Efficient Synthesis of Substituted Terphenyls by Suzuki Coupling Reaction[1]

Hélène Chaumeil,* Claude Le Drian, Albert Defoin

Laboratoire de Chimie Organique et Bio-organique, U.M.R. 7015, Ecole Nationale Supérieure de Chimie de Mulhouse, 3, rue Alfred Werner, 68093 Mulhouse Cedex, France
Fax +33(3)89336860; E-mail: h.chaumeil@uha.fr

Received 26 November 2001; revised 14 February 2002

Abstract: The Suzuki cross-coupling reactions of phenyl-1,4-diboronic acid bis-pinacol ester with a range of aryl halides are reported. The reaction proceeded smoothly, even with sterically hindered aryl halides, to give symmetrical terphenyls often quantitatively.

Key words: cross-coupling reaction, boronic esters, aryl halides, steric hindrance, terphenyls

The Suzuki cross-coupling reaction which is based on the Pd-catalysed reaction between arylboronic acids and aryl halides, triflates or diazonium salts is the most useful approach for the synthesis of biaryls.[2] This method is highly valuable for the synthesis of unsymmetrical biaryls as it is compatible with a large variety of functional groups. The synthesis of many hindered biaryls bearing bulky *ortho*-substituents has been reported.[2e,h,3] However in some cases, the protonolysis of the C–B bond predominated, leading to moderate yields.[2e,3c,e,4] To avoid this undesirable side reaction, various strategies have been developed. Thus, the replacement of the triphenylphosphine of the palladium catalyst by expensive and bulky monodendate ligands has been recommended.[5] We took interest in an other alternative which allows anhydrous conditions in which no protonolysis occurs,[2e,3d,6] namely the use of arylboronic esters instead of arylboronic acids. Thus, we wish to report, herein, our results on the synthesis of symmetrical and even hindered terphenyls from aryl-1,4-diboronic acid esters, expanding our previous studies on the synthesis of biaryls with three *ortho*-substituents.[7] Actually, terphenyls play an important role in a number of high performance engineering materials,[8a–d] including liquid crystals[8e] and non linear optical materials,[8f–h] as well as spacers in some catenanes and porphyrins.[9]

We first examined the cross-coupling reaction between phenyl-1,4-diboronic acid bis-pinacol ester **(1)** and 1-fluoro-3-iodobenzene **(2b)** in the presence of thallium(I) carbonate, sodium phenoxide and silver carbonate which proved to be efficient for arylboronic ester coupling (Table 1).[7] Using Tl_2CO_3, the reaction between the diboronic ester **1** and the iodide **2b** proceeded rather slowly requiring 64 hours under reflux for its completion (Scheme and Table 1, entry 2). Using sodium phenoxide, the reaction proceeded even more slowly and required 110 hours to reach an 82% yield (Table 1, entry 4). This result is consistent with our previous studies.[7] With Ag_2CO_3, only 6 hours were required to achieve a quantitative yield (Table 1, entry 5). In the latter case, the amount of catalyst could be lowered to 12 mmol equivalent without decreasing the reaction yield, however with a longer reaction time (16 h) (Table 1, entry 8).

We then studied the synthesis of a range of substituted terphenyls **3a–i** (Scheme and Table 2). The yields obtained were excellent in most cases, being well above those reported in the literature.[10] The reaction of electron rich aryl iodides with phenyl-1,4-diboronic acid is known to give low yields.[10a] Furthermore, the relative reactivity of aryl halides decreases in the order I>OTf>Br>>Cl.[2] All these explain the moderate and more especially the low yield obtained for the coupling of **1** with iodoanisole **2d** and with bromoanisole **2k** respectively (Table 2, entries 4 and 11).

