

Note

Short syntheses of 8-substituted 8'-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyls from Suzuki coupling reactions. A strategy for generating new chiral ligands and charge-transfer complexes

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Abstract

8'-Iodo-8-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl, a precursor of chiral phosphines, and 8'-(4-methylphenyl)-8-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl, a model compound for the preparation of charge-transfer complexes were synthesized via Suzuki coupling reactions of ferrocenylboronic acids and 8-substituted 8'-iodo-1,1'-binaphthyls. Sequential substitution of 8,8'-diiodo-1,1'-binaphthyl provided a facile method of generating unsymmetrical 8,8'-disubstituted 1,1'-binaphthyls. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chiral phosphines; Charge-transfer complexes; Suzuki coupling; Unsymmetrical 8,8'-disubstituted 1,1'-binaphthyls

1. Introduction

Despite a large number of chiral ferrocenyl derivatives that have been designed and synthesized in asymmetric catalysis and material sciences [1a,1b], no 8-ferrocenyl-1,1'-binaphthyls [1c,1d] (nonracemic or racemic) have been reported. Our recent interest in using enantiopure 8'-substituted 8-(diphenylphosphinyl)-1,1'-binaphthyls [2] in asymmetric intramolecular Heck reactions [2c,2d] prompted us to synthesize chiral 8-(diphenylphosphino)-8'-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl (**1**). Herein, we report the syntheses of 8'-iodo-8-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl (**2**), a precursor of chiral phosphine **1**, and 8'-(4-methylphenyl)-8-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl (**3**), a model compound for the preparation of charge-transfer complexes [3] from Suzuki coupling reactions [4] of ferrocenylboronic acids and 8-substituted 8'-iodo-1,1'-binaphthyls. Since ferrocenyl sulfides

can be enantioselectively oxidized with titanium tetrakisopropoxide, (*R,R*)-diethyl tartrate, and cumene hydroperoxide (CHP) [5], and the resulting ferrocenyl sulfoxide may facilitate the resolution of atropisomeric (axially dissymmetric) binaphthyls, these studies were undertaken.

2. Results and discussion

Our approach leading to 8-substituted 8'-ferrocenyl 1,1'-binaphthyls is based upon the Suzuki coupling of 8,8'-diiodo-1,1'-binaphthyl (**4**) [6] with 1'-substituted 1-ferrocenylboronic acids. Successful replacements of the iodo groups in **4** sequentially at C8 and C8' with different substituents will provide a facile method for the generation of various useful unsymmetrical 8,8'-disubstituted 1,1'-binaphthyls. Diiodide **4** is readily prepared from a palladium-catalyzed Ullmann coupling reaction [6a] of 1,8-diiodonaphthalene [6b]. 1'-Substituted 1-ferrocenylboronic acids can be prepared from a selective sequential lithiation-sulfonylation and lithia-

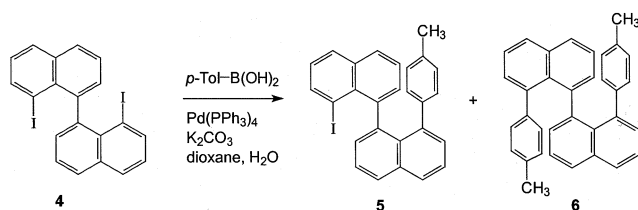
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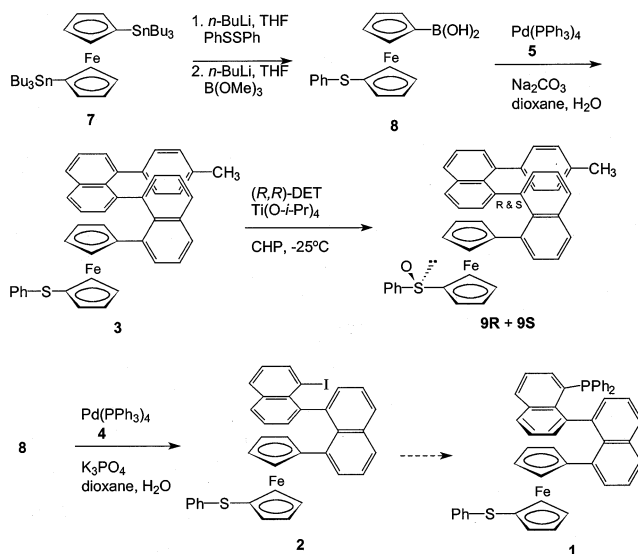
tion-boronylation of 1,1'-ferrocenyl ditelluride [7] or 1,1'-bis(tri-*n*-butylstannyl)ferrocene [8].

