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Synthetic protocols and building blocks for molecular electronics

Nicolai Stuhr-Hansen, Jakob Kryger Sørensen, Kasper Moth-Poulsen, Jørn Bolstad Christensen, Thomas Bjørnholm and Mogens Brøndsted Nielsen*

Department of Chemistry, Nano-Science Center and Molecular Engineering Group, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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Abstract—Simple and readily accessible aryl bromides are useful building blocks for thiol end-capped molecular wires. Thus, 4-bromophenyl *tert*-butyl sulfide and 1-bromo-4-(methoxymethyl)benzene serve as precursors for a variety of oligo(phenylenevinylene) and oligo(phenyleneethynylene) wires via efficient synthetic transformations as presented in this paper.

1. Introduction

The development of molecular wires for molecular electronics has attracted immense interest in recent years.[1] Thus, molecules are designed to interconnect molecular devices, such as single electron transistors, electron turnstiles, molecular switches, and chemical sensors. Especially sp^2-carbon based molecular wires have been intensely targeted due to their conducting properties. Compared to semiconductors such as silicon, it is possible to fabricate much smaller and better defined carbon based nanodevices. Much work has focused on thiol-terminated conjugated π-systems, such as oligo(phenylenevinylene)s (OPVs),[2] oligo(phenyleneethynylene)s (OPEs),[3] and oligothiophenes.[4]

Some of us have recently developed several new procedures for the synthesis and applications of OPVs[5] that have been found to exhibit some of the best conducting properties.[6] In order to utilize a molecular wire in a device, it has to be placed between electrodes. One method is direct evaporation of the molecular wire into a nanogap.[2a] However, manufacture of stable devices with wires fixed between electrodes requires 'molecular alligator clips'. Adhesion to gold electrodes can be accomplished with terminal end-groups such as thiols.[2b]

It is important to establish how small changes in molecular structure will affect the single molecule conductivity. Parameters to vary are the nature of the wire (choice of conjugated π-system, alternating π- and σ-systems, non-covalent junctions, etc.), the wire length, the number of electrode attachment sites and the nature of these. Figure 1 shows schematically five important classes of molecular wires (**A**–**E**) with protected thiol end-groups.[7] The acetyl group has found general applicability as a thiol protecting

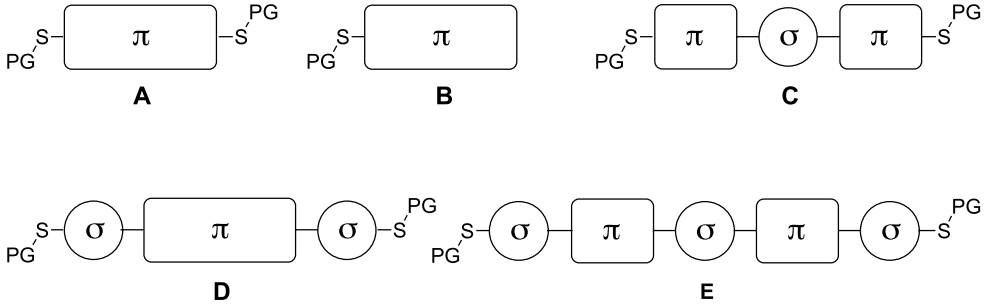

Figure 1. Schematic representation of five classes of molecular wires (**A**–**E**). PG = thiol protecting group.

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* Corresponding author. Tel.: +45 3532 0210; fax: +45 3532 0212; e-mail: mbn@kiku.dk

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group (PG), since it is readily cleaved in situ under mild basic conditions.[2b]

In this paper we present synthetic protocols for wires of type **A**, **B**, **D**, and **E**. Thus, we have developed: (i) a new synthesis of OPE3 with terminal acetylthio groups (class **A**) via a *tert*-butylthio precursor, a procedure that may be generalized to related molecules, (ii) new synthetic procedures for molecular wires where the conjugation is disrupted by methylene bridges (classes **D** and **E**), and (iii) efficient synthesis of unsymmetrical OPVs (class **B**).

In our previous synthesis of thiol end-capped molecular OPV wires,[5] we adopted an approach where the aryl thiol functionality was introduced as the *t*-Bu sulfide at the beginning of the synthetic sequence via the building block 4-bromophenyl *tert*-butyl sulfide (**1**) and maintained through the subsequent steps owing to the resistance of *t*-Bu-S-Ar to both strongly basic and acidic conditions. In a final step, the *t*-BuS group was converted into the AcS moiety by means of AcCl/BBr_3.[8] We became interested to employ the same approach to prepare acetyl-protected OPEs, providing an alternative procedure to that of Tour and co-workers.[9] It deserves mention that the lability of the acetyl protecting group has stimulated the exploitation of other protecting groups as well. Thus, recently Bryce and co-workers[10] successfully utilized cyanoethyl as a thiolate protecting group.

