Modular Access to 9,9-Spirobifluorenes by Oxidative Coupling Using Molybdenum Pentachloride

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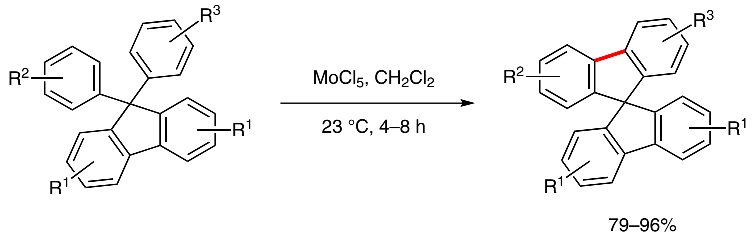
Abstract: The strong oxidizing agent molybdenum pentachloride was used for an efficient direct C–C bond formation of 9,9-diarylfluorenes to the corresponding 9,9-spirobifluorenes. Thus, a versatile method that is compatible with labile groups, such as iodo moieties, was established. By this approach important building blocks for light emitting polymers were synthesized in high yields.

Key words: molybdenum pentachloride, oxidative coupling, spiro compounds, biaryls, C–C bond formation



Scheme 1 Direct oxidative coupling of 9,9-diarylfluorenes to the corresponding spirobifluorenes

In the past decades, the unique electronic structure of spirobifluorenes turned out to be an important feature for optoelectronic applications[1] such as solar cells,[2] light-emitting devices,[3] and field-effect transistors.[4] Furthermore, the molecular vertex can generate a chiral cavity, which can be exploited for molecular recognition.[3g,5] Additionally, the rigid skeleton can be functionalized to form chiral ligands for transition metal catalysts.[6] Analogues of natural products containing spirobifluorenes were reported as well.[7]

The most prominent method for synthesizing 9,9-spirobifluorenes represents the protocol by Clarkson and Gomberg. 9-(Biphen-2-yl)fluoren-9-ols undergo a Friedel–Crafts type reaction.[8] The fluorenol derivative was obtained by addition of a biphenyl Grignard reagent to the corresponding fluorenone. However, the method requires sophisticated 2-halobiphenyls as starting materials. In addition, the Friedel–Crafts reaction occurs in the position para to the electron-releasing substituent limiting the scope. Direct oxidative methods for the formation of the aryl–aryl bond using DDQ/MeSO$_3$H or DDQ/FeCl$_3$ mixtures were reported, but are established only on two spirobifluorene derivatives.[9] An elegant Friedel–Crafts approach was established by Zhou et al. starting from 2,2′-diarylbenzophenones;[10] however, the latter have to be prepared in several steps.

Molybdenum pentachloride is a versatile and easily available oxidizing agent.[11] Because of its strong oxidative power and fast coupling reaction several labile moieties are tolerated.[12] In many cases, Lewis acids are added for intercepting hydrogen chloride formed during the reaction[13] or for providing a preorientation of the substrate by a precoordination[14] to enhance the performance of the Mo(V) reagent. MoCl$_5$ is often considered as a comparable reagent to hypervalent iodine reagents like phenyliodine bis(trifluoroacetate) (PIFA).[11] But in several examples MoCl$_5$ yields superior results.[11a,b,15] The molybdenum salts generated during the reaction can determine the stereoselectivity of the coupling,[16] cause domino oxidations,[17] or induce subsequent reductions by a redox play.[18]

Herein, we report a convenient synthesis of highly functionalized 9,9-spirobifluorenes (Scheme 1), which tolerates a variety of functionalities and is complementary to existing methods. Diiodinated and dibrominated species are obtainable, which can be used as building blocks for polymers with crucial optoelectronic features.

Scope and Limitations

The starting materials are easily accessible from the corresponding fluorenones by a double Friedel–Crafts type reaction or by an initial Grignard addition followed by a Friedel–Crafts type reaction (Scheme 2, and Supporting Information).

