Supporting Information

Highly Stereoselective Anti-Markovnikov Hydrothiolation of Alkynes and Electron-Deficient Alkenes by a Supported Cu-NHC Complex

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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 hexane-ethyl acetate. ^{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. Nitrogen physical adsorption was performed on a Micromeritics ASAP-2020 volumetric apparatus at -196^{o}C. Each sample (150 mg) was degassed at 473 K for 3 h before an adsorption measurement. ^{13}C and ^{29}Si solid-state CP-MAS NMR spectra (MAS rate: 5 kHz) were recorded with a Chemagnetics Bruker AV-300 spectrometer operating at 75.5 and 59.7, MHz, respectively. ^{13}C MAS NMR spectra with cross polarization (CP) were acquired with a contact time of 3.0 ms. A cross polarization detection method with hydrogen decoupling was used in ^{29}Si NMR measurements, using a contact time of 4.0 s. The rotor spin rate was 5 kHz, with a delay time of 5 s (^{13}C) or 4 s (^{29}Si). Hexamethylbenzene (^{13}C: 17.4 and 132.2 ppm) and tetrakis-silane (^{29}Si: -9.7 and -135.2 ppm) were used as external standard for the calibration of chemical shifts, respectively. The low-angle powder XRD patterns were recorded at room temperature on an X'Pert PRO X-ray diffractometer with Cu-Kα radiation at 45 kV and 40 mA. The 2θ angles were scanned from 0.5 º to 8º at a rate of 1º/min. High resolution transmission electron microscopy (HR-TEM) was performed on a JEOL JEM-2010F operating at an accelerating voltage of 200 kV. The sample was dispersed in dry ethanol and supported on holey carbon-coated Cu grids. FT-IR spectra were recorded on a Mattson Research Series FTIR spectrometer using a DRIFT cell with a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1}. The sample was mixed and grounded with KBr prior to measurement.

UV/Vis spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer in the range of 200-800 nm. XPS measurements were made with a Kratos Ultra X-ray Photoelectron spectrometer, equipped with Al Kα X-ray source. All binding energy values were calibrated using C1s =284.6 eV. The Cu loading in the supported catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin-Elmer-Optima 5300). A 40% hydrofluoric acid solution was used to dissolve the sample.

2. Preparation of the Cu-NHC-SBA-15 catalyst

a. Preparation of SH-SBA-15

SBA-15 silica was prepared by the method of Stucky et al.[1] After synthesis, the tri-block co-polymer template washing in ethanol, followed by calcination in air at 550°C at 12 h. The silica was stored in scintillation vial under either an air or nitrogen environment. Prior to grafting, the SBA-15 silica (1.5 g) was calcined at 673 K for 4 h under vacuum, and then refluxed in an anhydrous toluene solution of 3-mercapto-propyltriethoxysilane (0.09 mL) at 383 K for 24 h under a N_2 atmosphere. The SBA-15 was filtered by Soxhlet extraction with anhydrous dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as SH-SBA-15 and stored under a N_2 atmosphere.

b. Preparation of Cu-NHC-SBA-15

The immobilization of the homogeneous Cu-NHC complex onto SH-SBA-15 was performed according to a similar approach employed by Jones et al.[2] Assuming all of the 3-mercapto-propyltriethoxysilane (0.323 mmol) grafted to the SBA-15 surface, the –SH groups are ~1.5 fold excess (relative to 2:1 –SH:Cu-NHC molar stoichiometry). An anhydrous toluene solution of Cu-NHC complex (0.09 g, 0.11 mmol) and AIBN (2-2'-azoisobutyronitrile, 12.6 mg) was added to SH-SBA-15 (1.0 g) under a N_2 atmosphere. The resulting mixture was refluxed for 24 h. The solid was filtered by Soxhlet extraction with anhydrous toluene and then dried under vacuum for 24 h. The solid powder was labeled as Cu-NHC-SBA-15 and stored under a N_2 atmosphere. The Cu loading was determined to be 0.69 wt% by ICP-AES analysis, which is equivalent to the nominal loading of Cu based on the quantities of the starting reagents.

c. Preparation of Cu-NHC-SiO_2

The Cu-NHC-SiO_2 catalyst was prepared according to the same procedure as Cu-NHC-SBA-15. Cab-O-Sil fumed silica was chosen as the support. The Cu loading was determined to be 0.71 wt% by ICP-AES analysis.

