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Solvent free, phosphine free Pd-catalyzed annulations of aryl bromides with diarylacetylenes†

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Palladium nanoparticles and sodium acetate catalyze the reaction of aryl bromide with diarylacetylene to produce annulated products in good yield. One equivalent of PEG-600 serves as the solvent. This procedure is compatible with a wide variety of functional groups.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been the subject of popular research due to their high stability, enhanced ability to transport charges, fluorescent properties in the solid state, and their applications in organic optoelectronic devices and organic semiconductor luminescent materials.[1] The recent discovery of graphene, which can be regarded as giant PAHs, has further stimulated interest in this area.[2]

Several approaches have been reported in the literature for efficient assemblage of fused aromatic rings.[3] Among these, metal mediated annulation reactions have received particular attention in recent time.[4] Palladium mediated annulation[5] of aryl halide with alkynes, emerged as a useful route for the synthesis of a wide variety of polycyclic aromatics. An intriguing yet fascinating aspect of these palladium mediated reactions is the change in product selectivity as a function of reaction parameters[6] as depicted in Scheme 1.

In this report we describe the first example of nano-sized palladium catalyzed annulation reaction of aryl bromides with alkynes leading to 1,2,3,4-tetrasubstituted naphthalene derivatives.

There are several advantages of this reaction: it is free of phosphine, highly regio-selective, operationally simple, and produces good to excellent yield of product with high catalytic efficiency. No solvent other than PEG was necessary. An equivalent amount of PEG-600 (needed to prepare Pd-nanoparticles[7]) with respect to the aryl bromides was found to be adequate. Accordingly, this protocol appears to be highly competitive, if not superior to many of the methods reported earlier.[4e,5b,q]

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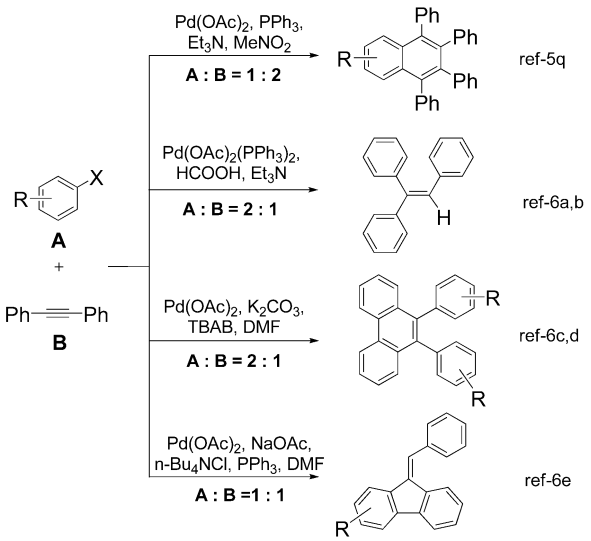
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of annulated products **3a–3y**, and X-ray crystal data of compound **3b** and **3i**. CCDC 928656 and 928657. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra41924j

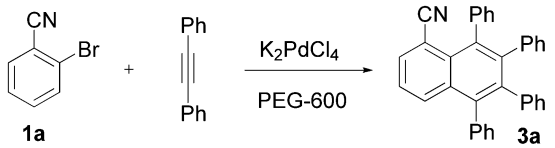
The Pd-nanoparticles were prepared by heating K_2PdCl_4 and PEG-600 at 70 °C for 15 mins. The colloidal solution was cooled to room temperature and it was found to be stable for several days. In a preliminary experiment, 2-bromobenzonitrile, diphenylacetylene and potassium carbonate were added to a dispersion of freshly prepared palladium nanoparticles (average size ~3.8 nm, see ESI†) and the mixture was stirred at 80 °C. 5,6,7,8-Tetraphenylnaphthalene-2-carbonitrile was formed as the major product along with some biaryls typically in 3–5 h (Table 1). No other product[6] was formed if the equivalents of arylbromide and alkyne were altered (Table 1, entries 13 and 14). It was eventually found that heating the substrates (aryl bromide and alkyne) at 80 °C with palladium nanoparticles and sodium acetate afforded excellent yield of desired annulated product in 2.5 h (entry 8, Table 1).

This reaction condition is compatible with a variety of functional groups such as keto, ester, cyano, nitro and carboxylic acid. Reactions with electron-deficient aryl bro-



Scheme 1

Table 1 Screening of conditions for annulation reactions



Entry	Ar–Br (eq)	Alkyne (eq)	K_2PdCl_4 (mol%)	Base	*T* (°C)	Time (h)	Yield (%)
1	1	2	3	K_2CO_3	80	3	30
2	1	2	5	K_2CO_3	80	3	50
3	1	2	5	K_2CO_3	80	5	57
4	1	2	5	K_2CO_3	100	5	55
5	1	2	3	NaOAc	r.t.	5	0
6	1	2	3	NaOAc	60	5	45
7	1	2	3	NaOAc	80	5	57
8[a]	**1**	**2**	**5**	**NaOAc**	**80**	**2.5**	**82**
9	1	2	5	NaOAc	80	5	82
10	1	2	5	KOAc	80	5	70
11	1	2	3	NaOH	60	5	0
12	1	2	5	NaOH	100	5	0
13	1	1	5	NaOAc	80	3	40
14	2	1	5	K_2CO_3	80	3	35

[a] Typical conditions subsequently used for most of the reactions studied.

mides afford product with better yield (Table 2) than those with electron-rich aryl bromides or bromoheterocycles (Table 3). There was no significant change in the yield of the annulation product as a result of positioning of substituents (*ortho*, *meta* and *para*).

