Regio and Stereoselective Synthesis of Aziridino-Epoxides from Cyclic Dienes

Devarajulu Sureshkumar, Susama Maity, Srinivasan Chandrasekaran*

Department of Organic Chemistry,

Tel : + 91 80 2293 2404

Indian Institute of Science,

Fax : + 91 80 2360 2423

Bangalore-560 012,

e-mail : scn@orgchem.iisc.ernet.in

India.

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General Experimental Procedure

All reactions were carried out in oven-dried apparatus using dry solvents under anhydrous conditions, unless otherwise stated. Reaction mixtures were stirred magnetically unless otherwise stated. Commercial grade solvents were distilled and dried according to literature procedures. Analytical TLC was performed on commercial plates coated with silica gel GF₂₅₄ (0.25 mm). Silica gel (230 - 400 mesh) was used for column chromatography. Melting points determined are uncorrected. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated. NMR spectra were recorded on 300 or 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations explain the multiplicity, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a FT-IR spectrometer.

Compound 5c: R_f = 0.75 (EtOAc/hexanes, 1 : 4); Yield: 0.548 g, 66%; m. p: 116 °C; IR (neat): 1314, 1153, 1089, 950, 898 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.13 – 2.53 (m, 1H), 3.21 (d, J = 3.0 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.42 (s, 3H), 2.30 – 2.06 (m, 3H), 1.76 (s, 3H), 1.55 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 143.4, 138.9, 129.4, 127.9, 126.9, 116.5, 49.1, 46.9, 32.3, 29.0, 23.3, 21.5, 19.6; HR - MS m/z: calcd for C₁₅H₁₉NO₂SN⁺[M+Na⁺]: 300.1034; found: 300.1040; Anal. Calcd for C₁₅H₁₉NO₂S: C, 64.95; H, 6.90; N, 5.05; S, 11.56; Found: C, 64.90; H, 6.99; N, 4.98; S, 11.48.

Compound 5d: R_f = 0.75 (EtOAc/hexanes, 1 : 4); Yield: 0.540 g, 65%; m. p: 91 °C; IR (neat): 1317, 1153, 1091, 946 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.79 (d, J = 8.1 Hz,

2H), 7.27 (d, $J = 8.1$ Hz, 2H), 5.07 – 5.05 (m, 1H), 3.17 (d, $J = 3.6$ Hz, 1H), 2.44 (d, $J = 18.3$ Hz, 1H), 2.40 (s, 3H), 2.35 – 2.29 (m, 1H), 2.24 – 2.17 (m, 1H), 2.05 (d, $J = 18.3$ Hz, 1H), 1.78 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.3, 138.7, 129.3, 129.1, 126.8, 115.0, 50.1, 45.8, 36.5, 24.7, 23.2, 21.4, 19.6; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{SNa}^+[\text{M}+\text{Na}^+]$: 300.1034; found: 300.1046; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$: C, 64.95; H, 6.90; N, 5.05; S, 11.56; Found: C, 64.83; H, 6.74; N, 5.13; S, 11.41.

Compound 5e: $R_f = 0.75$ (EtOAc/hexanes, 1 : 4); Yield: 0.503 g, 55%; IR (neat): 1322, 1153, 1084, 948 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 5.16 (t, $J = 2.7$ Hz, 1H), 2.63 – 2.54 (m, 1H), 2.40 (s, 3H), 2.31 – 2.19 (m, 2H), 2.15 (s, 3H), 2.11 – 1.99 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.2, 138.9, 137.6, 129.2, 126.8, 113.9, 49.9, 47.2, 34.5, 32.2, 25.0, 21.4, 20.9, 20.8, 19.4; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{SNa}^+[\text{M}+\text{Na}^+]$: 328.1347; found: 328.1350; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{S}$: C, 66.85; H, 7.59; N, 4.59; S, 10.50; Found: C, 66.88; H, 7.74; N, 4.43; S, 10.41.

Compound 5f: $R_f = 0.75$ (EtOAc/hexanes, 1 : 4); Yield: 0.457 g, 55%; m. p: 126 °C; IR (neat): 1597, 1313, 1154, 1091, 967, 813, 709, 649 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 5.41 (dd, $J = 2.5, 1.5$ Hz, 1H), 2.49 (t, $J = 2.7$ Hz, 1H), 2.43 (t, $J = 2.3$ Hz, 1H), 2.40 (s, 3H), 2.14 (d, $J = 15.9$ Hz, 2H), 1.69 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 142.9, 140.1, 129.2, 126.6, 122.5, 51.5, 32.7, 21.4, 16.5; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{SNa}^+[\text{M}+\text{Na}^+]$: 300.1034; found: 300.1045; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$: C, 64.95; H, 6.90; N, 5.05; S, 11.56; Found: C, 64.98; H, 6.96; N, 5.13; S, 11.59.

Compound 5h: $R_f = 0.70$ (EtOAc/hexanes, 1 : 4); Yield: 0.455 g, 50%; m. p: 181 °C IR (neat): 1318, 1149, 1076, 951 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 5.64 (s, 2H), 3.03 (d, $J = 18.0$ Hz, 2H), 2.41 – 2.31 (m, 2H), 2.39 (s, 3H), 2.14 – 2.05 (m, 2H), 1.69 – 1.66 (m, 2H), 1.54 – 1.43 (m, 3H), 1.34 – 1.28 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 142.8, 142.0, 129.1, 125.6, 122.9, 52.2, 30.8, 30.3, 21.4, 20.3; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{SNa}^+[\text{M}+\text{Na}^+]$: 326.1191; found: 326.1201; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$: C, 67.29; H, 6.98; N, 4.62; S, 10.57; Found: C, 67.38; H, 6.91; N, 4.53; S, 10.59.

