SYNTHETIC AND STRUCTURAL STUDIES ON NOVEL 4,3'-BICOUMARINS

Kiran K. Pujar,^a Manohar V. Kulkarni,^{a,*} Ganesh N. Alawandi,^b G. N. Anilkumar,^c

Mahantesha Basanagouda^d

^aP.G. Department of Chemistry, Karnatak University, Dharwad, Karnataka, India.

^bSigma-Aldrich Chemicals Pvt. Ltd, Research and Development Section, Bangalore, Karnataka, India.

^cDepartment of Physics, M. S. Ramaiah Institute of Technology, Bangalore, Karnataka, India.

^dP.G. Department of Chemistry, P.C. Jabin Science College, Hubli, Karnataka, India.

Supplementary Information

EXPERIMENTAL SECTION

Materials and methods

The melting points were determined by open capillary method and are uncorrected. The IR spectra (KBr disc) were recorded on a Nicolet-5700 FT-IR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on Bruker 400 MHz spectrometer using DMSO-*d*₆ as solvent and TMS as an internal standard. The chemical shifts are expressed in δ ppm. The mass spectra were recorded using Agilent-single Quartz GC-MS. The elemental analysis was carried out using Heraeus CHN rapid analyzer at the University Scientific Instrumentation Centre (USIC), Karnatak University Dharwad. The purity of the compound was checked by TLC. UV spectra were recorded on U-3310-UV-VIS spectrophotometer and fluorescence spectra were recorded on F-7000 Fluorescence spectrometer. The NOE difference spectra were measured with an

Avance Bruker 600 MHz, in DMSO-*d*₆, against TMS, at 298.1 K. NOE difference spectra were measured, at concentration 0.01 M, using NOE mul sequence. All the chemicals purchased were of analytical grade, and were used without further purification unless otherwise stated. The dry acetic acid, piperidine, sodium hydride were purchased from Sigma-Aldrich Chemicals (India) and remaining chemicals by S.D Fine Chemicals (India).

Synthesis of 4,3'-bicoumarins

Method- 1.

The coumarins-4-acetates (0.01 mol) and salicylaldehydes (0.01 mol) were stirred in round bottom flask containing catalytic amount of piperidine in ethanol for about 12 h. The reaction was monitored by TLC. The separated solid was dried and recrystallized from DMF.

Method- 2.

The coumarin-4-acetic acids (0.01 mol) and salicylaldehydes (0.01 mol) were taken in a round bottom flask containing NaH (1.5 eq) and acetic anhydride (3 mL). The flask was fitted with guard tube and stirred for 1-1.5 h. The progress of reaction was monitored by TLC, the solid separated was filtered off, washed with ether and 5% NaHCO₃ to remove unreacted coumarins-4-acetic acids. Then the remaining residue was dried and recrystallized from DMF. Numbering scheme of bicoumarins is given in figure 7.

1. 6'6-Dimethyl-[4,3']bichromenyl-2',2-dione (4a)

Colourless (Dimethyl formamide), m.p. 240-241 °C, yield: 58 % (method 1); 81% (method 2). IR (KBr, ν in cm⁻¹): 1712 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.33 (*s*, 3H, C6-CH₃), 2.52 (*s*, 3H, C6'-CH₃), 6.64 (*s*, 1H, C3-H), 7.39-7.62 (*m*, 6H, Ar-H), 8.27 (*s*, 1H, C4'-H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 20.17, 21.01, 115.47, 115.62, 116.01, 116.60, 118.35, 122.75, 125.46, 126.74, 128.60, 133.65, 134.09, 143.22,

143.94, 149.87, 151.91, 153.17, 158.71, 159.70; GCMS m/z : 318 [M⁺]; Anal.calcd. for C₂₀H₁₄O₄; C, 75.46; H, 4.43. Found: C, 75.40; H, 4.42.

2. 6'-Chloro-6-methyl-[4,3']bichromenyl-2',2-dione (4b)

Colourless (Dimethyl formamide), m.p. 258-259 °C, yield: 62 % (method 1); 76 % (method 2). IR (KBr, ν in cm⁻¹): 1716 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.31 (*s*, 3H, C6-CH₃), 6.62 (*s*, 1H, C3-H), 7.38-7.94 (*m*, 6H, Ar-H), 8.25 (*s*, 1H, C4'-H); GCMS m/z : 338, 340 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁ClO₄; C, 67.37; H, 3.27. Found: C, 67.31; H, 3.24.

3. 6'-Bromo-6-methyl-[4,3']bichromenyl-2',2-dione (4c)

Colourless (Dimethyl formamide), m.p. 275-276 °C, yield: 61 % (method 1); 73 % (method 2). IR (KBr, ν in cm⁻¹): 1718 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.33 (*s*, 3H, C6-CH₃), 6.60 (*s*, 1H, C3-H), 7.37-8.07 (*m*, 6H, Ar-H), 8.24 (*s*, 1H, C4'-H); GCMS m/z : 383, 385 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁BrO₄; C, 59.55; H, 2.89. Found: C, 59.51; H, 2.86.

