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Preparation of unsymmetrical terphenyls via the nickel-catalyzed cross-coupling of alkyl biphenylsulfonates with aryl Grignard reagents

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Abstract—Unsymmetrical terphenyl derivatives were prepared by sequential transition metal-catalyzed cross-coupling reactions of neopentyl bromobenzenesulfonates with arylboronic acids and arylmagnesium bromides in good yields. Biphenylsulfonates undergo nickel-catalyzed coupling reactions more rapidly than the corresponding benzenesulfonates. The stepwise palladium- and nickel-catalyzed reaction of the bromobenzenesulfonates appears to be a promising and conceptually straightforward route for preparing unsymmetrical terphenyls.

1. Introduction

Transition metal-catalyzed cross-coupling reaction is an extremely powerful tool for constructing carbon–carbon bonds.[1] The palladium- and nickel-catalyzed coupling reactions of aryl halides and pseudohalides with arylboronic acids,[2] arylstannanes,[3] arylzincs,[4] and arylmagnesium halides[5] have been extensively examined to produce unsymmetrical biaryls, which are of great interest due to their biological[6] and optical[7] properties. However, the preparation of unsymmetrical terphenyl derivatives has not been well-known.

Terphenyl derivatives are known to exhibit a variety of optical[8] and electrical[9] properties. They are particularly of interest in the area of liquid crystals.[10] Naturally isolated *p*-terphenyl metabolites[11] including terphenyllin,[12] terferol,[13] and terprenin[14] have potent biological activities. The efforts for substituting terphenyl-based architectures for the alkenyl bridge of stilbene-based compounds[15] and the biphenyl nucleus of biologically active compounds[16] have also been reported.

The most familiar synthetic pathway for symmetric terphenyls is the double C–C cross-coupling reaction of the dihalobenzene derivatives with two equivalents of aryl nucleophiles.[17] Among those processes, the Suzuki–Miyaura reaction is the most preferred due to the stability and low toxicity of the boronic acids as well as the mild reaction conditions. Recently, the double coupling reactions of the phenyl diboronic acids with aryl iodides[18] and aryl distannanes with phenyl bromides[19] for the preparation of symmetric terphenyls were also reported.

The traditional approach for unsymmetrical terphenyls requires the halogenation or boration of the biphenyl intermediates generated by the initial cross-coupling reactions of the two aryl moieties. The brominations of the biaryl compounds obtained by the initial coupling reactions of the aryl halides with arylboronic acids produce bromobiaryl intermediates, which undergo the following Suzuki–Miyaura reactions with arylboronic acids to generate the unsymmetrical terphenyls.[20] An alternative synthetic pathway by generating biphenyboronic acids as intermediates was also reported.[21]

More efficient method for introducing two different aryl groups into a benzene ring is the stepwise chemoselective cross-couplings of aryl compounds containing two dissimilar reactive sites. The order of reactivity for the cross-coupling reaction with organoboronic acids is I>Br>OTf≫Cl. Therefore, the sequential cross-coupling reaction of the bromoiodobenzene derivatives[22] and bromophenyl tosylates[23] with two dissimilar arylboronic acids furnished the unsymmetrical terphenyls. The stepwise cross-coupling reactions of chlorophenylboronic acids with aryl triflates and arylboronic acids[24] as well as the sequential reactions of the bromophenylboronic acids with the iodobenzenes and arylboronic acids[15] also produced the desired unsymmetrical terphenyls. Similarly, the stepwise couplings of aryl Grignard reagents with *p*- and *m*-bromochlorobenzenes

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catalyzed by non-ligated $NiCl_2$ gave unsymmetrical terphenyls.[25]

It is known that alkylthio and alkylsulfonyl groups, bonded directly to arenes or alkenes, can be substituted for nucleophilic aromatic substitution reactions with aryl and alkyl Grignard reagents in the presence of a Ni(0) catalyst.[26] Chlorobenzene is slightly more reactive than methylthiobenzene in the reaction with BuMgBr in the presence of $dpppNiCl_2$.[27] Therefore, the alkylthio groups were demonstrated to serve as less reactive leaving groups compared to halogens in the preparation of unsymmetrical terphenyls. The chemoselective sequential couplings of chlorophenyl alkyl sulfides with two different arylmagnesium halides gave unsymmetrical terphenyls in moderate yields.[28] The sequential coupling reactions of bis(alkylthio)benzenes, in which the selectivity originates from the difference in the steric effects as a result of the two dissimilar alkylthio groups, have also been reported to give terphenyls in low yields.[29] However, these approaches have not been thoroughly explored presumably due to the inefficient yield and the difficulty in obtaining the appropriate substrates.

Recently, it was reported that the reaction of alkyloxysulfonylarenes with arylmagnesium bromides produced unsymmetrical biaryls in the presence of a nickel catalyst.[30] The alkyloxysulfonyl group acts as an excellent leaving group, while it is not reactive towards the typical palladium catalysts. These results suggested that alkyl bromoarenesulfonates could be used as chemoselective precursors for unsymmetrical terphenyls.

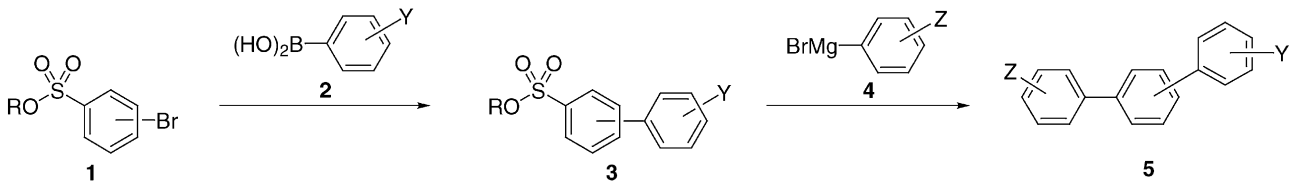
This paper reports our efforts in preparing a variety of unsymmetrical terphenyls via the sequential carbon–carbon cross-coupling reactions of neopentyl bromobenzenesulfonates with arylboronic acids and arylmagnesium bromides (Scheme 1). The results of this study are presented and discussed.