3. Characterization of the Cu-SBA-15 catalyst

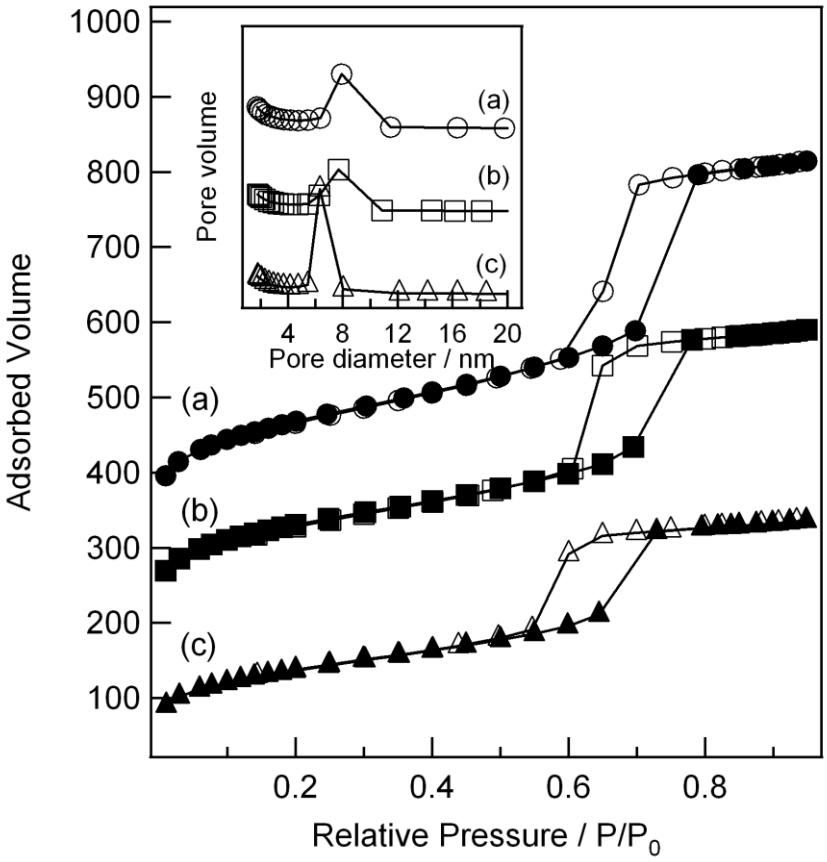


Figure S1. N_2 adsorption-desorption isotherms at -196°C for (a) SBA-15; (b) SH-SBA-15; and (c) Cu-NHC-SBA-15. The inset plot displays their corresponding pore size distribution.