Disruption of the conjugated system or changes in the conjugation pathway may lead to significant changes in the tunnelling mechanism of the molecules inserted between metal electrodes.[2b,11] Several examples where the conjugation is broken within the wire (class **C**) have been reported by Tour and co-workers.[9] Synthetic methods for two-terminal wires where the conjugation is instead broken between the intact wire and the thiol end-caps are less common. To our knowledge, only one example of a two-terminal class **D** OPV3 (with –OBu substitution at the central phenylene) has been reported in the literature with a focus on the current-voltage characteristics rather than the synthesis.[12,13]

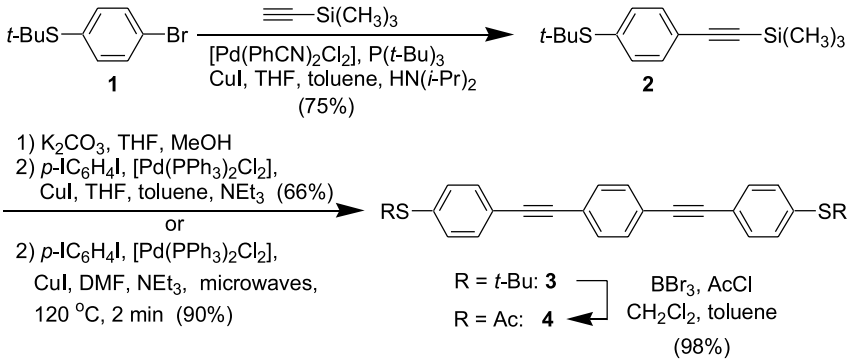
The next logical step in synthetic manipulations towards functional wires is further development of molecules having isolated aromatic units (π-islands) between thiols, again applying methylene spacers as isolating units between individual islands (class **E**).

Finally, we report the synthesis of unsymmetrical OPVs of class **B**. Highly ordered self-assembled monolayers (SAMs) of such molecules on electrode surfaces are interesting with respect to mediating electron transfer across the interfacial barrier represented by the monolayer.[4a,14]

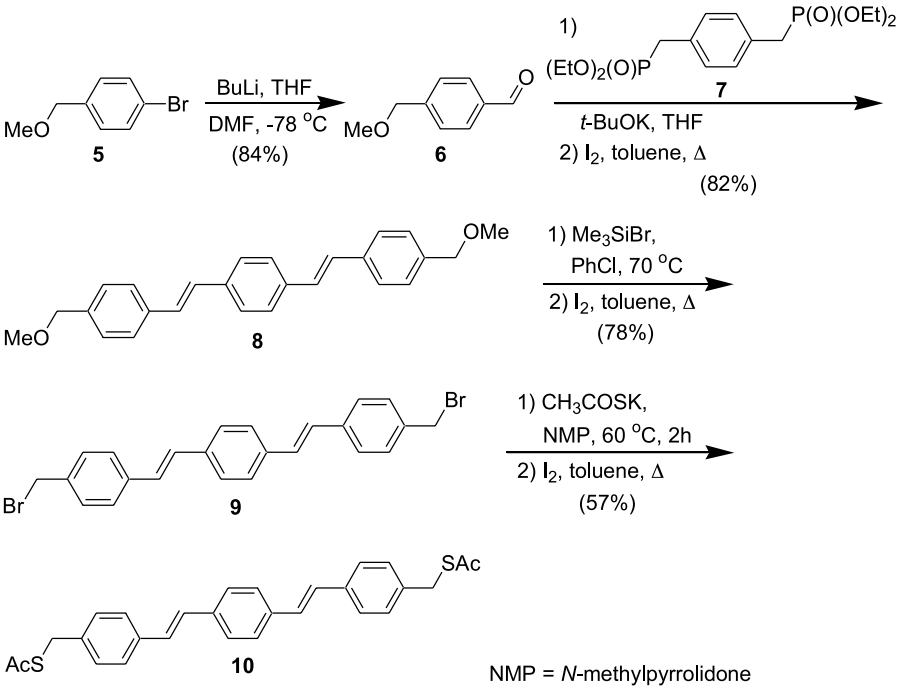
2. Results and discussion

The synthesis of SAc end-capped OPE3 proceeds according to Scheme 1. First, bromide **1** was subjected to a Pd-catalyzed cross-coupling with trimethylsilylacetylene, employing the [$Pd(PhCN)_2Cl_2$]/P(*t*-Bu)$_3$/CuI catalyst system. Hundertmark et al.[15] have shown that this system allows room temperature Sonogashira coupling[16] of aryl bromides with a wide variety of terminal acetylenes. Indeed, we managed to obtain **2** under these conditions in a yield of 75%.[17] This same compound was previously prepared by Mayor et al.[18] from the more reactive, but less accessible, 4-iodophenyl *tert*-butyl sulfide. After silyl deprotection using K_2CO_3 in THF/MeOH, **2** was subjected to a two-fold cross-coupling with 1,4-diiodobenzene, which afforded the OPE3 **3** in 66% yield. The yield was increased significantly, however, by employing microwave heating at 120 °C for 5 min, which gave **3** in 90%. This OPE was finally converted quantitatively into the acetyl-protected wire **4** by means of AcCl/BBr_3.

