SUPPLEMENTARY INFORMATION

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

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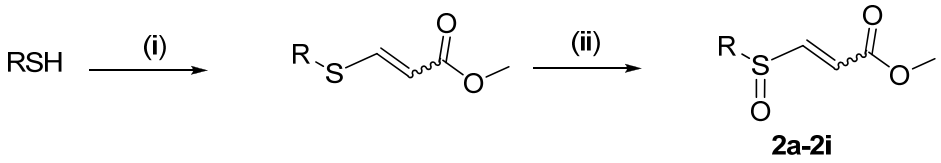
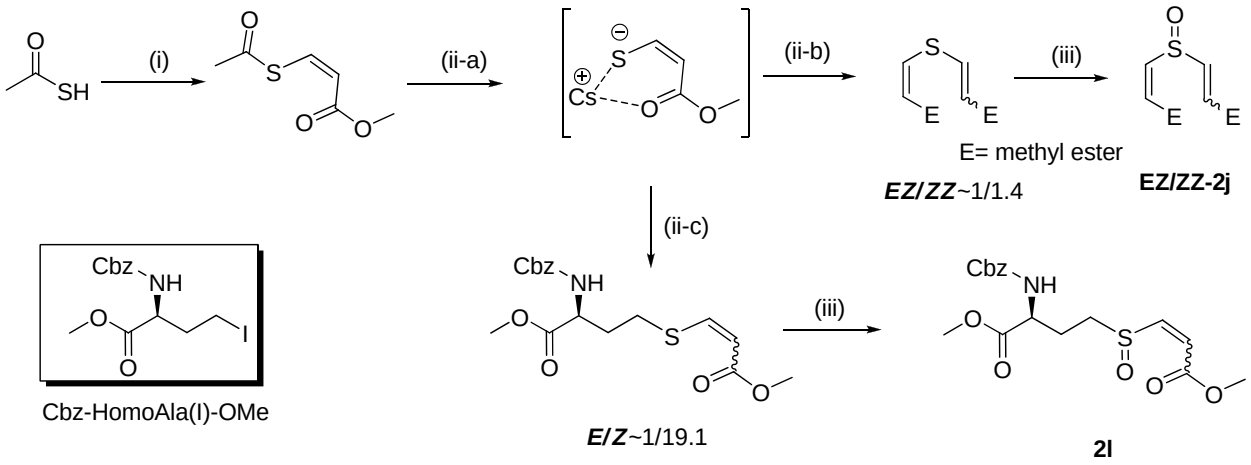
Preparation of α,β-Unsaturated Sulfoxides (2)

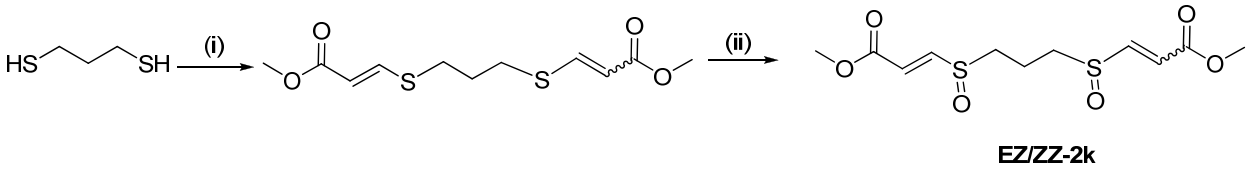


2a-2i

Scheme 1:- (i) methyl propiolate, Et_3N, CH_2Cl_2, 0 °C (ii) MCPBA, CH_2Cl_2, -78 °C.



Scheme 2:- (i) methyl propiolate, imidazole, CH_3CN, 45 °C[1] (ii) (a) Cs_2CO_3, CH_3OH, -10 °C and then, (b) methyl propiolate or (c) Cbz-HomoAla(I)-OMe in methanol. (iii) MCPBA, CH_2Cl_2, -78 °C.

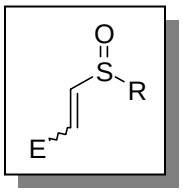


Scheme 3:- (i) methyl propiolate, Et_3N, CH_2Cl_2 (ii) MCPBA, CH_2Cl_2, -78 °C.

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_2Cl_2 or $CDCl_3$). NMR spectra for ^1H 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. ^1H 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 Pheonix, 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. MeO^-Na^+ 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 F_{254} precoated glass-backed silica gel plates, or Silicycle 0.25mm, extra hard layer, 60 Å F_{254} 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]

A solution of the thiol (1 eq.) was prepared in CH_2Cl_2 (1 mL/mmol) and cooled to 0 °C. Methyl propiolate was added (1.3 eq.),[b] followed by the slow addition of triethylamine (TEA) (1.1 eq.) upon which the solution turned dark brown.[c] The mixture was stirred for 30-60 minutes,[d] 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 CH_2Cl_2 (3x) and the organic layers combined. The organic layer was then washed with H_2O, brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting sulfide was isolated using flash chromatography through recycled silica gel using EtOAc/hexanes as the eluant.[e] Sulfide yields were calculated from the thiol.

The sulfide (1 eq.) was then dissolved in CH_2Cl_2 (5 mL/mmol)[f] and cooled to -78 °C[g,h] 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,[i] 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.[j] 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 CH_2Cl_2) 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.

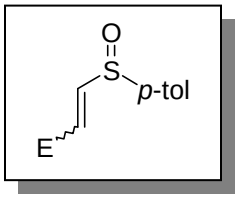
[f] **2g** was oxidised with 30% H_2O_2 rather than MCPBA.

[g] MCPBA was added at 40 °C for the synthesis of **2h** and the reaction time was 1 hr at this temp.

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

[i] oxidation reaction for the synthesis of **2i** was complete within 1 hr at -78 °C .

[j] workup procedure was different for the oxidation reactions to synthesize **2h**, **2i** and **2j** (washing with $Na_2S_2O_3$, $NaHCO_3$, 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.

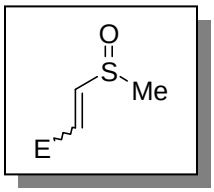


Synthesis of *E/Z*-2-Carbomethoxyethenyl *p*-Tolyl Sulfoxide (2a) [2,3]

p-Thiocresol (1.74 g, 13.7 mmol) in CH_2Cl_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[4] (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, $CDCl_3$), δ: 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, $CDCl_3$), δ: 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_2Cl_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; ^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 164.6, 156.2, 141.9, 140.9, 130.0, 124.9, 123.3, 52.4, 21.4; IR ($CDCl_3$), cm^{-1}: 3029, 2954, 1719, 1615, 1492, 1437, 1347, 1227, 1208, 1078, 1037, 1016, 816. ***E*-isomer** (***E*-2a**) (R_f = 0.21, 30% EtOAc/hexanes): Mp: 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 164.4, 151.5, 142.7, 138.1, 130.5, 125.0, 123.5, 52.3, 21.5; IR ($CDCl_3$), 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 $C_{11}H_{12}O_3S$: C, 58.95; H, 5.35; Found: C, 58.80; H, 5.13.

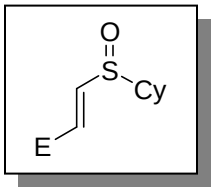


Synthesis of *E/Z*-2-Carbomethoxyethenyl Methyl Sulfoxide (2b)[2,5]

Sodium thiomethoxide (1.90 g, 24.0 mmol) in CH_3CN (25 mL) was treated with methyl propiolate (2.78 mL, 31.2 mmol). Sulfide[6] (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:** ^{1}H NMR (300 MHz, $CDCl_3$), 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 CH_2Cl_2 (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**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.61 (d, *J* = 15.0 Hz, 1H), 6.97 (d, *J* =

10.4 Hz, 1H), 6.62 (d, *J* = 15.0 Hz, 1H), 6.26 (d, *J* = 10.4 Hz, 1H), 3.76 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 165.0, 164.1, 159.3, 151.1, 125.3, 123.8, 52.4, 52.3, 42.3, 39.6; IR ($CDCl_3$), cm^{-1}: 3035, 2954, 1719, 1624, 1437, 1308, 1277, 1149, 1061, 965. MS (EI), m/z (%): 148 (M^+, 100), 117 (45), 103 (42), 102 (60), 88 (23), 71 (27), 63 (22) 59 (42), 53 (22); MS (HREI), Calc'd for $C_5H_8O_3S$ $(M)^+$: 268.0102; Found: 148.0194.

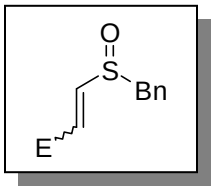


Synthesis of *E*-2-Carbomethoxyethenyl Cyclohexyl Sulfoxide (2c) [2]

Cyclohexanethiol (1.22 mL, 10.0 mmol) in CH_2Cl_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, $CDCl_3$), δ: 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, $CDCl_3$), δ: 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, 1624, 1584, 1437, 1310, 1043, 953, 833.

Sulfide (833 mg, 4.16 mmol) was dissolved in CH_2Cl_2 (50 mL) and cooled to -78 °C followed by the dropwise addition of MCPBA (75.7%, 1.2 eq., 10 mL CH_2Cl_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.^{TM} 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 (CI, 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 $C_{10}H_{16}O_3S$: C, 55.53; H, 7.40; Found: C, 55.43; H, 7.41.

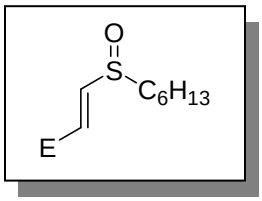


Synthesis of *E/Z*-2-Carbomethoxyethenyl Benzyl Sulfoxide (2d) [2,7]

Benzyl mercaptan (1.65 mL, 14.4 mmol) in CH_2Cl_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[8] (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_2Cl_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_q, *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,

52.5; IR ($CDCl_3$), cm^{-1}: 3067, 3034, 2955, 1715, 1612, 1438, 1349, 1227, 1041, 819. ***E*-isomer** (***E*-2d**) (R_f = 0.07, 20% EtOAc/hexanes): Mp: 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 149.0, 130.2, 129.0, 128.8, 128.5, 126.5, 60.0, 52.3; IR ($CDCl_3$), cm^{-1}: 3034, 2954, 1725, 1621, 1496, 1437, 1301, 1230, 1193, 1059, 960. MS (CI, NH_3), m/z (%): 242 ($(M + NH_4)^+$, 100), 225 (13), 108 (2); Analysis calc'd for $C_{11}H_{12}O_3S$: C, 58.95; H, 5.35; Found: C, 59.09; H, 5.26.