Suzuki coupling of diiodide **4** with *p*-tolylboronic acid (derived from *p*-bromotoluene with *tert*-BuLi in ether followed by trimethyl borate), a catalytic amount of tetrakis(triphenylphosphine)palladium (0.05 equivalents), and potassium carbonate in dioxane–water (3:1) at 70 °C for 11 h provided monoiodide **5** (37% yield) and biscoupling product **6** (37% yield), along with diiodide **4** (18% recovery) (Scheme 1).

1,1'-Bis-(tri-*n*-butylstannyl)ferrocene (**7**) [8] was selected as our starting material to prepare the unsymmetrical disubstituted ferrocene **8**. Hence, treatment of **7** with one equivalent of *n*-BuLi in THF at –78 °C for 30 min followed by diphenyl disulfide (–78 to 25 °C for 1 h) gave an 89% yield of 1-(tri-*n*-butylstannyl)-1'-(phenylthio)ferrocene. Subsequent treatment with *n*-BuLi in THF at –78 °C for 30 min followed by trimethyl borate [4a] provided a 74% yield of boronic acid **8** after aqueous work-up (with 0.5 N HCl) (Scheme 2). Attempted coupling of 1-(tri-*n*-butylstannyl)-1'-(phenylthio)ferrocene with diiodide **4** and 0.1 equivalents of tetrakis(triphenylphosphine)palladium in toluene at 90 °C for 24 h (the Stille coupling) [9] provided only a small amount of perylene (25% yield) and mainly starting stannylferrocene (85% recovery)



Scheme 1.



Scheme 2.

and diiodide **4** (60% recovery). The perylene by-product is a homo-coupling [6a] product from **4**.

First, Suzuki coupling of boronic acid **8** with iodide **5**, 0.1 equivalents of tetrakis(triphenylphosphine)palladium and three equivalents of sodium carbonate in dioxane–water (1:1) at 100–120 °C for 4 days gave a 27% yield of coupling product **3** along with 5% recovered iodide **5**. Asymmetric oxidation [5] of sulfide **3** with one equivalent each of titanium tetraisopropoxide, L-(*R,R*)-diethyl tartrate (DET), and CHP in methylene chloride and water at –25 °C gave sulfoxide (*SR*)-**9R** and (*SR*)-**9S**. Based on previous studies [5], the stereochemistry of **9** at sulfur should be the *R*-configuration. The two diastereomers, **9R** and **9S**, were separated by column chromatography, and the absolute configuration at the axially dissymmetric carbons (C1,1' of the naphthyl ring) remains to be determined by X-ray crystallography [10].

Second, Suzuki coupling of boronic acid **8** with iodide **4**, 0.1 equivalents of tetrakis(triphenylphosphine)palladium and three equivalents of potassium phosphate in dioxane–water (3:1) at 70 °C for 4 days afforded desired ferrocene **2** (38% yield) and perylene (12% yield) along with starting diiodide **4** (44% recovery). Under similar reaction conditions but using three equivalents of sodium carbonate in toluene and water (1:1) as solvents, we obtained products **2** and perylene in a ratio of 1:2 along with 15% of recovered diiodide **4**. Hence, use of a stronger base (sodium carbonate) and toluene as co-solvent increase the yield of the homo-coupling perylene by-product. Fortunately, the above three compounds are separable by silica gel column chromatography with hexane–ether (19:1) as eluent.

It should be noted that compound **2** may be converted to chiral phosphine **1** by the method reported by Imamoto et al. [11] involving metallation with *tert*-BuLi followed by reaction with dichlorophenylphosphine, displacement with L-menthol, complexation with borane-THF, separation of the diastereomers, and removal of the borane with diethylamine. The use of 3,5-dicyanophenylboronic acid instead of *p*-tolylboronic acid in the synthesis of compound **3** may provide the dicyano derivative, an intramolecular charge-transfer complex. This work and the synthesis of chiral 8-substituted 8'-(diphenylphosphino)-1,1'-binaphthyls from diiodide **4** will be reported in due course.

3. Conclusions

Couplings of 8,8'-diiodo-1,1'-binaphthyl (**4**) with *p*-tolylboronic acid and 1'-(phenylthio)-1-ferrocenylboronic acid (**8**) and of 8-iodo-8'-(*p*-tolyl)-1,1'-binaphthyl (**5**) with **8**, were successfully carried out. Despite its moderate yield, the sequential substitution of 8,8'-diiodo-1,1'-binaphthyl, as illustrated, should

prove to be one of the shortest routes to produce chiral unsymmetrical 8,8'-disubstituted 1,1'-binaphthyls.

