Supplementary material for

Co-cyclotrimerization of 6-Alkynylpurines with α,ω-Diynes as a Novel Approach to Biologically Active 6-Arylpurines

Pavel Turek, Martin Kotora,* Iva Tišlerová, Michal Hocek, Ivan Votruba, and Ivana Cisařová

Contents
I  General methods.
II  Preparation of starting material
III  General procedures for Ni- and Co-catalyzed co-cyclotrimerization
IV  General procedures for Ni-mediated co-cyclotrimerization
V  Crystallography
VI  References
VII  Spectra of all prepared compounds

I  General methods
All reactions were carried out under a protective atmosphere of Ar in 3 mL glass vials. Toluene was distilled from sodium and benzophenone under Ar. Unless mentioned, reagents were used as obtained without further purification.

II  Preparation of starting material
NiBr₂(PBu₃)₂, NiBr₂(PPh₃)₂, NiI₂(PPh₃)₂, NiBr₂(dpdm), NiBr₂(dppe), NiBr₂(dpdp), NiBr₂(dppe),¹ CoBr(PPh₃)₃,² 9-Bn-6-alkynylpurines³ were prepared according to the previously published procedures. Diynes that were not commercially available were prepared by C-alkylation of the corresponding C-acids with propargyl bromide in the presence of K₂CO₃.⁴

III  General procedures for Ni- and Co-catalyzed co-cyclotrimerization
Preparation of 9-benzyl-6-arylpurines 3xa₂.

General procedure for catalytic cyclotrimerization of 6-alkynylpurines with diynes.

Ni-catalyzed reactions. To a solution of 6-alkynylpurine 1xa (0.1 mmol), a diyne 2 (0.1 mmol) a Ni-complex (0.02 mmol) in MeCN (2 mL) under Ar was added Zn powder (5 mg, 0.08 mmol). The reaction mixture was initially stirred at 20 °C, if the reaction did not proceed or the rate was too slow the content was heated at 60 °C. Then the reaction mixture was filtered through a plug of wool and
concentrated under the reduced pressure. Further subjection to column chromatography afforded the product.

*Co or Rh-catalyzed reactions.* A solution of 6-alkynylpurine 1**a** (0.1 mmol), a diyne 2 (0.1 mmol) a Co- or Rh-complex (0.02 mmol) in toluene (2 mL) under Ar was initially stirred at 20 °C, if the reaction did not proceed or the rate was too slow the content was heated at 60 °C. Further steps followed the previously mentioned procedure.

**9-Benzyl-6-(1,3-dihydroisobenzofuran-5-yl)-9H-purine (3aad).** Column chromatography on silica gel (1/2 hexane/EtOAc) afforded 18 mg (55%) of a pale yellow oil. Recrystallization from hexane afforded a colorless crystals: mp 118-120 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.19 (s, 2H), 5.23 (s, 2H), 5.50 (s, 2H), 7.32–7.40 (m, 5H), 7.43 (d, J = 7.6 Hz, 1H), 8.11 (s, 1H), 8.70 (s, 1H), 8.76 (d, J = 8 Hz, 1H), 9.05 (s, 1H); IR (CHCl₃) ν 3027, 2859, 1583, 1570, 1504, 1455, 1327, 1231, 1222, 1218, 1212, 1046, 901, 838, 804 cm⁻¹; EI-MS m/z (% relative intensity) 328 (M⁺, 16), 300 (14), 91 (100), 65 (14); HR-MS calcd for C₂₀H₁₆N₄O: C 73.15, H 4.91, N 17.06, found: C 72.81, H 4.91, N 16.89. R_f (1/4 hexane/EtOAc) = 0.44.

