

Supporting Information

Diastereoselective deprotonative metalation of chiral ferrocene derived acetals and esters using mixed lithium-cadmium and lithium-zinc combinations

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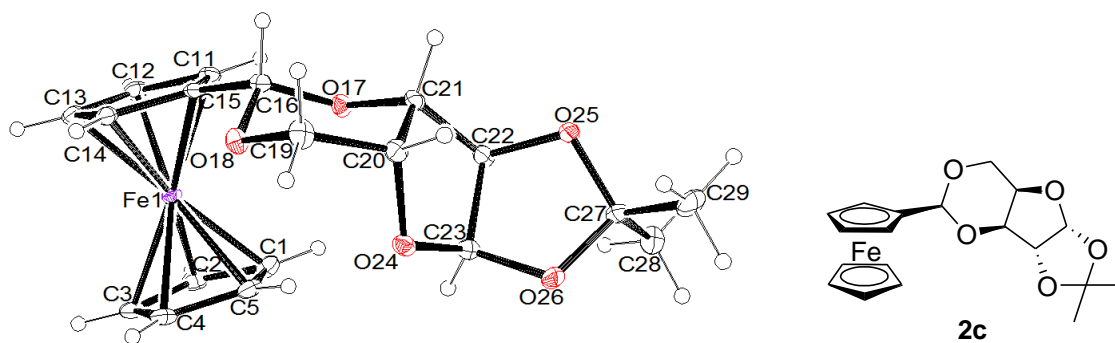
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1. X-ray crystallographic data for 2c, 6c-e, 6i-l, meso-10o and rac-10'o (APEXII, Bruker-AXS diffractometer)

Compound 2c

The sample was studied with graphite monochromatized Mo_Kα radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 3853 unique intensities and 228 parameters converged at $\omega R(F^2) = 0.0678$ ($R(F) = 0.0308$) for 3613 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

2c: C₁₉H₂₂FeO₅; $M = 386.22$; $T = 100(2) \text{ K}$; orthorhombic; space group $P2_12_12_1$, $a = 8.5565(6) \text{ \AA}$, $b = 10.2599(8) \text{ \AA}$, $c = 19.2947(14) \text{ \AA}$, $V = 1693.9(2) \text{ \AA}^3$, $Z = 4$; $d = 1.51 \text{ g.cm}^{-3}$; $\mu = 0.917 \text{ mm}^{-1}$.

CCDC 970485 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

¹ A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119.

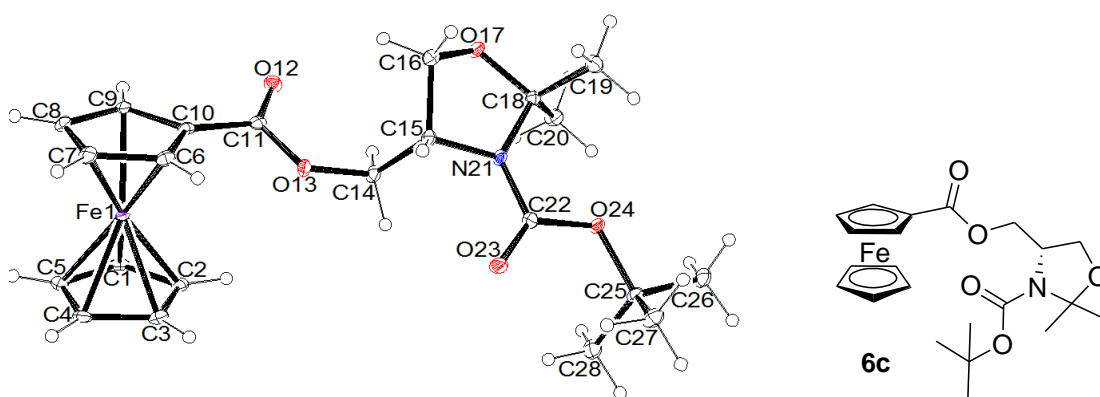
² G. M. Sheldrick, *Acta Cryst. A* **2008**, *A64*, 112-122.

³ L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849-854.

Compound 6c

The sample was studied with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm,⁴ implemented as the SQUEEZE option in PLATON.⁵ A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 5111 unique intensities and 267 parameters converged at $\omega R(F^2) = 0.0737$ ($R(F) = 0.0305$) for 4778 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

6c: $\text{C}_{22}\text{H}_{29}\text{FeNO}_5$; $M = 443.31$; $T = 100(2) \text{ K}$; monoclinic; space group $C2$, $a = 23.2862(18) \text{ \AA}$, $b = 5.9389(4) \text{ \AA}$, $c = 16.2631(13) \text{ \AA}$, $\beta = 90.645(4)^\circ$, $V = 2249.0(3) \text{ \AA}^3$, $Z = 4$; $d = 1.31 \text{ g.cm}^{-3}$; $\mu = 0.701 \text{ mm}^{-1}$.

CCDC 970486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

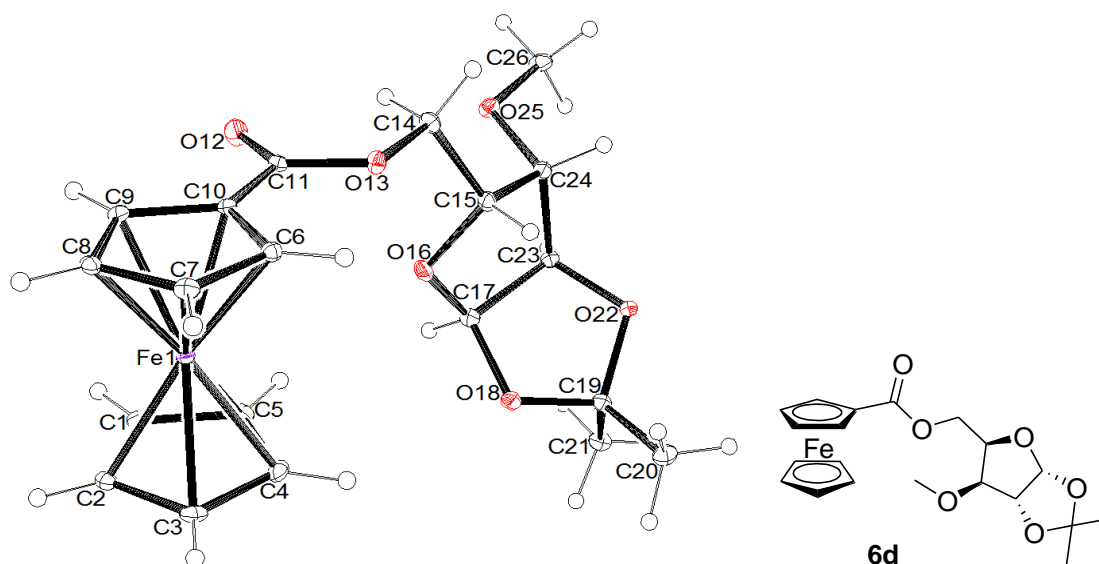
⁴ P. Van der Sluis, A. L. Spek, *Acta Cryst. A* **1990**, *A46*, 194-201.

⁵ A. L. Spek, *Acta Cryst. A* **1990**, *A46*, C34.

Compound 6d

The sample was studied with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 3747 unique intensities and 247 parameters converged at $\omega R(F^2) = 0.0555$ ($R(F) = 0.0226$) for 3679 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

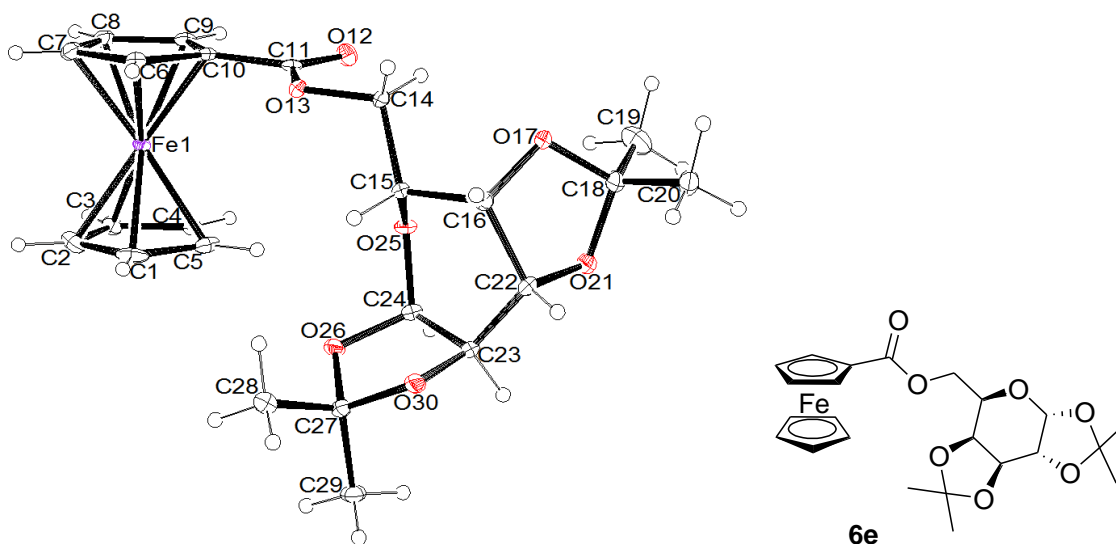
6d: $\text{C}_{20}\text{H}_{24}\text{FeO}_6$; $M = 416.24$; $T = 100(2) \text{ K}$; monoclinic; space group $P2_1$, $a = 8.9420(4) \text{ \AA}$, $b = 5.7179(2) \text{ \AA}$, $c = 18.0545(7) \text{ \AA}$, $\beta = 98.661(2)^\circ$, $V = 912.59(6) \text{ \AA}^3$, $Z = 2$; $d = 1.51 \text{ g.cm}^{-3}$; $\mu = 0.861 \text{ mm}^{-1}$.

CCDC 798861 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 6e

The sample was studied with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm,⁴ implemented as the SQUEEZE option in PLATON.⁵ A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 4456 unique intensities and 284 parameters converged at $\omega R(F^2) = 0.0805$ ($R(F) = 0.0347$) for 4236 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

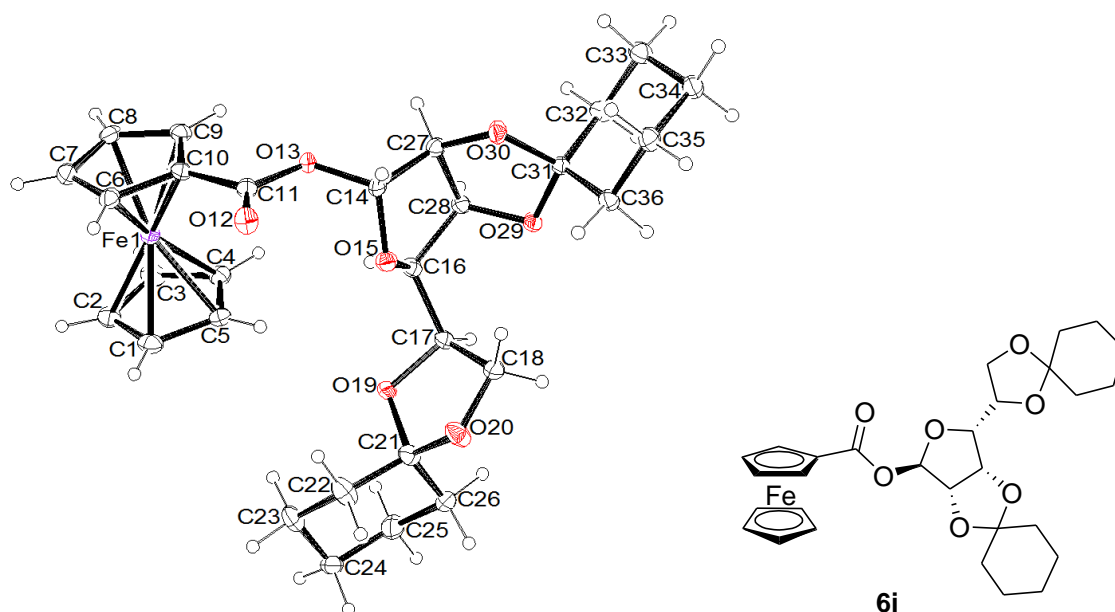
6e: C₂₃H₂₈FeO₇; $M = 472.30$; $T = 100(2) \text{ K}$; trigonal; space group $P6_5$, $a = 26.1720(14) \text{ \AA}$, $c = 5.6202(4) \text{ \AA}$, $V = 3333.9(3) \text{ \AA}^3$, $Z = 6$; $d = 1.41 \text{ g.cm}^{-3}$; $\mu = 0.720 \text{ mm}^{-1}$.

CCDC 798860 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 6i

The sample was studied with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 5763 unique intensities and 334 parameters converged at $\omega R(F^2) = 0.0959$ ($R(F) = 0.0462$) for 4064 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

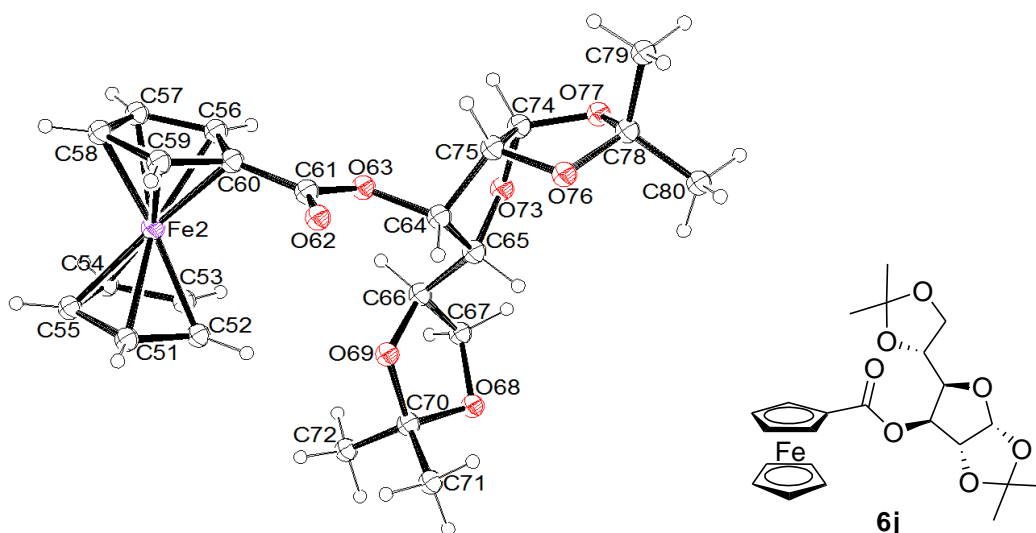
6i: C₂₉H₃₆FeO₇; $M = 552.43$; $T = 200(2) \text{ K}$; monoclinic; space group $P2_1$, $a = 17.3870(9) \text{ \AA}$, $b = 5.7126(4) \text{ \AA}$, $c = 12.8714(6) \text{ \AA}$, $\beta = 90.063(2)^\circ$, $V = 1278.5(2) \text{ \AA}^3$, $Z = 2$; $d = 1.43 \text{ g.cm}^{-3}$; $\mu = 0.637 \text{ mm}^{-1}$.

CCDC 798862 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 6j

The sample was studied with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 9694 unique intensities and 567 parameters converged at $\omega R(F^2) = 0.055$ ($R(F) = 0.0249$) for 9093 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

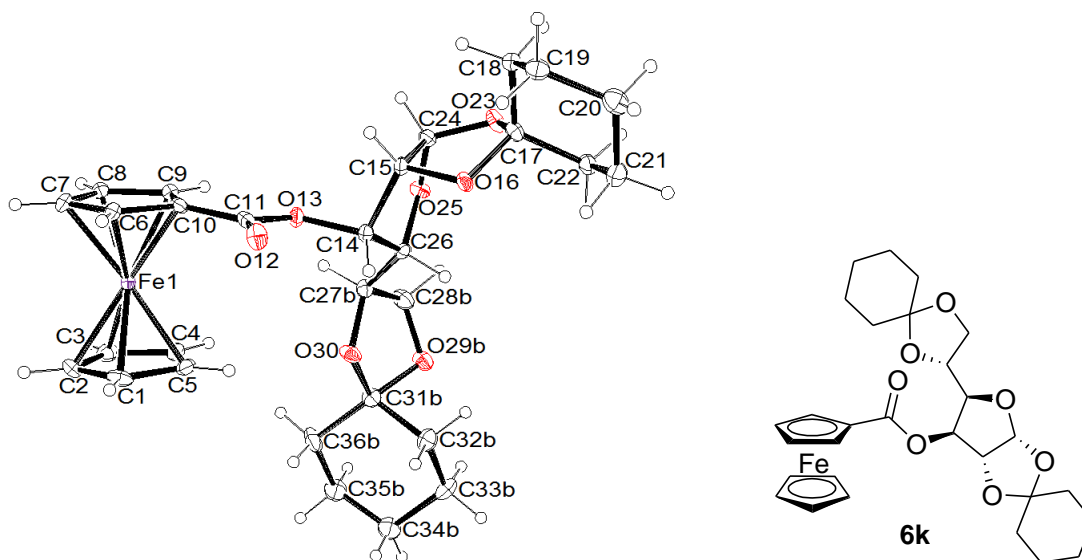
6j: $2(\text{C}_{23}\text{H}_{28}\text{FeO}_7)$; $M = 944.61$; $T = 100(2) \text{ K}$; monoclinic; space group $P2_1$, $a = 11.1999(4) \text{ \AA}$, $b = 12.2306(4) \text{ \AA}$, $c = 16.1208(6) \text{ \AA}$, $\beta = 97.150(2)^\circ$, $V = 2191.1(1) \text{ \AA}^3$, $Z = 2$; $d = 1.43 \text{ g.cm}^{-3}$; $\mu = 0.730 \text{ mm}^{-1}$.

CCDC 798863 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 6k

The sample was studied with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.⁶ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 5788 unique intensities and 346 parameters converged at $\omega R(F^2) = 0.1136$ ($R(F) = 0.0536$) for 4372 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

6k: $\text{C}_{29}\text{H}_{36}\text{FeO}_7$; $M = 552.43$; $T = 150(2) \text{ K}$; orthorhombic; space group $P2_12_12_1$, $a = 5.6582(4) \text{ \AA}$, $b = 19.1457(14) \text{ \AA}$, $c = 23.4462(17) \text{ \AA}$, $V = 2539.9(3) \text{ \AA}^3$, $Z = 4$; $d = 1.445 \text{ g.cm}^{-3}$; $\mu = 0.642 \text{ mm}^{-1}$.

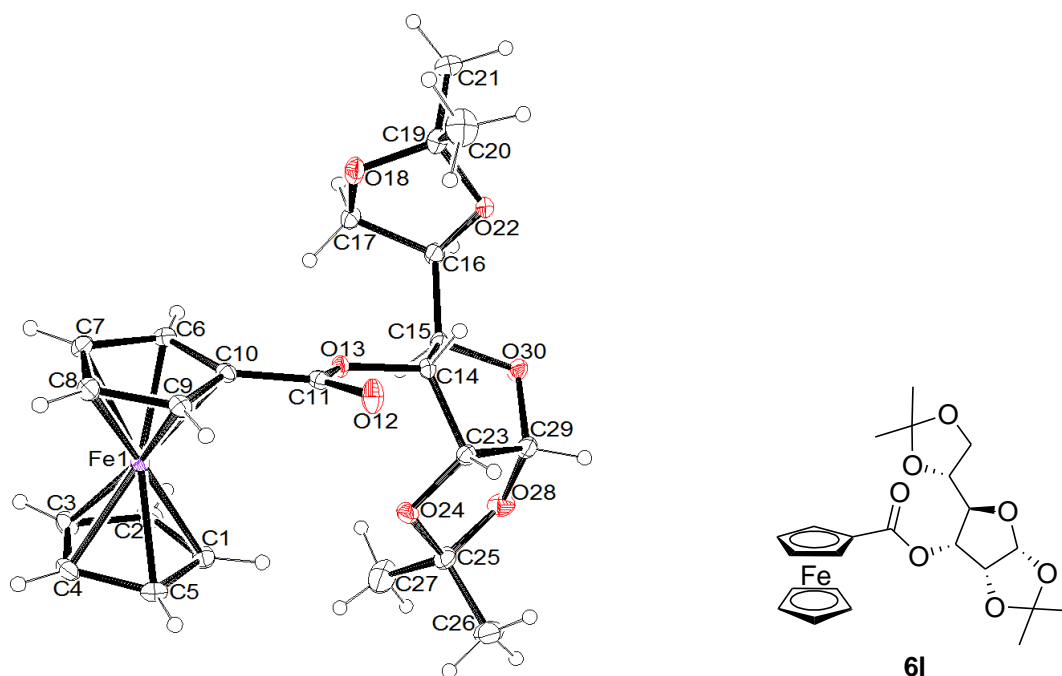
CCDC 970487 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

⁶ L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849-854.

Compound 6l

The sample was studied with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 4990 unique intensities and 285 parameters converged at $\omega R(F^2) = 0.0605$ ($R(F) = 0.0261$) for 4696 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

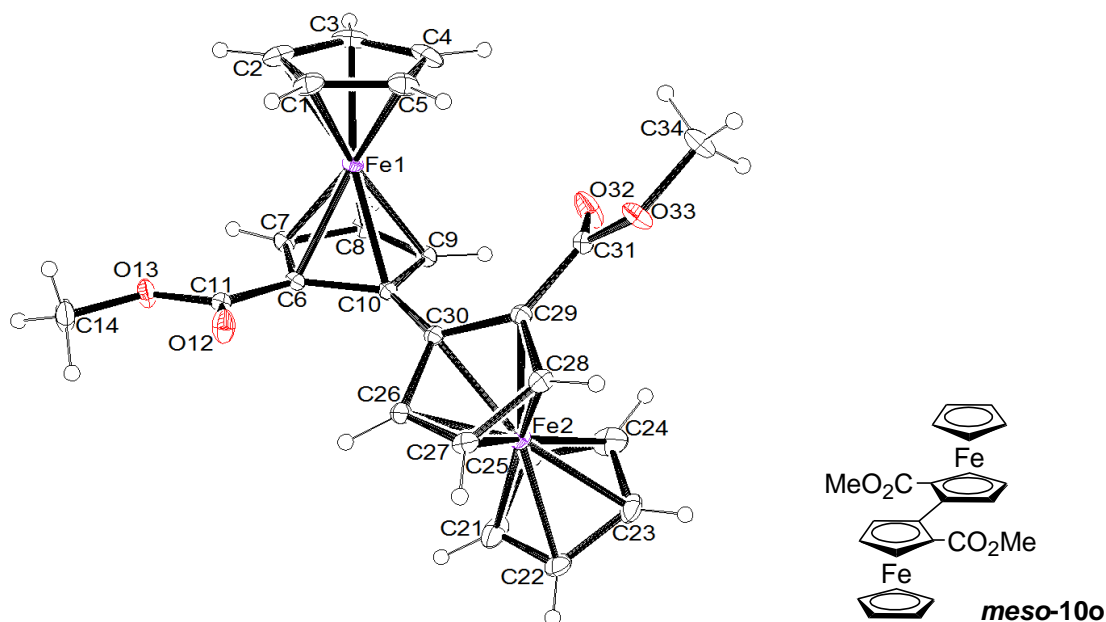
6l: $\text{C}_{23}\text{H}_{28}\text{FeO}_7$; $M = 472.30$; $T = 150(2) \text{ K}$; orthorhombic; space group $P2_12_12_1$, $a = 7.3390(1) \text{ \AA}$, $b = 9.7170(2) \text{ \AA}$, $c = 30.6157(6) \text{ \AA}$, $V = 2183.3(1) \text{ \AA}^3$, $Z = 4$; $d = 1.43 \text{ g.cm}^{-3}$; $\mu = 0.733 \text{ mm}^{-1}$.

