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One-Shot Double Elimination Process: A Practical and Concise Protocol for Diaryl Acetylenes

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Abstract: A variety of diaryl acetylenes were obtained in good yields when lithium hexamethyldisilazide was added to a solution of arylmethyl sulfone, aryl aldehyde, and chlorodiethylphosphate in THF. In this one-shot process, a number of transformations such as aldol reaction, phosphorylation of aldolate, and double elimination of the resulting β-substituted sulfone proceeded successively to afford the desired acetylenes. The one-shot process was accelerated by the substitution of halogen atoms on the phenyl groups, and unsymmetrically substituted diaryl acetylenes were obtained without contamination of the dehalogenated products. Diaryl acetylenes with other substituents such as CF_3, ethoxycarbonyl, dimethylamino, TMS-acetylene groups, as well as pyridinyl and thienyl moieties were also accessible with this method. However, methoxy-substituted compounds were obtained in moderate yields under the same conditions, but the yields were increased when lithium diisopropylamide was used instead.

Keywords: alkynes · elimination · halogens · lithium amides · sulfones

Introduction

Various acetylenic compounds are now synthesized as organic molecules with intriguing functionality.[1] The phenylene–ethynylene array is one of the most important components of liquid crystals,[2] organic electroluminescent displays,[3] and carbon-rich materials,[4] to name a few. For construction of phenylene–ethynylene arrays, Sonogashira coupling[5] between aryl halides with terminal acetylenes has been employed routinely. Although this transition-metal-catalyzed coupling reaction is indeed straightforward and versatile for aryl acetylenes, the synthesis of functionalized acetylenes requires sophisticated protection–deprotection technologies. Selective desilylation of terminal acetylenes protected with trimethylsilyl (TMS) and triisopropylsilyl (TIPS) or *tert*-butyldimethylsilyl (TBS) groups followed by Sonogashira coupling with aryl halides allow the preparation of unsymmetrically substituted phenylene–ethynylenes.[6a–d] The dialkyltriazene group can be used as a halide equivalent that is inert to Sonogashira coupling but can be easily transformed, on demand, to iodide by treatment with MeI.[6e,f] However, these protocols are somewhat tedious in spite of their remarkable usefulness. In the course of our research into the preparation of acetylenes with various functionalities, we succeeded in developing a practical and concise synthetic procedure from arylmethyl sulfones and aryl aldehydes to diaryl acetylenes with a variety of functional groups such as halogen, ether, ester, and heteroaromatics.

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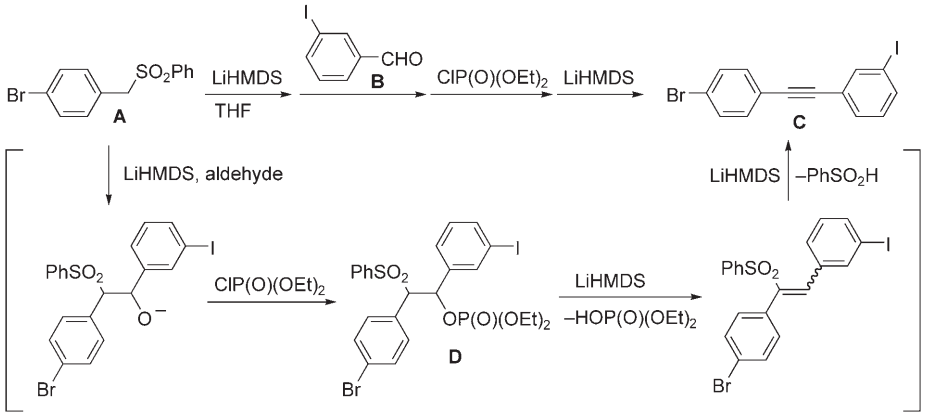
Results and Discussion

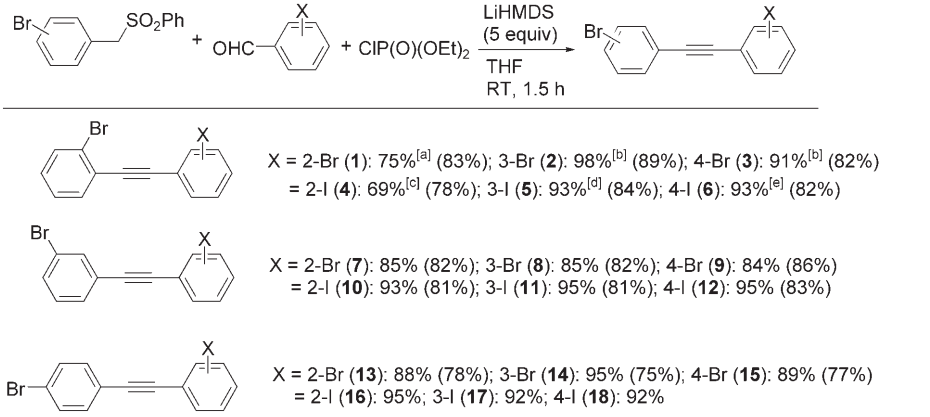
We have already developed a methodology for the preparation of acetylenes by utilizing sulfones and aldehydes as starting compounds.[7] When a solution of benzyl sulfone **A** in THF was treated successively with lithium hexamethyldisilazide (LiHMDS), benzaldehyde **B**, chlorodiethylphosphate, and LiHMDS again, the desired diphenyl acetylene **C** was obtained (Scheme 1). This protocol involves a number of transformations, such as aldol-type addition of **A** to **B**, phosphorylation of the aldolate, and double elimination of the resulting β-substituted sulfone **D**; these operations can be carried out successfully in a one-pot manner without disturbing base-labile halogen atoms.

