Synthesis of 3-(3-Methyl-1-aryl-1*H*-pyrazol-5-yl)-2*H*-2-chromen-2-one Derivatives *via* a One-Pot Three-Component Reaction

Abdolali Alizadeh,* Rashid Ghanbaripour

Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran. E-mail: aalizadeh@modares.ac.ir

SUPPORTING INFORMATION

3-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (3a).

Yield: 181 mg (60%); white powder; m.p. = 126-127 °C. IR (KBr): 1724 (CO₂), 1602, 1497, and 1464 (Ar), 1106 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.41 (3H, s, CH₃), 6.63 (1H, s, CH of pyrazole), 7.28 (1H, d, ³J_{HH} = 6.0 Hz, CH_{para} of Ph), 7.33-7.35 (4H, m, CH of Ar), 7.40-7.42 (4H, m, CH of Ar), 7.48 (1H, s, CH⁴ of chromene), 7.55 (1H, td, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.6 Hz, CH of Ar). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.56 (CH₃), 110.22 (CH³ of pyrazole), 116.68 (CH⁸ of chromene), 118.62 (C³ of chromene), 118.88 (C^{4a} of chromene), 124.68 (CH⁶ of chromene), 124.73 (2 CH_{ortho} of Ph), 127.70 (CH⁵ of chromene), 128.15 (CH_{para} of Ph), 129.30 (2 CH_{meta} of Ph), 132.19 (CH⁷ of chromene), 136.31 (C⁵ of pyrazole), 140.22 (C_{ipso}-N of Ph), 142.19 (CH⁴ of chromene), 149.59 (C³ of pyrazole) 153.56 (C^{8a} of chromene), 158.97 (CO₂). MS (EI, 70 eV): *m/z* (%) = 302 (*M*⁺, 100), 285 (19), 273 (62), 232 (21), 204 (34), 151 (25), 139 (28), 115 (33), 102 (28), 91 (34), 77 (77). Anal. calcd for C₁₉H₁₄N₂O₂ (302.33): C, 75.48; H, 4.67; N, 9.27%. Found: C, 75.37; H, 4.75; N, 9.20%.

6-Bromo-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (3b).

Yield: 278 mg (73%). white powder. m.p. = 160-162 °C. IR (KBr): 1726 (CO₂), 1596, 1541, and 1493 (Ar), 1235 and 1110 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.42 (3H, s, CH₃), 6.66 (1H, s, CH of pyrazole), 7.23 (1H, d, ³J_{HH} = 8.8 Hz, CH⁸ of chromene), 7.36 (1H, s, CH⁴ of chromene), 7.41-7.42 (5H, m, 5 CH of Ph), 7.45 (1H, d, ⁴J_{HH} = 2.0 Hz, CH⁵ of chromene), 7.63 (1H, dd, ³J_{HH} = 8.8 Hz, ⁴J_{HH} = 2.0 Hz, CH⁷ of chromene). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.54 (CH₃), 110.52 (CH³ of pyrazole), 117.27 (C-Br), 118.39 (CH⁸ of chromene), 119.92 (C³ of chromene), 120.13 (C^{4a} of chromene), 124.79 (2 CH_{ortho} of Ph), 127.93 (CH_{para} of Ph), 129.42 (2 CH_{meta} of Ph), 130.25 (CH⁵ of chromene), 134.84 (CH⁷ of chromene), 135.78 (C⁵ of pyrazole), 140.07 (C_{ipso}-N of Ph), 140.43 (CH⁴ of chromene), 149.71 (C³ of pyrazole), 152.30 (C^{8a} of chromene), 158.29 (CO₂). MS (EI, 70 eV): *m/z* (%) = 382 (*M*+2, 33), 380 (*M*⁺, 34), 241 (40), 188 (100), 173 (43), 161 (20), 145 (40), 118 (27), 107 (26), 91 (24), 77 (40). Anal. calcd for C₁₉H₁₃BrN₂O₂ (381.23): C, 59.86; H, 3.44; N, 7.35%. Found: C, 59.96; H, 3.37; N, 7.31%.

8-Methoxy-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (3c).

