Anionic Phospho-Fries Rearrangement at Ferrocene: One-Pot Approach to *P*,*O*-substituted Ferrocenes

Marcus Korb, Dieter Schaarschmidt and Heinrich Lang*

Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Anorganische Chemie, Straße der Nationen 62, 09107 Chemnitz, Germany

E-mail: heinrich.lang@chemie.tu-chemnitz.de

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Crystal structures of 10 and 18

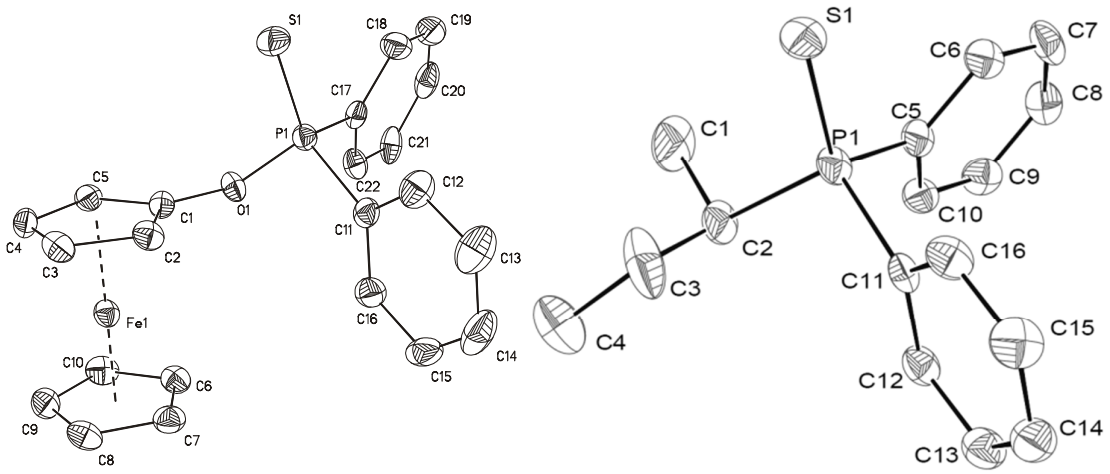


Figure SI1. ORTEP diagram (50 % probability level) of the molecular structure of **10** (left) and **18** (right) with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°) for **10**: C1–O1 1.394(4), C11–P1 1.806(3), C17–P1 1.805(3), O1–P1 1.616(2), P1–S1 1.9249(12), D1–Fe1 1.6453(5), D2–Fe1 1.6504(5); C1–O1–P1 121.30(19), O1–P1–S1 116.33(9), C17–P1–S1 115.05(12), C11–P1–C17 107.09(15), C11–P1–O1 105.46(15), O1–P1–C17 98.41(14), C11–P1–S1 113.04(12), D1–Fe1–D2 178.40(4) (D1 denotes the centroid of C_5H_4; D2 denotes the centroid of C_5H_5). Selected bond distances (Å), angles (°) for **18**: C2–P1 1.828(4), C5–P1 1.814(4), C11–P1 1.827(3), P1–S1 1.9632(13), C5–P1–C11 103.25(15), C5–P1–C2 107.56(18), C11–P1–C2 106.48(17), C5–P1–S1 112.36(13), C11–P1–S1 113.68(13), C2–P1–S1 112.84(13).

The thiophosphinate **10** and phosphine sulfide **18** crystallize in the monoclinic space group $P2_1/c$ (**10**) and the triclinic space group $P\bar{1}$ (**18**) with two independent molecules in the asymmetric unit. In case of phosphine sulfide **10** the asymmetric unit contains both enantiomers with respect to the chiral carbon atom C2. The P–C_{Ph} distances are equal for both molecules, whereas the P–S distance increases from 1.9249(12) (**10**) to 1.9632(13) Å (**18**) through the exchange of the ferrocenolato moiety by a ^{s}butyl group. The angle between the two phenyl rings is reduced from 107.09(15) ° (**10**) to 103.25(15) ° (**18**), due to the presence of a sterically more demanding secondary carbon in comparison to an oxygen atom. Thus, both phosphorous atoms possess a distorted tetrahedral geometry.

General Information.

All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques. Reaction vessels were heated at reduced pressure with a heat gun and flushed with argon. This procedure was repeated three times. If necessary, solvents were deoxygenated by standard procedures.

For column chromatography either silica with a particle size of 40−60 µm (230−400 mesh (ASTM), Fa. Macherey-Nagel) or alumina with a particle size of 90 µm (Standard, Fa. Macherey-Nagel) was used.

Instruments

FT IR spectra were recorded with a Nicolet IR 200 spectrometer (Fa. Thermo) between NaCl crystals or as KBr pellets.

NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 125.7 MHz for $^{13}C\{^{1}H\}$, and 202.5 MHz for $^{31}P\{^{1}H\}$ spectra). Chemical shifts are reported in δ (ppm) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR, $CHCl_3$ δ 7.26, C_6HD_5 δ 7.16; $^{13}C\{^{1}H\}$ NMR, $CDCl_3$ δ 77.00, C_6D_6 δ 128.06; $^{31}P\{^{1}H\}$ NMR, standard external relative to 85% H_3PO_4 δ 0.0, $P(OMe)_3$ δ 139.0). The melting points were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were measured with a Thermo FlashAE 1112 instrument. High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer.

Single-Crystal X-ray Diffraction Analysis.

Suitable single crystals of **1**, **10**, and **18** for X-ray diffraction analysis were obtained by recrystallization from n-hexane at ambient temperature. Data were collected with an Oxford Gemini S diffractometer at 100 K with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by fullmatrix least-squares procedures on F^2.[1] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions.

The HPLC measurements were performed with a Knauer system consisting of a WellChrom Mini-Star K-500 pump and a WellChrom K-2000 UV detector operating at 245 nm equipped with a Chiralcel OD-H column (4.6 x 250 mm) using 9/1 (v/v) hexane/isopropanol mixture (0.5 mL/min) as the solvent. Retention times are reported in *t* (minutes).

Reagents

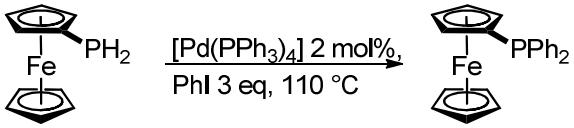
Tetrahydrofuran was purified by distillation from sodium/ benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride.

All starting materials were obtained from commercial suppliers and used without further purification. Acetocyferrocene,[2] ferrocenol[3], 1,1-bis(acetoxy)ferrocene,[2] 1,1'-ferrocenediol[2] and ferrocenylphosphine (**26**)[4] were prepared according to published procedures. The spectroscopic data of synthesized ferrocenyldiphenylphosphane (**27**) are in agreement with literature.[5]

Optimization of the Stelzer coupling of ferrocenylphosphine

The Palladium-catalyzed Stelzer *P*,*C*-bond formation between ferrocenylphosphine (**26**) and arylhalides has not been described so far in the literature. The phosphine is accessible in a multi gram scale, thus, we investigated **26** instead of **12** in a test reaction to explore the reaction conditions. The results for the formation of **27** are summarized in Table **SI1**. The best results were reached using two equivalents K_3PO_4 with toluene as the solvent (Table SI1, entry 4). The usage of other bases decreases the yield dramatically. With an increase of base also a significant amount of the corresponding phosphanoxide can be detected (up to 50 %, Table **SI1**, entry 2). Nevertheless, it is known that phosphaneoxides can be converted to the corresponding phosphane.[6]

Table SI1. Stelzer-coupling of ferrocenylphosphine



26 **27**

Entry	Base (eqiv)	solvent	Yield[a]
1	NEt_3 (4)	toluene	0 %
2	K_3PO_4 (4)	toluene	68 %[b]
3	CsF (4)	toluene	26 %
4	K_3PO_4 (2)	toluene	72 %
5	K_3PO_4 (4)	1,4-dioxane	65 %
6	K_3PO_4 (2)	1,4-dioxane	48 %

[a] isolated Yiel. Spectroscopic date are in agreement with literature.[5] [b] 50 % of corresponding phosphanoxide were formed.

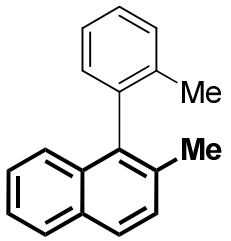
Experimental procedures

General Procedure for Suzuki-Miyaura cross-coupling reactions

A glass vessel (3 mL size) was charged with [$Pd_2(dba)_3$, 0.25 mol%], **1** [Pd/P = 1:2 (n/n)], boronic acid (1.5 mmol), powdered K_3PO_4 x H_2O (690 mg, 3.0 mmol), the appropriate aryl halide (1.0 mmol) and dry toluene (3 mL). The vessel was purged with argon and closed. The reaction mixture was heated at 70 °C, except otherwise noted, with vigorous stirring for 24 h. After cooling to room temperature, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 x 25 mL). The

combined organic extracts were filtered through alumina and concentrated under reduced pressure. The obtained crude material was purified by flash chromatography on silica (hexane/diethyl ether mixtures).

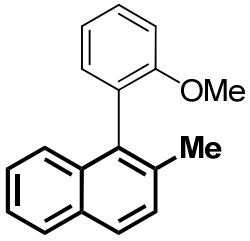
2-Methyl-1-(2'-methylphenyl)naphthalene (25a)



25a

The title compound was obtained as a colourless liquid from 2-methyl-1-bromnaphthalene (220 mg) and *o*-tolylboronic acid (205 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using hexane. The analytical data are in agreement with literature.[7] Yield: 230 mg (99 % based on the aryl halide). ^{1}H NMR ($CDCl_3$, δ): 1.94 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 7.14 (d, $J_{H,H}$ = 7.1 Hz, 1H), 7.26 (d, $J_{H,H}$ = 8.4 Hz, 1H), 7.31–7.34 (m, 2H), 7.35–7.39 (m, 2 H), 7.41 (ddd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.3 Hz, 1H), 7.44 (d, $J_{H,H}$ = 8.4 Hz, 1H), 7.80 (d, $J_{H,H}$ = 8.4 Hz, 1H), 7.85 (d, $J_{H,H}$ = 8.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.5, 20.3, 124.7, 125.87, 125.7, 125.9, 127.1, 127.4, 127.8, 128.6, 129.97, 130.04, 132.0, 132.6, 133.1, 136.8, 137.5, 139.2.

2-Methyl-1-(2-methoxyphenyl)naphthalene (25b)



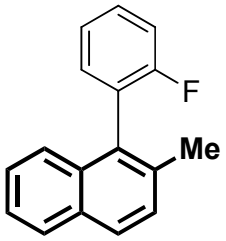
25b

The title compound was obtained as colourless liquid from 2-methyl-1-bromnaphthalene (220 mg) and 2-methoxyphenylboronic acid (230 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 98/2 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature.[8] Yield: 247 mg (99 % based on the aryl halide). ^{1}H NMR ($CDCl_3$, δ): 2.22 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 7.06–7.11 (m, 2H), 7.14 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.8 Hz, 1H), 7.29–7.32 (m, 1H), 7.35–7.40 (m, 2H), 7.42–7.45 (m, 2H), 7.78 (d, $J_{H,H}$ = 8.4 Hz, 1H), 7.83 (d, $J_{H,H}$ = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 20.5 (CH_3), 55.6 (OCH_3), 111.2, 120.7, 124.6, 125.6, 125.9, 127.2, 127.8, 128.3, 128.5, 128.8, 131.8, 132.0, 132.9, 133.9, 134.6, 157.4.

2-Methyl-1-(2-fluorphenyl)naphthalene (25c)

The title compound was obtained as a colourless oil from 2-methyl-1-bromnaphthalene (220 mg), 2-fluorphenylboronic acid (335 mg) and K_3PO_4 x $3H_2O$ (800 mg, 3.0 mmol) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 99/1 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature. Yield: 215 mg (91 % based on the

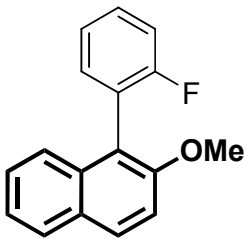
aryl halide). ^{1}H NMR ($CDCl_3$, δ): 2.27 (s, 3H, CH_3), 7.21–7.30 (m, 3H), 7.34–7.47 (m, 5H), 7.82 (d, $J_{H,H}$ = 8.5 Hz, 1H), 7.85 (d, $J_{H,H}$ = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 20.5 (s, CH_3), 115.8 (d, $J_{C,F}$ = 22.3 Hz), 124.1 (d, $J_{C,F}$ = 3.6 Hz), 124.9, 125.5, 126.1, 126.8 (d, $^2J_{C,F}$ = 17.7 Hz, C^i-Ph), 127.90, 127.96, 128.5, 129.4 (d, $J_{C,F}$ = 7.9 Hz), 131.6, 132.0, 132.4 (d, $J_{C,F}$ = 3.8 Hz), 132.7, 134.3, 160.2 (d, $^1J_{C,F}$ = 245.4 Hz, C–F). HRMS (ESI-TOF, *m/z*): calcd for $C_{17}H_{13}F$+H 237.1074, found 237.1065 $[M+H]^+$.



25c

2-Methoxy-1-(2-fluorphenyl)naphthalene (25d)

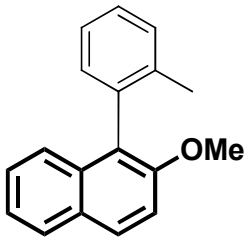
The title compound was obtained as a white solid from 2-methoxy-1-bromnaphthalene (235 mg), 2-fluorphenylboronic acid (210 mg) and K_3PO_4 x $3H_2O$ (800 mg, 3.0 mmol) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 94/6 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature.[9] Yield: 235 mg (93 % based on the aryl halide). ^{1}H NMR ($CDCl_3$, δ): 3.88 (s, 3H, OCH_3), 7.22 (ddd, $J_{H,H}$ = 9.3Hz, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 1.0 Hz, 1H), 7.28 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.2 Hz, 1H), 7.32–7.40 (m, 4H), 7.42–7.45 (m, 2H), 7.82–7.85 (m, 1H), 7.93 (d, $J_{H,H}$ = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.8 (OCH_3), 113.6, 115.7 (d, $J_{C,F}$ = 22.5 Hz), 118.8, 123.6, 123.8 (d, $^2J_{C,F}$ = 17.3 Hz), 123.8 (d, $J_{C,F}$ = 3.6 Hz), 124.7, 126.6, 128.0, 129.0, 129.3 (d, $J_{C,F}$ = 8.0 Hz), 129.9, 133.1 (d, $J_{C,F}$ = 3.7 Hz), 133.4, 154.4, 160.6 (d, $^1J_{C,F}$ = 246.3 Hz, C–F). HRMS (ESI-TOF, *m/z*): calcd. for $C_{17}H_{13}FO$+H 253.1023, found 253.1036 $[M+H]^+$.



25d

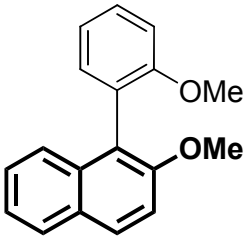
2-Methoxy-1-(2-methylphenyl)naphthalene (25e)

The title compound was obtained as a white solid from 2-methoxy-1-bromnaphthalene (235 mg) and *o*-tolylboronic acid (205 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 98/2 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature.[10] Yield 160 mg (64 % based on the aryl halide) ^{1}H NMR ($CDCl_3$, δ): 2.02 (CH_3), 3.85 (OCH_3), 7.21 (d, $J_{H,H}$ = 7.0 Hz, 1H), 7.28–7.40 (m, 7H), 7.85 (dd, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 2.5, 1H), 7.91 (d, $J_{H,H}$ = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.7 (CH_3), 56.6 (OCH_3), 113.6, 123.5, 124.5, 125.0, 125.6, 126.3, 127.5, 127.8, 128.97, 129.0, 129.8, 130.8, 133.5, 136.1, 137.6, 153.7.



25e

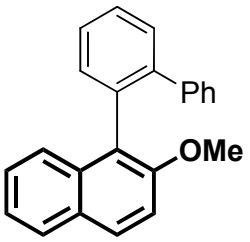
2-Methoxy-1-(2-methoxyphenyl)naphthalene (25f)



25f

The title compound was obtained as a white solid from 2-methoxy-1-bromnaphthalene (235 mg) and 2-methoxyphenylboronic acid (230 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 9/1 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature.[10] Yield: 243 mg (92 % based on the aryl halide). ^{1}H NMR ($CDCl_3$, δ): 3.69 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 7.05–7.11 (m, 2H), 7.22 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.8, 1H), 7.29–7.33 (m, 2H), 7.35–7.39 (m, 2H), 7.42 (ddd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 7.5 Hz, $J_{H,H}$ = 1.8 Hz, 1H), 7.80–7.83 (m, 1H), 7.88 (d, $J_{H,H}$ = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.1 (OCH_3), 57.0 (OCH_3), 111.3, 114.2, 120.6, 122.1, 123.4, 125.3, 125.4, 126.1, 127.8, 128.8, 129.05, 129.08, 132.4, 133.7, 154.3, 157.8.

2-Methoxy-1-(2-phenylphenyl)naphthalene (25g)



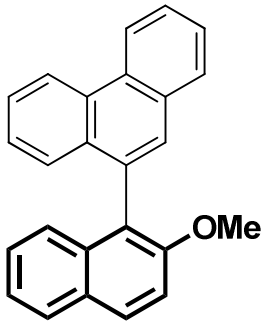
25g

The title compound was obtained as a white solid from 2-methoxy-1-bromnaphthalene (235 mg) and 2-phenylphenylboronic acid (290 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 98/2 (v/v) hexane/diethyl ether mixture. The analytical data are in agreement with literature.[9] Yield: 305 mg (99 % based on the arylhalide). ^{1}H NMR ($CDCl_3$, δ): 3.52 (s, 3H, OCH_3), 7.00–7.05 (m, 5H), 7.11 (d, $J_{H,H}$ = 9.0 Hz, 1H), 7.30 (ddd, $J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 7.4 Hz, 1H), 7.32–7.36 (m, 2H), 7.47 (td, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 2.1 Hz, 1H), 7.49–7.54 (m, 3H), 7.75–7.77 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.1 (OCH_3), 113.1, 123.3, 124.4, 125.2, 126.2, 126.3, 127.1, 127.2, 127.7, 127.9, 128.6, 128.8, 129.0, 129.8, 131.9, 133.9, 134.8, 141.8, 143.0, 153.5.

9-(2-Methoxy-1-naphthyl)phenanthrene (25h)

The title compound was obtained as a white solid from 2-methoxy-1-bromnaphthalene (235 mg) and 9-phenanthrylboronic acid (335 mg) by using the general procedure for Suzuki-Miyaura cross-coupling reactions and purified using a 98/2 (v/v) hexane/diethyl ether mixture. The

analytical data are in agreement with literature. Yield: 145 mg (43 % based on the aryl halide). ^{1}H NMR ($CDCl_3$, δ): 3.78 (s, 3H, OCH_3), 7.22 (ddd, $J_{H,H}$ = 8.6 Hz, $J_{H,H}$ = 6.6 Hz, $J_{H,H}$ = 1.3 Hz, 1H), 7.29–7.31 (m, 1H), 7.34 (ddd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 6.6, $J_{H,H}$ = 1.2, 1H), 7.39–7.40 (m, 2H), 7.48 (d, $J_{H,H}$ = 9.0, 1H), 7.62–7.66 (m, 2H), 7.71 (ddd, $J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.3 Hz, 1H), 7.73 (s, 1H), 7.89–7.91 (m, 2H), 8.01 (d, $J_{H,H}$ = 9.0 Hz, 1H), 8.81 (t, $J_{H,H}$ = 7.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 56.8 (OCH_3), 113.9, 122.6, 122.8, 123.2, 123.6, 125.5, 126.45, 126.52, 126.54, 126.6, 126.8, 127.8, 128.7, 129.1, 129.6, 130.3, 130.5, 131.9, 132.1, 133.2, 134.3, 154.8. HRMS (ESI-TOF, *m/z*): calcd. for $C_{25}H_{18}O$+Na 357.1250, found 357.1247 $[M+Na]^+$.