**9-Benzyl-6-(6-butyl-2,2-di(carboxyethyl)indan-5-yl)-9H-purine (3baa).** The reaction was catalyzed by NiI₂(PPh₃)₂/Zn. Column chromatography on silica gel (3/2 hexane/EtOAc) afforded 25 mg (48%) of a pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 0.70 (t, J = 7.3 Hz, 3H), 1.15–1.19 (m, 2H), 1.26 (t, J = 7.1 Hz, 6H), 1.35–1.43 (m, 2H), 2.72–2.76 (m, 2H), 3.63 (s, 2H), 3.64 (s, 2H), 4.19 (m, 4H), 5.50 (s, 2H), 7.22 (s, 1H), 7.33–7.41 (m, 5H), 7.42 (s, 1H), 8.05 (s, 1H), 9.07 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 14.0 (2C), 22.4, 32.9, 33.5, 40.1, 40.4, 47.3, 60.5, 61.7 (2C), 125.8, 126.2, 127.9 (2C), 128.6, 129.1 (2C), 132.1, 133.5, 134.1, 135.1, 137.5, 140.9, 141.9, 142.1, 151.1, 152.4, 159.6, 171.6 (2C); IR (CHCl₃) ν 3025, 2987, 1730, 1586, 1225 cm⁻¹; EI-MS m/z (% relative intensity) 526 (M⁺, 23), 497 (20), 435 (91), 289 (9), 245 (7), 91 (100); HR-MS calcd for C₃₁H₃₄N₄O₄: C 73.15, H 4.91, N 16.89. R_f (2/3 hexane/EtOAc) = 0.56.

**9-Benzyl-6-(6-butyl-2-acetyl-2-(carboxyethyl)indan-5-yl)-9H-purine (3bab).** The reaction was catalyzed by NiBr₂(dppe)/Zn. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 52 mg (52%) of a pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 0.70 (t, J = 7.2 Hz, 3H), 1.09-1.18 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.34–1.43 (m, 2H), 2.23 (s, 3H), 2.70-2.78 (m, 2H), 3.50-3.64 (m, 4H), 4.22 (q, J = 7.2 Hz, 2H), 5.49 (s, 2H), 7.21 (s, 1H), 7.32-7.41 (m, 5H), 7.43 (s, 1H), 8.04 (s, 1H), 9.05 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 14.0, 22.4, 26.1, 32.9, 33.5, 38.7, 38.9, 47.3, 61.8, 67.1, 125.9, 126.3, 127.9 (2C), 128.6, 129.1 (2C), 132.1, 133.6, 135.1, 137.3, 141.04, 141.8, 144.2, 151.7, 152.4, 159.5, 172.2, 202.7; IR (CHCl₃) ν 3024, 1716, 1588, 1225 cm⁻¹; EI-MS m/z (% relative intensity) 300 (100), 91 (100).
intensity) 496 (M⁺, 12), 467 (10), 405 (60), 91 (100); HR MS calcd for C₃₀H₃₂N₄O₃ 496.2474, found 496.2461. Rf(EtOAc) = 0.54.

9-Benzyl-6-(6-butyl-2,2-diacetylindan-5-yl)-9H-purine (3bac). The reaction was catalyzed by NiBr₂(dppe)/Zn. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 55 mg (59%) of a pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 0.70 (t, J = 7.2 Hz, 3H), 1.08-1.18 (m, 2H), 3.55 (s, 4H), 7.22 (s, 1H), 7.30-7.42 (m, 5H), 7.44 (s, 1H), 8.05 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 22.3, 26.5 (2C), 32.9, 33.5, 37.3, 47.3, 74.8, 126.0, 126.5, 127.6 (2C), 128.6, 129.1 (2C), 132.0, 133.7, 135.1, 137.1, 141.2, 141.6, 144.3, 151.7, 152.4, 159.3, 204.8 (2C); IR (CHCl₃) ν 3026, 1702, 1588, 1223, 1218 cm⁻¹; EI-MS m/z (% relative intensity) 466 (M⁺, 10), 375 (40), 333 (20), 224 (10), 91 (100), 43 (18); HR-MS calcd for C₂₉H₃₀N₄O₂ 466.2369, found 466.2389. Rf(EtOAc) = 0.48.