Compound 5i: $R_f = 0.70$ (EtOAc/hexanes, 1 : 4); Yield: 0.374 g, 45%; m. p: 161 °C IR (neat): 1321, 1159, 1091, 953, 882, 715 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 5.55 (bs, 2H), 2.44 (s, 3H), 2.40 – 2.36 (m, 4H), 2.02 – 1.94 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.0, 135.4, 129.5, 128.8, 127.5, 44.14, 27.1, 23.7, 21.5; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{SNa}^+[\text{M}+\text{Na}^+]$: 300.1034; found: 300.1046; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$: C, 64.95; H, 6.90; N, 5.05; S, 11.56; Found: C, 64.88; H, 6.92; N, 5.13; S, 11.59.

Compound 7b: $R_f = 0.75$ (EtOAc/hexanes, 3 : 7); Yield: 0.089 g, 32%; m. p: 104 °C; IR (neat): 1320, 1158, 1078, 967, 952 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 3.05 (t, $J = 3.6$ Hz, 1H), 2.99 - 2.95 (m, 2H), 2.43 (s, 3H), 2.41 (dd, $J = 16.5, 3.6$ Hz, 1H), 2.21 (dd, $J = 16.5, 4.8$ Hz, 1H), 2.04 – 1.94 (m, 2H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.7, 138.1, 129.4, 126.9, 49.7, 48.2, 47.5, 43.7, 30.6, 22.8, 21.4, 20.1; HR - MS m/z : calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 302.0827; found: 302.0828; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{S}$: C, 60.19; H, 6.13; N, 5.01; S, 11.48; Found: C, 60.01; H, 6.20; N, 5.18; S, 11.42.

Compound 6c: $R_f = 0.20$ (EtOAc/hexanes, 3 : 7); Yield: 0.200 g, 73%; m. p: 125 °C; IR (neat): 1320, 1158, 1078, 967, 952 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 2.98 (d, $J = 4.5$ Hz, 1H), 2.86 (d, $J = 1.8$ Hz, 1H), 2.73 (d, $J = 16.5$, 1H), 2.41 (s, 3H), 2.22 (d, $J = 16.5$ Hz, 1H), 2.11 – 1.99(m, 2H), 1.71 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.7, 138.1, 129.4, 126.9, 49.7, 48.2, 47.5, 43.7, 30.6, 22.8, 21.4, 20.1; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0989; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.46; H, 6.59; N, 4.73; S, 10.99.

Compound 7c: $R_f = 0.70$ (EtOAc/hexanes, 3 : 7); Yield: 0.067 g, 18%; m. p: 181 °C; IR (neat): 1601, 1330, 1152, 1079, 965, 720 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 2.98 (d, $J = 4.8$ Hz, 1H), 2.86 (d, $J = 3.3$ Hz, 1H), 2.44 (s, 3H), 2.43 (dd, $J = 16.5$, 3.9 Hz, 1H), 2.19 (dd, $J = 16.2$, 5.1 Hz, 3H), 2.03 (d, $J = 16.2$ Hz, 1H), 1.81 (d, $J = 16.5$ Hz, 1H), 1.71 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.8, 138.3, 129.5, 127.0, 57.0, 54.5, 47.8, 44.8, 31.9, 28.3, 23.5, 21.5, 20.2; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0983; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.60; H, 6.58; N, 4.63; S, 10.85.

Compound 6d: $R_f = 0.25$ (EtOAc/hexanes, 3 : 7); Yield: 0.211 g, 68%; m. p: 134 °C; IR (neat): 1601, 1330, 1152, 1079, 965, 720 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 2.95(d, $J = 2.4$ Hz, 1H), 2.80 (s, 1H), 2.62 (d, $J = 16.5$ Hz, 1H), 2.40 (s, 3H), 2.29 (d, $J = 16.5$ Hz, 1H), 2.20 – 2.12 (m, 1H), 1.93 (d, $J = 16.2$ Hz, 1H), 1.71 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.2, 138.8, 129.3, 126.8, 55.7, 54.6, 47.5, 43.9, 34.4, 23.5, 23.2, 21.4, 20.3; HR - MS m/z : calcd for

$\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0992; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.51; H, 6.64; N, 4.73; S, 10.98.

Compound 7d: $R_f = 0.65$ (EtOAc/hexanes, 3 : 7); Yield: 0.211 g, 22%; m. p: 135 °C; IR (neat): 1613, 1338, 1159, 1079, 965, 720 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 2.98 (d, $J = 5.1$ Hz, 1H), 2.81 (d = 3.0 Hz, 1H), 2.44 (s, 3H), 2.26 (d, $J = 15.9$ Hz, 1H), 2.23 (dd, $J = 16.5, 5.4$ Hz, 1H), 2.00 (d, $J = 16.5$ Hz, 1H), 1.99 (d, $J = 16.2$ Hz, 1H), 1.69 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.8, 138.3, 129.6, 127.1, 55.9, 55.8, 48.8, 43.9, 36.2, 24.1, 23.5, 21.6, 20.3; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0990; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.49; H, 6.54; N, 4.83; S, 10.89.

