Supporting information

Reactivity of epoxyynamides with metal halides: Nucleophile (Br/Cl/OH) assisted tandem intramolecular 5-exo-dig and 6-endo-dig cyclisation and AgF₂ promoted oxidation

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(1) General methods: All chemicals were procured from Aldrich or local manufacturers and used further without any purification, unless noted otherwise. Chemicals and solvents were purified when required according to standard procedures.\textsuperscript{1} \textsuperscript{1}H, \textsuperscript{13}C\textsuperscript{1}H\textsuperscript{1} and \textsuperscript{19}F NMR spectra were recorded using 5 mm tubes on 400 MHz and 500 NMR spectrometers [field strengths: 400, 100 and 376 MHz for 400 MHz NMR spectrometer and 500, 125 and 470 MHz for 500 MHz NMR spectrometer respectively] in CDCl\textsubscript{3}, DMSO-D\textsubscript{6} solutions (unless specified otherwise) with shifts referenced to SiMe\textsubscript{4} ( = 0). All \textit{J} values are in Hz. Infrared spectra were recorded neat or by using KBr pellets on a FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. For TLC, glass micro slides were coated with silica-gel-GF254 (mesh size 75) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100-200 mesh size was used. Microanalyses were performed using a CHNS analyzer. LC-MS equipment was used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization on a C-18 column at a flow rate 0.2 mL/ min using MeOH/water (90:10) as eluent. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. X-ray data were collected at 298 K using Mo-K\textsubscript{α} (\textit{λ} = 0.71073 Å) radiation. Structures were solved and refined using standard methods.\textsuperscript{2}

(2) Synthesis of epoxy-ynamides 1a-o

Our research group reported the synthesis of epoxy ynamides 1a-f and 1l by a known protocol with slight modification.\textsuperscript{3} In addition, in the current work, the new compounds 1h-l and 1n-o have been prepared (Scheme S1). The identities of all these substrates 1a-o were confirmed by IR and NMR spectra. IR spectra are particularly useful in identifying these compounds because the alkyne C≡C group shows a strong band at \textasciitilde 2200 cm\textsuperscript{-1}. In the \textsuperscript{13}C NMR spectra, two peaks at \textdelta \textasciitilde 80 and \textasciitilde 70 due to the presence of -C≡C- group are observed.
Scheme S1: Synthesis of epoxy-ynamides 1a-o

N-((4-bromophenyl)ethynyl)-4-methyl-N-(oxiran-2-ylmethyl)benzenesulfonamide (1h)

Yield: 1.50 g (84%, gummy liquid, \( R_f = 0.60 \) (9:1 hexane/ethyl acetate)); IR (neat) \( \nu_{\text{max}} \) 3064, 2999, 2925, 2237, 1596, 1488, 1367, 1171, 940, 819, 711 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.87-7.86 (m, 2H), 7.46-7.43 (m, 2H), 7.39 (m, 2H), 7.25-7.22 (m, 2H), 3.62 (d, \( J = 5.0 \) Hz, 2H), 3.24-3.21 (m, 1H), 2.85-2.83 (m, 1H), 2.66-2.65 (m, 1H), 2.48 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 145.1, 134.3, 132.8, 131.6, 129.9, 127.8, 122.1, 121.6, 83.4, 69.8, 53.9, 49.3, 45.5, 21.7; HRMS (ESI): Calcd for C\(_{18}\)H\(_{17}\)BrNO\(_3\)S (M\(^+\)+H), (M\(^+\)+H+2) \( m/z \) 406.0112, 408.0092. Found: 406.0111, 408.0090.

N-((oxiran-2-ylmethyl)-1-phenyl-N-(phenylethynyl)methanesulfonamide (1i)
Yield: 1.29 g (90%, gummy liquid, R<sub>f</sub> = 0.58 (9:1 hexane/ethyl acetate)); IR (neat)ν<sub>max</sub> 3062, 2999, 2929, 2237, 1495, 1361, 1258, 1202, 1158, 1135, 1007, 937, 796, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (m, 2H), 7.42 (m, 5H), 7.36-7.34 (m, 3H), 4.64 (AB multiplet, 2H), 3.40-3.30 (m, 2H), 3.10 (m, 1H), 2.81 (m, 1H), 2.63 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 131.7, 131.0, 129.4, 129.0, 128.4, 128.3, 127.7, 122.3, 81.8, 71.0, 57.5, 54.8, 49.4, 45.6; LC-MS: m/z 328 [M+1]<sup>+</sup>; Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>3</sub>S: C, 66.03; H, 5.23; N, 4.28. Found: C, 66.15; H, 5.18; N, 4.32.

4-chloro-2,5-dimethyl-N-(oxiran-2-ylmethyl)-N-(phenylethynyl)benzenesulfonamide (1j) Yield: 1.21 g (86%, gummy liquid, R<sub>f</sub> = 0.62 (9:1 hexane/ethyl acetate)); IR (neat)ν<sub>max</sub> 3059, 2997, 2926, 2858, 2236, 1599, 1543, 1479, 1370, 1169, 940, 755 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.92 (s, 1H), 7.36 (s, 1H), 7.34-7.29 (m, 5H), 3.72-3.68 (m, 1H), 3.64-3.60 (m, 1H), 3.32-3.28 (m, 1H), 2.87 (t, J = 4.3 Hz, 1H), 2.70 (d, J = 2.5 Hz, 1H), 2.69 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 140.2, 137.3, 134.5, 134.1, 133.2, 132.8, 131.2, 128.3, 128.1, 122.4, 81.9, 71.6, 53.5, 49.3, 45.7, 20.4, 19.6; HRMS (ESI): Calcd. for C<sub>19</sub>H<sub>18</sub>ClNO<sub>3</sub>SNa (M<sup>+</sup>+Na), (M<sup>+</sup>+Na+2) m/z 398.0594, 400.0564. Found: 398.0589, 400.0565.

4-methyl-N-(oxiran-2-ylmethyl)-N-((4-pentylphenyl)ethynyl)benzenesulfonamide (1k) Yield: 1.71 g (90%, gummy liquid, R<sub>f</sub> = 0.68 (9:1 hexane/ethyl acetate)); IR (neat)ν<sub>max</sub> 2955, 2927, 2857, 2236, 1597, 1366, 1170, 1114, 841, 745 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.89-7.87 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.30 (m, 2H), 7.12 (m, 2H), 3.68-3.64 (m, 1H) and 3.58-
3.54 (m, 1H) [as AB system], 3.24-3.21 (m, 1H), 2.81 (t, J = 4.3 Hz, 1H), 2.66-2.64 (m, 1H), 2.59 (t, J = 7.7 Hz, 2H), 2.46 (s, 3H), 1.64-1.58 (m, 2H), 1.37-1.32 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); 13C NMR (125 MHz, CDCl₃): δ 144.9, 143.3, 134.4, 131.6, 129.8, 128.4, 127.8, 119.6, 81.6, 70.7, 54.0, 49.2, 45.6, 35.8, 31.4, 31.0, 22.5, 21.7, 14.0; LC-MS: m/z 398 [M+1]+; Anal. Calcd. for C₂₃H₂₇NO₃S: C, 69.49; H, 6.85; N, 3.52. Found: C, 69.36; H, 6.81; N, 3.58.

N-(oxiran-2-ylmethyl)-N-(phenylethynyl)thiophene-2-sulfonamide (1I)
Yield: 1.136 g (78%, gummy liquid, Rₖ = 0.55 (9:1 hexane/ethyl acetate)); IR (neat) ν_max 3099, 3059, 3000, 2927, 2238, 1401, 1371, 1228, 1171, 1017, 856, 757 cm⁻¹; 1H NMR (500 MHz, CDCl₃): δ 7.78-7.77 (m, 1H), 7.72-7.70 (m, 1H), 7.43-7.41 (m, 2H), 7.31-7.30 (m, 3H), 7.17-7.15 (m, 1H), 3.68-3.58 (m, 2H), 3.26-3.23 (m, 1H), 2.82 (dd→t, J = 4.5 Hz, 1H); 13C NMR (100 MHz, CDCl₃): δ 150.7, 142.7, 131.7, 129.2, 128.6, 128.5, 124.4, 121.7, 80.8, 71.4, 54.4, 49.1, 45.5; LC-MS: m/z 320 [M+1]+; Anal. Calcd. for C₁₅H₁₄NO₂S₂: C, 56.41; H, 4.10; N, 4.39. Found: C, 56.32; H, 4.15; N, 4.31.

