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Liquid-Phase Synthesis of Biaryl Compounds by the Hydrogenolysis of Pentaerythritol-Supported Biarylsulfonates

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Unfunctionalized biaryl compounds were parallelly and combinatorially prepared by the traceless hydrogenolysis of biarylsulfonates supported on pentaerythritol. The hydrogenolysis using 2-propylmagnesium chloride in the presence of dppfNiCl$_2$ efficiently generated corresponding biaryl derivatives without any memory of the support. The strategy using pentaerythritol as a small soluble support was disclosed to have a potential to combine the benefits of both SPOS and solution-phase reaction with fast reaction rate, facile isolation of intermediates, easy analysis of intermediates and atom economical manner. The novel tetrapodal support is expected to be an efficient substitute for polymeric supports in many circumstances.

Key Words: Soluble support, Liquid-phase synthesis, Traceless, Parallel synthesis, Combinatorial synthesis, Biaryls

Introduction

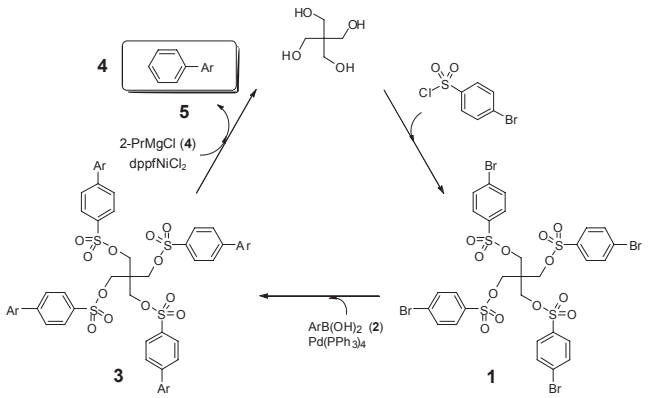
Combinatorial chemistry has been highlighted as a powerful tool to produce large libraries of structurally analogous compounds, especially in searching for lead molecules in drug discovery.[1] The combinatorial approach is now widely accepted as a good way to discover new functional materials, such as magnetic materials,[2] catalysts,[3] sensor materials,[4] agrochemicals,[5] and luminescent materials.[6]

In the field of combinatorial chemistry, solid-phase organic synthesis (SPOS) using polymer supports has been commonly used, because it makes the rapid preparation and screening of diverse compounds possible by allowing for the simple separation of the products and automation of the processes.[7] However, the heterogeneous nature of the polymeric support results in low reactivity, causing the prolongation of the reaction time and the usage of excess reagents. Difficulty in monitoring the reaction progress and identifying the reaction intermediates is also a significant drawback of this methodology.

Accordingly, a hybrid system, which still maintains the advantages of conventional solution reactions while allowing the fairly facile isolation of the product, has been actively sought. Liquid-phase combinatorial synthesis using a soluble polymeric support, such as poly(ethylene glycol) and non-cross-linked polystyrene, has been considered as an alternative.[8] However, these supports still exhibit several shortcomings, especially a low atomic efficiency and difficult mass production, due to their low loading capacity. Functionalized ionic liquids,[9] soluble dendrimers[10] and polyfunctionalized core molecules[11] have also been suggested as promising small soluble supports, although they seem to be still far from a satisfactory substitute, especially since their preparation is often labor intensive.

In a program designed to develop a suitable synthetic strategy for conjugated hydrocarbon libraries, we discovered that the sulfonate-based linker system using pentaerythritol as a soluble support had the potential to possess the benefits of SPOS and the conventional solution reaction.[12] However, the multifunctional cleavage/cross-coupling by aryl nucleophiles in the previous paper was destined to construct additional aryl moieties on the final products with their release. The truly 'traceless' cleavage of target substrates from their supports by simple hydrogenolysis was desirable as it has always been an important challenge in combinatorial syntheses.[13] Even if the definition of the term "traceless" is arguable,[14] an efficient strategy for the straightforward hydrogenolysis of the substrate-support linkage is quite necessary in various applications.[15]

Herein, we report our attempts to utilize the pentaerythritol as an efficient soluble tetrapodal support that permits the traceless release of various biaryl compounds attached through a sulfonate linkage. The last cleaving process of substrates from the support, which was the cross-coupling reaction in the previous paper,[12] is a simple hydrogenolysis in these reactions. Biaryl compounds play an important role as key building blocks for the syntheses of biologically active molecules,[16] liquid crystals,[17] and ligands of the transition metal catalysts.[18] Although the C-S bond in organosulfur compounds is known to be dis-



Scheme 1

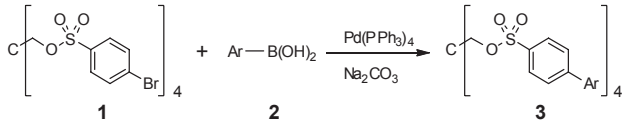
connected by photolysis or reducing agents such as Raney nickel and tin hydrides,[19] the reductive C-S bond cleavage has not often been applied in supported reactions.[20] The results of parallel and combinatorial syntheses of the unfunctionalized biaryl compounds **5** *via* the novel traceless hydrogenolysis of pentaerythritol-supported arenesulfonates **3** (Scheme 1) are presented and discussed below.

