JOC The Journal of Organic Chemistry

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Direct Arylation of Oligonaphthalenes Using PIFA/BF_3·Et_2O: From Double Arylation to Larger Oligoarene Products

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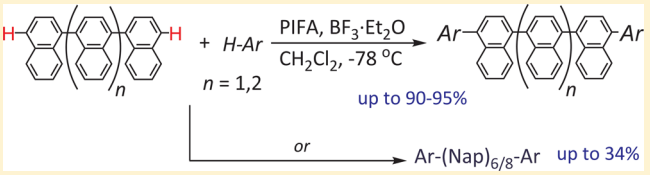
Supporting Information

ABSTRACT: Direct dehydrogenative coupling between the linear ter- and quaternaphthalenes and substituted benzenes was achieved under the Kita conditions using the hypervalent PIFA/BF_3 reagent. Products resulting from either the double arylation of the naphthalenic substrate or the formal dimerizative arylation have been prepared. For example, in the latter mode, ternaphthalene was converted into a series of linear octiarenes (counting the capping Ar). The process represents an alternative to the cross-coupling methodologies employed in related syntheses and proceeds via a selective functionalization of six relatively inert aromatic CH bonds.



The carbon—carbon coupling between arenes via the transformation of the CH groups is a particularly promising goal within the overall challenge of the CH bond functionalization. In this field, the earlier stoichiometric methods,[1−3] many in the form of the Scholl reaction, have recently been complemented by the development of the catalytic dehydrogenative coupling processes.[4,5] The challenge of finding a practical procedure applicable to a particular substrate lies both in the relative inertness of a CH bond and in our ability to direct the reaction toward a specific CH site. In an intermolecular system, the discrimination can be achieved through the use of an appropriate directing group,[6] or by employing a substrate with an inherently reactive CH position[7−9] in certain types of radical and electrophilic reactions.

This latter reactivity manifold was nicely illustrated by Kita and co-workers in an arylation of naphthalene with polyalkylbenzenes (e.g., mesitylene) using a combination of phenyliodine bis(trifluoroacetate), PIFA, and BF_3·Et_2O (Scheme 1A).[10] For this system, the arylation took place exclusively at the α-position of naphthalene, and the method complemented the existing metal-catalyzed cross-coupling protocols. The method was also extended to the direct coupling of heteroarenes.[11,12] Our group later showed that the outcome in the case of the naphthalene/mesitylene pair was highly dependent on the PIFA—naphthalene ratio. Thus, mesitylnaphthalene **1a** was the main product at a ratio of 1:1, whereas the arylated binaphthalene **2a** formed predominantly (45%) when this ratio was raised to ∼2:1 (Scheme 1A);[13] in both cases, the reaction was accompanied by the formation of small amounts of oligonaphthalenes Mes-$(nap)_3$-Mes (**3a**) and Mes-$(nap)_4$-Mes (**4a**) and longer oligomers, appearing as trailing fluorescent spots on a TLC plate (Figure 1A). Such products would be consistent with further oxidative coupling of the initially formed **1a** either through dimerization or by reacting with extra equivalents of naphthalene prior to a second arylation with mesitylene. We also found that, when naphthalene was replaced with 1,1′-binaphthalene (**Nap_2**), the corresponding coupling of four arene molecules (2 **Nap_2** and 2 ArH) became the predominant process, giving the diarylated tetranaphthalene **4a** in 87% (Scheme 1B).[13]

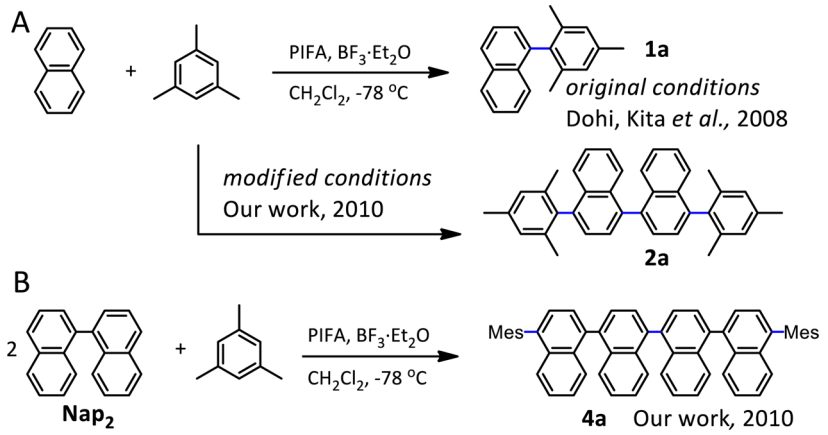
The TLC traces of the reaction mixtures for the arylation of naphthalene and 1,1′-binaphthalene (Figure 1) provide a nice visual comparison for the two outcomes. As mentioned above, arylation of naphthalene yields, in addition to **1a**, oligonaphthalenes (**2a**, **3a**, **4a**, etc.) capped on both sides by a mesityl (trace A). Under the same conditions, 1,1′-binaphthalene is expected to give an analogous mixture devoid of the *n*-odd components (trace B). Indeed, whereas the *n*-even **2a** and **4a** are found on both traces, product **3a** is absent in trace B.

