Supporting Information

Title: 24-Fold Endohedral Functinalization of a Self-assembled $M_{12}L_{24}$ Coordination Nanoball

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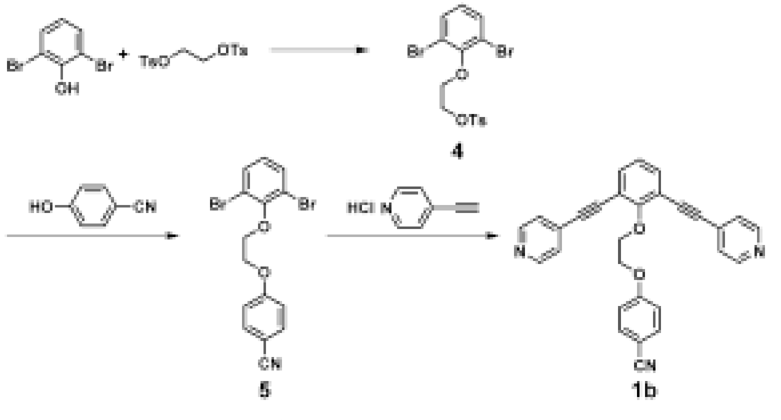
NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. The chemical shift values reported here are with respect to an internal TMS standard for CD_3Cl and DMSO-d_6, and an external TMS standard for CD_3CN. CSI-MS (cold-spray ionization mass spectroscopy) spectra were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without any further purification.

Synthesis of 2,6-bis(4-pyridylethynyl)toluene (1a)

Tri-*t*-butylphosphine (0.076 mL, 0.30 mmol; 10% solution in hexane) and diisopropylamine (0.68 mL, 4.8 mmol) was added to a mixture of 2,6-dibromotoluene (0.50 g, 2.0 mmol), 4-ethynylpyridine hydrochloride (0.67 g, 4.8 mmol), Pd(PhCN$_2$)Cl$_2$ (46.0 mg, 0.12 mmol) and copper (I) iodide (15 mg, 0.080 mmol), and the mixture was stirred in dioxane (2 mL) at room temperature for 17 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and filtered. After dilution with water (100mL), the mixture was washed with ethylenediamine (2 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 2:1) to give the title compound as a white solid (0.48 g, 1.6 mmol) in 81% yield. mp 102 ℃. ^{1}H NMR (500 MHz, DMSO-d_6, 27 ℃) δ 8.65 (d, J = 5.8 Hz, 4H), 7.68 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 6.3 Hz, 4H), 7.37 (t, J = 7.8 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 ℃) δ 150.0 (CH), 142.2 (C), 133.2 (CH), 129.9 (C), 126.6 (CH), 126.0 (CH), 122.0 (C), 91.5 (C), 91.0 (C), 18.9 (CH$_3$). IR (KBr, cm^{-1}) 3037, 2209, 1591, 1538, 1488, 1401, 1201, 988, 817, 799, 710. Elemental Analysis Calcd for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.45; H, 5.08; N, 9.22.

Ligand 1b was synthesized as follows:

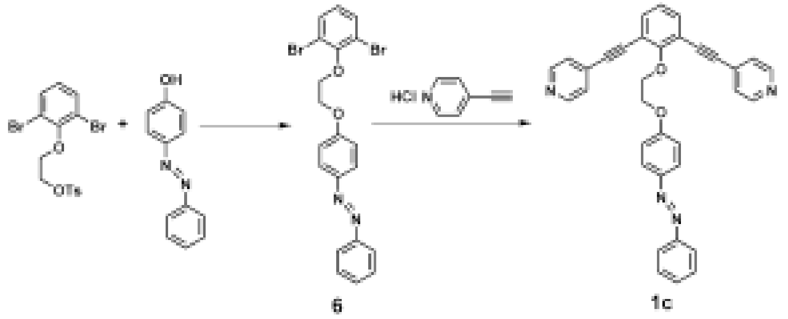


Synthesis of 1,3-dibromo-2-[2-(p-toluenesulfonyloxy)ethoxy]benzene (4) A mixture of 2,6-dibromophenol (10.0 g, 39.7 mmol), 1,2-bis(tosyloxy)ethane (20.0 g, 54.0 mmol) and potassium carbonate (8.72 g, 63.2 mmol) was stirred in acetone (300 mL) under argon atmosphere at 55 ℃ for 1 d. After dilution with water, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane: ethyl acetate = 2:1) to give the title compound as a white powder (15 g, 33 mmol) in 82% yield. mp 52 ℃. ^{1}H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 7.86 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.72 (t, J = 8.1 Hz, 1H), 4.42-4.46 (m, 2H), 4.20-4.24 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 152.5 (C), 144.9 (C), 132.8 (C), 132.7 (CH), 129.8 (CH), 128.0 (CH), 126.7 (CH), 118.1 (C), 70.1 (CH_2), 68.4 (CH_2), 21.6 (CH_3). IR (KBr, cm^{-1}) 3084, 2930, 1597, 1441, 1349, 1248, 1172, 1020, 921, 909, 816. Elemental Analysis Calcd for $C_{15}H_{22}Br_2O_5$: C, 40.75; H, 5.02. Found: C, 40.51; H, 5.29.

Synthesis of 1,3-dibromo-2-[4-(p-cyanophenyl)-1,4-dioxabutyl]benzene (5) A mixture of compound **4** (0.90 g, 2.0 mmol), 4-cyanophenol (0.28 g, 3.0 mmol) and potassium carbonate (0.83 g, 6.0 mmol) was stirred in *N*,*N*-dimethylformamide (50 mL) under argon atmosphere at 100 ℃ for 1 d. After dilution with water, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1:1) to give the title compound as a white powder (1.0 g, 2.6 mmol) in 87% yield. mp 85 ℃. ^{1}H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 7.54 (d, J =9.0 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 6.83 (t, J = 8.1 Hz, 1H), 4.32-4.42 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 161.9 (C), 152.8 (C), 134.0 (CH), 132.8 (CH), 126.7 (CH), 119.1 (C), 118.3 (C), 115.4 (CH), 104.3 (C), 70.9 (CH_2), 67.2 (CH_2). IR (KBr, cm^{-1}) 3079, 2929, 2226, 1605, 1507, 1428, 1367, 1244, 1173, 1042, 933, 830. Elemental Analysis Calcd for $C_{15}H_{11}NBr_2O_2{\cdot}0.3H_2O$: C, 44.76; H, 2.91; N, 3.48. Found: C, 45.03; H, 2.91; N, 3.18.

Synthesis of 2-[4-(p-cyanophenyl)-1,4-dioxabutyl]-1,3-bis(4-pyridylethynyl) benzene (1b) Tri-*t*-butylphosphine (0.12 mL, 0.48 mmol) and diisopropylamine (0.68 mL, 4.8 mmol) was added to a mixture of compound **5** (1.0 g, 2.5 mmol), 4-ethynylpyridine hydrochloride (1.0 g, 7.2 mmol), $Pd(PhCN_2)Cl_2$ (76.0 mg, 0.20 mmol) and copper (I) iodide (25.9 mg, 0.14 mmol), and the mixture was stirred in dioxane (9 mL) at 100 ℃ for 40 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and filtered. After dilution with water, the mixture was washed with ethylenediamine (2 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$:methanol = 50:1) to give the title compound as a pale yellow solid (1.0 g, 2.3 mmol) in 92% yield. mp 134 ℃. ^{1}H NMR (500 MHz, DMSO-d_6, 27 ℃) δ 8.59 (d, J = 5.8 Hz, 4H), 8.29 (d, J = 6.0 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 6.0 Hz, 4H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 6.2 Hz, 2H), 4.70-4.73 (m, 2H), 4.45-4.48 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 ℃) δ 161.7 (C), 161.1 (C), 149.8 (CH), 134.9 (CH), 134.1 (CH), 129.8 (C), 125.1 (CH), 124.5 (CH), 119.0 (C), 116.0 (C), 115.4 (CH), 102.9 (C), 91.3 (C), 89.1 (C), 72.7 (CH_2), 68.2 (CH_2). IR (KBr, cm^{-1}) 3045, 2945, 2224, 1597, 1504, 1429, 1294, 1246, 1171, 1068, 930, 840. Elemental Analysis Calcd for $C_{29}H_{19}N_3O_2$: C, 78.90; H, 4.34; N, 9.52. Found: C, 78.77; H, 4.54; N, 9.34.

Ligand 1c was synthesized as follows:



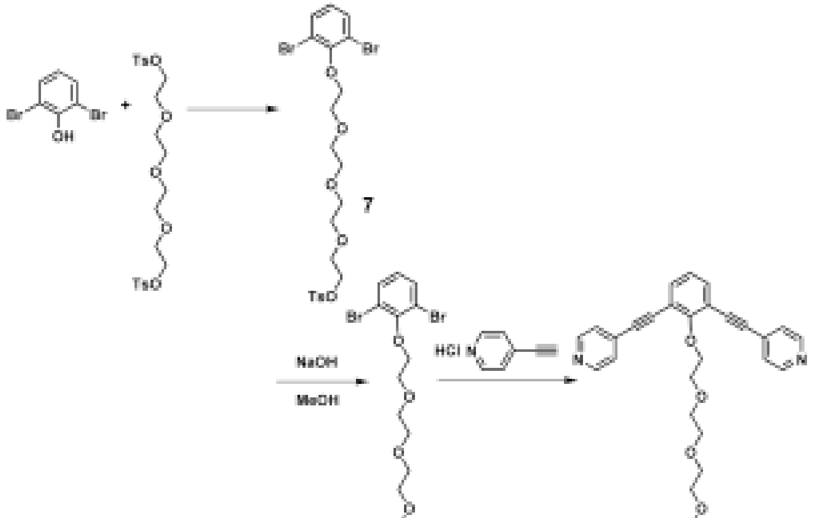
6

1c

Synthesis of 4-[2-(2,6-dibromophenyloxy)ethoxy]azobenzene (6) A mixture of compound **4** (1.0 g, 2.3 mmol), *p*-phenylazobenzene (0.68 g, 3.4 mmol) and potassium carbonate (1.0 g, 7.4 mmol) was stirred in *N*,*N*-dimethylformamide (50 mL) under argon atmosphere at 90 ℃ for 1 d. After dilution with water, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$) to give the title compound as a dark orange powder (1.1 g, 2.3 mmol) in 99% yield. mp 99.6-100.3 ℃. ^{1}H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 7.93 (d, *J* =8.8 Hz, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.5-4.9 (m, 2H), 4.5-4.9 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 161.1 (C), 153.1 (C), 152.8 (C), 147.2 (C), 132.8 (CH), 130.4 (CH), 129.0 (CH), 126.6. (CH), 124.7 (CH), 122.6 (CH), 118.4 (C), 114.9 (CH), 71.2 (CH_2), 67.2 (CH_2) IR (KBr, cm^{-1}) 3062, 2974, 2870, 2360, 1601, 1583, 1557, 1500, 1439, 1369, 1299, 1240, 1196, 1146, 1110, 1071, 1042, 932, 907, 838, 760, 721, 688, 615. Elemental Analysis Calcd for $C_{20}H_{16}Br_2N_2O_2$: C, 50.45; H, 3.39; N, 5.88. Found: C, 50.42; H, 3.56; N, 5.87.

Synthesis of 1,3-bis(4-pyridylethynyl)-2-[2-(4-phenylazophenyloxy)ethoxy] benzene (1c) Tti-*t*-butylphosphine (0.038 mL, 0.13 mmol) and diisopropylamine (1.5 mL, 11 mmol) was added to a mixture of compound **6** (0.50 g, 1.1 mmol), 4-ethynylpyridine hydrochloride (0.45 g, 3.2 mmol), $Pd(PhCN_2)Cl_2$ (26 mg, 0.068 mmol) and copper (I) iodide (8.8 mg, 0.046 mmol), and the mixture was stirred in dioxane (3 mL) at 50 ℃ for 27 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and filtered. After dilution with water, the mixture was washed with ethylenediamine (2 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$) to give the title compound as an orange solid (0.49 g, 0.95 mmol) in 90% yield. mp 167.6-168.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 8.57 (d, J = 6.0 Hz, 4H), 7.88 (d, J = 7.9 Hz, 2H), 7.85 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.9 Hz, 2H), 7.44 (t, J = 7.9 Hz, 1H), 7.31 (d, J = 6.0 Hz, 4H), 7.17 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 4.76-4.74 (m, 2H), 4.49-4.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 161.4 (C), 160.9 (C), 152.7 (C), 149.9 (CH), 147.3 (C), 134.6 (CH), 131.0 (CH), 130.5 (C), 129.1 (CH), 125.4 (CH), 124.7 (CH), 124.1 (CH), 122.6 (CH), 117.0 (C), 114.8 (CH), 91.6 (C), 89.3 (C), 72.7 (CH_2), 67.9 (CH_2). IR (KBr, cm^{-1}) 3038, 3020, 2940, 2218, 1918, 1823, 1596, 1537, 1499, 1453, 1424, 1412, 1324, 1306, 1294, 1258, 1242, 1213, 1159, 1143, 1106, 1068, 1031, 989, 967, 927, 889, 849, 811, 789, 778, 693. Elemental Analysis Calcd for $C_{34}H_{24}N_4O_2 \cdot H_2O$: C, 75.82; H, 4.87; N, 10.40. Found: C, 75.88; H, 4.63; N, 10.05.

Ligand 1d was synthesized as follows:

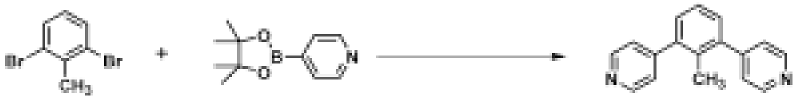


Synthesis of 1,3-dibromo-2-(12-tosyloxy-1,4,7,10-tetraoxadodecyl)benzene (**7**) A mixture of 2,6-dibromophenol (2.6 g, 10 mmol), tetra(ethylene glycol) di-*p*-toluenesulfonate (9.4 g, 19 mmol) and potassium carbonate (2.7 g, 20 mmol) was stirred in acetone (80 mL) under argon atmosphere at 55 ℃ for 1 d. The reaction mixture was treated with water (100 mL) and the products were extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$) to give the title compound as colorless oil (4.1 g, 7.1 mmol) in 68% yield. ^1H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.86 (t, *J* = 7.9 Hz, 1H), 4.19 (t, *J* = 4.9 Hz, 2H), 4.16 (t, *J* = 5.0 Hz, 2H), 3.91-3.94 (m, 2H), 3.74-3.77 (m, 2H), 3.68-3.71 (m, 2H), 3.64-3.67 (m, 2H), 3.58-3.60 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 153.3 (C), 144.8 (C), 133.0 (C), 132.7 (CH), 129.8 (CH), 128.0 (CH), 126.3 (CH), 118.4 (Cq), 72.4 (CH_2), 70.8 (CH_2), 70.7 (CH_2), 70.7 (CH_2), 70.6 (CH_2), 70.1 (CH_2), 69.2 (CH_2), 68.7 (CH_2), 21.6 (CH_3). IR (KBr, cm^{-1}) 2937, 1599, 1440, 1356, 1247, 1177, 1113, 920. Elemental Analysis Calcd for $C_{21}H_{26}Br_2O_7S$: C, 43.32; H, 4.50. Found: C, 43.51; H, 4.71.

