

Supplementary Information

Title:

Hydride-Induced Cleavage of C-O Bond in Pyran Ring of 2-Pyranylidene Carbene Complexes Followed by Ring Closure of Unsaturated Acylmetalates and Reductive Elimination: Mechanism and Synthetic Application

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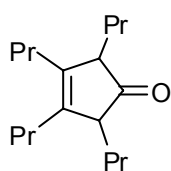
Contents

- 1) Experimental Details and Characterization Data of all new compounds;**
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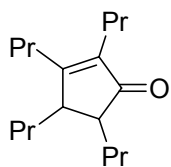
1. Experimental details and characterization data of all new compounds.

All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. 2-Pyranlydene carbene complexes¹ and 1-iodo-1,3-diene derivatives² were synthesized according to the reported procedure. NMR spectra were recorded on a JEOL-AL300 NMR spectrometer using CDCl₃ as the solvent with TMS as an internal standard at 25 °C.

(1) Demetalation Reaction of 2-Pyranlydene Carbene Complexes with LiAlH₄.

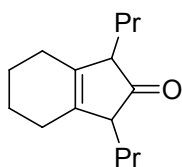


2a: To a THF solution (5 ml) of **1** (0.2 mmol) was added LiAlH₄ (0.1mmol, 1.0 mol/L in THF) at room temperature under N₂ atmosphere. After stirring for 1 h, the reaction mixture was quenched with H₂O and the organic phase was extracted with diethyl ether (5 mL × 3). The volatiles were removed under reduced pressure and the residue was purified with silica gel column chromatography (v/v, PE/Et₂O = 100 : 1). **2a** was isolated as colorless oil. From **1a1**: combined yield: 81% (*trans/cis* = 1/4). From **1b1**: combined yield: 87% (*trans/cis* = 1/4). ¹H NMR (CDCl₃, SiMe₄) of the main product: δ 0.84–0.95 (m, 12H), 1.16–1.72 (m, 12H), 1.94–2.03 (m, 2H), 2.26–2.35 (m, 2H), 2.83 (t, *J* = 5.4 Hz, 2H). ¹³C NMR (CDCl₃, SiMe₄) of the main product: δ 14.27, 14.46, 19.82, 21.32, 28.49, 31.20, 53.09, 136.63, 222.18. These data are consistent with the published data.³



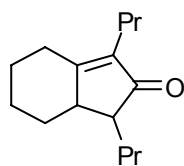
3a: To a THF solution (5 ml) of **1** (0.5 mmol) was added LiAlH₄ (0.25mmol, 1.0 mol/L in THF) at room temperature under N₂ atmosphere. After stirring for 1 h, the reaction mixture was quenched with 3N HCl followed by normal work up. **3a** was isolated as colorless oil. From **1a1**: combined yield: 90% (*trans/cis* = 5/6). From **1b1**: combined yield: 87% (*trans/cis* = 1/1). The *trans* isomer: ¹H NMR (CDCl₃, SiMe₄): δ 0.84–0.98 (m, 14H), 1.23–1.79 (m, 10H), 2.11–2.29 (m, 4H), 2.44–2.54 (m, 1H), 2.91–2.96 (m, 1H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.16, 14.29 (2 CH₃), 14.33, 19.73, 20.81, 21.86, 22.00, 25.16, 27.76, 30.63, 30.78, 42.68,

49.74, 139.17, 172.86, 210.40; The *cis* isomer: ^1H NMR (CDCl_3 , SiMe_4): δ 0.84–0.98 (m, 12H), 1.23–1.49 (m, 8H), 1.58–1.70 (m, 4H), 2.00–2.30 (m, 4H), 2.43–2.52 (m, 2H). ^{13}C NMR (CDCl_3 , SiMe_4): δ 14.00, 14.23, 14.30, 14.41, 20.03, 20.16, 20.76, 21.88, 25.07, 30.42, 34.80, 35.29, 46.37, 50.64, 139.40, 175.10, 211.31. These data are consistent with the published data.⁴

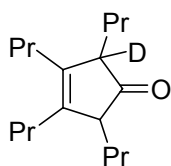


2b was obtained in a manner similar to that described for the synthesis of **2a**. Colorless oil. From **1a2**: combined yield: 83% (*trans/cis* = 1/5). From **1b2**: combined yield: 82% (*trans/cis* = 1/5). ^1H NMR (CDCl_3 , SiMe_4) of the main product: δ 0.80–0.84 (m, 6H), 1.19–1.64 (m, 12H), 1.87–2.05 (m, 4H), 2.64 (t, $J = 4.9$ Hz, 2H). ^{13}C NMR (CDCl_3 , SiMe_4) of the main product: δ 14.46, 19.92, 22.80, 24.16, 31.20, 54.37, 135.26, 222.34. These data are consistent with the published data.

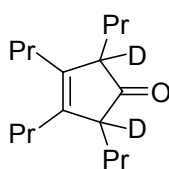
3



3b was obtained in a manner similar to that described for the synthesis of **3a**. Colorless oil. From **1a2**: combined yield: 86% (*trans/cis* = 1/3). From **1b2**: combined yield: 90% (*trans/cis* = 2/3). The *cis* isomer: ^1H NMR (CDCl_3 , SiMe_4): δ 0.83–0.95 (m, 6H), 1.27–1.52 (m, 8H), 1.71–2.19 (m, 9H), 2.83–2.88 (m, 1H). ^{13}C NMR (CDCl_3 , SiMe_4): δ 13.87, 14.18, 20.78, 21.97, 24.53, 25.66, 26.71, 28.57, 33.30, 35.09, 47.47, 52.11, 136.34, 174.48, 210.79. The *trans* isomer was difficult to be isolated and the *cis* isomer was isolated but its *trans* isomer still could be seen in NMR spectrum. These data are consistent with the published data.⁵

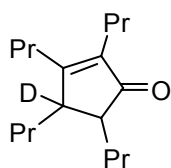


2a-D₁ was obtained in a manner similar to that described for the synthesis of **2a**. The reduction mixture of **1b1** with LiAlH_4 was quenched with D_2O followed by normal work up. Colorless oil **2a-D₁** was isolated as a mixture of *trans* and *cis* isomers (*trans/cis* = 1/4) in 86% combined yield. ^1H NMR (CDCl_3 , SiMe_4) of the main product: δ 0.84–0.95 (m, 12H), 1.15–1.71 (m, 12H), 1.92–2.01 (m, 2H), 2.24–2.34 (m, 2H), 2.83 (t, $J = 5.4$ Hz, 1H). ^{13}C NMR (CDCl_3 , SiMe_4) of the main product: δ 14.27 (2 CH_3), 14.46 (2 CH_3), 19.75, 19.78, 21.26 (2 CH_2), 28.42 (2 CH_2), 31.10, 31.19, 52.64 (t, $J = 19$ Hz), 53.08, 136.51, 136.60, 222.53. These data are consistent with the published data.³



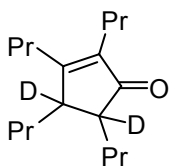
2a-D₂ was obtained in a manner similar to that described for the synthesis of **2a**. The reduction mixture of **1b1** with LiAlD₄ was quenched with D₂O followed by normal work up. **2a-D₂** was isolated as a mixture of *trans* and *cis* isomers (*trans/cis* = 1/4) in 85% combined yield. ¹H NMR (CDCl₃, SiMe₄)

of the main product: δ 0.86–0.95 (m, 12H), 1.15–1.71 (m, 12H), 1.92–2.02 (m, 2H), 2.24–2.34 (m, 2H). ¹³C NMR (CDCl₃, SiMe₄) of the main product: δ 14.26, 14.46, 19.74, 21.25, 28.41, 31.13, 52.66 (t, *J* = 19 Hz), 136.55, 222.67. These data are consistent with the published data.^{4,6}



3a-D₁ was formed in a fashion similar to that of **2a**. The reduction mixture of **1b1** with LiAlH₄ was quenched with 20% DCl followed by normal work up to give **3-D₁** as colorless oil. **3a-D₁** was isolated in 85% combined yield as a mixture of *trans* and *cis* isomers (*trans/cis* = 1/1). The *trans* isomer: ¹H

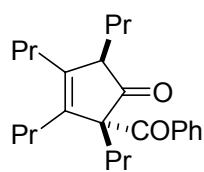
NMR (CDCl₃, SiMe₄): δ 0.84–0.98 (m, 14H), 1.23–1.75 (m, 10H), 2.11–2.27 (m, 4H), 2.44–2.51 (m, 1H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.18, 14.32 (2 CH₃), 14.35, 19.70, 20.83, 21.92, 22.05, 25.19, 27.77, 30.57, 30.81, 42.30 (t, *J* = 20 Hz), 49.75, 139.49, 173.20, 210.91; The *cis* isomer: ¹H NMR (CDCl₃, SiMe₄): δ 0.84–0.98 (m, 12H), 1.21–1.49 (m, 8H), 1.58–1.68 (m, 4H), 2.00–2.30 (m, 4H), 2.43–2.53 (m, 1H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.03, 14.25, 14.33, 14.45, 20.03, 20.20, 20.78, 21.93, 25.10, 30.46, 34.85, 35.25, 45.98 (t, *J* = 19 Hz), 50.66, 139.73, 175.44, 211.82; HRMS Calcd. for C₁₇H₂₉DO: 251.2359. Found: 251.2361.



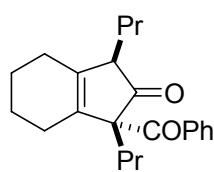
3a-D₂ was formed in a fashion similar to that of **2a**. The reduction mixture of **1b1** with LiAlD₄ was quenched with 20% DCl followed by normal work up to give **3a-D₂** as colorless oil. The major *cis* isomer **3a-D₂** was isolated in 75% yield with trace amount of *trans* isomer. ¹H NMR (CDCl₃, SiMe₄): δ

0.84–0.98 (m, 12H), 1.16–1.74 (m, 12H), 2.09–2.30 (m, 3H), 2.42–2.53 (m, 1H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.03, 14.25, 14.33, 14.44, 20.04, 20.17, 20.78, 21.93, 25.10, 30.47, 34.77, 35.23, 45.93 (t, *J* = 19 Hz), 50.22 (t, *J* = 19 Hz), 139.75, 175.46, 211.84; HRMS Calcd. for C₁₇H₂₈D₂O: 252.2422. Found: 252.2424.

(2) Trapping of the Demetalation Reaction Mixture with PhCOCl: Formation of α -Acylated 3-cyclopentenones **4**.



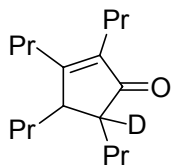
4a: To a THF solution (5 ml) of **1** (0.2 mmol) was added LiAlH₄ (0.1 mmol, 1.0 mol/L in THF) at room temperature under N₂ atmosphere. After stirring for 1 h, benzoyl chloride (0.4 mmol) was added to the mixture. Keeping at room temperature for another 1 h and TLC analysis shows **4a** was formed. Quenching the mixture with 3N HCl followed by normal work up gave **4a** as colorless oil. From **1a1**: yield: 75%. From **1b1**: 89%. ¹H NMR (CDCl₃, SiMe₄): δ 0.84–0.97 (m, 12H), 1.26–1.80 (m, 11H), 1.99–2.39 (m, 5H), 3.00 (t, J = 5.6 Hz, 1H), 7.26–7.62 (m, 5H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.31, 14.33, 14.54, 14.77, 17.77, 20.51, 20.69, 22.84, 28.68, 28.95, 31.60, 35.57, 53.86, 74.88, 127.60 (2C), 128.11, 131.70, 137.55, 139.04, 141.29, 198.88, 217.91. HRMS Calcd. for C₂₄H₃₄O₂: 354.2559. Found: 354.2549; IR (neat): ν (C=O) = 1774, 1738 cm⁻¹.



4b was formed in a fashion similar to that of **4a** as colorless oil. From **1a1**: yield: 91%. From **1b1**: 75%. ¹H NMR (CDCl₃, SiMe₄): δ 0.81–1.07 (m, 10H), 1.26–2.19 (m, 12H), 2.83 (br, 1H), 7.26–7.60 (m, 5H). ¹³C NMR (CDCl₃, SiMe₄): δ 14.32, 14.61, 18.02, 20.80, 22.53, 22.56, 22.82, 24.58, 31.41, 34.70, 55.20, 74.33, 127.34, 128.18, 131.57, 135.64, 139.04, 139.32, 198.46, 216.92. HRMS Calcd. for C₂₂H₂₈O₂: 324.2089. Found: 324.2089; IR (neat): ν (C=O) = 1774, 1724 cm⁻¹.

(3) General Procedure for the Reaction of 1-Lithio-1,3-diene and Metal Carbonyls Followed by Hydrolysis or Acylation with RCOCl:

To a THF solution of 1-iodo-1,3-diene (1mmol) was added *t*-BuLi (2mmol, 1.6 mol/L in hexane) at -78 °C. After stirring at the same temperature for 1 h, M (CO)₆ (M = Cr, W) was added and the mixture was allowed to stir at 60 °C for 3 h. Quenching the mixture with 3N HCl followed by normal workup affords 2-cyclopentenone in high yield with 3-cyclopentenone as a byproduct (*Note*: Under acidic condition, we found 3-cyclopentenone could smoothly convert to 2-cyclopentenone and *trans* isomer of 2-cyclopentenone could convert to its *cis* isomer.). Trapping of the reaction intermediate with benzoyl chloride afforded α -acylated 3-cyclopentenones **4**.



3a-D₁' was formed from the reaction of deuterated 1-lithio-4-deuteo-1,3-diene derivative **5a-D₁** and Cr(CO)₆ and quenched with 3N HCl. **2a-D₁** was generated as a byproduct. **2a-D₁**: Colorless oil. Combined yield: 10% (*trans/cis* = 1/4). **3a-D₁'**: Colorless oil. Combined yield: 85% (*trans/cis* = 1/3).

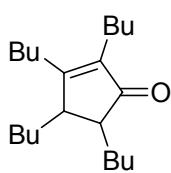
¹H NMR (CDCl₃, SiMe₄) of the *trans* isomer: δ 0.84–0.98 (m, 14H), 1.26–1.75 (m, 10H), 2.11–2.26 (m, 3H), 2.44–2.54 (m, 1H), 2.92 (t, *J* = 4.8 Hz, 1H). ¹³C NMR (CDCl₃, SiMe₄) of the *trans* isomer: δ 14.18, 14.32 (2 CH₃), 14.36, 19.79, 20.85, 21.84, 22.04, 25.20, 27.74, 30.67, 30.83, 42.68, 49.36 (t, *J* = 19 Hz), 139.49, 173.30, 210.93; HRMS Calcd. for C₁₇H₂₉DO: 251.2359. Found: 251.2361. Note: Because under acidic condition, the deuterium incorporated into the α position of 2-cyclopentenone tends to be replaced by hydrogen via its enolate structure, we quenched the mixture followed by purification on silica gel quickly. Only high deuterated *trans* isomer was obtained and its *cis* isomer was obtained with relatively low deuterated product, which indicates the conversion from *trans* isomer to *cis* isomer leads to the loss of deuterium.

3a was also formed from the reaction of 1-lithio-1,3-diene and M (CO)₆. M = Cr, Yield: 85%; M = W, Yield: 75% (*trans/cis* = 1/3).

4a was obtained by trapping the intermediate with benzoyl chloride. For Cr(CO)₆, Yield: 72%; For W(CO)₆, Yield: 88%. (only *cis*)

3b was also formed from the reaction of 1-lithio-1,3-diene and M (CO)₆. M = Cr, Yield: 87%; M = W, Yield: 84% (*cis/trans* > 99/1).

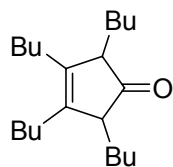
4b was obtained by trapping the reaction intermediate with benzoyl chloride. For Cr(CO)₆, Yield: 70%; For W(CO)₆, Yield: 75%. (only *cis*)



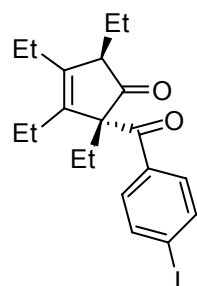
3c was formed in a fashion similar to that of **3a**. **3c**: Colorless oil. For Cr(CO)₆, combined yield: 86% (*trans/cis* = 1/3). For W(CO)₆, combined yield: 62% (*trans/cis* = 1/3). ¹H NMR (CDCl₃, SiMe₄) of the *trans* isomer: δ 0.87-0.98 (m, 12H), 1.24–1.75 (m, 20H), 1.98-2.28 (m, 4H), 2.41–2.56 (m, 2H). ¹³C

NMR (CDCl₃, SiMe₄) of the *trans* isomer: δ 13.92, 13.94, 13.96, 13.99, 22.73 (2C), 22.93 (2C), 23.00, 28.26, 28.85, 29.12, 29.70, 30.93, 32.30, 32.60, 46.55, 50.76, 139.81, 175.50, 211.77. ¹H NMR (CDCl₃, SiMe₄) of the *cis* isomer: δ 0.83–0.97 (m, 14H), 1.27–1.54 (m, 18H), 2.13–2.16 (m, 4H), 2.48–2.57 (m, 1H), 2.92–2.97 (m, 1H). ¹³C NMR (CDCl₃, SiMe₄)

of the *cis* isomer: δ 13.94 (3CH₃), 14.04, 22.82, 22.95 (2CH₂), 22.99 (2 CH₂), 25.24, 27.96, 28.56 (2 CH₂), 29.68, 30.97, 31.00, 42.68, 50.04, 139.54, 173.27, 210.90. These data are consistent with the published data.⁴



2c was generated as a byproduct of the above reaction. **2c**: Colorless oil. For Cr(CO)₆, combined yield: < 10% (*trans/cis* = 1/3). For W(CO)₆, combined yield: 30% (*trans/cis* = 1/3). ¹H NMR (CDCl₃, SiMe₄) of the main product: δ 0.84–0.95 (m, 12H), 1.26–1.43 (m, 18H), 1.68–1.75 (m, 2H), 1.96–2.04 (m, 2H), 2.32–2.39 (m, 2H), 2.78–2.83 (m, 2H). ¹³C NMR (CDCl₃, SiMe₄) of the main product: δ 13.93, 14.01, 22.85, 23.08, 26.07, 28.49, 28.62, 30.27, 53.07, 136.49, 222.46. These data are consistent with the published data.⁶

