

General Synthesis of Thiophene and Selenophene-Based Heteroacenes

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Experimental Section

General. Melting point (mp) determination was performed using a Yanaco MP-S3 instrument. ^1H and ^{13}C NMR spectra were measured with a JEOL EX-270 spectrometer, a JEOL A-400 spectrometer, or a VARIAN INOVA-500 spectrometer. IR spectra were measured with a JASCO FTIR 430 spectrometer. Cyclic voltammograms were recorded on a CHI600A instrument. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck) or 0.25 mm thick aluminum oxide 60F-254 (Merck). Column chromatography was performed using a Fuji SiliSia silica gel PSQ60B (60 μm). The starting material **1a**¹ and compounds **2a** and **3a**² are the literature known compounds. Copper nanopowder was purchased from Aldrich. All reactions were carried out under argon atmosphere except where noted.

1,4-Bis(*o*-bromophenyl)diacetylene (1a**).** To a suspension of copper iodide (1.67 mmol, 319 mg) and 0.50 mL of *N,N,N',N'*-tetramethylethylenediamine (3.35 mmol) in 35 mL of acetone was added *o*-bromophenylacetylene (6.06 g, 33.5 mmol). The mixture was stirred at room temperature for 1 h while oxygen gas was bubbled through the solution. After removal of the solvent under reduced pressure, 1N HCl aqueous solution was added and the mixture was extracted with CH_2Cl_2 . The organic layer was washed with water and brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The obtained solid was further washed with hexane to give pure **1a** (5.21 g, 14.5 mmol) in 86% yield: ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.57 (m, 4H), 7.32-7.21 (m, 4H).

1,4-Bis(2-bromo-4-anisyl)diacetylene (1c**).** This compound was prepared from (2-bromo-4-anisyl)acetylene essentially in the same manner as described for **1a** in 94% yield as white solid: mp. 145-147 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 2.4 Hz, 2H), 6.82 (dd, J = 8.8, 2.4 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (67.5 MHz, CDCl_3): δ 160.35, 135.16, 126.99, 117.92, 116.25, 113.61, 80.64, 76.70, 55.71. Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{Br}_2\text{O}_2$: C, 51.46; H, 2.88. Found: C, 51.65; H, 2.83.

1,4-Bis(2-bromo-4-trifluoromethylphenyl)diacetylene (1d). This compound was prepared from (2-bromo-4-trifluoromethylphenyl)acetylene essentially in the same manner as described for **1a** in 92% yield as white solid: mp. 90-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 134.73, 132.06 (q, *J*_{C-F} = 33.3 Hz), 129.62 (q, *J*_{C-F} = 4.1 Hz), 127.48, 126.55, 124.08, 124.04 (q, *J*_{C-F} = 4.1 Hz), 80.81, 79.55. Anal. Calcd for C₁₈H₆Br₂F₆: C, 43.58; H, 1.22. Found: C, 43.76; H, 1.16.

1,4-Bis(3-bromo-5-trimethylsilyl-2-thienyl)diacetylene (1e). This compound was prepared from (3-bromo-5-trimethylsilyl-2-thienyl)acetylene essentially in the same manner as described for **1a** in 73% yield as white solid: mp. 122-124 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.06 (s, 2H), 0.32 (s, 18H). ¹³C NMR (67.5 MHz, CDCl₃): δ 146.28, 136.09, 123.92, 119.37, 82.02, 76.39. MS(EI): m/e 516 (M⁺). Anal. Calcd for C₁₈H₂₀Br₂S₂Si₂: C, 41.86; H, 3.90. Found: C, 41.99; H, 3.93.

1,4-Bis(3-bromo-2-benzothienyl)diacetylene (1f). This compound was prepared from 3-bromo-2-benzothienylacetylene essentially in the same manner as described for **1a** in 73% yield as white solid: mp. 272-273 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.83-7.81 (m, 2H), 7.77-7.76 (m, 2H), 7.51-7.47 (m, 4H). HRMS(EI): 471.8437 (M⁺). Calcd for C₂₀H₈Br₂S₂: 471.8414.

A Typical Procedure of the Intramolecular Triple Cyclization.

