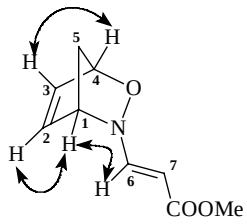
Supporting Information

General Remarks: NMR spectra were recorded on Bruker AM-300 instrument in $CDCl_3$ as a solvent. Chemical shifts were measured relative to internal reference (δ = 0 ppm) $SiMe_4$ (^1H, ^{13}C). Methyl 3-nitropropionate **1** was obtained according to the known procedure (Belikov, V. M. *Bull. Acad. Sci. USSR. Div. Chem. Sci.*, **1956**, 855 (Russ.); *Chem. Abstr*. **1957** *51*, 1837i.). Reagents: commercially available cyclopentadiene dimer (for preparation of cyclopentadiene **3a**), cyclohexadiene **3b** and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) were freshly distilled before use. Reactions were carried out in a dry argon atmosphere. MeOH, CH_2Cl_2 and hexane were distilled *prior* to use.

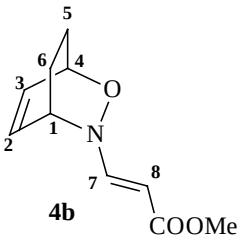
Methyl (*E*)-3-(2-oxa-3-azabicyclo[2.2.1]hept-5-en-3-yl)-2-propenoate 4a, white crystals, m.p. 71—76°C (dec.).



4a

NMR: δ (^1H): 1.79 (d, 1 H, C^5H_2, H^A, ^2J = 8.6 Hz); 2.02 (dt, 1 H, C^5H_2, H^B, ^2J = 8.6 Hz, ^3J = 1.9 Hz); 3.67 (s, 3 H, OMe); 4.73 (br.s, 1 H, C^1H); 5.11 (d, 1 H, C^7H, ^3J = 13.0 Hz); 5.28 (br.s, 1 H, C^4H); 6.23 (m, 1 H, C^2H); 6.33 (m, 1 H, C^3H); 7.45 (d, 1 H, C^6H, ^3J = 13.0 Hz). NOE: the irradiation of C^1H signal at δ 4.73 and C^4H signal at δ 5.28 (NOE is presented in the figure). δ (^{13}C): 47.8 (C^5); 51.0 (MeO); 67.2 (C^1); 84.3 (C^4); 96.4 (C^7); 131.3 (C^2), 132.1 (C^3); 149.0 (C^6); 168.6 (C=O). **4a**: $C_9H_{11}NO_3$ (181.19): calcd. (%) C 59.66, H 6.12, N 7.73; found (%) C, 59.94; H, 5.80; N, 7.81.

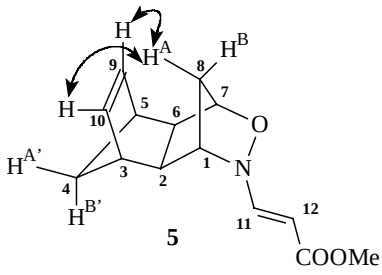
Methyl (*E*)-3-(2-oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)-2-propenoate 4b, white crystals, m.p. 70—76°C (dec.).



4b

NMR: δ (^1H): 1.45 (m, 2 H, C^6H_2); 2.19 (m, 2 H, C^5H_2); 3.64 (s, 3 H, MeO); 4.13 (br.s, 1 H, C^1H); 4.72 (br.s, 1 H, C^4H); 5.06 (d, 1 H, C^8H, ^3J = 14.0 Hz); 6.42 (m, 1 H, C^2H); 6.52 (m, 1 H, C^3H); 7.25 (d, 1 H, C^7H, ^3J = 14.0 Hz). δ (^{13}C): 21.7 (C^5); 23.5 (C^6); 50.8 (MeO); 55.3 (C^1); 71.4 (C^4); 92.4 (C^8); 130.3 (C^2), 130.8 (C^3); 148.8 (C^7); 168.6 (C=O). **4b**: $C_{10}H_{13}NO_3$ (195.21): calcd. (%) C 61.53, H 6.71, N 7.17; found (%) C, 60.94; H, 6.04; N, 7.25.

Methyl (*E*)-3-(4-oxa-5-azatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-5-yl)-2-propenoate 5, white crystals, m.p. 125—135°C (dec.).



5

NMR: δ (^1H): 1.28 (d, 1 H, C^4H_2, $H^{B'}$, ^2J = 9.8 Hz); 1.46 (d, 1 H, C^4H, $H^{A'}$, ^2J = 9.9 Hz); 1.49 (d, 1 H, C^8H_2, H^B, ^2J = 11.6 Hz); 2.48 (d, 1 H, C^8H_2, H^A, ^2J = 11.4 Hz); 2.50 (m, 1 H, C^2H); 2.61 (m, 1 H, C^6H); 2.95 (m, 2 H, C^3H + C^5H); 3.67 (s, 3 H, MeO); 3.88 (br.s, 1 H, C^1H); 4.43 (br.s, 1 H, C^7H); 5.14 (d, 1 H, $C^{12}H$, ^3J = 12.9 Hz); 5.98 (m, 2 H, C^9H + $C^{10}H$); 7.39 (d, 1 H, $C^{11}H$, ^2J = 12.9 Hz). NOE: the irradiation of C^9H + $C^{10}H$ signals at δ 5.98 (NOE is presented in the figure). δ (^{13}C): 34.2 (C^8); 44.6, 45.0 (C^3 and C^5); 46.4 (C^2); 47.9 (C^6); 50.7 (MeO); 53.9 (C^4); 63.7 (C^1); 80.6 (C^7); 92.7 (C^{12}); 134.8, 135.1 (C^9 and C^{10}); 147.5 (C^{11}); 168.9 (C=O). **5**: $C_{14}H_{17}NO_3$ (247.29): calcd. (%) C 68.00, H 6.93, N 5.66; found (%) C, 67.53; H, 6.78; N, 5.68.

Methyl 6-ethoxy-5,6-dihydro-4H-1,2-oxazine-4-carboxylate 6, yellowish oil. The ^1H NMR for **6** was in good agreement with literature data (Ioffe, S. L.; Lyapkalo, I. M.; Tishkov, A. A.; Danilenko, V. M.; Strelenko, Yu. A.; Tartakovsky, V. A. *Tetrahedron*, **1997**, *53*, 13085). The same isomeric ratio 2 : 1 as in previously reported work was observed.