2. Results and discussion

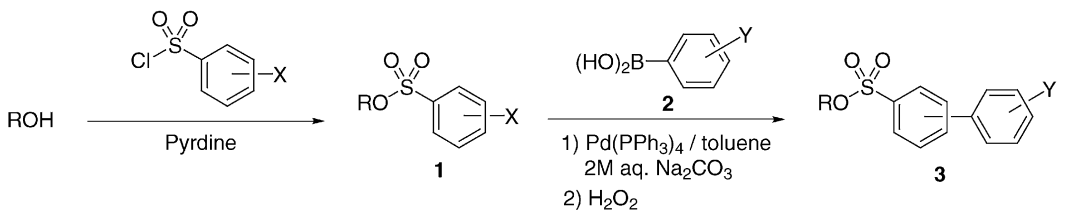
The bromobenzenesulfonates **1** were prepared using a previously reported procedure (Scheme 2).[31] Two types of neopentyl moieties, 2,2-dimethyl-3-phenyl-1-propyl and neopentyl, were selected as alkyl groups in those sulfonates to avoid the competitive substitution and elimination of the arenesulfonate anions in the reactions with the Grignard reagents **4**. All the reactions proceeded well in 68–87% isolated yields. The products **1a**, **1b**, and **1c** were purified by recrystallization from *n*-hexane to give white solids, while **1d** was isolated by column chromatography (Et_2O:*n*-hexane=1:4) as a colorless oil.

Bromobenzenesulfonates **1** underwent a palladium-catalyzed cross-coupling reaction with arylboronic acids **2** smoothly in the presence of sodium carbonate. Since the preparation of biaryls via the reactions of the arylboronic acids with the aryl halides was first reported,[32] the Suzuki–Miyaura reaction has been used successfully to produce biaryl derivatives from a variety of aryl halides and triflates. However, the reaction of the aryl electrophiles containing sulfur-substituents has not been examined intensively.[33] Although a detailed study to optimize the reaction conditions has not been undertaken in this effort, most of the reactions were complete within 6 h at the refluxing temperature of toluene. The displacement of arenesulfonates[34] was not observed under the standard reaction conditions.

The result of the cross-coupling reactions between **1** and **2** is summarized in Table 1. 2,2-Dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (**1a**) reacted rapidly with phenyl- (**2a**), 4-tolyl- (**2b**), and 4-methoxyphenylboronic acid (**2c**) in the presence of $Pd(PPh_3)_4$ to give the corresponding biphenylsulfonates **3a**–**3c** in good yields (entries 1–3). Neopentyl 4-bromobenzenesulfonate (**1b**) showed a similar reactivity with **1a** toward **2b** (entry 4), which shows that the remote alkyl moiety does not influence the reaction.



Scheme 1.

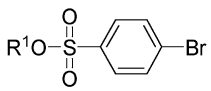
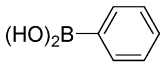
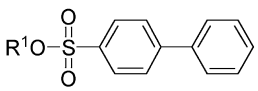
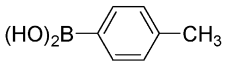
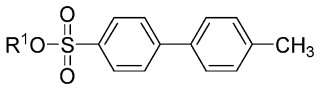
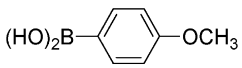
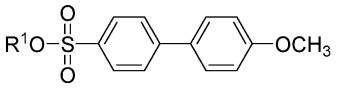
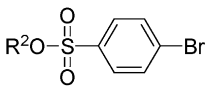
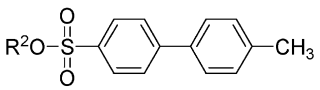
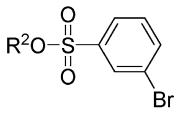
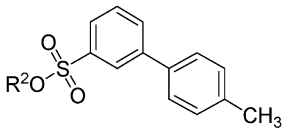
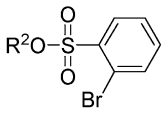
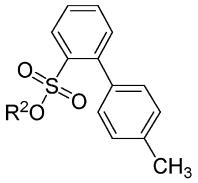
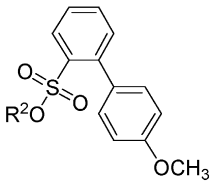


1a: R = 2,2-dimethyl-3-phenyl-1-propyl, X = 4-Br
1b: R = neopentyl, X = 4-Br
1c: R = neopentyl, X = 3-Br
1d: R = neopentyl, X = 2-Br

2a: Y = H
2b: Y = 4-Me
2c: Y = 4-MeO

Scheme 2.

Table 1. Coupling reaction of bromobenzenesulfonates **1** with arylboronic acids **2**

Entry	Bromobenzenesulfonate	Arylboronic acid	Time (h)	Biphenylsulfonate[a]	Yield (%)[b]
1	 **1a**	 **2a**	6	 **3a**	71
2	**1a**	 **2b**	6	 **3b**	73
3	**1a**	 **2c**	6	 **3c**	74
4	 **1b**	**2b**	6	 **3d**	71
5	 **1c**	**2b**	15	 **3e**	67
6	 **1d**	**2b**	6	 **3f**	72
7	**1d**	**2c**	6	 **3g**	69

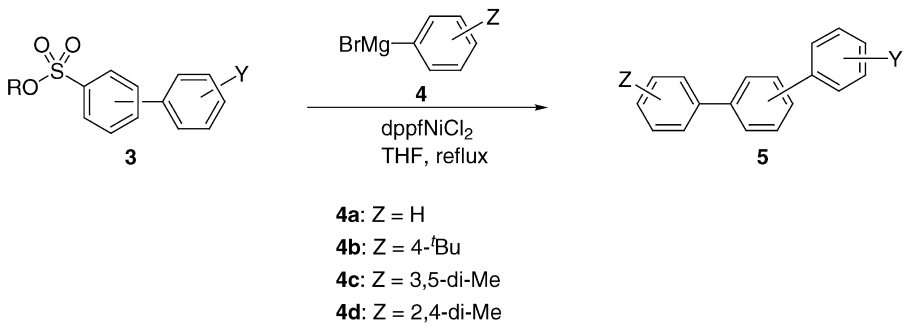
[a] R^1=2,2-dimethyl-3-phenyl-1-propyl, R^2=neopentyl.
[b] Isolated yields based on **1**.

The reaction of 3-bromobenzenesulfonate (**1c**) with **2b** also produced the desired coupling product **3e** in a competitive yield, although it required more time (15 h) for a complete reaction (entry 5). 2-Bromobenzenesulfonate (**1d**) underwent the coupling process with **2b** and **2c** in a similar way as with **1b** (entries 6 and 7). There was no evidence showing that the neighboring neopentyloxysulfonyl group provided a noticeable steric hindrance in the coupling reaction. Products **3a**-**3d** were purified by recrystallization, while **3e**-**3g** was isolated by column chromatography.