It has been observed that the *ortho* and *para* substituted aryl bromides reacted with diphenylacetylene to provide only one product. In case of *meta* substituted aryl bromides (Table 2, entries 3, 4, 6, 9, 15, 17, and Table 3, entry 2) a small amount of the isomeric product (5–10%) was also formed. Again, the heteroaryl bromides or iodide (Table 3, entries 6, 7 and 9) furnished only one regioisomer. 3-Iodopyridine, on the other hand, produced about 5% of the regioisomeric product (Table 3, entry 7).

It may be pertinent, at this point, to compare some of these results with related reactions reported earlier using homogeneous palladium catalysis. It was reported earlier[8] that a similar reaction between methyl 2-iodobenzoate and diphenylacetylene yielded isocoumarin as the only identified product in moderate yield after a prolonged reaction. Under the present reaction condition, methyl 2-bromobenzoate and diphenylacetylene afforded tetrasubstituted naphthalene only (Table 2, entry 7). Use of a mild base like NaOAc and absence of a strong electrolyte like LiCl appears to have suppressed participation of the carbomethoxy group in the present case and consequently no isocoumerin was produced in the present study.

Another report described the reaction between aryl iodide and diphenylacetylene (2 equiv.) at 100 °C for 24 h in presence of PPh_3 or P(*o*-tol)$_3$ and Et_3N to produce naphthalene derivatives in moderate yield.[5q] In the Pd-nanoparticle catalyzed reaction described herein, the reaction is complete in 2.5–4 h at 80 °C in absence of any phosphine ligand. Moreover, the present protocol uses aryl bromides rather than aryl iodides. Nitro substituted aryl bromides (Table 2, entries 5 and 6) yielded desired products in 80–83%, at variance with an earlier observation.[9]

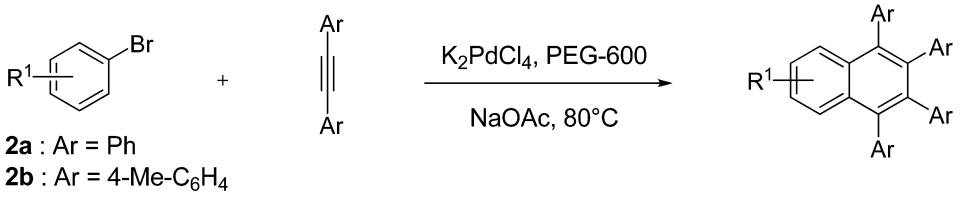
A possible mechanistic pathway is depicted in Scheme 2. After the first insertion of the acetylene, the intermediate can undergo a second insertion followed by *ortho*-metalation and finally reductive elimination (path A).[4c,5b,k] Alternatively, *ortho*-palladation might precede insertion of the second alkyne molecule (path B).[5b,k] In both pathways, intermediacy of Pd^{IV} has been invoked in keeping with current observations.[12]

If Pd^{IV} is not an intermediate, we could envisage an alternative pathway where the Pd^{II} is involved in an insertion reaction leading to C–C bond formation, followed by a β-hydride elimination to afford the desired product as shown in Scheme 3.

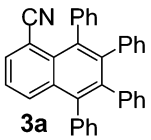
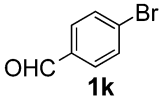
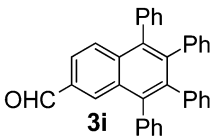
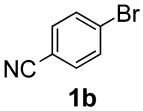
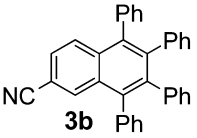
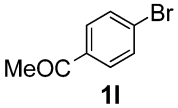
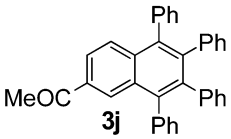
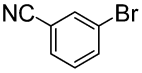
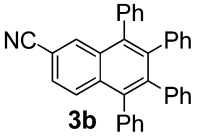
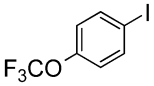
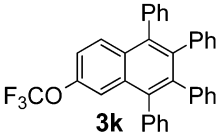
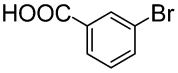
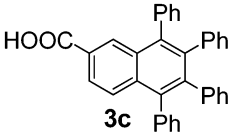
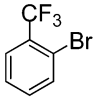
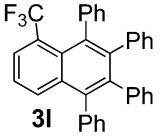
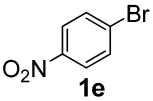
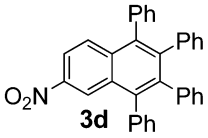
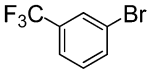
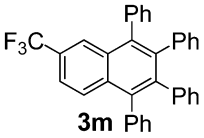
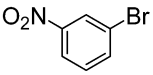
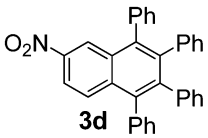
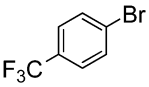
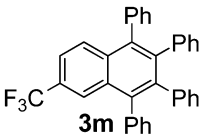
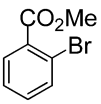
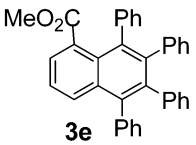
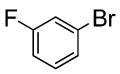
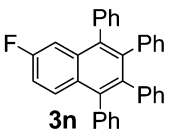
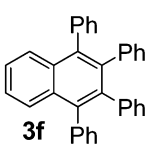
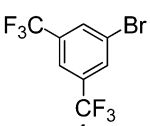
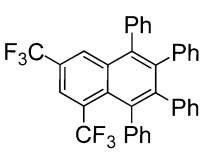
Conclusions