Table 1 Effect of the Nature of the Base on the Cross-Coupling Reaction Between **1** and **2b**[a]

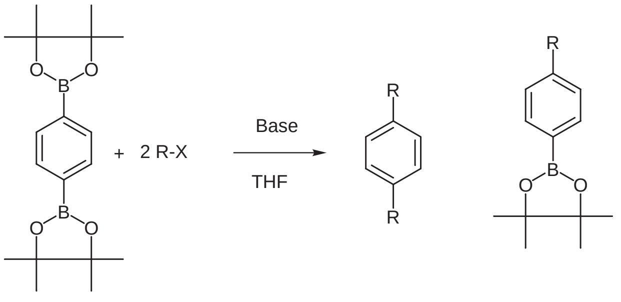
Entry	Base	Catalyst (mol equiv)	Time (h)	Yield (%)
1	Tl_2CO_3	0.09	16	40[b]
2	Tl_2CO_3	0.09	64	98
3	PhONa	0.09	16	21[c]
4	PhONa	0.09	110	82
5	Ag_2CO_3	0.04	6	93
6	Ag_2CO_3	0.026	6	81
7	Ag_2CO_3	0.028	16	97
8	Ag_2CO_3	0.012	16	96
9	Ag_2CO_3	0.004	16	47

[a] 1 Equiv of **1**, 1.8 equiv of **2b**, 2 equiv of base, and anhyd THF, at reflux (a slight excess of **1** was used to complete the reaction).
[b] Yield of monocoupled product **4b** = 18%.
[c] Yield of monocoupled product **4b** = 9%.

Attempts to couple **1** with 1-*tert*-butyl-2-iodobenzene (**2i**) failed to yield the corresponding terphenyl. Even after an extended reaction time (115 h instead of 16 h), only 24% of the monocoupled product **4i** was obtained (Table 2, en-

Synthesis 2002, No. 6, 29 04 2002. Article Identifier:
1437-210X,E;2002,0,06,0757,0760,ftx,en;T11001SS.pdf.

ISSN 0039-7881



1

2a-i X = I
2j-k X = Br

3a-i

4b, 4d, 4i

a R = Ph
b R = 3-FC_6H_4
c R = 4-$NO_2C_6H_4$
d R = 4-$MeOC_6H_4$
e R = 3-pyridyl
f R = 2-MeC_6H_4
g R = 1-naphthyl
h R = mesityl
i R = 2-*t*-BuC_6H_4
j R = 4-$MeO_2CC_6H_4$
k R = 4-$MeOC_6H_4$

Scheme

Table 2 Synthesis of Substituted Terphenyls by Cross-Coupling Reaction Between **1** and **2a**–**k**[a]

Entry	(Hetero)Aryl Halide	Product	Yield (%)[b]
1	**2a**	**3a**	quant[c]
2	**2b**	**3b**	quant[c]
3	**2c**	**3c**	86
4	**2d**	**3d**	55
5	**2e**	**3e**	quant[c]
6	**2f**	**3f**	quant[c]
7	**2g**	**3g**	quant[c]
8	**2h**	**3h**	quant[c]
9[d]	**2i**	**4i**	24
10	**2j**	**3j**	85
11	**2k**	**3d**	7[e]

[a] 1 equiv of **1**, 1.8 equiv of (hetero)aryl halide, 0.025 equiv of $Pd(PPh_3)_4$, 2 equiv of Ag_2CO_3, and anhyd THF, 16 h at reflux.

[b] Yields are determined, after chromatography, based on (hetero)aryl halide.

[c] Yield: 98–100%.

[d] Reaction time-extended to 115 h.

[e] Yield of mono-coupled product = 27%.

try 9). This is probably due to the extreme steric hindrance of the *ortho tert*-butyl group.

In summary, the double Suzuki cross-coupling reaction of the aryl diboronic ester with aryl halides proceeded readily, with very high yields, using Ag_2CO_3 as base. This provides a very convenient and simple procedure for the preparation of substituted and even hindered, symmetrical terphenyls.

THF and Et_2O were freshly distilled from sodium/benzophenone, and MeOH from Mg. All melting points were taken on a capillary melting point apparatus (Mettler FP51). IR spectra were recorded on a Nicolet 205 FTIR spectrometer. ^1H NMR (250 MHz) and ^{13}C NMR (62,9 MHz) spectra were measured in $CDCl_3$ (unless otherwise noted) on a Bruker ACF 250 spectrometer. EI mass spectra were obtained at the laboratoire de spectrométrie de Masse Bio-Organique of the ECPM in Strasbourg, and the microanalyses were done by the Service de Microanalyses de l'ICSN in Gif-sur-Yvette.

