Supporting Information of

[3]Rotaxane-Based Dinuclear Palladium Catalysts for Ring-closure Mizoroki-Heck Reaction

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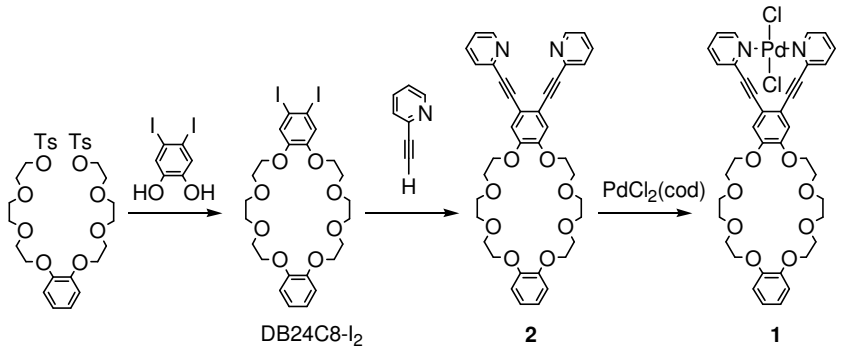
Experimental Section

General.

4,5-Diiododibenzo[24]crown-8 (DB24C8-I_2),[1] 4,4',5,5'-tetraiododibenzo[24]crown-8 (DB24C8-I_4),[2] $[FcCH_2NH_2CH_2C_6H_4\text{-}4\text{-}OCH_2CH_2CH{=}CH_2]PF_6$ (**3**) (Fc = $Fe(C_5H_4)(C_5H_5)$),[3] $IC_6H_4\text{-}4\text{-}OCH_2(CH_2OCH_2)_3CH_2OC_6H_4\text{-}4\text{-}I$[4] and tetra(ethyleneglycol) diacrylate[5] were prepared by literature methods. Other chemicals were commercially available. NMR spectra (^1H, $^{13}C\{^1H\}$) were recorded on Varian MERCURY300 or JEOL EX-400 spectrometers. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Fast atom bombardment mass spectra (FABMS) were obtained from a JEOL JMS-700 (matrix, 2-nitrophenyl *n*-octyl ether (NPOE)) spectrometer. ESI-TOF-MS were obtained from a micrOTOF II (Bruker) spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. Thermogravimetric analysis (TGA) was recorded on a Seiko TG/DTA6200R. Differential scanning calorimetry (DSC) was recorded on a Seiko DSC6200S. Gel permeation chromatography was performed by using an LC-908 recycling preparative

HPLC (Japan Analytical Industry Co., Ltd.) with two columns for the separation of low-molecular-weight organic compounds: JAIGEL-1H and JAIGEL-2H (styrene polymer gels).



Scheme S1 Synthesis of **1** and **2**

4,5-di(pyridinylethynyl)benzo[24]crown-8 (2)

A THF solution (24 mL) of 4,5-diiododibenzo[24]crown-8 (DB24C8-I_2) (1.40 g, 2.00 mmol), CuI (15 mg, 0.040 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.020 mmol), 2-ethynylpyridine (0.50 mL, 4.8 mmol), 0.5 M aqueous ammonia (16 mL, 8.0 mmol) was stirred for 8 h at room temperature. The organic product was extracted with CH_2Cl_2 and the solution was dried over $MgSO_4$. Evaporation of the solvent gave a crude product which was washed with hexane to yield 4,5-di(pyridinylethynyl)benzo[24]crown-8 (**2**) as a gray solid (1.23 g, 1.9 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 3.84 (br, 8H, CH_2), 3.91-3.94 (m, 8H, CH_2), 4.14-4.17 (m, 8H, CH_2), 6.87 (m, 4H, C_6H_4), 7.09 (s, 2H, C_6H_2), 7.23 (ddd, 2H, H5-pyridyl, J = 6, 5, 2 Hz), 7.64-7.66 (4H, H3 and H4-pyridyl), 8.62 (dd, 2H, H6-pyridyl, J = 5, 1 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, r.t.): δ 69.4 (2C, CH_2), 69.6 (CH_2), 67.0 (CH_2), 71.3 (CH_2), 71.5 (CH_2), 88.0 (C≡C), 91.7 (C≡C), 114.0, (C_6H_4), 116.0 (C_6H_2), 118.5, 121.3 (C_6H_4), 122.6 (C5-pyridyl), 127.2, (C3 or C4-pyridyl), 136.0 (C3 or C4-pyridyl), 143.5, 148.8, 149.2 (C6-pyridyl), 149.9; Anal. Calcd. for $C_{38}H_{38}N_2O_8(H_2O)_{0.5}$: C, 69.18; H, 5.96; N, 4.25. Found: C, 69.32; H, 5.77; N, 4.61.