In conclusion, a new, highly regioselective, phosphine-free protocol was developed for efficient synthesis of densely substituted naphthalene derivatives. It is an operationally simple and mild method that uses essentially solvent-free (a small amount of PEG is used as a 'green' reagent[13] and stabilizer of nanoparticles) and ligand-less condition in tune with the current thrust on ''green'' technology.

Table 2 Pd-catalyzed annulation of aryl bromides[a]



2a : Ar = Ph
2b : Ar = 4-Me-C_6H_4

Entry	Ar-Br	Time (h)	Product	Yield (%)[b]	Entry	Ar-Br	Time (h)	Product	Yield (%)[b]
1	 **1a**	2.5	 **3a**	82	11	 **1k**	3	 **3i**	84
2	 **1b**	2.5	 **3b**	85	12	 **1l**	3	 **3j**	76
3	 **1c**	2.5	 **3b**	80	13	 **1m**	3	 **3k**	73
4	 **1d**	3	 **3c**	75	14	 **1n**	3	 **3l**	61
5	 **1e**	3	 **3d**	83	15[c]	 **1o**	3	 **3m**	72
6[c]	 **1f**	3	 **3d**	80	16	 **1p**	3	 **3m**	75
7	 **1g**	3	 **3e**	76	17[c]	 **1q**	3	 **3n**	62
8	 **1h**	3	 **3f**	70	18	 **1r**	3	 **3o**	73

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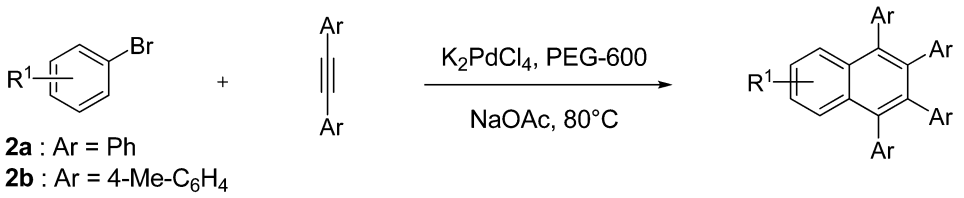
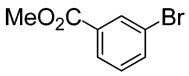
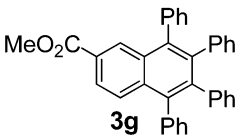
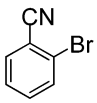
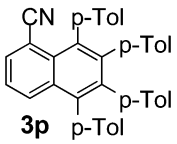
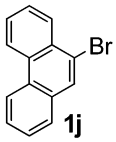
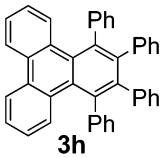
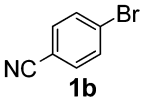
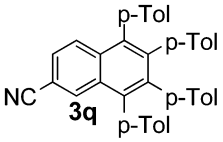


Entry	Ar-Br	Time (h)	Product	Yield (%)[b]	Entry	Ar-Br	Time (h)	Product	Yield (%)[b]
9	 **1i**	3	 **3g**	73	19	 **1a**	4	 **3p**	59
10	 **1j**	3	 **3h**	65	20	 **1b**	4	 **3q**	59

[a] Reaction condition: aryl bromide (1 mmol), diphenylacetylene (2 mmol), K_2PdCl_4 (5 mol%), NaOAc (2 mmol), PEG-600 (1.16 mmol), 80 °C under Argon. [b] Yield of the isolated product. [c] Isomeric products were obtained in 7%, 4% and 5% for entries 6, 15 and 17 respectively.

Experimental section

General comments

All chemicals were purchased from commercial suppliers (Aldrich, Merck, Avra and SRL) and used as received. All ^{1}H, ^{13}C NMR spectra were recorded on a Bruker-Avance DPX300 and Bruker-Avance III DPX500 for a $CDCl_3$ solution and reported in ppm (δ). Electrospray ionisation mass spectroscopy (ESI-MS) experiments were carried out on Microtek QtoF Micro YA 263 spectrometer in positive ion ESI mode.

