DABCO-Catalyzed Reaction of Allenic Esters and Ketones with Salicyl *N*-Tosylimines: Synthesis of Highly Functionalized Chromenes

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Experimental Procedures

General Remarks. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Other commercially available reagents were used without further purification. Salicyl *N*-tosylimines,¹ ethyl 2,3-butadienoate,² penta-3,4-dien-2-one³ were prepared according to the literature. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. ¹H NMR, ¹³C NMR and NOESY spectra were recorded on a Varian Mercury vx 300 NMR spectrometer in CDCl₃ using tetramethylsilane as the internal standard. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by an Ion Spec 4.7 Tesla FTMS mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points were obtained by means of a micro melting point apparatus and are uncorrected.

Characterization Data for the New Salicyl *N*-Tosylimines are Presented as Below.

***N*-(2-Hydroxy-3-methoxybenzylidene)-4-methylbenzenesulfonamide:** a yellow solid: mp. 107-109 °C; IR (CH₂Cl₂) ν 3396, 1596, 1567, 1257, 1159, 1089 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.44 (3H, s, Me), 3.90 (3H, s, MeO), 6.92-6.97 (1H, m, Ar), 7.08-7.16 (2H, m, Ar), 7.34 (2H, d, *J* = 8.1 Hz, Ar), 7.86 (2H, d, *J* = 8.1 Hz, Ar), 9.12 (1H, s, OH), 10.74 (1H, s, CH). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 21.5, 56.2, 116.6, 118.0, 119.8, 125.6, 127.7, 129.8, 134.8, 144.9, 148.2, 151.9, 171.0. MS (EI) *m/e* 305 (M⁺, 84.0), 150 (M⁺-155, 100). Anal. Calcd. for C₁₅H₁₅NO₄S requires C, 59.00; H, 4.95; N, 4.59%. Found: C, 58.93; H, 4.94; N, 4.56%.

***N*-(2-Hydroxy-4-methoxybenzylidene)-4-methylbenzenesulfonamide:** a colorless solid: mp. 115-117 °C; IR (CH₂Cl₂) ν 3067, 1632, 1586, 1504, 1158, 1087 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.44 (3H, s, Me), 3.86 (3H, s, MeO), 6.44 (1H, d, J = 2.4 Hz, Ar), 6.56 (1H, dd, J = 8.7, 2.4 Hz, Ar), 7.32-7.39 (3H, m, Ar), 7.84 (2H, d, J = 8.7 Hz, Ar), 8.96 (1H, s, OH), 11.21 (1H, s, CH). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 21.6, 55.8, 100.9, 109.4, 110.6, 127.6, 129.9, 135.7, 136.9, 144.6, 164.9, 167.4, 169.9. MS (EI) m/e 305 (M⁺, 79.0), 91 (M⁺-206, 100). Anal. Calcd. for C₁₅H₁₅NO₄S requires C, 59.00; H, 4.95; N, 4.59%. Found: C, 58.86; H, 4.98; N, 4.59%.

***N*-(2-Hydroxy-5-methoxybenzylidene)-4-methylbenzenesulfonamide:** a yellow solid: mp. 158-159 °C; IR (CH₂Cl₂) ν 3067, 2951, 1562, 1487, 1275, 1160 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.44 (3H, s, Me), 3.79 (3H, s, MeO), 6.92-6.95 (2H, m, Ar), 7.12-7.16 (1H, m, Ar), 7.35 (2H, d, J = 8.4 Hz, Ar), 7.86 (2H, d, J = 8.4 Hz, Ar), 9.06 (1H, s, OH), 10.49 (1H, s, CH). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 21.6, 55.8, 115.9, 116.1, 118.9, 125.9, 127.8, 130.0, 135.0, 145.0, 152.8, 156.7, 171.2. MS (EI) m/e 305 (M⁺, 63.8), 150 (M⁺-155, 100). Anal. Calcd. for C₁₅H₁₅NO₄S requires C, 59.00; H, 4.95; N, 4.59%. Found: C, 58.90; H, 5.02; N, 4.44%.

***N*-(2-Hydroxy-5-methylbenzylidene)-4-methylbenzenesulfonamide:** a yellow solid: mp. 188-190 °C; IR (CH₂Cl₂) ν 3074, 1596, 1486, 1324, 1285, 1159 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.31 (3H, s, Me), 2.44 (3H, s, Me), 6.90 (1H, d, J = 8.7 Hz, Ar), 7.26-7.36 (4H, m,

Ar), 7.85 (2H, d, $J = 8.4$ Hz, Ar), 9.04 (1H, s, OH), 10.64 (1H, s, CH). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 20.1, 21.6, 116.2, 117.6, 127.8, 129.5, 129.9, 134.9, 135.0, 138.5, 144.9, 160.0, 171.4. MS (EI) m/e 289 (M^+ , 96.0), 91 ($\text{M}^+ - 191$, 100). Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$ requires C, 62.26; H, 5.23; N, 4.84%. Found: C, 62.21; H, 5.20; N, 4.64%.

***N*-(5-Bromo-2-hydroxybenzylidene)-4-methylbenzenesulfonamide:** a yellow solid: mp. 183-185 °C; IR (CH_2Cl_2) ν 3052, 1594, 1472, 1337, 1280, 1159 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 2.46 (3H, s, Me), 6.91 (1H, d, $J = 8.7$ Hz, Ar), 7.37 (2H, d, $J = 8.4$ Hz, Ar), 7.56-7.62 (2H, m, Ar), 7.86 (2H, d, $J = 8.4$ Hz, Ar), 9.01 (1H, s, OH), 10.82 (1H, s, CH). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 21.7, 111.6, 117.8, 119.8, 128.0, 130.0, 134.4, 136.8, 139.6, 145.3, 160.9, 170.1. MS (EI) m/e 355 ($\text{M}^+ + 2$, 26.4), 353 (M^+ , 25.7), 91 ($\text{M}^+ - 262$, 100). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{BrNO}_3\text{S}$ requires C, 47.47; H, 3.41; N, 3.95%. Found: C, 47.41; H, 3.33; N, 3.93%.

***N*-(3,5-Dichloro-2-hydroxybenzylidene)-4-methylbenzenesulfonamide:** a yellow solid: mp. 183-184 °C; IR (CH_2Cl_2) ν 3071, 1594, 1557, 1334, 1294, 1161 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 2.46 (3H, s, Me), 7.37 (2H, d, $J = 8.1$ Hz, Ar), 7.44 (1H, d, $J = 2.4$ Hz, Ar), 7.58 (1H, d, $J = 2.4$ Hz, Ar), 7.86 (2H, d, $J = 8.1$ Hz, Ar), 9.03 (1H, s, OH), 11.35 (1H, s, CH). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 21.7, 117.8, 123.6, 124.8, 128.1, 130.1, 132.2, 134.1, 136.2, 145.6, 156.1, 169.5. MS (EI) m/e 343 (M^+ , 31.2), 91 ($\text{M}^+ - 252$, 100). Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3\text{Cl}_2\text{S}$ requires C, 48.85; H, 3.22; N, 4.07%. Found: C, 48.86; H, 3.28; N, 4.04%.

Typical Reaction Procedure for PPh₂Me-catalyzed Reaction of Ethyl 2,3-butadienoate **2a with Salicyl *N*-tosylimine **1a**.**

To a solution of salicyl *N*-tosylimine **1a** (138 mg, 0.50 mmol) and ethyl 2,3-butadienoate **2a** (69 μ L, 0.60 mmol) in THF (2.0 mL) at room temperature was added PPh₂Me (23 μ L, 0.0625 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When **1a** disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (eluent: EtOAc:Petroleum ether = 1:4) to yield **3a** (159 mg, 82 %) as a colorless solid.

2-(2-Hydroxy-phenyl)-1-(toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole-3-carboxylic acid ethyl ester (3a**):** a colorless solid: mp. 156-158 °C; IR (CH₂Cl₂) ν 3427, 1718, 1344, 1258, 1162, 1094 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.12 (3H, t, J = 7.2 Hz, CH₃), 2.38 (3H, s, Me), 3.98-4.16 (2H, m, CH₂), 4.35-4.53 (2H, m, CH₂), 6.07 (1H, t, J = 2.7 Hz), 6.77-6.91 (4H, m, Ar), 7.00-7.03 (1H, m, Ar), 7.12-7.22 (3H, m, Ar), 7.56 (2H, d, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 13.8, 21.5, 54.9, 61.3, 63.2, 118.3, 121.1, 126.6, 127.3, 128.0, 129.3, 129.6, 134.5, 135.1, 136.3, 143.7, 153.8, 162.6. MS (EI) m/e 387 (M⁺, 28.3), 91 (M⁺-296, 100). Anal. Calcd. for C₂₀H₂₁NO₅S requires C, 62.00; H, 5.46; N, 3.62%. Found: C, 62.08; H, 5.38; N, 3.54%.

