Synthesis of Neopentyl Biphenylsulfonates Using the Suzuki-Miyaura Reaction

Chul-Hee Cho, Chul-Bae Kim, Myungchul Sun, and Kwangyong Park*

Department of Chemical Engineering, Chung-Ang University, Seoul 156-756, Korea
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Palladium-catalyzed cross-coupling reactions of neopentyloxysulfonylphenyl bromides with arylboronic acids provided a variety of neopentyl biphenylsulfonates in good yields. 2-Bromo- and 4-bromobenzenesulfonates underwent the coupling reaction more rapidly than 3-bromobenzenesulfonate, while chlorobenzenesulfonate did not produce the coupling product under the standard reaction conditions.

Key Words : Cross-coupling, Bromobenzenesulfonates, Biphenylsulfonates, Arylboronic acid, Suzuki-Miyaura reaction

Introduction

Transition metal-catalyzed coupling reaction is one of the most important synthetic tools for constructing carbon-carbon bonds.[1] In particular, nickel- and palladium-catalyzed coupling reactions of organic halides and pseudohalides with organoboronic acids,[2] organostannanes,[3] organozincs,[4] and Grignard reagents[5] have emerged as extremely powerful methods during the last several decades. Among those processes, the Suzuki-Miyaura reaction of aryl and vinyl halides/triflates with organoboronic acids is preferred in many situations. This popularity can be attributed to the stability and low toxicity of boronic acids as well as the mild reaction conditions.

The preparation of asymmetric biaryls, which are of great interest due to their biological[6] and optical[7] properties, has been the object of transition metal-catalyzed coupling processes. Since the preparation of biaryls via the palladium-catalyzed reaction of arylboronic acids with aryl halides was first reported,[8] this reaction has been used successfully for a variety of aryl halides and triflates. Recently, it has become widely applied in solid-phase organic synthesis (SPOS) for the rapid and convenient preparation of asymmetric biaryl libraries.[9] However, the coupling reaction of aryl electrophiles containing sulfur-substituents, such as thio, sulfinyl, and sulfonyl groups, with organoboronic acids has not been explored except for the reactions of *p*-$BrC_6H_4SO_3Na$[10] and bromobenzenesulfonamide.[11]

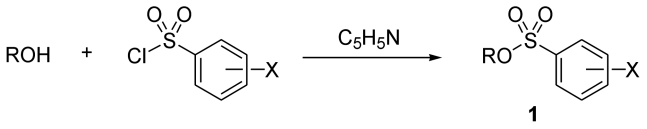
As part of an ongoing study directed toward the development of cross-coupling reactions between alkyloxysulfonylarenes and aryl nucleophiles,[12] a variety of neopentyl biphenylsulfonates were required. They could be produced by the palladium-catalyzed coupling reactions of alkyl bromobenzenesulfonates with aryl boronic acids in good yields. To the best of our knowledge, this is the first general case of a cross-coupling reaction of sulfur-substituted aryl electrophiles with organo-boronic acids. This paper reports our efforts in preparing neopentyl biphenylsulfonates via the Suzuki-Miyaura reaction.

*To whom correspondence should be addressed. e-mail: kypark @cau.ac.kr

Results and Discussion

The alkyl halobenzenesulfonates **1** were prepared using a previously reported procedure (Scheme 1).[12] Two types of neopentyl moieties, 2,2-dimethyl-3-phenyl-1-propyl and 2,2-dimethyl-1-propyl, were selected as the alkyl groups for these intermediates. All the sulfonates **1** were produced in good yields (Table 1). Products **1a**, **1b**, and **1d** were purified by recrystallization from *n*-hexane to give white solids, while **1c** was isolated by column chromatography (Et_2O : *n*-hexane = 1 : 4) to afford a clear oil.

