Supporting Information

A Computationally Designed Rh(I)-Catalyzed Two-Component [5 + 2 + 1] Cycloaddition of Ene-Vinylcyclopropanes and CO to Synthesize Fused Bicyclic Cyclooctenones

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Contents

1. Strategy for the New [5 + 2 + 1] Design and the Computational Details

Strategy for the new [5+2+1] reaction design. The strategy for our computational design of the new [5+2+1] reaction is to compute the energy surface of a postulated three-component [5+2+1] cycloaddition of vinylcyclopropane, alkene, and CO (Figure S1). The reductive elimination (RE) transition structure **S8** leading to [5+2] product is higher than **S1** by 26.6 kcal/mol. In contrast, in the [5+2+1] pathway, CO coordination (**S1** to **S2**, exothermic by 10.3 kcal/mol), CO insertion (or it is actually carbon migration) (**S2** to **S4** via transition structure **S3** with an activation energy of 18.7 kcal/mol), migratory reductive elimination (MRE) (**S4** to **S6**, and **S7** via transition structure **S5**, with an activation energy of 21.5 kcal/mol) are easier. The RE transition structure **S8** is higher in energy than **S3** and **S5**, suggesting that [5+2+1] pathway is favored with respect to the [5+2] pathway.

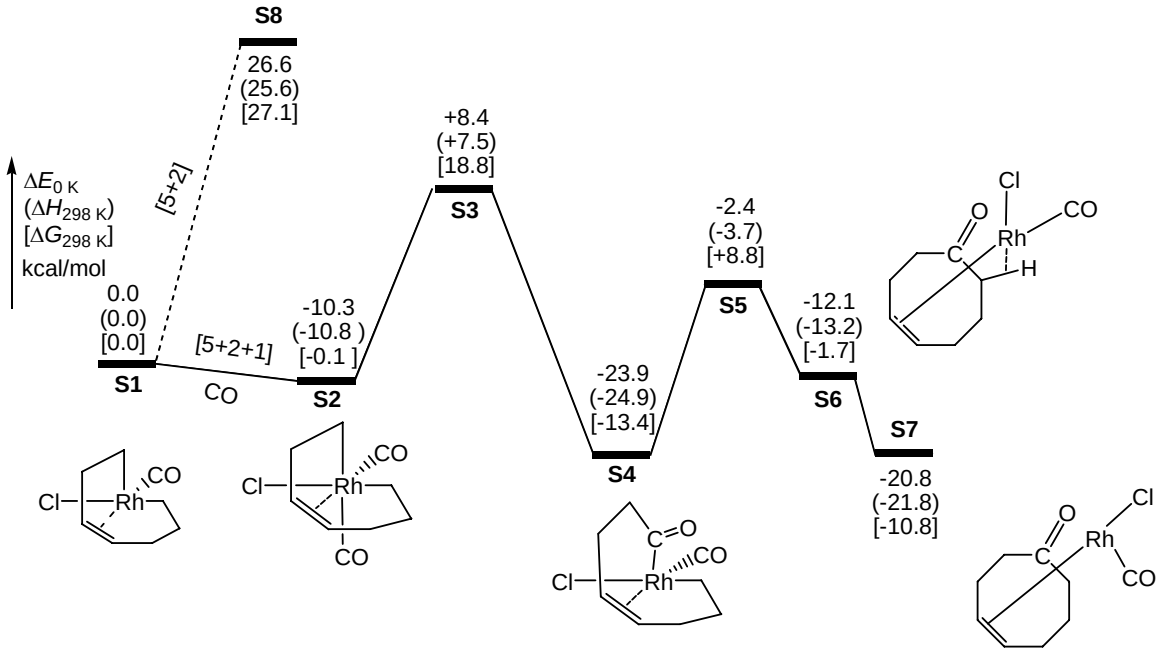
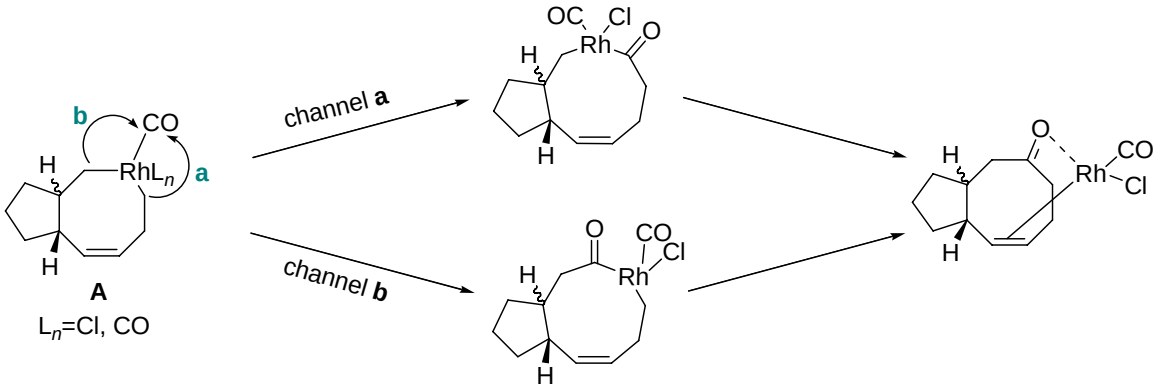


Figure S1. The Energy Surfaces of the [5+2+1] and [5+2] Pathways of Three-Component Reactions of VCP, Alkene, and CO.

The above calculations predicted that [5+2+1] path is favored over the [5+2] path. We then experimentally tested this prediction. Excitingly, experiments supported the DFT prediction that [5+2+1] path is favored. During the experimental test of the scope of the substrates for the [5+2+1] reaction, we have also done some preliminary calculations on the two-component [5+2+1] reaction of Ene-VCP and CO, in order to show that [5+2+1] path is preferred over the [5+2] path for the two-component reaction of Ene-VCP and CO.

Our present preliminary calculations only focus on the energetic difference of RE and MRE steps starting from intermediates **A** (Scheme S1). Intermediate **A** is generated through VCP cleavage, alkene insertion, and CO coordination. In the followed steps, the CO insertion can occur via either channel **a** or channel **b** or via both. Calculations indicate that channel **a** is preferred over channel **b** for the formation of cis-fused 5/8 [5+2+1] cycloadduct, whereas both channels **a** and **b** are very competitive for the formation of trans-fused 5/8 [5+2+1] cycloadduct (see below for details).



Scheme S1. Pathways of CO Insertion and Reductive Elimination

Figure S2 shows the DFT computed energy surfaces for the competitive [5+2] and [5+2+1] paths starting from the cis-fused intermediate **S9**. Here channel **a** is preferred over channel **b** since the CO insertion transition state **S11** (channel **a**) is lower in energy than the competitive CO insertion transition state **S16** (channel b) by 3.1 kcal/mol. In the favored channel **a**, the RE step via transition structure **S15** leading to the [5+2] product has an activation energy of 24.7 kcal/mol. However, in the [5+2+1] path, the CO coordination (**S9** to **S10**, exothermic by 8.5 kcal/mol), CO insertion (**S10** to **S12** via transition structure **S11** with an activation energy of 13 kcal/mol), and MRE step (**S12** to **S14** via transition structure **S13** with an activation energy of 22.9 kcal/mol) are easier. **S15** lies higher than **S11** and **S13** in the energy surfaces in Figure S2, suggesting [5+2+1] path is favored over the [5+2] path to generate cis-fused 5/8 [5+2+1] cycloadduct.

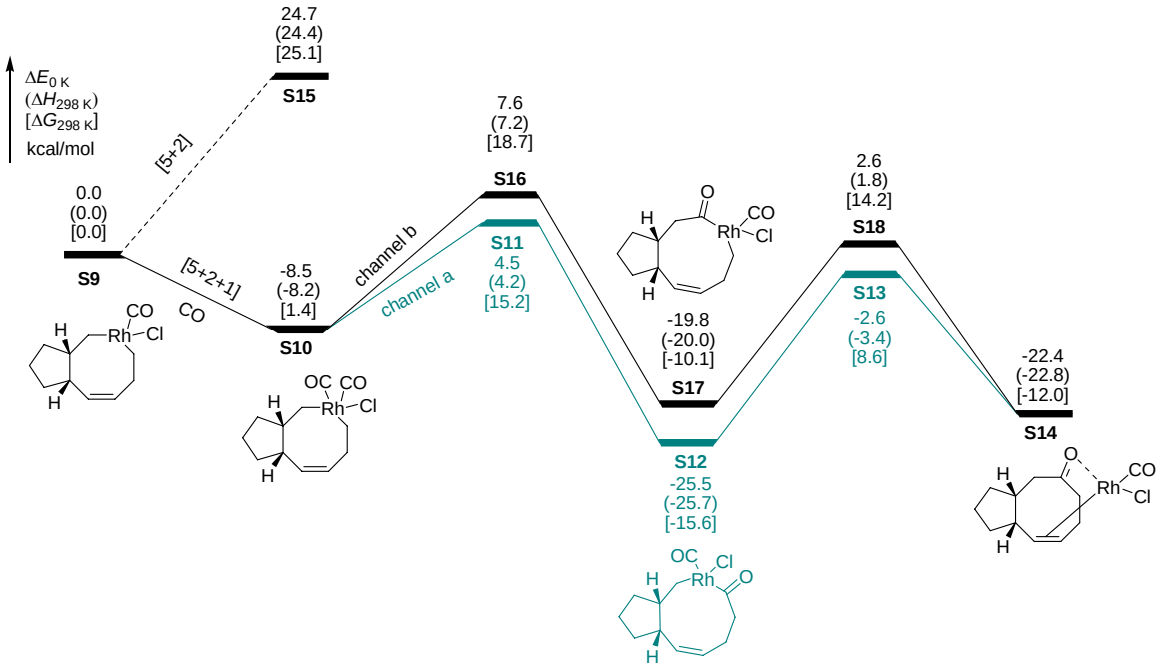


Figure S2. The Energy Surfaces of the *cis*-[5+2+1] and *cis*-[5+2] Pathways of Two-Component Reactions of Ene-VC and CO

Figure S3 shows the DFT computed energy surfaces for the competitive [5+2] and [5+2+1] paths starting from the trans-fused intermediate **S19**. Here channel **a** and channel **b** are very competitive, since the CO insertion transition state **S21** (channel **a**) is only higher in energy than the competitive CO insertion transition state **S26** (channel b) by 0.5 kcal/mol. In channel **a**, the RE step via transition structure **S25** leading to the [5+2] product has an activation energy of 30.4 kcal/mol. However, in the [5+2+1] path, the CO coordination (**S19** to **S20**, exothermic by 10.0 kcal/mol), CO insertion (**S20** to **S22** via transition structure **S21** with an activation energy of 13.8 kcal/mol), and MRE step (**S22** to **S24** via transition structure **S23** with an activation energy of 23.5 kcal/mol) are easier. **S25** lies higher than **S21** and **S23** in the energy surfaces in Figure S3, suggesting [5+2+1] path is favored than the [5+2] path to generate trans-fused 5/8 [5+2+1] cycloadduct.

In the [5+2+1] path of channel **b**, the CO coordination (**S19** to **S20**, exothermic by 10.0 kcal/mol), CO insertion (**S20** to **S27** via transition structure **S26** with an activation energy of 13.3 kcal/mol), and MRE step (**S27** to **S24** via transition structure **S28** with an activation energy of 18.8 kcal/mol) are easier. **S25** lies higher than **S26** and **S28** in the energy surfaces in Figure S3, suggesting [5+2+1] path is favored than the [5+2] path to generate trans-fused 5/8 [5+2+1] cycloadduct.

Therefore, in the case of generation of trans-fused 5/8 [5+2+1] cycloadduct, both channels **a** and **b** are competitive, and the formation of [5+2+1] cycloadduct is favored over the formation of [5+2] cycloadduct.

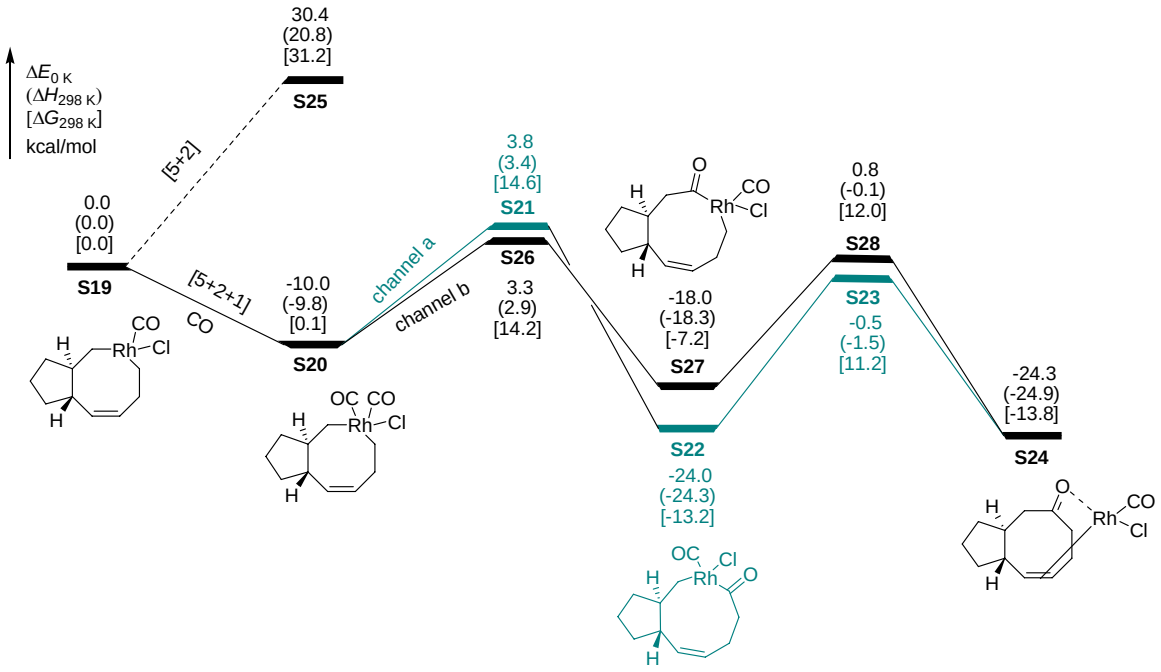


Figure S3. The Energy Surfaces of the *trans*-[5+2+1] and *trans*-[5+2] Pathways of Two-Component Reactions of Ene-VCP and CO.

Further study of the regio- and stereo-chemistry of the two-component [5+2+1] reaction, especially how **S9** and **S19** are generated, is in progress and will be reported in due course.

Computational Details. All of the calculations were performed with the Gaussian 03 progam.[1] Density functional B3LYP[2] were used to locate all the transition structures and intermediates. 6-31G* basis set is applied for all elements except for Rh, which uses the basis set of LANL2DZ+ECP.[3,4] This method has been successfully applied to predict structures and reaction mechanisms for reactions of dirhodium tetracarboxylate complexes and other Rh-catalyzed cycloadditions.[5] Frequency calculations at the same level have been performed to confirm each stationary point to be either a minimum or a transition structure. The reported energies are Zero-point energy-corrected electronic energies ($\Delta E_{0\,\mathrm{K}}$), enthalpies ($\Delta H_{298\,\mathrm{K}}$) and free energies ($\Delta G_{298\,\mathrm{K}}$)

Computational References

(1) Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

(2) (a) Becke, A. D. J. *Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(3) For LANL2DZ basis set: (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III. Ed.; Plenum Press: New York, 1977; pp 1-28.

(4) Each d orbital (for all elements) includes 5d functions (the keyword used in the Gaussian 98 calculations is 5D, 7F).

(5) (a) Nowlan, D. T., III; Gregg, T. M.; Davies, H. M. L.; Singleton, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 15902. (b) Sheehan, S. M.; Padwa, A.; Snyder, J. P. *Tetrahedron Lett.* **1998**, *39*, 949. (c) Padwa, A.; Snyder, J. P.; Curtis, E. A.; Sheehan, S. M.; Worsencroft, K. J.; Kappe, C. O. *J. Am. Chem. Soc.* **2000**, *122*, 8155. (d) Nakamura, E.; Yoshikai, N.; Yamanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 7181. (e) Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004,** *126*, 9451. (f) Baik, M.-H.; Baum, E. W.; Burland, M. C.; Evans, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 1602. (g) Bayden, A. S.; Brummond, K. M.; Jordan, K. D. *Organometallics* **2006**, *25*, 5204. (h) For a discussion of theoretical methods applied to transition-metal containing systems, see: Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Rev.* **2000**, *100*, 421.

2. General Methods of Synthesis

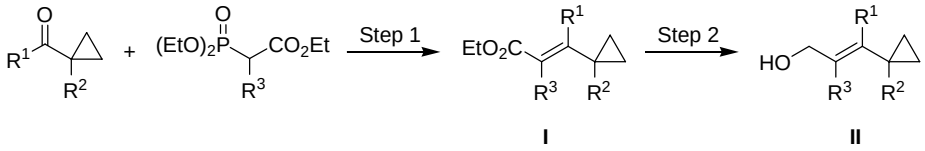
Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry CO mixed gas or nitrogen from a balloon, unless otherwise indicated. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone prior to use. Toluene was distilled from sodium prior to use. Dioxane (extra dry, water < 50 ppm), AgOTf, $[Rh(CO)_2Cl]_2$, and $Rh(PPh_3)_3Cl$ were commercially available and used as received. Analytical TLC was performed with 0.25 mm silica gel 60F plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on a Varian Mercury 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz), Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), or Varian INOVA 600 (^{1}H at 600 MHz, ^{13}C at 150 MHz) magnetic resonance spectrometer. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak. Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) and are reported in wavenumbers (cm^{-1}). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a VG-ZAB-HS mass spectrometer (EI, 70 eV).

3. General Procedure for the Preparation of Ene-VCP Substrates

Ene-VCP substrates **1**,[1] **4**,[2] **6**,[1] **8**,[1] **10**,[2] **22**,[1] and **24**[1] were prepared according to published procedures. Other ene-VCP substrates were prepared as described below.

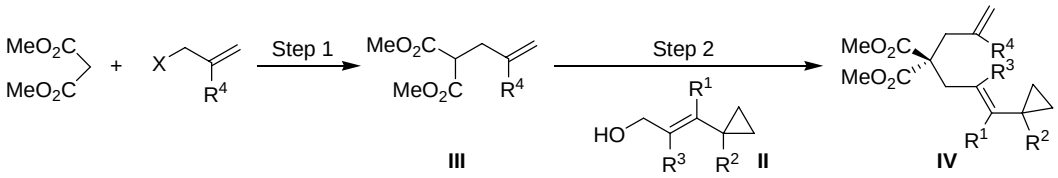
(1) General Procedure for the Preparation of Vinyl Cyclopropyl Alcohols



Step 1: To a flask containing NaH (1.2 equiv.) and THF at 0 °C was added triethyl phosphonoacetate (R^3 = H, 1.2 equiv.) or triethyl 2-phosphonopropionate (R^3 = CH_3, 1.2 equiv.) dropwise. After stirred at room temperature for 30 min, corresponding cyclopropyl carbonyl compound (1.0 equiv.) was added dropwise and the reaction was allowed to stir overnight. After quenching with brine, extraction with Et_2O, and drying over $MgSO_4$, concentration of the organic phase *in vacuo* gave a crude oil that was further purified by flash chromatography (petroleum ether/EtOAc = 9:1). Ester **I** was obtained as a clear, colorless oil.

Step 2: To a Schlenk flask charged with ester **I** (1 equiv.) and THF at −78 °C was added DIBAL-H (20% wt in toluene, 2.2 equiv.) dropwise. The reaction was warmed to room temperature overnight and was quenched with ethylacetate and aqueous potassium tartrate tetrahydrate. Stirring was continued until the solution is clear. Extraction with Et_2O, washed with brine, drying over $MgSO_4$, evaporation, and purification by flash column chromatography (petroleum ether/EtOAc = 4:1) provided alcohol **II** as a clear, colorless oil.

(2) General Procedure for the Preparation of Geminal Diester-Tether Substrates



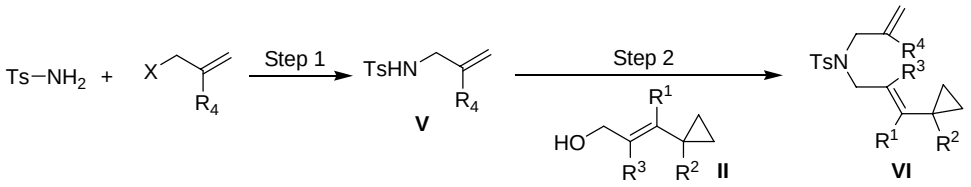
Step 1: To a flask charged with NaH (1.8 equiv.) and THF at 0 °C was added dimethyl malonate (1.8 equiv.) dropwise. After stirring for 30 min, allyl iodide or allyl bromide (1.0 equiv.) was added and the reaction mixture was stirred at room temperature overnight. Quenched with brine, extracted with Et_2O, dried over $MgSO_4$, evaporation, and purification by flash column chromatography (petroleum ether/EtOAc = 9:1) provided **III** as a clear, colorless oil.

Step 2: (a) To a 250 mL flask containing alcohol **II** (1.0 equiv.) and THF at −78 °C was added *n*-BuLi (1.6 M in hexane, 1.2 equiv.), followed 10 min later by methane sulfonyl chloride (1.2 equiv.), and then immediately by lithium bromide (4.5 equiv.) in one portion. The reaction mixture was stirred for 30 min. (b) To a second flask charged with NaH (1.6 equiv.) and THF was added **III** (1.6 equiv.)

(1) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A.; Pleuss, N. *Tetrahedron* **1998**, *54*, 7203.
(2) Wender, P. A.; Haustedt, L. O.; Lim, J.; Love, J. A.; Williams, T. J.; Yoon, J.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 6302.

dropwise over 15 min. After 30 min at room temperature, the solution was cooled to −78 °C and the solution of the first flask was transferred in via cannula. The reaction mixture was stirred for 2 h at −78 °C, then allowed to warm to room temperature. Quenching with water, extraction with Et_2O, drying over $MgSO_4$, evaporation, and purification by flash column chromatography (petroleum ether/EtOAc = 9:1) provided geminal diester derivative **IV** as a clear colorless oil.

(3) General Procedure for the Preparation of Tosylamide-Tether Substrates

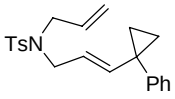


Step 1: To a flask was added $TsNH_2$ (1.1 equiv.), K_2CO_3 (1.5 equiv.) and acetone at 0 °C. After stirring for 30 min, allyl iodide or alyl bromide (1.0 equiv.) was added and the reaction mixture was refluxed for 7 h. Quenched with brine, extracted with Et_2O, dried over $MgSO_4$, evaporation, and purification by flash column chromatography (petroleum ether/EtOAc = 2:1) provided **V** as a white solid.

Step 2: To a solution of alcolol **II** (1.0 equiv.)**, V** (1.2 equiv.), and PPh_3 (2.2 equiv.) in THF was added DEAD (2.2 equiv.) at room temperature and the reaction mixture was stirred for 20 h at room temperature. The resulting mixture was diluted with Et_2O, washed with water and brine, and the organic layer was dried over Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography with Et_3N-impregnated silica gel (petroleum ether/EtOAc = 9:1) to give **VI** as a colorless oil.

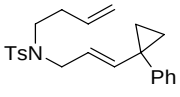
Physical data for new Ene-VCP substrates:

Substrate 14



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.62 (d, 2H), 7.31-7.15 (m, 7H), 5.66-5.53 (m, 1H), 5.40 (d, J = 15.3 Hz, 1H), 5.16-5.07 (m, 2H), 4.74 (dt, J = 15.3 and 6.9 Hz, 1H), 3.74 (d, J = 6.6 Hz, 4H), 2.42 (s, 3H), 1.08-1.02 (m, 2H), 0.97-0.84 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.9, 142.71, 142.66, 137.4, 132.9, 129.6, 129.5, 128.2, 127.0, 126.4, 121.7, 118.6, 49.0, 48.5, 27.6, 21.5, 14.6. IR (FT-IR): ν = 3027 (w), 1597 (w), 1496 (m), 1445 (w), 1346 (s), 1161 (s), 1092 (m), 1025 (w), 933 (m), 908 (m), 816 (m) cm^{-1}. MS (EI): m/z (%) = 367 (M^+, 0.5), 224 (53), 155 (43), 91 (100). HRMS calcd for $C_{22}H_{25}NO_2S$: 367.1606. Found: 367.1595.

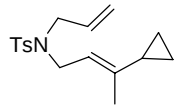
Substrate 20



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.23-7.15 (m, 5H),

5.68 (m, 1H), 5.44 (d, J = 15.3 Hz, 1H), 5.06-4.99 (m, 2H), 4.77 (dt, J = 15.3 and 6.9 Hz, 1H), 3.73 (d, J = 6.6 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H), 2.27 (s, 3H), 2.26-2.19 (m, 2H), 1.09-1.03 (m, 2H), 0.88-0.82 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.9, 142.7, 142.3, 137.0, 134.8, 129.6, 129.5, 128.2, 127.0, 126.4, 122.3, 116.9, 49.8, 46.3, 33.0, 27.7, 21.5, 14.6. IR (FT-IR): ν = 2912 (w), 1727 (w), 1658 (w), 1630 (w), 1588 (w), 1444 (w), 1341 (m), 1157 (s), 1091 (m), 1019 (w), 949 (m), 917 (m), 815 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 381 (M^+, 1.0), 340 (12), 264 (6), 238 (43), 226 (10), 184 (25), 157 (96), 129 (48), 91 (100). HRMS calcd for $C_{23}H_{27}NO_2S$: 381.1762. Found: 381.1758.

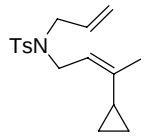
Substrate 25



(*E* configuration)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.64 (ddt, J = 17.1, 9.6, and 6.6 Hz, 1H), 5.13-5.17 (m, 2H), 4.97 (t, J = 6.6 Hz, 1H), 3.81 (d, J = 7.2 Hz, 2H), 3.76 (d, J = 6.3 Hz, 2H), 2.43 (s, 3H), 1.47 (s, 3H), 1.28 (m, 1H), 0.50-0.57 (m, 2H), 0.31-0.37 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 141.0, 137.6, 133.2, 129.6, 127.1, 118.4, 116.7, 49.2, 44.2, 21.3, 18.5, 14.0, 4.4. IR (FT-IR): ν = 2918 (w), 1444 (w), 1339 (s), 1158 (s), 1092 (m), 1049 (w), 908 (m), 812 (m) cm^{-1}. MS (EI): m/z (%) = 305 (M^+, 1), 224 (13), 155 (29), 150 (34), 149 (16), 146 (13), 134 (16), 108 (23), 95 (31), 94 (22), 91 (100). HRMS calcd for $C_{17}H_{23}NO_2S$: 305.1450. Found: 305.1444.

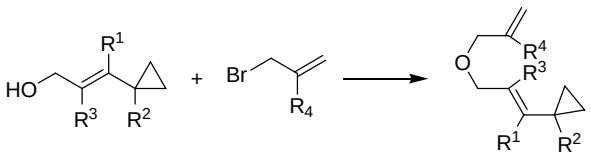
Substrate 27[3]



(*Z* configuration)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 5.67 (m, 1H), 5.10-5.21 (m, 2H), 5.05 (t, J = 7.2 Hz, 1H), 3.96 (d, J = 7.2 Hz, 2H), 3.82 (d, J = 6.0 Hz, 2H), 2.42 (s, 3H), 1.59 (m, 1H), 1.34 (s, 3H), 0.49-0.63 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.9, 140.1, 137.5, 133.1, 129.4, 127.1, 119.4, 118.3, 49.1, 43.7, 21.4, 18.5, 12.1, 4.2. IR (FT-IR): ν = 2922 (w), 1444 (w), 1339 (s), 1158 (s), 1092 (m), 1054 (w), 922 (m), 908 (m), 815 (m) cm^{-1}. MS (EI): m/z (%) = 305 (M^+, 3), 224 (30), 155 (38), 150 (69), 91 (100). HRMS calcd for $C_{17}H_{23}NO_2S$: 305.1450. Found: 305.1444.

(4) General Procedure for the Preparation of Ether-Tether Substrates



II **VII**

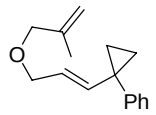
To a solution of NaH (1.2 equiv.) in THF was added a solution of alcohol **II** (1.0 equiv.) in THF at 0 °C and the mixture was refluxed for 2 h. The solution was cooled to room temperature, then allyl bromide (1.2 equiv.) was added and the mixture was refluxed overnight. After being cooled to room

(3) The synthesis refers to Trost, B. M., Shen, H. C.; Horne, D. B.; Toste, F. D.; Steinmetz, B. G.; Koradin, C. *Chem. Eur. J.* **2005**, *11*, 2577.

temperature, the reaction was quenched with water and extracted with Et_2O. Washed with brine, dried over $MgSO_4$, evaporation to remove the solvent, and purification by flash column chromatography (petroleum ether/EtOAc = 9:1) gave **VII** as a colorless oil.

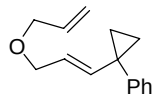
Physical data for new Ene-VCP substrates:

Substrate 12



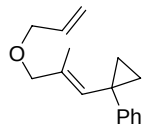
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.31-7.20 (m, 5H), 5.60 (d, J = 15.3 Hz, 1H), 5.14 (dt, J = 15.3 and 6.3 Hz, 1H), 4.92 (d, J = 0.9 Hz, 1H), 4.86 (d, J = 0.9Hz, 1H), 3.87 (d, J = 6.0 Hz, 2H), 3.85 (s, 2H), 1.71 (s, 3H), 1.11-1.07 (m, 2H), 1.01-0.96 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.2, 142.3, 141.0, 129.8, 128.2, 126.4, 124.4, 112.1, 73.9, 70.3, 27.7, 19.5, 14.8. IR (FT-IR): v = 3026 (w), 2850 (w), 1660 (w), 1602 (w), 1497 (m), 1446 (m), 1350 (w), 1107 (m), 1078 (m), 971 (m), 934 (m) cm^{-1}. MS (EI): m/z (%) = 228 (M^+, 1), 156 (24), 143 (100), 128 (61), 91 (54). HRMS calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1508.

Substrate 16



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 5H), 5.96-5.82 (m, 1H), 5.62 (dt, J = 15.4 and 1.0 Hz, 1H), 5.30-5.09 (m, 3H), 3.95-3.88 (m, 4H), 1.12-1.06 (m, 2H), 1.01-0.88 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 141.3, 134.8, 129.8, 128.2, 126.4, 124.2, 117.1, 71.0, 70.6, 27.7, 14.7. IR (FT-IR): v = 3026 (w), 2853 (w), 1685 (w), 1602 (w), 1497 (m), 1446 (m), 1425 (w), 1348 (w), 1076 (m), 1025 (m), 972 (m), 934 (m) cm^{-1}. MS (EI): m/z (%) = 214 (M^+, 1), 156 (15), 143 (100), 128 (61), 91 (43). HRMS calcd for $C_{15}H_{18}O$: 214.1358. Found: 214.1353.

Substrate 18



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.26-7.01 (m, 5H), 5.97-5.87 (m, 1H), 5.78 (s, 1H), 5.26 (dt, J = 17.1 and 0.9 Hz, 1H), 5.17 (dt, J = 10.2 and 0.9Hz, 1H), 3.95 (d, J = 0.6 Hz, 2H), 3.88 (s, 2H), 1.66 (s, 3H), 1.14-1.10 (m, 2H), 1.02-0.98 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 145.2, 137.2, 134.9, 130.5, 128.1, 126.1, 125.2, 116.9, 75.6, 70.7, 22.9, 17.9, 15.2. IR (FT-IR): v = 3080 (m), 3006 (m), 2930 (m), 2850 (m), 1601 (w), 1495 (m), 1446 (m), 1087 (s), 1028 (w), 925 (m) cm^{-1}. MS (EI): m/z (%) = 228 (M^+, 5), 157 (100), 141 (30), 129 (59), 91 (50). HRMS calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1517.

4. General Procedure for the [5 + 2 + 1] Cycloaddition Reactions

(1) General [5 + 2 + 1] Cycloaddition Procedure Using $[Rh(CO)_2Cl]_2$ as Catalyst

$[Rh(CO)_2Cl]_2$ (5 mol % to the substrate) was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen, and then a solution of the ene-VCP substrate in degassed dioxane (0.05 M) was added. The solution was bubbled with the mixed CO (0.2 atm CO + 0.8 atm N_2) for 5 min. The reaction mixture was stirred at 80 °C under the mixed CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to afford the cycloaddition products.

(2) Cycloaddition Procedure Using $RhCl(PPh_3)_3$ as Catalyst

$RhCl(PPh_3)_3$ (10 mol % to the substrate) and degassed dioxane was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen, and bubbled with CO for 10 min. Then a solution of the Ene-VCP substrate in degassed dioxane (0.05 M) was added. The solution was bubbled with CO for 5 min and then stirred at 80 °C under the CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to give the cycloaddition products.

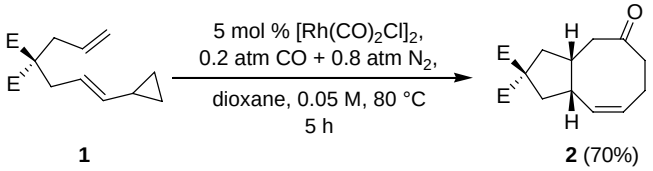
(3) Cycloaddition Procedure Using $RhCl(PPh_3)_3$ and AgOTf as Catalyst System

$RhCl(PPh_3)_3$ (10 mol % to the substrate), AgOTf (10 mol % to the substrate), and degassed dioxane was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen and stirred at room temperature for 5 min. Then, the catalyst mixture was bubbled with CO for 10 min. To the catalyst mixture was added a solution of the substrate in degassed dioxane (0.05 M) and then CO was bubbled again through the solution for 5 min. The mixture was stirred at 80 °C under the CO atmosphere until TLC indicated the completion of the reaction. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to give the cycloaddition products.

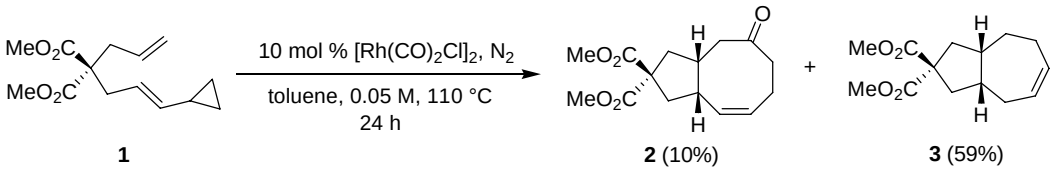
(4) Cycloaddition Procedure Using $[Rh(CO)_2Cl]_2$ and AgOTf as Catalyst System

$[Rh(CO)_2Cl]_2$ (5 mol % to the substrate), AgOTf (10 mol % to the substrate), and degassed dioxane was charged in a base-washed, oven-dried Schlenk flask under an atmosphere of nitrogen and stirred at room temperature for 5 min. Then the catalyst mixture was bubbled with CO for 10 min. To the catalyst mixture was added a solution of the substrate in degassed dioxane (0.05 M) and then CO was bubbled again through the solution for 5 min. The mixture was stirred at 80 °C for the indicated time under the CO atmosphere. After being cooled to room temperature, the mixture was concentrated and the residue was purified by flash column chromatography with silica gel to give the cycloaddition products.

