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Synthesis and characterisation of an unprecedented, figure-of-eight, dinuclear Iridium(I) dicarbene and Iridium(III) 'pincer' complexes

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S1. Synthesis and characterisation of the compounds

S2. Crystallographic data

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S1. Synthesis and characterisation of the compounds

General procedures. All operations were carried out using standard Schlenk techniques under inert atmosphere. The synthesis of the imidazolium salts **1**, **3** and **4** was conducted under nitrogen whereas that of complexes **2**, **5**, **6**, **7**, **8** and **9** was performed under argon. Solvents were dried and degassed, and freshly distilled prior to use. THF and Et_2O were dried over sodium/benzophenone and CH_2Cl_2 and CH_3CN were distilled from CaH_2. d_6-DMSO and CD_3CN were degassed and stored over 4 Å molecular sieves. CD_2Cl_2 was dried over 4 Å molecular sieves, degassed by freeze-pump-thaw cycles and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz) and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC and ^{1}H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000-100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université Louis Pasteur, Strasbourg and by the "Service Central d'Analyse", USR-59/CNRS, Solaize. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulising gas and Maldi-TOF analyses were carried out on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1.8.9 trihydroxyanthracene) as a matrix.

α, α'-bis(3-ethylimidazolium)-*m*-xylene dichloride[1] and 1,3-bis(imidazolyl)benzene[2] were prepared according to methods described in the literature, and 1,3-bis(3-butylimidazolium-1-yl)benzene diiodide **3** was obtained by a modification of a previously reported procedure.[3] All other reagents were used as received from commercial suppliers. Yields of the metal complexes are based on iridium.

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[1] E. Alcalde, N. Mesquida, M. Alemany, C. Alvarez-Rúa, S. García-Granda, P. Pacheco and L. Pérez-García, *Eur. J. Org. Chem.* 2002, 1221.

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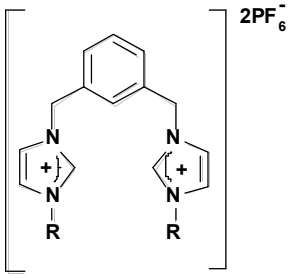
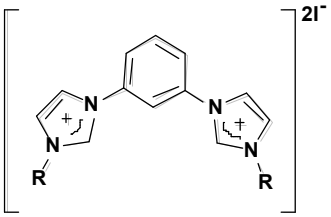
[2] V. C. Vargas, R. J. Rubio, T. K. Hollis and M. E. Salcido, *Org. Lett.* 2003, **5**, 4847.

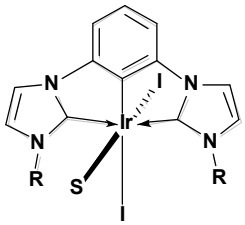
[3] R. *J.* Rubio, G. T. S. Andavan, E. B. Bauer, T. K. Hollis, J. Cho, F. S. Tham and B. Donnadieu, *J. Organomet. Chem.* 2005, **690**, 5353.



^{R}(CH^CH^CH)(PF$_6$)$_2$

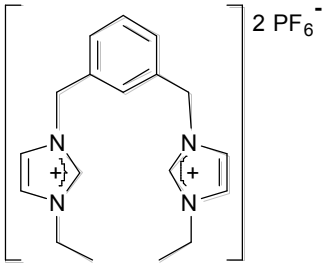


^{R}(CHCHCH)I$_2$



Ir^{R}(C$_{NHC}$CC$_{NHC}$)I$_2$S

Formula of ligands and complexes described in this paper.



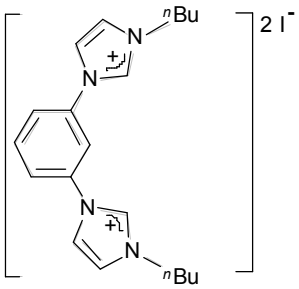
1

Synthesis of α,α'-bis(3-ethylimidazolium)-*m*-xylene dihexafluorophosphate, ^{Et}(CH^CH^CH)(PF$_6$)$_2$, 1. α,α'-bis(3-ethylimidazolium)-*m*-xylene dichloride (1.44 g, 3.9 mmol) and NH_4PF_6 (1.34 g, 7.8 mmol) were refluxed in MeOH (100 mL) for two days. The suspension was then allowed to cool to room temperature and the solvent was removed *in vacuo*. The solid was washed with methanol and water and then dried under reduced pressure. **1** was obtained as a colourless solid in 75% yield (1.71 g). ^{1}H NMR (d_6-DMSO): δ 1.43 (t, ^3J(HH) = 7.3 Hz, 6H, CH_3), 4.22 (q, ^3J(HH) = 7.3 Hz, 4H, CH_3CH_2), 5.42 (s, 4H, CH_2), 7.39-7.42 (m, 2H, CH arom.), 7.47-7.52 (m, 2H, CH arom.), 7.76 (br s, 2H, CH imid.), 7.83 (br s,

2H, CH imid.), 9.29 (br s, 2H, NCHN). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 15.0 (CH_3), 44.4 (CH_3CH_2), 51.7 (CH_2), 122.5 (CH imid.), 122.6 (CH imid.), 128.2 (CH arom.), 128.6 (CH arom.), 129.8 (CH arom.), 135.5 (C arom.), 136.0 (NCHN). $^{19}F\{^1H\}$ NMR (d_6-DMSO): δ -70.6 (d, ^1J(FP) = 711.6 Hz). $^{31}P\{^1H\}$ NMR (d_6-DMSO): δ -143.0 (sept., ^1J(PF) = 711.6 Hz). ESI-MS (CH_3OH, 50 V, *m/z*): 441.2 $[M-PF_6]^+$, 295.2 $[M-2PF_6-H]^+$. HRMS (ESI) $[M-PF_6]^+$: 441.1637 calcd for $C_{18}H_{24}F_6N_4P$: 441.1595. Anal. Calc. for $C_{18}H_{24}F_{12}N_4P_2$ (586.34): C, 36.87; H, 4.13; N, 9.56. Found: C, 36.43; H, 4.62; N, 9.43%.

Synthesis of $[Ir(cod)(\mu\text{-}^{Et}C_{NHC}\text{^}CH\text{^}C_{NHC})]_2(PF_6)_2$, 2. Solid α,α'-bis(3-ethylimidazolium)-*m*-xylene dihexafluorophosphate (**1**, 0.600 g, 1.02 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.345 g, 0.51 mmol) and Cs_2CO_3 (0.834 g, 2.50 mmol) were mixed and heated in acetonitrile (15 mL) at 60 °C for 15 h. The suspension was then allowed to cool to room temperature, filtered and the solvent was removed *in vacuo*. The red solid was dissolved in CH_3CN (10 mL) and addition of Et_2O (100 mL) led to the precipitation of a solid which was discarded by filtration. The solvent was removed *in vacuo* yielded **2** as a red solid in a 33% yield (0.250 g). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of $^iPr_2O$ in a saturated acetonitrile solution of the complex. ^1H NMR (CD_2Cl_2): a rather complicated spectrum was obtained, probably due to the presence of different conformers in solution. We report here an overall assignment for each chemical moiety, except for the ^1H NMR cod signals owing to their complexity: 1.35, 1.43, 1.53, 1.54, 1.58 (t, ^3J(HH) = 7.3 Hz, CH_3), 4.14-4.40 and 4.58-4.80 (m, CH_2CH_3), 5.08 and 5.75 (d, ^2J(HH) = 14.8 Hz, 2 × 1H, CH_2), 5.21 and 5.81 (d, ^2J(HH) = 14.8 Hz, 2 × 1H, CH_2), 5.18 and 5.55 (d, ^2J(HH) = 15.1 Hz, 2 × 1H, CH_2) second order system, 5.27 and 5.46 (d, ^2J(HH) = 15.2 Hz, 2 × 1H, CH_2) second order system,

6.36 (br s, CH arom.), 6.61-6.65 (m, CH arom. and CH imid.), 6.68 (d, ^3J(HH) = 2.1 Hz, CH imid.), 6.83-6.85 (m, CH imid.), 6.88 (d, ^3J(HH) = 2.1 Hz, CH imid.), 6.90-6.93 (m, CH arom.), 6.94 (d, ^3J(HH) = 2.1 Hz, CH imid.), 6.97 (d, ^3J(HH) = 2.1 Hz, CH imid.), 7.07 (d, ^3J(HH) = 2.1 Hz, CH imid.), 7.14 (d, ^3J(HH) = 2.1 Hz, CH imid.), 7.15-7.17 (m, CH imid.), 7.24 (t, ^3J(HH) = 7.7 Hz, CH arom.), 7.26 (d, ^3J(HH) = 2.1 Hz, CH imid.), 7.30-7.37 (m, CH arom.), 7.43 (d, ^3J(HH) = 2.1 Hz, CH imid.), 7.51-7.56 (m, CH arom.). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 16.0, 16.1 (CH_3), 31.2, 32.0, 32.1 (CH_2 cod), 46.1, 46.3 (CH_2CH_3), 77.1, 77.5 (CH cod), 121.3, 122.3 (CH imid.), 127.7, 129.0, 130.8, 131.0, 136.5, 136.9 (aromatic), 177.5 (br s, C-Ir). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ -73.4 (d, ^1J(FP) = 711.4 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -143.2 (sept., ^1J(PF) = 711.4 Hz). MALDI TOF-MS (CH_3CN, *m/z*): 1333.5 $[M-PF_6]^+$. IR (pure, diamond orbit): 3642br, 3470br, 3395br, 3177m, 2979m, 2936m, 2871m, 2834w, 1668s, 1610m, 1566m, 1423m, 1401s, 1355w, 1250s, 1231s, 1185m, 1154w, 1121w, 1038w, 995w, 976w, 948w, 835vs (PF_6), 739w, 699w.



3

Synthesis of 1,3-bis(3-butylimidazolium-1-yl)benzene diiodide, ^{n}Bu(CHCHCH)I$_2$, 3. Solid 1,3-bis(imidazolyl)benzene (4.000 g, 19.04 mmol) and iodobutane (10.0 mL) were mixed and refluxed for two days. The suspension was then allowed to cool to room temperature and filtered. The crude solid was washed with THF (2 × 20 mL) leading to an off-white product. Recrystallisation from MeOH/Et_2O yielded the product as a microcrystalline white solid in 66% yield (7.300 g). ^1H NMR (d_6-DMSO): δ 0.94 (t, ^3J(HH) = 7.5 Hz, 6H, CH_3), 1.35 (*pseudo* sextet, ^3J(HH) = 7.5 Hz, 4H, CH_2), 1.92 (*pseudo* quintet, ^3J(HH) = 7.5 Hz, 4H, CH_2), 4.31 (t, ^3J(HH) = 7.5 Hz, 4H, NCH_2), 7.95-8.07 (m, 3H, CH arom.), 8.16 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.8 Hz, 2H, CH imid.), 8.39 (t, *J*(HH) = 2.0 Hz, 1H, CH arom.), 8.46 (*pseudo* t, ^3J(HH) =

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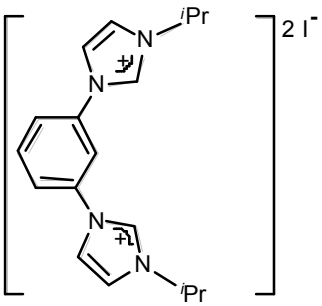
^4J(HH) = 1.8 Hz, 2H, CH imid.), 10.03 (*pseudo* t, ^4J(HH) = 1.8 Hz, 2H, NCHN). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 13.3 (CH_3), 18.8 (CH_2), 31.0 (CH_2), 49.3 (NCH_2), 115.8 (CH arom.), 121.1 (CH imid.), 122.6 (2 × CH arom.), 123.6 (CH imid.), 131.9 (CH arom.), 135.6 (C arom.), 135.7 (NCHN). Anal. Calc. for $C_{20}H_{28}I_2N_4$ (578.27): C, 41.54; H, 4.88; N, 9.69. Found: C, 41.12; H, 4.97; N, 9.64%. IR (pure, orbit diamond): 3130w, 3063mbr, 2960mw, 2931w, 2869w, 1613m, 1572m, 1551vs, 1487w, 1459br, 1386w, 1356w, 1334w, 1258w, 1200s, 1085m, 1076m, 859m, 783vs, 768s, 676vs, 656m cm^{-1}.

