**Ruthenium(II) and Iridium(III) complexes featuring NHC-Sulfonate chelate**

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# Supporting Information

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**General Information:**

All reactions were carried out under argon atmosphere using Schlenk tube techniques. Unless stated, reagents were purchased from commercial sources and used as received. Solvents (toluene, dichloromethane) were dried using a MBraun Solvent Purification System. Chloroform was HPLC grade and used as received. The reactions were monitored using a Shimadzu 2014 gas chromatograph equipped with an Equity$^{TM}$ – 1 Fused Silica capillary column (30 m x 0.25 mm x 0.25 μm) and a FID detector. $^{1}$H NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer and reported in ppm with reference to $CDCl_3$ (7.26 ppm) or $CD_2Cl_2$ (5.32 ppm). Data are reported as follows: s=singlet, d=doublet, t=triplet, q=quartet, qu=quintet, sept=septuplet, m=multiplet, br=broad. Coupling constants are reported in Hz. $^{13}$C NMR spectra were recorded at 100.6 MHz on the same spectrometer and reported in ppm with reference to $CDCl_3$ (76 ppm) or $CD_2Cl_2$ (53.8 ppm).

- Mesithyl imidazole **3** was prepared according to reported procedure[1]

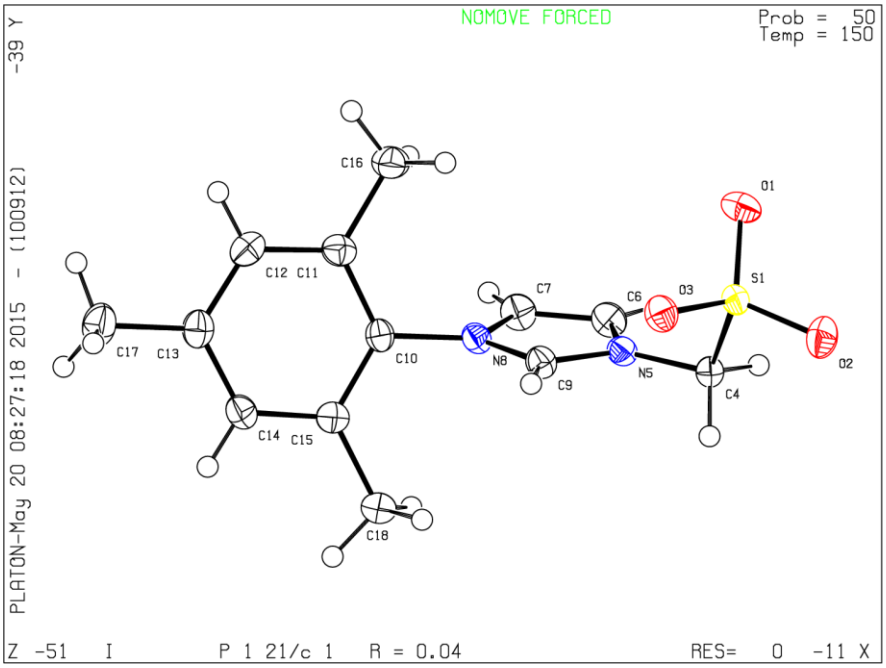
- *N*-(2,4,6-Trimethylphenyl)-*N*'-sulfomethylimidazolium **4**

A dried 500 mL Schlenk tube was loaded with 1 g (5.37 mmol) of mesithyl imidazole **4**, 40 mL of dibromomethane and 40 mL of water. This biphasic reaction mixture was vigourously stirred at 90 °C for 16 h. 1.7 g (13.4 mmol, 2.5 equiv.) of sodium sulfite were then added and the reaction stirred for 7 h at 90 °C (See $^{1}$H NMR Imidazolium crude). The reaction mixture was allowed to cool down to r.t. and the two phases were separated. The aqueous phase was washed by 3x20 mL of dichloromethane. The aqueous phase was placed at + 4°C to crystallize the desired imidazolium salt. If necessary, crystallization was repeated to decrease the amount of residual $BrCH_2SO_3Na$. The desired product was obtained as white crystals in 30-40 % yield. $^{1}$H NMR (400 MHz, $(CD_3)_2SO$) δ 9.44 (s, 1H), 7.98 (s, 1H), 7.88 (s, 1H), 7.14 (s, 2H), 5.04 (s, 2H), 2.33 (s, 3H), 2.01 (s, 6H). $^{13}$C NMR (75 MHz, $(CD_3)_2SO$) δ 140.7, 138.7, 134.7, 131.7, 129.7, 124.7, 123.5, 63.6, 21.1, 17.3. NMR data were consistent with reported data.[2]

CCDC 1414725 contains the supplementary crystallographic data for **4**

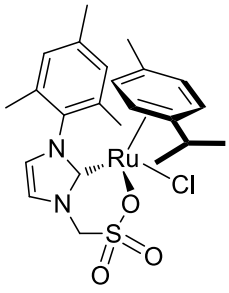
[1] M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, *J. Organomet. Chem.*, **1999**, *572*, 239-247.
[2] Y. Nagai, T. Kochi, K. Nozaki, K. *Organometallics*, **2009**, *28*, 6131

An X-ray molecular structure of compound **4** was recorded

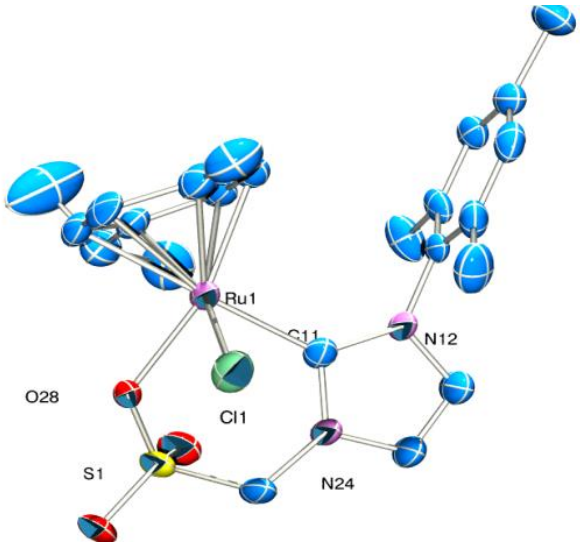



- Silver-NHC complex **Ag-1** was prepared according to the reported procedure.[1]
NMR data were consistent with reported data
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.75 (brs, 1H), 6.96 (brs, 1H), 6.77 (brs, 2H), 5.52 (brs, 2H), 2.06 (s,3H), 1.70 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 23.1, 27.8, 65.6, 122.2, 129.0, 134.8, 145.8, 181.9.

**- Synthesis of Ruthenium(NHC) complex Ru-1:**
To a vacuum dried Schlenk tube containing [Ru(*p*-cymene)$Cl_2$]$_2$ (80 mg, 0.13 mmol, 0.5 eq.) in DCM, silver NHC complex **Ag-1** (100 mg, 0.26mmol, 1.0 eq) was added and the reaction mixture was stirred at 45 $^{o}$C for 16 h. The reaction mixture was filtered over celite to remove AgCl. Concentration in vacuo of the red solution afforded the expected complex. Crystallization by layering with pentane and dichloromethane provided orange crystals (85 %). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.18 (br, 1H, $C_{mes}$-H), 7.07 (br, 1H, $C_{mes}$-H), 7.04 (d, *J* = 2.0 Hz, 1H, $C_{NHC}$-H), 6.91 (d, *J* = 2.0 Hz, 1H, $C_{NHC}$-H), 5.73 (d, *J* = 6.2 Hz, 1H, $C_{cym}$-H), 5.45 (d, *J* = 13.2 Hz, 1H, $CH_2SO_3$), 5.35 (brs, 1H, $C_{cym}$-H), 5.22 (d, *J* = 4.0 Hz, 1H, $C_{cym}$-H), 4.47 (d, *J* = 13.2 Hz, 1H, $CH_2SO_3$), 3.30 (brs, 1H, $C_{cym}$-H), 2.77 (sept, *J* = 7.2 Hz, 1H, H-$CMe_2$), 2.43 (s, 3H, $C_{mes}$-$CH_3$), 2.39 (s, 3H,



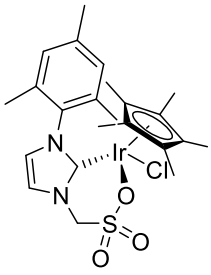
$C_{mes}$-$CH_3$), 2.02 (s, 3H, $C_{mes}$-$CH_3$), 1.84 (s, 3H, $C_{cym}$-$CH_3$), 1.18 (2dd, t app., *J* = 7.2 Hz, 6H, H-C(Me)$_2$); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) δ 171.1 ($C_{NHC}$-Ru), 141.5 ($C_{mes}$-quat.), 138.0 ($C_{mes}$-quat.), 137.9 ($C_{mes}$-quat.), 135.7 ($C_{mes}$-quat.), 130.1 ($C_{mes}$-H), 130.0 ($C_{mes}$-H), 125.4 ($C_{NHC}$-H), 123.2 ($C_{NHC}$-H), 104.1 ($C_{cym}$), 94.6 (br, $C_{cym}$-H), 93.0 ($C_{cym}$), 78.8 (br, $C_{cym}$-H), 78.7 ($C_{cym}$-H), 77.7 ($C_{cym}$-H), 63.6 ($CH_2SO_3$), 30.4 ($CHMe_2$), 24.0, 21.5, 20.4, 18.7, 18.6, 18.2 ($CH_3$).
HRMS (ESI) $[M\text{-}.Cl]^+$ ($C_{23}H_{29}N_2O_3SRu$) Th: 515.09369; Exp: 515.0943
Elemental analysis for $C_{23}H_{29}ClN_2O_3RuS$
Theoretical: C, 50.22; H, 5.31; N, 5.09; S, 5.83
Measured: C, 49.69; H, 5.62; N; 4.93; S, 5.84
CCDC 1414617 contains the supplementary crystallographic data for **Ru-1**




**Ru-1 Complex:** Selected bonds lengths (Å): Ru(1)-Cl(1), 2.405; Ru(1)-O(28), 2.157; Ru(1)-C(1), 2.088; Selected bond angles (deg): O(28)-Ru(1)-C(1), 88.7; O(28)-Ru(1)-Cl(1), 88.11; Cl(1)-Ru(1)-C(1), 83.18

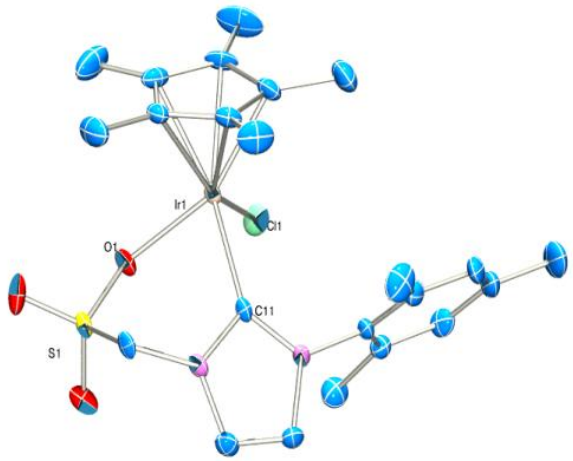
**- Synthesis of Iridium(NHC) complex Ir-1:**

To a vacuum dried Schlenk tube containing $[Ir(Cp^*)Cl_2]_2$ (0.5 eq) in DCM, silver NHC complex (1.0 eq) was added and the reaction mixture was stirred at 45 $^oC$ for 16h. Then solution was filtered over celite to remove AgCl. Concentration in vacuo of the reddish yellow solution afforded the expected complex. Crystalization by layering with pentane and dichloromethane gave the yellow crystals (81 %). $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.33 (d, *J* = 2.0 Hz, 1H, $C_{NHC}$-H), 6.99 (s, 2H, $C_{mes}$-H), 6.52 (d, *J* = 2.0 Hz, 1H, $C_{NHC}$-H), 5.20 (d, *J* = 13.2 Hz, 1H, $CH_2SO_3$), 4.77 (d, *J* = 13.2 Hz, 1H, $CH_2SO_3$), 2.34 (s, 3H, $C_{mes}$-$CH_3$), 2.14 (s, 3H, $C_{mes}$-$CH_3$), 2.08 (s, 3H, $C_{mes}$-$CH_3$), 1.35 (s, 15H, Cp*); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 161.5 ($C_{NHC}$-Ir), 140.3 ($C_{mes}$-quat.), 138.4 ($C_{mes}$-



quat.), 136.2 ($C_{mes}$-quat.), 135.4 ($C_{mes}$-quat.), 130.1 ($C_{mes}$-quat.), 129.0 ($C_{mes}$-quat.), 125.1 ($C_{mes}$-H), 125.0 ($C_{mes}$-H), 90.9 (Cp*), 64.8 ($CH_2SO_3$), 21.3 ($C_{mes}$-Me), 19.8 ($C_{mes}$-Me), 18.8 ($C_{mes}$-Me), 9.7 (Cp*)

HRMS (ESI) $[M\text{-}.Cl]^+$ ($C_{23}H_{30}N_2O_3SIr$) Th: 607.16011; Exp: 607.1603
Elemental analysis for $C_{23}H_{30}N_2O_3ClSIr$
Theoretical: C, 43.01; H, 4.71; N, 4.36; S, 4.99
Measured: C, 42.82; H, 4.38; N, 4.39; S, 4.74
CCDC 1414618 contains the supplementary crystallographic data for **Ir-1**

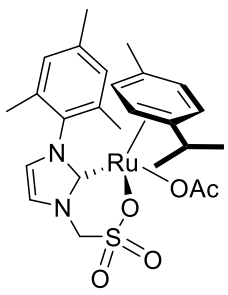



**Crystal structure of Ir(NHC) Complex**

**Ir(NHC) Complex :** Selected bonds lengths (Å): Ir(1)-Cl(1) , 2.374; Ir(1)-O(1) , 2.226; Ir(1)-C(1), 2.058; Selected bond angles (deg): C(1)-Ir(1)-Cl(1), 89.35; C(1)-Ir(1)-O(31), 89.27; Cl(1)-Ir(1)-O(31), 82.31.

**- Synthesis of Ruthenium(NHC) complex Ru-2:**

To a vacuum dried Schlenk tube containing [Ru(*p*-cymene)$(OAc)_2$] (1 eq) in DCM, silver NHC complex **Ag-1** (1.0 eq) was added and the reaction mixture was stirred at 45 °C for 16 h. The reaction mixture was filtered over celite to remove AgCl. Concentration in vacuo of the brown solution afforded the expected complex **Ru-2**. Precipitation by layering with pentane and dichloromethane provided brown powder (40 %). An alternative pathway involves the reaction of **Ru-1** (1 eq.) with potassium acetate (1.8 eq.) in dichloromethane at 50 °C overnight followed by cannulation and concentration *in vacuo* to yield **Ru-2;** This complex could not be crystallized. Its purity was estimated to 95% by $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (brs, 1H, $C_{NHC}$-H), 7.06 (brs, 1H, $C_{mes}$-H), 6.98 (s, 1H, $C_{mes}$-H), 6.96 (d, *J*= 2.0 Hz, 1H, $C_{NHC}$-H), 6.06 (d, *J* = 5.8

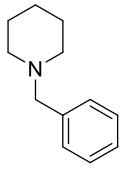


Hz, 1H, $C_{cym}$-H), 5.99-5.98 (m, 1H, $C_{cym}$-H), 5.61-5.59 (m, 1H, $C_{cym}$-H), 5.16 (d, *J*= 5.8 Hz, 1H, $C_{cym}$-H), 4.82 (d, *J*= 13.3 Hz, 1H, $CH_2SO_3$), 4.76 (d, *J*= 13.3 Hz, 1H, $CH_2SO_3$), 2.36 (s, 3H, $C_{mes}$-$CH_3$), , 2.27 (s, 3H, $C_{mes}$-$CH_3$), 1.96 (s, 3H, $C_{mes}$-$CH_3$), 1.85 (s, 3H), 1.63 (s, 3H), 1.60-1.52 (m, 1H, H-$CMe_2$), 1.09 (d, *J*= 6.9 Hz, 3H), 0.98 (d, *J*= 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 187.4 (C=O) , 174.7 ($C_{NHC}$-Ru), 138.7 ($C_{mes}$-quat.), 135.7 ($C_{mes}$-quat.), 135.3 ($C_{mes}$-quat.), 134.8 ($C_{mes}$-quat.), 128.6 ($C_{mes}$-H), 127.7 ($C_{mes}$-H), 124.2 ($C_{NHC}$-H), 123.6 ($C_{NHC}$-H), 99.2 ($C_{cym}$quat.), 91.1 ($C_{cym}$quat.), 87.8 ($C_{cym}$H), 85.1 ($C_{cym}$H), 81.4 ($C_{cym}$H), 79.9 ($C_{cym}$H), 64.1 ($CH_2SO_3$), 29.5 ($CHMe_2$), 22.5, 22.3, 20.6, 19.9, 17.4, 16.5, 16.3.

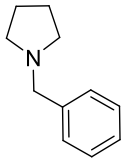
## General procedure for *N*-alkylation:

A 25 mL Schlenk tube was flushed with argon and equipped with a magnetic stirring bar. The flask was charged with alcohol (1.2 eq) and catalyst (1 mol%). The mixture was stirred at room temperature for 5 minutes before adding amine (1.0 eq). Afterwards, the mixture was stirred at 130 °C for 24 hours. Then the reaction mixture was cooled down to room temperature and was analyzed by GC. The crude mixture was purified by column chromatography using neutral alumina and a mixtures of pentane and diethyl ether as eluent. $^{1}$H NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer and reported in ppm with reference to $(CD_3)_2CO$ (2.05 ppm). $^{13}$C NMR spectra were recorded at 100.6 MHz on the same spectrometer and reported in ppm with reference to $(CD_3)_2CO$ (206.26 ppm).

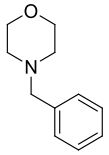
**1-benzylpiperidine:** Colourless oil (85%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.33-7.27 (m, 4H), 7.23-7.22 (m, 1H), 3.42(s, 2H), 2.35 (br, 4H), 1.57-1.51(m, 4H), 1.44-1.42 (m, 2H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 140.5, 130.0, 129.2, 127.8, 64.6, 55.5, 27.1, 25.5.
NMR data were consistent with reported data[3]



**1-benzylpyrrolidine:** Colourless oil (90%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.34-7.27 (m, 4H), 7.23-7.21 (m, 1H), 3.58 (s, 2H), 2.46-2.43 (m, 4H), 1.72 (qu, *J* = 3.2 Hz, 2H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 141.2, 129.6, 129.2, 127.7, 61.2, 54.8, 24.5.
NMR data were consistent with reported data[4]

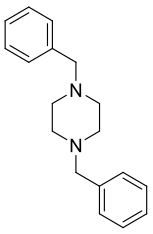


**4-benzylmorpholine:** Colourless oil (65%).$^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.35-7.29 (m, 4H), 7.25-7.22 (m, 1H), 3.60 (t, *J* = 4.8 Hz, 4H), 3.47 (s, 2H), 2.38 (t, *J* = 4.8 Hz, 4H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 139.4, 129.9, 129.1, 127.9, 67.6, 64.0, 54.6.
NMR data were consistent with reported data[5]

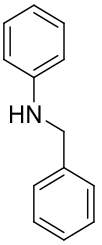


[3] G. A. Molander, P. E. Gormisky, D. L. Sandrock, *J. Org. Chem.*, **2008**, *73*, 2052-2057.
[4] J. M. J. Williams, A. Pettman, D. van der Waals, *RSC Advances*, **2014**, *4*, 51845-51849.

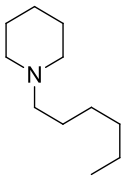
**1,4-dibenzylpiperazine:** White solid (81%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.33-7.28 (m, 8H), 7.24-7.22 (m, 2H), 3.48 (s, 4H), 2.43 (br, 8H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 140.0, 129.9, 129.2, 127.9, 63.7, 54.2.
NMR data were consistent with reported data[6]



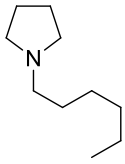
***N*-benzylaniline:** White solid (64%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 5.39 (s, 1H), 4.35 (d, *J* = 5.6 Hz, 2H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 149.8, 141.3, 129.8, 129.2, 128.2, 127.6, 117.4, 113.6, 48.2.
NMR data were consistent with reported data.[7]

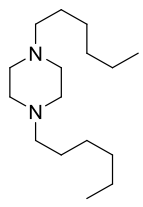


**1-hexylpiperidine:** Colourless oil (85%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 2.30 (br, 4H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.54-1.49 (m, 4H), 1.45-1.38 (m, 4H), 1.32-1.28 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 60.3, 55.7, 32.9, 28.3, 28.1, 27.2, 25.7, 23.7, 14.7.
NMR data were consistent with reported data.[8]



**1-hexylpyrrolidine:** Colourless oil (71%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 3.17 (br, 4H), 3.00 (t, *J* = 8.0 Hz, 2H), 2.02-1.98 (m, 4H), 1.83-1.75 (m, 2H), 1.38-1.29 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 55.6, 53.8, 32.2, 27.4, 26.7, 24.0, 23.2, 14.3.
NMR data were consistent with reported data.[9]

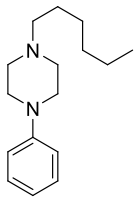




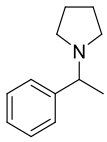
[5] O. O. Kovalenko, A. Volkov, H. Adolfson, *Org. Lett.*, **2015**, *17*, 446-449.
[6] L. L. R. Lorentz-Petersen, L. U. Nordstrom, R. Madsen, *Eur. J. Org. Chem.*, **2012**, *34*, 6752-6759.
[7] A. S. Kumari, D. D. Pathak, *Tetrahedron Lett.*, **2015**, *56*, 4135-4142.
[8] G. Liu, Z. Li, H. Geng, X. Zhang, *Catal. Sci. Technol.*, **2014**, *4*, 917-921.
[9] X. Li, Z. Zheng, S. Garg, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.*, **2008**, *21*, 3353-3358.

