

Summary

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1. General information

All reactions were carried out in anhydrous solvents in flame-dried glassware with magnetic stirring under nitrogen or argon atmosphere, unless otherwise stated. Solvents were purchased from commercial suppliers (Sigma Aldrich: THF, DMF, toluene, 1,4-dioxane; Carlo Erba: DCM, THF, toluene) and stored under argon over molecular sieves. Commercially available reagents were purchased from commercial suppliers (TCI Chemicals, Fluorochem, Sigma Aldrich) and were used as received. Known compounds **2**,^[1] **3**^[2] and **5**^[3] were prepared following modified literature procedures (see Supporting Information). The reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 pre-coated glass or aluminum plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or by treatment with staining agents (potassium permanganate alkaline solution, vanillin/H₂SO₄ ethanolic solution, or phosphomolybdic acid ethanolic solution). Purifications through flash column chromatography were performed using silica gel (60 Å, particle size 40-64 µm) as stationary phase, following the procedure by Still and co-workers.^[4] ¹H-NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. Proton chemical shifts are reported in ppm (δ) using solvent signal is used as reference (CDCl₃ δ = 7.26 ppm; CD₂Cl₂ δ = 5.32 ppm; (CD₃)₂CO δ = 2.05 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal, dd = doublet-doublet, td = triplet-doublet, ddd = doublet-doublet-doublet. Coupling constant values are reported in Hz. ¹³C-NMR spectra were recorded on a Bruker spectrometer operating at 100 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) using solvent signal as reference (CDCl₃ δ = 77.16 ppm; CD₂Cl₂ δ = 54.00 ppm; (CD₃)₂CO δ = 29.84 ppm, 206.26 ppm). Infrared spectra were recorded on standard FT/IR spectrometers. Wave numbers were reported in cm⁻¹. Optical rotation values were measured on an automatic polarimeter with a 1 dm cell at the sodium D line (λ = 589 nm). High resolution mass spectra (HRMS) were recorded on a ESI QToF SYNAPT G2 Si mass spectrometer (Waters), available at the UNITECH-COSPECT laboratories (Università degli Studi di Milano). Melting points were determined on a Büchi B-540 instrument.

2. Experimental Procedures

2.1. Synthesis of intermediate 2

(*R*)-BINOL (1.00 g, 3.49 mmol, 1 eq) was dissolved in dry THF (18 mL). NaH (209 mg, 8.73 mmol, 2.5 eq) was added in one portion at 0 °C. The mixture was allowed to warm up to room temperature, and it was stirred for 1 hour. Chloromethyl methyl ether (610 µL, 647 mg, 8.03 mmol, 2.3 eq) was added at 0 °C, and the reaction was left under stirring at room temperature for 16 additional hours. The product was purified through precipitation from iPr₂O. Compound **2** was isolated as a white crystalline solid. Yield: 880 mg (2.35 mmol, 67%).

Characterization data are in agreement with the literature.^[1]

R_f = 0.53 (SiO₂, EtOAc/petroleum ether 1:4)

¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 7.99 (d, ³J = 9.0 Hz, 2H), 7.91 (d, ³J = 8.2 Hz, 2H), 7.61 (d, ³J = 9.0 Hz, 2H), 7.41-7.34 (m, 2H), 7.29-7.24 (m, 2H), 7.19 (d, ³J = 8.4 Hz, 2H), 5.12 (d, ²J = 6.8 Hz, 2H), 5.01 (d, ²J = 6.8 Hz, 2H), 3.18 (s, 6H).

2.2. Synthesis of intermediate 3

Intermediate **2** (500 mg, 1.34 mmol, 1 eq) was dissolved in dry THF (19 mL) under nitrogen atmosphere. The solution was cooled to -78 °C. *n*-BuLi (1.6 M in hexane, 1 mL, 1.60 mmol, 1.2 eq) was added dropwise. The mixture was left under stirring at -78 °C for 5 hours. A solution of iodine (407 mg, 1.60 mmol, 1.2 eq) in THF (2 mL) was added dropwise and the reaction was left at -78 °C for one more hour. The reaction was allowed to slowly warm up to room temperature and it was left under stirring for 16 hours. The reaction was quenched with a 5% aqueous solution of Na₂SO₃ (7 mL). After 2 more hours, THF was removed under reduced pressure and the residue was extracted with EtOAc (2 x 15 mL). The organic layers were dried over Na₂SO₄. The product was purified through chromatographic column (EtOAc/petroleum ether 1:10, then 1:9). Compound **3** was isolated as a white crystalline solid.

Yield: 391 mg (0.78 mmol, 59%).

Characterization data are in agreement with the literature.^[2]

R_f = 0.47 (SiO₂, EtOAc/petroleum ether 1:9)

¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.52 (s, 1H), 7.97 (d, ³J = 9.1 Hz, 1H), 7.86 (d, ³J = 8.1 Hz, 1H), 7.78 (d, ³J = 8.2 Hz, 1H), 7.58 (d, ³J = 8.2 Hz, 1H), 7.41-7.34 (m, 2H), 7.29-7.23 (m, 2H), 7.20-7.13 (m, 2H), 5.14 (d, ²J = 6.9 Hz, 1H), 5.04 (d, ²J = 6.9 Hz, 1H), 4.73 (d, ²J = 5.2 Hz, 1H), 4.49 (d, ²J = 5.2 Hz, 1H), 3.20 (s, 3H), 2.72 (s, 3H).

2.3. Synthesis of intermediate 5

Iodobenzene (200 µL, 365 mg, 1.79 mmol, 1 eq) and 1,7-octadiyne (474 µL, 380 mg, 3.57 mmol, 2 eq) were dissolved in dry THF (24 mL) under nitrogen atmosphere. Freshly degassed *i*PrNH₂ (751 µL, 5.36 mmol, 3 eq) was added and the solution was purged with a flow of nitrogen. Pd(PPh₃)₄ (103 mg, 0.089 mmol, 0.05 eq) and CuI (34 mg, 0.179 mmol, 0.1 eq) were added and the mixture was left under stirring at room temperature for 4 hours. The reaction was quenched with a saturated aqueous solution of NH₄Cl (5 mL). THF was removed under reduced pressure. The residue was extracted with DCM (2 x 10 mL). The collected organic layers were washed with water (10 mL), brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified through chromatographic column (DCM/petroleum ether 1:10 to 1:9). Compound **5** was isolated as a colorless oil. Yield: 130 mg (0.72 mmol, 40%).

Characterization data are in agreement with the literature.^[3]

$R_f = 0.42$ (SiO₂, DCM/petroleum ether 1:9)

¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 7.47-7.35 (m, 2H), 7.35-7.20 (m, 3H), 2.52-2.38 (m, 2H), 2.32-2.22 (m, 2H), 1.99-1.93 (m, 1H), 1.80-1.67 (m, 4H).

2.4. Synthesis of diyne 4

Iodide **3** (807 mg, 1.61 mmol, 1 eq) was dissolved in a 1:1 mixture of Et₃N (6.5 mL) and MeCN (6.5 mL). The solution was degassed with a stream of argon, then 1,7-octadiyne (107 μ L, 86 mg, 0.81 mmol, 1 eq), CuI (15 mg, 0.08 mmol, 0.1 eq), and Pd(PPh₃)₄ (94 mg, 0.08 mmol, 0.1 eq) were added. The mixture was heated to 80 °C for 2 hours. The reaction was allowed to cool down to rt, and volatiles were removed in vacuo. The residue was purified through chromatographic column on silica gel (EtOAc/petroleum ether 1:9). **4** was isolated as a white crystalline solid. Yield: 556 mg (0.65 mmol, 81%). $R_f = 0.42$ (SiO₂, EtOAc/petroleum ether 1:4). M.p. = 147-149 °C. ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.08 (s, 2H), 7.94 (d, ³J = 9.0 Hz, 2H), 7.85 (d, ³J = 8.1 Hz, 2H), 7.78 (d, ³J = 8.2 Hz, 2H), 7.56 (d, ³J = 9.0 Hz, 2H), 7.38-7.32 (m, 4H), 7.26-7.13 (m, 8H), 5.13 (d, ²J = 6.8 Hz, 2H), 4.97 (d, ²J = 6.2 Hz, 4H), 4.87 (d, ²J = 5.7 Hz, 2H), 3.14 (s, 6H), 2.61-2.54 (s, 10H), 1.89-1.84 (m, 4H). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 153.1, 152.9, 134.2, 133.9, 133.5, 130.6, 129.8, 129.8, 127.8, 127.6, 126.8, 126.6, 126.2, 126.1, 125.9, 125.4, 124.2, 120.8, 118.2, 116.8, 98.7, 95.2, 94.1, 78.2, 56.2, 56.0, 28.0, 19.5. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 1616.4, 1592.0, 1507.2, 1259.2, 1242.6, 1152.0, 1073.4, 1034.3, 1013.0, 983.7, 922.6, 896.7, 809.3, 763.5. HRMS (ESI+): $m/z = 873.3391$ [M+Na]⁺ (calculated for C₅₆H₅₀O₈Na⁺ = 873.3398).

2.5. Procedure for the synthesis of (cyclopentadienone)iron tricarbonyl complexes **1a**, **15**, **16**, **17**, **18** (General procedure A).

Diiron nonacarbonyl (2 eq) and the diyne precursor (1 eq) were charged in a flame-dried Schlenk under inert atmosphere. Toluene (C_{0,diyne}) = 0.1 M) was added and the mixture was heated to 110 °C for 18 h. The reaction was allowed to cool to room temperature and filtered through celite, rinsing with DCM. The corresponding products were purified through chromatographic column on silica gel.

2.5.1. Complex **1a**

Complex **1a** was prepared according to general procedure A starting from diyne **4** (610 mg, 0.72 mmol). The product was purified through chromatographic column on silica gel (EtOAc/petroleum ether 1:4 to 3:7). **1a** was isolated as a yellow crystalline solid. Yield: 466 mg (0.46 mmol, 64%). $R_f = 0.39$ (SiO₂, EtOAc/petroleum ether 3:7). M.p. = 245-250 °C (dec.). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.08-7.90 (m, 6H), 7.85 (t, ³J = 9.1 Hz, 2H), 7.62 (d, ³J = 9.1 Hz, 1H), 7.57 (d, ³J = 9.0 Hz, 1H), 7.49-7.41 (m, 2H), 7.40-7.19 (m, 10H), 7.17 (d, ³J = 8.4 Hz, 1H), 5.14-4.97 (m, 4H), 4.69 (d, ²J = 4.8 Hz, 1H), 4.63 (d, ²J = 5.0 Hz, 1H), 4.54 (d, ²J = 4.8 Hz, 1H), 4.40 (d, ²J = 4.2 Hz, 1H), 3.23 (s, 3H), 3.19 (s, 3H), 3.03-2.81 (m, 2H), 2.53-2.33 (m, 5H), 2.28 (s, 3H), 1.98-1.80 (m, 4H). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 209.2, 171.6, 153.6, 153.0, 152.3, 152.1, 136.2, 136.1, 134.4, 134.3, 134.2, 134.0, 131.2, 131.1, 129.9, 129.8, 129.8, 129.5, 128.4, 128.1, 127.7, 126.9, 126.7, 126.6, 126.6, 126.5, 126.3, 126.2, 126.1, 125.8, 125.4, 125.4, 125.2, 125.0, 124.9, 124.3, 123.9, 121.1, 120.0, 117.1, 115.9, 106.0, 105.2, 99.4, 99.4, 95.5, 94.6, 84.0, 83.8, 56.2, 56.1, 55.8, 22.5, 22.4, 22.3, 22.1. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2060 (Fe(CO)₃), 2013 (Fe(CO)₃), 1978 (Fe(CO)₃), 1731, 1639 (C=O), 1591, 1305.8, 1239.3, 1196.1, 1147.8, 1084.7, 1039.5, 1008.0, 924.1, 901.0, 811.4, 744.2, 722.0. HRMS (ESI+): m/z 1019.2739 [M+H]⁺ (calculated for C₆₀H₅₁FeO₁₂⁺ = 1019.2724).

2.5.2. Synthesis of complex **1b**

Complex **1a** (156 mg, 0.15 mmol, 1 eq) was dissolved in THF (1.2 mL). Concentrated aqueous HCl (0.9 mL) was added, and the mixture was heated to 40 °C for 3 hours. The solution was diluted with water (5 mL) and extracted with Et₂O (2 x 5 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated in vacuo. The product was purified through chromatographic column on silica gel (EtOAc/petroleum ether 3:7). **1b** was isolated as a yellow solid. Yield: 100 mg (0.12 mmol, 77%). $R_f = 0.36$ (SiO₂, EtOAc/petroleum ether 2:3). M.p. = 311-313 °C (dec.). $[\alpha]_D^{25} = +253.2$ (c = 0.13 in CH₂Cl₂). ¹H-NMR (400 MHz, (CD₃)₂CO) δ [ppm] = 9.72 (s, 1H), 9.41 (s, 1H), 8.30 (d, ³J = 10.9 Hz, 2H), 8.01-7.82 (m, 8H), 7.42-7.15 (m, 10H), 7.15-7.01 (m, 4H), 3.24-3.09 (m, 1H), 3.04-2.90 (m, 3H), 2.17-1.88 (m, 4H). ¹³C-NMR (100 MHz, (CD₃)₂CO) δ [ppm] = 209.9, 166.9, 154.7, 154.3, 154.3, 153.7, 135.7, 135.7, 135.7, 135.6, 133.5, 132.6, 130.8, 130.5, 130.2, 130.1, 129.5, 129.5, 129.3, 129.1, 129.0, 127.9, 127.8, 127.3, 127.1, 125.7, 125.6, 125.5, 124.5, 124.5, 123.8, 123.7, 122.2, 121.6, 119.7, 119.6, 118.4, 117.9, 116.1, 115.5, 104.9, 102.4, 85.4, 83.9, 25.3, 24.2, 23.2, 23.1. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2853, 2074 (Fe(CO)₃), 2019 (Fe(CO)₃), 1620 (C=O), 1596, 1512, 1500, 1345, 1210, 1148, 817, 749, 722. MS (ESI+): $m/z = 843.00$ [M+H]⁺, 864.95 [M+Na]⁺ (calculated for C₅₂H₃₅FeO₈⁺ = 843.17, C₅₂H₃₅FeO₈Na⁺ = 865.15). HRMS (ESI-): $m/z = 841.1522$ [M-H]⁻ (calculated for C₅₂H₃₃FeO₈⁻ = 841.1530).

2.5.3. Synthesis of complex **1c**

Complex **1b** (30 mg, 0.036 mmol, 1 eq) was dissolved in dry THF (0.7 mL). 4-dimethylaminopyridine (0.9 mg, 0.007 mmol, 0.2 eq), triethylamine (40 μ L, 0.29 mmol, 8 eq), and acetyl chloride (15 μ L, 17 mg, 0.21 mmol, 6 eq) were added. The mixture was stirred at room temperature for 4 hours. The reaction was quenched with water (5 mL) and extracted with Et₂O (2 x 5 mL). The organic phase was washed with a 0.5 M HCl solution (5 mL), water (5 mL), and brine, then dried over Na₂SO₄, filtered, and concentrated in vacuo. The product was purified through chromatographic column on silica gel (EtOAc/petroleum ether 3:7). **1c** was isolated as a pale-yellow solid. Yield: 24.8 mg (0.024 mmol, 68%). $R_f = 0.29$ (SiO₂, EtOAc/petroleum ether 3:7). M.p. = 180 °C (dec.). $[\alpha]_D^{25} = +25.4$ (c = 0.05 in CH₂Cl₂). ¹H-NMR (400 MHz, (CD₃)₂CO) δ [ppm] = 8.24 (s, 1H), 8.22-8.13 (m, 3H), 8.13-8.04 (m, 2H), 8.04-7.95 (m, 2H), 7.62-7.42 (m, 6H), 7.40-7.26 (m, 2H), 7.26-7.18 (m, 2H), 7.09 (d, ³J = 8.4 Hz, 1H), 7.03 (d, ³J = 8.4 Hz,

1H), 3.04-2.88 (m, 1H), 2.69-2.43 (m, 3H), 2.02-1.73 (m, 4H), 1.94 (s, 3H), 1.90 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H). ¹³C-NMR (100 MHz, (CD₃)₂CO) δ [ppm] = 210.4, 171.2, 170.1, 169.5, 169.3, 168.3, 148.1, 148.0, 147.8, 147.5, 136.7, 136.0, 134.4, 134.2, 134.1, 132.7, 132.6, 132.6, 132.5, 130.7, 130.4, 129.4, 129.3, 129.1, 129.0, 128.2, 128.2, 127.8, 127.8, 127.6, 127.3, 127.3, 127.2, 126.9, 126.7, 126.6, 126.2, 125.5, 125.4, 124.2, 123.7, 123.7, 123.2, 105.2, 103.7, 84.3, 83.4, 24.0, 23.2, 23.2, 22.8, 21.1, 20.9, 20.8, 20.6. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2064 (Fe(CO)₃), 2007 (Fe(CO)₃), 1987 (Fe(CO)₃), 1762, 1654 (C=O), 1194.

2.5.4. Synthesis of complex 1d

Complex **1b** (39 mg, 0.046 mmol, 1 eq) was dissolved in dry THF (1.2 mL). 4-dimethylaminopyridine (1.1 mg, 0.009 mmol, 0.2 eq), triethylamine (52 μ L, 38 mg, 0.37 mmol, 8 eq), and benzoyl chloride (32 μ L, 39 mg, 0.28 mmol, 6 eq) were added. The mixture was stirred at room temperature for 4 hours. The reaction was quenched with water (5 mL) and extracted with Et₂O (2 x 5 mL). The organic phase was washed with a 0.5 M HCl solution (5 mL), water (5 mL), and brine, then dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified through chromatographic column on silica gel (EtOAc/petroleum ether 1:3). **1d** was isolated as a yellow solid. Yield: 24.8 mg (0.024 mmol, 68%). *R*_f = 0.51 (SiO₂, EtOAc/petroleum ether 3:7). M.p. = 176-182 °C (dec.). [α]_D = -32.8 (*c* = 0.21 in CH₂Cl₂). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.02-7.69 (m, 12H), 7.54-7.21 (m, 26H), 7.08 (dd, ³*J* = 7.6 Hz, 2H), 6.99 (dd, ³*J* = 7.1 Hz, 2H), 2.48 (ddd, ³*J* = 17.1 Hz, ³*J* = ²*J* = 6.6 Hz, 1H), 2.39-2.25 (m, 2H), 2.03-1.89 (m, 1H), 1.75-1.60 (m, 1H), 1.54-1.39 (m, 2H), 1.39-1.29 (m, 1H). ¹³C-NMR (100 MHz, (CD₂Cl₂) δ [ppm] = 209.3, 169.7, 165.4, 165.3, 165.1, 164.3, 147.7, 147.6, 147.1, 135.8 (br s), 134.6 (br s), 133.9, 133.8, 133.8, 133.7, 133.6, 133.6, 133.5, 132.1, 132.0, 131.8, 130.8, 130.4, 130.3, 130.1, 130.1, 130.1, 129.9, 129.6, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 127.8, 127.7, 127.3, 127.2, 127.0, 126.7, 126.6, 126.4, 126.2, 126.1, 125.8, 125.8, 124.9, 124.5, 124.1, 124.0, 122.2, 122.1, 83.5, 83.2, 23.7, 22.8, 22.6, 22.0. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2066 (Fe(CO)₃), 2011 (Fe(CO)₃), 1991 (Fe(CO)₃), 1738, 1654 (C=O), 1600, 1263, 1212, 1177, 1079, 1063, 1022, 707. HRMS (ESI⁺): *m/z* = 1259.2717 [M+H]⁺, *m/z* = 1281.2535 [M+Na]⁺ (calculated for C₈₀H₅₁FeO₁₂⁺ = 1259.2724, C₈₀H₅₀FeO₁₂Na⁺ = 1281.2544).

2.6. Procedure for the synthesis of diynes **6**, **7**, **8** (General procedure B).

1,7-octadiyne (3 eq) and the aryl iodide substrate (1 eq) were dissolved in dry 1,4-dioxane (C_{0,iodide}) = 0.075 M). Cs₂CO₃ (4 eq) was added, and the suspension was degassed with an argon stream. SPhos (0.1 eq), and Pd(OAc)₂ (0.05 eq) were added. The reaction mixture was heated to 100 °C for 4 hours. The reaction was allowed to cool to room temperature, and filtered through celite, rinsing with DCM. The corresponding products were purified through chromatographic column on silica gel.

2.6.1. Diyne **6**

Diyne **6** was prepared according to general procedure B starting from iodomesitylene (150 mg, 0.61 mmol). The product was purified through chromatographic column (DCM/petroleum ether 1:9). **6** was isolated as a yellowish oil. Yield: 89 mg (0.397 mmol, 65%). *R*_f = 0.53 (SiO₂, DCM/petroleum ether 1:9). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 6.84 (s, 2H), 2.57-2.50 (m, 2H), 2.37 (s, 6H), 2.31-2.22 (m, 2H), 2.25 (s, 3H), 1.96 (t, ⁴*J* = 2.6 Hz, 1H), 1.79-1.72 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 140.0, 136.9, 127.6, 120.8, 97.3, 84.3, 78.7, 68.6, 28.1, 27.7, 21.4, 21.2, 19.3, 18.1. HRMS (ESI⁺): *m/z* = 224.1573 [M+H]⁺ (calculated for C₁₇H₂₁⁺ = 224.1565).