25h

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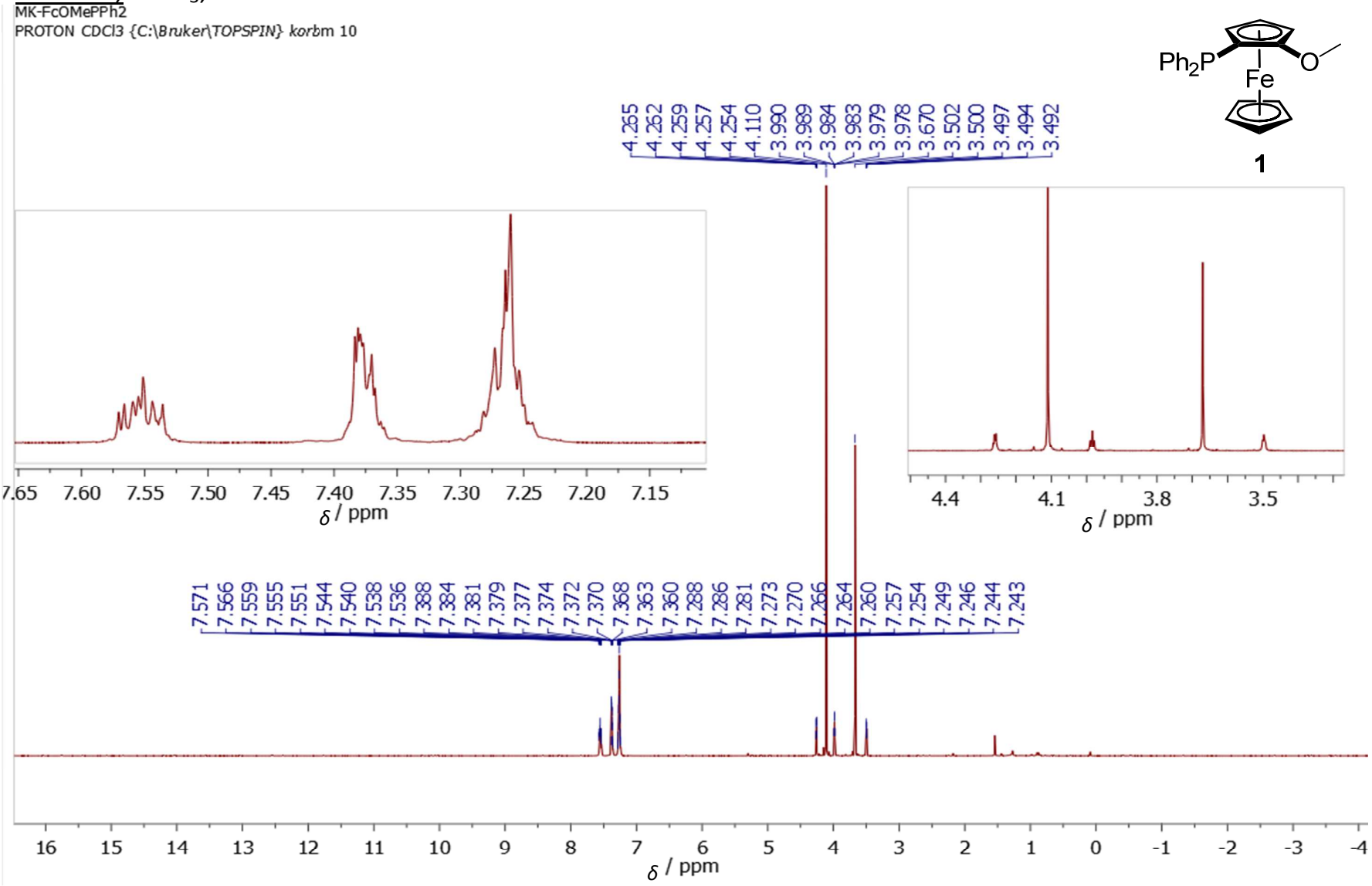
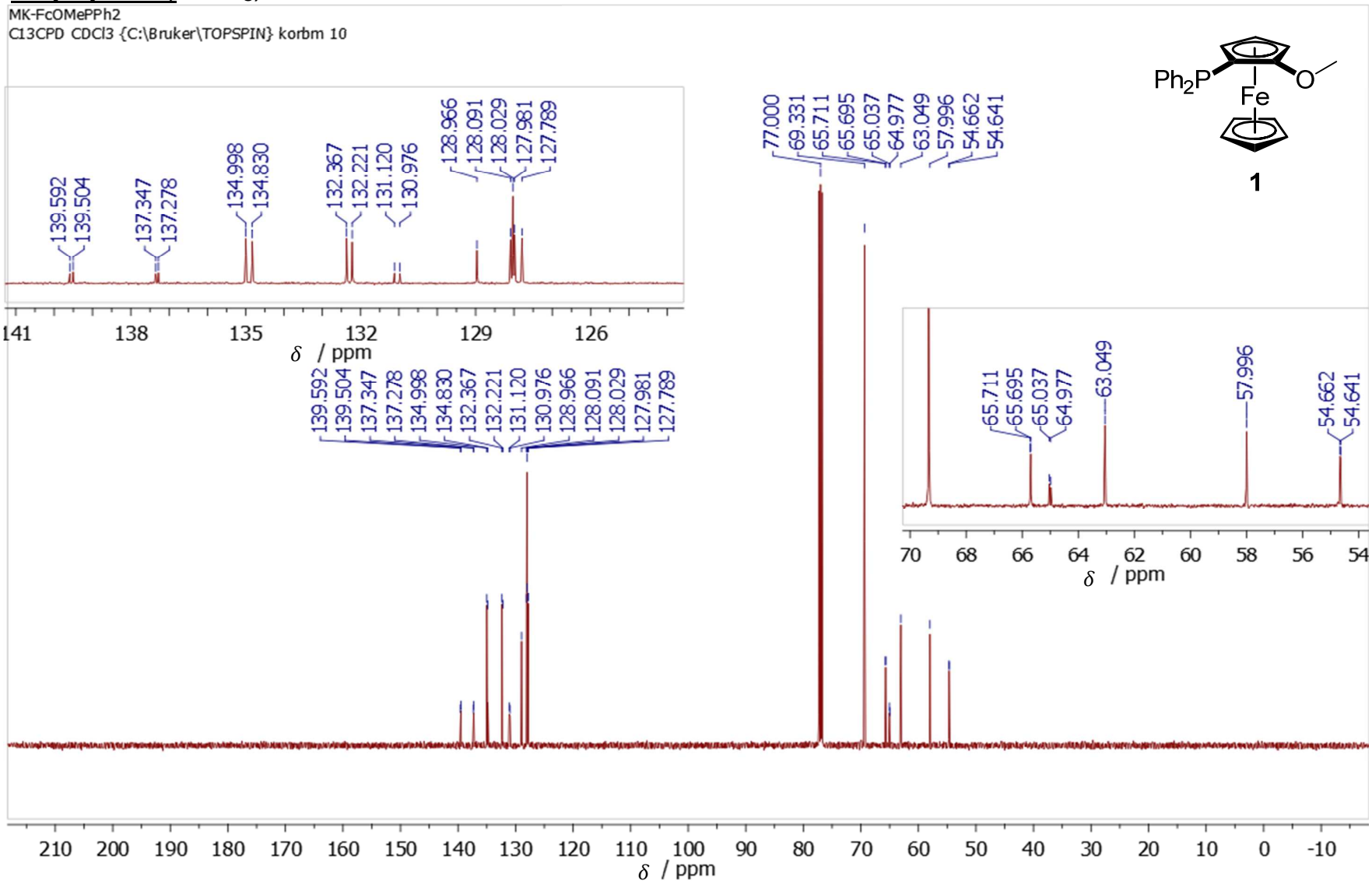
^{1}H and ^{13}C NMR spectra of the new compounds

^{1}H NMR, $CDCl_3$, 25 °C

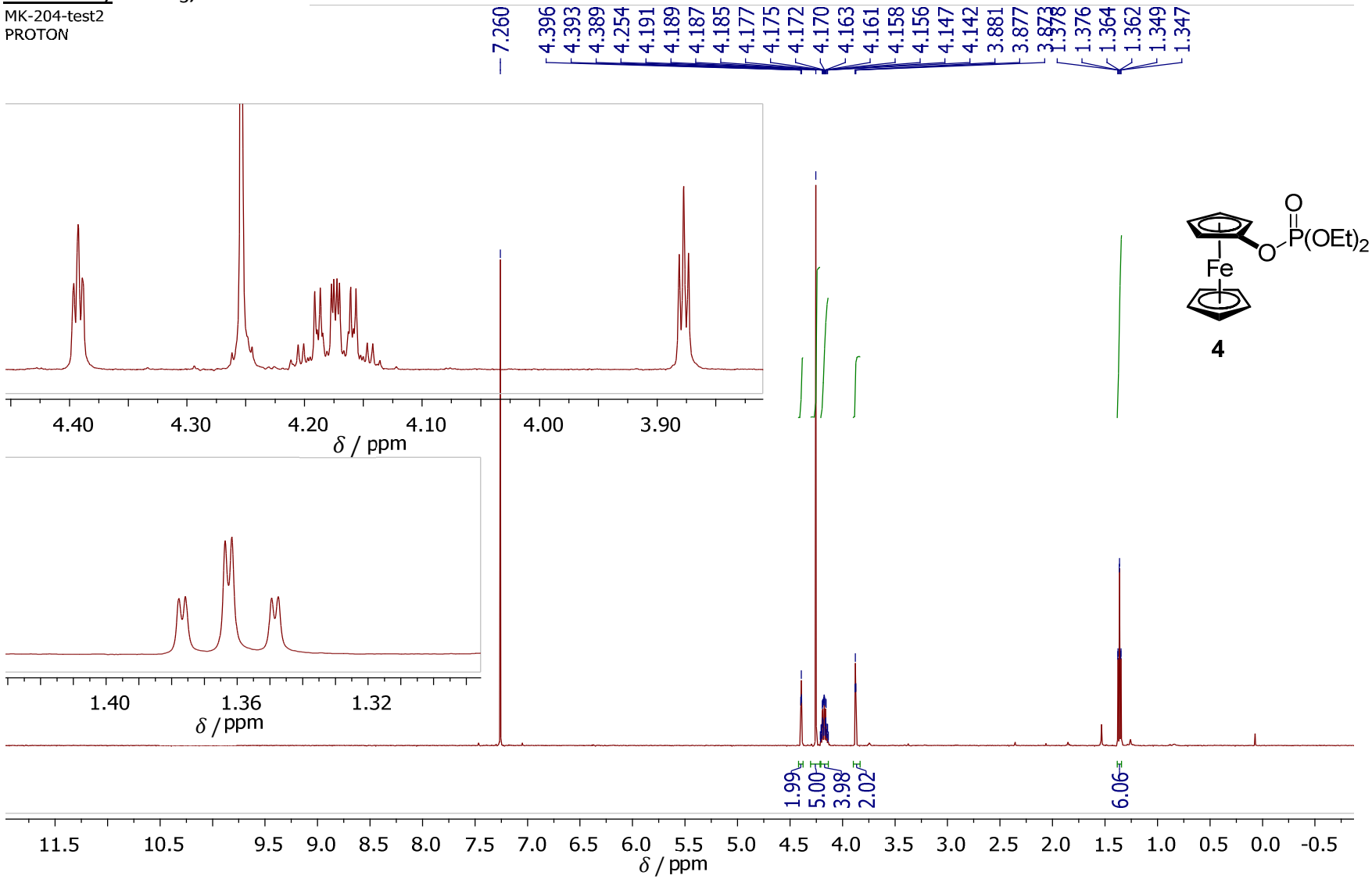


$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C



^{1}H NMR, $CDCl_3$, 25 °C

MK-204-test2
PROTON

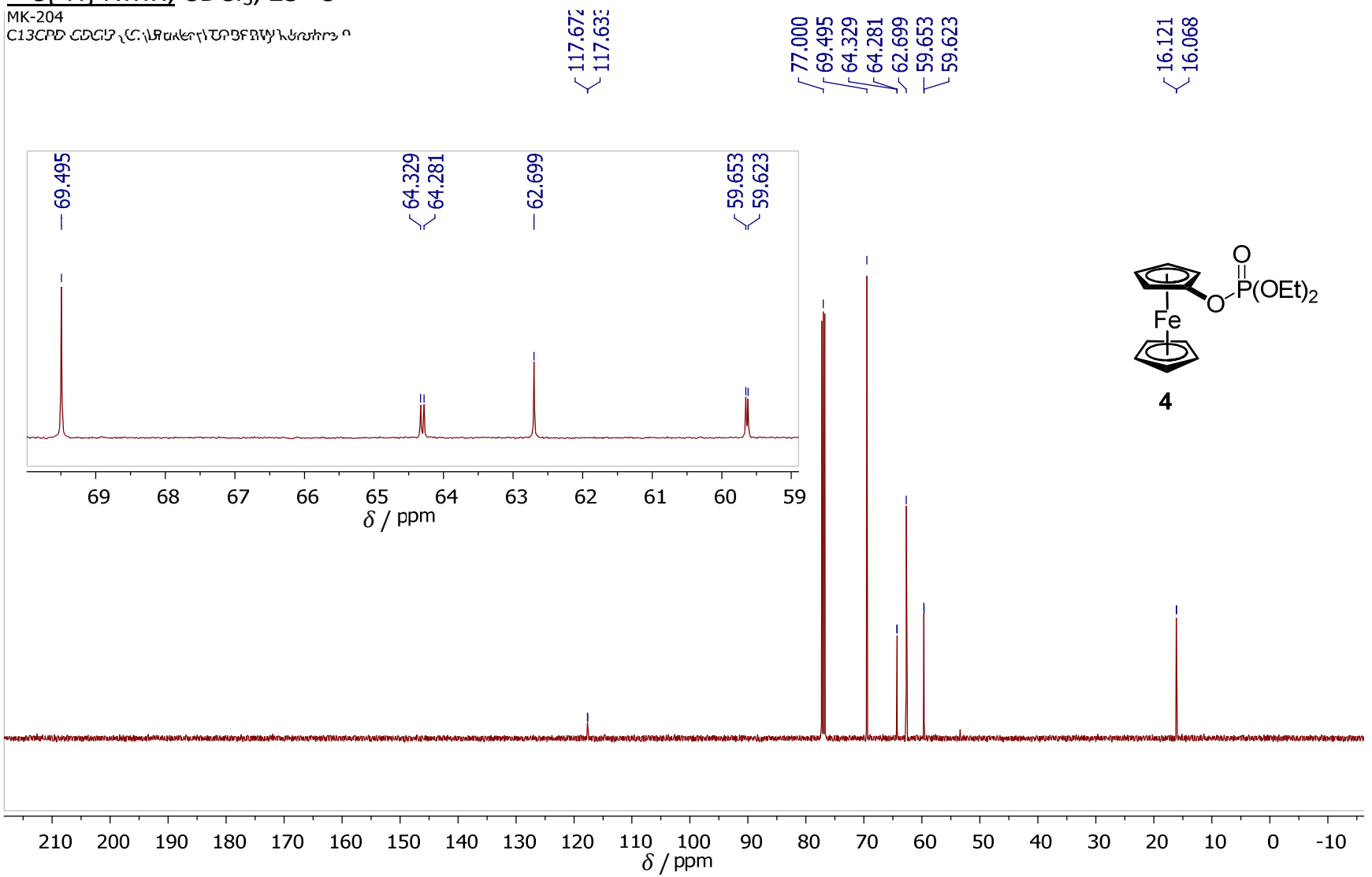


4

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

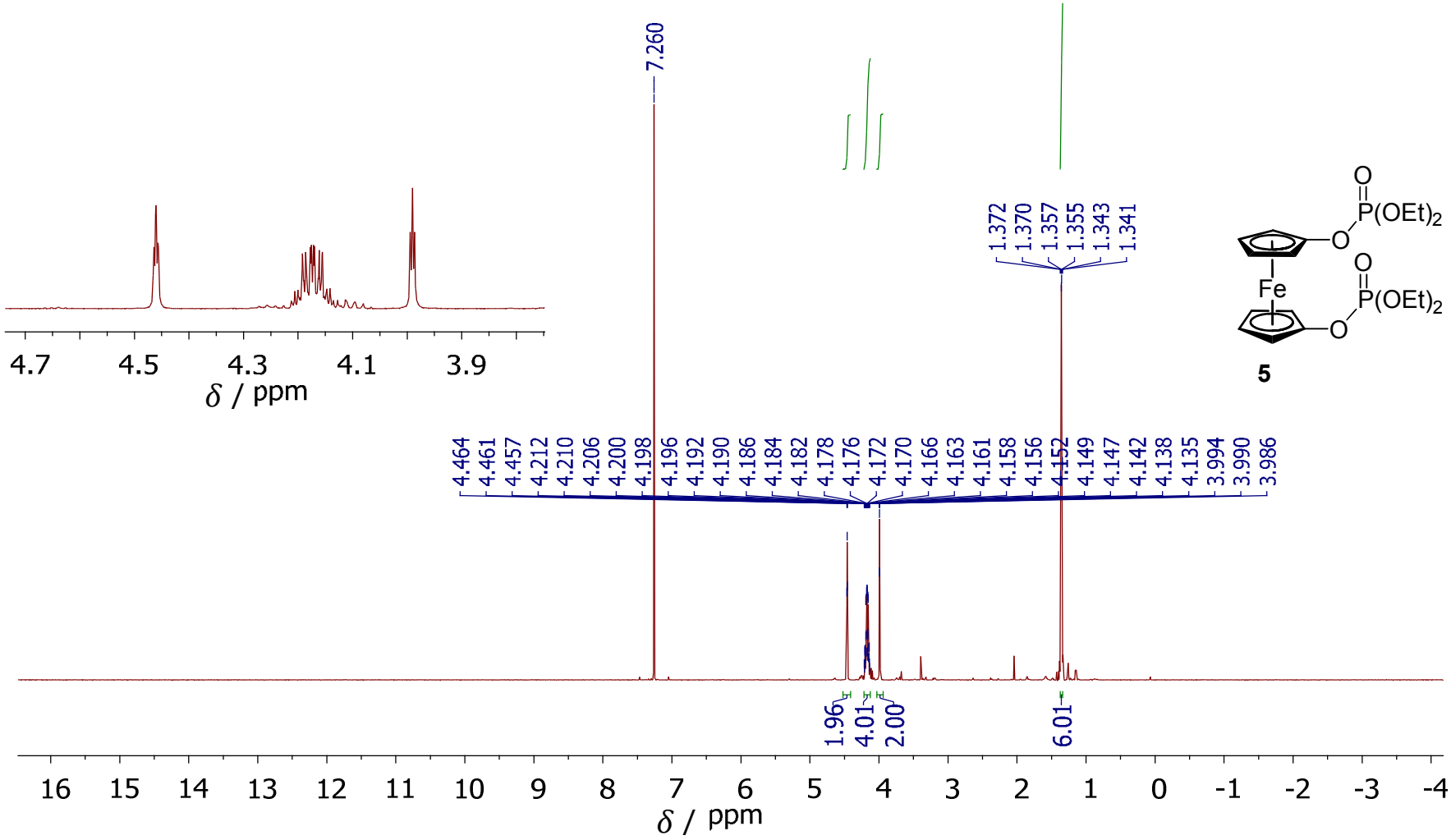
MK-204

C13CPD CDCl3 {C:\Bruker\TOPSPIN} kbrahm 0



^{1}H NMR, $CDCl_3$, 25 °C

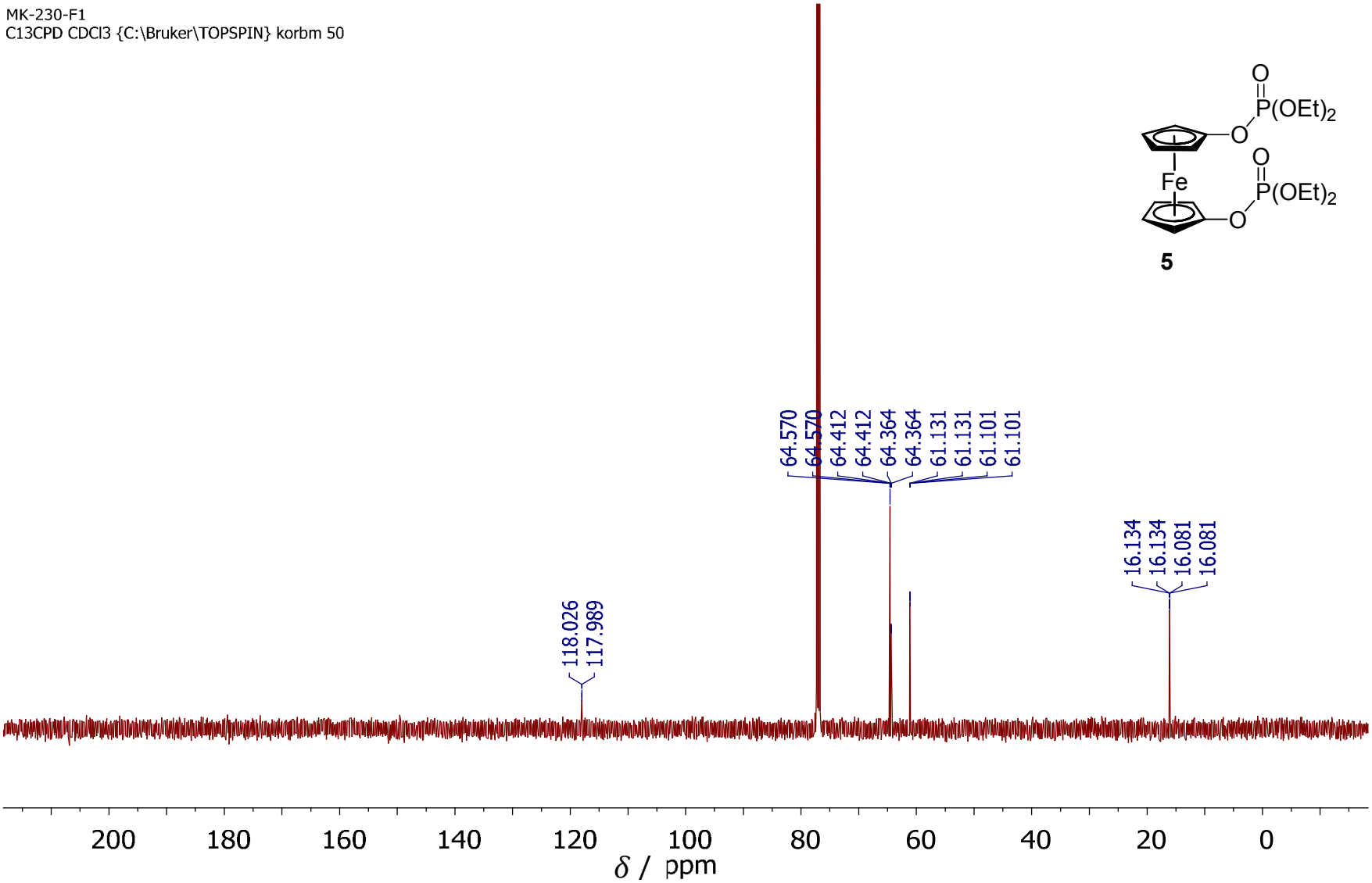
MK-230-F1
PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 50



