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New Journal of Chemistry

Visible-Light-Induced Radical Cascade Cyclization of pyrazoles bearing a coumarin unit

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Experimental Section

General Information

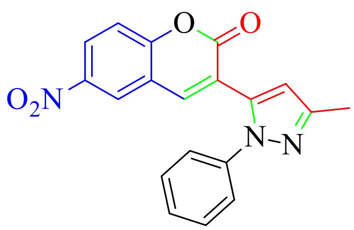
All chemicals were reagent grade and purchased from Aldrich, Alfa Aesar, Merck, Spectrochem and Qualigens and were used without purification. The reactions were monitored using pre-coated TLC plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254). NMR spectra were recorded on a Bruker Avance Neo 500FT spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) in $CDCl_3$ using TMS as an internal reference. Mass spectra were recorded on a JEOL SX-102 (FAB) mass spectrometer at 70 eV. Mass Spectra (ESIMS) were obtained on Micromassquadro II spectrometer. Melting points were determined by open glass capillary method and were uncorrected.

General Experimental Procedure

In a tube equipped with a magnetic stirrer bar salicylaldehyde (**1**, 1 mmol), 1,4-hydroxy-6-methyl-2H-pyran-2-one (**2**, 1 mmol) and phenylhydrazine (**3**, 1 mmol), were added in 3 mL acetonitrile and Eosin Y (2 mol%). The resulting mixture was stirred under irradiation with 23W

CFL at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with cold water (3 ml) and compound was dissolved in EtOAc. The EtOAc layer was separated and the aqueous fraction was extracted with EtOAc (3X3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo and the crude product was purified by silica gel chromatography (100-200 mesh silica gel; EtOAc/Hexane) to obtain the pure product **4a-l**. All the products are well known which were characterized by the comparison of their spectra and melting point with those reported in the literature.[37,38]

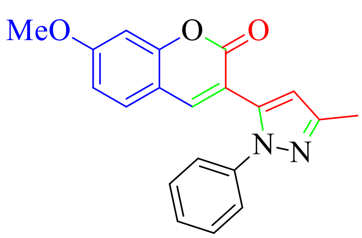
Spectral data of synthesized compounds:



4a 84%

3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-6-nitro-2H-chromen-2-one (4a).

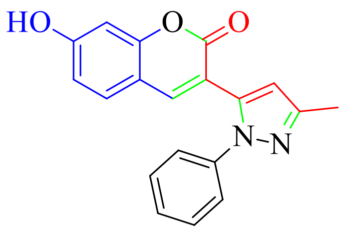
White Solid, M.P. 169^0C; IR (KBr): 3073, 1738, 1648, 1612, 1525 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.40 (s, 1H), 7.39 (s, 3H), 7.37–7.34 (m, 1H), 7.31 (t, J = 4.5 Hz, 1H), 7.27–7.26 (m, 1H,), 7.25–7.23 (m, 1H), 7.03-7.00 (m, 1H), 6.64 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 157.7, 155.9, 154.2, 143.8, 140.3, 130.4, 122.1, 120.2, 119.5, 118.4, 118.2, 117.2, 116.5, 115.3, 114.9, 113.4, 22.6, ESI-MS *m/z*: 347; found 348 $(M + H)^+$; Anal. Calcd for $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.10. Found; C, 65.91; H, 3.54; N, 12.32.



4b 77%

7-methoxy-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4b).

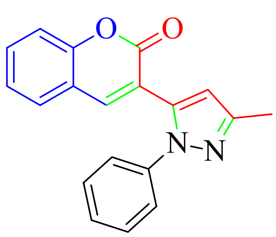
Yellow oil; IR (KBr): 3069, 1740, 1620, 1525, 1471 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.51 (s, 1H), 7.78–7.76 (m, 1H), 7.58–7.56 (m, 1H), 7.56–7.54 (m, 3H,), 7.51–7.48 (m, 2H), 7.08 (s, 1H), 6.91 (s, 1H), 3.92 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 163.2, 156.4, 147.1, 140.9, 139.2, 133.4, 132.3, 129.9, 129.6, 129.1, 128.5, 126.2, 113.4, 111.8, 108.8, 101.6, 66.3, 20.7, ESI-MS *m/z*: 332; found 333 $(M + H)^+$; anal. calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found; C, 72.49; H, 4.62; N, 8.57.



4c 75 %

7-hydroxy-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4c).