CCDC 798864 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound *meso*-10o

The sample was studied with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 4653 unique intensities and 273 parameters converged at $\omega R(F^2) = 0.067$ ($R(F) = 0.0274$) for 4070 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



Crystal data

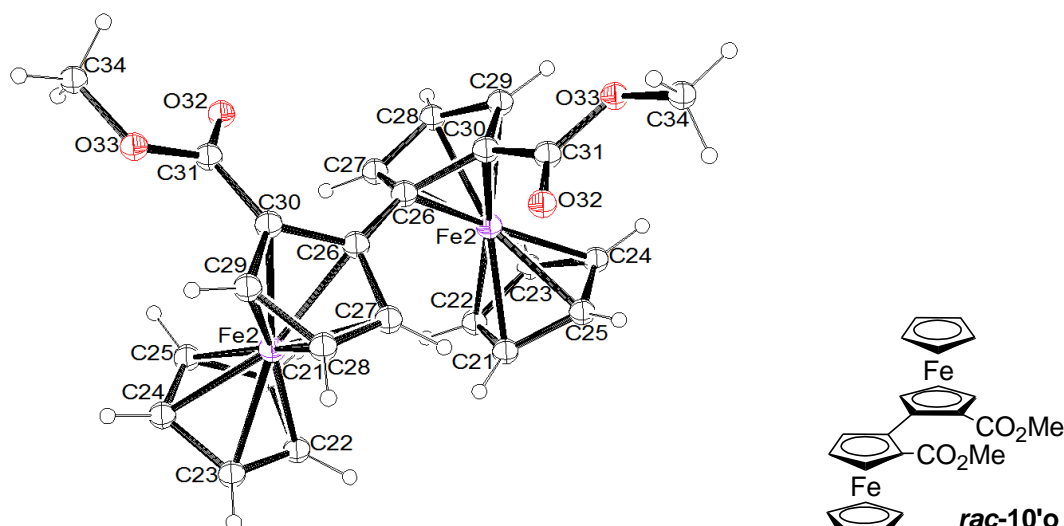
***meso*-10o**: C₂₄H₂₂Fe₂O₄; $M = 486.12$; $T = 150(2) \text{ K}$; monoclinic; space group $P2_1/c$, $a = 10.3467(3) \text{ \AA}$, $b = 16.5401(5) \text{ \AA}$, $c = 12.6568(3) \text{ \AA}$, $\beta = 109.903(1)^\circ$, $V = 2036.6(1) \text{ \AA}^3$, $Z = 4$; $d = 1.58 \text{ g.cm}^{-3}$; $\mu = 1.453 \text{ mm}^{-1}$.

CCDC 970488 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound *rac-10'o*

The sample was studied with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SIR97 program,¹ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)² with the aid of the WINGX program.³ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 4572 unique intensities and 273 parameters converged at $\omega R(F^2) = 0.0706$ ($R(F) = 0.0286$) for 3949 observed reflections with $I > 2\sigma(I)$.

ORTEP figure



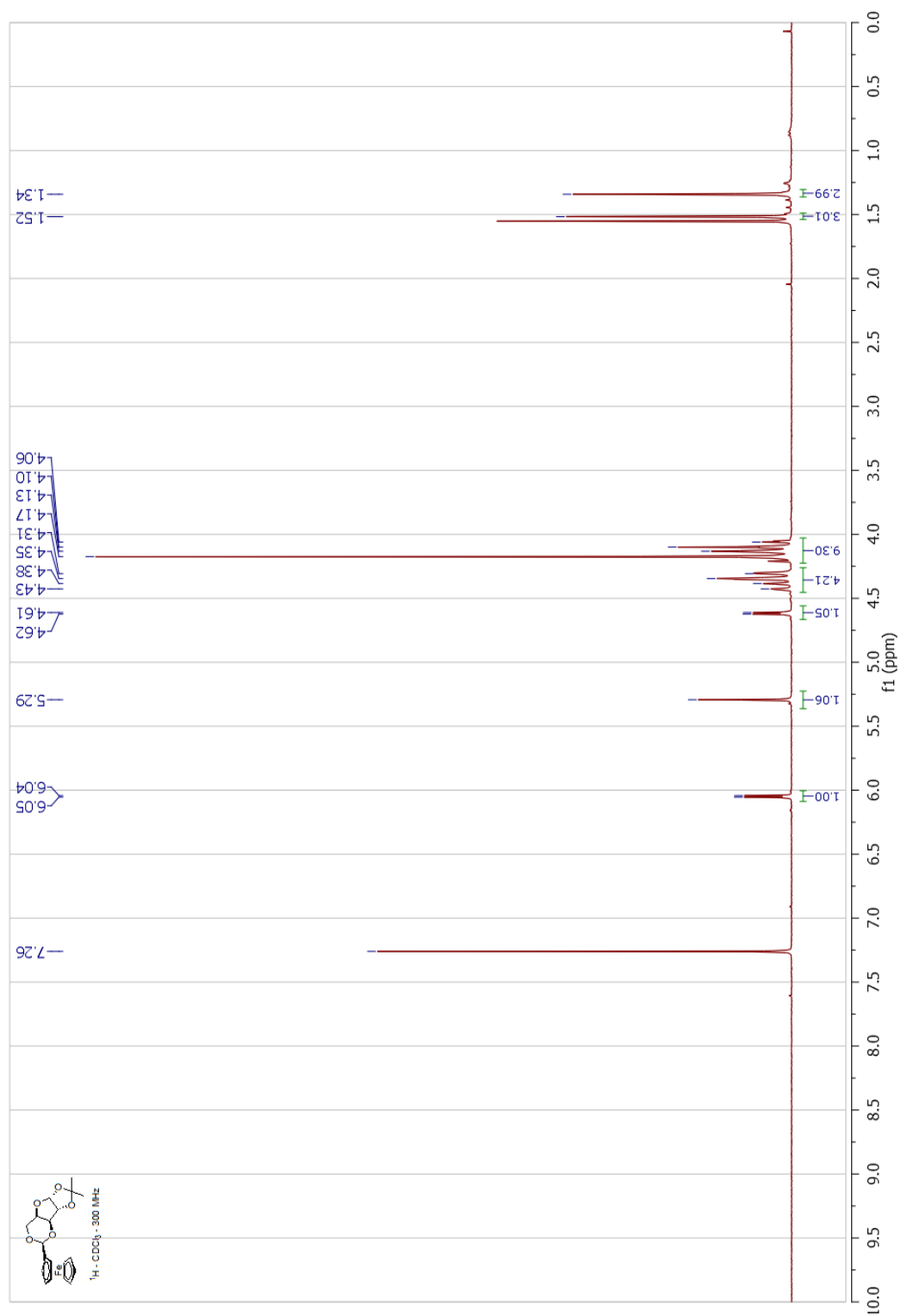
Crystal data

rac-10'o: $2(\text{C}_{24}\text{H}_{22}\text{Fe}_2\text{O}_4)$; $M = 972.23$; $T = 150(2) \text{ K}$; monoclinic; space group $C2/c$, $a = 15.4067(3) \text{ \AA}$, $b = 17.6978(4) \text{ \AA}$, $c = 15.0585(3) \text{ \AA}$, $\beta = 102.373(1)^\circ$, $V = 4010.5(2) \text{ \AA}^3$, $Z = 4$; $d = 1.61 \text{ g.cm}^{-3}$; $\mu = 1.476 \text{ mm}^{-1}$.

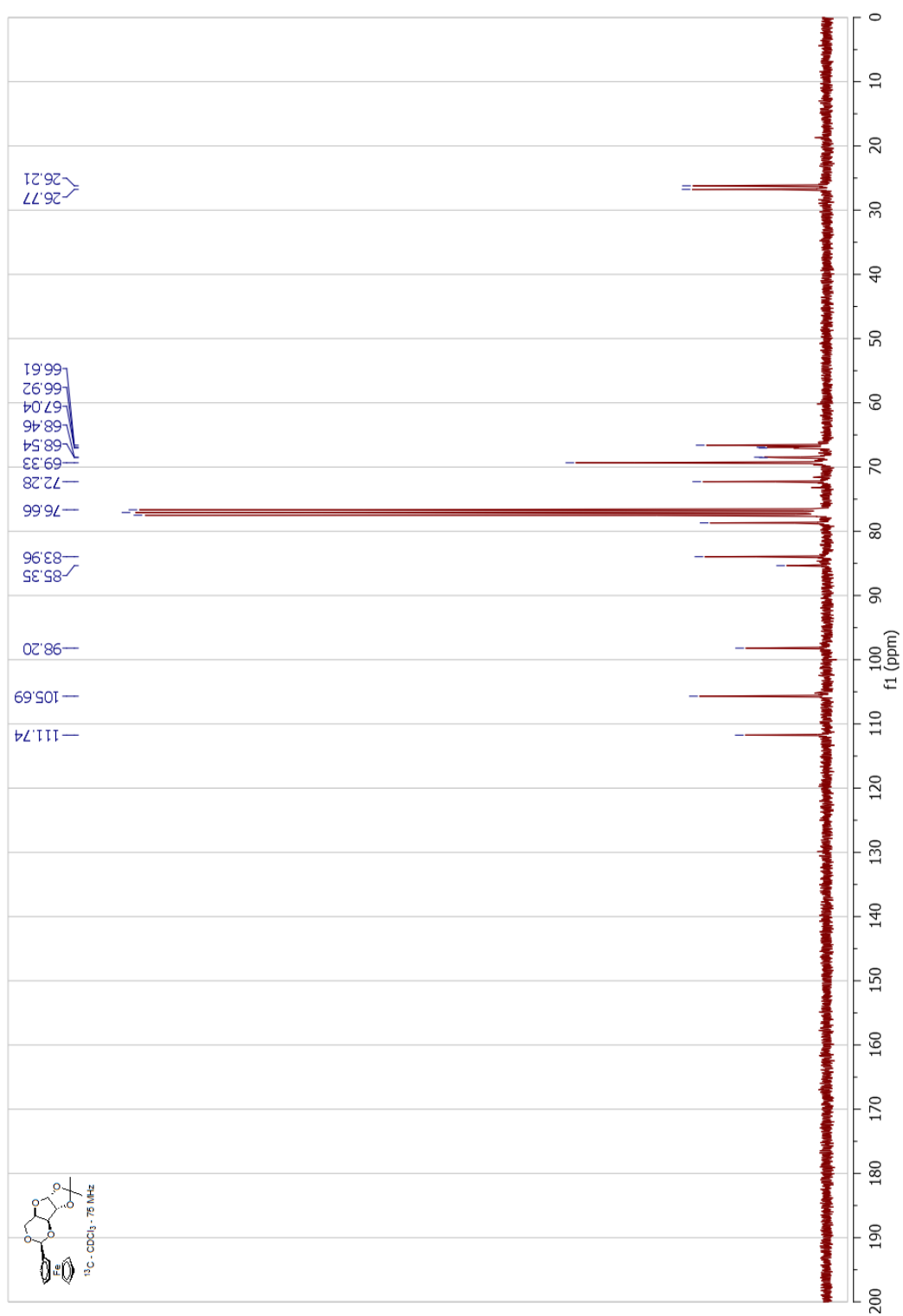
CCDC 970489 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. NMR spectra for 2c, 5g, 6a-c, 6f,g, 7a,b,f,g, 8a,d-f,n, meso-10o, rac-10'o, R_P-11j, S_P-11n and rac-11o

