Supplemental materials for:

The Development of a Facile Tandem Wolff/Cope Rearrangement for the Synthesis of Fused Carbocyclic Skeletons

Richmond Sarpong, Julius T. Su, Brian M. Stoltz*

The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

Table of Contents:

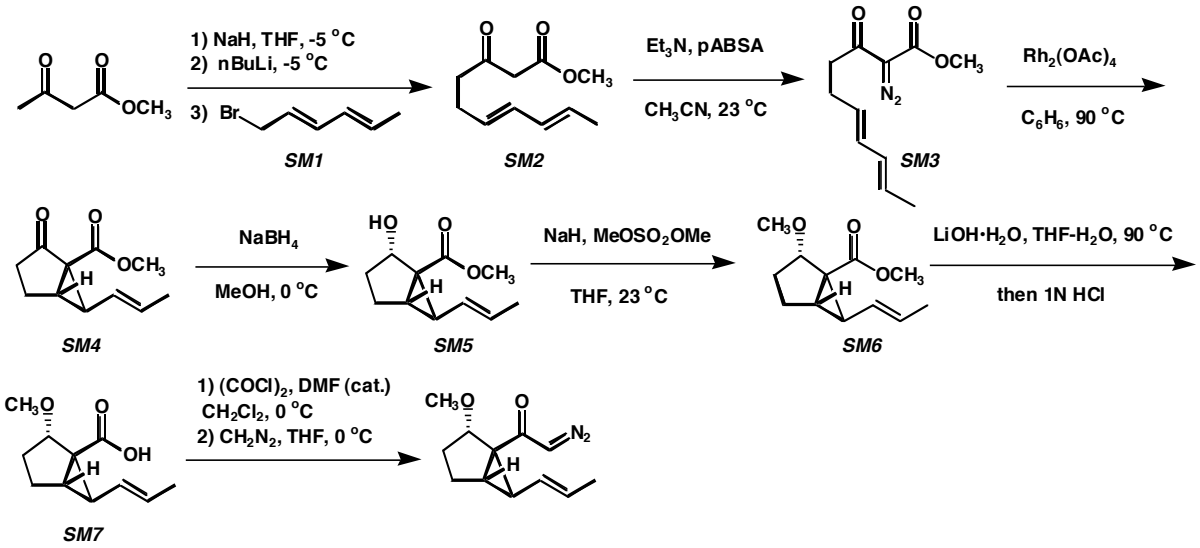
Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen or argon atmosphere using dry, deoxygenated solvents. Silver benzoate was purchased from Aldrich Chemical Company, dried by heating under vacuum (2 mmHg) at 100 °C for 1 h and stored in the dark under a nitrogen atmosphere. All other commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe or stainless steel cannula. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV, anisaldehyde or permanganate staining. ICN silica gel (particle size 0.032 - 0.063 mm) was used for flash chromatography. Sonochemical irradiation of samples was typically performed in sealed glass vials placed in a VWR Model 75D cleaning ultrasonic bath. Photochemical irradiation was performed in septum sealed quartz tubes with a Luzchem® Photochemical reactor or with a Hanovia® medium pressure Hg lamp. ^{1}H and ^{13}C NMR were recorded on a Varian Mercury 300 (at 300 MHz and 75 MHz respectively). Chemical shifts are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, comp. m = complicated multiplet, app. q = apparent quartet, app. t = apparent triplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra data were obtained from the Caltech Mass Spectral Facility.

Additional References

Approaches to guanacastepene (footnote 3):
(a) Shi, B.; Hawryluk, N.A.; Snider, B. B. *J. Org. Chem.* **2003**, *68*, 1030 - 1042. (b) Snider, B. B.; Hawryluk, N. A. *Org. Lett.* **2001**, *3*, 569 - 572. (c) Snider, B. B.; Shi, B. *Tetrahedron Lett.* **2001**, *42*, 9123 - 9126. (d) Du, X.; Chu, H. V.; Kwon, O. *Org. Lett.* **2003**, *5*, 1923 - 1926. (e) Boyer, F. D.; Hanna, I. *Tetrahedron Lett.* **2002**, *43*, 7469 - 7472. (f) Nakazaki, A.; Sharma, U.; Tius, M. *Org. Lett.* **2002**, *4*, 3363 - 3366. (g) Nguyen, T. M.; Seifert, R.; Mowrey, D. R.; Lee, D. *Org. Lett*. **2002**, *4*, 3959 - 3962. (h) Nguyen, T. M.; Lee, D. *Tetrahedron Lett.* **2002**, *43*, 4033 - 4036. (i) Shipe, W.D.; Sorensen, E. *J. Org. Lett.* **2002**, *4*, 2063 - 2066. (j) Gradl, S. N.; Kennedy-Smith, J. J.; Kim, J.; Trauner, D. *Synlett* **2002**, 411 - 414. (k) Mehta, G.; Umarye, J. D.; Gagliardini, V. *Tetrahedron Lett.* **2002**, *43*, 6975 - 6978. (l) Mehta, G.; Umarye, J. D. *Org. Lett.* **2002**, *4*, 1063 - 1066. (m) Magnus, P.; Ollivier, C. *Tetrahedron Lett.* **2002**, *43*, 9605 - 9609. (n) Magnus, P.; Waring, M. J.; Ollivier, C. Lynch, V. *Tetrahedron Lett.* **2001**, *42*, 4947 - 4950.

Representative Synthesis of β-Diazo ketone Substrates (Entry 1, Table 1 and Table 2 is used as an example): For each substrate, the dienyl halide (e.g., **SM1**) was synthesized according to a known procedure which is referenced with the characterization data.

Scheme S1. Synthesis of β-Diazo ketone Substrate (Entry 1, Table 2 and 3).



Dienyl Bromide SM1.[1] To a cooled heterogeneous solution (-5 °C; salt water-ice bath) of sorbyl alcohol (10 g, 102 mmol) and CaH_2 (6.4 g) in ether (170 mL) under an N_2 atmosphere was added a solution of PBr_3 (3.55 mL, 37.4 mmol) in ether (14 mL) dropwise via syringe pump over 30 min in the dark. The resulting mixture was stirred at -5 °C for 1 h at which time the salt-water bath was removed and stirring was continued at 23 °C for 30 min. The gray suspension was re-cooled to -5 °C and methanol (333 μL) was added dropwise. Stirring was continued for 15 min then filtration through a pad of celite (8 cm X 4 cm) and concentration of the filtrate provided crude dienyl bromide **SM1** which was ~80% pure (by NMR) and used without further purification.

β-Keto ester SM2.[2] To a cooled solution (-5 °C; salt water-ice bath) of methyl acetoacetate (13.2 mL, 123 mmol) in anhydrous THF (250 mL) under an N_2 atmosphere was added NaH (60% dispersion in oil, 6.4 g, 160 mmol) portionwise over 5 min. The resulting gray suspension was stirred 15 min after which time a clear solution had formed. A solution of *n*BuLi (2.3 M in hexanes, 67 mL, 154 mmol) was added as a constant stream via syringe down the walls of the flask over 10 min. The resulting dark red solution was stirred a further 10 min at which time a solution of sorbyl bromide (**SM1**) in THF (50 mL) was added rapidly via syringe (<3 min). The red color dissipates and a bright yellow orange solution with an off-white precipitate forms. Stirring was continued for another 20 min at which time the reaction was judged complete (TLC

analysis) and quenched by slow addition of saturated NH_4Cl (100 mL). The solution was warmed to 23 °C and extracted with ether (3 X 200 mL). The combined organic layers were washed with brine (1 X 200 mL), dried over magnesium sulfate, and evaporated under reduced pressure. The crude yellow oil was purified by flash chromatography (10:1 hexanes:ethyl acetate eluent) to yield **SM2** (9.6 g, 48% yield) as a faint yellow oil: All physical data compares favorably with reported literature data.[2] R_F 0.40 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) Complicated by enol form (not indicated) □ 5.98 (m, 2H), 5.53 (m, 2H), 3.70 (s, 3H), 3.43 (s, 2H), 2.61 (t, J = 7.3 Hz, 2H), 2.32 (app. q, J = 7.0 Hz, 2H), 1.70 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Complicated by enol form (not indicated) □ 202.2, 167.8, 131.7, 131.5, 129.3, 128.2, 52.6, 49.3, 42.8, 26.6, 18.2; IR (film) 3018, 2955, 1756, 1748, 1716, 1652, 1627, 1432 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{16}O_3]^+$: *m/z* 196.1100, found 196.1102.

□-Diazo-□-Keto ester SM3. To a solution of □-keto ester **SM2** (1.0 g, 5.1 mmol) in acetonitrile (15 mL) at 23 °C was added triethylamine (1.42 mL, 10.2 mmol) via syringe followed by *para*-acetamidobenzenesulfonyl azide, pABSA[3] (1.59 g, 6.6 mmol). An off-white precipitate forms (ca. 2 min) and stirring was continued until the reaction was judged complete by TLC (ca. 30 min). The crude mixture was diluted with ether (100 mL) and filtered through a pad of celite (4 cm X 2 cm). The residue was extracted with ether (2 X 100 mL) and the combined filtrate was concentrated. Purification by flash column chromatography (dry load; 5:1 hexane:ethyl acetate) provided **SM3** (1.01 g, 89% yield) as a bright yellow oil: All physical data compares favorably with reported literature data.[1] R_F 0.45 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) □ 6.01 (app. q, 1H), 5.57 (m, 1H), 3.83 (s, 3H), 2.93 (t, J = 7.0 Hz, 1H), 2.38 (app. q, J = 7.3 Hz, 1H), 1.71 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 192.2, 162.0, 131.6, 131.7, 129.8, 128.0, 52.4, 40.1, 27.3, 18.3, (10 of 11 peaks); IR (film) 3083, 2950, 2136, 1722, 1657, 1437, 1320, 1227 cm^{-1}; HRMS (EI$^+$) calc'd for (m-N_2) $[C_{11}H_{14}O_3]^+$: *m/z* 194.0943, found 194.0930.

Bicyclo[3.1.0] hexane SM4.[1, 4] A flask containing a solution of □-diazo-□-keto ester **SM3** (1.0 g, 4.5 mmol) and $Rh_2(OAc)_4$ (20 mg, 0.0045 mmol) in benzene (200 mL) was heated and held at reflux (oil bath temperature of 90 °C) for 6 h. The resulting green solution was cooled to 23 °C and concentrated under reduced pressure. Flash column chromatography (gradient of 10:1 hexanes: ethyl acetate, 1L; then 4:1 hexanes:ethyl acetate) of the crude product gave the bicycle **SM4** (560 mg, 64% yield) as a clear oil: All physical data compares favorably with reported literature data.[1, 4] R_F 0.15 (4:1 hexanes: EtOAc): ^{1}H NMR (300 MHz, $CDCl_3$) □ 5.65 (d, J = 15.2, 6.5 Hz, 1H), 5.17 (ddd, J = 15.2, 8.8 Hz, 1H), 3.68 (s, 3H), 2.56 (t, J = 5.3 Hz, 1H), 2.26 (dd, J = 8.8, 5.6 Hz, 1H), 2.02 - 2.21 (comp. m, 2H), 1.95 (m, 1H), 1.59 (dd, J = 6.7, 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) □206.1, 166.8, 130.7, 124.4, 52.4, 45.4, 38.3, 34.7, 33.7, 21.0,

18.2; IR (film) 2951, 1750, 1716, 1438, 1365, 1320, 1230 cm^{-1}; HRMS (EI^+) calc'd for $[C_{11}H_{14}O_3]^+$: *m/z* 194.0943, found 194.0938.

Alcohol SM5. To a cooled solution (0 °C) of bicycle **SM4** (330 mg, 1.71 mmol) in methanol (20 mL) was added sodium borohydride (24.1 mg, 0.63 mmol) at once. The resulting solution was stirred at 0 °C until the reaction was judged complete by TLC (30 min) and then quenched by addition of 1N HCl (20 mL). The mixture was stirred with warming to 23 °C over 2 h and then extracted with ethyl acetate (3 X 50 mL). The combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and then dried over $MgSO_4$. Concentration under reduced pressure followed by flash column chromatography (2:1 hexanes:ethyl acetate) provided **SM5** (320 mg, 95% yield) as a clear, colorless oil: R_F 0.4 (1:1 hexanes:EtOAc): ^{1}H NMR (300 MHz, $CDCl_3$) □ 5.65 (ddd, *J* = 15.4, 14.1, 6.5 Hz, 1H), 5.37 (ddd, *J* = 15.4, 9.1, 1.5 Hz, 1H), 4.75 (td, *J* = 8.4, 2.4 Hz, 1H), 3.74 (s, 3H), 2.50 (d, *J* = 2.4 Hz, 1H), 2.27 (dd, *J* = 9.1, 5.3 Hz, 1H), 1.95 (comp. m, 2H), 1.80 (comp. m, 2H), 1.64 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 173.0, 127.6, 127.1, 74.1, 52.0, 42.6, 34.0, 29.7, 28.5, 24.6, 18.3; IR (film) 3479, 2953, 1716, 1436, 1300, 1090 cm^{-1}; HRMS (FAB^+) calc'd for $[C_{11}H_{16}O_3]^+$: *m/z* 196.1100, found 195.1105.

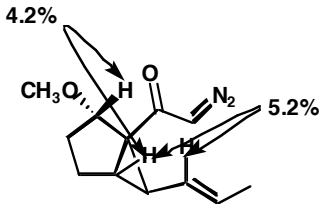
Methyl Ether SM6. To a solution of alcohol **SM5** (264 mg, 1.34 mmol) in anhydrous THF (13 mL) at 23 °C under a N_2 atmosphere was added NaH (60% dispersion in mineral oil, 81 mg, 2.01 mmol). The resulting heterogeneous solution was stirred 15 min and then dimethyl sulfate (165 □L, 1.74 mmol) was added via syringe. The resulting solution was stirred at 23 °C for 10 h and quenched by addition of saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with ether (3 X 20 mL) and the combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. Concentration by rotary evaporation gave a yellow oil residue which was purified by flash column chromatography (10:1 hexanes:ethyl acetate) to afford methyl ether **SM6** (268 mg, 95% yield) as a colorless oil: R_F 0.70 (1:1 hexanes: EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) □ 5.48 - 5.72 (comp. m, 2H), 4.43 (t, *J* = 7.6 Hz, 1H), 3.65 (s, 3H), 3.38 (s, 3H), 2.22 (dd, *J* = 8.6, 5.9 Hz, 1H), 2.06 (m, 1H), 1.94 (m, 1H), 1.84 (m, 2H), 1.64 (dt, *J* = 6.2, 1.8 Hz, 3H), 1.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 173.0, 127.4, 82.7, 57.7, 51.9, 41.6, 36.3, 31.5, 29.1, 25.1, 18.2, (11 of 12 peaks observed); IR (film) 2951, 1718, 1436, 1341, 1090 cm^{-1}; HRMS (FAB^+) calc'd for $[C_{12}H_{18}O_3]^+$: *m/z* 210.1256, found 210.1254.

Carboxylic Acid SM7. To a 100 mL round-bottom flask charged with methyl ester **SM6** (208 mg, 0.989 mmol) was added THF (15 mL) and H_2O (5 mL) followed by $LiOH•H_2O$ (208 mg, 6.67 mmol). The flask was fitted with a reflux condensor and held at reflux (oil bath temperature of 80 °C) until the reaction was judged complete by TLC (ca. 10 h). The resulting mixture was

cooled to 23 °C, diluted with ether (100 mL) and poured into cold 1N HCl (50 mL). The aqueous layer (pH = 2) was extracted with ether (2 X 100 mL) and the combined organic layer was washed with brine (100 mL) and dried over $MgSO_4$. Concentration in vacuo afforded the crude acid which was purified by flash column chromatography (2:1 hexanes:ethyl acetate) to give the acid **SM7** (190 mg, 98% yield) as a clear, colorless oil: R_F 0.30 (1:1 hexanes: EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) 11.5 (br s, 1H), 5.64 (comp. m, 2H), 4.48 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 2.31 (dd, *J* = 8.3, 5.8 Hz, 1H), 2.07 (comp. m, 2H), 1.87 (comp. m, 2H), 1.67 (dd, *J* = 5.7, 1.2 Hz, 3H), 1.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.2, 127.8, 127.2, 82.4, 57.7, 41.4, 37.4, 32.5, 29.1, 25.2, 18.2; IR (film) 2935, 2599, 1716, 1682, 1435, 1339, 1291, 1107 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{16}0_3]^+$: *m/z* 196.1100, found 196.1100.

