One Pot Synthesis of *p*-Polyphenyls *via* the Intramolecular Cyclization of 3-Dimethylaminohex-5-en-1-ynes

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Para linked polyphenyls of various molecular weights are conveniently synthesized from *p*-bis(3-dimethylamino-1-propynyl)arenes and 1-aryl-2-propenyl bromides in moderate yields using a three step, one-pot procedure.

As part of our ongoing research effort directed toward the synthesis and characterization of rigid rod molecules, the synthesis of all *para* linked polyphenyls became necessary. Synthetic routes to polyphenyls have been reviewed extensively.[1,2] The major shortfall of the previously investigated synthetic procedures is that usually mixtures of products are obtained which are contaminated with a variety of halogenated or metallic impurities. In addition, the synthesis of *p*-polyphenyls containing an odd number of phenyl rings is difficult to accomplish by the standard, often used, aromatic coupling procedures. Such routes inevitably lead to difficult-to-separate mixtures containing both the desired cross-coupled products contaminated with homo-coupled side products.

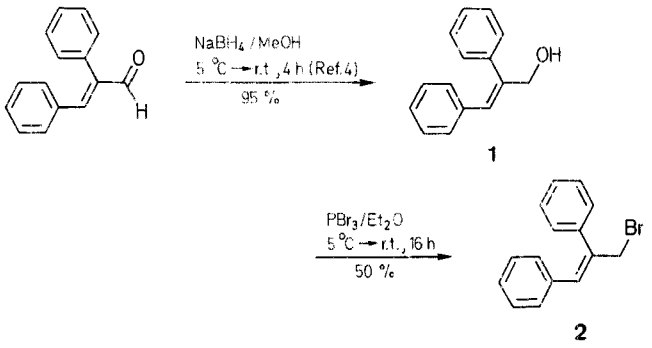
One synthetic method that appeared particularly attractive and had potential for the ability to circumvent the previously described problems had been described in the literature for the preparation of *p*-terphenyl.[3] The method as described involved the condensation of *N,N*-dimethyl-(3-phenyl-2-propynyl)-

amine with 3-bromo-1-phenyl-1-propene to form the corresponding ammonium bromides in high yield. The ammonium salts undergo both [3,2]- and [1,2]-base catalyzed Stevens rearrangements to the corresponding 3-dimethylamino-1,4-diphenylhex-5-en-1-ynes. Subsequent heating of the rearranged products initiates closure of the [3,2]-acyclic enyne with elimination of dimethylamine to form *p*-terphenyl.

It was the intention of the current research to optimize the experimental conditions of the reaction scheme and to generalize the scope of the reaction to include both the synthesis of longer chain *p*-polyphenyls with and without pendant phenyl substituents.

1. Synthesis of 1-Aryl-2-propenyl Bromides

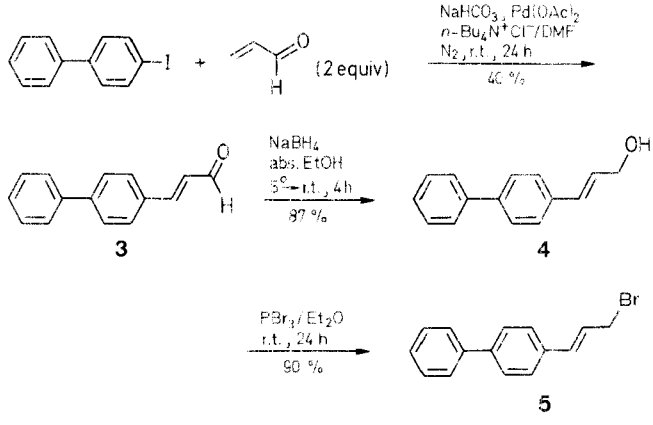
All the 1-aryl-2-propenyl bromide starting materials were prepared *via* the corresponding aldehyde and alcohol intermediates. The alcohol, (*E*)-2,3-diphenyl-2-propen-1-ol (**1**), was obtained with slight modifications of the known procedure[4] in 95% yield by the sodium borohydride reduction of the corresponding aldehyde.[5] Treatment of **1** with phosphorous tribromide afforded the aryl propenyl bromide **2** in 50% yield.[6]



1 2

The palladium catalyzed phase transfer reaction of 4-iodobiphenyl with acrolein was carried out using conditions similar to those described in the literature[7] to afford the resulting biphenyl olefinic aldehyde **3** in 40% yield. Reduction to form **4** followed by the standard treatment with phosphorus tribromide produced the desired bromide **5** in high yield.