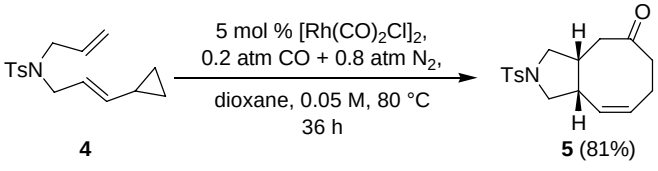
5. Summary of All [5 + 2 + 1] Cycloaddition Reactions



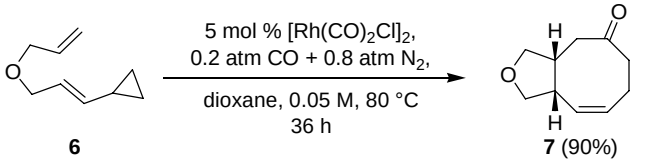
1 **2** (70%)



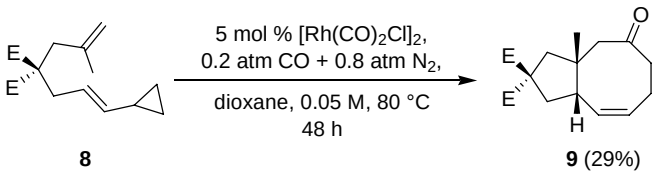
1 **2** (10%) **3** (59%)



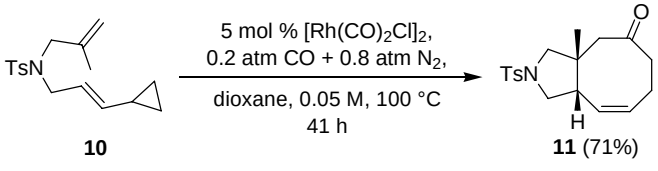
4 **5** (81%)



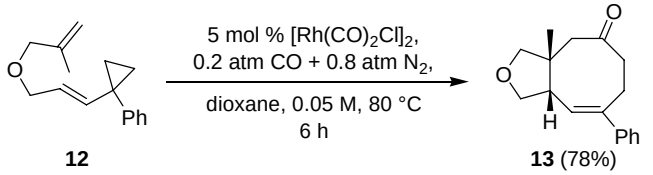
6 **7** (90%)



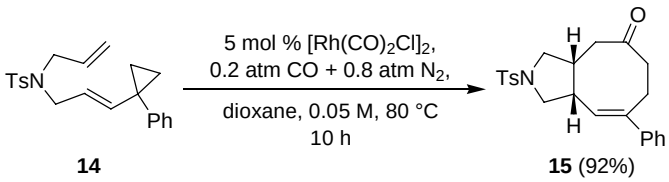
8 **9** (29%)



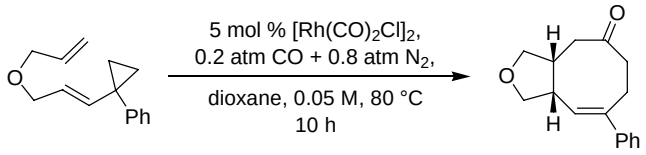
10 **11** (71%)



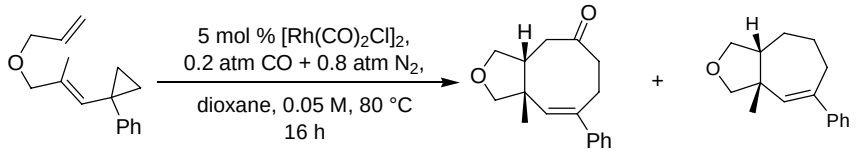
12 **13** (78%)



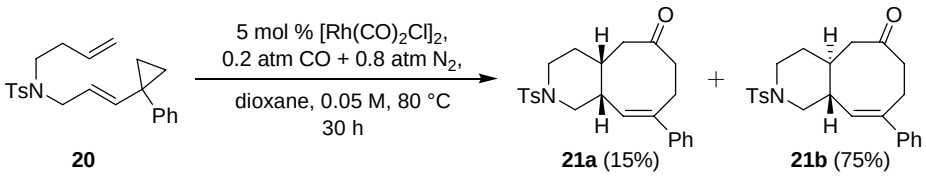
14 **15** (92%)



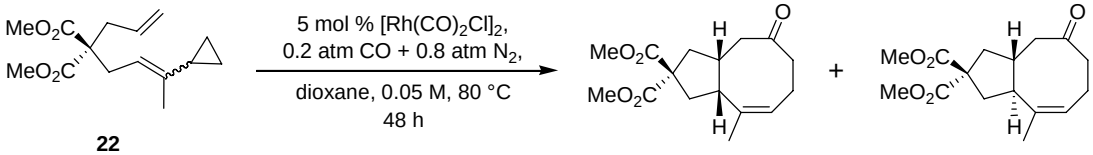
16 **17** (73%)



18 **19** (83%) **28** (11%)

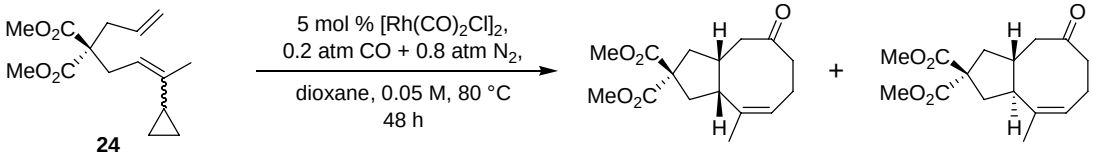


20 **21a** (15%) **21b** (75%)



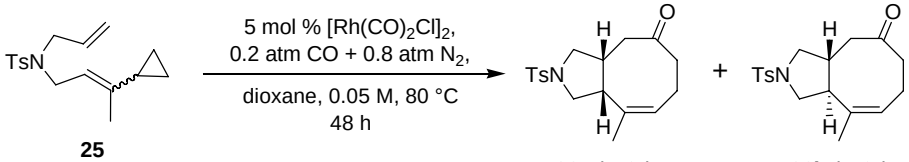
22
(*E* / *Z* = 3 : 1)

23a (16%) **23b** (50%)



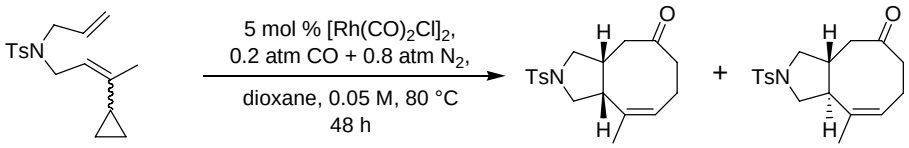
24
(*E* / *Z* = 1 : 3)

23a (52%) **23b** (17%)



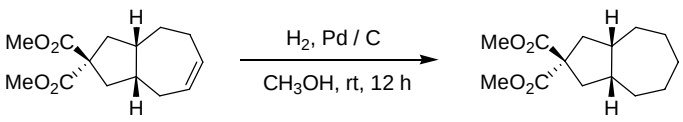
25
(*E* / *Z* = 3 : 1)

26a (15%) **26b** (44%)



27
(*E* / *Z* = 1 : 3)

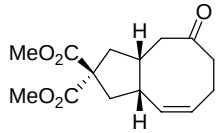
26a (31%) **26b** (10%)



3 **29** (quant.)

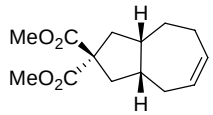
6. Physical Data for Cycloadducts

Dimethyl *cis*-3-oxobicyclo[6.3.0]undec-6-en-10,10-dicarboxylate (2)



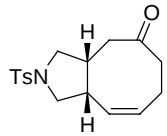
^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.92 (dddd, J = 9.4, 9.4, 8.1, and 1.8 Hz, 1H), 5.46 (ddd, J = 10.3, 9.4, and 1.8 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.83 (t, J = 7.5 Hz, 1H), 2.62-2.16 (m, 10H), 1.77 (t, J = 12.9 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 213.0, 172.9, 172.8, 132.8, 129.6, 59.0, 52.9, 46.5, 43.2, 40.5, 39.7, 39.1, 23.6. The spectroscopic data was identical to that reported in literature.[4]

Dimethyl *cis*-bicyclo[5.3.0]dec-3-en-9,9-dicarboxylate (3)



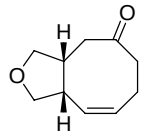
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.56-5.54 (m, 2H), 3.73 (s, 3H), 3.71(s, 3H), 2.58-2.46 (m, 2H), 2.43 (dd, J = 12.6 and 7.1 Hz, 1H), 2.35-2.22 (m, 3H), 2.05-2.16 (m, 1H), 1.92-1.63 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.8, 172.7, 130.9, 127.8, 60.0, 52.57, 52.52, 41.8, 41.5, 41.3, 40.9, 30.1, 29.3, 28.5. IR (FT-IR): ν = 2916 (w), 2849 (w), 1733 (s), 1435 (w), 1251 (m), 1200 (m), 1157 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 252 (21), 220 (28), 192 (60), 160 (27), 133 (73), 105 (100), 91 (61). HRMS calcd for $C_{14}H_{20}O_4$: 252.1362. Found: 252.1356.

***Cis*-*N*-*p*-Toluenesulfonyl-3-oxo-10-azabicyclo[6.3.0]-undec-6-ene (5)**



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 6.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.87 (m, 1H), 5.10 (m, 1H), 3.30-3.35 (m, 2H), 3.21 (dd, J = 9.9 Hz, 5.3 Hz, 1H), 2.71 (m, 2H), 2.44 (m, 1H), 2.27-2.38 (m, 2H), 2.37 (s, 3H), 1.97-2.26 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 211.7, 143.6, 133.6, 130.6, 129.7, 129.6, 127.3, 53.3, 51.0, 46.3, 41.1, 38.5, 38.4, 23.5, 21.4. MS (EI, 70 eV): m/z (%) = 319 (M^+, 23), 261 (34), 235 (11), 164 (100), 155 (22), 135 (11), 106 (48), 91 (87). HRMS calcd for $C_{17}H_{21}NO_3S$: 319.1242. Found: 319.1248. The spectroscopic data was identical to that reported in literature.[4]

***Cis*-3-Oxo-10-oxabicyclo[6.3.0]undec-6-ene (7)**

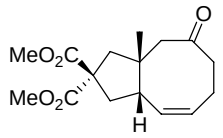


^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.96-5.93 (m, 1H), 5.49-5.44 (m, 1H), 3.91-3.77 (m, 3H), 3.20-3.16 (m, 1H), 2.87-2.82 (m, 1H), 2.52-2.36 (m, 4H), 2.26-2.15 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 212.3, 131.2, 130.2, 74.0, 71.5, 46.3, 40.6, 39.9, 39.8, 23.7. IR (FT-IR): ν = 2925 (m), 2863 (m), 1702 (s),

(4) Wender, P. A.; Correa, A. G.; Sato, Y.; Sun, R. *J. Am. Chem. Soc.* **2000**, *122*, 7815.

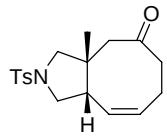
1455 (w), 1344 (w), 1178 (w), 1122 (m), 1078 (w), 1049 (w), 899 (w), 801 (w) cm^{-1}. HRMS calcd for $C_{10}H_{14}O$: 166.0994. Found: 166.0994. The spectroscopic data was identical to that reported in literature.[4]

Dimethyl *cis*-1-methyl-3-oxobicyclo[6.3.0]undec-6-en-10,10-dicarboxylate (9)



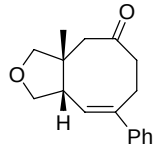
^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.92-5.83 (m, 1H), 5.60-5.54 (t, J = 9 Hz, 1Hz), 3.75 (s, 6H), 2.83 (dd, J = 7.2 and 14.4 Hz, 1H), 2.74 (d, J = 11.1 Hz, 1H), 2.57 (t, J = 7.5 Hz, 1H), 2.50-2.14 (m, 6H), 2.12 (d, J = 13.8 Hz, 1H), 2.08 (d, J = 11.4 Hz, 1H), 1.05 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 211.6, 173.0, 169.6, 133.8, 129.5, 58.7, 53.1, 53.0, 50.3, 47.0, 46.2, 45.9, 45.2, 38.8, 24.2, 23.2. MS (EI, 70 eV): m/z (%) = 294 (38), 276 (16), 263 (34), 248 (20), 234 (96), 212 (25), 202 (66), 177 (63), 154 (66), 145 (43), 133 (42), 122 (100), 105 (58), 91(85). HRMS calcd for $C_{16}H_{22}O_5$: 294.1467. Found: 294.1463. The spectroscopic data was identical to that reported in literature.[4]

***Cis*-*N*-*p*-Toluenesulfonyl-1-methyl-3-oxo-10-azabicyclo[6.3.0]undec-6-ene (11)**



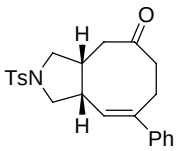
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.92-5.83 (m, 1H), 5.15 (t, J = 9.5Hz, 1H), 3.49 (dd, J = 9.9 and 5.1 Hz, 1H), 3.35 (d, J = 9.9 Hz, 1H), 3.11 (d, J = 9.3 Hz, 1H), 2.93 (d, J = 9.9 Hz, 1H), 2.66 (d, J = 11.7 Hz, 1H), 2.54-2.35 (m, 3H), 2.42 (s, 3H), 2.24-2.16 (m, 2H), 2.00 (d, J = 11.4 Hz, 1H), 0.87 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 210.4, 143.6, 134.1, 131.6, 130.6, 129.7, 127.3, 58.6, 52.7, 47.5, 45.8, 44.7, 42.9, 23.4, 23.2, 21.5. MS (EI, 70 eV): m/z (%) = 333 (33), 275 (43), 262 (8), 249 (13), 236 (9), 178 (60), 155 (18), 134 (22), 120 (92), 91 (92), 42 (100). HRMS calcd for $C_{18}H_{23}NO_3S$: 333.1399. Found: 333.1399. The spectroscopic data was identical to that reported in literature.[4]

***Cis*-1-methyl-3-oxo-6-phenyl-10-oxabicyclo[6.3.0]undec-6-ene (13)**



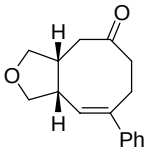
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44-7.29 (m, 5H), 5.92 (d, J = 8.4 Hz, 1H), 4.25 (dd, J = 5.2 and 8.6 Hz, 1H), 3.94 (d, J = 8.6 Hz, 1H), 3.59 (d, J = 7.8 Hz, 1H), 3.45 (d, J = 7.8 Hz, 1H), 2.69-2.74 (m, 1H), 2.63-2.69 (m ,4H), 2.57 (dd, J = 3.2 and 12.8 Hz, 1H), 2.09 (d, J = 12.8 Hz, 1H), 1.25 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 210.2, 141.2, 141.0, 130.3, 128.6, 127.6, 125.8, 79.0, 74.4, 47.9, 46.7, 45.7, 44.3, 26.3, 24.0. IR (FT-IR): ν = 2960 (m), 2925 (m), 2851 (m), 1699 (s), 1458 (m), 1173 (w), 1090 (m), 1065 (m), 1024 (w), 904 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 256 (30), 238 (5), 227 (8), 209 (7), 198 (74), 185 (18), 171 (76), 159 (43), 141 (47), 129 (54), 128 (67), 115 (72), 105 (100), 91 (82). HRMS calcd for $C_{17}H_{20}O_2$: 256.1463. Found: 256.1467.

***Cis*-*N*-*p*-Toluenesulfonyl-3-oxo-6-phenyl-10-azabicyclo[6.3.0]undec-6-ene (15)**



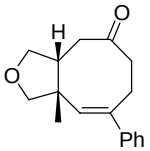
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.27-7.14 (m, 5H), 7.13(d, J = 8.2 Hz, 2H), 5.16 (d, J = 9.1 Hz, 1H), 3.41 (d, J = 10.2 Hz, 2H), 3.31 (dd, J = 5.1 and 10.2 Hz, 1H), 2.77-2.60 (m, 3H), 2.54-2.39 (m, 3H), 2.33 (s, 3H), 2.26-2.17 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 211.2, 143.6, 141.3, 141.0, 133.4, 129.7, 128.4, 127.5, 127.3, 126.0, 125.6, 53.6, 51.2, 46.3, 41.2, 40.2, 39.1, 26.9, 21.4. IR (FT-IR): ν = 2954 (w), 1704 (s), 1343 (s), 1160 (s), 1095 (m), 1064 (m), 912 (m), 816 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 395 (16), 337 (13), 324 (4), 241 (9), 240 (48), 222 (16), 182 (29), 155 (25), 141 (16), 115 (19), 91 (100). HRMS calcd for $C_{23}H_{25}NO_3S$: 395.1555. Found: 395.1552.

***Cis*-3-Oxo-6-phenyl-10-oxabicyclo[6.3.0]undec-6-ene (17)**



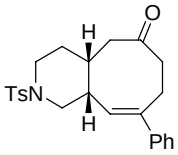
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.30 (m, 5H), 5.88 (d, J = 8.7 Hz, 1H), 4.05-3.92 (m, 3H), 3.34 (dd, J = 8.1 and 10.2 Hz, 1H), 3.02-2.97 (m, 1H), 2.87-2.82 (m, 1H), 2.72-2.55 (m, 4H), 2.46 (t, J = 11.4 Hz, 1H), 2.32 (dd, J = 4.2 and 11.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 211.7, 141.6, 141.1, 128.6, 128.1, 127.5, 125.8, 74.2, 71.7, 46.3, 41.7, 40.9, 40.6, 27.2. IR (FT-IR): ν = 2961 (m), 2969 (m), 2867 (m), 1702 (s), 1494 (w), 1444 (w), 1122 (m), 1078 (m), 1051 (m), 904 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 242 (68), 224 (7), 195 (8), 184 (44), 172 (53), 155 (100), 141 (60), 129 (68), 128 (86), 115 (89). HRMS calcd for $C_{16}H_{18}O_2$: 242.1307. Found: 242.1308.

***Cis*-8-Methyl-3-oxo-10-oxabicyclo[6.3.0]undec-6-ene (19)**



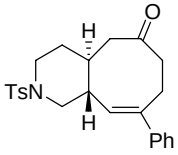
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.33-7.23 (m, 5H), 5.72 (s, 1H), 4.27 (dd, J = 9.6 and 13.2 Hz, 1H), 3.80 (d, J = 12.3 Hz, 1H), 3.69 (d, J = 12.3 Hz, 1H), 3.64 (dd, J = 5.7 and 13.2 Hz, 1H), 2.92-2.38 (m, 7H), 1.39 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 210.0, 142.1, 141.1, 130.4, 128.4, 127.5, 126.1, 79.6, 74.5, 46.8, 45.8, 44.8, 42.6, 25.5, 24.2. IR (FT-IR): ν = 2953 (m), 2924 (m), 2850 (m), 1701 (s), 1458 (w), 1070 (w), 1059 (w), 1034 (w), 1009 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 256 (40), 238 (5), 226 (4), 199 (16), 183 (21), 169 (100), 159 (86), 141 (40), 128 (42), 115 (44), 91 (62). HRMS calcd for $C_{17}H_{20}O_2$: 256.1463. Found: 256.1463. This structure was confirmed by X-ray crystallographic analysis.

Cis-_N_-_p_-Toluenesulfonyl-6-phenyl-3-oxo-10-azabicyclo[6.4.0]dodec-6-ene (21a)



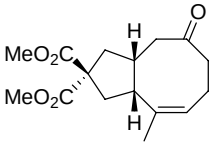
^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.64 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.37-7.26 (m, 5H), 6.23 (d, J = 9.6 Hz, 1H), 3.88-3.85 (m, 1H), 3.76 (dt, J = 11.8 and 2.1 Hz, 1H), 2.81-2.77 (m, 1H), 2.71-2.52 (m, 2H), 2.57-2.52 (m, 2H), 2.44 (s, 3H), 2.42-2.35 (m, 2H), 2.30-2.24 (m, 2H), 1.84-1.79 (m, 1H), 1.60-1.52 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 213.2, 143.6, 142.3, 140.5, 133.1, 129.7, 128.5, 127.6, 127.4, 126.2, 126.1, 50.0, 46.9, 46.6, 46.5, 36.2, 35.5, 28.1, 27.2, 21.5. IR (FT-IR): ν = 2925 (w), 1702 (s), 1597 (w), 1494 (w), 1463 (w), 1340 (m), 1329 (m), 1163 (s), 1093 (m), 940 (m), 916 (m), 819 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 409 (M^+, 32), 291 (10), 254 (100), 236 (14), 155 (28), 141 (16), 128 (17), 91 (92). HRMS calcd for $C_{24}H_{27}NO_3S$: 409.1712. Found: 409.1718.

Trans-_N_-_p_-Toluenesulfonyl-6-phenyl-3-oxo-10-azabicyclo[6.4.0]dodec-6-ene (21b)



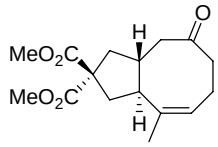
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.32-7.23 (m, 5H), 5.24 (d, J = 7.9 Hz, 1H), 3.86-3.79 (m, 2H), 3.20 (td, J = 13.2 and 4.3 Hz, 1H), 2.69 (tt, J = 10.3 and 3.9 Hz, 2H), 2.63-2.54 (m, 2H), 2.44 (s, 3H), 2.42-2.33 (m, 1H), 2.27 (dd, J = 11.9 and 3.4 Hz, 1H), 2.20 (dd, J = 11.9 and 2.7 Hz, 1H), 2.09-2.04 (m,1H), 2.81-1.73 (m, 1H), 1.66 (qd, J = 12.5 and 4.2 Hz, 1H), 1.60-1.41 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 211.3, 143.6, 142.5, 141.2, 132.9, 129.7, 128.4, 128.0, 127.6, 127.5, 126.1, 51.3, 47.0, 46.3, 46.2, 41.4, 38.0, 32.2, 26.4, 21.5. IR (FT-IR): ν = 2955 (m), 2923 (m), 2874 (m), 1700 (s), 1493 (w), 1466 (w), 1444 (w), 1240 (w), 1068 (s), 1035 (w), 950 (w), 899 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 409 (M^+, 28), 291 (6), 254 (100), 236 (10), 198 (15), 196 (10), 184 (5), 168 (4), 155 (21), 141 (8), 128 (10), 117 (6), 115 (10), 105 (9), 91 (55), 65 (11), 42 (35). HRMS calcd for $C_{24}H_{27}NO_3S$: 409.1712. Found: 409.1720.

Dimethyl _cis_-7-methyl-3-oxobicyclo[6.3.0]undec-6-en-10,10-dicarboxylate (23a)



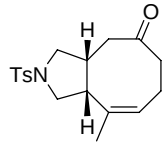
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.68 (t, J = 8.3 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.99 (td, J = 7.6 and 3.1 Hz, 1H), 2.59 (dd, J = 15.1 and 8.4 Hz, 1H), 2.46 (dd, J = 15.1 and 3.6 Hz, 1H), 2.39 (d, J = 8.9 Hz, 1H), 2.38 (d, J = 8.3 Hz, 1H), 2.24-2.34 (m, 3H), 2.06-2.16 (m, 3H), 1.79-1.86 (m, 1H), 1.64 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 213.0, 172.9, 172.3, 136.4, 125.9, 59.2, 53.0, 52.8, 46.1, 43.1, 41.1, 40.8, 40.6, 35.5, 23.8, 23.6. IR (FT-IR): ν = 2955 (m), 1732 (s), 1701 (s), 1435 (m), 1259 (s), 1198 (m), 1160 (m), 1113(m), 1076 (w), 1028 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 294 (12), 276 (100), 248 (30), 234 (65), 216 (90), 202 (76), 177 (82), 159 (30). HRMS calcd for $C_{16}H_{22}O_5$: 294.1467. Found: 294.1465.

Dimethyl *trans*-7-methyl-3-oxobicyclo[6.3.0]undec-6-en-10,10-dicarboxylate (23b)



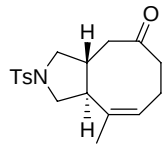
Colorless crystals, m.p. 128 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.49 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.82-2.90 (m, 2H), 2.60-2.70 (m, 2H), 2.53 (dd, J = 13.8 and 8.1 Hz, 1H), 2.29-2.42 (m, 4H), 2.08-2.14 (m, 1H), 2.01 (dd, J = 13.8 and 10.3 Hz, 1H), 1.86 (m, 1H), 1.66 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 211.7, 172.9, 172.5, 137.4, 126.1, 57.9, 52.80, 52.77, 47.7, 46.0, 45.4, 40.5, 40.1, 37.5, 21.8, 20.8. IR (FT-IR): ν = 2957 (w), 2920 (s), 2850 (m), 1730 (s), 1702 (w), 1461 (w), 1432 (w), 1377 (w), 1257 (m), 1173 (w), 1097 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 294 (M^+, 21), 276 (100), 263 (24), 248 (24), 235 (23), 234 (70), 217 (36), 216 (88), 206 (25), 203 (39), 202 (54), 191 (22), 188 (24), 177 (78), 176 (25) 175 (56), 157 (29), 147 (30), 145 (50), 133 (36), 131 (34). HRMS calcd for $C_{16}H_{22}O_5$: 294.1467. Found: 294.1468. This structure was confirmed by X-ray crystallographic analysis.

***Cis*-*N*-*p*-Toluenesulfonyl-7-methyl-3-oxo-10-azabicyclo[6.3.0]undec-6-ene (26a)**



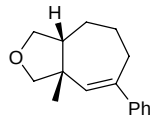
Colorless crystals, m.p. 157 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 5.79 (t, J = 8.3 Hz, 1H), 3.67 (d, J = 10.1 Hz, 1H), 3.49 (dd, J = 10.2 and 8.2 Hz, 1H), 3.20 (dd, J = 10.1 and 6.1Hz, 1H), 2.95 (t, J = 6.4 Hz, 1H), 2.83 (t, J = 10.8 Hz, 1H), 2.40-2.49 (m, 2H), 2.44 (s, 3H), 2.33 (t, J = 11.4 Hz, 1H), 2.23 (m, 1H), 1.96-2.14 (m, 3H), 1.75 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 212.2, 143.6, 134.8, 134.0, 129.8, 127.3, 126.6, 51.5, 50.3, 46.6, 40.8, 40.7, 39.1, 23.8, 21.5, 21.4. IR (FT-IR): ν = 2923 (m), 2853 (w), 1703 (s), 1454 (w), 1343 (s), 1132 (s), 1200 (w), 1162 (s), 1091 (w), 1065 (w), 815 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 333 (28), 275 (18), 262 (5), 249 (6), 222 (7), 178 (66), 160 (8), 155 (19), 120 (46), 134 (6), 91 (100). HRMS calcd for $C_{18}H_{23}NO_3S$: 333.1399. Found: 333.1392. This structure was confirmed by X-ray crystallographic analysis.

***Trans*-*N*-*p*-Toluenesulfonyl-7-methyl-3-oxo-10-azabicyclo[6.3.0]undec-6-ene (26b)**



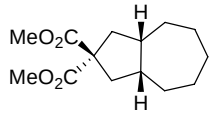
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.48 (m, 1H), 3.56-3.51 (m, 2H), 3.25 (t, J = 10.4 Hz, 1H), 2.96 (t, J = 10.2 Hz, 1H), 2.93 (m, 1H), 2.76 (m, 1H), 2.61 (m, 1H), 2.59 (t, J = 11.4 Hz, 1H), 2.46 (s, 3H), 2.34 (td, J = 13.0 and 4.8 Hz, 1H), 2.26 (dd, J = 11.4 and 3.1 Hz, 1H), 2.12 (m, 1H), 1.82 (m, 1H), 1.54 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 210.4, 143.7, 134.7, 133.7, 129.8, 127.49, 127.47, 52.7, 50.5, 47.5, 45.4, 42.9, 39.6, 21.8, 21.5, 20.9. IR (FT-IR): ν = 2923 (m), 2853 (w), 1703 (s), 1454 (w), 1343 (s), 1132 (s), 1200 (w), 1162 (s), 1091 (w), 1065 (w), 815 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 333 (28), 275 (18), 262 (5), 249 (6), 222 (7), 178 (66), 160 (8), 155 (19), 120 (46), 134 (6), 91 (100). HRMS calcd for $C_{18}H_{23}NO_3S$: 333.1399. Found: 333.1392.

Cis-1-Methyl-3-phenyl-9-oxabicyclo[5.3.0]dec-2-ene (28)



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37-7.20 (m, 5H), 5.61 (s, 1H), 4.30 (t, J = 8.2 Hz, 1H), 3.60 (d, J = 8.4 Hz, 1H), 3.54 (d, J = 8.2 Hz, 1H), 3.40 (dd, J = 5.7 and 8.7 Hz, 1H), 2.74-2.66 (m, 1H), 2.02 (dt, J = 14.1 and 3.6 Hz, 1H), 2.05-1.99 (m, 1H), 1.81-1.62 (m, 3H), 1.50-1.30 (m, 1H), 1.23 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.7, 137.4, 129.9, 128.2, 126.7, 125.7, 79.0, 76.1, 47.6, 44.9, 28.8, 28.4, 25.4, 24.3. IR (FT-IR): ν = 2925 (w), 2856 (w), 1724 (w), 1493 (w), 1448 (w), 1069 (m), 928 (w), 759 (s), 699 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 228 (24), 193 (9), 169 (27), 155 (12), 141 (9), 129 (10), 128 (9), 115 (10), 105 (6), 91 (20), 86 (19), 84 (30), 77 (8), 58 (98), 43 (100). HRMS calcd for $C_{16}H_{20}O$: 228.1514. Found: 228.1517.

Dimethyl _cis_-bicyclo[5.3.0]decane-9,9-dicarboxylate (29)



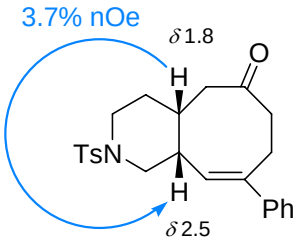
^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 3H), 3.69 (s, 3H), 2.51-2.45 (m, 2H), 2.26-2.21 (m, 2H), 1.82-1.62 (m, 7H), 1.36-1.14 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.8, 172.7, 60.3, 52.43, 52.35, 42.2, 41.8, 32.1, 31.4, 29.1. MS (EI, 70 eV): m/z (%) = 254 (0.5), 223 (11), 194 (10), 163 (8), 145 (100), 135 (50), 113 (68). The spectroscopic data was identical to that reported in literature.[5]

Stereochemical Determination

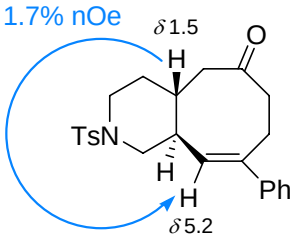
Compounds **2**, **5**, **7**, **9**, and **11** are identical to published structures.[4] The structures of **19**, **23b**, and **26a** were determined by X-ray crystallographic analysis. The stereochemistry of compounds **13**, **15**, and **17** was assigned by analogy to compounds **5**, **7**, and **19**. Compound **23a** was a diastereomer of **23b**, which has been confirmed to possess a trans ring fusion, therefore, compound **23a** must be a *cis*-fused [5+2+1] cycloadduct. Compound **26b** was a diastereomer of **26a**, which has been confirmed to possess a cis ring fusion, therefore, compound **26b** must be a *trans*-fused [5+2+1] cycloadduct. The assignment of cis configuration of **3** was based on its hydrogenation product **29**, which has a cis configuration with planar symmetry judged by its ^{1}H and ^{13}C NMR spectra.[5,6] The cis configuration of **28** is based on the geometry of *cis*- [5+2+1] cycloadduct **19**. Compounds **28** and **19** are expected to be generated from the same intermediate that can undergo both [5+2] and [5+2+1] reactions. The stereochemistry of cycloadduct **21** was determined by nOe experiments (Figure S4).

(5) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348.
(6) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940.