4. Experimental

4.1. General comments

Nuclear magnetic resonance spectra were obtained at 400 MHz for ^1H and 100 MHz for ^{13}C in deuteriochloroform and recorded in ppm. Infrared spectra are reported in wavenumbers (cm^{-1}) and recorded from a Nicolet 320 FTIR. Mass spectra were taken from a Hewlett–Packard 5890 Series II, GC–MS. FAB spectra were taken by using Xe beam (8 kV) and *m*-nitrobenzyl alcohol as matrix. *n*-Butyllithium, trimethyl borate, diphenyl disulfide, tri-*n*-butyltin chloride, titanium tetrakis(isopropoxide), (*R,R*)-diethyl tartrate, CHP and tetrakis(triphenylphosphine)palladium were purchased from Aldrich Chem. Co. Davisil silica gel, grade 643 (200–425 mesh), was used for the flash column chromatographic separation, and thin-layer chromatography on silica gel (0.25 mm thickness; purchased from Aldrich Chem. Co.) was used for TLC analysis. THF and Et_2O were distilled over sodium and benzophenone before use. Methylene chloride was distilled over CaH_2 and toluene and *p*-dioxane were distilled over LiAlH_4 . H_2O was degassed before use.

4.2. 8,8'-Diiodo-1,1'-binaphthyl (**4**) [6]

M.p. 122–125 °C. IR (film, cm^{-1}): ν 3051, 1553, 1492, 1358, 1331, 1194, 1141, 1019, 946, 816, 806, 763, 714, 640. $^1\text{H-NMR}$: δ 8.23 (d, $J = 7$ Hz, 2H), 7.95 (t, $J = 7$ Hz, 4H), 7.48 (t, $J = 7$ Hz, 2H), 7.32 (d, $J = 7$ Hz, 2H), 7.11 (t, $J = 8$ Hz, 2H). $^{13}\text{C-NMR}$: δ 142.3, 139.7, 135.6, 133.4, 133.3, 130.1, 130.0, 126.6, 124.9, 93.9. CIMS; m/z : 507 [$\text{M} + 1$]. This compound has been reported previously [6], although the $^{13}\text{C-NMR}$ data was not reported.

4.3. 8-Iodo-8'-(*p*-tolyl)-1,1'-binaphthyl (**5**). A general procedure for the Suzuki coupling reactions

A solution of 0.20 g (0.40 mmol) of diiodide **4**, 54 mg (0.40 mmol) of *p*-tolylboronic acid, 0.11 g (0.80 mmol) of K_2CO_3 , and 23 mg (0.02 mmol) of $\text{Pd}(\text{PPh}_3)_4$ in 6 ml of *p*-dioxane and 2 ml of H_2O under Ar was heated at 70 °C for 11 h. The reaction solution was cooled, diluted with 20 ml of aqueous NH_4Cl , and extracted three times with Et_2O . The combined ether layer was washed with brine, dried (MgSO_4), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and toluene as solvent to give 70 mg (37% yield) of **5**, 64 mg (37% yield) of **6**, and 36 mg (18% recovery) of diiodide **4**. Compound **5**: IR (film,

cm^{-1}): ν 3050, 2917, 1555, 1513, 1494, 1359, 1194, 1182, 1021, 957, 813, 764. $^1\text{H-NMR}$: δ 8.03 (d, $J = 8$ Hz, 1H), 8.00 (d, $J = 8$ Hz, 1H), 7.95 (d, $J = 8$ Hz, 1H), 7.58–7.46 (m, 4H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.19 (m, 2H), 6.93 (t, $J = 8$ Hz, 1H), 6.62 (d, $J = 8$ Hz, 1H, *p*-Tol ring), 6.41 (d, $J = 8$ Hz, 1H, *p*-Tol ring), 6.33 (d, $J = 8$ Hz, 1H, *p*-Tol ring), 6.08 (d, $J = 8$ Hz, 1H, *p*-Tol ring), 1.99 (s, 3H, Me). $^{13}\text{C-NMR}$: δ 142.1, 141.7, 140.9, 139.1, 139.0, 134.8, 134.7, 134.1, 132.6, 132.2, 131.9, 131.0, 130.5, 129.7, 129.1, 128.9, 128.8, 128.4, 128.0, 126.5, 126.1, 126.0, 125.0, 124.9, 92.7, 20.9. CIMS; m/z : 471 [$\text{M} + 1$]. Anal. Found: C, 68.69; H, 4.33. Calc. for $\text{C}_{27}\text{H}_{19}\text{I}$: C, 68.95; H, 4.07%.