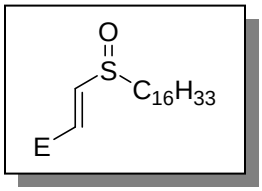


Synthesis of *E*-2-Carbomethoxyethenyl Hexyl Sulfoxide (2e) [2,9]

1-Hexanethiol (2.44 mL, 17.3 mmol) in CH_2Cl_2 (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**: ^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 165.7, 147.2, 113.1, 51.3, 31.9, 31.2, 28.5, 28.4, 22.4, 13.9; IR ($CDCl_3$), cm^{-1}: 3023, 2953, 2933, 1701, 1624, 1584, 1437, 1309, 1258, 1141, 1043, 1020, 832.

Sulfide (3.20 g, 15.8 mmol) in CH_2Cl_2 (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 (R_f = 0.24, 30% EtOAc/hexanes). ***E*-isomer** (***E*-2a**): Mp: 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 15.0 Hz, 1H), 6.65 (d, *J* = 15.0 Hz, 1H), 3.80 (s, 3H), 2.80 (ABXY, J_{AX} = 5.3 Hz, J_{AY} = 9.8 Hz, J_{BX} = 6.3 Hz, J_{BY} = 6.2 Hz, J_{AB} = 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, $CDCl_3$), δ: 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 (CI, 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 $C_{10}H_{18}O_3S$: C, 55.02; H, 8.25; Found: C, 55.23; H, 8.12.

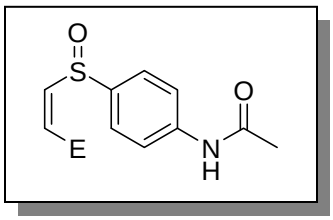


Synthesis of *E*-2-Carbomethoxyethenyl Hexadecyl Sulfoxide (2f) [2,9]

1-Hexadecanethiol (7.19 mL, 23.4 mmol) in CH_2Cl_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, $CDCl_3$), δ: 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, $CDCl_3$), δ: 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_2Cl_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, $CDCl_3$), δ: 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, $CDCl_3$), δ: 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 ($CDCl_3$), cm^{-1}: 3058, 2928, 2855, 1725, 1622, 1438, 1301, 1231, 959.MS (CI, NH_3), 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 $C_{20}H_{38}O_3S$: C, 66.99; H, 10.60; Found: C, 67.12; H, 10.69.

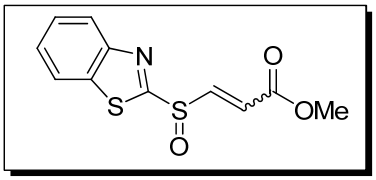


Synthesis of *Z*-2-Carbomethoxyethenyl 4-Acetamidophenyl Sulfoxide (2g)[2]

4-Acetamidothiophenol (2.50 g, 15.0 mmol) in CH_2Cl_2 (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); ^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 168.9, 167.0, 150.7, 138.4, 132.1, 130.6, 120.6, 112.7, 51.4, 24.5; IR ($CDCl_3$), 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 H_2O_2 (0.135 mL/mmol substrate, 30% solution in H_2O). The reaction was stirred at RT for 5 days. H_2O (5 mL) was added and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with H_2O (2 mL), brine (5 mL), dried over $MgSO_4$ 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; ^{1}H NMR (400 MHz), ***Z*-isomer** (***Z*-2g**)**:**^{1}H NMR (400 MHz, $CDCl_3$),, 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 169.4, 164.5, 155.3, 141.7, 137.6, 125.9, 123.7, 120.2, 52.5, 24.3; IR (CH_2Cl_2), 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 $C_{12}H_{13}NO_4S$: C, 53.93; H, 4.87; Found: C, 54.24; H, 4.65.

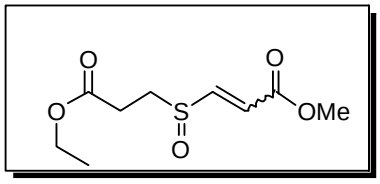


Synthesis of *E/Z*-2-Carbomethoxyethenyl Benzothiazolyl Sulfoxide (2h)

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 CH_2Cl_2 (30 mL) under N_2 gas, followed by immediate dropwise addition of 2-mercaptobenzothiazole (1.00 g, 5.96 mmol) in dry CH_2Cl_2 (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 $MgSO_4$ 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): ^{1}H NMR (400 MHz, $CDCl_3$), 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 CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of the sulfide (1.31 g, 5.2 mmol) in CH_2Cl_2 (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 $Na_2S_2O_3$ (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 combine 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*-2h** (0.32 g, 23 %, EtOAc/hexanes 30:70) as a white solid and compound ***Z*-2h** (0.62 g, 45 %, EtOAc/hexanes 50:50) as a yellow solid. ***E*-isomer** (***E*-2h**): Mp: 128-129 °C; ^{1}H NMR(400 MHz, $CDCl_3$) , δ 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, $CDCl_3$), δ 173.5, 163.7, 152.8, 149.0, 135.7, 127.1, 126.7, 125.8, 124.2, 122.3, 52.5; IR (CH_2Cl_2) cm^{-1} 3059, 2951, 1726, 1620, 1434, 1296, 1222, 1145, 1088, 954, 760, 702; HRMS (TOF CI$^+$), Calc'd for $C_{24}H_{25}NO_6S$ $(M+H)^+$: 268.0102; Found: 268.0100; ***Z*-isomer** (***Z*-2h**): Mp: 83-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 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, $CDCl_3$), δ 173.4, 163.9, 152.8, 152.7, 135.9, 126.6, 126.5, 126.2, 124.0, 121.7, 52.4; IR (CH_2Cl_2) cm^{-1} 3031, 2951, 1725, 1615, 1457, 1434, 1345, 1222, 1183, 1058, 990, 816, 761, 729; Analysis calc'd for $C_{11}H_9NO_3S_2$: C, 49.42; H, 3.39; Found: C, 49.50; H, 3.47.



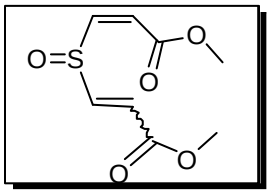
Synthesis of *E/Z*-2-Carboethoxyethyl 2-Carbomethoxyethenyl Sulfoxide (2i)

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_2Cl_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_2Cl_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_2Cl_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_2Cl_2 (10 mL) was added dropwise to a CH_2Cl_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 $Na_2S_2O_3$ (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

(100), 73 (60), 55 (64); MS (EI,), m/z (%): 242 ((M + NH_4)$^+$, 100), 225 (13), 108 (2); MS (HREI), Calc'd for $C_9H_{14}O_5S$: 234.0562; Found: 234.0562.

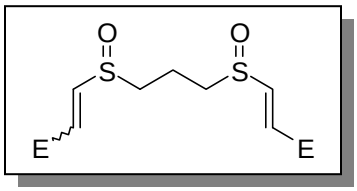


Synthesis of *E,Z/Z,Z*-Bis(2-Carbomethoxyethenyl) Sulfoxide (*2j*)

A methanolic solution (5 ml) of Cs_2CO_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_2Cl_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**:[10] ^{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**:[10] ^{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_2Cl_2 (10 mL) was added dropwise to a stirred solution of the sulfide (0.68 g, 3.3 mmol) in CH_2Cl_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 $Na_2S_2O_3$ (30 mL) and stirred for 1 hr at room temperature. The organic layer was extracted

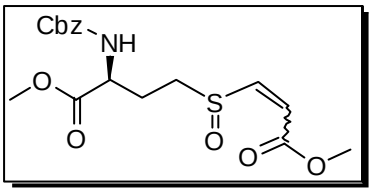
and washed with $NaHCO_3$ (2 x 20 mL) and brine (1 x 20 mL). The combine organic layer was dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford compound ***E,Z*-2j** (0.28 g, 38 %, EtOAc/hexanes 30:70 and then 50:50) liquid 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 ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.88 (d, *J* = 10.3 Hz, 2H), 6.31 (d, *J* = 10.3 Hz, 2H), 3.73 (s, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 164.2, 150.6, 126.0, 52.2. IR (CH_2Cl_2) cm^{-1} 3031, 2954, 1728, 1614, 1436, 1351, 1224, 1040, 816; Analysis calc'd for $C_8H_{10}O_5S$: C, 44.03; H, 4.62; Found: C, 44.00; H, 4.52. ***E,Z* isomer (*E,Z*-2j)**: Mp: 52-54 °C;^{1}H NMR (400 MHz, $CDCl_3$), 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 164.6, 163.7, 154.7, 147.9, 125.0, 124.1, 52.4, 51.8. IR (CH_2Cl_2) cm^{-1} 3033, 2954, 1724, 1612, 1437, 1347, 1295, 1066, 961, 816; Analysis calc'd for $C_8H_{10}O_5S$: 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 CH_2Cl_2 (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** ^{1}H NMR (400 MHz, $CDCl_3$), 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 CH_2Cl_2 (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, $CDCl_3$), δ: 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, $CDCl_3$), δ: 164.6, 163.9, 157.7, 149.0, 126.5, 124.8, 52.9, 52.6, 52.3, 50.5, 16.2; IR ($CDCl_3$), 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 $C_{11}H_{16}O_6S_2$: 308.0388; Found: 308.0371; Analysis calc'd for $C_{11}H_{16}O_6S_2$: C, 42.84; H, 5.23; Found: C, 43.06; H, 5.15.

