

Visible-Light-Promoted Photoredox Synthesis of Thioacetylenes by Dehydrogenation Coupling of Thiophenols and Alkynes

Xianya Wang,^{†, #, *} Xun Wu,[†] Yong Zhu,[†] Yaowu Liu^{†, #}

[†] School of pharmacy, Bozhou Vocational and Technical College, 236800 Bozhou, P. R. China.

[#] Huatuo Institute of Traditional Chinese Medicine, 236800 Bozhou, P. R. China.

Email: xywang21@outlook.com

Table of Contents

General procedure for the photoredox dehydrocoupling of diphenyl phosphine with thiophenols.....	1
Supporting Figures	2
Products Characterization.....	7
NMR Spectra.....	18

General procedure for the photoredox dehydrocoupling of diphenyl phosphine with thiophenols

A 20 mL Schlenk tube was charged with 0.2 mmol phenylacetylenes, 0.4 mmol thiophenols, CuBr (10 mol%), 0.4 mmol Cs₂CO₃ and 1.0 mL of MeCN, then the vials were sealed and stand on a 25 W white LED plate for 12 h. When completed, the reactions were detected by GC-MS and isolated with flash chromatography using petroleum ether or a mixed solvent of ethyl acetate(EA) and petroleum ether(PE) as eluent.

Supporting Figures

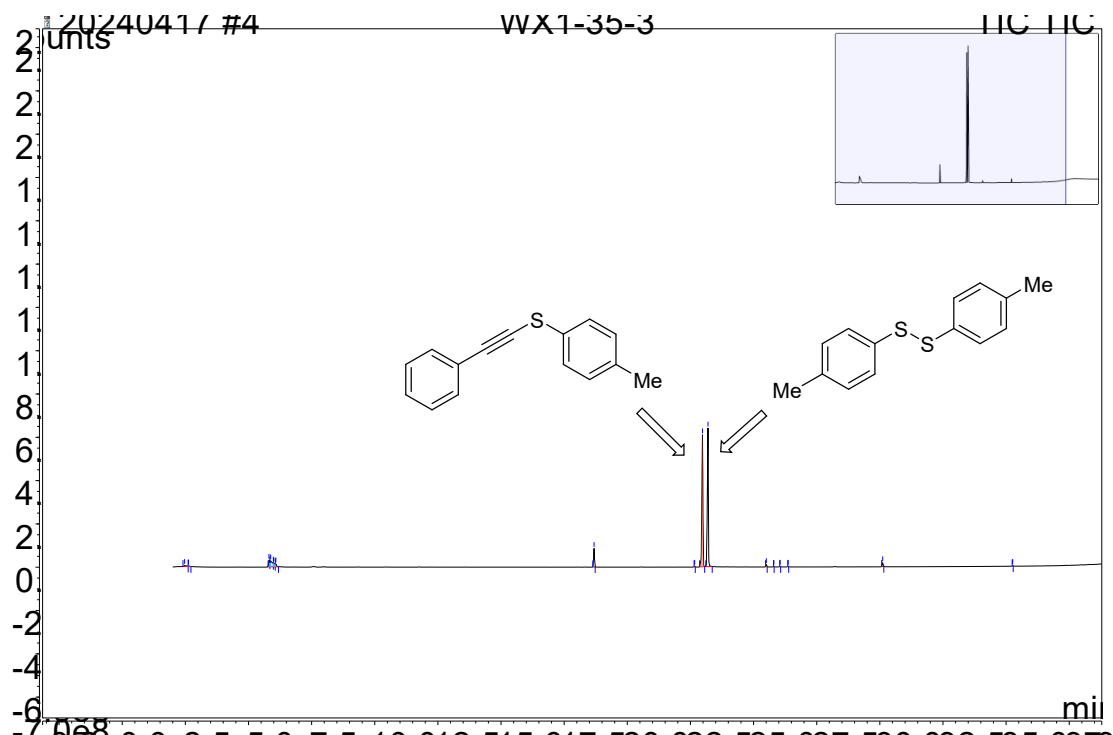


Figure S1. GC-MS spectrum of “standard conditions”: visible-light-promoted photoredox synthesis of thioacetylenes with dehydrogenation coupling of thiophenols and phenylacetylenes

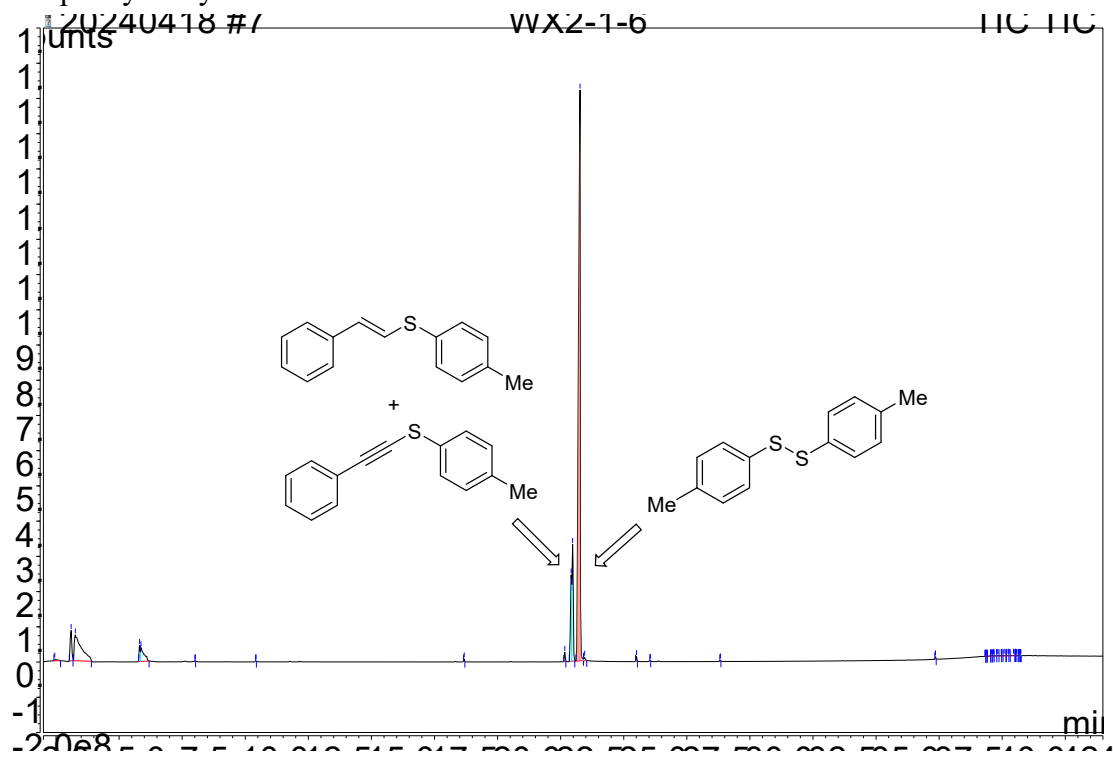


Figure S2. GC-MS spectrum of “standard conditions” **without light** to show the crucial role of visible light.

