Supporting information

Chiral Triazolylidene-Pd-PEPPSI: Synthesis, Characterization, and Application in Asymmetric Suzuki-Miyaura Cross-Coupling

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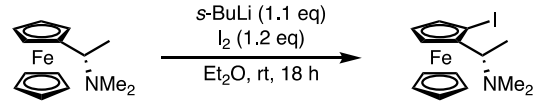
Contents

Instrumentation and chemicals

All manipulations of oxygen- and moisture-sensitive materials were conducted under argon or nitrogen atmosphere in a flame dried Schlenk flask. Nuclear magnetic resonance spectra were taken on a JEOL ECA spectrometer using tetramethylsilane for ^{1}H NMR as an internal standard (δ = 0 ppm) and $CDCl_3$ for ^{13}C NMR as an internal standard (δ = 77.16 ppm). ^{1}H NMR and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High performance liquid chromatography (HPLC) was performed on a JASCO MD-2010 Plus system with UV and CD detectors and chiral column of Daicel, Chiralpak OJ-H. Optical rotations were measured on a JASCO P-2200 Polarimeter. High-resolution mass spectra (HRMS) were measured by a JEOL JMS-T100LC AccuTOF. Infrared (IR) spectra were measured by an FT/IR-4100ST spectrometer. Melting points were determined using a YANAKO MP-500D. X-ray crystallographic analysis was performed on VariMax/Saturn CCD diffractometer. Flash column chromatography was carried out using silica gel (Fuji Silysia PSQ100B). Silver(I) oxide was purchased from Sigma-Aldrich Co. LLC (226831, >99%). Tetramethylammonium chloride was purchased from Tokyo Chemical Industry Co., Ltd. (T0136, 98%). Dichloromethane was purchased from Kanto Chemical Co., Inc., distilled from calcium hydride and stored under a nitrogen atmosphere. 3-Chloropyridine was purchased from Tokyo Chemical Industry Co., Ltd. (C0280, 95%). Palladium(II) chloride was purchased from Sigma-Aldrich Co. LLC (520659, >99%). 1-Naphthaleneboronic acid was purchased from Tokyo Chemical Industry Co., Ltd. (N0630, >97%). Potassium hydroxide was purchased from nacalai tesque (28616-45, 85%). Di-*n*-butyl ether was purchased from Kanto Chemical Co., Inc. (04662-00, >99%). 1-Bromo-2-methoxynaphthalene was prepared according to the literature.[1]

Experimental procedure

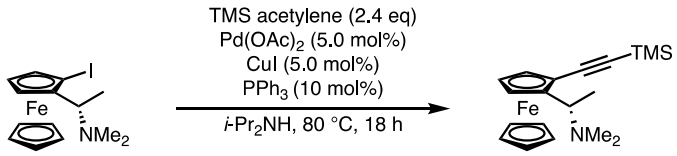
Procedure for preparation of (S,R_p)-1-[1-(dimethylamino)ethyl]-2-iodoferrocene[2]



(*S*)-Ugi's amine
2

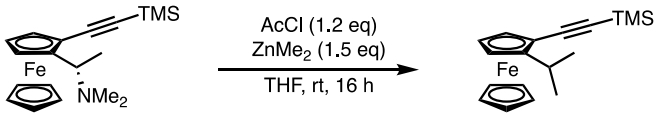
(*S*)-Ugi's amine **2** (1.0 g, 3.9 mmol) was placed in a 200-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in diethyl ether (20 mL). After the flask was cooled in an ice bath, *sec*-butyllithium (1.0 M in hexane, 4.3 mL, 4.3 mmol) was added to the solution at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. After the mixture was cooled to −78 °C, iodine (0.24 M in diethyl ether, 20 mL, 4.7 mmol) was added to the mixture at −78 °C. And then, the mixture was warm to room temperature and stirred for an additional 18 h. The reaction was quenched with saturated aqueous solution of sodium thiosulfate (30 mL), and the resulting mixture was then extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant residue was used for the next reaction without purification.

Procedure for preparation of (S,R_p)-1-[1-(dimethylamino)ethyl]-2-[(2-trimethylsilyl)ethynyl]ferrocene[3]



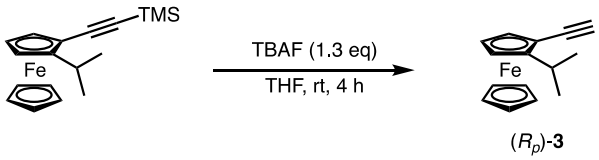
(S,R_p)-1-[1-(dimethylamino)ethyl]-2-iodoferrocene was placed in a 200-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in diisopropylamine (50 mL). Palladium(II) acetate (44 mg, 0.20 mmol), copper(I) iodide (37 mg, 0.20 mmol), triphenylphosphine (0.10 g, 0.39 mmol), and trimethylsilylacetylene (1.3 mL, 9.4 mmol) were added to the solution at 0 °C. After stirring at 0 °C for 30 min, the mixture was warm to room temperature and stirred for an additional 30 min. And then, the mixture was stirred at 80 °C for 18 h. After the mixture was filtered through a pad of Celite, the organic phase was concentrated under reduced pressure. The resultant residue was used for the next reaction without purification.

Procedure for preparation of (R_p)-1-isopropyl-2-[2-(trimethylsilyl)ethynyl]ferrocene[4]



(S,R_p)-1-[1-(dimethylamino)ethyl]-2-[(2-trimethylsilyl)ethynyl]ferrocene was placed in a 100-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in tetrahydrofuran (30 mL). To a stirred solution acetyl chloride (0.34 mL, 4.7 mmol) was added dropwise at −30 °C, followed by the addition of dimethylzinc (1.0 M in hexane, 5.9 mL, 5.9 mmol). The reaction mixture was warm to room temperature and stirred for 16 h. The reaction was quenched with saturated aqueous solution of ammonium chloride (20 mL), and the resulting mixture was then extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant residue was purified by flash silica gel column chromatography using hexane as an eluent, affording (R_p)-1-isopropyl-2-[2-(trimethylsilyl)ethynyl]ferrocene (973 mg, 3.0 mmol) in 77% yield over 3 steps from **2**. Red liquid; $[\alpha]_D^{25}$ –22.3 (*c* 0.52, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.36 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.12 (s, 5H), 4.09 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.05 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.87 (qq, *J* = 6.9, 6.9 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.22 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 104.3, 99.3, 92.7, 70.9, 70.6, 66.7, 65.9, 64.1, 27.5, 24.6, 21.8, 0.4 ppm; IR (KBr) 3096.2, 2959.2, 2927.4, 2897.5, 2149.3, 1658.5, 1633.4, 1464.7, 1362.5, 1106.9, 883.2, 841.8, 758.9, 748.2 cm^{-1}; ESI-HRMS (*m/z*): $[M]^+$ calcd for $C_{18}H_{24}FeSi$ 324.0997, found 324.1002.

Procedure for preparation of (R_p)-1-ethynyl-2-isopropylferrocene 3[3]

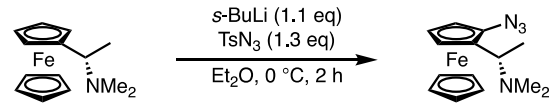


(R_p)-**3**

(R_p)-1-isopropyl-2-[2-(trimethylsilyl)ethynyl]ferrocene (0.97 g, 3.0 mmol) was placed in a 100-mL Schlenk tube under a nitrogen atmosphere and dissolved in tetrahydrofuran (20 mL). To a stirred solution tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 3.9 mL, 3.9 mmol) was added at 0 °C, and the mixture was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous solution of ammonium chloride (20

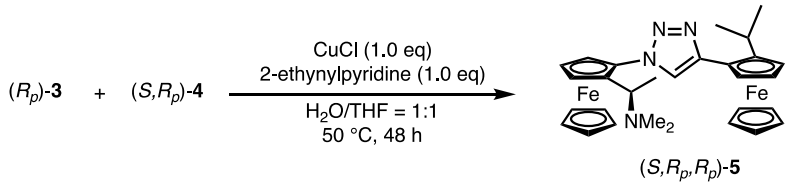
mL), and the resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant residue was purified by flash silica gel column chromatography using hexane as an eluent, affording (R_p)-1-ethynyl-2-isopropylferrocene **3** (756 mg, 3.0 mmol) in 99% yield. Red liquid; $[\alpha]_D^{25}$ –43.9 (*c* 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.40 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.15 (s, 5H), 4.10 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.08 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.89 (qq, *J* = 6.9, 6.9 Hz, 1H), 2.81 (s, 1H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 99.3, 82.4, 75.5, 71.2, 70.5, 66.8, 65.7, 63.0, 27.4, 25.0, 21.9 ppm; IR (KBr) 3292.9, 3095.2, 2961.2, 2925.5, 2896.6, 2755.8, 2703.7, 2458.8, 2368.2, 2234.1, 2107.8, 1766.5, 1637.3, 1472.4, 1456.9, 1380.8, 1360.5, 1106.9, 1060.7, 1000.9, 819.6, 656.6, 613.3, 592.0, 581.4 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{17}Fe$ 253.0680, found 253.0688.

Procedure for preparation of (S,R_p)-1-azido-2-[1-(dimethylamino)ethyl]ferrocene 4



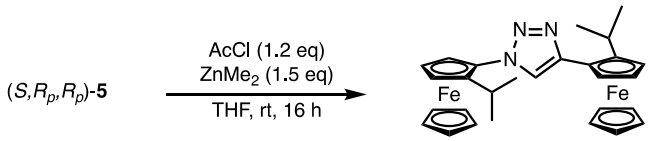
(*S*)-Ugi's amine **2** (1.0 g, 3.9 mmol) was placed in a 200-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in diethyl ether (20 mL). The flask was cooled in an ice bath, and *sec*-butyllithium (1.0 M in hexane, 4.3 mL, 4.3 mmol) was then added to the mixture, followed by the stirring at 0 °C for 2 h. After *p*-toluenesulfonyl azide (0.26 M in diethyl ether, 20 mL, 5.2 mmol) was added to the mixture at 0 °C, the mixture was stirred at 0 °C for 2 h. The reaction was quenched with water (20 mL), and the resulting mixture was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant crude **4** was used for the next reaction without purification.