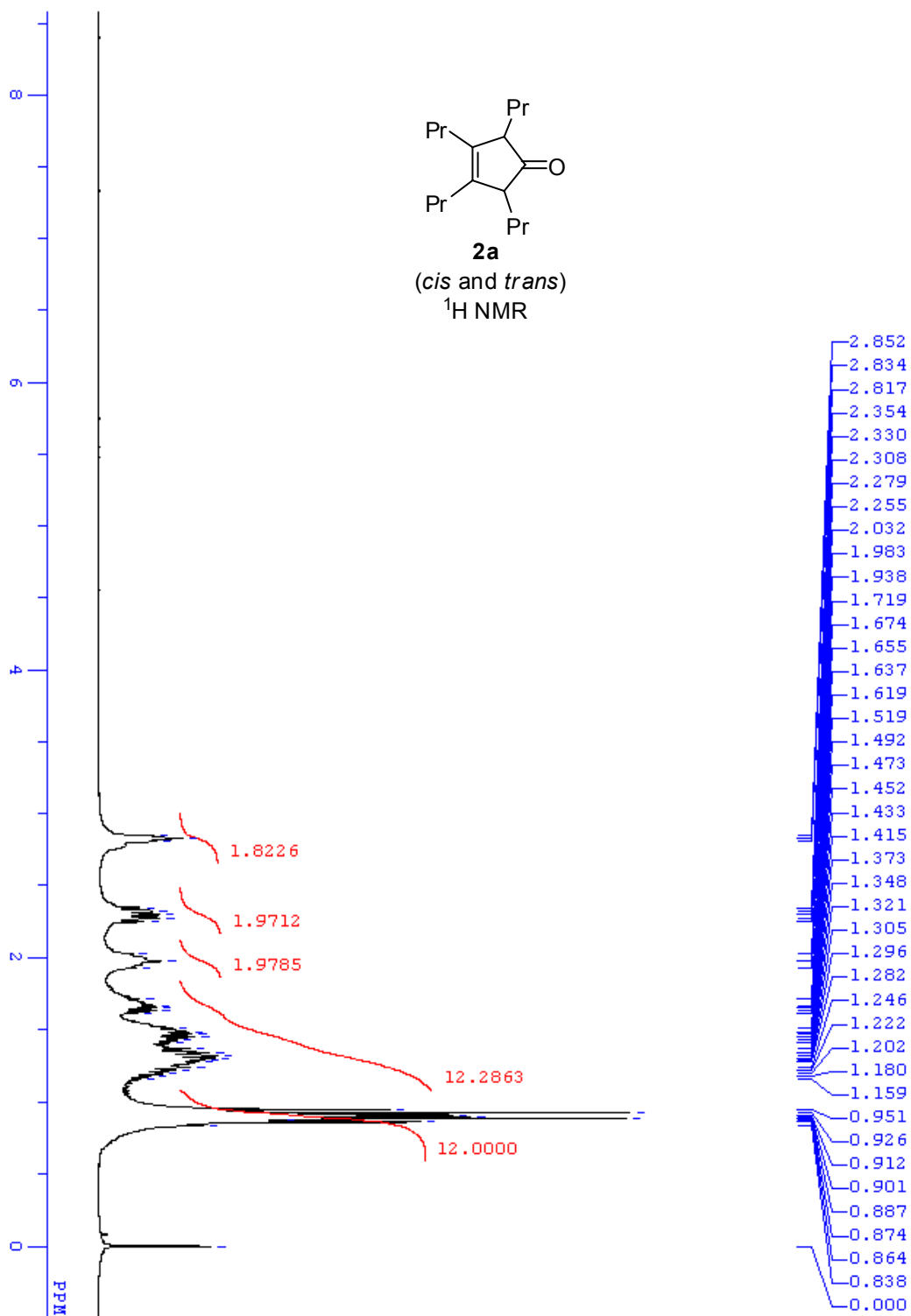


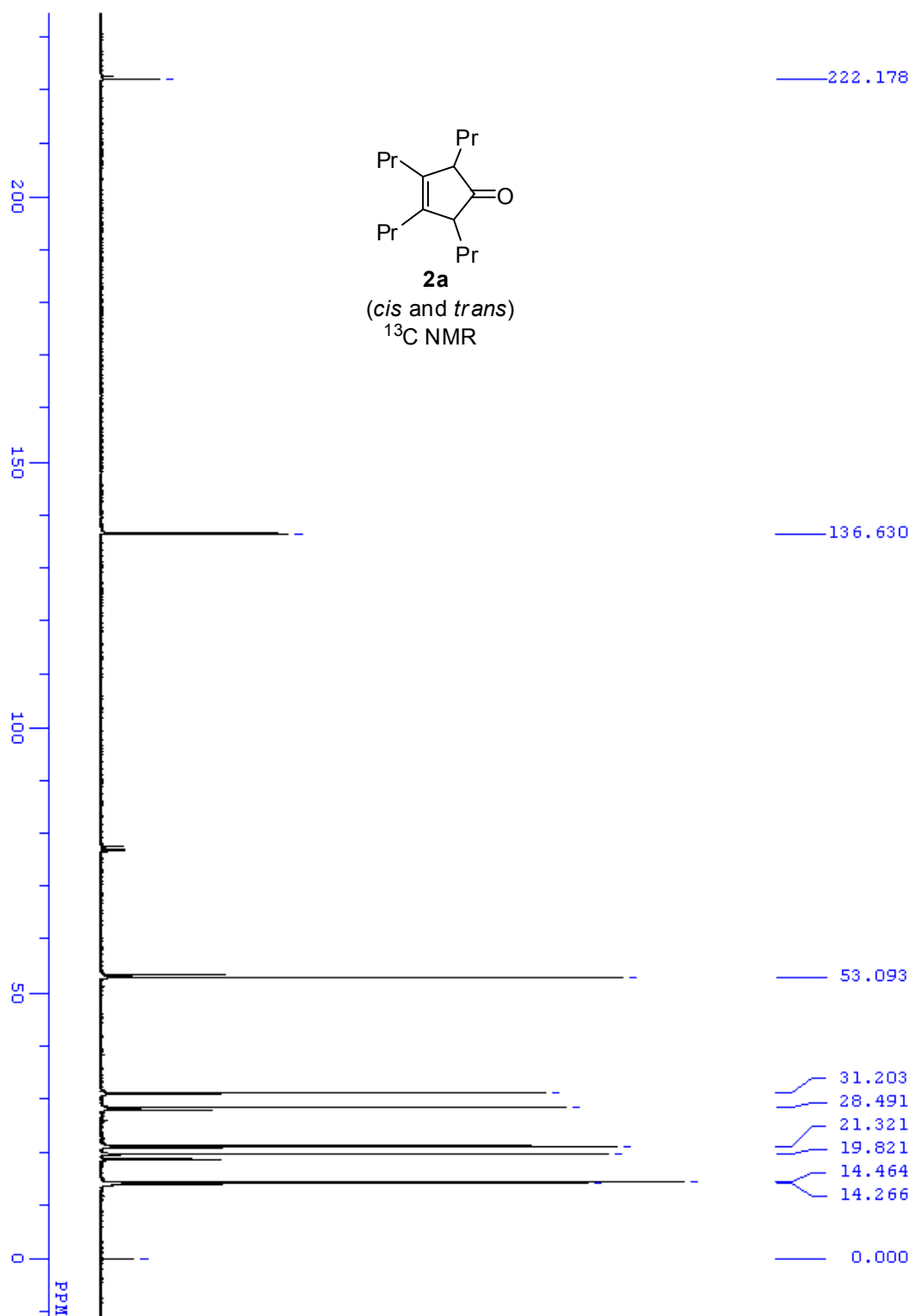
4c was obtained by the reaction of 1-lithio-1,3-diene derivative with W(CO)₆ followed by trapping of the intermediate with 4-iodobenzoyl chloride. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in hexane at –40 °C for one day. Yield: 65%. ¹H NMR (CDCl₃, SiMe₄): δ 0.68 (t, *J* = 7.5 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.42–1.57 (m, 1H), 1.64–1.82 (m, 2H), 1.94–2.25 (m, 4H), 2.39–2.51 (m, 1H), 2.93 (t, *J* = 6.0 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (CDCl₃, SiMe₄): δ 8.88, 11.78, 11.83, 14.00, 19.04, 19.72, 22.16, 26.16, 54.77, 74.92, 99.32, 129.18, 137.34, 138.19, 138.21, 142.34, 197.76, 217.24.

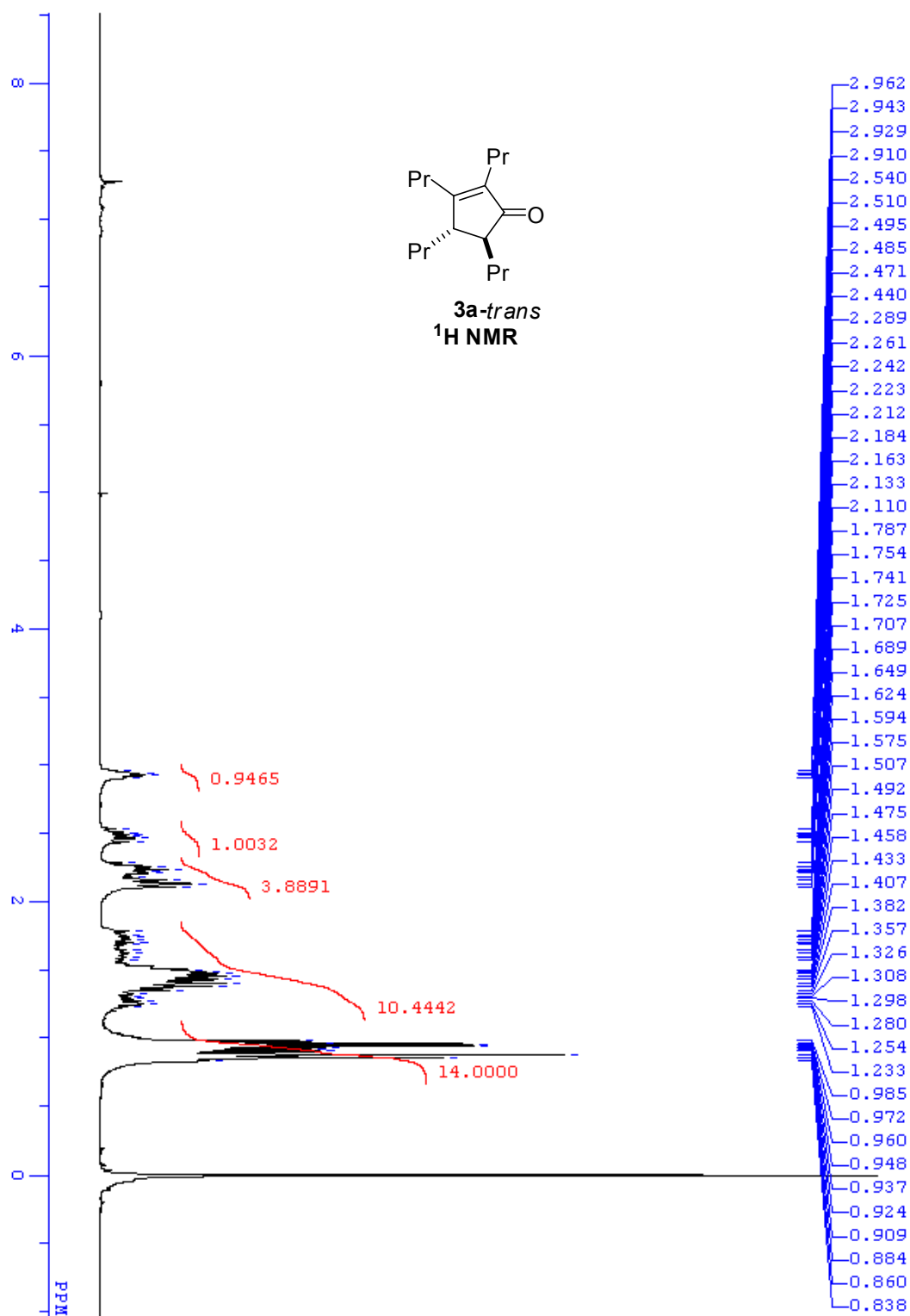
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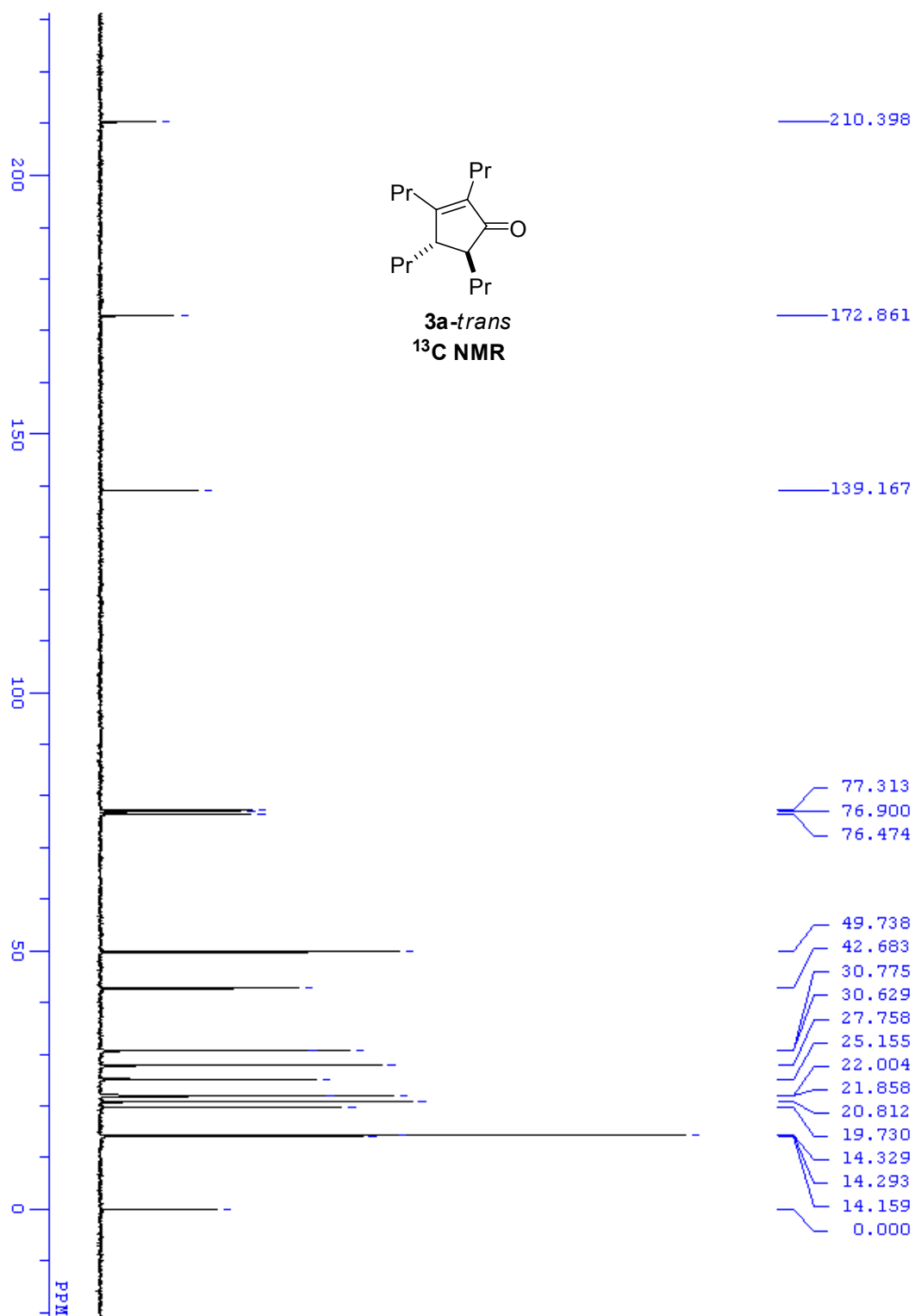
1. Wang, Q.; Zhang, W.-X.; Xi, Z. *Organometallics* **2008**, *27*, 3627–3629.
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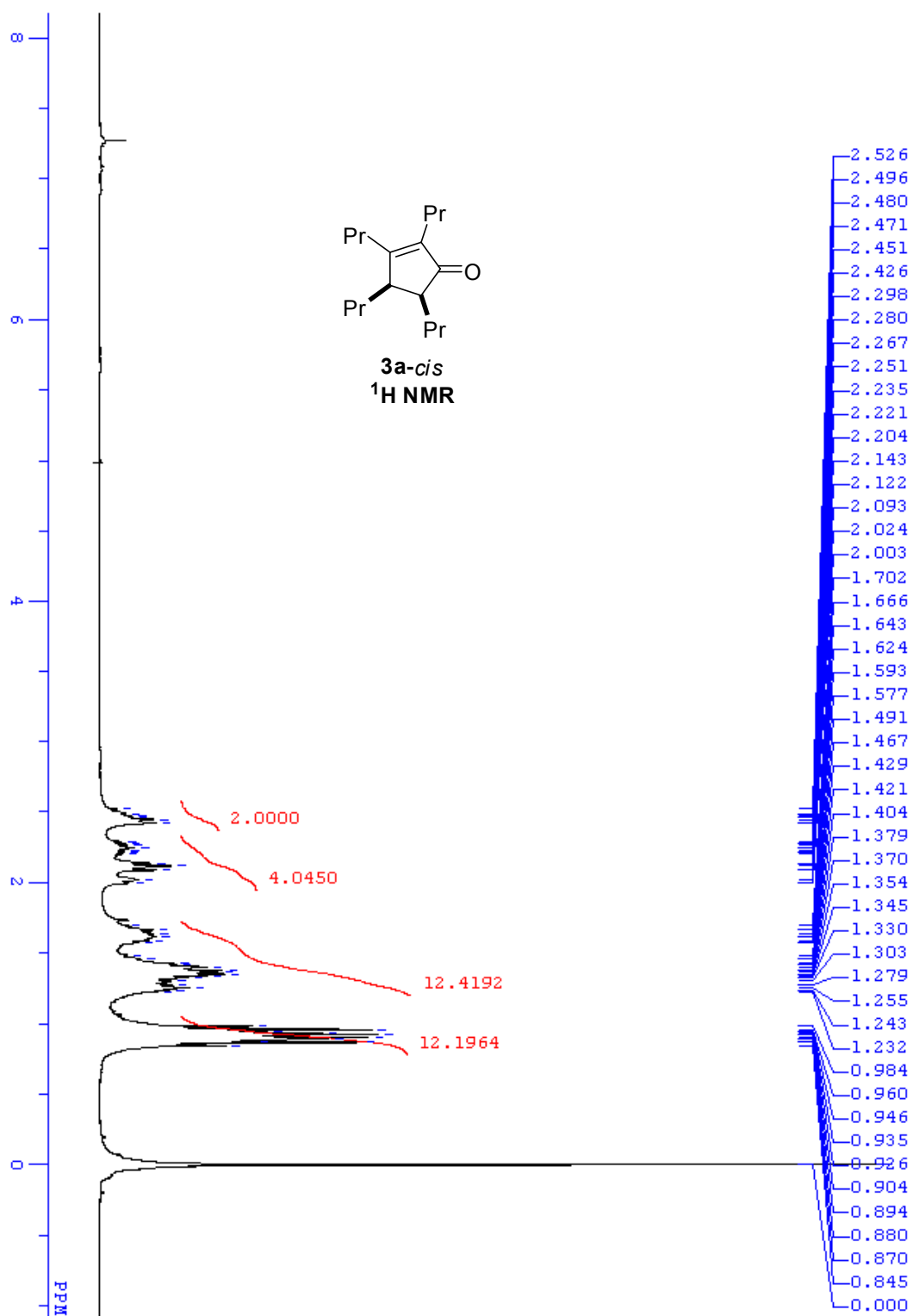
2. Copies of ^1H NMR and ^{13}C NMR spectra for all compounds.

