A Convenient One-Pot Synthesis of Bis[(*E*)-4-halostyryl]arene Derivatives

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Abstract: A new convenient synthetic protocol for the one-pot stereoselective synthesis of bis[(E)-4-bromo(or chloro)styryl]arene derivatives via the sequential reaction of silylative-coupling of 4-halostyrenes with vinylsilanes followed by palladium-catalyzed cross-coupling 4-halostyrylsilanes with diiodoarenes, is described. The reaction leads to symmetrical bis[(E)-4-halostyryl]arene derivatives obtained in a stereocontrolled manner with high efficiency.

Key words: vinylsilanes, transition metals catalysis, silylative cross-coupling

Organic molecules with extended π -conjugated double bond systems have found wide application in optoelectronic devices including light-emitting diodes (LED), nonlinear optics (NLO), photovoltaic cells, plastic lasers, and field-effect transistors.¹ The search for novel electrophores and chromophores is still of fundamental and practical interest. Stilbenoid compounds with extended π systems show interesting photophysical and photochemical properties and are therefore suited for various applications in material science.² Due to similar basic structure and interesting photophysical properties of bis(halostyryl)arenes to those of poly(phenylene vinylene), they have gained significant attention as potential unsaturated monomeric building blocks in polymer synthesis.³

Symmetrical derivatives of 1,4-distyrylbenzene belong to disperse optical brightening agents⁴ and can be used as a core of stilbenoid dendrimers.⁵ Despite their importance, only few methods of their synthesis have been proposed. Conventional approaches to the synthesis of bis(styryl)arenes are: Wittig–Horner-type condensation,^{3g,5b,6} Heck,^{3c,7} Suzuki–Miyaura,^{3c,f,8} or Hiyama⁸ reaction.

On the other hand, in the series of our studies we have developed in the last two decades, the silylative coupling reaction of vinylsilane with styrene derivatives in the presence of transition-metal complexes (e.g., ruthenium and rhodium) initially containing or generating M–H and M–Si bonds.⁹ The silylative coupling reaction of monovi-

nyl organosilicon compounds occurs by cleavage of the =C–Si bond of the vinylsilane and the activation of the =C–H bond of the styrene molecule. Thus obtained styrylsilanes can be easily transformed into the desired styryl-arenes in desilylative coupling reaction with haloarenes (Hiyama coupling, HC)¹⁰ in the presence of a palladium catalyst and TBAF (Bu₄NF) as an activator. This sequence of highly-stereoselective reactions allows the use of the vinyl group in vinylsilanes as a synthon for C=C double bond in the obtained arylene-vinylene derivatives.

We have recently reported a new and efficient protocol for the synthesis of unsymmetrical (*E*)-4-chlorostilbene and its derivatives via Hiyama coupling (HC) of 1-aryl-2-silylethenes with aryl iodides in the presence of $[Pd_2(dba)_3]^{10c}$ and a one-pot palladium-catalyzed Hiyamatype strategy for the stereoselective synthesis of (*E*)poly(arylene vinylene)s using aryl dihalides and isomeric bis(silyl)ethenes as new double bond equivalents.^{10d}

Herein, we present the results of our synthetic studies of halo-substituted symmetrical bis[(E)-styryl] arenes. The desired products were obtained via the sequential reaction of silvlative coupling (SC) of divinyltetramethyldisiloxane with 4-halostyrenes, followed by desilylative coupling of bis(4-halostyryl)tetramethyldisiloxane in the presence of a palladium catalyst. This one-pot reaction leads to a wide range of symmetrical bis[(E)-4-halostyryl]arenes in high yield and with stereoselectivity. In an initial experiment, we synthesized (E)-[1-(4-bromophenyl)-2-(pentamethyldisiloxane)]ethene (1) via silylative cross-coupling between vinylpentamethyldisiloxane and 4-bromostyrene using ruthenium complex fRu-HCl(CO)(PPh₃)₃] as a catalyst (Scheme 1).

