Supplementary Material (ESI) for Chemical Communications

A straightforward asymmetric synthesis of 1,2-disubstituted ferrocenylalkyl amines with the unusual (S_{Fc},S) configuration

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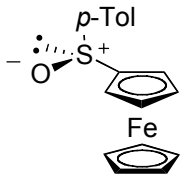
General Information

For moisture-sensitive reactions, glassware was oven-dried (120 °C, > 4 h), assembled hot and cooled under a stream of nitrogen gas before use. Reactions involving air-sensitive materials were carried out by standard syringe techniques. THF was purified by a PURESOLV^{TM} apparatus developed by Innovative Technology Inc. Temperature of –78 °C were obtained by the addition of dry ice to acetone. Melting points are uncorrected. Thin-layer chromatography (TLC) analyses were performed on Merck 0.2 mm aluminum-backed silica gel 60 F254 plates and components were visualized by illumination with UV light or by staining with phosphomolybdic acid solution (1 g in 100 mL of *i*-PrOH). Flash column chromatography was performed using Merck 0.040 to 0.063 mm, 230 to 400 mesh silica gel. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DRX 400 spectrometer. Chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS), using residual chloroform (δ 7.26 ppm) as an integral standard. The following abbreviations are used to describe NMR signals: δ, chemical shift; s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants *J* are quoted in Hertz (Hz). ^{13}C NMR spectra were recorded on a 100.6 MHz Bruker DRX 400 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from TMS, using the middle resonance of $CDCl_3$ (77.2 ppm) as an integral standard. Lithium bases were purchased from Aldrich and Acros and concentrations were checked before experiments by titration with diphenylacetic acid.

(S_S)-*p*-Tolylsulfinylferrocene 1b



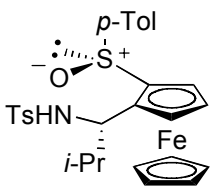
To a solution of ferrocene (2.0 g, 10.75 mmol) in THF (90 mL) was added *t*-BuOK (1.29 mL, 1 M in THF, 1.29 mmol). The mixture was cooled to –78

°C and *t*-BuLi (13,4 mL, 21.50 mmol, 1.6 M in hexanes) was added dropwise. The reaction mixture was kept at –78 °C for 1.5 h and 1 h at room temperature. The red solution was then cannulated dropwise into a cold solution (–55 °C) of (-)-(*1R*)-Menthyl (S_S)-*p*-toluenesulfinate (3.17 g, 10.75 mmol) in THF (55 mL). After 1 h at –55 °C, water (90 mL) was added. The aqueous layer was extracted with Et_2O (2 × 90 mL). The combined organic layers were washed with brine (100 ml), dried over $MgSO_4$, and evaporated to dryness. Column chromatography using *n*-heptane/ethyl acetate (v/v: 5/5) gave **1b** (2.86 g, 82%) as a yellow cotton-like solid (ee 94%) which can be recrystallized in *n*-heptane/ethyl acetate (5/5) (2.39 g, 68%) as a yellow crystals (ee 99%); Mp 149-150°C; δ_H(400 MHz; $CDCl_3$) 7.52 (2 H, d, *J* 8.4, Ar), 7.24 (2 H, d, *J* 8.4, Ar), 4.60-4.61 (1H, m, Cp-H), 4.35-4.38 (7 H, m, Cp-H), 4.31-4.33 (1 H, m, Cp-H), 2.37 (3 H, s, Me); δ_C(100.6 MHz; $CDCl_3$) 142.9, 141.0, 129.6, 124.4, 94.6, 70.0, 69.9, 67.8, 65.3, 21.4; HPLC [Daicel Chiralpak OD-H column 250 × 4.6 (L × I.D.) 5 µm, *n*-heptane/*i*-PrOH (v/v: 9/1) at 0.8 mL.min^{-1}, 204 nm, 20 °C]: 16.22 min (*R*), 18.26 min (*S*).

General procedure for addition of imines 2a on (S_S)-*p*-Tolylsulfinylferrocene 1b

To a cold solution (–78 °C) of LDA [1.2 eq, 0.15 M in dry THF, freshly prepared by treating DIPA (1.2 eq) with *n*-BuLi (1.2 eq)] was added (S_S)-*p*-Tolylsulfinylferrocene **1b** (1 eq) in dry THF (1 mL for 100 mg of **1b**). After stirring for 30 min at –78 °C, a solution of the imine **2a** (1.2 eq) in dry THF (1 mL for 100 mg of **1b**) was added dropwise. The reaction mixture was stirred at –78 °C. After completion, a 10% water solution in THF (4 mL for 100 mg of **1b**) was added at –78 °C. The reaction mixture was warmed at room temperature, then brine (4 mL for 100 mg of **1b**) was added. The aqueous layer was extracted with Et_2O (4 mL for 100 mg of **1b**). The combined organic layers were dried over $MgSO_4$ and then evaporated to dryness.

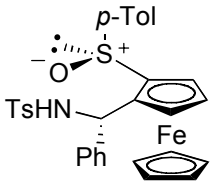
(S_{Fc},S_S,*S*)-*N*-tosyl-1-[2-(*p*-tolylsulfinyl)ferrocenyl]-2-methylpropylamine 3ba



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (1.0 g, 3.08 mmol) and imine **2a** (R_2 = *i*-Pr) (834 mg, 3.70 mmol). The mixture was stirred for 15 min at –78 °C. The crude product was purified by column chromatography on silica using *n*-heptane/diethylether (3/7) as eluent, to afford **3ba** (1.12 g, 66%) as a yellow solid (Found: C, 61.26; H, 6.07; N, 2.93.

$C_{28}H_{31}FeNO_3S_2$ requires C, 61.20; H, 5.69; N, 2.55%); Mp 133-135°C; $[\alpha]_D^{20}$ –270.0 (c 1.0 in $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 7.86 (2 H, d, *J* 8.4, Ar), 7.66 (2 H, d, *J* 8.4, Ar), 7.33 (2 H, d, *J* 8.0, Ar), 7.32 (2 H, d, *J* 8.0, Ar), 5.02 (1 H, d, *J* 8.0, C-NH), 4.63 (1 H, dd, *J* 8.0 and 4.0, CH-N), 4.30-4.32 (1 H, m, Cp), 4.26-4.27 (1 H, m, Cp), 4.20 (5 H, s, Cp), 4.16-4.17 (1 H, m, Cp), 2.44 (3 H, s, Me), 2.43 (3 H, s, Me), 1.85-1.90 (1 H, m C*H*Me_2), 0.57 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.49 (3 H, d, *J* 6.8, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.6 (Ar), 141.9 (Ar), 141.2 (Ar), 139.2 (Ar), 130.0 (2 C, Ar), 129.9 (2 C, Ar), 127.5 (2 C, Ar), 125.7 (2 C, Ar), 93.2 (C_{quat}, Cp), 91.3 (C_{quat}, Cp), 71.4 (5 C, Cp), 69.1 (Cp), 68.5 (Cp), 67.9 (Cp), 56.9 (CH-N), 34.7 (*C*HMe_2), 22.0 (Me), 21.9 (Me), 19.8 (Me of *i*-Pr), 17.0 (Me of *i*-Pr); HRMS (ESI): Found: 550.1181. $C_{28}H_{32}FeNO_3S_2$ (MH^+) requires 550.1173.

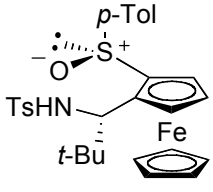
(S_{Fc},S_S,*S*)-*N*-tosyl-1-[2-(*p*-tolylsulfinyl)ferrocenyl]-1-phenylmethylamine 3bb



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (1.0 g, 3.08 mmol) and imine **2a** (R_2 = Ph) (834 mg, 3.70 mmol). The mixture reaction was stirred for 15 min at –78 °C. The crude product was purified by column chromatography, using *n*-heptane/diethylether (3/7) as eluent, to afford **3bb** (1.12 g, 66%) as a yellow solid; Mp 168-169 °C; $[\alpha]_D^{20}$ +252 (c 1.0 in $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 7.49 (1 H, d, *J* 2.8, C-NH), 7.42 (2 H, d, *J* 8.0, Ar), 7.31 (2 H, d, *J* 8.0, Ar), 7.15 (2 H, d, *J* 8.0, Ar), 7.04-7.10 (3 H, m, Ar), 6.95-7.01 (4 H, m, Ar), 5.00 (1 H, d, *J* 2.8, CH-N), 4.53 (1 H, dd, *J* 2.4 and 1.6, Cp), 4.49 (5 H, s, Cp), 4.24 (1 H, t, *J* 2.8, Cp), 3.73-3.75 (1 H, m, Cp), 2.35(6 H, s, Me × 2); δ_C(100.6 MHz; $CDCl_3$) 142.8 (Ar), 141.1 (Ar), 140.6 (Ar), 139.1 (Ar), 138.5 (Ar), 130.0 (2 C, Ar), 129.4 (2 C, Ar), 128.6 (2 C, Ar), 128.1 (2 C, Ar), 127.8 (2 C, Ar), 127.8 (Ar), 124.9 (2 C, Ar), 91.2 (Cp), 89.8 (Cp), 73.1 (Cp), 71.4 (6 C, Cp), 68.6 (Cp), 55.7 (CH-NH), 21.9 (Me), 20.3 (Me). HRMS (ESI): Found: 606.0839. $C_{31}H_{29}FeNO_3S_2Na$ (MNa^+) requires 606.0836.

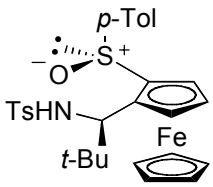
(S_{Fc},S_S)-*N*-tosyl-1-[2-(*p*-tolylsulfinyl)ferrocenyl]-2,2-dimethylpropylamine 3bc

The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (250 mg, 0.77 mmol) and imine **2a** (R_2 = *t*-Bu) (223 mg, 0.93 mmol). The mixture was stirred 30 min at –78 °C. The two diastereoisomers (dr 84:16) were separated by column chromatography, using pentane/diethylether (5/5) as eluent. The major diastereoisomer **(S_{Fc},S_S,*S*)-3bc** (302 mg, 69%, R_f 0.10) was isolated as a yellow solid (Found: C, 61.95; H, 6.14; N,



2.70. $C_{29}H_{33}FeNO_3S_2$ requires C, 61.81; H, 5.90; N, 2.49%); Mp 157-158 °C; $[\alpha]_D^{20}$ –484 (c 1.0 in $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 7.91 (2 H, d, *J* 8.4, Ar), 7.87 (2 H, d, *J* 8.4, Ar), 7.42 (2 H, d, *J* 8.0, Ar), 7.34 (2 H, d, *J* 8.0, Ar), 5.23 (1 H, d, *J* 8.9, NH), 4.42 (1 H, d, *J* 8.9, CH-N), 4.36 (1 H, t, *J* 2.4, Cp), 4.31-4.32 (1 H, m, Cp), 4.25-4.27 (1 H, m, Cp), 4.08 (5 H, s, Cp), 2.46 (3 H, s, Me), 2.43 (3 H, s, Me), 0.60 (9 H, s, *t*-Bu); δ_C(100.6 MHz; $CDCl_3$) 143.1 (Ar), 141.7 (Ar), 141.5 (Ar), 139.2 (Ar), 129.5 (4C, Ar), 127.3 (2 C, Ar), 125.7 (2 C, Ar), 94.6 (Cp), 94.4 (Cp), 71.3 (5 C, Cp), 69.2 (Cp), 65.4 (Cp), 65.1 (Cp), 59.4 (CH-N), 36.8 (C_{quat} *t*-Bu), 27.2 (3C, *t*-Bu), 21.5 (2C, Me×2); HRMS (ESI): Found: 586.1154. $C_{29}H_{33}FeNO_3S_2Na$ (MNa^+) requires 586.1149.

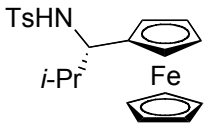
The minor diastereoisomer **(*S*$_{Fc}$,*S*$_S$,*R*)- 3bc** (56 mg, 13%, R*f* 0.45) was isolated as a yellow oil; $[\alpha]_D^{20}$ +480 (c 1.0 in $CHCl_3$); δ_H(400 MHz; $CDCl_3$) 8,04 (1 H, d, *J* 8.4, NH), 7.84 (2 H, d, *J* 8.3, Ar), 7.54 (2 H, d, *J* 8.3, Ar), 7.28 (2 H, d, *J* 8.8, Ar), 7.25 (2 H, d, *J* 8.8, Ar), 4.55 (5 H, s, Cp), 4.43-4.46 (1 H, m, Cp), 4.38-4.40 (2 H, m, Cp), 4.31 (1 H, d, *J* 8.4, CH-N), 2.41 (3 H, s, Me), 2.37 (3 H, s, Me), 0.38 (9 H, s, *t*-Bu); δ_C(100.6 MHz; $CDCl_3$) 141.9 (Ar), 141.3 (Ar), 141.1 (Ar), 140.9 (Ar), 129.5 (2 C, Ar), 129.14 (2 C, Ar), 126.3 (2 C, Ar), 124.9 (2 C, Ar), 90.5 (Cp), 87.6 (Cp), 73.4 (Cp), 71.7 (5 C, Cp), 69.8 (Cp), 68.3 (Cp), 63.8 (CH-N), 37.1 (C_{quat} *t*-Bu), 27.5 (3 C, *t*-Bu), 21.5 (Me), 21.3 (Me); HRMS (ESI): Found: 586.1147. $C_{29}H_{33}FeNO_3S_2Na$ (MNa^+) requires 586.1149.



General procedure for one pot reaction with (*S*$_S$)-*p*-Tolylsulfinylferrocene 1b

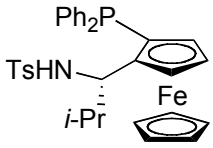
To a cold solution (–78 °C) of LDA [1.2 eq, 0.15 M in dry THF, freshly prepared by treating DIPA (1.2 eq) with *n*-BuLi (1.2 eq)] was added (*S*$_S$)-*p*-tolylsulfinylferrocene (1 eq) in dry THF (1 mL for 100 mg of **1b**). After stirring for 30 min at –78 °C, a solution of 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (1.2 eq) in dry THF (1 mL for 100 mg of **1b**) was added slowly. The resulting mixture was stirred for 20 min at –78 °C, and then *t*-BuLi (in pentane; 2.2 eq) was slowly added. After a further 20 min the chosen electrophile (2.2 eq) was added. The reaction mixture was stirred at –78 °C for 30 min. After completion, a 10% water solution in THF (4 mL for 100 mg of **1b**) was added at –78 °C. The reaction mixture was warmed up at room temperature, and then brine (4 mL for 100 mg of **1b**) was added. The aqueous layer was extracted with diethyl ether (4 mL for 100 mg of **1b**). The combined organic layers were dried over $MgSO_4$ and then evaporated to dryness.

(*S*)-*N*-tosyl-1-ferrocenyl-2-methylpropylamine 4a



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol) and 4-methyl-*N*-(isopropylmethylene)-benzenesulfonamide **2a** (84 mg, 0.370 mmol). The crude product was purified by column chromatography, using *n*-heptane/ethylacetate (8/2) as eluent, to afford **4a** (62 mg, 49%) as a yellow solid; Mp 157 °C; er > 99; $[\alpha]_D^{20}$ +32.2 (c 1.0 in $CHCl_3$); HPLC [(Daicel AD-H column 250 × 4.6 (L × I.D.) 5 μm, 95% *n*-Heptane: 5% Porpoan-2-ol at 1 mL.min^{-1}, 203 nm, 20 °C]: 20.01 min (*R*), 38.40 min (*S*); δ_H(400 MHz; $CDCl_3$) 7.83 (2 H, d, *J* 8.4, Ar), 7.34 (2 H, d, *J* 8.4, Ar), 4.95 (1 H, d, *J* 4.8, C-NH), 4.00-4.13 (10 H, m, CH-N and Cp), 2.45 (3 H, s, Me), 2.01-2.09 (1 H, m, C*H*Me$_2$), 0.69 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.63 (3 H, d, *J* 7.2, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.8 (Ar), 138.7 (Ar), 130.1 (2 C, Ar), 127.5 (2 C, Ar), 88.1 (Cp), 69.3 (5 C, Cp), 69.2 (Cp), 68.2 (Cp), 67.9 (Cp), 66.7 (Cp), 59.2 (CH-N), 31.9 (*C*HMe$_2$), 22.0 (Me of Ts), 19.1 (Me of *i*-Pr), 17.3 (Me of *i*-Pr). HRMS (ESI): Found: 412.1029. $C_{21}H_{26}FeNO_2S$ (MH^+) requires 412.1034.

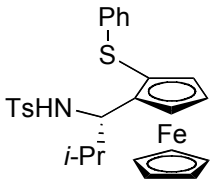
(S_{Fc},*S*)-*N*-tosyl-1-[2-(diphenylphosphino)ferrocenyl]-2-methylpropylamine 4b



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (700 mg, 2.16 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (583 mg, 2.59 mmol) and diphenylphosphine chloride (853 μL, 1.05 g, 4.75 mmol). The crude product was purified by column chromatography, using *n*-heptane/ethylacetate (8/2) as eluent, to afford **4b** (542 mg, 42%) as a yellow solid (Found: C, 66.26; H, 6.19; N, 2.67. $C_{33}H_{34}FeNO_2PS$ requires C, 66.56; H, 5.75; N, 2.35%); Mp 147-148°C; Er > 99:1; δ_H(400 MHz; $CDCl_3$) 7.91 (2 H, d, *J* 8.4, Ar), 7.50-7.57 (2 H, m, Ar), 7.35-7.41 (5 H, m, Ar), 7.18-7.23 (5 H, m, Ar), 5.05 (1 H, d, *J* 6.0, C-NH), 4.67 (1 H, dd, *J* 6.0 and 5.4, CH-N), 4.37-4.39 (1 H, m, Cp), 4.30-4.32 (1 H, m, Cp), 4.11-4.12 (1 H, m, Cp), 3.82 (5 H, s, Cp), 2.49 (3 H, s, Me of Ts), 1.80-1.84 (1 H, m, C*H*Me$_2$), 0.55 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.32 (3 H, d, *J* 6.8, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.5 (1 C, Ar of Ts), 140.3 (1 C, d, *J* 7.9, PPh_2), 139.1 (1 C, Ar of Ts), 138.7 (1 C, d, *J* 8.4, PPh_2), 135.7 (2 C, d, *J* 22.8, PPh_2), 132.7 (2 C, d, *J* 17.8, PPh_2), 130.1 (2 C, Ar of Ts), 129.7 (1 C, PPh_2), 128.5 (2 C, d, *J* 8.4, PPh_2), 128.2 (2 C, d, *J* 5.9, PPh_2), 128.0 (1 C, PPh_2), 127.7 (2 C, Ar of Ts), 97.5 (1 C, d, *J* 29.1, Cp), 75.7 (1 C, d, *J* 13.1, Cp), 71.6 (1 C, d, *J* 4.5, Cp), 70.3 (5

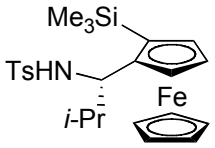
C, Cp), 70.1 (1 C, Cp), 68.0 (1 C, d, *J* 4.4, Cp), 57.3 (1 C, d, *J* 11.3, CH-N), 34.0 (1 C, d, *J* 1.7, C*H*Me_2), 22.0 (1 C, Me of Ts), 18.6 (1 C, Me of *i*-Pr), 17.8 (1 C, d, *J* 1.7, Me of *i*-Pr); δ_P(162.0 MHz; $CDCl_3$) –26.5; HRMS (ESI): Found: 596.1471. $C_{33}H_{35}FeNO_2PS$ (MH^+) requires 596.1476; HPLC [(Daicel OD-H column 250 × 4.6 (L × I.D.) 5 μm, 90% *n*-Heptane: 10% Porpoan-2-ol at 1 $mL.min^{-1}$, 204 nm, 20 °C]: 9.98 min (R_{Fc},*R*), 12.68 min (S_{Fc},*S*).

(S_{Fc},*S*)-*N*-tosyl-1-[2-(phenylsulfanyl)ferrocenyl]-2-methylpropylamine 4c



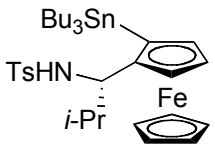
The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and phenyldisulfide (148 mg, 0.678 mmol, in 1 mL of dry THF). The crude product was purified by column chromatography, using pentane/ethylacetate (9/1) as eluent, to afford **4c** (82 mg, 52%) as a yellow solid (Found: C, 62.31; H, 5.91; N, 2.77. $C_{27}H_{29}FeNO_2S_2$ requires C, 62.42; H, 5.63; N, 2.70%); Mp 124-127 °C; δ_H(400 MHz; $CDCl_3$) 7.87 (2 H, d, *J* 8.1, Ar), 7.34 (2 H, d, *J* 8.1, Ar), 7.11-7.18 (2 H, m, Ar), 6.90-7.06 (3 H, m, Ar), 4.88 (1 H, d, *J* 5.7, C-NH), 4.58-4.61 (1 H, m, Cp), 4.50-4.55 (1 H, m, CH-N), 4.37-4.40 (1 H, m, Cp), 4.26-4.28 (1 H, m, Cp), 4.27 (5 H, s, Cp), 2.44 (3 H, s, Me of Ts), 1.70-1.79 (1 H, m, $CHMe_2$), 0.50 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.30 (3 H, d, *J* 7.2, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.6 (Ar), 140.2 (Ar), 139.2 (Ar), 130.0 (2C, Ar), 128.9 (2C, Ar), 127.4 (2C, Ar), 126.2 (2C, Ar), 125.3 (Ar), 93.3 (Cp), 76.3 (Cp), 75.4 (Cp), 71.3 (5C, Cp), 69.1 (Cp), 67.5 (Cp), 57.5 (CH-N), 33.1 (CHMe$_2$), 21.9 (Me of Ts), 18.5 (Me of *i*-Pr), 17.4 (Me of *i*-Pr). HRMS (ESI): Found: 542.0865. $C_{27}H_{29}FeNO_2S_2Na$ (MNa^+) requires 542.0887.

(S_{Fc},*S*)-*N*-tosyl-1-[2-(trimethylsilyl)ferrocenyl]-2-methylpropylamine 4d



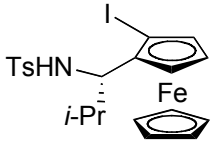
The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and chlorotrimethylsilane (86 μL, 74 mg, 0.678 mmol). The crude product was purified by column chromatography, using dichloromethane/pentane (5/5) as eluent, to afford **4d** (77 mg, 51%) as a yellow solid Found: C, 59.76; H, 7.14; N, 3.13. $C_{24}H_{33}FeNO_2SSi$ requires C, 59.62; H, 6.88; N, 2.90%); Mp 101-102 °C; δ_H(400 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 8.4, Ar), 7.34 (2 H, d, *J* 8.0, Ar), 5.11 (1 H, d, *J* 4.8, C-NH), 4.31-4.33 (1 H, m, Cp), 4.22-4.24 (1 H, m, Cp), 4.17 (5 H, s, Cp), 4.10-4.12 (1 H, m, CH-N), 4.04-4.06 (1 H, m, Cp), 2.44 (3 H, s, Me of Ts), 1.94 (1 H, dsept, *J* 7.2 and 3.6, CHMe$_2$), 0.64 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.54 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.22 (9 H, s, Me_3Si); δ_C(100.6 MHz; $CDCl_3$) 142.4 (Ar), 137.7 (Ar), 128.8 (2 C, Ar), 126.3 (2 C, Ar), 94.2 (Cp), 72.9 (Cp), 70.7 (Cp), 69.2 (Cp), 68.4 (5 C, Cp), 67.4 (Cp), 57.2 (CH-N), 32.3 (CHMe$_2$), 20.7 (Me of Ts), 17.2 (Me of *i*-Pr), 16.9 (Me of *i*-Pr), 0.0 (3 C, Me_3Si); HRMS (ESI): Found: 506.1233. $C_{24}H_{33}FeNO_2SSiNa$ (MH^+) requires 506.1248.

