**Iron(II)-Catalyzed Sulfimidation and [2,3]-Sigmatropic Rearrangement of Propargyl
Sulfides with *t*-Butoxycarbonylazide. Access to *N*-Allenylsulfenimides.**

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Experimental Procedures

General Methods

Tetrahydrofuran was dried by passage through alumina by the method of Grubbs.¹ *n*-Butyllithium solutions in hexanes were titrated with BHT/fluorene immediately prior to use. Benzaldehyde and acetic anhydride were distilled prior to use. All other commercially available reagents and solvents were used as purchased without further purification. All metal catalysts with the exception of dppeFeCl₂ were handled under an argon atmosphere in a glove bag. All reactions were performed under an atmosphere of dry nitrogen unless otherwise indicated. NMR spectra were recorded at 400 MHz or 500 MHz for ¹H and 100 MHz or 125 MHz for ¹³C as indicated. Mass spectral analysis was performed at the UC Irvine Mass Spectrometry facility.

1-Phenyl-4-phenylsulfanyl-2-butyne-1-ol (1d). To a flame-dried round bottom flask equipped with a magnetic stir bar was added 2-propynylsulfanylbenzene (1.50 g, 10.1 mmol) and 10 mL anhydrous THF under N₂. The resulting solution was stirred and cooled to –78 °C. To the cooled solution was added *n*-BuLi (5.18 mL, 11.1 mmol, 2.15 M solution in hexanes) dropwise. The resulting yellow solution was added dropwise via cannula to a stirring solution of benzaldehyde (1.29 mL, 13.16 mmol) in 10 mL anhydrous THF at –78 °C. After 15 min the reaction mixture was allowed to warm to room temperature. Upon warming, the color of the solution changed from yellow to brown. The reaction was quenched by addition of 1.16 mL glacial AcOH and 30 mL H₂O. The layers were separated and the aqueous phase was extracted with Et₂O (2 × 30 mL). The combined organic layers were washed with 10% NaHCO₃ solution

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(2 × 20 mL) and dried over MgSO₄. After filtration and concentration *in vacuo*, 3.24 g of yellow oil was obtained. The crude oil was purified by silica gel chromatography (20% EtOAc/hexanes) to afford **1d** as a pale yellow oil (1.283 g, 50%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.24–7.45 (m, 10H), 5.43 (dd, *J* = 2.0, 6.2 Hz, 1H) 3.70 (d, *J* = 2.0 Hz, 2H), 2.07 (d, *J* = 6.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 140.4, 134.8, 130.6, 129.0, 128.6, 128.4, 127.1, 126.6, 83.1, 82.9, 64.7, 23.1; IR (thin film) 3386, 3062, 3033, 1584, 1024, 1002 cm⁻¹; TLC R_f = 0.31 (20% EtOAc/hexanes); LRMS (ESI) *m/z* (relative intensity) 254(35), 147(87), 110(100); HRMS (CI/NH₃) *m/z* calcd for C₁₆H₁₄OS [M]⁺ 254.0765, found 254.0763.

1-Phenyl-4-phenylsulfanyl-2-butyrylacetate (1e). To a solution of 1-phenyl-4-phenylsulfanyl-2-butyryl-1-ol (600 mg, 2.36 mmol) and DMAP (14.4 mg, 0.118 mmol) in 24 mL of pyridine was added Ac₂O (0.45 mL, 4.7 mmol). The resulting red-brown solution was stirred under N₂ at room temperature. After 1 h, 25 mL of Et₂O was added and the reaction mixture was washed with 1N HCl (4 × 25 mL), 10% NaHCO₃ (3 × 20 mL) and saturated NaCl (2 × 20 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo* to afford 700 mg of a dark red oil. The crude oil was purified by silica gel chromatography (10% EtOAc/hexanes) to afford **1e** as a pale yellow oil (666 mg, 96%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.23–7.44 (m, 10H), 6.42 (t, *J* = 2.0 Hz, 1H), 3.68 (d, *J* = 2.0 Hz, 2H), 2.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 170.0, 137.1, 134.9, 131.1, 129.2, 129.1, 128.9, 128.0, 127.4, 83.7, 80.2, 66.0, 23.5, 21.3; IR (thin film) 3061, 3032, 2938, 2237, 1742, 1584, 1227, 1144 cm⁻¹; TLC R_f = 0.28 (10% EtOAc/hexanes); GC-MS (CI/NH₃) *m/z* (relative intensity) 296 (25), 187 (100); HRMS (CI/NH₃) *m/z* calcd for C₁₈H₁₆O₂S [M]⁺ 296.0871, found 296.0875.

