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Highly (*Z*)-Selective Hydrosilylation of Terminal Alkynes Catalyzed by a Diphosphinidenecyclobutene-Coordinated Ruthenium Complex: Application to the Synthesis of (*Z*,*Z*)-Bis(2-bromoethenyl)arenes

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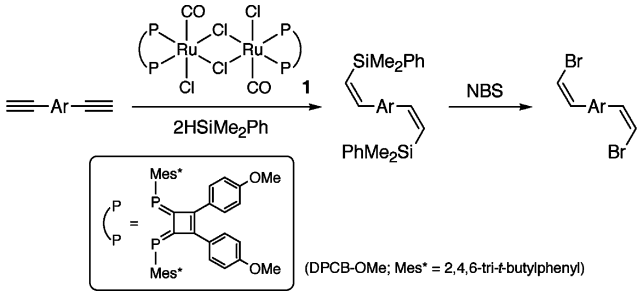

Complex **1** bearing a diphosphinidenecyclobutene ligand (DPCB-OMe) catalyzes highly stereoselective hydrosilylation of diethynylarenes with $HSiMe_2Ph$ to afford (*Z*,*Z*)-bis(2-silylethenyl)arenes. Treatment of the hydrosilylation products with *N*-bromosuccinimide causes bromodesilylation in a stereospecific manner, giving (*Z*,*Z*)-bis(2-bromoethenyl)arenes in high geometrical purity (>98%).

Introduction

Poly(phenylene vinylene) (PPV) and its analogues have found wide application in light-emitting diodes (LEDs), lasers, and solar cells.[1] We have reported that *cis*-PPV having (*Z*)-vinylene units in the polymer backbone exhibits a unique photochemical property that enables microscale patterning of PPV onto a quartz substrate in an extremely simple procedure.[2] This phenomenon, which should be useful for constructing functional materials used in optoelectronics, takes place only when the vinylene units are highly stereoregulated to (*Z*)-geometry. Since *cis*-PPV is prepared by palladium-catalyzed polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)benzene with benzenediboronic acid, the stereoregularity of *cis*-PPV depends heavily on the geometrical purity of starting dibromide.

Several methods have been reported for the preparation of (*Z*)-bromoalkenes, e.g., stereoselective hydrogenolysis of 1,1-dibromoalkenes,[3] Wittig-type condensations,[4] (*Z*)-selective hydrogenation of 1-bromoalkynes,[5] and carboxyl-bromo-elimination from bromine adducts of cinnamic acid derivatives.[6] Although these methods have proven to be effective for the synthesis of monofunctional bromoalkenes, their application to bifunctional homologues such as (*Z*,*Z*)-bis(2-bromoethenyl)benzene has remained almost unexplored.[7] Herein, we report that (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**4**) are successfully prepared by (*Z*,*Z*)-selective hydrosilylation of diethynylarenes (**2**) catalyzed by **1**, followed by bromodesilylation of the hydrosilylation products (**3**) (Scheme 1). (*Z*)-Selective hydrosilylation of simple alkynes such as phenylacetylene and 1-octyne has been accomplished by rhodium and ruthenium catalysts.[8] However, none of them provide sufficient results for (*Z*,*Z*)-selective double hydrosilylation

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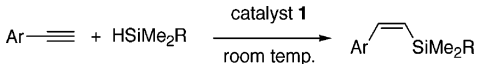
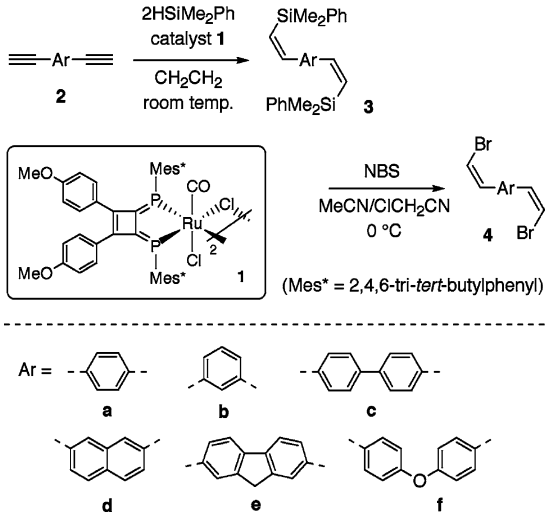
TABLE 1. Hydrosilylation of Terminal Alkynes Catalyzed by 1[a]