Compound 6e: $R_f = 0.20$ (EtOAc/hexanes, 3 : 7); Yield: 0.254 g, 79%; m. p: 173 °C; IR (neat): 1330, 1162, 1079, 840, 690, 660 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.04 – 3.02 (m, 1H), 2.84 (s, 1H), 2.71 (d, $J = 16.5$ Hz, 1H), 2.42 (s, 3H), 2.12 (s, 2H), 1.99 (dd, $J = 16.5, 3.0$ Hz, 1H), 1.71 (s, 3H), 1.49 – 1.36 (m, 1H), 0.90 (d, $J = 3.3$ Hz, 3H), 0.88 (d, $J = 3.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.3, 138.8, 129.4, 126.9, 59.67, 55.1, 47.2, 44.8, 34.6, 30.6, 21.9, 21.5, 20.1, 18.1, 17.4; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 344.1296; found: 344.1285; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{S}$: C, 63.52; H, 7.21; N, 4.36; S, 9.98; Found: C, 63.59; H, 7.32; N, 4.28; S, 9.91.

Compound 7e: $R_f = 0.70$ (EtOAc/hexanes, 3 : 7); Yield: 0.045 g, 14%; m. p: 80 °C; IR (neat): 1330, 1162, 1079, 840, 690, 660 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 3.03 – 3.01 (m, 1H), 2.79 (d, $J = 4.5$ Hz, 1H), 2.49

(d, $J = 4.5$ Hz, 1H), 2.43 (s, 3H), 1.97 – 1.87 (m, 3H), 1.74 (s, 3H), 1.34 – 1.22 (m, 1H), 0.80 (d, $J = 7.2$ Hz, 3H), 0.56 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.7, 138.3, 129.4, 127.1, 60.3, 55.6, 48.5, 45.1, 34.9, 31.8, 23.0, 21.5, 19.6, 17.6, 16.9; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 344.1296; found: 344.1296; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{S}$: C, 63.52; H, 7.21; N, 4.36; S, 9.98; Found: C, 63.49; H, 7.34; N, 4.26; S, 10.01.

Compound 6f: $R_f = 0.25$ (EtOAc/hexanes, 3 : 7); Yield: 0.136 g, 56%; m. p: 144 °C; IR (neat): 1299, 1143, 1087, 1025, 957, 707, 687 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.04 (d, $J = 1.0$ Hz, 2H), 2.58 (d, $J = 16.5$ Hz, 2H), 2.42 (s, 3H), 1.96 (dd, $J = 16.5, 1.2$ Hz, 2H), 1.61 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.1, 139.9, 129.2, 127.1, 49.4, 48.9, 30.6, 21.5, 16.8; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0993; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.54; H, 6.62; N, 4.56; S, 11.10.

Compound 7f: $R_f = 0.65$ (EtOAc/hexanes, 3 : 7); Yield: 0.090 g, 38%; m. p: 126 °C; IR (neat): 1314, 1152, 1086, 966, 814, 707 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.09 (d, $J = 3.3$ Hz, 2H), 2.45 (dd, $J = 16.5, 3.6$ Hz, 2H), 2.43 (s, 3H), 1.98 (d, $J = 16.5$ Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.4, 139.6, 129.4, 126.7, 49.8, 49.6, 31.0, 21.5, 18.1; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0986; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.44; H, 6.54; N, 4.66; S, 10.81.

Compound 7h: $R_f = 0.65$ (EtOAc/hexanes, 3 : 7); Yield: 0.258 g, 81%; m. p: 162 °C; IR (neat): 1333, 1169, 1089, 846, 702, 653 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.29 (d, $J = 2.1$ Hz, 2H), 3.02 (dd, $J = 17.0, 2.4$ Hz,

2H), 2.42 (s, 3H), 2.15 (d, $J = 17.0$ Hz, 2H), 2.03 – 1.94 (m, 2H), 1.57 – 1.36 (m, 4H), 1.29 – 1.18 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.2, 140.6, 129.4, 126.4, 50.6, 49.5, 32.3, 28.5, 21.5, 19.8; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 342.1140; found: 342.1144; calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 342.1140; found: 342.1144; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$: C, 63.92; H, 6.63; N, 4.39; S, 10.04; Found: C, 63.74; H, 6.52; N, 4.26; S, 10.21.

Compound 6i: $R_f = 0.45$ (EtOAc/hexanes, 3 : 7); Yield: 0.231 g, 79%; m. p: 94 °C; IR (neat): 1321, 1159, 1091, 846, 958 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 2.95 – 2.82 (m, 4H), 2.45 (s, 3H), 2.02 – 1.81 (m, 6H), 1.69 – 1.59 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.3, 135.4, 129.7, 127.6, 55.5, 43.5, 22.0, 21.6, 21.1; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0987; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.52; H, 6.73; N, 4.64; S, 10.86.

Compound 7j: $R_f = 0.45$ (EtOAc/hexanes, 3 : 7); Yield: 0.206 g, 82%; m. p: 124 °C; IR (neat): 1324, 1159, 1090, 846, 843 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 3.66 – 3.64 (m, 2H), 3.23 – 3.21 (m, 1H), 3.06 – 3.03 (m, 1H), 2.46 (s, 3H), 2.15 (dddd, $J = 15.3, 3.6, 1.2$ Hz, 1H), 2.02 (dd, $J = 15.3, 2.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.8, 134.8, 129.8, 127.8, 58.4, 52.8, 48.1, 40.3, 30.6, 21.6; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 274.0514; found: 274.0519; Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3\text{S}$: C, 57.35; H, 5.21; N, 5.57; S, 12.76; Found: C, 57.43; H, 5.34; N, 5.44; S, 12.86.