The palladium-catalyzed cross-coupling reaction of **1** with arylboronic acids proceeded smoothly in the presence of



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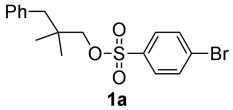
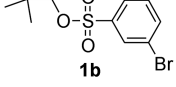
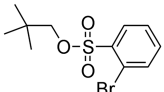
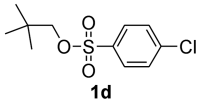
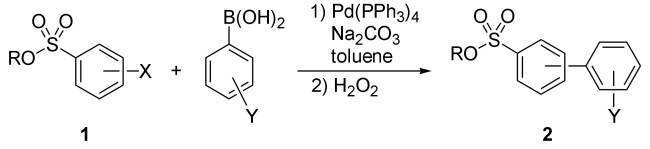
Scheme 1

Table 1. Preparation of Neopentyl halobenzenesulfonates **1**[a]

Entry	R[b]	X	Sulfonate **1**	Yield (%)[c]
1	R^1	4-Br	 **1a**	87
2	R^2	3-Br	 **1b**	81
3	R^2	2-Br	 **1c**	68
4	R^2	4-Cl	 **1d**	87

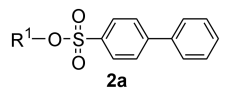
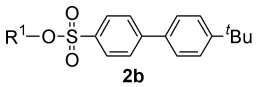
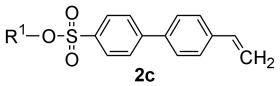
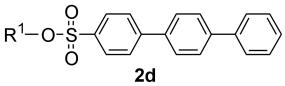
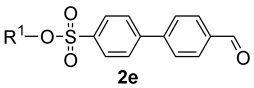
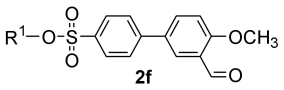
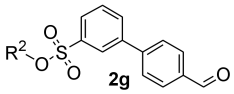
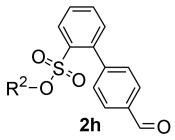
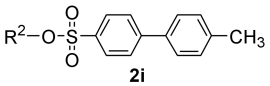
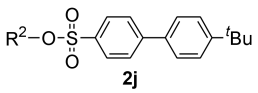
[a]Reactions of the alcohols (51.7 mmol) with sulfonyl chlorides (47.0 mmol) were carried out in chloroform (50 mL) in the presence of pyridine (103.0 mmol). [b]R^1 = 2,2-dimethyl-3-phenyl-1-propyl, R^2 = neopentyl. [c]Isolated yields based on sulfonyl chlorides.



1 2

Scheme 2

Table 2. Coupling Reactions of **1** with arylboronic acids[a]

Entry	1	Boronic acid (Y)	Time (h)	Product **2**[b]	Yield (%)[c]
1	**1a**	H	6	 **2a**	71
2	**1a**	4-^{t}Bu	6	 **2b**	78
3	**1a**	4-vinyl	6	 **2c**	76
4	**1a**	4-Ph	6	 **2d**	68
5	**1a**	4-CHO	6	 **2e**	64
6	**1a**	3-CHO-4-OCH$_3$	6	 **2f**	74
7	**1b**	4-CHO	15	 **2g**	69
8	**1c**	4-CHO	6	 **2h**	66
9	**1d**	4-CH$_3$	15	 **2i**	–
10	**1d**	4-^{t}Bu	15	 **2j**	–

[a]Reactions of **1** (5.22 mmol) with arylboronic acids (5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.157 mmol) and aqueous sodium carbonate (2.0 M, 6.0 mL) were carried out at the refluxing temperature of toluene (12.0 mL) under an Ar atmosphere. [b]R^1 = 2,2-dimethyl-3-phenyl-1-propyl, R^2 = neopentyl. [c]Isolated yields based on **1**.

sodium carbonate (Scheme 2). Although a detailed study to optimize the reaction conditions was not undertaken, most of the reactions were complete within 6 h at the refluxing temperature of toluene. The displacement of arenesulfonates[13] or alkyloxysulfonyl groups[12] was not observed under the standard reaction conditions.

The result of the cross-coupling reactions between **1** and the various arylboronic acids is summarized in Table 2. 4-Bromobenzenesulfonate **1a** reacted rapidly with phenyl-, 4-*tert*-butylphenyl-, 4-vinylphenyl-, and biphenylboronic acids in the presence of $Pd(PPh_3)_4$ catalyst to give the corresponding biphenyl- and terphenylsulfonates **2** in good yields (entries 1-4). While formylphenylboronic acid, which has an electron-withdrawing substituent, showed a slightly lower reactivity than the above nucleophiles (entry 5), 3-formyl-4-methoxyphenylboronic acid underwent the coupling reaction rapidly (entry 6).

