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Supporting information

Planar-chiral ferrocene-based triazolylidene copper complexes: synthesis, characterization, and catalysis in asymmetric borylation of α,β-unsaturated ester

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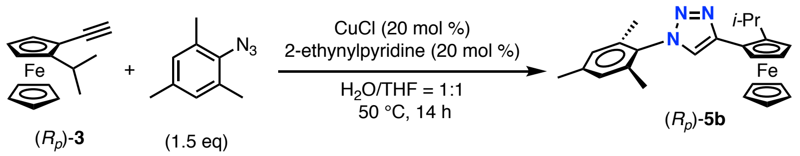
Contents

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 ($\delta = 0$ ppm) when $CDCl_3$ was used as a solvent and $CDCl_3$ for ^{13}C NMR as an internal standard ($\delta = 77.16$ ppm) when $CDCl_3$ was used as a solvent. ^{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 OD-H. High-resolution mass spectra (HRMS) were measured by a JEOL JMS-T100LC AccuTOF. Infrared (IR) spectra were measured by an FT/IR-4100ST spectrometer. 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 FUJIFILM Wako Pure Chemical Corporation. (199-00882, >99%). Copper(I) Chloride was purchased from nacalai tesque (09508-42, 95%). Bis(pinacolato)diboron was purchased from Tokyo Chemical Industry Co., Ltd. (B1964, >99%). Sodium *tert*-butoxide was purchased from Tokyo Chemical Industry Co., Ltd. (S0450, >98%) Potassium *tert*-butoxide was purchased from Tokyo Chemical Industry Co., Ltd. (P1008, >97%). Trimethyloxonium tetrafluoroborate was purchased from Tokyo Chemical Industry Co., Ltd. (T1507, >95%). Trimethylaluminium was purchased from Kanto Chemical Co., Inc. (40935-25). Tetramethylammonium chloride was purchased from Tokyo Chemical Industry Co., Ltd. (T0136, >98%) Acetyl chloride was purchased from nacalai tesque (00524-05, 95%). 2-Ethynylpyridine was purchased from Tokyo Chemical Industry Co., Ltd. (E0340, >97%). Tetrahydrofuran was purchased from Kanto Chemical Co., Inc. (41001-84, >99.5%). Dichloromethane was purchased from Kanto Chemical Co., Inc. (10158-81, >99%), distilled from calcium hydride and stored under nitrogen. Unless otherwise noted, commercially available reagents were used without purification. (R_p)-1-Ethynyl-2-isopropylferrocene [(R_p)-**3**][1], (S,R_p)-2-{1-(dimethylamino)ethyl}ferrocenyl azide [(S,R_p)-**4**][1], (R_p,R_p)-1,4-di-{2-(isopropyl)ferrocenyl}-1*H*-1,2,3-triazole [(R_p,R_p)-**5**][1], 2-ethynyl-1,3,5-trimethylbenzene[2], and 2-azide-1,3,5-trimethylbenzene[3], were prepared according to the literature.

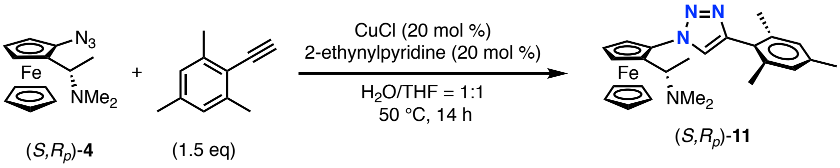
Experimental Procedure

Procedure for preparation of **(R_p)-4-[2-(isopropyl)ferrocenyl]-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole** (R_p)-**5b**



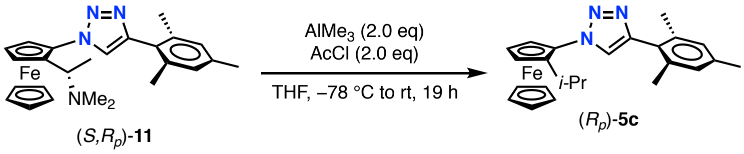
Copper(I) chloride (20 mg, 0.2 mmol) and 2-ethynylpyridine (21 mg, 0.2 mmol) were placed in a 100-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in water (5 mL) and tetrahydrofuran (5 mL). To the mixture were added (R_p)-**3** (0.25 g, 1.0 mmol) and mesityl azide (0.24 g, 1.5 mmol) at room temperature. After being stirred at 50 °C for 14 h, the reaction mixture was quenched with ammonia aqueous solution (10 mL) and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. The resultant residue was purified by flash silica gel column chromatography using a mixture of ethyl acetate/hexane (5/1), affording (R_p)-**5b** (0.28 g, 0.67 mmol) in 67% yield.

Procedure for preparation of **(S,R_p)-1-[2-{1-(dimethylamino)ethyl}ferrocenyl]-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole** (*S*,$\mathrm{R_p}$)-**11**



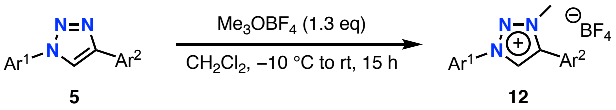
Copper(I) chloride (0.51 g, 0.52 mmol) and 2-ethynylpyridine (0.54 g, 0.52 mmol) were placed in a 100-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in water (10 mL) and tetrahydrofuran (10 mL). To the mixture were added 2,4,6-timethylphenylacethylene (0.56 g, 3.9 mmol) and (S,R_p)-**4** (0.78 g, 2.6 mmol) at room temperature. After being stirred at 50 °C for 14 h, the reaction mixture was quenched with ammonia aqueous solution (10 mL) and extracted with ethyl acetate three times. The combined organic layers were washed with Brine, dried over magnesium sulfate, and concentrated *in vacuo*. The resultant crude (*S*,*R*$_p$)-**11** was used for the next reaction without purification.

Procedure for preparation of (*R*$_p$)-1-[2-(isopropyl)ferrocenyl]-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole (*R*$_p$)-5c



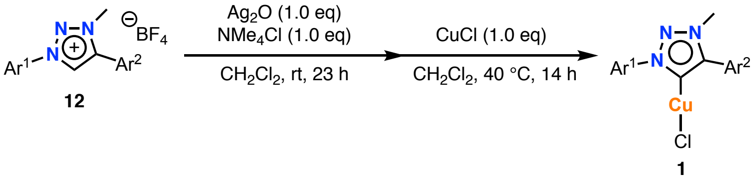
(*S*,*R*$_p$)-**11** was placed in a 200-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in dry tetrahydrofuran (15 mL). To the stirred solution was added acetyl chloride (0.31 mL, 2.4 mmol) dropwise at −78 °C, followed by the addition of trimethylaluminum (1.8 M in toluene, 1.3 mL, 2.4 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 19 h. The reaction was quenched with saturated aqueous solution of sodium hydrogen carbonate (15 mL), and the solution was extracted with dichloromethane. The combined organic layers were washed with Brine, dried over magnesium sulfate, and concentrated *in vacuo*. The resultant residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (5/1) as an eluent, affording (*R*$_p$)-**5c** in 33% yield over 2 steps from (*S*,*R*$_p$)-**4**.

General Procedure for preparation of the triazolium salt 12



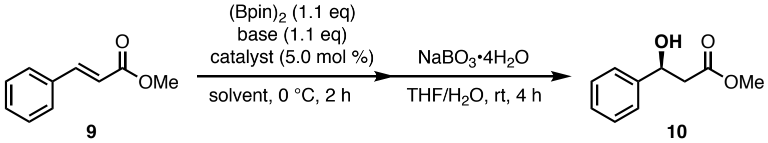
Triazole **5** was placed in a 50-mL three-neck round-bottom flask under a nitrogen atmosphere and dissolved in dry dichloromethane. After the addition of Me_3OBF_4 (1.3 eq) at −10 °C, the resulting mixture was allowed to warm to room temperature. The mixture was stirred at room temperature for 15 h and was quenched with methanol (25 mL). The volatiles were removed under reduced pressure, and the resultant residue was washed with diethyl ether to afford triazolium salt **12**.

General Procedure for preparation of the triazolylidene copper complexes 1



Triazolium salt **12** (1.0 eq), silver(I) oxide (1.0 eq), and NMe_4Cl (1.0 eq) were placed in a 50-mL Schlenk flask under a nitrogen atmosphere and dissolved in dry dichloromethane. The mixture was stirred in the dark at room temperature for 23 h. To the solution was added CuCl (1.0 equiv.), and the resultant mixture was stirred at 40 °C for further 14 h, followed by filtration through a pad of Celite. The filtrate was concentrated *in vacuo* to give the crude product, which was purified by flash silica gel column chromatography to afford triazolylidene copper complex **1**.