Compound 2c. To a solution of compound **1c** (840 mg, 2.0 mmol) in THF (20 mL) was added a pentane solution of *t*-BuLi (1.60 M, 5.0 mL, 8.06 mmol) dropwise at -78 °C. After stirred for 1 h, sulfur (257 mg, 8.0 mmol) was added as a powder under a stream of argon. The mixture was kept at the same temperature for 5 min and then was allowed to warm to room temperature with stirring over 2 h. After concentrated under reduced pressure, 1M sodium hydroxide aqueous solution was added and the mixture was washed with dichloromethane for several times. Potassium ferricyanide(III) was added to the resulting aqueous solution and stirred for 1 h. The mixture was extracted with CH₂Cl₂ and the organic layer was washed with water and brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (1/1 CH₂Cl₂/hexane) to give 380 mg (0.98 mmol) of **2c** in 49% yield as purple powders: mp. 203-205 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 2.4 Hz, 2H), 7.08 (dd, *J* = 8.5, 2.4 Hz, 2H), 3.90 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 158.24, 139.82, 131.69, 131.03, 123.78, 119.04, 115.32, 105.33, 55.72. Anal. Calcd for C₁₈H₁₂O₂S₄: C, 55.64; H, 3.11. Found: C, 55.67; H, 2.99.

Compound 2b. 62% yield as purple powders: mp. 198.5-199.0 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.89-7.86 (m, 4H), 7.49 (td, J = 7.5, 1.0 Hz, 2H), 7.34 (td, J = 8.0, 1.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): 140.85, 140.29, 138.74, 126.90, 125.68, 125.58, 125.49, 116.07. MS(EI): m/e 520 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_8\text{Se}_4$: C, 37.24; H, 1.56. Found: C, 37.31; H, 1.56.

Compound 2d. 47% yield as purple powders: mp. 205-206 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.15 (s, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.98, 138.28, 136.41, 128.16 (q, $J_{\text{C-F}}$ = 33 Hz), 123.95 (q, $J_{\text{C-F}}$ = 142 Hz), 122.66, 122.40 (q, $J_{\text{C-F}}$ = 3.3 Hz), 121.85, 120.30 (q, $J_{\text{C-F}}$ = 4.1 Hz). MS(EI): m/e 464 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_6\text{F}_6\text{S}_4$: C, 46.54; H, 1.30. Found: C, 46.57; H, 1.19.

Compound 2e. 42% yield as yellow powders: mp. 193.5-194.0 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.33 (s, 2H), 0.39 (s, 18H). ^{13}C NMR (67.5 MHz, CDCl_3): δ 145.38, 143.20, 136.86, 132.80, 125.54, 115.79, -0.25. MS(EI): m/e 484 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{S}_6\text{Si}_2$: C, 44.58; H, 4.16. Found: C, 44.35; H, 4.02.

Compound 2f. This compound was purified by recrystallization from *o*-dichlorobenzene. 68% yield as yellow powders: mp. >300 °C. ^1H NMR (500 MHz, 1/9 $\text{CDCl}_3/\text{CS}_2$): δ 7.86-7.80 (m, 4H), 7.47-7.38 (m, 4H). ^{13}C NMR spectrum was not able to obtain due to low solubility. MS(EI): m/e 440 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_8\text{S}_6$: C, 54.51; H, 1.83. Found: C, 54.47; H, 1.90.

Compoun 2g. This compound was purified by recrystallization from *o*-dichlorobenzene. 47% yield as yellow brown powders: mp. >300 °C. ^1H NMR (500 MHz, 1/9 $\text{CDCl}_3/\text{CS}_2$): δ 7.90-7.87 (m, 2H), 7.77-7.74 (m, 2H), 7.48-7.37 (m, 4H). ^{13}C NMR spectrum was not able to obtain due to low solubility. HRMS(EI): 629.6729 (M^+). Calcd for $\text{C}_{20}\text{H}_8\text{S}_2\text{Se}_4$: 629.6736.

