Supporting Information

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Highly Chemoselective Baylis-Hillman and Aldol Reactions of 2*H*-Thiopyran-4(3*H*)-one Using Tertiary Amine Catalysts in Aqueous Media

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Contents:

General procedure of DBU-catalysed BH reaction of 1	SI-2
Spectroscopic data of compounds 3a-e	SI-2
Spectroscopic data of compounds 4	SI-3
General procedure of DABCO-catalysed aldol reaction of 1	SI-3
Spectroscopic data of compounds 5a-f	SI-4
General procedure of DMAP or Et ₃ N-catalysed domino aldol-rearrangement reactions of 1	SI-6
¹ H NMR data of compounds 6c,d	SI-6
General procedure of tertiary amine-catalysed BH reaction of 2	SI-7
¹ H NMR and ¹³ C NMR of 3a-e , 5a-f , 4 and 6c,d	SI-8
X-ray crystallographic data of 5d	SI-21

General procedure of DBU-catalysed BH reaction of 1:

In a 5 ml round bottomed flask, to the mixture of **1** (2 mmol) and aldehyde (2 mmol) in 2 ml water was added 10 mol% of DBU at room temperature and stirred at the same temperature for appropriate time. After completion of the reaction (monitored by TLC using EtOAc/hexane: 3/7 as eluent) 5 ml HCl (5%) was added to the reaction mixture and extracted three times with 5 ml dichloromethane. The organic solvents were collected, washed with brine, dried on anhydrous Na₂SO₄ and evaporated under vacuum. The obtained crud product was purified by column chromatography using EtOAc/hexane (3/7) as eluent.

5-[(Phenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3a):

As a yellow oil, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.37-7.40 (m, 5H; Ph), 7.33 (s, 1H; CH), 5.7 (s, 1H; CH), 3.40 (s, 1H; OH), 3.16-3.26 (m, 2H; CH₂), 2.77-2.80 ppm (m, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=194.6 (C=O), 144.5, 141.8, 136.2, 128.8, 128.1, 126.9, 73.0, 38.3, 27.1 ppm; IR (KBr): ν=3404 (m, br; OH), 3028 (w, C-H_{Ar}), 2910 (w; C-H_{alkyl}), 1647 cm⁻¹ (s; C=O); MS (70 eV): *m/z* (%): 220 (99) [M⁺], 203 (100) [M⁺-OH], 163 (15), 146 (22), 105 (31), 77 (33) [C₆H₅⁺]; HRMS (ESI-Pos): *m/z* [M+Na]⁺ calcd for C₁₂H₁₂O₂S: 243.0450; found: 243.0448.

5-[(4-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3b):

As a green oil, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.31-7.37 (m, 5H; Ar and CH), 5.65 (d, ³*J*(H,H)=3.5 Hz, 1H; CH), 3.39 (d, ³*J*(H,H)=2.5 Hz, 1H; OH), 3.18-3.23 (m, 2H; CH₂), 2.76-2.79 ppm (m, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=194.5, 144.7, 140.4, 135.8, 133.8, 129.0, 128.2, 72.5, 38.2, 27.1 ppm; IR (KBr): ν=3414 (w, br; OH), 3030 (w; C-H_{Ar}), 2920 (w; C-H_{alkyl}), 1647 cm⁻¹ (s; C=O); MS (70 eV): *m/z* (%): 254 (88) [M⁺], 256 (41) [M⁺+2], 237 (100) [M⁺-OH], 139 (30) [M⁺-C₅H₇OS⁺], 113 (14) [C₅H₅OS⁺]; HRMS (ESI-Pos): *m/z* [M+Na]⁺ calcd for C₁₂H₁₁ClO₂S: 277.0061; found: 277.0043.

5-[(4-fluorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3c):

As a pale yellowish oil, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.37-7.40 (m, 2H; Ar), 7.30 (s, 1H; CH), 7.06-7.11 (m, 2H; Ar), 5.68 (d, ³*J*(H,H)=3.7 Hz, 1H; CH), 3.31 (d, ³*J*(H,H)=4.6 Hz, 1H; OH), 3.18-3.25 (m, 2H; CH₂), 2.78-2.81 ppm (m, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=194.6, 144.5, 128.7, 128.6, 115.9, 115.8, 115.6, 72.5, 38.2, 27.1 ppm; IR (KBr): ν=3421 (w, br; OH), 3043 (w; C-H_{Ar}), 2920 (w; C-H_{alkyl}), 1647 cm⁻¹ (s; C=O); MS (70 eV): *m/z* (%): 238 (42)

[M⁺], 237 (100) [M⁺-1], 143 (8) [C₆H₇O₂S⁺], 113 (15) [C₅H₅OS⁺], 77 (25); HRMS (ESI-Pos): *m/z* [M+Na]⁺ calcd for C₁₂H₁₁FO₂S: 261.0356; found: 261.0320.