-Diazo ketone (Entry 1, Table 1 and 2). To a cooled (0 °C) solution of acid **SM7** (1.36 g, 6.93 mmol) in anhydrous CH_2Cl_2 (30 mL) under a N_2 atmosphere was added oxalyl chloride (726 L, 8.32 mmol) via syringe followed by DMF (10 mL). Immediate gaseous evolution was observed and the solution was stirred 1 h at 0 °C and an additional 20 min at 23 °C. At this time, the reaction was judged complete (TLC analysis of an aliquot in MeOH) and the crude reaction solution was concentrated by rotary evaporation. The crude acid chloride residue was dried azeotropically with anhydrous toluene (3 X 5 mL), taken up in anhydrous THF (30 mL), and cooled to 0 °C. To the solution was added Et_3N (2.90 mL, 20.8 mmol) followed by the addition of a cooled solution of CH_2N_2 (0.2 M in Et_2O, 100 mL). **Caution**! Diazomethane is potentially explosive and hazardous and should be handled in a fume hood. The resulting mixture was allowed to stir with warming to 10 °C over 30 min at which time TLC analysis indicated the reaction was complete. The reaction mixture was quenched by careful addition of saturated $NaHCO_3$ (30 mL) and extracted with ether (3 X 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated in vacuo. Flash column chromatography of the bright yellow concentrate gave the -diazo ketone (1.07 g, 70% yield), along with methyl ester **SM6** (200 mg). Characterization of -diazo ketone: R_F 0.60 (1:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) 5.81 (br s, 1H), 5.63 (dq, *J* = 152, 6.5 Hz, 1H), 5.34 (ddd, *J* = 15.4, 9.1, 1.5 Hz, 1H), 4.17 (t, *J* = 7.8 Hz, 1H), 2.26 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.08 (comp. m, 2H), 1.83 (comp. m, 1H), 1.63 (dd, *J* = 6.6, 1.5 Hz, 3H), 1.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 192.5, 127.2, 126.7, 82.8, 57.2, 54.8, 47.5, 32.6, 31.9, 27.0, 24.4, 18.2; IR (film) 2937, 2103, 1624, 1450, 1412, 1344, 1313, 1070 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{17}N_2O_2]^+$: *m/z* 221.1290, found 221.1293.

NOE measurements of β-diazo ketone:



Spectral Data for β-Diazo ketones

Table 1 and 2, Entry 2. Bright yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (s, 1H), 5.60 (ddd, *J* = 15.3, 12.8, 6.4 Hz, 1H), 5.35 (ddd, *J* = 15.3, 9.0, 1.3 Hz, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.64 (d, *J* = 6.6 Hz, 1H), 4.46 (t, *J* = 7.7 Hz, 1H), 3.38 (s, 3H), 2.5 (dd, *J* = 9.0, 5.3 Hz, 1H), 2.00 - 2.13 (comp. m, 2H), 1.74 - 1.82 (comp. m, 2H), 1.61 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 126.9, 126.6, 96.0, 79.6, 56.0, 54.6, 47.1, 32.8, 31.7, 28.2, 24.3, 18.0; IR (film) 3118, 2938, 2104, 1622, 1410, 1360, 1330, 1216, 1153, 1112, 1042 cm^{-1}; HRMS (FAB$^+$) calc'd for (m + H) $[C_{13}H_{19}N_2O_3]^+$: *m/z* 251.1396, found 251.1396.

Table 1 and 2, Entry 3. Bright yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.72 (s, 1H), 5.63 (dq, *J* = 15.2, 6.5 Hz, 1H), 5.36 (ddd, *J* = 15.2, 9.1, 1.2 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 4.33 (t, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 2.32 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.02 - 2.14 (comp. m, 2H), 1.76 - 1.89 (comp. m, 2H), 1.64 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 159.6, 130.2, 129.9, 127.1, 126.9, 114.1, 80.2, 71.2, 55.5, 54.8, 47.5, 32.6, 31.9, 27.5, 24.5, 18.3; IR (film) 3110, 2936, 2869, 2102, 1616, 1512, 1367, 1348, 1328, 1249, 1113, 1084, 1035 cm^{-1}; HRMS (FAB$^+$) calc'd for (m + H) $[C_{19}H_{23}N_2O_3]$: *m/z* 327.1709, found 327.1696.

Table 1, Entry 4. Bright yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 (br s, 1H), 5.48 - 5.67 (comp. m, 2H), 4.26 (dd, *J* = 4.4, 1.8 Hz, 1H), 3.60 (s, 3H), 2.56 (ddd, *J* = 16.1, 6.6, 2.0 Hz, 1H), 2.36 (app. t, *J* = 5.3 Hz, 1H), 2.25 (dd, *J* = 16.3, 2.6 Hz, 1H), 1.83 (dd, *J* = 8.3, 5.9 Hz, 1H), 1.66 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.5, 189.9, 160.5, 127.7, 93.6, 57.6, 55.9, 48.2, 44.9, 32.8, 29.7, 18.3; IR (film) 3128, 2915, 2849, 2102, 1627, 1610, 1340, 1236, 1172 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{14}N_2O_2]^+$: *m/z* 218.1055, found 218.1052.

Table 1, Entry 5.[5] Bright yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (s, 1H), 4.96 (d, *J* = 1.5 Hz, 1H), 4.84 (s, 1H), 4.26 (t, *J* = 7.9 Hz, 1H), 3.39 (s, 3H), 2.27 (m, 1H), 2.22 (d, *J* = 6.2 Hz, 1H), 2.12 (m, 1H), 1.80 - 1.88 (comp. m, 2H), 1.73 (s, 3H), 1.30 (m, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 191.6, 140.1, 114.0, 82.6, 57.4, 54.1, 47.8, 35.1, 30.5, 27.8, 24.6, 23.7; IR (film)

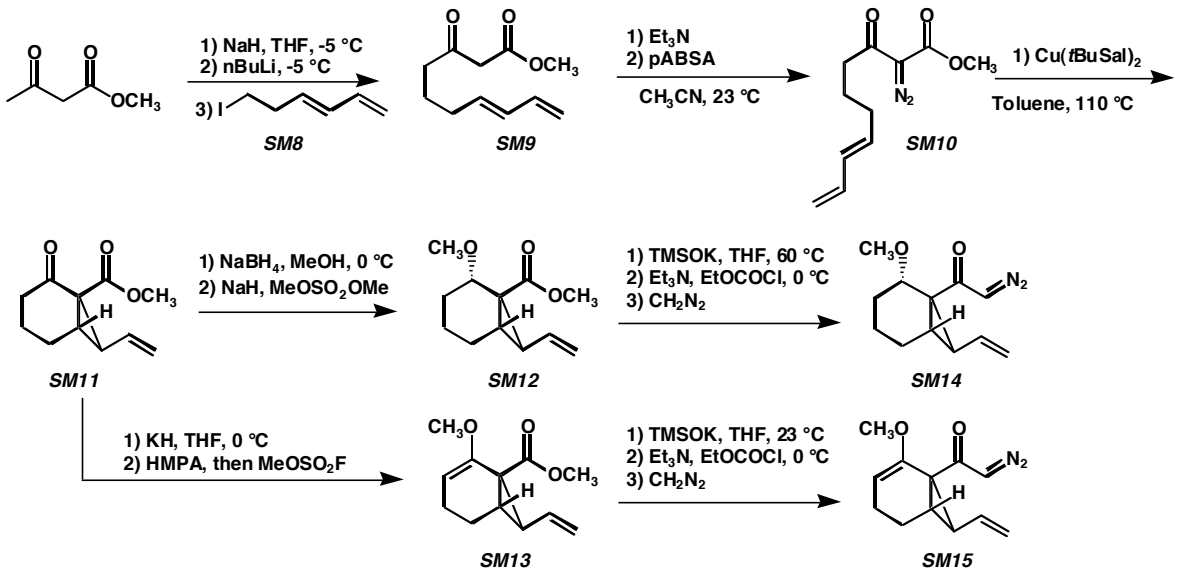
3111, 2936, 2101, 1627, 1373, 1351, 1327, 1110, 1097 cm^{-1}; HRMS (EI^+) calc'd for (m - N_2) $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1141.

Table 1, Entry 6.[4] Bright yellow oil: ^1H NMR (300 MHz, $CDCl_3$) □ 5.80 (s, 1H), 5.67 (dt, *J* = 17.3, 9.4 Hz, 1H), 5.17 (dd, *J* = 17.4, 1.5 Hz, 1H), 4.97 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.17 (t, *J* = 7.9 Hz, 1H), 3.35 (s, 3H), 2.27 (dd, *J* = 9.2, 5.0 Hz, 1H), 2.03 - 2.17 (m, 2H), 1.74 - 1.90 (m, 2H), 1.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 192.2, 134.4, 116.0, 82.8, 57.2, 54.9, 47.7, 32.5, 32.3, 26.9, 24.3; IR (film) 3113, 2940, 2105, 1622, 1394, 1352, 1097 cm^{-1}; HRMS (EI^+) calc'd for (m -N_2) $[C_{11}H_{14}O_2]^+$: *m/z* 178.0994, found 178.0994.

Table 1, Entry 7.[6] Bright yellow oil: ^1H NMR (300 MHz, $CDCl_3$) □ 5.88 (br s, 1H), 5.68 (m, 1H), 5.46 (m, 1H), 4.29 (m, 1H), 3.28 (s, 3H), 1.96 - 2.08 (comp. m, 2H), 1.74 - 1.94 (comp. m, 4H), 1.62 (m, 2H), 1.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 229.5, 127.9, 122.8, 86.8, 57.5, 56.3, 52.0, 36.8, 31.6, 26.1, 22.1, 21.6, 20.5; IR (film) 2924, 2100, 1622, 1352, 1324, 1112 cm^{-1}; HRMS (EI^+) calc'd for (m -N_2) $[C_{13}H_{16}O_2]^+$: *m/z* 204.1150, found 204.1150.

Table 2, Entry 4. Bright yellow oil: ^1H NMR (300 MHz, $CDCl_3$) □ 5.71 (s, 1H), 5.62 (dd, *J* = 17.3, 11.4 Hz, 1H), 5.03 (d, *J* = 17.3 Hz, 1H), 4.94 (dd, *J* = 10.7, 1.5 Hz, 1H), 4.33 (dd, *J* = 9.2, 6.5 Hz, 1H), 3.28 (s, 3H), 2.26 (m, 1H), 2.00 - 2.16 (comp. m, 2H), 1.86 (m, 1H), 1.62 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) □ 193.3, 141.2, 112.8, 85.6, 57.9, 54.8, 53.3, 36.5, 31.9, 23.5, 13.4, (11 of 12 peaks); IR (film) 3111, 2934, 2102, 1633, 1392, 1338, 1193, 1160, 1098, 1007 cm^{-1}; HRMS (EI^+) calc'd for $[C_{12}H_{16}N_2O_2]^+$: *m/z* 220.1212, found 220.1218.

Scheme S2. Synthesis of β-Diazo ketone Substrates (Table 1, Entry 8; Table 2, Entries 5 and 6):



β-Keto ester SM9.[7] To a cooled solution (-5 °C; salt water-ice bath) of methyl acetoacetate (10.2 mL, 95 mmol) in anhydrous THF (450 mL) under an atmosphere of N_2 was added NaH (60% dispersion in oil, 3.5 g, 87.6 mmol) portionwise over 5 min. The resulting gray suspension was stirred 15 min after which time a clear solution had formed. To this solution was added *n*BuLi (2.3 M in hexanes, 36.5 mL, 87.6 mmol) in a constant stream via syringe down the walls of the flask over 10 min. The resulting dark red solution was stirred a further 10 min at which time a solution of dienyl iodide **SM8**[8] (15.2 g, 73 mmol) in THF (100 mL) was added rapidly (< 5 min). The red color dissipates and a bright orange solution forms. Stirring is continued for 30 min at -5 °C then the ice-bath is removed and the reaction mixture is stirred with warming to 23 °C for a further 2 h. At this time the reaction is judged complete (TLC) and quenched by pouring into cold saturated NH_4Cl (300 mL). The solution is warmed to 23 °C and extracted with ether (3 X 200 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude yellow oil was purified by flash column chromatography (10:1 hexanes:ethyl acetate eluent) to yield **SM9** (6.5 g, 45% yield) as a faint yellow oil: R_F 0.50 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.01 (s, enol H), 6.28 (dt, J = 17.0, 10.3 Hz, 1H), 6.04 (dd, J = 13.3, 11.1 Hz, 1H), 5.62 (m, 1H), 5.09 (d, J = 17.6 Hz, 1H), 4.97 (d, J = 9.4 Hz, 1H), 3.73 (s, 3H), 3.41 (s, 2H), 2.53 (t, J = 7.3 Hz, 2H), 2.09 (app. t, J = 7.0 Hz, 2H), 1.70 (app. q, J = 7.3 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 202.7, 167.8, 137.2, 134.0, 132.1, 115.6, 52.6, 49.3, 42.4, 31.8, 22.9; IR (film) 2953, 1748, 1716, 1651, 1631, 1603, 1438, 1408, 1371, 1323, 1257, 1006 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{16}O_3]^+$: *m/z* 196.1100, found 196.1099.

β-Diazo-α-Keto ester SM10. To a solution of β-keto ester **SM9** (1.93 g, 9.83 mmol) in acetonitrile (20 mL) at 23 °C was added triethylamine (2.74 mL, 19.7 mmol) via syringe followed by *para*-acetamidobenzenesulfonyl azide, pABSA (2.83 g, 11.8 mmol). An off-white precipitate forms (ca. 2 min) and stirring is continued until the reaction is judged complete by TLC (ca. 30 min). The crude mixture is diluted with ether (100 mL) and filtered through a pad of celite (4 cm X 2 cm). The residue was extracted with ether (2 X 100 mL) and the combined filtrate was concentrated. Purification by flash column chromatography (dry load; 5:1 hexane:ethyl acetate) provided **SM10** (2.13 g, 98% yield) as a bright yellow oil: R_F 0.73 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (dt, *J* = 16.8, 10.3 Hz, 1H), 6.05 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.67 (m, 1H), 5.08 (dd, *J* = 17.2, 0.7 Hz, 1H), 4.95 (d, *J* = 10.3 Hz, 1H), 3.82 (s, 3H), 2.84 (app. t, *J* = 7.3 Hz, 2H), 2.13 (dd, *J* = 7.3, 7.0 Hz, 2H), 1.61 - 1.79 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 161.9, 137.3, 134.3, 131.9, 115.4, 52.4, 39.8, 32.2, 24.1, (10 of 11 peaks observed); IR (film) 2955, 2136, 1724, 1659, 1603, 1437, 1310, 1220, 1190, 1107 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{14}N_2O_3]^+$: *m/z* 222.1005, found 222.1004.

Bicyclo[4.1.0]heptane SM11.[9] To a refluxing solution of bis - (N-t-butylsalicyladiminato)copper (II) catalyst[10] (280 mg, 0.700 mmol) in toluene (200 mL) was added a solution of β-diazo-α-keto ester **SM10** (3.6 g, 16.2 mmol) in toluene (200 mL) at a rate of 10 mL/h via syringe pump. The solution was held at reflux 20 min after complete addition (ca. 20 h), cooled, concentrated and purified by flash chromatography (9:1 hexanes:ethyl acetate eluent) to afford **SM11** (1.87 g, 59%) as a clear oil: R_F 0.35 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 (app. m, 1H), 5.23 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.10 (dd, *J* = 10.1, 1.2 Hz, 1H), 3.71 (s, 3H), 2.29 - 2.42 (m, 3H), 2.17 (ddd, *J* = 17.0, 11.0, 6.5 Hz, 1H), 1.96 - 2.04 (comp. m, 2H), 1.60-1.80 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.5, 201.4, 133.4, 118.5, 52.7, 43.6, 38.2, 33.8, 30.2, 21.0, 19.1; IR (film) 2951, 1728, 1683, 1636, 1435, 1349, 1250, 1140 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{11}H_{14}O_3]^+$: *m/z* 194.0943, found 194.0946.

Methyl Ether SM12. To a cooled solution (0 °C) of bicycle **SM11** (635 mg, 3.05 mmol) in methanol (50 mL) was added sodium borohydride (43 mg, 1.13 mmol) at once. The resulting solution was stirred at 0 °C until the reaction was judged complete by TLC (ca. 30 min) and then quenched by addition of 1N HCl (50 mL). The mixture was stirred with warming to 23 °C over 1 h and then extracted with ethyl acetate (3 X 100 mL). The combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and then dried over $MgSO_4$. Filtration followed by concentration of the filtrate under reduced pressure afforded a crude oil which was dissolved in anhydrous DMF (10 mL) under an atmosphere of N_2. To this solution was added sodium hydride (60% dispersion in oil, 176 mg, 3.66 mmol) and the resulting heterogenous solution was stirred for 15 min, followed by the addition of dimethyl sulfate (3.18 mL, 3.36

mmol). The resulting clear yellow reaction mixture was stirred 12 h with warming to 23 °C then quenched by pouring into saturated $NaHCO_3$ (50 mL) and extracted with ether (3 X 100 mL). The combined organic layer was dried over $MgSO_4$, concentrated by rotary evaporation and purified by flash column chromatography (15:1 hexanes:ethyl acetate) to provide **SM12** (384 mg, 60% yield) and the β-diastereomer (151 mg, 24% yield). Characterization data for **SM12**: R_F 0.30 (4:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (m, 1H), 5.23 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.03 (dd, *J* = 10.1, 2.1 Hz, 1H), 4.38 (t, *J* = 3.2 Hz, 1H), 3.68 (s, 3H), 3.31 (s, 3H), 2.08 - 2.17 (m, 2H), 1.84 (m, 1H), 1.70 (m, 1H), 1.56 (m, 1H), 1.20 - 1.32 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 136.2, 116.8, 72.2, 56.1, 52.1, 34.6, 32.1, 29.3, 29.1, 22.4, 14.7; IR (film) 2939, 1717, 1633, 1436, 1228, 1090, 1046 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{12}H_{18}O_3]^+$: *m/z* 210.1256, found 210.1251.
Characterization data for α diastereomer: R_F 0.28 (4:1 hexanes:ethyl acetate eluent) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (ddd, *J* = 17.0, 16.3, 8.8 Hz, 1H), 5.12 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.96 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.05 (t, *J* = 2.3 Hz, 1H), 3.70 (s, 3H), 3.33 (s, 3H), 2.11 (m, 1H), 1.93 (dd, *J* = 7.6, 6.2 Hz, 1H), 1.81 (m, 1H), 1.48 - 1.61 (m, 3H), 1.09 - 1.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 135.8, 116.0, 74.7, 57.4, 52.0, 37.3, 34.0, 22.8, 22.6, 21.3, 14.7; IR (film) 2941, 1730, 1635, 1437, 1228, 1182, 1031 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{12}H_{18}O_3]^+$: *m/z* 210.1256, found 210.1262.