**1,4-dihexylpiperazine:** Colourless oil (56%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 2.37 (br, 8H), 2.25 (t, *J* = 7.2 Hz, 4H), 1.44-1.41 (m, 4H), 1.32-1.29 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 59.5, 54.5, 32.8, 28.1, 27.9, 23.5, 14.6.

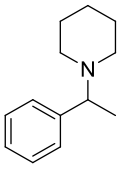
**1-hexyl-4-phenylpiperazine:** White solid (47%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.20 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 8.4 Hz, 1H), 3.16 (t, *J* = 5.2 Hz, 4H), 2.53 (t, *J* = 5.2 Hz, 4H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.54-1.48 (m, 2H), 1.38-1.29 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): δ 152.7, 129.8, 119.9, 116.6, 59.3, 54.3, 49.9, 32.7, 28.0, 27.8, 23.4, 14.5.
NMR data were consistent with reported data.[10]



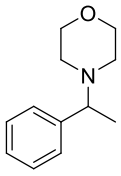
**1-(1-phenylethyl)pyrrolidine:** Yellow oil (70%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.34-7.27(m, 4H), 7.22-7.18 (m, 1H), 3.16 (q, *J* = 6.8 Hz, 1H), 2.52-2.47 (m, 2H), 2.35-2.30 (m, 2H), 1.73-1.66 (m, 4H), 1.31 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): 147.6, 129.2, 128.0, 127.7, 66.6, 53.5, 24.4, 24.3.
NMR data were consistent with reported data.[11]



**1-(1-phenylethyl)piperidine:** Yellow oil (51%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.33-7.27 (m, 4H), 7.22-7.18 (m, 1H), 3.36 (q, *J* = 6.8 Hz, 1H), 2.39-2.38 (m, 2H), 2.32-2.31 (m, 2H), 1.53-1.48 (m, 4H), 1.41-1.34(m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): 145.9, 129.0, 128.4, 127.6, 65.8, 52.3, 27.3, 25.7, 19.8.
NMR data were consistent with reported data.[12]



**4-(1-phenylethyl)morpholine:** Yellow oil (46%). $^{1}$H NMR (400 MHz, *acetone-d6*): δ 7.34-7.29 (m, 4H), 7.24-7.20 (m, 1H), 3.61-3.55 (m, 4H), 3.29 (q, *J* = 6.8 Hz, 1H), 2.45-2.42 (m, 2H), 2.32-2.27 (m, 2H), 1.30 (d, *J* = 6.4 Hz, 3H); $^{13}$C NMR (100.6 MHz, *acetone-d6*): 144.2, 128.0, 127.2, 126.6, 66.6, 64.8, 51.0, 19.2.
NMR data were consistent with reported data.[12]



[10] I. Yavari, M. J. Bayat, M. Ghazanfarpour-Darjani, *Tetrahedron Lett.*, **2014**, *55*, 5595-5596.
[11] A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *J. Org. Chem.*, **2011**, *76*, 2328-2331.
[12] Y. Miki, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.*, **2013**, *52*, 10830-10834.

**General procedure for etherification**

A 25 mL Schlenk tube was flushed with argon, equipped with a magnetic stirring bar. The flask was charged with phenyl ethanol **6c** (0.1 mmol), and catalyst **Ru-1** (1 mol%). The reaction mixture was stirred at 130 °C for 24 h. The reaction progress was monitored by gas chromatography. The reaction mixture was then allowed to cool down to r.t. and the product isolated by column chromatography on silica gel employing a mixture of petroleum ether and ethyl acetate (95/5, v/v) as eluent. The product **12** was isolated in 45 % yield as a white oil.

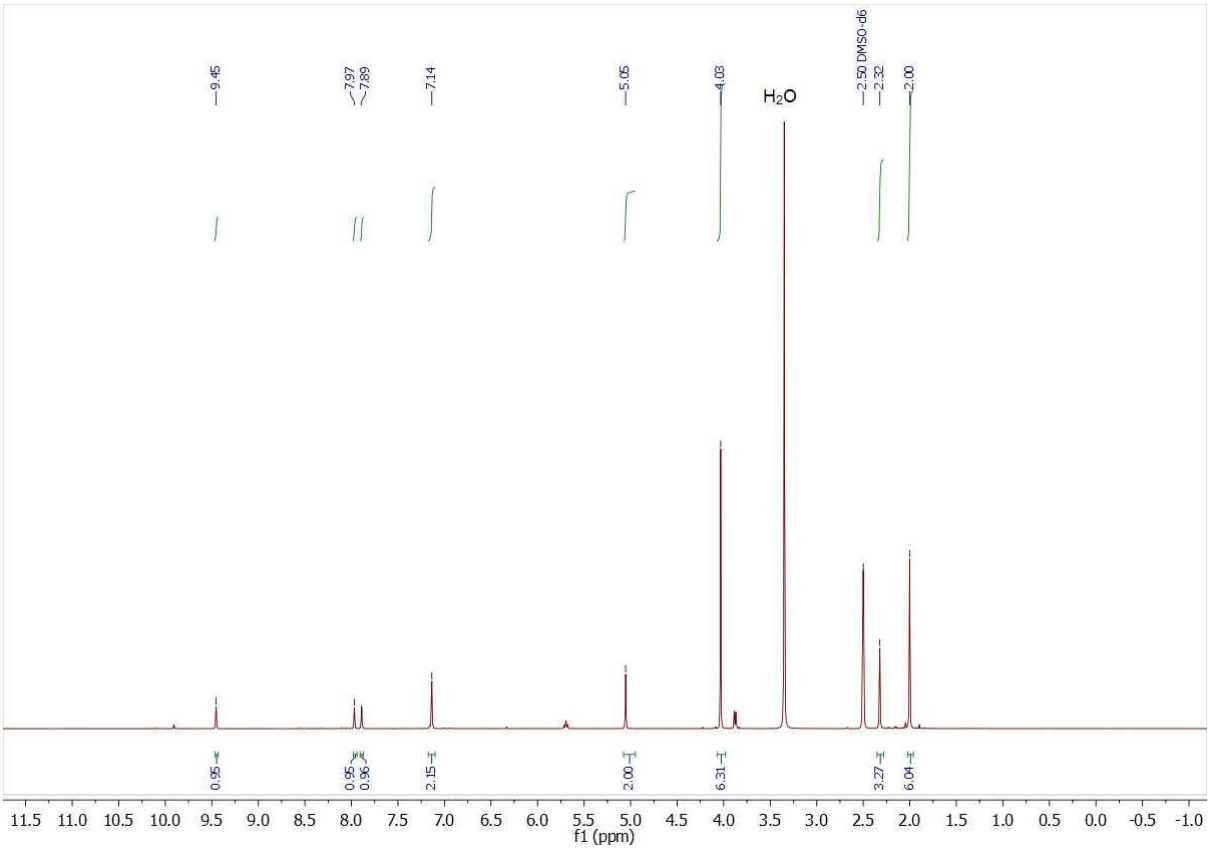
$^{1}$H NMR (400 MHz, $CD_2Cl_2$): δ 7.40-7.34 (m, 4H), 7.33-7.20(m, 14H), 4.54 (q, *J* = 8.0 Hz, 1,6H), 4.25 (q, *J* = 8.0 Hz, 2H), 1.46 (d, *J* = 8.0 Hz, 4,9H), 1.36 (d, *J* = 8.0 Hz, 6H); $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): 145.0, 144.9, 129.0, 128.8, 127.9, 127.7, 126.9, 126.8, 75.2, 75.0, 54.3, 54.0, 54.00, 53.7, 25.1, 23.4

Compound **12** was obtained as a mixture of *dl* enantiomers and meso compounds in a 45/55 ratio

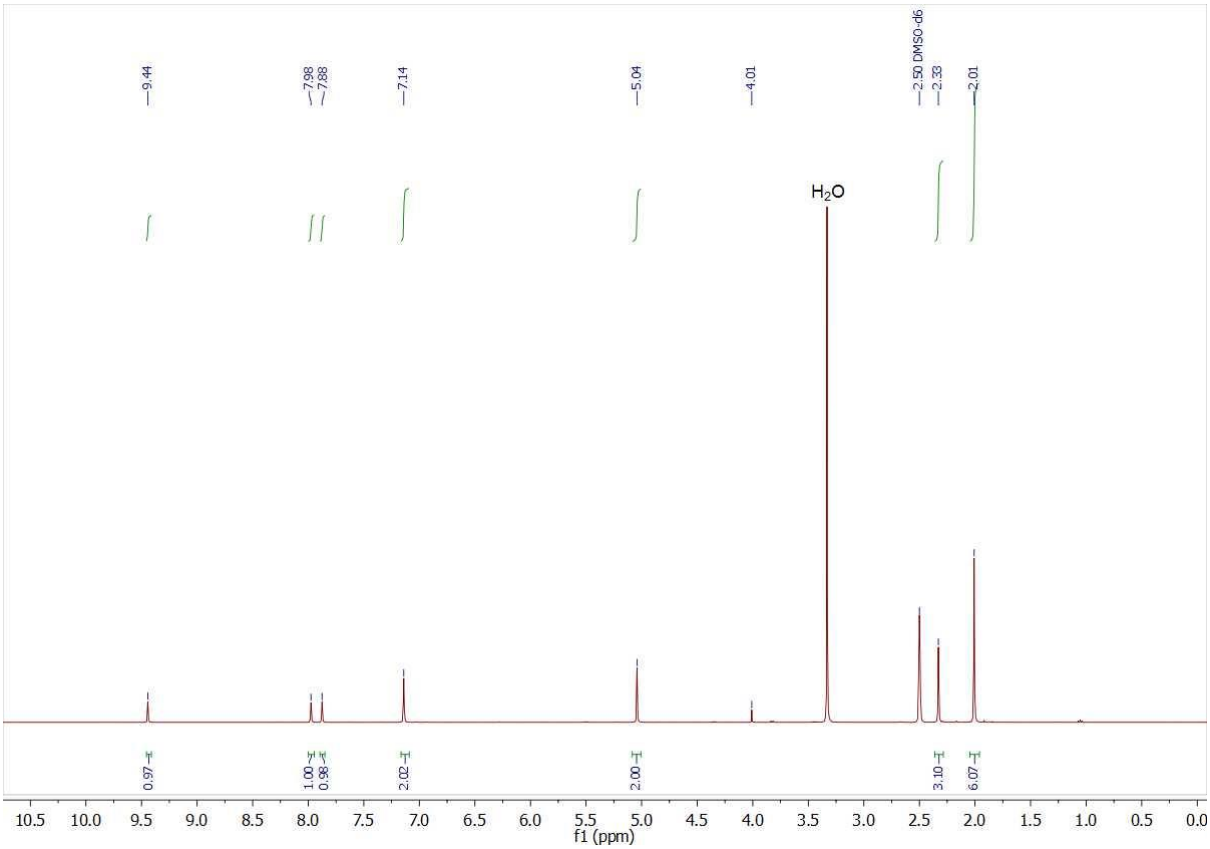
NMR data were consistent with reported data[13]

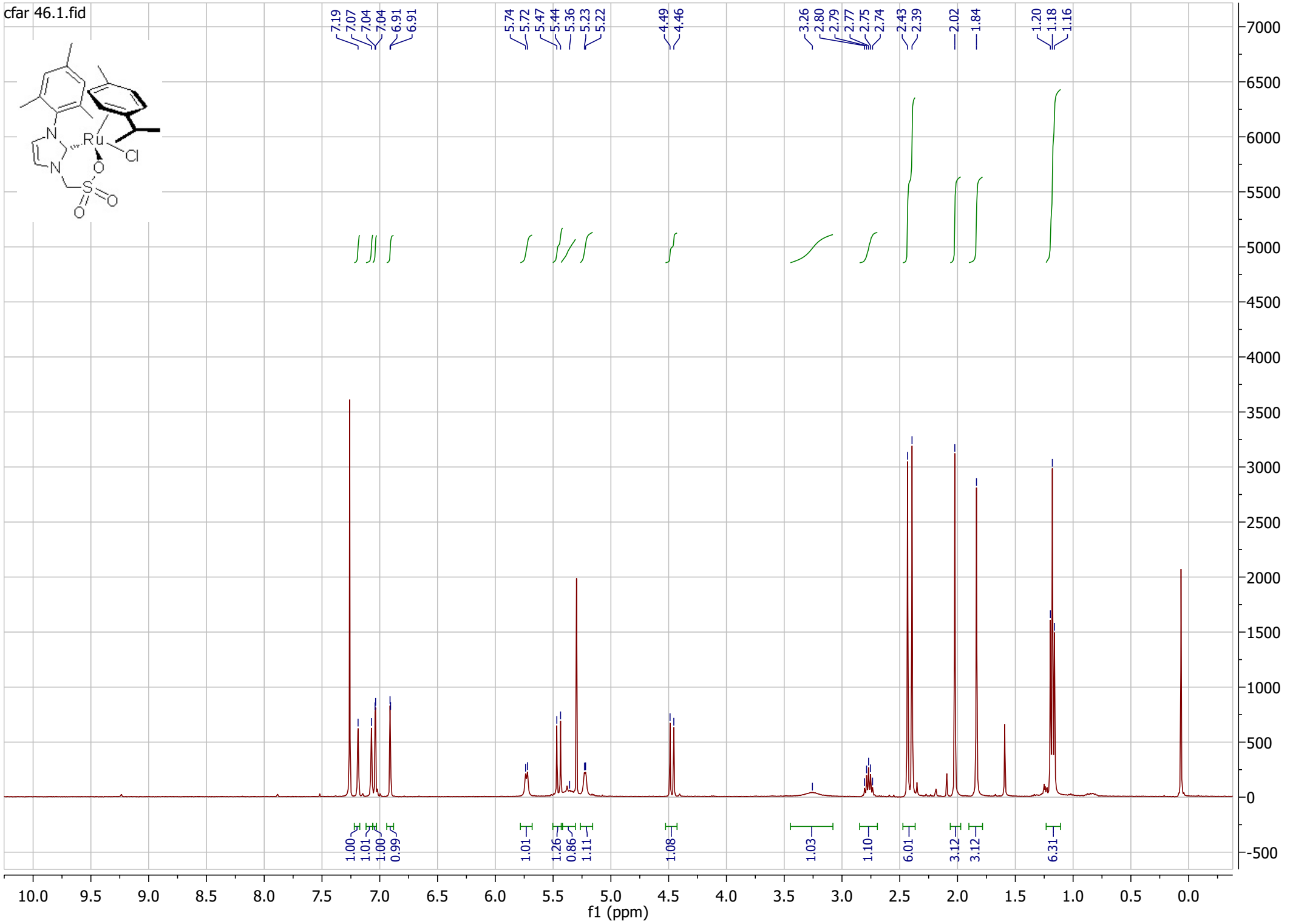
[13] C. H. Jin, H. Y. Lee, S. H. Lee, I. S. Kim, Y. H. Jung, *Synlett*, **2007**, 2695-2698.

## Imidazolium salt 4 crude




## Imidazolium salt 4 crystallised

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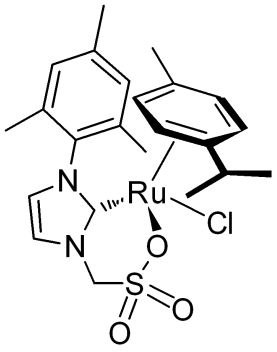
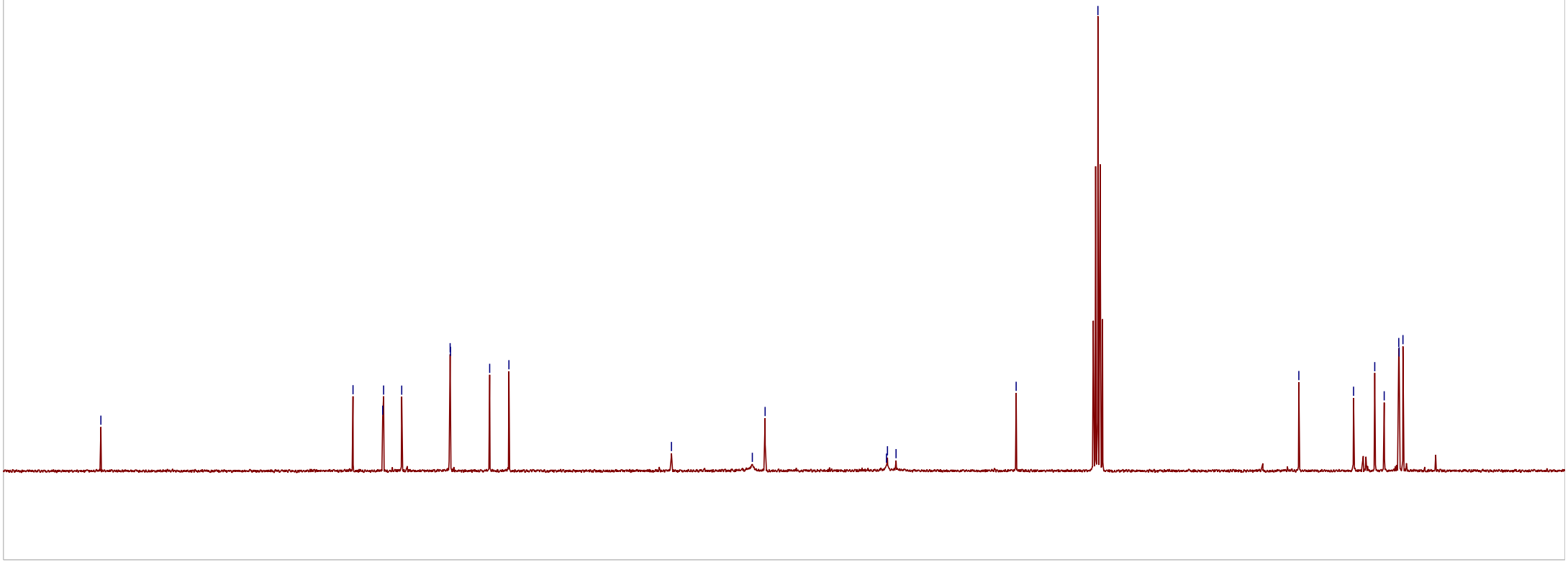
7.19
7.07
7.04
7.04
6.91
6.91
5.74
5.72
5.47
5.44
5.36
5.23
5.22
4.49
4.46
3.26
2.80
2.79
2.77
2.75
2.74
2.43
2.39
2.02
1.84
1.20
1.18
1.16
1.00
1.01
1.00
0.99
1.01
1.26
0.86
1.11
1.08
1.03
1.10
6.01
3.12
3.12
6.31
f1 (ppm)

M3-CFFH-80.50.fid



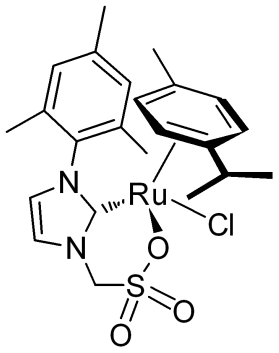

171.06
141.46
137.97
137.87
135.74
130.05
130.01
125.41
123.15
104.07
94.57
93.07
78.82
78.71
77.70
63.60
54.00 CD2Cl2
30.41
23.99
21.50
20.39
18.68
18.64
18.19



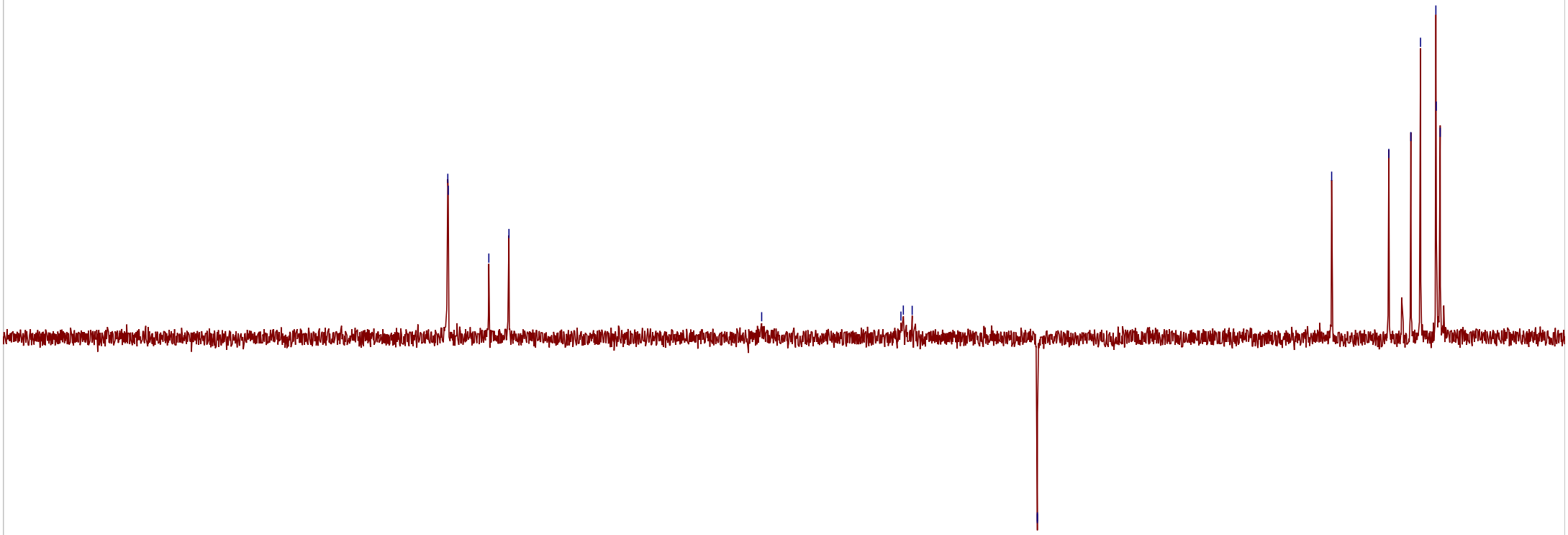
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