4. 6-Methyl-[4,3']bichromenyl-2',2-dione (4d)

Colourless (Dimethyl formamide), m.p. 265-266 °C, yield: 55 % (method 1); 83 % (method 2). IR (KBr, ν in cm⁻¹): 1716 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.31 (*s*, 3H, C6-CH₃), 6.62 (*s*, 1H, C3-H), 7.37-7.83 (*m*, 7H, Ar-H), 8.32 (*s*, 1H, C4'-H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 20.15, 116.06, 116.38, 116.62, 117.83, 118.44,

122.85, 126.58, 128.62, 133.19, 133.61, 133.84, 134.10, 143.89, 149.96, 151.24, 151.96, 158.76, 159.67; GCMS m/z : 304 [M⁺]; Anal.calcd. for C₁₉H₁₂O₄ ; C, 74.99; H, 3.97. Found: C, 74.92; H, 3.96.

5. 8'-Ethoxy-6-methyl-[4,3']bichromenyl-2',2-dione (4e)

Colourless (Dimethyl formamide), m.p. 212-213 °C, yield: 61 % (method 1); 79 % (method 2). IR (KBr, ν in cm⁻¹): 1714 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.41 (t, 3H, CH₃), 2.30 (s, 3H, C6-CH₃), 4.20 (q, 2H, OCH₂), 6.61 (s, 1H, C3-H), 7.04-8.00 (m, 6H, Ar-H), 8.28 (s, 1H, C4'-H); GCMS m/z : 348 [M⁺]; Anal.calcd. for C₂₁H₁₆O₅; C, 72.41; H, 4.63. Found: C, 72.36; H, 4.60.

6. 6',7-Dimethyl-[4,3']bichromenyl-2',2-dione (5a)

Colourless (Dimethyl formamide), m.p. 225-226 °C, yield: 60 % (method 1); 79 % (method 2). IR (KBr, ν in cm⁻¹): 1722 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.42 (s, 3H, C7-CH₃), 2.39 (s, 3H, C6'-CH₃), 6.56 (s, 1H, C3-H), 7.12-7.94 (m, 6H, Ar-H), 8.24 (s, 1H, C4'-H); GCMS m/z : 318 [M⁺]; Anal.calcd. for C₂₀H₁₄O₄ ; C, 75.46; H, 4.43. Found: C, 75.39; H, 4.42.

7. 6'-Chloro-7-methyl-[4,3']bichromenyl-2',2-dione (5b)

Colourless (Dimethyl formamide), m.p. 265-266 °C, yield: 59 % (method 1); 73 % (method 2). IR (KBr, ν in cm⁻¹): 1705 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.43 (s, 3H, C7-CH₃), 6.57 (s, 1H, C3-H), 7.14-7.93 (m, 6H, Ar-H), 8.25 (s, 1H, C4'-H);

GCMS m/z : 338, 340 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁ClO₄; C, 67.37; H, 3.27. Found: C, 67.32; H, 3.26.

8. 6'-Bromo-7-methyl-[4,3']bichromenyl-2',2-dione (5c)

Colourless (Dimethyl formamide), m.p. 280-281 °C, yield: 52 % (method 1); 77 % (method 2). IR (KBr, ν in cm⁻¹): 1703 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.43 (*s*, 3H, C7-CH₃), 6.57 (*s*, 1H, C3-H), 7.14-8.07 (*m*, 6H, Ar-H), 8.25 (*s*, 1H, C4'-H); GCMS m/z : 383, 385 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁BrO₄; C, 59.55; H, 2.89. Found: C, 59.51; H, 2.88.

9. 7-Methyl-[4,3']bichromenyl-2',2-dione (5d)

Colourless (Dimethyl formamide), m.p. 240-241 °C, yield: 54 % (method 1); 89 % (method 2). IR (KBr, ν in cm⁻¹): 1727 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.42 (*s*, 3H, C7-CH₃), 6.59 (*s*, 1H, C3-H), 7.32-7.85 (*m*, 7H, Ar-H), 8.33 (*s*, 1H, C4'-H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 20.15, 116.29, 116.37, 116.64, 117.81, 118.73, 122.99, 124.80, 126.65, 129.08, 132.76, 133.20, 133.84, 143.95, 149.94, 151.23, 153.82, 158.64, 159.68; GCMS m/z : 304 [M⁺]; Anal.calcd. for C₁₉H₁₂O₄; C, 74.99; H, 3.97. Found: C, 74.91; H, 3.96.

10. 8'-Ethoxy-7-methyl-[4,3']bichromenyl-2',2-dione (5e)

Colourless (Dimethyl formamide), m.p. 192-193 °C, yield: 62 % (method 1); 78 % (method 2). IR (KBr, ν in cm⁻¹): 1720 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ

1.41 (*t*, 3H, CH₃), 2.43 (*s*, 3H, C7-CH₃), 4.20 (*q*, 2H, OCH₂), 6.58 (*s*, 1H, C3-H), 7.13-7.53 (*m*, 6H, Ar-H), 8.30 (*s*, 1H, C4'-H); GCMS *m/z*: 348 [M⁺]; Anal.calcd. for C₂₁H₁₆O₅; C, 72.41; H, 4.63. Found: C, 72.37; H, 4.62.

11. 1-(6'-Methyl-2'-oxo-2'H-chromen-3'-yl)-benzo[f]chromen-3-one (6a)

Yellow (Dimethyl formamide), m.p. 238-239 °C, yield: 59 % (method 1); 75 % (method 2). IR (KBr, ν in cm⁻¹): 1729 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.93 (*s*, 3H, C6'-CH₃), 6.52 (*s*, 1H, C3-H), 7.55-8.71 (*m*, 10H, Ar-H); GCMS *m/z*: 354 [M⁺]; Anal.calcd. for C₂₃H₁₄O₄; C, 77.96; H, 3.98. Found: C, 77.90; H, 3.97.

