SUPPLEMENTARY INFORMATION

Nucleophilic attack of 2-sulfinyl acrylates: A mild and general approach to sulfenic acid anions

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Preparation of \( \alpha, \beta \)-Unsaturated Sulfoxides (2)

\[
\text{RSH} \quad \xrightarrow{(i)} \quad \text{R-S=CHCOO} \quad \xrightarrow{(ii)} \quad \text{R-S=CHCOO}
\]

Scheme 1: (i) methyl propiolate, Et\(_3\)N, CH\(_2\)Cl\(_2\), 0 °C (ii) MCPBA, CH\(_2\)Cl\(_2\), -78 °C.
Scheme 2: (i) methyl propiolate, imidazole, CH$_3$CN, 45 °C$^1$ (ii) (a) Cs$_2$CO$_3$, CH$_3$OH, -10 °C and then, (b) methyl propiolate or (c) Cbz-HomoAla(I)-OMe in methanol. (iii) MCPBA, CH$_2$Cl$_2$, -78 °C.

Scheme 3: (i) methyl propiolate, Et$_3$N, CH$_2$Cl$_2$ (ii) MCPBA, CH$_2$Cl$_2$, -78 °C.

**Experimental section**

Melting points were determined using a MEL-TEMP melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Bomen FT-IR spectrometer in a solution cell (CH$_2$Cl$_2$ or CDCl$_3$). NMR spectra for $^1$H NMR and $^{13}$C NMR were recorded on either a Bruker model spectrometer at 400 and 100.6 MHz or 300 and 75.5 MHz, respectively in CDCl$_3$ unless otherwise noted. $^1$H NMR and $^{13}$C NMR chemical shifts are referenced to CHCl$_3$ or tetramethylsilane and are recorded in parts per million (ppm). Mass Spectra (MS) were
performed at either the McMaster Regional Centre for Mass Spectrometry, McMaster University or the WATSPEC Mass Spectrometry Facility at the University of Waterloo using either chemical ionization or electron impact techniques. Elemental analyses were performed by MHW Laboratories of Phoenix, AZ. Tetrahydrofuran (THF) was freshly distilled from benzophenone and sodium. Triethylamine (TEA) was dried and distilled from KOH and stored over 4 Å molecular sieves. MeONa+ was purchased from Aldrich as a 25% solution in methanol, purged with nitrogen and stored over 4 Å molecular sieves. m-CPBA was obtained from Acros and was dried and calibrated with benzyl sulfide before use. n-BuLi was purchased from Aldrich as either a 1.6 M or 2.5 M solution in hexanes. All air and water sensitive reagents were transferred via oven-dried nitrogen-purged syringes into flame-dried flasks. Flash chromatography was performed on 200-450 mesh Type 60 Å silica gel. Analytical thin-layer chromatography (TLC) was performed using 0.25 mm Merck Kieselgel 60 F254 precoated glass-backed silica gel plates, or Silicycle 0.25mm, extra hard layer, 60 Å F254 glass-backed silica gel plates. Optical rotations were measured by a Rudolph Research Autopol III automatic polarimeter in 1 dm tubes.

**General Procedure for the Synthesis of 2-Carbomethoxyethenyl Ar(alk)yl Sulfoxides**

A solution of the thiol (1 eq.) was prepared in CH₂Cl₂ (1 mL/mmol) and cooled to 0 °C. Methyl propiolate was added (1.3 eq.), followed by the slow addition of triethylamine (TEA) (1.1 eq.) upon which the solution turned dark brown. The mixture was stirred for 30-60 minutes, allowing the ice bath to warm to RT, until complete by TLC and no smell of the thiol lingered. A 5% solution of HCl was added and the organic layer separated. The
aqueous layer was extracted with CH₂Cl₂ (3x) and the organic layers combined. The organic layer was then washed with H₂O, brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting sulfide was isolated using flash chromatography through recycled silica gel using EtOAc/hexanes as the eluant. Sulfide yields were calculated from the thiol.

The sulfide (1 eq.) was then dissolved in CH₂Cl₂ (5 mL/mmol) and cooled to -78 °C followed by the dropwise addition of MCPBA (42% or 75%, 1.05 eq., 20 mL/mmol). The oxidation reaction was stirred at -78 °C for 6 hours, warmed to -40 °C and stirred overnight. The reaction was then cooled back down to -78 °C and filtered through a bed of Celite. The filtrate was then placed in the cold bath and the surface impinged with dry ammonia and refiltered, and repeated twice more. The clear filtrate was then concentrated under reduced pressure and purified by flash chromatography using EtOAc/hexanes as the eluant. Sulfoxide yields were obtained from the sulfide. All spectral data is presented for the mixture of E/Z isomers unless otherwise noted.

a precursor sulfide of 2j was synthesized through a different method.
b 2.6 eq. methyl propiolate was used for the synthesis of precursor sulfide of 2k.
c order of adding reagents was reversed (thiol was added to a ice cold solution of methyl propiolate, TEA and CH₂Cl₂) in the synthesis of precursor sulfide of 2h and 2i. Reverse addition for the synthesis of precursor sulfide of 2a gave almost similar or slightly better results.
d reaction time for the synthesis of precursor sulfide of 2i was 5 min.
e in some cases where the yield is good, sulfide could be taken to the next oxidation step without purification.
f 2g was oxidised with 30% H₂O₂ rather than MCPBA.
MCPBA was added at 40 °C for the synthesis of 2h and the reaction time was 1 hr at this temp.

Although, MCPBA was added at -78 °C for the synthesis of 2j, reaction mixture was stirred for 2 h at room temperature for completion.

Oxidation reaction for the synthesis of 2i was complete within 1 hr at -78 °C.

Workup procedure was different for the oxidation reactions to synthesize 2h, 2i and 2j (washing with Na$_2$S$_2$O$_3$, NaHCO$_3$, brine solution). This procedure could be used as an alternate to the ammonia protocol as we have successfully used it in the synthesis of above mentioned compound as well as 2a and other α,β-unsaturated sulfoxides synthesized in our lab.

Synthesis of E/Z-2-Carbomethoxyethenyl p-Tolyl Sulfoxide (2a)$^{2,3}$

p-Thiocresol (1.74 g, 13.7 mmol) in CH$_2$Cl$_2$ (14 mL) was treated with methyl propiolate (1.59 mL, 17.8 mmol) followed by the addition of TEA (2.10 mL, 15.1 mmol). Sulfide$^d$ (2.81 g, 98%) was isolated as an oil after flash chromatography (10% EtOAc/hexanes) as a mixture of isomers. Mixture of E/Z isomers: $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.72 (d, $J = 15.0$ Hz, 1H), 7.30 (m, 4H), 7.19 (d, $J = 10.1$ Hz), 7.14 (m, 4H), 5.84 (d, $J = 10.1$ Hz, 1H), 5.54 (d, $J = 15.0$ Hz, 1H), 3.72 (s, 3H), 3.63 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$: 166.6, 165.3, 150.6, 147.5, 139.3, 138.1, 133.0, 132.3, 130.9, 130.2, 129.8, 126.3, 114.4, 112.3, 51.1, 51.0, 20.9, 20.8; IR (CDCl$_3$), cm$^{-1}$: 3026, 2951, 2925, 2847, 1698, 1586, 1496, 1039, 1018, 834, 817.

Sulfide (1.14 g, 5.49 mmol) in CH$_2$Cl$_2$ (15 mL) was treated dropwise with MCPBA (42 %, 2.37 g, 5.60 mmol, 85 mL). Sulfoxide (1.02 g, 83%) was isolated after flash chromatography (20% EtOAc/hexanes, then 100% EtOAc). Z-isomer (Z-2a) (R$_f$ = 0.42, 30%
EtOAc/hexanes): Mp: 57-58 °C; ¹H NMR (400 MHz, CDCl₃), δ: 7.72 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 10.2 Hz, 1H), 6.21 (d, J = 10.3 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 164.6, 156.2, 141.9, 140.9, 130.0, 124.9, 123.3, 52.4, 21.4; IR (CDCl₃), cm⁻¹: 3029, 2954, 1719, 1615, 1492, 1437, 1347, 1227, 1208, 1078, 1037, 1016, 816. E-isomer (E-2a) (Rᵣ = 0.21, 30% EtOAc/hexanes): Mp: 68-69 °C; ¹H NMR (400 MHz, CDCl₃), δ: 7.51 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 14.9 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 14.9 Hz, 1H), 3.77 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 164.4, 151.5, 142.7, 138.1, 130.5, 125.0, 123.5, 52.3, 21.5; IR (CDCl₃), cm⁻¹: 3058, 2954, 1726, 1621, 1437, 1299, 1228, 1148, 1057, 809. MS (EI), m/z (%): 224 (M⁺, 4), 177 (8), 176 (100), 145 (60), 139 (18), 123 (21), 91 (12), 77 (6), 65 (8); Analysis calc’d for C₁₁H₁₂O₃S: C, 58.95; H, 5.35; Found: C, 58.80; H, 5.13.

