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Supporting Information

Structural Analysis of Chiral Complexes of Palladium(0) with 15-Membered Triolefinic Macrocyclic Ligands

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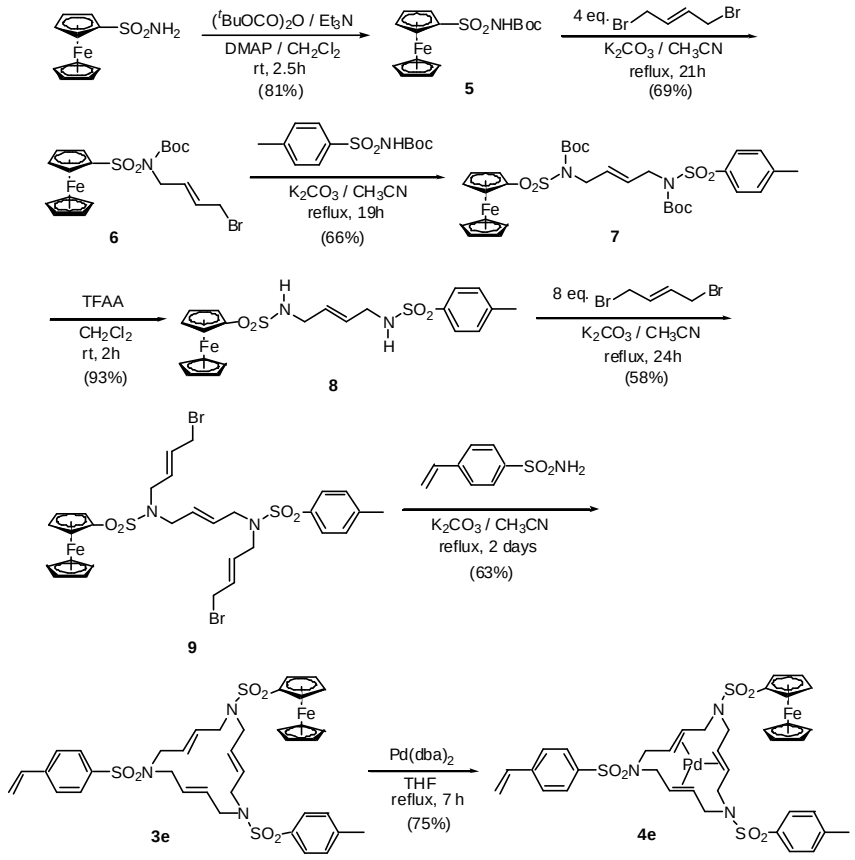
Supporting Information. Schematic details of synthesis and spectroscopic data for macrocyclic ligand **3e** and its Pd(0) complex **4e**.

General Remarks. IR spectra were recorded with a FT-IR using a single reflection ATR system as a sampling accessory. ^{1}H NMR (^{13}C NMR) were recorded at 200 MHz (50 MHz) using Me_4Si as internal standard. Chemical shifts are given in δ units. ESI mass spectra were acquired using a Navigator quadrupole instrument. Elemental analyses were determined at "Servei d'Anàlisi Química de la Universitat de Girona" and "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona". HRMS spectra were determined at "RIAIDT, Unidade de Espectrometria de Masas, de la Universidade de Santiago de Compostela".

Scheme S1. Synthesis of the macrocyclic ligand **3e** and its Pd(0) complex **4e**.



(*E*)-1,4-Dibromobutene and (4-methylphenyl)sulfonamide are commercially available and were used without further purification. Ferrocenesulfonamide was prepared from ferrocene as previously reported.[1] 4-Vinylbenzenesulfonamide was prepared from commercially available sodium 4-vinylbenzenesulfonate as previously reported by us.[2] ***N*-(*tert*-Butyloxycarbonyl)ferrocenylsulfonamide (5)** and ***N*-[(*E*)-4-bromo-2-butenyl]-*N*-(*tert*-butyloxycarbonyl)ferrocenylsulfonamide (6)** were prepared as previously reported by us.[3]

Spectral data for all other intermediates are described bellow:

(*E*)-*N,N'*-Bis(*tert*-butyloxycarbonyl)-*N*-ferrocenylsulfonyl-*N'*-[(4-methylphenyl)sulfonyl]-2-buten-1,4-diamine, (7): yellow solid; m.p. 122-124°C (*n*-hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): *d* = 1.33 (s, 9H), 1.41 (s, 9H), 2.43 (s, 3H), 4.31-4.42 (m, 6H), 4.39 (s, 5H), 4.80 (*ap* t, ^{3}J(H,H) = 1.9 Hz, 2H), 5.77 (br abs, 2H), 7.30 (AA' part of the AA'BB' system, *J* = 8.4 Hz, 2H), 7.79 (BB' part of the AA'BB' system, *J* = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 21.6, 27.9, 28.0, 47.4, 47.8, 70.3, 70.6, 70.9, 83.8, 84.2, 87.2, 128.0, 128.2, 129.3, 129.6, 137.2, 144.0, 150.6, 151.0; IR (ATR): *n* = 2982, 1720, 1354, 1155 cm^{-1}; ESI-MS: *m/z* = 711 $[M + Na]^+$, 706 $[M + NH_4]^+$; elemental analysis calcd (%) for $C_{31}H_{40}FeN_2O_8S_2$ (688.6): C 54.07, H 5.85, N 4.07; found: C 53.68 and 53.76, H 5.91 and 5.89, N 4.02 and 4.02.

(*E*)-*N*-ferrocenylsulfonyl-*N'*-[(4-methylphenyl)sulfonyl]-2-buten-1,4-diamine, (8): yellow solid; m.p. 97-99°C (Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): 2.43 (s, 3H), 3.45 (br abs, 4H), 4.38 (s, 5H), 4.37-4.39 (m, 2H), 4.53 (t, *J* = 6.2 Hz, 1H), 4.61 (*ap* t, ^{3}J (H,H) = 1.8 Hz, 2H), 4.94 (t, ^{3}J(H,H) = 6.0 Hz, 1H), 5.45-5.48 (m, 2H), 7.30 (AA' part of the AA'BB' system, *J* = 8.1 Hz, 2H), 7.79 (BB' part of the AA'BB' system, *J* = 8.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 21.5, 44.4, 68.6, 70.5, 70.7, 87.5, 127.1, 128.0, 128.7, 129.7, 136.8, 143.5; IR (ATR): *n* = 3302, 2914, 1320, 1152 cm^{-1}; ESI-MS: *m/z* = 506 $[M + NH_4]^+$, 489 $[M + H]^+$; elemental analysis calcd (%) for $C_{21}H_{24}FeN_2O_4S_2$ (488.4): C 51.64, H 4.95, N 5.74; found: C 51.41 and 51.34, H 5.01 and 4.98, N 5.73 and 5.73.

(*E,E,E*)-1,14-Dibromo-*N*-ferrocenylsulfonyl-*N'*-[(4-methylphenyl)sulfonyl]-5,10-diazatetradeca-2,7,12-triene, (9): yellow solid; m.p. 68-70°C (Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): 2.44 (s, 3H), 3.46-3.88 (m, 12H), 4.40 (s, 5H), 4.37-4.40 (m, 2H), 4.58 (*ap* t, ^{3}J(H,H) = 1.9 Hz, 2H), 5.21-5.84 (m, 6H), 7.31 (AA' part of the AA'BB' system, *J* = 8.1 Hz, 2H), 7.67 (BB'part of the AA'BB' system, *J* = 8.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 21.5, 31.4, 31.5, 48.0, 48.2, 48.4, 68.6, 70.6, 70.8, 87.1, 127.2, 128.7, 129.4, 129.6, 129.8, 129.9, 130.1, 130.5, 136.9, 143.5; IR (ATR): *n* = 2915, 1336, 1151 cm^{-1}; ESI-MS: *m/z* = 772 $[M + NH_4]^+$, 755 $[M + H]^+$; HRMS (ESI): calcd for $C_{29}H_{34}Br_2FeN_2NaO_4S_2$ $[M + Na]^+$: 774.9568; found: 774.9597.