The cross-coupling reactions of **3** with **4** were performed in the presence of dppfNiCl$_2$ in refluxing THF, which were previously demonstrated to be the most efficient reaction conditions for the reactions of benzenesulfonates (Scheme 3).[30] Most of those processes proceeded in high yields to give the corresponding unsymmetrical terphenyls **5** via the substitution of the neopentyloxysulfonyl groups. The highest yields were generally obtained when 5 equiv. of **4** were added in two portions, 3 equiv. initially and 2 equiv. after 8 h.

The biphenylsulfonates showed a higher reactivity than the benzenesulfonates under the standard reaction conditions. Most of **3** were completely consumed within 16 h, while the benzenesulfonates typically required almost 30 h for the completion. The faster reaction of more conjugated arenesulfonates has been previously observed in the case of naphthalenesulfonates. The π-electrons appear to play an important role by precomplexing with the catalyst prior to oxidative addition.

The results of the cross-coupling reactions between various **3** and **4** are summarized in Table 2. 2,2-Dimethyl-3-phenyl-1-propyl-4-biphenylsulfonate (**3a**) reacted with phenyl- (**4a**), 4-*tert*-butylphenyl- (**4b**), and 3,5-dimethylphenylmagnesium



Scheme 3.

bromide (**4c**) to generate the unsymmetrical *p*-terphenyls **5a**-**5c** respectively in good yields within 16 h (entries 1–3). There was no significant difference in the reactivities of those nucleophiles. However, the sterically hindered **4d** showed a reduced reactivity. Even though more time (50 h) was allowed, the reaction of **3a** with **4d** generated the coupling product **5d** in only a moderate yield (entry 4).

The coupling reaction of **3b** with **4a**, **4b**, and **4c** also efficiently produced the corresponding unsymmetrical terphenyls **5e**-**5g** within 16 h in refluxing THF (entries 5–7). The methyl group on the 4′-position of biphenylsulfonates did not have any significant effect on the reactivity of those reactions. On the other hand, the reactions of **3c** possessing the 4′-methoxy group with **4a** and **4b** resulted in slightly lower yields, although the products produced by the cleavage of the C–O bond were not detected (entries 8 and 9).[35] The reaction of **3c** with **4d** proceeded slowly, as expected, and gave the reduced yield (entry 10).

The alkyl moiety of the biphenylsulfonates had a significant influence in the progress of the reactions. Neopentyl 4′-methyl-4-biphenylsulfonate (**3d**) required only 3 h for the complete reaction with 3 equiv. of **4a** (entry 11) while **3b** required 16 h for the reaction with 5 equiv. of **4a** (entry 5). This result was quite unexpected considering that both alkyl groups were bulky neopentyl groups. The higher reactivity of the neopentyl compounds compared to the 2,2-dimethyl-3-phenyl-1-propyl substrates was constantly observed in the reactions of **3e**-**3g**.

The bulkiness of the biphenyl moieties also had a great effect on the reactivity of biphenylsulfonates **3**. The reaction of 3-biphenylsulfonate (**3e**) and 2-biphenylsulfonate (**3f**) required 8 and 15 h, respectively for the complete reaction with only 3 equiv. of **4a** (entries 12 and 13). The *ortho*-phenyl group to the alkyloxysulfonyl substituent appears to significantly hinder the approach of the Ni catalyst to C–S bonds. The 4′-methoxy-2-biphenylsulfonate (**3g**), which even contains a slightly deactivating methoxy group, required 16 h for the complete reaction with 5 equiv. of **4b** to produce **5m**, and showed a reduced yield (entry 14). The reaction of **3g** with the sterically hindered **4d** was exceptionally slow in forming the *o*-terphenyl (**5n**) in a lower yield.

Even though no significant levels of byproducts originating from the biphenylsulfonates **3** were observed in this study, the large amount of biphenyls derived by the dimerization of **4** made the purification of **5** by column chromatography difficult in most cases. However, the products **5a**-**5j** could be easily purified by recrystallization from methanol to give white solids.

3. Conclusion

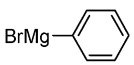
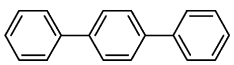
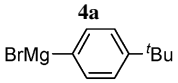
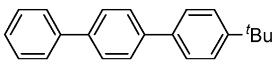
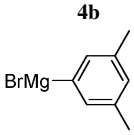
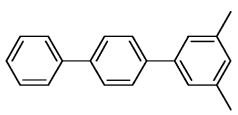
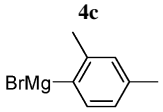
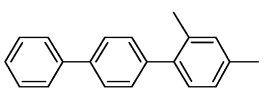
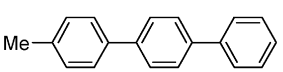
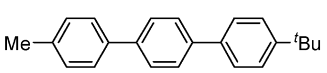
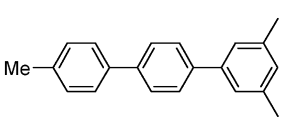
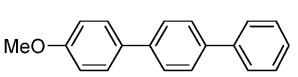
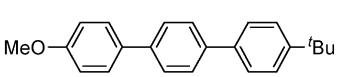
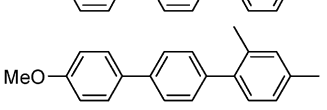
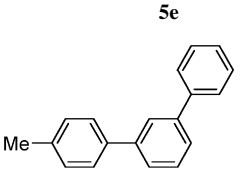
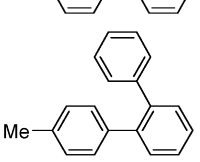
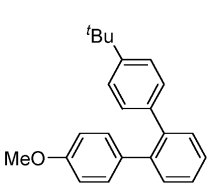
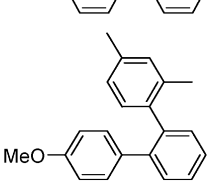
The Suzuki–Miyaura reaction followed by a nickel-catalyzed cross-coupling reaction allows the introduction of two different aryl groups into the benzene nucleus by the sequential substitution of the bromo and neopentyloxysulfonyl groups of the neopentyl bromobenzenesulfonates. The coupling reaction of biphenylsulfonates with the arylmagnesium bromides proceeds faster than the corresponding benzenesulfonates. Neopentyl biphenylsulfonates undergo nickel-catalyzed reactions much faster than the 2,2-dimethyl-3-phenyl-1-propyl biphenylsulfonates. 2-Biphenylsulfonate showed a lower reactivity than the 3- and 4-biphenylsulfonates.