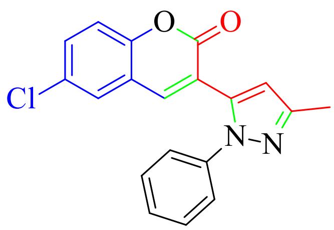
White Solid, M.P. 151^{0}C; IR (KBr): 3512, 3148, 1739, 1665, 1625 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.33-7.31 (m, 5H), 7.26–7.24 (m, 3H), 6.91 (s, 1H), 6.88 (s, 1H), 5.49 (s, 1H), 1.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 156.8, 143.7, 140.1, 135.4, 133.2, 132.5, 131.2, 127.6, 125.9, 122.1, 120.8, 119.4, 114.2, 112.1, 109.3, 103.7, 30.5, ESI-MS *m/z*: 318; found 319 $(M + H)^+$; anal. calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found; C, 71.82; H, 4.28; N, 8.93.



4d 78 %

3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4d).

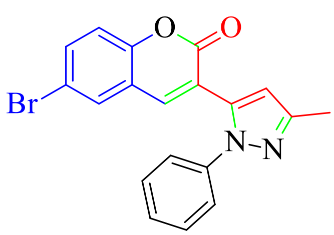
White solid, M.P. 132^{0}C; IR (KBr): 3057, 1785, 1692, 1644, 1537 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.57–7.54 (m, 1H), 7.48 (s, 1H), 7.45–7.43 (m, 3H,), 7.40 (s, 1H), 7.36-7.33 (m, 3H), 7.27 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 157.9, 156.3, 154.2, 143.8, 140.7, 130.6, 125.3, 122.5, 120.1, 118.8, 117.3, 116.9, 115.6, 115.2, 113.8, 108.6, 29.7, ESI-MS *m/z*: 302; found 303 $(M + H)^+$; anal. calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found; C, 75.69; H, 4.53; N, 9.47.



4e 88%

6-chloro-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4e).

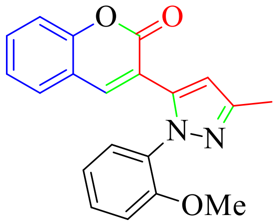
White Solid, M.P. 176^{0}C; IR (KBr): 3184, 1765, 1715, 1637, 1517 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.95 (d, J = 8.0 Hz, 1H), 7.76–7.74 (m, 1H), 7.58-7.56 (m, 2H), 7.51 (s, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.39 (s, 1H), 7.12 (t, J = 8.5 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 157.8, 154.9, 150.6, 143.5, 142.1, 137.3, 135.2, 131.8, 128.5, 128.1, 123.3, 119.3, 118.6, 116.1, 113.4, 105.3, 22.7, ESI-MS *m/z*: 336; found 337 (M + H)$^+$; anal. calcd for $C_{19}H_{13}ClN_2O_2$: C, 67.76; H, 3.89; N, 8.32. Found; C, 67.87; H, 3.75; N, 8.53.



4f 92%

6-bromo-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4f).

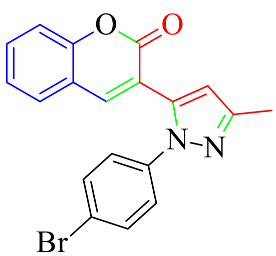
White solid; M.P. 163^{o}C ; IR (KBr): 3053, 1785, 1644, 1614, 1518 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.83 (s, 1H), 7.39 (s, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.48 (s, 1H), 6.41 (s, 1H), 2.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 157.8, 151.4, 146.8, 144.3, 140.7, 139.6, 134.3, 132.1, 129.9, 126.8, 126.7, 125.3, 122.5, 117.8, 115.2, 112.1, 32.2, ESI-MS *m/z*: 380; found 381 (M + H)$^+$; anal. calcd for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found; C, 60.05; H, 3.32; N, 7.54.



4g 83 %

3-(1-(2-methoxyphenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (**4g**).

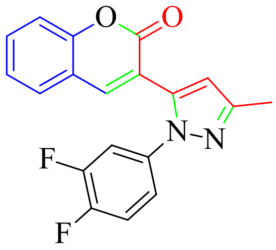
White solid; M.P. 191^{0}C; IR (KBr): 3047, 1752, 1677, 1634,1524 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.53 (s, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 5.5 Hz, 2H), 7.41 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 3.85 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 161.2, 155.5, 150.1, 143.3, 137.6, 134.7, 131.8, 131.3, 130.4, 129.3, 129.0, 128.3, 128.2, 127.5, 126.4, 122.1, 118.6, 113.4, 62.7, 15.3, ESI-MS *m/z*: 332; found 333 $(M + H)^+$; anal. calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found; C, 72.41; H, 4.72; N, 8.57.



4h 74%

3-(1-(4-bromophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4h).

