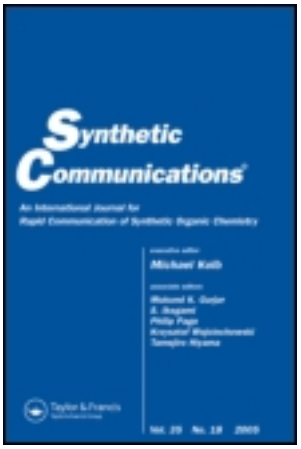


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of p-Quinquephenyl from E,E-1,4-Bis(4-bromophenyl)-1,3-butadiene

Matthew C. Davis [a] & Thomas J. Groshens [a]
[a] Chemistry and Materials Division, Michelson Laboratory, Naval Air Warfare Center, China Lake, California, USA
Published online: 15 Dec 2010.

To cite this article: Matthew C. Davis & Thomas J. Groshens (2010) Synthesis of p-Quinquephenyl from E,E-1,4-Bis(4-bromophenyl)-1,3-butadiene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:2, 206-218, DOI: 10.1080/00397910903533991

To link to this article: http://dx.doi.org/10.1080/00397910903533991

Synthetic Communications®, 41: 206–218, 2011
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903533991

Taylor & Francis
Taylor & Francis Group

SYNTHESIS OF *p*-QUINQUEPHENYL FROM *E,E*-1,4-BIS(4-BROMOPHENYL)-1,3-BUTADIENE

Matthew C. Davis and Thomas J. Groshens
Chemistry and Materials Division, Michelson Laboratory, Naval Air Warfare Center, China Lake, California, USA

p-*Quinquephenyl was synthesized in five steps from* E,E-*1,4-bis(4-bromophenyl)-1,3-butadiene in 34% overall yield. The butadiene was prepared in six steps from 4-bromobenzaldehyde in 35% overall yield.*

Keywords: Diels–Alder reaction; oxidative decarboxylation; *p*-quinquephenyl; *p*-terphenyl; Suzuki reaction

Rigid-rod polymers such as poly(*p*-phenylene) (PPP), Fig. 1, are of interest because of their resistance to solvents and high temperatures.[1–8] Lohaus[9] and others[10–14] synthesized *p*-terphenyl by cycloaddition of diethyl acetylenedicarboxylate to 1,4-diphenylbutadiene, followed by hydrolysis and finally oxidative decarboxylation. Polymers such as PPP are extremely difficult to process as they are insoluble in common organic solvents. An attempt was made to make an intermediate similar to Lohaus's that could be polymerized to a soluble polymer and then transformed into PPP.

The Perkin reaction on 4-bromobenzaldehyde (**1**) gave trans-4-bromocinnamic acid (**2**)[15–17] in 56% yield (Scheme 1). Initially, the methyl ester **4**[18,19] was prepared by refluxing **2** in methanol in the presence of catalytic sulfuric acid, but this reaction took days to complete, so an alternate method was found. In a one-pot, two-step process, **2** was transformed into the acid chloride **3**[17,20] with thionyl chloride. The excess thionyl chloride was then evaporated and methanol was added to form **4** in 96% yield over two steps. Reaction of ester **4** with diisobutylaluminum hydride in toluene at $-78\,^{\circ}C$ gave the allylic alcohol **5**[21–23] in 99% yield.

The synthesis of the unreported 1,3-butadiene **10** from **5** could be accomplished by two methods (Scheme 2). Reaction of **5** with thionyl chloride in 1,2-dichloroethane gave the allylic chloride **6**[21,23] in 97% yield. Arbuzov reaction of **6** with triethyl phosphite gave the corresponding phosphonate **7**[24] in 86% yield. Finally, the Horner–Wadsworth–Emmons (HWE) reaction of **1** and **7** in tetrahydrofuran (THF) with potassium *tert*-butoxide as base gave **10** in 85% yield. Alternately, oxidation of **5** using pyridinium chlorochromate gave the cinnamaldehyde **8**[16,25]

Received June 24, 2009.

Address correspondence to Matthew C. Davis, Chemistry and Materials Division, Michelson Laboratory, Naval Air Warfare Center, China Lake, CA, 93555, USA. E-mail: matthew.davis@navy.mil

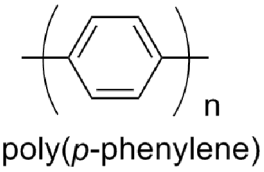
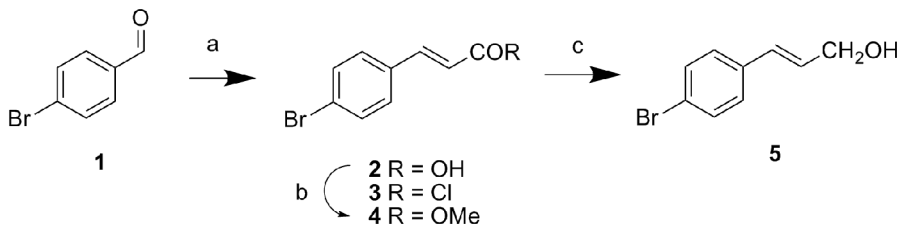


Figure 1.