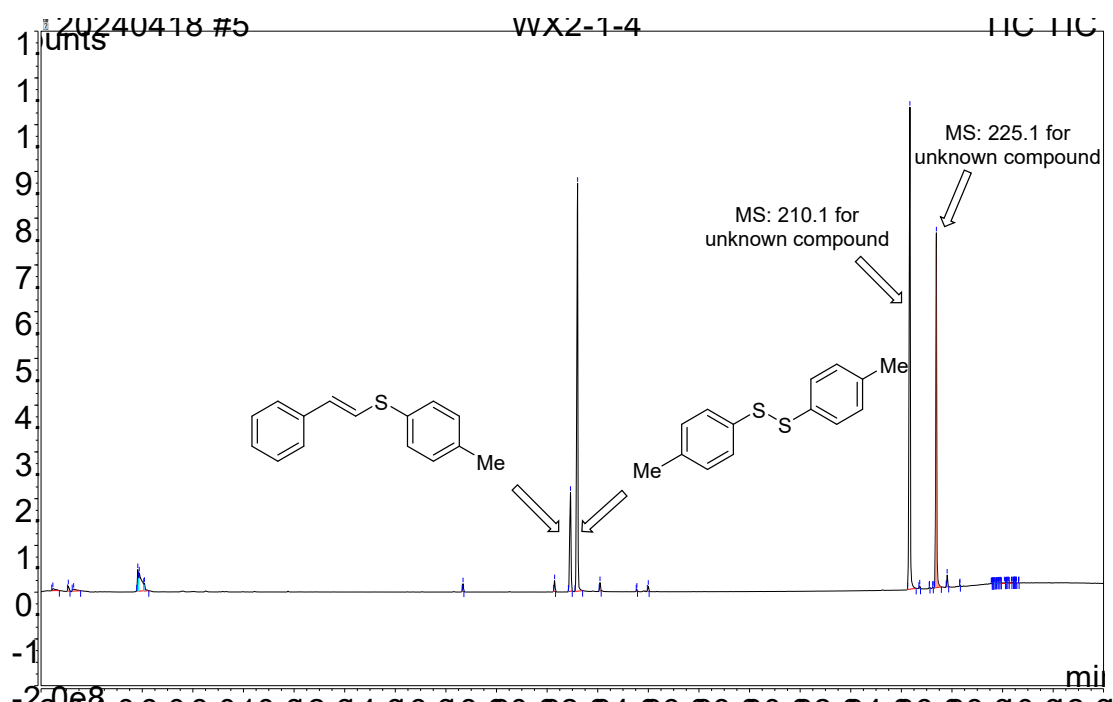


Figure S3. GC-MS spectrum of “standard conditions” **without CuBr** to show the crucial role of catalyst.

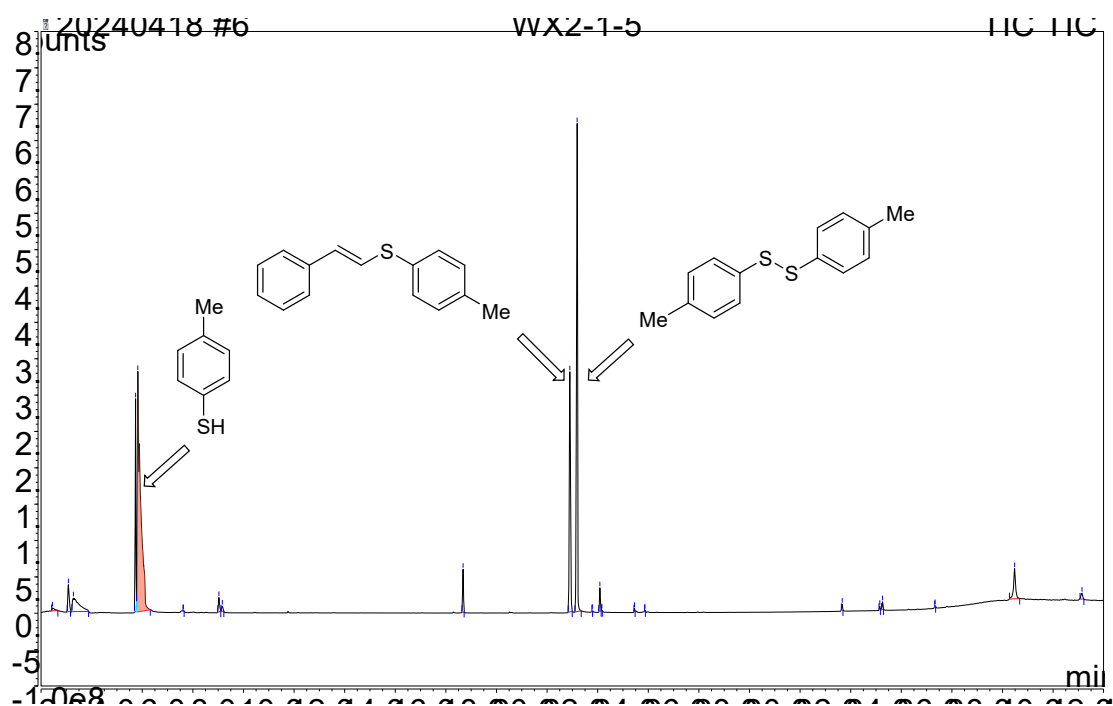


Figure S4. GC-MS spectrum of “standard conditions” **without Cs₂CO₃** to show the crucial role of base.