An AcS-CH_2 end-capped OPV3 was prepared according to Scheme 2. The synthesis starts from 1-bromo-4-(methoxymethyl)benzene **5**[19] (that we conveniently prepared from 4-bromobenzylbromide by treatment with sodium methoxide). Compound **5** was treated with butyllithium and DMF, which provided aldehyde **6**. Several procedures are available in the literature for synthesis of **6**,[20] but since the existing procedures involve either carcinogenic compounds,[20a] long reaction times (several days for one reaction),[20b] or a starting material not readily available,[20c] the present procedure is more convenient. The aldehyde was subsequently coupled with tetraethyl 1,4-xylylenediphosphonate **7**[21] in a typical Horner–Wadsworth–Emmons (HWE) reaction[22] upon treatment with potassium *tert*-butoxide. Treatment of the product with iodine in toluene provided the pure all-*trans* OPV3 **8**. Demasking this new wire with bromotrimethylsilane gave the dibromide **9** that was subsequently treated with potassium thioacetate to give the protected thiomethyl wire **10**.

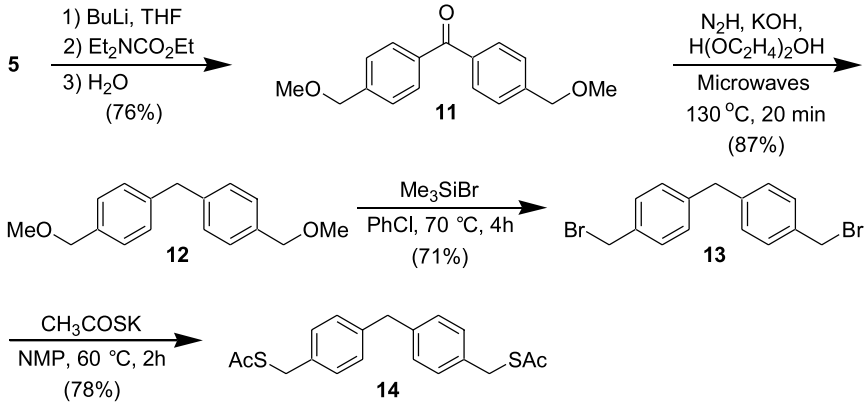


Scheme 1.

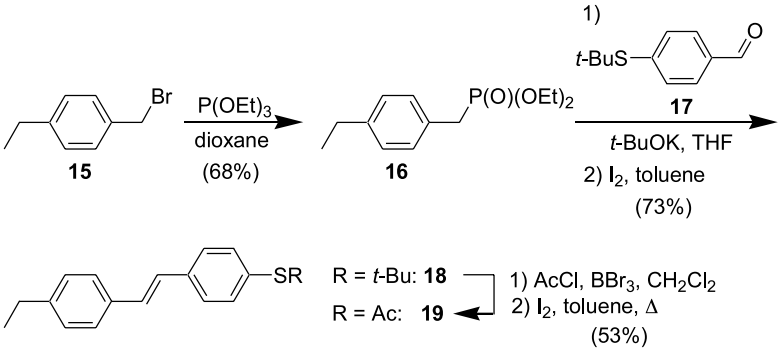


Scheme 2.

Synthesis of bis[4-(*S*-acetylthiomethyl)phenyl]methane (**14**) was carried out according to Scheme 3. First, Br/Li-exchange on **5** with butyllithium followed by reaction of the lithium reagent with ethyl *N*,*N*-diethylcarbamate[23] gave the ketone **11**. Subjecting **11** to a microwave-assisted Huang–Minlon modification[24] of the Wolff–Kishner procedure produced **12** containing a central methylene unit. Demasking the methoxymethyl functionalities by means of bromotrimethylsilane gave the dibromide **13**[25] that was treated with potassium thioacetate to provide the acetyl-protected wire **14** with three methylene bridges.



Scheme 3.



Scheme 4.

An unsymmetrical OPV wire was prepared in analogy to our previous two-terminal OPV synthesis (Scheme 4).[5a] The bromide **15**,[26] prepared from the corresponding alcohol,[27] was first converted to the phosphonate **16**. A HWE reaction between **16** and aldehyde **17** (obtained from **1**[5]) gave, after iodine-induced isomerization, the *trans*-stilbene **18**. Finally, the *tert*-butyl group was converted into an acetyl group to provide **19**.

3. Conclusion

In conclusion, we have devised efficient protocols for the synthesis of a selection of wires for molecular electronics applications. The protocols are both simple and reliable and may allow future synthesis of more complex systems. The successful development of molecular electronics and the establishment of structure-property relationships is strongly dependent on such synthetic advances.