(S_{Fc},*S*)-*N*-tosyl-1-[2-(tributylstannyl)ferrocenyl]-2-methylpropylamine 4e



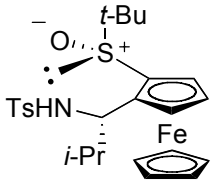
The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and tributyltin chloride (175 μL, 211 mg, 0.678 mmol). The crude product was purified by column chromatography, using dichloromethane/pentane (8/2) as eluent, to afford **3e** (90 mg, 42%) as an orange oil; δ_H(400 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 8.4, Ar), 7.33 (2 H, d, *J* 8.0, Ar), 5.14 (1 H, d, *J* 4.8, C-NH), 4.31 (1 H, t, *J* 2.4, Cp), 4.21-4.23 (1 H, m, Cp), 4.12 (5 H, s, Cp), 3.95-3.98 (2 H, m, CH-N and Cp), 2.44 (3 H, s, Me of Ts), 1.91 (1 H, dsept, *J* 6.8 and 3.2, C*H*Me_2), 1.50-1.58 (6 H, m, *n*-Bu_3Sn), 1.36 (6 H, sext, *J* 7.4, *n*-Bu_3Sn), 0.99-1.04 (6 H, m, *n*-Bu_3Sn), 0.93 (9 H, t, *J* 7.4, *n*-Bu_3Sn), 0.59 (3 H, d, *J* 6.8, Me of *i*-Pr), 0.53 (3 H, d, *J* 7.0, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.6 (Ar), 139.0 (Ar), 130.0 (2 C, Ar), 127.5 (2 C, Ar), 95.0 (Cp), 74.9 (Cp), 70.8 (Cp), 70.4 (Cp), 69.3 (5 C, Cp), 68.0 (Cp), 59.8 (CH-N), 33.0 (*C*HMe_2), 29.7 (3 C, *n*-Bu_3Sn), 27.8 (3 C, *n*-Bu_3Sn), 22.0 (Me of Ts), 18.6 (Me of *i*-Pr), 17.5 (Me of *i*-Pr), 14.1 (3 C, *n*-Bu_3Sn), 11.3 (3 C, *n*-Bu_3Sn); HRMS (ESI): Found: 724.1930. $C_{33}H_{51}FeNO_2SSnNa$ (MNa^+) requires 724.1910.

(S_{Fc},*S*)-*N*-tosyl-1-(2-iodoferrocenyl)-2-methylpropylamine 4f



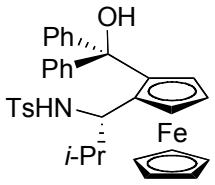
The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and iodine (172 mg, 0.678 mmol). The crude product was purified by column chromatography, using pentane/ethylacetate (95/5) as eluent, to afford **3f** (75 mg, 46%) as a yellow solid (Found: C, 47.23; H, 4.95; N, 2.65. $C_{21}H_{24}FeINO_2S$ requires C, 46.95; H, 4.50; N, 2.61%); Mp 59-61 °C; δ_H(400 MHz; $CDCl_3$) 7.89 (2 H, d, *J* 8.0, Ar), 7.36 (2 H, d, *J* 8.0, Ar), 5.10 (1 H, d, *J* 4.0, C-NH), 4.44-4.46 (1 H, m, Cp), 4.19-4.24 (2 H, m, CH-N and Cp), 4.16 (5 H, s, Cp), 4.07-4.09 (1 H, m, Cp), 2.45 (3 H, s, Me of Ts), 2.02-2.09 (1 H, m, C*H*Me_2), 0.62 (6 H, t, *J* 6.0, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.8 (Ar), 138.7 (Ar), 130.1 (2 C, Ar), 127.5 (2 C, Ar), 90.9 (Cp), 74.7 (Cp), 72.5 (5 C, Cp), 69.2 (Cp), 64.9 (Cp), 58.5 (CH-N), 44.5 (Cp), 33.4 (*C*HMe_2), 22.0 (Me of Ts), 18.9 (Me of *i*-Pr), 17.6 (Me of *i*-Pr). HRMS (ESI): Found: 559.9797. $C_{21}H_{24}FeNO_2SNa$ (MNa^+) requires 559.9820.

(S_{Fc},R_S,S)-*N*-tosyl-1-[2-(*t*-butylsulfinyl)ferrocenyl]-2-methylpropylamine 4g



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and (R_S)-(-)-*t*-butyl-*t*-butanethiosulfinate (132 mg, 0.678 mmol, in 1 mL of dry THF). The crude product was purified by column chromatography, using dichloromethane/ethyl acetate (8/2) as eluent, to afford **3g** (68 mg, 43%) as a yellow solid (Found: C, 58.02; H, 6.78; N, 2.87. $C_{25}H_{33}FeNO_3S_2$ requires C, 58.25; H, 6.45; N, 2.72%); Mp 79-81 °C. δ_H(250 MHz; $CDCl_3$) 7.87 (2 H, d, *J* 8.3, Ar), 7.35 (2 H, d, *J* 8.3, Ar), 5.21 (1 H, d, *J* 6.4, C-NH), 4.46 (5 H, s, Cp), 4.43-4.46 (1 H, m, Cp), 4.34-4.36 (1 H, m, Cp), 4.19 (1 H, dd, *J* 6.4 and 3.6, CH-N), 2.44 (3H, s, Me), 2.80 (1 H, dsept, *J* 6.8 and 3.6, C*H*Me_2), 0.76 (3 H, d, *J* 6.9, Me of *i*-Pr), 0.73 (3 H, d, *J* 6.9, Me of *i*-Pr). δ_C(100.6 MHz; $CDCl_3$) 143.7 (Ar), 139.3 (Ar), 130.1 (2 C, Ar), 127.6 (2 C, Ar), 96.7.1 (Cp), 88.271(Cp), 71.6 (5 C, Cp), 68.9 (Cp), 68.5 (Cp), 65.7 (Cp), 56.9 (C_{quat} *t*-Bu), 56.1 (CH-N), 34.5 (*C*HMe_2), 23.9 (3 C, C*Me*$_3$), 22.0 (Me of Ts), 20.8 (Me of *i*-Pr), 17.4 (Me of *i*-Pr); HRMS (ESI): Found: 538.1127. $C_{25}H_{33}FeNO_3S_2Na$ (MNa^+) requires 538.1149.

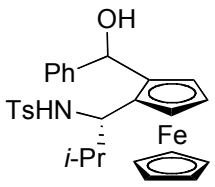
(S_{Fc},S)-2-(*N*-Tosyl-1-amino-2-methylpropyl)-1-(1-hydroxy-1,1-diphenylmethyl) ferrocene 4h



The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and benzophenone (124 mg, 0.678 mmol, in 1 mL of dry THF). The crude product was purified by column chromatography, using dichloromethane/pentane (8/2) as eluent, to afford **4h** (79 mg, 44%) as a yellow solid (Found: C, 68.73; H, 6.30; N, 2.57. $C_{34}H_{35}FeNO_3S$ requires C, 68.80; H, 5.94; N, 2.36%); Mp 96-98 °C; δ_H(400 MHz; $CDCl_3$) 7.84 (2 H, d, *J* 8.0, Ar), 7.58 (2 H, d, *J* 8.0, Ar), 7.10-7.34 (10 H, m, Ar), 4.73 (1 H, d, *J* 8.8, C-NH), 4.32-4.36 (2 H, m, CH-N and OH), 4.34 (5 H, s, Cp), 4.21 (1 H, t, *J* 2.4, Cp), 4.14-4.15 (1 H, m, Cp), 3.78-3.80 (1 H, m, Cp), 2.41 (3 H, s, Me of Ts), 0.88-0.92 (1 H, m, C*H*Me_2), 0.38 (3 H, d, *J* 8.0, Me of *i*-Pr), –0.28 (3 H, d, *J* 8.0, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 146.7 (Ar), 146.6 (Ar), 143.6 (Ar), 138.9

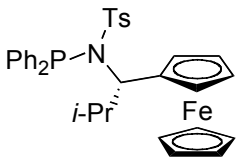
(Ar), 129.9 (2 C, Ar), 127.9 (2 C, Ar), 127.8 (2 C, Ar), 127.7 (2 C, Ar), 127.4 (2 C, Ar), 127.3 (2 C, Ar), 127.1 (Ar), 127.0 (Ar), 98.1 (Cp), 92.1 (Cp), 70.7 (Cp), 70.5 (5 C, Cp), 66.9 (Cp), 65.9 (Cp), 56.0 (CH-N), 34.1 (*C*HMe$_2$), 21.9 (Me of Ts), 20.9 (Me of *i*-Pr), 16.3 (Me of *i*-Pr); HRMS (ESI): Found: 616.1573. $C_{34}H_{35}FeNO_3SNa$ (MNa^+) requires 616.1585.

(S_{Fc},*S*)-2-(*N*-Tosyl-1-amino-2-methylpropyl)-1-(1-hydroxy-1-phenylmethyl) ferrocene 4i



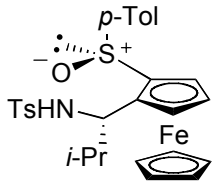
The reaction was performed with (S_S)-*p*-tolylsulfinylferrocene **1b** (100 mg, 0.308 mmol), 4-methyl-*N*-(isopropylmethylene)benzenesulfonamide **2a** (84 mg, 0.370 mmol) and benzaldehyde (69 µL, 72 mg, 0.678 mmol). The crude product was purified by column chromatography, using dichloromethane/pentane (8/2) as eluent, to afford **4i** (79 mg, 44%, inseparable 53:47 mixture of 2 diastereoisomers) as a yellow solid; δ_H(400 MHz; $CDCl_3$) 8.88 (2 H, d, *J* 8.4, Ar major), 8.87 (2 H, d, *J* 8.4, Ar minor), 7.25-7.38 (14 H, m, Ar), 5.53 (1 H, d, *J* 2.4, CH-O major), 5.39 (1 H, d, *J* 4.4, CH-O minor), 5.10 (1 H, d, *J* 6.8, NH major), 5.03 (1 H, d, *J* 6.0, NH minor), 4.34 (5 H, s, Cp), 4.28-4.31 (2 H, m, Cp), 4.16-4.18 (2 H, m, Cp), 4.11-4.15 (1 H, m, Cp major), 4.11 (5 H, s, Cp), 4.10-4.12 (1 H, m, Cp), 4.06 (1 H, t, *J* 2.0, Cp major), 3.98-3.99 (1 H, m, Cp minor), 2.62 (1 H, d, *J* 4.4, OH minor), 2.53 (1 H, d, *J* 2.4, OH major), 2.47 (3 H, s, Me of Ts), 2.45 (3 H, s, Me of Ts), 1.59-1.69 (2 H, m, C*H*Me$_2$ major and minor), 0.49 (3 H, d, *J* 7.0, Me of *i*-Pr minor), 0.44 (3 H, d, *J* 7.0, Me of *i*-Pr major), 0.42 (3 H, d, *J* 7.0, Me of *i*-Pr major), 0.37 (3 H, d, *J* 7.0, Me of *i*-Pr minor); HRMS (ESI): Found: 540.1245. $C_{28}H_{31}FeNO_3SNa$ (MNa^+) requires 540.1272.

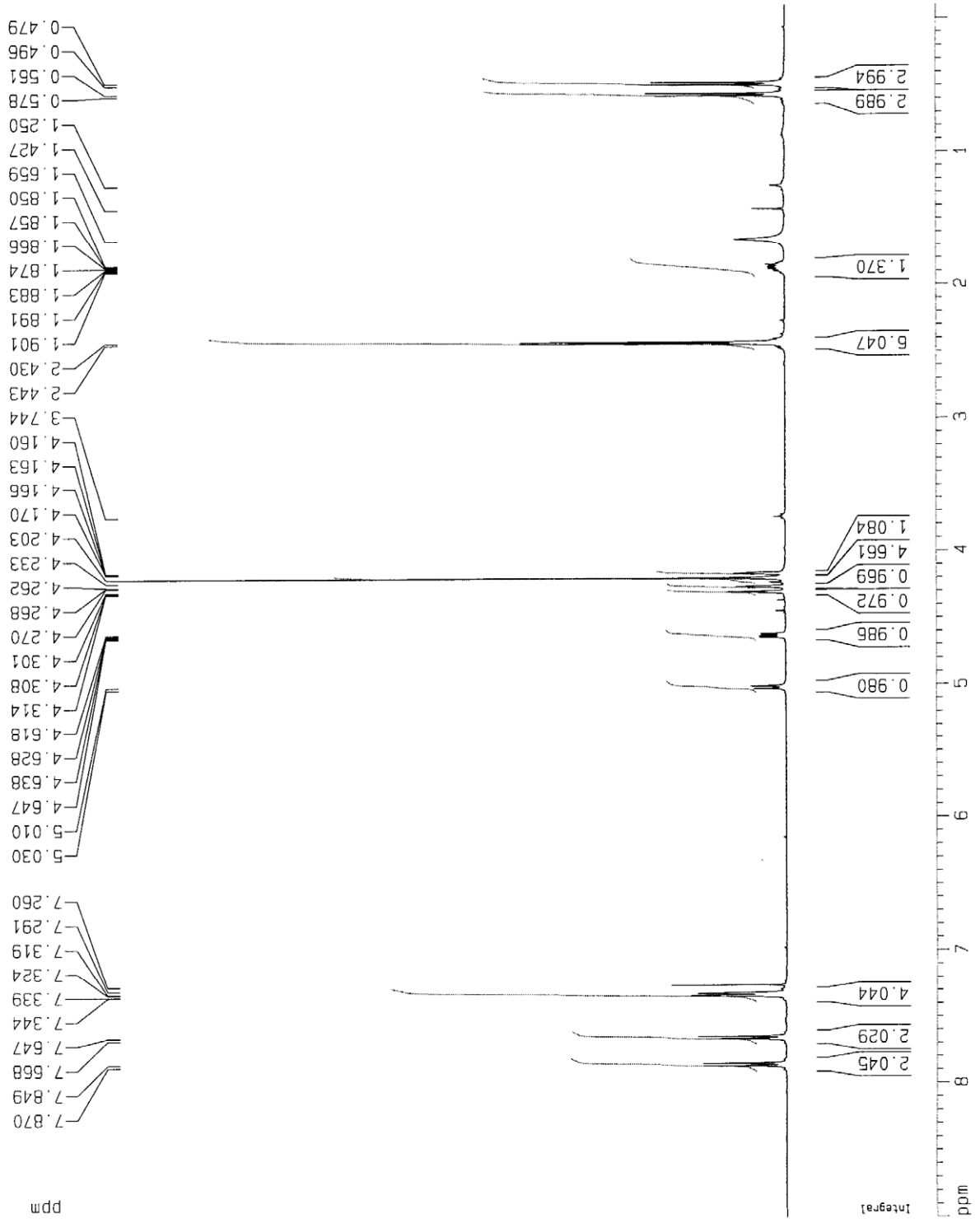
(*S*)-[*N*-tosyl-*N*-diphenylphosphino]-1-ferrocenyl-2-methylpropylamine 5

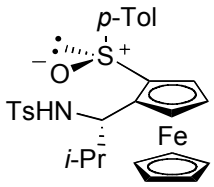


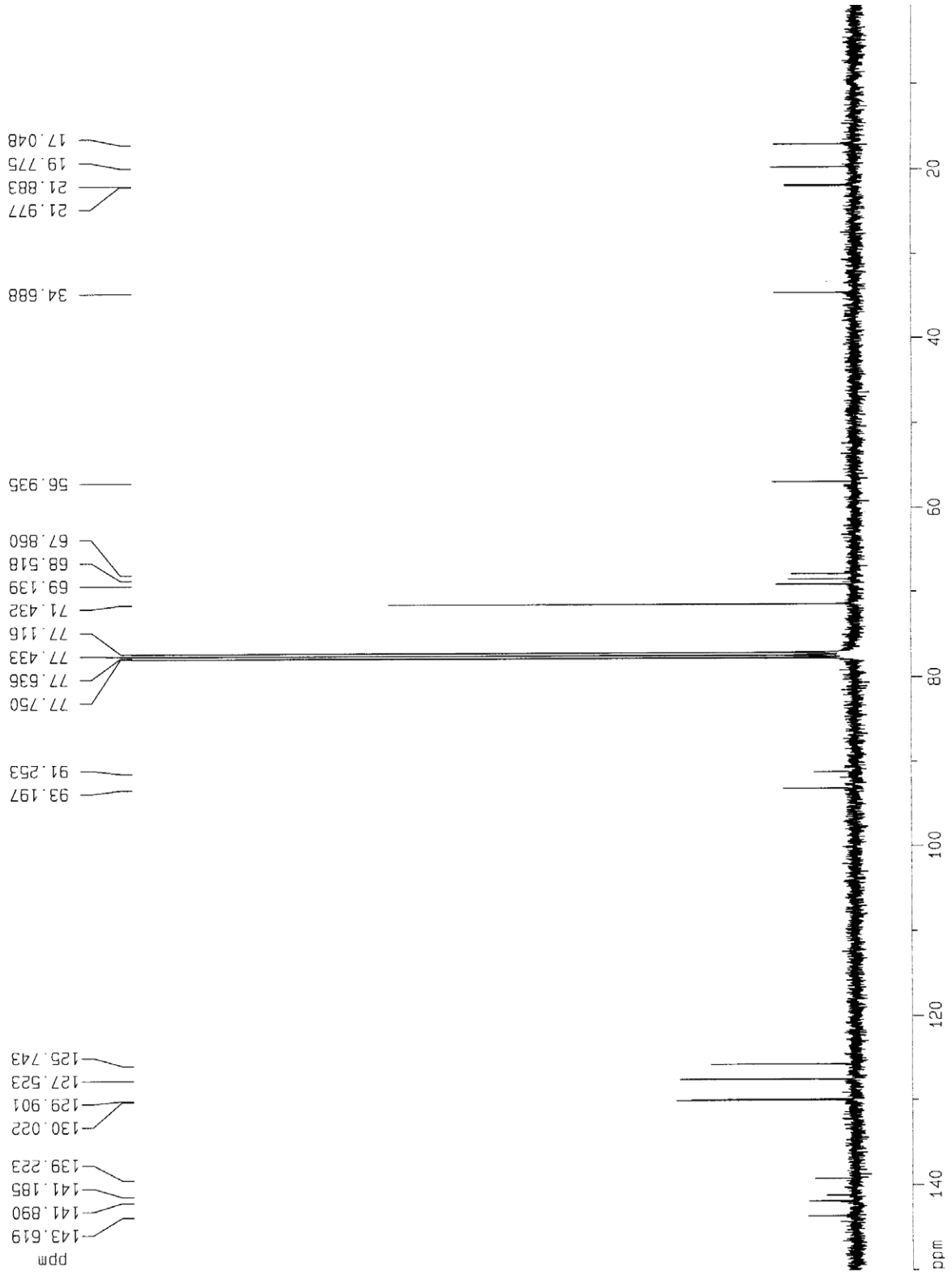
To a cold solution (–78 °C) of sulfoxide **3ba** (150 mg, 0.273 mmol) in THF (3 mL) was slowly added *t*-BuLi (0.4 mL, 0.601 mmol, 1.5 M in hexanes). After stirring for 15 min at –78 °C, chlorodiphenylphosphine (0.11 mL, 133 mg, 10.75 mmol) was added dropwise. The reaction mixture was stirred for 15 min and a 10% water solution in THF (3 mL) was added at –78 °C. The reaction mixture was warmed up at room temperature, and then brine (3 mL) was added. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by column chromatography on silica using *n*-heptane/ethylacetate (9/1) as eluent, to afford **4b**

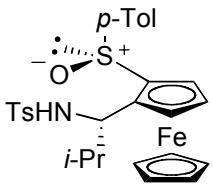
(44 mg, 27%) and **5** (102 mg, 62%) as a yellow solid; Mp 137-138 °C; δ_H(400 MHz; $CDCl_3$) 7.63-7.68 (2 H, m, PPh_2), 7.23-7.38 (8 H, m, PPh_2), 7.08 (2 H, d, *J* 8.0, Ar of Ts), 6.88 (2 H, d, *J* 8.0, Ar of Ts), 4.75 (1 H, dd, *J* 6.0 and 21.2, CH-N-P), 4.33 (1 H, br, Cp), 4.16-4.18 (1 H, m, Cp), 4.01 (5 H, s, Cp), 3.96-3.98 (1 H, m, Cp), 3.12 (1 H, br, Cp), 2.60-2.66 (1 H, m, C*H*Me_2), 2.41 (3 H, s, Me of Ts), 1.42 (3 H, d, *J* 7.0, Me of *i*-Pr), 1.01 (3 H, d, *J* 7.0, Me of *i*-Pr); δ_C(100.6 MHz; $CDCl_3$) 143.6 (1 C, Ar of Ts), 138.4 (1 C, Ar of Ts), 136.8 (1 C, d, *J* 13.3, PPh_2), 135.9 (1 C, d, *J* 23.5, PPh_2), 135.9 (2 C, d, *J* 24.6, PPh_2), 133.3 (2 C, d, *J* 23.5, PPh_2), 129.9 (1 C, PPh_2), 129.5 (2 C, Ar of Ts), 128.9 (1 C, PPh_2), 128.6 (2 C, Ar of Ts), 128.1 (2 C, d, *J* 6.8, PPh_2), 127.8 (2 C, d, *J* 7.3, PPh_2), 88.7 (1 C, d, *J* 8.4, Cp), 69.6 (1 C, d, *J* 4.2, Cp), 69.6 (5 C, Cp), 69.5 (1 C, Cp), 68.1 (1 C, Cp), 67.9 (1 C, Cp), 66.0 (1 C, d, *J* 21.4, CH-N-P), 33.0 (1 C, d, *J* 6.0, *C*HMe_2), 22.7 (1 C, Me of *i*-Pr), 22.0 (1 C, Me of Ts), 21.2 (1 C, d, *J* 4.6, Me of *i*-Pr); δ_P(162.0 MHz; $CDCl_3$) 47.4; HRMS (ESI): Found: 596.1480. $C_{33}H_{35}FeNO_2PS$ (MH^+) requires 596.1476.