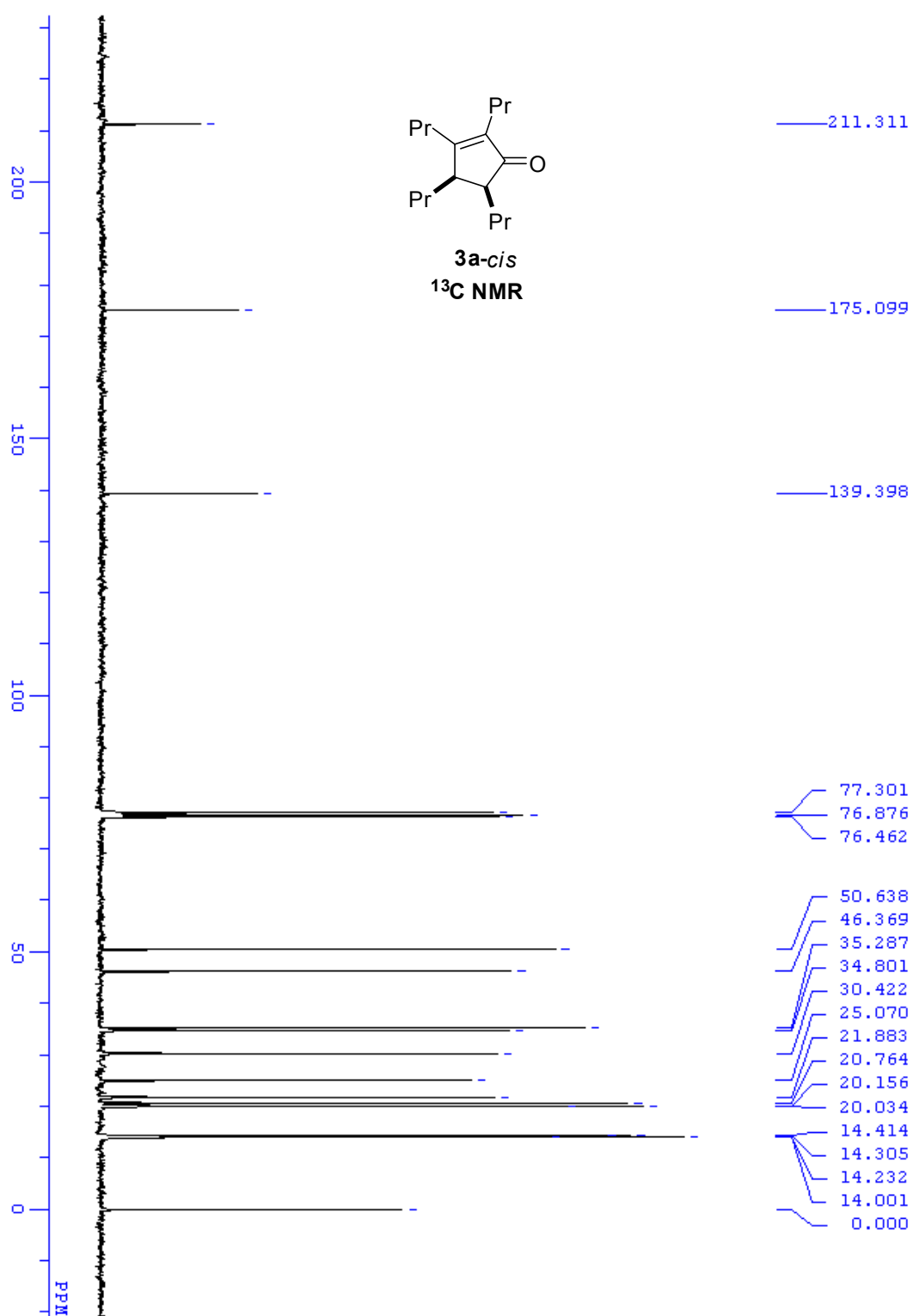


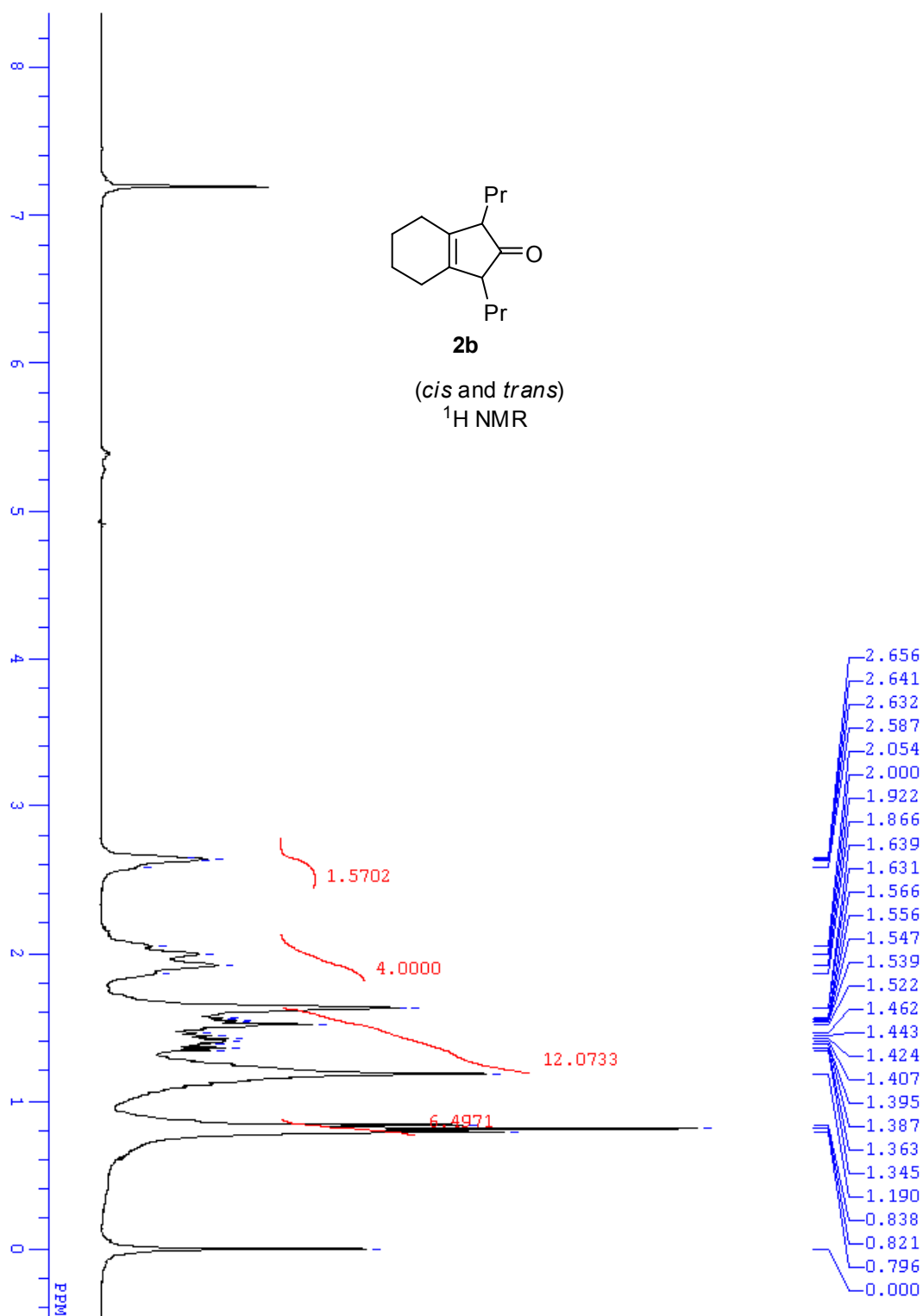


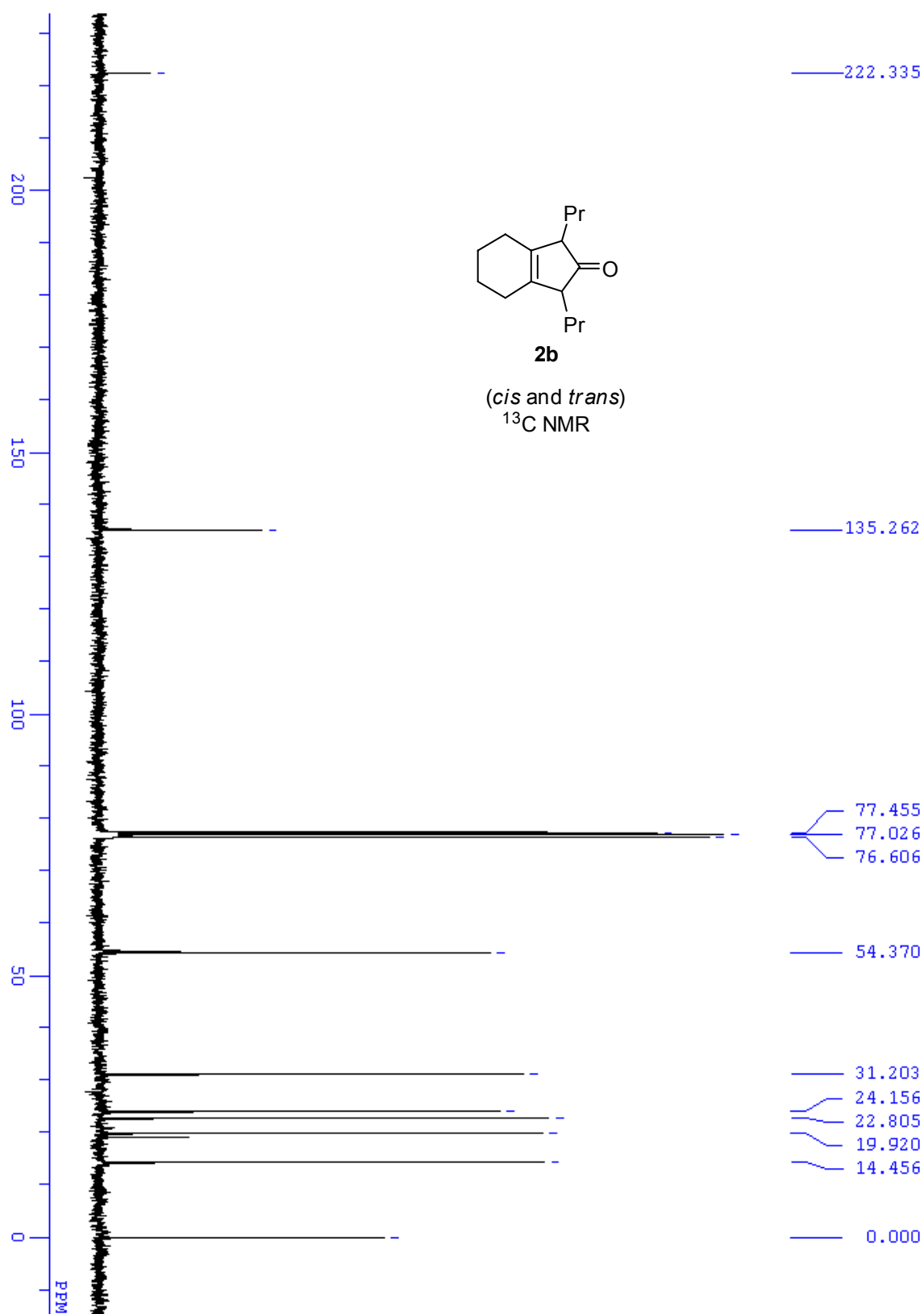


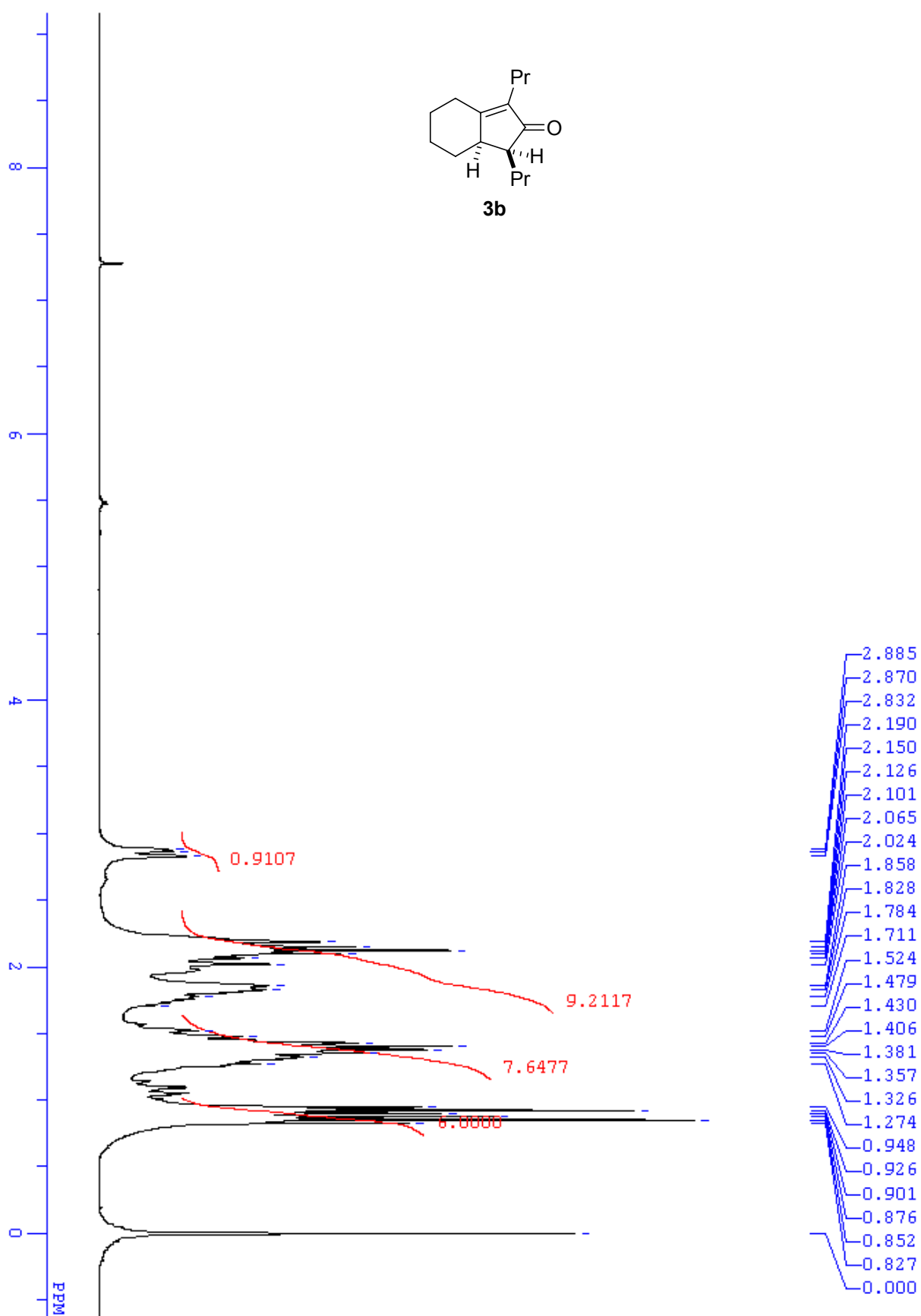


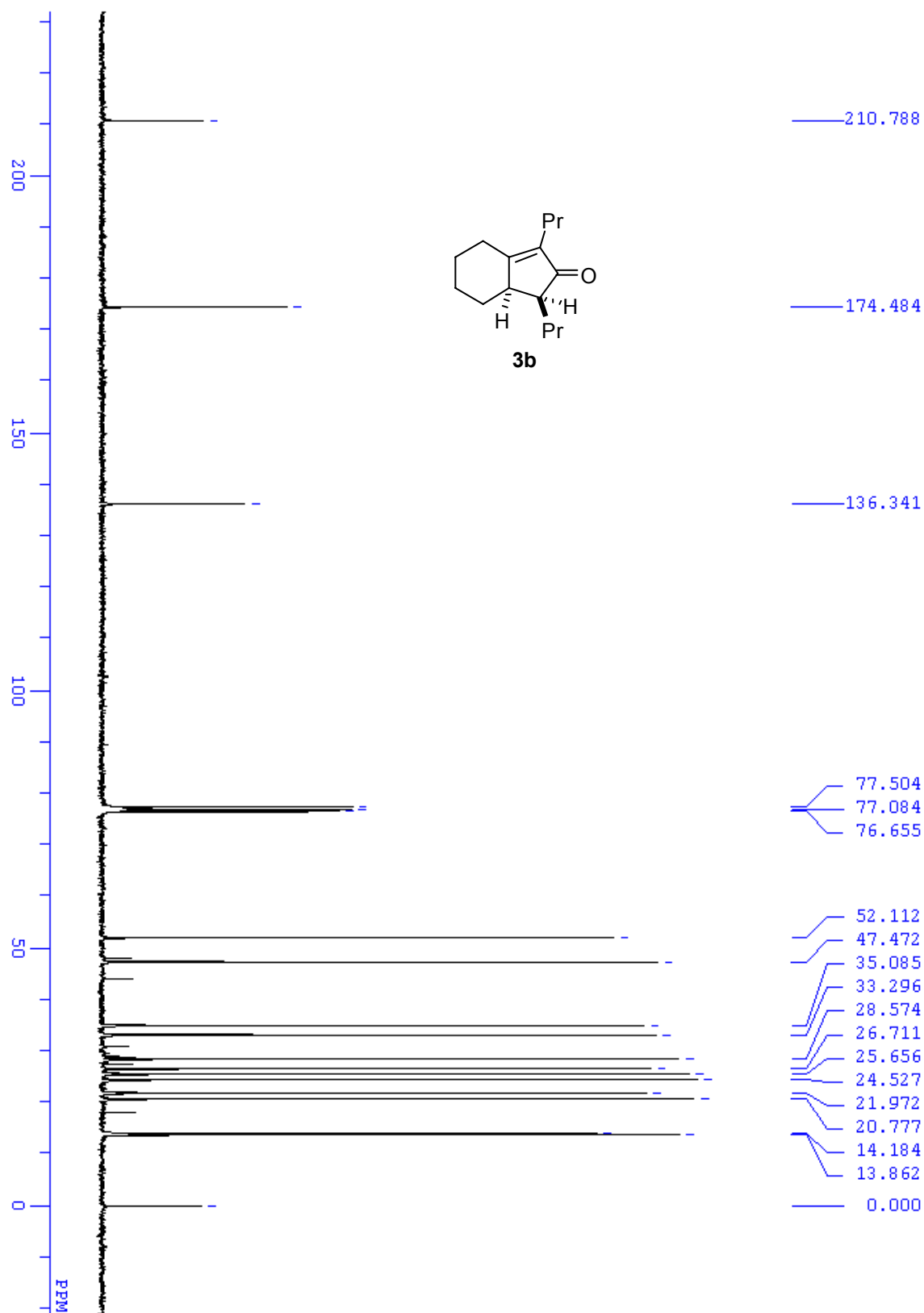


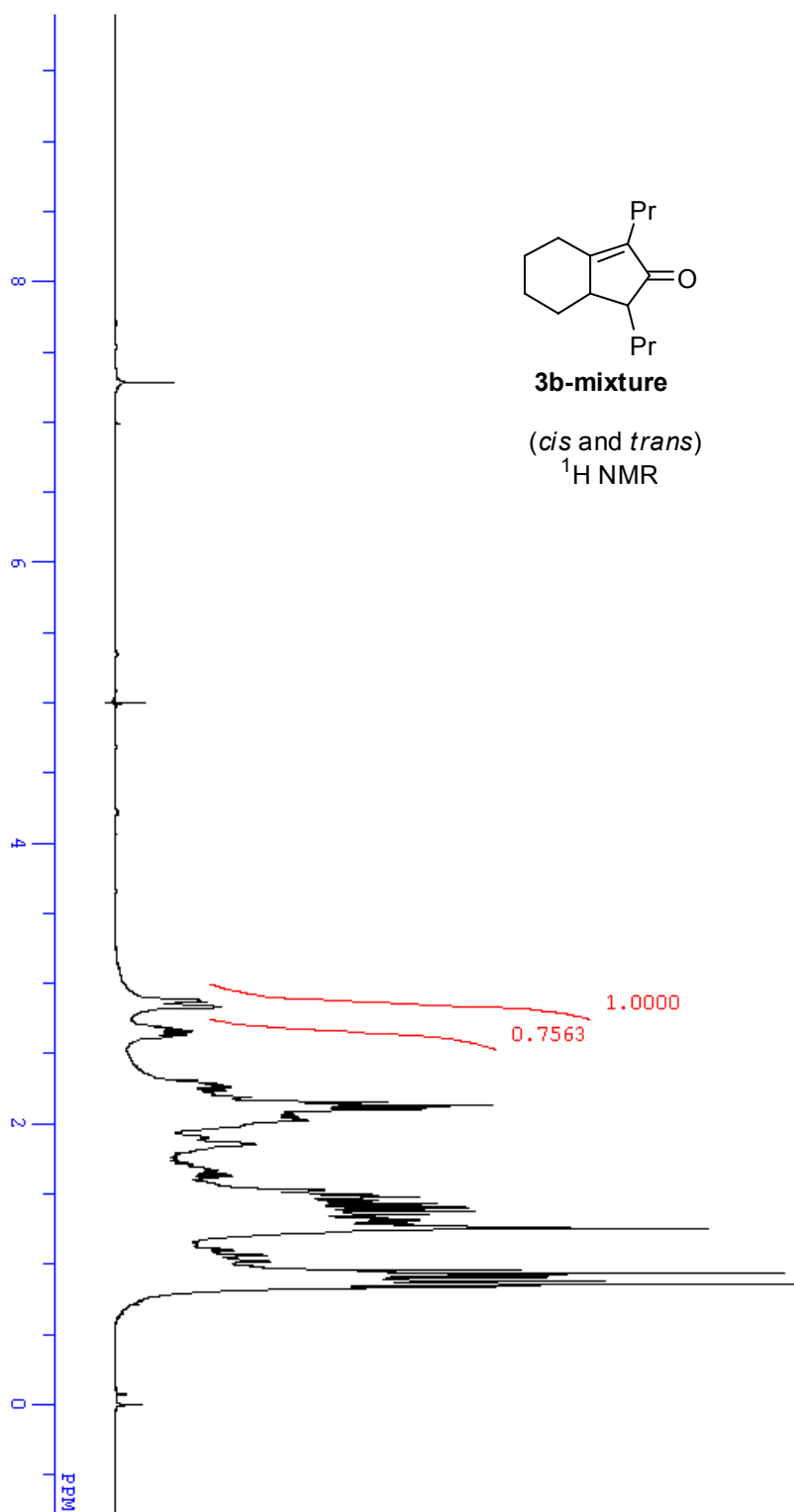


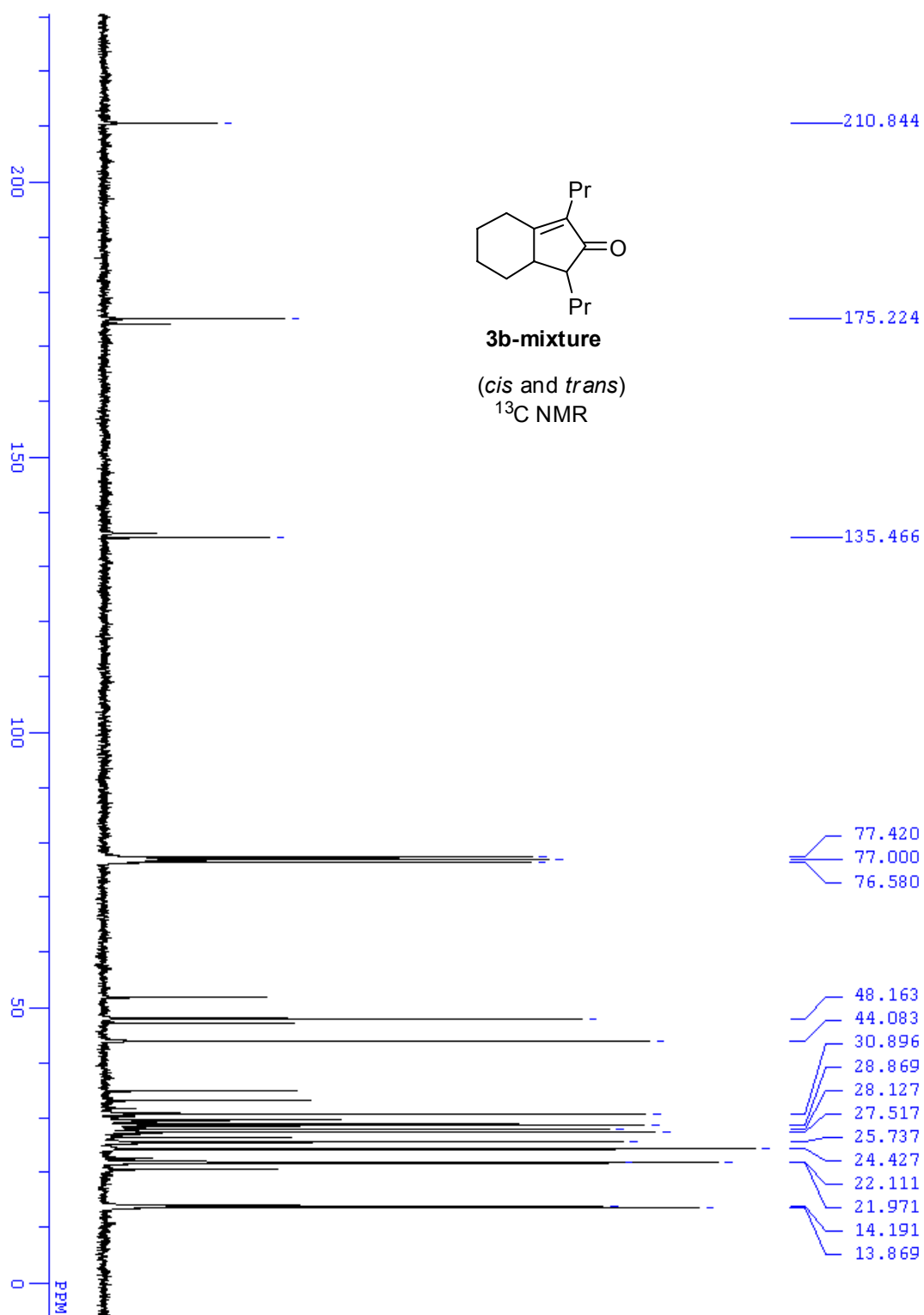


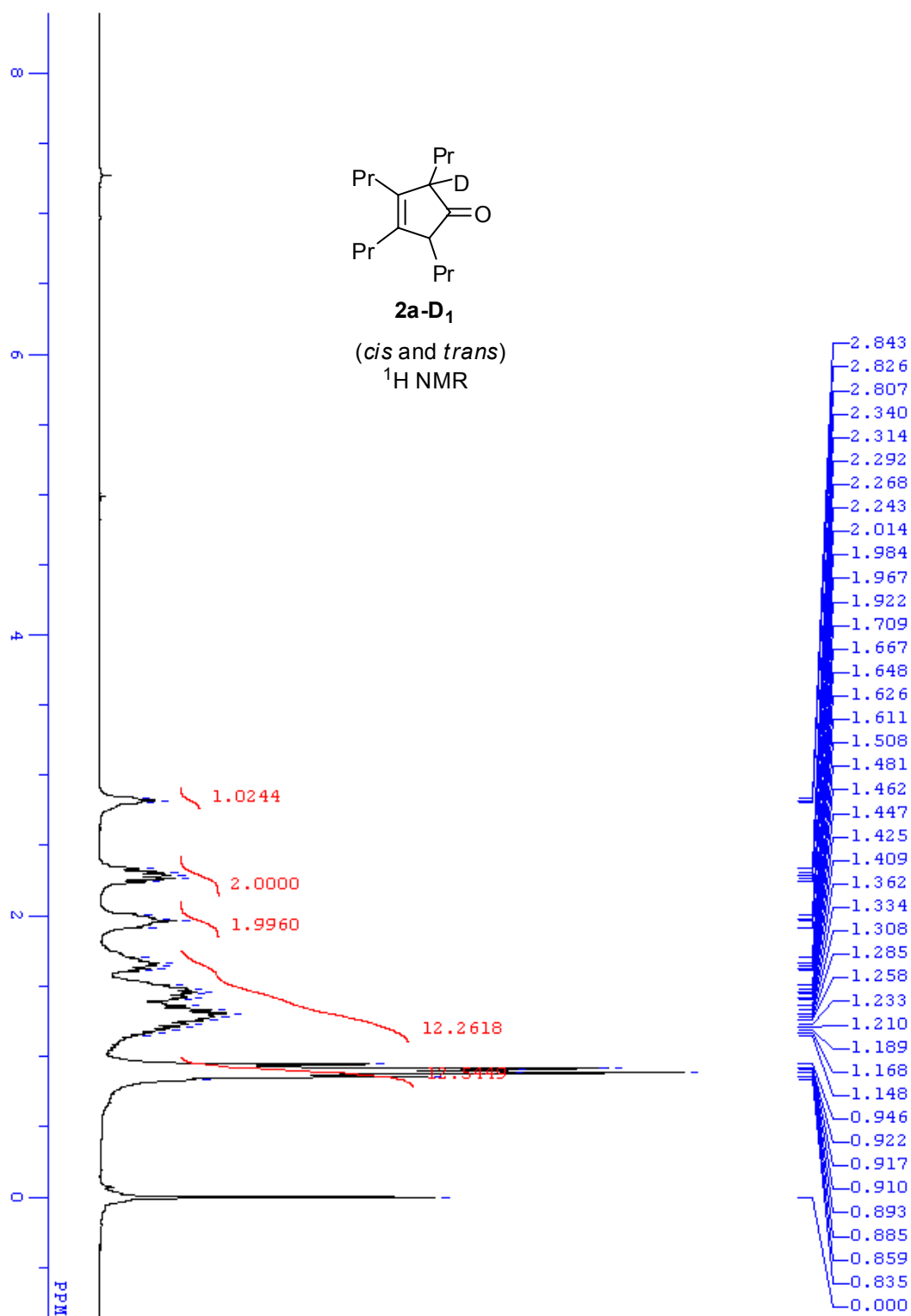


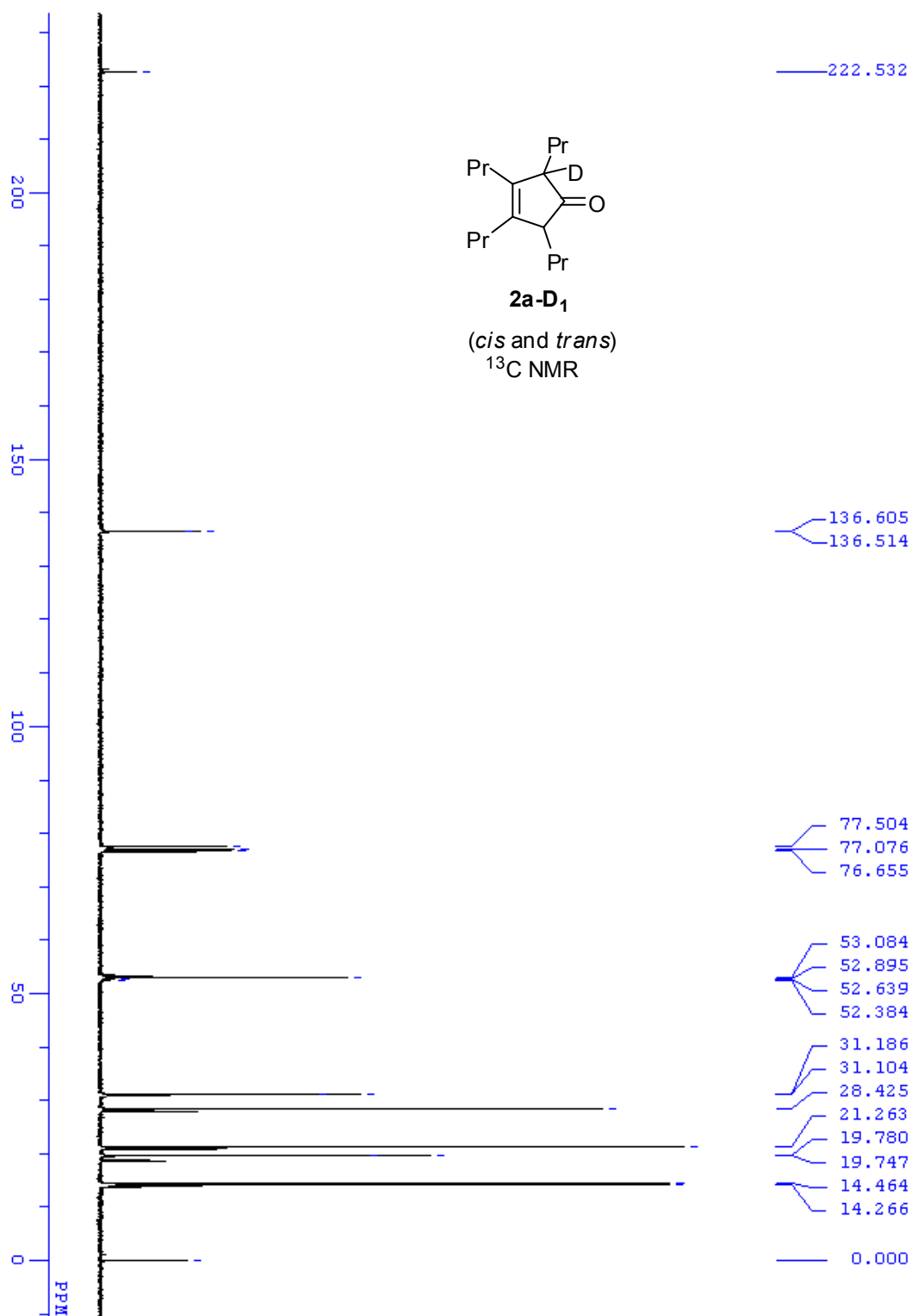


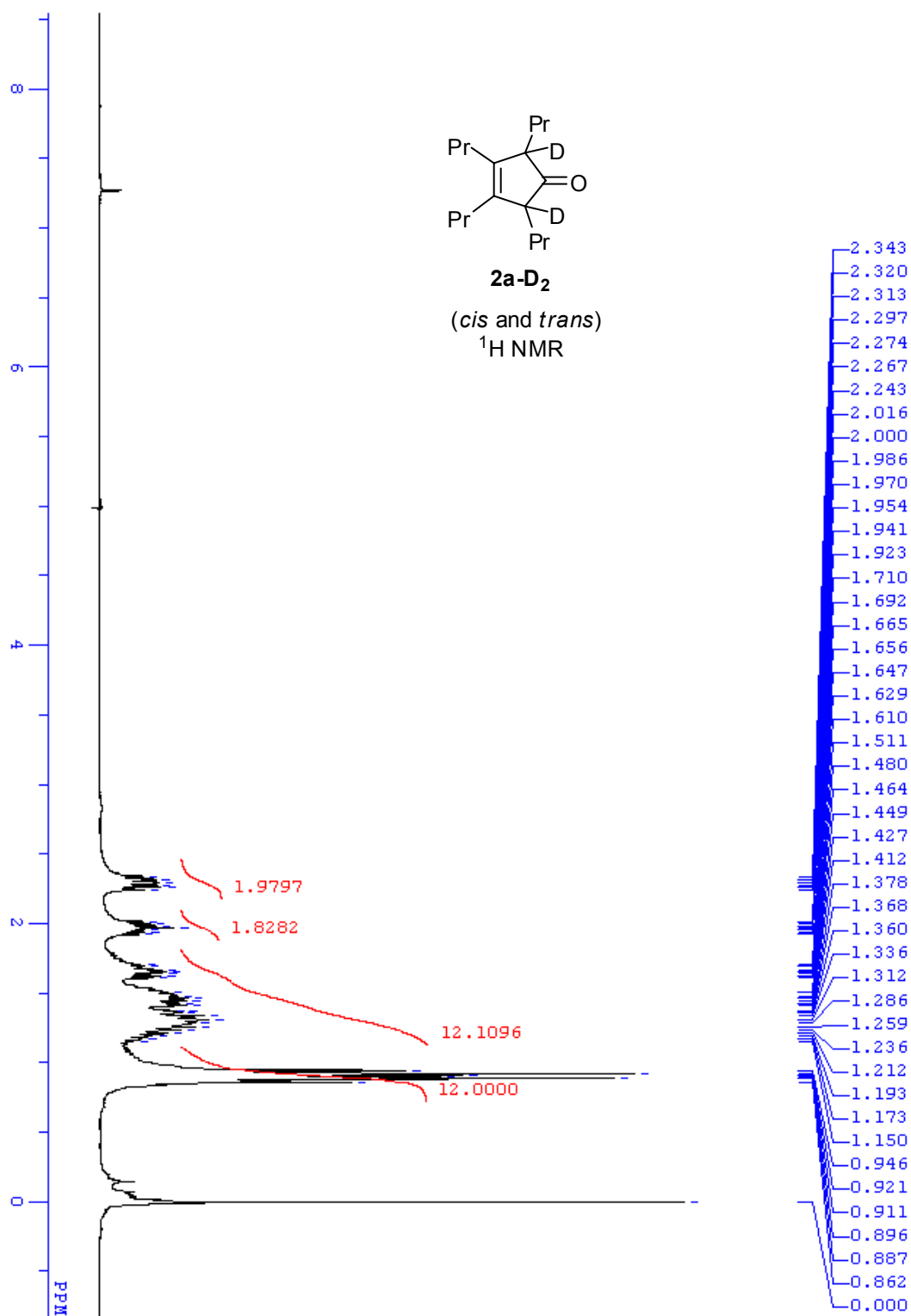


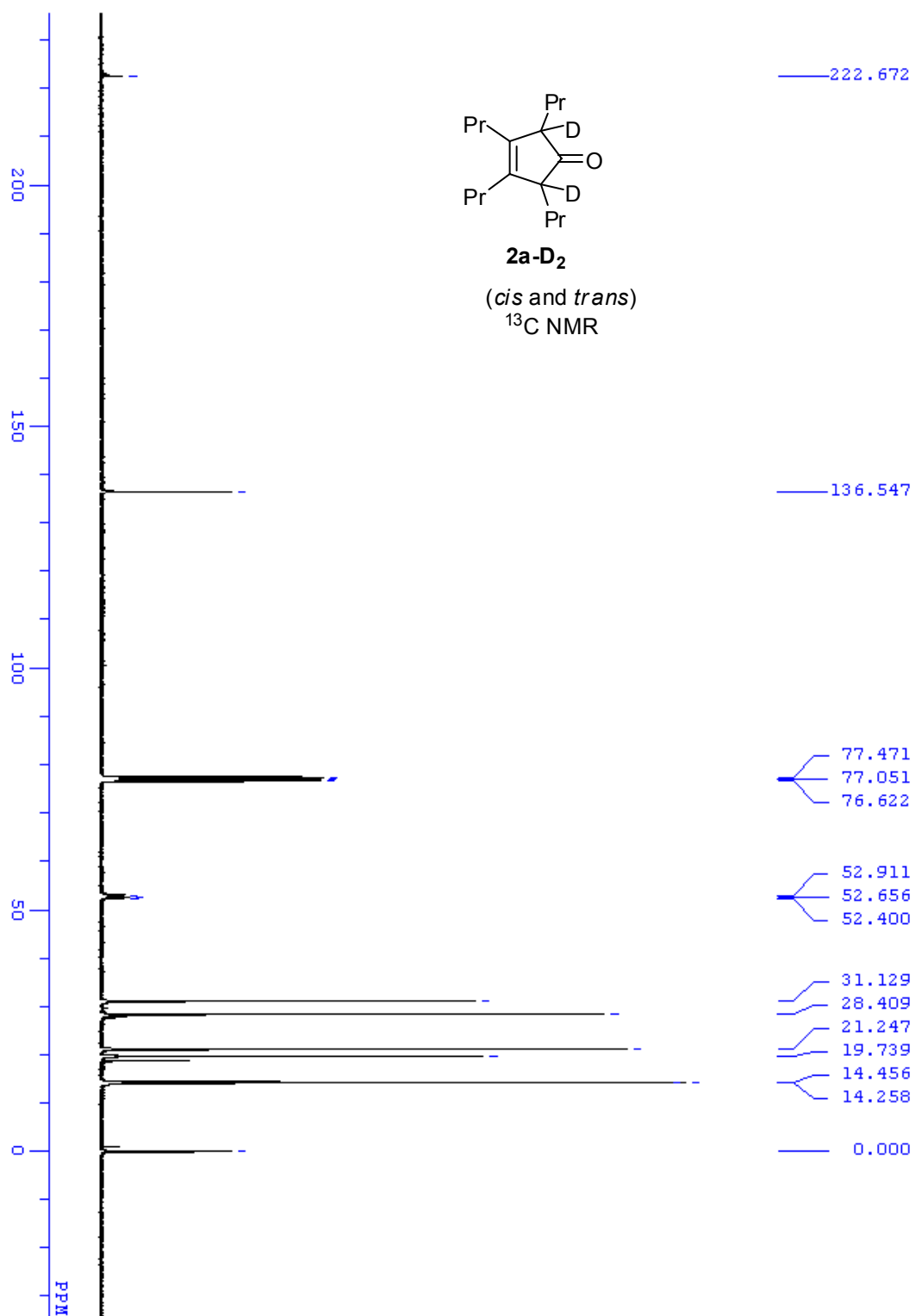


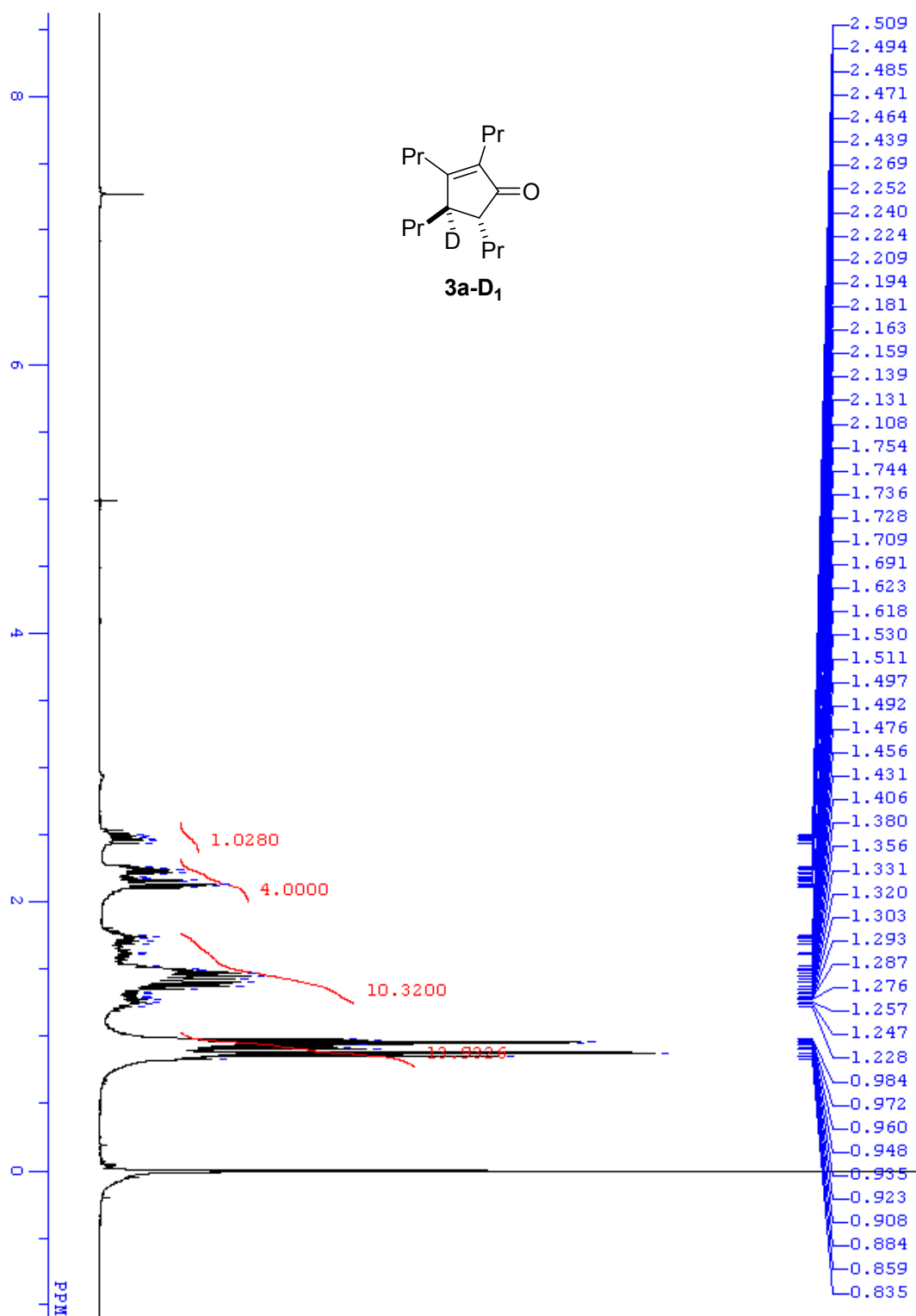


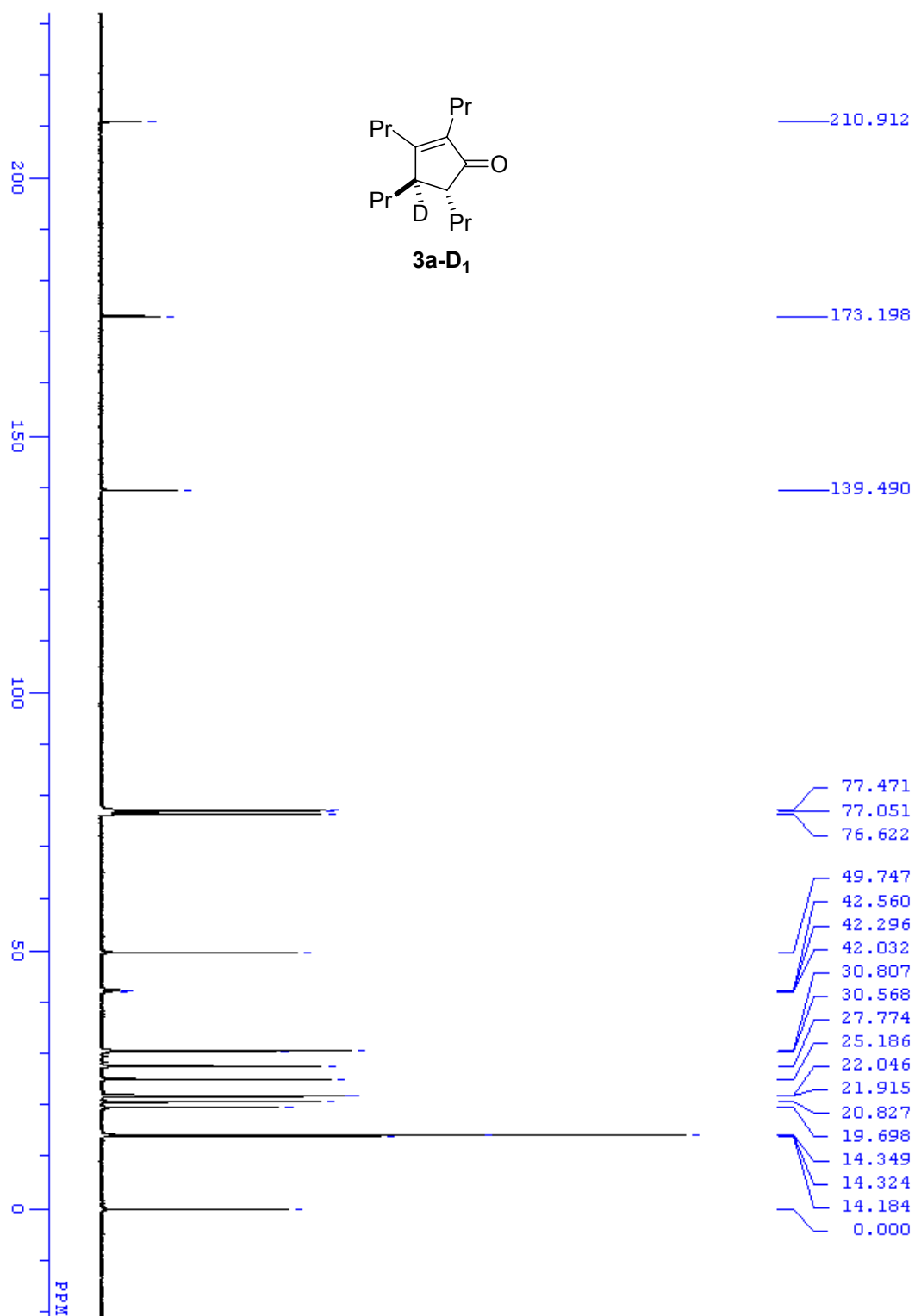


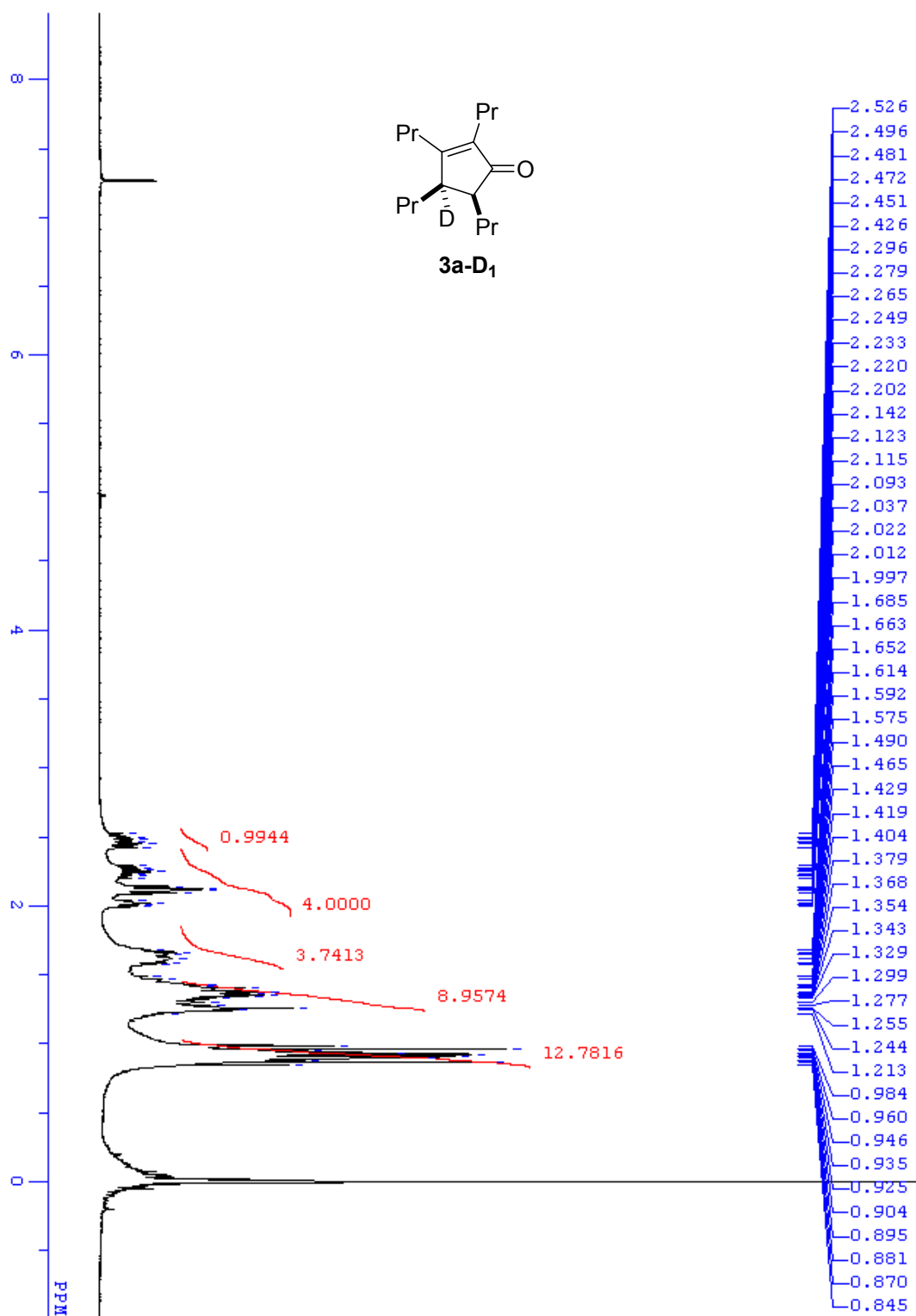


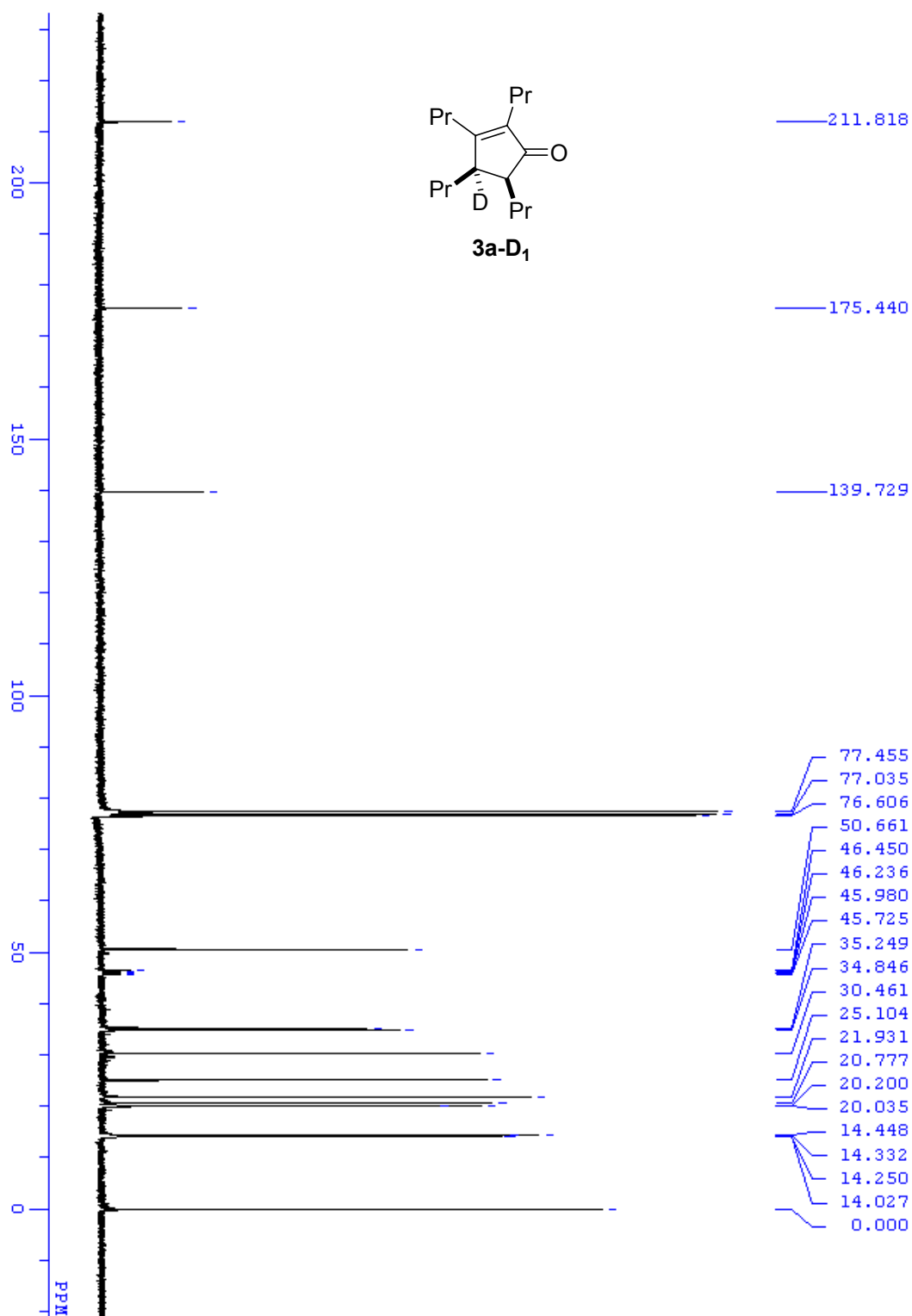


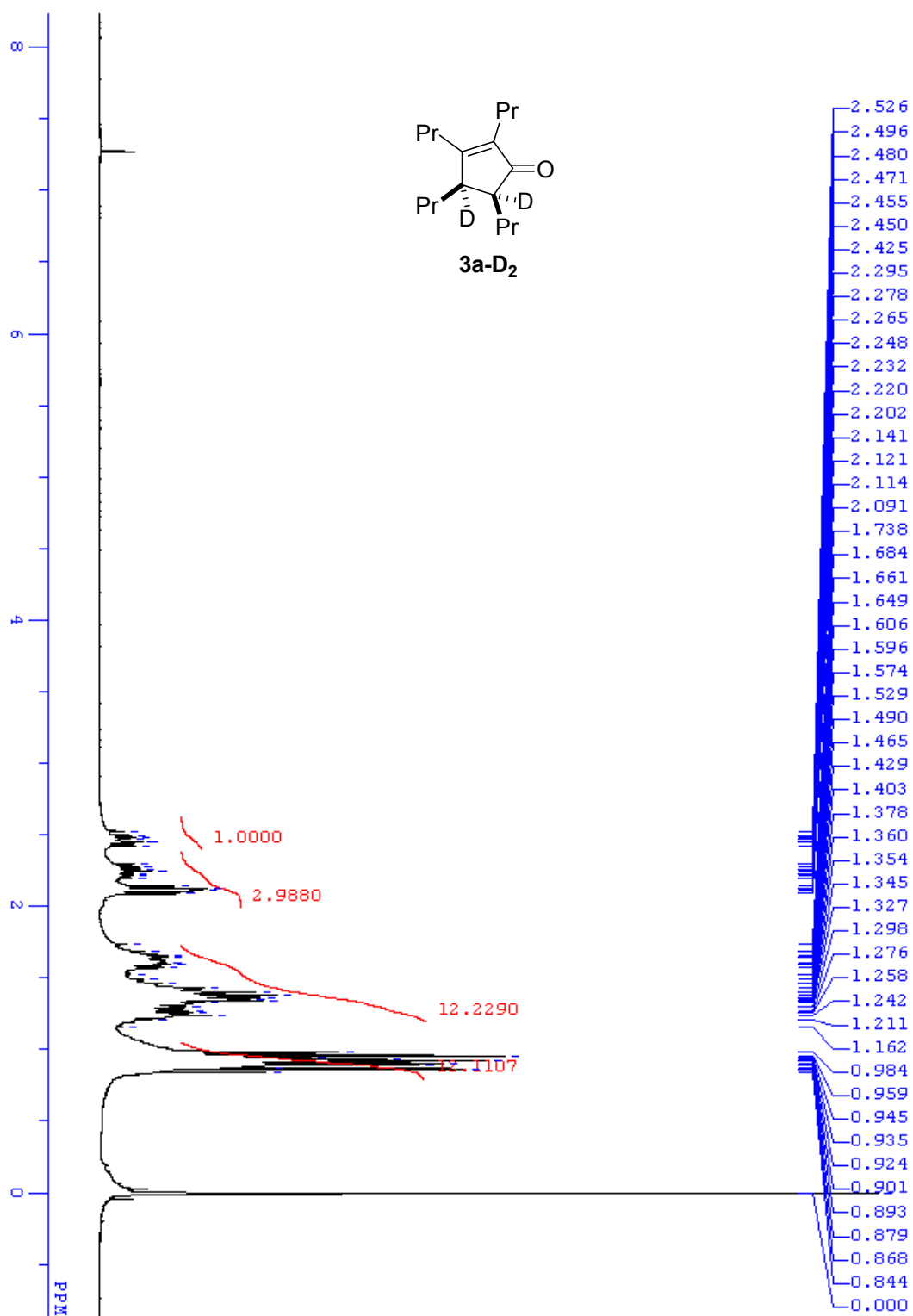


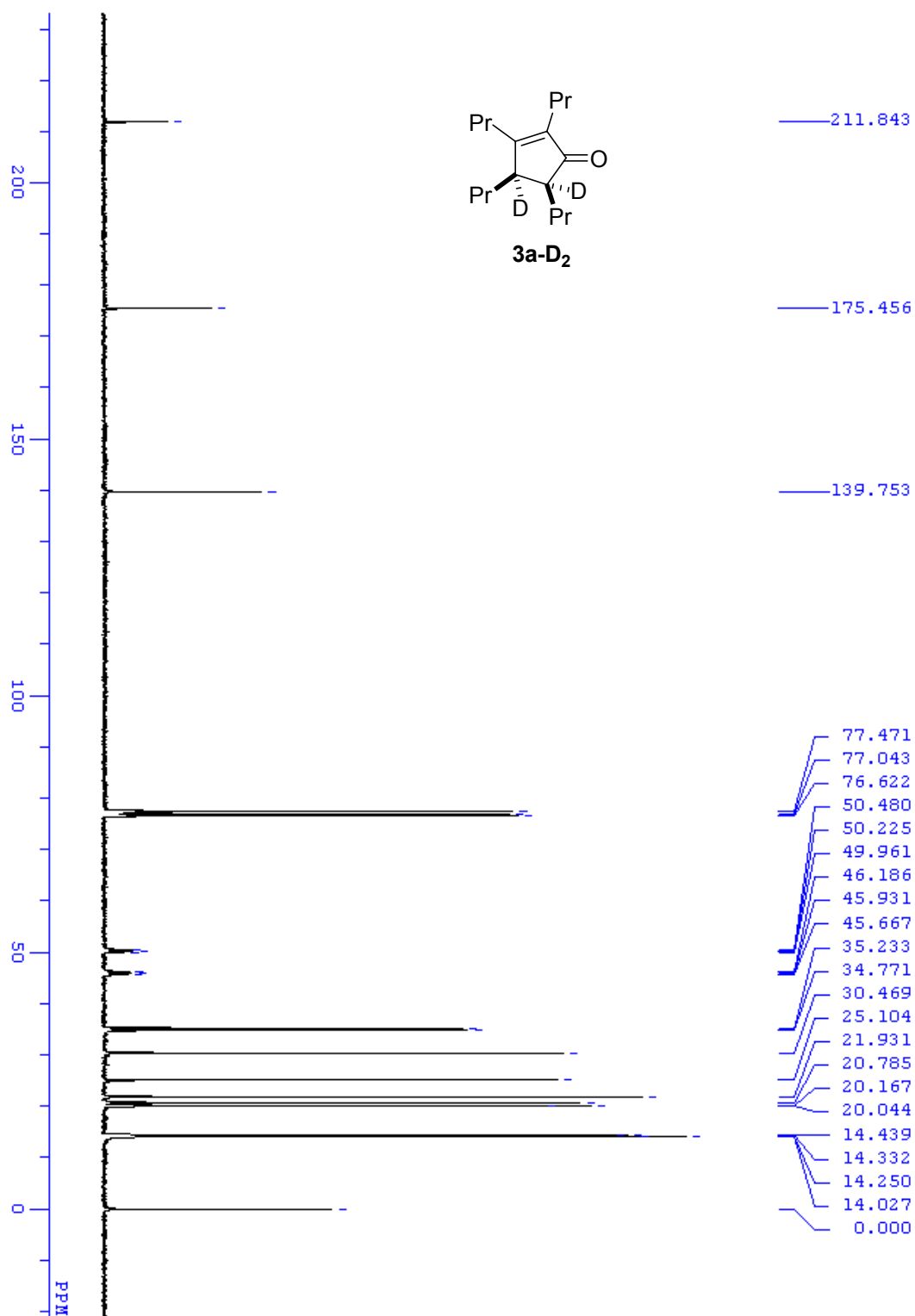


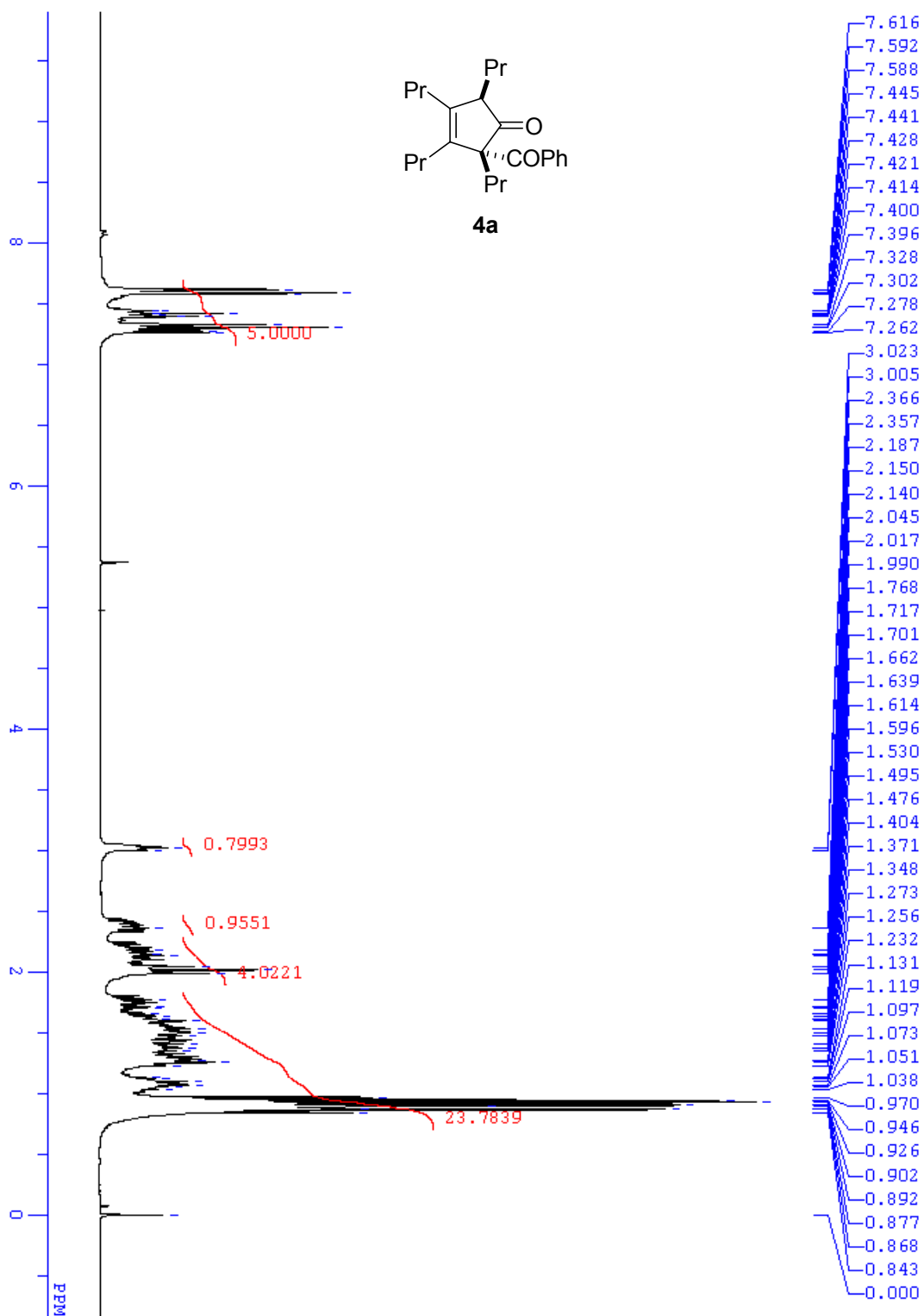


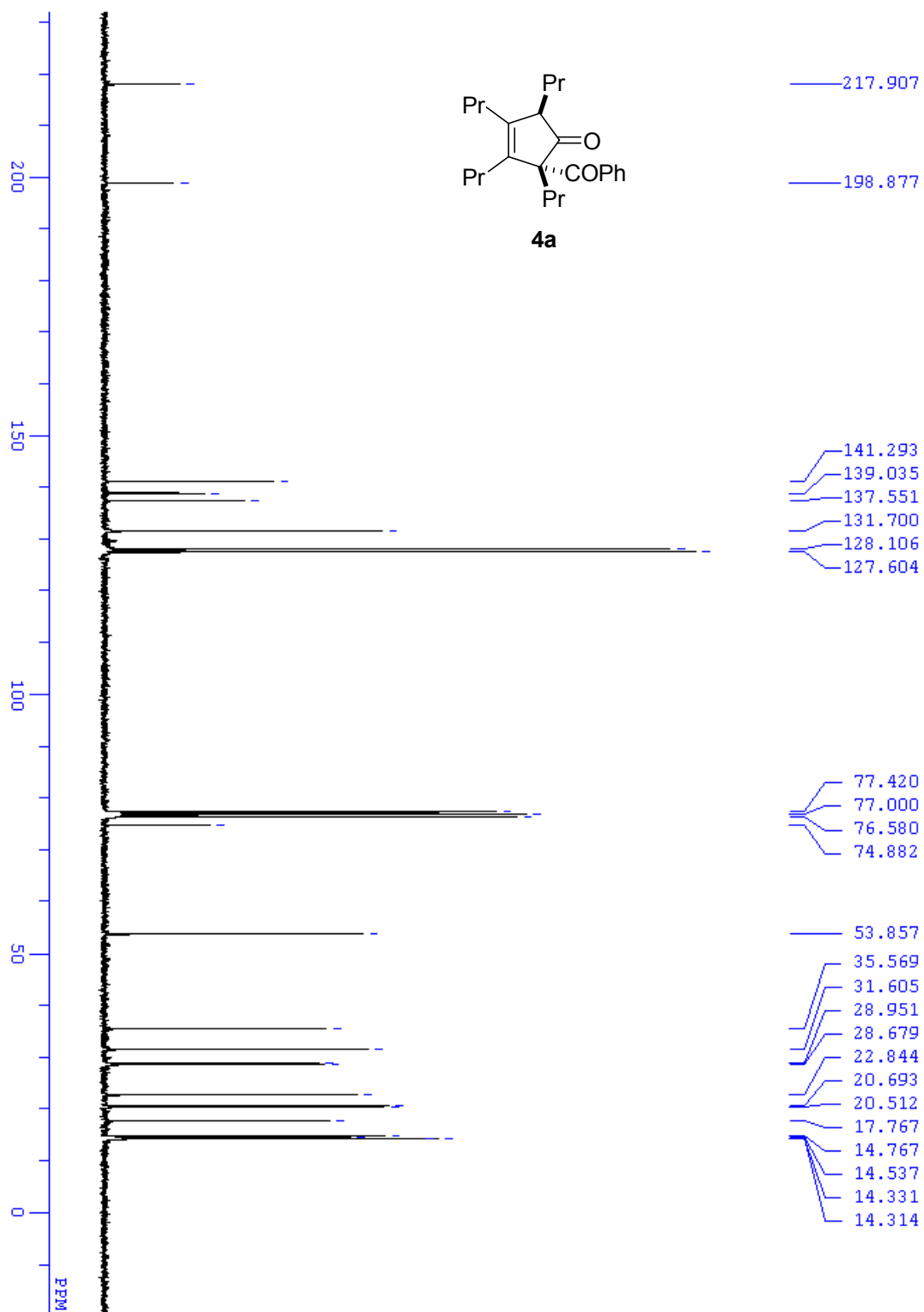


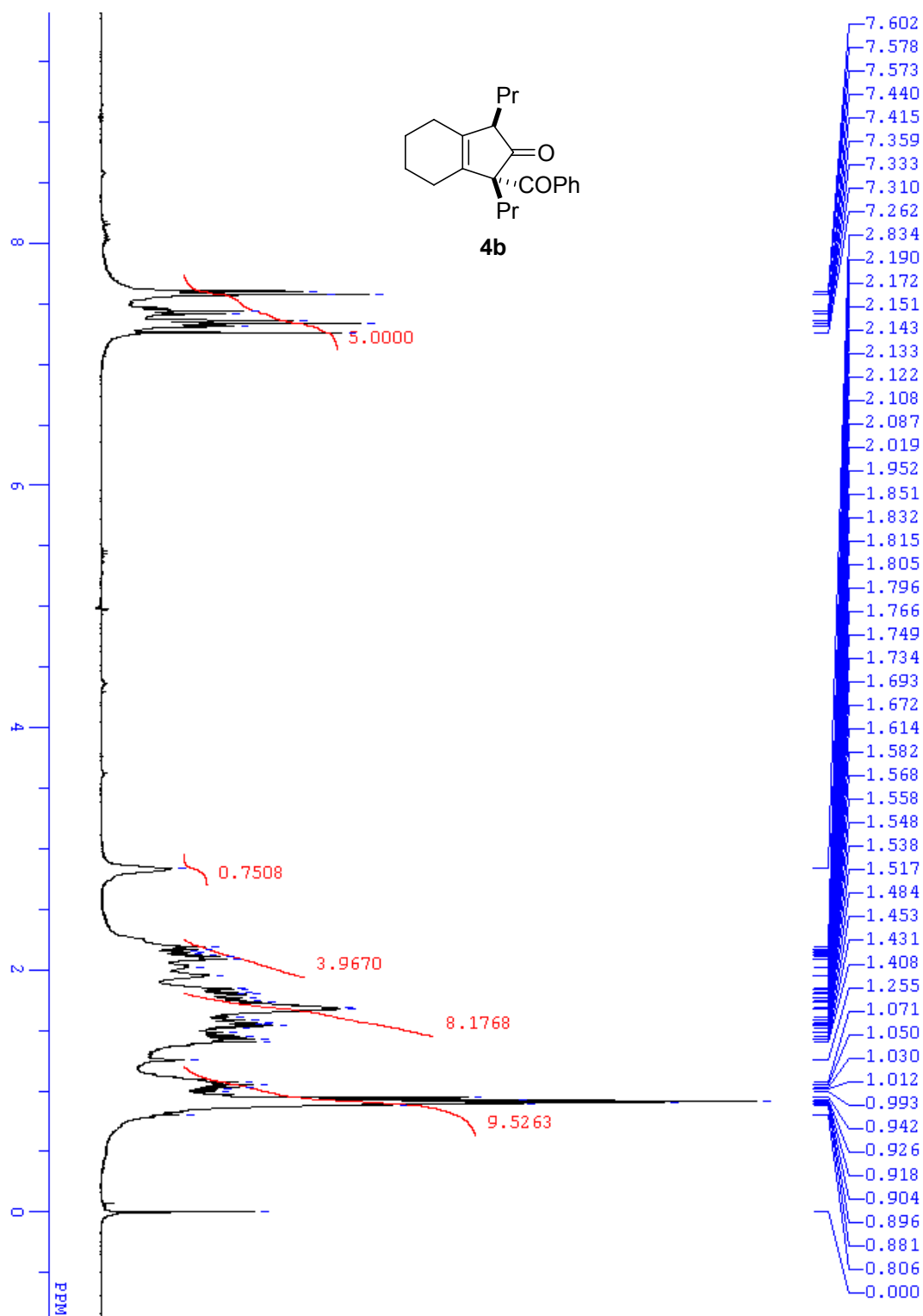


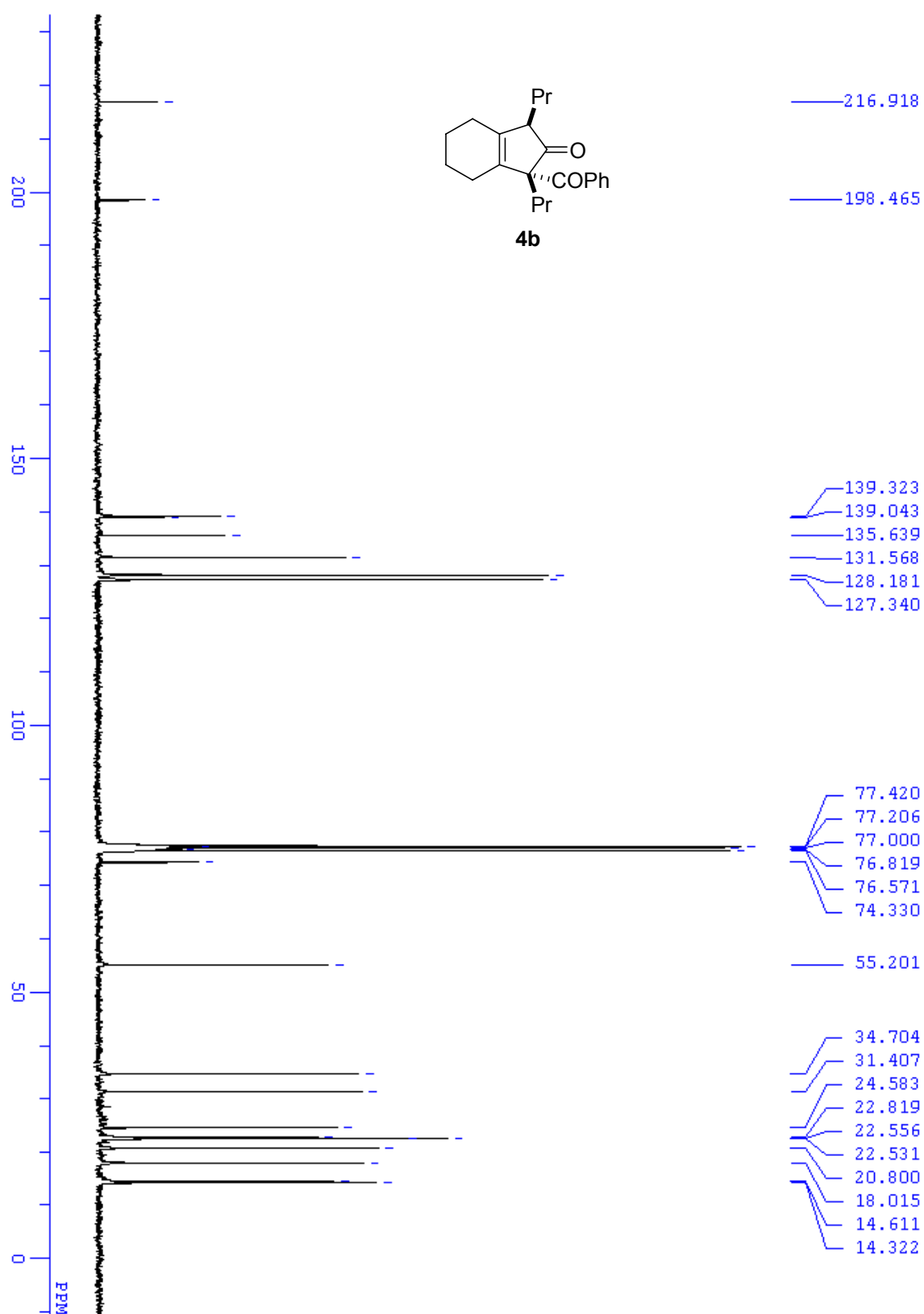


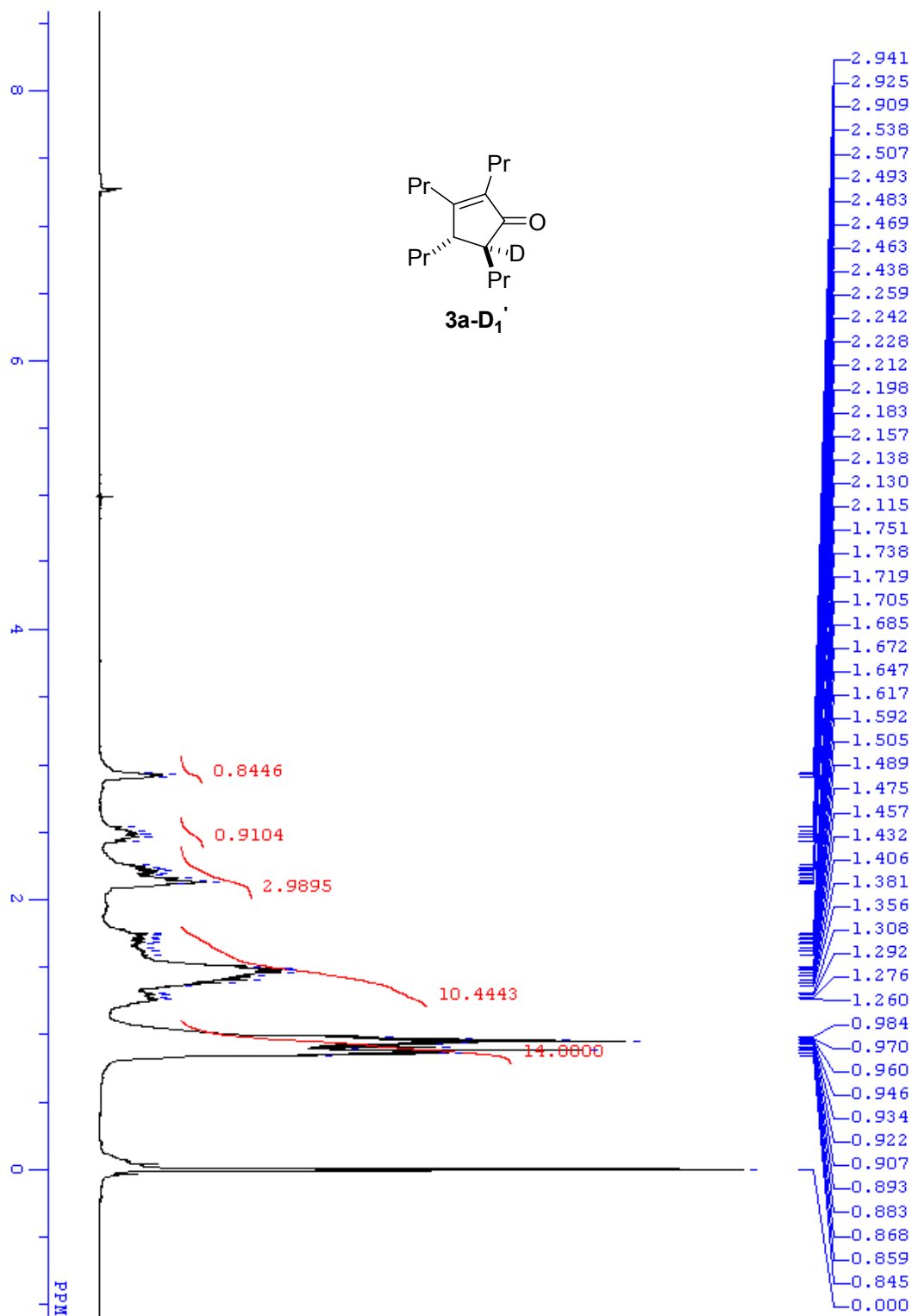


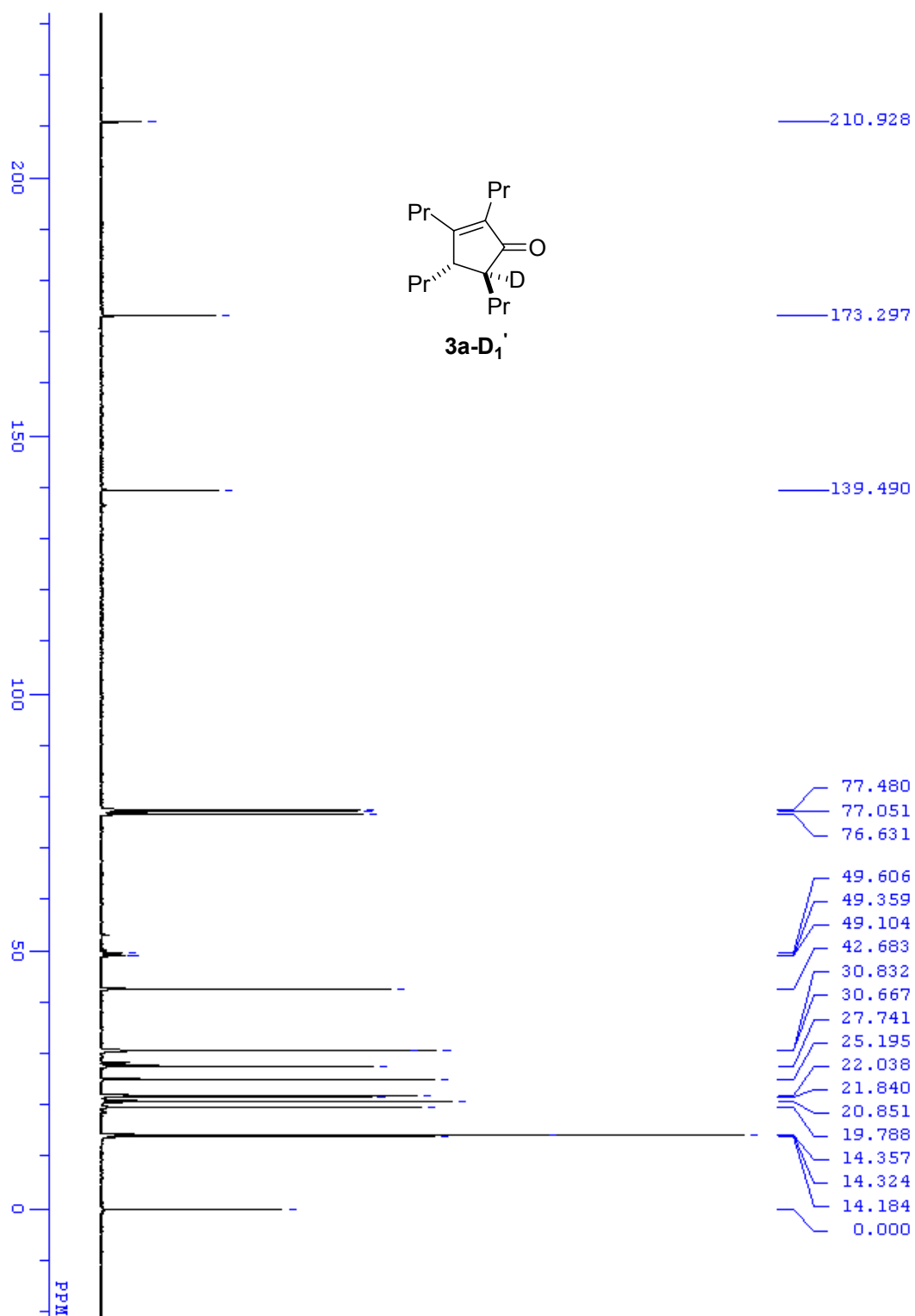


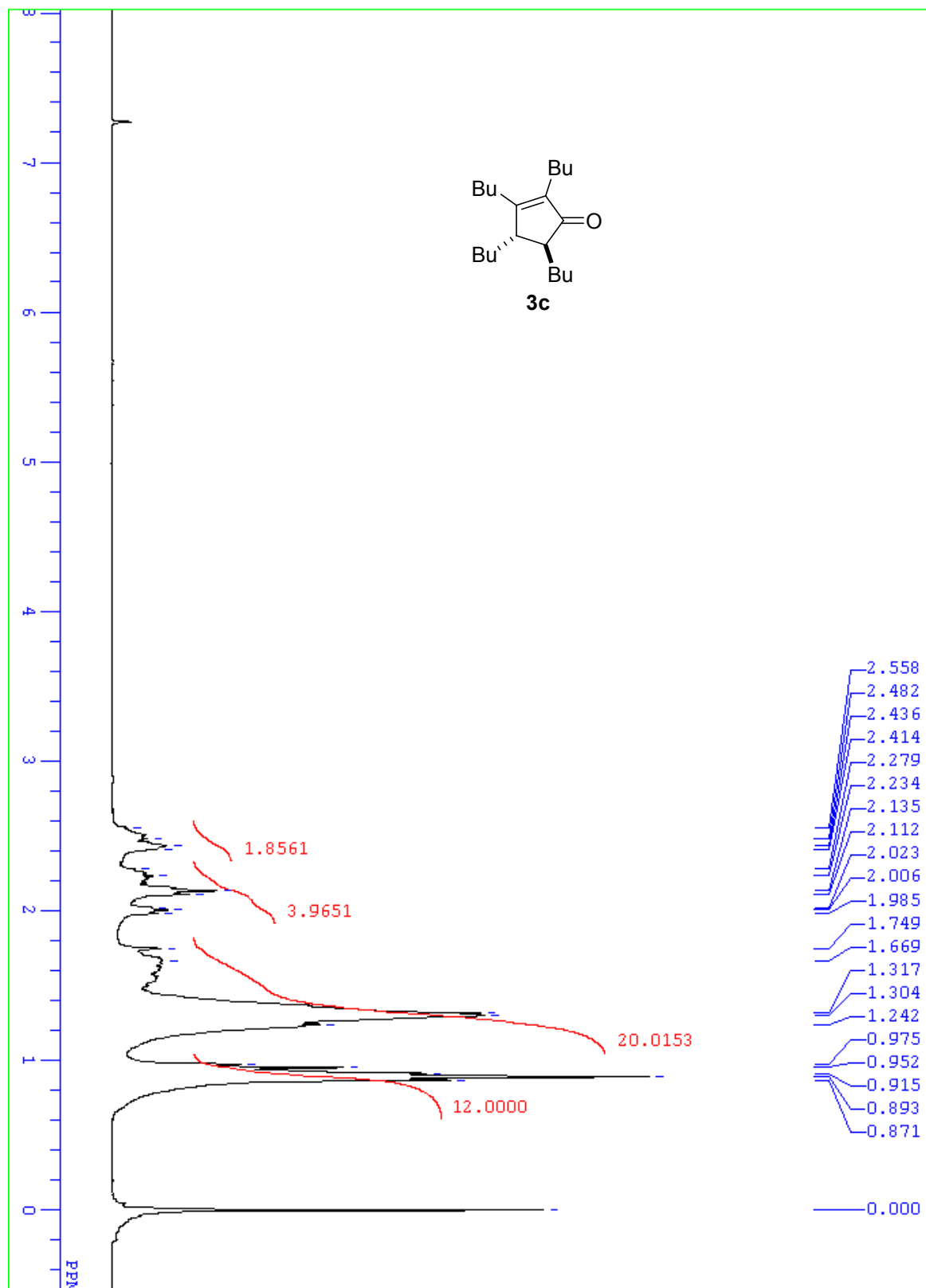


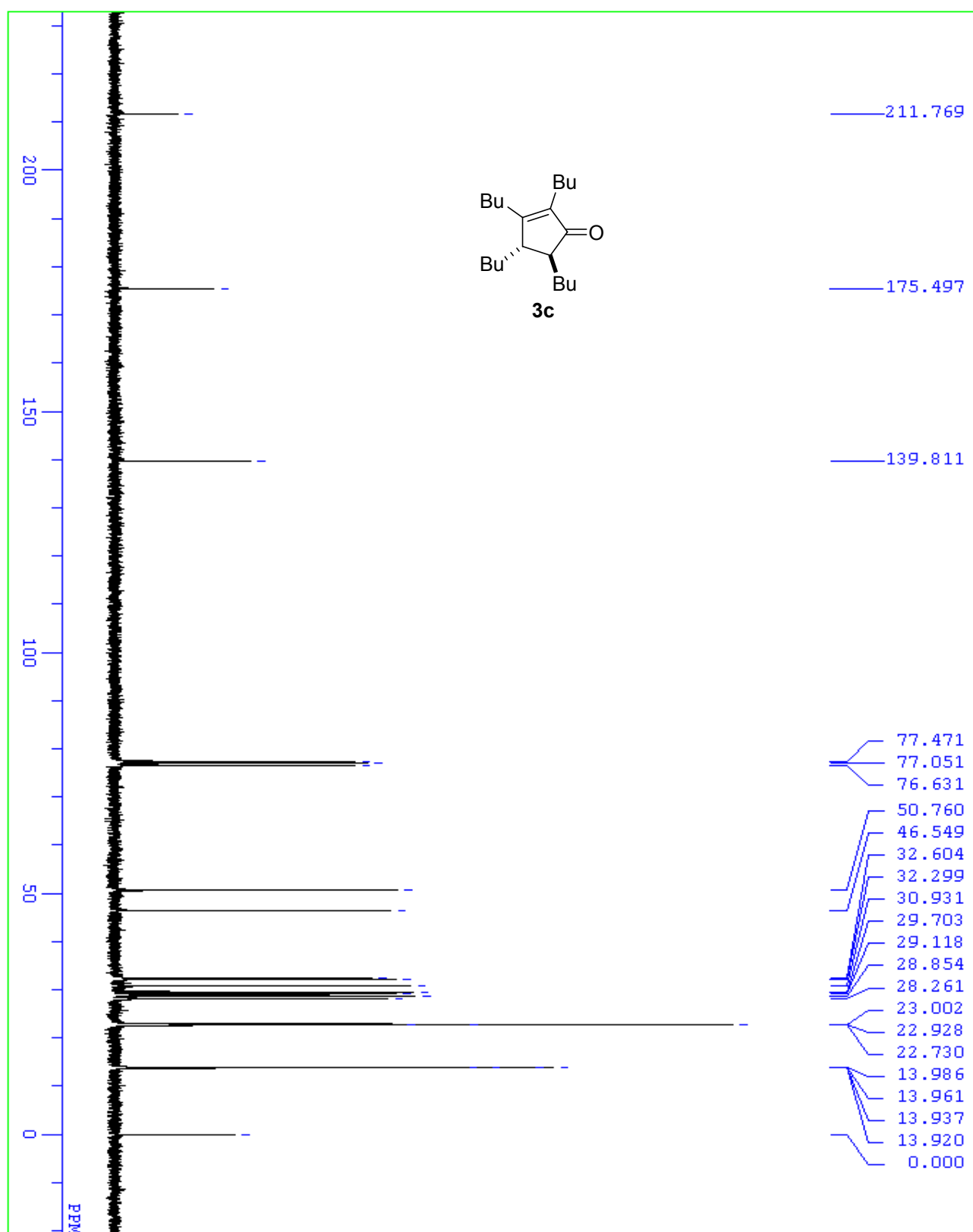


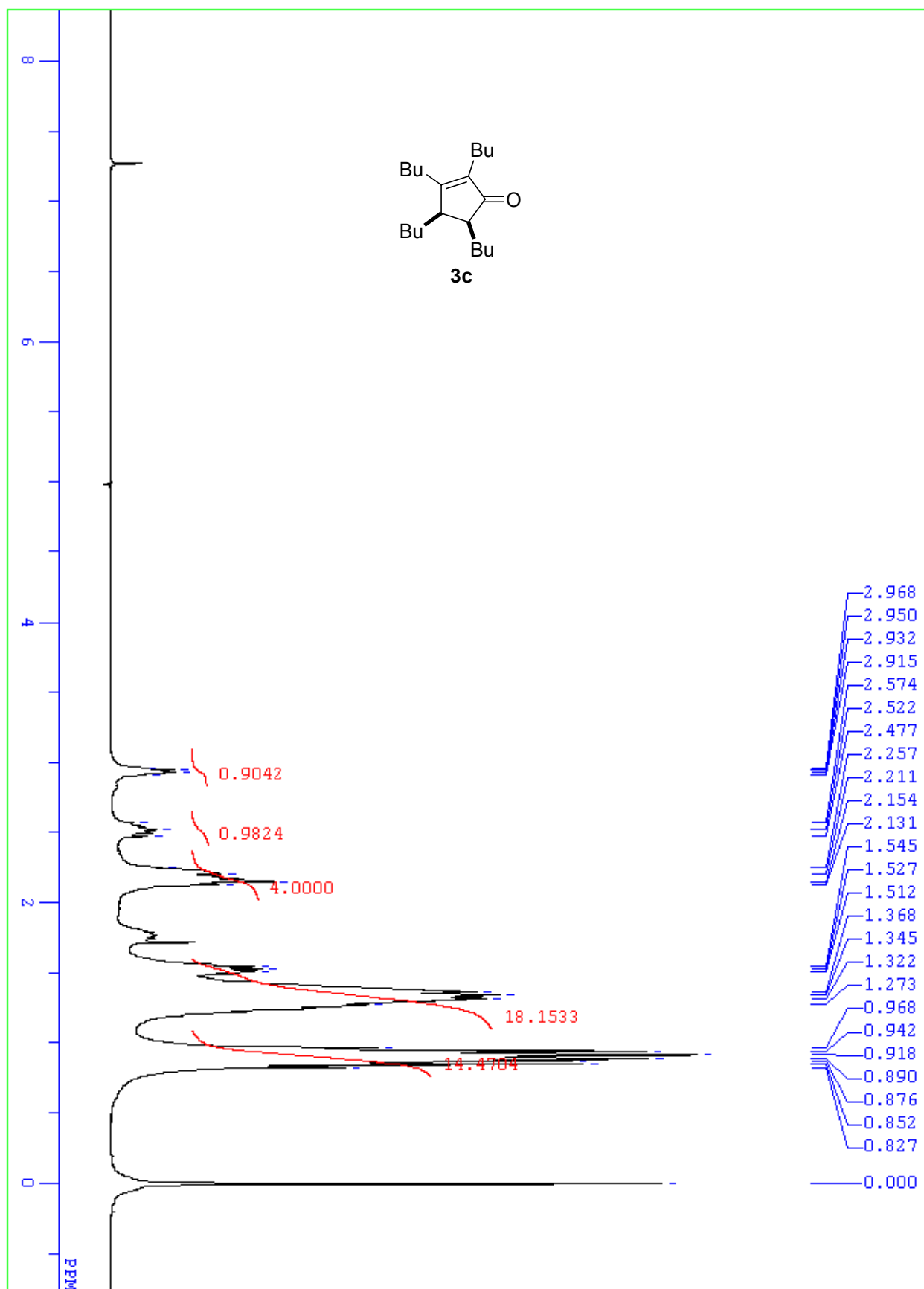


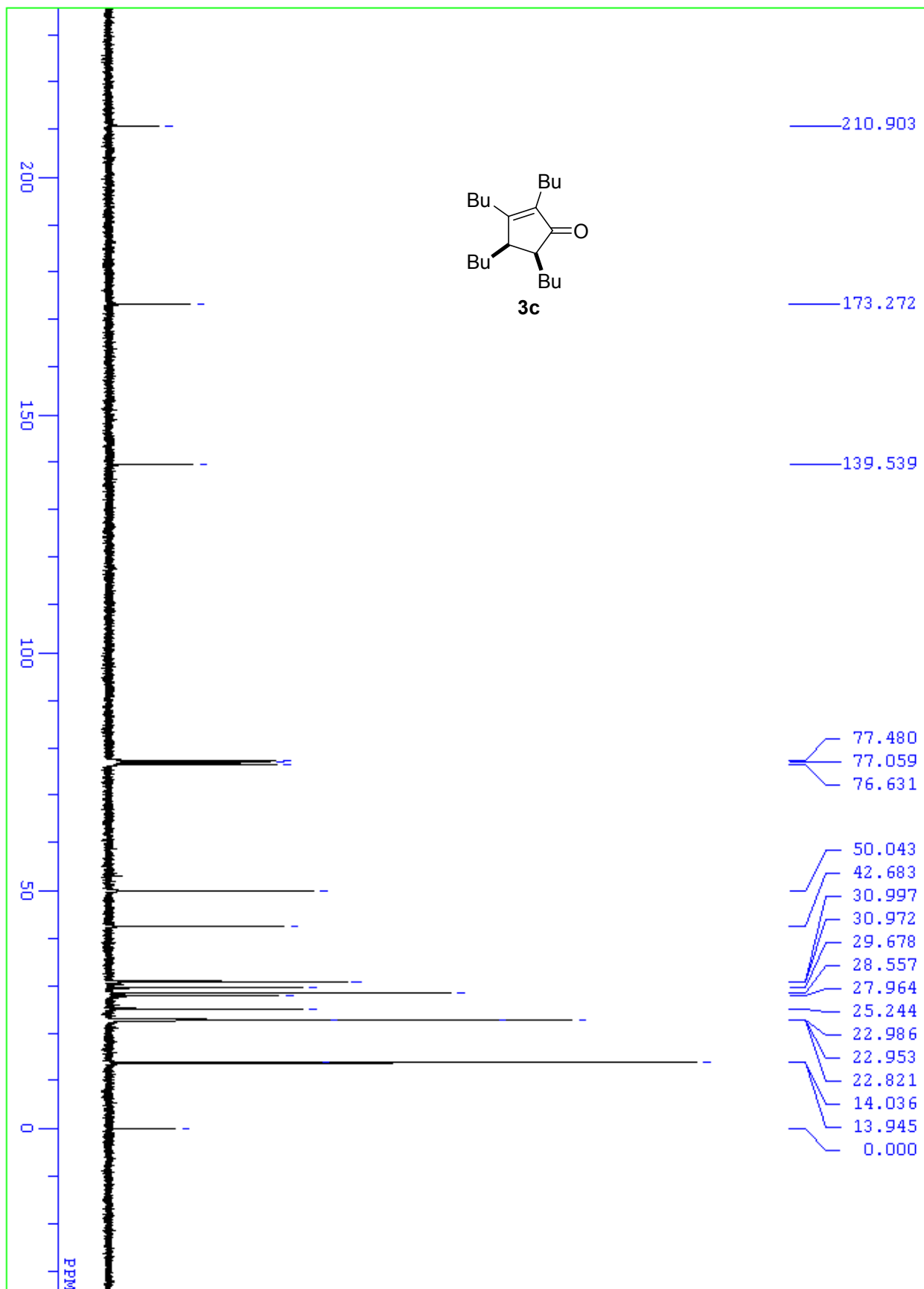


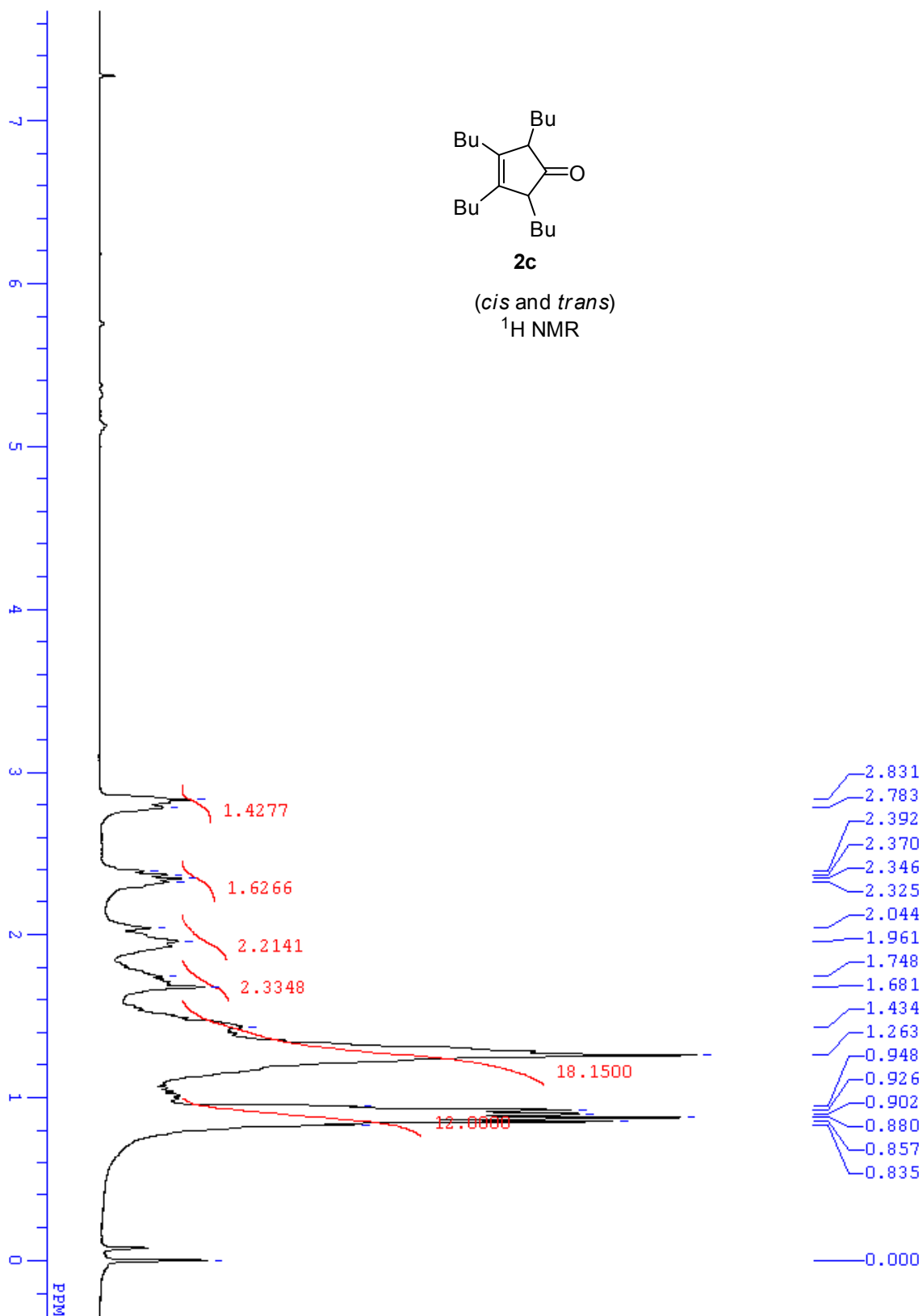


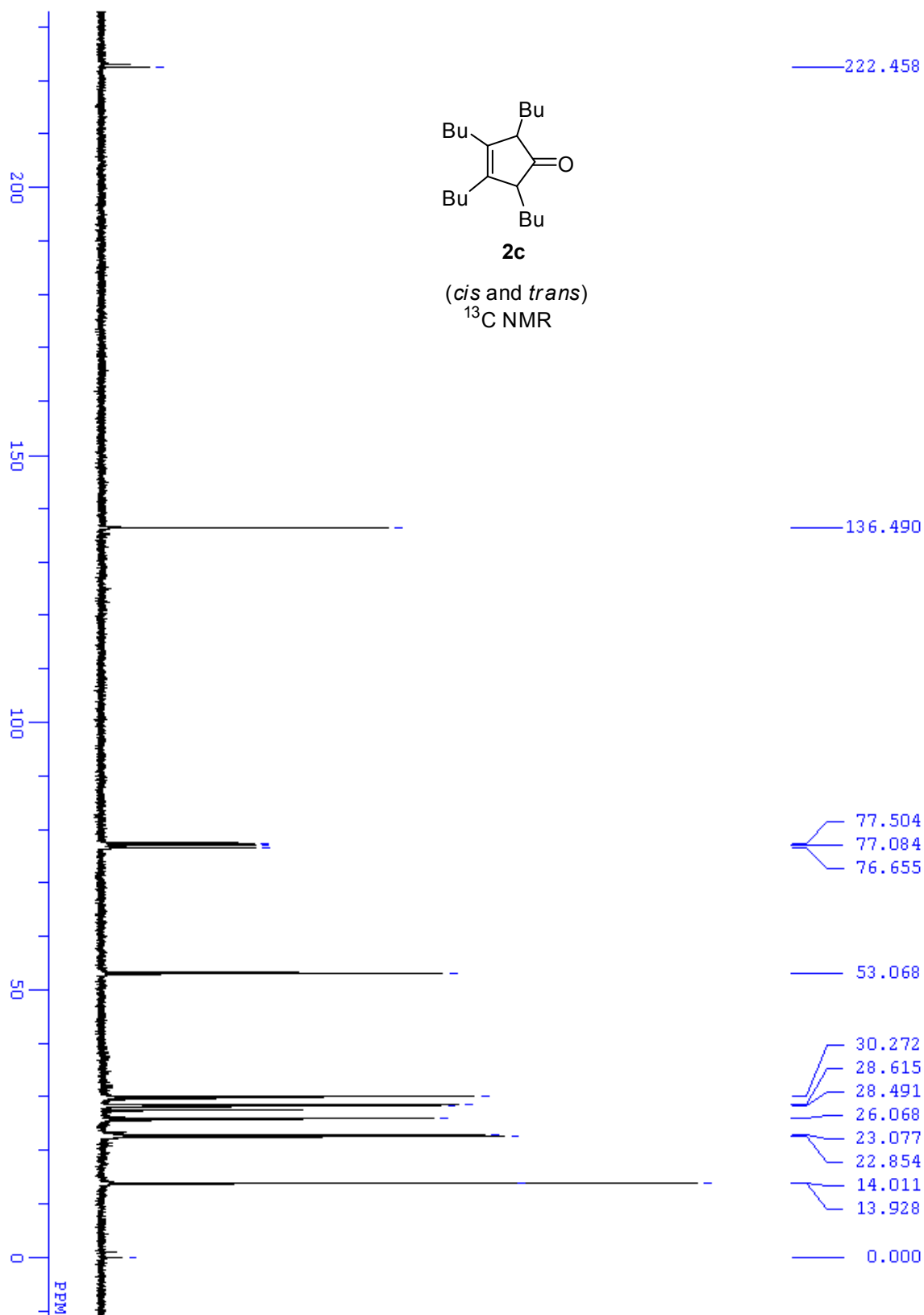


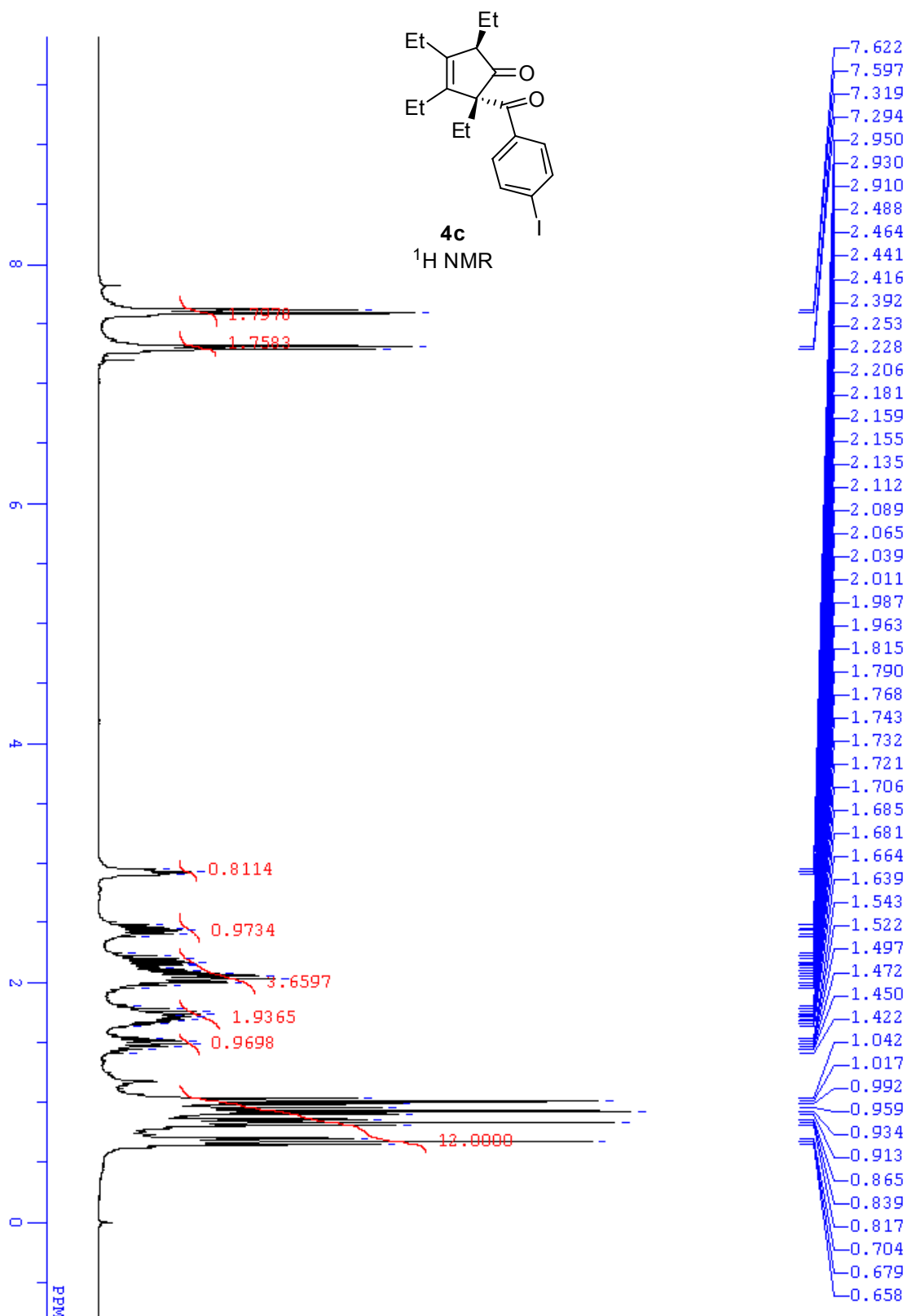


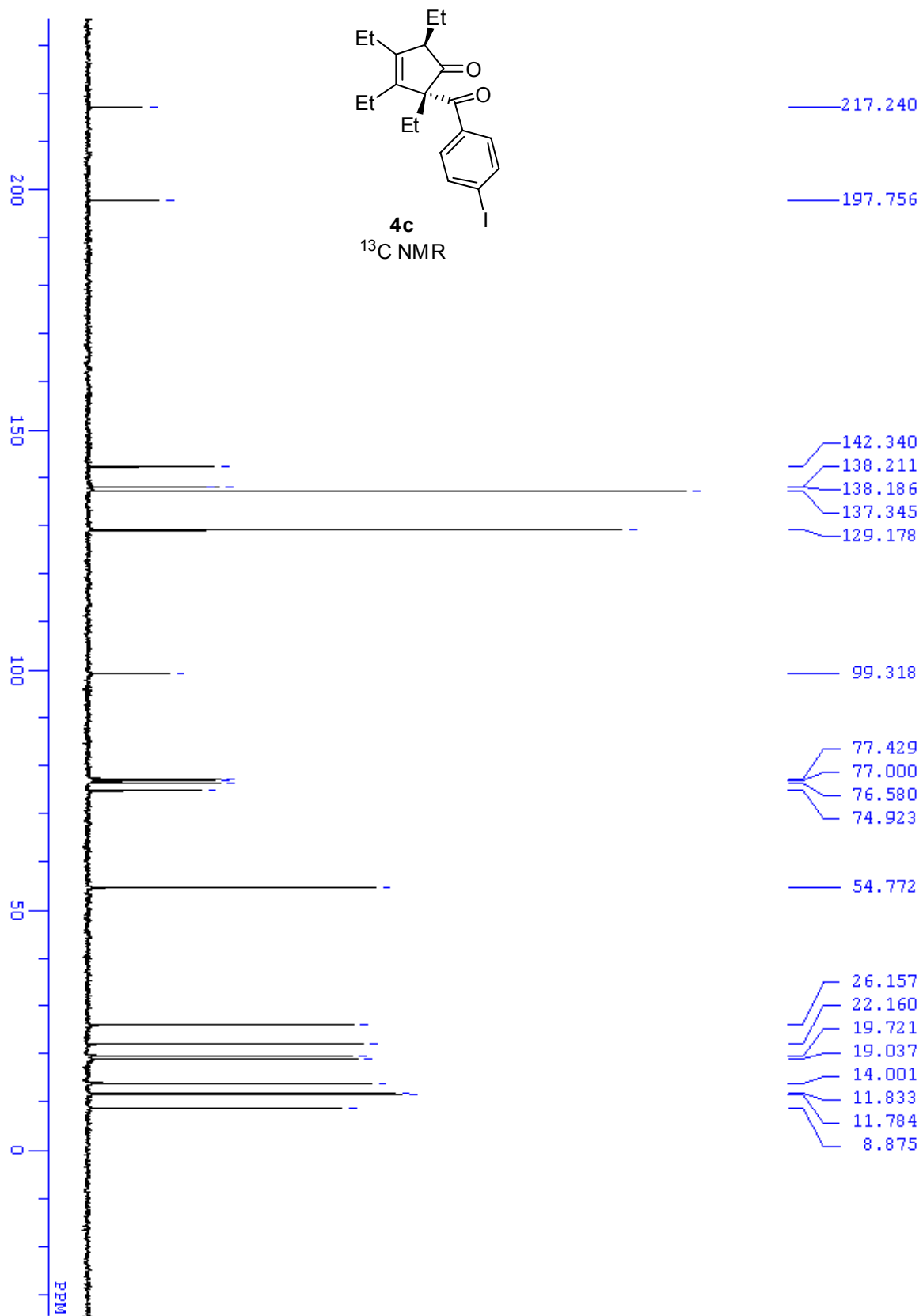












3) X-ray crystallographic studies of **4c**

