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Solid-Phase Synthesis of Unfunctionalized Arenes *Via* the Traceless Cleavage of Sulfonate Linkers

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The hydrogenolysis of polymer-bound arenesulfonates by 2-propylmagnesium chloride was performed through reductive cleavage of the C–S bond in the presence of a nickel catalyst. The reaction underwent in the highest efficiency by adding 15 equiv of the nucleophile in two additions with dppfNiCl$_2$ in THF. Various unfunctionalized naphthalene, biphenyl, and stilbene derivatives were produced in good yields by the traceless sulfonate linker system at room temperature.

Key Words : Solid-phase synthesis, Traceless cleavage, Parallel synthesis, Unfunctionalized arenes, Sulfonate linker

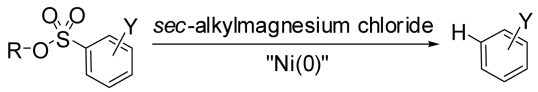
Introduction

Since Merrifield introduced cross-linked polystyrene for the synthesis of oligopeptides,[1] solid-phase organic synthesis (SPOS) with parallel or combinatorial synthesis has been developed for the preparation of numerous classes of compounds.[2] It can be automated and can simply achieve pure products, making it attractive for a range of syntheses beyond the peptide and nucleotide libraries. For example, it has been used in the discovery of drug candidates and other new materials.[3] A range of standard solution-phase reactions have now been adapted for SPOS.

The selection of linker, which facilitates substrates' attachment, functionalization, and release, is a key consideration in SPOS.[4] Linker units are typically classified as traditional/classical, multifunctional or traceless according to the functionality of the target molecules at the cleavage sites. Most traditional linkers leave polar functionality on the target compound released from the resin because the substrate is linked to the polymeric support through its existing functionality. Most organic compounds prepared by this approach possess functional moieties, typically hydroxyl, amino, or carboxyl groups. However, this polar functionality is not always desired, necessitating the development of traceless linkers that leave no polar traces on the cleaved substrates.

A variety of traceless linker systems have been reported.[5] The traceless cleavage of C–S bonds in polymer-bound thioethers,[6] sulfones,[7] thioesters,[8] sulfonamides,[9] and trialkylsulfonium salts[10] has been investigated for the release of substrates without functional groups. The large demand for various unfunctionalized conjugated hydrocarbons in organic electronics necessitates the development of an efficient traceless linker system. However, the preparation of a library of unfunctionalized hydrocarbons via SPOS remains challenging due to the lack of appropriate traceless linkers.

Solid-phase[11] and liquid-phase[12] parallel syntheses of biphenyl and terphenyl compounds have been reported through the traceless multifunctional cleavage of arenesulfonate linkers that involved *ipso*-nucleophilic aromatic substitution of alkyloxysulfonyl moieties by aryl nucleophiles. This approach was useful in the preparation of unfunctionalized oligophenyl libraries by allowing additional diversity through the aryl moieties and traceless multifunctional release of the target compounds. However, reactions of arylmagnesium bromides resulted in large amounts of biphenyls through the dimerization of aryl groups that hindered the purification of the desired products. While the term "traceless" has not been precisely defined,[13] truly traceless cleavage of target substrates from supports by simple hydrogenolysis is desirable in many applications.



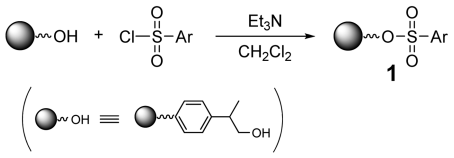
Scheme 1. Hydrogenolysis of arenesulfonates.

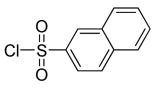
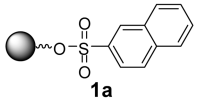
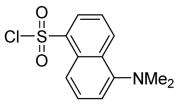
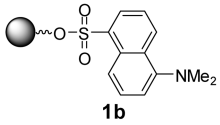
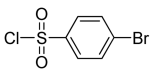
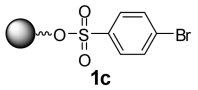
Previous work directed towards the development of unfunctionalizing cleavage of C–S bonds in arenesulfonates reported 2-propylmagnesium chloride as an efficient reducing agent (Scheme 1).[14] The development of a novel sulfur-based traceless linker system through the nickel-catalyzed hydrogenolysis of polymer-bound arenesulfonate linkers is reported here. Biphenyl and stilbene compounds, with a variety of biological,[15] optical,[16] and electrical[17] properties, were prepared by solid-phase parallel synthesis.