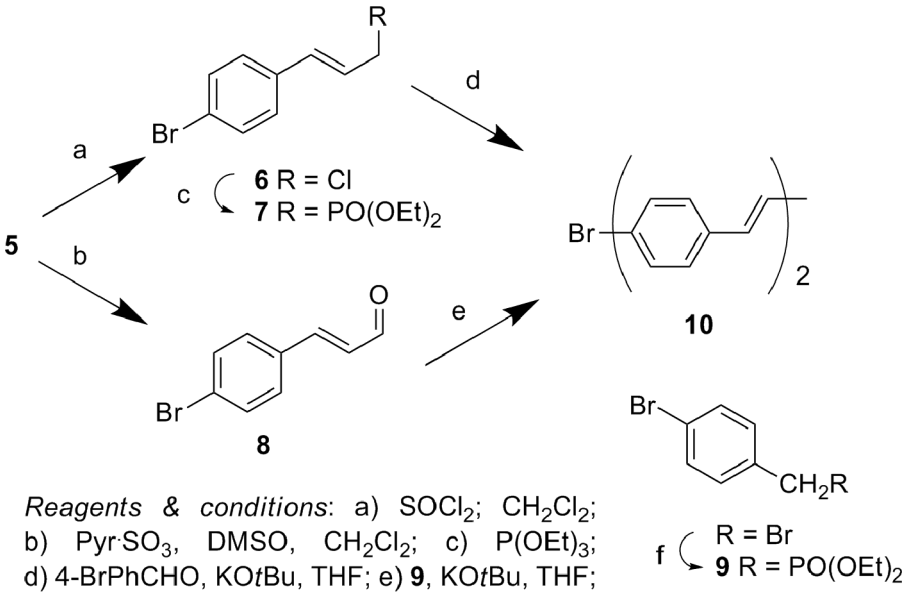
contaminated with ~20% of the *cis* isomer. A very clean oxidation was found using conditions of Parikh and Doering[26] that gave **8** in 84% yield. Reaction of **8** with diethyl 4-bromobenzylphosphonate (**9**)[27,28] using the HWE conditions gave **10** in 79% yield. The phosphonate **9** was readily synthesized by Arbuzov reaction of 4-bromobenzylbromide and triethyl phosphite.

Diels–Alder [$_{\pi}2_{s} + _{\pi}4_{s}$] cycloaddition of **10** and diethyl acetylenedicarboxylate following conditions similar to Fieser and Haddadin[11] gave the 1,4-cyclohexadiene **11** in the modest yield of 68%, (Scheme 3). Progress of this reaction could be observed by proton nuclear magnetic resonance spectroscopy after dissolving an aliquot of the reaction mixture in dueterochloroform. A crystal structure for **11** was obtained (Fig. 2), showing that both aryl groups lie on the same side of the 1,4-cyclohexadiene ring in keeping with Woodward-Hoffmann rules.[29–31] Brief treatment of **11** with potassium hydroxide in hot methanol brought about isomerization to the 3,5-cyclohexadiene **12**. The two ester moieties are assumed to have the trans configuration as Fieser and Haddadin[11] concluded on the des-bromo analog. Unfortunately, many attempts to prepare single crystals of **12** for crystallographic experiments were unsuccessful. Palladium-catalyzed Suzuki cross-coupling reaction between **12** and phenylboronic acid pinacol ester ($PhBO_2Pin$) gave the bis-biphenyl derivative **13** in good yield.

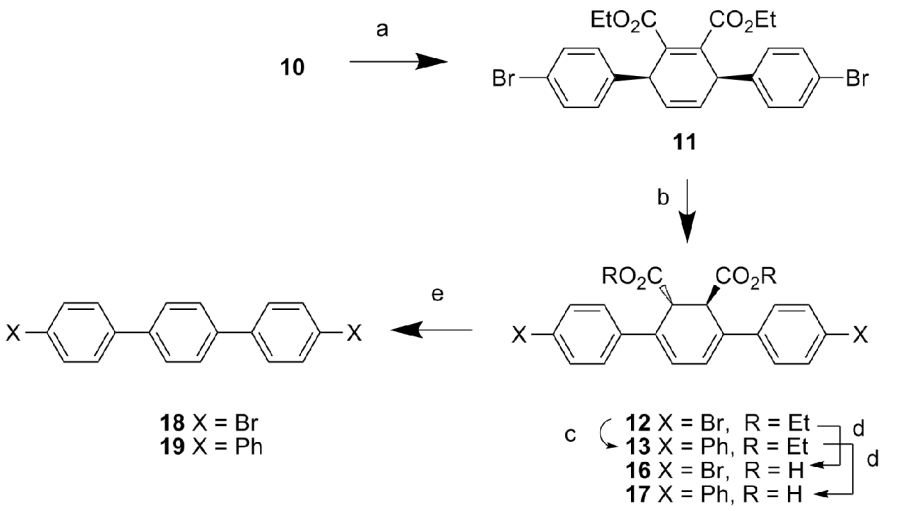
Hydrolysis of **12** and **13** with potassium hydroxide in refluxing ethanol gave a small amount of insoluble materials that were found to be dehydrogenated by-products **14** and **15** (Fig. 3). Changing the solvent to ethylene glycol containing 2 equivalents of water eliminated these impurities to give the two diacids **16** and **17**. A suitable solvent for recrystallization of either diacid could not be found. In the final oxidative decarboxylation reaction, a water-miscible, organic cosolvent was necessary as the diacids **16** and **17** would not dissolve in aqueous base. Adding



Scheme 1. Synthesis of the 4-bromocinnamyl alcohol.



Scheme 2. Synthesis of 1,3-butadiene **10**.



Scheme 3. Synthesis of 4,4″-dibromo-*p*-terphenyl (**17**) and *p*-quinuephenyl (**18**).

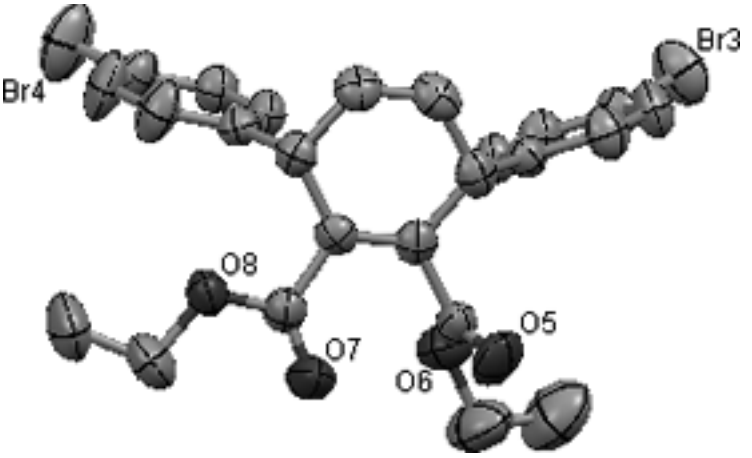


Figure 2. Crystal structure of **11**.