Halogen-substituted acetylenes can be used as building blocks for more complicated acetylenes, and our previous research exemplified the usefulness of unsymmetrically substituted acetylenes as building blocks for tailor-made phenyl-

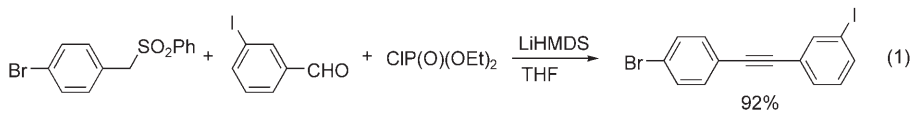


Scheme 1. One-pot process for the preparation of diphenyl acetylenes.

ene–ethynylenes.[7a] In this one-pot protocol, LiHMDS was added separately for the aldol-type reaction and the double elimination of β-substituted sulfones. Therefore, we postulated that if a carbanion of benzyl sulfone could be generated by LiHMDS in the presence of aldehyde and chlorodiethylphosphate, the aldol reaction, phosphorylation, and LiHMDS-induced double elimination that follow would give rise to the desired acetylene in a one-shot manner [Eq. (1)]. This is indeed the case; when a solution of LiHMDS (5.0 mmol) in THF (5 mL) was added to a solution of 4-bromobenzyl sulfone (1.2 mmol), 3-iodobenzaldehyde (1.0 mmol), and chlorodiethylphosphate (1.2 mmol) in THF (10 mL) at 0 °C, and the mixture stirred at room temperature for 1.5 h, the reaction for



Scheme 2. One-shot process for the preparation of **1**–**18** from bromobenzyl sulfones. Yields of isolated products are shown; those for the corresponding one-pot process are in parentheses. [a] 45 h. [b] 20 h. [c] LiHMDS (10 equiv), 20 h. [d] 8 h. [e] 18 h.



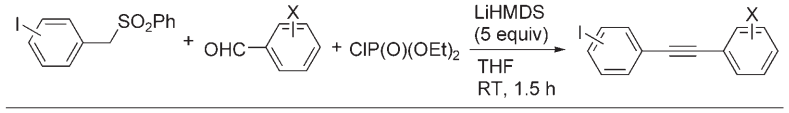
acetylene proceeded smoothly as expected, and 1-(4-bromophenyl)-2-(3-iodophenyl)ethyne was obtained in 92% yield. This process is clean, and after the reaction, the desired acetylene could be observed as the sole product with TLC. Thus, purification of the product was facile, and the usual aqueous workup followed by filtration with a thin pad of silica gel produced the pure products. This one-shot protocol was versatile for access to various halogen-substituted diphenyl acetylenes. The reaction between bromo- and/or iodo-substituted benzyl sulfones with benzaldehyde derivatives afforded the corresponding dibromo, bromoiodo, and diiododiphenyl acetylenes in good to excellent yields (Schemes 2 and 3). The one-shot protocol enabled easier operations than the one-pot process and afforded comparable or better yields. When 2-bromo and 2-iodobenzyl sulfones were used, a longer reaction time or 10 equivalents of LiHMDS was necessary for completion of the reaction, otherwise the vinyl sulfone intermediates remained, thus resulting in low yields of the desired acetylenes. For instance, in the reaction of 2-bromobenzyl sulfone with 2-iodobenzaldehyde to give **4**, the yield was improved from 24% to 69% by the introduction of 10 equivalents of LiHMDS and stirring for 20 h. The yield of the reaction of 2-iodobenzyl sulfone with 3-bromobenzaldehyde to give **10** was also improved from 53% to 91% by increasing the reaction time from 1.5 to 8 h. We found that trimethylsilyl chloride can be used instead of chlorodiethylphosphate, but chemical yields decreased slightly: **11** was obtained from 3-bromobenzyl sulfone and 3-iodobenzaldehyde in 82% yield, and **21** was obtained from 4-iodobenzyl sulfone and 3-iodobenzaldehyde in 75% yield.

This one-shot protocol is also applicable to the preparation of monohalogen-substituted acetylenes (Scheme 4). When monohalogen-substituted aldehydes were used, the reactions proceeded smoothly to give satisfactory results (73–93%). These can be carried out on a larger scale. For

instance, when benzyl sulfone was treated with 3- and 4-bromobenzaldehyde on a 20-mmol scale, more than 4 g of **24** and **25** were obtained in 78 and 85% yield, respectively. When bromo-substituted sulfones were used, however, the reactions proceeded rather sluggishly, and longer reaction times were required. Similarly, the vinyl sulfone intermediates were not consumed completely after 1.5 h of reaction time and furnished only modest yields (21% for **23**, 69% for **24**, and 57% for **25**).

Whereas LiHMDS worked well as a base for access to mono- and dihalodiphenyl acetylenes, other bases such as *t*BuOK and lithium diisopropylamide (LDA) were not suitable. When *t*BuOK (15 equiv) was used in the reaction between benzyl sulfone and 3-bromobenzaldehyde, the reaction proceeded rather sluggishly to afford **24** in only 71% yield, though LiHMDS (5 equiv) provided **24** in 93% yield (Scheme 4). In the preparation of **11**, *t*BuOK resulted in low yields and contamination of dehalogenated acetylenes **24** which were inseparable from **11** (Scheme 5). The use of LDA also failed to give a satisfactory outcome.

Next, we investigated the preparation of methoxy-substituted diphenyl acetylenes. The one-shot protocol was carried out by means of several combinations of bromobenzyl sulfones and methoxybenzaldehydes and their reverse (Scheme 6). These reactions proceeded rather sluggishly, and the desired acetylenes were obtained in moderate yields with LiHMDS (5 equiv) or *t*BuOK (10 equiv). Surprisingly, in the preparation of the 3-bromo-4′-methoxy derivative **29** from 3-bromobenzyl sulfone and 4-methoxybenzaldehyde,

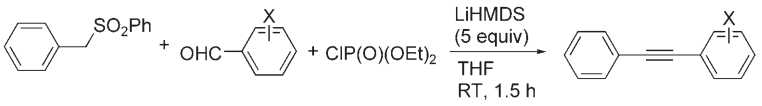


X = 2-Br (**4**): 51%[a] (61%); 3-Br (**10**): 91%[b] (82%); 4-Br (**16**): 88%[c] (76%)

X = 2-Br (**5**): 93% (79%); 3-Br (**11**): 93% (83%); 4-Br (**17**): 95% (86%)
= 2-I (**19**): 98% (71%); 3-I (**20**): 94% (75%)