run	Ar	R	solvent	time, min	yield,[b] %	product ratio [(*Z*)/(*E*)/*gem*][c]
1	Ph	Ph	CH_2Cl_2	10	91 (100)	98/1/1
2	Ph	Ph	toluene	30	− (100)	98/1/1
3	Ph	Ph	THF	60	− (10)	87/7/6
4	Ph	Ph	DMF	60	− (24)	84/9/7
5	Ph	4-$MeOC_6H_4$	CH_2Cl_2	10	81	94/2/4
6	Ph	3,5-$(CF_3)_2C_6H_3$	CH_2Cl_2	10	92	100/0/0
7	4-$MeO_2CC_6H_4$	Ph	CH_2Cl_2	180	92	97/1/2
8	4-$MeCOC_6H_4$	Ph	CH_2Cl_2	180	99	98/1/1
9	4-BrC_6H_4	Ph	CH_2Cl_2	10	96	98/0/2
10[d]	4-$CF_3C_6H_4$	Ph	toluene	300	91	97/1/2
11[d]	4-MeC_6H_4	Ph	toluene	30	94	100/0/0
12[e]	4-$MeOC_6H_4$	Ph	toluene	120	91	99/1/0
13[e]	2-MeC_6H_4	Ph	toluene	60	89	94/1/5
14[e]	*n*-C_6H_{13}	Ph	toluene	300	90	100/0/0

[a] Reactions were run at room temperature with ArC≡CH (1.05 mmol), $HSiMe_2R$ (1 mmol), **1** (0.25 mol %), and solvent (1 mL), unless otherwise noted. [b] Isolated yield based on the amount of hydrosilane initially employed. Values in parentheses are GLC yields determined by using tridecane as an internal standard. [c] Determined by ^1H NMR spectroscopy. [d] 0.5 mol % of **1** was used. [e] 1 mol % of **1** was used.

SCHEME 1



of diethynylarenes.[9] Therefore, we tested several ruthenium catalysts and found complex **1** bearing an sp^2-hybridized phosphorus ligand[10] to exhibit extremely high selectivity and reactivity. The synthesis of **4a** and **4b** was briefly described previously.[2] This paper reports full details including those results.

Results and Discussion

(*Z*)-Selective Hydrosilylation of Terminal Alkynes. The reaction conditions were optimized with use of phenylacetylenes as substrates (Table 1). The reaction of PhC≡CH with $HSiMe_2Ph$ (0.95 equiv) in CH_2Cl_2 in the presence of **1** (0.25 mol %) was completed within 10 min at room temperature, giving (*Z*)-PhCH=CHSiMe_2Ph in 98% selectivity, together with small amounts of (*E*) and geminal (*gem*) isomers, (*E*)-PhCH=CHSiMe_2Ph and Ph(PhMe_2Si)C=CH_2, respectively (run 1). A comparable result was obtained with toluene as a solvent (run 2). There is a tendency that CH_2Cl_2 provides higher reactivity, whereas toluene gives better selectivity. THF and DMF caused a notable drop in both selectivity and reactivity (runs 3 and 4). The selectivity was also lowered when $HSiMe_2(C_6H_4OMe\text{-}4)$ having an electron-donating substituent was used instead of $HSiMe_2Ph$ (run 5). On the other hand, $HSiMe_2[C_6H_3(CF_3)_2\text{-}3,5]$ bearing electron-withdrawing CF_3 groups afforded (*Z*)-styrylsilane in almost perfect selectivity (run 6). The hydrosilylation did not proceed with alkoxysilanes such as $HSi(OEt)_3$ and $HSiMe_2(OEt)$. Under optimal conditions, a variety of para-substituted phenylacetylenes were hydrosilylated in over 97% selectivity (runs 7−12). Moreover, (2-methylphenyl)acetylene and 1-octyne were converted to the corresponding (*Z*)-alkenylsilanes in 94% and 100% selectivities, respectively (runs 13 and 14).