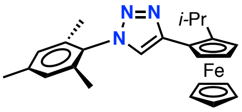
Representative procedure for the asymmetric borylation of methyl cinnamate with bis(pinacolato)diboron



To a 5-mL vial were added sequentially lithium *tert*-butoxide (0.22 mmol, 18 mg), catalyst **1a** (0.010 mmol, 6.3 mg) in a glovebox. After the vial was take out of the glovebox, THF (1 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 20 min, and a THF (0.5 mL) solution of bis(pinacolato)diboron (0.22 mmol, 56 mg) was added to the reaction mixture at 0 °C. After the resulting mixture was stirred at 0 °C for 10 min, a THF solution of methyl cinnamate (0.20 mmol, 32 mg) was added to the mixture. The mixture was stirred at 0 °C for 2 h and then was quenched with $NaBO_3·4H_2O$ and water. After the resulting mixture was stirred at room temperature for 4 h, the mixture was extracted by ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated in *vacuo*. Purification by preparative TLC (PTLC) (hexane/ethyl acetate = 4/1) gave **10** as a colorless oil. Enantio excess of **10** was determined by HPLC analysis with a chiral stationary phase column (Daicel, Chiralpak OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 225 nm, 30 °C): t_{major} = 31.1 min, t_{minor} = 46.7 min).

Characterization Data

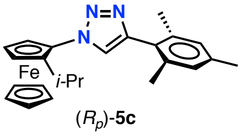
(*R*$_p$)-4-[2-(isopropyl)ferrocenyl]-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole [(*R*$_p$)-5b].



(*R*$_p$)-**5b**

Yield: 67% (0.28 g); orange solid; R_f 0.33 (hexane/ethyl acetate = 5/1); $[\alpha]_D^{25}$ –31.6 (c 0.15, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.58 (s, 1H), 7.00 (s, 2H), 4.84–4.77 (m, 1H), 4.26 (s, 1H), 4.24 (s, 1H), 4.07 (s, 5H), 3.25 (qq, *J* = 6.8, 6.8 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 6H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ: 146.4, 140.0, 135.2, 133.7, 129.2, 121.5, 95.1, 70.9, 70.2, 67.9, 67.0, 66.2, 27.1, 25.0, 22.0, 21.2, 17.4 ppm; IR (KBr): 3455.8, 3095.2, 2959.2, 2921.6, 2865.7, 2737.5, 1609.3, 1577.5, 1496.5, 1458.9, 1398.1, 1377.9, 1327.8, 1290.1, 1247.7, 1222.7, 1161.9, 1129.1, 1105.0, 1038.5, 1012.5, 999.9, 988.3, 938.2, 852.4, 814.8, 753.1, 634.5, 613.3, 587.2, 534.2 cm^{-1}; ESI-HRMS (*m/z*): [M+Na]$^+$ calcd for $C_{24}H_{27}N_3FeNa$ 436.1452, found 436.1446.

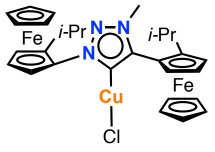
(*R*$_p$)-1-[2-(isopropyl)ferrocenyl]-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole [(*R*$_p$)-5c].



(*R*$_p$)-**5c**

Yield: 20% (0.35 g); orange solid; R_f 0.13 (hexane/ethyl acetate = 5/1); $[\alpha]_D^{25}$ –8.7 (c 0.07, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.73 (s, 1H), 6.97 (s, 2H), 4.70–4.66 (m, 1H), 4.29 (s, 5H), 4.23–4.17 (m, 2H), 2.96 (qq, *J* = 6.8, 6.8 Hz, 1H), 2.34 (s, 3H), 2.18 (s, 6H), 1.35 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ: 145.1, 138.3, 137.9, 128.6, 127.1, 125.6, 92.6, 91.6, 71.6, 70.6, 65.4, 64.7, 26.0, 24.4, 22.1, 21.3, 20.9 ppm; IR (KBr): 3155.9, 3093.3, 2963.1, 2919.7, 2863.8, 1612.2, 1577.5, 1570.7, 1560.1, 1542.8, 1525.4, 1508.1, 1501.3, 1467.6, 1458.9, 1450.2, 1439.6, 1409.7, 1385.6, 1376.9, 1361.5, 1321.0, 1290.1, 1260.3, 1212.0, 1183.1, 1170.6, 1106.0, 1031.7, 1101.8, 941.1, 899.6, 884.2, 848.5, 825.4, 807.1, 743.4, 675.9, 639.3, 619.0, 576.6, 551.5, 540.9 cm^{-1}; ESI-HRMS (*m/z*): [M+H]$^+$ calcd for $C_{24}H_{28}N_3Fe$ 414.1633, found 414.1623.

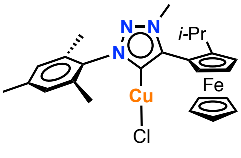
(*R*$_p$,*R*$_p$)-1,4-Di-[2-(isopropyl)ferrocenyl]-3-methyl-1*H*-1,2,3-triazol-5-ylidene copper(I) chloride (1a)



1a

Yield: 57% (0.12 g); orange solid; R_f 0.23 (hexane/ethyl acetate = 5/1); $[\alpha]_D^{25}$ +90.7 (c 0.1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ: 5.16 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.44 (s, 5H), 4.39–4.33 (m, 2H), 4.35 (s, 5H), 4.33–4.31 (m, 1H), 4.27–4.25 (m, 1H), 4.24–4.21 (m, 1H), 3.94 (s, 3H), 3.60 (qq, $J = 6.8, 6.8$ Hz, 1H), 3.06 (qq, $J = 6.8, 6.8$ Hz, 1H), 1.40–1.34 (m, 6H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.64 (d, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.7(C_{carbene}), 146.2($C_{\text{trz-4}}$), 98.0(C_{Fero}), 96.1(C_{Fero}), 91.8(C_{Fero}), 71.2(C_{Fero}), 71.1(C_{Fero}), 71.1(C_{Fero}), 67.6(C_{Fero}), 67.1(C_{Fero}), 66.4(C_{Fero}), 66.3(C_{Fero}), 65.3(C_{Fero}), 64.8(C_{Fero}), 37.0(C_{Me}), 26.7($C_{i\text{-Pr}}$), 25.9($C_{i\text{-Pr}}$), 25.4($C_{i\text{-Pr}}$), 24.6($C_{i\text{-Pr}}$), 22.1($C_{i\text{-Pr}}$), 21.6($C_{i\text{-Pr}}$) ppm; IR (KBr): 3455.8, 3092.3, 2958.3, 2924.5, 2866.7, 1628.6, 1560.1, 1542.8, 1457.9, 1424.2, 1410.7, 1380.8, 1360.5, 1262.2, 1231.3, 1170.6, 1106.9, 1067.4, 1036.5, 1000.9, 970.0, 946.9, 875.5, 824.4, 749.2, 733.8, 720.3, 688.5, 678.8, 669.2, 644.1, 621.9, 566.0, 540.0 cm^{-1}; ESI-HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{29}H_{33}N_3ClCuFe_2Na$ 656.0256, found 656.0257.

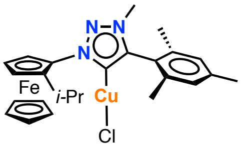
(*R*$_p$)-4-[2-(isopropyl)ferrocenyl]-3-methyl-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazol-5-ylidene copper(I) chloride (1b).



1b

Yield: 71% (0.047 g); orange solid; R_f 0.69 (dichloromethane); $[\alpha]_D^{25}$ –40.3 (c 0.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.02 (s, 1H), 6.99 (s, 1H), 4.42 (s, 5H), 4.40–4.36 (m, 2H), 4.36–4.33 (m, 1H), 3.98 (s, 3H), 3.79–3.68 (m, 1H), 2.36 (s, 3H), 2.16 (s, 3H), 2.00 (s, 3H), 1.41 (d, $J = 6.8$ Hz, 3H), 0.70 (d, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.8(C_{carbene}), 146.9($C_{\text{trz-4}}$), 140.5(C_{benz}), 136.4(C_{benz}), 134.1(C_{benz}), 133.9(C_{benz}), 129.6(C_{benz}), 129.6(C_{benz}), 98.0(C_{Fero}), 71.2(C_{Fero}), 70.8(C_{Fero}), 67.7(C_{Fero}), 67.2(C_{Fero}), 66.6(C_{Fero}), 37.0(C_{Me}), 26.9(C_{Me}), 25.3(C_{Me}), 21.5(C_{Me}), 21.3($C_{i\text{-Pr}}$), 17.9($C_{i\text{-Pr}}$), 17.5($C_{i\text{-Pr}}$) ppm;; IR (KBr): 3464.5, 3092.3, 3080.7, 2956.3, 2920.7, 2862.8, 1654.6, 1638.2, 1628.6, 1618.0, 1609.3, 1560.1, 1542.8, 1509.0, 1490.7, 1458.9, 1449.2, 1439.6, 1407.8, 1337.9, 1360.5, 1322.0, 1291.1, 1266.0, 1230.4, 1185.0, 1131.1, 1106.0, 1071.3, 1035.6, 1001.8, 960.4, 852.4, 823.5, 812.8, 756.9, 737.6, 681.7, 671.1, 654.7, 622.9, 594.9, 583.4, 569.9, 537.1 cm^{-1}; ESI-HRMS (*m/z*): $[2M-CuCl_2]^+$ calcd for $C_{50}H_{58}N_6CuFe_2$ 917.2718, found 917.2748.