This reaction was examined in an open system under a gentle stream of argon. The reaction was effectively catalyzed by ruthenium catalyst (0.1 mol%) in toluene at 110 °C for 7 hours. Such a small amount of catalyst needs CuCl as a co-catalyst (0.4 mol%). The exclusive forma-





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Scheme 2 Palladium-catalyzed cross-coupling of (E)-[1-(4-bromophenyl)-2-(pentamethyldisiloxane)]ethene (1) with 1,4-diiodobenzene

tion of the *E*-isomer of [1-(4-bromophenyl)-2-(pentamethyldisiloxane)]ethene (1) was confirmed by ¹H NMRspectroscopy. The expected product 1 was isolated as acolorless liquid by column chromatography and furtherpurified by distillation under low pressure (89%).

The synthesized **1** was used for a catalytic examination in the synthesis of 1,4-bis[(E)-4-bromostyryl]benzene (**2**) (Scheme 2). Compound **1** underwent desilylative coupling reaction (HC) with 1,4-diiodobenzene catalyzed by palladium catalyst [Pd₂(dba)₃] in the presence of TBAF as an activator.

The reaction was performed in an open system under a gentle flow of argon at 30 °C for 72 hours (Table 1). Conversion of substrates, selectivity, and yield of the process were determined using a GC method with an internal standard. The results clearly showed that the best catalytic system contains at least 0.2% of $[Pd_2(dba)_3]$ relative to the silyl compound. However, the reduction of the catalyst amount to 0.2 mol% required longer reaction time (24 h). The use of the catalyst in a lower amount (0.1%) gave a low yield of desired product **2**. On the other hand, the use of higher amount of palladium catalyst (0.5%) reduced the reaction time to 8 hours (Table 1).

Table 1 Synthesis of 1,4-Bis[(E)-4-bromostyryl]benzene (2)

Entry	[Pd]:[Si]	Time (h)	Conv. (IArI) (%)	Yield (%) ^a
1	1:10000	72	0	_
2	1:1000	24	23	_
3	1:500	24	~99	96
4	1:200	8	100	98

^a Isolated yield of chromatographically pure product.

The results of the catalytic study prompted us to perform experiments aiming at an elaboration of the one-pot reaction system [without isolation of (E)-4-halostyryldisiloxane (1)]. However, instead of vinylpentamethyldisiloxane substrate, commercially available divinyl substituted disiloxane was initially used as a substrate in the silylative coupling reaction to get bis[(E)-4-halostyryl]tetramethyldisiloxane as a 'product-substrate' and followed without isolation by Hiyama coupling, according to Scheme 3.

The silylative coupling reaction of divinyltetramethyldisiloxane with 4-bromostyrene and desilylative coupling 'product-substrate' with 1,4-diiodobenzene were tested in some common solvents such as: THF, dioxane, DMF,





Scheme 3 One-pot silylative coupling of 4-halostyrenes with divinyltetramethyldisiloxane and Hiyama coupling reaction of bis[(E)-4-halostyryl]tetramethyldisiloxane with diiodobenzene

benzene, toluene, and DMSO. Due to solubility of substrates and favorable properties, dioxane appeared the best one for both steps of 'one-pot' reaction.

The first step (SC) of the one-pot reaction was the synthesis of bis[(E)-4-bromo(or chloro)styryl]tetramethyldisiloxane in a mini-reactor. The use of dioxane as a solvent entailed the lower temperature (100 °C), higher excess of catalyst (1 mol%), co-catalyst (1 mol%), and a longer time (16 h) of the reaction. These reaction conditions were also necessary to totally transform vinyl groups in divinyltetramethyldisiloxane, because in the second step of the onepot synthesis they can produce some by-products. Twofold excess of 4-bromo(or chloro)styrene relative to divinyltetramethyldisiloxane was enough to complete silylative coupling reaction of both vinyl groups, and still homopolymerization of halostyrene was not observed. Conversion of substrates (>99%), selectivity (>99%) and the yield of the process were determined using the GC method with an internal standard. Then, the components for the Hiyama coupling (additional amount of dioxane, IArI, TBAF, and catalyst) were introduced. The dilution was necessary for dissolving the diiodoarene. The second step of the one-pot reaction was performed at a lower temperature (30 °C) for 8–48 hours (Table 2).