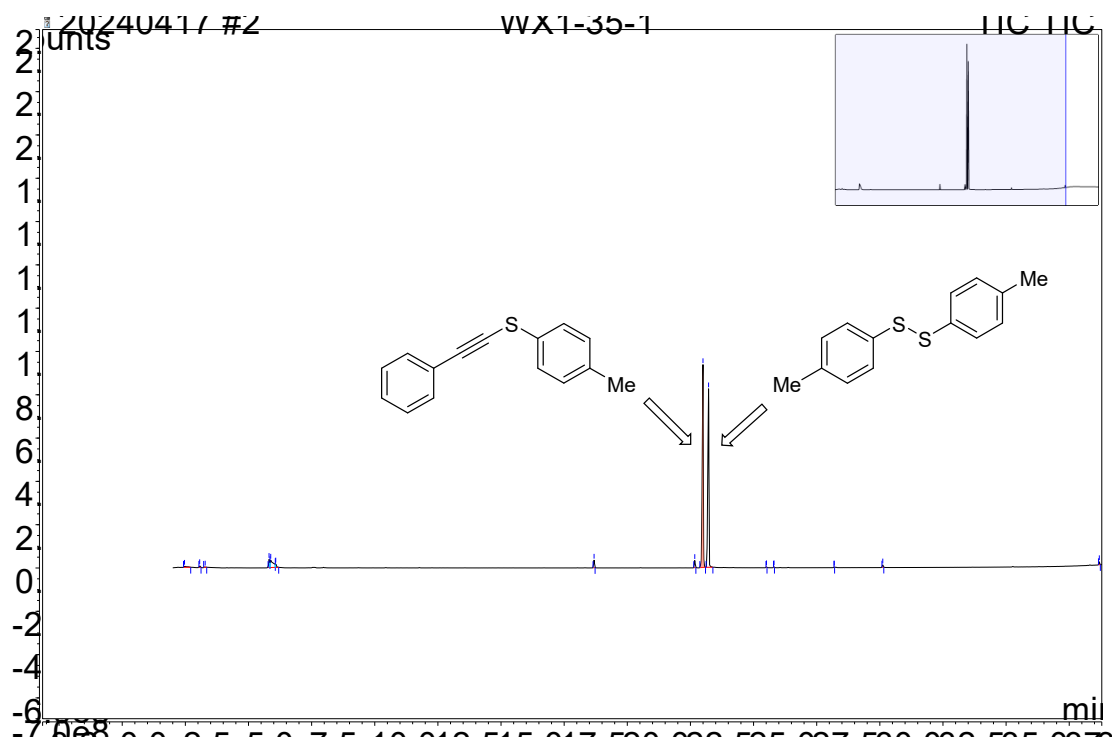


Figure S5. GC-MS spectrum of “standard conditions” **O₂ instead of air** to show the crucial role of air.

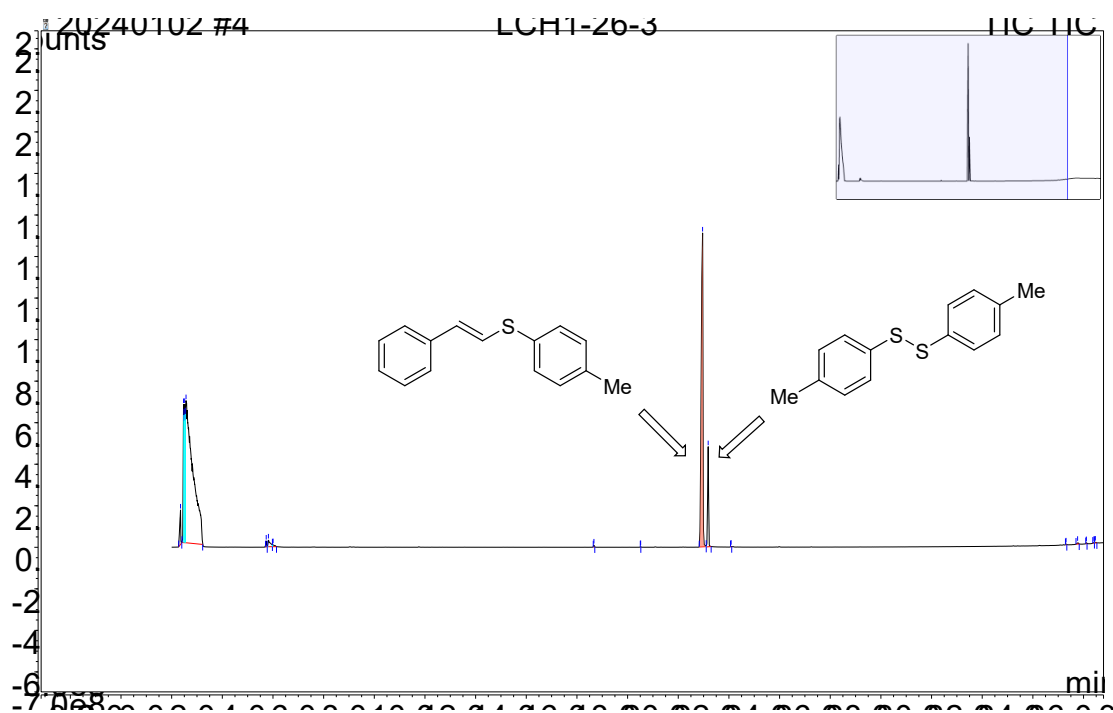


Figure S6. GC-MS spectrum of “standard conditions” **Ar instead of air** to show the crucial role of O₂ in the air.