Results and Discussion

Polymer-bound arenesulfonates **1a-c** were prepared by reported reactions of hydroxymethylethyl resin with corresponding arenesulfonyl chlorides[11] (Table 1). Yields of 79-85% were calculated based on the initial loading of sulfonate moieties. The products were determined by elemental analyses. Efficient sulfonylation was confirmed by IR analyses.

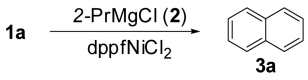
Table 1. Preparation of polymer-bound arenesulfonates **1**[a]



Entry	Sulfonyl chloride	Arenesulfonate **1**	Yield (%)[b]
1		 **1a**	82
2		 **1b**	79
3		 **1c**	85

[a]Reactions between hydroxyl resin (4.55 mmol) and sulfonyl chlorides (18.20 mmol) were carried out in CH_2Cl_2 (75 mL) in the presence of Et_3N (22.75 mmol). [b]Yields were determined by elemental analyses of polymer-bound sulfonates **1**.

Table 2. Effects of Conditions on the Reaction of **1a** with **2**[a]



Entry	**2** (equiv)	Solvent	Yield (%)[b]
1	15	Et_2O	55
2	8+7	Et_2O	58
3	15	THF	84
4	8+7	THF	96
5	15	DME	65
6	8+7	DME	63
7	15	1,4-dioxane	58
8	8+7	1,4-dioxane	58
9[c]	5+5	THF	89
10	10+10	THF	96

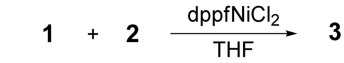
[a]Reactions of **1a** (0.157 mmol) with the indicated amounts of **2** were carried out in the presence of $dppfNiCl_2$ (0.048 mmol) in the indicated solvents (4.0 mL) for 24 h at room temperature. [b]Yields were determined by GC analyses using biphenyl as an internal standard. [c]Reaction for 48 h.

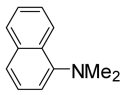
The unreacted hydroxyl groups of **1** were converted to methoxy groups by treatment with excess CH_3I.

The hydrogenolysis of polymer-bound 2-naphthalenesulfonate, **1a**, by 2-propylmaginesium chloride, **2**, was first investigated to establish optimal reaction conditions (Table 2). All reactions were performed using [1,1'-bis(diphenylphosphino)ferrocene]dichloronickel ($dppfNiCl_2$), which had previously shown the best catalytic activity for the 24 h hydrogenolysis of neopentylarenesulfonates[14] at room temperature.

The use of 15 equiv of Grignard reagent in tetrahydrofuran (THF) led to more efficient reactions than in other common ethereal solvents (entries 1, 3, 5 and 7). Diethylether, which gave the best results in the corresponding solution-phase reactions, was inappropriate for this heterogeneous cleavage, likely due to its poor swelling and shrinking effects (entry 1). Yield generally increased when the Grignard reagent was added in two portions – 8 equiv added initially and a further 7 equiv added after 12 h (denoted as 8 + 7 equiv, entries 2, 4, 6, and 8) – rather than a similar single addition (entries 3 and 4). 10 equiv of **2** was insufficient for complete reaction, even when the system was left for an extended time (entry 9). Using **2** at over 15 equiv did not significantly improve efficiency (entry 10). Naphthalenesulfonate was not liberated via the cleavage of C–O bonds by the Ni catalyst under any of the tested conditions. In summary, the highest yield was obtained by adding 8 equiv, then later another 7 equiv of **2** in the presence of $dppfNiCl_2$ in THF at room temperature.

Table 3. Hydrogenolysis of **1** to **3**[a]



Entry	Sulfonate **1**	Product **3**	Yield (%)[b]
1	**1a**	**3a**	82
2	**1b**	 **3b**	75

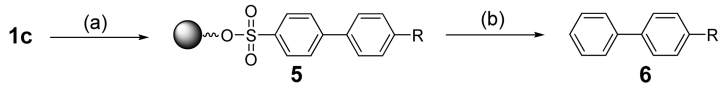
[a]Reactions of **1** (0.157 mmol) with **2** (2.36 mmol) were carried out in the presence of $dppfNiCl_2$ (0.048 mmol) in THF (4.0 mL) for 24 h at room temperature. [b]Yields based on the loading of **1**.