Iodobenzene (**2a**), 1-fluoro-3-iodobenzene (**2b**), 4-iodo-1-nitrobenzene (**2c**), 4-iodoanisole (**2d**), 4-bromoanisole (**2k**), 2-iodotoluene (**2f**) and iodonaphtalene (**2g**) were commercially available and used without further purification. Reported procedures were used to prepare 1-*tert*-butyl-2-iodobenzene (**2i**),[11] iodomesitylene (**2h**),[12] Ag_2CO_3,[13] and sodium phenoxide.[14] $Pd(PPh_3)_4$ was prepared according to the literature[15] and used fresh or within 3 months at the longest when stored under N_2 at –30 °C. 3-Iodopyridine (**2e**) was prepared according to the literature[16] and isolated as the hydrochloride. Methyl 4-bromobenzoate (**2j**) was obtained by esterification of the corresponding acid with anhyd HCl in MeOH and further recrystallisation from cyclohexane.

Phenyl-1,4-diboronic Acid

The published procedures[17] were slightly modified. A solution of *p*-dibromobenzene (6.00 g, 25.4 mmol) in anhyd THF (50 mL) was added dropwise to Mg (1.20 g, 50 mmol) in THF (5 ml) under reflux. After refluxing overnight, the mixture was placed in an acetone-dry ice bath and trimethyl borate (4.41 g, 4.73 mL, 42.4 mmol) was added dropwise at –70 °C. The mixture was stirred at –70 °C for 2 h and allowed to warm gradually to r.t. After hydrolysis by addition of aq 2M HCl until pH 3, the solution was extracted with Et_2O (3 × 100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The desired product was recrystallised from H_2O and isolated as colourless crystals (1.5 g, 35%).

Phenyl-1,4-diboronic Acid Bis-pinacol Ester (1)

This procedure was adapted from a brief description in the literature.[10a] A suspension of phenyl-1,4-diboronic acid (1.00 g, 6.03 mmol), pinacol (1.71 g, 14 mmol) and $MgSO_4$ (2.00 g, 16 mmol) in anhyd MeOH (10 mL) was stirred overnight at 30 °C. The solvent was evaporated under reduced pressure and the residue was extracted with EtOAc (30 mL). The organic phase was washed with H_2O (10 mL), dried ($MgSO_4$) and then concentrated in vacuo. The crude product was purified by silica gel chromatography (petroleum ether–CH_2Cl_2, 70:30 to CH_2Cl_2 pure) and isolated as a colourless solid (1.93 g, 97%); mp 237–238 °C (Lit.[18] mp 226 °C).

Coupling Reaction; General Procedure

In a flask equipped with a Dean–Stark apparatus, a stirred suspension of **1** (100 mg, 0.3 mmol), aryl halide (0.51 mmol), Ag_2CO_3 (167 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (9 mg, 0.025 mmol) in anhyd THF (20 mL) was refluxed in the dark for 16 h under N_2. The suspension was then filtered through Celite. The solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and successively washed with aq 2 M HCl (10 mL) and H_2O (10 mL). The aqueous layers were extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layers were successively washed with aq $NaHCO_3$ (40 mL) and brine (40 mL), dried ($MgSO_4$) and concentrated in vacuo. The coupling product was purified by silica gel column chromatography and further recrystallisation.

p-Terphenyl (3a)

Chromatography: petroleum ether–Et_2O (95:5); mp 212–214 °C (Lit.[10d] mp 212–213 °C).

The IR, ^1H and ^{13}C NMR spectral data were identical to those reported in the literature.[10d]

1,4-Bis(3-fluorophenyl)benzene (3b)

Chromatography: petroleum ether–Et_2O (95:5); mp 141.3 °C (petroleum ether).

