One-Pot Synthesis of 1,4-Diarylnaphthalenes via a Wittig–Horner Reaction/ [4+2] Cycloaddition/Dehydrogenation Sequence

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Abstract: A one-pot synthesis of 1,4-diarylnaphthalenes from cinnamaldehydes, dimethyl benzylphosphonates, and benzenediazonium-2-carboxylate is described. The tandem process involves the Wittig–Horner reaction of the cinnamaldehyde with the benzylphosphonate, [4+2] cycloaddition of the thus-formed diene with benzyne, and subsequent dehydrogenation. The procedure is general and efficient and the substrates are readily available.

Key words: diphenylnaphthalene, tandem reaction, Wittig–Horner reaction, cycloaddition, benzyne

Substituted naphthalenes are very important building blocks for the synthesis of pharmaceuticals[1] and polycyclic aromatic materials.[2] Traditionally, the regioselective construction of substituted naphthalenes has been carried out by the stepwise introduction of substituents through electrophilic substitution.[3] More modern achievements in the regioselective construction of substituted naphthalenes include annulation of benzene molecules bearing an unsaturated carbonyl side chain,[4] cross-coupling reactions of naphthalenes[5a] or halonaphthalenes,[5b,c] reactions of aryl halides with alkynes,[6] cyclization of alkynes and benzynes,[7] annulations via Fisher carbenes,[8] and the coupling of alkynes with arylacetaldehydes or aryl epoxides.[9] However, these methods involve either expensive transition metal catalysts or multistep procedures. In some cases, the reactions produce mixtures of isomers.

Benzynes are highly reactive intermediates that have found numerous applications in organic synthesis.[10] The dienophilic nature of the benzynes have been exploited in [2+2] and [4+2] cycloaddition reactions.[11] Benzenediazonium-2-carboxylate (**1**) is a benzyne precursor (Figure 1) that is easily prepared from anthranilic acid.[12] Previously, we reported a tandem reaction of aromatic aldehydes and anilines with benzyne generated in situ from **1** for the preparation of 6-arylphenanthridines.[13] In connection with this work, we herein report a one-pot tandem approach to 1,4-diarylnaphthalenes from benzenediazonium-2-carboxylate, cinnamaldehydes, and dimethyl benzylphosphonates.

In our initial experiments, we examined the model reaction using **1** as the benzyne precursor, cinnamaldehyde (**2a**), and dimethyl benzylphosphonate (**3a**). It was anticipated that the Wittig–Horner reaction of **2a** and **3a** would result in the diene **5**, which would subsequently react with the in situ generated benzyne via a tandem [4+2] cycloaddition[11a] and dehydrogenation process to afford 1,4-diphenylnaphthalene (**4a**) (Scheme 1). We found that **2a** reacted with **3a** in the presence of excess potassium *tert*-butoxide (2.6 equiv) in anhydrous tetrahydrofuran, followed by treatment with excess **1** (2.5 equiv) in 1,2-dichloroethane at 65–75 °C to give the desired product **4a** in 63% isolated yield (Table 1, entry 1).

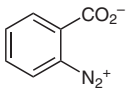

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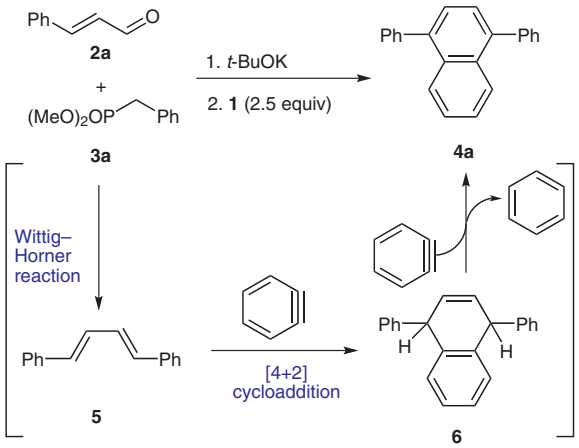
Figure 1



Scheme 1 Synthesis of 1,4-diphenylnaphthalene (**4a**)

With this result in hand, we went on to study the scope of the methodology. Using the established reaction conditions, a variety of cinnamaldehydes **2** and dimethyl benzylphosphonates **3** were investigated. As shown in Table 1, all of the reactions generated the desired 1,4-diarylnaphthalenes **4**. The yields of the isolated products ranged from 55–85%. The benzylphosphonates substituted with strongly electron-donating groups (Table 1, entries 3, 7, 11, 16, and 21) gave higher yields than those with strongly electron-withdrawing groups (Table 1, entries 5 and 13). The products were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS, and HRMS spectra.