Compound 7k: $R_f = 0.65$ (EtOAc/hexanes, 3 : 7); Yield: 0.228 g, 86%; m. p: 113 °C; IR (neat): 1322, 1159, 1092, 982, 953, 851, 674 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.82 (d,

$J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 3.29 – 3.24 (m, 2H), 3.11 – 3.09 (m, 1H), 2.99 – 2.96 (m, 1H), 2.45 (s, 3H), 1.93 – 1.72 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.6, 134.9, 129.7, 127.7, 52.5, 48.3, 40.1, 38.2, 21.6, 18.8, 17.5; HR - MS m/z : calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 288.0670; found: 288.0671; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$: C, 58.85; H, 5.70; N, 5.28; S, 12.09; Found: C, 58.82; H, 5.67; N, 5.34; S, 11.98.

Compound 17: $R_f = 0.75$ (EtOAc/hexanes, 3 : 7); Yield: 0.560 g, 67%; m. p: 95 °C; IR (neat): 1597, 1322, 1159, 1092, 822, 718, 668 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 2.86 (s, 3H), 2.43 (s, 3H), 2.29 – 2.09 (m, 4H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 134.9, 129.6, 127.6, 56.0, 54.9, 37.2, 36.1, 27.0, 23.3, 22.9, 21.5; HR - MS m/z : calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{SNa}^+[\text{M}+\text{H}^+]$: 280.1007; found: 280.1018; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{S}$: C, 60.19; H, 6.13; N, 5.01; S, 11.48; Found: C, 60.32; H, 6.21; N, 5.20; S, 11.32.

Compound 18: $R_f = 0.60$ (EtOAc/hexanes, 3 : 7); Yield: 0.211 g, 60%; m. p: 103 °C; IR (neat): 1324, 1157, 1089, 950, 921, 829, 727, 671 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 2.88 (dd, $J = 3.9, 1.5$ Hz, 2H), 2.45 (s, 3H), 2.29 (dd, $J = 3.9, 1.5$ Hz, 1H), 2.24 (dd, $J = 4.2, 1.8$ Hz, 1H), 1.96 (d, $J = 16.2$ Hz, 2H), 1.26 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 135.1, 129.7, 127.7, 59.3, 37.5, 29.2, 21.6, 20.0; HR - MS m/z : calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 316.0983; found: 316.0981; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}$: C, 61.41; H, 6.53; N, 4.77; S, 10.93; Found: C, 61.32; H, 6.62; N, 4.87; S, 10.78.

Compound 19: $R_f = 0.70$ (EtOAc/hexanes, 3 : 7); Yield: 0.640 g, 70%; m. p: 141 °C; IR (neat): 1320, 1162, 976, 941, 870, 813, 721, 667 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 2.89 (s, 2H), 2.45 (s, 3H), 2.29 (d, $J = 16.5$

Hz, 2H), 2.07 (d, $J = 16.5$ Hz, 2H), 1.97 – 1.90 (m, 2H), 1.54 – 1.26 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 134.9, 129.6, 127.7, 64.3, 37.7, 37.4, 31.07, 24.84, 21.6, 18.8; HR - MS m/z : calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 328.0983; found: 328.0991; Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}$: C, 62.93; H, 6.27; N, 4.59; S, 10.50; Found: C, 62.79; H, 6.38; N, 4.42; S, 10.67.

Compound 20: $R_f = 0.70$ (EtOAc/hexanes, 3 : 7); Yield: 0.689 g, 72%; m. p: 155 °C; IR (neat): 1318, 1158, 951, 841, 726, 671 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.83 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 2.89 – 2.83 (m, 2H), 2.46 (s, 3H), 2.33 – 2.22 (m, 2H), 1.91 (d, $J = 15.9$ Hz, 2H), 1.85 – 1.80 (m, 2H), 1.61 – 1.18 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.4, 135.1, 129.7, 127.8, 59.5, 37.2, 30.2, 28.9, 21.6, 20.2; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{SNa}^+[\text{M}+\text{Na}^+]$: 342.1140; found: 342.1132; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$: C, 63.92; H, 6.63; N, 4.39; S, 10.04; Found: C, 63.78; H, 6.56; N, 4.53; S, 10.36.

Compound 22d: $R_f = 0.50$ (EtOAc/hexanes, 3 : 7); Yield: 0.405 g, 40%; m. p: 123 °C; $[\alpha]_D^{27} = -48.00$ ($c=1.0$, CHCl_3); IR (neat): 1709, 1319, 1159, 846, 715 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 3.42 (d, $J = 3.3$ Hz, 1H), 2.63 (s, 1H), 2.57-2.50 (m, 1H), 2.44 (s, 3H), 2.36-2.29 (m, 1H), 2.24 (s, 1H), 2.13-1.95 (m, 2H), 1.88-1.79 (m, 1H), 1.66 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 204.3, 144.0, 137.5, 129.5, 127.3, 60.7, 58.7, 50.9, 40.3, 39.0, 35.4, 25.6, 21.5, 15.2, 15.2; HR - MS m/z : calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{SNa}^+[\text{M}+\text{Na}^+]$: 358.1089; found: 358.1095; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$: C, 60.87; H, 6.31; N, 4.18; S, 9.56; Found: C, 60.64; H, 6.51; N, 4.34; S, 9.65.