2.6.2. Diyne **7**

Diyne **7** was prepared according to general procedure B starting from iodopentafluorobenzene (133 μ L, 294 mg, 1.00 mmol). The product was purified through chromatographic column (DCM/petroleum ether 1:15). **7** was isolated as a colorless liquid. Yield: 128 mg (0.47 mmol, 47%). *R*_f = 0.48 (SiO₂, DCM/petroleum ether 1:15). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 2.54 (t, ³*J* = 6.6 Hz, 2H), 2.26 (td, ³*J* = 6.5 Hz, ⁴*J* = 2.3 Hz, 2H), 1.97 (t, ⁴*J* = 2.4 Hz, 1H), 1.86-1.62 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 149.1-146.1, 142.7-139.5, 139.2-136.2, 103.6-103.3, 101.0-100.0, 84.0, 68.8, 65.4-65.0, 27.5, 27.2, 19.5, 18.1. ¹⁹F-NMR (377 MHz, CDCl₃) δ [ppm] = -136.99--137.26 (m, 2F), -154.20 (t, ³*J* = 20.8 Hz, 1F), -162.33--162.51 (m, 2F). IR (neat): $\tilde{\nu}$ [cm⁻¹] = 2949.4, 2868.0, 2666.2, 2438.1, 2247.9, 2119.2, 1737.3, 1649.4, 1626.7, 1518.6, 1496.9, 1459.7, 1430.5, 1374.2, 1320.7, 1273.9, 1176.6, 1148.5, 1048.7, 989.4, 923.1, 838.3, 816.9, 793.2.

2.6.3. Diyne **8**

Diyne **8** was prepared according to general procedure B starting from 2-iodo-1,3-dimethoxybenzene (200 mg, 0.757 mmol). The product was purified through chromatographic column (DCM/petroleum ether 1:4 to 2:3). **8** was isolated as a yellowish oil. Yield: 101 mg (0.417 mmol, 55%). *R*_f = 0.15 (SiO₂, DCM/petroleum ether 1:4). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 7.17 (t, ³*J* = 8.4 Hz, 1H), 6.51 (d, ³*J* = 8.4 Hz, 2H), 3.87 (s, 6H), 2.60-2.54 (m, 2H), 2.33-2.21 (m, 2H), 1.95 (t, ⁴*J* = 2.6 Hz, 1H), 1.86-1.69 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 161.6, 128.9, 103.6, 98.6, 84.6, 73.1, 68.4, 56.2, 27.9, 27.7, 19.8, 18.2. IR (neat): $\tilde{\nu}$ [cm⁻¹] = 3286.4, 3003.1, 2933.3, 2837.8, 2538.8, 2229.8, 2188.7, 2115.2, 1927.2, 1713.6, 1583.5, 1473.9, 1432.2, 1329.1, 1300.8, 1252.7, 1173.5, 1110.6, 1033.3, 958.4, 902.2, 776.9, 725.8. HRMS (ESI⁺): *m/z* = 243.1358 [M+H]⁺, 265.1205 [M+Na]⁺ (calculated for C₁₆H₁₉O₂⁺ = 243.1358, C₁₆H₁₈O₂Na⁺ = 265.1204).

2.7. Procedure for the coupling of iodide **3** with diynes **5**, **6**, **7**, **8** (General procedure C).

Iodide **3** (1 eq) and the mono-substituted diyne substrate (1 eq) were dissolved in a 1:1 mixture of MeCN and triethylamine (C₀(3): 0.1 M). The solution was degassed with a stream of argon. Cul (0.1 eq) and Pd(PPh₃)₄ (0.05 eq) were added, and the reaction was heated to 80 °C for 2 hours. Volatiles were removed and the crude was suspended in a saturated solution of NH₄Cl. The

residue was extracted with DCM. The collected organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The corresponding products were purified through chromatographic column on silica gel.

2.7.1. Diyne 9

Diyne **9** was prepared according to general procedure C starting from mono-substituted diyne **5** (55 mg, 0.30 mmol). **9** was isolated through chromatographic column on silica gel (EtOAc/petroleum ether 1:9 to 1:4) as a thick yellow oil. Yield: 125 mg (0.23 mmol, 75%). *R_f* = 0.61 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.09 (s, 1H), 7.95 (d, ³J = 9.0 Hz, 1H), 7.85 (d, ³J = 8.2 Hz, 1H), 7.81 (d, ³J = 8.2 Hz, 1H), 7.57 (d, ³J = 9.0 Hz, 1H), 7.43-7.31 (m, 4H), 7.31-7.23 (m, 4H), 7.23-7.13 (m, 3H), 5.14 (d, ²J = 6.9 Hz, 1H), 4.99 (d, ²J = 7.0 Hz, 1H), 4.99 (d, ²J = 5.7 Hz, 1H), 4.88 (d, ²J = 5.7 Hz, 1H), 3.16 (s, 3H), 2.57 (s, 3H), 2.62-2.53 (m, 2H), 2.53-2.46 (m, 2H), 1.94-1.75 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 153.1, 152.9, 134.2, 133.9, 133.5, 131.7, 130.6, 129.8, 129.8, 128.3, 127.8, 127.7, 127.6, 126.8, 126.6, 126.2, 126.1, 126.0, 125.4, 124.2, 124.1, 120.8, 118.2, 116.9, 98.7, 95.2, 94.2, 89.9, 81.2, 78.2, 56.2, 56.0, 28.1, 28.0, 19.5, 19.2. HRMS (ESI+): *m/z* 577.2355 [M+Na]⁺ (calculated for C₃₈H₃₄NaO₄⁺: 577.2355).

2.7.2. Diyne 10

Diyne **10** was prepared according to general procedure C starting from mono-substituted diyne **6** (80 mg, 0.36 mmol). **10** was isolated through chromatographic column on silica gel (EtOAc/petroleum ether 1:9) as a yellow oil. Yield: 139 mg (0.233 mmol, 65%). *R_f* = 0.71 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.07 (s, 1H), 7.94 (d, ³J = 9.1 Hz, 1H), 7.85 (d, ³J = 8.1 Hz, 1H), 7.80 (d, ³J = 8.1 Hz, 1H), 7.57 (d, ³J = 9.0 Hz, 1H), 7.41-7.31 (m, 2H), 7.30-7.12 (m, 4H), 6.83 (s, 2H), 5.14 (d, ²J = 6.9 Hz, 1H), 5.02-4.93 (m, 2H), 4.87 (d, ²J = 5.7 Hz, 1H), 3.15 (s, 3H), 2.63-2.50 (m, 7H), 2.37 (s, 6H), 2.25 (s, 3H), 1.93-1.77 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 153.1, 152.9, 140.0, 136.9, 134.2, 133.9, 133.5, 130.6, 129.8, 129.8, 127.8, 127.6, 127.6, 126.2, 126.1, 126.0, 125.4, 124.2, 120.9, 120.8, 118.3, 116.9, 98.7, 97.4, 95.2, 94.3, 78.8, 78.1, 56.2, 56.0, 28.4, 28.0, 21.4, 21.2, 19.5, 19.4. HRMS (ESI+): *m/z* = 619.2817 [M+Na]⁺ (calculated for C₄₁H₄₀O₄Na⁺: 619.2819).

2.7.3. Diyne 11

Diyne **11** was prepared according to general procedure C starting from mono-substituted diyne **7** (56 mg, 0.21 mmol). **11** was isolated through chromatographic column on silica gel (EtOAc/n-hexane 1:9) as a yellow oil. Yield: 102 mg (0.16 mmol, 77%). *R_f* = 0.26 (SiO₂, EtOAc/petroleum ether 1:9). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.08 (s, 1H), 7.94 (d, ³J = 9.0 Hz, 1H), 7.85 (d, ³J = 8.1 Hz, 1H), 7.81 (d, ³J = 8.2 Hz, 1H), 7.57 (d, ³J = 9.0 Hz, 1H), 7.42-7.30 (m, 2H), 7.30-7.11 (m, 4H), 5.14 (d, ²J = 6.9 Hz, 1H), 5.03-4.93 (m, 2H), 4.86 (d, ²J = 5.7 Hz, 1H), 3.15 (s, 3H), 2.65-2.50 (m, 4H), 2.57 (s, 3H), 1.94-1.74 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 153.1, 152.9, 149.0-146.2, 142.7-139.5, 139.2-136.2, 134.2, 133.9, 133.5, 130.6, 129.8, 129.8, 127.9, 127.6, 126.8, 126.6, 126.2, 126.1, 125.9, 125.4, 124.2, 120.8, 118.1, 116.9, 103.6-103.4, 100.9-100.4, 98.7, 95.2, 93.8, 78.3, 65.4-65.2, 56.2, 56.0, 27.8, 27.5, 19.5, 19.4. ¹⁹F-NMR (377 MHz, CDCl₃) δ [ppm] = -136.95--137.13 (m, 2F), -154.18 (t, 3J = 20.8 Hz, 1F), -162.27--162.51 (m, 2F). IR (neat): $\tilde{\nu}$ [cm⁻¹] = 1612.8, 1594.0, 1334.7, 1260.8, 1241.9, 1214.8, 1155.7, 1069.8, 1033.8, 1014.3, 976.5, 923.1, 809.1, 761.2, 691.1. HRMS (ESI+): *m/z* = 667.1884 [M+Na]⁺ (calculated for C₃₈H₂₉O₄NaF₅⁺ = 667.1884).

2.7.4. Diyne 12

Diyne **12** was prepared according to general procedure C starting from mono-substituted diyne **8** (77 mg, 0.32 mmol). **12** was isolated through chromatographic column on silica gel (EtOAc/petroleum ether 1:4 to 3:7) as a yellow solid. Yield: 152 mg (0.247 mmol, 78%). *R_f* = 0.39 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.07 (s, 1H), 7.94 (d, ³J = 9.1 Hz, 1H), 7.85 (d, ³J = 8.1 Hz, 1H), 7.80 (d, ³J = 8.2 Hz, 1H), 7.57 (d, ³J = 9.0 Hz, 1H), 7.41-7.30 (m, 2H), 7.30-7.10 (m, 5H), 6.51 (d, ³J = 8.4 Hz, 2H), 5.14 (d, ²J = 6.9 Hz, 1H), 5.01-4.94 (m, 2H), 4.87 (d, ²J = 5.8 Hz, 1H), 3.86 (s, 6H), 3.16 (s, 3H), 2.68-2.51 (m, 4H), 2.56 (s, 3H), 1.97-1.79 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 161.6, 153.1, 153.0, 134.2, 133.9, 133.5, 130.6, 129.8, 128.9, 127.8, 127.6, 127.8, 127.6, 126.8, 126.6, 126.1, 126.0, 125.3, 124.2, 120.9, 118.3, 116.9, 103.6, 98.7, 98.6, 95.2, 94.6, 78.0, 73.2, 56.2, 56.2, 56.0, 28.2, 27.9, 19.9, 19.6. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 3058.4, 3007.4, 2934.7, 2836.7, 2227.0, 2191.1, 1711.5, 1622.1, 1529.6, 1584.1, 1473.4, 1432.3, 1393.1, 1357.7, 1334.5, 1301.7, 1253.8, 1217.2, 1199.4, 1155.8, 1112.6, 1071.3, 1033.9, 1014.3, 978.5, 923.5, 904.9, 810.9, 752.9, 725.3. HRMS (ESI+): *m/z* 637.2565 [M+Na]⁺ (calculated for C₄₀H₃₈O₆Na⁺ = 637.2566).

2.8. Synthesis of compound 13

Iodide **3** (500 mg, 1.00 mmol, 1 eq) was dissolved in a 1:1 mixture of MeCN (5 mL) and triethylamine (5 mL). The solution was degassed with a stream of argon. CuI (19 mg, 0.10 mmol, 0.1 eq), Pd(PPh₃)₄ (115 mg, 0.10 mmol, 0.1 eq), and propargyl alcohol (116 μ L, 112 mg, 2.00 mmol, 2 eq) were added. The reaction was heated to 80 °C for 2 hours. Volatiles were removed in vacuo, and the residue was suspended in a saturated solution of NH₄Cl (15 mL). The residue was extracted with DCM (2 x 15 mL). The organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The product was purified through chromatographic column on silica gel (EtOAc/petroleum ether 2:3). **13** was isolated as a pale-yellow solid. Yield: 355 mg (0.83 mmol, 83%). M.p. = 109-110 °C. *R_f* = 0.41 (SiO₂, EtOAc/petroleum ether 2:3). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.12 (s, 1H), 7.96 (d, ³J = 9.0 Hz, 1H), 7.89-7.80 (m, 2H), 7.58 (d, ³J = 9.0 Hz, 1H), 7.44-7.32 (m, 2H), 7.30-7.22 (m, 2H), 7.20-7.13 (m, 2H), 5.14 (d, ²J = 6.9 Hz, 1H), 5.00 (d, ²J = 6.9 Hz, 1H), 4.90 (d, ²J = 5.6 Hz, 1H), 4.82 (d, ²J = 5.6 Hz, 1H), 4.55 (d, ³J = 3.5 Hz, 2H), 3.16 (s, 3H), 2.71 (s, 3H), 1.91 (br s, 1H, OH). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 153.1, 152.8, 134.2, 134.1, 134.0, 130.5, 130.0, 129.8, 127.9, 127.3, 126.8, 126.4, 126.2, 125.7, 125.6, 124.3, 120.4, 117.0, 116.8, 99.0, 95.2, 91.5, 83.1, 56.5, 56.1, 52.0. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 3417.4, 2226.9, 1621.7, 1593.5, 1261.1, 1241.7, 1214.9, 1154.5, 1120.5, 1068.4, 1032.7, 1013.7, 974.0, 921.3, 864.4, 809.5, 761.4.

2.9. Synthesis of diyne 14

NaH (60% in mineral oil, 16.6 mg, 0.693 mmol, 1.5 eq) was suspended in THF (3 mL). **13** (198 mg, 0.462 mmol, 1 eq) was dissolved in THF (1.6 mL), and the solution was slowly added to the suspension of NaH under argon atmosphere at 0 °C. The mixture was left for 0.5 hours at rt. Propargyl bromide (80% in toluene, 77 μ L, 82.5 mg, 0.693 mmol, 1.5 eq) was added at 0 °C. The mixture was left under stirring for 3 hours at rt. The reaction was quenched with sat. aq. NH₄Cl (10 mL). The crude was extracted with EtOAc (3 x 10 mL). The collected organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The product was purified through chromatographic column on silica gel (EtOAc/n-hexane 1:9 to 1:4). **14** was isolated as a thick yellow oil. Yield: 188 mg (0.40 mmol, 87%). *R*_f = 0.56 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CDCl₃) δ [ppm] = 8.14 (s, 1H), 7.96 (d, ³*J* = 9.1 Hz, 1H), 7.89-7.80 (m, 2H), 7.58 (d, ³*J* = 9.1 Hz, 1H), 7.48-7.31 (m, 2H), 7.31-7.20 (m, 2H), 7.20-7.13 (m, 2H), 5.14 (d, ²*J* = 6.9 Hz, 1H), 5.00 (d, ²*J* = 6.9 Hz, 1H), 4.93 (d, ²*J* = 5.7 Hz, 1H), 4.82 (d, ²*J* = 5.7 Hz, 1H), 4.57 (s, 2H), 4.37 (d, ⁴*J* = 2.3 Hz, 2H), 3.16 (s, 3H), 2.66 (s, 3H), 2.47 (t, ⁴*J* = 2.3 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ [ppm] = 153.1, 152.9, 134.5, 134.1, 134.1, 130.5, 130.0, 129.8, 127.9, 127.9, 127.3, 126.8, 126.4, 126.2, 125.8, 125.6, 124.3, 120.4, 116.9, 116.7, 99.0, 95.2, 88.2, 84.3, 79.1, 75.2, 57.6, 56.7, 56.4, 56.1. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 3286.5, 3058.6, 2945.5, 2853.1, 2225.1, 2116.7, 1738.6, 1621.9, 1594.1, 1508.8, 1469.9, 1428.0, 1393.3, 1357.2, 1242.5, 1156.1, 1077.6, 1033.6, 1014.0, 979.5, 923.0, 810.3, 751.6. HRMS (ESI+): *m/z* 489.1676 [M+Na]⁺ (calculated for C₃₀H₂₆O₅Na⁺ = 489.1672).

2.10. Synthesis and isolation of the pairs of diastereoisomerically pure complexes.

2.10.1. Complexes (pR,aR)-15 and (pS,aR)-15

Iron complexes (pR,aR)-**15** and (pS,aR)-**15** were prepared according to general procedure A, starting from diyne **9** (125 mg, 0.225 mmol). (pR,aR)-**15** and (pS,aR)-**15** were isolated through chromatographic column on silica gel (Et₂O/n-hexane 1:1 to 3:2) as yellow solids.

(pR,aR)-**15**. Yield: 59 mg (0.082 mmol, 36%). M.p. = 112-114 °C. *R*_f = 0.34 (SiO₂, Et₂O/petroleum ether 3:2). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.03-7.97 (m, 2H), 7.94-7.87 (m, 2H), 7.77-7.72 (m, 2H), 7.63 (d, ³*J* = 9.1 Hz, 1H), 7.50-7.44 (m, 1H), 7.44-7.31 (m, 4H), 7.31-7.22 (m, 2H), 7.19 (d, ³*J* = 8.5 Hz, 1H), 7.13 (d, ³*J* = 8.5 Hz, 1H), 5.14-5.08 (m, 2H), 4.50 (d, ²*J* = 5.1 Hz, 1H), 4.34 (d, ²*J* = 5.1 Hz, 1H), 3.24 (s, 3H), 2.95-2.78 (m, 2H), 2.78-2.65 (m, 1H), 2.72 (s, 3H), 2.39 (ddd, ³*J* = 17.0 Hz, ³*J* = ²*J* = 5.3 Hz, 1H), 2.01-1.80 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 209.8, 171.4, 153.5, 153.1, 153.9, 134.7, 134.7, 132.3, 131.5, 130.5, 130.3, 130.2, 129.0, 128.7, 128.5, 128.5, 127.4, 127.3, 126.6, 126.4, 126.3, 125.9, 125.7, 124.7, 120.9, 117.4, 105.3, 101.8, 99.9, 95.9, 85.7, 81.2, 56.7, 56.2, 24.0, 23.2, 22.9, 22.6. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2059.7 (Fe(CO)₃), 1984.9 (Fe(CO)₃), 1639.7 (C=O), 1592.6, 1240.9, 1197.8, 1148.4, 1074.8, 1034.1, 1013.7, 965.6, 925.0, 749.7, 721.5. HRMS (ESI+): *m/z* 723.1678 [M+H]⁺, 745.1500 [M+Na]⁺ (calculated for C₄₂H₃₅FeO₈⁺ = 723.1676, C₄₂H₃₄FeO₈Na⁺ = 745.1495).

(pS,aR)-**15**. Yield: 56 mg (0.077 mmol, 34%). M.p. = 105-110 °C. *R*_f = 0.21 (SiO₂, Et₂O/petroleum ether 3:2). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.05-7.97 (m, 2H), 7.95-7.89 (m, 2H), 7.78-7.72 (m, 2H), 7.67 (d, ³*J* = 9.1 Hz, 1H), 7.50-7.45 (m, 1H), 7.45-7.27 (m, 6H), 7.24 (d, ³*J* = 8.5 Hz, 1H), 7.15 (d, ³*J* = 8.5 Hz, 1H), 5.19 (d, ²*J* = 7.1 Hz, 1H), 5.10 (d, ²*J* = 7.1 Hz, 1H), 4.69 (d, ²*J* = 5.1 Hz, 1H), 4.53 (d, ²*J* = 5.1 Hz, 1H), 3.25 (s, 3H), 2.91-2.76 (m, 3H), 2.87 (s, 3H), 2.76-2.65 (m, 1H), 2.48-2.36 (m, 1H), 2.00-1.78 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 209.8, 171.6, 153.8, 152.8, 136.1, 134.6, 134.3, 132.3, 131.6, 130.6, 130.2, 130.2, 129.0, 128.8, 128.7, 128.5, 127.4, 127.2, 126.9, 126.0, 126.0, 125.7, 125.4, 124.6, 120.2, 116.4, 105.5, 101.9, 100.0, 95.2, 85.5 (s, 1C), 81.2, 57.0, 56.6, 23.8, 23.2, 22.9, 22.6. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2059.5 (Fe(CO)₃), 1984.9 (Fe(CO)₃), 1640.5 (C=O), 1592.6, 1258.8, 1241.4, 1197.7, 1148.1, 1062.3, 1032.9, 1012.1, 964.8, 924.2, 749.7, 721.0. HRMS (ESI+): *m/z* 723.1677 [M+H]⁺, 745.1500 [M+Na]⁺ (calculated for C₄₂H₃₅FeO₈⁺ = 723.1676, C₄₂H₃₄FeO₈Na⁺ = 745.1495).