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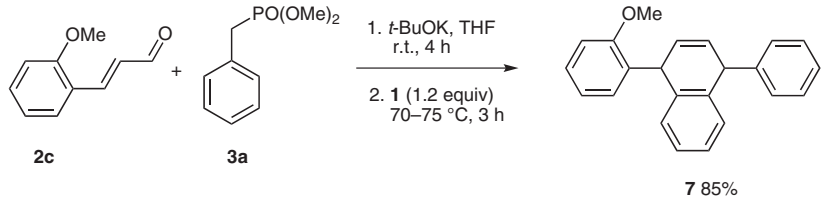
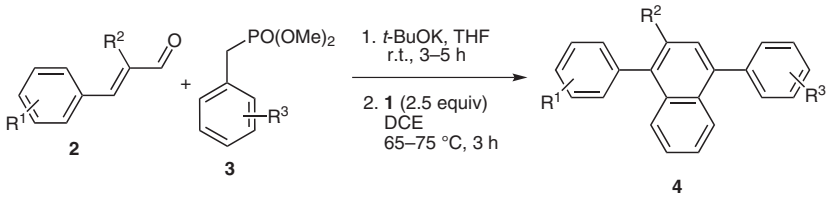


Scheme 2 Synthesis of the 1,4-dihydronaphthalene intermediate **7**

Table 1 One-Pot Synthesis of Substituted 1,4-Diarylnaphthalenes **4**[a]



Entry	R^1	R^2	R^3	Product	Yield[b] (%)
1	H	H	H	**4a**	63
2	H	H	3-Me	**4b**	64
3	H	H	4-MeO	**4c**	73
4	H	H	4-Br	**4d**	61
5	H	H	4-NO_2	**4e**	55
6	H	Me	H	**4f**	69
7	H	Me	4-MeO	**4g**	75
8	H	Me	4-Br	**4h**	68
9	4-MeO	H	H	**4c**	72
10	4-MeO	H	3-Me	**4i**	78
11	4-MeO	H	4-MeO	**4j**	82
12	4-MeO	H	4-Br	**4k**	70
13	4-MeO	H	4-NO_2	**4l**	60
14	2-MeO	H	H	**4m**	79
15	2-MeO	H	3-Me	**4n**	76
16	2-MeO	H	4-MeO	**4o**	85
17	2-MeO	H	4-Br	**4p**	73
18	2-Me	H	H	**4q**	68
19	2-Me	H	4-Br	**4r**	65
20	2-Cl	H	3-Me	**4s**	66
21	2-Cl	H	4-MeO	**4t**	74
22	2-Cl	H	4-Br	**4u**	70

[a] Reaction conditions: (1) **2** (5 mmol), **3** (5 mmol), *t*-BuOK (13 mmol), THF (45 mL), r.t., 3–5 h; (2) **1** (12.5 mmol), DCE (60 mL), 65–75 °C, 3 h.
[b] Isolated yield.

We obtained the 1,4-dihydronaphthalene intermediate **7** as a mixture of *cis*- and *trans*-isomers by using 1.2 equivalents of benzyne to perform the reaction (Scheme 2). This result supports the proposed mechanism as shown in Scheme 1.

In conclusion, we have developed a one-pot synthesis of 1,4-diarylnaphthalenes from cinnamaldehydes, dimethyl benzylphosphonates, and benzenediazonium-2-carboxylate. The tandem process involves the Wittig–Horner reaction of cinnamaldehyde with benzylphosphonate, [4+2] cycloaddition of the thus formed diene with benzyne, and subsequent dehydrogenation. The procedure is general and efficient and the substrates are readily available. Considering the importance of naphthalene derivatives, this method should find wide application in the synthesis of polycyclic aromatic hydrocarbons.

IR spectra were obtained on a FT-IR spectrophotometer. NMR spectra were recorded for ^{1}H NMR at 500 MHz, for ^{13}C NMR at 125 MHz. For ^{1}H NMR, TMS served as internal standard (δ = 0 ppm). For ^{13}C NMR, $CDCl_3$ was used as internal standard (δ = 77.25 ppm) and spectra were obtained with complete proton decoupling. LR-MS and HRMS were obtained using EI ionization. Melting points were measured with micro melting point apparatus.