Typical Reaction Procedure for DABCO-catalyzed Reaction of Ethyl 2,3-butadienoate **2a with Salicyl *N*-tosylimine **1a**.**

To a flame-dried Schlenk tube at room temperature was in turn added molecular sieve 4A (100

mg), DABCO (5.6 mg, 0.05 mmol), salicyl *N*-tosylimine **1a** (138 mg, 0.50 mmol), THF (2.0 mL) and ethyl 2,3-butadienoate **2a** (69 μ L, 0.60 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When **1a** disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (eluent: EtOAc:Petroleum ether = 1:4-2:1) to yield **4a** (169 mg, 87 %) as a colorless solid.

2-Methyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4a): a colorless solid: mp. 130-132 °C; IR (CH₂Cl₂) ν 3273, 1710, 1638, 1347, 1223, 1157 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.22 (3H, t, *J* = 7.2 Hz, CH₃), 2.39 (3H, s, Me), 2.40 (3H, s, Me), 3.90 (1H, dq, *J* = 10.8, 7.2 Hz), 4.10 (1H, dq, *J* = 10.8, 7.2 Hz), 5.00 (1H, d, *J* = 6.6 Hz, NH), 5.60 (1H, d, *J* = 6.6 Hz, CH), 7.00-7.05 (2H, m, Ar), 7.18-7.28 (3H, m, Ar), 7.34-7.36 (1H, m, Ar), 7.55 (2H, d, *J* = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 14.1, 19.7, 21.4, 47.8, 60.5, 102.9, 116.1, 120.0, 124.6, 126.7, 129.0, 129.1, 129.6, 139.2, 142.6, 150.5, 163.1, 166.3. MS (EI) *m/e* 232 (*M*⁺-155, 39.7), 217 (*M*⁺-170, 100). Anal. Calcd. for C₂₀H₂₁NO₅S requires C, 62.00; H, 5.46; N, 3.62%. Found: C, 61.73; H, 5.52; N, 3.55%.

6-Methoxy-2-methyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4b): a colorless solid: mp. 150-151 °C; IR (CH₂Cl₂) ν 3275, 1710, 1498, 1218, 1156, 1070 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.23 (3H, t, *J* = 7.2 Hz, CH₃), 2.39 (6H, s, 2Me), 3.65 (3H, s, MeO), 3.92 (1H, dq, *J* = 10.5, 7.2 Hz), 4.12 (1H, dq, *J* = 10.5, 7.2 Hz), 5.05 (1H, d, *J* = 6.3 Hz, NH), 5.56 (1H, d, *J* = 6.3 Hz, CH), 6.74 (1H, d, *J* = 2.7 Hz, Ar), 6.79 (1H,

dd, $J = 8.7, 2.7$ Hz, Ar), 6.97 (1H, d, $J = 8.7$ Hz, Ar), 7.18 (2H, d, $J = 7.8$ Hz, Ar), 7.53 (2H, d, $J = 7.8$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 14.1, 19.8, 21.4, 48.4, 55.3, 60.5, 102.0, 111.9, 116.5, 117.2, 120.1, 126.6, 129.1, 139.3, 142.6, 144.7, 156.1, 163.3, 166.5. MS (EI) m/e 417 (M^+ , 3.3), 247 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_6\text{S}$ requires C, 60.42, H, 5.55; N, 3.36%. Found: C, 60.31; H, 5.34; N, 3.31%.

8-Methoxy-2-methyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4c): a white solid: mp. 163-164 °C; IR (CH_2Cl_2) ν 3305, 1705, 1329, 1212, 1155, 1098 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 1.22 (3H, t, $J = 7.2$ Hz, CH_3), 2.35 (3H, s, Me), 2.39 (3H, s, Me), 3.88 (3H, s, MeO), 3.89 (1H, dq, $J = 10.5, 7.2$ Hz), 4.10 (1H, dq, $J = 10.5, 7.2$ Hz), 5.03 (1H, d, $J = 6.6$ Hz, NH), 5.64 (1H, d, $J = 6.6$ Hz, CH), 6.80-6.83 (1H, m, Ar), 6.98-7.00 (2H, m, Ar), 7.21 (2H, d, $J = 7.8$ Hz, Ar), 7.61 (2H, d, $J = 7.8$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 14.1, 19.3, 21.4, 47.5, 55.9, 60.5, 103.0, 110.8, 120.8, 121.5, 124.5, 126.7, 129.1, 139.4, 140.1, 142.6, 147.1, 162.7, 166.3. MS (EI) m/e 417 (M^+ , 1.5), 247 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_6\text{S}$ requires C, 60.42, H, 5.55; N, 3.36%. Found: C, 60.62; H, 5.56; N, 3.36%.

2,6-Dimethyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4d): a white solid: mp. 118-120 °C; IR (CH_2Cl_2) ν 3275, 1709, 1499, 1339, 1219, 1157 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 1.25 (3H, t, $J = 6.9$ Hz, CH_3), 2.14 (3H, s, Me), 2.39 (6H, s, 2Me), 3.95 (1H, dq, $J = 11.4, 6.9$ Hz), 4.12 (1H, dq, $J = 11.4, 6.9$ Hz), 5.07 (1H, d, $J = 6.6$ Hz, NH), 5.52 (1H, d, $J = 6.6$ Hz, CH), 6.90-7.03 (3H, m, Ar), 7.18 (2H, d, $J = 8.1$ Hz, Ar),

7.51 (2H, d, $J = 8.1$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 14.1, 19.8, 20.5, 21.4, 48.0, 60.5, 102.8, 115.9, 119.1, 126.7, 129.0, 129.6, 129.7, 134.1, 139.3, 142.5, 148.6, 163.2, 166.5. MS (EI) m/e 401 (M^+ , 1.4), 231 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_5\text{S}$ requires C, 62.82, H, 5.77; N, 3.49%. Found: C, 62.92; H, 5.85; N, 3.34%.

6,8-Dichloro-2-methyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4e): a white solid: mp. 141-142 °C; IR (CH_2Cl_2) ν 3272, 1716, 1463, 1245, 1201, 1158 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 1.26 (3H, t, $J = 7.2$ Hz, CH_3), 2.41 (3H, s, Me), 2.46 (3H, s, Me), 4.02 (1H, dq, $J = 10.8, 7.2$ Hz), 4.15 (1H, dq, $J = 10.8, 7.2$ Hz), 5.07 (1H, d, $J = 6.3$ Hz, NH), 5.49 (1H, d, $J = 6.3$ Hz, CH), 7.06 (1H, d, $J = 2.4$ Hz, Ar), 7.21 (2H, d, $J = 8.4$ Hz, Ar), 7.27 (1H, d, $J = 2.4$ Hz, Ar), 7.52 (2H, d, $J = 8.4$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 14.1, 19.5, 21.4, 47.5, 60.9, 103.3, 122.2, 122.3, 126.6, 127.7, 129.1, 129.28, 129.34, 138.7, 143.2, 145.4, 162.9, 165.7. MS (EI) m/e 300 ($\text{M}^+ - 155$, 63.3), 285 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{NO}_5\text{S}$ requires C, 52.64, H, 4.20; N, 3.07%. Found: C, 52.92; H, 4.08; N, 2.94%.

6-Bromo-2-methyl-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4f): a colorless solid: mp. 150-151 °C; IR (CH_2Cl_2) ν 3273, 1712, 1336, 1225, 1157, 1071 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 1.24 (3H, t, $J = 7.2$ Hz, CH_3), 2.38 (3H, s, Me), 2.40 (3H, s, Me), 3.97 (1H, dq, $J = 10.8, 7.2$ Hz), 4.11 (1H, dq, $J = 10.8, 7.2$ Hz), 5.44 (1H, d, $J = 6.6$ Hz, NH), 5.61 (1H, d, $J = 6.6$ Hz, CH), 6.88 (1H, d, $J = 9.0$ Hz, Ar), 7.17-7.19 (3H, m, Ar), 7.25-7.28 (1H, m, Ar), 7.48 (2H, d, $J = 7.8$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS,

75.44 MHz) δ 14.1, 19.7, 21.5, 47.3, 60.7, 102.9, 116.7, 118.0, 121.3, 126.5, 129.2, 131.9, 132.0, 138.9, 143.0, 149.7, 163.0, 166.1. MS (EI) m/e 465 (M^+ , 1.3), 295 (M^+ -170, 100). Anal. Calcd. for $C_{20}H_{20}BrNO_5S$ requires C, 51.51, H, 4.32; N, 3.00%. Found: C, 51.39; H, 4.28; N, 2.85%.