Crystals for X-ray analyses of **4c** were obtained as described above. Data collections were performed at -150 °C on a Rigaku RAXIS RAPID IP, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the Rapid Auto (Rigaku 2001) program package. The raw frame data were processed using Rapid Auto (Rigaku 2001) to yield the reflection data file. These structures were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

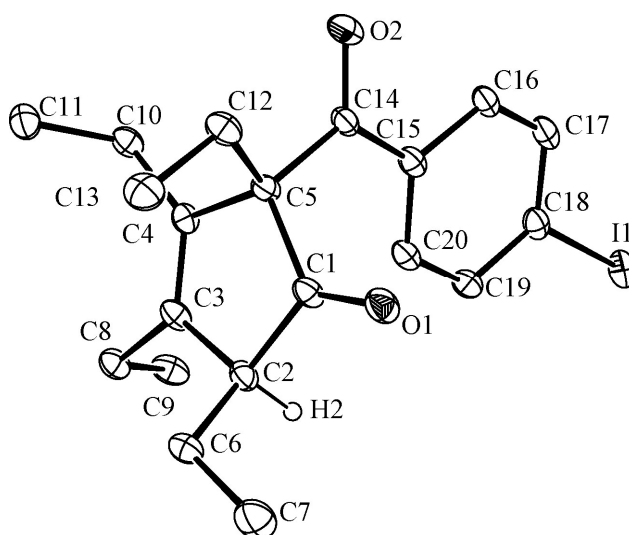


Figure 1. ORTEP drawing of **4c** with 30% thermal ellipsoids.

Table 1. Crystal data and structure refinement for **4c**.

Identification code	4c	
Empirical formula	C ₂₀ H ₂₅ I O ₂	
Formula weight	424.30	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5377(15) Å	$\alpha = 87.68(3)^\circ$
	b = 11.101(2) Å	$\beta = 75.05(3)^\circ$

	$c = 11.695(2) \text{ \AA}$	$\gamma = 74.76(3)^\circ$
Volume	$911.8(3) \text{ \AA}^3$	
Z	2	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	1.764 mm^{-1}	
F(000)	428	
Crystal size	$0.40 \times 0.20 \times 0.10 \text{ mm}^3$	
Theta range for data collection	2.58 to 27.48° .	
Index ranges	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	
Reflections collected	5338	
Independent reflections	3471 [R(int) = 0.0566]	
Completeness to theta = 27.48°	83.1 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8434 and 0.5389	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3471 / 0 / 216	
Goodness-of-fit on F^2	1.031	
Final R indices [I > 2sigma(I)]	R1 = 0.0555, wR2 = 0.1489	
R indices (all data)	R1 = 0.0675, wR2 = 0.1549	