2.10.2. Complexes (pR,aR)-16 and (pS,aR)-16

Iron complexes (pR,aR)-**16** and (pS,aR)-**16** were prepared according to general procedure A, starting from diyne **10** (112 mg, 0.19 mmol). (pR,aR)-**16** and (pS,aR)-**16** were isolated through chromatographic column on silica gel (Et₂O/n-hexane 2:3 to 3:2) as yellow solids.

(pR,aR)-**16**. Yield: 45 mg (0.058 mmol, 31%). M.p. = 234-236 °C. [α]_D = +56.4 (c = 0.02 in CH₂Cl₂). *R*_f = 0.30 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 7.99 (d, ³*J* = 9.2 Hz, 2H), 7.93 (s, 1H), 7.89 (d, ³*J* = 8.2 Hz, 1H), 7.62 (d, ³*J* = 9.0 Hz, 1H), 7.46 (t, ³*J* = 7.4 Hz, 1H), 7.37 (t, ³*J* = 7.3 Hz, 1H), 7.32-7.16 (m, 3H), 7.12 (d, ³*J* = 8.5 Hz, 1H), 6.98 (s, 1H), 6.94 (s, 1H), 5.10 (s, 2H), 4.59 (d, ²*J* = 4.8 Hz, 1H), 4.35 (d, ²*J* = 4.7 Hz, 1H), 3.23 (s, 3H), 3.04-2.91 (m, 1H), 2.62 (s, 3H), 2.47-2.35 (m, 4H), 2.34-2.21 (m, 5H), 2.11 (s, 3H), 2.00-1.73 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 210.2, 171.0, 153.7, 152.6, 138.6, 138.2, 137.2, 136.1, 131.4, 130.4, 130.3, 129.8, 128.7, 128.3, 127.3, 127.1, 126.8, 126.6, 126.5, 126.4, 125.9, 125.7, 124.7, 121.2, 117.5, 105.5, 103.0, 99.8, 96.1, 86.4, 85.6, 56.4, 56.2, 23.3, 23.2, 23.1, 22.9, 21.4, 21.1. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2060.8 (Fe(CO)₃), 2008.4 (Fe(CO)₃), 1987.5 (Fe(CO)₃), 1644.0 (C=O), 1240.5, 1151.4, 1084.4, 1035.9, 1014.8, 969.9, 925.6, 721.5. HRMS (ESI⁺): *m/z* 765.2145 [M+H]⁺, 787.1967 [M+Na]⁺ (calculated for C₄₅H₄₁FeO₈⁺ = 765.2145, C₄₅H₄₀FeO₈Na⁺ = 787.1965).

(pS,aR)-**16**. Yield: 32 mg (0.041 mmol, 22%). M.p. = 194-198 °C. [α]_D = +80.4 (c = 0.04 in CH₂Cl₂). *R*_f = 0.16 (SiO₂, EtOAc/petroleum ether 1:4). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.01 (d, ³*J* = 9.2 Hz, 1H), 7.98 (d, ³*J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.91 (d, ³*J* = 8.2 Hz, 1H), 7.67 (d, ³*J* = 9.1 Hz, 1H), 7.52-7.43 (m, 1H), 7.38 (t, ³*J* = 7.0 Hz, 1H), 7.35-7.26 (m, 3H), 7.21 (d, ³*J* = 8.4 Hz, 1H), 6.98 (s, 1H), 6.95 (s, 1H), 5.16 (d, ²*J* = 7.2 Hz, 1H), 5.11 (d, ²*J* = 7.2 Hz, 1H), 4.70 (d, ²*J* = 4.7 Hz, 1H), 4.51 (d, ²*J* = 4.7 Hz, 1H), 3.26 (s, 3H), 2.97-2.84 (m, 1H), 2.63 (s, 3H), 2.54-2.41 (m, 4H), 2.35-2.21 (m, 5H), 2.11 (s, 3H), 2.05-1.84 (m, 2H), 1.84-1.65 (m, 2H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 210.2, 171.2, 154.1, 152.1, 138.5, 138.2, 137.3, 136.1, 134.5, 134.4, 131.5, 130.5, 130.3, 130.1, 129.8, 128.7, 128.6, 127.3, 127.1, 126.8, 126.5, 126.1, 126.0, 125.8, 125.4, 124.4, 120.1, 116.3, 105.9, 102.7, 99.9, 95.2, 86.2, 85.7, 56.7, 56.6, 23.3, 23.3, 23.1, 23.1, 22.9, 21.4, 21.1. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2060.6 (Fe(CO)₃), 2004.0 (Fe(CO)₃), 1989.5 (Fe(CO)₃), 1642.6 (C=O), 1241.6, 1148.3, 1032.7, 1012.2, 963.6, 925.6, 721.4. HRMS (ESI+): *m/z* 765.2144 [M+H]⁺, 787.1966 [M+Na]⁺ (calculated for C₄₅H₄₁FeO₈⁺ = 765.2145, C₄₅H₄₀FeO₈Na⁺ = 787.1965).

2.10.3. Complexes (pS,aR)-17 and (pR,aR)-17

Iron complexes (pS,aR)-17 and (pR,aR)-17 were prepared according to general procedure A, starting from diyne **11** (95 mg, 0.147 mmol). (pS,aR)-17 and (pR,aR)-17 were isolated through chromatographic column on silica gel (Et₂O/*n*-hexane 35:65) as yellow solids.

(pS,aR)-17. Yield: 51 mg (0.063 mmol, 43%). M.p. = 135-140 °C (dec.). [α]_D = 0.0 (c = 0.14 in CH₂Cl₂). R_f = 0.32 (SiO₂, Et₂O/*n*-hexane 2:3). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.04-7.96 (m, 2H), 7.93-7.85 (m, 2H), 7.63 (d, ³J = 9.1 Hz, 1H), 7.51-7.43 (m, 1H), 7.40-7.33 (m, 1H), 7.33-7.21 (m, 2H), 7.20-7.10 (m, 2H), 5.17-5.07 (m, 2H), 4.41 (d, ²J = 5.2 Hz, 1H), 4.37 (d, ²J = 5.2 Hz, 1H), 3.25 (s, 3H), 2.97-2.87 (m, 1H), 2.84 (s, 3H), 2.72-2.59 (m, 1H), 2.50-2.34 (m, 2H), 2.08-1.73 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 208.7, 169.8, 153.5, 153.2, 144.0-140.0 (m), 140.0-136.5 (m), 135.5, 134.8, 134.6, 131.4, 130.6, 130.3, 128.7, 128.5, 127.5, 127.3, 126.6, 126.3, 126.2, 126.0, 125.0, 124.8, 120.6, 117.2, 107.7, 106.6 (m), 101.4, 100.0, 95.8, 86.7, 67.2, 56.9, 56.2, 23.3, 22.9, 22.7, 22.2. ¹⁹F-NMR (377 MHz, CD₂Cl₂) δ [ppm] = -133.78 (br s, 1F), -137.62 (br s, 1F), -153.81 (t, ³J = 20.7 Hz), -161.58 (br s, 1F), -162.72 (br s, 1F). IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2060.7 (Fe(CO)₃), 1996.3 (Fe(CO)₃), 1648.2 (C=O), 1525.6, 1241.2, 1150.9, 1077.4, 1034.6, 1012.8, 988.7, 967.3, 721.2. HRMS (ESI⁺): *m/z* 813.1205 [M+H]⁺, 835.1029 [M+Na]⁺ (calculated for C₄₂H₃₀F₅FeO₈⁺ = 813.1205, C₄₂H₂₉F₅FeO₈Na⁺ = 835.1024).

(pR,aR)-17. Yield: 40.6 mg (0.050 mmol, 34%). M.p. = 161-163 °C (dec.). [α]_D = 120.4 (c = 0.11 in CH₂Cl₂). R_f = 0.25 (SiO₂, Et₂O/*n*-hexane 2:3). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.05-7.96 (m, 2H), 7.95-7.86 (m, 2H), 7.66 (d, ³J = 9.1 Hz, 1H), 7.52-7.43 (m, 1H), 7.43-7.36 (m, 1H), 7.36-7.27 (m, 2H), 7.22 (d, ³J = 8.5 Hz, 1H), 7.13 (d, ³J = 8.5 Hz, 1H), 5.17 (d, ²J = 7.1 Hz, 1H), 5.08 (d, ²J = 7.1 Hz, 1H), 4.61 (d, ²J = 5.1 Hz, 1H), 4.50 (d, ²J = 5.1 Hz, 1H), 3.23 (s, 3H), 3.00-2.79 (m, 1H), 2.95 (s, 3H), 2.69-2.57 (m, 1H), 2.52-2.32 (m, 2H), 2.05-1.77 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 208.7, 169.9, 153.8, 152.7, 143.6-140.3 (m), 140.3-136.7 (m), 135.8, 134.7, 134.2, 131.5, 130.7, 130.2, 128.8, 128.7, 127.6, 127.2, 126.9, 126.1, 126.0, 125.3, 125.0, 124.6, 120.0, 116.5, 108.0, 106.6 (m), 101.5, 100.1, 95.2, 86.3, 57.2, 56.6, 23.2, 22.9, 22.7, 22.2. ¹⁹F-NMR (377 MHz, CD₂Cl₂) δ [ppm] = -133.70 (br s, 1F), -137.61 (br s, 1F), -153.80 (t, ³J = 21.0 Hz), -161.53 (br s, 1F), -162.63 (br s, 1F). IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2071.4 (Fe(CO)₃), 2021.1 (Fe(CO)₃), 1995.6 (Fe(CO)₃), 1651.4 (C=O), 1592.4, 1524.7, 1493.2, 1258.4, 1241.5, 1198.7, 1148.1, 1097.2, 1077.8, 1033.6, 1012.8, 989.1, 967.4, 921.6, 811.2, 802.1, 746.7, 721.8, 666.61. HRMS (ESI⁺): *m/z* 813.1204 [M+H]⁺, 835.1028 [M+Na]⁺ (calculated for C₄₂H₃₀F₅FeO₈⁺ = 813.1205, C₄₂H₂₉F₅FeO₈Na⁺ = 835.1024).

2.10.4. Complexes (pS,aR)-18 and (pR,aR)-18

Iron complexes (pS,aR)-18 and (pR,aR)-18 were prepared according to general procedure A, starting from diyne **12** (145 mg, 0.236 mmol). (pS,aR)-18 and (pR,aR)-18 were isolated through chromatographic column on silica gel (Et₂O/*n*-hexane 4:1 to 100% Et₂O).

(pS,aR)-18. Yield: 61 mg (0.076 mmol, 32%). M.p. = 196-199 °C (dec.). [α]_D = 18.7 (c = 0.09 in CH₂Cl₂). R_f = 0.30 (SiO₂, EtOAc/*n*-hexane 1:1). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.02-7.96 (m, 2H), 7.92 (s, 1H), 7.88 (d, ³J = 8.1 Hz, 1H), 7.63 (d, ³J = 9.1 Hz, 1H), 7.48-7.41 (m, 1H), 7.39-7.30 (m, 2H), 7.30-7.21 (m, 2H), 7.21-7.15 (m, 1H), 7.12 (d, ³J = 8.2 Hz, 1H), 6.69 (d, ³J = 8.1 Hz, 1H), 6.61 (d, ³J = 8.1 Hz, 1H), 5.11 (s, 2H), 4.58 (d, ²J = 4.9 Hz, 1H), 4.39 (d, ²J = 4.9 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 3.25 (s, 3H), 2.98-2.84 (m, 1H), 2.59 (s, 3H), 2.52-2.42 (m, 1H), 2.37 (ddd, ³J = 12.1 Hz, ³J = ²J = 5.8 Hz, 1H), 2.27 (ddd, ³J = 16.6 Hz, ³J = ²J = 5.2 Hz, 1H), 1.92-1.73 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 210.4, 171.0, 159.7, 157.7, 153.6, 152.8, 136.1, 134.8, 134.6, 131.5, 130.4, 130.3, 130.3, 128.7, 128.3, 127.2, 127.1, 126.6, 126.5, 126.4, 126.3, 125.7, 124.7, 121.2, 117.5, 107.5, 104.8, 104.7, 104.1, 104.1, 99.7, 95.9, 86.3, 75.6, 56.6, 56.2, 56.2, 55.5, 23.2, 23.0, 22.5. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2059.7 (Fe(CO)₃), 2012.3 (Fe(CO)₃), 1988.7 (Fe(CO)₃), 1655.0 (C=O), 1593.0, 1251.0, 1149.4, 1109.2, 1030.5, 1005.5, 721.7. MS (ESI⁺): *m/z* = 783.1885 [M+H]⁺, 805.1707 [M+Na]⁺ (calculated for C₄₄H₃₉FeO₁₀⁺ = 783.1887, C₄₄H₃₈FeO₁₀Na⁺ = 805.1707).

(pR,aR)-18. Yield: 46 mg (0.058 mmol, 25%). M.p. = 239-241 °C (dec.). [α]_D = 95.9 (c = 0.09 in CH₂Cl₂). R_f = 0.12 (SiO₂, EtOAc/*n*-hexane 1:1). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.04-7.96 (m, 2H), 7.93 (s, 1H), 7.91 (d, ³J = 8.2 Hz, 1H), 7.66 (d, ³J = 9.1 Hz, 1H), 7.50-7.42 (m, 1H), 7.42-7.27 (m, 4H), 7.24 (d, ³J = 8.3 Hz, 1H), 7.19 (d, ³J = 8.4 Hz, 1H), 6.70 (d, ³J = 8.4 Hz, 1H), 6.62 (d, ³J = 8.3 Hz, 1H), 5.17 (d, ²J = 7.2 Hz, 1H), 5.09 (d, ²J = 7.2 Hz, 1H), 4.68 (d, ²J = 4.7 Hz, 1H), 4.58 (d, ²J = 4.7 Hz, 1H), 3.95 (s, 3H), 3.70 (s, 3H), 3.25 (s, 3H), 2.86 (ddd, ³J = 17.4 Hz, ³J = ²J = 6.3 Hz, 1H), 2.79 (s, 3H), 2.54-2.35 (m, 2H), 2.26 (ddd, ³J = 17.2 Hz, ³J = ²J = 6.3 Hz, 1H), 1.95-1.74 (m, 4H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 210.4, 171.1, 159.6, 157.7, 153.9, 152.3, 136.3, 134.4, 134.4, 131.6, 130.4, 130.1, 128.7, 128.6, 127.1, 127.1, 126.8, 126.4, 126.0, 125.8, 125.5, 124.4, 120.3, 116.4, 107.4, 105.3, 104.8, 104.0, 103.9, 99.9, 95.2, 86.0, 75.6, 57.0, 56.6, 56.2, 55.5, 23.1, 23.1, 23.0, 22.6. IR (nujol): $\tilde{\nu}$ [cm⁻¹] = 2060.7 (Fe(CO)₃), 2000.4 (Fe(CO)₃), 1991.4 (Fe(CO)₃), 1733.1, 1636.0 (C=O), 1253.8, 1244.9, 1162.0, 1150.3, 1106.2, 1058.6, 1031.8, 1012.9, 989.8, 964.9, 932.7, 721.0. HRMS (ESI⁺): *m/z* 783.1885 [M+H]⁺, 805.1708 [M+Na]⁺ (calculated for C₄₄H₃₉FeO₁₀⁺ = 783.1887, C₄₄H₃₈FeO₁₀Na⁺ = 805.1707).

2.10.4. Complexes (pR,aR)-19 and (pS,aR)-19

Iron complexes (pR,aR)-19 and (pS,aR)-19 were prepared according to general procedure A, starting from diyne **14** (168 mg, 0.360 mmol). The reaction was conducted at 85 °C. (pR,aR)-19 and (pS,aR)-19 were isolated through chromatographic column on silica gel (EtOAc/*n*-hexane 7:3 to 4:1) as yellow solids.

(pR,aR)-19. Yield: 59 mg (0.093 mmol, 26%). M.p. = 190-193 °C (dec.). [α]_D = -20.2 (c = 0.20 in CH₂Cl₂). R_f = 0.37 (SiO₂, EtOAc/*n*-hexane 7:3). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.39 (s, 1H), 8.03-7.94 (m, 2H), 7.90 (d, ³J = 8.1 Hz, 1H), 7.61 (d, ³J = 9.1 Hz, 1H), 7.44 (t, ³J = 7.5 Hz, 1H), 7.37 (t, ³J = 7.4 Hz, 1H), 7.29-7.22 (m, 2H), 7.13 (d, ³J = 8.4 Hz, 1H), 7.09 (d, ³J = 8.5 Hz, 1H), 5.10-5.02 (m, 3H), 4.80 (d, ²J = 13.4 Hz, 1H), 4.76 (s, 2H), 4.47 (d, ²J = 4.9 Hz, 1H), 4.35 (s, 1H), 4.23 (d, ²J = 4.9 Hz, 1H), 3.21 (s, 3H), 2.59 (s, 3H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 208.5, 173.1, 153.8, 151.3, 134.9, 134.7, 134.6, 134.3, 131.3, 130.6, 130.3, 128.9, 128.6, 127.6, 127.3, 126.3, 126.2, 126.1, 124.7, 124.5, 120.6, 117.6, 107.4, 103.9, 99.8, 95.9, 80.1, 69.9, 67.8, 57.4, 57.2, 56.2. HRMS (ESI⁺): *m/z* 635.0999 [M+H]⁺, 657.0823 [M+Na]⁺ (calculated for C₃₄H₂₇FeO₉⁺ = 635.0999, C₃₄H₂₆FeO₉Na⁺ = 657.0818).

(pS,aR)-19. Yield: 42 mg (0.066 mmol, 18%). M.p. = 130-132 °C (dec.). [α]_D = 119.6 (c = 0.13 in CH₂Cl₂). R_f = 0.24 (SiO₂, EtOAc/*n*-hexane 7:3). ¹H-NMR (400 MHz, CD₂Cl₂) δ [ppm] = 8.41 (s, 1H), 8.01 (d, ³J = 8.7 Hz, 1H), 7.97 (d, ³J = 8.2 Hz, 1H), 7.90 (d, ³J = 8.1 Hz, 1H), 7.65 (d, ³J = 8.6 Hz, 1H), 7.45 (t, ³J = 7.3 Hz, 1H), 7.38 (t, ³J = 7.1 Hz, 1H), 7.34-7.21 (m, 3H), 7.13 (d, ³J = 8.5 Hz, 1H), 5.20-5.08 (m, 2H), 4.97 (d, ²J = 13.6 Hz, 1H), 4.76 (d, ²J = 13.7 Hz, 1H), 4.74 (s, 2H), 4.67 (d, ²J = 4.9 Hz, 1H), 4.42 (d, ²J = 4.9 Hz, 1H), 4.36 (s, 1H), 3.24 (s, 3H), 2.73 (s, 3H). ¹³C-NMR (100 MHz, CD₂Cl₂) δ [ppm] = 208.6, 173.1, 153.7, 151.1, 134.9,

134.2, 134.1, 130.8, 130.2, 128.9, 128.6, 127.5, 127.3, 126.4, 126.2, 126.0, 125.2, 124.7, 124.5, 119.8, 116.1, 107.7, 103.9, 100.1, 95.2, 79.9, 69.9, 67.8, 57.5, 57.4, 56.7. HRMS (ESI+): m/z 635.1002 [M+H]⁺, 657.0824 [M+Na]⁺ (calculated for C₃₄H₂₇FeO₉⁺ = 635.0999, C₃₄H₂₆FeO₉Na⁺ = 657.0818).

2.11. General procedure for the AH of ketones

The pre-catalyst (0.010 mmol, 0.02 eq) was weighted in a 3 mL glass vial. A magnetic stirring bar was added, and the vial was charged in an autoclave. After purging the system with argon, the solvent (0.35 mL) was added. Me₃NO (1.5 mg, 0.020 mmol, 0.04 eq) was added and the mixture was stirred for 5 minutes under argon. The ketone (0.500 mmol, 1 eq) was then added. The autoclave was sealed and, after purging 2 times with hydrogen, it was charged with H₂ (30 bar). The reaction was heated to 70 °C. After 18 h the reaction was allowed to cool to rt. Hydrogen was removed, and the reaction mixture was filtered through celite, rinsing with AcOEt/petroleum ether 1:1. Conversion was evaluated through ¹H-NMR analysis and chiral GC analysis. Enantiomeric excesses were evaluated through GC analysis with a chiral column. The absolute configurations of the alcohol products was determined by comparison with literature data.