2-Methyl-6-nitro-4-(toluene-4-sulfonylamino)-4H-chromene-3-carboxylic acid ethyl ester (4g): a white solid: mp. 194-196 °C; IR (CH_2Cl_2) ν 3312, 1678, 1339, 1249, 1158, 1028 cm^{-1} ; 1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.30 (3H, t, J = 7.2 Hz, CH_3), 2.35 (3H, s, Me), 2.46 (3H, s, Me), 4.06-4.25 (2H, m, CH_2), 5.42 (1H, d, J = 6.0 Hz, NH), 5.52 (1H, d, J = 6.6 Hz, CH), 7.12-7.16 (3H, m, Ar), 7.41-7.45 (2H, m, Ar), 7.97 (1H, d, J = 2.7 Hz, Ar), 8.07 (1H, dd, J = 9.0, 2.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 14.1, 19.6, 21.3, 47.4, 61.1, 103.4, 117.3, 119.9, 124.6, 126.1, 126.5, 129.3, 138.9, 143.3, 143.8, 154.9, 162.8, 165.7. MS (EI) m/e 432 (M^+ , 0.51), 262 (M^+ -170, 100). Anal. Calcd. for $C_{20}H_{20}N_2O_7S$ requires C, 55.55, H, 4.66; N, 6.48%. Found: C, 55.48; H, 4.60; N, 6.25%.

Typical Reaction Procedure for DABCO-catalyzed Reaction of Penta-3,4-dien-2-one **2b with Salicyl *N*-Tosylimine **1a**.**

To a flame-dried Schlenk tube at room temperature was in turn added molecular sieve 4A (100 mg), DABCO (5.6 mg, 0.05 mmol), salicyl *N*-tosylimine **1a** (138 mg, 0.50 mmol), THF (2.0 mL) and penta-3,4-dien-2-one **2b** (55 μ L, 0.60 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When **1a** disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash

chromatography (eluent: EtOAc:Petroleum ether = 1:4-2:1) to yield **5a** (156 mg, 87 %) as a colorless solid.

***N*-(3-Acetyl-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5a):** a colorless solid: mp. 146-147 °C; IR (CH₂Cl₂) ν 3263, 1680, 1573, 1381, 1244, 1222, 1156 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.28 (3H, s, Me), 2.36 (3H, s, Me), 2.40 (3H, s, Me), 4.99 (1H, d, J = 7.2 Hz, NH), 5.59 (1H, d, J = 7.2 Hz, CH), 6.93-6.98 (1H, m, Ar), 7.02-7.05 (1H, m, Ar), 7.17-7.25 (4H, m, Ar), 7.53 (2H, d, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 20.3, 21.4, 29.7, 48.1, 111.8, 116.2, 120.2, 124.5 (2C), 126.7, 129.0, 129.3, 138.7, 143.0, 150.3, 162.2, 198.2. MS (EI) m/e 357 (M⁺, 4.32), 187 (M⁺-170, 100). Anal. Calcd. for C₁₉H₁₉NO₄S requires C, 63.85, H, 5.36; N, 3.92%. Found: C, 64.12; H, 5.53; N, 3.84%.

***N*-(3-Acetyl-8-methoxy-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5b):** a white solid: mp. 163-164 °C; IR (CH₂Cl₂) ν 3263, 1678, 1565, 1491, 1243, 1211, 1155, 1095 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.28 (3H, s, Me), 2.30 (3H, s, Me), 2.40 (3H, s, Me), 3.87 (3H, s, MeO), 4.98 (1H, d, J = 7.5 Hz, NH), 5.64 (1H, d, J = 7.5 Hz, CH), 6.79-6.96 (3H, m, Ar), 7.20 (2H, d, J = 8.4 Hz, Ar), 7.59 (2H, d, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 19.7, 21.4, 29.5, 48.0, 55.8, 110.8, 111.3, 120.5, 121.6, 124.3, 126.7, 129.3, 138.9, 139.8, 143.0, 147.1, 161.6, 198.4. MS (EI) m/e 387 (M⁺, 2.54), 217 (M⁺-170, 100). Anal. Calcd. for C₂₀H₂₁NO₅S requires C, 62.00, H, 5.46; N, 3.62%. Found: C, 62.05; H, 5.51; N, 3.44%.

***N*-(3-Acetyl-7-methoxy-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5c):**

a colorless solid: mp. 150-152 °C; IR (CH₂Cl₂) ν 3259, 1665, 1610, 1330, 1280, 1212, 1162 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.28 (3H, s, Me), 2.35 (3H, s, Me), 2.40 (3H, s, Me), 3.78 (3H, s, MeO), 4.83 (1H, d, J = 7.5 Hz, NH), 5.55 (1H, d, J = 7.5 Hz, CH), 6.51-6.55 (2H, m, Ar), 7.13 (1H, d, J = 8.4 Hz, Ar), 7.20 (2H, d, J = 8.1 Hz, Ar), 7.55 (2H, d, J = 8.1 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 20.3, 21.4, 29.7, 48.0, 55.4, 100.6, 111.6, 112.2, 112.5, 126.8, 129.3, 130.0, 138.8, 143.0, 151.2, 160.1, 161.7, 198.4. MS (EI) m/e 387 (M⁺, 4.00), 91 (M⁺-296, 100). Anal. Calcd. for C₂₀H₂₁NO₅S requires C, 62.00, H, 5.46; N, 3.62%. Found: C, 62.20; H, 5.56; N, 3.44%.

***N*-(3-Acetyl-6-methoxy-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5d):**

a colorless solid: mp. 134-135 °C; IR (CH₂Cl₂) ν 3263, 1679, 1576, 1498, 1338, 1220, 1156 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.30 (3H, s, Me), 2.36 (3H, s, Me), 2.39 (3H, s, Me), 3.62 (3H, s, MeO), 5.04 (1H, d, J = 6.6 Hz, NH), 5.55 (1H, d, J = 6.6 Hz, CH), 6.65 (1H, d, J = 2.7 Hz, Ar), 6.77 (1H, dd, J = 8.7, 2.7 Hz, Ar), 6.97 (1H, d, J = 8.7 Hz, Ar), 7.18 (2H, d, J = 8.4 Hz, Ar), 7.52 (2H, d, J = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 20.5, 21.4, 29.8, 48.6, 55.3, 111.1, 111.9, 116.3, 117.3, 120.4, 126.6, 129.2, 138.9, 142.9, 144.5, 156.0, 162.5, 198.2. MS (EI) m/e 387 (M⁺, 6.98), 217 (M⁺-170, 100). Anal. Calcd. for C₂₀H₂₁NO₅S requires C, 62.00, H, 5.46; N, 3.62%. Found: C, 62.05; H, 5.44; N, 3.39%.

***N*-(3-Acetyl-2,6-dimethyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5e):** a

colorless solid: mp. 150-151 °C; IR (CH₂Cl₂) ν 3262, 1680, 1574, 1499, 1329, 1220, 1157

cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.07 (3H, s, Me), 2.34 (3H, s, Me), 2.35 (3H, s, Me), 2.39 (3H, s, Me), 5.22 (1H, d, *J* = 7.2 Hz, NH), 5.50 (1H, d, *J* = 7.2 Hz, CH), 6.76 (1H, s, Ar), 6.88-6.98 (2H, m, Ar), 7.16 (2H, d, *J* = 8.4 Hz, Ar), 7.50 (2H, d, *J* = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 20.4 (2C), 21.4, 29.8, 48.4, 111.8, 115.9, 119.4, 126.7, 129.2, 129.3, 129.7, 133.9, 138.9, 142.8, 148.4, 162.4, 198.3. MS (EI) *m/e* 371 (M⁺, 1.63), 201 (M⁺-170, 100). Anal. Calcd. for C₂₀H₂₁NO₄S requires C, 64.67, H, 5.70; N, 3.77%. Found: C, 64.95; H, 5.56; N, 3.74%.

***N*-(3-Acetyl-6-bromo-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5f):** a colorless solid: mp. 150-152 °C; IR (CH₂Cl₂) ν 3259, 1682, 1571, 1480, 1334, 1243, 1225, 1157 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.37 (3H, s, Me), 2.39 (3H, s, Me), 2.42 (3H, s, Me), 5.06 (1H, d, *J* = 6.9 Hz, NH), 5.46 (1H, d, *J* = 6.9 Hz, CH), 6.91 (1H, d, *J* = 8.7 Hz, Ar), 7.06 (1H, d, *J* = 2.4 Hz, Ar), 7.20 (2H, d, *J* = 8.4 Hz, Ar), 7.27 (1H, dd, *J* = 8.7, 2.4 Hz, Ar), 7.49 (2H, d, *J* = 8.4 Hz, Ar). ¹³C NMR (CDCl₃, TMS, 75.44 MHz) δ 20.2, 21.5, 29.7, 47.6, 111.5, 116.4, 118.0, 121.6, 126.4, 129.4, 131.6, 131.8, 138.3, 143.2, 149.3, 162.2, 198.0. MS (EI) *m/e* 435 (M⁺, 0.52), 265 (M⁺-170, 100). Anal. Calcd. for C₁₉H₁₈BrNO₄S requires C, 52.30, H, 4.16; N, 3.21%. Found: C, 52.25; H, 4.07; N, 2.98%.