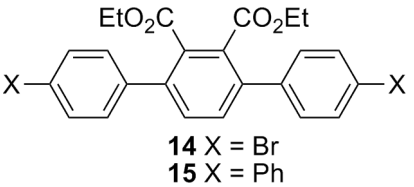


Figure 3. Dehydrogenation by-products.

excess potassium ferricyanide to a warm mixture of the diacids in one molar aqueous sodium hydroxide and tetrahydrofuran or ethylene glycol gave the terphenyl **18**[32,33] and quinquephenyl (**19**)[34] in good yields.

A yellow solid precipitated during the Suzuki polycondensation of dibromide **12** with 1,4-phenylenebisboronic acid bis(pinacol) ester, (1,4-Ph(BO_2Pin)$_2$. Unfortunately, further characterization was not possible as the material was insoluble in common organic solvents including dimethylsulfoxide and dimethylformamide.

EXPERIMENTAL

The melting point for **19** was determined by Dupont Instruments DSC2910 differential scanning calorimeter; all other melting points were collected on a Mel-Temp II from Laboratory Devices (Holliston, MA) and are not corrected. All NMR data were collected on a Bruker Avance II 300-MHz spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz). Nuclear magnetic resonance data (free-induction decays) were processed using NUTS software from Acorn NMR (Livermore, CA). All spectra are referenced to solvent or tetramethylsilane. The phenylboronic acid pinacol ester (PhBO_2Pin)[35,36] and 1,4-phenyldiboronic bis(pinacol) ester (1,4-Ph(BO_2Pin)$_2$)[37] were prepared by esterification of the corresponding boronic

acids with pinacol and were purified by reduced pressure distillation or recrystallization, respectively, before use. Ethylene glycol (99 + %), acetic anhydride (Ac_2O, 99.5%), acetic acid (HOAc, 99.8%), acetonitrile (MeCN, 99%), sodium acetate (NaOAc, 99.9%), 1,2-dichloroethane (DCE, 99+%), thionyl chloride ($SOCl_2$, 97%), 1 M diisobutylaluminum hydride (DIBAL) in hexanes, phenol (99+%), diethyl acetylenedicarboxylate (95%), triethyl phosphite ($P(OEt)_3$, 98%), 4-bromobenzyl bromide (98%), triphenylphosphine ($P(Ph)_3$, 99%), palladium acetate ($Pd(OAc)_2$, 99%) THF 99+%, inhibited with 250 ppm 2,6-di-*tert*-butyl-4-methylphenol), potassium *tert*-butoxide (KO*t*Bu, 95%), 4-bromobenzaldehyde (**1**, 99+%), triethylamine (TEA, 99.5%), sulfur trioxide pyridine complex ($Pyr \cdot SO_3$, 98%), and potassium ferricyanide ($K_3Fe(CN)_6$, 99%) were purchased from Sigma-Aldrich (Milwaukee). All other reagents were obtained commercially and used as received. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

4-Bromocinnamic Acid (2)

A 500-mL, round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with 76.6 g **1** (0.41 mol), 153 g Ac_2O (1.5 mol), and 26 g NaOAc (317 mmol). The mixture was heated to reflux by heating mantle. After 8 h, the heating mantle was removed and an addition funnel was equipped atop the condenser. The addition funnel was charged with 200 mL H_2O. The H_2O was added with care over 30 min. The crude product precipitated during the hydrolysis. The solid was filtered on a coarse-porosity glass frit and washed with HOAc. Recrystallization of the crude from HOAc gave 53.2 g of the title compound as a tan, microcrystalline powder (56%). Mp 260–262 °C (lit.[16] 250 °C). δ_H (DMSO): 12.29 (bs, CO_2H), 7.62 (q, $J = 8.7$ Hz, 4H), 7.56 (d, $J = 16.0$ Hz, 1H), 6.56 (d, $J = 15.9$ Hz, 1H); δ_C (DMSO): 167.34, 142.46, 133.53, 131.79, 130.07, 123.43, 120.20. Elemental analysis calculated for $C_9H_7BrO_2$: C, 47.61; H, 3.11. Found: C, 47.48; H, 2.93.

4-Bromocinnamoyl Chloride (3)

A 250-mL, round-bottomed flask equipped with magnetic stirbar and was charged with 25 g **2** (110 mmol) and 25 mL $SOCl_2$. A N_2 bubbler was equipped that piped the effluent gases through a caustic scrubber. The mixture was heated to 55 °C for 5 h. After cooling to rt, the precipitated formed. Heptane (100 mL) was added, and the solid was filtered on a medium-porosity glass frit. Recrystallization of the crude solid from heptane gave 17.38 g of the title compound as colorless needles (64%). Mp 97–100 °C (lit.[17] 104–106 °C). δ_H ($CDCl_3$): 7.77 (d, $J = 15.0$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 6.64 (d, $J = 15.6$ Hz, 1H); δ_C ($CDCl_3$): 166.06, 149.21, 132.76, 132.13, 130.50, 126.82, 123.21. Elemental analysis calculated for C_9H_6BrClO: C, 44.03; H, 2.46. Found: C, 44.33; H, 2.27.

Methyl 4-Bromocinnamate (4)

A 250-mL, round-bottomed flask equipped with magnetic stirbar was charged with 25 g **2** (110 mmol). An N_2 bubbler was equipped that piped the effluent gas into a caustic scrubber. In one portion, 25 mL $SOCl_2$ were added to the flask. The mixture

was heated to 50 °C to complete the chlorination. After 2 h, the excess $SOCl_2$ was evaporated to leave a crude solid of the acid chloride **3**. To the flask, 100 mL MeOH were added, and the solids dissolved with some gentle heating. After 30 min, the mixture was cooled to rt whereby the title compound precipitated as the spectacular needles. The colorless crystals were filtered on a coarse-porosity glass frit, and no further purification was necessary (25.5 g, 96%). Mp 78–81 °C (lit.[18] 79–80 °C). δ_H ($CDCl_3$): 7.61 (d, $J = 15.9$ Hz, 1H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 6.42 (d, $J = 16.0$ Hz, 1H), 3.80 (s, 3H); δ_C ($CDCl_3$): 167.23, 143.59, 133.50, 132.31, 129.59, 124.69, 118.72, 51.90. Elemental analysis calculated for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76. Found: C, 49.81; H, 3.66.