1-Phenylethanol (P1)

Conversion and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 95 °C for 20 min. $t_{\text{substrate}}$ = 4.9 min; t_R = 8.8 min; t_S = 11.0 min.^[5a]

1-Phenylpropan-1-ol (P2)

Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen programmed flow: 42 mL/min; oven temperature: 95 °C for 20 min. $t_{\text{substrate}}$ = 7.8 min; t_R = 11.5 min; t_S = 12.6 min.^[5a]

1-(Naphthalen-2-yl)ethan-1-ol (P3)

Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 150 °C for 20 min. $t_{\text{substrate}}$ = 8.3 min; t_R = 12.4 min; t_S = 13.3 min.^[5a]

1-(4-(Trifluoromethyl)phenyl)ethan-1-ol (P4)

Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 90 °C; 1 °C/min gradient; 100 °C; 0.5 °C/min gradient; 110 °C for 5 min. $t_{\text{substrate}}$ = 8.4 min; t_R = 19.0 min; t_S = 20.6 min.^[5a]

1-(4-Methoxyphenyl)ethan-1-ol (P5)

Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 110 °C for 10 min; 30 °C/min gradient; 120 °C for 10 min; 30 °C/min gradient; 130 °C for 10 min. $t_{\text{substrate}}$ = 16.6 min; t_R = 16.3 min; t_S = 18.7 min.^[5a]

2,2,2-Trifluoro-1-phenylethanol (P6)

Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 100 °C for 20 min. $t_{\text{substrate}}$ = 1.8 min; t_S = 7.8 min; t_R = 8.5 min.^[6]

1,2,3,4-Tetrahydronaphthalen-2-ol (P7)

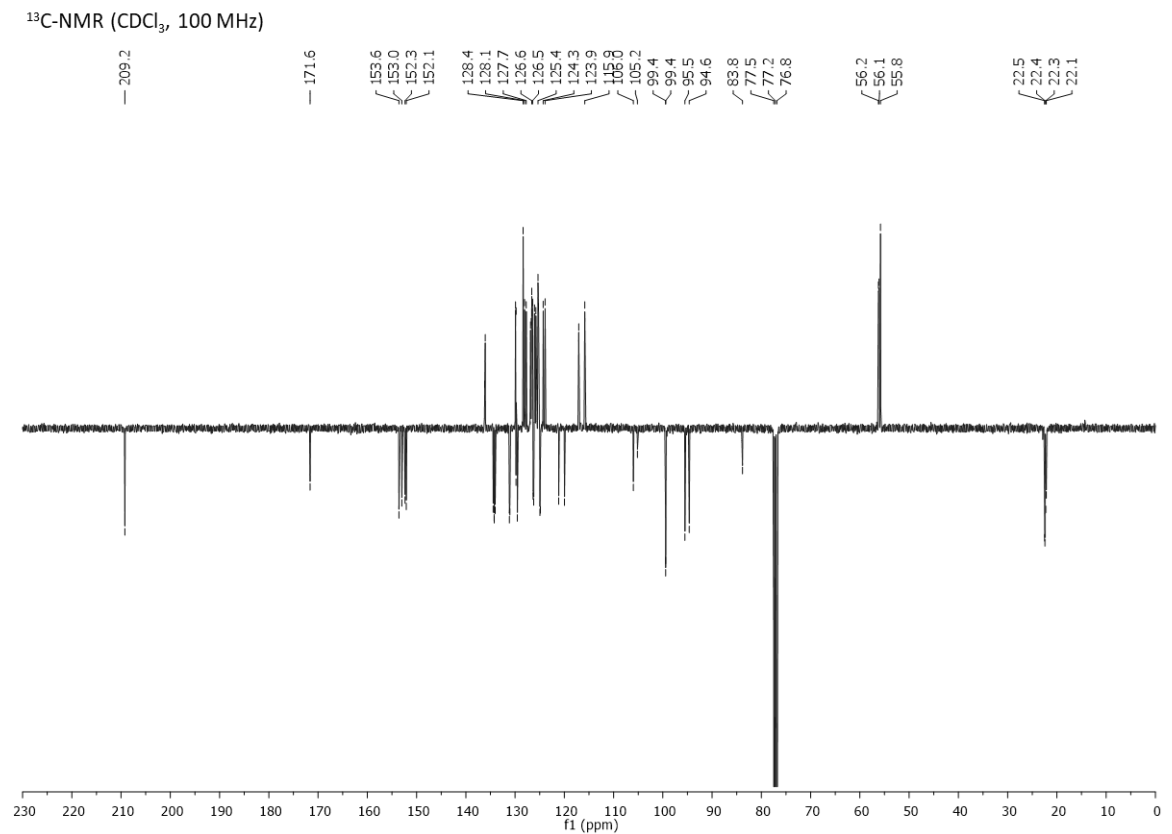
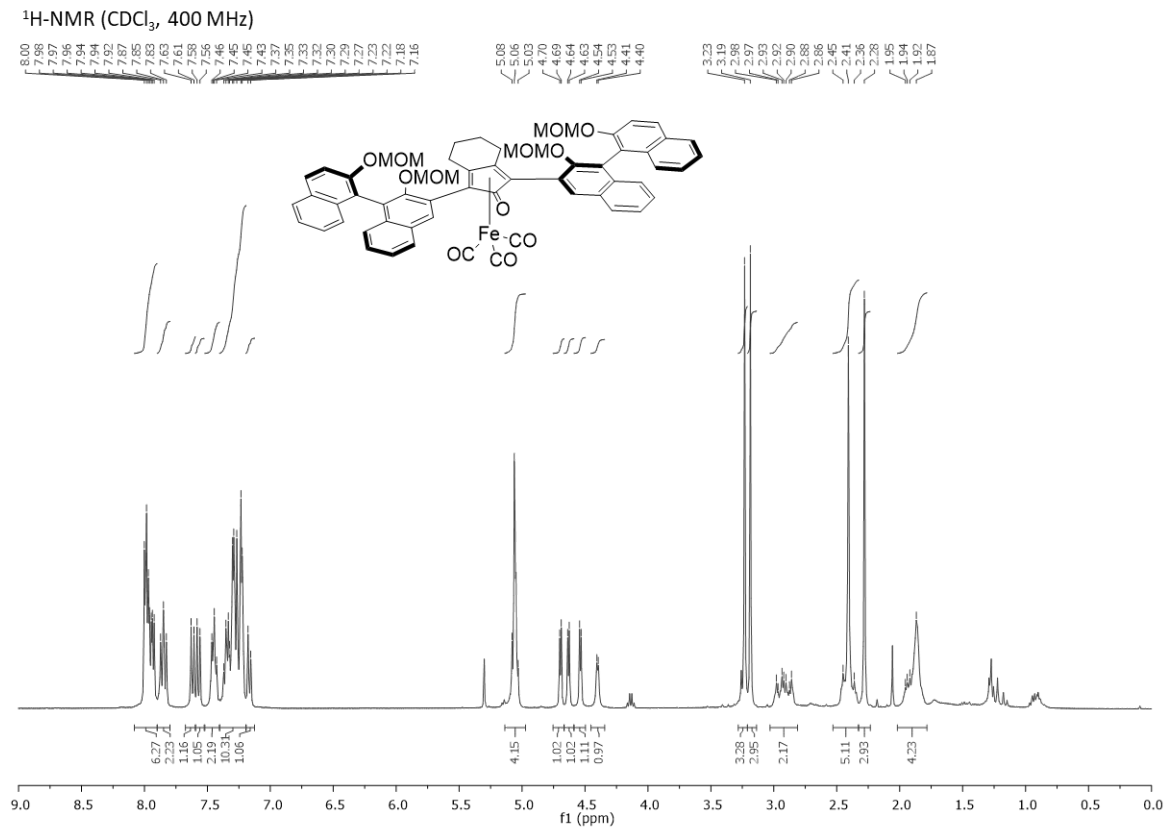
Conversions and ee's were determined via chiral GC analysis. Column: MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 120 °C for 40 min. t_R = 17.7 min; t_S = 18.1 min; $t_{\text{substrate}}$ = 44 min.^[5a]

3,3-Dimethylbutan-2-ol (P8)

Conversion was determined via ¹H-NMR analysis. ee's were determined via chiral GC analysis. MEGA-DEX DAC Beta, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 mm; diameter: 0.25 mm; length: 25 m; carrier: hydrogen; programmed flow: 42 mL/min; oven temperature: 40 °C; 2 °C/min gradient; 100 °C. t_S = 6.8 min; t_R = 8.0 min; $t_{\text{substrate}}$ = 8.9 min.^[5a] Absolute configurations were assigned by comparing the sign of optical rotation with literature data ($[\alpha_D^{20}] = +0.0496 \pm 0.0048$, $c = 0.25$ in CHCl₃ at $T = 27.8$ °C).^[7]

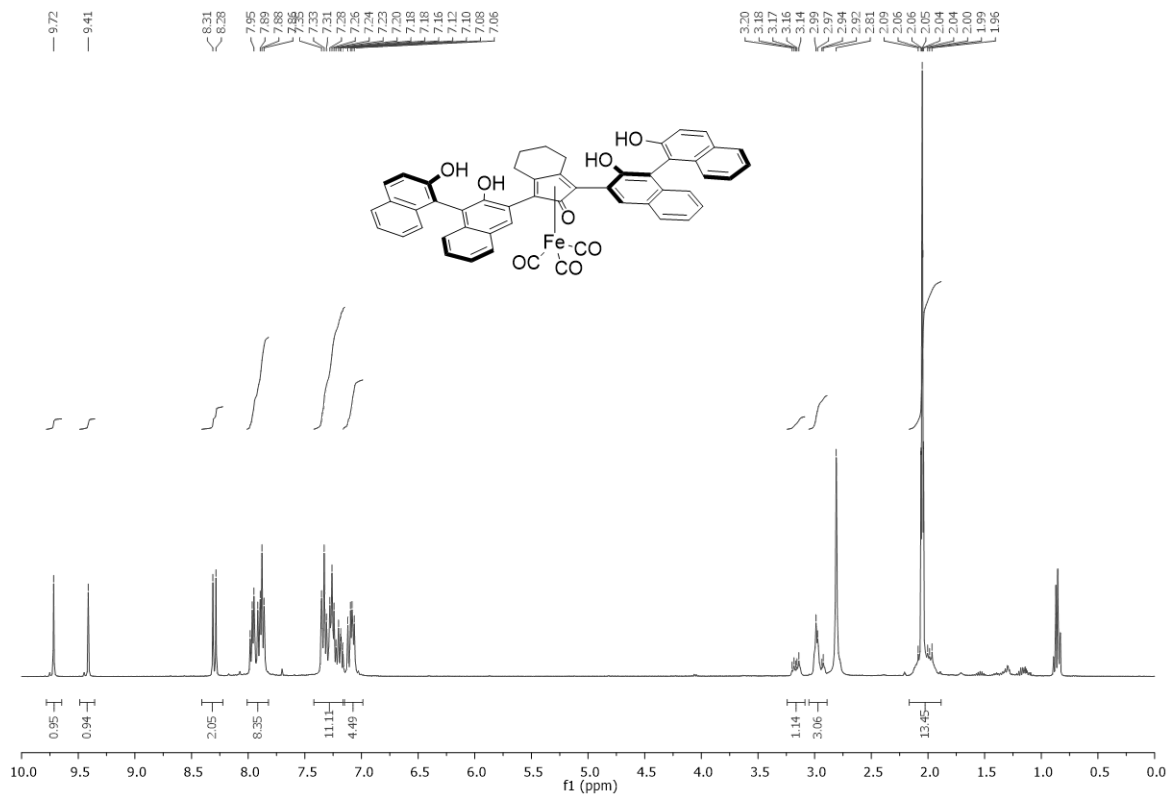
3. NMR Spectra

3.1. Complex 1a

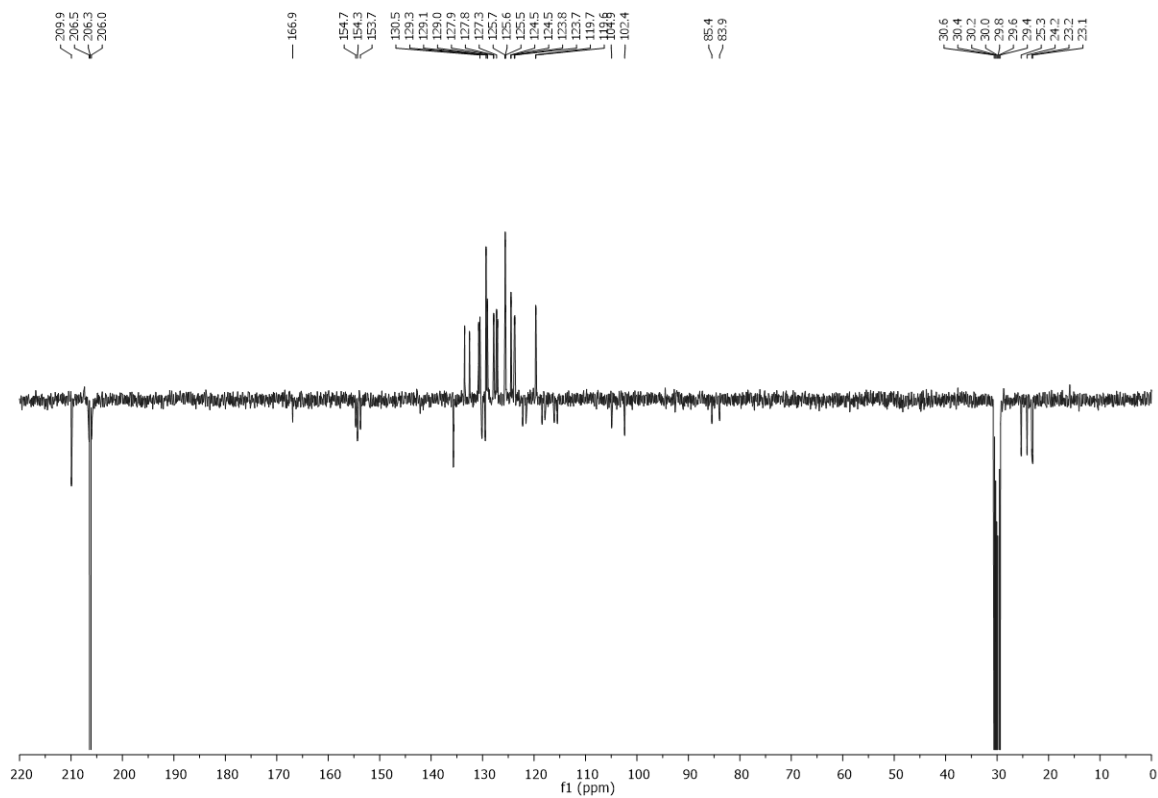


3.2. Complex 1b

$^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{CO}$, 400 MHz]

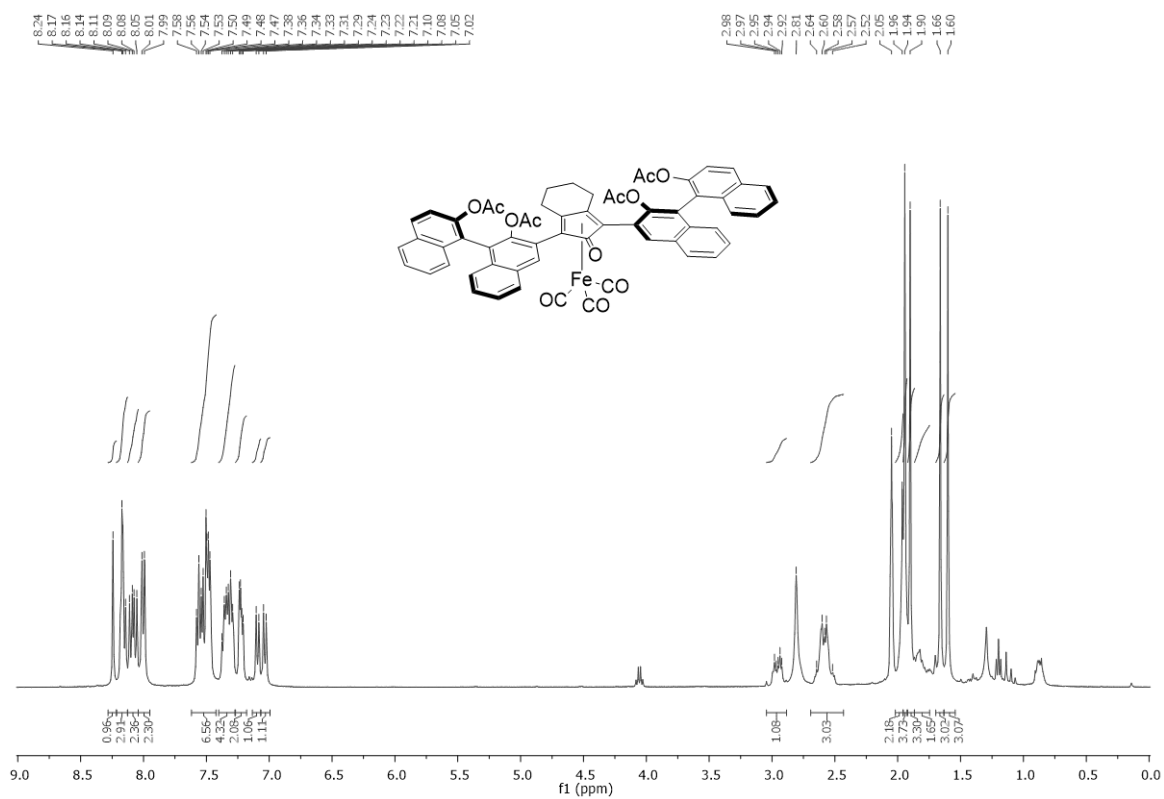


$^{13}\text{C-NMR}$ [$(\text{CD}_3)_2\text{CO}$, 100 MHz]

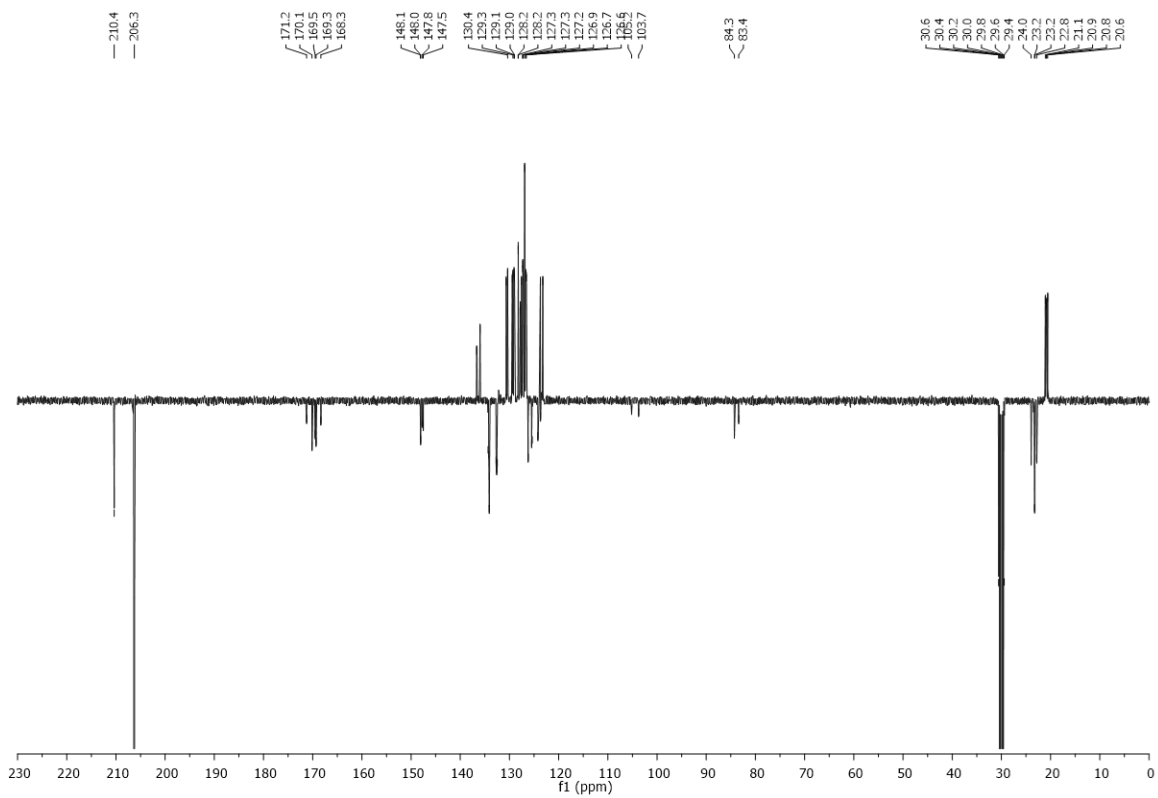


3.3. Complex 1c

$^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{CO}$, 400 MHz]