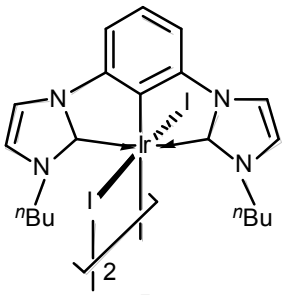
The spectroscopic data of **3** are in good accordance with those given in the literature.[3]



4

Synthesis of 1,3-bis(3-isopropylimidazolium-1-yl)benzene diiodide, ^{iPr}(CHCHCH)I_2, 4. Solid 1,3-bis(imidazolyl)benzene (1.000 g, 4.78 mmol) and 2-iodopropane (10.0 mL) were mixed and refluxed for two days. The suspension was then allowed to cool to room temperature and filtered. 2-Iodopropane (5 mL) was added and the mixture was refluxed overnight. The suspension was then allowed to cool to room temperature and filtered. The crude solid was washed with THF (2 × 20 mL) leading to an off-white product. Two recrystallisations from MeOH/Et_2O yielded a white solid in a 42% yield (1.100 g). ^1H NMR (d_6-DMSO): δ 1.59 (d, ^3J(HH) = 6.7 Hz, 12H, CH_3), 4.77 (septuplet, ^3J(HH) = 6.7 Hz, 2H, $(CH_3)_2CH$), 7.96-8.08 (m, 3H, CH arom.), 8.26 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.8 Hz, 2H, CH imid.), 8.36 (t, ^4J(HH) = 2.0 Hz, 1H, CH arom.), 8.44 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.8 Hz, 2H, CH imid.), 9.94 (*pseudo* t, ^4J(HH) = 1.8 Hz, 2H, NCHN). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 22.2

(CH_3), 53.2 ($(CH_3)_2CH$), 115.8 (CH arom.), 121.2 (CH imid.), 121.8 (CH imid.), 122.7 (CH arom.), 131.8 (CH arom.), 134.5 (NCHN), 135.6 (C arom.). ESI-MS (CH_3OH, 50 V, *m/z*): 423.1 $[M-I]^+$, 295.2 $[M-2I-H]^+$. HRMS (ESI) $[M-I]^+$: 423.108 calcd for $C_{18}H_{24}IN_4$: 423.104. Anal. Calc. for $C_{18}H_{24}I_2N_4$ (550.22): C, 39.29; H, 4.40; N, 10.18. Found: C, 38.52; H, 4.13; N, 10.24%. (Despite several attempts, no better elemental analyses could be obtained owing to the heavily hygroscopic property of this compound). IR (pure, orbit diamond): 3069wbr, 3001wbr, 1613m, 1564m, 1551ms, 1499w, 1460w, 1432w, 1378w, 1348w, 1321 m, 1258w, 1199s, 1162w, 1139w, 1081m, 875sh, 858m, 791m, 753s, 679vs, 652s cm^{-1}.

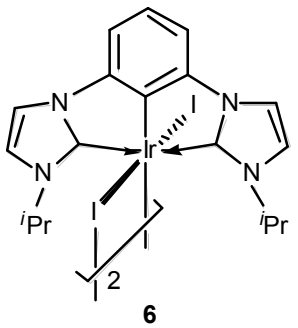


5

Synthesis of bis[1,3-bis(3-butylimidazol-2-ylidene)benzene(iodo)(μ_2-iodo) iridium(III)], $[Ir^{nBu}(C_{NHC}CC_{NHC})(\mu_2\text{-}I)I]_2$, 5. A mixture of 1,3-bis(3-butylimidazolium-1-yl)benzene diiodide (**3**, 0.690 g, 1.20 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.400 g, 0.60 mmol), NEt_3 (0.38 mL, 0.272 g, 2.70 mmol) and KI (0.595 g, 3.60 mmol) in CH_3CN (20 mL) was refluxed for 15 h. The resulting orange suspension was filtered and the solvent was removed *in vacuo*. The residue was extracted with THF (200 mL), filtered and the solvent was removed *in vacuo*. The orange solid was dissolved in CH_2Cl_2 (150 mL) and washed with deionised water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (1 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallised from CH_2Cl_2/pentane yielding pure **5** as an orange solid in a 30% yield (0.275 g). MALDI TOF-MS (CH_2Cl_2, *m/z*): 1407.0 $[M-I]^+$, 768.0 $[0.5\ M]^+$. Anal. Calc. for $C_{40}H_{50}I_4Ir_2N_8$ (1534.93): C, 31.30 ; H, 3.28; N, 7.30. Found: C, 30.32; H, 2.99; N, 6.89%. IR (pure, orbit diamond): 3110w, 2955w, 2922w, 2871w, 1593w, 1481s, 1457sh, 1428m, 1383m, 1329w, 1268s, 1239w, 1104w, 1092w, 1029w, 945w, 778m,

766m, 730m, 700s, 588br, 374wbr, 282wbr, 249wbr, 173s cm^{-1}.

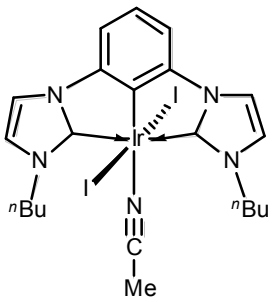
This dinuclear complex is almost insoluble in common organic solvents. We shall see below that in donor solvents, such as CH_3CN or DMSO, the iodide bridges are readily cleaved.



6

Synthesis of bis[1,3-bis(3-isopropylimidazol-2-ylidene)benzene(iodo)(μ_2-iodo) iridium(III)], [Ir^{iPr}($C_{NHC}CC_{NHC}$)(μ_2-I)I]$_2$, 6. A mixture of 1,3-bis(3-isoproprylimidazolium-1-yl)benzene diiodide (**4**, 0.488 g, 0.89 mmol), [Ir(μ-Cl)(cod)]$_2$ (0.300 g, 0.45 mmol), NEt_3 (0.28 mL, 0.202 g, 2.00 mmol) and KI (0.443 g, 2.66 mmol) in CH_3CN (15 mL) was refluxed for 15 h. The resulting orange suspension was filtered and the solvent was removed *in vacuo*. The residue was extracted with THF (200 mL), filtered and the solvent was removed *in vacuo*. The orange solid was dissolved in CH_2Cl_2 (150 mL) and washed with deionised water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (1 × 10 mL). The combined organic extracts were dried over magnesium sulphate, filtered and the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallised from CH_2Cl_2/pentane yielding pure **6** as an orange solid in 30% yield (0.200 g). This dimeric species **6** leads to the mononuclear DMSO-adduct whilst being heated in DMSO. MALDI TOF-MS (CH_2Cl_2, *m/z*): 1351.9 $[M-I]^+$, 739.4 $[0.5\ M]^+$. Anal. Calc. for $C_{36}H_{42}I_4Ir_2N_8$ (1478.82): C, 29.24; H, 2.86; N, 7.58. Found: C, 29.64; H, 2.95; N, 7.88%. IR (pure, orbit diamond): 3116w, 2975w, 2926w, 1592w, 1479s, 1427m, 1399w, 1369w, 1328w, 1312w, 1267s, 1236m, 1227m, 1133w, 1017w, 951w, 878w, 824w, 779m, 761m, 731m, 697vs, 599br, 440wbr, 396wbr, 343wbr, 320wbr, 278wbr, 247wbr, 202wbr, 173s cm^{-1}.

This dinuclear complex is almost insoluble in common organic solvents. We shall see below that in donor solvents, such as CH_3CN or DMSO, iodide bridges are readily cleaved.



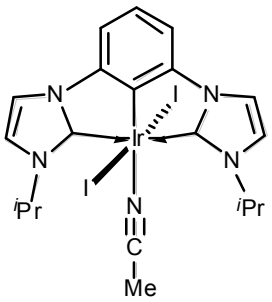
7

Synthesis of 1,3-bis(3-butylimidazol-2-ylidene)benzene(acetonitrile)bis(iodo) iridium (III), Ir$^{n\mathrm{Bu}}$($C_{NHC}CC_{NHC}$)I_2(CH_3CN), 7.

a/ directly from the bis(imidazolium) salt 3. A mixture of 1,3-bis(3-butylimidazolium-1-yl)benzene diiodide (**3**, 0.344 g, 0.60 mmol), [Ir(μ-Cl)(cod)]$_2$ (0.200 g, 0.30 mmol), NEt_3 (0.19 mL, 0.139 g, 1.37 mmol) in CH_3CN (5 mL) was refluxed for 15 h. The resulting orange suspension was filtered and the solvent was removed *in vacuo*. The residue was extracted with THF (200 mL), filtered and the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO_2, CH_3CN) and obtained as an orange solid in 30% yield (0.143 g).

b/ from dinuclear 5. A CH_3CN (10 mL) suspension of the dinuclear **5** (0.300 g, 0.20 mmol) was refluxed for 1 h. The resulting solution was then allowed to cool to room temperature and the solvent was removed *in vacuo* leading to an orange solid. Recrystallisation from CH_3CN yielded pure **7** in 90% yield (0.290 g). Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of an acetonitrile solution of the complex. ^{1}H NMR (CD_3CN): δ 1.01 (t, ^3J(HH) = 7.5 Hz, 6H, CH_3), 1.46 (*pseudo* sextet, ^3J(HH) = 7.5 Hz, 4H, CH_2), 2.08 (*pseudo* quintet, ^3J(HH) = 7.5 Hz, 4H, CH_2), 4.39 (t, ^3J (HH) = 7.5 Hz, 4H, NCH_2), 6.93 (t, ^3J(HH) = 8.2 Hz, 1H, CH arom.) and 7.16 (d, ^3J(HH) = 8.2 Hz, 2H, CH arom) second order signals, 7.25 (d, ^3J(HH) = 2.1 Hz, 2H, CH imid.), 7.71 (d, ^3J(HH) = 2.1 Hz, 2H, CH imid.). ^{13}C{^{1}H} NMR (CD_3CN): δ 14.2 (CH_3), 20.8 (CH_2), 33.8 (CH_2), 50.6 (NCH_2), 107.9 (CH arom.), 116.9 (CH imid.), 122.0 (CH imid.), 123.3 (CH arom.), 136.1 (metallated C arom.), 147.0 (C arom.), 164.1 (C-Ir). ESI-MS (CH_3CN, 70 V, *m/z*): 682.1[M-I]$^+$, 556.2 [M-2I+H]$^+$. HRMS (ESI) [M-I]$^+$: 682.0979 calcd for $C_{22}H_{28}IIrN_5$: 682.1013. Anal. Calc. for $C_{22}H_{28}I_2IrN_5$ (808.52): C, 32.68; H, 3.49; N, 8.66. Found: C, 32.52; H, 3.39; N, 8.29%. IR (pure, orbit

diamond): 3154w, 3108w, 2960br, 2923w, 2848w, 1594w, 1480s, 1458m, 1427m, 1380br, 1328w, 1266s, 1238m, 1164w, 1092br, 1026br, 945w, 835s, 802br, 779s, 771s, 729m, 700s, 686m, 556s cm^{-1}.



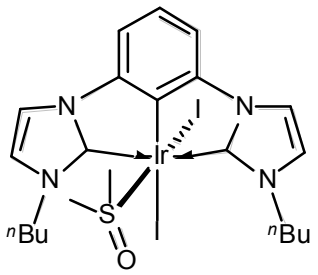
8

Synthesis of 1,3-bis(3-isopropylimidazol-2-ylidene)benzene(acetonitrile)bis(iodo) iridium (III), $Ir^{iPr}(C_{NHC}CC_{NHC})I_2(CH_3CN)$, 8

a/ directly from the bis(imidazolium) salt 4. A mixture of 1,3-bis(3-isopropylimidazolium-1-yl)benzene diiodide (**4**, 0.344 g, 0.63 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.217 g, 0.32 mmol), NEt_3 (0.19 mL, 0.141 g, 1.39 mmol) in CH_3CN (5 mL) was refluxed for 15 h. The resulting orange suspension was filtered and the solvent was removed *in vacuo*. The residue was extracted with THF (200 mL), filtered and the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO_2, CH_3CN) and obtained as an orange solid in 30% yield (0.148 g).

b/ from dinuclear 6. A CH_3CN (10 mL) suspension of the dinuclear **6** (0.300 g, 0.20 mmol) was refluxed for 1 h. The resulting solution was then allowed to cool to room temperature and the solvent was removed *in vacuo* leading to an orange solid. Recrystallisation from CH_3CN yielded pure **8** in 92% yield (0.290 g). Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of an acetonitrile solution of the complex. ^1H NMR (CD_3CN): δ 1.64 (d, $^3J(HH)$ = 6.8 Hz, 12H, CH_3), 5.13 (septet, $^3J(HH)$ = 6.8 Hz, 2H, $(CH_3)_2CH$), 6.93 (t, $^3J(HH)$ = 8.2 Hz, 1H, CH arom.) and 7.16 (d, $^3J(HH)$ = 8.2 Hz, 2H, CH arom) second order signals, 7.35 (d, $^3J(HH)$ = 2.1 Hz, 2H, CH imid.), 7.75 (d, $^3J(HH)$ = 2.1 Hz, 2H, CH imid.). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 23.5 (CH_3), 52.5 ($(CH_3)_2CH$), 107.9 (CH arom.),

117.2 (CH imid.), 117.3 (CH imid.), 123.4 (CH arom.), 135.6 (metallated C arom.), 146.9 (C arom.), 163.7 (C-Ir). ESI-MS (CH_3CN, 30V, *m/z*): 741.0 $[M-CH_3CN+H]^+$, 654.1 $[M-I]^+$, 528.2 $[M-2I+H]^+$. HRMS (ESI) $[M-I]^+$: 654.0746 calcd for $C_{20}H_{24}I_1Ir_1N_5$: 654.0701. Anal. Calc. for $C_{20}H_{24}I_2Ir_1N_5$ (780.46): C, 30.78; H, 3.10; N, 8.97%. Found: C, 30.59; H, 3.16; N, 8.52%.