4-Bromocinnamyl Alcohol (5)

A 500-mL, round-bottomed flask equipped with magnetic stirbar, 250-mL addition funnel, and N_2 bubbler was charged with 12.12 g **4** (0.05 mol) and 300 mL toluene. The mixture was cooled to −78 °C with a dry ice/acetone bath. The addition funnel was charged with 126 mL 1 M DIBAL in hexanes (0.126 mol, 2.5 equiv), which were then added over 30 min. After the addition, the cooling bath was removed, and the mixture was stirred at rt overnight. Then the addition funnel was charged with a mixture of 50 mL conc. HCl in 300 mL H_2O, which was carefully added to the reaction. After stirring to allow all the solids to dissolve, the mixture was poured into a separatory funnel. The aqueous phase was discarded, and the organic layer was further washed with 200 mL H_2O followed by 100 mL saturated aqueous Na_2CO_3 and finally 100 mL brine. After drying over anhydrous $MgSO_4$, the solvent was rotary evaporated, leaving 11.49 g of a crude white solid. The solid was recrystallized from heptane to give the title compound as colorless needles (10.6 g, 99%). Mp 58–62 °C (lit.[22] 68–69 °C). δ_H ($CDCl_3$): 7.44 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 6.56 (dt, $J = 15.8$ and 1.4 Hz, 1H), 6.34 (dt, $J = 16.0$ and 5.5 Hz, 1H), 4.31 (t, $J = 4.6$ Hz, 2H), 1.59 (t, $J = 5.2$ Hz, OH); δ_C ($CDCl_3$): 135.93, 131.93, 130.03, 129.61, 128.20, 121.68, 63.72. Elemental analysis calculated for C_9H_9BrO: C, 50.73; H, 4.26. Found: C, 50.54; H, 4.13.

4-Bromocinnamyl Chloride (6)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 4.18 g **5** (18 mmol) and 50 mL DCE. An N_2 bubbler was attached that piped the effluent gas into an aqueous base scrubbing bottle. To the mixture, 4.3 g $SOCl_2$ (36 mmol mol, 2.63 mL, 2 equiv), were added over 1 h. After the addition, the mixture was heated to 50 °C to facilitate the reaction. NMR and thin-layer chromatography (TLC) were used to determine reaction completion. The mixture was extracted with 50 mL H_2O followed by 50 mL saturated aqueous Na_2CO_3 and finally 50 mL brine. After drying over anhydrous $MgSO_4$, the solvent was evaporated, leaving a 4.0 g of a white solid (97%). No further purification was necessary. Mp 49–50 °C. δ_H ($CDCl_3$): 7.45 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.29 (dt, $J = 15.5$ Hz and 7.1 Hz, 1H), 4.21 (dt, $J = 7.0$ and 1.0 Hz, 2H); δ_C ($CDCl_3$): 135.08, 133.07, 132.01, 128.41, 125.94, 122.35, 45.26. Elemental analysis calculated for C_9H_8BrCl: C, 46.69; H, 3.48. Found: C, 46.74; H, 3.33.

Diethyl 4-Bromocinnamyl Phosphonate (7)

A 50-mL, round-bottomed flask equipped with magnetic stirbar and condenser was charged with 4.16 g **6** (18 mmol) and 2.98 g $P(OEt)_3$ (1 equiv). The mixture was heated to 150 °C for 12 h. Reduced pressure distillation (0.1 torr) of the reaction mixture gave 5.17 g of title compound as a colorless oil (86%). δ_H ($CDCl_3$): 7.43 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 6.47 (dd, $J = 15.8$ and 5.3 Hz, 1H), 6.17 (d, $J = 15.7$ and 7.4 Hz, 1H), 4.13 (pent of mult, $J = 7.7$ Hz, 4H), 2.75 (ddd, $J = 22.5$ and 7.5 and 1.3 Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 6H); δ_C ($CDCl_3$): 135.98 (d, $J_{CP} = 3.8$ Hz), 133.68 (d, $J_{CP} = 14.8$ Hz), 131.86 (d, $J_{CP} = 1.1$ Hz), 127.94 (d, $J_{CP} = 2.2$ Hz), 121.55 (d, $J_{CP} = 1.6$ Hz), 120.06 (d, $J_{CP} = 11.9$ Hz), 62.25 (d, $J_{CP} = 6.7$ Hz), 31.30 (d, $J_{CP} = 140.4$ Hz), 16.66 (d, $J_{CP} = 5.8$ Hz). Elemental analysis calculated for $C_{13}H_{18}BrO_3P$: C, 46.87; H, 5.45. Found: C, 46.73; H, 5.43.

4-Bromocinnamaldehyde (8)

A 250-mL, round-bottomed flask equipped with magnetic stirbar was charged with 3.76 g **5** (18 mmol), 5.78 g TEA (57 mmol, 3.16 equiv), 30 mL DMSO, and 100 mL CH_2Cl_2. The mixture was cooled in an ice bath, and 6.75 g $Pyr \cdot SO_3$ (42 mmol, 2.3 equiv) were added in portions over 15 min. The cooling bath was removed, and the mixture was stirred for 12 h. The mixture was poured into a separatory funnel and washed with 100 mL H_2O twice, followed by 100 mL brine. The organic layer was dried over anhydrous $MgSO_4$ and rotary evaporated to a crude solid. Recrystallization from hexanes gave 3.13 g of the title compound as colorless needles (84%). Mp 70–72 °C (lit.[16] 81 °C). δ_H ($CDCl_3$): 9.71 (d, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 15.9$ Hz, 1H), 6.70 (dd, $J = 16.3$ and 7.6 Hz, 1H); δ_C ($CDCl_3$): 193.43, 151.16, 133.15, 132.61, 129.97, 129.27, 125.86. Elemental analysis calculated for C_9H_7BrO: C, 51.22; H, 3.34. Found: C, 51.26; H, 3.25.