IR (KBr): 682, 780, 833, 873, 1192, 1397, 1477 cm^{-1}.

^1H NMR: δ = 7.00–7.12 (m, 2 H), 7.33 (dm, 2 H, J = 9 Hz), 7.38–7.45 (m, 4 H), 7.66 (s, 4 H).

^{13}C NMR: δ = 113.88 (2 CH, J = 22 Hz), 114.26 (2 CH, J = 21 Hz), 122.63 (2 CH, J = 2.7 Hz), 127.54 (4 CH), 130.31 (2 CH, J = 8.4 Hz), 139.34 (2 C), 142.79 (2 C), 163.23 (2 CF, J = 245.68 Hz).

Anal. Calcd for $C_{18}H_{12}F_2$ (266.3): C, 81.18; H, 4.54; F, 14.27. Found: C, 81.3; H, 4.55; F 13.3.

1,4-Bis(4-Nitrophenyl)benzene (3c)

Chromatography: petroleum ether–CH_2Cl_2 (60:40); mp 272.3 °C (chlorobenzene) (Lit.[19] mp 273 °C).

IR (KBr): 746, 820, 856, 1342, 1507, 1594, 2342, 2361 cm^{-1}.

^1H NMR: δ = 7.77 (s, 4 H), 7.80 (d, 4 H, J = 8.9 Hz), 8.34 (d, 4 H, J = 8.9 Hz).[19]

^{13}C NMR ($C_2D_2Cl_4$): δ = 124.21 (4 CH), 127.81 (4 CH), 128.12 (4 CH), 138.99 (2 C), 146.49 (2 C), 147.05 (2 C).

Anal. Calcd for $C_{18}H_{12}N_2O_4\cdot0.5C_6H_5Cl$ (376.6): C, 66.98; H, 3.88; N, 7.44. Found: C, 67.0; H, 3.85; N, 7.55.

1,4-Bis(4-Methoxyphenyl)benzene (3d)

Chromatography: petroleum ether–CH_2Cl_2 (60:40 to 0:100); mp 271.7 °C (chlorobenzene) (Lit.[20] mp 273–274 °C).

IR (KBr): 811, 820, 828, 1026, 1042, 1188, 1252, 1261, 1291, 1493, 1607 cm^{-1}.

^1H NMR: δ = 3.86 (s, 6 H), 6.99 (d, 4 H, J = 8.75 Hz), 7.57 (d, 4 H, J = 8.75 Hz), 7.61 (s, 4 H).

^{13}C NMR ($C_2D_2Cl_4$): δ = 55.5 (2 CH_3), 114.31 (4 CH), 127.00 (4 CH), 128.02 (4 CH), 132.96 (2 C), 138.81 (2 C), 158.99 (2 C).

HRMS: m/z Calcd for $C_{20}H_{18}O_2$: 290.13068, found: 290.130953

1,4-Bis(2-Methylphenyl)benzene (3f)

Chromatography: cyclohexane–EtOAc (95:5); mp 145 °C (EtOAc) (Lit.[10c,21] mp 145.5–146 °C)

IR (KBr): 456, 589, 720, 760, 844, 1005, 1028.5, 1373, 1395.5, 1468.5, 1476, 2952, 3019 cm^{-1}.

^1H NMR: δ = 2.34 (s, 6 H), 7.2–7.33 (m, 8 H), 7.37 (s, 4 H)

^{13}C NMR: δ = 20.61 (2 CH_3), 125.84 (2 CH), 127.28 (2 CH), 128.92 (2 CH), 129.91 (4 CH), 130.41 (2 CH), 135.45 (2 C), 140.39 (2 C), 141.69 (2 C).

Anal. Calcd for $C_{20}H_{18}$ (258.4): C, 92.98; H, 7.02. Found: C, 93.1; H, 7.1.