(2-But-2-ynylsulfanylethyl)benzene (1f). To a round bottom flask was added EtOH (20 mL) and 1N NaOH (10.5 mL). The mixture was stirred at room temperature for 5 min. To the resulting solution was added 2-phenyl-ethanethiol (0.77 mL, 5.8 mmol) and the mixture was stirred until homogeneous. 1-Bromo-2-butyne (0.47 mL, 5.3 mmol) was added and the reaction mixture was stirred for 1.5 h at room temperature under N₂. Water (50 mL) was added and the aqueous layer extracted with Et₂O (4 × 30 mL). The combined organic layers were washed with 1N NaOH (4 × 30 mL) and saturated NaCl (40 mL). Organics were dried over MgSO₄, filtered and concentrated *in vacuo* to afford 1.18 g of a yellow oil. The crude oil was purified by silica gel chromatography (2% EtOAc/hexanes) to afford **1f** as a yellow oil (1.00 g, quantitative): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.29 – 7.32 (m, 2H), 7.20 – 7.23 (m, 3H), 3.24 (q, *J* = 2.5 Hz, 2H), 2.92 (s, 4H), 1.84 (t, *J* = 2.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 140.5, 128.5, 128.5, 126.4, 78.9, 74.8, 35.8, 33.0, 19.9, 3.7; IR (thin film) 3064, 3027, 2916, 2850, 1496, 1454 cm⁻¹; TLC R_f = 0.47 (5% EtOAc/hexanes); GC-MS (EI) *m/z* (relative intensity) 190(85), 104(100); HRMS (CI/NH₃) *m/z* calcd for C₁₂H₁₄S [M]⁺ 190.0816, found 190.0812.

General Procedure for Preparation of *N*-allenylsulfenimides.

To a flame-dried round bottom flask equipped with a magnetic stir bar was added dppeFeCl₂ and 1,2-dichloroethane. The resulting mixture was heated to reflux and stirred under N₂ until a clear brown solution was obtained. The solution was allowed to cool to room temperature and was then cooled to 0 °C in an ice bath. To this solution was added a solution of propargyl sulfide and *t*-butoxycarbonylazide in 1,2-dichloroethane via syringe. The reaction mixture was stirred under N₂ at 0 °C. The crude reaction mixture was filtered through a plug of

silica gel with Et₂O as eluant and concentrated *in vacuo*. The crude *N*-allenylsulfenimide product was purified by silica gel chromatography (EtOAc/hexanes).

***t*-Butylbenzenesulfanyl-(1-methyl-1,2-propadienyl)carbamate (2a).** As described in the general procedure, dppeFeCl₂ (53 mg, 0.10 mmol) was dissolved in 0.9 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1a** (162 mg, 1.0 mmol) and *t*-butoxycarbonylazide (143 mg, 1.0 mmol) in 0.1 mL 1,2-dichloroethane. The resulting mixture was stirred for 6 h (comparable yields obtained when reaction was run for 2 h). The crude oil was purified by silica gel chromatography with gradient elution (1% → 3% EtOAc/hexanes) to yield **2a** as a clear oil (193 mg, 70%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.27–7.35 (m, 4H), 7.17–7.20 (m, 1H), 4.90 (q, *J* = 3.2 Hz, 2H), 1.95 (t, *J* = 3.2 Hz, 3H), 1.47 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 207.5, 155.2, 138.8, 128.9, 126.8, 125.7, 110.4, 82.4, 80.4, 28.2, 18.6; IR (thin film) 3061, 2979, 2931, 1717, 1585, 1292 cm⁻¹; TLC R_f = 0.40 (10% EtOAc/hexanes); GC-MS (CI/NH₃) *m/z* (relative intensity) 278(10), 239(38), 178(100); HRMS (CI/NH₃) *m/z* calcd for C₁₅H₂₀NO₂S [M+H]⁺ 278.1214 found 278.1206.