X = 2-Br (**6**): 88% (84%); 3-Br (**12**): 92% (78%); 4-Br (**18**): 92% (84%)
= 3-I (**21**): 87%; 4-I (**22**): 66%[d]

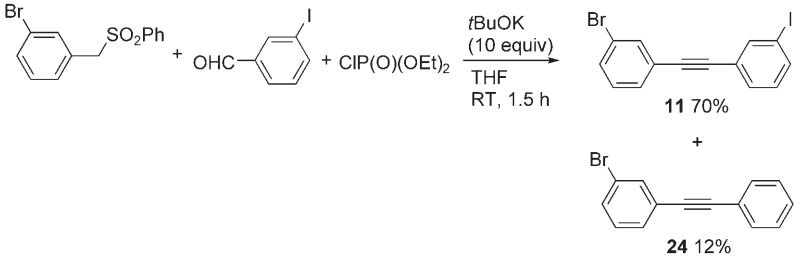
Scheme 3. One-shot process for the preparation of **4**–**22** from iodobenzyl sulfones. Yields of isolated products are shown; those for the corresponding one-pot process are in parentheses. [a] LiHMDS (10 equiv), 20 h. [b] 8 h. [c] 18 h. [d] 3 h.



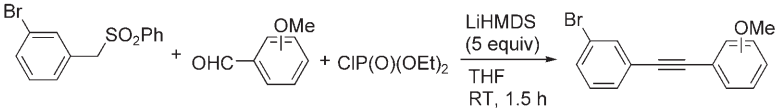
X = 2-Br (**23**): 90% (85%); 3-Br (**24**): 93% (85%), 71%[a], 78%[b]; 4-Br (**25**): 87% (86%), 85%[b]; 3-I (**26**) 73%

X = 2-Br (**23**): 81%[c] (80%); 3-Br (**24**): 95%[c] (79%); 4-Br (**25**): 84%[d]

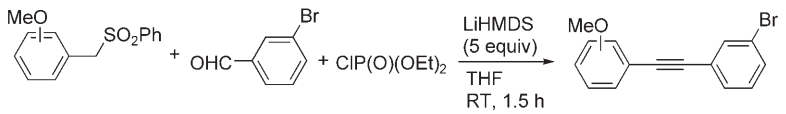
Scheme 4. One-shot process for the preparation of **23**–**26**. Yields of isolated products are shown; those for the corresponding one-pot process are in parentheses. [a] *t*BuOK (15 equiv). [b] 20-mmol scale. [c] 18 h. [d] 20 h.



Scheme 5. One-shot process for the preparation of **11** with *t*BuOK.



X = 2-MeO (**27**): 39%, 31%[a]; 3-MeO (**28**): 64%, 27%[a]



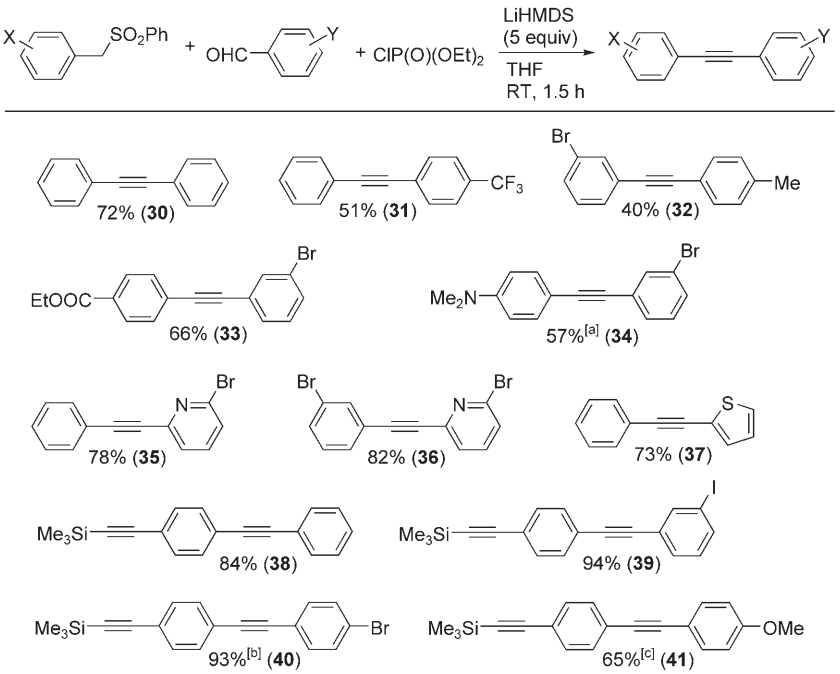
X = 2-MeO (**27**): 72%, 57%[a]; 3-MeO (**28**): 86%, 59%[a] (88%); 4-MeO (**29**): 58%[a]

Scheme 6. One-shot process for the preparation of **27**–**29**. Yields of isolated products are shown; those for the corresponding one-pot process are in parentheses. [a] *t*BuOK (10 equiv).

CHEMISTRY
AN ASIAN JOURNAL

the last elimination did not occur, and the corresponding vinyl sulfone was obtained as the sole product. On the other hand, the reverse combination, namely, 4-methoxybenzyl sulfone with 3-bromobenzaldehyde, with *t*BuOK resulted in the formation of **29** (58%), though LiHMDS afforded the vinyl sulfone again.