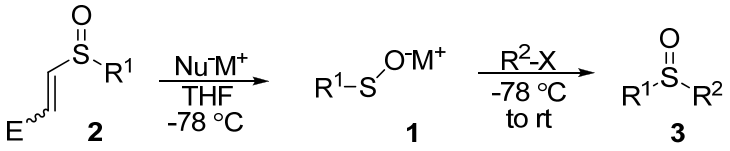


Synthesis of Cbz-HomoCys((O)-*Z*-2-Carbomethoxyethenyl)-OMe (2l)

Z-Isomer of the sulfide[1] (1.06 g, 2.89 mmol) was dissolved in CH_2Cl_2 (7 mL) and cooled to -78 °C. A solution of MCPBA (77.1%, 711 mg, 3.18 mmol) in CH_2Cl_2 (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

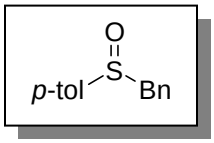
impinged with dry ammonia and refiltered, and repeated twice more. The clear filtrate was then concentrated under reduced pressure. *Z*-Isomer of sulfoxide **(*Z*-2l)** (737 mg, 67%) was obtained as oil as a pair of diastereomers (S_C,S_S/S_C,R_S) after flash chromatography (50% EtOAc/hexanes, then 3% MeOH/EtOAc). ***Z*-isomer (*Z*-2l)**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 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, $CDCl_3$), δ: 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 $C_{16}H_{21}NO_5S$ $(M-44)^+$: 339.1141; Found: 339.1148.

Preparation of Ar(alk)yl Sulfoxides (3)



Scheme 4: synthesis of ar(alk)yl sulfoxides via sulfenate anions.

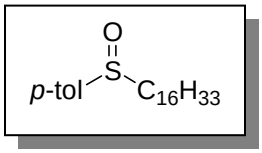
See main manuscript for general procedure.



Synthesis of *p*-Tolyl Benzyl Sulfoxide (3a)[2,11] (Method A/B)

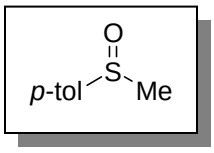
2-Carbomethoxyethenyl *p*-tolyl sulfoxide (*E*-**2a** or *Z*-**2a** or *E/Z*-**2a**) (200 mg, 0.892 mmol) in THF (15 mL) was treated with *n*-BuLi (556 μL, 0.892 mmol) followed by the addition of a solution of benzyl bromide (128 μL, 1.07 mmol) in THF (1 mL). Sulfoxide (130 mg, 78-88%, see table 1 for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

EtOAc/hexanes, then 100% EtOAc). Mp: 140-141 °C (EtOAc/hexanes), Lit:[6] 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.21 (m, 7H), 6.96 (d, J = 7.8 Hz, 2H), 3.99 (AB_q, J = 12.5 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 141.3, 139.4, 130.1 (2C), 129.3 (2C), 129.1, 128.2 (2C), 127.9, 124.2 (2C), 63.4, 21.2; IR ($CDCl_3$), cm^{-1}: 3034, 2925, 1494, 1040, 808.



Synthesis of *p*-Tolyl Hexadecyl Sulfoxide (3aa) (Method B)[12]

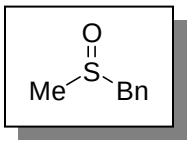
2-Carbomethoxyethenyl *p*-tolyl sulfoxide (***E/Z*-2a**) (120 mg, 0.535 mmol) in THF (12 mL) was treated with MeO^-Na^+ (125 μL, 0.546 mmol) followed by the addition of a solution of hexadecyl iodide (226 mg, 0.642 mmol) in THF (1 mL). Sulfoxide (170 mg, 87%) was isolated as a white solid after chromatography (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)[2,13] (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,

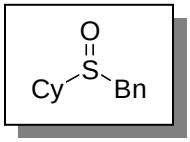
2H), 2.54 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 142.1, 140.9, 129.5, 123.0, 43.5, 20.9; IR ($CDCl_3$), cm^{-1}: 3052, 2925, 2871, 1598, 1495, 1411, 1295, 1082, 1016, 959, 813.



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).

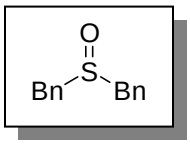
Method B:- 2-Carbomethoxyethenyl benzyl sulfoxide (***E/Z*-2d**) (100 mg, 0.446 mmol) in THF (12 mL) was treated with MeO^-Na^+ (102 μL, 0.446 mmol) followed by the addition of a solution of methyl iodide (33.3 μL, 0.535 mmol) in THF (1 mL). Sulfoxide (8-32 mg, 12-48%) was isolated as an oil after chromatography. ^{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]

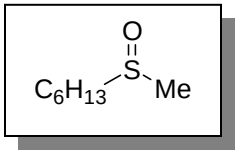
2-Carbomethoxyethenyl cyclohexyl sulfoxide (***E*-2c**) (120 mg, 0.555 mmol) in THF (12 mL) was treated with MeO^-Na^+ (130 μL, 0.566 mmol) followed by the addition of a solution of benzyl bromide (79.2 μL, 0.666 mmol) in THF (1 mL). Sulfoxide (79.9 mg, 65%) was isolated as a white solid after chromatography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

Mp: 83-84 °C (EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.31 (m, 5H), 3.90 (AB_q, J = 13.0 Hz, 2H), 2.42 (tt, J = 3.5 & 11.7 Hz, 1H), 2.06 (m, 1H), 1.89 (m, 3H), 1.65 (m, 1H), 1.49 (m, 2H), 1.26 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 130.4, 129.8, 128.7, 127.9, 56.7, 54.5, 26.7, 25.3, 25.2, 24.5, 23.8; IR ($CDCl_3$), cm^{-1}: 3155, 2938, 2859, 1496, 1453, 1031; Analysis calc'd for $C_{13}H_{18}OS$: C, 70.29; H, 8.10; Found: C, 70.10; H, 7.97.



Synthesis of Benzyl Sulfoxide (3d)[2,16] (Method A/B)

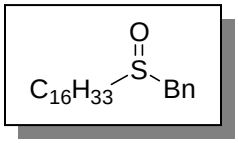
2-Carbomethoxyethenyl benzyl sulfoxide (***E/Z*-2d**) (100 mg, 0.446 mmol) in THF (5 mL) was treated with a solution of CySH/*n*-BuLi (54.6 μL, 0.446 mmol; 2.5 M, 182 μL, 0.455 mmol) followed by the addition of a solution of benzyl bromide (63.6 μL, 0.535 mmol) in THF (5 mL). Sulfoxide (76.7 mg, 75%) 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; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.31 (m, 10H), 3.87 (AB_q, J = 13.0 Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 130.0, 129.9, 128.7, 128.1, 57.0; IR ($CDCl_3$), cm^{-1}: 3033, 2921, 1496, 1043.



Synthesis of Hexyl Methyl Sulfoxide (3e)[2,17] (Method B)

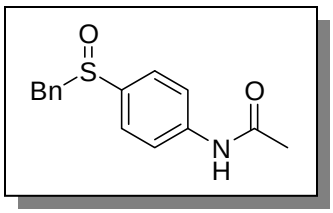
2-Carbomethoxyethenyl hexyl sulfoxide (***E*-2e**) (150 mg, 0.686 mmol) in THF (15 mL) was treated with MeO^-Na^+ (161 μL, 0.700 mmol) followed by the addition of a solution of methyl iodide (51.2 μL, 0.823 mmol) in THF (1 mL). Sulfoxide (64.1 mg, 63%) was isolated as an oil after chromatography (30% EtOAc/hexanes, then 100% EtOAc, then 10% MeOH/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.78 (ABXY, J_{AX} = 6.1 Hz, J_{AY} = 8.9 Hz, J_{BX} = 7.2 Hz, J_{BY} = 8.9 Hz, J_{AB} = 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); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 54.1, 38.2, 31.3, 28.4, 22.5,

22.3, 13.9; IR ($CDCl_3$), cm^{-1}: 3155, 2959, 2931, 1425, 1036, 791. MS (EI), m/z (%): 148 (M^+, 1), 131 (100), 84 (18), 64 (29).



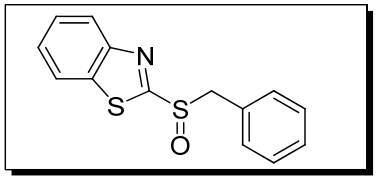
Synthesis of Hexadecyl Benzyl Sulfoxide (3f)[2] (Method B)

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]



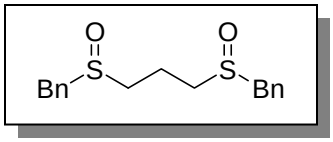
Synthesis of Benzyl 4-Acetamidophenyl Sulfoxide (3g)[2] (Method B)

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, $CDCl_3$), 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 (AB_q, J = 12.6 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 168.9, 141.3, 136.6, 130.4, 129.0, 128.4, 125.8, 125.5, 119.6, 63.6, 24.6; IR ($CDCl_3$), cm^{-1}: 3434, 3033, 2925, 1695, 1592, 1511, 1310, 1040, 834. MS (CI, NH_3), 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 $C_{15}H_{15}NO_2S$: C, 65.95; H, 5.49; Found: C, 66.16; H, 5.33.



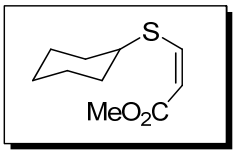
Synthesis of Benzothiazolyl Benzyl Sulfoxide (3h)[18] (Method A/B)

2-Carbomethoxyethenyl *p*-tolyl sulfoxide (*E*-**2h** or *E*-**2h** or ***E/Z*-2h**) (150 mg, 0.559 mmol) in THF (20 mL) was treated with CySH/*n*-BuLi (68 μL, 0.559 mmol; 1.6 M, 349 μL, 0.559 mmol) followed by the immediate addition of a solution of benzyl bromide (132 μL, 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; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.00 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.47 (m, 1H), 7.37 (m, 1H), 7.21-7.14 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 2H), 4.32 (AB_q, *J* = 13.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$), δ:176.8, 153.6, 135.8, 130.3, 128.5, 128.2, 126.8, 126.0, 123.7, 122.1, 62.6; IR (CH_2Cl_2), cm^{-1}: 3061, 3031, 2920, 1494, 1472, 1454, 1425, 1313, 1059, 1001, 760, 729, 697.



