Supporting Information
for DOI: 10.1055/s-0039-1691586
© 2020. Thieme. All rights reserved.
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany
Supporting Information

Unusual transformations of cyclic allenes with an enamine moiety into complex frameworks

Alexander A. Titov*, Maxim S. Kobzev, Tatiana N. Borisova, Elena A. Sorokina, Erik Van der Eycken, Alexey V. Varlamov, and Leonid G. Voskressensky

Organic Chemistry Department, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow, 117198, Russian Federation;
*Corresponding authors. E-mail: titov-aa@rudn.ru
Laboratory for Organic & Microwave-Assisted Chemistry (LOMAC), Department of Chemistry, University of Leuven (KU Leuven), Celestijnenlaan 200F, Leuven, Belgium.

Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General information and General procedures</td>
<td>2</td>
</tr>
<tr>
<td>X-ray crystal structures</td>
<td>7</td>
</tr>
<tr>
<td>Copies of $^1$H and $^{13}$C NMR spectra</td>
<td>8</td>
</tr>
</tbody>
</table>
General information.

MW-assisted reactions were carried out in a Monowave 400 reactor from Anton Paar GmbH; the reaction temperature was monitored by an IR sensor. Standard 10-mL G10 reaction vials, sealed with silicone septa, were used for the MW irradiation experiments. Elemental analysis was performed on a Euro Vector EA-3000 Elemental Analyzer. IR spectra were registered on an Infralum FT-801 FTIR spectrometer in KBr pellets. Mass spectra for compounds 7 and 8 were recorded with an LCMS-8040 triple quadrupole LCMS from Shimadzu (electrospray ionization).

1H and 13C NMR spectra were registered on a JEOL JNM-ENM 600 spectrometer (600 and 150 MHz, respectively) in CDCl3 for compounds 4b, 7a-c,e and 8a-e with the solvent signal as the internal standard (7.26 ppm for 1H nuclei, and 77.2 ppm for 13C nuclei) and in DMSO-d6 for compound 4d, with solvent signal as internal standard (2.50 ppm for 1H nuclei, 39.5 ppm for 13C nuclei). Melting points were determined on an SMP 10 apparatus in open capillaries. Sorbfil PTH-AF-A-UF plates were used for TLC, visualization in an iodine chamber or using KMnO4 and H2SO4 solutions. Silica gel (40–60 μm, 60 Å) was used for column chromatography for compounds 7a-c,e. All solvents were purified by distillation before use.

8-Substituted 3-methyl-6-phenyl-benzo[d]-3-aza-cyclodeca-4,6,7-trienes (4) were synthesized from 1-R-1-phenylethynyl-1,2,3,4-tetrahydroisoquinolines and activated alkynes; see Ref. 9.

**Methyl 10,11-dimethoxy-3-methyl-6-phenyl-8-(propan-2-yl)benzo[d]-3-aza-cyclodeca-4,6,7-trien-5-carboxylate (4b).** Colorless crystals. Mp 175-176 °C. Yield 92%. Rf = 0.44 (1:2 EtOAc:Hex). IR spectrum, ν, cm⁻¹: 1956, 1055 (C=C=C), 1684 (C=O). 1H NMR (600 MHz, CDCl3) δ 7.61 (s, 1H), 7.33–7.30 (m, 2H), 7.25–7.23 (m, 2H), 7.14–7.12 (m, 1H), 6.88 (s, 1H), 6.59 (s, 1H), 4.18–4.14 (m, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.61 (s, 3H), 3.50–3.46 (m, 1H), 3.16 (s, 3H), 2.94 (sep, J = 6.7, 1H), 2.81–2.70 (m, 2H), 1.35 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.7 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 206.0, 170.7, 147.9, 147.6, 147.4, 138.3, 129.3, 128.7, 128.2 (2C), 126.3, 125.7 (2C), 112.9, 111.5, 110.5, 103.5, 96.0, 56.1, 55.9, 51.8, 51.1, 45.1, 31.7, 31.0, 22.2, 21.2. m/z: 434 [M+H]+. Anal Calcd for C27H31NO4 (%): C 74.80, H 7.21, N 3.23. Found (%): C 74.95, H 7.41, N 3.37.

