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Supporting Information

Palladium-catalyzed Formation of Highly Substituted Naphthalenes from Arene and Alkyne Hydrocarbons

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5,8-Dimethyl-1,2,3,4-tetraphenylnaphthalene (**3aa**): a white solid, m. p. 211–212 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.88 (s, 6 H), 6.60–6.71 (m, 4 H), 6.75–6.80 (m, 6 H), 7.08 (br. s, 10 H), 7.11 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.2, 124.8, 125.9, 126.2, 126.8, 129.8, 131.2 and 131.7 (all +), 132.9, 134.0, 138.1, 139.2, 140.7 and 143.1 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 460 (100) [M^+], 445 (13) [$M^+ - CH_3$], 97 (10). – HRMS (EI) calcd for $C_{36}H_{28}$: 460.2191; found: 460.2193.

An inseparable mixture of 5-methyl-1,2,3,4-tetraphenylnaphthalene (**3ca-a**) and **6-methyl-1,2,3,4-tetraphenylnaphthalene** (**3ca-b**): These two compounds were prepared according to the general procedure, and their ^{1}H-NMR spectra are identical to the reference.[S1]

5,8-Diethyl-1,2,3,4-tetraphenylnaphthalene (**3da**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 168–169 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.90 (t, ^{3}J = 7.3 Hz, 6 H), 2.16 (q, ^{3}J = 7.3 Hz, 4 H), 6.64–6.69 (m, 4 H), 6.78–6.82 (m, 6 H), 7.08 (br. s, 10 H), 7.26 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 16.1 (+), 28.8 (–), 124.8, 125.9, 126.2, 126.9, 127.3, 131.4 and 131.5 (all +), 132.8, 137.5, 138.7, 139.9, 140.8 and 143.2 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 488 (100) [M^+], 473 (11) [$M^+ - CH_3$], 431 (13), 367 (16), 365 (14). – Elemental analysis calcd (%) for $C_{38}H_{32}$ (488.7): C 93.40, H 6.60; found: C 93.32, H 6.60. – HRMS (EI) calcd for $C_{38}H_{32}$: 488.2504; found: 488.2502.

5-*n*-Butyl-8-methyl-1,2,3,4-tetraphenylnaphthalene (**3ea**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 169–170 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.71 (t, ^{3}J = 7.3 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 0.89 (sex, ^{3}J = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.26 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.87 (s, 3 H, CH_3), 2.09 (t, ^{3}J = 7.7 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 6.64–6.72 (m, 4 H), 6.70–6.85 (m, 6 H), 7.08 (br. s, 10 H), 7.13 (d, ^{3}J = 9.2 Hz, 1 H), 7.16 (d, ^{3}J = 9.2 Hz, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 13.9 (+), 22.6 (–), 25.2 (+), 34.3 and 36.3 (all –), 124.8, 125.9, 126.2, 126.8, 126.9, 128.4, 129.8, 131.3 and 131.8 (all +), 132.5, 133.3, 133.7, 137.5, 138.1, 138.96, 139.0, 139.3, 140.8, 143.0 and 143.2 (all C_{quat}). Five CH and one C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 502 (100) [M^+], 445 (19) [$M^+ - C_4H_9$], 381 (12), 367 (13), 365 (14), 289 (14), 194 (13), 167 (17), 97 (12), 95 (12), 91 (13). – Elemental analysis calcd (%) for $C_{39}H_{34}$ (502.7): C 93.18, H 6.82; found: C 93.03, H 6.81. – HRMS (EI) calcd for $C_{39}H_{34}$: 502.2661; found: 502.2663.

5-Isopropyl-8-methyl-1,2,3,4-tetraphenylnaphthalene (**3fa**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 179–180 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.93 (d, ^3J = 6.7 Hz, 6 H), 1.88 (s, 3 H), 2.85 (sep, ^3J = 6.7 Hz, 1 H), 6.65–6.72 (m, 4 H), 6.78–6.83 (m, 6 H), 7.05–7.12 (m, 10 H), 7.21 (d, ^3J = 7.4 Hz, 1 H), 7.37 (d, ^3J = 7.4 Hz, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 24.8, 25.1 and 29.7 (all +), 124.6, 124.80, 124.81, 125.8, 125.9, 126.2, 126.3, 126.8, 127.1, 129.9, 131.1, 131.4×2 and 131.9 (all +), 132.3, 133.1, 133.4, 137.0, 138.0, 138.8, 138.9, 140.8, 140.9, 143.2, 143.6 and 145.8 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 488 (100) [M^+], 473 (11) [$M^+ - CH_3$], 445 (25) [$M^+ - C_3H_7$], 381 (13), 365 (13). – HRMS (EI) calcd for $C_{38}H_{32}$: 488.2504; found: 488.2503.