Figure S4. Stereochemical Determination of Cycloadduct *cis*-**21a** and *trans*-**21b**



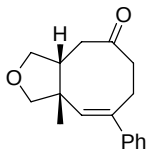
21a



21b

7. X-Ray Structure for Cycloadducts 19, 23b, and 26a

Figure S5. Chemical Structure and ORTEP Figure of Cycloadduct **19**



CCDC 641318

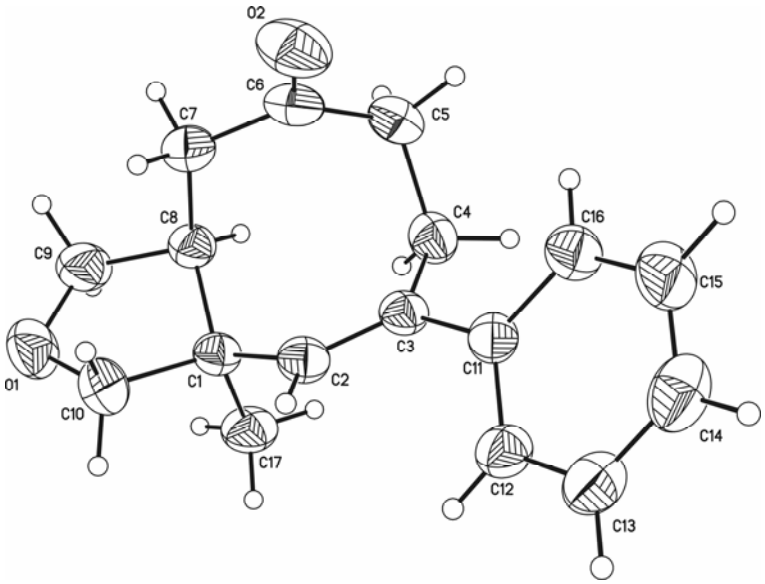
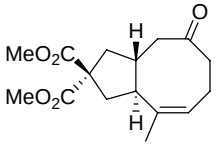


Figure S6. Chemical Structure and ORTEP Figure of Cycloadduct **23b**



CCDC 639277

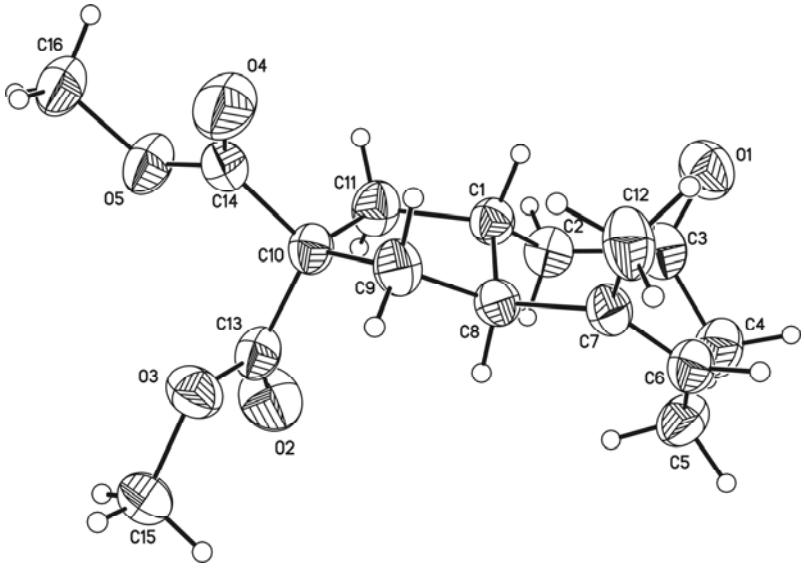
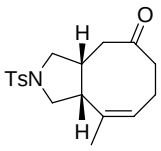
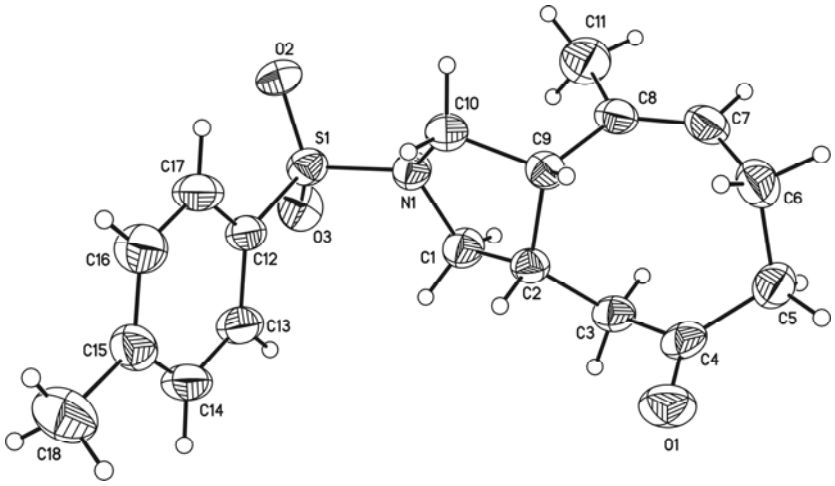


Figure S7. Chemical Structure and ORTEP Figure of Cycloadduct **26a**

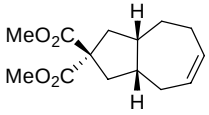


CCDC 639278

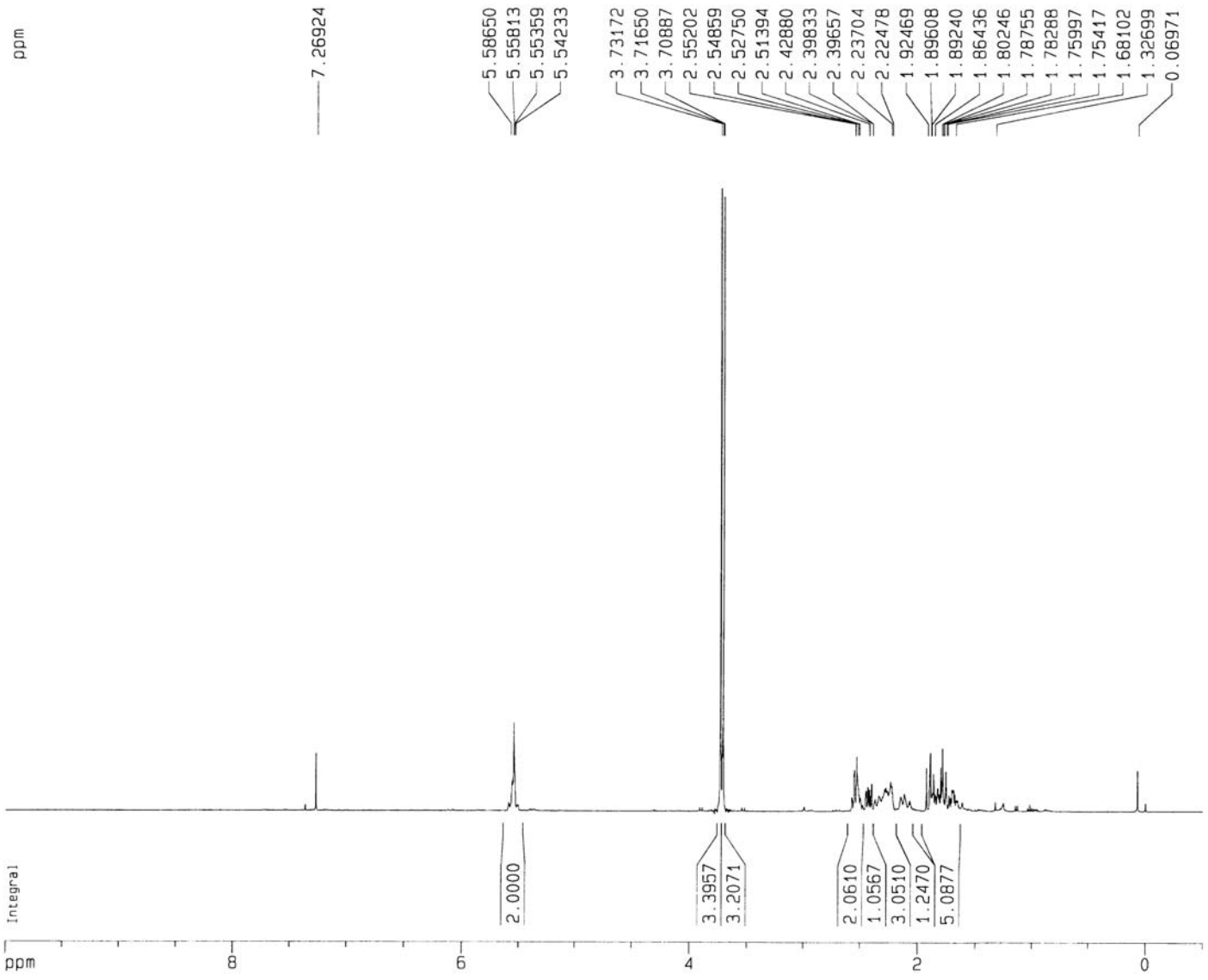


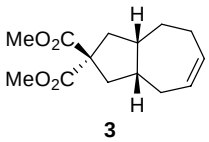
CCDC 641318, 639277, and 639278 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

8. ^{1}H and ^{13}C-NMR Spectra for New Compounds



3





3

ppm

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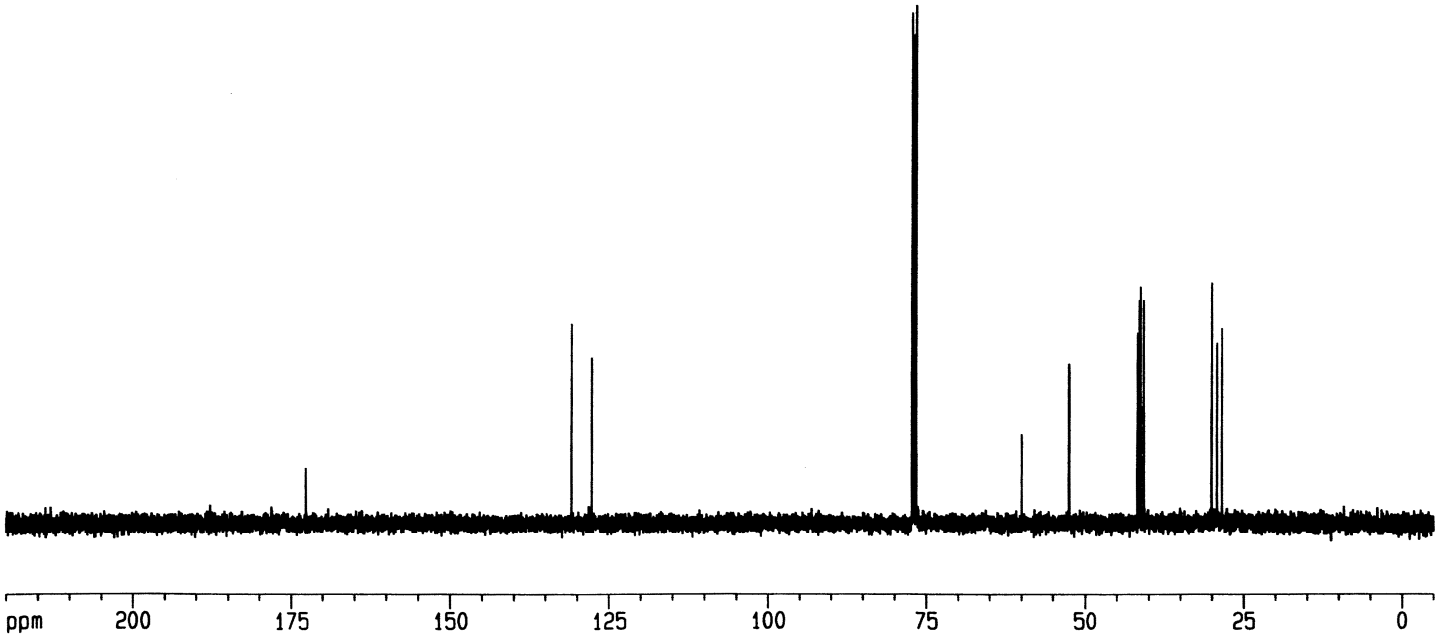
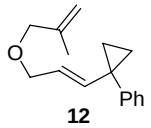
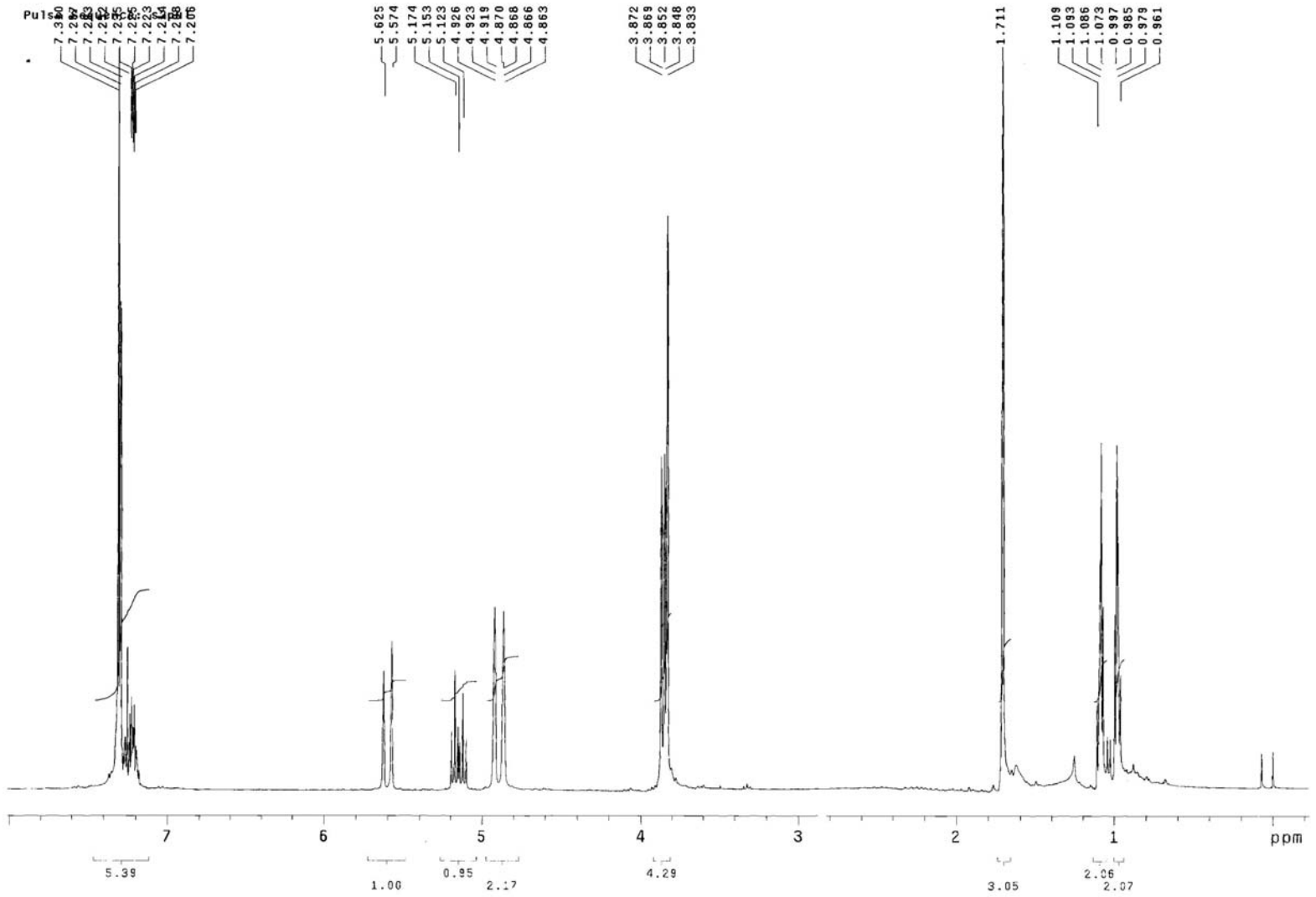
127.750
77.278
76.960
76.644
60.008
52.574
52.515
41.778
41.468
41.334
40.872
30.111
29.250
28.495




O
Ph

12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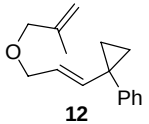
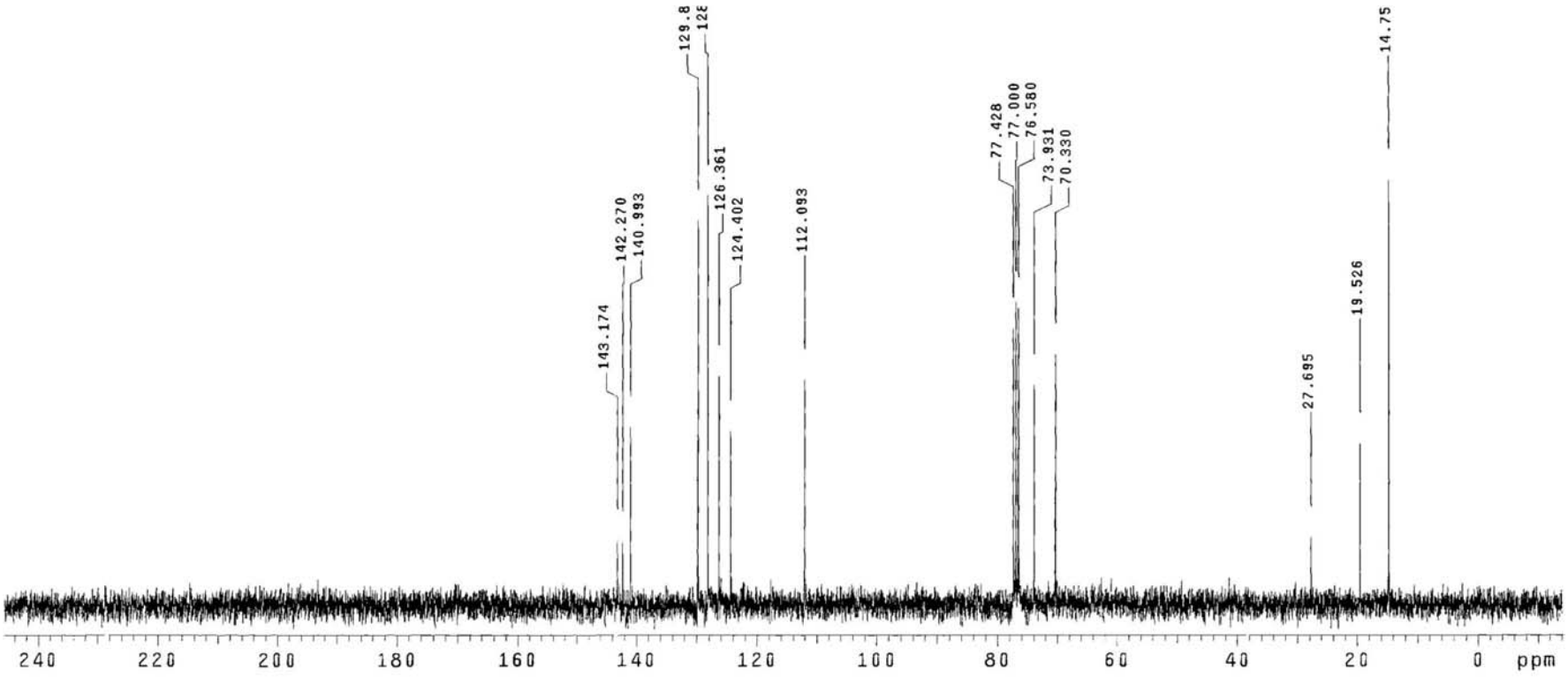
5.174
5.153
5.123
4.926
4.923
4.918
4.870
4.868
4.866
4.863
3.872
3.869
3.852
3.848
3.833
1.711
1.109
1.093
1.086
1.073
0.997
0.985
0.979
0.961
7
6
5
4
3
2
1
ppm
5.39
1.00
0.95
2.17
4.29
3.05
2.06
2.07


O
Ph

12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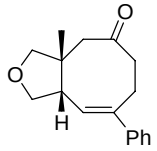
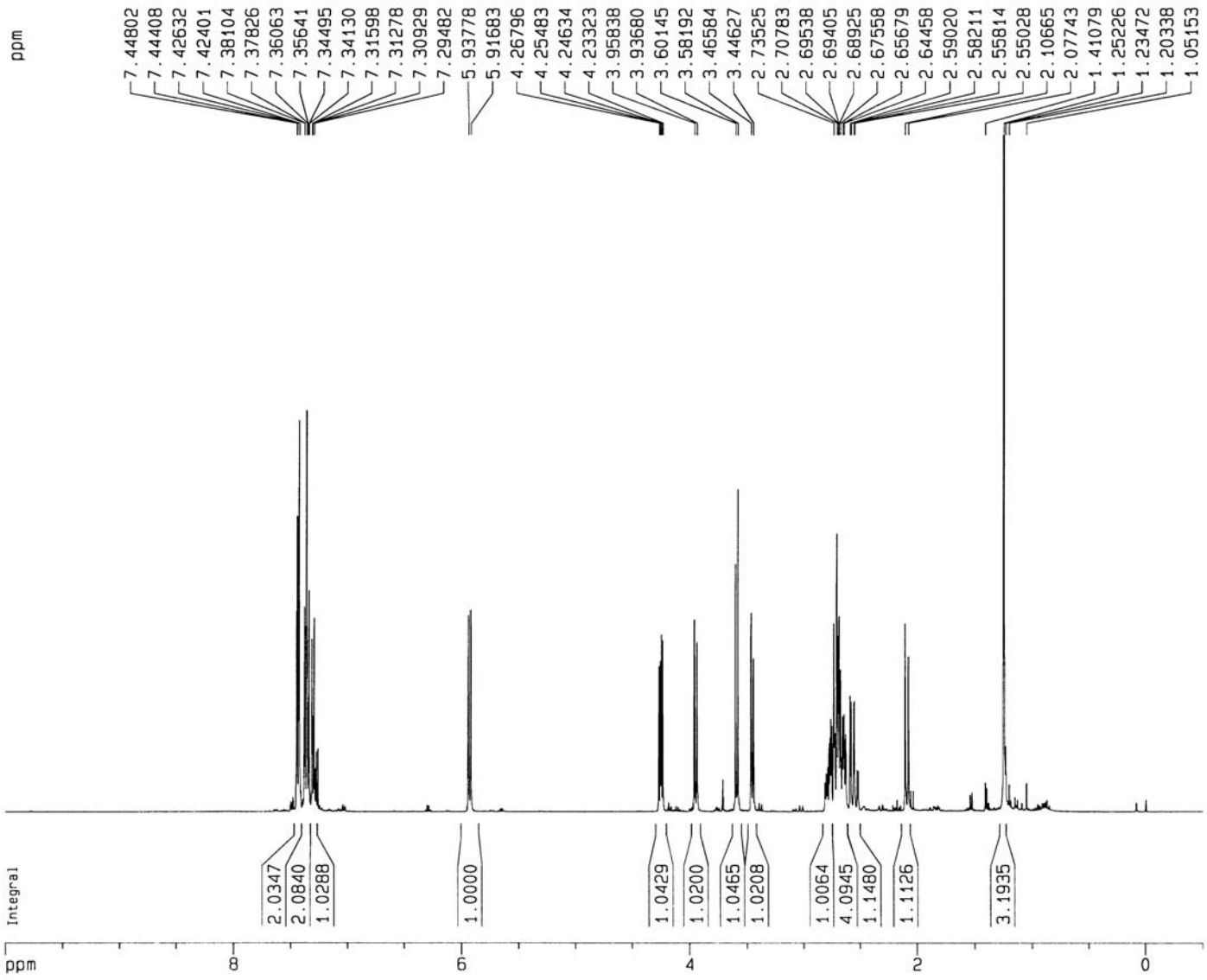
128
126.361
124.402
112.093
77.428
77.000
76.580
73.931
70.330
14.75
143.174
142.270
140.993
27.695
19.526
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
H
Ph

13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7.42401
7.38104
7.37826
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7.35641
7.34495
7.34130
7.31598
7.31278
7.30929
7.29482
5.93778
5.91683
4.26796
4.25483
4.24634
4.23323
3.95838
3.93680
3.60145
3.58192
3.46584
3.44627
2.73525
2.70783
2.69538
2.69405
2.68925
2.67558
2.65679
2.64458
2.59020
2.58211
2.55814
2.55028
2.10665
2.07743
1.41079
1.25226
1.23472
1.20338
1.05153
Integral
2.0347
2.0840
1.0288
1.0000
1.0429
1.0200
1.0465
1.0208
1.0064
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1.1480
1.1126
3.1935
ppm
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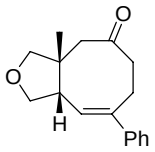
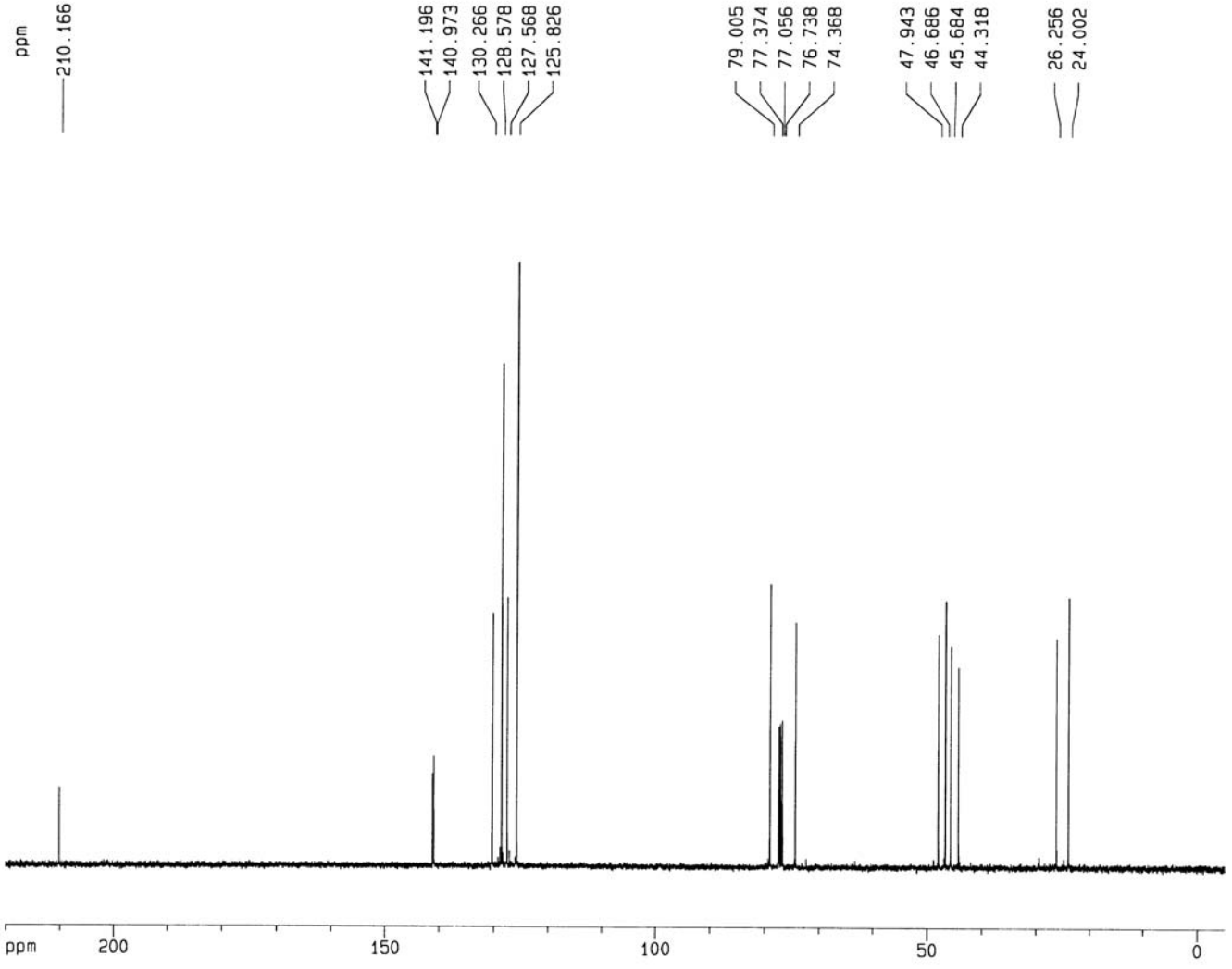
6
4
2
0


O
O
H
Ph

13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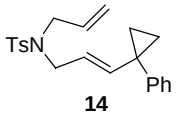
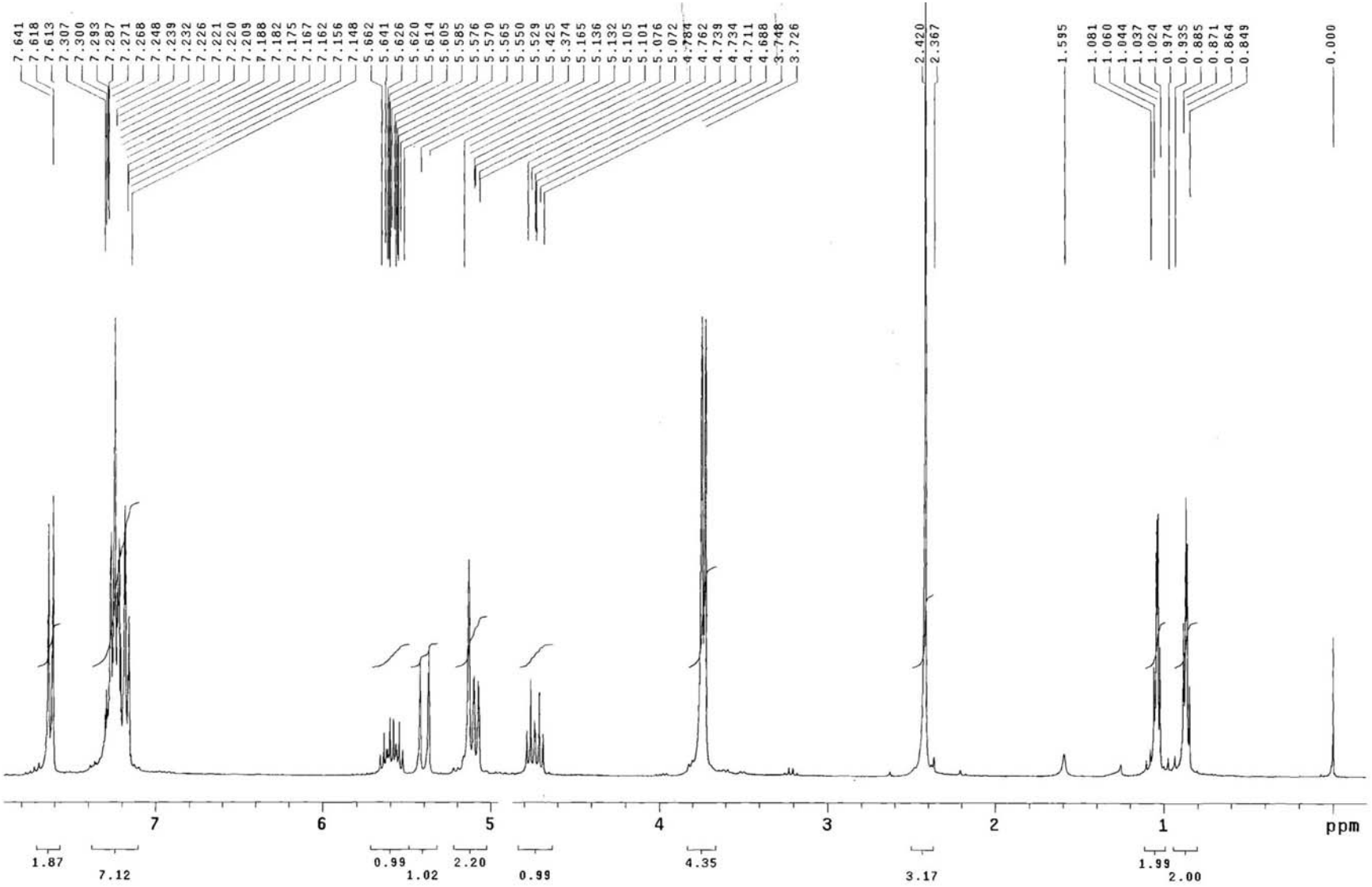
128.578
127.568
125.826
79.005
77.374
77.056
76.738
74.368
47.943
46.686
45.684
44.318
26.256
24.002
ppm
200
150
100
50
0


TsN
Ph

14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7.293
7.287
7.271
7.268
7.248
7.239
7.232
7.226
7.221
7.220
7.209
7.188
7.182
7.175
7.167
7.162
7.156
7.148
5.662
5.641
5.626
5.620
5.614
5.605
5.585
5.576
5.570
5.565
5.550
5.529
5.425
5.374
5.165
5.136
5.132
5.105
5.101
5.076
5.072
4.784
4.762
4.739
4.734
4.711
4.688
3.748
3.726
2.420
2.367
1.595
1.081
1.060
1.044
1.037
1.024
0.974
0.935
0.885
0.871
0.864
0.849
0.000
7
6
5
4
3
2
1
ppm
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7.12
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1.02
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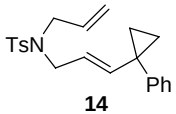
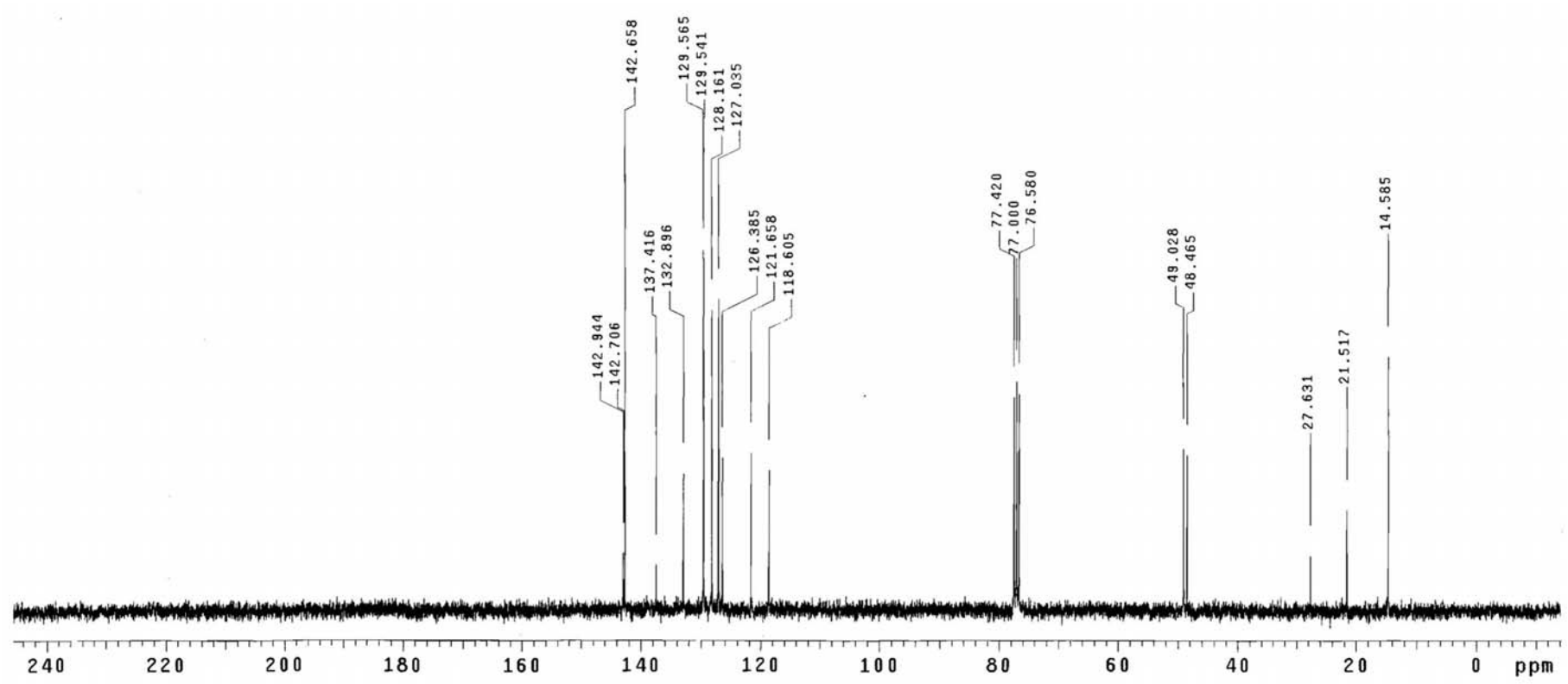
0.99
4.35
3.17
1.99
2.00


TsN
Ph

14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129.541
128.161
127.035
137.416
132.896
126.385
121.658
118.605
142.944
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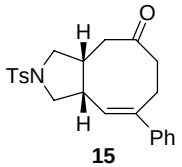
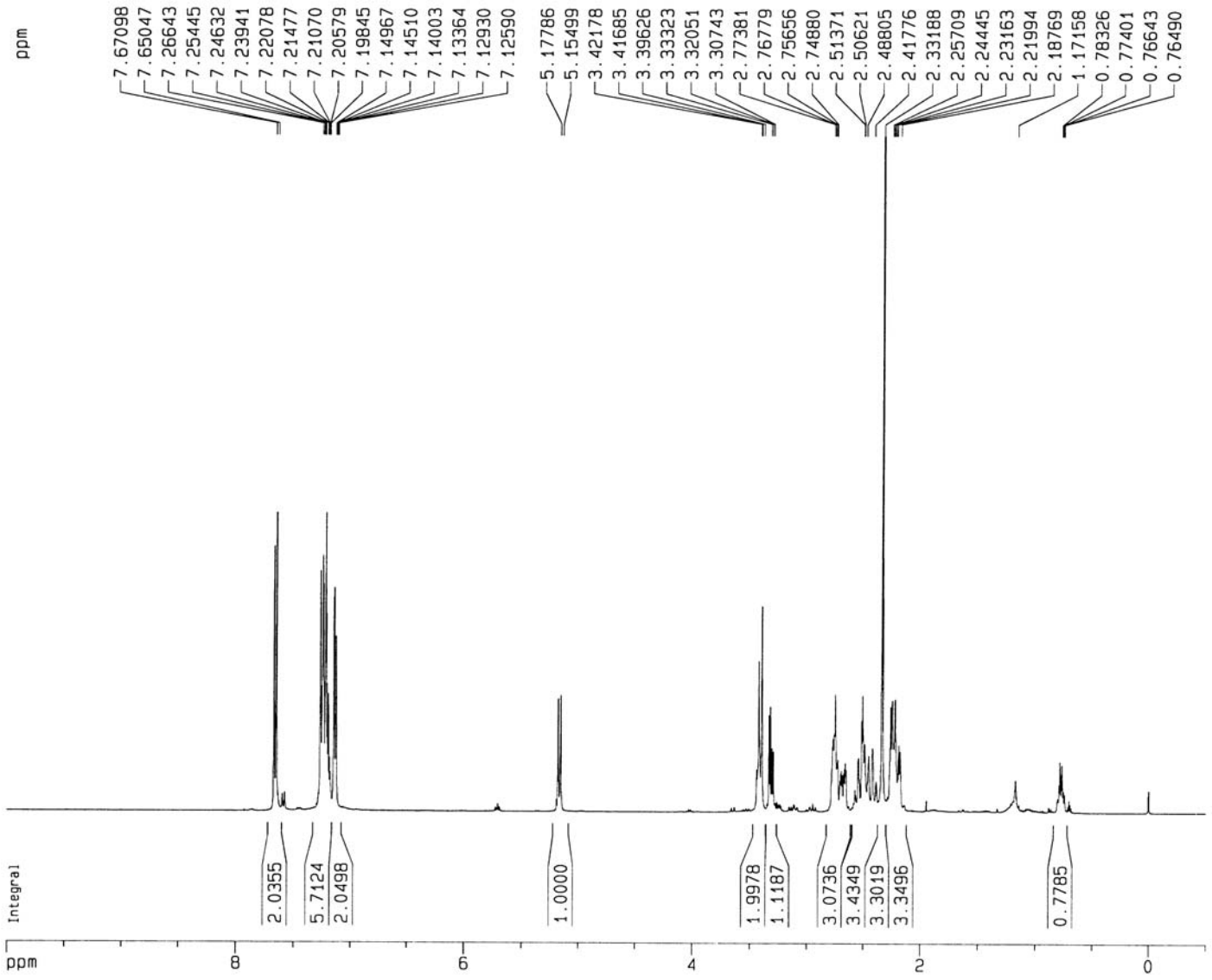
77.420
77.000
76.580
49.028
48.465
27.631
21.517
14.585
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
H
TsN
H
Ph