**Methyl 10,11-dimethoxy-3-methyl-6,8-diphenyl-benzo[d]-3-aza-cyclodeca-4,6,7-trien-5-carboxylate (4d).** Colorless crystals. Mp 210-212 °C. Yield 92%. Rf = 0.47 (1:1 EtOAc:Hex). IR spectrum, ν, cm⁻¹: 1947, 1059 (C=C=C), 1690 (C=O). 1H NMR (600 MHz, DMSO-d6) δ 7.58 (s, 1H), 7.42–7.38 (m, 4H), 7.34–7.29 (m, 5H), 7.22–7.20 (m, 1H), 6.93 (s, 1H), 6.70 (s, 1H), 3.89–
3.85 (m, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 3.47 (s, 3H), 3.29–3.25 (m, 1H), 3.17 (s, 3H), 3.07–3.02 (m, 1H), 2.98–2.92 (m, 1H). 13C NMR (150 MHz, DMSO-d6) δ 209.1, 168.4, 148.1, 147.7, 147.2, 137.4, 136.5, 129.5, 128.8 (2C), 128.7 (2C), 127.4, 127.3 (2C), 127.1, 125.9, 125.5 (2C), 113.7, 112.8, 107.0, 104.7, 93.1, 55.6, 55.5, 50.9, 50.7, 44.6, 30.2. m/z: 468 [M+H]+. Anal Calcd for C30H29NO4 (%): C 77.06, H 6.25, N 3.00. Found (%): C 77.19, H 6.33, N 3.13.

**General procedure A**: A solution of the allene derivative (0.68 mmol) in absolute toluene (6.0 mL) was placed in a microwave reactor. The reaction was carried out at 150°C for 30 min, monitoring the reaction progress by TLC (eluent EtOAc–hexane, 1:1, for 4a,c; eluent EtOAc–hexane, 1:2, for 4b,d,e). The solvent was evaporated in vacuum. Products 7a-c,e and 8a-e were isolated by chromatography on silica gel. Compounds 7a,c, 7b/8b, 7e, 8a, 8c, and 8e were eluted with EtOAc–hexane; 1:3, 1:5, 1:12, 1:2, 1:1, and 1:10, respectively.

**General procedure B**: A solution of the allene derivative (0.16 mmol) in absolute toluene (6.0 mL) was irradiated in a microwave reactor at 150°C for 3–7.5 hrs with stirring. The reaction progress was monitored by TLC (eluent EtOAc–hexane, 1:1, for 4a,c; eluent EtOAc–hexane, 1:2, for 4b,d,e). The solvent was evaporated in vacuum. Product 8a-e was crystallized in ether.

**General procedure C**: A solution of the compound 7a (0.24 mmol) in absolute toluene (6.0 mL) was irradiated in a microwave reactor at 150°C for 2 hrs with stirring. The reaction progress was monitored by TLC (eluent EtOAc–hexane, 1:1). The solvent was evaporated in vacuum. Product 8a was crystallized in ether. Yield 49 mg, 50%.

Methyl 6,7-dimethoxy-2,4b-dimethyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[cd]cyclopropa[cd]azulene-4-carboxylate (7a). Colorless crystals. Mp 153-155°C. Yield 162 mg, 59% (procedure A). Rf = 0.47 (1:1 EtOAc:Hex). IR spectrum, ν, cm⁻¹: 1682 (C=O).