***N*-(3-Acetyl-6,8-dichloro-2-methyl-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5g):** a colorless solid: mp. 155-157 °C; IR (CH₂Cl₂) ν 3258, 1686, 1573, 1464, 1251, 1206, 1157 cm⁻¹; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 2.34 (3H, s, Me), 2.41 (3H, s, Me), 2.43 (3H, s, Me), 5.17 (1H, d, *J* = 7.2 Hz, NH), 5.47 (1H, d, *J* = 7.2 Hz, CH), 6.91 (1H, d, *J* = 2.4 Hz, Ar),

7.20-7.24 (3H, m, Ar), 7.50-7.53 (2H, m, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 20.2, 21.5, 29.9, 47.7, 112.0, 122.3, 122.5, 126.6, 127.3, 128.9, 129.3, 129.5, 138.2, 143.5, 145.2, 162.0, 197.6. MS (EI) m/e 425 (M^+ , 0.85), 255 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{NO}_4\text{S}$ requires C, 53.53; H, 4.02; N, 3.29%. Found: C, 53.43; H, 3.98; N, 3.09%.

***N*-(3-Acetyl-2-methyl-6-nitro-4H-chromen-4-yl)-4-methyl-benzenesulfonamide (5h):** a white solid: mp. 157-159 °C; IR (CH_2Cl_2) ν 3263, 1686, 1527, 1341, 1245, 1213, 1157 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 2.34 (3H, s, Me), 2.36 (3H, s, Me), 2.39 (3H, s, Me), 5.53 (1H, d, $J = 7.2$ Hz, NH), 5.84 (1H, d, $J = 7.2$ Hz, CH), 7.10-7.13 (3H, m, Ar), 7.44 (2H, d, $J = 8.4$ Hz, Ar), 7.84 (1H, d, $J = 3.0$ Hz, Ar), 7.99-8.03 (1H, m, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 20.1, 21.3, 30.0, 47.4, 112.1, 117.3, 120.3, 124.4, 125.6, 126.4, 129.4, 138.4, 143.5, 143.6, 154.5, 161.7, 197.6. MS (EI) m/e 402 (M^+ , 1.46), 232 ($\text{M}^+ - 170$, 100). Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_6\text{S}$ requires C, 56.71; H, 4.51; N, 6.96%. Found: C, 57.00; H, 4.73; N, 6.86%.

***N*-(2-Acetyl-3-methyl-1H-benzo[f]chromen-1-yl)-4-methyl-benzenesulfonamide (5i):** a yellow solid: mp. 160-161 °C; IR (CH_2Cl_2) ν 3270, 2924, 1682, 1642, 1594, 1332, 1231, 1155 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 2.16 (3H, s, Me), 2.44 (3H, s, Me), 2.48 (3H, s, Me), 5.67 (1H, d, $J = 4.8$ Hz, NH), 6.05 (1H, d, $J = 4.8$ Hz, CH), 6.70 (2H, d, $J = 8.4$ Hz, Ar), 7.07 (2H, d, $J = 8.4$ Hz, Ar), 7.19 (1H, d, $J = 9.0$ Hz, Ar), 7.29-7.38 (2H, m, Ar), 7.59-7.67 (2H, m, Ar), 7.89 (1H, d, $J = 8.1$ Hz, Ar). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 20.9, 21.2, 31.1, 45.3, 110.8, 113.5, 116.4, 122.7, 124.8, 126.2, 127.1, 128.0, 128.3, 130.2, 130.66, 130.69, 137.7,

141.9, 149.4, 162.6, 197.9. MS (EI) m/e 407 (M^+ , 2.91), 91 (M^+-316 , 100). Anal. Calcd. for $C_{23}H_{21}NO_4S$ requires C, 67.79; H, 5.19; N, 3.44%. Found: C, 67.73; H, 5.16; N, 3.26%.

Typical Reaction Procedure for DABCO-catalyzed Reaction of Penta-3,4-dien-2-one **2b with Salicylaldehyde.**

To a solution of salicylaldehyde (55 μ L, 0.50 mmol) and penta-3,4-dien-2-one **2b** (55 μ L, 0.60 mmol) in THF (2.0 mL) at room temperature was added DABCO (18 mg, 0.0625 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When salicylaldehyde disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (eluent: EtOAc:Petroleum ether = 1:10) to yield **13a** (78 mg, 76 %) as a colorless liquid.

***E*-2-(1-Methyl-3-oxo-but-1-enyloxy)-benzaldehyde (13a):** a colorless liquid: IR (CH_2Cl_2) ν 2855, 1693, 1596, 1578, 1389, 1274, 1238, 1209, 1151 cm^{-1} ; 1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.04 (3H, s, Me), 2.54 (3H, s, Me), 5.25 (1H, s), 7.10–7.13 (1H, m, Ar), 7.37–7.42 (1H, m, Ar), 7.65–7.70 (1H, m, Ar), 7.95–7.98 (1H, m, Ar), 10.14 (1H, d, J = 0.6 Hz, CHO). ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 18.6, 32.0, 105.3, 122.8, 126.3, 128.1, 129.1, 135.9, 155.3, 172.0, 188.1, 196.9. MS (EI) m/e 205 (M^++1 , 64.7), 204 (M^+ , 17.7), 161 (M^+-43 , 100). HRMS Calcd. for $C_{12}H_{12}O_3Na^+$ requires 227.0679, Found 227.0690.

Typical Reaction Procedure for DABCO-catalyzed Reaction of Ethyl 2,3-butadienoate **2a with Salicylaldehyde.**

To a solution of salicylaldehyde (55 μ L, 0.50 mmol) and ethyl 2,3-butadienoate **2a** (69 μ L, 0.60 mmol) in THF (2.0 mL) at room temperature was added DABCO (18 mg, 0.0625 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When salicylaldehyde disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (eluent: EtOAc:Petroleum ether = 1:10) to yield **13b** (83 mg, 71 %) as a colorless liquid.

***E*- 3-(2-Formyl-phenoxy)-but-2-enoic acid ethyl ester (**13b**):** a colorless liquid: IR (CHCl_3) ν 2981, 1712, 1639, 1601, 1387, 1274, 1247, 1212, 1131 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 1.21 (3H, t, J = 7.2 Hz, CH_3), 2.57 (3H, s, Me), 4.10 (2H, q, J = 7.2 Hz, CH_2), 4.84 (1H, s), 7.11-7.14 (1H, m, Ar), 7.35-7.40 (1H, m, Ar), 7.63-7.69 (1H, m, Ar), 7.94-7.97 (1H, m, Ar), 10.14 (1H, d, J = 0.6 Hz, CHO). ^{13}C NMR (CDCl_3 , TMS, 75.44 MHz) δ 14.2, 18.0, 59.8,

98.0, 122.8, 126.3, 128.1, 129.2, 135.9, 155.4, 166.9, 172.6, 188.2. MS (EI) m/e 234 (M^+ , 7.23), 147 ($M^+ - 87$, 100). HRMS Calcd. for $C_{13}H_{14}O_4Na^+$ requires 257.0784, Found 257.0793.

Reference:

- (1) Wynne, J. H.; Price, S. E.; Rorer, J. R.; Stalick, W. M. *Synth. Commun.* **2003**, 33, 341.
- (2) Anderson, J. C.; Cubbon, R. J.; Harling, J. D. *Tetrahedron: Asymmetry* **2001**, 12, 923.
- (3) Buono, G. *Synthesis* **1981**, 272.

Figure 1. The ORTEP draw of **3a**.

The crystal data of **3a** has been deposited in CCDC with number 266106. Empirical Formula: $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$; Formula Weight: 387.44; Temperature: 293(2)K; Crystal Dimensions: 0.516 x 0.427 x 0.344 mm; Crystal System: Orthorhombic; Space group: Pbc_a; Unit cell dimensions: $a = 15.9518(12)\text{\AA}$, $b = 12.6973(9)\text{\AA}$, $c = 19.0989(13)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 3868.4(5)\text{\AA}^3$; $Z = 8$; $D_{\text{calc.}} = 1.330 \text{ mg/m}^3$; $F_{000} = 1632$; Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0435$, $R_2 = 0.1235$.

Table 1. Crystal data and structure refinement for cd24432.