Synthesis of E/Z-2-Carbomethoxyethenyl Methyl Sulfoxide (2b)²,⁵

Sodium thiomethoxide (1.90 g, 24.0 mmol) in CH₃CN (25 mL) was treated with methyl propiolate (2.78 mL, 31.2 mmol). Sulfide (1.27 g, 40%) was isolated as an oil after flash chromatography (15% EtOAc/hexanes) as a mixture of isomers.

Mixture of E/Z-isomers: ¹H NMR (300 MHz, CDCl₃), δ: 7.75 (d, J = 15.0 Hz, 1H), 7.04 (d, J = 10.3 Hz, 1H), 5.82 (d, J = 10.3 Hz, 1H), 5.62 (d, J = 15.0 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H).

Sulfide 542 mg, 4.11 mmol) in CH₂Cl₂ (10 mL) was treated dropwise with MCPBA (42 %, 1.77 g, 4.32 mmol, 50 mL). Sulfoxide (0.314 g, 52%) was isolated as a oil after flash chromatography (30% EtOAc/hexanes, then 100% EtOAc) as a mixture of isomers.

Mixture of E/Z-isomers: ¹H NMR (400 MHz, CDCl₃), δ: 7.61 (d, J = 15.0 Hz, 1H), 6.97 (d, J =
Synthesis of E-2-Carbomethoxyethenyl Cyclohexyl Sulfoxide (2c)

Cyclohexanethiol (1.22 mL, 10.0 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with methyl propiolate (1.16 mL, 13.0 mmol) followed by the addition of TEA (1.53 mL, 11.0 mmol). Sulfide (1.90 g, 95%) was isolated as oil after flash chromatography (10% EtOAc/hexanes) as a mixture of isomers. **Mixture of E/Z-isomers:** $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.67 (d, $J = 15.3$ Hz, 1H), 7.23 (d, $J = 10.3$ Hz, 1H), 5.84 (d, $J = 10.3$ Hz, 1H), 5.76 (d, $J = 15.3$ Hz, 1H), 3.67 (s, 3H), 3.02 (tt, $J = 10.2$ & 3.4 Hz, 1H), 1.98 (m, 2H), 1.73 (m, 2H), 1.59 (m, 2H), 1.27 (br m, 4H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$: 167.0, 165.8, 148.6, 146.6, 113.6, 112.0, 51.3, 51.0, 47.5, 45.0, 33.5, 33.0, 25.70, 27.51, 25.4, 25.3; IR (CDCl$_3$), cm$^{-1}$: 2936, 2857, 1701, 1584, 1437, 1310, 1043, 953, 833.

Sulfide (833 mg, 4.16 mmol) was dissolved in CH$_2$Cl$_2$ (50 mL) and cooled to -78 °C followed by the dropwise addition of MCPBA (75.7%, 1.2 eq., 10 mL CH$_2$Cl$_2$). The oxidation reaction was stirred at -78 °C for 6 hours, warmed to -40 °C and stirred overnight. The reaction was then cooled back down to -78 °C and filtered through a bed of Celite. The filtrate was then placed in the cold bath and the surface impinged with dry ammonia and refiltered, and repeated twice more. The clear filtrate was then concentrated under reduced pressure. Sulfoxide (741 mg, 82%) was isolated as a white solid after flash chromatography (30% EtOAc/hexanes, then 100% EtOAc) as the E-isomer exclusively. **E-isomer (E-2c)** ($R_f = 0.30$, 30%
EtOAc/hexanes): Mp: 58-59 °C;  $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.56 (d, $J = 15.0$ Hz, 1H), 6.63 (d, $J = 15.0$ Hz, 1H), 3.80 (s, 3H), 2.72 (tt, $J = 11.9$ & 3.6 Hz, 1H), 1.70 (m, 10 H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 164.3, 148.2, 126.6, 60.6, 52.3, 26.5, 25.6, 25.3 (2C), 24.2; IR (CDCl$_3$), cm$^{-1}$: 3060, 2939, 2860, 1723, 1620, 1437, 1302, 1231, 1058, 848. MS (Cl, NH$_3$), m/z (%): 217 ((M+H)$^+$, 45), 135 (22), 134 (41), 103 (15), 102 (100), 83 (75), 55 (58), 41 (14); Analysis calc’d for C$_{10}$H$_{16}$O$_3$S: C, 55.53; H, 7.40; Found: C, 55.43; H, 7.41.

**Synthesis of E/Z-2-Carbomethoxyethenyl Benzyl Sulfoxide (2d)**

Benzyl mercaptan (1.65 mL, 14.4 mmol) in CH$_2$Cl$_2$ (15 mL) was treated with methyl propiolate (1.67 mL, 18.7 mmol) followed by the addition of TEA (2.21 mL, 15.8 mmol). Sulfide (2.90 g, 97%) was isolated as an oil after flash chromatography (10% EtOAc/hexanes) as a mixture of isomers, which solidifies on standing. **Mixture of E/Z isomers:** Mp: 47-51 °C; $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.71 (d, $J = 15.1$ Hz, 1H), 7.30 (m, 10H), 7.06 (d, $J = 10.2$ Hz, 1H), 5.83 (d, $J = 15.0$ Hz, 1H), 5.82 (d, $J = 10.3$ Hz, 1H), 4.00 (s, 2H), 3.95 (s, 2H), 3.71 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 166.8, 165.4, 148.7, 146.1, 137.0, 135.3, 128.8, 128.7, 128.6 (2C), 127.6, 127.4, 113.9, 113.0, 51.3, 51.1, 39.2, 36.4; IR (CDCl$_3$), cm$^{-1}$: 3066, 3032, 2951, 2846, 1708, 1585, 1496, 1435, 1312, 1042, 828.

Sulfide (2.50 g, 12.0 mmol) in CH$_2$Cl$_2$ (50 mL) was treated dropwise with MCPBA (42 %, 5.18 g, 12.6 mmol, 125 mL). Sulfoxide (2.15 g, 80%) was isolated as a white solid after flash chromatography (20% EtOAc/hexanes, then 100% EtOAc). **Z-isomer (Z-2d)** (R$_f$ = 0.17, 20% EtOAc/hexanes): Mp: 54-55 °C; $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.36 (br s, 5H), 6.72 (d, $J = 10.4$ Hz, 1H), 6.31 (d, $J = 10.4$ Hz, 1H), 4.20 (AB, $J = 12.7$ Hz, 2H), 3.81 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 164.7, 157.7, 130.4, 130.2, 128.7, 128.4, 125.5, 124.5, 60.0,
E-isomer (E-2d) (Rf = 0.07, 20% EtOAc/hexanes): Mp: 79-80 °C; 1H NMR (400 MHz, CDCl₃), δ: 7.55 (d, J = 15.0 Hz, 1H), 7.33 (m, 3H), 7.27 (d, J = 3.5 Hz, 2H), 6.55 (d, J = 15.0 Hz, 1H), 4.11 (s, 2H), 3.79 (s, 3H); 13C NMR (100.6 MHz, CDCl₃), δ: 149.0, 130.2, 129.0, 128.8, 128.5, 126.5, 60.0, 52.3; IR (CDCl₃), cm⁻¹: 3034, 2954, 1725, 1621, 1496, 1437, 1301, 1230, 1193, 1059, 960. MS (Cl, NH₃), m/z (%): 242 ((M + NH₄)⁺, 100), 225 (13), 108 (2); Analysis calc’d for C₁₁H₁₂O₃S: C, 58.95; H, 5.35; Found: C, 59.09; H, 5.26.