1H NMR (600 MHz, CDCl3) δ 7.57–7.56 (m, 2H), 7.26–7.24 (m, 2H), 7.15–7.13 (m, 1H), 6.87 (s, 1H), 6.74 (s, 1H), 6.50 (s, 1H), 4.22 (dd, J = 14.1, 1.5 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.77–3.75 (m, 1H), 3.58 (dd, J = 14.1, 5.6 Hz, 1H), 3.44 (s, 3H), 3.00 (s, 3H), 2.12 (d, J = 6.6 Hz, 1H), 1.71 (s, 3H). 13C NMR (150 MHz, CDCl3) δ 168.7, 147.5, 147.4, 146.7, 144.1, 140.1, 134.6, 131.1 (2C), 127.3 (2C), 125.3, 107.5, 106.8, 98.0, 55.8, 55.6, 51.4, 49.8, 46.5, 42.1, 39.1, 37.8, 37.0, 16.2. m/z: 406 [M+H]+. Anal Calcd for C25H27NO4 (%): C 74.05, H 6.71, N 3.45. Found (%): C 74.21, H 6.86, N 3.55.
Methyl 6,7-dimethoxy-2-methyl-4a-phenyl-4b-(propan-2-yl)-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7b). Colorless crystals. Mp 178-179°C. Yield 15 mg, 5% (procedure A). Rf = 0.48 (1:2 EtOAc:Hex). IR spectrum, ν, см–1: 1682 (C=O). 1H NMR (600 MHz, CDCl3) δ 7.62–7.61 (m, 2H), 7.26–7.25 (m, 2H), 7.16–7.13 (m, 1H), 7.08 (s, 1H), 6.71 (s, 1H), 6.48 (s, 1H), 4.22 (d, J = 14.1, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.79–3.77 (m, 1H), 3.55 (dd, J = 14.1, 5.1 Hz, 1H), 3.47 (s, 3H), 2.98 (s, 3H), 1.98 (d, J = 6.6 Hz, 1H), 1.79 (sep, J = 6.6 Hz, 1H), 1.72 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 169.6, 147.9, 147.6, 146.8, 144.0, 140.1, 137.9, 136.5, 131.4 (2C), 127.7 (2C), 125.7, 110.1, 105.7, 100.2, 56.2, 56.0, 52.7, 50.7, 48.3, 47.2, 42.7, 38.9, 30.8, 29.8, 21.9, 21.4. m/z: 434 [M+H]+. Anal Calcd for C27H31NO4 (%): C 74.80, H 7.21, N 3.23. Found (%): C 74.49, H 7.51, N 3.46.

Methyl 4b-benzyl-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7c). Colorless crystals. Mp 161-162°C. Yield 29 mg, 9% (procedure A). Rf = 0.45 (1:1 EtOAc:Hex). IR spectrum, ν, см–1: 1684 (C=O). 1H NMR (600 MHz, CDCl3) δ 7.62–7.61 (m, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.18–7.16 (m, 1H), 7.12–7.06 (m, 4H), 7.05–7.03 (m, 1H), 6.87 (s, 1H), 6.75 (s, 1H), 6.42 (s, 1H), 4.22 (dd, J = 14.0, 1.5 Hz, 1H), 3.92 (d, J = 15.6 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.72–3.70 (m, 1H), 3.55 (dd, J = 14.0, 5.4 Hz, 1H), 3.47 (s, 3H), 2.99 (s, 3H), 2.98 (d, J = 15.6 Hz, 1H), 2.43 (d, J = 6.6 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 169.4, 147.8, 147.5, 147.0, 143.3, 141.1, 138.5, 134.4, 131.3 (2C), 128.7 (2C), 127.9 (2C), 127.7 (2C), 125.7, 125.5, 108.1, 105.6, 99.7, 56.1, 55.9, 52.4, 50.3, 47.0, 44.1, 42.7, 38.6, 38.4, 35.4. m/z: 482 [M+H]+. Anal Calcd for C31H31NO4 (%): C 77.31, H 6.49, N 2.91. Found (%): C 77.43, H 6.59, N 2.79.