The reaction of 3-bromobenzenesulfonate **1b** with 4-formylphenylboronic acid also produced the desired coupling product in good yield, although it required more time (15 h) for a complete reaction (entry 7). 2-Bromobenzenesulfonate **1c** underwent the coupling process with formyl-phenylboronic acid in a similar way as with **1a** (entry 8). There was no evidence showing that the neighboring neopentyloxysulfonyl group provided a significant steric hindrance for the coupling reaction.

Chlorobenzenesulfonate **1d** was quite inert under our standard reaction conditions. Even though it is well known that chlorobenzene derivatives are generally not reactive toward the oxidative addition of a palladium catalyst, some electron-deficient aryl chlorides have been reported to undergo the palladium-catalyzed coupling reaction with organoboronic acids successfully.[14] However, reactions of **1d** with 4-methylphenyl- and 4-*tert*-butylphenylboronic acids did not give any noticeable amounts of the desired coupling products in this effort (entries 9 and 10).

Conclusion

In conclusion, the palladium-catalyzed cross-coupling reaction of neopentyloxysulfonylphenyl bromides with arylboronic acids in the presence of base was described. A variety of neopentyl biphenylsulfonates were prepared in good yields. To our knowledge, this is the first general exploration of the Suzuki-Miyaura reaction of sulfur-substituted aryl electrophiles. Investigations into applying this coupling strategy for preparing asymmetric terphenyl and stilbene derivatives are currently underway and will be reported in due course.

Experimental Section

^{1}H NMR (300 or 500 MHz) and ^{13}C NMR (75 or 125 MHz) were registered in $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.2 ppm. All coupling constants, *J*, are reported in hertz (Hz). Column chromatography was performed on silica gel 60, 70-230 mesh. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light (254 and 365 nm) or by iodine vapor staining. GC

analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.). Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry. Melting points were obtained using a Barnstead/Thermolyne MEL-TEMP apparatus and are uncorrected. Toluene was distilled from calcium hydride. 4-Tolyl-, 4-*tert*-butylphenyl-, 4-vinylphenyl-, and biphenylboronic acid were prepared according to a literature procedure.[15] Phenyl-, 4-formylphenyl-, and 3-formyl-4-methoxyphenylboronic acid were used as obtained commercially.

General Procedure for the Preparation of Neopentyl Halobenzenesulfonates (1). To the solution of alcohol (51.7 mmol) in chloroform (50 mL) at 0 °C were added pyridine (103.0 mmol) dropwise over a period of 20 min and halobenzenesulfonyl chloride (47.0 mmol) in small portions. The reaction mixture was stirred at room temperature for 12 h and diluted with Et_2O. The solution was washed with a 0.1% aqueous HCl, water, and brine; dried over $MgSO_4$; filtered; and concentrated in vacuo.

2,2-Dimethyl-3-phenyl-1-propyl 4'-bromobenzenesulfonate (**1a**) was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propanol (8.48 g, 51.7 mmol) with *p*-bromobenzenesulfonyl chloride (12.0 g, 47.0 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1a** (15.66 g, 87%) as a white solid: TLC R_f 0.38 (Et_2O : *n*-hexane = 1 : 4); mp 82-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (s, 6H), 2.55 (s, 2H), 3.68 (s, 2H), 6.99-7.03 (m, 2H), 7.19-7.22 (m, 3H), 7.71 (d, J = 8.73 Hz, 2H), 7.79 (d, J = 8.73 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (×2), 35.4, 44.3, 77.7, 126.6, 128.2 (×2), 129.2, 129.7 (×2), 130.6 (×2), 132.9 (×2), 135.3, 137.5; HRMS (EI, 70 eV) calcd for $C_{17}H_{19}BrO_3S$ (M^+) 382.0238, found 382.0231.

Neopentyl 3-bromobenzenesulfonate (**1b**) was prepared by the reaction of neopentyl alcohol (0.36 g, 4.09 mmol) with *m*-bromobenzenesulfonyl chloride (0.95 g, 3.72 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1b** (0.93 g, 81%) as a white solid: TLC R_f 0.51 (Et_2O : *n*-hexane = 1 : 1); mp 44-45 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H), 3.72 (s, 2H), 7.45 (dd, J = 8.06, 7.89 Hz, 1H), 7.79 (ddd, J = 8.06, 2.01, 1.00 Hz, 1H), 7.85 (ddd, J = 7.89, 1.68, 1.00 Hz, 1H), 8.06 (dd, J = 2.01, 1.68 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2 (×3), 31.9, 80.3, 123.3, 126.5, 130.9, 130.9, 136.9, 138.1; HRMS (EI, 70 eV) calcd for $C_{11}H_{15}BrO_3S$ (M^+) 305.9925, found 305.9969.