Identification code	cd24432
Empirical formula	C ₂₀ H ₂₁ N O ₅ S
Formula weight	387.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 15.9518(12) Å alpha = 90 deg. b = 12.6973(9) Å beta = 90 deg. c = 19.0989(13) Å gamma = 90 deg.
Volume	3868.4(5) Å ³
Z, Calculated density	8, 1.330 Mg/m ³
Absorption coefficient	0.198 mm ⁻¹
F(000)	1632
Crystal size	0.516 x 0.427 x 0.344 mm
Theta range for data collection	2.13 to 27.00 deg.
Limiting indices	-20 ≤ h ≤ 14, -15 ≤ k ≤ 16, -19 ≤ l ≤ 24
Reflections collected / unique	21440 / 4224 [R(int) = 0.0476]
Completeness to theta = 27.00	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.62973
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4224 / 0 / 318

Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0435$, $wR2 = 0.1235$
R indices (all data)	$R1 = 0.0523$, $wR2 = 0.1290$
Extinction coefficient	$0.0012(5)$
Largest diff. peak and hole	0.331 and -0.316 e. Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd24432.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	2407(1)	8769(1)	1605(1)	41(1)
O(1)	770(1)	10326(1)	295(1)	57(1)
O(2)	82(1)	7780(1)	-236(1)	65(1)
O(3)	601(1)	6206(1)	-496(1)	54(1)
O(4)	2186(1)	9852(1)	1533(1)	54(1)
O(5)	3181(1)	8481(1)	1925(1)	59(1)
N(1)	2420(1)	8273(1)	817(1)	40(1)
C(1)	2697(1)	7163(1)	745(1)	51(1)
C(2)	2024(1)	6672(1)	323(1)	46(1)
C(3)	1449(1)	7367(1)	136(1)	39(1)
C(4)	1655(1)	8464(1)	386(1)	35(1)
C(5)	1803(1)	9242(1)	-198(1)	40(1)
C(6)	2409(1)	9079(2)	-702(1)	56(1)
C(7)	2530(2)	9804(2)	-1240(1)	74(1)
C(8)	2033(2)	10675(2)	-1274(1)	76(1)
C(9)	1423(2)	10857(2)	-779(1)	63(1)
C(10)	1319(1)	10152(1)	-232(1)	44(1)
C(11)	646(1)	7159(1)	-218(1)	43(1)
C(12)	-197(1)	5920(2)	-818(1)	65(1)
C(13)	-72(2)	4921(2)	-1196(2)	83(1)
C(14)	1590(1)	8131(1)	2051(1)	42(1)
C(15)	779(1)	8515(1)	2007(1)	50(1)
C(16)	133(1)	7969(1)	2312(1)	56(1)
C(17)	266(1)	7044(1)	2670(1)	55(1)
C(18)	1075(1)	6680(2)	2717(1)	69(1)
C(19)	1742(1)	7211(2)	2416(1)	61(1)
C(20)	-444(2)	6440(2)	2990(1)	80(1)

Table 3. Bond lengths [Å] and angles [deg] for cd24432.

S(1)-O(5)	1.4258(12)
S(1)-O(4)	1.4261(12)
S(1)-N(1)	1.6329(13)
S(1)-C(14)	1.7546(16)
O(1)-C(10)	1.352(2)
O(1)-H(23)	0.87(3)
O(2)-C(11)	1.1975(19)
O(3)-C(11)	1.3225(18)
O(3)-C(12)	1.461(2)
N(1)-C(1)	1.483(2)
N(1)-C(4)	1.4926(18)
C(1)-C(2)	1.481(2)
C(1)-H(1)	0.98(2)
C(1)-H(2)	0.93(2)
C(2)-C(3)	1.322(2)
C(2)-H(3)	0.929(19)
C(3)-C(11)	1.472(2)
C(3)-C(4)	1.5085(19)
C(4)-C(5)	1.507(2)
C(4)-H(4)	0.891(16)
C(5)-C(6)	1.381(2)
C(5)-C(10)	1.390(2)
C(6)-C(7)	1.392(3)
C(6)-H(6)	0.962(18)
C(7)-C(8)	1.363(4)
C(7)-H(7)	1.02(3)
C(8)-C(9)	1.375(3)
C(8)-H(8)	1.03(3)
C(9)-C(10)	1.387(2)
C(9)-H(9)	0.97(2)
C(12)-C(13)	1.473(3)
C(12)-H(10)	0.91(2)
C(12)-H(11)	1.07(2)
C(13)-H(12)	1.08(3)
C(13)-H(13)	0.85(3)
C(13)-H(14)	0.99(3)
C(14)-C(19)	1.382(2)
C(14)-C(15)	1.384(2)
C(15)-C(16)	1.372(3)
C(15)-H(15)	0.95(2)

C(16)-C(17)	1.376(3)
C(16)-H(16)	0.90(2)
C(17)-C(18)	1.373(3)
C(17)-C(20)	1.499(3)
C(18)-C(19)	1.385(3)
C(18)-H(18)	0.90(2)
C(19)-H(19)	0.98(2)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

O(5)-S(1)-O(4)	120.19(8)
O(5)-S(1)-N(1)	106.56(7)
O(4)-S(1)-N(1)	106.58(7)
O(5)-S(1)-C(14)	108.49(8)
O(4)-S(1)-C(14)	108.00(7)
N(1)-S(1)-C(14)	106.21(7)
C(10)-O(1)-H(23)	114.2(16)
C(11)-O(3)-C(12)	116.35(13)
C(1)-N(1)-C(4)	110.32(11)
C(1)-N(1)-S(1)	117.10(11)
C(4)-N(1)-S(1)	115.81(9)
C(2)-C(1)-N(1)	103.55(12)
C(2)-C(1)-H(1)	111.6(11)
N(1)-C(1)-H(1)	108.7(11)
C(2)-C(1)-H(2)	113.9(13)
N(1)-C(1)-H(2)	113.6(12)
H(1)-C(1)-H(2)	105.5(18)
C(3)-C(2)-C(1)	111.66(14)
C(3)-C(2)-H(3)	127.3(11)
C(1)-C(2)-H(3)	121.1(11)
C(2)-C(3)-C(11)	127.42(14)
C(2)-C(3)-C(4)	112.35(13)
C(11)-C(3)-C(4)	120.02(12)
N(1)-C(4)-C(5)	112.70(12)
N(1)-C(4)-C(3)	101.67(11)
C(5)-C(4)-C(3)	113.94(12)
N(1)-C(4)-H(4)	111.6(10)
C(5)-C(4)-H(4)	104.5(9)
C(3)-C(4)-H(4)	112.6(9)
C(6)-C(5)-C(10)	118.75(15)
C(6)-C(5)-C(4)	121.78(15)
C(10)-C(5)-C(4)	119.47(14)
C(5)-C(6)-C(7)	120.8(2)

C(5)-C(6)-H(6)	121.3(11)
C(7)-C(6)-H(6)	117.9(11)
C(8)-C(7)-C(6)	119.4(2)
C(8)-C(7)-H(7)	121.8(14)
C(6)-C(7)-H(7)	118.6(14)
C(7)-C(8)-C(9)	121.02(19)
C(7)-C(8)-H(8)	130.1(16)
C(9)-C(8)-H(8)	108.8(16)
C(8)-C(9)-C(10)	119.6(2)
C(8)-C(9)-H(9)	120.7(14)
C(10)-C(9)-H(9)	119.7(14)
O(1)-C(10)-C(9)	122.16(16)
O(1)-C(10)-C(5)	117.46(13)
C(9)-C(10)-C(5)	120.36(17)
O(2)-C(11)-O(3)	123.41(15)
O(2)-C(11)-C(3)	123.27(14)
O(3)-C(11)-C(3)	113.28(13)
O(3)-C(12)-C(13)	107.60(19)
O(3)-C(12)-H(10)	108.4(15)
C(13)-C(12)-H(10)	112.7(15)
O(3)-C(12)-H(11)	104.2(12)
C(13)-C(12)-H(11)	113.9(13)
H(10)-C(12)-H(11)	110(2)
C(12)-C(13)-H(12)	105.3(16)
C(12)-C(13)-H(13)	110.0(18)
H(12)-C(13)-H(13)	107(3)
C(12)-C(13)-H(14)	114.3(18)
H(12)-C(13)-H(14)	109(2)
H(13)-C(13)-H(14)	111(2)
C(19)-C(14)-C(15)	119.42(15)
C(19)-C(14)-S(1)	120.35(13)
C(15)-C(14)-S(1)	120.14(12)
C(16)-C(15)-C(14)	119.96(16)
C(16)-C(15)-H(15)	120.4(12)
C(14)-C(15)-H(15)	119.5(12)
C(15)-C(16)-C(17)	121.67(18)
C(15)-C(16)-H(16)	120.0(13)
C(17)-C(16)-H(16)	118.1(13)
C(18)-C(17)-C(16)	117.75(17)
C(18)-C(17)-C(20)	120.73(18)
C(16)-C(17)-C(20)	121.52(19)
C(17)-C(18)-C(19)	122.04(17)
C(17)-C(18)-H(18)	115.6(13)
C(19)-C(18)-H(18)	122.3(13)