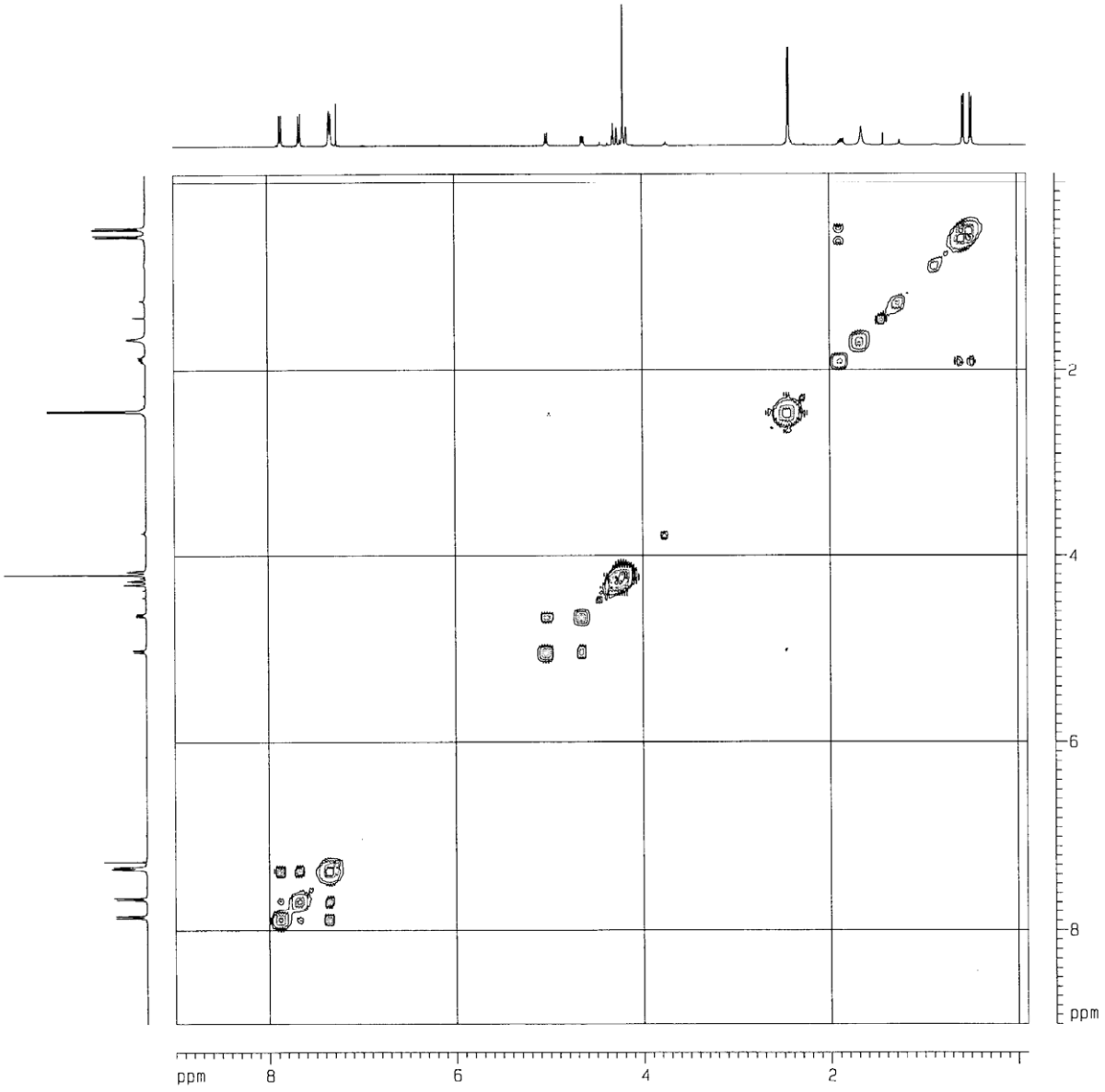
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},S_S,S)-3ba**	

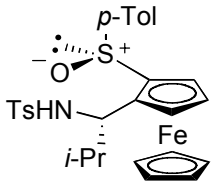


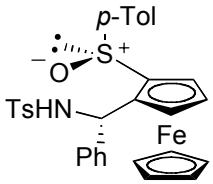
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},S_S,S)-3ba**	

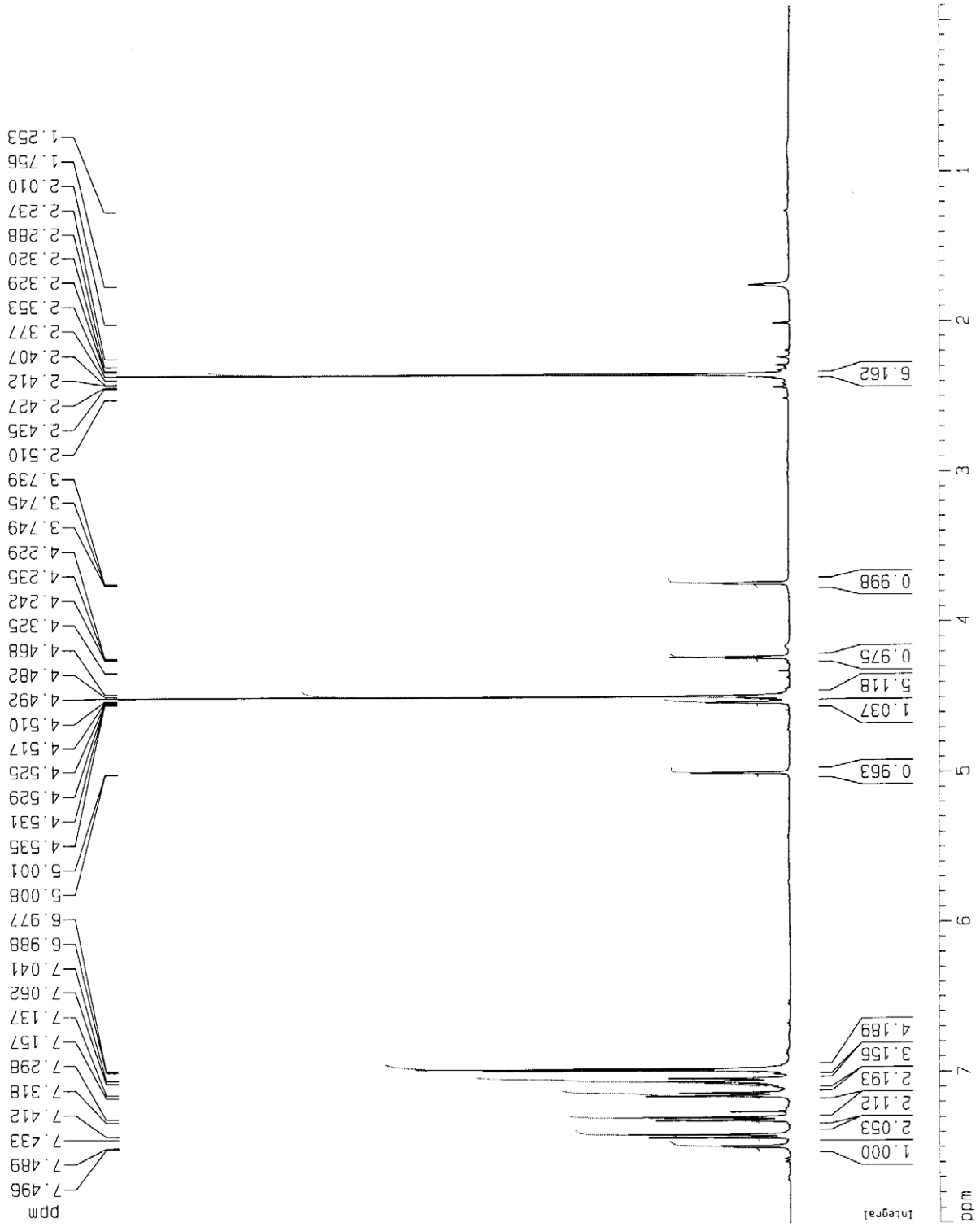


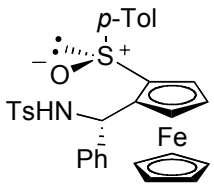
COSY H-H of **(S_{Fc},S_S,*S*)-3ba**	

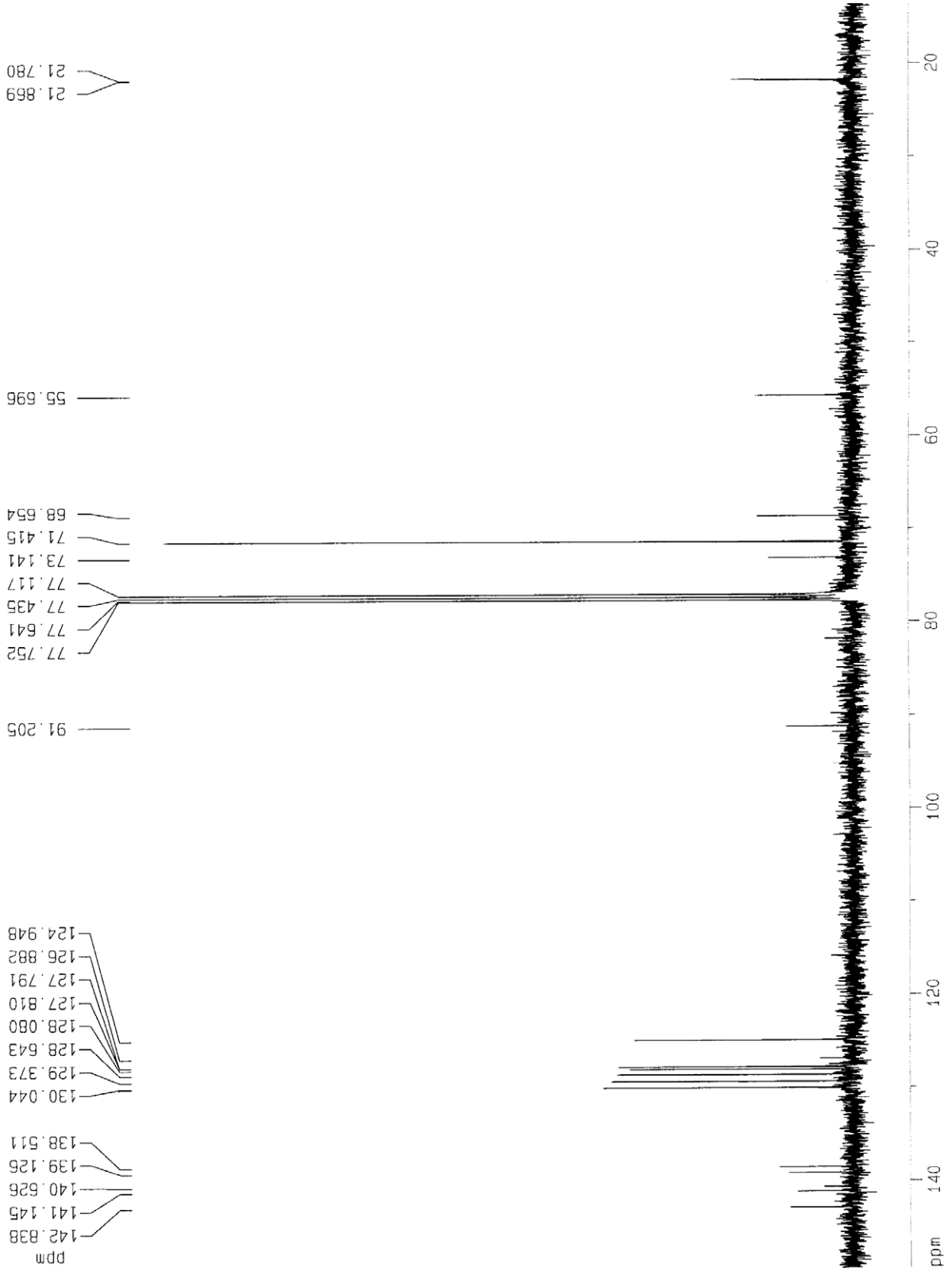


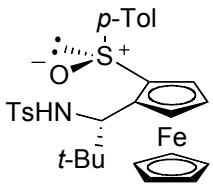
HMQC of **(S_{Fc},S_S,S)-3ba**	

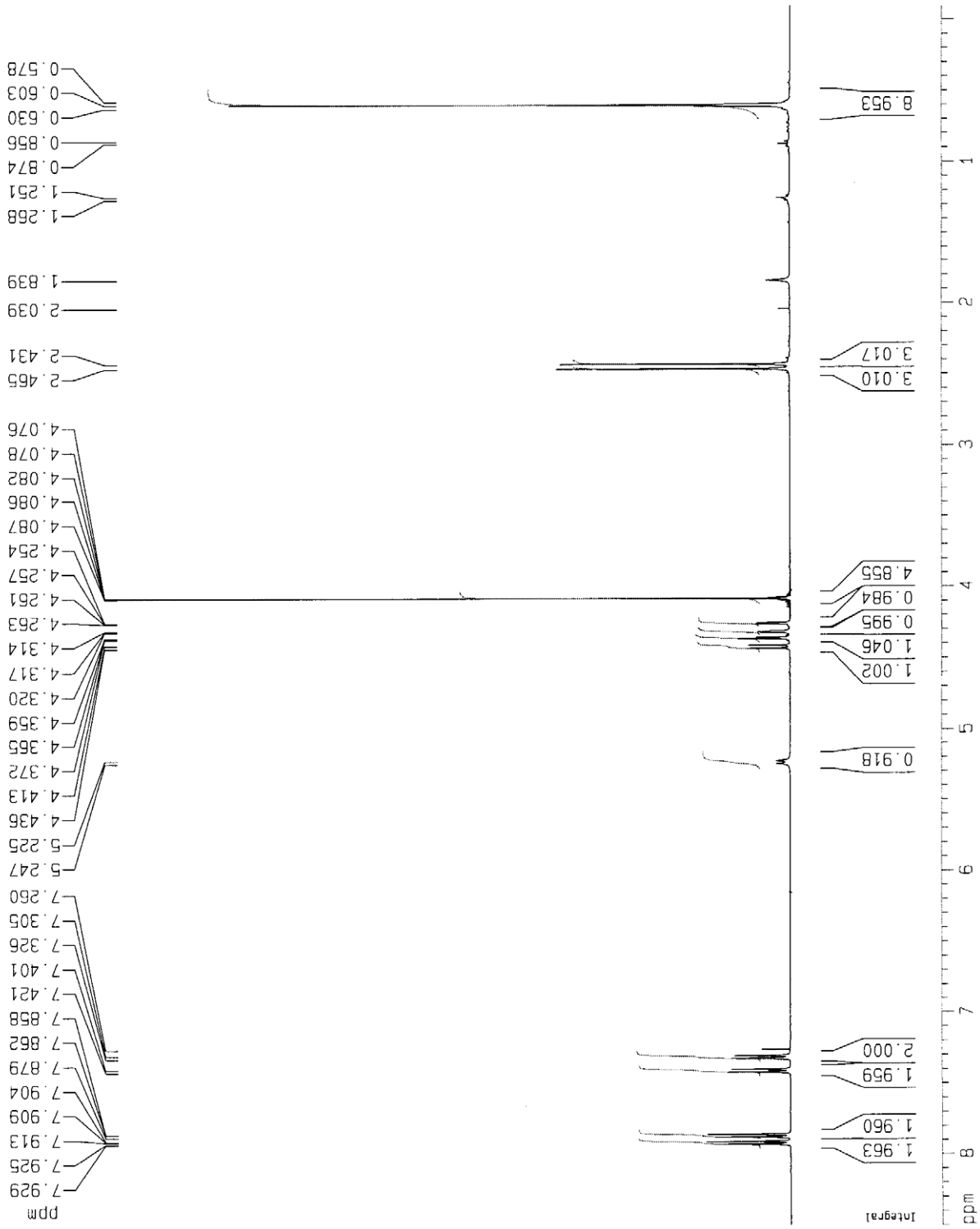
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},S_S,S)-3bb**	

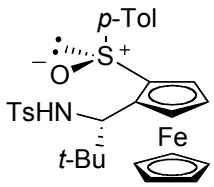


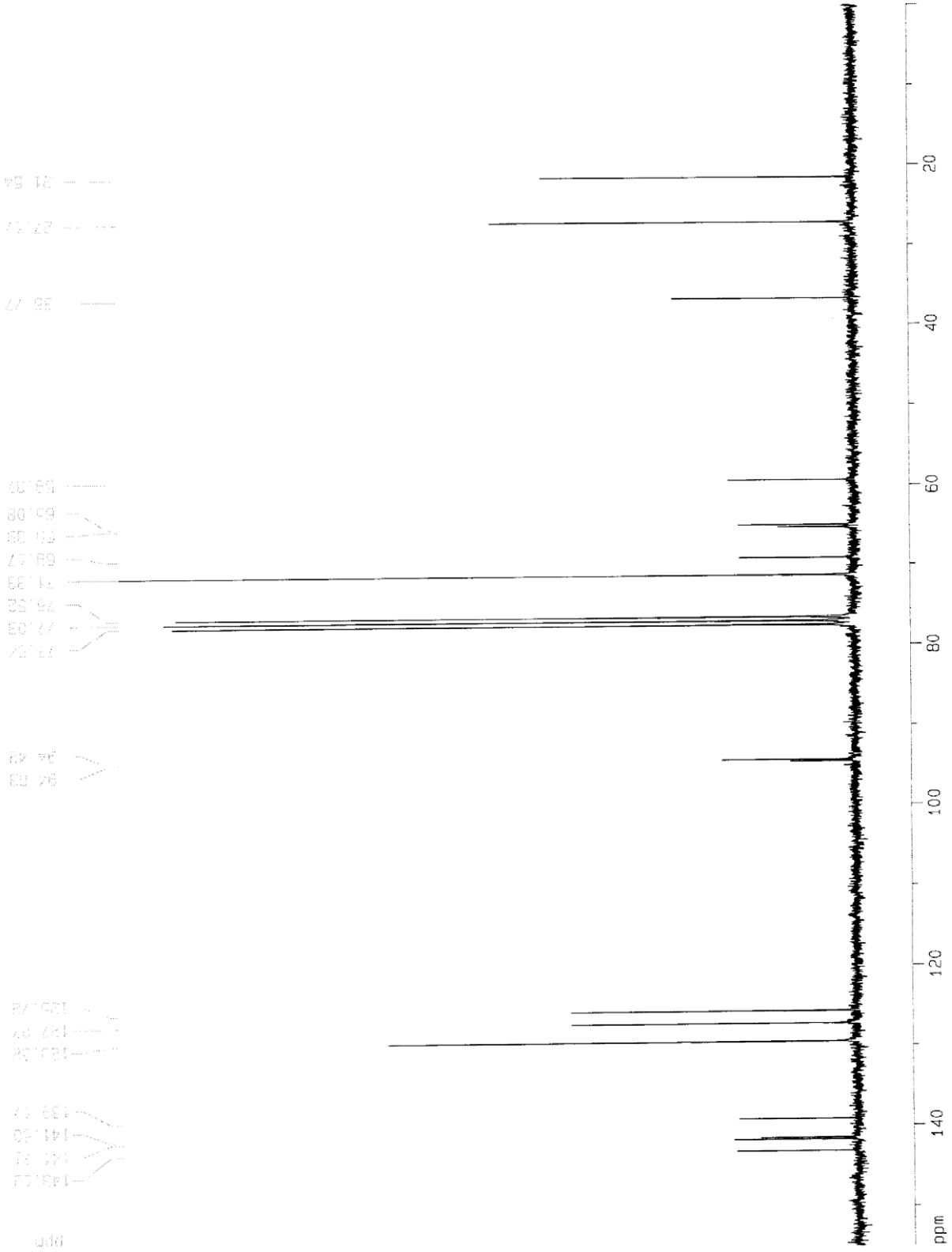
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},S_S,S)-3bb**	

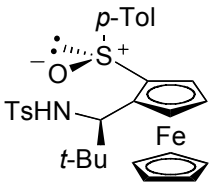


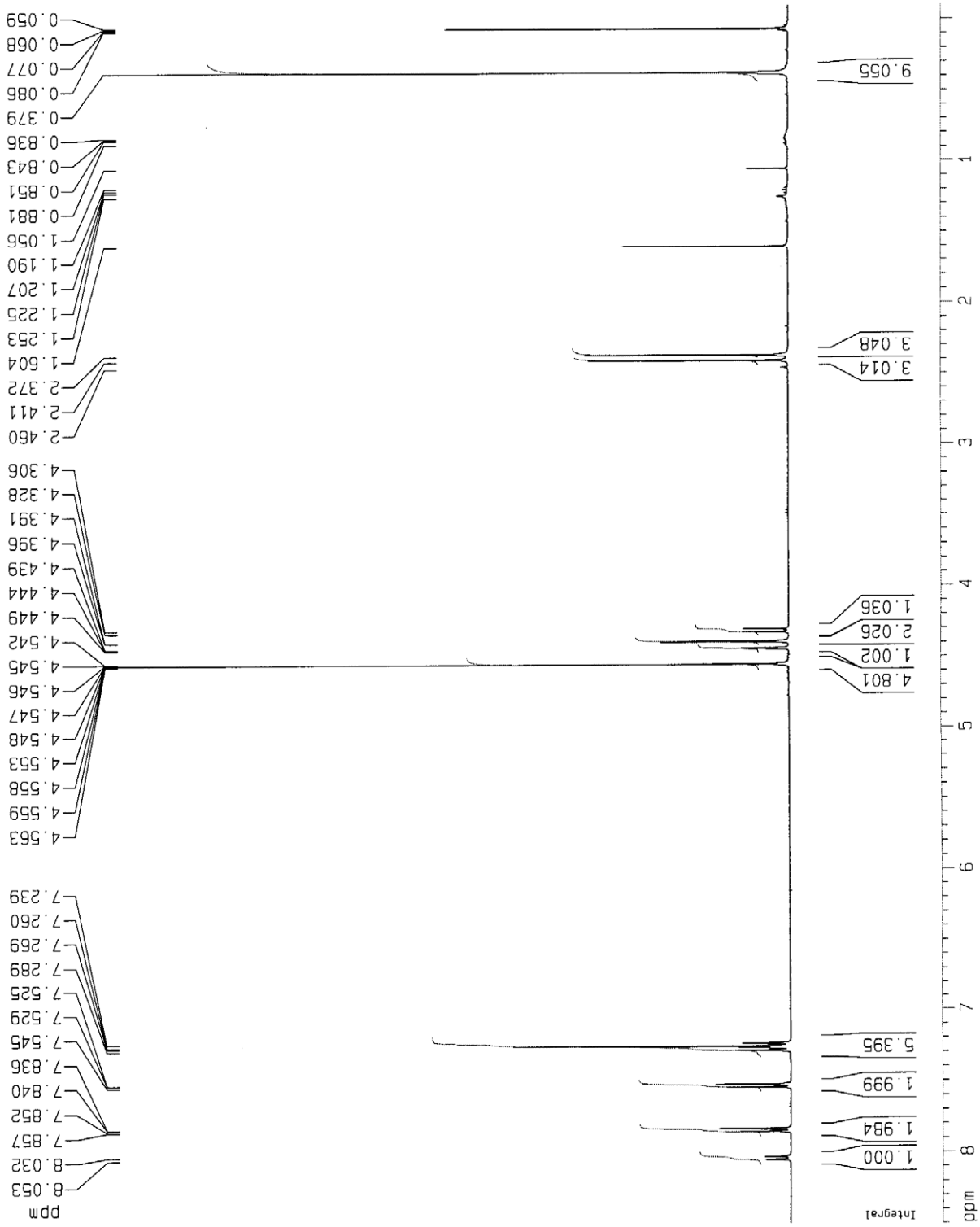
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},S_S,S)-3bc**	

