**Supplementary Data**

A Novel Three-Component Reaction Involving Terminal Alkynes, Elemental Sulfur, and Strained Heterocycles

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1. Experimental Section

1.1 General

Terminal alkynes (1), elemental sulfur (2), and Epoxides (3) were obtained from *Merck* and were used without further purification. THF was distilled over sodium and other solvents were dried over 4Å molecular sieve prior to use. N-Ts Aziridines 4a and 4b were prepared using the literature procedures. M.p.: *Electrothermal-9100* apparatus. IR spectra (KBr, cm⁻¹): *Shimadzu IR-460* spectrometer; in cm⁻¹. ¹H- and ¹³C-NMR spectra: *Bruker DRX-500 Avance* instrument; in CDCl₃ at 500.1 and 125.7 MHz, resp.; δ in ppm, J in Hz. MS: *Finnigan-MAT-8430* mass spectrometer, at 70 eV; in m/z (rel. %). Elemental analyses (C, H, N): *Heraeus CHN-O-Rapid* analyzer. All the reactions were monitored by thin-layer chromatography (TLC) using pre-coated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F254) using UV light for visualization.

1.2 Typical procedure for preparation of 5 and 6.
A mixture of NaH (60%w in paraffine, 40 mg) in DMF (3 ml) was treated drop-wise (10 min) with a solution of terminal alkyne (1 mmol) in THF (2 ml) at -10 °C. After 30 min S₈ (1.1 mmol) was added and allowed the mixture to warm to room temperature. Then, 3 or 4 (1 mmol) was added and the resulting yellowish mixture was stirred for 16-22 h at 50 °C. Afterward, the mixture was treated with 10 ml H₂O that saturated with ammonium chloride for 30 min, followed by extraction with CH₂Cl₂ (3× 6 ml). Organic layers were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by chromatography (silica gel, hexane: EtOAc 4:1) to give desired product.

1.3 Experimental data

2-benzylidene-5-phenyl-1,3-oxathiolane (5c)

Yellow oil; Yield: 0.24g (96%). IR (KBr) (νmax, cm⁻¹): 3036, 2961, 1658, 1540, 1325, 1120. ¹H NMR (500.1 MHz, CDCl₃): δ_H = 3.26 (H, dd, ²J = 11.8 Hz, ³J = 6.8 Hz, CH), 3.41 (H, dd, ²J = 11.8 Hz, ³J = 4.6 Hz, CH), 4.90-4.94 (H, m, CH), 5.16 (H, s, CH), 7.10 (2 H, d, ³J = 6.1 Hz), 7.14 (H, t, ³J = 6.4 Hz), 7.19-7.32 (7 H, m). ¹³C NMR (125.7 MHz, CDCl₃): δ_C = 36.2 (CH₂), 89.2 (CH), 125.2 (2 CH), 126.7 (2 CH), 127.2 (CH), 127.8 (CH), 129.4 (2 CH), 130.1 (2 CH), 131.1 (CH), 136.3 (C), 142.5 (C), 164.2 (C). MS: m/z (%) = 254 (M⁺, 3), 221 (57), 164 (41), 151 (85), 119 (65), 101 (64), 91 (36), 77 (100). Anal. Calcd for C₁₃H₁₄OS (254.35): C, 75.55, H, 5.55, S, 12.61. Found: C, 75.61, H, 5.63, S, 12.60.

2-benzylidene-5-(phenoxy methyl)-1,3-oxathiolane (5d)