Procedure for preparation of (S,R_p,R_p)-1-[2-{1-(dimethylamino)ethyl}ferrocenyl]-4-(2-isopropylferrocenyl)-1*H*-1,2,3-triazole 5[5]



Copper(I) chloride (0.39 g, 3.9 mmol) and 2-ethynylpyridine (0.40 g, 3.9 mmol) were placed in a 100-mL Schlenk tube under a nitrogen atmosphere and dissolved in water (20 mL) and tetrahydrofuran (20 mL). (R_p)-1-Ethynyl-2-isopropylferrocene **3** (0.98 g, 3.9 mmol) and (S,R_p)-1-azido-2-[1-(dimethylamino)ethyl]ferrocene **4** (1.2 g, 3.9 mmol) were added to the mixture at room temperature. After stirring at 50 °C for 48 h, the reaction mixture was quenched with ammonia aqueous solution (20 mL) and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant crude **5** was used for the next reaction without purification.

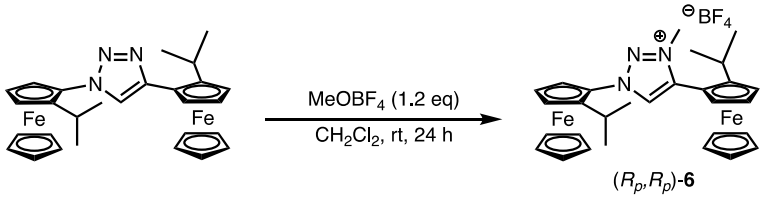
Procedure for preparation of (R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-1*H*-1,2,3-triazole[4]



(S,R_p,R_p)-1-[2-{1-(dimethylamino)ethyl}ferrocenyl]-4-(2-isopropylferrocenyl)-1*H*-1,2,3-triazole **5** was placed in a 100-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in tetrahydrofuran (30 mL). To a stirred solution acetyl chloride (0.34 mL, 4.7 mmol) was added dropwise at −30 °C, followed by the addition of dimethylzinc (1.0 M in hexane, 5.9 mL, 5.9 mmol). The reaction mixture was warm to room temperature and stirred for 16 h. The reaction was quenched with saturated aqueous solution of ammonium chloride (20 mL), and the solution was extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The resultant residue was purified by flash silica gel column chromatography using hexane/ethyl acetate (v/v = 4/1), affording (R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-1*H*-1,2,3-triazole (0.78 g, 1.5 mmol) in 38% yield over 2 steps from **3**. Red liquid; $[\alpha]_D^{25}$ +53.4 (*c* 0.54, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (s, 1H), 4.68 (dd, J = 2.4, 1.4 Hz, 1H), 4.62 (dd, J = 2.5, 1.6 Hz, 1H), 4.31 (s, 5H),

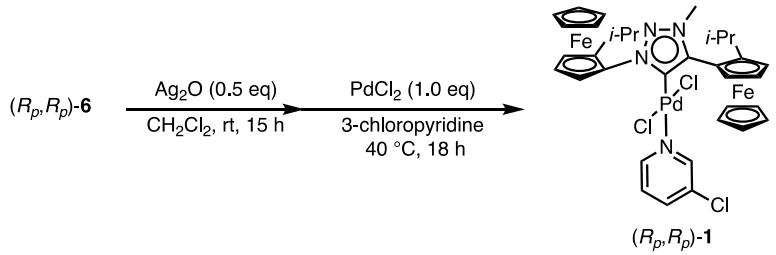
4.23 (dd, J = 2.3, 1.4 Hz, 1H), 4.22-4.20 (m, 2H), 4.18 (dd, J = 2.5, 2.5 Hz, 1H), 4.07 (s, 5H), 3.31 (qq, J = 6.8, 6.8 Hz, 1H), 2.98 (qq, J = 6.8, 6.8 Hz, 1H), 1.44 (d, J = 6.8 Hz, 3H), 1.35 (d, J = 6.8 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.1, 122.7, 95.2, 92.6, 91.9, 73.4, 70.6, 70.1, 67.7, 66.8, 66.1, 65.3, 64.6, 64.6, 27.1, 25.9, 25.4, 24.6, 22.1, 22.1 ppm; IR (KBr) 3305.4, 3100.0, 2961.2, 2925.5, 2868.6, 2374.9, 2247.6, 2140.6, 2103.9, 1718.3, 1626.7, 1587.1, 1503.2, 1443.5, 1351.9, 1264.1, 1220.7, 1105.9, 1034.6, 929.5, 819.6, 746.3, 662.4 cm^{-1}; ESI-HRMS (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{32}N_3Fe_2$ 522.1295, found 522.1299.

Procedure for preparation of (R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-3-methyl-1*H*-1,2,3-triazolium tetrafluoroborate 6[5]



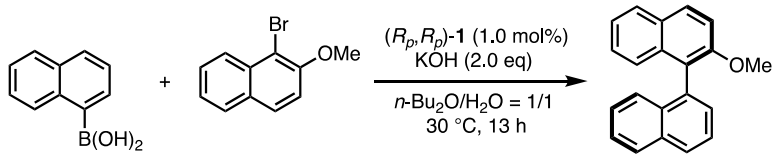
(R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-1*H*-1,2,3-triazole (78 mg, 0.15 mmol) was placed in a 50-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in dichloromethane (3.0 mL). After the addition of trimethyloxonium tetrafluoroborate (27 mg, 0.18 mmol) at 0 °C, the mixture was stirred at room temperature for 24 h. The reaction was quenched with methanol (1.0 mL), and the volatiles were removed under reduced pressure. The crude product was washed with diethyl ether and dried to give (R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-3-methyl-1*H*-1,2,3-triazolium tetrafluoroborate **6** (81 mg, 0.13 mmol) in 84% yield. Red solid; $[\alpha]_D^{25}$ +196.2 (*c* 0.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 5.17 (dd, J = 2.5, 1.5 Hz, 1H), 4.92 (dd, J = 2.5, 1.4 Hz, 1H), 4.49 (dd, J = 2.5, 2.5 Hz, 1H), 4.45 (s, 5H), 4.39-4.36 (m, 2H), 4.34 (s, 5H), 4.32 (dd, J = 2.5, 1.4 Hz, 1H), 4.18 (s, 3H), 2.93 (qq, J = 6.8, 6.8 Hz, 1H), 2.64 (qq, J = 6.8, 6.8 Hz, 1H), 1.41 (d, J = 6.8 Hz, 3H), 1.37 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.2, 131.0, 98.3, 92.5, 91.5, 71.9, 71.2, 69.8, 69.5, 67.6, 66.6, 66.3, 65.8, 64.7, 39.0, 26.5, 25.7, 25.7, 24.9, 22.2, 22.1 ppm; IR (KBr) 3294.8, 3096.2, 2961.2, 2937.1, 2864.7, 2367.2, 2148.3, 2100.1, 1658.5, 1598.7, 1451.2, 1105.9, 1083.8, 1034.6, 1001.8, 834.1, 682.7, 619.0 cm^{-1}; ESI-HRMS (*m/z*): $[M-BF_4]^+$ calcd for $C_{29}H_{34}N_3Fe_2$ 536.1446, found 536.1444.

Procedure for preparation of (R_p,R_p)-[Pd(TFc*)(3-ClPy)Cl_2] 1[5]



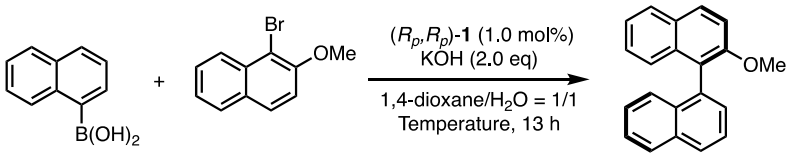
(R_p,R_p)-1,4-bis(2-isopropylferrocenyl)-3-methyl-1*H*-1,2,3-triazolium tetrafluoroborate **6** (62 mg, 0.1 mmol) and silver(I) oxide (12 mg, 0.05 mmol) were placed in a 20-mL Schlenk flask under a nitrogen atmosphere and dissolved in dichloromethane (2.0 mL). The mixture was stirred at room temperature for 15 h. The solvent was removed under reduced pressure, and the residue was dissolved with dichloromethane and filtered to another 20-mL Schlenk flask. The solvent was removed under vacuum, followed by the addition of palladium(II) chloride (18 mg, 0.1 mmol) and 3-chloropyridine (2.0 mL). After stirring at 50 °C for 16 h under a nitrogen atmosphere, the reaction mixture was cooled to room temperature, diluted with dichloromethane (3.0 mL), and passed through a silica pad. The volatiles were removed under reduced pressure to give the crude product, which was purified by flash silica gel column chromatography using dichloromethane as an eluent to give (R_p,R_p)-[Pd(TFc*)(3-ClPy)Cl_2] **1** (29 mg, 0.035 mmol) in 35% yield. Red solid; $[\alpha]_D^{25}$ +73.4 (*c* 0.59, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.00 (d, *J* = 2.3 Hz, 1H), 8.92 (dd, *J* = 5.5, 1.2 Hz, 1H), 7.67 (ddd, *J* = 8.2, 2.3, 1.2 Hz, 1H), 7.20 (dd, *J* = 8.2, 5.5 Hz, 1H), 6.20 (dd, *J* = 2.6, 1.5 Hz, 1H), 4.87 (s, 5H), 4.53 (dd, *J* = 2.2, 1.5 Hz, 1H), 4.41 (dd, *J* = 2.4, 2.4 Hz, 1H), 4.39-4.37 (m, 1H), 4.35 (dd, *J* = 2.6, 2.6 Hz, 1H), 4.33-4.30 (m, 1H), 4.28 (s, 5H), 3.78 (s, 3H), 2.98 (qq, *J* = 6.8, 6.8 Hz, 1H), 2.91 (qq, *J* = 6.8, 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.5, 149.5, 141.3, 137.7, 132.6, 128.1, 124.8, 97.4, 96.1, 92.6, 72.6, 71.0, 70.9, 70.2, 68.6, 67.8, 66.8, 65.0, 65.0, 37.3, 25.8, 25.3, 24.2, 24.2, 23.0, 22.3 ppm; IR (KBr) 1689.3, 1609.3, 1403.9, 1323.9, 1169.6, 1129.1, 1063.6, 1017.3, 837.9, 768.5, 743.4, 720.3, 698.1 cm^{-1}; ESI-HRMS (*m/z*): $[M–Cl]^+$ calcd for $C_{34}H_{37}N_4Cl_2Fe_2Pd$ 789.0129, found 789.0112.