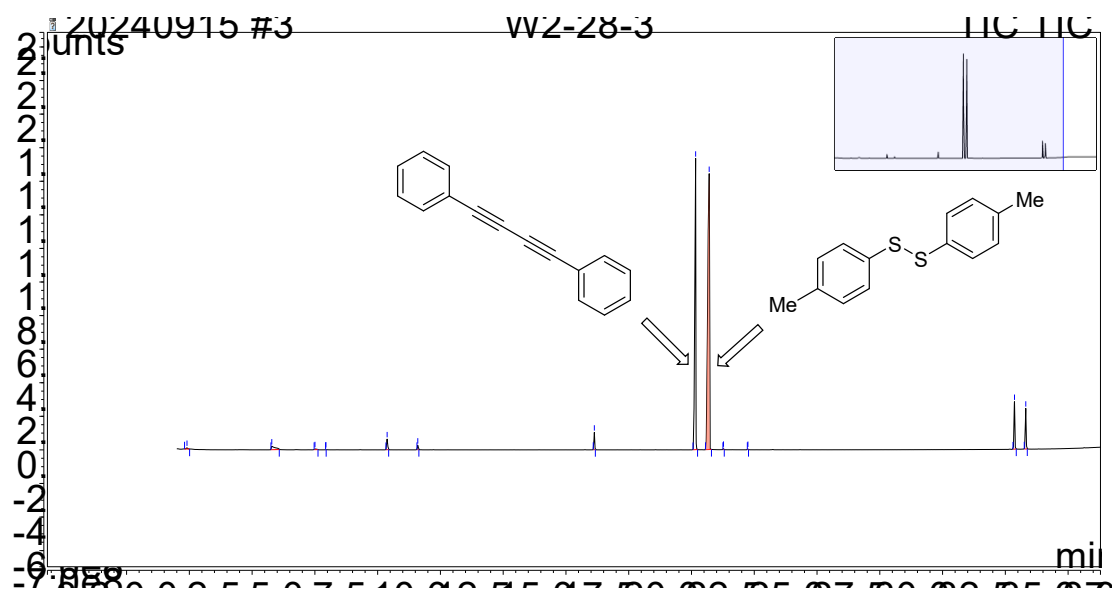


Figure S9. GC-MS spectrum of “standard conditions” with 0.25 equiv. diyne to show the pathway of catalytic cycle.

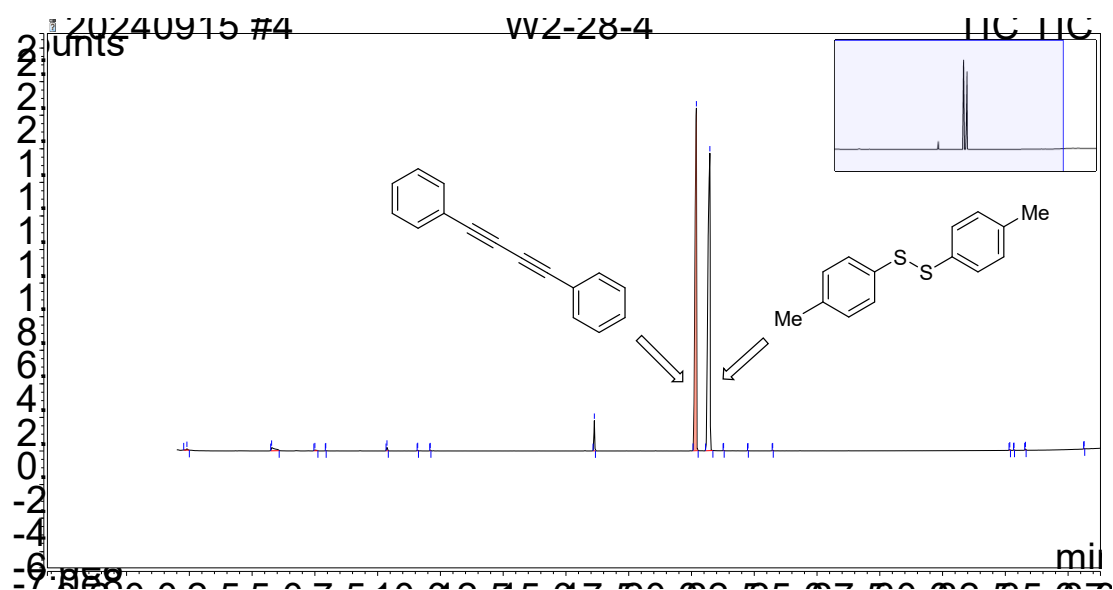
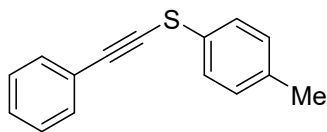


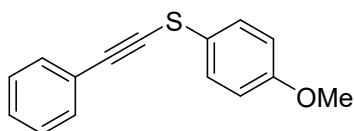
Figure S10. GC-MS spectrum of “standard conditions” diyne with 2 equiv. disulfide to show the pathway of catalytic cycle.

Products Characterization



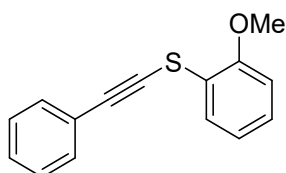
(phenylethynyl)(p-tolyl)sulfane 3a

Eluent: petroleum ether, R_f = 0.6, colorless liquid, 38.1 mg, 85% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.42 (dd, J = 6.7, 3.0 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.27 – 7.25 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 135.61, 131.48, 130.65, 129.02, 128.76, 128.16, 127.48, 127.34, 125.55, 96.22, 75.09, 19.98. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{S}^+$: 225.0735; found: 225.0731.



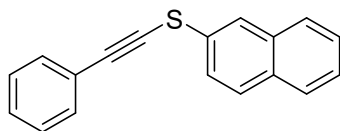
(4-methoxyphenyl)(phenylethynyl)sulfane 3b

Eluent: petroleum ether, R_f = 0.3, colorless liquid, 45.1 mg, 94% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.54 – 7.49 (m, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.38 – 7.33 (m, 3H), 6.94 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 159.04, 128.93, 128.47, 128.37, 123.09, 123.04, 115.08, 96.30, 55.47. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{OS}^+$: 241.0682; found: 241.0680.



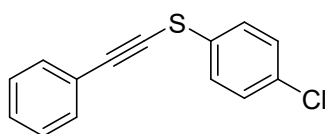
(2-methoxyphenyl)(phenylethynyl)sulfane 3c

Eluent: petroleum ether, R_f = 0.3, colorless liquid, 44.4 mg, 92% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.60 (dd, J = 7.8, 1.6 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.31 – 7.25 (m, 3H), 7.16 – 7.12 (m, 1H), 6.96 (td, J = 7.6, 1.2 Hz, 1H), 6.79 (dd, J = 8.1, 1.0 Hz, 1H), 3.83 (s, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 154.19, 127.54, 127.37, 126.25, 125.52, 122.03, 120.66, 109.38, 97.41, 74.24, 54.92. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{OS}^+$: 241.0682; found: 241.0680.



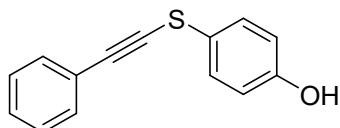
naphthalen-2-yl(phenylethynyl)sulfane 3d

Eluent: petroleum ether, R_f = 0.4, colorless liquid, 39.2 mg, 75% yield. **^1H NMR** (600 MHz, CDCl_3) δ 7.98 (s, 1H), 7.88 – 7.83 (m, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.58 (t, J = 7.1 Hz, 3H), 7.51 (dt, J = 22.5, 7.3 Hz, 2H), 7.42 – 7.38 (m, 3H). **^{13}C NMR** (150 MHz, CDCl_3) δ 133.78, 132.06, 131.84, 130.26, 129.03, 128.75, 128.47, 127.87, 127.18, 126.90, 126.01, 124.61, 124.18, 122.92, 98.06, 75.49. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{13}\text{S}^+$: 261.0732; found: 261.0731.