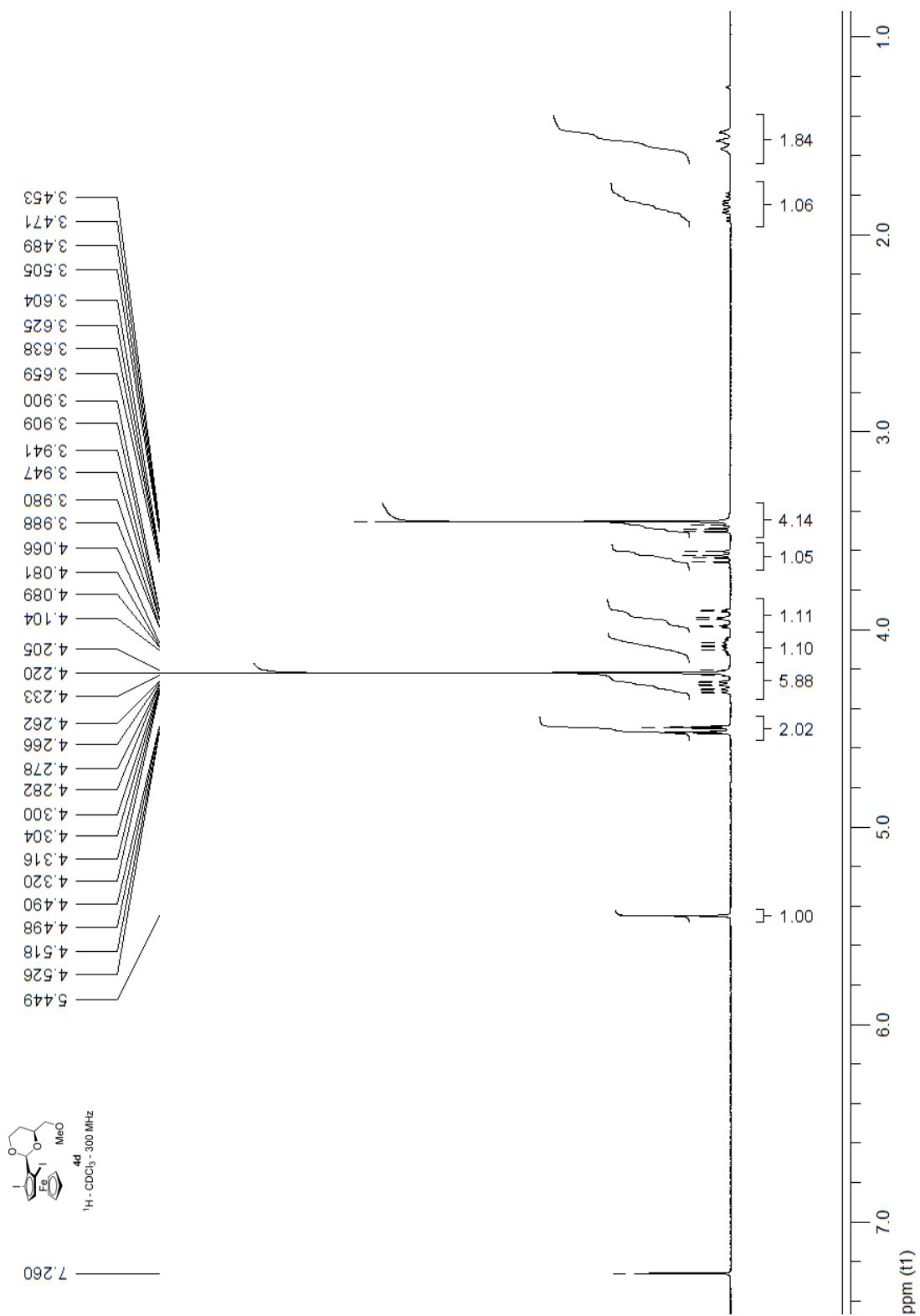
Compound 2c, ¹H-NMR



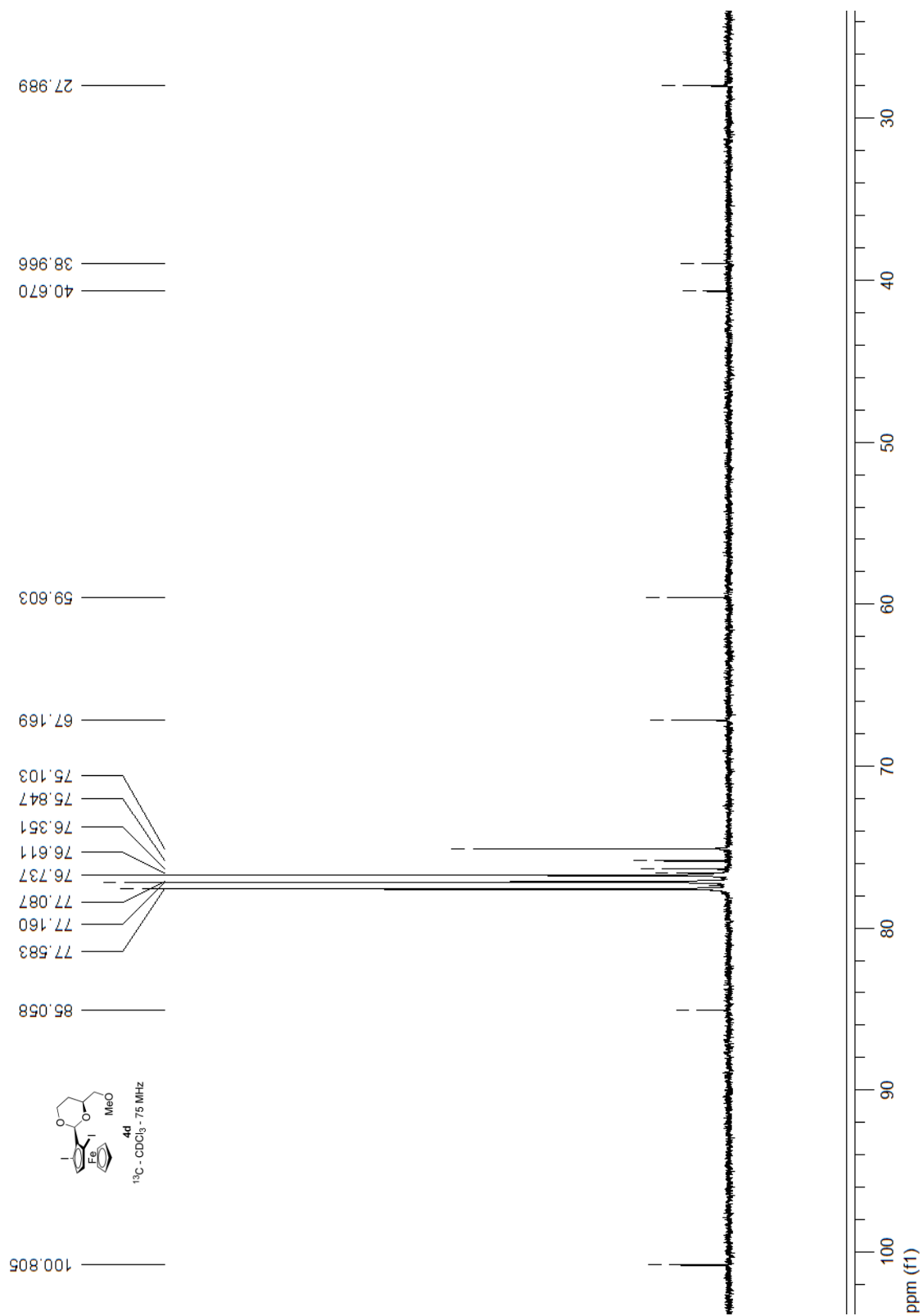
Compound 2c, ¹³C-NMR



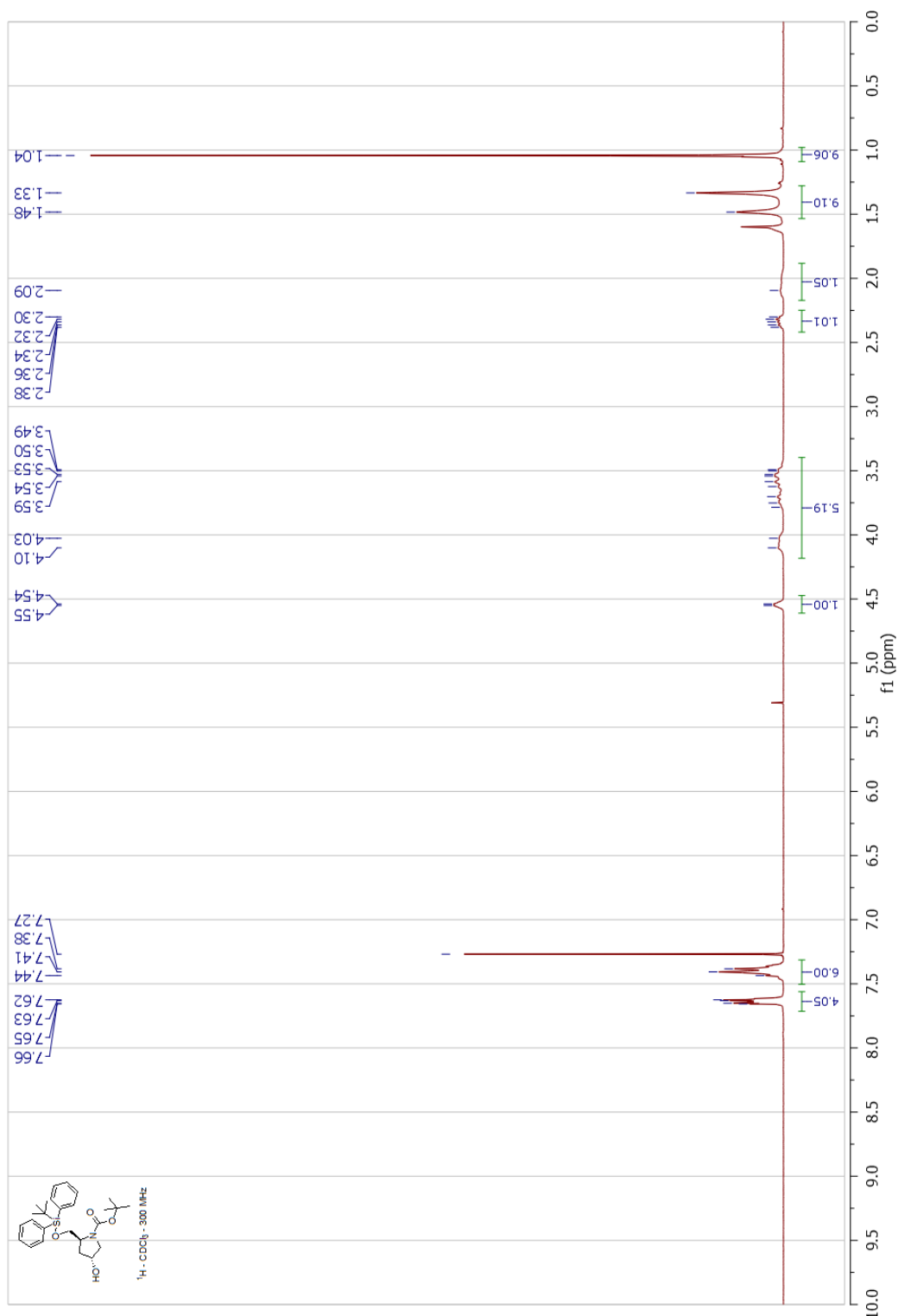
Compound 4d, ¹H-NMR



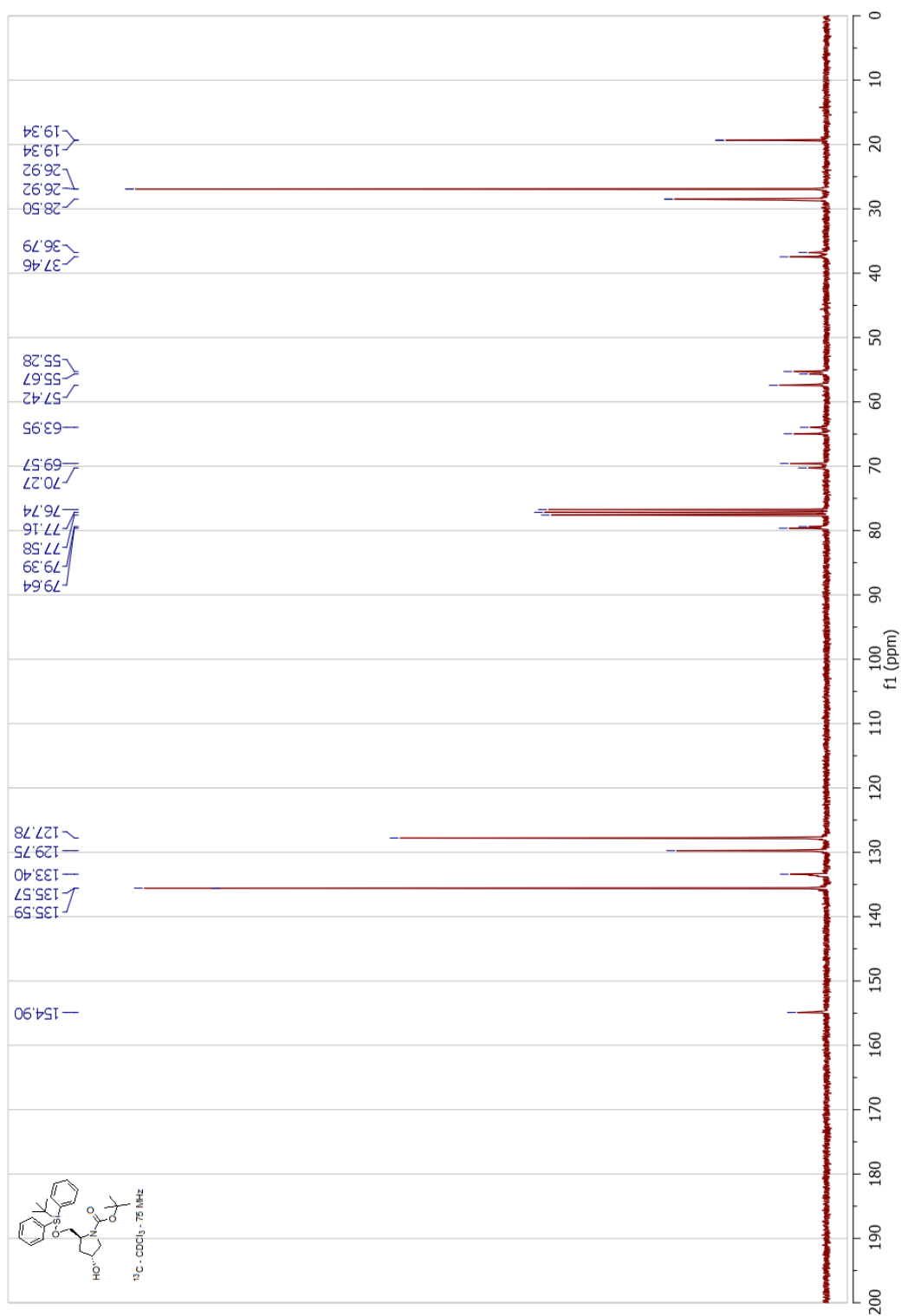
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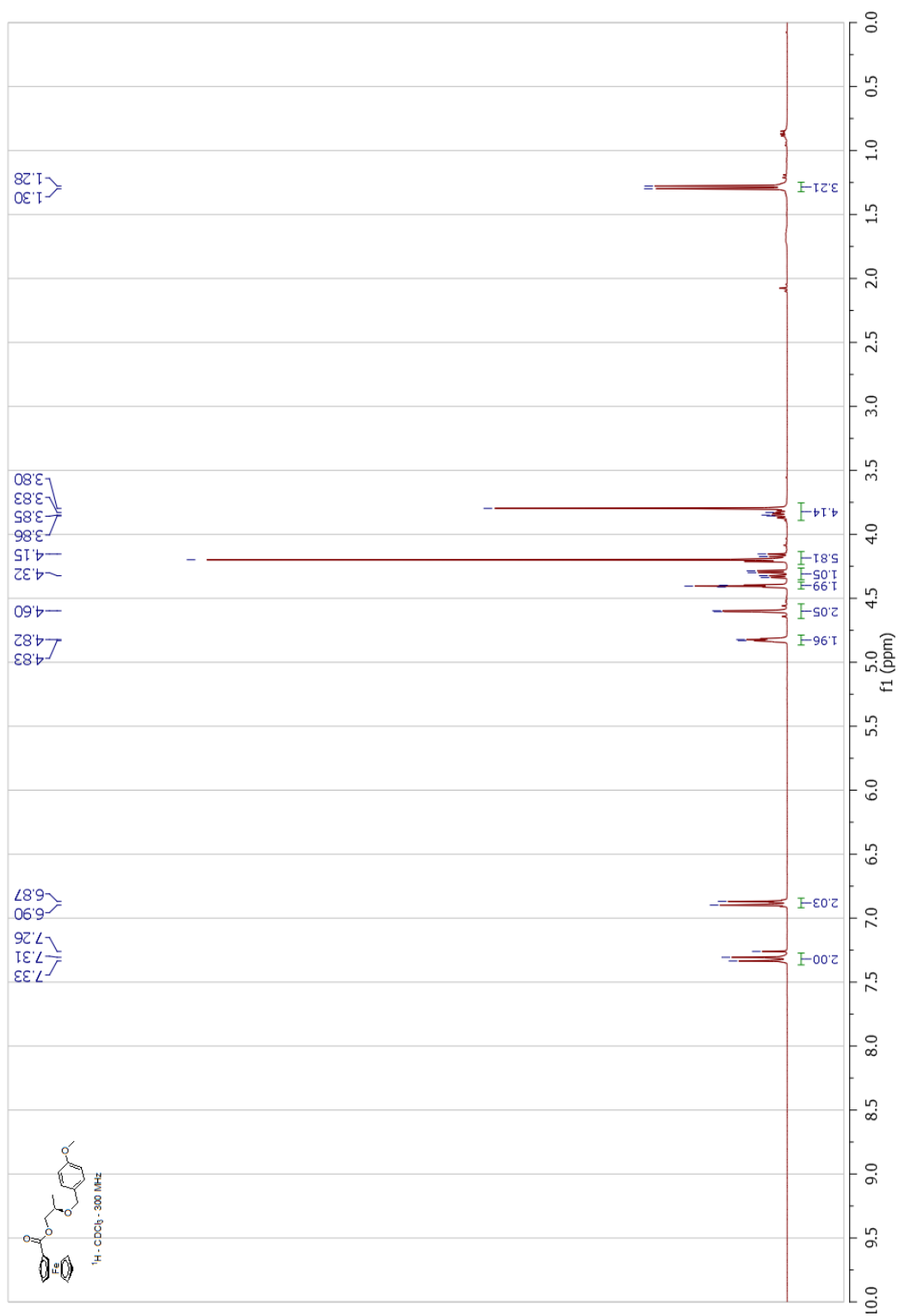
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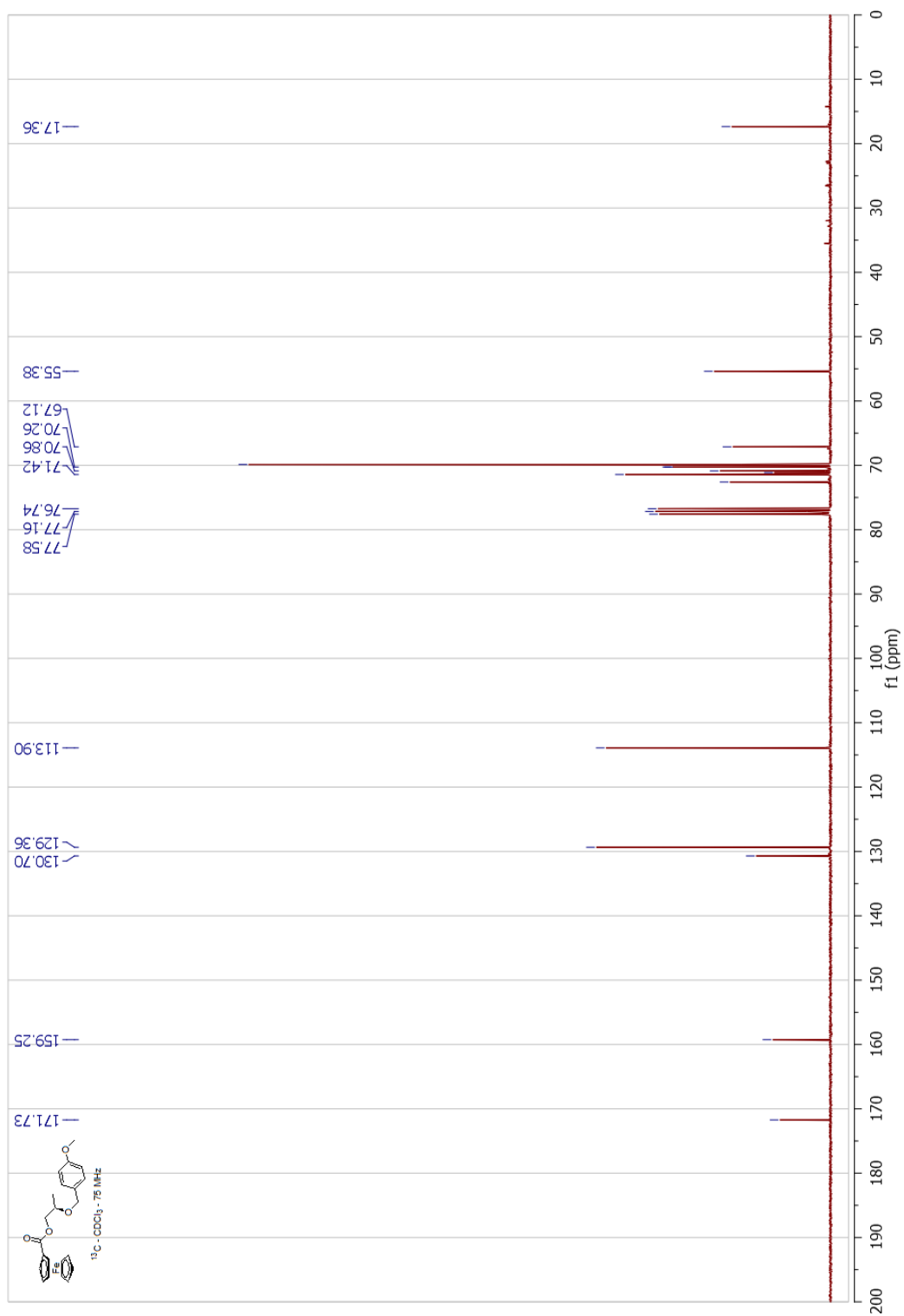
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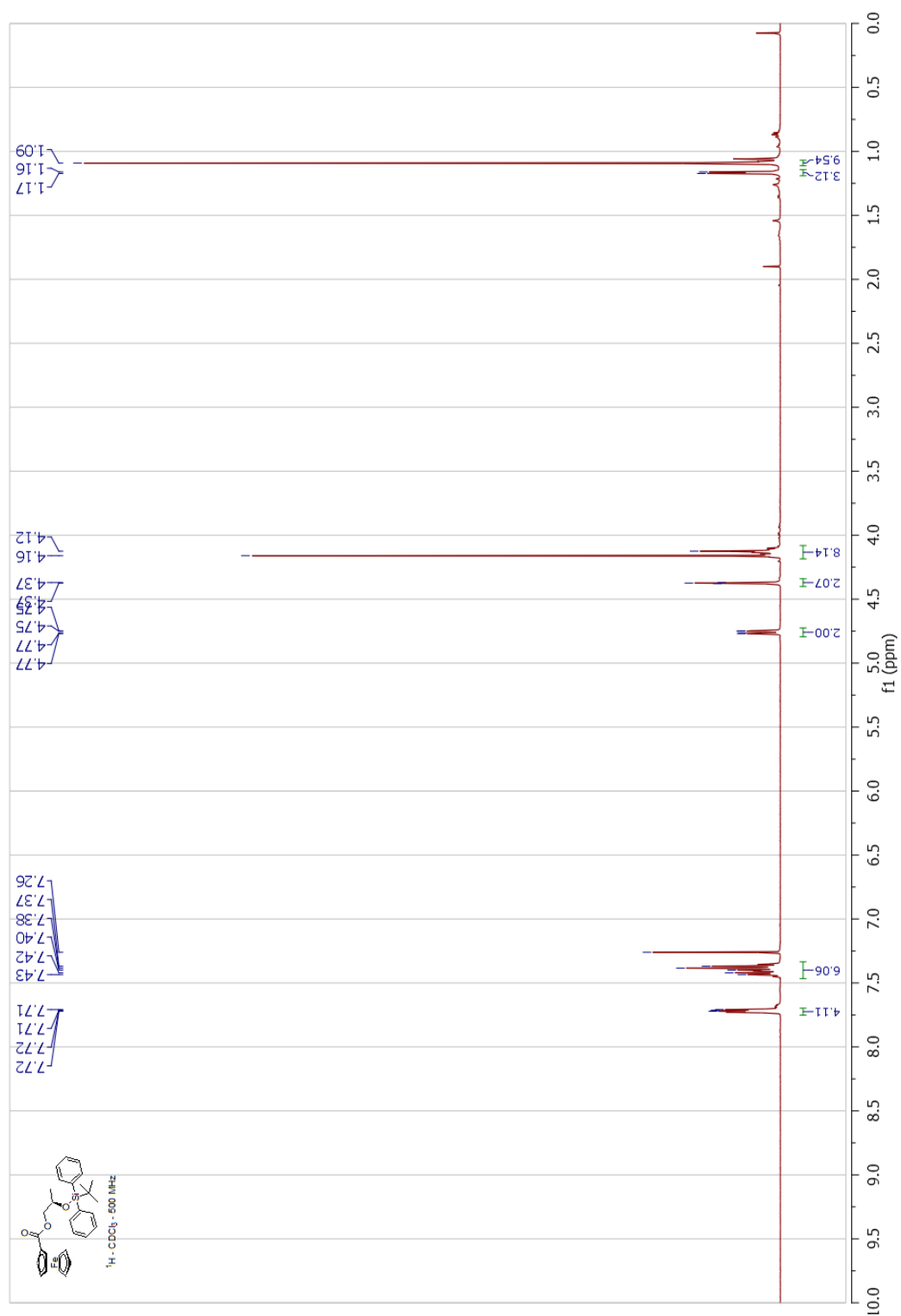
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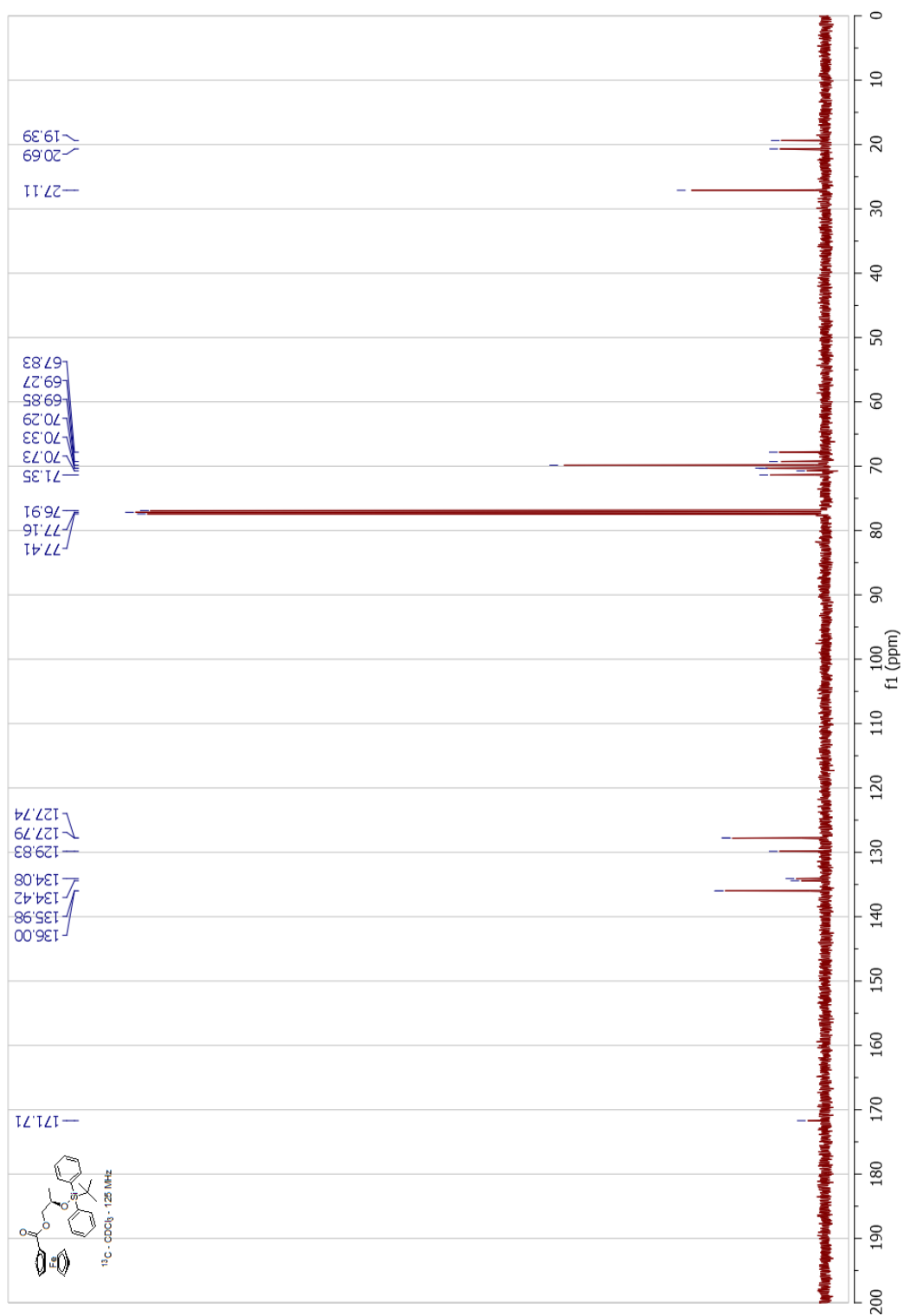
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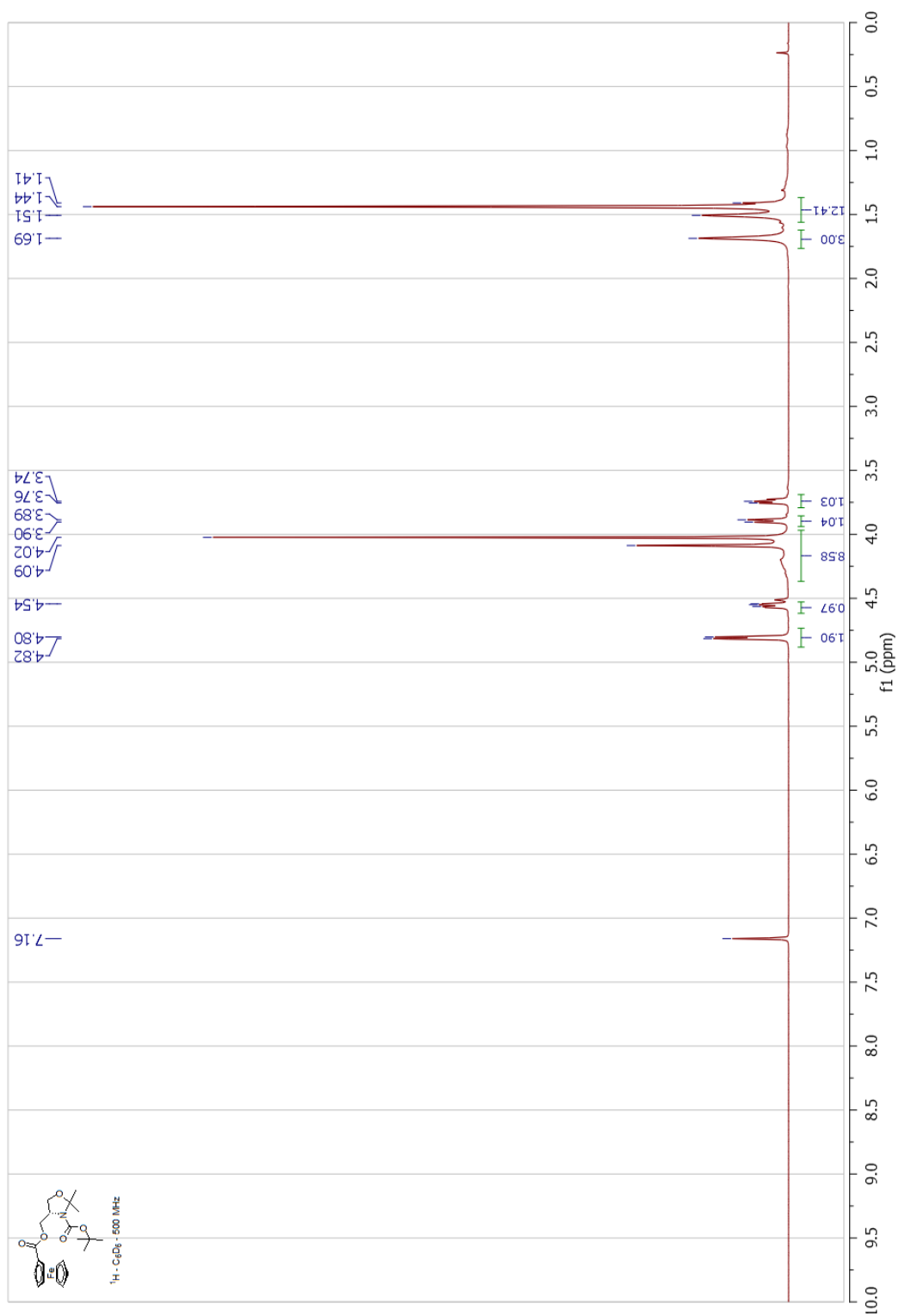
Compound 6b, ¹H-NMR