4. Experimental

4.1. General experimental procedures

Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). For microwave-assisted reactions, a CEM925110 Discover microwave oven was employed. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian instrument. Samples were prepared using $CDCl_3$ purchased from Cambridge Isotope Labs. Electron impact ionisation mass spectrometry (EI-MS) was performed on a Varian MAT 311A. Fast atom bombardment (FAB) spectra were ontained on a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode using 3-nitrobenzyl alcohol (NBA) as matrix. Gas chromatography–Mass spectrometry (GC–MS) was performed on a HP5890 Series II plus gas chromatograph coupled with a HP5972 Series Mass analyzer. Microanalyses were performed at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen.

4.1.1. 1-*tert*-Butylthio-4-trimethylsilylethynylbenzene (2). $[Pd(PhCN)_2Cl_2]$ (0.04 g, 0.104 mmol) and CuI (0.005 g, 0.026 mmol) were dissolved in dry and argon-degassed THF (2.5 mL) and toluene (2.5 mL) and stirred under a flow of argon for 10 min. Then $HN(i\text{-}Pr)_2$ (1 mL) and $P(t\text{-}Bu)_3$ (10% in hexane, 0.63 mL) were added followed by 1-bromo-4-(*tert*-butylthio)benzene **1** (1.25 g, 5 mmol) and trimethylsilylacetylene (0.85 g, 8.7 mmol). The dark solution was heated to 50 °C for 2 h. The reaction was stopped by pouring the reaction mixture onto H_2O (100 mL) and extracting with diethyl ether (3×100 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated to a yellow oil. Column chromatography (SiO_2, heptane) afforded **2** (994 mg, 75%) as a semi-crystalline oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25 (s, 9H), 1.27 (s, 9H), 7.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.1, 31.0, 46.4, 96.0, 104.4, 123.4, 131.8, 133.5, 137.1. MS (EI) (%): *m*/*z* 262 (M^+, 36%), 206 (60%), 191 (100%). HR-MS (EI): *m*/*z* 262.1207 (M^+, calcd for $C_{15}H_{22}SSi$ 262.1211).

4.1.2. 4.1.2. Desilylation of 2. To a solution of **2** (0.335 g, 1.28 mmol) in MeOH (40 mL) and THF (7 mL) was added K_2CO_3 (0.190 g, 1.37 mmol), and the mixture was stirred for 45 min at room temperature. Then it was poured into water (200 mL) and extracted with diethyl ether (3×100 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated to an orange oil of 1-*tert*-butylthio-4-ethynylbenzene that can be cross-coupled without further purification. A pure sample (semi-crystalline oil) can be obtained by column chromatography (SiO_2, heptane/EtOAc gradual increase from 1:0 to 50:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (s, 9H), 3.19 (s, 1H), 7.45 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.9, 46.1, 78.6, 83.1, 123.4, 131.6, 131.8, 138.9. MS (GC): *m*/*z* 190 (M^+).

4.1.3. 1,4-Bis(4-*tert*-butylthiophenylethynyl)benzene (3). *Procedure (i)*. Compound **2** (0.307 g, 1.17 mmol) was desilylated according to the procedure described above. $[Pd(PPh_3)_2Cl_2]$ (0.020 g, 0.03 mmol) and CuI (0.010 g, 0.05 mmol) were dissolved in dry and argon-degassed THF (3.5 mL), toluene (3.5 mL), and NEt_3 (3 mL). The mixture was stirred under a flow of argon for about 30 min, whereupon the desilylated **2** and 1,4-diiodobenzene (0.126 g, 0.383 mmol) were added. The solution turned black immediately. After 30 min of stirring under argon, a white precipitate had formed. After 2 h the mixture was poured onto aqueous NH_4Cl and extracted with CH_2Cl_2 (3×100 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo until the precipitation of a white precipitate. Cooling on ice provided further precipitation, and the solid was filtered and washed with cold diethyl ether. The crude product was recrystallized from hot diethyl ether to afford **3** (115 mg, 66%) as a white powder. *Procedure (ii)*. Compound **2** (0.131 g, 0.50 mmol) was desilylated according to the procedure described above. $[Pd(PPh_3)_2Cl_2]$ (9.5 mg, 0.014 mmol) and CuI (5 mg, 0.026 mmol) were dissolved in dry and argon-degassed DMF (2 mL) and NEt_3 (1 mL). The mixture was stirred under a flow of argon for about 10 min and then transferred to a heavy-walled reaction vessel (sealed with a teflon septum), containing the desilylated **2** and 1,4-diiodobenzene (0.072 g, 0.22 mmol). The solution turned black immediately. The mixture was heated in a microwave oven (ramp time: 2 min, temperature: 120 °C, hold time: 5 min, pressure: 1.5 bar). After cooling to room temperature, the mixture was evaporated to dryness and purified by column chromatography (SiO_2, heptane). After recrystallization from hot heptane, the product **3** (90.5 mg, 90%) was obtained as a white powder. Mp 205–207 °C. Sublimation temperature 170 °C at 2×10^{-2} mbar. IR(KBr): ν (cm^{-1}) 2951, 2927, 2860, 1920, 1799, 1736, 1670, 1586, 1506, 1466, 1397, 1366, 1300, 1263, 1160, 1101, 1015, 833, 730, 535. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 18H), 7.51 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 31.3, 46.8, 90.8, 91.1,