5

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

MK-230-F1
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 50

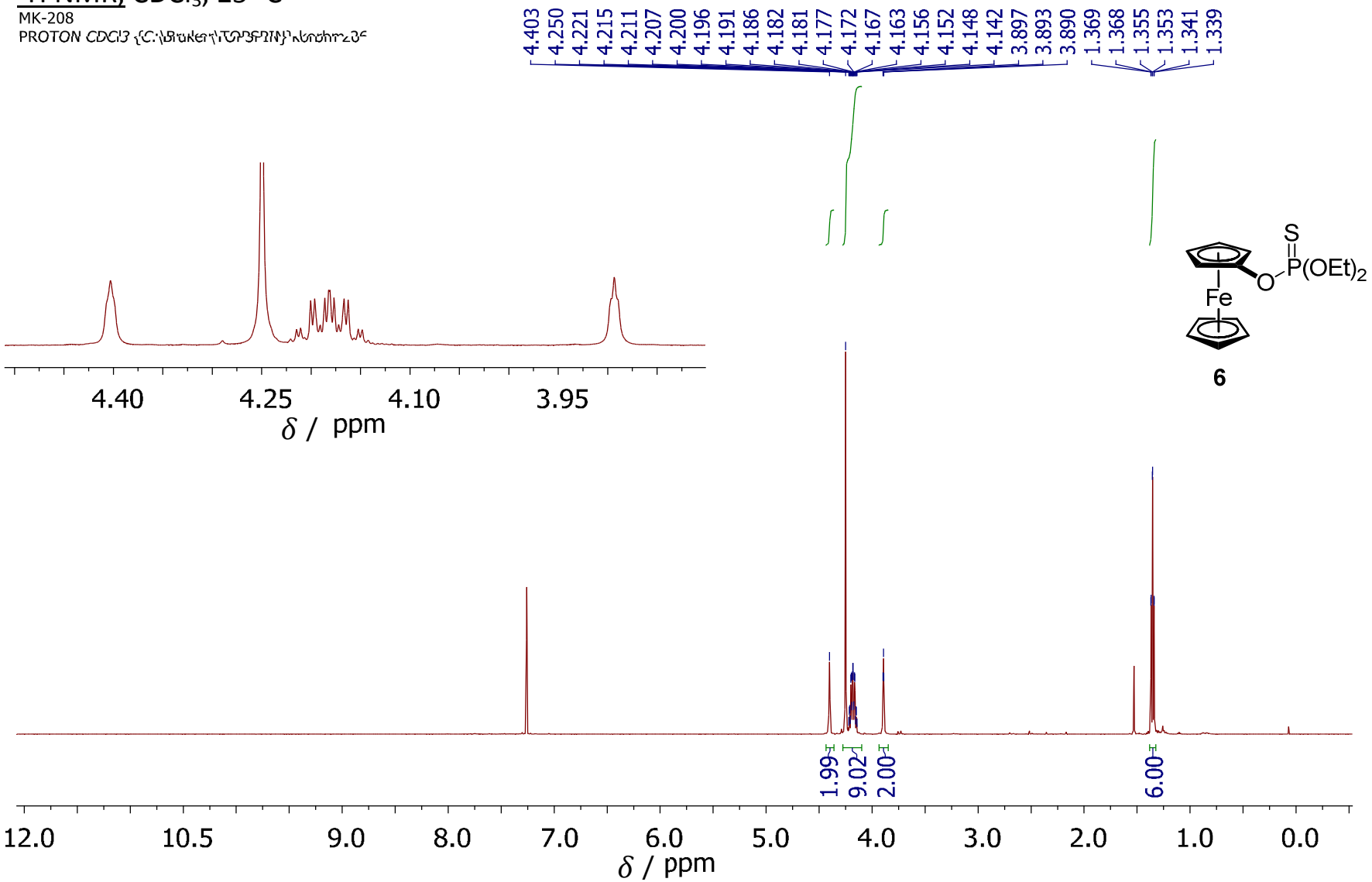


5

^{1}H NMR, $CDCl_3$, 25 °C

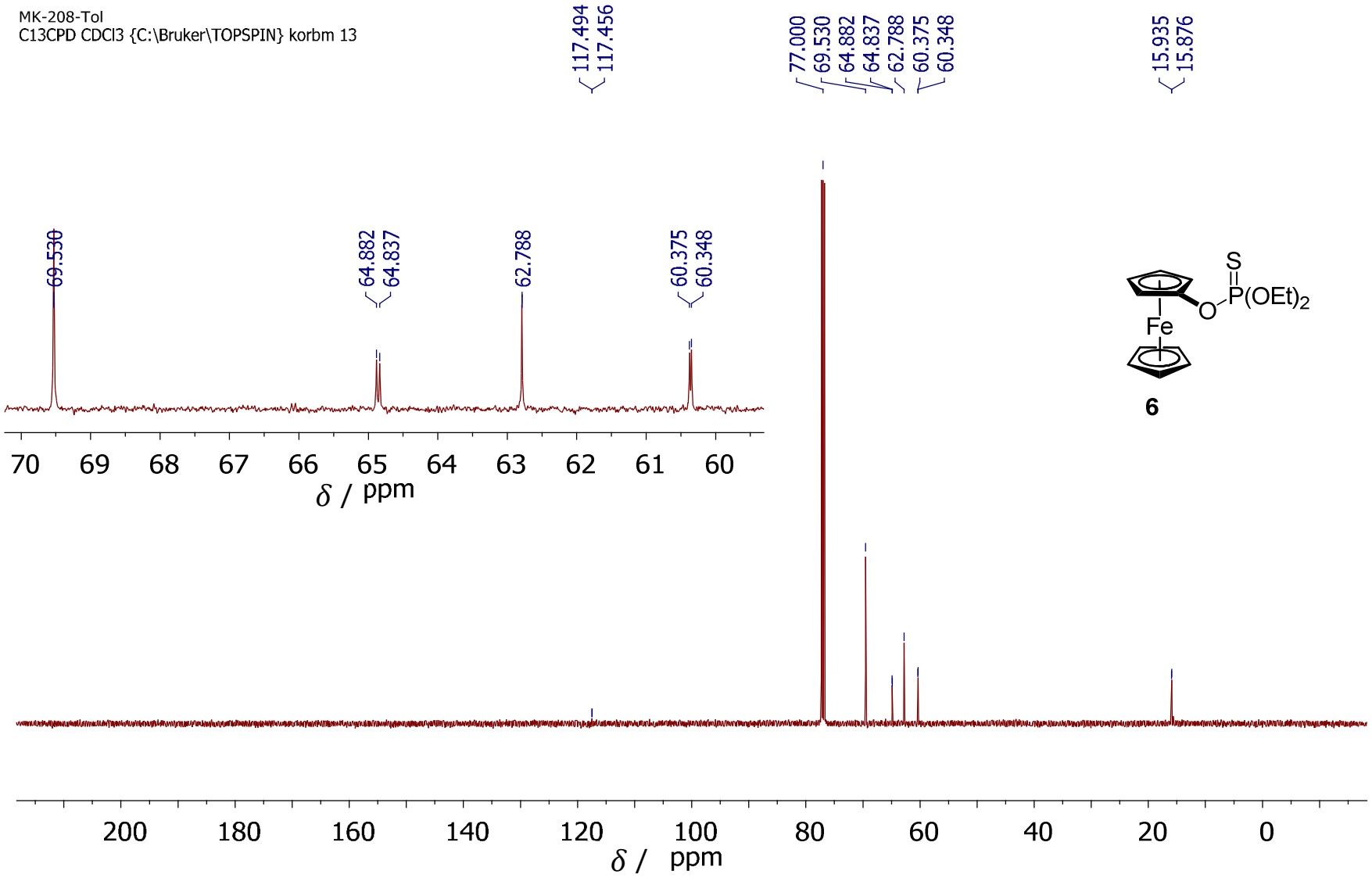
MK-208

PROTON CDCl3 {C:\Bruker\TOPSPIN\...

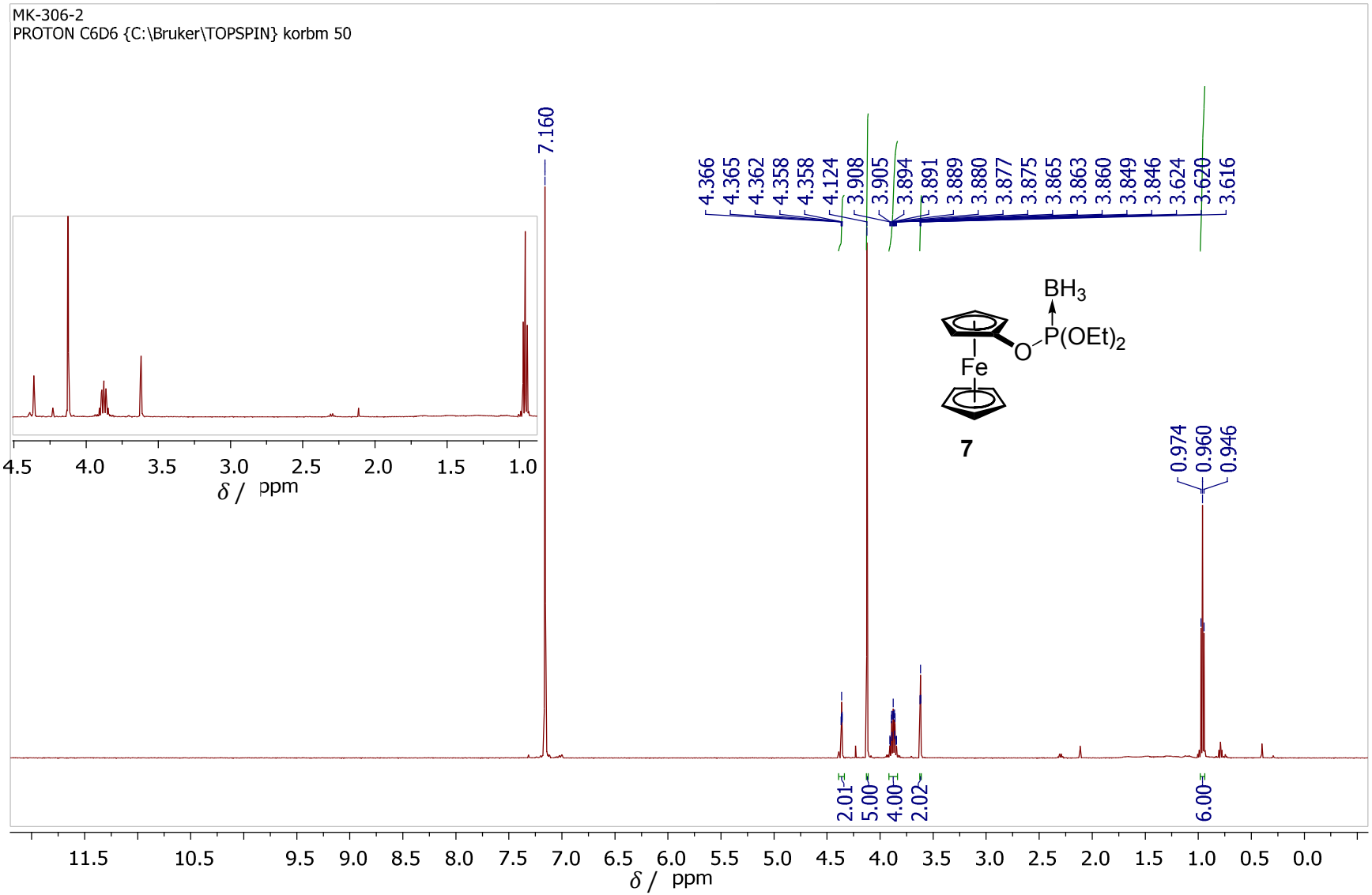


$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

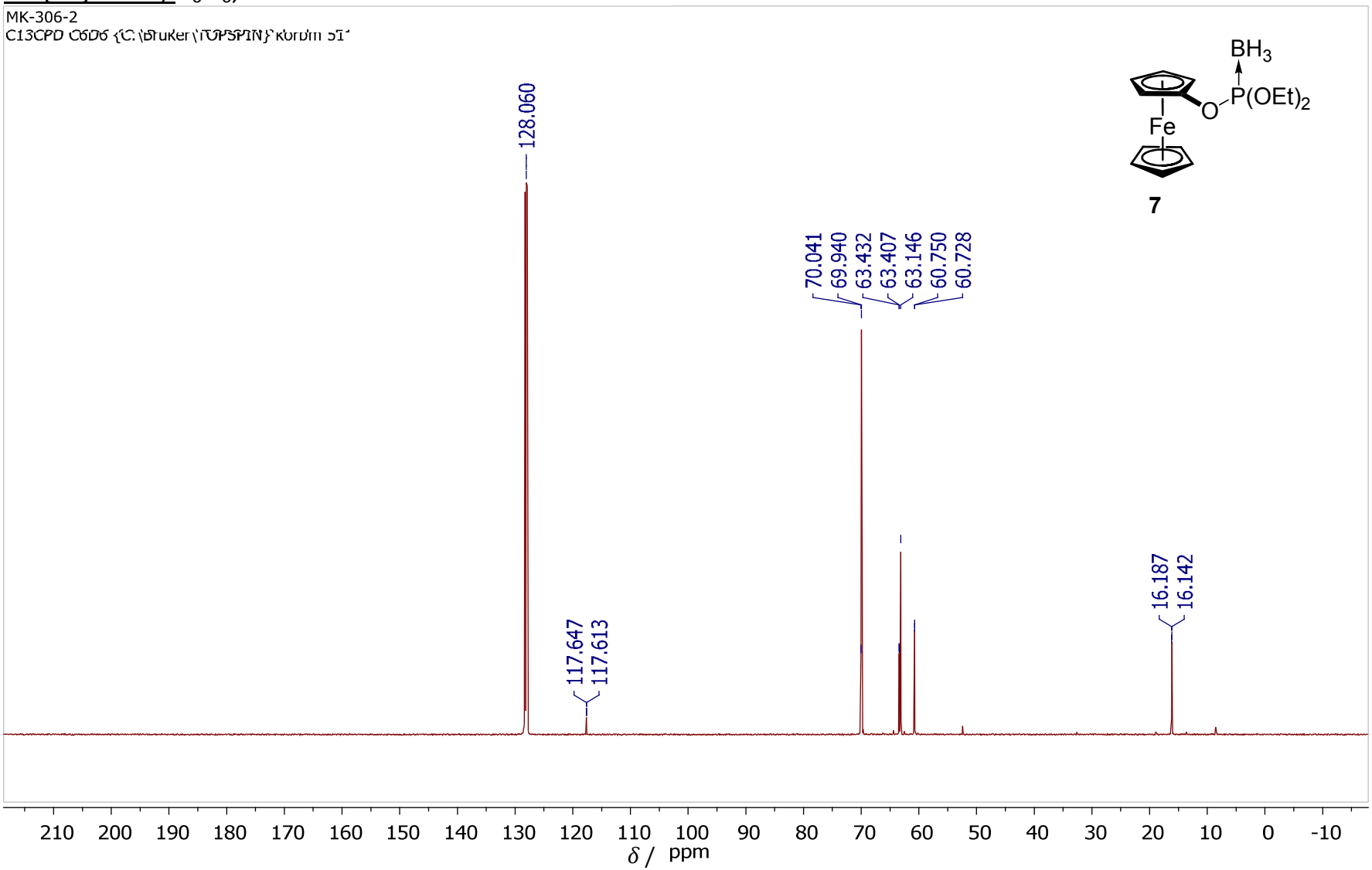
MK-208-Tol
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 13