The dialdehyde **6** was synthesized in low yield (10%) *via* the crossed aldol condensation of phenylacetaldehyde with terephthaldehyde. Treatment with sodium borohydride gave essentially a quantitative yield of the dialcohol **7**. Conversion to the dibromide **8** was smoothly carried out as before with phosphorus tribromide in ether.



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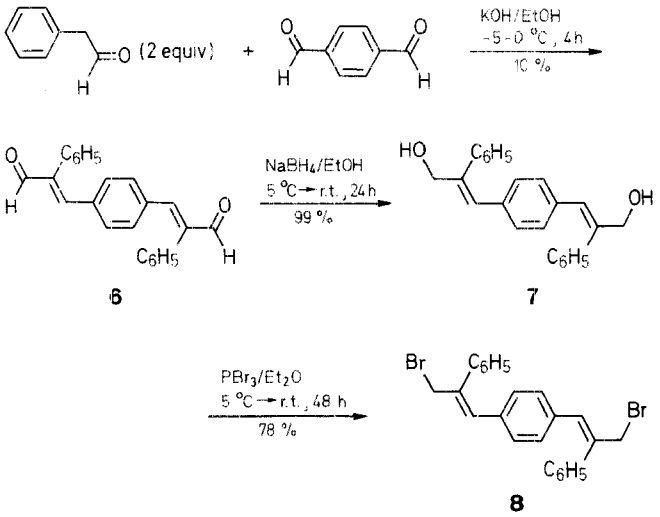
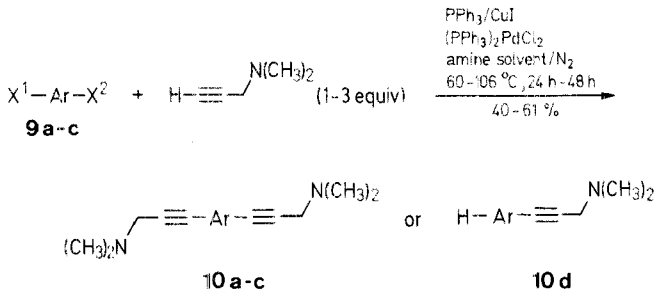


6 7 8

2. Synthesis of *N,N*-Dimethyl-(3-aryl-2-propynyl)amines 10a–d

The previously published method[8] for the synthesis of *N,N*-dimethyl-(3-phenyl-2-propynyl)amine was found to be unsatisfactory for the synthesis of the *N,N*-dimethyl-(3-aryl-2-propynyl)amine starting materials. A one-step method, similar to one previously described[9] involving the palladium catalyzed substitution of halide by the alkyne functionality of 1-(*N,N*-dimethylamino)-2-propyne gave the desired products **10a–d** in moderate yield (40–61%) (Scheme **A**). Piperidine is a superior solvent to triethylamine when using the more insoluble *p*-terphenyl halides. Analytical and spectroscopic data for the amines prepared are summarized in Table 1.



9	X^1	X^2	Ar
a	I	I	*p*-C_6H_4
b	Br	Br	biphenyl-4,4'-diyl
c	I	I	*p*-terphenyl-4,4''-diyl
d	H	I	*p*-terphenyl-4,4''-diyl

Scheme **A**

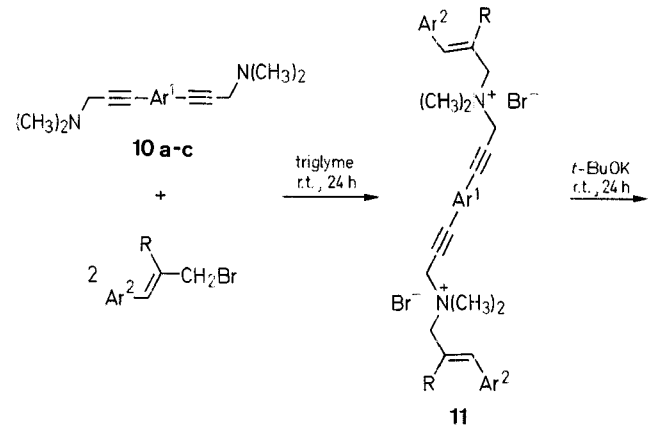
3. Synthesis of Polyphenyls 15a–g and 21a–b