15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7.25445
7.24632
7.23941
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7.19845
7.14967
7.14510
7.14003
7.13364
7.12930
7.12590
5.17786
5.15499
3.42178
3.41685
3.39626
3.33323
3.32051
3.30743
2.77381
2.76779
2.75656
2.74880
2.51371
2.50621
2.48805
2.41776
2.33188
2.25709
2.24445
2.23163
2.21994
2.18769
1.17158
0.78326
0.77401
0.76643
0.76490
Integral
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5.7124
2.0498
1.0000
1.9978
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3.0736
3.4349
3.3019
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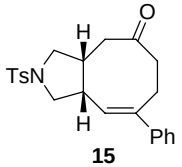
4
2
0



15

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129.700
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127.258
125.985
125.590
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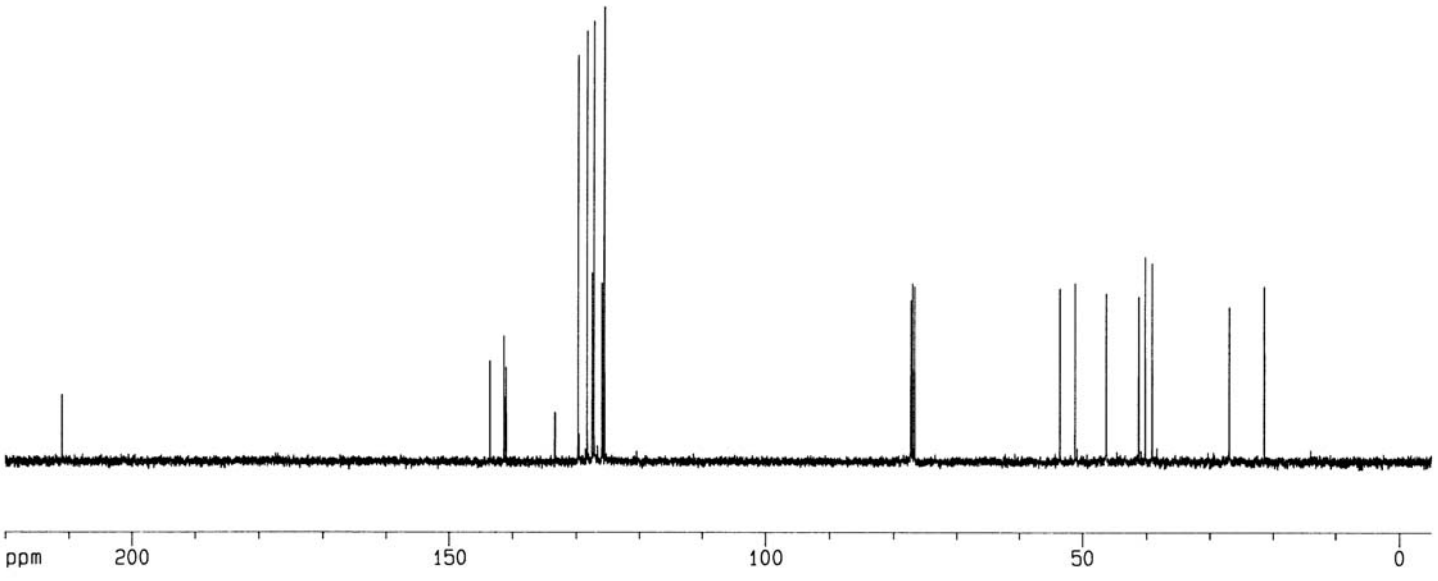
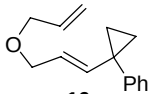
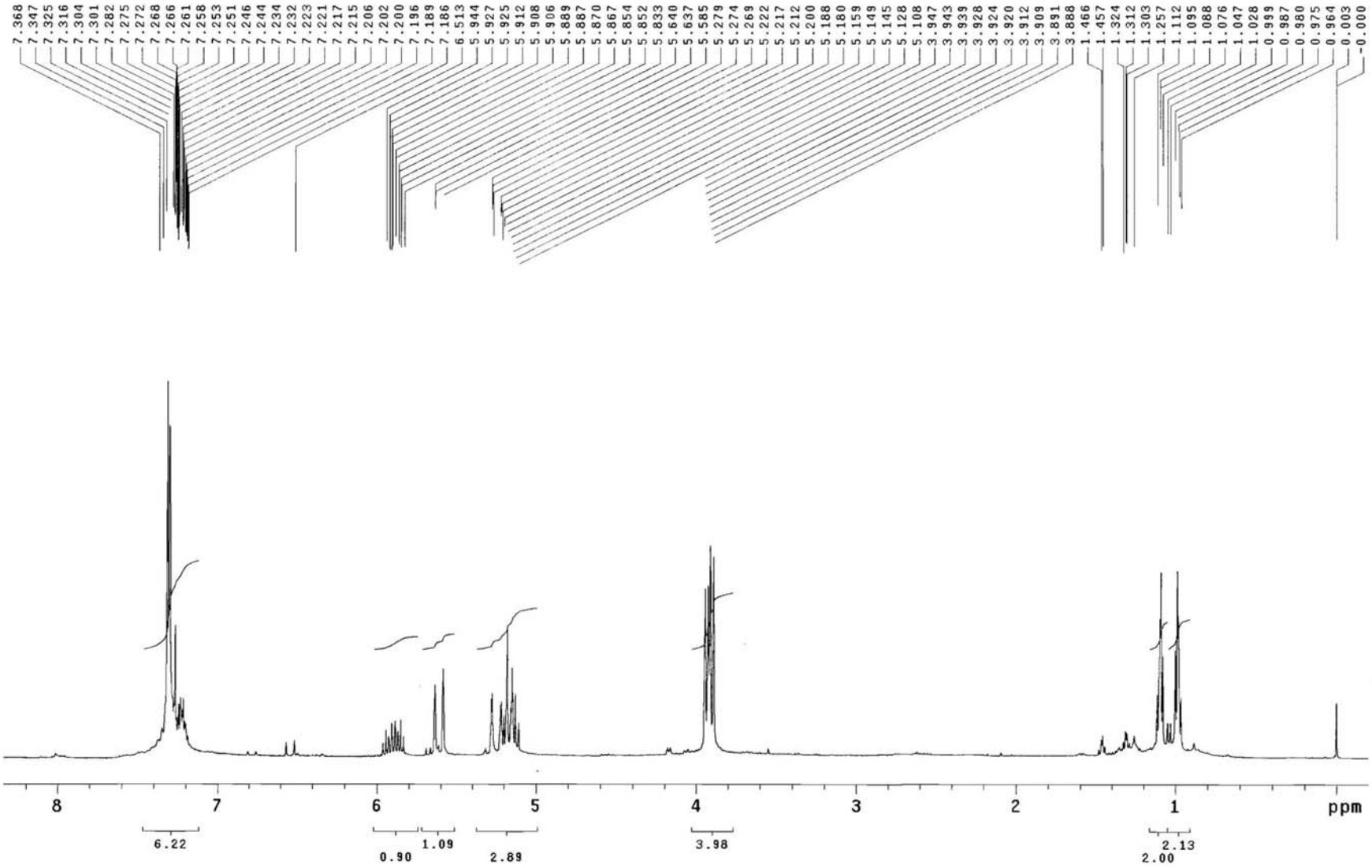
76.680
53.562
51.176
46.315
41.231
40.191
39.094
26.949
21.417




O
Ph

16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7.301
7.282
7.275
7.272
7.268
7.266
7.261
7.258
7.253
7.251
7.246
7.244
7.234
7.232
7.223
7.221
7.217
7.215
7.206
7.202
7.200
7.196
7.189
7.186
6.513
5.944
5.927
5.925
5.912
5.908
5.906
5.889
5.887
5.870
5.867
5.854
5.852
5.833
5.640
5.637
5.585
5.279
5.274
5.269
5.222
5.217
5.212
5.200
5.188
5.180
5.159
5.149
5.145
5.128
5.108
3.947
3.943
3.939
3.928
3.924
3.920
3.912
3.909
3.891
3.888
1.466
1.457
1.324
1.312
1.303
1.257
1.112
1.095
1.088
1.076
1.047
1.028
0.999
0.987
0.980
0.975
0.964
0.003
-0.000
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7
6
5
4
3
2
1
ppm
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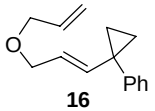
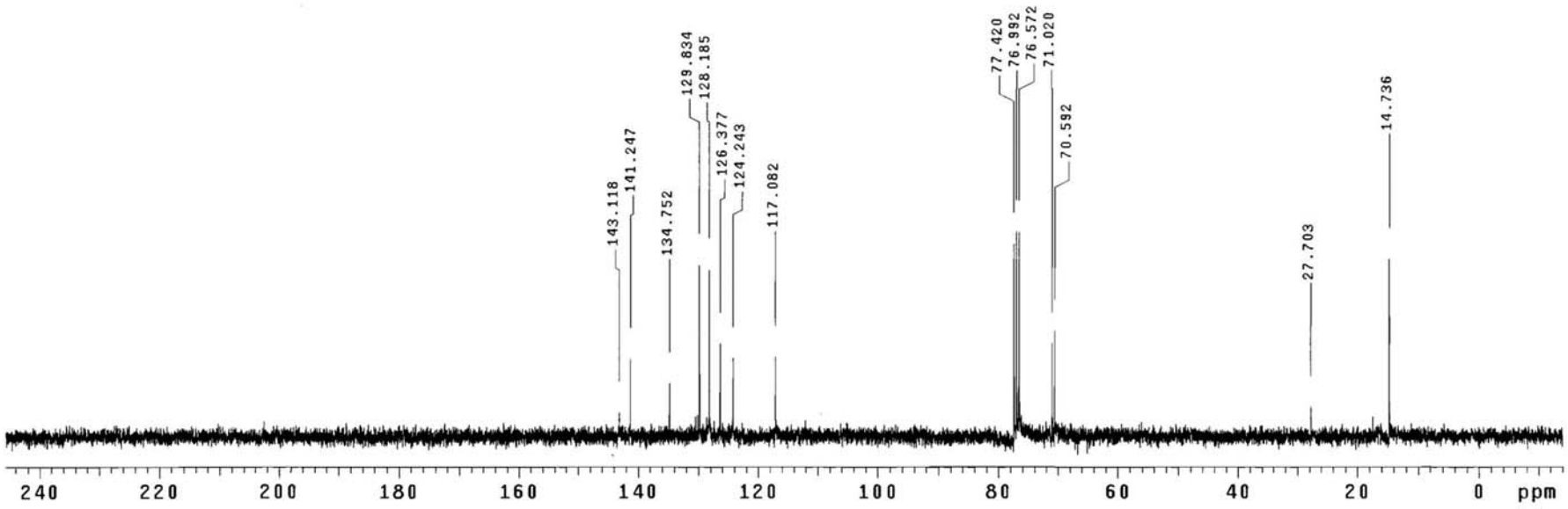
0.90
1.09
2.89
3.98
2.00
2.13


O
Ph

16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128.185
126.377
124.243
117.082
77.420
76.992
76.572
71.020
70.592
27.703
14.736
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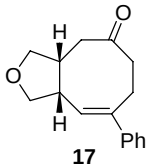
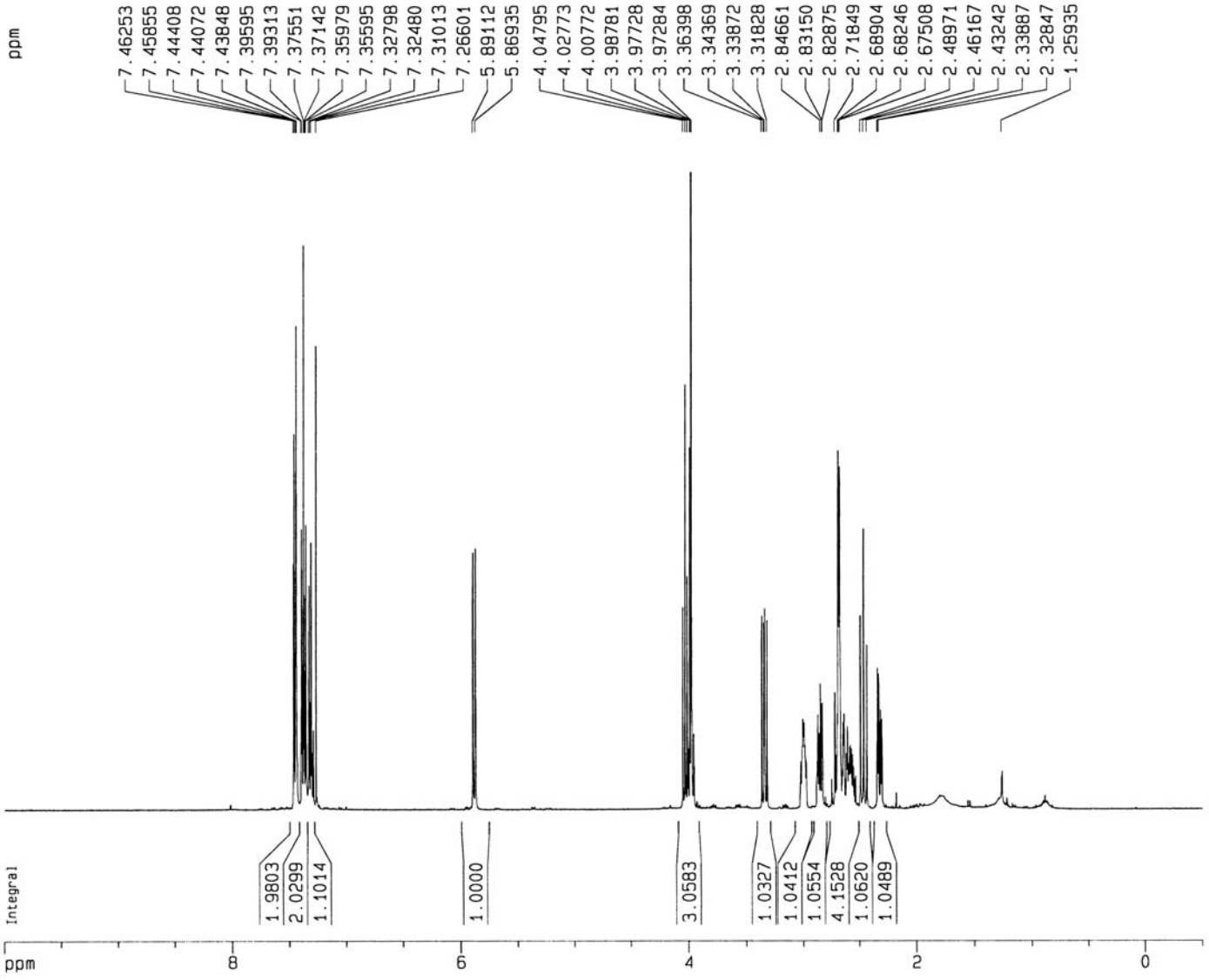
220
200
180
160
140
120
100
80
60
40
20
0
ppm


H
O
O
H
Ph

17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7.32798
7.32480
7.31013
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4.00772
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3.33872
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2.71849
2.68904
2.68246
2.67508
2.48971
2.46167
2.43242
2.33887
2.32847
1.25935
Integral
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1.1014
1.0000
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1.0412
1.0554
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1.0489
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6
4
2
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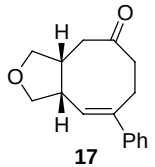
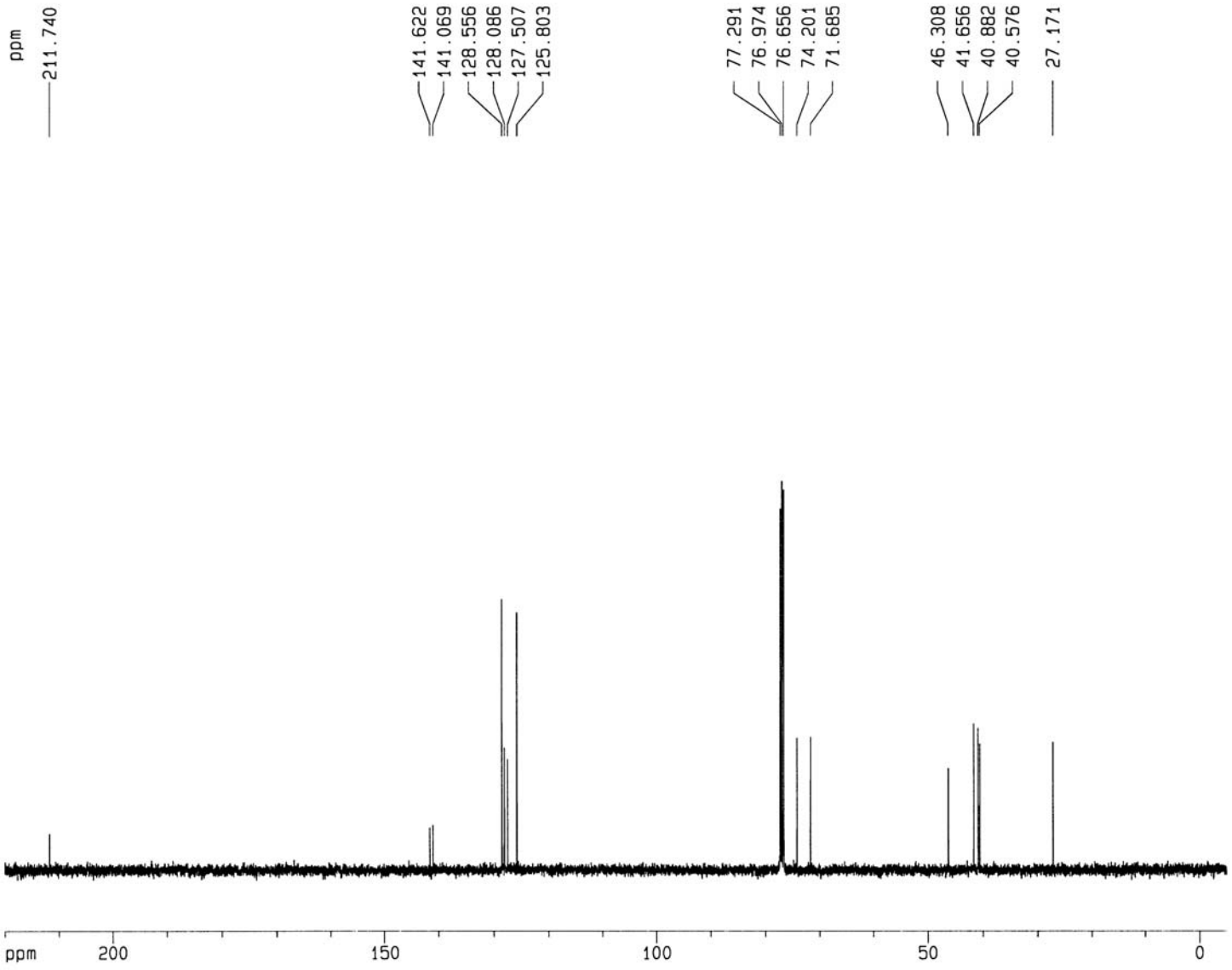

H
O
O
H
Ph

17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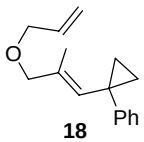
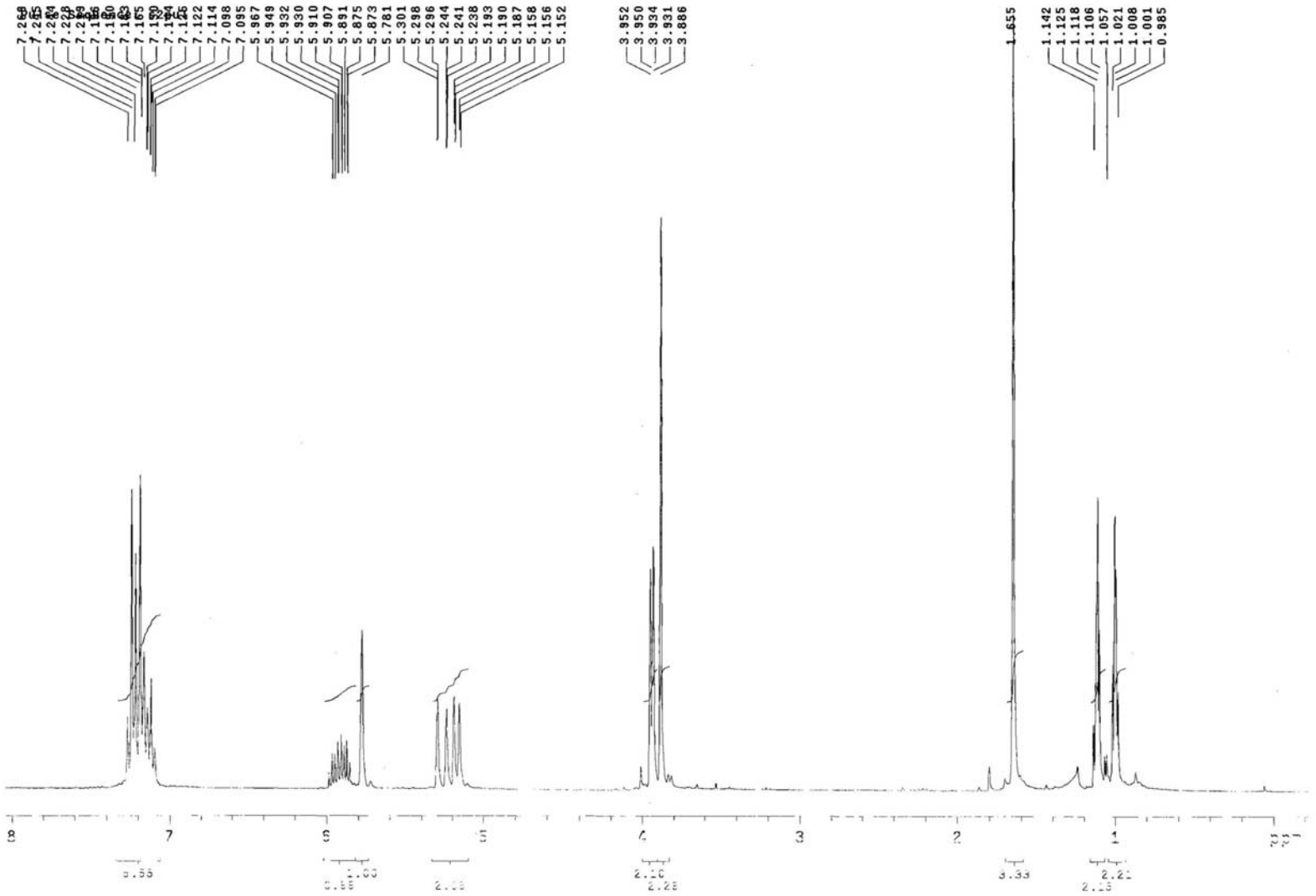
40.576
27.171
ppm
200
150
100
50
0


O
Ph

18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7.261
7.256
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7.226
7.221
7.216
7.211
7.206
7.201
7.196
7.191
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7.181
7.176
7.171
7.166
7.161
7.156
7.151
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7.106
7.101
7.096
7.091
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5.949
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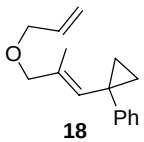
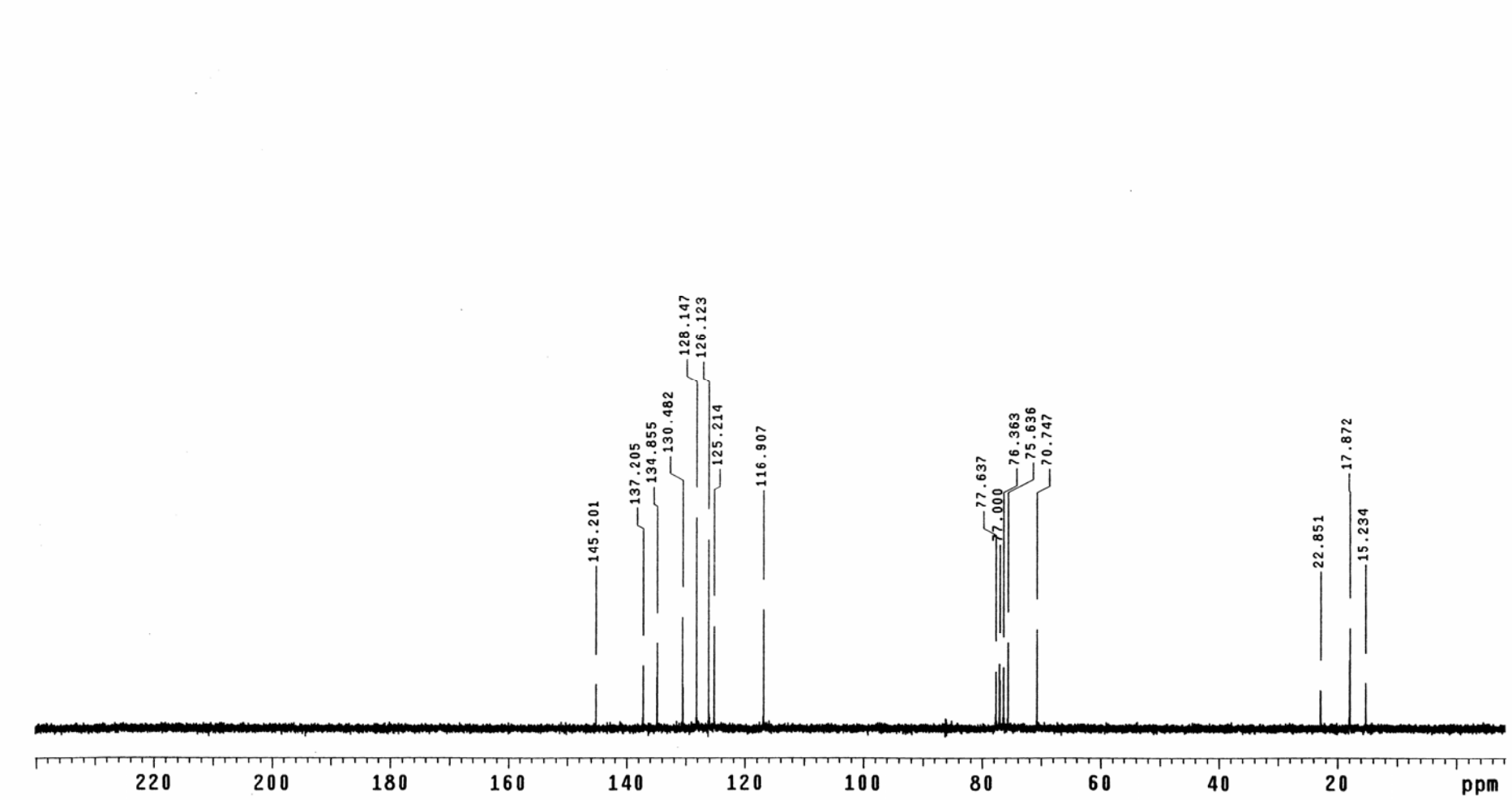
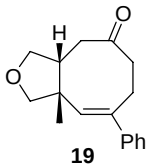
5.907
5.881
5.875
5.873
5.781
5.301
5.298
5.296
5.244
5.241
5.238
5.193
5.190
5.187
5.158
5.156
5.152
3.952
3.950
3.934
3.931
3.886
1.655
1.142
1.125
1.118
1.106
1.057
1.021
1.008
1.001
0.985
8
7
6
5
4
3
2
1
3.33
2.21

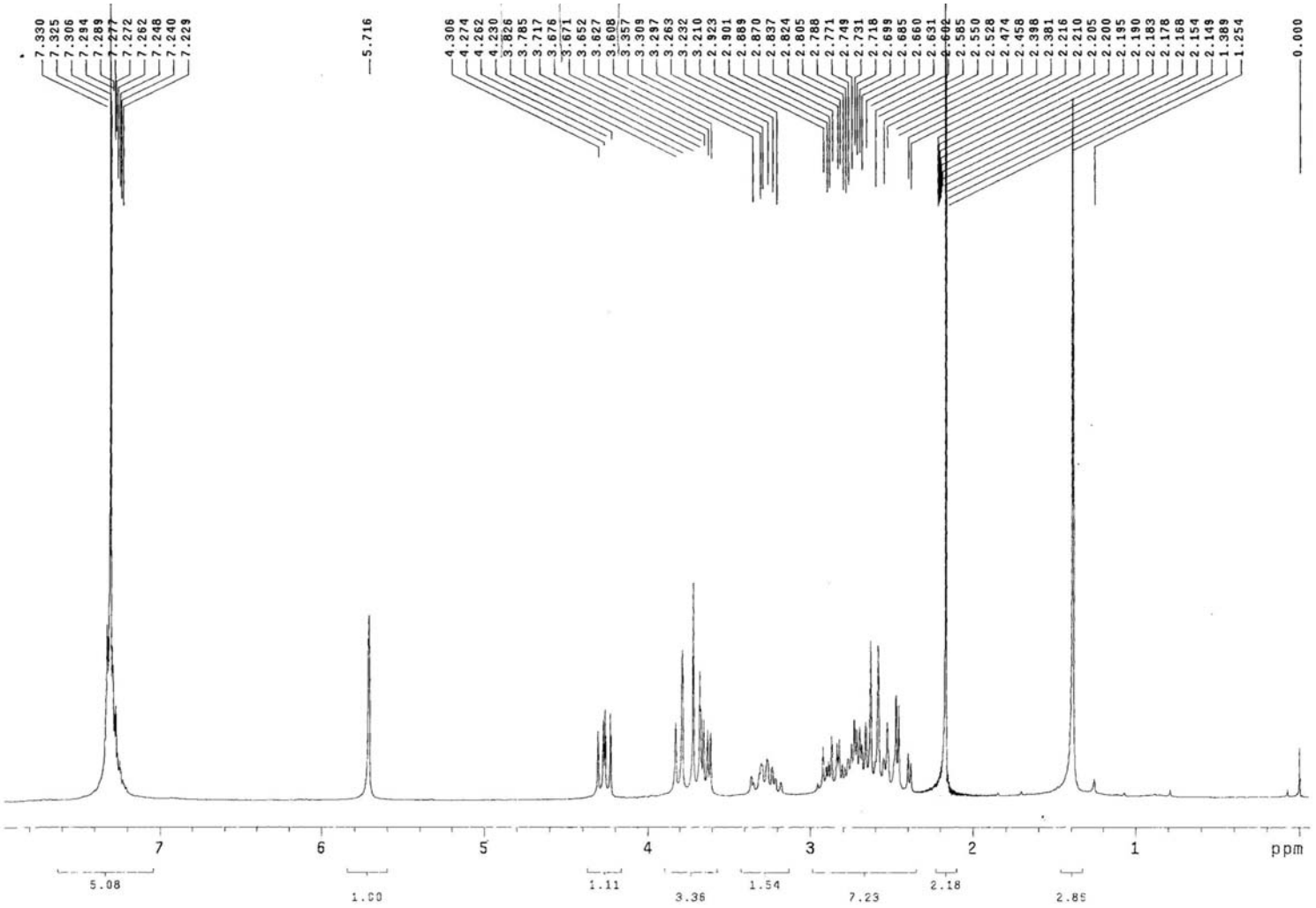

O
Ph

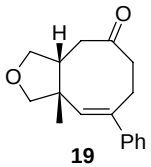
18


145.201
137.205
134.855
130.482
128.147
126.123
125.214
116.907
77.637
77.000
76.363
75.636
70.747
22.851
17.872
15.234
220
200
180
160
140
120
100
80
60
40
20
ppm

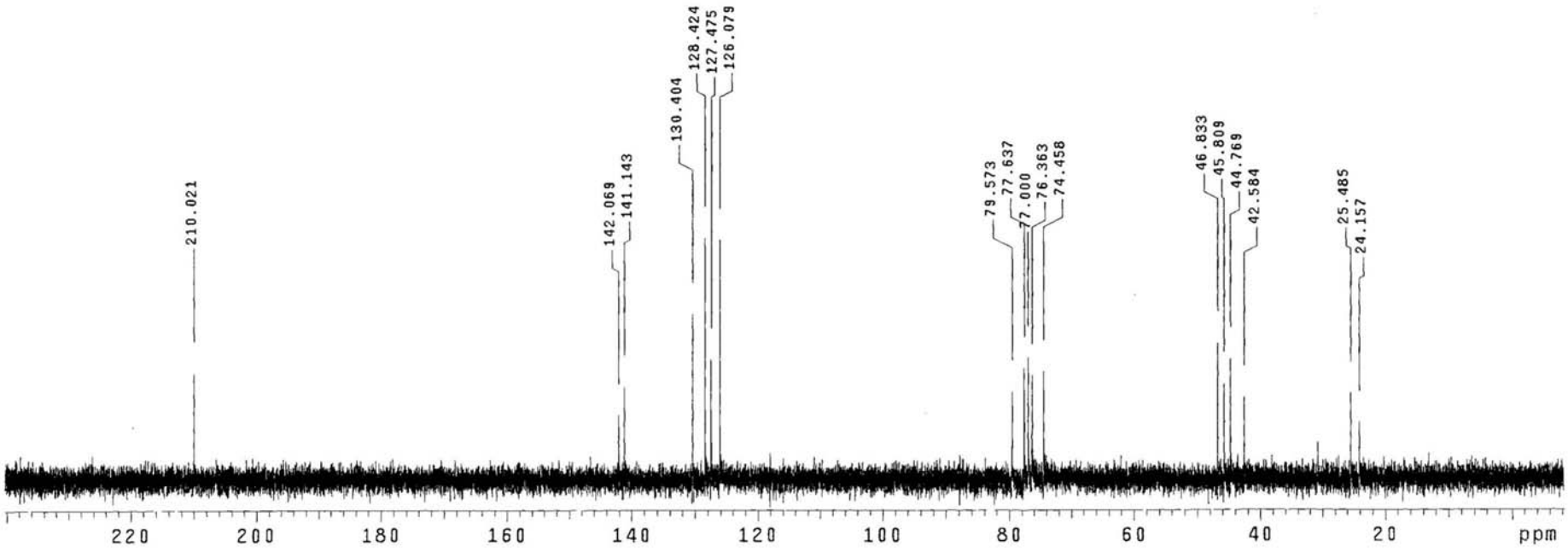

H
O
O
Ph

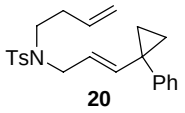
19


7.330
7.325
7.306
7.284
7.269
7.277
7.272
7.262
7.248
7.240
7.229
5.716
4.306
4.274
4.262
4.230
3.826
3.785
3.717
3.676
3.671
3.652
3.627
3.608
3.357
3.309
3.297
3.263
3.232
3.210
2.923
2.901
2.889
2.870
2.837
2.824
2.805
2.788
2.771
2.749
2.731
2.718
2.699
2.685
2.660
2.631
2.602
2.585
2.550
2.528
2.474
2.458
2.398
2.381
2.216
2.210
2.205
2.200
2.195
2.190
2.183
2.178
2.168
2.154
2.149
1.389
1.254
0.000
7
6
5
4
3
2
1
ppm
5.08
1.00
1.11
3.36
1.54
7.23
2.18
2.89