Yellow oil; Yield: 0.26g (92%). IR (KBr) (νmax, cm⁻¹): 3038, 3012, 2958, 1639, 1542, 1326, 1118. ¹H NMR (500.1 MHz, CDCl₃): δ_H = 3.28 (H, dd, ²J = 11.7 Hz, ³J = 6.8 Hz, CH), 3.41 (H, dd, ²J = 11.7 Hz, ³J = 4.5 Hz, CH), 4.64 (H, dd, ²J = 11.6 Hz, ³J = 7.0 Hz, CH), 4.76 (H, dd, ²J = 11.6 Hz, ³J = 4.5 Hz, CH), 4.84-4.89 (H, m, CH), 5.15 (H, s, CH), 6.81 (2 H, d, ³J = 6.5 Hz), 6.87
(H, t, $^3J = 6.7$ Hz), 7.12-7.31 (7H, m). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta_C = 37.5$ (CH$_2$), 73.2 (CH$_2$), 84.1 (CH), 114.1 (2 CH), 121.2 (CH), 125.5 (2 CH), 127.8 (CH), 129.1 (2 CH), 130.3 (2 CH), 131.1 (CH), 135.8 (C), 159.9 (C), 163.2 (C). MS: m/z (%) = 284 (M$^+$, 3), 251 (64), 194 (41), 151 (87), 133 (36), 119 (78), 91 (21), 77 (100). Anal. Calcd for C$_{17}$H$_{16}$O$_2$S (284.37): C, 71.80, H, 5.67, S, 11.28. Found: C, 71.94, H, 5.72, S, 11.32.

2-benzylidene-hexahydrobenzo[d][1,3]oxathiole (5e)

Yellow solid, D.p: 221 °C; Yield: 0.20g (87%). IR (KBr) ($\nu_{\max}$, cm$^{-1}$): 3034, 3014, 2953, 1647, 1548, 1321, 1141. $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta_H = 1.27-1.46$ (4H, m, 2 CH$_2$), 1.69-1.79 (2 H, m, CH$_2$), 1.90-2.11 (2 H, m, CH$_2$), 3.12-3.17 (H, m, CH), 3.96-4.04 (H, m, CH), 5.15 (H, s, CH), 7.12 (H, $^3J = 6.2$ Hz), 7.23 (2 H, d, $^3J = 6.7$ Hz), 7.29 (2 H, d, $^3J = 6.9$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta_C = 20.3$ (CH$_2$), 27.1 (CH$_2$), 29.0 (CH$_2$), 32.5 (CH$_2$), 49.7 (CH), 87.0 (CH), 125.3 (2 CH), 127.6 (CH), 129.9 (2 CH), 131.5 (CH), 136.2 (C), 163.7 (C). MS: m/z (%) = 232 (M$^+$, 3), 199 (34), 151 (87), 142 (61), 101 (48), 97 (82), 77 (100). Anal. Calcd for C$_{14}$H$_{16}$OS (232.34): C, 72.37, H, 6.94, S, 13.80. Found: C, 72.46, H, 7.10, S, 13.85.

2-butylidene-5-methyl-1,3-oxathiolane (5f)

Yellow oil; Yield: 0.11g (71%). IR (KBr) ($\nu_{\max}$, cm$^{-1}$): 3025, 2961, 1644, 1547, 1328, 1115. $^1$H NMR (500.1 MHz, CDCl$_3$): $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta_H = 0.90$ (3 H, t, $^3J = 6.4$ Hz, Me), 1.29 (3 H, d, $^3J = 6.5$ Hz, Me), 1.35 (2 H, m, CH$_2$), 2.10-2.14 (2 H, m, CH$_2$), 3.27-3.40 (2 H, m, CH$_2$), 4.64 (H, m, CH), 4.98 (H, t, $^3J = 6.3$ Hz, CH). $^{13}$C NMR (125.7 MHz, CDCl$_3$): 13.6 (Me), 21.3 (Me), 24.1 (CH$_2$), 26.5 (CH$_2$), 43.2 (CH$_2$), 78.5 (CH), 129.1 (CH), 163.4 (C). MS: m/z (%) = 158 (M$^+$, 3), 125 (53), 117 (100), 102 (41), 85 (73), 69 (48), 57 (25). Anal. Calcd for C$_8$H$_{14}$OS (158.26): C, 60.71, H, 8.92, S, 20.26. Found: C, 60.83, H, 8.98, S, 20.32.