^{1}H NMR, C_6D_6, 25 °C



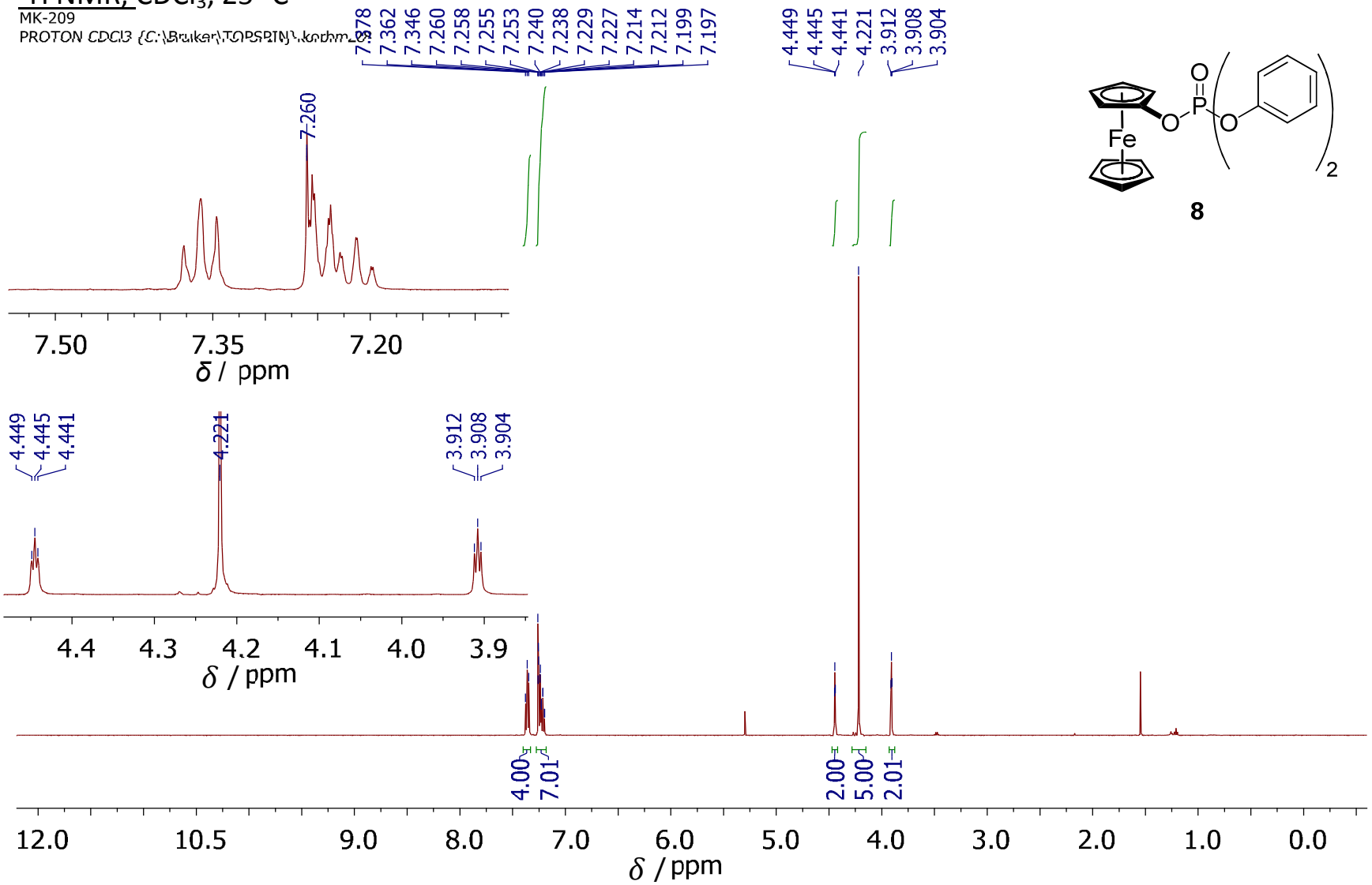
$^{13}C\{^{1}H\}$ NMR, C_6D_6, 25 °C



^{1}H NMR, $CDCl_3$, 25 °C

MK-209

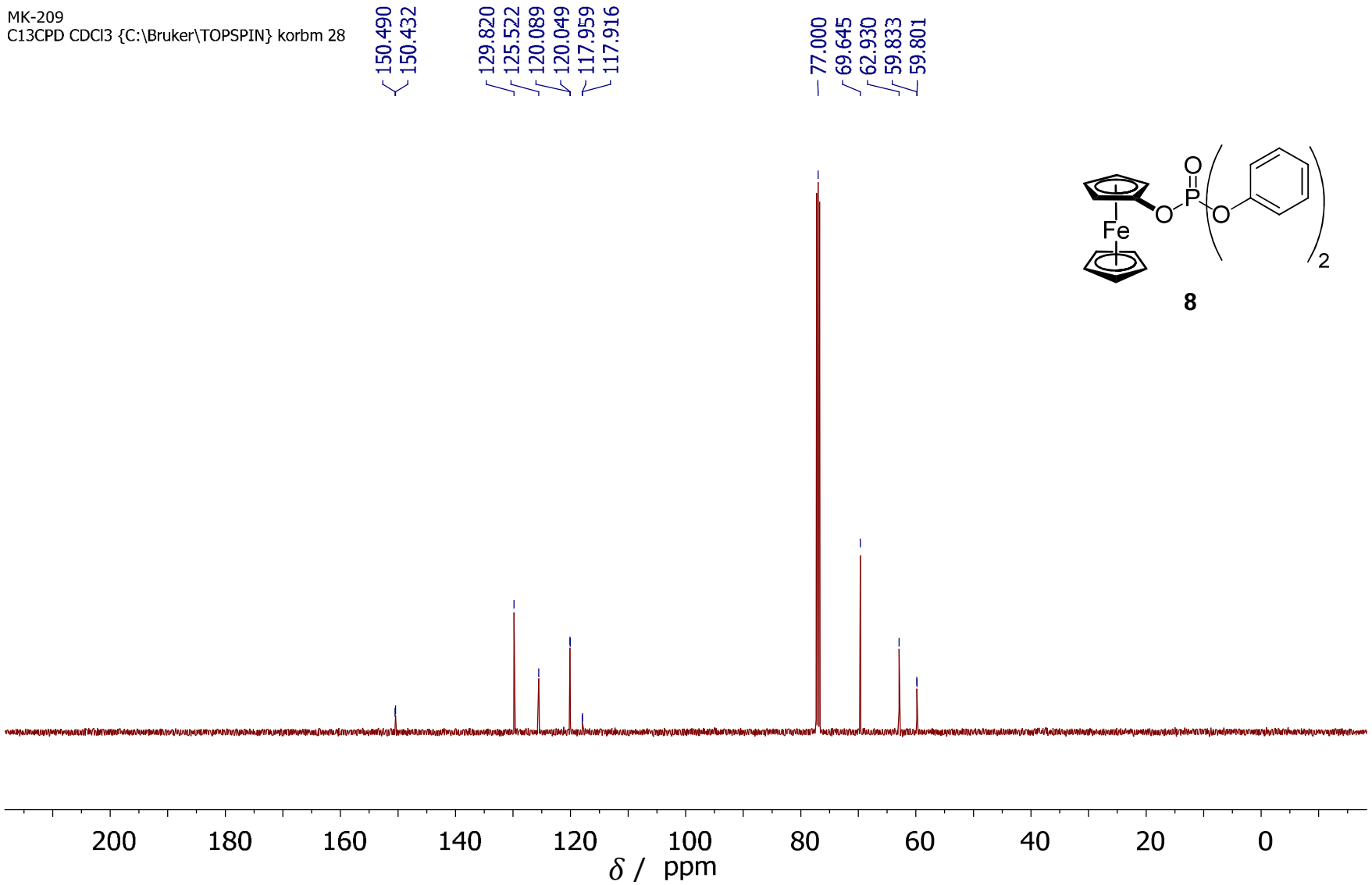
PROTON CDCl3 {C:\Bruker\TOPSPIN\...}



8

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

MK-209
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 28

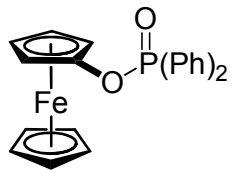


8

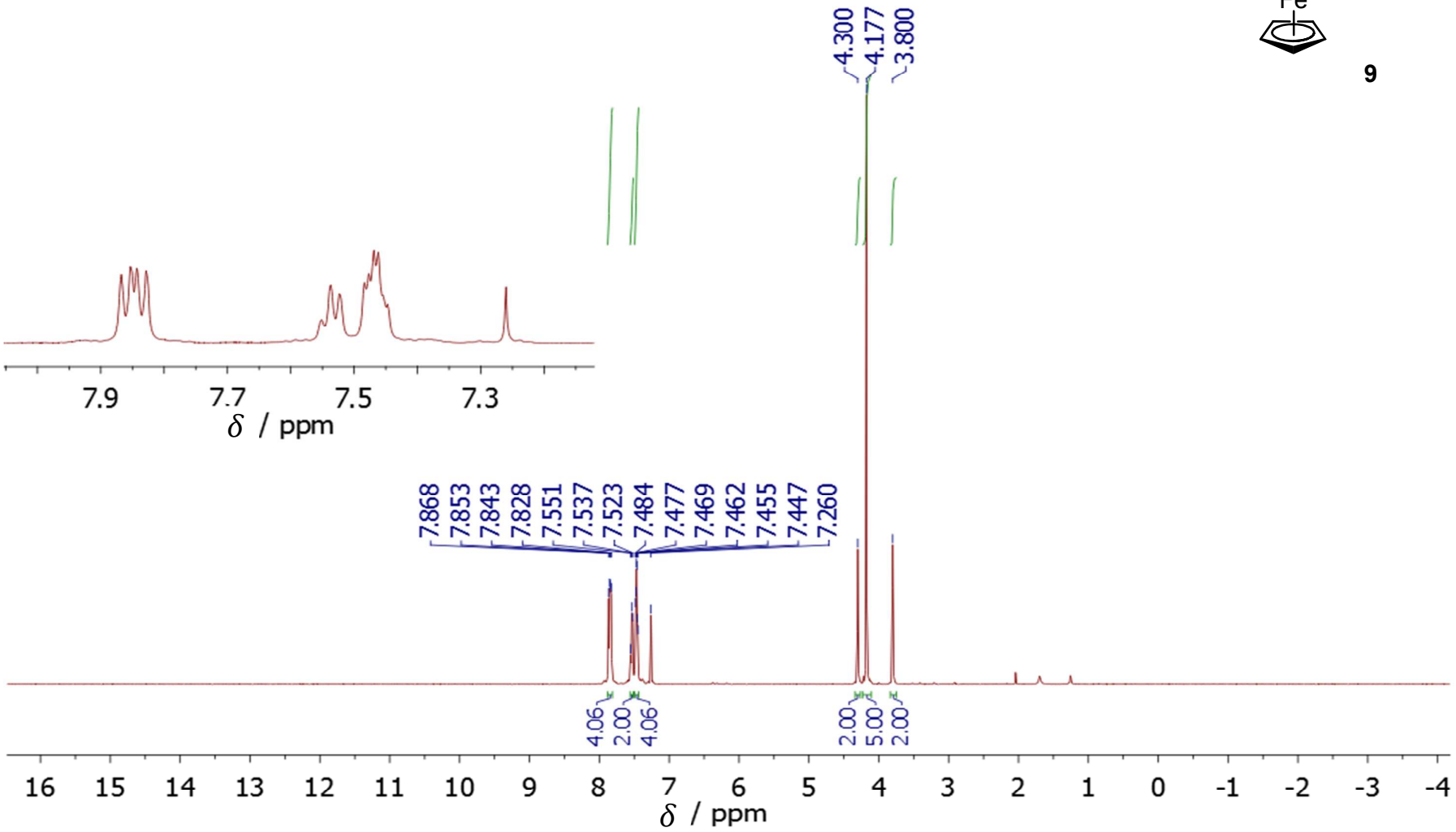
^{1}H NMR, $CDCl_3$, 25 °C

MK-211

PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 15



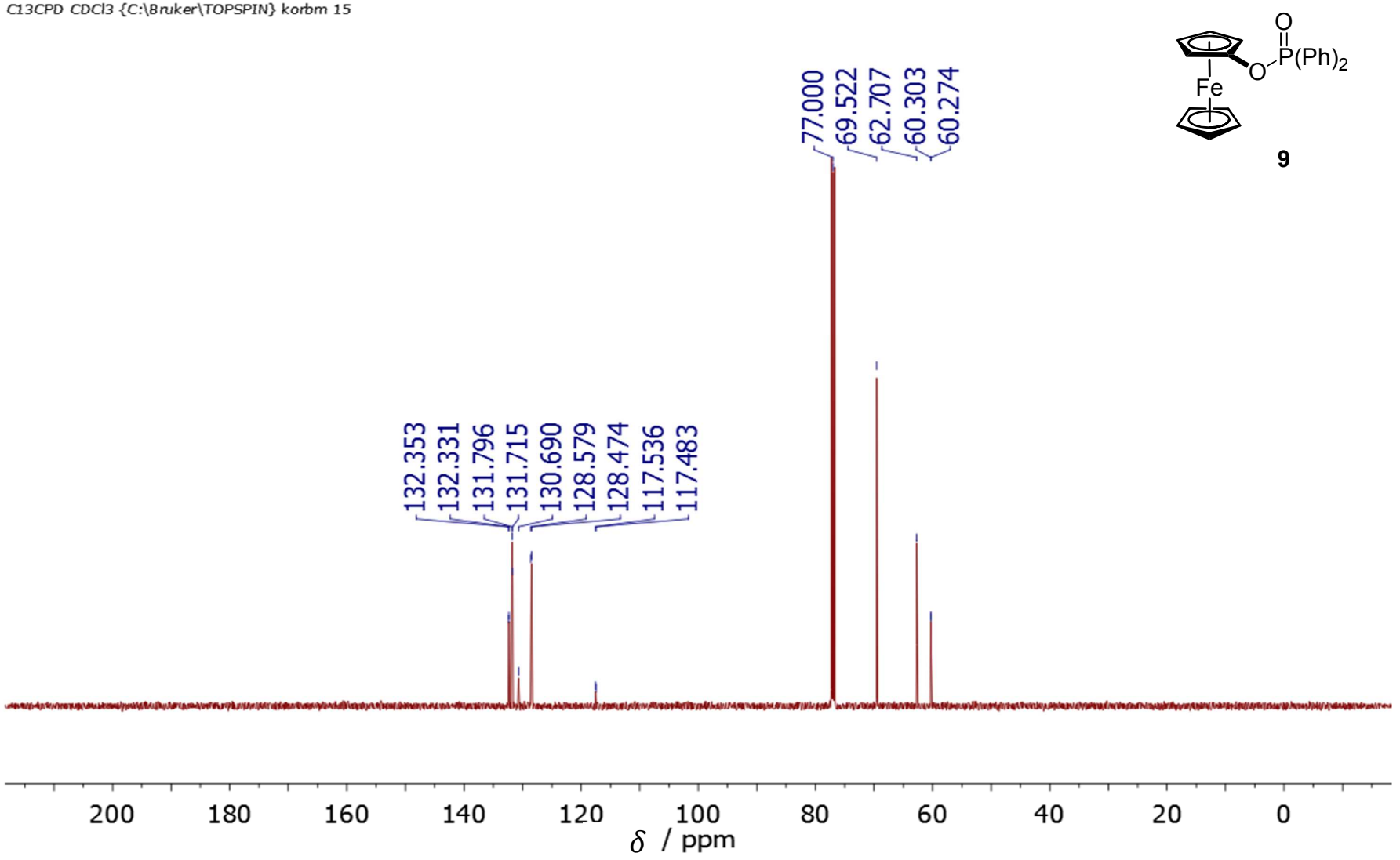
9



$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

MK-211

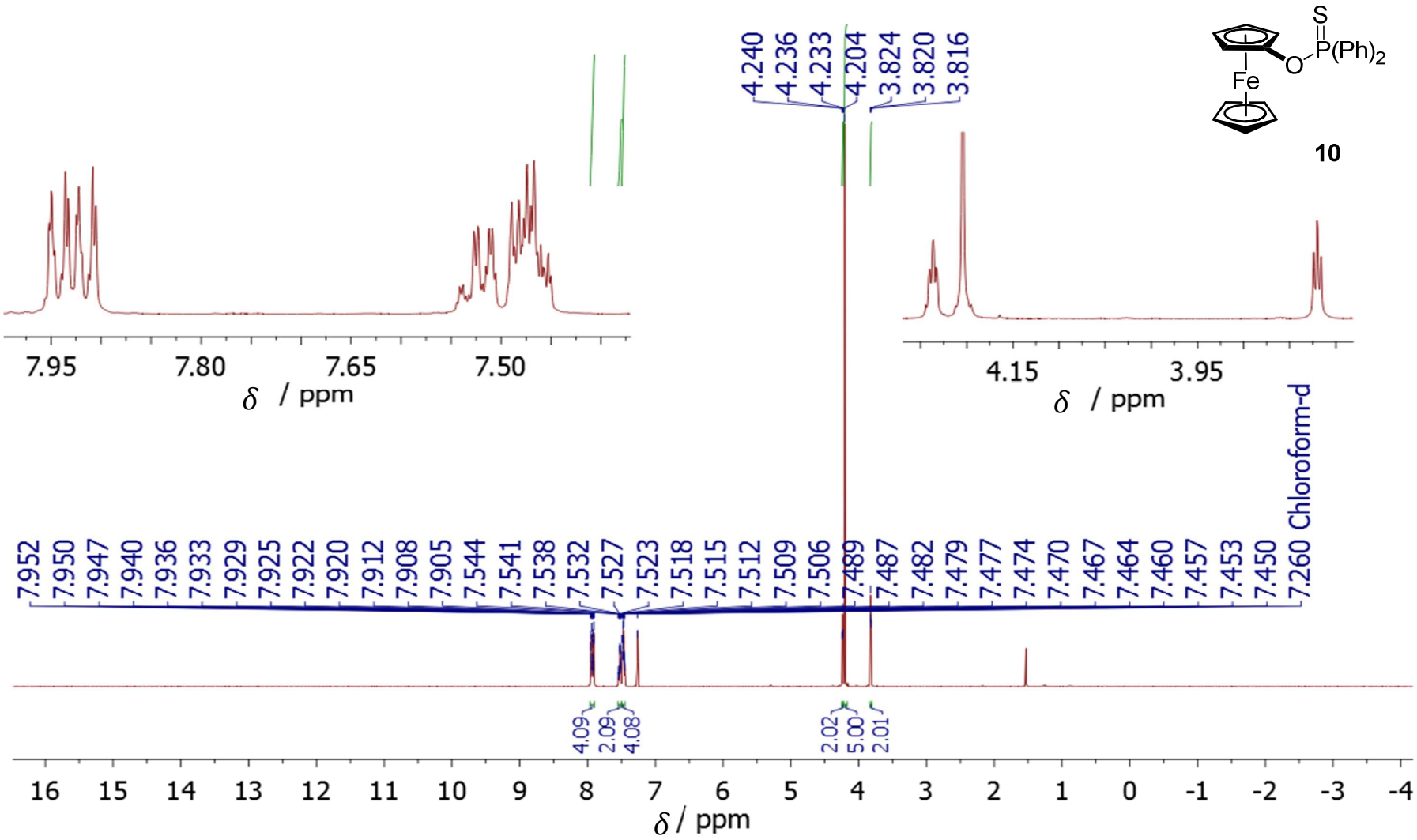
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 15



9

^{1}H NMR, $CDCl_3$, 25 °C

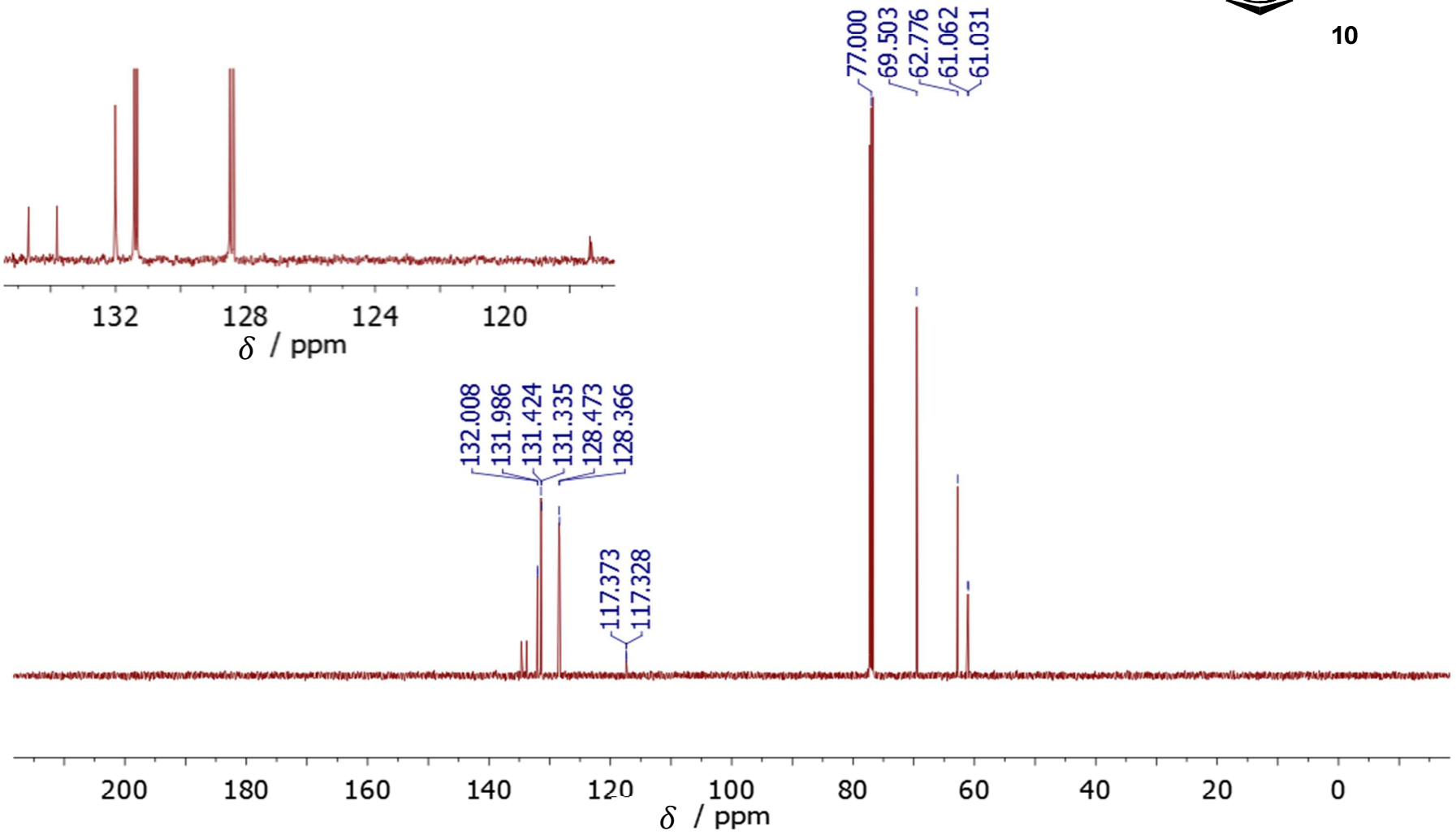
MK-214
PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 58