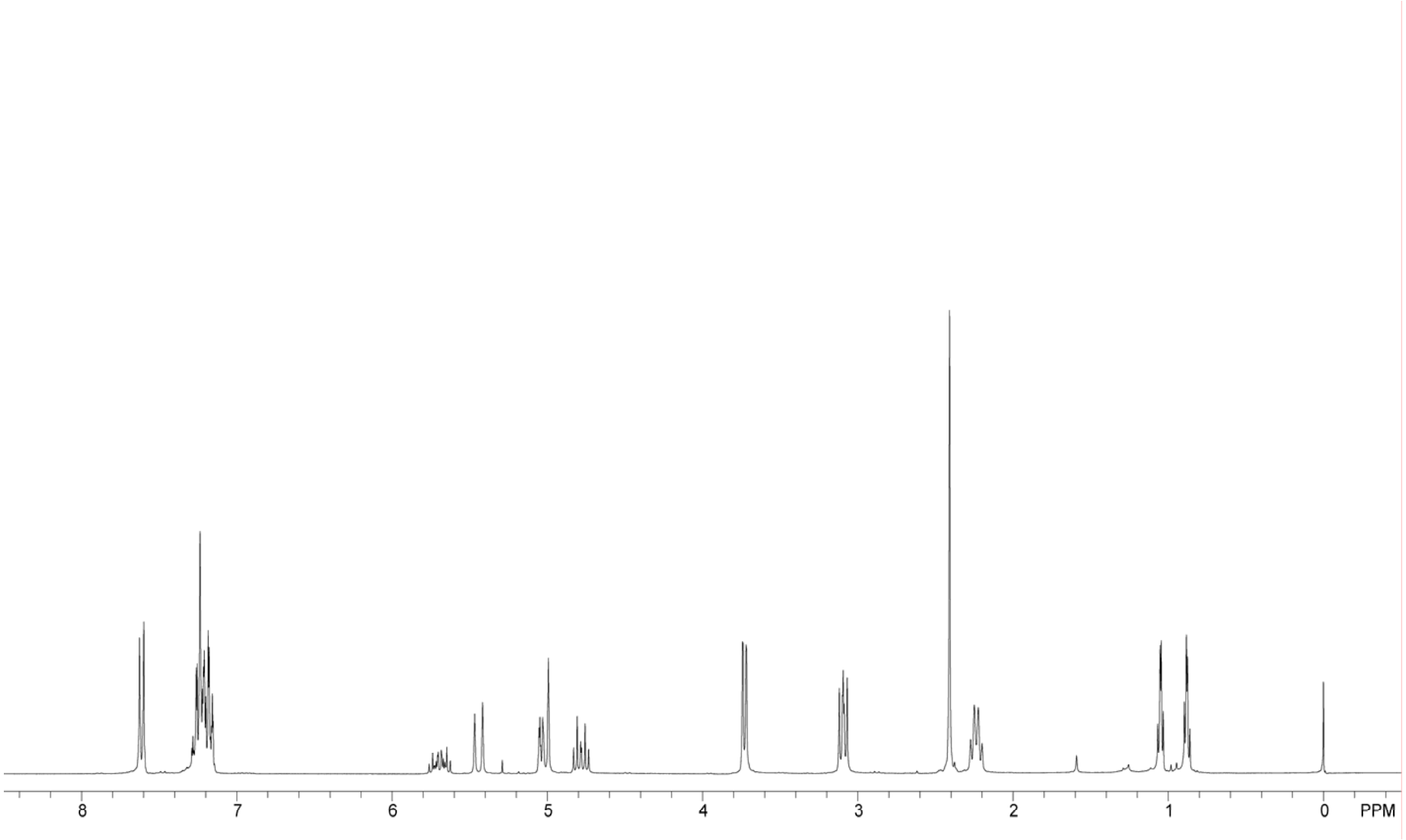

H
O
O
Ph

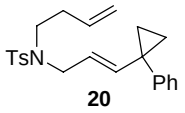
19


210.021
142.069
141.143
130.404
128.424
127.475
126.079
79.573
77.637
77.000
76.363
74.458
46.833
45.809
44.769
42.584
25.485
24.157
220
200
180
160
140
120
100
80
60
40
20
ppm

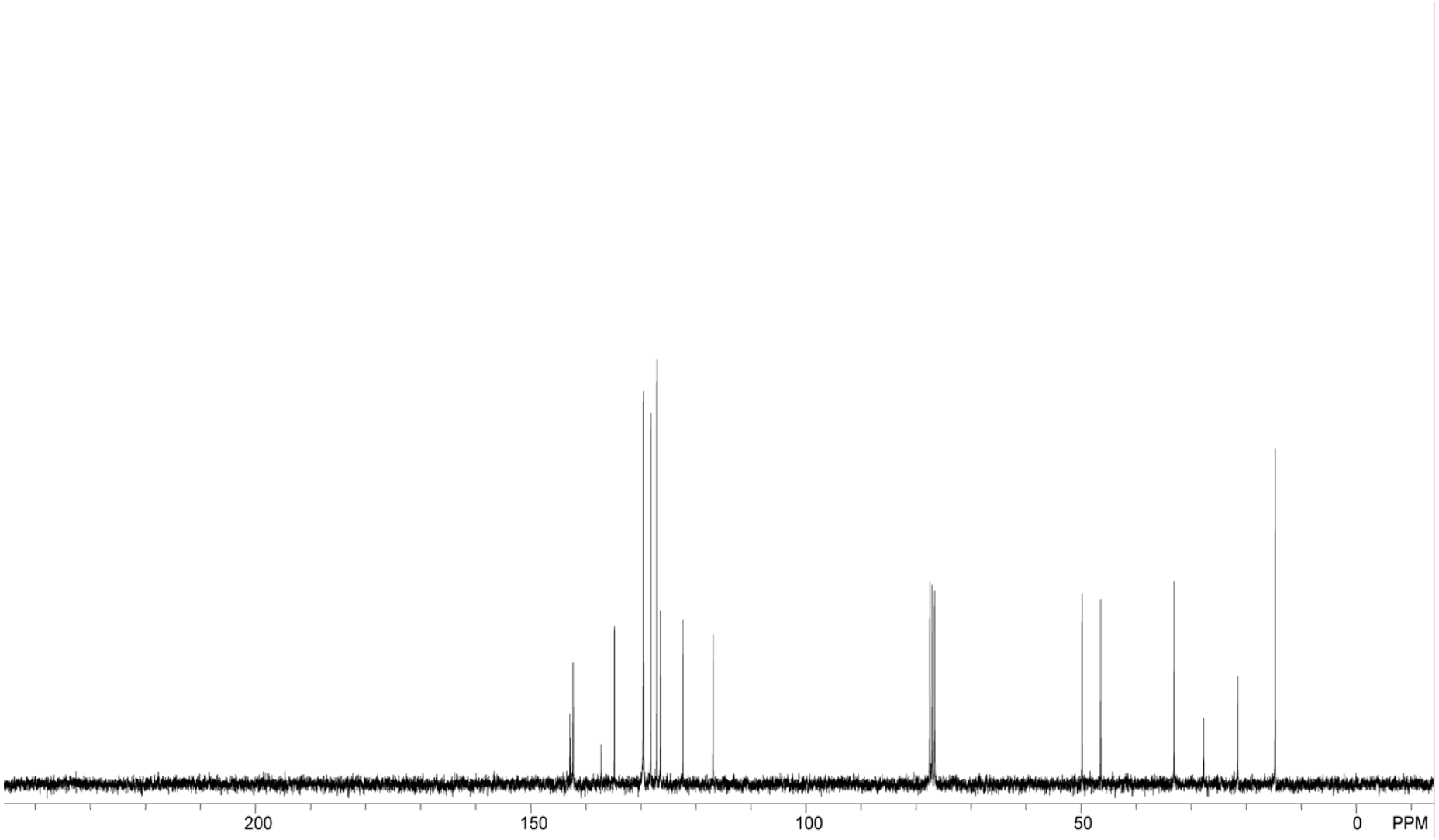


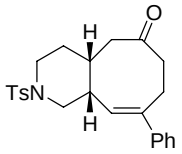
20



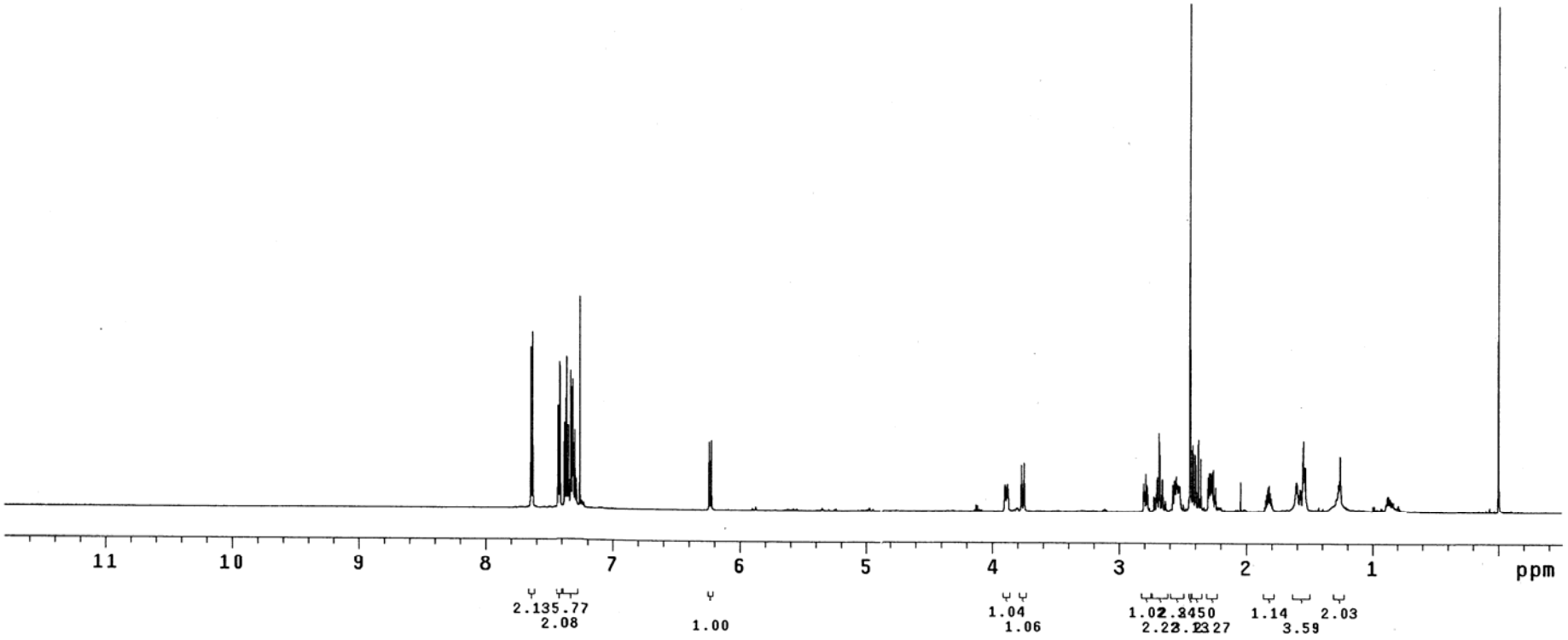


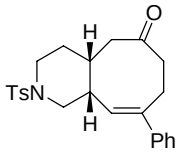
20



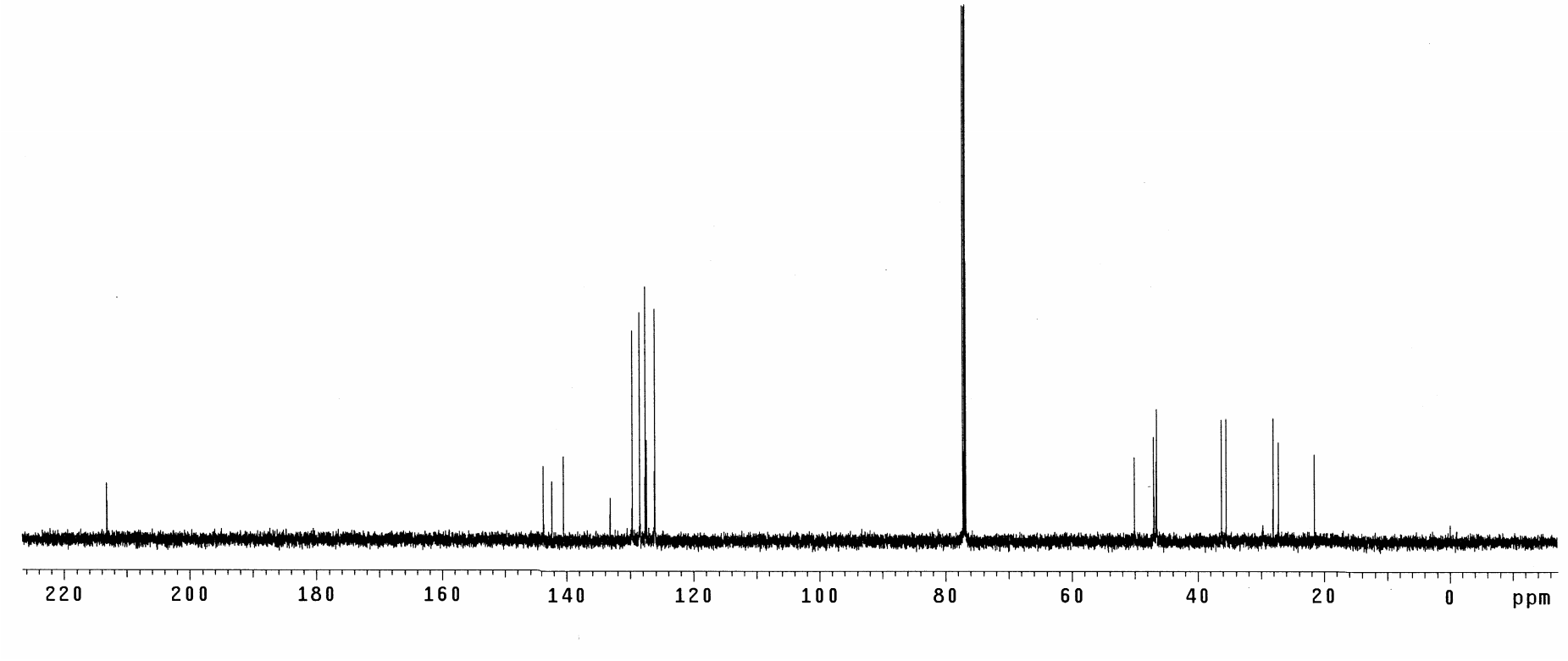

O
H
TsN
H
Ph

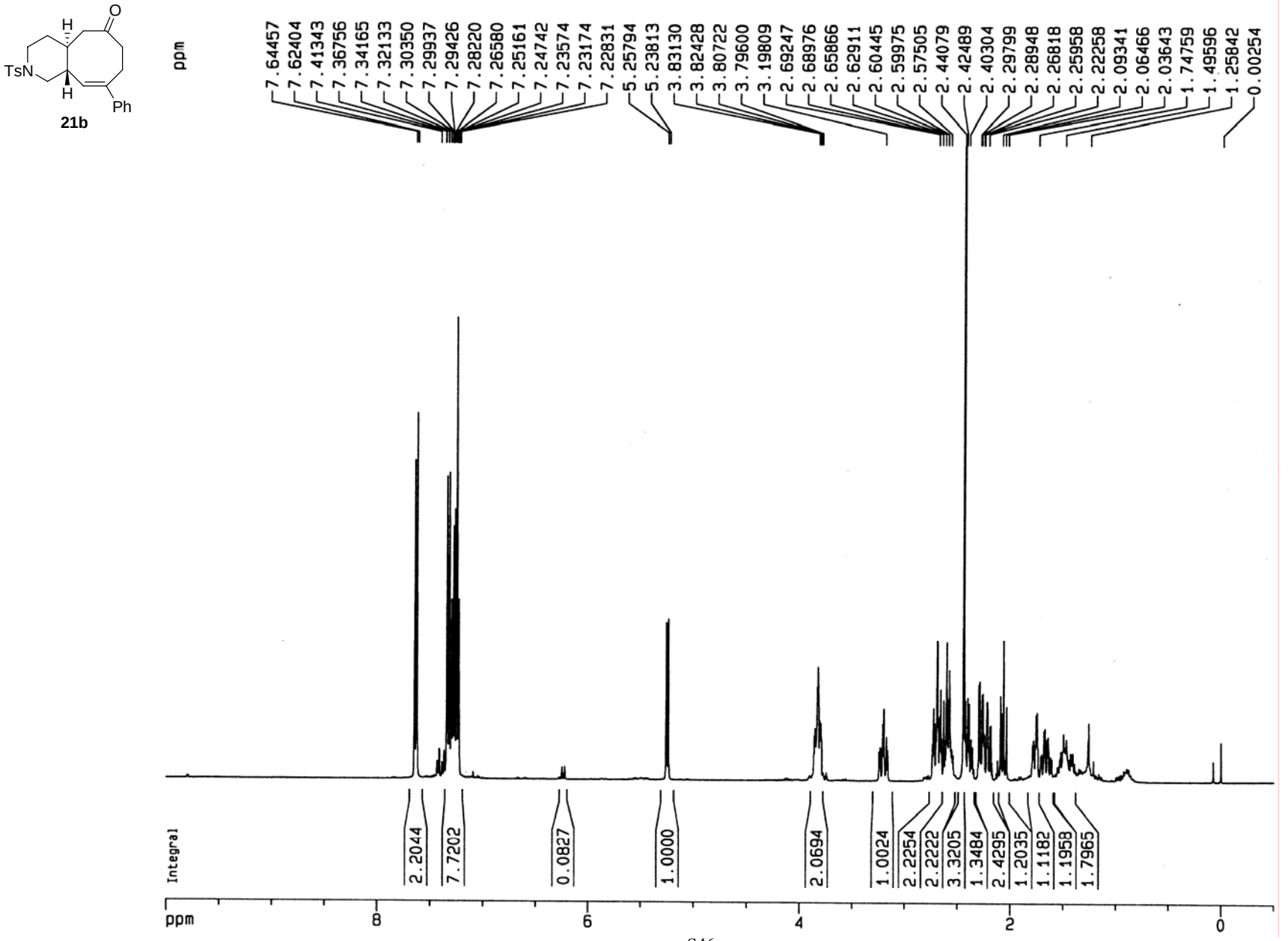
21a

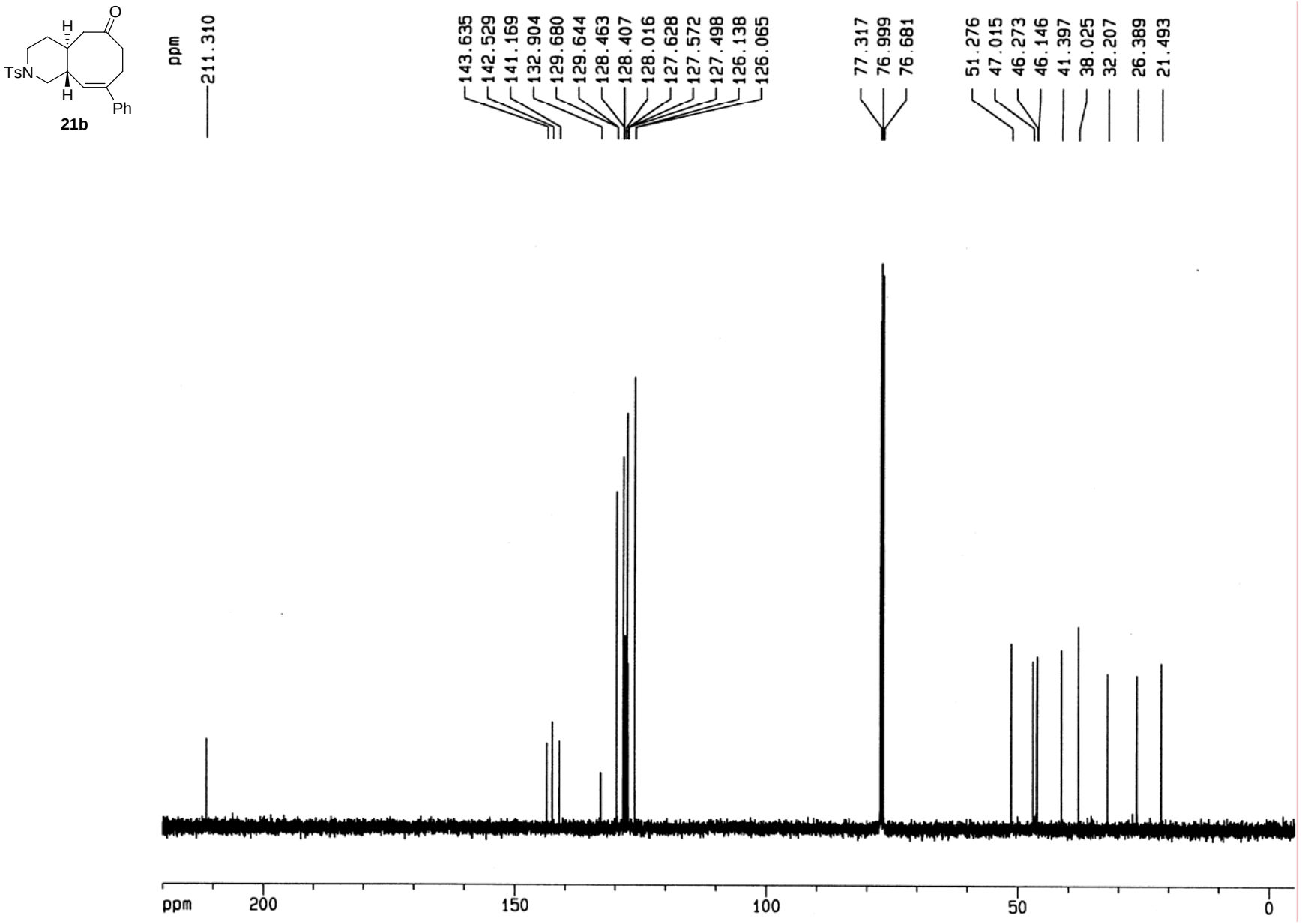

11
10
9
8
7
6
5
4
3
2
1
ppm
2.13
5.77
2.08
1.00
1.04
1.06
1.02
2.23
2.34
2.50
2.27
1.14
3.59
2.03

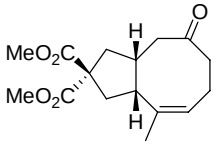


21a

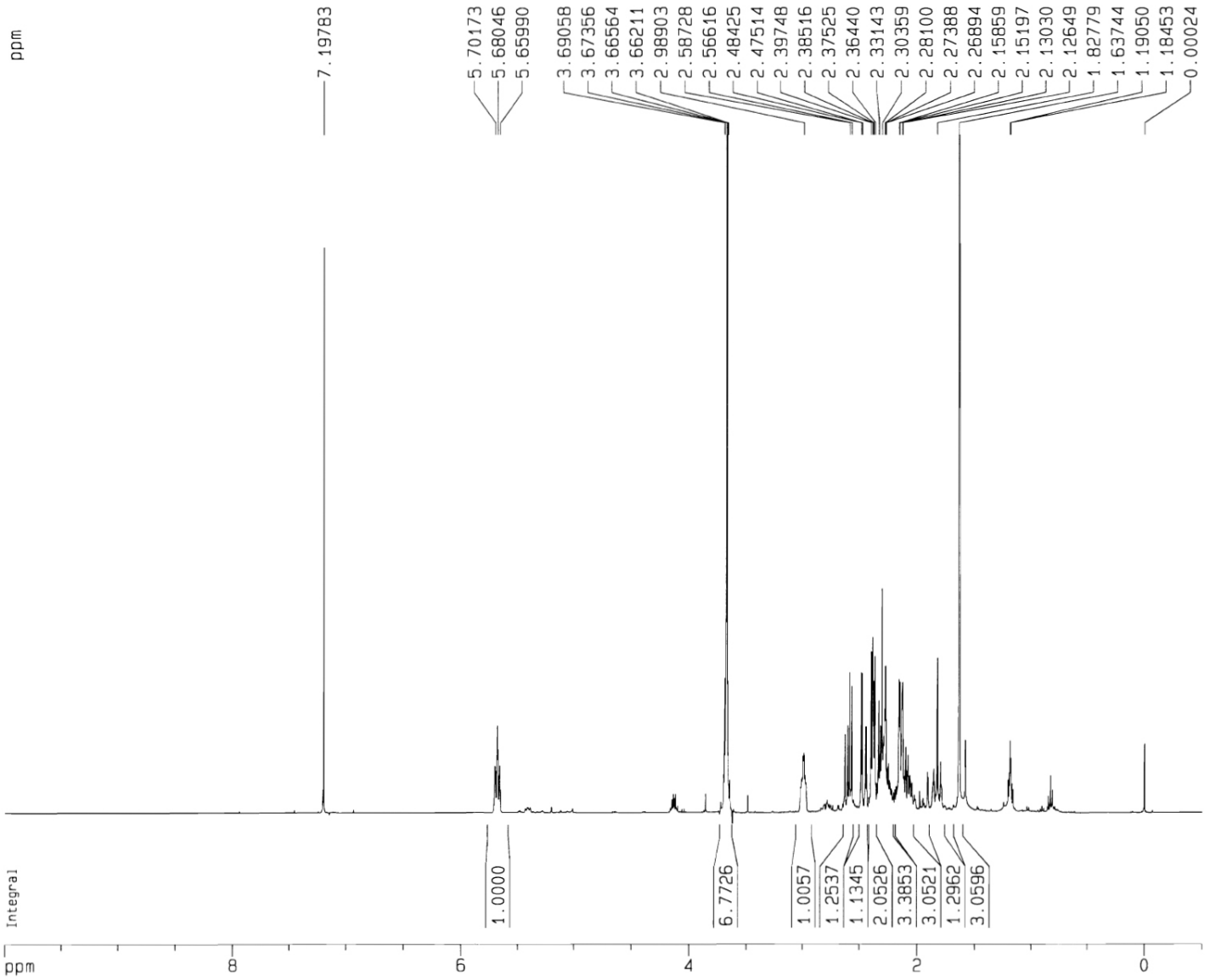


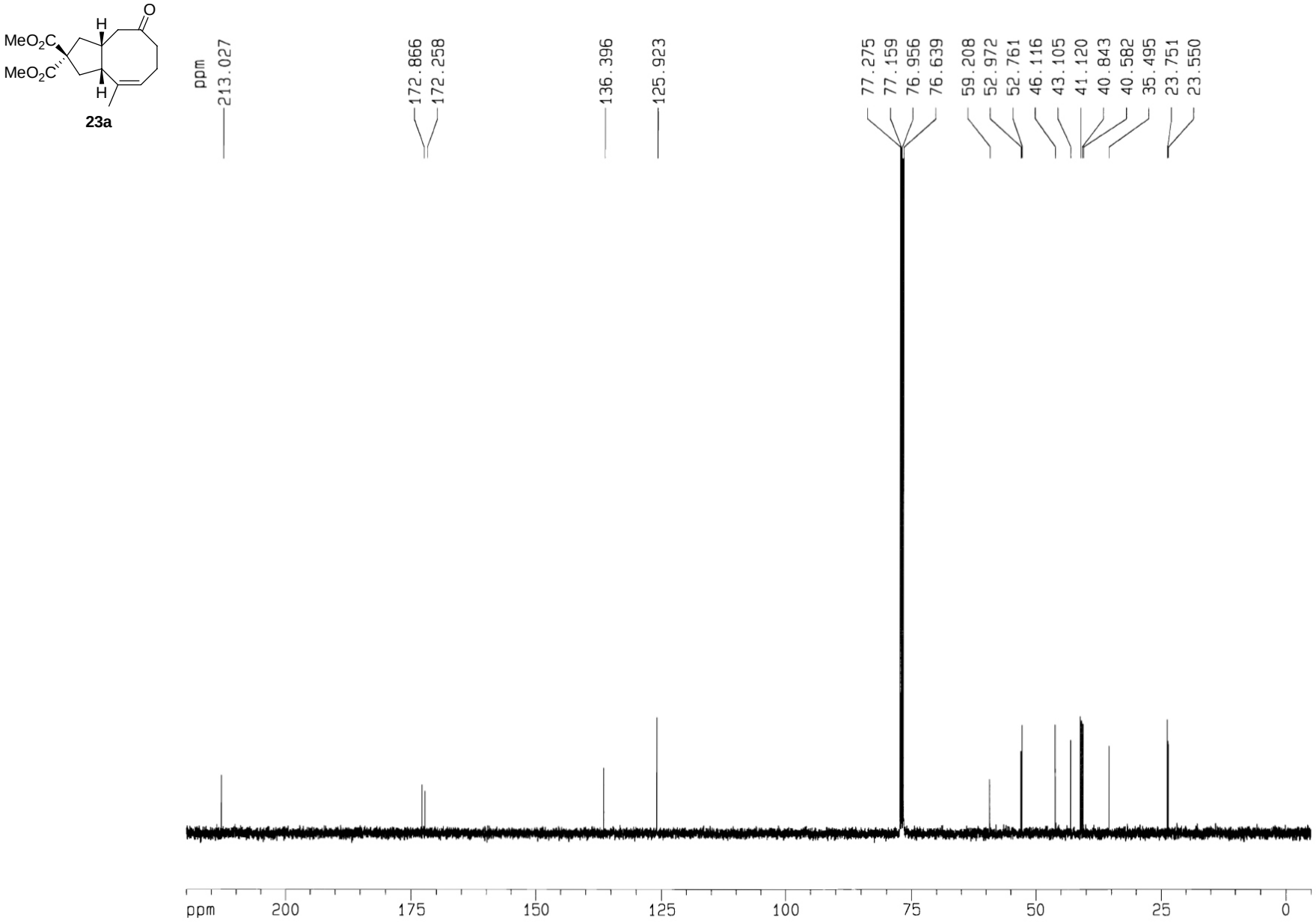

O
H
TsN
H
Ph
21b
ppm
7.64457
7.62404
7.41343
7.36756
7.34165
7.32133
7.30350
7.29937
7.29426
7.28220
7.26580
7.25161
7.24742
7.23574
7.23174
7.22831
5.25794
5.23813
3.83130
3.82428
3.80722
3.79600
3.19809
2.69247
2.68976
2.65866
2.62911
2.60445
2.59975
2.57505
2.44079
2.42489
2.40304
2.29799
2.28948
2.26818
2.25958
2.22258
2.09341
2.06466
2.03643
1.74759
1.49596
1.25842
0.00254
Integral
2.2044
7.7202
0.0827
1.0000
2.0694
1.0024
2.2254
2.2222
3.3205
1.3484
2.4295
1.2035
1.1182
1.1958
1.7965
ppm
8
6
4
2
0

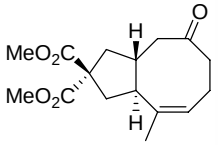

O
H
TsN
H
Ph
21b
ppm
211.310
143.635
142.529
141.169
132.904
129.680
129.644
128.463
128.407
128.016
127.628
127.572
127.498
126.138
126.065
77.317
76.999
76.681
51.276
47.015
46.273
46.146
41.397
38.025
32.207
26.389
21.493
ppm
200
150
100
50
0


O
H
MeO2C
MeO2C
H

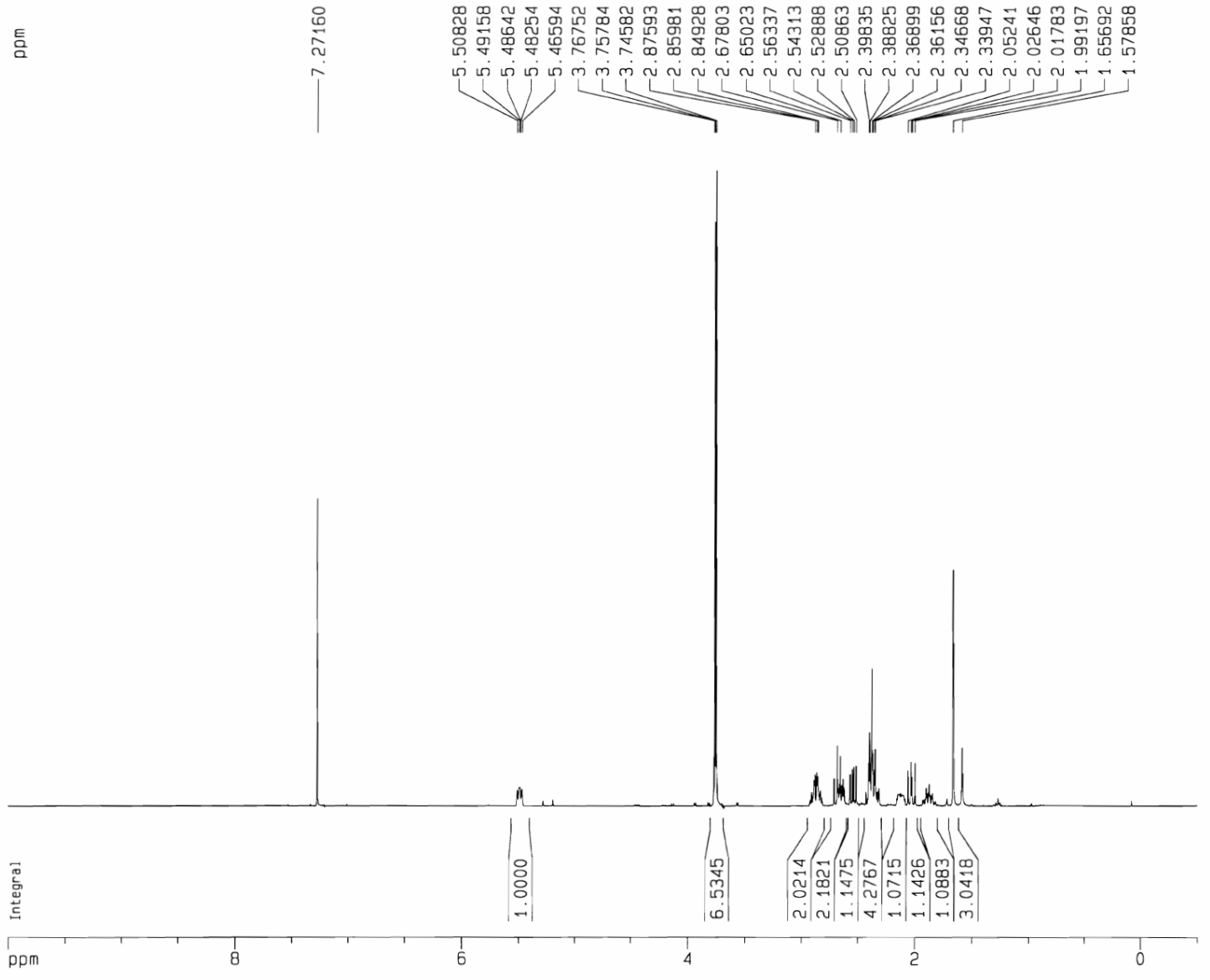
23a

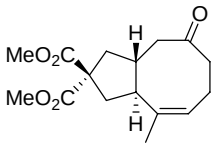

ppm
7.19783
5.70173
5.68046
5.65990
3.69058
3.67356
3.66564
3.66211
2.98903
2.58728
2.56616
2.48425
2.47514
2.39748
2.38516
2.37525
2.36440
2.33143
2.30359
2.28100
2.27388
2.26894
2.15859
2.15197
2.13030
2.12649
1.82779
1.63744
1.19050
1.18453
0.00024
Integral
1.0000
6.7726
1.0057
1.2537
1.1345
2.0526
3.3853
3.0521
1.2962
3.0596
ppm
8
6
4
2
0