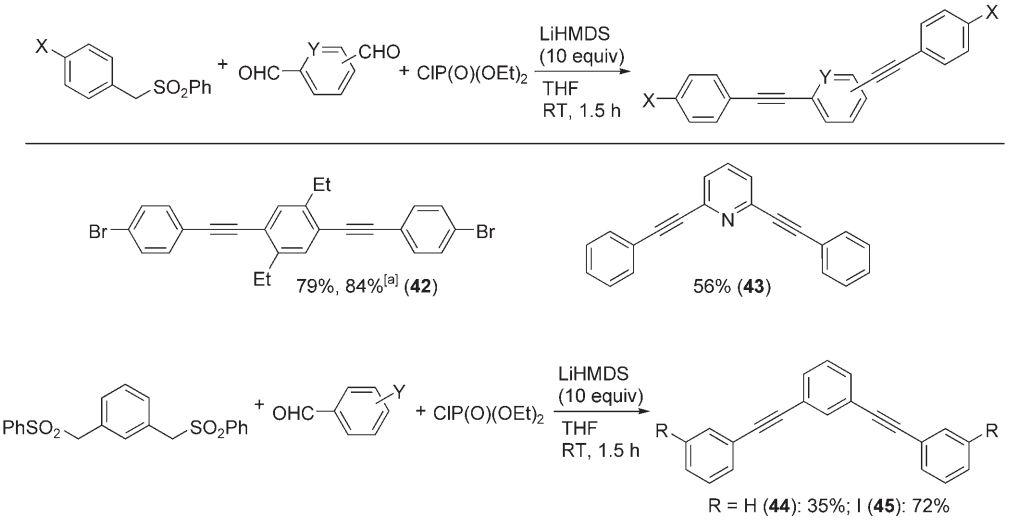
To evaluate the one-shot process for acetylene, we prepared acetylenes that bear other groups. As shown in Scheme 7, various acetylenes were produced in fair to excellent yields by treatment of the corresponding sulfones and aldehydes with chlorodiethylphosphate and LiHMDS. Trifluoromethyl **31** and methyl derivatives **32** were obtained in moderate yields. Ester and amine groups (**33** and **34**) were tolerated in this protocol. The incorporation of heteroaromatic rings such as pyridine and thiophene was effected as seen in **35**–**37**. TMS-acetylene-substituted benzyl sulfones could also be used, and the corresponding bisacetylene derivatives **38**–**41** were prepared in high yields. Dialdehydes or disulfones gave the desired bisacetylenes **42**–**45** in good yields (Scheme 8). In these reactions, the halogen-substituted sulfone and aldehyde enabled smooth elimination and resulted in high yields. In the preparation of **42**, trimethylsilyl chloride gave a better yield than chlorodiethylphosphate.



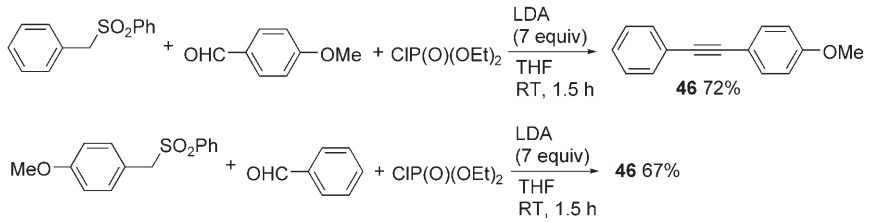
Scheme 7. One-shot process for the preparation of **30**–**41**. Yields of isolated products are shown. [a] 18 h. [b] 3 h. [c] 0–30 °C, 30 min.

When the one-shot protocol for 4-methoxydiphenylacetylene (**46**) was attempted by use of LiHMDS or *t*BuOK, the desired acetylene was not obtained at all, but the vinyl sulfone intermediate was observed as the sole product with TLC analysis. However, LDA enabled smooth elimination of sulfonic acid from the intermediate to give **46** in good yields (Scheme 9).

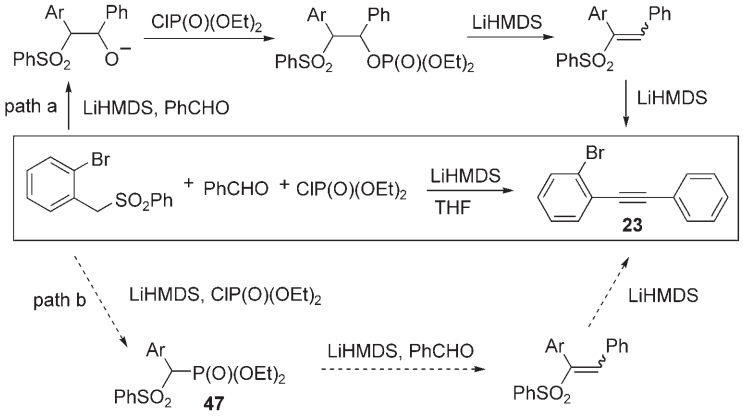
For this one-shot process, two pathways are plausible (Scheme 10): In path a (solid line), the aldol reaction occurs first, followed by transformation of the aldolate to the phosphate and double elimination. In path b (dashed line), phosphonate **47**, which was derived from the reaction of the sulfonyl anion with chlorophosphate,



Scheme 8. One-shot process for the preparation of **42**–**45**. Yields of isolated products are shown. [a] Me_3SiCl was used instead of $ClP(O)(OEt)_2$.

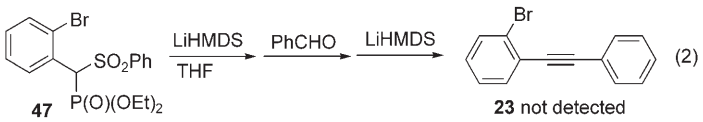


Scheme 9. One-shot process for the preparation of **46** with LDA.



Scheme 10. Plausible mechanism of the one-shot process for the preparation of acetylenes.

undergoes a Wittig–Horner reaction with the aldehyde followed by elimination. To differentiate the two possibilities, we chose the reaction of 3-bromobenzylsufone with benzaldehyde. When this reaction was carried out in a sequential one-pot manner, the desired acetylene was obtained in 79% yield. By contrast, Wittig–Horner reaction of **47** with benzaldehyde did not proceed at all, and on the basis of TLC and ^{1}H NMR spectroscopic analyses of the crude mixture, no evidence of the formation of **23** was observed [Eq. (2)]. These results strongly support the aldol-reaction path of the one-shot process.[8]



Conclusions

In summary, we have presented a convenient synthesis for acetylenes by use of sulfones and aldehydes. This protocol can be carried out easily by introduction of a solution of LiHMDS in THF to a mixture of sulfone and aldehyde to afford various acetylenes in good to excellent yield. When the reagents contain electron-withdrawing substituents, the reaction proceeds smoothly, but if electron-releasing substituents are present, longer reaction times and/or more base are required for completion of reaction.