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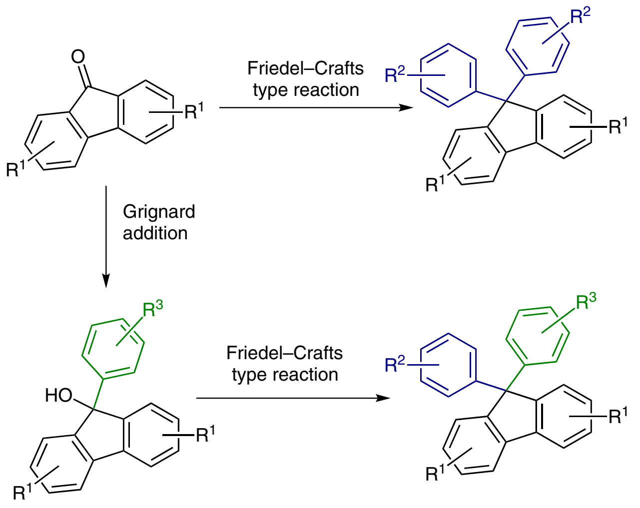
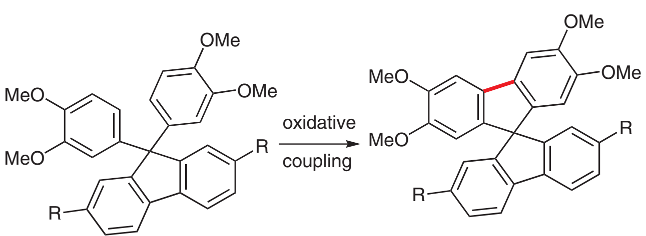


Scheme 2 Synthesis of starting materials

The commonly used reagent mixture consisting of molybdenum pentachloride with titanium tetrachloride provides in the oxidative coupling reaction to **1** inferior yields than $MoCl_5$ as sole reagent (Table 1, entries 1, 2). The addition of titanium tetrachloride leads to the formation of a sparingly soluble precipitate with the substrate (entry 3). The spiro product **1** is generated in excellent yield if reaction times are prolonged (entry 4). Application of ferric chloride at analogous reaction conditions resulted in complete decomposition of the starting material and no traces of **1** could be detected (entry 5). The unique and superior character of $MoCl_5$ as reagent is demonstrated in the oxidative coupling reaction to the diiodinated spirobifluorene **4**. Using the conditions reported, neither DDQ/$MeSO_3H$ nor DDQ/$FeCl_3$ could form the desired and valuable building block **4** as effectively as $MoCl_5$ (entries 6–8). The dichlorodicyanoquinone-based reagent mixtures cause protodeiodination as a dominant side reaction. The physical properties of **4** and its partially and fully deiodinated species are very similar. Consequently, the content was determined in the product mixture. The formation of the diiodinated compound was verified by X-ray analysis of a suitable single crystal (Figure 1).

Table 1 Comparison of Different Coupling Conditions



1: R = H
4: R = I

Entry	Conditions	Result
1	$MoCl_5/TiCl_4$, 2 h, 23 °C	64%[a] (**1**)
2	$MoCl_5$, 2 h, 23 °C	78%[a] (**1**)
3	$TiCl_4$, 2 min, 23 °C	–[b]
4	$MoCl_5$, 5 h, 23 °C	96%[a] (**1**)
5	$FeCl_3$, 5 h, 23 °C	<1%[c] (**4**)
6	DDQ, $FeCl_3$, 1 h, 0 °C	34%[c] (**4**)
7	DDQ, $MeSO_3H$, 1 h, 0 °C	60%[c] (**4**)
8	$MoCl_5$, 4 h, 23 °C	92%[a] (**4**)

[a] Isolated yield.
[b] Formation of a sparingly soluble precipitate.
[c] Determined by ^1H NMR spectroscopy.