4-nitro-N-(oxiran-2-ylmethyl)-N-(phenylethynyl)benzenesulfonamide (1n) Yield: 0.735 g (53%, gummy liquid, Rₖ = 0.62 (9:1 hexane/ethyl acetate)); IR (neat) ν_max 3103, 2925, 2239, 1605, 1528, 1401, 1368, 1345, 1311, 1172, 1107, 1088, 1027, 938, 896, 810, 736, 687 cm⁻¹; 1H NMR (400 MHz, CDCl₃): δ 8.43 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H), 7.41-7.32 (m, 5H), 3.81-3.66 (m, 2H), 3.28-3.24 (m, 1H), 2.86 (t, J = 4.4 Hz, 1H); 13C NMR (100 MHz, CDCl₃): δ 150.7, 142.7, 131.7, 129.2, 128.6, 128.5, 124.4, 121.7, 80.8, 71.4, 54.4, 49.1, 45.5; HRMS (ESI): Calcd for C₁₇H₁₄N₂O₅S (M⁺+Na) m/z 381.0521. Found: 381.0524.
4-methyl-N-(oxiran-2-ylmethyl)-N-((3-(trifluoromethyl)phenyl)ethynyl)benzenesulfonamide *(10)* Yield: 1.47 g (85%, gummy liquid, *R* = 0.62 (9:1 hexane/ethyl acetate)); IR (neat) *ν* max 3163, 3002, 2944, 2252, 1756, 1611, 1501, 1375, 1201, 1171, 1039, 918, 739 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 1H), 7.55-7.54 (m, 2H), 7.45-7.39 (m, 3H), 3.69-3.59 (m, 2H), 3.26-3.23 (m, 1H), 2.85 (t, *J* = 4.3 Hz, 1H), 2.67-2.66 (m, 1H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 145.3, 134.3, 130.9 (q, *J* = 65.0 Hz), 129.9, 128.8, 127.9 (q→t, *J* = 3.7 Hz), 127.8, 124.4 (q, *J* = 7.7 Hz), 123.7 (q, *J* = 270.8 Hz), 123.6, 83.9, 69.6, 53.9, 49.3, 45.4, 21.7; ¹⁹F NMR (470 MHz, CDCl₃) -62.9; HRMS (ESI): Calcd. for C₁₉H₁₇F₃NO₃S (M⁺+H): m/z 396.0881. Found: 396.0880.

(3) Synthesis of 1,3 oxazolidines 3-11 from epoxy ynamides

To an oven dried RBF (10 mL), 4-methyl-N-(oxiran-2-ylmethyl)-N-(phenylethynyl)benzenesulfonamide (1a; 0.100 g, 0.3 mmol) in dry DMF (1 mL), CuBr (0.088 g, 0.6 mmol) was added. The mixture was heated with stirring at 80 °C for 1-2 h. After completion of the reaction as monitored by TLC, ethyl acetate (25 mL) was added and the solution was washed with water (3 x 30 mL). The aqueous layer was extracted with ethyl acetate (3x 20 mL). The combined organic portion was dried over anh. Na₂SO₄ and the solvent removed under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded 1,3-oxazolidine 3. Compounds 4-11 were prepared following the same procedure and by using the same molar quantities.
(E)-2-(bromo(phenyl)methylene)-5-(bromomethyl)-3-tosyloxazolidine (3)

Yield: 0.131g (88% with E:Z in 96:4, R_f = 0.78 (9:1 hexane/ethyl acetate)); IR (neat) \( \nu_{\text{max}} \) 3054, 3030, 2959, 2923, 2852, 1649, 1490, 1443, 1367, 1346, 1165, 1088, 1052, 1018, 753 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\( D_6 \)): \( \delta \) 7.91 (d, \( J = 8.0 \) Hz, 2H), 7.54 (m, 4H), 7.38 (dd→t, \( J \sim 7.4 \) Hz, 2H), 7.29 (t, \( J \sim 7.4 \) Hz, 1H), 4.24-4.20 (m, 1H), 3.97 (br m, 1H), 3.62-3.56 (m, 2H), 3.53-3.49 (m, 1H), 2.46 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\( D_6 \)): \( \delta \) 146.4, 145.8, 136.6, 134.8, 130.7, 130.2, 129.8, 129.4, 128.6, 128.4, 128.2, 127.0, 93.6, 77.7, 51.8, 33.2, 21.6; HRMS (ESI): Calcd. for C\(_{18}\)H\(_{18}\)Br\(_2\)NO\(_3\)S (M\(^{+}\)+H), (M\(^{+}\)+H+2), (M\(^{+}\)+H+4) \( m/z \) 485.9374, 487.9354, 489.9334. Found: 485.9376, 487.9356, 489.9338.

(E)-2-(bromo(3-fluorophenyl)methylene)-5-(bromomethyl)-3-tosyloxazolidine (4)

Yield: 0.121 g (83% with E:Z in 78:22, R_f = 0.76 (9:1 hexane/ethyl acetate)); Mp: 118-120 °C; IR (KBr) \( \nu_{\text{max}} \) 3068, 3033, 2958, 1648, 1608, 1582, 1487, 1434, 1348, 1265, 1165, 1088, 1054, 1019, 953, 779, 680 cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-\( D_6 \)): Major isomer: \( \delta \) 7.90 (d, \( J = 8.4 \) Hz, 2H), 7.53 (d, \( J = 8.4 \) Hz, 2H), 7.45-7.42 (m, 2H), 7.37-7.32 (m, 2H), 4.25-4.20 (m, 1H), 4.03-3.97 (m, 1H), 3.66-3.62 (m, 2H), 3.56-3.53 (m, 1H), 2.45 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\( D_6 \)): Major isomer: \( \delta \) 162.0 (d, \( J = 241.4 \) Hz), 147.3, 145.9, 138.8 (d, \( J = 8.3 \) Hz), 134.7, 130.74, 130.68, 128.2, 127.8, 126.9 (d, \( J = 3.3 \) Hz), 125.6 (d, \( J = 2.8 \) Hz), 115.9 (d, \( J = 23.3 \) Hz), 115.1 (d, \( J = 20.8 \) Hz), 91.8, 78.1, 51.8, 33.2, 21.6; \(^{19}\)F NMR: -113.30 (major isomer); -114.06 (minor isomer); HRMS (ESI): Calcd. for C\(_{18}\)H\(_{17}\)Br\(_2\)FNO\(_3\)S (M\(^{+}\)+H), (M\(^{+}\)+H+2), (M\(^{+}\)+H+4): \( m/z \) 503.9280, 505.9260, 507.9240. Found:
This compound was crystallized from hexane/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for the E-isomer.

(E)-2-(bromo(phenyl)methylene)-5-(bromomethyl)-3-(phenylsulfonyl)oxazolidine (5)
Yield: 0.121 g (80% with E:Z in 88:12, R_t = 0.66 (9:1 hexane/ethyl acetate)); IR (neat)_ν_max 3061, 2955, 2926, 2854, 1651, 1446, 1367, 1348, 1168, 1088, 1053, 1023, 754, 726, 689 cm⁻¹; \(^1\)H NMR (400 MHz, DMSO-D₆): Major isomer: δ 8.04-8.02 (m, 2H), 7.86-7.82 (m, 1H), 7.75-7.72 (m, 2H), 7.56-7.54 (m, 2H), 7.39-7.36 (m, 2H), 7.31-7.27 (m, 1H), 4.26-4.22 (m, 1H), 4.01-3.96 (m, 1H), 3.64-3.58 (m, 2H), 3.52-3.49 (m, 1H); \(^{13}\)C NMR (100 MHz, DMSO-D₆): Major isomer: δ 146.3, 137.8, 136.6, 135.0, 130.3, 129.4, 128.6, 128.4, 128.2, 127.7, 93.6, 77.8, 51.9, 33.1; HRMS (ESI): Calcd. for C₁₇H₁₆Br₂NO₃S (M⁺+H), (M⁺+H+2), (M⁺+H+4): m/z 471.9217, 473.9197, 475.9177. Found: 471.9218, 473.9195, 475.9178.

(E)-2-(bromo(phenyl)methylene)-5-(bromomethyl)-3-((4-(tert-butyl)phenyl)sulfonyl)oxazolidine (6)
Yield: 0.117 g (82% with E:Z in 92:8, R_t = 0.72 (9:1 hexane/ethyl acetate)); IR (neat)_ν_max 2925, 2870, 2854, 1752, 1596, 1496, 1399, 1331, 1267, 1164, 1113, 1088, 1027, 837, 753, 629 cm⁻¹.; \(^1\)H NMR (400 MHz, DMSO-D₆): Major isomer: δ 7.95 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.38 (dd→t, J ~ 7.4 Hz, 2H), 7.29 (t, J ~ 7.4 Hz, 1H), 4.22-4.17 (m, 1H), 4.03-3.98 (m, 1H), 3.61-3.55 (m, 2H), 3.49-3.45 (m, 1H), 1.34 (s, 9H); \(^{13}\)C NMR (100 MHz, DMSO-
D₆): Major isomer: δ 158.4, 146.4, 136.6, 134.7, 129.5, 128.6, 128.4, 127.1, 93.6, 78.0, 51.8, 35.6, 33.1, 31.2; HRMS (ESI): Calcd. for C₂₁H₂₄Br₂NO₃S (M⁺+H), (M⁺+H+2), (M⁺+H+4): m/z 527.9843, 529.9823, 531.9803. Found: 527.9842, 529.9824, 531.9801.