12. 1-(6'-Chloro-2'-oxo-2'H-chromen-3'-yl)-benzo[f]chromen-3-one (6b)

Yellow (Dimethyl formamide), m.p. 264-265 °C, yield: 60 % (method 1); 77 % (method 2). IR (KBr, ν in cm⁻¹): 1734 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.53 (*s*, 1H, C3-H), 6.72-8.72 (*m*, 10H, Ar-H); GCMS *m/z*: 374, 376 [M⁺, M+2]; Anal.calcd. for C₂₂H₁₁ClO₄; C, 70.51; H, 2.96. Found: C, 70.47; H, 2.95.

13. 1-(6'-Bromo-2'-oxo-2'H-chromen-3'-yl)-benzo[f]chromen-3-one (6c)

Yellow (Dimethyl formamide), m.p. 240-241 °C, yield: 54 % (method 1); 76 % (method 2). IR (KBr, ν in cm⁻¹): 1729 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.53 (*s*, 1H, C3-H), 7.34-8.71 (*m*, 10H, Ar-H); GCMS *m/z*: 419, 421 [M⁺, M+2]; Anal.calcd. for C₂₂H₁₁BrO₄; C, 63.03; H, 2.64. Found: C, 63.01; H, 2.62.

14. 1-(2'-Oxo-2'H-chromen-3'-yl)-benzo[f]chromen-3-one (6d)

Yellow (Dimethyl formamide), m.p. 273-274 °C, yield: 57 % (method 1); 74 % (method 2). IR (KBr, ν in cm^{-1}): 1727 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 6.51 (*s*, 1H, C3-H), 7.54-8.70 (*m*, 11H, Ar-H); GCMS *m/z*: 340 [M^+]; Anal.calcd. for $\text{C}_{22}\text{H}_{12}\text{O}_4$; C, 77.64; H, 3.55. Found: C, 77.58; H, 3.54.

15. 1-(8'-Ethoxy-2'-oxo-2'H-chromen-3'-yl)-benzo[f]chromen-3-one (6e)

Yellow (Dimethyl formamide), m.p. 188-189 °C, yield: 59 % (method 1); 79 % (method 2). IR (KBr, ν in cm^{-1}): 1711 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.42 (*t*, 3H, CH_3), 4.23 (*q*, 2H, OCH_2), 6.45 (*s*, 1H, C3-H), 7.24-8.31 (*m*, 10H, Ar-H); GCMS *m/z*: 384 [M^+]; Anal.calcd. for $\text{C}_{24}\text{H}_{16}\text{O}_5$; C, 74.99; H, 4.20. Found: C, 74.90; H, 4.19.

16. 4-(6'-Methyl-2'-oxo-2'H-chromen-3'-yl)-benzo[h]chromen-2-one (7a)

Yellow (Dimethyl formamide), m.p. 245-246 °C, yield: 60 % (method 1); 81 % (method 2). IR (KBr, ν in cm^{-1}): 1715 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.18 (*s*, 3H, C6'-CH_3), 6.53 (*s*, 1H, C3-H), 7.20-8.21 (*m*, 10H, Ar-H); GCMS *m/z*: 354 [M^+]; Anal.calcd. for $\text{C}_{23}\text{H}_{14}\text{O}_4$; C, 77.96; H, 3.98. Found: C, 77.89; H, 3.97.

17. 1-(6'-Chloro-2'-oxo-2'H-chromen-3'-yl)-benzo[h]chromen-2-one (7b)

Yellow (Dimethyl formamide), m.p. 283-286 °C, yield: 57 % (method 1); 88 % (method 2). IR (KBr, ν in cm^{-1}): 1712 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 6.53 (*s*,

1H, C3-H), 6.77-8.43 (*m*, 10H, Ar-H); GCMS *m/z*: 374, 376 [M⁺, M+2]; Anal.calcd. for C₂₂H₁₁ClO₄; C, 70.51; H, 2.96. Found: C, 70.47; H, 2.95.

18. 4-(6'-Bromo-2'-oxo-2'H-chromen-3'-yl)-benzo[h]chromen-2-one (7c)

Yellow (Dimethyl formamide), m.p. 235-236 °C, yield: 59 % (method 1); 79 % (method 2). IR (KBr, ν in cm⁻¹): 1712 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.68 (*s*, 1H, C3-H), 7.43-8.36 (*m*, 10H, Ar-H); GCMS *m/z*: 419, 421 [M⁺, M+2]; Anal.calcd. for C₂₂H₁₁BrO₄; C, 63.03; H, 2.64. Found: C, 63.00; H, 2.63.

19. 4-(2'-Oxo-2'H-chromen-3'-yl)-benzo[h]chromen-2-one (7d)

Yellow (Dimethyl formamide), m.p. 230-231 °C, yield: 54 % (method 1); 80 % (method 2). IR (KBr, ν in cm⁻¹): 1716 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.70 (*s*, 1H, C3-H), 7.35-8.36 (*m*, 11H, Ar-H); GCMS *m/z*: 340 [M⁺]; Anal.calcd. for C₂₂H₁₂O₄; C, 77.64; H, 3.55. Found: C, 77.58; H, 3.54.