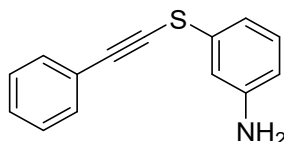
(4-chlorophenyl)(phenylethynyl)sulfane 3e

Eluent: petroleum ether, R_f = 0.6, white solid, 43.3 mg, 88% yield. **^1H NMR** (600 MHz, CDCl_3) δ 8.14 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 8.0, 1.6 Hz, 1H), 7.44 (dd, J = 7.3, 2.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 (d, J = 8.7 Hz, 1H). **^{13}C NMR** (150 MHz, CDCl_3) δ 131.03, 130.80, 128.43, 128.37, 127.85, 127.56, 127.43, 126.45, 124.68, 123.28, 97.37, 73.73. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{10}\text{ClS}^+$: 245.0186; found: 245.0183.



4-((phenylethynyl)thio)phenol 3f

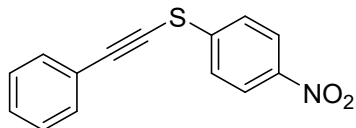
Eluent: EA:PE=1:5, R_f = 0.3, white solid, 44.3 mg, 98% yield. **^1H NMR** (600 MHz, CDCl_3) δ 7.52 – 7.48 (m, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.37 – 7.34 (m, 3H), 6.87 (d, J = 8.7 Hz, 2H), 4.97 (s, 1H). **^{13}C NMR** (150 MHz, CDCl_3) δ 154.97, 131.68, 129.09, 128.51, 128.38, 123.30, 123.03, 116.53, 96.44. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{OS}^+$: 227.0525; found: 227.0526.



3-((phenylethynyl)thio)aniline 3g

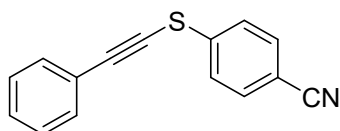
Eluent: EA:PE=1:3, R_f = 0.3, colorless liquid, 34.3 mg, 76% yield. **^1H NMR** (600 MHz, CDCl_3) δ 7.63 – 7.46 (m, 2H), 7.45 – 7.32 (m, 3H), 7.15 (t, J = 7.9 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.84 (s,

1H), 6.57 (d, J = 7.9 Hz, 1H), 4.15 – 3.36 (m, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 147.22, 133.78, 131.83, 130.07, 128.64, 128.41, 123.00, 116.31, 113.48, 112.31, 97.91, 75.63. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₄H₁₂NS⁺: 226.0685; found: 226.0683.



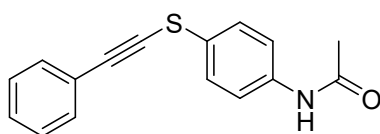
(4-nitrophenyl)(phenylethynyl)sulfane 3h

Eluent: petroleum ether, R_f = 0.5, yellow solid, 46.5 mg, 91% yield. **¹H NMR** (600 MHz, CDCl₃) δ 8.14 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 7.48 (dd, J = 8.0, 1.6 Hz, 2H), 7.34 – 7.31 (m, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 145.22, 141.98, 131.02, 130.79, 128.43, 127.56, 127.43, 126.45, 124.67, 123.27, 120.96, 99.50, 71.41. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₄H₁₀NO₂S⁺: 256.0427; found: 256.0427.



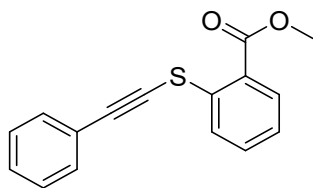
4-((phenylethynyl)thio)benzonitrile 3i

Eluent: EA:PE=1:20, R_f = 0.5, yellow liquid, 33.3 mg, 70% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.65 (d, J = 8.5 Hz, 2H), 7.60 (s, 1H), 7.56 (s, 3H), 7.41 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 140.59, 132.65, 132.03, 129.37, 128.58, 125.92, 122.09, 118.55, 109.78, 100.37, 72.56. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₅H₁₀NS⁺: 236.0528; found: 236.0528.



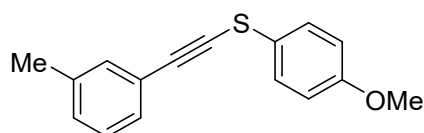
N-(4-((phenylethynyl)thio)phenyl)acetamide 3j

Eluent: EA:PE=1:1, R_f = 0.3, white solid, 45.6 mg, 85% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.57 – 7.49 (m, 4H), 7.44 (dd, J = 19.3, 8.3 Hz, 3H), 7.38 – 7.35 (m, 2H), 2.20 (s, 3H), 1.71 (s, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 168.45, 136.80, 131.74, 131.33, 128.75, 128.67, 128.43, 128.35, 127.73, 127.33, 122.86, 120.78, 120.54, 97.58, 75.75, 24.62. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₄NOS⁺: 268.0791; found: 268.0790.



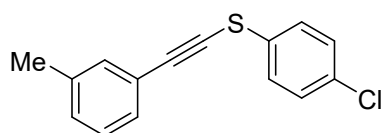
methyl 2-((phenylethynyl)thio)benzoate 3k

Eluent: EA:PE=1:5, R_f = 0.5, yellow liquid, 50.4 mg, 94% yield. **¹H NMR** (600 MHz, CDCl₃) δ 8.14 – 8.06 (m, 2H), 7.63 – 7.55 (m, 3H), 7.42 – 7.37 (m, 3H), 7.29 (d, J = 10.7 Hz, 1H), 3.98 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 166.45, 138.40, 133.22, 131.89, 131.36, 128.82, 128.46, 127.14, 125.79, 125.51, 122.84, 99.92, 52.40. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₃O₂S⁺:269.0631; found: 269.0632.



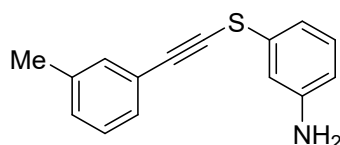
(4-methoxyphenyl)(m-tolylethynyl)sulfane 4a

Eluent: EA:PE=1:20, R_f = 0.3, colorless liquid, 46.3 mg, 91% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.46 (d, J = 8.8 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 159.00, 138.08, 132.23, 129.40, 128.85, 128.75, 128.27, 123.16, 122.88, 115.06, 96.55, 76.50, 55.46, 21.25. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₅OS⁺:255.0838; found: 255.0841.