123.3, 123.6, 131.8, 131.8, 133.8, 137.5. HR-MS (FAB): *m/z* 454.1793 (M^+, calcd for $C_{30}H_{30}S_2$ 454.1789).

4.1.4. 1,4-Bis(4-acetylthiophenylethynyl)benzene (4). OPE3 **3** (0.100 g, 0.220 mmol) was dissolved in CH_2Cl_2 (10 mL) and toluene (10 mL). Then acetyl chloride (2 mL) and boron tribromide (1 M in CH_2Cl_2, 4 mL, 4 mmol) were added while stirring. The reaction was stirred for 3 h under inert atmosphere and then poured onto ice and extracted with CH_2Cl_2 (4×100 mL). The combined organic phases were dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography (SiO_2, heptane/EtOAc gradual increase from 10:1 to 0:1) to afford **4** as an off-white powder (96 mg, 98%). Mp 188–189 °C. IR(KBr): ν (cm^{-1}) 2922, 2852, 1916, 1696, 1591, 1513, 1480, 1422, 1407, 1396, 1354, 1304, 1269, 1117, 1013, 964, 873, 824, 695, 621, 542, 508. UV–vis ($CHCl_3$): λ_{max} (nm) (ε (M^{-1} cm^{-1})) 318 (sh, 50400), 332 (61800), 350 (sh, 38300). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 6H), 7.41 (d, J=7.8 Hz, 4H), 7.52 (s, 4H), 7.56 (d, J=7.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.3, 90.6, 90.7, 123.0, 124.2, 128.3, 131.6, 132.2, 134.2, 199.4. HR-MS (FAB): *m/z* 426.0728 (M^+, calcd for $C_{26}H_{18}O_2S_2$ 426.0748).

4.1.5. 1-Bromo-4-(methoxymethyl)benzene (5). To a slurry of 4-bromobenzylbromide (37.5 g, 150 mmol) in MeOH (100 mL) was added NaOMe (25% in MeOH, 35.7 g, 0.165 mmol). The resulting reaction mixture was refluxed for 2 h under nitrogen and poured into water (350 mL) and extracted with pentane (3×50 mL). The pooled organic extracts were filtered through basic alumina (10 g) and evaporated. Bulb-to-bulb distillation (0.5 mmHg, air bath 100 °C) gave **5** (25.1 g, 83%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 3H), 4.40 (s, 2H), 7.20 (d, J=8.2 Hz, 2H), 7.47 (d, J=8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.0, 73.7, 121.3, 129.1, 131.3, 137.1. MS (EI, 70 eV) (%): *m/z* 202 (M^+, 15), 171 (37), 157 (5), 121 (100).

4.1.6. 4-(Methoxymethyl)benzaldehyde (6). Compound **5** (10.05 g, 50 mmol) was added dropwise under an argon atmosphere to a solution of butyllithium (2.5 M in hexanes, 20 mL, 50 mmol) in THF (50 mL) cooled in a dry ice/acetone bath. The reaction mixture was stirred at −78 °C for 15 min, then DMF (10 mL) was added in one portion, and stirring was maintained at room temperature for 30 min. The clear reaction mixture was poured into H_2O (200 mL) and extracted with pentane (3×50 mL). The combined organic layers were washed with H_2O (30 mL), dried ($MgSO_4$), filtered, and concentrated by rotary evaporation (30 °C, 20 mmHg). Distillation at 77–79 °C (0.40–0.45 mmHg) in a column-free standard Claisen equipment gave **6** (6.28 g, 84%) as a colorless liquid. Purity >98% (GC–MS). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (s, 3H), 4.50 (s, 2H), 7.46 (d, J=7.9 Hz, 2H), 7.83 (d, J=7.9 Hz, 2H), 9.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.3, 73.7, 127.5, 129.7, 135.6, 145.2, 191.8. MS (EI, 70 eV) (%): *m/z* 150 (M^+, 40), 135 (100), 121 (71). HR-MS (EI): *m/z* 150.0699 (M^+, calcd for $C_9H_{10}O_2$ 150.0681).