Control experiments showed that, in the case of the 1,1′-binaphthalene, the process likely begins with the formation of the monoarylated product, which then dimerizes. We showed, however, that alternative paths may also be operational. Thus, the coupling between the monoarylated product with a second binaphthalene may be followed by the second arylation; finally, dimerization of 1,1′-binaphthalene followed by a double arylation was also shown to be feasible.[13] In fact, these experiments and the surprisingly high efficiency for this formal dimerizative arylation process suggested that the use of longer-chain oligonaphthalenes, such as ter- and quaternaphthalenes, might also be feasible.[14] To this end, we developed the synthesis of the parent linear **Nap_3** and **Nap_4** through a two-step procedure involving selective dibromination,[15,16] followed by Suzuki—Miyaura coupling with the 1-naphthaleneboronic acid (Scheme 2; see the Supporting Information). Even for the simple trinaphthalene **Nap_3**, the fairly complex ^{13}C NMR spectrum, consisting of a large number of the somewhat broadened peaks,[17,18] suggested that the product exists as a mixture of the slowly interconverting atropisomeric *aRaR*/*aSaS*

Received: May 14, 2013
Published: July 16, 2013

   dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

Scheme 1. Previous Results on Oxidative Arylation of Naphthalenes Using PIFA/BF_3·Et_2O



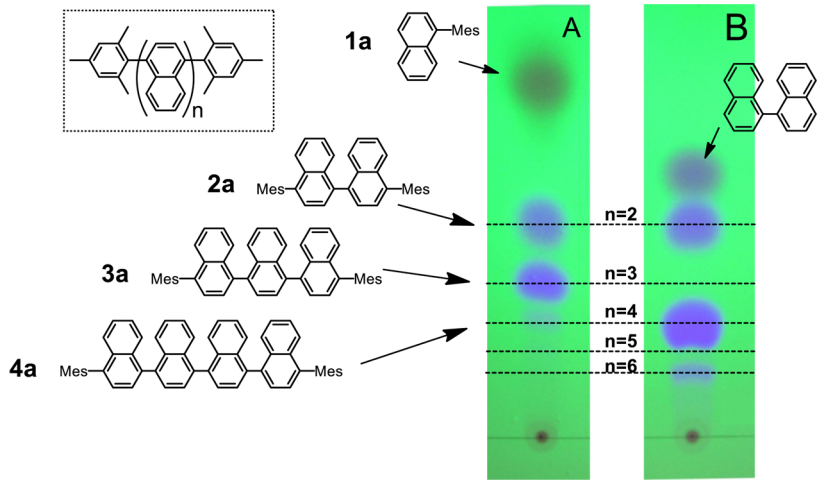
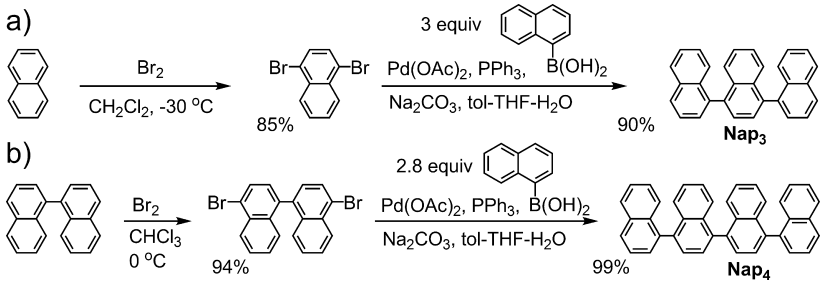


Figure 1. TLC traces for the coupling of mesitylene with (A) naphthalene and (B) 1,1′-binaphthalene.

Scheme 2. Preparation of Substrates Nap_3 and Nap_4



(*rac*, C_2) and *aRaS* (*meso* σ) forms. The procedure afforded multigram quantities of **Nap_3** and **Nap_4** in, respectively, 77% and 93% yields over the two steps.[19]

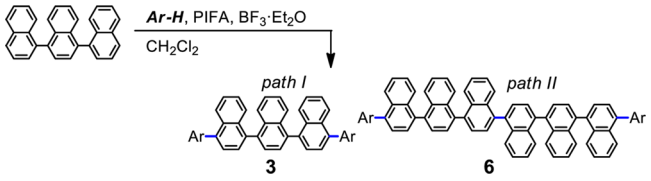
As was the case for the parent 1,1′-binaphthalene, the next higher homologue, **Nap_3**, could be envisaged undergoing, in addition to the monarylation, a double arylation to **3** (Table 1, path I), or a formal dimerizative arylation to give the linear sexinaphthalene **6** (path II).

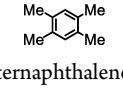
Thus, the reactivity of **Nap_3** with mesitylene was examined under the conditions similar to those used for the binaphthalene. The test revealed that, unlike for **Nap_2**, the simple double arylation path I is somewhat preferred for **Nap_3**. Specifically, the addition of the PIFA/BF_3 reagent (0.6 mmol/1.2 mmol) to a mixture of **Nap_3** (0.3 mmol) and mesitylene (1.2 mmol) led to a 90% yield of **3a**, a compound previously identified (see Figure 1) as a minor fraction in the arylation of naphthalene (Table 1, entry 1). The reactivity difference between **Nap_2** and **Nap_3** in the Kita-type arylation is noteworthy. Assuming the monoarylation as the first step, the preference for arylative dimerization in **Nap_2** and for selective diarylation in **Nap_3** indicates a significantly more favored second arylation in the latter.

As previously documented for **2a**,[13] two singlets are observed in the ^{1}H NMR spectrum of **3a** due to the diastereotopic *ortho* Me resonances within each mesityl; signal doubling is also observed for the aromatic *m*-H. A diastereotopic relationship between the two halves of the "hindered" mesityl group is a

dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

Table 1. Oxidative Arylation of Nap_3 Using PIFA/$BF_3{\cdot}Et_2O$[a,b]



Entry	Ar-H				
1		**3a**	90	**6a**	--
2		**3b**	89	**6b**	--
3		**3c**	71	**6c**	<5%
4		**3d**	33	**6d**	31
5		**3e**	32	**6e**	22
6		**3f**	31	**6f**	34

[a]Using ternaphthalene 0.3 mmol of **Nap_3**, 1.2 mmol of PIFA, and 1.2 mmol of $BF_3{\cdot}Et_2O$ in CH_2Cl_2 at −78 °C. [b]Yields of isolated products.

consequence of their disposition over the two diastereotopic faces of the adjacent naphthalene (Figure 2).[20]

A good yield of the double arylation product was also obtained using pentamethylbenzene (Table 1, entry 2, 89%), and triethylbenzene (entry 3, 71%). In contrast, the use of bulkier arenes drastically lowered the efficiency of the double arylation, and only a modest 33% of **3d** was isolated using 1-*tert*-butyl-3,5-dimethylbenzene (entry 4). Similarly, the use of 2,4,6-trimethyl-1,1′-biphenyl gave **3e** in 32% yield (entry 5). In the latter two cases, however, the decrease in the yield of **3** was compensated by the appearance of non-negligible quantities of the octiarene products **6d** (31%, entry 4) and **6e** (22%, entry 5). An approximately 1:1 mixture of **3f**:**6f** was also obtained using 1,2,4,5-tetramethylbenzene (entry 6).