M3-CFFH-80.70.fid

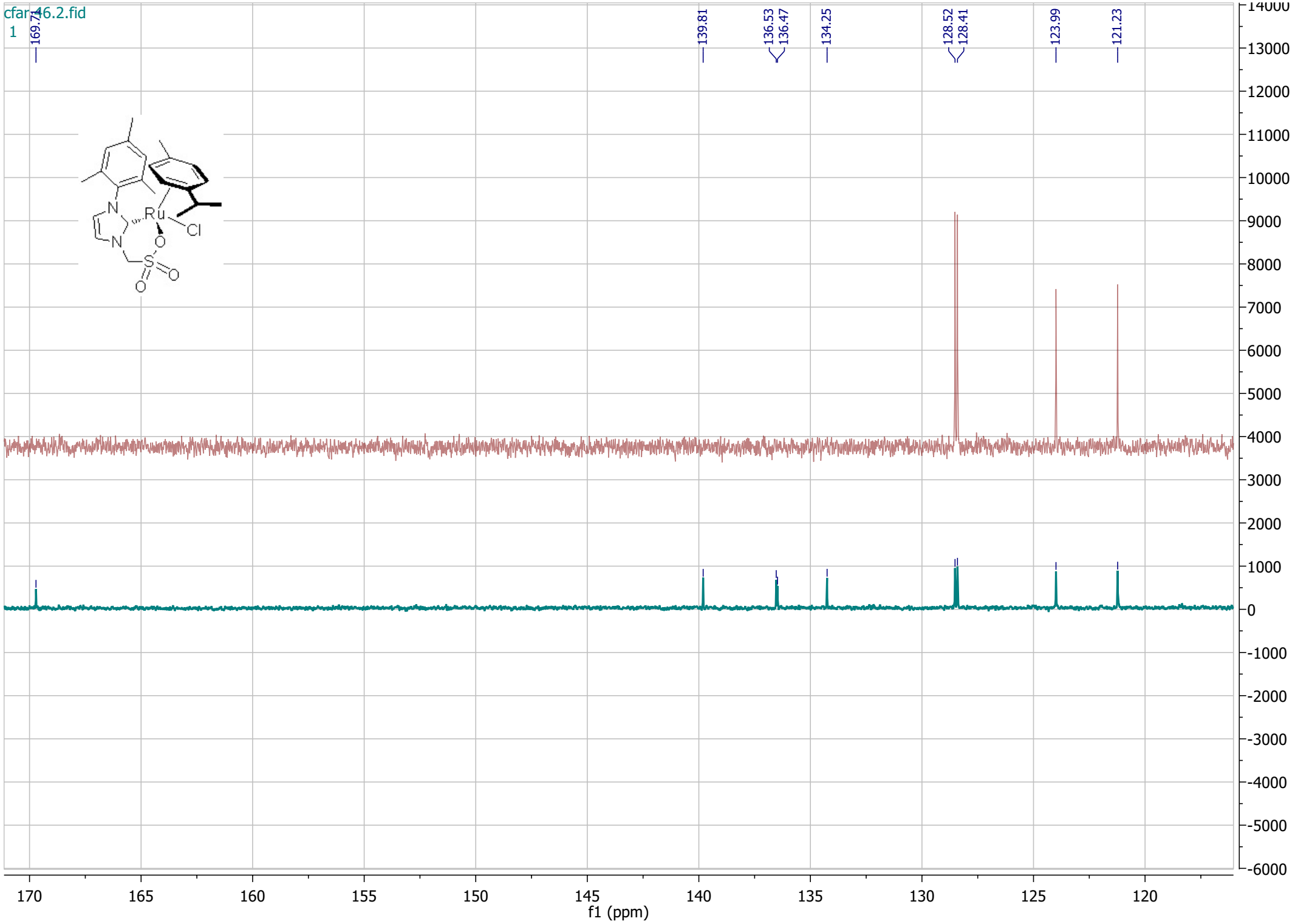


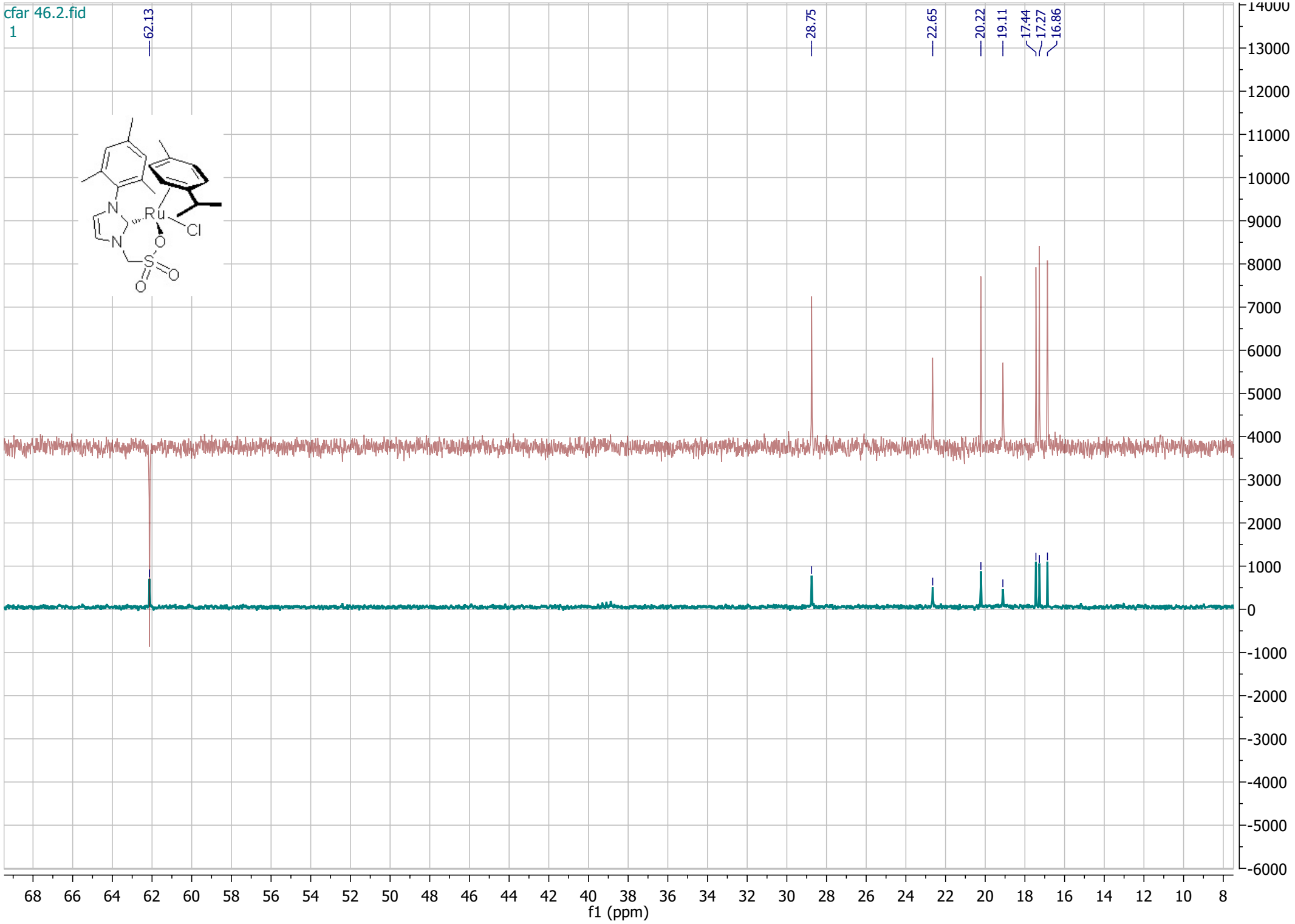

130.06
130.02
125.43
123.17
94.68
78.98
78.71
77.71
63.60
63.60
30.42
23.98
21.49
20.40
18.67
18.63
18.19



30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)


cfar-46.2.fid
1
169.74
139.81
136.53
136.47
134.25
128.52
128.41
123.99
121.23
Ru
Cl
N
N
O
S
O
O
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
170
165
160
155
150
145
140
135
130
125
120
f1 (ppm)


cfar 46.2.fid
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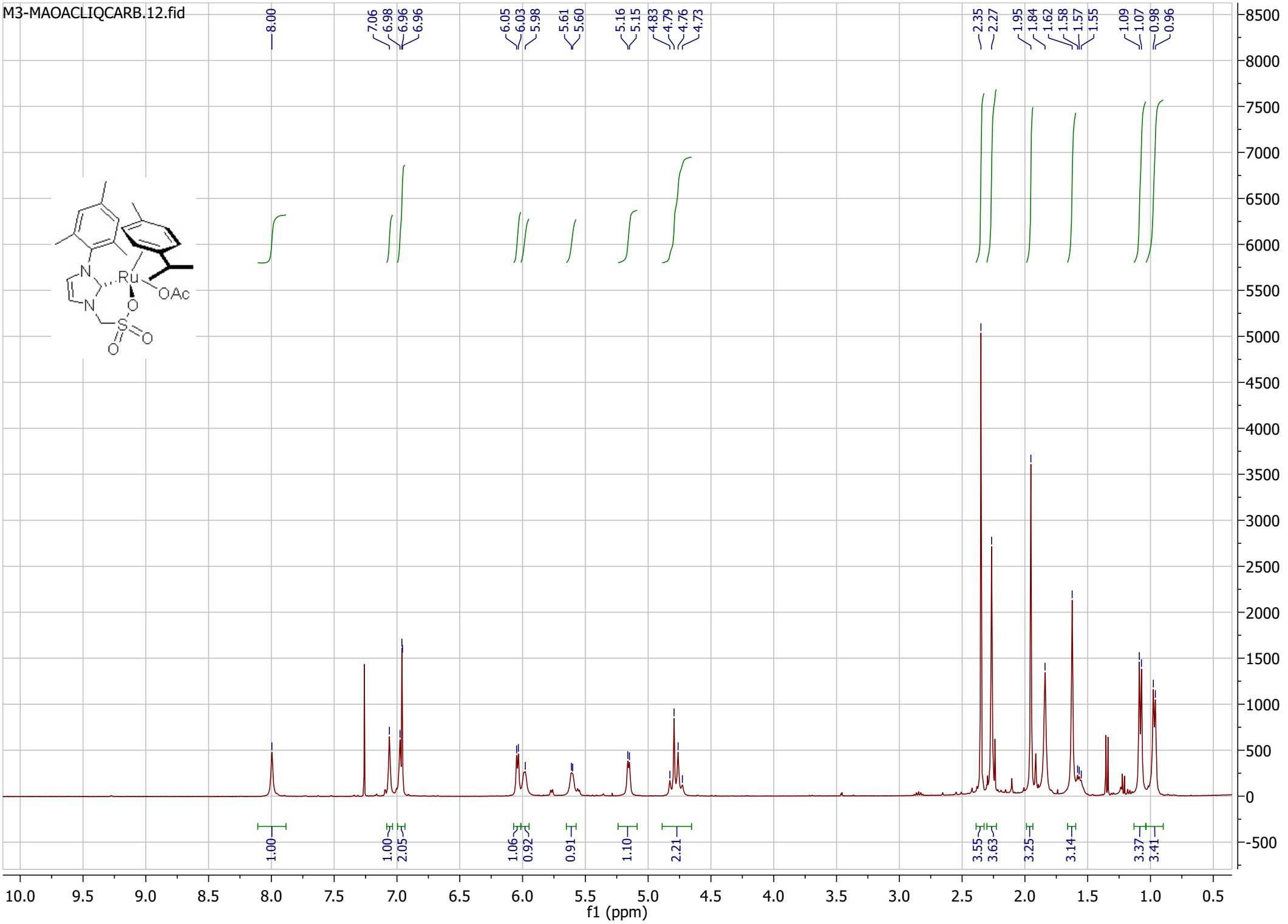
62.13
28.75
22.65
20.22
19.11
17.44
17.27
16.86
Ru
Cl
N
N
O
S
O
O
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8
f1 (ppm)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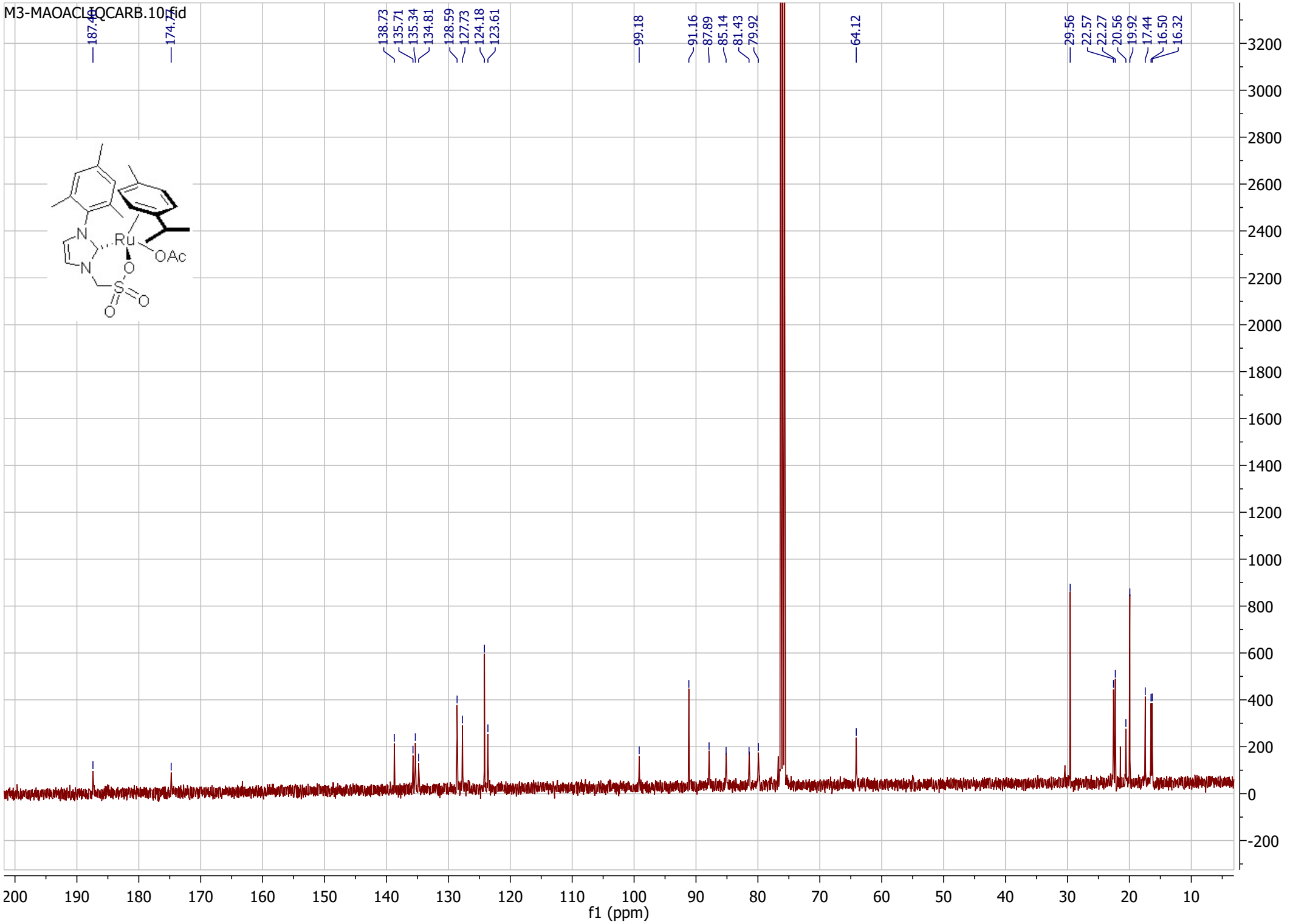
6.98
6.96
6.96
6.05
6.03
5.98
5.61
5.60
5.16
5.15
4.83
4.79
4.76
4.73
2.35
2.27
1.95
1.84
1.62
1.58
1.57
1.55
1.09
1.07
0.98
0.96
Ru
OAc
N
N
O
S
O
O
1.00
1.00
2.05
1.06
0.92
0.91
1.10
2.21
3.55
3.63
3.25
3.14
3.37
3.41
f1 (ppm)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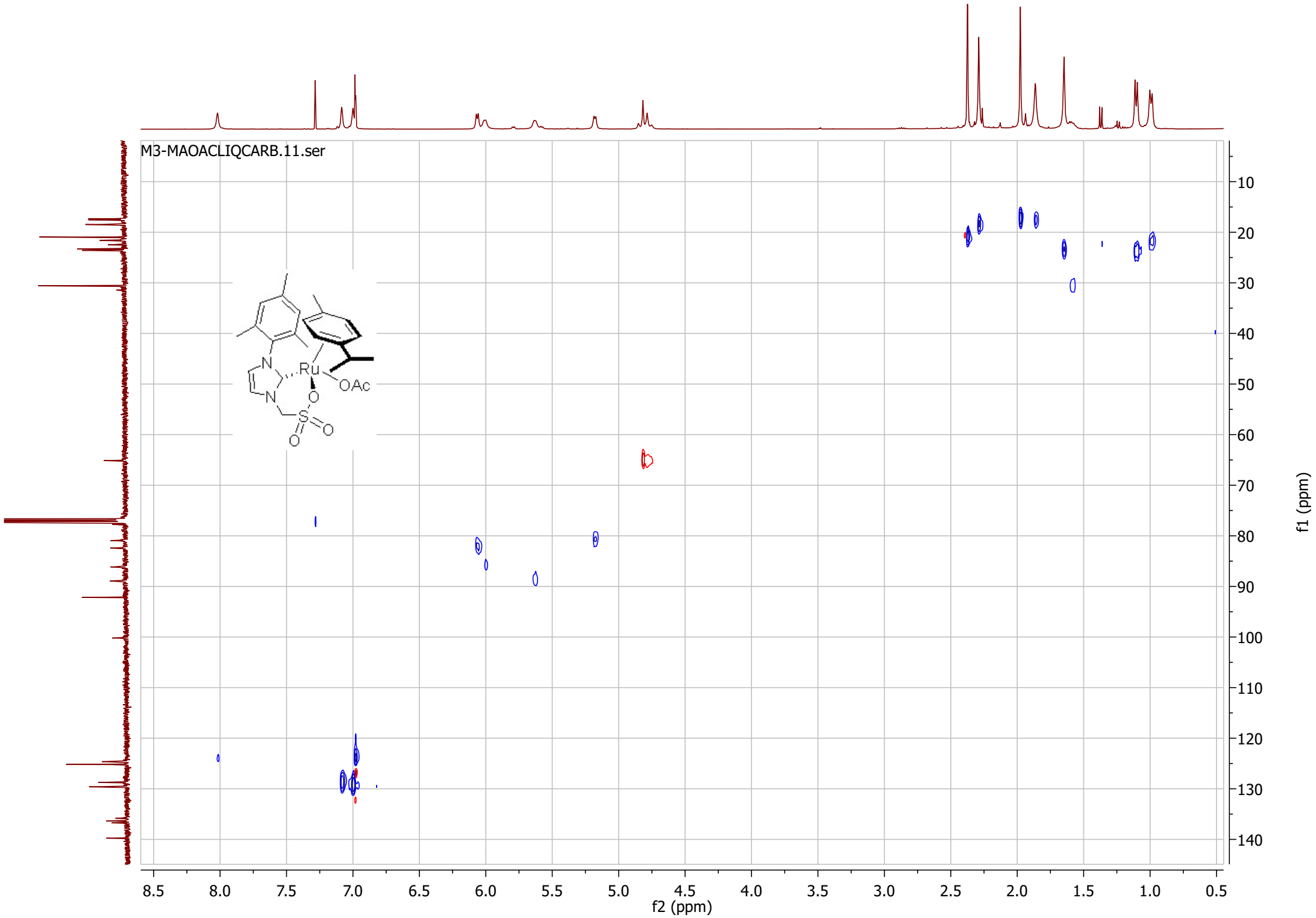
187.45
174.77
138.73
135.71
135.34
134.81
128.59
127.73
124.18
123.61
99.18
91.16
87.89
85.14
81.43
79.92
64.12
29.56
22.57
22.27
20.56
19.92
17.44
16.50
16.32
Ru
OAc
N
N
O
S
O
O
O
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