(4,5-dipyridinylethynylbenzo[24]crown-8)$PdCl_2$ (1)

A DMSO solution (3.0 mL) of **2** (330 mg, 0.50 mmol) and $PdCl_2$(cod) (95 mg, 0.30 mmol) was stirred for 30 min at 50 ^oC. The resulting solid was collected by filtration, washed with methanol and diethyl ether, and dried in vacuo to form **1** as yellow solid (230 mg, 0.28 mmol, 92%). ^1H NMR (300 MHz, $CDCl_3$, r.t.): δ 3.86 (br, 8H, CH_2), 3.92-3.98 (m, 8H, CH_2), 4.15-4.18 (m, 4H, CH_2), 4.23-4.26 (m, 4H, CH_2), 6.88 (m, 4H, C_6H_4), 7.15 (s, 2H, C_6H_2), 7.31 (m, 2H, H5-pyridyl), 7.60 (d, 2H, H3-pyridyl, J = 8 Hz), 7.73 (m, 2H, H4-pyridyl), 8.86 (d, 2H, H6-pyridyl, J = 6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, r. t.): δ 69.3 (CH_2), 69.5 (CH_2), 69.6 (CH_2), 69.9 (CH_2), 71.3 (CH_2), 71.5 (CH_2), 90.1 (C≡C), 96.3 (C≡C), 113.9 (C_6H_4), 116.0 (C_6H_2), 118.6, 121.3 (C_6H_4), 123.7 (C5-pyridyl), 128.8 (C3 or C4-pyridyl), 137.6 (C3 or C4-pyridyl), 145.1, 148.7, 150.0, 153.0 (C6-pyridyl); IR (KBr disk, r.t.) ν 2919, 2812, 2213, 1592, 1514, 1256 cm^{-1}; m.p.: ca. 240 ^oC (by DSC. decomp.); 5% weight loss temperature: 238 ^oC (by TGA. scan rate = 5 ^oC/min); Anal. Calcd. for $C_{38}H_{38}N_2Cl_2O_8Pd(H_2O)_3$: C, 51.74; H, 5.03; N, 3.18; Found: C, 51.76; H, 4.67; N, 3.22. ESI-TOF-MS (eluent: MeCN): Calcd. for $C_{38}H_{38}N_2O_8Na$: 851.1. Found: *m/z* = 851.1 ($[M + Na]^+$).

[($FcCH_2NH_2CH_2C_6H_4$-4-OCH_2CH_2CH=$CHCH_2CH_2OC_6H_4$-4-$CH_2NH_2CH_2Fc$)(3)$_2$](PF_6)$_2$ (4) (Fc = $Fe(C_5H_4)(C_5H_5)$)

1 (331 mg, 0.40 mmol) and **3** (172 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (3.0 mL), followed by addition of a Ru–carbene complex, (H_2IMes)(PCy_3)Cl_2Ru=CHPh, (14 mg, 0.017 mmol). The mixture was refluxed for 15 h. The resulting solid was collected by filtration, washed with dichloromethane, and dried in vacuo to form **4** as yellow solid (241 mg, 0.10 mmol, 62%). ^1H NMR (300 MHz, dmso-d_6, r.t.): δ 2.25 (m, 4H, CH_2), 3.68-4.23 (66H, CH_2-crown, C_5H_4, C_5H_5), 4.38 (s, 4H, NCH_2), 4.43 (s, 4H, NCH_2), 5.38 (2H, CH_2=*CH*), 6.59 (d, 4H, C_6H_4-axle, J

= 9 Hz), 6.88 (m, 4H, C_6H_4-crown), 6.93 (m, 4H, C_6H_4-crown), 7.04 (brs, 2H, NH_2), 7.15 (d, 4H, C_6H_4-axle, J = 9 Hz), 7.41 (s, 4H, C_6H_2), 7.55 (m, 4H, H5-pyridyl), 7.77 (d, 4H, H3-pyridyl, J = 8 Hz), 8.01 (dd, 4H, H4-pyridyl), 8.89 (d, 4H, H6-pyridyl, J = 6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, dmso-d_6, r.t.): δ 31.9 ($OCH_2\mathit{CH_2}$), 47.9 (NCH_2), 51.1 (NCH_2), 67.0 ($O\mathit{C}H_2CH_2$), 67.6 (CH_2-crown), 68.7 (C_5H_5 and C_5H_4), 68.8 (CH_2-crown), 68.9 (C_5H_5 or C_5H_4), 69.2 (CH_2-crown), 69.6 (C_5H_5 or C_5H_4), 69.9 (CH_2-crown), 70.2 (CH_2-crown), 70.4 (CH_2-crown), 76.4, 90.2, (C≡C), 94.8 (C≡C), 112.4 (C_6H_4-crown), 114.0 (C_6H_4-axle), 115.9 (C_6H_2), 117.6, 121.0 (C_6H_4-crown), 123.5, 124.8 (C5-pyridyl), 128.1 (C3-pyridyl), 128.7 (CH_2=CH), 130.4 (C_6H_4-axle), 140.0 143.7, 147.1, 148.9, (C4-pyridyl), 152.8 (C6-pyridyl), 158.6; IR (KBr disk, r.t.) ν 2211, 1592, 1514, 1252, 1105, 843 (PF_6), 558 (PF_6) cm^{-1}; m.p.: ca. 200 ^oC (by DSC. decomp.); 5% weight loss temperature: 235 ^oC (by TGA. scan rate = 5 ^oC/min); Anal. Calcd. for $C_{118}H_{124}Cl_4F_{12}FeN_6O_{18}P_2Pd_2(H_2O)_3$: C, 52.02; H, 4.81; N, 3.08. Found: C, 51.91; H, 4.81; N, 3.03; ESI-TOF-MS (eluent: MeCN): Calcd. for $C_{118}H_{124}Cl_4N_6O_{18}Pd_2$: 1190.2 (dication), Found: m/z = 1190.2 ($[M - (PF_6)_2]^{2+}$) The assignments of the NMR signals were supported by ^1H-^1H COSY, $^{13}C\{^1H\}$-^1H COSY and DEPT135 spectroscopy.