5-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3d):

As a pale green oil, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.41 (s, 1H; Ar), 7.34 (s, 1H; CH), 7.28-7.33 (m, 3H; Ar), 5.66 (d, ³*J*(H,H)=4.2 Hz, 1H; CH), 3.37 (d, ³*J*(H,H)=4.7 Hz, 1H; OH), 3.18-3.25 (m, 2H; CH₂), 2.80 (t, ³*J*(H,H)=6.24 Hz, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=194.4, 144.9, 144.0, 135.6, 134.8, 130.1, 128.2, 127.0, 125.0, 72.6, 38.2, 27.2 ppm; IR (KBr): ν=3419 (w, br; OH), 3030 (w; C-H_{Ar}), 2934 (w; C-H_{alkyl}), 1647 cm⁻¹ (s; C=O); MS (70 eV): *m/z* (%): 254 (38) [M⁺], 256 (13) [M⁺+2], 180 (52) [M⁺-C₃H₆S], 141 (45) [C₇H₆ClO⁺], 77 (100); HRMS (ESI-Pos): *m/z* [M+Na]⁺ calcd for C₁₂H₁₁ClO₂S: 277.0061; found: 277.0056.

5-[(3-bromophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3e):

As a yellow oil, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ= 7.57 (s, 1H; Ar), 7.45 (d, ³*J*(H,H)=7.9 Hz, 1H; Ar), 7.33-7.34 (m, 2H; CH, Ar), 7.25 (t, ³*J*(H,H)=7.8 Hz, 1H; H), 5.65 (d, ³*J*(H,H)=4.9 Hz, 1H; CH), 3.36 (d, ³*J*(H,H)=5.0 Hz, 1H; OH), 3.19-3.25 (m, 2H; CH₂), 2.80 ppm (t, ³*J*(H,H)=6.4 Hz, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=194.4, 144.3, 135.6, 131.1, 130.4, 129.9, 125.5, 123.0, 115.0, 72.5, 38.2, 27.2 ppm; IR (KBr): ν=3417 (m, br; OH), 3026 (w; C-H_{Ar}), 2920 (w; C-H_{alkyl}), 1647 cm⁻¹ (s; C=O); MS (70 eV): *m/z*(%): 298 (100) [M⁺], 300 (87) [M⁺+2], 281 (16) [M⁺-OH], 219 (22) [M⁺-Br], 115 (5) [C₅H₅OS⁺]; HRMS (ESI-Pos): *m/z* [M+Na]⁺ calcd for C₁₂H₁₁BrO₂S: 320.9555; found: 320.9538.

3-(4-fluorobenzyl)-5-[(4-fluorophenyl)hydroxymethyl]-4H-thiopyran-4-one (4):

As a pale green pasty solid, ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ= 7.61 (d, ³*J*(H,H)=4.1 Hz, 1H), 7.44-7.47 (m, 2H; Ar), 7.36-7.37 (m, 1H; CH), 7.20-7.23 (m, 2H; Ar), 7.04-7.12 (m, 4H; Ar), 5.94 (d, ³*J*(H,H)=4.1 Hz, 1H; CH-O), 4.28 (d, ³*J*(H,H)=4.3 Hz, 1H; OH), 3.9 ppm (s, 2H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=186.3, 143.2, 134.6, 134.3, 131.4, 131.3, 129.0, 128.9, 116.1, 115.9, 115.8, 73.6, 36.9 ppm; IR (KBr): ν=3420 (m, br; OH), 3021 (w; C-H_{Ar}), 2922 (w; C-H_{alkyl}), 1602 cm⁻¹ (s; C=O).