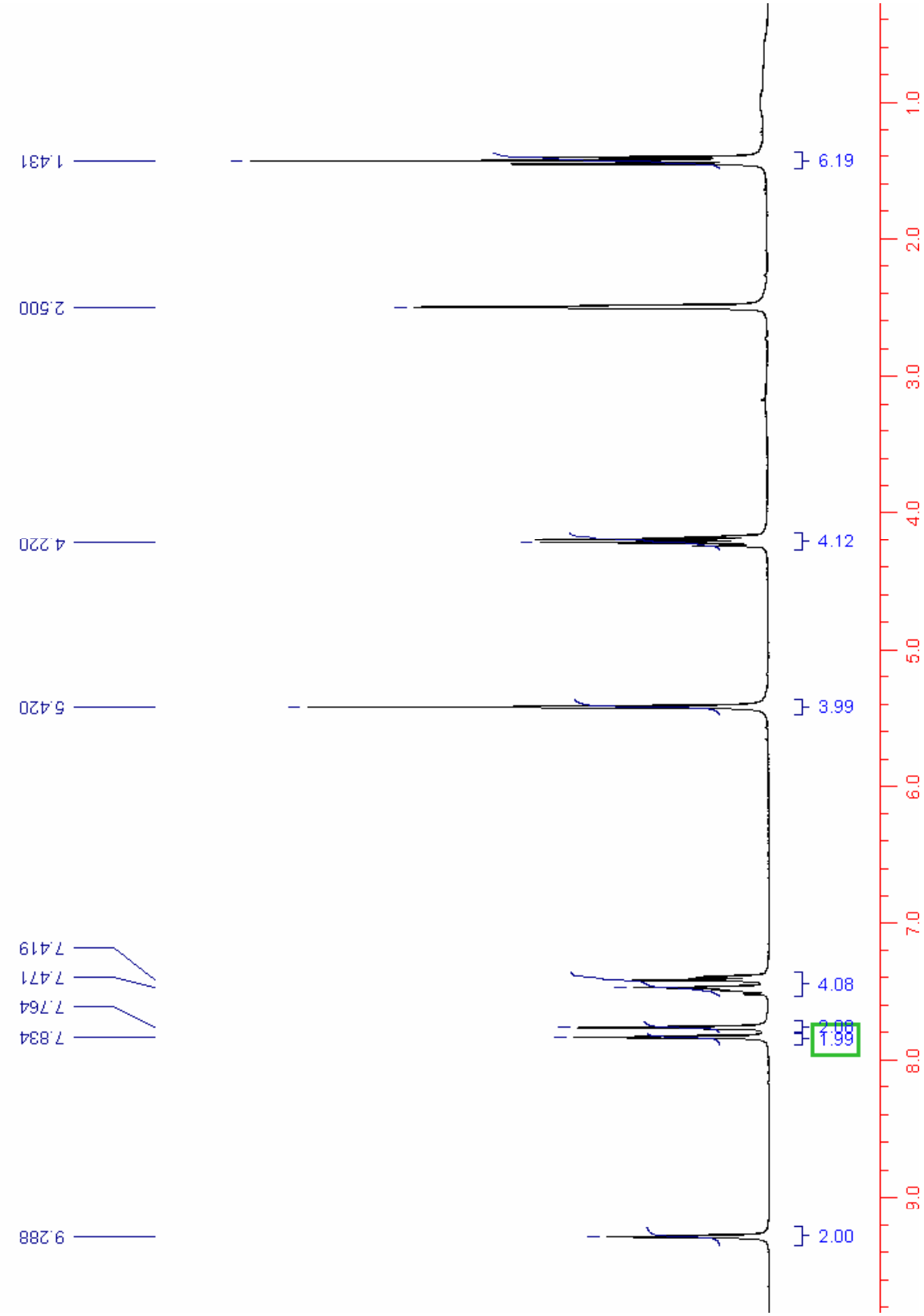
9

Synthesis of 1,3-bis(3-butylimidazol-2-ylidene)benzene(dimethylsulfoxide)bis (iodo)iridium(III), $Ir^{nBu}(C_{NHC}CC_{NHC})I_2$(DMSO), 9. A DMSO (10 mL) solution of the dinuclear complex **5** (0.300 g, 0.20 mmol) was heated to 50 °C for 5 min. Dichloromethane (50 mL) was added to the orange solution and the organic layer was washed with deionised water (50 mL). The organic extract was dried over $MgSO_4$, filtered and the solvent was removed in vacuo, which afforded an orange oil. Recrystallisation from CH_2Cl_2/pentane yielded pure **9** as a yellow solid in a 70% yield (0.241 g). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of Et_2O in a saturated dichloromethane solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.03 (t, ^3J(HH) = 7.4 Hz, 6H, CH_3), 1.46-1.67 (m, 4H, CH_2), 1.85-2.02 (m, 2H, CH_2), 2.03-2.18 (m, 2H, CH_2), 3.12 (s, 6H, CH_3, coord. DMSO), 4.33-4.43 (m, 2H, CH_2), 5.33-5.42 (m, 2H, CH_2), 7.18-7.28 (m, 5H, 3 × CH arom. + 2 × CH imid.), 7.66 (d, ^3J(HH) = 2.1 Hz, 2H, CH imid.). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.3 (CH_3), 20.3 (CH_2), 33.8 (CH_2), 48.0 (CH_3, coord. DMSO), 52.0 (NCH_2), 108.8 (CH arom.), 116.6 (CH imid.), 122.3 (CH imid.), 124.7 (CH arom.), 138.6 (metallated C arom.), 144.7 (C arom.), 155.7 (C-Ir). MALDI TOF-MS (THF, *m/z*): 767.8 $[M-DMSO]^+$, 718.9 $[M-I]^+$. ESI-MS (CH_3OH, 80 V, *m/z*): $[M-I]^+$ 719.1. HRMS (ESI) $[M-I]^+$: 719.0814 calcd for $C_{22}H_{31}IIrN_4OS$: 719.0887. Anal. Calc. for $C_{22}H_{31}I_2IrN_4OS\cdot\frac{1}{2}CH_2Cl_2$ (888.06): C, 30.43; H, 3.63; N, 6.31. Found: C, 30.42; H, 3.47; N, 5.96%. IR (pure, orbit diamond): 3112w, 3085w, 2952w, 2925w, 2868w, 1598m, 1555w, 1481vs, 1458s 1425ms, 1383m, 1326w, 1309w, 1268s, 1239m, 1205w, 1118br, 1043m, 1011vs,

969m, 945m, 926br, 768m, 725m, 698m, 434mbr, 377mbr, 332w, 154w, 116vs cm^{-1}.

We also provide below the NMR analysis, in d_6-DMSO, of the d_6-analogue of **9**, obtained by cleavage of the dinuclear complex **5** in this solvent: ^{1}H-NMR (d_6-DMSO): δ 0.93 (t, ^3J(HH) = 7.4 Hz, 6H, CH_3), 1.33-1.52 (m, 4H, CH_2), 1.72-1.89 (m, 2H, CH_2), 1.90-2.03 (m, 2H, CH_2), 4.27-4.36 (m, 2H, CH_2), 5.14-5.23 (m, 2H, CH_2), 7.16 (t, ^3J(HH) = 7.8 Hz, 1H, CH arom.), 7.41 (d, ^3J(HH) = 7.8 Hz, 2H, CH arom.), 7.64 (d, ^3J(HH) = 2.0 Hz, 2H, CH imid.), 8.21 (d, ^3J(HH) = 2.0 Hz, 2H, CH imid.). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 13.9 (CH_3), 19.2 (CH_2), 32.8 (CH_2), 50.1 (NCH_2), 108.4 (CH arom.), 116.8 (CH imid.), 122.5 (CH imid.), 123.9 (CH arom.), 136.9 (metallated C arom.), 144.1 (C arom.), 154.4 (C-Ir).

compound **1** (^{1}H NMR, DMSO)


1.431
2.500
4.220
5.420
7.419
7.471
7.764
7.834
9.288
6.19
4.12
3.99
4.08
1.99
2.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0

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compound **1** (^{13}C NMR, DMSO)

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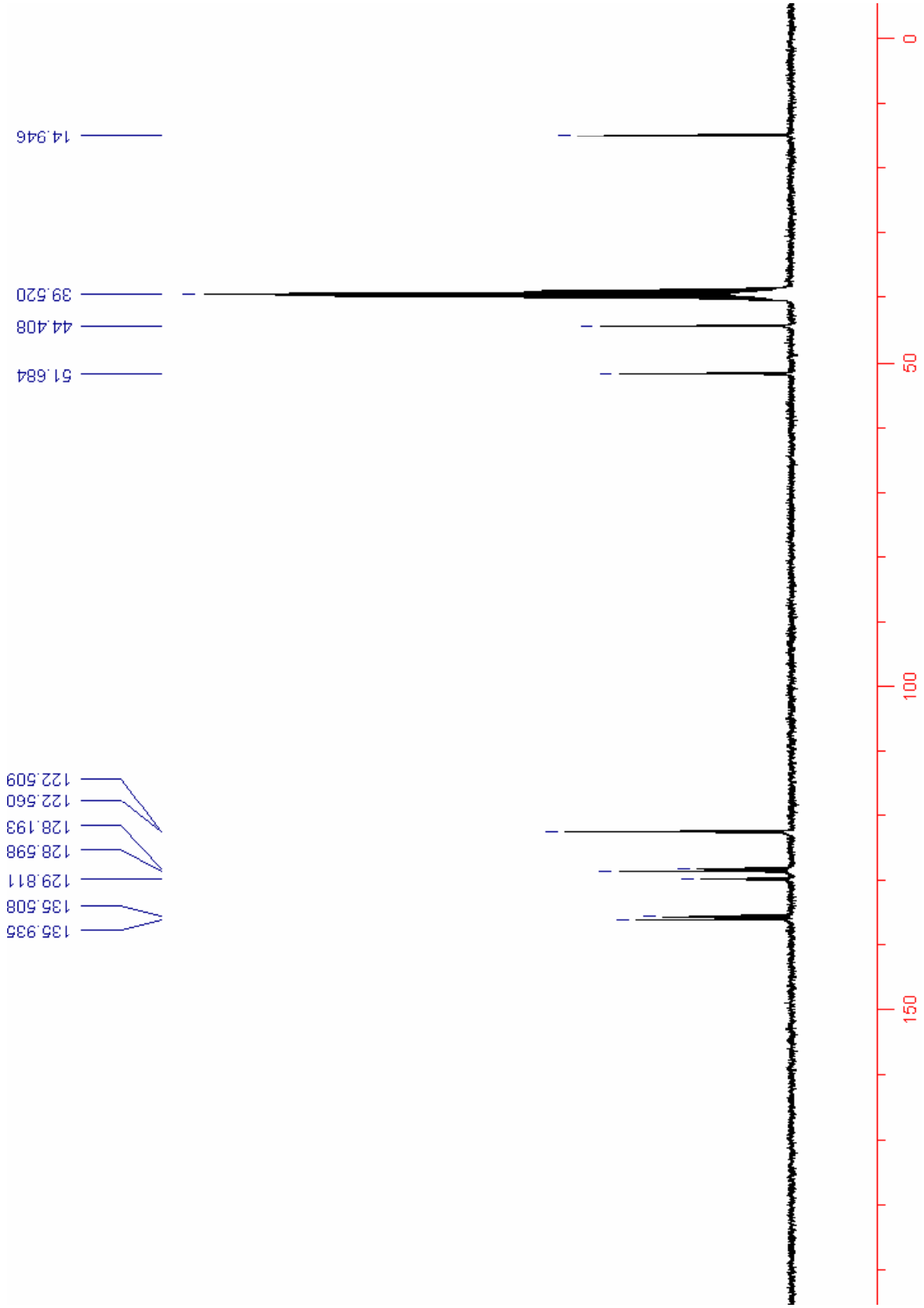
14.946
39.520
44.408
51.684
122.509
122.560
128.193
128.598
129.811
135.508
135.935
0
50
100
150

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compound **2** (^{13}C NMR, CD_2Cl_2)