Result and Discussion

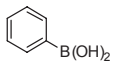
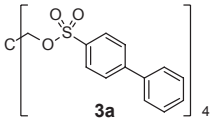
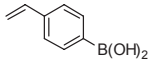
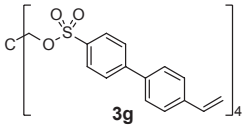
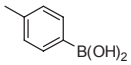
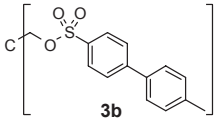
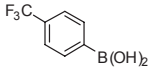
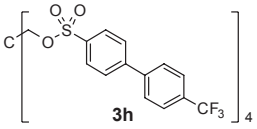
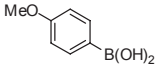
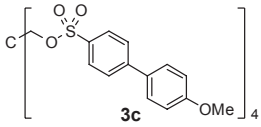
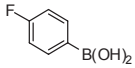
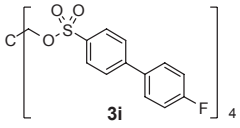
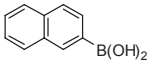
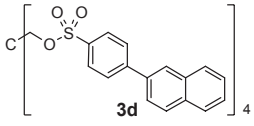
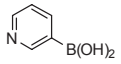
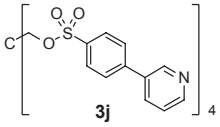
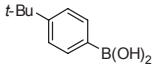
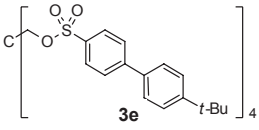
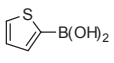
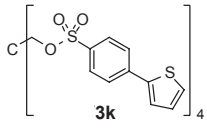
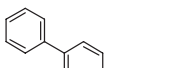
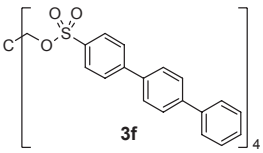
Pentaerythritol tetrakis(4-bromobenzenesulfonate) (**1**) was prepared by the reaction of pentaerythritol with 1.2 equiv of 4-bromobenzenesulfonyl chloride using NaH in DME.[12] The solid product **1** after conventional work-up was purified by washing with hot 2-PrOH to give a white powder in 82% yield.

Bromobenzenesulfonate **1** reacted with arylboronic acids **2a-k** in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 to produce the corresponding biarylsulfonates **3a-k** in good yields (Table 1). All coupling reactions were completed within 8 h at 110 °C in toluene/EtOH/water. No cleavage of the C-S bonds or C-O bonds was observed under the standard reaction conditions. Although 2-naphthylboronic acid **2d** showed a relatively lower reactivity, conversion of each reactive site of **1** was still much more than 90% with common phenylboronic acids **2a-g** (entries 1-7). On the other hand, electron-deficient arylboronic acids **2h**, **i** (entries 8, 9), which possess an electron-withdrawing moiety, showed a reduced reactivity, and heteroarylboronic acids **2j**, **k** produced the corresponding products in noticeably reduced yields (entries 10, 11). However, the conversions of each reactive site of **1** are still over 87% for **2h-k**, which are not so disappointing. The products **3** were able to be easily isolated as reasonably pure powders by simply washing the resulting solids

Table 1. Preparation of tetrakis(biarylsulfonate)s **3**[a]

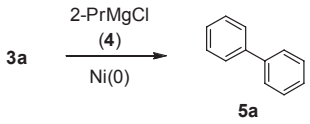


1 **2** **3**

entry	boronic acid **2**	product **3**	yield (%)[b]	entry	boronic acid **2**	product **3**	yield (%)[b]
1	 **2a**	 **3a**	82	7	 **2g**	 **3g**	75
2	 **2b**	 **3b**	80	8	 **2h**	 **3h**	61
3	 **2c**	 **3c**	75	9	 **2i**	 **3i**	63
4	 **2d**	 **3d**	69	10	 **2j**	 **3j**	59
5	 **2e**	 **3e**	76	11	 **2k**	 **3k**	58
6	 **2f**	 **3f**	78				

[a]The reactions of sulfonate **1** (1.976 mmol) with **2** (8.692 mmol) were carried out in the presence of $Pd(PPh_3)_4$ (0.237 mmol, 3 mol %) and 2.0 M aq Na_2CO_3 (8.0 mL) in toluene (20.0 mL) and EtOH (5.0 mL) for 8 h at 110 °C. [b]Isolated yields based on **1**.