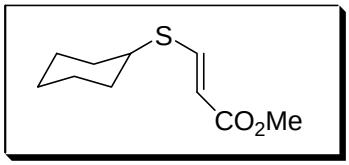
Synthesis of 1,3-*Bis*(Benzylsulfinyl) Propane (3k)[2] (Method A)

1,3-Bis(2-carbomethoxyethenylsulfinyl)propane **(*E,E/E,Z*-2k)** (100 mg, 0.325 mmol) in THF (10 mL) was treated with a solution of CySH/*n*-BuLi (79.4 μL, 0.649 mmol; 2.5 M, 262 μL, 0.656 mmol) followed by the addition of benzyl bromide (92.7 μL, 0.779 mmol). Sulfoxide (77.4 mg, 74%) was isolated as a white solid (*dr* 56:44) after chromatography (5% EtOH/CH_2Cl_2, then 10% EtOH/CH_2Cl_2). Mp: 176-177 °C (EtOAc/hexanes).[2]



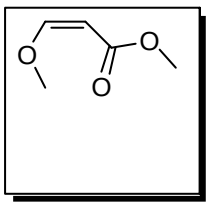
(Z)-Methyl 3-(Cyclohexylthio)acrylate (*Z*-4)[19]

^{1}H NMR (300 MHz) δ ; 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), 1.80-176 (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_2Cl_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).



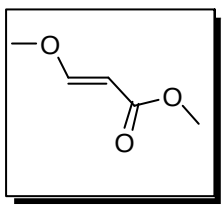
(E)-Methyl 3-(Cyclohexylthio)acrylate (*E*-4) [19]

^{1}H NMR (300 MHz) δ ; 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) δ; 166.0, 146.7, 113.7, 51.4, 45.1, 33.1, 25.8, 25.5; IR (CH_2Cl_2) cm^{-1} 2932, 2854, 1713, 1582, 1306, 1160, 948, 831. GC-MS, m/z (%): 201 (M +1)$^+$, 30), 167 (100), 135 (20).



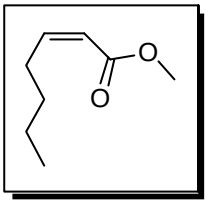
(Z)-Methyl 3-(Methoxy)acrylate (Z-5)[20]

^{1}H NMR (300 MHz), δ: 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_2Cl_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+1)$^+$, 75), 85 (100).



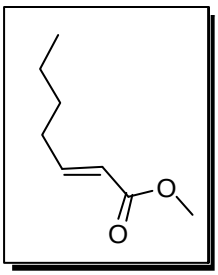
(E)-Methyl 3-(Methoxy)acrylate (E-5)[20]

^{1}H NMR (300 MHz), δ: 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_2Cl_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).



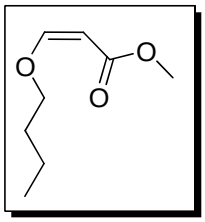
(*Z*)- Methyl 2-Heptenoate (*Z*-6)[21]

^{1}H NMR (300 MHz), δ: 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), δ: 166.9, 151.0, 119.1, 50.9, 31.1, 28.7, 22.4, 13.9; IR (CH_2Cl_2), cm^{-1}: 3034, 2925, 1635, 1457, 1428. GC-MS (EI), m/z (%): 143 ($(M+1)^+$, 100).



(*E*)-Methyl 2-Heptenoate (*E*-6)[21]

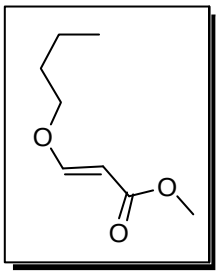
^{1}H NMR (300 MHz), δ: 7.00 (dt, *J* = 7.8 Hz, 15.7 Hz, 1H), 5.84 (dt, *J* = 1.7 Hz, 15.7 Hz, 1H), 3.74 (s, 3H), 2.22 (m, 2H), 1.49-1.35 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75.5 MHz), δ: 149.8, 137.8, 120.8, 51.4, 31.9, 30.9, 22.2, 14.2; IR (CH_2Cl_2), cm^{-1}: 3031, 2956, 1718, 1652, 1496, 1455, 1227. GC-MS (EI), m/z (%): 143 $(M+1)^+$, 100).



(Z)-Methyl 3-(Butoxy)acrylate (Z-7)[22]

^{1}H NMR (300 MHz), δ: 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), δ: 174.4, 159.3, 95.5, 66.2, 50.8, 31.8, 18.8, 14.1; IR

(CH_2Cl_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)[22]

^{1}H NMR (400 MHz), δ: 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), δ: 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_2Cl_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).

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Selected NMR spectra of new compounds

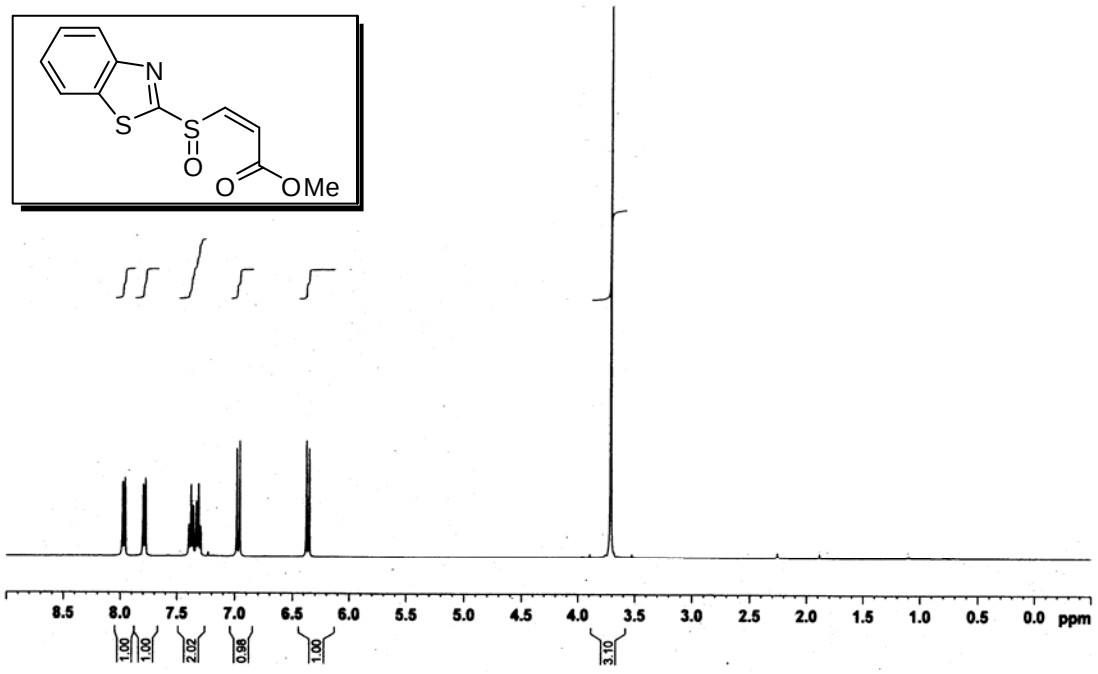

Figure 1. ^{1}H NMR spectrum of ***Z*-2h** in $CDCl_3$ (400 MHz)

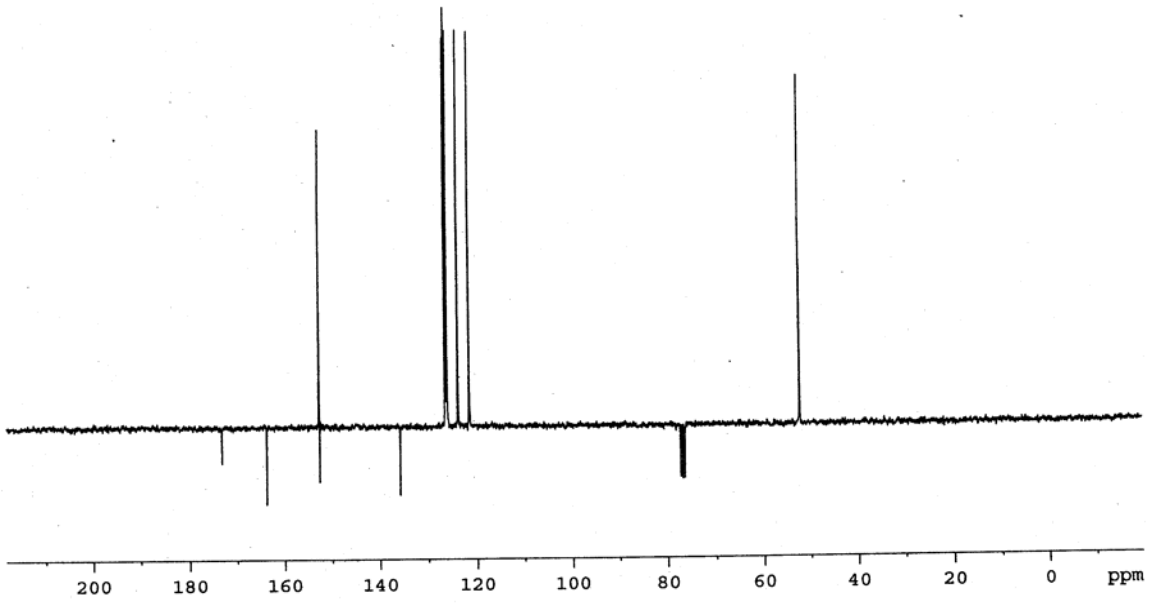

Figure 2. ^{13}C (JMOD) NMR spectrum of ***Z*-2h** in $CDCl_3$ (100.6 MHz)