9-Benzyl-6-(6-butyl-1,3-dihydroisobenzofuran-5-yl)-9H-purine (3bad). The reaction was catalyzed by CoBr₂(PPh₃)₃. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 48 mg (63%) of a pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 0.71 (t, J = 7.2 Hz, 3H), 1.11-1.21 (m, 2H), 1.38-1.46 (m, 2H), 2.75-2.85 (m, 2H), 5.15 (s, 4H), 5.50 (s, 2H), 7.26 (s, 1H), 7.34-7.42 (m, 5H), 7.49 (s, 1H), 8.06 (s, 1H), 9.08 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 22.3, 32.9, 33.5, 47.3, 73.4, 73.4, 122.5, 123.1, 127.9 (2C), 128.6, 129.1 (2C), 132.1, 133.8, 135.0, 136.6, 140.9, 141.5, 144.4, 151.8, 152.4, 159.2; IR (CHCl₃) ν 3022, 2996, 2863, 1587, 1501, 1456, 1402, 1331, 1222, 1218, 1211, 1197, 1050, 901 cm⁻¹; EI-MS m/z (% relative intensity) 384 (M⁺, 11), 355 (10), 293 (48), 91 (100), 65 (11); HR-MS calcd for C₂₄H₂₄N₄O 384.1950, found 384.1944. Rf(EtOAc) = 0.40.

9-Benzyl-6-(6-butylindan-5-yl)-9H-purine (3bae). The reaction was catalyzed by NiI₂(PPh₃)₂/Zn. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 8 mg (11%) of a pale yellow oil. Recrystallization from hexane furnished colorless crystals: mp 124-127 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.71 (t, J = 7.4 Hz, 3H), 1.10-1.20 (m, 2H), 1.36-1.45 (m, 2H), 2.04-2.14 (m, 2H), 2.72-2.80 (m, 2H), 2.93 (t, J = 7.2 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H), 5.49 (s, 2H), 7.23 (s, 1H), 7.32-7.42 (m, 5H), 7.46 (s, 1H), 8.03 (s, 1H), 9.05 (1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 22.4, 25.5, 32.5, 32.9 (2C), 33.8, 47.3, 126.0, 126.4, 127.9 (2C), 128.6, 129.2 (2C), 132.2, 132.4, 135.2, 139.9, 141.6, 144.1, 146.2, 151.7, 152.4, 160.2; IR (CHCl₃) ν 3028, 2960, 2870, 1586, 1500, 1456, 1379, 1329, 1223, 1227, 879 cm⁻¹; EI-MS m/z (% relative intensity) 383 (M⁺, 11), 215 (5), 201 (13), 181 (7), 110 (19), 91 (100), 75 (22), 57 (28); HR-MS calcd for C₂₅H₂₆N₄ (M⁺-H) 382.2157, found 382.2171. Rf(2/3 hexane/EtOAc) = 0.57.

9-Benzyl-6-(6-pfenyl-2,2-(dicarboxyethyl)indan-5-yl)-9H-purine (3caa). The reaction was catalyzed by NiBr₂(dppe)/Zn. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 35 mg (64%) of a pale yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 1.27 (t, J = 7.2 Hz, 6H), 3.70 (s, 2H), 3.72 (s, 2H),
4.23 (q, $J = 7.2$ Hz, 4H), 5.37 (s, 2H), 7.06-7.14 (m, 5H), 7.14-7.18 (m, 2H), 7.28-7.36 (m, 3H), 7.38 (s, 1H), 7.62 (s, 1H), 7.82 (s, 1H); 13C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0 (2C), 40.1, 40.4, 47.0, 60.6, 61.7 (2C), 126.2, 126.4 (2C), 127.4 (2C), 127.1 (2C), 128.4, 129.0 (2C), 129.2 (2C), 132.0, 133.4, 135.15, 139.3, 141.1, 141.3, 142.2, 144.0, 151.4, 152.3, 159.2, 171.4 (2C); IR (CHCl$_3$) ν 3037, 3025, 2987, 1731, 1588, 1499, 1447, 1369, 1329, 1230, 1217, 1214, 1196, 1159, 1069, 907 cm$^{-1}$; EI-MS m/z (% relative intensity) 545 (M$^+$, 22), 473 (6), 399 (6), 91 (100); HR-MS cacld for C$_{33}$H$_{30}$N$_4$O$_5$ 546.2267, found 546.2274. R$_f$(1/2 hexane/EtOAc) = 0.40.