The procedure described in this paper appears to be a promising and conceptually straightforward route to the unsymmetrical terphenyls. The application of this coupling strategy in the solid-phase organic synthesis (SPOS) is also in progress and will be reported in due course.

4. Experimental

All reactions were carried out under an inert atmosphere of Ar. Solvents were distilled from an appropriate drying agent prior to use: toluene from calcium hydride and THF from sodium-benzophenone ketyl. Pyridine was dried over CaH_2 and distilled. ^1H 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 ^1H 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). Analytical and preparative HPLC was performed with an instrument equipped with a UV detector set at 254 nm. Octadecylsilane coated columns, 4.6×250 mm or 20×250 mm, with 5 or 10 μm particle size were used for analytical or preparative runs, respectively. A flow rate of 5 mL/min was used. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.).

Table 2. Nickel-catalyzed coupling of biphenylsulfonates **3** with aryl Grignard reagents **4**

Entry	Biphenylsulfonate	Grignard reagent	Time (h)	Product	Yield (%)[a]
1	**3a**	 **4a**	16	 **5a**	84
2	**3a**	 **4b**	16	 **5b**	82
3	**3a**	 **4c**	16	 **5c**	80
4	**3a**	 **4d**	50	 **5d**	54
5	**3b**	**4a**	16	 **5e**	81
6	**3b**	**4b**	16	 **5f**	76
7	**3b**	**4c**	16	 **5g**	75
8	**3c**	**4a**	16	 **5h**	73
9	**3c**	**4b**	16	 **5i**	75
10	**3c**	**4d**	50	 **5j**	51
11	**3d**	**4a**[b]	3	**5e**	83
12	**3e**	**4a**[b]	8	 **5k**	75
13	**3f**	**4a**[b]	15	 **5l**	66
14	**3g**	**4b**	16	 **5m**	69
15	**3g**	**4d**	72	 **5n**	38

[a] Isolated yields based on **3**.
[b] 3 equiv. only.

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. Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry. Mass data are reported in mass units (*m*/*z*). Melting points were obtained using a Barnstead/Thermolyne MEL-TEMP apparatus and are uncorrected. 4-Tolyl- (**2b**), 4-methoxyphenylboronic acid (**2c**) were prepared according to a literature procedure.[36] 3,5-Dimethylphenyl- (**4c**, 0.5 M, THF) and 2,4-dimethylphenylmagnesium bromide (**4d**, 0.5 M, THF) were prepared by reacting magnesium turnings with the appropriate organic halides in THF. $DppfNiCl_2$ was prepared according to a literature procedure.[37] [mp 282–283 °C (lit. mp 283–284 °C)]. Phenylboronic acid **2a** and phenyl- (**4a**, 1.0 M, THF) and 4-*tert*-butylphenylmagnesium bromide (**4b**, 2.0 M, Et_2O) were purchased and used as received.

4.1. General procedure for the preparation of neopentyl bromobenzenesulfonates 1

To the alcohol (51.7 mmol) in chloroform (50 mL) at 0 °C, was added pyridine (103 mmol) dropwise over a period of 20 min and bromobenzenesulfonyl chloride (47.0 mmol) in small portions. This reaction mixture was stirred at room temperature for 12 h and diluted with Et_2O and then 0.1% aqueous HCl. The separated organic layer was washed with 0.1% aq. HCl (2×30 mL), water (3×50 mL), and a brine; dried over $MgSO_4$; and concentrated in vacuo. The crude bromobenzenesulfonates **1** were purified by either recrystallization or column chromatography.

4.1.1. 2,2-Dimethyl-3-phenyl-1-propyl 4-bromobenzenesulfonate (1a). The title compound was prepared by the reaction of 2,2-dimethyl-3-phenyl-1-propanol (8.49 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** (15.7 g, 87%) as a white solid: TLC R_f 0.38 (Et_2O:*n*-hexane=1:4); mp 82–83 °C; ^1H 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*=8.7 Hz, 2H), 7.79 (d, *J*=8.7 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. Anal. Calcd for $C_{17}H_{19}BrO_3S$: C, 53.27; H, 5.00. Found: C, 53.26; H, 4.94.

4.1.2. Neopentyl 4-bromobenzenesulfonate (1b). The title compound was prepared by the reaction of neopentyl alcohol (0.45 g, 5.11 mmol) with *p*-bromobenzenesulfonyl chloride (1.19 g, 4.65 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1b** (0.47 g, 78%) as a white needle solid: TLC R_f 0.48 (Et_2O:*n*-hexane=1:1); mp 71 °C (lit.[38] mp 70–71 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 9H), 3.70 (s, 2H), 7.74 (dd, *J*=8.9, 8.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1 (×3), 31.8, 80.1, 129.1, 129.6 (×2), 132.8 (×2), 135.4; HRMS (EI, 70 eV) Calcd for $C_{11}H_{15}BrO_3S$ (M^+): 305.9925. Found: 305.9936. Anal. Calcd for $C_{11}H_{15}BrO_3S$: C, 43.01; H, 4.92. Found: C, 42.95; H, 4.89.

4.1.3. Neopentyl 3-bromobenzenesulfonate (1c). The title compound 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 **1c** (0.93 g, 81%) as a white solid: TLC R_f 0.51 (Et_2O:*n*-hexane=1:1); mp 44–45 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H), 3.72 (s, 2H), 7.45 (dd, *J*=8.1, 7.9 Hz, 1H), 7.79 (ddd, *J*=8.1, 2.0, 1.0 Hz, 1H), 7.85 (ddd, *J*=7.9, 1.7, 1.0 Hz, 1H), 8.06 (dd, *J*=2.0, 1.7 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.

4.1.4. Neopentyl 2-bromobenzenesulfonate (1d). The title compound was prepared by the reaction of neopentyl alcohol (0.57 g, 6.46 mmol) with *o*-bromobenzenesulfonyl chloride (1.5 g, 5.87 mmol). The crude compound was purified by column chromatography (Et_2O:*n*-hexane=1:4) to afford **1d** (1.23 g, 68%) as a viscous colorless oil: TLC R_f 0.56 (Et_2O:*n*-hexane=1:1); ^1H 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.