Diethyl 4-Bromobenzylphosphonate (9)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 25 g 4-bromobenzyl bromide (0.1 mol) and 18.85 mL $P(OEt)_3$ (0.11 mol, 1.1 equiv), and the mixture was heated to 130 °C for 18 h. Reduced pressure distillation (0.1 torr) of the reaction mixture gave 30.37 g of title compound as a colorless oil (99%). δ_H ($CDCl_3$): 7.44 (dd, $J = 8.5$ and 1.0 Hz, 2H), 7.18 (dd, $J = 8.7$ and 2.4 Hz, 2H), 4.03 (pent, $J = 7.7$ Hz, 4H), 3.09 (d, $J = 22$ Hz, 2H), 1.26 (t, $J = 6.6$ Hz, 6H); δ_C ($CDCl_3$): 131.82 (d, $J_{CP} = 2.8$ Hz), 131.63 (d, $J_{CP} = 6.6$), 131.02 (d, $J_{CP} = 9.2$ Hz), 121.10 (d, $J_{CP} = 4.9$ Hz), 62.37 (d, $J_{CP} = 6.7$ Hz), 33.50 (d, $J_{CP} = 139.2$ Hz), 16.56 (d, $J_{CP} = 5.5$ Hz). Elemental analysis calculated for $C_{11}H_{16}BrO_3P$: C, 43.02; H, 5.25. Found: C, 42.73; H, 5.47.

E,E-1,4-Bis(4-bromophenyl)-1,3-butadiene (10)

From 1 and 7. A 50-mL, round-bottomed flask equipped with magnetic stirbar was charged with 550 mg **1** (2.9 mmol), 1 g **7** (3 mmol, 1 equiv), and 20 mL THF. In one portion, 370 mg KO*t*Bu (3.3 mmol, 1.1 equiv) was added. The mixture became

warm and reddish in color with a precipitate. The mixture was refluxed briefly, then cooled to rt, and 25 mL cold H_2O was added to the reaction. A yellow solid precipitated. The precipitate was filtered on a medium-porosity glass frit and air dried. Recrystallization from toluene gave 890 mg of the title compound as colorless plates (85%). Mp 220–223 °C. δ_H (DMSO, 360 K): 7.52 (d, $J_{ab} = 8.6$ Hz, 4H), 7.44 (d, $J_{ab} = 8.6$ Hz, 4H), 7.06 (dd, $J = 12.3$ and 2.9 Hz, 2H), 6.75 (dd, $J = 11.9$ and 2.5 Hz, 2H); δ_C (DMSO, 360 K): 135.95, 131.41, 131.08, 129.63, 127.76, 120.04. Elemental analysis calculated for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.78; H, 3.24.

From 8 and 9. A 50 mL round-bottomed flask equipped with magnetic stirbar was charged with 13.26 g **8** (62.8 mmol), 22.93 g **9** (74.6 mmol, 1.2 equiv), and 300 mL THF. In one portion, 8.4 g KO*t*Bu (75 mmol, 1.2 equiv) were added. The mixture became warm and yellow-orange in color with a precipitate. The mixture was refluxed briefly, then cooled to rt, and 25 mL cold H_2O were added to the reaction. A yellow solid precipitated. The precipitate was filtered on a medium-porosity glass frit and air dried. Recrystallization from toluene gave 18.2 g of the title compound as colorless plates (79%). Analytical data for the product were identical to those obtained from the previous method.

cis-Diethyl 3,6-Bis(4-bromophenyl)-1,4-cyclohexadiene-1,2-dicarboxylate (11)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 2.85 g **10** (7.8 mmol), 10 g phenol, and 1.5 g diethyl acetylenedicarboxylate (8.6 mmol, 1.1 equiv). The mixture was heated in a controlled oil bath at 130 °C for 6 h. The mixture was cooled to rt and dissolved in 100 mL Et_2O. The mixture poured into a separatory funnel and extracted twice with 100 mL cold 1 M aqueous NaOH. After further extracting with 100 mL H_2O and finally 100 mL brine, the organic phase was dried over anhydrous $MgSO_4$. The solvent was evaporated, leaving 2.84 g of a pale yellow powder (68%). Recrystallization from a mixture of heptane/toluene gave the title compound as colorless, microcrystalline needles. Mp 218–220 °C. δ_H ($CDCl_3$): 7.47 (d, $J = 8.4$ Hz, 4H), 7.14 (d, $J = 8.4$ Hz, 4H), 5.75 (d, $J = 1.7$ Hz, 2H), 4.43 (d, $J = 1.5$ Hz, 2H), 4.05 (q, $J = 7.2$ Hz, 2H), 4.04 (q, $J = 7.1$ Hz, 2H), 1.06 (t, $J = 7.1$ Hz, 6H); δ_C ($CDCl_3$): 167.15, 140.45, 135.48, 131.99, 130.24, 126.18, 121.31, 61.32, 43.65, 13.95. Elemental analysis calculated for $C_{24}H_{22}Br_2O_4$: C, 53.96; H, 4.15. Found: C, 54.08; H, 4.08.

Diethyl 3,6-Bis(4-bromophenyl)-3,5-cyclohexadiene-1,2-*trans*-dicarboxylate (12)

A 250-mL, Erlenmeyer flask equipped with magnetic stirbar was charged with 14.86 g **11** (28 mmol) and a solution of 779 mg KOH (14 mmol, 0.5 equiv) in 100 mL MeOH. The mixture refluxed for 10 min; the starting material did not dissolve completely but changed into a new solid, and the supernatant became orange in color. The mixture was cooled to rt and filtered on a medium-porosity glass frit. Vacuum drying gave 13.85 g of the title compound as a white powder (93%). Recrystallization from MeCN to gave the title compound as colorless needles. Mp 155–158 °C.

δ_H ($CDCl_3$): 7.56 (d, $J = 3.6$ Hz, 8H), 6.72 (s, 2H), 4.44 (s, 2H), 3.99 (q, $J = 7.0$ Hz, 2H), 3.96 (q, $J = 7.0$ Hz, 2H), 0.98 (t, $J = 7.0$ Hz, 6H); δ_C ($CDCl_3$): 170.42, 138.04, 132.86, 131.27, 127.62, 122.46, 120.63, 60.74, 43.48, 13.71. Elemental analysis calculated for $C_{24}H_{22}Br_2O_4$: C, 53.96; H, 4.15. Found: C, 53.69; H, 3.96.