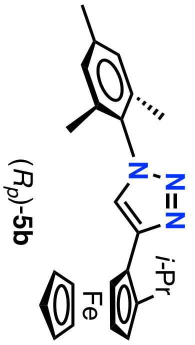
(*R*$_p$)-1-[2-(isopropyl)ferrocenyl]-3-methyl-4-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazol-5-ylidene copper(I) chloride (1c).



1c

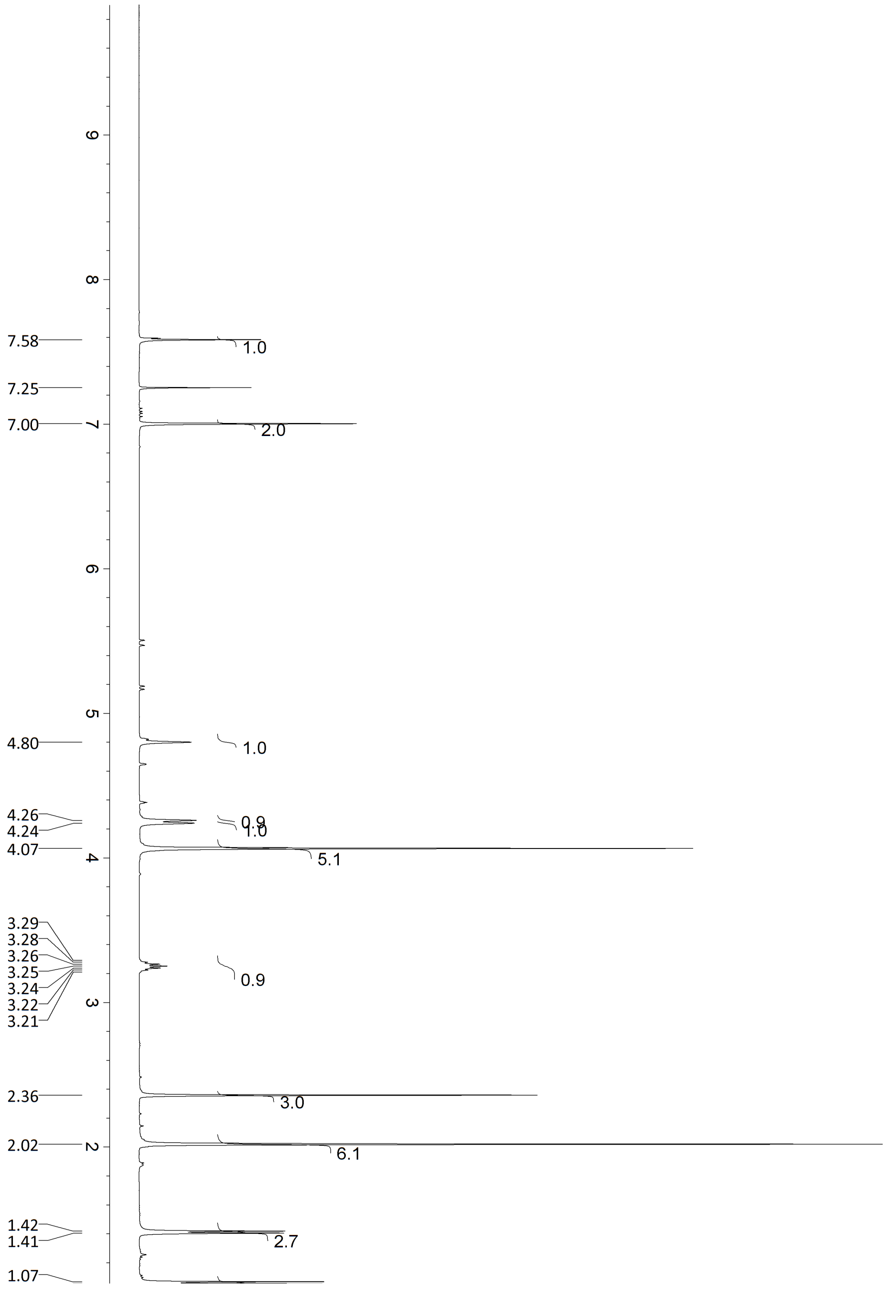
Yield: 76% (0.40 g); orange solid; R_f 0.19 (dichloromethane); $[\alpha]_D^{25}$ +83.1 (c 0.008, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.99 (s, 1H), 6.98 (s, 1H), 5.22–5.11 (m, 1H), 4.35 (s, 5H), 4.30–4.21 (m, 2H), 3.81 (s, 3H), 3.32–3.12 (m, 1H), 2.34 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.39 (d, $J = 6.8$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.9(C_{carbene}), 146.8($C_{\text{trz-4}}$), 140.6(C_{benz}), 138.0(C_{benz}), 138.0(C_{benz}), 129.1(C_{benz}), 129.1(C_{benz}), 123.2(C_{benz}), 95.8(C_{Fero}), 91.7(C_{Fero}), 71.2(C_{Fero}), 66.2(C_{Fero}), 65.4(C_{Fero}), 64.9(C_{Fero}), 36.1(C_{Me}), 26.2(C_{Me}), 24.7(C_{Me}), 22.1(C_{Me}), 21.4($C_{i\text{-}\mathrm{Pr}}$), 20.6($C_{i\text{-}\mathrm{Pr}}$), 20.4($C_{i\text{-}\mathrm{Pr}}$) ppm; IR (KBr): 2962.1, 2947.7, 2919.7, 2859.2, 2126.1, 1654.6, 1647.9, 1637.3, 1611.2, 1560.1, 1458.9, 1439.6, 1406.8, 1379.8, 1364.4, 1324.9, 1304.6, 1262.2, 1235.2, 1170.6, 1148.4, 1106.0, 1064.5, 1038.5, 1024.0, 998.0, 960.4, 874.6, 853.3, 845.6, 826.3, 813.8, 763.7, 691.4, 672.1, 661.5, 641.2, 623.9, 592.0, 568.9, 557.3, 539.0 cm^{-1}; ESI-HRMS (*m/z*): $[2M-CuCl_2]^+$ calcd for $C_{50}H_{58}N_6CuFe_2$ 917.2718, found 917.2690.