(E)-2-(bromo(phenyl)methylene)-5-(bromomethyl)-3-(naphthalen-2-ylsulfonyl)oxazolidine (7)

Yield: 0.112 g (78% with E:Z in 96: 4, Rᵣ = 0.70 (9:1 hexane/ethyl acetate)); IR (neat)νₘₐₓ 3058, 2923, 2853, 1748, 1591, 1504, 1455, 1444, 1336, 1260, 1157, 1131, 1073, 1027, 900, 814, 749, 659 cm⁻¹; ¹H NMR (500 MHz, DMSO-D₆): Major isomer: δ 8.75 (s, 1H), 8.28-8.24 (m, 2H), 8.12 (d, J = 8.0 Hz, 1H), 8.02-8.00 (m, 1H), 7.81-7.72 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.37 (dd→t, J ~ 7.7 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 4.34-4.30 (m, 1H), 4.01-3.97 (m, 1H), 3.68-3.64 (m, 1H), 3.59-3.56 (m, 1H), 3.51-3.50 (m, 1H); ¹³C NMR (125 MHz, DMSO-D₆): Major isomer: δ 146.4, 136.6, 135.4, 134.8, 132.1, 130.4, 130.2, 130.1, 130.0, 129.5, 128.6, 128.5, 128.4, 122.8, 93.6, 77.8, 52.0, 33.2; HRMS (ESI): Calcd. for C₂₁H₂₂Br₂NO₃SNa (M⁺+Na), (M⁺+Na+2), (M⁺+Na+4): m/z 543.9194, 545.9174, 547.9154. Found: 543.9193, 545.9180, 547.9155.

(E)-2-(bromo(phenyl)methylene)-5-(bromomethyl)-3-((4-bromophenyl)sulfonyl)oxazolidine (8)

Yield: 0.113 g (81% with E:Z in 89:11, Rᵣ = 0.73 (9:1 hexane/ethyl acetate)); Mp: 138-140 °C; IR (KBr)νₘₐₓ 3105, 3035, 2959, 2922, 2852, 1678, 1606, 1531, 1350, 1311, 1169, 856, 772, 739 cm⁻¹; ¹H NMR (400 MHz, DMSO-D₆): Major isomer: δ 7.97-7.91 (m, 4H), 7.56-7.54 (m, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 4.27-4.23 (m, 1H), 4.11-4.06 (m, 1H), 3.66-3.62 (m, 2H), 3.56-3.53 (m, 1H); ¹³C NMR (100 MHz, DMSO-D₆): Major isomer: δ 146.1, 137.1, 136.5, 133.4, 130.1, 130.0, 129.4, 129.2, 128.6, 128.5, 93.7, 77.9, 51.9, 33.2; HRMS (ESI): Calcd. for C₁₇H₁₅Br₃NO₅S (M⁺+H), (M⁺+H+2), (M⁺+H+4), (M⁺+H+6) : m/z 549.8323, 551.8303, 553.8283,
555.8263. Found: 549.8321, 551.8305, 553.8284, 555.8258. This compound was crystallized from hexane/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for this sample.

\[(E)-2\text{-}(\text{bromo}(p\text{-tolyl})\text{methylene})-5\text{-}(\text{bromomethyl})-3\text{-tosyloxazolidine} (9)\]

Yield: 0.126 g (86% with \(E:Z\) in 86:14, \(R_f = 0.74\) (9:1 hexane/ethyl acetate)); IR (neat)\(\nu_{\text{max}}\) 2960, 2923, 2855, 1747, 1597, 1513, 1422, 1330, 1260, 1159, 1090, 1018, 811, 752 cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(D_6\)): Major isomer: \(\delta 7.88\) (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.5\) Hz, 2H), 7.43 (d, \(J = 8.0\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 4.21-4.17 (m, 1H), 3.93-3.90 (m, 1H), 3.59-3.53 (m, 2H), 3.50-3.47 (m, 1H), 2.44 (s, 3H), 2.30 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(D_6\)): Major isomer: \(\delta 146.0, 145.7, 137.9, 134.8, 133.8, 130.7, 129.3, 129.1, 128.2, 127.7, 93.9, 77.6, 51.8, 33.2, 21.6, 21.2; HRMS (ESI): Calcd. for \(C_{19}H_{20}Br_{2}NO_{3}S\) (M\(^{+}\)H), (M\(^{+}\)H+2), (M\(^{+}\)H+4): \(m/z\) 499.9530, 501.9500, 503.9480. Found: 499.9523, 501.9504, 503.9484.

\[(E/Z)-2\text{-}(\text{bromo}(4\text{-bromophenyl})\text{methylene})-5\text{-}(\text{bromomethyl})-3\text{-tosyloxazolidine} (10) (two isomers)\]

Yield: 0.108 g (78% with \(E:Z\) in 54:46, \(R_f = 0.76\) (9:1 hexane/ethyl acetate)); IR (near)\(\nu_{\text{max}}\) 2956, 2925, 2854, 1748, 1657, 1596, 1488, 1338, 1163, 1090, 1011, 814, 756, 669 cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(D_6\)): Major isomer: \(\delta 7.88\) (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.5\) Hz, 2H), 7.43 (d, \(J = 8.0\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 4.21-4.17 (m, 1H), 3.93-3.90 (m, 1H), 3.59-3.53 (m, 2H), 3.50-3.47 (m, 1H), 2.44 (s, 3H), 2.30 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(D_6\)): Major isomer: \(\delta 146.0, 145.7, 137.9, 134.8, 133.8, 130.7, 129.3, 129.1, 128.2, 127.7, 93.9, 77.6, 51.8, 33.2, 21.6, 21.2; HRMS (ESI): Calcd. for \(C_{20}H_{21}Br_{2}NO_{3}S\) (M\(^{+}\)H), (M\(^{+}\)H+2), (M\(^{+}\)H+4): \(m/z\) 509.9545, 511.9515, 513.9555. Found: 509.9538, 511.9512, 513.9552.
MHz, DMSO-D$_6$): Isomer 1: δ 7.89 (d, $J = 8.5$ Hz, 2H), 7.53-7.48 (m, 6H), 4.23-4.19 (m, 1H), 4.00-3.94 (m, 1H), 3.59-3.56 (m, 2H), 3.52-3.49 (m, 1H), 2.44 (s, 3H). Isomer 2: δ 7.59-7.57 (m, 2H), 7.38-7.36 (m, 2H), 4.34-4.30 (m, 1H); 4.00-3.94 (m, 1H), 3.82-3.78 (m, 1H); 3.64-3.60 (m, 2H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, DMSO-D$_6$): Isomer 1: δ 146.9, 145.8, 135.9, 134.8, 132.0, 131.4, 130.7, 130.3, 128.2, 121.3, 92.1, 77.9, 51.9, 33.1, 21.6. Isomer 2: 146.5, 145.7, 137.2, 134.3, 131.5, 131.3, 130.6, 127.7, 121.0, 88.9, 76.9, 52.9, 32.8, 21.6; HRMS (ESI): Calcd. for C$_{18}$H$_{17}$Br$_3$NO$_3$S (M$^+$+H), (M$^+$+H+2), (M$^+$+H+4), (M$^+$+H+6): m/z 563.8479, 565.8459, 567.8439, 569.8419. Found: 563.8470, 565.8450, 567.8432, 569.8412.

(E)-3-(benzylsulfonyl)-2-(bromo(phenyl)methylene)-5-(bromomethyl)oxazolidine (11)

Yield: 0.126 g (85% with $E$:Z in 94:6, $R_f = 0.80$ (9:1 hexane/ethyl acetate)); IR (neat) $\nu_{\text{max}}$ 2929, 1745, 1495, 1455, 1327, 1212, 1127, 1029, 830, 751, 695 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.68-7.65 (m, 2H), 7.59-7.57 (m, 2H), 7.48-7.46 (m, 3H), 7.38-7.34 (m, 2H), 7.29-7.25 (m, 1H), 4.77 (AB pattern, 2H), 4.49-4.42 (m, 1H), 3.43-3.33 (m, 3H), 3.27-3.23 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.2, 135.9, 131.4, 129.3, 128.9, 128.1, 128.0, 127.9, 92.1, 78.1, 60.7, 52.5, 30.0; HRMS (ESI): Calcd. for C$_{18}$H$_{18}$Br$_2$NO$_3$S (M$^+$+H), (M$^+$+H+2), (M$^+$+H+4): m/z 485.9374, 487.9354, 489.9334. Found: 485.9368, 487.9353, 489.9331.

(4) Synthesis of compound 12

To an oven dried 10 mL RBF, 4-methyl-$N$-(oxiran-2-ylmethyl)-$N$-phenylbenzenesulfonyamide (0.1 g, 0.3 mmol) in DMF/H$_2$O (0.9+0.1 mL), and CuBr (0.94 g, 0.6 mmol) were added. The mixture was heated with stirring at 80 °C for 2 h. After completion of the reaction as monitored by TLC, ethyl acetate (25 mL) was added and the solution was washed with water (3 x 30 mL); the aqueous layer was extracted with ethyl acetate (3x 20 mL). The combined organic portion was

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dried over anh. Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded compound 12.

