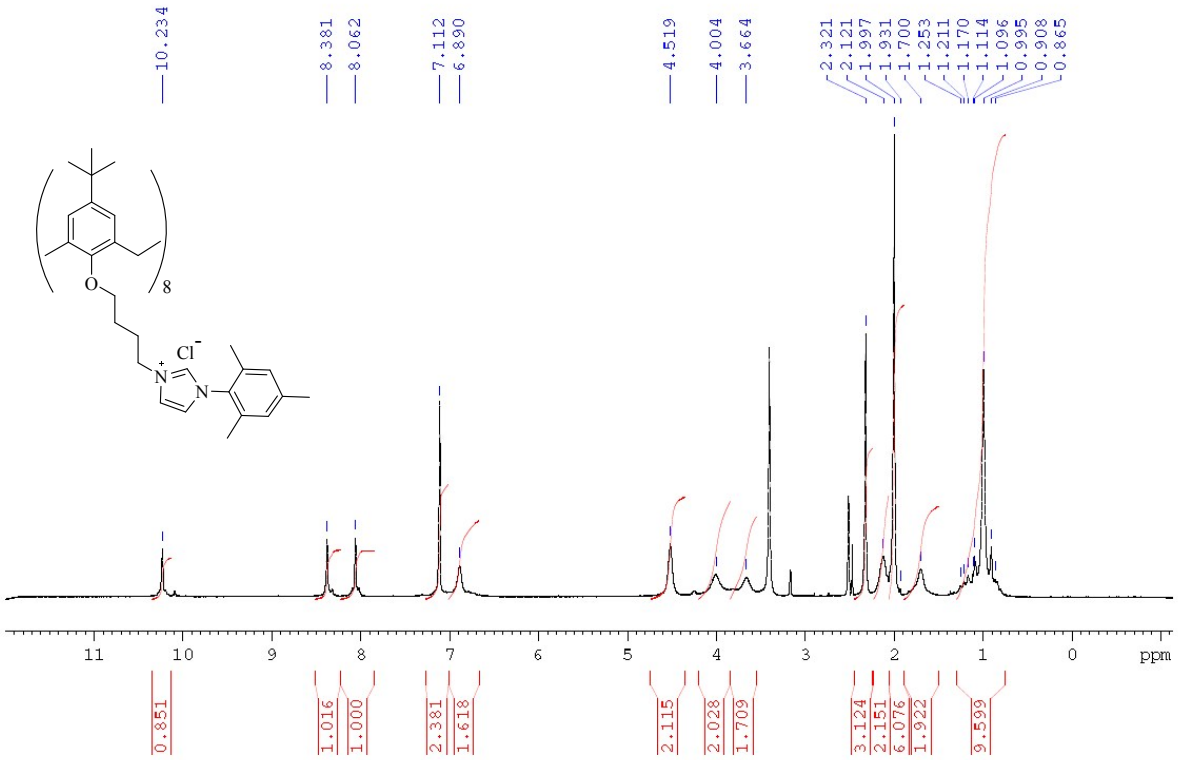

154.130
151.706
148.512
146.443
138.268
136.835
134.981
134.602
129.976
128.033
127.296
126.900
124.586
123.690
122.048
114.395
73.345
68.846
50.820
29.583
28.018
26.662
26.051
24.882
23.143
Bn
O
8
Br
Pd
N
ppm