MeO2C
MeO2C
H
H
O
23a
ppm
213.027
172.866
172.258
136.396
125.923
77.275
77.159
76.956
76.639
59.208
52.972
52.761
46.116
43.105
41.120
40.843
40.582
35.495
23.751
23.550
ppm
200
175
150
125
100
75
50
25
0


MeO2C
MeO2C
H
H
O

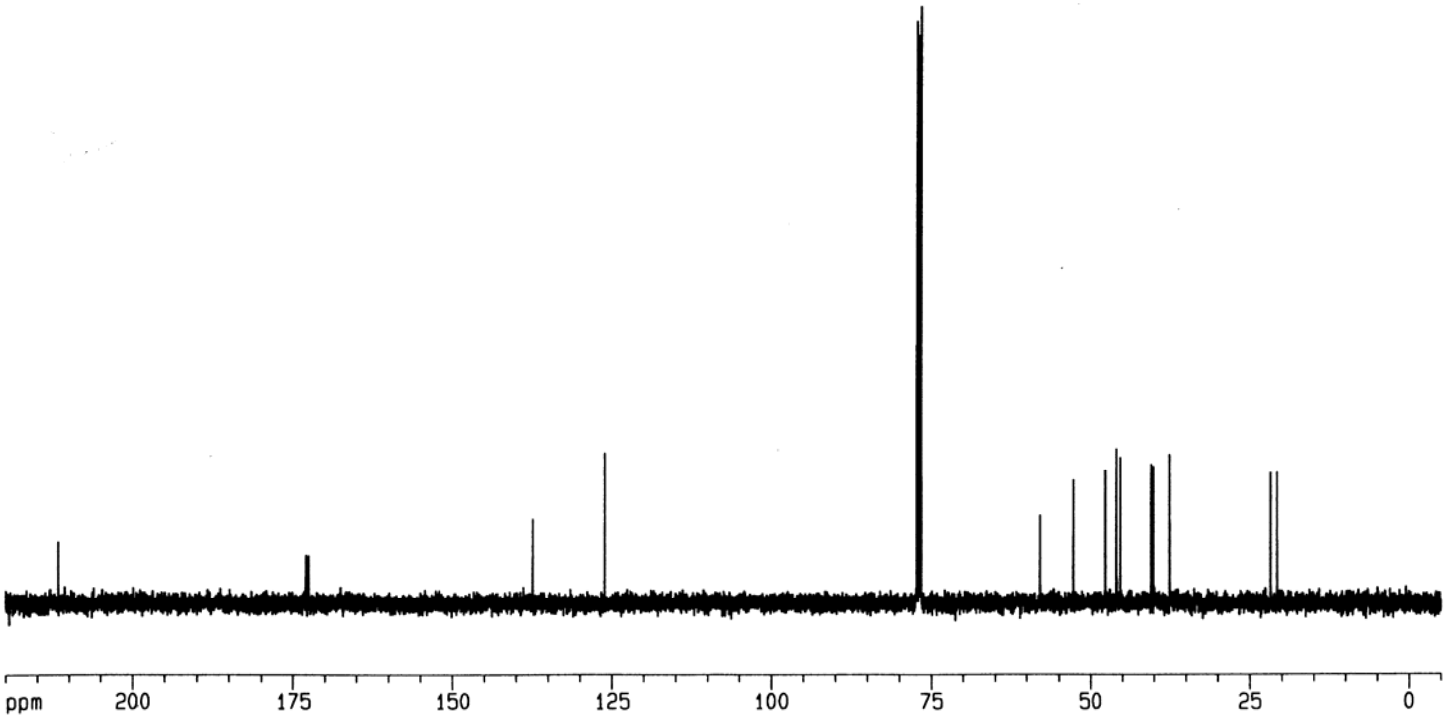
23b

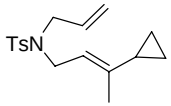

ppm
7.27160
5.50828
5.49158
5.48642
5.48254
5.46594
3.76752
3.75784
3.74582
2.87593
2.85981
2.84928
2.67803
2.65023
2.56337
2.54313
2.52888
2.50863
2.39835
2.38825
2.36899
2.36156
2.34668
2.33947
2.05241
2.02646
2.01783
1.99197
1.65692
1.57858
Integral
1.0000
6.5345
2.0214
2.1821
1.1475
4.2767
1.0715
1.1426
1.0883
3.0418
ppm
8
6
4
2
0



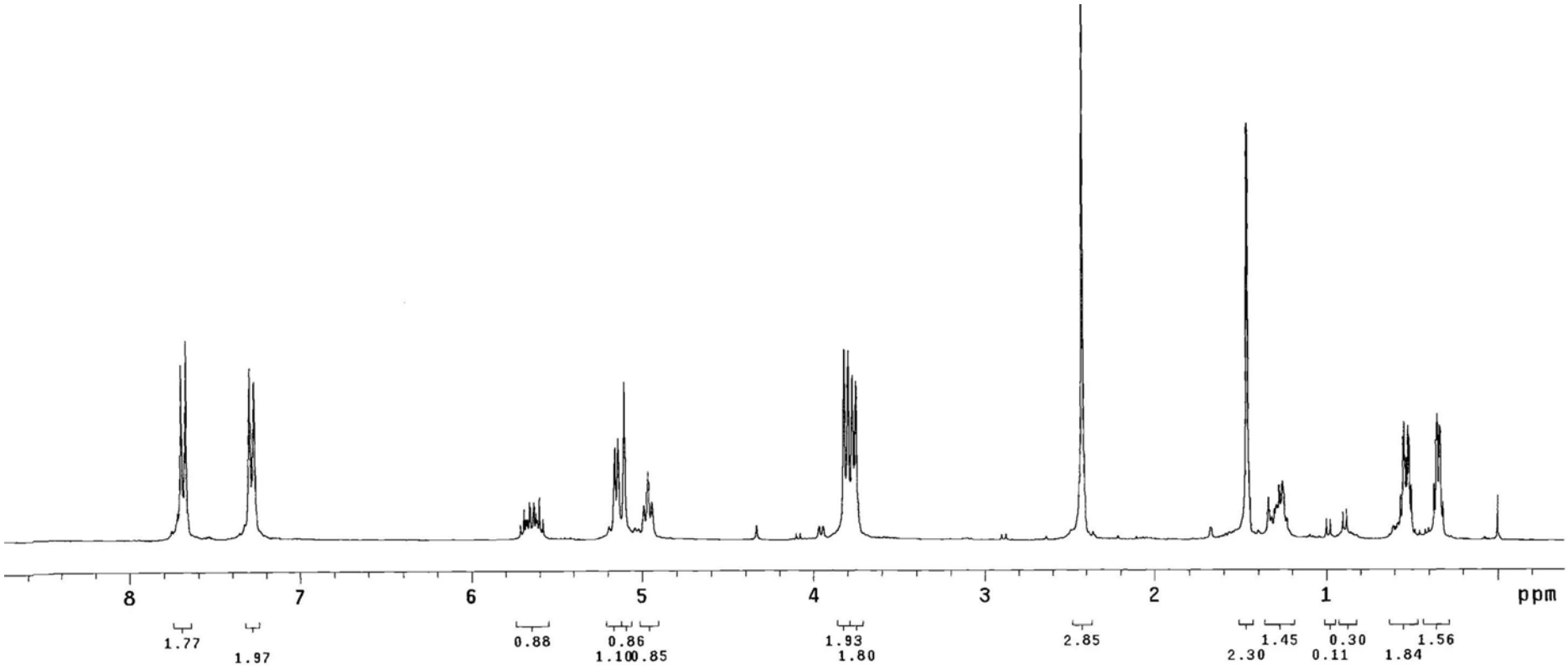
23b

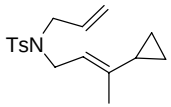
ppm
211.732
172.931
172.522
137.355
126.103
77.271
76.954
76.636
57.896
52.803
52.765
47.667
45.960
45.371
40.471
40.110
37.540
21.766
20.803



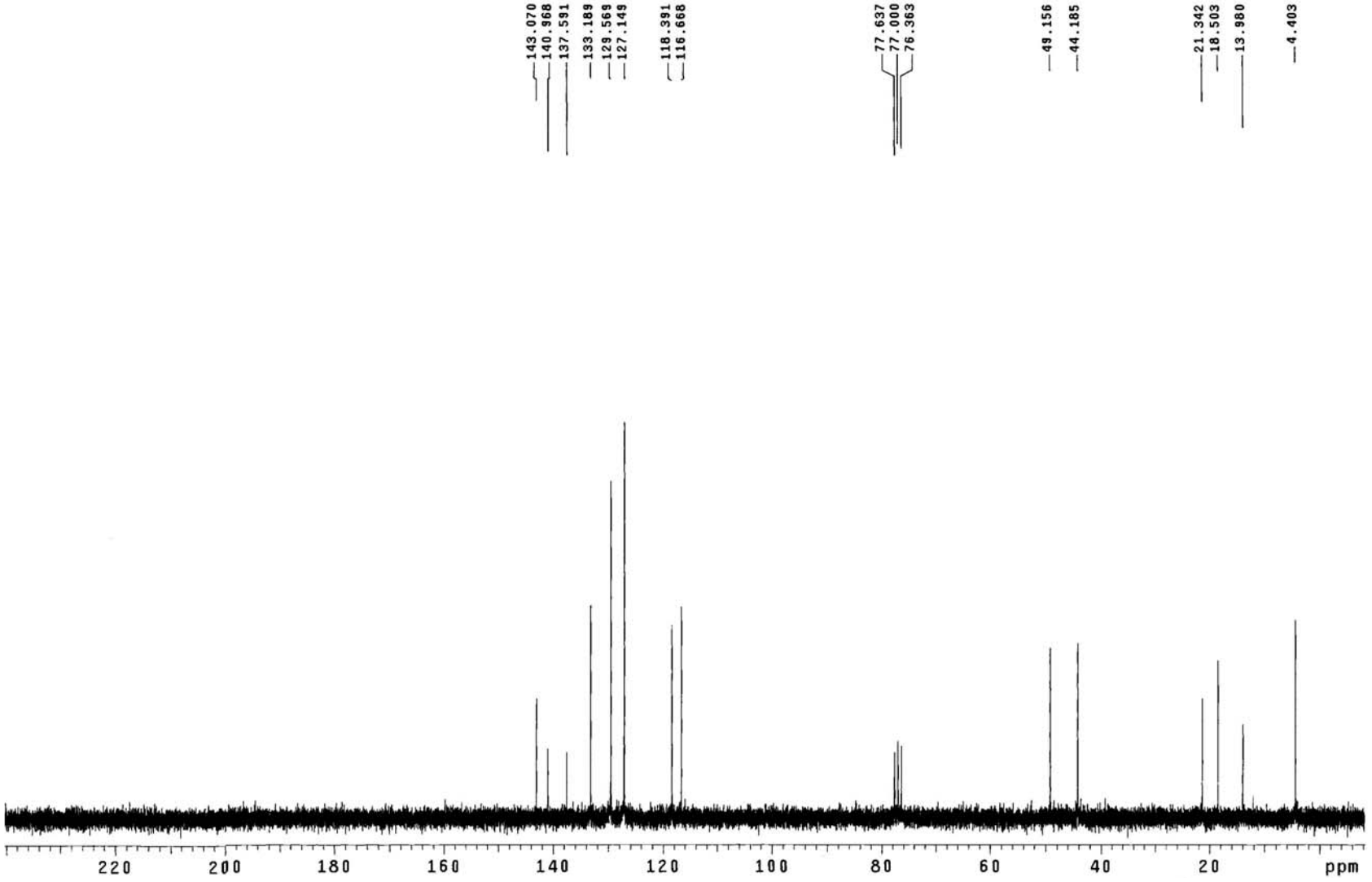

TsN

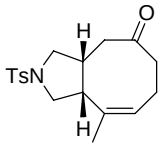
25


8
7
6
5
4
3
2
1
ppm
1.77
1.97
0.88
0.86
1.10
0.85
1.93
1.80
2.85
2.30
1.45
0.30
0.11
1.84
1.56

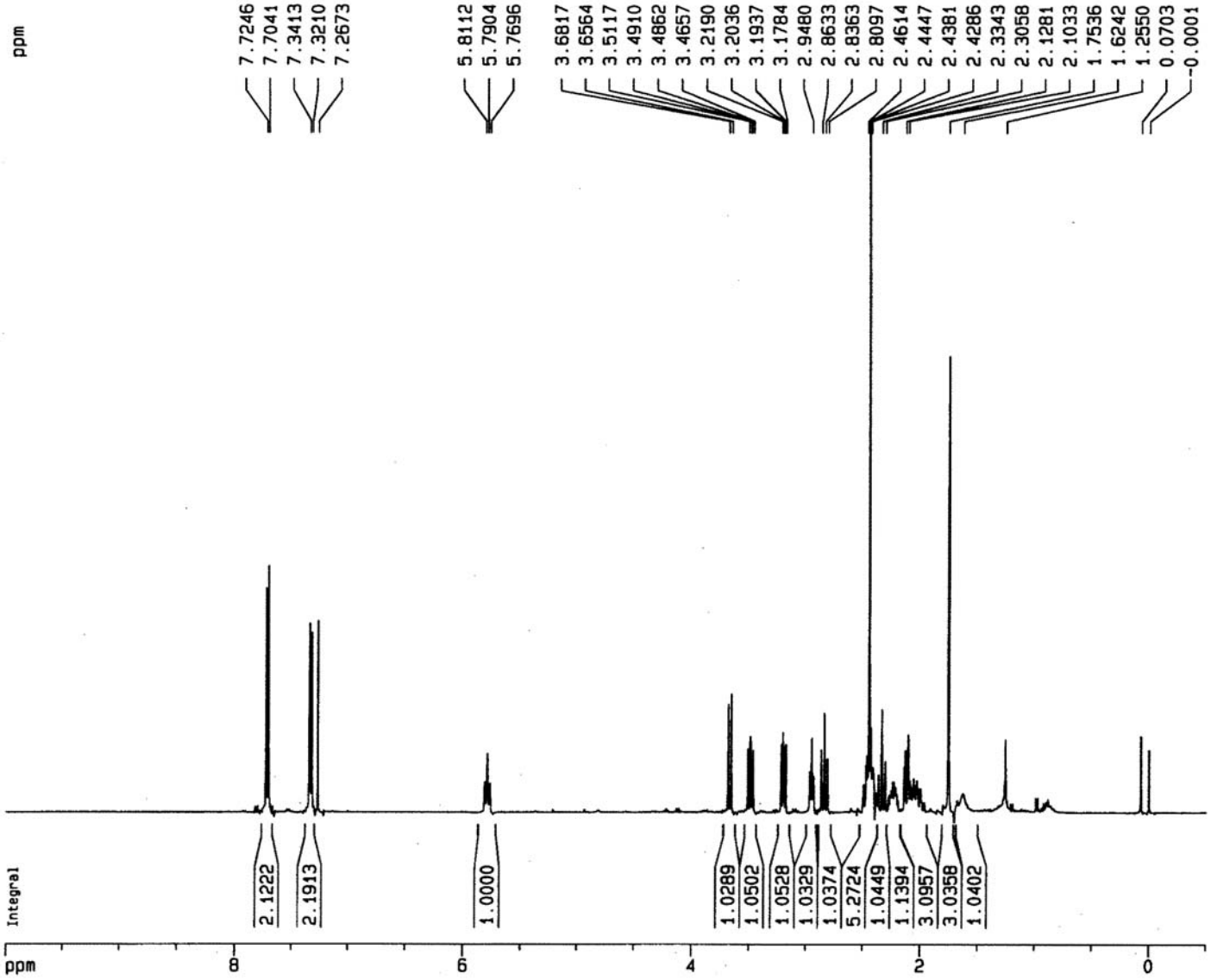

TsN

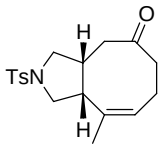
25


143.070
140.968
137.591
133.189
129.569
127.149
118.391
116.668
77.637
77.000
76.363
49.156
44.185
21.342
18.503
13.980
4.403
220
200
180
160
140
120
100
80
60
40
20
ppm

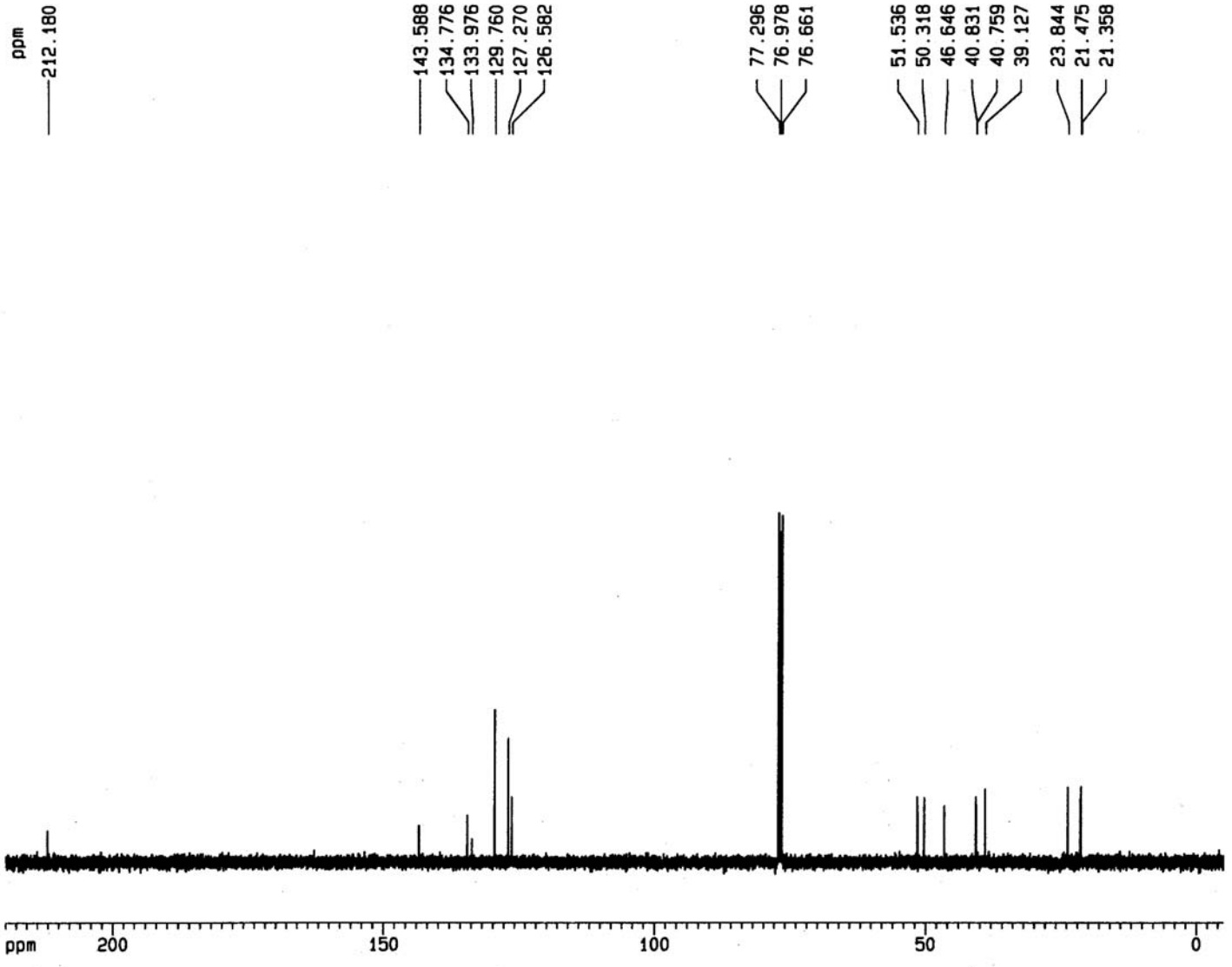

O
H
TsN
H

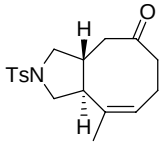
26a


ppm
7.7246
7.7041
7.3413
7.3210
7.2673
5.8112
5.7904
5.7696
3.6817
3.6564
3.5117
3.4910
3.4862
3.4657
3.2190
3.2036
3.1937
3.1784
2.9480
2.8633
2.8363
2.8097
2.4614
2.4447
2.4381
2.4286
2.3343
2.3058
2.1281
2.1033
1.7536
1.6242
1.2550
0.0703
-0.0001
Integral
2.1222
2.1913
1.0000
1.0289
1.0502
1.0528
1.0329
1.0374
5.2724
1.0449
1.1394
3.0957
3.0358
1.0402
ppm
8
6
4
2
0

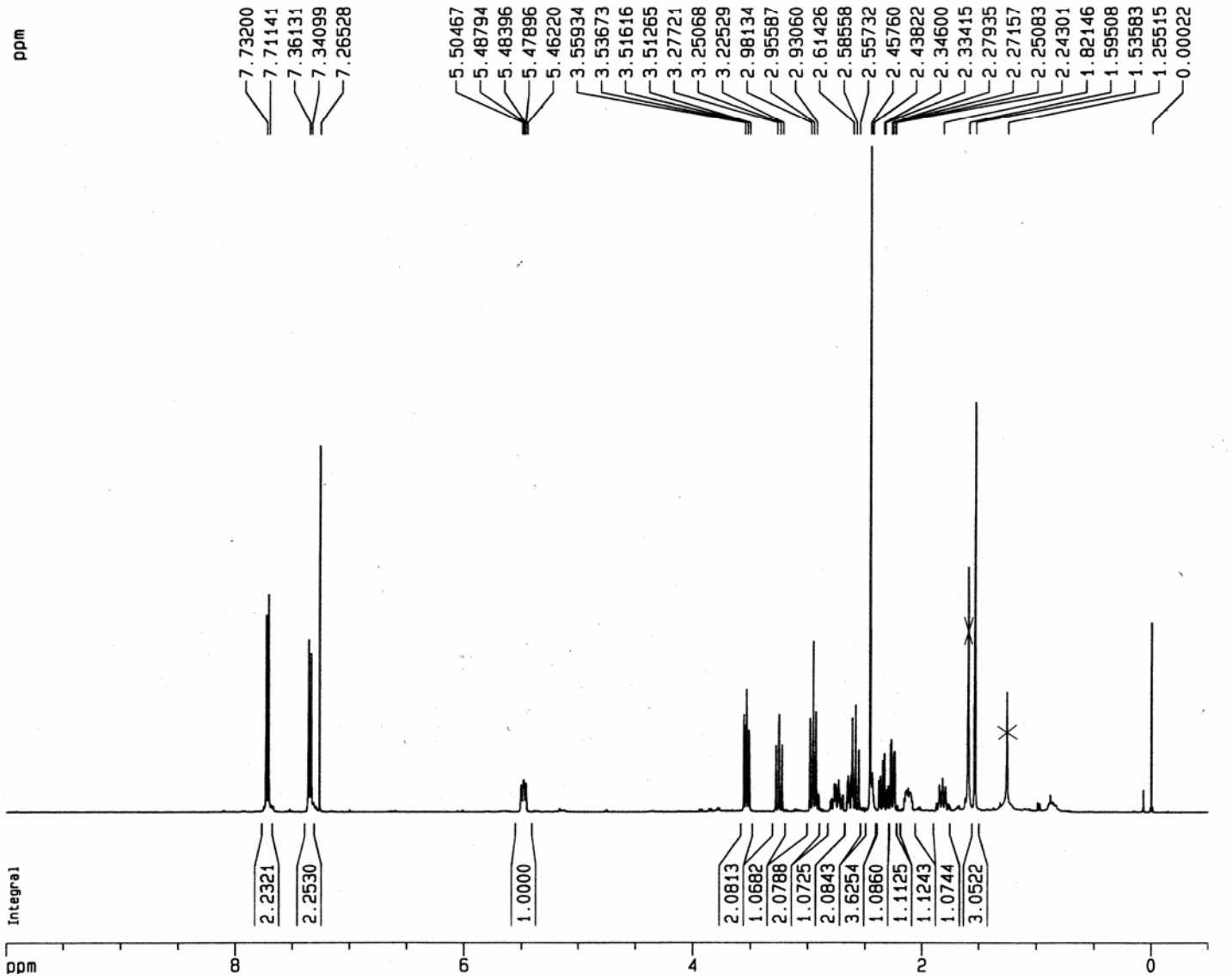

O
H
TsN
H

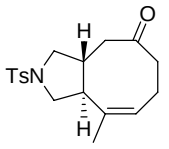
26a


ppm
212.180
143.588
134.776
133.976
129.760
127.270
126.582
77.296
76.978
76.661
51.536
50.318
46.646
40.831
40.759
39.127
23.844
21.475
21.358
ppm
200
150
100
50
0

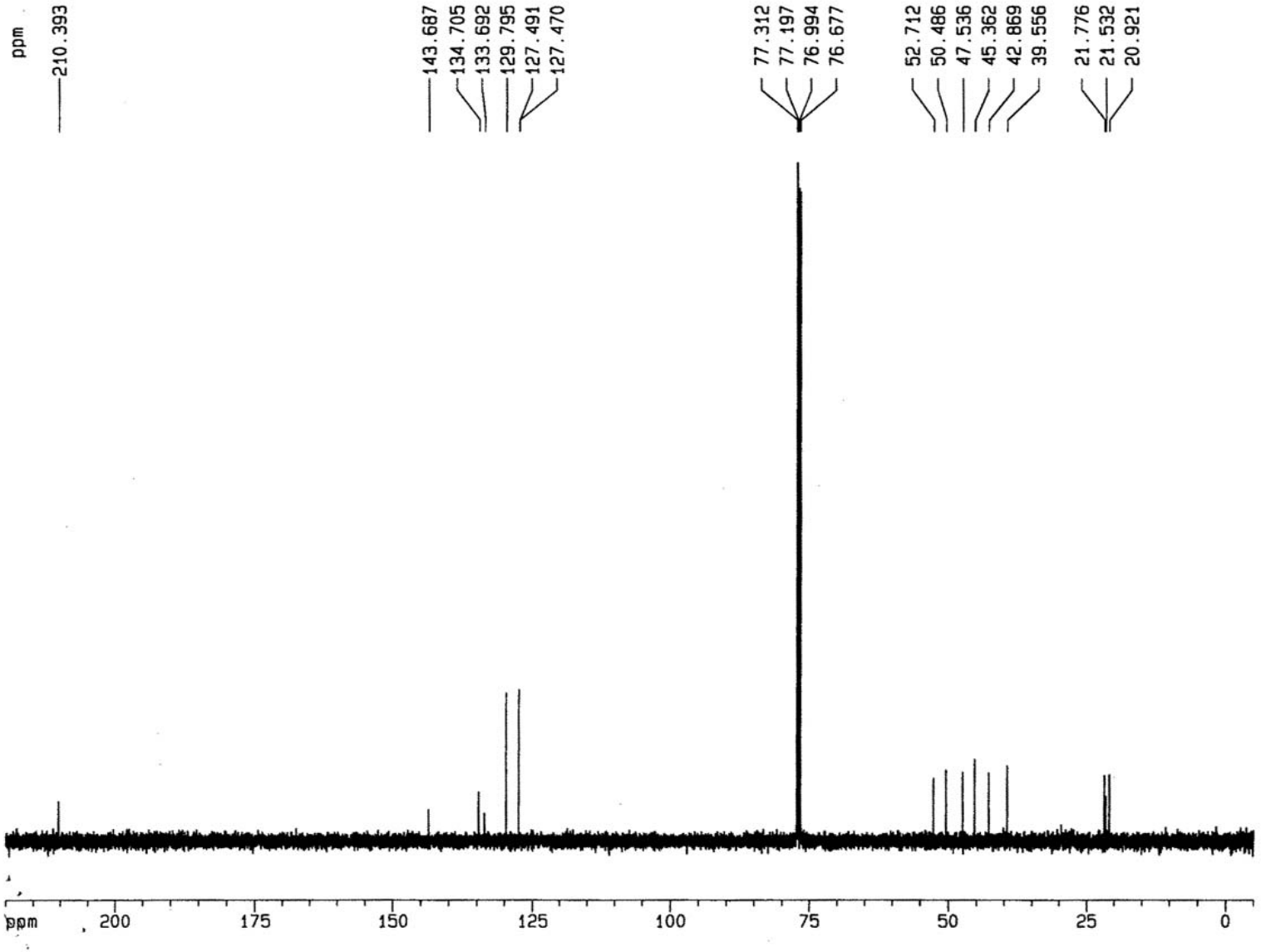

H
O
TsN
H

26b


ppm
7.73200
7.71141
7.36131
7.34099
7.26528
5.50467
5.48794
5.48396
5.47896
5.46220
3.55934
3.53673
3.51616
3.51265
3.27721
3.25068
3.22529
2.98134
2.95587
2.93060
2.61426
2.58558
2.55732
2.45760
2.43822
2.34600
2.33415
2.27935
2.27157
2.25083
2.24301
1.82146
1.59508
1.53583
1.25515
0.00022
Integral
2.2321
2.2530
1.0000
2.0813
1.0682
2.0788
1.0725
2.0843
3.6254
1.0860
1.1125
1.1243
1.0744
3.0522
ppm
8
6
4
2
0


H
O
TsN
H

26b


ppm
210.393
143.687
134.705
133.692
129.795
127.491
127.470
77.312
77.197
76.994
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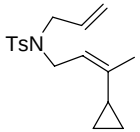
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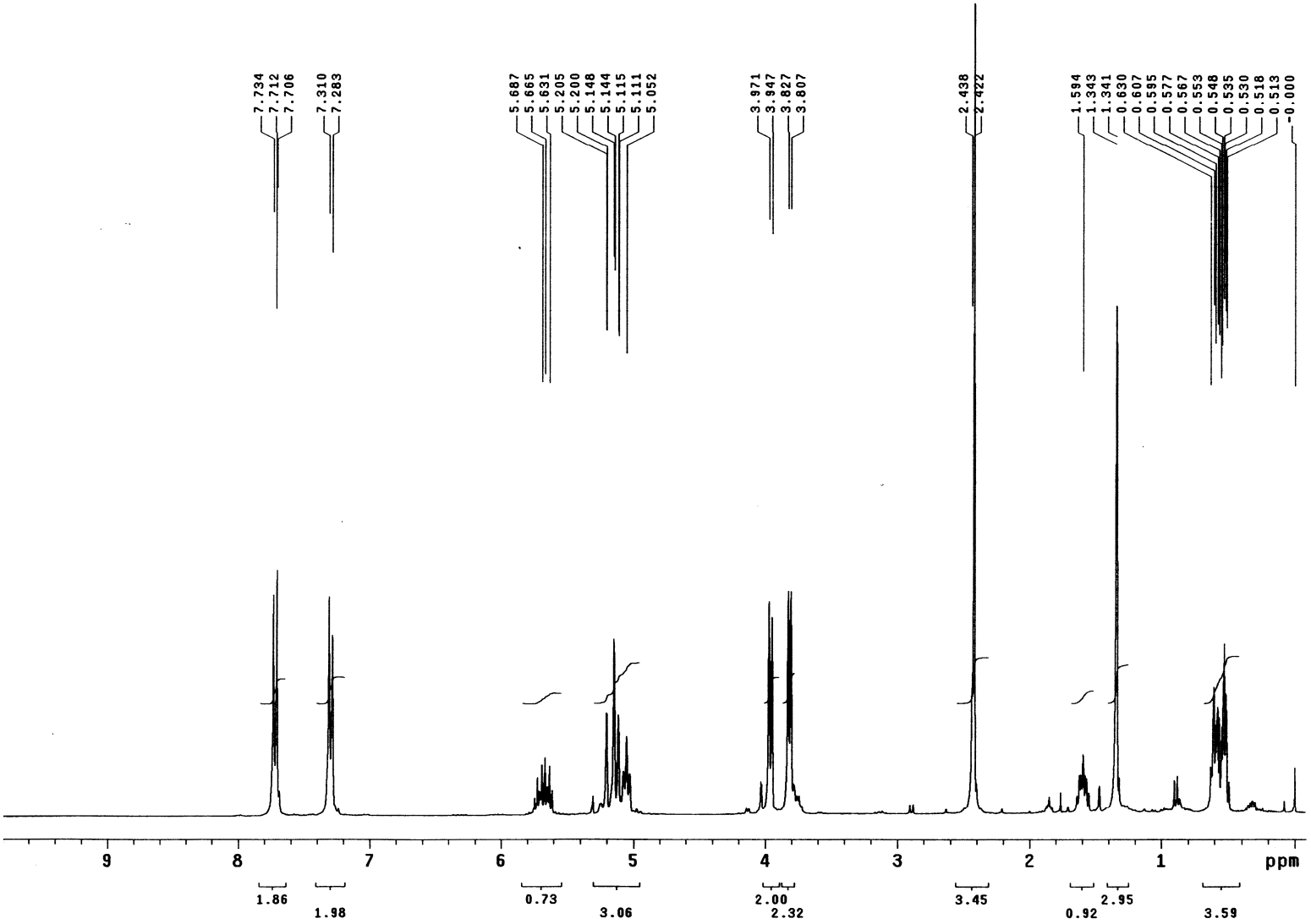
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2.422
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0.595
0.577
0.567
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7
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5
4
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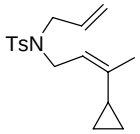
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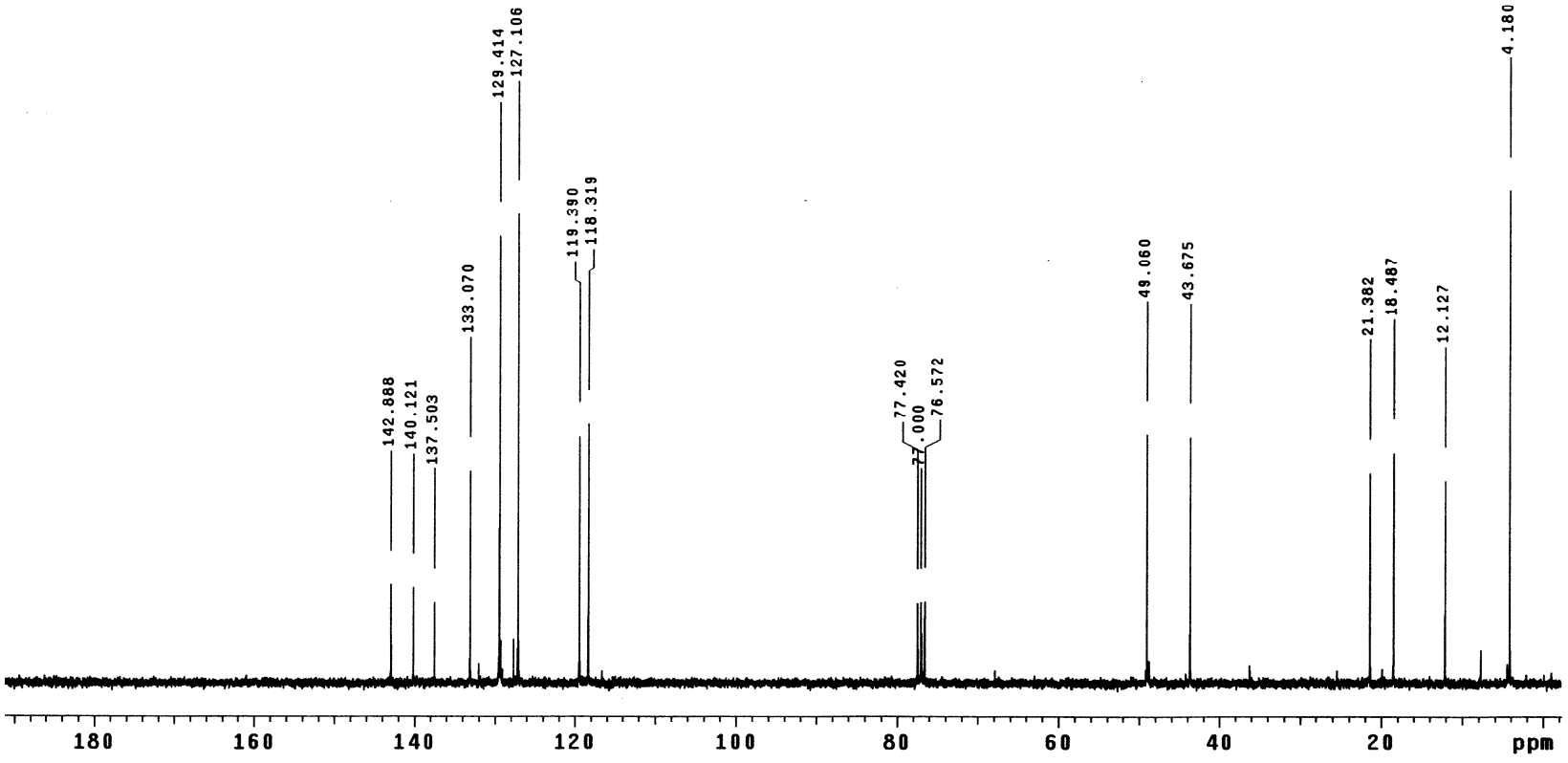
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77.000
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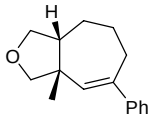
4.180
180
160
140
120
100
80
60
40
20
ppm



