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Protolysis of five-membered metallacyclocumulene complexes of zirconocene and hafnocene

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Table S1. Crystal data, data collection and structure refinement parameters for **3a**

Identification code	**3a**
Empirical formula	$C_{22}H_{27}ClHf$
Formula weight	505.37
Temperature/K	120
Crystal system	Orthorhombic
Space group	Pnma
a/Å	9.6720(7)
b/Å	11.2652(8)
c/Å	18.5235(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2018.3(2)
Z	4
ρ_{calc}g/cm^3	1.663
μ/mm^{-1}	5.301
F(000)	992.0
Crystal size/mm^3	0.18 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.232 to 59.994
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	34457
Independent reflections	3082 [R_{int} = 0.0293, R_{sigma} = 0.0128]
Data/restraints/parameters	3082/0/126
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0159, wR_2 = 0.0389

[a] $R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

2. EXPERIMENTAL SECTION

Experiments were carried out under Ar with careful exclusion of air and moisture using standard Schlenk techniques. The starting five-membered zirconacyclocumulene **1a**[S1], hafnacyclocumulene **1b**[S2] and bis(trimethylsilyl)acetylene complex of zirconocene **6**[S3] were prepared according to the published procedure. Commercial ^{t}BuC≡C–C≡C^{t}Bu was purchased from Sigma Aldrich and used without additional purification. A 4M solution of HCl in dioxane was also purchased from Sigma Aldrich. Solvents (THF, toluene, *n*-pentane, *n*-hexane) were purified by conventional methods and freshly distilled prior to use over metallic sodium under Ar. The ^{1}H and ^{13}C NMR spectra were recorded on AV-400 spectrometer. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of benzene-d_6 (δ_H 7.16 ppm, δ_C 128.0 ppm). The Raman spectra were registered on a JY LABRAM 300 spectrometer (He−Ne laser, 632.8 nm, 5 mW). The mass spectra were recorded on MAT 95-XP and Finnigan Polaris Q instruments. Melting points are uncorrected and were measured in sealed capillaries.

Protolysis of complex **1a** *and synthesis of* **3a**. Complex **1a** (0.795 g, 2.07 mmol) was dissolved in toluene (15 ml), and the resulting yellow-brown solution was treated with a 4M solution (0.5 ml, 2.0 mmol) of HCl in dioxane at room temperature. Immediately, the reaction mixture turned yellow. After 1-2 min, the solution was evaporated *in vacuo* to dryness and the obtained residue was extracted with *n*-hexane (15 ml) at 60°C. Then, the resulting extract was filtrated and placed in dry ice. After day, the formed light yellow crystals of complex **3a** were separated by decanting of the mother liquor, washed with cold *n*-hexane and dried in vacuo. Yield: 0.536 g (61.5 %). M.p. 136-137°C (under Ar). Elemental analysis calcd (%) for $C_{22}H_{29}ClZr$: C 62.89; H 6.96%; found: C 62.81; H 6.97%. ^{1}H NMR (C_6D_6, 297 K, δ): 1.21 (s, 18H, CMe_3); 6.24 (s, 10H, Cp); 6.48 (s, 1H, C=CH). ^{13}C NMR (C_6D_6, 297 K, δ): 28.4 ($\underline{C}Me_3$); 31.3 ($C\underline{Me}_3$); 32.1

(C<u>Me</u>$_3$); 42.2 (<u>C</u>Me$_3$); 83.4, 99.8 (C≡C); 113.3 (C=<u>C</u>H); 114.0 (Cp); 206.8 (Zr<u>C</u>). Raman spectrum (cm^{-1}): 2196 (ν C≡C). MS (70 eV, *m*/*z*): 418 [M]$^+$; 382 [M-HCl]$^+$; 361 [M-^{t}Bu]$^+$; 255 [Cp$_2$ZrCl]$^+$; 220 [Cp$_2$Zr]$^+$.