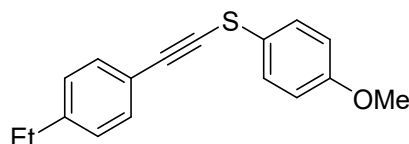
(4-chlorophenyl)(m-tolylethynyl)sulfane 4b

Eluent: petroleum ether, R_f = 0.4, colorless liquid, 42.5 mg, 82% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.44 (d, J = 8.5 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.27 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 2.38 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 138.22, 132.45, 132.39, 131.71, 129.83, 129.39, 128.93, 128.37, 127.43, 122.42, 98.68, 74.26, 21.25. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₅H₁₂ClS⁺:259.0343; found: 259.0345.



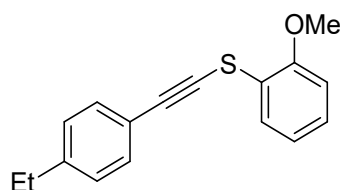
3-((m-tolylethynyl)thio)aniline 4c

Eluent: EA:PE=1:2, R_f = 0.4, yellow liquid, 44.7 mg, 93% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.38 – 7.31 (m, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.9 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.84 (s, 1H), 6.57 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H), 1.28 (s, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 147.20, 138.12, 133.90, 132.38, 130.04, 129.56, 128.92, 128.30, 122.79, 116.27, 113.43, 112.27, 98.14, 75.11, 21.25. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₅H₁₄NS⁺:240.0841; found: 240.0843.



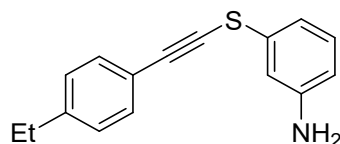
((4-ethylphenyl)ethynyl)(4-methoxyphenyl)sulfane 4d

Eluent: EA:PE=1:20, R_f = 0.4, colorless liquid, 50.5 mg, 94% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.44 (t, J = 8.7 Hz, 4H), 7.19 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 2.68 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 158.94, 145.10, 131.86, 128.73, 127.95, 123.33, 120.22, 115.04, 96.56, 75.90, 55.46, 28.88, 15.37, 1.05. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₇H₁₇OS⁺:269.0995; found: 269.0993.



((4-ethylphenyl)ethynyl)(2-methoxyphenyl)sulfane 4e

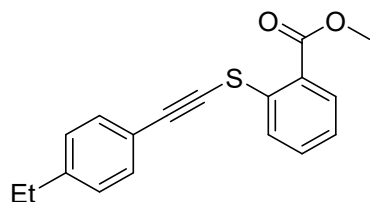
Eluent: EA:PE=1:20, R_f = 0.4, colorless liquid, 47.8 mg, 89% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.70 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 3H), 7.05 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 3.93 (s, 3H), 2.69 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 155.18, 145.23, 131.96, 127.99, 127.18, 126.50, 121.67, 120.20, 110.35, 98.68, 74.21, 55.95, 28.90, 15.39, 1.06. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₇H₁₇OS⁺:269.0995; found: 269.0993.



3-(((4-ethylphenyl)ethynyl)thio)aniline 4f

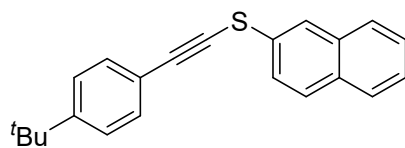
Eluent: EA:PE=1:3, R_f = 0.4, colorless liquid, 43.3 mg, 85% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.47 (d, J = 7.7 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.14 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H),

6.85 (s, 1H), 6.57 (d, J = 7.9 Hz, 1H), 3.54 (s, 2H), 2.69 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 147.08, 145.31, 134.08, 132.03, 130.03, 128.00, 120.13, 116.29, 113.44, 112.27, 98.18, 74.57, 28.90, 15.39. HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₆NS⁺: 254.0998; found: 254.0996.



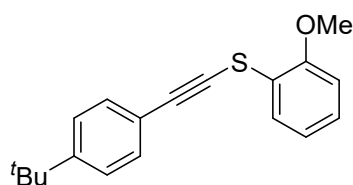
methyl 2-(((4-ethylphenyl)ethynyl)thio)benzoate 4g

Eluent: EA:PE=1:5, R_f = 0.5, yellow liquid, 47.5 mg, 80% yield. ¹H NMR (600 MHz, CDCl₃) δ 8.09 (t, J = 7.1 Hz, 2H), 7.58 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 3.7 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.46, 145.49, 138.68, 133.18, 132.07, 131.33, 128.04, 127.15, 125.75, 125.41, 119.98, 100.12, 75.71, 52.37, 28.92, 15.39. HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₈H₁₇O₂S⁺: 297.0944; found: 297.0946.



((4-(tert-butyl)phenyl)ethynyl)(naphthalen-2-yl)sulfane 4h

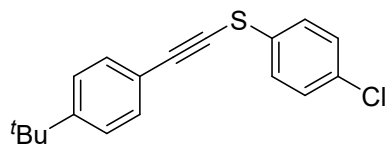
Eluent: petroleum ether, R_f = 0.3, colorless liquid, 56.7 mg, 90% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.97 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.1 Hz, 1H), 7.54 (dt, J = 15.6, 8.1 Hz, 4H), 7.51 – 7.47 (m, 1H), 7.42 (d, J = 8.1 Hz, 2H), 1.36 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 152.27, 133.79, 132.01, 131.83, 130.59, 128.95, 127.86, 127.16, 126.86, 125.93, 125.50, 124.39, 124.09, 119.86, 98.30, 74.43, 34.91, 31.18. HRMS (ESI) m/z: [M+H]⁺ calcd for C₂₂H₂₁S⁺: 317.1358; found: 317.1361.



((4-(tert-butyl)phenyl)ethynyl)(2-methoxyphenyl)sulfane 4i

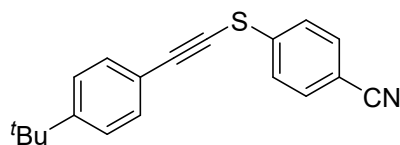
Eluent: petroleum ether, R_f = 0.3, colorless liquid, 43.4 mg, 73% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.23 (t, J = 7.7 Hz,

1H), 7.05 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 3.93 (s, 3H), 1.36 (s, 9H). **¹³C NMR** (150 MHz, CDCl₃) δ 155.19, 152.07, 131.74, 127.18, 126.50, 125.44, 121.86, 121.67, 120.00, 110.36, 98.64, 74.24, 55.95, 34.88, 31.19. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₂₁OS⁺: 297.1308; found: 297.1311.