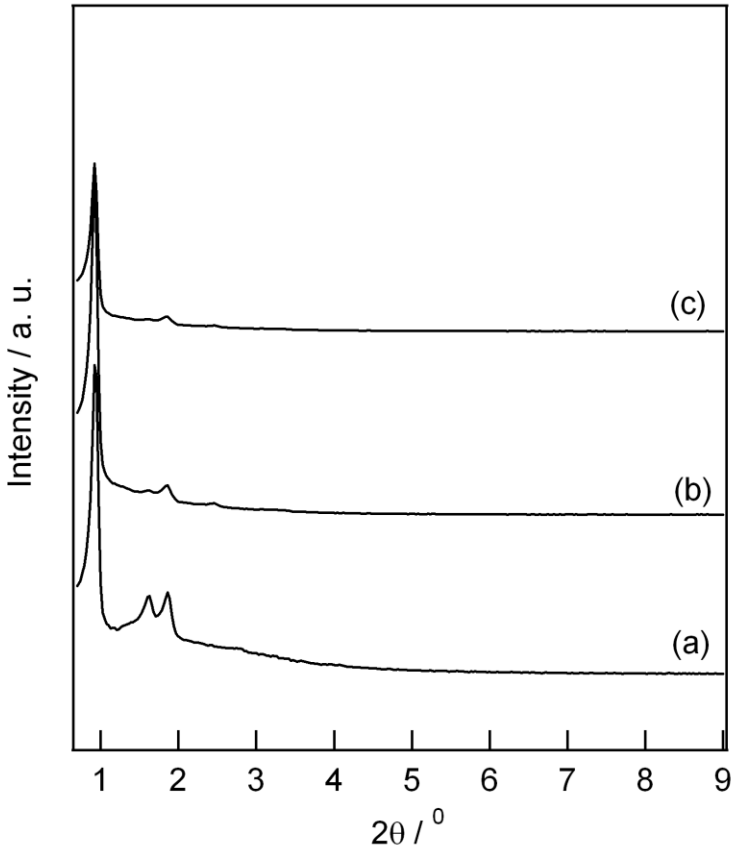


Figure S2. Low-angle XRD pattern of (a) SBA-15; (b) SH-SBA-15; and (c) Cu-NHC-SBA-15.

Table S1. Structural and textual properties of various SBA-15 samples.

Sample	Cu loading (wt%)	d_{100} (Å) [a]	a_0 (Å)[b]	Wall thickness (Å)[c]	S_{BET} (m^2g^{-1})[d]	D_{BJH} (Å)[e]	V_u (cm^3g^{-1})[f]	V_p (cm^3g^{-1})[g]
SBA-15	-	90.8	104.8	40.8	587	64	0.046	0.75
SH-SBA-15	-	94.5	109.3	47.3	469	62	0.031	0.59
Cu-NHC-SBA-15	0.69	95.6	110.3	52.3	327	58	0.013	0.46
Cu-NHC-SiO_2	0.71	-	-	-	166	97	-	0.39

[a] XRD (100) interplanar spacing, $\lambda = 2d_{100}\sin\theta$.

[b] Hexagonal unit cell parameter, $a_0 = \lambda/\sqrt{3}\sin\theta$.

[c] Size of wall thickness, wall thickness = $a_0 - D_{BJH}$.

[d] BET specific surface area.

[e] Mean pore diameter.

[f] Micropore volume.

[g] Total pore volume.