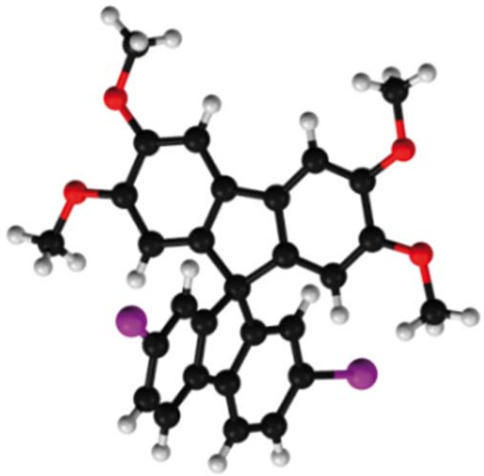


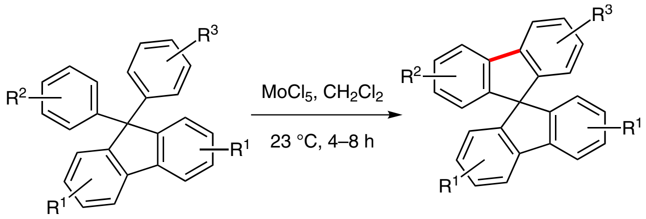
Figure 1 Molecular structure of **4** determined by X-ray analysis of a suitable single crystal

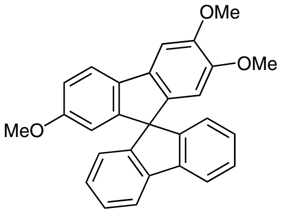
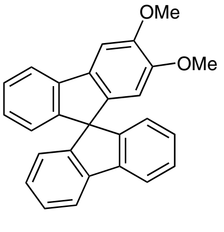
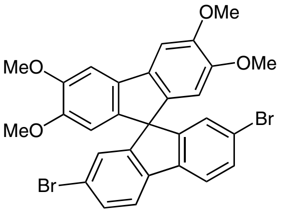
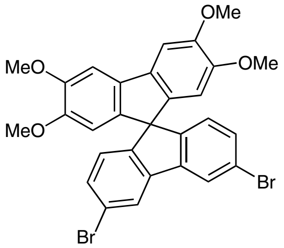
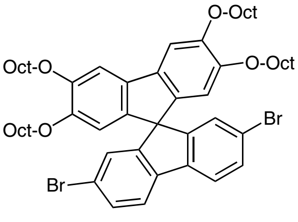
The screening of the oxidative coupling conditions indicated that $MoCl_5$ is capable to construct effectively the spirobifluorene skeleton. Subsequently, the scope of substrates was elucidated (Table 2). A variety of 9,9-diphenylfluorenes with differently substituted phenyl groups were subjected to the oxidative coupling protocol. As found in previous studies, a 1,2-dimethoxy substitution pattern is very beneficial for the oxidative coupling process since a precoordination of $MoCl_5$ prior to electron transfer is anticipated.[11g] This was underlined by the excellent yield of **1** and **4**, respectively. If only three electron-releasing groups are present in the substrate, product **2** can still be obtained in 86% yield (Table 2, entry 1). If only one coupling moiety is activated, no intramolecular C–C bond formation is observed (entry 3). When the corresponding diarylfluorene is treated with $MoCl_5$, even after 14 hours no coupling process is observed, whereas chlorination reactions of the starting material occur.

Iodo and bromo substituents are splendid leaving groups for transition metal catalysis. Consequently, spirobifluorenes exhibiting two of such functionalities are very useful building blocks for polymer synthesis.[19,20]

By the oxidative coupling of the corresponding substrates the 2,7-dibromo- and 3,6-dibromospirobifluorenes **3** and **5** are accessible in excellent to good yields, respectively (Table 2, entries 3, 4). The coupling protocol is not only compatible with labile moieties on the aromatic core but