1,4-Bis(1-Naphthyl)benzene (3g)

Chromatography: cyclohexane–CH_2Cl_2–Et_2O (90:5:5); mp 207–208 °C (cyclohexane) (Lit.[10b] mp 201–202 °C)

The IR, ^1H and ^{13}C NMR spectral data were identical to those reported in the literature.[10b]

1,4-Bis(2,4,6-Trimethylphenyl)benzene (3h)

Chromatography: petroleum ether–EtOAc (95:5); mp 182 °C (cyclohexane) (Lit.[10d] mp 181–183 °C).

The IR, ^1H and ^{13}C NMR spectral data were identical to those reported in the literature.[10d]

2′-(*tert*-Butyl)biphenyl-4-boronic Acid Pinacol Ester (4i)

Chromatography: cyclohexane–EtOAc (95:5); **4i** was obtained impure; mp 133–134 °C.

IR (KBr): 663, 754, 858, 1084, 1098, 1144, 1255, 1295, 1315, 1334, 1354, 1391.5, 2361, 2962, 2976 cm^{-1}.

^1H NMR: δ = 1.18 (s, 9 H), 1.37 (s, 12 H), 6.97 (dd, 1 H, J = 1.6, 7.5 Hz), 7.16 (td, 1 H, J = 7.5, 1 Hz), 7.21–7.35 (m, 3 H), 7.52 (br d, 1 H, J = 7 Hz), 7.78 (br d, 2 H, J = 7.9 Hz).

2-(4-Pyridin-3-ylphenyl)pyridine (3e)

The general procedure was used starting from **1** (100 mg, 0.3 mmol), 3-iodopyridine hydrochloride (132 mg, 0.54 mmol), Ag_2CO_3 (250 mg, 0.9 mmol), and $Pd(PPh_3)_4$ (9 mg, 0.025 mmol) in anhyd THF (20 mL). After the reaction, the suspension was filtered through Celite and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography [from EtOAc–cyclohexane (70:30) to pure EtOAc and EtOAc–EtOH (90:10)]; mp 107–110 °C (cyclohexane).

IR (KBr): 571, 622, 683.5, 709, 796, 845.5, 851.5, 1002, 1569, 3010, 3028 cm^{-1}.

^1H NMR: δ = 7.40 (dd, 1 H, J = 7.9, 4.8 Hz), 7.71 (s, 4 H), 7.93 (dt, 1 H, J = 1.5, 2.0, 7.9 Hz), 8.63 (dd, 1 H, J = 4.8, 1.5 Hz), 8.90 (d, 1 H, J = 2.0 Hz).

^{13}C NMR: δ = 123.59 (2 CH), 127.72 (4 CH), 134.21 (2 CH), 135.77 (2 C), 137.47 (2 C), 148.1 (2 CH), 148.65 (2 CH).

HRMS: m/z Calcd for $C_{16}H_{12}N_2$: 232.100048, found: 232.100034

Dimethyl [1,1′;4′,1″]Terphenyl-4,4″-dicarboxylate (3j)

The general procedure was used starting from **1** (100 mg, 0.3 mmol), methyl 4-bromobenzoate (**2j**; 118 mg, 0.54 mmol), Ag_2CO_3 (167 mg, 0.9 mmol), and $Pd(PPh_3)_4$ (9 mg, 0.025 mmol) in anhyd THF (20 mL). After 16 h at reflux, the suspension was quickly centrifuged and the still hot supernatant organic phase was recovered. The reaction flask was washed three times with chlorobenzene at reflux which was quickly centrifuged as above. The combined organic phases were evaporated in vacuo. The crude crystals were washed with EtOAc (10 mL) and recrystallised from chlorobenzene; mp 297–302 °C (chlorobenzene) (Lit.[22] mp 305–306 °C).

IR (KBr) = 766, 820, 1112, 1195, 1277, 1299, 1434, 1721 cm^{-1}.

^1H NMR: δ = 3.95 (s, 6 H), 7.72 (d, 4 H, J = 8.4 Hz), 7.74 (s, 4 H), 8.13 (d, 4 H, J = 8.4 Hz).

^{13}C NMR ($C_2D_2Cl_4$): δ = 52.32 (2 CH_3), 126.95 (4 CH), 127.77 (4 CH), 128.94 (2 C), 130.12 (4 CH), 139.46 (2 C), 144.61(2 C), 166.89 (2 C=O).