Methyl 2,4b-dimethyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7e). Colorless crystals. Mp 149-150°C. Yield 61 mg, 26% (procedure A). Rf = 0.54 (1:2 EtOAc:Hex). IR spectrum, ν, см–1: 1682 (C=O). 1H NMR (600 MHz, CDCl3) δ 7.58–7.57 (m, 2H), 7.33–7.32 (m, 1H), 7.27–7.25 (m, 2H), 7.17–7.13 (m, 2H), 7.12–7.09 (m, 1H), 6.98–6.97 (m, 1H), 6.76 (s, 1H), 4.25 (dd, J = 14.1, 1.5 Hz, 1H), 3.81–3.79 (m, 1H), 3.65 (dd, J = 14.1, 5.6 Hz, 1H), 3.44 (s, 3H), 3.00 (s, 3H) 2.15 (d, J = 6.6 Hz, 1H), 1.74 (s, 3H). 13C NMR (150 MHz, CDCl3) δ 169.5, 148.6, 146.7, 143.8, 142.4, 131.3, 127.4 (2C), 126.4 (2C), 125.7, 125.5, 123.6, 122.0, 99.7, 52.2, 50.3, 46.8, 42.8, 38.9, 38.7, 37.5, 16.1. m/z: 346 [M+H]+. Anal Calcd for C23H23NO2 (%): C 79.97, H 6.71, N 4.05. Found (%): C 79.80, H 6.84, N 4.23.
Methyl 5,6-dimethoxy-3a,10-dimethyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8a). Colorless crystals. Mp 149-151°C. Yield 32 mg, 50% (procedure B), 3 mg, 1% (procedure A). Rf = 0.52 (1:1 EtOAc:Hex). IR spectrum, ν, см⁻¹: 1694 (C=O). ¹H NMR (600 MHz, CDCl₃) δ 7.49–7.47 (m, 2H), 7.41–7.35 (m, 3H), 6.74 (s, 1H), 6.73 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.70 (s, 3H), 3.68 (d, J = 1.7 Hz, 1H), 3.23 (d, J = 4.1 Hz, 1H), 3.12–3.11 (m, 1H), 2.66 (dd, J = 10.7, 2.5 Hz, 1H), 2.48 (dd, J = 10.7, 2.5 Hz, 1H), 2.22 (s, 3H), 1.48 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.3, 151.1, 148.3, 147.8, 137.3, 137.1, 135.1, 128.5, 128.0 (2C), 127.9 (2C), 124.9, 107.1, 106.9, 72.8, 67.9, 59.6, 55.8, 55.7, 51.2, 51.1, 42.6, 42.3, 18.3. m/z: 406 [M+H]⁺. Anal Calcd for C₂₅H₂₇NO₄ (%): C 74.05, H 6.71, N 3.45. Found (%): C 74.28, H 6.91, N 3.56.

Methyl 5,6-dimethoxy-10-methyl-1-phenyl-3a-(propan-2-yl)-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8b). Colorless crystals. Mp 135-136°C. Yield 40 mg, 58% (procedure B), 6 mg, 2% (procedure A). Rf = 0.46 (1:2 EtOAc:Hex). IR spectrum, ν, см⁻¹: 1709 (C=O). ¹H NMR (600 MHz, CDCl₃) δ 7.49–7.47 (m, 2H), 7.42–7.39 (m, 2H), 7.37–7.35 (m, 1H), 6.85 (s, 1H), 6.70 (s, 1H), 4.00 (d, J = 1.5 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.69 (s, 3H), 3.44 (dd, J = 5.6, 1.5 Hz, 1H), 3.11–3.10 (m, 1H), 2.61 (dd, J = 10.9, 2.5 Hz, 1H), 2.47 (dd, J = 10.9, 2.5 Hz, 1H), 2.34 (sep, J = 7.1 Hz, 1H), 2.23 (s, 3H), 1.20 (d, J = 7.1 Hz, 3H), 1.02 (d, J = 7.1 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.6, 153.2, 148.3, 147.6, 138.2, 135.5, 134.8, 128.6, 128.1 (2C), 127.9 (2C), 125.0, 107.2, 105.9, 70.9, 68.0, 64.7, 55.9, 56.0, 52.4, 51.2, 43.5, 43.0, 29.0, 19.6, 19.2. m/z: 434 [M+H]⁺. Anal Calcd for C₂₇H₃₁NO₄ (%): C 74.80, H 7.21, N 3.23. Found (%): C 74.93, H 7.36, N 3.37.