***t*-Butylbenzenesulfanyl-(1,2-propadienyl)carbamate (2b).** As described in the general procedure, dppeFeCl₂ (52.5 mg, 0.10 mmol) was dissolved in 0.9 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1b** (148 mg, 1.0 mmol) and *t*-butoxycarbonylazide (143 mg, 1.0 mmol) in 0.1 mL 1,2-dichloroethane. The reaction mixture was stirred for 2 h. The crude oil was purified by silica gel chromatography with gradient elution (1% EtOAc/hexanes → 3% EtOAc/hexanes) to yield **2b** as a clear oil (193 mg, 73%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.21–7.32 (m, 6H), 5.33 (d, *J* = 6.3 Hz, 2H), 1.47 (s, 9H); ¹³C NMR (125 MHz, CDCl₃,

298 K) δ 202.2, 154.1, 138.3, 129.2, 127.2, 126.2, 104.2, 87.9, 83.3, 28.3; IR (thin film) 3061, 2978, 2931, 1966, 1714, 1582, 1061 cm^{-1} ; TLC R_f = 0.43 (10% EtOAc/hexanes); GC-MS (CI/ NH_3) m/z (relative intensity) 281(10), 264(12), 225(100), 164(32); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$ [$\text{M}-t\text{Bu}+\text{H}$] $^+$ 207.0354, found 207.0363.

***t*-Butylbenzenesulfanyl-(1-trimethylsilyl-1,2-propadienyl)carbamate (2c).** As described in the general procedure, dppeFeCl_2 (52.5 mg, 0.10 mmol) was dissolved in 0.9 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1c** (220 mg, 1.0 mmol) and *t*-butoxycarbonylazide (143 mg, 1.0 mmol) in 0.1 mL 1,2-dichloroethane. The reaction mixture was stirred for 4.5 hours. The crude oil was purified by silica gel chromatography with gradient elution (1% $\rightarrow$ 40% EtOAc/hexanes) to yield **2c** as a clear oil (119 mg, 54%): ^1H NMR (500 MHz, CDCl_3 , 298 K) δ 7.27–7.32 (m, 4H), 7.19–7.26 (m, 1H), 4.84 (s, 2H), 1.45 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ 209.6, 155.5, 138.9, 128.7, 126.6, 125.8, 111.9, 82.0, 79.1, 28.0, -0.5; IR (thin film) 3061, 2980, 2900, 1933, 1707, 1584, 1072 cm^{-1} ; TLC R_f = 0.61 (10% EtOAc/hexanes); GC-MS (CI/ NH_3) m/z (relative intensity) 336(13), 297(100), 280(34), 236(10), 189(13); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{SSi}$ [$\text{M}+\text{Na}$] $^+$ 358.1273, found 358.1259.

***t*-Butylbenzenesulfanyl-(1-hydroxy-1-phenyl-1,2-propadienyl)carbamate (2d).** As described in the general procedure, dppeFeCl_2 (29.0 mg, 0.055 mmol) was dissolved in 0.4 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1d** (141 mg, 0.55 mmol) and *t*-butoxycarbonylazide (79 mg, 0.55 mmol) in 0.15 mL 1,2-dichloroethane. The reaction mixture was stirred for 2.5 h. The crude oil was purified by silica gel chromatography with gradient

elution (10% → 50% EtOAc/hexanes) to yield **2d** as a pale yellow oil (108 mg, 53%): ^1H NMR (500 MHz, CDCl_3 , 298 K) δ 7.38–7.21 (m, 10H), 5.46 (m, 1H), 5.06 (m, 2H), 3.41 (br s, 1H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ 206.8, 156.2, 140.6, 138.0, 128.7, 128.1, 127.7, 127.1, 126.7, 126.3, 117.6, 83.8, 83.0, 73.9, 27.9; IR (thin film) 3450, 3063, 2979, 2931, 1720, 1583 cm^{-1} ; TLC R_f = 0.26 (20% EtOAc/hexanes); LRMS (ESI) m/z (relative intensity) 369(10), 312(5), 296(15), 204(100), 186(15); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{S}$ $[\text{M}]^+$ 369.1399, found 369.1411.