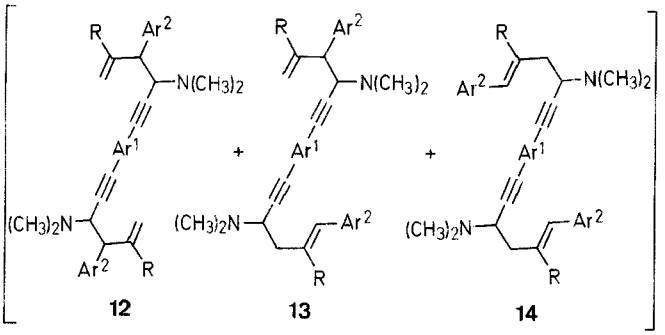
The syntheses of the *p*-polyphenyls were carried out employing a three step, one-pot procedure starting from the appropriate aryl-2-propenyl bromide and the corresponding *N,N*-dimethyl-(3-aryl-2-propynyl)amine (Scheme **B**). Room temperature addition in triglyme afforded high yields of the bis ammonium salt **11**. Upon treatment with potassium *t*-butoxide the ammonium salts undergo a Stevens rearrangement to three possible isomeric unconjugated enynes **12–14**. The reaction mixture containing the various isomers was then heated to 190° at which

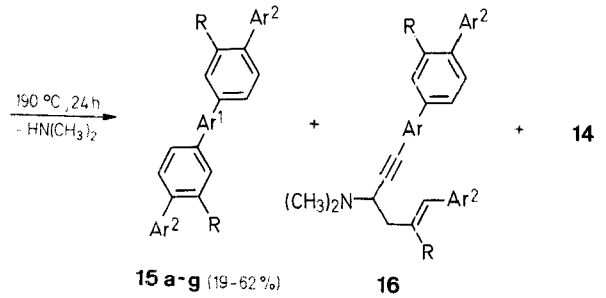
Table 1. *p*-Bis(3-dimethylamino-1-propynyl)arenes **10a–c** and 4-(3-Dimethylamino-1-propynyl)-*p*-terphenyl **(10d)** Prepared

Product	Solvent	Temp. (°C)	Yield[a] (%)	m.p. (°C)[b] (solvent)	Molecular Formula[c]	IR (KBr)[d] ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[e] δ	MS (70eV)[f] *m/e* (%)
10a	Et_3N	60	45	44–45[g]	$C_{16}H_{20}N_2$ (240.3)	1507, 1327, 1034, 835	2.35 (s, 12H); 3.45 (s, 4H); 7.35 (s, 4H)	240 (M^+, 48); 42 (100)
10b	Et_3N	89	61	115–116 (hexane)	$C_{22}H_{24}N_2$ (316.4)	1492, 1324, 1035, 819	2.35 (s, 12H); 3.45 (s, 4H); 7.59 (s, 8H)	361 (M^+, 57); 42 (100)
10c	Piperidine	106	40	240–242 (dec) (benzene/cyclohexane, 1 : 1)	$C_{28}H_{28}N_2$ (392.5)	1326, 1035, 825	2.40 (s, 12H); 3.52 (s, 4H); 7.70 (m, 12H)	392 (M^+, 30); 42 (100)
10d	Piperidine	85	54	209–211 (toluene/hexane, 1 : 1)	$C_{23}H_{21}N$ (311.4)	1483, 1326, 1035, 824	2.40 (s, 6H); 3.52 (s, 2H); 7.70 (m, 13H)	311 (M^+, 26); 42 (100)

[a] Yield of isolated product **10** based on **9**.
[b] Uncorrected, measured on a Mel-Temp melting point apparatus.
[c] Satisfactory microanalyses obtained: C ±0.30, H ±0.10, N ±0.27.
[d] Recorded on a Beckman FT 1100 spectrophotometer.
[e] Recorded on a Varian EM-360A spectrometer.
[f] Recorded on a Finnegan GC/MS/DS System Model 4021.
[g] Purified by column chromatography on silica gel (ether/THF, 8 : 1).