General procedure for the Pd catalyzed annulation reaction

Weighted amount of K_2PdCl_4 (16 mg, 5 mol%) and PEG 600 (700 mg, 1.16 mmol) was heated at 70 °C for 15 min to form colloidal Pd. Then it was cooled to room temperature, aryl bromide (1 mmol) and diphenylacetylene (2 mmol) and NaOAc (182 mg, 2 eq) were added then stirred at 80 °C for the specified time. Then the reaction mixture was allowed to cool at room temperature, extracted with dichloromethane and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue thus obtained was purified by flash column chromatography on silica gel (230 ~ 400 mesh) with a mixture of ethyl acetate (2–10%) and petroleum ether as eluent.

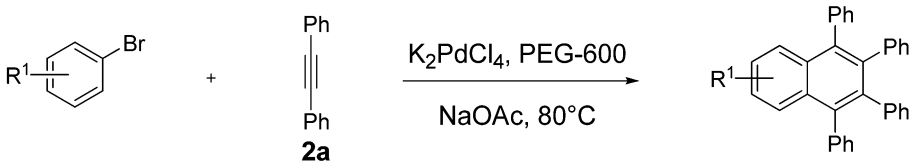
5,6,7,8-Tetraphenylnaphthalene-1-carbonitrile (3a). mp > 240 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.93–7.89 (m, 2H), 7.40 (dd, J = 7.0, 8.25 Hz, 1H), 7.31–7.17 (m, 10H), 6.87–6.79 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.4, 140.6, 139.8, 139.7, 139.5, 138.8, 138.6, 137.4, 137.2, 132.8, 132.7, 132.3, 131.3, 131.0, 130.8, 128.2, 127.9, 127.7, 127.1 126.8, 126.7, 125.84, 125.8, 124.8, 117.8, 110.4; IR (KBr): 3391, 3080, 3053, 3026, 2218, 1599, 1493, 1443, 1383, 1338, 1072, 1028 cm^{-1}; HRMS calcd for $C_{35}H_{24}N$ $[M + H]^+$: 458.1909 found 458.1902.

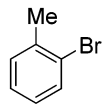
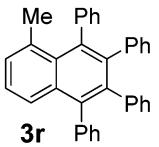
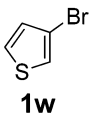
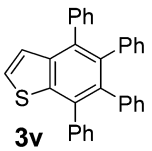
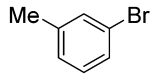
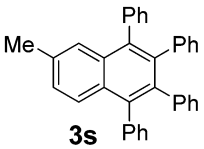
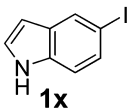
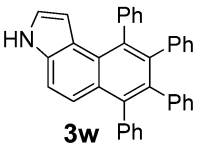
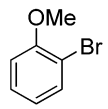
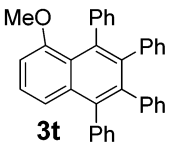
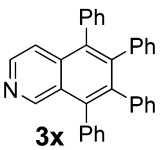
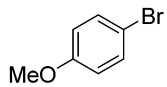
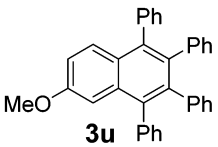
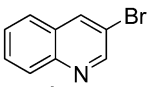
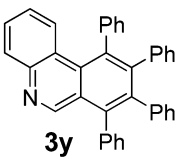
5,6,7,8-Tetraphenylnaphthalene-2-carbonitrile (3b). mp 230–232 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.04 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 8.25 Hz, 1H), 7.30–7.17 (m, 10H), 6.90–6.82 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.3, 140.9, 139.8, 139.7, 139.3, 138.9, 138.6, 138.2, 133.6, 133.5, 131.5, 131.2, 131.17, 131.13, 131.0, 128.5, 128.1, 127.9, 127.3, 127.1, 126.9, 126.7, 126.3, 125.9, 119.7, 109.4; IR (KBr): 3435, 3418, 3078, 3057, 3022, 1950, 1897, 1880, 1603, 1497, 1439, 1367, 1068, 1030 cm^{-1}; HRMS calcd for $C_{35}H_{23}NNa$ $[M + Na]^+$: 480.1728 found 480.1728.

5,6,7,8-Tetraphenylnaphthalene-2-carboxylic acid (3c). mp 235–238 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.42 (s, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.20–7.12 (m, 10H), 6.80–6.75 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 171.9, 141.8, 140.2, 140.1, 139.1, 138.7, 138.6, 134.8, 131.5, 131.3, 131.2, 131.1, 127.8, 127.6, 127.0, 126.8, 126.5, 125.8, 125.7, 125.4; IR (KBr): 3055, 3012, 2654, 2536, 1689, 1599, 1564, 1493, 1441, 1367, 1306, 1279, 1072, 1026 cm^{-1}; HRMS calcd for $C_{35}H_{24}O_2Na$ $[M + Na]^+$: 499.1674 found 499.1675.

6-Nitro-1,2,3,4-tetraphenylnaphthalene (3d)[14]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.60 (s, 1H), 8.11 (dd, J = 2.5, 9.25 Hz,1H), 7.76 (d, J = 9.5 Hz, 1H), 7.29–7.18 (m, 10H), 6.89–6.81 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 145.7, 142.9, 141.3, 140.8, 139.8, 139.7, 138.9, 138.6, 138.1, 134.8, 131.3, 131.2, 131.1, 130.9, 129.0, 128.1, 128.0, 127.4, 127.2, 126.9, 126.0, 125.9, 123.9, 119.2; HRMS calcd for $C_{34}H_{24}NO_2$ $[M + H]^+$: 478.1807 found 478.1802.