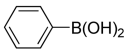
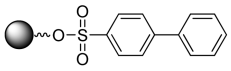
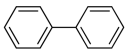
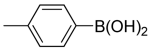
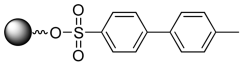
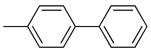
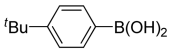
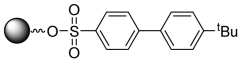
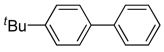
Reactions of naphthalenesulfonates **1a** and **1b** were performed under the optimized conditions (Table 3). Reasonably pure solid products could be easily isolated from the reaction mixtures by filtration using hexane through a sintered glass funnel containing a small pad of silica gel after standard work-up. Pure **3a** and **3b** were produced with good yields after additional chromatographic isolation.

The generality of this traceless strategy was explored by synthesizing several unfunctionalized biphenyls **6** (Table 4). Polymer-bound 4-bromobenzenesulfonate, **1c**, was initially subjected to Suzuki coupling with three phenylborinic acids **4a-c** in the presence of $Pd(PPh_3)_4$ and aqueous Na_2CO_3 in DME. These palladium-catalyzed coupling reactions produced resin-bound biphenylsulfonates **5a-c**. Free biphenylsulfonates were not liberated via the cleavage of CO bonds by the Pd catalyst under any of the tested conditions. Biphenylsulfonates **5** were allowed to undergo nickel-catalyzed hydrogenolysis with **2** to produce biphenyl derivatives, **6**. Treating **5** with 8 + 7 equiv of **2** in the presence of $dppfNiCl_2$ in THF produced **6** with good yields: 76–79% based on the initial loading of bromobenzenesulfonate **1c**. Filtration using hexane after standard work-up resulted in good purities. Samples were further purified by chromatography for the calculation of final yields. The desired products **6a-c** were obtained as white solids.

The sulfonate-based traceless linker system was tested in the solid-phase synthesis of unfunctionalized *trans*-stilbene derivatives **9**. Unfunctionalized stilbene derivatives have been studied as part of efforts to understand emission mechanisms and the effects of substitution on light emission

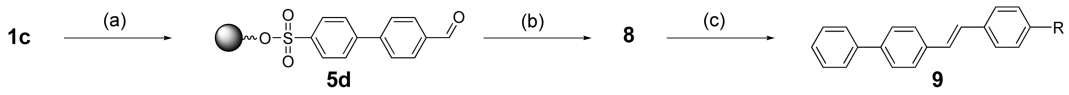
Table 4. Solid-phase preparation of biphenyl compounds **6**[a]

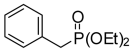
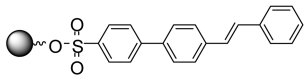
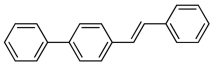
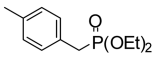
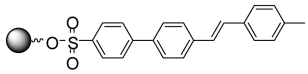
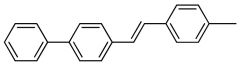
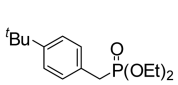
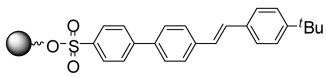
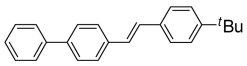


Entry	boronic acid **4**		Biphenylsulfonate **5**		Biphenyl **6**		Yield (%)[b]
1		**4a**		**5a**		**6a**	79
2		**4b**		**5b**		**6b**	78
3		**4c**		**5c**		**6c**	76

[a]Reagents and conditions: (a) **1c** (0.157 mmol), boronic acid **4** (0.518 mmol), DME (4 mL), $Pd(PPh_3)_4$ (0.014 mmol), aqueous Na_2CO_3 (0.314 mmol), 85 °C, 30 h; (b) **5** (0.157 mmol), **2** (2.355 mmol), $dppfNiCl_2$ (0.048 mmol), THF (4.0 mL), 110 °C, 24 h. [b]Yields based on **1c**.