Methyl 3a-benzyl-5,6-dimethoxy-10-methyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8c). Colorless crystals. Mp 159-160°C. Yield 39 mg, 50% (procedure B), 52 mg, 16% (procedure A). Rf = 0.35 (1:1 EtOAc:Hex). IR spectrum, ν, см⁻¹: 1711 (C=O). ¹H NMR (600 MHz, CDCl₃) δ 7.39–7.37 (m, 2H), 7.36–7.35 (m, 3H), 7.13–7.12 (m, 3H), 7.04–7.03 (m, 2H), 6.97 (s, 1H), 6.67 (s, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.83 (s, 1H), 3.73 (s, 3H), 3.45 (d, J = 14.1 Hz, 1H), 3.10–3.09 (m, 1H), 3.05 (d, J = 14.1 Hz, 1H), 3.02–3.00 (m, 1H), 2.60 (dd, J = 10.8, 1.8 Hz, 1H), 2.43 (dd, J = 10.8, 1.8 Hz, 1H), 2.24 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.8, 151.2, 148.9, 148.1, 138.6, 138.0, 135.4, 135.3, 130.4 (2C), 129.2, 128.6 (2C), 128.5 (2C), 128.3 (2C), 126.4, 125.9, 108.6, 107.5, 73.5, 65.1, 64.1, 56.6, 56.1, 52.4, 51.7, 43.2, 42.7, 36.4. m/z: 482 [M+H]⁺. Anal Calcd for C₃₁H₃₁NO₄ (%): C 77.31, H 6.49, N 2.91. Found (%): C 77.45, H 6.33, N 2.78.
Methyl 5,6-dimethoxy-10-methyl-1,3a-diphenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8d). Colorless crystals. Mp 184-185°C. Yield 61 mg, 81% (procedure B), 95 mg, 30% (procedure A). Rf = 0.47 (1:2 EtOAc:Hex). IR spectrum, ν, см⁻¹: 1714 (C=O). ¹H NMR (600 MHz, CDCl₃) δ 7.41–7.40 (m, 2H), 7.39–7.38 (m, 4H), 7.35–7.34 (m, 3H), 7.27–7.25 (m, 1H), 6.87 (s, 1H), 6.19 (s, 1H), 4.24 (d, J = 1.4 Hz, 1H), 3.94 (dd, J = 5.5, 1.4 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 3.55 (s, 3H), 3.31–3.29 (m, 1H), 2.58 (dd, J = 10.5, 2.2 Hz, 1H), 2.38 (dd, J = 10.5, 2.2 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.2, 152.6, 148.7, 142.2, 141.8, 137.1, 135.3, 128.5, 128.2 (2C), 128.1 (2C), 127.8 (3C), 127.4 (2C), 126.6, 125.5, 107.7, 106.0, 70.5, 70.0, 68.6, 56.1, 55.8, 52.2, 51.3, 43.6, 43.0. m/z: 468 [M+H]⁺. Anal Calcd for C₃₀H₂₉NO₄ (%): C 77.06, H 6.25, N 3.00. Found (%): C 77.15, H 6.38, N 3.11.

Methyl 3a,10-dimethyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8e). Colorless crystals. Mp 147-148°C. Yield 28 mg, 50% (procedure B), 5 mg, 2% (procedure A). Rf = 0.6 (1:2 EtOAc:Hex). IR spectrum, ν, см⁻¹: 1703 (C=O). ¹H NMR (600 MHz, CDCl₃) δ 7.51–7.48 (m, 2H), 7.42–7.39 (m, 2H), 7.38–7.35 (m, 1H), 7.29–7.28 (m, 1H), 7.25–7.23 (m, 1H), 7.19 (d, J = 6.6 Hz, 1H), 7.16 (d, J = 7.1 Hz, 1H), 3.72 (d, J = 1.5 Hz, 1H), 3.70 (s, 3H), 3.26–3.25 (m, 1H), 3.21–3.19 (m, 1H), 2.65 (dd, J = 10.6, 2.5 Hz, 1H), 2.54 (dd, J = 10.6, 2.5 Hz, 1H), 2.19 (s, 3H), 1.50 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.2, 151.2, 145.7, 145.4, 135.0, 128.5, 128.0 (2C), 127.9 (2C), 127.1, 126.4, 124.6, 121.8, 121.5, 73.4, 67.6, 59.5, 51.3, 51.1, 42.6, 42.5, 18.2. m/z: 346 [M+H]⁺. Anal Calcd for C₂₃H₂₃NO₂ (%): C 79.97, H 6.71, N 4.05. Found (%): C 79.75, H 6.91, N 4.32.
The structures of 7a was elucidated using X-ray crystal structure analyses (Fig. S1). Tables of the coordinates of atoms, bond lengths, valence and torsion angles, and the anisotropic temperature parameters of compound 7a was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1830405).

![Figure S1. Molecular structure of 7a.](image1)

The structures of 8a was elucidated using x-ray crystal structure analyses (Fig. S2). Tables of the coordinates of atoms, bond lengths, valence and torsion angles, and the anisotropic temperature parameters of compound 8a was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1579823).