Experimental Section

General

All reactions were carried out under argon atmosphere with freshly distilled solvents, unless otherwise noted. THF and Et_2O were distilled from sodium/benzophenone. Other solvents such as toluene, diisopropylamine, and *N*,*N*-dimethylformamide (DMF) were distilled from CaH_2. LiHMDS solution in THF was purchased and used without titration. BuLi solution in hexane was purchased and titrated by the Gilman method prior to use. Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded at 25 °C on JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with tetramethylsilane as an internal reference. Elemental analyses were performed with a Perkin–Elmer PE 2400 instrument.

Synthesis

Halogen-substituted sulfones were prepared according to the reported method,[7a] and other sulfones were prepared by reaction of the corresponding benzyl bromides and sodium benzenesulfinate.

2-Methoxyphenylmethyl phenyl sulfone: A solution of 2-methoxyphenylmethyl bromide (3.13 g, 20.0 mmol) and $PhSO_2Na{\cdot}2H_2O$ (4.80 g, 24.0 mmol) in DMF (50 mL) was heated at 80 °C for 12 h. After workup with CH_2Cl_2 and water, the combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was subjected to recrystallization from CH_2Cl_2/hexane to afford pure 2-methoxyphenylmethyl phenyl sulfone (4.35 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.33 (s, 3H), 4.45 (s, 2H), 6.65 (d, J = 8.3 Hz, 1H), 6.94 (t, J = 6.8 Hz, 1H), 7.27–7.33 (m, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.61 ppm (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 54.9, 56.5, 110.2, 116.7, 120.6, 128.3, 128.7, 130.3, 132.4, 133.2, 138.6, 157.3 ppm.

3- and 4-methoxyphenylmethyl phenyl sulfones: These compounds were prepared according to the same procedure above. 3-Methoxyphenylmethyl phenyl sulfone: 4.52 g, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.71 (s, 3H), 4.29 (s, 2H), 6.61 (s, 1H), 6.45 (d, J = 6.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.66 ppm (d, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 62.9, 114.8, 115.8, 123.1, 128.6, 128.9, 129.4, 129.5, 133.7, 137.8, 159.5 ppm. 4-Methoxyphenylmethyl phenyl sulfone: 4.20 g, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 4.25 (s, 2H), 6.79 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.61 (t, J = 7.7 Hz, 1H), 7.64 ppm (d, J = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 62.2, 114.0, 119.9, 128.6, 128.9, 132.0, 133.6, 137.9, 160.0 ppm.

4-(Trimethylsilylethynyl)phenylmethyl phenyl sulfone: Trimethylsilylacetylene (4.24 mL, 30.0 mmol), [$(Ph_3P)_4Pd$] (1.16 g, 1.0 mmol), CuI (190 mg, 1.0 mmol), diisopropylamine (20 mL), and toluene (20 mL) were added to a solution of 4-bromophenylmethyl phenyl sulfone (5.00 g, 20.0 mmol) in THF (150 mL). The mixture was heated at 60 °C for 12 h. The mixture was filtered through a pad of celite, and the filtrate was washed with aqueous NH_3. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over silica gel (CH_2Cl_2/hexane (40%) to CH_2Cl_2 (100%)) to afford pure 4-(trimethylsilylethynyl)phenylmethyl phenyl sulfone (5.98 g, 91% yield). M.p.: 155–160 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 4.29 (s, 2H), 7.01 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.7, 2H), 7.59–7.62 ppm (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −0.14, 62.6, 95.6, 104.2, 123.7, 128.4, 128.6, 129.0, 130.6, 132.1, 133.8, 137.6 ppm.

4-Ethoxycarbonylphenylmethyl phenyl sulfone: A solution of ethyl 4-methylbenzoate (3.28 g, 20.0 mmol), *N*-bromosuccinimide (3.92 g, 22.0 mmol), and benzoyl peroxide (484.5 mg, 2.0 mmol) in CCl_4 (100 mL)

was heated at reflux for 12 h. The mixture was filtered, and the filtrate was washed with aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 three times, and the combined organic layer was washed with brine and dried over $MgSO_4$. After the mixture was filtered, the filtrate was evaporated, and the residue was subjected to column chromatography over silica gel (EtOAc/hexane (5%)) to afford an inseparable mixture of 4-ethoxycarbonylphenylmethyl bromide and dibromide (4.67 g). A solution of this mixture (4.67 g) and $PhSO_2Na{\cdot}2H_2O$ (4.80 g, 24.0 mmol) in DMF (50 mL) was then heated at 80 °C for 12 h. After workup with CH_2Cl_2 and water, the combined organic layer was washed with water and brine. After drying over $MgSO_4$ followed by evaporation, the residue was subjected to recrystallization from CH_2Cl_2/hexane to afford pure 4-ethoxycarbonylphenylmethyl phenyl sulfone (4.80 g, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.39$ (t, $J = 7.2$ Hz, 3H), 4.36 (s, 2H), 4.37 (q, $J = 7.2$ Hz, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.47 (t, $J = 8.3$ Hz, 2H), 7.60–7.64 (m, 3H), 7.94 ppm (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.3$, 30.9, 61.2, 62.6, 128.6, 129.0, 129.7, 130.8, 132.9, 133.9, 137.5, 166.0 ppm.