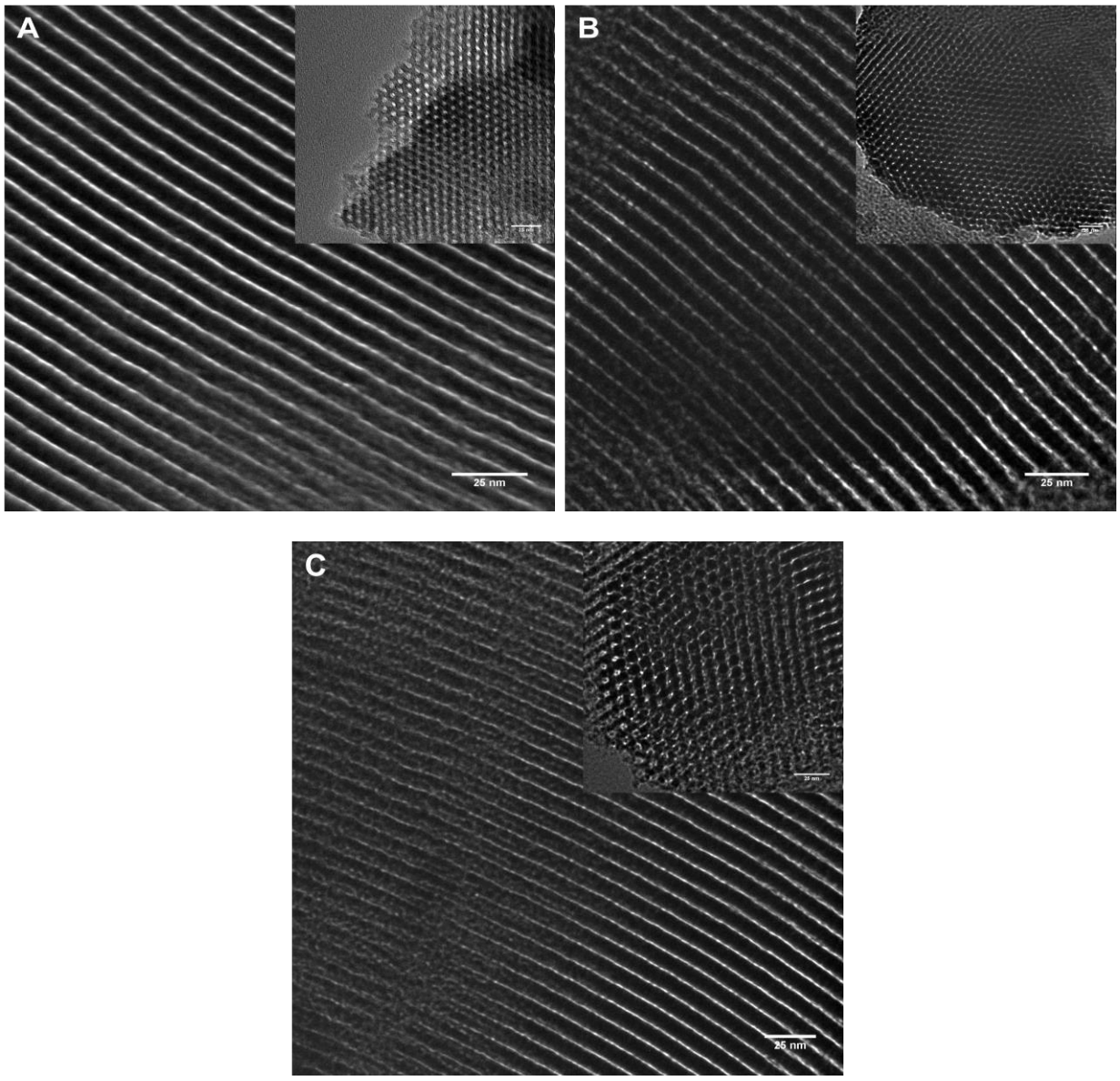


Figure S3. HR-TEM images for (A) SBA-15; (B) SH-SBA-15; and (C) Cu-NHC-SBA-15.

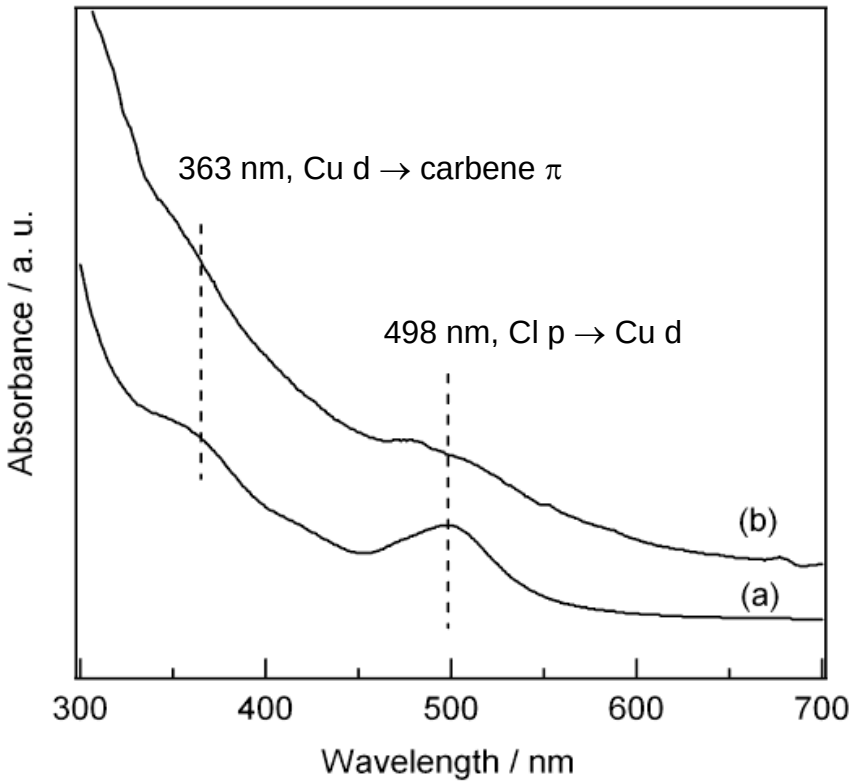
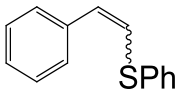
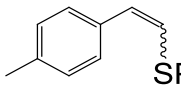


Figure S4. Diffuse-reflectance UV/Vis spectra for (a) Cu-NHC complex and (b) Cu-NHC-SBA-15.