Typical procedure for the Mizoroki-Heck reaction of methyl acrylate and iodobenzene. (Table 1, run 1)

A DMF solution (8.0 mL) of methyl acrylate (0.090 mL, 1.0 mmol) and triethylamine (0.56 mL, 4.0 mmol) was stirred for 10 min at room temperature, followed by addition of iodobenzene (0.11 mL, 1.0 mmol) and Pd catalyst **1** (1.7 mg, 0.02 mmol). The solution was stirred at 100 ^oC for 1 h and the resulting solid was removed by filtration. The solvent was removed by evaporation to give a crude product, which is dissolved in CH_2Cl_2 and partitioned by addition of water. The separated organic phase was dried over $MgSO_4$, filtered and evaporated. The obtained crude dried in vacuo to give methyl cinnamate, PhCH=CHCOOMe, in quantitative yield.

The product was determined by ^{1}H NMR spectroscopy.

O($CH_2CH_2OC_6H_4$-4-I)$_2$ (5a)

A mixture of IC_6H_4-4-OH (2.75 g, 12.5 mmol) and K_2CO_3 (1.80 g, 13 mmol) in MeCN (12 mL) was stirred for 30 min at 90 °C, followed by addition of di(ethylene glycol) di-p-tosylate (2.48 g, 6.0 mmol) in MeCN (18 mL). The mixture was stirred for another 24 h at 90 °C, before being cooled to r.t.. The product was extracted with CH_2Cl_2, and the organic extract was washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a crude product, which was purified by SiO_2 column chromatography (CH_2Cl_2, R_f = 0.8) to yield O($CH_2CH_2OC_6H_4$-4-I)$_2$ (**5a**) as a white powder (1.65 g, 3.22 mmol, 54%). ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 3.90 (t, 4H, CH_2, J = 5 Hz), 4.11 (t, 4H, CH_2, J = 5 Hz), 6.69 (d, 4H, C_6H_4, J = 9 Hz), 7.54 (d, 4H, C_6H_4, J = 9 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, r.t.): δ 67.6 (CH_2), 69.8 (CH_2), 83.0 (C_6H_4), 117.1 (C_6H_4), 138.2 (C_6H_4), 158.6 (C_6H_4); Anal. Calcd. for $C_{16}H_{16}I_2O_3$: C, 37.67; H, 3.16. Found: C, 37.27; H, 2.99; m.p.: 123 °C (by DSC).

Typical procedure of the Mizoroki-Heck reaction of 5b and 6b. (Table 2, run 3)

5b used for the following reaction was purified by SiO_2 column chromatography to remove stabilizer. A DMF solution (100 mL) of **6b** (151 mg, 0.50 mmol), triethylamine (0.28 mL, 2.0 mmol), **5b** (299 mg, 0.50 mmol) and Pd catalyst **4** (13 mg, 5.0×10^{-4} mmol) was stirred at 100 °C. After 2 h, 10 ml of the solution was sampled and then extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, evaporated and dried in vacuo. The obtained solid was analyzed by ^{1}H NMR spectroscopy (in $CDCl_3$) and GPC (eluent: THF) to find the formation of **7b** and **8b**. The yields of the compounds, **7b** and **8b**, were calculated based on the comparison of the integration of the ^{1}H NMR signal with that of the internal standard, 1,3,5-triphenylbenzene, added to the $CDCl_3$ solution. Similar samplings were also

conducted after 4, 8, 12, 24, 48 and 90 h.