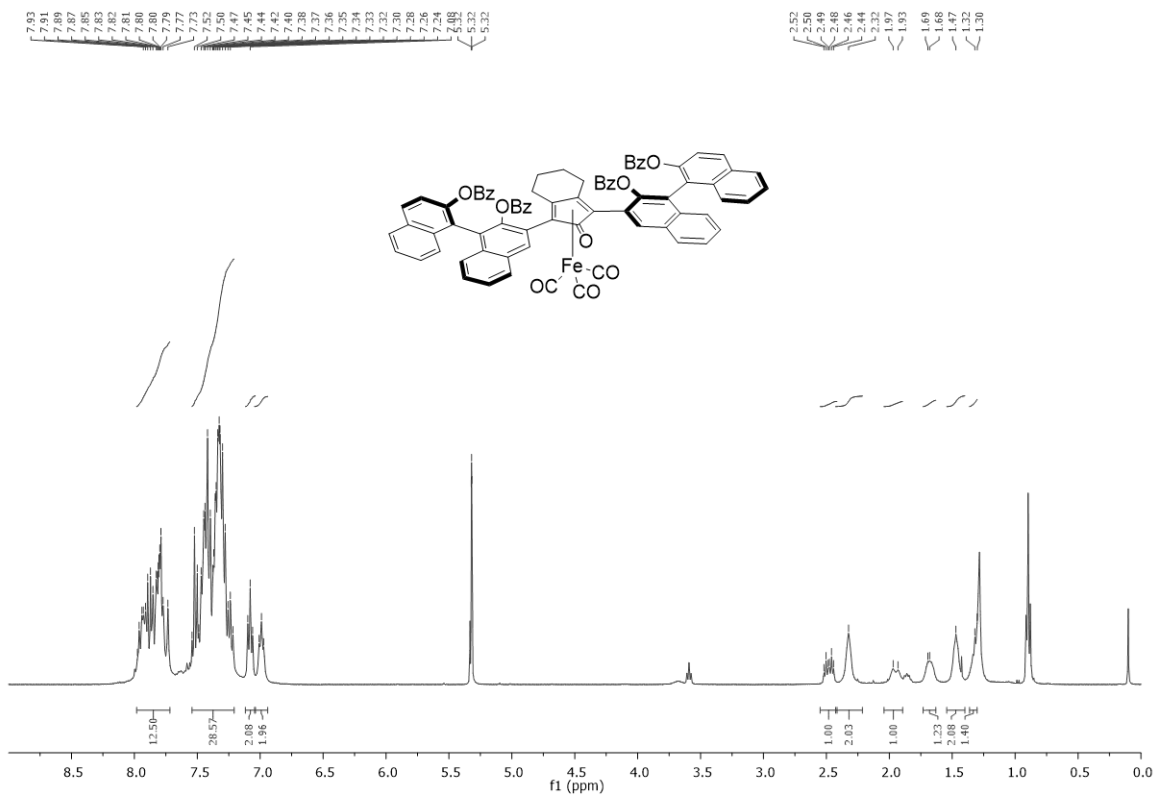


$^{13}\text{C-NMR}$ [$(\text{CD}_3)_2\text{CO}$, 100 MHz]

