Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Cu(I)-Catalyzed Aerobic Cross-Dehydrogenative Coupling of Terminal Alkynes with Thiols for Construction of Alkynyl Sulfides

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1. General information

Unless otherwise noted, all chemicals were purchased from Sigma Aldrich and used as received without further purification. All operations were carried out in an argon-filled glovebox and Schlenk techniques. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 and compounds were visualized by irradiation with UV light. Column chromatography was carried out on silica gel (200-300 mesh) by elution with appropriate solvent. ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Advance 300 or 400 NMR spectrometer. The spectra were recorded in $CDCl_3$ at room temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0.0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Regioselectivity and stereroselectivity of the product was determined by NMR analysis of the crude product. High resolution mass spectrometry analysis (HR-MS) was performed on a Waters LCT Classic TOF Mass Spectrometer.

EPR Spectroscopy. X-band (9.4 GHz) continuous-wave EPR spectra were recorded under non-saturating, slow-passage conditions using a Bruker Elexsys E500 spectrometer equipped with super high Q cavity. Cryogenic temperatures were achieved and controlled using an Oxford Instruments ESR900 liquid helium cryostat in conjunction with an Oxford Instruments ITC4 temperature controller. Spectrometer settings for the experiment included the following: temperature, 45 K; excitation frequency, 9.4 G; microwave power, 0.05 mW; modulation amplitude, 1 G; modulation frequency, 100 kHz. During the catalytic reactions, 50 µL aliquots were removed from reaction mixtures and immediately frozen at 77 K to stop further reaction, and EPR spectra were acquired at 45 K. The EPR data were analyzed in terms of the standard spin Hamiltonian (Eq. 1):

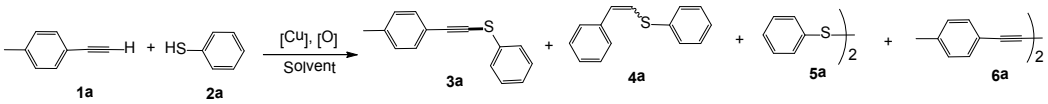
$$H = \beta \mathbf{B} \cdot \vec{g} \cdot \boldsymbol{S} + \boldsymbol{I} \cdot \vec{A} \cdot \boldsymbol{S} \qquad (1)$$

where all parameters have their standard meaning. Simulation of the spectra used the Windows software package SpinCount provided by Prof. Michael P. Hendrich at the Department of Chemistry at Carnegie Mellon University.

2. Typical copper catalyzed oxidative coupling reaction

Typical experimental procedure for the copper-catalyzed oxidative coupling synthesis of alkynyl sulfides: CuCl (5 mol%), K_2CO_3 (10 mol%), 2 mL DMSO were added to a Schlenk tube under argon atmosphere. Then 0.5 mmol alkyne and 0.55 mmol thiol were added using syringe. The tube was sealed with an oxygen balloon, then stirred at 70^{o}C, and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and washed with 1 mM HCl solution, and the aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product.

Table S1. Solvent effect on the oxidative cross-coupling of 4-methylphenylacetylene with thiophenol.[a]

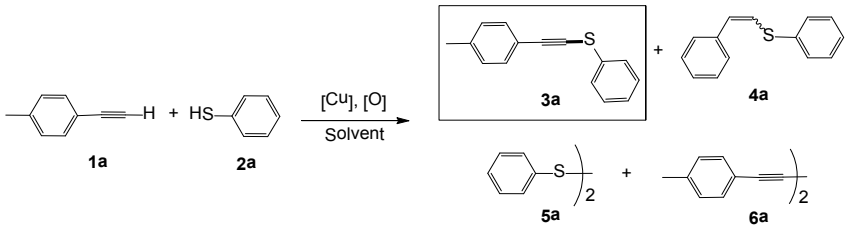


Entry	Solvent	Conv.[%][b]	Yield [%][c]			
			3a	**4a** [*Z*/*E*][d]	**5a**	**6a**
1	DMSO	100	96	2 (100/0)	0	0
2	DMF	100	91	4 (100/0)	0	0
3	Toluene	100	0	72 (24/76)	24	0
4	Hexane	88	0	74 (21/79)	6	0
5	CH_2Cl_2	99	0	80 (57/43)	12	0
6	1,2-DCE	100	0	87 (14/86)	8	0
7	THF	76	0	65 (77/23)	31	0
8	1,4-dioxane	100	0	80 (18/82)	13	0