Neopentyl 2-bromobenzenesulfonate (**1c**) was prepared by the reaction of neopentyl alcohol (0.57 g, 6.46 mmol) with *o*-bromobenzenesulfonyl chloride (1.50 g, 5.87 mmol). The crude compound was purified by column chromatography (Et_2O : *n*-hexane = 1 : 4) to afford **1c** (1.23 g, 68%) as a viscous colorless oil; TLC R_f 0.56 (Et_2O : *n*-hexane = 1 : 1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (s, 9H), 3.73 (s, 2H), 7.48-7.55 (m, 2H), 7.77-7.82 (m, 1H), 8.09-8.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0 (×3), 31.5, 80.4, 120.6, 127.8, 132.0, 132.2, 134.8, 135.7; HRMS (EI, 70 eV) calcd for $C_{11}H_{15}BrO_3S$ (M^+) 305.9925, found 305.9948.

Neopentyl 4-chlorobenzenesulfonate (**1d**) was prepared by the reaction of neopentyl alcohol (1.84 g, 20.85 mmol) with *p*-chlorobenzenesulfonyl chloride (4.00 g, 18.95 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1d** (4.33 g, 87%) as a white solid: TLC R_f 0.63 (Et_2O : *n*-hexane = 1 : 1); mp 64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 9H), 3.70 (s, 2H), 7.54 (d, J = 8.56 Hz, 2H), 7.85 (d, J = 8.56 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0 (×3), 31.7, 80.1, 129.5 (×2), 129.8 (×2), 134.8, 140.5; HRMS (EI, 70 eV) calcd for $C_{11}H_{15}ClO_3S$ (M^+) 262.0430, found 262.0434.

General Procedure for the Coupling Reaction of 1 with arylboronic acid. To the solution of halobenzenesulfonate (5.22 mmol) and $Pd(PPh_3)_4$ (0.157 mmol) in toluene (12 mL) was added 2.0 M aqueous Na_2CO_3 (6.0 mL) under an Ar atmosphere. To the resulting mixture was added arylboronic acid (5.74 mmol), which was dissolved in ethanol (3 mL). The reaction mixture was heated at reflux for 6 h with vigorous stirring. To the resulting mixture was added 30% hydrogen peroxide (0.3 mL) to oxidize the residual boronic acid. The mixture was stirred at room temperature for 1 h and diluted with EtOAc. The organic layer was washed with water and brine; dried over $MgSO_4$; filtered through a small pad of silica gel in a sintered glass filter; and concentrated in vacuo.

2,2-Dimethyl-3-phenyl-1-propyl 1',1''-biphenyl-4'-sulfonate (**2a**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with phenylboronic acid (0.70 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **2a** (1.41 g, 71%) as a white solid: TLC R_f 0.43 (Et_2O : *n*-hexane = 1 : 4); mp 74-75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 6H), 2.57 (s, 2H), 3.72 (s, 2H), 7.00-7.05 (m, 2H), 7.15-7.21 (m, 3H), 7.42-7.53 (m, 3H), 7.63 (d, J = 6.72 Hz, 2H), 7.76 (d, J = 8.73 Hz, 2H), 7.99 (d, J = 8.73 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (×2), 35.4, 44.3, 77.4, 126.5, 127.6 (×2), 128.1 (×2), 128.2 (×2), 128.7 (×2), 129.0, 129.4 (×2), 130.7 (×2), 134.7, 137.6, 139.3, 147.0; HRMS (EI, 70 eV) calcd for $C_{23}H_{24}O_3S$ (M^+) 380.1446, found 380.1403.

2,2-Dimethyl-3-phenyl-1-propyl 4''-*tert*-butyl-1',1''-biphenyl-4'-sulfonate (**2b**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with *p*-*tert*-butylphenylboronic acid (1.02 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **2b** (1.78 g, 78%) as a fluffy white solid: TLC R_f 0.44 (Et_2O : *n*-hexane = 1 : 4); mp 76-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 6H), 1.38 (s, 9H), 2.57 (s, 2H), 3.71 (s, 2H), 6.98-7.04 (m, 2H), 7.15-7.23 (m, 3H), 7.53 (d, J = 8.56 Hz, 2H), 7.59 (d, J = 8.56 Hz, 2H), 7.81 (d, J = 8.73 Hz, 2H), 7.98 (d, J = 8.73 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.2 (×2), 31.5 (×3), 34.9, 35.5, 44.4, 77.5, 126.3 (×2), 126.5, 127.2 (×2), 127.8 (×2), 128.1 (×2), 128.6 (×2), 130.6 (×2), 134.3, 136.3, 137.6, 146.7, 152.2; HRMS (EI, 70 eV) calcd for $C_{27}H_{32}O_3S$ (M^+) 436.2072, found 436.2071.