Data of **7b**: ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 3.70 (m, 16H, OCH_2), 3.78 (m, 4H, OCH_2), 3.82 (m, 4H, OCH_2), 4.02 (m, 4H, OCH_2), 4.36 (m, 4H, OCH_2), 6.29 (d, 2H, CH, *J* = 16 Hz) 6.84 (d, 4H, C_6H_4, *J* = 9 Hz), 7.40 (d, 4H, C_6H_4, *J* = 9 Hz), 7.74 (d, 2H, CH, *J* = 16 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, r.t.): δ 63.6 (OCH_2), 67.6 (OCH_2), 69.3(OCH_2), 69.5 (OCH_2), 70.6 (OCH_2), 70.8 (OCH_2), 70.8 (OCH_2), 70.8 (OCH_2), 114.8 (C_6H_4), 115.3 (CH), 127.1, 130.0 (C_6H_4), 144.4 (CH), 160.4, 167.0; IR (KBr disk, r.t.) ν 2919, 2815, 1707 (C=O), 1636, 1609, 1179 cm^{-1}; Anal. Calcd. for $C_{34}H_{44}O_{12}(H_2O)_{0.5}$: C, 62.47; H, 6.94. C, 62.76; H, 6.67; m.p.: 95 ^{o}C (by DSC. decomp.); 5% weight loss temperature: 362 ^{o}C (by TGA. scan rate = 5 ^{o}C/min); FABMS: Calcd. for $C_{34}H_{45}O_{12}$: 645. Found: *m/z* = 645 ($[M + H]^+$) (Matrix = NPOE).
Data of **7a**: ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 3.77-3.80 (m, 4H, CH_2), 3.86-3.89 (m, 4H, CH_2), 4.15-4.18 (m, 4H, CH_2), 4.38-4.40 (m, 4H, CH_2), 6.23 (d, 2H, CH=CH, *J* = 16 Hz), 6.63 (d, 4H, C_6H_4, *J* = 9 Hz), 7.17 (d, 4H, C_6H_4, *J* = 9 Hz), 7.60 (d, 2H, CH=CH, *J* = 16 Hz); FABMS: Calcd. for $C_{26}H_{29}O_8$: 469. Found: *m/z* = 469 ($[M + H]^+$) (Matrix = NPOE); Anal. Calcd. for $C_{26}H_{28}O_8(H_2O)_{0.5}$: C, 65.40; H, 6.12. Found: C, 65.73; H, 6.01; m.p.: 141 ^{o}C (by DSC.)

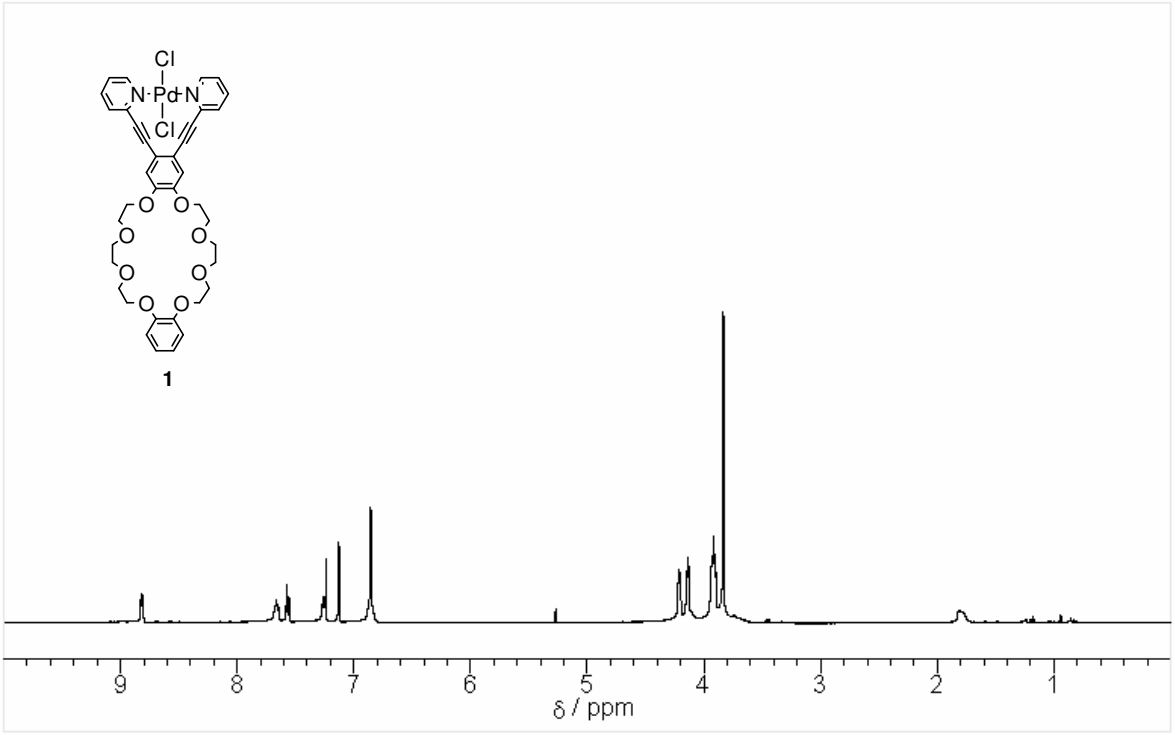
X-ray structure analyses of 1

Crystals of **1** suitable for X-ray diffraction study were obtained by recrystallization from NMP/AcOEt. All measurements were made on Rigaku AFC-10R Saturn CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were carried out by using a program package Crystal Structure™ for Windows.[6] All hydrogen atoms were included at the calculated positions with fixed thermal parameters.