Synthesis of 1,3-dibromo-2-(1,4,7,10,13-pentaoxatetradecyl)benzene (8) A mixture of compound **7** (0.80 g, 1.4 mmol), and sodium hydrate (1.1 g, 27 mmol) was stirred in methanol (40 mL) under argon atmosphere at 90 ℃ for 24 h. The reaction mixture was treated with water (80 mL) and the products were extracted with $CHCl_3$. The combined organic layer was evaporated to give the title compound as colorless oil (0.59 g, 1.3 mmol) in 97% yield. ^1H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 7.50 (d, *J* = 8.1 Hz, 2H), 6.86 (t, *J* = 8.1 Hz, 1H), 4.20 (t, *J* = 5.0 Hz, 2H), 3.94 (t, *J* = 5.1 Hz, 2H), 3.76-3.79 (m, 2H), 3.68-3.72 (m, 4H), 3.64-3.68 (m, 4H), 3.54-3.57 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 ℃) δ 153.3 (C), 132.7 (CH), 126.3 (CH), 118.4 (C), 72.4 (CH_2), 71.9 (CH_2), 70.8 (CH_2), 70.7 (CH_2), 70.7 (CH_2), 70.6 (CH_2), 70.5 (CH_2), 70.1 (CH_2), 59.0 (CH_3). IR (KBr, cm^{-1}) 2963, 1440, 1260, 1094, 1068, 1017, 863, 798. Elemental Analysis Calcd for $C_{15}H_{22}Br_2O_5$: C, 40.75; H, 5.02. Found: C, 40.51; H, 5.29.

Synthesis of 2-(1,4,7,10,13-pentaoxatetradecyl)-1,3-bis(4-pyridylethynyl) benzene (1d) Tti-*t*-butylphosphine (0.076 mL, 0.30 mmol) and diisopropylamine (1.5 mL, 11 mmol) was added to a mixture of compound **8** (0.54 g, 1.2 mmol), 4-ethynylpyridine hydrochloride (0.48 g, 3.4 mmol), $Pd(PhCN_2)Cl_2$ (28 mg, 0.074 mmol) and copper (I) iodide (9.4 mg, 0.049 mmol), and the mixture was stirred in dioxane (2.5 mL) at 90 ℃ for 1d under argon atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and filtered. After dilution with water, the mixture was washed with ethylenediamine (2 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$:methanol = 50:1) to give the title compound as colorless oil (0.47 g, 0.97 mmol) in 81% yield. ^1H NMR (500 MHz, CD_3CN, 27 ℃) δ 9.47 (d, *J* = 5.8 Hz, 4H), 8.46 (d, *J* = 7.6 Hz, 2H), 8.33 (d, *J* = 6.2 Hz, 4H), 8.05 (t, J = 7.9 Hz, 1H), 5.31-5.34 (m, 2H), 4.72-4.75 (m, 2H), 4.46-4.49 (m, 2H), 4.32-4.37 (m, 8H), 4.25-4.28 (m, 2H), 4.10 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 27 ℃) δ 162.5 (C), 150.9 (CH), 135.6 (CH), 131.5 (C), 126.1 (CH), 125.0 (CH), 117.6 (C), 92.0 (C), 90.0 (C), 74.7 (CH_2), 72.4 (CH_2), 71.4 (CH_2), 71.2 (CH_2), 71.1 (CH_2), 71.0 (CH_2), 71.0 (CH_2), 70.8 (CH_2), 58.7 (CH_3). IR (KBr, cm^{-1}) 2877, 2215, 1594, 1407, 1238, 1105, 989, 820. Elemental Analysis Calcd for $C_{29}H_{30}N_2O_5{\cdot}0.6H_2O$: C, 70.03; H, 6.32; N, 5.63. Found: C, 70.25; H, 6.53; N, 5.34.

Synthesis of 2,6-bis(4-pyridyl)toluene (3)



A mixture of 2,6-dibromotoluene (0.25 g, 1.0 mmol), 4-pyridylboronic acid pinacol ester (0.62 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.10 mmol), and potassium phosphate (1.7 g, 8.0 mmol) was refluxed in 1,4-dioxane (30 mL) for 2 d under argon atmosphere. After dilution with water, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel ($CHCl_3$:methnol = 10:1) to give the title compound as a white solid (0.19 g, 0.77 mmol) in 77% yield. mp 149 ℃. ^{1}H NMR (500 MHz, $CDCl_3$, 27 ℃) δ 8.66 (d, J = 5.6 Hz, 4H), 7.41-7.45 (m, 5H), 7.32 (d, J = 7.6 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 ℃) δ 149.6 (CH), 148.9 (C), 140.0 (C), 131.9 (C), 129.4 (CH), 126.3 (CH), 124.3(CH), 18.1 (CH_3). IR (KBr, cm^{-1}) 3062, 2013, 1595, 1542, 1410, 1215, 1069, 990, 822, 797. Elemental Analysis Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.70; H, 5.85; N, 11.10.

Synthesis of 2a Compound **1a** (5.9 mg, 0.02 mmol) was treated with $Pd(NO_3)_2$ (2.3 mg, 0.01 mmol) in dimethyl sulfoxide (1.0 mL) at 70 °C for 4 h. The quantitative formation of **2a** was confirmed by ^{1}H NMR. By addition of diethyl ether to the resulting solution, precipitated a white solid, which was separated by centrifugation and dried *in vacuo* to give the title complex (6.4 mg, 78% yield). mp >260 ℃ (decomposed). ^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) δ 9.24 (br, 96H), 7.90 (br, 96H), 7.68 (br, 48H), 7.39 (br, 24H), 2.67 (s, 72H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 °C) δ 151.0 (CH), 143.8 (C), 134.4 (C), 134.1 (CH), 128.6 (CH), 126.9 (CH), 121.2 (C), 95.9 (C), 89.7 (C), 18.7 (CH_3). IR (KBr, cm^{-1}) 3088, 2208, 1608, 1497, 1316, 1270, 1204, 973, 825, 795, 709. Mass spectrometry was performed after **2a** was converted to its $CF_3SO_3^-$ salt by adding $NaCF_3SO_3$ to the DMSO solution of **2a**. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN:DMSO = 20:1): m/z 1837.1 $[M-6(CF_3SO_3^-)]^{6+}$, 1553.2 $[M-7(CF_3SO_3^-)]^{7+}$, 1340.3 $[M-8(CF_3SO_3^-)]^{8+}$, 1174.8

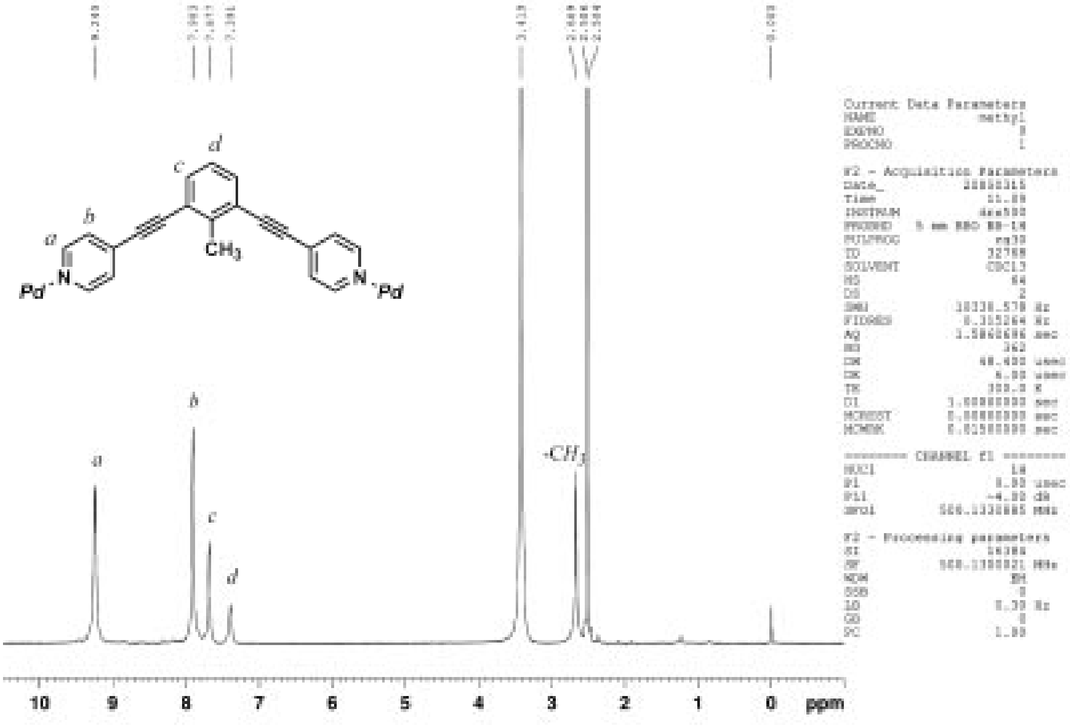
$[M{-}9(CF_3SO_3^-)]^{9+}$, 1058.2 $[M{-}10(CF_3SO_3^-)+2(DMSO)]^{10+}$, 955.7 $[M{-}11(CF_3SO_3^-)+3(DMSO)]^{11+}$, 870.1 $[M{-}12(CF_3SO_3^-)+4(DMSO)]^{12+}$, 809.5 $[M{-}13(CF_3SO_3^-)+7(DMSO)]^{13+}$, 746.5 $[M{-}14(CF_3SO_3^-)+8(DMSO)]^{14+}$.

Synthesis of 2b Compound **1b** (8.8 mg, 0.02 mmol) was treated with $Pd(NO_3)_2$ (2.3 mg, 0.01 mmol) in dimethyl sulfoxide (1.0 mL) at 70 °C for 4 h. Isolated yield was 78 % (NMR yield 100 %). mp >270 °C (decomposed). ^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) δ 9.23 (br s, 96H), 7.75 (br s, 96H), 7.68 (br s, 24H), 7.44 (t, *J* = 8.0 Hz, 24H), 7.29 (br s, 24H), 6.94 (t, *J* = 8.0 Hz, 24H), 4.70 (br s, 48H), 4.43 (br s, 48H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 °C) δ 163.3 (C), 162.6 (C), 152.0 (CH), 137.1 (CH), 135.1 (C), 134.9 (CH), 129.5 (CH), 125.8 (CH), 120.0 (C), 116.6 (CH), 116.2 (C), 103.8 (C), 94.9 (C), 90.9 (C), 74.2 (CH_2), 69.4 (CH_3). IR (KBr, cm^{-1}) 3097, 2941, 2221, 1610, 1504, 1429, 1383, 1262, 1173, 1062, 926, 837. Elemental Analysis Calcd for $C_{696}H_{336}N_{72}O_{72}Pd_{12}\cdot32DMSO$, C, 57.55; H, 4.12; N, 8.48. Found: C, 57.71; H, 4.22; N, 8.22. Mass spectrometry was performed after **2b** was converted to its $CF_3SO_3^-$ salt by adding $NaCF_3SO_3$ to the DMSO solution of **2b**. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN:DMSO = 20:1): *m/z* 2058.3 $[M{-}7(CF_3SO_3^-)]^{7+}$, 1781.1 $[M{-}8(CF_3SO_3^-)]^{8+}$, 1575.3 $[M{-}9(CF_3SO_3^-)+(DMSO)]^{9+}$, 1410.7 $[M{-}10(CF_3SO_3^-)+2(DMSO)]^{10+}$, 1276.11 $[M{-}11(CF_3SO_3^-)+3(DMSO)]^{11+}$, 1163.8 $[M{-}12(CF_3SO_3^-)+4(DMSO)]^{12+}$.

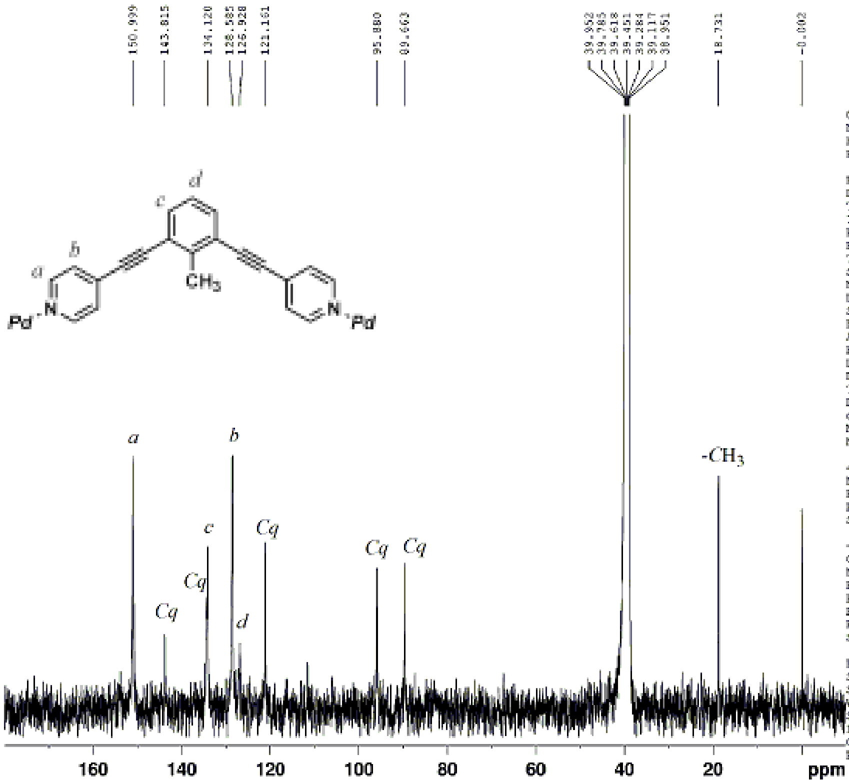
Synthesis of 2c Compound **1c** (7.3 mg, 0.014 mmol) was treated with $Pd(NO_3)_2$ (1.6mg, 0.007 mmol) in dimethyl sulfoxide (0.7 mL) at 70 °C for 12 h. Isolated yield was 98 % (NMR yield 100 %). mp > 194 °C (decomposed). ^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) δ 9.23 (br s, 96H), 7.82 (d, *J* = 7.4 Hz, 48H), 7.76 (br s, 96H), 7.64 (br s, 48H), 7.59 (d, *J* = 8.7 Hz, 48H), 7.56 (t, *J* = 7.4 Hz, 48H), 7.48 (t, *J* = 7.4 Hz, 24H), 7.26 (br s, 24H) 6.81 (d, *J* = 8.7 Hz, 48H), 4.59 (br s, 48H), 4.34 (br s, 48H). ^{13}C NMR (125 MHz, DMSO-d_6, 27 °C) δ 161.9 (C), 160.6 (C), 151.9 (C), 151.0 (CH), 146.1 (C), 135.9 (CH), 134.1 (C), 130.8 (CH), 129.3 (CH), 128.3 (CH), 124.24 (CH), 124.16 (CH), 122.1 (CH), 115.2 (C), 114.8 (CH), 93.7 (C), 89.8 (C), 72.8 (CH_2), 67.9 (CH_2). IR (KBr, cm^{-1}) 3094, 3048, 3015, 2214, 1612, 1582, 1538, 1500, 1454, 1432, 1384, 1369, 1338, 1320, 1270, 1256, 1224, 1205, 1142, 1105, 1064, 1040, 1031, 1001, 926, 838, 788, 770, 722, 690. Elemental Analysis Calcd for $C_{816}H_{576}N_{120}O_{120}Pd_{12}\cdot30DMSO$, C, 59.77; H, 4.34; N, 9.55. Found: C, 59.92; H, 4.11; N, 9.27. Mass spectrometry was performed after **2c** was converted to its $CF_3SO_3^-$ salt by adding $NaCF_3SO_3$ to the DMSO solution of **2c**. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN): m/z 2019.6 $[M{-}8(CF_3SO_3^-)]^{8+}$, 1778.5 $[M{-}9(CF_3SO_3^-)]^{9+}$, 1585.6 $[M{-}10(CF_3SO_3^-)]^{10+}$, 1428.2 $[M{-}11(CF_3SO_3^-)]^{11+}$.