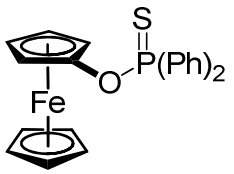


$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

MK-214

C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 58



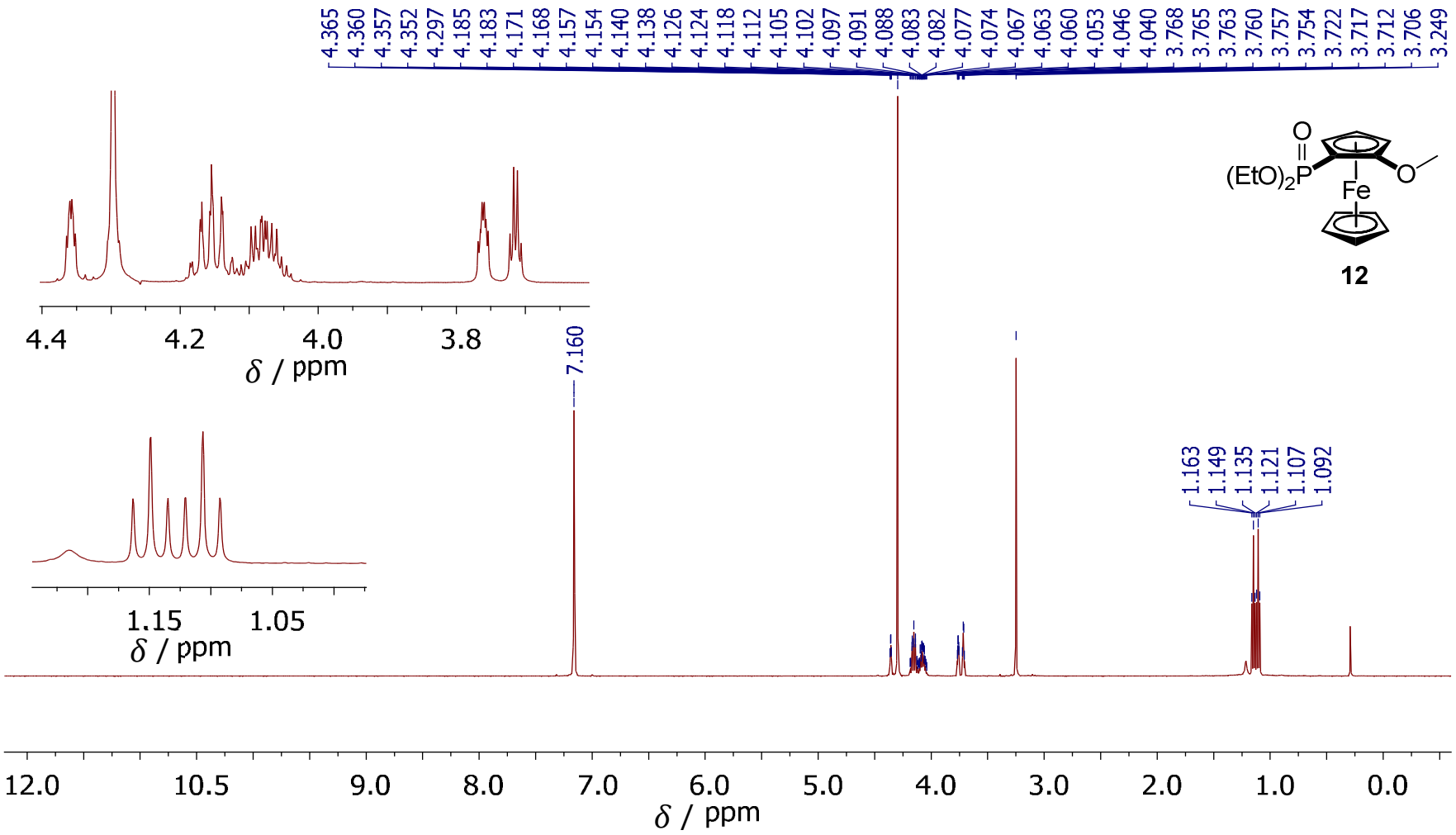


10

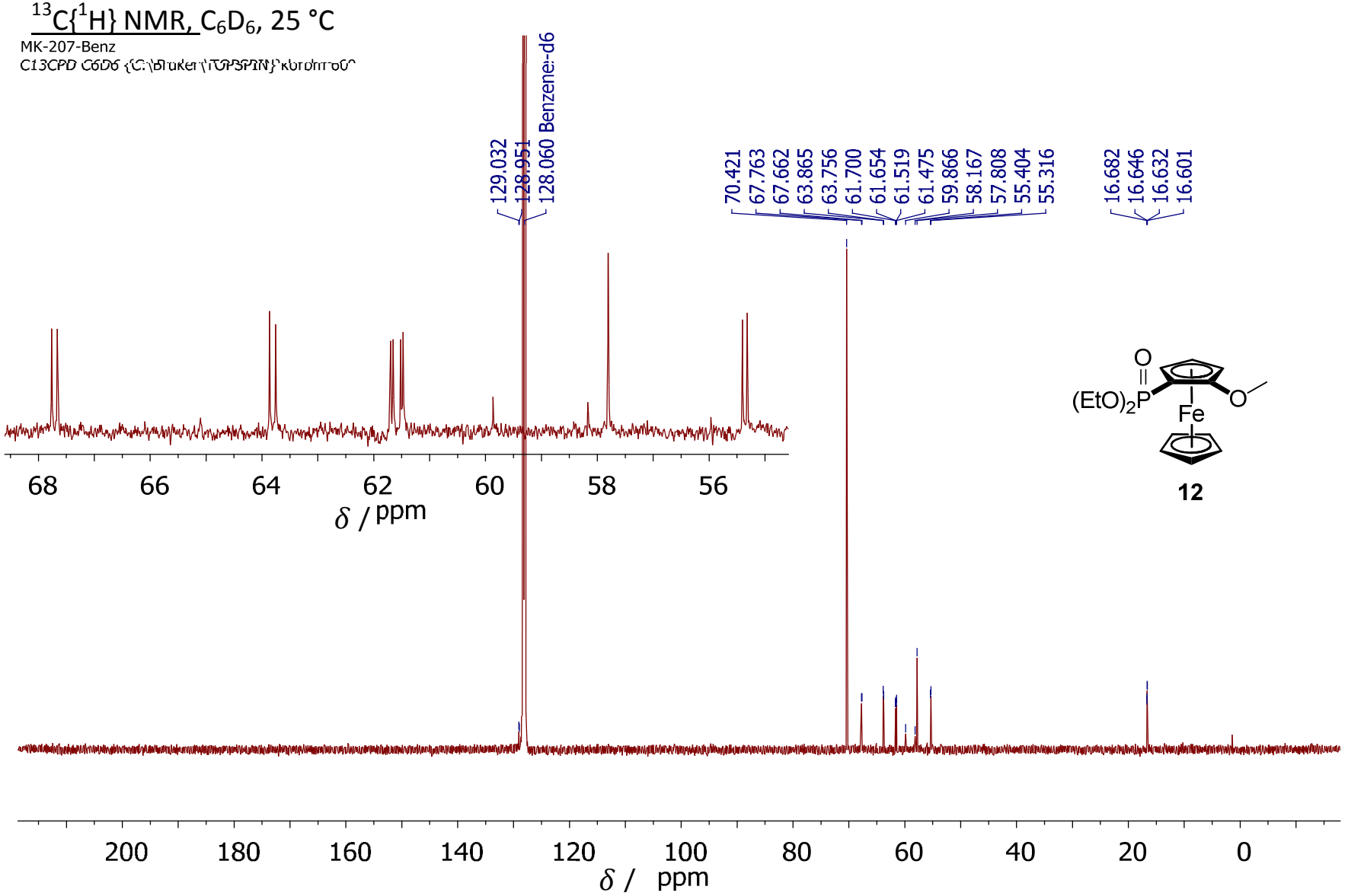
^{1}H NMR, C_6D_6, 25 °C

MK-207-Benz

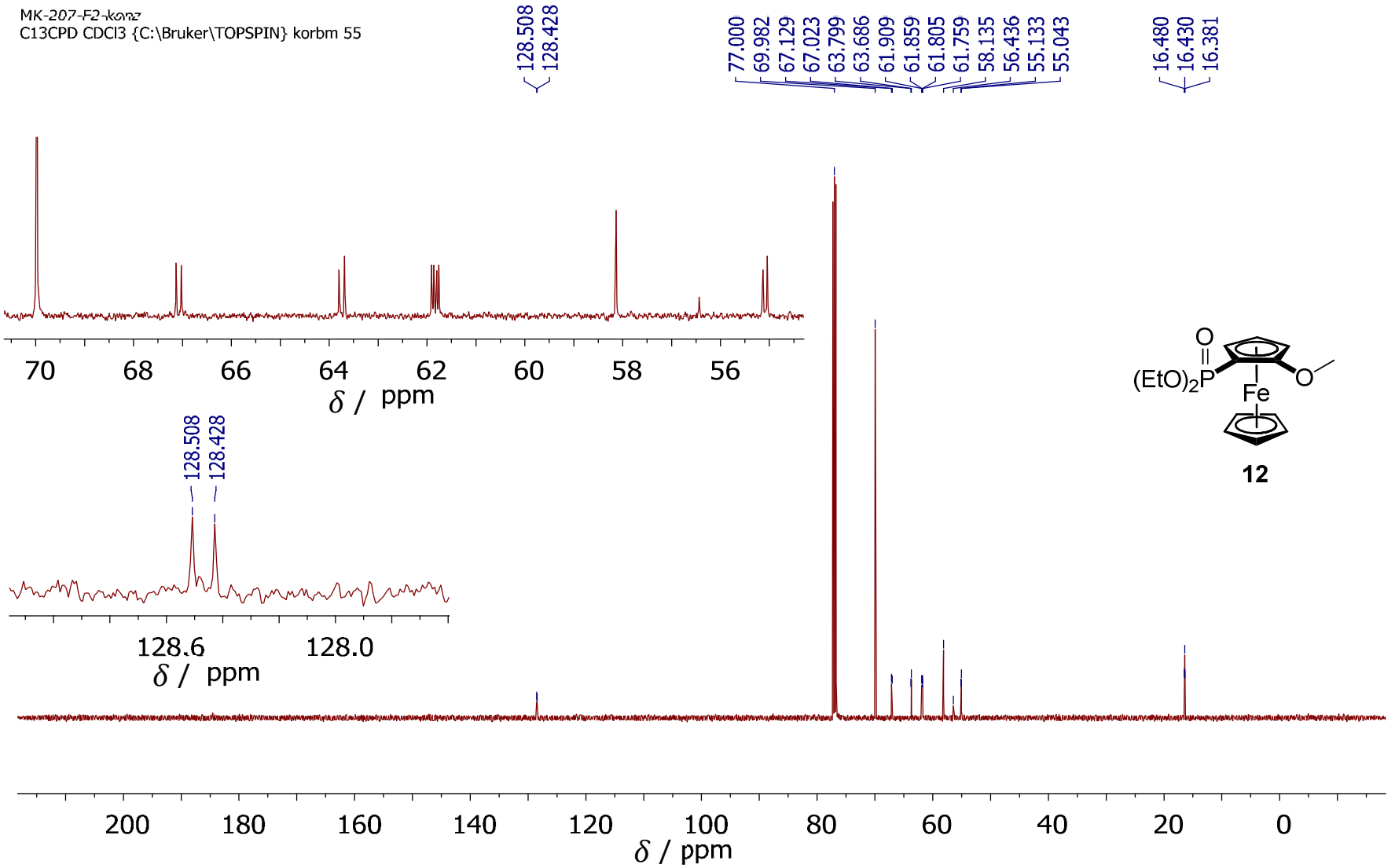
PROTON C6D6 {C:\Bruker\TOPSPIN\...}



12

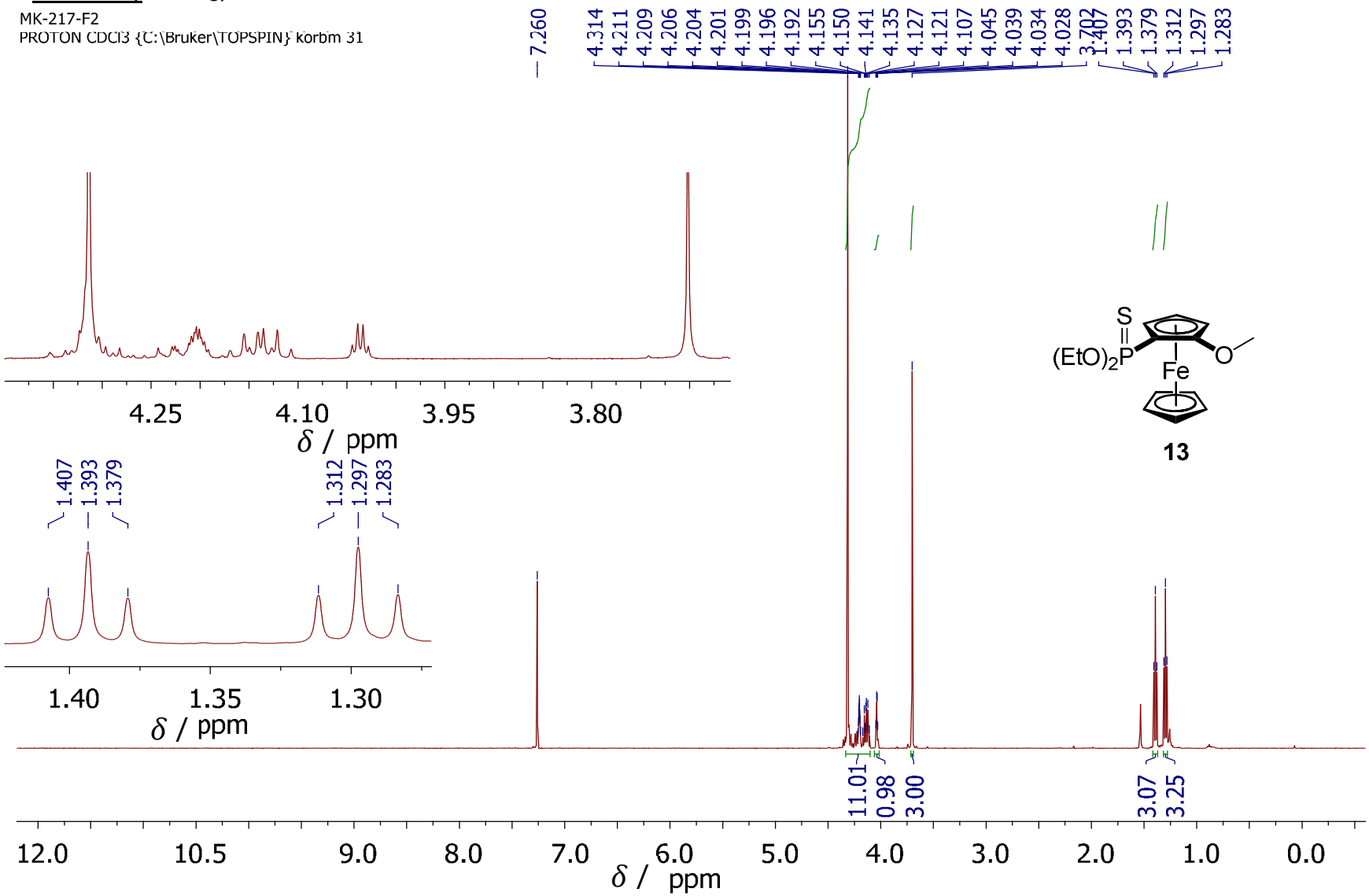

13C{1H} NMR, C6D6, 25 °C
MK-207-Benz
129.032
128.951
128.060 Benzene-d6
70.421
67.763
67.662
63.865
63.756
61.700
61.654
61.519
61.475
59.866
58.167
57.808
55.404
55.316
16.682
16.646
16.632
16.601
68
66
64
62
60
58
56
δ / ppm
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
O
(EtO)2P
Fe
O
12

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

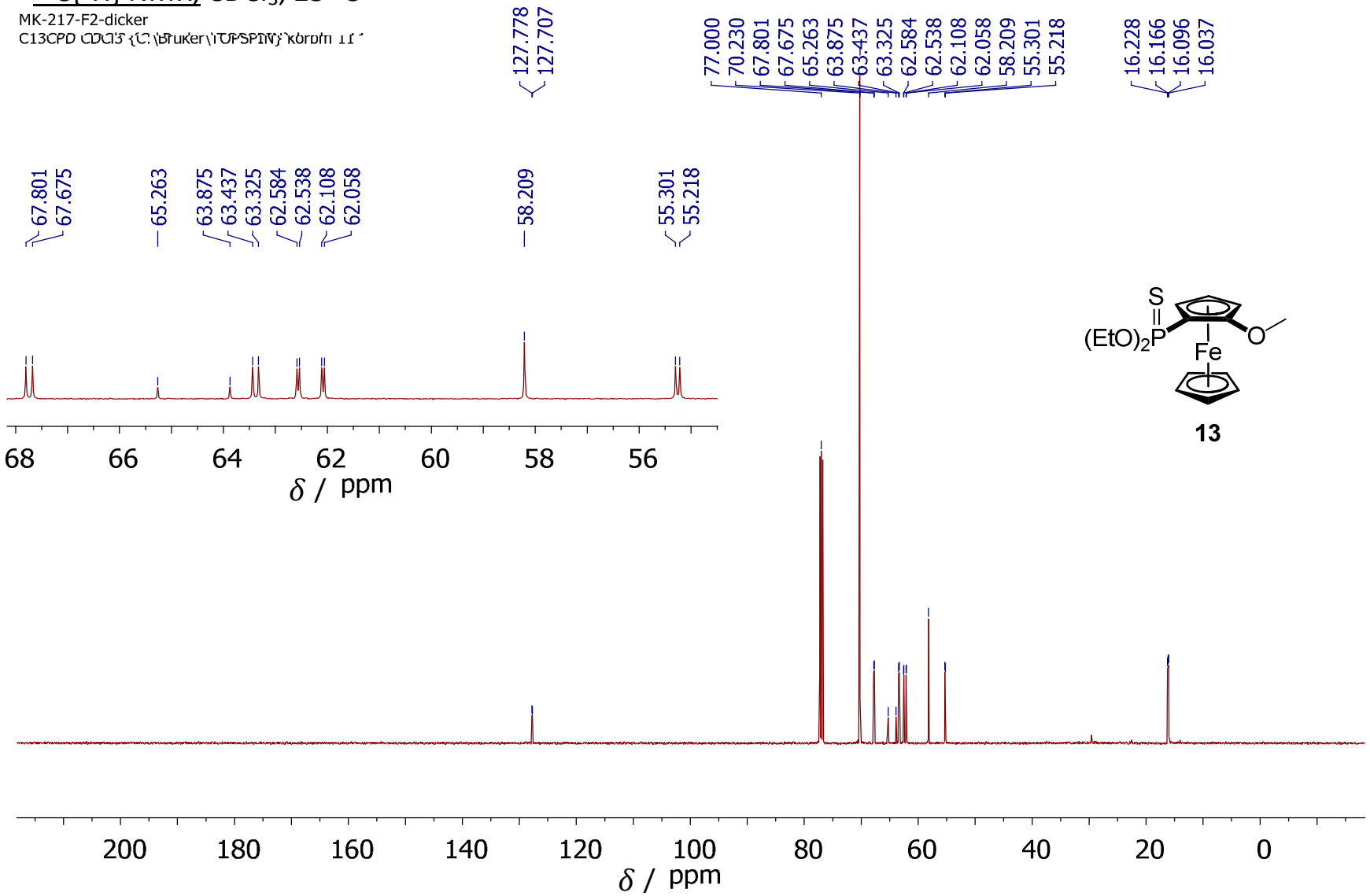


12

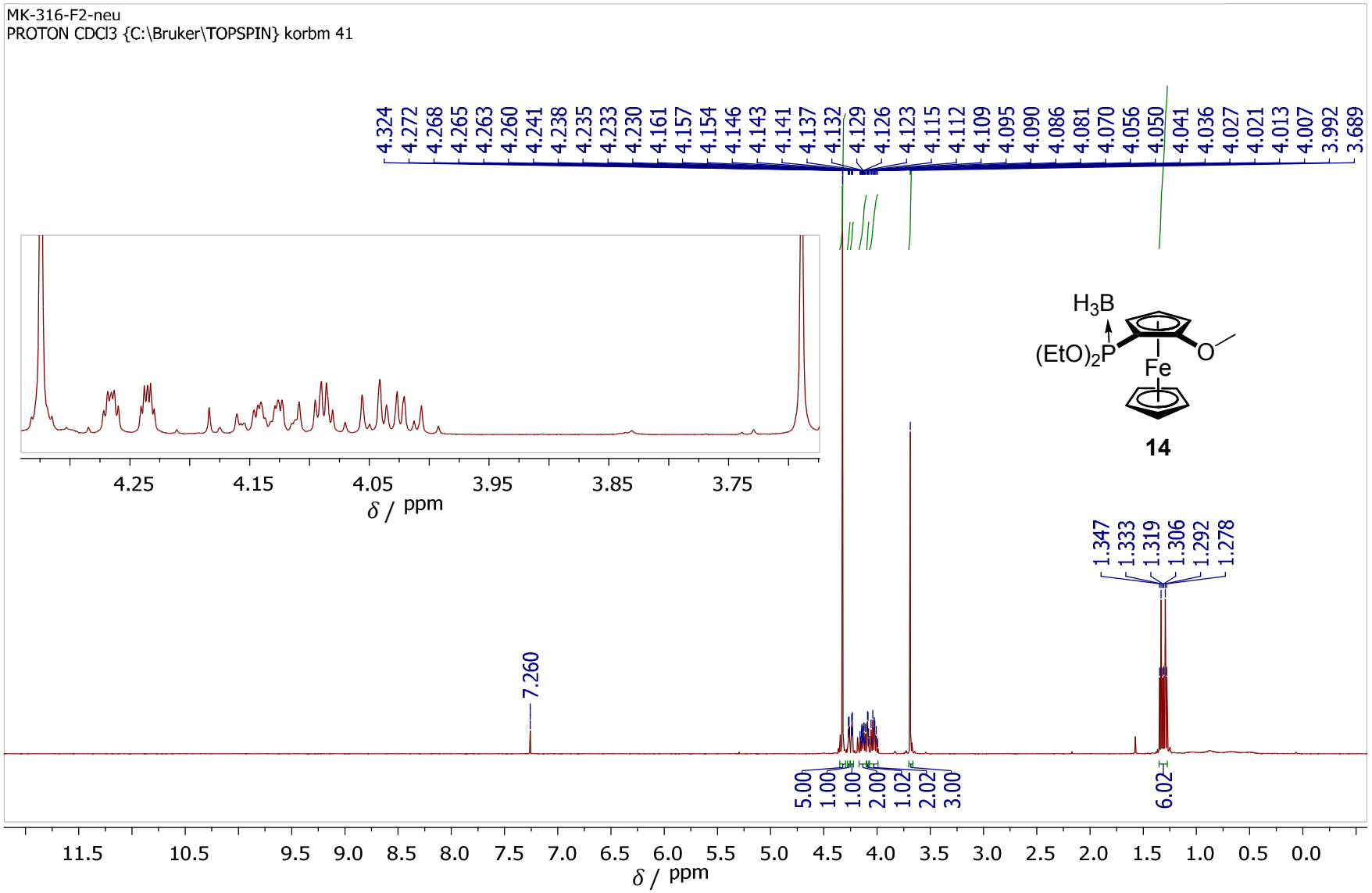
^{1}H NMR, $CDCl_3$, 25 °C



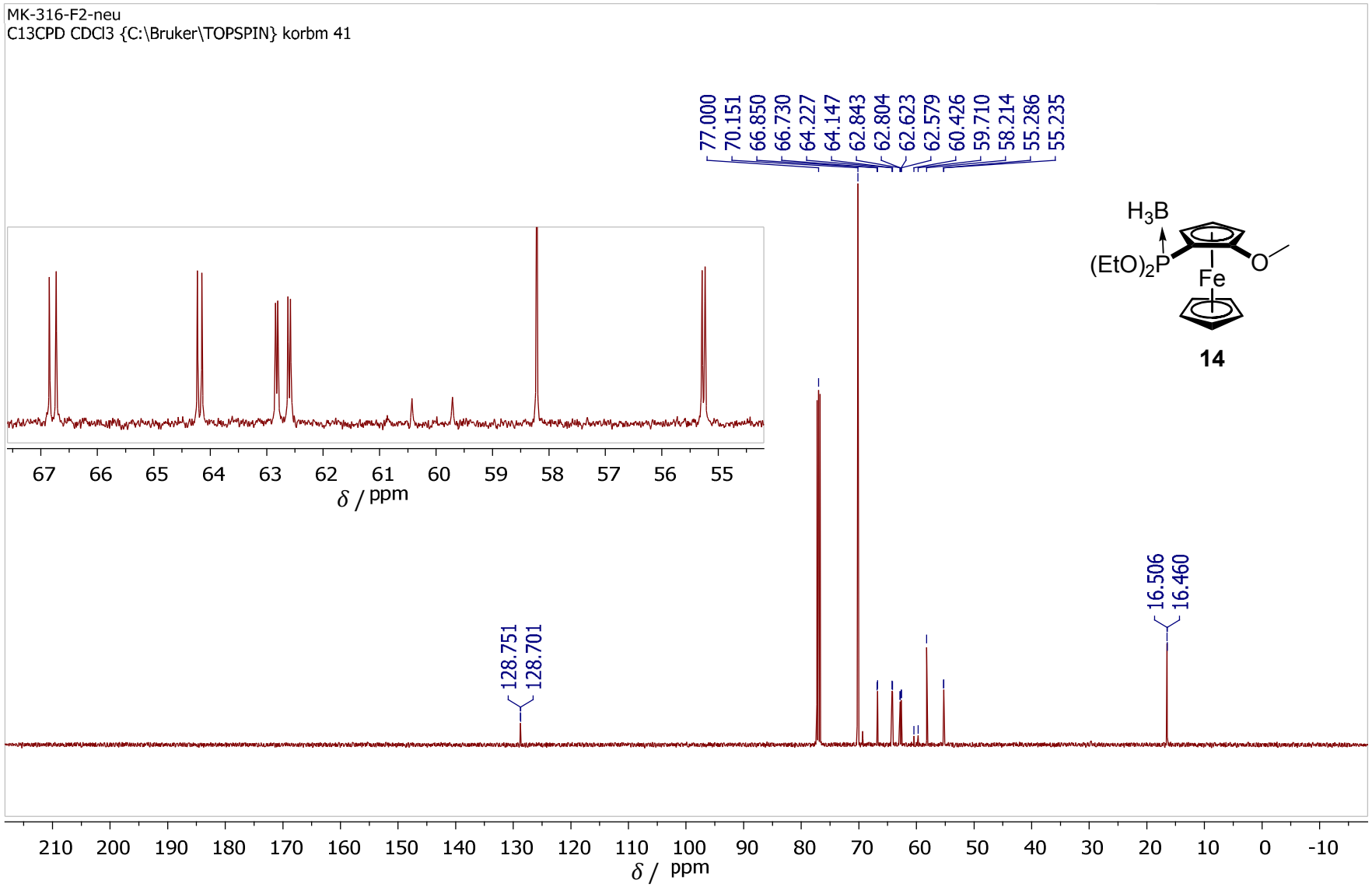
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C