9-Benzyl-6-(6-phenyl-2-acetyl-2-(carboxyethyl)indan-5-yl)-9$H$-purine (3cab). The reaction was catalyzed by NiBr$_2$(dppe)/Zn. Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 55 mg (53%) of a pale yellow oil: 1H NMR (400 MHz, CDCl$_3$) $\delta$ 1.29 (t, $J = 7.2$ Hz, 3H), 2.27 (s, 3H), 3.58-3.72 (m, 4H), 4.24 (q, $J = 7.1$ Hz, 2H), 5.39 (s, 2H), 7.06-7.13 (m, 5H), 7.14-7.20 (m, 2H), 7.31-7.37 (m, 3H), 7.38 (s, 1H), 7.62 (s, 1H), 7.83 (s, 1H), 8.88 (s, 1H); 13C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 26.1, 38.7, 38.9, 47.0, 61.9, 67.1, 126.2, 126.5, 126.5, 127.4 (2C), 127.6 (2C), 128.4, 129.0 (2C), 129.1 (2C), 132.0, 133.5, 135.1, 139.1, 141.2, 141.3, 142.0, 144.1, 151.4, 152.3, 159.1, 172.1, 202.4; IR (CHCl$_3$) ν 3019, 1703, 1589, 1215, 1212, 1200 cm$^{-1}$; EI-MS m/z (% relative intensity) 516 (M$^+$, 27), 515 (35), 473 (10), 443 (8), 399 (6), 311 (35), 221 (9), 91 (100); HR MS cacld for C$_{32}$H$_{28}$N$_4$O$_3$ 516.2161, found 516.2195. R$_f$(EtOAc) = 0.46.

9-Benzyl-6-(6-phenyl-1,3-dihydroisobenzofuran-5-yl)-9$H$-purine (3cad). The reaction was catalyzed by NiBr$_2$(dppe)/Zn. Column chromatography on silica gel (1/2 hexane/EtOAc) afforded 66 mg (68%) of a pale yellow oil: 1H NMR (400 MHz, CDCl$_3$) $\delta$ 2.21 (s, 6H), 3.63 (s, 4H), 5.39 (s, 2H), 7.04-7.14 (m, 5H), 7.14-7.22 (m, 2H), 7.32-7.38 (m, 3H), 7.39 (s, 1H), 7.62 (s, 1H), 7.83 (s, 1H), 8.88 (s, 1H); 13C NMR (100 MHz, CDCl$_3$) $\delta$ 26.5 (2C), 37.3, 37.5, 47.0, 74.9, 126.3, 126.5, 126.6 (2C), 127.5 (2C), 128.4, 129.0 (2C), 129.1 (2C), 132.0, 133.6, 135.1, 138.9, 141.1, 141.3, 141.9, 144.1, 151.4, 152.3, 159.0, 204.5 (2C); IR (CHCl$_3$) ν 3019, 1703, 1589, 1215, 1212, 1200 cm$^{-1}$; EI-MS m/z (% relative intensity) 486 (M$^+$, 16), 485 (17), 443 (60), 91 (100); HR MS cacld for C$_{31}$H$_{26}$N$_4$O$_2$ 486.2056, found 486.2073. R$_f$(EtOAc) = 0.35.