**N-(3-bromo-2-hydroxypropyl)-4-methyl-N-phenylbenzenesulfonamide (12)**

Yield: 0.117 g (93%, $R_f$ = 0.46 (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{\text{max}}$ 3495, 3063, 2924, 1595, 1490, 1344, 1160, 1088, 1023, 814 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J = 8.5$ Hz, 2H), 7.34-7.31 (m, 3H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.09-7.07 (m, 2H), 3.92-3.87 (m, 1H), 3.76-3.65 (m, 2H), 3.58-3.55 (m, 1H, 3.48-3.45 (m, 1H), 3.02 (d, $J = 5.5$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.0, 139.8, 134.5, 129.6, 129.3, 128.7, 128.4, 127.8, 69.0, 55.0, 36.4, 21.6; HRMS (ESI): Calcd. for C$_{16}$H$_{18}$BrNO$_3$SNa ($M^+$+Na), ($M^+$+Na+2): $m/z$ 406.0089, 408.0069. Found: 406.0089, 408.0070.

(5) **Synthesis of chloromethyl-1,4-oxazines 13-20 from epoxy ynamides**

To an oven dried 10 mL RBF, 4-methyl-N-(oxiran-2-ylmethyl)-N-(phenylethynyl)benzenesulfonamide (1a; 0.1 g, 0.3 mmol) in DMF/H$_2$O(0.9+0.1 mL), anhy. LiCl (0.024 g, 0.6 mmol) was added. The mixture was heated with stirring at 80 °C for 12 h. After completion of the reaction as monitored by TLC, ethyl acetate (25 mL) was added and the solution was washed with water (3 x 30 mL); the aqueous layer was extracted with ethyl acetate (3x 20 mL). The combined organic portion was dried over anh. Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded compound 1,4-oxazine 13. Compounds 13' and 14-20 were prepared following the same procedure and by using the same molar quantities.
2-{(chloromethyl)-6-phenyl-4-tosyl-3,4-dihydro-2H-1,4-oxazine (13)}

Yield: 0.086 g (78%, $R_f = 0.80$ (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{max}$ 3112, 3059, 3028, 2960, 2924, 2872, 1651, 1597, 1494, 1353, 1306, 1164, 1005, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J = 8.0$ Hz, 2H), 7.51-7.48 (m, 2H), 7.37-7.30 (m, 5H), 6.75 (s, 1H), 4.03-4.00 (m, 1H), 3.70-3.64 (m, 2H), 3.53-3.48 (m, 1H), 3.26-3.21 (m, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 1.44.4, 139.8, 133.1, 130.1, 128.4, 128.2, 127.4, 123.8, 101.8, 71.9, 45.1, 42.4, 21.6; HRMS (ESI): Calcd. for C$_{18}$H$_{19}$ClNO$_3$S (M$^+$+H), (M$^+$+H+2): m/z 364.0774, 366.0744. Found: 364.0772, 366.0747.

2-{(chloromethyl)-5-deutero-6-phenyl-4-tosyl-3,4-dihydro-2H-1,4-oxazine (13’)}

Yield: 0.061 g (55%, $R_f = 0.79$ (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{max}$ 2957, 2925, 2855, 1725, 1637, 1598, 1494, 1356, 1167, 1089, 760 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J = 8.5$ Hz, 2H), 7.50-7.48 (m, 2H), 7.37-7.34 (m, 4H), 7.32-7.30 (m, 1H), 6.75 (s, 0.1H), 4.02-4.00 (m, 1H), 3.70-3.64 (m, 2H), 3.52-3.49 (m, 1H), 3.26-3.22 (m, 1H), 2.45 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.3, 139.7, 133.7, 133.2, 130.0, 128.4, 128.2, 127.4, 123.8, 101.8, 101.4 (d, $J = 28.4$ Hz), 72.0, 45.0, 42.4, 21.6; HRMS (ESI): Calcd. for C$_{18}$H$_{17}$ClNO$_3$SNa (M$^+$+Na), (M$^+$+Na+2): m/z 387.0657, 389.0627. Found: 387.0654, 389.0628.

2-{(chloromethyl)-6-phenyl-4-(phenylsulfonyl)-3,4-dihydro-2H-1,4-oxazine (14)}

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Yield: 0.082 g (74%, Rf = 0.78 (9:1 hexane/ethyl acetate)); IR (neat)νmax 3027, 2960, 2925, 2873, 1652, 1446, 1354, 1309, 1166, 1088, 1007, 749, 688 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.58 (dd→t, J ~ 7.6 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.39-7.30 (m, 3H), 6.77 (s, 1H), 4.03 (d, J = 13.2 Hz, 1H), 3.70-3.63 (m, 2H), 3.52-3.48 (m, 1H), 3.29-3.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 139.9, 136.5, 133.5, 133.1, 129.5, 128.5, 128.3, 127.3, 123.8, 101.6, 72.0, 45.1, 42.4; HRMS (ESI): Calcd. for C₁₇H₁₇ClNO₃S (M⁺+H), (M⁺+H+2): m/z 350.0617, 352.0587. Found: 350.0616, 352.0584.

2-(chloromethyl)-4-(naphthalen-2-ylsulfonfonyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazine (15)

Yield: 0.076 g (69%, Rf = 0.74 (9:1 hexane/ethyl acetate)); IR (neat)νmax 3027, 2959, 2926, 1653, 1498, 1448, 1350, 1308, 1164, 1133, 1074, 1007, 858, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.43 (s, 1H), 8.02-7.99 (m, 2H), 7.94 (d, J = 8.5 Hz, 1H), 7.82-7.80 (m, 1H), 7.71-7.63 (m, 2H), 7.50-7.48 (m, 2H), 7.37-7.30 (m, 3H), 6.84 (s, 1H), 4.12-4.09 (m, 1H), 3.68-3.62 (m, 2H), 3.50-3.46 (m, 1H), 3.33-3.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 139.9, 135.1, 133.6, 133.1, 133.1, 132.2, 129.8, 129.4, 129.3, 128.9, 128.5, 128.3, 128.0, 127.9, 123.9, 122.3, 101.7, 72.0, 45.1, 42.4; HRMS (ESI): Calcd. for C₂₁H₁₈ClNO₃SNa (M⁺+Na), (M⁺+Na+2): m/z 422.0594, 424.0564. Found: 422.0595, 424.0559.

4-((4-chloro-2,5-dimethylphenyl)sulfonyl)-2-(chloromethyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazine (16)
Yield: 0.068 g (65%, \( R_f = 0.79 \) (9:1 hexane/ethyl acetate)); IR (near)\( \nu_{max} \) 2961, 2926, 2870, 2857, 1724, 1658, 1599, 1448, 1365, 1341, 1165, 1087, 1016, 758 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.84 (s, 1H), 7.51-7.50 (m, 2H), 7.38-7.30 (m, 4H), 6.75 (s, 1H), 3.95-3.90 (m, 2H), 3.77-3.73 (m, 1H), 3.60-3.56 (m, 1H), 3.29-3.25 (m, 1H), 2.62 and 2.42 (2 s, 6H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 139.8, 139.1, 136.7, 134.8, 133.8, 133.4, 133.1, 132.4, 128.5, 128.2, 123.8, 101.6, 72.4, 44.6, 42.3, 20.5, 19.6; HRMS (ESI): Calcd. for C\(_{19}\)H\(_{19}\)Cl\(_2\)NO\(_3\)SNa (M\(^+\)+Na), (M\(^+\)+Na+2): \( m/z \) 434.0361, 436.0331. Found: 434.0363, 436.0329.

![Chemical Structure](image1)

**6-(4-bromophenyl)-2-(chloromethyl)-4-tosyl-3,4-dihydro-2H-1,4-oxazine (17)**

Yield: 0.067 g (62%, \( R_f = 0.80 \) (9:1 hexane/ethyl acetate)); IR (neat)\( \nu_{max} \) 3110, 3028, 2960, 2924, 1651, 1596, 1490, 1355, 1308, 1166, 1088, 1006, 752 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.72-7.70 (m, 2H), 7.48-7.45 (m, 2H), 7.36-7.34 (m, 4H), 6.75 (s, 1H), 4.01-3.98 (m, 1H), 3.68-3.64 (m, 2H), 3.52-3.50 (m, 1H), 3.25-3.21 (m, 1H), 2.45 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 143.5, 137.7, 132.7, 131.1, 130.5, 129.1, 126.3, 124.2, 121.0, 101.2, 71.0, 44.0, 41.3, 20.6; HRMS (ESI): Calcd. for C\(_{18}\)H\(_{17}\)BrClNO\(_3\)SNa (M\(^+\)+Na), (M\(^+\)+Na+2), (M\(^+\)+Na+4): \( m/z \) 463.9699, 465.9679, 467.9659. Found: 463.9702, 465.9681, 467.9657.