Table 2. Effect of varying reaction conditions on the reaction of **3a** with **4**[a]



entry	catalyst	solvent	**4** (equiv)	time (h)	yield (%)[b]
1	$dppfNiCl_2$	Et_2O	3	12	35
2	$dppfNiCl_2$	THF	3	12	86
3	$dppfNiCl_2$	DME	3	12	72
4	$dppfNiCl_2$	THF	3	18	92
5	$dppfNiCl_2$	THF	3	24	92
6	$(PPh_3)_2NiCl_2$	THF	3	18	76
7	$Ni(acac)_2$	THF	3	18	65
8	$dppfNiCl_2$	THF	3	18	26
9	$dppfNiCl_2$	THF	2	18	81
10	$dppfNiCl_2$	THF	4	18	92
11	$dppfNiCl_2$	THF	4	24	91
12[c]	$dppfNiCl_2$	THF	3	18	92

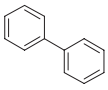
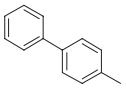
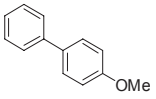
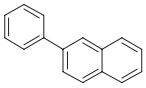
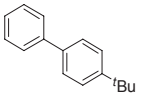
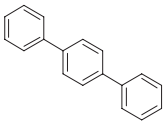
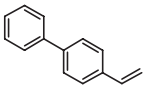
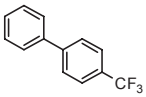
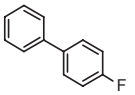
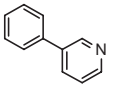
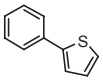
[a]Reactions of sulfonate **3a** (0.300 mmol) with indicated amount of **4** were carried out in the presence of the indicated nickel catalyst (0.060 mmol) in the indicated solvent (6.0 mL) for the indicated hours at 25 °C. [b]All yields were determined by GC analyses using naphthalene as an internal standard. [c]Reaction was performed at 65 °C.

after standard work-up with EtOAc or acetone, and further purified by a facile precipitation from EtOAc or acetone.

The hydrogenolysis of pentaerythritol tetrakis(4-biphenylsulfonate) (**3a**) using 2-propylmagnesium chloride (**4**), which was most effective for the hydrogenolysis of neopentyl arenesulfonates,[21] was preliminarily investigated in order to determine optimum reaction conditions (Table 2). A brief solvent survey was initially performed in the presence of [1,2'-bis(diphenylphosphino)ferrocene]dichloronickel ($dppfNiCl_2$). The results indicated that tetrahydrofuran (THF) gives the highest reaction efficiency (entries 1-3). Diethyl ether (Et_2O) did not give a satisfactory result primarily due to its poor solubility (entry 1). 18 h was necessary to complete the reaction of **3a** (entries 2, 4 and 5). $DppfNiCl_2$ was proved to be best for the hydrogenolysis among selected nickel catalysts again. Bis(triphenylphosphine) nickel(II) dichloride ($(PPh_3)_2NiCl_2$), nickel(II) acetylacetonate ($Ni(acac)_2$) and [1,2'-bis(diphenylphosphiono)ethane]dichloronickel ($dppeNiCl_2$) were not as effective as $dppfNiCl_2$ under the standard reaction conditions (entries 6-8). While 2 equiv of **4** could not complete the reaction (entry 9), additional amount of **4** over 3 equiv did not improve the reaction efficiency at all (entry 10, 11). Increasing the reaction temperature did not raise the conversion (entry 12). In summary, the optimization studies demonstrated that the highest yield was obtained by performing the reaction with 3 equiv of **4** in the presence of $dppfNiCl_2$ in THF for 18 h.

Hydrogenolysis reactions of **3a-k** were performed under the optimized conditions and the results are summarized in Table 3. The arenesulfonate moieties tethered to a flexible neopentyl core effectively underwent the desired traceless cleavage step.

Table 3. Hydrogenolysis of **3** producing **5**[a]

entry	sulfonate **3**	product **5**		yield (%)[b]
1	**3a**		**5a**	91
2	**3b**		**5b**	92
3	**3c**		**5c**	87
4	**3d**		**5d**	90
5	**3e**		**5e**	91
6	**3f**		**5f**	94
7	**3g**		**5g**	79
8	**3h**		**5h**	67
9	**3i**		**5i**	52
10	**3j**		**5j**	61
11	**3k**		**5k**	55

[a]Reactions of sulfonate **3** (0.300 mmol) with **4** (3.600 mmol) were carried out in the presence of $dppfNiCl_2$ (0.060 mmol) in THF (6.0 mL) for 18 h at 25 °C. [b]Isolated yields were based on **3**.

Most of the reactions produced the corresponding biaryl compounds **5a-k** in good yields within 18 h. The fluoro- and trifluoromethyl-substituted biphenylsulfonates **3h**, **i** showed relatively low reactivity, presumably due to their poor solubility (entries 8, 9). The cleavages of the pyridyl- and thiophenylbenzene sulfonates **3j**, **k** proceeded with lower efficiency (entries 10, 11).