Protolysis of complex **1b** *and synthesis of* **3b**. Complex **1b** (0.561 g, 1.19 mmol) was dissolved in *n*-hexane (25 ml) at 60°C, and the resulting light yellow solution was treated with a 4M solution (0.26 ml, 1.2 mmol) of HCl in dioxane at room temperature with active stirring. After 1-2 min, the solution was evaporated *in vacuo* to dryness and the obtained residue was extracted with *n*-hexane (15 ml) at 50ºC. Then, the resulting solution was filtrated and placed in the refrigerator at –15°C. After 1 day, the deposited crystals were separated from the solution by the decanting of the mother liquor, washed with cold *n*-hexane and dried *in vacuo*. Yield of **3b**: 0.356 g (59 %). M.p. 144-145°C (under Ar). Elemental analysis calcd (%) for C$_{22}$H$_{29}$ClHf: C 52,08%; H 5,76%; found: C 52,12; H 5,81%. ^{1}H NMR (C$_6$D$_6$, 297 K, δ): 1.22 (s, 9H, CMe$_3$); 1.24 (s, 9H, CMe$_3$); 6.15 (s, 10H, Cp); 6.70 (s, 1H, C=CH). ^{13}C NMR (C$_6$D$_6$, 297 K, δ): 28.4 (<u>C</u>Me$_3$); 31.4 (C<u>Me</u>$_3$); 32.1 (C<u>Me</u>$_3$); 42.8 (<u>C</u>Me$_3$); 83.6, 100.3 (C≡C); 113.0 (Cp); 113.9 (C=<u>C</u>H); 214.4 (Hf<u>C</u>). Raman spectrum (cm^{-1}): 2196 (ν C≡C). MS (70 eV, *m*/*z*): 508 [M]$^+$; 493 [M-Me]$^+$; 473 [M-Cl]$^+$; 451 [M-^{t}Bu]$^+$; 415 [M-^{t}Bu-HCl]$^+$; 345 [Cp$_2$HfCl]$^+$.

Protolysis of complex **1a** *and synthesis of* **4**. Complex **1a** (1.20 g, 3.13 mmol) was dissolved in toluene (10 ml), and the resulting yellow-brown solution was treated with a 4M solution (1.36 ml, 6.26 mmol) of HCl in dioxane at room temperature which resulted in the immediate deposition of a colorless precipitate and discoloration of the solution. After 1-2 min, the solution was evaporated *in vacuo* during 4 h with solvent trap. By the NMR, the obtained residue is Cp$_2$ZrCl$_2$. The solution in the trap was evaporated by an Ar stream which led to pure **4**. Yield: 0.32 g (62.3 %). M.p. Elemental analysis calcd (%) for C$_{12}$H$_{20}$: C 87.73; H 12.27%; found: C 87.61; H 12.08%.. ^{1}H NMR (C$_6$D$_6$, 297 K, δ): 0.84 (s, 9H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 5.51 (d, ^{2}J = 16.2 Hz, CH); 6.15 (d, ^{2}J = 16.1 Hz, CH). ^{13}C NMR (C$_6$D$_6$, 297 K, δ): 28.1 (<u>C</u>Me$_3$); 29.0 (C<u>Me</u>$_3$); 31.3 (C<u>Me</u>$_3$); 33.6 (<u>C</u>Me$_3$); 78.7, 97.3 (C≡C); 106.4, 153.0 (C=C). MS (70 eV, *m*/*z*): 164 [M]$^+$.

Protolysis of complex **1b** *and synthesis of* **4**. Was used a procedure for the compound **1a** presented above.