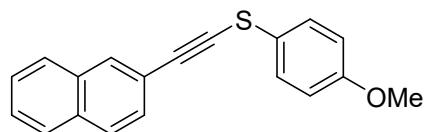
((4-(tert-butyl)phenyl)ethynyl)(4-chlorophenyl)sulfane 4j

Eluent: petroleum ether, R_f = 0.4, white solid, 57.3 mg, 95% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.49 (d, J = 8.3 Hz, 2H), 7.42 (dd, J = 14.2, 8.4 Hz, 4H), 7.34 (d, J = 8.5 Hz, 2H), 1.35 (s, 9H). **¹³C NMR** (150 MHz, CDCl₃) δ 152.45, 132.36, 131.90, 131.83, 129.36, 127.33, 125.51, 119.57, 98.69, 73.74, 34.91, 31.17. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₂₁OS⁺: 301.0812; found: 301.0816.



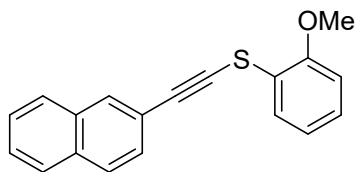
4-(((4-(tert-butyl)phenyl)ethynyl)thio)benzonitrile 4k

Eluent: EA:PE=1:20, R_f = 0.3, white solid, 54.3 mg, 93% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.63 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 1.36 (s, 9H). **¹³C NMR** (150 MHz, CDCl₃) δ 152.99, 140.92, 132.60, 132.01, 125.85, 125.61, 119.02, 118.60, 109.65, 100.62, 71.64, 34.97, 31.14. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₁₈NS⁺: 292.1154; found: 292.1152.



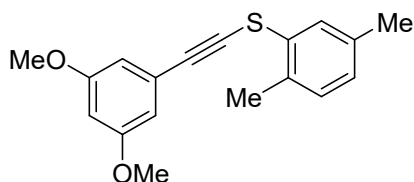
(4-methoxyphenyl)(naphthalen-2-ylethynyl)sulfane 4l

Eluent: EA:PE=1:20, R_f = 0.3, white solid, 56.7 mg, 98% yield. **¹H NMR** (600 MHz, CDCl₃) δ 8.02 (s, 1H), 7.87 – 7.79 (m, 3H), 7.57 – 7.48 (m, 5H), 6.96 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 159.10, 132.95, 131.53, 129.04, 128.29, 128.06, 127.80, 126.81, 126.66, 123.02, 120.38, 115.13, 96.70, 55.48. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₉H₁₅OS⁺: 291.0838; found: 291.0835.



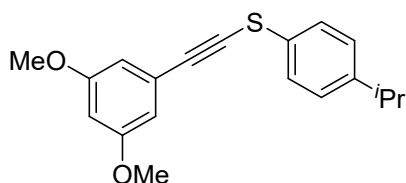
(2-methoxyphenyl)(naphthalen-2-ylethynyl)sulfane 4m

Eluent: EA:PE=1:20, R_f = 0.3, colorless liquid, 47.8 mg, 82% yield. **^1H NMR** (600 MHz, CDCl_3) δ 8.09 (s, 1H), 7.88 – 7.82 (m, 3H), 7.78 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.30 – 7.23 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (150 MHz, CDCl_3) δ 155.26, 132.97, 131.69, 128.36, 128.12, 127.84, 127.83, 127.36, 126.88, 126.70, 126.61, 121.75, 121.58, 120.34, 110.45, 98.94, 75.68, 55.98. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{OS}^+$: 291.0838; found: 291.0839.



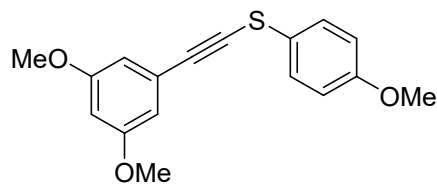
((3,5-dimethoxyphenyl)ethynyl)(2,5-dimethylphenyl)sulfane 4n

Eluent: EA:PE=1:20, R_f = 0.4, colorless liquid, 47.9 mg, 80% yield. **^1H NMR** (600 MHz, CDCl_3) δ 7.53 (s, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.70 (s, 2H), 6.50 (s, 1H), 3.83 (s, 7H), 2.38 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (150 MHz, CDCl_3) δ 160.56, 136.73, 132.39, 131.25, 130.23, 127.60, 127.44, 124.33, 109.46, 101.96, 97.25, 75.72, 55.47, 21.15, 19.10. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2\text{S}^+$: 299.1100; found: 299.1104.



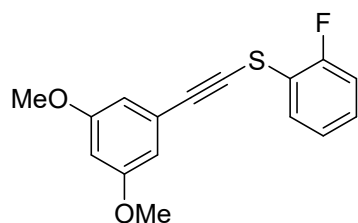
((3,5-dimethoxyphenyl)ethynyl)(4-isopropylphenyl)sulfane 4o

Eluent: EA:PE=1:20, R_f = 0.4, colorless liquid, 46.8 mg, 75% yield. **^1H NMR** (600 MHz, CDCl_3) δ 7.44 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.68 (s, 2H), 6.49 (s, 1H), 3.82 (s, 6H), 2.93 (p, J = 6.9 Hz, 1H), 1.28 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (150 MHz, CDCl_3) δ 160.54, 147.80, 129.36, 127.54, 126.74, 124.29, 109.38, 102.00, 97.19, 75.94, 55.47, 33.75, 23.97. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{S}^+$: 313.1257; found: 313.1260.



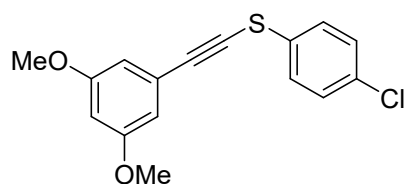
((3,5-dimethoxyphenyl)ethynyl)(4-methoxyphenyl)sulfane 4p

Eluent: EA:PE=1:20, R_f = 0.2, colorless liquid, 56.8 mg, 95% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.45 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 2.1 Hz, 2H), 6.47 (s, 1H), 3.83 (s, 3H), 3.81 (s, 6H). **¹³C NMR** (150 MHz, CDCl₃) δ 160.52, 159.09, 129.05, 124.31, 122.85, 115.09, 109.34, 101.95, 96.23, 55.46. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₇H₁₇O₃S⁺: 301.0893; found: 301.0898.