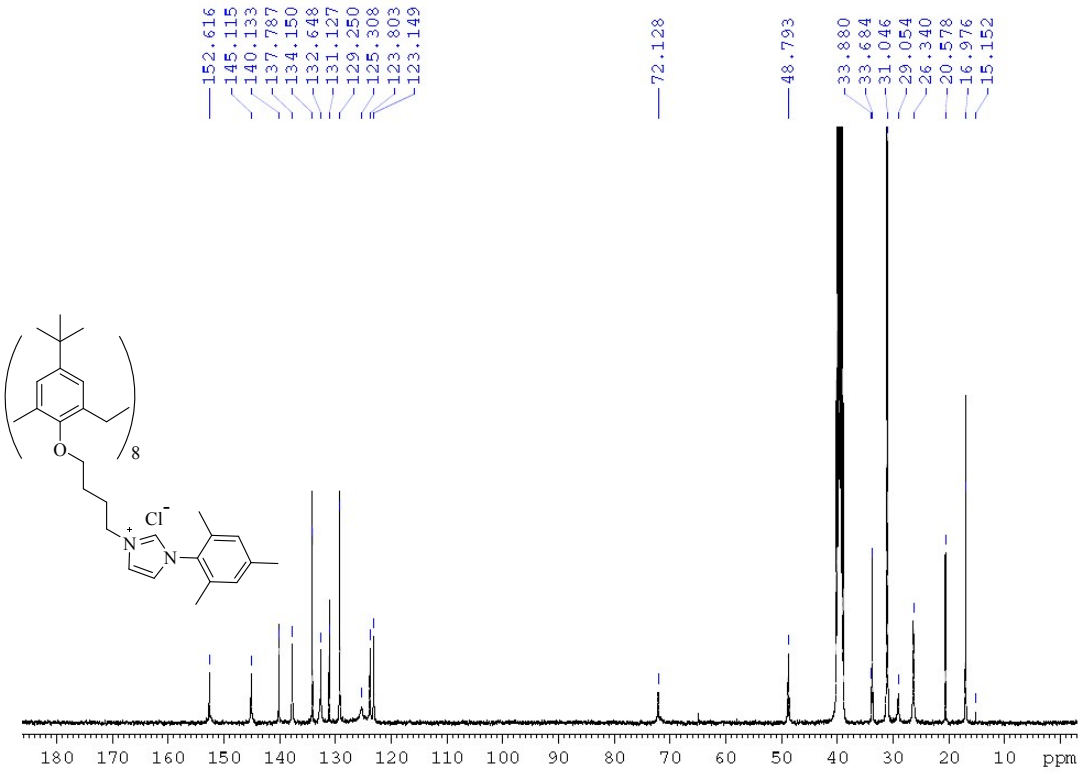
Compound D


6.948
4.032
3.530
3.444
3.428
3.412
1.873
1.857
1.840
1.703
1.090
O
8
Cl
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.937
1.759
2.220
1.990
2.071
9.293

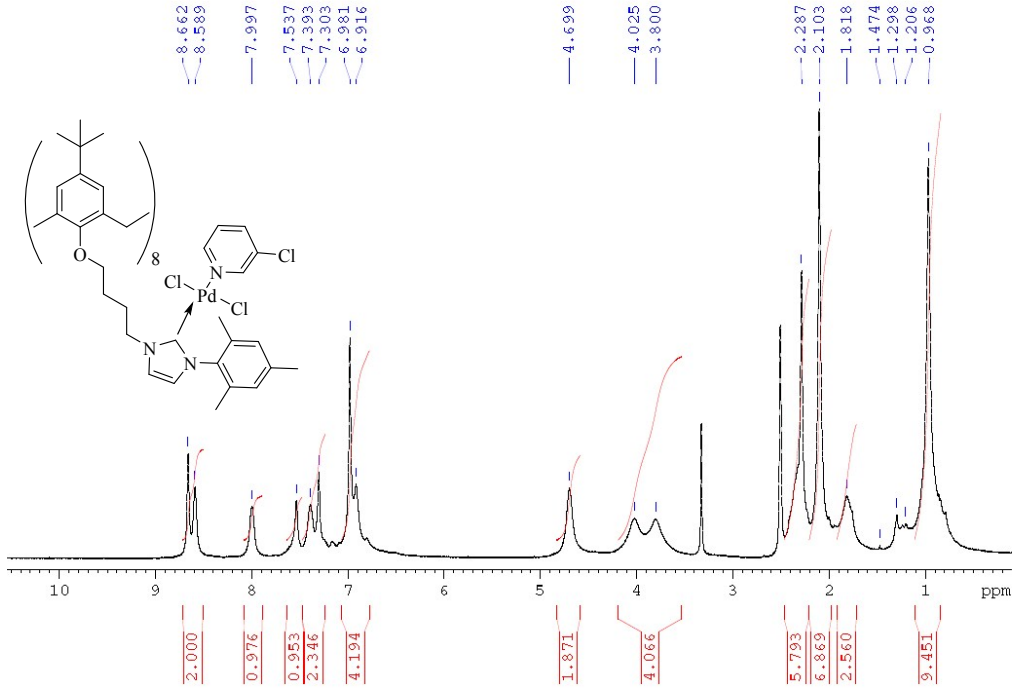

153.162
146.027
132.896
125.902
72.104
44.967
34.319
31.553
29.974
29.669
27.839
O
8
Cl
180
160
140
120
100
80
60
40
20
0
ppm