***t*-Butylbenzenesulfanyl-(1-acetoxy-1-phenyl-1,2-propadienyl)carbamate (2e).** As described in the general procedure, dppeFeCl_2 (52.5 mg, 0.10 mmol) was dissolved in 0.9 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1e** (286 mg, 0.97 mmol) and *t*-butoxycarbonylazide (138 mg, 0.97 mmol) in 0.1 mL 1,2-dichloroethane. The reaction mixture was stirred for 2 h. The crude oil was purified by silica gel chromatography with gradient elution (5% → 20% EtOAc/hexanes) to yield **2e** as a pale yellow oil (277 mg, 69%): ^1H NMR (500 MHz, CDCl_3 , 298 K) δ 7.36–7.37 (m, 2H), 7.26–7.33 (m, 7H), 7.21–7.22 (m, 1H), 6.57 (t, J = 2.9 Hz, 1H), 4.99 (d, J = 2.9 Hz, 2H), 2.03 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ 207.5, 169.7, 155.0, 138.0, 137.1, 128.7, 128.4, 128.2, 127.7, 127.2, 126.8, 114.3, 83.6, 82.6, 73.5, 27.9, 21.1; IR (thin film) 3064, 2981, 2934, 1957, 1748, 1731, 1715, 1584, 1025 cm^{-1} ; TLC R_f = 0.40 (20% EtOAc/hexanes); LRMS (ESI) m/z (relative intensity) 434(100), 378(20); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 434.1402, found 434.1402.

***t*-Butyl-(2-phenylethane)sulfanyl-(1-methyl-1,2-propadienyl)carbamate (2f).** As described in the general procedure, dppeFeCl_2 (52.5 mg, 0.10 mmol) was dissolved in 0.9 mL 1,2-

dichloroethane. To the cooled solution was added a solution of **1f** (190 mg, 1.0 mmol) and *t*-butoxycarbonylazide (143 mg, 1.0 mmol) in 0.1 mL 1,2-dichloroethane. The reaction mixture was stirred for 4.5 h. The crude oil was purified by silica gel chromatography with gradient elution (1% → 4% EtOAc/hexanes) to yield **2f** as a clear oil (96 mg, 31%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.28–7.31 (m, 2H), 7.20–7.23 (m, 3H), 5.01 (q, *J* = 3.2 Hz, 2H), 3.05–3.08 (m, 2H), 2.91–2.94 (m, 2H), 1.95 (t, *J* = 3.2 Hz, 3H), 1.49 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 208.0, 155.6, 140.4, 128.5, 128.4, 126.4, 110.2, 81.8, 79.8, 39.7, 34.4, 28.2, 18.3; IR (thin film) 3062, 3028, 2980, 2931, 1712, 1073 cm⁻¹; TLC R_f = 0.43 (10% EtOAc/hexanes); LRMS (ESI) *m/z* (relative intensity) 249(15), 205(10), 137(33); HRMS (CI/NH₃) *m/z* calcd for C₁₃H₁₅NO₂S [M-*t*Bu+H]⁺ 249.0823, found 249.0821.

***t*-Butyl-*N*-benzenesulfanyl-*N*-(buta-1,2-dienyl)carbamate (2g).** As described in the general procedure, dppeFeCl₂ (53 mg, 0.10 mmol) was dissolved in 0.8 mL 1,2-dichloroethane. To the cooled solution was added a solution of **1g** (160 mg, 1.0 mmol) and *t*-butoxycarbonylazide (153 mg, 1.1 mmol) in 0.2 mL 1,2-dichloroethane. The reaction mixture was stirred for 2 h. The crude oil was purified by silica gel chromatography with gradient elution (5% → 10% EtOAc/hexanes) to yield **2g** as a clear oil (137 mg, 52%): ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.17–7.37 (m, 5H), 7.04–7.11 (m, 1H), 5.68 (quint., *J* = 7.0 Hz, 1H), 1.61 (dd, *J* = 2.7, 7.0 Hz, 3H), 1.49 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 196.7, 154.3, 138.3, 129.0, 126.9, 126.0, 102.9, 99.1, 83.0, 28.2, 16.0; IR (thin film) 3059, 2979, 2932, 1970, 1712, 1293, 853 cm⁻¹; TLC R_f = 0.28 (5% EtOAc/hexanes); LRMS (ESI) *m/z* (relative intensity) 300(100); HRMS (CI/NH₃) calcd for C₁₅H₂₀NO₂S [M+H]⁺ 278.1215, found: 278.1215.