The biaryl products could be easily isolated as pure solids from the reaction mixtures by filtration using hexane through a sintered glass funnel containing a small pad of silica gel after standard work-up. This was because the remaining arenesulfonates **3** were not dissolvable in hexane and no significant level of byproducts originating from arenesulfonates and alkyl nucleophiles were produced. This simple purification procedure

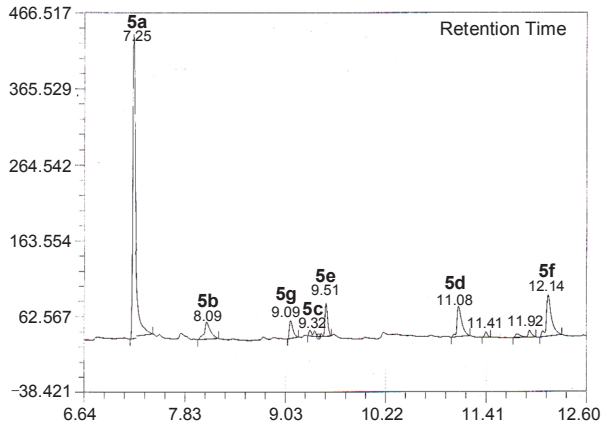


Figure 1. GC analysis of the reaction mixture from the combinatorial preparation of **5** using and equimolar mixture of **2a-k**, 1.2 equiv each and 13.2 equiv overall.

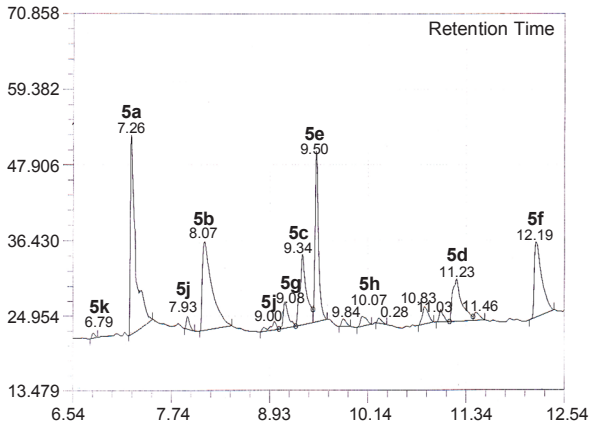
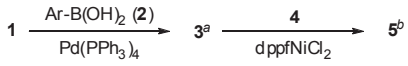


Figure 2. GC analysis of the reaction mixture from the combinatorial preparation of **5** using and equimolar mixture of **2a-k**, 1.2 equiv each and 13.2 equiv overall.

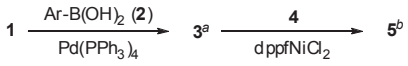
Table 4. Composition of the reaction mixture from the combinatorial preparation of **5** using **2a-k**, 1.2 equiv each and 13.2 equiv overall



entry	Ar	biphenyl **5**	composition (%)[c]
1	Ph	**5a**	84.1
2	4-Me-Ph	**5b**	2.5
3	4-MeO-Ph	**5c**	0.8
4	2-naphtyl	**5d**	3.5
5	*t*-Bu-Ph	**5e**	2.3
6	*p*-BiPh	**5f**	5.3
7	4-vinyl-Ph	**5g**	1.5
8	4-CF_3-Ph	**5h**	none
9	4-F-Ph	**5i**	none
10	3-pyridine	**5j**	none
11	2-thiophene	**5k**	none

[a]Bromobenzenesulfonate **1** (0.300 mmol) was reacted with an equimolar mixture of eleven boronic acids **2**, 1.2 equiv each (1.440 mmol), in the presence of $Pd(PPh_3)_4$ (0.060 mmol) and 2.0 M aq Na_2CO_3 (1.2 mL) in toluene (5.0 mL) and EtOH (1.0 mL) for 8 h at 110 °C. [b]The reactions of sulfonate **3** (0.300 mmol) with **4** (6.000 mmol) were carried out in the presence of $dppfNiCl_2$ (0.060 mmol) in THF (6.0 mL) for 18 h at 25 °C. [c]Relative GC ratio.