20. 4-(8'-Ethoxy-2'-oxo-2'H-chromen-3'-yl)-benzo[h]chromen-2-one (7e)

Yellow (Dimethyl formamide), m.p. 243-244 °C, yield: 42 % (method 1); 78 % (method 2). IR (KBr, ν in cm⁻¹): 1713 (lactone C=O); ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.43 (*t*, 3H, CH₃), 4.22 (*q*, 2H, OCH₂), 6.78 (*s*, 1H, C3-H), 7.36-8.45 (*m*, 10H, Ar-H); GCMS *m/z*: 384 [M⁺]; Anal.calcd. for C₂₄H₁₆O₅; C, 74.99; H, 4.20. Found: C, 74.91; H, 4.19.

21. 6-Methoxy-6'-methyl-[4,3']bichromenyl-2',2-dione (8a)

Colourless (Dimethyl formamide), m.p. 212-213 °C, yield: 53 % (method 1); 84 % (method 2). IR (KBr, ν in cm^{-1}): 1715 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): 2.41 (s, 3H, C6'-CH₃), 3.82 (s, 3H, C6-OCH₃), 6.48 (s, 1H, C3-H), 6.90-7.62 (m, 6H, Ar-H), 8.22 (s, 1H, C4'-H); GCMS m/z : 334 [M⁺]; Anal.calcd. for C₂₀H₁₄O₅; C, 71.85; H, 4.22. Found: C, 71.81; H, 4.21.

22. 6'-Chloro-6-methoxy-[4,3']bichromenyl-2',2-dione (8b)

Colourless (Dimethyl formamide), m.p. 250-251 °C, yield: 59 % (method 1); 83 % (method 2). IR (KBr, ν in cm^{-1}): 1719 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.79 (s, 3H, C6-OCH₃), 6.40 (s, 1H, C3-H), 6.89-7.81 (m, 6H, Ar-H), 8.25 (s, 1H, C4'-H); GCMS m/z : 354, 356 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁ClO₅; C, 64.33; H, 3.13. Found: C, 64.25; H, 3.12.

23. 6'-Bromo-6-methoxy-[4,3']bichromenyl-2',2-dione (8c)

Colourless (Dimethyl formamide), m.p. 234-235 °C, yield: 56 % (method 1); 78 % (method 2). IR (KBr, ν in cm^{-1}): 1712 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.78 (s, 3H, C6-OCH₃), 6.41 (s, 1H, C3-H), 6.79-7.68 (m, 6H, Ar-H), 8.19 (s, 1H, C4'-H); GCMS m/z : 399, 401 [M⁺, M+2]; Anal.calcd. for C₁₉H₁₁BrO₅; C, 57.17; H, 2.78. Found: C, 57.11; H, 2.77.

24. 6-Methoxy-[4,3'-bichromenyl-2',2-dione (8d)

Colourless (Dimethyl formamide), m.p. 216-217 °C, yield: 52 % (method 1); 86 % (method 2). IR (KBr, ν in cm^{-1}): 1716 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.79 (*s*, 3H, C6-OCH₃), 6.40 (*s*, 1H, C3-H), 6.84-7.52 (*m*, 7H, Ar-H), 8.18 (*s*, 1H, C4'-H); GCMS *m/z*: 320 [M⁺]; Anal.calcd. for C₁₉H₁₂O₅; C, 71.25; H, 3.78. Found: C, 71.18; H, 3.77.

25. 8'-Ethoxy-6-methoxy-[4,3']bichromenyl-2',2-dione (8e)

Colourless (Dimethyl formamide), m.p. 243-244 °C, yield: 57 % (method 1); 80 % (method 2). IR (KBr, ν in cm^{-1}): 1719 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.33 (*t*, 3H, CH₃), 3.77 (*s*, 3H, C6-OCH₃), 4.18 (*s*, 2H, -OCH₂), 6.41 (*s*, 1H, C3-H), 6.88-7.58 (*m*, 6H, Ar-H), 8.18 (*s*, 1H, C4'-H); GCMS *m/z*: 364 [M⁺]; Anal.calcd. for C₂₁H₁₆O₆; C, 69.23; H, 4.43. Found: C, 69.16; H, 4.42.

26. 7-Methoxy-6'-methyl-[4,3']bichromenyl-2',2-dione (9a)

Colourless (Dimethyl formamide), m.p. 261-262 °C, yield: 55 % (method 1); 88 % (method 2). IR (KBr, ν in cm^{-1}): 1717 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.40 (*s*, 3H, C6'-CH₃), 3.88 (*s*, 3H, C7-OCH₃), 6.45 (*s*, 1H, C3-H), 6.88-7.59 (*m*, 6H, Ar-H), 8.24 (*s*, 1H, C4'-H); GCMS *m/z*: 334 [M⁺]; Anal.calcd. for C₂₀H₁₄O₅; C, 71.85; H, 4.22. Found: C, 71.79; H, 4.21.

27. 6'-Chloro-7-methoxy-[4,3']bichromenyl-2',2-dione (9b)

Colourless (Dimethyl formamide), m.p. 226-227 °C, yield: 50 % (method 1); 83 % (method 2). IR (KBr, ν in cm^{-1}): 1713 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 3.80 (*s*, 3H, C7-OCH₃), 6.39 (*s*, 1H, C3-H), 6.86-7.76 (*m*, 6H, Ar-H), 8.24 (*s*, 1H, C4'-H); GCMS *m/z*: 354, 356 [*M*⁺, *M*+2]; Anal.calcd. for C₁₉H₁₁ClO₅; C, 64.33; H, 3.13. Found: C, 64.28; H, 3.12.

