

# A New Ring Expansion for a Chiral Hexahydroazulene Skeleton Possessing an Angular Methyl Group

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## Supporting Information

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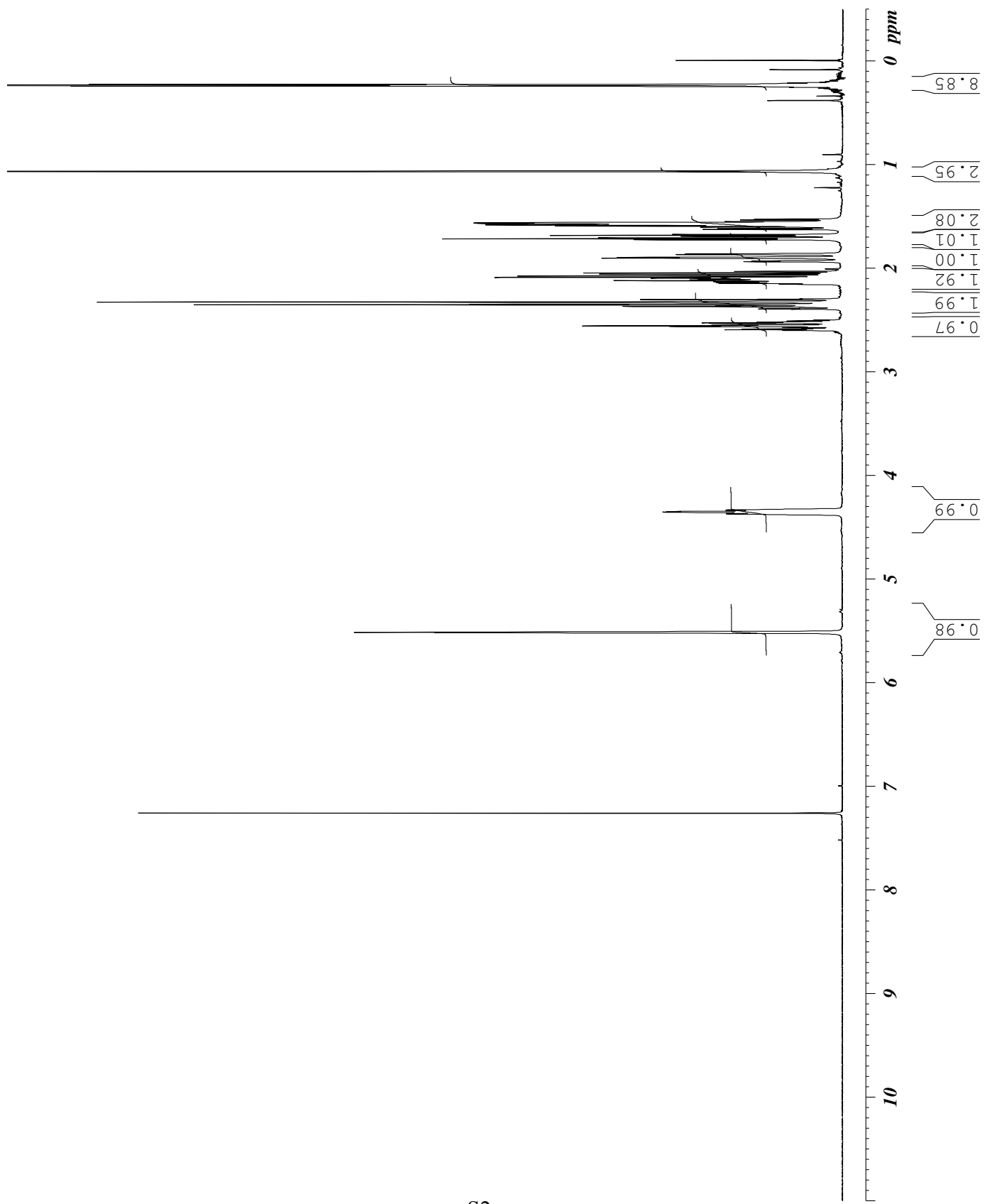
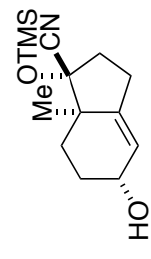
**General Experimental:** Melting points (mp) are not corrected. Infrared spectra (IR) are reported in wave number ( $\text{cm}^{-1}$ ). Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on 600 MHz or 400 MHz spectrometer. NMR samples were dissolved in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $\text{C}_6\text{D}_6$ , and chemical shifts are reported in ppm relative to the residual undeuterated solvent ( $\text{CDCl}_3$  as  $\delta = 7.26$  ppm,  $\text{CD}_3\text{OD}$  as  $\delta = 3.31$  ppm,  $\text{C}_6\text{D}_6$  as  $\delta = 7.15$  ppm).  $^1\text{H}$  NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broadened, m = multiplet), coupling constant, and assignment.  $^{13}\text{C}$  NMR spectra were recorded on 150 MHz or 100 MHz spectrometer. The samples were dissolved in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  and  $\text{C}_6\text{D}_6$ , and chemical shifts are reported in ppm relative to the solvent ( $\text{CDCl}_3$  as  $\delta = 77.0$  ppm,  $\text{CD}_3\text{OD}$  as  $\delta = 49.0$  ppm,  $\text{C}_6\text{D}_6$  as  $\delta = 128.0$  ppm).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured at 300 K unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel coated glass plate 60 F<sub>254</sub> (Merck, #1.05715). Silica gel 60 (particle size 63-200  $\mu\text{m}$ , 70-230 mesh ASTM, purchased from Merck Ltd.) was used for open column chromatography. Silica gel 60 (spherical, particle size 40-50  $\mu\text{m}$ , purchased from Kanto Chemical Co., Inc.) or Silica gel 60 N (spherical, neutral, particle size 40-50  $\mu\text{m}$ , purchased from Kanto Chemical Co., Inc.) were used for flash column chromatography. Unless otherwise noted, non-aqueous reactions were carried out in oven-dried (120  $^\circ\text{C}$ ) or flame-dried glassware under nitrogen. All commercially available reagents were used as received.

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PROCNO 1

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PL13 14.80 dB
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