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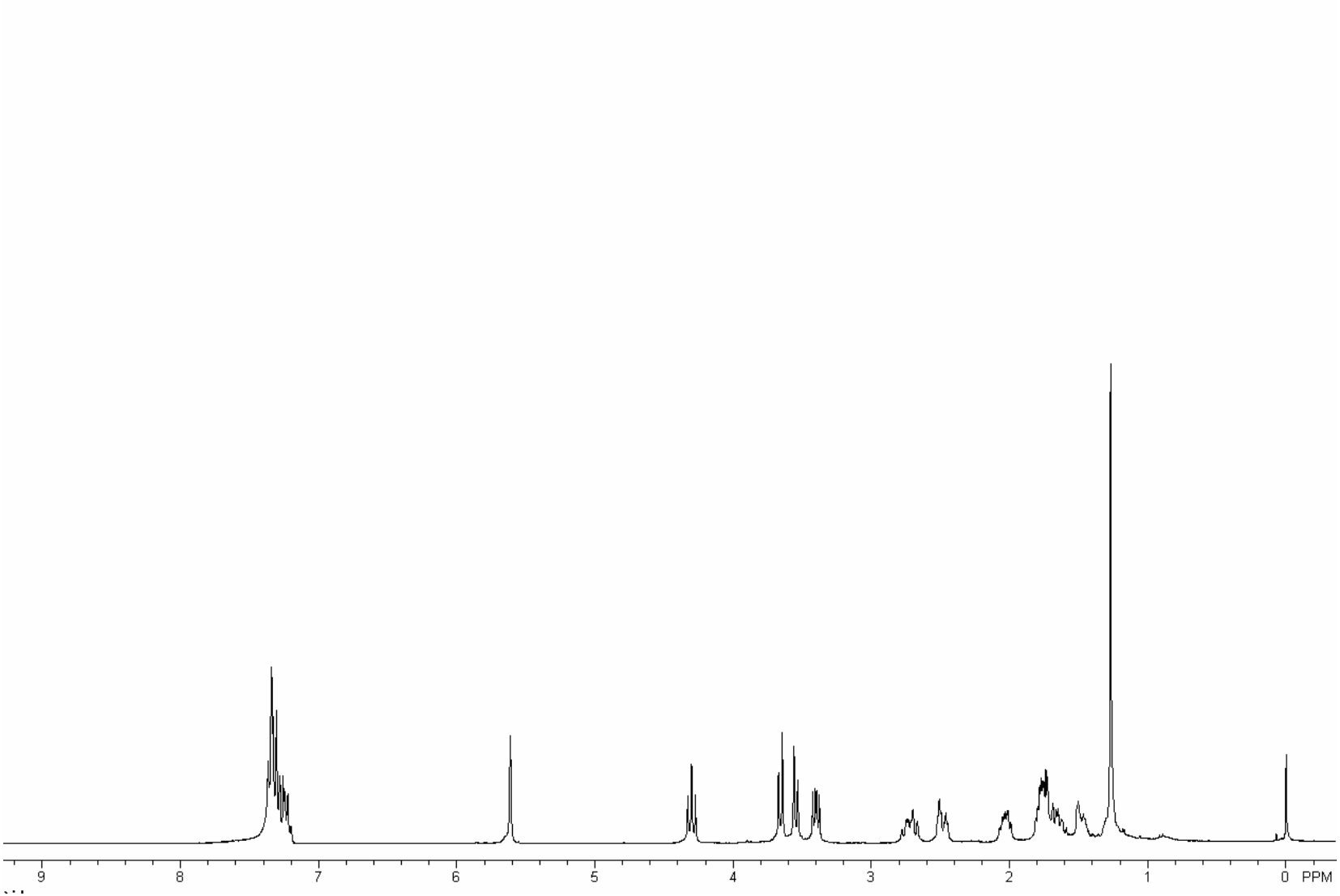

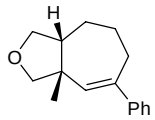

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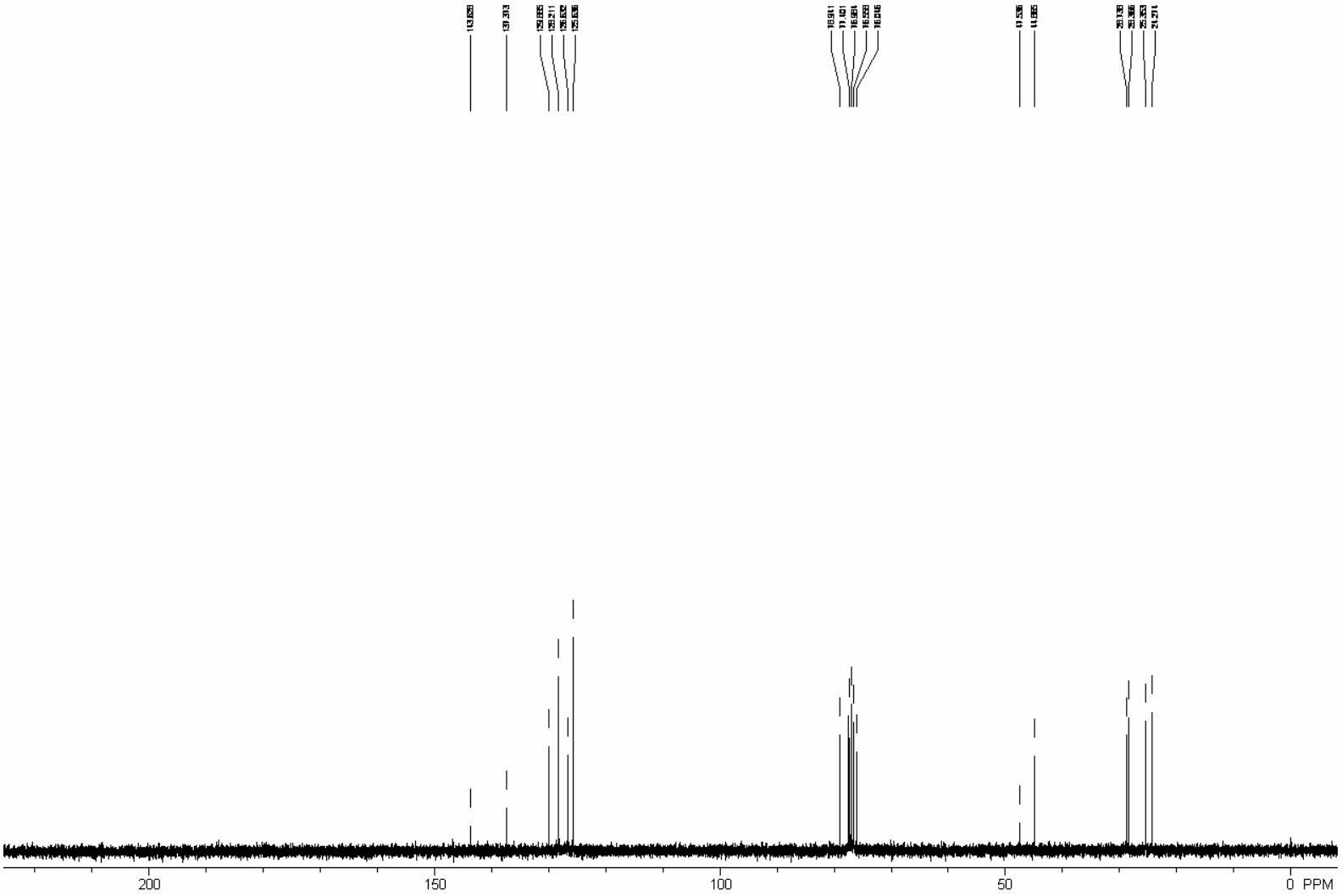

9. Cartesian Coordinates and Energies of all Computed Structures

Table S1. The Computed Energies and Other Thermal Parameters for the Three-Component [5+2+1] Reaction (in Hartree)

Structure	E_{ele}	$E_{0\ K}$	$H_{298\ K}$	$G_{298\ K}$
S1	–957.026001	–956.841081	–956.827585	–956.880773
S2	–1070.352574	–1070.159363	–1070.143291	–1070.202005
S3	–1070.322564	–1070.129586	–1070.114134	–1070.171761
S4	–1070.376280	–1070.181119	–1070.165808	–1070.223143
S5	–1070.341230	–1070.146858	–1070.132085	–1070.187723
S6	–1070.357971	–1070.162303	–1070.147153	–1070.204513
S7	–1070.372355	–1070.176127	–1070.160899	–1070.219064
S8	–956.983271	–956.798727	–956.786734	–956.837544

S1 :

C	0.308091	-0.321233	-2.134724
Rh	0.341213	-0.341861	-0.029817
C	2.199085	-0.361590	0.075044
O	3.344821	-0.372807	0.140312
C	-1.203572	-0.362215	-2.402020
C	-1.788090	-0.748450	-1.052608
C	-2.129597	0.114598	-0.054243
C	-2.138361	1.619380	-0.129937
C	-0.930292	2.201082	0.632382
C	0.392809	1.740973	0.040067
Cl	0.043597	-0.877569	2.360817
H	0.811258	0.543665	-2.573933
H	0.816799	-1.236709	-2.456225
H	-1.485223	-1.091198	-3.171401
H	-1.580144	0.613411	-2.724897
H	-1.888967	-1.815313	-0.846295
H	-2.452822	-0.315667	0.891207
H	-2.114638	1.962308	-1.170377
H	-3.067885	1.993240	0.316688
H	-0.964929	3.302319	0.590891
H	-0.984039	1.909179	1.685383
H	0.559281	2.108861	-0.976401
H	1.236593	2.015504	0.676950

S2 :

C	-1.652994	-0.124616	-1.194584
C	-1.456117	0.546609	1.510445
Rh	-0.114062	0.127072	0.252523
C	-0.823102	-0.409698	-2.452195
C	0.592670	-0.074313	-2.010953
H	0.912431	0.947007	-2.198777
H	-0.907263	-1.446205	-2.790319
H	-1.110402	0.234239	-3.289760
H	-2.175972	0.829163	-1.243419
H	-2.328320	-0.933940	-0.913597
Cl	0.016538	2.623636	-0.254905
C	-0.300648	-1.946268	0.741309
C	0.055975	-2.821533	-0.458360
C	1.382230	-2.380007	-1.090431
C	1.479690	-0.889385	-1.359112
H	2.455327	-0.445397	-1.160592
H	2.205093	-2.652196	-0.418236
H	1.565049	-2.924356	-2.029165
H	-0.748546	-2.790482	-1.198467
H	0.135533	-3.874729	-0.146845
H	-1.317063	-2.153177	1.088146
H	0.384964	-2.123580	1.576456
C	1.530574	0.482824	1.454564
O	-2.295725	0.810044	2.241968
O	2.412110	0.778946	2.114323

S3 :

C	-1.763700	0.210483	-1.231283
C	-1.763700	0.210483	0.738877
Rh	0.044538	0.210483	0.353255
C	-0.866788	-0.398420	-2.336287
C	0.614942	-0.148309	-2.116088
H	0.965715	0.850677	-2.360680
H	-1.064347	-1.467799	-2.427876
H	-1.177396	0.057863	-3.287038
H	-1.895888	1.285030	-1.351853
H	-2.721449	-0.308662	-1.193484
Cl	0.331283	2.624976	-0.244949
C	0.132374	-1.864596	0.901008

C	0.115574	-2.769562	-0.325271
C	1.294641	-2.496295	-1.280325
C	1.518325	-1.041649	-1.649061
H	2.547581	-0.689873	-1.582324
H	2.212520	-2.865306	-0.807404
H	1.172203	-3.091534	-2.197411
H	-0.841878	-2.685181	-0.849437
H	0.174147	-3.819139	0.005076
H	-0.684981	-2.102140	1.587247
H	1.072387	-1.986905	1.448626
C	1.050489	0.601996	1.910090
O	-2.769093	0.233625	1.322552
O	1.595642	0.879111	2.879235

S4 :

C	0.113050	0.020117	1.631910
C	-0.655417	1.304854	1.982690
Rh	0.385572	-0.155094	-0.349115
C	-0.734932	-1.948869	-0.291936
C	-2.220072	-1.667832	-0.074638
C	-2.720955	-0.631165	-1.095033
C	-1.745130	0.518230	-1.285849
H	-1.377815	0.674640	-2.301542
H	-3.706512	-0.241463	-0.805301
H	-2.854576	-1.121468	-2.065803
H	-2.813968	-2.590824	-0.162334
H	-2.382109	-1.303306	0.946979
C	-1.404285	1.480927	-0.378392
C	-1.855671	1.557803	1.057435
H	-2.654290	0.840325	1.266547
H	-2.256342	2.558579	1.260142
H	-0.790573	2.308636	-0.724864
H	0.078432	2.113855	1.871021
H	-0.944496	1.238161	3.037315
H	-0.342041	-2.629600	0.468394
H	-0.562517	-2.396459	-1.281738
Cl	1.809662	1.811637	-0.862913
C	1.971416	-1.171375	-0.081612
O	2.931091	-1.772981	0.070205
O	0.569385	-0.732746	2.440221

S5 :

C	-1.575635	-0.340115	-1.206079
C	-1.575635	-0.340115	0.664886
Rh	0.437578	-0.340115	-0.009763
C	0.229670	1.954401	0.323388
C	0.560988	1.738042	-0.993611
C	-0.382903	1.711246	-2.180343
C	-1.723215	0.994392	-1.939156
H	-2.190087	0.796428	-2.914214
H	-2.429203	1.638644	-1.407947
H	-0.939616	-1.033379	-1.774273
H	-2.530509	-0.862141	-1.136361
H	0.140329	1.213129	-3.005258
H	-0.563546	2.743062	-2.519643
H	1.622021	1.742150	-1.236409
C	-1.160002	2.258528	0.848854
C	-1.910811	1.005496	1.337630
H	-2.998384	1.145057	1.274581
H	-1.690536	0.818587	2.394411
H	-1.061753	2.954240	1.689429
H	-1.739897	2.787441	0.087844
H	1.052625	2.081346	1.021785
O	-1.998703	-1.373163	1.147996
Cl	2.639373	-0.180278	0.834523
C	0.627293	-2.253381	0.180957
O	0.777410	-3.380037	0.296927

S6 :

C	-1.774634	-0.267295	-1.013622
C	-2.105615	-0.244050	0.493465
Rh	0.601770	-0.395708	-0.071303
C	0.225574	1.918378	0.307189
C	0.506987	1.724444	-1.020897
C	-0.495532	1.679636	-2.158780
C	-1.860574	1.022403	-1.859967
H	-2.322647	0.768475	-2.820203
H	-2.548690	1.726849	-1.384108
H	-0.772852	-0.776819	-1.263848
H	-2.437670	-1.046985	-1.403075
H	-0.024762	1.134654	-2.986062
H	-0.654260	2.703063	-2.532379

H	1.552298	1.776030	-1.321191
C	-1.144671	2.210001	0.888385
C	-1.931834	0.987439	1.393274
H	-2.944045	1.301849	1.683896
H	-1.469229	0.600755	2.307723
H	-1.002460	2.877785	1.746042
H	-1.739105	2.777559	0.166145
H	1.071939	2.057101	0.974598
O	-2.603316	-1.245129	0.981218
Cl	2.737608	-0.110672	0.836346
C	0.785415	-2.250349	0.285036
O	0.908539	-3.366824	0.511115

S7 :

Rh	-0.232211	0.802290	-0.341004
C	-0.404233	0.484712	1.816714
C	0.961203	0.476315	1.478024
C	-0.974700	-2.076684	1.620912
H	-0.155186	-2.481245	2.224658
H	-1.829794	-2.730471	1.819716
C	-1.345241	-0.669314	2.110252
H	-2.329620	-0.398663	1.702901
H	-0.775643	1.419637	2.235105
H	-1.485599	-0.704345	3.202161
H	1.476120	1.414971	1.672739
C	1.929169	-0.703914	1.371835
H	1.805073	-1.364019	2.239367
H	2.934763	-0.281900	1.465399
C	1.946205	-1.552496	0.073111
H	1.914824	-0.879449	-0.798048
H	2.891441	-2.100336	0.017957
C	0.846317	-2.594111	-0.092502
C	-0.611021	-2.185938	0.112005
H	-1.222945	-2.943538	-0.384240
H	-0.858910	-1.249380	-0.434115
O	1.116927	-3.749475	-0.356559
Cl	-0.836020	0.789548	-2.603955
C	-0.098497	2.608196	-0.274094
O	-0.016664	3.756072	-0.224531

S8 :

SCF Done: E(RB+HF-LYP) = -956.983271424

Zero-point vibrational energy 484522.0 (Joules/Mol)
115.80355 (Kcal/Mol)

Zero-point correction=	0.184545 (Hartree/Particle)
Thermal correction to Energy=	0.196537
Thermal correction to Enthalpy=	0.197482
Thermal correction to Gibbs Free Energy=	0.145728
Sum of electronic and zero-point Energies=	-956.798727
Sum of electronic and thermal Energies=	-956.786734
Sum of electronic and thermal Enthalpies=	-956.785790
Sum of electronic and thermal Free Energies=	-956.837544

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	123.329	44.374	108.925
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.589
Rotational	0.889	2.981	31.087
Vibrational	121.552	38.413	35.250

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.074229	1.221906	1.269122
2	6	0	1.224110	1.445720	-0.744008
3	45	0	-0.449229	0.073215	0.003797
4	6	0	2.539576	0.719100	-1.008123
5	6	0	2.296350	-0.781000	-1.257905
6	6	0	1.326477	-1.474228	-0.319105
7	6	0	1.108668	-1.246092	1.016264
8	6	0	1.696492	-0.084712	1.798580
9	1	0	1.451807	-0.194285	2.860871
10	1	0	2.789737	-0.069417	1.725773
11	1	0	0.207871	1.555199	1.845234
12	1	0	1.792627	2.039252	1.280826
13	6	0	-1.885898	1.296433	-0.142974
14	8	0	-2.781241	2.011952	-0.215674
15	1	0	3.010407	1.151553	-1.902027

16	1	0	3.252482	0.875219	-0.191512
17	17	0	-2.041813	-1.680343	-0.165188
18	1	0	1.908214	-0.908733	-2.275676
19	1	0	3.251940	-1.327677	-1.233694
20	1	0	0.855348	-2.364619	-0.730506
21	1	0	0.504920	-1.971821	1.554491
22	1	0	1.317295	2.525616	-0.638923
23	1	0	0.553374	1.282480	-1.603254

CO ：

SCF Done: E(RB+HF-LYP) = -113.306913781

Zero-point vibrational energy 13222.8 (Joules/Mol)
3.16034 (Kcal/Mol)

Zero-point correction= 0.005036 (Hartree/Particle)
Thermal correction to Energy= 0.007397
Thermal correction to Enthalpy= 0.008341
Thermal correction to Gibbs Free Energy= -0.014102
Sum of electronic and zero-point Energies= -113.301877
Sum of electronic and thermal Energies= -113.299517
Sum of electronic and thermal Enthalpies= -113.298573
Sum of electronic and thermal Free Energies= -113.321016

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	4.642	4.973	47.235
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	35.923
Rotational	0.592	1.987	11.312
Vibrational	3.160	0.005	0.001

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-0.650130
2	8	0	0.000000	0.000000	0.487597

S9 :

SCF Done: E(RB+HF-LYP) = -1073.75138044

Zero-point vibrational energy 655753.4 (Joules/Mol)
156.72882 (Kcal/Mol)

Zero-point correction=	0.249763 (Hartree/Particle)
Thermal correction to Energy=	0.264716
Thermal correction to Enthalpy=	0.265660
Thermal correction to Gibbs Free Energy=	0.206640
Sum of electronic and zero-point Energies=	-1073.501617
Sum of electronic and thermal Energies=	-1073.486664
Sum of electronic and thermal Enthalpies=	-1073.485720
Sum of electronic and thermal Free Energies=	-1073.544740

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	166.112	56.196	124.218
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.013
Rotational	0.889	2.981	32.313
Vibrational	164.335	50.234	48.893

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.594839	-0.045374	1.369205
2	6	0	2.148755	-1.438855	0.973767
3	6	0	3.369789	-1.170218	0.048894
4	6	0	3.516130	0.369544	-0.028406
5	6	0	2.099830	0.917838	0.254284
6	6	0	1.229798	0.855441	-0.981395
7	6	0	0.224865	1.715677	-1.315421
8	6	0	-0.374358	2.774505	-0.406262
9	6	0	-1.522342	2.019774	0.276000
10	45	0	-0.963896	0.031425	-0.131834
11	6	0	-2.423112	-0.711291	0.759532
12	8	0	-3.324865	-1.154689	1.313971
13	6	0	0.104930	0.045258	1.668316
14	17	0	-0.579898	-1.974779	-1.508588
15	1	0	4.191932	0.729670	0.757048

16	1	0	3.923185	0.714385	-0.985538
17	1	0	2.130543	1.947762	0.627687
18	1	0	2.104287	0.267186	2.297318
19	1	0	1.388490	-2.015988	0.439925
20	1	0	2.423122	-2.007074	1.869017
21	1	0	1.484354	0.091965	-1.713849
22	1	0	-0.231299	1.595682	-2.299136
23	1	0	-0.709784	3.649004	-0.977682
24	1	0	0.361996	3.121128	0.325589
25	1	0	-1.649579	2.255681	1.334840
26	1	0	-2.477749	2.146889	-0.245064
27	1	0	-0.240616	-0.822962	2.237434
28	1	0	-0.151008	0.954681	2.217284
29	1	0	4.288501	-1.638397	0.416458
30	1	0	3.181404	-1.588793	-0.945648

S10 :

SCF Done: E(RB+HF-LYP) = -1187.07473493

Zero-point vibrational energy 676672.1 (Joules/Mol)
161.72852 (Kcal/Mol)

Zero-point correction= 0.257731 (Hartree/Particle)
Thermal correction to Energy= 0.275485
Thermal correction to Enthalpy= 0.276429
Thermal correction to Gibbs Free Energy= 0.211240
Sum of electronic and zero-point Energies= -1186.817004
Sum of electronic and thermal Energies= -1186.799250
Sum of electronic and thermal Enthalpies= -1186.798306
Sum of electronic and thermal Free Energies= -1186.863495

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.869	64.952	137.202
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.941

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	3.701057	0.714748	-0.339260
2	6	0	2.283404	0.897762	0.256156
3	6	0	2.091956	-0.390470	1.084949
4	6	0	2.722333	-1.501897	0.210657
5	6	0	3.819279	-0.803344	-0.643410
6	6	0	1.254335	0.994145	-0.845141
7	6	0	0.242237	1.906183	-0.929701
8	6	0	-0.217091	2.809397	0.206865
9	6	0	-1.006606	1.890446	1.156324
10	45	0	-0.842275	0.016639	0.154891
11	17	0	-0.525289	-2.013653	-1.330449
12	6	0	0.647650	-0.616880	1.549269
13	6	0	-1.981970	-0.878801	1.341060
14	8	0	-2.665133	-1.427718	2.078860
15	6	0	-2.338926	0.393398	-1.270312
16	8	0	-3.151613	0.440171	-2.068057
17	1	0	4.434304	1.012216	0.419835
18	1	0	3.880062	1.344462	-1.218232
19	1	0	2.223314	1.787726	0.893074
20	1	0	2.713372	-0.286760	1.990441
21	1	0	1.957993	-1.949509	-0.429982
22	1	0	3.128986	-2.303931	0.835950
23	1	0	1.424082	0.364777	-1.717256
24	1	0	-0.285156	1.987439	-1.877524
25	1	0	-0.841826	3.615113	-0.192371
26	1	0	0.636703	3.280371	0.707150
27	1	0	-0.563274	1.808968	2.148994
28	1	0	-2.060297	2.160508	1.242389
29	1	0	0.475588	-1.681698	1.733304
30	1	0	0.453424	-0.074043	2.479267
31	1	0	4.824990	-1.167985	-0.410071
32	1	0	3.658041	-1.002060	-1.708610

S11 ：

SCF Done: E(RB+HF-LYP) = -1187.05388086

Zero-point vibrational energy 676367.2 (Joules/Mol)
161.65563 (Kcal/Mol)

Zero-point correction= 0.257615 (Hartree/Particle)
Thermal correction to Energy= 0.274479

Thermal correction to Enthalpy=	0.275423
Thermal correction to Gibbs Free Energy=	0.212362
Sum of electronic and zero-point Energies=	-1186.796266
Sum of electronic and thermal Energies=	-1186.779402
Sum of electronic and thermal Enthalpies=	-1186.778458
Sum of electronic and thermal Free Energies=	-1186.841519

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.238	62.584	132.723
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.986
Vibrational	170.461	56.622	56.460
Vibration 1	0.595	1.979	4.981

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.686470	-1.925361	-0.547479
2	6	0	-0.375162	-2.589478	-0.068855
3	6	0	0.247933	-1.821006	1.081854
4	6	0	1.413941	-1.134856	1.050317
5	6	0	2.410241	-1.071668	-0.089127
6	6	0	-2.087657	-0.160608	-1.300982
7	6	0	3.841834	-0.755135	0.420367
8	6	0	4.005300	0.793989	0.330053
9	6	0	2.705975	1.321231	-0.326276
10	6	0	2.125178	0.103148	-1.069085
11	6	0	0.694150	0.192949	-1.599080
12	8	0	-2.906993	-0.033787	-2.116104
13	6	0	-0.579438	2.097194	0.118456
14	8	0	-0.557821	3.241129	0.190393
15	17	0	-2.280409	0.293882	1.944118
16	45	0	-0.780090	0.223050	-0.051091
17	1	0	-2.485826	-1.979281	0.191453
18	1	0	-1.995325	-2.352997	-1.501860
19	1	0	-0.622646	-3.615920	0.243175
20	1	0	0.322605	-2.672823	-0.905870
21	1	0	-0.332432	-1.803769	2.001524
22	1	0	1.691106	-0.608117	1.963866
23	1	0	2.392875	-2.024729	-0.630866

24	1	0	4.006459	-1.135857	1.433940
25	1	0	4.575079	-1.253232	-0.222868
26	1	0	2.769909	-0.063311	-1.951013
27	1	0	4.878804	1.047283	-0.280305
28	1	0	4.169676	1.247557	1.312621
29	1	0	2.879789	2.171259	-0.995059
30	1	0	2.006372	1.660178	0.446903
31	1	0	0.570796	1.073699	-2.236697
32	1	0	0.467351	-0.684303	-2.215118

S12 ：

SCF Done: E(RB+HF-LYP) = -1187.10468345

Zero-point vibrational energy 682239.4 (Joules/Mol)
163.05914 (Kcal/Mol)

Zero-point correction= 0.259851 (Hartree/Particle)
Thermal correction to Energy= 0.276817
Thermal correction to Enthalpy= 0.277761
Thermal correction to Gibbs Free Energy= 0.214085
Sum of electronic and zero-point Energies= -1186.844832
Sum of electronic and thermal Energies= -1186.827867
Sum of electronic and thermal Enthalpies= -1186.826923
Sum of electronic and thermal Free Energies= -1186.890598

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.705	62.842	134.016
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.124

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.438774	0.372465	1.526158
2	6	0	-1.342997	1.903342	1.639956
3	6	0	-0.021206	2.461982	1.095459
4	6	0	0.159226	2.014414	-0.331294
5	6	0	1.149861	1.225914	-0.835203

6	6	0	2.300843	0.595993	-0.109234
7	6	0	3.694028	0.715705	-0.758330
8	6	0	4.498992	-0.483327	-0.167820
9	6	0	3.454568	-1.425965	0.502476
10	6	0	2.088948	-0.930566	-0.023145
11	6	0	0.833161	-1.259604	0.769315
12	45	0	-0.769847	-0.282947	-0.248657
13	8	0	-2.430954	-2.804271	-0.014040
14	6	0	-1.802420	-1.852037	-0.093929
15	17	0	-2.388812	0.610313	-1.887509
16	8	0	-1.926718	-0.328918	2.361832
17	1	0	-2.187003	2.292941	1.055276
18	1	0	-1.504530	2.160565	2.692673
19	1	0	-0.057187	3.558352	1.133769
20	1	0	0.810178	2.141704	1.730284
21	1	0	-0.571446	2.404080	-1.036456
22	1	0	1.120369	1.040517	-1.911694
23	1	0	2.354925	0.978346	0.918781
24	1	0	3.601557	0.615658	-1.847457
25	1	0	4.168848	1.683219	-0.565705
26	1	0	5.239238	-0.140970	0.562763
27	1	0	5.055402	-0.999118	-0.957089
28	1	0	3.482521	-1.317194	1.594284
29	1	0	3.630981	-2.482986	0.278960
30	1	0	1.972301	-1.304175	-1.054409
31	1	0	0.647349	-2.337882	0.812049
32	1	0	0.905400	-0.900143	1.802393

S13 ：

SCF Done: E(RB+HF-LYP) = -1187.06679896

Zero-point vibrational energy 680349.8 (Joules/Mol)
162.60751 (Kcal/Mol)

Zero-point correction= 0.259132 (Hartree/Particle)
Thermal correction to Energy= 0.275271
Thermal correction to Enthalpy= 0.276215
Thermal correction to Gibbs Free Energy= 0.214733
Sum of electronic and zero-point Energies= -1186.807667
Sum of electronic and thermal Energies= -1186.791528
Sum of electronic and thermal Enthalpies= -1186.790584
Sum of electronic and thermal Free Energies= -1186.852066

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.735	61.082	129.399
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.939

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.694557	1.457418	1.185408
2	6	0	0.903269	0.196506	1.298697
3	6	0	-0.376697	2.766755	0.453155
4	6	0	0.312632	2.598936	-0.904934
5	6	0	-0.084862	1.304352	-1.590517
6	6	0	2.186640	0.450683	0.498740
7	6	0	3.377272	-0.394413	1.077503
8	6	0	3.844733	-1.331728	-0.062847
9	6	0	2.635565	-1.424469	-1.003060
10	6	0	2.081930	0.014419	-0.994644
11	6	0	0.713919	0.157121	-1.630534
12	45	0	-0.820217	-0.234663	-0.121494
13	8	0	-3.174036	-0.946120	-1.936187
14	6	0	-2.266025	-0.710523	-1.277945
15	17	0	-1.770596	-1.851122	1.395884
16	8	0	-1.387587	1.423220	2.161313
17	1	0	-1.355862	3.247449	0.339975
18	1	0	0.201875	3.400177	1.138269
19	1	0	0.039206	3.439946	-1.551850
20	1	0	1.398599	2.643213	-0.790968
21	1	0	-0.866621	1.395538	-2.340927
22	1	0	0.501550	-0.569288	-2.415911
23	1	0	2.779860	0.635029	-1.582524
24	1	0	2.893375	-1.771102	-2.010275
25	1	0	1.883173	-2.114898	-0.598430
26	1	0	4.690986	-0.882626	-0.598474
27	1	0	4.176558	-2.307734	0.305003
28	1	0	4.187900	0.248427	1.436213
29	1	0	3.036739	-0.978370	1.939736
30	1	0	2.435872	1.513668	0.567127
31	1	0	0.737679	-0.864480	1.523281

32	1	0	0.959054	0.666814	2.281818

S14 :

SCF Done: E(RB+HF-LYP) = -1187.10095360

Zero-point vibrational energy 687155.0 (Joules/Mol)
164.23400 (Kcal/Mol)

Zero-point correction= 0.261724 (Hartree/Particle)
Thermal correction to Energy= 0.278287
Thermal correction to Enthalpy= 0.279232
Thermal correction to Gibbs Free Energy= 0.216050
Sum of electronic and zero-point Energies= -1186.839230
Sum of electronic and thermal Energies= -1186.822666
Sum of electronic and thermal Enthalpies= -1186.821722
Sum of electronic and thermal Free Energies= -1186.884904

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	174.628	61.424	132.977
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.097
Vibrational	172.850	55.462	56.603