28. 6'-Bromo-7-methoxy-[4,3']bichromenyl-2',2-dione (9c)

Colourless (Dimethyl formamide), m.p. 218-219 °C, yield: 56 % (method 1); 79 % (method 2). IR (KBr, ν in cm^{-1}): 1715 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 3.77 (*s*, 3H, C7-OCH₃), 6.37 (*s*, 1H, C3-H), 6.81-7.85 (*m*, 6H, Ar-H), 8.17 (*s*, 1H, C4'-H); GCMS *m/z*: 399, 401 [*M*⁺, *M*+2]; Anal.calcd. for C₁₉H₁₁BrO₅; C, 57.17; H, 2.78. Found: C, 57.10; H, 2.77.

29. 7-Methoxy-[4,3']bichromenyl-2',2-dione (9d)

Colourless (Dimethyl formamide), m.p. 256-257 °C,¹⁵ yield: 52 % (method 1); 80 % (method 2). IR (KBr, ν in cm^{-1}): 1712 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 3.77 (*s*, 3H, C7-OCH₃), 6.37 (*s*, 1H, C3-H), 6.81-7.99 (*m*, 7H, Ar-H), 8.16 (*s*, 1H, C4'-H); GCMS *m/z*: 320 [*M*⁺]; Anal.calcd. for C₁₉H₁₂O₅; C, 71.25; H, 3.78. Found: C, 71.21; H, 3.77.

30. 8'-Ethoxy-7-methoxy-[4,3']bichromenyl-2',2-dione (9e)

Colourless (Dimethyl formamide), m.p. 214-215 °C, yield: 54 % (method 1); 78 % (method 2). IR (KBr, ν in cm^{-1}): 1718 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.34 (t, 3H, CH_3), 3.79 (s, 3H, C7- OCH_3), 4.15 (s, 2H, - OCH_2), 6.38 (s, 1H, C3-H), 6.82-7.49 (m, 6H, Ar-H), 8.21 (s, 1H, C4'-H); GCMS m/z : 364 $[\text{M}^+]$; Anal.calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_6$; C, 69.23; H, 4.43. Found: C, 69.15; H, 4.42.

31. 6',5,7-Trimethyl-[4,3']bichromenyl-2',2-dione (10a)

Colourless (Dimethyl formamide), m.p. 210-211 °C, yield: 56 % (method 1); 83 % (method 2). IR (KBr, ν in cm^{-1}): 1706 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.32 (s, 3H, C5- CH_3), 2.59 (s, 3H, C7- CH_3), 2.66 (s, 3H, C6'- CH_3), 6.24 (s, 1H, C3-H), 6.99-7.95 (m, 5H, Ar-H), 8.21 (s, 1H, C5'-H); GCMS m/z : 332 $[\text{M}^+]$; Anal.calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_4$; C, 75.89; H, 4.85. Found: C, 75.81; H, 4.84.

32. 6'-Chloro-5,7-dimethyl-[4,3']bichromenyl-2',2-dione (10b)

Colourless (Dimethyl formamide), m.p. 245-246 °C, yield: 59 % (method 1); 79 % (method 2). IR (KBr, ν in cm^{-1}): 1717 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.33 (s, 3H, C5- CH_3), 2.60 (s, 3H, C7- CH_3), 6.24 (s, 1H, C3-H), 7.00-7.92 (m, 5H, Ar-H), 8.19 (s, 1H, C5'-H); GCMS m/z : 352, 354 $[\text{M}^+, \text{M}+2]$; Anal.calcd. for $\text{C}_{20}\text{H}_{13}\text{ClO}_4$; C, 68.09; H, 3.71. Found: C, 68.00; H, 3.70.

33. 6'-Bromo-5,7-dimethyl-[4,3']bichromenyl-2',2-dione (10c)

Colourless (Dimethyl formamide), m.p. 238-239 °C, yield: 57 % (method 1); 80 % (method 2). IR (KBr, ν in cm^{-1}): 1720 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.34 (*s*, 3H, C5-CH₃), 2.60 (*s*, 3H, C7-CH₃), 6.25 (*s*, 1H, C3-H), 7.00-8.05 (*m*, 5H, Ar-H), 8.18 (*s*, 1H, C5'-H); GCMS *m/z*: 397, 399 [*M*⁺, *M*+2]; Anal.calcd. for C₂₀H₁₃BrO₄; C, 60.47; H, 3.30. Found: C, 60.41; H, 3.29.

34. 5,7-Dimethyl-[4,3']bichromenyl-2',2-dione (10d)

Colourless (Dimethyl formamide), m.p. 115-116 °C, yield: 60 % (method 1); 82 % (method 2). IR (KBr, ν in cm^{-1}): 1712 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.22 (*s*, 3H, C5-CH₃), 2.56 (*s*, 3H, C7-CH₃), 6.39 (*s*, 1H, C3-H), 6.89-7.70 (*m*, 6H, Ar-H), 8.14 (*s*, 1H, C5'-H); GCMS *m/z*: 318 [*M*⁺]; Anal.calcd. for C₂₀H₁₄O₄; C, 75.46; H, 4.43. Found: C, 75.40; H, 4.42.

35. 8'-Ethoxy-5,7-dimethyl-[4,3']bichromenyl-2',2-dione (10e)

Colourless (Dimethyl formamide), m.p. 113-114 °C, yield: 58 % (method 1); 80 % (method 2). IR (KBr, ν in cm^{-1}): 1713 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.25 (*t*, 3H, CH₃), 2.34 (*s*, 3H, C5-CH₃), 2.60 (*s*, 3H, C7-CH₃), 4.08 (*q*, 2H, OCH₂), 6.25 (*s*, 1H, C3-H), 6.49-7.49 (*m*, 5H, Ar-H), 8.22 (*s*, 1H, C5'-H); GCMS *m/z*: 362 [*M*⁺]; Anal.calcd. for C₂₂H₁₈O₅; C, 72.92; H, 5.01. Found: C, 72.83; H, 5.00.

