

**Phosphine-catalyzed [3 + 2] cycloaddition of ethyl buta-2,3-dienoate to adamantane-containing N-substituted maleimides**

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*Experimental*

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros and Aldrich-Sigma Co and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with Bruker Avance-400 spectrometer in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ , using the residual signals of  $\text{CHCl}_3$  or  $\text{CHD}_2\text{S(O)CD}_3$  as internal standards. High resolution mass spectra (HRMS) of compounds **20**, **21**, **23-26** using electrospray ionization (ESI) were registered with a Thermo Scientific Orbitrap Elite high-field orbitrap hybrid mass spectrometer. Preparative column chromatography was carried out using silica gel 40/60 from Merck Co. Toluene was distilled over sodium under argon,  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$  under argon,  $\text{CHCl}_3$  was distilled over  $\text{P}_2\text{O}_5$  under argon, MeOH, ethyl acetate and petroleum ether were used freshly distilled.

**1-[2-(1-Adamantyl)ethyl]-1H-pyrrole-2,5-dione (14)** was obtained from maleic anhydride (980 mg, 10 mmol) and amine **6** (895 mg, 5 mmol) in the presence of *p*-toluenesulfonic acid (860 mg, 5 mmol). Eluent: petroleum ether- $\text{CH}_2\text{Cl}_2$ , 2:1, yield 479 mg (37%), white crystalline powder, mp 135-136°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.32 (t,  $J$  = 8.1 Hz, 2 H), 1.53 (br. s., 6 H), 1.60-1.71 (m, 6 H), 1.93 (br. s., 3 H), 3.50 (t,  $J$  = 8.1 Hz, 2 H), 6.65 (s, 2 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 28.5 (3 C), 31.8 (1 C), 33.0 (1 C), 37.0 (3 C), 32.0 (3 C), 42.1 (1 C), 134.1 (2 C), 170.7 (2 C). Anal. calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_2$ : C 74.10, H 8.16, N 5.40%; found: C 74.03, H 8.15, N 5.41%.

**1-[2-(1-Adamantyloxy)ethyl]-1H-pyrrole-2,5-dione (15)** was obtained from maleic anhydride (980 mg, 10 mmol) and amine **7** (975 mg, 5 mmol) in the presence of *p*-toluenesulfonic acid (860 mg, 5 mmol). Eluent: petroleum ether- $\text{CH}_2\text{Cl}_2$ , 2:1, yield 605 mg (44%), white crystalline powder, mp 121-122°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.52-1.70 (m, 12 H), 2.09 (br. s., 3 H),

3.53 (t,  $J = 5.9$  Hz, 2 H), 3.65 (t,  $J = 5.9$  Hz, 2 H), 6.68 (s, 2 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 30.4$  (3 C), 36.3 (3 C), 38.7 (1 C), 41.3 (3 C), 56.8 (1 C), 72.4 (1 C), 134.0 (2 C), 170.7 (2 C). Anal. calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_3$ : C 69.79, H 7.69, N 5.09%; found: C 69.81, H 7.72, N 5.03%.

**1-[2-(2-Adamantyl)ethyl]-1H-pyrrole-2,5-dione (17)** was obtained from maleic anhydride (980 mg, 10 mmol) and benzylamine **5** (895 mg, 5 mmol) in presence of *p*-toluenesulfonic acid (860 mg, 5 mmol). Eluent: petroleum ether- $\text{CH}_2\text{Cl}_2$ , 2:1, yield 596 mg (46%); white crystalline powder; mp 144-145°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.47$ -1.51 (m, 2 H), 1.60-1.83 (m, 15 H), 3.48 (t,  $J = 7.7$  Hz, 2 H), 6.66 (s, 2 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 27.8$  (1 C), 28.0 (1 C), 31.3 (1 C), 31.5 (4 C), 36.4 (1 C), 38.2 (1 C), 38.9 (2 C), 41.8 (1 C), 134.0 (2 C), 170.8 (2 C). Anal. calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_2$ : C 74.10, H 8.16, N 5.40%; found: C 74.01, H 8.23, N 5.41%.

**Ethyl 2-[4-(1-adamantyl)phenyl]-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxylate (21)** was obtained from compound **12** (92 mg, 0.3 mmol) and allene **18** (67 mg, 0.6 mmol) in the presence of  $\text{PPh}_3$  (8 mg, 10 mol%). Eluent:  $\text{CH}_2\text{Cl}_2$ , yield 117 mg (93%), white crystalline powder, mp 173-174°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.31$  (t,  $J = 7.3$  Hz, 3 H), 1.70-1.79 (m, 6 H), 1.88-1.89 (m, 6 H), 2.07 (br. s., 3 H), 3.01-3.04 (m, 2 H), 3.66-3.71 (m, 1 H), 4.19-4.34 (m, 3 H), 6.82-6.85 (m, 1 H), 7.18 (d,  $J = 8.6$  Hz, 2 H), 7.42 (d,  $J = 8.6$  Hz, 2 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  (1 C), 28.7 (3 C), 35.8 (1 C), 36.1 (1 C), 36.5 (3 C), 42.9 (3 C), 43.1 (1 C), 51.5 (1 C), 60.9 (1 C), 125.6 (2 C), 125.8 (2 C), 128.8 (1 C), 133.2 (1 C), 144.0 (1 C), 151.7 (1 C), 163.0 (1 C), 174.4 (1 C), 178.1 (1 C). HRMS (ESI):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{29}\text{NNaO}_4$ : 422.1994; found: 442.1982.