4-Dimethylaminophenylmethyl phenyl sulfone: $NaBH_4$ (340 mg, 9.0 mmol) was added to a solution of 4-dimethylaminobenzaldehyde (2.24 g, 15.0 mmol) in methanol (10 mL), and the mixture was heated at 60 °C for 2.5 h. After introduction of water at 0 °C, workup with EtOAc and water was carried out, and the combined organic layer was washed with brine and dried over Na_2SO_4. After filtration followed by evaporation, the residue was subjected to column chromatography over silica gel (EtOAc/hexane (40%)) to afford pure 4-dimethylaminophenylmethanol (2.21 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.94$ (s, 6H), 4.55 (s, 2H), 6.73 (d, $J = 8.6$ Hz, 2H), 7.23 ppm (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.6$, 65.3, 112.6, 128.6, 128.9, 150.3 ppm. 4-Dimethylaminophenylmethanol (998 mg, 6.6 mmol) and HCl (12 N, 2.5 mL) were then placed in a stainless autoclave, and the mixture was heated at 100 °C for 15 h. Evaporation provided crude 4-(dimethylhydroammonium)phenylmethyl chloride, which was used for sulfonylation without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.20$ (s, 6H), 4.61 (s, 2H), 7.56 (br s, 2H), 7.82 ppm (br s, 2H); ^{13}C NMR (75 HMz, $CDCl_3$): $\delta = 44.6$, 47.2, 121.4, 130.6, 139.7, 142.5 ppm. A solution of 4-(dimethylhydroammonium)phenylmethyl chloride (4.12 g, 20.0 mmol) and $PhSO_2Na{\cdot}2H_2O$ (3.94 g, 24.0 mmol) in DMF (50 mL) was then heated at 80 °C for 12 h. After workup with CH_2Cl_2 and water, the combined organic layer was washed with water, aqueous $NaHCO_3$, and brine. After drying over Na_2SO_4 followed by evaporation, the residue was subjected to column chromatography over silica gel (Et_3N was eluted prior to use to deactivate the silica gel. EtOAc/hexane (5%) was used for elution of the remaining chloride, and EtOAc/hexane (40%) was used for elution of the desired sulfone) followed by recrystallization from ethanol to afford pure 4-dimethylaminophenylmethyl phenyl sulfone (2.86 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.93$ (s, 6H), 4.22 (s, 2H), 6.58 (d, $J = 8.6$ Hz, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 7.46 (t, $J = 8.3$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.66 ppm (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.3$, 62.4, 112.1, 114.8, 128.7, 128.8, 131.6, 133.4, 138.2, 150.6 ppm.

1,3-Bis(phenylsulfonylmethyl)benzene: A solution of 1,3-bis(bromomethyl)benzene (1.32 g, 5.0 mmol) and $PhSO_2Na{\cdot}2H_2O$ (3.94 g, 24.0 mmol) in DMF (10 mL) was heated at 80 °C for 12 h. After workup with CH_2Cl_2 and water, the combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was subjected to recrystallization from CH_2Cl_2/hexane to afford pure 1,3-bis(phenylsulfonylmethyl)benzene (1.72 g, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.24$ (s, 4H), 6.98 (s, 1H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 4H), 7.61–7.66 ppm (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 62.4$, 128.5, 128.6, 128.8, 129.0, 131.2, 133.2, 133.9, 137.8 ppm.

Benzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, thiophene-2-carboaldehyde, 2,6-dibromopyridine, and 2-, 3-, and 4-bromobenzaldehyde were commercially available. 2-, 3-, and 4-iodobenzaldehyde were prepared according to the reported method,[9] and other aldehydes such as 1,4-diethyl-2,5-diformylbenzene and 2-bromo-6-formylpyridine were prepared as described below.

1,4-Diethyl-2,5-diiodobenzene: Iodine (6.10 g, 24.0 mmol) and H_5IO_6 (2.74 g, 12.0 mmol) were added to a mixture of 1,4-diethylbenzene (4.03 g, 30.0 mmol), acetic acid (45 mL), water (9.0 mL), and H_2SO_4 (1.35 mL). The mixture was heated at 80 °C for 16 h, after which aqueous $NaHSO_3$ was added at 0 °C and the mixture stirred for 2 h. After filtration, the solids obtained were washed with water and dissolved in EtOAc. After drying over $MgSO_4$, the solution was evaporated, and the residue was subjected to recrystallization from hexane to furnish pure 1,4-diethyl-2,5-diiodobenzene (9.74 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7.5$ Hz, 6H), 2.65 (q, $J = 7.5$ Hz, 4H), 7.62 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.4$, 33.1, 100.3, 138.6, 145.9 ppm.

1,4-Diethyl-2,5-diformylbenzene: A solution of *t*BuLi (1.46 M, 33.0 mL, 48.2 mmol) in pentane was added to a solution of 1,4-diethyl-2,5-diiodobenzene (3.86 g, 10.0 mmol) in THF (60 mL) at −78 °C, and the mixture was stirred at −78 °C for 1 h. DMF (4.62 mL, 61.3 mmol) was then added at −78 °C, and the mixture was stirred at room temperature for 3 h. After workup with EtOAc and aqueous NH_4Cl, the combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over silica gel (CH_2Cl_2/hexane (40%)) to furnish pure 1,4-diethyl-2,5-diformylbenzene (1.63 g, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.30$ (t, $J = 7.7$ Hz, 6H), 3.11 (q, $J = 7.6$ Hz, 4H), 7.76 (s, 2H), 10.4 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.2$, 25.0, 132.7, 136.7, 144.5, 191.8 ppm.

2-Bromo-6-formylpyridine: A solution of BuLi (1.41 M, 14.2 mL, 20.0 mmol) in hexane was added to a solution of 2,6-dibromopyridine (4.73 g, 20.0 mmol) in Et_2O (100 mL) at −78 °C, and the mixture was stirred at −78 °C for 30 min. DMF (1.81 mL, 24.0 mmol) was then added at −78 °C, and the mixture was stirred for 20 min. After warming to 0 °C, HCl (1 N) was added, followed by saturated aqueous $NaHCO_3$ until the pH of the solution was greater than 7. After workup with EtOAc and water, the combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over silica gel (EtOAc/hexane (10%)) to furnish pure 2-bromo-6-formylpyridine (3.01 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.72–7.79 (m, 2H), 7.90–7.95 (m, 1H), 10.01 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 120.3$, 132.7, 139.4, 142.6, 153.4, 191.7 ppm.

11: A solution of LiHMDS (1.0 M, 10.0 mL, 10.0 mmol) in THF was added to a solution of 3-bromophenylmethyl phenyl sulfone (747 mg, 2.4 mmol), 3-iodobenzaldehyde (464 mg, 2.0 mmol), and diethyl chlorophosphate (0.35 mL, 2.4 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. After workup with EtOAc and aqueous NH_4Cl, the mixture was dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over a thin pad of silica gel ($R_f = 0.40$, hexane) to furnish pure **11** (728 mg, 95%).