Largest diff. peak and hole	1.095 and -1.464 e. \AA^{-3}	

STable 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4c**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6013(7)	2873(5)	3031(5)	27(1)
C(2)	7793(7)	2019(5)	3325(5)	27(1)
C(3)	7973(7)	800(5)	2726(5)	29(1)
C(4)	6545(7)	824(5)	2250(4)	24(1)
C(5)	5103(7)	2098(4)	2401(5)	25(1)
C(6)	7648(8)	1913(5)	4664(5)	31(1)
C(7)	7517(11)	3112(6)	5292(6)	47(2)
C(8)	9742(7)	-279(5)	2605(5)	30(1)
C(9)	11232(8)	-208(6)	1451(5)	36(1)
C(10)	6285(7)	-259(5)	1618(5)	30(1)
C(11)	5430(9)	-1156(5)	2466(6)	37(1)
C(12)	3112(7)	2092(5)	3196(5)	33(1)
C(13)	3072(8)	1710(6)	4475(6)	39(1)
C(14)	4858(7)	2620(5)	1192(5)	28(1)
C(15)	6376(7)	3048(5)	323(5)	27(1)
C(16)	5925(8)	3664(5)	-680(5)	29(1)
C(17)	7254(8)	4086(5)	-1525(5)	32(1)
C(18)	9077(8)	3923(5)	-1373(5)	30(1)
C(19)	9564(8)	3322(5)	-383(5)	32(1)
C(20)	8220(8)	2900(5)	447(5)	32(1)
I(1)	11121(1)	4596(1)	-2607(1)	40(1)
O(1)	5368(6)	3972(4)	3277(4)	35(1)
O(2)	3401(6)	2603(4)	904(4)	44(1)
H(6A)	6512	1617	5045	37
H(6B)	8777	1272	4776	37
H(7A)	8594	3444	4894	70
H(7B)	7550	2941	6117	70
H(7C)	6324	3725	5273	70

H(8A)	9393	-1080	2615	36
H(8B)	10287	-254	3286	36
H(9A)	10694	-236	777	55
H(9B)	12353	-917	1386	55
H(9C)	11604	574	1450	55
H(10A)	7536	-724	1119	36
H(10B)	5447	73	1088	36
H(11A)	6258	-1494	2989	55
H(11B)	5312	-1841	2013	55
H(11C)	4170	-709	2942	55
H(12A)	2251	2939	3211	39
H(12B)	2602	1513	2831	39
H(13A)	3993	901	4473	59
H(13B)	1794	1644	4887	59
H(13C)	3403	2341	4882	59