Table 2	One-Pot Synthesis of Bis[(E)-4-bromo(or chloro)styr-
yl]arenesa	

Entry	Aryl diiodide	R	Time (h)	Product	Yield (%) ^b
1	$1,4-I_2C_6H_4$	Br	8	2	97
2	$1,4-I_2C_6H_4$	Cl	8	3	98
3	$1,3-I_2C_6H_4$	Br	24	4	91
4	$1,3-I_2C_6H_4$	Cl	24	5	90
5	$1,2-I_2C_6H_4$	Br	24	6	82
6	$1,2-I_2C_6H_4$	Cl	24	7	86
7	$1,4-I_2C_6F_4$	Br	48	8	43
8	$1,4-I_2C_6F_4$	Cl	48	9	51
9	$4-IC_{6}H_{4}-C_{6}H_{4}-4'-I$	Br	16	10	98
10	$4-IC_{6}H_{4}-C_{6}H_{4}-4'-I$	Cl	16	11	94
11	$2,5-I_2C_4H_2S$	Br	24	12	89
12	$2,5-I_2C_4H_2S$	Cl	24	13	95

^a SC conditions: [Si–O–Si]:[RuHCl(CO)(PPh₃)₃]:[CuCl] =

1:0.02:0.02; dioxane (1 M), 100 °C. HC conditions: [Si-O-Si]:

 $[XArX]:[TBAF]:[Pd_2(dba)_3] = 1:0.8:2.4:0.02$, dioxane, 30 °C.

^b Isolated yields of products.

The desilylative coupling reaction required a small excess of silyl compounds (10% per one iodo substituent) and TBAF (20% per one silyl group). This reaction needs at least 1 mol% catalyst loading ([Pd₂(dba)₃]) per one silyl group for exclusive formation of the products expected. In the above specified reaction conditions, the desired bis[(E)-4-bromo(or chloro)styryl]arenes 2–13 were obtained with perfect stereoselectivity (Table 2). With 1,4diiobenzene and 4,4'-diiodobiphenyl as substrates, this one-pot procedure provided almost quantitative yields (97–99%) of the expected products (Table 2, entries 1, 2, 9, and 10). These compounds 2, 3, 10, and 11 were almost insoluble in dioxane and they could be easily separated from the reaction mixture by filtration. Only when 1,4-diiodotetrafluorobenzene was used, low transformation (43% for 8 and 51% for 9) was observed (Table 2, entries 7 and 8). The extended reaction time (48 h) did not cause a significant increase in the yield of products 8 and 9 (Table 2). Compounds 4-9 and 12,13 were separated on a silica gel chromatographic column (EtOAc-THF).

The structures of the obtained products **2–13** were confirmed by FT-IR, ¹H NMR, ¹³C NMR, and EI-MS spectroscopy. The presence of *E*-vinylene functionality was unambiguously confirmed by the appearance of FT-IR bands attributable to CH bending of *trans*-vinylene at 929–998 cm⁻¹. Unfortunately, the corresponding ¹H NMR signals (J = 14.8-16.2 Hz) fell in the region of aromatic protons and could not be assigned for 4,4'-bis[(*E*)-4-chlorostyryl]biphenyl (**11**). In two compounds **6** and **10** only one signal was assigned to CH in the *trans*-vinylene group. Because of the lack of polar substituents, compounds **2**, **3**, and **11** were found to be only poorly soluble in common deuterated solvents (C_6D_6 , $CDCl_3$, $DMSO-d_6$, THF- d_8) and their ¹³C NMR spectra could not be recorded. The molecular weights of obtained bis[(*E*)-4-bromo(or chlorostyryl)]arenes **2–13** were confirmed by EI-MS and high-resolution mass spectroscopic analyses.

In conclusion, we have developed a new efficient, highly stereoselective, one-pot synthetic methodology for the construction of bis[(E)-4-bromo(or chloro)styryl]arenes based on ruthenium catalyzed silylative cross-coupling of divinyltetramethyldisiloxane with 4-bromo(or chloro)styrenes followed by palladium-catalyzed desilylative coupling of the intermediate bis[(E)-4-halostyryl]tetramethyldisiloxane with diiodoarenes. The availability of the starting materials, simplicity of the experimental technique and the possibility of mild reaction conditions are favorable features of this new catalytic approach to synthesis of bis[(E)-4-halostyryl]arenes.