2-butylidene-5-phenyl-1,3-oxathiolane (5g)
Yellow oil; Yield: 0.17 g (78%). IR (KBr) ($\nu_{\text{max}}$, cm$^{-1}$): 3026, 2951, 1650, 1567, 1334, 1126. $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta_H = 0.91$ (3 H, t, $^3J = 6.1$ Hz, Me), 1.35-1.39 (2 H, m, CH$_2$), 2.09-2.13 (2 H, m, CH$_2$), 3.28 (H, dd, $^2J = 11.8$ Hz, $^3J = 7.0$ Hz, CH), 3.41 (H, dd, $^2J = 11.8$ Hz, $^3J = 4.7$ Hz, CH), 4.87 (H, m, CH), 5.03 (H, t, $^3J = 6.5$ Hz, CH), 7.15 (H, t, $^3J = 6.4$ Hz), 7.20 (2 H, d, $^3J = 6.5$ Hz), 7.25 (2 H, d, $^3J = 6.6$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): 13.6 (Me), 23.0 (CH$_2$), 25.2 (CH$_2$), 43.5 (CH$_2$), 87.4 (CH), 126.0 (2 CH), 127.5 (CH), 129.1 (2 CH), 129.8 (CH), 139.4 (C), 164.2 (C). MS: m/z (%) = 220 (M$^+$, 1), 187 (36), 164 (53), 143 (72), 117 (89), 77 (100), 69 (40). Anal. Calcd for C$_{13}$H$_{16}$OS (220.33): C, 70.87; H, 7.32, S, 14.55. Found: C, 70.94; H, 7.47, S, 14.60.

2-butyldiene-5-(phenoxy)methyl)-1,3-oxathiolane (5h)

Yellow oil; Yield: 0.18 g (74%). IR (KBr) ($\nu_{\text{max}}$, cm$^{-1}$): 3036, 3012, 2963, 1647, 1540, 1340, 1120. $^1$H NMR (500.1 MHz, CDCl$_3$): $\delta_H = 0.91$ (3 H, t, $^3J = 6.1$ Hz, Me), 1.40-1.46 (2 H, m, CH$_2$), 2.13-2.17 (2 H, m, CH$_2$), 3.30 (H, dd, $^2J = 11.9$ Hz, $^3J = 6.8$ Hz, CH), 3.44 (H, dd, $^2J = 11.9$ Hz, $^3J = 4.7$ Hz, CH), 4.66 (H, dd, $^2J = 12.0$ Hz, $^3J = 7.0$ Hz, CH), 4.71 (H, dd, $^2J = 12.0$ Hz, $^3J = 4.9$ Hz, CH), 4.86-4.91 (H, m, CH), 4.99 (H, t, $^3J = 6.3$ Hz, CH), 6.80 (2 H, d, $^3J = 6.5$ Hz), 6.87 (H, t, $^3J = 6.2$ Hz), 7.12 (2 H, t, $^3J = 6.7$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): 13.7 (Me), 23.5 (CH$_2$), 27.2 (CH$_2$), 43.5 (CH$_2$), 76.5 (CH$_2$), 87.1 (CH), 114.3 (2 CH), 121.1 (CH), 130.2 (2 CH), 130.4 (CH), 160.0 (C), 162.4 (C). MS: m/z (%) = 250 (M$^+$, 1), 217 (40), 194 (53), 149 (78), 133 (37), 117 (86), 85 (58), 77 (100). Anal. Calcd for C$_{14}$H$_{18}$O$_2$S (250.36): C, 67.16; H, 7.25, S, 12.81. Found: C, 67.28; H, 7.36, S, 12.85.