Table 2 Scope of the Coupling Reaction to Spirobifluorenes

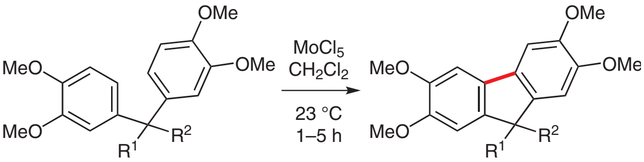


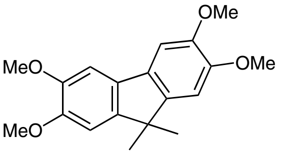
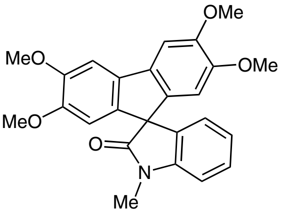
Entry	Product	Time (h)	Yield (%)
1	 **2**	8	86
2	 **10**	14	–
3	 **3**	5	94
4	 **5**	4	79
5	 **6**	4	92

also useful for substrates with larger side chains (entry 5). This tetrakisoctyloxylated spirobifluorene **6** was employed as building block for light emitting polymers. The synthesis reported for **6** involves seven steps with a total yield of 7% starting from 2,7-dibromofluorenone, catechol, and 1-bromooctane.[20] In our work, the synthesis of **6** is accomplished in three steps with an overall yield of 71% starting from the same chemicals.

The scope for oxidative coupling reaction yielding five-membered ring systems is not limited to spirobifluorenes and can be expanded to substrates exhibiting a geminal disubstitution with veratryl moieties (Table 3). By our protocol, the 9,9-dimethylfluorene **7** was synthesized in very good yield (Table 3, entry 1). Even alkyl-substituted amides are useful substrates, which are usually prone to an oxidative overfunctionalization of the alkyl group.[21] The spiro[indole-3,9′-fluorene] **8** was obtained in 77% yield (entry 2). The required starting material is made in a single step from the *N*-methylisatine (see the Supporting Information).

Table 3 Oxidative Coupling Reaction of Analogue Architectures



Entry	Product	Time (h)	Yield (%)
1	 **7**	5	90
2	 **8**	1	77

In conclusion, a reliable and an easy to perform synthetic access to 9,9-spirobifluorenes was established. The oxidative coupling reaction represents the key step and was conducted by the powerful reagent $MoCl_5$ at room temperature. The cyclization was compatible with a variety of labile groups, for example, iodo moieties and amides. The yield for the coupling reaction for all derivatives is in the range of 77 to 96%. By this approach a valuable building block for light emitting polymers was synthesized in excellent yield.

Commercial reagents were used as supplied. All reagents were used of analytical grades. Solvents were dried if necessary by standard methods. Flash chromatography was performed on silica gel (40–60 μm, Merck, Darmstadt, Germany) by using mixtures of cyclohexane with EtOAc or CH_2Cl_2 with MeOH as eluents. Silica gel 60 sheets on glass (F254, Merck, Darmstadt, Germany) were used for TLC. Melting points were determined by a Melting Point Apparatus B-545 (Büchi, Flawil, Switzerland) and are uncorrected. Microanalysis was performed with a VarioMICRO cube (Elementaranalysensysteme, Hanau, Germany). ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C by using a Bruker AC 300 instrument (Analytische Messtechnik, Karlsruhe, Germany). All ^1H NMR experiments are reported in δ units, parts per million (ppm) downfield from TMS (internal standard) and were measured relative to the signal for residual $CHCl_3$ (7.26 ppm) or DMSO-d_5 (2.50 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.16 ppm) or deuterated DMSO (39.52 ppm), and all were obtained by ^1H decoupling. Mass spectra and high-resolution mass spectra were obtained by using a QTof Ultima 3 (Waters, Milford, Massachusetts) apparatus employing ESI. All X-ray analysis data were collected on a STOE IPDS-2T diffractometer at –80 °C using graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system[22] (for details, see the Supporting Information).