¹H NMR (300 MHz), ¹³C NMR (75 MHz), and ²⁹Si NMR were recorded on Varian XL 300 MHz spectrometer in CDCl₃ (or DMSO d_6 , THF- d_8) solution. IR spectra (KBr pellets) were recorded on a Bruker ITS 113v spectrometer. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m \times 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GCMS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. TLC was performed on plates coated with 250 μm thick silica gel (Merck), and column chromatography was performed with silica gel 60 (70-230 mesh, Fluka). Toluene and hexane were dried by distillation from NaH; THF and dioxane were distilled from Na under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon. Melting points are uncorrected and were determined by using Boetius melting point apparatus.

The chemicals were obtained from the following sources: toluene, THF, dioxane, EtOAc, decane, and hexane were purchased from Fluka; CDCl₃ from Dr. Glaser A.G. Basel; vinylpentamethyldisiloxane and 1,3-divinyltetramethyldisiloxane were purchased from ABCR company; 1,4-diodobenzene, 1,3-diodobenzene, 1,2-diodobenzene, 4,4'-diiodobiphenyl, 4,4'-diiodobiphenyl, 2,5-diiodothiophene, Bu₄NF and pentane, were bought from Aldrich. The ruthenium and palladium complexes – [RuHCl(CO)(PPh₃)₃]¹¹ and [Pd₂(dba)₃]¹² – were prepared according to procedures described in literature.

Catalytic Examination of Hiyama Coupling Reaction

In a typical catalytic test, the reagents (0.5 mmol) and decane as an internal standard (5% by volume of all components) were dissolved in dioxane (5 mL) and placed in a glass ampoule under argon (usually used in the molar ratio: [Si]:[XArX]:[TBAF] = 1:0.8:2.4). Then the palladium catalyst (0.1–1.0 mol%) was added and the ampoule was heated at 30 °C for 16–48 h. The conversion of the substrates was calculated using the internal standard method. The composition of the reaction mixture was analyzed by GC, GCMS, or TLC.

(E)-[1-(4-Bromophenyl)-2-(pentamethyldisiloxane)]ethene (1)

A toluene solution (1 M) of the reagents, vinylpentamethyldisiloxane (10.0 mL, 45.13 mmol) and 4-bromostyrene (11.8 mL, 90.26 mmol) was placed in a two-necked glass flask equipped with a magnetic stirring bar and a condenser connected to a bubbler. Then the mixture was stirred and heated at 110 °C under a flow of argon. After 5 min, the ruthenium complex [RuHCl(CO)(PPh₃)₃] (43 mg, 0.1 mol%) was added and then, after 10 min CuCl (17.8 mg, 0.4 mol%) was added as a co-catalyst. The color of the solution changed from yellow through green to yellow again. The synthesis process was carried out for the next 7 h. After cooling, the resulting mixture was flushed through a short column chromatography with hexane elution in order to separate the final mixture from the remains of complex. The product was further purified by distillation under low pressure (72 °C/0.8 mmHg) to give 13.23 g (89%) of a colorless liquid.

¹H NMR (CDCl₃): δ = 7.46 (d, *J* = 8.4 Hz, 2 H, C₆H₄Br), 7.31 (d, J = 8.7 Hz, 2 H, C₆ H_4 Br), 6.85 (d, J = 19.2 Hz, 1 H, SiHC=CH), 6.41 (d, J = 19.5 Hz, 1 H, SiHC=CH), 0.23 [s, 6 H, Si(CH₃)₂], 0.12 [s, 9 H, OSi(CH₃)₃].

¹³C NMR (CDCl₃): δ = 142.6, 137.0, 131.5, 129.7, 127.9, 121.9, 2.1, 0.9.

²⁹Si NMR (CDCl₃): $\delta = -2.53, 9.29$.

MS (EI): *m*/*z* (%) = 328 (5), 313 (82), 249 (38), 233 (100), 193 (31), 149 (48), 133 (33).

HRMS (EI): *m/z* calcd for C₁₃H₂₁⁷⁹Br⁸¹BrOSi₂: 328.03143; found: 328.03138.