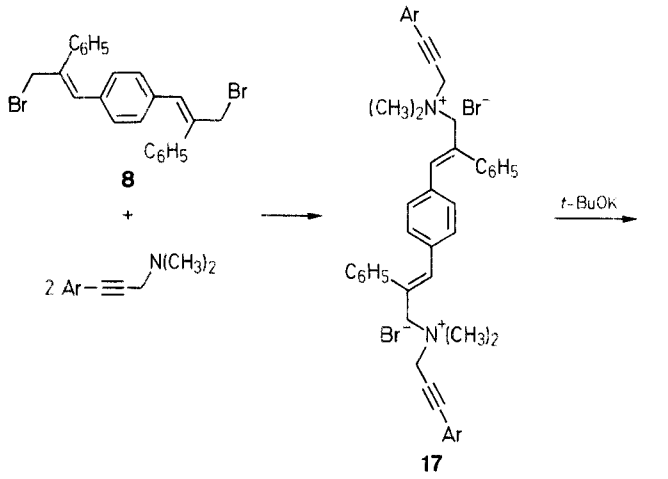


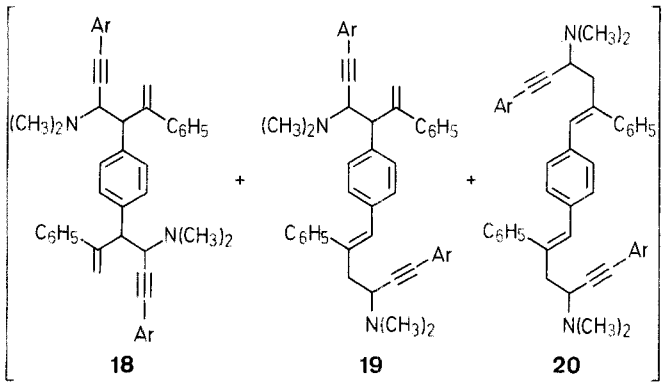


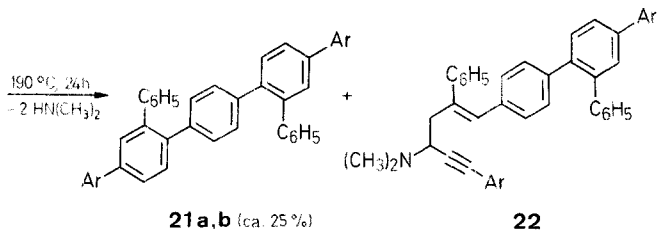


15	Ar^1	R	Ar^2
a	*p*-C_6H_4	H	C_6H_5
b	*p*-C_6H_4	C_6H_5	C_6H_5
c	biphenyl-4,4′-diyl	H	C_6H_5
d	biphenyl-4,4′-diyl	C_6H_5	C_6H_5
e	*p*-terphenyl-4,4″-diyl	H	C_6H_5
f	*p*-terphenyl-4,4″-diyl	C_6H_5	C_6H_5
g	biphenyl-4,4′-diyl	H	4-biphenylyl