H(16)	4676	3793	-776	35
H(17)	6931	4484	-2205	38
H(19)	10809	3204	-284	38
H(20)	8552	2498	1124	39
H(2)	8830(80)	2390(60)	2900(60)	31(16)

STable 3. Bond lengths [Å] and angles [°] for **4c**.

C(1)-O(1)	1.205(6)	C(12)-H(12A)	0.9900
C(1)-C(2)	1.537(6)	C(12)-H(12B)	0.9900
C(1)-C(5)	1.541(7)	C(13)-H(13A)	0.9800
C(2)-C(3)	1.507(8)	C(13)-H(13B)	0.9800
C(2)-C(6)	1.543(7)	C(13)-H(13C)	0.9800
C(2)-H(2)	0.99(6)	C(14)-O(2)	1.234(6)
C(3)-C(4)	1.328(7)	C(14)-C(15)	1.488(8)
C(3)-C(8)	1.520(7)	C(15)-C(20)	1.401(7)
C(4)-C(10)	1.517(7)	C(15)-C(16)	1.406(7)
C(4)-C(5)	1.525(6)	C(16)-C(17)	1.377(8)
C(5)-C(14)	1.543(7)	C(16)-H(16)	0.9500
C(5)-C(12)	1.550(8)	C(17)-C(18)	1.395(8)
C(6)-C(7)	1.514(8)	C(17)-H(17)	0.9500
C(6)-H(6A)	0.9900	C(18)-C(19)	1.396(7)
C(6)-H(6B)	0.9900	C(18)-I(1)	2.094(6)
C(7)-H(7A)	0.9800	C(19)-C(20)	1.376(8)
C(7)-H(7B)	0.9800	C(19)-H(19)	0.9500
C(7)-H(7C)	0.9800	C(20)-H(20)	0.9500
C(8)-C(9)	1.532(8)		
C(8)-H(8A)	0.9900	O(1)-C(1)-C(2)	126.3(5)
C(8)-H(8B)	0.9900	O(1)-C(1)-C(5)	124.2(4)
C(9)-H(9A)	0.9800	C(2)-C(1)-C(5)	109.5(4)
C(9)-H(9B)	0.9800	C(3)-C(2)-C(1)	102.2(4)
C(9)-H(9C)	0.9800	C(3)-C(2)-C(6)	113.5(4)
C(10)-C(11)	1.523(8)	C(1)-C(2)-C(6)	113.9(4)
C(10)-H(10A)	0.9900	C(3)-C(2)-H(2)	110(4)
C(10)-H(10B)	0.9900	C(1)-C(2)-H(2)	104(3)
C(11)-H(11A)	0.9800	C(6)-C(2)-H(2)	113(4)
C(11)-H(11B)	0.9800	C(4)-C(3)-C(2)	113.4(4)
C(11)-H(11C)	0.9800	C(4)-C(3)-C(8)	125.3(5)
C(12)-C(13)	1.533(8)	C(2)-C(3)-C(8)	121.0(5)

C(3)-C(4)-C(10)	126.1(4)	C(4)-C(10)-C(11)	112.9(5)