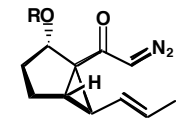
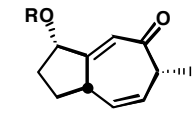
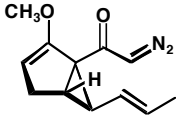
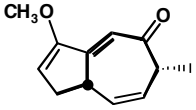
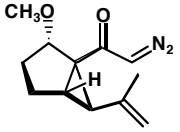
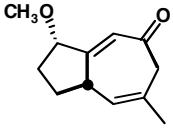
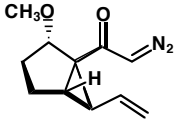
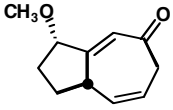
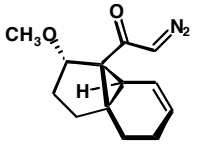
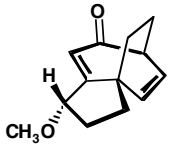
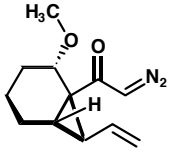
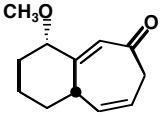
Methyl Enol Ether SM13. To a cooled (0 °C) heterogenous solution of KH (35% dispersion in oil, 346 mg, 3.03 mmol) in anhydrous THF (20 mL) was added via syringe a solution of the ketone **SM11** (392 mg, 2.02 mmol) in THF (20 mL) over 2 min. The resulting solution was stirred at 0 °C for 20 min at which time the cooling bath was removed and stirring continued at 23 °C for 20 min. The reaction mixture was then cooled to -78 °C and anhydrous HMPA (6 mL) was added via syringe with vigorous stirring. After 10 min, methyl fluorosulfonate[11] (235 μL, 2.83 mmol) was added via syringe and stirring continued at -78 °C until the reaction was judged complete by TLC (ca. 20 min). The reaction was quenched at -78 °C by the addition of saturated $NaHCO_3$ (50 mL). After warming to 23 °C, the aqueous layer was extracted with ether (3 X 20 mL) and the combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. Concentration by rotary evaporation gave a clear yellow oil which was purified by flash chromatography (10:1 hexanes: ethyl acetate with 1% Et_3N) to afford methyl enol ether **SM13** (343 mg, 82% yield) as a colorless oil: R_F 0.80 (2:1 hexanes: EtOAc). This material was subjected directly to the saponification conditions to make **SM15**.

α-Diazo ketone SM14 (Table 1, Entry 8 and Table 2, Entry 6). To a solution of methyl ether **SM12** (284 mg, 1.35 mmol) in anhydrous THF (15 mL) in a 100 mL round-botton flask under an atmosphere of N_2 was added TMSOK[12] (189 mg, 1.49 mmol) at once. The flask was fitted with

a reflux condensor and the resulting clear, yellow solution was held at reflux (oil bath temperature of 70 °C) until the reaction was judged complete by TLC (ca. 4 h). The reaction was cooled to 0 °C and Et_3N (564 μL, 4.05 mmol) was added via syringe followed by dropwise addition of ethyl chloroformate (168 μL, 1.76 mmol). The reaction mixture was stirred for 2 h at 0 °C at which time CH_2N_2 (0.2 M in Et_2O, 20 mL; **Caution**!) was added and the resulting mixture was stirred with warming to 23 °C over 12 h. The reaction was quenched by careful addition of saturated $NaHCO_3$ (30 mL) and extracted with ether (3 X 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated in vacuo. Flash column chromatography (6:1 hexanes:ethyl acetate) of the bright yellow concentrate gave α-diazo ketone **SM14** (163 mg, 55% yield): R_F 0.20 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (s, 1H), 5.53 (ddd, J = 17.2, 10.0, 1.1 Hz, 1H), 5.18 (dd, J = 17.0, 2.1 Hz, 1H), 4.98 (dd, J = 10.3, 1.7 Hz, 1H), 3.86 (dd, J = 7.1, 5.6 Hz, 1H), 3.39 (s, 3H), 2.21 (t, J = 6.7 Hz, 1H), 2.03 (dd, J = 9.1, 7.0 Hz, 1H), 1.89 (m, 1H), 1.71 (m, 1H), 1.58 (m, 1H), 1.42 (m, 1H), 1.28 (m, 1H), 1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 135.7, 116.0, 75.7, 55.6, 55.0, 41.4, 34.5, 26.8, 26.1, 22.6, 18.5; IR (film) 2938, 2103, 1616, 1356, 1340, 1125 cm^{-1}; HRMS (EI$^+$) calc'd for (m-N_2) $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1150.

α-Diazo ketone SM15 (Table 2, Entry 5). To a solution of methyl enol ether **SM13** (343 mg, 1.65 mmol) in anhydrous THF (17 mL) in a 100 mL round-botton flask under an atmosphere of N_2 was added TMSOK (231 mg, 1.82 mmol) at once. The reaction was stirred at 23 °C until judged complete by TLC (ca. 48 h) then cooled to 0 °C. Addition of Et_3N (1.15 mL, 8.25 mmol) via syringe was followed by dropwise addition of ethyl chloroformate (474 μL, 4.95 mmol). The reaction mixture was stirred for 2 h at 0 °C at which time CH_2N_2 (0.2 M in Et_2O, 20 mL; **Caution**!) was added and the resulting mixture was stirred with warming to 23 °C over 12 h. The reaction was quenched by careful addition of saturated $NaHCO_3$ (30 mL) and extracted with ether (3 X 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated in vacuo. Flash column chromatography (9:1 hexanes: ethyl acetate) of the bright yellow concentrate gave α-diazo ketone **SM15** (206 mg, 57% yield): R_F 0.70 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (comp. m, 2H), 5.16 (dd, J = 17.0, 1.8 Hz, 1H), 5.01 (dd, J = 10.2, 1.8 Hz, 1H), 4.74 (br s, 1H), 3.58 (s, 3H), 2.25 (br s, 1H), 1.83 - 2.18 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 154.5, 135.5, 116.0, 96.3, 56.3, 54.7, 45.3, 30.8, 24.7, 22.3, 21.8; IR (film) 2936, 2856, 2104, 1806, 1651, 1621, 1443, 1347, 1254, 1210, 1169, 1105 cm^{-1}; HRMS (EI$^+$) calc'd for (m-N_2) $[C_{12}H_{14}O_2]^+$: *m/z* 190.0994, found 190.0991.

Table 1. The Tandem Wolff/Cope Rearrangement.

entry	substrate	product	conditions[a]		% yield
1.			R = CH_3	A	95
2.			R = MOM	A	88
3.			R = PMB	A	92
4.				A	98
5.				A	98
6.				B	80
7.				A B	76 94[b]
8.				B	88

[a] Condition A: AgOBz (0.1 equiv), Et_3N (1.0 equiv), THF, 45 °C, sonication for 30 min. Condition B: *hν* (310 nm), THF, 23 °C, 1h. [b] Experiment performed in PhH for 2 h.

Representative Sonochemical Procedure for the Preparation of Fused [5-7] Bicycles (Entry 1 is used as an example):[13] A 125 mL Erlenmeyer flask was charged with the α-diazo ketone substrate (390 mg, 1.79 mmol) and dry AgOBz (41 mg, 0.179 mmol). The vial was septum sealed, evacuated and backfilled with N_2 (3 X) then anhydrous, degassed THF (65 mL) was added via syringe, followed immediately by Et_3N (247 μL, 1.80 mmol). The reaction mixture, which darkens slightly, was placed in an ultrasonic bath (VWR Model 75D) preheated to 45 °C and sonochemically irradiated (degas setting = 7) for 30 min. The resulting solution, which had darkened appreciably and developed a precipitate, was filtered through a short column of silica gel (5.0 cm X 10 cm; EtOAc eluent) to provide essentially pure [5-7] bicycle (327 mg, 95% yield) as a colorless oil. An analytical sample was obtained by preparative TLC (2:1 hexanes:ethyl acetate; 0.25 mm thickness): R_F 0.30 (2:1 hexanes: EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 6.09 (d, J = 2.5 Hz, 1H), 5.88 (dt, J = 9.2, 2.9 Hz, 1H), 5.40 (ddd, J = 9.2, 4.8, 2.9 Hz, 1H), 4.07 (t, J = 3.7 Hz, 1H), 3.56 (comp. m, 2H), 3.33 (s, 3H), 2.10 (m, 1H), 1.87 (comp.

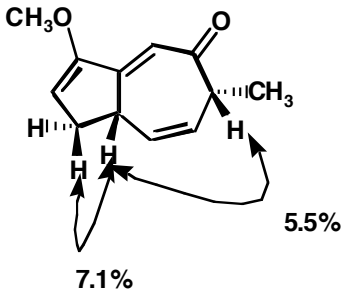
m, 3H), 1.24 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 165.0, 136.4, 132.0, 126.7, 84.3, 56.9, 47.9, 43.6, 31.3, 29.6, 14.6; IR (film) 2933, 1671, 1456, 1136, 1090, 1045 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1144.

Entry 2. β-Diazo ketone substrate sonochemically irradiated over 30 min at 45 °C. Purification by flash chromatography (2:1 hexanes: ethyl acetate) provided the desired [5-7] bicycle as a clear oil. R_F 0.63 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (dd, J = 3.1, 1.6 Hz, 1H), 5.94 (dt, J = 9.0, 2.7 Hz, 1H), 5.46 (m, 1H), 4.75 (d, J = 7.2 Hz, 1H), 4.71 (d, J = 7.2 Hz, 1H), 4.53 (td, J = 5.6, 1.3 Hz, 1H), 3.54 - 3.72 (comp. m, 2H), 3.40 (s, 3H), 2.18 (m, 1H), 1.80 - 2.00 (m, 3H), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 165.5, 136.5, 132.0, 126.2, 95.0, 79.3, 55.6, 47.7, 42.9, 31.6, 29.3, 14.4; IR (film) 2935, 1713, 1668, 1454, 1149, 1039 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{13}H_{19}O_3]^+$: *m/z* 223.1334, found 223.1337.

Entry 3. β-Diazo ketone substrate sonochemically irradiated over 30 min at 45 °C. Purification by flash chromatography (2:1 hexanes:ethyl acetate) provided the desired [5-7] bicycle as a clear oil. R_F 0.70 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 14.2 Hz, 2H), 6.91 (d, J = 14.2 Hz, 2H), 6.18 (dd, J = 3.1, 1.6 Hz, 1H), 5.94 (dt, J = 9.0, 2.9 Hz, 1H), 5.45 (ddd, J = 9.0, 4.5, 2.9 Hz, 1H), 4.53 (s, 2H), 4.30 (td, J = 4.8, 1.1 Hz, 1H), 3.82 (s, 3H), 3.62 (comp. m, 2H), 2.16 (m, 1H), 1.80 - 2.06 (comp. m, 2H), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 167.5, 160.1, 138.5, 131.1, 130.5, 130.0, 128.3, 114.5, 82.5, 71.4, 56.2, 48.5, 44.2, 31.2, 30.0, 14.2; IR (film) 2934, 1667, 1613, 1514, 1249, 1034 cm^{-1}; HRMS (FAB$^+$) calc'd for (m - H) $[C_{19}H_{21}O_3]^+$: *m/z* 297.1491, found 297.1492.

Entry 4. β-Diazo ketone substrate sonochemically irradiated over 30 min at 45 °C. Purification by flash chromatography (2:1 hexanes:ethyl acetate) provided the desired [5-7] bicycle as a clear oil. R_F 0.50 (2:1 hexanes:EtOAc) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (d, J = 2.93 Hz, 1H), 5.91 (dt, J = 9.1, 2.6 Hz, 1H), 5.46 (ddd, J = 10.8, 4.7, 2.9 Hz, 1H), 5.38 (t, J = 2.9 Hz, 1H), 4.05 (m, 1H), 3.75 (s, 3H), 3.63 (m, 1H), 2.90 (ddd, J = 17.2, 7.2, 3.2 Hz, 1H), 2.51 (dt, J = 17.3, 2.6 Hz, 1H), 1.27 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 161.0, 157.0, 135.8, 132.4, 118.5, 110.8, 57.1, 47.2, 42.3, 35.2, 14.7; IR (film) 2933, 1721, 1655, 1611, 1243 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{14}O_2]^+$: *m/z* 190.0994, found 190.0999.

NOE measurements of [5-7] bicycle:



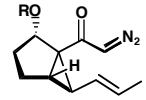
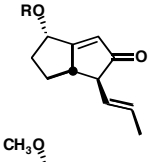
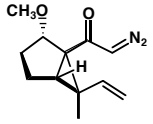
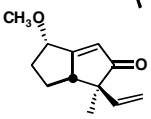
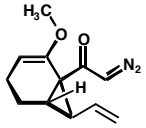
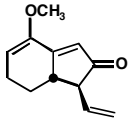
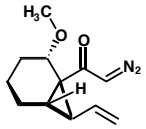
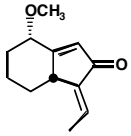
Entry 5. α-Diazo ketone substrate sonochemically irradiated over 30 min at 45 °C. Purification by flash chromatography (2:1 hexanes:ethyl acetate) provided the desired [5-7] bicycle as a clear oil. R_F 0.60 (2:1 hexanes:EtOAc) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (m, 1H), 5.61 (m, 1H), 4.07 (td, J = 4.4, 1.2 Hz, 1H), 3.67 (dd, J = 13.6, 0.6 Hz, 1H), 3.55 (m, 1H), 3.37 (s, 3H), 3.00 (t, J = 1.8 Hz, 1H), 2.95 (t, J = 1.8 Hz, 1H), 2.08 (m, 1H), 1.82 - 1.94 (comp. m, 2H), 1.80 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 195.3, 167.1, 133.2, 131.3, 126.3, 84.4, 60.0, 51.2, 43.1, 31.2, 29.8, 23.8; IR (film) 2965, 1656, 1264, 1091 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1143.

Entry 6. Prepared by photochemical irradiation of α-diazo ketone substrate in THF (0.001 M) at 310 nm for 1 h. The product bicycle isomerizes to multiple compounds upon attempted purification. Yield determined on crude reaction product using an added standard (1,4-dichlorobenzene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.98 (m, 1H), 5.84 (m, 1H), 4.13 (t, 1H), 3.65 (m, 1H), 3.42 - 3.51 (m, 1H), 3.40 (s, 3H), 3.21 (dd, 1H), 2.2 (m, 1H), 1.80 - 1.98 (m, 2H).

Entry 7. Prepared by either sonochemical irradiation (THF, 0.003 M, 30 min, 45 °C) or photochemical irradiation (PhH, 0.001 M, 310 nm, 23 °C, 2 h). Purification by flash chromatography (8:1 CH_2Cl_2: EtOAc) provided a white solid. An analytical sample was prepared by slow recrystallization of an ether solution as -15 °C. R_F 0.60 (4:1 CH_2Cl_2: EtOAc); mp = 65-67 °C (relative to biphenyl 69-72 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (d, J = 7.9 Hz, 1H), 6.05 (t, J = 7.6 Hz, 1H), 5.80 (t, J = 1.8 Hz, 1H), 4.13 (m, 1H), 3.51 (m, 1H), 3.37 (s, 3H), 2.04 - 2.18 (comp. m, 2H), 1.80 -1.99 (comp. m, 4H), 1.62 - 1.76 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 171.5, 143.7, 127.5, 122.4, 83.6, 56.9, 52.8, 49.8, 35.9, 34.7, 30.8, 23.1; IR (film) 2939, 1660, 1459, 1282, 1195, 1125, 1094 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{13}H_{16}O_2]^+$: *m/z* 204.1150, found 204.1141.