Table 5. Composition of the reaction mixture from the combinatorial preparation of **5** using **2a-k**, 0.11 equiv each and 1.21 equiv overall



entry	Ar	biphenyl **5**	composition (%)[c]
1	Ph	**5a**	18.5
2	4-Me-Ph	**5b**	13.7
3	4-MeO-Ph	**5c**	13.8
4	2-naphtyl	**5d**	11.3
5	*t*-Bu-Ph	**5e**	17.3
6	*p*-BiPh	**5f**	16.5
7	4-vinyl-Ph	**5g**	4.0
8	4-CF_3-Ph	**5h**	1.8
9	4-F-Ph	**5i**	1.6
10	3-pyridine	**5j**	1.2
11	2-thiophene	**5k**	0.5

[a]Bromobenzenesulfonate **1** (0.300 mmol) was reacted with an equimolar mixture of eleven boronic acids **2**, 0.11 equiv (0.132 mmol) each, in the presence of $Pd(PPh_3)_4$ (0.060 mmol) and 2.0 M aq Na_2CO_3 (1.2 mL) in toluene (5.0 mL) and EtOH (1.0 mL) for 8 h at 110 °C. [b]The reactions of sulfonate **3** (0.300 mmol) with **4** (6.000 mmol) were carried out in the presence of $dppfNiCl_2$ (0.060 mmol) in THF (6 mL) for 18 h at 25 °C. [c]Relative GC ratio.

should allow this small tetrapodal support to be an efficient substitute for polymeric supports. The relatively rapid reaction rate obtained using less reactant makes this approach more attractive.

The application of this strategy to the combinatorial synthesis of a biaryl library was demonstrated. Bromobenzenesulfonate **1** was treated with an equimolar mixture of eleven boronic acids **2a-k**, containing 1.2 equivalents each and 13.2 equiv overall, in the presence of $Pd(PPh_3)_4$ for 8 h. The resulting mixture of **3** was able to be isolated as a light brown solid by a simple precipitation using 2-PrOH, and was pure enough to undergo the subsequent hydrogenolysis without any further purification.

The final reductive cleavage of **3** with 5 equiv of **4** was performed in the presence of $dppfNiCl_2$ in THF. After 18 h of reaction and standard work-up, GC analysis of the reaction mixture indicated that only seven products, **5a-g**, were generated in detectable quantity (Figure 1). The relative composition of **5** was calculated and summarized in Table 4. The predominant reactivity of phenylboronic acid (**2a**) was disclosed by the presence of 84.1% of **5a** in the mixture. The lack of **5h-k** was explained by the combination of their lower reactivities in both steps, as shown in Table 1 and Table 3.

Bromobenzenesulfonate **1** was allowed to react with an equimolar mixture of eleven boronic acids **2a-k**, 0.11 equiv each and 1.21 equiv overall, in the presence of $Pd(PPh_3)_4$ for 8 h. The resulting mixture of **3** was isolated by simple precipitation using 2-PrOH and was treated with 5 equiv of **4** in the presence

of dppfNiCl$_2$ in THF. After 18 h of reaction and standard work-up, all of the expected biaryls **5a-k** were able to be identified by GC analysis (Figure 2). The relative composition of the mixture of biaryls **5** is shown in Table 5.

Biphenyl and methyl-, methoxy- and aryl-substituted biphenyls **5a-f** were relatively abundant, while vinyl-, trifluoromethyl- and fluoro-substituted biphenyls **5g-i**, 3-phenylpyridine (**5j**) and 2-phenylthiophene (**5k**) were not plentiful according to the GC analysis. The composition was also in good agreement with the results in Table 1 and Table 3. Although the final yields of each eleven biaryls **5a-k** were not uniform, this pentaerythritol-supported synthesis allowed for the facile combinatorial preparation of biphenyl compounds by an efficient traceless cleavage method.

Conclusion

Unfunctionalized biaryl compounds were prepared by the traceless parallel and combinatorial hydrogenolysis of pentaerythritol-supported arenes. To the best of our knowledge, this method is the first general application of the traceless hydrogenolysis of sulfonate-based linkers on supports. This strategy using pentaerythritol as a soluble support was disclosed to have the potential to combine the benefits of both SPOS and the solution-phase reaction. First, its relatively faster reaction rate using less reactant allows this approach to share the advantages of homogeneous reactions. Second, this method is comparable to SPOS in terms of its facile isolation of the reaction intermediates and final products. The large tetrapodal intermediates **1** and **3** were able to be isolated by simple wash in purities sufficient for the subsequent reactions and further purified by simple precipitation if necessary. Biaryl derivatives could be isolated from the reaction mixtures by facile filtration through a small pad of silica gel after standard work-up. This extremely easy isolation without a complex chromatographic technique, while possessing the rapid reaction rate of conventional homogeneous syntheses, is the considerable benefit of this approach. Third, the fact that the reaction progress could be monitored by TLC analysis during every reaction and the reaction intermediate could be analyzed after every step makes this approach as researcher-friendly as the conventional synthetic methods. Finally, these syntheses proceeded in an atom economical manner compared not only to the corresponding polymer-supported preparations, but also to the original preparations from neopentyl arenesulfonates, by generating only one equiv of the small byproduct, pentaerythritol, while producing 4 equiv of **5**. Further application of this novel tetrapodal support, which is commercially available at a very cheap price, to prepare larger libraries of highly conjugated hydrocarbons is underway.