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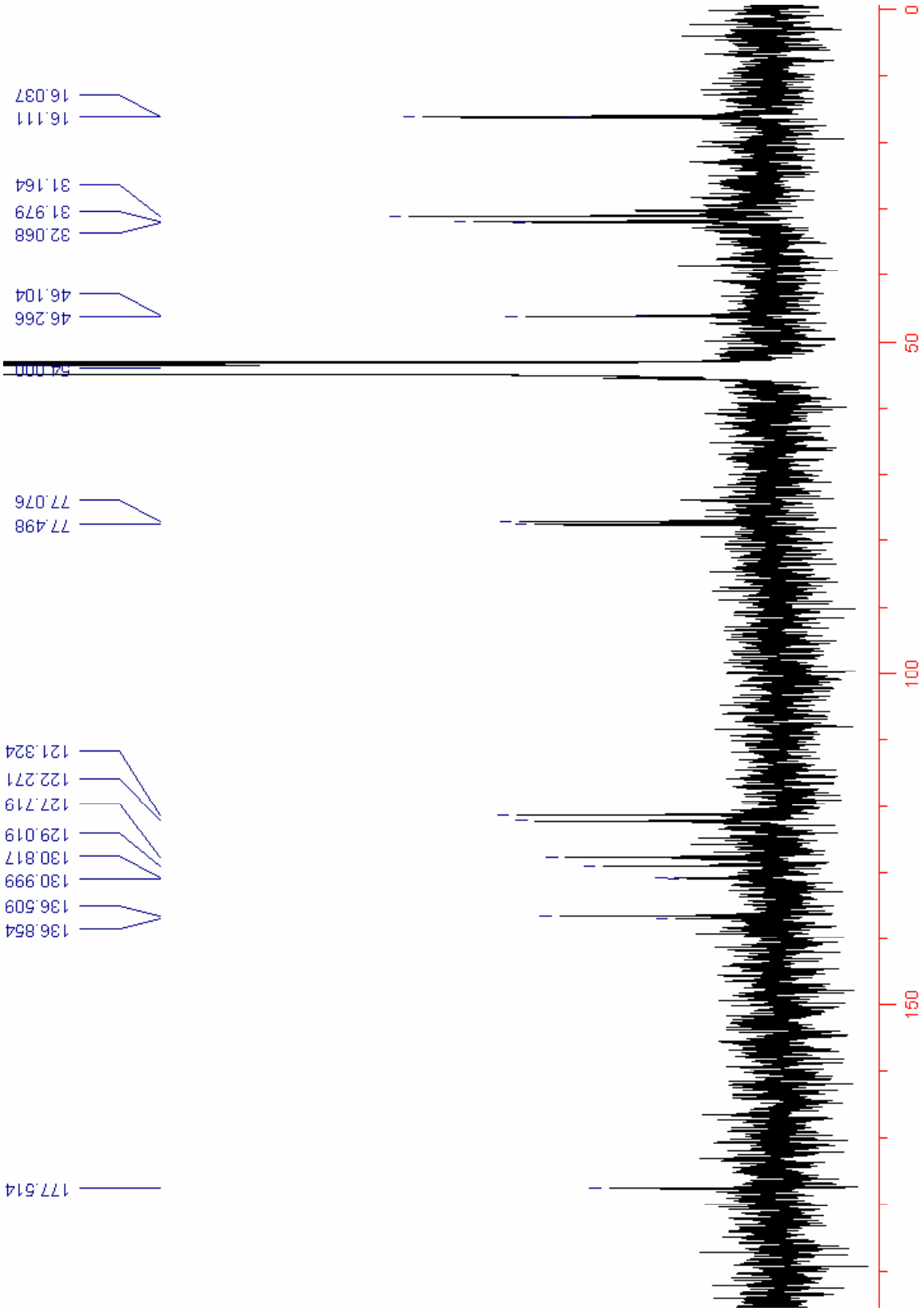

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compound **3** (^{1}H NMR, DMSO)

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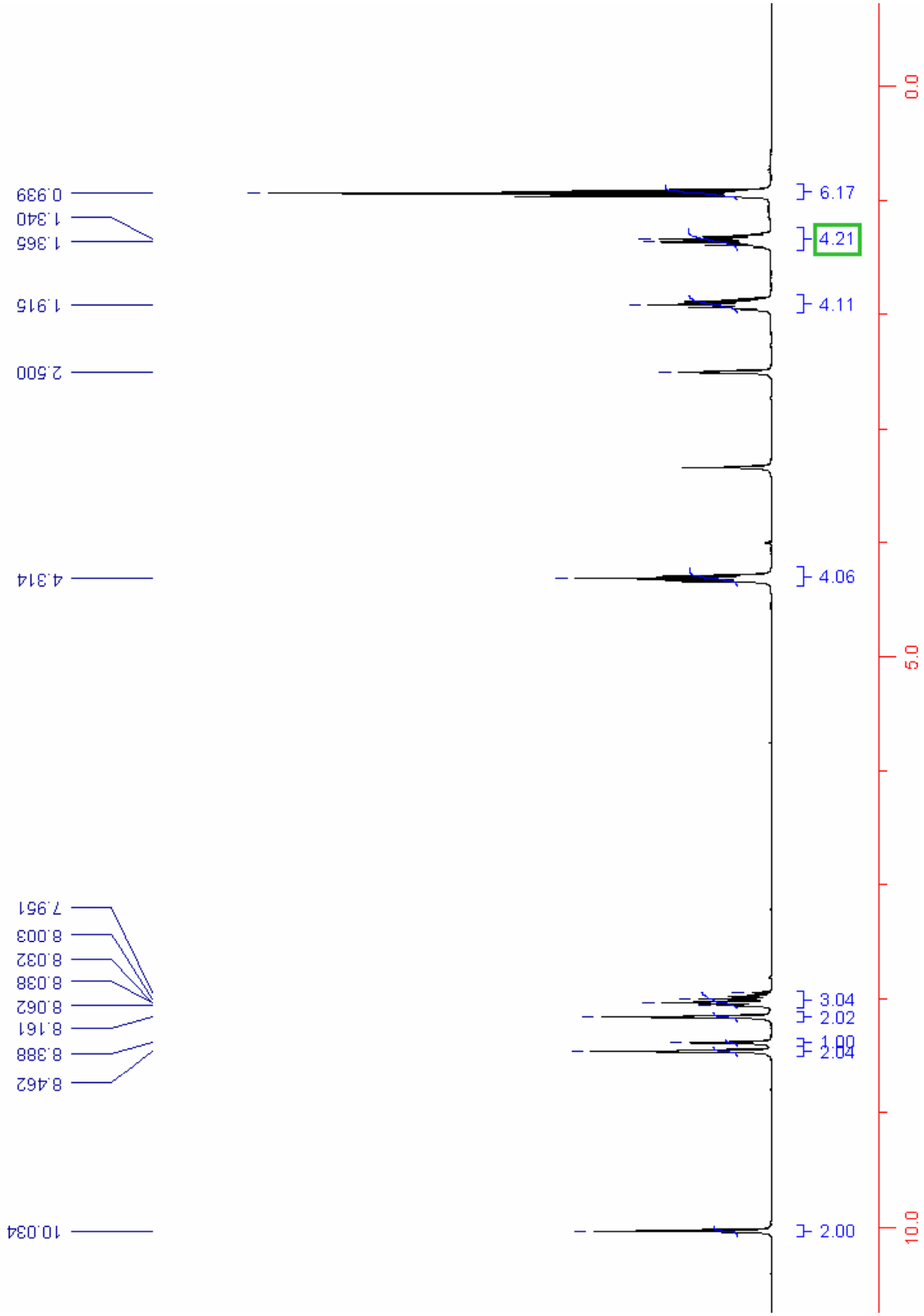
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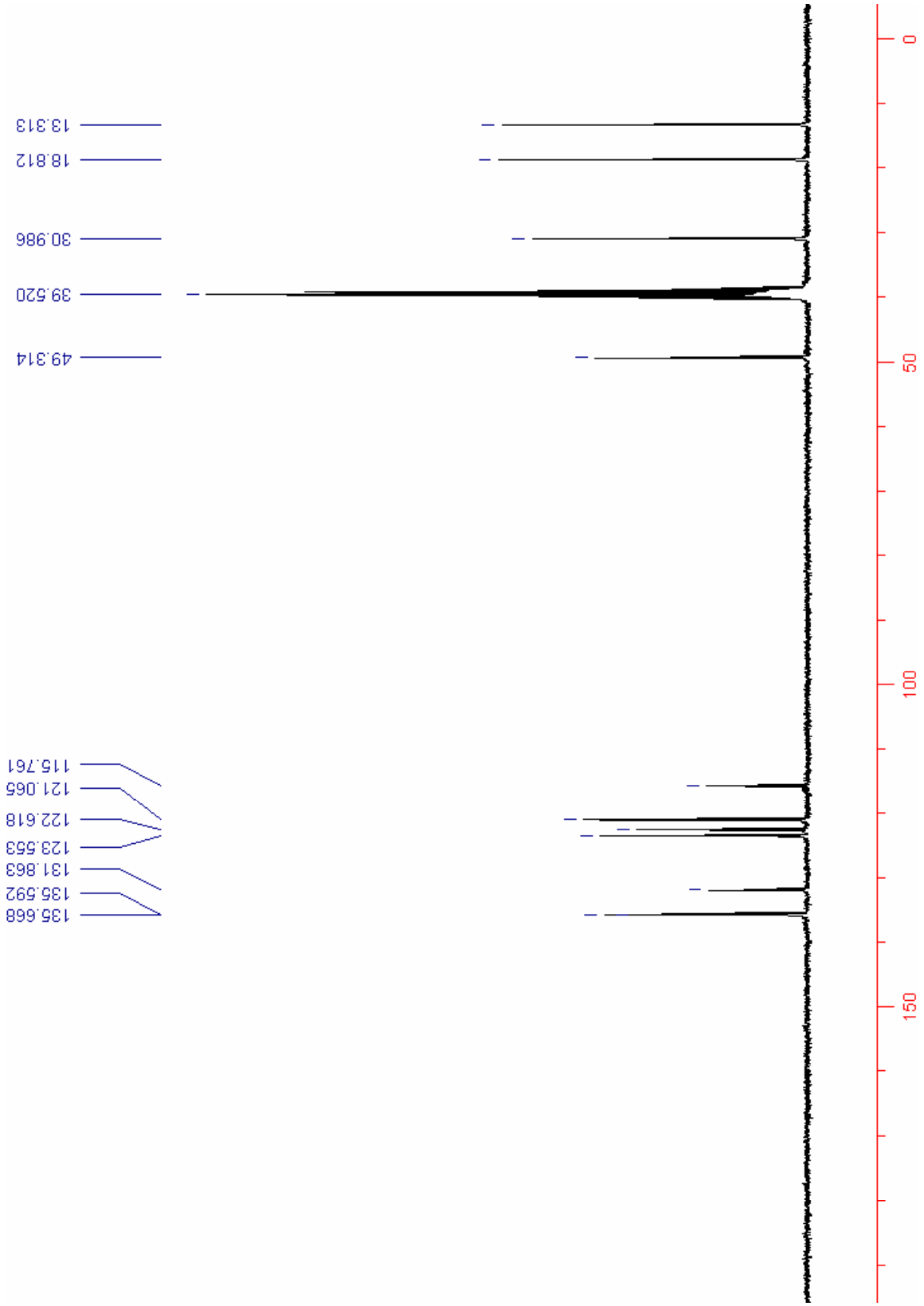
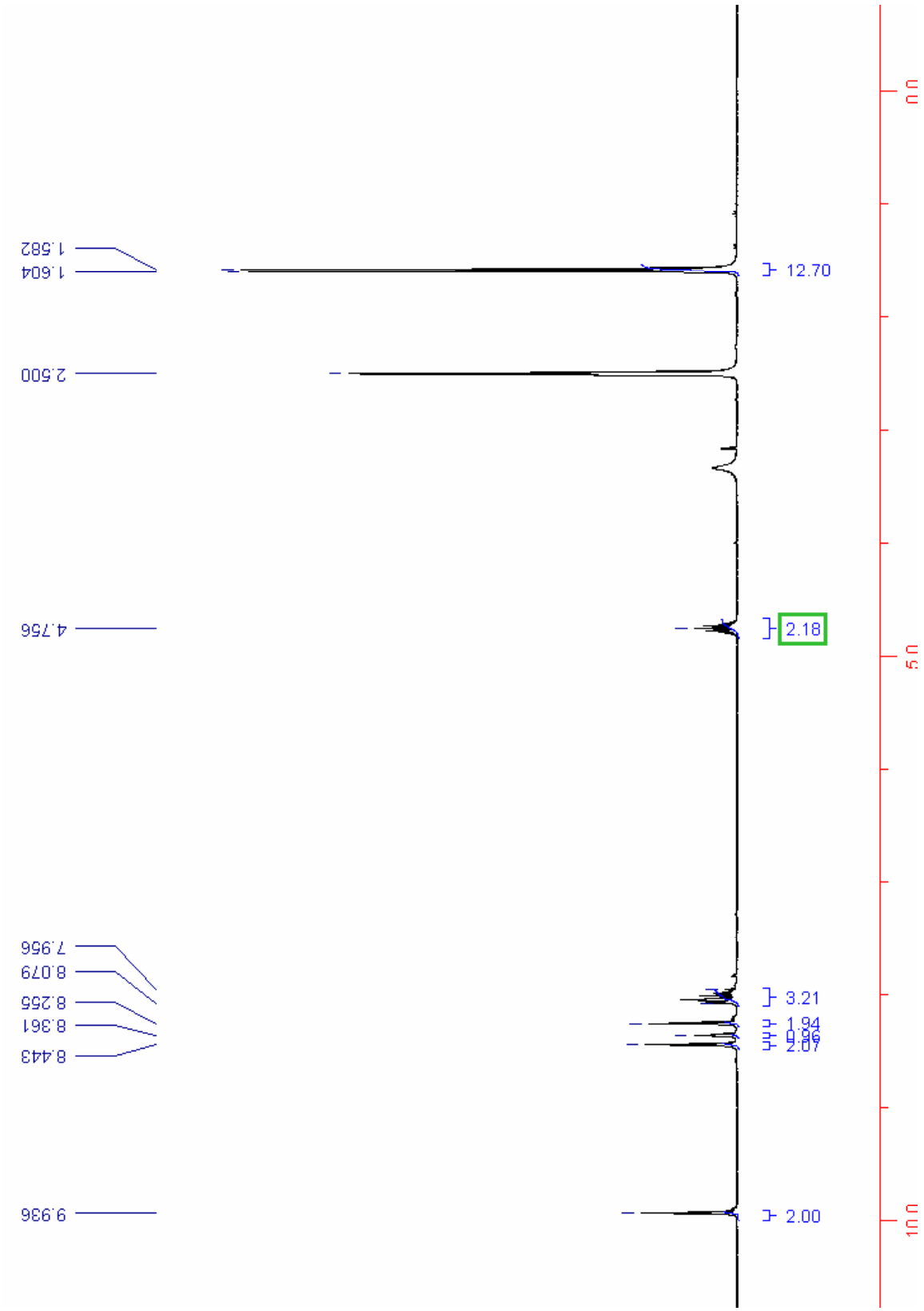
1.365
1.915
2.500
4.314
7.951
8.003
8.032
8.038
8.062
8.161
8.388
8.462
10.034
6.17
4.21
4.11
4.06
3.04
2.02
1.00
2.04
2.00
0.0
5.0
10.0