Procedure for asymmetric Suzuki-Miyaura cross-coupling of 1-naphthaleneboronic acid and 1-bromo-2-methoxynaphthalene



n-Dibutyl ether (1 mL) and water (1 mL) were placed in a 20-mL Schlenk flask under a nitrogen atmosphere. To a stirred solution potassium hydroxide (18 mg, 0.32 mmol), 1-naphthaleneboronic acid (41 mg, 0.24 mmol), 1-bromo-2-methoxynaphthalene (38 mg, 0.16 mmol), and (R_p,R_p)-palladium complex **1** (1.3 mg, 0.0016 mmol) were added at room temperature. After stirring at 30 °C for 13 h, the reaction mixture was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by PTLC (hexane as an eluent) gave (*S*)-2-methoxy-1,1'-binaphthyl (40 mg, 0.13 mmol) in 84% yield with 75% ee. The enantiomeric purity was determined by chiral HPLC analysis. The stereochemistry of the product was consistent with the literature data.[6] White solid; $[\alpha]_D^{25}$ +8.6 (*c* 0.79, $CHCl_3$) for 75% ee, {lit[6], (*S*)-isomer, $[\alpha]_D^{25}$ +12.4 (*c* 0.92, $CHCl_3$) for 90% ee}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 9.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.61 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.47-7.40 (m, 3H), 7.34-7.28 (m, 2H), 7.28-7.24 (m, 1H), 7.23-7.19 (m, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.8, 134.7, 134.4, 133.8, 133.1, 129.6, 129.2, 128.6, 128.4, 127.9, 127.9, 126.5, 126.3, 126.0, 125.8, 125.7, 125.7, 123.7, 123.4, 114.0, 56.9 ppm; HPLC (Daicel Chiralpak OJ-H, *n*-hexane/2-propanol = 4/1, flow rate = 1.0 mL/min, T = 25 °C, λ = 220 nm): t_R 8.6 min (major) and 14.5 min (minor).

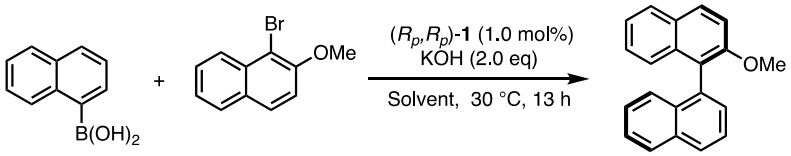
Table S1. Screening of the reaction temperature[a]



Entry	Temperature (°C)	Yield (%)	ee (%)[b]
1	60	35	61
2	50	62	67
3	40	57	65
4	**30**	**73**	**66**
5	20	trace	-

[a]Reaction conditions: 1-naphthaleneboronic acid (0.24 mmol), 1-bromo-2-methoxynaphthalene (0.16 mmol), (R_p,R_p)-**1** (1.6 μmol), and KOH (0.32 mmol) in 1,4-dioxane (1.0 mL) and H_2O (1.0 mL) for 13 h. [b]Determined by HPLC.

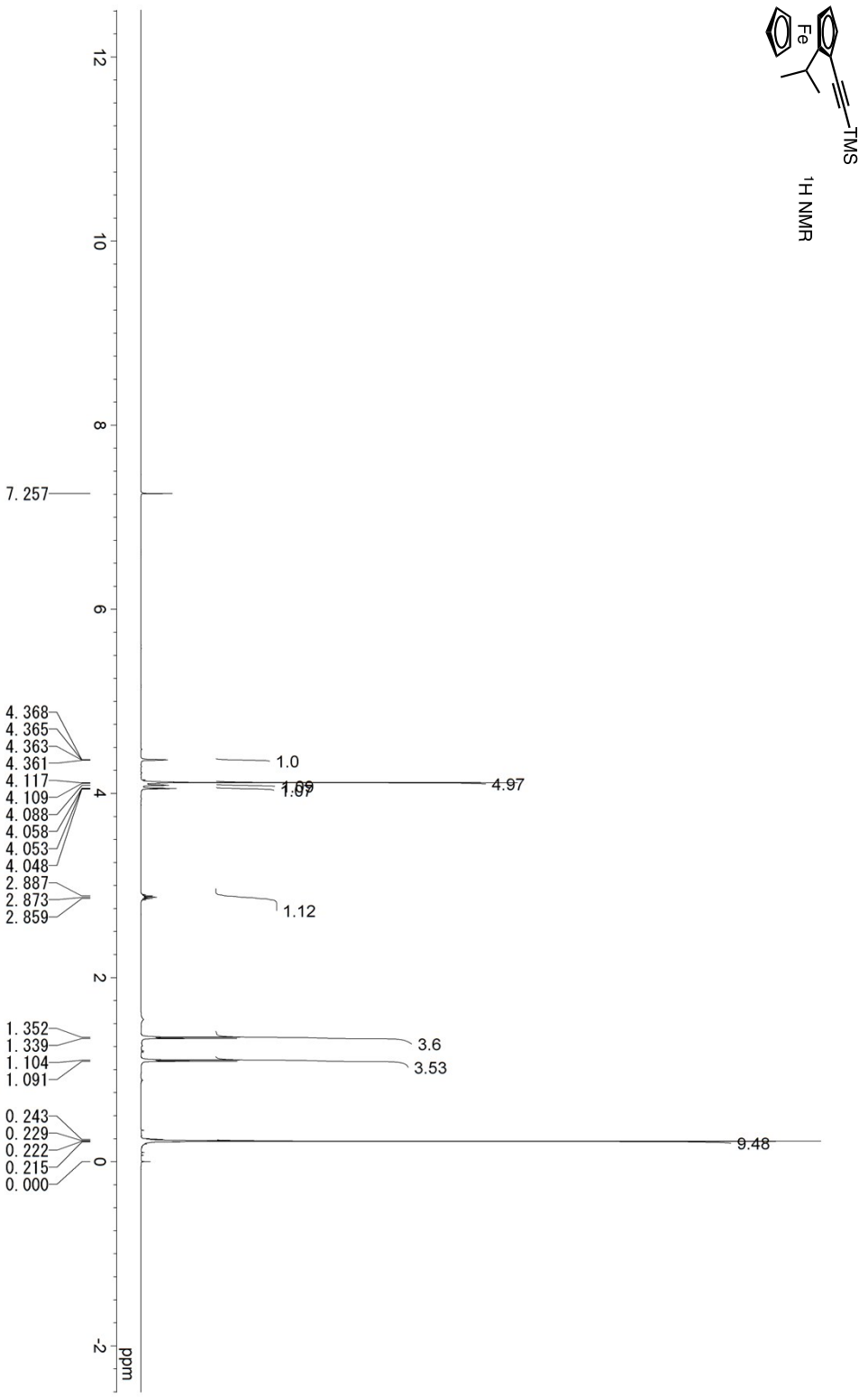
Table S2. Screening of solvents[a]