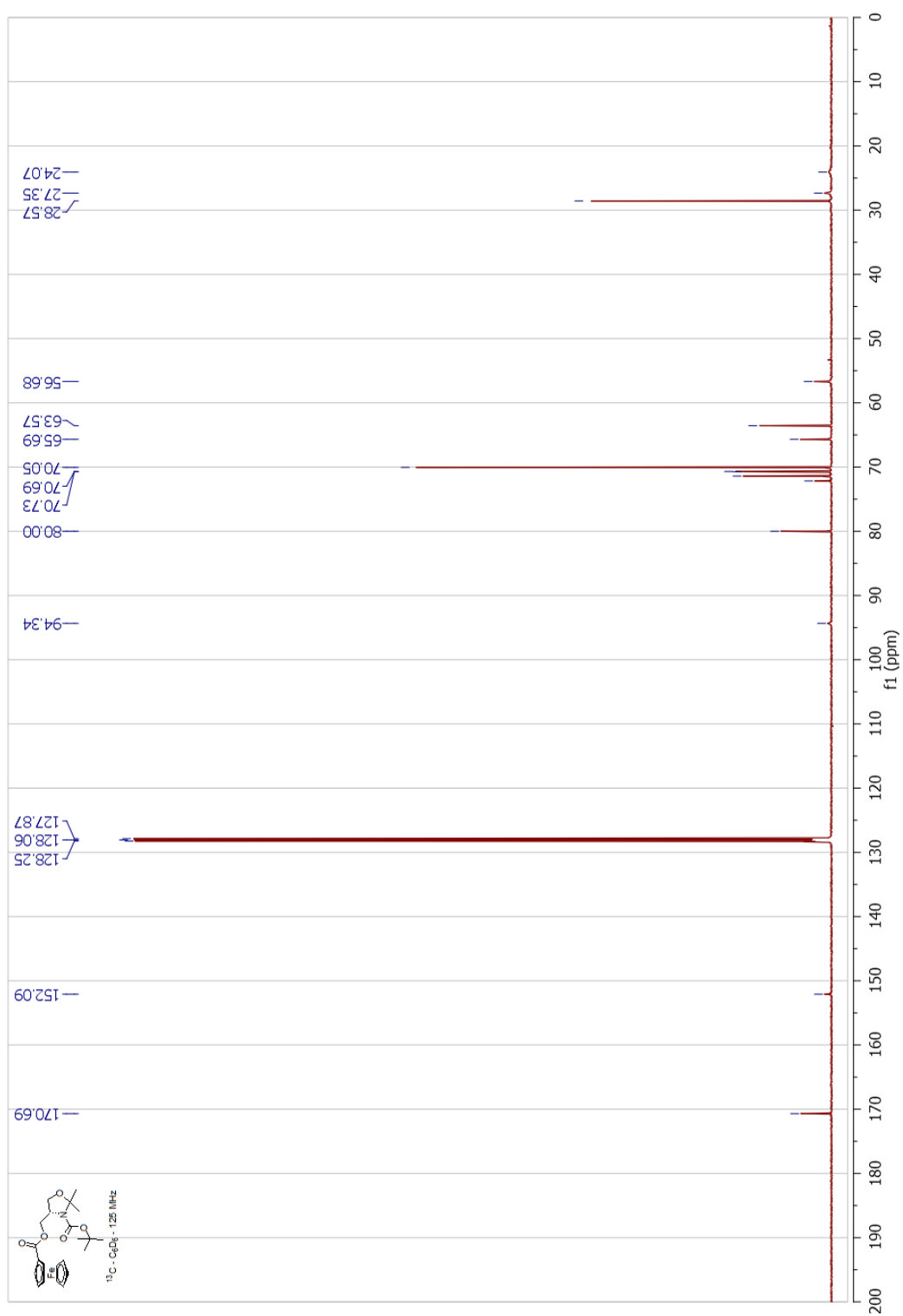
Compound 6b, ^{13}C -NMR



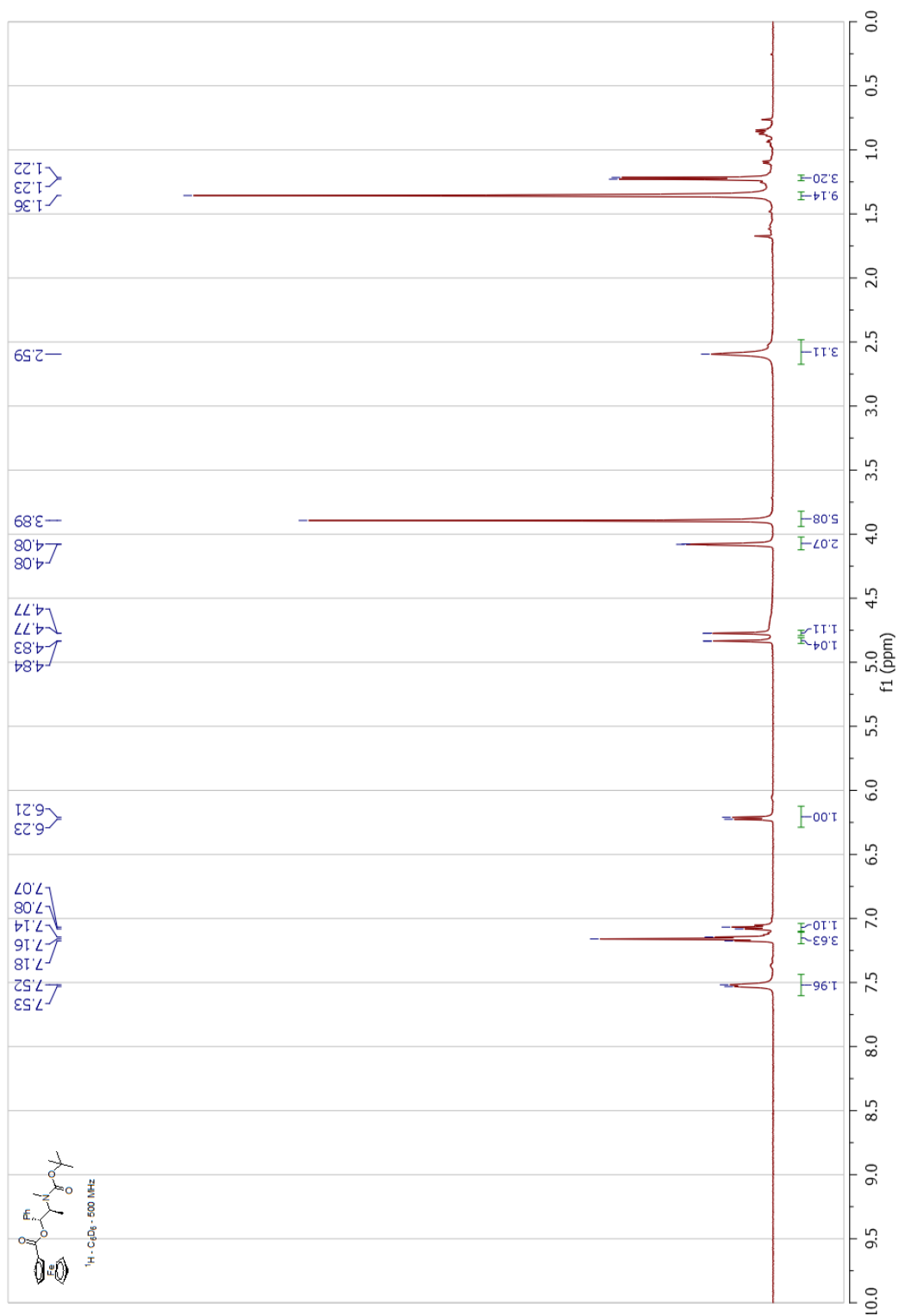
Compound 6c, ¹H-NMR



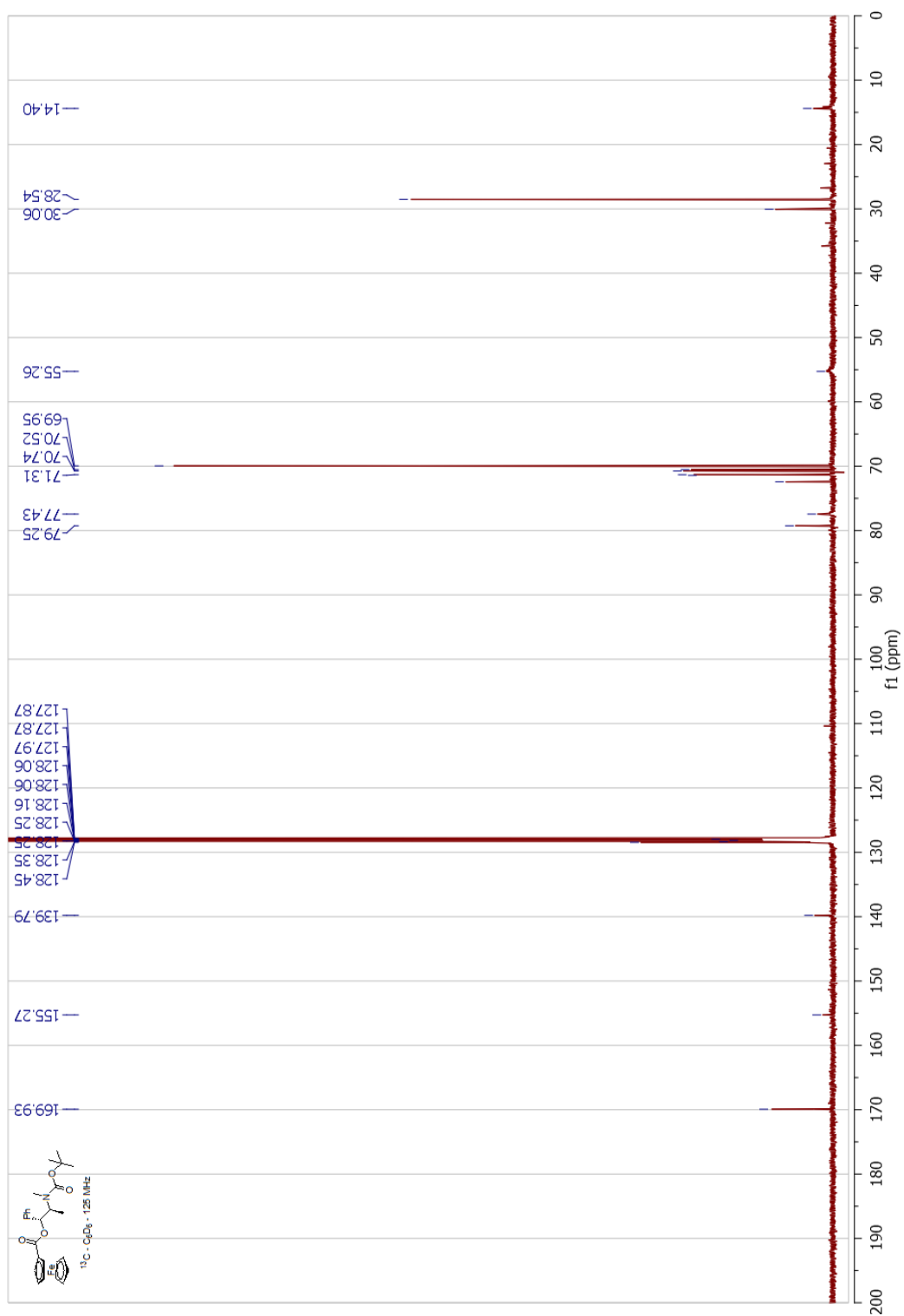
Compound 6c, ¹³C-NMR



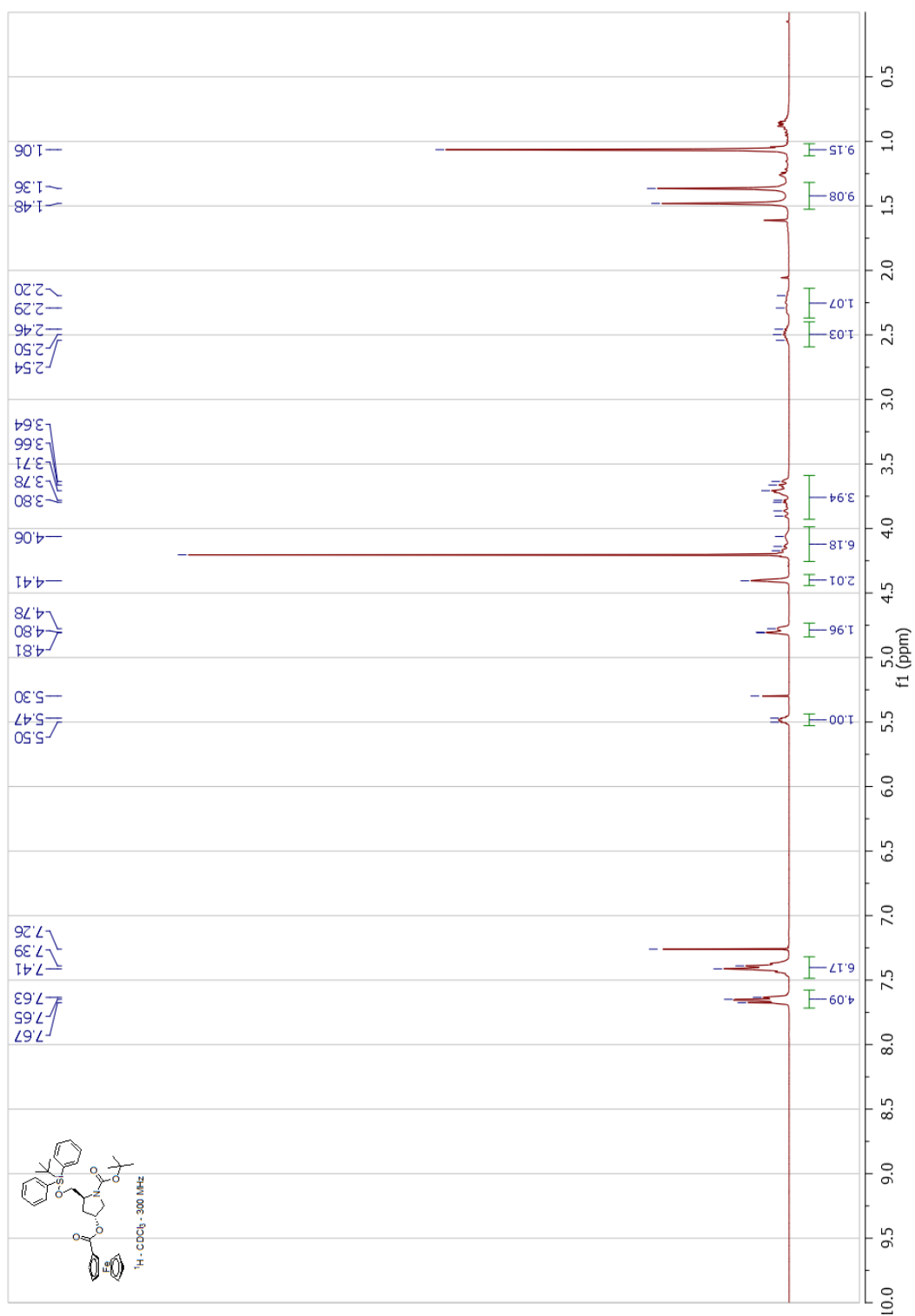
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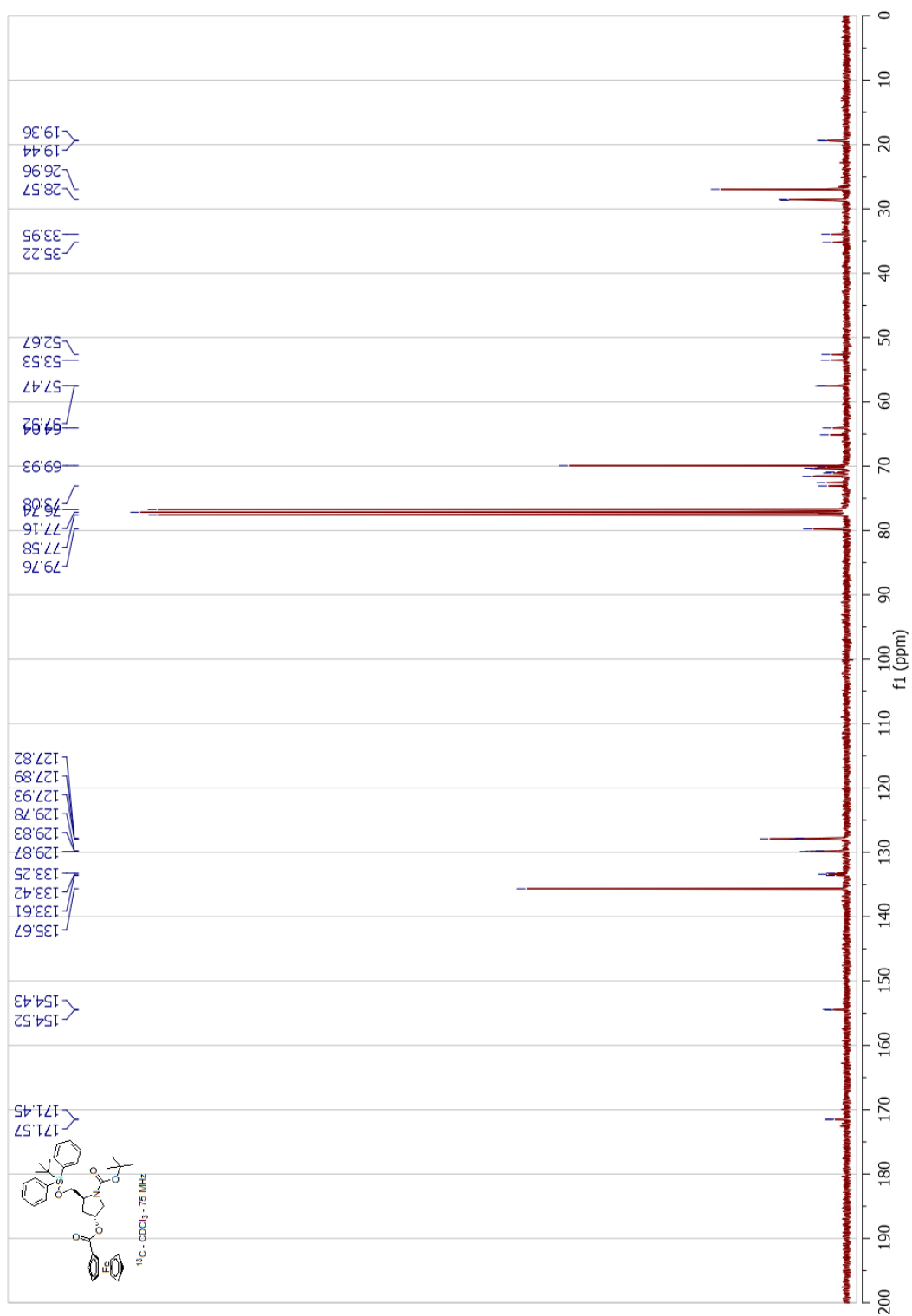
Compound 6f, ^{13}C -NMR