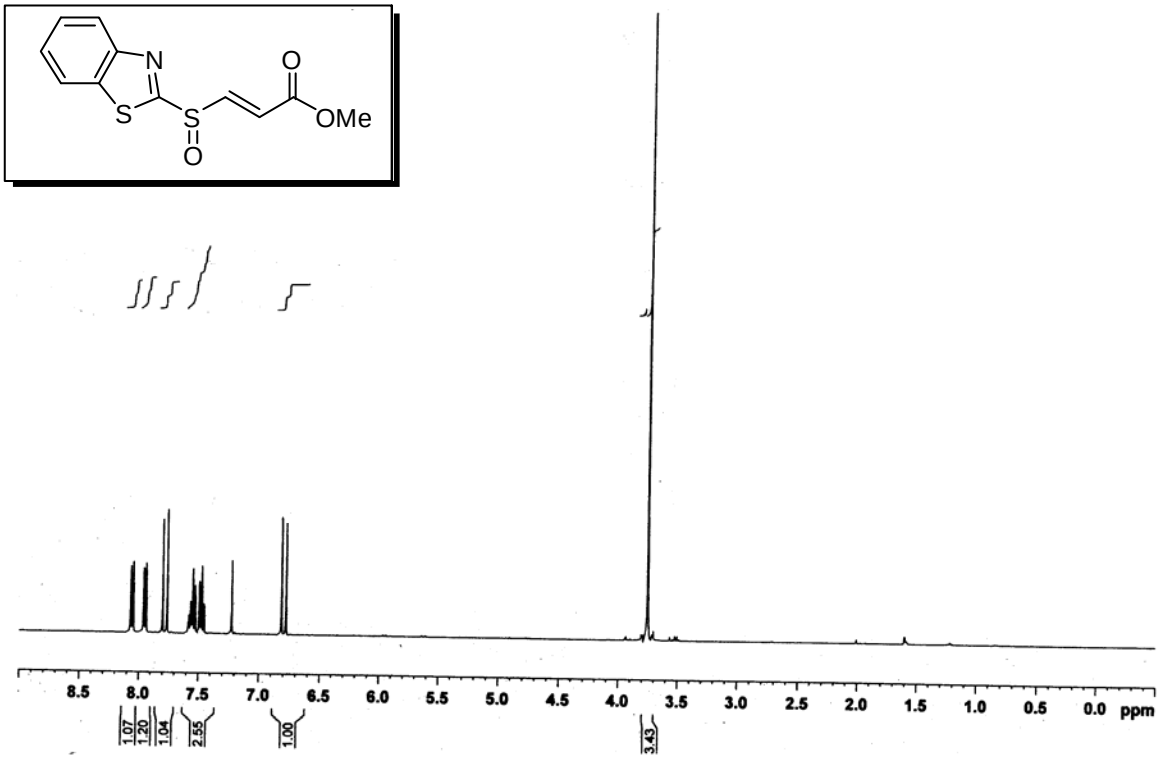

Figure 3. ^{1}H NMR spectrum of ***E*-2h** in $CDCl_3$ (400 MHz)

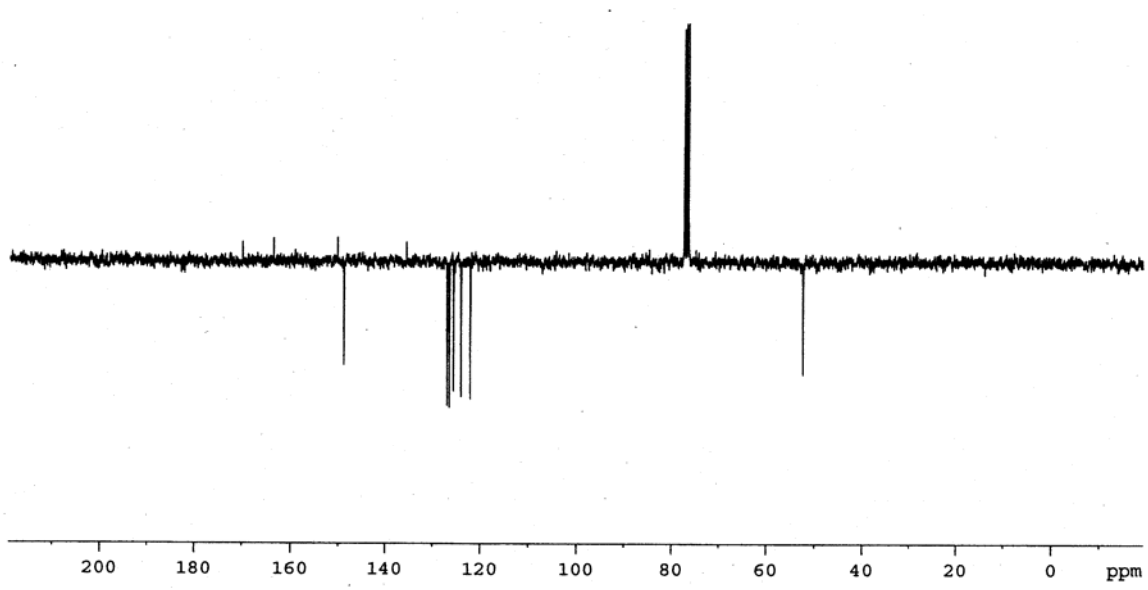

Figure 4. ^{13}C (JMOD) NMR spectrum of ***E*-2h** in $CDCl_3$ (100.6 MHz)

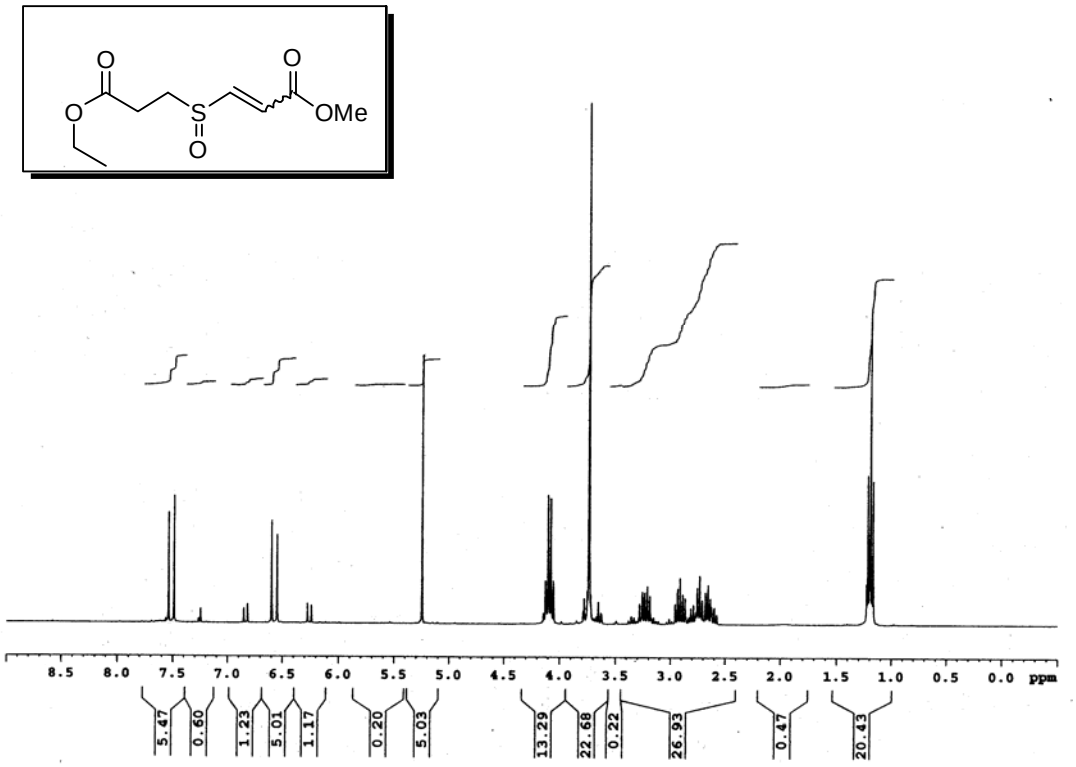

Figure 5. ^{1}H NMR spectrum of ***E/Z*-2i** in $CDCl_3$ (400 MHz)

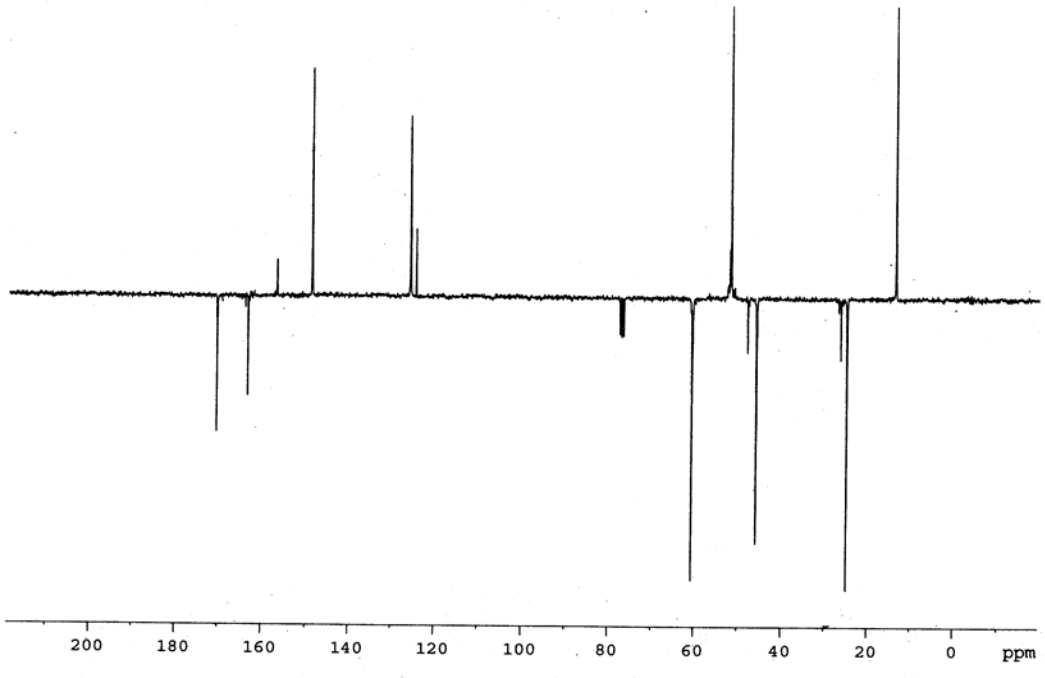

Figure 6. ^{13}C (JMOD) NMR spectrum of ***E/Z*-2i** in $CDCl_3$ (100.6 MHz)