Entry 8. Photochemical irradiation (THF, 0.001 M, 310 nm, 1 h) and purification by flash chromatography (9:1 hexanes: EtOAc) provided the [5-7] bicycle as a clear oil. R_F 0.44 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) □6.28 (s, 1H), 5.81 (ddd, *J* = 10.9, 5.8, 2.1 Hz, 1H), 5.69 (ddd, *J* = 10.9, 6.8, 4.5 Hz, 1H), 3.58 (ddd, *J* = 10.0, 4.8, 1.3 Hz, 1H), 3.45 (s, 3H), 3.39 (m, 1H), 1.96 (m, 1H), 1.65 (comp. m, 2H), 1.45 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) □196.3, 158.5, 132.9, 122.2, 120.9, 83.2, 57.7, 44.9, 44.3, 35.2, 33.4, 24.0; IR (film) 2937, 2861, 1659, 1279, 1120, 1079 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1154.

Table 2. The Wolff/Cope/1,3-Acyl Shift Rearrangement.

entry	substrate	product		conditions[a]	time	% yield
1.			R = CH_3	B	12 h	72
2.			R = MOM	B	6 h	69
3.			R = PMB	B	6 h	75
4.				B[b]	2 h	80
5.				A	0.5 h	57
6.				B[c]	6 h	55
				A	0.5 h	72

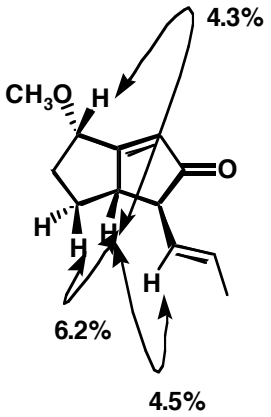
[a] Condition A: AgOBz (0.1 equiv), Et_3N (1.0 equiv), THF, 45 °C, sonication. Condition B: *h*□(254 nm), THF, 23 °C. [b] Performed with a 450 Watt medium pressure Hg lamp in THF at 40 °C. [c] *h*□(310 nm)

Representative Photolytic Procedure for the Preparation of Fused [5-5] Bicycles (Entry 3 is used as an example): In a 10 mL quartz test-tube was placed the □-diazo ketone substrate(18.9 mg, 0.0579 mmol). The test-tube was tightly capped with a rubber septum wrapped in teflon tape then evacuated and backfilled with N_2 (3 X). To the flask was added anhydrous THF (6 mL) and the resulting solution was irradiated at 254 nm in a Luzchem photoreactor for 6 h. The resulting reaction mixture was concentrated under reduced pressure and purified by preparative TLC (2:1 hexanes:ethyl acetate; 0.5 mm thickness) to yield [5-5] bicycle (12.9 mg, 74% yield) along with the corresponding [5-7] bicycle (2 mg, 12% yield). Characterization data for [5-5] bicycle: R_F 0.35 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) □7.32 (d, *J* = 14.2 Hz, 2H), 6.93 (d, *J* = 14.2 Hz, 2H), 6.16 (t, *J* = 1.9 Hz, 1H), 5.65 (dqd, *J* = 15.4, 13.6, 0.8 Hz, 1H), 5.50 (ddd, *J* = 15.4, 6.9, 1.3 Hz, 1H), 4.73 (m, 1H), 4.65 (d, *J*

= 11.4 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 3.80 (s, 3H), 2.76 - 2.87 (comp. m, 2H), 2.15 - 2.36 (comp. m, 2H), 2.05 (m, 1H), 1.76 (d, *J* = 6.1 Hz, 3H), 1.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 209.9, 186.7, 159.5, 129.7, 129.5, 129.2, 126.9, 123.9, 114.0, 75.7, 71.9, 59.0, 55.3, 49.9, 32.3, 28.5, 18.2; IR (film) 2936, 2868, 1714, 1644, 1614, 1586, 1515, 1464, 1460, 1302, 1249, 1174, 1112, 1083, 1035 cm^{-1}; HRMS (FAB$^+$) calc'd for (m + H) $[C_{19}H_{23}O_3]^+$: *m/z* 299.1647, found 299.1640.

Entry 1. -Diazo ketone substrate photolytically irradiated (THF, 0.001 M, 254 nm, 6 h, 23 °C) and purified by flash chromatography (2:1 hexanes:ethyl acetate) to provide the [5-5] bicycle as a clear oil (72% yield) along with a minor amount of [5-7] bicycle (10% yield): R_F 0.48 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) 6.11 (t, *J* = 1.8 Hz, 1H), 5.40 - 5.70 (comp. m, 2H), 4.55 (m, 1H), 3.48 (s, 3H), 2.78 (m, 1H), 2.24 (m, 1H), 2.01 (m, 1H), 1.73 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 210.2, 186.4, 129.5, 127.0, 124.1, 78.4, 59.1, 58.0, 50.3, 32.0, 28.7, 18.4; IR (film) 2935, 1706, 1645, 1456, 1362, 1200 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1150.

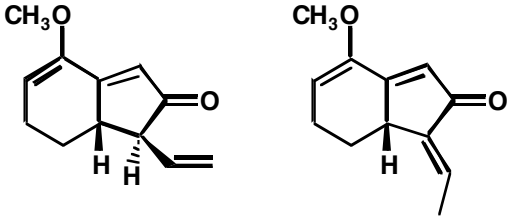
NOE measurements of [5-5] Bicycle:



Entry 2. -Diazo ketone substrate photolytically irradiated (THF, 0.001M, 254 nm, 6h, 23 °C) and purified by flash chromatography (2:1 hexanes:ethyl acetate) to provide the [5-5] bicycle as a clear oil (69% yield) along with a minor amount of [5-7] bicycle (12% yield): R_F 0.50 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) 6.13 (t, *J* = 1.9 Hz, 1H), 5.66 (dq, *J* = 15.3, 6.4 Hz, 1H), 5.51 (ddd, *J* = 15.4, 6.9, 1.3 Hz, 1H), 4.92 (m, 1H), 4.76 (s, 2H), 3.41 (s, 3H), 2.76 - 2.88 (m, 2H), 3.37 (m, 1H), 2.22 (m, 1H), 2.01 (m, 1H), 1.76 (d, *J* = 6.1 Hz, 3H), 1.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 209.8, 186.6, 129.3, 126.8, 123.9, 96.1, 74.0, 59.2, 55.7, 49.6, 32.8, 28.4, 18.2; IR (film) 2939, 1713, 1644, 1451, 1151, 1050 cm^{-1}; HRMS (FAB$^+$) calc'd for (m + H) $[C_{13}H_{19}O_3]^+$: *m/z* 223.1334, found 223.1325.

Entry 4. -Diazo ketone substrate photolytically irradiated (THF, 0.001 M, medium pressure Hg lamp, 450 W, 2 h, 23 °C) and purified by flash chromatography (20:1 CH_2Cl_2:EtOAc) to

provide the [5-5] bicycle as a clear oil (80% yield): R_F 0.46 (10:1 CH_2Cl_2:EtOAc) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10 (t, *J* = 2.4 Hz, 1H), 6.01 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.19 (dd, *J* = 1.9, 1.1 Hz, 1H), 5.14 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.58 (ddd, *J* = 8.5, 3.7, 1.6 Hz, 1H), 3.50 (s, 3H), 3.08 (m, 1H), 2.28 (m, 1H), 1.87 - 2.07 (comp. m, 2H), 1.71 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 141.0, 121.9, 114.2, 78.1, 77.2, 57.7, 55.0, 53.7, 31.8, 23.1, 20.2; IR (film) 2932, 1713, 1646, 1635, 1456, 1200, 1088 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{12}H_{17}O_2]^+$: *m/z* 193.1229, found 193.1231.

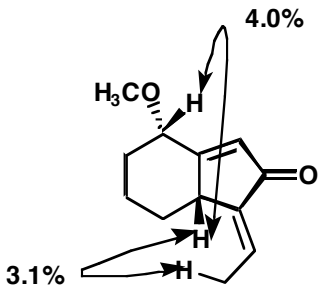


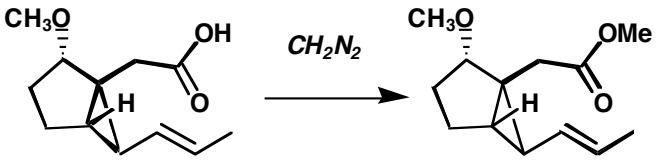
Entry 5. Sonochemical irradiation (30 min, 45 °C) of diazo ketone substrate and purification by flash chromatography (9:1 hexanes:ethyl acetate) provided the [6-5] bicycle bearing a terminal olefin (57% yield) along with an isomer in which the olefin had migrated into conjugation with the carbonyl (14% yield) : Characterization data for terminal olefin product: R_F 0.46 (2:1 hexanes:EtOAc) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.86 (ddd, *J* = 17.2, 10.4, 7.0 Hz, 1H), 5.20 - 5.36 (m, 3H), 3.63 (s, 3H), 2.76 (comp. m, 2H), 2.44 (comp. m, 2H), 2.16 (m, 1H), 1.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 167.8, 150.4, 134.3, 121.9, 118.6, 108.1, 58.6, 54.8, 45.6, 28.2, 25.2; IR (film) 2929, 1694, 1621, 1590, 1442, 1386, 1238, 1023 cm^{-1}; HRMS calc'd for (m + H)$[C_{12}H_{15}O_2]^+$: *m/z* 191.1072, found 191.1070. Characterization data for conjugated olefin product: R_F 0.36 (2:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (qd, *J* = 7.2, 1.6 Hz, 1H), 6.30 (d, *J* = 1.86 Hz, 1H), 5.29 (dd, *J* = 5.8, 3.2 Hz, 1H), 3.68 (s, 3H), 3.46 (m, 1H), 2.40 - 2.59 (m, 3H), 2.95 (d, *J* = 7.1 Hz, 3H), 1.49 (m, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 195.6, 164.6, 150.4, 139.4, 130.6, 124.7, 106.3, 54.6, 42.4, 27.4, 25.2, 14.7; IR (film) 2936, 2834, 1732, 1688, 1652, 1621, 1585, 1236, 1187, 1109, 1088, 1026 cm^{-1}; HRMS (FAB$^+$) calc'd for (m + H)$[C_{12}H_{15}O_2]^+$: *m/z* 191.1072, found 191.1069

Entry 6. Sonochemical irradiation (30 min, 45 °C) of α-diazo ketone substrate and purification by flash chromatography (9:1 hexanes:ethyl acetate) provided the [6-5] bicycle (72% yield) as a clear oil: R_F 0.50 (2:1 hexanes:ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (qd, *J* = 7.2, 1.6 Hz, 1H), 6.23 (s, 1H), 4.00 (ddd, *J* = 12.2, 5.8 Hz, 1H), 3.52 (s, 3H), 3.21 (dd, *J* = 12.0, 5.1 Hz, 1H), 2.35 (comp. m, 2H), 1.98 (m, 1H), 1.91 (d, *J* = 7.2 Hz, 3H), 1.64 (m, 1H), 1.38 (ddd, *J* = 17.4, 11.6, 3.5 Hz, 1H), 1.09 (ddd, *J* = 17.3, 12.5, 3.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 177.2, 139.6, 130.0, 125.4, 79.7, 57.4, 43.8, 33.8, 32.7, 23.5, 14.7; IR (film) 2940, 2861,

1701, 1657, 1615, 1445, 1378, 1256, 1207, 1129, 1103 cm^{-1}; HRMS (EI^+) calc'd for $[C_{12}H_{16}O_2]^+$: *m/z* 192.1150, found 192.1156.

NOE measurements of [6-5] bicycle:



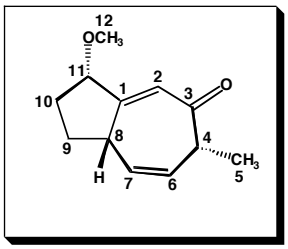


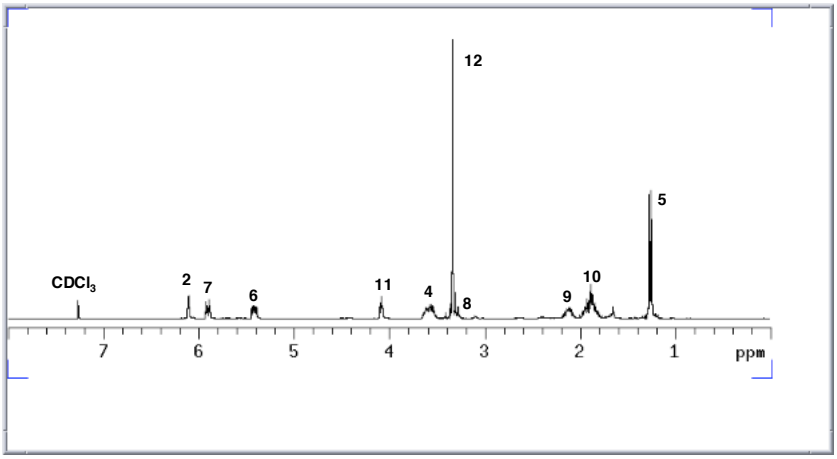
7

Homologated Methyl Ester. R_F 0.56 (2:1 hexanes:ethyl acetate) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (dqd, *J* = 15.3, 6.4, 0.8 Hz, 1H), 5.21 (ddd, *J* = 15.2, 7.6, 1.6 Hz, 1H), 4.06 (t, *J* = 7.7 Hz, 1H), 3.71 (s, 3H), 3.34 (s, 3H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.2 Hz, 1H), 1.73 - 2.04 (comp. m, 4H), 1.70 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.31 (t, *J* = 4.0 Hz, 1H), 1.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 128.4, 126.7, 85.7, 57.6, 51.5, 34.4, 33.2, 28.7, 26.7, 24.9, 23.7, 18.1; IR (film) 2953, 2865, 2821, 1740, 1436, 1375, 1338, 1248, 1203, 1171, 1106, 1031 cm^{-1}. HRMS (EI^+) calc'd for $[C_{13}H_{20}O_3]^+$: *m/z* 224.1413, found 224.1408.

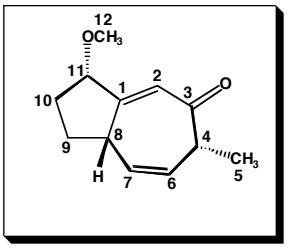
Advanced NMR Spectra for [5-7] Bicycle

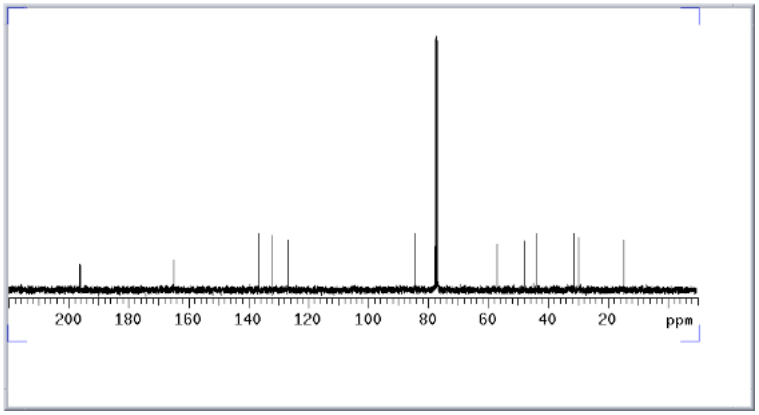
Proton NMR Assignments for [5-7] Bicycle