Table 5. Solid-phase preparation of *trans*-stilbene compounds **9**[a]



Entry	Phosphonate **7**		Stilbenesulfonate **8**		Stilbene **9**		Yield (%)[b]
		**7a**		**8a**		**9a**	53
2		**7b**		**8b**		**9b**	56
3		**7c**		**8c**		**9c**	57

[a]Reagents and conditions: (a) **1c** (10.4 mmol), **4d** (34.2 mmol), DME (230 mL), $Pd(PPh_3)_4$ (0.933 mmol), Na_2CO_3 (0.090 mmol), 85 °C, 24 h; (b) **5d** (1.86 mmol), **7** (7.44 mmol), DME (40 mL), NaH (7.07 mmol), 85 °C, 48 h; (c) **8** (0.282 mmol), **2** (4.230 mmol), THF (6.0 mL), $dppfNiCl_2$ (0.113 mmol), 25 °C, 36 h. [b]Yields based on **1c**.

by conjugated skeletons,[18] because they are short subunits of poly(*p*-phenylenevinylene), the first light-emitting polymer.[19] Stilbene derivatives can also exhibit blue photoluminescence.[20] Polymer-bound *trans*-stilbenesulfonates **8** were prepared by Horner-Wadsworth-Emmons reactions of formylbiphenylsulfonate **5d** itself prepared by the Suzuki coupling of **1c** and **4d** with benzyl phosphonates **7**. The hydrogenolysis of **8** produced high-purity white solids **9** (Table 5) after filtration. The yields of the *trans*-stilbenes **9a-c** were calculated after additional chromatography.

Conclusions

The hydrogenolysis of polymer-bound arenesulfonates and stilbenesulfonates using 2-propylmagnesium chloride produced naphthalene, biphenyl, and stilbene derivatives with good yields. The sulfonate linker system could generate unfunctionalized oligophenyl and stilbene libraries without any polar remnants of resin attachment. This traceless technique is efficient in that it does not require additional reactions for the preparation of the linker units and the regeneration and reuse of the hydroxyl resin appears plausible. Isolating the final target compounds is also convenient due to the absence of significant by-products caused by the homo-coupling of the Grignard reagent. This traceless strategy shows potential applicability for parallel and combinatorial solid-phase syntheses of various aromatic hydrocarbon derivatives.

Experimental Section

Solvents were distilled from appropriate drying agents 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. Polymer-bound stilbenesulfonates were prepared by a reported procedure.[21]

Preparation of Polymer-Bound Arylsulfonate, 1. Triethylamine (TEA) (22.75 mmol) and arylsulfonyl chloride (18.20 mmol) were added to the resin (BT Core™ Resin, 0.91 mmol/g, 100-200 mesh, 5 g, 4.55 mmol) in CH_2Cl_2 (75 mL) in a three-necked round-bottomed flask at 0 °C. An ice

bath maintained the flask at 5-10 °C during the addition. The mixture was stirred at room temperature for 35 h. Excess reagent was removed by filtration and rinsing with MeOH (×3), 0.1 N aq HCl (×2), water (×3), and MeOH (×3). After thorough washing, **1** was treated with triethylamine (TEA) (2.21 mL, 15.9 mmol) and methyl iodide (0.85 mL, 13.7 mmol) for 3 h to protect the remaining hydroxyl groups as methoxy groups.

Polymer-bound 2-naphthalenesulfonate (1a) was prepared by the reaction of resin (5.00 g, 4.55 mmol) with 2-naphthalenesulfonyl chloride (4.13 g, 18.22 mmol) in CH_2Cl_2 (75 mL) in the presence of TEA (3.15 mL, 22.80 mmol): Anal. Found: S, 2.04 (0.636 mmol/g, 82%); FT-IR (KBr) 1358, 1172, 961.

Polymer-bound Dansylsulfonate (1b) was prepared by the reaction of resin (5.00 g, 4.55 mmol) with dansylsulfonyl chloride (4.91 g, 18.22 mmol) in CH_2Cl_2 (75 mL) in the presence of TEA (3.15 mL, 22.80 mmol): Anal. Found: S, 1.91 (0.597 mmol/g, 79%); FT-IR (KBr) 1358, 949, 787.

Polymer-bound 4-bromobenzenesulfonate (1c) was prepared by the reaction of resin (5.00 g, 4.55 mmol) with 4-bromobenzenesulfonyl chloride (4.65 g, 18.22 mmol) in CH_2Cl_2 (75 mL) in the presence of TEA (3.15 mL, 22.80 mmol): Anal. Found: S, 2.05 (0.639 mmol/g, 85%); FT-IR (KBr) 1364, 1186, 814.