M3-MAOACLIQCARB.11.ser
Ru
OAc
N
N
O
S
O
O
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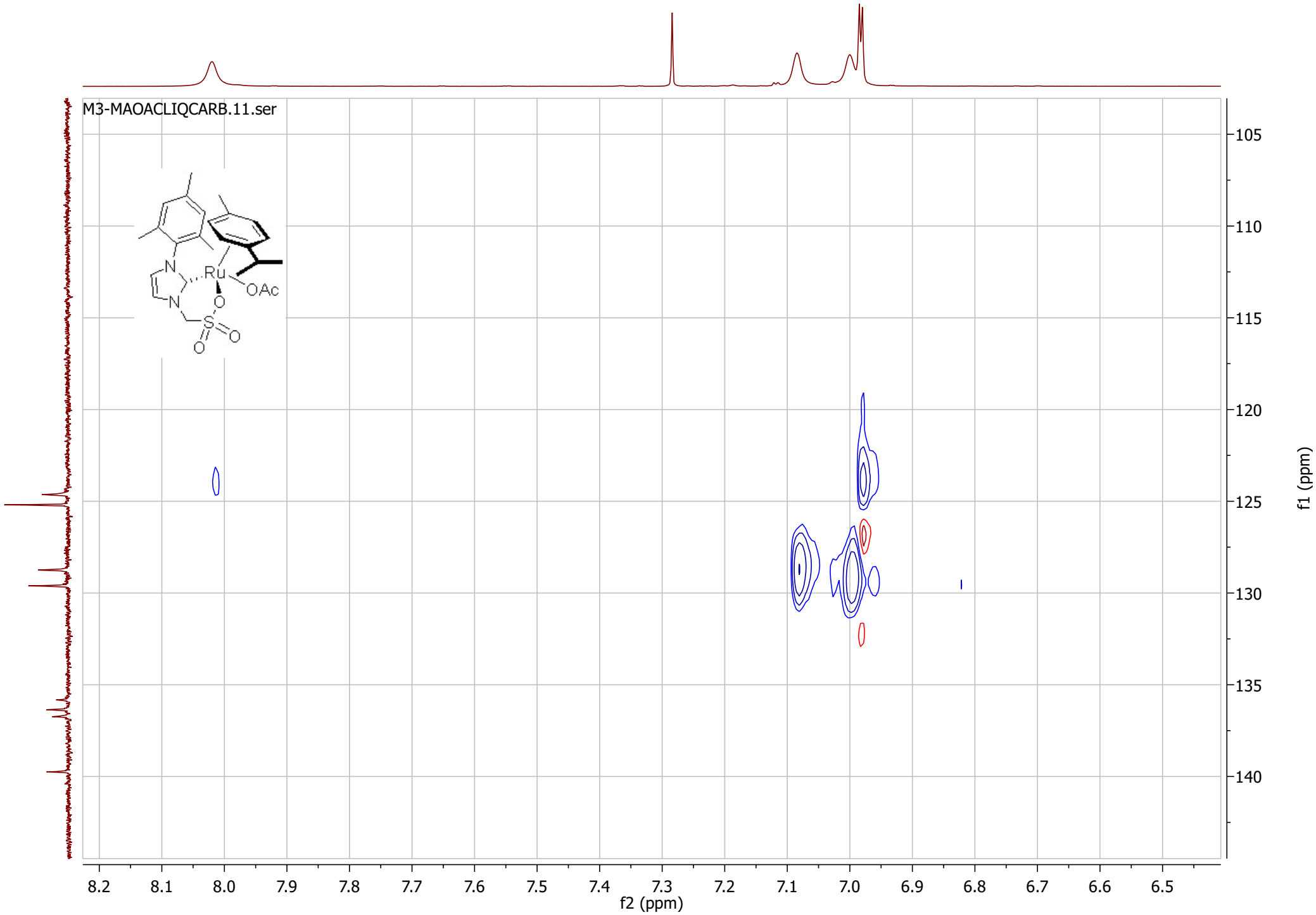
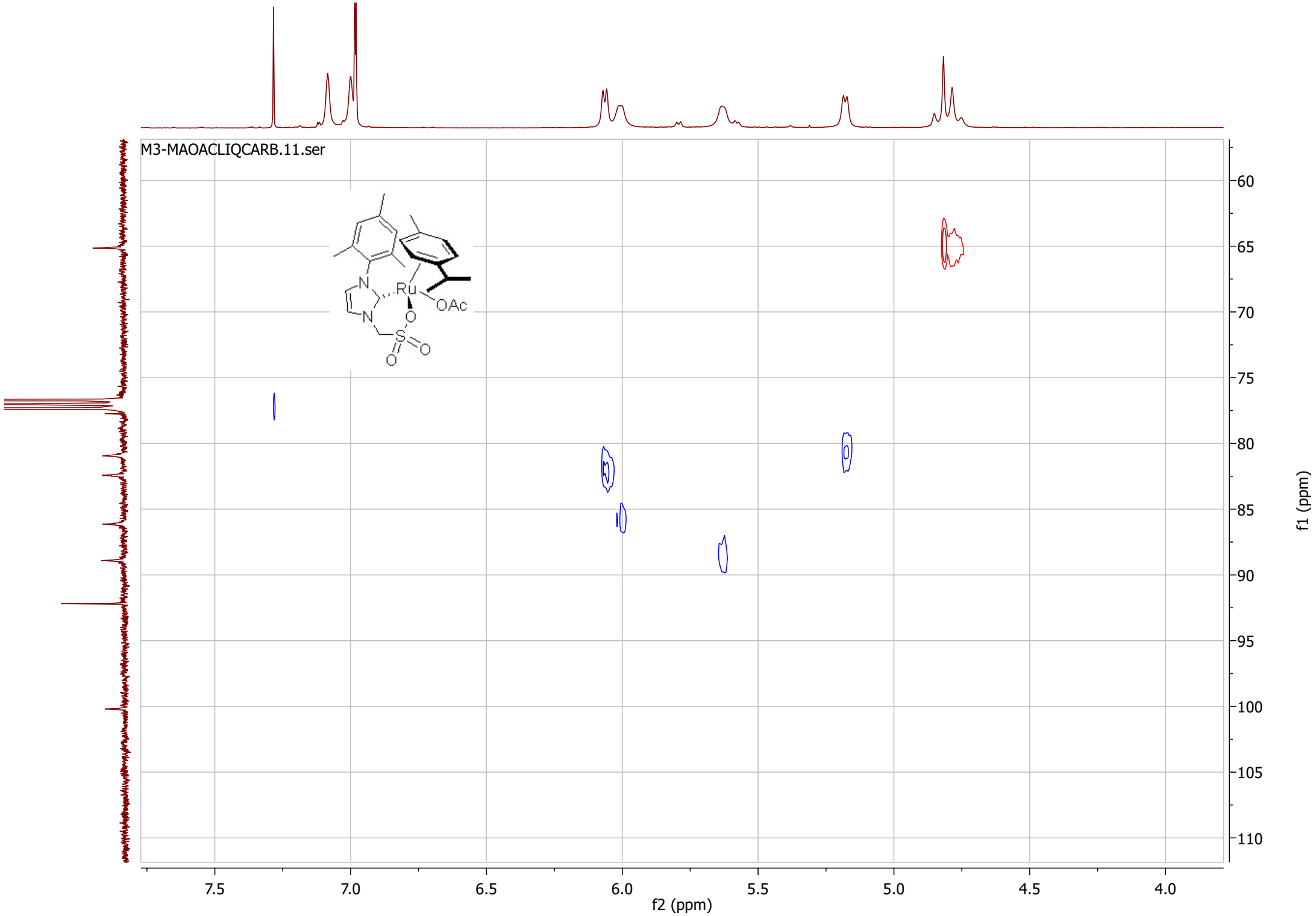
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)


M3-MAOACLIQCARB.11.ser
Ru
OAc
N
N
O
S
O
O
O
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f2 (ppm)
105
110
115
120
125
130
135
140
f1 (ppm)


M3-MAOACLIQCARB.11.ser
Ru
OAc
N
N
O
S
O
O
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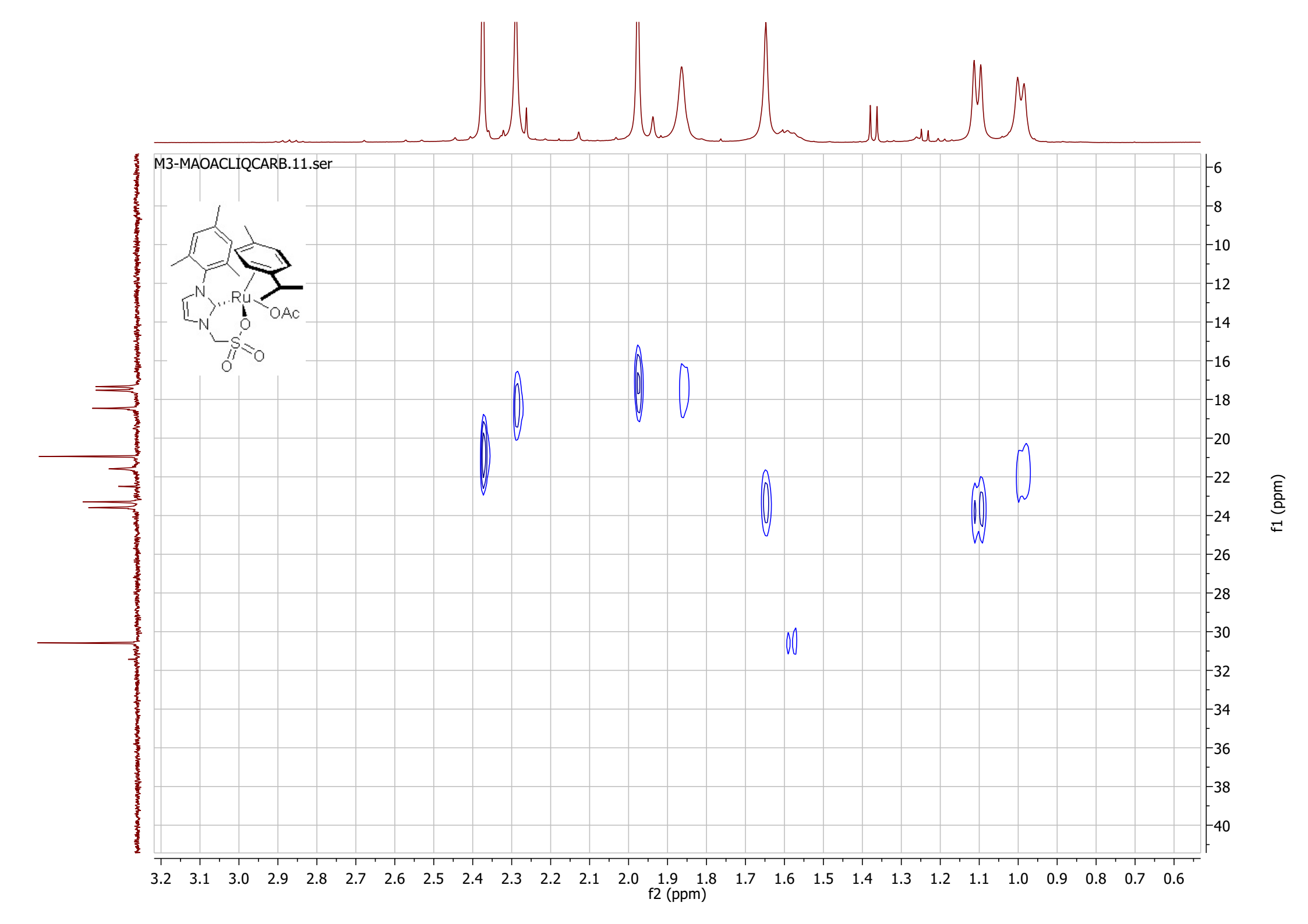
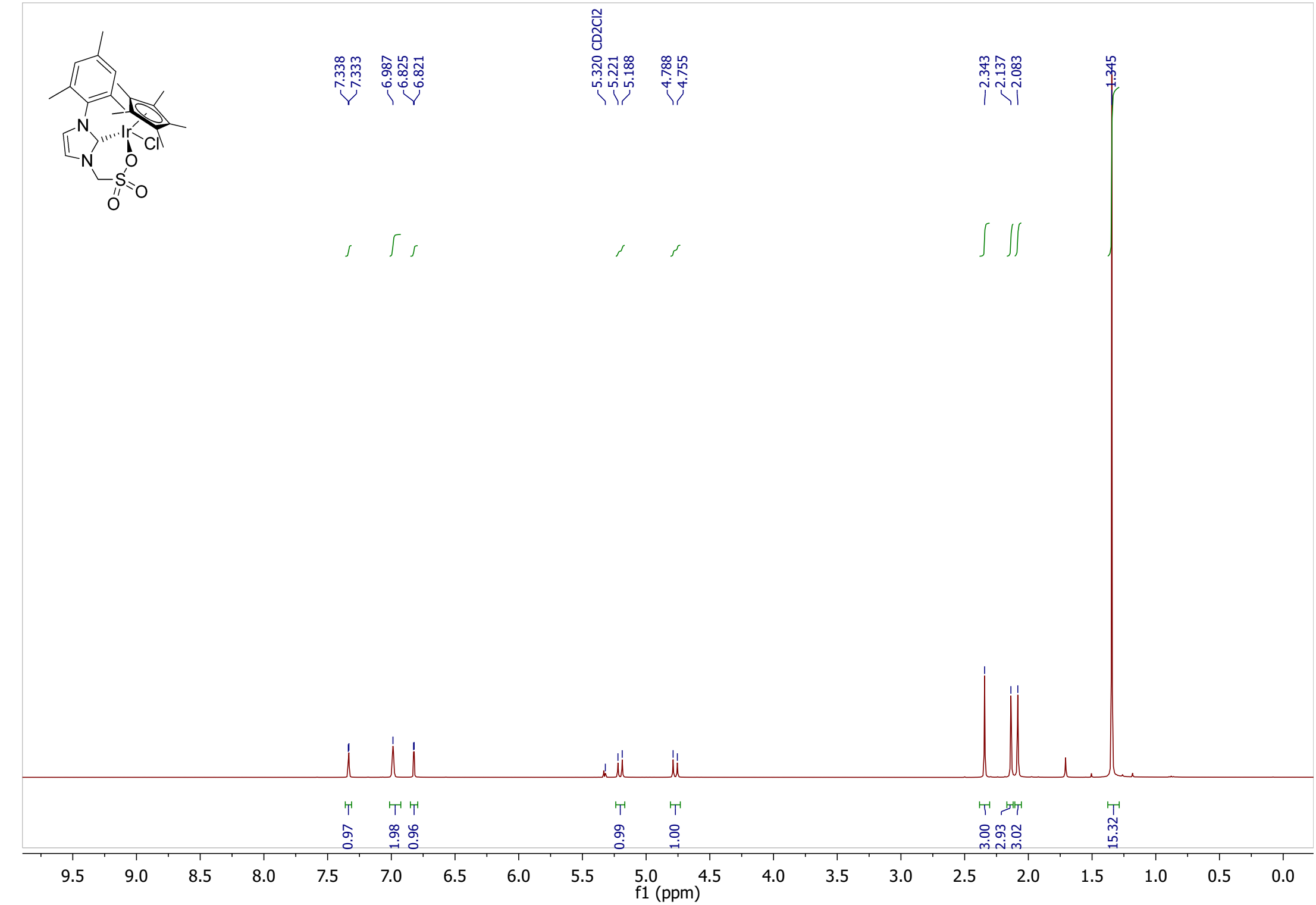
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f2 (ppm)
60
65
70
75
80
85
90
95
100
105
110
f1 (ppm)


M3-MAOACLIQCARB.11.ser
Ru
OAc
N
N
O
S
O
O
O
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
f2 (ppm)
6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
f1 (ppm)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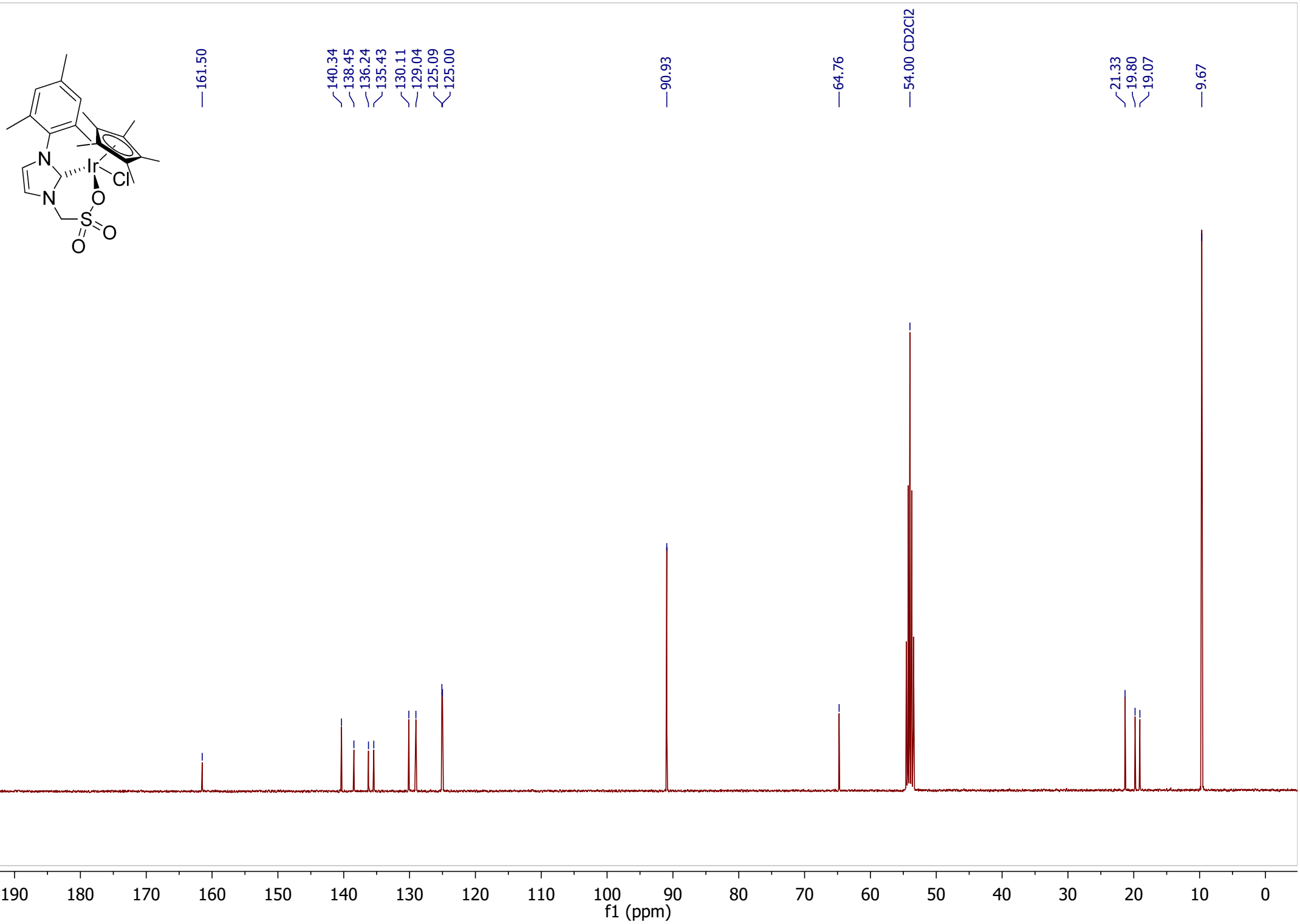
6.821
5.320 CD2Cl2
5.221
5.188
4.788
4.755
2.343
2.137
2.083
1.345
0.97
1.98
0.96
0.99
1.00
3.00
2.93
3.02
15.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.50
140.34
138.45
136.24
135.43
130.11
129.04
125.09
125.00
90.93
64.76
54.00 CD2Cl2
21.33
19.80
19.07
9.67
N
Ir
Cl
N
O
S
O
O
O
190
180
170
160
150
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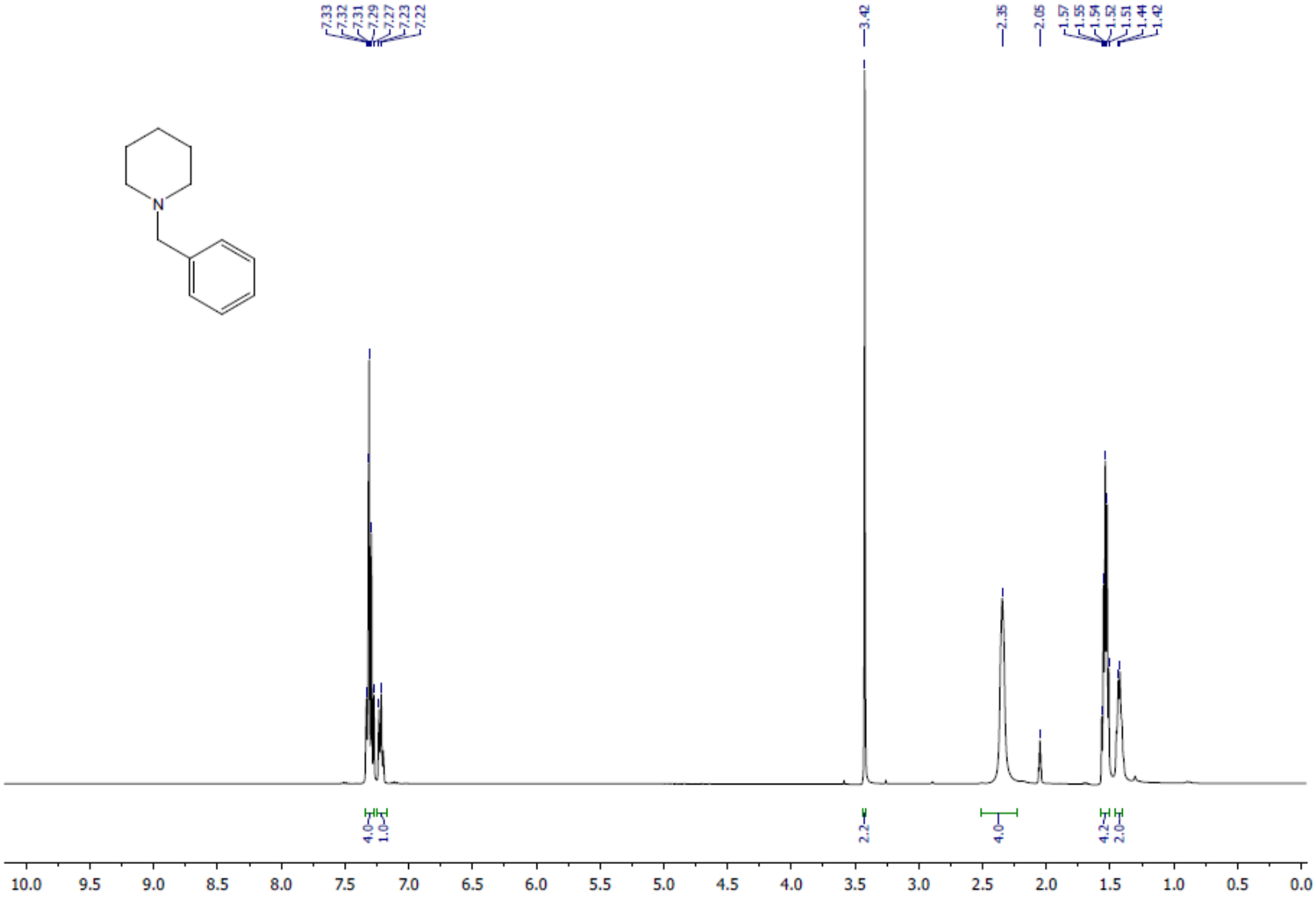
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.29
7.27
7.23
7.22
3.42
2.35
2.05
1.57
1.55
1.54
1.52
1.51
1.44
1.42
N
4.0
1.0
2.2
4.0
4.2
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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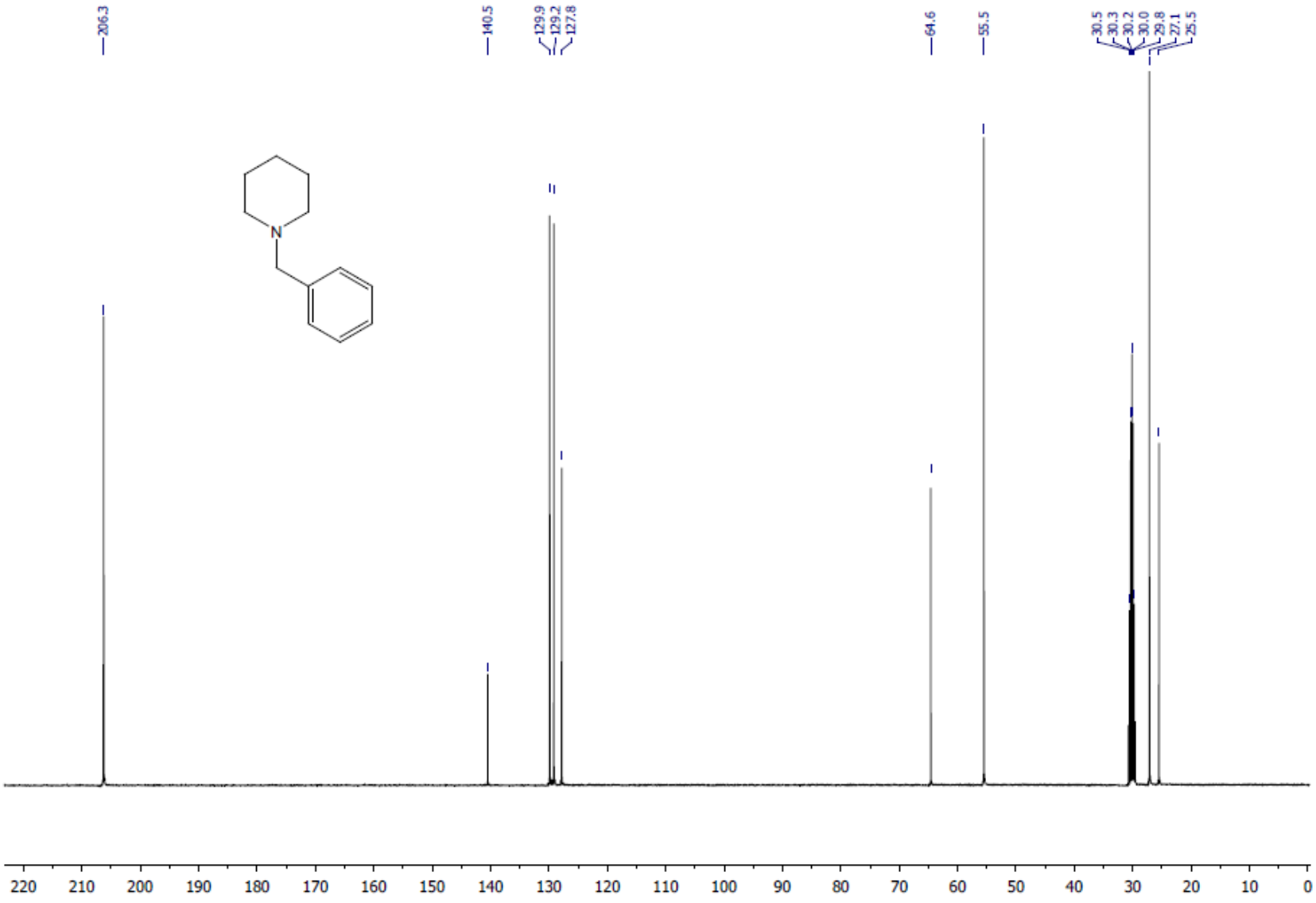
0.0