C(14)-C(19)-C(18)	119.15(18)
C(14)-C(19)-H(19)	119.5(14)
C(18)-C(19)-H(19)	121.2(14)
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd24432.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	43(1)	39(1)	41(1)	-5(1)	-2(1)	-5(1)
O(1)	57(1)	43(1)	72(1)	2(1)	0(1)	14(1)
O(2)	48(1)	45(1)	101(1)	-9(1)	-22(1)	11(1)
O(3)	50(1)	40(1)	72(1)	-13(1)	-17(1)	1(1)
O(4)	67(1)	35(1)	59(1)	-7(1)	5(1)	-8(1)
O(5)	46(1)	73(1)	56(1)	-6(1)	-13(1)	-6(1)
N(1)	37(1)	40(1)	41(1)	-6(1)	-3(1)	5(1)
C(1)	46(1)	45(1)	62(1)	-11(1)	-11(1)	14(1)
C(2)	44(1)	38(1)	57(1)	-10(1)	-4(1)	7(1)
C(3)	39(1)	33(1)	46(1)	-4(1)	0(1)	1(1)
C(4)	33(1)	33(1)	40(1)	-3(1)	0(1)	3(1)
C(5)	41(1)	38(1)	40(1)	-4(1)	-4(1)	-8(1)
C(6)	59(1)	61(1)	48(1)	-6(1)	7(1)	-7(1)
C(7)	83(2)	90(2)	48(1)	-4(1)	14(1)	-31(1)
C(8)	103(2)	73(1)	51(1)	15(1)	-11(1)	-32(1)
C(9)	81(1)	50(1)	58(1)	12(1)	-19(1)	-14(1)
C(10)	50(1)	36(1)	47(1)	0(1)	-13(1)	-8(1)
C(11)	43(1)	33(1)	52(1)	1(1)	-5(1)	0(1)
C(12)	63(1)	57(1)	76(1)	-8(1)	-26(1)	-8(1)
C(13)	94(2)	71(2)	84(2)	-23(1)	-24(2)	-18(1)
C(14)	49(1)	39(1)	39(1)	-1(1)	1(1)	-1(1)
C(15)	56(1)	41(1)	54(1)	4(1)	14(1)	11(1)
C(16)	54(1)	55(1)	61(1)	2(1)	17(1)	9(1)
C(17)	65(1)	47(1)	52(1)	-4(1)	13(1)	-7(1)
C(18)	78(1)	53(1)	74(1)	26(1)	2(1)	0(1)
C(19)	54(1)	60(1)	71(1)	22(1)	-7(1)	4(1)
C(20)	92(2)	62(1)	87(2)	1(1)	33(1)	-18(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd24432.

	x	y	z	U(eq)
H(20A)	-764	6105	2628	121
H(20B)	-798	6913	3247	121
H(20C)	-224	5914	3302	121
H(1)	3236(13)	7151(15)	499(10)	57(5)
H(2)	2794(13)	6832(16)	1170(11)	62(5)
H(3)	2028(11)	5955(15)	227(9)	50(5)
H(4)	1243(10)	8748(11)	639(8)	34(4)
H(6)	2762(11)	8463(15)	-694(9)	49(5)
H(7)	3018(16)	9694(19)	-1574(13)	94(8)
H(8)	2038(18)	11290(20)	-1623(14)	106(9)
H(9)	1056(15)	11460(18)	-817(12)	87(7)
H(10)	-360(14)	6453(18)	-1105(13)	81(7)
H(11)	-622(15)	5863(19)	-387(12)	82(7)
H(12)	370(20)	5100(20)	-1604(18)	133(11)
H(13)	-523(18)	4740(20)	-1397(15)	97(8)
H(14)	151(19)	4340(30)	-903(15)	119(10)
H(15)	681(12)	9175(16)	1793(9)	58(5)
H(16)	-384(13)	8245(16)	2317(11)	66(6)
H(18)	1139(13)	6064(16)	2944(10)	64(5)
H(19)	2312(14)	6917(18)	2425(12)	78(6)
H(23)	449(16)	10870(20)	232(12)	91(8)

Table 6. Torsion angles [deg] for cd24432.

O(5)-S(1)-N(1)-C(1)	46.06(13)
O(4)-S(1)-N(1)-C(1)	175.55(12)
C(14)-S(1)-N(1)-C(1)	-69.47(13)
O(5)-S(1)-N(1)-C(4)	178.97(10)
O(4)-S(1)-N(1)-C(4)	-51.55(12)
C(14)-S(1)-N(1)-C(4)	63.44(12)
C(4)-N(1)-C(1)-C(2)	-6.03(18)
S(1)-N(1)-C(1)-C(2)	129.29(13)
N(1)-C(1)-C(2)-C(3)	2.7(2)
C(1)-C(2)-C(3)-C(11)	-172.96(16)
C(1)-C(2)-C(3)-C(4)	1.7(2)
C(1)-N(1)-C(4)-C(5)	-115.60(14)
S(1)-N(1)-C(4)-C(5)	108.45(12)
C(1)-N(1)-C(4)-C(3)	6.79(16)
S(1)-N(1)-C(4)-C(3)	-129.16(11)
C(2)-C(3)-C(4)-N(1)	-5.22(17)
C(11)-C(3)-C(4)-N(1)	169.87(13)
C(2)-C(3)-C(4)-C(5)	116.30(15)
C(11)-C(3)-C(4)-C(5)	-68.60(18)
N(1)-C(4)-C(5)-C(6)	57.95(19)
C(3)-C(4)-C(5)-C(6)	-57.24(19)
N(1)-C(4)-C(5)-C(10)	-121.92(14)
C(3)-C(4)-C(5)-C(10)	122.89(15)
C(10)-C(5)-C(6)-C(7)	-0.7(3)
C(4)-C(5)-C(6)-C(7)	179.41(17)
C(5)-C(6)-C(7)-C(8)	-1.1(3)
C(6)-C(7)-C(8)-C(9)	1.0(3)
C(7)-C(8)-C(9)-C(10)	0.9(3)
C(8)-C(9)-C(10)-O(1)	175.37(17)
C(8)-C(9)-C(10)-C(5)	-2.8(3)
C(6)-C(5)-C(10)-O(1)	-175.58(15)
C(4)-C(5)-C(10)-O(1)	4.3(2)
C(6)-C(5)-C(10)-C(9)	2.7(2)
C(4)-C(5)-C(10)-C(9)	-177.44(14)
C(12)-O(3)-C(11)-O(2)	-1.8(3)
C(12)-O(3)-C(11)-C(3)	176.28(16)
C(2)-C(3)-C(11)-O(2)	163.17(18)
C(4)-C(3)-C(11)-O(2)	-11.1(2)
C(2)-C(3)-C(11)-O(3)	-14.9(2)
C(4)-C(3)-C(11)-O(3)	170.82(13)

C(11)-O(3)-C(12)-C(13)	170.50(19)
O(5)-S(1)-C(14)-C(19)	-24.54(17)
O(4)-S(1)-C(14)-C(19)	-156.31(15)
N(1)-S(1)-C(14)-C(19)	89.68(16)
O(5)-S(1)-C(14)-C(15)	159.09(13)
O(4)-S(1)-C(14)-C(15)	27.32(15)
N(1)-S(1)-C(14)-C(15)	-86.69(14)
C(19)-C(14)-C(15)-C(16)	-1.4(3)
S(1)-C(14)-C(15)-C(16)	175.02(14)
C(14)-C(15)-C(16)-C(17)	0.5(3)
C(15)-C(16)-C(17)-C(18)	0.3(3)
C(15)-C(16)-C(17)-C(20)	-178.85(19)
C(16)-C(17)-C(18)-C(19)	-0.3(3)
C(20)-C(17)-C(18)-C(19)	178.9(2)
C(15)-C(14)-C(19)-C(18)	1.4(3)
S(1)-C(14)-C(19)-C(18)	-175.02(16)
C(17)-C(18)-C(19)-C(14)	-0.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd24432 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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Figure 1. The ORTEP draw of **4a**.

The crystal data of **4a** has been deposited in CCDC with number 266105. Empirical Formula: $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$; Formula Weight: 387.44; Temperature: 293(2)K; Crystal Dimensions: 0.516 x 0.354 x 0.220 mm; Crystal System: Monoclinic; Space group: $P2(1)/c$; Unit cell dimensions: $a = 11.8337(13)\text{\AA}$, $b = 17.2263(18)\text{\AA}$, $c = 9.9628(10)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 106.880(2)^\circ$, $\gamma = 90^\circ$, $V = 1943.4(4)\text{\AA}^3$; $Z = 4$; $D_{\text{calc.}} = 1.324 \text{ mg/m}^3$; $F_{000} = 816$; Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0642$, $R_2 = 0.1617$.