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.974299	1.843037	-0.521874
2	6	0	-0.575667	2.630621	0.701538
3	45	0	1.252758	0.043501	-0.086724
4	6	0	-2.427212	1.578444	-0.804364
5	6	0	-2.766119	0.072743	-0.581860
6	6	0	-2.301256	-0.898760	-1.692241
7	6	0	-2.332820	-2.309574	-1.037777
8	6	0	-2.795219	-2.081748	0.422145
9	6	0	-2.351741	-0.637162	0.751841
10	6	0	-0.900921	-0.636663	1.243999
11	6	0	-0.260762	0.388597	1.869478

12	6	0	-0.831511	1.785278	1.982593
13	17	0	2.434631	-1.570206	1.152854
14	8	0	-0.128641	1.262038	-1.217256
15	1	0	-3.062184	2.209385	-0.173406
16	1	0	-2.644899	1.822489	-1.851562
17	1	0	-3.864332	0.045809	-0.564914
18	1	0	-2.957989	-0.823267	-2.566546
19	1	0	-1.290952	-0.648044	-2.023571
20	1	0	-2.997019	-3.001512	-1.564976
21	1	0	-1.332115	-2.753708	-1.055133
22	1	0	-3.888064	-2.145060	0.491520
23	1	0	-2.385957	-2.818144	1.121327
24	1	0	-2.954403	-0.223874	1.574244
25	1	0	0.655937	0.169142	2.412988
26	1	0	-0.383717	2.312304	2.830709
27	1	0	-1.912122	1.734800	2.170833
28	1	0	-1.154254	3.561907	0.754953
29	1	0	0.490072	2.865720	0.620563
30	8	0	3.557782	0.297049	-1.984814
31	6	0	2.668602	0.193123	-1.258770
32	1	0	-0.420405	-1.612284	1.295313

S15 :

SCF Done: E(RB+HF-LYP) = -1073.71128906

Zero-point vibrational energy 653958.1 (Joules/Mol)
156.29974 (Kcal/Mol)

Zero-point correction= 0.249079 (Hartree/Particle)
Thermal correction to Energy= 0.263588
Thermal correction to Enthalpy= 0.264532
Thermal correction to Gibbs Free Energy= 0.206619
Sum of electronic and zero-point Energies= -1073.462210
Sum of electronic and thermal Energies= -1073.447701
Sum of electronic and thermal Enthalpies= -1073.446757
Sum of electronic and thermal Free Energies= -1073.504670

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	165.404	54.765	121.888
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.013

Rotational	0.889	2.981	32.400
Vibrational	163.627	48.804	46.475

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.983762	-1.224155	-0.580560
2	6	0	-0.063369	-1.943399	1.003765
3	45	0	-0.923662	-0.097077	-0.034885
4	8	0	-2.797985	-1.281942	-2.116631
5	6	0	-2.070191	-0.846406	-1.342211
6	17	0	-2.374081	1.784963	0.022962
7	6	0	2.246684	-0.721818	0.119321
8	6	0	3.438225	-0.588701	-0.857829
9	6	0	3.237434	0.766944	-1.570950
10	6	0	2.412949	1.642360	-0.588444
11	6	0	2.054276	0.734117	0.628811
12	6	0	0.707059	1.082563	1.233149
13	6	0	-0.084965	0.305299	2.040420
14	6	0	0.171871	-1.165616	2.313346
15	1	0	1.079642	-2.224335	-1.002214
16	1	0	0.754955	-0.561414	-1.431055
17	1	0	2.516352	-1.398944	0.937162
18	1	0	3.508389	-1.433105	-1.552925
19	1	0	4.368732	-0.575778	-0.275627
20	1	0	2.689300	0.629520	-2.509282
21	1	0	4.194860	1.227104	-1.834823
22	1	0	2.968930	2.525309	-0.256737
23	1	0	1.499215	2.008444	-1.067774
24	1	0	2.806529	0.908474	1.415070
25	1	0	0.421735	2.129858	1.149163
26	1	0	-0.918926	0.785902	2.544790
27	1	0	-0.520770	-1.529528	3.080234
28	1	0	1.185906	-1.324900	2.697327
29	1	0	-1.072961	-2.352157	0.917497
30	1	0	0.623759	-2.781971	0.908803

S16 :

SCF Done: E(RB+HF-LYP) = -1187.05388086

Zero-point vibrational energy 676367.2 (Joules/Mol)
161.65563 (Kcal/Mol)

Zero-point correction= 0.257615 (Hartree/Particle)
Thermal correction to Energy= 0.274479
Thermal correction to Enthalpy= 0.275423
Thermal correction to Gibbs Free Energy= 0.212362
Sum of electronic and zero-point Energies= -1186.796266
Sum of electronic and thermal Energies= -1186.779402
Sum of electronic and thermal Enthalpies= -1186.778458
Sum of electronic and thermal Free Energies= -1186.841519

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.238	62.584	132.723
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.986

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.686470	-1.925361	-0.547479
2	6	0	-0.375162	-2.589478	-0.068855
3	6	0	0.247933	-1.821006	1.081854
4	6	0	1.413941	-1.134856	1.050317
5	6	0	2.410241	-1.071668	-0.089127
6	6	0	-2.087657	-0.160608	-1.300982
7	6	0	3.841834	-0.755135	0.420367
8	6	0	4.005300	0.793989	0.330053
9	6	0	2.705975	1.321231	-0.326276
10	6	0	2.125178	0.103148	-1.069085
11	6	0	0.694150	0.192949	-1.599080
12	8	0	-2.906993	-0.033787	-2.116104
13	6	0	-0.579438	2.097194	0.118456
14	8	0	-0.557821	3.241129	0.190393
15	17	0	-2.280409	0.293882	1.944118
16	45	0	-0.780090	0.223050	-0.051091
17	1	0	-2.485826	-1.979281	0.191453
18	1	0	-1.995325	-2.352997	-1.501860
19	1	0	-0.622646	-3.615920	0.243175

20	1	0	0.322605	-2.672823	-0.905870
21	1	0	-0.332432	-1.803769	2.001524
22	1	0	1.691106	-0.608117	1.963866
23	1	0	2.392875	-2.024729	-0.630866
24	1	0	4.006459	-1.135857	1.433940
25	1	0	4.575079	-1.253232	-0.222868
26	1	0	2.769909	-0.063311	-1.951013
27	1	0	4.878804	1.047283	-0.280305
28	1	0	4.169676	1.247557	1.312621
29	1	0	2.879789	2.171259	-0.995059
30	1	0	2.006372	1.660178	0.446903
31	1	0	0.570796	1.073699	-2.236697
32	1	0	0.467351	-0.684303	-2.215118

S17 :

SCF Done: E(RB+HF-LYP) = -1187.09479687

Zero-point vibrational energy 682084.3 (Joules/Mol)
163.02205 (Kcal/Mol)

Zero-point correction= 0.259792 (Hartree/Particle)
Thermal correction to Energy= 0.276822
Thermal correction to Enthalpy= 0.277766
Thermal correction to Gibbs Free Energy= 0.212947
Sum of electronic and zero-point Energies= -1186.835005
Sum of electronic and thermal Energies= -1186.817975
Sum of electronic and thermal Enthalpies= -1186.817031
Sum of electronic and thermal Free Energies= -1186.881850

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.709	62.918	136.424
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.095
Vibrational	171.931	56.956	60.052

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-4.483670	-0.268579	-0.080815
2	6	0	-3.609526	0.862620	0.491691
3	6	0	-2.186613	0.662950	-0.134784
4	6	0	-2.236092	-0.765402	-0.795352
5	6	0	-3.499426	-1.437238	-0.221688
6	6	0	-1.134146	0.867348	0.925908
7	6	0	-0.201358	1.864178	0.956364
8	45	0	1.211339	0.169456	0.167796
9	6	0	2.878994	-0.386624	-0.519278
10	8	0	3.901565	-0.701844	-0.927507
11	6	0	-0.965714	-1.615149	-0.636567
12	6	0	0.260873	-0.910933	-1.235451
13	8	0	0.614007	-1.013476	-2.371779
14	6	0	0.173489	2.766691	-0.211014
15	6	0	1.150725	1.908618	-1.040017
16	17	0	1.275120	-1.330143	2.131373
17	1	0	-2.399794	-0.611285	-1.869609
18	1	0	-3.867835	-2.246385	-0.861499
19	1	0	-3.283302	-1.869819	0.765095
20	1	0	-3.549702	0.760318	1.582724
21	1	0	-4.004049	1.863269	0.289291
22	1	0	-2.029741	1.397845	-0.929192
23	1	0	-1.231441	0.259885	1.824916
24	1	0	0.350432	1.998769	1.888325
25	1	0	0.645315	3.679898	0.166072
26	1	0	-0.706337	3.071221	-0.788094
27	1	0	2.153885	2.336362	-1.103011
28	1	0	0.789726	1.676384	-2.042910
29	1	0	-0.774614	-1.862350	0.409697
30	1	0	-1.072178	-2.546188	-1.206389
31	1	0	-4.875439	0.010862	-1.067625
32	1	0	-5.342002	-0.500200	0.558338

S18 :

SCF Done: E(RB+HF-LYP) = -1187.06313063

Zero-point vibrational energy 681597.8 (Joules/Mol)
162.90578 (Kcal/Mol)

Zero-point correction= 0.259607 (Hartree/Particle)
Thermal correction to Energy= 0.275829
Thermal correction to Enthalpy= 0.276774

Thermal correction to Gibbs Free Energy=	0.215233
Sum of electronic and zero-point Energies=	-1186.803524
Sum of electronic and thermal Energies=	-1186.787301
Sum of electronic and thermal Enthalpies=	-1186.786357
Sum of electronic and thermal Free Energies=	-1186.847898

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.086	60.847	129.523
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.819

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.685226	1.322941	1.428256
2	6	0	-0.718873	1.840889	0.726312
3	6	0	1.962527	0.509620	1.021760
4	6	0	2.024545	-0.915607	1.656967
5	6	0	2.828956	-1.803044	0.671954
6	6	0	3.407464	-0.824798	-0.369859
7	6	0	-0.695889	2.703543	-0.541908
8	6	0	2.356731	0.300017	-0.471345
9	6	0	1.202524	-0.085570	-1.379899
10	6	0	0.302857	0.815351	-1.890697
11	6	0	0.338080	2.299797	-1.597280
12	8	0	-2.688460	-1.372720	1.979661
13	6	0	-1.940036	-0.958503	1.218516
14	45	0	-0.700440	-0.306138	-0.073444
15	17	0	-1.685918	-1.787569	-1.599249
16	8	0	-1.639643	1.981432	1.522814
17	1	0	-1.710647	2.647389	-0.949325
18	1	0	-0.543905	3.746227	-0.226832
19	1	0	0.138825	2.852433	-2.522915
20	1	0	1.339230	2.597300	-1.266242
21	1	0	-0.385710	0.476610	-2.660741
22	1	0	1.200239	-1.094256	-1.788344
23	1	0	2.814675	1.215860	-0.867045
24	1	0	4.352458	-0.398888	-0.009634
25	1	0	3.611791	-2.384699	1.168705
26	1	0	2.160232	-2.521121	0.184156

27	1	0	2.498257	-0.861934	2.643584
28	1	0	1.018432	-1.320213	1.810444
29	1	0	2.797328	1.077637	1.454843
30	1	0	0.346195	0.975284	2.407340
31	1	0	1.029485	2.355893	1.595054
32	1	0	3.613678	-1.296147	-1.337330

S19 :

SCF Done: E(RB+HF-LYP) = -1073.75411686

Zero-point vibrational energy 654653.6 (Joules/Mol)
156.46598 (Kcal/Mol)

Zero-point correction= 0.249344 (Hartree/Particle)
Thermal correction to Energy= 0.264614
Thermal correction to Enthalpy= 0.265558
Thermal correction to Gibbs Free Energy= 0.205570
Sum of electronic and zero-point Energies= -1073.504772
Sum of electronic and thermal Energies= -1073.489503
Sum of electronic and thermal Enthalpies= -1073.488559
Sum of electronic and thermal Free Energies= -1073.548546

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	166.048	56.650	126.254
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.013
Rotational	0.889	2.981	32.507
Vibrational	164.270	50.688	50.734

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.839811	-1.185636	-1.361644
2	6	0	-4.047007	-0.715778	-0.495269
3	6	0	-3.456587	0.186161	0.627255
4	6	0	-2.024957	0.508277	0.154400
5	6	0	-1.590978	-0.816414	-0.523321
6	6	0	-1.044782	0.910144	1.216572
7	6	0	-0.126076	1.912870	1.136915

8	45	0	1.084469	0.100341	0.075107
9	17	0	1.119364	-1.688662	1.771563
10	6	0	-0.293570	-0.681959	-1.290546
11	6	0	0.142275	2.772224	-0.090524
12	6	0	1.140472	1.951588	-0.923852
13	6	0	2.448837	-0.627754	-0.944221
14	8	0	3.298596	-1.072313	-1.576216
15	1	0	-4.050849	1.088191	0.806203
16	1	0	-3.411102	-0.363258	1.575777
17	1	0	-2.071770	1.278013	-0.627893
18	1	0	-1.453796	-1.567680	0.263874
19	1	0	-2.875327	-2.253759	-1.597044
20	1	0	-2.818432	-0.643472	-2.315670
21	1	0	-1.078720	0.329718	2.137411
22	1	0	0.500018	2.088053	2.012781
23	1	0	0.544173	3.747535	0.207794
24	1	0	-0.784105	2.960324	-0.642501
25	1	0	0.878791	1.883978	-1.982735
26	1	0	2.167317	2.320798	-0.830438
27	1	0	0.104923	-1.647153	-1.611494
28	1	0	-0.364027	-0.000664	-2.143842
29	1	0	-4.768870	-0.165215	-1.107484
30	1	0	-4.584190	-1.567339	-0.066007

S20 :

SCF Done: E(RB+HF-LYP) = -1187.08008964

Zero-point vibrational energy 676177.9 (Joules/Mol)
161.61039 (Kcal/Mol)

Zero-point correction= 0.257543 (Hartree/Particle)
Thermal correction to Energy= 0.275416
Thermal correction to Enthalpy= 0.276360
Thermal correction to Gibbs Free Energy= 0.210681
Sum of electronic and zero-point Energies= -1186.822547
Sum of electronic and thermal Energies= -1186.804674
Sum of electronic and thermal Enthalpies= -1186.803729
Sum of electronic and thermal Free Energies= -1186.869409

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	172.826	65.143	138.234

Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.067

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.973733	-0.766844	-0.186894
2	6	0	-3.345872	-1.239365	-0.715154
3	6	0	-4.386783	-0.438353	0.125452
4	6	0	-3.587912	0.675158	0.867754
5	6	0	-2.229554	0.718469	0.140321
6	6	0	-1.079627	1.302424	0.905705
7	6	0	-0.122676	2.144738	0.425324
8	6	0	0.058171	2.554343	-1.029321
9	6	0	0.968363	1.485286	-1.653532
10	45	0	0.914008	-0.038899	-0.166051
11	6	0	2.551665	0.658256	0.944532
12	8	0	3.442532	0.901971	1.612109
13	6	0	-0.773390	-0.940624	-1.104333
14	17	0	0.720612	-1.588249	1.827769
15	6	0	1.879499	-1.234537	-1.212832
16	8	0	2.463321	-1.973562	-1.866709
17	1	0	-4.102857	1.641728	0.864636
18	1	0	-3.430039	0.396360	1.917211
19	1	0	-2.354376	1.253548	-0.811609
20	1	0	-1.761987	-1.284896	0.755963
21	1	0	-3.473242	-2.322835	-0.623791
22	1	0	-3.441767	-0.990745	-1.780402
23	1	0	-1.033410	1.040825	1.962433
24	1	0	0.588568	2.556345	1.138885
25	1	0	0.495949	3.557850	-1.089311
26	1	0	-0.909198	2.591865	-1.539263
27	1	0	0.598182	1.100981	-2.604783
28	1	0	2.002219	1.816098	-1.767326
29	1	0	-0.567417	-2.001992	-1.271718
30	1	0	-0.924232	-0.456602	-2.076216
31	1	0	-5.157201	-0.005400	-0.521419
32	1	0	-4.905699	-1.083426	0.841616

S21 ：

SCF Done: E(RB+HF-LYP) = -1187.05789559

Zero-point vibrational energy 675598.1 (Joules/Mol)
161.47182 (Kcal/Mol)

Zero-point correction=	0.257322 (Hartree/Particle)
Thermal correction to Energy=	0.274390
Thermal correction to Enthalpy=	0.275334
Thermal correction to Gibbs Free Energy=	0.211621
Sum of electronic and zero-point Energies=	-1186.800574
Sum of electronic and thermal Energies=	-1186.783506
Sum of electronic and thermal Enthalpies=	-1186.782561
Sum of electronic and thermal Free Energies=	-1186.846274

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.182	62.892	134.095
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.152

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.841387	0.078089	1.574310
2	6	0	1.419154	-1.785389	1.130673
3	6	0	0.150710	-2.472247	0.579139
4	6	0	-0.212796	-2.012282	-0.820253
5	6	0	-1.296900	-1.286927	-1.171313
6	6	0	-2.370333	-0.762065	-0.259084
7	6	0	-3.774126	-0.619642	-0.879849
8	6	0	-4.512613	0.407732	0.026855
9	6	0	-3.416130	1.076330	0.906537
10	6	0	-2.074411	0.672531	0.250638
11	6	0	-0.847482	0.757907	1.149890
12	8	0	1.067105	3.105239	-0.998143
13	6	0	0.947058	2.019879	-0.650645
14	45	0	0.884638	0.241378	0.005721
15	17	0	2.669366	-0.322446	-1.638665
16	8	0	2.478730	0.343135	2.510250
17	1	0	2.324010	-2.052534	0.584746

18	1	0	1.521330	-2.001537	2.194534
19	1	0	0.353456	-3.554717	0.576910
20	1	0	-0.679917	-2.312175	1.271263
21	1	0	0.493964	-2.286463	-1.599939
22	1	0	-1.395740	-1.020763	-2.224896
23	1	0	-2.449633	-1.403891	0.629875
24	1	0	-4.299662	-1.577467	-0.952535
25	1	0	-3.681086	-0.229447	-1.901848
26	1	0	-5.265613	-0.082845	0.652270
27	1	0	-5.044676	1.147948	-0.579412
28	1	0	-3.530976	2.162792	0.978576
29	1	0	-3.451545	0.681202	1.930094
30	1	0	-1.925446	1.310809	-0.634390
31	1	0	-0.721886	1.758644	1.573214
32	1	0	-0.922309	0.049541	1.983149

S22 ：

SCF Done: E(RB+HF-LYP) = -1187.10468345

Zero-point vibrational energy 682239.4 (Joules/Mol)
163.05914 (Kcal/Mol)

Zero-point correction= 0.259851 (Hartree/Particle)
Thermal correction to Energy= 0.276817
Thermal correction to Enthalpy= 0.277761
Thermal correction to Gibbs Free Energy= 0.214085
Sum of electronic and zero-point Energies= -1186.844832
Sum of electronic and thermal Energies= -1186.827867
Sum of electronic and thermal Enthalpies= -1186.826923
Sum of electronic and thermal Free Energies= -1186.890598

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	173.705	62.842	134.016
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.124

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-1.438774	0.372465	1.526158
2	6	0	-1.342997	1.903342	1.639956
3	6	0	-0.021206	2.461982	1.095459
4	6	0	0.159226	2.014414	-0.331294
5	6	0	1.149861	1.225914	-0.835203
6	6	0	2.300843	0.595993	-0.109234
7	6	0	3.694028	0.715705	-0.758330
8	6	0	4.498992	-0.483327	-0.167820
9	6	0	3.454568	-1.425965	0.502476
10	6	0	2.088948	-0.930566	-0.023145
11	6	0	0.833161	-1.259604	0.769315
12	45	0	-0.769847	-0.282947	-0.248657
13	8	0	-2.430954	-2.804271	-0.014040
14	6	0	-1.802420	-1.852037	-0.093929
15	17	0	-2.388812	0.610313	-1.887509
16	8	0	-1.926718	-0.328918	2.361832
17	1	0	-2.187003	2.292941	1.055276
18	1	0	-1.504530	2.160565	2.692673
19	1	0	-0.057187	3.558352	1.133769
20	1	0	0.810178	2.141704	1.730284
21	1	0	-0.571446	2.404080	-1.036456
22	1	0	1.120369	1.040517	-1.911694
23	1	0	2.354925	0.978346	0.918781
24	1	0	3.601557	0.615658	-1.847457
25	1	0	4.168848	1.683219	-0.565705
26	1	0	5.239238	-0.140970	0.562763
27	1	0	5.055402	-0.999118	-0.957089
28	1	0	3.482521	-1.317194	1.594284
29	1	0	3.630981	-2.482986	0.278960
30	1	0	1.972301	-1.304175	-1.054409
31	1	0	0.647349	-2.337882	0.812049
32	1	0	0.905400	-0.900143	1.802393

S23 :

SCF Done: E(RB+HF-LYP) = -1187.06670712

Zero-point vibrational energy 680840.5 (Joules/Mol)
162.72478 (Kcal/Mol)

Zero-point correction= 0.259318 (Hartree/Particle)
Thermal correction to Energy= 0.275604
Thermal correction to Enthalpy= 0.276549

Thermal correction to Gibbs Free Energy=	0.214956
Sum of electronic and zero-point Energies=	-1186.807389
Sum of electronic and thermal Energies=	-1186.791103
Sum of electronic and thermal Enthalpies=	-1186.790158
Sum of electronic and thermal Free Energies=	-1186.851751

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.944	61.148	129.632
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.023

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.850848	1.488081	-0.638397
2	6	0	0.575242	1.894162	0.261823
3	45	0	0.877828	-0.252390	-0.144702
4	6	0	-1.800879	0.271282	-0.789905
5	6	0	-3.202952	0.616873	-1.337611
6	6	0	-4.066231	-0.635597	-1.004684
7	6	0	-3.244503	-1.466368	0.026820
8	6	0	-2.141663	-0.503328	0.502436
9	6	0	-0.917473	-1.114959	1.140739
10	6	0	-0.102923	-0.450639	2.020634
11	6	0	-0.349228	0.957398	2.521304
12	6	0	0.516140	1.996332	1.797154
13	8	0	1.302887	2.658693	-0.353145
14	8	0	2.679059	0.242074	-2.548493
15	6	0	1.998665	0.073191	-1.643178
16	17	0	2.273387	-2.065324	0.372094
17	1	0	-0.585919	1.881415	-1.621096
18	1	0	-1.428039	2.271741	-0.123252
19	1	0	-1.349644	-0.447785	-1.487609
20	1	0	-3.590469	1.503591	-0.817544
21	1	0	-3.187272	0.851646	-2.406693
22	1	0	-4.272382	-1.226693	-1.902332
23	1	0	-5.036849	-0.339591	-0.594244
24	1	0	-2.786309	-2.337356	-0.458594
25	1	0	-3.856754	-1.843444	0.852243
26	1	0	-2.596172	0.212284	1.202187

27	1	0	-0.721339	-2.168992	0.951480
28	1	0	0.707516	-1.006775	2.485535
29	1	0	-0.125571	0.998003	3.593816
30	1	0	-1.406886	1.220637	2.416107
31	1	0	0.190550	3.016174	2.045732
32	1	0	1.560032	1.918515	2.120543

S24 :

SCF Done: E(RB+HF-LYP) = -1187.10694518

Zero-point vibrational energy 686510.4 (Joules/Mol)
164.07991 (Kcal/Mol)

Zero-point correction= 0.261478 (Hartree/Particle)
Thermal correction to Energy= 0.278197
Thermal correction to Enthalpy= 0.279141
Thermal correction to Gibbs Free Energy= 0.215401
Sum of electronic and zero-point Energies= -1186.845467
Sum of electronic and thermal Energies= -1186.828748
Sum of electronic and thermal Enthalpies= -1186.827804
Sum of electronic and thermal Free Energies= -1186.891545

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	174.571	61.629	134.154
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.325

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.736887	1.926290	-0.050157
2	6	0	-0.336773	2.313947	1.350857
3	45	0	1.426396	-0.008964	-0.144790
4	6	0	-2.188736	1.778964	-0.428969
5	6	0	-2.436985	0.279868	-0.741758
6	6	0	-3.895472	-0.022360	-1.135154
7	6	0	-4.076998	-1.549931	-0.923379
8	6	0	-2.837643	-2.013327	-0.114005

9	6	0	-2.177515	-0.723170	0.423503
10	6	0	-0.765059	-0.971450	0.936019
11	6	0	-0.090639	-0.193430	1.827460
12	6	0	-0.607170	1.136963	2.335624
13	8	0	0.103306	1.537813	-0.873692
14	8	0	3.749612	0.690061	-1.904250
15	6	0	2.853184	0.416819	-1.233284
16	1	0	-0.336097	-1.945298	0.705279
17	17	0	2.536665	-1.956292	0.568640
18	1	0	-2.851980	2.135431	0.367473
19	1	0	-2.392409	2.367576	-1.332161
20	1	0	-1.769540	0.011032	-1.568826
21	1	0	-4.575006	0.535672	-0.477372
22	1	0	-4.112601	0.296855	-2.160089
23	1	0	-4.138326	-2.081646	-1.877917
24	1	0	-5.007963	-1.759448	-0.386960
25	1	0	-2.123175	-2.527123	-0.769005
26	1	0	-3.089409	-2.711043	0.691245
27	1	0	-2.775469	-0.362868	1.277564
28	1	0	0.807202	-0.598115	2.289796
29	1	0	-0.133141	1.386388	3.289841
30	1	0	-1.686622	1.070605	2.524558
31	1	0	0.732240	2.547642	1.341742
32	1	0	-0.902021	3.196591	1.676521

S25 :

SCF Done: E(RB+HF-LYP) = -1073.70539274

Zero-point vibrational energy 653945.3 (Joules/Mol)
156.29667 (Kcal/Mol)

Zero-point correction= 0.249075 (Hartree/Particle)
Thermal correction to Energy= 0.263707
Thermal correction to Enthalpy= 0.264652
Thermal correction to Gibbs Free Energy= 0.206518
Sum of electronic and zero-point Energies= -1073.456318
Sum of electronic and thermal Energies= -1073.441685
Sum of electronic and thermal Enthalpies= -1073.440741
Sum of electronic and thermal Free Energies= -1073.498875

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total	165.479	55.045	122.353
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.013
Rotational	0.889	2.981	32.499
Vibrational	163.701	49.084	46.841

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.737045	-1.619119	-0.333657
2	6	0	-0.420027	-1.827215	1.339012
3	45	0	-1.014033	-0.053661	0.021094
4	6	0	1.641117	-0.451176	-0.741348
5	6	0	3.008061	-0.834990	-1.352831
6	6	0	3.880787	0.443499	-1.173026
7	6	0	3.124083	1.350227	-0.156205
8	6	0	2.061239	0.425779	0.462126
9	6	0	0.877089	1.076653	1.137212
10	6	0	0.084946	0.459490	2.063284
11	6	0	0.239649	-1.007007	2.447833
12	8	0	-2.989851	-1.206036	-1.942080
13	6	0	-2.226531	-0.774207	-1.196750
14	17	0	-2.051169	2.048956	-0.300656
15	1	0	1.365827	-2.343683	0.185095
16	1	0	0.266734	-2.133153	-1.172853
17	1	0	1.120647	0.197676	-1.456731
18	1	0	3.438673	-1.676862	-0.793821
19	1	0	2.924694	-1.149315	-2.398032
20	1	0	4.879088	0.182014	-0.807407
21	1	0	4.022145	0.964147	-2.125271
22	1	0	3.788386	1.790693	0.594459
23	1	0	2.628439	2.179554	-0.675911
24	1	0	2.561769	-0.236919	1.185341
25	1	0	0.677754	2.122221	0.911275
26	1	0	-0.684997	1.044041	2.561230
27	1	0	-0.248213	-1.207530	3.409583
28	1	0	1.297638	-1.272661	2.561990
29	1	0	-1.513904	-1.800319	1.425243
30	1	0	-0.149254	-2.880710	1.320478

S26 :

SCF Done: E(RB+HF-LYP) = -1187.05872899

Zero-point vibrational energy 675655.6 (Joules/Mol)
161.48557 (Kcal/Mol)

Zero-point correction=	0.257344 (Hartree/Particle)
Thermal correction to Energy=	0.274386
Thermal correction to Enthalpy=	0.275330
Thermal correction to Gibbs Free Energy=	0.211753
Sum of electronic and zero-point Energies=	-1186.801385
Sum of electronic and thermal Energies=	-1186.784343
Sum of electronic and thermal Enthalpies=	-1186.783399
Sum of electronic and thermal Free Energies=	-1186.846976

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.180	62.883	133.810
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	32.992
Vibrational	170.402	56.922	57.541

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.887064	-1.369551	-0.944589
2	6	0	0.971153	-1.523639	-1.172439
3	45	0	0.942007	-0.043368	-0.053694
4	6	0	-1.908659	-0.777666	0.056673
5	6	0	-3.351699	-1.290083	-0.261937
6	6	0	-4.290290	-0.063943	-0.097059
7	6	0	-3.447131	0.993127	0.639418
8	6	0	-2.023986	0.770699	0.084020
9	6	0	-0.947158	1.426020	0.914496
10	6	0	0.018128	2.279746	0.491276
11	6	0	0.307782	2.621380	-0.967690
12	6	0	0.787089	1.337438	-1.669959
13	8	0	1.396291	-2.348684	-1.878974
14	17	0	0.926129	-1.317645	2.090503
15	8	0	3.841981	0.702603	0.454742

16	1	0	1.733325	1.455898	-2.199016
17	1	0	-0.950881	-2.457663	-0.867521
18	1	0	-1.117434	-1.065649	-1.970603
19	1	0	-3.414603	-1.697622	-1.277971
20	1	0	-3.619483	-2.103479	0.420263
21	1	0	-5.214724	-0.308541	0.435973
22	1	0	-4.582942	0.320877	-1.081489
23	1	0	-3.448483	0.799387	1.720614
24	1	0	-3.806298	2.016946	0.489637
25	1	0	-1.990622	1.149106	-0.947144
26	1	0	-1.626208	-1.111878	1.059757
27	1	0	-0.994690	1.209100	1.981055
28	1	0	0.666670	2.721582	1.245616
29	1	0	-0.579892	3.044775	-1.455839
30	1	0	1.083108	3.393081	-1.002100
31	1	0	0.044557	0.929627	-2.360254
32	6	0	2.734822	0.467244	0.274544

S27 :

SCF Done: E(RB+HF-LYP) = -1187.09481067

Zero-point vibrational energy 681439.8 (Joules/Mol)
162.86803 (Kcal/Mol)

Zero-point correction= 0.259547 (Hartree/Particle)
Thermal correction to Energy= 0.276595
Thermal correction to Enthalpy= 0.277539
Thermal correction to Gibbs Free Energy= 0.213683
Sum of electronic and zero-point Energies= -1186.835264
Sum of electronic and thermal Energies= -1186.818216
Sum of electronic and thermal Enthalpies= -1186.817272
Sum of electronic and thermal Free Energies= -1186.881128

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.566	63.105	134.396
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.049
Vibrational	171.788	57.143	58.070

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.574805	0.717589	-0.643342
2	6	0	2.129206	0.609130	-0.106354
3	6	0	1.997787	-0.886761	0.298458
4	6	0	3.450626	-1.369108	0.610534
5	6	0	4.372970	-0.157318	0.336090
6	6	0	1.042142	-1.102459	1.469911
7	6	0	-0.366714	-0.467551	1.493992
8	8	0	-0.986353	-0.408879	2.517367
9	6	0	1.091061	0.999274	-1.116012
10	6	0	0.152933	1.983960	-1.035964
11	6	0	-0.269059	2.772159	0.188534
12	6	0	-1.536450	2.021086	0.604069
13	45	0	-1.158920	0.117664	-0.267296
14	17	0	-0.789477	-1.774407	-1.809129
15	6	0	-2.825698	-0.563922	0.293602
16	8	0	-3.850432	-0.962646	0.612164
17	1	0	1.609608	-1.438813	-0.562321
18	1	0	3.553267	-1.728780	1.640854
19	1	0	3.710126	-2.209742	-0.041528
20	1	0	3.623845	0.296818	-1.656982
21	1	0	3.928916	1.752645	-0.698029
22	1	0	2.049300	1.234676	0.792973
23	1	0	1.170367	0.475312	-2.067910
24	1	0	-0.426070	2.186216	-1.939599
25	1	0	-0.436621	3.830353	-0.051555
26	1	0	0.493944	2.726722	0.971643
27	1	0	-2.431611	2.413875	0.111235
28	1	0	-1.697786	1.948637	1.679576
29	1	0	0.837985	-2.175181	1.590826
30	1	0	1.496333	-0.759692	2.409251
31	1	0	4.550861	0.402100	1.263501
32	1	0	5.352679	-0.449372	-0.055774

S28 :

SCF Done: E(RB+HF-LYP) = -1187.06397429

Zero-point vibrational energy 678960.1 (Joules/Mol)

162.27537 (Kcal/Mol)

Zero-point correction=	0.258602 (Hartree/Particle)
Thermal correction to Energy=	0.275072
Thermal correction to Enthalpy=	0.276017
Thermal correction to Gibbs Free Energy=	0.213575
Sum of electronic and zero-point Energies=	-1186.805372
Sum of electronic and thermal Energies=	-1186.788902
Sum of electronic and thermal Enthalpies=	-1186.787958
Sum of electronic and thermal Free Energies=	-1186.850400

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.611	61.579	131.420
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	43.277
Rotational	0.889	2.981	33.052
Vibrational	170.833	55.618	55.092

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.331465	-1.728758	-0.394545
2	6	0	-0.797127	-1.685513	1.421074
3	45	0	-1.107905	0.216031	0.135061
4	6	0	1.188689	-1.789522	-0.628084
5	6	0	1.965498	-0.476687	-0.787155
6	6	0	3.400280	-0.708586	-1.320143
7	6	0	4.249146	0.494886	-0.821488
8	6	0	3.322924	1.301356	0.121384
9	6	0	2.202790	0.317255	0.522052
10	6	0	1.003710	1.013896	1.117386
11	6	0	0.139809	0.510593	2.051591
12	6	0	0.086675	-0.951051	2.447077
13	8	0	-3.712292	-0.345182	-1.347957
14	6	0	-2.715467	-0.164708	-0.816001
15	1	0	-0.557748	-2.751087	1.392292
16	17	0	-1.376889	2.438872	-0.612528
17	8	0	-1.083536	-2.414934	-1.060017
18	1	0	1.636741	-2.376928	0.187743
19	1	0	1.290289	-2.387746	-1.540158
20	1	0	1.424424	0.175003	-1.486300

21	1	0	3.795868	-1.647549	-0.911043
22	1	0	3.408088	-0.813158	-2.409895
23	1	0	4.604324	1.116194	-1.649491
24	1	0	5.139286	0.142641	-0.289640
25	1	0	2.874308	2.146410	-0.415993
26	1	0	3.847731	1.714449	0.989422
27	1	0	2.607365	-0.394577	1.258775
28	1	0	0.909504	2.072338	0.885284
29	1	0	-0.538030	1.198403	2.554112
30	1	0	-0.330215	-1.071367	3.453940
31	1	0	1.092586	-1.385883	2.463727
32	1	0	-1.867809	-1.637398	1.637348