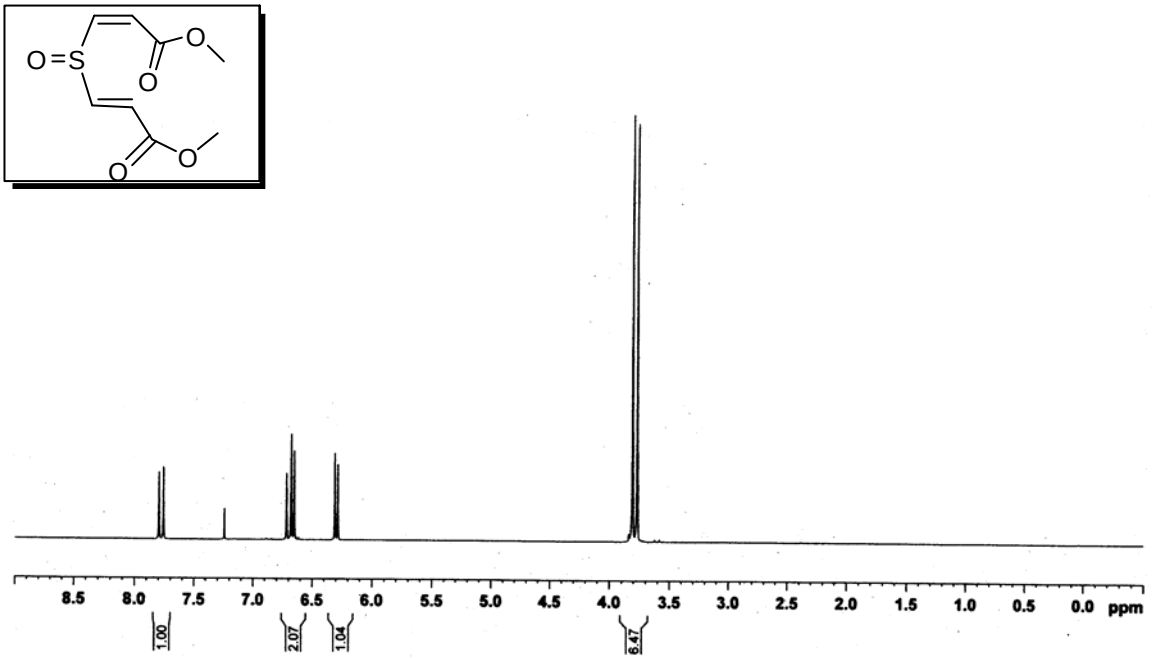

Figure 7. ^{1}H NMR spectrum of ***E,Z*-2j** in $CDCl_3$ (400 MHz)

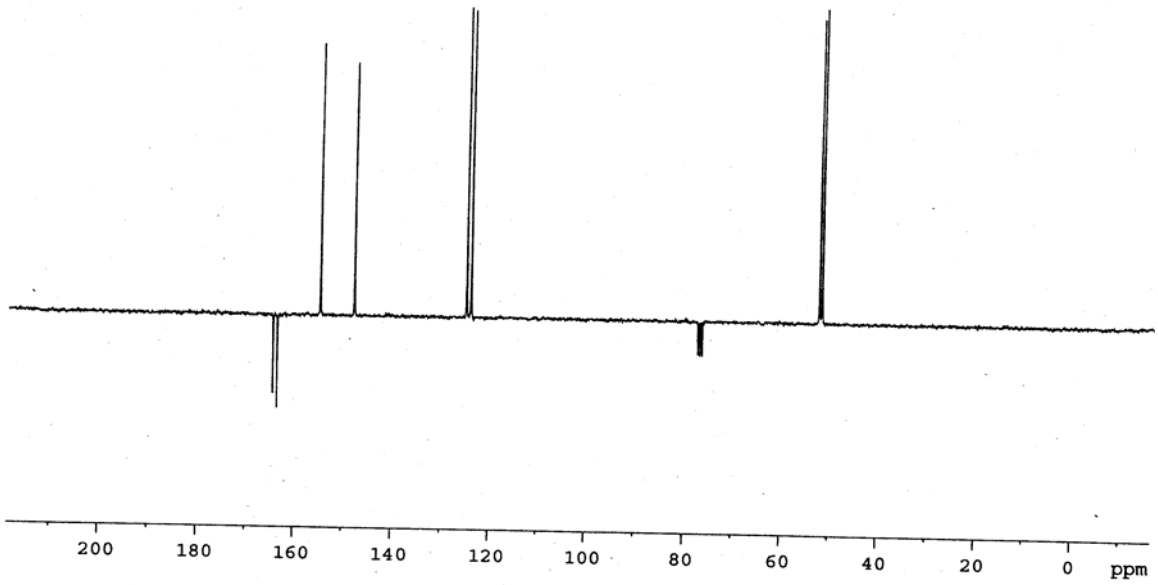

Figure 8. ^{13}C (JMOD) NMR spectrum of ***E,Z*-2j** in $CDCl_3$ (100.6 MHz)

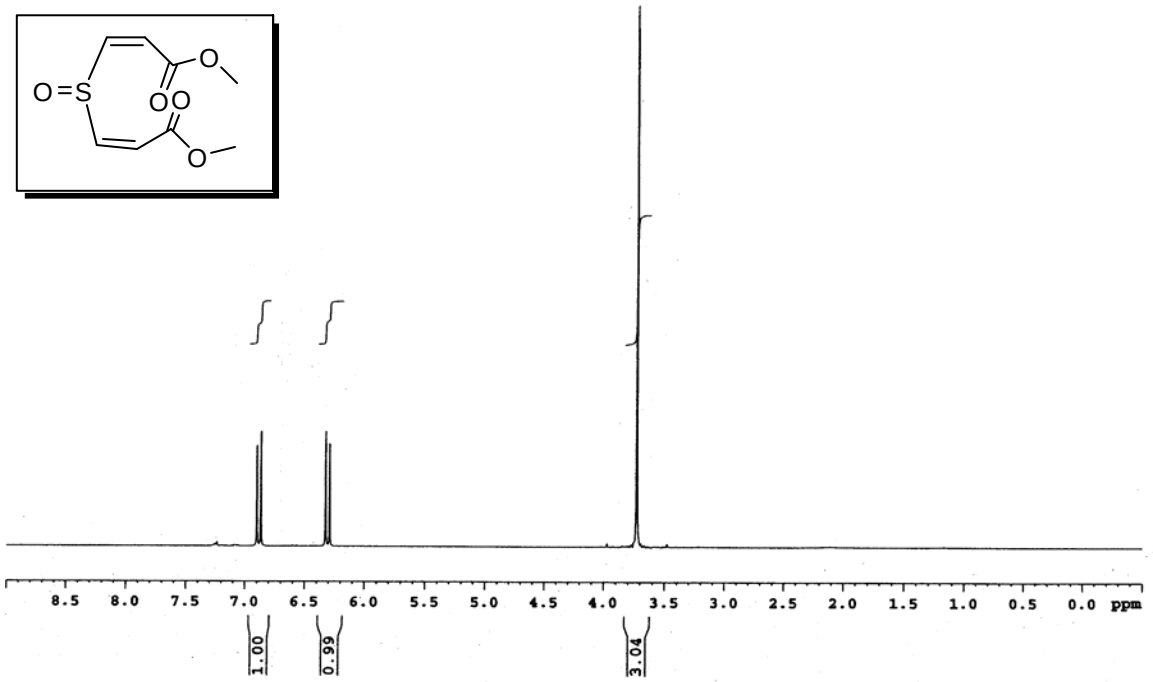

Figure 9. ^{1}H NMR spectrum of ***Z,Z*-2j** in $CDCl_3$ (400 MHz)

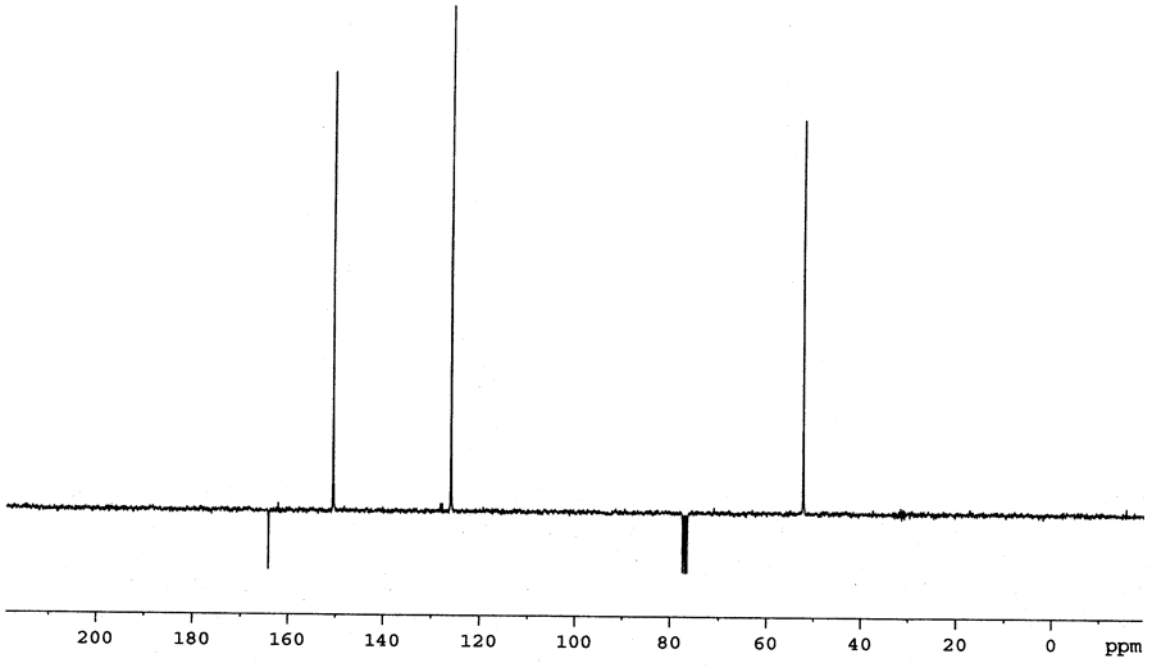

Figure 10. ^{13}C (JMOD) NMR spectrum of ***Z,Z*-2j** in $CDCl_3$ (100.6 MHz)