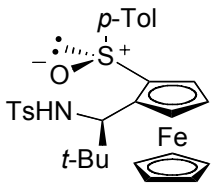


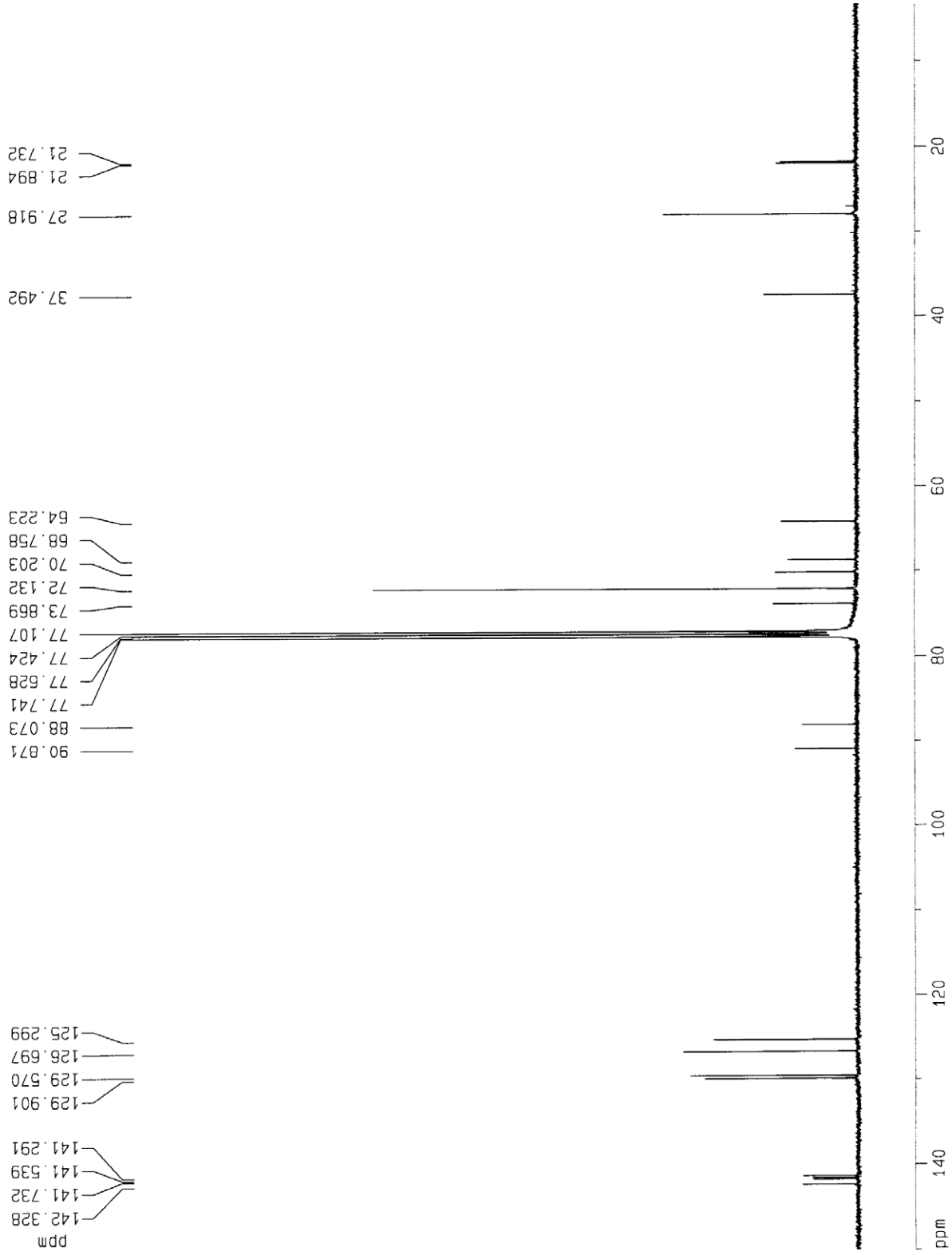
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},S_S,S)-3bc**	

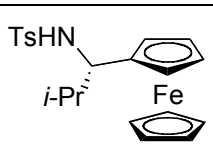


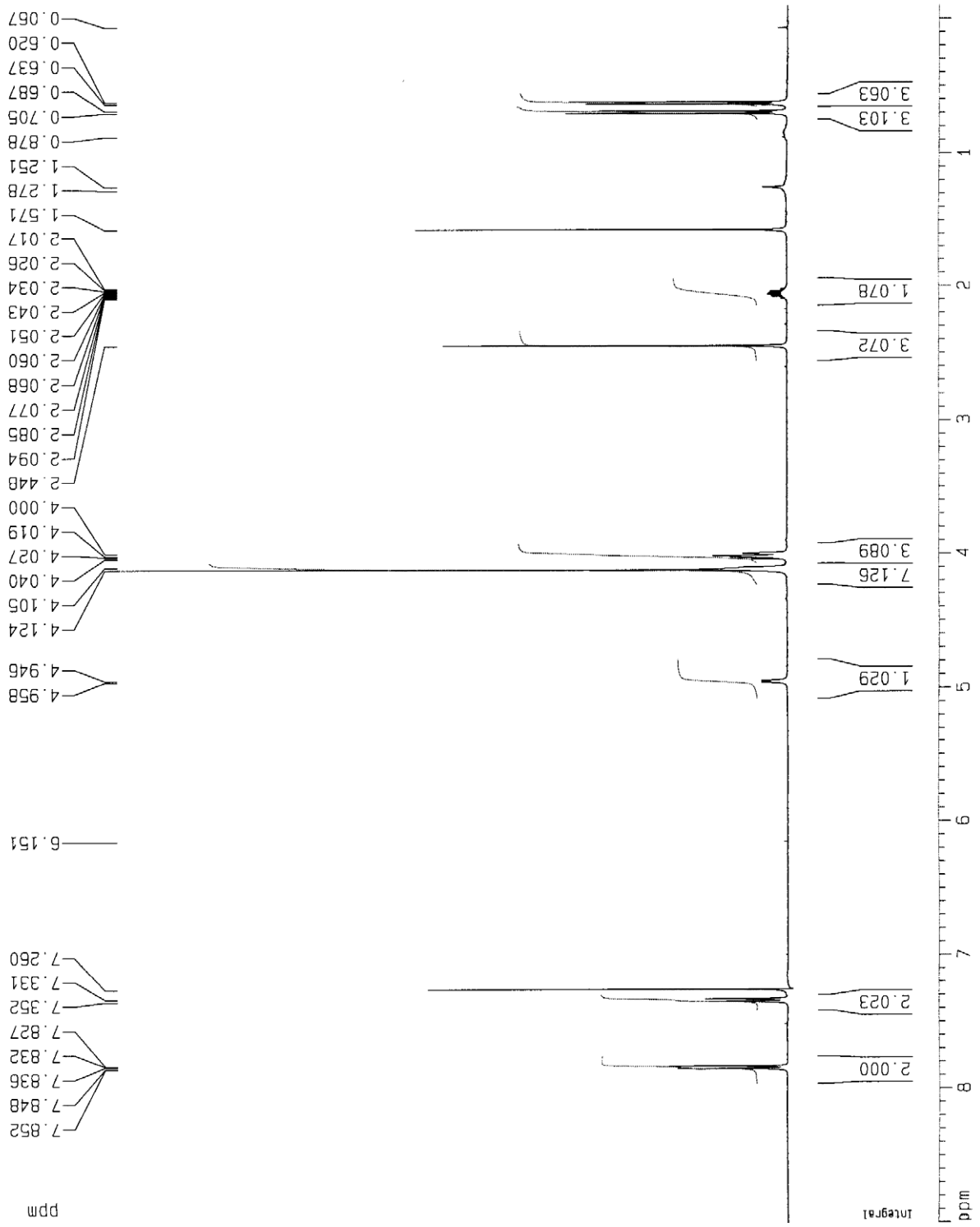
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},S_S,R)- 3bc**	

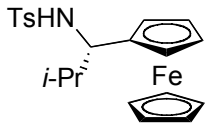


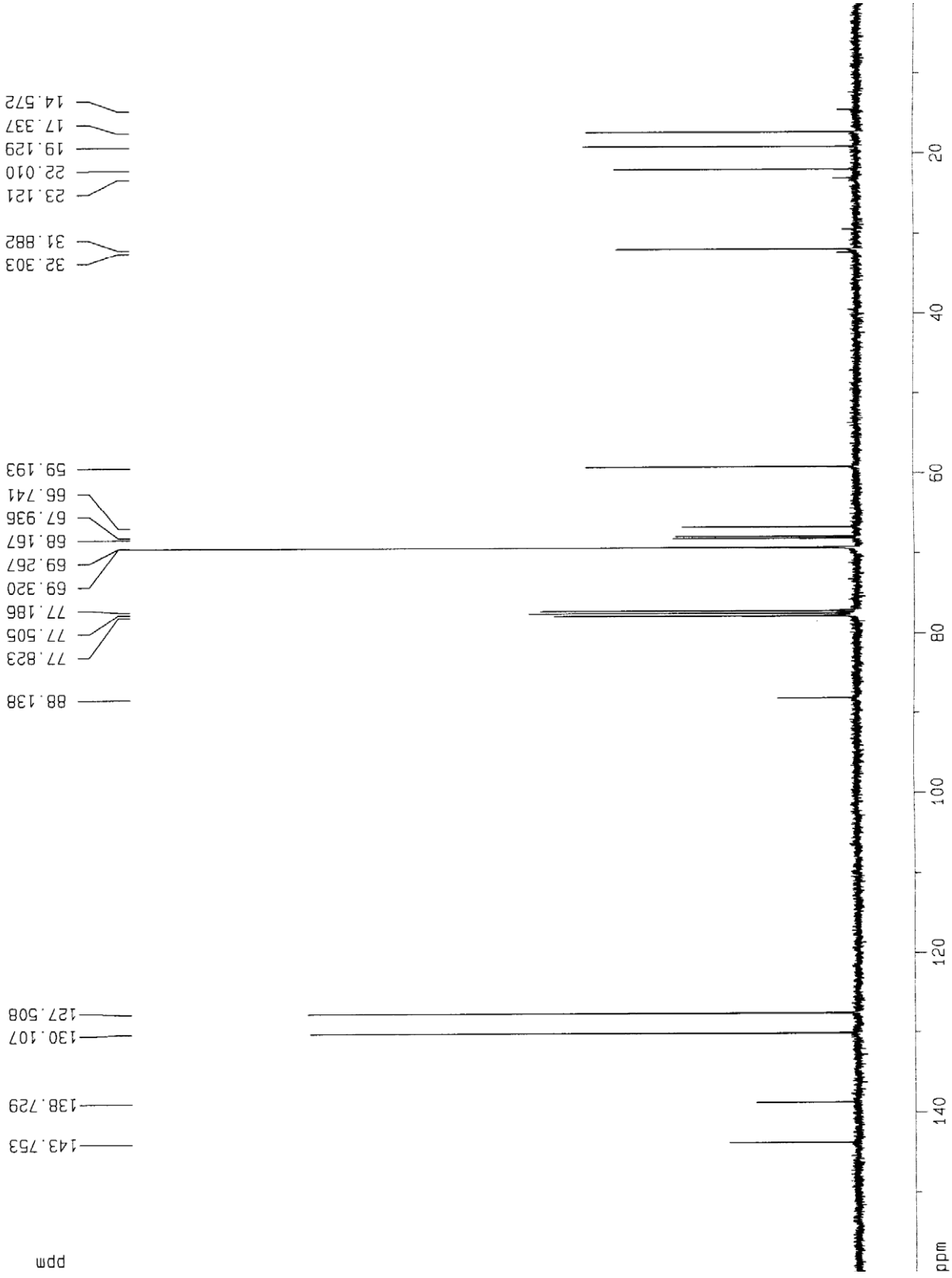
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},S_S,S)-3bc**	

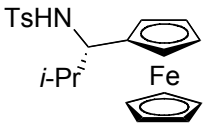


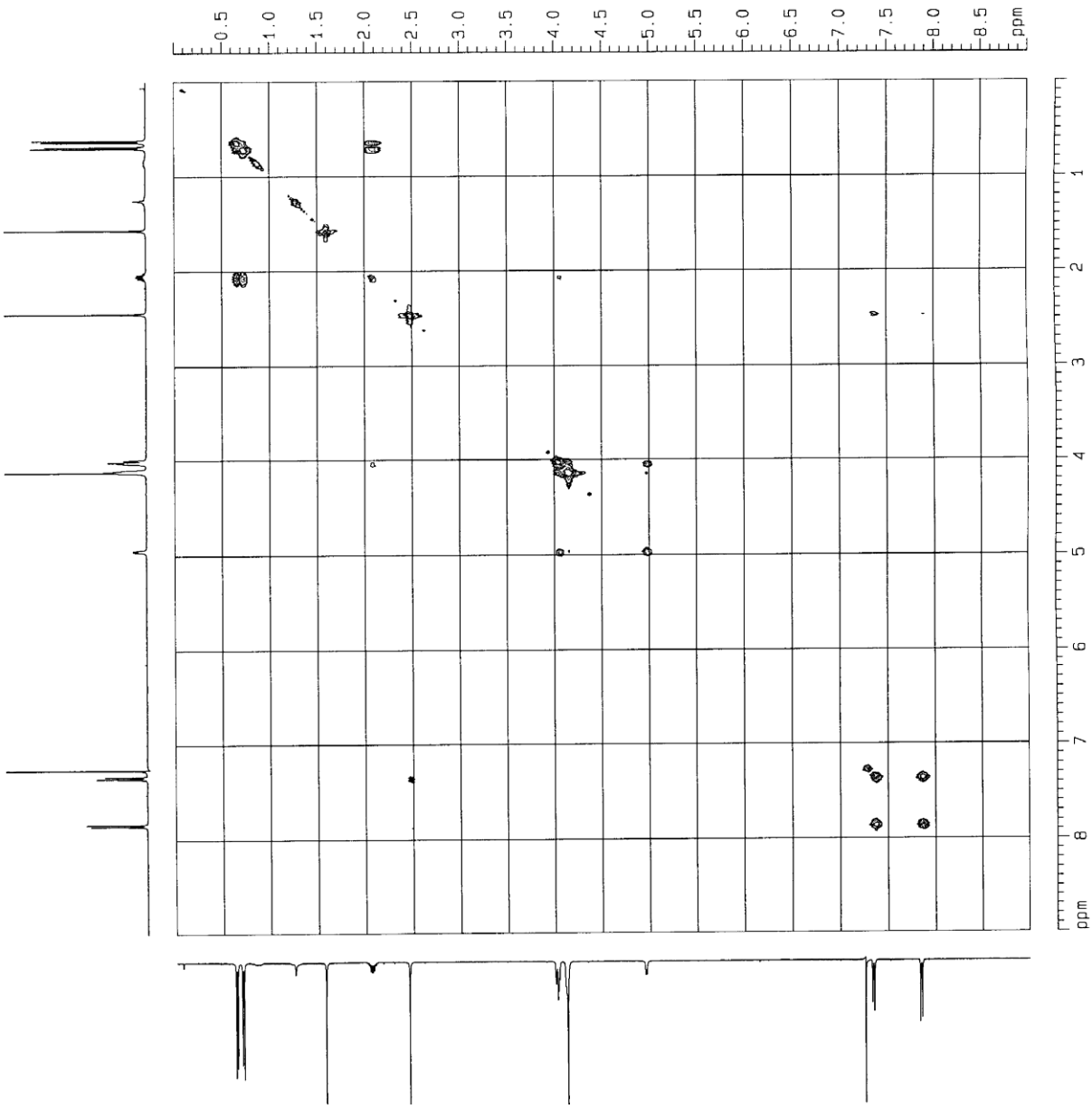
^{1}H NMR ($CDCl_3$, 400 MHz) of **(*S*)-4a**	

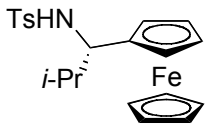


^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(*S*)-4a**	



COSY H-H of **(*S*)-4a**	

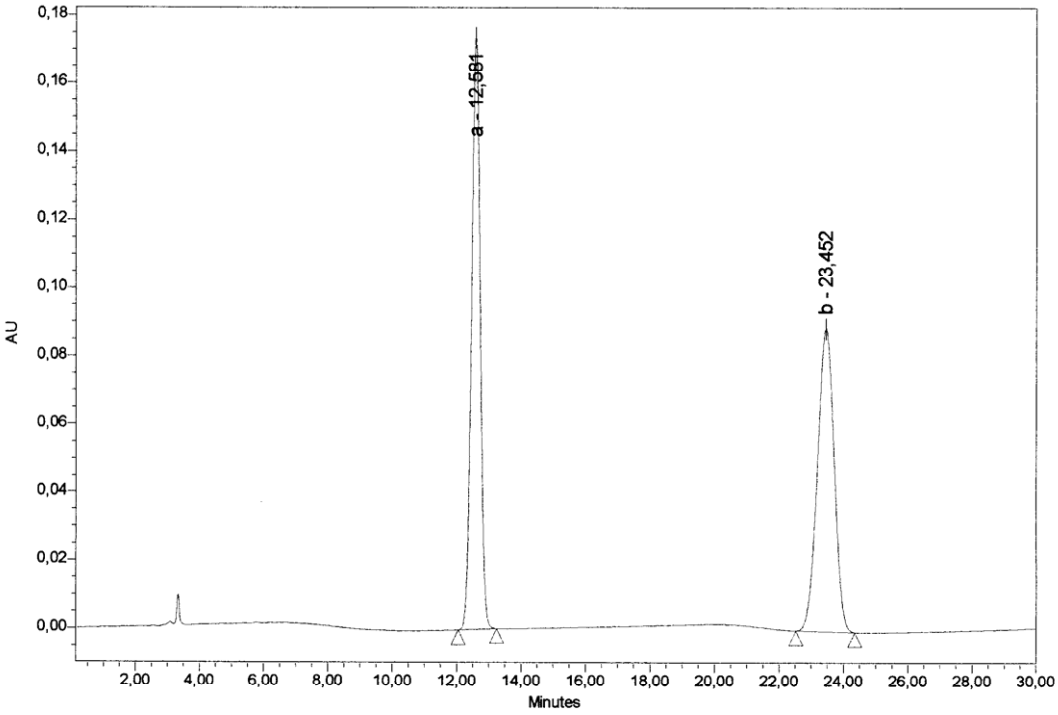


HPLC of rac-**4a**	

Instrument Method: IM 1mL 90 10

Comments Col. Daicel AD-H 250mmx4,6mm 5µm 1mL/mn 90%n-heptane 10% propanol-2 20°C

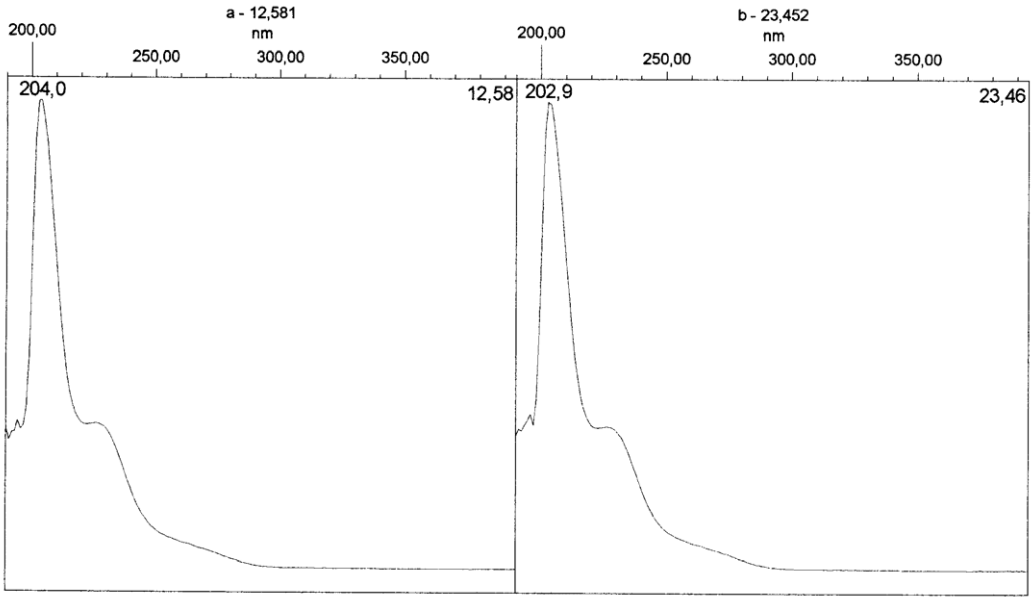
Auto-Scaled Chromatogram

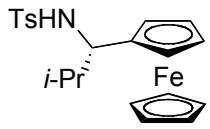


Peak Results

	Name	RT	Start Time	End Time	% Area
1	a	12,581	12,055	13,247	50,38
2	b	23,452	22,522	24,347	49,62