[a] Reaction conditions: 5 mol% CuCl with respect to 1a, 10 mol% K_2CO_3 with respect to **1a**, 0.5 mmol **1a**, 0.55 mmol **2a**, 2 mL DMSO, 70ºC, 1 atm O_2. [b] Conversion was determined by ^{1}H NMR of the reaction mixture, based on **1a**. [c] NMR yield based on **1a** using CH_2Br_2 as an internal standard. [d] Stereoselecivity was determined by ^{1}H NMR.

Although dimethylformamide (DMF) provided high yield to **3a**, comparable to DMSO; no **3a** was yielded when other solvents, e.g. toluene, hexane, CH_2Cl_2, 1,2-dichloroethane (1,2-DCE), THF, 1,4-dioxane, were employed. These latter solvents exhibited good yield to **4a** with variable stereoselectivity accompanied with the formation of **5a**.

Table S2. Optimization results for Cu-catalyzed oxidative cross-coupling of 4-methylphenylacetylene and thiophenol.[a]



Entry	[Cu]	Base	Conv. [%][b]	Yield [%][c]			
				3a	**4a** [*Z*/*E*][d]	**5a**	**6a**
1	CuBr	K_2CO_3	100	92	4 (100/0)	0	0
2	CuI	K_2CO_3	100	93	2 (100/0)	0	0
3	$CuCl_2$	K_2CO_3	100	93	7 (90/10)	0	0
4	$Cu(NO_3)_2$	K_2CO_3	100	93	8 (85/15)	0	0

[a] Reaction conditions: 5 mol% [Cu] with respect to 1a, 10 mol% base with respect to **1a**, 0.5 mmol **1a**, 0.55 mmol **2a**, 2 mL DMSO, 70ºC, 1 atm O_2, 1 h. [b] Conversion was determined by ^{1}H NMR of the reaction mixture, based on **1a**. [c] NMR yield based on **1a** using CH_2Br_2 as an internal standard. [d] Stereoselecivity was determined by ^{1}H NMR.

Cu^IBr, Cu^II also worked efficiently and selectively afforded **3a** in high yield under otherwise identical reaction conditions (entries 1 and 1). Other copper (II) salts such as $CuCl_2$ and $Cu(NO_3)_2$ displayed similar catalytic performance to copper (I) salts (entries 3 and 4).