4. $^{1}H/^{13}C$ NMR and HR-MS Data for vinyl sulfides

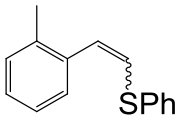


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): 6.61 (d, 1H, major), 6.67 (d, 1H, major), 6.86 (d, minor), 6.96 (d, minor), 7.34-7.64 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): 123.9, 126.5, 127.5, 127.6, 127.7, 127.8, 128.0, 128.8, 129.2, 129.6, 129.7, 130.3, 130.6, 132.2. HR-MS (ESI): theoretical, $C_{14}H_{12}S$, 212.0660, found 212.0487.

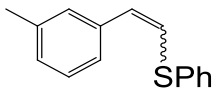


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 2.39 (s, 3H), 2.42 (s, minor), 6.17 (d, 1H, major), 6.51 (d, 1H, major), 6.62 (d, minor), 6.86 (d, minor), 7.19-7.54 (m, 12H). ^{13}C NMR

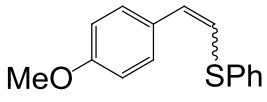
(75 MHz, $CDCl_3$): 21.3, 21.7, 122.3, 125.3, 126.4, 127.5, 127.9, 129.1, 129.4, 129.6, 129.9, 130.4, 132.9, 133.8, 134.2, 136.0, 138.0. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0319.



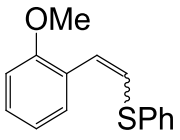
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): 2.49 (s, 3H), 6.37 (d, 1H, major), 6.63 (d, 1H, major), 6.78 (d, minor), 6.86 (d, minor), 7.23-7.66 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.3, 124.7, 125.8, 126.7, 127.5 (d), 128.0 (d), 129.6, 130.0, 130.5 (d), 130.9, 135.6, 135.7, 136.0, 136.6, 137.5. (d). HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0809.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): 2.48 (s, 3H), 2.50 (s, minor), 6.39 (d, 1H, major), 6.58 (d, 1H, major), 6.83 (d, minor), 6.94 (d, minor), 7.10-7.34 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.9, 22.0 (minor), 123.6 (d), 126.2 (d), 127.4 (d), 127.8, 128.9, 129.6 (d), 130.2, 132.6, 135.9, 136.9, 138.4, 138.7. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0786.

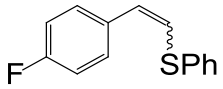


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid, ^1H NMR (300 MHz, $CDCl_3$): 3.84 (s, 3H, major), 3.87 (s, minor), 6.52 (d, 1H, major), 6.61 (d, 1H, major), 6.74 (d, minor), 6.87 (d, minor), 7.27-7.58 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): 55.8, 111.3, 114.6, 120.5, 1121.5, 123.4, 126.2, 127.0, 127.8, 129.5, 129.6 (d), 129.8, 133.2, 136.4, 159.1, 159.8. HR-MS (ESI): theoretical, $C_{15}H_{14}SO$, 242.0765, found 242.0278.

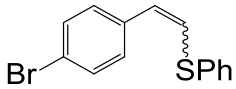


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (18/1, v/v) as an eluent, colorless liquid, ^1H NMR (300 MHz, $CDCl_3$): 3.88 (s, 3H), 6.61 (d, 1H, major), 6.64 (d, 1H, major), 6.95 (d, minor), 7.06 (d, minor), 7.30-7.54 (m, 10H). ^{13}C NMR (75 MHz,

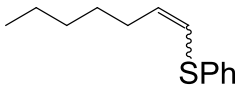
$CDCl_3$): 55.9, 110.9, 111.4, 120.7, 121.2, 123.1, 124.2, 126.5 (d), 127.5 (d), 129.4 (d), 130.3, 136.4, 157.0, 157.1. HR-MS (ESI): theoretical, $C_{15}H_{14}SO$, 242.0765, found 242.0795.