![Chemical Structure](image2)

**2-(chloromethyl)-6-(4-pentylphenyl)-4-tosyl-3,4-dihydro-2H-1,4-oxazine (18)**

Yield: 0.081 g (74%, \( R_f = 0.81 \) (9:1 hexane/ethyl acetate)); IR (neat)\( \nu_{max} \) 3112, 3029, 2956, 2927, 2856, 1658, 1597, 1356, 1310, 1261, 1218, 1167, 1124, 1055, 1009, 813, 770 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.84 (s, 1H), 7.51-7.50 (m, 2H), 7.38-7.30 (m, 4H), 6.75 (s, 1H), 3.95-3.90 (m, 2H), 3.77-3.73 (m, 1H), 3.60-3.56 (m, 1H), 3.29-3.25 (m, 1H), 2.62 and 2.42 (2 s, 6H); \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 139.8, 139.1, 136.7, 134.8, 133.8, 133.4, 133.1, 132.4, 128.5, 128.2, 123.8, 101.6, 72.4, 44.6, 42.3, 20.5, 19.6; HRMS (ESI): Calcd. for C\(_{19}\)H\(_{19}\)Cl\(_2\)NO\(_3\)SNa (M\(^+\)+Na), (M\(^+\)+Na+2), (M\(^+\)+Na+4): \( m/z \) 463.9699, 465.9679, 467.9659. Found: 463.9702, 465.9681, 467.9657.

![Chemical Structure](image3)
MHz, CDCl$_3$): $\delta$ 7.71 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.70 (s, 1H), 4.01-3.98 (m, 1H), 3.68-3.59 (m, 2H), 3.51-3.47 (m, 1H), 3.24-3.20 (m, 1H), 2.61 (t, $J = 7.7$ Hz, 2H), 2.45 (s, 3H), 1.64-1.58 (m, 2H), 1.36-1.30 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.3, 143.3, 140.0, 133.7, 130.6, 130.0, 128.5, 127.4, 123.8, 101.1, 71.9, 45.1, 42.4, 35.6, 31.4, 31.0, 22.5, 21.6, 14.0; HRMS (ESI): Calcd. for C$_{23}$H$_{28}$ClNO$_3$SNa (M$^+$+Na), (M$^+$+Na+2): m/z 456.1376, 458.1346. Found: 456.1375, 458.1350.

2-(chloromethyl)-6-(p-toly1)-4-tosyl-3,4-dihydro-2H-1,4-oxazine (19)
Yield: 0.085 g (77%, $R_f = 0.78$ (9:1 hexane/ethyl acetate)); Mp: 124-126 °C; IR (KBr)$\nu_{\text{max}}$ 3111, 3031, 2957, 2922, 2871, 1655, 1597, 1514, 1354, 1308, 1165, 1089, 1007, 818, 758 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.71 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.70 (s, 1H), 4.02-4.00 (m, 1H), 3.68-3.60 (m, 2H), 3.51-3.48 (m, 1H), 3.25-3.20 (m, 1H), 2.45 and 2.40 (2s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.3, 140.0, 138.2, 133.7, 130.4, 130.0, 129.1, 127.4, 123.8, 101.1, 72.0, 45.1, 42.4, 21.6, 21.2; HRMS (ESI): Calcd. for C$_{19}$H$_{20}$ClNO$_3$SNa (M$^+$+Na), (M$^+$+Na+2): m/z 400.0750, 402.0720. Found: 400.0743, 402.0714. This compound was crystallized from hexane/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for this sample.

2-(chloromethyl)-6-phenyl-4-(thiophen-2-ylsulfonyl)-3,4-dihydro-2H-1,4-oxazine (20)
Yield: 0.076 g (69%, $R_f = 0.70$ (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{\text{max}}$ 3110, 3028, 2958, 2926, 1652, 1448, 1403, 1360, 1310, 1226, 1165, 1092, 1014, 757, 724 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.66-7.65 (m, 1H), 7.64-7.63 (m, 1H), 7.53-7.51 (m, 2H), 7.38-7.32 (m, 3H), 7.18-7.16
(m, 1H), 6.71 (s, 1H), 4.08-4.05 (m, 1H), 3.74-3.67 (m, 2H), 3.58-3.55 (m, 1H), 3.30-3.26 (m, 1H); 
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 140.7, 136.6, 133.0, 132.8, 132.8, 130.4, 128.5, 128.4, 127.9, 123.9, 101.1, 72.0, 45.2, 42.4; HRMS (ESI): Calcd. for C$_{15}$H$_{15}$ClNO$_3$S$_2$ (M$^+$+H), (M$^+$+H+2): m/z 356.0182, 358.0152. Found: 356.0187, 358.0160.

(6) Synthesis of hydroxymethyl-1,4-oxazines 21-26 from epoxy ynamides

To an oven dried 10 mL RBF, epoxy ynamide (1a; 0.1 g, 0.3 mmol) in NMP/H$_2$O(0.9+0.1 mL), and CuF$_2$ (0.62 g, 0.6 mmol) were added. The mixture was heated with stirring at 80 °C for 4 h. After completion of the reaction as monitored by TLC, ethyl acetate (25 mL) was added and the solution was washed with water (3 x 30 mL); the aqueous layer was extracted with ethyl acetate (3x 20 mL). The combined organic portion was dried over anh. Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded compound 1,4-oxazine 21. Compounds 22-26 were prepared by following the same procedure and by using the same molar quantities.

(6-phenyl-4-tosyl-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (21)

Yield: 0.082 g (78%, $R_f = 0.61$ (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{max}$ 3531, 3064, 2987, 2881, 1651, 1448, 1349, 1263, 1214, 1162, 1061, 1005, 751 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.70 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.35-7.31 (m, 5H), 6.74 (s, 1H), 3.90-3.87 (m, 1H), 3.83-3.80 (m, 1H), 3.75-3.72 (m, 1H), 3.61-3.57 (m, 1H), 3.24-3.19 (m, 1H), 2.43 (s, 3H), 1.93 (br, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.2, 139.9, 133.8, 133.5, 130.0, 128.4, 128.1, 127.3, 123.8, 101.8, 72.9, 62.5, 44.3, 21.6; HRMS (ESI): Calcd. for C$_{18}$H$_{20}$NO$_4$S (M$^+$+H): m/z 346.1111. Found: 346.1117.
(4-((4-tert-buty)phenyl)sulfonyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (22)

Yield: 0.078 g (75%, R<sub>f</sub> = 0.62 (9:1 hexane/ethyl acetate)); Mp: 106-110 °C; IR (KBr)\(\nu_{\text{max}}\) 3437, 2960, 2927, 2869, 1726, 1597, 1455, 1262, 1165, 1085, 1005, 843, 798 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): \(\delta\) 7.77-7.74 (m, 2H), 7.56-7.50 (m, 4H), 7.37-7.28 (m, 3H), 6.77 (s, 1H), 3.92-3.88 (m, 1H), 3.85-3.81 (m, 1H), 3.75-3.72 (m, 1H), 3.71-3.67 (m, 1H), 3.26-3.20 (m, 1H), 2.24 (br s, 1H), 1.35 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): \(\delta\) 157.2, 139.7, 133.7, 133.5, 128.4, 128.1, 127.2, 126.4, 123.7, 101.8, 73.1, 62.4, 44.3, 35.3, 31.1; HRMS (ESI): Calcd. for C<sub>21</sub>H<sub>25</sub>NO<sub>4</sub>SNa (M<sup>+</sup>+Na): m/z 410.1402. Found: 410.1407. This compound was crystallized from hexane/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for this sample.

(4-((4-bromophenyl)sulfonyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (23)

Yield: 0.073 g (71%, R<sub>f</sub> = 0.63 (9:1 hexane/ethyl acetate)); IR (neat)\(\nu_{\text{max}}\) 3532, 3093, 2927, 1573, 1389, 1355, 1310, 1167, 1087, 1067, 1006, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): \(\delta\) 7.70-7.65 (m→s, 4H), 7.50-7.47 (m, 2H), 7.37-7.30 (m, 3H), 6.69 (s, 1H), 3.92-3.88 (m, 1H), 3.84-3.74 (m, 2H), 3.65-3.60 (m, 1H), 3.25-3.19 (m, 1H), 2.27 (br, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): \(\delta\) 140.6, 135.7, 133.2, 132.7, 128.8, 128.5, 128.3, 123.9, 101.2, 73.0, 62.3, 44.4; HRMS (ESI): Calcd. for C<sub>17</sub>H<sub>16</sub>BrNO<sub>4</sub>SNa (M<sup>+</sup>+Na), (M<sup>+</sup>+Na+2): m/z 431.9881, 433.9851. Found: 431.9885, 433.9852.
(4-((4-chloro-2,5-dimethylphenyl)sulfonyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (24)

Yield: 0.071 g (68%, Rf = 0.62 (9:1 hexane/ethyl acetate)); IR (neat) \( \nu_{max} \) 3437, 3064, 2923, 2857, 1697, 1452, 1365, 1320, 1224, 1158, 1026, 980, 702, 605 cm\(^{-1}\); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.83 (s, 1H), 7.49 (d, \( J = 7.5 \) Hz, 2H), 7.36-7.29 (m, 4H), 6.74 (s, 1H), 3.89-3.86 (m, 2H), 3.82-3.78 (m, 2H), 3.28-3.24 (m, 1H), 2.60 (s, 3H), 2.41 (s, 3H), 2.06 (br, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 139.6, 139.1, 136.7, 134.6, 134.0, 133.5, 133.3, 132.3, 128.8, 128.4, 128.1, 123.7, 101.6, 73.4, 62.3, 43.8, 20.3, 19.6; HRMS (ESI): Calcd. for C\(_{19}\)H\(_{20}\)ClNO\(_4\)SNa (M\(^{+}\)+Na), (M\(^{+}\)+Na+2): \( m/z \) 416.0700, 418.0670. Found: 416.0700, 418.0671.