NMR Spectra Data

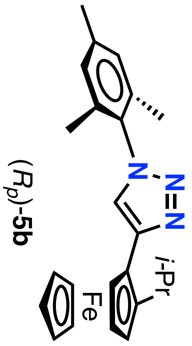


(*R*$_p$)-**5b**

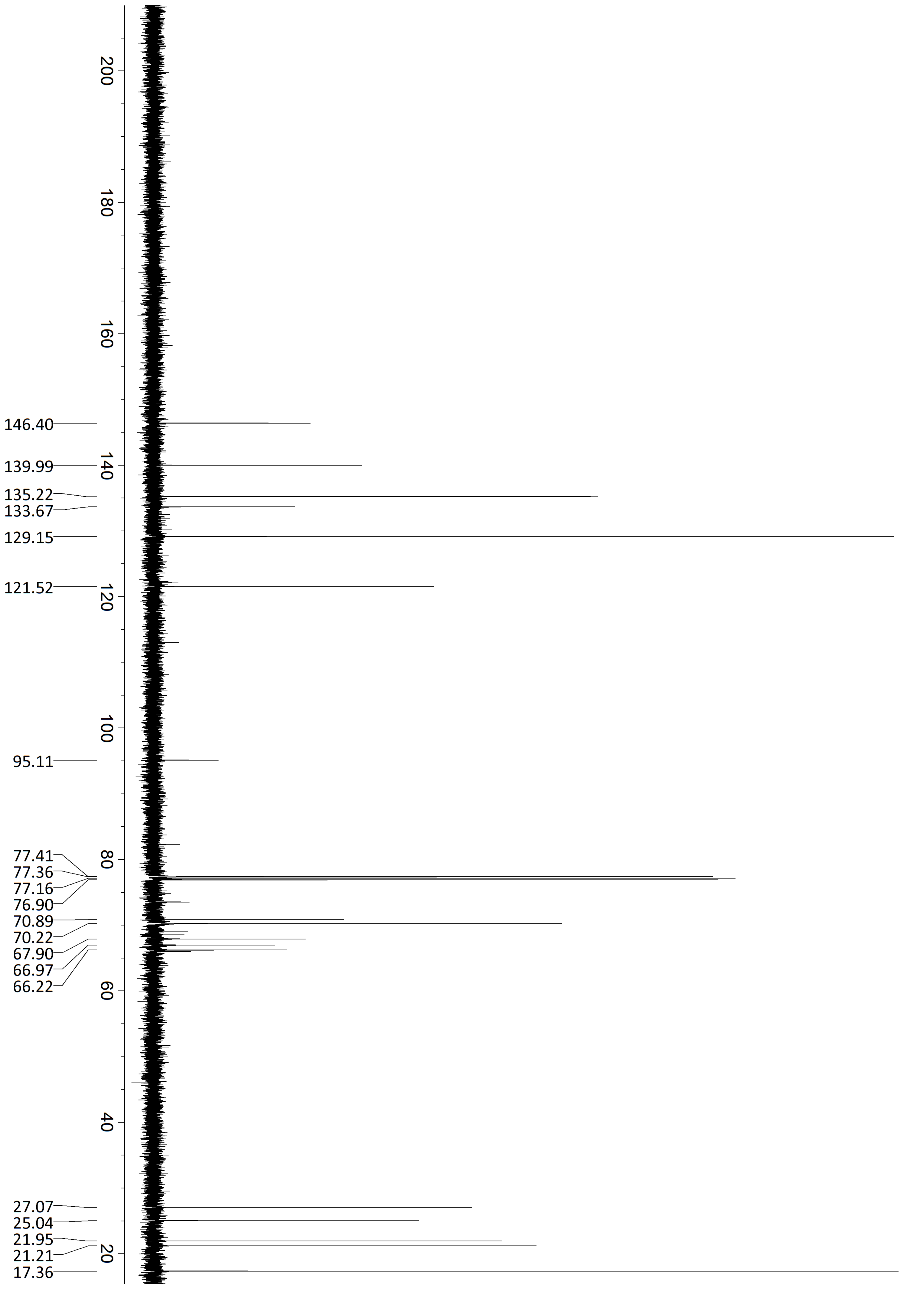
^{1}H NMR



^{13}C NMR



(*R*$_p$)-**5b**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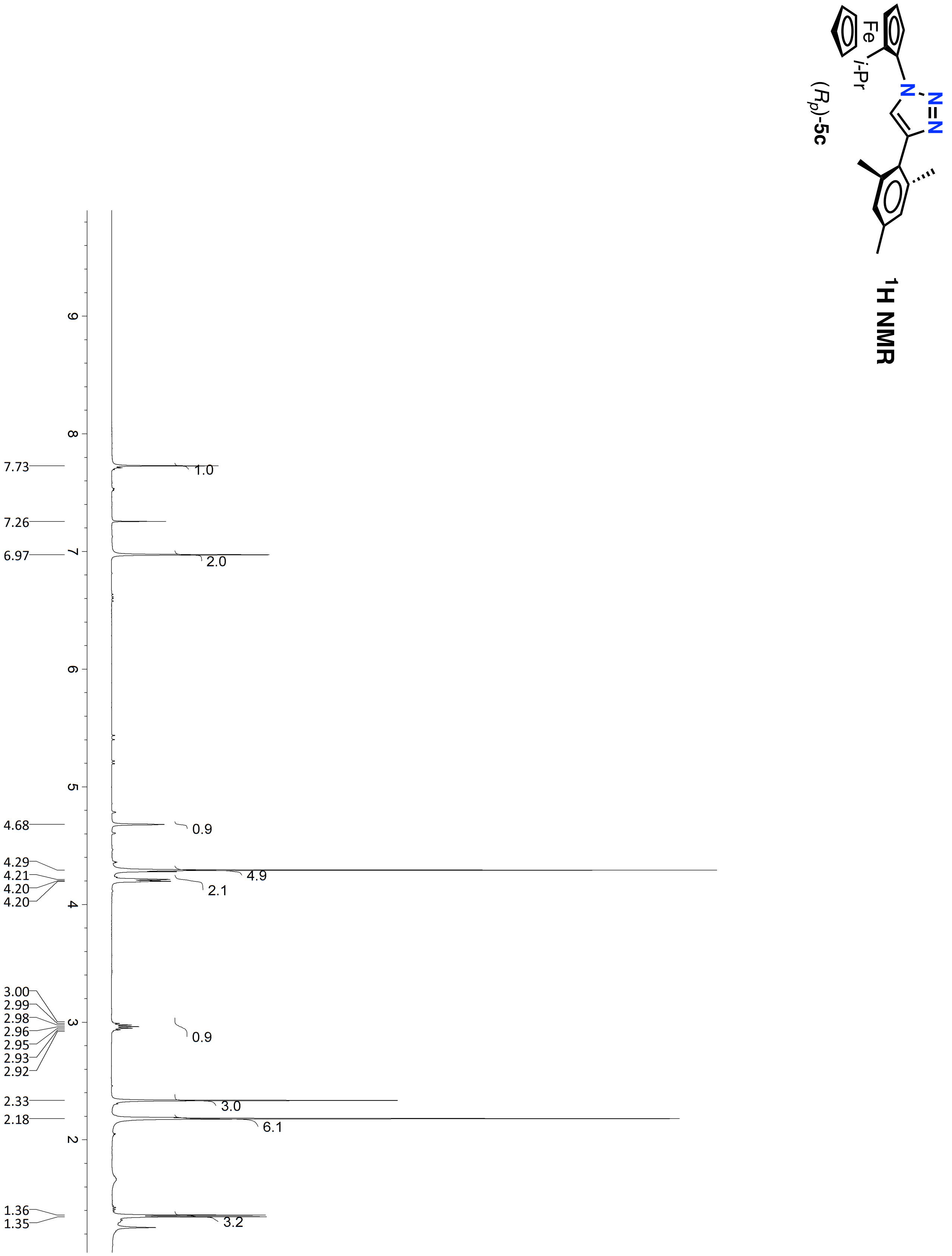
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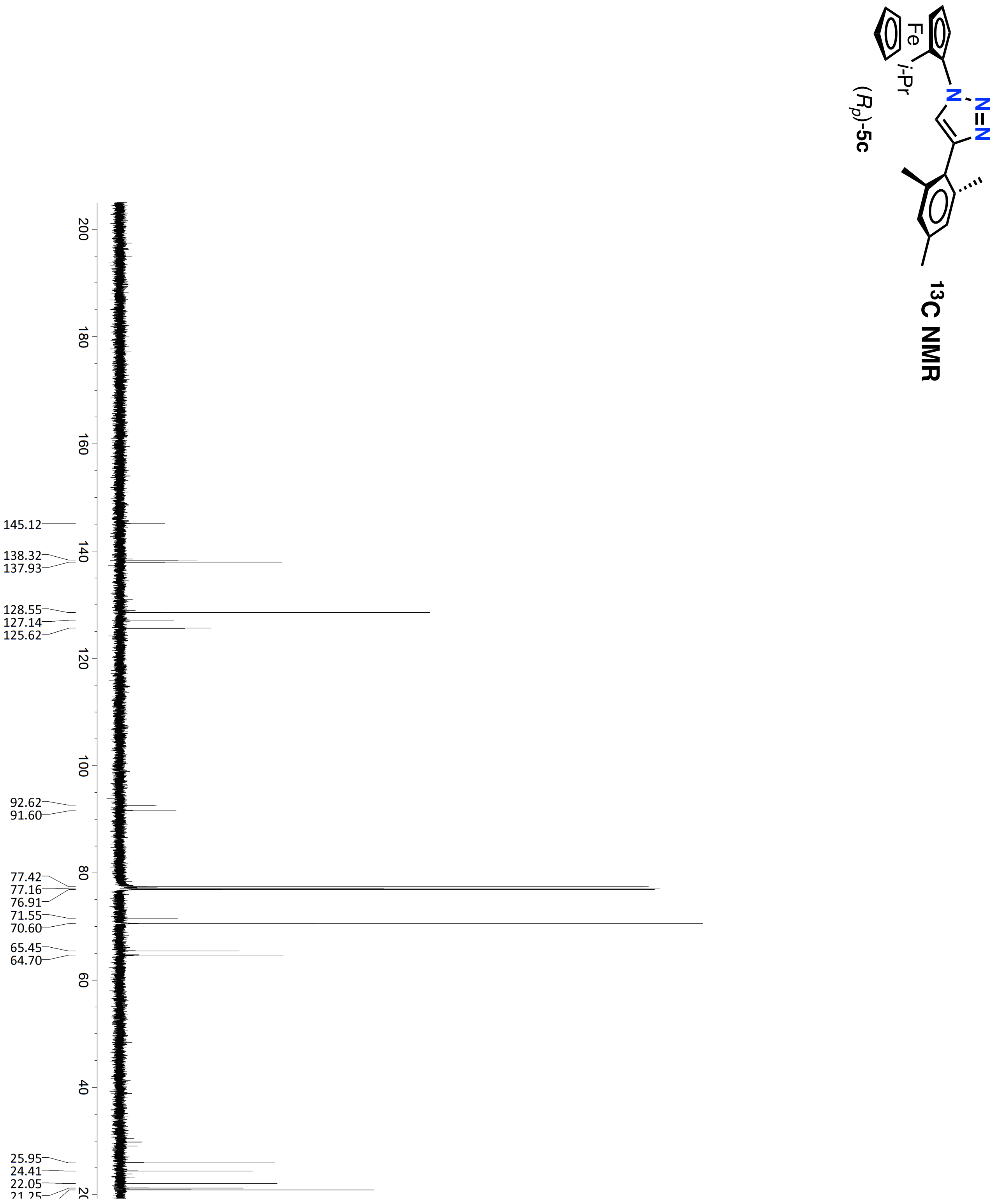
0.9
3.0
6.1
3.2