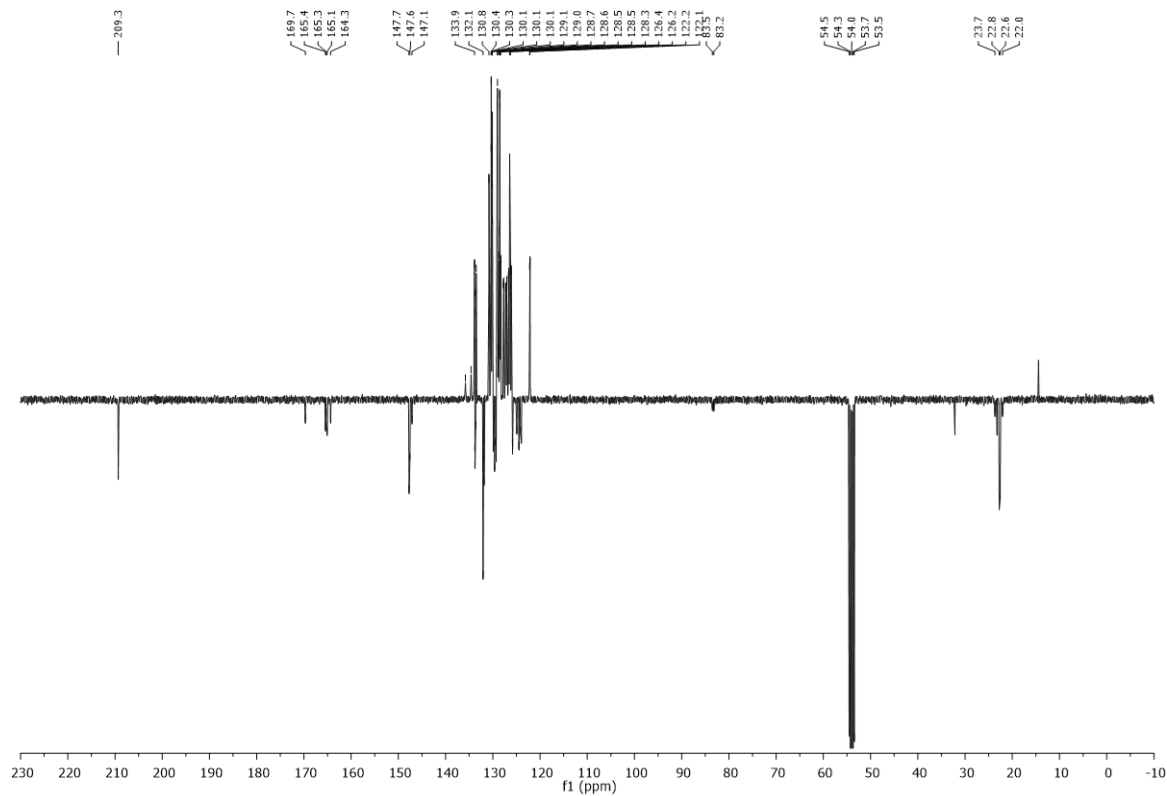


3.4. Complex 1d

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

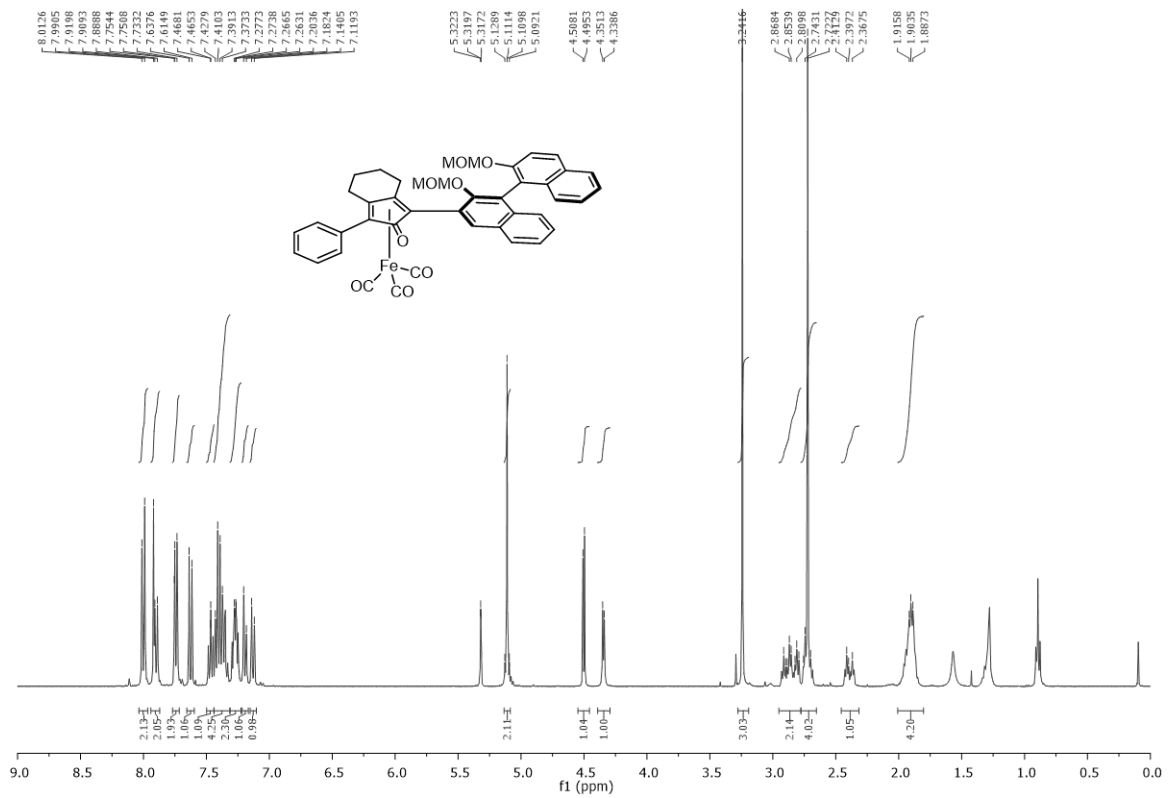


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

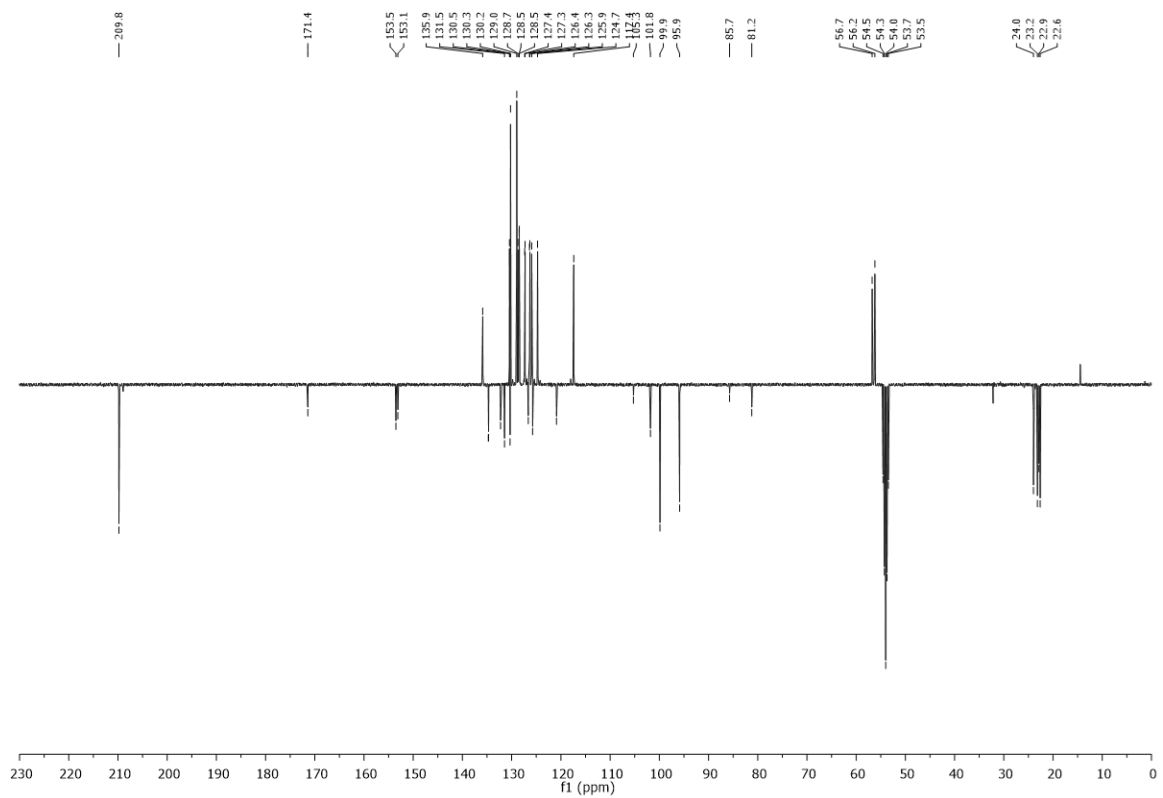


3.5. Complex (pR,aR)-15

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

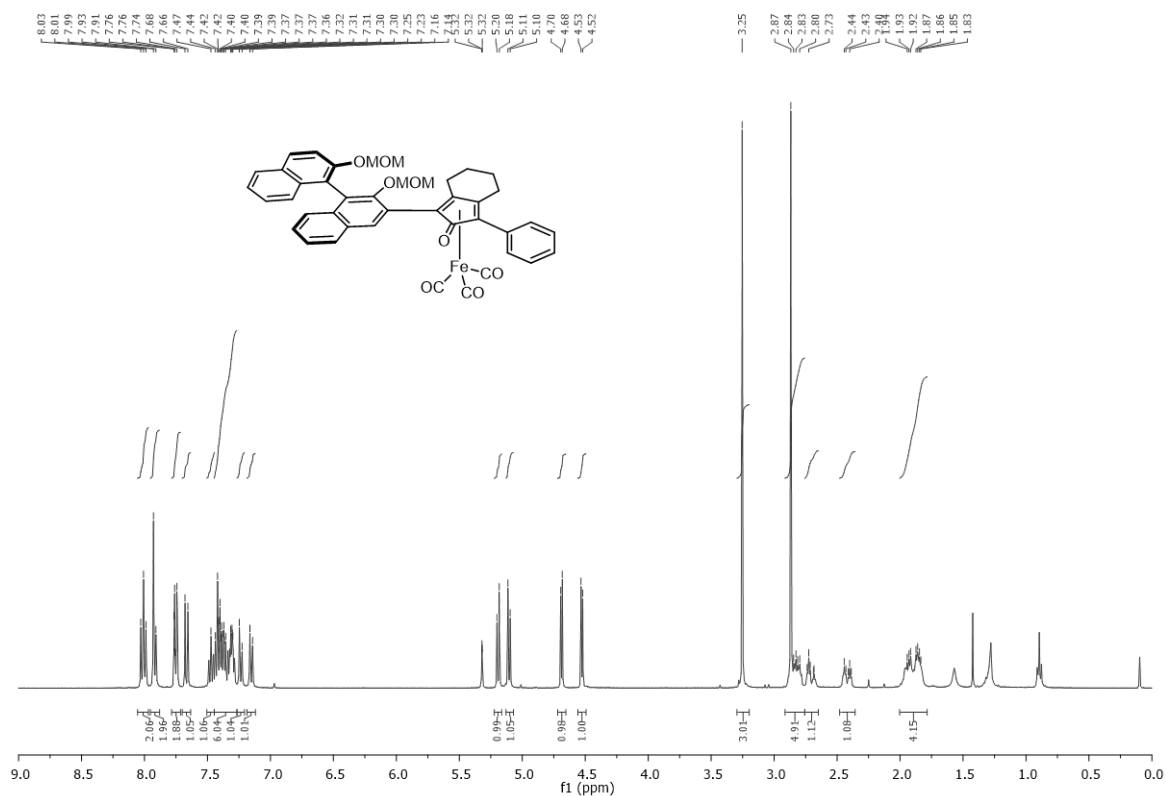


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

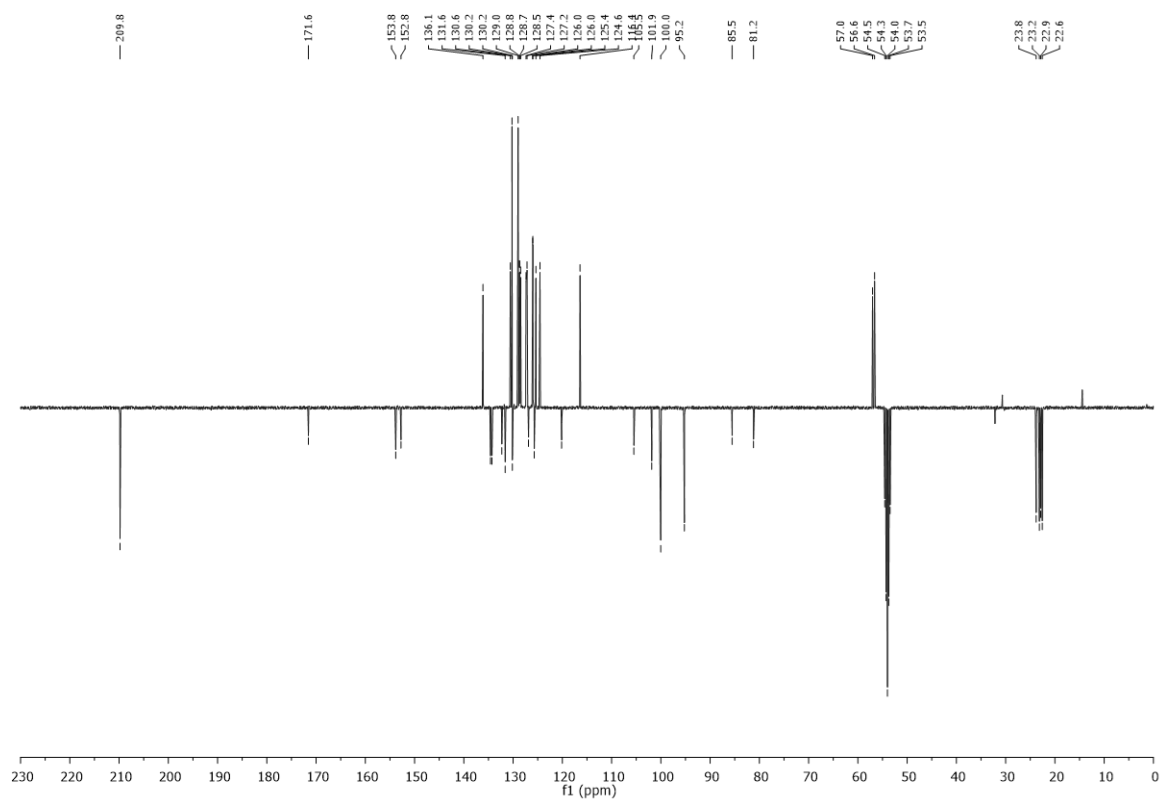


3.6. Complex (pS,aR)-15

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

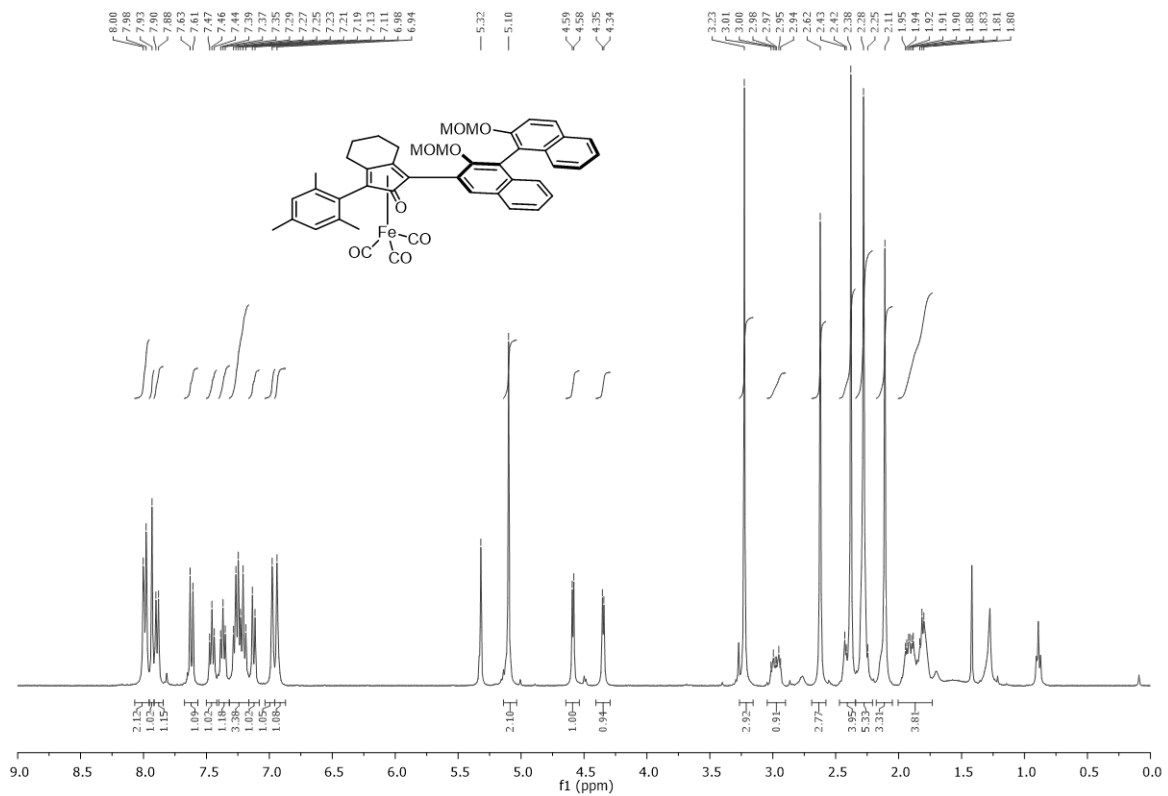


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

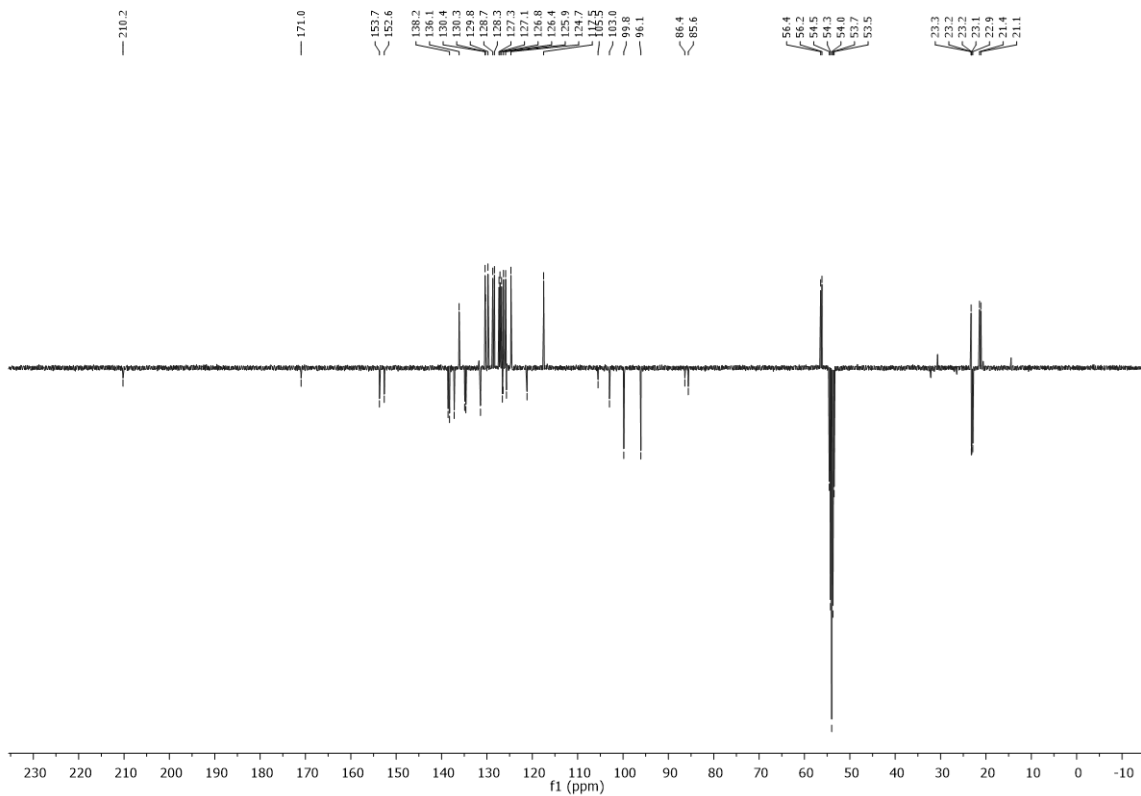


3.7. Complex (pR,aR)-16

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

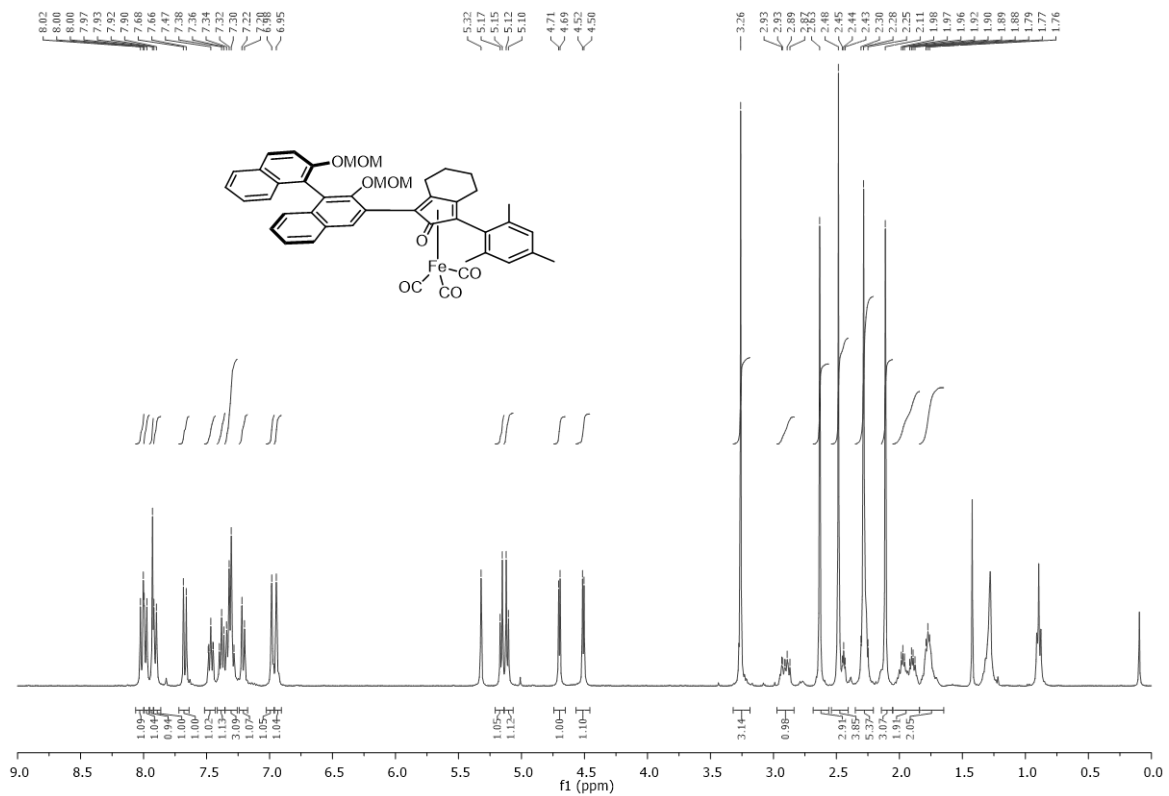


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

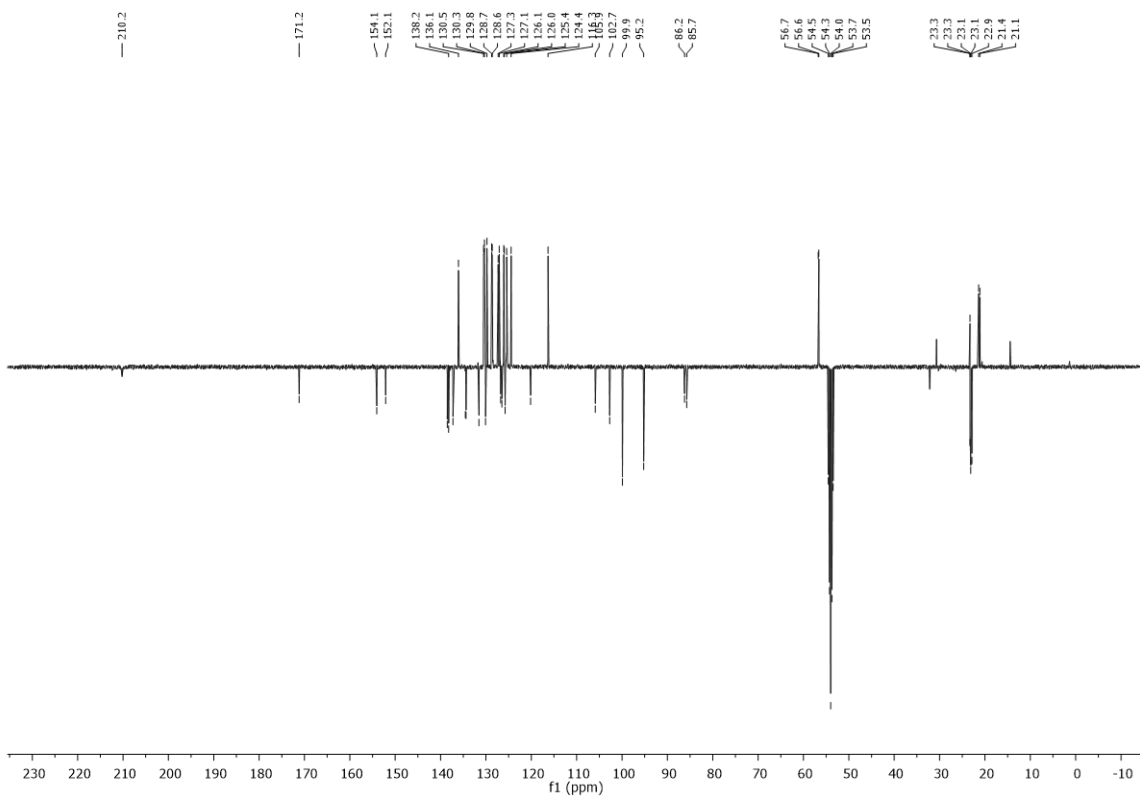


3.8. Complex (pS,aR)-16

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

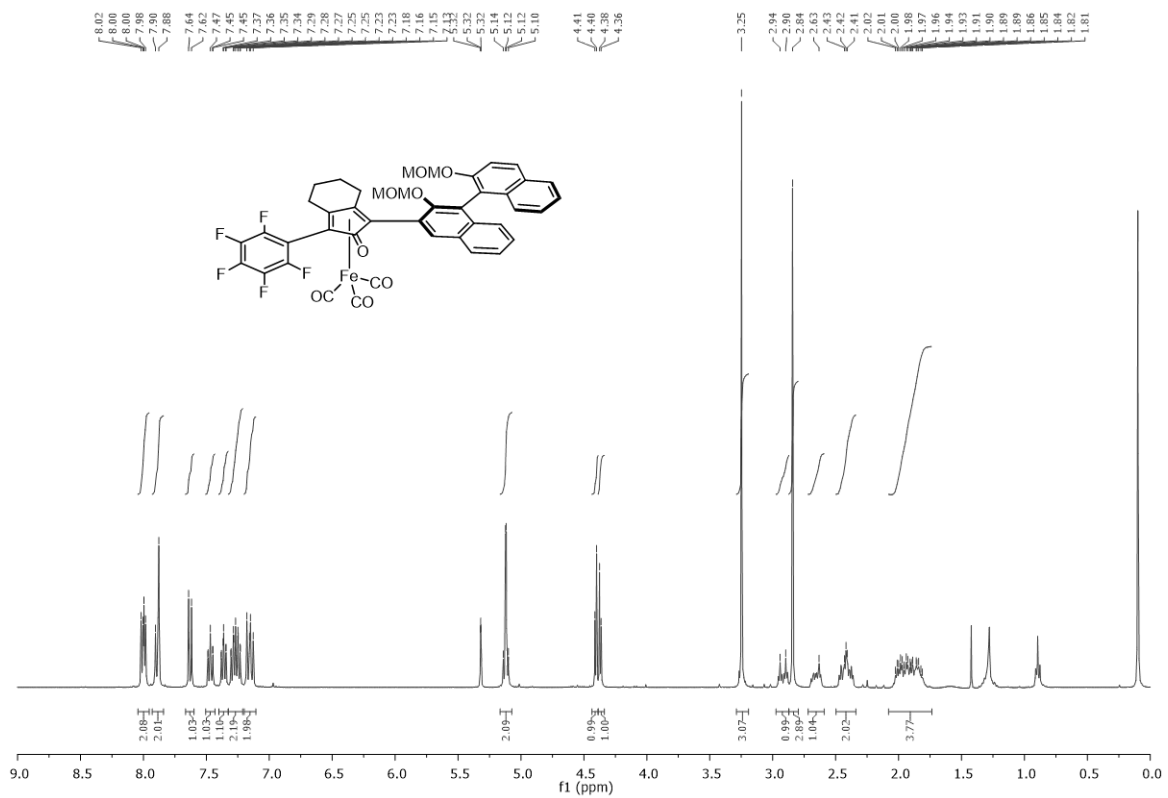


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

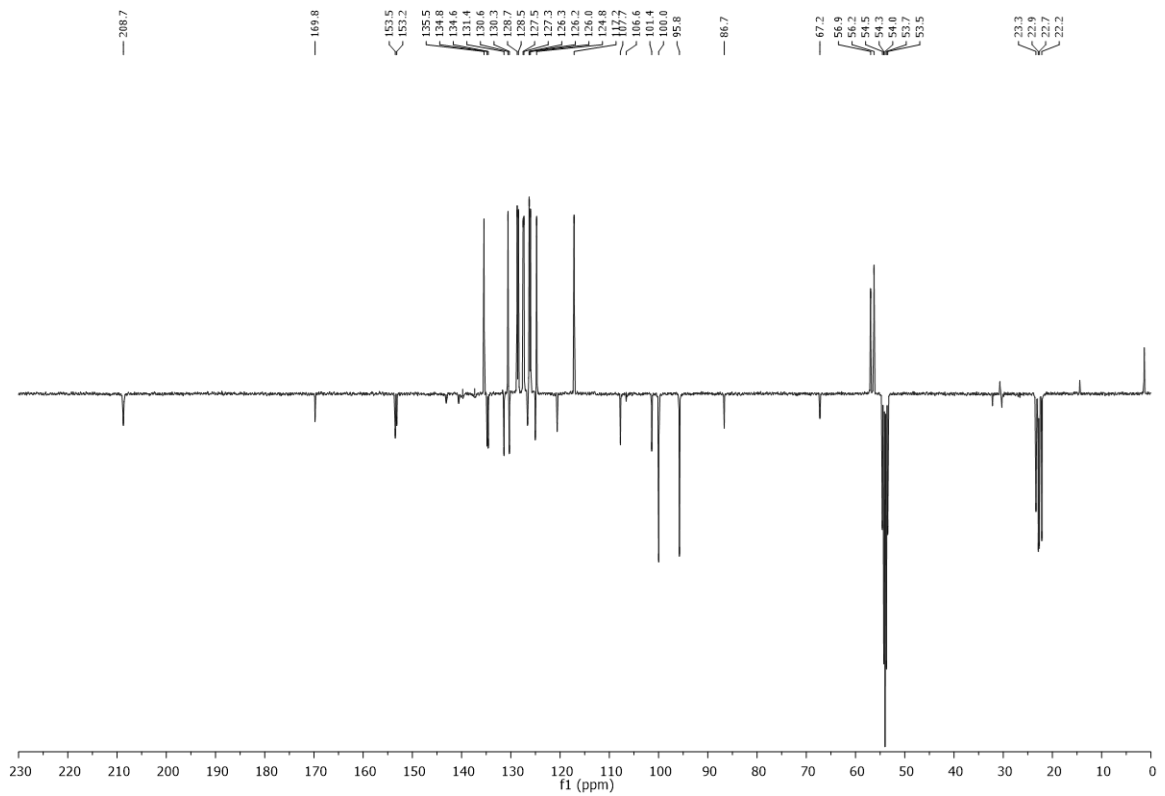


3.9. Complex (pS,aR)-17

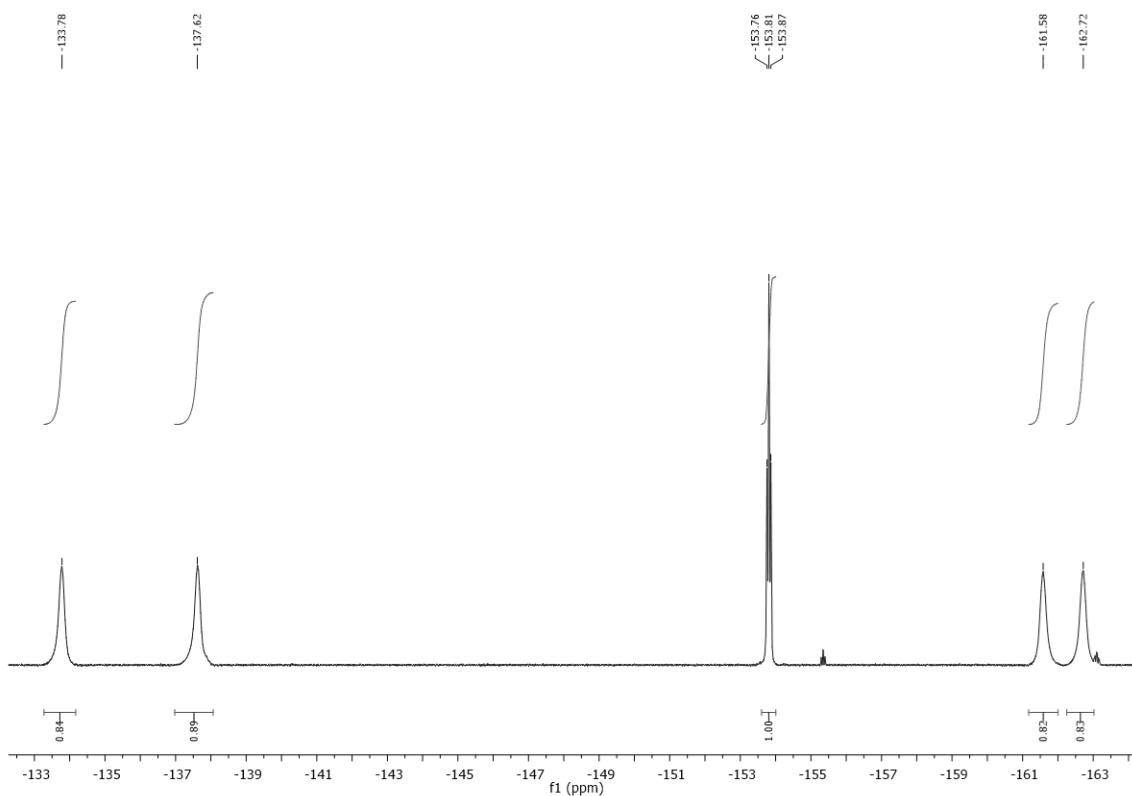
$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)



$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

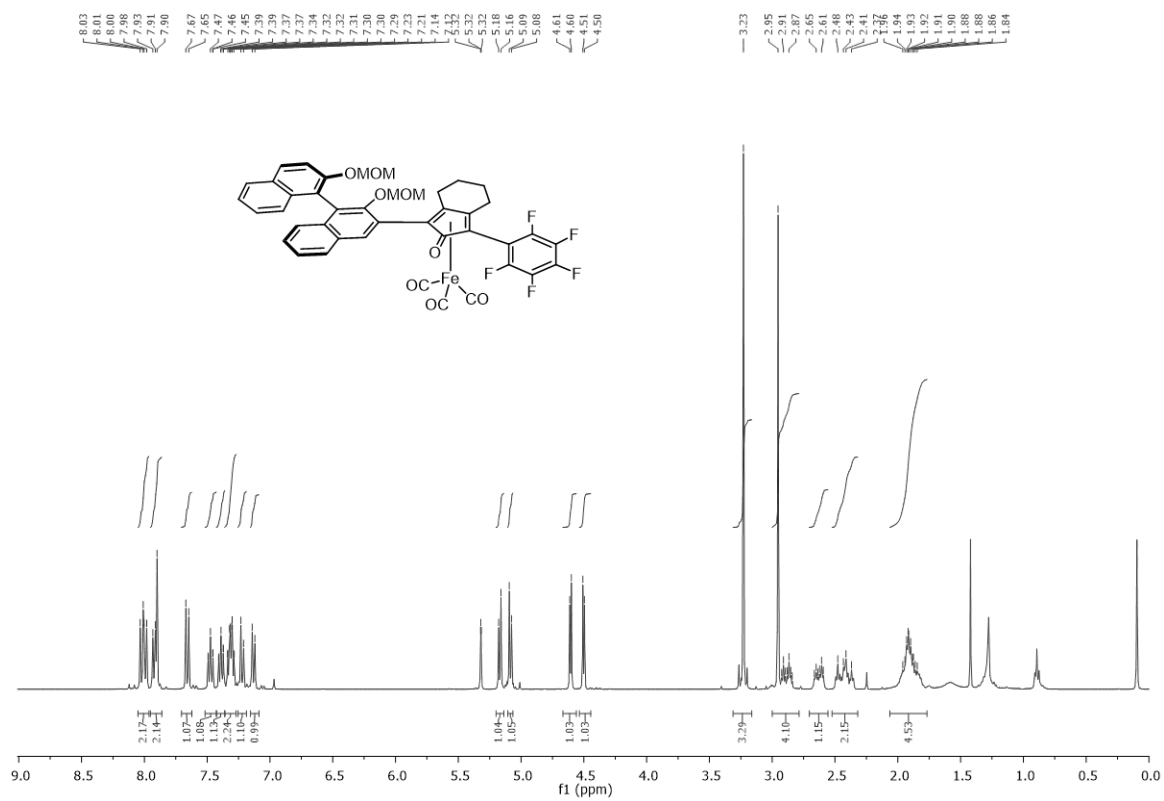


^{19}F -NMR (CD_2Cl_2 , 377 MHz)