Yield: 229 mg (69%). yellow oil. IR (KBr): 1720 (CO₂), 1601, 1484 and 1449 (Ar), 1276 and 1100 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.41 (3H, s, CH₃), 3.97 (3H, s, OCH₃), 6.63 (1H, s, CH of pyrazole), 6.90 (1H, dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.2 Hz, CH⁷ of chromene), 7.09 (1H, dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.2 Hz, CH⁵ of chromene), 7.19 (1H, t, ³J_{HH} = 8.0 Hz, CH⁶ of chromene), 7.32-7.41 (5H, m, 5 CH of Ph), 7.45 (1H, s, CH⁴ of chromene). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.55 (CH₃), 56.27 (OCH₃), 110.26 (CH³ of pyrazole), 113.92 (CH⁷ of chromene), 119.12 (C³ of chromene), 119.23 (C^{4a} of chromene), 119.46 (CH⁵ of chromene), 124.54 (CH⁶ of chromene), 124.76 (2 CH_{ortho} of Ph), 127.66 (CH_{para} of Ph), 129.28 (2 CH_{meta} of Ph), 136.31 (C⁵ of pyrazole), 140.19 (C_{ipso}-N of Ph), 142.35 (CH⁴ of chromene), 143.23 (C^{8a} of chromene), 147.08 (C³ of pyrazole), 149.56 (C-OCH₃), 158.41 (CO₂). MS (EI, 70 eV): *m/z* (%) = 332 (*M*⁺, 100), 315 (30),

303 (20), 261 (11), 191 (11), 91 (27), 84 (52), 76 (31), 51 (43). Anal. calcd for C₂₀H₁₆N₂O₃ (332.36): C, 72.28; H, 4.85; N, 8.43%. Found: C, 72.45; H, 4.97; N, 8.30%.

6,8-Dibromo-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (3d).

Yield: 409 mg (89%). yellow powder. m.p. = 263-265 °C. IR (KBr): 3058 (CH of aromatic), 1738 (CO₂), 1595, 1498 and 1451 (Ar), 1396, 1364 (Me), 1247 and 1098 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.42 (3H, s, CH₃), 6.69 (1H, s, CH of pyrazole), 7.29 (1H, s, CH⁴ of chromene), 7.38 (1H, d, ⁴J_{HH} = 2.0 Hz, CH⁵ of chromene), 7.40-7.43 (5H, m, 5CH of Ph), 7.88 (1H, d, ⁴J_{HH} = 2.0 Hz, CH⁷ of chromene). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.54 (CH₃), 110.83 (CH³ of pyrazole), 111.19 (C⁸-Br), 117.17 (C³ of chromene), 120.52 (C^{4a} of chromene), 120.86 (C⁶-Br), 124.86 (2 CH_{ortho} of Ph), 128.09 (CH_{para} of Ph), 129.44 (CH⁵ of chromene), 129.51 (2 CH_{meta} of Ph), 135.25 (C⁵ of pyrazole), 137.46 (CH⁴ of chromene), 139.87 (CH⁷ of chromene), 139.92 (C_{ipso}-N of Ph), 149.26 (C³ of pyrazole), 149.80 (C^{8a} of chromene), 157.39 (CO₂). MS (EI, 70 eV): *m/z* (%) = 462 (*M*+4, 52), 460 (*M*+2, 100), 458 (*M*⁺, 52), 431 (38), 297 (36), 201 (30), 139 (22), 77 (79), 51 (31). Anal. calcd for C₁₉H₁₂Br₂N₂O₂ (460.12): C, 49.60; H, 2.63; N, 6.09%. Found: C, 49.74; H, 2.58; N, 6.18%.

6,8-Dibromo-3-[3-methyl-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]-2*H*-chromen-2-one (3e).

Yield: 398 mg (84%). white powder. m.p. = 258-261 °C. IR (KBr): 1739 (CO₂), 1553, 1515 and 1452 (Ar), 1284 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.40 (3H, s, CH₃), 2.41 (3H, s, CH₃), 6.66 (1H, s, CH of pyrazole), 7.21 (2H, d, ³J_{HH} = 8.4 Hz, CH of Ar), 7.26 (2H, d, ³J_{HH} = 8.4 Hz, CH of Ar), 7.30 (1H, s, CH⁴ of chromene), 7.39 (1H, d, ⁴J_{HH} = 2.0 Hz, CH⁵ of chromene), 7.88 (1H, d, ⁴J_{HH} = 2.0 Hz, CH⁷ of chromene). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.53 (CH₃ of pyrazole), 21.17 (CH₃ of chromene), 110.55 (CH³ of pyrazole), 111.16 (C⁸-Br), 117.11 (C³ of chromene), 120.66 (C^{4a} of chromene), 120.92 (C⁶-Br), 124.71 (2 CH of Ar), 129.44 (CH⁵ of

chromene), 130.06 (2 CH of Ar), 135.19 (C⁵ of pyrazole), 137.38 (CH⁴ of chromene), 137.49 (C-N of Ar), 138.02 (C-CH₃ of Ar), 139.75 (CH⁷ of chromene), 149.47 (C³ of pyrazole), 149.54 (C^{8a} of chromene), 156.43 (CO₂). MS (EI, 70 eV): m/z (%) = 476 ($M+4$, 51), 474 ($M+2$, 100), 472 (M^+ , 59), 445 (28), 216 (15), 189 (11), 139 (16), 91 (45), 65 (41). Anal. calcd for C₂₀H₁₄Br₂N₂O₂ (474.15): C, 50.66; H, 2.98; N, 5.91%. Found: C, 50.61; H, 2.87; N, 6.02%.