5,8-Diisopropyl-1,2,3,4-tetraphenylnaphthalene (**3ga**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 233–234 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.90 (d, ^3J = 6.7 Hz, 12 H), 2.82 (sep, ^3J = 6.7 Hz, 2 H), 6.60–6.70 (m, 4 H), 6.77–6.84 (m, 6 H), 6.95–7.08 (m, 10 H), 7.42 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 24.7, 29.7, 124.5, 124.7, 125.7, 126.2, 127.0, 131.3 and 131.4 (all +), 132.7, 136.7, 138.2, 140.9, 143.6 and 144.5 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 516 (100) [M^+], 443 (15), 431 (34), 365 (15). – HRMS (EI) calcd for $C_{40}H_{36}$: 516.2817; found: 516.2820.

5-*tert*-Butyl-8-methyl-1,2,3,4-tetraphenylnaphthalene (**3ha**): a white solid (from CH_2Cl_2/MeOH), m. p. 310 °C. – ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.23 [s, $C(CH_3)_3$, 9 H], 1.97 (s, 3 H, CH_3), 6.72–6.83 (m, 10 H, Ph-H), 7.05–7.24 (m, 10 H, Ph-H), 7.38 (d, ^3J = 2.0 Hz, 1 H, 8-H), 7.49 (d, ^3J = 2.0 Hz, 1 H, 7-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.6 (+, CH_3), 30.9 [+, $C(CH_3)_3$], 34.5 [C_{quat}, $C(CH_3)_3$], 121.6, 124.9, 125.1, 126.1, 126.2, 126.4, 126.7, 127.3, 129.1, 131.2, 131.3, 131.4 and 131.6 (all +), 133.3, 135.3, 137.7, 138.4, 139.1, 139.9, 140.4, 140.9, 143.0 and 147.6 (all C_{quat}). One CH and two C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 502 (100) [M^+], 487 (30) [$M^+ - CH_3$], 97 (16), 83 (22), 69 (31). – HRMS (EI) calcd for $C_{39}H_{34}$: 502.2660; found: 502.2658.

5,7-Diisopropyl-1,2,3,4-tetraphenylnaphthalene (**3ja**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 238–239 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.97 (d, ^3J = 6.7 Hz, 6 H), 1.22 (d, ^3J = 6.7 Hz, 6 H), 2.90 (sep, ^3J = 6.7 Hz, 1 H), 2.95 (sep, ^3J = 6.7 Hz, 1 H), 6.71–6.86 (m, 10 H), 7.08–7.24 (m, 10 H), 7.32 (d, ^4J = 1.9 Hz, 1 H), 7.44 (d, ^4J = 1.9 Hz, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 23.7, 25.0, 28.7, 34.1, 122.2,

124.8, 125.0, 125.1, 125.9, 126.1, 126.2, 126.3, 127.1, 127.3, 130.7, 131.1, 131.3 and 131.5 (all +), 128.6, 133.8, 136.9, 138.2, 138.9, 139.7, 140.6, 140.9, 141.0, 143.5, 145.4 and 147.5 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 516 (100) [M^+], 443 (13), 431 (16), 381 (11), 365 (15). – HRMS (EI) calcd for $C_{40}H_{36}$: 516.2817; found: 516.2819.

An inseparable mixture of **5,6-dimethyl-1,2,3,4-tetraphenylnaphthalene** (**3ka-a**) and **6,7-dimethyl-1,2,3,4-tetraphenylnaphthalene** (**3ka-b**): a colorless crystal (from CH_2Cl_2/MeOH). – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.89 (s, 3 H, CH_3 of **3ka-a**), 2.34 (s, 6 H, CH_3 of **3ka-b**), 2.40 (s, 3 H, CH_3 of **3ka-a**), 6.75–6.89 (m, 20 H), 7.14 (br. s, 6 H), 7.16–7.26 (m, 15 H), 7.43 (s, 2 H, 5,8-H of **3ka-b**), 7.45 (d, ^3J = 7.9 Hz, 1 H, 8-H of **3ka-a**). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 20.1, 20.3, 21.6, 124.9, 125.1, 125.8, 126.26, 126.29, 126.4, 126.5, 127.0, 127.4, 127.5, 129.0, 131.2, 131.35, 131.41, 131.49 and 131.53 (all +), 130.8, 131.9, 132.2, 133.1, 135.6, 135.9, 137.3, 137.5, 137.6, 138.0, 138.7, 139.9, 140.27, 140.32, 140.8, 140.9 and 143.6 (all C_{quat}). Five CH and one C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 460 (100) [M^+], 200 (11), 194 (16), 182 (11), 176 (16), 97 (22). – Elemental analysis calcd (%) for $C_{36}H_{28}$ (460.6): C 93.87, H 6.13; found: C 93.88, H 6.08. – HRMS (EI) calcd for $C_{36}H_{28}$: 460.2191; found: 460.2193.