The formation, albeit in modest yields, of **6d**−**6f**, represents an assembly of a linear octiarene (counting the capping arenes) using simple aromatic building blocks, whereby three new C−C bonds have been formed from six unactivated arene molecules. The new products appear at R_f lower than those of the corresponding **3d**−**3f**. The identity of the new oligoarenes was confirmed, in addition to the ^1H and ^{13}C NMR spectra, via high-resolution MALDI TOF spectrometry.

Given that the product distribution in the arylation of **Nap_2** was dependent on the amount of PIFA, we looked for a similar influence for **Nap_3**. Taking as a model the coupling between 1-*tert*-butyl-3,5-dimethylbenzene (entry 4, Table 1) and **Nap_3** (ratio 4:1), the yields of the simple and formal dimerizative arylation products **3d** and **6d** were determined as a function of the equivalents of PIFA employed (Figure 3A).[21] Thus, both yields grew steadily with increasing amounts of PIFA, with the **6d** reaching a maximum yield (32%) at 2 equiv. In turn, the yield of **3d** reached its maximum (40%) with 3 equiv of PIFA (at the expense of **6d**); a further increase in the PIFA loading was found to be detrimental to both. In a separate experiment, the yields of both **3d** and **6d** were found to peak at ∼4−5 equiv of ArH added, with **3d** slightly favored (as expected) at higher ratios of ArH (Figure 3B).

Finally, the oxidative arylation of the next higher homologue **Nap_4** was explored (Scheme 3, Figure 4). Previously,[13] we showed that the arylation of this substrate with mesitylene gave predominantly the doubly arylated product **4a**, indicating the substrate's decreased ability to undergo the formation of the larger formally dimeric products.

Expanding on that preliminary result, and after some optimization, we found that, in addition to the 91% yield obtained for **4a**, good yields were reached for the pentamethylphenyl and triethylphenyl derivatives, **4b** (95%) and **4c** (77%), respectively. Once again, arylation using the bulkier 1-*tert*-butyl-3,5-dimethylbenzene and 2,4,6-trimethyl-1,1′-biphenyl gave moderate yields of the corresponding products **4d** (52%) and **4e** (60%), respectively. In the case of 1,2,4,5-tetramethylbenzene, only a 37% yield of the double arylation product **4f** was obtained. This low yield was attributed to the further oxidative coupling at the *p*-H at the tetramethylphenyl unit of the newly formed **4f**, leading to an intractable oligomer.

Unlike in the case of **Nap_3**, however, the use of **Nap_4** as a substrate did not afford any significant quantities of the larger oligoarene **8** (i.e., Ar-nap_8-Ar). Nevertheless, small amounts of **8** were, indeed, detected in some cases. For example, the TLC analysis in the reaction mixture using 1,2,4,5-tetramethylbenzene as a substrate showed the principal leading fraction (product **4d**) trailed by a minor component, consistent with the presence of a larger oligomer. Repeated purification of this fraction by preparative TLC afforded small quantities of the deciarene **8f**, whose identity was confirmed by the observation of a peak at 1274.5852 in the high-resolution MALDI-TOF analysis (see the Supporting Information).

In summary, the Kita-type direct dehydrogenative arylation protocol using the BF_3-activated phenyliodine bis(trifluoroacetate) (**PIFA**) has now been successfully applied to the arylation of the linear ter- and quaternaphthalenes. In contrast to the reactions using naphthalene and binaphthalene, the arylation of oligonaphthalenes has led predominantly to the

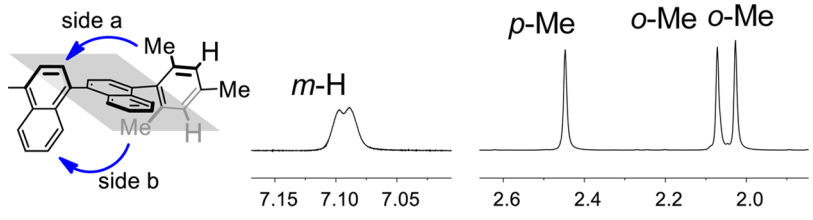


Figure 2. Different chemical environments for the two halves of the mesitylene and the resulting doubling of the ^1H pattern.

dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

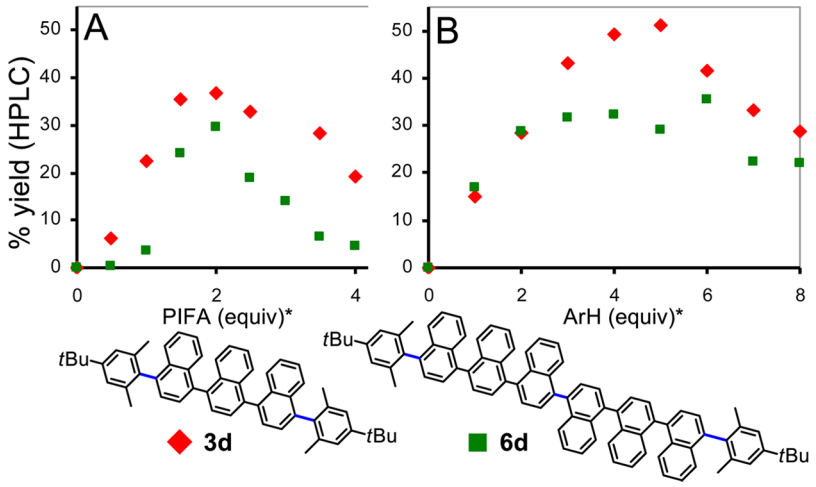


Figure 3. Yields of **3d** and **6d** (% by HPLC, corrected), as a function of the amount of PIFA (A) and ArH (B) used. * equiv PIFA = mmol(PIFA)/mmol(**Nap$_3$**).