4.2. General procedure for the preparation of biphenylsulfonates 3

To a solution of **1** (5.22 mmol) and $Pd(PPh_3)_4$ (0.157 mmol, 0.181 g) 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 **2** (5.74 mmol), which was dissolved in ethanol (3 mL). The reaction mixture was heated at reflux for 6 h (15 h for **1c**) with vigorous stirring. Upon cooling to room temperature, 30% hydrogen peroxide (0.3 mL) was added to oxidize the residual boronic acid. The mixture was stirred at room temperature for ca. 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. The biphenylsulfonates **3** were purified by recrystallization and/or column chromatography.

4.2.1. 2,2-Dimethyl-3-phenyl-1-propyl 4-biphenylsulfonate (3a). The title compound was prepared by the reaction of **1a** (2.0 g, 5.2 mmol) with **2a** (0.7 g, 5.7 mmol) in the presence of $Pd(PPh_3)_4$ (184.9 mg, 0.16 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 **3a** (1.41 g, 71%) as a white solid: TLC R_f 0.43 (Et_2O:*n*-hexane=1:4); mp 74–75 °C; ^1H 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*=6.7 Hz, 2H), 7.76 (d, *J*=8.7 Hz, 2H), 7.99 (d, *J*=8.7 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. Anal. Calcd for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36. Found: C, 72.67; H, 6.37.

4.2.2. 2,2-Dimethyl-3-phenyl-1-propyl 4′-methyl-4-biphenylsulfonate (3b). The title compound was prepared by the reaction of **1a** (2.0 g, 5.2 mmol) with **2b** (0.78 g, 5.7 mmol) in the presence of $Pd(PPh_3)_4$ (184.9 mg, 0.16 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 **3b** (1.50 g, 73%) as a fluffy white solid: TLC R_f 0.45 (Et_2O:*n*-hexane=1:4); mp 89–91 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 6H), 2.42 (s, 3H), 2.56 (s, 2H), 3.71 (s, 2H), 7.00–7.03 (m, 2H), 7.15–7.19 (m, 3H), 7.31 (d, J=8.1 Hz, 2H), 7.53 (d, J=8.1 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 7.97 (d, J=8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 24.1 (×2), 35.4, 44.4, 77.4, 126.5, 127.5 (×2), 127.8 (×2), 128.2 (×2), 128.7 (×2), 130.1 (×2), 130.7(×2), 134.4, 136.4, 137.7, 139.1, 146.9; HRMS (EI, 70 eV) Calcd for $C_{24}H_{26}O_3S$ (M^+): 394.1603. Found: 394.1567. Anal. Calcd for $C_{24}H_{26}O_3S$: C, 73.06; H, 6.64. Found: C, 73.18; H, 6.65.

4.2.3. 2,2-Dimethyl-3-phenyl-1-propyl 4′-methoxy-4-biphenylsulfonate (3c). The title compound was prepared by the reaction of **1a** (2.0 g, 5.2 mmol) with **2c** (0.87 g, 5.7 mmol) in the presence of $Pd(PPh_3)_4$ (184.9 mg, 0.16 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 **3c** (1.58 g, 74%) as a white solid: TLC R_f 0.33 (Et_2O:*n*-hexane=1:4); mp 84–85 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 6H), 2.57 (s, 2H), 3.71 (s, 2H), 3.88 (s, 3H), 7.00–7.05 (m, 2H), 7.03 (d, J=9.1 Hz, 2H), 7.16–7.21 (m, 3H), 7.59 (d, J=9.1 Hz, 2H), 7.73 (d, J=8.7 Hz, 2H), 7.96 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (×2), 35.4, 44.3, 55.5, 77.3, 114.8 (×2), 126.5, 127.4 (×2), 128.2 (×2), 128.7 (×2), 128.8 (×2), 130.7(×2), 131.6, 134.0, 137.6, 146.5, 160.6; HRMS (EI, 70 eV) Calcd for $C_{24}H_{26}O_4S$ (M^+): 410.1552. Found: 410.1597. Anal. Calcd for $C_{24}H_{26}O_4S$: C, 70.22; H, 6.38. Found: C, 70.25; H, 6.33.

4.2.4. Neopentyl 4′-methyl-4-biphenylsulfonate (3d). The title compound was prepared by the reaction of **1b** (2.0 g, 6.5 mmol) with **2b** (0.98 g, 7.2 mmol) in the presence of $Pd(PPh_3)_4$ (231.1 mg, 0.2 mmol) and 2 M aq. Na_2CO_3 (7.0 mL) by using toluene (14.0 mL) as solvent. The crude product was purified by recrystallization from *n*-hexane to give **3d** (1.47 g, 71%) as a white solid: TLC R_f 0.36 (Et_2O:*n*-hexane=1:4); mp 116–118 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 6H), 2.42 (s, 3H), 3.72 (s, 2H), 7.31 (d, J=7.7 Hz, 2H), 7.52 (d, J=8.2 Hz, 2H), 7.74 (d, J=8.9 Hz, 2H), 7.95 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 26.1 (×3), 31.8, 79.8, 127.4 (×2), 127.7 (×2), 128.7 (×2), 130.1 (×2), 134.5, 136.4, 139.1, 146.8; HRMS (EI, 70 eV) Calcd for $C_{18}H_{22}O_3S$ (M^+): 318.1290. Found: 318.1280.

4.2.5. Neopentyl 4′-methyl-3-biphenylsulfonate (3e). The title compound was prepared by the reaction of **1c** (0.4 g, 1.3 mmol) with **2b** (0.19 g, 1.4 mmol) in the presence of $Pd(PPh_3)_4$, (46.22 mg, 0.04 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 (Et_2O:*n*-hexane=1:4) to give **3e** (0.28 g, 67%) as a white solid: TLC R_f 0.45 (Et_2O:*n*-hexane=1:4); mp 89–90 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, 9H), 2.42 (s, 3H), 3.72 (s, 2H), 7.30 (d, J=8.2 Hz, 2H), 7.52 (d, J=8.2 Hz, 2H), 7.61 (t, J=7.7 Hz, 1H), 7.85 (dd, J=7.7, 1.9 Hz, 2H), 8.11 (t, J=1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 26.2 (×3), 31.9, 80.0, 126.2, 126.3, 127.2 (×2), 129.8, 130.0 (×2), 132.1, 136.2, 136.8, 138.6, 142.6; HRMS (EI, 70 eV) Calcd for $C_{18}H_{22}O_3S$ (M^+): 318.1290. Found: 318.1259. Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96. Found: C, 67.75; H, 6.91.