4.4. 8,8'-Bis-(*p*-tolyl)-1,1'-binaphthyl (**6**)

M.p. 177–179 °C. IR (film, cm^{-1}): ν 3047, 2916, 1512, 1367, 1182, 832, 808, 786, 771, 607. $^1\text{H-NMR}$: δ 7.55 (d, $J = 7$ Hz, 2H), 7.50–7.45 (m, 4H), 7.35–7.30 (m, 2H), 7.28 (d, $J = 7$ Hz, 2H), 7.02 (d, $J = 7$ Hz, 2H), 6.50 (d, $J = 8$ Hz, 2H, *p*-Tol ring), 6.27 (d, $J = 8$ Hz, 2H, *p*-Tol ring), 6.17 (d, $J = 8$ Hz, 2H, *p*-Tol ring), 6.08 (d, $J = 8$ Hz, 2H, *p*-Tol ring), 2.05 (s, 6H, Me). $^{13}\text{C-NMR}$: δ 141.9, 140.7, 138.4, 134.7, 133.8, 131.3, 130.8, 130.5, 128.8, 128.2, 127.9, 126.0, 125.9, 125.7, 125.0, 124.6, 21.0. EIMS; m/z : 434 [$\text{M} + 1$]. Anal. Found: C, 93.72; H, 5.88. Calc. for $\text{C}_{34}\text{H}_{26}$: C, 93.97; H, 6.03%.

4.5. 1-(Tri-*n*-butylstannyl)-1'-(phenylthio)ferrocene

To a cold (-78 °C) solution of 1.56 g (2.0 mmol) of bis-stannane **7** in 20 ml of THF under Ar, was added 1.3 ml (2.0 mmol) of *n*-BuLi (1.6 M in hexanes). After the reaction solution was stirred at -78 °C for 30 min, a solution of 0.436 g (2.0 mmol) of diphenyl disulfide in 4 ml of THF was added via cannula, and the solution was stirred at -78 °C for 1 h and 25 °C for 3 h. The reaction solution was diluted with aqueous NH_4Cl , extracted three times with Et_2O , and the combined ether layer was washed with brine, dried (MgSO_4), concentrated, and column chromatographed on silica gel using hexane as solvent to give 1.04 g (89% yield) of 1-(tri-*n*-butylstannyl)-1'-(phenylthio)ferrocene. IR (neat, cm^{-1}): ν 3070, 2955, 2934, 2851, 1582, 1477, 1376, 1025, 828, 736, 689. $^1\text{H-NMR}$: δ 7.16 (m, 2H, PhS), 7.05 (m, 3H, PhS), 4.44 (bs, 2H, Cp), 4.34 (bs, 2H, Cp), 4.26 (bs, 2H, Cp), 4.09 (bs, 2H, Cp), 1.58 (m, 6H), 1.36 (sextet, $J = 8$ Hz, 6H), 1.05 (t, $J = 8$ Hz, 6H), 0.92 (t, $J = 8$ Hz, 9H). CIMS; m/z : 584 [$\text{M} + 1$], 583. $^{13}\text{C-NMR}$: δ 141.0, 128.5 (2C), 125.7 (2C), 124.7, 76.0, 75.3, 74.9, 72.2, 70.5, 70.1, 29.2, 27.4, 13.7, 10.3. Anal. Found: C, 57.44; H, 7.13. Calc. for $\text{C}_{28}\text{H}_{40}\text{FeSSn}$: C, 57.66; H, 6.91%.

4.6. 1'-(Phenylthio)-1-ferrocenylboronic acid (**8**)