A Trapping Experiment of the Dianionic Intermediate 5 with Benzyl Bromide. 3,3'-Bis(benzylthio)-2,2'-bi(benzothiophene) (6). To a solution of 1,4-bis(*o*-bromophenyl)diacetylene (**1a**) (360 mg, 1.0 mmol) in THF (10 mL) was added a pentane solution of *t*-BuLi (1.46 M, 2.74 mL, 4.0 mmol) dropwise at -78 °C. After stirred for 1 h, sulfur (128 mg, 4.0 mmol) was added as a powder. The mixture was kept at the same temperature for 5 min and was allowed to warm to room temperature. After stirring for 2 h, benzyl bromide (262 μL , 2.2 mmol) was added. 1M sodium hydroxide solution was added and the mixture was extracted with CH_2Cl_2 . The organic layer was washed with water and

brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (1/1 CH_2Cl_2 /hexane) to give 350 mg (0.685 mmol) of the bis(benzylthio) compound in 69% as yellow powders: mp. 194 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.00-7.98 (m, 2H), 7.84-7.82 (m, 2H), 7.45-7.42 (m, 4H), 7.12-7.07 (m, 6H), 7.01-6.99 (m, 4H), 3.90 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.29, 139.67, 138.84, 137.35, 128.83, 128.27, 127.09, 126.58, 125.48, 124.76, 123.82, 122.13, 40.63. HRMS(FAB): 511.0669 ($\text{M}+\text{H}^+$). Calcd for $\text{C}_{30}\text{H}_{24}\text{S}_2$: 511.0683.

A Typical Procedure for the Dechalcogenation.

Compound 3c. The mixture of **2c** (219 mg, 0.471 mmol) and copper nanopowder (120 mg, 1.89 mmol) was heated at 240-270 °C for 10 min using a sand bath. The reaction mixture was dissolved with CH_2Cl_2 , and the soluble compounds were collected by filtration with a celite. The filtrate was concentrated under reduced pressure, followed by recrystallization from toluene to give 52.8 mg (0.148 mmol) of **3c** in 58% yield as a colorless crystal: mp. > 300 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 2.2 Hz, 2H), 7.06 (dd, J = 8.8, 2.2 Hz, 2H), 3.92 (s, 6H). ^{13}C NMR spectrum was not able to obtain due to low solubility. IR (KBr): 3013 (w), 2955 (w), 2932 (w), 2831 (w), 1600 (s), 1556 (m), 1474 (s), 1435 (s), 1304 (m), 1268 (s), 1226 (s), 1061 (m), 1030 (s), 868 (s), 814 (s) cm^{-1} . HRMS(EI): 355.9987 (M^+). Calcd for $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}_3$: 355.9999.

Compound 3b. 62% yield as a colorless crystal: mp. > 300 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 7.1 Hz, 2H), 7.82 (d, J = 7.1 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H). ^{13}C NMR (67.5 MHz, 4/1 CS_2 / CDCl_3): δ 148.27, 141.97, 137.93, 137.52, 126.60, 125.35, 124.79, 122.85 (against 77.00 ppm of CDCl_3 peak as a standard). IR (KBr): 3054 (w), 2924 (w), 2923 (m), 2851 (w), 1444 (s), 1338 (s), 1250 (m), 744 (s), 716 (s) cm^{-1} . MS(EI): m/e 438 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_8\text{Se}_4$: C, 43.96; H, 1.84. Found: C, 43.97; H, 1.79.

Compound 3d. 60% yield as a colorless crystal: mp. 270.4-273.0 °C (sublimed). ^1H NMR (400 MHz, CDCl_3): δ 8.21 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, 4/1 CS_2 / CDCl_3): δ 142.09, 137.13, 135.13, 132.43, 127.41, 127.09, 121.94 (q, $J_{\text{C-F}} = 3.3$ Hz), 121.27 (q, $J_{\text{C-F}} = 4.1$ Hz), 120.99 (against 77.00 ppm of CDCl_3 peak as a standard). MS(EI): m/e 432 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_6\text{F}_6\text{S}_3$: C, 50.00; H, 1.40; F, 26.36; S, 22.25. Found: C, 50.15; H, 1.47; F, 26.21; S, 22.13.

Compound 3e. 54% yield as colorless powders: mp. 298.5-300 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 2H), 0.39 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.73, 142.23, 136.66, 134.21, 131.09, 126.70, -0.15. IR (KBr): 3065 (w), 2953 (m), 2923 (m), 2898 (w),

2852 (w), 1463 (m), 1375 (s), 1249 (s), 983 (s), 860 (s), 842 (s), 829 (s) cm^{-1} . MS(EI): m/e 452. (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{S}_5\text{Si}_2$: C, 47.74; H, 4.45. Found: C, 47.72; H, 4.36.