Diethyl 3,6-Bis(*p*-biphenyl)-3,5-cyclohexadiene-1,2-*trans*-dicarboxylate (13)

A 250-mL, round-bottomed flask equipped with magnetic stirbar, condenser, and N_2 bubbler was charged with 2.67 g **12** (5 mmol), 4.08 g Ph(BO_2Pin) (20 mmol, 4 equiv), 50 mL THF, and a solution of 2.75 g K_2CO_3 (20 mmol, 4 equiv) in 5 mL H_2O. After deaerating the reaction mixture with a gentle streaming of N_2 for 30 min, the catalyst mixture was added in one portion [11 mg $Pd(OAc)_2$ (1 mol%), 52 mg PPh_3 (4 mol%)]. The mixture was refluxed for 18 h. The yellow mixture was cooled to rt, diluted with 200 mL EtOAc, washed with 50 mL H_2O, dried over anhydrous $MgSO_4$, and rotary evaporated to a yellow-brown solid. The crude was dissolved in $CHCl_3$ and filtered through a pad of SiO_2, removing most of the dark brown color. The filtrate was rotary evaporated, leaving 3.95 g of a bright yellow solid. The solid was slurried with MeCN and filtered on a medium frit to give 2.15 g (81%) of the title compound as a bright yellow solid that exhibits strong fluorescence under shortwave ultraviolet light exposure. The product can be further recrystallized from MeCN to give microcrystalline needles. Mp 183–185 °C. δ_H (DMSO): 7.76–7.65 (m, 12H), 7.48 (t, $J = 7.9$ Hz, 4H), 7.38 (t, $J = 7.4$ Hz, 2H), 6.81 (s, 2H), 4.54 (s, 2H), 4.09–3.91 (m, 4H), 1.01 (t, $J = 6.9$ Hz, 6H); δ_C (DMSO): 170.75, 139.49, 139.04, 137.86, 132.99, 128.93, 127.47, 126.62, 126.43, 126.03, 122.23, 60.76, 43.69, 13.82. Elemental analysis calculated for $C_{36}H_{32}O_4$: C: 81.79; H, 6.10. Found: C, 81.63; H, 6.09.

4,4″-Dibromo-2′,3′-bis(ethoxycarbonyl)-*p*-terphenyl (14)

A 100-mL, round-bottomed flask equipped with magnetic stirbar and condenser was charged with 1 g **12** (1.8 mmol), 50 mL EtOH, 5 mL H_2O, and 420 mg KOH (7.5 mmol, 4 equiv). The mixture was refluxed overnight. The resulting bright yellow solution was filtered on a medium-porosity glass frit to remove a small amount of precipitate. The crude white solid was recrystallized from toluene to give ~50 mg of the title compound as fine, colorless needles. Mp 217–220 °C. δ_H ($CDCl_3$): 7.55 (d, $J = 8.4$ Hz, 4H), 7.45 (s, 2H), 7.24 (d, $J = 8.4$ Hz, 4H), 4.10 (q, $J = 7.3$ Hz, 4H), 1.05 (t, $J = 7.3$ Hz, 6H); δ_C ($CDCl_3$): 168.02, 139.31, 138.91, 132.61, 131.74, 131.61, 130.28, 122.46, 61.93, 13.83. Elemental analysis calculated for $C_{24}H_{20}Br_2O_4$: C, 54.16; H, 3.79. Found: C, 54.36; H, 3.75.

2‴,3‴-Bis(ethoxycarbonyl)-*p*-quinquephenyl (15)

A procedure analogous to that for **14** using starting material **13** obtained ~50 mg of the title compound as colorless needles from toluene. Mp 206–209 °C. δ_H (DMSO, 370 K): 7.79–7.68 (m, 8H), 7.66 (s, 2H), 7.54–7.35 (m, 10H), 4.07 (q, $J = 7.0$ Hz, 4H), 1.03 (t, $J = 7.4$ Hz, 6H). Elemental analysis calculated for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 82.32; H, 5.69.

3,6-Bis(4-bromophenyl)-3,5-cyclohexadiene-1,2-*trans*-dicarboxylic Acid (16)

A 100-mL, round-bottomed flask equipped with magnetic stirbar and condenser was charged with 3 g **12** (5.67 mmol), 20 mL ethylene glycol, 200 mg H_2O (2 equiv), and 1.27 g KOH (22.68 mmol, 4 equiv) and heated near reflux for 2 h. The solids eventually dissolved to a clear yellow solution. The mixture was cooled to rt and filtered through filter paper. The filtrate was poured into a vigorously stirred mixture of 2.34 mL conc. HCl in 100 mL H_2O. The yellow precipitate was filtered on a medium-porosity glass frit and then dried under vacuum (20 torr, 65 °C) overnight to obtain the 2.5 g of title compound as a pale yellow powder (93%). Mp > 300 °C. δ_H (DMSO): 12.68 (bs, 2 CO_2H), 7.56 (s, 8H), 6.73 (s, 2H), 4.34 (s, 2H); δ_C (DMSO): 172.63, 138.49, 133.48, 131.48, 127.74, 122.37, 120.72, 43.89. Elemental analysis calculated for $C_{20}H_{14}Br_2O_4$: C, 50.24; H, 2.95. Found: C, 50.72; H, 2.78.

3,6-Bis(*p*-biphenyl)-3,5-cyclohexadiene-1,2-*trans*-dicarboxylic Acid (17)

A procedure similar to that for **16** was used on 3 g **13** to obtain 2.6 g of the title compound as a pale yellow powder (96%). Mp > 300 °C. δ_H (DMSO): 12.64 (s, 2 CO_2H), 7.87–7.57 (m, 12H), 7.55–7.29 (m, 6H), 6.80 (s, 2H), 4.48 (s, 2H); δ_C (DMSO): 172.74, 139.64, 138.95, 138.17, 133.42, 128.96, 127.47, 126.69, 126.47, 126.03, 121.88, 43.83. Elemental analysis calculated for $C_{32}H_{24}O_4$: C: 81.34; H, 5.12. Found: C, 79.56; H, 5.01.