5,6,8-Trimethyl-1,2,3,4-tetraphenylnaphthalene (**3la**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 199–200 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.76 (s, 3 H), 1.84 (s, 3 H), 2.31 (s, 3 H), 6.63–6.70 (m, 4 H), 6.78–6.82 (m, 6 H), 7.00–7.16 (m, 11 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 20.3, 20.8, 24.8, 124.9×2, 125.6, 126.0, 126.28, 126.34, 126.9, 127.0, 131.44, 131.45, 131.79, 131.84 and 133.4 (all +), 131.3, 132.8, 134.4, 135.2, 137.3, 137.7, 138.3, 139.0, 140.9, 141.0, 143.2 and 143.8 (all C_{quat}). One C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 474 (100) [M^+], 459 (13) [$M^+ - CH_3$], 194 (14), 183 (11), 97 (14). – HRMS (EI) calcd for $C_{37}H_{30}$: 474.2347; found: 474.2349.

5,6,7-Trimethyl-1,2,3,4-tetraphenylnaphthalene (**3ma**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 279–280 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.92 (s, 3 H), 2.31 (s, 3 H), 2.37 (s, 3 H), 6.75–6.80 (m, 2 H), 6.80–6.90 (m, 8 H), 7.10–7.15 (m, 5 H), 7.15–7.28 (m, 5 H), 7.32 (s, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 16.8, 20.9, 21.8, 124.9, 125.0, 125.2, 125.7, 126.2, 126.3, 126.4, 127.1, 127.4, 131.2, 131.4, 131.5 and 131.6 (all +), 130.9, 131.8, 133.0, 135.1, 135.8, 137.1, 137.6, 138.0, 139.4, 140.3, 140.96, 141.05

and 143.7 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 474 (100) [M^+], 84 (11), 77 (14). – Elemental analysis calcd (%) for $C_{37}H_{30}$ (474.6): C 93.63, H 6.37; found: C 93.38, H 6.39. – HRMS (EI) calcd for $C_{37}H_{30}$: 474.2348; found: 474.2349.

6,7,8,9-Tetraphenyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (**3na**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 270 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.85 (tt, ^3J = 7.4, ^3J = 7.2 Hz, 2 H), 2.32 (t, ^3J = 7.2 Hz, 2 H), 2.96 (t, ^3J = 7.4 Hz, 2 H), 6.82–6.86 (m, 10 H), 7.11–7.26 (m, 10 H), 7.36 (d, ^3J = 8.6 Hz, 1 H), 7.55 (d, ^3J = 8.6 Hz, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.5, 33.3 and 35.2 (all –), 123.5, 125.1, 125.2, 126.3, 126.4, 126.6, 126.7, 127.5, 131.26, 131.27, 131.33 and 131.66 (all +), 129.3, 131.8, 137.4, 137.7, 139.1, 139.9, 140.1, 140.5, 140.72, 140.76, 142.1 and 143.3 (all C_{quat}). Two CH cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 472 (100) [M^+], 182 (21), 77 (19), 69 (18). – HRMS (EI) calcd for $C_{37}H_{28}$: 472.2191; found: 472.2189.

An inseparable mixture of **5,6,7,8-Tetraphenyl-1,2,3,4-tetrahydrophenanthrene** (**3oa-a**) and **5,6,7,8-Tetraphenyl-1,2,3,4-tetrahydroanthrathene** (**3oa-b**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 179 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.43–1.48 (m, 2 H, 3-H of **3oa-a**), 1.65–1.72 (m, 2 H, 2-H of **3oa-a**), 1.80 (br. s, 4 H, 2,3-H of **3oa-b**), 2.22 (t, ^3J = 5.5 Hz, 2 H, 4-H of **3oa-a**), 2.83 (br. s, 4 H, 1,4-H of **3oa-b**), 2.91 (t, ^3J = 6.2 Hz, 2 H, 1-H of **3oa-a**), 6.70–6.91 (m, 21 H), 7.09–7.25 (m, 20 H), 7.35 (s, 2 H, 9,10-H of **3oa-b**), 7.42 (d, ^3J = 8.7 Hz, 1 H, 9-H of **3oa-a**). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 22.3, 24.0, 31.0 and 31.3 (all –, C-1,2,3,4 of **3oa-a**), 23.3 and 29.8 (all –, C-1,2,3,4 of **3oa-b**), 124.8, 125.07, 125.08, 125.2, 125.74, 125.75, 126.2, 126.38, 126.43, 126.7, 127.37, 127.38, 128.5, 131.1, 131.3, 131.38, 131.4 and 131.5 (all +), 130.6, 131.6, 131.7, 134.4, 136.0, 136.4, 137.3, 137.5, 137.7, 137.9, 138.8, 139.9, 140.3, 140.6, 140.76, 140.77, 140.9 and 143.7 (all C_{quat}). Three CH cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 486 (100) [M^+], 194 (13), 97 (18), 83 (32), 77 (27). – HRMS (EI) calcd for $C_{38}H_{30}$: 486.2347; found: 486.2345.