General procedure of DABCO-catalysed aldol reaction of 1:

In a 5 ml round bottomed flask, to the mixture of **1** (2 mmol) and aldehyde (2 mmol) in 2 ml water was added 10 mol% of DABCO at room temperature and stirred at the same temperature for appropriate time. After completion of the reaction (monitored by TLC using EtOAc/hexane: 3/7 as

eluent) 5 ml HCl (5%) was added to the reaction mixture and extracted three times with 5 ml dichloromethane. The organic solvents were collected, washed with brine, dried on anhydrous Na₂SO₄ and evaporated under vacuum. The obtained oil was purified by column chromatography using EtOAc/hexane (3/7) as eluent.

3-[(4-chlorophenyl)hydroxymethyl]-2*H*-thiopyran-4(3*H*)-one (5a):

Only *syn* isomer; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.48 (dd, ⁴*J*(H,H)=2.01, ³*J*(H,H)=10.1 Hz, 1H; CH), 7.38 (d, ³*J*(H,H)=8.5 Hz, 2H; Ar), 7.32 (d, ³*J*(H,H)=8.5 Hz, 2H; Ar), 6.25 (d, ³*J*(H,H)=10.1 Hz, 1H; CH), 5.69-5.70 (m, 1H; CH–O), 3.43 (dd, ³*J*(H,H)=13.7, ²*J*(H,H)=13.8 Hz, 1H; CH₂axial), 2.92 (ddd, ³*J*(H,H)=3.32, ³*J*(H,H)=3.35, ³*J*(H,H)=13.7 Hz, 1H; CH), 2.87 (d, ³*J*(H,H)=4.3 Hz, 1H; OH), 2.78 ppm (ddd, ⁴*J*(H,H)=2.1, ³*J*(H,H)=3.8, ²*J*(H,H)=13.14 Hz, 1H; CH₂equatorial); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=195.7, 147.4, 139.6, 133.7, 129.1, 127.5, 124.2, 69.8, 52.7, 26.6 ppm; IR (KBr): ν=3407 (w, br; OH), 3030 (w; C–H_{Ar}), 2899 (w; C–H_{alkyl}), 1622 cm^{–1} (vs; C=O), 806 (s; C–Cl); MS (70 eV): *m/z* (%): 254 (3) [M⁺], 256 (1) [M⁺+2], 141 (17) [C₇H₆ClO⁺], 113 (31) [C₅H₅OS⁺], 77 (100); Anal. Calcd for C₁₂H₁₁ClO₂S: C, 56.58; H, 4.35. Found: C, 56.52; H, 4.35.

3-[(4-nitrophenyl)hydroxymethyl]-2*H*-thiopyran-4(3*H*)-one (5b):

Only *syn* isomer; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=8.28 (d, ³*J*(H,H)=8.7 Hz, 2H; Ar), 7.58 (d, ³*J*(H,H)=8.7 Hz, 2H; Ar), 7.50 (dd, ⁴*J*(H,H)=1.9, ³*J*(H,H)=10.1 Hz, 1H; CH), 6.27 (d, ³*J*(H,H)=10.1 Hz, 1H; CH), 5.83 (m, 1H; CH–O), 3.47 (dd, ³*J*(H,H)=13.8, ³*J*(H,H)=13.9 Hz, 1H; CH₂axial), 2.98-3.02 (m, 2H; CH and OH), 2.68 ppm (ddd, ⁴*J*(H,H)=2.1, ³*J*(H,H)=3.8, ²*J*(H,H)=13.6 Hz, 1H; CH₂equatorial); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ=195.1, 148.6, 147.8, 128.4, 127.1, 124.1, 123.8, 69.7, 52.6, 26.4 ppm; IR (KBr): ν=3458 (m, br; OH), 3016 (w; C–H_{Ar}), 2939 (w; C–H_{alkyl}), 1643 cm^{–1} (s; C=O); MS (70 eV): *m/z* (%): 265 (10) [M⁺], 218 (12) [M⁺–HNO₂], 152 (11) [C₇H₆NO₃⁺], 113 (100) [C₅H₅OS⁺]; Anal. Calcd for C₁₂H₁₁NO₄S: C, 54.33; H, 4.18. Found: C, 54.71; H, 4.23.