36. 6',7,8-Trimethyl-[4,3']bichromenyl-2',2-dione (11a)

Colourless (Dimethyl formamide), m.p. 240-241 °C, yield: 59 % (method 1); 79 % (method 2). IR (KBr, ν in cm^{-1}): 1713 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 2.31 (s, 3H, C7-CH₃), 2.56 (s, 3H, C8-CH₃), 2.61 (s, 3H, C6'-CH₃), 6.28 (s, 1H, C3-H), 6.61-7.84 (m, 5H, Ar-H), 8.18 (s, 1H, C5'-H); GCMS m/z : 332 [M⁺]; Anal.calcd. for C₂₁H₁₆O₄; C, 75.89; H, 4.85. Found: C, 75.81; H, 4.84.

37. 6'-Chloro-7,8-dimethyl-[4,3']bichromenyl-2',2-dione (11b)

Colourless (Dimethyl formamide), m.p. 273-274 °C, yield: 51 % (method 1); 85 % (method 2). IR (KBr, ν in cm^{-1}): 1722 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 2.35 (s, 3H, C7-CH₃), 2.56 (s, 3H, C8-CH₃), 6.42 (s, 1H, C3-H), 7.08-7.99 (m, 5H, Ar-H), 8.22 (s, 1H, C5'-H); GCMS m/z : 352, 354 [M⁺, M+2]; Anal.calcd. for C₂₀H₁₃ClO₄; C, 68.09; H, 3.71. Found: C, 68.01; H, 3.70.

38. 6'-Bromo-7,8-dimethyl-[4,3']bichromenyl-2',2-dione (11c)

Colourless (Dimethyl formamide), m.p. 280-281 °C, yield: 62 % (method 1); 79 % (method 2). IR (KBr, ν in cm^{-1}): 1733 (lactone C=O); ^1H NMR (400 MHz, DMSO- d_6): δ 2.39 (s, 3H, C7-CH₃), 2.58 (s, 3H, C8-CH₃), 6.28 (s, 1H, C3-H), 7.05-8.10 (m, 5H, Ar-H), 8.22 (s, 1H, C5'-H); GCMS m/z : 397, 399 [M⁺, M+2]; Anal.calcd. for C₂₀H₁₃BrO₄; C, 60.47; H, 3.30. Found: C, 60.38; H, 3.29.

39. 7,8-Dimethyl-[4,3']bichromenyl-2',2-dione (11d)

Colourless (Dimethyl formamide), m.p. 230-231 °C, yield: 58 % (method 1); 80 % (method 2). IR (KBr, ν in cm^{-1}): 1728 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.39 (*s*, 3H, C7-CH₃), 2.52 (*s*, 3H, C8-CH₃), 6.32 (*s*, 1H, C3-H), 6.78-8.18 (*m*, 7H, Ar-H); GCMS *m/z*: 318 [M⁺]; Anal.calcd. for C₂₀H₁₄O₄; C, 75.46; H, 4.43. Found: C, 75.34; H, 4.42.

40. 8'-Ethoxy-7,8-dimethyl-[4,3']bichromenyl-2',2-dione (11e)

Colourless (Dimethyl formamide), m.p. 178-179 °C, yield: 59 % (method 1); 83 % (method 2). IR (KBr, ν in cm^{-1}): 1719 (lactone C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.28 (*t*, 3H, CH₃), 2.35 (*s*, 3H, C7-CH₃), 2.55 (*s*, 3H, C8-CH₃), 4.12 (*q*, 2H, OCH₂), 6.29 (*s*, 1H, C3-H), 6.82-8.25 (*m*, 6H, Ar-H); GCMS *m/z*: 362 [M⁺]; Anal.calcd. for C₂₂H₁₈O₅; C, 72.92; H, 5.01. Found: C, 72.86; H, 5.00S.