This one-shot double elimination method was also used to prepare **1**–**41** and **46**. The preparation of all dihalogen-substituted diphenyl acetylenes **1**–**22** were reported in the previous paper,[7a] and **30** is commercially available.

23:[10] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.18$ (t, $J = 8.2$ Hz, 1H), 7.30 (t, $J = 8.2$ Hz, 1H), 7.34–7.38 (m, 3H), 7.53–7.64 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 88.0$, 93.9, 122.9, 125.4, 125.6, 127.0, 128.4, 128.6, 129.4, 131.7, 132.4, 133.2 ppm.

24:[11] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.22$ (t, $J = 7.9$ Hz, 1H), 7.33–7.38 (m, 3H), 7.43–7.48 (m, 2H), 7.51–7.55 (m, 2H), 7.67–7.69 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 87.8$, 90.7, 122.1, 122.7, 125.3, 128.4, 128.6, 129.7, 130.1, 131.3, 131.6, 134.0 ppm.

25:[12] M.p.: 80–83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.34–7.41 (m, 5H), 7.47–7.54 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 88.3$, 90.5, 122.2, 122.5, 122.9, 128.4, 128.5, 131.6, 131.7, 133.0 ppm.

26:[13] M.p.: 45–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.08$ (t, $J = 7.7$ Hz, 1H), 7.33–7.37 (m, 3H), 7.46–7.54 (m, 3H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.90 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 87.6$, 90.7, 93.8, 122.7, 125.3, 128.4, 128.6, 129.8, 130.7, 131.6, 137.2, 140.1 ppm.

27: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.92$ (s, 3H), 6.90–6.97 (m, 2H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.30–7.37 (m, 1H), 7.43–7.50 (m, 3H), 7.71 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.8$, 87.1, 91.8, 110.6, 111.9, 120.5, 122.0, 125.6, 129.7, 130.1, 130.2, 131.2, 133.6, 134.3, 160.0 ppm; elemental

analysis: calcd (%) for $C_{15}H_{11}BrO$: C 62.74, H 3.86; found: C 62.94, H 3.64.

28:[14] M.p.: 78–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.88–6.95 (m, 1H), 7.03–7.07 (m, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.19–7.30 (m, 2H), 7.44–7.49 (m, 2H), 7.67–7.71 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, 87.6, 90.6, 115.3, 116.3, 122.1, 123.7, 124.2, 125.2, 129.5, 129.8, 130.1, 131.4, 134.3, 159.3 ppm.

29:[15] M.p.: 65–67 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.90–6.93 (m, 1H), 7.04–7.06 (m, 1H), 7.12 (d, J = 6.3 Hz, 1H), 7.20–7.28 (m, 2H), 7.44–7.48 (m, 2H), 7.68–7.69 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, 86.6, 90.7, 114.0, 114.8, 122.1, 125.6, 129.7, 129.9, 131.0, 133.1, 134.1, 159.8 ppm.

31:[16] M.p.: 100–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.39 (m, 3H), 7.53–7.58 (m, 2H), 7.58–7.65 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.9, 91.7, 122.5, 123.9 (J = 271.9 Hz), 125.2 (J = 3.6 Hz), 127.1, 128.4, 128.8, 129.8 (J = 32.6 Hz), 131.7, 131.8 ppm.

32: M.p.: 89–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 7.16 (d, J = 4.8 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H), 7.40–7.45 (m, 4H), 7.67 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 87.2, 90.9, 119.6, 122.1, 125.5, 129.2, 129.7, 130.1, 131.2, 131.6, 134.2, 138.8 ppm; elemental analysis: calcd (%) for $C_{15}H_{11}Br$: C 66.44, H 4.09; found: C 66.50, H 4.03.

33: M.p.: 70–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.3 Hz, 3H), 4.39 (q, J = 7.3 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 7.48 (dd, J = 8.0, 7.7 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.70 (s, 1H), 8.03 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3, 61.2, 89.8, 90.5, 122.2, 124.7, 127.2, 129.5, 129.8, 130.2, 130.2, 131.5, 131.8, 134.4, 165.9 ppm; elemental analysis: calcd (%) for $C_{17}H_{13}BrO_2$: C 62.03, H 3.98; found: C 62.34, H 3.61.

34: M.p.: 116–118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.99 (s, 6H), 6.65 (d, J = 9.2 Hz, 2H), 7.17 (t, J = 7.7 Hz, 1H), 7.38–7.41 (m, 4H), 7.63–7.65 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.1, 85.9, 92.2, 109.3, 111.7, 122.0, 126.2, 129.6, 129.7, 130.4, 132.8, 133.9, 150.3 ppm; elemental analysis: calcd (%) for $C_{16}H_{14}BrN$: C 64.02, H 4.70, N 4.67; found: C 64.22, H 4.43, N 4.75.

35:[17] M.p.: 79–81 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.40 (m, 3H), 7.43–7.49 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.57–7.61 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 87.4, 90.8, 121.7, 126.0, 127.4, 128.4, 129.3, 132.1, 138.3, 141.8, 143.8 ppm.

36: M.p.: 116–118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (t, J = 7.9 Hz, 1H), 7.45–7.49 (m, 2H), 7.51–7.57 (m, 3H), 7.73–7.75 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.4, 88.9, 122.2, 123.7, 126.1, 127.7, 129.9, 130.6, 132.4, 134.7, 138.4, 141.9, 143.4 ppm; elemental analysis: calcd (%) for $C_{13}H_7Br_2N$: C 46.33, H 2.09, N 4.16; found: C 46.54, H 1.92, N 4.14.

37:[18] M.p.: 48–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (dd, J = 5.0, 3.5 Hz, 1H), 7.27–7.30 (m, 2H), 7.33–7.37 (m, 3H), 7.50–7.53 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 82.6, 93.0, 122.8, 123.1, 127.0, 127.2, 128.3, 128.3, 131.3, 131.8 ppm.