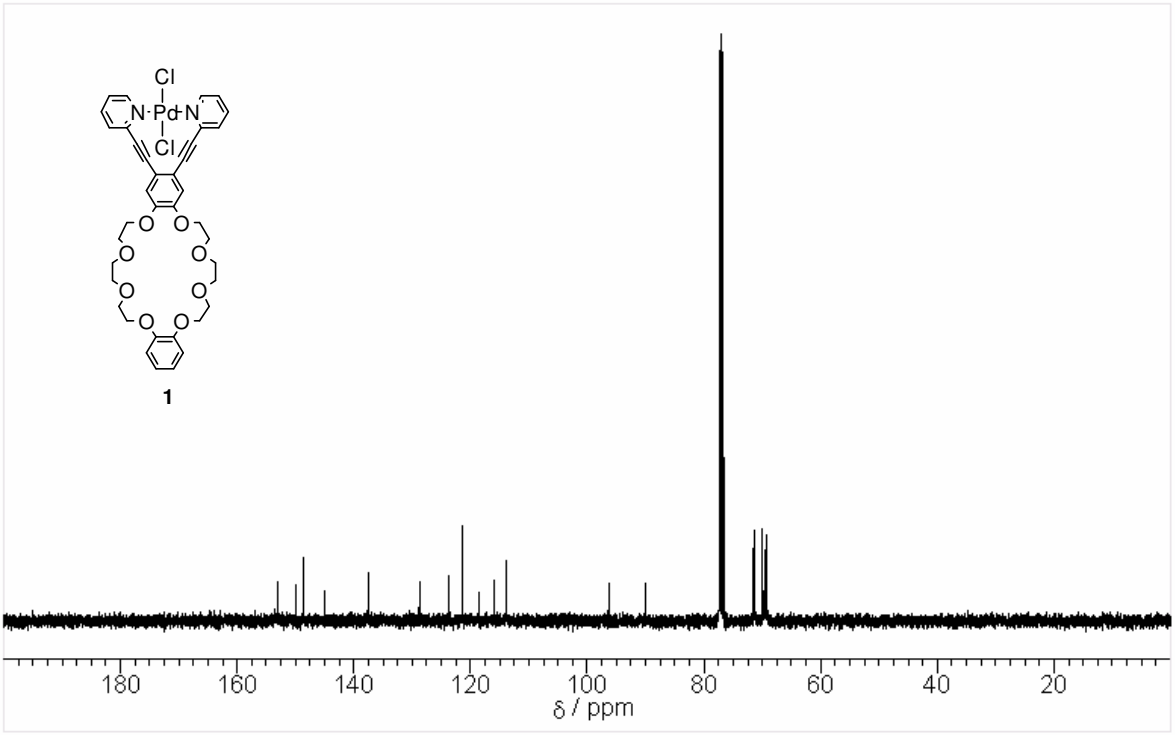
References

1. Park, J. J.; Weakley, T. J. R.; Haley, M. M.; Lau, D. Y. K.; Stoddart, J. F. *Synthesis* **2002,** *9,* 1256.
2. Joshua J. P.; Jaime L. M.; Endrit, S. *Tetrahedron Lett.* **2006**, *47*, 233.
3. Suzaki, Y.; Osakada, K. *Chem. Lett*. **2006**, *35*, 374.
4. (a) Virtue, G. A.; Coyne, N. E.; Hamilton, D. G. *J. Org. Chem.* **2002**, *67*, 6856; (b) Suzaki, Y.; Osakada, K. *Organometallics* **2003**, *22*, 2193.
5. Kim, B. H.; Jeong, E. J.; Jung, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 6390.
6. *Crystal Structure*: Crystal analysis package, Rigaku and Rigaku/MSC (2000-2011).