4-[hydroxy(4-oxo-3,4-dihydro-2*H*-thiopyran-3-yl)methyl]benzonitrile (5c):

dr (*syn/anti* ratio)=60/40; ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.69-7.72 (m, 2H; CH_{Ar}, *syn* and *anti*), 7.48-7.58 (m, 3H; CH and CH_{Ar}, *syn* and *anti*), 6.26 (d, ³*J*(H,H)=10.1 Hz, 0.4H; CH, *anti*), 6.25 (d, ³*J*(H,H)=10.1 Hz, 0.6H; CH, *syn*), 5.77 (dd, ³*J*(H,H)=3.6, ³*J*(H,H)=3.7 Hz, 0.6H; CH–O, *syn*), 5.10 (dd, ³*J*(H,H)=7.2, ³*J*(H,H)=2.5 Hz, 0.4H; CH–O, *anti*), 4.35 (d, ³*J*(H,H)=2.5 Hz, 0.4H; OH, *anti*), 3.45 (dd, ³*J*(H,H)=13.8, ²*J*(H,H)=13.9 Hz, 0.6H; CH₂axial, *syn*), 3.07 (d, ³*J*(H,H)=4.4 Hz, 0.6H; OH,

syn), 2.95 (ddd, $^3J(\text{H,H})=3.4$, $^3J(\text{H,H})=3.5$, $^3J(\text{H,H})=14.1$ Hz, 0.6H; CH, *syn*), 2.89-2.91 (m, 0.8H; CH and CH₂axial, *anti*), 2.67-2.70 ppm (m, 1H: CH₂equatorial, *syn* and *anti*); ^{13}C NMR (125 MHz, CDCl₃, 25°C, TMS): $\delta=196.9$, 195.2, 147.9, 147.6, 146.8, 145.8, 132.9, 132.8, 128.3, 127.0, 124.1, 123.8, 119.1, 118.9, 111.8, 112.8, 73.9, 69.7, 52.6, 52.0, 28.9, 26.5 ppm; IR (KBr): $\nu=3416$ (m, br; OH), 3056 (w; C–H_{Ar}), 2967 (w; C–H_{alkyl}), 2221 (m; C $\equiv$ N), 1640 cm⁻¹ (s; C=O); MS (70 eV): m/z (%): 245 (8) [M^+], 228 (13) [$\text{M}^+-\text{H}_2\text{O}$], 113 (100) [$\text{C}_5\text{H}_5\text{OS}^+$], 102 (37) [$\text{C}_7\text{H}_4\text{N}^+$], 86 (82) [$\text{C}_3\text{H}_2\text{OS}^+$].

3-[(2,4-dichlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5d):

Only *syn* isomer; ^1H NMR (500 MHz, CDCl₃, 25°C, TMS): $\delta=7.58$ (d, $^3J(\text{H,H})=8.3$ Hz, 1H; CH_{Ar}), 7.46 (dd, $^4J(\text{H,H})=2.1$, $^3J(\text{H,H})=10.1$ Hz, 1H; CH), 7.40 (d, $^4J(\text{H,H})=2.1$ Hz, 1H; CH_{Ar}), 7.33 (dd, $^4J(\text{H,H})=2.1$, $^3J(\text{H,H})=8.4$ Hz, 1H; CH_{Ar}), 6.25 (d, $^3J(\text{H,H})=10.1$ Hz, 1H; CH), 6.02 (dd, $^3J(\text{H,H})=2.7$, $^3J(\text{H,H})=4.4$ Hz, 1H; CH), 3.47 (dd, $^2J(\text{H,H})=13.1$, $^3J(\text{H,H})=14.4$ Hz, 1H; CH₂axial), 3.25 (d, $^3J(\text{H,H})=4.4$ Hz, 1H; OH, exchanged with D₂O), 3.10 (ddd, $^3J(\text{H,H})=2.7$, $^3J(\text{H,H})=3.8$, $^3J(\text{H,H})=14.6$ Hz, 1H; CH), 2.65 ppm (ddd, $^4J(\text{H,H})=2.2$, $^3J(\text{H,H})=3.85$, $^2J(\text{H,H})=13.4$ Hz, 1H; CH₂equatorial); ^{13}C NMR (125 MHz, CDCl₃, 25°C, TMS): $\delta=195.4$, 147.3, 137.3, 134.3, 132.1, 129.8, 129.7, 127.6, 124.3, 67.1, 49.6, 26.5 ppm; IR (KBr): $\nu=3410$ (m, br; OH), 3035 (w; C–H_{Ar}), 2918 (w; C–H_{alkyl}), 1639 (s; C=O), 1589 (w; C=C), 1201 (m; C–O), 1037 cm⁻¹ (m; C–Cl); MS (70 eV): m/z (%): 288 (31) [M^+], 290 (23) [M^++2], 292 (5) [M^++4], 173 (61) [$\text{C}_7\text{H}_3\text{Cl}_2\text{O}^+$], 111 (100) [$\text{C}_5\text{H}_3\text{OS}^+$], 86 (98) [$\text{C}_3\text{H}_2\text{OS}^+$]; Anal. Calcd for C₁₂H₁₀Cl₂O₂S: C, 49.84; H, 3.49. Found: C, 49.96; H, 3.68.