List of spectra

Spectrum No. 1. IR spectrum of compound 4a

Spectrum No. 2. ^1H NMR spectrum of compound 4a

Spectrum No. 3. ^{13}C NMR spectrum of compound 4a

Spectrum No. 4. GCMS spectrum of compound 4a

Spectrum No. 5 IR spectrum of compound 4d

Spectrum No. 6. ^1H NMR spectrum of compound 4d

Spectrum No. 7. ^{13}C NMR spectrum of compound 4d

Spectrum No. 8. GCMS spectrum of compound 4d

Spectrum No. 9 IR spectrum of compound 5d

Spectrum No. 10. ^1H NMR spectrum of compound 5d

Spectrum No. 11. ^{13}C NMR spectrum of compound 5d

Spectrum No. 12. GCMS spectrum of compound 5d

Spectrum No. 13 IR spectrum of compound 6a

Spectrum No. 14. ^1H NMR spectrum of compound 6a

Spectrum No. 15. GCMS spectrum of compound 6a

Spectrum No. 16 IR spectrum of compound 7a

Spectrum No. 17. ^1H NMR spectrum of compound 7a

Spectrum No. 18. GCMS spectrum of compound 7a

Spectrum No. 1. IR spectrum of compound 4a

Unlabeled 27-04-2013 11:47:18 AM TBE

6-Me-1
PROTON DMSO {D:\OUTSIDE} (Sigma Aldrich) 1

Spectrum No. 2. ¹H NMR spectrum of compound 4a

Spectrum No. 3. ^{13}C NMR spectrum of compound 4a

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1-5 in
brow
109 → 49

Sample Information

Analyzed by : Admin
 Analyzed : 10/4/2012 2:29:51 AM
 Sample Type : Unknown
 Level # : 1
 Sample Name : 6-me (a)
 Sample ID :
 IS Amount : [1]=1
 Sample Amount : 1
 Dilution Factor : 1
 Vial # : 1
 Injection Volume : 1
 Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran7.qgd
 Org Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran7.qgd
 Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Org Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Report File :
 Tuning File : C:\GCMSsolution\system tune\SEPTEMBER 3.qgt
 Modified by : Admin
 Modified : 10/4/2012 2:35:26 AM

Spectrum

Line#:1 R.Time:3.1(Scan#:373)
 MassPeaks:113
 RawMode:Single 3.1(373) BasePeak:290(69796)
 BG Mode:None Group 1 - Event 1

Spectrum No. 4. GCMS spectrum of compound 4a

Spectrum No. 5 IR spectrum of compound 4d

Unlabeled 27-04-2013 11:47 18 AM.THF

6-Me-4
PROTON DMSO {D:\OUTSIDE} {Sigma Aldrich} 1

Current Data Parameters
NAME 6-Me-4
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130427
Time 10.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 24
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TDO 1

Page 10 of 21

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
S1 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

4d

Spectrum No. 6. ¹H NMR spectrum of compound 4d

Spectrum No. 7. ^{13}C NMR spectrum of compound 4d

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Analyzed by : Admin
 Analyzed : 10/4/2012 2:47:02 AM
 Sample Type : Unknown
 Level # : 1
 Sample Name : 6-me (20 Cal)
 Sample ID :
 IS Amount : [1]=1
 Sample Amount : 1
 Dilution Factor : 1
 Vial # : 1
 Injection Volume : 1
 Data File : C:\GCMSolution\Data\Project1\Kiran\Kiran8.qgd
 Org Data File : C:\GCMSolution\Data\Project1\Kiran\Kiran8.qgd
 Method File : C:\GCMSolution\Data\Project1\DI METHOD.qgm
 Org Method File : C:\GCMSolution\Data\Project1\DI METHOD.qgm
 Report File :
 Tuning File : C:\GCMSolution\system tune\SEPTEMBER 3.qgt
 Modified by : Admin
 Modified : 10/4/2012 2:52:26 AM

Sample Information

Spectrum

Line#:1 RTime:1.5(Scan#:186)

MassPeaks:43

RawMode:Single 1.5(186) BasePeak:63(21440)

BG Mode:None Group 1 - Event 1

Spectrum No. 8. GCMS spectrum of compound 4d

Spectrum No. 9 IR spectrum of compound 5d

Untitled-27-04-2013 11:47:18 AM TIF

7-Me-4
PROTON DMSO {D:\OUTSIDE} {Sigma Aldrich} 1

Current Data Parameters
NAME 7-Me-4
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130427
Time 11.30
INSTRUM spect
PROBHD 5 mm PABBO 88-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
CW 60.800 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

Page 18 of 21

----- CHANNEL f1 -----
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
SFO1 400.1324719 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Spectrum No. 10. ¹H NMR spectrum of compound 5d

```

F2 - Acquisition Parameters
Date      20140212
Time      18.09
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT    DMSO
NS         15000
DS         4
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         812
DE         20.800 use
DW         6.00 use
TE         300.0 K
d1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999999 sec
TDO        1

```

```

===== CHANNEL f2 =====
CPDPRG2          waltz16
NUC2              1H
PCPD2            100.00 usec
PL2              -1.00 dB
PL12             16.39 dB
PL13             17.00 dB
SFO2             400.1316005 MHz

```

```
F2 - Processing parameters
SI              32768
SF              100.6128193 MHz
WDW             EM
SSB             0
LB              1.00 Hz
GB              0
PC              1.40
```

Spectrum No. 11. ^{13}C NMR spectrum of compound 5d

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11d

Sample Information

Analyzed by : Admin
 Analyzed : 10/5/2012 1:08:46 AM
 Sample Type : Unknown
 Level # : 1
 Sample Name : 7-me (d)
 Sample ID :
 IS Amount : [1]=1
 Sample Amount : 1
 Dilution Factor : 1
 Vial # : 1
 Injection Volume : 1
 Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran13.qgd
 Org Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran13.qgd
 Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Org Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Report File :
 Tuning File : C:\GCMSsolution\system tune\SEPTEMBER 3.qgt
 Modified by : Admin
 Modified : 10/5/2012 1:14:36 AM

Spectrum

Line#:1 R.Time:3.8(Scan#:457)
 MassPeaks:126
 RawMode:Single 3.8(457) BasePeak:276(119416)
 BG Mode:None Group 1 - Event 1

Spectrum No. 12. GCMS spectrum of compound 5d

Spectrum No. 13 IR spectrum of compound 6a

Untitled-03-05-2013 07:56:21 AM.TIF

5-6 BENZO SERIES-1
PROTON DMSO (D:\OUTSIDE) (Sigma Aldrich) 1

Current Data Parameters
NAME 5-6 BENZO SERIES-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130501
Time 14.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 256
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TDO 1

Page 1 of 24

----- CHANNEL f1 -----
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Spectrum No. 14. ^1H NMR spectrum of compound 6a