All reactions listed in Table 1 were carried out with a slight excess of alkyne to hydrosilane ([alkyne]/[hydrosilane] = 1.05). This condition was essential to obtain (*Z*)-hydrosilylation products in high selectivity. Thus, the reaction of PhC≡CH with 1.05 equiv of $HSiMe_2Ph$ under otherwise the same conditions as run 1 formed a 45:54:1 mixture of (*Z*)-, (*E*)-, and *gem*-isomers. An elongated reaction time led to a further drop in the (*Z*)-selectivity. This is due to the occurrence of cis−trans isomerization of styrylsilane, as confirmed by ^1H NMR observation of the reaction system. It was also confirmed that the isomerization is effectively suppressed by addition of free phenylacetylene to the system.

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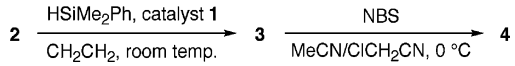
(9) (a) It has been reported that the reaction of **2a** with $HSiMe_2Ph$ catalyzed by $RhI(PPh_3)_3$ forms **3a** in 65% yield and 92% selectivity.[8c] (b) The same reaction with $RuCl_2(CO)(PPr^i_3)_2$ as a catalyst affords **3a** in 40% yield and 91% selectivity.[8e]

(10) (a) 1,2-Bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*tert*-butylphenylphosphinidene)cyclobutene (DPCB-OMe): Ozawa, F.; Kawagishi, S.; Ishiyama, T.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1325. (b) The synthesis of **1** has been reported as Supporting Information for ref 2.

TABLE 2. Synthesis of Bis(2-bromoethenyl)arenes[a,b]



		2 → 3		3 → 4	
run	2	time, min	yield,[c] % [(Z)/(E)/gem]	time, h	yield,[d] % [(Z)/(E)]
1	**2a**	10	88 [98.5/0.5/1]	2	70 [>99/1]
2	**2b**	30	92 [97/1/2]	6	{77 [>99/1]}[e]
3	**2c**	30	88 [99/0.5/0.5]	2	66 [>99/1]
4	**2d**	30	87 [97.5/1.5/1]	2	59 [99/1]
5	**2e**	30	96 [98/1.5/0.5]	1	{62 [>99/1]}[e]
6	**2f**	30	91 [98/1.5/0.5]	2	66 [98/2]

[a] Hydrosilylation was performed in CH_2Cl_2 at room temperature with **2** (1.03−1.05 mmol), $HSiMe_2Ph$ (2 mmol), and **1** (5.0 μmol, 0.5 mol %). [b] Bromodesilylation of **3** was carried out with 12 equiv of NBS in MeCN/$ClCH_2CN$ (9/1) at 0 °C. [c] Isolated yield based on the amount of $HSiMe_2Ph$ initially employed. [d] Isolated yield based on **3**. [e] Yield and purity after recycle GPC purification of the product.

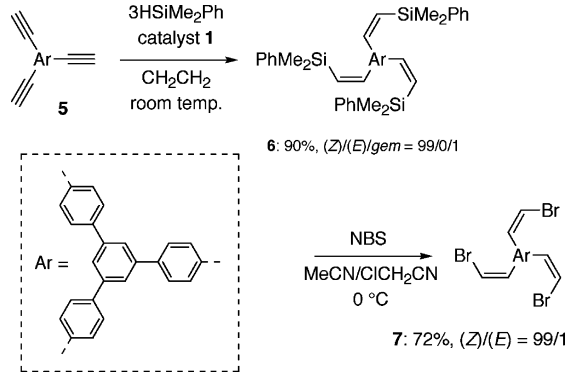
Synthesis of (*Z*,*Z*)-Bis(2-bromoethenyl)arenes. Accordingly, catalytic hydrosilylation of six kinds of diethynylarenes (**2**, Scheme 1) was examined in CH_2Cl_2, using 1.9 equiv of $HSiMe_2Ph$ and 0.5 mol % of **1** (Table 2). All reactions proceeded at room temperature to give bis(2-silylethenyl)arenes (**3**) in over 97% (*Z*)-selectivity. Although the geometrical purity of **3** could be further improved by recrystallization or recycle GPC, they were subjected to bromodesilylation without purification.