Computational method:

All calculations were performed using the Gaussian98 suite of quantum chemical programs.¹ The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange correlation functional was applied for DFT calculations.² Geometries were fully optimized at the B3LYP level of theory using the 6-31G(d) basis sets. All stationary points were characterized as minima by corresponding Hessian indices.

B3LYP/6-31G(d) level optimized coordinates of *cis*- and *trans*-epoxy bromonium ion I

trans-epoxy bromonium ion I	cis-epoxy bromonium ion I

E = -2879.909318 HF	E = -2879.913070 HF $\Delta E = 2.35$ kcal/mol
Br -1.219750 -1.077111 -.452827	Br -1.509154 -.000037 -.345385
O 2.316679 1.535363 .361368	O 1.394192 -.000277 -1.360840
C -.868970 .898030 .220444	C -.176079 -.730760 1.114196
C -.383756 -.066327 1.207759	C -.175814 .731365 1.114073
C 1.975022 .152926 .276466	C .988059 -1.518696 .590461
C 1.075115 -.348310 1.395213	C 1.961646 -.736228 -.269713
C .061791 1.665933 -.666706	C 1.961802 .735885 -.269964
C 1.483679 1.129562 -.723310	C .988334 1.518858 .589897
H 2.798416 -.506573 .006927	H .630763 -2.418480 .075649
H -.380696 1.760627 -1.663912	H -.834951 1.232030 1.819942
H .081884 2.687683 -.251911	H 1.509862 -1.883301 1.491858
H 1.351935 .163132 2.332358	H -.835132 -1.231051 1.820406
H 1.958216 1.163500 -1.702713	H 2.883508 -1.265934 -.505870
H 1.217702 -1.416702 1.588588	H 2.883771 1.265350 -.506249
H -1.871079 1.297034 .365291	H 1.510185 1.883910 1.491100
H -1.055830 -.323619 2.024169	H .631138 2.418454 .074671

Reference:

- (1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (2) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

Crystal Data and Structure Refinement Tables

Identification code	Compound 5b
Empirical formula	C ₁₄ H ₁₇ N O ₂ S
Formula weight	263.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.6976(14) Å α = 90°.
	b = 8.1596(10) Å β = 107.932(2)°.
	c = 15.0502(18) Å γ = 90°.
Volume	1366.7(3) Å ³
Z	4
Density (calculated)	1.280 mg/m ³
Absorption coefficient	0.231 mm ⁻¹
F(000)	560
Crystal size	0.34 x 0.26 x 0.24 mm ³
Theta range for data collection	1.83 to 24.99°.
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	12639
Independent reflections	2398 [R(int) = 0.0205]
Completeness to theta = 24.99°	99.9 %
Max. and min. transmission	0.9467 and 0.9257
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2398 / 0 / 165
Goodness-of-fit on F ²	1.128
Final R indices [I > 2σ(I)]	R1 = 0.0490, wR2 = 0.1257
R indices (all data)	R1 = 0.0563, wR2 = 0.1301
Largest diff. peak and hole	0.296 and -0.231 e.Å ⁻³

Identification code	Compound 5c
Empirical formula	C ₁₅ H ₁₉ N O ₂ S
Formula weight	277.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 21.774(5) Å α = 90°.
	b = 8.4311(18) Å β = 98.761(4)°.
	c = 16.261(3) Å γ = 90°.
Volume	2950.5(11) Å ³
Z	8
Density (calculated)	1.249 mg/m ³
Absorption coefficient	0.217 mm ⁻¹
F(000)	1184
Crystal size	0.74 x 0.21 x 0.17 mm ³
Theta range for data collection	0.95 to 25.00°.
Index ranges	-25 ≤ h ≤ 25, -10 ≤ k ≤ 10, -19 ≤ l ≤ 18
Reflections collected	19757
Independent reflections	5174 [R(int) = 0.0336]
Completeness to theta = 25.00°	99.9 %
Max. and min. transmission	0.9640 and 0.8558
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5174 / 0 / 349
Goodness-of-fit on F ²	1.265
Final R indices [I > 2σ(I)]	R1 = 0.0706, wR2 = 0.1559
R indices (all data)	R1 = 0.0838, wR2 = 0.1657
Largest diff. peak and hole	0.228 and -0.343 e.Å ⁻³

Identification code	Compound 6b
Empirical formula	C ₁₄ H ₁₇ N O ₃ S
Formula weight	279.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 12.336(8) Å α = 90°.
	b = 8.151(5) Å β = 104.232(11)°.
	c = 14.536(10) Å γ = 90°.
Volume	1416.7(16) Å ³
Z	4
Density (calculated)	1.310 mg/m ³
Absorption coefficient	0.232 mm ⁻¹
F(000)	592
Crystal size	0.27 x 0.26 x 0.12 mm ³
Theta range for data collection	1.94 to 25.00°.
Index ranges	-13 ≤ h ≤ 14, -9 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	9793
Independent reflections	2494 [R(int) = 0.0165]
Completeness to theta = 24.99°	99.9 %
Max. and min. transmission	0.9727 and 0.9401
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2494 / 0 / 174
Goodness-of-fit on F ²	1.082
Final R indices [I > 2σ(I)]	R1 = 0.0413, wR2 = 0.1121
R indices (all data)	R1 = 0.0476, wR2 = 0.1160
Largest diff. peak and hole	0.217 and -0.150 e.Å ⁻³