Scheme **B**







21	Ar
a	C_6H_5
b	*p*-terphenyl-4-yl

Scheme C

Table 2. *p*-Polyphenyls **15a–g**, **21a–b** Prepared

Product	Yield[a] (%)	m.p. (°C)[b] (solvent)	Molecular Formula[c] or Lit. m.p. (°C)	IR (KBr)[d] ν(cm^{-1})	MS (70 eV)[e] *m/e* (%)
15a	42	388 (1,2,4-TCB)[f]	387.5–388.5[10] 385–390[11], 388[12]	820.0[g]	382 (M^+, 100)
15b	19	288 (xylenes)	$C_{42}H_{30}$ (534.7)	1473, 815, 764	534 (M^+, 100); 267 (M^{++}, 99)
15c	46	437 (1,2,4-TCB)[f]	429[12], 475[13]	815.0[g]	458 (M^+, 32); 229 (M^{++}, 100)
15d	62	341 (1,2,4-TCB)[f]	$C_{48}H_{34}$ (610.8)	1474, 814, 762	610 (M^+, 68); 305 (M^{++}, 100)
15e	49	468 (insoluble)[h]	545[13]	812.0[g]	534 (M^+, 100)
15f	39	375 (1,2,4-TCB)[f]	$C_{54}H_{38}$ (686.8)	1473, 813, 764	686 (M^+, 100); 343 (M^{++}, 96)
15g	46	491 (insoluble)[i]	$C_{48}H_{28}$ (610.8)	809.9[g]	610 (M^+, 21); 305 (M^{++}, 100)
21a	29	255 (xylenes)	$C_{42}H_{30}$ (534.7)	1473, 823, 763	534 (M^+, 100); 267 (M^{++}, 7)
21b	25	416 (1,2,4-TCB)[f]	$C_{66}H_{46}$ (839.0)	1473, 817, 766	839 (M^+, 100); 419 (M^{++}, 12)

[a] Yield of isolated product **15** based on **10a–c**.
[b] Measured by differential scanning calorimetry (ΔT = 10 °C/min) on a DuPont 910 DSC apparatus with Omnitherm 35053 three-module controller.
[c] Satisfactory microanalyses obtained: C ± 0.26, H ± 0.23 (Exception: **15g**; C −1.3).
[d] Recorded on a Beckman FT 1100 spectrophotometer.
[e] Recorded on a Finnigan GC/MS/DS system Model 4021.
[f] 1,2,4-Trichlorobenzene.
[g] Absorption defines C–H out-of-plane deformation of adjacent hydrogens on consecutively *para*-linked benzene rings.[14,15]
[h] Purified by sublimation.
[i] Purified by Soxhlet extraction in boiling xylenes.
[j] Yield of isolated product **21** based on **8**.

temperature only the linkages containing terminal olefinic bonds aromatize. Due to extreme differences in solubility only the fully aromatized polyphenyls **15a–g** precipitate from the reaction mixture with the partially closed **16** and unreacted **14** remaining in solution.

Polyphenyls containing pendant phenyl groups **21a–b** were synthesized in an analogous manner (Scheme **C**). Analytical and spectroscopic data for all polyphenyls prepared are summarized in Table 2. In all cases the products containing pendant phenyl groups exhibited increased solubility and lowered melting points when compared to their corresponding unsubstituted analogs. The *p*-septiphenyl **15e**, *p*-octiphenyl **15g** and the phenyl substituted *p*-noniphenyl **21b** showed very limited solubility in boiling 1,2,4-trichlorobenzene and final purification could only be accomplished by vacuum sublimation or soxhlet extraction.

All amine solvents, commercially available, were distilled and stored over molecular sieves (Linde, 4 Å) before use. The following reagents were obtained from Aldrich Chemical Co. and were used without further purification: 1,2,4-trichlorobenzene, triglyme, 1,4-diiodobenzene (**9a**, X^1=X^2=I, Scheme **A**), 4,4'-dibromobiphenyl (**9b**, X^1=X^2=Br, Scheme **A**), and 3-bromo-1-phenyl-1-propene.

(*E*)-2,3-Diphenyl-2-propen-1-ol (1):
The alcohol **1** is prepared by modification of a known procedure[4] in which $NaBH_4$ (3.11 g, 82.0 mmol) is added in increments over a 5 min period to a suspension of (*E*)-2,3-diphenyl-2-propenal[5] (17.05 g, 82.0 mmol) in cold (5 °C) methanol (400 mL). The flask is allowed to warm to room temperature and is stirred for 4 h. The pure product **1** is obtained by precipitation of the colorless solution into water (1000 mL) to give white needles; yield: 16.07 g (95%); m.p. 72–73 °C (Lit.[4] m.p. 68–69 °C).