Synthesis of 2d Compound **1d** (9.7 mg, 0.02 mmol) was treated with $Pd(CF_3SO_3)_2(CH_3CN)_4$ (5.7 mg, 0.01 mmol) in acetonitrile (1.0 mL) at 50 ℃ for 12 h. The quantitative formation of **2d** was confirmed by ^{1}H NMR. The solution was dried *in vacuo* and recrystallized from acetonitrile to give the title complex (11 mg, 78% yield) as an orange solid. mp >270 ℃ (decomposed). ^{1}H NMR (500 MHz, CD_3CN, 27 ℃) δ 9.87 (d, J = 6.7 Hz, 96H), 8.52 (d, J = 6.8 Hz, 96H), 8.47 (d, J = 7.8 Hz, 48H), 8.04 (t, J = 7.7 Hz, 24H), 5.24-5.27 (m, 48H), 4.69-4.72 (m, 48H), 4.45-4.48 (m, 48H), 4.35-4.38 (m, 48H), 4.27-4.30 (m, 48H), 4.21-4.24 (m, 48H), 4.17-4.20 (m, 47H), 4.07-4.10 (m, 48H), 3.94 (s, 72H). ^{13}C NMR (125 MHz, CD_3CN, 27 ℃) δ 163.6 (C), 151.8 (CH), 137.0 (CH), 136.4 (C), 129.61 (CH), 125.3 (CH), 116.6 (C), 95.4 (C), 90.5 (C), 75.1 (CH_2), 72.3 (CH_2), 71.4 (CH_2), 71.2 (CH_2), 71.0 (CH_2), 70.9 (CH_2), 70.9 (CH_2), 70.8 (CH_2), 58.7 (CH_3). IR (KBr, cm^{-1}) 2864, 2208, 1610, 1431, 1275, 1247, 1205, 1027, 836. CSI-MS ($CF_3SO_3^-$ salt, CH_3CN:DMSO = 1:1): *m/z* 1916.8 $[M-8(CF_3SO_3^-)]^{8+}$, 1687.4 $[M-9(CF_3SO_3^-)]^{9+}$, 1503.6 $[M-10(CF_3SO_3^-)]^{10+}$, 1353.4 $[M-11(CF_3SO_3^-)]^{11+}$, 1228.1 $[M-12(CF_3SO_3^-)]^{12+}$, 1128.2 $[M-13(CF_3SO_3^-)+(DMSO)]^{13+}$, 1042.4 $[M-14(CF_3SO_3^-)+2(DMSO)]^{14+}$.

^{1}H NMR of **2a**



^{13}C NMR of **2a**



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EXPNO                 6
PROCNO                1

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TD                65536
SOLVENT           CDCl3
NS                17131
DS                    2
SWH           39682.539 Hz
FIDRES         0.605507 Hz
AQ            0.8258162 sec
RG                 3251
DW               12.600 usec
DE                 6.00 usec
TE                300.0 K
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d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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PL1                2.00 dB
SFO1        125.7736214 MHz

======== CHANNEL f2 ========
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NUC2                 1H
PCPD2             80.00 usec
PL2               -4.00 dB
PL12              15.50 dB
PL13              15.50 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
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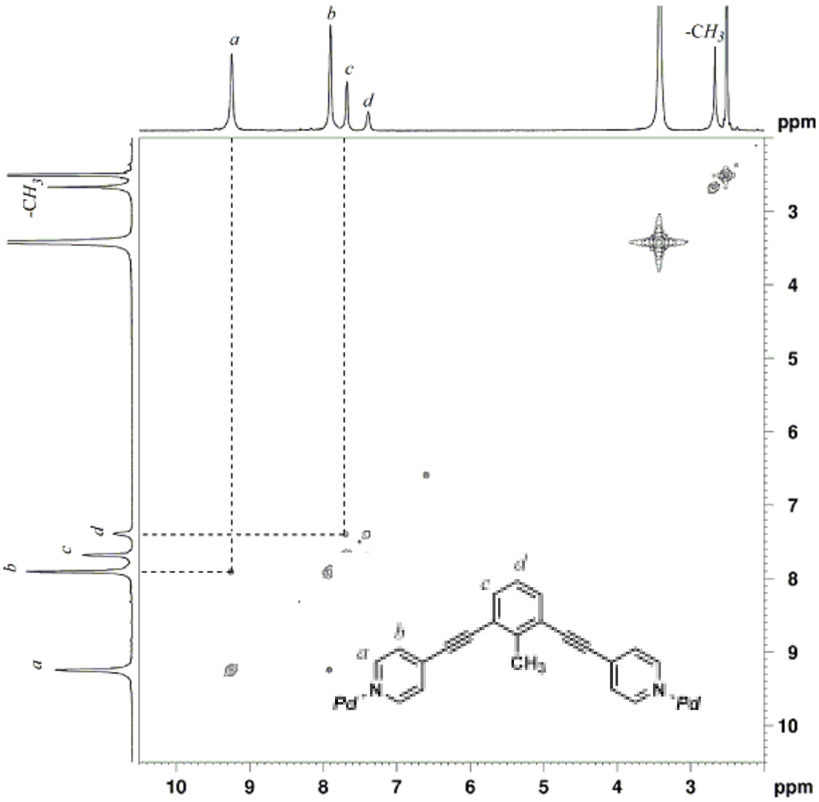
H-H COSY of **2a**



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EXPNO              1010
PROCNO                1

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PULPROG        cosygpqf
TD                 2048
SOLVENT            DMSO
NS                   32
DS                    8
SWH            7002.801 Hz
FIDRES         3.419337 Hz
AQ            0.1463486 sec
RG               1448.2
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DE                 6.00 usec
TE                300.0 K
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D1           1.48689198 sec
d13          0.00000400 sec
D16          0.00010000 sec
IN0          0.00014280 sec
MCREST       0.00000000 sec
MCWRK        1.48689198 sec

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P1                 9.00 usec
PL1               -4.00 dB
SFO1        500.1325027 MHz

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GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              10.00 %
GPZ2              10.00 %
P16             1000.00 usec

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TD                  128
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FIDRES        54.709385 Hz
SW               14.002 ppm
FnMODE               QF

F2 - Processing parameters
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SF          500.1300001 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

F1 - Processing parameters
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MC2                  QF
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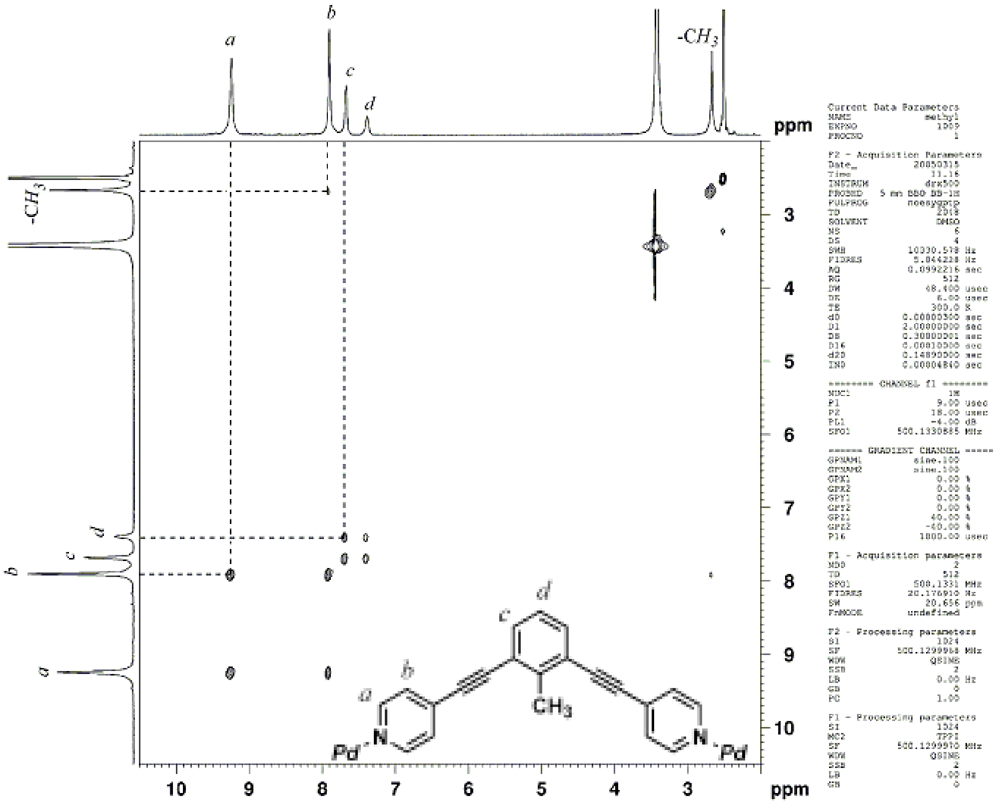
NOESY of **2a**



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EXPNO               1009
PROCNO                 1

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PULPROG         noesygptp
TD                  2048
SOLVENT             DMSO
NS                     6
DS                     4
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FIDRES          5.044228 Hz
AQ             0.0992216 sec
RG                   512
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DE                  6.00 usec
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D1            2.00000000 sec
D8            0.30000001 sec
D16           0.00010000 sec
d20           0.14890000 sec
IN0           0.00004840 sec

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P2                 18.00 usec
PL1                -4.00 dB
SFO1         500.1330885 MHz

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GPY1                0.00 %
GPY2                0.00 %
GPZ1               40.00 %
GPZ2              -40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
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FIDRES         20.176910 Hz
SW                20.656 ppm
FnMODE         undefined

F2 - Processing parameters
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WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
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MC2                 TPPI
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WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
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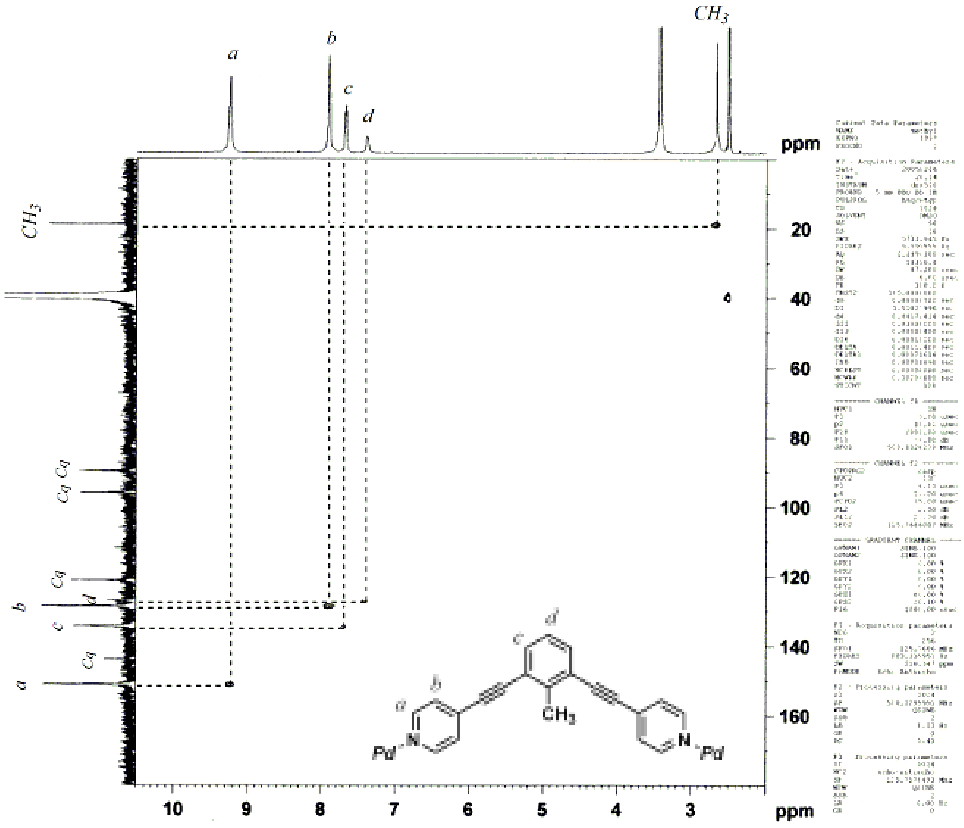
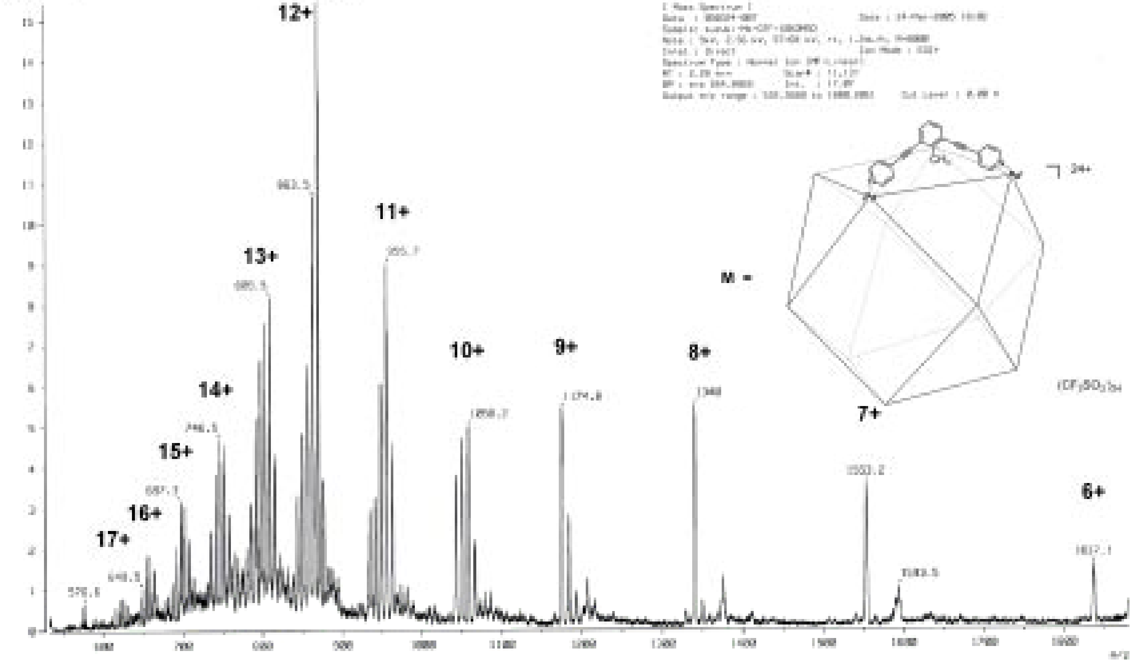
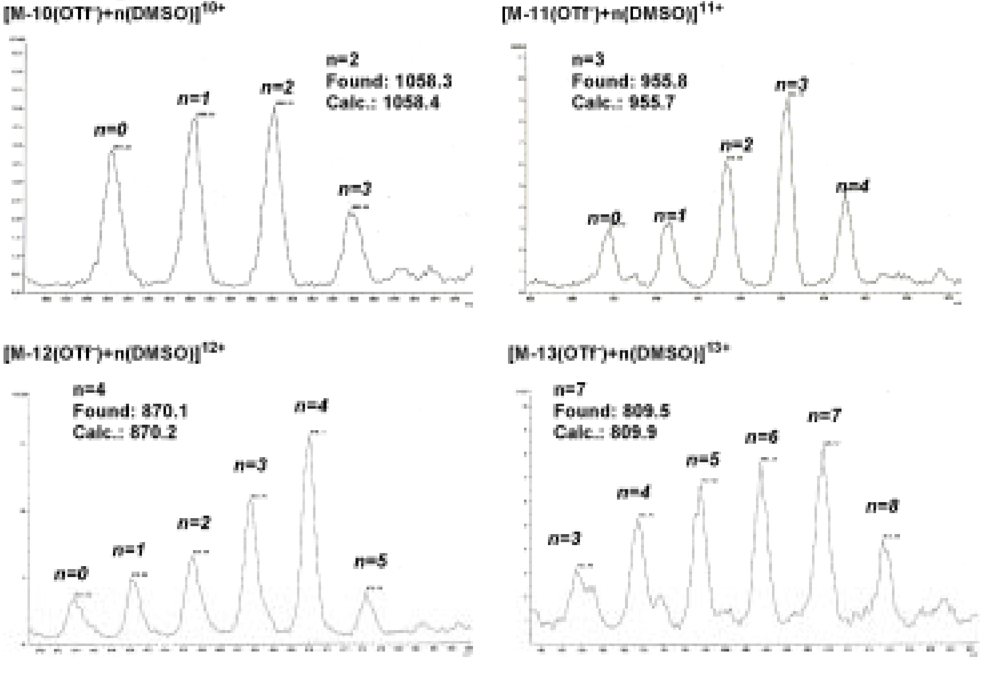
HSQC of **2a**