Experimental Section

Solvents were distilled from appropriate drying agent prior to use: THF and DME from sodium-benzophenone ketyl; Et_2O and toluene from CaH_2. Commercially available reagents were used without further purification unless otherwise stated. ^{1}H NMR (300, 500 or 600 MHz) and ^{13}C NMR (75 or 150 MHz) were registered in $CDCl_3$ and DMSO-d_6 as solvent and tetramethylsilane (TMS) as an 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). 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.

General procedure for the preparation of pentaerithritol tetrakis(biarylsulfonate) 3. To a solution of pentaerythritol tetrakis (4-bromobenzenesulfonate) (**1**) (1.976 mmol), which was prepared according to the literature procedure,[12] and Pd(PPh$_3$)$_4$ (0.237 mmol) in toluene (20 mL) was added 2.0 M aq Na_2CO_3 (8.0 mL) under an Ar atmosphere. To the resulting mixture was added **2** (8.692 mmol) dissolved in EtOH (5.0 mL). The reaction mixture was stirred vigorously at 110 °C for 8 h and then diluted with $CHCl_3$. The organic layer was washed with water; dried over $MgSO_4$; and concentrated in vacuo. The crude sulfonates **3** were easily purified by facile precipitation from acetone or EtOAc. The sulfonates **3a-d** were identified according to the literature.[12]

Pentaerythritol tetrakis(4'-*tert*-butyl-4-biphenylsulfonate) (3e): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2e** (1.548 g, 8.692 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.274 g, 0.237 mmol) and 2.0 M *aq* Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3e** (1.841 g, 76%) as a white solid: TLC R_f 0.28 ($CHCl_3$); mp 319 - 321 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 36H), 3.96 (s, 8H), 7.50 (d, *J* = 8.7 Hz, 8H), 7.55 (d, *J* = 8.7 Hz, 8H), 7.69 (d, *J* = 8.6 Hz, 8H), 7.83 (d, *J* = 8.6 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.4 (×9), 34.8 (×4), 43.6, 65.7 (×4), 126.4 (×8), 127.4 (×8), 128.2 (×8), 128.8 (×8), 132.7 (×4), 136.2 (×4), 147.5 (×4), 152.4 (×4). Anal. Calcd for $C_{69}H_{76}O_{12}S_4$: C, 67.62; H, 6.25; S, 10.47. Found: C, 67.49; H, 6.01; S, 10.27.

Pentaerythritol tetrakis(1,1',4',1"-terphenylsulfonate) (3f): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2f** (1.721 g, 8.692 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from acetone to give **3f** (2.012 g, 78%) as a white solid: TLC R_f 0.21 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 8H), 7.44 (d, *J* = 7.4 Hz, 4H), 7.51 (t, *J* = 7.7, 7.4 Hz, 8H), 7.69 (d, *J* = 7.7 Hz, 8H), 7.74 (s,16 H), 7.83 (d, *J* = 8.7 Hz, 8H), 8.01 (d, *J* = 8.7 Hz, 8H). Anal. Calcd for $C_{77}H_{60}O_{12}S_4$: C, 70.84; H, 4.63; S, 9.82. Found: C, 70.81; H, 4.34; S, 9.67.

Pentaerythritol tetrakis(4'-vinyl-4-biphenylsulfonate) (3g): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2g** (1.286 g, 8.692 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3g** (1.638 g, 75%) as a white solid: TLC R_f 0.29 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 8H), 5.34 (d, *J* = 10.9 Hz, 4H), 5.83 (d, *J* = 17.6 Hz, 4H), 6.76 (dd, *J* = 10.9, 17.6 Hz, 4H), 7.49 (d, *J* = 8.7 Hz, 8H), 7.55 (d, *J* = 8.7 Hz, 8H), 7.69 (d, *J* = 8.7 Hz, 8H), 7.84 (d, *J* = 8.7 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 65.7 (×4), 115.2 (×4), 127.1 (×8), 127.7 (×8), 128.0 (×8), 128.7 (×8), 132.9 (×4), 136.2 (×4),

138.2 (×4), 138.3 (×4), 147.0 (×4). Anal. Calcd for $C_{61}H_{52}O_{12}S_4$: C, 66.28; H, 4.74; S, 11.60. Found: C, 65.94; H, 4.51; S, 11.43.

Pentaerythritol tetrakis(4'-trifluoromethyl-4-biphenylsulfonate) (3h): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2h** (1.651 g, 8.692 mmol) in the presence of Pd$(PPh_3)_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3h** (1.535 g, 61%) as a white solid: TLC R_f 0.19 ($CHCl_3$); mp 283 - 285 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 8H), 7.71 (d, J = 8.4 Hz, 8H), 7.73-7.77 (m, 16H), 7.91 (d, J = 8.4 Hz, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.6, 65.1 (×4), 123.9 (q, J = 272.3 Hz, ×4), 126.1 (q, J = 3.6 Hz, ×8), 127.9 (×8), 128.6 (×8), 128.7 (×8), 130.9 (q, J = 32.1 Hz, ×4), 133.6 (×4), 142.4 (×4), 146.1 (×4). Anal. Calcd for $C_{57}H_{40}F_{12}O_{12}S_4$: C, 53.77; H, 3.17; S, 10.07. Found: C, 53.69; H, 3.10; S, 9.97.