Table 3 Pd-catalyzed annulation of aryl bromides[a]



Entry	Ar-Br	Time (h)	Product	Yield (%)[b]	Entry	Ar-Br	Time (h)	Product	Yield (%)[b]
1	 **1s**	4	 **3r**	51[d]	5	 **1w**	3	 **3v**	62
2[c]	 **1t**	3	 **3s**	53[d]	6	 **1x**	4	 **3w**	52
3	 **1u**	4	 **3t**	46[d]	7[c]	 **1y**	4	 **3x**	60
4	 **1v**	4	 **3u**	49[d]	8	 **1z**	4	 **3y**	49

[a] Reaction conditions: aryl bromide (1 mmol), diphenylacetylene (2 mmol), K_2PdCl_4 (5 mol%), NaOAc (2 mmol), PEG-600 (1.16 mmol), 80 °C under Argon. [b] Yield of the isolated product. [c] Isomeric products were obtained in 5% and 10% for entries 2 and 7 respectively. [d] Homo-coupling products were isolated in 5%,7%,7% and 10% from corresponding aryl bromides in entries 1,2,3,4 respectively and identified after comparison with literature[7b,10,11] data.

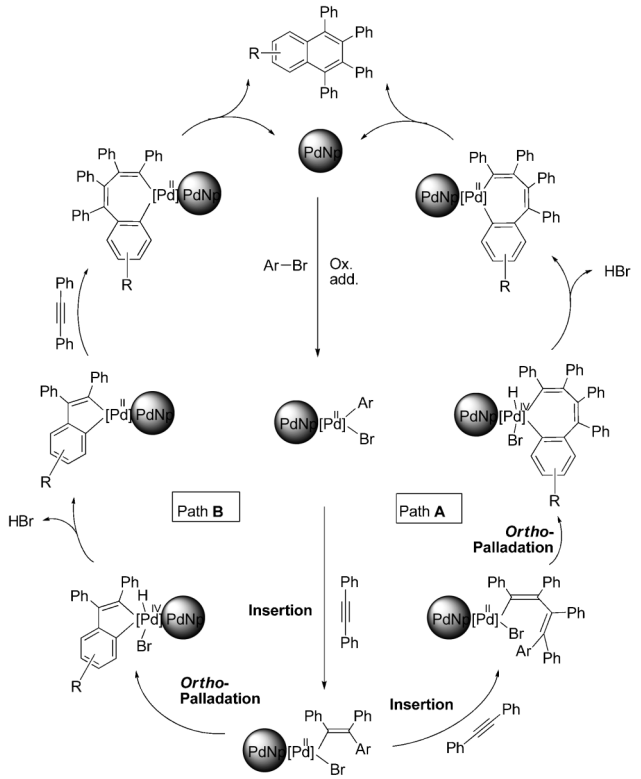
Methyl 5,6,7,8-tetraphenylnaphthalene-1-carboxylate (3e). mp 165–167 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.72 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 6.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H) 7.25–7.08 (m, 10H), 6.86–6.70 (m, 10H), 3.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 170.5, 141.3, 140.4, 140.1, 139.9, 139.5, 139.0, 137.2, 133.4, 132.4, 132.3, 131.4, 131.3, 131.1, 130.4, 128.7, 128.5, 127.7, 127.1, 126.8, 126.7, 126.6, 126.5, 125.6, 125.4, 124.6, 51.9; IR (KBr): 3078, 3055, 3043, 1722, 1599, 1564, 1495, 1443, 1271, 1192, 1134, 1086, 1026 cm^{-1} HRMS calcd for $C_{36}H_{26}O_2Na$ $[M + Na]^+$: 513.1830 found 513.1830.

1,2,3,4-Tetraphenylnaphthalene (3f)[4a]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.65 (dd, J = 3.5, 6.5 Hz, 2H), 7.39 (dd, J = 3.5, 6.5 Hz, 2H), 7.26–7.18 (m, 10H), 6.88–6.82 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 140.7, 139.7, 139.0, 138.6, 132.2, 131.4, 127.7, 127.1, 126.7, 126.6, 126.0, 125.5.

Methyl 5,6,7,8-tetraphenylnaphthalene-2-carboxylate (3g)[4a]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.44 (s, 1H), 7.97 (d, J = 9.5 Hz, 1H), 7.71 (d, J = 9.5 Hz, 1H), 7.29–7.21 (m, 10H), 6.90–6.85 (m, 10H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 167.4, 141.4, 140.26, 140.24, 140.0, 139.9, 139.2, 138.9, 138.6, 134.3, 131.5, 131.4, 131.3, 131.2, 130.1, 128.5, 127.8, 127.5, 126.9, 126.8, 125.7, 125.6, 125.3, 52.3.