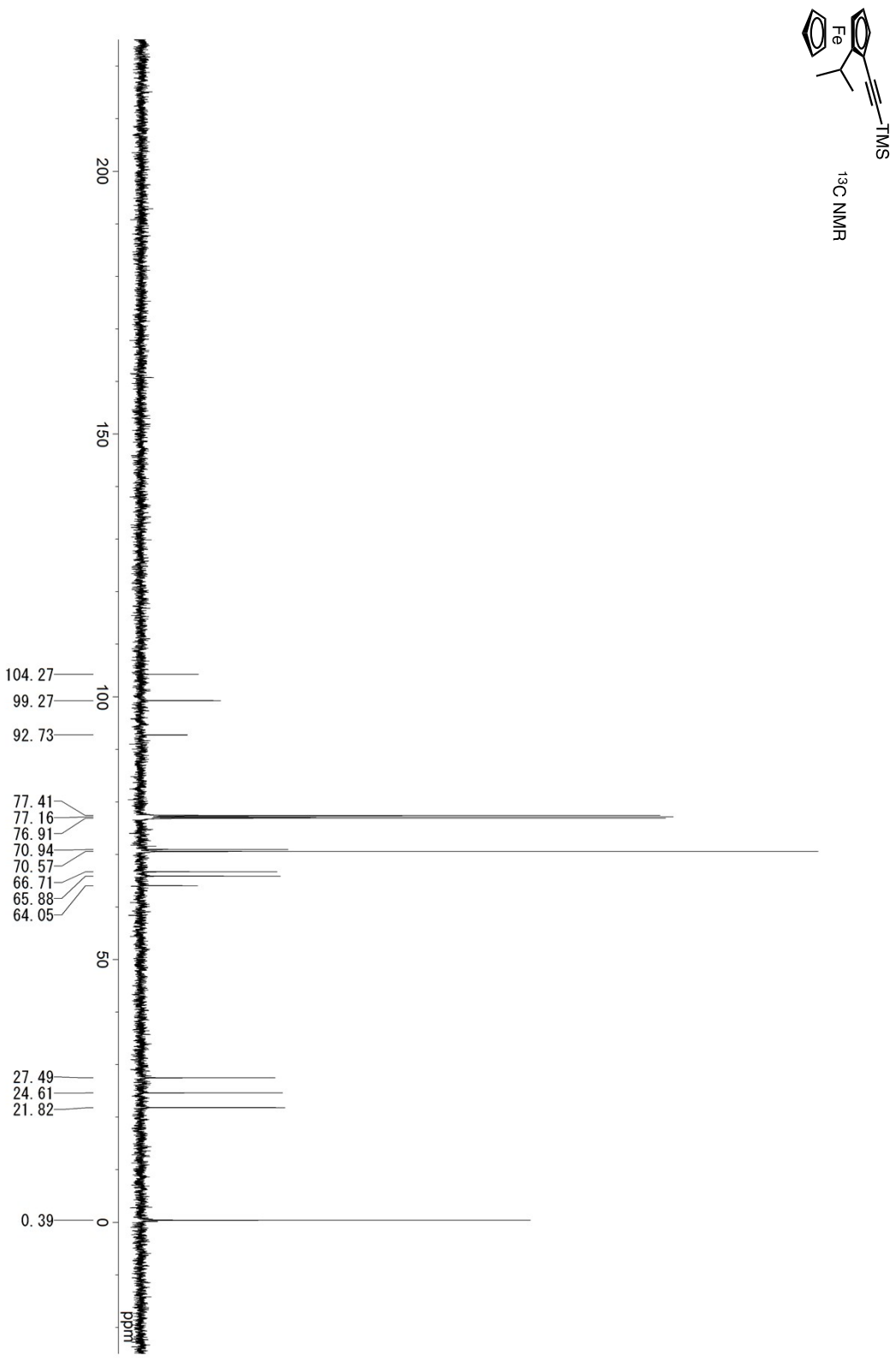


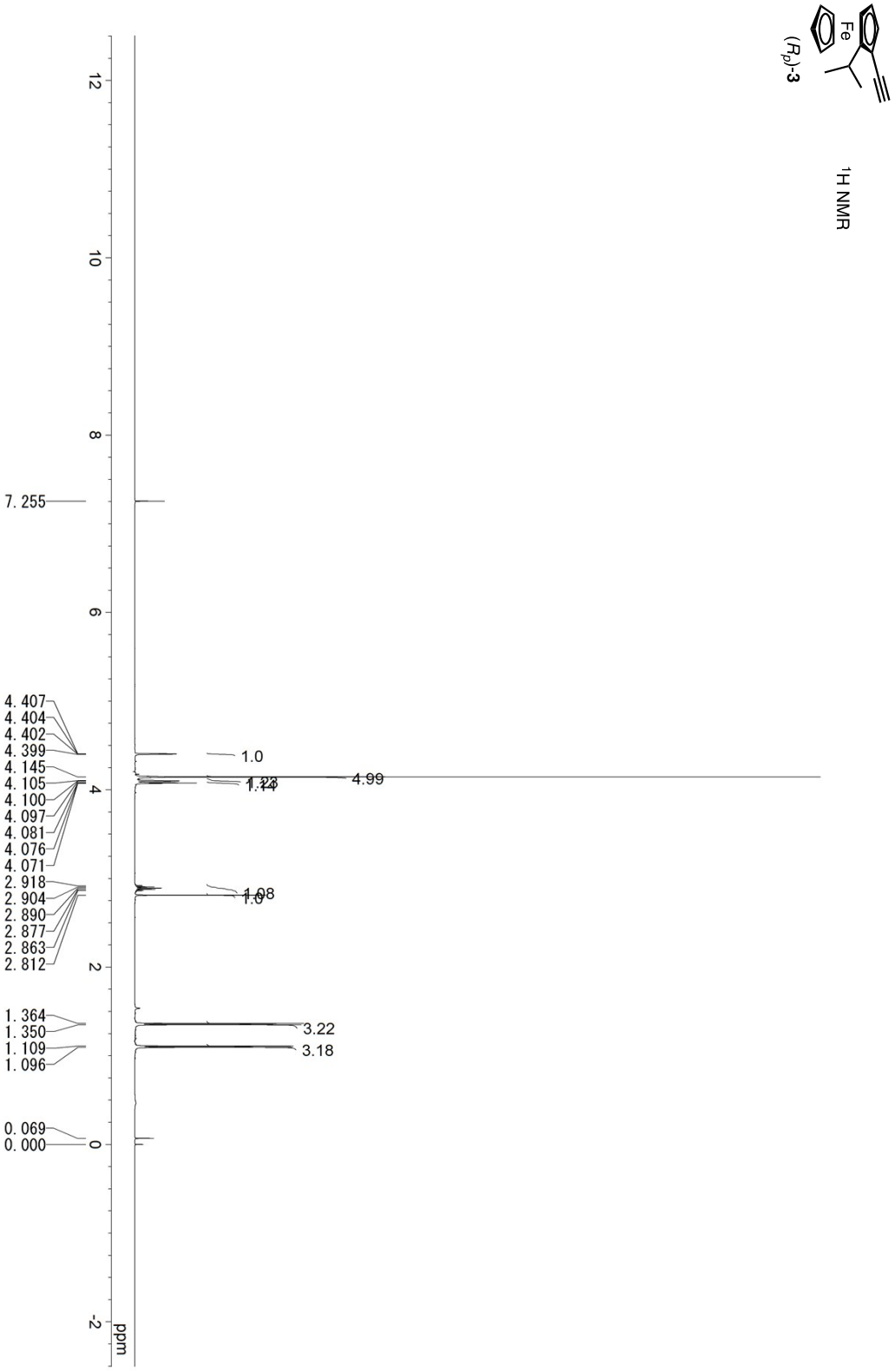
Entry	Solvent	Yield (%)	ee (%)[b]
1	1,4-dioxane/H_2O = 1/1	73	66
2	THF/H_2O = 1/1	65	72
3	MTBE/H_2O = 1/1	62	75
4	***n*-Bu_2O/H_2O = 1/1**	**86**	**75**
5	Et_2O/H_2O = 1/1	77	68

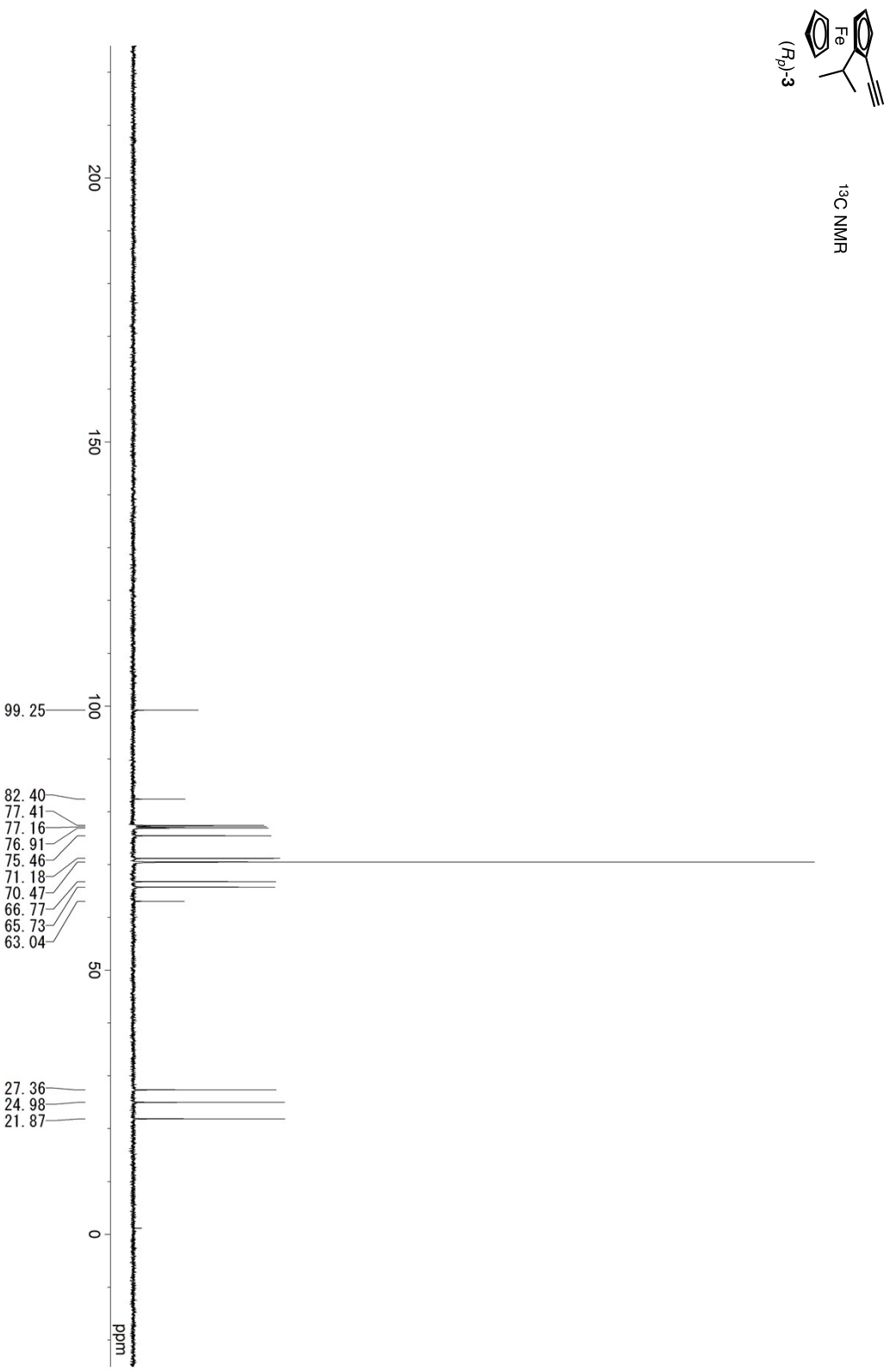
[a]Reaction conditions: 1-naphthaleneboronic acid (0.24 mmol), 1-bromo-2-methoxynaphthalene (0.16 mmol), (R_p,R_p)-**1** (1.6 μmol), and KOH (0.32 mmol) in Solvent (2.0 mL) at 30 °C for 13 h. [b]Determined by HPLC.