4,4″-Dibromo-*p*-terphenyl (18)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 580 mg **16** (1.2 mmol) dissolved in a warm mixture of 20 mL THF and 20 mL 1 M NaOH. In one portion, 1.97 g $K_3Fe(CN)_6$ (6 mmol, 5 equiv) was added, and the mixture became milky with a precipitate. After 3 h, the mixture was filtered on a medium-porosity glass frit. The solid was suspended in 20 mL H_2O, and a small amount of conc. HCl was added to make pH 3. The solid was filtered again on a medium-porosity glass frit, washed with methanol, and air dried on the frit. The off-white powder was recrystallized from DMSO to give 420 mg of the title compound as microscopic needles (89%). Mp 310–315 °C (lit.[33] 309–311 °C). δ_H (DMSO, 370 K): 7.75 (s, 4H), 7.65 (s, 8H). Elemental analysis calculated for $C_{18}H_{12}Br_2$: C, 55.71; H, 3.12. Found: C, 55.33; H, 3.05.

p-Quinquephenyl (19)

A procedure similar to that for **18** was used, except ethylene glycol was used as cosolvent. From 400 mg **17** (0.8 mmol), 220 mg of the title compound were obtained as a green-tinged microcrystalline powder after recrystallization from DMSO (68%). Mp 390.45 °C (DSC; lit.[3] 388 °C). δ_H (DMSO, 370 K): 7.88–7.60 (m, 16H), 7.47 (t, $J = 7.4$ Hz, 4H), 7.36 (t, $J = 7.1$ Hz, 2H). Elemental analysis calculated for $C_{30}H_{22} \cdot 0.16$ DMSO: C, 92.11; H, 5.86. Found: C, 92.35; H, 5.60.

Table 1. Crystal structure data and refinement details for **11**

Parameter	Value
Empirical formula	$C_{24}H_{22}Br_2O_4$
Formula weight	534.24
Crystal color	Clear colorless
Crystal size	$0.28 \times 0.31 \times 0.48$ mm
Crystal system	Monoclinic
Space group	P12(1)/c1
A (Å)	12.1874(5)
B (Å)	24.4922(10)
C (Å)	15.4897(5)
α	90°
β	94.8640(10)°
γ	90°
V (Å^3)	4607.0(3)
Z	8
λ	1.540 Mg/cm^3
Reflections collected	44874
Independent reflections	8171
Data/parameters	8171/546
Final R indices (all data)	$R1 = 0.0830$, $wR_2 = 0.0961$
Goodness-of-fit on F^2	1.001
Largest difference peak and hole	0.564 and -0.458 eÅ^{-3}

X-Ray Structure Determination of 11

Some selected data and refinement details are collected in Table 1. CCDC 736728 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ACKNOWLEDGMENTS

The financial support from the In-House Laboratory Independent Research (ILIR) program of the Research and Intelligence Department (NAWCWD) is gratefully acknowledged. Thanks to Dan E. Bliss (NAWCWD) for assistance with the differential scanning calorimeter experiment.

REFERENCES

1. Stille, J. K.; Gilliams, Y. Poly(*p*-phenylene). *Macromolecules* **1971**, *4*, 515–517.
2. (a) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. A biotech route to polyphenylene. *J. Chem. Soc. Chem. Commun.* **1983**, 954–955; (b) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. Synthesis of polyphenylene from a *cis*-dihydrocatechol, a biologically produced monomer. *Macromolecules* **1988**, *21*, 294–304.
3. Unroe, M. R.; Reinhardt, B. A. One-pot synthesis of *p*-polyphenyls via the intramolecular cyclization of 2-dimethylaminohex-5-en-1-ynes. *Synthesis* **1987**, 981–986.