2,7-Diiodo-2′,3′,6′,7′-tetramethoxy-9,9-spirobifluorene (4); Typical Procedure

2,7-Diiodo-9,9-bis(3,4-dimethoxyphenyl)fluorene (109.8 mg, 0.16 mmol) was added to a mixture of $MoCl_5$ (132 mg, 0.48 mmol) and CH_2Cl_2 (8 mL) and stirred at 23 °C for 4 h under an argon atmosphere. Then, sat. aq $NaHCO_3$ (10 mL) was added and the reaction mixture was stirred for additional 2 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were dried ($MgSO_4$), and the solvent was evaporated. The crude product was purified by flash-column chromatography (eluent: CH_2Cl_2) to yield the desired spirobifluorene **4** as a colorless solid (100.1 mg, 92%). For analytical purposes the product can be recrystallized from CH_2Cl_2–MeOH by slow evaporation of the solvent; mp 258.1 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (dd, J = 8.1, 1.4 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 2 H), 7.23 (s, 2 H), 7.03 (d, J = 1.4 Hz, 2 H), 6.14 (s, 2 H), 5.29 (s, 2 H), 4.03 (s, 6 H), 3.65 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 150.1, 149.1, 140.6, 139.4, 137.3, 135.0, 133.4, 122.1, 107.3, 102.8, 94.0, 65.6, 56.6, 56.5.

HRMS-ESI (+): m/z calcd for $C_{29}H_{22}I_2O_4$ + Na [M + Na]$^+$: 710.9505; found: 710.9503.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

References

(1) For excellent reviews, see: (a) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011. (b) Grätzel, M. *Curr. Opin. Colloid Interface Sci.* **1999**, 314. (c) Kanibolotsky, A. L.; Perepichka, I. F.; Skabara, P. J. *Chem. Soc. Rev.* **2010**, *39*, 2695.

(2) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583. (c) Bach, U.; Tachibana, Y.; Moser, J. E.; Haque, S. A.; Durrant, J. R.; Grätzel, M.; Klug, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7445. (d) Schmidt-Mende, L.; Bach, U.; Humphry-Baker, R.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2005**, *17*, 813. (e) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Grätzel, M. *Nano Lett.* **2005**, *5*, 1315.

(3) (a) Steuber, F.; Staudigl, J.; Stössel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissörtel, F.; Salbeck, J. *Adv. Mater.* **2000**, *12*, 130. (b) Omer, K. M.; Ku, S.-Y.; Cheng, J.-Z.; Chou, S.-H.; Wong, K.-T.; Bard, A. J. *J. Am. Chem. Soc.* **2011**, *133*, 5492. (c) Polo, F.; Rizzo, F.; Veiga-Gutierrez, M.; De Cola, L.; Quici, S. *J. Am. Chem. Soc.* **2012**, *134*, 15402. (d) Nakagawa, T.; Ku, S.-Y.; Wong, K.-T.; Adachi, C. *Chem. Commun.* **2012**, *48*, 9580. (e) Okuda, H.; Seto, R.; Koyama, Y.; Takata, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4192. (f) Lei, T.; Cheng, C.-Y.; Guo, Z.-H.; Zheng, C.; Zhou, Y.; Liang, D.; Pei, J. *J. Mater. Chem.* **2012**, *22*, 4306. (g) Weber, J.; Thomas, A. *J. Am. Chem. Soc.* **2008**, *130*, 6334. (h) Luo, J.; Lei, T.; Wang, L.; Ma, Y.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2009**, *131*, 2076. (i) Shen, J. Y.; Lee, C. Y.; Huang, T. H.; Lin, J. T.; Tao, Y. T.; Chien, C. H.; Tsai, C. *J. Mater. Chem.* **2005**, *15*, 2455. (j) Wu, C. C.; Lin, Y. T.; Wong, K. T.; Chen, R. T.; Chien, Y. Y. *Adv. Mater.* **2004**, *16*, 61. (k) Oyston, S.; Wang, C.; Hughes, G.; Batsanov, A. S.; Perepichka, I. F.; Bryce, M. R.; Ahn, J. H.; Pearson, C.; Petty, M. C. *J. Mater. Chem.* **2005**, *15*, 194. (l) He, G.; Pfeiffer, M.; Leo, K.; Hofmann, M.; Birnstock, J.; Pudzich, R.; Salbeck, J. *Appl. Phys. Lett.* **2004**, *85*, 3911.