1,4-Diarylnaphthalenes 4; General Procedure

Cinnamaldehyde **2** (5 mmol) and dimethyl benzylphosphonate **3** (5 mmol) were dissolved in anhyd THF (20 mL). The resulting soln was added dropwise slowly to *t*-BuOK (13 mmol) in anhyd THF (25 mL) at 0 °C, the mixture was stirred at r.t. for 3–5 h. To the mixture was added a suspension of benzenediazonium-2-carboxylate (**1**, 12.5 mmol) in DCE (60 mL) at 65–75 °C over a period of 3 h. The solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1) to afford pure **4**, which was recrystallized (hexane–EtOAc).

1,4-Diphenylnaphthalene (4a)

White solid; mp 136 °C (Lit.[2] 135–136 °C).

IR (KBr): 1599, 1491, 1446, 1384, 1157 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 2 H), 7.54–7.41 (m, 14 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 140.1, 132.2, 130.4, 128.6, 127.5, 126.71, 126.65, 126.1.

MS (EI): *m*/*z* (%) = 280 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{16}$: 280.1252; found: 280.1246.

1-Phenyl-4-(3-tolyl)naphthalene (4b)

White solid; mp 88–89 °C.

IR (KBr): 1602, 1490, 1442, 1381, 1155 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98–7.95 (m, 2 H), 7.55–7.49 (m, 4 H), 7.46–7.38 (m, 6 H), 7.35–7.33 (m, 2 H), 7.26 (d, *J* = 7.4 Hz, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 141.0, 140.2, 140.0, 138.2, 132.24, 132.18, 131.1, 130.4, 128.5, 128.4, 128.3, 127.5, 126.75, 126.70, 126.6, 126.05, 126.03, 21.8.

MS (EI): *m*/*z* (%) = 294 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}$: 294.1409; found: 294.1403.

1-(4-Methoxyphenyl)-4-phenylnaphthalene (4c)

White solid; mp 134–135 °C.

IR (KBr): 1607, 1506, 1442, 1387, 1285, 1241, 1179 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.95 (m, 2 H), 7.55–7.42 (m, 11 H), 7.06–7.05 (m, 2 H), 3.91 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 141.1, 139.8, 139.7, 133.4, 132.4, 132.2, 131.4, 130.4, 128.5, 127.5, 126.74, 126.70, 126.68, 126.62, 126.04, 126.01, 114.0, 55.6.

MS (EI): *m*/*z* (%) = 310 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}O$: 310.1358; found: 310.1351.

1-(4-Bromophenyl)-4-phenylnaphthalene (4d)

White solid; mp 118–119 °C.

IR (KBr): 1586, 1490, 1443, 1382, 1170 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01–7.99 (m, 1 H), 7.94–7.92 (m, 1 H), 7.68–7.66 (m, 2 H), 7.57–7.52 (m, 4 H), 7.50–7.42 (m, 7 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.9, 140.5, 140.0, 138.7, 132.2, 132.0, 131.9, 131.7, 130.3, 128.6, 127.6, 126.8, 126.7, 126.34, 126.26, 121.8.

MS (EI): *m*/*z* (%) = 358 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{15}Br$: 358.0357; found: 358.0359.

1-(4-Nitrophenyl)-4-phenylnaphthalene (4e)

Yellow solid; mp 160–161 °C.

IR (KBr): 1594, 1509, 1441, 1387, 1343 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.38–8.37 (m, 2 H), 8.00–7.98 (m, 1 H), 7.85–7.83 (m, 1 H), 7.72–7.70 (m, 2 H), 7.53–7.46 (m, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.0, 147.5, 141.5, 140.6, 137.6, 132.3, 131.6, 131.3, 130.3, 128.7, 127.8, 127.0, 126.9, 126.8, 126.62, 126.56, 125.8, 123.9.

MS (EI): *m*/*z* (%) = 325 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{15}NO_2$: 325.1103; found: 325.1107.

2-Methyl-1,4-diphenylnaphthalene (4f)

White solid; mp 120–121 °C.