4.1.7. (*E*,*E*)-1,4-Bis[4-(methoxymethyl)styryl]benzene (8). To a solution of **6** (3.00 g, 20 mmol) and tetraethyl 1,4-xylylenediphosphonate **7** (3.78 g, 10 mmol) in THF (80 mL) cooled in an ice bath was added *t*-BuOK (2.47 g, 22 mmol) in small portions during a period of 10 min. The reaction mixture was further stirred at room temperature for 6 h under nitrogen and then poured into water (300 mL). A yellow material was filtered off, washed with H_2O, and dried in a vacuum oven (120 °C, 1 mmHg). The product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling at room temperature, the pure *trans*-stilbene **8** (3.05 g, 82%) precipitated as yellow crystals. Mp 259–260 °C. IR(KBr): ν (cm^{-1}) 3021, 2985, 2923, 2891, 2821, 2066, 1914, 1693, 1650, 1632, 1610, 1567, 1518, 1456, 1423, 1381, 1336, 1322, 1306, 1278, 1209, 1196, 1112, 1017, 970, 949, 927, 830, 803, 781, 713, 601, 549. Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.45; H, 7.06. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (s, 6H), 4.47 (s, 4H), 7.12 (s, 4H), 7.33 (d, J=8.1 Hz, 4H), 7.50 (s, 4H), 7.51 (d, J=8.1 Hz, 4H). Crystals not soluble enough for ^{13}C NMR. MS (EI, 70 eV) (%): *m/z* 370 (M^+, 100), 354 (10), 339 (17).

4.1.8. (*E*,*E*)-1,4-Bis[4-(bromomethyl)styryl]benzene (9). To a slurry of **8** (0.74 g, 2 mmol) in chlorobenzene (15 mL) was added bromotrimethylsilane (0.70 g, 4.6 mmol) and the resulting slurry was stirred at 75 °C for 4 h under nitrogen. The grey slurry was poured into MeOH (150 mL), and a yellow powder was filtered off. The product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling at room temperature, the product **9** (0.73 g, 78%) precipitated as yellow crystals. Mp >280 °C. Anal. Calcd for $C_{24}H_{20}Br_2$: C, 61.56; H, 4.31. Found: C, 61.20; H, 4.21. Crystals not soluble enough for NMR. MS (EI, 70 eV) (%): *m/z* 468 (M^+, 63), 389 (100), 308 (26).

4.1.9. (*E*,*E*)-1,4-Bis[4-(*S*-acetylthiomethyl)styryl]benzene (10). A slurry of **9** (0.23 g, 0.5 mmol) and potassium thioacetate (0.14 g, 1.2 mmol) in NMP (15 mL) was heated at 60 °C for 2 h. The clear solution was poured into ice (200 g). Filtration and separation on silica gel 60F (30 g) by means of CH_2Cl_2 gave yellow crystalline material which was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM). Reflux was maintained for 12 h. By slow cooling at room temperature, the product **10** (0.13 g, 57%) precipitated as light-yellow plates. Mp 257–258 °C. Anal. Calcd for $C_{28}H_{26}O_2S_2$: C, 73.33; H, 5.71; S, 13.98. Found: C, 73.32; H, 5.70; S, 13.84. IR(KBr): ν (cm^{-1}) 3015, 2909, 1910, 1698, 1654, 1604, 1515, 1422, 1352, 1335, 1141, 1099, 1015, 961, 947, 889, 833, 779, 751, 701, 633, 570, 546, 540. UV–vis ($CHCl_3$): λ_{max} (nm) (ε (M^{-1} cm^{-1})) 350 (sh, 61100), 362 (68700), 383 (sh, 43800). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H), 4.13 (s, 4H), 7.08 (s, 4H), 7.28 (d, J=8.2 Hz, 4H), 7.45 (d, J=8.2 Hz, 4H), 7.49 (s, 4H). Crystals not soluble enough for ^{13}C NMR. MS (EI, 70 eV) (%): *m/z* 458 (M^+, 100), 415 (11), 383 (72), 339 (14).

4.1.10. 4,4′-Bis(methoxymethyl)benzophenone (11). Compound **5** (10.05 g, 50 mmol) was added dropwise under an argon atmosphere to a solution of butyllithium (2.5 M in hexanes, 20 mL, 50 mmol) in THF (50 mL) cooled in a dry ice/acetone bath. After stirring the reaction mixture at −8 °C for 15 min, ethyl *N*,*N*-diethylcarbamate