Anal. Calcd for C₁₃H₂₁BrOSi₂: C, 47.40; H, 6.43. Found: C, 47.38; H, 6.42.

One-Pot Synthesis of Bis[(E)-4-halostyryl]tetramethyldisiloxanes 2-13; General Procedure

The glass mini-reactor (15 mL, equipped with a magnetic stirring bar, argon bubbling tube, and thermostated heating oil bath) was evacuated and flushed with argon. [RuHCl(CO)(PPh₃)₃] (9.52 mg, 0.01 mmol), CuCl (0.99 mg, 0.01 mmol), 1,3-divinyltetramethyldisiloxane (0.1 g, 0.5 mmol), 4-bromo(or chloro)styrene (2.0 mmol), and anhydrous dioxane (1.0 mL) were added to the reactor. The mixture was heated at 100 °C for 16 h under an argon flow. After completion of the reaction (GCMS and ¹H NMR analyses confirmed the formation of bis[(E)-4-halostyryltetramethyldisiloxane]), palladium catalyst [Pd₂(dba)₃] (9.16 mg, 0.01 mmol), TBAF (320 mg, 1.2 mmol), dioxane (4.0 mL or 9 mL in the case of reaction with 4,4'-diiodobiphenyl and 1,4-diiodotetrafluorobenzene) and the respective dihaloarene (0.4 mmol) were added and the mixture was heated at 30 °C for 8-48 h under argon. The degree of conversion of the substrates was estimated by GC and TLC analyses. Then the mixture was cooled and the precipitated solid (2, 3, 10-11) was filtered and washed extensively with dioxane or chromatographed on a silica gel column (4-9, 12, 13) (EtOAc-THF).

1,4-Bis[(*E*)-4-bromostyryl]benzene (2)

Yellow powder; yield: 0.17 g (97%); mp 345-348 °C.

IR (KBr): 3016.9, 2957.9, 2873.2, 1907.8, 1701.3, 1636.3, 1583.2, 1484.4, 1419.9, 1076.7, 1009.1, 971.2, 830.2 cm⁻¹.

¹H NMR (DMSO- d_6): $\delta = 7.92$ (d, J = 8.5 Hz, 4 H, BrC₆H₄), 7.85 (m, 4 H, C_6H_4), 7.58 (m, 4 H, BrC_6H_4), 7.60 (d, J = 16.0 Hz, 2 H, C_6H_4CH , 7.32 (d, J = 16.1 Hz, 2 H, BrC_6H_4CH).

MS (EI): *m*/*z* (%) = 440 (100), 438 (61), 279 (35), 278 (32), 202 (29), 178 (37), 132 (22).

HRMS (EI): m/z calcd for $C_{22}H_{16}^{-79}Br^{81}Br$: 439.9598; found: 439.9572.

Anal. Calcd for C₂₂H₁₆Br₂: C, 60.03; H, 3.66; Br, 36.31. Found: C, 60.05; H, 3.78; Br, 36.17.

1,4-Bis[(E)-4-chlorostyryl]benzene (3)^{6c}

Yellow powder; yield: 0.137 g (98%); mp 299-302 °C.

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The analytical data were in accord with the literature values.

1,3-Bis[(E)-4-bromostvrvl]benzene (4)

Yellow powder; yield: 0.16 g (91%); mp 192-195 °C.

IR (KBr): 3012.0, 2970.7, 1605.5, 1486.3, 1251.9, 1109.3, 1022.9, 987.4, 883.0, 846.0, 791.2 cm⁻¹.

¹H NMR (CDCl₃): δ = 7.63 (s, 1 H, C₆H₄), 7.48 (d, J = 16.0 Hz, 2 H, C₆H₄CH), 7.01 (d, J = 16.2 Hz, 2 H, BrC₆H₄CH), 7.50–7.10 (m, 11 H, Ar).

¹³C NMR (CDCl₂): δ = 137.4, 136.1, 131.8, 131.4, 130.5, 129.1, 128.0, 127.8, 126.0, 125.5.

MS (EI): m/z (%) = 440 (9), 438 (12), 286 (57), 205 (100), 202 (62), 178 (69), 103 (41).

HRMS (EI): m/z calcd for $C_{22}H_{16}^{-79}Br^{81}Br$: 439.9598; found: 439.9584.