4. Baker, K. N.; Fratini, A. V.; Resch, T., Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. Crystal structures, phase transitions, and energy calculations of poly(*p*-phenylene) oligomers. *Polymer* **1993**, *34*, 1571–1587.
5. Takahashi, T.; Tsai, F. U.; Li, Y. A convenient preparative method of dibromoterphenyl and bis(bromophenyl)diene monomers using zirconacyclopentadienes. *Chem. Lett.* **1999**, *11*, 1173–1174.
6. Annan, K. O.; Scherf, U.; Müllen, K. Visible-emitting poly[(3′,4′-dialkoxycarbonyl-2′-hydroxy-1,1′:5′,1″-terphenyl-4,4″-ylene)]. *Synth. Met.* **1999**, *99*, 9–16.
7. Kadokawa, J.; Suenaga, M.; Kaneko, Y. Synthesis of poly(*p*-phenylene) having phthalic anhydride moieties in the main chain and its conversion into fluorescein derivative. *Macromolecules* **2008**, *41*, 3750–3754.
8. Li, S.; Li, Z.; Fang, X.; Chen, G. Q.; Huang, Y.; Xu, K. Synthesis and characterization of polyparaphenylene from *cis*-dihydrocatechol. *J. Appl. Polym. Sci.* **2008**, *110*, 2085–2093.
9. Lohaus, H. Eine dien-synthese mit acetylen-dicärbonsaure-diäthylester. *Ann.* **1935**, *516*, 295–297.
10. (a) McDonald, R. N.; Campbell, T. W. Synthesis of hydrocarbon derivatives by the Wittig reaction, II: Diarylbutadienes and quinquephenyls. *J. Org. Chem.* **1959**, *24*, 1969–1975; (b) Campbell, T. W.; McDonald, R. M. *p*-Quinquephenyl. *Org. Synth. Coll. Vol.* **1973**, *5*, 985–986.
11. Fieser, L. F.; Haddadin, M. Oxidative decarboxylation. *J. Am. Chem. Soc.* **1964**, *86*, 2392–2395.
12. Courtot, P.; Rumin, R. Photoisomérisation en série cyclohexadiénique-1,3, IV: Synthèse de dérivés *cis* et *trans*-disubstitués en 5,6. *Bull. Soc. Chim. Fr.* **1969**, 3662–3665.
13. Schuster, G. B. New chemiluminescent reaction systems: Light formation from the reaction of a vicinal diacid dichloride. *J. Am. Chem. Soc.* **1977**, *99*, 651–653.
14. Ikeda, H.; Takasaki, T.; Takahashi, Y.; Konno, A.; Matsumoto, M.; Hoshi, Y.; Aoki, T.; Suzuki, T.; Goodman, J. L.; Miyashi, T. The Photoinduced electron-transfer Cope rearrangments of 3,6-diaryl-2,6-octadienes and 2,5-diaryl-3,4-dimethyl-1,5-hexadienes: Stereospecificity and an unexpected formation of the bicyclo[2.2.0]hexane derivatives. *J. Org. Chem.* **1999**, *64*, 1640–1649.
15. Perkin, W. H. On the formation of coumarin and of cinnamic and of other analogous acids from the aromatic aldehydes. *J. Chem. Soc.* **1877**, *31*, 388–427.
16. Braun, J. V.; Nelles, J. Synthese von zimtsäuren. *Ber.* **1933**, *66*, 1464–1470.
17. Mikroyannidis, J. A.; Spiliopoulos, I. K.; Kasimis, T. S.; Kulkarni, A. P.; Jenekhe, S. A. Synthesis, photophysics, and electroluminescence of conjugated poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazoles in the backbone. *Macromolecules* **2003**, *36*, 9295–9302.
18. Krauss, R. Ueber halogensubstitutionsproducte der α- und γ-truxillsäuren. *Ber.* **1904**, *37*, 216–224.
19. Plevyak, J. E.; Dickerson, J. E.; Heck, R. F. Selective palladium-catalyzed vinylic substitutions with bromoiodo aromatics. *J. Org. Chem.* **1979**, *44*, 4078–4080.
20. Wand, M.; Thurmes, W. N.; Moré, K.; Vohra, R. T. High birefringence liquid crystal compounds. U.S. Patent 5,626,792, May 6, 1997.
21. Malet, R.; Moreno-Mañas, M.; Parella, T.; Pleixats, R. (1-Dimethylamino)-2-(diphenylphosphino)ethane)(3–1-arylallyl)palladium tetrafluoroborates: Preparation, isomeric equilibria, and correlations of NMR chemical shifts with Hammett substituent constants. *J. Org. Chem.* **1996**, *61*, 758–763.
22. Couladouros, E. A.; Soufli, I. C.; Moutsos, V. I.; Chadha, R. K. Total synthesis of combrestatins D. *Chem. Eur. J.* **1998**, *4*, 33–43.
23. Bouziane, A.; Hélou, M.; Bertrand Carboni, B.; Carreaux, F.; Demerseman, B.; Bruneau, C.; Renaud, J.-L. Ruthenium-catalyzed synthesis of allylic alcohols: Boronic acid as a hydroxide source. *Chem. Eur. J.* **2008**, *14*, 5630–5637.

24. Demik, N. N.; Kabachnik, M. M.; Novikova, Z. S.; Beletskaya, I. P. Palladium-catalyzed arylation of diethyl allylphophonate. *Russ. J. Org. Chem.* **1994**, *30*, 935–940.
25. Pastushak, N. O.; Dombrovskii, A. V. Preparation of some unsaturated alkaryl aldehydes by reduction of nitriles of β-arylacrylic acids. *Russ. J. Org. Chem. (Engl. Trans.)* **1965**, *1*, 323–325.
26. Parikh, J. R.; Doering, W. V. E. Sulfur trioxide in the oxidation of alcohols by dimethyl sulfoxide. *J. Am. Chem. Soc.* **1967**, *89*, 5505–5507.
27. Peyman, A.; Uhlmann, E.; Budt, K.; Knolle, J.; Winkler, I.; Helsberg, M. Use of benzylphosphonic acid derivatives for the treatment of diseases caused by viruses. U.S. Patent 5,242,908, Sept. 7, 1993.
28. Taylor, S. D.; Kotoris, C. C.; Dinaut, A. N.; Chen, M.-J. Synthesis of aryl(difluoromethylenephosphonates) via electrophilic fluorination of α-carbanions of benzylic phosphonates with N-fluorobenzenesulfonimide. *Tetrahedron* **1998**, *54*, 1691–1714.
29. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.
30. Jain, P. C.; Mukergee, Y. N.; Anand, N. Novel aspects of the Diels–Alder reaction with 1,4- and 1,2-diphenylbutadienes under thermal and Lewis acid–catalyzed conditions. *J. Am. Chem. Soc.* **1974**, *96*, 2996–2997.
31. Langler, R. F. Unambiguous assessments of reaction paths for selected pericyclic reactions. *Química Nova* **2000**, *23*, 703–705.
32. Braun, J. V.; Irmisch, G.; Nelles, J. Synthesen in der di- und terphenylreihe II: Mitteil. *Ber.* **1933**, *66*, 1471–1483.
33. France, H.; Heilbron, I. M.; Hey, D. H. Studies in the terphenyl series, part I: *p*-Terphenyl, nitro-, amino-, and halogeno-*p*-terphenyls. *J. Chem. Soc.* **1938**, 1364–1375.
34. Müller, E.; Töpel, T. Zur kenntnis des reaktiven verhaltens der organolithiumverbindungen. *Ber.* **1939**, *72*, 273–290.
35. Kuivila, H. G.; Keough, A. H.; Soboczenski, E. J. Areneboronates from diols and triols. *J. Org. Chem.* **1954**, *19*, 780–783.
36. Bowie, R. A.; Musgrave, O. C. Organoboron compounds, part V: The hydrolysis of cyclic phenylboronates. *J. Chem. Soc.* **1963**, 3945–3949.
37. Pickup, D. F.; Yi, H.; Iraqi, A. Preparation and properties of alternating 2,7-linked carbazole copolymers with phenylene units with varying number of fluorine substituents. *J. Mat. Chem.* **2009**, *44*, 3172–3178.