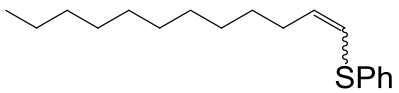
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, ^1H NMR (300 MHz, $CDCl_3$): 6.33 (d, 1H, major), 6.54 (d, 1H, major), 6.79 (d, minor), 6.84 (d, minor), 7.05 (t, 2H), 7.31-7.57 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 114.8(d), 115.9 (d), 122.9, 125.9, 126.7, 127.1, 128.9, 129.5, 129.7, 130.3, 132.5, 134.8, 136.7. HR-MS (ESI): theoretical, $C_{14}H_{11}FS$, 230.0565, found 230.0488.



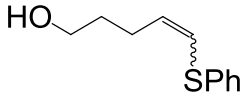
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid, ^1H NMR (300 MHz, $CDCl_3$): 6.29 (d, 1H, major), 6.52 (d, 1H, major), 6.93 (d, minor), 7.23 (d, 2H), 7.32-7.56 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 125.3, 126.3, 127.6, 127.8, 129.5, 129.7, 130.1, 130.7, 131.9, 132.2, 135.3, 136.6. HR-MS (ESI): theoretical, $C_{14}H_{11}BrS$, 289.9765, found 289.9589.



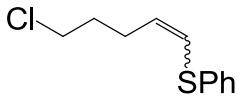
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (18/1, v/v) as an eluent, colorless liquid, ^1H NMR (300 MHz, $CDCl_3$): 0.93 (t, 3H), 1.28-1.48 (m, 4H), 1.92 (d, 2H), 2.19 (q, 2H), 5.84 (d, 1H, major), 6.04 (d, 1H, major), 6.12 (d, minor), 6.16 (d, minor), 7.21-7.37 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.4, 22.9, 29.1, 29.5, 31.7, 31.8, 33.5, 121.0, 122.9, 126.4, 126.5, 128.8, 129.1, 129.3, 134.2, 138.3. HR-MS (ESI): theoretical, $C_{13}H_{18}S$, 206.1129, found 206.1108.



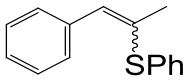
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil, ^1H NMR (300 MHz, $CDCl_3$): 0.91 (t, 3H), 1.32-1.48 (m, 16H), 2.18-2.33 (m, 2H), 5.86 (d, 1H, major), 6.02 (d, 1H, major), 6.07 (d, minor), 6.18 (d, minor), 7.23-7.55 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.6, 23.2, 29.4, 29.6, 29.8, 29.9, 30.1, 32.4, 33.5, 121.1, 122.9, 126.4, 126.5, 127.9, 128.8, 129.1, 129.3, 129.5, 134.2, 138.3. HR-MS (ESI): theoretical, $C_{18}H_{28}S$, 276.1912, found 276.1513.



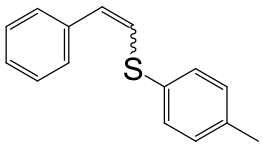
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (18/1, v/v) as an eluent, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): 1.71-1.79 (m, 2H), 2.27-2.38 (m, 2H), 3.53-3.58 (m, 2H), 5.83 (d, 1H, major), 6.02 (d, 1H, major), 6.19 (d, minor), 6.27 (d, minor), 7.25-7.56 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 26.9, 30.5, 32.1, 32.4, 44.6, 44.8, 123.4, 125.2, 126.8, 129.2, 129.4, 129.5, 131.2, 134.5, 136.5. HR-MS (ESI): theoretical, $C_{11}H_{14}OS$, 194.0765, found 194.0801.



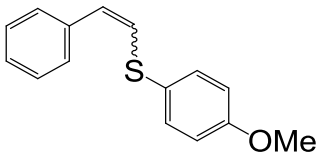
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): 1.89-1.99 (m, 2H), 2.34-2.49 (m, 2H), 3.60-3.64 (m, 2H), 5.79 (d, 1H, major), 5.93 (d, 1H, major), 6.24 (d, minor), 6.32 (d, minor), 7.25-7.56 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 26.9, 30.5, 32.1, 32.4, 44.6, 44.8, 123.4, 125.2, 126.8, 129.2, 129.4, 129.5, 131.2, 134.5, 136.5. HR-MS (ESI): theoretical, $C_{11}H_{13}ClS$, 212.0426, found 212.0411.