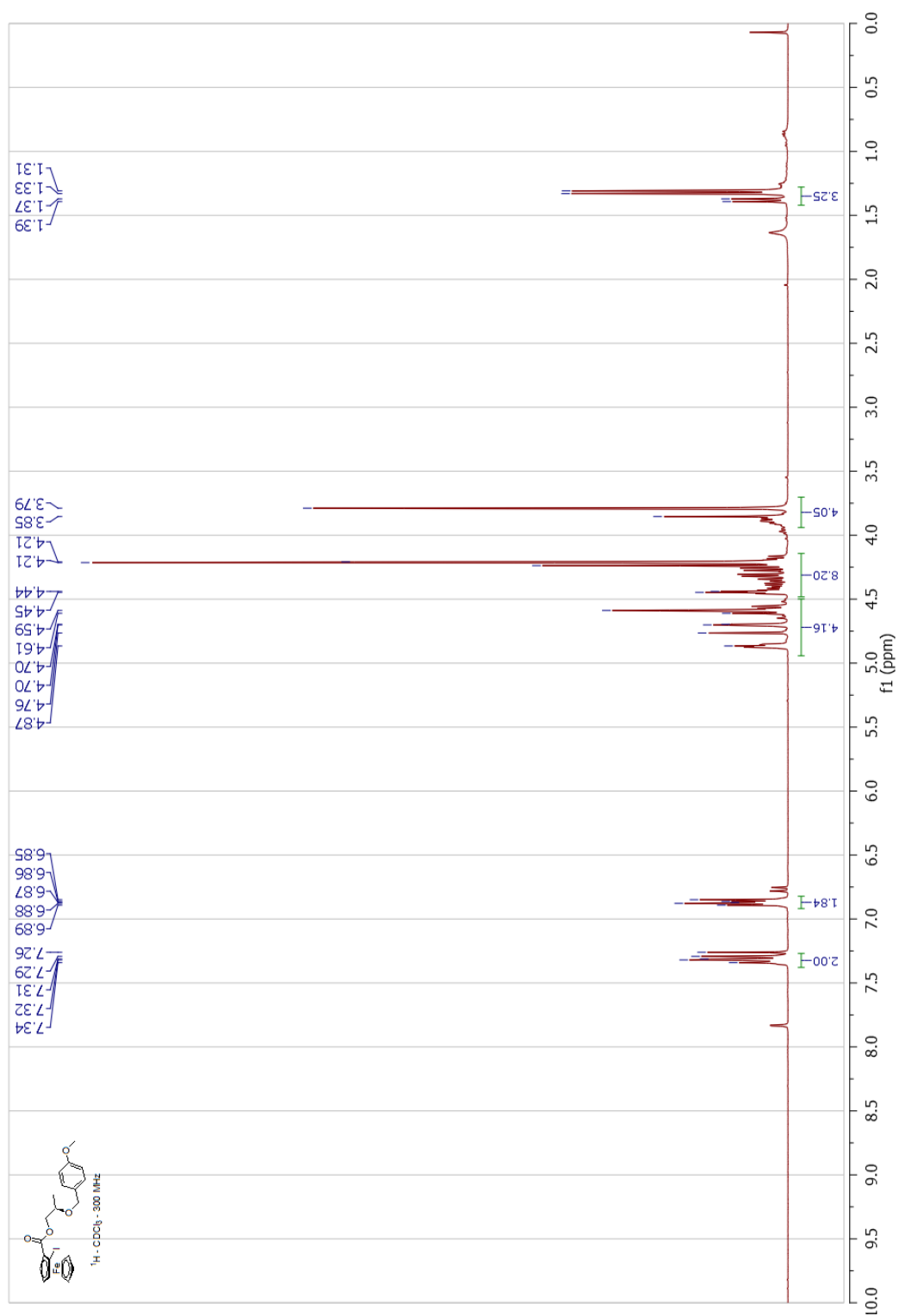
Compound 6g, ¹H-NMR



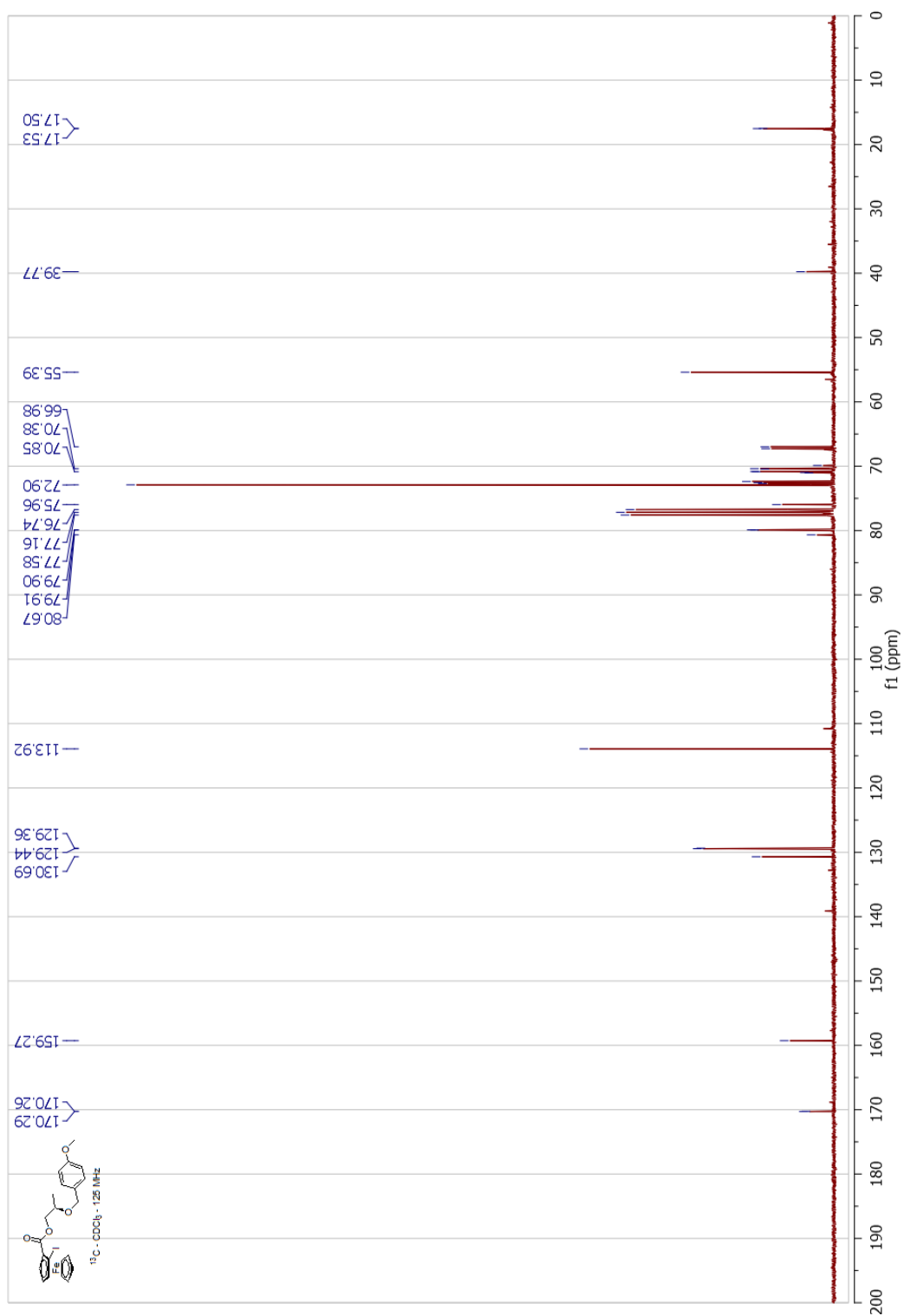
Compound 6g, ¹³C-NMR



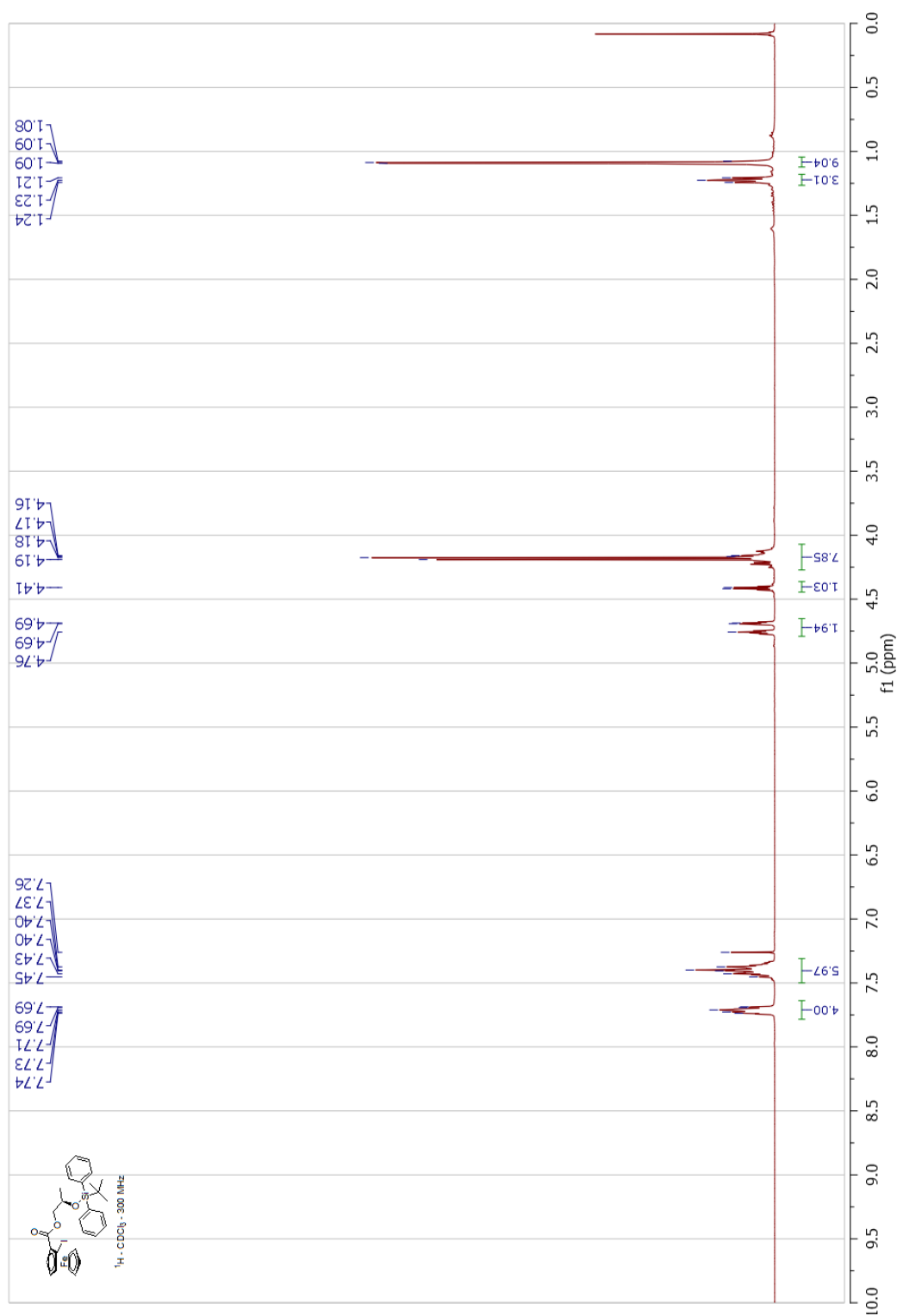
Compound 7a, ¹H-NMR



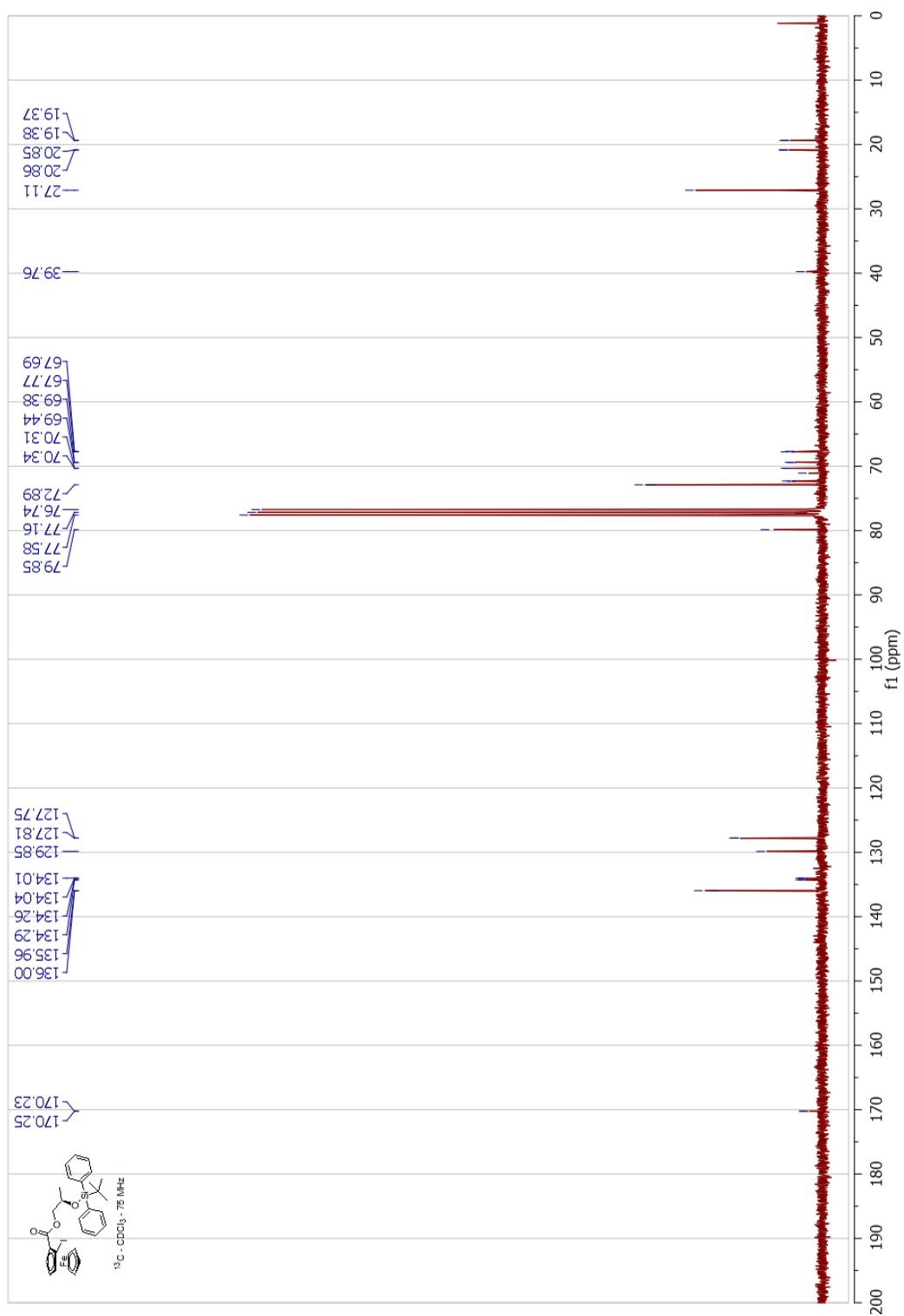
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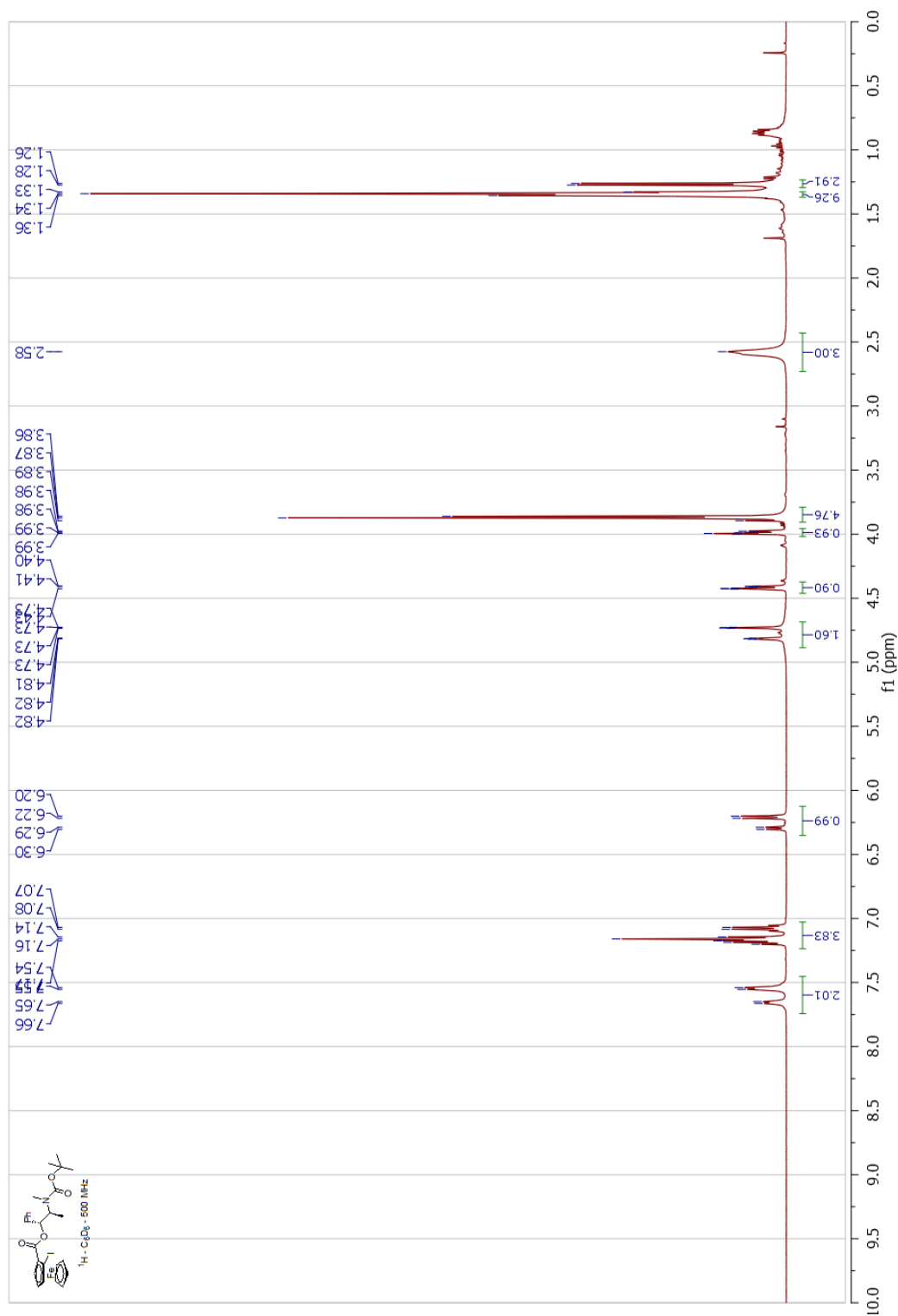
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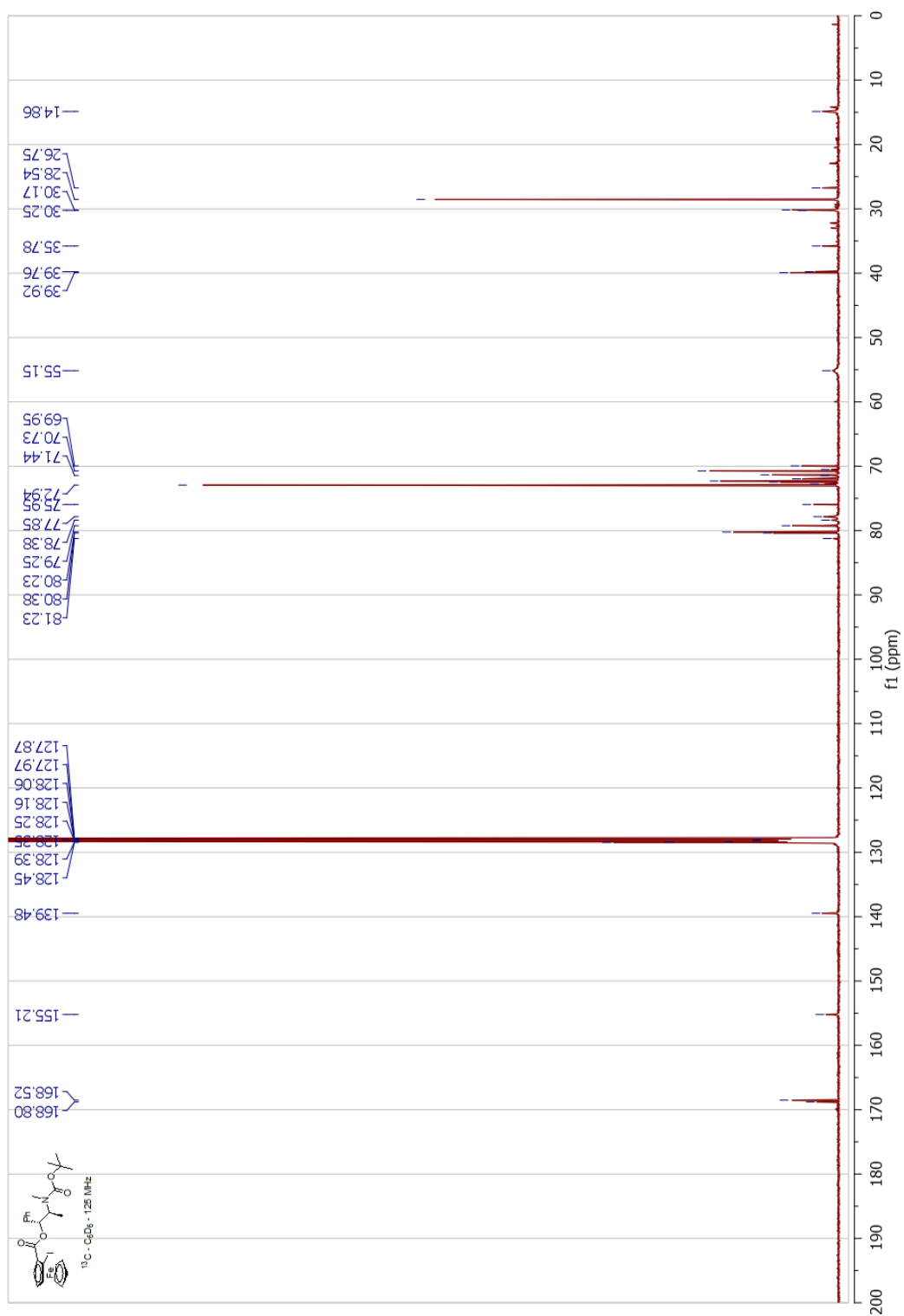
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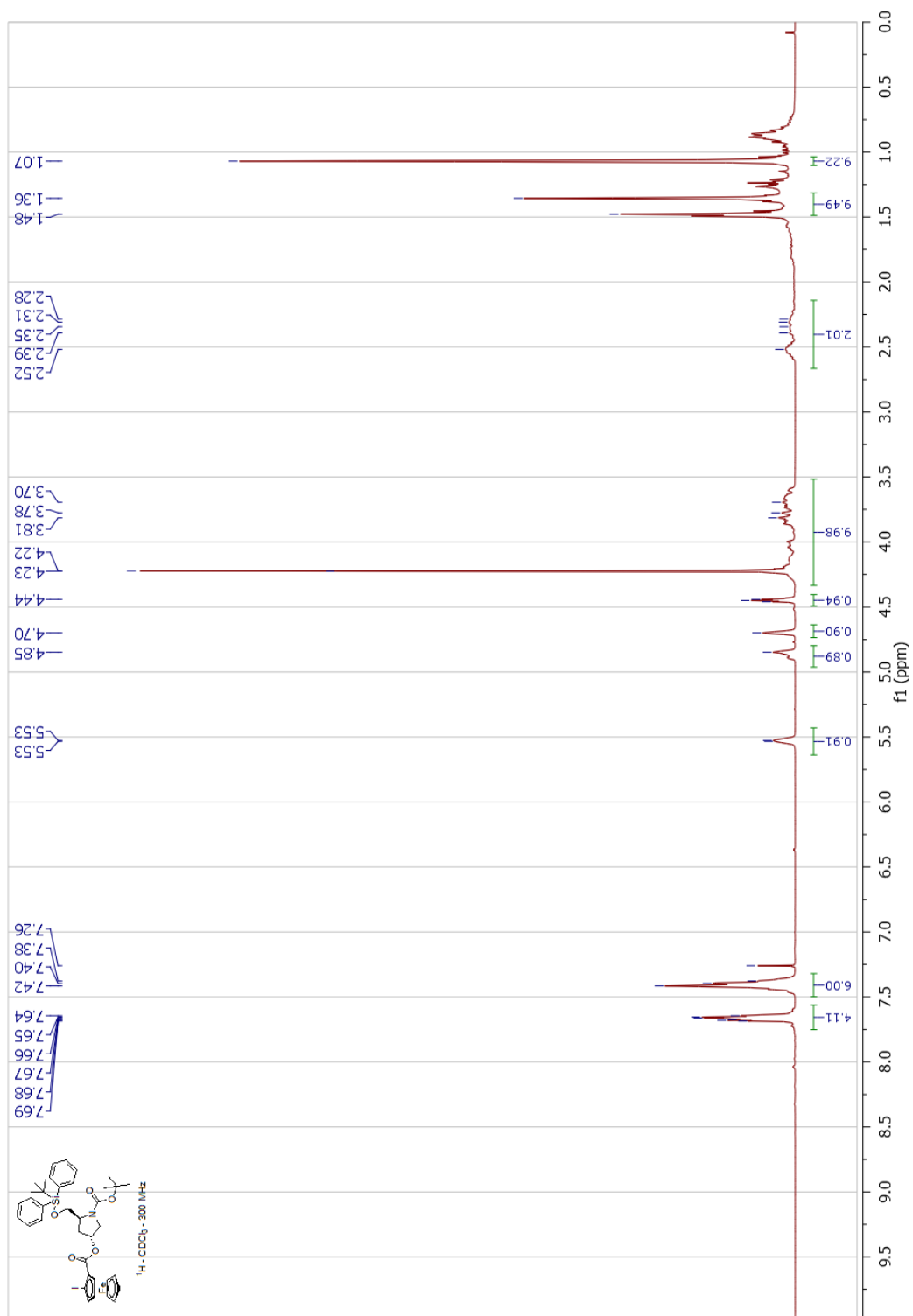
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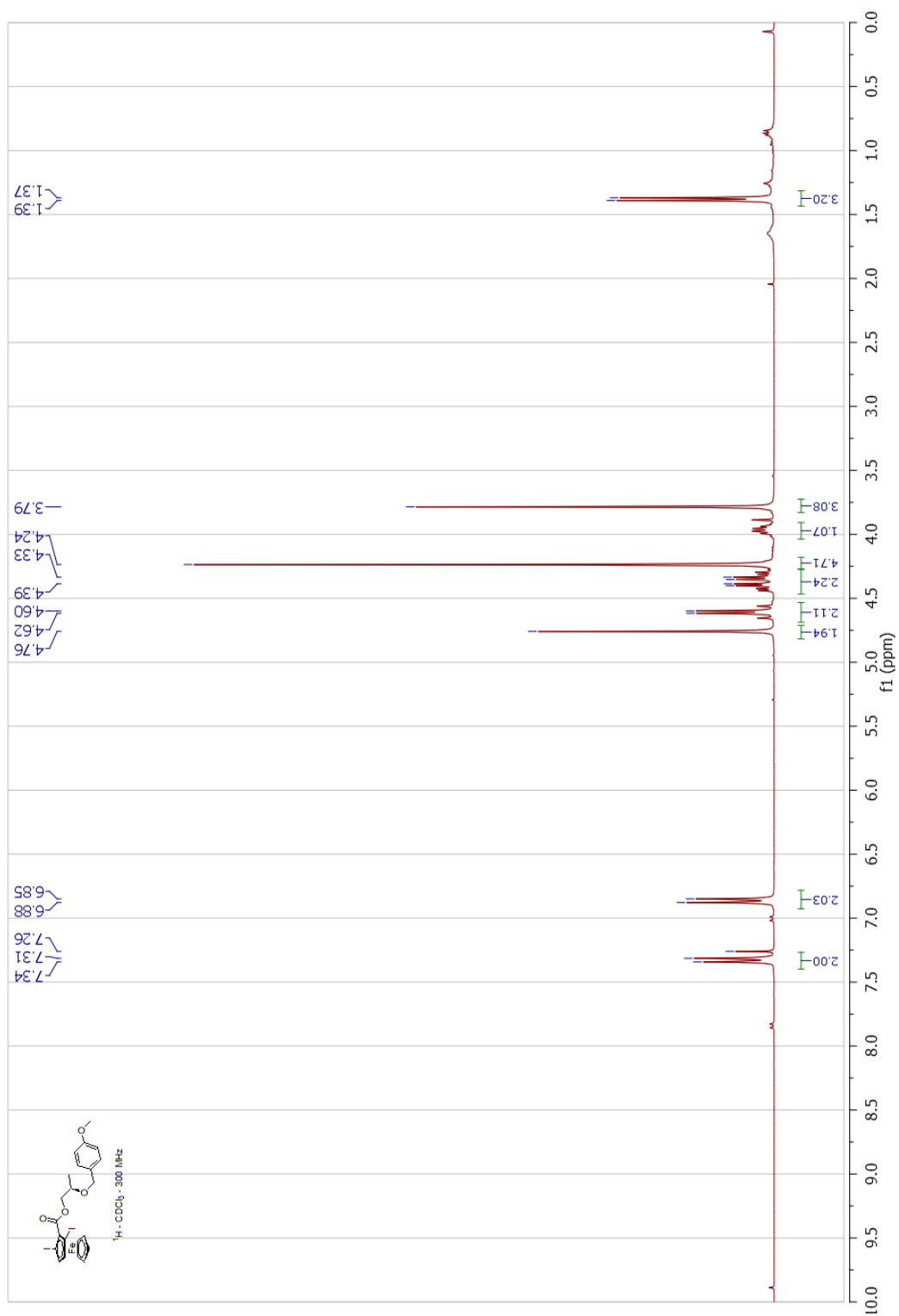
Compound 7f, ¹³C-NMR