5-methyl-2-pentyldiene-5-propyl-1,3-oxathiolane (5i)
Yellow oil; Yield: 0.15 g (70%). IR (KBr) (ν_max, cm⁻¹): 3010, 2947, 1651, 1326, 1120. ¹H NMR (500.1 MHz, CDCl₃): δ_H = 0.91-0.98 (6 H, m, 2 Me), 1.29-1.41 (6 H, m, 3 CH₂), 1.49 (3 H, s, Me), 1.54 (2 H, t, ³J = 6.3 Hz, CH₂), 2.09-2.13 (2 H, m, CH₂), 3.31 (H, dd, ²J = 11.8 Hz, ³J = 6.8 Hz, CH), 3.52 (H, dd, ²J = 11.8 Hz, ³J = 4.7 Hz, CH), 5.04 (H, t, ³J = 6.7 Hz, CH). ¹³C NMR (125.7 MHz, CDCl₃): 13.4 (Me), 14.1 (Me), 14.5 (CH₂), 21.6 (CH₂), 23.5 (CH₂), 26.0 (Me), 32.5 (CH₂), 39.7 (CH₂), 47.2 (CH₂), 89.7 (C), 129.7 (CH), 162.8 (C). MS: m/z (%) = 214 (M⁺, 1), 197 (53), 144 (40), 131 (100), 115 (76), 85 (82), 83 (51). Anal. Calcd for C₁₂H₂₂OS (214.37): C, 67.23; H, 10.34, S, 14.96. Found: C, 67.31; H, 10.41, S, 14.99.

2-pentylidene-5-(phenoxy methyl)-1,3-oxathioline (5j)

Yellow oil; Yield: 0.19 g (73%). IR (KBr) (ν_max, cm⁻¹): 3048, 3014, 2946, 1641, 1539, 1327, 1123. ¹H NMR (500.1 MHz, CDCl₃): δ_H = 0.91 (3 H, t, ³J = 6.5 Hz, Me), 1.26-1.37 (4 H, m, 2 CH₂), 2.11-2.16 (2 H, m, CH₂), 3.31 (H, dd, ²J = 12.1 Hz, ³J = 6.8 Hz, CH), 3.52 (H, dd, ²J = 12.1 Hz, ³J = 4.5 Hz, CH), 4.67 (H, dd, ²J = 11.6 Hz, ³J = 7.1 Hz, CH), 4.74 (H, dd, ²J = 11.6 Hz, ³J = 4.5 Hz, CH), 4.87-4.91 (H, m, CH), 5.01 (H, t, ³J = 6.6 Hz, CH), 6.79 (2 H, d, ³J = 6.4 Hz), 6.88 (H, t, ³J = 6.3 Hz), 7.13 (2 H, t, ³J = 6.7 Hz). ¹³C NMR (125.7 MHz, CDCl₃): 13.5 (Me), 23.1 (CH₂), 24.8 (CH₂), 33.1 (CH₂), 43.5 (CH₂), 76.9 (CH₂), 87.4 (CH), 114.3 (2 CH), 121.1 (CH), 129.6 (2 CH), 130.3 (CH), 160.1 (C), 163.8 (C). MS: m/z (%) = 264 (M⁺, 1), 231 (40), 149 (75), 133 (61), 131 (86), 99 (36), 77 (100). Anal. Calcd for C₁₅H₂₆O₂S (264.38): C, 68.14; H, 7.62, S, 12.13. Found: C, 68.21; H, 7.75, S, 12.20.

trimethyl((S-(phenoxy methyl)-1,3-oxathiolan-2-ylidene)methyl) silane (5k)
Yellow oil; Yield: 0.20 g (71%). IR (KBr) (ν<sub>max</sub>, cm<sup>-1</sup>): 3054, 3016, 2964, 1641, 1540, 1328, 1119. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 0.03 (9 H, s, 3 Me), 3.31 (H, dd, <sup>2</sup>J = 11.8 Hz, <sup>3</sup>J = 6.7 Hz, CH), 3.47 (H, dd, <sup>2</sup>J = 11.8 Hz, <sup>3</sup>J = 4.5 Hz, CH), 4.68 (H, dd, <sup>2</sup>J = 11.7 Hz, <sup>3</sup>J = 7.0 Hz, CH), 4.75 (H, dd, <sup>2</sup>J = 11.7 Hz, <sup>3</sup>J = 4.7 Hz, CH), 4.84-4.89 (H, m, CH), 5.27 (H, s, CH), 6.79 (2 H, d, <sup>3</sup>J = 6.8 Hz), 6.84 (H, t, <sup>3</sup>J = 6.5 Hz), 7.13 (2 H, t, <sup>3</sup>J = 6.2 Hz). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): 1.8 (3 Me), 43.0 (CH<sub>2</sub>), 76.1 (CH<sub>2</sub>), 87.4 (CH), 94.1 (CH), 114.2 (2 CH), 120.6 (CH), 128.5 (2 CH), 159.8 (C), 179.4 (C). MS: m/z (%) = 280 (M<sup>+</sup>, 1), 247 (40), 149 (61), 147 (83), 133 (39), 115 (72), 77 (100). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>S (280.46): C, 59.96; H, 7.19, S, 11.43. Found: C, 60.08; H, 7.25, S, 11.50.