6,8-Dichloro-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (3f).

Yield: 297 mg (80%). white powder. m.p. = 244-246 °C. IR (KBr): 1737 (CO₂), 1565, 1498 and 1456 (Ar), 1243 (C-O) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ_H = 2.42 (3H, s, CH₃), 6.69 (1H, s, CH of pyrazole), 7.20 (1H, d, ⁴J_{HH} = 2.4 Hz, CH⁵ of chromene), 7.32 (1H, s, CH⁴ of chromene), 7.32-7.43 (5H, m, 5CH of Ph), 7.58 (1H, d, ⁴J_{HH} = 2.4 Hz, CH⁷ of chromene). ¹³C NMR (100.6 MHz, CDCl₃): δ_C = 13.54 (CH₃), 110.80 (CH³ of pyrazole), 120.41 (C⁸-Cl), 120.59 (C³ of chromene), 122.56 (C^{4a} of chromene), 124.86 (2 CH_{ortho} of Ph), 125.75 (CH⁵ of chromene), 128.07 (CH_{para} of Ph), 129.49 (2 CH_{meta} of Ph), 128.81 (C⁶-Cl), 131.94 (CH⁷ of chromene), 135.31 (C⁵ of pyrazole), 139.94 (C_{ipso}-N of Ph), 139.99 (CH⁴ of chromene), 147.74 (C^{8a} of chromene), 149.79 (C³ of pyrazole), 157.30 (CO₂). MS (EI, 70 eV): m/z (%) = 374 ($M+4$, 9), 372 ($M+2$, 52), 370 (M^+ , 81), 353 (20), 341 (32), 297 (49), 241 (56), 201 (31), 188 (29), 174 (65), 77 (100), 51 (47). Anal. calcd for C₁₉H₁₂Cl₂N₂O₂ (371.22): C, 61.48; H, 3.26; N, 7.55%. Found: C, 61.44; H, 3.41; N, 7.69%.

3-[(Z)-1-Hydroxy-3-oxo-1-butenyl]-2H-chromen-2-one (4a).

Yield: 207 mg (90%). green-yellow powder. m.p. = 148-150 °C. ¹H NMR (500.13 MHz, CDCl₃): δ_H = 2.26 (s, 3H, CH₃), 7.02 (s, 1H, CH of vinylic), 7.33 (d, ³J = 7.6 Hz, 1H, CH of Ar), 7.36 (d, ³J = 7.6 Hz, 1H, CH of Ar), 7.63 (t, ³J = 7.6 Hz, 2H, 2 CH of Ar), 8.64 (s, 1H, Ch of chromene), 15.86 (s, 1H, OH). ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 27.30 (CH₃), 101 (CH of vinylic), 116.57 (CH of

Ar), 118.53 (C³), 120.63 (C^{4a}), 124.94 (CH of Ar), 129.55 (CH of Ar), 133.96 (CH of Ar), 145.43 (CH⁴), 154.40 (C^{8a}), 158.03 (CO₂), 171.97 (C-OH), 199.69 (CO).

Figure S1 ¹H NMR of **3a**

Figure S2 ¹³C NMR of **3a**

Figure S3 ¹H NMR of **3b**

Figure S4 ¹³C NMR of **3b**

Figure S5 ¹H NMR of **3c**

Figure S6 ^{13}C NMR of **3c**

Figure S7 ¹H NMR of **3d**

Figure S8 ¹³C NMR of **3d**

Figure S9 ¹H NMR of **3e**

Figure S10 ^{13}C NMR of 3e

Figure S11 ¹H NMR of **3f**

Figure S12 ^{13}C NMR of **3f**

Figure S13 ¹H NMR of **4a**

Figure S14 ¹H NMR of **4a** (expand)

Current Data Parameters
 NAME ghanbaripour
 EXPNO 119
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120214
 Time_ 16.37
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg
 TD 65536
 SOLVENT CDCl3
 NS 140
 DS 0
 SWH 31446.541 Hz
 FIDRES 0.479836 Hz
 AQ 1.0420883 sec
 RG 1625.5
 DW 15.900 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 125.7716224 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 20.00 dB
 PL13 20.00 dB
 SFO2 500.1320005 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7577912 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

Figure S15 ^{13}C NMR of 4a