(*E*)-1,1'-[1-(Bromomethyl)-1,2-ethenediyl]bis[benzene] (2):
A solution[6] of PBr_3 (6.99 g, 25.8 mmol) in ether (30 mL) is added dropwise over a period of 20 min to a cold (5 °C) solution of alcohol **1** (16.25 g, 77.4 mmol) in ether (200 mL). The flask is warmed to room temperature and stirred for 16 h. The solution is poured into 5% aqueous NaOH and the ethereal layer is separated from the base. After washing with water (2 × 1200 mL), the ether is removed by distillation to give a yellow oil consisting of crude product. Pure product **2** is isolated by chromatography on a silica gel column (Woelm DCC, 5 cm dia X 60 cm H) using petroleum ether/CH_2Cl_2 (4:1) as the eluent and the drying of similar fractions of eluate in a warm oven (50 °C) at reduced pressure (40 mbar) to afford a light yellow oil; yield: 10.5 g (50%).

$C_{15}H_{13}Br$ (273.1) calc. C 65.93 H 4.76 Br 29.30
found 67.46 4.91 29.46

IR (Neat): ν = 3080, 3060, 3010, 2950, 1600, 1560, 1200, 765, 750, 690 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 4.40 (s, 2H, CH_2); 7.10 (s, 1H, H); 6.40–7.50 (m, 10 H_{arom}).

MS (70 eV): *m/e* (%) = 274 (M^+, 6, ^{81}Br); 272 (M^+, 6, ^{79}Br); 193 (100).

(*E*)-3-(4-Biphenylyl)-2-propenal (3):
The aldehyde **3** is prepared by modification of a known procedure[7] in which a mixture of 4-iodobiphenyl (10 g, 35.7 mmol), acrolein (4.03 g, 71.9 mmol), $NaHCO_3$ (7.56 g, 90.0 mmol), tetra-*n*-butylammonium chloride (11.60 g, 41.7 mmol), and $Pd(OAc)_2$ (2.24 g, 10.0 mmol) in degassed DMF (100 mL) is stirred at room temperature under nitrogen for 24 h. The mixture is poured into water (700 mL) and the resulting precipitate is filtered and air dried. The precipitate is stirred vigorously in boiling heptane (600 mL) for 15 min and filtered hot. The pure product **3** is afforded as a light yellow solid upon cooling of the filtrate to room temperature; yield: 3 g (40%); m.p. 110–112 °C.

$C_{15}H_{12}O$ (208.3) calc. C 86.51 H 5.81
found 86.30 5.91

^{1}H-NMR ($CDCl_3$/TMS): δ = 6.55–7.00 (m, 2H, CH=CH); 7.40–7.80 (m, 9 H_{arom}); 9.85 (d, 1H, CHO, J = 8.5 Hz).
MS (70 eV): *m/e* (%) = 208 (M^+, 100).

(*E*)-3-(4-Biphenylyl)-2-propen-1-ol (4):
The alcohol **4** is prepared in a manner similar to **1** using aldehyde **3** (4 g, 19.2 mmol), $NaBH_4$ (0.36 g, 9.5 mmol) and absolute ethanol (40 mL). Upon recrystallization from isopropanol/water (3:1, 200 mL) pure product **4** is afforded as a white powder; yield: 3.52 g (87%); m.p. 161–162 °C.

$C_{15}H_{14}O$ (210.3) calc. C 85.68 H 6.71
found 85.42 6.80

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.15 (s, 1H, OH); 4.25 (d, 2H, CH_2, J = 4 Hz); 6.40–6.48 (m, 2H, CH=CH); 7.40–7.80 (m, 9H$_{arom}$).

MS (70 eV): m/e (%) = 210 (M^+, 89); 167 (100).

(*E*)-4-(3-Bromo-1-propenyl)biphenyl (5):

PBr_3 (288 g, 10.6 mmol) in dry ether (5 mL) is added dropwise over a period of 15 min to a cold (5°C) suspension of alcohol **4** (3.85 g, 18.3 mmol) in ether (50 mL). The flask is allowed to warm to room temperature and stirred for 24 h. The product **5** is obtained from precipitation of the ethereal solution into water (400 mL) and recrystallization of the resulting solid from hexane (100 mL); yield: 4.42 g (90%); m.p. 130–131°C.