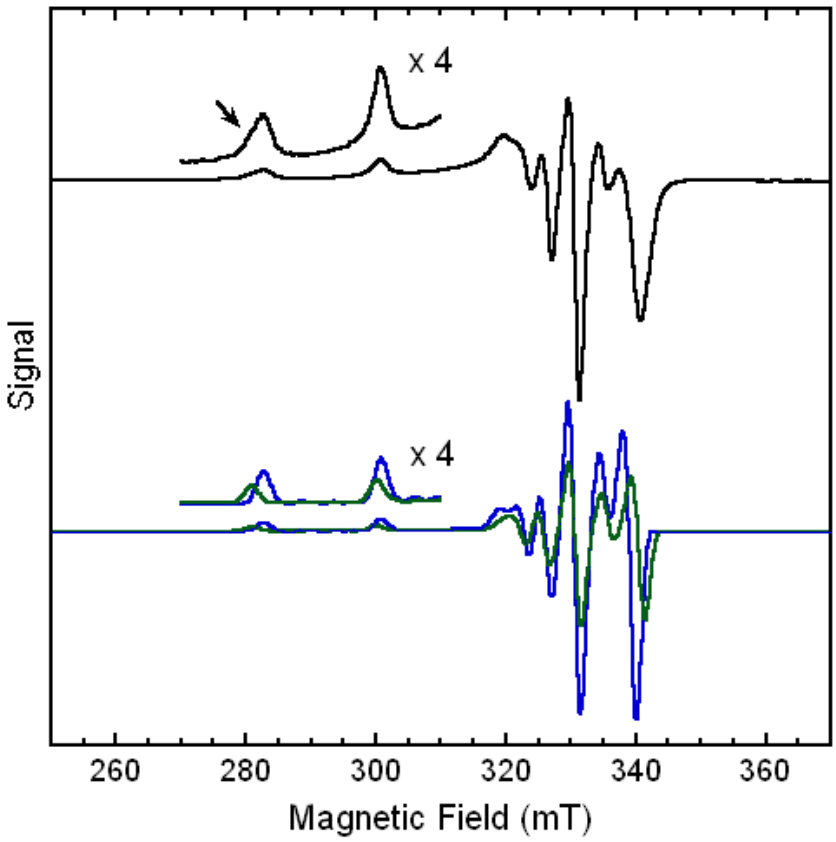


Figure S1. X-band EPR spectrum acquired at 30 min time point of the reaction (black curve), and the spectral simulations using ^{63}Cu (blue curve) and ^{65}Cu (green curve) isotopes. The presence of ^{65}Cu isotope in the experimental data is indicated by the black arrow. Reaction conditions: 5 mol% CuCl, 10 mol% K_2CO_3, 0.5 mmol phenylacetylene, 0.55 mmol thiophenol, 2 mL DMSO, 70°C, 1 atm O_2.

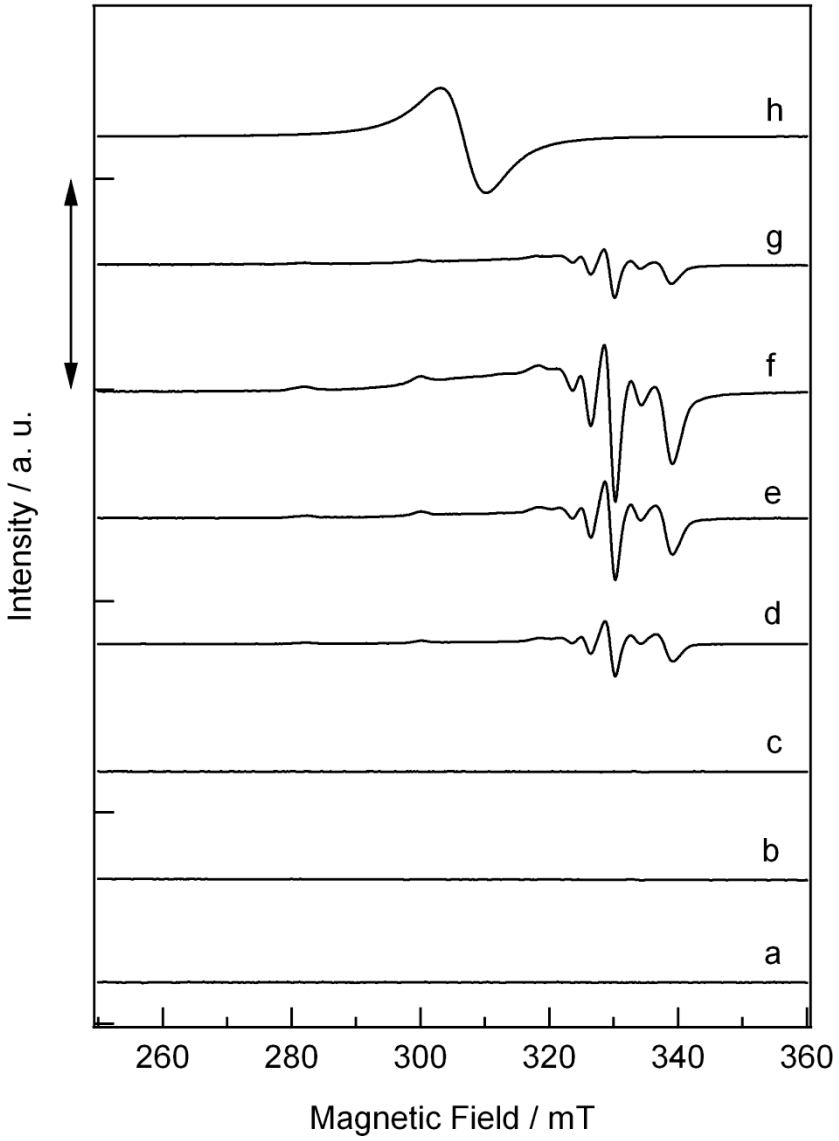
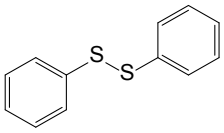
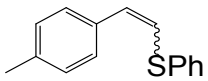


Figure S2. X-band EPR spectra acquired from monitoring the reaction catalyzed by $CuCl_2$ at variable reaction time (a) 0 min; (b) 5 min; (c) 10 min;(d) 20 min; (e) 30 min; (f) 50 min; (g) 60 min; and (h) $CuCl_2$ in DMSO. Reaction conditions: 5 mol% $CuCl_2$, 10 mol% K_2CO_3, 0.5 mmol phenylacetylene, 0.55 mmol thiophenol, 2 mL DMSO, 70°C, 1 atm O_2.