9-Benzyl-6-(6-phenyl-1,3-dihydroisobenzofuran-5-yl)-9$H$-purine (3cad). The reaction was catalyzed by NiBr$_2$(dppe)/Zn. Column chromatography on silica gel (1/2 hexane/EtOAc) afforded 36 mg (88%) of a pale yellow oil: 1H NMR (400 MHz, CDCl$_3$) $\delta$ 5.22 (s, 4H), 5.40 (s, 2H), 7.08-7.16 (m, 5H), 7.16-7.22 (m, 2H), 7.32-7.38 (m, 3H), 7.41 (s, 1H), 7.66 (s, 1H), 7.86 (s, 1H), 8.89 (s, 1H); 13C NMR (100 MHz, CDCl$_3$) $\delta$ 47.1, 73.4, 73.5, 123.2, 123.3, 126.5, 127.6 (2C), 127.8 (2C), 128.5, 129.1 (2C), 129.2 (2C), 132.1, 133.8, 135.1, 138.4, 141.1, 141.2, 141.7, 144.3, 151.5, 152.4, 158.6; IR (CHCl$_3$) ν 3021, 2989, 2859, 1589, 1499, 1455, 1438, 1332, 1216, 1213, 1121, 1048, 902, 855 cm$^{-1}$; EI-MS m/z (% relative
intensity) 404 (M^+, 6), 403 (11), 277 (100), 201 (24), 183 (20), 91 (25), 77 (44), 59 (58); HR-MS calcd for C_{26}H_{20}N_{4}O_{4} 404.1637, found 404.1614. R_f(EtOAc) = 0.32.

9-Benzyl-6-(6-phenyl-2-cyano-2-(carboxyethyl)indan-5-yl)-9H-purine (3cag). The reaction was catalyzed by NiBr_2(dppe)/Zn. Column chromatography on silica gel (3/1 toluene/EtOAc) afforded 62 mg (62%) of a yellow oil: \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 1.36 (t, \(J = 7.2\) Hz, 3H), 3.69 (d, \(J = 16.4\) Hz, 1H), 3.70 (d, \(J = 16.5\) Hz, 1H), 3.82 (d, \(J = 16.5\) Hz, 1H), 3.84 (d, \(J = 16.3\) Hz, 2H), 4.33 (q, \(J = 7.2\) Hz, 2H), 5.40 (s, 2H), 7.08-7.14 (m, 5H), 7.16-7.20 (m, 2H), 7.30-7.40 (m, 3H), 7.43 (s, 1H), 7.67 (s, 1H), 7.85 (s, 1H), 8.88 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\) 14.0, 42.9, 42.9, 47.1, 47.5, 63.3, 120.4, 126.6, 126.7, 127.5 (2C), 127.8 (2C), 128.5, 129.1 (2C), 129.2 (2C), 132.0, 134.3, 135.1, 137.4, 140.3, 140.9, 142.1, 144.3, 151.5, 152.4, 158.6, 168.2; IR (CHCl_3) \(\nu\) 2986, 2244, 1740, 1587, 1495, 1457, 1236, 905 cm\(^{-1}\); EI-MS m/z (% relative intensity) 499 (M^+, 2), 498 (M^+-1, 4), 311 (62), 221 (18), 91 (100). R_f(1/3 toluene/EtOAc) = 0.55.

IV General procedure for cyclotrimerization of 6-alkynylpurines with diynes in the presence of a stoichimetric amount of Ni-complex.

To a solution of 6-alkynylpurine 1 (0.1 mmol), a diyne 2 (0.1 mmol) a NiI_2(PPh_3)_2 (0.1 mmol) in MeCN (2 mL) under Ar was added Zn powder (13 mg, 0.2 mmol). The reaction mixture was initially stirred at 20 °C, if the reaction did not proceed or the rate was too slow the content was heated at 60 °C. Further steps followed the previously mentioned procedure.