Reaction of complex **6** *with* **4**, *synthesis of* **5**. Complex **6** (0.377 g, 0.81 mmol) and enyne **4** (0.135 g, 0.82 mmol) were dissolved in THF (1.5 ml). After 1 day, the light green-yellow solution was evaporated *in vacuo* to dryness, and the obtained residue was extracted with *n*-hexane (15 ml) at 60ºC. The warm solution was filtered and placed in in refrigerator at -40°C. After 2 days, the deposited yellow crystals of **5** were separated from the solution by the decanting of the mother liquor, washed with cold *n*-hexane and dried *in vacuo*. The mother liquor was evaporated to 8 ml and placed in a refrigerator at -40°C which afforded additional crop of **5**. Yield: 0.231 g (74.0 %). M.p. 171-173ºC (with dec., under Ar). Elemental analysis calcd (%) for $C_{22}H_{30}Zr$: C 68.51; H 7.84%; found: C 68.76; H 7.87%. ^{1}H NMR (C_6D_6, 297 K, δ): 1.29 (s, 9H, CMe_3); 1.34 (d, ^{2}J = 14.9 Hz, CH); 1.42 (s, 9H, CMe_3); 4.42 (d, ^{2}J = 14.9 Hz, CH); 5.03 (s, 5H, Cp); 5.42 (s, 5H, Cp). ^{13}C NMR (C_6D_6, 297 K, δ): 33.1 ($C\underline{Me}_3$); 33.5 ($C\underline{Me}_3$); 34.7 ($\underline{C}Me_3$); 36.2 ($\underline{C}Me_3$); 87.4 (Zr$\underline{C}$-C); 94.2 (ZrC-$\underline{C}$); 100.3, 103.6 (Cp); 113.2 (ZrC=$\underline{C}$); 160.9 (Zr$\underline{C}$=C). Raman spectrum (cm^{-1}): 1621 (ν C=C=C). MS (70 eV, *m*/*z*): 384 $[M]^+$; 220 $[Cp_2Zr]^+$.

One-pot synthesis of complex **5** *from complex* **1a.** Complex **1a** (0.553 g, 1.44 mmol) was dissolved in *n*-pentane (7-8 ml), and the resulting light yellow solution with undissolved residue was treated with a 4M solution (0.75 ml, 3.0 mmol) of HCl in dioxane at room temperature with stirring, which resulted in the immediate deposition of a colorless precipitate and discoloration of the solution. The solution was evaporated by an Ar stream at room temperature. After 3 h, magnesium turnings (0.040 g, 1.65 mmol) and THF (10 ml) were added under Ar to the above residue, and the obtained mixture was stirred at room temperature. After 1 day, the resulting dark solution contained 60% of complex **5** according to ^{1}H NMR spectrum.

Crystal data for **3b.** Single-crystal X-ray diffraction experiments of **3b** were carried out with Bruker APEX-II CCD diffractometer. The crystal was kept at 120 K during data collection. Using Olex2,[S4] the

structure was solved with the SHELXT [S5] structure solution program using Intrinsic Phasing and refined with the XL [S6] refinement package using Least Squares minimisation.