Scheme 3. Oxidative Arylation of Nap$_4$ Using PIFA/BF$_3$·Et$_2$O

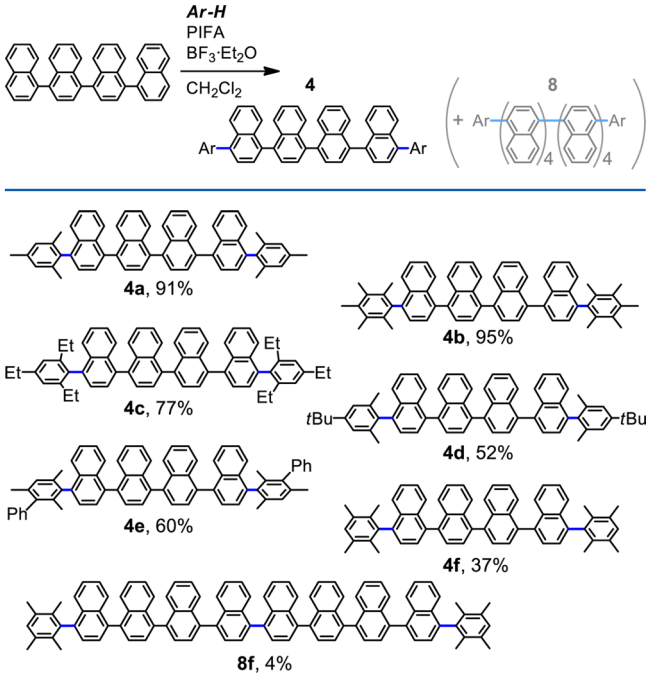


Figure 4. Products obtained via oxidative arylation of **Nap$_4$** using PIFA/BF$_3$·Et$_2$O.

double-arylation products **3** and **4**. Still, moderate yields of the larger multiarene **6** could be obtained in some cases for **Nap$_3$**. Such a synthesis of an octiarene is remarkable, in that it constitutes a direct oxidative metal-free assembly of four unfunctionalized building block molecules. The interest in practical syntheses of such large oligonaphthalenes lies in their optoelectronic properties relevant in the design of solar cells or OLED devices.[22] Finally, small quantities of the formal dimerizative arylation products **8d** and **8f** have also been detected (4% isolated yield for **8f**), representing the one-pot assembly of a linear deciarene.

EXPERIMENTAL SECTION

General. All reagents were purchased from commercial sources and used as received. 1,4-Dibromonaphthalene was prepared following a reported procedure,[15] 2-phenylmesitylene was prepared following a Suzuki coupling protocol as previously described,[13] and 4,4′-dibromo-1,1′-binaphthalene was prepared as already described.[16] Dichloromethane was dried by passing through a column of activated molecular sieves. Silica gel used corresponds to 230−440 mesh. Routine ^{1}H and ^{13}C NMR spectra were recorded on 250 and 360 MHz instruments. ^{1}H NMR chemical shifts are given relative to the residual proton signal of CDCl$_3$ (7.26 ppm). ^{13}C NMR spectra are given relative to the ^{13}C resonance of CDCl$_3$ (77.16 ppm). High-resolution MALDI-TOF spectra were recorded using dithranol as the matrix and polyethylene glycol as the internal reference. IR data were obtained using a spectrometer equipped with an ATR probe. The yields of compound **3d** and **6d** related to condition optimization were determined by HPLC, using a column packed with diphenyl silica as a stationary phase (Pursuit XRs Diphenyl from Agilent Technologies) and a mixture of hexane/acetonitrile/isopropanol (10/20/70) as a mobile phase with a flow rate of 0.6 mL/min. For all the analyses, 1,1′-binaphthalene was used as an internal standard.

Synthesis and Characterization Details. *1,4-Dibromonaphthalene.*[15] A stirred solution of naphthalene (8.970 g, 69.692 mmol) in dichloromethane (70 mL) was cooled to −30 °C, and then bromine (33.600 g, 10.8 mL, 210 mmol) was added dropwise over 10 min in the dark while maintaining the temperature at −30 °C with constant magnetic stirring. The mixture was then stirred for 20 h in the dark at −25 °C. At this point, the excess of bromine was quenched with an aqueous solution of NaHSO$_3$. The organic layer was separated and further washed with aqueous solutions of NaHSO$_3$ and NaOH (2 M). The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness to afford the crude compound, which was further purified by silica gel chromatography using hexane as eluent. White powder, yield: 17.000 g, 85%; mp 79−81 °C; lit.[15] 80−82 °C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 8.25 (dd, J = 6.5, 3.3 Hz, 2H), 7.65 (dd, J = 6.4, 3.3 Hz, 2H), 7.63 (s, 2H) ppm; ^{13}C{^{1}H} NMR (90 MHz, CDCl$_3$) δ 133.1, 130.2, 128.3, 127.9, 122.7 ppm; IR (ATR) ν (cm^{-1}) 3067, 1583, 1492, 1365, 1251, 959, 812, 749.

4,4′-Dibromo-1,1′-binaphthalene.[13,16] A stirred solution of 1,1′-binaphthalene (3.050 g, 11.993 mmol) in chloroform (96 mL) was cooled to 0 °C. Bromine (9.010 g, 2.9 mL, 56.383 mmol) was added dropwise over 10 min in the dark while maintaining the temperature at 0 °C and with a steady magnetic stirring. The mixture was stirred for 4 h in the dark at 0 °C. At this point, aqueous NaHSO$_3$ solution was added to quench the excess of bromine. The organic layer was separated and washed successively with aqueous NaHSO$_3$ solution, aqueous NaOH solution (2 M), and water. The organic layer was

dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

dried over anhydrous Na_2SO_4 and concentrated to dryness to afford the crude compound, which was recrystallized from boiling chloroform. White needle crystals, yield: 4.600 g, 94%; mp 214−216 °C; lit.[16] 215−217 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.37 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.62−7.58 (m, 2H), 7.35−7.31 (m, 6H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 137.8, 134.0, 132.1, 129.6, 128.3, 127.6, 127.1, 123.1 ppm; IR (ATR) ν (cm^{-1}) 3071, 1582, 1450, 1366, 1248, 954, 817, 754.