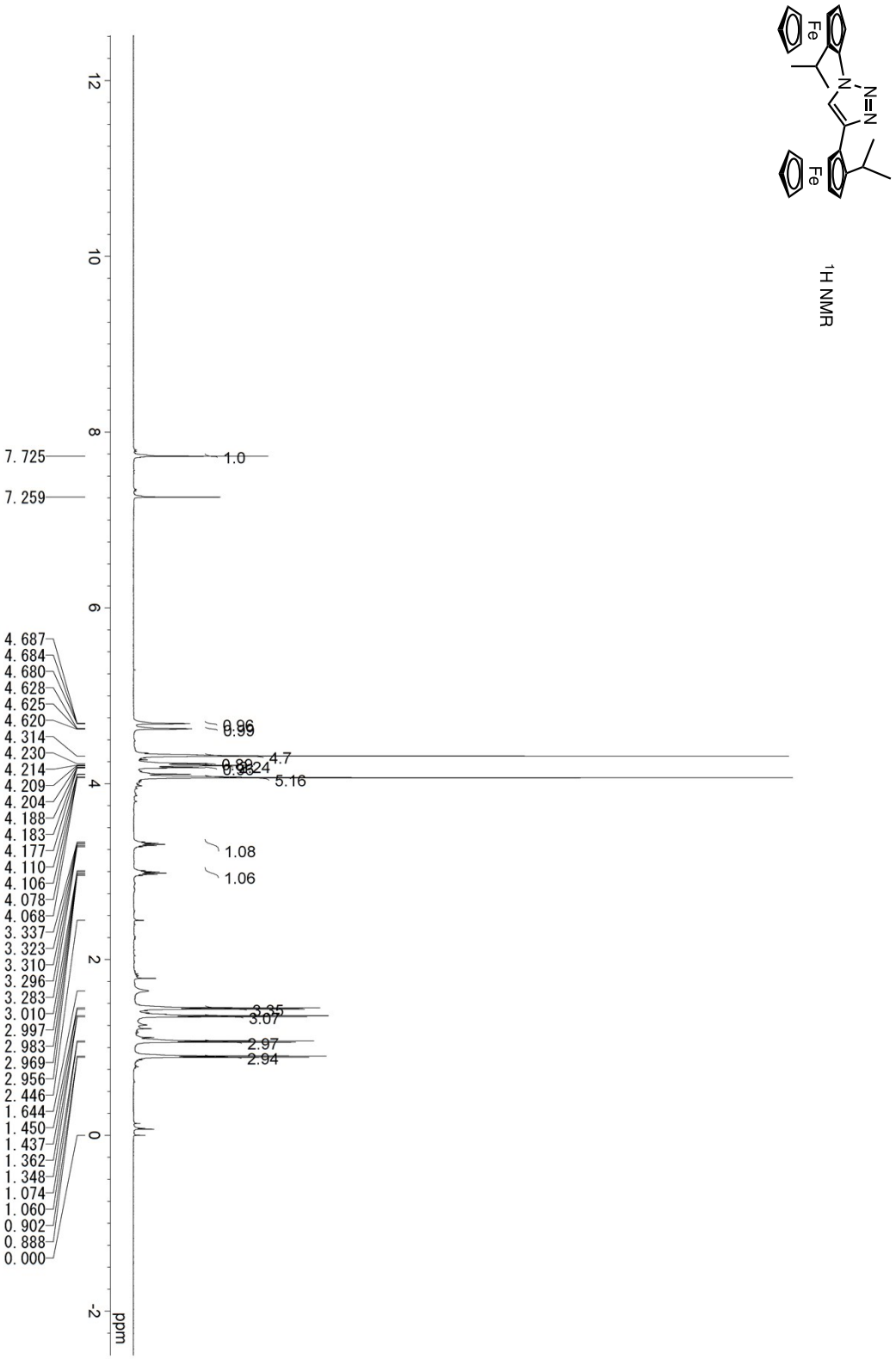
NMR Spectra Data

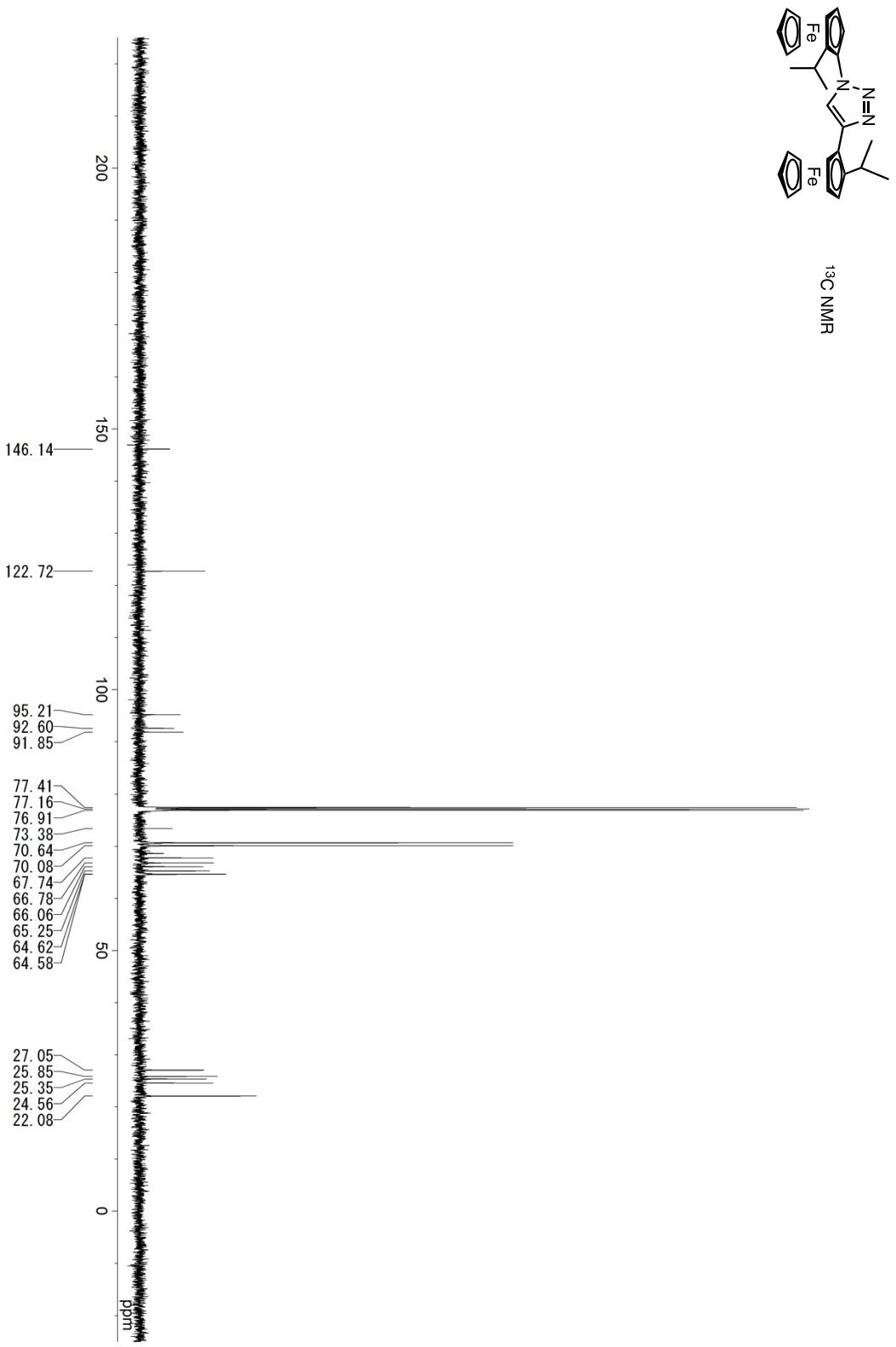


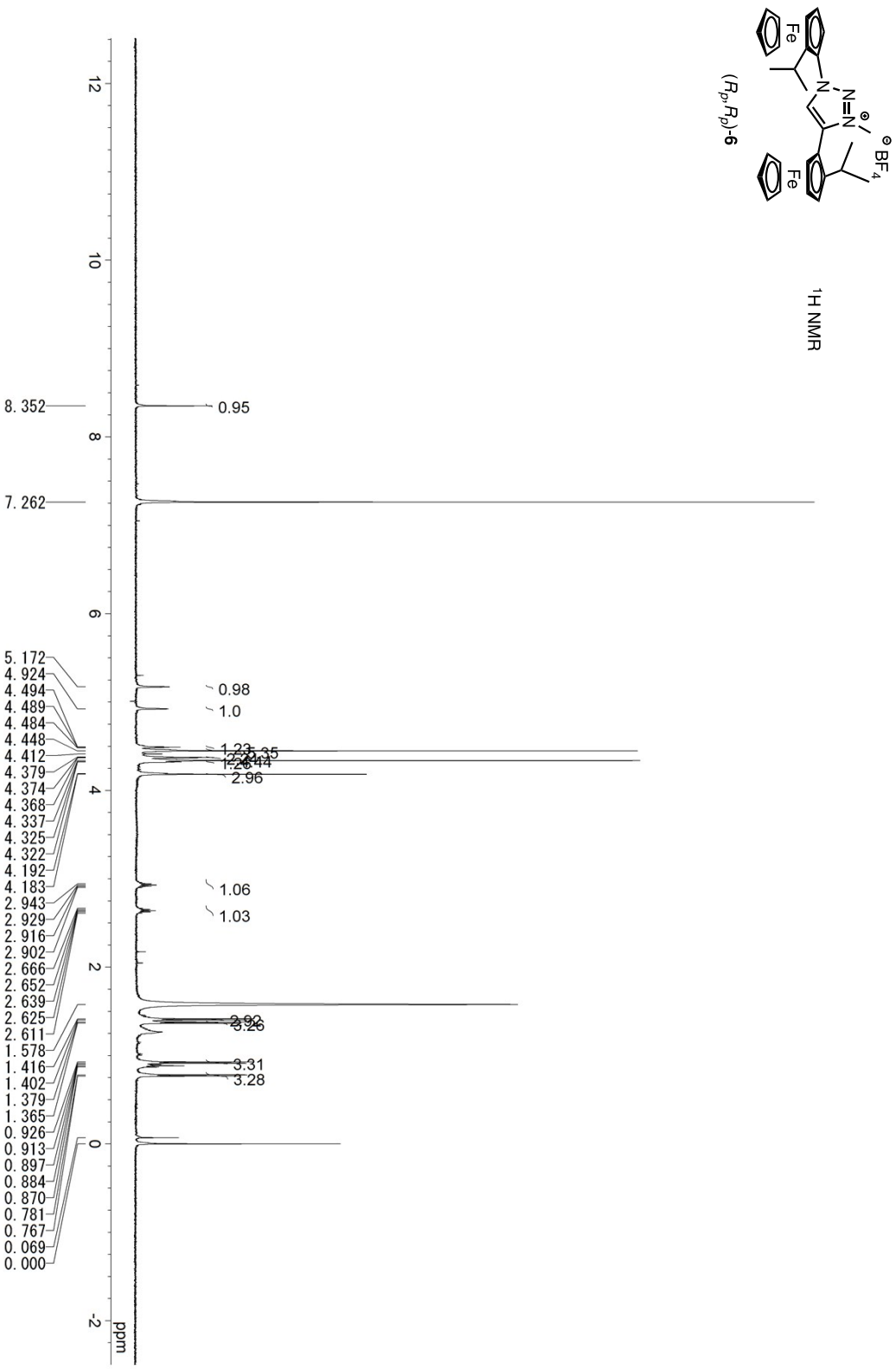

Fe
TMS
^{13}C NMR
200
150
100
50
0
104.27
99.27
92.73
77.41
77.16
76.91
70.94
70.57
66.71
65.88
64.05
27.49
24.61
21.82
0.39
ppm