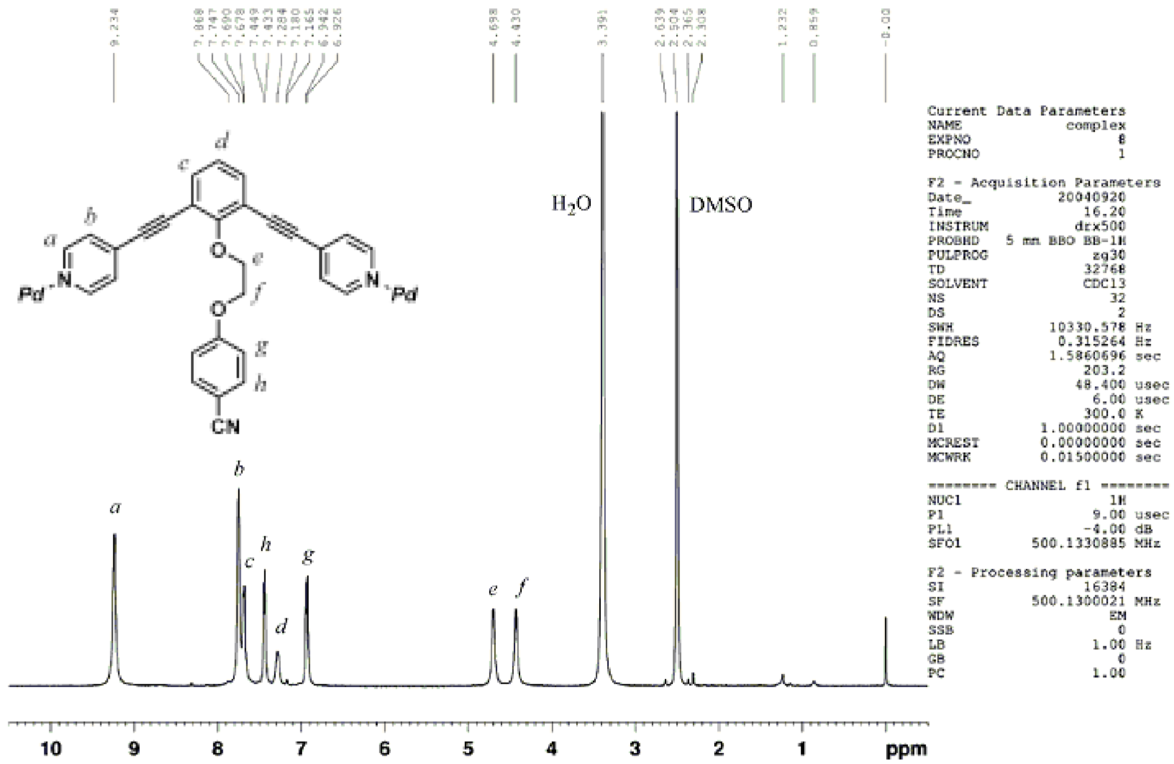
CSI-MS of **2a** (CH_3CN:DMSO = 20:1, r.t.)



Title Enlarged spectra of CSI-MS of **2a**



^{1}H NMR of **2b**



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EXPNO                   8
PROCNO                  1

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PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             10330.578 Hz
FIDRES           0.315264 Hz
AQ              1.5860696 sec
RG                  203.2
DW                 48.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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NUC1                   1H
P1                   9.00 usec
PL1                 -4.00 dB
SFO1          500.1330885 MHz

F2 - Processing parameters
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SSB                     0
LB                   1.00 Hz
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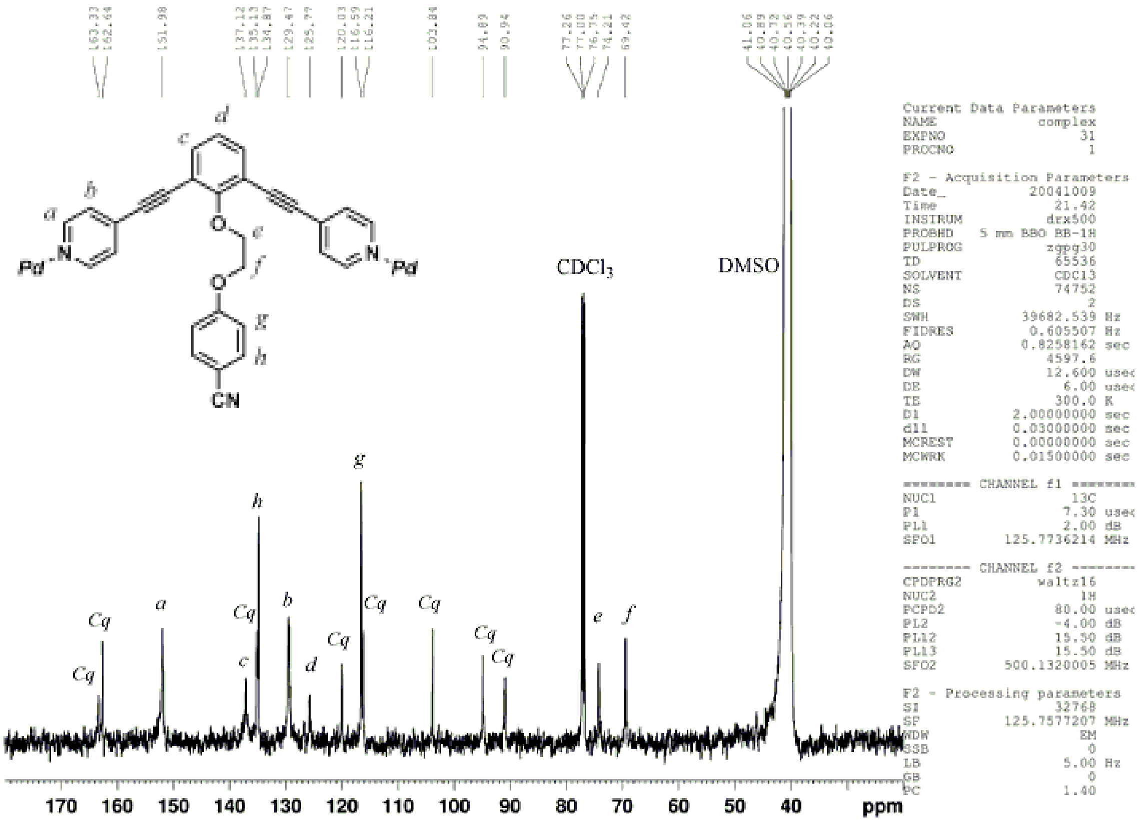
^{13}C NMR of **2b**



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EXPNO                  31
PROCNO                  1

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PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  74752
DS                      2
SWH             39682.539 Hz
FIDRES           0.605507 Hz
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RG                 4597.6
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DE                   6.00 use
TE                  300.0 K
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MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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P1                   7.30 use
PL1                  2.00 dB
SFO1          125.7736214 MHz