*1,1′:4′,1″-Ternaphthalene (**Nap$_3$**).* To a mixture of 1,4-dibromonaphthalene (2.000 g, 6.994 mmol), naphthalene-1-boronic acid (3.610 g, 20.990 mmol), $Pd(OAc)_2$ (94 mg, 0.419 mmol), PPh_3 (0.330 g, 1.258 mmol), and Na_2CO_3 (2.230 g, 21.038 mmol) were added H_2O (14 mL), THF (53 mL), and toluene (140 mL), and the resulting suspension was heated to reflux for 22 h. The reaction mixture was then cooled to room temperature, and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, hexane:AcOEt 20:1; R_f = 0.43), affording 1,1′:4′,1″-ternaphthalene. Cotton-like white solid, yield: 2.400 g, 90%; mp 188−190 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.00−7.97 (m, 4H), 7.68−7.48 (m, 12H), 7.43−7.35 (m, 2H), 7.29−7.26 (m, 2H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 138.7, 138.5, 138.4, 133.7, 133.10, 133.07, 133.0, 128.37, 128.33, 128.1, 127.5, 127.0, 126.8, 126.23, 126.18, 126.03, 126.00, 125.96, 125.6; HRMS (MALDI-TOF) m/z calcd for $C_{30}H_{20}$ $[M]^+$: 380.1554, found: 380.1569; IR (ATR) ν (cm^{-1}) 3043, 1571, 1505, 1375, 1256, 776, 758.

*1,1′:4′,1″:4″,1‴-Quaternaphthalene (**Nap$_4$**).*[13] To a mixture of 4,4′-dibromo-1,1′-binaphthalene (2.470 g, 5.993 mmol), naphthalene-1-boronic acid (2.890 g, 16.803 mmol), $Pd(OAc)_2$ (135 mg, 0.601 mmol), PPh_3 (488 mg, 1.861 mmol), and Na_2CO_3 (1.910 g, 18.019 mmol) were added H_2O (9 mL), THF (36 mL), and toluene (108 mL), and the resulting suspension was heated to reflux for 24 h, at which point all of the aryl halide has been consumed as gauged by GC. The reaction mixture was cooled to room temperature, and the solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel, neat hexane; R_f = 0.1). Cotton-like white solid, yield: 3.000 g, 99%; mp 178−181 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01−7.99 (m, 4H), 7.77−7.49 (m, 16H), 7.45−7.32 (m, 6H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 138.7, 138.6, 138.5, 133.7, 133.13, 133.09, 128.40, 128.36, 128.2, 127.7, 127.6, 127.1, 126.8, 126.3, 126.2, 126.1, 125.6 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{40}H_{26}$ $[M]^+$: 506.2029, found: 506.2019; IR (ATR) ν (cm^{-1}) 3041, 1592, 1506, 1373, 1256, 800, 761.

General Procedure for the Oxidative Arylation. To a solution of 1,1′:4′,1″-ternaphthalene, **Nap$_3$**, or 1,1′:4′,1″:4″,1‴-quaternaphthalene, **Nap$_4$**, (0.300 mmol), and the chosen arene (1.200 mmol) in dry dichloromethane (2 mL) at −78 °C and under a nitrogen atmosphere were added $BF_3{\cdot}Et_2O$ (170 mg, 150 μL, 1.200 mmol) and a solution of PIFA (258 mg, 0.600 mmol) in dichloromethane (anhydrous, 2 mL). The resulting deep purple reaction mixture was kept below −50 °C for 3 h and then was allowed to warm up to room temperature for an additional 20 h. The mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and was transferred to a separatory funnel. The organic layer was separated, and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic fraction was dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude product was purified by flash chromatography. Given the difficult separation due to similar R_f values for the major and the minor, a second or even a third purification by flash chromatography were performed when needed. In some cases, preparatory paper TLC was used to obtain samples suitable for analysis.

*4,4″-Dimesityl-1,1′:4′,1″-ternaphthalene (**3a**).* Following the general procedure, ternaphthalene, **Nap$_3$** (150 mg, 0.394 mmol), was allowed to react with 1,3,5-trimethylbenzene (230 μL, 0.846 g/mL, 1.610 mmol). Column chromatography: silica gel, hexane:AcOEt 70:1, R_f = 0.25. Light yellow powder, 223 mg, yield: 90%; mp 212−214 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.72−7.59 (m, 8H), 7.52−7.44 (m, 2H), 7.41−7.33 (m, 8H), 7.10−7.09 (two overlapping s, 2H + 2H), 2.45 (s, 6H), 2.07 (s, 6H), 2.03 (s, 6H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 138.9, 138.6, 137.7, 137.2, 137.1, 137.0, 133.42, 133.36, 133.3, 133.2, 132.1, 128.3, 128.0, 127.7, 127.2, 127.0, 126.5, 126.0, 125.6, 21.3, 20.7 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{48}H_{40}$ $[M]^+$: 616.3124, found: 616.3125; IR (ATR) ν (cm^{-1}) 3038, 2919, 2854, 1374, 1260, 844, 762.

*4,4″-Bis(2,3,4,5,6-pentamethylphenyl)-1,1′:4′,1″-ternaphthalene (**3b**).* Following the general procedure, ternaphthalene (114 mg, 0.300 mmol) was allowed to react with 2,3,4,5,6-pentamethylbenzene (178 mg, 1.201 mmol). Column chromatography: silica gel, hexane:AcOEt 70:1, R_f = 0.16. Light yellow powder, 180 mg, yield: 89%; mp 198−201 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.73−7.62 (m, 8H), 7.56−7.52 (m, 2H), 7.46−7.34 (m, 8H), 2.42 (s, 6H), 2.37−2.36 (two overlapping s, 6H + 6H), 2.01 (s, 6H), 1.96 (s, 6H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 140.9, 138.7, 138.6, 137.6, 137.55, 137.45, 134.4, 133.2, 132.73, 132.70, 132.65, 132.56, 128.0, 127.7, 127.1, 126.70, 126.67, 126.6, 126.0, 125.9, 18.6, 18.5, 17.1, 16.9 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{52}H_{48}$ $[M]^+$: 672.3751, found: 672.3752; IR (ATR) ν (cm^{-1}) 3040, 2990, 2916, 1372, 906, 761, 731.