Anal. Calcd for $C_{22}H_{18}O_4$ (346.4): C, 76.29; H, 5.24. Found: C, 76.1; H, 5.2.

Acknowledgements

We thank the ‘Centre National de la Recherche Scientifique’ (UMR 7015) for financial support of this work. We also gratefully acknowledge the help of Dr P. Bisseret for valuable comments and suggestions during the preparation of the manuscript.

References

(1) Chaumeil H., Le Drian C. 31ème séminaire Hors-Ville d'Automne and 21st Regio Symposium in Organic and Bioorganic chemistry, 16–20th September 2001, Champery, Switzerland.

(2) (a) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, **1985**. (c) Matteson, D. S. *Tetrahedron* **1989**, *45*, 1859. (d) Martin, A. R.; Yang, Y. *Acta Chem. Scand.* **1993**, *47*, 221. (e) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (f) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (g) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, **1995**. (h) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263. (i) Suzuki, A. *J. Organomet. Chem.* **1999**, 147.

(3) (a) Schlüter, A. D. *J. Polym. Sci., Polym. Chem.* **2001**, 1533; and references cited therein. (b) Synthesis of biaryls possessing three or four *ortho*-substituents by cross-coupling in the presence of $Pd(PPh_3)_4$: Miller, R. B.; Dugar, S. *Organometallics* **1984**, *3*, 1261. (c) See also: Muller, D.; Fleury, J.-P. *Tetrahedron Lett.* **1991**, *32*, 2229. (d) See also: Fu, J.-M.; Zhao, B.-P.; Sharp, M. J.; Sniekus, V. *J. Org. Chem.* **1991**, *56*, 1653. (e) See also: Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, 207. (f) See also: Zhang, H.; Xue, F.; Mak, T. C. W.; Chan, K.-S. *J. Org. Chem.* **1996**, *61*, 8002. (g) See also: Zhang, H.; Chan, K.-S. *Tetrahedron Lett.* **1996**, *37*, 1043. (h) See also: Anderson, J. C.; Namli, H.; Roberts, C. A. *Tetrahedron* **1997**, *53*, 15123. (i) See also: Jonhson, M. G.; Foglesong, R. J. *Tetrahedron Lett.* **1997**, *38*, 7001. (j) See also: Zhang, H.; Kwong, F.-Y.; Tian, Y.; Chan, K.-S. *J. Org. Chem.* **1998**, *63*, 6886. (k) See also: Kamikawa, T.; Hayashi, T. *Tetrahedron* **1999**, *55*, 3455.

(4) (a) Thomson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237. (b) Gronowitz, S.; Bobosik, V.; Lawitz, K. *Chem. Scr.* **1984**, *23*, 120. (c) Gronowitz, S.; Honfelt, A.-B.; Yang, Y. *Chem. Scr.* **1988**, *28*, 281. (d) Abraham, M. H.; Grellier, P. L. *The Chemistry of the Metal Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; Wiley: New York, **1985**.

(5) Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2001**, *42*, 6667; and references cited therein.

(6) Hoshino, Y.; Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3008.

(7) Chaumeil, H.; Signorella, S.; Le Drian, C. *Tetrahedron* **2000**, *56*, 9655.