======== CHANNEL f2 =======
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NUC2                   1H
PCPD2               80.00 use
PL2                 -4.00 dB
PL12                15.50 dB
PL13                15.50 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
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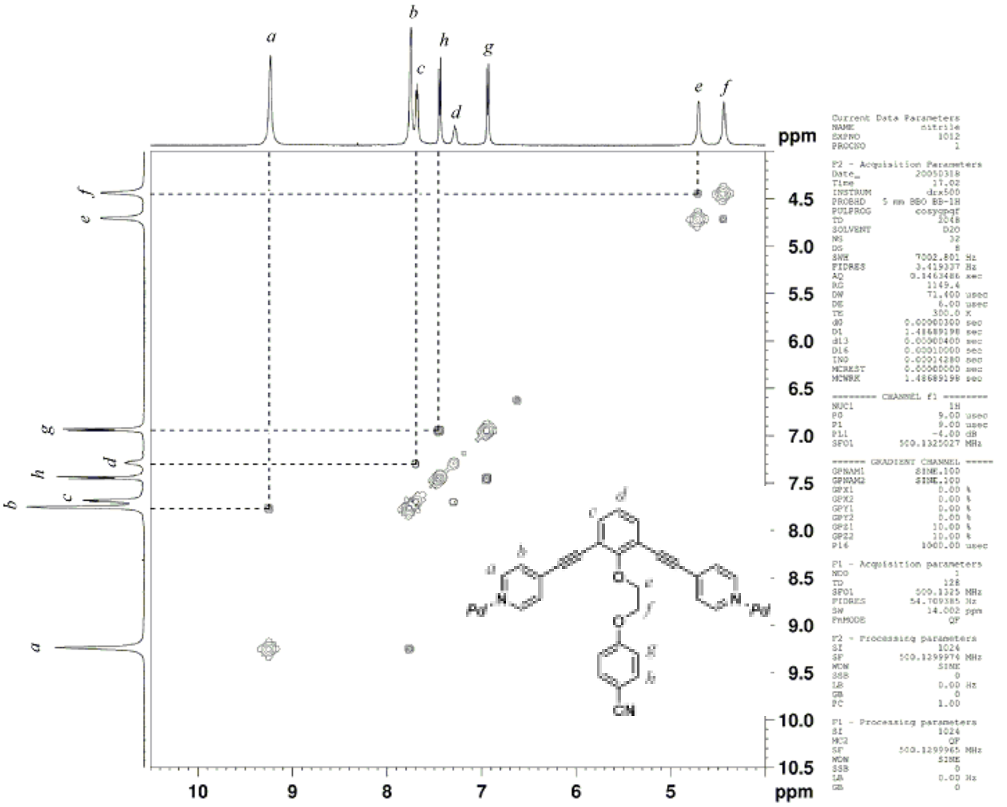
WDW                    EM
SSB                     0
LB                   5.00 Hz
GB                      0
PC                   1.40
```

H-H COSY of **2b**



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EXPNO                1012
PROCNO                  1

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PULPROG          cosygpqf
TD                   2048
SOLVENT               D2O
NS                     32
DS                      8
SWH              7002.801 Hz
FIDRES           3.419337 Hz
AQ              0.1463486 sec
RG                 1149.4
DW                 71.400 usec
DE                   6.00 usec
TE                  300.0 K
d0             0.00000300 sec
D1             1.48689198 sec
d13            0.00000400 sec
D16            0.00010000 sec
IN0            0.00014280 sec
MCREST         0.00000000 sec
MCWRK          1.48689198 sec

======== CHANNEL f1 ========
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GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                10.00 %
GPZ2                10.00 %
P16               1000.00 usec

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TD                    128
SFO1             500.1325 MHz
FIDRES          54.709385 Hz
SW                 14.002 ppm
FnMODE                 QF

F2 - Processing parameters
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WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
SI                   1024
MC2                    QF
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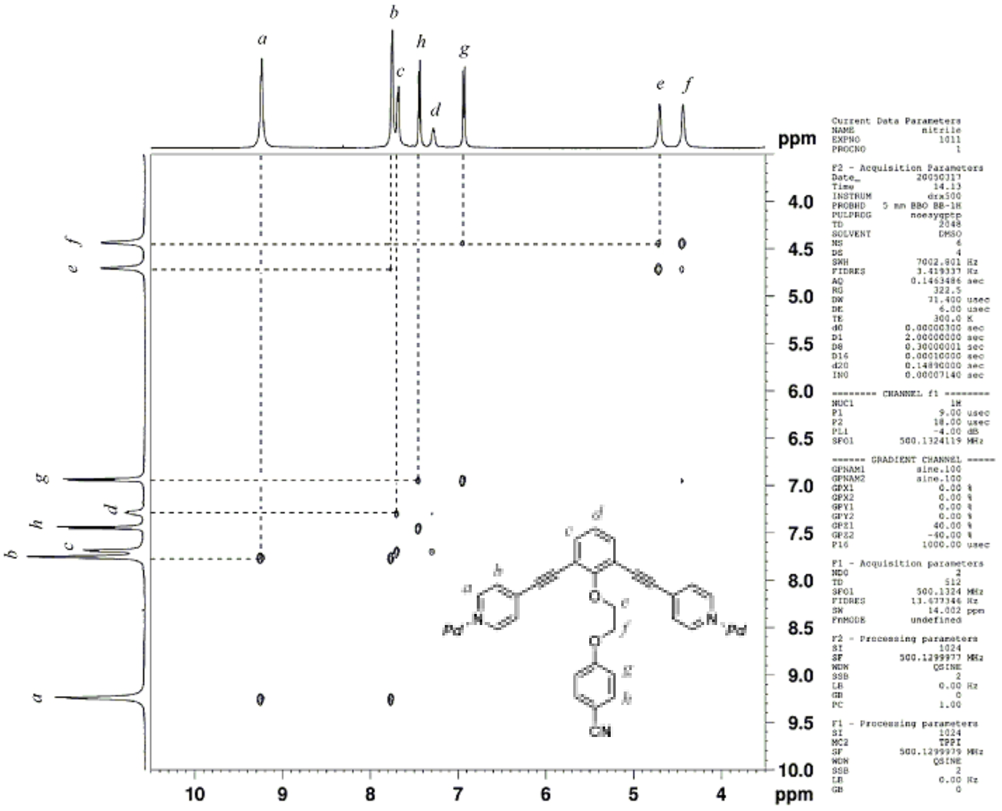
NOESY of **2b**



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Current Data Parameters
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EXPNO                1011
PROCNO                  1

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PULPROG          noesygptp
TD                   2048
SOLVENT              DMSO
NS                      6
DS                      4
SWH              7002.801 Hz
FIDRES           3.419337 Hz
AQ              0.1463486 sec
RG                  322.5
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DE                   6.00 usec
TE                  300.0 K
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D1             2.00000000 sec
D8             0.30000001 sec
D16            0.00010000 sec
d20            0.14890000 sec
IN0            0.00007140 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.00 usec
P2                  18.00 usec
PL1                 -4.00 dB
SFO1          500.1324119 MHz

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GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                40.00 %
GPZ2               -40.00 %
P16               1000.00 usec

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TD                    512
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FIDRES          13.677346 Hz
SW                 14.002 ppm
FnMODE          undefined

F2 - Processing parameters
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SF            500.1299977 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
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MC2                  TPPI
SF            500.1299979 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
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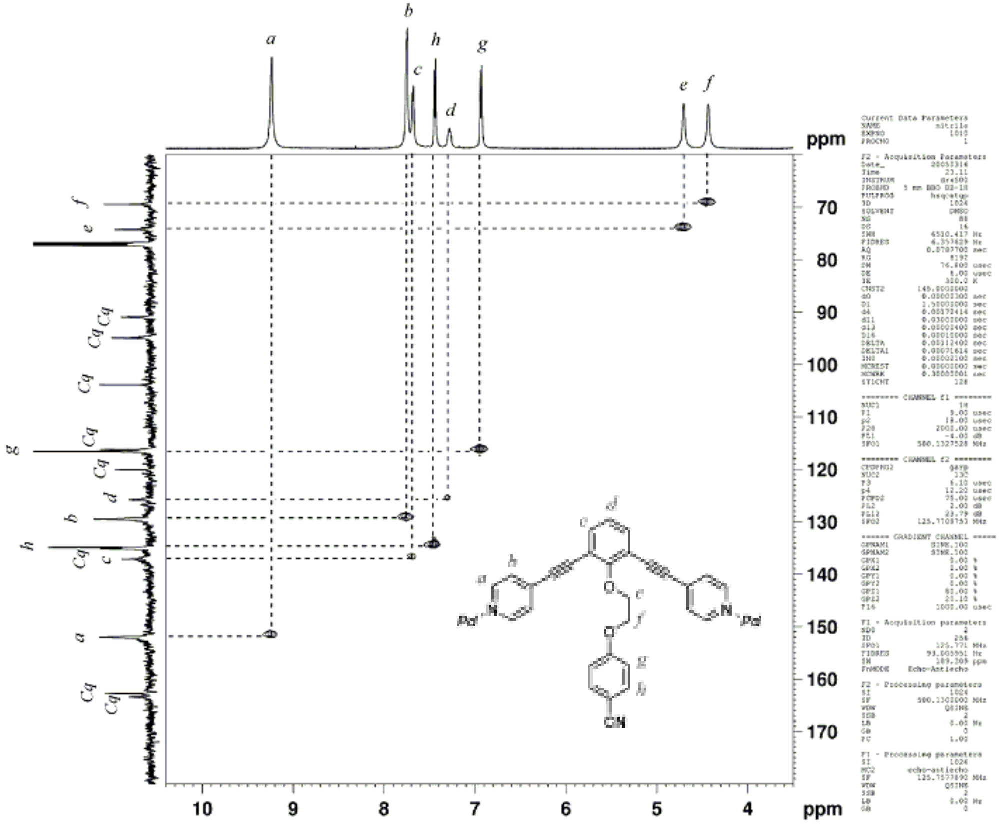
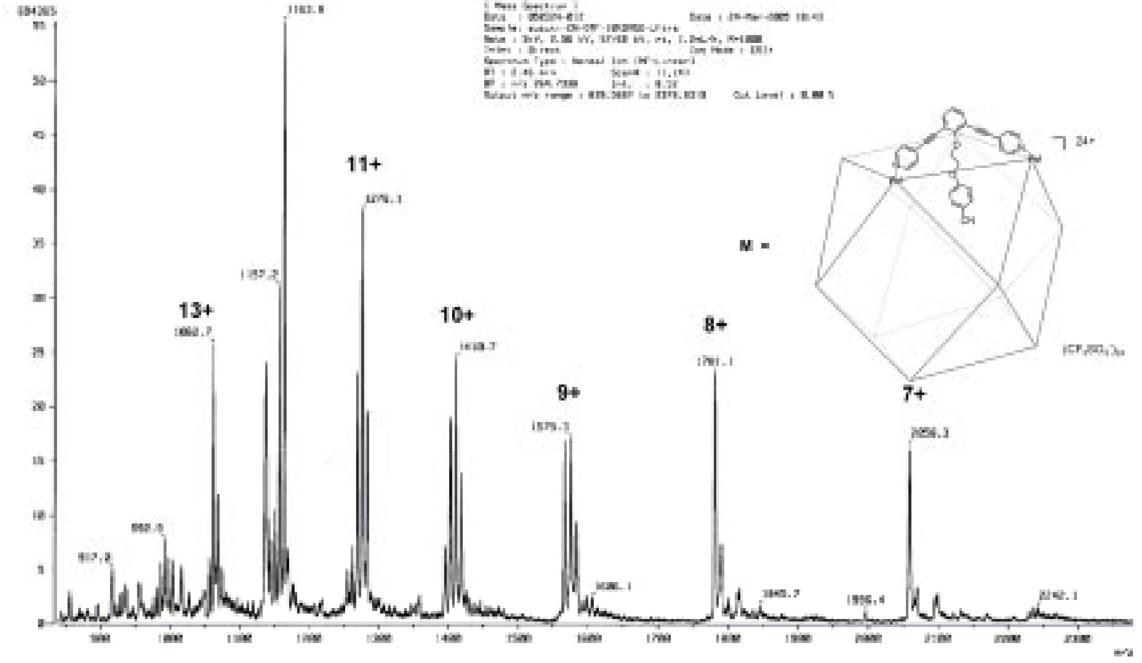
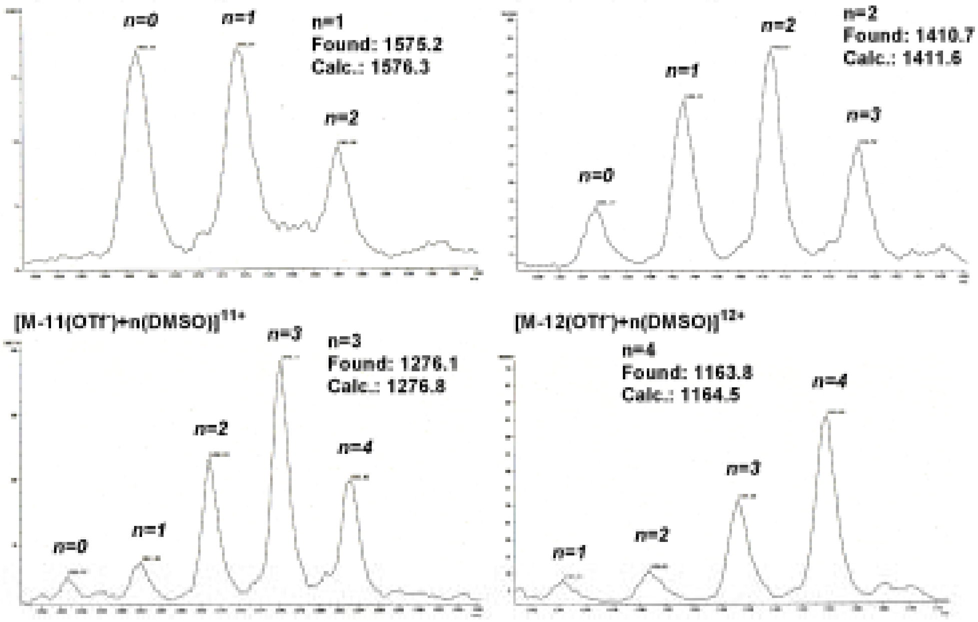
HSQC of **2b**



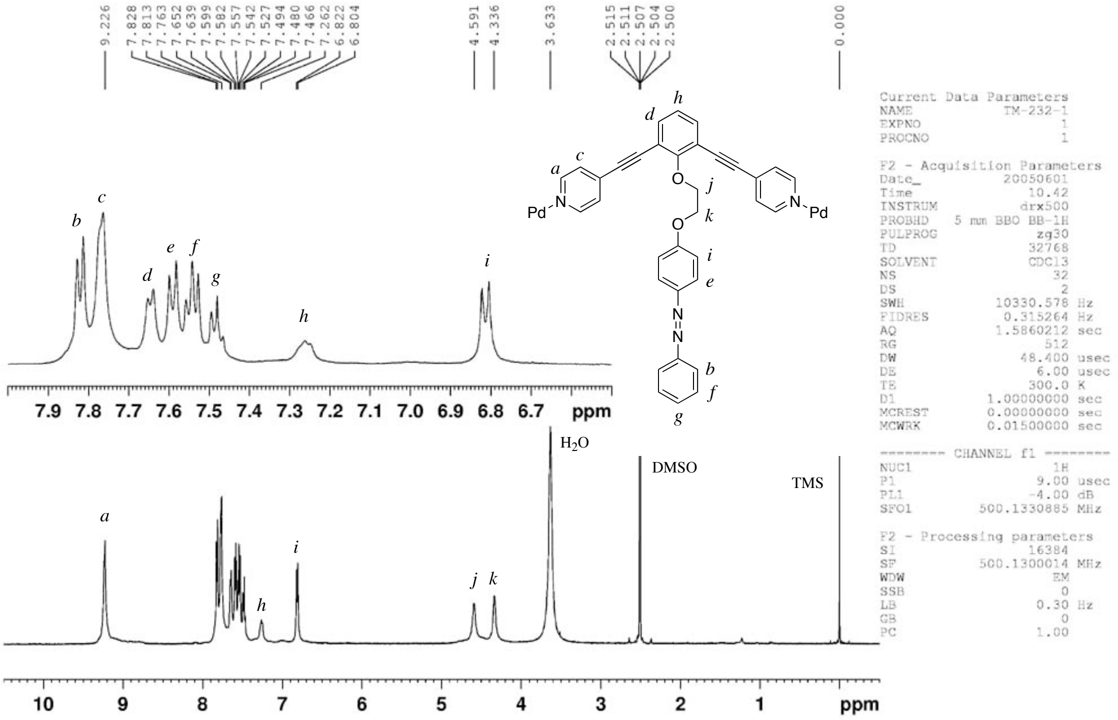
CSI-MS of **2b** (CH$_3$CN:DMSO = 20:1, r.t.)



Enlarged spectra of CSI-MS of **2b**



^{1}H NMR of **2c**



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PROCNO                   1

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PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              10330.578 Hz
FIDRES            0.315264 Hz
AQ               1.5860212 sec
RG                     512
DW                  48.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.00 usec
PL1                  -4.00 dB
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   16384
SF             500.1300014 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```
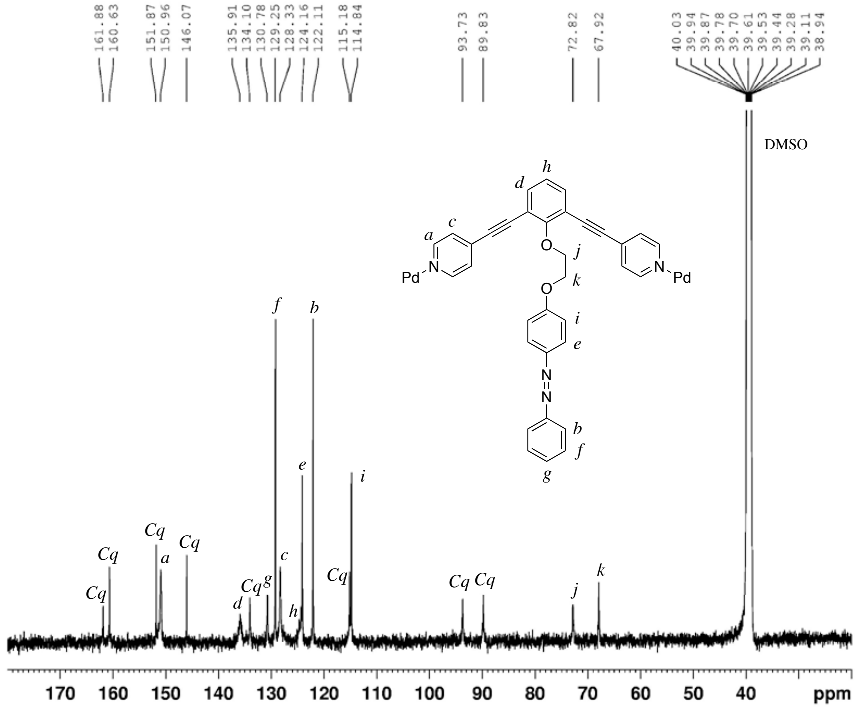

^{13}C NMR of **2c**



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Current Data Parameters
NAME          13C TM-232-1
EXPNO                    1
PROCNO                   1

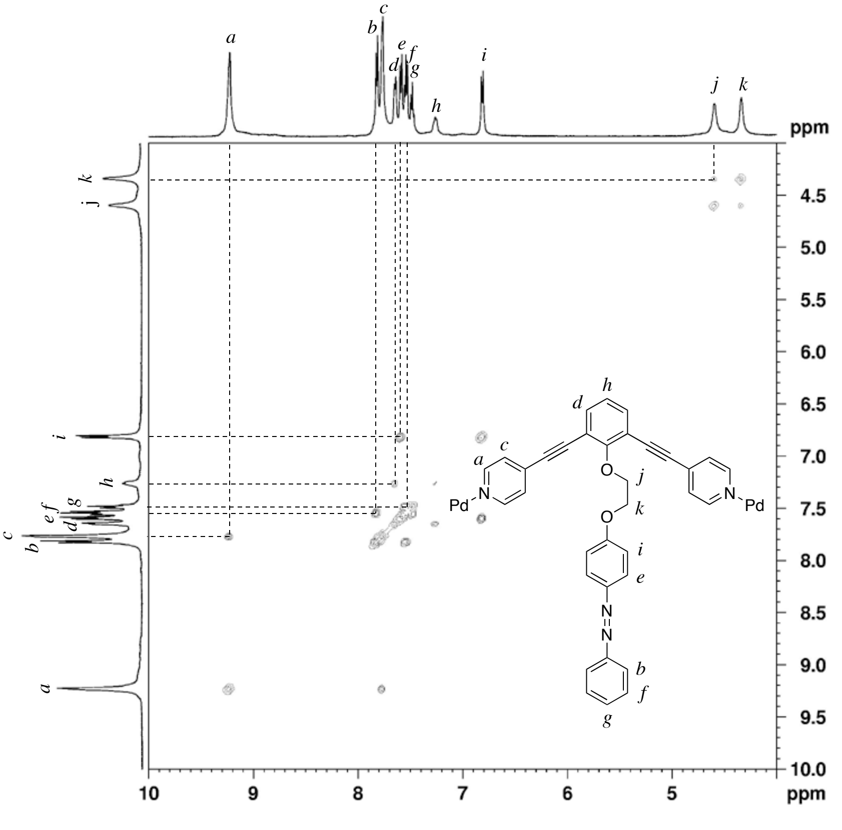
F2 - Acquisition Parameters
Date_             20050604
Time                 23.46
INSTRUM             drx500
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                   26223
DS                       2
SWH             39682.539 Hz
FIDRES           0.605507 Hz
AQ              0.8258036 sec
RG                  4597.6
DW                  12.600 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.30 usec
PL1                   2.00 dB
SFO1           125.7736214 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 15.50 dB
PL13                 15.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF             125.7578613 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

H-H COSY of **2c**



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Current Data Parameters
NAME          COSY TM-232-1
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20050601
Time                  22.23
INSTRUM              drx500
PROBHD    5 mm BBO BB-1H
PULPROG            cosygpqf
TD                     2048
SOLVENT                DMSO
NS                        6
DS                        8
SWH                6009.615 Hz
FIDRES             2.934382 Hz
AQ                0.1704436 sec
RG                   1824.6
DW                   83.200 usec
DE                     6.00 usec
TE                    300.0 K
d0               0.00000300 sec
D1               1.48689198 sec
d13              0.00000400 sec
D16              0.00010000 sec
IN0              0.00016640 sec
MCREST           0.00000000 sec
MCWRK            1.48689198 sec

======== CHANNEL f1 ========
NUC1                     1H
P0                     9.00 usec
P1                     9.00 usec
PL1                   -4.00 dB
SFO1            500.1325021 MHz

====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPNAM2             SINE.100
GPX1                   0.00 %
GPX2                   0.00 %
GPY1                   0.00 %
GPY2                   0.00 %
GPZ1                  10.00 %
GPZ2                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
ND0                       1
TD                      256
SFO1               500.1325 MHz
FIDRES            23.475060 Hz
SW                   12.016 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300006 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1299981 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
```
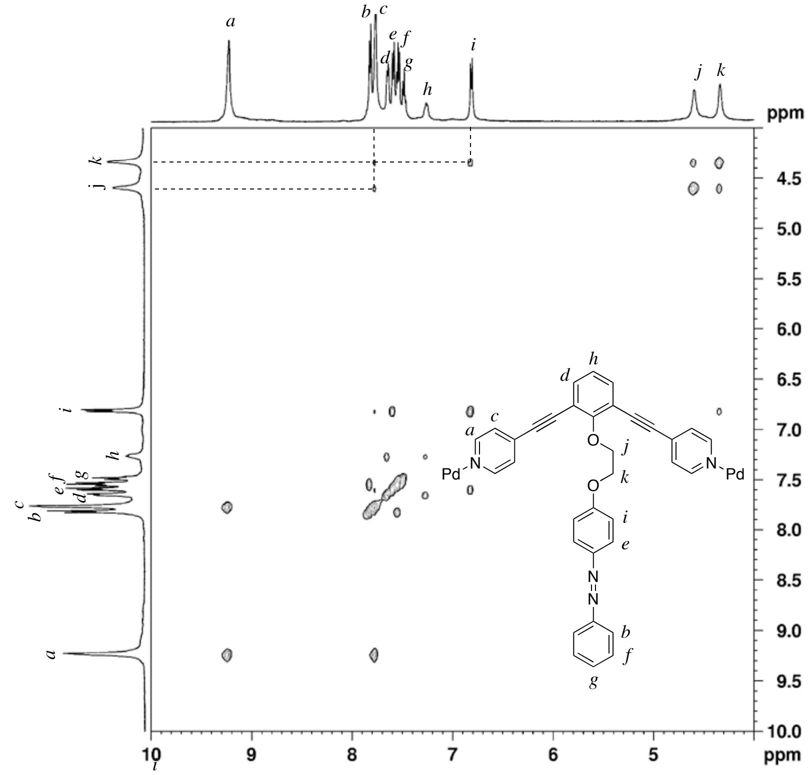
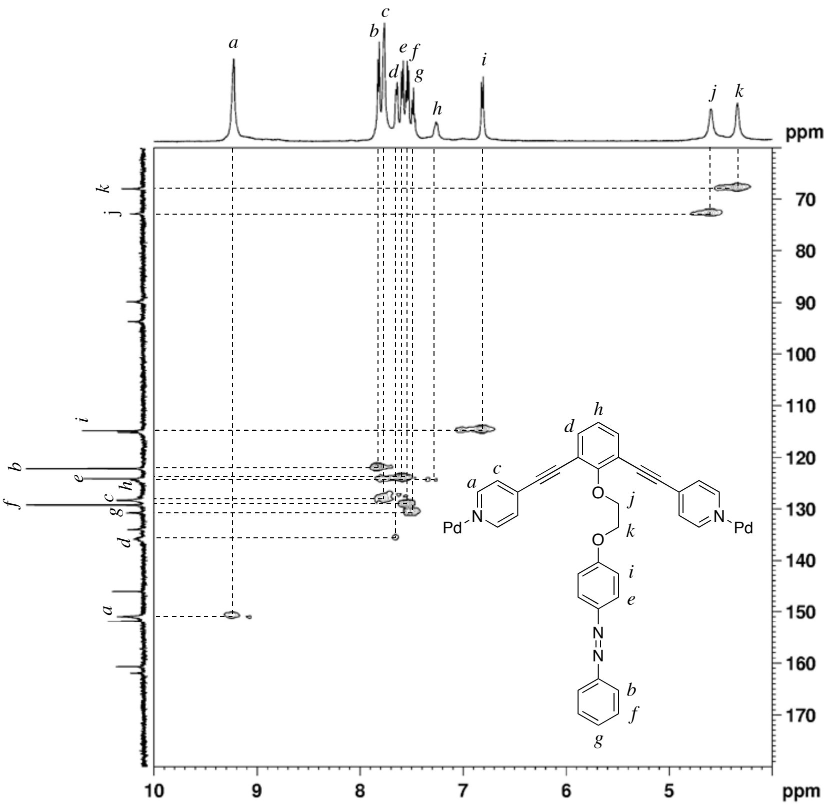