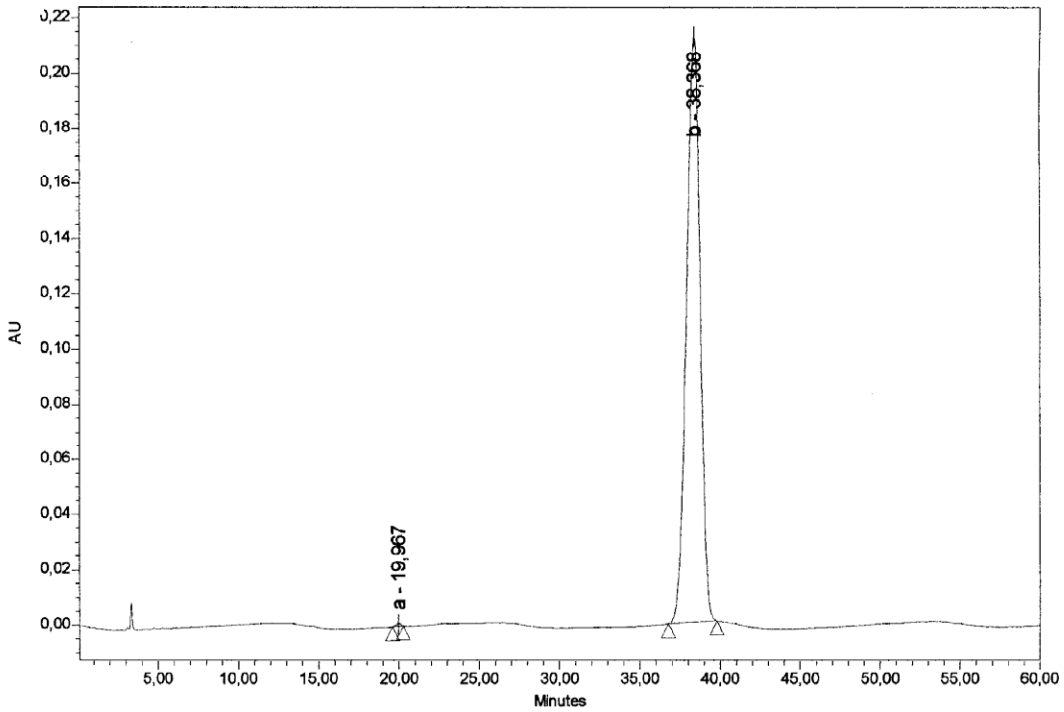
Spectrum Index Plot



HPLC of **(*S*)-4a**	

Col. Daicel AD-H 250mmx4,6mm 5µm 1mL/mn 95%n-heptane 5% propanol-2

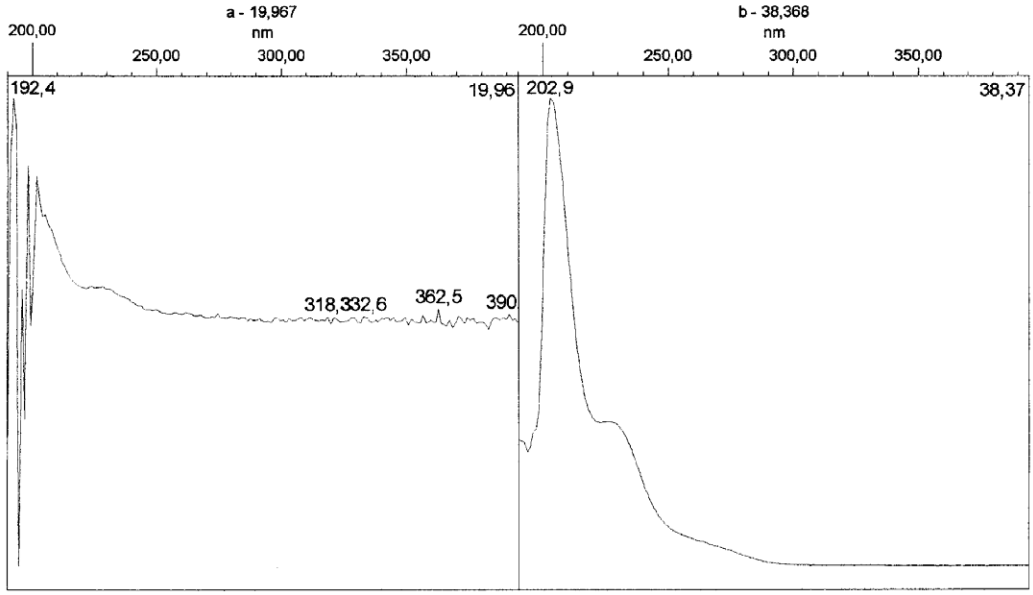
Auto-Scaled Chromatogram

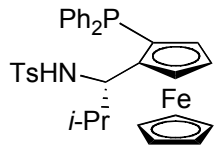


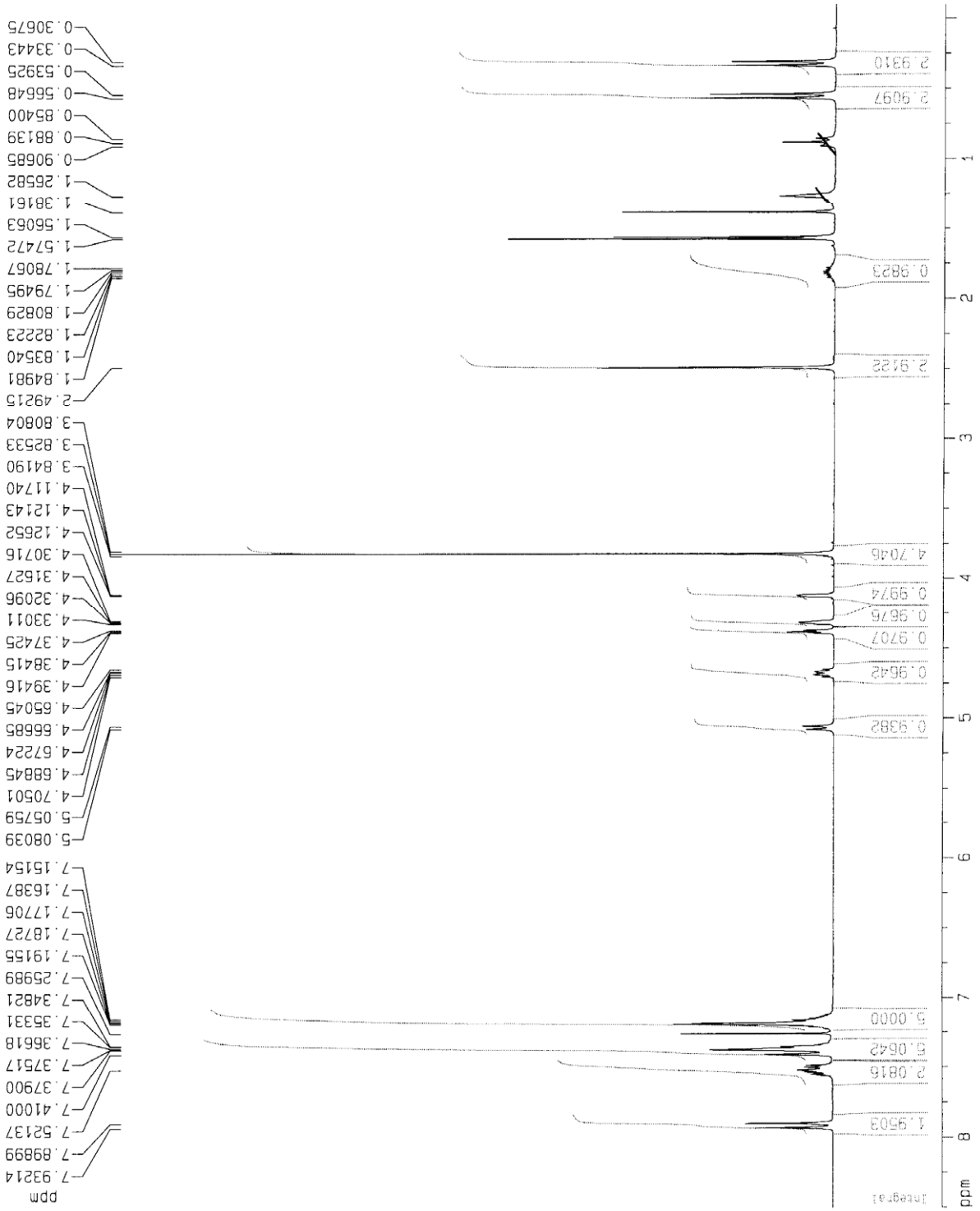
Peak Results

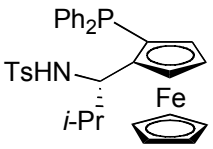
	Name	RT	Start Time	End Time	% Area
1	a	19,967	19,600	20,258	0,15
2	b	38,368	36,767	39,792	99,85

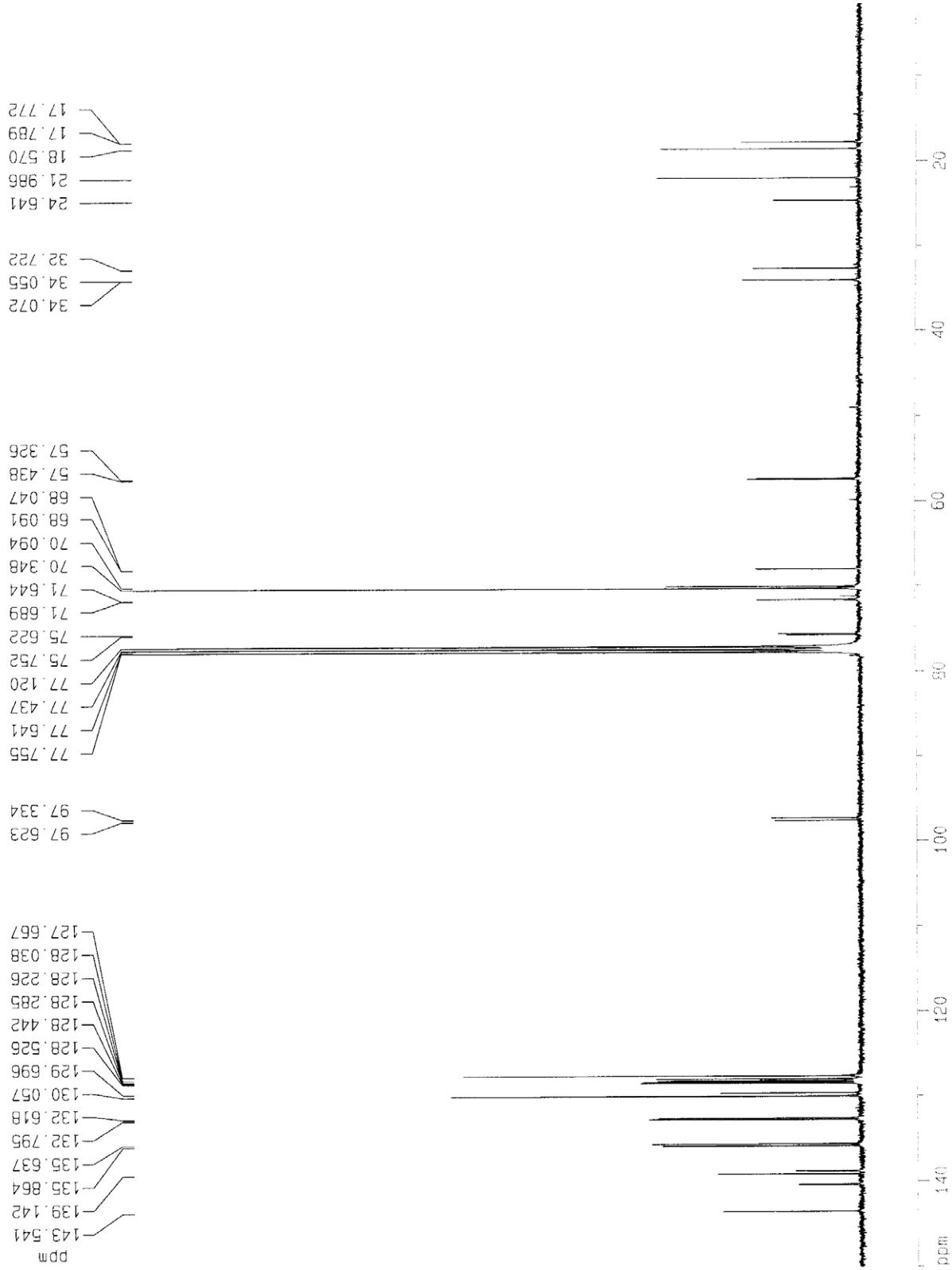
Spectrum Index Plot

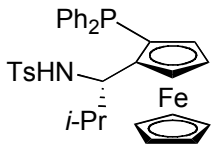


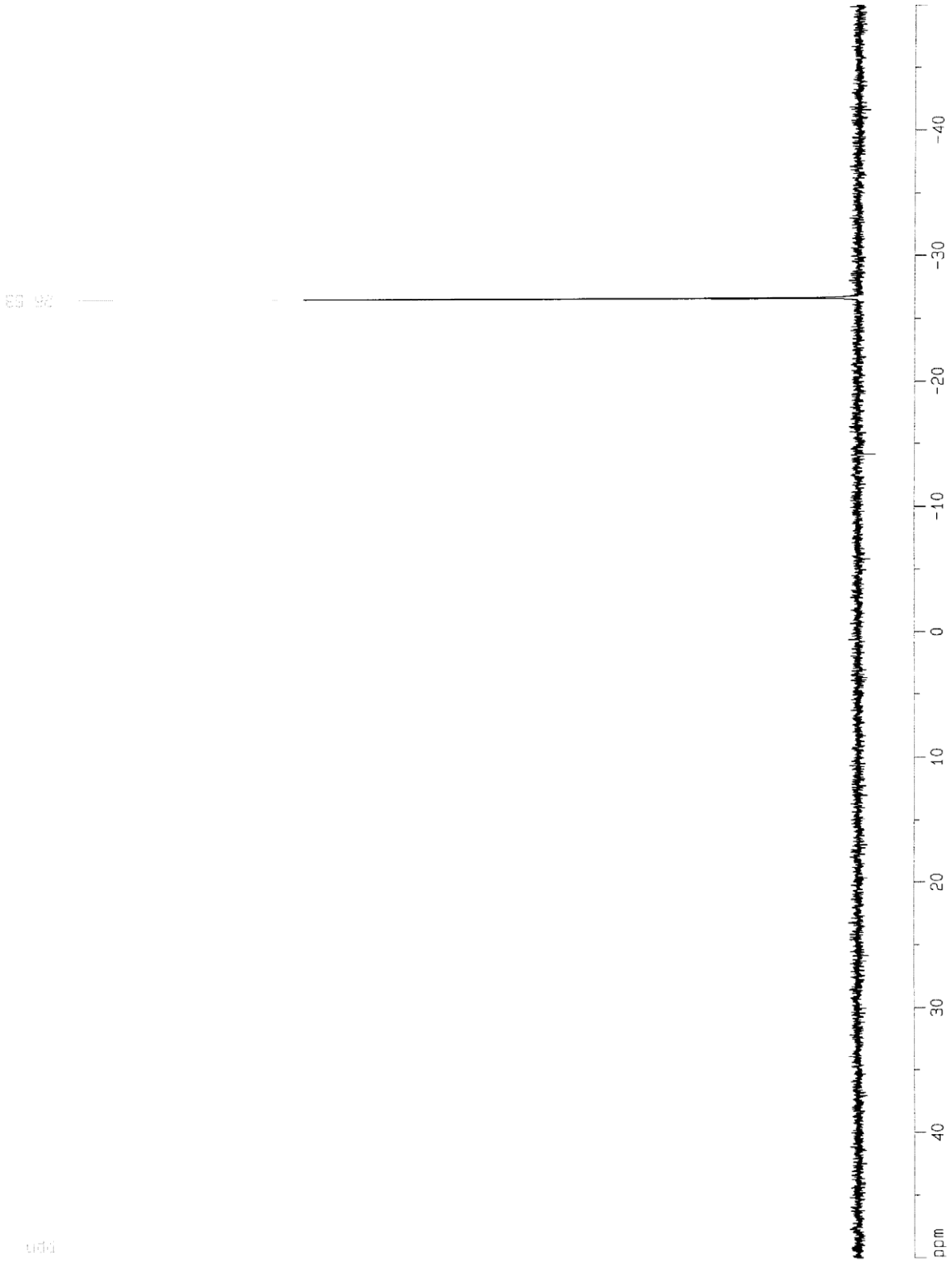
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},*S*)-4b**	

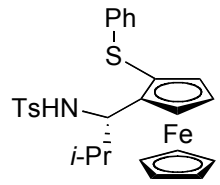


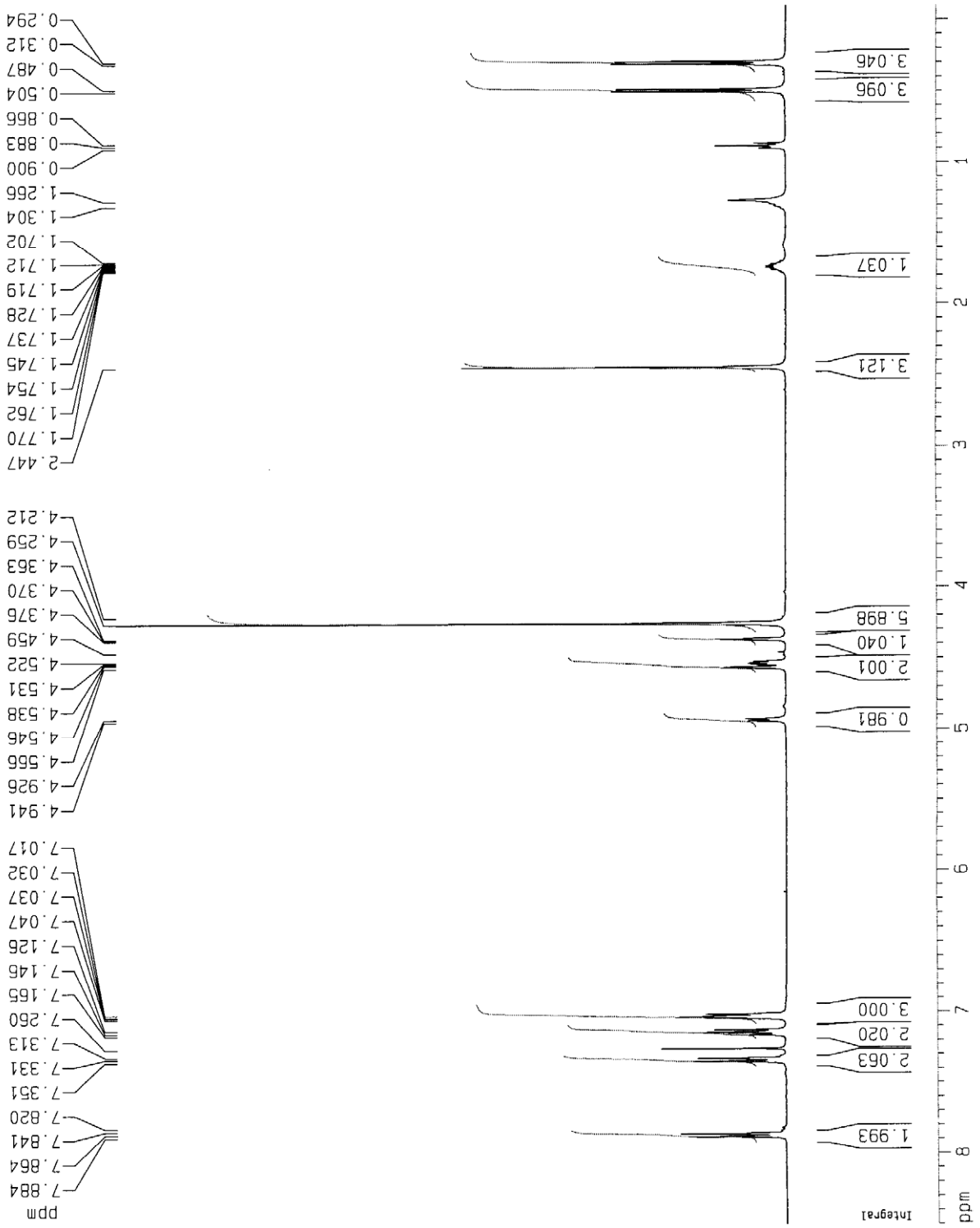
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4b**	

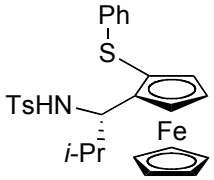


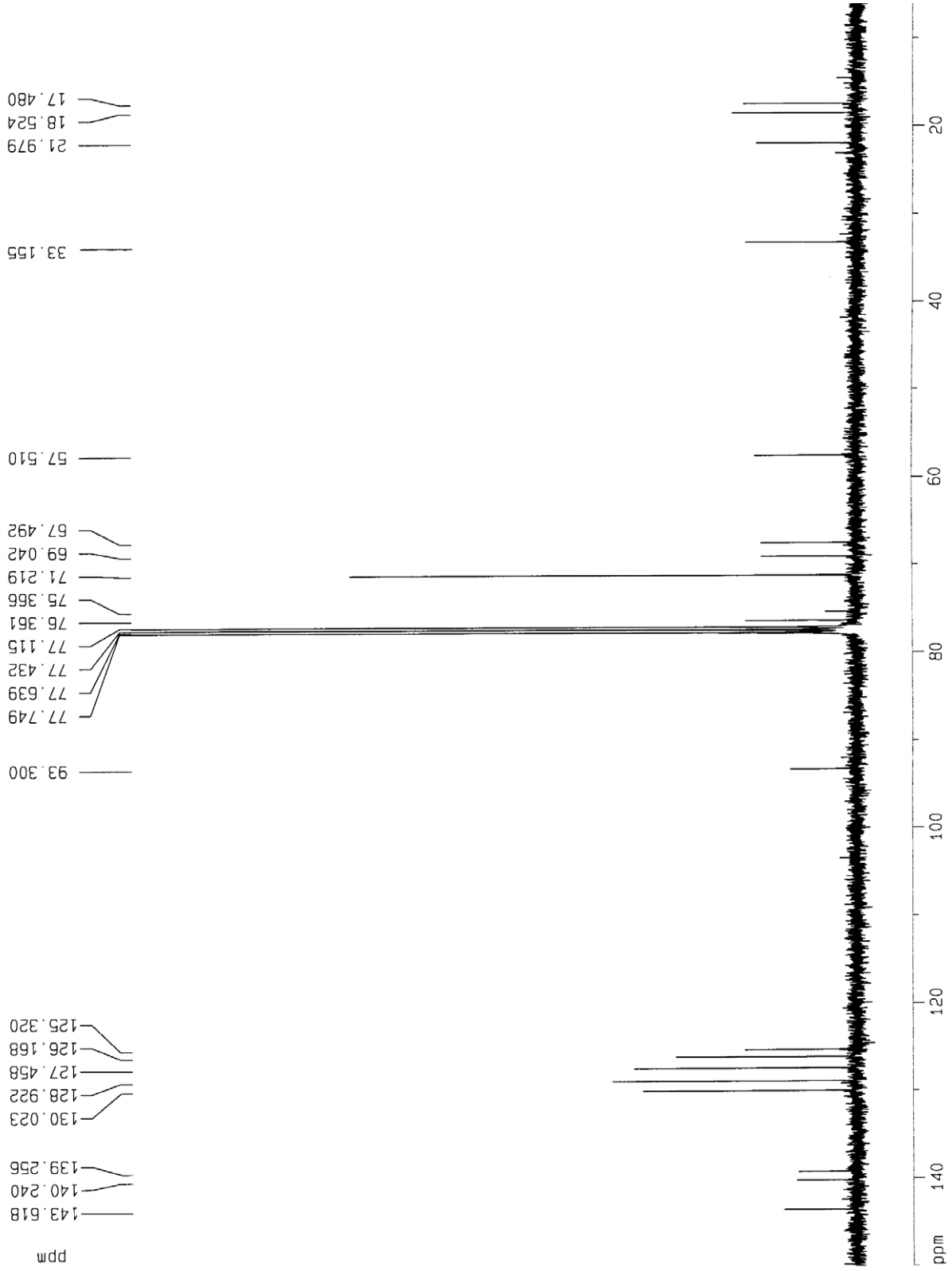
^{31}P NMR ($CDCl_3$, 161,9 MHz) of **(S_{Fc},*S*)-4b**	