Identification code	Compound 6c
Empirical formula	C ₁₅ H ₁₉ N O ₃ S
Formula weight	293.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 7.7208(14) Å α = 90°.
	b = 18.301(3) Å β = 104.458(3)°.
	c = 10.857(2) Å γ = 90°.
Volume	1485.6(5) Å ³
Z	4
Density (calculated)	1.312 mg/m ³
Absorption coefficient	0.224 mm ⁻¹
F(000)	624
Crystal size	0.40 x 0.38 x 0.36 mm ³
Theta range for data collection	2.23 to 25.00°.
Index ranges	-9 ≤ h ≤ 8, -21 ≤ k ≤ 21, -12 ≤ l ≤ 12
Reflections collected	10592
Independent reflections	2621 [R(int) = 0.0222]
Completeness to theta = 24.99°	100.0 %
Max. and min. transmission	0.9236 and 0.9156
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2621 / 0 / 184
Goodness-of-fit on F ²	1.123
Final R indices [I > 2σ(I)]	R1 = 0.0496, wR2 = 0.1136
R indices (all data)	R1 = 0.0605, wR2 = 0.1181
Largest diff. peak and hole	0.242 and -0.186 e.Å ⁻³

Identification code	Compound 6e
Empirical formula	C ₁₇ H ₂₃ N O ₃ S
Formula weight	321.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 6.4314(17) Å α = 90°.
	b = 10.997(3) Å β = 91.696(4)°.
	c = 24.165(6) Å γ = 90°.
Volume	1708.4(8) Å ³
Z	4
Density (calculated)	1.250 mg/m ³
Absorption coefficient	0.201 mm ⁻¹
F(000)	688
Crystal size	0.64 x 0.19 x 0.11 mm ³
Theta range for data collection	1.69 to 25.00°.
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	11915
Independent reflections	3003 [R(int) = 0.0284]
Completeness to theta = 25.00°	99.7 %
Max. and min. transmission	0.9782 and 0.8821
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3003 / 0 / 199
Goodness-of-fit on F ²	1.431
Final R indices [I > 2σ(I)]	R1 = 0.0856, wR2 = 0.1640
R indices (all data)	R1 = 0.1046, wR2 = 0.1701
Largest diff. peak and hole	0.319 and -0.231 e.Å ⁻³

Identification code	Compound 7b
Empirical formula	C ₁₄ H ₁₇ N O ₃ S
Formula weight	279.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 6.484(4) Å α = 90°.
	b = 11.763(7) Å β = 98.903(10)°.
	c = 18.062(11) Å γ = 90°.
Volume	1360.9(15) Å ³
Z	4
Density (calculated)	1.363 mg/m ³
Absorption coefficient	0.241 mm ⁻¹
F(000)	592
Crystal size	0.37 x 0.16 x 0.10 mm ³
Theta range for data collection	2.07 to 26.36°.
Index ranges	-7 ≤ h ≤ 8, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	10291
Independent reflections	2725 [R(int) = 0.0183]
Completeness to theta = 25.00°	100.0 %
Max. and min. transmission	0.9763 and 0.9160
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2725 / 0 / 174
Goodness-of-fit on F ²	1.066
Final R indices [I > 2σ(I)]	R1 = 0.0398, wR2 = 0.1066
R indices (all data)	R1 = 0.0468, wR2 = 0.1123
Largest diff. peak and hole	0.293 and -0.233 e.Å ⁻³

Identification code	Compound 7d
Empirical formula	C ₁₅ H ₁₉ N O ₃ S
Formula weight	293.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 31.917(7) Å α = 90°.
	b = 5.9247(13) Å β = 91.371(4)°.
	c = 15.929(4) Å γ = 90°.
Volume	3011.4(12) Å ³
Z	8
Density (calculated)	1.294 mg/m ³
Absorption coefficient	0.221 mm ⁻¹
F(000)	1248
Crystal size	0.29 x 0.26 x 0.07 mm ³
Theta range for data collection	1.28 to 25.00°.
Index ranges	-37 ≤ h ≤ 37, -7 ≤ k ≤ 7, -17 ≤ l ≤ 18
Reflections collected	10244
Independent reflections	2645 [R(int) = 0.0363]
Completeness to theta = 25.00°	99.8 %
Max. and min. transmission	0.9847 and 0.9386
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2645 / 0 / 181
Goodness-of-fit on F ²	0.985
Final R indices [I > 2σ(I)]	R1 = 0.0866, wR2 = 0.2230
R indices (all data)	R1 = 0.1069, wR2 = 0.2415
Largest diff. peak and hole	0.519 and -0.240 e.Å ⁻³