![Figure S2. Molecular structure of 8a.](image2)
Methyl 10,11-dimethoxy-3-methyl-6-phenyl 8-(propan-2-yl)benzo[d]-3-aza-cyclodeca-4,6,7-trien-5-carboxylate (4b).

$^1$H NMR spectra for 4b.
$^1$H NMR spectra for 4b.
$^{13}$C NMR spectra for 4b.
$^{13}$C NMR spectra for 4b.
Methyl 10,11-dimethoxy-3-methyl-6,8-diphenyl-benzo[d]-3-aza-cyclodeca-4,6,7-trien-5-carboxylate (4d).

$^1$H NMR spectra for 4d.
$^1$H NMR spectra for 4d.
$^{13}$C NMR spectra for 4d.
$^{13}$C NMR spectra for 4d.
Methyl 6,7-dimethoxy-2,4b-dimethyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7a)

$^1$H NMR spectra for 7a.
$^{13}$C NMR spectra for 7a.
$^1$H NMR spectra for 7a.
$^1$H NMR spectra for 7a.
$^{13}$C NMR spectra for 7a.
$^{13}$C NMR spectra for 7a.
Methyl 6,7-dimethoxy-2-methyl-4a-phenyl-4b-(propan-2-yl)-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7b)

$^1$H NMR spectra for 7b.
$^{13}$C NMR spectra for 7b.
$^1$H NMR spectra for 7b.
$^1$H NMR spectra for 7b.
$^{13}$C NMR spectra for 7b.
$^{13}$C NMR spectra for 7b.
Methyl 4b-benzyl-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7c)

$^1$H NMR spectra for 7c.
$^{13}$C NMR spectra for 7c.
$^1$H NMR spectra for 7c.
$^1$H NMR spectra for 7c.
$^{13}$C NMR spectra for 7c.
$^{13}$C NMR spectra for 7c.
Methyl 2,4b-dimethyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2 azabenzo[a]cyclopropa[cd]azulene-4-carboxylate (7e)

\(^1\)H NMR spectra for 7e.
$^{13}$C NMR spectra for 7e.
$^1$H NMR spectra for 7e.
$^1$H NMR spectra for 7e.
$^{13}$C NMR spectra for 7e.
$^{13}$C NMR spectra for 7e.
Methyl 5,6-dimethoxy-3a,10-dimethyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8a)

$^1$H NMR spectra for 8a.
$^{13}$C NMR spectra for 8a.
$^1$H NMR spectra for 8a.
$^{1}H$ NMR spectra for 8a.
$^{13}$C NMR spectra for 8a.
$^{13}$C NMR spectra for 8a.
Methyl 5,6-dimethoxy-10-methyl-1-phenyl-3a-(propan-2-yl)-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8b)

$^1$H NMR spectra for 8b.
$^{13}$C NMR spectra for 8b.
$^1$H NMR spectra for 8b.
$^1$H NMR spectra for 8b.
$^{13}$C NMR spectra for 8b.
$^{13}$C NMR spectra for 8b.
Methyl 3a-benzyl-5,6-dimethoxy-10-methyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-
(epiminomethano)cyclopenta[a]indene-2-carboxylate (8c)

1H NMR spectra for 8c.
$^{13}$C NMR spectra for 8c.
$^1$H NMR spectra for 8c.
$^1$H NMR spectra for 8c.
$^{13}$C NMR spectra for 8c.
$^{13}$C NMR spectra for 8c.
Methyl 5,6-dimethoxy-10-methyl-1,3a-diphenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8d)

$^1$H NMR spectra for 8d.
$^{13}$C NMR spectra for 8d.
\(^1\)H NMR spectra for 8d.
$^1$H NMR spectra for 8d.
$^{13}$C NMR spectra for 8d.
$^{13}$C NMR spectra for 8d.
Methyl 3a,10-dimethyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]indene-2-carboxylate (8e)

\(^1\)H NMR spectra for 8e.

Chemical Shift (ppm)
$^{13}$C NMR spectra for 8e.
$^{1}H$ NMR spectra for 8e.
$^1$H NMR spectra for 8e.
$^{13}$C NMR spectra for 8e.
$^{13}$C NMR spectra for 8e.