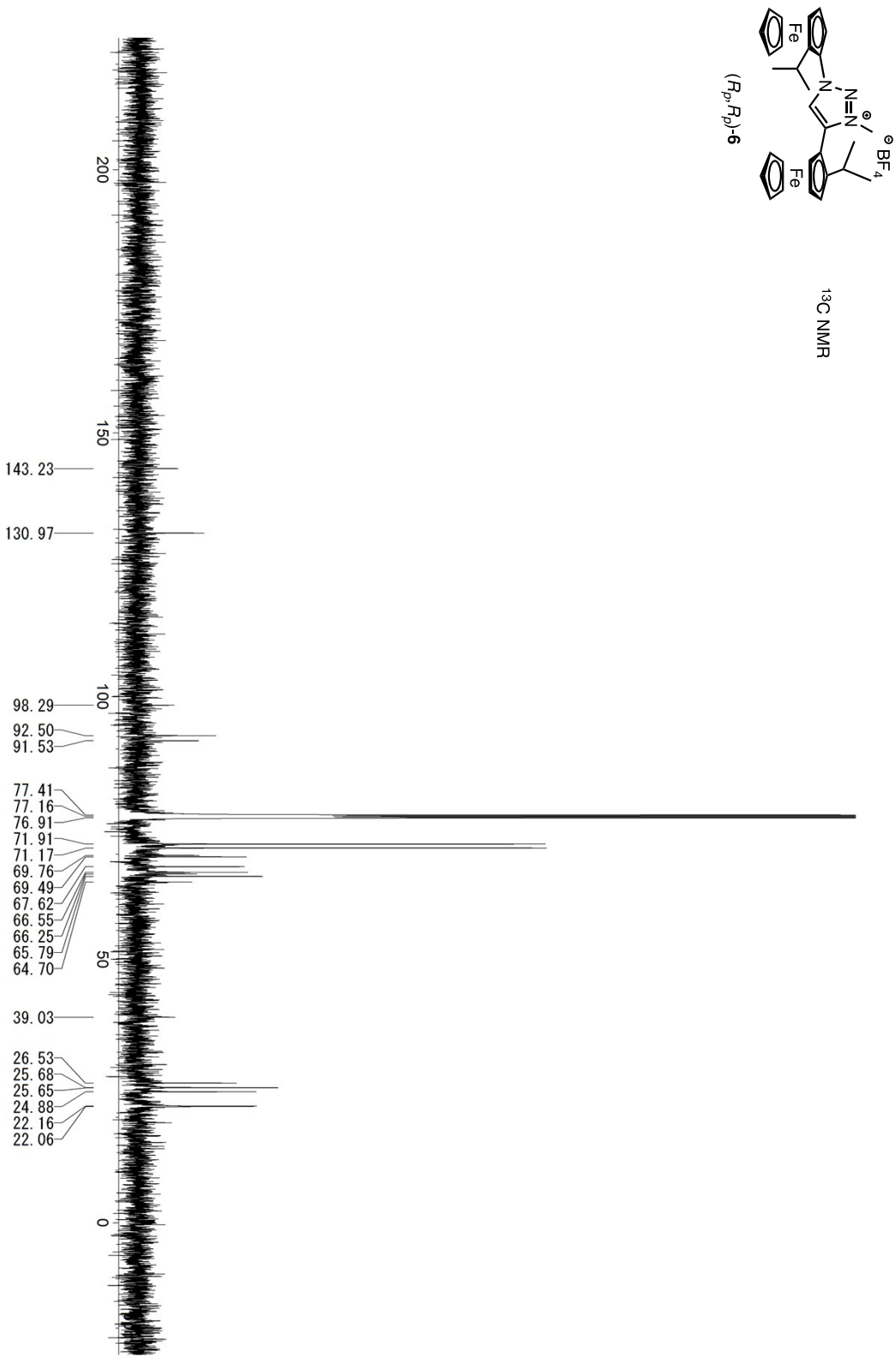

Fe
(Rp)-3
1H NMR
7.255
4.407
4.404
4.402
4.399
4.145
4.105
4.100
4.097
4.081
4.076
4.071
2.918
2.904
2.890
2.877
2.863
2.812
1.364
1.350
1.109
1.096
0.069
0.000
1.0
4.99
3.22
3.18
ppm

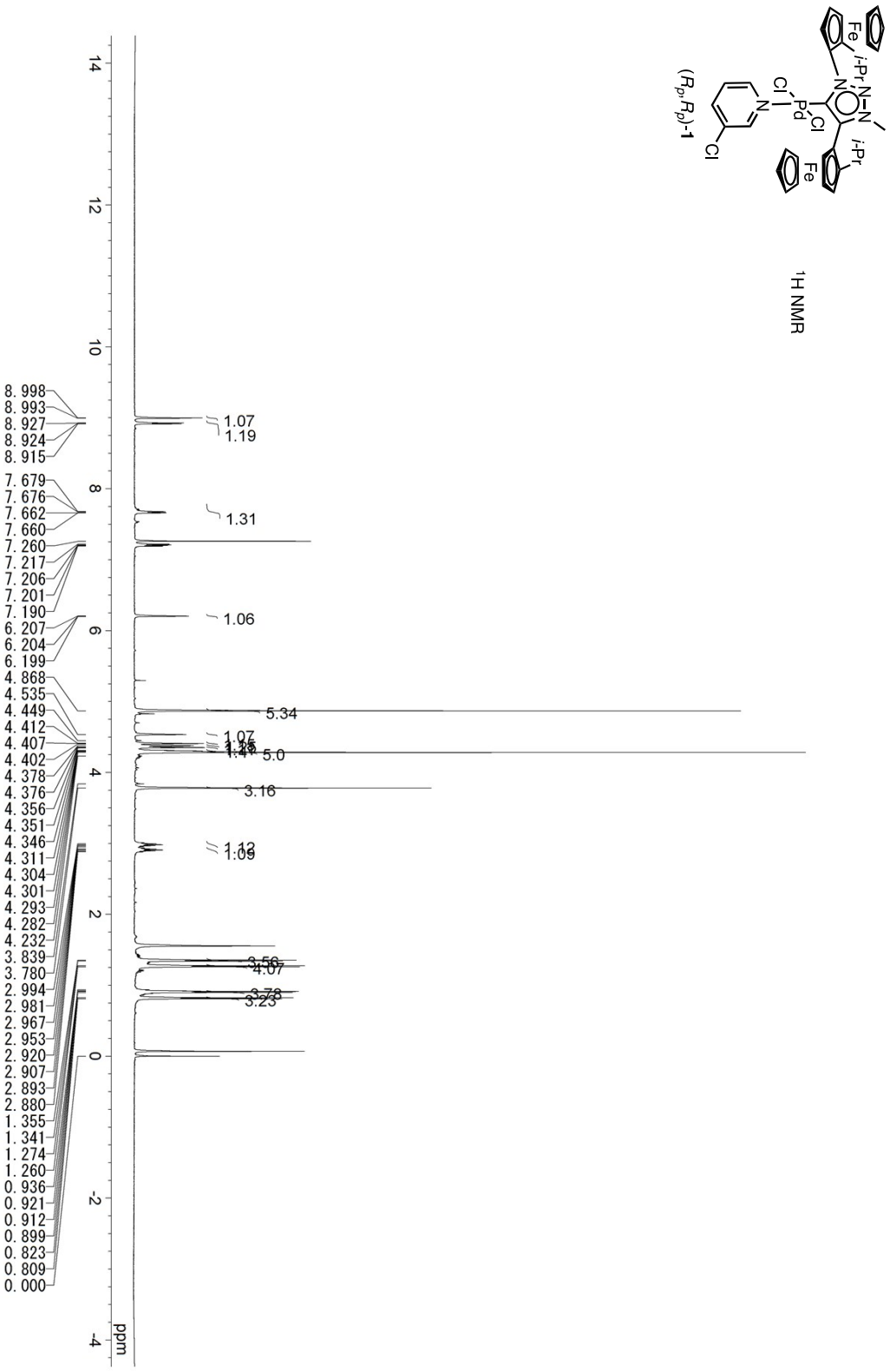

Fe
(Rp)-3
13C NMR
200
150
100
50
0
ppm
99.25
82.40
77.41
77.16
76.91
75.46
71.18
70.47
66.77
65.73
63.04
27.36
24.98
21.87