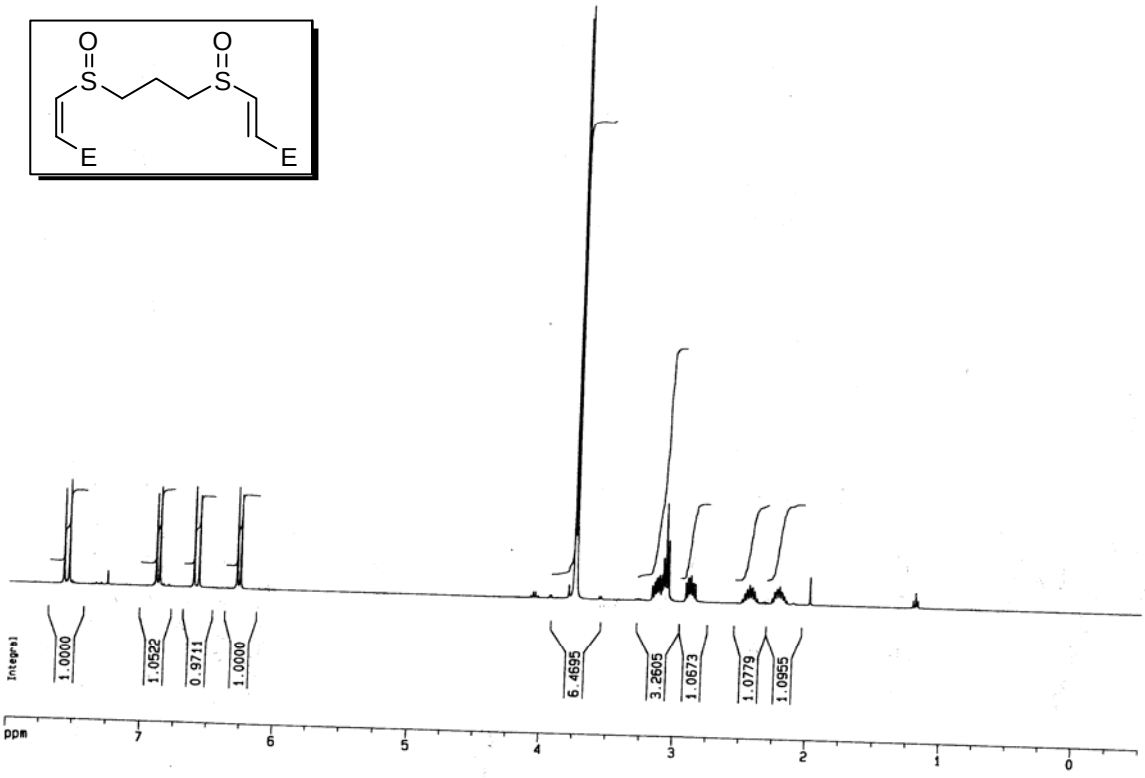

Figure 11. ^{1}H NMR spectrum of ***E,Z*-2k** in $CDCl_3$ (400 MHz)

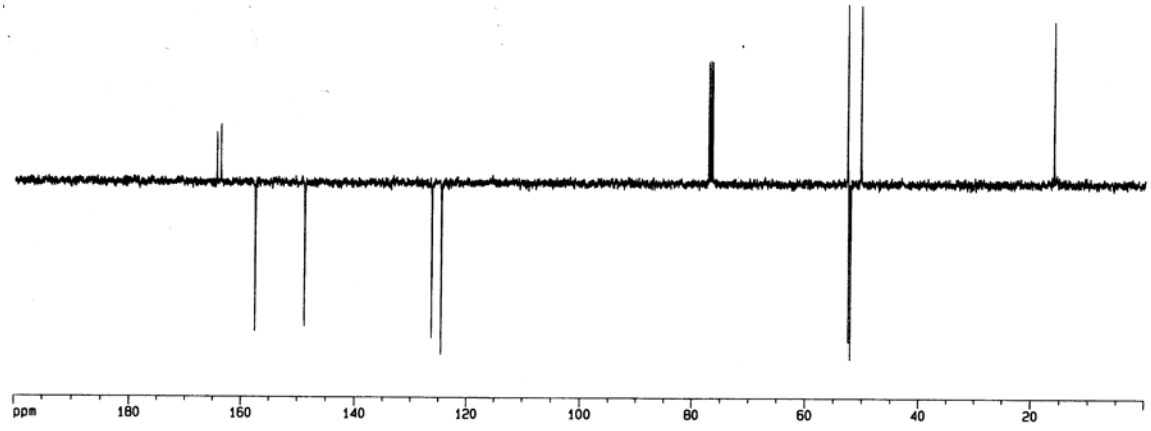

Figure 12. ^{13}C (JMOD) NMR spectrum of ***E,Z*-2k** in $CDCl_3$ (100.6 MHz)

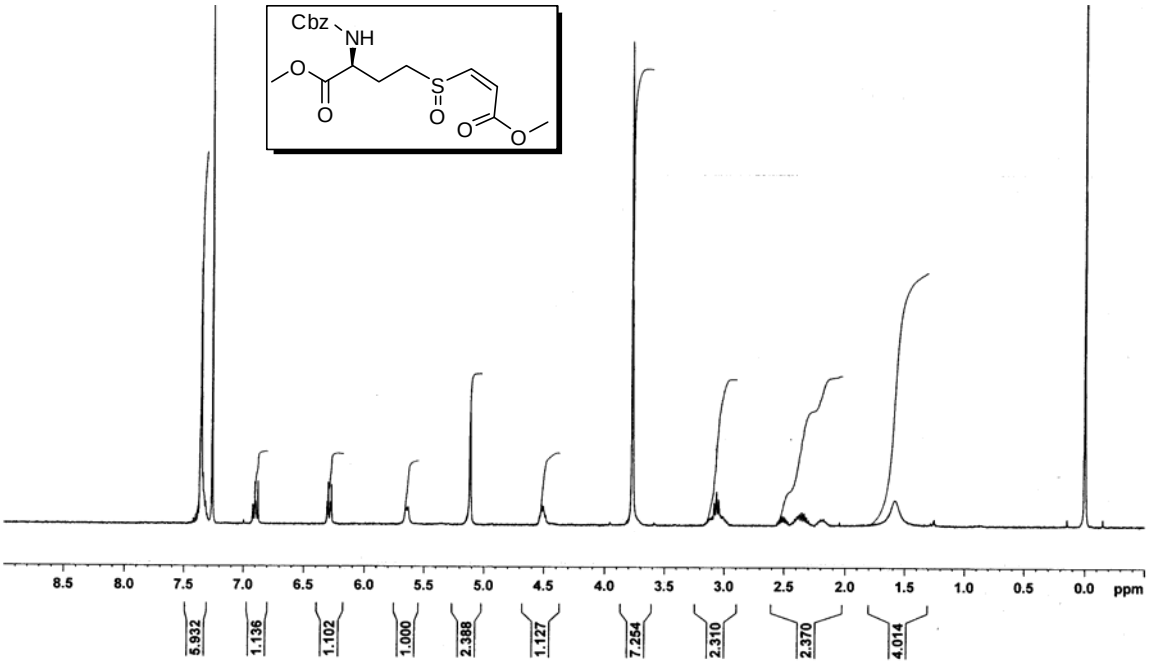

Figure 13. ^{1}H NMR spectrum of *Z*-**2l** in $CDCl_3$ (400 MHz)

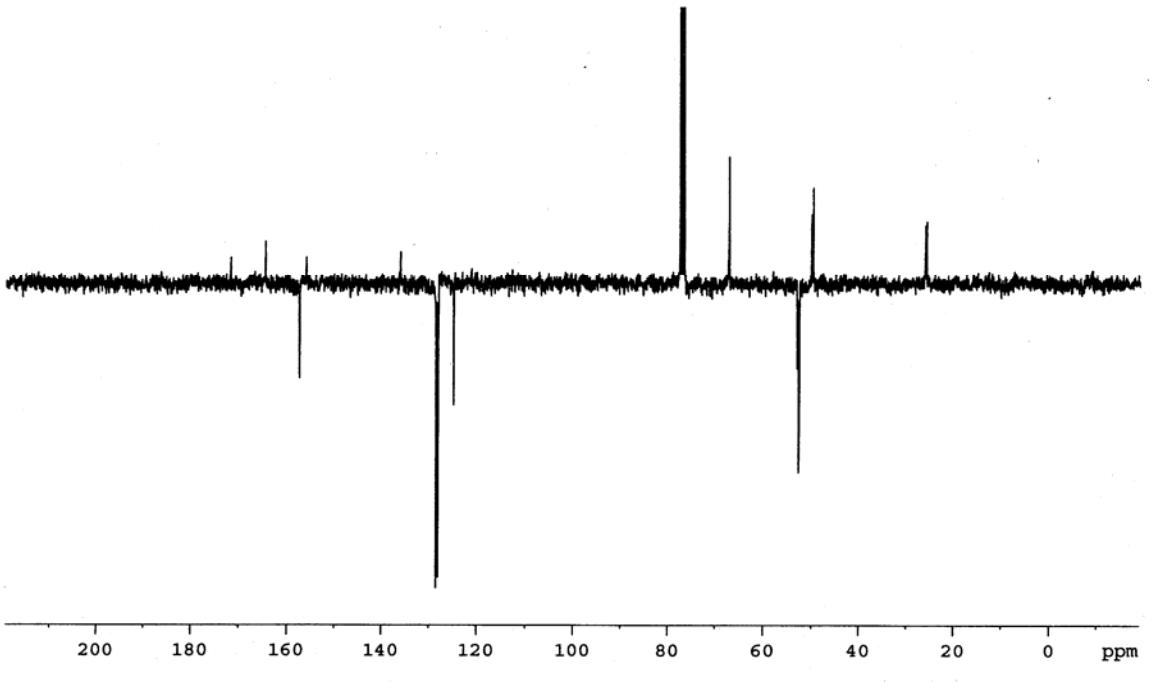

Figure 14. ^{13}C (JMOD) NMR spectrum of ***Z*-2l** in $CDCl_3$ (75.5 MHz)