Table 1. Crystal data and structure refinement for cd2b44.

Identification code	cd2544
Empirical formula	C20 H21 N O5 S
Formula weight	387.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.8337(13) Å alpha = 90 deg. b = 17.2263(18) Å beta = 106.880(2) deg. c = 9.9628(10) Å gamma = 90 deg.
Volume	1943.4(4) Å ³
Z, Calculated density	4, 1.324 Mg/m ³
Absorption coefficient	0.197 mm ⁻¹
F(000)	816
Crystal size	0.516 x 0.354 x 0.220 mm
Theta range for data collection	1.80 to 26.50 deg.
Limiting indices	-14<=h<=13, -17<=k<=21, -12<=l<=12
Reflections collected / unique	10931 / 4005 [R(int) = 0.1340]
Completeness to theta = 26.50	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.60697
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4005 / 0 / 287
Goodness-of-fit on F ²	0.921
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1617
R indices (all data)	R1 = 0.1008, wR2 = 0.1801
Largest diff. peak and hole	0.293 and -0.226 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd2544. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	3938(1)	10465(1)	2851(1)	66(1)
O(1)	1437(2)	9749(1)	6393(2)	82(1)
O(2)	3180(2)	11055(1)	2064(2)	83(1)
O(3)	5127(2)	10664(1)	3634(2)	77(1)
O(4)	1241(2)	9177(2)	1807(3)	104(1)
O(5)	1512(2)	8143(2)	3182(3)	131(1)
N(1)	3344(2)	10112(2)	3948(3)	65(1)
C(1)	2023(2)	10759(2)	5057(3)	60(1)
C(2)	2295(3)	11539(2)	4989(4)	78(1)
C(3)	2241(3)	12043(2)	6047(5)	93(1)
C(4)	1889(3)	11778(3)	7145(5)	98(1)
C(5)	1622(3)	11008(2)	7257(4)	83(1)
C(6)	1702(2)	10514(2)	6200(3)	67(1)
C(7)	1395(2)	9224(2)	5356(4)	75(1)
C(8)	1628(2)	9413(2)	4174(4)	67(1)
C(9)	2105(2)	10199(2)	3951(3)	61(1)
C(10)	1025(3)	8462(2)	5790(4)	106(1)
C(11)	1474(3)	8836(2)	3044(5)	89(1)
C(12)	1054(4)	8678(3)	591(5)	129(2)
C(13)	108(5)	8808(4)	-406(5)	126(3)
C(14)	4043(2)	9723(2)	1693(3)	65(1)
C(15)	4633(3)	9047(2)	2215(4)	83(1)
C(16)	4734(3)	8471(2)	1319(4)	90(1)
C(17)	4257(3)	8535(2)	-117(4)	81(1)
C(18)	3698(3)	9226(3)	-622(4)	98(1)
C(19)	3592(3)	9813(2)	268(3)	88(1)
C(20)	4345(3)	7885(3)	-1091(4)	116(1)

Table 3. Bond lengths [Å] and angles [deg] for cd2544.

S(1)-O(2)	1.4305(18)
S(1)-O(3)	1.4381(18)
S(1)-N(1)	1.583(3)
S(1)-C(14)	1.750(3)
O(1)-C(7)	1.363(4)
O(1)-C(6)	1.381(3)
O(4)-C(11)	1.321(4)
O(4)-C(12)	1.450(4)
O(5)-C(11)	1.200(4)
N(1)-C(9)	1.474(4)
N(1)-H(1)	0.77(3)
C(1)-C(6)	1.367(4)
C(1)-C(2)	1.387(4)
C(1)-C(9)	1.490(4)
C(2)-C(3)	1.382(5)
C(2)-H(2)	0.95(3)
C(3)-C(4)	1.358(6)
C(3)-H(3)	0.95(3)
C(4)-C(5)	1.374(6)
C(4)-H(4)	1.02(4)
C(5)-C(6)	1.379(5)
C(5)-H(5)	0.97(3)
C(7)-C(8)	1.326(4)
C(7)-C(10)	1.488(4)
C(8)-C(11)	1.474(4)
C(8)-C(9)	1.507(4)
C(9)-H(9)	0.87(3)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(12)-C(13)	1.282(5)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.372(4)
C(14)-C(15)	1.379(4)
C(15)-C(16)	1.363(5)
C(15)-H(15)	0.92(3)
C(16)-C(17)	1.381(5)
C(16)-H(16)	0.94(4)
C(17)-C(18)	1.384(5)
C(17)-C(20)	1.505(5)
C(18)-C(19)	1.375(5)
C(18)-H(18)	0.96(3)
C(19)-H(19)	1.09(4)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
O(2)-S(1)-O(3)	119.12(13)
O(2)-S(1)-N(1)	108.54(14)
O(3)-S(1)-N(1)	106.10(12)
O(2)-S(1)-C(14)	108.13(12)
O(3)-S(1)-C(14)	106.67(14)
N(1)-S(1)-C(14)	107.81(14)
C(7)-O(1)-C(6)	119.1(3)
C(11)-O(4)-C(12)	117.1(3)
C(9)-N(1)-S(1)	127.1(2)
C(9)-N(1)-H(1)	114(2)
S(1)-N(1)-H(1)	118(2)
C(6)-C(1)-C(2)	117.6(3)
C(6)-C(1)-C(9)	120.6(3)
C(2)-C(1)-C(9)	121.7(3)
C(3)-C(2)-C(1)	120.6(4)
C(3)-C(2)-H(2)	124(2)
C(1)-C(2)-H(2)	114(2)

C(4)-C(3)-C(2)	119.7(4)
C(4)-C(3)-H(3)	129(2)
C(2)-C(3)-H(3)	111(2)
C(3)-C(4)-C(5)	121.4(4)
C(3)-C(4)-H(4)	123(2)
C(5)-C(4)-H(4)	115(2)
C(4)-C(5)-C(6)	117.7(4)
C(4)-C(5)-H(5)	114.7(19)
C(6)-C(5)-H(5)	127.5(19)
C(1)-C(6)-C(5)	122.9(3)
C(1)-C(6)-O(1)	122.7(3)
C(5)-C(6)-O(1)	114.4(3)
C(8)-C(7)-O(1)	122.6(3)
C(8)-C(7)-C(10)	129.0(3)
O(1)-C(7)-C(10)	108.3(3)
C(7)-C(8)-C(11)	120.1(3)
C(7)-C(8)-C(9)	122.3(3)
C(11)-C(8)-C(9)	117.5(3)
N(1)-C(9)-C(1)	110.2(2)
N(1)-C(9)-C(8)	108.9(2)
C(1)-C(9)-C(8)	111.4(3)
N(1)-C(9)-H(9)	105.0(19)
C(1)-C(9)-H(9)	112.3(18)
C(8)-C(9)-H(9)	108.7(19)
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(5)-C(11)-O(4)	122.7(4)
O(5)-C(11)-C(8)	126.3(4)
O(4)-C(11)-C(8)	111.0(3)
C(13)-C(12)-O(4)	115.5(4)
C(13)-C(12)-H(12A)	108.4
O(4)-C(12)-H(12A)	108.4
C(13)-C(12)-H(12B)	108.4
O(4)-C(12)-H(12B)	108.4
H(12A)-C(12)-H(12B)	107.5
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	119.2(3)
C(19)-C(14)-S(1)	121.2(3)
C(15)-C(14)-S(1)	119.5(2)
C(16)-C(15)-C(14)	119.9(3)
C(16)-C(15)-H(15)	115.9(19)
C(14)-C(15)-H(15)	124.1(19)
C(15)-C(16)-C(17)	122.2(4)
C(15)-C(16)-H(16)	121(2)
C(17)-C(16)-H(16)	117(2)
C(16)-C(17)-C(18)	117.0(4)
C(16)-C(17)-C(20)	121.7(4)
C(18)-C(17)-C(20)	121.4(3)
C(19)-C(18)-C(17)	121.5(3)
C(19)-C(18)-H(18)	121.6(19)
C(17)-C(18)-H(18)	116.5(19)
C(14)-C(19)-C(18)	120.2(4)
C(14)-C(19)-H(19)	116.7(19)
C(18)-C(19)-H(19)	123.0(19)
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd2544.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	68(1)	55(1)	64(1)	12(1)	1(1)	5(1)
O(1)	89(2)	61(1)	86(1)	13(1)	9(1)	0(1)
O(2)	96(2)	59(1)	80(1)	24(1)	3(1)	21(1)
O(3)	70(1)	74(1)	75(1)	11(1)	-1(1)	-14(1)
O(4)	98(2)	81(2)	106(2)	-41(2)	-14(1)	17(1)
O(5)	136(2)	48(2)	195(3)	-35(2)	26(2)	6(1)
N(1)	61(2)	66(2)	59(1)	13(1)	0(1)	13(1)
C(1)	52(2)	43(2)	72(2)	-4(1)	-3(1)	1(1)
C(2)	76(2)	50(2)	99(2)	-8(2)	13(2)	-2(1)
C(3)	94(3)	49(2)	122(3)	-21(2)	8(2)	-6(2)
C(4)	95(3)	89(3)	96(3)	-37(3)	5(2)	6(2)
C(5)	80(2)	84(3)	77(2)	-9(2)	9(2)	9(2)
C(6)	55(2)	55(2)	77(2)	-2(2)	-2(1)	6(1)
C(7)	59(2)	48(2)	101(2)	5(2)	-4(2)	5(1)
C(8)	50(2)	41(2)	95(2)	-5(2)	-3(2)	5(1)
C(9)	53(2)	48(2)	67(2)	-1(1)	-4(1)	6(1)
C(10)	93(2)	53(2)	152(3)	25(2)	5(2)	-8(2)
C(11)	55(2)	60(2)	134(3)	-31(2)	-3(2)	8(1)
C(12)	121(3)	137(4)	150(4)	-98(3)	-20(3)	33(3)
C(13)	173(5)	240(7)	102(3)	-76(4)	-29(3)	87(5)
C(14)	58(2)	66(2)	63(2)	10(1)	3(1)	5(1)
C(15)	106(3)	67(2)	68(2)	12(2)	10(2)	14(2)
C(16)	103(3)	68(2)	99(3)	7(2)	29(2)	15(2)
C(17)	72(2)	87(3)	84(2)	-13(2)	24(2)	-8(2)
C(18)	87(2)	128(4)	65(2)	-6(2)	2(2)	11(2)
C(19)	88(2)	97(3)	64(2)	3(2)	-2(2)	22(2)
C(20)	111(3)	117(3)	125(3)	-38(3)	46(2)	-13(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd2544.