*4,4″-Bis(2,4,6-triethylphenyl)-1,1′:4′,1″-ternaphthalene (**3c**).* Following the general procedure, ternaphthalene (114 mg, 0.300 mmol) was allowed to react with 1,3,5-triethylbenzene (226 μL, 0.862 g/mL, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt gradient from 250:1 to 100:1 (R_f = 0.09). Light brown powder, 150 mg, yield: 71%; mp 135−138 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.74−7.62 (m, 8H), 7.50−7.47 (m, 4H), 7.37−7.35 (m, 6H), 7.14 (two overlapping s, 2H + 2H), 2.82−2.76 (q, 4H, J = 7.4 Hz), 2.39−2.29 (m, 8H), 1.41−1.37 (t, 6H, J = 7.6 Hz), 1.11−1.03 (m, 12 H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 143.7, 143.2, 143.1, 138.3, 137.7, 136.0, 133.20, 133.18, 133.0, 127.8, 127.7, 127.12, 127.05, 126.0, 125.94, 125.91, 125.32, 125.29, 29.0, 27.02, 26.95, 15.9, 15.8, 15.7 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{54}H_{52}$ $[M]^+$: 700.4064, found: 700.4078; IR (ATR) ν (cm^{-1}) 3044, 2967, 2933, 2873, 1570, 1460, 1375, 840, 764.

*4,4″-Bis(4-(tert-butyl)-2,6-dimethylphenyl)-1,1′:4′,1″-ternaphthalene (**3d**).* Following the general procedure, ternaphthalene (114 mg, 0.300 mmol) was allowed to react with 5-*tert*-butyl-*m*-xylene (195 mg, 225 μL, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt gradient from 250:1 to 100:1 (R_f = 0.21). Light yellow powder, 70 mg, yield: 33%; mp > 300 °C; ^{1}H NMR ($CDCl_3$): δ 7.72−7.58 (m, 8H), 7.52−7.44 (m, 4H), 7.40−7.33 (m, 6H), 7.25 (two overlapping s, 2H + 2H), 2.09 (s, 6H), 2.05 (s, 6H), 1.44 (s, 18H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 150.2, 139.1, 138.64, 138.58, 137.6, 136.9, 136.7, 133.3, 132.2, 128.0, 127.7, 127.2, 127.1, 126.4, 126.1, 126.0, 124.5, 34.6, 31.7, 21.1 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{54}H_{52}$ $[M]^+$: 700.4064, found: 700.4068; IR (ATR) ν (cm^{-1}) 3040, 2952, 2864, 1456, 1375, 841, 763.

*4,4‴′′′′′-Bis(4-tert-butyl-2,6-dimethylphenyl)-1,1′:4′,1″:4″,1‴:4‴,1′′′′:4′′′′,1′′′′′-sexinaphthalene (**6d**).* From the same experiment used to obtain **3d**, an additional product was isolated that corresponded to the hexanaphthalene **6d**. Light brown powder, 50 mg, yield: 31%. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.87−7.65 (m, 20H), 7.56−7.54 (m, 2H), 7.52−7.39 (m, 14H), 7.29 (two overlapping s, 2H + 2H), 2.14−2.09 (two s, 6H + 6H), 1.47 (s, 18H). ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 150.2, 139.1, 138.6, 137.6, 136.9, 136.7, 133.4, 133.2, 132.3, 128.0, 127.8, 127.2, 126.4, 126.1, 126.02, 125.97, 124.5, 34.6, 31.7, 21.1 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{84}H_{70}$ $[M]^+$: 1078.5472, found: 1078.5488; IR (ATR) ν (cm^{-1}) 3039, 2951, 1509, 1372, 837, 760.

*4,4″-Bis(2,4,6-trimethyl-[1,1′-biphenyl]-3-yl)-1,1′:4′,1″-ternaphthalene (**3e**).* Following the general procedure, ternaphthalene (114 mg, 0.300 mmol) was allowed to react with 2-phenylmesitylene (235 mg, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 70:1 (R_f = 0.15). Orange powder, 74 mg, yield: 32%; mp 209−212 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.73−7.60 (m, 10H), 7.49−7.28 (m, 18H), 7.21 and 7.20 (two overlapping s, 1H + 1H), 2.16 (s, 6H), 2.11 (s, 3H), 2.06 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H) ppm; ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 141.7, 140.0, 139.3, 137.7, 137.6, 136.1, 135.4, 135.2, 133.4, 133.1, 132.2, 129.6, 129.5, 128.8, 128.6, 128.0, 127.7, 127.2, 127.0, 126.7, 126.5, 126.1, 126.0, 21.2, 20.8, 19.0, 18.9 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{60}H_{48}$ $[M]^+$: 768.3756, found: 768.3774; IR (ATR) ν (cm^{-1}) 3038, 2918, 1601, 1441, 1373, 763, 702.

dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

*4,4′′′′′′-Bis(2,4,6-trimethylbiphenyl-3-yl)-1,1′:4′,1″:4″,1‴:4‴,1′′′′:4′′′′,1′′′′′:4′′′′′-sexinaphthalene (**6e**).* From the same experiment used to obtain **3e**, an additional product was isolated that corresponded to the hexanaphthalene **6e**. Light red powder, 38 mg, yield: 22%; mp 278−281 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.85−7.62 (m, 22H), 7.53−7.29 (m, 24H), 7.23 and 7.21 (two overlapping s, 1H + 1H), 2.17 (two overlapping s, 3H + 3H), 2.12 (s, 3H), 2.08 (s, 3H), 1.79 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.0, 139.4, 138.7, 137.6, 136.1, 135.4, 135.2, 133.4, 133.2, 132.3, 129.7, 129.5, 128.8, 128.6, 127.8, 126.7, 126.6, 126.1, 21.2, 20.1, 19.0 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{90}H_{66}$ $[M]^+$: 1146.5159, found: 1146.5198; IR (ATR) ν (cm^{-1}) 3038, 2918, 2856, 1371, 838, 760, 702.