To a cold ($-78\text{ }^{\circ}\text{C}$) solution of 0.60 g (1.0 mmol) of 1-(tri-*n*-butylstannyl)-1'-(phenylthio)ferrocene in 10 ml of THF under Ar, was added 0.75 ml (1.2 mmol) of *n*-BuLi (1.6 M in hexanes). After the reaction solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, a solution of 0.13 ml (1.2 mmol) of trimethyl borate in 2 ml of THF was added. The solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and $25\text{ }^{\circ}\text{C}$ for 1 h, diluted with 10 ml of 0.5 N HCl, and stirred at $0\text{ }^{\circ}\text{C}$ for 1 h. The mixture was extracted with Et₂O three times, and the combined ether layer was washed with brined, dried (MgSO₄), and concentrated. The resulting mixture was triturated with cold hexane twice, and the remaining yellow solids were dried under vacuo to give 0.25 g (74% yield) of **8** (as a ferrocenylboroxine; a trimeric boric anhydride). IR (film, cm⁻¹): ν 3399 (broad s, OH), 3062 (CH), 1790, 1705, 1580, 1471, 1377; ¹H-NMR: δ 7.16 (m, 1H, Ph), 7.07 (m, 2H, Ph), 6.97 (m, 2H, Ph), 4.79 (bs, 2H, Cp), 4.63 (bs, 2H, Cp), 4.40 (bs, 2H, Cp), 4.33 (bs, 2H, Cp). ¹³C-NMR: δ 132.0, 128.6, 125.9, 124.9, 75.9, 75.5, 74.6, 70.8, 69.6. Anal. Found: C, 56.37; H, 4.61. Calc. for C₁₆H₁₅BFeO₂S: C, 56.85; H, 4.47%.

4.7. 8-(4-Methylphenyl)-8'-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl (**3**)

A mixture of 22 mg (0.064 mmol) of ferrocene **8**, 10 mg (0.021 mmol) of iodide **5**, 2 mg (0.002 mmol) of Pd(PPh₃)₄, and 22 mg (0.21 mmol) of Na₂CO₃ in 0.2 ml of *p*-dioxane and 0.1 ml of H₂O was stirred in a sealed tube under Ar at 110–120 $^{\circ}\text{C}$ for 4 days. The mixture was cooled to $25\text{ }^{\circ}\text{C}$, diluted with aqueous NH₄Cl, and extracted three times with Et₂O. The combined ether layers were washed with brine, dried (MgSO₄), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ether as solvent to give 3.5 mg (27% yield) of **3** and 0.5 mg (5% recovery) of **5**. Compound **3**: IR (film, cm⁻¹): ν 3049, 2920, 1731, 1607, 1477, 1365, 1024. ¹H-NMR: δ 7.98 (d, $J = 7\text{ Hz}$, 1H), 7.68 (d, $J = 8\text{ Hz}$, 1H), 7.60 (d, $J = 7\text{ Hz}$, 2H), 7.51 (d, $J = 7\text{ Hz}$, 1H), 7.44–7.36 (m, 3H), 7.32–7.24 (m, 3H), 7.10 (m, 2H), 7.02–6.92 (m, 4H), 6.35 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol ring), 6.24 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol ring), 6.09 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol ring), 5.95 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol ring), 4.02 (bs, 1H, Cp), 3.99 (bs, 1H, Cp), 3.98 (bs, 1H, Cp), 3.92 (bs, 1H, Cp), 3.62 (bs, 1H, Cp), 3.36 (bs, 2H, Cp), 3.31 (bs, 1H, Cp), 2.03 (s, 3H, Me). Anal. Found: C, 80.86; H, 5.32. Calc. for C₄₃H₃₂FeS: C, 81.12; H, 5.07%.

4.8. (aR)-8-(4-Methylphenyl)-8-[(SR)-1-(1'-phenylsulfanyl)ferrocenyl]-1,1'-binaphthyl (**9R**)

A chiral oxidation reaction procedure as that re-

ported in Ref. [5b] was followed, and compounds **9R** and **9S** were separated by silica gel column chromatography using a gradient mixture of hexane and Et₂O as solvent. The stereochemistry at C1,1' has not been determined and is tentatively assigned. Less polar isomer; TLC: $R_f = 0.16$ in hexane–ether = 1:1. IR (film, cm⁻¹): ν 3051, 2924, 2854, 1600, 1442, 1365, 1083, 1046 (s, SO), 1022. ¹H-NMR: δ 7.90 (d, $J = 7\text{ Hz}$, 1H), 7.69 (d, $J = 7\text{ Hz}$, 1H), 7.61 (t, $J = 7\text{ Hz}$, 2H), 7.54 (d, $J = 7\text{ Hz}$, 1H), 7.46–7.34 (m, 5H), 7.32–7.24 (m, 6H), 6.97 (d, $J = 7\text{ Hz}$, 1H), 6.34 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 6.23 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 6.09 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 5.94 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 4.33 (bs, 1H, Cp), 3.99 (bs, 1H, Cp), 3.96 (bs, 1H, Cp), 3.91 (bs, 1H, Cp), 3.77 (bs, 1H, Cp), 3.56 (bs, 1H, Cp), 3.51 (bs, 1H, Cp), 3.45 (bs, 1H, Cp), 2.03 (s, 3H, Me). Anal. Found: C, 78.97; H, 5.23. Calc. for C₄₃H₃₂FeOS: C, 79.14; H, 4.94%.