206.3
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129.9
129.2
127.8
64.6
55.5
30.5
30.3
30.2
30.0
29.8
27.1
25.5
N
220
210
200
190
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150
140
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120
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70
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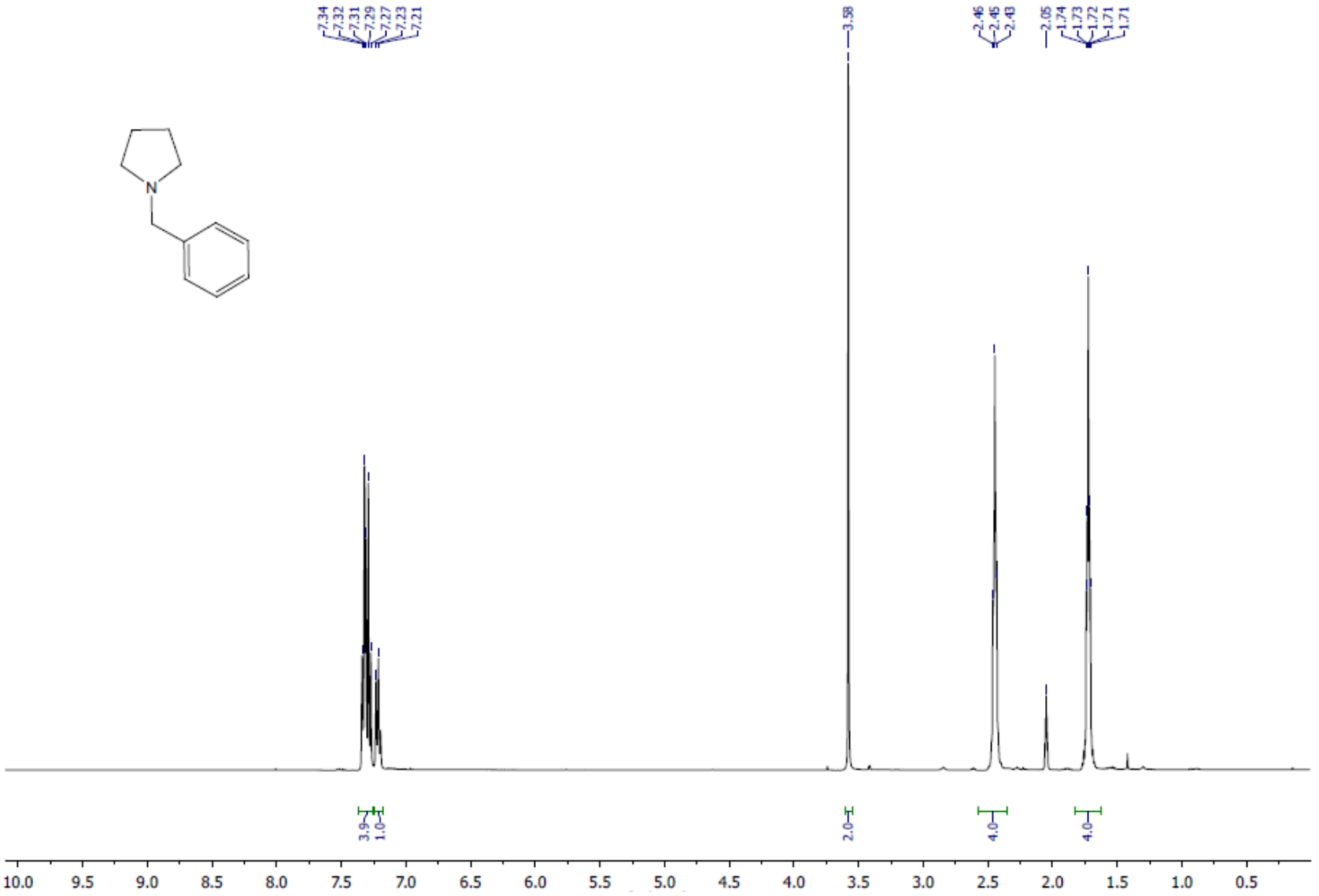
30
20
10
0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7.32
7.31
7.29
7.27
7.23
7.21
3.58
2.46
2.45
2.43
2.05
1.74
1.73
1.72
1.71
1.71
N
3.9
1.0
2.0
4.0
4.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


206.260
141.215
129.563
129.150
127.724
61.208
54.855
30.687
30.494
30.302
30.110
29.917
29.725
29.533
24.477
N
220
210
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70
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10
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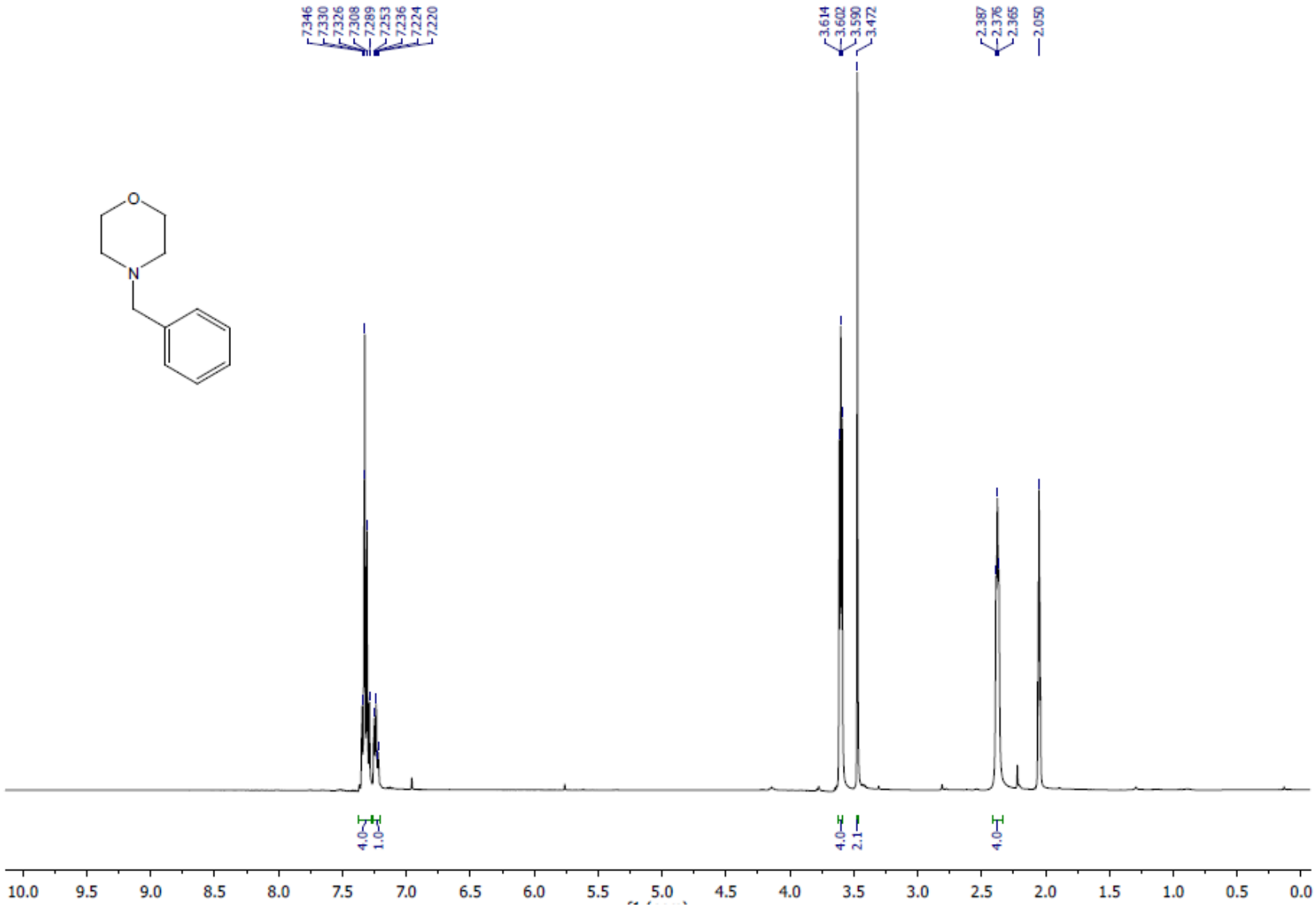
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7.224
7.220
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3.602
3.590
3.472
2.387
2.376
2.365
2.050
O
N
4.0
1.0
4.0
2.1
4.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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2.5
2.0
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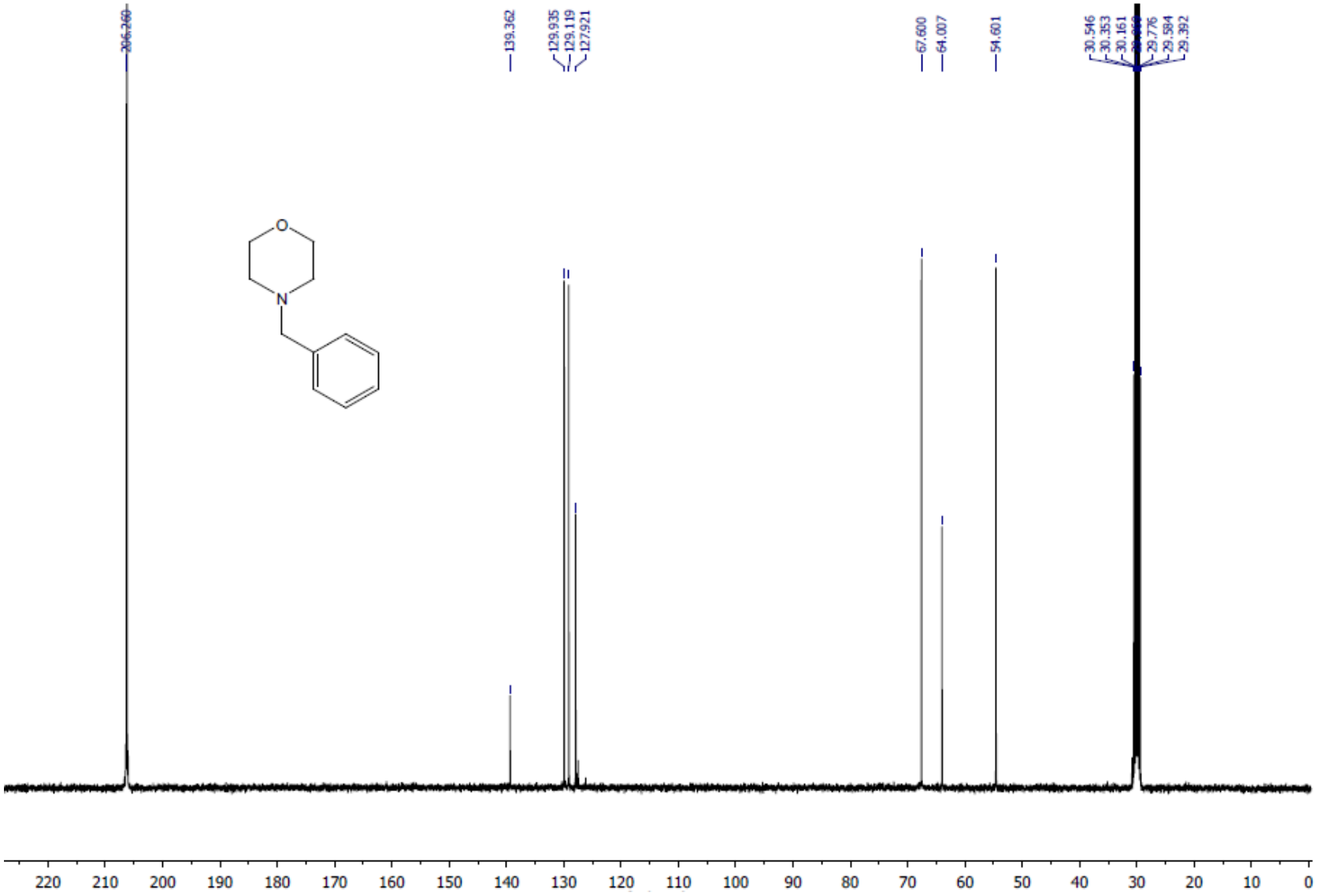
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29.584
29.392
O
N
220
210
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150
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130
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70
60
50
40
30
20
10
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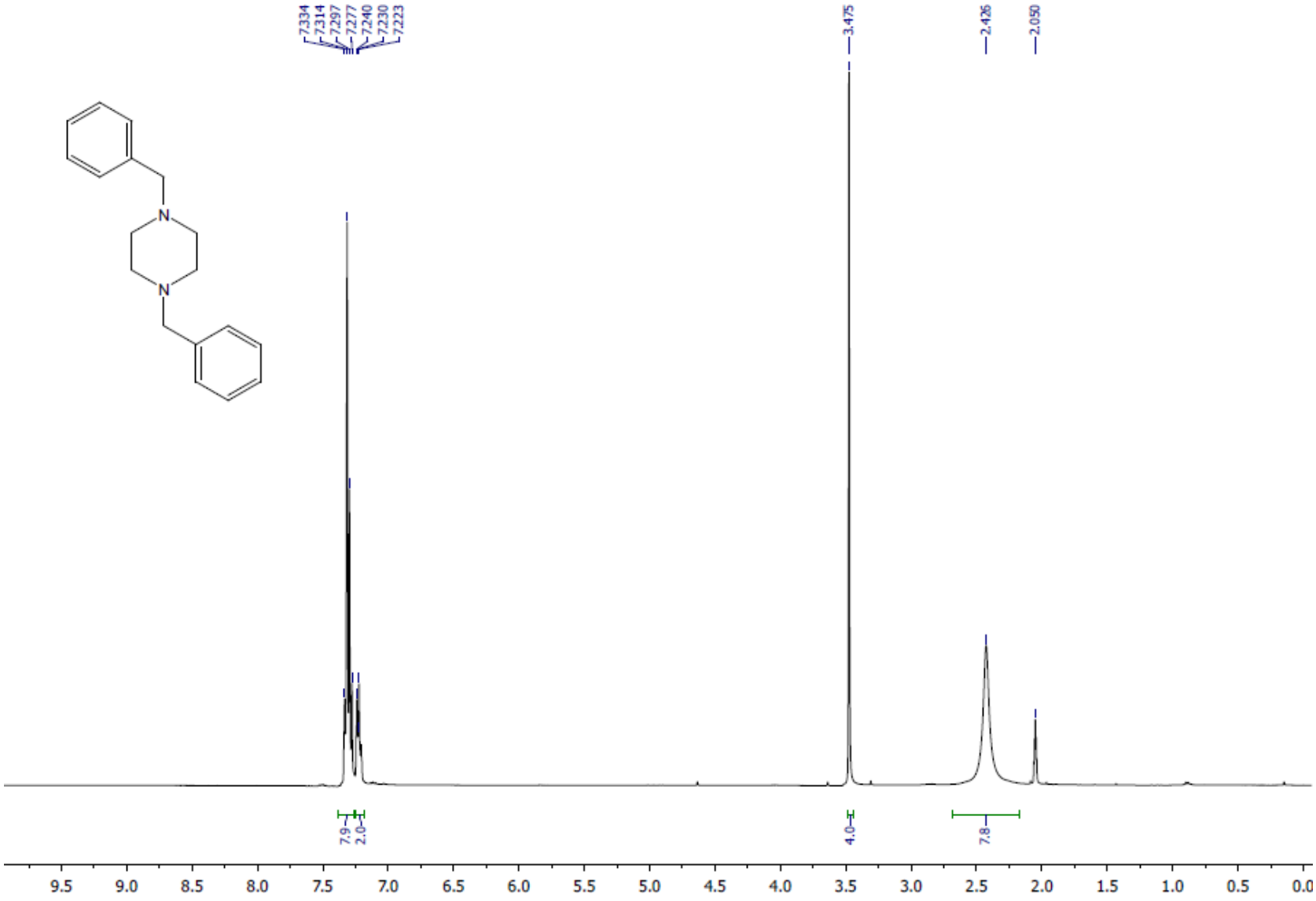
7334
7314
7297
7277
7240
7230
7223
3.475
2.426
2.050
N
N
7.9
2.0
4.0
7.8
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