3-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5e):

dr (*syn/anti* ratio)= >95/5; ^1H NMR (500 MHz, CDCl₃, 25°C, TMS): $\delta=7.45$ -7.49 (m, 1H; CH, *syn* and *anti*), 7.43 (s, 0.05H; CH_{Ar}, *anti*), 7.40 (s, 0.95H; CH_{Ar}, *syn*), 7.27-7.34 (m, 2H; CH_{Ar}, *syn* and *anti*, and 0.05H; CH_{Ar}, *anti*), 7.23 (d, $^3J(\text{H,H})=7.35$ Hz, 0.95H; CH_{Ar}, *syn*), 6.24 (d, $^3J(\text{H,H})=10.1$ Hz, 0.05H; CH, *anti*), 6.23 (d, $^3J(\text{H,H})=10.1$ Hz, 0.95H; CH, *syn*), 5.69 (m, 0.95H; CH–O, *syn*), 5.03 (m, 0.05H; CH–O, *anti*), 4.33 (d, $^3J(\text{H,H})=2.3$ Hz, 0.05H; OH, *anti*), 3.44 (dd, $^3J(\text{H,H})=13.8$, $^2J(\text{H,H})=13.8$ Hz, 0.95H; CH₂axial, *syn*), 3.17 (d, $^3J(\text{H,H})=3.6$ Hz, 0.95H; OH, *syn*), 2.90 (ddd, $^3J(\text{H,H})=3.5$, $^3J(\text{H,H})=3.4$, $^3J(\text{H,H})=14.0$ Hz, 0.95H; CH, *syn*), 2.84-2.86 (m, 0.1H; CH and CH₂axial, *anti*), 2.74-2.79 ppm (m, 1H: CH₂equatorial, *syn* and *anti*); ^{13}C NMR (125 MHz, CDCl₃, 25°C, TMS): $\delta=197.2$, 195.5, 148.0, 147.5, 146.9, 143.5, 135.0, 130.3, 130.2, 129.1, 128.1, 127.6, 126.5, 125.6, 124.3, 124.2, 123.8, 74.0, 69.6, 52.8, 52.2, 27.8, 26.5 ppm; IR (KBr): $\nu=3417$ (m, br; OH), 3041 (w; C–H_{Ar}), 2916 (w; C–H_{alkyl}), 1639 (s; C=O), 1203 (m; C–O), 1045 cm⁻¹ (m; C–Cl); MS (70 eV): m/z (%): 254 (<1) [M^+], 113 (17) [$\text{C}_5\text{H}_5\text{OS}^+$], 85 (71) [C_3HOS^+], 58 (100) [$\text{C}_2\text{H}_2\text{S}^+$]; Anal. Calcd for C₁₂H₁₁ClO₂S: C, 56.58; H, 4.35. Found: C, 56.49; H, 4.32.

3-[(3-nitrophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5f):