Bromodesilylation of **3** was carried out referring to the procedure for iododesilylation of alkenylsilanes.[11] Compound **3a** with 98.5% (*Z*)-content was treated with excess *N*-bromosuccinimide (NBS, 12 equiv) in a mixed solvent of MeCN and $ClCH_2CN$ (9/1) at 0 °C for 2 h. The reaction was quenched with aqueous $Na_2S_2O_3$, extracted with $CHCl_3$, washed with aqueous NaOH, and concentrated to dryness. Recrystallization of the resulting solid from cold MeOH afforded a white crystalline solid of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene (**4a**) in 70% yield, which was sufficiently pure for NMR and elemental analysis (run 1 in Table 2). In this procedure, the geminal isomer of **3a** was unreactive toward NBS, and readily removed from the product by recrystallization. Compounds **4c**, **4d**, and **4f** were similarly obtained as white solids in high purity. Compounds **4b** and **4e** were purified by recycle GPC. Accordingly, six kinds of bis(2-bromoethenyl)arenes (**4a**−**f**) were isolated in over 98% geometrical purity.

In a previous study,[2] we showed the synthesis of **4a** and **4b** using $HSiMe_2(C_6H_4OMe\text{-}4)$ instead of $HSiMe_2Ph$. However, we found later that the hydrosilylation with $HSiMe_2(C_6H_4OMe\text{-}4)$ is rather sensitive to reaction conditions and involves a reproducibility problem. The hydrosilylation reactions with $HSiMe_2Ph$ are more reliable, yielding hydrosilylation products in high stereoselectivities.

Finally, (*Z*,*Z*,*Z*)-1,3,5-tris[4-(2-bromoethenyl)phenyl]-benzene (**7**) was prepared by the present synthetic route (Scheme 2). The reaction of 1,3,5-tris(4-ethynylphenyl)-benzene (**5**) with $HSiMe_2Ph$ (2.85 equiv) in CH_2Cl_2 in the presence of **1** (0.5 mol %) proceeded at room temperature in 30 min to give 1,3,5-tris[4-(2-silylethenyl)phenyl]-benzene (**6**, (*Z*)/(*E*)/*gem* = 99/0/1) in 90% yield. This product was subsequently treated with NBS (18 equiv) in MeCN/$ClCH_2CN$ (9/1) at 0 °C for 2 h. The desired product **7** ((*Z*)/(*E*) = 99/1) was isolated in 72% yield (61% based on **5**).

SCHEME 2



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Conclusion

The diphosphinidenecyclobutene-coordinated ruthenium complex **1** has proven to be a highly effective catalyst for (*Z*)-selective hydrosilylation of terminal alkynes. The successive hydrosilylation of ethynyl groups in di- and triethynylarenes (**2** and **5**, respectively) could be performed in over 97% (*Z*)-selectivity. The hydrosilylation products were readily converted to the corresponding (*Z*)-bromoalkenes without loss of geometrical purity. The overall process provides an efficient approach to (*Z*,*Z*)-bis- and (*Z*,*Z*,*Z*)-tris(2-bromoethenyl)arenes. Application of this highly stereoselective route to the synthesis of all-cis poly(arylene vinylene)s will be reported elsewhere.

Experimental Section

The diphosphinidenecyclobutene complex **1** is stable toward air. However, since this complex has a strong affinity for water to lose catalytic activity and selectivity, the hydrosilylation reactions were carried out under an atmosphere of dry nitrogen.

Hydrosilylation of Phenylacetylene (run 1, Table 1). To a solution of phenylacetylene (108 mg, 1.05 mmol) and **1** (5.1 mg, 2.5 μmol) in CH_2Cl_2 (1.0 mL) was added $HSiMe_2Ph$ (137 mg, 1.00 mmol) at room temperature. The color quickly changed from red to deep red with gentle generation of heat. The solution was stirred for 10 min. The solvent was removed by pumping, and the resulting dark red oil was purified by flash chromatography (hexane) to give $PhCH{=}CHSiMe_2Ph$[8d] as a colorless oil (217 mg, 91%; (*Z*):(*E*):*gem* = 98:1:1). Identification of the products given in Table 1 is reported as Supporting Information.

Synthesis of (*Z*,*Z*)-Bis(2-silylethenyl)arenes (3) (Table 2). A typical procedure is reported for the synthesis of **3c** in run 3. To a solution of 4,4′-diethynylbiphenyl (**2c**, 106 mg, 052 mmol) and **1** (5.1 mg, 2.5 μmol) in CH_2Cl_2 (1 mL) was added $HSiMe_2Ph$ (138 mg, 1.01 mmol) at room temperature. The deep red solution was stirred for 30 min and concentrated to dryness. The resulting dark red oil was purified by flash chromatography (hexane/CH_2Cl_2 = 10/1) to give **3c** as a white solid (214 mg, 88%; (*Z*):(*E*):*gem* = 99:0.5:0.5).