$C_{15}H_{13}Br$	calc.	C 65.95	H 4.80	Br 29.25
(273.2)	found	67.77	4.80	29.06

^{1}H-NMR ($CDCl_3$/TMS): δ = 4.20 (d, 2H, CH_2, J = 6 Hz); 6.40–6.65 (m, 2H, CH=CH); 7.45–7.85 (m, 9H$_{arom}$).

MS (70 eV): m/e (%) = 274 (M^+, 4, ^{81}Br); 272 (M^+, 4, ^{79}Br); 193 (100).

(*E,E*)-3,3-(1,4-Phenylene)bis(2-phenyl-2-propenal) (6):

Potassium hydroxide (56 g, 1.0 mol) is dissolved in absolute ethanol (2.4 L) in a 5 L three-necked round-bottom flask fitted with a mechanical stirrer and a nitrogen inlet. The flask is cooled to 20°C by ice bath under a nitrogen atmosphere and terephthaldehyde (200 g, 1.5 mol) is added to the solution. The mixture is then further cooled (−5°C) in a salt-ice bath for 30 min before the dropwise addition of phenylacetaldehyde (396 g, 3.3 mol) over a 2 h period. The reaction is stirred under nitrogen for an additional 2 h maintaining the temperature at −5 to 0°C. The bright yellow precipitate is filtered from the solution, washed with ethanol (0.56 L), hexane (0.5 L), and air dried to afford the crude product **6** (120 g, 19%). Upon treatment with decolorizing carbon (5 g) the product is recrystallized twice from ethyl EtOAc (4 L) to give **6** as small yellow plates; yield: 43 g (10%); m.p. 198–199°C.

$C_{24}H_{18}O_2$	calc.	C 85.18	H 5.36	
(338.4)	found	84.91	5.52	

IR (KBr): ν = 3080, 3060, 2830, 2720, 1665, 1660, 1395 cm^{-1}.

^{1}H-NMR (CD_2Cl_2/TMS): δ = 1.4 (s, 2H, CH=CH); 6.50–7.10 (m, 14H$_{arom}$); 9.30 (s, 2H, CHO).

MS (70 eV): m/e (%) = 338 (M^+, 100).

(*E,E*)-3,3-[1,4-Phenylene]bis]2-phenyl-2-propen-1-ol] (7):

Sodium borohydride (2.81 g, 74.0 mmol) is added in increments over a 5 min period to a cold (5°C) suspension of aldehyde **6** (25 g, 74.0 mmol) in absolute ethanol (220 mL). The flask is warmed to room temperature and stirred for 24 h. The reaction is precipitated into water (1500 mL) and the precipitate is collected on a Buchner funnel. After drying in a 100°C oven at reduced pressure **7** is afforded as a white powder which is used without further purification; yield: 25 g (99%); m.p. 195–196°C.

$C_{24}H_{22}O_2$	calc.	C 84.18	H 6.48	
(342.5)	found	83.88	6.48	

(*E,E*)-1,4-Bis(3-bromo-2-phenyl-1-propenyl)benzene (8):

PBr_3 (5.28 g, 19.5 mmol) in dry ether (30 mL) is added dropwise over a period of 15 min to a cold (5°C) suspension of bis alcohol **7** (10.00 g, 29.2 mmol) in ether (350 mL). The flask is warmed to room temperature and stirred for 48 h. The resulting white precipitate is collected on a Buchner funnel, and dried in a 100°C oven at reduced pressure 40 mbar to give **8** as a white powder which is used without purification; yield: 10.76 g (78%); m.p. 141–142°C.

$C_{24}H_{20}Br_2$	calc.	C 61.54	H 4.27	Br 34.19
(468.3)	found	61.53	4.28	34.19

MS (70 eV): m/e (%) = 470, (M^+, 3, ^{81}Br^{81}Br); 468 (M^+, 4, ^{81}Br^{79}Br); 466 (M^+, 2, ^{79}Br^{79}Br); 307 (100).