**Synthesis of E-2-Carbomethoxyethenyl Hexyl Sulfoxide (2e)**

1-Hexanethiol (2.44 mL, 17.3 mmol) in CH₂Cl₂ (18 mL) was treated with methyl propiolate (2.00 mL, 22.5 mmol) followed by the addition of TEA (2.65 mL, 19.0 mmol). Sulfide (2.94 g, 84%) was isolated as an oil after flash chromatography (10% EtOAc/hexanes) as the E-isomer exclusively. **E-isomer:** 1H NMR (400 MHz, CDCl₃), δ: 7.66 (d, J = 15.2 Hz, 1H), 5.70 (d, J = 15.2 Hz, 1H), 3.68 (s, 3H), 2.75 (t, J = 7.5 Hz, 2H), 1.63 (p, J = 7.6 Hz, 2H), 1.32 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H); 13C NMR (100.6 MHz, CDCl₃), δ: 165.7, 147.2, 113.1, 51.3, 31.9, 31.2, 28.5, 28.4, 22.4, 13.9; IR (CDCl₃), cm⁻¹: 3023, 2953, 2933, 1701, 1624, 1584, 1437, 1309, 1258, 1141, 1043, 1020, 832.

Sulfide (3.20 g, 15.8 mmol) in CH₂Cl₂ (20 mL) was treated dropwise with MCPBA (42 %, 6.82 g, 16.6 mmol, 250 mL). Sulfoxide (1.88 g, 54%) was isolated as a white solid after flash chromatography (30% EtOAc/hexanes) as the E-isomer exclusively (Rf = 0.24, 30% EtOAc/hexanes). **E-isomer (E-2a):** Mp: 57-58 °C; 1H NMR (400 MHz, CDCl₃), δ: 7.58 (d, J = 15.0 Hz, 1H), 6.65 (d, J = 15.0 Hz, 1H), 3.80 (s, 3H), 2.80 (ABXY, Jₓₓ = 5.3 Hz, Jₙₙ = 9.8 Hz, Jₓᵧ = 6.3 Hz, Jᵧᵧ = 6.2 Hz, Jₐₐ = 13.2 Hz, 2H), 1.75 (m, 2H), 1.38 (m, 6H), 0.88 (t, J = 7.0
Hz, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$: 164.2, 149.7, 125.9, 52.9, 52.3, 31.2, 28.3, 22.3, 21.8, 13.9; IR (CDCl$_3$), cm$^{-1}$: 3035, 2957, 2932, 2873, 2861, 1724, 1622, 1437, 1302, 1230, 1149, 1055, 960. MS (Cl, NH$_3$), m/z (%): 219 ((M+H)$^+$, 100), 202 (11), 201 (23), 171 (14), 158 (15), 141 (12), 109 (21), 102 (65), 43 (21); Analysis calc’d for C$_{10}$H$_{18}$O$_3$S: C, 55.02; H, 8.25; Found: C, 55.23; H, 8.12.

**Synthesis of E-2-Carbomethoxyethenyl Hexadecyl Sulfoxide (2f)**

1-Hexadecanethiol (7.19 mL, 23.4 mmol) in CH$_2$Cl$_2$ (30 mL) was treated with methyl propiolate (2.70 mL, 30.4 mmol) followed by the addition of TEA (3.58 mL, 25.7 mmol). Sulfide (7.01 g, 88%) was isolated as a white solid after flash chromatography (10% EtOAc/hexanes) as the E-isomer exclusively. **E-isomer**: Mp: 32-33 °C; $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.67 (d, $J = 15.2$ Hz, 1H), 5.73 (d, $J = 15.2$ Hz, 1H), 3.71 (s, 3H), 2.77 (t, $J = 7.4$ Hz, 2H), 1.66 (p, $J = 7.5$ Hz, 2H), 1.32 (br s, 26H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$: 165.8, 147.3, 113.1, 51.4, 32.0, 31.9, 29.7 (4C), 29.6 (2C), 29.5, 29.4 (2C), 29.1, 28.7, 25.6, 22.7, 14.1; IR (CDCl$_3$), cm$^{-1}$: 3023, 2936, 2896, 2855, 1702, 1582, 1437, 1307, 1258, 1193, 1173, 1043, 1019, 832.

Sulfide (1.00 g, 2.92 mmol) in CH$_2$Cl$_2$ (15 mL) was treated dropwise with MCPBA (42%, 1.26 g, 3.07 mmol, 50 mL). Sulfoxide (0.677 g, 65%) was isolated as a white solid after flash chromatography (30% EtOAc/hexanes). **E-isomer (E-2f)**: Mp: 80-81 °C; $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.58 (d, $J = 15.0$ Hz, 1H), 6.67 (d, $J = 15.0$ Hz, 1H), 3.81 (s, 3H), 2.80 (ABXY, $J_{AX} = 5.3$ Hz, $J_{AY} = 9.8$ Hz, $J_{BX} = 6.2$ Hz, $J_{BY} = 9.9$ Hz, $J_{AB} = 13.2$ Hz, 2H), 1.76 (m, 2H), 1.25 (br s, 26H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$: 164.3, 149.8, 126.0, 52.9, 52.3, 31.9, 29.7 (4C), 29.6 (2C), 29.5, 29.4 (2C), 29.1, 28.7, 22.7, 21.9, 14.1;
IR (CDCl₃), cm⁻¹: 3058, 2928, 2855, 1725, 1622, 1438, 1301, 1231, 959. MS (Cl, NH₃), m/z (%): 359 ((M+H)+, 5), 343 (42), 311 (32), 223 (53), 217 (67), 201 (50), 169 (39), 167 (38), 135 (50), 102 (77), 91 (100), 83 (56), 55 (44); Analysis calc'd for C₂₀H₃₈O₃S: C, 66.99; H, 10.60; Found: C, 67.12; H, 10.69.

Synthesis of Z-2-Carbomethoxyethenyl 4-Acetamidophenyl Sulfoxide (2g)²

4-Acetamidothiophenol (2.50 g, 15.0 mmol) in CH₂Cl₂ (20 mL) and MeOH (10 mL) was treated with methyl propiolate (1.73 mL, 19.4 mmol) followed by the addition of TEA (2.30 mL, 16.4 mmol). Sulfide (3.35 g, 89%) was isolated as a white solid as the Z-isomer exclusively and used crude in the oxidation to the sulfoxide. Z-isomer: Mp: 143-145 °C (EtOH); ¹H NMR (400 MHz, CDCl₃), δ: 8.11 (br s, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 10.1 Hz, 1H), 5.89 (d, J = 10.1 Hz, 1H), 3.76 (s, 3H), 2.17 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 168.9, 167.0, 150.7, 138.4, 132.1, 130.6, 120.6, 112.7, 51.4, 24.5; IR (CDCl₃), cm⁻¹: 3434, 3330, 2952, 1696, 1670, 1590, 1513, 1438, 1361, 1228, 1173, 1010, 833.

To a solution of the sulfide (200 mg, 0.796 mmol) in acetic acid (2.2 mL) was added H₂O₂ (0.135 mL/mmol substrate, 30% solution in H₂O). The reaction was stirred at RT for 5 days. H₂O (5 mL) was added and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with H₂O (2 mL), brine (5 mL), dried over MgSO₄ and concentrated under reduced pressure. Sulfoxide (91.5 mg, 43%) was isolated as a solid after flash chromatography (60% EtOAc/hexanes, then 80% EtOAc/hexanes, then 100% EtOAc). Mp: 122-123 °C; ¹H NMR (400 MHz), Z-isomer (Z-2g): ¹H NMR (400 MHz, CDCl₃), δ: 9.10 (br s, 1H),
7.69 (br s, 4H), 6.79 (d, J = 10.2 Hz, 1H), 6.22 (d, J = 10.2 Hz, 1H), 3.77 (s, 3H), 2.11 (s, 3H); 13C NMR (100.6 MHz, CDCl3), δ: 169.4, 164.5, 155.3, 141.7, 137.6, 125.9, 123.7, 120.2, 52.5, 24.3; IR (CH2Cl2), cm⁻¹: 3426, 3312, 3035, 2955, 1721, 1702, 1590, 1512, 1347, 1217, 1042, 818; MS (EI), m/z (%): 267 (M⁺, 2), 251 (45), 241 (18), 219 (100), 209 (24), 178 (15), 177 (66), 146 (23), 140 (68), 124 (18); Analysis calc’d for C12H13NO4S: C, 53.93; H, 4.87; Found: C, 54.24; H, 4.65.