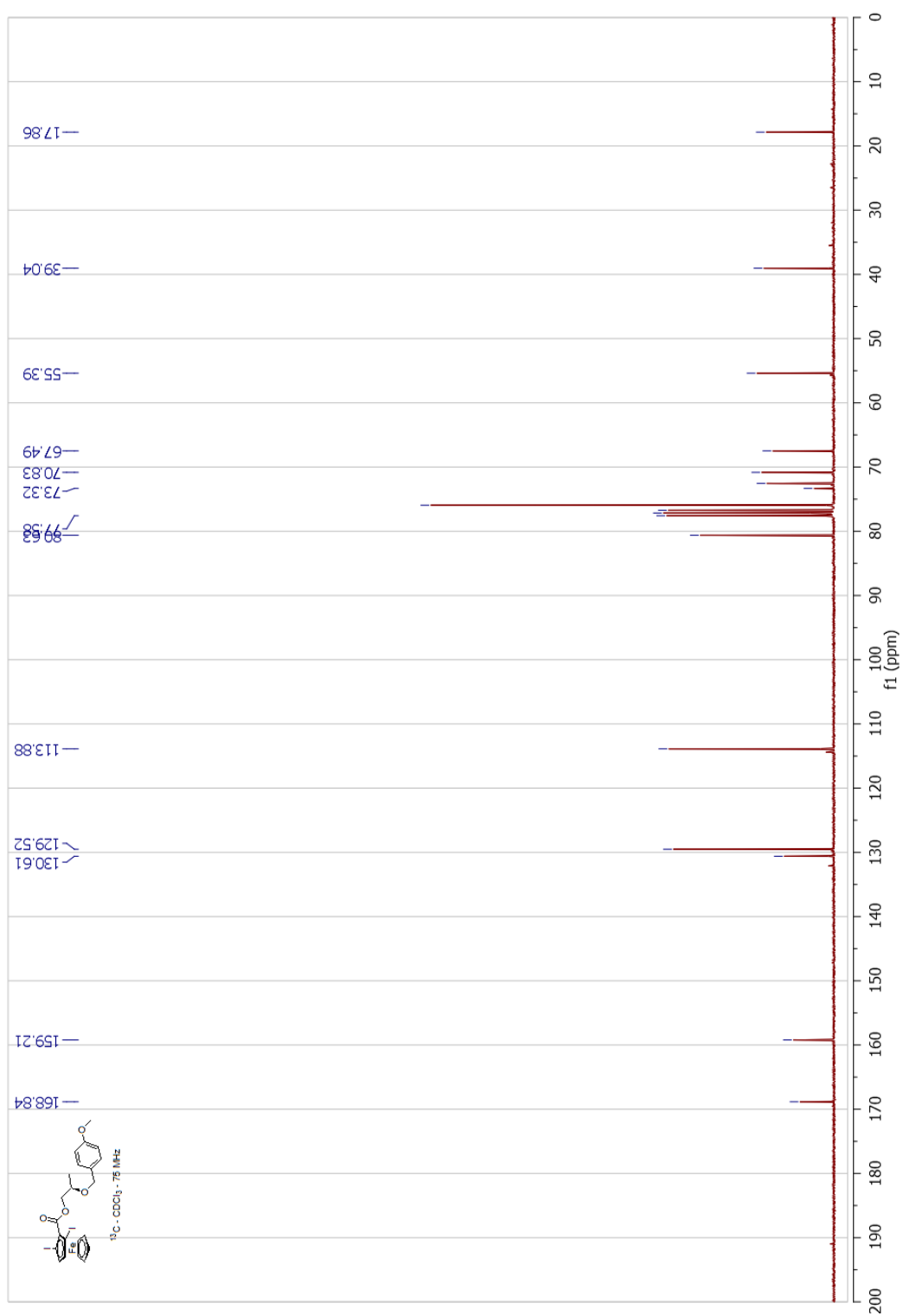
Compound 7g, ¹H-NMR



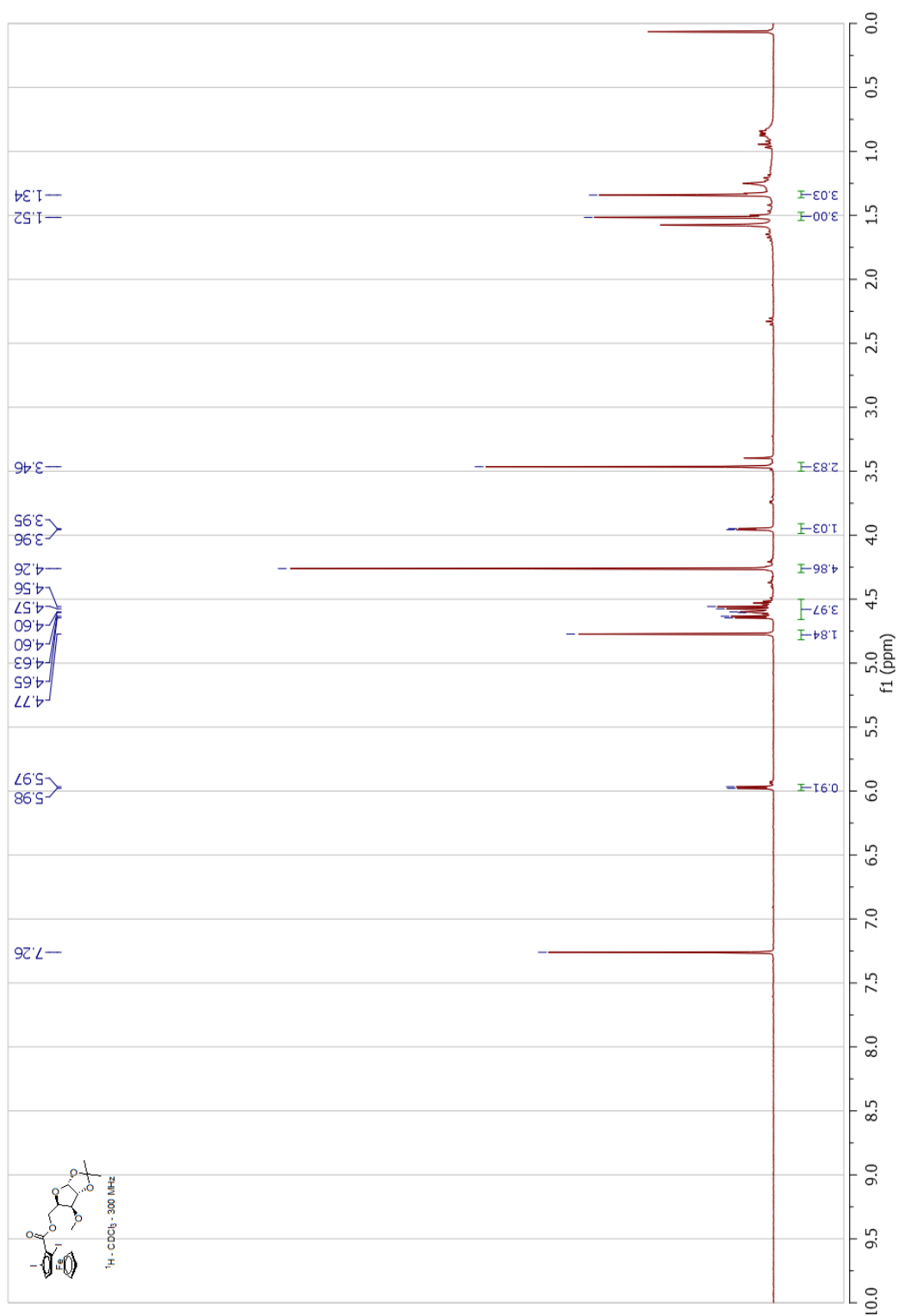
Compound 8a, ¹H-NMR



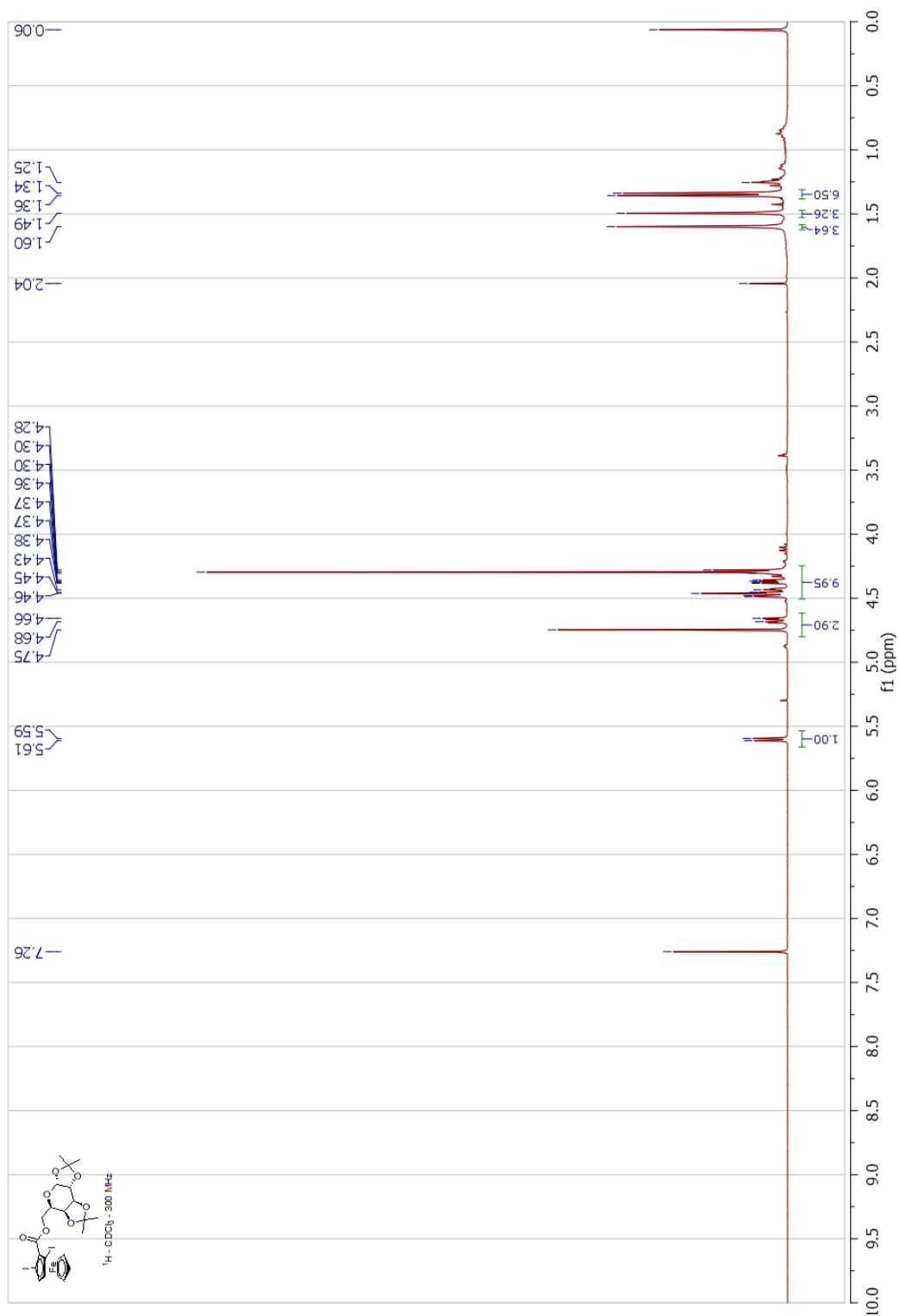
Compound 8a, ¹³C-NMR



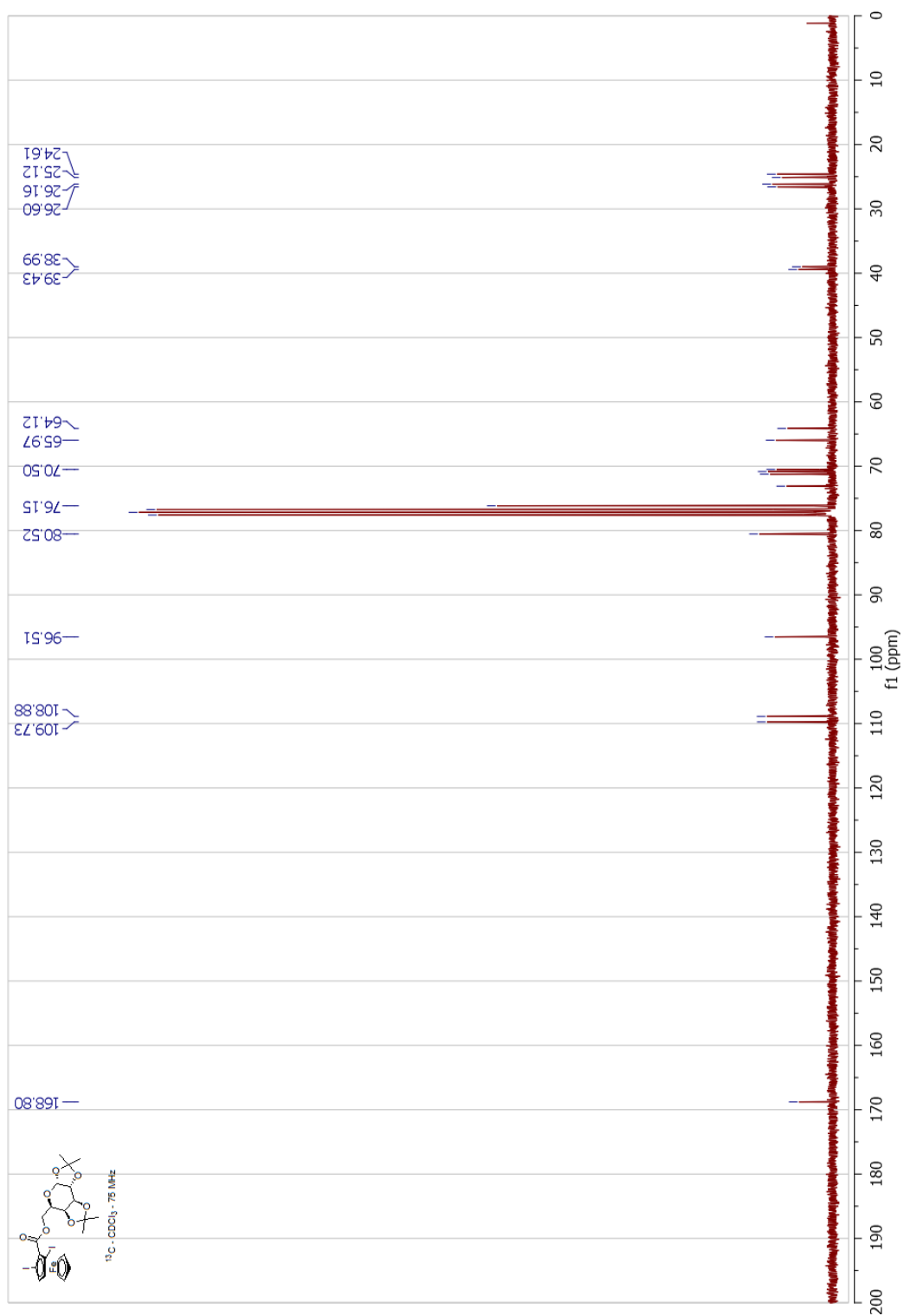
Compound 8d, ¹H-NMR



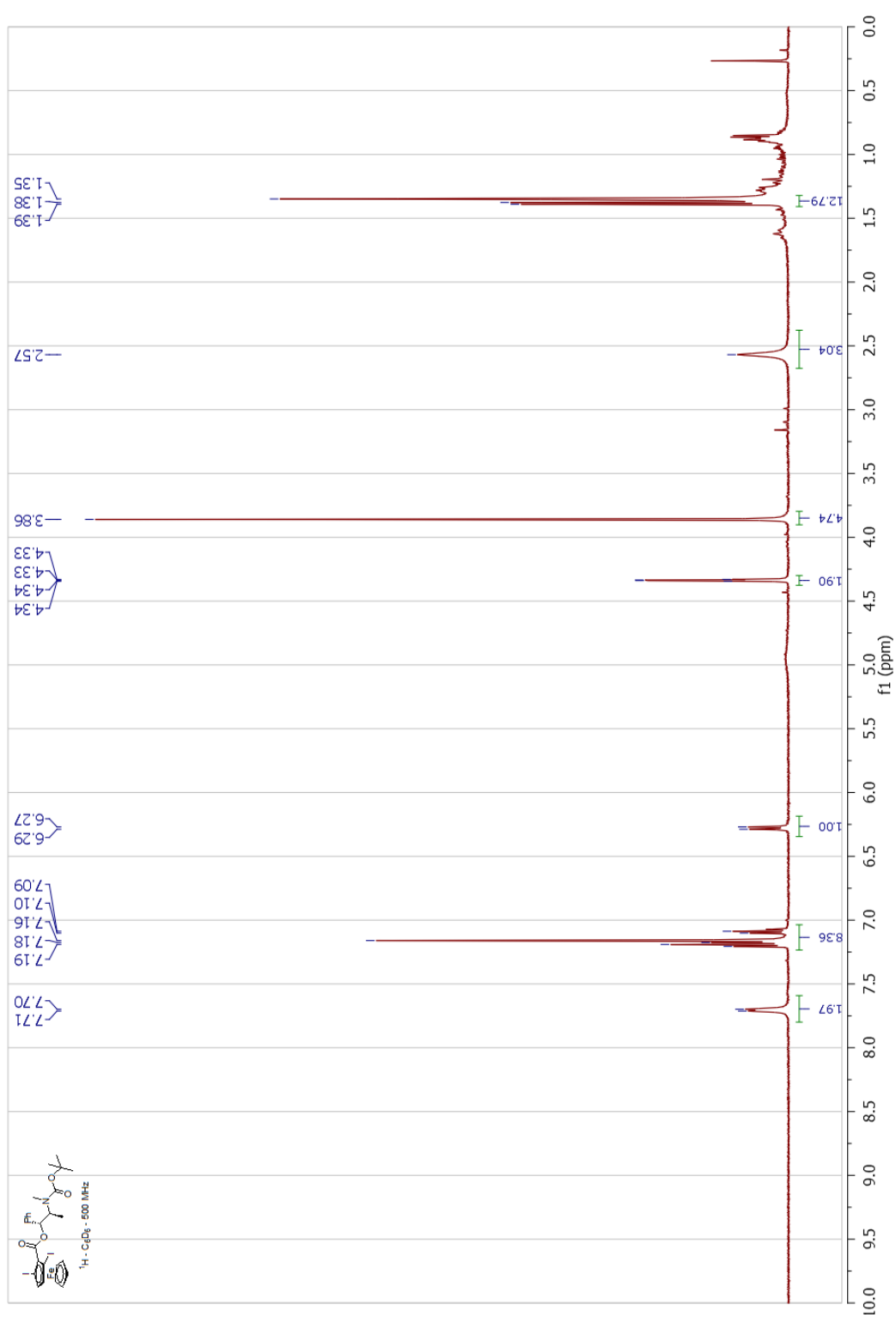
Compound 8e, ¹H-NMR



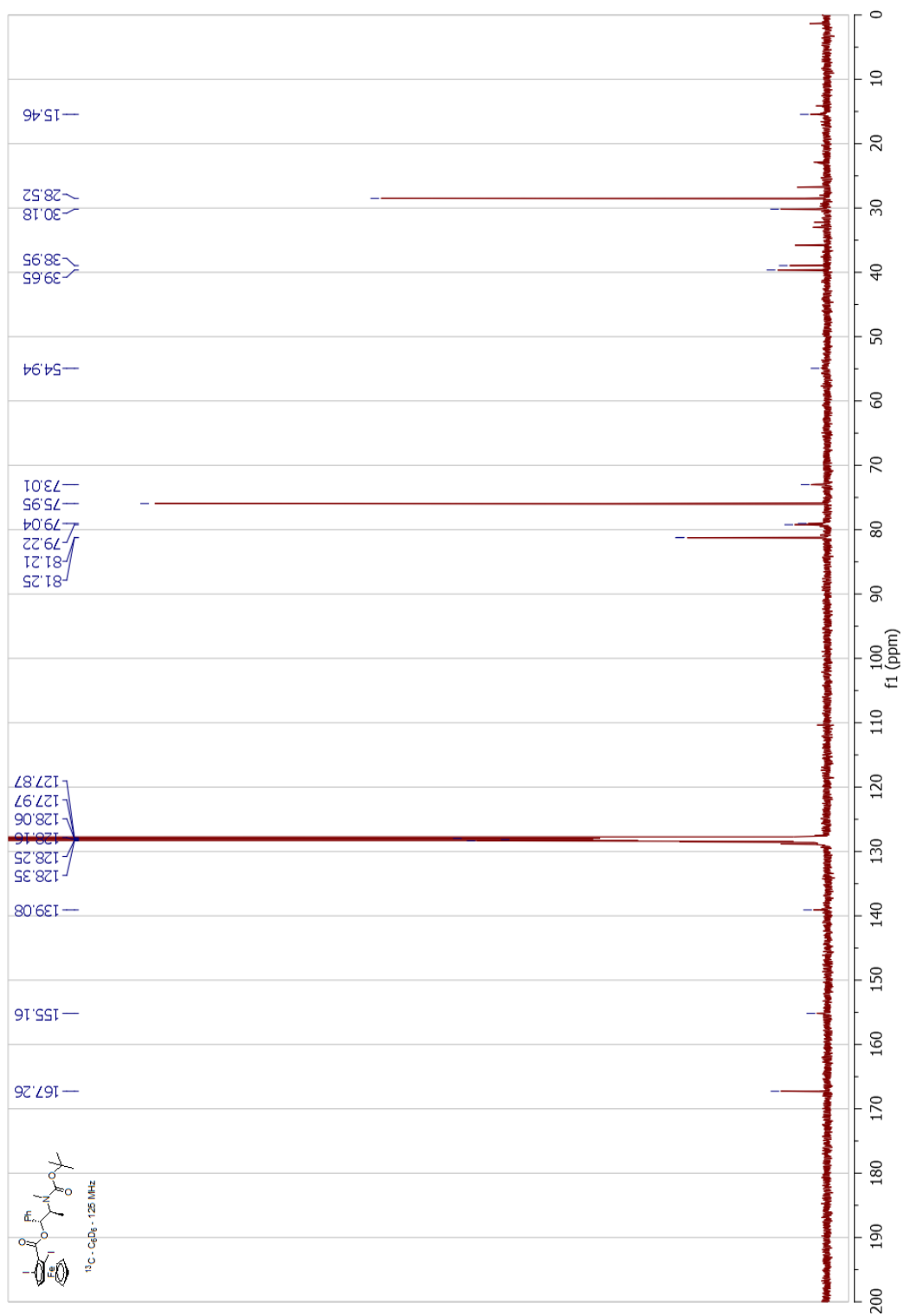
Compound 8e, ¹³C-NMR



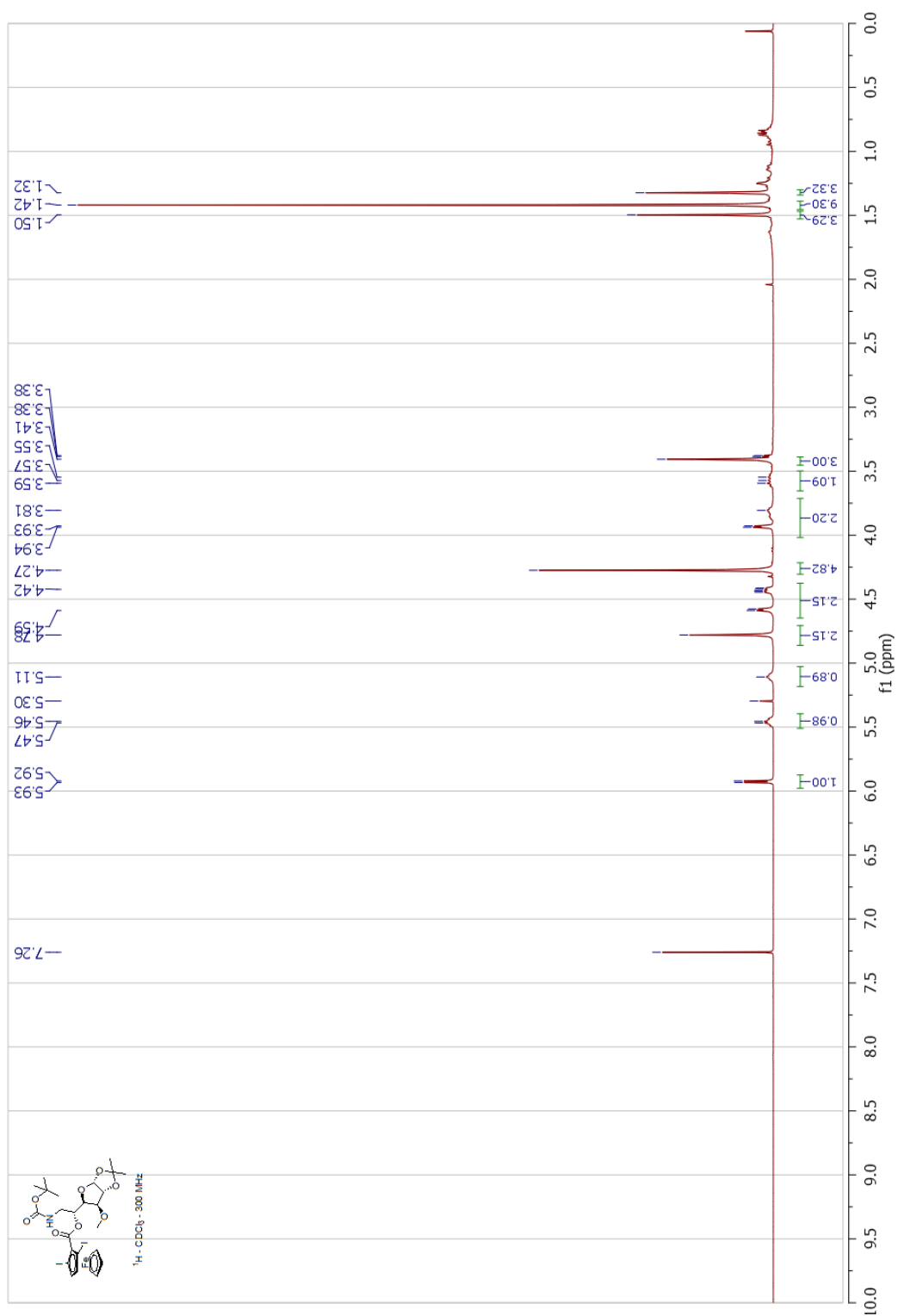