Pentaerythritol tetrakis(4'-fluoro4-biphenylsulfonate) (3i): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2i** (1.216 g, 8.692 mmol) in the presence of Pd$(PPh_3)_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3i** (1.336 g, 63%) as a white solid: TLC R_f 0.20 ($CHCl_3$); mp 170 - 171 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 8H), 7.18 (t, J = 8.6 Hz, 8H), 7.57-7.59 (m, 8H), 7.71 (d, J = 8.5 Hz, 8H), 7.87 (d, J = 8.5 Hz, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.5, 65.3 ('4), 116.1 (d, J = 21.7 Hz, '8), 128.1 ('8), 128.6 ('8), 129.2 (d, J = 8.3 Hz, '8), 132.7 ('4), 135.0 (d, J = 3.3, '4), 146.5 ('4), 163.3 (d, J = 249.3, '4). Anal. Calcd for $C_{53}H_{40}F_4O_{12}S_4$: C, 59.32; H, 3.76; S, 11.95. Found: C, 59.15; H, 3.66; S, 11.72.

Pentaerythritol tetrakis[4-(3-pyridyl)-bezenesulfonate)] (3j): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2j** (1.060 g, 8.692 mmol) in the presence of Pd$(PPh_3)_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3j** (1.172 g, 59%) as a white solid: TLC R_f 0.15 ($CHCl_3$); mp 106 - 108 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 8H), 7.43 (ddd, J = 7.9, 4.9, 0.8 Hz, 4H), 7.78 (d, J = 8.7 Hz, 8H), 7.93 (d, J = 8.7 Hz, 8H), 7.91-7.94 (m, 4H), 8.69 (dd, J = 4.9, 1.7 Hz, 4H), 8.89 (d, J = 2.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 65.7 ('4), 126.4 ('8), 127.4 ('8), 128.2 ('4), 128.8 ('4), 128.9 ('4), 132.7 ('4), 136.2 ('4), 147.5 ('4), 152.4 ('4). Anal. Calcd for $C_{49}H_{40}N_4O_{12}S_4$: C, 58.55; H, 4.01; N, 5.57; S, 12.76. Found: C, 58.21; H, 3.88; N, 5.37; S, 12.40.

Pentaerythritol tetrakis[4-(2-thienyl)-bezenesulfonate)] (3k): It was prepared by the reaction of **1** (2.000 g, 1.976 mmol) with **2k** (1.112 g, 8.692 mmol) in the presence of Pd$(PPh_3)_4$ (0.274 g, 0.237 mmol) and 2.0 M aq Na_2CO_3 (8.0 mL) by using toluene (20 mL) as a solvent. The crude product was purified by precipitation from EtOAc to give **3k** (1.175 g, 58%) as a white solid: TLC R_f 0.25 ($CHCl_3$); mp 195 - 197 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 8H), 7.14 (dd, J = 5.0, 3.7 Hz, 4H), 7.43-7.45 (m, 8H), 7.71 (d, J = 8.6 Hz, 8H), 7.77 (d, J = 8.6 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.5, 65.8 ('4), 125.9 ('4), 126.6 ('8), 127.7 ('4), 128.9 ('4), 129.0 ('8), 132.7 ('4), 140.6 ('4), 141.9 ('4). Anal. Calcd for $C_{45}H_{36}O_{12}S_8$: C, 52.72; H, 3.54; S, 25.02. Found: C, 52.48; H, 3.45; S, 24.77.

General procedure for the preparation of biaryl compounds 5. To a stirred solution of **3** (0.300 mmol) and dppfNiCl_2 (0.0600 mmol, 41.0 mg) in THF (6.0 mL) was slowly added 2-propylmagnesium chloride (**4**) (3.60 mmol) at 25 °C under an argon atmosphere. The reaction mixture was stirred for 18 h. The resulting mixture was diluted with Et_2O. The organic layer was washed with 1% aqueous HCl, water, and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude biphenyls **5** were purified by simple filtration using hexane through a sintered glass funnel containing a small pad of silica gel. The biphenyls **5a-f** were identified according to the literature.[22]

4-Vinylbiphenyl (5g): It was prepared by the reaction of **3g** (0.332 g, 0.300 mmol) with **4** (2.0 M in THF, 1.8 mL, 3.60 mmol) in the presence of dppfNiCl_2 (41.0 mg, 0.0600 mmol) by using THF (6.0 mL) as a solvent. The crude product was purified by simple filtration using hexane through a sintered glass funnel containing a small pad of silica gel to give **5g** (112 mg, 79%) as a white solid: TLC R_f 0.90 (Et_2O:*n*-hexane = 1:1); mp 120 - 121 °C (lit.[23] 118 - 120 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.28 (d, J = 10.9 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 6.77 (dd, J = 10.9, 17.6 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.59-7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.1, 126.8 ('2), 127.2 ('2), 127.4 ('2), 127.5, 129.0 ('2), 136.6, 136.8, 140.8, 140.9. HRMS (EI, 70eV): calcd for $C_{14}H_{12}$, 180.0939; found, 180.0942.