(*Z*,*Z*)-1,4-Bis[2-(dimethylphenylsilyl)ethenyl]benzene (3a).[8c] White solid. R_f 0.25 (hexane/CH_2Cl_2 = 20/1). Mp 60 °C. ^1H NMR ($CDCl_3$): δ 7.55−7.51 (m, 4H), 7.42 (d, *J* = 15.2 Hz, 2H), 7.39−7.32 (m, 6H), 7.08 (s, 4H), 5.98 (d, *J* =

15.2 Hz, 2H), 0.26 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 147.6, 139.6, 138.8, 133.7, 130.3, 128.8, 127.8, −1.1. Anal. Calcd for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.29; H, 7.59.

(*Z*,*Z*)-1,4-Bis[2-(dimethylphenylsilyl)ethenyl]benzene (3b). Colorless oil. R_f 0.35 (hexane/CH_2Cl_2 = 10/1). ^{1}H NMR ($CDCl_3$): δ 7.57−7.48 (m, 4H), 7.38 (d, J = 15.2 Hz, 2H), 7.37−7.24 (m, 6H), 7.10−7.02 (m, 4H), 5.99 (d, J = 15.2 Hz, 2H), 0.26 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 147.7, 139.6, 139.2, 133.7, 130.4, 128.8, 128.6, 127.8, 127.3, 127.1, −1.1. MS, *m/z* (rel intensity, %): 398 (M^+, 4), 383 (2), 320 (16), 305 (7), 263 (25), 247 (28), 227 (13), 145 (20), 135(100), 121 (39), 105 (17), 73 (9), 59 (42), 43 (58). Anal. Calcd for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.58; H, 7.63.

(*Z*,*Z*)-4,4′-Bis[2-(dimethylphenylsilyl)ethenyl]biphenyl (3c). White solid. R_f 0.34 (hexane/CH_2Cl_2 = 10/1). Mp 91 °C. ^{1}H NMR ($CDCl_3$): δ 7.58−7.53 (m, 4H), 7.49 (d, J = 15.0 Hz, 2H), 7.37−7.32 (m, 6H), 7.43 (d, J = 8.2 Hz, 4H), 7.27 (d, J = 7.3 Hz, 4H), 6.03 (d, J = 15.0 Hz, 2H), 0.31 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 147.5, 139.6, 139.5, 138.5, 133.7, 130.2, 128.9, 128.8, 127.9, 126.3, −1.1. Anal. Calcd for $C_{32}H_{34}Si_2$: C, 80.95; H,7.22. Found: C, 80.88; H, 7.28.

(*Z*,*Z*)-2,7-Bis[2-(dimethylphenylsilyl)ethenyl]naphthalene (3d). Colorless oil. R_f 0.33 (hexane/CH_2Cl_2 = 10/1). ^{1}H NMR ($CDCl_3$): δ 7.62 (s, 2H), 7.60−7.53 (m, 6H), 7.35−7.29 (m, 8H), 6.07 (d, J = 15.2 Hz, 2H), 0.27 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 147.9, 139.6, 137.4, 133.7, 132.6, 132.0, 130.8, 128.9, 127.9, 127.7, 127.4, 127.1, −1.0. Anal. Calcd for $C_{30}H_{32}Si_2$: C, 80.30; H, 7.19. Found: C, 80.29; H, 7.25.

(*Z*,*Z*)-2,7-Bis[2-(dimethylphenylsilyl)ethenyl]fluorene (3e). Pale yellow solid. Mp 52 °C. ^{1}H NMR ($CDCl_3$): δ 7.62−7.55 (m, 6H), 7.55 (d, J = 15.0 Hz, 2H), 7.40−7.33 (m, 8H), 7.25 (d, J = 8.4 Hz, 2H), 6.02 (d, J = 15.0 Hz, 2H), 3.66 (s, 2H), 0.32 (s, 12H). ^{13}C NMR: δ 148.2, 143.1, 140.8, 139.7, 138.2, 133.7, 129.7, 128.8, 127.8, 127.2, 124.9, 119.2, 36.5, −1.1. Anal. Calcd for $C_{33}H_{34}Si_2$: C, 81.42; H, 7.04. Found: C, 81.19; H, 7.27.