Compound 8f, $^1\text{H-NMR}$



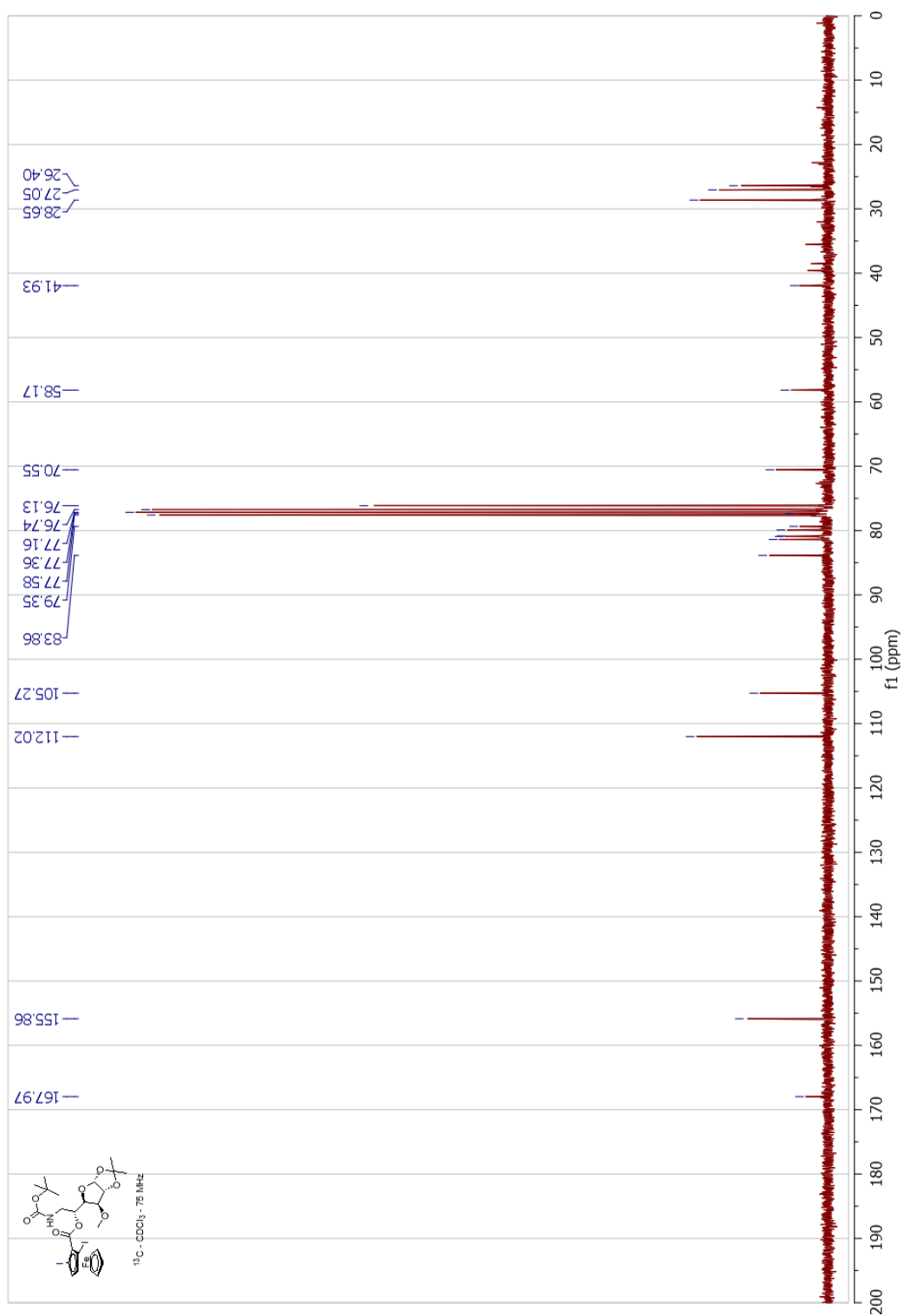
Compound 8f, ¹³C-NMR



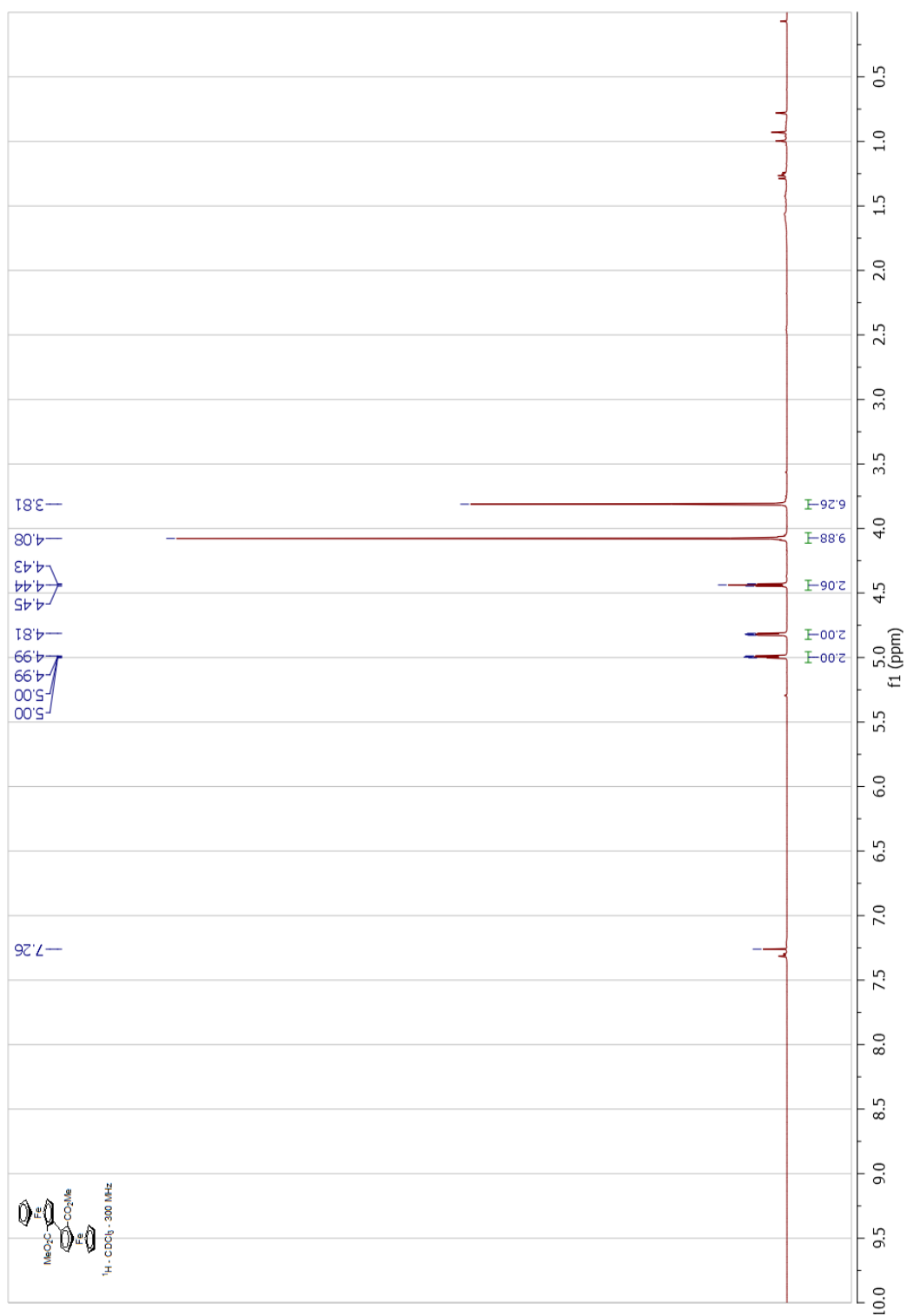
Compound 8n, ¹H-NMR



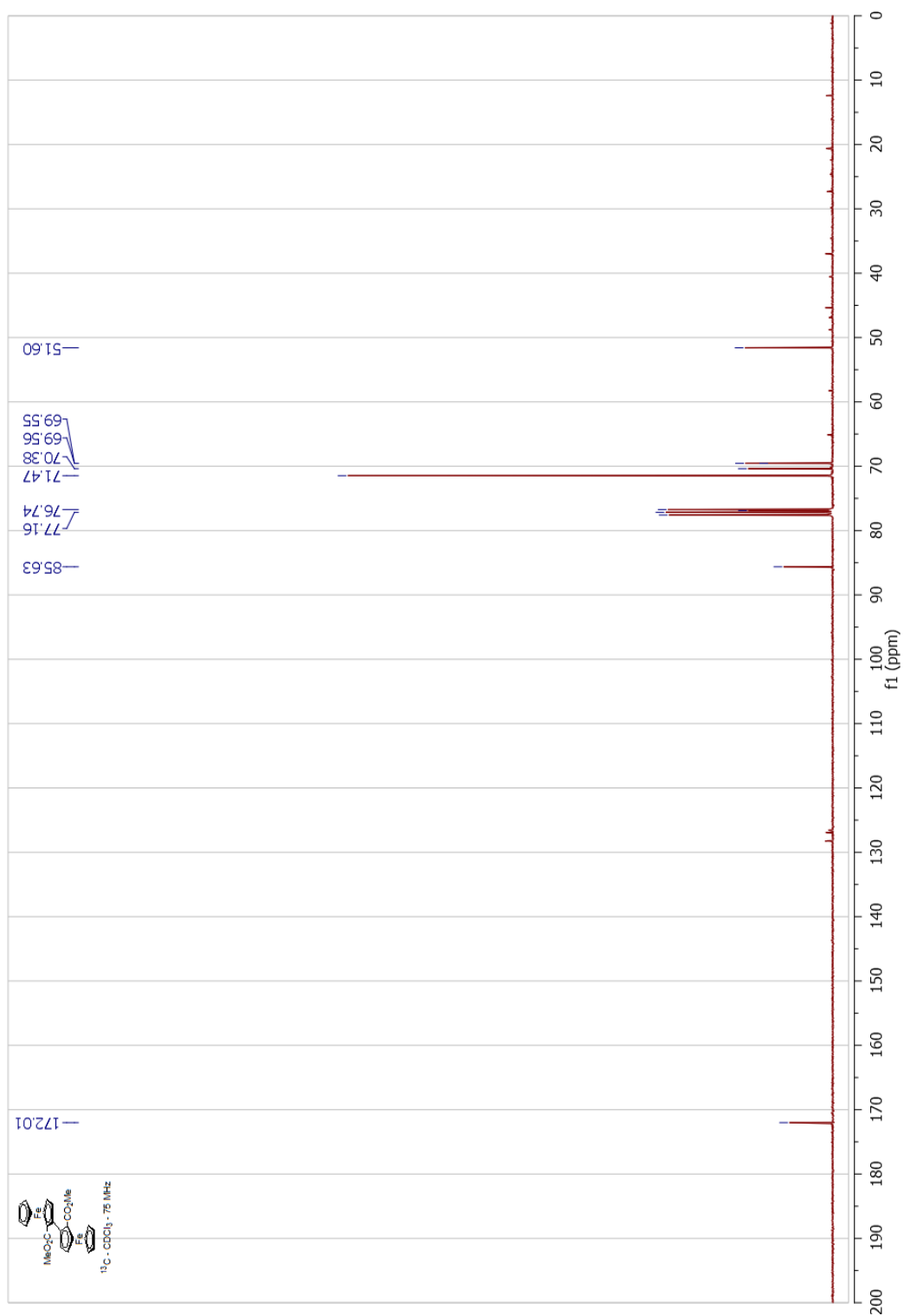
Compound 8n, ¹³C-NMR



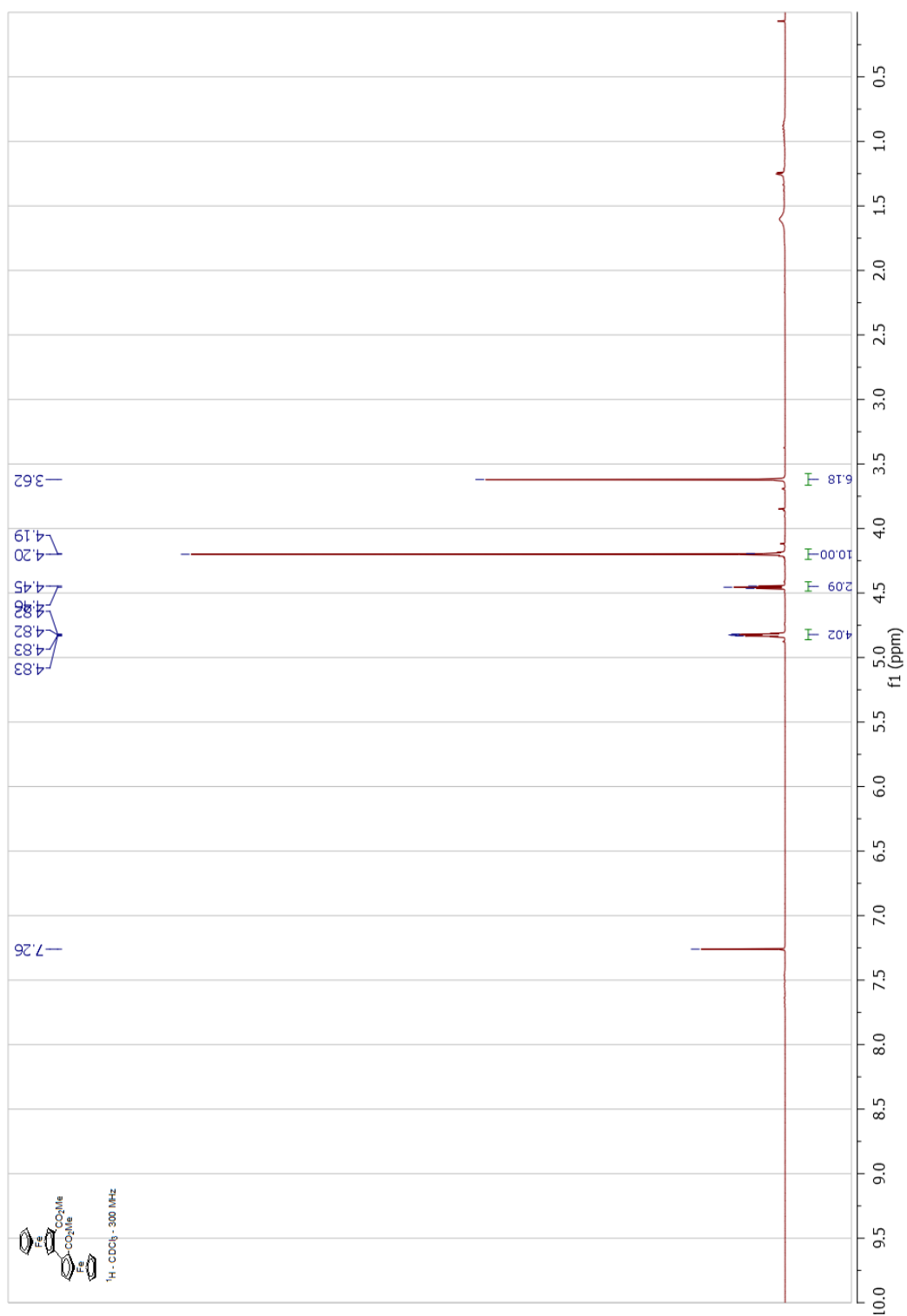
Compound *meso*-10o, ¹H-NMR



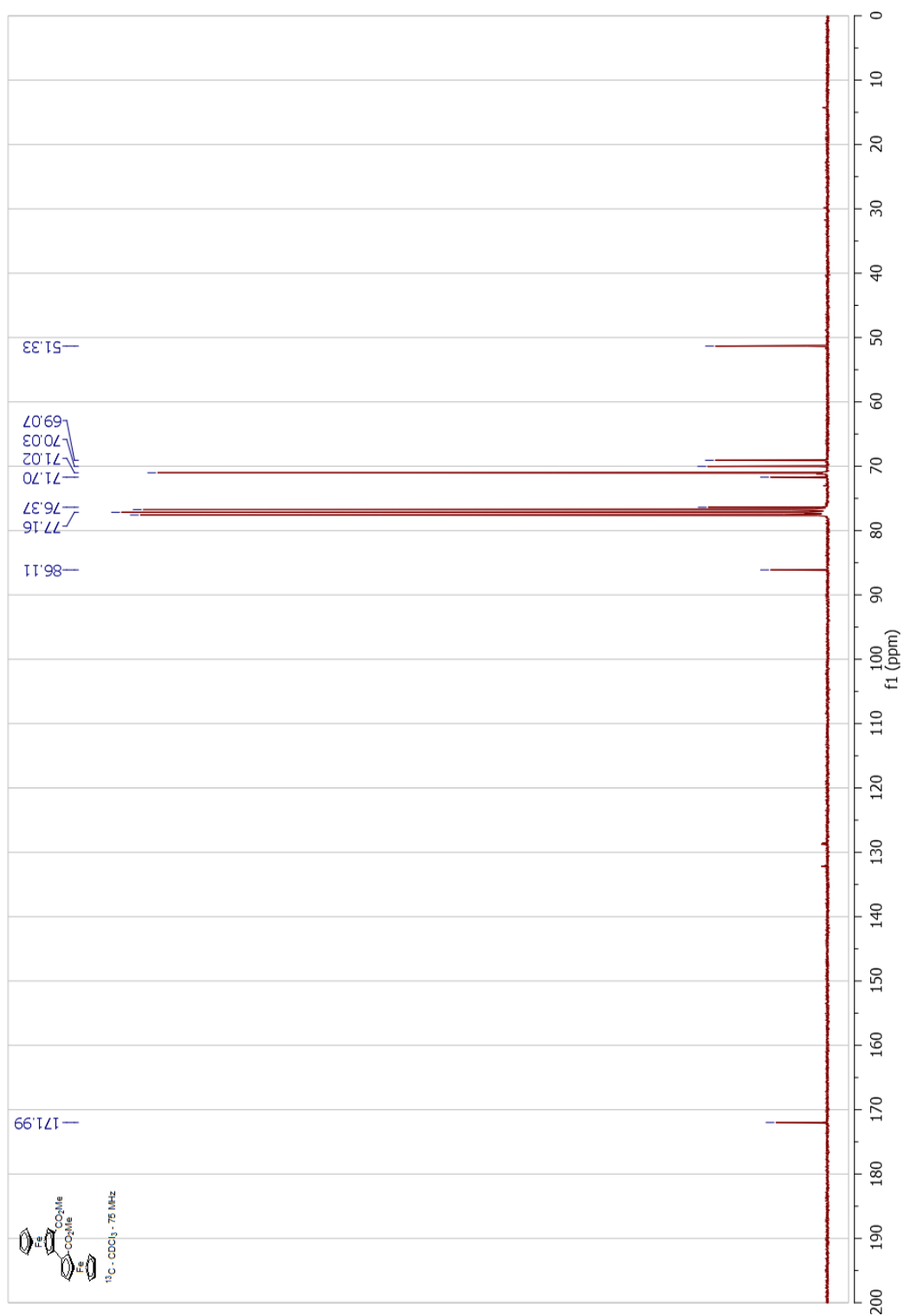
Compound *meso*-10o, ¹³C-NMR



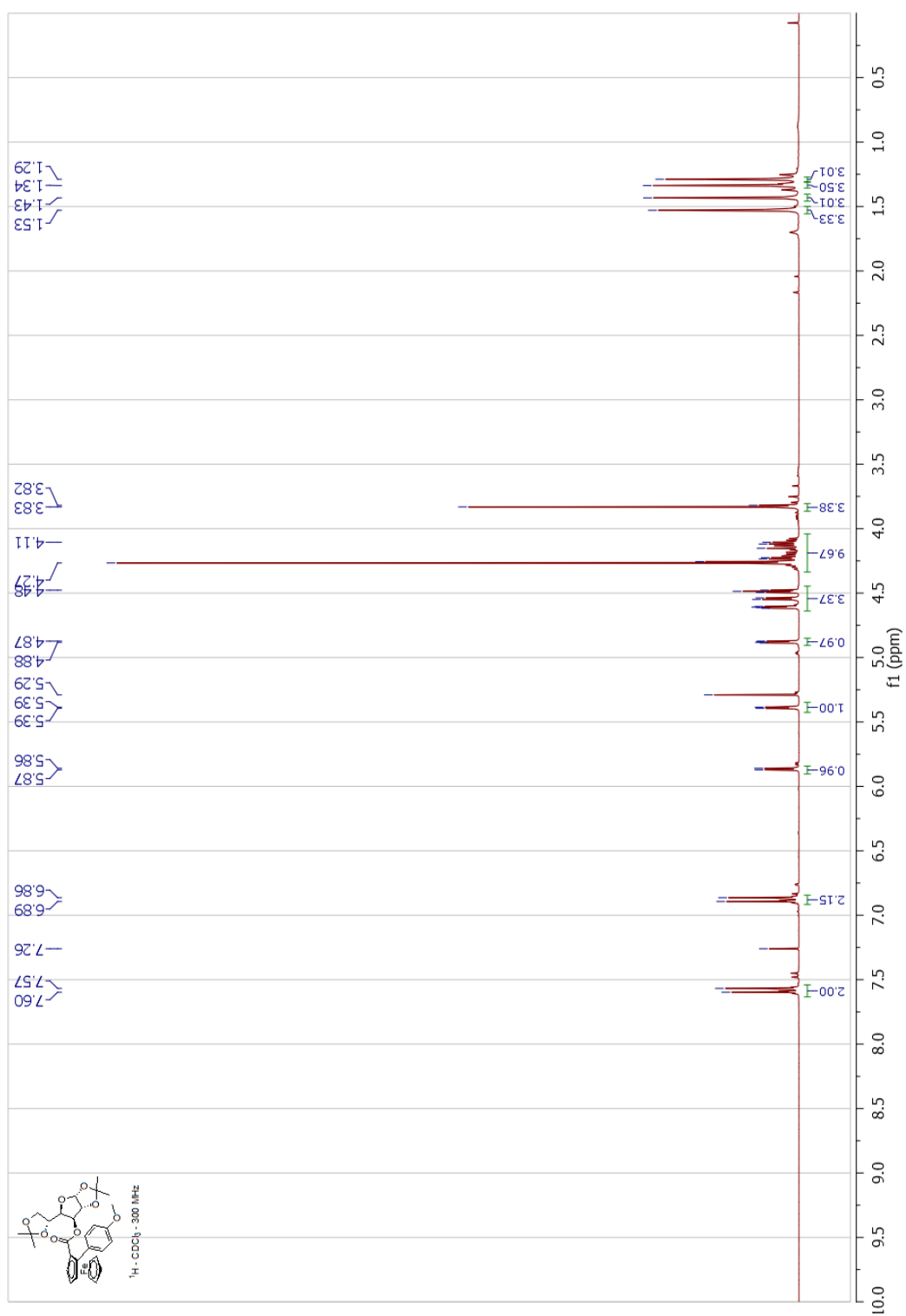