i

NOESY of **2c**



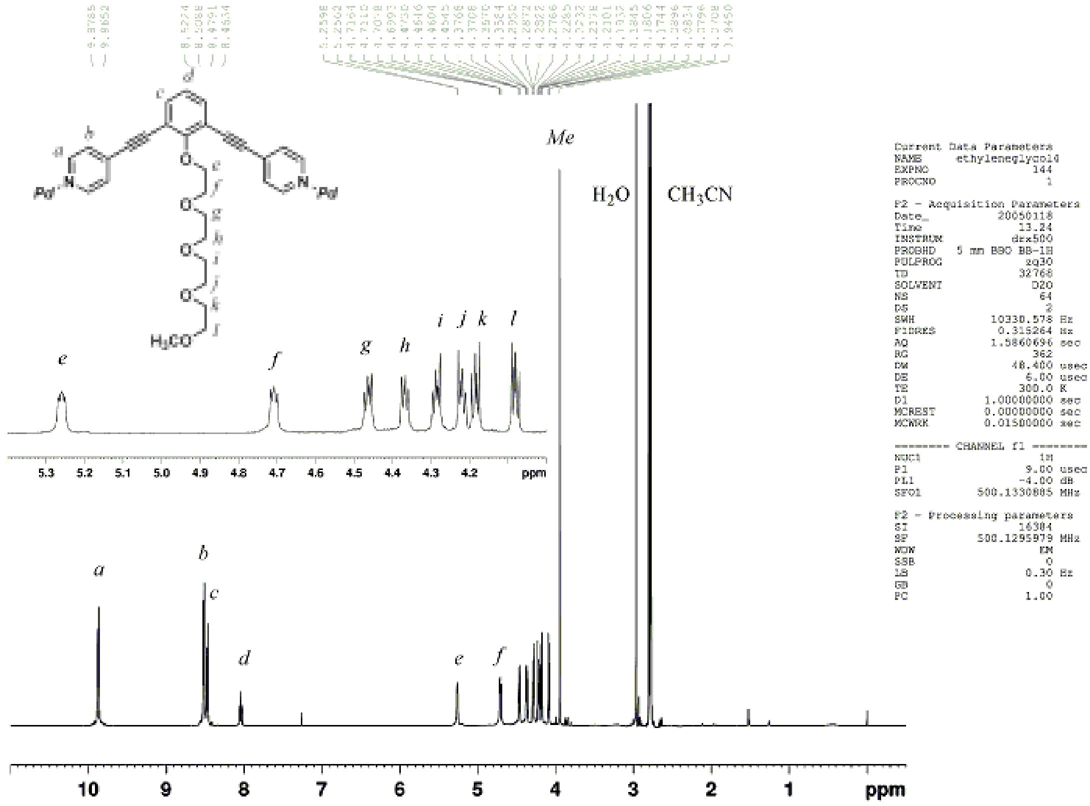
```
Current Data Parameters
NAME       NOESY TM-232-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20050603
Time                18.19
INSTRUM            drx500
PROBHD    5 mm BBO BB-1H
PULPROG         noesygptp
TD                   2048
SOLVENT              DMSO
NS                      6
DS                      4
SWH              6510.417 Hz
FIDRES           3.178914 Hz
AQ              0.1573364 sec
RG                    362
DW                 76.800 usec
DE                   6.00 usec
TE                  300.0 K
d0             0.00000300 sec
D1             2.00000000 sec
D8             0.30000001 sec
D16            0.00010000 sec
d20            0.14890000 sec
IN0            0.00007680 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.00 usec
P2                  18.00 usec
PL1                 -4.00 dB
SFO1          500.1322520 MHz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                40.00 %
GPZ2               -40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
ND0                     2
TD                    512
SFO1             500.1323 MHz
FIDRES          12.715657 Hz
SW                 13.017 ppm
FnMODE          undefined

F2 - Processing parameters
SI                   1024
SF            500.1299980 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.00

F1 - Processing parameters
SI                   1024
MC2                  TPPI
SF            500.1299970 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

HSQC of **2c**



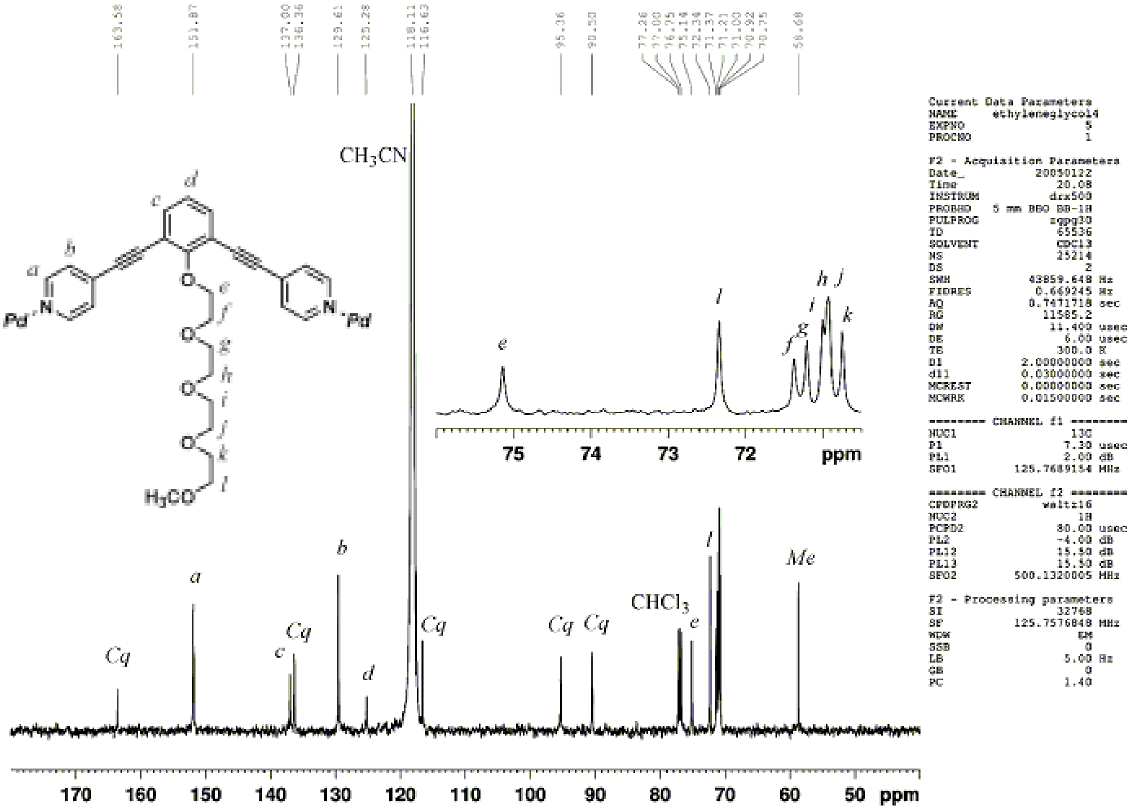
```
Current Data Parameters
NAME        HSQC TM-232-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20050605
Time                20.03
INSTRUM            drx500
PROBHD    5 mm BBO BB-1H
PULPROG          hsqcetgp
TD                   1024
SOLVENT               D2O
NS                    108
DS                     16
SWH              6009.615 Hz
FIDRES           5.868765 Hz
AQ              0.0852468 sec
RG                  13004
DW                 83.200 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
d0             0.00000300 sec
D1             1.51023996 sec
d4             0.00172414 sec
d11            0.03000000 sec
d13            0.00000400 sec
D16            0.00010000 sec
DELTA          0.00112400 sec
DELTA1         0.00071614 sec
IN0            0.00001890 sec
MCREST         0.00000000 sec
MCWRK          0.30204800 sec
ST1CNT                128