![Chemical structure](image)

(4-((4-chlorophenyl)sulfonyl)-6-phenyl-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (25)

Yield: 0.079 g (76%, Rf = 0.63 (9:1 hexane/ethyl acetate)); IR (neat) \( \nu_{max} \) 3436, 3089, 2927, 1696, 1650, 1583, 1475, 1354, 1307, 1165, 1089, 1005, 828 cm\(^{-1}\); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.78-7.74 (m, 2H), 7.53-7.47 (m, 4H), 7.37-7.31 (m, 3H), 6.70 (s, 1H), 3.92-3.88 (m, 1H), 3.85-3.74 (m, 2H), 3.65-3.60 (m, 1H), 3.26-3.20 (m, 1H), 2.19 (br, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 140.5, 139.9, 135.2, 133.3, 129.7, 128.7, 128.4, 128.3, 123.9, 101.2, 73.0, 62.4, 44.4; HRMS (ESI): Calcd. for C\(_{17}\)H\(_{16}\)ClNO\(_4\)SNa (M\(^{+}\)+Na), (M\(^{+}\)+Na+2): \( m/z \) 388.0387, 390.0357. Found: 388.0385, 390.0356.

![Chemical structure](image)

(6-((4-pentylphenyl)-4-tosyl)-3,4-dihydro-2H-1,4-oxazin-2-yl)methanol (26)
Yield: 0.076 g (74%, R<sub>f</sub> = 0.58 (9:1 hexane/ethyl acetate)); IR (neat) ν<sub>max</sub> 3540, 2956, 2927, 2861, 1701, 1597, 1456, 1353, 1164, 1089, 1010, 734, 663 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.70 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.69 (s, 1H), 3.89-3.86 (m, 1H), 3.82-3.79 (m, 1H), 3.74-3.71 (m, 1H), 3.58-3.54 (m, 1H), 3.23-3.18 (m, 1H), 2.61 (t, J = 7.7 Hz, 2H), 2.43 (s, 3H), 1.64-1.59 (m, 2H), 1.36-1.29 (m, 5H), 0.90 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 144.1, 143.2, 140.2, 133.8, 130.9, 129.9, 128.5, 127.3, 123.6, 101.1, 72.8, 62.5, 44.3, 35.6, 31.4, 31.0, 22.5, 21.6, 14.0; HRMS (ESI): Calcd. for C<sub>23</sub>H<sub>29</sub>NO<sub>4</sub>SNa (M<sup>+</sup>Na): m/z 438.1715. Found: 438.1714.

(7) Synthesis of 3,5-dimethylphenoxy-1,4-oxazine 27

To an oven dried 5 mL RBF, epoxy-ynamide (1a; 0.100 g, 0.3 mmol), 3,5-dimethylphenol (0.055 g, 0.45 mmol), CuF<sub>2</sub> (0.015 g, 0.015 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.021 g, 0.015 mmol) were added. The contents were mixed thoroughly and the mixture was heated in a microwave oven [MW; 120 °C/10 min]. After completion of the reaction as monitored by TLC, DCM (15 mL) was added, the mixture filtered and the filtrate concentrated under reduced pressure. The crude product was purified by using flash column chromatography (neutral alumina; slow column led to decomposition of the product) to obtain pure 3,5-dimethylphenoxy-1,4-oxazine 27 by using hexane-ethyl acetate (9:1) mixture as the eluent. [Note: In silica gel compound decomposed very fast]

![Chemical structure of 3,5-dimethylphenoxy-1,4-oxazine 27](image)

2-((3,5-dimethylphenoxy)methyl)-6-phenyl-4-tosyl-3,4-dihydro-2H-1,4-oxazine (27)

Yield: 0.121 g (89%, gummy liquid, R<sub>f</sub> = 0.89 (hexane, neutral alumina ); IR (neat) ν<sub>max</sub> 3281, 2922, 1663, 1594, 1495, 1329, 1295, 1159, 911 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.81 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.31-7.24 (m, 4H), 7.15-7.11 (m, 1H), 6.66 (s, 1H), 6.41 (s, 2H), 5.97 (s, 1H), 4.59-4.53 (m, 1H), 4.09-4.04 (m, 1H), 3.98-3.89 (m, 2H), 3.54-3.50 (m, 1H),
2.40 (s, 3H), 2.29 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.9, 146.8, 144.9, 139.3, 135.4, 133.6, 129.9, 128.3, 127.6, 127.5, 125.1, 123.3, 112.3, 88.6, 74.9, 66.9, 48.7, 21.6, 21.4; HRMS (ESI): Calcd for C$_{26}$H$_{28}$NO$_4$S (M$^+$+H) $m/z$ 450.1739. Found: 450.1739.

(8) Synthesis of 1,2-dioxo-amides 28-31 and 33

To an oven dried 10 mL RBF, epoxy ynamide (1f; 0.1 g, 0.25 mmol) in dry DMC (1 mL), AgF$_2$ (0.185 g, 1.27 mmol) was added. The mixture was kept for stirring at 30 °C for 12 h. After completion of the reaction as monitored by TLC, the mixture was passed through celite and concentrated in vacuum. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded compound 1,2-dioxoenamide 28. Compounds 29-31 and 33 were prepared following the same procedure and by using the same molar quantities.

$\begin{align*}
\text{N-((4-bromophenyl)sulfonyl)-N-(oxiran-2-ylmethyl)-2-oxo-2-phenylacetamide (28)}
\end{align*}$

Yield: 0.076 g (71%, $R_f = 0.73$ (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{max}$ 3092, 3068, 2925, 1682, 1573, 1450, 1371, 1210, 1171, 1069, 1008, 945, 823, 741, 612 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98-7.93 (m, 4H), 7.79-7.77 (m, 2H), 7.71-7.68 (m, 1H), 7.59-7.56 (m, 2H), 4.03-3.92 (m, 2H), 3.24-3.21 (m, 1H), 2.83 (t, $J = 4.2$ Hz, 1H), 2.71-2.69 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 187.5, 167.1, 136.2, 134.8, 132.7, 132.5, 130.3, 130.1, 129.8, 128.9, 49.1, 47.0, 46.4; HRMS (ESI): Calcd. for C$_{17}$H$_{14}$BrNO$_5$SNa (M$^+$+Na): $m/z$ 445.9674, 447.9654. Found: 445.9674, 447.9656.

$\begin{align*}
\text{N-((4-chlorophenyl)sulfonyl)-N-(oxiran-2-ylmethyl)-2-oxo-2-phenylacetamide (29)}
\end{align*}$

Yield: 0.081 g (73%, $R_f = 0.72$ (9:1 hexane/ethyl acetate)); Mp 104-108 °C (white solid); IR (KBr)$\nu_{max}$ 3089, 3068, 2924, 1682, 1583, 1370, 1209, 1169, 1086, 1011, 924, 757, 713, 688 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.03-8.01 (m, 2H), 7.98-7.96 (m, 2H), 7.71-7.68 (m, 1H), 7.62-7.56
(m, 4H), 4.03-3.92 (m, 2H), 3.24-3.21 (m, 1H), 2.82 (t, J = 4.5 Hz, 1H), 2.70-2.69 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 187.6, 167.2, 141.6, 135.6, 134.8, 132.5, 130.1, 129.8, 129.0, 129.7, 49.1, 47.0, 46.4; HRMS (ESI): Calcd. for C$_{17}$H$_{14}$ClNO$_5$SNa (M$^+$+Na), (M$^+$+Na+2): m/z 402.0179, 404.0149. Found: 402.0179, 404.0149.

**N-((4-nitrophenyl)sulfonyl)-N-(oxiran-2-ylmethyl)-2-oxo-2-phenylacetamide (30)**

Yield: 0.082 g (74%; purity ~97%, R$_f$ = 0.61 (9:1 hexane/ethyl acetate)); Mp 168-170 °C (white solid); IR (KBr)$\nu_{max}$ 3108, 1684, 1597, 1533, 1404, 1376, 1350, 1258, 1210, 1173, 1086, 1045, 924, 855, 739, 617 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.48-8.46 (m, 2H), 8.31-8.29 (m, 2H), 7.99-7.97 (m, 2H), 7.73-7.70 (m, 1H), 7.61-7.57 (m, 2H), 4.26-4.23 (m, 1H), 3.96-3.92 (m, 1H), 3.23-3.20 (m, 1H), 2.82 (t, J = 4.5 Hz, 1H), 2.68-2.67 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 187.4, 166.9, 151.1, 142.9, 135.0, 132.2, 130.2, 129.9, 129.0, 124.4, 49.1, 47.4, 46.0; HRMS (ESI): Calcd. for C$_{17}$H$_{15}$N$_2$O$_7$S (M$^+$+H): m/z 391.0600. Found: 391.0600. This compound was crystallized from hexane/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for this sample.