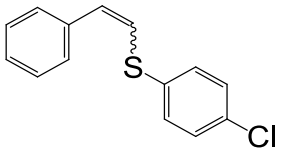
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$): 2.12 (s, minor), 2.23 (s, 3H, major), 6.79 (s, 1H), 7.37-7.71 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.1, 26.2, 127.3, 127.5, 127.6, 128.7, 129.3, 129.5, 129.7, 131.9, 132.6, 134.3, 137.6. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0513.



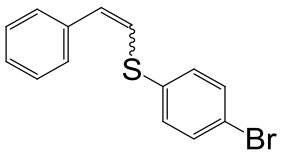
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 2.43 (s, 1H), 6.36 (d, 1H, major), 6.56 (d, 1H, major), 6.75 (d, minor), 6.94 (d, minor), 7.19-7.62 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.6, 124.9, 126.4, 127.5, 127.8, 128.9, 129.1, 130.5, 130.9, 131.1, 137.1, 137.7. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0809.



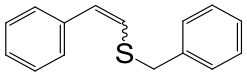
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 3.84 (s, 3H, major), 3.89 (s, minor), 6.23 (d, 1H, major), 6.43 (d, 1H, major), 6.57 (d, minor), 6.89 (d, minor), 6.97 (d, 2H), 7.20-7.41 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): 55.3, 55.8, 115.3, 122.3, 123.8, 124.9, 126.2, 126.3, 127.6, 129.1, 129.4, 129.8, 132.8, 133.9, 136.4, 137.7. HR-MS (ESI): theoretical, $C_{15}H_{14}OS$, 242.0765, found 242.0759.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 6.23 (d, 1H, major), 6.48 (d, major), 6.76 (d, 1H, minor), 6.85 (d, 1H, minor), 7.31-7.59 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 121.3, 122.7, 126.6, 128.3, 128.8, 129.2, 129.8, 131.4, 132.7 (d), 134.4, 135.1, 136.7. HR-MS (ESI): theoretical, $C_{14}H_{11}ClS$, 246.0270, found 246.0259.

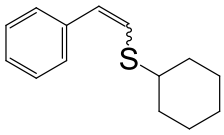


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): 6.44 (d, 1H, major), 6.64 (d, 1H, major), 6.78 (d, minor), 6.84 (d, minor), 7.28-7.55 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): 122.9, 125.6, 126.5, 127.8, 128.3, 129.2, 131.5, 133.2, 135.0, 136.7. HR-MS (ESI): theoretical, $C_{14}H_{11}BrS$, 289.9765, found 289.9682.

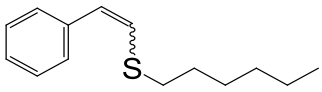


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 4.06 (s, 2H, major), 4.08 (s, minor), 6.33 (d, 2H, major), 6.51 (d, 2H, major), 6.62 (d, minor), 6.80 (d, minor), 7.26-7.56 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 37.8, 39.9, 124.9, 126.1, 126.3, 126.5, 127.2, 127.5, 128.7,

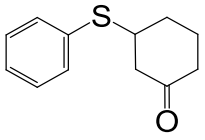
128.9, 129.3, 129.5, 129.9, 137.4, 137.9. HR-MS (ESI): theoretical, $C_{15}H_{14}S$, 226.0816, found 226.0693.



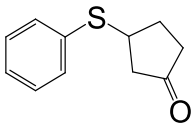
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (40/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 1.30-1.42 (m, 6H), 1.50-1.67 (m, 4H), 2.10 (m, 1H), 6.39 (d, 1H, major), 6.47 (d, 1H, major), 6.65 (d, minor), 6.82 (d, minor), 7.24-7.55 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$):26.1, 26.2, 33.3, 34.1, 45.7, 48.2, 50.4, 124.5, 125.4, 126.0, 127.3, 128.6, 129.1, 137.6. HR-MS (ESI): theoretical, $C_{14}H_{18}S$, 218.1129, found 218.1132.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (40/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 0.97 (t, 3H), 1.38-1.48 (m, 6H), 1.73-1.78 (m, 2H), 2.73-2.88 (m, 2H), 6.31 (d, 1H, major), 6.50 (d, 1H, major), 6.56 (d, minor), 6.80 (d, minor), 7.24-7.58 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$):17.8, 26.5, 32.2, 33.4, 34.2, 36.5, 129.1, 129.4, 130.5, 131.7, 132.2, 132.5, 141.0. HR-MS (ESI): theoretical, $C_{14}H_{20}S$, 220.1286, found 220.1300.