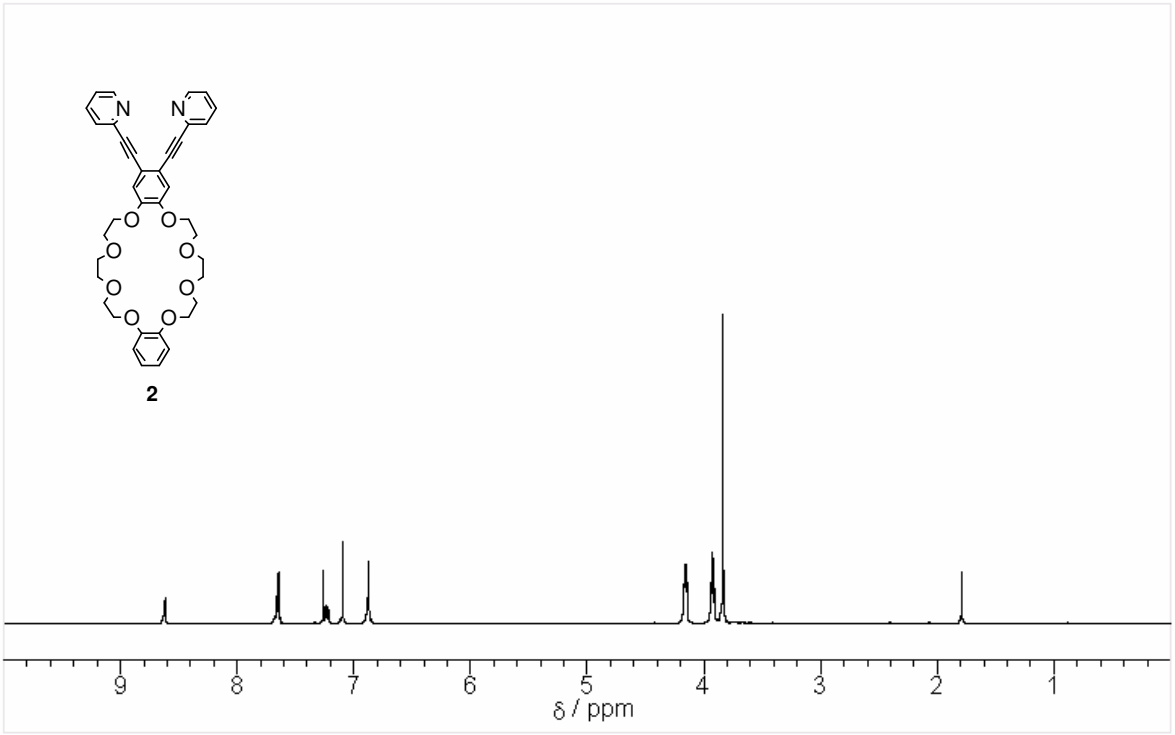
^{1}H NMR spectrum of 1 ($CDCl_3$, 400 MHz, r.t.)



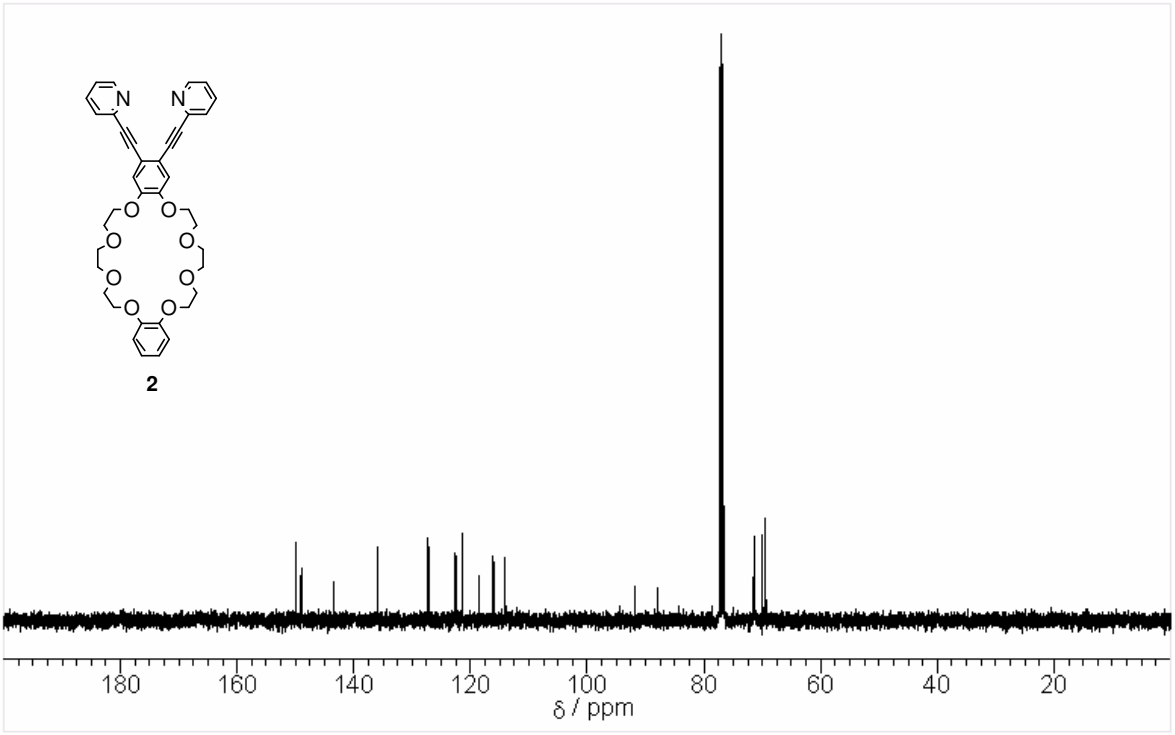
^{13}C{^{1}H} NMR spectrum of 1 ($CDCl_3$, 100 MHz, r.t.)