Compound *rac*-10'o, ¹H-NMR



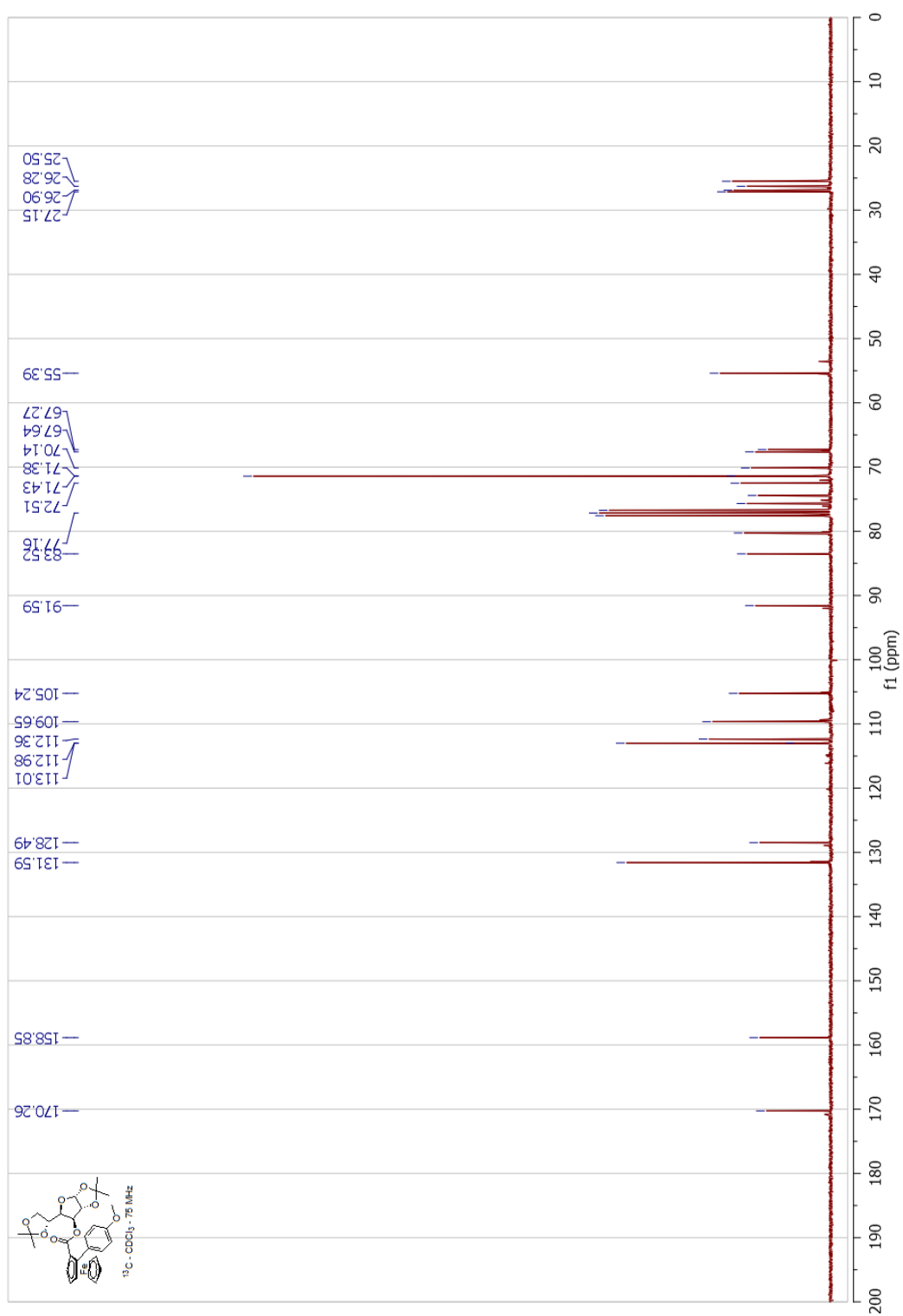
Compound *rac*-10'o, ¹³C-NMR



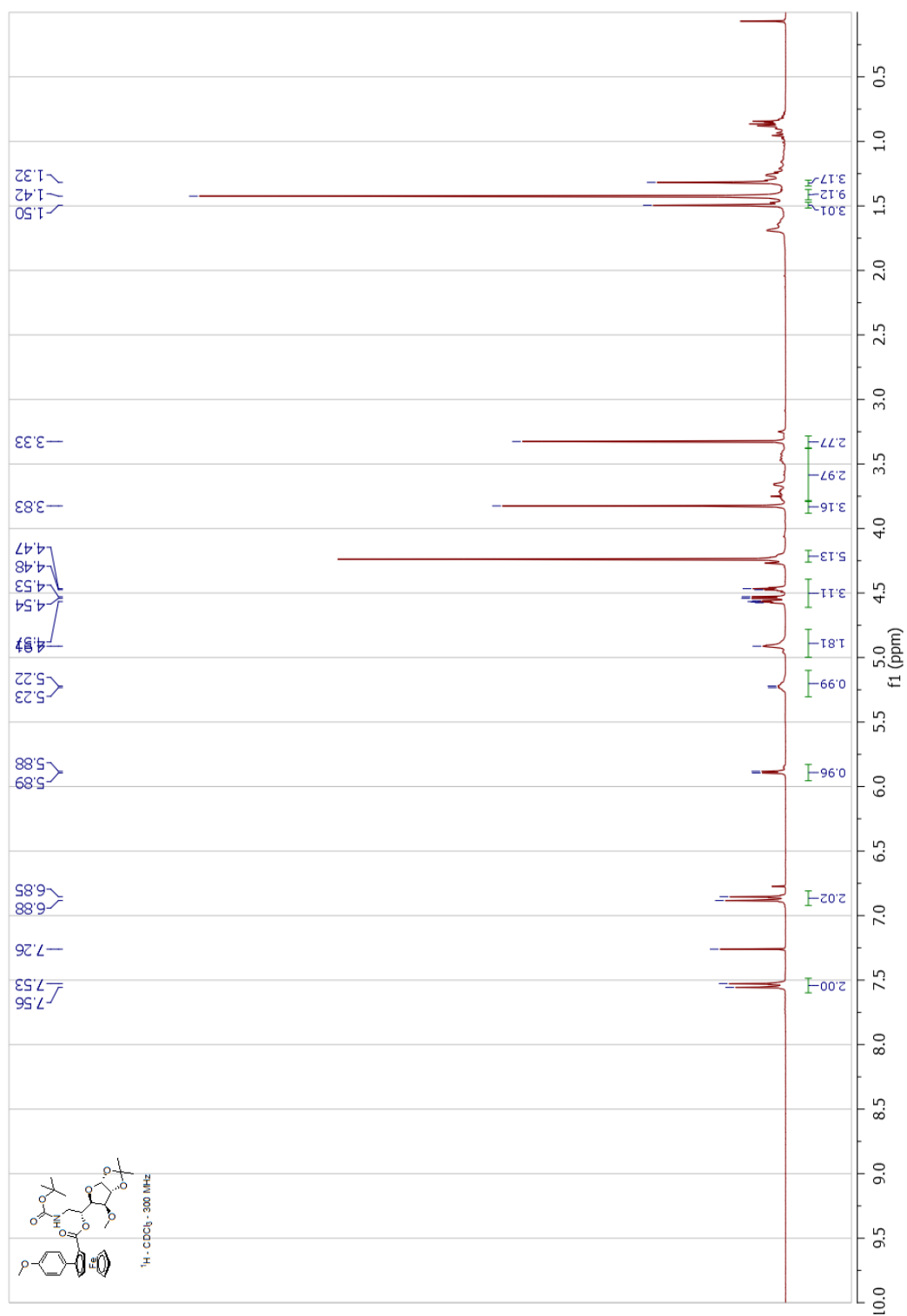
Compound *R_p*-11j, ¹H-NMR



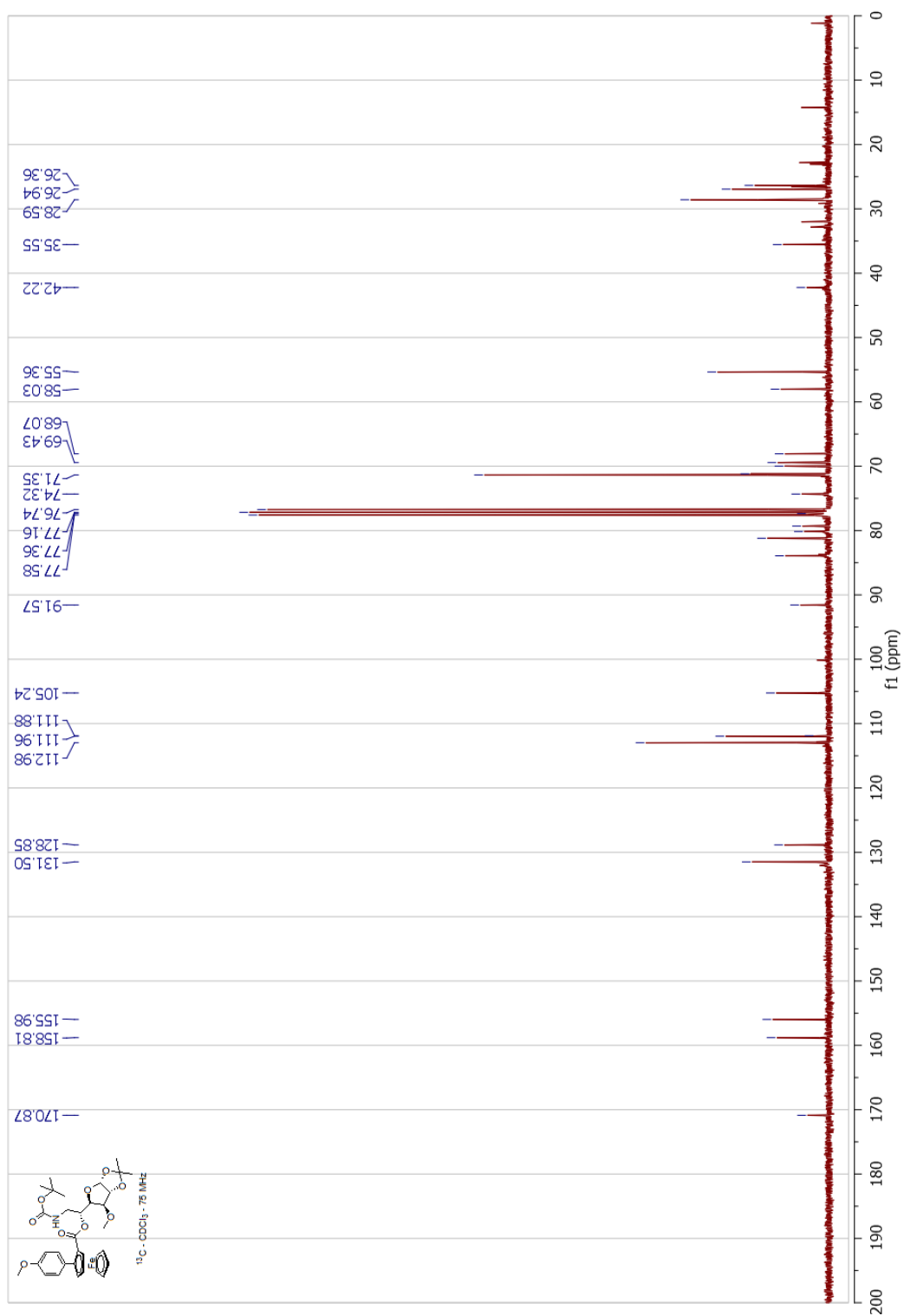
Compound *R_p-11j*, ¹³C-NMR



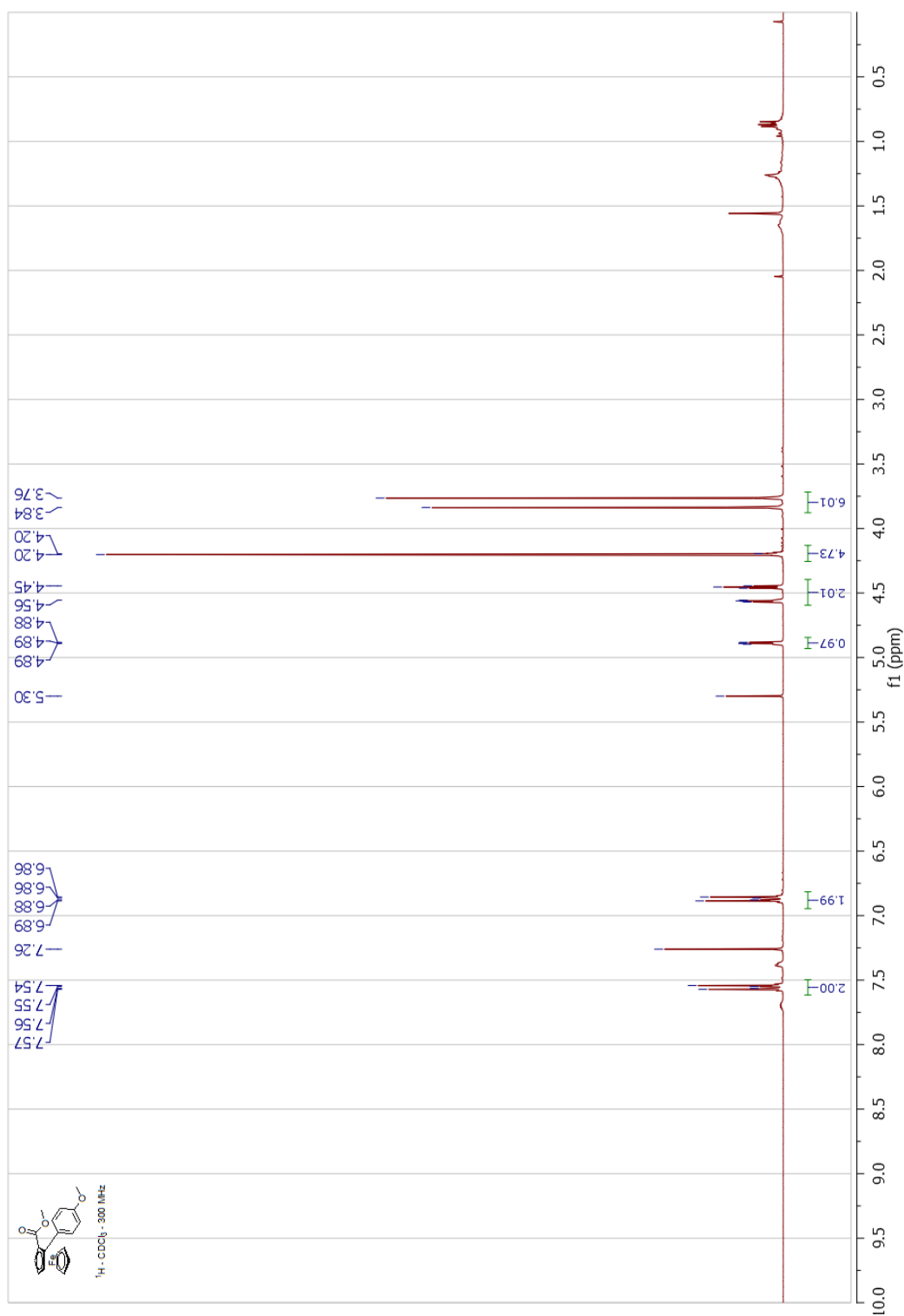
Compound Sp-11n, ¹H-NMR



Compound Sp-11n, ¹³C-NMR



Compound *rac*-11o, ¹H-NMR



Compound *rac*-11o, ^{13}C -NMR