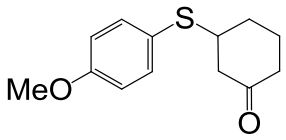


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 1.69-1.75 (m, 2H), 2.09-2.15 (m, 2H), 2.28-2.71 (m, 4H), 3.43 (m, 1H), 7.28-7.43 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 24.4, 31.6, 41.2, 46.95, 48.1, 128.2, 129.5 (d), 133.4, 209.1. HR-MS (ESI): theoretical, $C_{12}H_{14}OS$, 206.0765, found 206.0754.

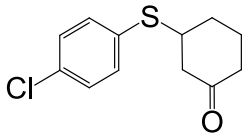


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 2.04 (m, 2H), 2.24-2.61 (m, 4H),

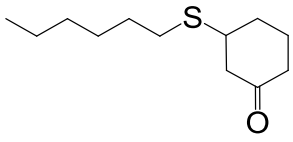
3.92 (m, 1H), 7.31-7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 29.7, 37.2, 43.8, 45.6, 127.8, 129.5 (d), 132.4, 216.8. HR-MS (ESI): theoretical, $C_{11}H_{12}OS$, 192.0609, found 192.0603.



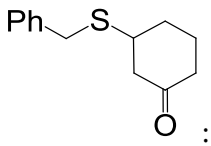
: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 1.62 (t, 2H), 2.12 (m, 2H), 2.25-2.37 (m, 3H), 2.64 (m, 1H), 3.40 (t, 1H), 3.85 (s, 3H), 7.25-7.28 (d, 2H), 7.34-7.50 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 24.3, 31.5, 41.2, 46.8, 47.9, 55.8, 129.6, 132.0, 134.9, 208.7. HR-MS (ESI): theoretical, $C_{13}H_{16}O_2S$, 236.0871, found 236.0876.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): 1.68 (t, 2H), 2.10 (m, 2H), 2.28-2.36 (m, 3H), 2.62 (m, 1H), 3.38 (t, 1H), 7.23-7.26 (d, 2H), 7.31-7.33 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 24.3, 31.5, 41.2, 46.8, 47.9, 129.6, 132.0, 134.9, 208.7. HR-MS (ESI): theoretical, $C_{12}H_{13}ClOS$, 240.0376, found 240.0289.

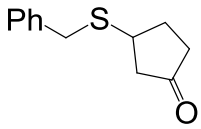


: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, 3H), 1.31 (m, 6H), 1.38 (t, 2H), 1.59 (t, 2H), 2.14 (t, 2H), 2.34 (m, 3H), 2.69 (m, 2H), 2.74 (m, 1H), 3.06 (t, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5, 22.9, 24.7, 29.0, 30.1, 30.9, 31.8, 32.1, 41.4, 43.2, 48.7, 209.4. HR-MS (ESI): theoretical, $C_{12}H_{22}OS$, 214.1391, found 214.1387.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 1.68 (t, 2H), 2.08 (d, 2H), 2.32-2.72 (m, 4H), 2.93 (t, 1H), 3.76 (s, 2H), 7.24-7.32 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 24.5, 31.7,

35.3, 41.4, 42.4, 48.2, 127.6, 129.1 (d), 138.4, 209.1. HR-MS (ESI): theoretical, $C_{13}H_{16}OS$, 220.0922, found 220.0931.



: Purified by column chromatography using SiO_2 gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 1.95-2.32 (m, 4H), 2.39-2.57 (m, 2H), 3.29 (t, 1H), 3.80 (s, 2H), 7.30-7.36 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): 30.0, 36.3, 37.6, 40.1, 45.9, 127.6, 129.1 (d), 138.4, 217.1. HR-MS (ESI): theoretical, $C_{12}H_{14}OS$, 206.0765, found 206.0812.

5. References

[1] D. Y. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024-6036.

[2] K. Q. Yu, C. W. Jones, *Organometallics* **2003**, *22*, 2571-2580.