4.9. (aS)-8-(4-Methylphenyl)-8-[(SR)-1-(1'-phenylsulfanyl)ferrocenyl]-1,1'-binaphthyl (**9S**)

The stereochemistry at C1,1' has not been determined and is tentatively assigned. More polar isomer; TLC: $R_f = 0.10$ in hexane–ether = 1:1. ¹H-NMR: δ 7.83 (d, $J = 7\text{ Hz}$, 1H), 7.68 (d, $J = 7\text{ Hz}$, 1H), 7.59 (d, $J = 7\text{ Hz}$, 2H), 7.53 (d, $J = 7\text{ Hz}$, 1H), 7.47–7.33 (m, 5H), 7.32–7.24 (m, 6H), 6.97 (d, $J = 7\text{ Hz}$, 1H), 6.34 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 6.24 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 6.09 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 5.94 (d, $J = 7.5\text{ Hz}$, 1H, *p*-Tol), 4.21 (bs, 1H, Cp), 4.07 (bs, 1H, Cp), 3.96 (bs, 1H, Cp), 3.92 (bs, 1H, Cp), 3.76 (bs, 1H, Cp), 3.57 (bs, 1H, Cp), 3.47 (bs, 1H, Cp), 3.42 (bs, 1H, Cp), 2.03 (s, 3H, Me). Anal. Found: C, 79.40; H, 5.19. Calc. for C₄₃H₃₂FeOS: C, 79.14; H, 4.94%.

The sulfoxide, **9S**, was oxidized with *m*-chloroperbenzoic acid to give the corresponding sulfone which ¹H-NMR spectrum is different from that of sulfoxide **9S**, and IR spectrum of the sulfone shows absorptions at 1315 and 1141 cm⁻¹ indicating the asym. and sym. stretching of the SO₂ moiety.

4.10. 8-Iodo-8'-[1-(1'-phenylthio)ferrocenyl]-1,1'-binaphthyl (**2**)

A mixture of 82 mg (0.24 mmol) of ferrocene **8**, 98 mg (0.19 mmol) of iodide **4**, 30 mg (0.025 mmol) of Pd(PPh₃)₄, and 0.16 g (0.73 mmol) of potassium phosphate in 1.5 ml of *p*-dioxane and 0.5 ml of H₂O was stirred under Ar at $70\text{ }^{\circ}\text{C}$ for 4 days. The mixture was cooled to $25\text{ }^{\circ}\text{C}$, diluted with aqueous NH₄Cl, and extracted three times with Et₂O. The combined ether layer was washed with brine, dried (MgSO₄), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and ether as solvent to

give 38 mg (29% yield) of **2** and 43 mg (44% recovery) of **4** along with 6 mg (12% yield) of perylene. Compound **2**: IR (film, cm^{-1}): ν 3051, 2924, 1733 (w), 1580, 1556, 1477, 1438, 1359, 1193, 1024, 819. EIMS; m/z : 672 $[\text{M} +]$. $^1\text{H-NMR}$: δ 8.34 (dd, $J = 7.2$, 1.6 Hz, 1H), 8.07 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.97 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.91 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.75 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.62 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.46 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.27–7.10 (m, 6H), 7.04–6.96 (m, 3H), 4.20–4.14 (m, 4H, Cp), 3.89 (m, 1H, Cp), 3.85 (m, 1H, Cp), 3.56 (m, 1H, Cp), 3.21 (m, 1H, Cp). $^{13}\text{C-NMR}$: δ 142.0, 141.8, 141.0, 138.2, 135.5, 134.9, 134.8, 134.4, 133.9, 133.5, 132.1, 131.8, 130.0, 129.5, 129.0, 128.8 (2C), 126.1, 125.9 (2C), 125.0, 124.9 (2C), 124.7, 95.3, 92.7, 73.5 (Cp), 72.9 (Cp), 72.1 (Cp), 72.0 (Cp), 67.9 (Cp), 67.1 (Cp). Anal. Found: C, 64.56; H, 3.91. Calc. for $\text{C}_{36}\text{H}_{25}\text{FeS}$: C, 64.31; H, 3.75%.

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