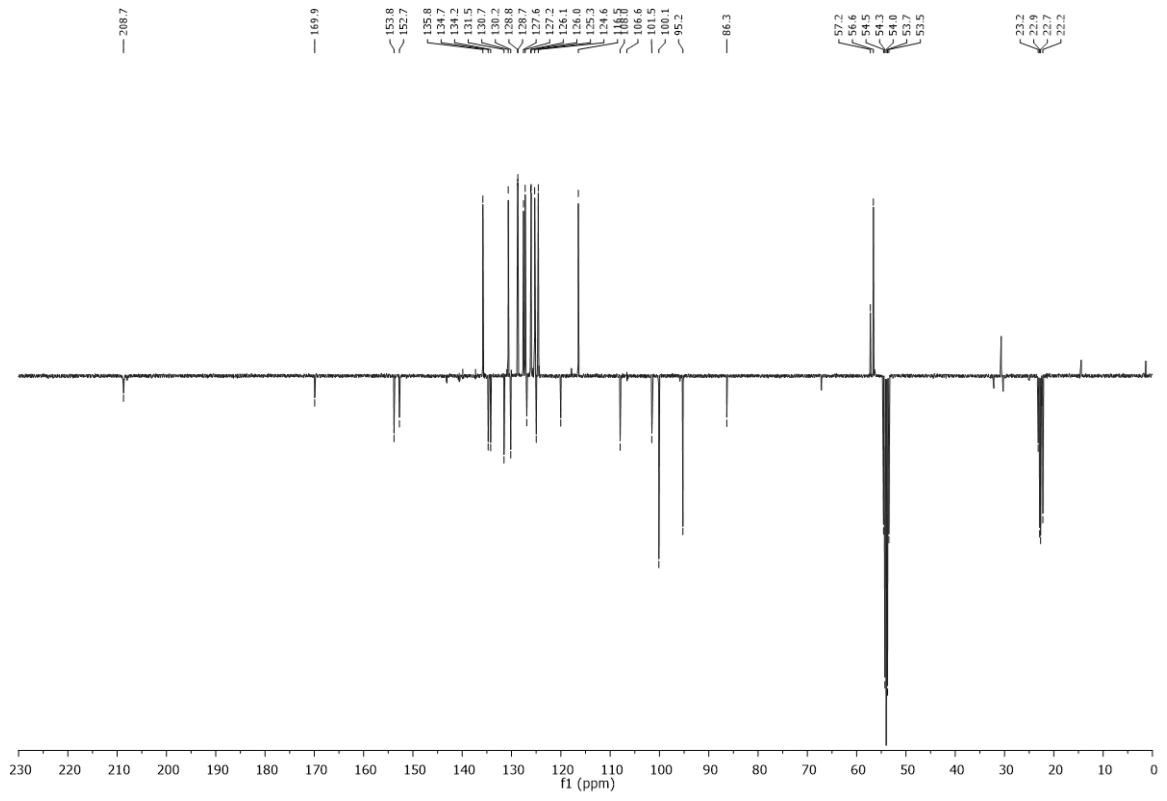


3.10. Complex (pR,aR)-17

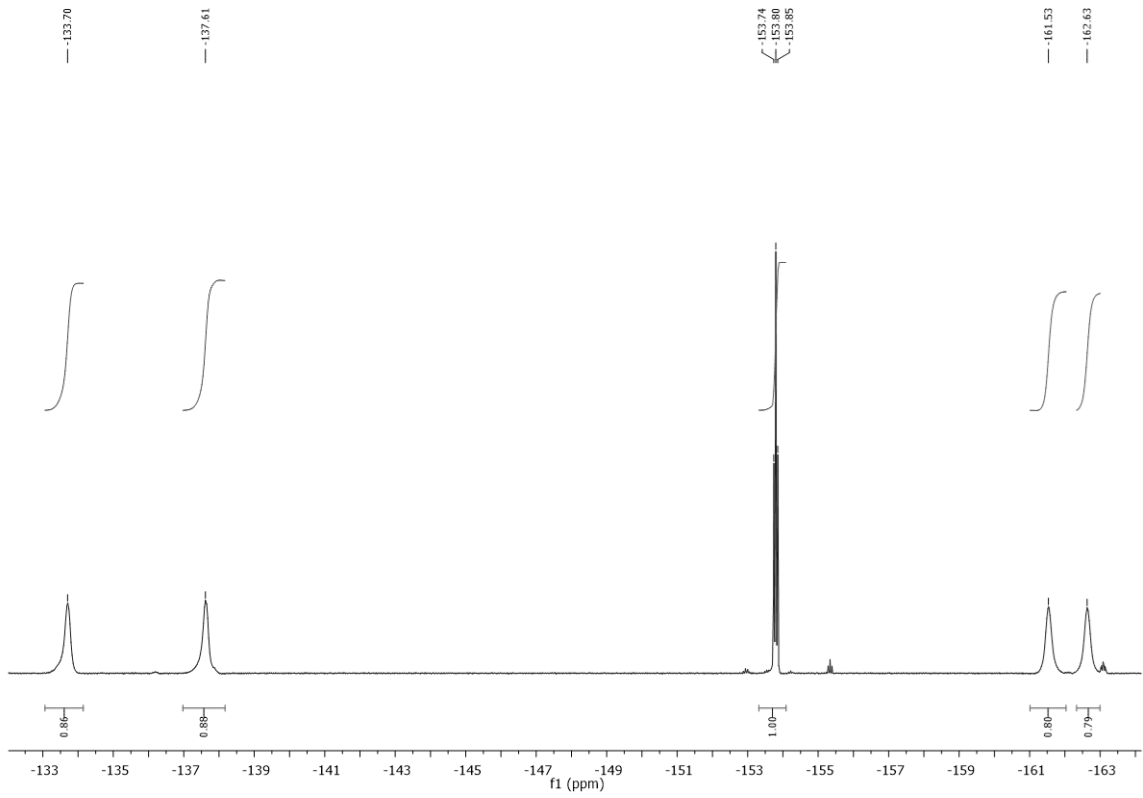
^1H -NMR (CD_2Cl_2 , 400 MHz)



¹³C-NMR (CD₂Cl₂, 100 MHz)

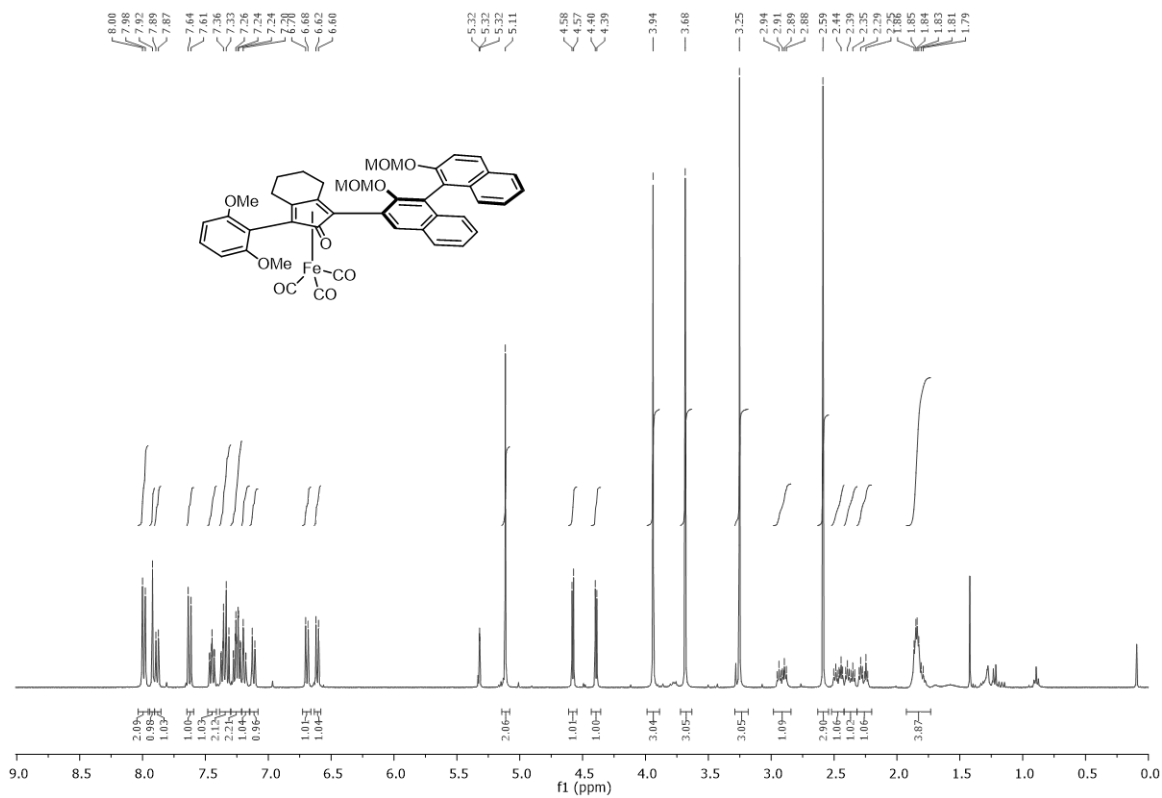


¹⁹F-NMR (CD₂Cl₂, 377 MHz)

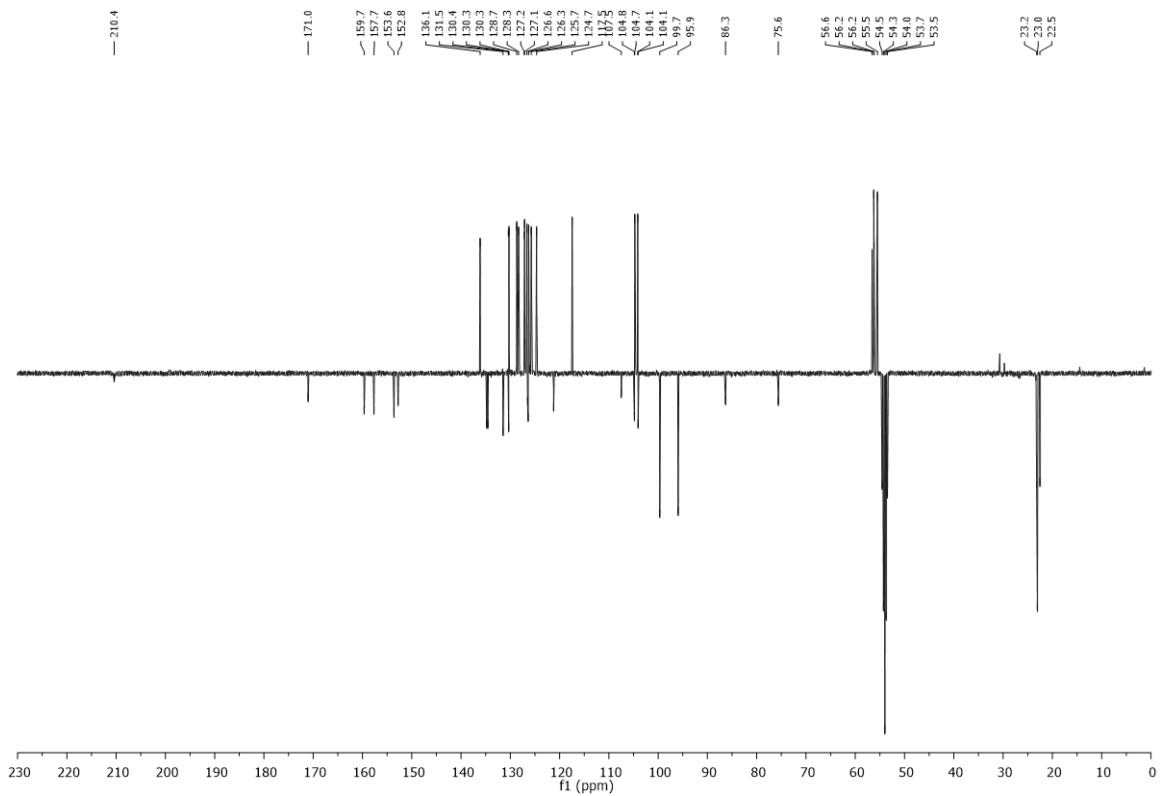


3.11. Complex (pS,aR)-18

¹H-NMR (CD₂Cl₂, 400 MHz)

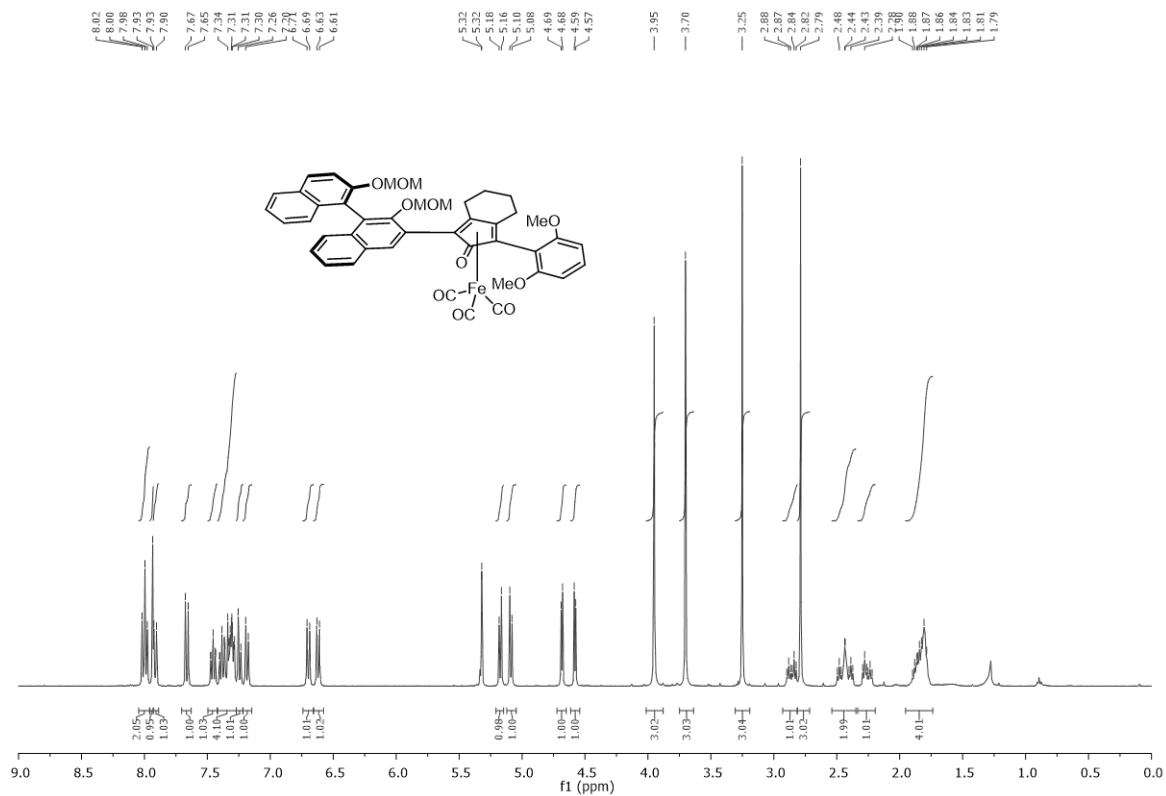


¹³C-NMR (CD₂Cl₂, 100 MHz)

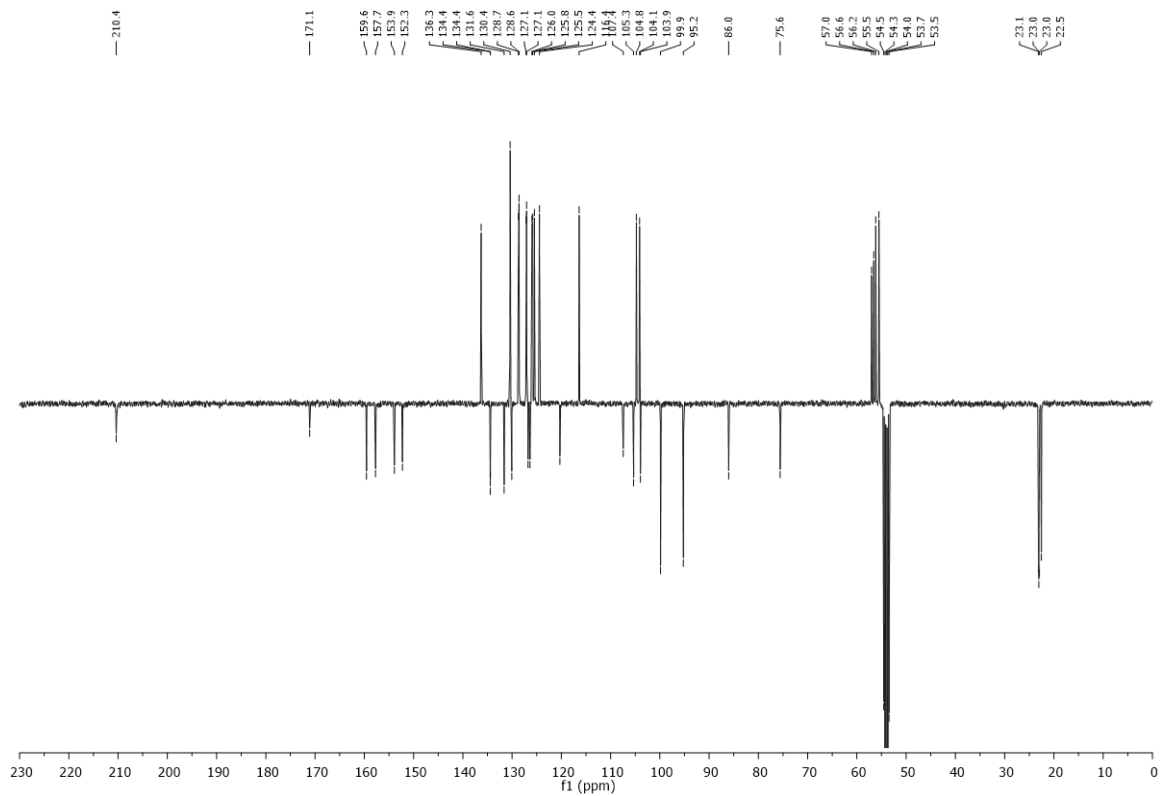


3.12. Complex (pR,aR)-18

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)

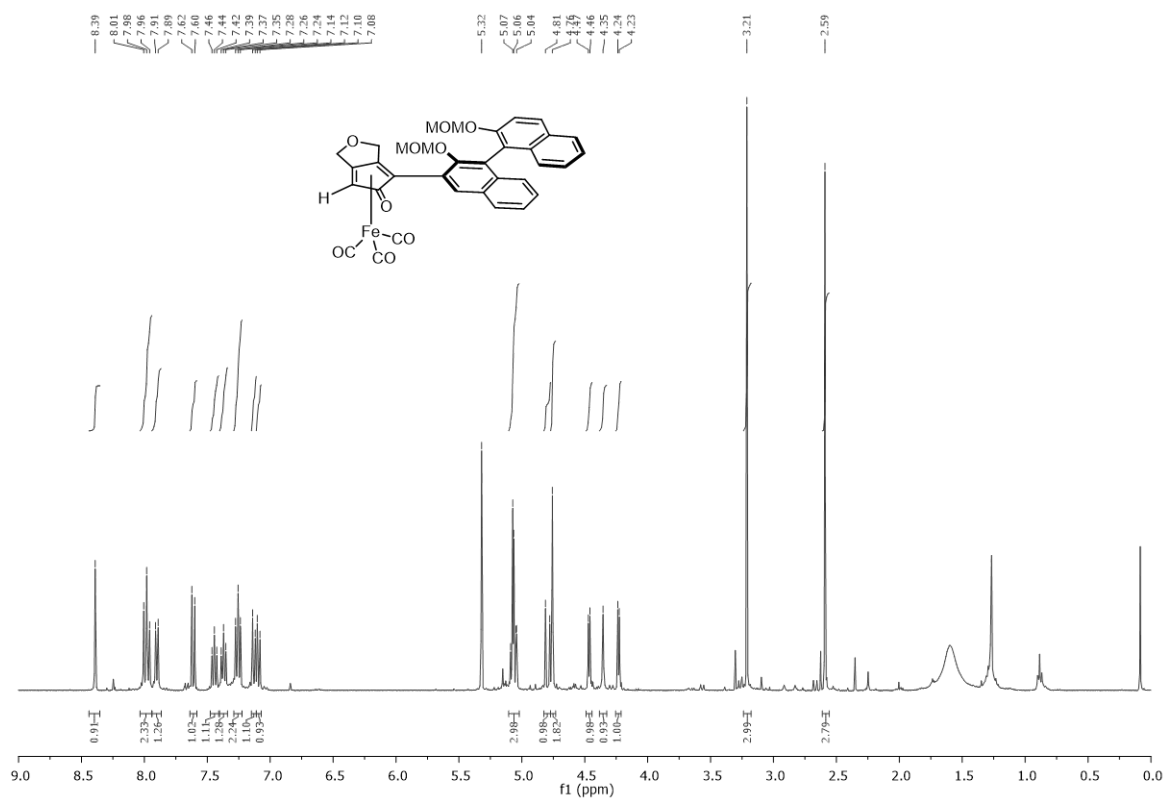


$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)