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11-15 in
books

129

Sample Information

Analyzed by : Admin
 Analyzed : 10/5/2012 2:05:24 AM
 Sample Type : Unknown
 Level # : 1
 Sample Name : 5-6 Benzo (a)
 Sample ID :
 IS Amount : [1]=1
 Sample Amount : 1
 Dilution Factor : 1
 Vial # : 1
 Injection Volume : 1
 Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran16.qgd
 Org Data File : C:\GCMSsolution\Data\Project1\Kiran\Kiran16.qgd
 Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Org Method File : C:\GCMSsolution\Data\Project1\DI METHOD.qgm
 Report File :
 Tuning File : C:\GCMSsolution\system tune\SEPTEMBER 3.qgt
 Modified by : Admin
 Modified : 10/5/2012 2:12:02 AM

Spectrum

Line#:1 R.Time:4.9(Scan#:587)
 MassPeaks:178
 RawMode:Single 4.9(587) BasePeak:354(153772)
 BG Mode:None Group 1 - Event 1

Spectrum No. 15. GCMS spectrum of compound 6a

Spectrum No. 16 IR spectrum of compound 7a

7-8 BENZO SERIES-1
 PROTON DMSO {D:\OUTSIDE} (Sigma Aldrich) 1

Current Data Parameters
 NAME 7-8 BENZO SERIES-1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20130510
 Time 14.40
 INSTRUM spect
 PROBD 5 mm PAB90 BB-
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 322
 DW 60.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

Page 1 of 12

===== CHANNEL f1 =====
 NUC1 1H
 P1 13.50 usec
 PL1 -1.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300972 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Spectrum No. 17. ¹H NMR spectrum of compound 7a

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16-20 in
base

139

Sample Information

Analyzed by	: Admin
Analyzed	: 10/9/2012 3:52:33 AM
Sample Type	: Unknown
Level #	: 1
Sample Name	: 7-8 Benzo (a)
Sample ID	:
IS Amount	: [1]=1
Sample Amount	: 1
Dilution Factor	: 1
Vial #	: 1
Injection Volume	: 1
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Org Data File	: C:\GCMSsolution\Data\Project1\Kiran\Kiran30.qgd
Method File	: C:\GCMSsolution\Data\Project1\DI METHOD.qgm
Org Method File	: C:\GCMSsolution\Data\Project1\DI METHOD.qgm
Report File	: C:\GCMSsolution\system tune\SEPTEMBER 3.qgt
Tuning File	: Admin
Modified by	: Admin
Modified	: 10/9/2012 4:01:09 AM

Spectrum

Line#:1 R.Time:6.8(Scan#:815)
MassPeaks:75
RawMode:Single 6.8(815) BasePeak:182(25481)
BG Mode:None Group 1 - Event 1

Spectrum No. 18. GCMS spectrum of compound 7a

Table 2. Crystallographic data of intermediate chalcone **12** and bicoumarins **4a**, **4d** and **10d**.

Details	4a	4d	10d	12
CCDC No.	946935	936965	946936	936917
Chemical formula	C ₂₀ H ₁₄ O ₄	C ₁₉ H ₁₂ O ₄	C ₂₀ H ₁₄ O ₄	C ₂₆ H ₂₁ O ₆
Formula weight	318.31	304.29	318.31	429.43
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	296	296	296	296
a (Å)	7.834 (1)	8.5537 (4)	6.9972 (2)	7.3062 (4)
b (Å)	8.0455 (9)	12.5000 (6)	20.0661 (7)	11.7920 (7)
c (Å)	12.7952 (15)	13.7885 (8)	11.1578 (4)	13.1435 (8)
α (°)	79.492 (5)	90		80.054 (4)
β (°)	77.096 (4)	108.07	91.407 (2)	82.714 (3)
γ (°)	86.637 (5)	90		79.179 (3)
V (Å ³)	772.78 (16)	1401.57 (12)	1566.16 (9)	82.714 (3)
Z	2	4	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.10	0.10	0.09	0.09
Crystal size (mm)	0.35 x 0.31 x 0.25	0.32 x 0.30 x 0.26	0.34 x 0.32 x 0.24	0.33 x 0.32 x 0.26
Data collection				
Diffractometer	Bruker SMART CCD area detector	BRUKER SMART APEX diffractometer	BRUKER SMART APEX diffractometer	BRUKER SMART APEX diffractometer
Absorption correction	Multi-scan (SADABS; Sheldrick, 1996)	Multi-scan (SADABS; Sheldrick, 1996)	Multi-scan (SADABS; Sheldrick, 1996)	Multi-scan (SADABS; Sheldrick, 1996)
No. of measured, independent and observed [$I > 2 \sigma(I)$] reflections	12862, 3499, 2509	4282, 2061, 1319	24605, 3880, 3005	16917, 4041, 3207

R_{int}	0.027	0.028	0.026	0.025
$(\sin \theta/\lambda)_{\text{max}} (\text{\AA}^{-1})$	0.648	0.606	0.668	0.606
Refinement				
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.046, 0.140, 1.05	0.041, 0.094, 0.88	0.045, 0.130, 1.01	0.040, 0.118, 1.05
No. of reflections	3499	2061	3880	4041
No. of parameters	219	209	219	291
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} (\text{e \AA}^{-3})$	0.19, -0.20	0.14, -0.11	0.25, -0.16	0.47, -0.18

Computer programs: *SHELXL97* (Sheldrick, 1997).