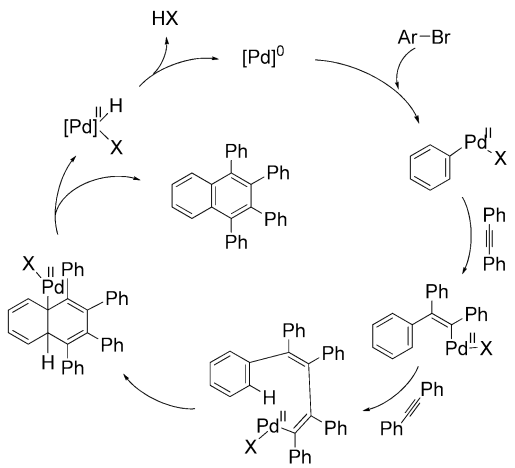
1,2,3,4-Tetraphenyltriphenylene (3h)[5i]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.44 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.13–7.08 (m, 10H), 7.04 (t, J = 7.75 Hz, 2H) 6.95–6.87 (m, 6H), 6.72 (d, J = 6.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.9, 140.53, 140.5, 137.3, 132.3, 131.7, 131.3, 130.9, 130.1, 128.1, 126.7, 126.5, 126.3, 125.6, 125.4, 123.3; HRMS calcd for $C_{42}H_{29}$ $[M + H]^+$: 533.2269 found 533.2264.

5,6,7,8-Tetraphenylnaphthalene-2-carbaldehyde (3i)[4a]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 10.01 (s, 1H), 8.18 (s, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.34–7.23 (m, 10H), 6.93–6.87 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 192.6, 142.3, 140.4, 140.2, 140.1, 139.9, 138.9, 138.7, 135.2, 134.3, 134.0, 131.7, 131.4, 131.3, 131.2, 131.1, 128.4, 127.9, 127.8, 127.1, 126.9, 126.88, 126.85, 125.84, 125.8, 122.4; HRMS calcd for $C_{35}H_{25}O$ $[M + H]^+$: 461.1905 found 461.1901.



Scheme 2 Plausible mechanism of annulation reaction.

1-(1,2,3,4-Tetraphenylnaphthalen-7-yl)ethanone (3j). mp 236–237 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 8.28 (s, 1H), 7.93 (dd, J = 1.5, 8.9 Hz, 1H), 7.69 (d, J = 8.9 Hz, 1H), 7.26–7.18 (m, 10H), 6.89–6.84 (m, 10H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ: 198.3, 141.6, 140.2, 140.1, 139.9, 139.1, 138.8, 138.6, 134.4, 134.3, 131.5, 131.3, 131.2, 131.1, 129.5, 127.8, 127.0, 126.8, 125.7, 123.8, 26.6; IR (KBr): 3055, 3026, 1682, 1603, 1495, 1441, 1420, 1367, 1354, 1294, 1246, 1072, 1026 cm^{-1}; HRMS calcd for $C_{36}H_{27}O$ $[M + H]^+$: 475.2062 found 475.2055.



Scheme 3

1,2,3,4-Tetraphenyl-6-(trifluoromethoxy)naphthalene (3k). mp 170–172 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.71 (d, J = 9.5 Hz, 1H), 7.49 (s, 1H), 7.29–7.21 (m, 11H), 6.90–6.83 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 147.2, 140.4, 140.3, 140.2, 139.6, 139.2, 138.9, 138.7, 138.6, 132.8, 131.33, 131.30, 131.2, 130.7, 129.5, 127.9, 127.8, 126.9, 126.86, 126.82, 126.7, 125.7, 125.6, 121.7, 119.8, 117.8; IR (KBr): 3060, 1620, 1601, 1491, 1443, 1261, 1221, 1171, 1157, 1072, 1026 cm^{-1}; HRMS calcd for $C_{35}H_{23}F_3ONa$ $[M + Na]^+$: 539.1599 found 539.1599.

5-(Trifluoromethyl)-1,2,3,4-tetraphenylnaphthalene (3l)[15]. mp 178–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.01 (d, J = 7.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.30–7.08 (m, 10H), 6.90–6.73 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.8, 140.5, 140.4, 140.2, 139.9, 139.5, 139.3, 137.2, 133.9, 132.8, 132.2, 131.4, 131.05, 131.0, 128.9, 128.23, 128.18, 128.12, 128.1, 127.8, 127.0, 126.9, 126.7, 126.5, 126.4, 126.2, 125.6, 125.4, 123.9, 123.2; IR (KBr): 3055, 3032, 1601, 1493, 1443, 1352, 1286, 1182, 1163, 1138, 1121, 1099,1074, 1061, 1024 cm^{-1}; HRMS calcd for $C_{35}H_{23}F_3Na$ $[M + Na]^+$: 523.1650 found 523.1649.

6-(Trifluoromethyl)-1,2,3,4-tetraphenylnaphthalene (3m)[4a]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.86 (s, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.18–7.09 (m, 10H), 6.78–6.72 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 141.2, 140.4, 140.1, 139.6, 139.0, 138.7, 138.6, 133.5, 131.3, 131.2, 128.5, 128.3, 127.9, 127.8, 127.6, 127.1, 126.9, 126.8, 125.8, 125.7, 125.6, 124.8, 124.78, 124.74, 123.5, 121.5; HRMS calcd for $C_{35}H_{23}F_3Na$ $[M + Na]^+$: 523.1650 found 523.1651.