dr (*syn/anti* ratio)=65/35; ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): δ =8.26 (s, 0.34H; CH_{Ar} , *anti*), 8.21 (s, 0.66H; CH_{Ar} , *syn*), 8.12-8.14 (m, 0.34H; CH_{Ar} , *anti*), 8.08-8.10 (m, 0.66H; CH_{Ar} , *syn*), 7.75 (d, $^3J(\text{H,H})$ =7.65 Hz, 0.34H; CH_{Ar} , *anti*), 7.67 (d, $^3J(\text{H,H})$ =7.75 Hz, 0.66H; CH_{Ar} , *syn*), 7.45-7.55 (m, 2H; CH_{Ar} , CH, *syn* and *anti*), 6.18 (d, $^3J(\text{H,H})$ =10.1 Hz, 0.34H; CH, *anti*), 6.17 (d, $^3J(\text{H,H})$ =10.1 Hz, 0.66H; CH, *syn*), 5.73 (d, $^3J(\text{H,H})$ =1.68 Hz, 0.66H; CH-O, *syn*), 5.17 (d, $^3J(\text{H,H})$ =7.41 Hz, 0.34H; CH-O, *anti*), 4.56 (s, 0.34H; OH, *anti*), 3.77 (s, 0.66H; OH, *syn*), 3.44 (dd, $^2J(\text{H,H})$ =13.5, $^3J(\text{H,H})$ =13.5 Hz, 0.66H; CH_2 axial, *syn*), 2.83-2.92 (m, 1H; CH, *syn* and *anti*, 0.34H; CH_2 axial, *anti*), 2.72-2.78 ppm (m, 1H; CH_2 equatorial, *syn* and *anti*); ^{13}C NMR (125 MHz, CDCl_3 , 25°C, TMS): δ =196.6, 194.9, 148.7, 148.7, 148.1, 147.9, 144.2, 143.0, 133.7, 132.5, 130.0, 129.9, 124.0, 123.7, 122.9, 122.4, 121.4, 73.1, 69.2, 52.7, 51.9, 28.8, 26.6 ppm; IR (KBr): ν =3396 (m, br; OH), 3047 (w; C-H_{Ar}), 2920 (w; C-H_{alkyl}), 1658 (s; C=O), 1527, 1352 (s; NO₂), 1201 cm^{-1} (m; C-O); MS (70 eV): m/z (%): 265 (2) [M^+], 218 (11) [$\text{M}^+ - \text{HNO}_2$], 150 (24) [$\text{C}_7\text{H}_4\text{NO}_3^+$], 113 (100) [$\text{C}_5\text{H}_5\text{OS}^+$], 86 (71) [$\text{C}_3\text{H}_2\text{OS}^+$], 58 (84) [$\text{C}_2\text{H}_2\text{S}^+$].

General procedure of DABCO, DMAP or Et₃N-catalysed domino aldol-rearrangement reactions of 1:

In a 5 ml round bottomed flask, to the mixture of **1** (2 mmol) and aldehyde (2 mmol) in 2 ml water was added 10 mol% of DABCO, DMAP or Et₃N at room temperature and stirred at 45-50 °C for 6h. After completion of the reaction (monitored by TLC using EtOAc/hexane: 3/7 as eluent) 10 ml saturated NaHCO₃ was added to the reaction mixture and extracted three times with 5 ml dichloromethane. The organic solvents were collected, washed with brine, dried on anhydrous Na₂SO₄ and evaporated under vacuum. The obtained oil was purified by column chromatography using EtOAc/hexane (3/7) as eluent. All compounds are known and were identified by m.p. and ^1H NMR spectrum. Selected compounds ^1H NMR spectrum:

3-benzyl-4H-thiopyran-4-one (6a): m.p. 74-76°C (reported: 73-75°C).

3-(4-chlorobenzyl)-4H-thiopyran-4-one (6b): m.p. 63-65°C (reported: 63-65°C).

3-(2,6-dichlorobenzyl)-4H-thiopyran-4-one (6c): m.p. 125-126°C (reported: 126-127°C); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): δ =7.78 (dd, $^4J(\text{H,H})$ =4.0, $^3J(\text{H,H})$ =10.2 Hz, 1H; CH), 7.39 (d, $^3J(\text{H,H})$ =8.0 Hz, 2H; CH_{Ar}), 7.23 (t, $^3J(\text{H,H})$ =8.0 Hz, 1H; CH_{Ar}), 7.13 (d, $^3J(\text{H,H})$ =10.2 Hz, 1H; CH), 6.90 (dt, $^4J(\text{H,H})$ =4.0, $^4J(\text{H,H})$ =1.4 Hz, 1H; CH), 4.26 ppm (d, $^4J(\text{H,H})$ =1.4 Hz, 2H; CH₂).