Synthesis of E/Z-2-Carbomethoxyethyl Benzothiazolyl Sulfoxide (2h)

Triethylamine (0.81 ml, 5.96 mmol) was added to a stirred ice cold solution of methyl propiolate (0.69 ml, 7.76 mmol) and dry CH2Cl2 (30 mL) under N2 gas, followed by immediate dropwise addition of 2-mercaptobenzothiazole (1.00 g, 5.96 mmol) in dry CH2Cl2 (5 mL). The mixture was stirred at 0°C for 1 hr and then quenched with 1.0 M HCl (20 mL). The organic layer was extracted, dried with MgSO4 and the solvent was removed under reduced pressure. Sulfide (1.31 g, 87%) was recovered as a mixture of isomers (E/Z = 1/2.7). Mixture of E/Z isomers (1/2.7): 1H NMR (400 MHz, CDCl3), δ: 8.29 (d, J = 9.8 Hz, 1H, Z isomer), 8.26 (d, J = 15.6 Hz, 1H, E isomer), 7.90 (d, J = 8.2 Hz, 1H, E isomer), 7.86 (d, J = 8.1 Hz, 1H, Z isomer), 7.73-7.70 (m, 2H, E/Z isomers), 7.39-7.36 (m, 2H, E/Z isomers), 7.29-7.23 (m, 2H, E/Z isomers), 6.16 (d, J = 15.6 Hz, 1H, E isomer), 6.10 (d, J = 9.8 Hz, 1H, Z isomer), 3.73 (s, 3H, Z isomer), 3.71 (s, 3H, E isomer).

The sulfide was taken to the next step without further purification. MCPBA (1.16 g, 77%, 5.2 mmol) in CH2Cl2 (10 mL) was added dropwise to a stirred solution of the sulfide (1.31 g, 5.2 mmol) in CH2Cl2 (30 mL) at 40 °C for 15 min and the reaction was allowed to stir for 1 hr. The
reaction was stirred with a saturated solution of Na$_2$S$_2$O$_3$ (30 mL) for 1 hr at room temperature. The organic layer was extracted and washed with NaHCO$_3$ (3 x 20 mL) and brine (2 x 20 mL). The combined organic layer was dried with MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (EtOAc/hexanes 30:70 to 50:50) to afford compound $E$-$2$h (0.32 g, 23 %, EtOAc/hexanes 30:70) as a white solid and compound $Z$-$2$h (0.62 g, 45 %, EtOAc/hexanes 50:50) as a yellow solid. $E$-isomer ($E$-$2$h): Mp: 128-129 °C; $^1$H NMR(400 MHz, CDCl$_3$), $\delta$ 8.05 (d, $J$ = 8.3 Hz, 1H), 7.94 (d, $J$ = 8.0 Hz, 1H), 7.78 (d, $J$ = 15.0 Hz, 1H), 7.54 (m, 1H), 7.47 (m, 1H), 6.81 (d, $J$ = 15.0 Hz, 1H), 3.75 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$ 173.5, 163.7, 152.8, 149.0, 135.7, 127.1, 126.7, 125.8, 124.2, 122.3, 52.5; IR (CH$_2$Cl$_2$) cm$^{-1}$ 3059, 2951, 1726, 1620, 1434, 1345, 1296, 1145, 1088, 954, 760, 702; HRMS (TOF Cl$^+$), Calc’d for C$_{24}$H$_{25}$NO$_6$S (M+H)$^+$: 268.0102; Found: 268.0100; $Z$-isomer ($Z$-$2$h): Mp: 83-84 °C; $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ 7.96 (d, $J$ = 8.2 Hz, 1H), 7.78 (d, $J$ = 7.9 Hz, 1H), 7.37 (m, 1H), 7.31 (m, 1H), 6.97 (d, $J$ = 10.0 Hz, 1H), 6.37 (d, $J$ = 10.0 Hz, 1H), 3.71 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), $\delta$ 173.4, 163.9, 152.8, 152.7, 135.9, 126.6, 126.5, 126.2, 124.0, 121.7, 52.4; IR (CH$_2$Cl$_2$) cm$^{-1}$ 3031, 2951, 1725, 1615, 1457, 1434, 1345, 1222, 1183, 1058, 990, 816, 761, 729; Analysis calc’d for C$_{11}$H$_9$NO$_3$S$_2$: C, 49.42; H, 3.39; Found: C, 49.50; H, 3.47.

**Synthesis of $E/Z$-2-Carboethoxyethyl 2-Carbomethoxyethenyl Sulfoxide (2i)**

Triethylamine (1.07 ml, 7.74 mmol) was added to a stirred ice cold solution of methyl propiolate (0.89 ml, 10.06 mmol) and dry CH$_2$Cl$_2$ (20 mL) under N$_2$ gas, followed by immediate dropwise addition of ethyl-3-mercaptopropanoate (1.00 ml, 7.74 mmol).
The mixture was stirred at 0 °C for 5 min and then quenched with 5 % HCl (20 mL). The organic layer was extracted with CH$_2$Cl$_2$, dried with MgSO$_4$ and the solvent was removed under reduced pressure. Sulfide (1.63 g, 97%) was recovered as a mixture of isomers (E/Z = 5.6/1).

**E/Z isomers (5.6/1):** Yellow liquid, $^1$H NMR (300 MHz, CDCl$_3$), δ: 7.58 (d, $J$ = 15.0 Hz, 1H, E isomer), 7.05 (d, $J$ = 10.1 Hz, 1H, Z isomer), 5.80 (d, $J$ = 10.1 Hz, 1H, Z isomer), 5.71 (d, $J$ = 15.0 Hz, 1H, E isomer), 4.08 (m, $J$ = 6.3 Hz, 2H, E/Z isomers), 3.65 (s, 3H, E/Z isomers), 3.00 (t, $J$ = 7.2 Hz, 2H, E/Z isomers), 2.62 (t, $J$ = 7.2 Hz, 2H, E/Z isomers), 1.19 (m, 3H, E/Z isomers); IR (CH$_2$Cl$_2$), cm$^{-1}$: 2983, 2954, 1728, 1621, 1436, 1298, 1227, 1147, 1061, 962, 856.

A solution of MCPBA (77 %, 1.67 g, 7.47 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise to a CH$_2$Cl$_2$ (25 mL) solution of the sulfide (1.63 g, 7.47 mmol) at -78 °C. The reaction was stirred 1 hr and quenched with a saturated solution of Na$_2$S$_2$O$_3$ (30 mL) with stirring for another 1 hr at room temperature. The organic layer was extracted and washed with NaHCO$_3$ (3 x 20 mL) and brine (2 x 20 mL). The combined organic layer was dried with MgSO$_4$. The solvent was removed under reduced pressure to afford compound $^{E/Z}$-2i (1.57 g, 90 %, E/Z = 4.3/1) as a yellow liquid. **$^{E/Z}$-isomer ($^{E/Z}$-2i) (4.3/1):** $^1$H NMR (300 MHz, CDCl$_3$), δ: 7.51 (d, $J$ = 15.0 Hz, 1H, E isomer), 6.83 (d, $J$ = 10.2 Hz, 1H, Z isomer), 6.57 (d, $J$ = 15.0 Hz, 1H), 6.25 (d, $J$ = 10.2 Hz, 1H, Z isomer), 4.08 (m, 2H, E/Z isomers), 3.73 (s, 3H, E/Z isomers), 3.24-3.0 (m, 1H, E/Z isomers), 2.94-2.53 (m, 3H, E/Z isomers), 1.18 (m, 3H, E/Z isomers); $^{13}$C NMR (75.5 MHz, CDCl$_3$), δ: 170.6 (Z isomer), 170.5 (E isomer), 163.6 (Z isomer), 163.4 (E isomer), 156.9 (Z isomer), 148.9 (E isomer), 125.9 (E isomer), 124.5 (Z isomer), 60.7(E/Z isomers), 52.0 (Z isomer), 51.7 (E isomer), 47.8 (Z isomer), 45.8 (E isomer), 26.4 (Z isomer), 24.9 (E isomer), 13.6 (E/Z isomers); IR (CDCl$_3$), cm$^{-1}$: 2984, 2954, 1727, 1621, 1437, 1373, 1349, 1298, 1227, 1147, 1037, 1060, 963. MS (EI), m/z (%): 234 (M$^+$, 56), 218 (18), 189 (27), 133 (99), 117 (70), 102
Synthesis of $E,Z/Z,Z$-Bis(2-Carbomethoxyethenyl) Sulfoxide (2j)