6-Fluoro-1,2,3,4-tetraphenylnaphthalene (3n)[4a]. ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.43 (d, J = 9.0 Hz, 1H), 7.32–6.94 (m, 13H), 6.85–6.78 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 160.7, 158.7, 141.9, 141.8, 140.9, 140.3, 140.1, 139.9, 139.6, 138.5, 135.1, 135.0, 134.53, 134.51, 131.4, 131.3, 131.2, 130.2, 130.1, 127.7, 126.9, 126.7, 126.6, 126.1, 125.9, 125.8, 125.6, 125.5, 123.6, 123.5, 122.2, 122.1, 111.8, 111.6; HRMS calcd for $C_{34}H_{23}FNa$ $[M + Na]^+$: 473.1681 found 473.1683.

5,7-*Bis*(trifluoromethyl)-1,2,3,4-tetraphenylnaphthalene (3o). mp 195–197 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.11 (s, 1H), 8.08 (s, 1H), 7.26–7.01 (m, 10H), 6.86–6.80 (m, 6H), 6.74 (dd, J = 1.75, 7.75 Hz, 2H), 6.66–6.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 145.0, 141.3, 140.7, 140.5, 139.8, 139.6, 138.3, 137.6, 133.3, 132.7, 131.6, 131.4, 131.3, 130.8, 130.7, 130.2, 129.6, 129.5, 128.6, 128.4, 128.1, 127.5, 127.3, 126.9, 126.8, 126.7, 126.4, 126.3, 126.0, 125.9, 125.8, 125.7, 125.5, 125.3, 124.8, 124.6, 123.8, 123.7, 122.7 122.5; IR (KBr): 3099, 1680, 1653, 1558, 1497, 1319, 1286, 1267, 1163, 1128, 1068, 1027 cm^{-1}; HRMS calcd for $C_{36}H_{22}F_6Na$ $[M + Na]^+$: 591.1523 found 591.1524.

5,6,7,8-Tetra *p*-tolylnaphthalene-1-carbonitrile (3p). mp > 240 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.90–7.86 (m, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.08–7.02 (m, 8H), 6.68–6.66 (m, 8H), 2.34 (s, 3H), 2.31 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.7, 140.8, 139.4, 137.7, 137.4, 137.0, 136.99, 136.95, 136.3, 136.1, 135.8, 134.9, 134.8, 132.9, 132.7, 132.1, 131.1, 131.0, 130.8, 128.5, 128.4, 127.5, 127.3, 124.4, 117.9, 110.4, 21.6, 21.4, 21.2; IR (KBr): 3435, 3045, 3022, 2991, 2949, 2920, 2866, 2831, 2214, 1898, 1512, 1479, 1445, 1404, 1379, 1350, 1337, 1209,

1182, 1111, 1034, 1020 cm^{-1}; HRMS calcd for $C_{39}H_{32}N$ $[M + H]^+$: 514.2535 found 514.2529.

5,6,7,8-Tetra *p*-tolylnaphthalene-2-carbonitrile (3q). mp > 240 °C; ^1H NMR (500 MHz, $CDCl_3$): δ: 8.00 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.45 (dd, J = 1.5, 9.0 Hz, 1H), 7.08–7.02 (m, 8H), 6.68 (s, 8H), 2.34 (s, 3H), 2.32 (s, 3H) 2.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.5, 141.1, 139.2, 138.7, 137.1, 136.9, 136.6, 136.4, 135.8, 135.4, 135.03, 135.0, 133.8, 133.6, 131.6, 131.1, 131.0, 130.9, 130.8, 128.7, 128.6, 128.4, 127.6, 127.5, 125.9, 119.9, 108.9, 21.4, 21.2; IR (KBr): 3045, 3020, 2993, 2968, 2729, 2221, 1900, 1609, 1558, 1514, 1487, 1441, 1402, 1371, 1292, 1213, 1184, 1107, 1080, 1035, 1024 cm^{-1}; HRMS calcd for $C_{39}H_{31}NNa$ $[M + Na]^+$: 536.2354 found 536.2355.

5-Methyl-1,2,3,4-tetraphenylnaphthalene (3r)[4a]. ^1H NMR (500 MHz, $CDCl_3$): δ: 7.52 (dd, J = 1.5, 8.0 Hz, 1H), 7.28–7.10 (m, 12H), 6.93–6.75 (m, 10H), 1.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 143.1, 140.9, 140.8, 140.6, 140.5, 138.6, 138.2, 136.1, 131.8, 131.5, 131.4, 131.3, 131.1, 130.4, 127.6, 126.9, 126.6, 126.5, 126.4, 126.3, 125.6, 125.3, 125.1, 25.4; HRMS calcd for $C_{35}H_{27}$ $[M + H]^+$: 447.2113 found 447.2108.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (3s)[4a]. ^1H NMR (500 MHz, $CDCl_3$): δ: 7.52 (d, J = 9.0 Hz, 1H), 7.39 (s, 1H), 7.25–7.16 (m, 11H), 6.86–6.79 (m, 10H) 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 140.8, 140.7, 139.9, 139.1, 138.3, 138.1, 137.9, 135.7, 132.3, 131.5, 131.48, 131.43, 131.2, 130.4, 128.2, 127.6, 127.0, 126.6, 126.5, 125.9, 125.4, 21.9; HRMS calcd for $C_{35}H_{27}$ $[M + H]^+$: 447.2113 found 447.2106.