(8) (a) 1,4-bis(4-methoxyphenyl)benzene: Danjo, S.; Saito, T.; Kadomachi, H.; Kishimoto, D. Japanese Patent 03250021, **1991**; *Chem. Abstr.* **1992**, *116*, 129935. (b) 1,4-bis(2-methylphenyl)benzene: Dowen, M.; Majewski, S.; Pettey, D.; Walker, J.; Wojcik, R.; Zorn, C. *Trans. Nucl. Sci.* **1989**, *36*, 562. (c) See also: De Vol, T. A.; Wehe, D. K.; Knoll, G. K. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *348*, 156. (d) See also: Ikoma, Y.; Taya, F.; Naoi, Y. Japanese Patent 0183030, **1989**; *Chem. Abstr.* **1989**, *111*, 153333. (e) 1,4-Bis(4-methoxyphenyl)benzene: Yamada, S.; Tanabe, S. Japanese Patent 07101900, **1995**; *Chem. Abstr.* **1995**, *123*, 170537. (f) Linear optical materials, 1,4-bis(4-methoxyphenyl)benzene: Kauffman, J. M.; Kelley, C. S.; Ghiorghis, A.; Neister, E.; Seliskar, C. J.; Steppel, R. N. *Proc. Int. Conf. Lasers* **1989**, 420. (g) 1,4-Bis(2-methylphenyl)benzene: Golovkin, S. V.; Konstantinchenko, A. A.; Koslov, V. A.; Kushnirenko, A. E.; Pyschchev, A. I.; Shershukov, V. M.; Vasil'chenko, V. G.; Zimyn, K. V. *Nucl. Instrum. Methods Phys. Res,. Sect. A* **1995**, *362*, 283.
(h) See also: Kessler, W. J.; Davis, S. J.; Ferguson, D. R.; Pugh, E. R. US Patent 5610932, **1997**; *Chem. Abstr.* **1997**, *126*, 256922.

(9) (a) Banfi, S.; Montanari, F.; Pozzi, G.; Quici, S. *Tetrahedron* **1994**, *50*, 9025. (b) Houk, K. N.; Menzer, S.; Newton, S. P.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 1479.

(10) (a) Todd, M. H.; Balasubramanian, S.; Abell, C. *Tetrahedron Lett.* **1997**, *38*, 6781. (b) Schilling, B.; Kaufmann, D. E. *Eur. J. Org. Chem.* **1998**, 701.
(c) Newnan, M. S.; Hung, W. *J. Org. Chem.* **1974**, *39*, 3950.
(d) Hart, H.; Harada, K.; Frank Du, C.-J. *J. Org. Chem.* **1985**, *50*, 3104. (e) Ikoma, Y.; Taya, F.; Ozaki, E.-I.; Higuchi, S.; Naoi, Y.; Fuji-i, K. *Synthesis* **1990**, 147.
(f) Ikoma, Y.; Ando, K.; Naoi, Y.; Akiyama, T.; Sugimori, A. *Synth. Commun.* **1991**, 481.

(11) Shoesmith, J. B.; Mackie, A. *J. Am. Chem. Soc.* **1928**, 2338.

(12) Wirth, H. O.; Königstein, O.; Kern, W. *Liebigs Ann. Chem.* **1960**, *634*, 84.

(13) Mc Closkey, C. M.; Coleman, G. H. *Org. Synth. Coll. Vol. 3*; Wiley: New York, **1955**, 434.

(14) Kornblum, N.; Lurie, A. P. *J. Am. Chem. Soc.* **1959**, *81*, 2710.

(15) Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 121.

(16) Uemura, S.; Tanaka, S.; Okamo, R. M.; Hamana, M. *J. Org. Chem.* **1983**, *48*, 3297.

(17) (a) Coutts, I. G. C.; Goldschmid, H. R.; Musgrave, O. C. *J. Chem. Soc. C* **1970**, 488. (b) Miller, W. T.; Koch, S. D. *J. Am. Chem. Soc.* **1957**, *79*, 3081.

(18) Wasgindt, M.; Klemm, E. *Synth. Commun.* **1999**, *29*, 103.

(19) Colonge, J.; Buendia, J.; Sabadie, J. *Bull. Soc. Chim. Fr.* **1967**, 4370.

(20) Prince, C. C.; Mueller, G. P. *J. Am. Chem. Soc.* **1944**, *66*, 632.

(21) (a) Böckmann, K.; Vögtle, F. *Liebigs Ann. Chem.* **1981**, 467. (b) Wirth, H. O.; Gönner, K. H.; Stück, R.; Kern, W. *Makromol. Chem.* **1963**, *63*, 30.

(22) Campbell, T. W. *J. Am. Chem. Soc.* **1960**, *82*, 3126.