IR (KBr): 1589, 1495, 1441, 1387 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 1 H), 7.55–7.43 (m, 9 H), 7.37 (s, 1 H), 7.34–7.31 (m, 4 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 140.1, 139.7, 138.0, 133.5, 132.9, 130.5, 130.4, 129.9, 128.7, 128.5, 127.5, 127.3, 126.8, 126.1, 125.9, 125.1, 21.1.

MS (EI): *m*/*z* (%) = 294 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}$: 294.1409; found: 294.1402.

4-(4-Methoxyphenyl)-2-methyl-1-phenylnaphthalene (4g)

White solid; mp 120–121 °C.

IR (KBr): 1608, 1505, 1463, 1389, 1286, 1244, 1171 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 1 H), 7.52–7.43 (m, 6 H), 7.35–7.30 (m, 5 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 3.89 (s, 3 H), 2.25 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 140.1, 139.3, 137.8, 133.6, 133.4, 132.9, 131.4, 130.6, 130.5, 129.9, 128.7, 127.3, 126.7, 126.2, 125.9, 125.0, 114.0, 55.6, 21.1.

MS (EI): *m*/*z* (%) = 324 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{20}O$: 324.1514; found: 324.1510.

4-(4-Bromophenyl)-2-methyl-1-phenylnaphthalene (4h)

White solid; mp 145–146 °C.

IR (KBr): 1599, 1494, 1441, 1389 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 1 H), 7.64–7.62 (m, 2 H), 7.53–7.50 (m, 2 H), 7.48–7.40 (m, 4 H), 7.36–7.29 (m, 5 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 139.9, 138.5, 138.3, 133.6, 132.9, 132.0, 131.7, 130.4, 130.1, 129.9, 128.7, 127.4, 126.9, 126.1, 125.8, 125.3, 121.7, 21.0.

MS (EI): *m*/*z* (%) = 372 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}Br$: 372.0514; found: 372.0510.

1-(4-Methoxyphenyl)-4-(3-tolyl)naphthalene (4i)
White solid; mp 105–106 °C.

IR (KBr): 1605, 1504, 1445, 1387, 1287, 1246, 1171 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 2 H), 7.46–7.37 (m, 7 H), 7.34–7.32 (m, 2 H), 7.25–7.23 (m, 1 H), 7.05–7.03 (m, 2 H), 3.89 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 139.9, 139.6, 138.1, 133.5, 132.4, 132.3, 131.4, 131.1, 128.4, 128.2, 127.5, 126.72, 126.68, 126.65, 126.0, 55.6, 21.8.

MS (EI): *m*/*z* (%) = 324 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{20}O$: 324.1514; found: 324.1507.

1,4-Bis(4-methoxyphenyl)naphthalene (4j)
White solid; mp 155–156 °C.

IR (KBr): 1609, 1509, 1445, 1383, 1284, 1246, 1175 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02–8.00 (m, 2 H), 7.49–7.44 (m, 8 H), 7.09–7.06 (m, 4 H), 3.92 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 139.4, 133.5, 132.4, 131.4, 126.74, 126.67, 125.9, 114.0, 55.6.

MS (EI): *m*/*z* (%) = 340 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{20}O_2$: 340.1463; found: 340.1462.

1-(4-Bromophenyl)-4-(4-methoxyphenyl)naphthalene (4k)
White solid; mp 176–177 °C.

IR (KBr): 1605, 1504, 1458, 1385, 1285, 1242, 1174 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.98 (m, 1 H), 7.89–7.88 (m, 1 H), 7.63 (d, *J* = 8.3 Hz, 2 H), 7.46–7.39 (m, 8 H), 7.05 (d, *J* = 8.6 Hz, 2 H), 3.90 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 140.2, 140.0, 138.4, 133.2, 132.4, 132.03, 131.96, 131.7, 131.4, 126.8, 126.69, 126.66, 126.3, 126.25, 126.16, 121.7, 55.6.

MS (EI): *m*/*z* (%) = 388 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}BrO$: 388.0463; found: 388.0457.

1-(4-Methoxyphenyl)-4-(4-nitrophenyl)naphthalene (4l)
Yellow solid; mp 160–161 °C.