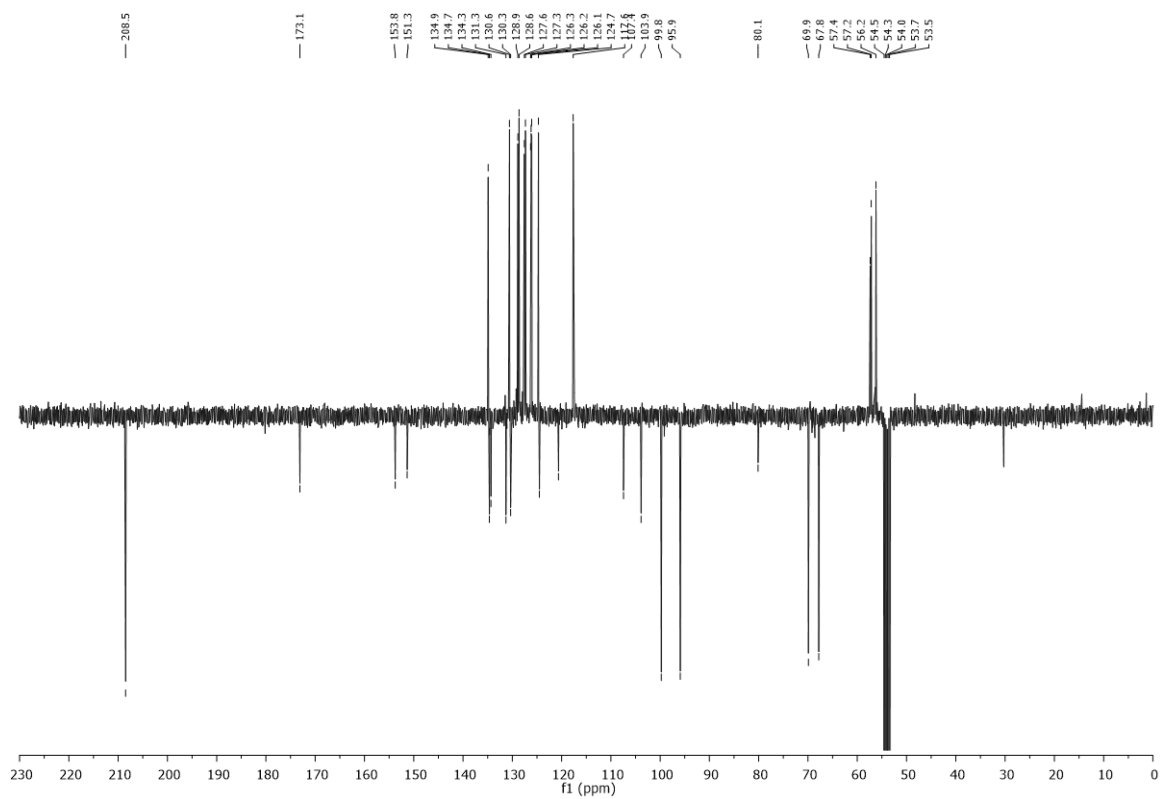


3.13. Complex (p*R*,a*R*)-19

¹H-NMR (CD₂Cl₂, 400 MHz)

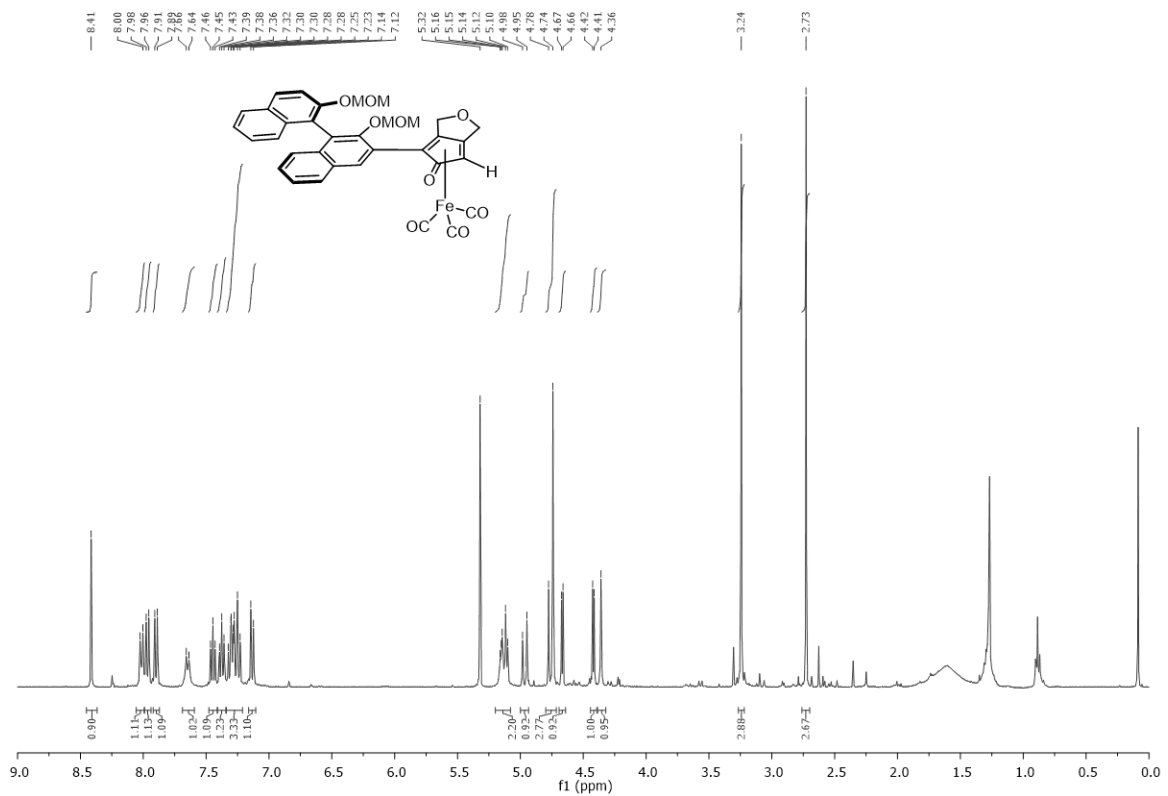


¹³C-NMR (CD₂Cl₂, 100 MHz)

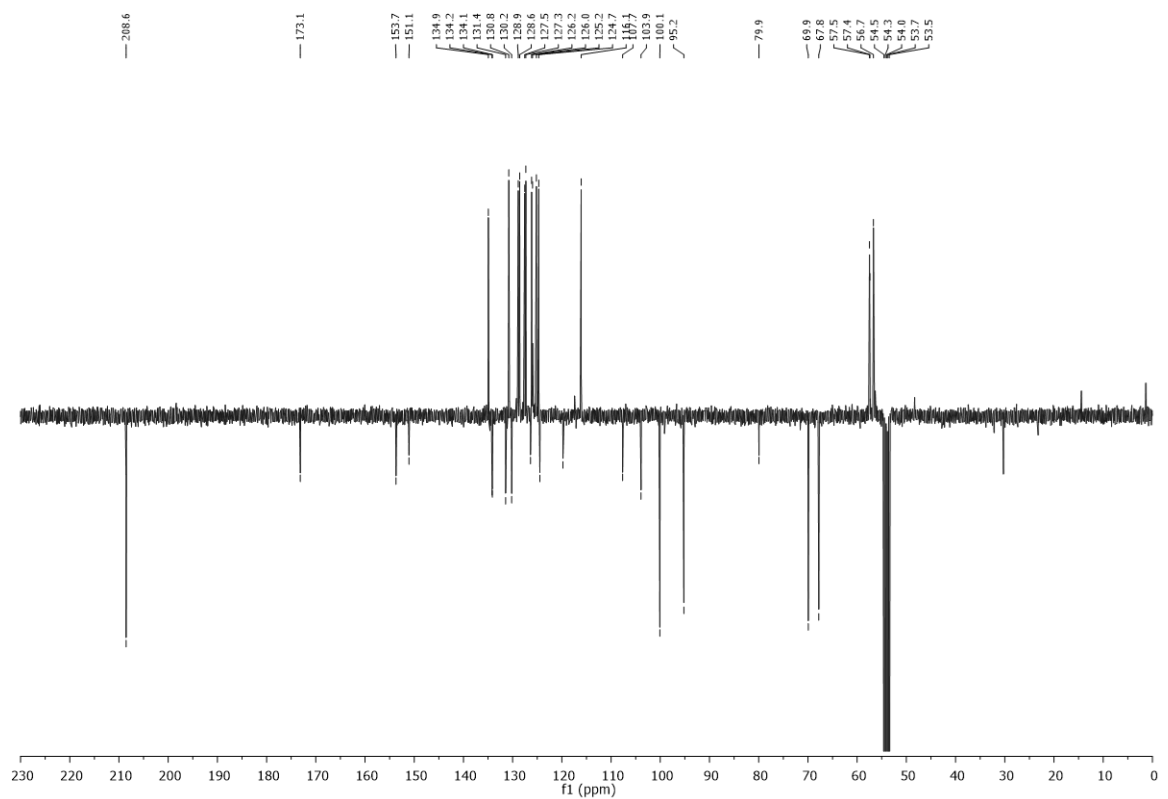


3.14. Complex (pS,aR)-19

$^1\text{H-NMR}$ (CD_2Cl_2 , 400 MHz)



$^{13}\text{C-NMR}$ (CD_2Cl_2 , 100 MHz)



4. X-ray Crystallographic data

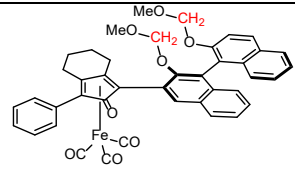
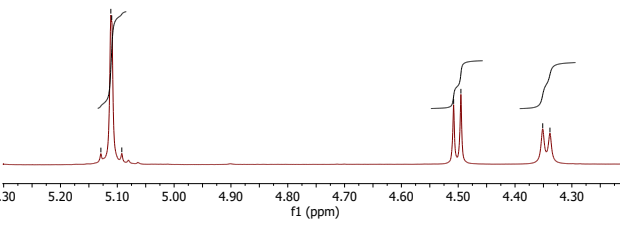
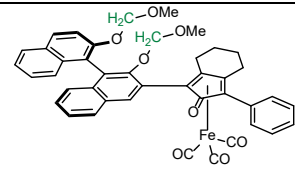
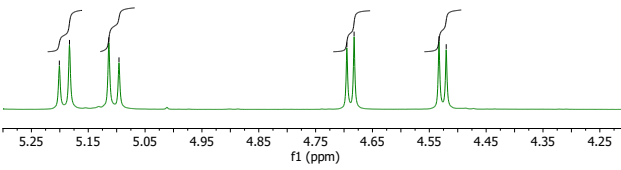
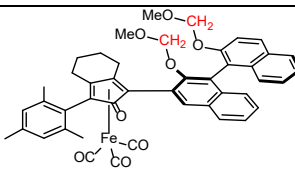
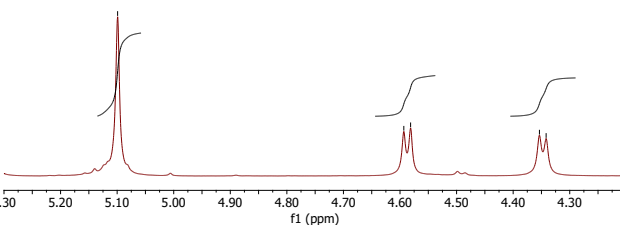
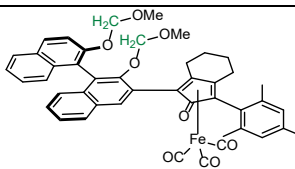
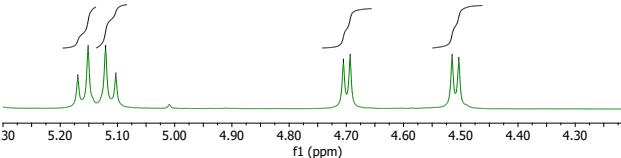
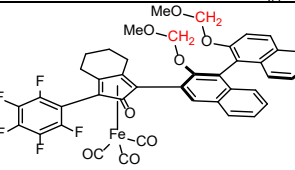
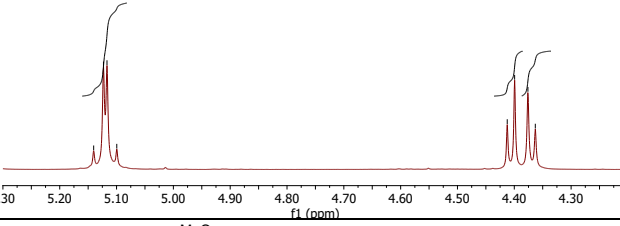
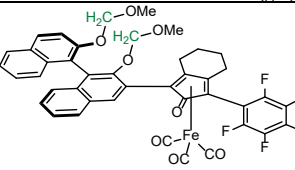
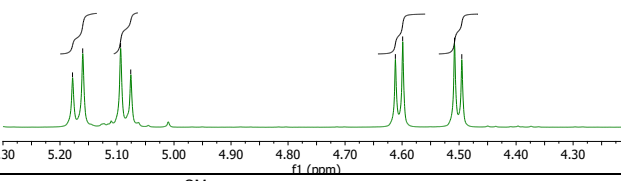
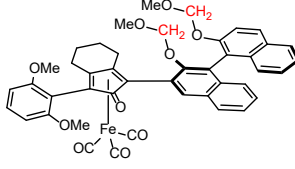
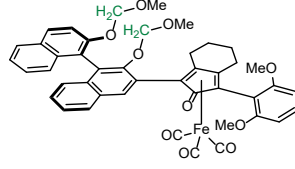
Table S1. Crystallographic table of compounds **1a**, **15** and **19**.

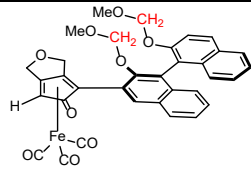
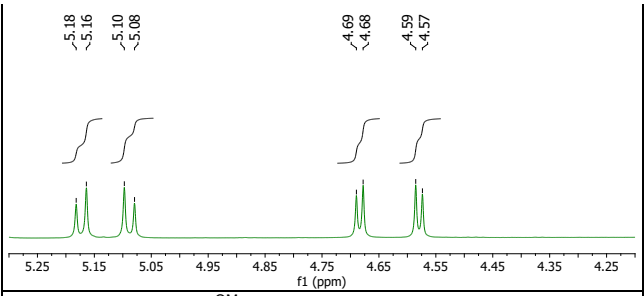
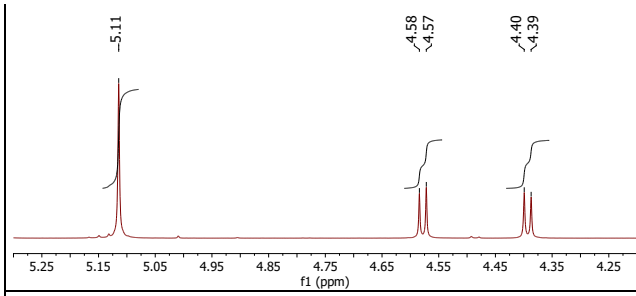
Compound	1a	15	19
CCDC No.	2280105	2280106	2280107
Formula	C ₃₄ H ₂₆ FeO ₉	C ₄₆ H ₄₄ FeO ₉	C ₆₀ H ₅₀ FeO ₁₂
Formula weight	634.40	796.66	1018.85
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>I</i> 2
a [Å]	11.1027(2)	11.1419(3)	25.7074(18)
b [Å]	11.3177(2)	10.4175(3)	8.2601(6)
c [Å]	11.3346(2)	18.1708(5)	27.8632(19)
α [°]	90	90	90
β [°]	94.746(2)	105.678(3)	103.171(7)
γ [°]	90	90	90
V [Å ³]	1419.39(4)	2030.63(10)	5761.0(7)
Z	2	2	4
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα
Temp. [K]	120(2)	120(2)	295(2)
ρ _(calcd) [g·cm ⁻³]	1.484	1.303	1.175
μ [mm ⁻¹]	0.590	0.427	0.319
F(000)	656	836	2128
Cryst. size [mm ³]	0.210 x 0.180 x 0.170	0.340 x 0.130 x 0.100	0.125 x 0.080 x 0.070
θ range [°]	1.803-31.494	1.898-31.481	1.627-25.345
Limiting indices	-16<=h<=15 -16<=k<=15 -16<=l<=15	-15<=h<=15 -14<=k<=14 -25<=l<=26	-30<=h<=30 -9<=k<=9 -33<=l<=33
Reflections collected/unique ^a	16023 / 8357 [R(int) = 0.0068]	23664 / 12048 [R(int) = 0.0125]	27972 / 10510 [R(int) = 0.0401]
Data/restraints/param	8357 / 1 / 399	12048 / 2 / 536	10510 / 3 / 662
Completeness to θ = 25.242° [%]	100.0	99.9	99.9
Max. and min. transmission	1.00000 and 0.89928	1.00000 and 0.88134	1.00000 and 0.74093
Final R indices (I > 2σ(I)) ^b	R ₁ = 0.0198, wR ₂ = 0.0545	R ₁ = 0.0354, wR ₂ = 0.0940	R ₁ = 0.0718, wR ₂ = 0.1841
R indices (all data)	R ₁ = 0.0199, wR ₂ = 0.0546	R ₁ = 0.0383, wR ₂ = 0.0960	R ₁ = 0.1074, wR ₂ = 0.2058
Absolute Structure Parameter	-0.006(3)	0.009(3)	0.036(11)
Goodness of fit ^c on F ²	1.044	1.028	1.032
Largest diff. peak and hole [Å ⁻³]	0.338 and -0.264	0.891 and -0.569	0.914 and -0.404

^a R_{int} = Σ|F_o² - F_o(mean)|/ΣF_o², ^b R₁ = Σ||F_o| - |F_c||/Σ|F_o|, wR₂ = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]}^{1/2}, ^c GooF = {S/(n - p)}^{1/2} = {Σ[w(F_o² - F_c²)²]/(n - p)}^{1/2}.

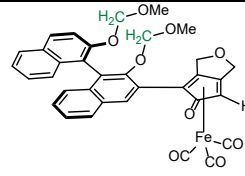
5. NMR patterns of the stereoplane epimers

Table S2. Typical ¹H NMR patterns of the MOM CH₂ groups of the stereoplane-containing CIC diastereomers.

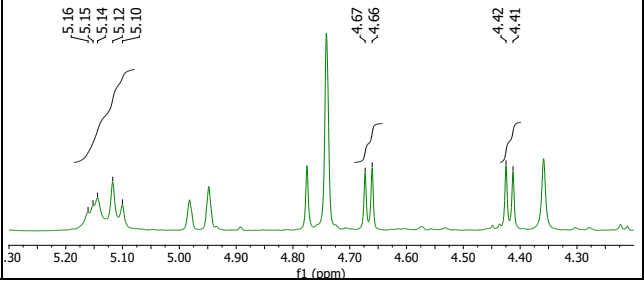
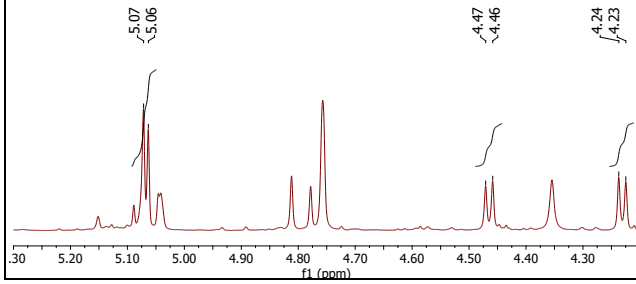
First Eluted Complex	Second Eluted Complex
<p>(pR,aR)-15</p>  <p>5.13 5.11 5.11 5.09</p> <p>4.51 4.50</p> <p>4.35 4.34</p> 	<p>(pS,aR)-15 X-ray structure</p>  <p>5.20 5.18 5.11 5.10</p> <p>4.70 4.68</p> <p>4.53 4.52</p> 
<p>(pR,aR)-16</p>  <p>5.10</p> <p>4.59 4.58</p> <p>4.35 4.34</p> 	<p>(pS,aR)-16</p>  <p>5.17 5.15 5.12 5.10</p> <p>4.71 4.69</p> <p>4.52 4.50</p> 
<p>(pS,aR)-17</p>  <p>5.14 5.12 5.12 5.10</p> <p>4.41 4.40 4.38 4.36</p> 	<p>(pR,aR)-17</p>  <p>5.18 5.16 5.09 5.08</p> <p>4.61 4.60</p> <p>4.51 4.50</p> 
<p>(pS,aR)-18</p> 	<p>(pR,aR)-18</p> 



(pR,aR)-19
X-ray structure



(pS,aR)-19



6. References

- [1] N. Li, H. Feng, Q. Gong, C. Wu, H. Zhou, Z. Huang, J. Yang, X. Chen, N. Zhao, *J. Mater. Chem.* **2015**, *3*, 11458-11463.
- [2] F. Yang, S. Wei, C. A. Chen, P. Xi, L. Yang, J. Lan, H. M. Gau, J. You, *Chem. Eur. J.* **2008**, *14*, 2223-2231.
- [3] H. T. Chang, M. Jeganmohan, C. H. Cheng, *Org. Lett.* **2007**, *9*, 505-508.
- [4] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.
- [5] a) P. Gajewski, M. Renom-Carrasco, S. Vailati Facchini, L. Pignataro, L. Lefort, J.G. de Vries, R. Ferraccioli, A. Forni, U. Piarulli, C. Gennari, *Eur. J. Org. Chem.* **2015**, 1887-1893; b) P. Gajewski, M. Renom-Carrasco, S. Vailati Facchini, L. Pignataro, L. Lefort, J.G. de Vries, R. Ferraccioli, U. Piarulli, C. Gennari, *Eur. J. Org. Chem.* **2015**, 5526-5536.
- [6] X. Bai, M. Cettolin, G. Mazzocanti, M. Pierini, U. Piarulli, V. Colombo, A. Dal Corso, L. Pignataro, C. Gennari, *Tetrahedron* **2019**, *75*, 1415-1424.
- [7] C. A. Swamy P, A. Varenikov, G. de Ruiter *Organometallics* **2020**, *39*, 247-257.