4.2.6. Neopentyl 4′-methyl-2-biphenylsulfonate (3f). The title compound was prepared by the reaction of **1d** (0.49 g, 1.6 mmol) with **2b** (0.25 g, 1.8 mmol) in the presence of $Pd(PPh_3)_4$ (57.78 mg, 0.05 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 (Et_2O:*n*-hexane=1:4) to give **3f** (0.37 g, 72%) as a colorless oil: TLC R_f 0.47 (Et_2O:*n*-hexane=1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 0.73 (s, 9H), 2.30 (s, 3H), 3.45 (s, 2H), 7.12 (d, J=8.0 Hz, 2H), 7.24 (d, J=8.0 Hz, 2H), 7.28 (dd, J=7.7, 1.3 Hz, 1H), 7.40 (td, J=7.7, 1.3 Hz, 1H), 7.52 (td, J=7.6, 1.2 Hz, 1H), 8.01 (dd, J=7.9, 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 26.1 (×3), 31.6, 79.4, 127.7, 128.6, 128.7, 129.5 (×2), 130.1, 133.2 (×2), 135.4, 136.4, 138.1, 142.4; HRMS (EI, 70 eV) Calcd for $C_{18}H_{22}O_3S$ (M^+): 318.1290. Found: 318.1280.

4.2.7. Neopentyl 4′-methoxy-2-biphenylsulfonate (3g). The title compound was prepared by the reaction of **1d** (0.49 g, 1.6 mmol) with **2c** (0.27 g, 1.8 mmol) in the presence of $Pd(PPh_3)_4$ (57.58 mg, 0.05 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 (Et_2O:*n*-hexane=1:4) to give **3g** (0.37 g, 69%) as a pale yellow oil: TLC R_f 0.28 (Et_2O:*n*-hexane=1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 9H), 3.55 (s, 2H), 3.85 (s, 3H), 6.95 (d, J=8.9 Hz, 2H), 7.38 (d, J=8.9 Hz, 2H), 7.36–7.41 (m, 1H), 7.50 (ddd, J=8.1, 7.6, 1.5 Hz, 1H), 7.63 (ddd, J=7.6, 7.6, 1.5 Hz, 1H), 8.11(dd, J=8.1, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1 (×3), 31.7, 55.5, 79.5, 113.4, 127.6 (×2), 130.0, 130.9(×2), 131.6, 133.3, 133.4, 125.4, 142.2, 159.8; HRMS (EI, 70 eV) Calcd for $C_{18}H_{22}O_4S$ (M^+): 334.1239. Found: 334.1232.

4.3. General procedure for the preparation of unsymmetrical terphenyls 5

To a stirred solution of **3** (0.3 mmol) and $dppfNiCl_2$ (0.015 mmol) in dry THF (6 mL) was slowly added aryl Grignard reagents **4** (0.9 mmol) via syringe at room temperature. This resulted in a color change from dark green to dark brown. The reaction mixture was heated at reflux for ca. 8 h, cooled to room temperature, and an additional 0.6 mmol of **4** was added to the solution. After the resulting mixture was heated at reflux for 8–64 h, cooled to room temperature, and diluted with Et_2O. The organic layer was washed with a 1% aqueous HCl (2×10 mL), water, and brine; dried over $MgSO_4$; and concentrated in vacuo. The product **5a-j** were purified by recrystallization from MeOH to give white solids, and the product **5k-n** were purified by preparative HPLC (CH_3CN:MeOH=2:3).

4.3.1. *p*-Terphenyl (5a). The title compound was prepared by the reaction of **3a** (114.15 mg, 0.30 mmol) with **4a** (1.0 M in THF, 0.9 mL, 0.9 mmol+0.6 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5a** (58.05 mg, 84%) as a white solid: TLC R_f 0.72 (Et$_2$O:*n*-hexane=1:4); mp 211–213 °C [an authentic sample[39] (mp 212–213 °C)]; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (t, J=7.4 Hz, 2H), 7.46 (t, J=7.7 Hz, 4H), 7.64 (d, J=7.2 Hz, 4H), 7.68 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 127.3 (×4), 127.6 (×2), 127.8 (×4), 129.1 (×4), 140.4 (×2), 141.0 (×2).

4.3.2. 4-*tert*-Butyl-*p*-terphenyl (5b). The title compound was prepared by the reaction of **3a** (114.15 mg, 0.30 mmol) with **4b** (2.0 M in THF, 0.45 mL, 0.9 mmol+0.3 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5b** (70.47 mg, 82%) as a white solid: TLC R_f 0.70 (Et$_2$O:*n*-hexane=1:4); mp 180–181 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.38 (s, 9H), 7.35 (t, J=7.4 Hz, 1H), 7.46 (t, J=7.7 Hz, 2H), 7.49 (d, J=8.3 Hz, 2H), 7.59 (d, J=8.3 Hz, 2H), 7.64 (d, J=7.5 Hz, 2H), 7.67 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 31.5 (×3), 34.7, 126.0 (×2), 127.0 (×2), 127.3 (×2), 127.5, 127.6 (×2), 127.7 (×2), 129.1 (×2), 138.0, 140.1, 140.3, 141.1, 150.7; HRMS (EI, 70 eV) Calcd for $C_{22}H_{22}$ (M^+): 286.1721. Found: 286.1724. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.69.

4.3.3. 3,5-Dimethyl-*p*-terphenyl (5c). The title compound was prepared by the reaction of **3a** (114.15 mg, 0.30 mmol) with **4c** (0.5 M in THF, 1.8 mL, 0.9 mmol+1.2 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5c** (62.00 mg, 80%) as a white solid: TLC R_f 0.70 (Et$_2$O:*n*-hexane=1:4); mp 88–90 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.39 (s, 6H), 7.00 (s, 1H), 7.26 (s, 2H), 7.35 (t, J=7.4 Hz, 1H), 7.45 (t, J=7.7 Hz, 2H), 7.64 (d, J=7.7 Hz, 2H), 7.65 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.5 (×2), 125.3 (×2), 127.3 (×2), 127.5, 127.7 (×2), 127.8 (×2), 129.1 (×2), 129.3, 138.6 (×2), 140.2, 140.7, 141.0, 141.1; HRMS (EI, 70 eV) Calcd for $C_{20}H_{18}$ (M^+): 258.1409. Found: 258.1403. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.70; H, 7.12.