Preparation of Polymer-Bound Biphenylsulfonates 5. 2.0 M aqueous Na_2CO_3 (1.60 mL) and arylboronic acid, **4**, (5.28 mmol) were dissolved in a minimal amount of EtOH:DME (1:1) and added to the suspension of 4-bromobenzenesulfonate resin **1c** (2.50 g, 1.60 mmol) with $Pd(PPh_3)_4$ (166 mg, 0.14 mmol) in DME (38 mL) at room temperature. After heating for 30 h, 30% hydrogenperoxide (0.08 mL) was added at room temperature, and the reaction mixture was stirred for 10 min. The resulting resin **5** was isolated by filtration through a sintered glass filter and rinsed with DME (×3), 0.1 N aq HCl (×2), water (×3), MeOH (×3). The resin was dried under vacuum, resulting in brown biphenylsulfonate resin **5**.

Polymer-bounded Biphenylsulfonate (5a) was prepared by the reaction of **1c** (2.50 g, 1.60 mmol) with phenylboronic acid **4a** (0.64 g, 5.28 mmol) in DME (38 mL) in presence of $Pd(PPh_3)_4$ (166 mg, 0.14 mmol) and 2.0 M aqueous Na_2CO_3 (1.60 mL); FT-IR (KBr) 1362, 1174, 958, 832.

Polymer-bounded 4-methylbiphenylsulfonate (5b) was prepared by the reaction of **1c** (2.50 g, 1.60 mmol) with tolylboronic acid **4b** (0.72 g, 5.28 mmol) in DME (38 mL) in presence of $Pd(PPh_3)_4$ (166 mg, 0.14 mmol) and 2.0 M aqueous Na_2CO_3 (1.60 mL); FT-IR (KBr) 1364, 1178, 960, 830.

Polymer-bounded 4-*tert*-butylbiphenylsulfonate (5c) was prepared by the reaction of **1c** (2.50 g, 1.60 mmol) with 4-*tert*-butyl-phenylboronic acid **4c** (0.94 g, 5.28 mmol) in DME (38 mL) in presence of $Pd(PPh_3)_4$ (166 mg, 0.14 mmol) and 2.0 M aqueous Na_2CO_3 (1.60 mL); FT-IR (KBr) 1363, 1178, 960, 821.

General Procedure for The Hydrogenolysis. Grignard reagent **2** (1.256 mmol) was slowly added to the polymer-bound **8** (0.157 mmol) and $dppfNiCl_2$ (0.0480 mmol, 32.8 mg) in THF (4 mL) at room temperature under Ar. The reaction mixture was stirred for 12 h at room temperature. Additional **2** (1.099 mmol) was added to the mixture, and it was stirred for 12 h at room temperature. The resulting mixture was filtered using Et_2O through a sintered glass filter. The filtrate was washed with 1% aqueous HCl, water, and brine. It was then dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was dissolved in a small amount of EtOAc and filtered through a sintered glass funnel containing a small pad of silica gel. The filtrate was concentrated to give a pure stilbene **9**.

(*E*)-4-Styryl-[1,1']biphenyl (9a) was prepared by the reaction of **8a** (0.704 mmol/g, 0.4 g) with **2** (2.0 M in THF, 3.5 mL, 3.38 mmol) in the presence of $dppfNiCl_2$. The products could be easily isolated as pure solids from the reaction mixtures by a facile filtration through a sintered glass funnel containing a small pad of silica gel using EtOAc to give **9a** (38.3 mg, 53%) as a white solid: TLC R_f 0.57 (CH_2Cl_2:*n*-hexane = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.33-7.39 (m, 3H), 7.45 (t, J = 7.5 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.60 (s, 4H), 7.62 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.7 (×2), 127.1 (×4), 127.5 (×2), 127.8, 128.4, 128.9 (×2), 129.0 (×2), 136.5, 137.5, 140.5, 140.8; HRMS (EI, 70 eV) calcd for $C_{20}H_{16}$ (M^+) 256.3410, found 256.3452.