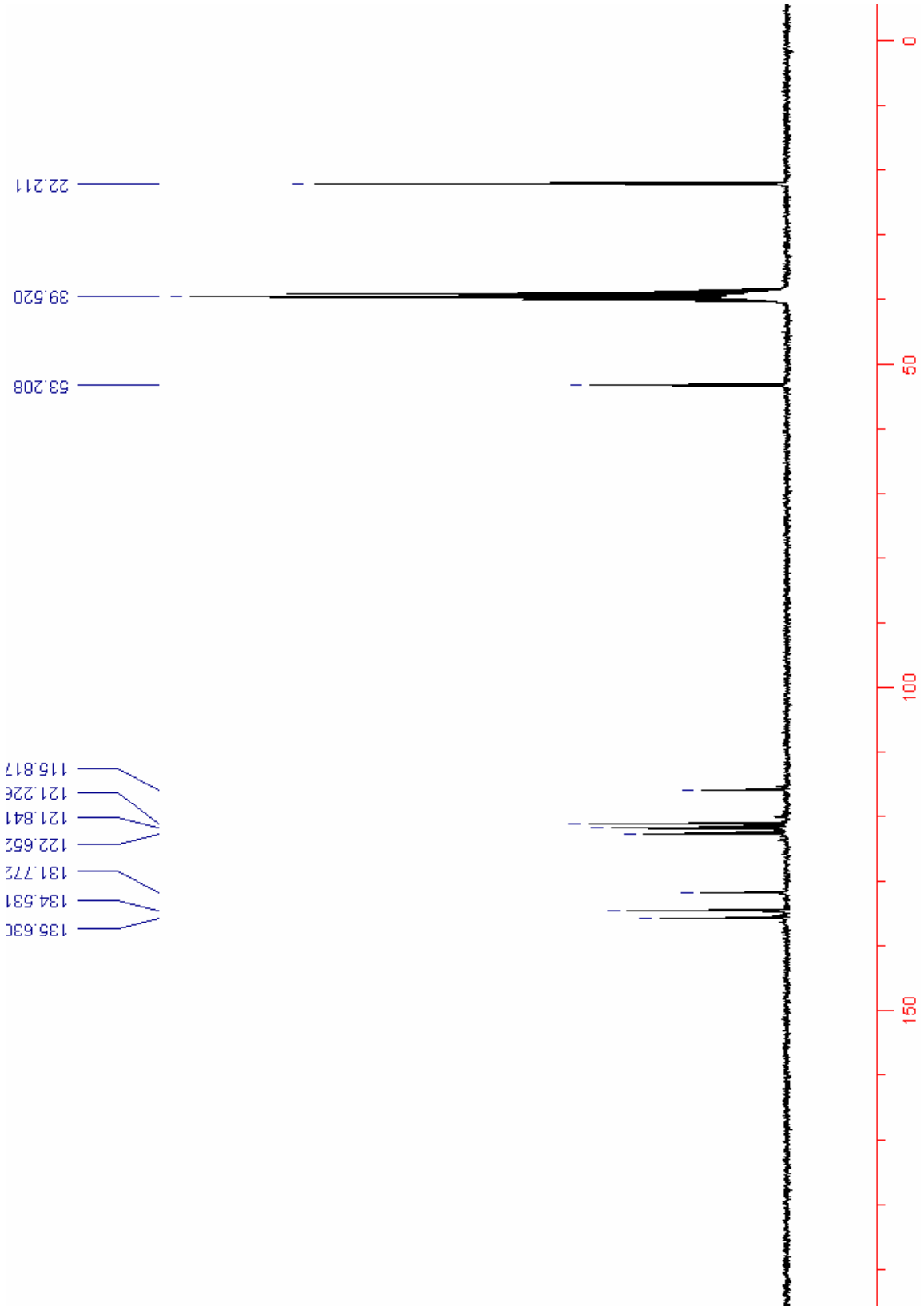
compound **3** (^{13}C NMR, DMSO)



compound **4** (^{1}H NMR, DMSO)



compound **4** (^{13}C NMR, DMSO)



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compound **7** (^{1}H NMR, CD_3CN)

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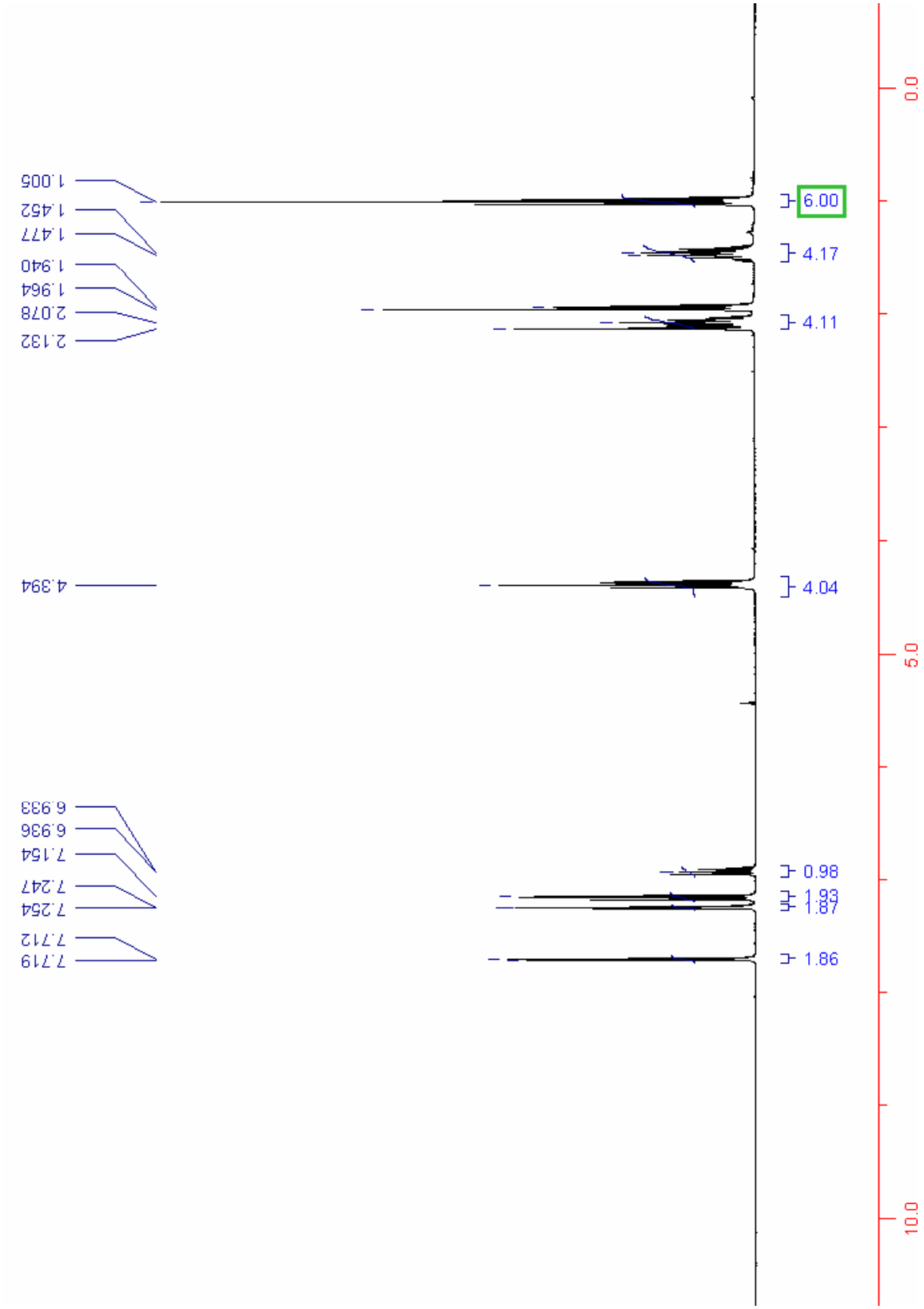
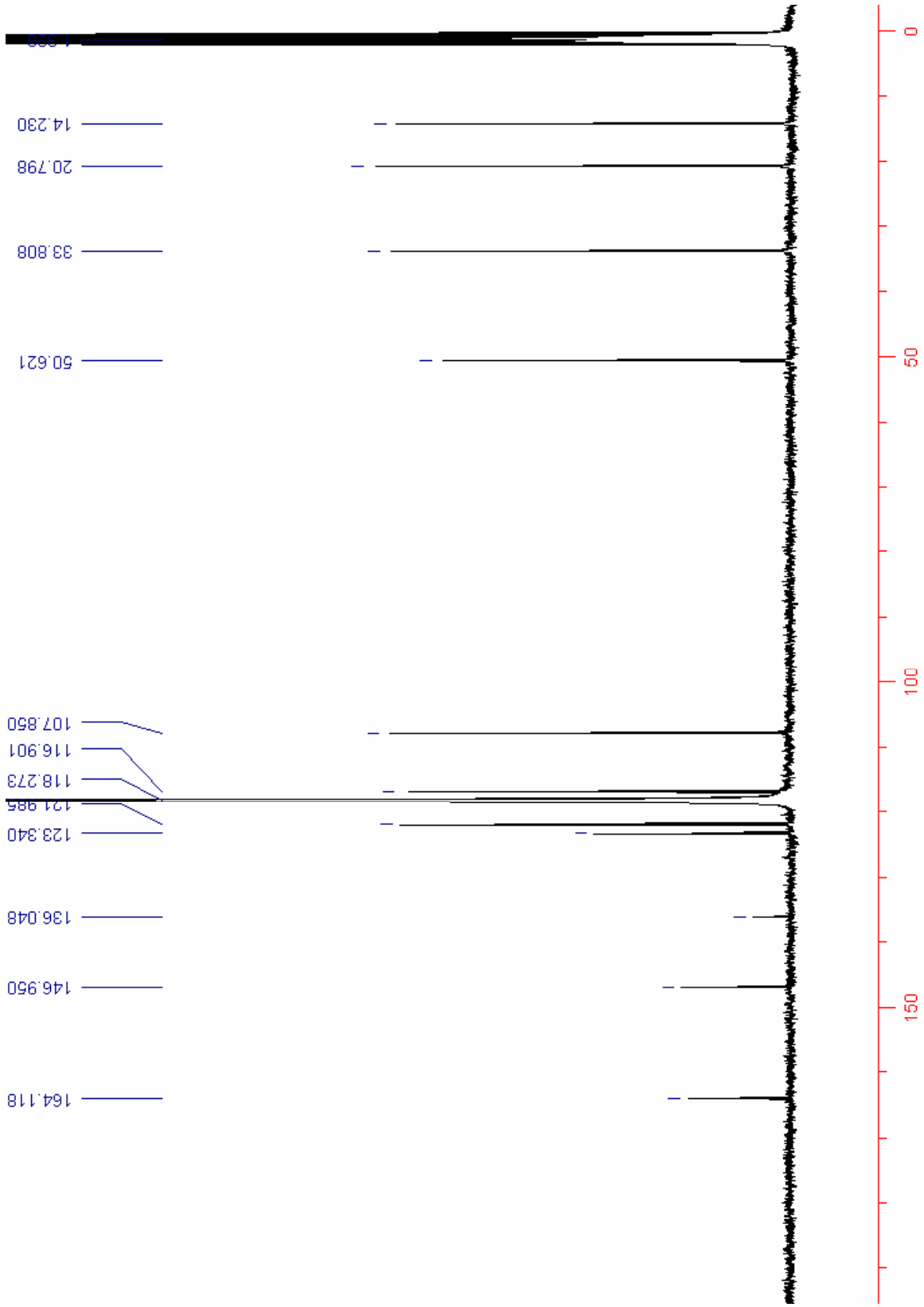
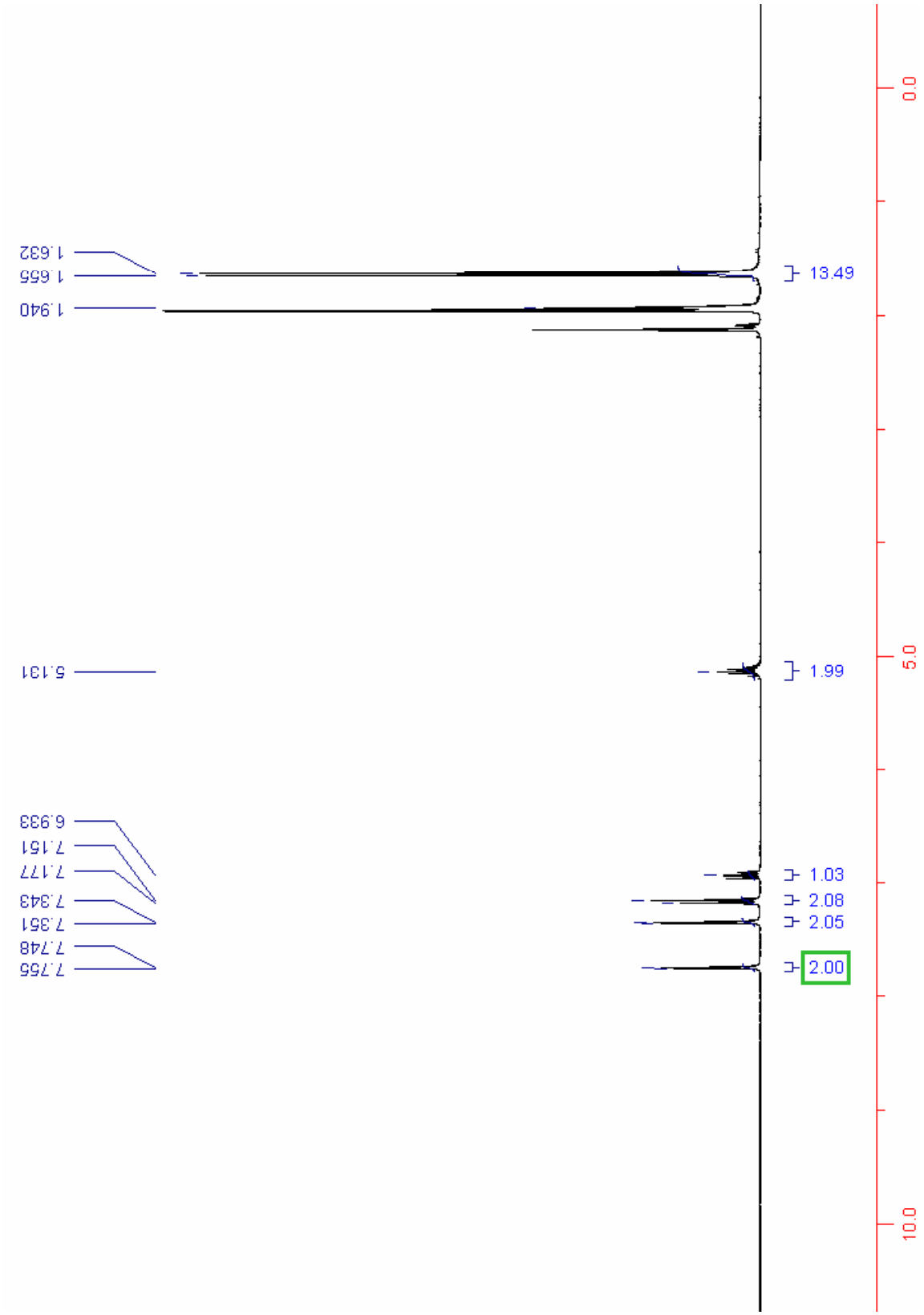