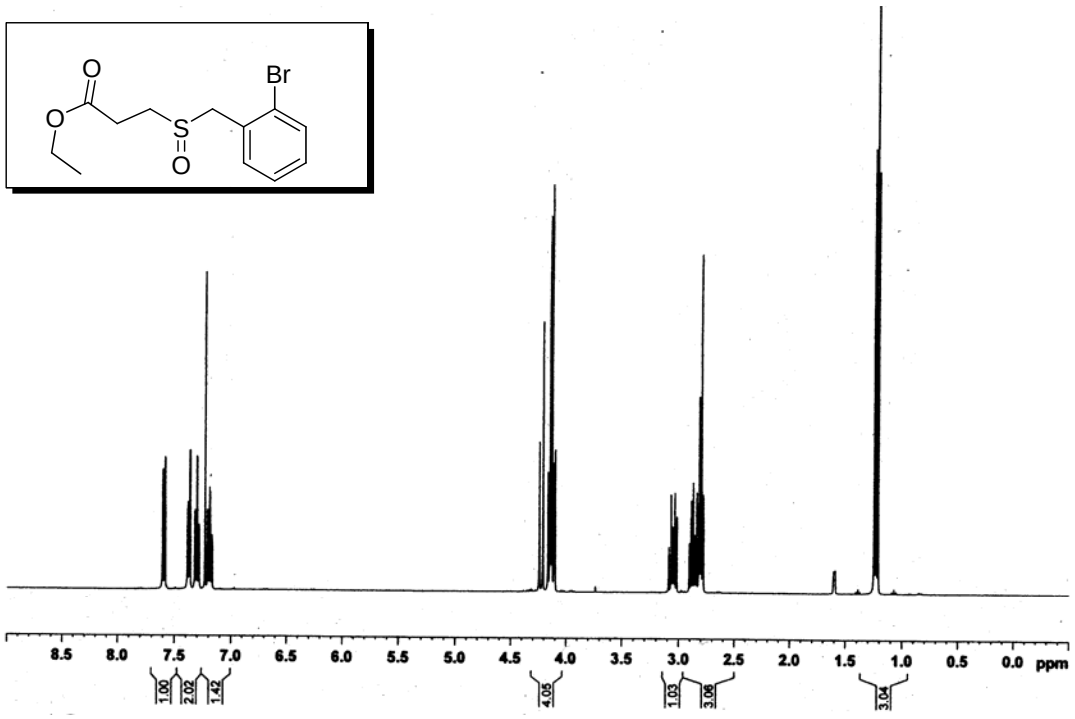

Figure 15. ^{1}H NMR spectrum of **3i** in $CDCl_3$ (400 MHz)

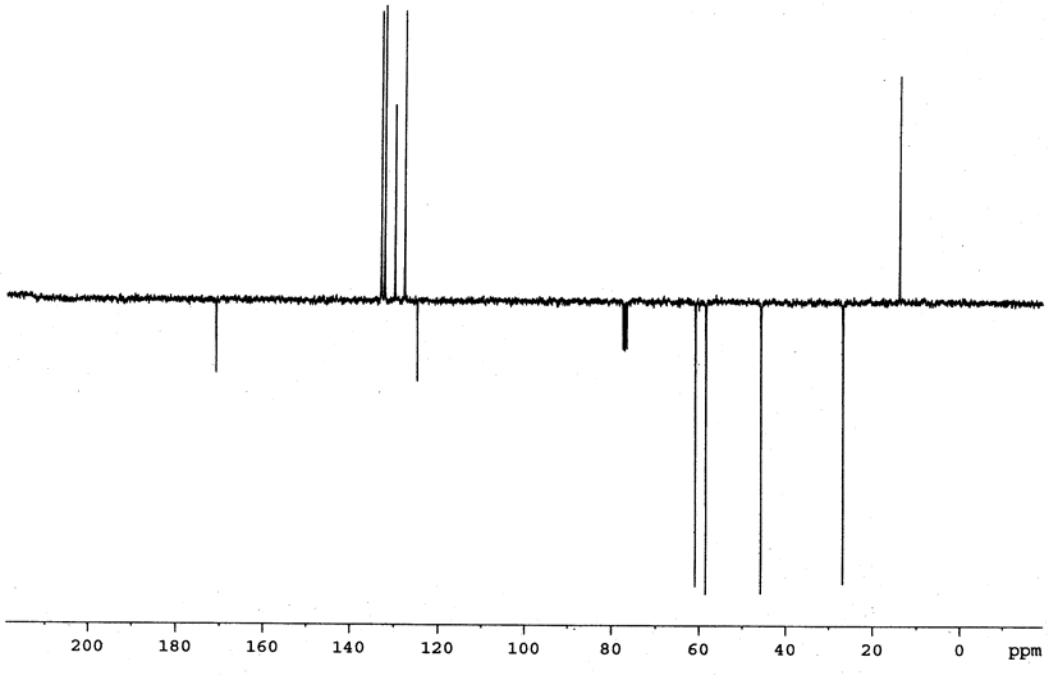

Figure 16. ^{13}C (JMOD) NMR spectrum of **3i** in $CDCl_3$ (75.5 MHz)

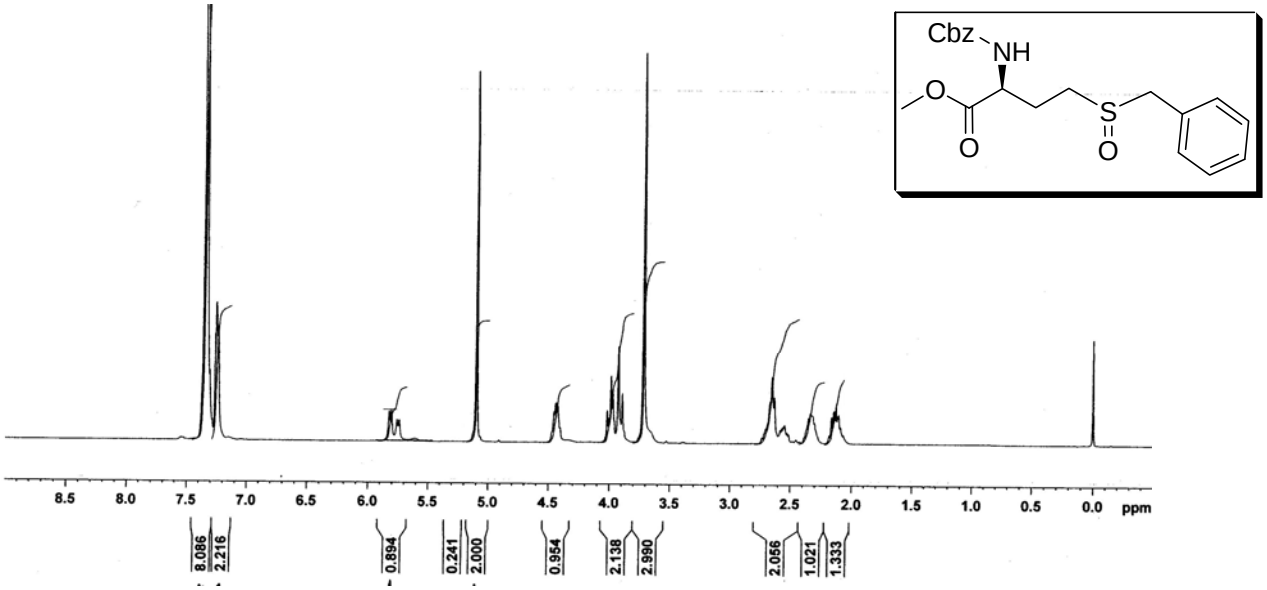

Figure 17. ^{1}H NMR spectrum of **3l** in $CDCl_3$ (400 MHz)

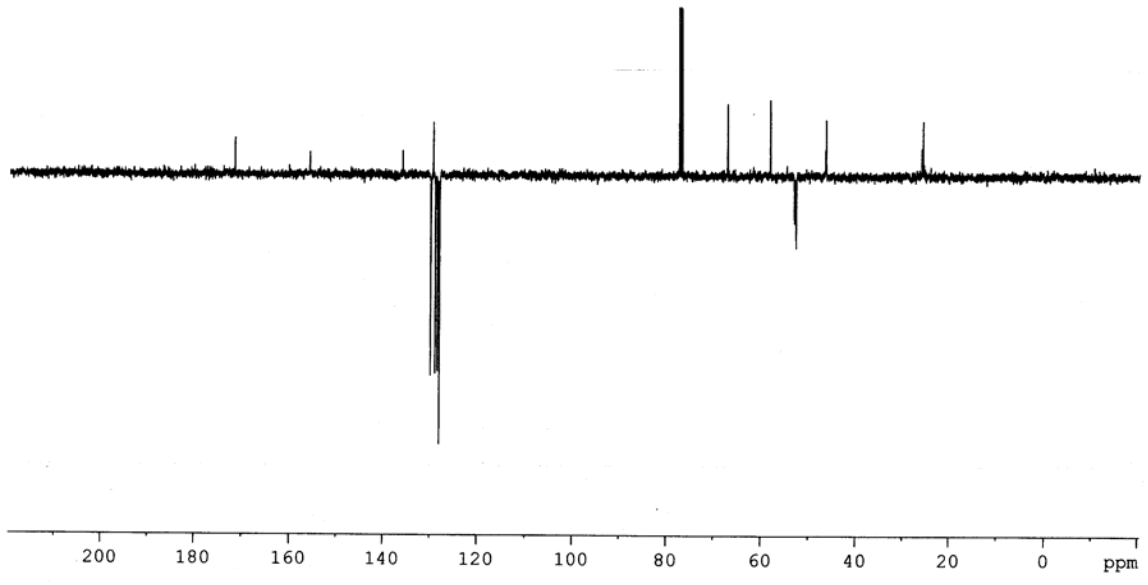

Figure 18. ^{13}C (JMOD) NMR spectrum of **3l** in $CDCl_3$ (100.6 MHz).