(5-(isopropoxymethyl)-1,3-oxathiolan-2-ylidene)methyl)trimethylsilane (5l)

Yellow oil; Yield: 0.16 g (67%). IR (KBr) (ν<sub>max</sub>, cm<sup>-1</sup>): 3023, 2958, 1641, 1538, 1325, 1117. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 0.04 (9 H, s, 3 Me), 1.16 (6 H, d, <sup>3</sup>J = 6.2 Hz, 2 Me), 3.30 (H, dd, <sup>2</sup>J = 11.9 Hz, <sup>3</sup>J = 6.9 Hz, CH), 3.42 (H, dd, <sup>2</sup>J = 11.9 Hz, <sup>3</sup>J = 4.7 Hz, CH), 4.39-4.44 (H, m, CH), 4.52 (H, dd, <sup>2</sup>J = 11.8 Hz, <sup>3</sup>J = 7.2 Hz, CH), 4.64 (H, dd, <sup>2</sup>J = 11.8 Hz, <sup>3</sup>J = 6.9 Hz, CH), 4.83-4.87 (H, m, CH), 5.30 (H, s, CH). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): 1.7 (3 Me), 22.7 (Me), 22.9 (Me), 42.1 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 70.2 (CH), 84.7 (CH), 100.6 (CH), 180.9 (C). MS: m/z (%) = 246 (M<sup>+</sup>, 1), 213 (40), 147 (100), 141 (69), 115 (81), 101 (34), 99 (53). Anal. Calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>S (246.44): C, 53.61; H, 9.00, S, 13.01. Found: C, 53.67; H, 9.11, S, 13.08.

4-benzyl-2-((trimethylsilyl)methylene)-3-tosylthiazolidine (6c)

Pale yellow solid, mp: 81-83 °C; Yield: 0.28 g (67%). IR (KBr) (ν<sub>max</sub>, cm<sup>-1</sup>): 3046, 3021, 2954, 1648, 1537, 1324, 1315, 1123. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 0.03 (9 H, s, 3 Me), 2.23 (3 H, s, Me), 3.21 (H, dd, <sup>2</sup>J = 11.6 Hz, <sup>3</sup>J = 6.9 Hz, CH), 3.33 (H, dd, <sup>2</sup>J = 11.6 Hz, <sup>3</sup>J = 6.9 Hz, CH).
Hz, $^3J = 4.9$ Hz, CH), 3.50-3.56 (2 H, m, CH$_2$), 5.20-5.24 (H, m, CH), 5.31 (H, t, $^3J = 6.5$ Hz, CH), 7.08-7.14 (3 H, m), 7.23 (2 H, d, $^3J = 6.3$ Hz), 7.35 (2 H, d, $^3J = 6.7$ Hz), 7.81 (2 H, d, $^3J = 6.3$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): 1.6 (3 Me), 23.5 (Me), 37.2 (CH$_2$), 43.0 (CH$_2$), 65.7 (CH), 101.7 (CH), 123.8 (CH), 126.1 (2 CH), 127.9 (2 CH), 128.4 (2 CH), 130.1 (2 CH), 136.3 (C), 138.5 (C), 143.0 (C), 174.8 (C). MS: \( m/z \) (%) = 417 (M$^+$, 1), 384 (40), 331 (57), 300 (87), 286 (78), 268 (81), 117 (38), 99 (51), 77 (100). Anal. Calcd for C$_{21}$H$_{27}$NO$_2$S$_2$Si (417.66): C, 60.39; H, 6.52, N, 3.35, S, 15.35. Found: C, 60.48; H, 6.67, N, 3.42, S, 15.44.

2. References