A methanolic solution (5 ml) of Cs$_2$CO$_3$ (448 mg, 1.37 mmol) was added to a cold (-10°C) stirred methanolic (10 ml) solution of $Z$-2-carbomethoxyethenyl thiolacetate (200 mg, 1.25 mmol) under N$_2$ atmosphere. After 10 min., methyl propiolate (0.122 ml, 1.37 mmol) was added dropwise and the mixture was stirred at -10°C. After 3 hr solvent evaporated under vacuum and reaction mixture dissolved in CH$_2$Cl$_2$. The organic layer was washed with water, brine and then, dried with MgSO$_4$. The solvent was removed under reduced pressure to give $E,Z/Z,Z$-bis(2-carbomethoxyethenyl) sulfide (190 mg, 76%) as a mixture of isomers ($E,Z/Z,Z = 1/1.4$). Both isomers could be purified and separated by flash chromatography (20:80% EtOAc/hexanes), or they could be taken to the next step without further separation and purification. **Z,Z isomer:** $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.07 (d, $J = 7.5$ Hz, 2H), 5.95 (d, $J = 7.5$ Hz, 2H), 3.75 (s, 6H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 166.0, 147.6, 115.7, 51.5. **E,Z isomer:** $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.68 (d, $J = 15.5$ Hz, 1H), 7.17 (d, $J = 10.0$ Hz, 1H), 6.06 (d, $J = 15.5$ Hz, 1H), 6.02 (dd, $J = 10.0$ Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 166.0, 164.8, 145.7, 143.5, 117.6, 115.3, 51.3, 51.2.

MCPBA (0.75 g, 77%, 3.3 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise to a stirred solution of the sulfide (0.68 g, 3.3 mmol) in CH$_2$Cl$_2$ (40 mL) at -78 °C for 15 min and the reaction was allowed to stir for 2 hr at room temperature. The reaction was quenched with a saturated solution of Na$_2$S$_2$O$_3$ (30 mL) and stirred for 1 hr at room temperature. The organic layer was extracted.
and washed with NaHCO₃ (2 x 20 mL) and brine (1 x 20 mL). The combine organic layer was
dried with MgSO₄. The solvent was removed under reduced pressure and the residue was
purified by flash chromatography to afford compound **E,Z-2j** (0.28 g, 38 %, EtOAc/hexanes
30:70 and then 50:50 ) liquid which becomes white solid on keeping in freezer and compound
**Z,Z-2j** (0.38 g, 52 %, EtOAc/hexanes 50:50) as a liquid which becomes solid on keeping in
freezer and semisolid at room temperature. **Z,Z isomer (Z,Z-2j):** Mp: 28-30 °C ¹H NMR (400
MHz, CDCl₃), δ: 6.88 (d, J = 10.3 Hz, 2H), 6.31 (d, J = 10.3 Hz, 2H), 3.73 (s, 6H); ¹³C NMR
(100.6 MHz, CDCl₃), δ: 164.2, 150.6, 126.0, 52.2. IR (CH₂Cl₂) cm⁻¹ 3031, 2954, 1728, 1614,
1436, 1351, 1224, 1040, 816; Analysis calc’d for C₈H₁₀O₅S: C, 44.03; H, 4.62; Found: C, 44.00;
H, 4.52.  **E,Z isomer (E,Z-2j):** Mp: 52-54 °C;¹H NMR (400 MHz, CDCl₃), δ: 7.77 (d, J = 15.0
Hz, 1H), 6.69 (d, J = 15.0 Hz, 1H), 6.66 (d, J = 9.9 Hz, 1H), 6.30 (dd, J = 9.9 Hz, 1H), 3.81 (s,
3H), 3.77 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 164.6, 163.7, 154.7, 147.9, 125.0, 124.1,
52.4, 51.8. IR (CH₂Cl₂) cm⁻¹ 3033, 2954, 1724, 1612, 1437, 1347, 1295, 1066, 961, 816;
Analysis calc’d for C₈H₁₀O₅S: C, 44.03; H, 4.62; Found: C, 44.21; H, 4.40.

**Synthesis of 1,3-Bis(2-Carbomethoxy Ethenylsulfinyl)propane (2k)**

1,3-Propanethiol (928 μL, 9.24 mmol) in CH₂Cl₂ (25 mL) was
treated with methyl propiolate (2.14 mL, 24.0 mmol) followed by the addition of TEA (1.42 mL,
10.2 mmol). Sulfide (**E,E/E,Z isomer**) was used crude in the preparation of the corresponding
sulfoxide.  **E,E-isomer** ¹H NMR (400 MHz, CDCl₃), δ: 7.63 (d, J = 15.4 Hz, 1H), 5.77 (d, J =
15.4 Hz, 1H), 3.72 (s, 6H), 2.90 (t, J = 7.0 Hz, 4H), 2.06 (pent, J = 7.3 Hz, 2H).
Crude bis sulfide (2.12 g, 7.65 mmol) in CH₂Cl₂ (20 mL) was treated dropwise with MCPBA (42 %, 6.29 g, 15.3 mmol, 200 mL). Sulfoxide (0.876 g, 37%) was isolated as a mixture of sulfoxide and sulfone (1.74 g) after flash chromatography (5% MeOH/EtOAc, then 15% MeOH/EtOAc). Mixture recrystallized from EtOAc/hexanes to yield both yellow and white crystals, which were separated manually. Further recrystallization (2x) afforded white crystals (199 mg) and yellow crystals (98.9 mg) and a mixture of both (578 mg) for a total yield of 37%. \(E,E\)-isomer (\(E,E\)-2k).² White crystals, Mp: 122-125 °C (EtOAc/hexanes); \(E,Z\)-isomer (\(E,Z\)-2k): Yellow crystals, Mp: 150-151 °C (EtOAc/hexanes); \(^1\)H NMR (400 MHz, CDCl₃), \(\delta\): 7.57, (d, \(J = 15.0\) Hz, 1H), 6.89 (d, \(J = 10.4\) Hz, 1H), 6.60 (d, \(J = 15.0\) Hz, 1H), 6.28 (d, \(J = 10.4\) Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.14 (m, 1H), 3.08 (t, \(J = 6.2\) Hz, 2H), 2.89 (m, 1H), 2.44 (m, 1H), 2.22 (m, 1H); \(^13\)C NMR (100.6 MHz, CDCl₃), \(\delta\): 164.6, 163.9, 157.7, 149.0, 126.5, 124.8, 52.9, 52.6, 52.3, 50.5, 16.2; IR (CDCl₃), cm\(^{-1}\): 3033, 2955, 1727, 1717, 1621, 1437, 1224, 1350, 1148, 1066, 1047, 959; MS (EI), m/z (%): 308 (M⁺, 1), 175 (100), 133 (19), 117 (51), 102 (39), 89 (19), 59 (13), 41 (22); MS (HREI), Calc’d for C₁₁H₁₆O₆S₂: 308.0388; Found: 308.0371; Analysis calc’d for C₁₁H₁₆O₆S₂: C, 42.84; H, 5.23; Found: C, 43.06; H, 5.15.