9-Benzyl-6-(2,2-di(carboxyethyl)indan-5-yl)-9H-purine (3aaa). Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 9 mg (9%) of a pale yellow oil: \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 1.27 (t, \(J = 7.1\) Hz, 6H), 3.67 (s, 2H), 3.72 (s, 2H), 4.22 (q, \(J = 7\) Hz, 4H), 5.49 (s, 2H), 7.30–7.40 (m, 6H), 8.09 (s, 1H), 8.62 (s, 1H), 8.66 (dd, \(J = 9.5\) Hz, \(J = 1.5\) Hz, 1H), 9.03 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\) 14.0 (2C), 40.5, 40.5, 47.3, 60.5, 61.8 (2C), 124.5, 125.4, 127.8 (2C), 128.6, 129.1, 129.2 (2C), 130.8, 134.7, 135.2, 140.7, 143.6, 144.0, 152.5, 152.5, 155.0, 171.5 (2C); IR (CHCl_3) \(\nu\) 3032, 2989, 1730, 1581, 1449, 1253, 1215, 1182, 1062, 863 cm\(^{-1}\); EI-MS m/z (% relative intensity) 470 (M^+, 6), 396 (15), 91 (100), 65 (6); HR-MS calcd for C_{27}H_{26}N_{4}O_{4} 470.1954, found 470.1950. R_f(1/2 hexane/EtOAc) = 0.47.

9-Benzyl-6-(6-butylindan-5-yl)-9H-purine (3bae). Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 22 mg (29%) of a pale yellow oil.

9-Benzyl-6-(6-butyl-2,2-di(carboxyethyl)indan-5-yl)-9H-purine (3baa). Column chromatography on silica gel (3/2 hexane/EtOAc) afforded 27 mg (52%) of a pale yellow oil.
9-Benzyl-6-(6-butyl-2-cyano-2-(carboxyethyl)indan-5-yl)-9H-purine (3bag). Column chromatography on silica gel (2/3 hexane/EtOAc) afforded 32 mg (33%) of a pale yellow oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.71 (t, $J = 7.2$ Hz, 3H), 1.11–1.20 (m, 2H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.37-1.45 (m, 2H), 2.74-2.80 (m, 2H), 3.60 (d, $J = 16.5$ Hz, 1H), 3.61 (d, $J = 16.5$ Hz, 1H), 3.73 (d, $J = 15.4$ Hz, 1H), 3.76 (d, $J = 16.0$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 5.50 (s, 2H), 7.26 (s, 1H), 7.33-7.42 (m, 5H), 7.48 (s, 1H), 8.06 (s, 1H), 9.07 (1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.7, 14.0, 22.4, 32.9, 33.5, 42.9, 43.0, 47.4, 47.4, 63.2, 120.5, 126.0, 126.5, 127.9 (2C), 128.7, 129.2 (2C), 132.1, 134.4, 135.0, 135.6, 140.0, 142.0, 144.4, 151.8, 152.5, 158.9, 168.4; IR (CHCl$_3$) $\nu$ 3025, 2988, 2963, 1745, 1587, 1502, 1370, 1329, 1217, 1209, 909 cm$^{-1}$; EI-MS m/z (% relative intensity) 479 (M$^+$,11), 450 (8), 388 (45), 91 (100), 65 (7); HR-MS calcd for C$_{29}$H$_{29}$N$_5$O$_2$ 479.2321, found 479.2309. $R_f$ (2/3 hexane/EtOAc) = 0.41.