(*E*)-4-[2-(4-Methylphenyl)vinyl]-[1,1']biphenyl (9b) was prepared by the reaction of **8b** (0.697 mmol/g, 0.4 g) with **2** (2.0 M in THF, 3.5 mL, 3.38 mmol) in the presence of $dppfNiCl_2$. The products could be easily isolated as pure solids from the reaction mixtures by a facile filtration through a sintered glass funnel containing a small pad of silica gel using EtOAc to give **9b** (42.2 mg, 56%) as a white solid: TLC R_f 0.58 (CH_2Cl_2:*n*-hexane = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.09 (d, J = 16.4 Hz, 1H), 7.14 (d, J = 16.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.43-7.46 (m, 4H), 7.58 (d, J = 8.5 Hz, 2H), 7.59-7.63 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 126.6 (×2), 127.0 (×2), 127.1 (×2), 127.3, 127.5, 127.5 (×2), 128.8, 129.0 (×2), 129.6 (×2), 134.7, 136.7, 137.8, 140.3, 140.9; HRMS (EI, 70 eV) calcd for $C_{21}H_{18}$ (M^+) 270.3676, found 270.3669.

(*E*)-4-[2-(4-*tert*-Butylphenyl)vinyl]-[1,1']biphenyl (9c) was prepared by the reaction of **8c** (0.677 mmol/g, 0.4 g) with **2** (2.0 M in THF, 3.5 mL, 3.38 mmol) in the presence of $dppfNiCl_2$. The products could be easily isolated as pure solids from the reaction mixtures by a facile filtration through a sintered glass funnel containing a small pad of silica gel using EtOAc to give **9c** (48.2 mg, 57%) as a white solid: TLC R_f 0.59 (CH_2Cl_2:*n*-hexane = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 7.11 (d, J = 16.3 Hz, 1H), 7.15 (d, J = 16.3 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.9, 7.4 Hz, 2H), 7.57-7.59 (m, 4H), 7.62 (d, J = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5 (×3), 34.8, 125.8 (×2), 126.4 (×2), 127.0 (×2), 127.1(×2), 127.5, 127.5 (×2), 127.6, 128.7, 129.0 (×2), 134.7, 136.8,

140.3, 140.9, 151.0; HRMS (EI, 70 eV) calcd for $C_{24}H_{24}$ (M^+) 312.4474, found 312.4472.