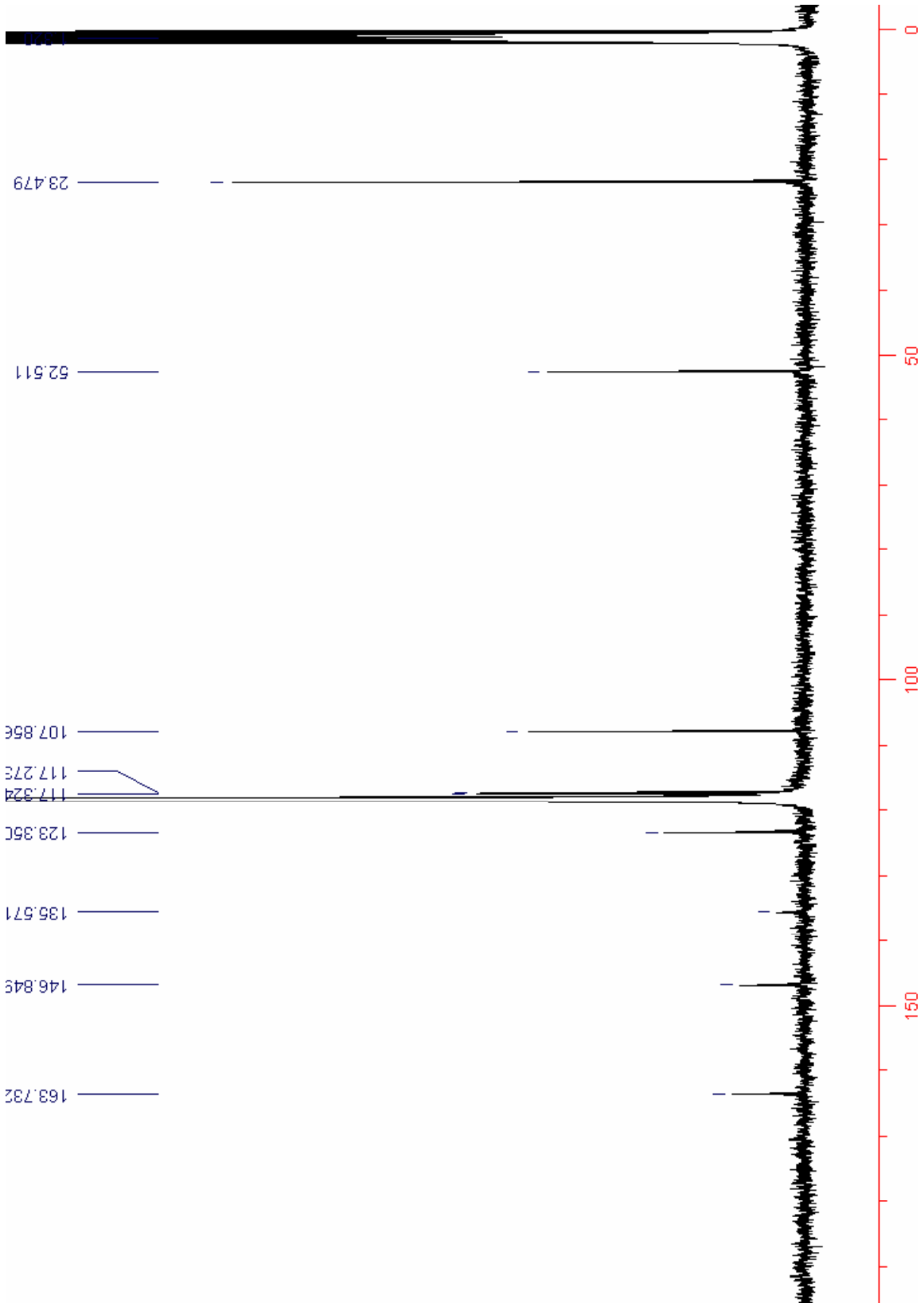
compound **7** (^{13}C NMR, CD_3CN)



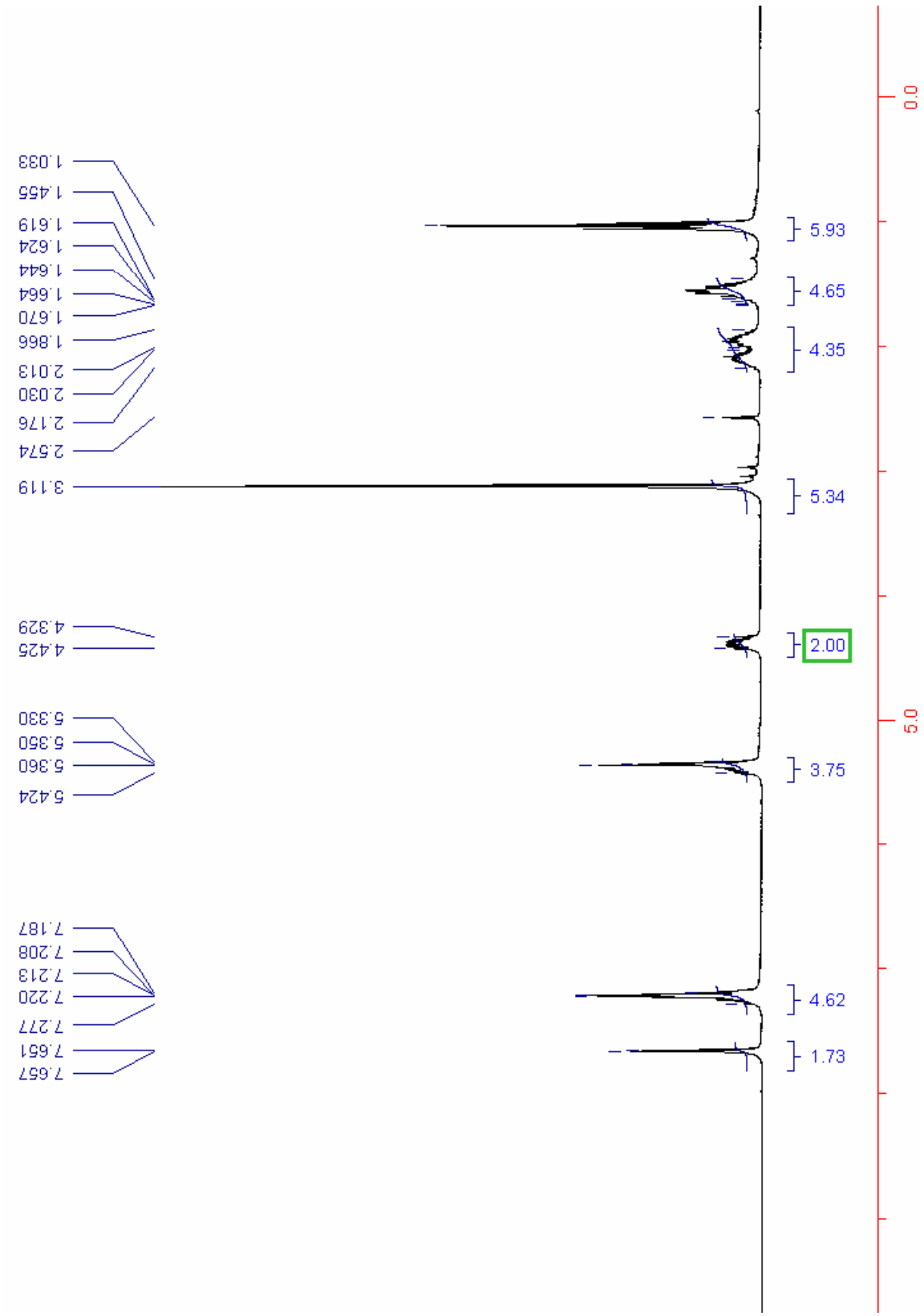
compound **8** (^{1}H NMR, CD_3CN)



compound **8** (^{13}C NMR, CD_3CN)