3-(4-methylbenzyl)-4*H*-thiopyran-4-one (6d): m.p. 71-73°C (reported: 71-73°C); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=7.73 (dd, ⁴*J*(H,H)=4.1, ³*J*(H,H)=10.2 Hz, 1H; CH), 7.26 (dt, ⁴*J*(H,H)=4.0, ⁴*J*(H,H)=1.0 Hz, 1H; CH), 7.13-7.18 (m, 4H; CH_{Ar}), 7.08 (d, ³*J*(H,H)=10.2 Hz, 1H; CH), 3.89 (d, ⁴*J*(H,H)=1.0 Hz, 2H; CH₂), 2.37 ppm (s, 3H; CH₃).

3-(4-methoxybenzyl)-4*H*-thiopyran-4-one (6e): m.p. 114-116°C (reported: 115-117°C)

General procedure of tertiary amine-catalysed BH reaction of 2:

Reaction was carried out as in the case of DBU-catalysed BH reaction of **1** using cyclohex-2-enone **2** instead of **1**. All products are known and were determined by ¹H NMR spectra in compared with authentic compounds.

¹H NMR of 5-[(Phenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3a) in CDCl₃ at 25°C.

¹³C NMR of 5-[(Phenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3a) in CDCl₃ at 25°C.

¹H NMR of 5-[(4-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3b) in CDCl₃ at 25°C.

¹³C NMR of 5-[(4-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3b) in CDCl₃ at 25°C.

¹H NMR of 5-[(4-fluorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3c) in CDCl₃ at 25°C.

¹³C NMR of 5-[(4-fluorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3c) in CDCl₃ at 25°C.

¹H NMR of 5-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3d) in CDCl₃ at 25°C.

¹³C NMR of 5-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3d) in CDCl₃ at 25°C.

¹H NMR of 5-[(3-bromophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3e) in CDCl₃ at 25°C.

¹³C NMR of 5-[(3-bromophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (3e) in CDCl₃ at 25°C.

¹H NMR of **3-(4-fluorobenzyl)-5-[(4-fluorophenyl)hydroxymethyl]-4H-thiopyran-4-one (4)** in CDCl₃ at 25°C.

¹³C NMR of **3-(4-fluorobenzyl)-5-[(4-fluorophenyl)hydroxymethyl]-4H-thiopyran-4-one (4)** in CDCl₃ at 25°C.

¹H NMR of 3-[(4-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5a) in CDCl₃ at 25°C.

¹³C NMR of 3-[(4-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5a) in CDCl₃ at 25°C.

¹H NMR of 3-[(4-nitrophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (**5b**) in CDCl₃ at 25°C.

¹³C NMR of 3-[(4-nitrophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (**5b**) in CDCl₃ at 25°C.

¹H NMR of 4-[hydroxy(4-oxo-3,4-dihydro-2H-thiopyran-3-yl)methyl]benzonitrile (5c) in CDCl₃ at 25°C.

¹³C NMR of 4-[hydroxy(4-oxo-3,4-dihydro-2H-thiopyran-3-yl)methyl]benzonitrile (5c) in CDCl₃ at 25°C.

¹H NMR of 3-[(2,4-dichlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5d) in CDCl₃ at 25°C.

¹³C NMR of 3-[(2,4-dichlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5d) in CDCl₃ at 25°C.

¹H NMR of 3-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5e) in CDCl₃ at 25°C.

¹³C NMR of 3-[(3-chlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5e) in CDCl₃ at 25°C.

¹H NMR of 3-[(3-nitrophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5f) in CDCl₃ at 25°C.

¹³C NMR of 3-[(3-nitrophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5f) in CDCl₃ at 25°C.

¹H NMR of 3-(2,6-dichlorobenzyl)-4H-thiopyran-4-one (6c) in CDCl₃ at 25°C.

¹H NMR of 3-(4-methylbenzyl)-4H-thiopyran-4-one (6d) in CDCl₃ at 25°C.

X-ray crystallographic data of 3-[(2,4-dichlorophenyl)hydroxymethyl]-2H-thiopyran-4(3H)-one (5d):

ORTEP representation of the crystal structure of **5d**:

CCDC 780479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for **5d**.