Anal. Calcd for C₂₂H₁₆Br₂: C, 60.03; H, 3.66; Br, 36.31. Found: C, 59.79; H, 3.74; Br, 36.09.

1,3-Bis[(*E*)-4-chlorostyryl]benzene (5)

Yellow crystals; yield: 0.126 g (90%); mp 178-182 °C.

IR (KBr): 3434.6, 3013.3, 2924.3, 1909.7, 1645.4, 1587.6, 1575.8, 1490.2, 1420.9, 1400.1, 1092.2, 1011.8, 970.2, 855.1, 820.4, 691.4, 514.1 cm⁻¹.

¹H NMR (THF- d_8): $\delta = 7.72$ (s, 1 H, C₆H₄), 7.54 (d, J = 16.0 Hz, 2 H, C_6H_4CH), 7.10 (d, J = 16.0 Hz, 2 H, ClC_6H_4CH), 7.50–7.10 (m, 11 H, Ar).

¹³C NMR (CDCl₃): δ = 138.6, 137.3, 133.8, 130.1, 129.7, 129.6, 128.7, 128.4, 126.8, 125.6.

MS (EI): *m*/*z* (%) = 352 (84), 350 (100), 280 (30), 278 (38), 276 (29), 202 (55), 178 (25).

HRMS (EI): m/z calcd for $C_{22}H_{16}^{35}Cl_2$: 350.0629; found: 350.0618. Anal. Calcd for C₂₂H₁₆Cl₂: C, 75.22; H, 4.59; Cl, 20.19. Found: C, 74.97; H, 4.72; Cl, 20.01.

1,2-Bis[(E)-4-bromostyryl]benzene (6)

Yellow oil; yield: 0.144 g (82%).

IR (KBr): 3058.2, 2957.4, 1669.0, 1591.7, 1437.6, 1182.4, 1120.1, 1028.1, 998.0, 754.3, 722.1, 694.5, 541.7 cm⁻¹.

¹H NMR (CDCl₃): δ = 7.50–7.10 (m, 14 H, Ar), 7.01 (d, J = 16.2 Hz, 2 H, BrC_6H_4CH).

¹³C NMR (CDCl₃): δ = 139.3, 131.7, 131.3, 130.2, 129.0, 128.9, 127.9, 125.4, 119.7.

MS (EI): *m*/*z* (%) = 440 (21), 438 (21), 286 (14), 219 (88), 205 (100), 203 (65), 169 (69).

HRMS (EI): m/z calcd for $C_{22}H_{16}^{79}Br^{81}Br$: 439.9598; found: 439.9606.

Anal. Calcd for C₂₂H₁₆Br₂: C, 60.03; H, 3.66; Br, 36.31. Found: C, 59.75; H, 3.41; Br, 36.03.

1,2-Bis[(*E*)-4-chlorostyryl]benzene (7)

Pale yellow powder; yield: 0.12 g (86%); mp 58-63 °C.

IR (KBr): 3025.2, 2955.8, 1685.7, 1591.1, 1489.2, 1449.9, 1402.9, 1259.6, 1176.7, 1088.4, 1011.0, 958.1, 855.8, 804.6, 747.1, 701.3, 523.4 cm^{-1} .

¹H NMR (CDCl₃): δ = 7.57 (d, J = 16.2 Hz, 2 H, C₆H₄CH), 7.50– 7.25 (m, 12 H, Ar), 6.94 (d, J = 16.2 Hz, 2 H, ClC₆H₄CH).

¹³C NMR (CDCl₃): δ = 135.9, 133.4, 130.3, 130.2, 128.9, 128.0, 127.8, 127.0, 126.7.

MS (EI): *m*/*z* (%) = 352 (25), 350 (36), 278 (13), 276 (16), 225 (100), 204 (44), 178 (31).

HRMS (EI): m/z calcd for $C_{22}H_{16}^{35}Cl_2$: 350.0629; found: 350.0642.

Anal. Calcd for $C_{22}H_{16}Cl_2$: C, 75.22; H, 4.59; Cl, 20.19. Found: C, 74.90; H, 4.35; Cl, 19.88.