^{1}H NMR, $CDCl_3$, 25 °C

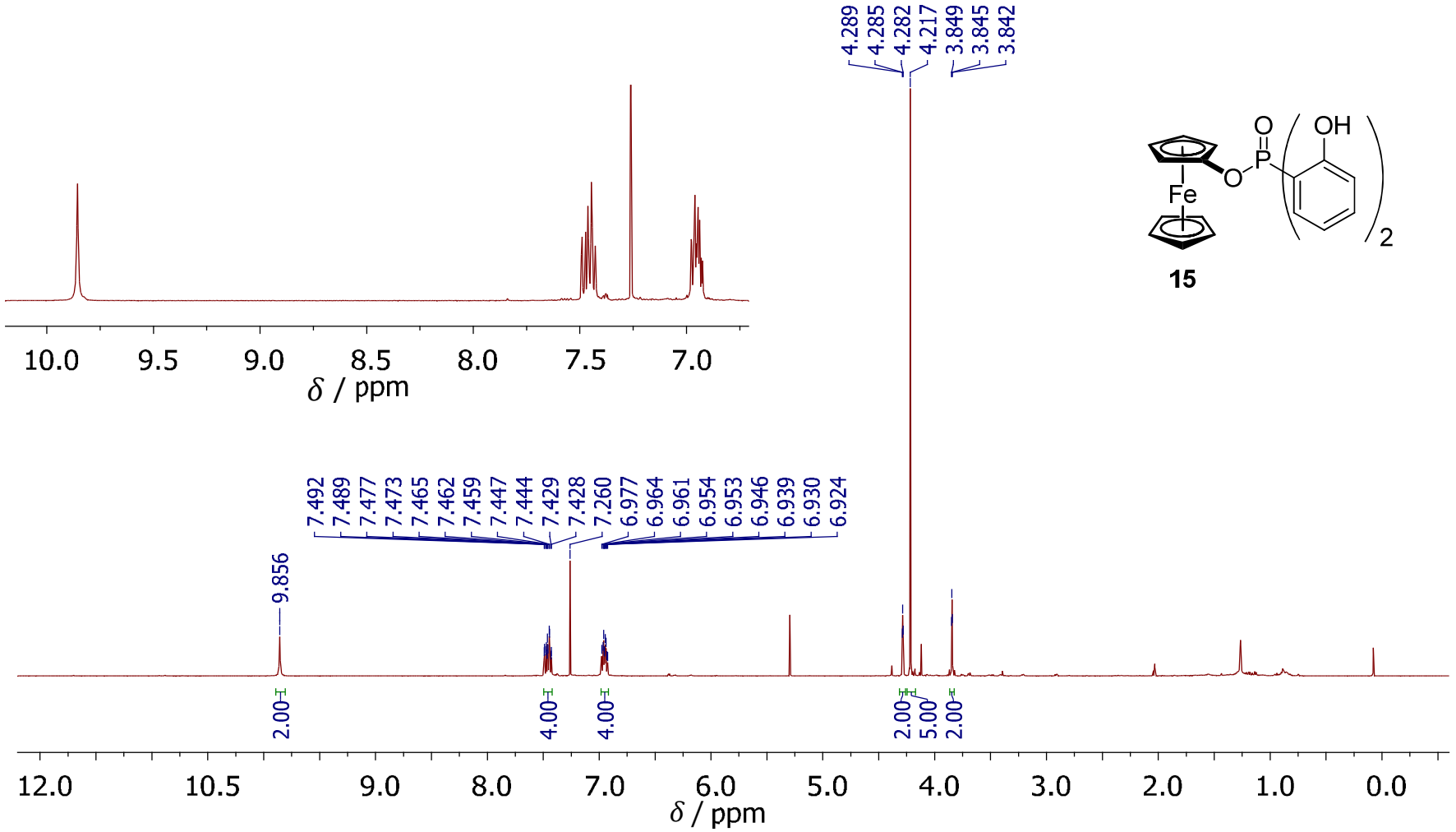


$^{13}C\{1H\}$ NMR, $CDCl_3$, 25 °C



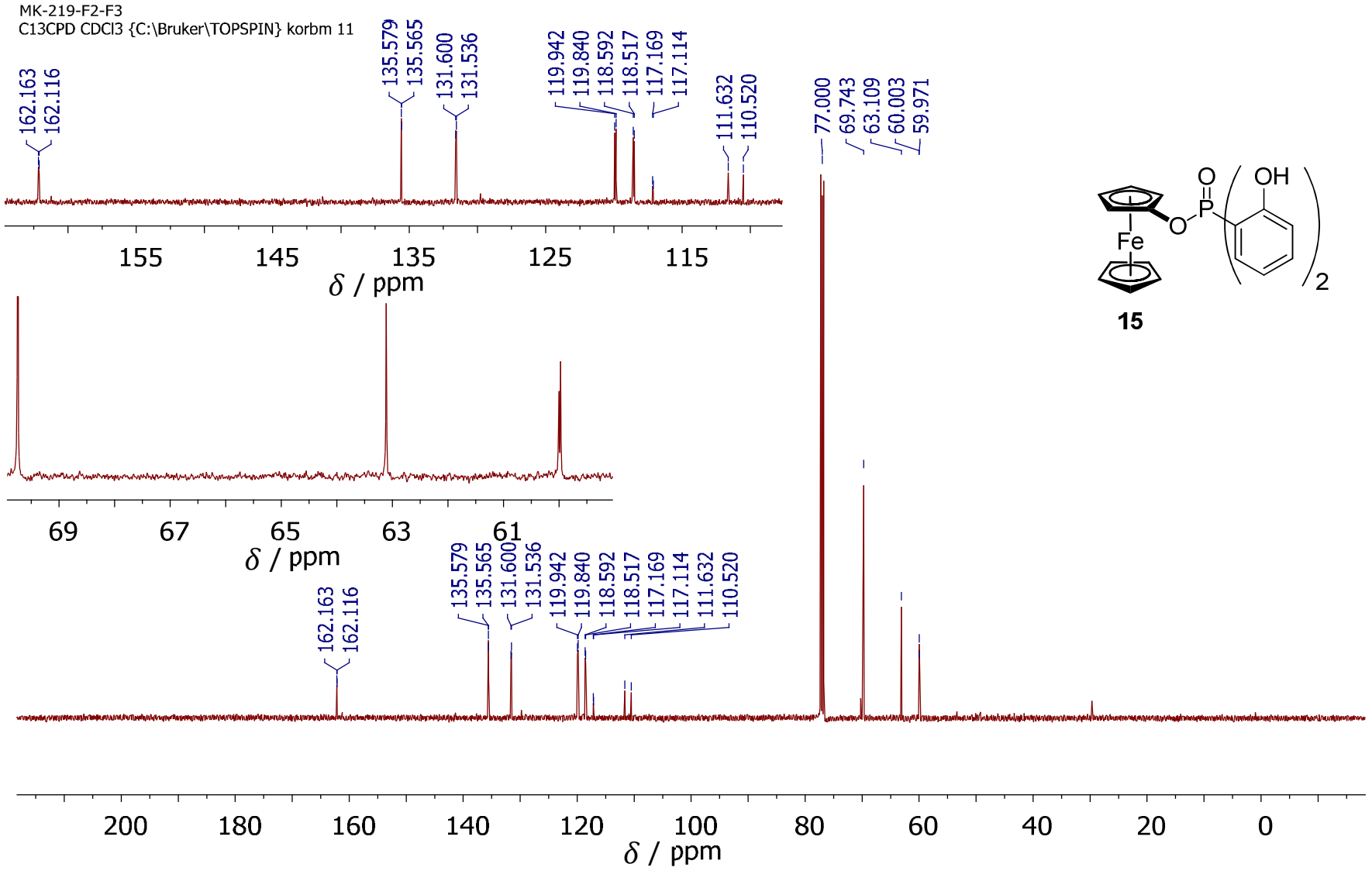
^{1}H NMR, $CDCl_3$, 25 °C

MK-219-F2-F3
PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 11



15

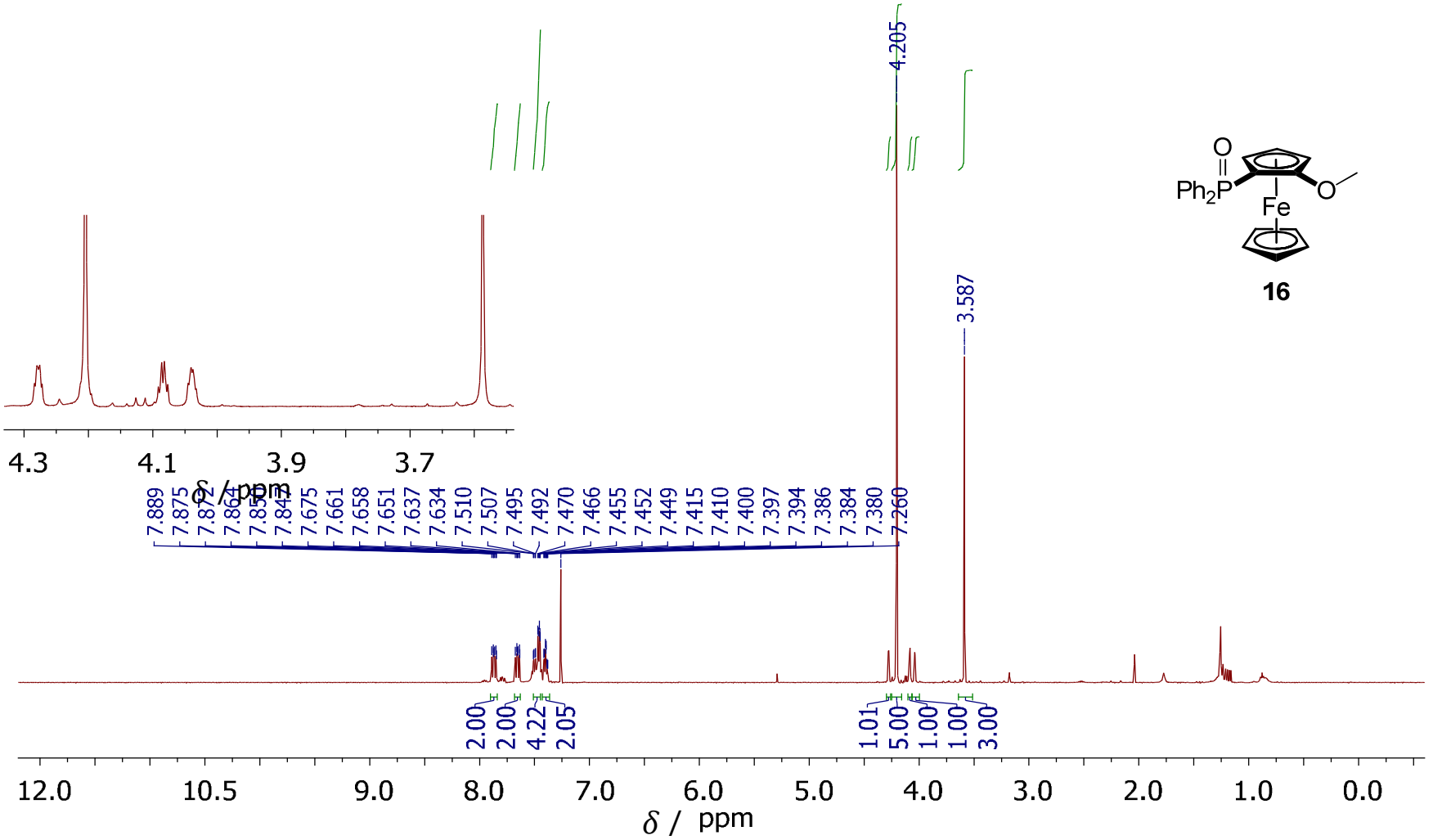
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C