**Synthesis of Cbz-HomoCys((O)-Z-2-Carbethoxyethenyl)-OMe (2l)**

Z-Isomer of the sulfide¹ (1.06 g, 2.89 mmol) was dissolved in CH₂Cl₂ (7 mL) and cooled to -78 °C. A solution of MCPBA (77.1%, 711 mg, 3.18 mmol) in CH₂Cl₂ (23 mL) was added dropwise. The oxidation reaction was stirred at -78 °C for 4 hours, warmed to -40 °C and stirred overnight. The reaction was then cooled back down to -78 °C and filtered through a bed of Celite™. The filtrate was then placed in the cold bath and the surface
impinged with dry ammonia and refiltered, and repeated twice more. The clear filtrate was then concentrated under reduced pressure. Z-Isomer of sulfoxide (Z-2l) (737 mg, 67%) was obtained as oil as a pair of diastereomers (S_C,S_C/R_S) after flash chromatography (50% EtOAc/hexanes, then 3% MeOH/EtOAc). Z-isomer (Z-2l): \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\): 7.35 (m, 5H), 6.89 (two d, J = 10.3 Hz and J = 10.4 Hz, 1H), 6.29 (two d, J = 10.3 Hz, J = 10.4 Hz, 1H), 5.65 (br d, J = 7.4 Hz, 1H), 5.11 (s, 2H), 4.51 (dt, J = 4.0 & 7.4 Hz, 1H), 3.78 (s, 6H), 3.05 (m, 2H), 2.43 (m, 2H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)), \(\delta\): 171.7, 164.6, 157.4, 156.0, 136.1, 128.5, 128.2, 128.1, 124.9, 67.1, 53.0, 52.7, 52.6, 50.1, 49.7, 25.9, 25.7; IR (CDCl\(_3\)), cm\(^{-1}\): 3426, 2956, 1742, 1718, 1260, 1041; MS (CI, NH\(_3\)), m/z (%): 384 ((M+H\(^+\)), 89), 267 (100), 250 (55), 206 (14), 117 (28); MS (HREI), Calc’d for C\(_{16}\)H\(_{21}\)NO\(_5\)S (M-44): 339.1141; Found: 339.1148.

**Preparation of Ar(alk)yl Sulfoxides (3)**

See main manuscript for general procedure.

**Synthesis of p-Tolyl Benzyl Sulfoxide (3a)**\(^{2,11}\) (Method A/B)

2-Carbomethoxyethenyl p-tolyl sulfoxide (E-2a or Z-2a or E/Z-2a) (200 mg, 0.892 mmol) in THF (15 mL) was treated with n-BuLi (556 \(\mu\)L, 0.892 mmol) followed by the addition of a solution of benzyl bromide (128 \(\mu\)L, 1.07 mmol) in THF (1 mL). Sulfoxide (130 mg, 78-88%, see table 1 for detail) was isolated as a white solid after flash chromatography (30%
Synthesis of p-Tolyl Hexadecyl Sulfoxide (3aa) (Method B)

2-Carbomethoxyethenyl p-tolyl sulfoxide \((E/Z-2a)\) (120 mg, 0.535 mmol) in THF (12 mL) was treated with MeO\(^+\)Na (125 μL, 0.546 mmol) followed by the addition of a solution of hexadecyl iodide (226 mg, 0.642 mmol) in THF (1 mL). Sulfoxide (170 mg, 87%) was isolated as a white solid after chromatography (10% EtOAc/hexanes, then 70% EtOAc/hexanes). Mp: 56-57 °C (hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)), δ: 7.51 (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 2.77 (m, 2H), 2.42 (s, 3H), 1.57 (m, 2H), 1.36 (m, 2H), 1.24 (br s, 24H), 0.88 (t, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)), δ: 141.4, 141.0, 129.9, 124.1, 57.4, 31.9, 29.7 (5C), 29.5, 29.3 (3C), 29.2, 28.7, 22.7, 22.2, 21.4, 14.1; IR (CDCl\(_3\)), cm\(^{-1}\): 2927, 2855, 1035, 809; Analysis calc’d for C\(_{23}\)H\(_{40}\)OS: C, 75.84; H, 10.98; Found: C, 75.94; H, 10.84.

Synthesis of p-Tolyl Methyl Sulfoxide (3ab) (Method B)

2-Carbomethoxyethenyl p-tolyl sulfoxide \((E-2a)\) (150 mg, 0.669 mmol) in THF (15 mL) was treated with MeO\(^+\)Na (156 μL, 0.682 mmol) followed by the addition of a solution of methyl iodide (50.0 μL, 0.803 mmol) in THF (1 mL). Sulfoxide (87.6 mg, 85%) was isolated as a yellow oil after chromatography (30% EtOAc/hexanes). Mp: 31-32 °C (EtOAc/hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)), δ: 7.39 (d, \(J = 7.7\) Hz, 2H), 7.17 (d, \(J = 7.7\) Hz,
2H), 2.54 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 142.1, 140.9, 129.5, 123.0, 43.5, 20.9; IR (CDCl$_3$), cm$^{-1}$: 3052, 2925, 2871, 1598, 1495, 1411, 1295, 1082, 1016, 959, 813.

**Synthesis of Methyl Benzyl Sulfoxide (3b)$^{14}$ (from $E/Z$-2b by Method A or from $E/Z$-2d by Method B)**

**Method A:** 2-Carbomethoxyethenyl methyl sulfoxide ($E/Z$-2b) (100 mg, 0.675 mmol) in THF (5 mL) was treated with a solution of CySH/n-BuLi (82.6 μL, 0.675 mmol; 2.5 M, 276 μL, 0.689 mmol) followed by the addition of a solution of benzyl bromide (96.3 μL, 0.810 mmol) in THF (5 mL). Sulfoxide (64.7 mg, 62%) was isolated as an oil after chromatography (30% EtOAc/hexanes, then 100% EtOAc, then 50% MeOH/EtOAc).

**Method B:** 2-Carbomethoxyethenyl benzyl sulfoxide ($E/Z$-2d) (100 mg, 0.446 mmol) in THF (12 mL) was treated with MeO$^-$Na$^+$ (102 μL, 0.446 mmol) followed by the addition of a solution of methyl iodide (33.3 μL, 0.535 mmol) in THF (1 mL). Sulfoxide (8-32 mg, 12-48%) was isolated as an oil after chromatography. $^1$H NMR (400 MHz, CDCl$_3$), δ: 7.29 (m, 5H), 3.93 (AB$_q$, J = 12.8 Hz, 2H), 2.39 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$), δ: 129.8, 129.5, 128.7, 128.2, 60.0, 37.0; IR (CDCl$_3$), cm$^{-1}$: 3067, 2918, 1497, 1424, 1073, 1030, 966. MS (EI), m/z (%): 154 (M$^+$, 5), 92 (8), 91 (100), 65 (8).

**Synthesis of Cyclohexyl Benzyl Sulfoxide (3c) (Method A/B)$^{2,15}$**

2-Carbomethoxyethenyl cyclohexyl sulfoxide ($E$-2c) (120 mg, 0.555 mmol) in THF (12 mL) was treated with MeO$^-$Na$^+$ (130 μL, 0.566 mmol) followed by the addition of a solution of benzyl bromide (79.2 μL, 0.666 mmol) in THF (1 mL). Sulfoxide (79.9 mg, 65%) was isolated as a white solid after chromatography (30% EtOAc/hexanes, then 100% EtOAc).
Synthesis of Benzyl Sulfoxide (3d)²¹⁶ (Method A/B)

2-Carbomethoxyethenyl benzyl sulfoxide (E/Z-2d) (100 mg, 0.446 mmol) in THF (5 mL) was treated with a solution of CySH/n-BuLi (54.6 μL, 0.446 mmol; 2.5 M, 182 μL, 0.455 mmol) followed by the addition of a solution of benzyl bromide (63.6 μL, 0.535 mmol) in THF (5 mL). Sulfoxide (76.7 mg, 75%) was isolated as a white solid after chromatography (30% EtOAc/hexanes, then 50% EtOAc). Mp: 129-130 °C (EtOAc/hexanes), Lit: ⁹ 57-58 °C; ¹H NMR (400 MHz, CDCl₃), δ: 7.31 (m, 10H), 3.87 (AB q, J = 13.0 Hz, 4H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 130.0, 129.9, 128.7, 128.1, 57.0; IR (CDCl₃), cm⁻¹: 3033, 2921, 1496, 1043.