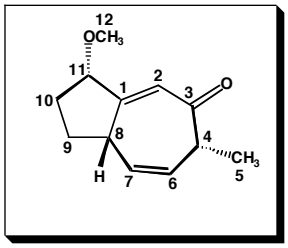


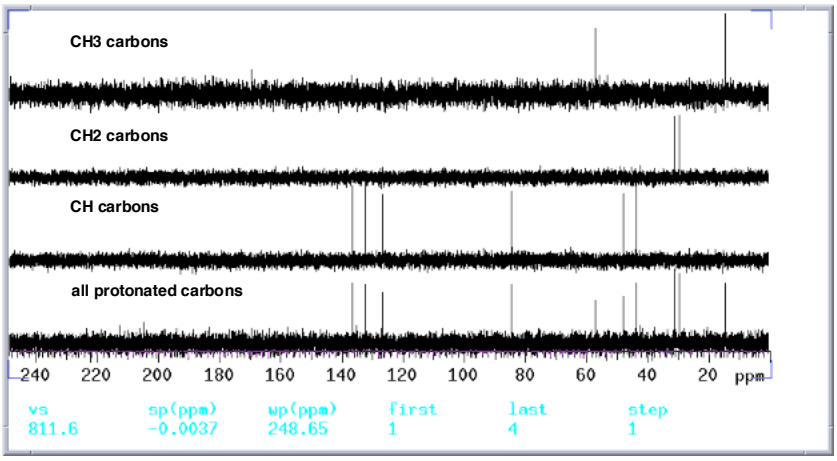
[5-7] Bicycle 13C NMR



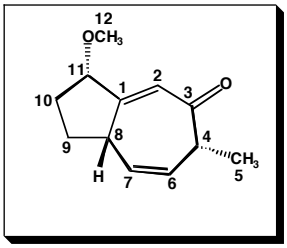


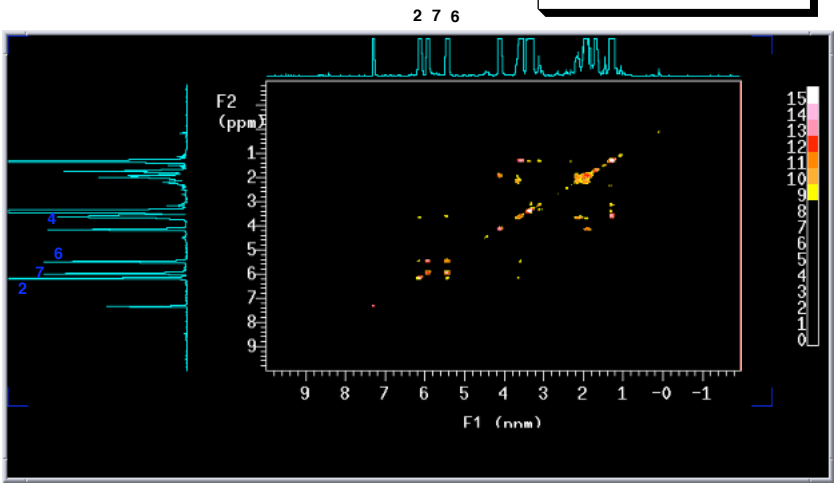
[5-7] Bicycle DEPT NMR



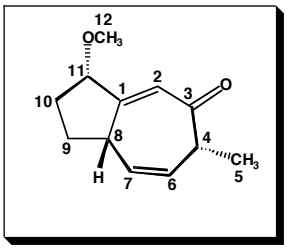


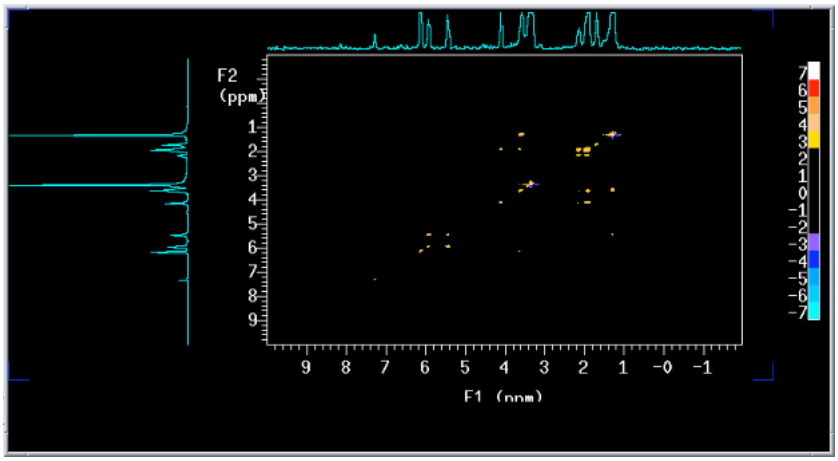
[5-7] Bicycle COSY NMR



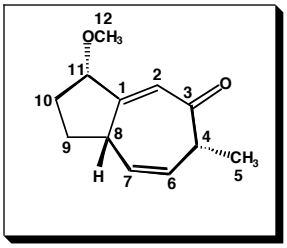


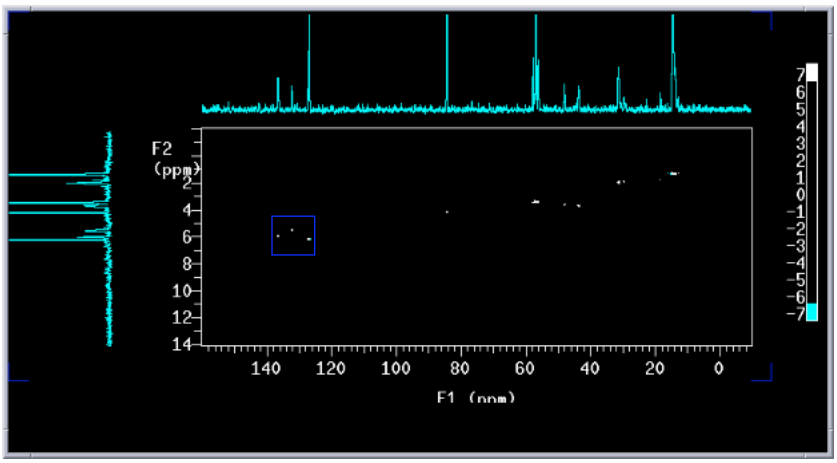
[5-7] Bicycle TOCSY NMR



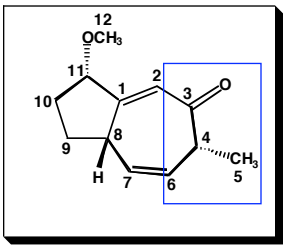


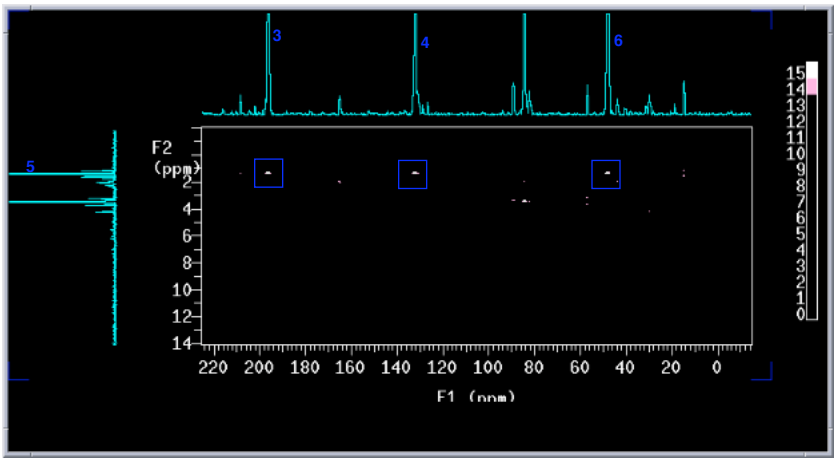
[5-7] Bicycle HMQC NMR





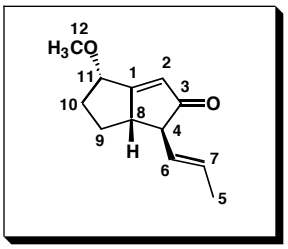
[5-7] Bicycle HMBC NMR

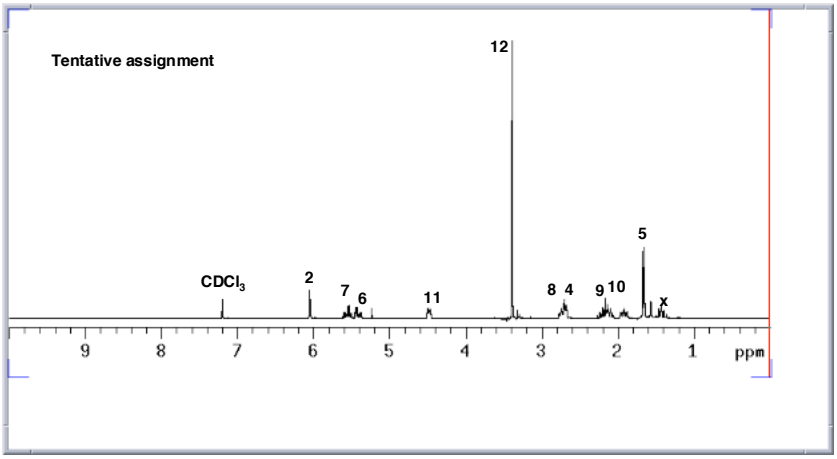




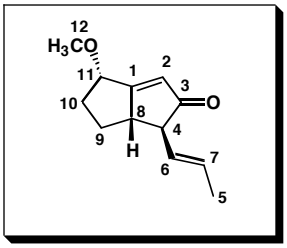
Advanced NMR Spectra for [5-5] Bicycle

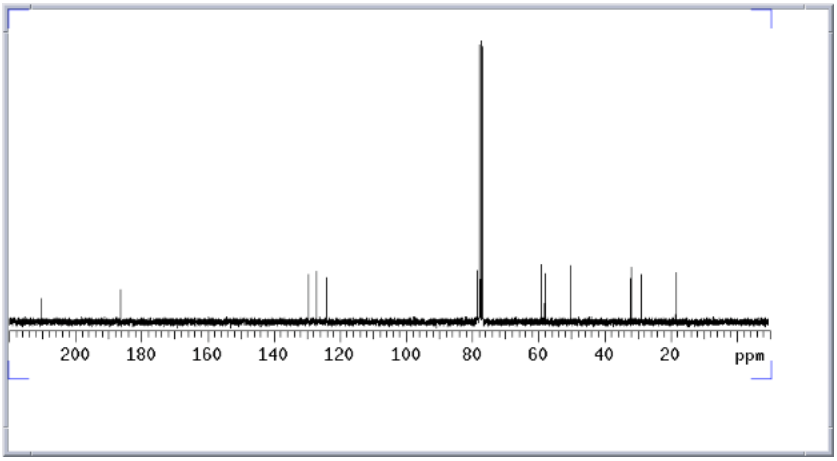
[5-5] Bicycle 1H NMR



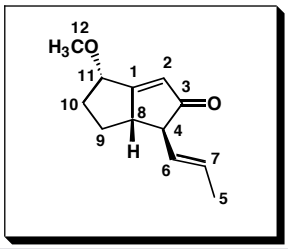


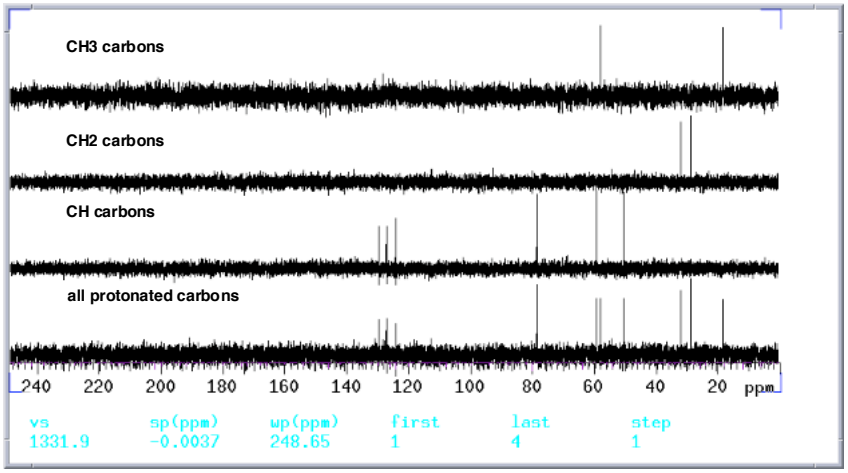
[5-5] Bicycle 13C NMR



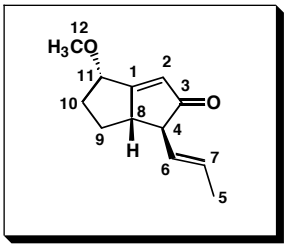


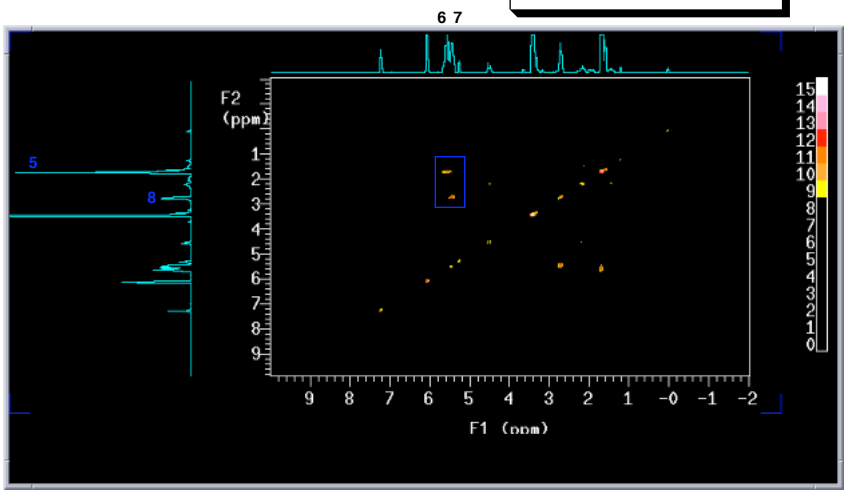
[5-5] Bicycle DEPT NMR



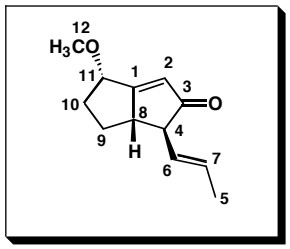


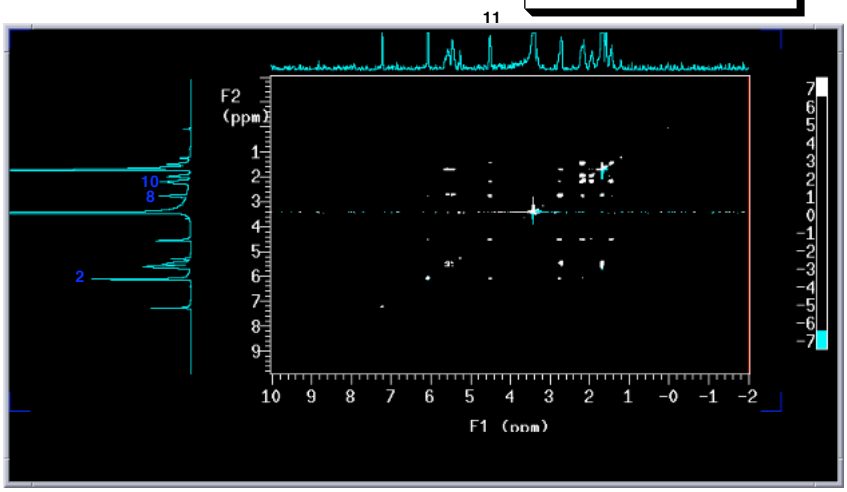
[5-5] Bicycle COSY NMR



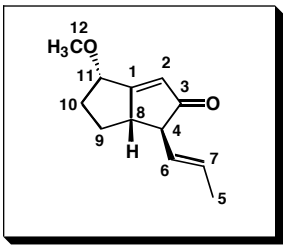


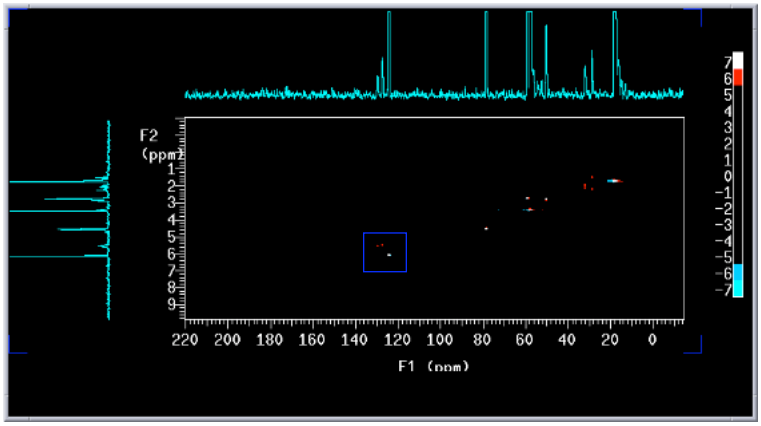
[5-5] Bicycle TOCSY NMR



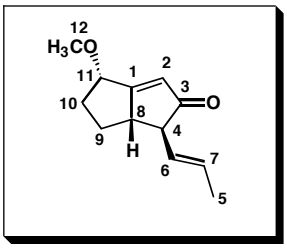


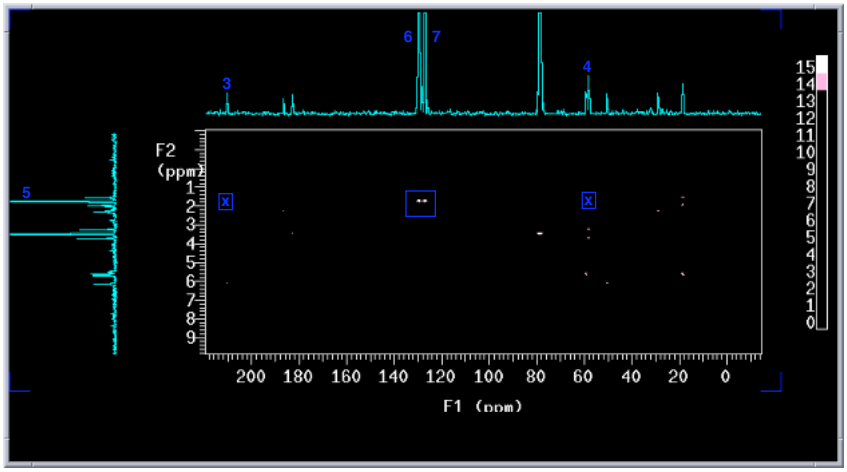
[5-5] Bicycle HMQC NMR



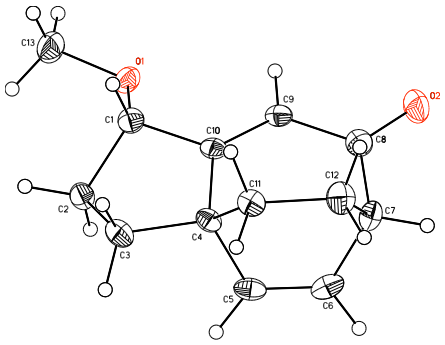


[5-5] Bicycle HMBC NMR





X-Ray Crystallography Material



[5-7] Bicycle Product (Table 1, Entry 7)

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 216172.