38:[19] M.p.: 115–118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 9H), 7.34–7.37 (m, 3H), 7.42–7.48 (m, 4H), 7.50–7.55 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 89.0, 91.4, 96.3, 104.7, 123.0, 123.1, 123.4, 128.5, 128.6, 131.5, 131.7, 132.0 ppm.

39: M.p.: 101–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 9H), 7.08 (t, J = 7.7 Hz, 1H), 7.43–7.48 (m, 5H), 7.67 (d, J = 7.9 Hz, 1H), 7.87–7.89 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 89.5, 90.4, 93.8, 96.6, 104.6, 122.9, 123.4, 125.1, 130.0, 130.8, 131.5, 132.0, 137.5, 140.2 ppm; elemental analysis: calcd (%) for $C_{19}H_{17}ISi$: C 57.00, H 4.28; found: C 57.26, H 4.43.

40:[20] M.p.: 145–148 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 9H), 7.38 (d, J = 8.5 Hz, 2H), 7.44 (s, 4H), 7.48 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0, 90.2, 90.3, 96.6, 104.6, 122.0, 122.8, 123.0, 123.3, 131.5, 131.8, 132.0, 133.1 ppm.

41:[21] M.p.: 155–157 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 3.83 (s, 3H), 6.88 (d, J = 8.9 Hz, 2H), 7.43–7.47 ppm (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −0.1, 55.3, 88.1, 92.0, 96.5, 104.4, 114.0, 115.0, 122.6, 123.8, 131.2, 131.8, 133.0, 160.4 ppm.

46:[22] M.p.: 57–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.89 (d, J = 8.7 Hz, 2H), 7.30–7.37 (m, 3H), 7.45–7.53 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2, 88.0, 89.3, 114.0, 115.3, 123.5, 127.9, 128.3, 131.4, 133.0, 159.6 ppm.

45: A solution of LiHMDS (1.0 M, 10.0 mL, 10.0 mmol) in hexane was added to a solution of 1,3-bis(phenylsulfonylmethyl)benzene (384 mg, 1.0 mmol), 3-iodobenzaldehyde (510 mg, 2.2 mmol), and diethyl chlorophosphate (0.35 mL, 2.4 mmol) in THF (20 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. After workup with EtOAc and aqueous NH_4Cl, the mixture was dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over silica gel (CH_2Cl_2/hexane (10%)) to furnish pure **45** (382 mg, 72%). M.p.: 159–161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (t, J = 7.9 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 4H), 7.67–7.70 (m, 3H), 7.88–7.91 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.3, 89.7, 93.8, 123.2, 125.0, 128.6, 129.9, 130.7, 131.6, 134.6, 137.5, 140.2 ppm; elemental analysis: calcd (%) for $C_{22}H_{12}I_2$: C 49.84, H 2.28; found: C 49.73, H 2.01. This one-shot double elimination method was also used to prepare **42**–**44**.

42: M.p.: 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, J = 7.5 Hz, 6H), 2.84 (q, J = 7.5 Hz, 4H), 7.38 (s, 2H), 7.39 (d, J = 8.4 Hz, 4H), 7.48 ppm (d, J = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 27.1, 89.3, 93.1, 122.2, 122.3, 122.5, 131.6, 131.7, 132.9, 143.5 ppm; elemental analysis: calcd (%) for $C_{26}H_{20}Br_2$: C 63.44, H 4.10; found: C 63.39, H 3.81.

43:[23] M.p.: 133–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.37 (m, 6H), 7.48 (d, J = 7.7 Hz, 2H), 7.59–7.63 (m, 4H), 7.68 ppm (t, J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.2, 89.6, 122.0, 126.1, 128.3, 129.0, 132.0, 136.3, 143.7 ppm.

44:[24] M.p.: 105–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.40 (m, 7H), 7.48–7.56 (m, 6H), 7.71–7.73 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.5, 89.9, 123.0, 123.6, 128.4, 128.4, 128.5, 131.3, 131.6, 134.6 ppm.

47: A solution of LiHMDS (1.0 M, 11.0 mL, 11.0 mmol) in THF was added to a solution of 2-bromophenylmethyl phenyl sulfone (3.11 g, 10.0 mmol) in THF (30 mL) at −78 °C, and the mixture was stirred at −78 °C for 30 min. Diethyl chlorophosphate (1.73 mL, 12.0 mmol) was then added to the mixture at −78 °C, which was then stirred at room temperature for 2 h. After workup with EtOAc and aqueous NH_4Cl, the mixture was dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography over silica gel (EtOAc/hexane (20%) to EtOAc (100%)) to furnish pure **47** (2.32 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16, 1.33 (1:1, t, J = 7.0 Hz, 3H), 3.96–4.03, 4.08–4.13, 4.26–4.32 (1:1:2, m, 2H), 5.57 (d, J = 21.7 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.35–7.42 (m, 4H), 7.56 (t, J = 7.3 Hz, 1H), 7.65 (d, J = 7.4 Hz, 2H), 8.11 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.0, 16.2 (J = 6.2 Hz), 64.0, 64.1 (J = 6.7 Hz), 67.4 (J = 136 Hz), 126.6 (J = 9.3 Hz), 127.6, 127.8 (J = 4.1 Hz), 128.6, 128.9, 130.6, 132.3 (J = 4.1 Hz), 132.6, 133.9, 138.4 ppm; elemental analysis: calcd (%) for $C_{17}H_{20}BrO_5PS$: C 45.65, H 4.51; found: C 45.66, H 4.28.

23: A solution of LiHMDS (1.0 M, 1.2 mL, 1.2 mmol) in THF was added to a solution of **47** (447 mg, 1.1 mmol) in THF (10 mL) at −78 °C, and the mixture was stirred at −78 °C for 30 min. Benzaldehyde (106 mg, 1.0 mmol) was then added to the mixture at −78 °C, and the mixture was stirred at room temperature for 1 h. Next, a solution of LiHMDS (1.0 M, 2.0 mL, 2.0 mmol) in THF was added to the mixture at −78 °C, and the mixture was stirred at room temperature for 2 h. According to TLC analysis, there was no evidence of the formation of **23**.

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