1,4-Bis[*(E)*-**4-bromostyryl]-2,3,5,6-tetrafluorobenzene (8)** Yellow powder; yield: 0.088 g (43%); mp 154–158 °C.

IR (KBr): 2988.0, 2958.1, 2873.4, 1628.1, 1585.7, 1472.7, 1396.9, 1242.1, 1109.2, 1070.9, 1029.9, 1008.2, 969.2, 922.0, 880.6, 808.2, 736.0 cm⁻¹.

¹H NMR (DMSO- d_6): δ = 7.55 (d, J = 8.5 Hz, 4 H, BrC₆H₄), 7.48 (d, J = 8.7 Hz, 4 H, BrC₆H₄), 7.12 (d, J = 14.8 Hz, 2 H, BrC₆H₄CH), 6.76 (d, J = 14.8 Hz, 2 H, C₆F₄CH).

¹³C NMR (DMSO- d_6): δ = 142.9, 139.3, 136.3, 134.2, 132.0, 131.7, 130.2, 128.4, 120.6.

MS (EI): m/z (%) = 512 (11), 364 (34), 219 (100), 185 (47), 171 (49), 169 (53), 131 (72).

HRMS (EI): m/z calcd for $C_{22}H_{12}^{79}Br^{81}BrF_4$: 511.9221; found: 511.9214.

Anal. Calcd for $C_{22}H_{12}Br_2F_4$: C, 51.60; H, 2.36; Br, 31.20. Found: C, 51.26; H, 2.63; Br, 30.98.

1,4-Bis[(E)-4-chlorostyryl]-2,3,5,6-tetrafluorobenzene (9)

Yellow crystals; yield: 0.086 g (51%); mp 162-166 °C.

IR (KBr): 3027.9, 3009.6, 2923.0, 1620.1, 1589.7, 1486.9, 1401.1, 1245.3, 1089.5, 1011.0, 994.3, 967.4, 929.6, 852.6, 800.9 $\rm cm^{-1}$

¹H NMR (DMSO-*d*₆): δ = 7.55 (d, *J* = 8.5 Hz, 4 H, ClC₆H₄), 7.41 (d, *J* = 8.5 Hz, 4 H, ClC₆H₄), 7.17 (d, *J* = 15.2 Hz, 2 H, ClC₆H₄CH), 6.76 (d, *J* = 14.9 Hz, 2 H, C₆F₄CH).

¹³C NMR (DMSO- d_6): δ = 169.2, 142.7, 135.7, 134.8, 133.4, 128.6, 127.9, 114.2, 105.2.

MS (EI): *m*/*z* (%) = 422 (32), 286 (55), 276 (58), 239 (70), 225 (57), 204 (100), 125 (66).

HRMS (EI): m/z calcd for $C_{22}H_{12}^{35}Cl_2F_4$: 422.0252; found: 422.0252.

Anal. Calcd for $C_{22}H_{12}Cl_2F_4$: C, 62.43; H, 2.86; Cl, 16.75. Found: C, 62.19; H, 2.99; Cl, 16.51.

4,4'-Bis[(E)-4-bromostyryl]biphenyl (10)

Yellow powder; yield: 0.202 g (98%); mp >340 °C.

IR (KBr): 3440.8, 3016.7, 2923.7, 2852.3, 1904.0, 1632.2, 1580.8, 1495.5, 1484.6, 1403.4, 1073.9, 1007.6, 969.7, 828.4, 819.9, 720.4, 529.0 cm⁻¹.

¹H NMR (THF- d_8): $\delta = 7.77$ (d, J = 8.6 Hz, 4 H, BrC₆H₄), 7.62–7.20 (m, 14 H, Ar), 7.18 (d, J = 14.8 Hz, 2 H, BrC₆H₄CH).

¹³C NMR (THF- d_8): δ = 140.9, 138.8, 137.7, 132.6, 129.7, 129.4, 129.0, 128.0, 127.7, 121.9.

MS (EI): *m/z* (%) = 516 (8), 462 (100), 253 (88), 178 (17), 152 (17), 126 (29), 102 (15).

HRMS (EI): m/z calcd for $C_{28}H_{20}^{-79}Br^{81}Br$: 515.9911; found: 515.9906.