Table 3. Crystal data and structure refinement for [5-7] Bicycle (Table 1, Entry 7) (CCDC 216172).

Empirical formula	$C_{13}H_{15}O_2$
Formula weight	203.25
Crystal Habit	Plate
Crystal size	0.31 x 0.30 x 0.17 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKa
Data Collection Temperature	100(2) K
q range for 8432 reflections used in lattice determination	2.70 to 28.04°
Unit cell dimensions	a = 9.2557(8) Å b = 10.1353(9) Å c = 11.2231(10) Å
Volume	1052.83(16) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.282 Mg/m^3
F(000)	436
Data collection program	Bruker SMART v5.054
q range for data collection	2.71 to 28.19°
Completeness to q = 28.19°	96.0%
Index ranges	$-11 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Data collection scan type	w scans at 5 f settings and 1 f scan
Data reduction program	Bruker SAINT v6.022
Reflections collected	17022
Independent reflections	2434 [R_{int}= 0.0586]
Absorption coefficient	0.085 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9857 and 0.9741

Table 3 (cont.)

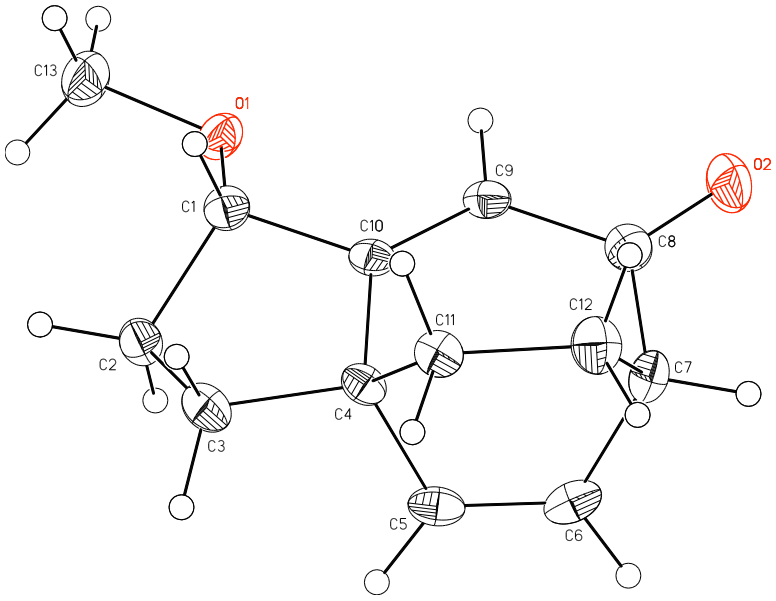
Structure solution and Refinement

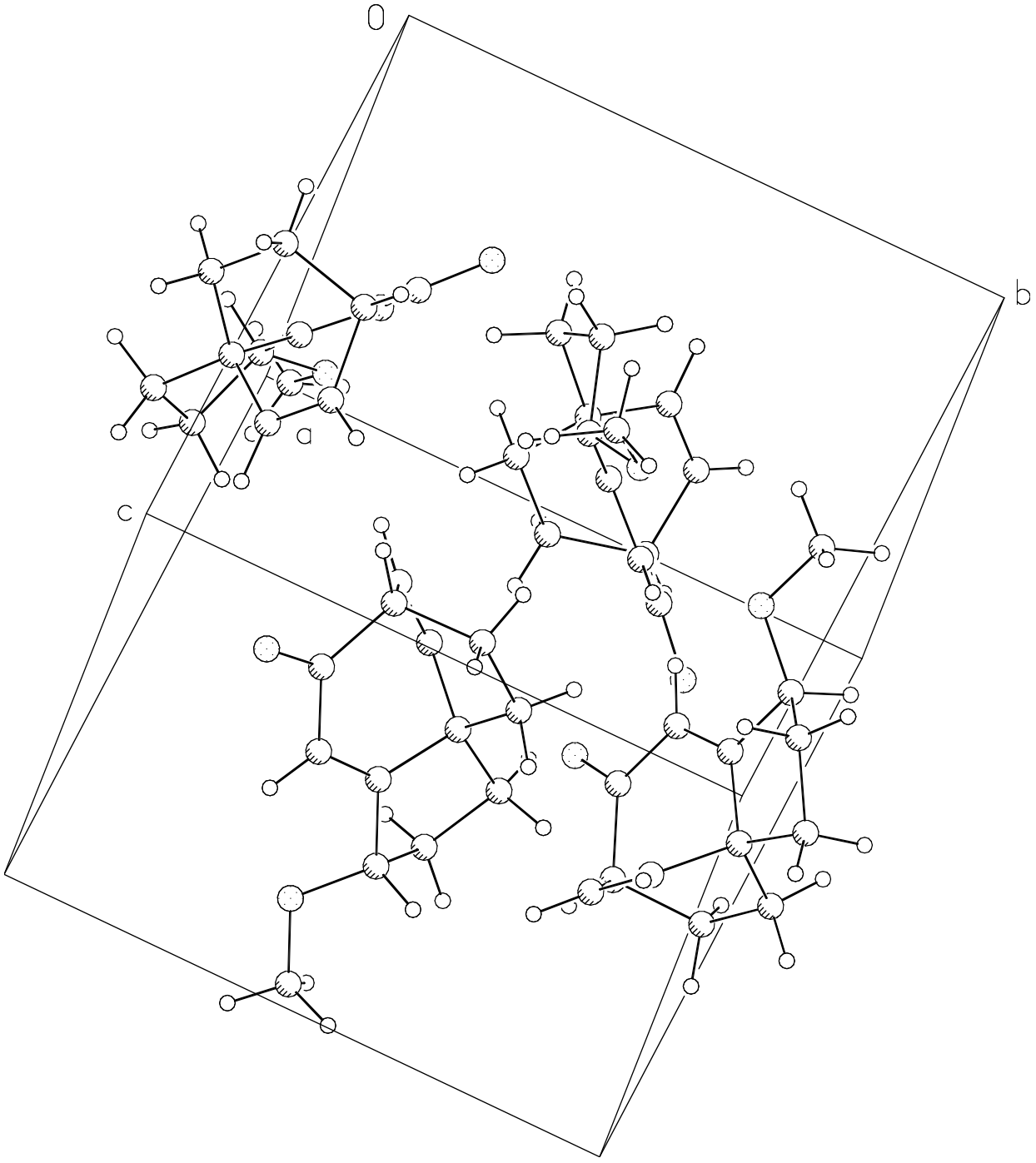
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2434 / 0 / 200
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.821
Final R indices [I>2s(I), 2135 reflections]	R1 = 0.0372, *w*R2 = 0.0557
R indices (all data)	R1 = 0.0448, *w*R2 = 0.0564
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/s^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.1(10)
Largest diff. peak and hole	0.212 and -0.309 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2s(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C13
O1
C1
C10
C9
O2
C8
C12
C11
C2
C7
C4
C3
C5
C6


0
b
a
c

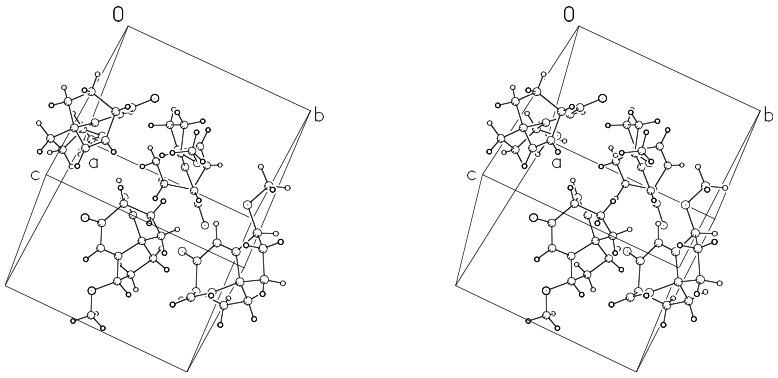

0
b
c
a
0
b
c
a

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [5-7] BICYCLE (TABLE 1, ENTRY 7) (CCDC 216172). U(eq) is defined as the trace of the orthogonalized U^{iJ} tensor.

	x	y	z	U_{eq}
O(1)	10831(1)	3964(1)	7633(1)	21(1)
O(2)	5811(1)	2200(1)	7260(1)	32(1)
C(1)	10099(1)	4931(1)	6966(1)	19(1)
C(2)	10808(2)	5401(1)	5809(1)	22(1)
C(3)	9545(2)	6089(1)	5203(1)	24(1)
C(4)	8237(1)	5186(1)	5428(1)	17(1)
C(5)	7980(2)	4205(1)	4429(1)	21(1)
C(6)	6829(2)	3444(1)	4487(1)	23(1)
C(7)	5829(2)	3590(1)	5542(1)	22(1)
C(8)	6475(1)	3022(1)	6676(1)	21(1)
C(9)	7890(1)	3493(1)	7081(1)	19(1)
C(10)	8651(1)	4442(1)	6551(1)	17(1)
C(11)	6819(2)	5960(1)	5637(1)	20(1)
C(12)	5492(2)	5076(1)	5736(1)	26(1)
C(13)	12151(2)	4456(2)	8116(2)	30(1)

Table 5. Bond lengths [Å] and angles [°] for [5-7] BICYCLE (TABLE 1, ENTRY 7) (CCDC 216172).

O(1)-C(1)	1.4069(14)	H(2A)-C(2)-H(2B)	107.6(10)
O(1)-C(13)	1.4262(16)	C(2)-C(3)-C(4)	104.98(10)
O(2)-C(8)	1.2252(15)	C(2)-C(3)-H(3A)	112.4(8)
C(1)-C(10)	1.5033(17)	C(4)-C(3)-H(3A)	113.0(9)
C(1)-C(2)	1.5313(17)	C(2)-C(3)-H(3B)	110.4(8)
C(1)-H(1)	1.011(11)	C(4)-C(3)-H(3B)	107.7(7)
C(2)-C(3)	1.521(2)	H(3A)-C(3)-H(3B)	108.2(11)
C(2)-H(2A)	0.989(13)	C(5)-C(4)-C(10)	109.13(9)
C(2)-H(2B)	0.990(14)	C(5)-C(4)-C(3)	113.07(11)
C(3)-C(4)	1.5391(18)	C(10)-C(4)-C(3)	103.47(10)
C(3)-H(3A)	0.989(14)	C(5)-C(4)-C(11)	108.16(11)
C(3)-H(3B)	1.001(14)	C(10)-C(4)-C(11)	109.90(10)
C(4)-C(5)	1.5171(18)	C(3)-C(4)-C(11)	112.98(10)
C(4)-C(10)	1.5182(17)	C(6)-C(5)-C(4)	118.26(12)
C(4)-C(11)	1.5476(18)	C(6)-C(5)-H(5)	125.3(8)
C(5)-C(6)	1.3171(19)	C(4)-C(5)-H(5)	116.4(8)
C(5)-H(5)	0.980(14)	C(5)-C(6)-C(7)	118.53(13)
C(6)-C(7)	1.5100(19)	C(5)-C(6)-H(6)	124.4(8)
C(6)-H(6)	0.963(14)	C(7)-C(6)-H(6)	117.0(8)
C(7)-C(8)	1.5190(18)	C(6)-C(7)-C(8)	112.24(11)
C(7)-C(12)	1.5533(19)	C(6)-C(7)-C(12)	109.14(11)
C(7)-H(7)	0.972(13)	C(8)-C(7)-C(12)	109.20(11)
C(8)-C(9)	1.4662(18)	C(6)-C(7)-H(7)	111.0(7)
C(9)-C(10)	1.3318(17)	C(8)-C(7)-H(7)	106.8(7)
C(9)-H(9)	0.959(12)	C(12)-C(7)-H(7)	108.5(7)
C(11)-C(12)	1.5245(19)	O(2)-C(8)-C(9)	120.23(12)
C(11)-H(11A)	0.992(14)	O(2)-C(8)-C(7)	120.52(12)
C(11)-H(11B)	1.000(13)	C(9)-C(8)-C(7)	119.23(12)
C(12)-H(12A)	0.958(13)	C(10)-C(9)-C(8)	124.65(13)
C(12)-H(12B)	0.966(15)	C(10)-C(9)-H(9)	119.8(7)
C(13)-H(13A)	0.972(16)	C(8)-C(9)-H(9)	115.6(7)
C(13)-H(13B)	0.988(15)	C(9)-C(10)-C(1)	124.84(12)
C(13)-H(13C)	1.015(16)	C(9)-C(10)-C(4)	126.58(12)
C(1)-O(1)-C(13)	111.80(10)	C(1)-C(10)-C(4)	108.56(10)
O(1)-C(1)-C(10)	111.35(10)	C(12)-C(11)-C(4)	113.32(10)
O(1)-C(1)-C(2)	117.45(11)	C(12)-C(11)-H(11A)	110.7(8)
C(10)-C(1)-C(2)	102.81(10)	C(4)-C(11)-H(11A)	105.1(8)
O(1)-C(1)-H(1)	109.0(6)	C(12)-C(11)-H(11B)	109.7(7)
C(10)-C(1)-H(1)	109.5(7)	C(4)-C(11)-H(11B)	107.6(7)
C(2)-C(1)-H(1)	106.3(6)	H(11A)-C(11)-H(11B)	110.4(10)
C(3)-C(2)-C(1)	101.08(11)	C(11)-C(12)-C(7)	113.46(11)
C(3)-C(2)-H(2A)	114.1(7)	C(11)-C(12)-H(12A)	110.9(7)
C(1)-C(2)-H(2A)	113.3(7)	C(7)-C(12)-H(12A)	108.3(8)
C(3)-C(2)-H(2B)	111.6(7)	C(11)-C(12)-H(12B)	108.4(8)
C(1)-C(2)-H(2B)	109.1(7)	C(7)-C(12)-H(12B)	106.8(8)

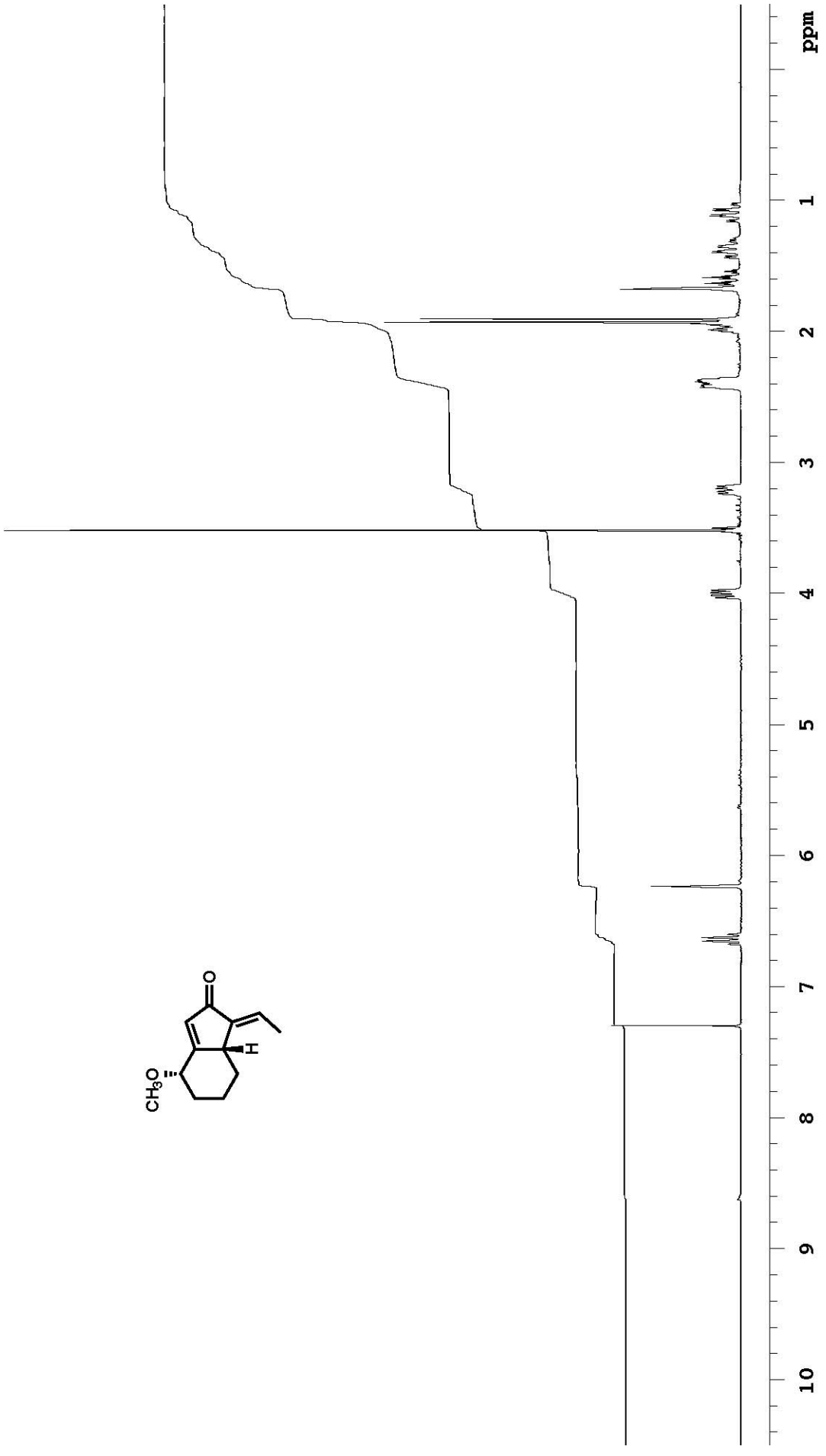
H(12A)-C(12)-H(12B)	108.8(12)
O(1)-C(13)-H(13A)	110.8(8)
O(1)-C(13)-H(13B)	104.0(8)
H(13A)-C(13)-H(13B)	113.4(12)
O(1)-C(13)-H(13C)	111.3(8)
H(13A)-C(13)-H(13C)	108.6(13)
H(13B)-C(13)-H(13C)	108.6(12)