	x	y	z	U(eq)
H(10A)	893	8101	5025	128
H(10B)	309	8525	6047	128
H(10C)	1634	8266	6579	128
H(12A)	1724	8732	222	138
H(12B)	1038	8143	893	138
H(13A)	-554	8825	-33	139
H(13B)	-7	8400	-1089	139
H(13C)	177	9296	-841	139
H(20A)	3924	7441	-909	133
H(20B)	5160	7752	-942	133
H(20C)	4008	8049	-2045	133
H(1)	3750(20)	9938(15)	4630(30)	53(8)
H(2)	2630(30)	11665(19)	4260(30)	89(11)
H(3)	2400(30)	12560(20)	5820(30)	96(11)
H(4)	1740(30)	12130(20)	7900(40)	109(11)
H(5)	1360(30)	10883(18)	8070(30)	80(10)
H(9)	1730(20)	10359(16)	3120(30)	69(9)
H(15)	4940(20)	8941(17)	3150(30)	81(9)
H(16)	5110(30)	8000(20)	1660(40)	117(13)
H(18)	3480(20)	9299(17)	-1620(30)	78(9)
H(19)	3100(30)	10350(20)	-100(40)	120(12)

Table 6. Torsion angles [deg] for cd2544.

O(2)-S(1)-N(1)-C(9)	15.4(3)
O(3)-S(1)-N(1)-C(9)	144.6(2)
C(14)-S(1)-N(1)-C(9)	-101.5(3)
C(6)-C(1)-C(2)-C(3)	0.0(4)
C(9)-C(1)-C(2)-C(3)	-178.3(3)
C(1)-C(2)-C(3)-C(4)	-1.7(5)
C(2)-C(3)-C(4)-C(5)	2.3(6)
C(3)-C(4)-C(5)-C(6)	-1.2(5)
C(2)-C(1)-C(6)-C(5)	1.2(4)
C(9)-C(1)-C(6)-C(5)	179.5(3)
C(2)-C(1)-C(6)-O(1)	-178.6(2)
C(9)-C(1)-C(6)-O(1)	-0.3(4)
C(4)-C(5)-C(6)-C(1)	-0.6(5)
C(4)-C(5)-C(6)-O(1)	179.2(3)
C(7)-O(1)-C(6)-C(1)	-5.5(4)
C(7)-O(1)-C(6)-C(5)	174.7(2)
C(6)-O(1)-C(7)-C(8)	1.6(4)
C(6)-O(1)-C(7)-C(10)	-176.7(2)
O(1)-C(7)-C(8)-C(11)	-175.0(2)
C(10)-C(7)-C(8)-C(11)	3.0(5)
O(1)-C(7)-C(8)-C(9)	7.9(4)
C(10)-C(7)-C(8)-C(9)	-174.1(3)
S(1)-N(1)-C(9)-C(1)	-104.8(3)
S(1)-N(1)-C(9)-C(8)	132.7(3)
C(6)-C(1)-C(9)-N(1)	-112.6(3)
C(2)-C(1)-C(9)-N(1)	65.6(3)
C(6)-C(1)-C(9)-C(8)	8.5(3)
C(2)-C(1)-C(9)-C(8)	-173.3(2)
C(7)-C(8)-C(9)-N(1)	109.5(3)
C(11)-C(8)-C(9)-N(1)	-67.8(3)
C(7)-C(8)-C(9)-C(1)	-12.4(4)
C(11)-C(8)-C(9)-C(1)	170.4(2)
C(12)-O(4)-C(11)-O(5)	-1.5(5)
C(12)-O(4)-C(11)-C(8)	-179.3(3)
C(7)-C(8)-C(11)-O(5)	-25.0(5)
C(9)-C(8)-C(11)-O(5)	152.3(3)
C(7)-C(8)-C(11)-O(4)	152.7(3)
C(9)-C(8)-C(11)-O(4)	-30.0(3)
C(11)-O(4)-C(12)-C(13)	128.9(6)
O(2)-S(1)-C(14)-C(19)	9.2(3)
O(3)-S(1)-C(14)-C(19)	-120.1(3)
N(1)-S(1)-C(14)-C(19)	126.3(3)
O(2)-S(1)-C(14)-C(15)	-173.7(3)
O(3)-S(1)-C(14)-C(15)	57.1(3)
N(1)-S(1)-C(14)-C(15)	-56.5(3)
C(19)-C(14)-C(15)-C(16)	-1.8(5)
S(1)-C(14)-C(15)-C(16)	-179.0(3)
C(14)-C(15)-C(16)-C(17)	-0.3(6)
C(15)-C(16)-C(17)-C(18)	2.1(6)
C(15)-C(16)-C(17)-C(20)	-178.2(3)
C(16)-C(17)-C(18)-C(19)	-1.9(6)
C(20)-C(17)-C(18)-C(19)	178.5(4)
C(15)-C(14)-C(19)-C(18)	2.0(6)
S(1)-C(14)-C(19)-C(18)	179.1(3)
C(17)-C(18)-C(19)-C(14)	-0.1(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd2544 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)#1	0.77(3)	2.12(3)	2.886(3)	173(3)

Symmetry transformations used to generate equivalent atoms:
 #1 -x+1,-y+2,-z+1

The 2D NOESY spectrum of 2-(1-methyl-3-oxo-but-1-enyl)benzaldehyde **13a**:

Archive directory: /export/home/sbi-m/vmrnsys/data
Sample directory: sy1-5-107-4noesy_17Jan2005

Pulse Sequence: NOESY

Solvent: CDCl₃

Temperature: 300 K

File: NOESY

Mercury-300BB "OMC300"

Relax. delay 2.000 sec

Acq. time 2.000 sec

Width 4807.7 Hz

2D Width 4807.7 Hz

32 repetitions

2.000 sec

DATA PROCESSING

Observed: 300.0275728 MHz

Gauss apodization 0.079 sec

Fourier processing

Gauss apodization 0.025 sec

FT size 2048 x 2048

Total time 7 hr, 24 min, 27 sec

The 2D NOESY spectrum of 3-(2-formyl-phenyl)-but-2-enoic acid ethyl ester
(13b):

Archive directory: /export/home/shi-m/vnmrsvs/data
Sample directory: spt-5-64-noesy_12Sep2004

Pulse Sequence: NOESY

Solvent: CDCl3

Antisolvent: none

Temperature

File: NOESY

Mercury-30068 "DMC300"

Relax. delay 2.000 sec

Mixing 0.800 sec

Time 21.00 sec

Width 4807.7 Hz

2D Width 4807.7 Hz

2 x 128 F1 points

2 x 128 F2 points

OBSERVE H1, 500.0279716 MHz

DATA PROCESSING

Acquisition 0.005 sec

Processing

FT size 2048 x 2048

Total time 7 hr, 24 min, 26 sec