9-Benzyl-6-(3-butyl-5,6,7,8-tetrahydronafthalen-2-yl)-9H-purine (3b af). Column chromatography on silica gel (3/2 hexane/EtOAc) afforded 31 mg (39%) of a pale yellow oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.70 (t, $J = 7.3$ Hz, 3H), 1.10-1.20 (m, 2H), 1.35-1.43 (m, 2H), 1.78-1.82 (m, 4H), 2.70-2.76 (m, 2H), 2.76-2.82 (m, 2H), 7.05 (s, 1H), 7.33 (s, 1H), 7.32-7.41 (m, 5H), 8.02 (s, 1H), 9.05 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.7, 22.4, 23.2, 23.3, 28.9, 29.4, 32.6, 33.6, 47.3, 127.9 (2C), 128.6, 129.2 (2C), 130.7, 131.2, 131.8, 132.1, 134.4, 135.2, 138.8, 138.8, 144.1, 151.7, 152.4, 159.7; IR (CHCl$_3$) $\nu$ 3025, 2935, 2866, 1683, 1586, 1456, 1402, 1330, 1211, 823 cm$^{-1}$; EI-MS m/z (% relative intensity) 396 (M$^+$, 9), 367 (11), 319 (12), 305 (42), 91 (100), 65 (9); HR-MS calcd for C$_{26}$H$_{28}$N$_4$ 396.2314, found 396.2289. $R_f$(2/3 hexane/EtOAc) = 0.54.

6-(6-Butyl-2-cyano-2-(carboxyethyl)indan-5-yl)-9-(tetrahydropyran-2-yl)-9H-purine (3bbg). Column chromatography on silica gel (2/1 toluene/EtOAc) afforded 25 mg (26%) of a yellow oil.

9-Benzyl-6-(6-pfenyl-2,2-(dicarboxyethyl)indan-5-yl)-9H-purine (3caa). Column chromatography on silica gel (1/1 hexane/EtOAc) afforded 24 mg (22%) of a pale yellow oil.

9-Benzyl-6-(6-phenyl-2-cyano-2-(carboxyethyl)indan-5-yl)-9H-purine (3cag). Column chromatography on silica gel (3/1 toluene/EtOAc) afforded 15 mg (15%) of a yellow oil.

6-(6-Phenyl-2-cyano-2-(carboxyethyl)indan-5-yl)-9-(tetrahydropyran-2-yl)-9H-purine (3cbg). Column chromatography on silica gel (2/1 toluene/EtOAc) afforded 12 mg (12%) of a yellow oil.

V Crystallography.

Crystal data for 3acd: C$_{13}$H$_{10}$N$_4$O, M=238.25, monoclinic, $P$ 2$_1$/c (No 2), $a$ = 14.7560(3) Å, $b$ = 9.7250(4) Å, $c$ = 7.2310(7) Å, $\beta$ = 93.467(3)$^\circ$, $V$ = 1035.76(11) Å$^3$, $Z$ = 4, $D_x$ = 1.528 Mg m$^{-3}$. A light blue plate of dimensions 0.4x0.3x0.025mm was mounted on glass capillary with epoxy glue and measured at Nonius KappaCCD diffractometer by monochromatized MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 150(2) K. An absorption was neglected ($\mu$ = 0.103 mm$^{-1}$); a total of 14549 measured reflections in the
range \( h = -19 \) to 19, \( k = -12 \) to 12, \( l = -9 \) to 9 (\( \theta_{\text{max}} = 27.5^\circ \)), from which 2369 were unique (\( R_{\text{int}} = 0.052 \)), 1738 observed according to the \( I > 2\sigma(I) \) criterion. The structure was solved by direct methods (SIR92)\(^5\) and refined by full-matrix least squares based on \( F^2 \) (SHELXL97).\(^6\) The refinement converged (\( \Delta/\sigma_{\text{max}} = 0.000 \)) to \( R = 0.0513 \) for observed reflections and \( wR = 0.1343, S = 1.104 \) for 167 parameters and all 2396 reflections. The final difference map displayed no peaks of chemical significance (\( \Delta\rho_{\text{max}} = 0.224, \Delta\rho_{\text{min}} -0.282 \text{ e.Å}^{-3} \)).

Fig. 1. View on the molecule of 3acd with atom numbering schema. The displacement ellipsoids are drawn on 50% probability level. The dihedral angle between least-square planes through atoms N1...C6 and C9...C16 is 35.82(3)\(^\circ\). The distance of O1 from C9...C16 plane -0.070(2)Å.
VI References


VII  Spectra of all prepared compounds