Synthesis of Hexyl Methyl Sulfoxide (3e)²¹⁷ (Method B)

2-Carbomethoxyethenyl hexyl sulfoxide (E-2e) (150 mg, 0.686 mmol) in THF (15 mL) was treated with MeO⁻Na⁺ (161 μL, 0.700 mmol) followed by the addition of a solution of methyl iodide (51.2 μL, 0.823 mmol) in THF (1 mL). Sulfoxide (64.1 mg, 63%) was isolated as an oil after chromatography (30% EtOAc/hexanes, then 100% EtOAc, then 10% MeOH/EtOAc). ¹H NMR (400 MHz, CDCl₃), δ: 2.78 (ABXY, JAX = 6.1 Hz, JAY = 8.9 Hz, JBX = 7.2 Hz, JBY = 8.9 Hz, JAB = 12.9 Hz, 2H), 2.64 (s, 3H), 1.68 (m, 2H), 1.39 (br m, 2H), 1.28 (br m, 4H), 0.85 (t, J = 7.0 Hz, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 54.1, 38.2, 31.3, 28.4, 22.5, 20.6.
Synthesis of Hexadecyl Benzyl Sulfoxide (3f)² (Method B)

2-Carbomethoxyethenyl hexadecyl sulfoxide (E-2f) (150 mg, 0.418 mmol) in THF (15 mL) was treated with MeO⁻Na⁺ (97.7 μL, 0.426 mmol) followed by the addition of a solution of benzyl bromide (59.7 μL, 0.502 mmol) in THF (1 mL). Sulfoxide (206 mg, 77%) was isolated as a white solid after chromatography (30% EtOAc/hexanes, then 100% EtOAc). Mp: 92-93 °C (EtOAc/hexanes).²

Synthesis of Benzyl 4-Acetamidophenyl Sulfoxide (3g)² (Method B)

2-Carbomethoxyethenyl 4-acetamidophenyl sulfoxide (Z-2g) (120 mg, 0.449 mmol) in THF (12 mL) was treated with MeO⁻Na⁺ (105 μL, 0.458 mmol) followed by the addition of benzyl bromide (64.1 μL, 0.539 mmol). Sulfoxide (61.2 mg, 50%) was isolated as a white solid after chromatography (30% EtOAc/hexanes, then 100% EtOAc). Mp: 158-161 °C; ¹H NMR (400 MHz, CDCl₃), δ: 8.31 (br s, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.43 (m, 5H), 6.99 (d, J = 8.1 Hz, 2H), 4.05 (ABq, J = 12.6 Hz, 2H), 2.14 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃), δ: 168.9, 141.3, 136.6, 130.4, 129.0, 128.4, 125.8, 125.5, 119.6, 63.6, 24.6; IR (CDCl₃), cm⁻¹: 3434, 3033, 2925, 1695, 1592, 1511, 1310, 1040, 834. MS (CI, NH₃), m/z (%): 274 ((M+H)⁺, 2), 273 (M⁺,2), 225 (5), 167 (4), 140 (5), 125 (7), 93 (5), 92 (11), 91 (100); Analysis calc’d for C₁₅H₁₅NO₂S: C, 65.95; H, 5.49; Found: C, 66.16; H, 5.33.

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Synthesis of Benzothiazolyl Benzyl Sulfoxide (3h)\textsuperscript{18} (Method A/B)

2-Carbomethoxyethenyl \textit{p}-tolyl sulfoxide (\textit{E}-2\textit{h} or \textit{E}-2\textit{h} or \textit{E/Z}-2\textit{h}) (150 mg, 0.559 mmol) in THF (20 mL) was treated with CySH/\textit{n}-BuLi (68 \textmu L, 0.559 mmol; 1.6 M, 349 \textmu L, 0.559 mmol) followed by the immediate addition of a solution of benzyl bromide (132 \textmu L, 1.12 mmol) in THF (1 mL). Sulfoxide (100-120 mg, 66-78%, see table-1 in the manuscript) was isolated as a white solid after flash chromatography (5\% EtOAc/hexanes, then 50\% EtOAc/hexanes). mp: 123-124 °C; \textit{\textsuperscript{1}H} NMR (400 MHz, CDCl\textsubscript{3}), \textdelta: 8.00 (d, \textit{J} = 8.2 Hz, 1H), 7.83 (d, \textit{J} = 8.1 Hz, 1H), 7.47 (m, 1H), 7.37 (m, 1H), 7.21-7.14 (m, 3H), 7.07 (d, \textit{J} = 7.6 Hz, 2H), 4.32 (AB\textit{q}, \textit{J} = 13.0 Hz, 2H); \textit{\textsuperscript{13}C} NMR (100.6 MHz, CDCl\textsubscript{3}), \textdelta:176.8, 153.6, 135.8, 130.3, 128.5, 128.2, 126.8, 126.0, 123.7, 122.1, 62.6; IR (CH\textsubscript{2}Cl\textsubscript{2}), cm\textsuperscript{-1}: 3061, 3031, 2920, 1494, 1472, 1454, 1425, 1313, 1059, 1001, 760, 729, 697.

Synthesis of 1,3-\textit{Bis}(Benzylsulfinyl) Propane (3k)\textsuperscript{2} (Method A)

1,3-\textit{Bis}(2-carbomethoxyethenylsulfinyl)propane (\textit{E,E/E,Z}-2k) (100 mg, 0.325 mmol) in THF (10 mL) was treated with a solution of CySH/\textit{n}-BuLi (79.4 \textmu L, 0.649 mmol; 2.5 M, 262 \textmu L, 0.656 mmol) followed by the addition of benzyl bromide (92.7 \textmu L, 0.779 mmol). Sulfoxide (77.4 mg, 74\%) was isolated as a white solid (\textit{dr} 56:44) after chromatography (5\% EtOH/CH\textsubscript{2}Cl\textsubscript{2}, then 10\% EtOH/CH\textsubscript{2}Cl\textsubscript{2}). Mp: 176-177 °C (EtOAc/hexanes).\textsuperscript{2}
(Z)-Methyl 3-(Cyclohexylthio)acrylate (Z-4)\textsuperscript{19}

\(^1\)H NMR (300 MHz) \(\delta\): 7.15 (d, \(J = 10.2\) Hz, 1H), 5.80 (d, \(J = 10.2\) Hz, 1H), 3.70 (s, 3H), 2.81 (m, 1H), 2.01-1.96 (m, 2H), 1.80-1.76 (m, 2H), 1.62-1.56 (m, 1H), 1.44-1.24 (m, 5 H); \(^{13}\)C NMR: 167.1, 148.7, 112.1, 51.2, 47.6, 33.5, 25.8, 25.4; IR (CH\(_2\)Cl\(_2\)) cm\(^{-1}\) 2930, 2852, 1701, 1561, 1434, 1367, 1217, 1165, 1011, 933, 800. GC-MS, m/z (%): 200 (M\(^+\), 5.2), 167 (100), 135 (32).

(E)-Methyl 3-(Cyclohexylthio)acrylate (E-4)\textsuperscript{19}

\(^1\)H NMR (300 MHz) \(\delta\): 7.68 (d, \(J = 15.3\) Hz, 1H), 5.78 (d, \(J = 15.3\) Hz, 1H), 3.69 (s, 3H), 3.03 (m, 1H), 2.01-1.98 (m, 2H), 1.76-1.73 (m, 2H), 1.62-1.59 (m, 1H), 1.44-1.24 (m, 5 H); \(^{13}\)C NMR (75.5 MHz) \(\delta\): 166.0, 146.7, 113.7, 51.4, 45.1, 33.1, 25.8, 25.5; IR (CH\(_2\)Cl\(_2\)) cm\(^{-1}\) 2932, 2854, 1713, 1582, 1306, 1160, 948, 831. GC-MS, m/z (%): 201 (M\(^+\)+, 30), 167 (100), 135 (20).

(Z)-Methyl 3-(Methoxy)acrylate (Z-5)\textsuperscript{20}

\(^1\)H NMR (300 MHz), \(\delta\): 6.42 (d, \(J = 7.0\) Hz, 1H), 4.83 (d, \(J = 7.0\) Hz, 1H), 3.86 (s, 3H), 3.67 (s, 3H). \(^{13}\)C NMR (75.5 MHz): 165.6, 160.0, 96.0, 62.5, 50.9; IR (CH\(_2\)Cl\(_2\)) cm\(^{-1}\) 2951, 2855, 1718, 1648, 1457, 1436, 1296, 1275, 1249, 1204, 1165, 1106, 1043, 1018, 804. GC-MS (EI), m/z (%): 117 (M\(^+\)+, 75), 85 (100).

(E)-Methyl 3-(Methoxy)acrylate (E-5)\textsuperscript{20}
$^1$H NMR (300 MHz), $\delta$: 7.56 (dd, $J = 12.6 \& 0.2$ Hz, 1H), 5.13 (d, $J = 12.6$, 1H), 3.63 (s, 3H), 3.62 (s, 3H). $^{13}$C NMR (75.5 MHz); 167.5, 162.7, 95.2, 56.8, 50.5; IR (CH$_2$Cl$_2$) cm$^{-1}$ 2956, 2852, 1717, 1629, 1436, 1332, 1251, 1223, 1196, 1174, 1139, 1102, 961, 918, 828, 747. GC-MS (EI), m/z (%): 117 (M+1$^+$), 63), 85 (100).