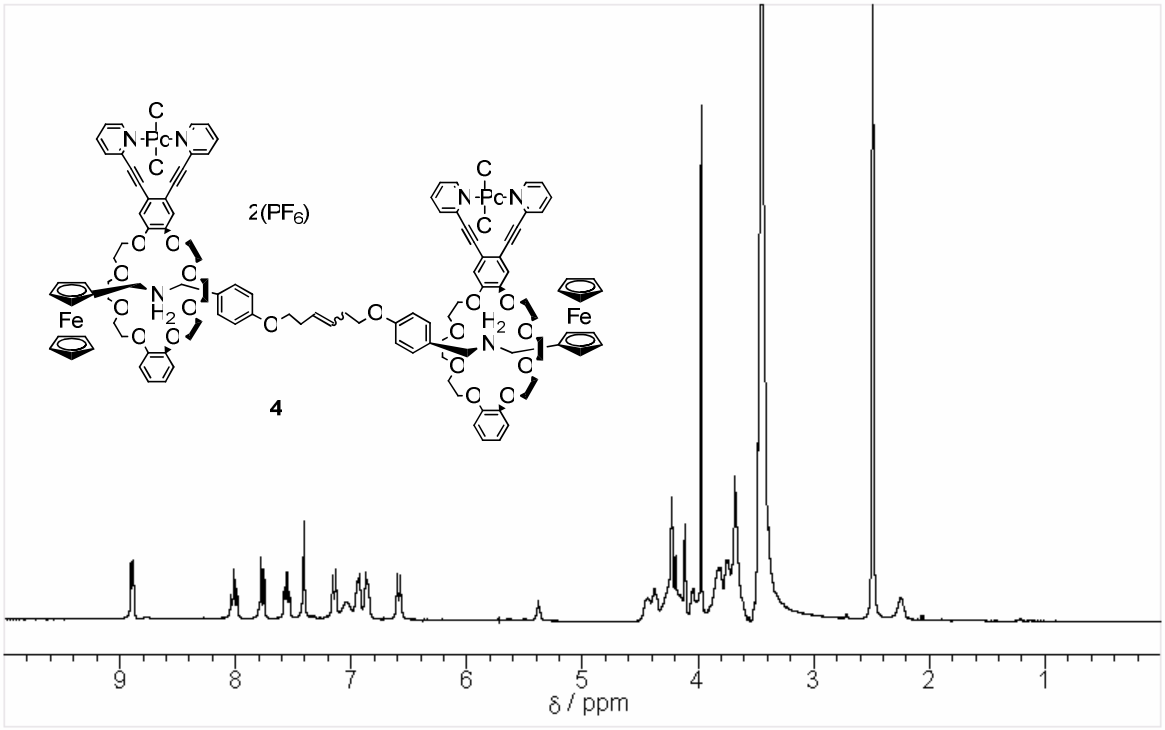
^{1}H NMR spectrum of 2 ($CDCl_3$, 400 MHz, r.t.)