15

^{1}H NMR, $CDCl_3$, 25 °C

MK-220-neu-F3
PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 26

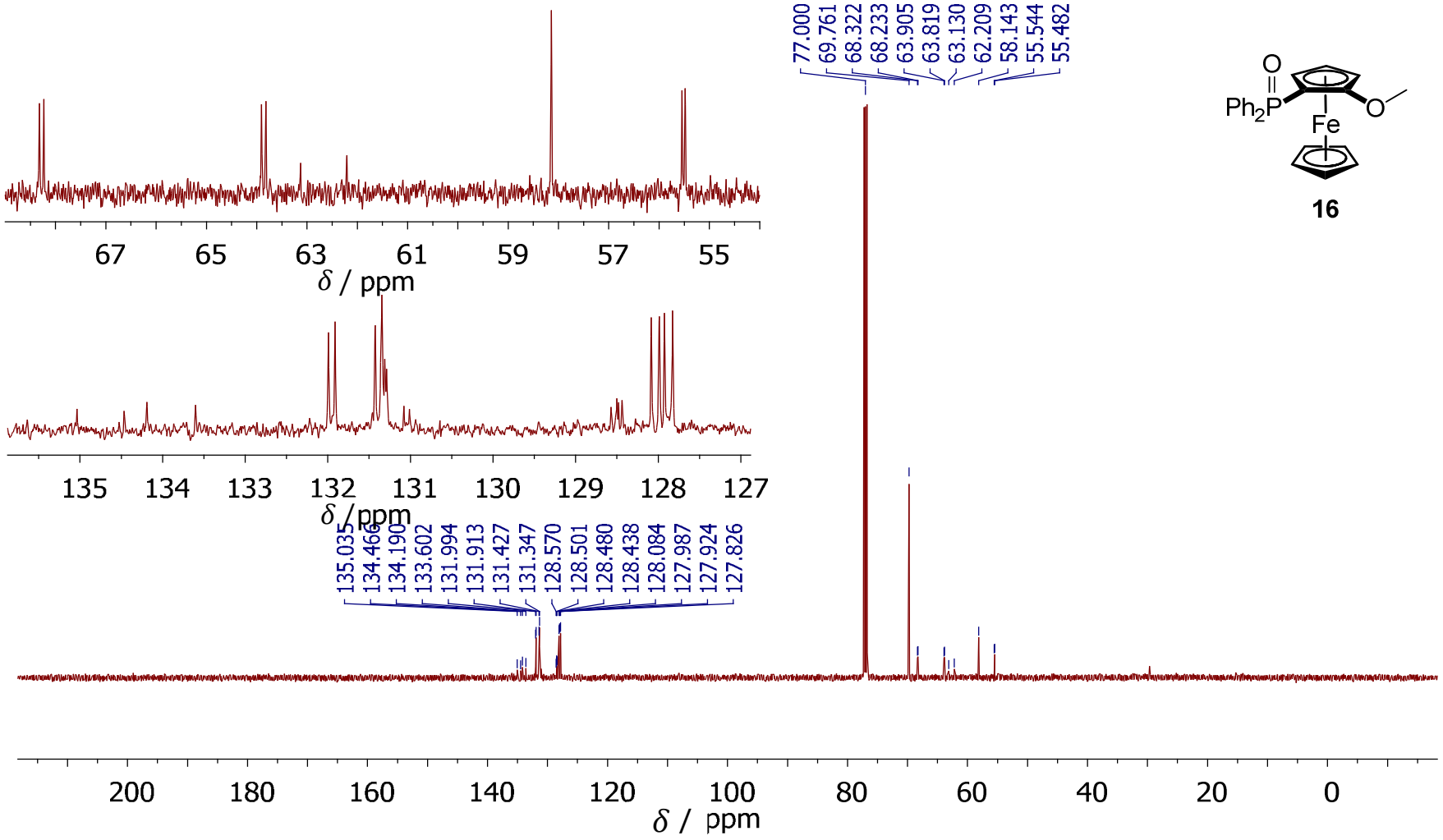


16

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

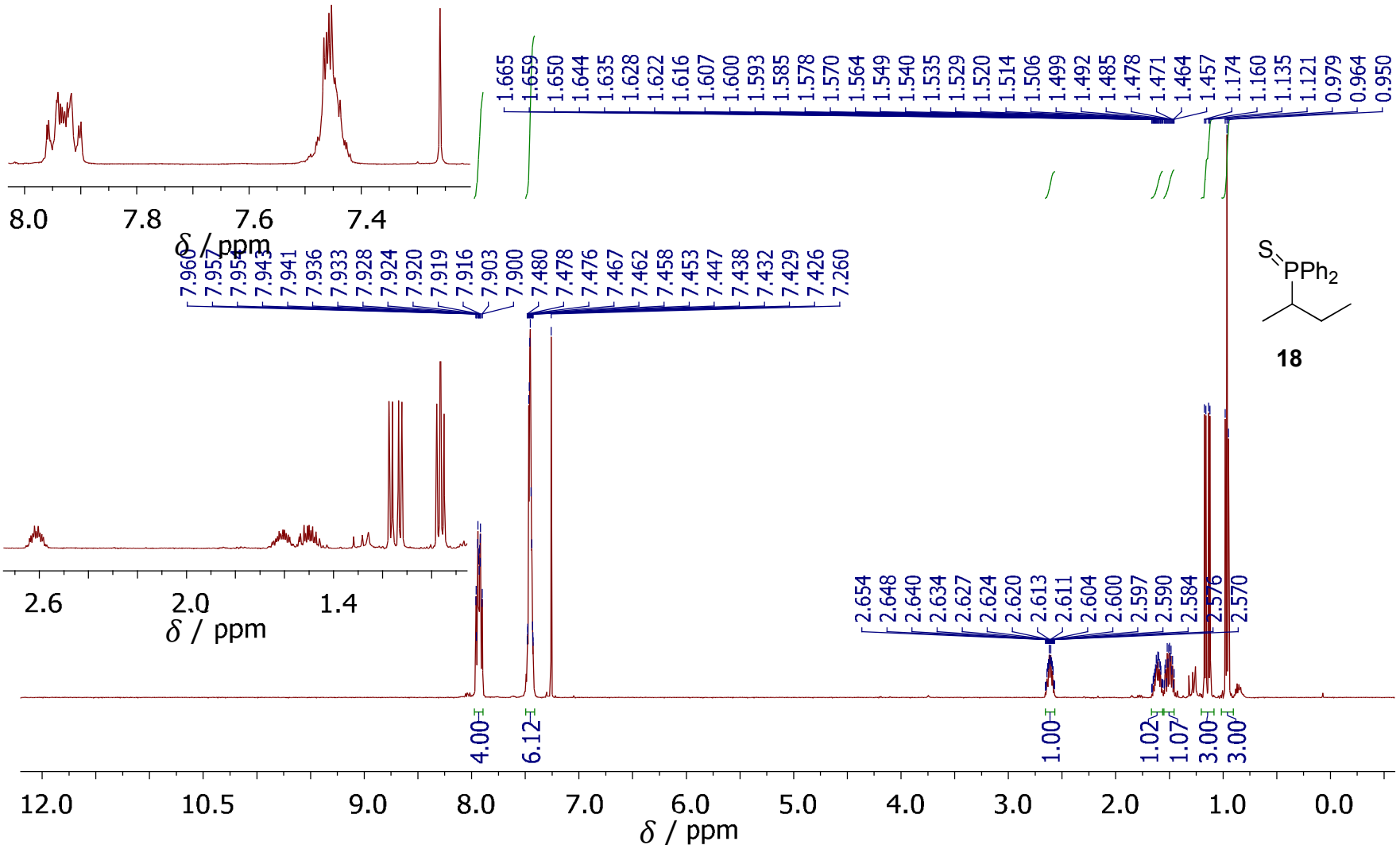
MK-220-neu-F3

C13CPD CDCl3 {C:\Bruker\TOPSPIN}`korbm 26



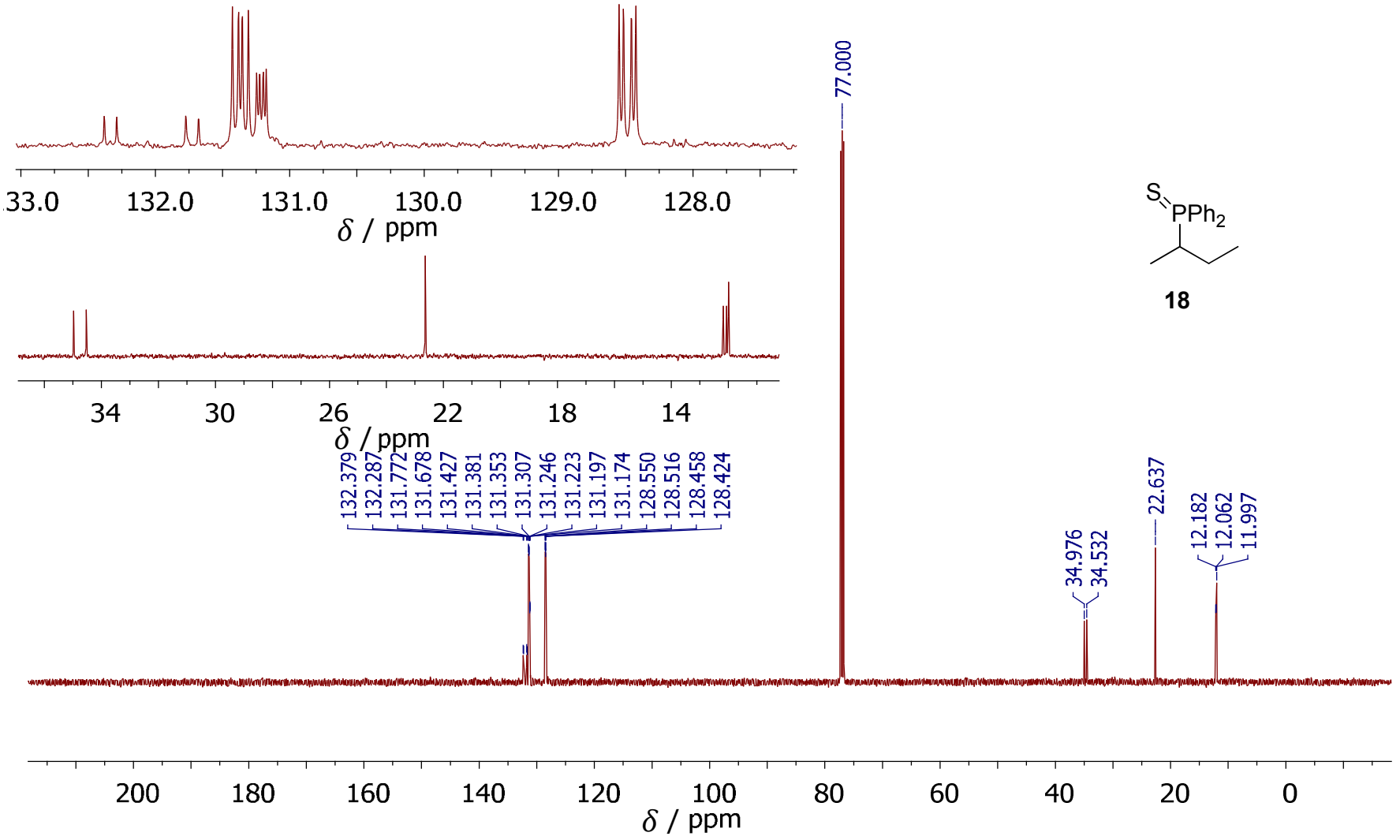
16

^{1}H NMR, $CDCl_3$, 25 °C



$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

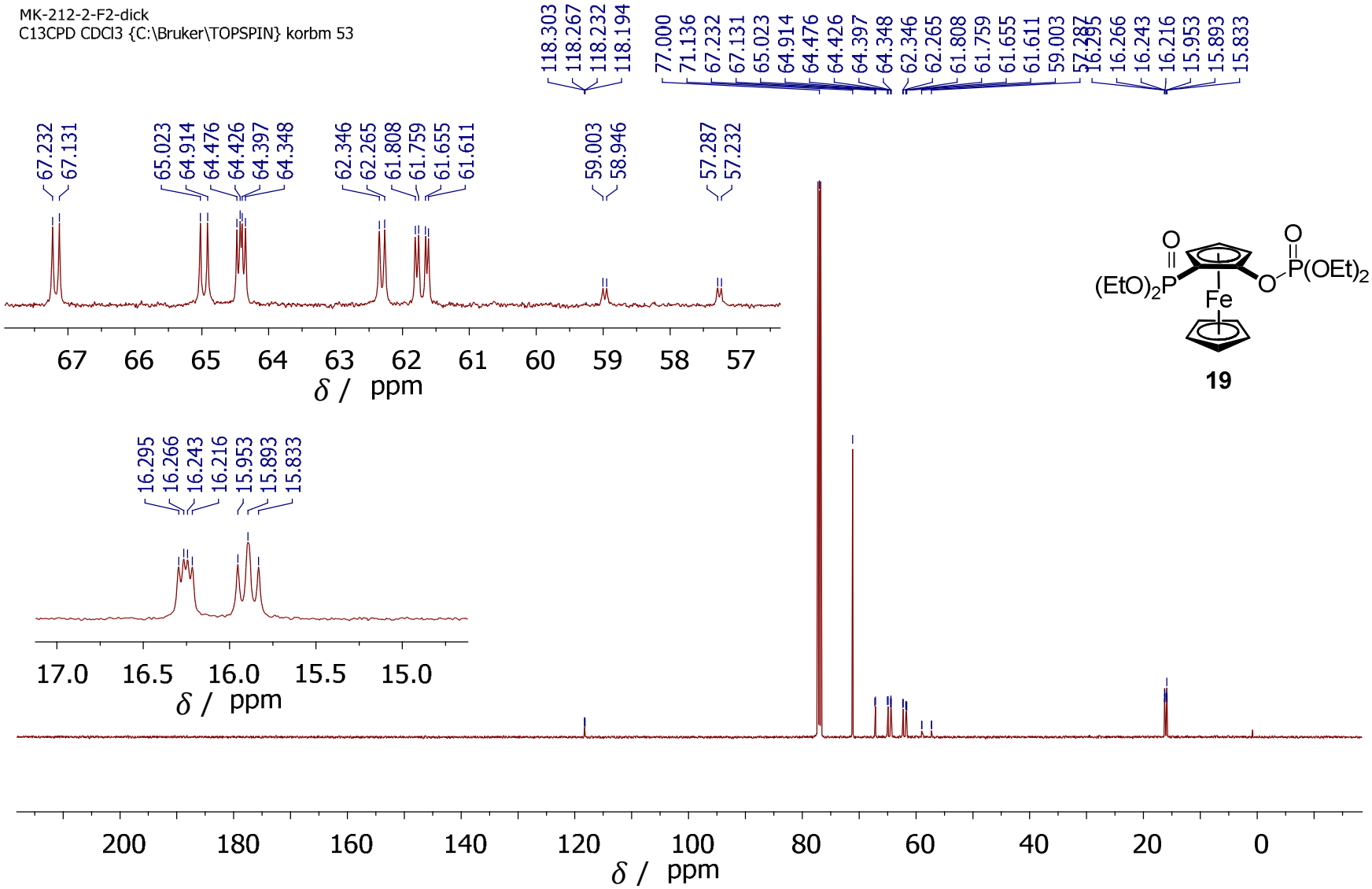
MK-226-F2-umkrist
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 33



18

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

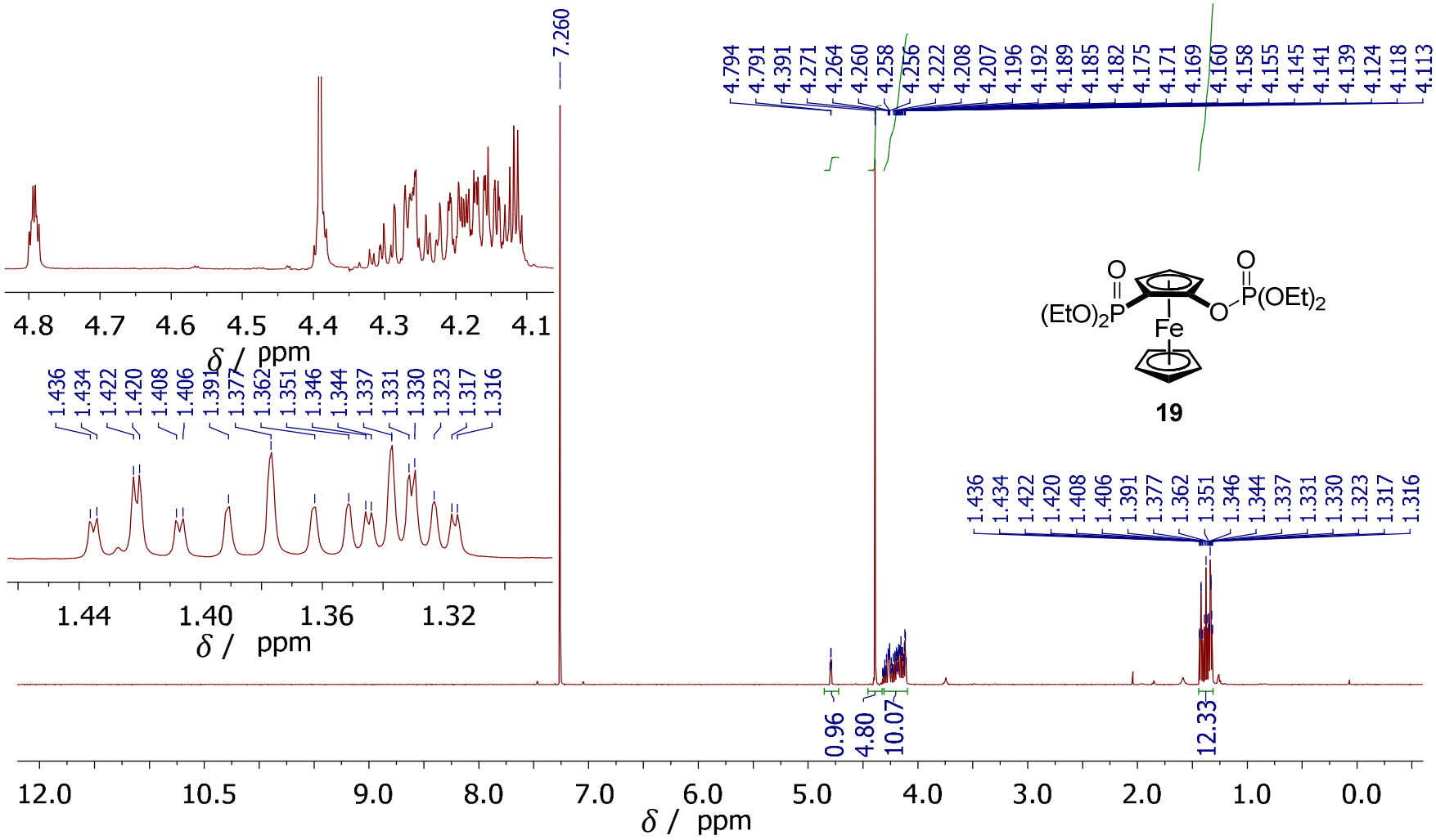
MK-212-2-F2-dick
C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 53



19

^{1}H NMR, $CDCl_3$, 25 °C

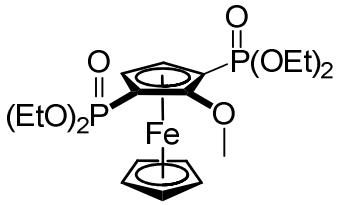
MK-212-2-F2
PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 38