*4,4″-Bis(2,3,5,6-tetramethylphenyl)-1,1′:4′,1″-ternaphthalene (**3f**).* Following the general procedure, ternaphthalene (114 mg, 0.300 mmol) was allowed to react with 1,2,4,5-tetramethylbenzene (161 mg, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 400:1 (hexane:AcOEt 50:1, R_f = 0.42). White powder, 60 mg, yield: 31%; mp 165−168 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.74−7.63 (m, 8H), 7.49−7.37 (m, 10H), 7.15 (s, 2H), 2.37 (two overlapping s, 6H + 6H), 1.96 (s, 6H), 1.91 (s, 6H) ppm; ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 140.2, 139.9, 138.62, 128.56, 137.5, 133.7, 133.3, 133.2, 133.14, 133.11, 132.4, 130.8, 127.9, 127.7, 127.1, 127.0, 126.5, 126.4, 126.33, 126.31, 125.98, 125.95, 20.4, 17.34, and 17.25 (partial overlap of the latter two signals) ppm; HRMS (MALDI-TOF) m/z calcd for $C_{50}H_{44}$ $[M]^+$: 644.3438, found 644.3441; IR (ATR) ν (cm^{-1}) 3039, 2918, 2863, 1466, 1369, 824, 761.

*4,4′′′′′-Bis(2,3,5,6-tetramethylphenyl)-1,1′:4′,1″:4″,1‴:4‴,1′′′′:4′′′′,1′′′′′:4′′′′′-sexinaphthalene (**6f**).* From the same experiment used to obtain **3f**, an additional product was isolated that corresponded to the hexanaphthalene **6f**. Peach powder, 52 mg, yield: 34%; mp 256−259 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.86−7.65 (m, 20H), 7.49−7.39 (m, 16H), 7.15 (s, 2H), 2.39−2.37 (two overlapping s, 6H + 6H), 1.97 (s, 6H), 1.93 (s, 6H); ^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) δ 140.29, 140.28, 139.9, 138.8, 138.7, 138.52, 138.48, 137.5, 133.8, 133.3, 133.14, 133.11, 132.5, 130.9, 128.0, 127.8, 127.1, 126.5, 126.4, 126.1, 126.0, 20.4, 17.4, 17.3; HRMS (MALDI-TOF) m/z calcd for $C_{80}H_{62}$ $[M]^+$: 1022.4852, found: 1022.4870; IR (ATR) ν (cm^{-1}) 3038, 2917, 1370, 826, 759.

*4,4‴-Dimesityl-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4a**).* Following the general procedure, quaternaphthalene (203 mg, 0.400 mmol) was allowed to react with mesitylene (192 mg, 222 μL, 1.600 mmol). Column chromatography: silica gel, hexane:AcOEt 70:1 (R_f = 0.29). Off-white powder, 271 mg, yield: 91%; mp 203−205 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.84−7.62 (m, 12H), 7.56−7.51 (m, 2H), 7.49−7.35 (m, 10H), 7.11−7.10 (two overlapping s, 2H + 2H), 2.46 (s, 6H), 2.08 (s, 6H), 2.04 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.0, 138.8, 138.7, 138.6, 138.5, 137.72, 137.71, 137.2, 133.4, 133.3, 133.2, 132.3, 128.3, 127.8, 127.2, 127.1, 126.5, 126.1, 126.0, 21.3, 20.7; HRMS (MALDI-TOF) m/z calcd for $C_{58}H_{46}$ $[M]^+$: 742.3594, found: 742.3605; IR (ATR) ν (cm^{-1}) 3040, 2952, 2917, 2861, 1571, 1375, 839, 762.

*4, 4‴-Bis(2,3,4,5,6-pentamethylphenyl)-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4b**).* Following the general procedure, quaternaphthalene (152 mg, 0.300 mmol) was allowed to react with 1,2,3,4,5-pentamethyl benzene (178 mg, 1.201 mmol). Column chromatography: silica gel, hexane:AcOEt 100:1, (hexane:AcOEt 70:1, R_f = 0.13). Off-white powder, 227 mg, yield: 95%; mp 212−215 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.83−7.37 (m, 24H), 2.44 (s, 6H), 2.38 (two overlapping s, 6H + 6H), 2.04 (s, 6H), 1.99 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 141.0, 138.82, 138.76, 138.54, 138.49, 137.6, 137.4, 134.4, 133.3, 133.2, 132.73, 132.69, 132.6, 128.0, 127.8, 127.1, 126.71, 126.69, 126.1, 125.9, 18.6, 18.55, 18.46, 17.1, 16.9, 16.8 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{62}H_{54}$ $[M]^+$: 798.4220, found: 798.4198; IR (ATR) ν (cm^{-1}) 3038, 2915, 1508, 1372, 839, 760.

*4,4‴-Bis(2,4,6-triethylphenyl)-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4c**).* Following the general procedure, quaternaphthalene (152 mg, 0.300 mmol) was allowed to react with 1,3,5-triethylbenzene (195 mg, 226 μL, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 60:1 (R_f = 0.26). Pale-yellow powder, 191 mg, yield: 77%; mp 165−168 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.83−7.62 (m, 12H), 7.55−7.49 (m, 4H), 7.43−7.33 (m, 8H), 7.16 (s, 2H), 7.15 (s, 2H), 2.80 (q, J = 7.5 Hz, 4H), 2.43−2.28 (m, 8H), 1.42 (t, J = 7.5 Hz, 6H), 1.14−1.06 (m, 12H); ^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) δ 143.8, 143.2, 143.1, 138.8, 138.7, 138.6, 138.5, 138.4, 137.7, 136.0, 133.23, 133.19, 133.15, 133.06, 127.79, 127.76, 127.66, 127.14, 127.07, 126.6, 126.1, 126.0, 125.9, 125.33, 125.30, 29.0, 27.03, 26.96, 15.9, 15.8, 15.7 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{64}H_{58}$ $[M]^+$: 826.4533, found 826.4538; IR (ATR) ν (cm^{-1}) 3040, 2962, 2931, 2870, 1458, 1421, 1372, 838, 761.