206.260
139.951
129.904
129.168
127.890
63.727
54.213
30.663
30.471
30.279
30.086
29.894
29.701
29.509
N
N
220
210
200
190
180
170
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150
140
130
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110
100
90
80
70
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30
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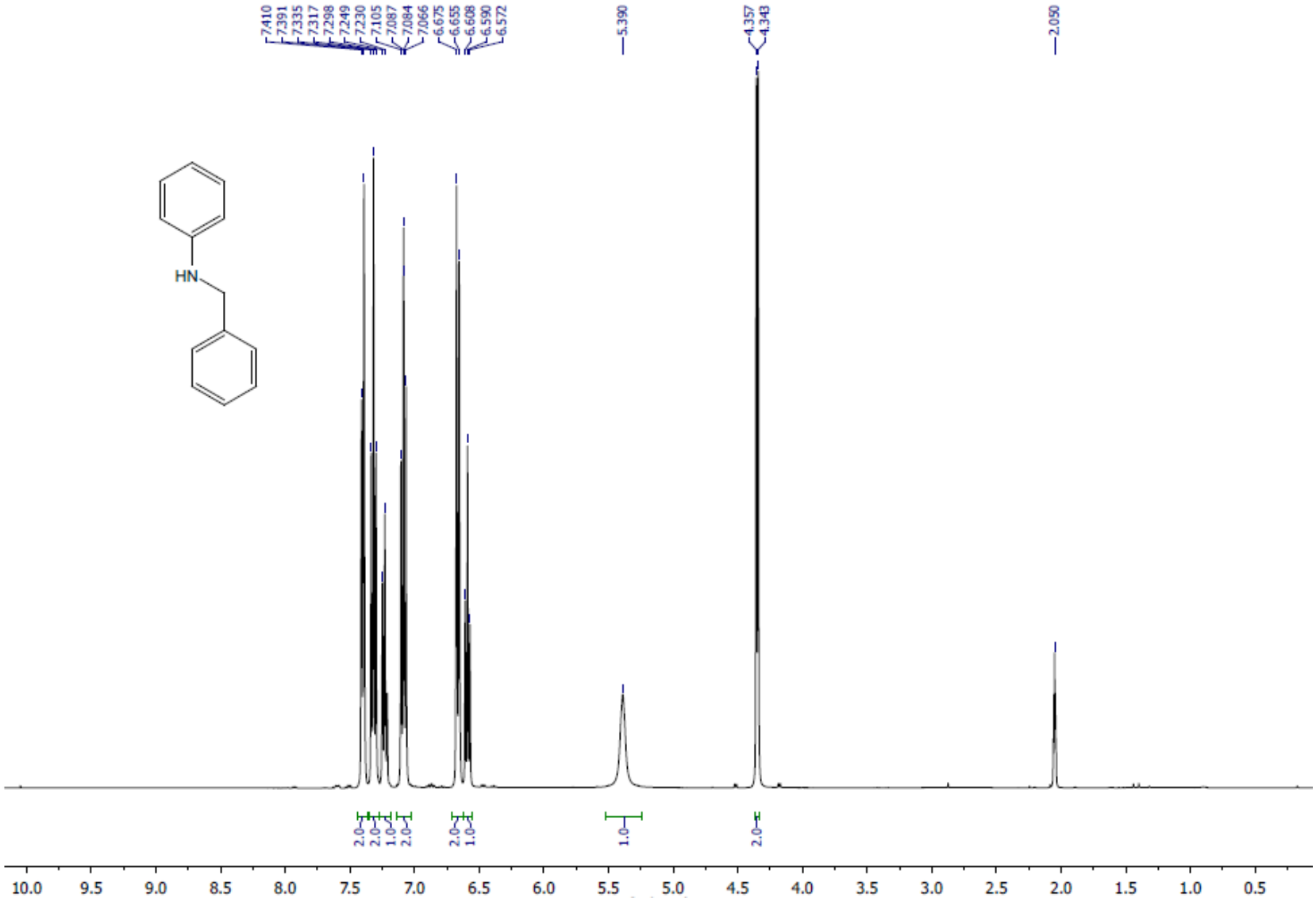
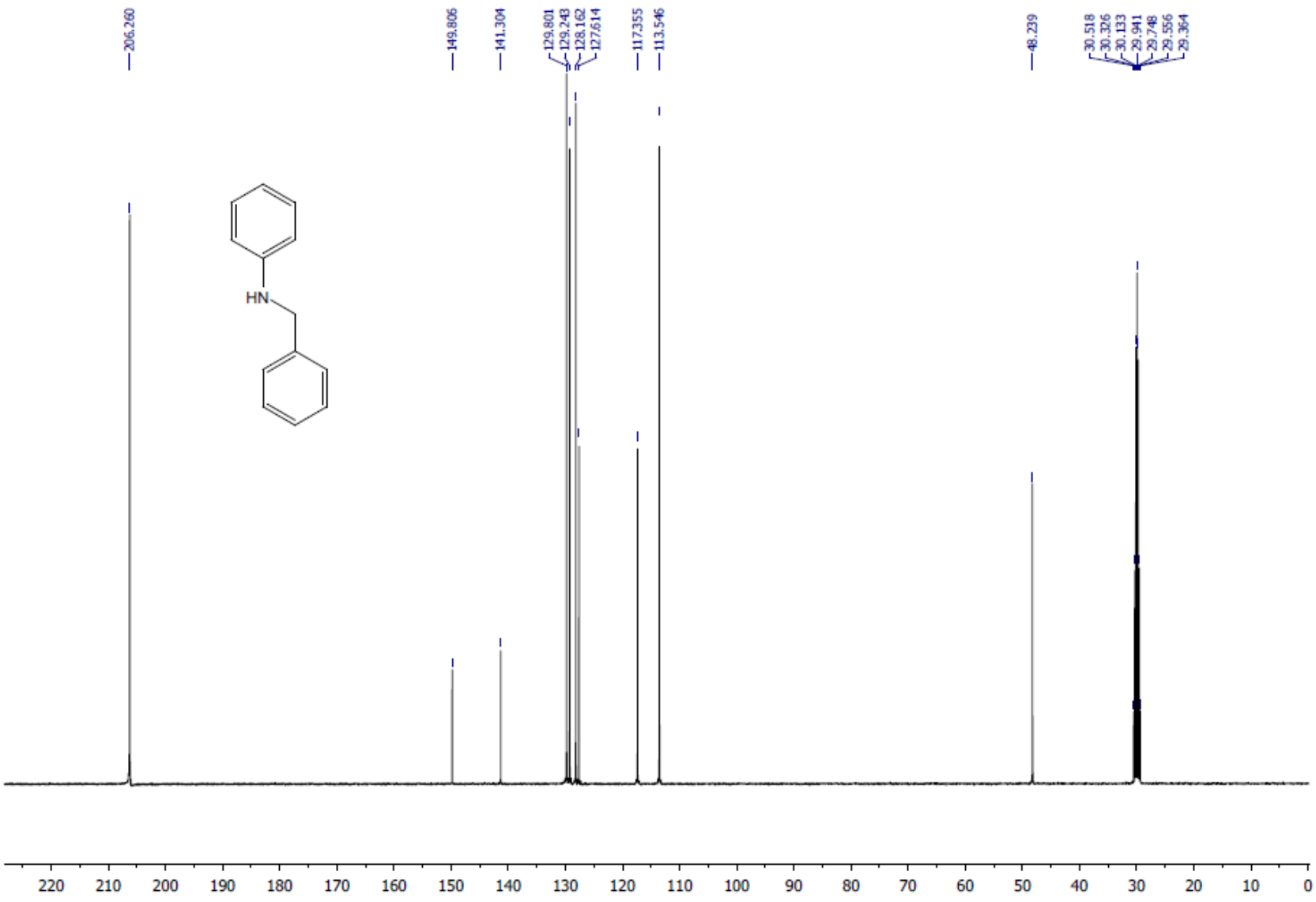
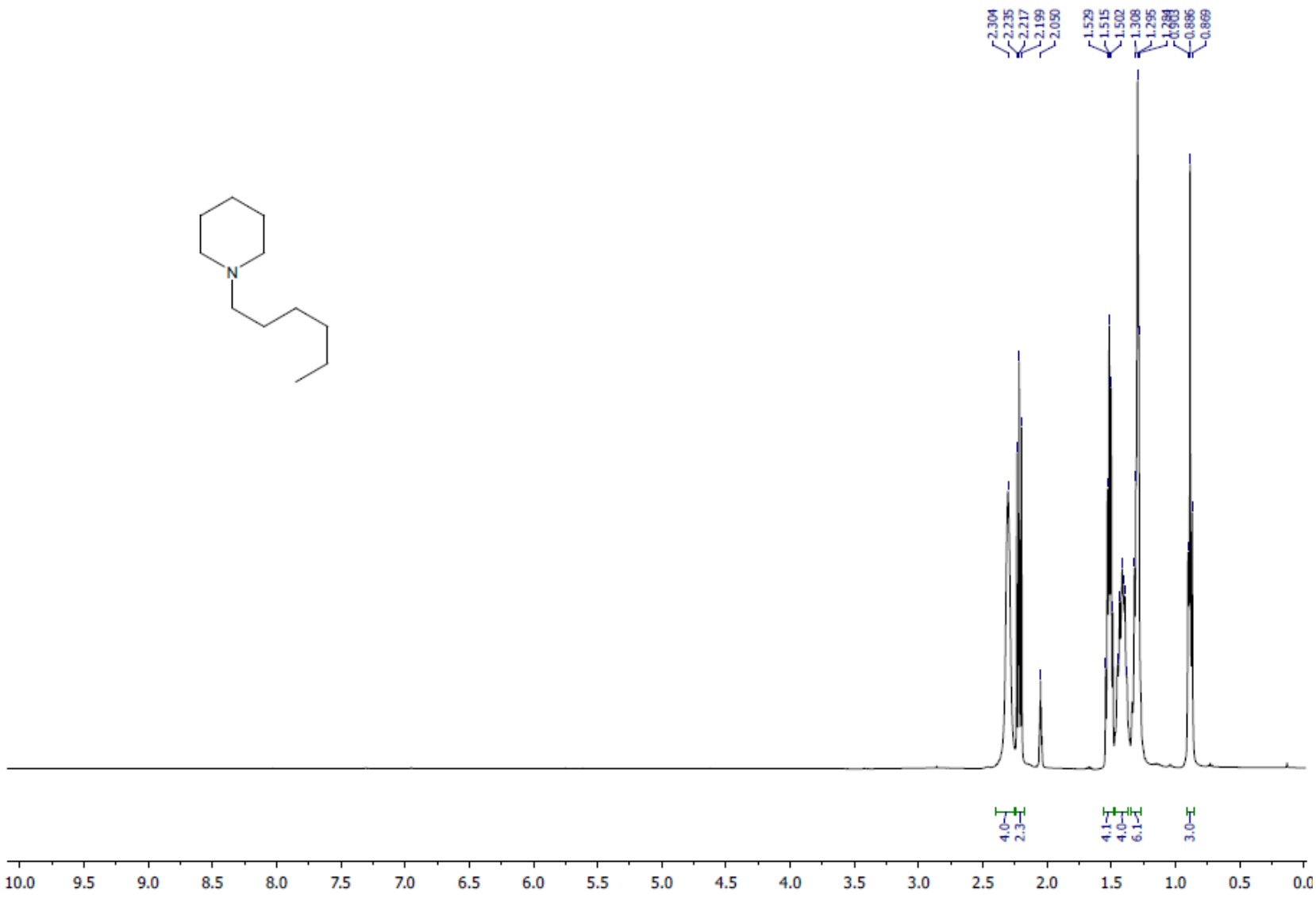
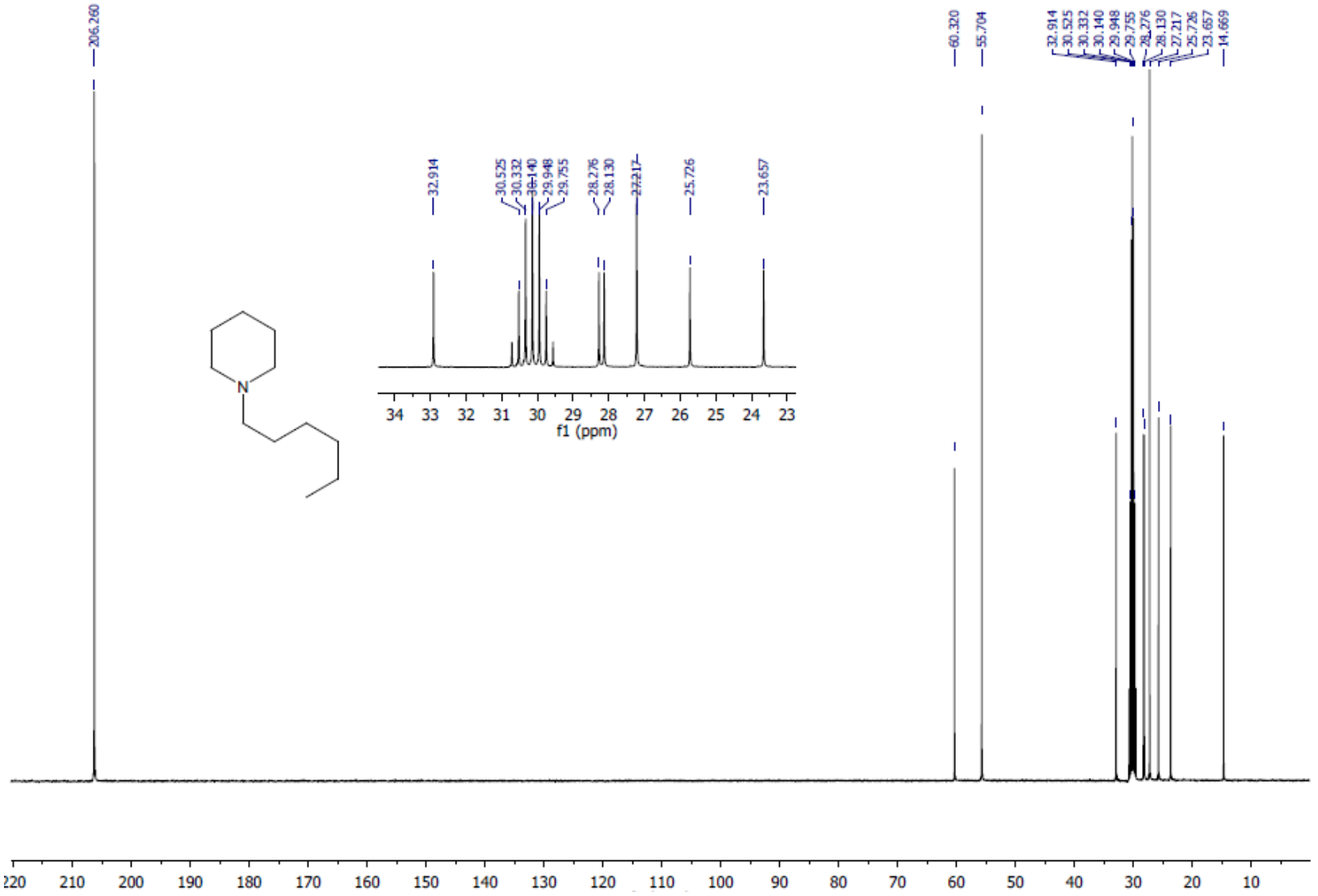
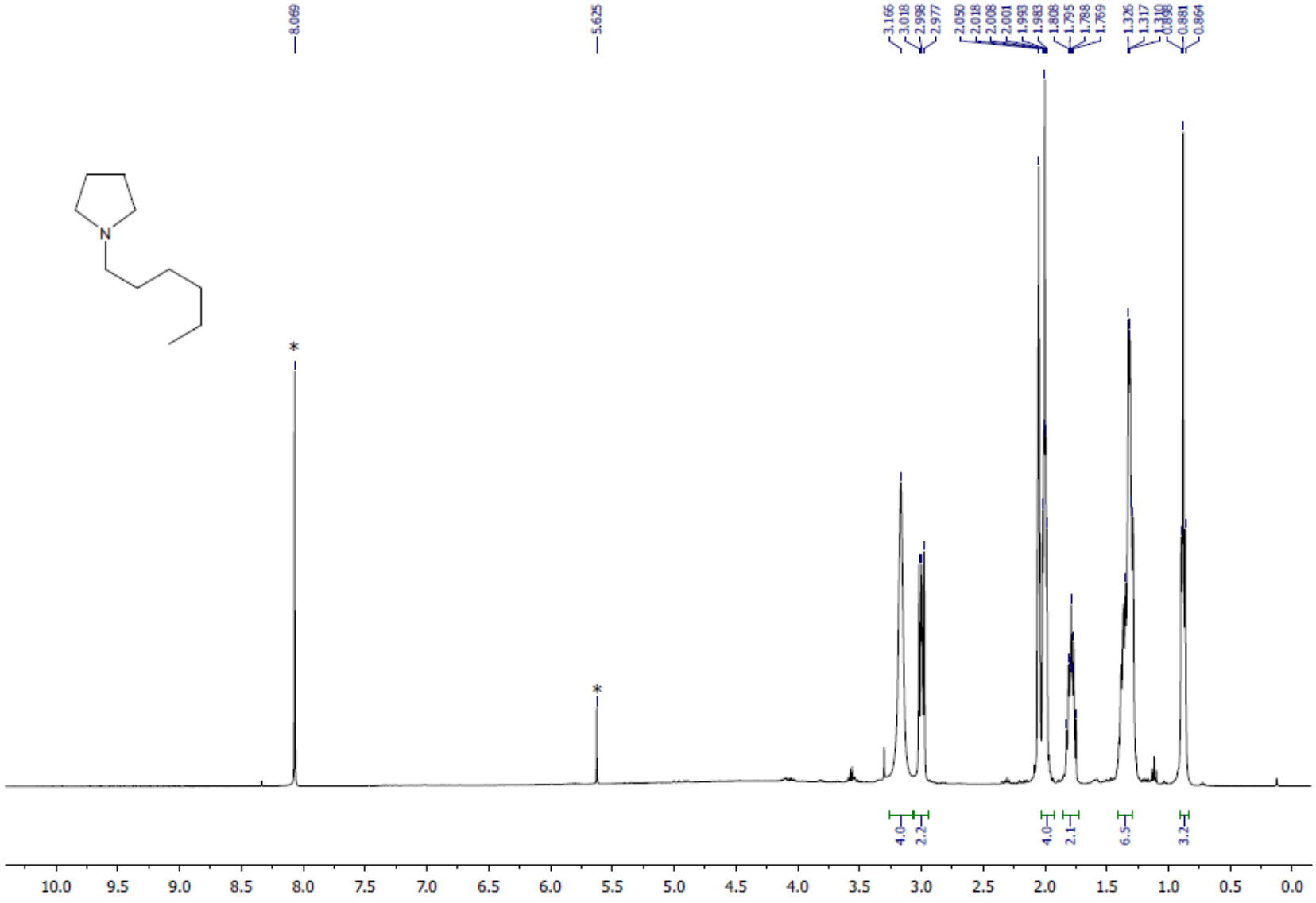
10
0


7.410
7.391
7.335
7.317
7.298
7.249
7.230
7.105
7.087
7.084
7.066
6.675
6.655
6.608
6.590
6.572
5.390
4.357
4.343
2.050
HN
2.0
2.0
1.0
2.0
2.0
1.0
1.0
2.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

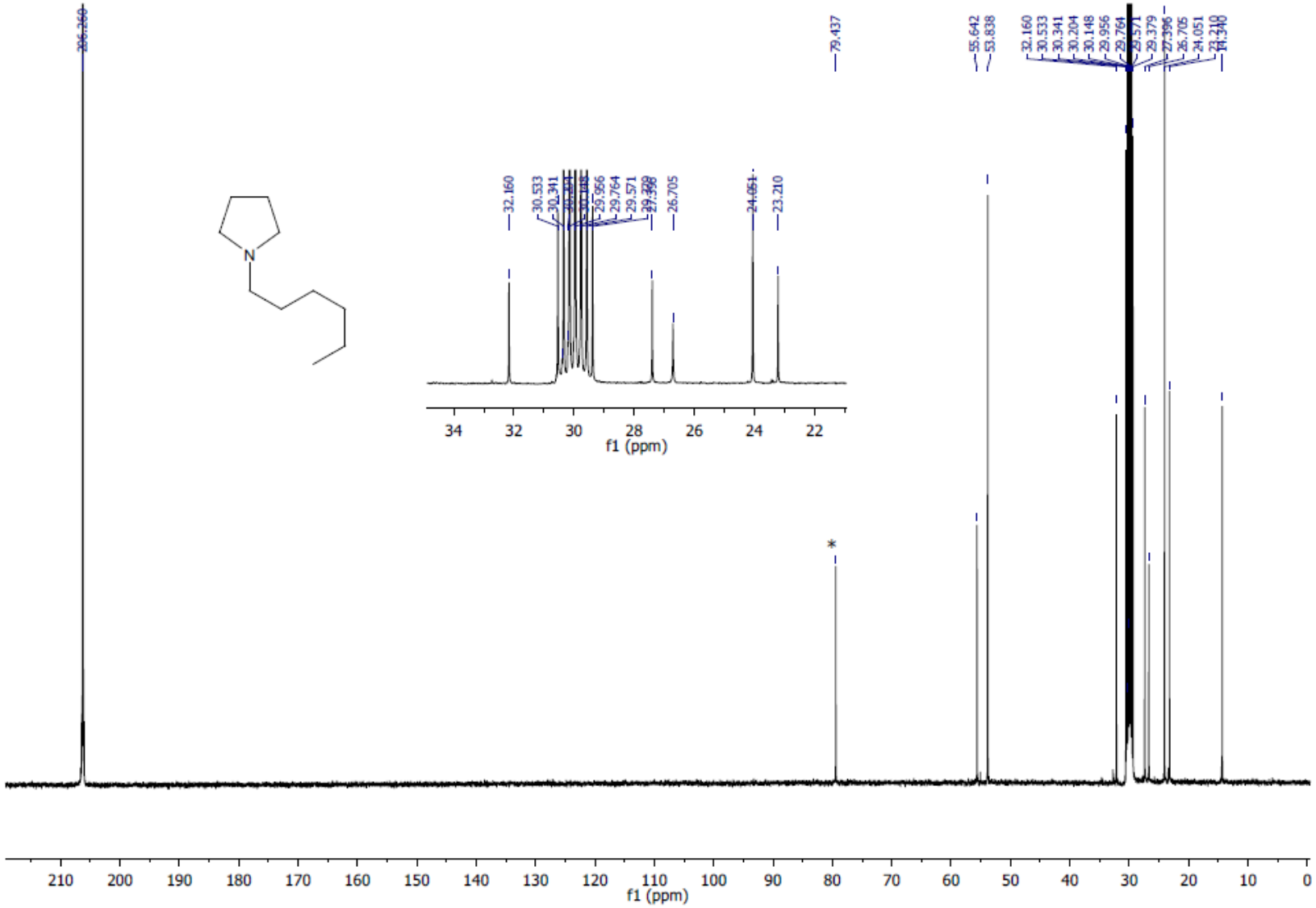

206.260
149.806
141.304
129.801
129.243
128.162
127.614
117.355
113.546
48.239
30.518
30.326
30.133
29.941
29.748
29.556
29.364
HN
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