(4) (a) Saragi, T. P. I.; Fuhrmann-Lieker, T.; Salbeck, J. *Adv. Funct. Mater.* **2006**, *16*, 966. (b) Saragi, T. P. I.; Fuhrmann-Lieker, T.; Salbeck, J. *Synth. Met.* **2005**, *148*, 267.

(5) (a) Montero, V. A.; Tomlinson, L.; Houk, K. N.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 5309. (b) Alcazar, V.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1521. (c) Cuntze, J.; Owens, L.; Alcazar, V.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 367. (d) Cuntze, J.; Diederich, F. *Helv. Chim. Acta* **1997**, *80*, 897. (e) Smith, D. K.; Diederich, F. *Chem. Commun.* **1998**, 2501. (f) Weber, E.; Ahrendt, J.; Czugler, M.; Csöregh, I. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 746. (g) Das, G.; Hamilton, A. D. *Tetrahedron Lett.* **1997**, *38*, 3675. (h) Tejeda, A.; Oliva, A. I.; Simon, L.; Grande, M.; Caballero, M. C.; Morán, J. R. *Tetrahedron Lett.* **2000**, *41*, 4563. (i) Czugler, M.; Stezowski, J. J.; Weber, E. *J. Chem. Soc., Chem. Commun.* **1983**, 154. (j) Demers, E.; Maris, T.; Wuest, J. D. *Cryst. Growth Des.* **2005**, *5*, 1227. (k) Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2004**, *69*, 1762. (l) Collins, C. S.; Sun, D.; Liu, W.; Zuo, J.-L.; Zhou, H.-C. *J. Mol. Struct.* **2008**, *890*, 163.

(6) (a) Lützen, A.; Thiemann, F.; Meyer, S. *Synthesis* **2002**, 2771. (b) Thiemann, F.; Piehler, T.; Saak, W.; Haase, D.; Lützen, A. *Eur. J. Org. Chem.* **2005**, 1991. (c) Piehler, T.; Lützen, A. *Z. Naturforsch., B* **2010**, *65*, 329. (d) Poriel, C.; Ferrand, Y.; Le Maux, P.; Paul, C.; Rault-Berthelot, J.; Simonneaux, G. *Chem. Commun.* **2003**, 2308. (e) Poriel, C.; Ferrand, Y.; Le Maux, P.; Raul-Berthelot, J.; Simonneaux, G. *Chem. Commun.* **2003**, 1104. (f) Poriel, C.; Ferrand, Y.; Le Maux, P.; Rault-Berthelot, J.; Simonneaux, G. *Tetrahedron Lett.* **2003**, *44*, 1759.

(7) Winter-Werner, B.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1996**, *79*, 1338.

(8) (a) Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881. (b) Thirion, D.; Poriel, C.; Métivier, R.; Rault-Berthelot, J.; Barrière, F.; Jeannin, O. *Chem. Eur. J.* **2011**, *17*, 10272. (c) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (d) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924. (e) Wong, K.-T.; Ku, S.-Y.; Cheng, Y.-M.; Lin, X.-Y.; Hung, Y.-Y.; Pu, S.-C.; Chou, P.-T.; Lee, G.-H.; Peng, S.-M. *J. Org. Chem.* **2006**, *71*, 456. (f) Wu, Y.; Li, J.; Fu, Y.; Bo, Z. *Org. Lett.* **2004**, *6*, 3485. (g) Fan, C.; Chen, Y.; Gan, P.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. *Org. Lett.* **2010**, *12*, 5648.

(9) (a) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474. (b) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748. (c) Chen, J.-J.; Onogi, S.; Hsieh, Y.-C.; Hsiao, C.-C.; Higashibayashi, S.; Sakurai, H.; Wua, Y.-T. *Adv. Synth. Catal.* **2012**, *354*, 1551.