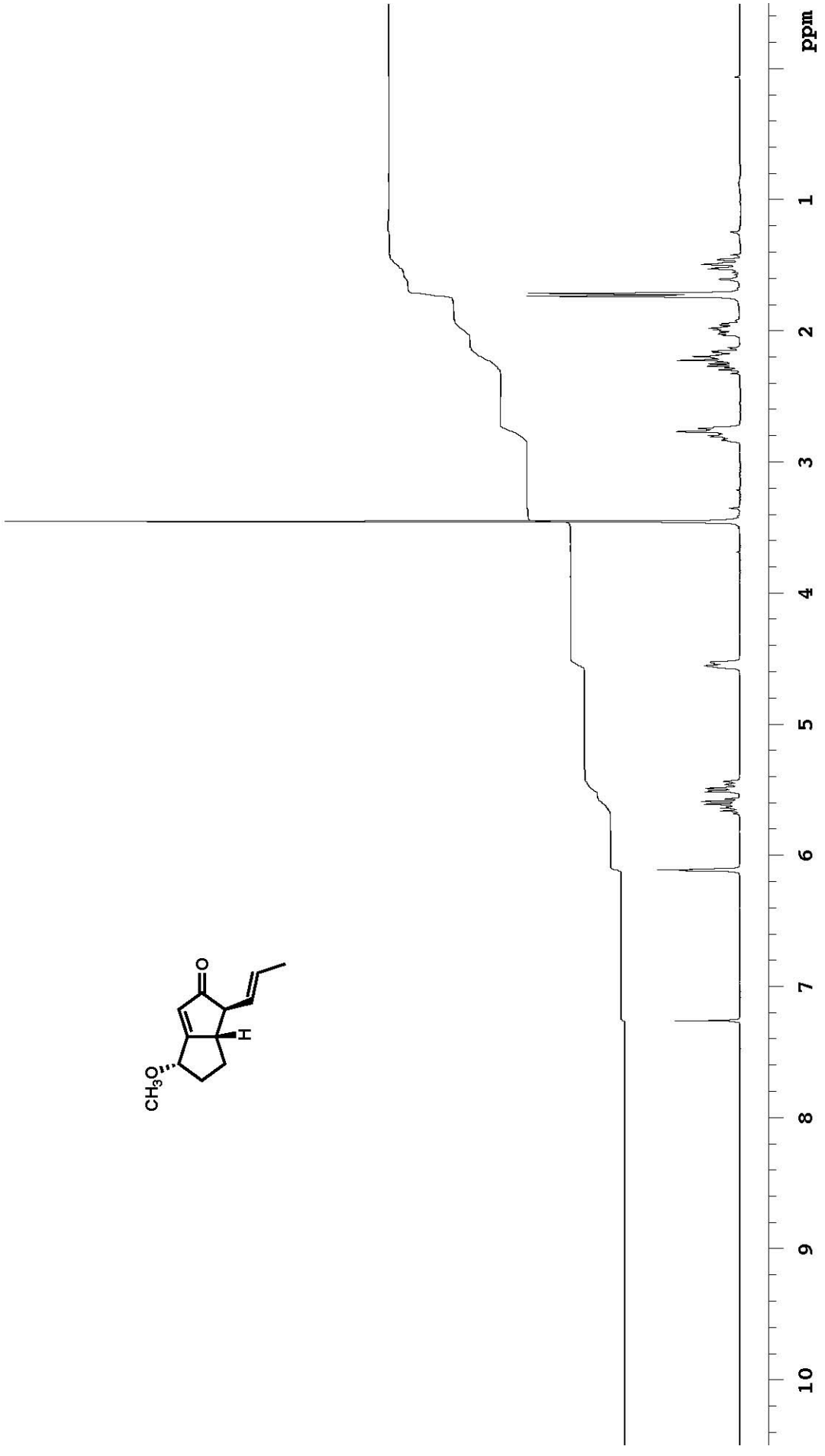
Table 6. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for [5-7] Bicycle (Table 1, Entry 7) (CCDC 216172). The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

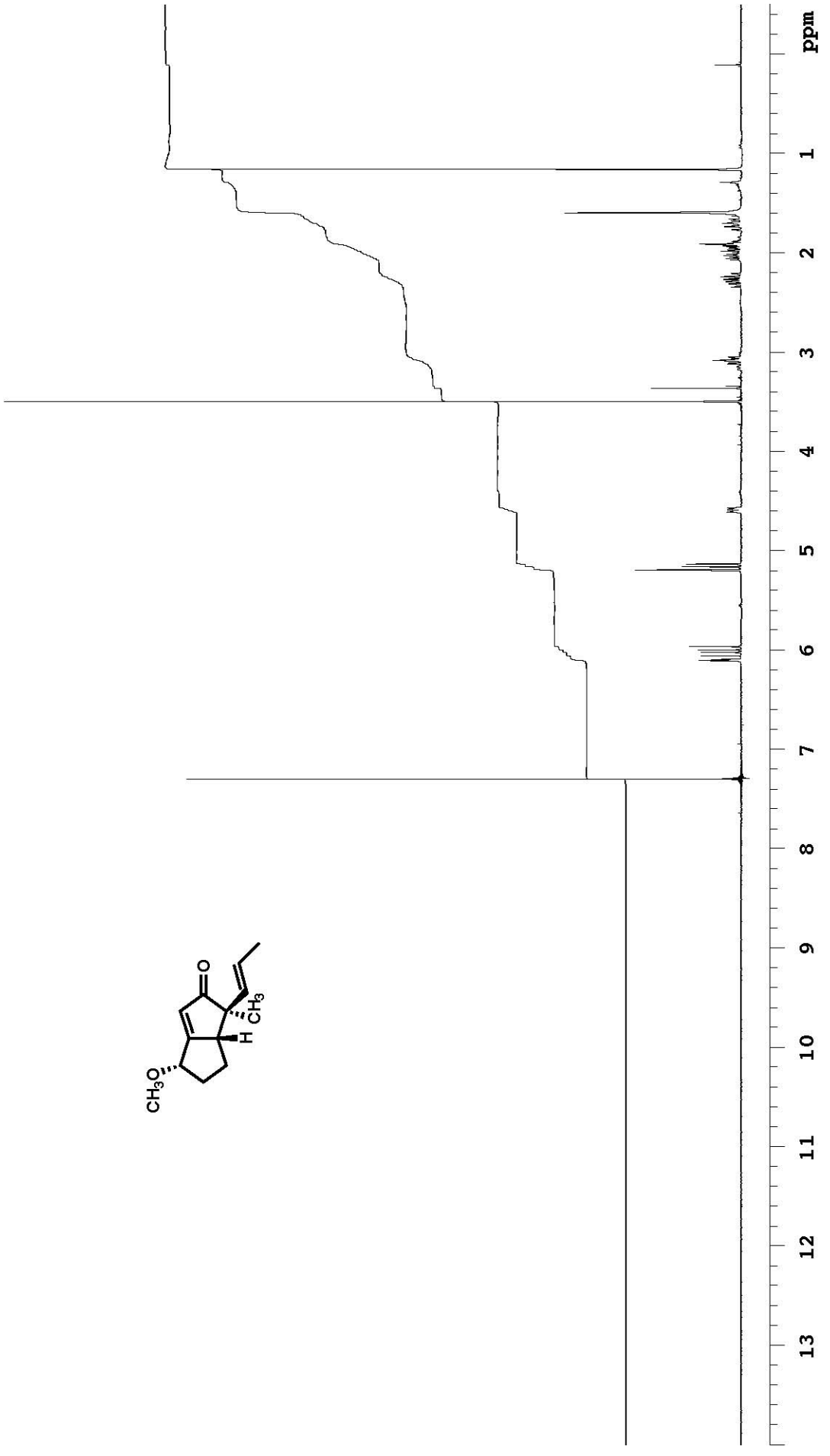
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	191(5)	234(5)	205(5)	5(4)	-51(4)	-11(4)
O(2)	316(6)	313(5)	328(6)	86(4)	-5(5)	-129(5)
C(1)	205(7)	180(6)	194(7)	-12(6)	1(6)	7(6)
C(2)	198(8)	227(7)	219(7)	-2(6)	27(6)	-26(7)
C(3)	261(8)	225(7)	230(8)	43(6)	44(6)	-11(6)
C(4)	178(7)	167(6)	166(6)	26(5)	27(6)	26(6)
C(5)	265(8)	208(7)	145(7)	30(6)	0(6)	77(6)
C(6)	303(8)	188(6)	188(7)	-30(6)	-74(6)	58(7)
C(7)	191(7)	187(7)	266(7)	-10(6)	-36(7)	-35(7)
C(8)	235(8)	164(6)	223(7)	-35(6)	33(6)	2(6)
C(9)	231(7)	188(6)	137(7)	7(6)	-6(6)	4(6)
C(10)	201(7)	160(6)	135(6)	-30(5)	29(5)	23(6)
C(11)	223(8)	174(6)	214(7)	-2(6)	17(6)	27(6)
C(12)	211(8)	246(7)	324(9)	-5(7)	11(7)	34(6)
C(13)	241(9)	375(9)	289(9)	56(8)	-79(7)	-61(7)

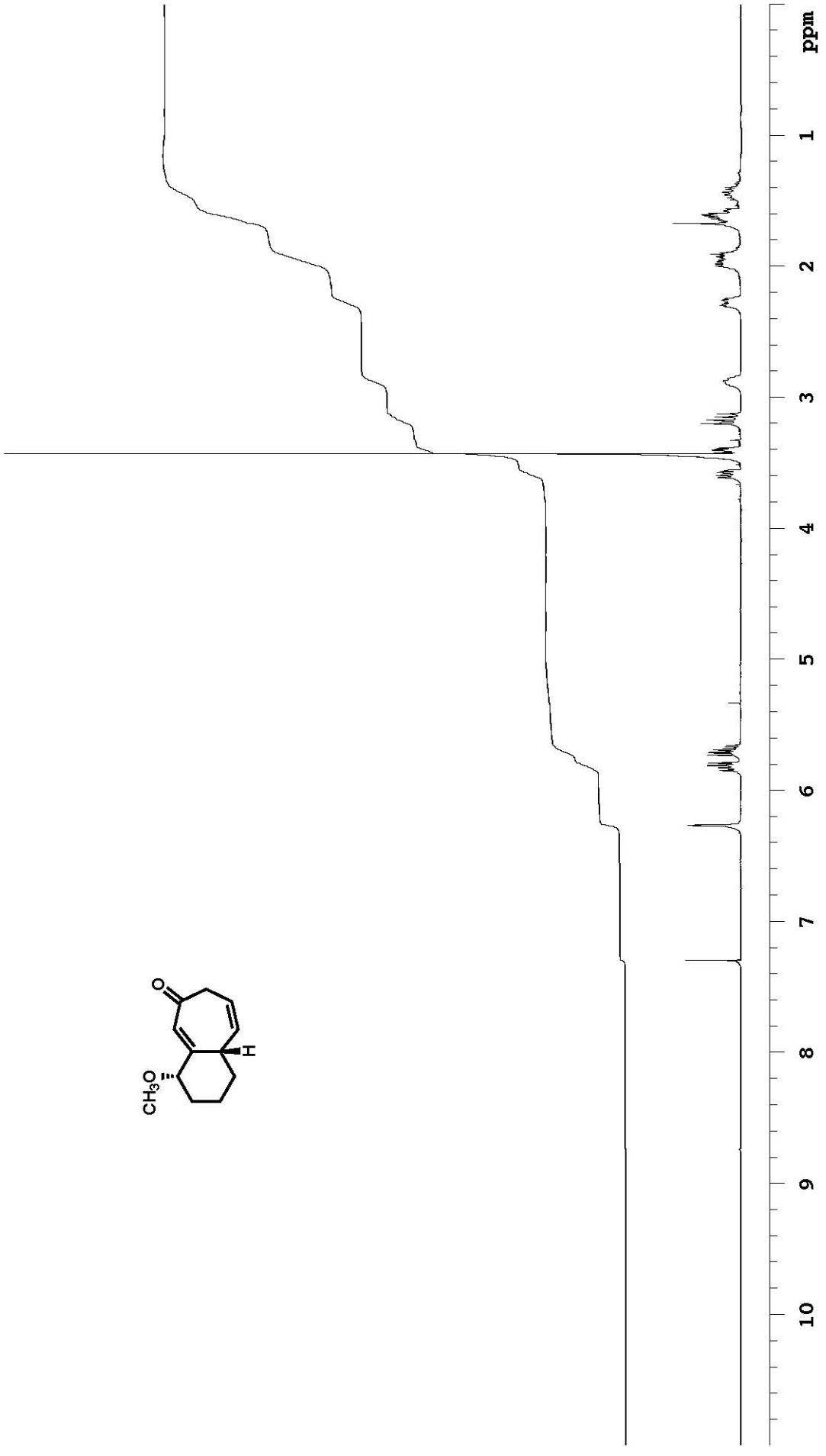
Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [5-7] Bicycle (Table 1, Entry 7) (CCDC 216172).