**N-(oxiran-2-ylmethyl)-2-oxo-N-tosyl-2-(3-(trifluoromethyl)phenyl)acetamide (31)**

Yield: 0.091 g (85%, R$_f$ = 0.70 (9:1 hexane/ethyl acetate)); IR (neat)$\nu_{max}$ 2928, 1740, 1699, 1597, 1363, 1331, 1165, 1125, 1092, 1075, 814 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.27 (br, 1H), 8.13 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.4 Hz, 3H), 7.72 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 4.00-3.91 (m, 2H), 3.23-3.19 (m, 1H), 2.82 (t, J = 4.2 Hz, 1H), 2.71-2.70 (m, 1H), 2.50 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 186.1, 166.8, 146.4, 133.8, 133.4, 133.1, 131.7 (q, J = 66.5 Hz), 130.8 (q, J =
7.0 Hz), 130.2, 129.6, 128.6, 126.1 (q, \( J = 8.0 \text{ Hz} \)), 123.5 (q, \( J = 270.8 \text{ Hz} \)), 49.0, 46.7, 46.5, 21.8; \(^{19} \text{F NMR (470 MHz, CDCl}_3\)): -62.9; HRMS (ESI): Calcd. for C\(_{19}\)H\(_{17}\)F\(_3\)NO\(_5\)S (M\(^{+}\)+H): \( m/z \) 428.0779. Found: 428.0779.

\[ \text{N-methyl-2-oxo-2-phenyl-N-tosylacetamide (33)} \]

Yield: 0.086 g (78%, \( R_f = 0.72 \) (9:1 hexane/ethyl acetate)); Mp 116-120 °C (white solid); IR (neat)\( \nu_{\text{max}} \): 2923, 2853, 1739, 1677, 1595, 1368, 1230, 1202, 1087, 945, 662 cm\(^{-1}\); \(^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta \) 7.98-7.90 (m, 4H), 7.70-7.65 (m, 1H), 7.56 (t, \( J = 7.8 \text{ Hz} \), 2H), 7.42 (d, \( J = 8.0 \text{ Hz} \), 2H), 3.27 (s, 3H), 2.50 (s, 3H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\)): \( \delta \) 188.1, 167.3, 145.9, 134.5, 133.5, 132.8, 130.1, 129.7, 128.9, 128.4, 30.7, 21.7; HRMS (ESI): Calcd. for C\(_{16}\)H\(_{15}\)NO\(_4\)S (M\(^{+}\)+Na): \( m/z \) 340.0620. Found: 340.0622. This compound has been prepared previously by a different method (S. W. Kim, T. -W. Um and S. Shin, \textit{J. Org. Chem.} 2018, \textbf{83}, 4703.)

\( \text{(9) Synthesis of ynamide 34 and } \alpha,\beta\text{-dibromo enamide 35} \)

\text{Synthesis of ynamide 34:} To a mixture of N-(2-bromoethyl)-4-methylbenzenesulfonylamine (1.00 g, 3.62 mmol), CuSO\(_4\)·5H\(_2\)O (0.180 g, 0.72 mmol), 1,10-phenanthroline monohydrate (0.287 g, 1.44 mmol) and K\(_2\)CO\(_3\) (1.25 g, 9.0 mmol) in dry THF (20 mL), (bromoethyl)benzene (0.786 g, 4.34 mmol) was added. The vessel was stoppered under nitrogen atmosphere and heated overnight on an oil-bath maintained at 70 °C. The mixture was filtered and concentrated in vacuum. The crude product was purified by using silica gel column chromatography to obtain the pure ynamide 34 by using hexane-ethyl acetate (8:2) as the eluent.

\[ \text{N-(2-bromoethyl)-4-methyl-N-(phenylethynyl)benzenesulfonylamide (34)} \]
Yield: 1.03 g (76%, R\text{f} = 0.67 (9:1 hexane/ethyl acetate)); IR (neat)\nu_{\text{max}} 3061, 2925, 2855, 2235, 1730, 1704, 1597, 1493, 1367, 1289, 1168, 1119, 1089, 1020, 958, 813, 755 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.89 (d, \(J = 8.4\) Hz, 2H), 7.40 - 7.33 (m, 7H), 3.83 (t, \(J = 7.4\) Hz, 2H), 3.58 (t, \(J = 7.4\) Hz, 2H), 2.49 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) \(\delta\) 145.2, 134.3, 131.6, 129.9, 128.4, 128.2, 127.8, 122.3, 81.4, 71.2, 52.7, 27.5, 21.7; HRMS (ESI): Calcd for C\(_{17}\)H\(_{17}\)BrNO\(_2\)S (M\(^+\)H), (M\(^+\)H+2) \(m/z\) 378.0163, 380.0143. Found 378.0164, 380.0145.

**Synthesis of \(\alpha,\beta\)-dibromo enamide 35:** To an oven dried 10 mL RBF (round bottom flask) N-(2-bromoethyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide 34 (0.3 mmol) in dry acetonitrile (1 mL), CuBr (0.6 mmol) was added at 25 °C. After completion of the reaction as monitored by TLC, the contents were passed through a pad of celite, washed with ethyl acetate (2 x 20 mL) and concentrated \textit{in vacuo}. Purification by column chromatography (hexane/ethyl acetate 9:1) afforded compound 35.

![Structure of \(\alpha,\beta\)-dibromo enamide 35](image)

\textbf{(E)-N-(2-bromoethyl)-N-(1,2-dibromo-2-phenylvinyl)-4-methylbenzenesulfonamide (35)}
Yield: 0.131 g (92%; \(E/Z\): 7:3; pure \(E\)-isomer was isolated), white solid, \(R_f = 0.76\) (9:1 hexane/ethyl acetate)); Mp: 132-134 °C IR (KBr)\nu_{\text{max}} 2954, 2923, 2853, 1597, 1492, 1445, 1361, 1165, 1087, 967, 899, 813, 695 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.90 (d, \(J = 8.0\) Hz, 2H), 7.47 - 7.37 (m, 7H), 3.92 - 3.86 (m, 1H), 3.75 - 3.70 (m, 1H), 3.60 - 3.47 (m, 2H), 2.48 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 145.1, 138.8, 134.6, 129.8, 129.6, 128.9, 128.5, 126.9, 116.2, 50.4, 27.2, 21.7; HRMS (ESI): Calcd. for C\(_{17}\)H\(_{16}\)Br\(_3\)NO\(_2\)SNa (M\(^+\)+Na), (M\(^+\)+Na+2), (M\(^+\)+Na+4), (M\(^+\)+Na+6): \(m/z\) 557.8350, 559.8330, 561.8310, 563.8290. Found: 557.8352, 559.8336, 561.8316, 563.8293. This compound was crystallized from DCM/ethyl acetate (2:1) mixture at 25 °C. X-ray structure was determined for this sample.
(10) X-ray data and crystal structures of 4, 8, 19, 22, 30, and 35

**Compound 4:** \( \text{C}_{18}\text{H}_{16}\text{Br}_2\text{FNO}_3\text{S} \), \( M = 505.20 \), Triclinic, Space group \( P\bar{1} \), \( a = 6.9921(3) \), \( b = 11.2113(6) \), \( c = 12.4434(7) \) Å, \( V = 959.19(9) \) \( \text{Å}^3 \), \( \alpha = 96.443(2) \), \( \beta = 95.376(2) \), \( \gamma = 95.626(2) \), \( Z = 2 \), \( \mu = 4.361 \text{mm}^{-1} \), data/restraints/parameters: 3377/0/237, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0479 \), \( wR2 \) (all data) = 0.1485. CCDC No. 1885280.

**Compound 8:** \( \text{C}_{17}\text{H}_{14}\text{Br}_3\text{NO}_3\text{S} \), \( M = 552.08 \), Triclinic, Space group \( P\bar{1} \), \( a = 6.9458(2) \), \( b = 10.9848(2) \), \( c = 12.6203(4) \) Å, \( V = 946.11(4) \) \( \text{Å}^3 \), \( \alpha = 95.166(2) \), \( \beta = 94.677(2) \), \( \gamma = 97.680(2) \), \( Z = 2 \), \( \mu = 6.522 \text{mm}^{-1} \), data/restraints/parameters: 3962/0/226, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0509 \), \( wR2 \) (all data) = 0.1223. CCDC No. 1885281.

**Compound 19:** \( \text{C}_{19}\text{H}_{20}\text{ClNO}_3\text{S} \), \( M = 377.87 \), Monoclinic, Space group \( C2/c \), \( a = 18.258(2) \), \( b = 13.0810(13) \), \( c = 15.4466(14) \) Å, \( V = 3687.2(6) \) \( \text{Å}^3 \), \( \alpha = 90 \), \( \beta = 91.845(3) \), \( \gamma = 90 \), \( Z = 8 \), \( \mu = 0.338 \text{mm}^{-1} \), data/restraints/parameters: 3227/0/229, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0488 \), \( wR2 \) (all data) = 0.1434. CCDC No. 1885282.

**Compound 22:** \( \text{C}_{21}\text{H}_{25}\text{NO}_4\text{S} \), \( M = 387.48 \), Triclinic, Space group \( P\bar{1} \), \( a = 10.994(13) \), \( b = 12.052(15) \), \( c = 16.90(2) \) Å, \( V = 2130(4) \) \( \text{Å}^3 \), \( \alpha = 95.131(11) \), \( \beta = 99.760(11) \), \( \gamma = 103.107(11) \), \( Z = 4 \), \( \mu = 0.176 \text{mm}^{-1} \), data/restraints/parameters: 5863/0/498, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0954 \), \( wR2 \) (all data) = 0.3278. CCDC No. 1885283.