***t*-Butyl-*N*-benzenesulfanyl-*N*-(bicyclo[2.2.1]hept-5-en-2-ylidenemethyl)carbamate (3).** To an oven dried glass reaction tube equipped with a magnetic stir bar was added **2b** (132 mg, 0.50 mmol) in toluene (0.5 mL) followed by cyclopentadiene monomer (0.10 mL, 1.2 mmol). The tube was sealed and heated and placed in an oil bath at 100 °C. After 5h, the reaction mixture was cooled to rt and concentrated *in vacuo* to afford the crude oil. Purification by silica gel chromatography (5% Et₂O/hexanes) followed by preparative reverse-phase HPLC (C₁₈, 60–100% MeCN/Aqueous 0.1% TFA buffer, 30 min) afforded **3** as a clear oil (94 mg, 57%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.50 (br s, 0.5H), 7.37 (br s, 0.5H), 7.23-7.28 (m, 4H), 7.16 (br s, 1H), 5.92 (br s, 0.5H), 5.80-5.82 (m, 1.5H), 4.91 (br s, 0.5 H) 4.81 (br s, 0.5 H), 2.52-2.58 (m, 2H), 1.98-2.12 (m, 3H), 1.54 (s, 9H); ¹³C NMR (125 MHz, CDCl₃, 323 K) δ 152.6, 137.2, 134.6, 132.3, 131.1, 129.1, 128.4, 125.9, 106.5, 81.8, 60.2, 38.4, 35.7, 30.9, 28.6; IR (thin film) 3065, 2967, 2932, 2852, 1707, 1639 cm⁻¹; TLC R_f = 0.16 (5% Et₂O/hexanes); GC-MS (CI/NH₃) *m/z* (relative intensity) 347(8), 330(30), 291(100), 274(30), 230(30); HRMS (CI/NH₃) calcd for C₁₉H₂₃NO₂S [M]⁺ 329.1449, found: 329.1452.

***t*-Butyl-*N*-benzenesulfanyl-*N*-propenylcarbamate (4).** To a flame dried round bottom flask equipped with a stir bar was added **2b** (132 mg, 0.50 mmol) and 4 mL EtOAc. To this stirring solution was added Pd/C (26 mg of 10% w/w powder). The flask was flushed three times with H₂ and the reaction stirred for 20 h under balloon pressure of H₂. The reaction mixture was filtered through Celite[®] with Et₂O as eluant and concentrated *in vacuo* to give a yellow oil. Silica gel chromatography with gradient elution (2% → 4% EtOAc/hexanes) afforded **4** as a colorless solid (96 mg, 72%): ¹H NMR (500 MHz, CDCl₃, 298 K) δ 7.27-7.32 (m, 4H). 7.21-7.24

(m, 1H), 6.23 (dq, $J = 1.7, 7.9$ Hz, 1H), 5.27 (dq, $J = 7.0, 7.9$ Hz, 1H), 1.60 (dd, $J = 1.7, 7.0$ Hz, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3 , 298 K) δ 155.3, 138.3, 130.4, 129.0, 127.0, 126.0, 120.8, 82.3, 28.0, 12.6; IR (thin film) 3038, 2979, 2933, 1716, 1658, 1583 cm^{-1} ; TLC $R_f = 0.36$ (10% EtOAc/hexanes); GC-MS (EI) m/z (relative intensity) 265(5), 209(9), 165(82), 109(83); HRMS (CI/ NH_3) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{S}$ $[\text{M}]^+$ 265.1136, found 265.1140.

¹³C and ¹H NMR Spectra

2g

2g

3

323 K

323 K

HMQC

HMQC

HMQC

323 K

NOESY

323 K

NOESY