4.3.4. 2,4-Dimethyl-*p*-terphenyl (5d). The title compound was prepared by the reaction of **3a** (114.15 mg, 0.30 mmol) with **4d** (0.5 M in THF, 1.8 mL, 0.9 mmol+1.2 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5d** (41.85 mg, 54%) as a white solid: TLC R_f 0.68 (Et$_2$O:*n*-hexane=1:4); mp 97–98 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.30 (s, 3H), 2.37 (s, 3H), 7.08 (d, J=7.7 Hz, 1H), 7.12 (s, 1H), 7.19 (d, J=7.7 Hz, 1H), 7.32–7.48 (m, 5H), 7.63 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.6, 21.2, 126.8, 127.0 (×2), 127.3 (×2), 127.5, 129.1 (×2), 130.0 (×2), 130.0, 131.5, 135.5, 137.3, 138.9, 139.7, 141.2, 141.2; HRMS (EI, 70 eV) Calcd for $C_{20}H_{18}$ (M^+): 258.1409. Found: 258.1406. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.84; H, 7.00.

4.3.5. 4-Methyl-*p*-terphenyl (5e). The title compound was prepared by the reaction of **3b** (118.35 mg, 0.30 mmol) with **4a** (1.0 M in THF, 0.9 mL, 0.9 mmol+0.6 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5e** (59.37 mg, 81%) as a white solid: TLC R_f 0.66 (Et$_2$O:*n*-hexane=1:4); mp 209–210 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.41 (s, 3H), 7.27 (d, J=8.0 Hz, 2H), 7.35 (t, J=7.4 Hz, 1H), 7.46 (t, J=7.6 Hz, 2H), 7.55 (d, J=8.0 Hz, 2H), 7.64 (d, J=7.6 Hz, 2H), 7.66 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.2, 127.2 (×2), 127.3 (×2), 127.6 (×2), 127.6, 127.7 (×2), 129.1 (×2), 129.8 (×2), 137.4, 138.1, 140.1, 140.4, 141.1; HRMS (EI, 70 eV) Calcd for $C_{19}H_{16}$ (M^+): 244.1252. Found: 244.1249.

4.3.6. 4-*tert*-Butyl-4″-methyl-*p*-terphenyl (5f). The title compound was prepared by the reaction of **3b** (118.35 mg, 0.30 mmol) with **4b** (2.0 M in THF, 0.45 mL, 0.9 mmol+0.3 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5f** (68.50 mg, 76%) as a pale yellowish solid: TLC R_f 0.68 (Et$_2$O:*n*-hexane=1:4); mp 203–205 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.37 (s, 9H), 2.41 (s, 3H), 7.27 (d, J=8.7 Hz, 2H), 7.49 (d, J=8.7 Hz, 2H), 7.55 (d, J=8.1 Hz, 2H), 7.59 (d, J=8.6 Hz, 2H), 7.65 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.2, 31.5 (×3), 34.7, 126.0 (×2), 126.9 (×2), 127.1 (×2), 127.5 (×2), 127.6 (×2), 129.8 (×2), 137.3, 138.1, 138.2, 139.9, 140.0, 150.6; HRMS (EI, 70 eV) Calcd for $C_{23}H_{24}$ (M^+): 300.1878. Found: 300.1898.

4.3.7. 3,5-Dimethyl-4″-methyl-*p*-terphenyl (5g). The title compound was prepared by the reaction of **3b** (118.35 mg, 0.30 mmol) with **4c** (0.5 M in THF, 1.8 mL, 0.9 mmol+1.2 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5g** (61.29 mg, 75%) as a white solid: TLC R_f 0.72 (Et$_2$O:*n*-hexane=1:4); mp 151–152 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.39 (s, 6H), 2.40 (s, 3H), 7.00 (s, 1H), 7.25 (s, 2H), 7.26 (d, J=8.1 Hz, 2H), 7.54 (d, J=8.1 Hz, 2H), 7.64 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.2, 21.5 (×3), 125.3 (×2), 127.1 (×2), 127.4 (×2), 127.8 (×2),129.1, 129.8 (×2), 137.4, 138.2, 138.6 (×2), 140.2, 140.4, 141.1; HRMS (EI, 70 eV) Calcd for $C_{21}H_{20}$ (M^+): 272.1565. Found: 272.1557. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.43; H, 7.51.

4.3.8. 4-Methoxy-*p*-terphenyl (5h). The title compound was prepared by the reaction of **3c** (123.15 mg, 0.30 mmol) with **4a** (1.0 M in THF, 0.9 mL, 0.9 mmol+0.6 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from MeOH to afford **5h** (57.01 mg, 73%) as a white solid: TLC R_f 0.54 (Et$_2$O:*n*-hexane=1:4); mp 224–225 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.86 (s, 3H), 7.13 (d, J=8.7 Hz, 2H), 7.35 (t, J=7.4 Hz, 1H), 7.45 (t, J=7.6 Hz, 2H), 7.58 (d, J=8.7 Hz, 2H), 7.61–7.65 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 55.5, 114.5 (×2), 127.3 (×2), 127.4 (×2), 127.5, 127.7 (×2), 128.3 (×2), 129.1 (×2), 133.5, 139.8, 140.0, 141.1; HRMS (EI, 70 eV) Calcd for $C_{19}H_{16}O$ (M^+): 260.1201. Found: 260.1210.

4.3.9. 4-*tert*-Butyl-4″-methoxy-*p*-terphenyl (5i). The title compound was prepared by the reaction of **3c** (123.15 mg, 0.30 mmol) with **4b** (2.0 M in THF, 0.45 mL, 0.9 mmol+0.3 mL, 0.6 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by recrystallization from

MeOH to afford **5i** (71.19 mg, 75%) as a white solid: TLC R_f 0.55 (Et_2O:*n*-hexane=1:4); mp 236–237 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 9H), 3.86 (s, 3H), 6.99 (d, J=8.7 Hz, 2H), 7.48 (d, J=8.3 Hz, 2H), 7.58 (d, J=8.7 Hz, 2H), 7.58 (d, J=8.2 Hz, 1H), 7.62 (d, J=8.2 Hz, 2H), 7.65 (d, J=8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5 (×3), 34.7, 55.5, 114.5 (×2), 126.0 (×2), 126.9 (×2), 127.3 (×2), 127.6 (×2), 128.3 (×2), 133.6, 138.2, 139.6, 139.7, 150.6, 159.5; HRMS (EI, 70 eV) Calcd for $C_{23}H_{24}O$ (M^+): 316.1827. Found: 316.1836. Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64. Found: C, 87.19; H, 7.59.