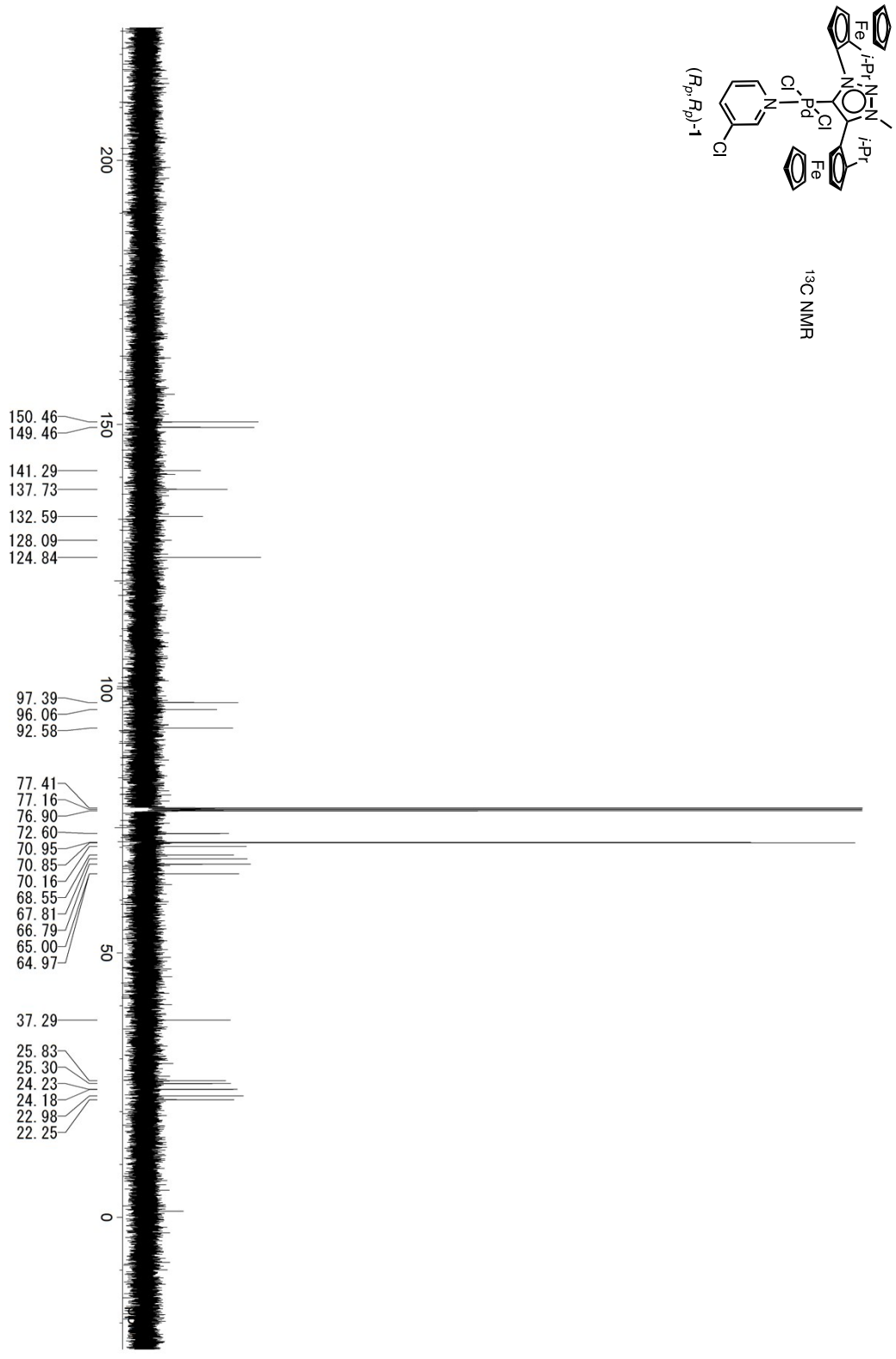

Fe
N
N≡N
Fe
1H NMR
12
10
8
6
4
2
0
-2
ppm
7.725
7.259
4.687
4.684
4.680
4.628
4.625
4.620
4.314
4.230
4.214
4.209
4.204
4.188
4.183
4.177
4.110
4.106
4.078
4.068
3.337
3.323
3.310
3.296
3.283
3.010
2.997
2.983
2.969
2.956
2.446
1.644
1.450
1.437
1.362
1.348
1.074
1.060
0.902
0.888
0.000
1.0
0.96
0.99
4.7
5.16
1.08
1.06
3.35
3.07
2.97
2.94

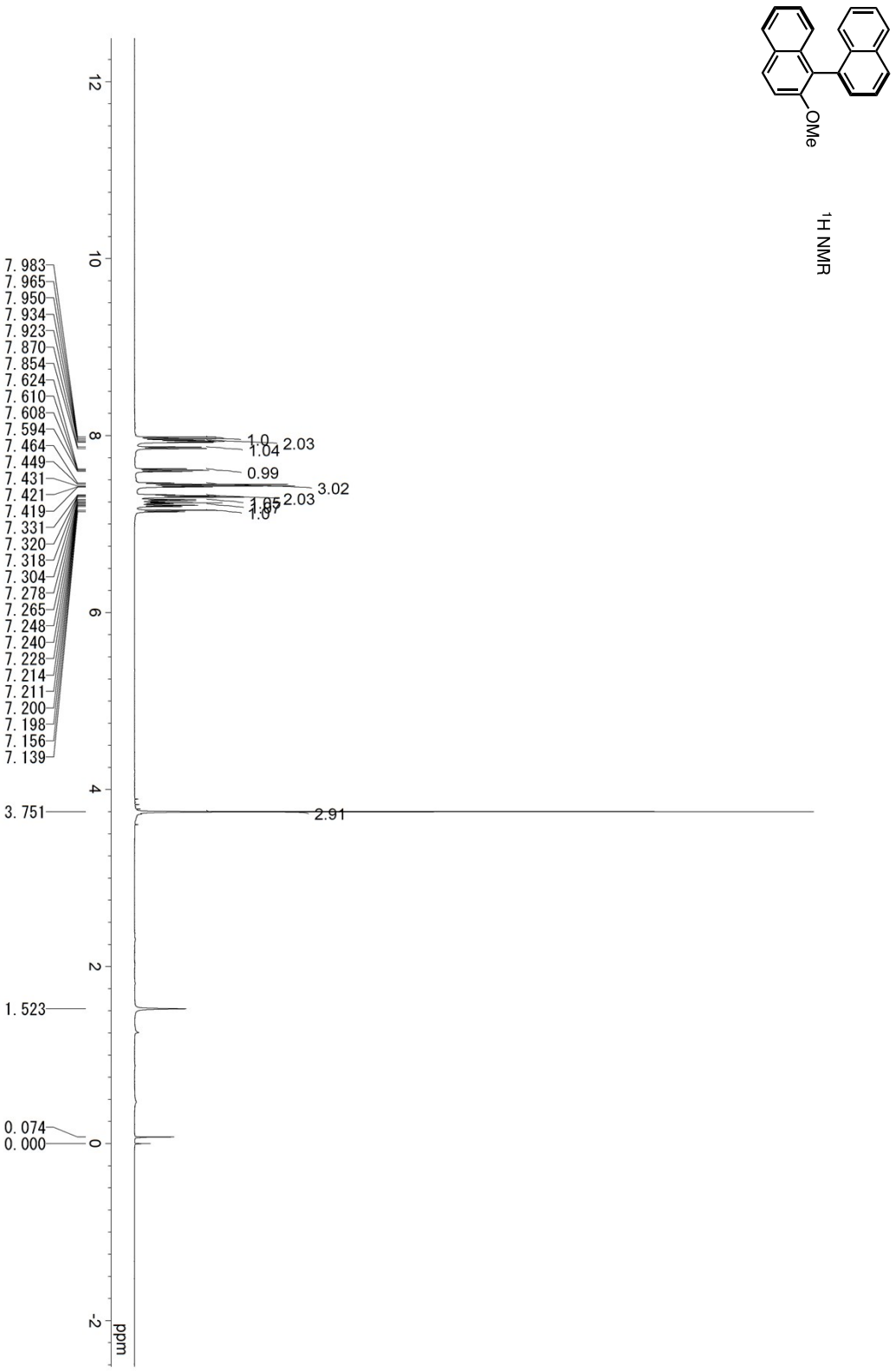

Fe
N
N≡N
Fe
^{13}C NMR
200
150
100
50
0
ppm
146.14
122.72
95.21
92.60
91.85
77.41
77.16
76.91
73.38
70.64
70.08
67.74
66.78
66.06
65.25
64.62
64.58
27.05
25.85
25.35
24.56
22.08

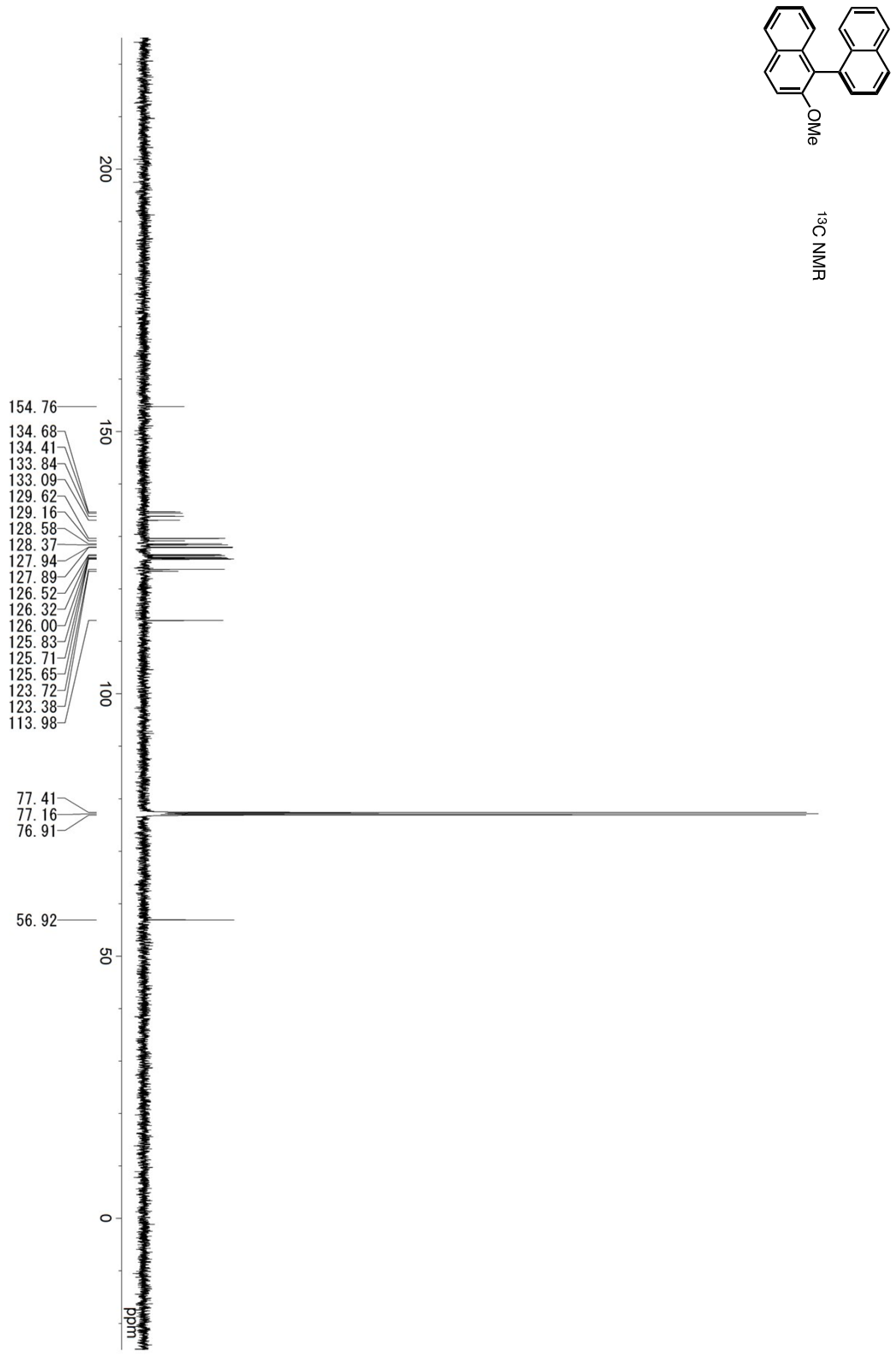

(Rp,Rp)-6
Fe
Fe
BF4
1H NMR
ppm
8.352
7.262
5.172
4.924
4.494
4.489
4.484
4.448
4.412
4.379
4.374
4.368
4.337
4.325
4.322
4.192
4.183
2.943
2.929
2.916
2.902
2.666
2.652
2.639
2.625
2.611
1.578
1.416
1.402
1.379
1.365
0.926
0.913
0.897
0.884
0.870
0.781
0.767
0.069
0.000
0.95
0.98
1.0
2.96
1.06
1.03
3.31
3.28