5-Methoxy-1,2,3,4-tetraphenylnaphthalene (3t). mp > 200 °C; ^1H NMR (500 MHz, $CDCl_3$): δ: 7.31 (t, J = 8.0 Hz, 1H), 7.26–7.17 (m, 6H), 7.11–7.02 (m, 5H), 6.85–6.77 (m, 11H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 157.4, 144.0, 140.7, 140.3, 140.0, 139.6, 138.3, 136.8, 134.3, 131.6, 131.4, 131.3, 129.9, 127.6, 126.6, 126.5, 126.3, 126.1, 125.3, 125.1, 124.9, 123.9, 120.3, 107.1, 55.9; IR (KBr): 3074, 3057, 300, 1599, 1560, 1547, 1491, 1450, 1441, 1425, 1373, 1354, 1257, 1234, 1115, 1057, 1026, 1003 cm^{-1}; HRMS calcd for $C_{35}H_{27}O$ $[M + H]^+$: 463.2062 found 463.2056.

6-Methoxy-1,2,3,4-tetraphenylnaphthalene (3u)[4a]. ^1H NMR (500 MHz, $CDCl_3$): δ: 7.55 (d, J = 9.0 Hz, 1H), 7.25–7.15 (m, 10H), 7.06 (dd, J = 2.5, 9.0 Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H) 6.86–6.79 (m, 10H), 3.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ: 157.7, 140.8, 140.7, 139.9, 139.8, 139.5, 138.5, 137.4, 136.9, 133.4, 132.4, 131.6, 131.4, 131.3, 128.8, 127.7, 127.6, 126.6, 126.5, 125.4, 125.3, 118.1, 105.8, 55.3; HRMS calcd for $C_{35}H_{26}ONa$ $[M + Na]^+$: 485.1881 found 485.1881.

4,5,6,7-Tetraphenylbenzo[*b*]thiophene (3v)[5b]. ^1H NMR (500 MHz, $CDCl_3$): δ: 7.37 (d, J = 5.5 Hz, 1H), 7.31–7.15 (m, 11H), 6.89–6.83 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 140.8, 140.4, 140.3, 140.1, 140.0, 138.6, 137.9, 137.1, 136.1, 135.2, 131.9, 131.8, 130.7, 130.1, 128.1, 127.7, 127.2, 126.85, 126.83, 126.6, 125.6, 125.5, 124.8.

6,7,8,9-Tetraphenyl-3*H*-benzo[*e*]indole (3w). mp > 240 °C; ^1H NMR (500 MHz, $CDCl_3$): δ: 8.33 (s, 1H), 7.44 (s, 2H), 7.29–7.17 (m, 10H), 6.91–6.79 (m, 11H), 5.12 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.5, 141.2, 141.1, 140.9, 139.5, 139.2, 137.1, 136.7, 133.5, 131.7, 131.6, 131.3, 128.3, 128.1, 127.5, 126.9, 126.7, 126.5, 126.4, 126.3, 125.2, 125.1, 122.6, 122.5, 120.9, 112.9, 106.2; IR (KBr): 3400, 3360, 3076, 3055, 3022, 1599, 1485, 1441, 1385, 1367, 1238, 1099, 1070, 1026 cm^{-1}; HRMS calcd for $C_{36}H_{26}N$ $[M + H]^+$: 472.2065 found 472.2060.

5,6,7,8-Tetraphenylisoquinoline (3x)[4a]. ^1H NMR (500 MHz, $CDCl_3$): δ: 9.04 (s, 1H), 8.44 (d, J = 5.5 Hz, 1H), 7.48 (d, J = 6.0 Hz, 1H), 7.29–7.17 (m, 10H), 6.90–6.81 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 151.4, 143.8, 142.1, 140.9, 139.7, 139.5, 139.4, 137.9, 137.7, 137.4, 135.1, 131.3, 131.26, 131.2, 130.9, 127.98, 127.9, 127.3, 127.2, 126.9, 126.1, 125.9, 119.6; HRMS calcd for $C_{33}H_{24}N$ $[M + H]^+$: 434.1903 found 434.1903.

7,8,9,10-Tetraphenylphenanthridine (3y). mp > 200 °C; ^1H NMR (500 MHz, $CDCl_3$): δ: 9.01 (s, 1H), 8.03(d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.25 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.23–7.07 (m, 10H), 7.02 (t, J = 7.75 Hz, 1H) 6.82–6.70 (m,10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 152.9, 145.7, 145.2, 141.9, 140.9, 140.7, 139.9, 139.7, 138.0, 137.9, 131.5, 131.2, 131.1, 130.9, 130.7, 129.9, 128.7, 128.1, 127.8, 127.6, 127.2, 127.1, 126.9, 126.7, 125.8, 125.7, 125.6, 124.5; IR (KBr): 3055, 3024, 1599, 1585, 1493, 1439, 1394, 1332, 1072, 1026 cm^{-1}; HRMS calcd for $C_{37}H_{26}N$ $[M + H]^+$: 484.2065 found 484.2060.

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