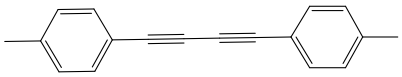
3. ^{1}H / ^{13}C NMR and HR-MS Data for disulfide, vinyl sulfide, diyne, and alkynyl sulfides



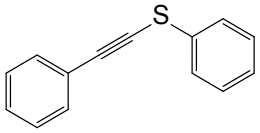
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$): 7.28-7.30 (m, 2H), 7.33-7.38 (m, 4H), 7.55-7.57(d, J = 7.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 127.6, 127.9, 129.6, 137.5. HR-MS (ESI): theoretical, $C_{12}H_{10}S_2$, 218.0244, found 218.0216.



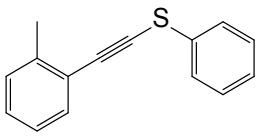
: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, white solid; ^{1}H NMR (400 MHz, $CDCl_3$): 2.39 (s, 3H), 2.42 (s, 3H), 6.51 (d, J = 4.9 Hz, 1H), 6.62 (d, J = 5.0 Hz, 1H), 6. 81 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 5.0 Hz, 1H), 7.19-7.54 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.3, 21.7, 122.3, 125.3, 126.4, 127.5, 127.9, 129.1, 129.4, 129.6, 129.9, 130.4, 132.9, 133.8, 134.2, 136.0, 138.0. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0319.



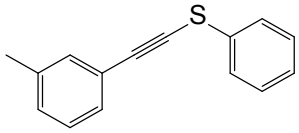
: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 2.41 (s, 6H), 7.17-7.19 (d, J = 8.0 Hz, 4H), 7.44-7.47 (d, J = 8.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 22.1, 73.9, 82.0, 119.2, 127.7 (d), 129.6 (d), 132.8. HR-MS (ESI): theoretical, $C_{18}H_{14}$, 230.1096, found 230.1096.



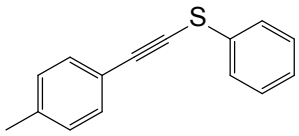
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 7.12-7.24 (m, 1H), 7.39-7.41 (m, 5H), 7.54-7.56(m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 75.9, 98.4, 123.4, 126.6, 127.0, 128.9, 129.1, 129.7, 132.2, 133.4. HR-MS (ESI): theoretical, $C_{14}H_{10}S$, 210.0503, found 210.0497.



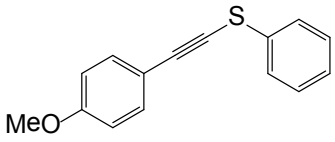
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 2.56 (s, 3H), 7.14-7.29 (m, 4H), 7.39-7.42 (m, 2H), 7.56-7.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.3, 79.3, 97.4, 123.2, 126.1, 126.5, 126.9, 129.1, 129.7, 130.0, 132.6, 133.7, 140.9. HR-MS (ESI): theoretical, $C_{15}H_{12}S$, 224.0660, found 224.0653.



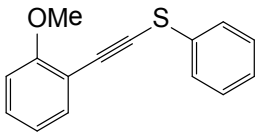
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 2.39 (s, 3H), 7.19-7.21 (d, J = 5.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.37-7.42 (m, 4H), 7.52-7.55 (d, J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.7, 75.4, 98.6, 123.2, 126.6, 126.9, 128.8, 129.3, 129.7, 130.1, 132.8, 133.5, 138.6. HR-MS (ESI): theoretical, $C_{15}H_{12}S$, 224.0660, found 224.0655.