(R_p)-**5c**

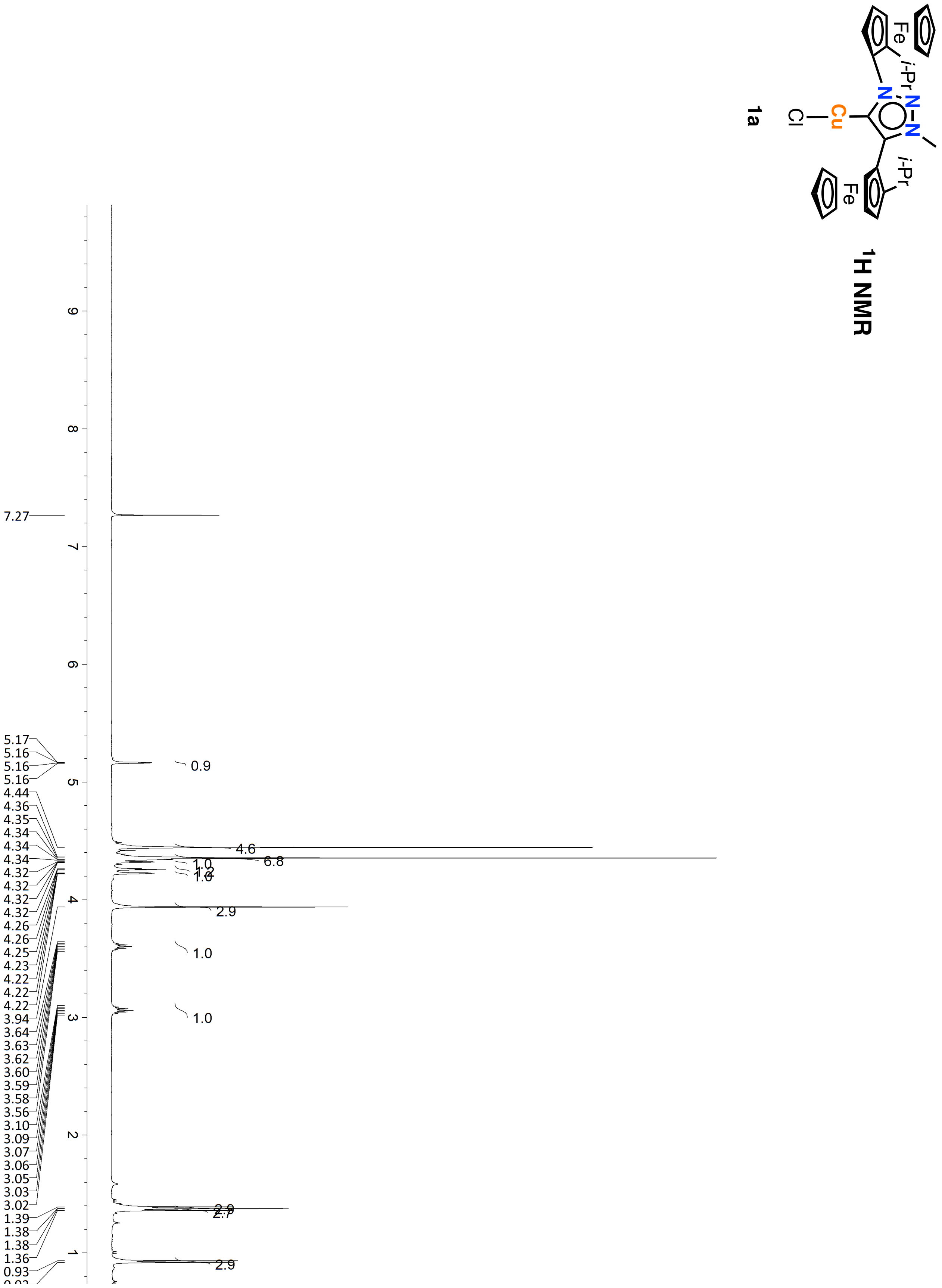
^{1}H NMR



^{13}C NMR

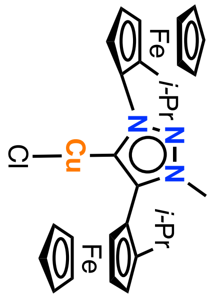
(R_p)-**5c**

Fe
i-Pr
N
N=N
200
180
160
140
120
100
80
60
40
20
145.12
138.32
137.93
128.55
127.14
125.62
92.62
91.60
77.42
77.16
76.91
71.55
70.60
65.45
64.70
25.95
24.41
22.05
21.25


Fe
i-Pr
N
N–N
Cu
Cl
i-Pr
Fe
9
8
7.27
7
6
5.17
5.16
5.16
5.16
4.44
4.36
4.35
4.34
4.34
4.34
4.32
4.32
4.32
4.32
4.26
4.26
4.25
4.23
4.22
4.22
4.22
3.94
3.64
3.63
3.62
3.60
3.59
3.58
3.56
3.10
3.09
3.07
3.06
3.05
3.03
3.02
1.39
1.38
1.38
1.36
0.93
5
4
3
2
1
0.9
4.6
6.8
1.0
1.2
1.0
2.9
1.0
1.0
2.9
2.7
2.9