IR (KBr): 1596, 1514, 1443, 1347, 1288, 1243, 1176 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41–8.39 (m, 2 H), 8.06–8.05 (m, 1 H), 7.87–7.86 (m, 1 H), 7.74–7.73 (m, 2 H), 7.52–7.47 (m, 6 H), 7.10–7.09 (m, 2 H), 3.94 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 148.1, 147.4, 141.2, 137.2, 132.9, 132.4, 131.6, 131.4, 131.2, 127.1, 126.9, 126.7, 126.6, 126.4, 125.7, 123.9, 114.1, 55.6.

MS (EI): *m*/*z* (%) = 355 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}NO_3$: 355.1208; found: 355.1206.

1-(2-Methoxyphenyl)-4-phenylnaphthalene (4m)
White solid; mp 131–132 °C.

IR (KBr): 1599, 1488, 1461, 1386, 1285, 1252, 1173 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95–7.93 (m, 1 H), 7.66–7.64 (m, 1 H), 7.55–7.32 (m, 11 H), 7.09–7.05 (m, 2 H), 3.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6, 141.3, 140.0, 136.8, 132.7, 132.3, 131.9, 130.5, 129.9, 129.3, 128.5, 127.4, 127.1, 127.0, 126.8, 126.5, 125.9, 125.7, 120.9, 111.3, 55.9.

MS (EI): *m*/*z* (%) = 310 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}O$: 310.1358; found: 310.1354.

1-(2-Methoxyphenyl)-4-(3-tolyl)naphthalene (4n)
Colorless oil.

IR (KBr): 1602, 1492, 1462, 1386, 1293, 1249, 1181 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–7.94 (m, 1 H), 7.64–7.63 (m, 1 H), 7.44–7.34 (m, 9 H), 7.32–7.30 (m, 1 H), 7.07–7.02 (m, 2 H), 3.69 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.5, 141.2, 140.1, 138.0, 136.7, 132.6, 132.3, 131.9, 131.2, 129.9, 129.2, 128.3, 128.1, 127.5, 127.1, 127.0, 126.65, 126.56, 125.8, 125.7, 120.8, 111.2, 55.8, 21.8.

MS (EI): *m*/*z* (%) = 324 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{20}O$: 324.1514; found: 324.1509.

1-(2-Methoxyphenyl)-4-(4-methoxyphenyl)naphthalene (4o)
White solid; mp 113–114 °C.

IR (KBr): 1598, 1507, 1461, 1387, 1283, 1246, 1176 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 1 H), 7.64–7.63 (m, 1 H), 7.48–7.31 (m, 8 H), 7.10–7.03 (m, 4 H), 3.88 (s, 3 H), 3.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 157.6, 139.7, 136.5, 133.6, 132.7, 132.3, 132.1, 131.5, 129.9, 129.2, 127.1, 127.0, 126.7, 126.5, 125.8, 125.7, 120.9, 114.0, 111.3, 55.9, 55.6.

MS (EI): *m*/*z* (%) = 340 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{20}O_2$: 340.1463; found: 340.1456.

1-(4-Bromophenyl)-4-(2-methoxyphenyl)naphthalene (4p)
White solid; mp 124–125 °C.

IR (KBr): 1604, 1491, 1459, 1386, 1296, 1238 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88–7.86 (m, 1 H), 7.65–7.61 (m, 3 H), 7.43–7.37 (m, 7 H), 7.32–7.30 (m, 1 H), 7.09–7.05 (m, 2 H), 3.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.5, 140.2, 138.7, 137.3, 132.7, 132.2, 132.1, 131.7, 129.7, 129.4, 127.15, 127.08, 126.7, 126.1, 125.9, 121.7, 120.9, 111.3, 55.9.

MS (EI): *m*/*z* (%) = 388 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}BrO$: 388.0463; found: 388.0465.

1-Phenyl-4-(2-tolyl)naphthalene (4q)
White solid; mp 112–113 °C.

IR (KBr): 1590, 1495, 1440, 1386 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 1 H), 7.55–7.43 (m, 9 H), 7.37–7.31 (m, 5 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 140.1, 139.7, 138.1, 133.6, 132.9, 130.5, 130.4, 129.9, 128.7, 128.5, 127.5, 127.3, 126.8, 126.2, 125.9, 125.1, 21.0.

MS (EI): *m*/*z* (%) = 294 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{18}$: 294.1409; found: 294.1405.

1-(4-Bromophenyl)-4-(2-tolyl)naphthalene (4r)
White solid; mp 142–143 °C.