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.00 usec
p2                  18.00 usec
P28               2000.00 usec
PL1                 -4.00 dB
SFO1          500.1325021 MHz

======== CHANNEL f2 ========
CPDPRG2              garp
NUC2                  13C
P3                   6.10 usec
p4                  12.20 usec
PCPD2               75.00 usec
PL2                  2.00 dB
PL12                23.79 dB
SFO2          125.7703648 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
ND0                     2
TD                    256
SFO1             125.7704 MHz
FIDRES         103.339951 Hz
SW                210.344 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF            500.1299989 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2         echo-antiecho
SF            125.7578994 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

^{1}H NMR of **2d**



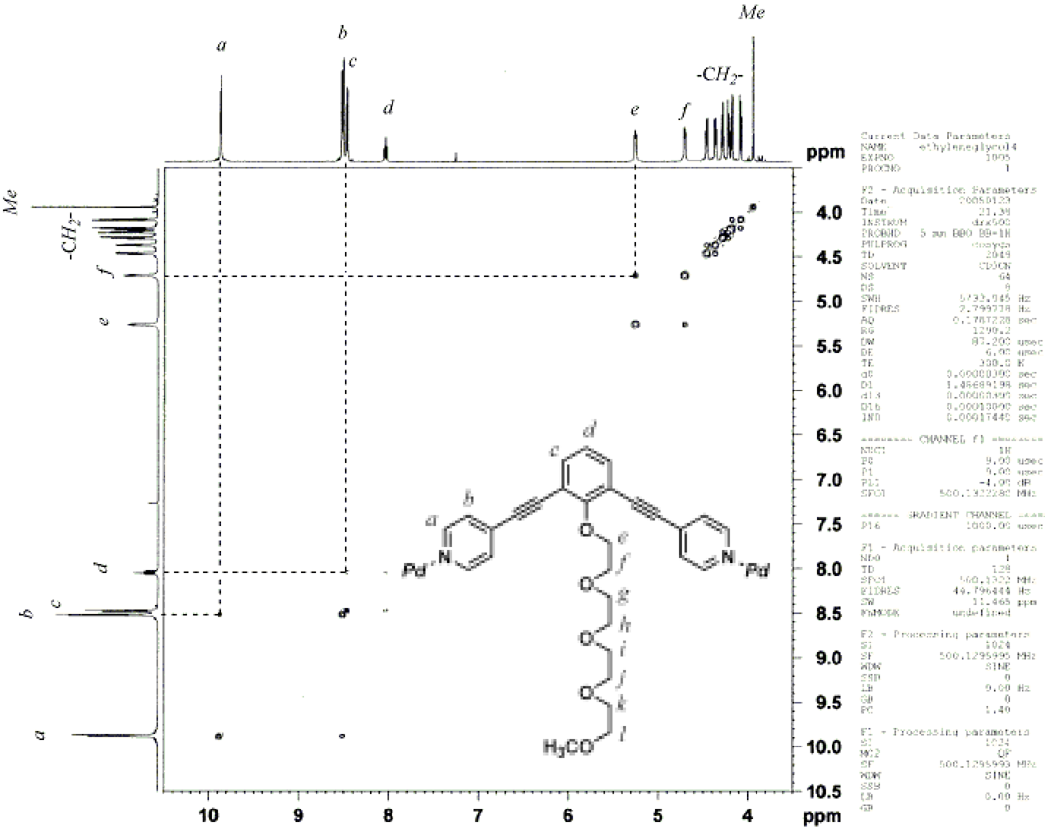
```
Current Data Parameters
NAME     ethyleneglycol4
EXPNO                144
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050118
Time               13.24
INSTRUM           drx500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    64
DS                     2
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860696 sec
RG                   362
DW                48.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.00 usec
PL1                -4.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 16384
SF           500.1295979 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C NMR of **2d**

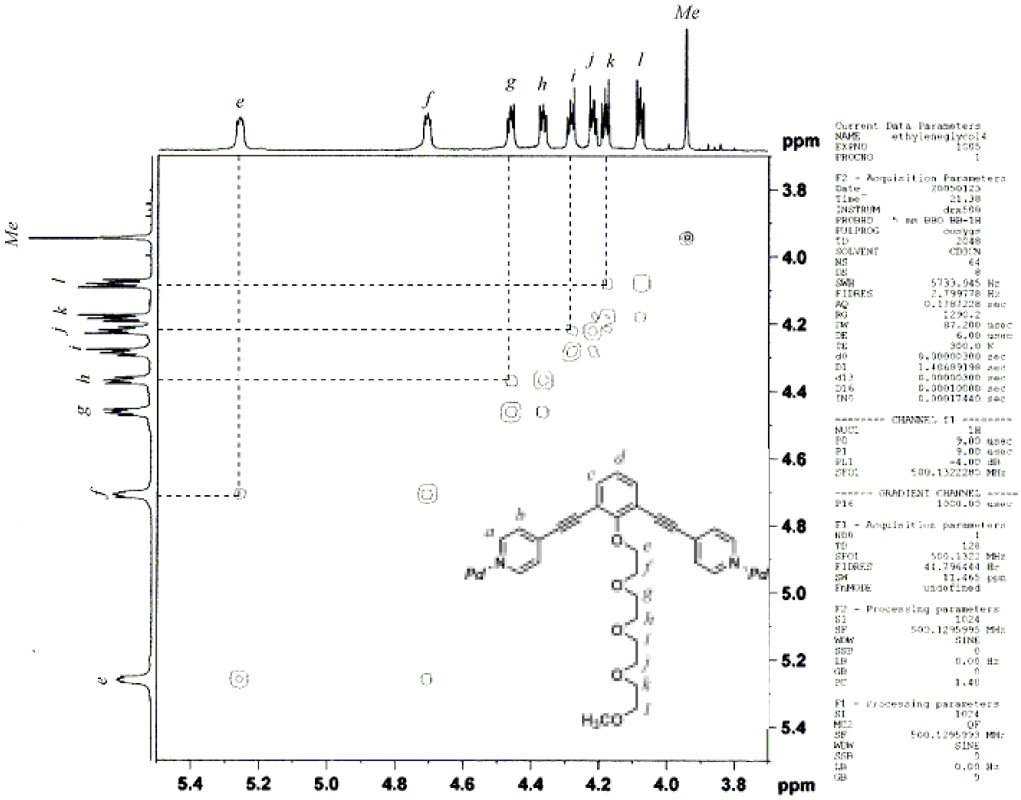


```
Current Data Parameters
NAME     ethyleneglycol4
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050122
Time               20.08
INSTRUM           drx500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 25214
DS                     2
SWH            43859.648 Hz
FIDRES          0.669245 Hz
AQ             0.7471718 sec
RG               11585.2
DW                11.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.30 usec
PL1                 2.00 dB
SFO1         125.7689154 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               15.50 dB
PL13               15.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7576848 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  1.40
```

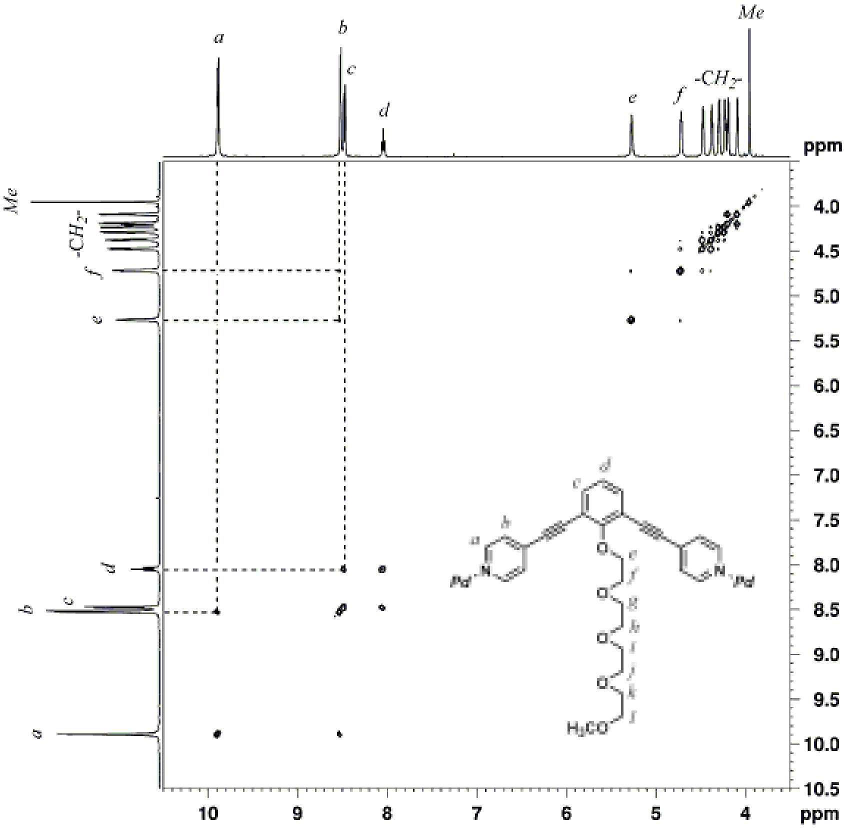
H-H COSY of **2d**



Enlarged spectrum of H-H COSY of **2d** (aliphatic region)

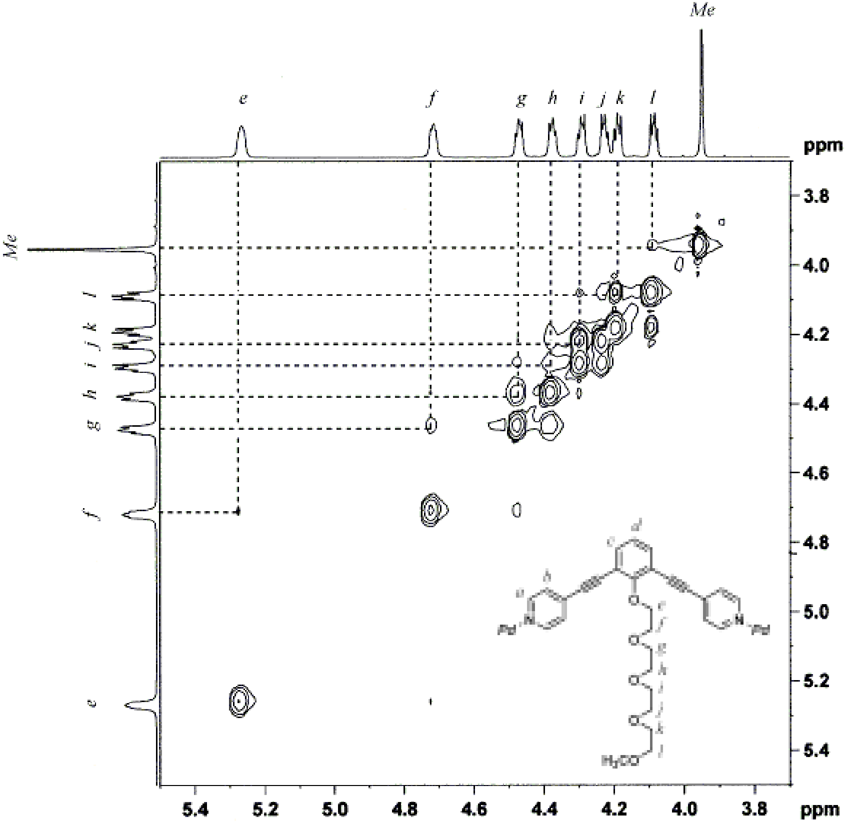


ROESY of **2d**



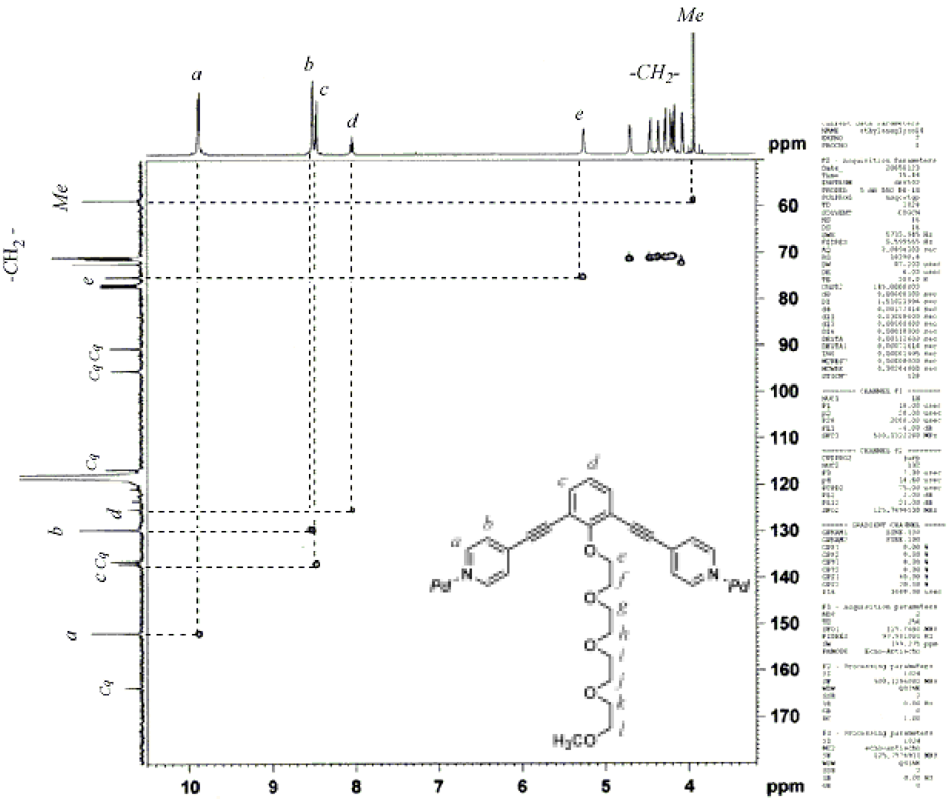
```
Current Data Parameters
NAME     ethyleneglycol4
EXPNO                523
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050402
Time               20.14
INSTRUM           drx500
PROBHD   5 mm BBO BB-1H
PULPROG          roesytp
TD                  2048
SOLVENT            CD3CN
NS                    54
DS                     4
SWH             6410.256 Hz
FIDRES          3.130008 Hz
AQ             0.1598720 sec
RG                5160.6
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
d0            0.00000300 sec
D1            2.00000000 sec
d12           0.00002000 sec
IN0           0.00007800 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.00 usec
P15            200000.00 usec
PL1                -4.00 dB
PL11               16.92 dB
SFO1         500.1323233 MHz