Anal. Calcd for $C_{28}H_{20}Br_2$: C, 65.14; H, 3.90; Br, 30.95. Found: C, 64.97; H, 3.96; Br, 30.71.

4,4'-Bis[(*E*)-4-chlorostyryl]biphenyl (11)

Yellow powder; yield: 0.16 g (94%); mp 303-307 °C.

IR (KBr): 3018.2, 2921.1, 1904.8, 1668.9, 1585.6, 1496.0, 1487.5, 1405.6, 1098.7, 1010.7, 999.5, 969.9, 829.4, 721.0, 530.8 cm⁻¹.

¹H NMR (DMSO- d_6): $\delta = 7.80-7.30$ (m, Ar).

MS (EI): *m*/*z* (%) = 428 (78), 426 (100), 265 (20), 253 (31), 213 (25), 178 (31), 126 (18).

HRMS (EI): m/z calcd for $C_{28}H_{20}^{35}Cl_2$: 426.0942; found: 426.0932.

Anal. Calcd for $C_{28}H_{20}Cl_2$: C, 78.69; H, 4.72; Cl, 16.59. Found: C, 78.64; H, 4.57; Cl, 16.41.

2,5-Bis[(*E*)-4-bromostyryl]thiophene (12)

Brown powder; yield: 0.158 g (89%); mp 188–191 °C.

IR (KBr): 3636.3, 3027.0, 2958.8, 2924.5, 2855.3, 1615.1, 1599.0, 1484.1, 1072.8, 1007.4, 960.7, 947.6, 854.7, 808.5, 540.8 cm $^{-1}$.

¹H NMR (CDCl₃): δ = 7.46 (d, *J* = 8.5 Hz, 4 H, BrC₆H₄), 7.32 (d, *J* = 8.5 Hz, 4 H, BrC₆H₄), 7.16 (d, *J* = 16.2 Hz, 2 H, C₄H₂SC*H*), 6.96 (s, 2 H, C₄H₂S), 6.83 (d, *J* = 16.2 Hz, 2 H, BrC₆H₄C*H*).

¹³C NMR (CDCl₃): δ = 141.7, 135.7, 131.8, 128.9, 127.7, 127.3, 122.3, 121.3.

MS (EI): *m*/*z* (%) = 448 (15), 446 (12), 184 (61), 142 (100), 100 (72), 57 (90).

HRMS (EI): m/z calcd for $C_{20}H_{14}S^{79}Br^{81}Br$: 445.9163; found: 445.9182.

Anal. Calcd for $C_{20}H_{14}Br_2S$: C, 53.84; H, 3.16; Br, 35.82. Found: C, 53.59; H, 3.24; Br, 35.67.

2,5-Bis[(*E*)-4-chlorostyryl]thiophene (13)

Brown powder; yield: 0.135 g (95%); mp 208-211 °C.

IR (KBr): 3028.2, 2923.6, 2852.3, 1731.6, 1650.3, 1615.5, 1587.4, 1487.0, 1403.8, 1092.0, 1010.7, 961.8, 948.1, 855.6, 811.9, 542.0 $\rm cm^{-1}.$

¹H NMR (CDCl₃): δ = 7.39 (d, *J* = 8.5 Hz, 4 H, ClC₆H₄), 7.30 (d, *J* = 8.5 Hz, 4 H, ClC₆H₄), 7.15 (d, *J* = 16.2 Hz, 2 H, C₄H₂SC*H*), 6.96 (s, 2 H, C₄H₂S), 6.84 (d, *J* = 16.0 Hz, 2 H, ClC₆H₄C*H*).

¹³C NMR (CDCl₃): δ = 141.7, 135.3, 133.2, 128.8, 127.4, 127.3, 127.2, 122.3.

MS (EI): m/z (%) = 358 (74), 356 (100), 320 (10), 284 (13), 252 (21), 142 (21), 126 (18).

HRMS (EI): m/z calcd for $C_{20}H_{14}^{35}Cl_2S$: 356.0193; found: 356.0201.

Anal. Calcd for $C_{20}H_{14}Cl_2S$: C, 67.23; H, 3.95; Cl, 19.85. Found: C, 67.01; H, 4.07; Cl, 19.59.

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