(*E,E,E*)-1-ferrocenylsulfonyl-11-[(4-methylphenyl)sulfonyl]-6-[(4-vinylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-triene, (3e): yellow solid; m.p. 142-144°C (*n*-hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): 2.43 (s, 3H), 3.65-4.11 (m, 12H), 4.39 (s, 5H), 4.37-4.41 (m, 2H), 4.57 (*ap* t, ^{3}J(H,H) = 1.7 Hz, 2H), 5.44 (d, ^{3}J(H,H) = 11 Hz, 1H), 5.46-5.54 (m, 6H), 5.89 (d, ^{3}J(H,H) = 17.5 Hz, 1H), 6.76 (dd, ^{3}J(H,H) = 17.5 and 11 Hz, 1H), 7.31 (AA' part of the AA'BB' system, *J* = 8.2 Hz, 2H), 7.52 (AA' part of the AA'BB' system, *J* = 8.3 Hz, 2H), 7.65 (BB' part of the AA'BB' system, *J* = 8.1 Hz, 2H), 7.72 (BB' part of the AA'BB' system, *J* = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 21.5, 50.5, 50.6, 68.5, 70.6, 70.7, 86.2, 117.4, 126.8, 127.1, 127.4, 128.8, 129.0, 129.2, 129.5, 129.6, 129.8, 135.2, 136.1, 137.9, 141.8, 143.5; IR (ATR): *n* = 2918, 1338, 1152 cm^{-1}; ESI-MS: *m/z* = 793 $[M + NH_4]^+$, 776 $[M + H]^+$; elemental analysis calcd (%) for $C_{37}H_{41}FeN_3O_6S_3$ (775.8): C 57.29, H 5.33, N 5.42; found: C 57.07 and 56.69, H 5.35 and 5.24, N 5.33 and 5.30.

(*E,E,E*)-1-ferrocenylsulfonyl-11-[(4-methylphenyl)sulfonyl]-6-[(4-vinylphenyl)sulfonyl]-1,6,11-triazaciclopentadeca-3,8,13-trienepalladium(0), (4e): yellow solid; m.p. 148-150°C (decomp) (*n*-hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): 1.56-1.73 (m, 4H), 2.38 (s, 3H), 2.76 (t, ^{3}J(H,H) = 12.0 Hz, 2H), 3.04 (q, ^{3}J (H,H) = 12.0 Hz, 2H), 3.70-3.74 (m, 2H), 3.88-3.94 (m, 2H), 4.40 (s, 5H), 4.30-4.82 (m, 10H), 5.41 (d, ^{3}J(H,H) = 11.0 Hz, 1H), 5.84 (d, ^{3}J(H,H) = 17.6 Hz, 1H), 6.71 (dd, ^{3}J(H,H) = 17.6 and 11.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.45-7.51 (m, 2H), 7.59-7.79 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS): 21.4, 45.0, 48.0, 48.1, 49.2, 49.3, 68.3, 68.4, 70.6, 70.7, 77.9, 78.0, 78.1, 78.2, 78.3, 78.4, 78.5, 78.6, 78.7, 82.3, 82.4, 82.5, 82.6, 82.8, 82.9, 85.2, 85.3, 85.7, 117.3, 117.4, 126.7, 126.8, 126.9, 127.0, 127.2, 127.3, 129.7, 129.8, 135.0, 135.1, 135.2, 135.9, 137.0, 137.1, 137.7, 141.6, 141.8, 143.3, 143.4; IR (ATR): *n* = 2920, 1334, 1156 cm^{-1}; ESI-MS: *m/z* = 904 $[M + Na]^+$, 899 $[M + NH_4]^+$, 882 $[M + H]^+$, 881 $[M]^+$; elemental analysis calcd (%) for $C_{37}H_{41}FeN_3O_6PdS_3$ (882.2): C 50.38, H 4.68, N 4.76; found: C 50.08 and 50.11, H 4.66 and 4.64, N 4.60 and 4.58.

References for the supporting information

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