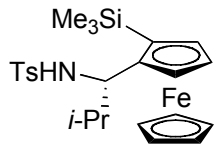


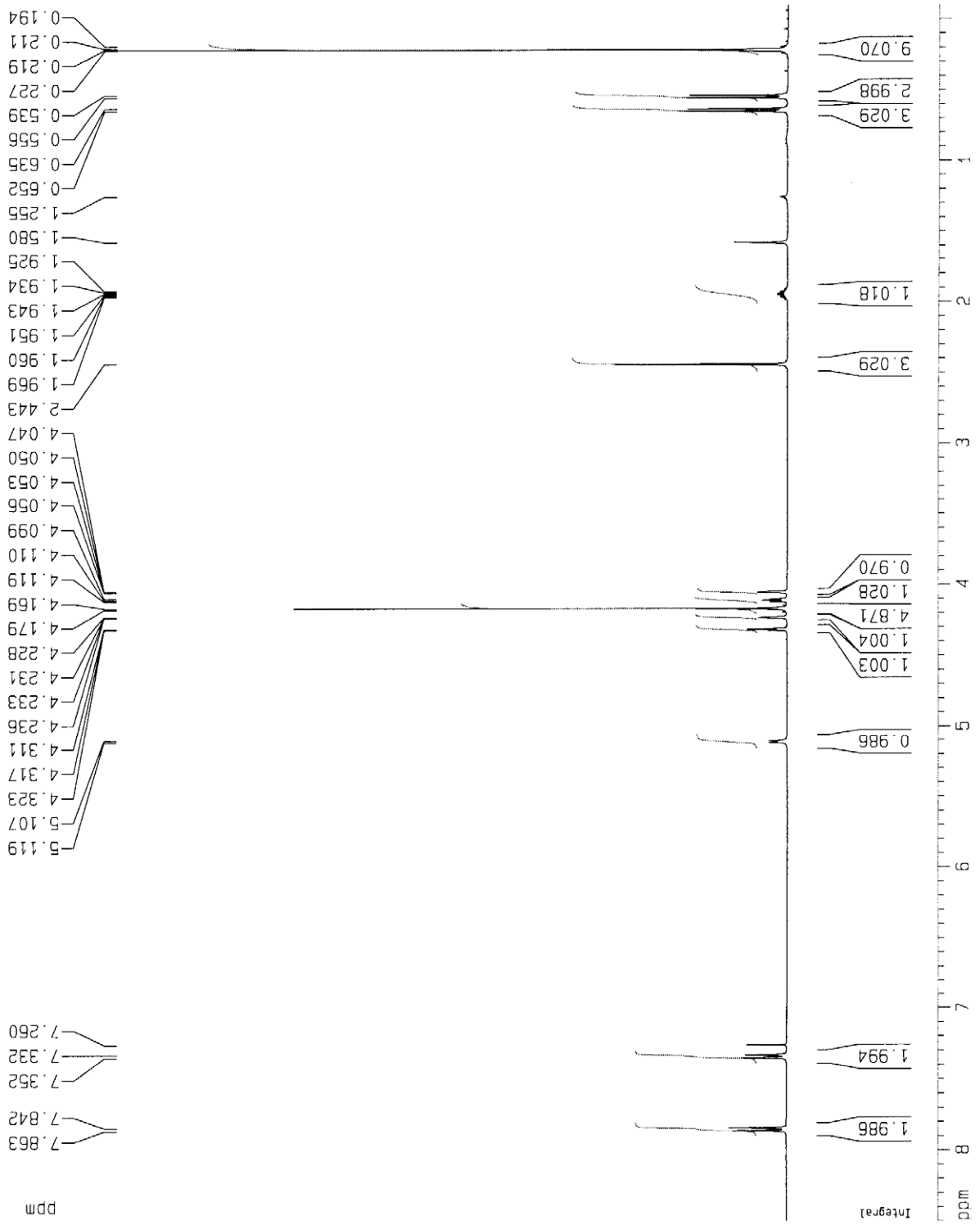
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},*S*)-4c**	

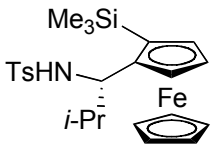


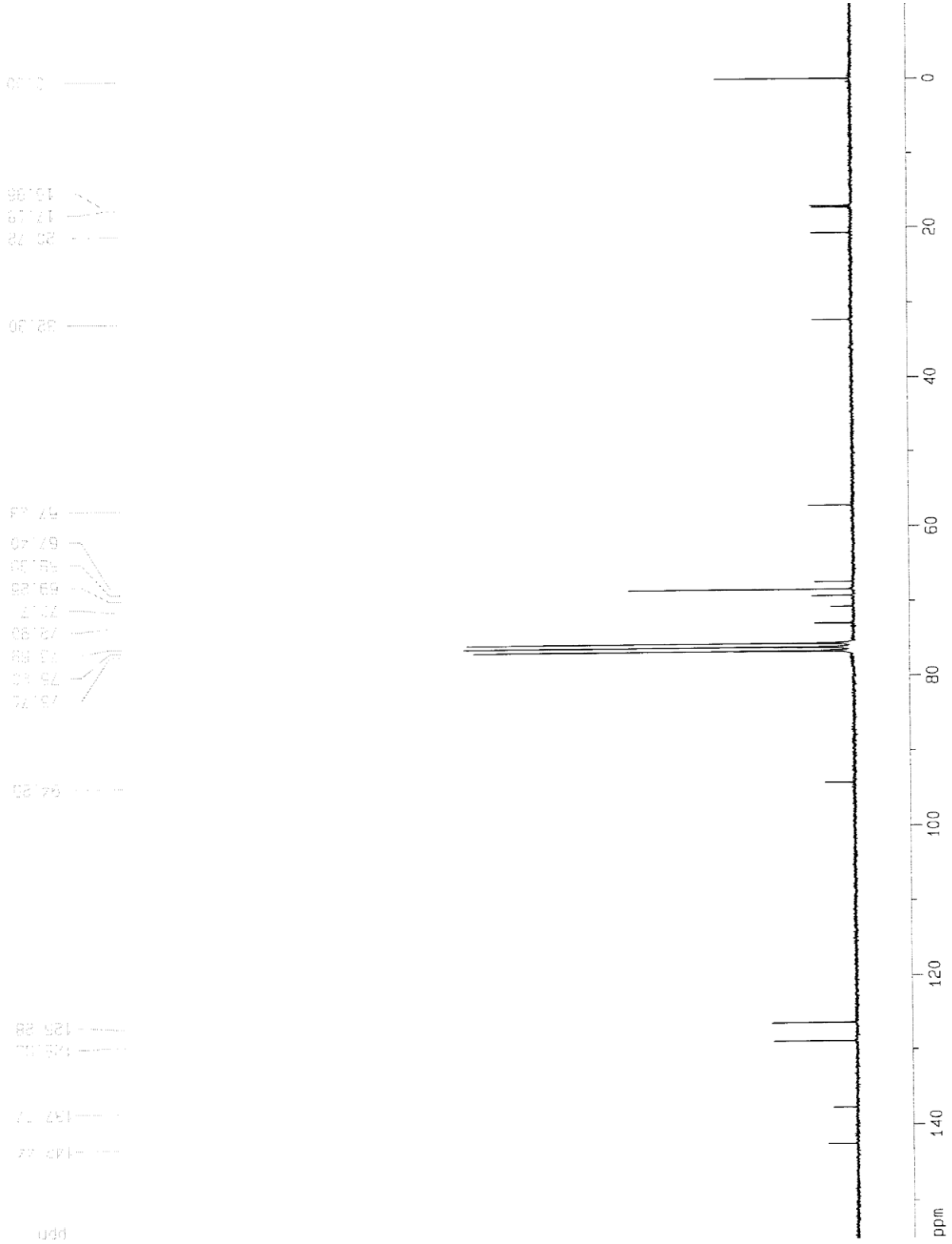
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4c**	

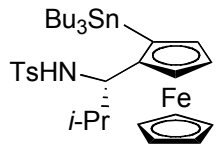


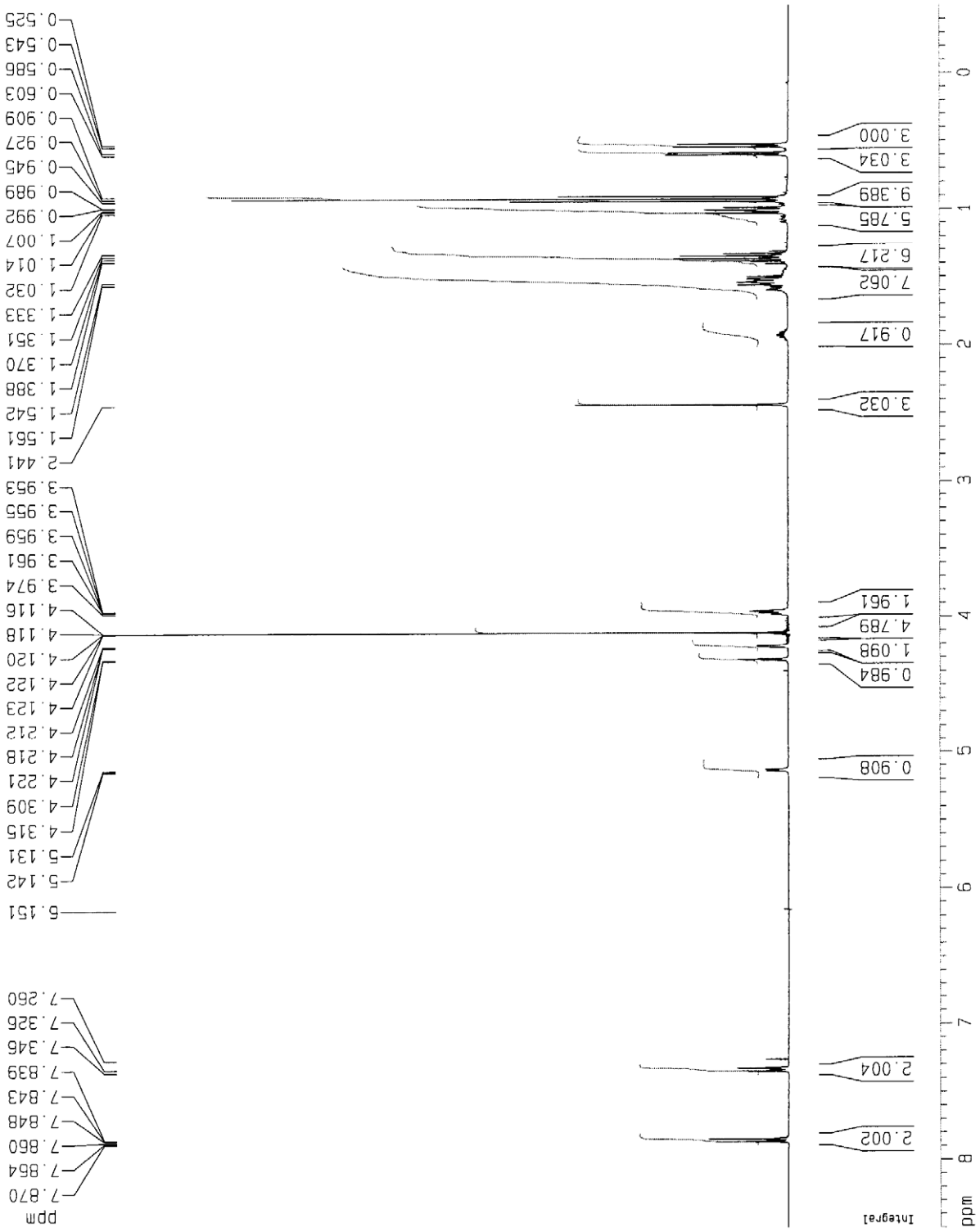
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},*S*)-4d**	

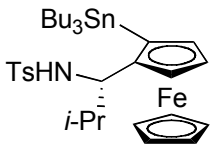


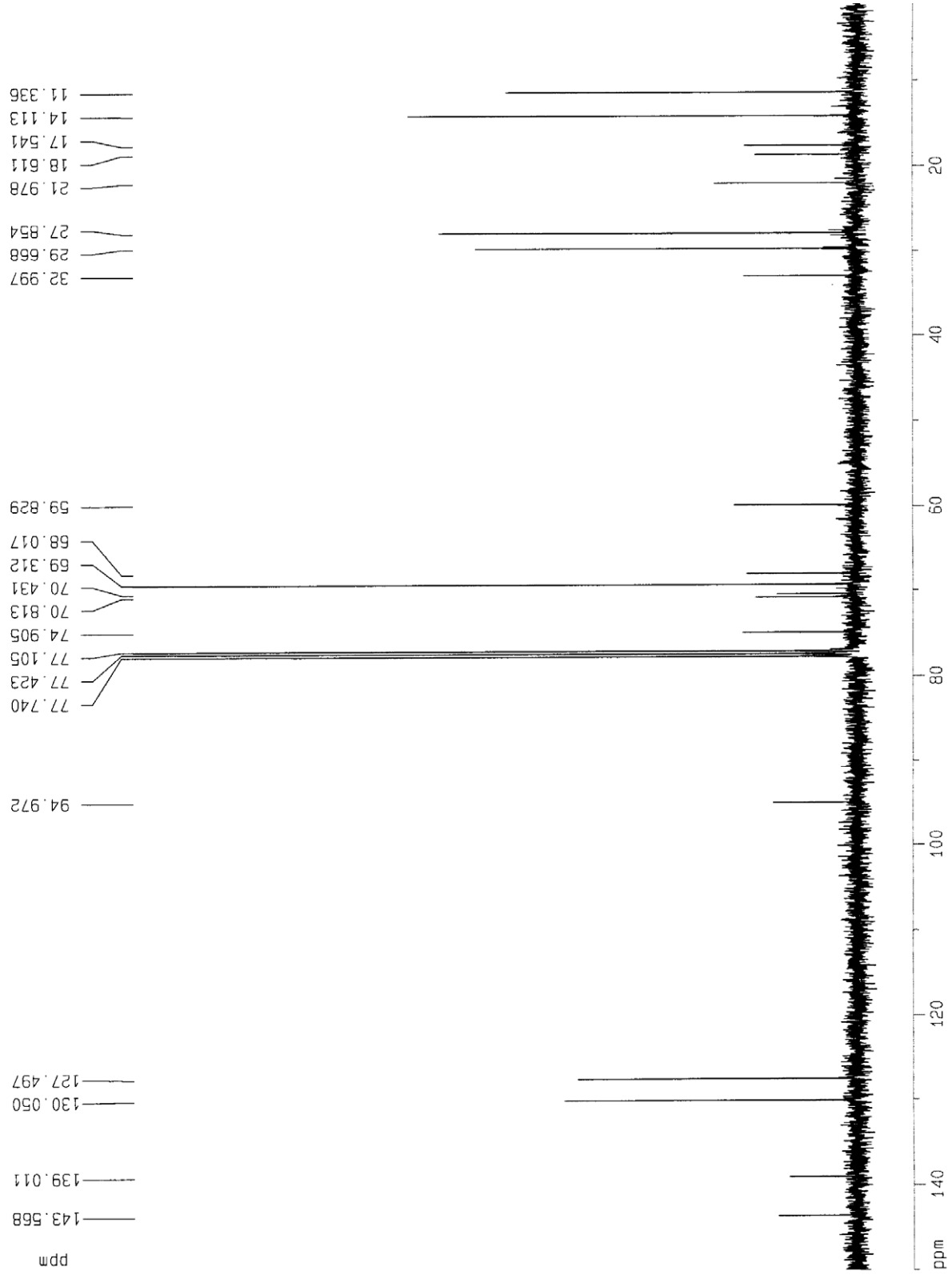
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4d**	

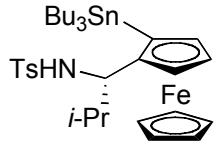


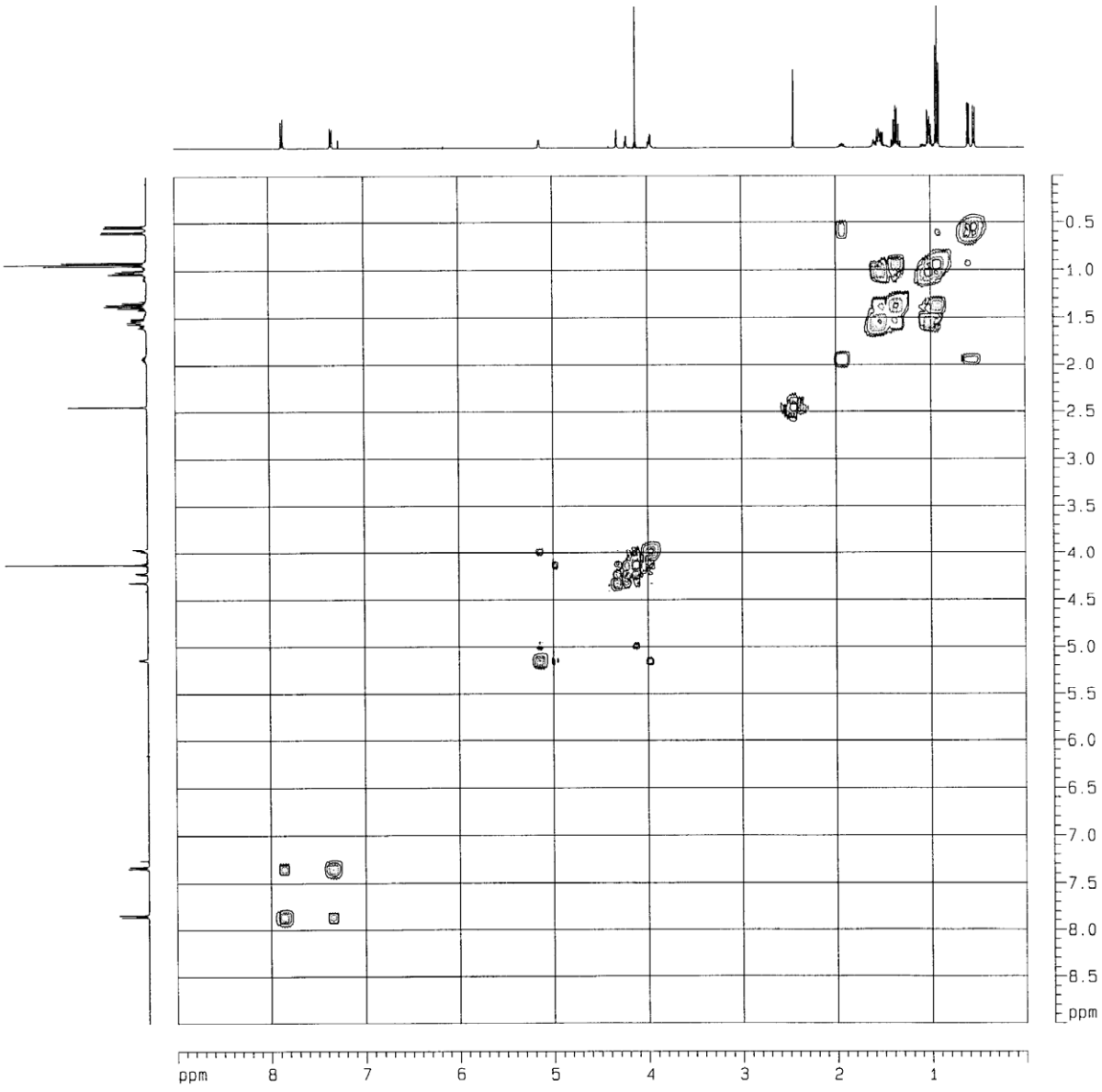
^{1}H NMR ($CDCl_3$, 400 MHz) of of **(S_{Fc},*S*)-4e**	

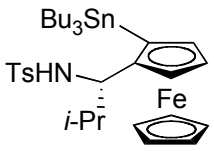


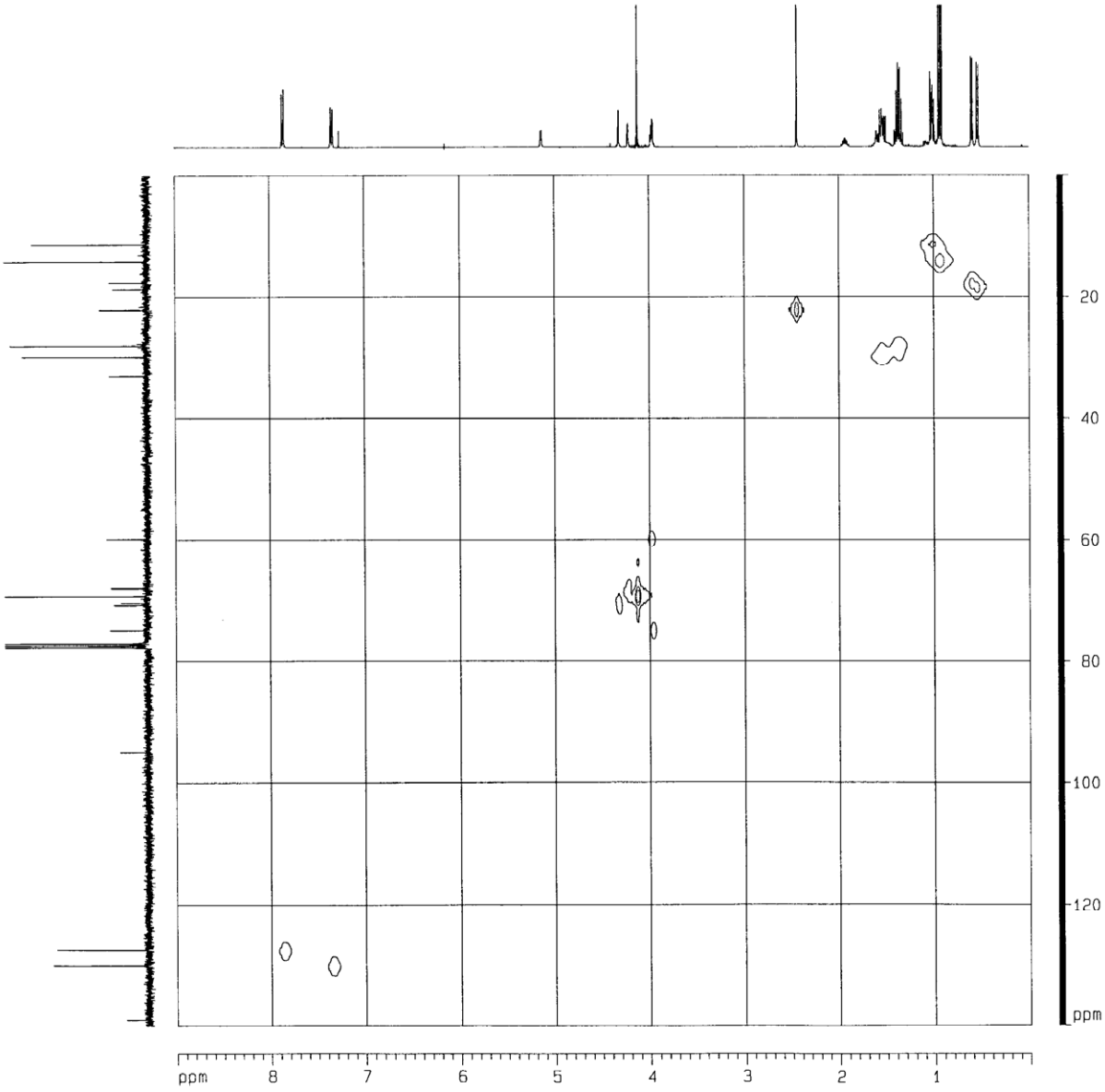
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4e**	