(3.63 g, 25 mmol) was added during a 10 min period in a dropwise fashion. After stirring the reaction mixture at −78 °C for an additional 15 min, H_2O (10 mL) was added dropwise, and the reaction mixture was poured into H_2O (300 mL) and extracted with pentane (3×50 mL). The combined organic layers were washed with H_2O (30 mL), dried ($MgSO_4$), filtered, and concentrated by rotary evaporation (30 °C, 20 mmHg). Bulb-to-bulb distillation (0.05 mmHg, air bath 200 °C) afforded **11** (5.14 g, 76%) as a colorless liquid that crystallized into white crystals upon standing. Mp 45–46 °C. Purity >98% (GC–MS). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.95; H, 6.72. IR(KBr): ν (cm^{-1}) 3037, 3000, 2982, 2926, 2893, 2861, 2824, 2732, 2069, 1934, 1824, 1733, 1651, 1609, 1571, 1510, 1469, 1455, 1409, 1379, 1310, 1277, 1211, 1195, 1175, 1148, 1104, 1017, 972, 928, 854, 841, 819, 754, 681, 629, 487, 474, 436. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 6H), 4.48 (s, 4H), 7.40 (d, J=8.2 Hz, 4H), 7.74 (d, J=8.2 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.1, 73.7, 126.8, 129.8, 136.5, 142.7, 195.7. MS (EI, 70 eV) (%): *m/z* 270 (M^+, 25), 255 (4), 225 (7), 210 (34), 195 (7), 180 (18), 165 (18), 149 (100).

4.1.11. 4,4′-Bis(methoxymethyl)diphenylmethane (12). A slurry of ketone **11** (1.08 g, 4 mmol), KOH (1.35 g, 24 mmol), and hydrazine monohydrate (0.30 g, 6 mmol) in diethylene glycol (25 mL) was stirred at room temperature for 10 min in order to become homogeneous and then heated in a microwave oven for 20 min at 130 °C under the influence of 20 W microwaves. The clear colorless solution was poured into H_2O (200 mL) and extracted with pentane (3×50 mL). The combined organic layers were washed with H_2O (30 mL), dried ($MgSO_4$), filtered, and concentrated by rotary evaporation (30 °C, 20 mmHg). Bulb-to-bulb distillation (0.05 mmHg, air bath 200 °C) afforded **12** (0.89 g, 87%) as a colorless liquid. Purity >98% (GC–MS). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.78; H, 7.66. IR(KBr): ν (cm^{-1}) 3050, 3010, 2983, 2925, 2894, 2852, 2820, 2736, 1912, 1803, 1721, 1656, 1612, 1577, 1512, 1450, 1417, 1381, 1364, 1304, 1278, 1193, 1155, 1099, 1021, 967, 919, 857, 806, 754, 616, 579, 485. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 6H), 3.98 (s, 2H), 4.43 (s, 4H), 7.17 (d, J=8.1 Hz, 4H), 7.26 (d, J=8.1 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.2, 57.9, 74.4, 127.9, 128.8, 135.8, 140.4. MS (EI, 70 eV) (%): *m/z* 256 (M^+, 47), 225 (19), 211 (26), 179 (42), 121 (100).

4.1.12. 4,4′-Bis(bromomethyl)diphenylmethane (13). To a mixture of **12** (0.51 g, 2 mmol) and chlorobenzene (10 mL) was added bromotrimethylsilane (0.67 g, 4.4 mmol). The resulting yellow slurry was stirred at 75 °C for 4 h under nitrogen and poured into H_2O (100 mL). The phases were separated, and the aqueous phase was further extracted with toluene (2×20 mL). The combined organic extracts were filtered through silica gel 60F (10 g) by means of CH_2Cl_2–pentane (1/9). Evaporation afforded **13** (0.89 g, 87%) as white crystals. Mp 146–147 °C (lit.:[25] 151.5–153.5 °C). Anal. Calcd for $C_{15}H_{14}Br_2$: C, 50.88; H, 3.99. Found: C, 51.18; H, 3.92. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.96 (s, 2H), 4.48 (s, 4H), 7.15 (d, J=8.1 Hz, 4H), 7.32 (d, J=8.1 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.3, 41.2, 129.1, 129.2, 135.6, 141.0. MS (EI, 70 eV) (%): *m/z* 354 (M^+, 5), 275 (100), 194 (100).

4.1.13. 4,4′-Bis(*S*-acetylthiomethyl)diphenylmethane (14). A slurry of dibromide **13** (0.35 g, 1 mmol) and potassium thioacetate (0.25 g, 2.2 mmol) in NMP (10 mL) was heated at 60 °C for 2 h. The clear colorless solution was poured into ice (100 g) and extracted with Et_2O (3× 20 mL). The combined organic layers were washed with H_2O (30 mL) and evaporated. Separation on silica gel 60F (20 g) by means of CH_2Cl_2 gave a white crystalline material upon evaporation. Recrystallization from heptane afforded **14** (0.27 g, 78%) as white needles. Mp 90–91 °C. Anal. Calcd for $C_{19}H_{20}O_2S_2$: C, 66.25; H, 5.85; S, 18.65. Found: C, 66.25; H, 5.84; S, 18.69. IR(KBr): ν (cm^{-1}) 3045, 3002, 2920, 2832, 1912, 1693, 1510, 1431, 1411, 1359, 1241, 1130, 1098, 1023, 1000, 964, 914, 866, 839, 823, 774, 728, 718, 687, 626, 568, 541, 513, 475. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 6H), 3.90 (s, 2H), 4.08 (s, 4H), 7.09 (d, J=6.3 Hz, 4H), 7.19 (d, J=6.3 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 33.0, 41.1, 128.8, 129.0, 135.2, 139.9, 195.0. MS (EI, 70 eV) (%): *m/z* 344 (M^+, 21), 301 (8), 269 (100).