C(3)-C(4)-C(5)	112.6(5)	C(4)-C(10)-H(10A)	109.0
C(10)-C(4)-C(5)	121.3(4)	C(11)-C(10)-H(10A)	109.0
C(4)-C(5)-C(1)	101.9(4)	C(4)-C(10)-H(10B)	109.0
C(4)-C(5)-C(14)	111.1(4)	C(11)-C(10)-H(10B)	109.0
C(1)-C(5)-C(14)	112.9(4)	H(10A)-C(10)-H(10B)	107.8
C(4)-C(5)-C(12)	113.8(4)	C(10)-C(11)-H(11A)	109.5
C(1)-C(5)-C(12)	109.0(4)	C(10)-C(11)-H(11B)	109.5
C(14)-C(5)-C(12)	108.2(4)	H(11A)-C(11)-H(11B)	109.5
C(7)-C(6)-C(2)	115.1(5)	C(10)-C(11)-H(11C)	109.5
C(7)-C(6)-H(6A)	108.5	H(11A)-C(11)-H(11C)	109.5
C(2)-C(6)-H(6A)	108.5	H(11B)-C(11)-H(11C)	109.5
C(7)-C(6)-H(6B)	108.5	C(13)-C(12)-C(5)	115.0(4)
C(2)-C(6)-H(6B)	108.5	C(13)-C(12)-H(12A)	108.5
H(6A)-C(6)-H(6B)	107.5	C(5)-C(12)-H(12A)	108.5
C(6)-C(7)-H(7A)	109.5	C(13)-C(12)-H(12B)	108.5
C(6)-C(7)-H(7B)	109.5	C(5)-C(12)-H(12B)	108.5
H(7A)-C(7)-H(7B)	109.5	H(12A)-C(12)-H(12B)	107.5
C(6)-C(7)-H(7C)	109.5	C(12)-C(13)-H(13A)	109.5
H(7A)-C(7)-H(7C)	109.5	C(12)-C(13)-H(13B)	109.5
H(7B)-C(7)-H(7C)	109.5	H(13A)-C(13)-H(13B)	109.5
C(3)-C(8)-C(9)	110.8(4)	C(12)-C(13)-H(13C)	109.5
C(3)-C(8)-H(8A)	109.5	H(13A)-C(13)-H(13C)	109.5
C(9)-C(8)-H(8A)	109.5	H(13B)-C(13)-H(13C)	109.5
C(3)-C(8)-H(8B)	109.5	O(2)-C(14)-C(15)	118.8(5)
C(9)-C(8)-H(8B)	109.5	O(2)-C(14)-C(5)	118.6(5)
H(8A)-C(8)-H(8B)	108.1	C(15)-C(14)-C(5)	122.5(4)
C(8)-C(9)-H(9A)	109.5	C(20)-C(15)-C(16)	117.6(5)
C(8)-C(9)-H(9B)	109.5	C(20)-C(15)-C(14)	124.4(5)
H(9A)-C(9)-H(9B)	109.5	C(16)-C(15)-C(14)	118.0(4)
C(8)-C(9)-H(9C)	109.5	C(17)-C(16)-C(15)	121.5(5)