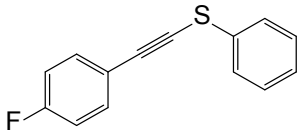
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 2.43 (s, 3H), 7.19-7.40 (m, 3H), 7.43-7.56 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 22.0, 74.9, 98.6, 120.3, 126.6, 126.9, 129.6, 129.7, 132.3, 133.7, 139.5. HR-MS (ESI): theoretical, $C_{15}H_{12}S$, 224.0660, found 224.0669.



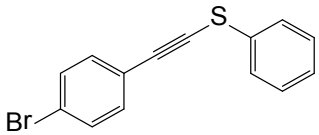
: Purified by column chromatography using SiO_2 gel with hexane) as an eluent, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): 3.85 (s, 3H), 6.89-6.92 (m, 2H), 7.26-7.27 (d, J = 7.2 Hz, 1H), 7.36-7.40 (m, 2H), 7.51-7.53 (d, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 55.8, 74.0, 98.4, 114.5, 115.4, 126.5, 126.8, 129.6, 133.9, 134.2, 160.5. HR-MS (ESI): theoretical, $C_{15}H_{12}OS$, 240.0609, found 240.0607.



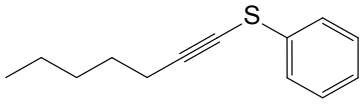
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 3.96 (s, 3H), 6.93-6.98 (m, 2H), 7.23-7.40 (m, 4H), 7.50-7.61 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 56.2, 79.5, 95.1, 111.1, 112.7, 120.9, 126.4, 126.7, 129.6, 130.5, 133.8, 160.7. HR-MS (ESI): theoretical, $C_{15}H_{12}OS$, 240.0609, found 240.0605.



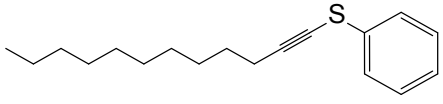
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 7.06-7.09 (m, 2H), 7.28-7.41 (m, 4H), 7.52-7.57 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 75.7, 97.2, 116.1 (d), 126.7 (d), 127.6 (d), 129.5 (d), 133.3, 134.3, 134.4, 137.5. HR-MS (ESI): theoretical, $C_{14}H_9FS$, 228.0409, found 228.0414.



: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$): 7.00-7.02 (m, 1H), 7.29-7.47 (m, 6H), 7.54-7.56 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 75.2, 98.9, 118.5, 123.0, 124.6, 125.4, 127.9, 128.9, 129.8, 132.8. HR-MS (ESI): theoretical, $C_{14}H_9BrS$, 287.9608, found 287.9602.

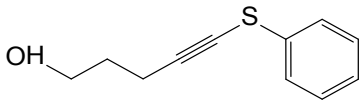


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 0.94 (t, J = 14.1 Hz, 3H), 1.38-1.47 (m, 4H), 1.62-1.67 (t, 2H), 2.48 (t, J = 14.1 Hz, 2H), 7.22-7.28 (m, 1H), 7.31-7.38 (m, 2H), 7.43-7.55 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.4, 20.7, 22.6, 28.8, 31.5, 64.9, 100.6, 126.3 (d), 127.6 (d), 129.5, 134.2, 137.4. HR-MS (ESI): theoretical, $C_{13}H_{16}S$, 204.0973, found 204.0966.

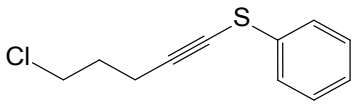


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 0.92 (t, J = 14.1 Hz, 3H), 1.32-

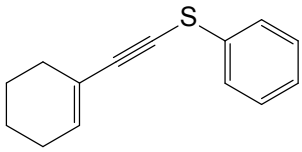
1.48 (m, 14H), 1.58-1.68 (m, 2H), 2.50 (t, J = 14.1 Hz, 2H), 7.21-7.26 (m, 1H), 7.34-7.39 (m, 2H), 7.45-7.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.6, 20.8, 23.2, 29.1, 29.4, 29.6, 29.8, 30.0, 30.1, 32.4, 65.0, 100.6, 126.2, 126.5, 127.9, 129.5, 134.3. HR-MS (ESI): theoretical, $C_{18}H_{26}S$, 274.1755, found 274.1770.