CCDC 2277259 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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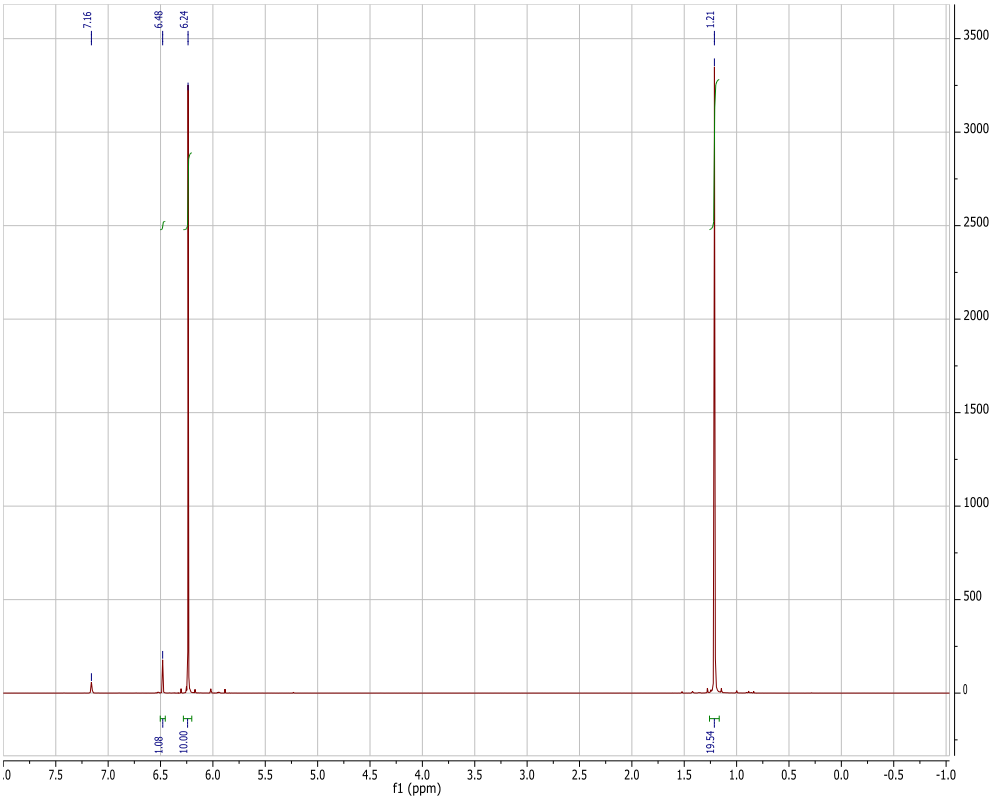
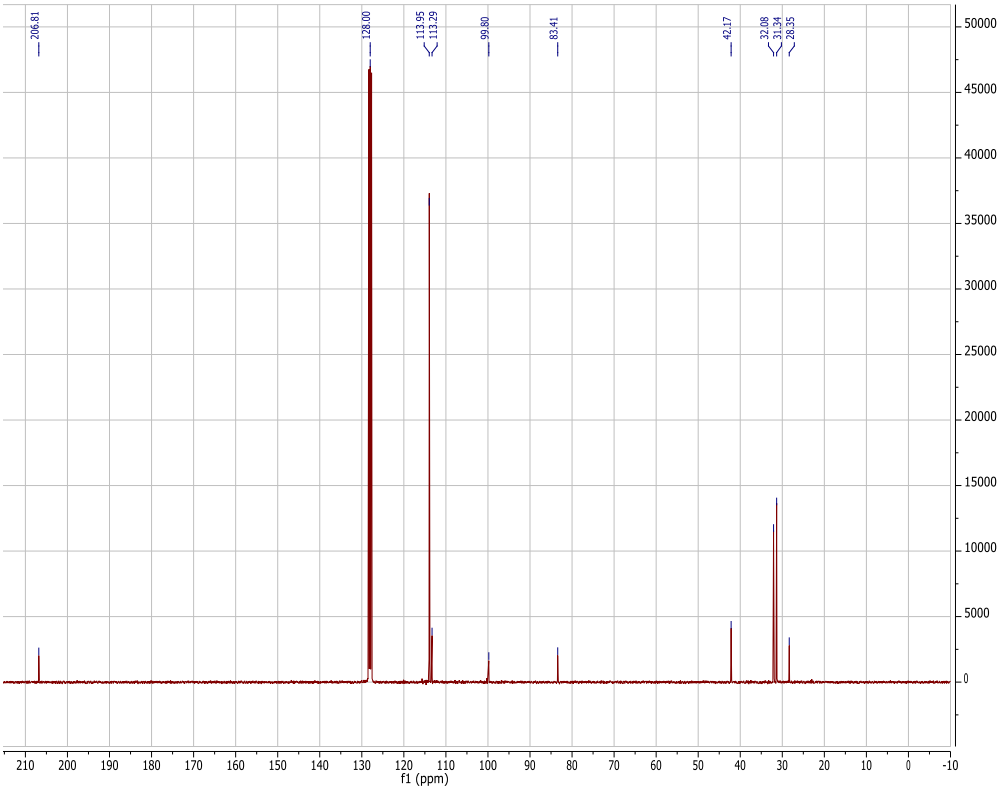