H(9A)-C(9)-H(9C)	109.5	C(17)-C(16)-H(16)	119.3
H(9B)-C(9)-H(9C)	109.5	C(15)-C(16)-H(16)	119.3

C(16)-C(17)-C(18)	119.4(5)	C(20)-C(19)-H(19)	120.4
C(16)-C(17)-H(17)	120.3	C(18)-C(19)-H(19)	120.4
C(18)-C(17)-H(17)	120.3	C(19)-C(20)-C(15)	121.8(5)
C(17)-C(18)-C(19)	120.4(5)	C(19)-C(20)-H(20)	119.1
C(17)-C(18)-I(1)	120.9(4)	C(15)-C(20)-H(20)	119.1
C(19)-C(18)-I(1)	118.7(4)		
C(20)-C(19)-C(18)	119.3(5)		

Symmetry transformations used to generate
equivalent atoms:

STable 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	31(3)	28(3)	21(2)	-1(2)	-10(2)	-1(2)
C(2)	24(2)	26(2)	31(3)	6(2)	-10(2)	-3(2)
C(3)	28(3)	28(2)	25(3)	0(2)	-9(2)	2(2)
C(4)	24(2)	23(2)	22(2)	1(2)	-4(2)	-2(2)
C(5)	25(2)	23(2)	27(3)	-1(2)	-12(2)	-2(2)
C(6)	31(3)	38(3)	24(3)	3(2)	-11(2)	-7(2)
C(7)	63(4)	42(3)	35(4)	-6(3)	-20(3)	-5(3)
C(8)	27(2)	28(3)	32(3)	0(2)	-10(2)	2(2)
C(9)	28(3)	44(3)	31(3)	-6(2)	-9(2)	3(2)
C(10)	28(2)	29(3)	29(3)	-1(2)	-9(2)	0(2)
C(11)	41(3)	31(3)	39(3)	6(2)	-13(3)	-8(2)
C(12)	24(2)	35(3)	34(3)	0(2)	-8(2)	1(2)
C(13)	27(3)	49(3)	39(3)	3(3)	-4(2)	-10(3)
C(14)	34(3)	24(2)	26(3)	3(2)	-16(2)	-4(2)
C(15)	33(3)	25(2)	23(3)	0(2)	-10(2)	-1(2)
C(16)	35(3)	24(2)	26(3)	3(2)	-13(2)	-2(2)
C(17)	45(3)	23(2)	26(3)	0(2)	-15(2)	2(2)
C(18)	40(3)	23(2)	25(3)	-1(2)	-9(2)	-3(2)
C(19)	34(3)	35(3)	25(3)	3(2)	-11(2)	-7(2)
C(20)	35(3)	33(3)	30(3)	9(2)	-15(2)	-7(2)
I(1)	45(1)	31(1)	34(1)	5(1)	-3(1)	-3(1)
O(1)	39(2)	28(2)	37(2)	-2(2)	-15(2)	0(2)
O(2)	40(2)	51(3)	49(3)	17(2)	-27(2)	-15(2)