**Ethyl 2-[2-(1-adamantyl)ethyl]-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxylate (23)** was obtained from compound **14** (78 mg, 0.3 mmol) and allene **18** (67 mg, 0.6 mmol) in the presence of  $\text{PPh}_3$  (8 mg, 10 mol%). Eluent:  $\text{CH}_2\text{Cl}_2$ , yield 110 mg (99%), white crystalline powder, mp 84-85°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.22$ -1.26 (m, 2 H), 1.31 (t,  $J = 7.2$  Hz, 3 H), 1.48-1.49 (m, 6 H), 1.57-1.68 (m, 6 H), 1.92 (br. s., 3 H), 2.82-3.00 (m, 2 H), 3.42-3.51 (m, 3 H), 4.12-4.16 (m, 1 H), 4.25 (qd,  $J = 7.2, 3.6$  Hz, 2 H), 6.73-6.74 (m, 1 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  (1 C), 28.4 (3 C), 31.8 (1 C), 34.1 (1 C), 35.5 (1 C), 36.9 (3 C), 41.9 (3 C), 43.0 (1 C), 51.5 (1 C), 60.9 (1 C), 133.2 (1 C), 143.6 (1 C), 163.1 (1 C), 175.2 (1 C), 178.7 (1 C). HRMS (ESI):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{29}\text{NNaO}_4$ : 394.1994; found: 394.1981.

**Ethyl 2-[2-(1-adamantyloxy)ethyl]-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxylate (24)** was obtained from compound **15** (83 mg, 0.3 mmol) and allene **18** (67 mg, 0.6 mmol) in the presence of PPh<sub>3</sub> (8 mg, 10 mol%). Eluent: CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 200:1, yield 107 mg (92%), yellowish oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.28 (t, *J* = 7.1 Hz, 3 H), 1.48-1.58 (m, 12 H), 2.05 (br. s., 3 H), 2.85-3.00 (m, 2 H), 3.47-3.53 (m, 3 H), 3.59 (t, *J* = 5.7 Hz, 2 H), 4.13-4.16 (m, 1 H), 4.19-4.27 (m, 2 H), 6.72-6.73 (m, 1 H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 14.1 (1 C), 30.3 (3 C), 35.6 (1 C), 36.2 (3 C), 39.4 (1 C), 41.2 (3 C), 43.0 (1 C), 51.4 (1 C), 55.8 (1 C), 60.8 (1 C), 72.2 (1 C), 133.4 (1 C), 143.5 (1 C), 163.0 (1 C), 175.2 (1 C), 178.8 (1 C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>29</sub>NNaO<sub>5</sub>: 410.1943; found: 410.1950.

**Ethyl 2-[2-(2-adamantyl)ethyl]-1,3-dioxo-1,2,3,3a,6,6a-hexahydrocyclopenta[*c*]pyrrole-4-carboxylate (26)** was obtained from compound **17** (78 mg, 0.3 mmol) and allene **18** (67 mg, 0.6 mmol) in the presence of PPh<sub>3</sub> (8 mg, 10 mol%). Eluent: CH<sub>2</sub>Cl<sub>2</sub>, yield 110 mg (99%), white crystalline powder, mp 108-109°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.31 (t, *J* = 7.2 Hz, 3 H), 1.47-1.49 (m, 2 H), 1.58-1.83 (m, 15 H), 2.86-3.01 (m, 2 H), 3.42-3.54 (m, 3 H), 4.15-4.17 (m, 1 H), 4.24-4.29 (m, 2 H), 6.75 (br. s., 1 H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 14.1 (1 C), 27.8 (1 C), 28.0 (1 C), 30.3 (1 C), 31.4 (2 C), 31.7 (1 C), 35.5 (2 C), 37.6 (1 C), 38.2 (1 C), 39.0 (2 C), 42.0 (1 C), 43.1 (1 C), 51.5 (1 C), 60.9 (1 C), 133.4 (1 C), 143.6 (1 C), 163.1 (1 C), 175.4 (1 C), 178.9 (1 C). HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>29</sub>NNaO<sub>4</sub>: 394.1994; found: 394.1993.