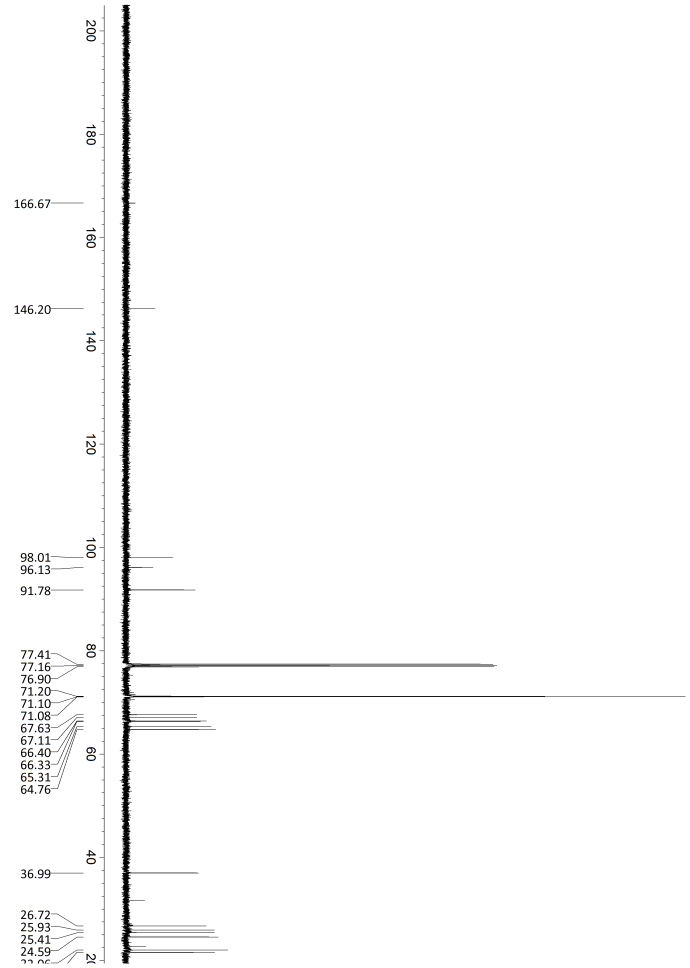
1a

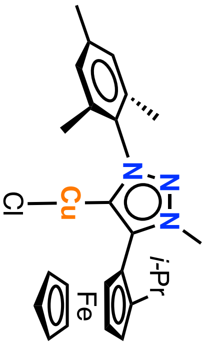
^{1}H NMR


Fe
i-Pr
N
N–N
Cu
Cl
i-Pr
Fe

1a

^{13}C NMR

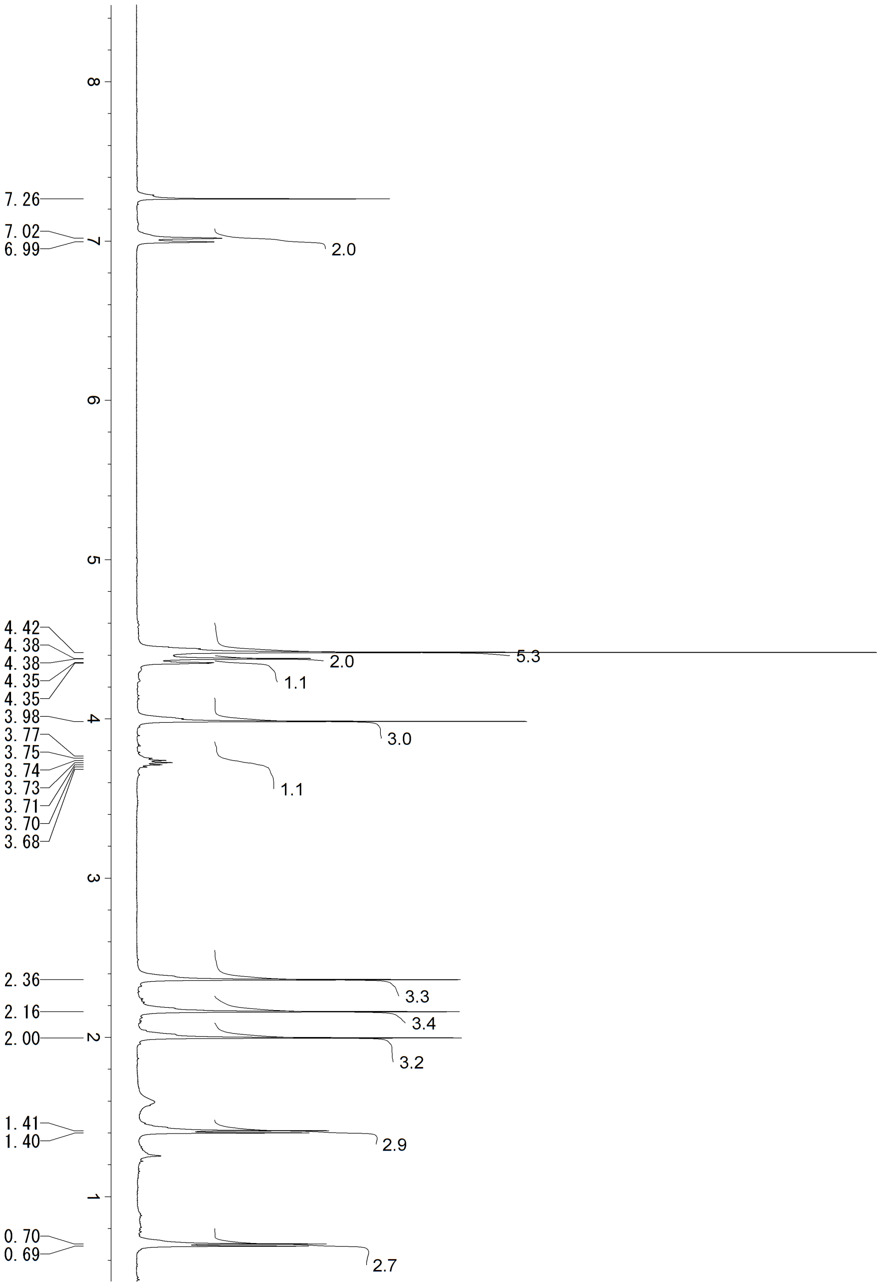

200
180
166.67
160
146.20
140
120
100
98.01
96.13
91.78
80
77.41
77.16
76.90
71.20
71.10
71.08
67.63
67.11
66.40
66.33
65.31
64.76
60
40
36.99
26.72
25.93
25.41
24.59