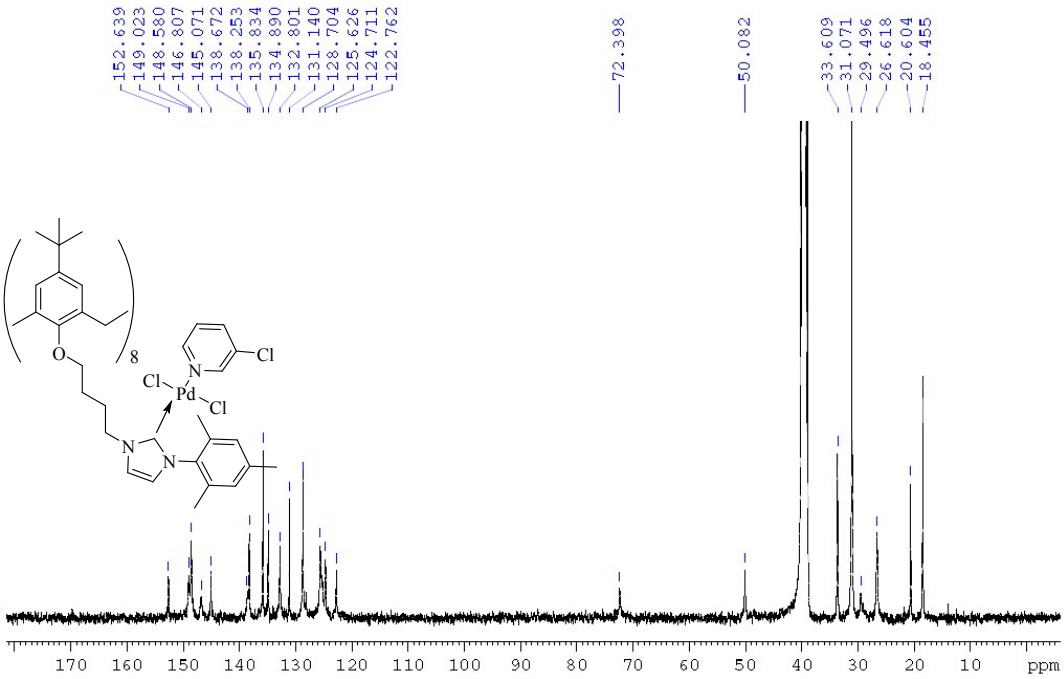
Compound E


10.234
8.381
8.062
7.112
6.890
4.519
4.004
3.664
2.321
2.121
1.997
1.931
1.700
1.253
1.211
1.170
1.114
1.096
0.995
0.908
0.865
0.851
1.016
1.000
2.381
1.618
2.115
2.028
1.709
3.124
2.151
6.076
1.922
9.599
ppm