Compound 3f. 81% yield as yellow powders: mp. >300 °C. IR (KBr): 3048 (w), 2922 (m), 2851 (w), 1467 (m), 1447 (m), 1388 (s), 1335 (m), 1297 (m), 1257 (m), 1129 (m), 737 (s), 719 (s) cm^{-1} . MS(EI): m/e 408. Anal. Calcd for $\text{C}_{20}\text{H}_8\text{S}_5$: C, 58.79; H, 1.97. Found: C, 58.79; H, 1.89. ^1H and ^{13}C NMR spectra were not able to obtain due to low solubility.

Compound 3g. 71% yield as yellow powders: mp. >300 °C. IR (KBr): 3046 (w), 2923 (m), 2850 (w), 1465 (m), 1445 (m), 1357 (s), 1298 (m), 1254 (m), 1127 (m), 739 (s), 718 (s) cm^{-1} . HRMS(EI): 549.7570 (M^+). Calcd for $\text{C}_{20}\text{H}_8\text{S}_2\text{Se}_3$: 549.7571. Anal. Calcd for $\text{C}_{20}\text{H}_8\text{S}_2\text{Se}_3$: C, 43.73; H, 1.47. Found: C, 43.75; H, 1.37. ^1H and ^{13}C NMR spectra were not able to obtain due to low solubility.

X-ray Crystal Structure Analysis of 2b and 3a.

Single crystals of **2b** and **3a** suitable for X-ray crystal analysis were obtained by recrystallization from toluene. Intensity data were collected at 173 K on a Rigaku single crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070$ Å) and graphite monochromator. The crystal data for these compounds are summarized in Table S-1. Their structures were solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares on F^2 (SHELXL-97).³ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions.

References

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Table S-1. Crystallographic Data for Compounds **2b** and **3a**.

compound	2b	3a
formula	$C_{16}H_8Se_4$	$C_{16}H_8S_3$
mol weight (g mol ⁻¹)	516.06	296.40
cryst dimens (mm)	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.02
cryst syst	monoclinic	orthorhombic
space group	$P2_1/a$	$Pnma$
a (Å)	12.632(8)	7.933(4)
b (Å)	7.864(4)	26.589(15)
c (Å)	14.964(10)	5.906(3)
α (deg)		
β (deg)	101.258(7)	
γ (deg)		
V (Å ³)	1457.8(15)	1245.9(11)
Z	4	4
D_{calcd} (g cm ⁻³)	2.351	1.580
$F(000)$	960	608
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	10.050	0.573
temp (K)	173(2)	173(2)
no. of measd reflns	8281	6907
no. of ind reflns	2467 ($I > 2\sigma(I)$)	1110 ($I > 2\sigma(I)$)
goodness of fit	1.085	1.218
final R indices		
$R1$	0.0510	0.0417
$wR2$ ($I > 2\sigma(I)$)	0.1309	0.0913

Table S-2. UV-vis Absorption Spectral Data for Fused 1,2-Dichalcogenins **2** and Heteroacenes **3**

cmpd	$\lambda_{\text{max}} / \text{nm}$ ($\log \epsilon$) ^a
2a	468 (3.41), 338 (4.25)
2b	498 (2.12), 366 (4.20)
2c	473 (3.56), 357 (4.46)
2d	471 (3.49), 334 (4.36)
2e	473 (3.81), 347 (4.40)
2f	480 (3.99), 343 (4.42)
2g	516 (3.51), 379 (4.18)
3a	344 (4.51), 327 (4.56)
3b	356 (4.56), 340 (4.59)
3c	356 (4.43), 340 (4.41), 321 (4.20)
3d	350 (4.59), 332 (4.62)
3e	370 (4.65), 354 (4.69), 337 (4.46), 323 (4.42)
3f^b	399 (3.98), 378 (3.93)
3g^b	418 (3.08), 394 (3.04)

^aIn THF, unless otherwise stated. ^bIn CS₂.