IR (KBr): 1599, 1493, 1440, 1388 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 1 H), 7.64–7.62 (m, 2 H), 7.53–7.40 (m, 6 H), 7.35–7.29 (m, 5 H), 2.25 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 139.9, 138.5, 138.4, 133.6, 132.9, 132.0, 131.7, 130.4, 130.1, 129.9, 128.7, 127.4, 126.9, 126.1, 125.8, 125.3, 121.7, 21.0.

MS (EI): *m*/*z* (%) = 372 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}Br$: 372.0514; found: 372.0517.

1-(2-Chlorophenyl)-4-(3-tolyl)naphthalene (4s)
White solid; mp 110–111 °C.

IR (KBr): 1603, 1508, 1433, 1386, 1157 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 1 H), 7.56–7.53 (m, 2 H), 7.47–7.46 (m, 1 H), 7.43–7.34 (m, 9 H), 7.26–7.25 (m, 1 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.91, 140.87, 139.7, 138.1, 137.1, 134.5, 132.5, 132.2, 132.0, 131.2, 129.8, 129.2, 128.4, 128.3, 127.5, 126.91, 126.88, 126.8, 126.4, 126.2, 126.1, 21.8.

MS (EI): *m*/*z* (%) = 328 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}Cl$: 328.1019; found: 328.1012.

1-(2-Chlorophenyl)-4-(4-methoxyphenyl)naphthalene (4t)
White solid; mp 100–101 °C.

IR (KBr): 1608, 1514, 1456, 1388, 1281, 1254, 1174 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.98 (m, 1 H), 7.56–7.52 (m, 2 H), 7.49–7.38 (m, 9 H), 7.05 (d, *J* = 8.7 Hz, 2 H), 3.90 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 140.4, 139.7, 136.9, 134.5, 133.3, 132.5, 132.3, 132.1, 131.5, 129.8, 129.2, 127.0, 126.9, 126.7, 126.51, 126.47, 126.2, 126.1, 114.0, 55.6.

MS (EI): *m*/*z* (%) = 344 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{17}ClO$: 344.0968; found: 344.0963.

1-(4-Bromophenyl)-4-(2-chlorophenyl)naphthalene (4u)
White solid; mp 114–115 °C.

IR (KBr): 1486, 1431, 1386, 1157 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 1 H), 7.64 (d, *J* = 8.3 Hz, 2 H), 7.57–7.54 (m, 2 H), 7.45–7.39 (m, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.9, 139.5, 139.4, 137.6, 134.4, 132.4, 132.2, 132.1, 131.73, 131.67, 129.9, 129.3, 126.9, 126.6, 126.5, 126.41, 126.40, 126.3, 121.9.

MS (EI): *m*/*z* (%) = 392 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{14}BrCl$: 391.9967; found: 391.9964.

1-(2-Methoxyphenyl)-4-phenyl-1,4-dihydronaphthalene (7)
2-Methoxycinnamaldehyde (**2c**, 5 mmol) and dimethyl benzylphosphonate (**3a**, 5 mmol) were dissolved in anhyd THF (20 mL). To the resulting soln was added dropwise slowly *t*-BuOK (13 mmol) in anhyd THF (25 mL) at 0 °C. The mixture was then stirred at r.t. for 4 h. A suspension of benzenediazonium-2-carboxylate (**1**, 6 mmol) in DCE (30 mL) was added dropwise at 70–75 °C over a period of 3 h. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, hexane–EtOAc, 50:1) and recrystallized (hexane–EtOAc) to afford **7** (85% yield) as a white solid; mp 80–81 °C.

IR (KBr): 1597, 1489, 1439, 1353, 1284, 1245, 1169 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 4 H), 7.23–7.18 (m, 2 H), 7.08–7.03 (m, 4 H), 6.96–6.94 (m, 2 H), 6.88–6.85 (m, 1 H), 5.97–5.96 (m, 1 H), 5.92–5.89 (m, 1 H), 5.30–5.28 (m, 1 H), 4.72–4.70 (m, 1 H), 3.92 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.1, 146.2, 137.5, 137.3, 134.5, 130.2, 129.74, 129.70, 129.1, 128.8, 127.83, 127.79, 127.6, 126.6, 126.5, 126.4, 121.1, 110.8, 55.8, 45.8, 38.1.

MS (EI): *m*/*z* (%) = 312 (M^+, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{20}O$: 312.1514; found: 312.1512.

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