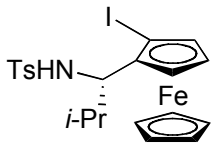


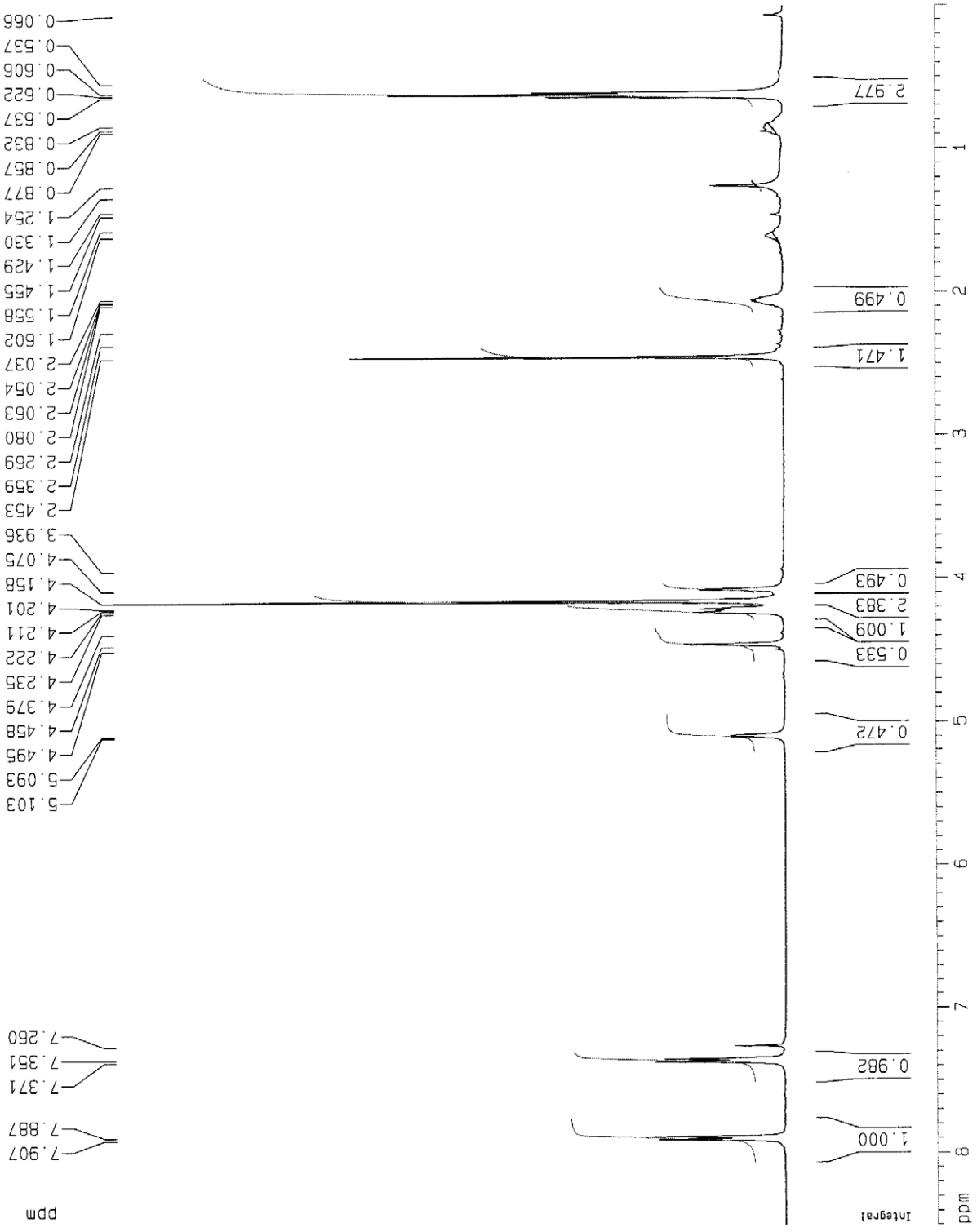
COSY H-H of **(S_{Fc},*S*)-4e**	

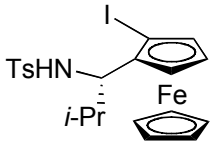


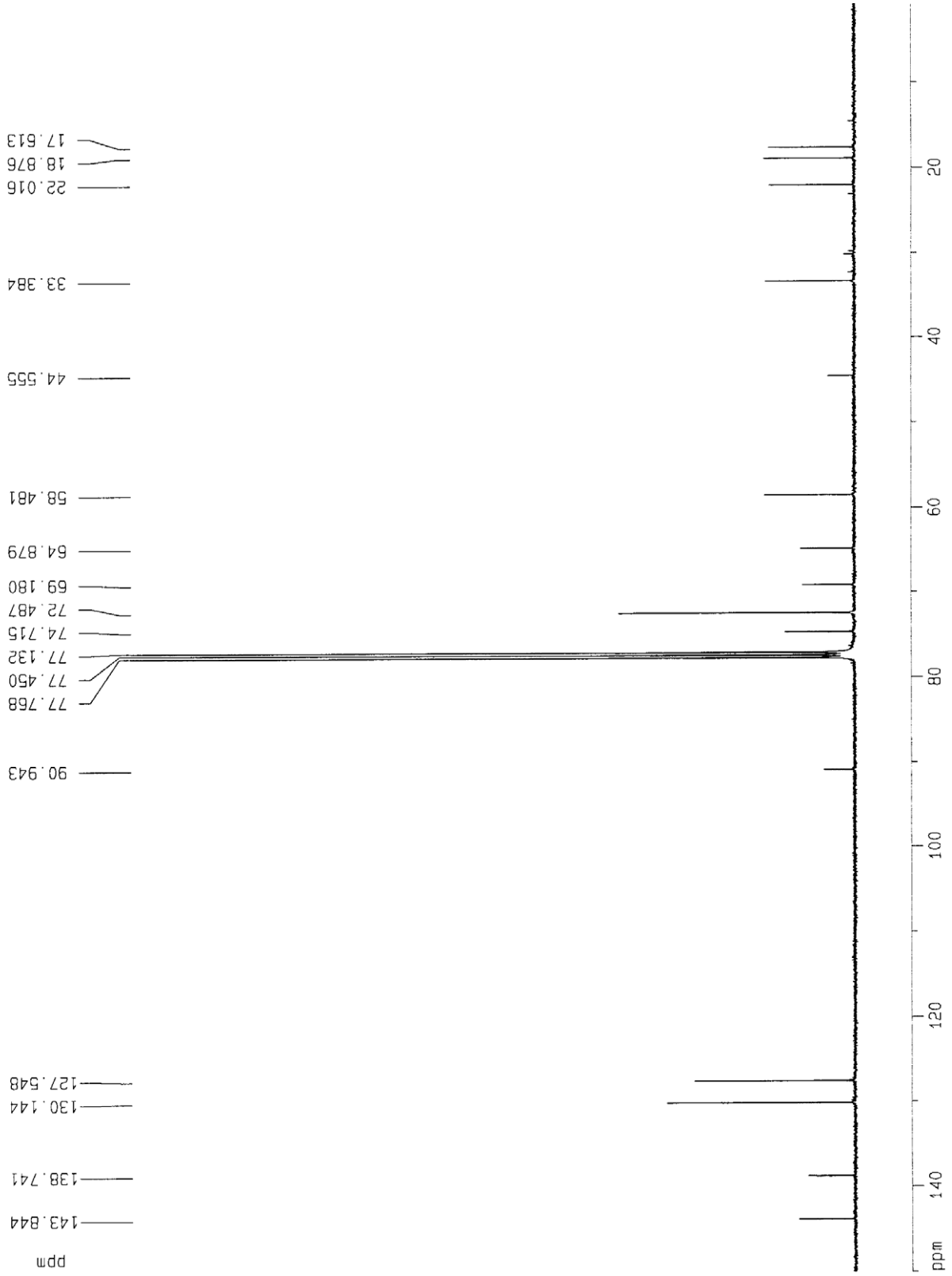
HMQC of **(S_{Fc},*S*)-4e**	

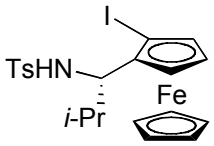


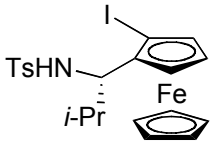
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},*S*)-4f**	

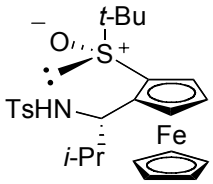


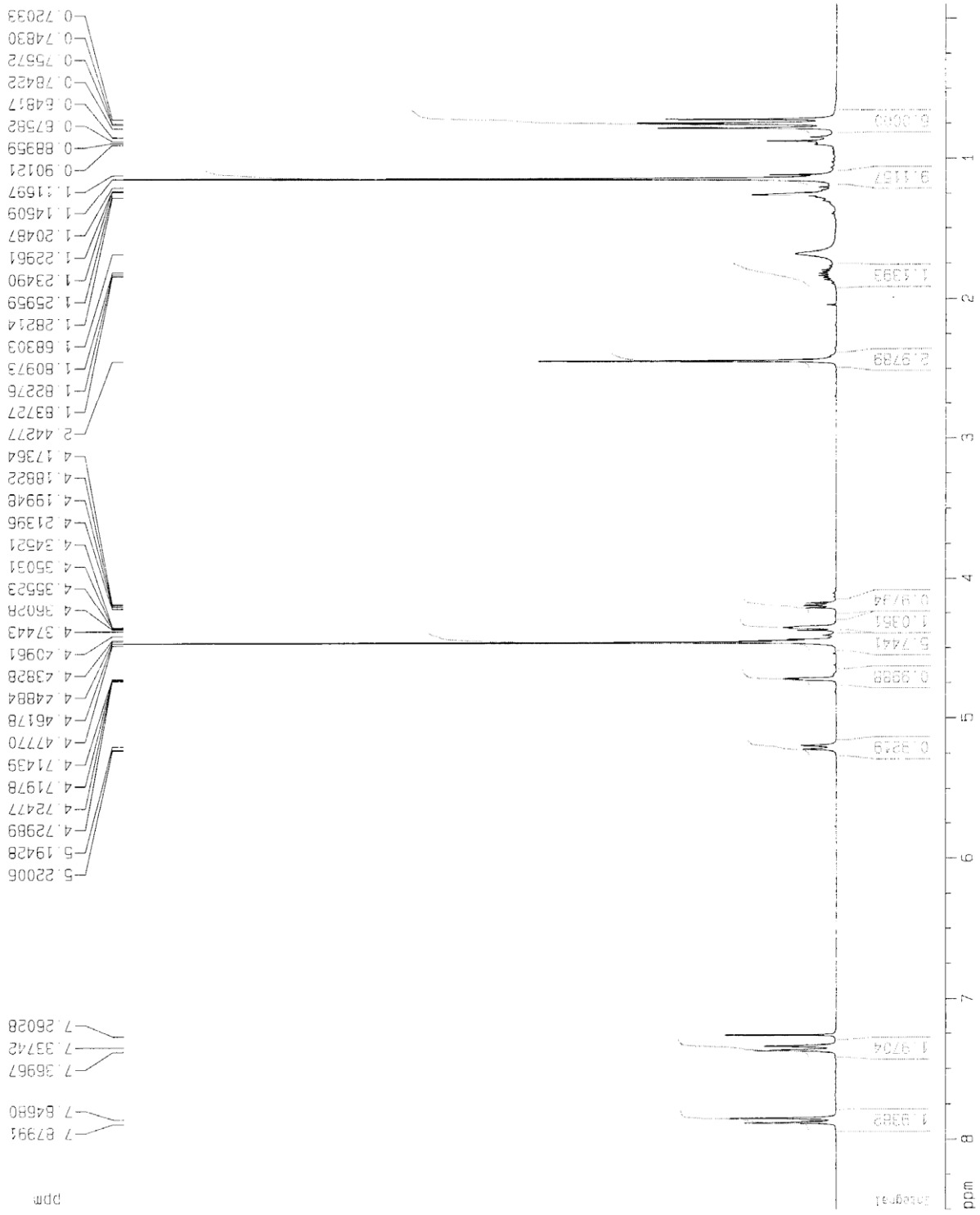
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4f**	

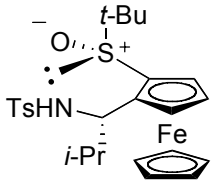


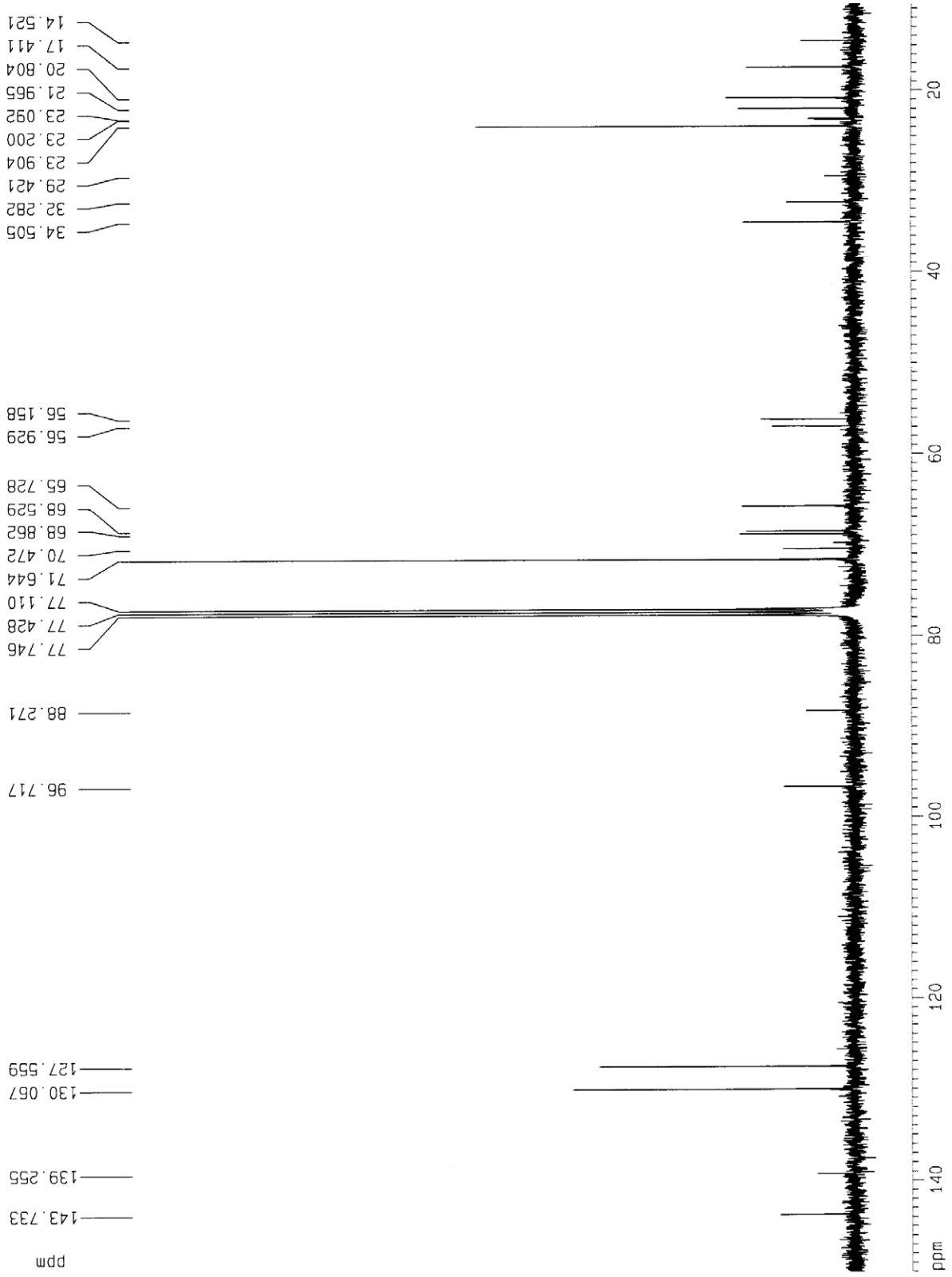
HMQC of **(S_{Fc},*S*)-4f**	

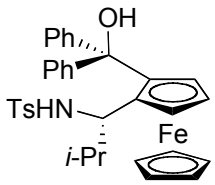
HMBC of **(S_{Fc},*S*)-4f**	

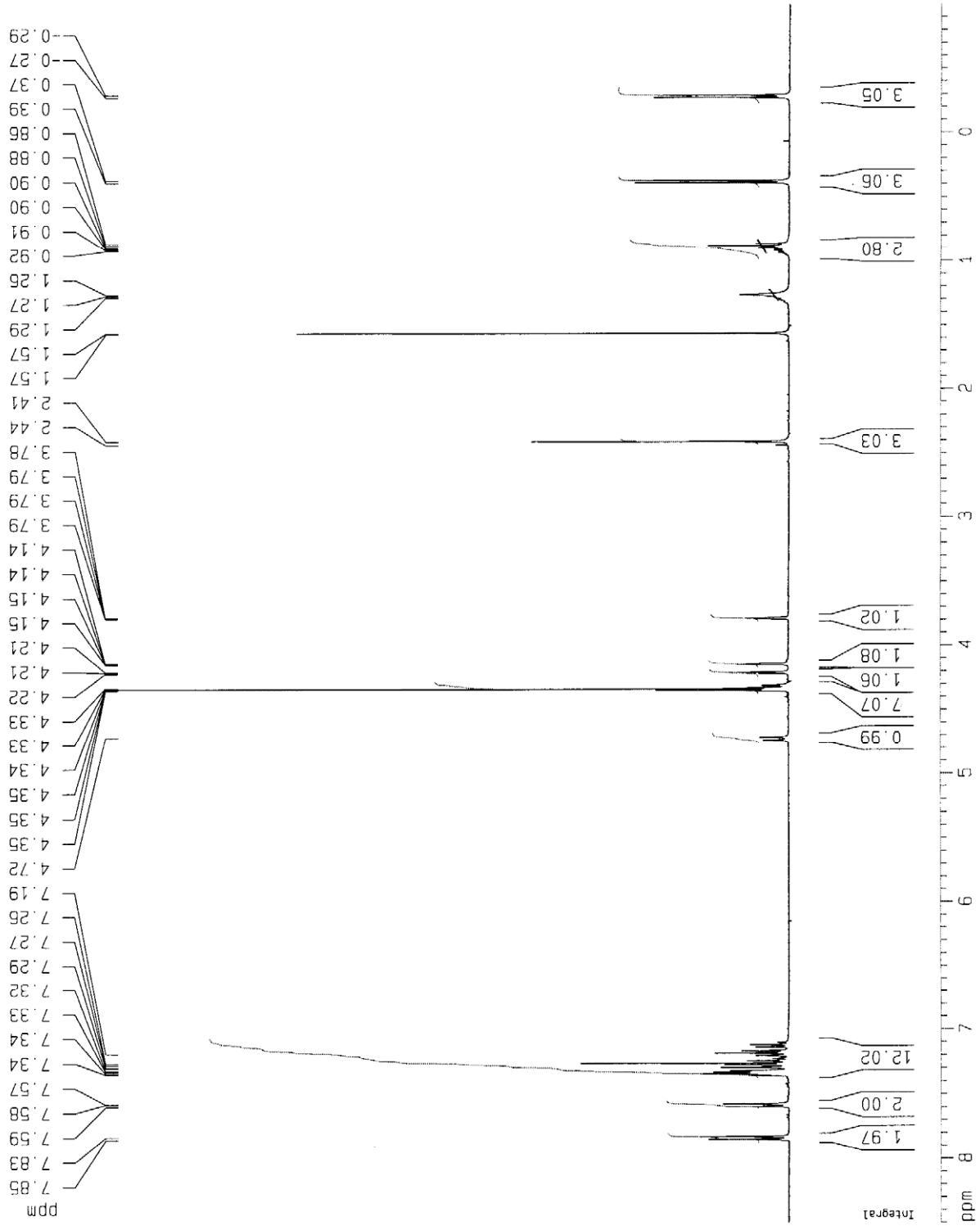
^{1}H NMR ($CDCl_3$, 400 MHz) of (S_{Fc},R_S,S)-**4g**	

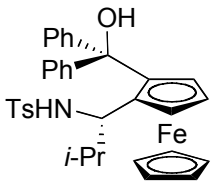


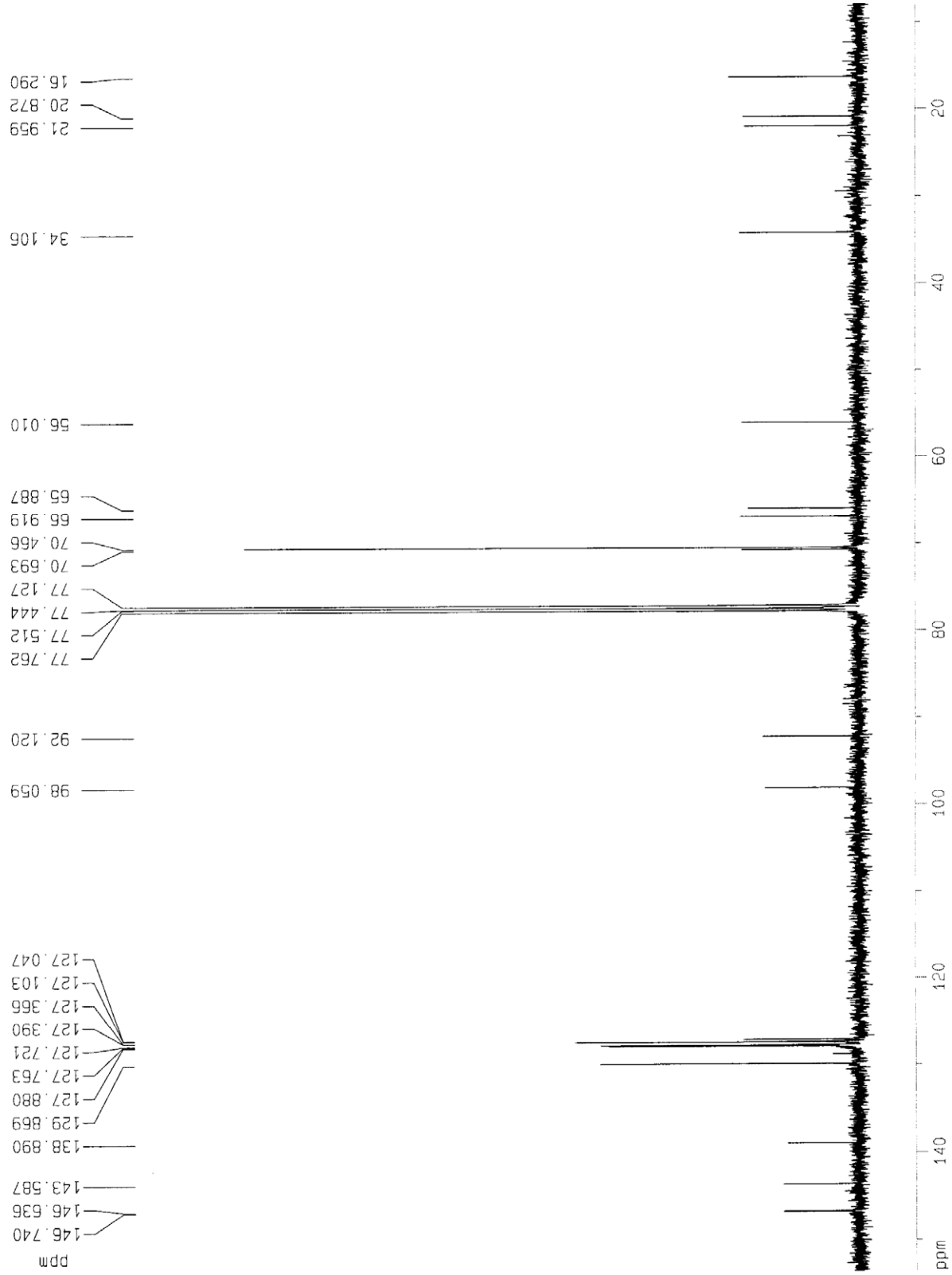
^{13}C NMR ($CDCl_3$, 100.6 MHz) of (S_{Fc},R_S,S)-**4g**	