compound **9** (^{1}H NMR, CD_2Cl_2)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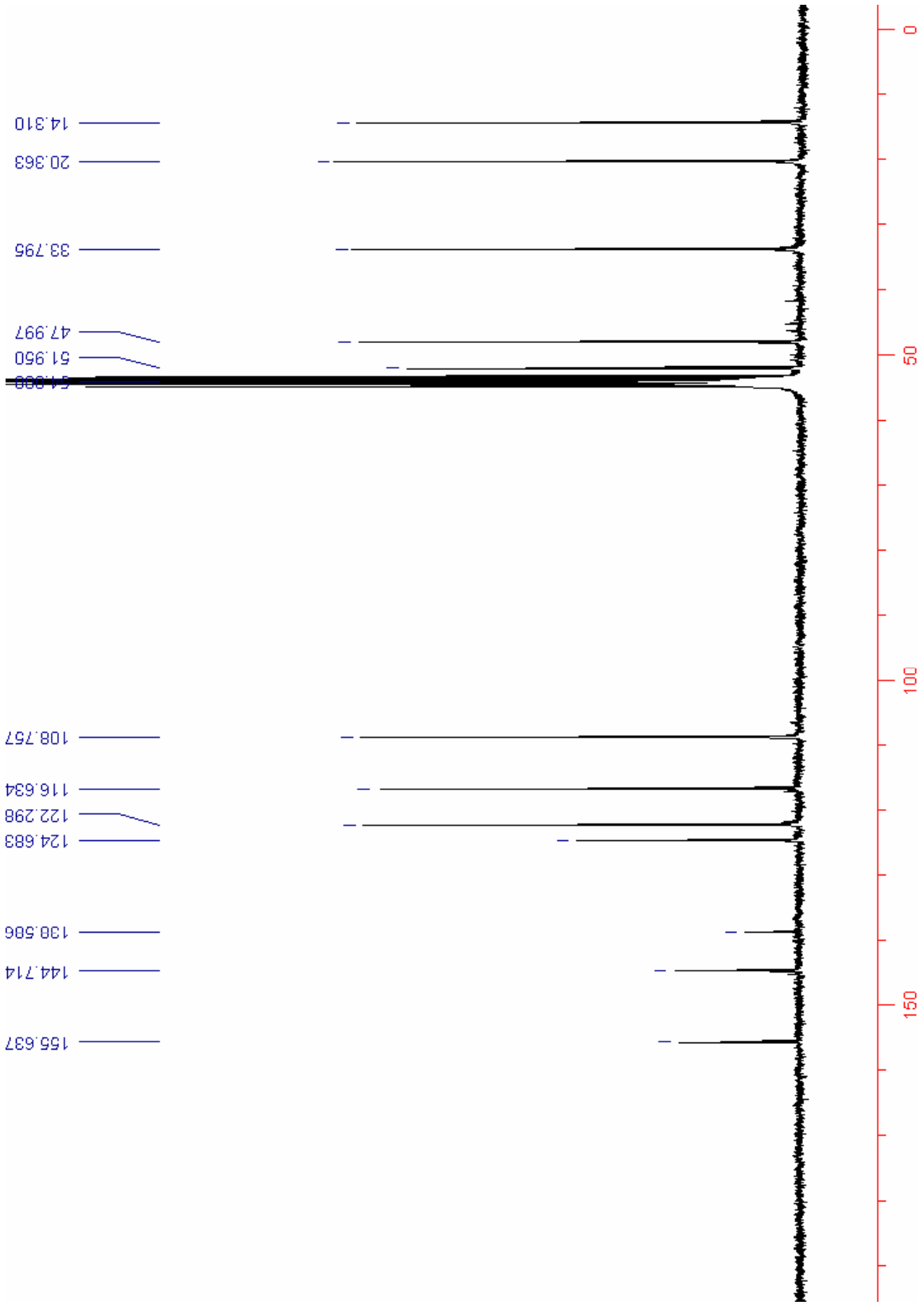
1.644
1.664
1.670
1.866
2.013
2.030
2.176
2.574
3.119
4.329
4.425
5.330
5.350
5.360
5.424
7.187
7.208
7.213
7.220
7.277
7.651
7.657
5.93
4.65
4.35
5.34
2.00
3.75
4.62
1.73
0.0
5.0

compound **9** (^{13}C NMR, CD_2Cl_2)



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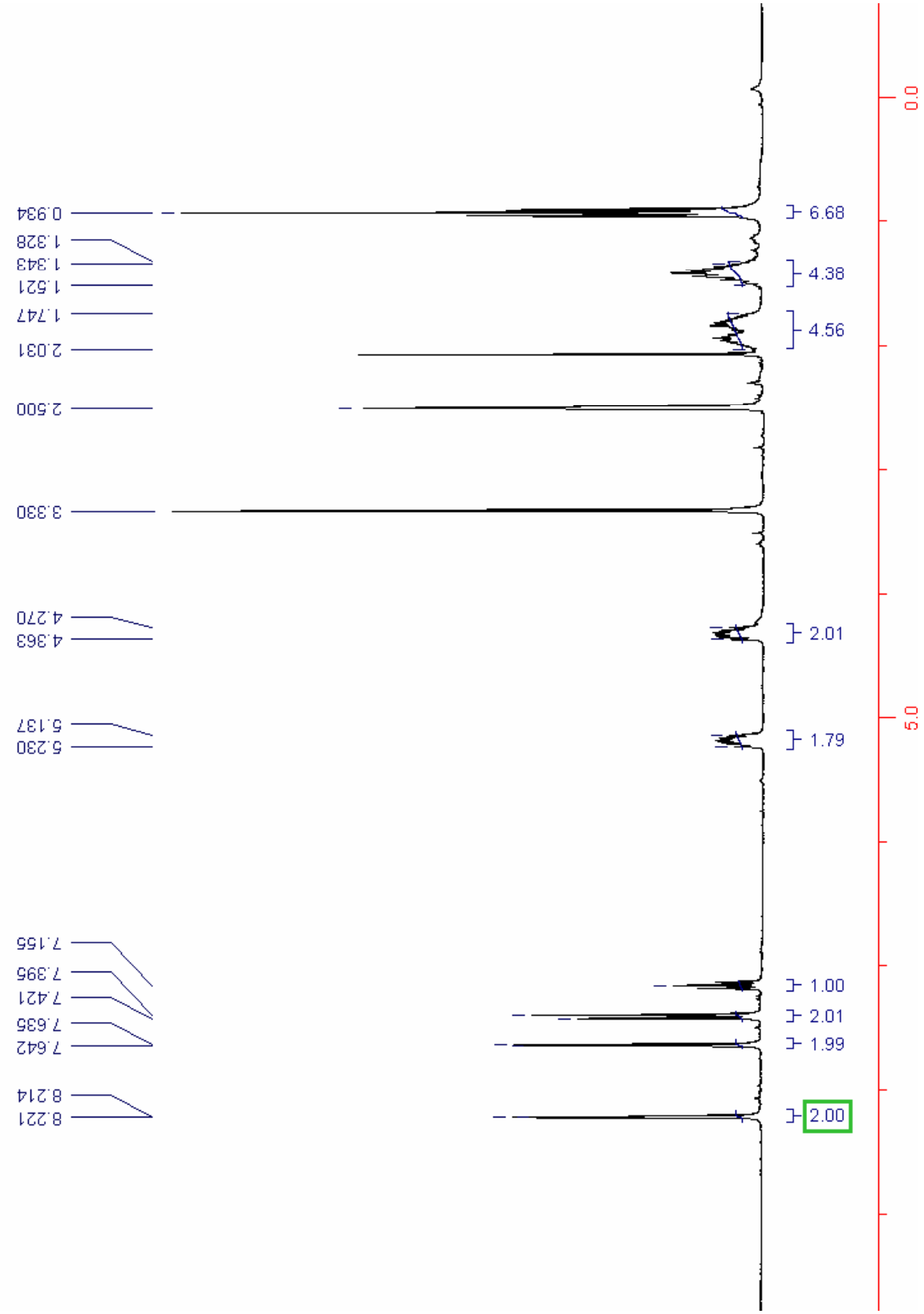
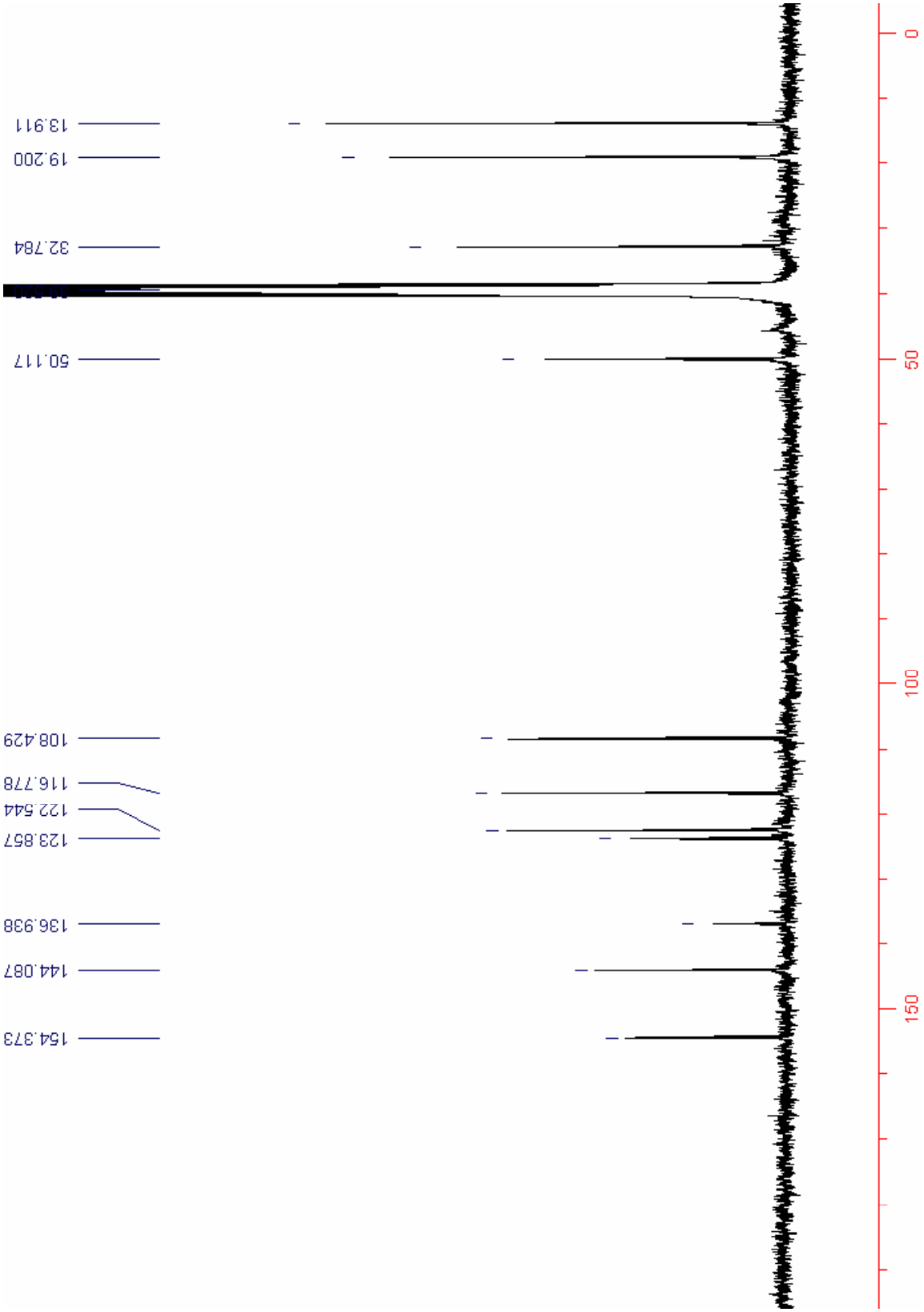
compound **9** (^{1}H NMR, DMSO)



compound **9** (^{13}C NMR, DMSO)



S2. Crystallographic data

The intensity data was collected at 173(2) K on a Kappa CCD diffractometer[S1] (graphite monochromated MoK_α radiation, λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S2] with anisotropic thermal parameters for all the non-hydrogen atoms, except those of the disordered PF_6^- in **2**·MeCN which were refined isotropically. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms.

S1 Bruker-Nonius, Kappa CCD Reference Manual, Nonius BV, The Netherlands, 1998.

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S2 M Sheldrick; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.