4.3.10. 2,4-Dimethyl-4″-methoxyterphenyl (5j). The title compound was prepared by the reaction of **3c** (123.15 mg, 0.30 mmol) with **4d** (0.5 M in THF, 1.8 mL, 0.9 mmol+1.2 mL, 0.6 mmol) in the presence of dppfNiCl_2. The crude compound was purified by recrystallization from MeOH to afford **5j** (44.12 mg, 51%) as a white solid: TLC R_f 0.56 (Et_2O:*n*-hexane=1:4); mp 136–137 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.38 (s, 3H), 3.86 (s, 3H), 7.00 (d, J=8.7 Hz, 2H), 7.08 (d, J=7.7 Hz, 1H), 7.12 (s, 1H), 7.19 (d, J=7.7 Hz, 1H), 7.37 (d, J=8.7 Hz, 2H), 7.59 (d, J=8.7 Hz, 2H), 7.60 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 21.2, 55.5, 114.5 (×2), 126.6 (×2), 126.8, 128.3 (×2), 129.9 (×2), 130.0, 131.4, 133.7, 135.5, 137.2, 139.0, 139.3, 140.6, 159.4; HRMS (EI, 70 eV) Calcd for $C_{21}H_{20}O$ (M^+): 288.1514. Found: 288.1522. Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.53; H, 7.06.

4.3.11. 4-Methyl-*p*-terphenyl (5e). The title compound was prepared by the reaction of **3d** (31.84 mg, 0.10 mmol) with **4a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in the presence of dppfNiCl_2. The crude compound was purified by recrystallization from MeOH to afford **5e** (20.28 mg, 83%) as a white solid.

4.3.12. 4-Methyl-(1,1′,3′,1″)-terphenyl (5k). The title compound was prepared by the reaction of **3e** (31.84 mg, 0.1 mmol) with **4a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in the presence of dppfNiCl_2. The crude compound was purified by preparative HPLC (CH_3CN:MeOH=2:3) to afford **5k** (18.32 mg, 75%) as a colorless oil that solidified upon standing to a yellow solid: TLC R_f 0.62 (EtOAc:*n*-hexane=1:4); ^1H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.27 (d, J=8.0 Hz, 2H), 7.37 (t, J=7.4 Hz, 1H), 7.46 (t, J=7.7 Hz, 2H), 7.50 (d, J=7.5 Hz, 1H), 7.38–7.58 (m, 4H), 7.65 (d, J=8.0 Hz, 2H), 7.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 126.1, 126.2, 126.2, 127.3 (×2), 127.5 (×2), 127.6, 129.0 (×2), 129.4, 129.7 (×2), 137.4, 138.5, 141.5, 141.9, 142.0; HRMS (EI, 70 eV) Calcd for $C_{19}H_{16}$ (M^+): 244.1252. Found: 244.1240. Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.28; H, 6.57.

4.3.13. 4-Methyl-(1,1′,2′,1″)-terphenyl (5l). The title compound was prepared by the reaction of **3f** (31.84 mg, 0.10 mmol) with **4a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in the presence of dppfNiCl_2. The crude compound was purified by preparative HPLC (CH_3CN:MeOH=2:3) to afford **5l** (16.13 mg, 66%) as a colorless oil that solidified upon standing to a yellow solid: TLC R_f 0.62 (EtOAc:*n*-hexane=1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.00–7.03 (m, 4H), 7.13–7.23 (m, 5H), 7.35–7.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 126.6, 127.5 (×2), 127.7 (×2), 128.1 (×2), 128.9 (×2), 130.0, 130.1 (×2), 130.9 (×2), 136.3, 138.8, 140.8, 142.0; HRMS (EI, 70 eV) Calcd for $C_{19}H_{16}$ (M^+): 244.1252. Found: 244.1247. Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.22; H, 6.57.

4.3.14. 4-*tert*-Butyl-4′-methoxy-(1,1′,2′,1″)-terphenyl (5m). The title compound was prepared by the reaction of **3g** (33.44 mg, 0.10 mmol) with **4b** (2.0 M in THF, 0.15 mL, 0.3 mmol+0.1 mL, 0.2 mmol) in the presence of dppfNiCl_2. The crude compound was purified by preparative HPLC (CH_3CN:MeOH=2:3) to afford **5m** (21.83 mg, 69%) as a pale yellow oil that solidified upon standing to a yellow solid: TLC R_f 0.53 (EtOAc:*n*-hexane=1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 3.79 (s, 3H), 6.73–6.78 (m, 2H), 7.04–7.10 (m, 4H), 7.22–7.26 (m, 2H), 7.35–7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.4 (×3), 34.5, 55.3, 113.5, 125.1, 127.3 (×2), 127.5 (×2), 129.7, 130.8 (×2), 131.0 (×2), 131.2, 134.4, 138.9, 140.4, 140.7, 149.5, 158.5; HRMS (EI, 70 eV) Calcd for $C_{23}H_{24}O$ (M^+): 316.1827. Found: 316.1844.

4.3.15. 2,4-Dimethyl-4′-methoxy-(1,1′,2′,1″)-terphenyl (5n). The title compound was prepared by the reaction of **3g** (33.44 mg, 0.10 mmol) with **4d** (0.5 M in THF, 0.6 mL, 0.3 mmol+0.4 mL, 0.2 mmol) in the presence of dppfNiCl_2. The crude compound was purified by preparative HPLC (CH_3CN:MeOH=2:3) to afford **5n** (10.96 mg, 38%) as a pale yellow oil that solidified upon standing to a yellow solid: TLC R_f 0.52 (EtOAc:*n*-hexane=1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (s, H), 2.30 (s, H), 3.75 (s, 3H), 6.68–6.73 (m, 2H), 6.89 (s, 1H), 6.92 (s, 1H), 6.95 (s, 1H), 7.01–7.06 (m, 3H), 7.31–7.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 21.2, 55.3, 113.4, 126.4, 126.9 (×2), 127.6 (×2), 130.1, 130.7 (×2), 131.2 (×2), 134.3, 135.8, 136.7, 138.9, 140.5, 141.0, 158.5; HRMS (EI, 70 eV) Calcd for $C_{19}H_{16}$ (M^+): 288.1514. Found: 288.1556.

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