2.304
2.235
2.217
2.199
2.050
1.529
1.515
1.502
1.308
1.295
0.886
0.869
N
4.0
2.3
4.1
4.0
6.1
3.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

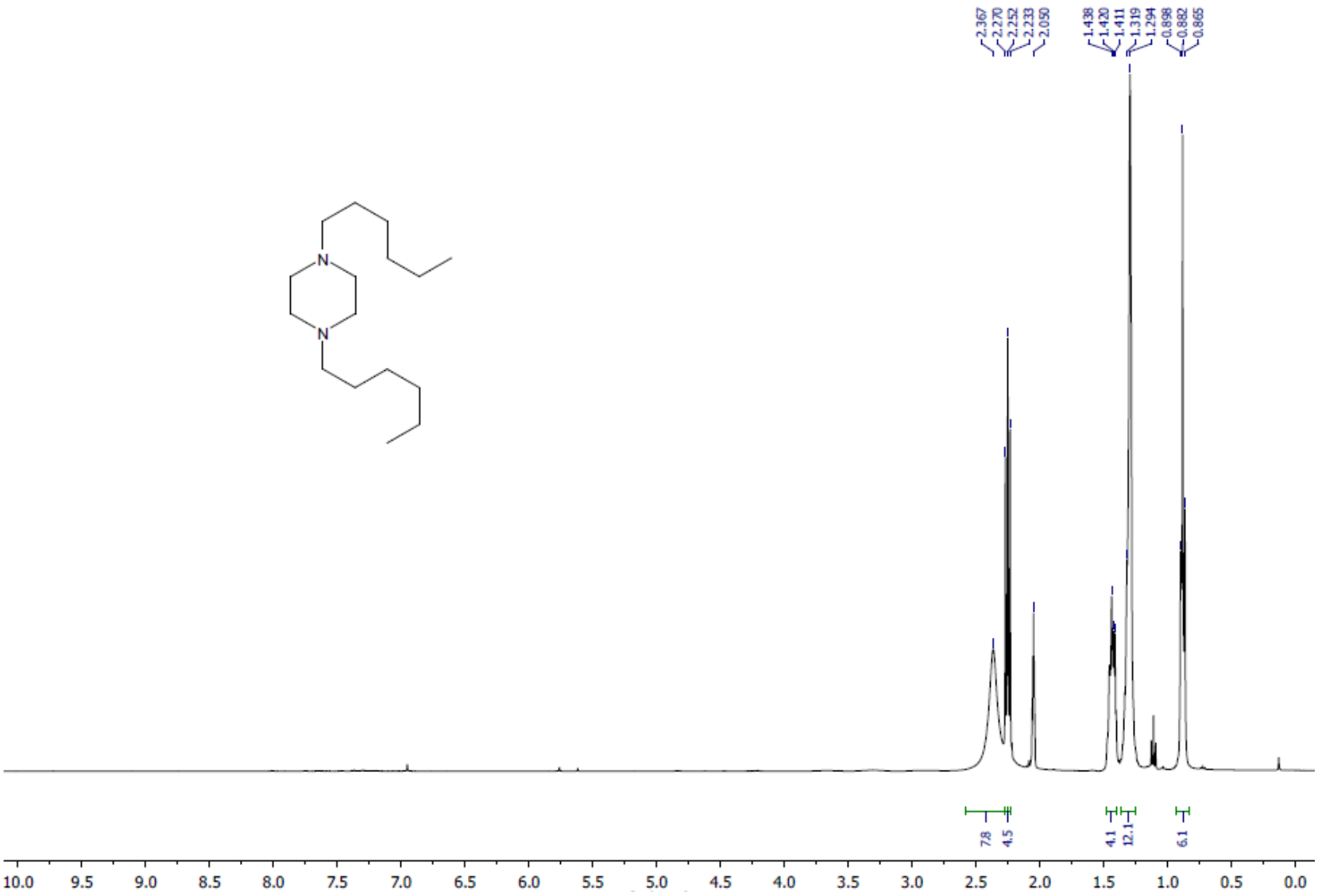

206.260
60.320
55.704
32.914
30.525
30.332
30.140
29.948
29.755
28.276
28.130
27.217
25.726
23.657
14.669
f1 (ppm)
N



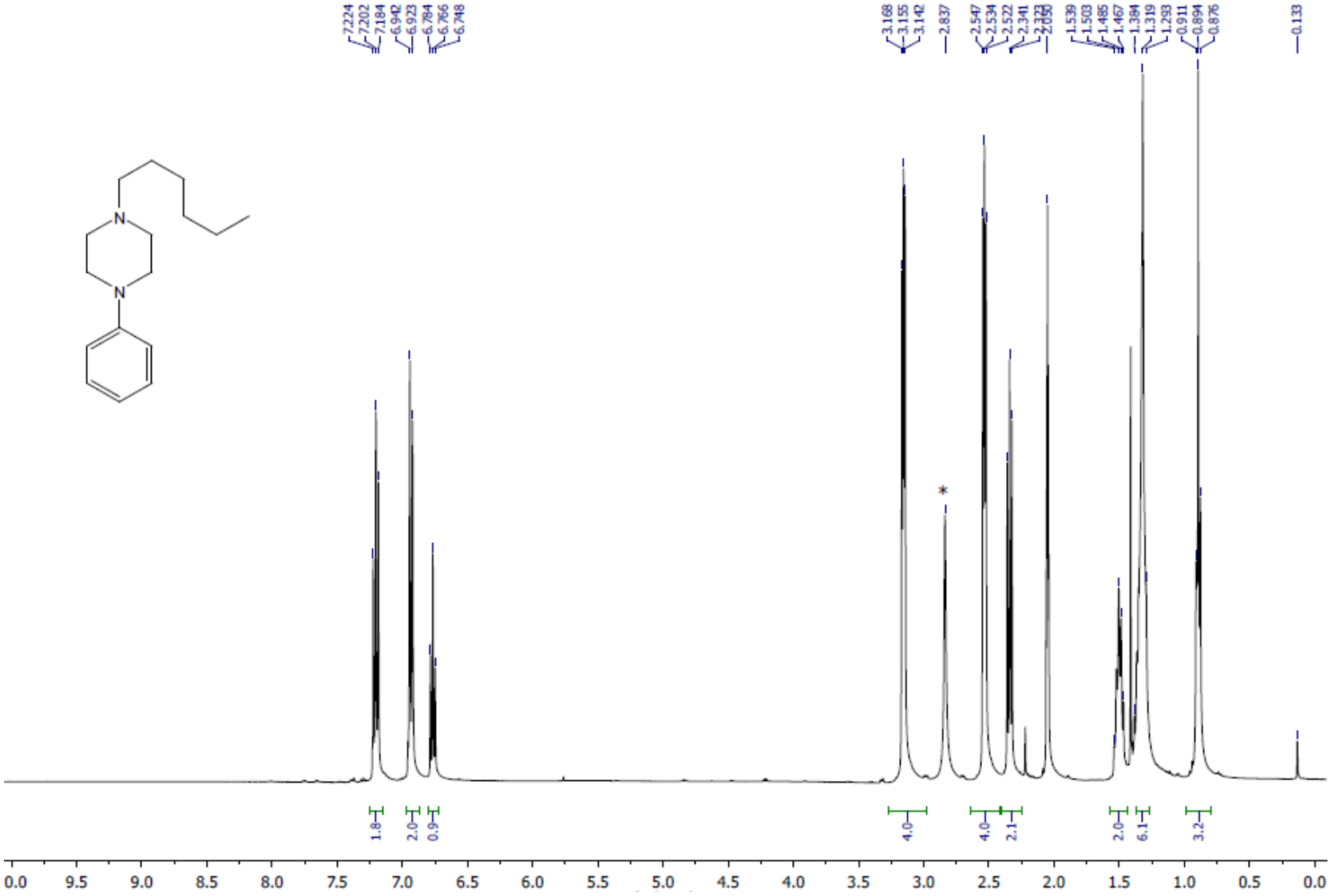

* solvent signals



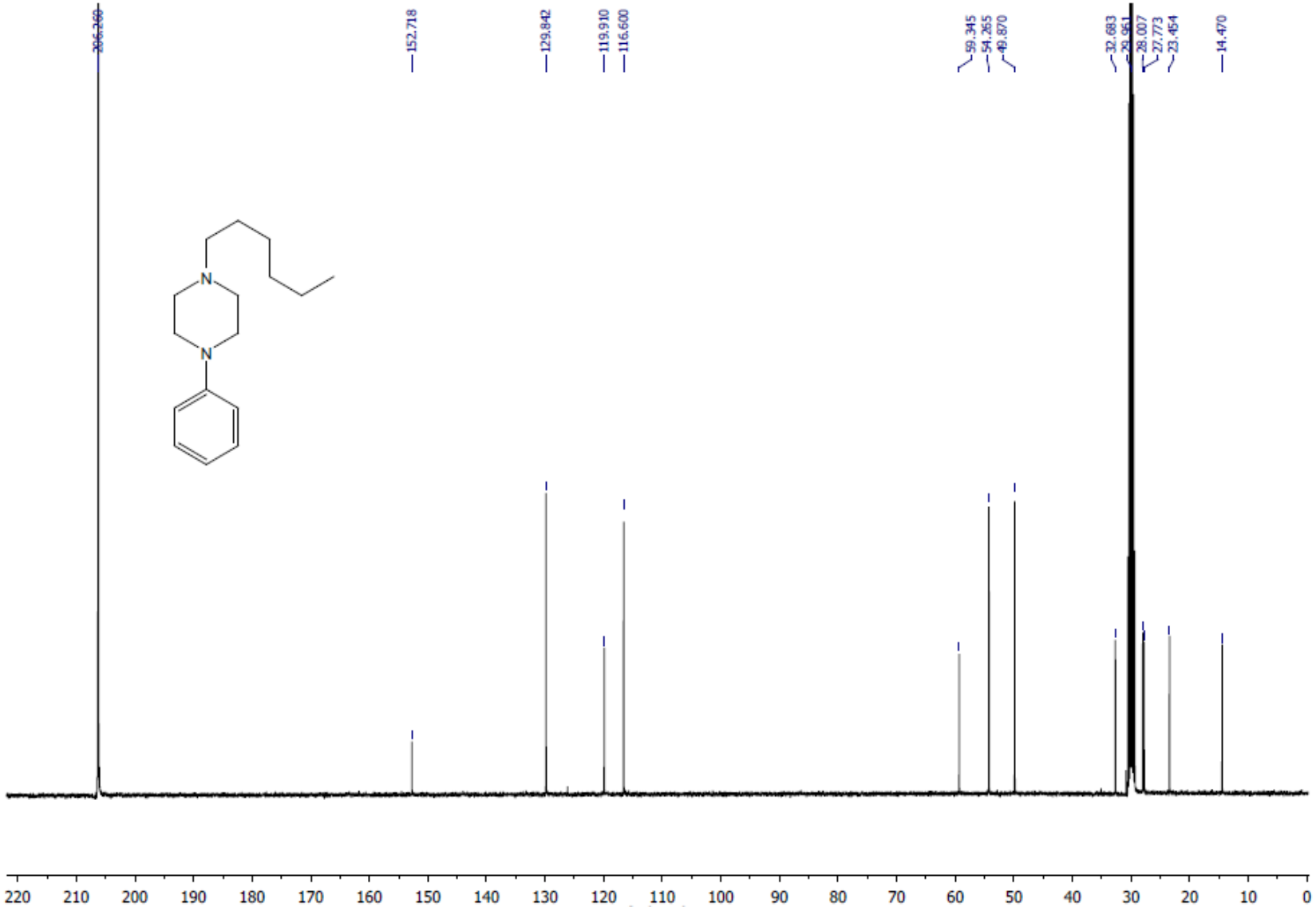

*solvent signals

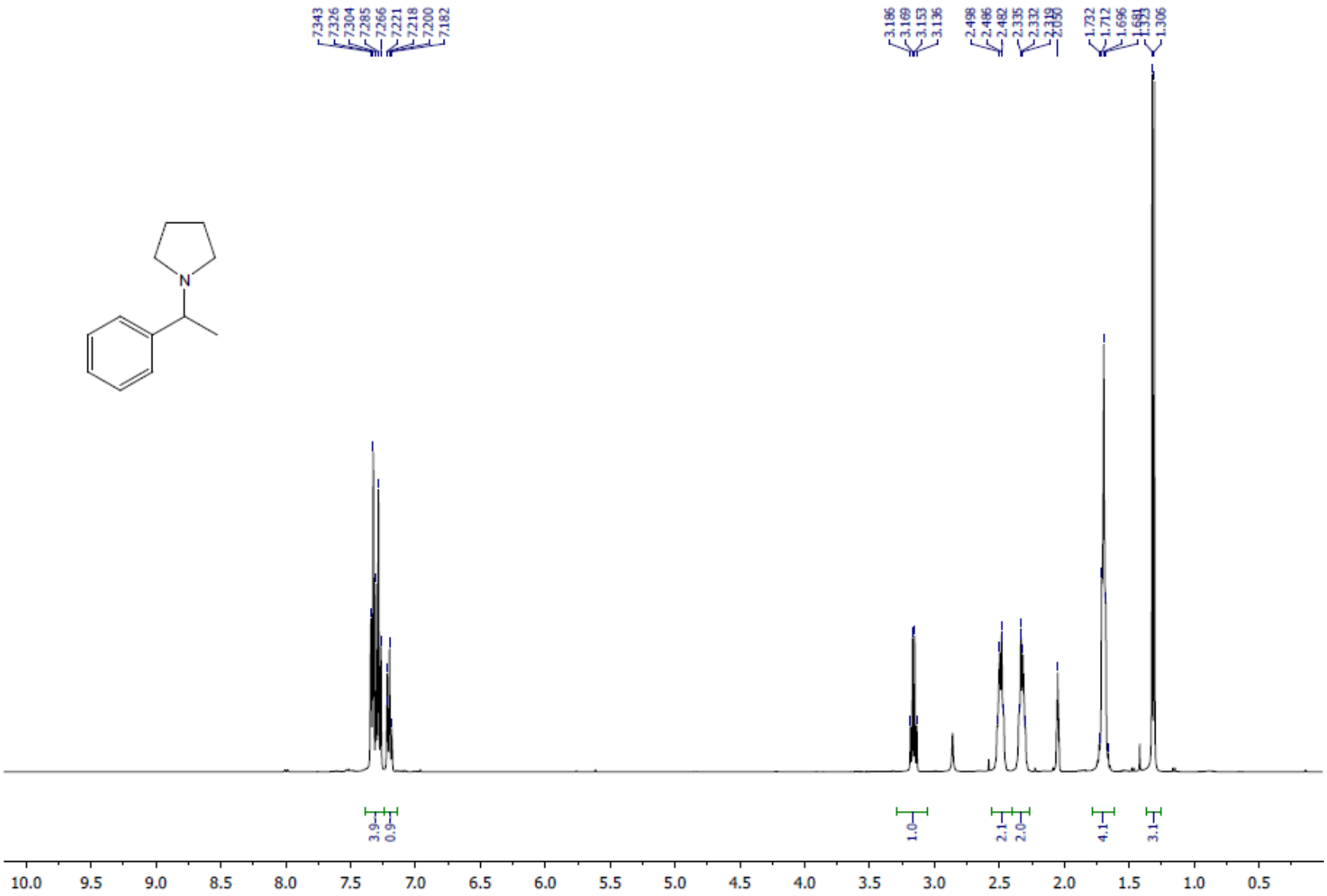

2.367
2.270
2.252
2.233
2.050
1.438
1.420
1.411
1.319
1.294
0.898
0.882
0.865
7.8
4.5
4.1
12.1
6.1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

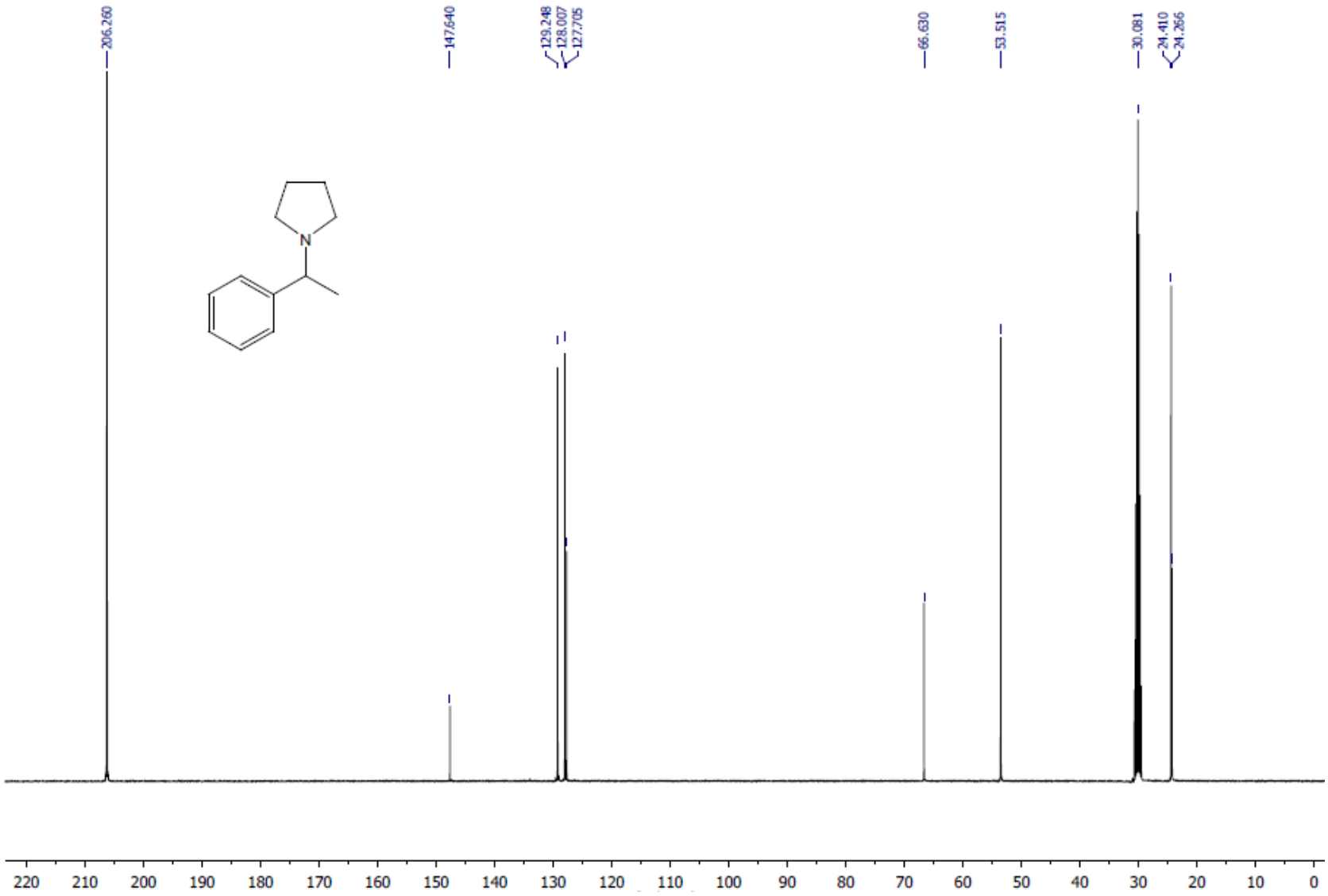

206.260
59.490
54.468
32.785
30.435
30.243
30.050
29.858
29.665
28.102
27.926
23.544
14.560
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