(Z)-Methyl 2-Heptenoate (Z-6)$^{21}$

$^1$H NMR (300 MHz), $\delta$: 6.21 (dt, $J = 1.5$, 11.5 Hz, 1H), 5.74 (dt, $J = 1.7$, 11.5 Hz, 1H), 3.68 (s, 3H), 2.63 (m, 2H), 1.43-1.29 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75.5 MHz), $\delta$: 166.9, 151.0, 119.1, 50.9, 31.1, 28.7, 22.4, 13.9; IR (CH$_2$Cl$_2$), cm$^{-1}$: 3034, 2925, 1635, 1457, 1428. GC-MS (EI), m/z (%): 143 ((M+1)$^+$, 100).

(E)-Methyl 2-Heptenoate (E-6)$^{21}$

$^1$H NMR (300 MHz), $\delta$: 7.00 (dt, $J = 7.8$ Hz, 15.7 Hz, 1H), 5.84 (dt, $J = 1.7$ Hz, 15.7 Hz, 1H), 3.74 (s, 3H), 2.22 (m, 2H), 1.49-1.35 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75.5 MHz), $\delta$: 149.8, 137.8, 120.8, 51.4, 31.9, 30.9, 22.2, 14.2; IR (CH$_2$Cl$_2$), cm$^{-1}$: 3031, 2956, 1718, 1652, 1496, 1455, 1227. GC-MS (EI), m/z (%): 143 (M+1$^+$, 100).

(Z)-Methyl 3-(Butoxy)acrylate (Z-7)$^{22}$

$^1$H NMR (300 MHz), $\delta$: 6.50 (d, $J = 7.0$ Hz, 1H), 4.81 (d, $J = 7.0$ Hz, 1H), 4.00 (d, $J = 6.7$ Hz, 2H), 1.69 (m, 2H), 1.41 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75.5 MHz), $\delta$: 174.4, 159.3, 95.5, 66.2, 50.8, 31.8, 18.8, 14.1; IR
(CH$_2$Cl$_2$), cm$^{-1}$: 3034, 2927, 1722, 1643, 1455, 1285, 1164, 1106. GC-MS (EI), m/z (%): 159 (M+1)$^+$, 100).

(E)-Methyl 3-(Butoxy)acrylate (E-7)\textsuperscript{22}

$^1$H NMR (400 MHz), $\delta$: 7.56 (dt, $J = 12.7$, 3.1 Hz, 1H), 5.15 (dt, $J = 12.6$, 2.6 Hz, 1H), 4.06 (m, 1H), 3.79 (m, 1H), 3.65 (m, 3H), 1.65-1.58 (m, 2H), 1.39-1.32 (m, 2H), 0.89 (dt, $J = 7.4$, 2.0 Hz, 3H); $^{13}$C NMR (100. MHz), $\delta$: 168.0, 167.7, 163.2, 163.0, 162.7, 162.5, 96.3, 96.0, 95.9, 95.6, 70.9, 70.7, 63.7 63.6, 57.2, 57.1, 51.05, 50.99, 30.8, 19.1, 19.0, 13.7, 13.6; IR (CH$_2$Cl$_2$), cm$^{-1}$: 2960, 2937, 2875, 1713, 1645, 1626, 1465, 1436, 1392, 1327, 1283, 1241, 1210, 1134, 1065, 1029, 962, 934, 824, 747. GC-MS (EI), m/z (%): 159 (M+1)$^+$, 100).

References:-

Selected NMR spectra of new compounds

Figure 1. $^1$H NMR spectrum of $Z$-2h in CDCl$_3$ (400 MHz)  S25

Figure 2. $^{13}$C (JMOD) NMR spectrum of $Z$-2h in CDCl$_3$ (100.6 MHz)  S25

Figure 3. $^1$H NMR spectrum of $E$-2h in CDCl$_3$ (400 MHz)  S26

Figure 4. $^{13}$C (JMOD) NMR spectrum of $E$-2h in CDCl$_3$ (100.6 MHz)  S26

Figure 5. $^1$H NMR spectrum of $E/Z$-2i in CDCl$_3$ (300 MHz)  S27

Figure 6. $^{13}$C (JMOD) NMR spectrum of $E/Z$-2i in CDCl$_3$ (75.5 MHz)  S27

Figure 7. $^1$H NMR spectrum of $E,Z$-2j in CDCl$_3$ (400 MHz)  S28

Figure 8. $^{13}$C (JMOD) NMR spectrum of $E,Z$-2j in CDCl$_3$ (100.6 MHz)  S28

Figure 9. $^1$H NMR spectrum of $Z,Z$-2j in CDCl$_3$ (400 MHz)  S29

Figure 10. $^{13}$C (JMOD) NMR spectrum of $Z,Z$-2j in CDCl$_3$ (100.6 MHz)  S29

Figure 11. $^1$H NMR spectrum of $E,Z$-2k in CDCl$_3$ (400 MHz)  S30

Figure 12. $^{13}$C (JMOD) NMR spectrum of $E,Z$-2k in CDCl$_3$ (100.6 MHz)  S30

Figure 13. $^1$H NMR spectrum of $Z$-2l in CDCl$_3$ (400 MHz)  S31

Figure 14. $^{13}$C (JMOD) NMR spectrum of $Z$-2l in CDCl$_3$ (75.5 MHz)  S31

Figure 15. $^1$H NMR spectrum of 3i in CDCl$_3$ (400 MHz)  S32

Figure 16. $^{13}$C (JMOD) NMR spectrum of 3i in CDCl$_3$ (75.5 MHz)  S32

Figure 17. $^1$H NMR spectrum of 3l in CDCl$_3$ (400 MHz)  S33

Figure 18. $^{13}$C (JMOD) NMR spectrum of 3l in CDCl$_3$ (100.6 MHz)  S33
Figure 1. $^1$H NMR spectrum of $Z-2h$ in CDCl$_3$ (400 MHz)

Figure 2. $^{13}$C (JMOD) NMR spectrum of $Z-2h$ in CDCl$_3$ (100.6 MHz)
Figure 3. $^1$H NMR spectrum of $E$-2h in CDCl$_3$ (400 MHz)

Figure 4. $^{13}$C (JMOD) NMR spectrum of $E$-2h in CDCl$_3$ (100.6 MHz)
Figure 5. $^1$H NMR spectrum of $E/Z$-2i in CDCl$_3$ (400 MHz)

Figure 6. $^{13}$C (JMOD) NMR spectrum of $E/Z$-2i in CDCl$_3$ (100.6 MHz)
Figure 7. $^{1}$H NMR spectrum of $E,Z$-2j in CDCl$_3$ (400 MHz)

Figure 8. $^{13}$C (JMOD) NMR spectrum of $E,Z$-2j in CDCl$_3$ (100.6 MHz)
Figure 9. $^1$H NMR spectrum of $Z,Z$-2j in CDCl$_3$ (400 MHz)

Figure 10. $^{13}$C (JMOD) NMR spectrum of $Z,Z$-2j in CDCl$_3$ (100.6 MHz)
Figure 11. $^1$H NMR spectrum of $E,Z$-2k in CDCl$_3$ (400 MHz)

Figure 12. $^{13}$C (JMOD) NMR spectrum of $E,Z$-2k in CDCl$_3$ (100.6 MHz)
Figure 13. $^1$H NMR spectrum of Z-2l in CDCl$_3$ (400 MHz)

Figure 14. $^{13}$C (JMOD) NMR spectrum of Z-2l in CDCl$_3$ (75.5 MHz)
Figure 15. $^1$H NMR spectrum of 3i in CDCl$_3$ (400 MHz)

Figure 16. $^{13}$C (JMOD) NMR spectrum of 3i in CDCl$_3$ (75.5 MHz)
Figure 17. $^1$H NMR spectrum of $3l$ in CDCl$_3$ (400 MHz)

Figure 18. $^{13}$C (JMOD) NMR spectrum of $3l$ in CDCl$_3$ (100.6 MHz).