2,2-Dimethyl-3-phenyl-1-propyl 4''-vinyl-1',1''-biphenyl-4'-sulfonate (**2c**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with *p*-vinylphenylboronic acid (0.85 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **2c** (1.61 g, 76%) as a slightly yellowish solid: TLC R_f 0.53 (Et_2O : *n*-hexane = 1 : 4); mp 90-91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 6H), 2.57 (s, 2H), 3.71 (s, 2H), 5.35 (d, J = 10.93 Hz, 1H), 5.85 (d, J = 17.60 Hz, 1H), 6.78 (dd, J = 17.60, 10.93 Hz, 1H), 7.00-7.03 (m, 2H), 7.15-7.20 (m, 3H), 7.54 (d, J = 8.39 Hz, 2H), 7.61 (d, J = 8.39 Hz, 2H), 7.78 (d, J = 8.56 Hz, 2H), 7.99 (d, J = 8.56 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (×2), 35.4, 44.4, 77.4, 115.3, 126.6, 127.2 (×2), 127.8 (×2), 127.9 (×2), 128.2 (×2), 128.8 (×2), 130.7 (×2), 134.8, 136.3, 137.7, 138.4, 138.6, 146.5; HRMS (EI, 70 eV) calcd for $C_{25}H_{26}O_3S$ (M^+) 406.1603, found 406.1440.

2,2-Dimethyl-3-phenyl-1-propyl 1',1'',1'''-terphenyl-4'-sulfonate (**2d**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with biphenylboronic acid (1.14 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.18 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **2d** (1.62 g, 68%) as a fluffy white solid: TLC R_f 0.50 (UV 254 nm blue tailing spot, Et_2O : *n*-hexane = 1 : 1); mp 161-162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (s, 6H), 2.57 (s, 2H), 3.72 (s, 2H), 7.01-7.03 (m, 2H), 7.15-7.21 (m, 3H), 7.39 (t, J = 7.35 Hz, 1H), 7.48 (dd, J = 7.80, 7.35 Hz, 2H), 7.65 (d, J = 7.80 Hz, 2H), 7.71 (d, J = 8.70 Hz, 2H), 7.73 (d, J = 8.70 Hz, 2H), 7.82 (d, J = 8.25 Hz, 2H), 8.00 (d, J = 8.25 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.2 (×2), 35.5, 44.4, 77.5, 126.5, 127.3 (×2), 127.6, 127.8 (×2), 127.9 (×2), 128.0 (×2), 128.1 (×2), 128.7 (×2), 129.1 (×2), 130.6 (×2), 134.7, 137.5, 138.0, 140.4, 141.8, 146.4; HRMS (EI, 70 eV) calcd for $C_{29}H_{28}O_3S$ (M^+) 456.1756, found 456.1766.

2,2-Dimethyl-3-phenyl-1-propyl 4''-formyl-1',1''-biphenyl-4'-sulfonate (**2e**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with *p*-formylphenylboronic acid (0.86 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane : CH_2Cl_2 (20 : 1) to give **2e** (1.37 g, 64%) as a pale yellowish solid: TLC R_f 0.36 (CH_2Cl_2); mp 122-123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 6H), 2.57 (s, 2H), 3.74 (s, 2H), 7.02-7.05 (m, 2H), 7.18-7.21 (m, 3H), 7.79-7.83 (m, 4H), 8.01-8.06 (m, 4H), 10.11 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 24.2 (×2), 35.9, 44.7, 78.3, 127.3, 129.0 (×2), 129.2 (×2), 129.5 (×2), 129.8 (×2), 131.3 (×2), 131.5 (×2), 136.9, 137.7, 138.6, 145.5, 146.1, 193.0; HRMS (EI, 70 eV) calcd for $C_{24}H_{24}O_4S$ (M^+) 408.1395, found 408.1229.