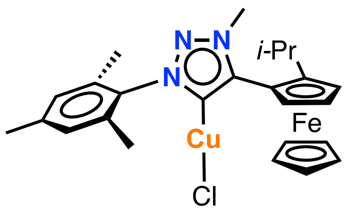
N
N
N
Cu
Cl
i-Pr
Fe

1b

^{1}H NMR

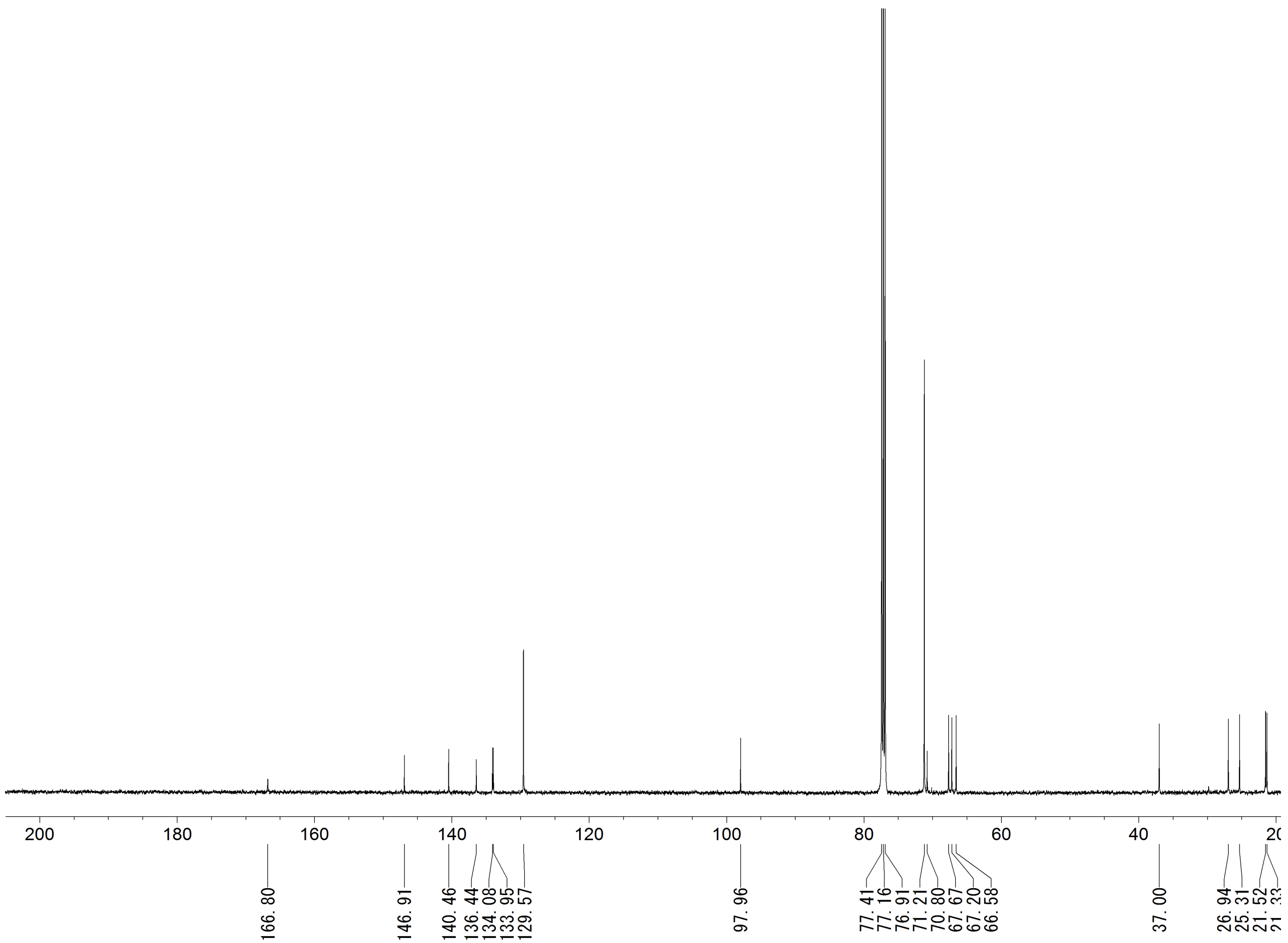


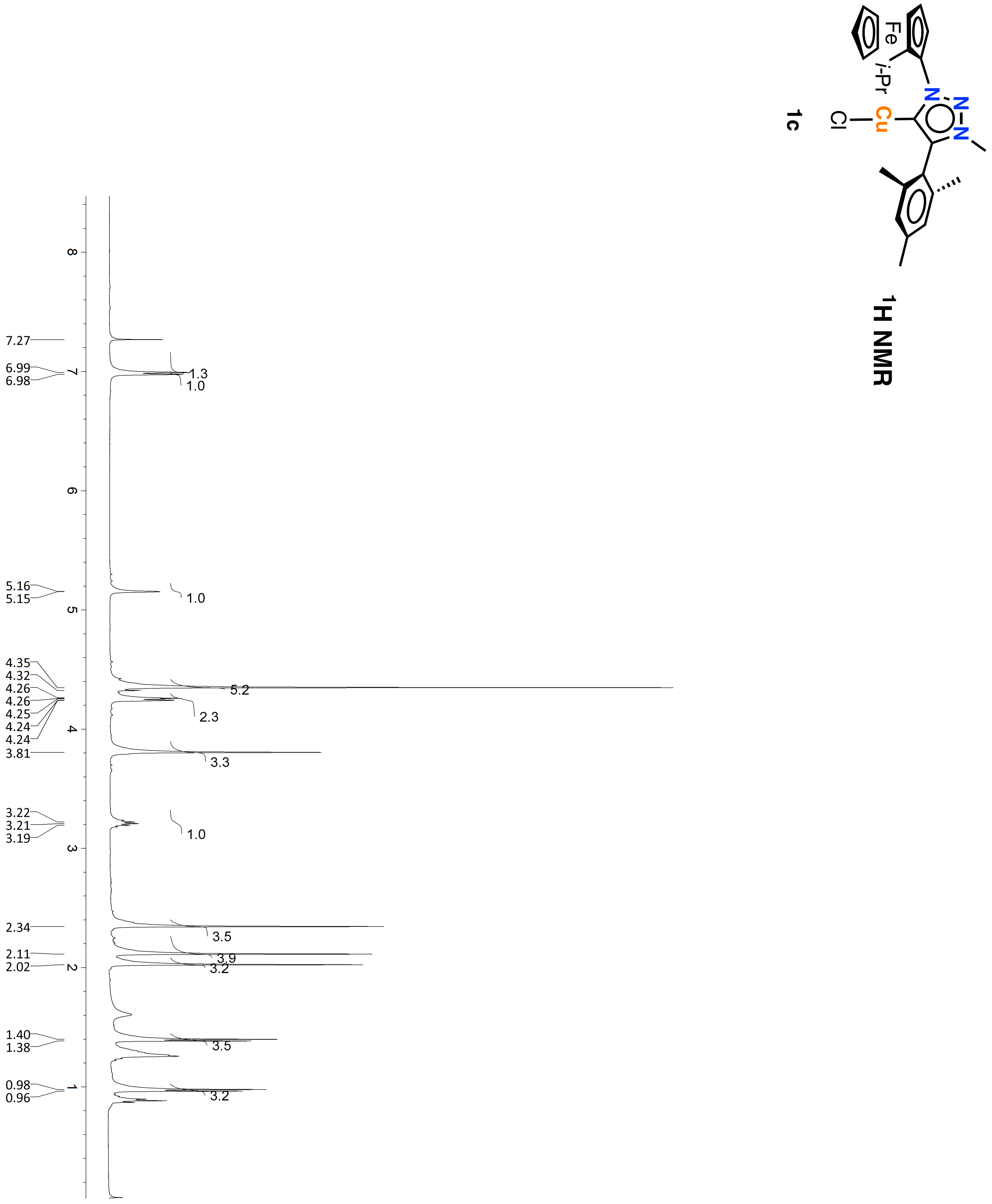
8
7
6
5
4
3
2
1
7.26
7.02
6.99
4.42
4.38
4.38
4.35
4.35
3.98
3.77
3.75
3.74
3.73
3.71
3.70
3.68
2.36
2.16
2.00
1.41
1.40
0.70
0.69
2.0
5.3
2.0
1.1
3.0
1.1
3.3
3.4
3.2
2.9
2.7


N
N
N
i-Pr
Cu
Cl
Fe

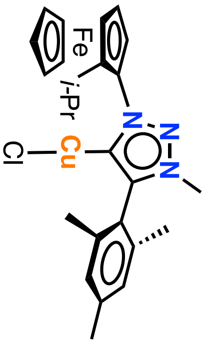
1b

^{13}C NMR

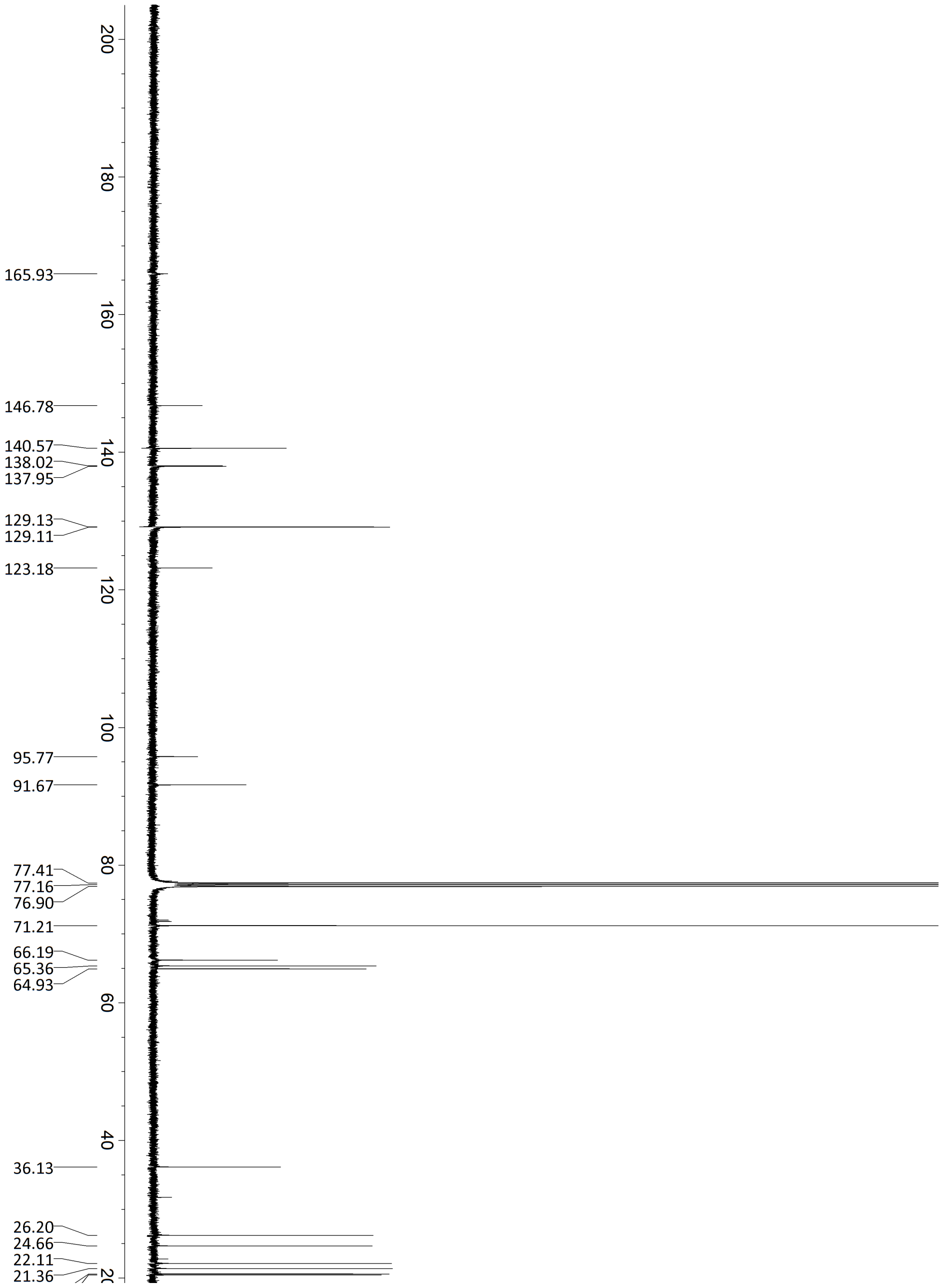

200
180
160
140
120
100
80
60
40
166. 80
146. 91
140. 46
136. 44
134. 08
133. 95
129. 57
97. 96
77. 41
77. 16
76. 91
71. 21
70. 80
67. 67
67. 20
66. 58
37. 00
26. 94
25. 31
21. 52