4,4″-Diiodo-*p*-terphenyl (9c) and 4-Iodo-*p*-terphenyl (9d):

A mixture of *p*-terphenyl (4.60 g, 20 mmol), iodine (4.05 g, 16 mmol), and HIO_4 (98%, 1.83 g, 8 mmol), in a solvent mixture of AcOH/H_2O/H_2SO_4 (10:2:0.3, 75 mL) is heated to 100°C in an oil bath and stirred mechanically for 24 h. After cooling to room temperature, the precipitate is collected and washed with 10% $Na_2S_2O_3$ (500 mL). The crude products are stirred in refluxing toluene (250 mL) for 15 min and filtered hot. The insoluble product **9c** is purified by extraction with boiling toluene (2 × 250 mL) and dried to afford a white solid; yield: 3 g (31%); m.p. 307–309°C (dec.) [Lit.[16] m.p. 307°C (dec.)].

$C_{18}H_{12}I_2$	calc.	C 44.84	H 2.51	I 53.27
(482.1)	found	44.81	2.55	52.36

MS (70 eV): m/e (%) = 482 (M^+, 14); 226 (100).

The toluene extracts are combined and concentrated to 33% of the original volume. Upon cooling to room temperature the precipitate is collected and purified by recrystallization in toluene (250 mL) to give **9d** as a white solid; yield: 4.50 g (63%); m.p. 246–247°C (Lit.[17] m.p. 246–247°C).

***p*-Bis(3-dimethylamino-1-propynyl)arenes 10a–c; General Procedure:**

The appropriate dihaloarene **9a–c** (101.7 mmol) and 1-dimethylamino-2-propyne (25.82 g, 310.6 mmol) in the designated amine solvent (1000 mL) are degassed for 30 min at room temperature before the addition of PPh_3 (1.0 g, 3.8 mmol), cuprous iodide (0.2 g, 1.1 mmol), and dichlorobis(triphenylphosphine)palladium(II) (0.7 g, 1.0 mmol). The flask is heated for 24–48 h and allowed to cool to room temperature. The precipitate of ammonium halide salts is filtered from solution and washed with amine solvent (200 mL). The solvent is reduced to one quarter of the original volume by distillation under vacuum. The resulting concentrated solution is then poured into 5% HCl (1000 mL) and the solution is adjusted to pH 9 by addition of 5% aqueous NaOH. The suspension is extracted with CH_2Cl_2 (3 × 300 mL) and separated. After drying $MgSO_4$ (10 g), the pure product **10a–c** is obtained upon distillation of the solvent and subsequent recrystallization (Table 1).

4-(3-Dimethylamino-1-propynyl)-*p*-terphenyl (10d):

The asymmetric N,N-dimethyl-2-propyn-1-amine **10d** is prepared in a manner similar to **10a–c** by reaction of 4-iodo-*p*-terphenyl (**9d**, X^1=H, X^2=I, 5.00 g, 14.0 mmol) and 1-dimethylamino-2-propyne (1.75 g, 21.1 mmol) in a degassed solution of piperidine (70 mL) (Table 1).

***para*-Polyphenyls 15a–g; General Procedure:**

A suspension of the bis amine **10a–c** (1.0 mmol) in triglyme (50 mL) is degassed for 20 min before the addition of **2**, **5**, or 3-bromo-1-phenyl-1-propene (2 mmol). The mixture is stirred at room temperature under nitrogen for 24 h. Anhydrous KOBu-*t* (2 mmol) is added to the solution and stirring is continued at room temperature under nitrogen for an additional 24 h. The temperature of the reaction mixture is raised to 190°C under nitrogen for 24 h and cooled to room temperature. The precipitate is filtered from solution through a Buchner funnel, washed with methanol (50 mL), distilled water (500 mL), and air dried. The product **15a–g** is purified *via* either sublimation or recrystallization (Table 2).

***para*-Polyphenyls 21a–b; General Procedure:**

The polyphenylenes **21a–b** are prepared in a manner similar to the preparation of **15a–g** by the reaction of (*E,E*)-1,4-bis(3-bromo-2-phenyl-1-propenyl)benzene **(8)** (1.0 mmol) with either *N,N*-dimethyl-3-phenyl-2-propyn-1-amine[8] or **10d** (2.0 mmol) (Table 2).

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