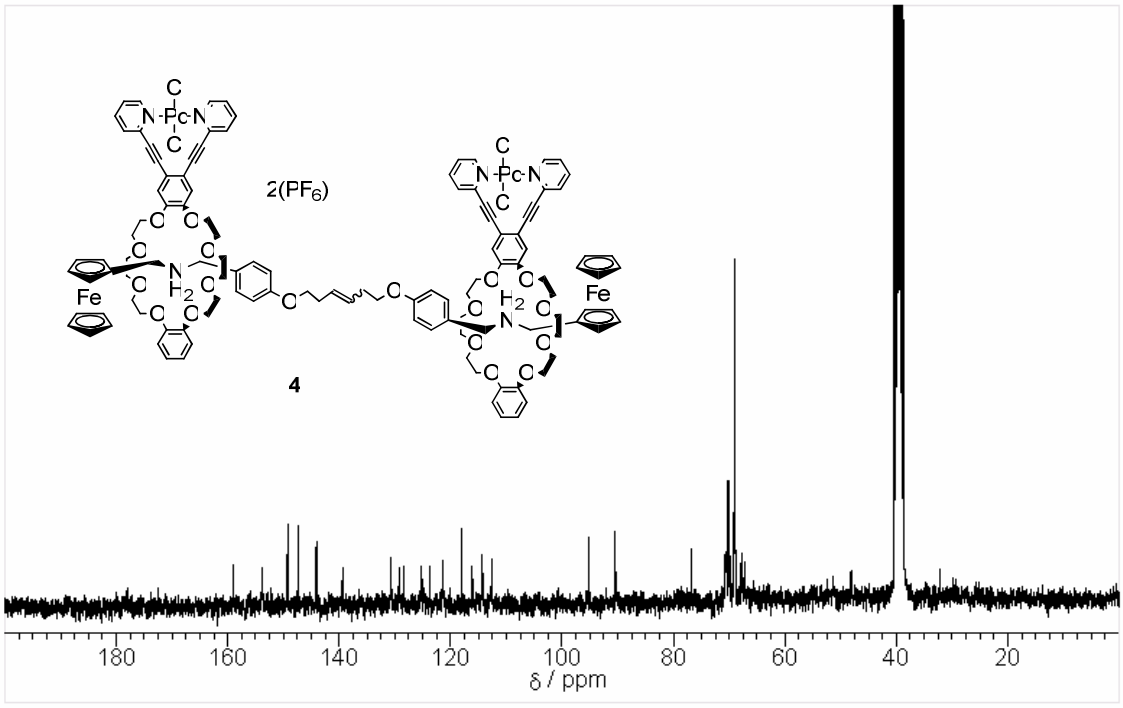
^{13}C{^{1}H} NMR spectrum of 2 ($CDCl_3$, 100 MHz, r.t.)



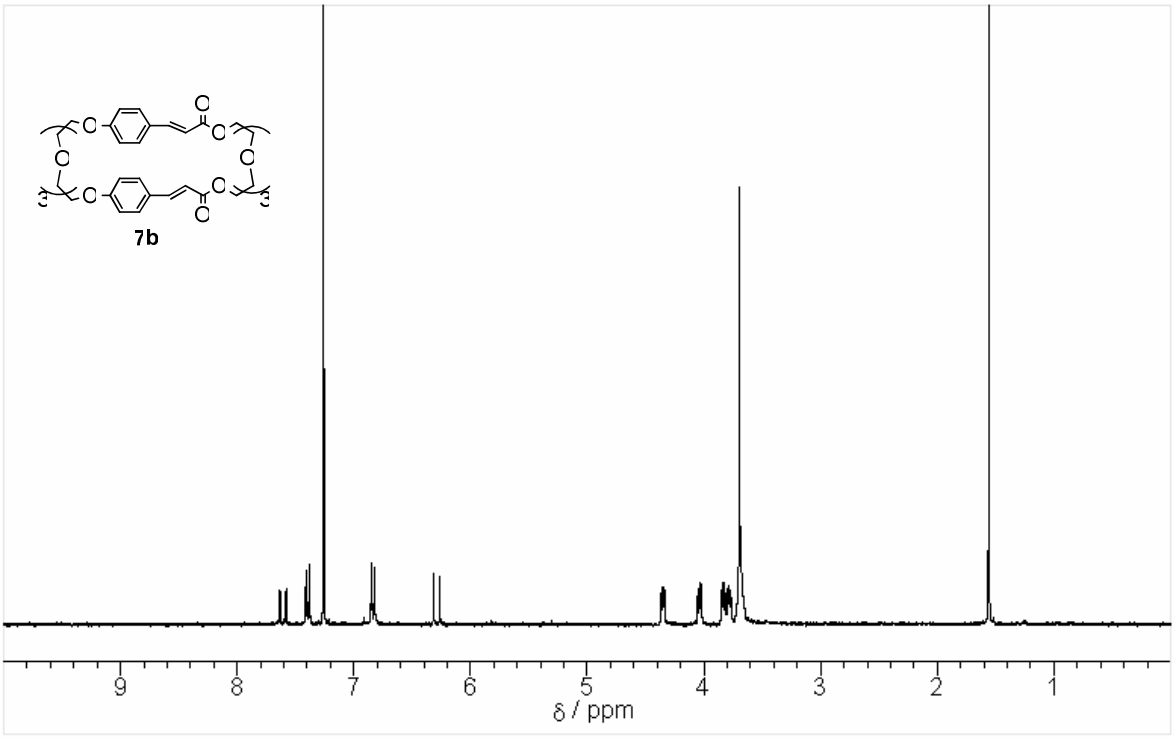
^{1}H NMR spectrum of 4 (dmso-d_6, 300 MHz, r.t.)



^{13}C{^{1}H} NMR spectrum of 4 (dmso-d_6, 100 MHz, r.t.)



^{1}H NMR spectrum of 7b ($CDCl_3$, 300 MHz, r.t.)



^{13}C{^{1}H} NMR spectrum of 7b ($CDCl_3$, 77.5 MHz, r.t.)