Fe
N
N≡N
BF4
Fe
(Rp,Rp)-6
13C NMR
200
150
100
50
0
143.23
130.97
98.29
92.50
91.53
77.41
77.16
76.91
71.91
71.17
69.76
69.49
67.62
66.55
66.25
65.79
64.70
39.03
26.53
25.68
25.65
24.88
22.16
22.06


(Rp,Rp)-1
1H NMR
8.998
8.993
8.927
8.924
8.915
7.679
7.676
7.662
7.660
7.260
7.217
7.206
7.201
7.190
6.207
6.204
6.199
4.868
4.535
4.449
4.412
4.407
4.402
4.378
4.376
4.356
4.351
4.346
4.311
4.304
4.301
4.293
4.282
4.232
3.839
3.780
2.994
2.981
2.967
2.953
2.920
2.907
2.893
2.880
1.355
1.341
1.274
1.260
0.936
0.921
0.912
0.899
0.823
0.809
0.000
1.07
1.19
1.31
1.06
5.34
5.0
3.16
1.12
1.09
4.07
3.23
14
12
10
8
6
4
2
0
-2
-4
ppm


150.46
149.46
141.29
137.73
132.59
128.09
124.84
97.39
96.06
92.58
77.41
77.16
76.90
72.60
70.95
70.85
70.16
68.55
67.81
66.79
65.00
64.97
37.29
25.83
25.30
24.23
24.18
22.98
22.25
200
150
100
50
0
(R_p,R_p)-1
^{13}C NMR


OMe
^{1}H NMR
7.983
7.965
7.950
7.934
7.923
7.870
7.854
7.624
7.610
7.608
7.594
7.464
7.449
7.431
7.421
7.419
7.331
7.320
7.318
7.304
7.278
7.265
7.248
7.240
7.228
7.214
7.211
7.200
7.198
7.156
7.139
3.751
1.523
0.074
0.000
1.0
1.04
2.03
0.99
3.02
2.03
1.07
1.0
2.91
12
10
8
6
4
2
0
-2
ppm

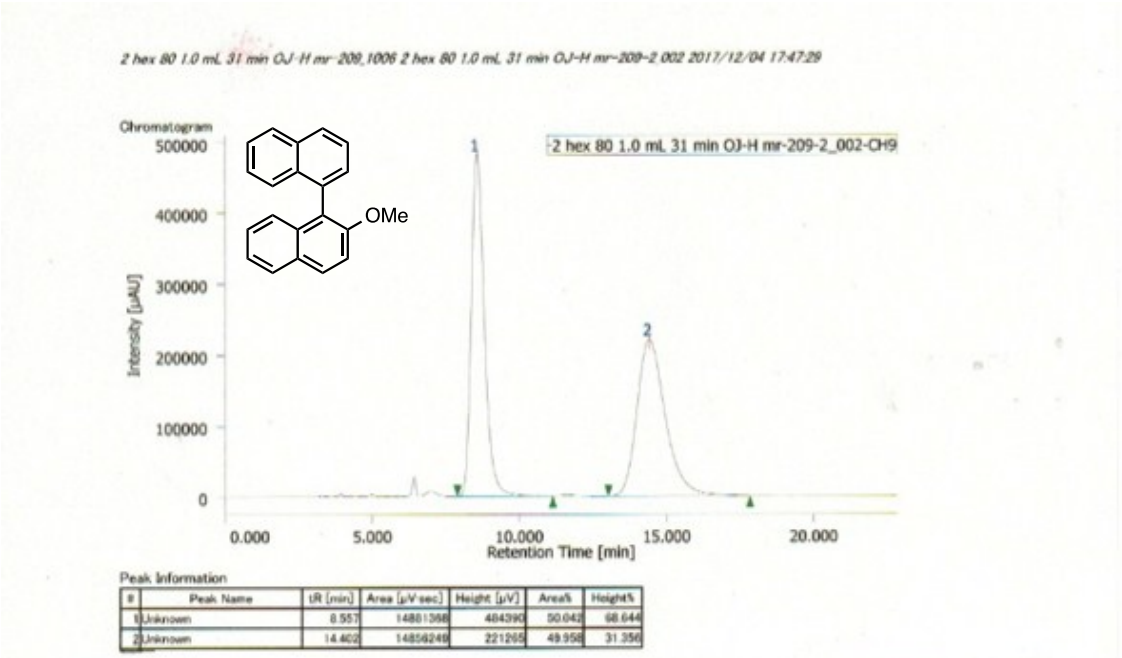

OMe
^{13}C NMR
154.76
134.68
134.41
133.84
133.09
129.62
129.16
128.58
128.37
127.94
127.89
126.52
126.32
126.00
125.83
125.71
125.65
123.72
123.38
113.98
77.41
77.16
76.91
56.92
200
150
100
50
0
ppm

Crystallographic Information

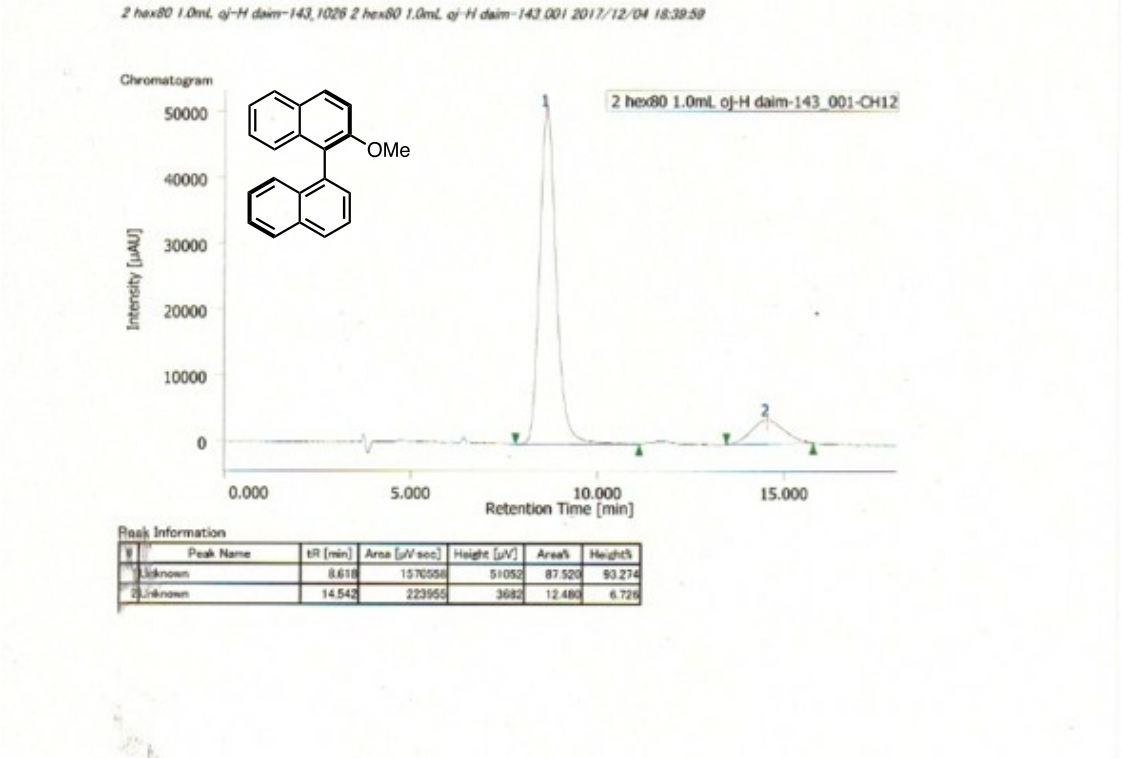
Table S3. Crystallographic data for (R_p,R_p)-[Pd(TFc*)(3-ClPy)Cl_2] **1**

	(R_p,R_p)-[Pd(TFc*)(3-ClPy)Cl_2] **1**
CCDC No	1812843
colour, shape	prism, red
crystal size/mm	0.20 x 0.07 x 0.06
empirical formula	$C_{34.67}H_{38.33}Cl_{4.33}Fe_2N_4Pd$
F_w	882.74
T/K	93(2)
crystal system	trigonal
space group	P 31
unit cell	
a/Å	23.629(3)
b/Å	23.629(3)
c/Å	16.877(2)
α/deg	90
β/deg	90
γ/deg	120
V/Å^3	8160(2)
Z	9
Flack parameter	0.055(15)
reflections collected	21272
independent reflections	1258
R_{int}	0.0880
R, R_w	0.1868, 0.2047
GOF	1.063

HPLC analytical data



#	Peak Name	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	8.557	14881368	484390	50.042	68.644
2	Unknown	14.402	14856248	221265	49.958	31.356



#	Peak Name	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	8.618	1570558	51052	87.520	93.274
2	Unknown	14.542	223955	3682	12.480	6.726

References

[1] C. Pan, Z. Zhu, M. Zhang and Z. Gu, *Angew. Chem., Int. Ed.,* 2017, **56**, 4777.

[2] S.-i. Fukuzawa, H. Oki, M. Hosaka, J. Sugasawa and S. Kikuchi, *Org. Lett.*, 2007, **9**, 5557.

[3] V. Mamane and O. Riant, *Tetrahedron*, 2001**, 57**, 2555.

[4] T. Takahashi, T. Konno, K. Ogata and S.-i. Fukuzawa, *J. Org. Chem.*, 2012, **77**, 6638.

[5] T. Mitsui, M. Sugihara, Y. Tokoro and S.-i. Fukuzawa, *Tetrahedron*, 2015, **71**, 1509.

[6] A. Bermejo, A. Ros, R. Fernández and J. M. Lassaletta, *J. Am. Chem. Soc.*, 2008, **130**, 15798.