F1 - Acquisition parameters
ND0                    2
TD                  1024
SFO1            500.1323 MHz
FIDRES          6.260016 Hz
SW                12.817 ppm
FnMODE         undefined

F2 - Processing parameters
SI                  1024
SF           500.1295922 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2                 TPPI
SF           500.1295940 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```

Enlarged spectrum of ROESY of **2d** (aliphatic region)

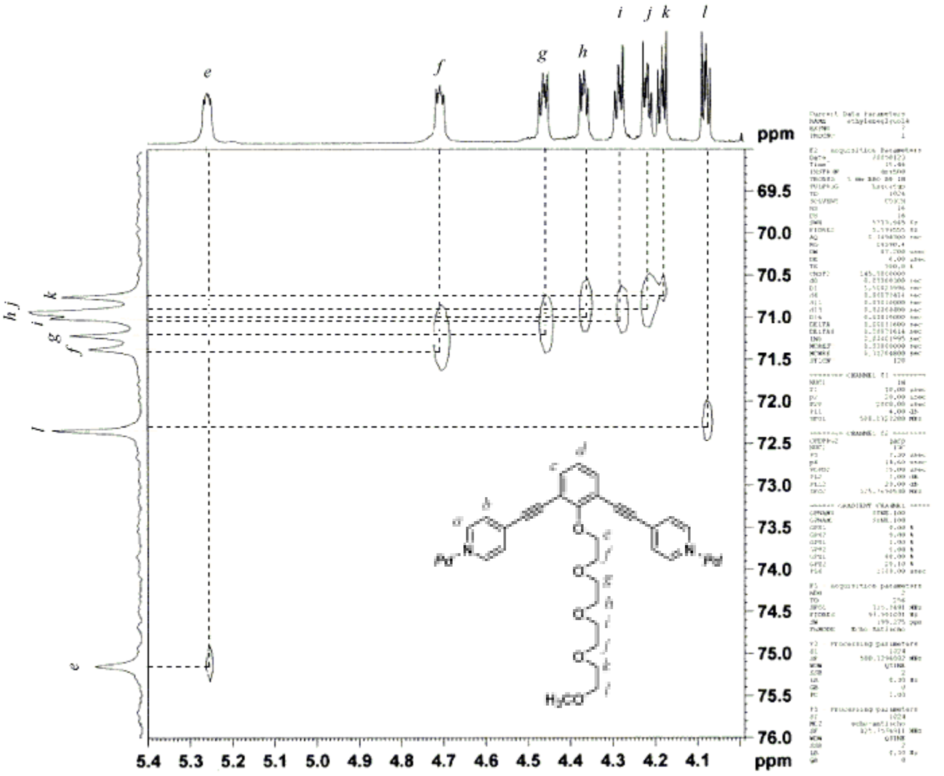


```
Current Data Parameters
NAME     ethyleneglycol4
EXPNO                523
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050402
Time               20.14
INSTRUM           drx500
PROBHD   5 mm BBO BB-1H
PULPROG          roesytp
TD                  2048
SOLVENT            CD3CN
NS                    54
DS                     4
SWH             6410.256 Hz
FIDRES          3.130008 Hz
AQ             0.1598720 sec
RG                5160.6
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
d0            0.00000300 sec
D1            2.00000000 sec
d12           0.00002000 sec
IN0           0.00007800 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.00 usec
P15            200000.00 usec
PL1                -4.00 dB
PL11               16.92 dB
SFO1         500.1323233 MHz

F1 - Acquisition parameters
ND0                    2
TD                   696
SFO1            500.1323 MHz
FIDRES          9.210138 Hz
SW                12.817 ppm
FnMODE         undefined

F2 - Processing parameters
SI                  1024
SF           500.1295908 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2                 TPPI
SF           500.1295997 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```

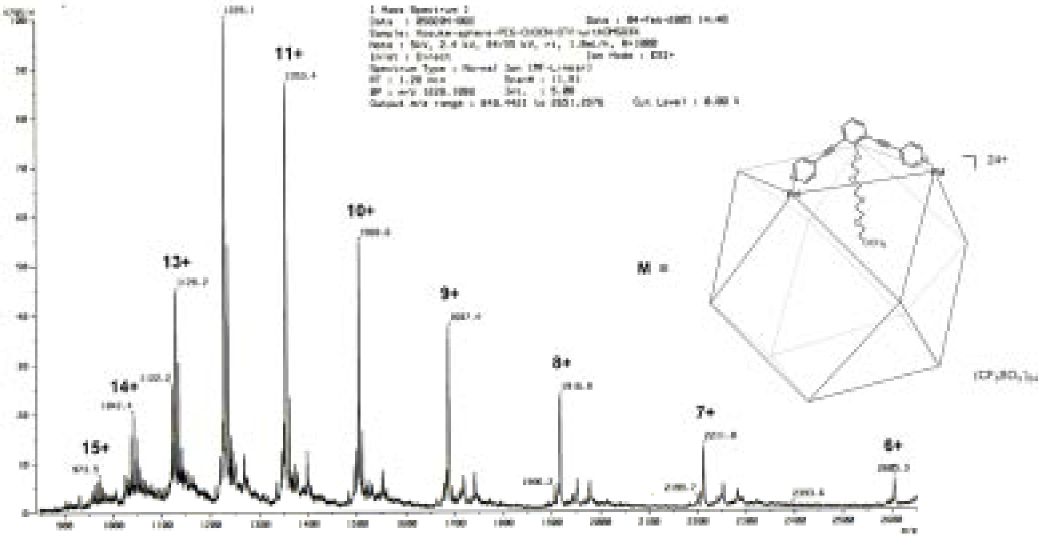
HSQC of **2d**



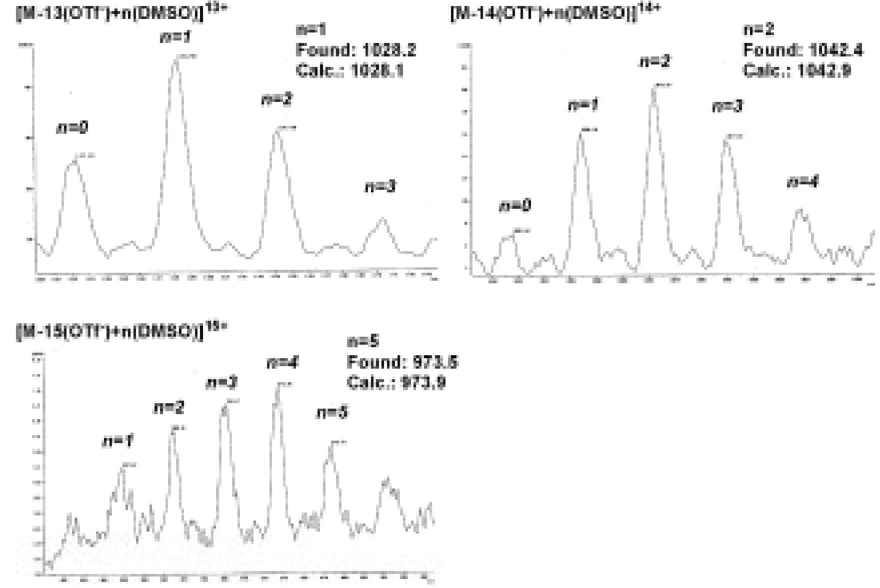
Enlarged spectrum of HSQC of **2d** (aliphatic region)



CSI-MS of **2d** (CH$_3$CN:DMSO = 20:1, r.t.)



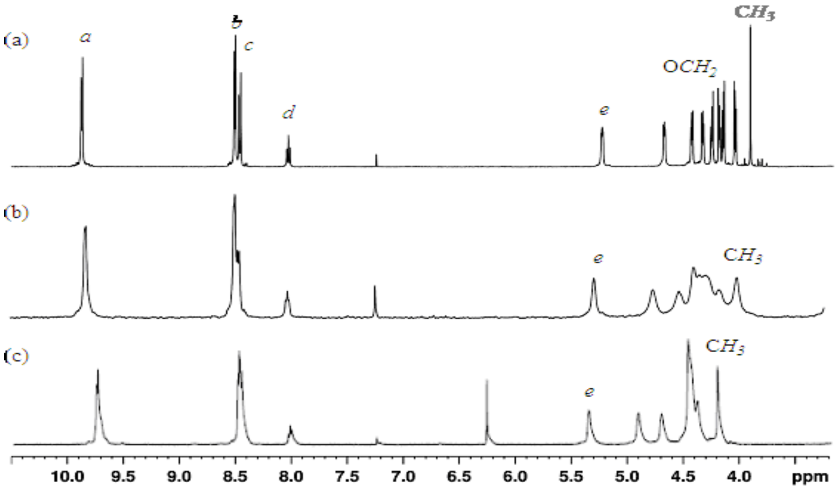
Enlarged spectra of CSI-MS of **2d**



^{1}H NMR spectra of 2d mixed with $La(CF_3SO_3)_3$ and $Ca(CF_3SO_3)_2$.

Metal ions such as Ca^{2+} and La3$^+$ were absorbed within complex **2d**.

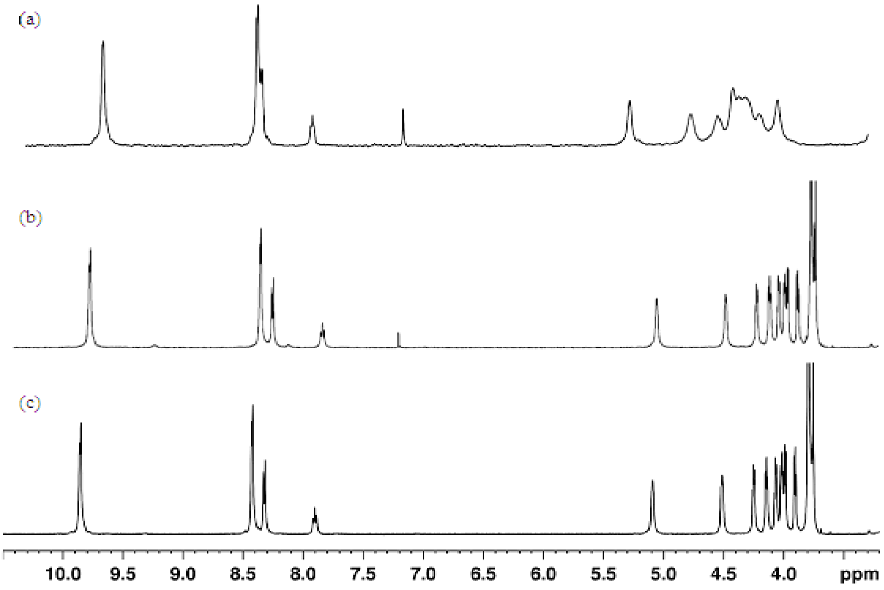
^{1}H NMR spectra of a) **2d** (0.83 mM) in CD_3CN, b) $La(OTf)_3$/**2d** (0.42 mM/0.83mM) in CD_3CN, c) $Ca(OTf)_2$/**2d** (0.42 mM/0.83mM) in CD_3CN.



^{1}H NMR spectra when DMSO was added to the mixtrure of 2d and $La(CF_3SO_3)_3$.

The absorbed metal ions were expelled by addition of a coordinative solvent such as DMSO.

^{1}H NMR spectra of a) $La(OTf)_3$/**2d** (0.42 mM/0.83mM) in CD_3CN (sample **a**), b) Addition of DMSO (5 vol%) to sample **a,** c) **2d** (0.83mM) in 5 vol% of DMSO-d_6/CD_3CN.

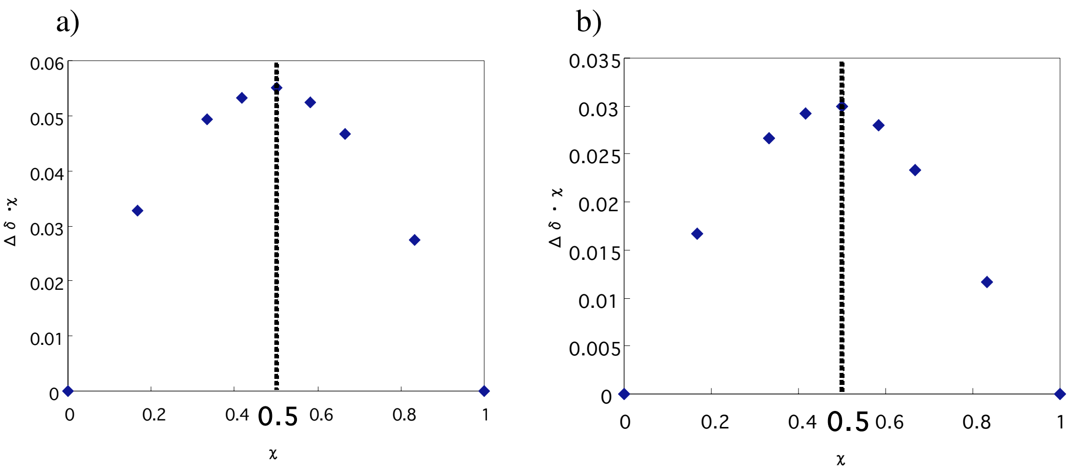


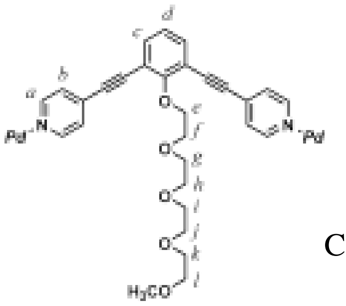
^{1}H NMR Job's plots for the complexation between ethyleneoxide chain of 2d and La^{3+} ions.

Plots of $\Delta\delta\cdot\chi$ versus χ : $\chi = [(OCH_2CH_2)_4OCH_3]/\{[(OCH_2CH_2)_4OCH_3]+[La^{3+}]\}$.

The sum of concentration of $[(OCH_2CH_2)_4OCH_3]+[La^{3+}]$ was kept to be 2.5 mM.

(a) Job's plot based on the shift value of the chemical shift of CH_3 group, (b) Job's plot based on the shift value of the chemical shift of H_e.





Complex **2d**