(10) (a) Cheng, X.; Hou, G.-H.; Xie, J.-H.; Zhou, Q.-L. *Org. Lett.* **2004**, *6*, 2381. (b) Cheng, X.; Zhu, S.-F.; Qiao, X.-C.; Yan, P.-C.; Zhou, Q.-L. *Tetrahedron* **2006**, *62*, 8077. (c) Chiang, C.-L.; Shu, C.-F.; Chen, C.-T. *Org. Lett.* **2005**, *7*, 3717.

(11) (a) Rempala, P.; Kroulik, J.; King, B. T. *J. Org. Chem.* **2006**, *71*, 5067. (b) King, B. T.; Kroulik, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279. (c) Danz, M.; Tonner, R.; Hilt, G. *Chem. Commun.* **2012**, *48*, 377. (d) Spurg, A.; Schnakenburg, G.; Waldvogel, S. R. *Chem. Eur. J.* **2009**, *15*, 13313. (e) Kramer, B.; Bergander, K.; Waldvogel, S. R. *Synthesis* **2003**, 91. (f) Mirk, D.; Waldvogel, S. R. *Tetrahedron Lett.* **2004**, *45*, 7911. (g) Waldvogel, S. R. *Synlett* **2002**, 622.

(12) (a) For reviews, see: Waldvogel, S. R.; Trosien, S. *Chem. Commun.* **2012**, *48*, 9109. (b) Waldvogel, S. R.; Fröhlich, R.; Schalley, C. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 2472. (c) Waldvogel, S. R.; Wartini, A. R.; Rasmussen, P. H.; Rebek, J. *Tetrahedron Lett.* **1999**, *40*, 3515. (d) Waldvogel, S. R.; Aits, E.; Holst, C.; Fröhlich, R. *Chem. Commun.* **2002**, 1278.

(13) (a) Kramer, B.; Fröhlich, R.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2003**, 3549. (b) Kramer, B.; Waldvogel, S. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 2446.

(14) Trosien, S.; Waldvogel, S. R. *Org. Lett.* **2012**, *14*, 2976.

(15) (a) Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002. (b) Hackelöer, K.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2011**, 6314. (c) Mirk, D.; Willner, A.; Fröhlich, R.; Waldvogel, S. R. *Adv. Synth. Catal.* **2004**, *346*, 675.

(16) (a) Boshta, N.; Bomkamp, M.; Schnakenburg, G.; Waldvogel, S. R. *Chem. Eur. J.* **2010**, *16*, 3459. (b) Boshta, N.; Bomkamp, M.; Schnakenburg, G.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2011**, 1985.

(17) Hackelöer, K.; Schnakenburg, G.; Waldvogel, S. R. *Org. Lett.* **2011**, *13*, 916.

(18) Hackelöer, K.; Waldvogel, S. R. *Tetrahedron Lett.* **2012**, *53*, 1579.

(19) (a) Chen, H.; He, M.; Pei, J.; Liu, B. *Anal. Chem.* **2002**, *74*, 6252. (b) Su, H.-J.; Wu, F.-I.; Shu, C.-F. *Macromolecules* **2004**, *37*, 7197. (c) Shin, W. S.; Kim, S. C.; Lee, E.-J.; Park, S.-M.; Jin, S.-H.; Lee, J. W.; Gal, Y.-S. *Mol. Cryst. Liq. Cryst.* **2007**, *471*, 335.

(20) Kang, J.-S.; Park, J.-W.; Lee, J.-H.; Oh, S.-Y. *Mol. Cryst. Liq. Cryst.* **2007**, *462*, 267.

(21) (a) Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264. (b) Shono, T.; Matsumura, Y.; Onomura, O.; Ogaki, M.; Kanazawa, T. *J. Org. Chem.* **1987**, *52*, 536. (c) Liotta, D.; Saindane, M.; Sunay, U.; Charles, W.; Jamison, L.; Grossman, J.; Phillips, P. *J. Org. Chem.* **1985**, *50*, 3243.

(22) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.