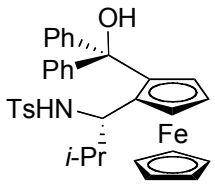


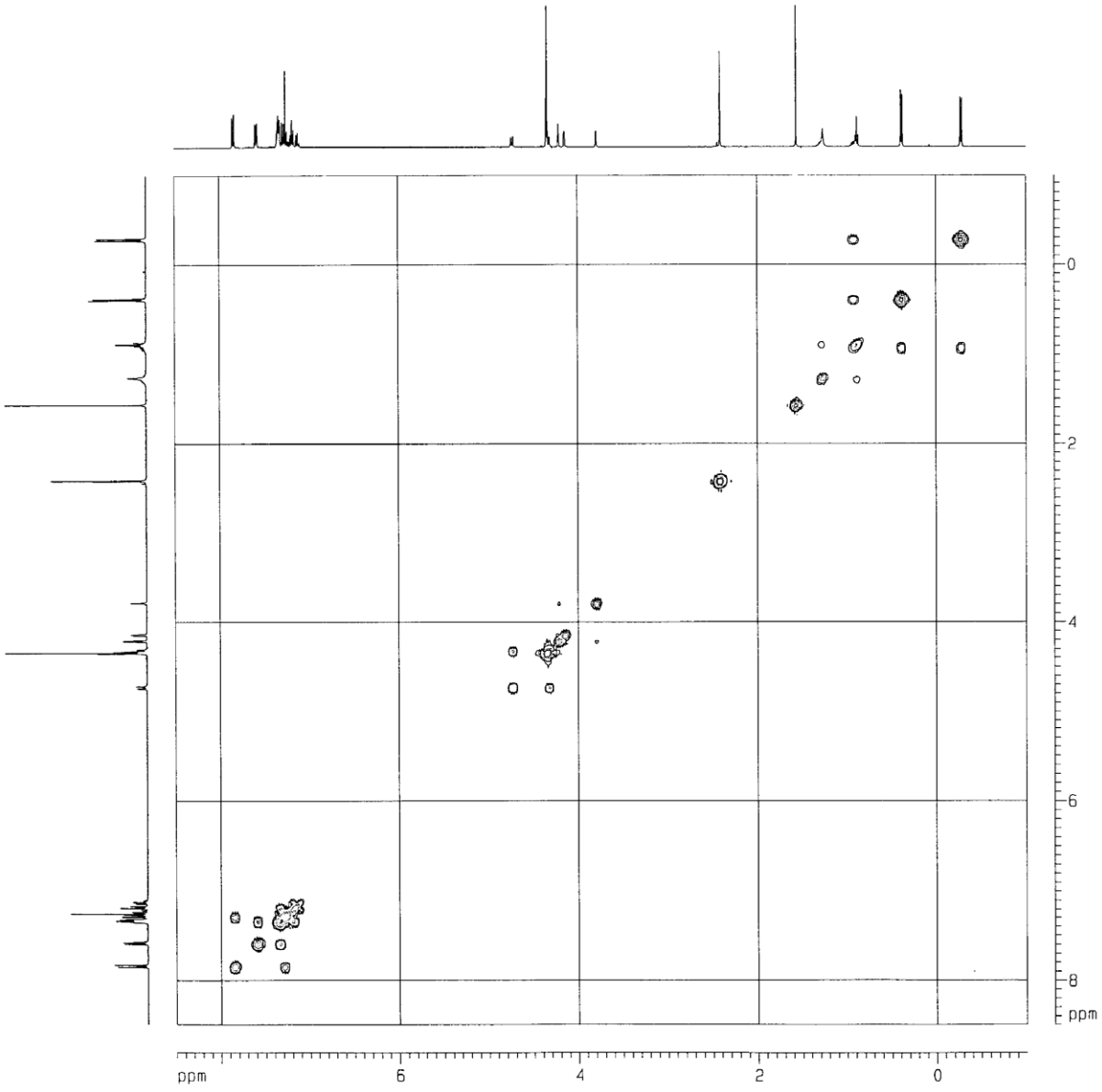
^{1}H NMR ($CDCl_3$, 400 MHz) of **(S_{Fc},*S*)-4h**	

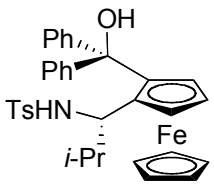


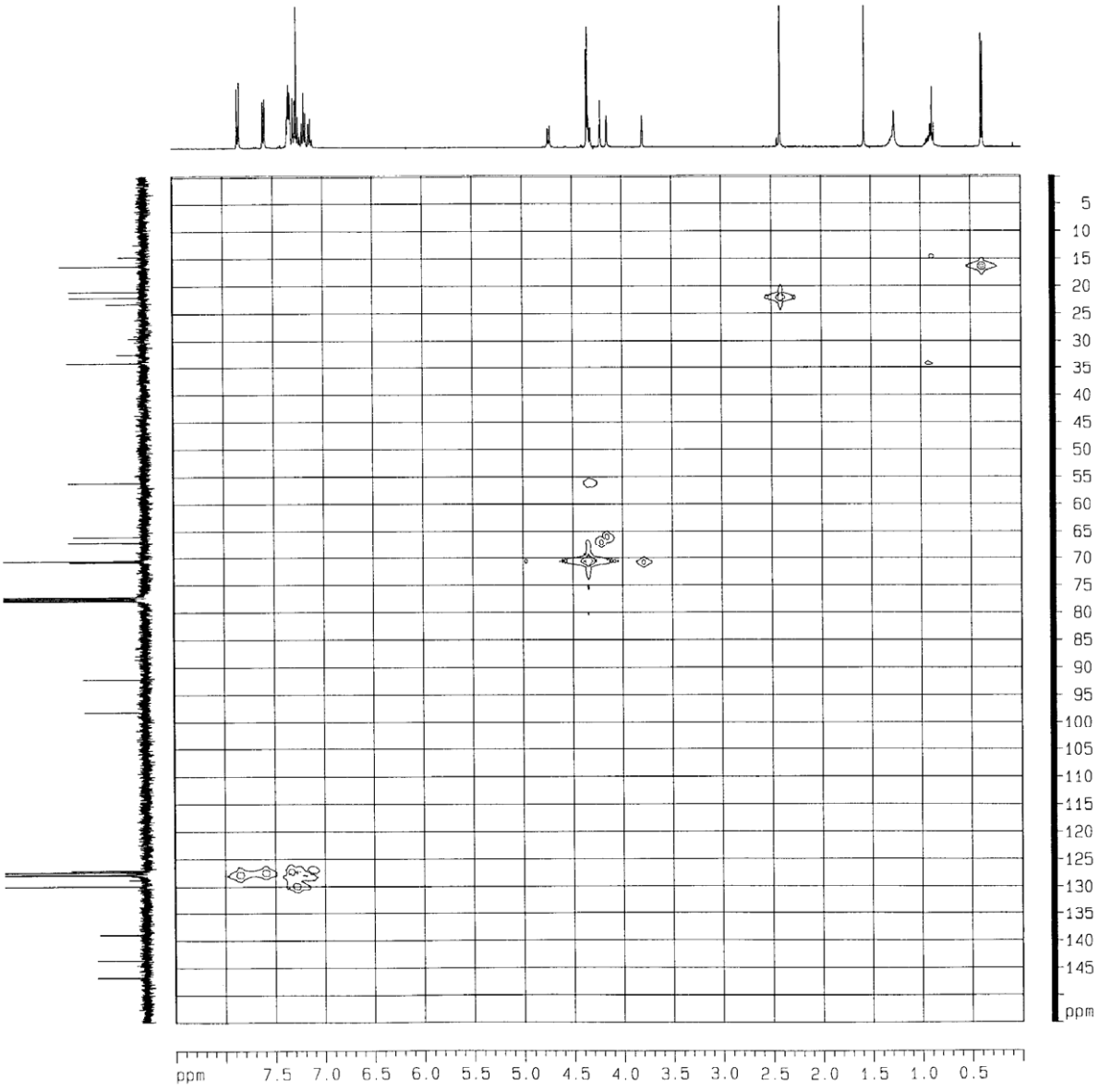
^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(S_{Fc},*S*)-4h**	

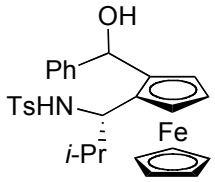


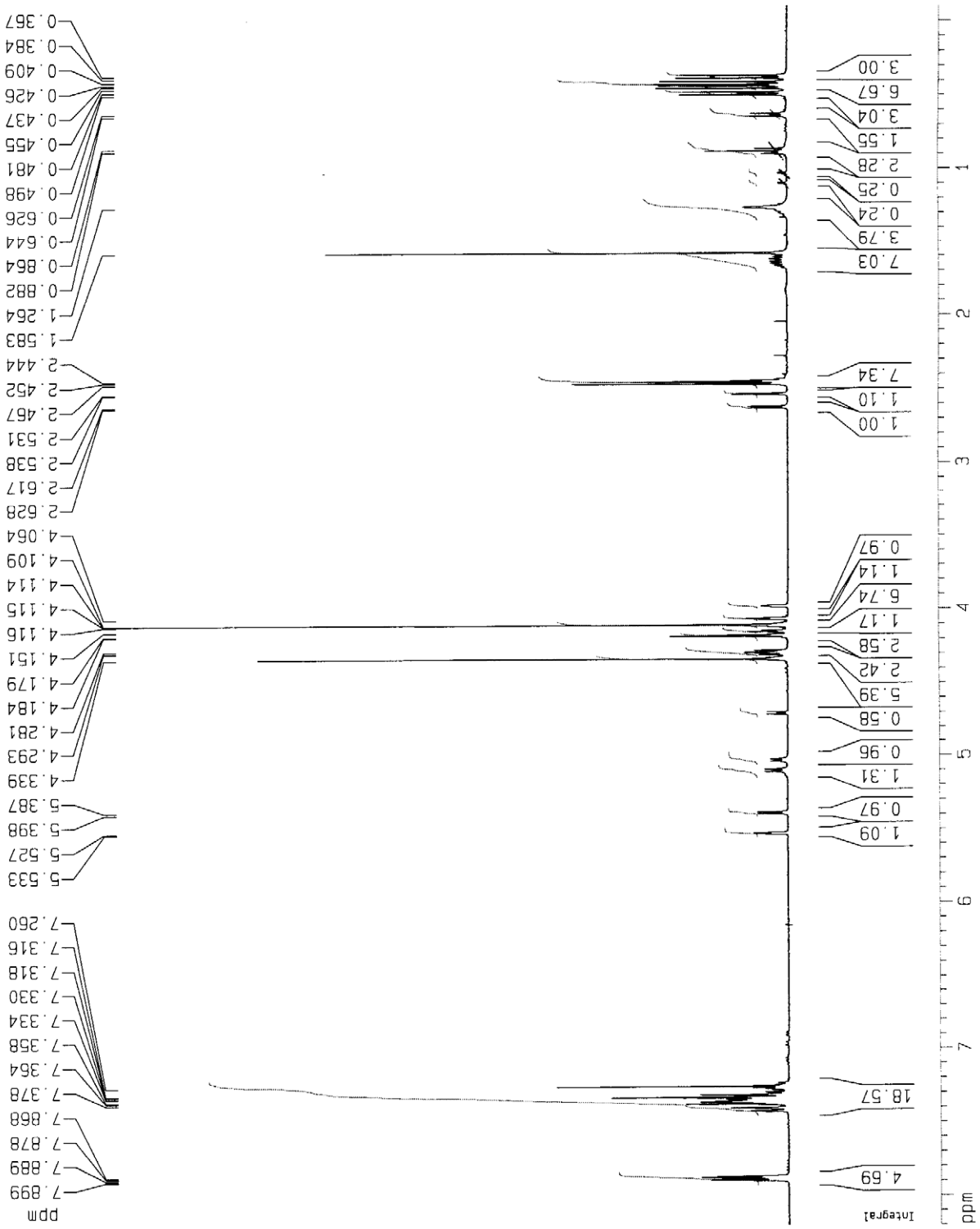
COSY H-H of **(S_{Fc},*S*)-4h**	

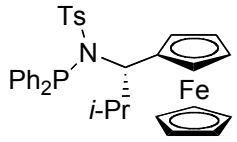


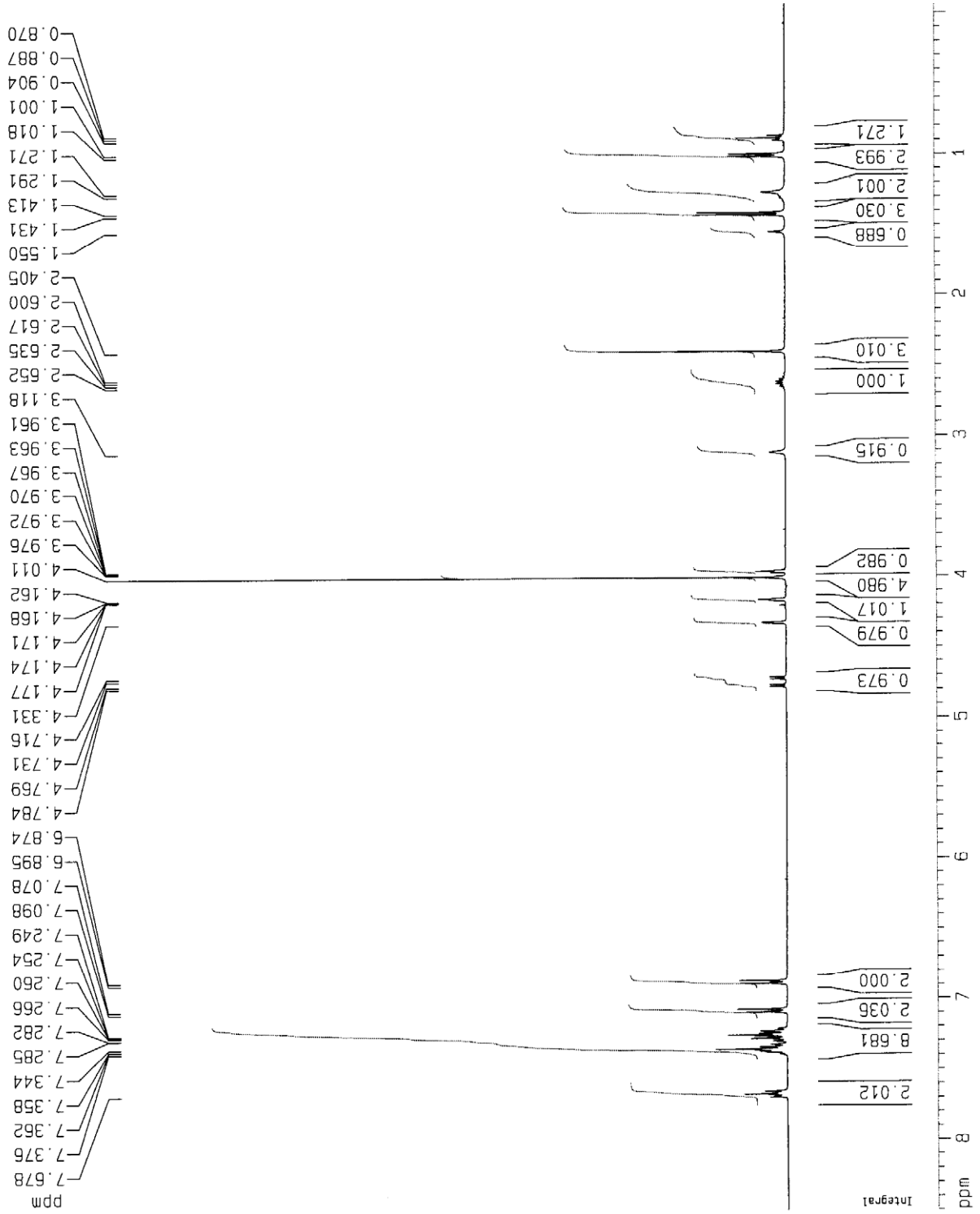
HMQC of **(S_{Fc},*S*)-4h**	

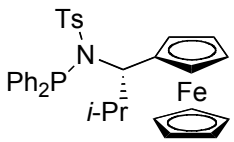


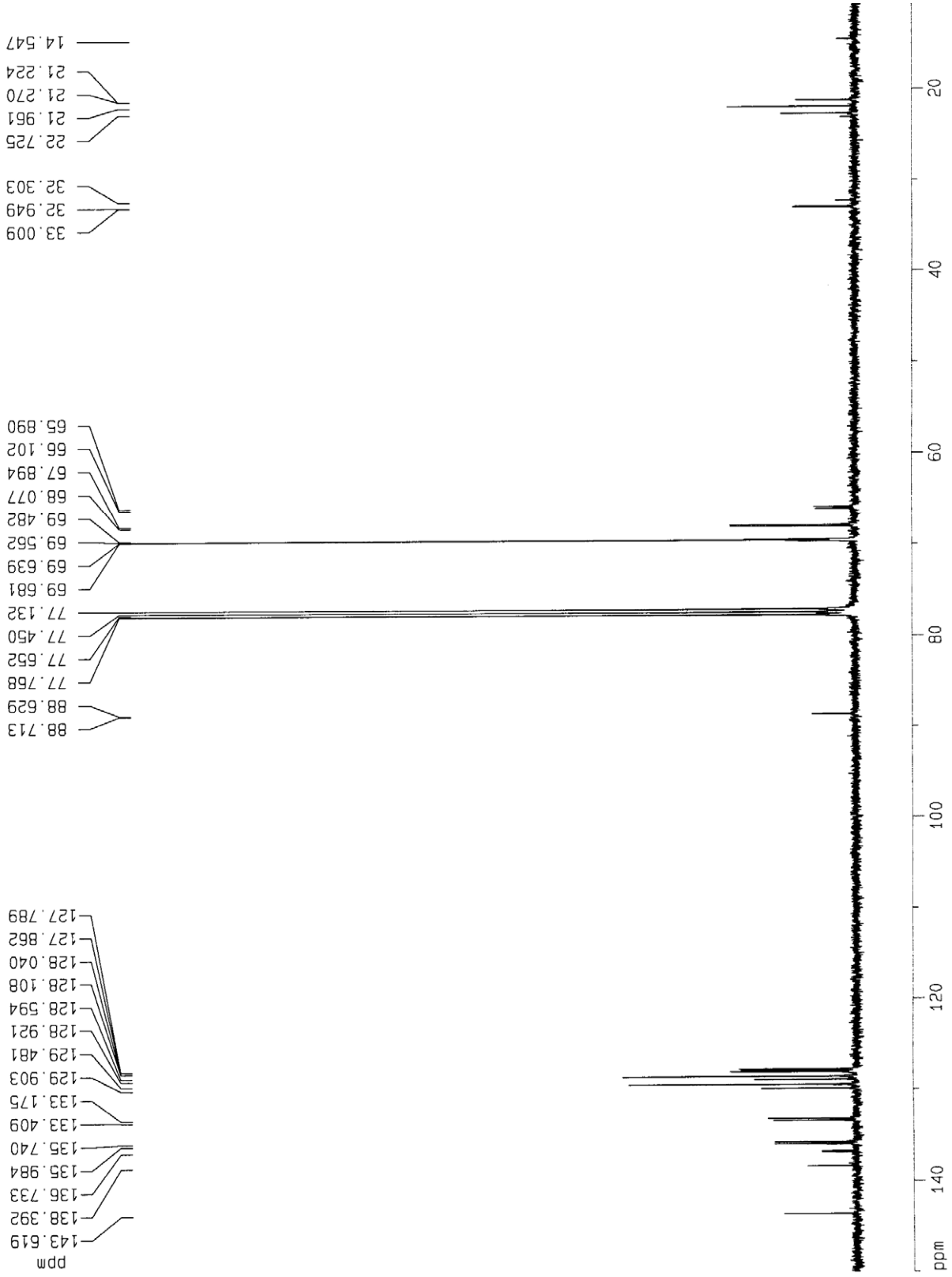
^{1}H NMR ($CDCl_3$, 400 MHz) of of **(S_{Fc},*S*)-4i** (mixture of 2 dia.)	

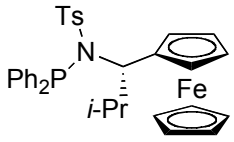


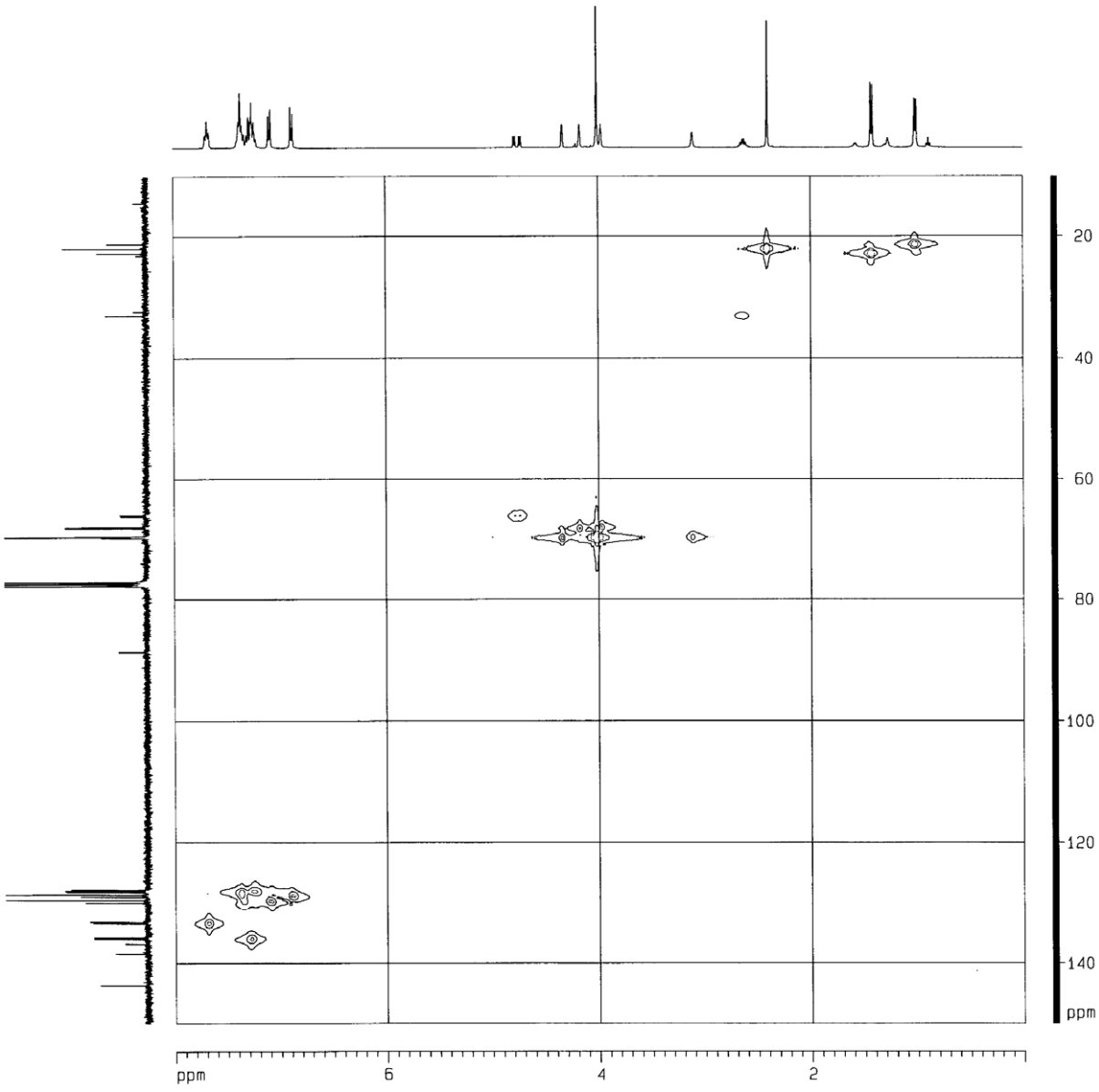
^{1}H NMR ($CDCl_3$, 400 MHz) of **(*S*)-5**	



^{13}C NMR ($CDCl_3$, 100.6 MHz) of **(*S*)-5**	



HMQC of **(*S*)-5**	



^{31}P NMR ($CDCl_3$, 161,9 MHz) of **(*S*)-5**