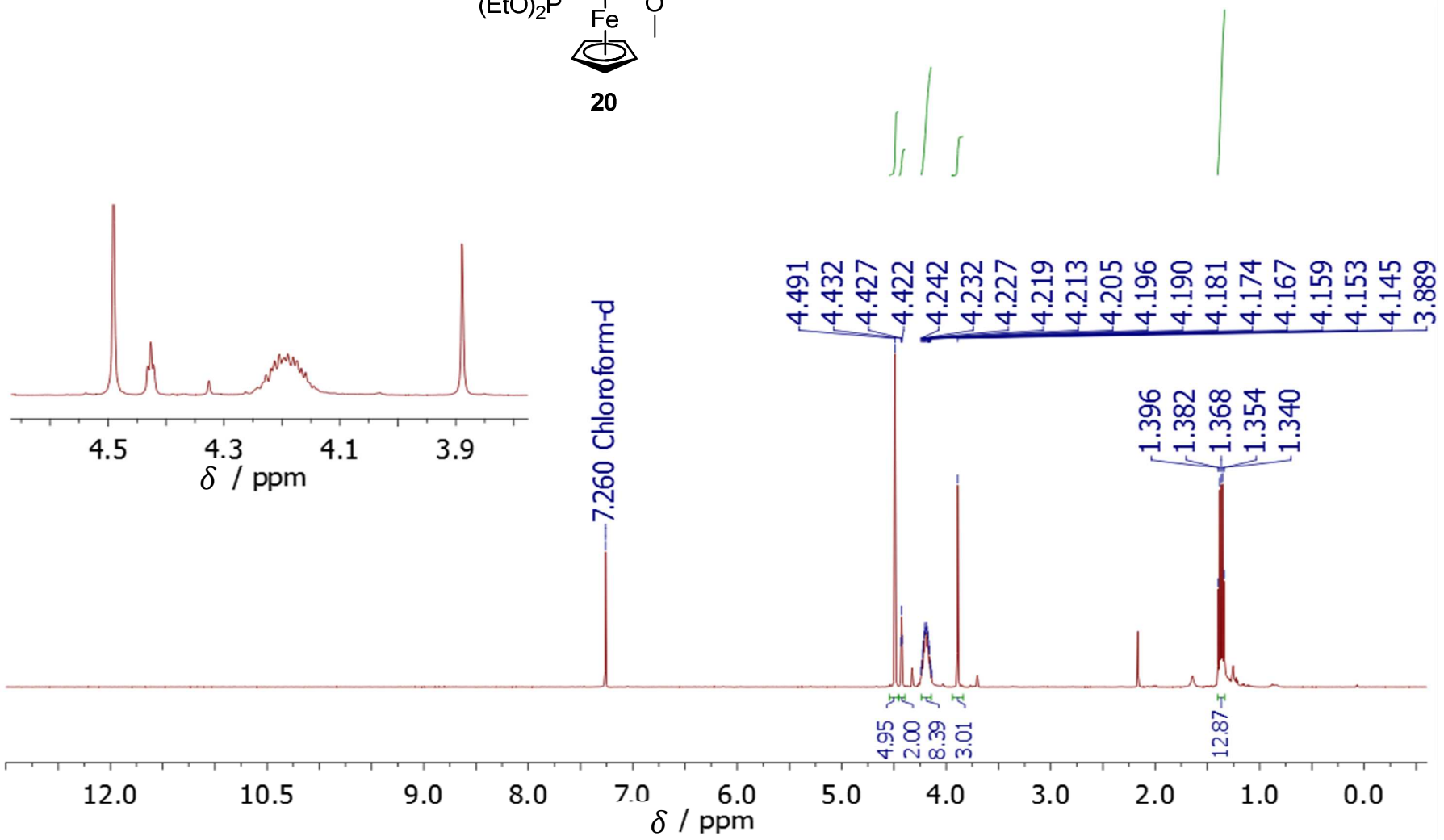
^{1}H NMR, $CDCl_3$, 25 °C

MK-218

PROTON CDCl3 {C:\Bruker\TOPSPIN} korbm 45



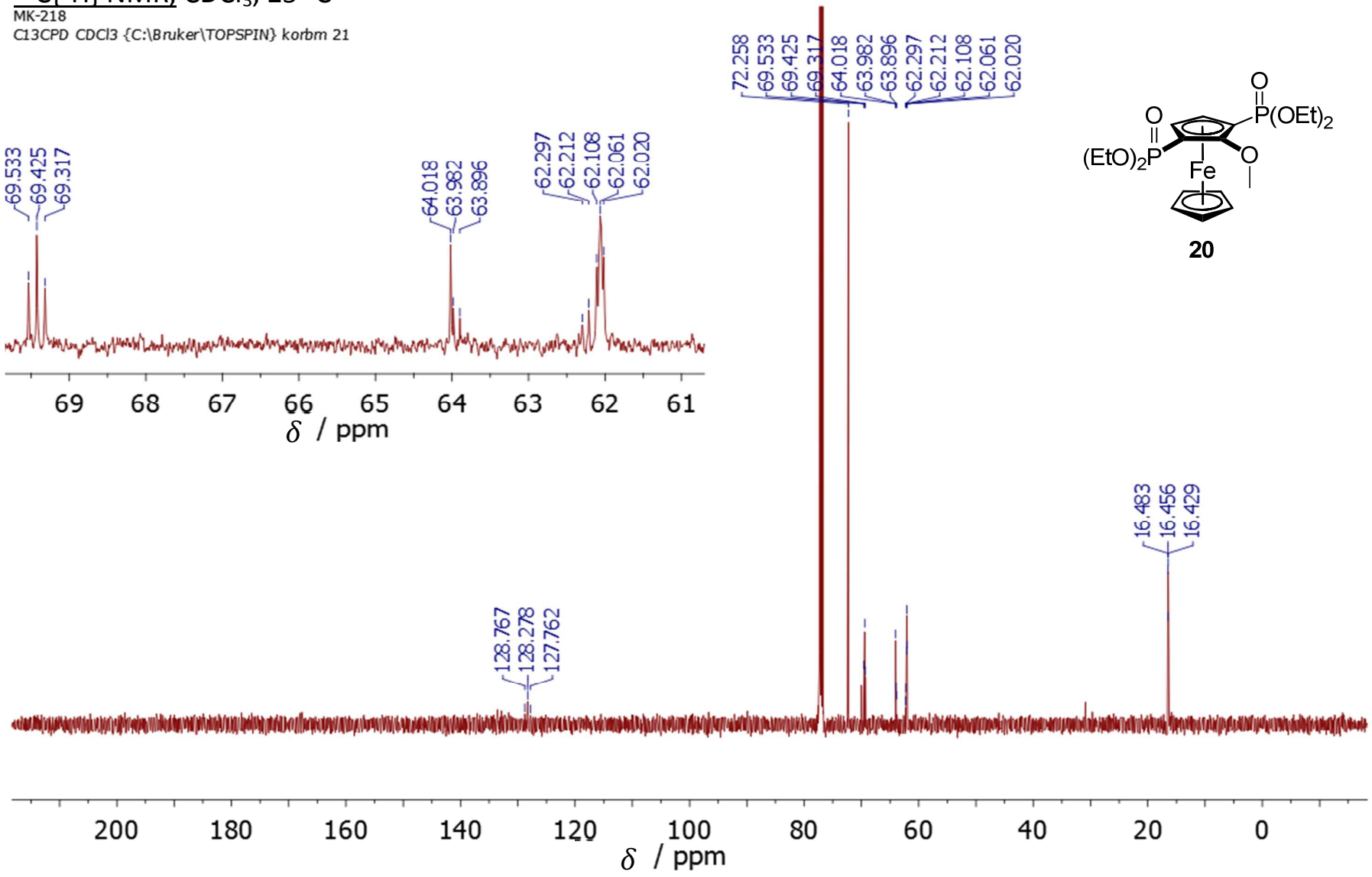
20



$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

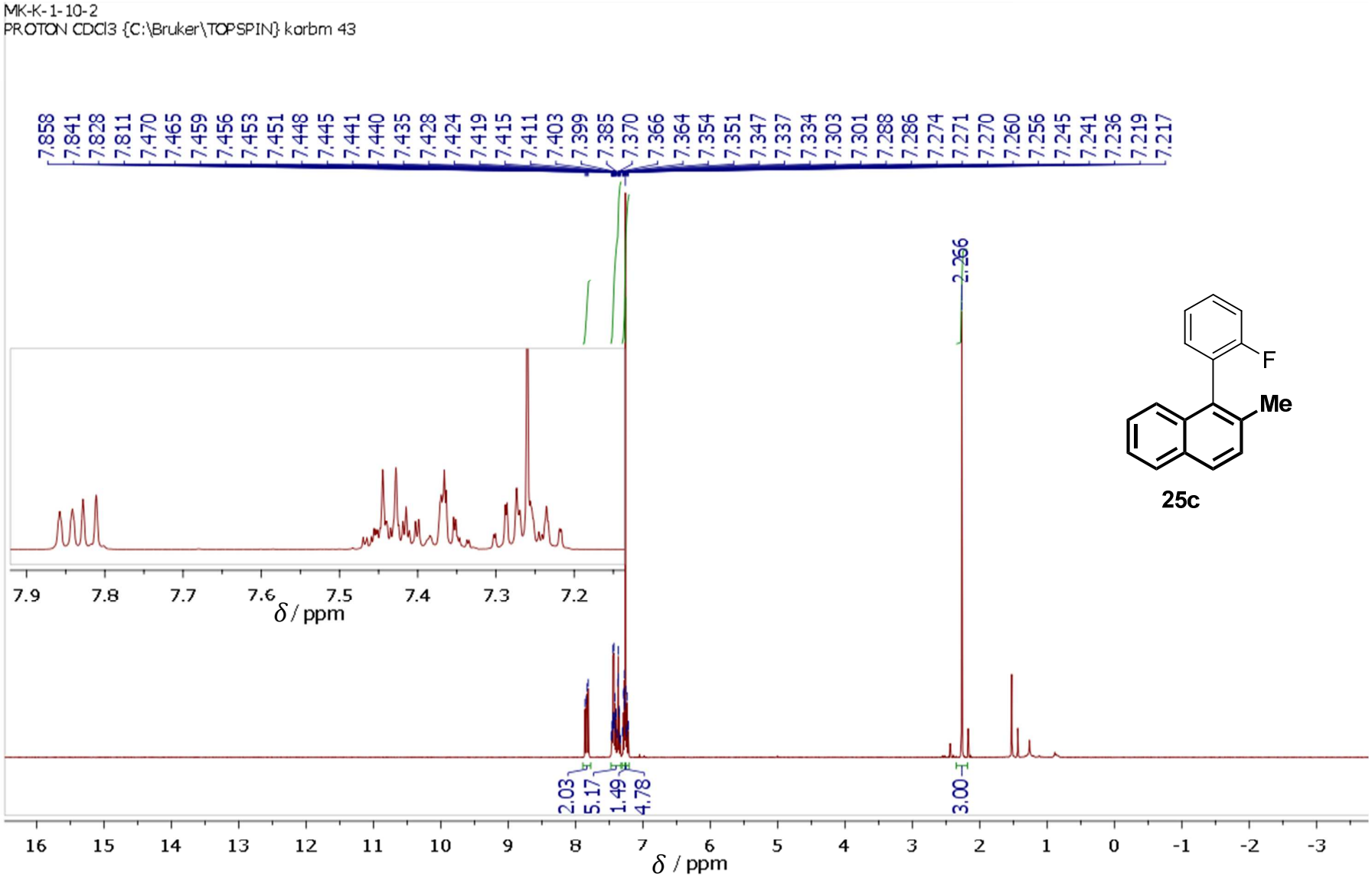
MK-218

C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 21

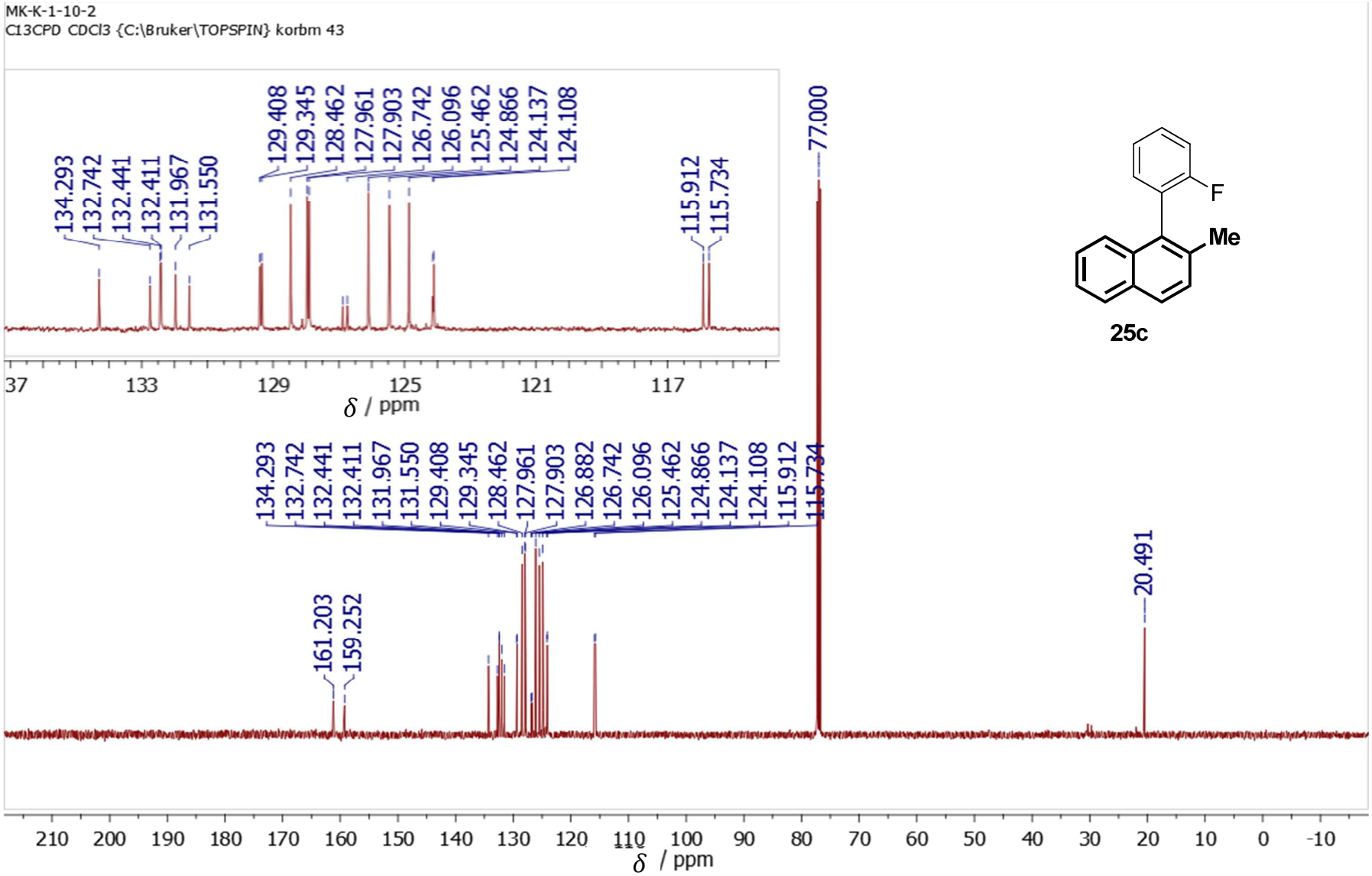


20

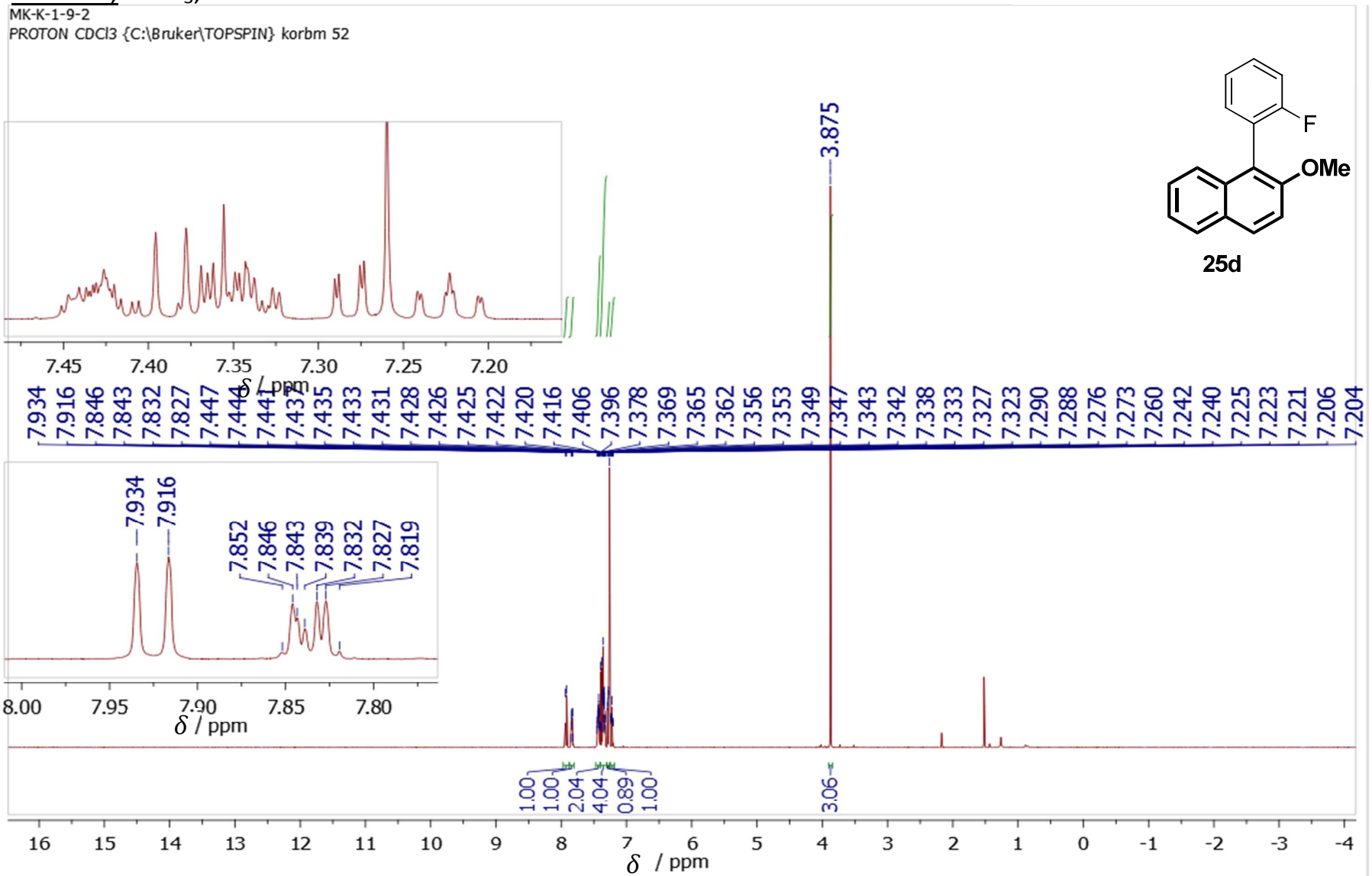
^{1}H NMR, $CDCl_3$, 25 °C



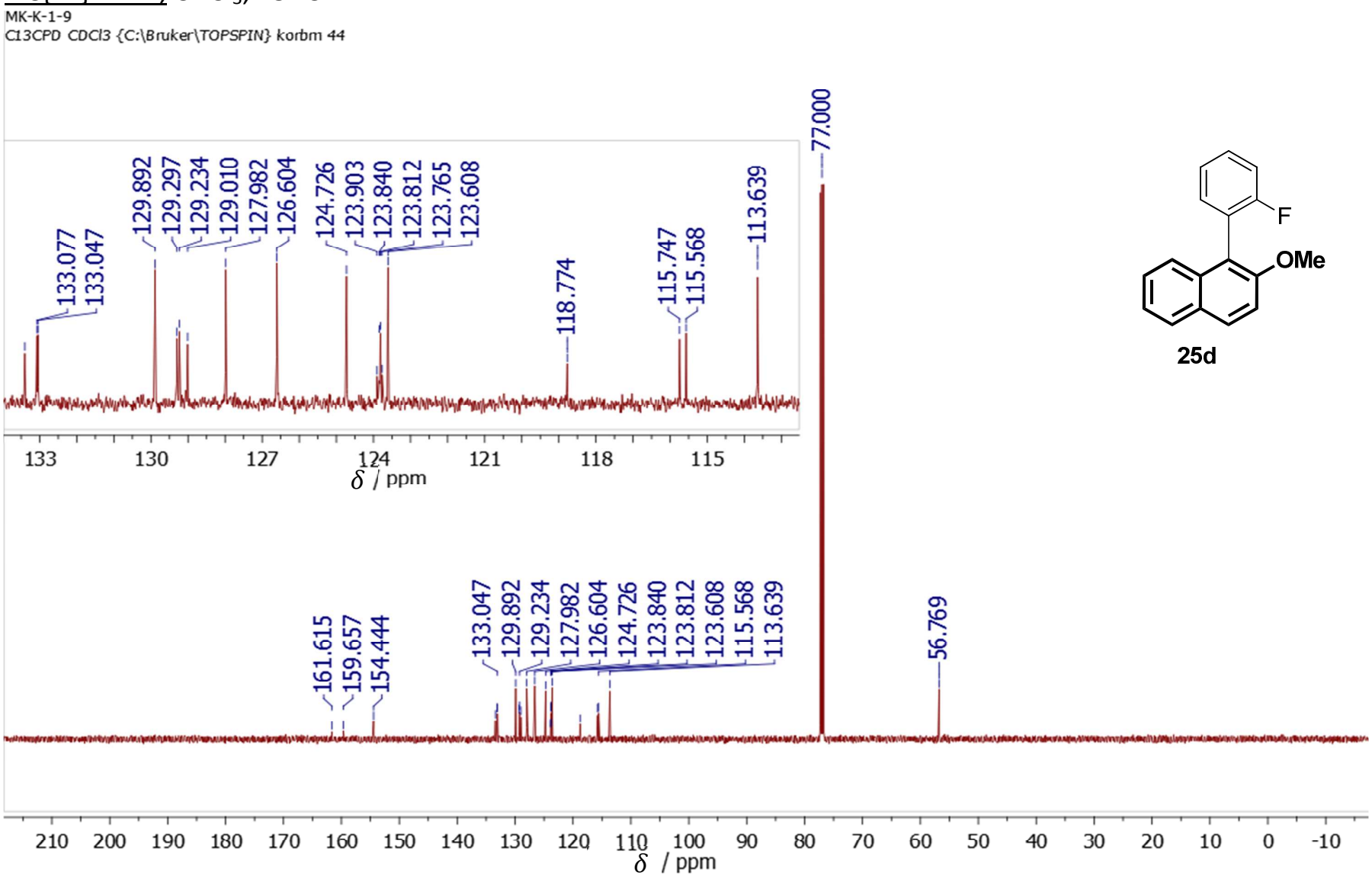
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C



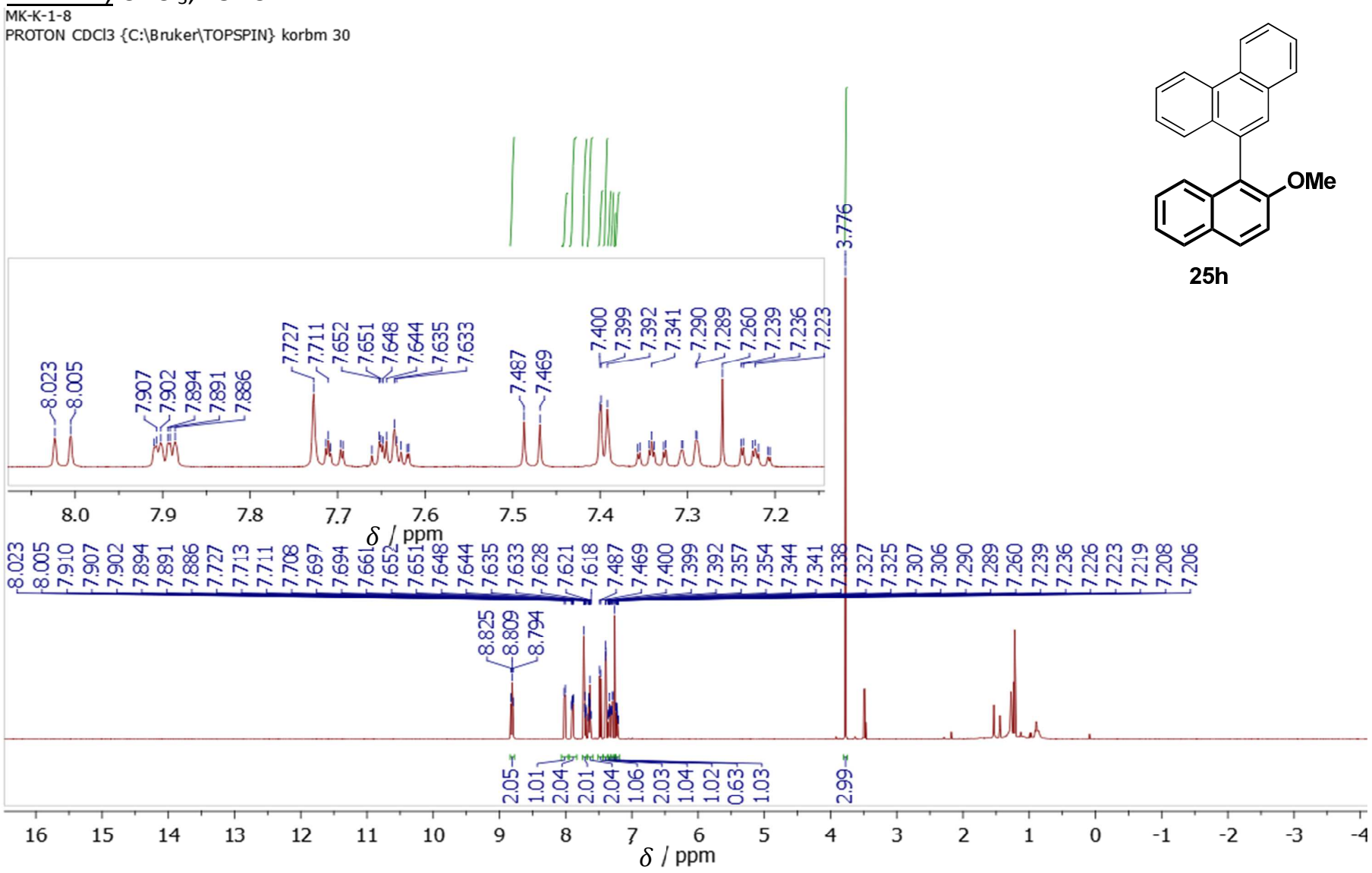
^{1}H NMR, $CDCl_3$, 25 °C



$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C



^{1}H NMR, $CDCl_3$, 25 °C

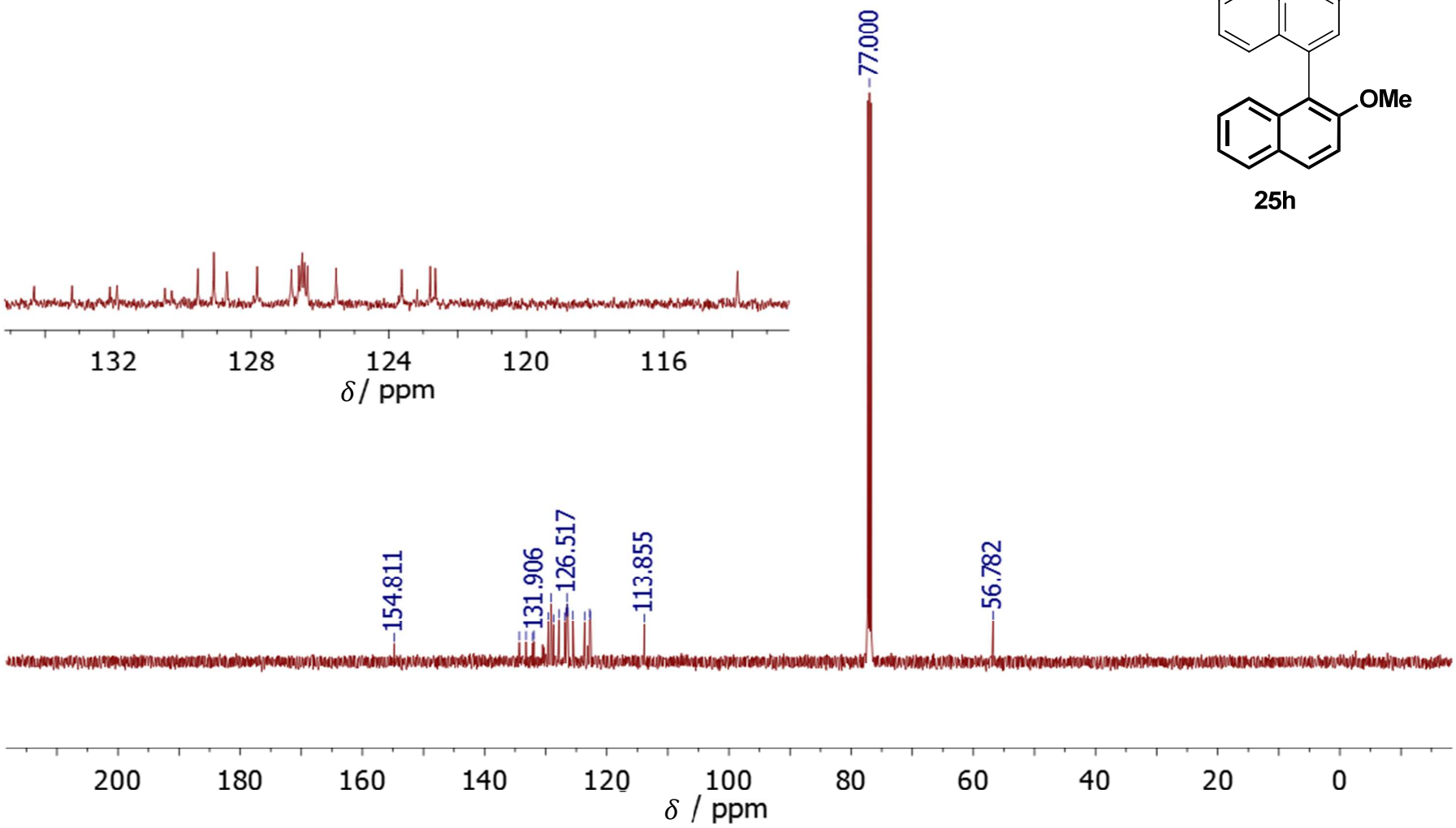


25h

$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 25 °C

MK-K-1-8

C13CPD CDCl3 {C:\Bruker\TOPSPIN} korbm 39



25h