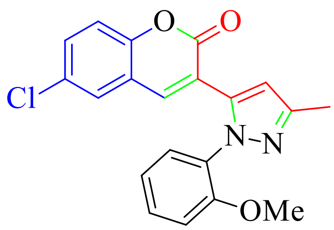
White solid; M.P. 213^{o}C; IR (KBr): 3034, 1746, 1672, 1638, 1512 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.53 (s, 1H), 7.68 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz , $CDCl_3$) (δ, ppm): 160.8, 154.3, 147.1, 140.9, 139.7, 133.5, 129.2, 128.7, 127.3, 126.9, 125.3, 123.0, 121.1, 120.4, 117.2, 109.7, 13.7; ESI-MS *m/z*: 380; found 381$(M + H)^+$; anal. calcd for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found; C, 60.05; H, 3.32; N, 7.54



4i 73%

3-(1-(3,4-difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4i).

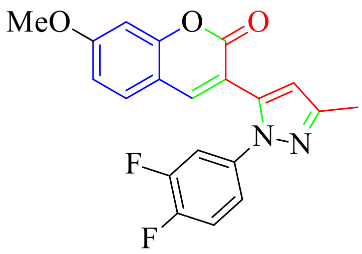
White solid; M.P. 210°C; IR (KBr): 3062, 1765, 1678, 1622, 1530 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.48 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.33-7.30 (m, 2H), 7.08 (s, 1H), 7.03-6.97 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz , $CDCl_3$) (δ, ppm): 161.2, 154.4, 151.3, 150.7, 146.7, 140.9, 138.5, 136.8, 132.5, 129.3, 125.4, 122.1, 120.9, 120.2, 118.5, 117.2, 115.6, 109.7 13.8; ESI-MS *m/z*: 338; found 339 $(M + H)^+$; anal. calcd for $C_{19}H_{12}F_2N_2O_2$: C, 67.45; H, 3.58; N, 8.28. Found; C, 67.68; H, 3.45; N, 8.41.



4j 87%

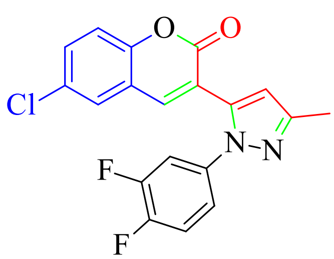
6-chloro-3-(1-(2-methoxyphenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4j).

White solid; M.P. 224°C; IR (KBr): 3065, 1755, 1672, 1627, 1531 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.43 (s, 1H), 7.48 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.10-7.08 (m, 2H), 3.84 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 155.4, 152.5, 149.3, 145.8, 143.2, 136.7, 132.1, 131.6, 129.7, 128.2, 127.5, 123.1, 121.9, 121.5, 119.0, 117.3, 112.8, 108.3, 63.4, 30.5; ESI-MS *m/z*: 366; found 367 $(M + H)^+$; anal. calcd for $C_{20}H_{15}ClN_2O_3$: C, 65.49; H, 4.12; N, 7.64. Found; C, 65.63; H, 4.32; N, 7.85.



4k 76%

3-(1-(3,4-difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-7-methoxy-2H-chromen-2-one (4k). Yellow oil; IR (KBr): 3124, 1748, 1677, 1626, 1543 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm): 7.58 (s, 1H), 7.49-7.43 (m, 1H), 7.13 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 5.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.83-7.82 (m, 1H), 6.49 (s, 1H), 3.90 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 164.4, 159.8, 159.2, 157.0, 150.9, 144.1, 138.7, 138.3, 130.2, 120.9, 118.2, 115.7, 115.3, 114.4, 114.0, 112.8, 110.9, 109.6, 56.5, 14.8; ESI-MS *m/z*: 368; found 369 $(M + H)^+$; anal. calcd for $C_{20}H_{14}F_2N_2O_3$: C, 65.22; H, 3.83; N, 7.61. Found; C, 65.37; H, 3.69; N, 7.83.



4l 80%

6-chloro-3-(1-(3,4-difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4l). White solid; M.P. 224°C; IR (KBr): 3034, 1762, 1723, 1640, 1523 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm): 8.43 (s, 1H), 7.55-7.53 (m, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.26-7.22 (m, 1H), 7.11 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 164.1, 160.3, 160.2, 153.0, 146.5, 141.6, 137.7, 132.8, 131.2, 128.4, 122.1, 121.8, 121.4, 119.2, 118.5, 115.7, 109.8, 108.4, 13.7; ESI-MS *m/z*: 372; found 373 $(M + H)^+$; anal. calcd for $C_{19}H_{11}ClF_2N_2O_2$: C, 61.22; H, 2.97; N, 7.52. Found; C, 61.42; H, 2.84; N, 7.74.

Reference:

37 X. T. Li, Y. H. Liu, X. L. and Z. H. Zhang, *RSC Adv*., 2015, **5**, 25625-25633.

38 A. Alizadeh and R. Ghanbaripour, *Synth. Commun*., 2014, **44**, 1635-1640.