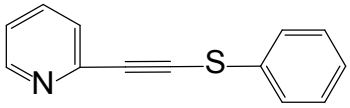
: Purified by column chromatography using SiO_2 gel with CH_2Cl_2 as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 1.83-1.89 (t, J = 12.0 Hz, 2H), 2.58-2.64 (m, 2H), 3.78-3.82 (t, J = 12.0 Hz, 2H), 7.19-7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 17.3, 31.7, 61.9, 65.9, 99.4, 126.3, 126.7, 129.6, 133.8. HR-MS (ESI): theoretical, $C_{11}H_{12}OS$, 192.0609, found 192.0623.



: Purified by column chromatography using SiO_2 gel with CH_2Cl_2 as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 2.04-2.09 (m, 2H), 2.68-2.72 (t, J = 12.0 Hz, 2H), 3.71-3.75 (t, J = 12.0 Hz, 2H), 7.24-7.45 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 18.2, 31.7, 44.1, 66.7, 98.1, 126.3, 126.7, 129.6, 133.7. HR-MS (ESI): theoretical, $C_{11}H_{11}ClS$, 210.0270, found 210.0274.

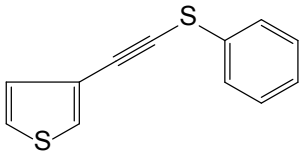


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 1.66-1.72 (m, 4H), 2.18-2.26 (m, 4H), 6.27 (s, 1H), 7.25-7.48 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.9, 22.7, 26.2, 29.6, 72.4, 100.6, 121.1, 126.4 (d), 129.6, 136.7. HR-MS (ESI): theoretical, $C_{14}H_{14}S$, 214.0816, found 214.0822.

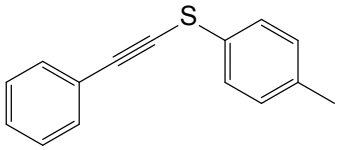


: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 1.66-1.72 (m, 4H), 2.18-2.26 (m, 4H), 6.27 (s, 1H), 7.25-7.48 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.9,

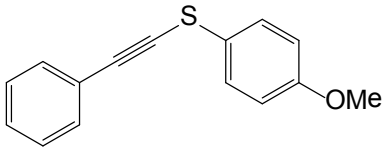
22.7, 26.2, 29.6, 72.4, 100.6, 121.1, 126.4 (d), 129.6, 136.7. HR-MS (ESI): theoretical, $C_{13}H_9NS$, 211.0546, found 211.0587.



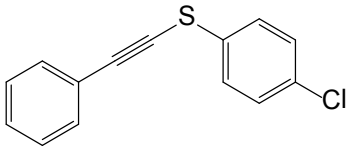
: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, yellow oil, ^1H NMR (300 MHz, $CDCl_3$): 7.24-7.36 (m, 5H), 7.38-7.63 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 75.4, 93.2, 122.4, 125.9, 126.7, 127.0, 129.7, 130.6, 130.7, 133.4. HR-MS (ESI): theoretical, $C_{12}H_8S_2$, 216.0067, found 216.0064.



: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil, ^1H NMR (300 MHz, $CDCl_3$): 2.41 (s, 3H), 7.22-7..24 (d, J = 8.1 Hz, 2H), 7.39-7.44 (m, 5H), 7.56-7.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.5, 76.6, 97.8, 118.8, 123.5, 126.6, 127.0, 128.8, 129.6, 130.5, 137.1. HR-MS (ESI): theoretical, $C_{15}H_{12}S$, 224.0660, found 224.0670.

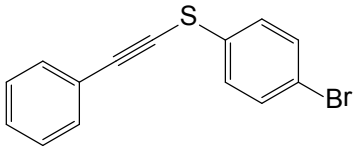


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil; ^1H NMR (300 MHz, $CDCl_3$): 3.83 (s, 3H), 6.94-6.97 (d, J = 8.9 Hz, 2H), 7.36-7.52 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 56.0, . HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 224.0609, 240.0619

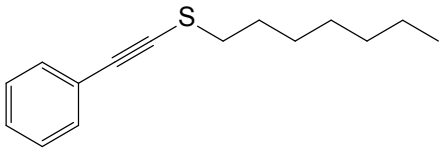


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil; ^1H NMR (300 MHz, $CDCl_3$): 7.04-7.45 (m, 9H). ^{13}C NMR (75 MHz,

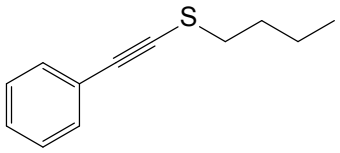
$CDCl_3$): 75.1, 99.2, 127.9, 128.9, 129.3, 129.8, 130.0, 132.3, 134.1, 135.6. HR-MS (ESI): theoretical, $C_{15}H_9ClS$, 244.0113, found 244.0119.