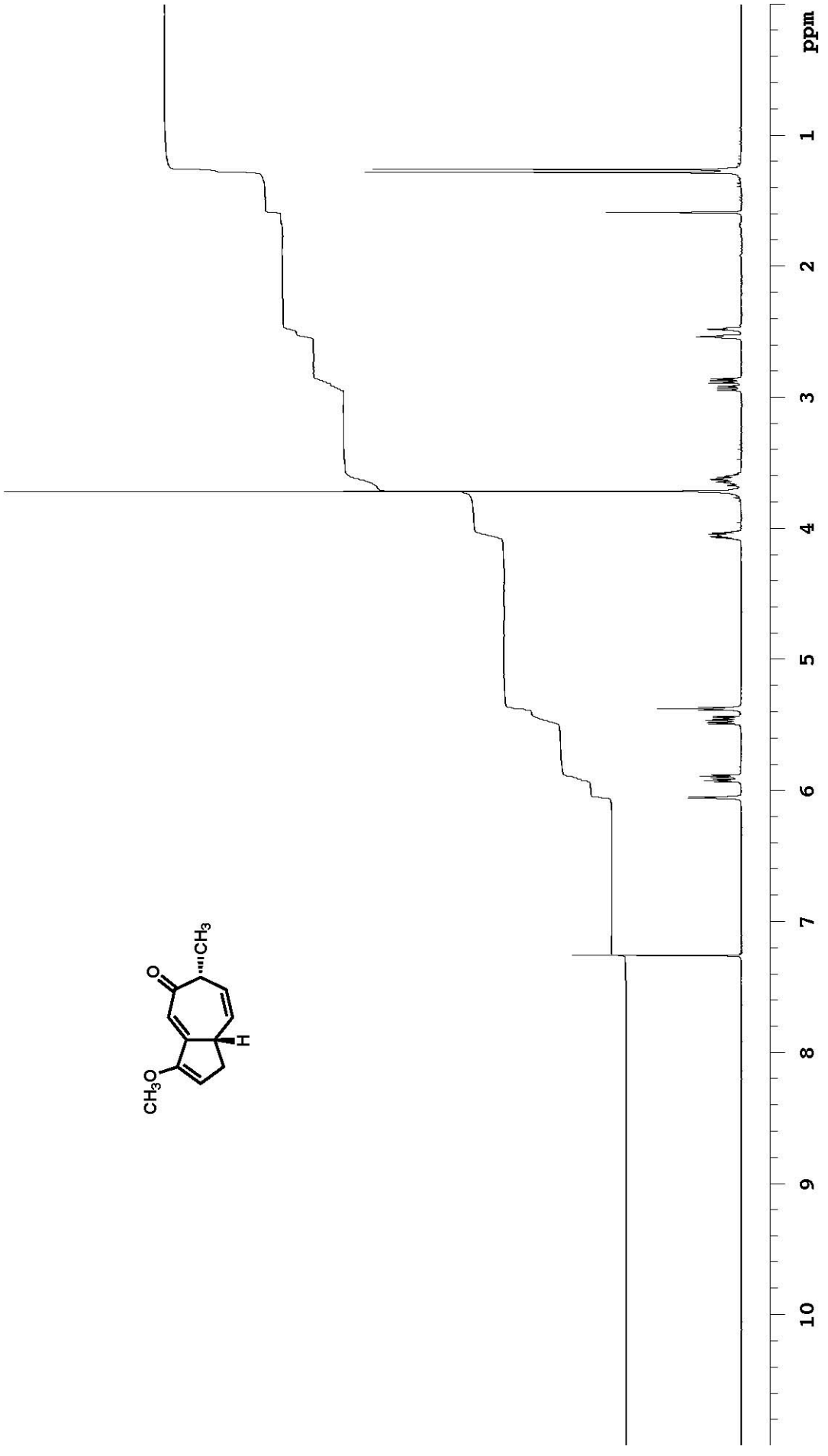
	x	y	z	U_{iso}
H(1)	9963(12)	5744(11)	7476(10)	10(3)
H(2A)	11658(14)	5974(13)	5941(11)	21(4)
H(2B)	11136(13)	4623(13)	5348(11)	23(4)
H(3A)	9725(15)	6252(14)	4347(13)	36(4)
H(3B)	9345(14)	6957(14)	5596(11)	23(3)
H(5)	8699(14)	4191(13)	3788(12)	26(4)
H(6)	6555(14)	2815(14)	3885(12)	29(4)
H(7)	4924(14)	3127(11)	5406(11)	17(3)
H(9)	8264(12)	3071(11)	7781(11)	9(3)
H(11A)	6732(15)	6559(13)	4942(12)	28(4)
H(11B)	6937(13)	6480(12)	6387(11)	14(3)
H(12A)	5039(13)	5174(12)	6498(12)	27(4)
H(12B)	4813(16)	5330(13)	5125(14)	42(4)
H(13A)	12841(15)	4645(15)	7485(14)	45(5)
H(13B)	12472(14)	3752(14)	8664(13)	34(4)
H(13C)	11985(15)	5293(16)	8594(13)	40(4)

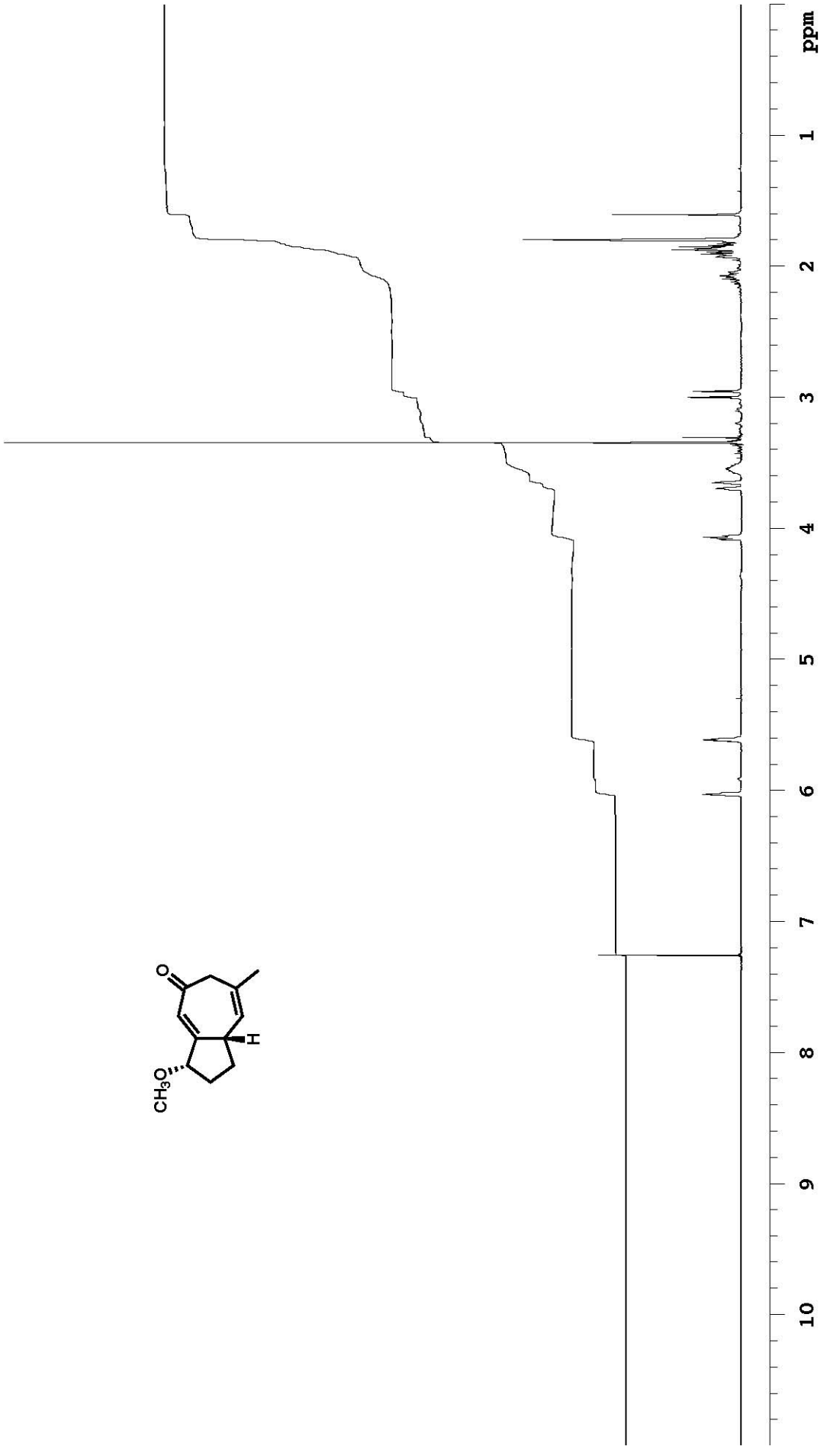

ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O

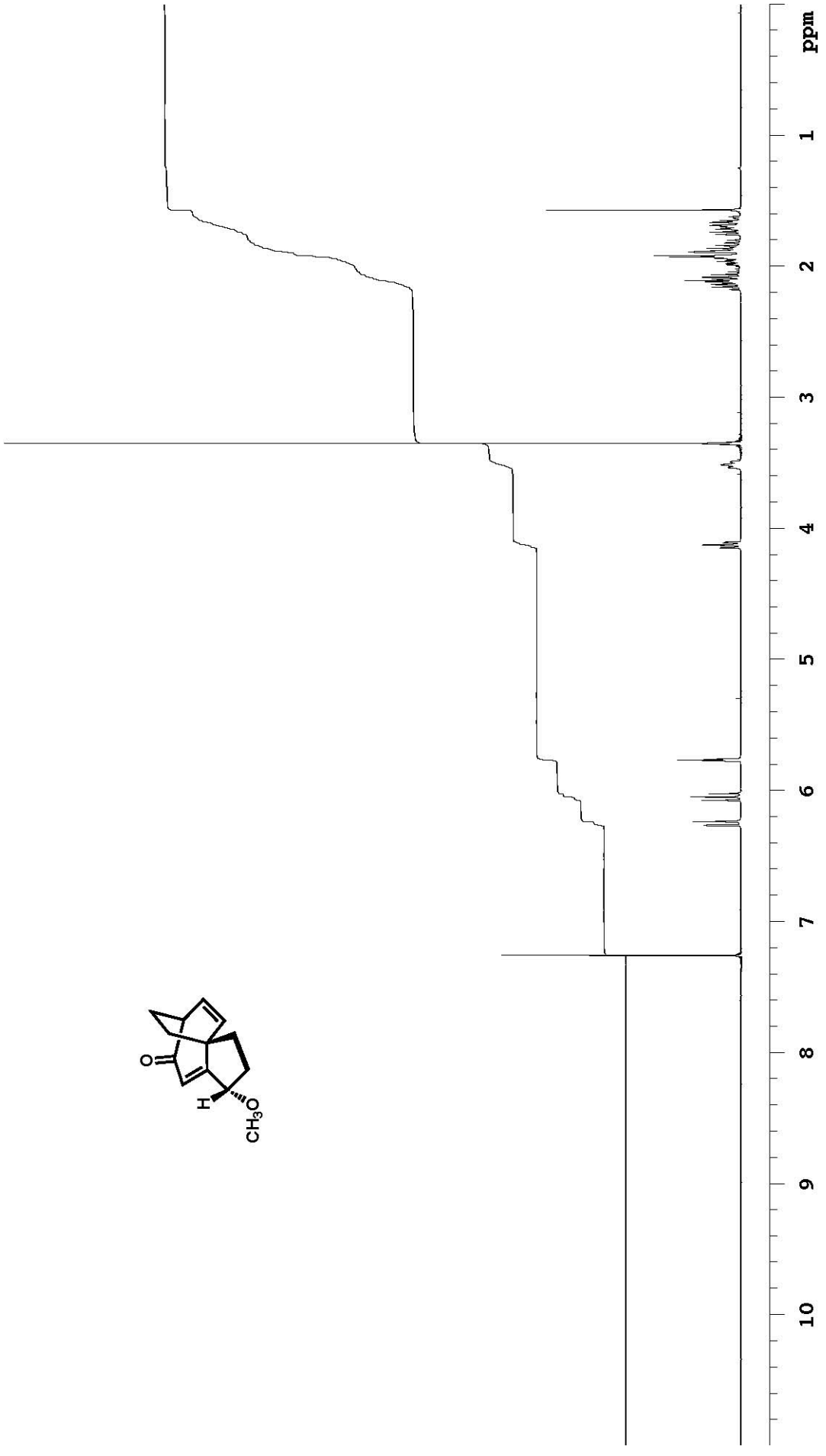

ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O

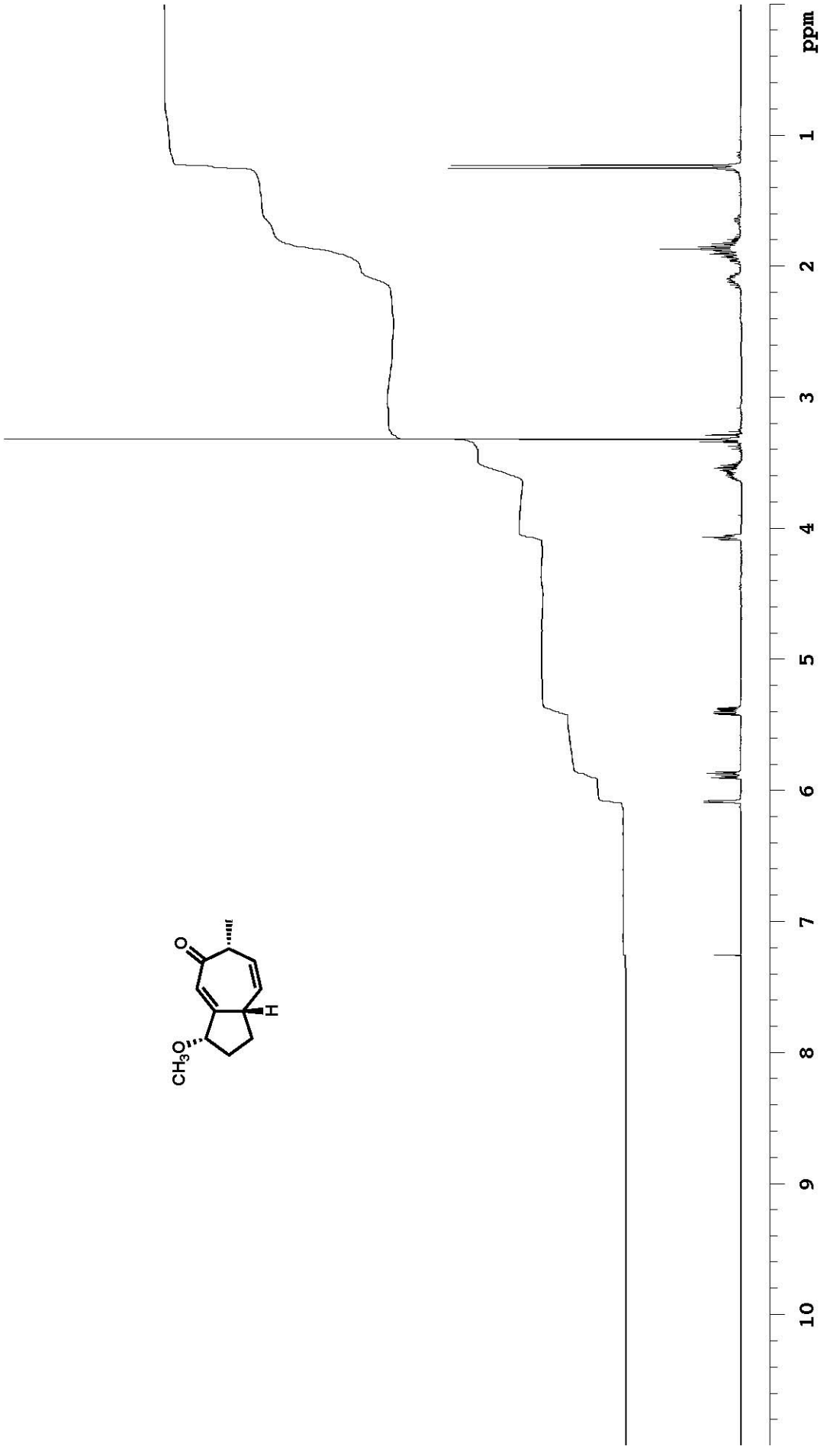

ppm
1
2
3
4
5
6
7
8
9
10
11
12
13
O
CH3
H
CH3O


ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O


ppm
1
2
3
4
5
6
7
8
9
10
O
CH3
H
CH3O


ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O


ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O


ppm
1
2
3
4
5
6
7
8
9
10
O
H
CH3O

References

1) Ziegler, F. E.; Petersen, A. K. *J. Org. Chem.* **1994**, *59*, 2707-2714.

2) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082-1087.

3) Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. *Syn. Comm*. **1987**, *17*, 1709-1716.

4) Piers. E.; Jung, G. L.; Ruediger, E. H. *Can. J. Chem.* **1987**, *65*, 670-682.

5) 3-methyl-2,4-pentadienoate was prepared according to the procedure of Liu: Liu, H. J.; Pednekar, P. R. *Syn. Comm.* **1982**, *12*, 395-400. Standard reduction (LAH) and bromination (PBr_3) provided the corresponding dienyl bromide.

6) Dienal prepared according to the procedure of Hünig: Hünig, S.; Kahanek, H. *Chem. Ber.* **1957**, *90*, 238-245. Also see Botica, I.; Mirrington, R. N. *Aust. J. Chem.* **1971**, *24*, 1467-1480. Standard reduction ($NaBH_4$) and bromination (PBr_3) provided the corresponding dienyl bromide.

7) The alkylation adduct **SM9** has been previously prepared using the corresponding dienyl bromide: Gassman, P. G.; Lee, C.-J.; Lee, C. *Syn Comm.* **1994**, *24*, 1465-1474.

8) Brodney, M. A.; O'Leary, J. P.; Hansen, J. A.; Giguere, R. J. *Syn Comm.* **1995**, *25*, 521-531.

9) Corey, E. J.; Myers, A. G. *Tetrahedron Lett.* **1984**, *25*, 3559-3562.

10) (a) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron*, **1968**, *24*, 3655-3669. (b) Charles, R. G. *J. Org. Chem.* **1957**, *22*, 677-679. (c) Sacconi, L.; Ciampolini, M. *J. Chem. Soc.* **1964**, 276-280.

11) Ahmed, M. G.; Alder, R. W.; James, G. H.; Sinnott, M. L.; Whiting, M. C. *Chem. Comm.* **1968**, 1533 - 1534.

12) Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, *25*, 5831-5834.

13) Sonochemical promotion of the Wolff Rearrangement is precedented: (a) Winum, J.-Y.; Kamal, M.; Leydet, A.; Roque, J.-P.; Montero, J.-L. *Tetrahedron Lett.* **1996**, *37*, 1781-1782. (b) Müller, A.; Vogt, C.; Sewald, N. *Synthesis* **1998**, 837-841.