(*Z*,*Z*)-4,4′-Bis[2-(dimethylphenylsilyl)ethenyl]biphenyl Ether (3f). Colorless oil. R_f 0.20 (hexane/CH_2Cl_2 = 10/1). ^{1}H NMR ($CDCl_3$): δ 7.53−7.50 (m, 4H), 7.44 (d, J = 15.2 Hz, 2H), 7.32−7.28 (m, 6H), 7.15 (d, J = 8.4 Hz, 4H), 6.76 (d, J = 8.4 Hz, 4H), 5.96 (d, J = 15.2 Hz, 2H), 0.30 (s, 12H). ^{13}C NMR: δ 156.5, 147.2, 139.4, 133.7, 129.7, 129.4, 128.8, 127.8, 118.1, −1.0. Anal. Calcd for $C_{32}H_{34}OSi_2$: C, 78.31; H, 6.98. Found: C, 78.05; H, 7.08.

Synthesis of (*Z*,*Z*)-Bis(2-bromoethenyl)arenes (4) (Table 2). A typical procedure for the synthesis of **4c** (run 3) is as follows. *N*-Bromosuccinimide (1.17 g, 6.6 mmol) was added to a suspension of **3c** (261 mg, 0.55 mmol) in CH_3CN (10 mL) and $ClCH_2CN$ (1 mL) at 0 °C. The mixture was stirred for 2 h, and then poured into aqueous $Na_2S_2O_3$ solution (10%, 150 mL) at 0 °C. The solution was extracted with $CHCl_3$ (3 × 100 mL), and the combined organic layer was washed with 1 N NaOH (2 × 100 mL) and brine (100 mL), dried over $MgSO_4$, and then concentrated to dryness. The pale yellow solid thus obtained was dissolved in MeOH (1 mL) and Et_2O (5.5 mL) at room temperature, and allowed to stand at −25 °C to give **4c** as white crystals (132 mg, 66%; (*Z*):(*E*) > 99:1). Compounds **4a** and **4b** have been reported previously.[2] The data for **4c**−**f** are as follows.

(*Z*,*Z*)-4,4′-Bis(2-bromoethenyl)biphenyl (4c). Pale yellow solid. Mp 109 °C. ^{1}H NMR ($CDCl_3$): δ 7.79 (d, J = 8.1 Hz, 4H), 7.64 (d, J = 8.1 Hz, 4H), 7.11 (d, J = 8.1 Hz, 2H), 6.47 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 140.3, 134.1, 131.8, 129.4, 126.7, 106.6. MS, *m/z* (rel intensity, %): 366 (M^+ + 2, 50), 364 (M^+, 100), 362 (M^+ − 2, 53), 285 (9), 283 (9), 202 (57), 176 (17), 152 (9), 102 (49), 88 (32), 76 (30), 63 (13), 51 (13). Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.97; H, 3.52.

(*Z*,*Z*)-2,7-Bis(2-bromoethenyl)naphthalene (4d). Recrystallized from MeOH/CH_2Cl_2. White solid. Mp 86 °C. ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 2H), 7.87−7.77 (m, 4H), 7.32 (d, J = 8.1 Hz, 2H), 6.30 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): 132.9, 132.7, 132.5, 132.2, 128.9, 127.5, 127.1, 107.0. MS, *m/z* (rel intensity, %): 340 (M^+ + 2, 50), 338 (M^+, 100), 336 (M^+ − 2, 51), 259 (10), 257 (11), 178 (74), 176 (52), 152 (40), 126 (9), 88 (85), 76 (91), 63 (33), 51 (15). Anal. Calcd for $C_{14}H_{10}Br_2$: C, 49.74; H, 2.98. Found: C, 49.71; H, 3.05.

(*Z*,*Z*)-2,7-Bis(2-bromoethenyl)fluorene (4e). Purified by recycle GPC. White solid. Mp 120 °C. ^{1}H NMR ($CDCl_3$): δ 7.94 (dd, J = 0.9 and 0.4 Hz, 2H), 7.76 (dd, J = 7.7 and 0.4 Hz, 2H), 7.69 (dd, J = 7.7 and 0.9 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 8.1 Hz, 2H), 3.96 (s, 2H). ^{13}C NMR ($CDCl_3$): 143.6, 141.4, 133.6, 132.5, 128.2, 125.4, 119.8, 105.8, 36.9. MS, *m/z*, (rel intensity, %): 378 (M^+ + 2, 30), 376 (M^+, 55), 374 (M^+ − 2, 32), 297 (11), 295 (12), 216 (62), 215 (87), 189 (55), 163 (11), 148 (11), 107 (76), 95 (100), 82 (25), 63 (12). Anal. Calcd for $C_{17}H_{12}Br_2$: C, 54.29; H, 3.22. Found: C, 54.01; H, 3.31.