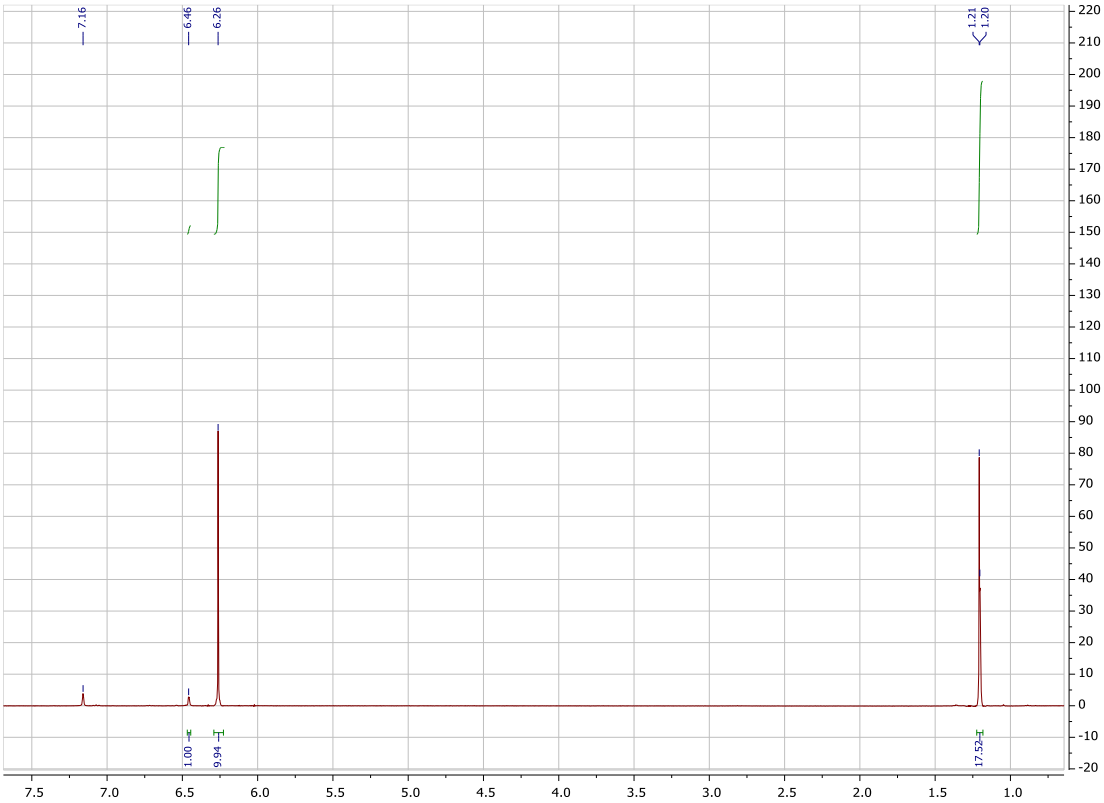
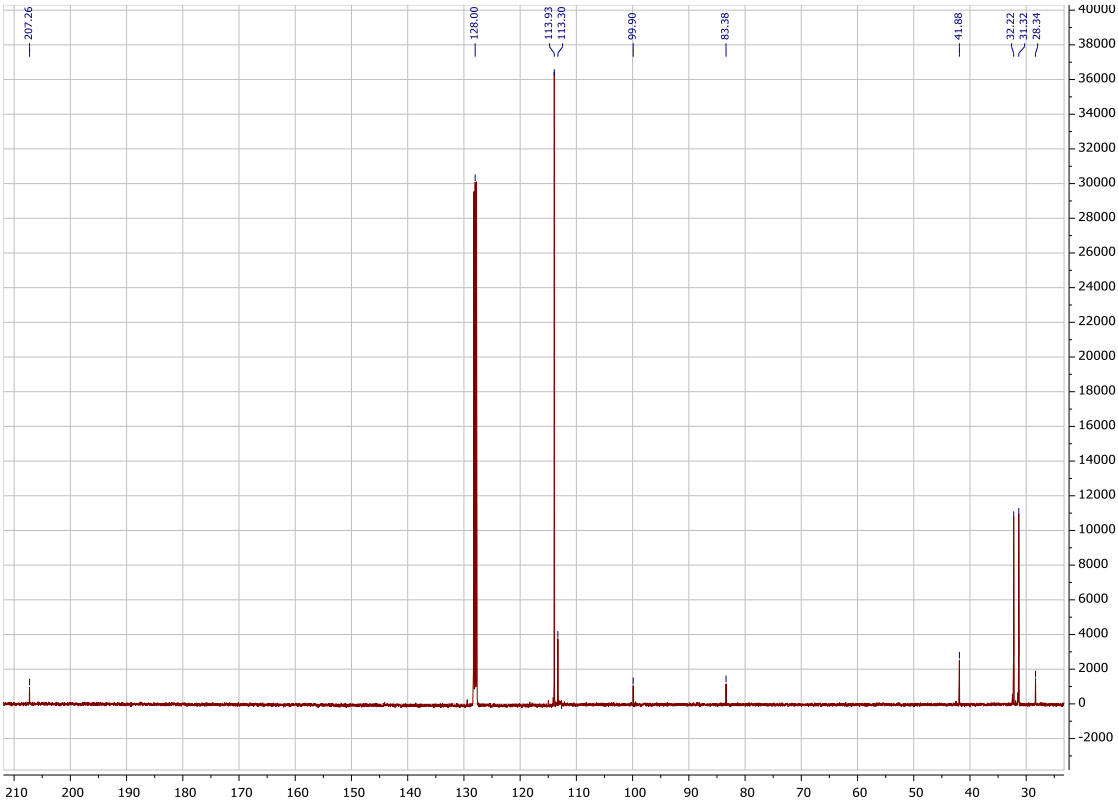
^{1}H and ^{13}C NMR spectra of **3a**