4.1.14. Diethyl 4-ethylbenzylphosphonate (16). A solution of bromide **15** (4.36 g, 22 mmol) and triethylphosphite (5 g, 30 mmol) in dioxane (40 mL) was refluxed under nitrogen for 12 h. The solvent was evaporated in vacuo, and bulb-to-bulb distillation (0.1 mbar, air bath 180 °C) gave the phosphonate **16** (3.8 g, 68%) as a colorless liquid. Anal. Calcd for $C_{13}H_{21}O_3P$: C, 60.93; H, 8.26. Found: C, 60.51; H, 8.69. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J=7.2 Hz, 3H), 1.24 (t, J=7.2 Hz, 6H), 2.62 (q, J=7.2 Hz, 2H), 3.23 (d, J=21 Hz, 2H), 4.01 (q, J=7.2 Hz, 4H), 7.13 (d, J=8.1 Hz, 2H), 7.22 (d, J=8.2, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 15.4, 16.2 (d, J=6 Hz), 28.3, 33.1 (d, J=138 Hz), 61.7 (d, J=7 Hz), 127.8 (d, J=3 Hz), 128.0 (d, J=3 Hz), 129.5 (d, J=3 Hz), 142.6 (d, J=3 Hz). MS–S (EI) (%): *m/z* 256 (M^+, 100).

4.1.15. *Trans*-4-*tert*-butylthio-4′-ethylstilbene (18). A solution of phosphonate **16** (0.77 g, 3 mmol) and aldehyde **17** (0.58 g, 3 mmol) in freshly distilled THF (50 mL) was cooled to 0 °C, and potassium *tert*-butoxide (0.37 g, 3.3 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and poured into water. The white crystalline precipitate was filtered off and dried in vacuo. Recrystallization and isomerization to the *trans* compound was achieved by refluxing the compound for 6 h in toluene (5 mL) containing iodine (0.1 mM), thus affording **18** (0.65 g, 73%). Mp 90.3–91.6 °C. Anal. Calcd for $C_{20}H_{24}S$: C, 81.02; H, 8.16; S, 10.82. Found: C, 80.55; H, 8.40; S, 10.51. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J=7.2 Hz, 3H), 1.30 (s, 9H), 2.62 (q, J=7.2 Hz, 2H), 7.04 (d, J= 16 Hz, 1H), 7.14 (d, J=16 Hz, 1H), 7.20 (d, J=7.7 Hz, 2H), 7.42–7.53 (m, 6H). ^{13}C (62.9 MHz, $CDCl_3$) δ 15.4, 28.6, 30.9, 46.1, 126.2, 126.5, 126.9, 128.1, 129.5, 131.6, 134.5, 137.6, 137.9, 144.1. MS (FAB): *m/z* 296 (M^+).

4.1.16. *Trans*-4-acetylthio-4′-ethylstilbene (19). To a solution of **18** (0.33 g, 1.1 mmol) and acetyl chloride (1 mL) in CH_2Cl_2 (20 mL) was added BBr_3 (1.5 mmol, 1 M in CH_2Cl_2). The black solution was stirred under

nitrogen for 2 h and poured into ice/water (100 mL). The precipitate was purified using coloumn chromatography (SiO_2, CH_2Cl_2). The product containing fraction was recrystallized and isomerized to the *trans* compound by refluxing the compound for 6 h in toluene (5 mL) containing iodine (0.1 mM). The product **19** precipitated as white crystals (170 mg, 53%). Mp 98.5–101.3 °C. Anal. Calcd for $C_{15}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35. Found: C, 76.44; H, 6.26; S, 11.24. IR(KBr): ν (cm^{-1}) 3019, 2961, 2928, 2870, 1911, 1704, 1587, 1508, 1455, 1411, 1350, 1179, 1121, 1008, 963, 831, 681, 617, 546. ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (t, $J=7.2$ Hz, 3H), 2.42 (s, 3H) 2.62 (q, $J=7.2$ Hz, 2H), 7.05 (d, $J=17$ Hz, 1H), 7.14 (d, $J=17$ Hz, 1H), 7.21 (d, $J=8.7$ Hz, 2H), 7.39 (d, $J=8.7$ Hz, 2H) 7.45 (d, $J=8.7$ Hz, 2H), 7.54 (d, $J=8.7$ Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 15.4, 28.6, 30.1, 126.4, 127.6, 126.9, 128.2, 130.1, 134.3, 134.6, 138.7, 144.3, 194.1; One signal overlapping. MS (EI) (%): *m/z* 282 (M^+, 55), 240 (100), 225 (25).

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