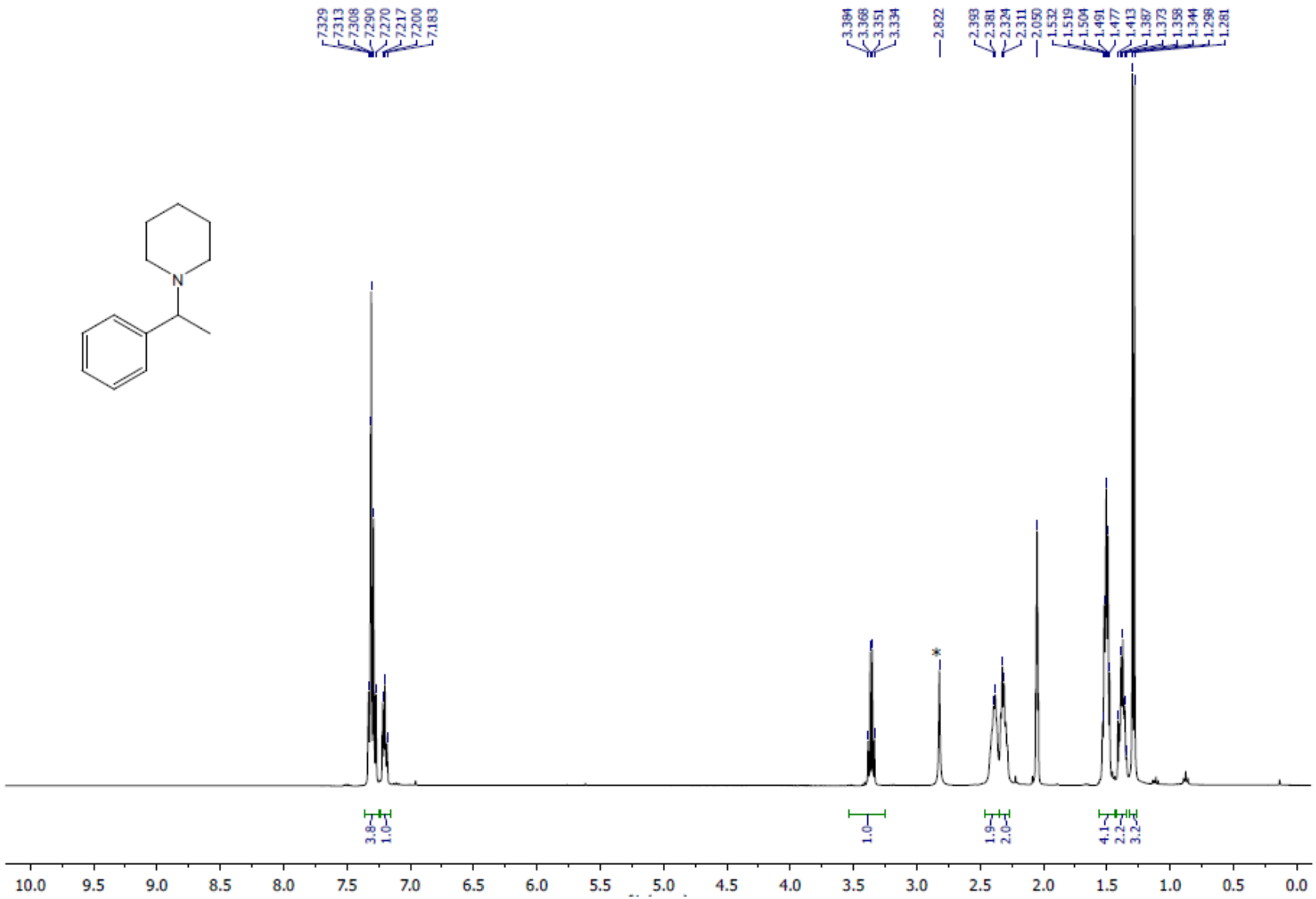



* signal from water

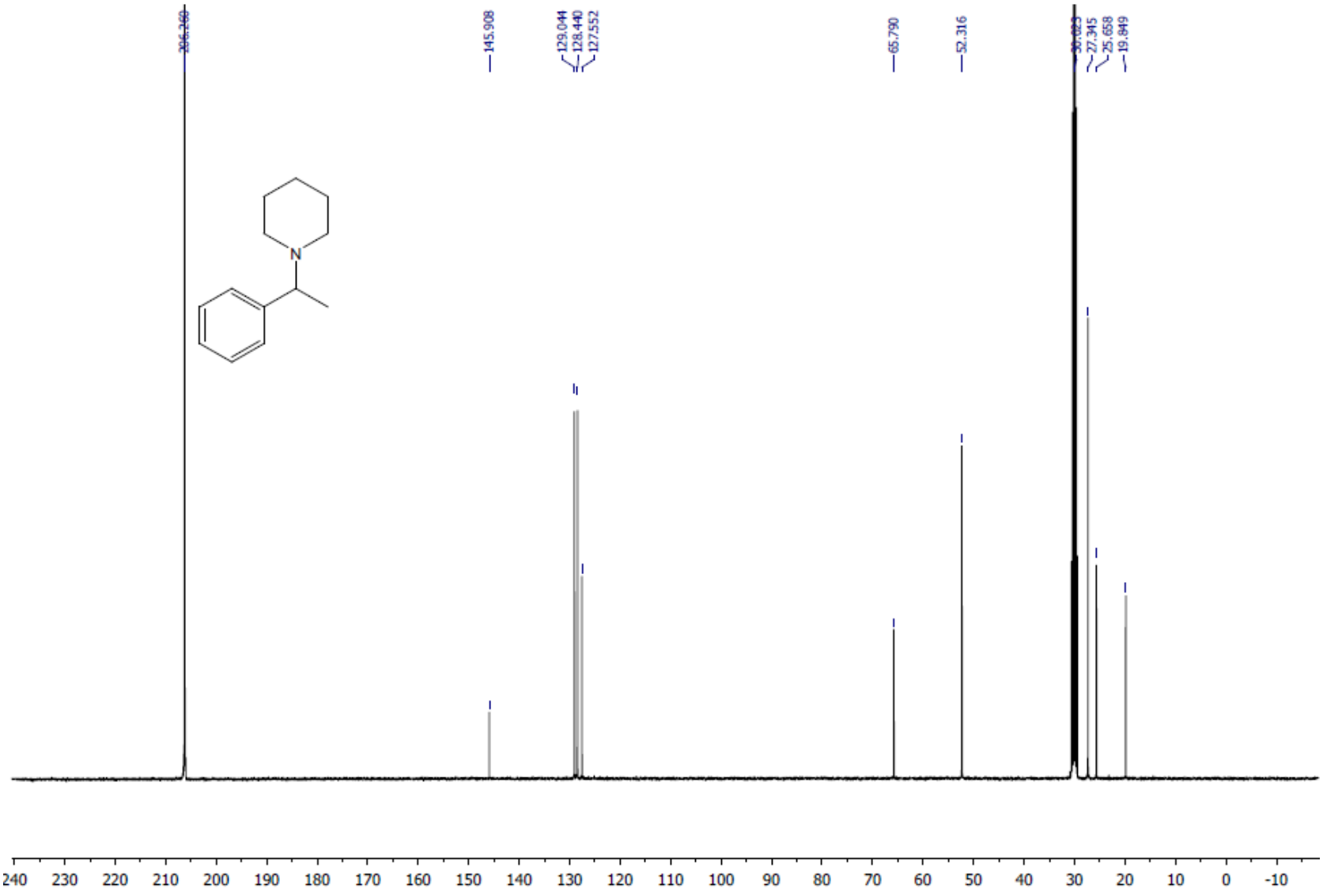

206.260
152.718
129.842
119.910
116.600
59.345
54.265
49.870
32.683
29.951
28.007
27.773
23.454
14.470
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

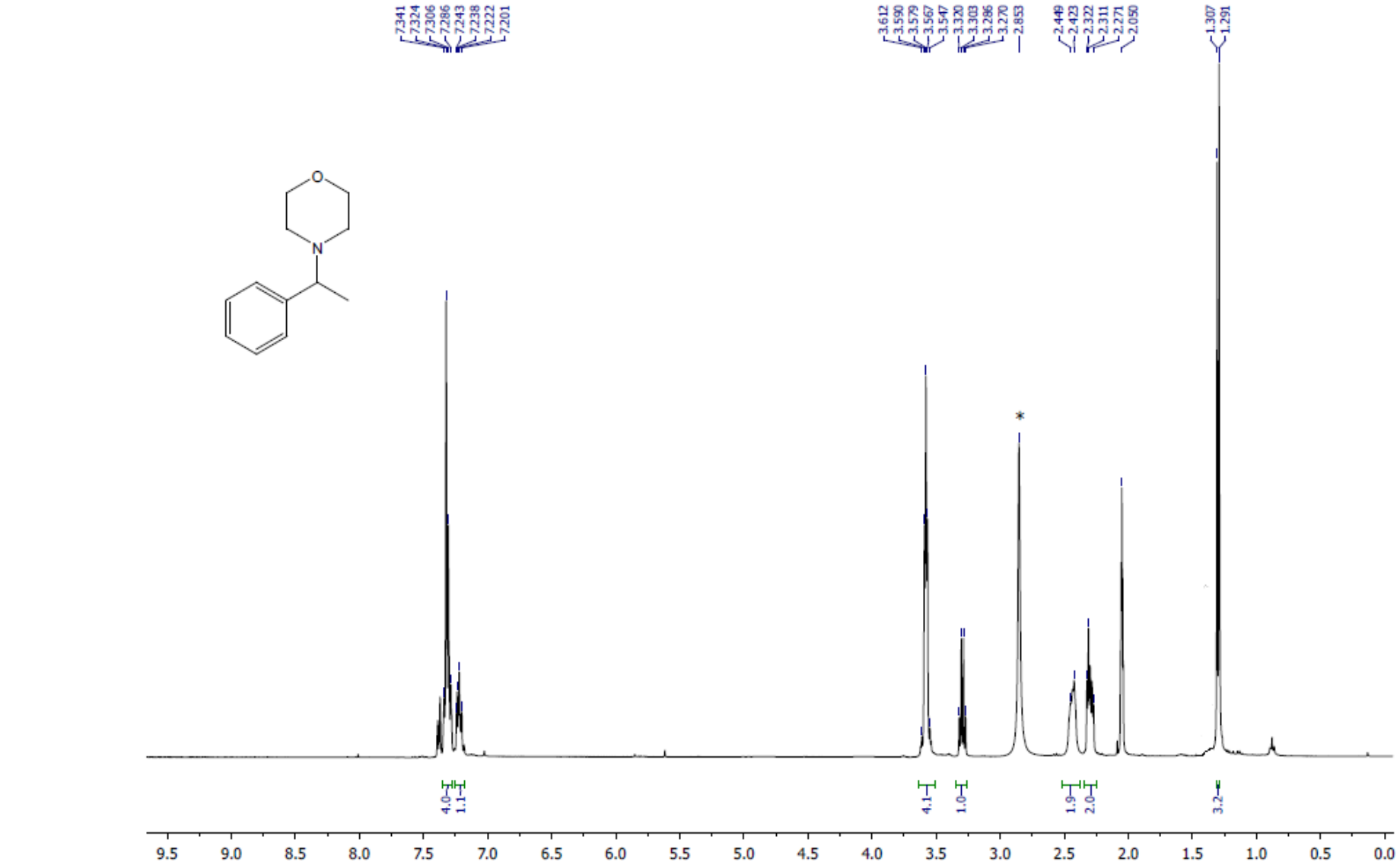

7.343
7.326
7.304
7.285
7.266
7.221
7.218
7.200
7.182
3.186
3.169
3.153
3.136
2.498
2.486
2.482
2.335
2.332
2.050
1.732
1.712
1.696
1.306
N
3.9
0.9
1.0
2.1
2.0
4.1
3.1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


206.260
147.640
129.248
128.007
127.705
66.630
53.515
30.081
24.410
24.366
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

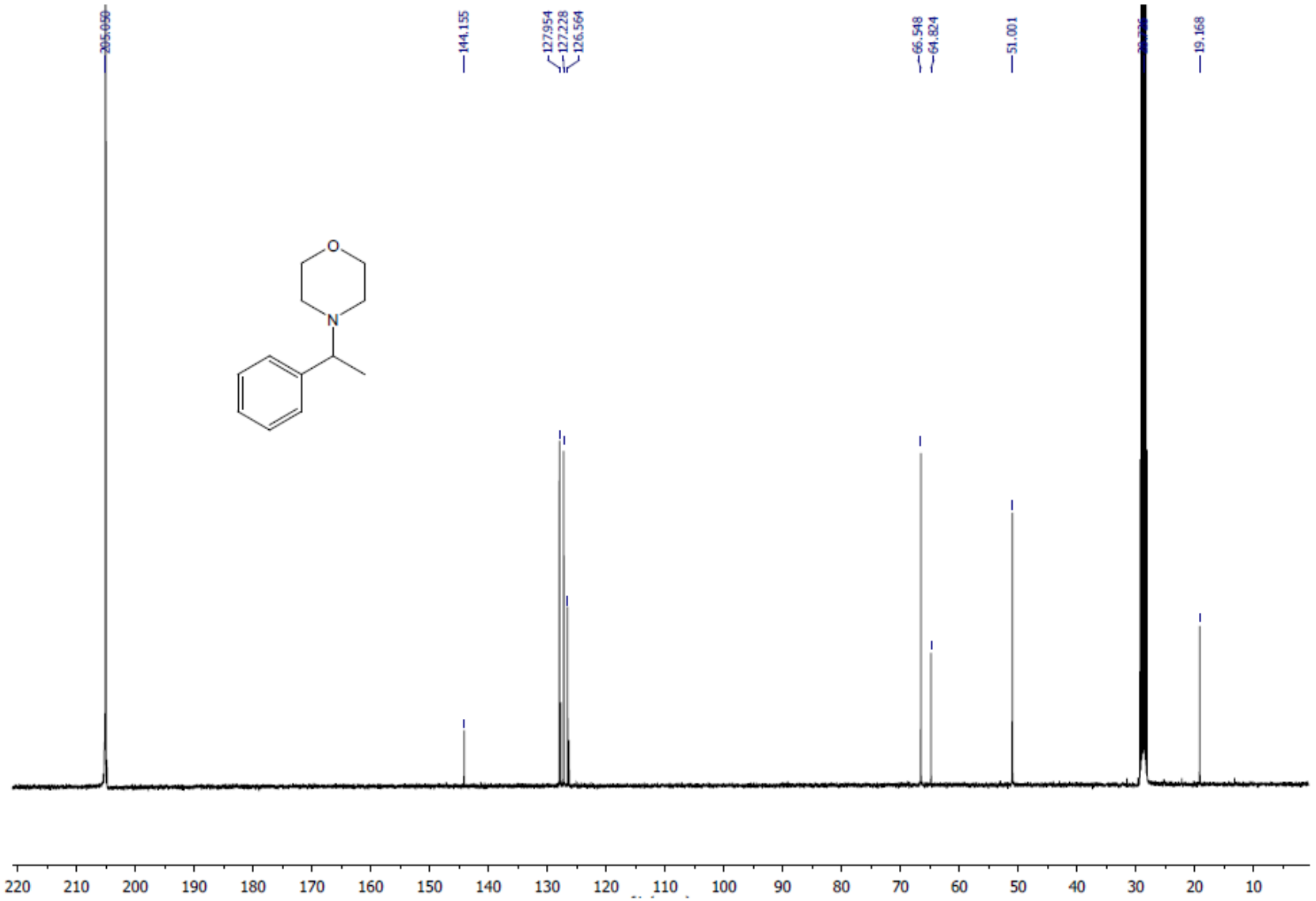


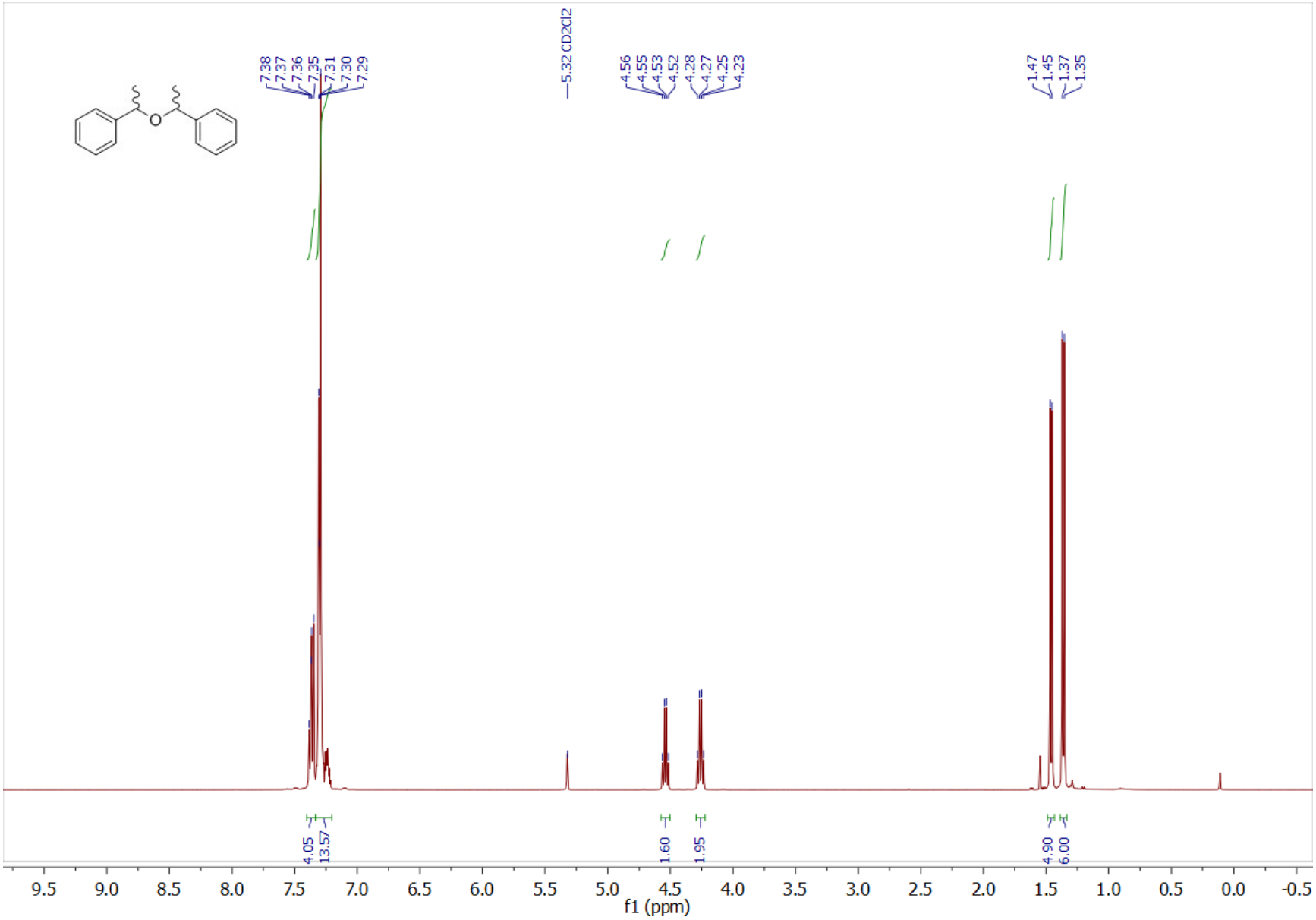

* signal from water

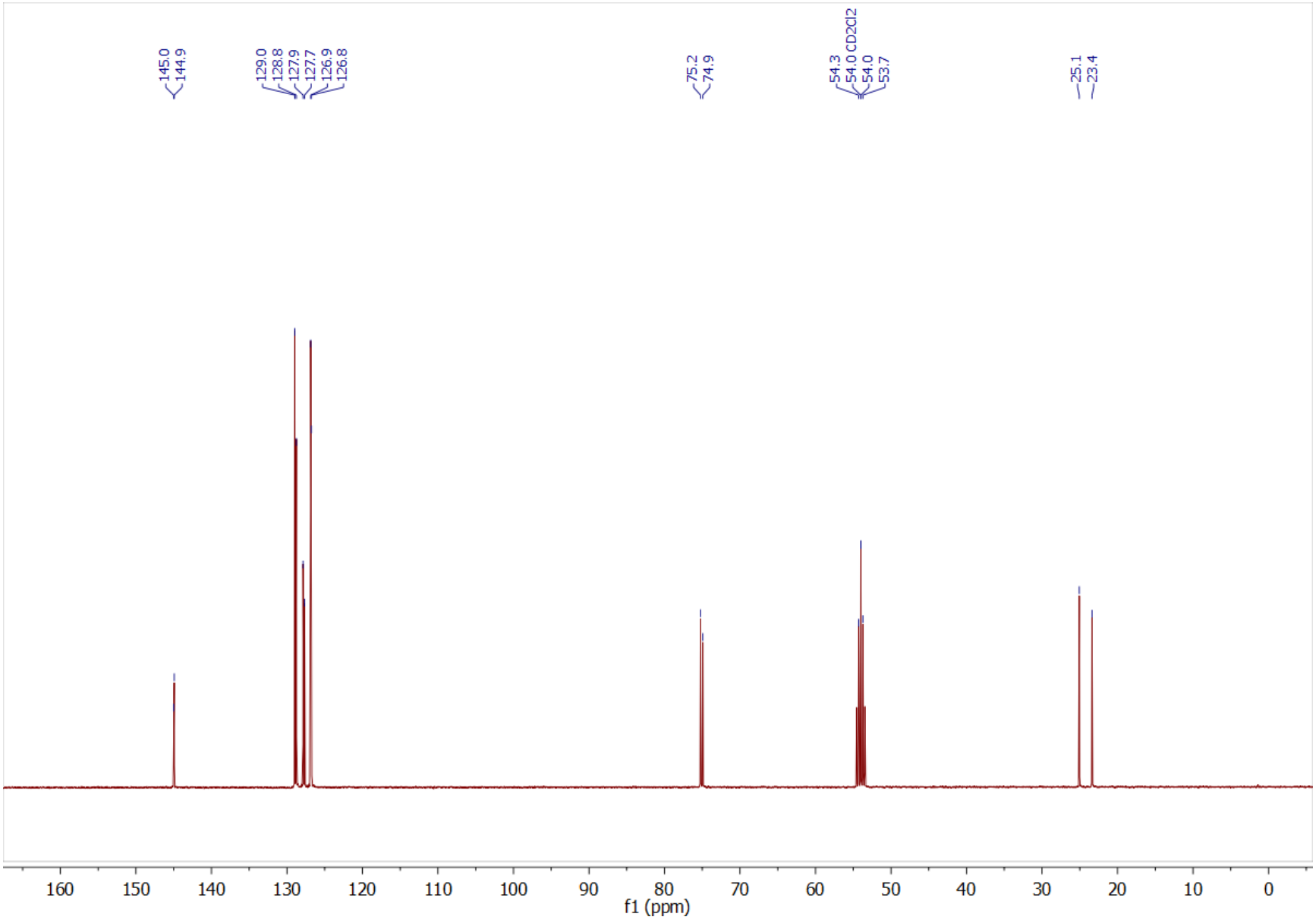

206.268
145.908
129.044
128.440
127.552
65.790
52.316
30.023
27.345
25.658
19.849
N
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10




* signal from water


205.650
144.155
127.954
127.228
126.564
66.548
64.824
51.001
19.168
O
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.38
7.37
7.36
7.35
7.31
7.30
7.29
5.32 CD2Cl2
4.56
4.55
4.53
4.52
4.28
4.27
4.25
4.23
1.47
1.45
1.37
1.35
4.05
13.57
1.60
1.95
4.90
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


145.0
144.9
129.0
128.8
127.9
127.7
126.9
126.8
75.2
74.9
54.3
54.0 CD2Cl2
54.0
53.7
25.1
23.4
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)