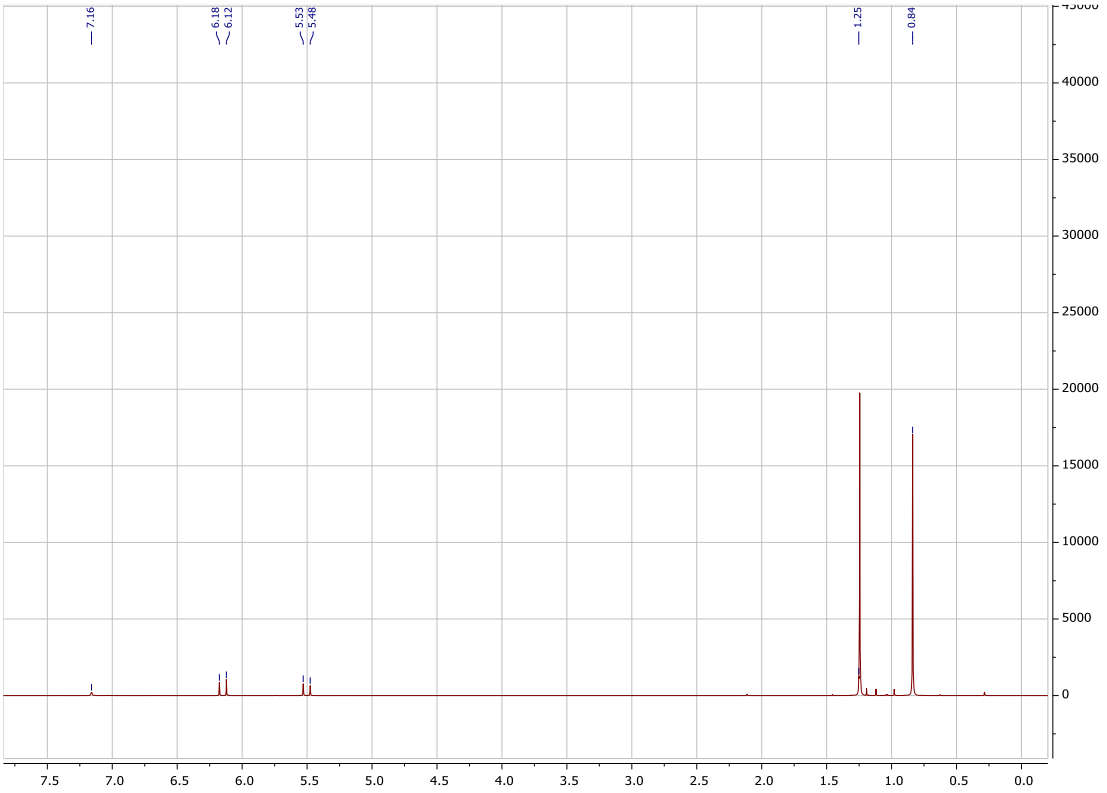


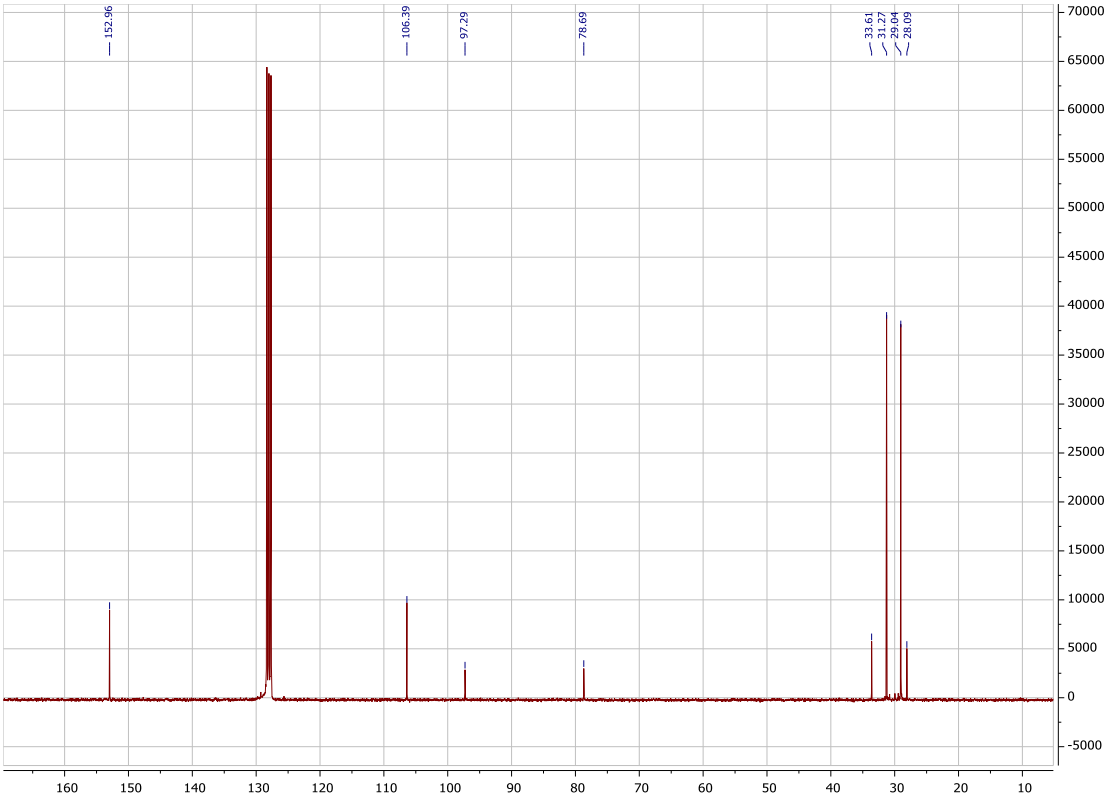
^{1}H and ^{13}C NMR spectra of **3b**





^{1}H and ^{13}C NMR spectra of **4**





^{1}H and ^{13}C NMR spectra of **5**