Fe
i-Pr
Cu
Cl
N
N
N
1c
1H NMR
7.27
6.99
6.98
5.16
5.15
4.35
4.32
4.26
4.26
4.25
4.24
4.24
3.81
3.22
3.21
3.19
2.34
2.11
2.02
1.40
1.38
0.98
0.96
8
7
6
5
4
3
2
1
1.3
1.0
1.0
5.2
2.3
3.3
1.0
3.5
3.9
3.2
3.5
3.2

^{13}C NMR


Fe
i-Pr
N
N–N
Cu
Cl

1c


165.93
146.78
140.57
138.02
137.95
129.13
129.11
123.18
95.77
91.67
77.41
77.16
76.90
71.21
66.19
65.36
64.93
36.13
26.20
24.66
22.11
21.36
200
180
160
140
120
100
80
60
40
20

Crystallographic Information

Table S1. Crystallographic data for copper complex **1b**

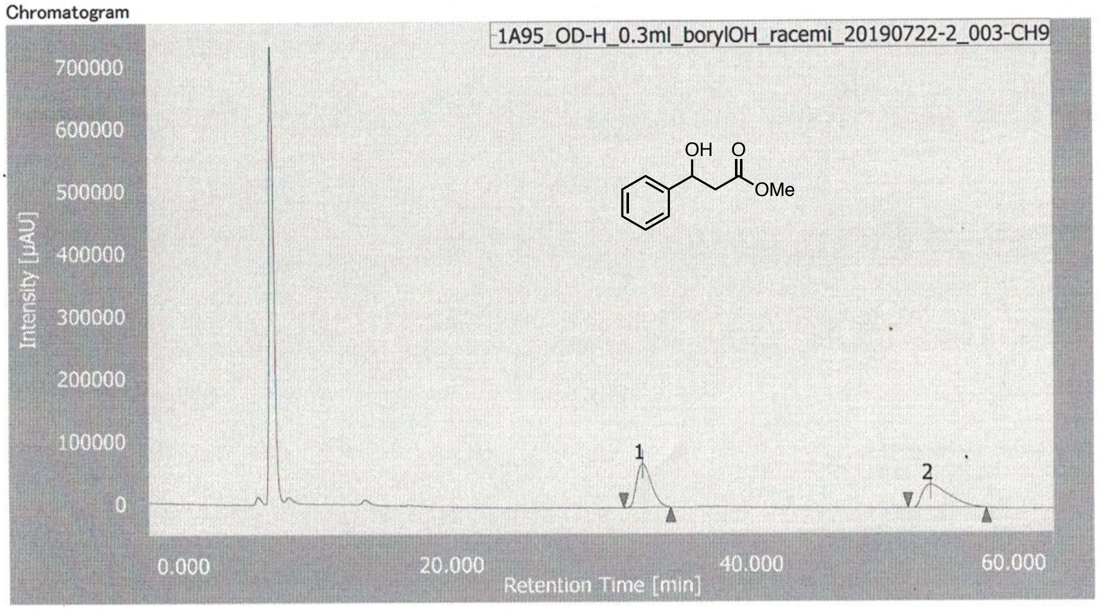
	Copper complex **1b**
CCDC No	2008346
colour, shape	prism, yellow
crystal size/mm	0.36 x 0.08 x 0.06
empirical formula	$C_{25}H_{29}ClCuFeN_3$
F_w	526.37
T/K	93
crystal system	monoclinic
space group	C 2
unit cell	
a/Å	15.573(6)
b/Å	10.617(4)
c/Å	31.122(13)
α/deg	90.000(0)
β /deg	98.741(5)
γ/deg	90.000(0)
V/Å^3	5086(4)
Z	8
Flack parameter	0.022(19)
reflections collected	20794
independent reflections	11178
R_{int}	0.0654
R, R_w	0.0845, 0.1018
GOF	1.000

Table S2. Crystallographic data for copper complex **1c**

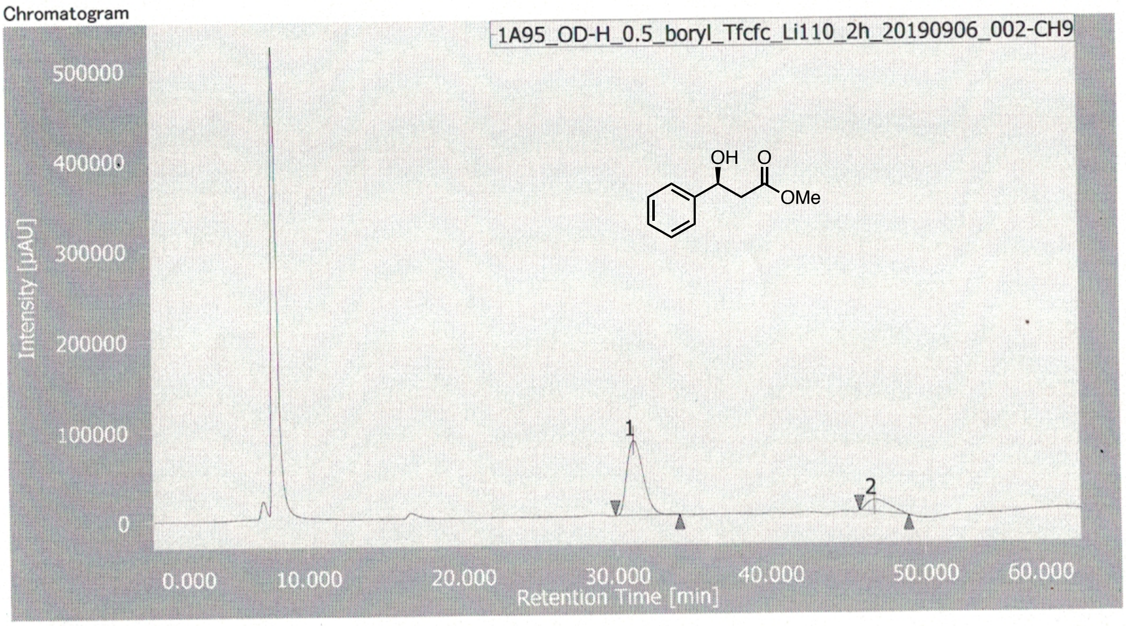
	Copper complex **1c**
CCDC No	2008348
colour, shape	prism, orange
crystal size/mm	0.40 x 0.23 x 0.08
empirical formula	$C_{25}H_{29}ClCuFeN_3$
F_w	526.37
T/K	93
crystal system	monoclinic
space group	P 21
unit cell	
a/Å	8.244(4)
b/Å	15.110(6)
c/Å	9.885(4)
α/deg	90.000(0)
β/deg	107.249(5)
γ/deg	90.000(0)
V/Å^3	1176.1(8)
Z	2
Flack parameter	-0.019(15)
reflections collected	9551
independent reflections	5343
R_{int}	0.0553
R, R_w	0.0472, 0.0991
GOF	1.000

HPLC Analytical Data

1A95_OD-H_0.3ml_borylOH_racemi_20190722-2_0722 1A95_OD-H_0.3ml_borylOH_racemi_20190722-2_003 2020/02/29 21:59:10



1A95_OD-H_0.5_boryl_Tfcfc_Li110_2h_20190906_0906 1A95_OD-H_0.5_boryl_Tfcfc_Li110_2h_20190906_002 2020/02/27 15:16:21



Peak Information

#	Peak Name	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	31.120	6045750	82736	80.608	85.796
2	Unknown	46.693	1454437	13698	19.392	14.204

References

[1] Haraguchi, R.; Hoshino, S.; Yamazaki, T.; Fukuzawa, S.-i. Chiral triazolylidene-Pd-PEPPSI: synthesis, characterization, and application in asymmetric Suzuki–Miyaura cross-coupling. *Chem. Commun*. **2018**, *54*, 2110−2113.

[2] Zhou, B.; Chen, H.; Wang, C. Mn-Catalyzed Aromatic C–H Alkenylation with Terminal Alkynes. *J. Am. Chem. Soc*. **2013**, *135*, 1264−1267.

[3] Kwok, S. W.; Fotsing, J. R.; Fraser, R. J.; Rodionov, V. O.; Fokin, V. V. Transition-Metal-Free Catalytic Synthesis of 1,5-Diaryl-1,2,3-triazoles. *Org. Lett*. **2010**, *12*, 4217−4219.