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References

1. Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149-2154.
2. For recent reviews, see (a) Nandy, P. J.; Prakesch, M.; Khadem, S.; Reddy, P. T.; Sharma, U.; Arya, P. *Chem. Rev.* **2009**, *109*, 1999-2060. (b) Kennedy, J. K.; Williams, L.; Bridges, T. M.; Daniels, R. N.; Weaver, D., Lindsley, C. W. *Journal of Combinatorial Chemistry* **2008**, *10*, 345-354.
3. For recent reviews, see (a) Potyrailo, R. A.; Mirsky, V. M. *Chem. Rev.* **2008**, *108*, 770-813. (b) Maier, W.; Stowe, K.; Sieg, S. *Angew. Chem., Int. Ed*. **2007**, *46*, 6016. (c) Potyrailo, R. A. *Angew. Chem. Int. Ed*. **2006**, *45*, 702-723. (d) Tacheuchi, I.; Lauterbach, J.; Fasolka, M. J. *Materialstoday* **2005**, 18.
4. For reviews, see (a) Boas, U.; Brask, J.; Jensen, K. J. *Chem. Rev.* **2009**, *109*, 2092-2118. (b) Zhang, W. *Chem. Rev.* **2009**, *109*, 749-795. (c) Scott, P. J. H.; Steel, P. G. *Eur. J. Org. Chem*. **2006**, 2251-2268. (d) James, I. W. *Tetrahedron* **1999**, *55*, 4855-4946.
5. For reviews, see (a) Gil, C.; Bräse, S. *Curr. Opin. Chem. Biol.* **2004**, *8*, 230-237. (b) Blaney, P.; Grigg, R.; Sridharan, V. *Chem. Rev.* **2002**, *102*, 2607-2624. (c) Phoon, C. W.; Sim, M. M. *Curr. Org. Chem*. **2002**, *6*, 937-964. (d) Bräse, S.; Dahmen, S. *Chem. Eur. J*. **2000**, *6*, 1899-1905.
6. (a) Jung, K. W.; Zhao, X.-Y.; Janda, K. D. *Tetrahedron* **1997**, *53*, 6645-6652. (b) Jung, K. W.; Zhao, X.-Y.; Janda, K. D. *Tetrahedron Lett.* **1996**, *37*, 6491-6494. (c) Sucholeiki, I. *Tetrahedron Lett.* **1994**, *35*, 7307-7310.
7. (a) Chen, Y.; Lam, Y.; Lai, Y.-H. *Org. Lett.* **2002**, *4*, 3935-3937. (b) Kroll, F. E. K.; Morphy, R.; Rees, D.; Gani, D. *Tetrahedron Lett.* **1997**, *38*, 8573-8576. (c) Zhao, X.-Y.; Jung, K. W.; Janda, K. D. *Tetrahedron Lett.* **1997**, *38*, 977-980. (d) Gayo, L. M.; Suto, M. J. *Tetrahedron Lett.* **1997**, *38*, 211-214.
8. May, P. J.; Bradley, M.; Harrowven, D. C.; Pallin, D. *Tetrahedron Lett.* **2000**, *41*, 1627-1630.
9. Pattarawarapan, M.; Chen, J.; Steffensen, M.; Burgess, K. *J. Comb. Chem.* **2001**, *3*, 102-116.
10. Vanier, C.; Lorgé, F.; Wagner, A.; Mioskowski, C. *Angew. Chem. Int. Ed.* **2000**, *39*, 1679-1683.
11. Cho, C.-H.; Park, H.; Park, M.-A.; Ryoo, T.-Y.; Lee, Y.-S.; Park, K. *Eur. J. Org. Chem*. **2005**, 3177-3181.
12. Kim, C.-B.; Cho, C.-H.; Kim, C. K.; Park, K. *J. Comb. Chem.* **2007**, *9*, 1157-1163.
13. Comely, A. C.; Gibson, S. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1012-1032.
14. Kim, C.-B.; Cho, C.-H.; Park, K. *Bull. Korean Chem. Soc*. **2007**, *28*, 281-284.
15. (a) Davies, D. R.; Mamat, B.; Magnusson, O. T.; Christensen, J.; Haraldsson, M. H.; Mishra, R.; Pease, B.; Hansen, E.; Singh, J.; Zembower, D.; Kim, H.; Kiselyov, A. S.; Burgin, A. B.; Gurney, M. E.; Stewart, L. J. *J. Med. Chem.* **2009**, *52*, 4694-4715. (b) Delomenède, M.; Bedos-Belval, F.; Duran, H.; Vindis, C.; Baltas, M.; Nègre-Salvayre, A. *J. Med. Chem.* **2008**, *51*, 3171-3181. (c) Lion, C. J.; Matthews, C. S.; Stevens, M. F. G.; Westwell, A. D. *J. Med. Chem.* **2005**, *48*, 1292-1295. (d) Walter, G.; Liebl, R.; von Angerer, E. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4659-4663. (e) Iliya, I.; Ali, Z.; Tanaka, T.; Iinuma, M.; Furusawa, M.; Nakaya, K.-I.; Murata, J.; Darnaedi, D.; Matsuura, N.; Ubukata, M. *Phytochemistry* **2003**, *62*, 601-606.
16. (a) Kawamoto, M.; Aoki, T.; Shiga, N.; Wada, T. *Chem. Mater.* **2009**, *21*, 564. (b) Mori, T.; Kyotani, M.; Akagi, K. *Macromolecules* **2008**, *41*, 607-613.
17. (a) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675-1688. (b) Momotake, A.; Arai, T. *J. Photochem. Photobiol. C* **2004**, *5*, 1-25. (c) Markham, J. P. J.; Namdas, E. B.; Anthopoulos, T. D.; Samuel, I. D. W.; Richards, G. J.; Burn, P. L. *Appl. Phys. Lett.* **2004**, *85*, 1463-1465. (d) Sengupta, S.; Muhuri, S. *Tetrahedron Lett.* **2004**, *45*, 2895-2898.
18. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539-541.
19. (a) Gierschner, J.; Cornil, J.; Egelhaaf, H.-J. *Adv. Mater.* **2007**, *19*, 173-191. (b) Hohnholz, D.; Schweikart, K.-H.; Subramanian, L. R.; Wedel, A.; Wischert, W.; Hanack, M. *Synth. Met.* **2000**, *110*, 141-152. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1351-1377.
20. (a) Um, S.-I.; Lee, J.-K.; Kang, Y.; Baek, D.-J. *Dyes Pigm.* **2006**, *70*, 84-90. (b) Sengupta, S. *Tetrahedron Lett.* **2003**, *44*, 307-310.
21. Cho, C.-H.; Kim, C.-B.; Park, K. *J. Comb. Chem.* **2010**, *12*, 45-50.