**Compound 30:** \( \text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_7\text{S} \), \( M = 390.36 \), Monoclinic, Space group \( P2(1)/n \), \( a = 7.4466(5) \), \( b = 24.7338(15) \), \( c = 9.6421(5) \) Å, \( V = 1718.87(18) \) \( \text{Å}^3 \), \( \alpha = 90 \), \( \beta = 104.560(2) \), \( \gamma = 90 \), \( Z = 4 \), \( \mu = 0.233 \text{mm}^{-1} \), data/restraints/parameters: 3032/0/247, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0435 \), \( wR2 \) (all data) = 0.1128. CCDC No. 1885284.

**Compound 35:** \( \text{C}_{17}\text{H}_{18}\text{Br}_3\text{NO}_3\text{S} \), \( M = 538.10 \), Monoclinic, Space group \( P2(1)/c \), \( a = 8.2985(3) \), \( b = 12.4303(6) \), \( c = 19.4432(8) \) Å, \( V = 1966.59(14) \) \( \text{Å}^3 \), \( \alpha = 90 \), \( \beta = 101.3220(10) \), \( \gamma = 90 \), \( Z = 4 \), \( \mu = 6.269 \text{mm}^{-1} \), data/restraints/parameters: 3431/0/218, R indices (I > 2\( \sigma(I) \)) \( R_1 = 0.0394 \), \( wR2 \) (all data) = 0.1036. CCDC No. 1885285.
Figure S1. ORTEP diagram of compound 4 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses: S1-N1 1.694(4), N1-C8 1.479(6), O3-C9 1.441(5), O3-C11 1.358(5), C11-C12 1.326(6), Br2-C12 1.899(4), Br1-C10 1.928(5), C9-C10 1.491(7), C12-C13 1.477(5).

Figure S2. ORTEP diagram of compound 8 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses:

Figure S3. ORTEP diagram of compound 19 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses: S1-N1 1.6563(19), N1-C8 1.470(3), N1-C12 1.419(3), C12-C11 1.332(3), C13-C11 1.471(3), O3-C11 1.377(2), O3-C9 1.436(3), Cl1-C10 1.770(3), C9-C8 1.504(3), C9-C10 1.514(3).
**Figure S4.** ORTEP diagram of compound 22 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses: S1-N1 1.668(8), N1-C14 1.409(11), N1-C11 1.446(13), C12-C11 1.388(16), C15-C14 1.346(13), O4-C15 1.373(11), O3-C13 1.422(17), C15-C16 1.433(13), O4-C12 1.357(13), C12-C13 1.402(17).

**Figure S5.** ORTEP diagram of compound 30 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses: N1-C10 1.393(3), C10-C11 1.539(3), O6-C10 1.204(3), O7-C11 1.206(3), C11-C12 1.476(3), N1-C7 1.479(3), C7-C8 1.506(4), C8-C9 1.432(4), O3-C8 1.409(3), O3-C9 1.431(4).

**Figure S6.** ORTEP diagram of compound 35 (probability ellipsoid at 30%). Selected bond lengths [Å] with esds in parentheses: S1-N1 1.663(3), N1-C8 1.394(5), C8-C9 1.309(6), C10-C9 1.488(5), Br2-C8 1.931(4), Br3-C9 1.890(4), Br1-C17 1.919(6), N1-C16 1.496(6), C16-C17 1.486(7).
(11) References:


2. (a) G. M. Sheldrick, SADABS, Siemens Area Detector Absorption Correction, University of Göttingen, Germany, 1996; (b) G. M. Sheldrick, SHELX-97- A program for crystal structure solution and refinement, University of Göttingen, 1997; (c) G. M. Sheldrick, SHELXTL NT Crystal Structure Analysis Package, Bruker AXS, Analytical X-ray System, WI, USA, 1999, version 5.10.

Figure S7. $^1$H NMR spectrum of compound 1h

Figure S8. $^{13}$C NMR spectrum of compound 1h
Figure S9. \(^1\)H NMR spectrum of compound 1i

Figure S10. \(^{13}\)C NMR spectrum of compound 1i
Figure S11. $^1$H NMR spectrum of compound 1j

Figure S12. $^{13}$C NMR spectrum of compound 1j
Figure S1. $^1$H NMR spectrum of compound 1k

Figure S13. $^1$H NMR spectrum of compound 1k

Figure S14. $^{13}$C NMR spectrum of compound 1k
Figure S15. $^1$H NMR spectrum of compound 1l

Figure S16. $^{13}$C NMR spectrum of compound 1l
Figure S17. $^1$H NMR spectrum of compound 1n

Figure S18. $^{13}$C NMR spectrum of compound 1n
Figure S19. $^1$H NMR spectrum of compound 1o

Figure S20. $^{13}$C NMR spectrum of compound 1o
Figure S21. $^1$H NMR spectrum of compound 3

Figure S22. $^{13}$C NMR spectrum of compound 3
Figure S23. $^1$H NMR spectrum of compound 4

Figure S24. $^{13}$C NMR spectrum of compound 4
Figure S25. $^1$H NMR spectrum of compound 5

Figure S26. $^{13}$C NMR spectrum of compound 5
Figure S27. $^1$H NMR spectrum of compound 6

Figure S28. $^{13}$C NMR spectrum of compound 6
Figure S29. $^1$H NMR spectrum of compound 7

Figure S30. $^{13}$C NMR spectrum of compound 7
Figure S31. $^1$H NMR spectrum of compound 8

Figure S32. $^{13}$C NMR spectrum of compound 8
Figure S33. $^1$H NMR spectrum of compound 9

Figure S34. $^{13}$C NMR spectrum of compound 9
Figure S35. $^1$H NMR spectrum of compound 10

Figure S36. $^{13}$C NMR spectrum of compound 10
Figure S37. $^1$H NMR spectrum of compound 11

Figure S38. $^{13}$C NMR spectrum of compound 11
Figure S39. $^1$H NMR spectrum of compound 12

Figure S40. $^{13}$C NMR spectrum of compound 12
Figure S41. $^1$H NMR spectrum of compound 13

Figure S42. $^{13}$C NMR spectrum of compound 13
Figure S43. $^1$H NMR spectrum of compound 13’

Figure S44. $^{13}$C NMR spectrum of compound 13’
Figure S45. $^1$H NMR spectrum of compound 14

Figure S46. $^{13}$C NMR spectrum of compound 14
Figure S47. $^1$H NMR spectrum of compound 15

Figure S48. $^{13}$C NMR spectrum of compound 15
Figure S49. $^1$H NMR spectrum of compound 16

Figure S50. $^{13}$C NMR spectrum of compound 16
Figure S51. $^1$H NMR spectrum of compound 17

Figure S52. $^{13}$C NMR spectrum of compound 17
Figure S53. $^1$H NMR spectrum of compound 18

Figure S54. $^{13}$C NMR spectrum of compound 18
Figure S5. $^1$H NMR spectrum of compound 19

Figure S56. $^{13}$C NMR spectrum of compound 19
**Figure S57.** $^1$H NMR spectrum of compound 20

**Figure S58.** $^{13}$C NMR spectrum of compound 20
Figure S59. $^1$H NMR spectrum of compound 21

Figure S60. $^{13}$C NMR spectrum of compound 21
Figure S61. $^1$H NMR spectrum of compound 22

Figure S62. $^{13}$C NMR spectrum of compound 22
Figure S63. $^{1}$H NMR spectrum of compound 23

Figure S64. $^{13}$C NMR spectrum of compound 23
Figure S65. $^1$H NMR spectrum of compound 24

Figure S66. $^{13}$C NMR spectrum of compound 24
Figure S67. $^1$H NMR spectrum of compound 25

Figure S68. $^{13}$C NMR spectrum of compound 25
**Figure S69.** $^1$H NMR spectrum of compound 26

**Figure S70.** $^{13}$C NMR spectrum of compound 26
Figure S71. $^1$H NMR spectrum of compound 27

Figure S72. $^{13}$C NMR spectrum of compound 27
Figure S73. $^1$H NMR spectrum of compound 28

Figure S74. $^{13}$C NMR spectrum of compound 28
Figure S75. $^1$H NMR spectrum of compound 29

Figure S76. $^{13}$C NMR spectrum of compound 29
Figure S77. $^1$H NMR spectrum of compound 30

Figure S78. $^{13}$C NMR spectrum of compound 29
Figure S79. $^1$H NMR spectrum of compound 31

Figure S80. $^{13}$C NMR spectrum of compound 31
Figure S81. $^1$H NMR spectrum of compound 33

Figure S82. $^{13}$C NMR spectrum of compound 33
Figure S83. $^1$H NMR spectrum of compound 34

Figure S84. $^{13}$C NMR spectrum of compound 34
Figure S85. $^1$H NMR spectrum of compound 35

Figure S86. $^{13}$C NMR spectrum of compound 35