S2.1 Crystallographic data of compound 2

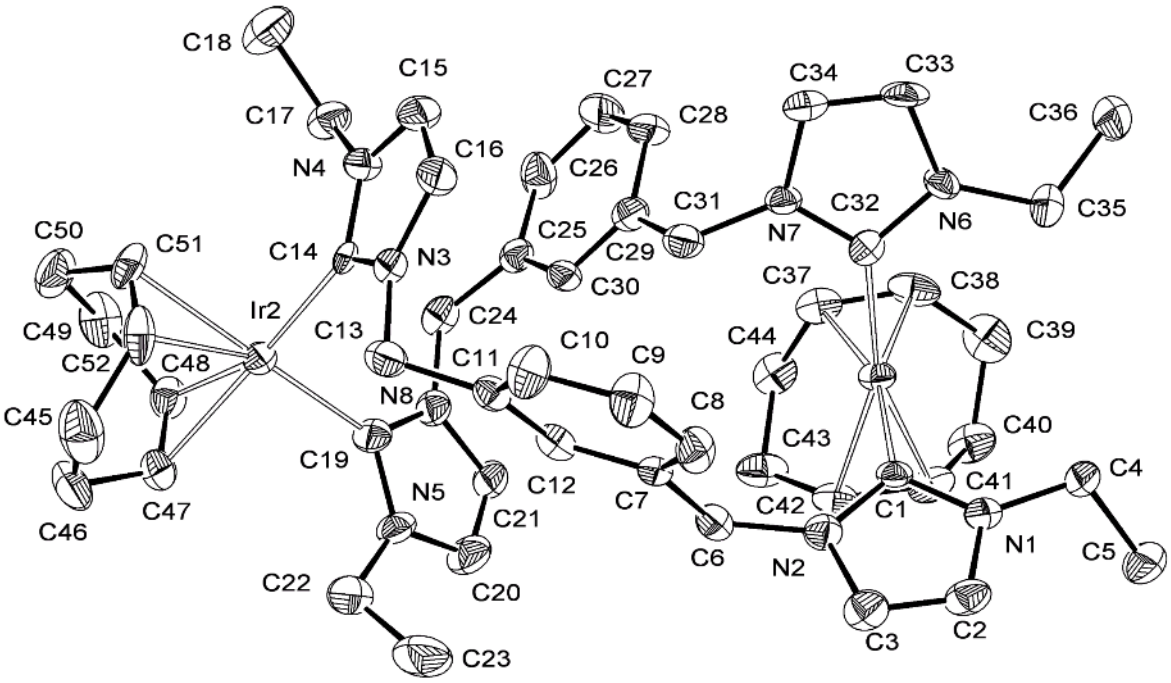

Figure S-1. Molecular structure of the dication in **2**·CH_3CN (50% probability chosen for the ellipsoids, hexafluorophosphate anions, molecule of solvent and hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Ir(1)-C(1) 2.050(6), Ir(1)-C(32) 2.068(6), Ir(1)-C(42) 2.185(6), Ir(1)-C(41) 2.197(6), Ir(1)-C(38) 2.200(6), Ir(1)-C(37) 2.215(6), Ir(2)-C(19) 2.058(6), Ir(2)-C(14) 2.059(6), Ir(2)-C(52) 2.177(6), Ir(2)-C(48) 2.187(6), Ir(2)-C(47) 2.210(6), Ir(2)-C(51) 2.225(6), C(1)-Ir(1)-C(32) 98.1(2), C(1)-Ir(1)-C(42) 86.1(2), C(32)-Ir(1)-C(42) 160.0(2), C(1)-Ir(1)-C(41) 88.8(2), C(32)-Ir(1)-C(41) 161.2(2), C(32)-Ir(1)-C(41) 161.2(2), C(1)-Ir(1)-C(38) 159.2(2), C(32)-Ir(1)-C(38) 87.7(2), C(42)-Ir(1)-C(38) 95.3(2), C(41)-Ir(1)-C(38) 80.2(2), C(1)-Ir(1)-C(37) 161.3(2), C(32)-Ir(1)- C(37) 91.2(2), C(42)-Ir(1)-C(37) 79.9(2), C(41)-Ir(1)-C(37) 87.6(2), C(19)-Ir(2)-C(14) 95.6(2), C(19)-Ir(2)-C(52) 151.5(3), C(14)-Ir(2)-C(52) 89.6(2), C(19)-Ir(2)-C(48) 92.5(2), C(14)-Ir(2)-C(48) 152.0(2), C(52)-Ir(2)-C(48) 96.0(3), C(19)-Ir(2)-C(47) 90.2(2), C(14)-Ir(2)-C(47) 168.2(2), C(52)-Ir(2)-C(47) 80.5(3), C(19)-Ir(2)-C(51) 170.5(2), C(14)-Ir(2)-C(51) 88.5(2), C(48)-Ir(2)-C(51) 80.1(2), C(47)-Ir(2)-C(51) 87.3(3).

Data collection and refinement parameters: formula $C_{54}H_{71}F_{12}Ir_2N_9P_2$, M = 1520.54, monoclinic, space group $C2/c$, a = 46.866(1), b = 12.7769(4), c = 20.6145(4) Å, β = 112.869(1), V = 11373.6(5) Å^3, Z = 8, Dc = 1.776 g cm^{-3}, μ = 4.817 mm^{-1} (Mo-Kα), T = 173, R (I>2σ(I)) = 0.0437, wR(I>2σ(I)) = 0.0883, S = 0.956 for all 8008 unique data (30420 meas., Rint = 0.0610, max 2θ = 53.0°) and 713 refined parameters.

S2.2 Crystallographic data of compound 7

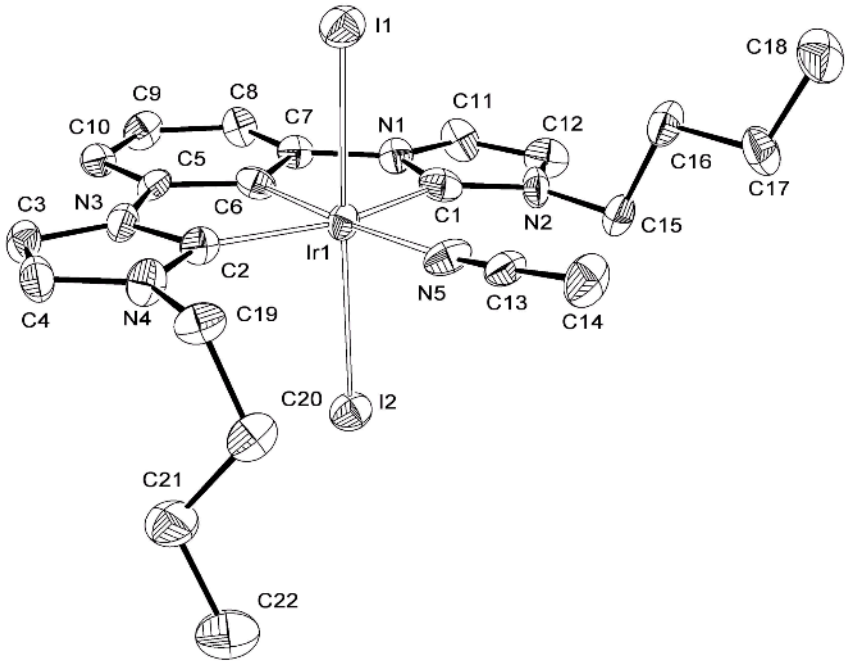

Figure S-2. ORTEP plot of the molecular structure of **7** in **7**·CH_3CN (50% probability chosen for the ellipsoids, molecule of solvent and hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Ir(1)-C(2) 2.047(10), Ir(1)-C(1) 2.053(10), Ir(1)-C(6) 1.987(9), Ir(1)-I(1) 2.6692(8), Ir(1)-I(2) 2.6835(8), Ir(1)-N(5) 2.120(8), C(2)-Ir(1)-C(6) 78.8(4), C(1)-Ir(1)-C(6) 77.8(4).

Data collection and refinement parameters: formula $C_{24}H_{31}I_2Ir_1N_6$, M = 849.55, orthorhombic, space group $P2_12_12_1$, a = 11.0172(5), b = 15.0514(7), c = 16.7082(4) Å, V = 2770.63(19) Å^3, Z = 4, Dc = 2.037 g cm^{-3}, μ = 7.070 mm^{-1} (Mo-Kα), T = 173, $R(I>2\sigma(I))$ = 0.0443, wR(I>2σ(I)) = 0.0928, S = 0.979 for all 5710 unique data (13336 meas., Rint = 0.0645, max 2θ = 53.0°) and 302 refined parameters.

S2.3 Crystallographic data of compound 8

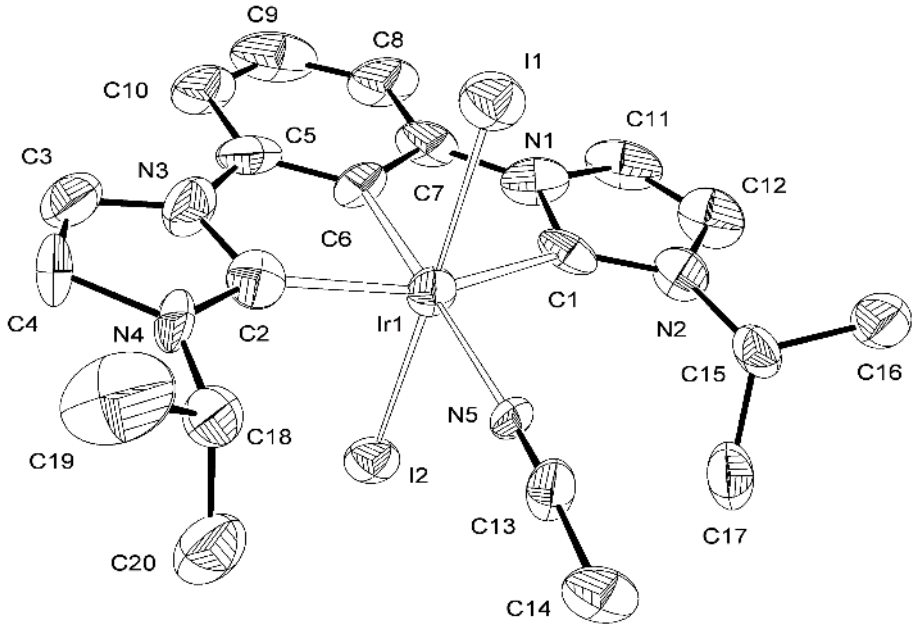

Figure S-3. ORTEP plot of the molecular structure of **8** in **8**·CH_3CN (50% probability chosen for the ellipsoids, molecule of solvent and hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Ir(1)-C(2) 2.051(14), Ir(1)-C(1) 2.068(12), Ir(1)-C(6) 1.975(10), Ir(1)-I(1) 2.6711(11), Ir(1)-I(2) 2.6832(11), Ir(1)-N(5) 2.122(9), C(2)-Ir(1)-C(6) 77.1(5), C(1)-Ir(1)-C(6) 78.5(5). Data collection and refinement parameters: formula $C_{22}H_{27}I_2Ir_1N_6$, M = 821.50, triclinic, space group P-1, a = 9.2130(6), b = 11.3480(8), c = 13.4060(10) Å, V = 1298.13(16) Å^3, Z = 2, Dc = 2.102 g cm^{-3}, μ = 7.541 mm^{-1} (Mo-Kα), T = 173, $R(I>2\sigma(I))$ = 0.0655, wR(I>2σ(I)) = 0.1391, S = 0.995 for all 2932 unique data (11389 meas., Rint = 0.1025, max 2θ = 52.0°) and 286 refined parameters.

S2.4 Crystallographic data of compound 9

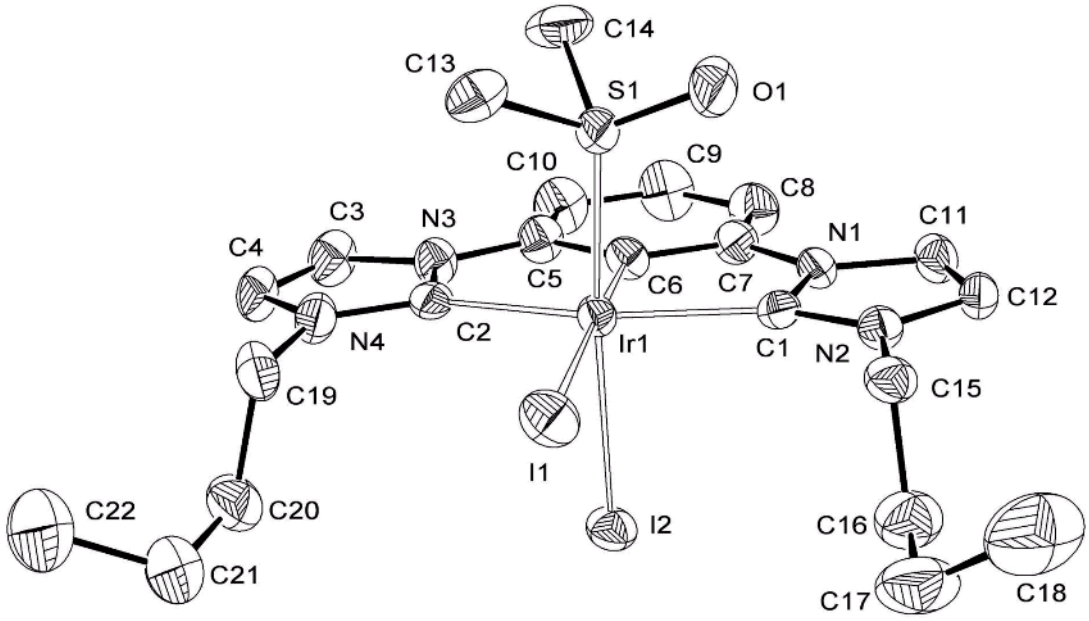

Figure 4. ORTEP plot of the molecular structure of one of the two crystallographically independent molecules of **9** in **9**·1/2CH_2Cl_2 (50% probability chosen for the ellipsoids, molecule of solvent and hydrogens omitted for clarity). Selected bond distances (Å) and angles (°): Ir(1)-C(2) 2.082(5), Ir(1)-C(1) 2.065(5), Ir(1)-C(6) 1.979(5), Ir(1)-I(1) 2.7947(4), Ir(1)-I(2) 2.7141(4), Ir(1)-S(1) 2.2405(14), C(2)-Ir(1)-C(6) 77.8(2), C(1)-Ir(1)-C(6) 77.7(2).

Data collection and refinement parameters: formula $C_{45}H_{64}Cl_2I_4Ir_2N_8O_2S_2$, M = 1776.06, triclinic, space group P-1, a = 13.1064(2), b = 14.8675(4), c = 16.7840(4) Å, α = 73.1480(10), β = 74.9320(10), γ = 64.7570(10), V = 2795.84(11) Å^3, Z = 2, Dc = 2.110 g cm^{-3}, μ = 7.176 mm^{-1} (Mo-Kα), T = 173, R (I>2σ(I)) = 0.0401, wR(I>2σ(I)) = 0.0918, S = 1.030 for all 11369 unique data (38805 meas., Rint = 0.0613, max 2θ = 58°) and 614 refined parameters.