Identification code	Compound 7h
Empirical formula	C ₁₇ H ₂₁ N O ₃ S
Formula weight	319.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 7.6464(16) Å α = 90°
	b = 28.747(6) Å β = 114.656(3)°
	c = 7.9681(17) Å γ = 90°
Volume	1591.8(6) Å ³
Z	4
Density (calculated)	1.333 Mg/m ³
Absorption coefficient	0.216 mm ⁻¹
F(000)	680
Crystal size	0.65 x 0.55 x 0.46 mm ³
Theta range for data collection	2.83 to 25.00°
Index ranges	-9 ≤ h ≤ 8, -34 ≤ k ≤ 34, -9 ≤ l ≤ 9
Reflections collected	11376
Independent reflections	2797 [R(int) = 0.0292]
Completeness to theta = 25.00°	99.9 %
Max. and min. transmission	0.9074 and 0.8726
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2797 / 0 / 201
Goodness-of-fit on F ²	1.163
Final R indices [I > 2σ(I)]	R1 = 0.0561, wR2 = 0.1288
R indices (all data)	R1 = 0.0626, wR2 = 0.1325
Extinction coefficient	0.042(3)
Largest diff. peak and hole	0.378 and -0.264 e.Å ⁻³

Identification code	Compound 6i
Empirical formula	C ₁₅ H ₁₉ N O ₃ S
Formula weight	293.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	a = 7.0977(16) Å α = 101.147(3)°.
	b = 9.111(2) Å β = 94.924(3)°.
	c = 12.314(3) Å γ = 106.198(3)°.
Volume	742.0(3) Å ³
Z	2
Density (calculated)	1.313 Mg/m ³
Absorption coefficient	0.225 mm ⁻¹
F(000)	312
Crystal size	0.50 x 0.45 x 0.09 mm ³
Theta range for data collection	2.39 to 25.00°.
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected	6480
Independent reflections	2612 [R(int) = 0.0150]
Completeness to theta = 25.00°	99.4 %
Max. and min. transmission	0.9801 and 0.8960
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2612 / 0 / 182
Goodness-of-fit on F ²	1.066
Final R indices [I > 2σ(I)]	R1 = 0.0458, wR2 = 0.1230
R indices (all data)	R1 = 0.0561, wR2 = 0.1281
Largest diff. peak and hole	0.285 and -0.133 e.Å ⁻³

Identification code	Compound 7j
Empirical formula	C ₁₂ H ₁₂ N O ₃ S
Formula weight	250.29
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	a = 6.136(2) Å α = 100.788(5)°.
	b = 9.040(3) Å β = 97.355(6)°.
	c = 11.057(4) Å γ = 92.065(6)°.
Volume	596.4(4) Å ³
Z	2
Density (calculated)	1.394 Mg/m ³
Absorption coefficient	0.266 mm ⁻¹
F(000)	262
Crystal size	0.30 x 0.25 x 0.06 mm ³
Theta range for data collection	1.89 to 25.00°.
Index ranges	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	5750
Independent reflections	2101 [R(int) = 0.0163]
Completeness to theta = 25.00°	99.7 %
Max. and min. transmission	0.9842 and 0.9243
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2101 / 0 / 200
Goodness-of-fit on F ²	1.121
Final R indices [I > 2σ(I)]	R1 = 0.0406, wR2 = 0.1108
R indices (all data)	R1 = 0.0436, wR2 = 0.1128
Largest diff. peak and hole	0.271 and -0.294 e.Å ⁻³

Identification code	Compound 17
Empirical formula	C ₁₄ H ₁₇ N O ₃ S
Formula weight	279.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁
Unit cell dimensions	a = 8.579(6) Å α = 90°
	b = 6.023(4) Å β = 96.762(11)°
	c = 13.590(9) Å γ = 90°
Volume	697.4(8) Å ³
Z	2
Density (calculated)	1.330 mg/m ³
Absorption coefficient	0.235 mm ⁻¹
F(000)	296
Crystal size	0.23 x 0.20 x 0.16 mm ³
Theta range for data collection	1.51 to 25.00°
Index ranges	-10 ≤ h ≤ 10, -7 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	4870
Independent reflections	2397 [R(int) = 0.0286]
Completeness to theta = 25.00°	99.2 %
Max. and min. transmission	0.9633 and 0.9479
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2397 / 1 / 172
Goodness-of-fit on F ²	1.159
Final R indices [I > 2σ(I)]	R1 = 0.0739, wR2 = 0.1874
R indices (all data)	R1 = 0.0878, wR2 = 0.1931
Absolute structure parameter	0.1(2)
Largest diff. peak and hole	0.704 and -0.310 e.Å ⁻³

Identification code	Compound 18
Empirical formula	C ₁₅ H ₁₉ NO ₃ S
Formula weight	293.37
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 15.656(4) Å α = 90°.
	b = 19.673(5) Å β = 90°.
	c = 19.736(5) Å γ = 90°.
Volume	6079(3) Å ³
Z	16
Density (calculated)	1.282 Mg/m ³
Absorption coefficient	0.219 mm ⁻¹
F(000)	2496
Crystal size	0.50 x 0.42 x 0.31 mm ³
Theta range for data collection	1.96 to 25.00°.
Index ranges	-18 ≤ h ≤ 18, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	41811
Independent reflections	5349 [R(int) = 0.0714]
Completeness to theta = 25.00°	100.0 %
Max. and min. transmission	0.9351 and 0.8982
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5349 / 0 / 367
Goodness-of-fit on F ²	1.274
Final R indices [I > 2σ(I)]	R1 = 0.1021, wR2 = 0.1937
R indices (all data)	R1 = 0.1403, wR2 = 0.2064
Largest diff. peak and hole	0.227 and -0.197 e.Å ⁻³