(*Z*,*Z*)-4,4′-Bis(2-bromoethenyl)biphenyl Ether (4f). Recrystallized from MeOH/CH_2Cl_2. White solid. Mp 77 °C. ^{1}H NMR ($CDCl_3$): δ 7.70 (d, J = 8.6 Hz, 4H), 7.03 (d, J = 8.6 Hz, 4H), 7.03 (d, J = 8.2 Hz, 2H), 6.39 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 156.7, 131.4, 130.7, 118.6, 105.6. MS, *m/z* (rel intensity, %): 382 (M^+ + 2, 50), 380 (M^+, 100), 378 (M^+ − 2, 52), 301 (5), 299 (5), 220 (5), 219 (7), 191 (30), 165 (17), 102 (75), 89 (33), 63 (37), 51 (41). Anal. Calcd for $C_{16}H_{12}Br_2O$: C, 50.56; H, 3.18. Found: C, 50.80; H, 3.25.

Synthesis of (*Z*,*Z*,*Z*)-1,3,5-Tris[4-(2-dimethylphenylsilylethenyl)phenyl]benzene (6). This compound was synthesized similarly to **3**, using 1,3,5-tris(4-ethynylphenyl)-benzene (**5**, 227 mg, 0.600 mmol), $HSiMe_2Ph$ (233 mg, 1.71 mmol), and **1** (6.0 mg, 3.0 μmol). The hydrosilylation was completed in CH_2Cl_2 at room temperature in 30 min. Purification of the crude product by flash chromatography (hexane/CH_2Cl_2 = 5/1) afforded **6** as a white solid (404 mg, 90%; (*Z*):(*E*):*gem* = 99:0:1). Mp 104 °C. ^{1}H NMR ($CDCl_3$): δ 7.70 (s, 3H), 7.59−7.50 (m, 12H), 7.54 (d, J = 15.0 Hz, 3H), 7.36−7.31 (m, 15H), 6.05 (d, J = 15.0 Hz, 3H), 0.33 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 147.5, 141.7, 140.0, 139.5, 138.7, 133.7, 130.4, 128.9, 128.8, 127.9, 126.6, 124.7, −1.02. Anal. Calcd for $C_{54}H_{54}Si_3$: C, 82.38; H, 6.91. Found: C, 82.31; H, 6.87.

Synthesis of (*Z*,*Z*,*Z*)-1,3,5-Tris[4-(2-bromoethenyl)phenyl]benzene (7). This compound was synthesized similarly to **4**, starting from (*Z*,*Z*,*Z*)-**6** (404 mg, 0.513 mmol, 99% (*Z*)) and NBS (1.65 g, 9.27 mmol) in CH_3CN/$ClCH_2CN$ (9/1, 14.1 mL). The bromodesilylation was completed in 2 h at 0 °C. The heterogeneous mixture was poured into aqueous $Na_2S_2O_3$ solution (10%, 150 mL) at 0 °C and extracted with $CHCl_3$ (3 × 75 mL). The extract was washed with 1 N NaOH (2 × 75 mL) and brine (75 mL), dried over $MgSO_4$, and concentrated to dryness. Recrystallization of the resulting solid from MeOH/CH_2Cl_2 gave **7** as pale yellow crystals (224 mg, 72%; (*Z*):(*E*) = 99:1). Mp 121 °C. ^{1}H NMR ($CDCl_3$): δ 7.83 (s, 3H), 7.83 (d, J = 8.3 Hz, 6H), 7.72 (d, J = 8.3 Hz, 6H), 7.14 (d, J = 8.1 Hz, 3H), 6.49 (d, J = 8.1 Hz, 3H). ^{13}C{^{1}H} NMR: δ 141.8, 140.3, 134.3, 131.8, 129.5, 126.7, 125.1, 106.6. Anal. Calcd for $C_{30}H_{21}Br_3$: C, 58.00; H, 3.41. Found. C, 57.73; H, 3.44.

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Supporting Information Available: General experimental details, identification data for the products in Table 1, and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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