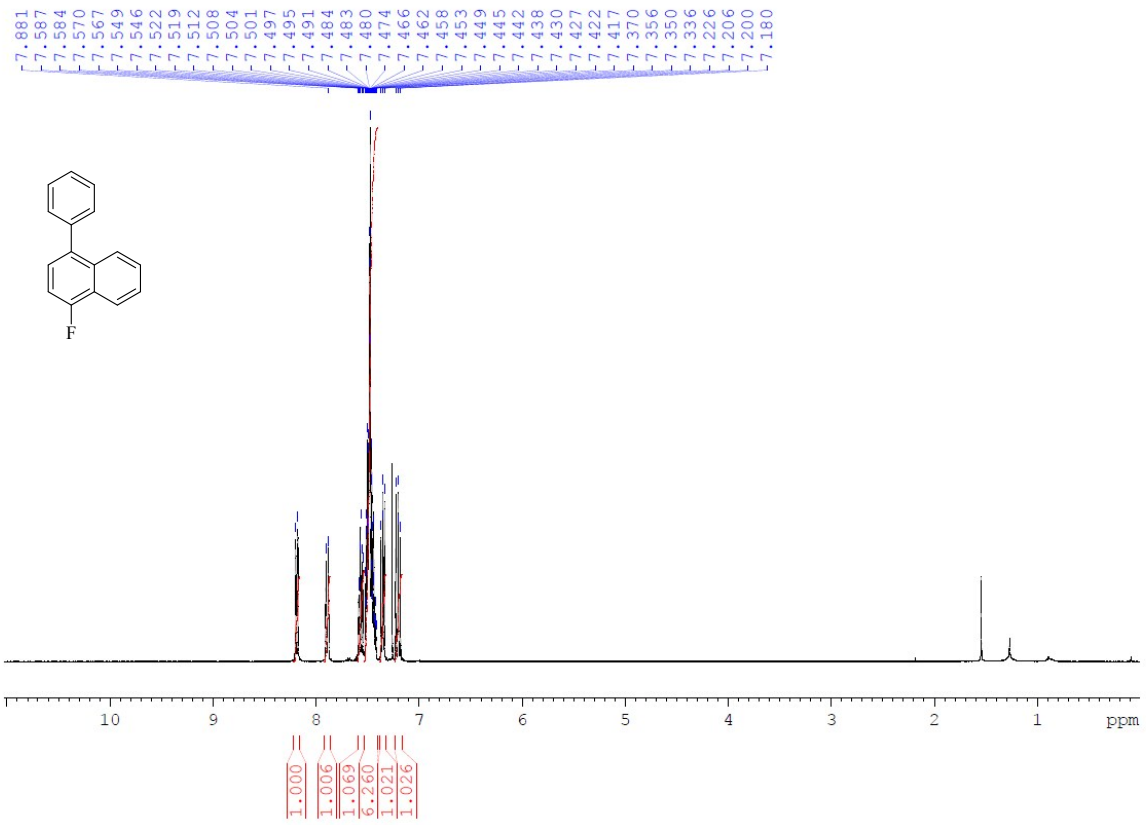

152.616
145.115
140.133
137.787
134.150
132.648
131.127
129.250
125.308
123.803
123.149
72.128
48.793
33.880
33.684
31.046
29.054
26.340
20.578
16.976
15.152
ppm

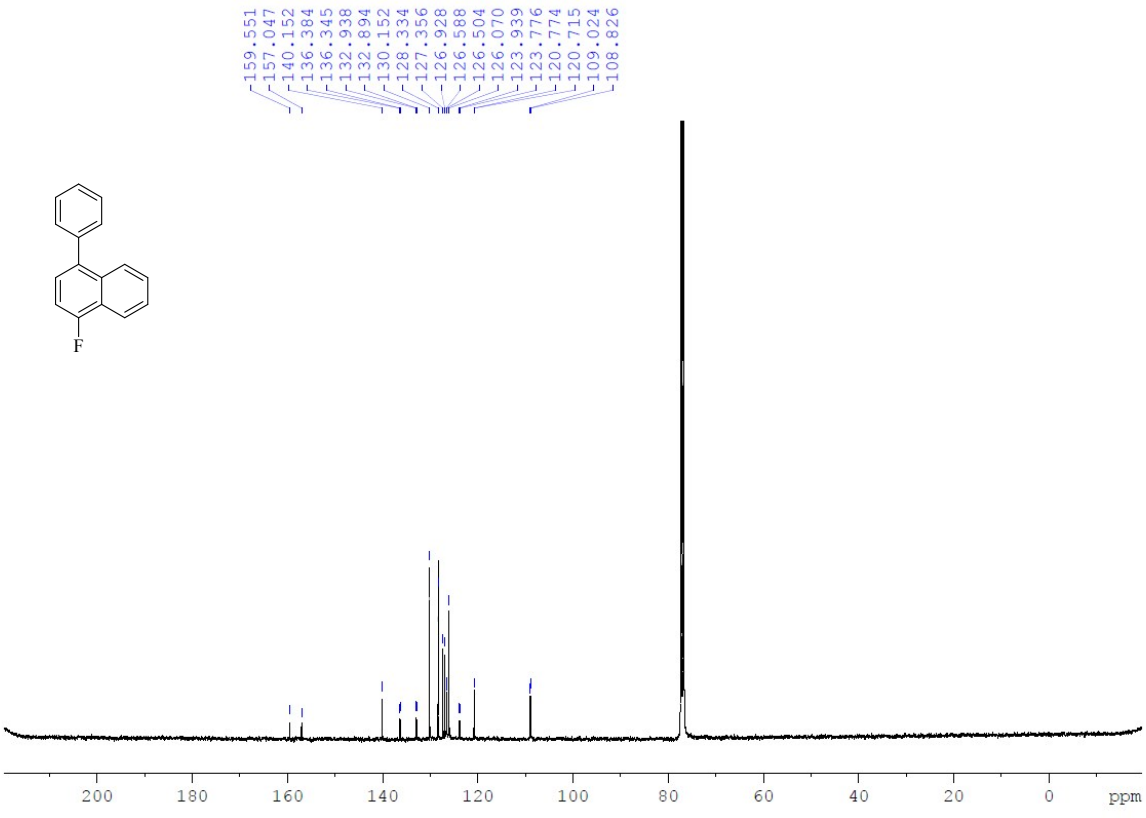
Complex 3


8.662
8.589
7.997
7.537
7.393
7.303
6.981
6.916
4.699
4.025
3.800
2.287
2.103
1.818
1.474
1.298
1.206
0.968
Cl
N
Cl
Pd
Cl
O
8
N
N
10
9
8
7
6
5
4
3
2
1
ppm
2.000
0.976
0.953
2.346
4.194
1.871
4.066
5.793
6.869
2.560
9.451


152.639
149.023
148.580
146.807
145.071
138.672
138.253
135.834
134.890
132.801
131.140
128.704
125.626
124.711
122.762
72.398
50.082
33.609
31.071
29.496
26.618
20.604
18.455
Cl
N
Cl
Pd
Cl
O
8
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

1-fluoro-4-phenylnaphthalene





4-phenyl-1-naphthoic acid