: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): 7.38-7.58 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 75.1, 99.0, 120.7, 123.1, 124.6, 128.2, 128.9, 129.4, 132.3, 132.7. HR-MS (ESI): theoretical, $C_{14}H_9BrS$, 287.9608, found 287.9622.

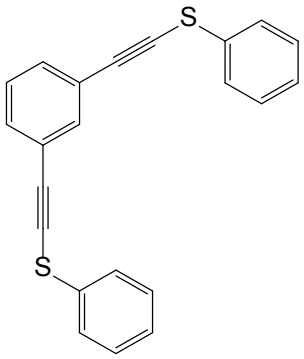


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 0.94 (t, J = 14.6 Hz 3H), 1.35-1.43 (m, 8H), 1.69-1.72 (m, 2H), 2.68-2.84 (t, J = 14.7 Hz, 2H), 7.29-7.58 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5, 23.0, 28.7, 29.6, 31.9, 39.6, 74.4, 82.0, 122.2, 128.6, 129.7, 132.9. HR-MS (ESI): theoretical, $C_{15}H_{20}S$, 232.1286, found 232.1285.

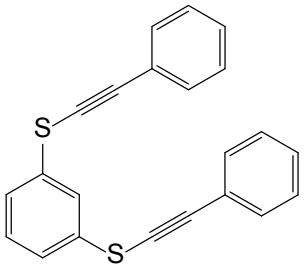


: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 0.94-0.99 (t, J = 14.6 Hz, 3H), 1.42-1.50 (m, 2H), 1.65-1.73 (m, 2H), 2.71-2.76 (t, J = 14.7 Hz, 2H), 7.29-7.42 (m, 3H), 7.56-7.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2, 22.1, 31.7, 39.3, 74.4, 82.0, 122.2, 128.9, 129.7, 132.9. HR-MS (ESI): theoretical, $C_{12}H_{14}S$, 190.0816, found 190.0802.

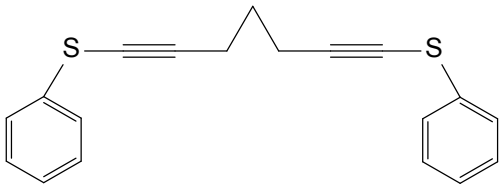
: Purified by column chromatography using SiO_2 gel with hexane as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 0.89-0.97 (t, J = 14.2 Hz, 6H), 1.31-1.68 (m, 12H), 2.23-2.28 (t, J = 14.2 Hz, 2H), 2.69-2.83 (t, J = 14.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.1, 14.4, 19.6, 22.1, 22.6, 28.5, 31.4, 31.7, 39.3, 65.6, 77.9. HR-MS (ESI): theoretical, $C_{11}H_{20}S$, 184.1286, found 184.1292.



: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 7.03-7.56 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$): 74.8, 99.3, 122.9, 123.4, 124.4, 128.8 (d), 129.2, 130.1, 132.2, 135.2. HR-MS (ESI): theoretical, $C_{22}H_{14}S_2$, 342.0537, found 342.0518.



: Purified by column chromatography using SiO_2 gel with hexane/ethyl acetate (10/1, v/v) as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 7.28-7.50 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$):77.2, 97.3, 123.7, 126.7, 127.2, 129.1, 129.7, 131.9, 132.9, 134.9. HR-MS (ESI): theoretical, $C_{22}H_{14}S_2$, 342.0537, found 342.0538.



: Purified by column chromatography using SiO_2 gel with hexane as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 1.89-1.98 (m, 2H), 2.68-2.70 (t, J = 13.7 Hz, 4H), 7.22-7.26 (m, 2H), 7.29-7.36 (m, 4H), 7.39-7.46 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$):19.9, 28.0, 66.3, 98.9, 126.3, 126.7, 129.6, 133.8. HR-MS (ESI): theoretical, $C_{19}H_{16}S_2$, 308.0693, found 308.0578.