Habitus, colour	prism, colorless	
Crystal size	0.44 x 0.36 x 0.18 mm ³	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	Z = 4
Unit cell dimensions	a = 14.9933(17) Å	α = 90°.
	b = 6.9057(5) Å	β = 104.389(12)°.
	c = 12.3749(13) Å	γ = 90°.
Volume	1241.1(2) Å ³	

Cell determination	6584 peaks with Theta 2.5 to 25°.
Empirical formula	C ₁₂ H ₁₀ Cl ₂ O ₂ S
Formula weight	289.16
Density (calculated)	1.548 Mg/m ³
Absorption coefficient	0.676 mm ⁻¹
F(000)	592

Data collection:

Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Temperature	193(2) K
Theta range for data collection	2.81 to 26.01°.
Index ranges	-18<=h<=18, -8<=k<=8, -15<=l<=15
Data collection software	STOE EXPOSE
Cell refinement software	STOE CELL
Data reduction software	STOE INTEGRATE

Solution and refinement:

Reflections collected	9446
Independent reflections	2430 [R(int) = 0.0528]
Completeness to theta = 25.00°	99.8 %
Observed reflections	1768[I>2(I)]
Reflections used for refinement	2430
Absorption correction	None
Largest diff. peak and hole	0.283 and -0.333 e.Å ⁻³
Solution	Direct methods
Refinement	Full-matrix least-squares on F ²
Treatment of hydrogen atoms	CH calculated, OH located
Programs used	SIR92 (Giacovazzo et al, 1993) SHELXL-97 (Sheldrick, 2008) DIAMOND 3.1 STOE IPDS software

Data / restraints / parameters	2430 / 0 / 158
Goodness-of-fit on F^2	0.938
R index (all data)	wR2 = 0.0824
R index conventional [$I > 2\sigma(I)$]	R1 = 0.0326

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **5d**.

C1-O1	1.418(2)	C11-C12	1.387(3)
C1-C7	1.515(2)	C11-H11	0.9500
C1-C2	1.541(3)	C12-H12	0.9500
C1-H1	1.0000	O1-H1A	0.87(3)
C2-C6	1.524(3)		
C2-C3	1.527(2)		
C2-H2	1.0000		
C3-O2	1.222(2)		
C3-C4	1.450(3)		
C4-C5	1.341(3)		
C4-H4	0.9500		
C5-S1	1.712(2)		
C5-H5	0.9500		
C6-S1	1.800(2)		
C6-H6A	0.9900		
C6-H6B	0.9900		
C7-C12	1.393(3)		
C7-C8	1.397(3)		
C8-C9	1.389(3)		
C8-Cl1	1.7418(19)		
C9-C10	1.377(3)		
C9-H9	0.9500		
C10-C11	1.375(3)		
C10-Cl2	1.7494(19)		

		S1-C6-H6A	108.9
O1-C1-C7	109.55(15)	C2-C6-H6B	108.9
O1-C1-C2	108.71(15)	S1-C6-H6B	108.9
C7-C1-C2	111.20(14)	H6A-C6-H6B	107.7
O1-C1-H1	109.1	C12-C7-C8	116.76(17)
C7-C1-H1	109.1	C12-C7-C1	120.87(17)
C2-C1-H1	109.1	C8-C7-C1	122.34(17)
C6-C2-C3	111.07(15)	C9-C8-C7	122.75(18)
C6-C2-C1	111.07(15)	C9-C8-Cl1	117.53(16)
C3-C2-C1	110.81(15)	C7-C8-Cl1	119.72(14)
C6-C2-H2	107.9	C10-C9-C8	117.85(19)
C3-C2-H2	107.9	C10-C9-H9	121.1
C1-C2-H2	107.9	C8-C9-H9	121.1
O2-C3-C4	121.42(17)	C11-C10-C9	121.82(18)
O2-C3-C2	120.17(18)	C11-C10-Cl2	119.68(16)
C4-C3-C2	118.26(17)	C9-C10-Cl2	118.50(17)
C5-C4-C3	124.19(19)	C10-C11-C12	119.1(2)
C5-C4-H4	117.9	C10-C11-H11	120.4
C3-C4-H4	117.9	C12-C11-H11	120.4
C4-C5-S1	127.32(17)	C11-C12-C7	121.7(2)
C4-C5-H5	116.3	C11-C12-H12	119.2
S1-C5-H5	116.3	C7-C12-H12	119.2
C2-C6-S1	113.48(14)	C1-O1-H1A	105.1(18)
C2-C6-H6A	108.9	C5-S1-C6	99.31(10)

Symmetry transformations used to generate equivalent atoms

Table 3. Hydrogen bonds for **5d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1A...O2#1	0.87(3)	1.97(3)	2.7659(19)	152(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+3/2