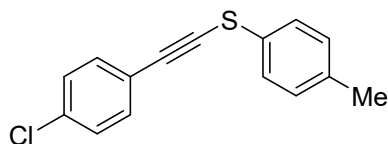
((3,5-dimethoxyphenyl)ethynyl)(2-fluorophenyl)sulfane 4q

Eluent: petroleum ether, R_f = 0.3, colorless liquid, 54.5 mg, 95% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.70 (t, J = 7.6 Hz, 1H), 7.24 (dt, J = 15.0, 7.2 Hz, 2H), 7.10 (t, J = 8.9 Hz, 1H), 6.70 (d, J = 2.2 Hz, 2H), 6.51 (s, 1H), 3.82 (s, 6H). **¹³C NMR** (150 MHz, CDCl₃) δ 160.58, 159.71, 158.08, 128.32, 125.08, 123.84, 120.40, 115.55, 109.61, 102.31, 98.24, 73.27, 55.49. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₄FO₂S⁺: 289.0693; found: 289.0692.



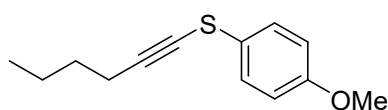
(4-chlorophenyl)((3,5-dimethoxyphenyl)ethynyl)sulfane 4r

Eluent: EA:PE=1:20, R_f = 0.5, colorless liquid, 55.5 mg, 91% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.43 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.68 (d, J = 1.9 Hz, 2H), 6.51 (s, 1H), 3.82 (s, 6H). **¹³C NMR** (150 MHz, CDCl₃) δ 160.59, 132.59, 131.43, 129.43, 127.55, 123.84, 109.54, 102.28, 98.37, 74.50, 55.49. **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₆H₁₄ClO₂S⁺: 305.0398; found: 305.0399.



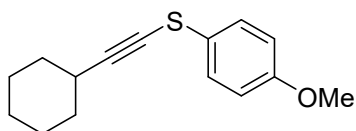
((4-chlorophenyl)ethynyl)(p-tolyl)sulfane 4s

Eluent: petroleum ether, $R_f = 0.5$, white solid, 50.2 mg, 97% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.44 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 136.88, 134.54, 132.86, 130.13, 128.81, 128.75, 126.78, 121.53, 95.96, 77.56, 21.05. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{12}\text{ClS}^+$: 259.0343; found: 259.0338.



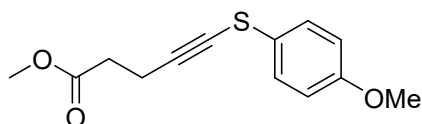
hex-1-yn-1-yl(4-methoxyphenyl)sulfane 4t

Eluent: petroleum ether, $R_f = 0.3$, colorless liquid, 41.6 mg, 94% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.37 (d, $J = 8.2$ Hz, 2H), 6.90 (d, $J = 8.2$ Hz, 2H), 3.82 (s, 3H), 2.44 (t, $J = 7.0$ Hz, 2H), 1.59 (d, $J = 7.5$ Hz, 2H), 1.47 (q, $J = 7.4$ Hz, 2H), 0.95 (t, $J = 7.3$ Hz, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 158.67, 128.30, 123.95, 114.89, 98.40, 65.91, 55.44, 30.76, 22.00, 19.99, 13.61. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{OS}^+$: 221.0995; found: 221.0989.



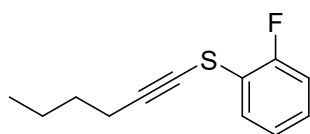
(cyclohexylethynyl)(4-methoxyphenyl)sulfane 4u

Eluent: petroleum ether, $R_f = 0.3$, colorless liquid, 42.8 mg, 87% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.36 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 3.82 (s, 3H), 2.61 (s, 1H), 1.88 (d, $J = 11.0$ Hz, 2H), 1.75 (s, 2H), 1.55 (s, 3H), 1.41 – 1.32 (m, 3H). **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 158.58, 128.00, 124.12, 114.88, 102.52, 65.82, 55.43, 32.61, 30.59, 25.84, 24.87. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{OS}^+$: 247.1151; found: 247.1148.



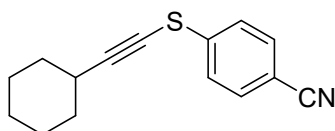
methyl 5-((4-methoxyphenyl)thio)pent-4-ynoate 4v

Eluent: EA:PE=1:20, R_f = 0.3, colorless liquid, 42.7 mg, 85% yield. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.36 (d, J = 7.5 Hz, 2H), 6.90 (d, J = 7.5 Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H), 2.76 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.24, 158.83, 128.59, 123.33, 114.94, 95.83, 67.60, 55.44, 51.89, 33.35, 16.21. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{S}^+$: 251.0736; found: 251.0736.



(2-fluorophenyl)(hex-1-yn-1-yl)sulfane 4w

Eluent: petroleum ether, R_f = 0.5, colorless liquid, 39.3 mg, 94% yield. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.67 – 7.58 (m, 1H), 7.24 – 7.16 (m, 2H), 7.08 – 7.01 (m, 1H), 2.48 (t, J = 7.1 Hz, 2H), 1.66 – 1.62 (m, 1H), 1.50 (dt, J = 14.8, 7.3 Hz, 2H), 1.28 (s, 1H), 0.97 (t, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 159.46, 157.84, 127.82, 127.61, 127.57, 124.83, 115.26, 115.13, 62.70, 30.66, 29.72, 22.00, 20.01, 13.59. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{FS}^+$: 209.0795; found: 209.0800.



4-((cyclohexylethynyl)thio)benzonitrile 4x

Eluent: EA:PE=1:10, R_f = 0.4, colorless liquid, 44.5 mg, 92% yield. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.60 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 2.68 (s, 1H), 1.92 (d, J = 10.5 Hz, 2H), 1.77 (s, 2H), 1.58 (s, 3H), 1.39 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 141.68, 132.45, 125.49, 118.70, 109.22, 106.77, 62.22, 32.45, 30.64, 25.74, 24.83. **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{NS}^+$: 242.0998; found: 242.0996.

NMR Spectra