Identification code	Compound 19
Empirical formula	C ₁₆ H ₁₉ N O ₃ S
Formula weight	305.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ P2 ₁ P2 ₁
Unit cell dimensions	a = 6.1762(14) Å α = 90°
	b = 14.029(3) Å β = 90°
	c = 17.742(4) Å γ = 90°
Volume	1537.2(6) Å ³
Z	4
Density (calculated)	1.320 mg/m ³
Absorption coefficient	0.220 mm ⁻¹
F(000)	648
Crystal size	0.56 x 0.17 x 0.15 mm ³
Theta range for data collection	1.85 to 25.00°.
Index ranges	-7<=h<=7, -16<=k<=15, -21<=l<=21
Reflections collected	10900
Independent reflections	2694 [R(int) = 0.0326]
Completeness to theta = 24.98°	99.8 %
Max. and min. transmission	0.9678 and 0.8868
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2694 / 0 / 190
Goodness-of-fit on F ²	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0976
R indices (all data)	R1 = 0.0449, wR2 = 0.0999
Absolute structure parameter	-0.05(9)
Largest diff. peak and hole	0.184 and -0.165 e.Å ⁻³

Identification code	Compound 20
Empirical formula	C ₁₇ H ₂₁ N O ₃ S
Formula weight	319.41
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.247(2) Å α = 90°
	b = 15.655(3) Å β = 107.586(3)°
	c = 9.4946(18) Å γ = 90°
Volume	1593.6(5) Å ³
Z	4
Density (calculated)	1.331 mg/m ³
Absorption coefficient	0.215 mm ⁻¹
F(000)	680
Crystal size	0.49 x 0.30 x 0.19 mm ³
Theta range for data collection	2.30 to 25.00°.
Index ranges	-12 ≤ h ≤ 13, -18 ≤ k ≤ 18, -11 ≤ l ≤ 11
Reflections collected	11163
Independent reflections	2795 [R(int) = 0.0298]
Completeness to theta = 25.00°	99.4 %
Max. and min. transmission	0.9602 and 0.9018
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2795 / 0 / 199
Goodness-of-fit on F ²	1.163
Final R indices [I > 2σ(I)]	R1 = 0.0533, wR2 = 0.1444
R indices (all data)	R1 = 0.0638, wR2 = 0.1511
Largest diff. peak and hole	0.426 and -0.314 e.Å ⁻³

Identification code	Compound 21d
Empirical formula	C ₁₇ H ₂₁ N O ₄ S
Formula weight	335.41
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ P2 ₁ P2 ₁
Unit cell dimensions	a = 8.4144(5) Å α = 90°
	b = 13.3381(8) Å β = 90°
	c = 15.0488(9) Å γ = 90°
Volume	1688.96(17) Å ³
Z	4
Density (calculated)	1.319 mg/m ³
Absorption coefficient	0.211 mm ⁻¹
F(000)	712
Crystal size	0.37 x 0.20 x 0.15 mm ³
Theta range for data collection	2.04 to 25.00°.
Index ranges	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	12271
Independent reflections	2965 [R(int) = 0.0197]
Completeness to theta = 24.99°	100.0 %
Max. and min. transmission	0.9691 and 0.9261
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2965 / 0 / 211
Goodness-of-fit on F ²	1.046
Final R indices [I > 2σ(I)]	R1 = 0.0291, wR2 = 0.0805
R indices (all data)	R1 = 0.0306, wR2 = 0.0818
Absolute structure parameter	0.01(6)
Largest diff. peak and hole	0.152 and -0.137 e.Å ⁻³

Identification code	Compound 22d
Empirical formula	C ₁₇ H ₂₁ N O ₄ S
Formula weight	335.41
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ P2 ₁ P2 ₁
Unit cell dimensions	a = 8.405(3) Å α = 90°.
	b = 13.343(5) Å β = 90°.
	c = 15.028(5) Å γ = 90°.
Volume	1685.3(10) Å ³
Z	4
Density (calculated)	1.322 mg/m ³
Absorption coefficient	0.211 mm ⁻¹
F(000)	712
Crystal size	0.40 x 0.35 x 0.22 mm ³
Theta range for data collection	2.04 to 25.00°.
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 12, -15 ≤ l ≤ 14
Reflections collected	8288
Independent reflections	1761 [R(int) = 0.0212]
Completeness to theta = 20.81°	100.0 %
Max. and min. transmission	0.9550 and 0.9202
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1761 / 0 / 211
Goodness-of-fit on F ²	1.096
Final R indices [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0676
R indices (all data)	R1 = 0.0283, wR2 = 0.0682
Absolute structure parameter	0.00(9)
Largest diff. peak and hole	0.134 and -0.177 e.Å ⁻³

^1H NMR, ^{13}C NMR and DEPT Spectra

Compound 5b:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5c:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5d:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5e:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5f:

¹H NMR – CDCl₃ (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5h:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 5i:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6b:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7b:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6c:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7c:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6d:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7d:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6e:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7e:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6f:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7f:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7h:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 6i:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7j:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 7k:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 17:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

Compound 18:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 19:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

Compound 20:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

Compound 21d:

^1H NMR – CDCl_3 (300 MHz)

^{13}C NMR – CDCl_3 (75 MHz)

DEPT – CDCl_3 (75 MHz)

$^1\text{H} - ^1\text{H}$ COSY

$^1\text{H} - ^{13}\text{C}$ COSY

Compound 22d:

 ^1H NMR – CDCl_3 (300 MHz) ^{13}C NMR – CDCl_3 (75 MHz)