*4,4‴-Bis(4-tert-butyl-2,6-dimethylphenyl)-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4d**).* Following the general procedure, quaternaphthalene (152 mg, 0.300 mmol) was allowed to react with 5-*tert*-butyl-*m*-xylene (195 mg, 225 μL, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 70:1 (R_f = 0.22). White powder, 130 mg, yield: 52%; mp 219−222 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.81−7.62 (m, 12H), 7.52−7.48 (m, 4H), 7.40−7.37 (m, 8H), 7.27 (broad s, 4H), 2.11 (s, 6H), 2.07 (s, 6H), 1.45 (s, 18H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 150.3, 139.2, 139.1, 138.80, 138.75, 138.6, 138.51, 138.49, 137.6, 136.9, 136.66, 136.65, 133.4, 133.3, 133.2, 132.3, 128.0, 127.8, 127.1, 126.4, 126.04, 125.96, 124.5, 34.6, 31.7, 21.1 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{64}H_{58}$ $[M]^+$: 826.4533, found: 826.4551; IR (ATR) ν (cm^{-1}) 3040, 2953, 2865, 1481, 1373, 964, 837, 761.

*Octinaphthalene **8d**.* From the same experiment used to obtain **4d**, a trace amount of an additional product was isolated that corresponded to the octinaphthalene **8d**. HRMS (MALDI-TOF) m/z calcd for $C_{104}H_{82}$ $[M]^+$: 1330.6411, found: 1330.6428.

*4,4‴-Bis(2,4,6-trimethylbiphenyl-3-yl)-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4e**).* Following the general procedure, quaternaphthalene (152 mg, 0.300 mmol) was allowed to react with 2-phenylmesitylene (235 mg, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 50:1 (R_f = 0.35). White powder, 160 mg, yield: 60%; mp 250−253 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.80−7.61 (m, 14H), 7.53−7.28 (m, 20H), 7.22 (s, 1H), 7.21 (s, 1H), 2.16 (s, 6H), 2.12 (s, 3H), 2.07 (s, 3H), 1.79 (s, 3H), 1.75 (s, 3H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 141.8, 140.0, 139.4, 138.8, 138.5, 137.7, 137.6, 136.1, 135.4, 135.2, 133.4, 133.2, 132.3, 129.7, 129.6, 128.9, 128.6, 128.1, 127.7, 127.1, 126.6, 126.1, 21.2, 20.8, 19.0, 18.9 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{70}H_{54}$ $[M]^+$: 894.4220, found: 894.4224; IR (ATR) ν (cm^{-1}) 3038, 2949, 2918, 2860, 1441, 1372, 952, 838, 761.

*4,4‴-Bis(2,3,5,6-tetramethylphenyl)-1,1′:4′,1″:4″,1‴-quaternaphthalene (**4f**).* Following the general procedure, quaternaphthalene (152 mg, 0.300 mmol) was allowed to react with 1,2,4,5-tetramethylbenzene (161 mg, 1.200 mmol). Column chromatography: silica gel, hexane:AcOEt 50:1, R_f = 0.35. Pale yellow powder, 86 mg, yield: 37%; mp 212−215 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.82−7.64 (m, 12H), 7.51−7.35 (m, 12H), 7.15 (s, 2H), 2.38 (s, 6H), 2.37 (s, 6H), 1.96 (s, 6H), 1.92 (s, 6H); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$) δ 140.3, 140.0, 138.80, 138.76, 138.74, 138.56, 138.55, 137.55, 137.54, 133.8, 133.31, 133.27, 133.23, 133.20, 133.14, 133.11, 132.5, 130.9, 128.0, 127.78, 127.76, 127.1, 126.49, 126.46, 126.38, 126.35, 126.07, 126.02, 126.00, 125.98, 20.41, 20.39, 17.34, 17.32, 17.25 ppm; HRMS (MALDI-TOF) m/z calcd for $C_{60}H_{50}$ $[M]^+$: 770.3907, found: 770.3874; IR (ATR) ν (cm^{-1}) 3038, 2918, 2864, 1450, 1378, 826, 764.

*Octinaphthalene **8f**.* From the same experiment used to obtain **4f**, an additional product was isolated that corresponded to the octinaphthalene **8f**. Purple powder, 8 mg, yield: 4%; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.87−7.66 (m, 28H), 7.48−7.42 (m, 20H), 7.15 (s, 2H), 2.37 (s, 12H), 1.97 (s, 6H), 1.93 (s, 6H); HRMS (MALDI-TOF) m/z calcd for $C_{90}H_{66}$ $[M]^+$: 1274.5785, found: 1274.5852.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of the NMR and MS spectra, and the details of experiment optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/jo401001k | J. Org. Chem. 2013, 78, 8169−8175

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from Ministerio de Ciencia e Innovación (MICINN) of Spain (Projects CTQ2008-05409-C02-01, CTQ2009-07881, CTQ2011-22649 and Consolider Ingenio 2010 (CSD2007-00006)), a Ramón y Cajal scholarship to A.S. (MEC, Spain, RYC-2006-001425), DURSI-Generalitat de Catalunya (SGR2009-1441), and the China Scholarship Council (CSC scholarship) are gratefully acknowledged. We thank Dr. J. Orduna for the MALDI-TOF spectra.

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(21) Since the products were not volatile enough to be quantified by GC, the yields were measured by HPLC equipped with a Ph_2MeSi-functionalized column (Agilent); binaphthalene was used as an internal standard.
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