4-(Trifluoromethyl)biphenyl (5h): It was prepared by the reaction of **3h** (0.382 g, 0.300 mmol) with **4** (2.0 M in THF, 1.8 mL, 3.60 mmol) in the presence of dppfNiCl_2 (41.0 mg, 0.0600 mmol) by using THF (6.0 mL) as a solvent. The crude product was purified by simple filtration using hexane through a sintered glass funnel containing a small pad of silica gel to give **5h** (179 mg, 67%) as a white solid: TLC R_f 0.76 (Et_2O:*n*-hexane = 1:1); mp 69 - 70 °C (lit.[24] 69.0 - 69.3 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.60 (dd, J = 8.4, 1.2 Hz, 2H), 7.69 (s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 124.3 (q, J = 272.0), 125.7 (q, J = 3.8 Hz, '2), 127.3 ('2), 127.4 ('2), 128.2, 129.0 ('2), 129.3 (q, J = 32.4 Hz), 139.8, 144.7. HRMS (EI, 70eV): calcd for $C_{13}H_9F_3$, 222.0656; found, 222.0669.

4-Fluorobiphenyl (5i): It was prepared by the reaction of **3i** (0.322 g, 0.300 mmol) with **4** (2.0 M in THF, 1.8 mL, 3.60 mmol) in the presence of dppfNiCl_2 (41.0 mg, 0.0600 mmol) by using THF (6.0 mL) as a solvent. The crude product was purified by simple filtration using hexane through a sintered glass funnel containing a small pad of silica gel to give **5i** (107 mg, 52%) as a white solid: TLC R_f 0.74 (Et_2O:*n*-hexane = 1:1); mp 71 - 72 °C (lit.[25] 72 - 73 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.14 (m, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.54-7.56 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 115.6 (d, J = 21.4 Hz, '2), 127.0 ('2), 127.2, 128.7 (d, J = 8.0 Hz, '2), 128.8 ('2), 137.3 (d, J = 3.2 Hz), 140.2, 162.4 (d, J = 246.4 Hz). HRMS (EI, 70eV): calcd for $C_{12}H_9F$, 172.0688; found, 172.0694.

3-Phenylpyridine (5j): It was prepared by the reaction of **3j** (0.302 g, 0.300 mmol) with **4** (2.0 M in THF, 1.8 mL, 3.60 mmol) in the presence of dppfNiCl_2 (41.0 mg, 0.0600 mmol) by using THF (6.0 mL) as a solvent. The crude product was purified by simple filtration using hexane through a sintered

glass funnel containing a small pad of silica gel to give **5j** (114 mg, 61%) as a brown oil: TLC R_f 0.69 (Et_2O:*n*-hexane = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.38 (m, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.58-7.60 (m, 2H), 7.87-7.89 (m, 1H), 8.60 (dd, J = 4.8, 1.6 Hz, 1H), 8.86 (d, J = 2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.7, 127.3 ('2), 128.2, 129.2 ('2), 134.5, 136.8, 138.0, 148.5, 148.6. HRMS (EI, 70eV): calcd for $C_{11}H_9N$, 155.0735; found, 155.0744.

2-Phenylthiophene (5k): It was prepared by the reaction of **3k** (0.308 g, 0.300 mmol) with **4** (2.0 M in THF, 1.8 mL, 3.60 mmol) in the presence of dppfNiCl_2 (41.0 mg, 0.0600 mmol) by using THF (6.0 mL) as a solvent. The crude product was purified by simple filtration using hexane through a sintered glass funnel containing a small pad of silica gel to give **5k** (106 mg, 55%) as a white solid: TLC R_f 0.78 (Et_2O:*n*-hexane = 1:1); mp 35 - 36 °C (lit.[23] 34 - 36 °C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.12 (dd, J = 5.1, 3.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.50 (dd, J = 3.6, 1.2 Hz, 1H), 7.53 (dd, 5.1, 1.2 Hz, 1H), 7.63-7.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.3, 125.0, 126.1 ('2), 127.6, 128.2, 129.1 ('2), 134.6, 144.6. HRMS (EI, 70eV): calcd for $C_{11}H_9N$, 160.0347; found, 160.0334.

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