2,2-Dimethyl-3-phenyl-1-propyl 3''-formyl-4''-methoxy-1',1''-biphenyl-4'-sulfonate (**2f**) was prepared by the reaction of **1a** (2.00 g, 5.22 mmol) with 3-formyl-4-methoxyphenylboronic acid (1.03 g, 5.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.181 g, 0.157 mmol) and 2 M aq. Na_2CO_3 (6.0 mL) by using toluene (12.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane : CH_2Cl_2 (20 : 1) to give **2f** (1.69 g, 74%) as a bright canary yellow solid: mp 83-84 °C; TLC R_f 0.38 (CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 6H), 2.57 (s, 2H), 3.71 (s, 2H), 4.02 (s, 3H), 7.00-7.06 (m, 2H), 7.17-7.23 (m, 3H), 7.14 (d, J = 8.73 Hz, 1H), 7.76 (d, J = 8.73 Hz, 2H), 7.85 (dd, J = 8.73, 2.52 Hz, 1H), 7.98 (d, J = 8.73 Hz, 2H), 8.13 (d, J = 2.52 Hz, 1H), 10.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (×2), 35.4, 44.3, 56.1, 77.5, 112.8, 125.3, 126.5, 127.5 (×2), 128.2 (×2), 128.9 (×2), 130.7 (×2), 131.7, 132.3, 132.4, 134.7, 137.6, 145.2, 162.5, 189.7; HRMS (EI, 70 eV) calcd for $C_{25}H_{26}O_4S$ (M^+) 438.1501, found 438.1548.

Neopentyl 4'-formyl-1,1'-biphenyl-3-sulfonate (**2g**) was prepared by the reaction of **1b** (0.40 g, 1.30 mmol) with 4-formylphenylboronic acid (0.21 g, 1.43 mmol) in the presence of $Pd(PPh_3)_4$ (0.045 g, 0.039 mmol) and 2 M aq. Na_2CO_3 (1.5 mL) by using toluene (10.0 mL) as solvent. The crude product was purified by column chromatography to give **2g** (0.30 g, 69%) as a pale ivorish solid: TLC R_f 0.31 (CH_2Cl_2); mp 68-70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (s, 9H), 3.74 (s, 2H), 7.68 (t, J = 7.80 Hz, 1H), 7.78 (d, J = 8.35 Hz, 2H), 7.90 (ddd, J = 7.80, 1.85, 0.90 Hz, 1H), 7.94 (ddd, J = 7.80, 1.85, 0.90 Hz, 1H), 8.00 (d, J = 8.35 Hz, 2H), 8.16 (t, J = 1.85 Hz, 1H), 10.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2 (×3), 31.9, 80.1, 126.7, 127.7, 128.0 (×2), 130.1, 130.7 (×2), 132.5, 136.2, 137.4, 141.3, 144.9; HRMS (EI, 70 eV) calcd for $C_{18}H_{20}O_4S$ (M^+) 332.1082, found 332.1092.

Neopentyl 4'-formyl-1,1'-biphenyl-2-sulfonate (**2h**) was prepared by the reaction of **1c** (0.50 g, 1.63 mmol) with *p*-formylphenylboronic acid (0.27 g, 1.79 mmol) in the presence of $Pd(PPh_3)_4$ (0.057 g, 0.049 mmol) and 2 M aq. Na_2CO_3 (2.0 mL) by using toluene (10.0 mL) as solvent. The crude product was purified by column chromatography to give **2h** (0.36 g, 66%) as a viscous colorless oil: TLC R_f 0.31 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (s, 9H), 3.59 (s, 2H), 7.39 (dd, J = 7.78, 0.90 Hz, 1H), 7.58 (td, J = 7.78, 0.90 Hz, 1H), 7.60 (d, J = 8.25 Hz, 2H), 7.68 (td, J = 7.80, 0.90 Hz, 1H), 7.93 (dd, J = 8.25 Hz, 2H), 8.13 (dd, J = 7.80, 0.90 Hz, 1H), 10.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2 (×3), 31.8, 79.7, 128.6, 129.2 (×2), 130.0, 130.3 (×2), 132.5, 133.4, 135.2, 136.0, 140.8, 145.4, 192.1; HRMS (EI, 70 eV) calcd for $C_{18}H_{20}O_4S$ (M^+) 332.1082, found 332.1059.

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