An inseparable mixture of **5-methoxy-1,2,3,4-tetraphenylnaphthalene** (**3pa-a**) and **6-methoxy-1,2,3,4-tetraphenylnaphthalene** (**3pa-b**): a colorless crystal (from CH_2Cl_2/ MeOH), m. p. 254 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.39 (s, 3 H, OCH_3 of **3pa-a**), 3.70 (s, 3 H, OCH_3 of **3pa-b**), 6.78–6.86 (m, 20 H), 6.97 (s, 1 H, 5-H of **3pa-b**), 7.05–7.32 (m, 24 H), 7.58 (d, ^3J = 9.2 Hz, 1 H, 8-H of **3pa-b**). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus

DEPT, ppm): δ = 55.1 and 55.8 (all +, OCH_3), 105.6, 106.9, 118.0, 120.1, 124.8, 125.0, 125.19, 125.24, 126.0, 126.19, 126.30, 126.38, 126.42, 126.50, 127.45, 127.47, 127.6, 128.7, 129.8, 131.1, 131.20, 131.23 and 131.5 (all +), 123.7, 133.3, 134.1, 136.6, 136.8, 137.3, 138.2, 138.3, 139.4, 139.69, 139.75, 139.86, 140.1, 140.53, 140.56, 140.59, 140.7, 143.8, 157.2 and 157.5 (all C_{quat}). Seven CH and two C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 462 (100) [M^+], 194 (14), 97 (23), 83 (33). – HRMS (EI) calcd for $C_{35}H_{26}O$: 462.1984; found: 462.1983.

6,7-Dimethoxy-1,2,3,4-tetraphenylnaphthalene (**3qa-b**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 324 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.73 (s, 6 H), 6.85 (br. s, 10 H), 6.95 (s, 2 H), 7.25 (br. s, 10 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 55.6 (+, OCH_3), 105.8, 125.1, 126.4, 126.5, 127.6, 131.1 and 131.4 (all +), 127.8, 137.0, 137.3, 139.9, 140.8 and 149.2 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 492 (100) [M^+], 478 (17), 416 (19), 170 (11), 149 (10), 105 (20), 97 (27), 85 (20), 83 (20), 77 (16), 71 (27). – HRMS (EI) calcd for $C_{36}H_{28}O_2$: 492.2089; found: 492.2091.

6-Chloro-5,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3ra**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 210 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.83 (s, 3 H), 1.91 (s, 3 H), 6.65–6.71 (m, 4 H), 6.78–6.83 (m, 6 H), 6.99–7.09 (m, 10 H), 7.22 (s, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 21.1, 24.6, 125.01, 125.04, 126.0, 126.2, 126.3, 126.4, 127.0, 127.2, 130.6, 131.21, 131.22, 131.65 and 131.69 (all +), 130.8, 132.0, 133.8, 135.0, 135.1, 137.7, 138.0, 139.4, 139.9, 140.36, 140.38, 142.5 and 142.9 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 494/495/496/497 (100/30/41/11) [M^+], 444 (31), 175 (30), 97 (45), 83 (57). – HRMS (EI) calcd for $C_{36}H_{27}Cl$: 494.1801; found: 494.1798.

6-Bromo-5,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3sa**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 230–231 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.81 (s, 3 H), 1.94 (s, 3 H), 6.62–6.67 (br. s, 4 H), 6.78–6.82 (br. s, 6 H), 6.98–7.08 (m, 10 H), 7.39 (s, 1 H). – MS (70 eV), *m*/*z* (%): 538/539/540/541 (100/28/100/35) [M^+], 340 (100), 444 (86), 365 (22), 289 (25), 230 (29), 222 (22), 208 (38), 201 (31), 194 (42), 175 (30). – HRMS (EI) calcd for $C_{36}H_{27}Br$: 538.1296; found: 538.1299.

5-Methoxy-6,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3ta**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 209–210 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.90 (s, 3 H),

2.38 (s, 3 H), 3.13 (s, 3 H), 6.69–6.87 (m, 10 H), 7.03–7.18 (br. s, 11 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 16.2, 25.1, 60.7, 124.8, 124.9, 125.0, 126.06, 126.12, 126.16, 126.21, 126.8, 130.1, 131.3, 131.7 and 134.2 (all +), 127.4, 127.7, 131.9, 135.7, 138.1, 139.7, 140.0, 140.75, 140.77, 142.8, 143.4 and 153.5 (all C_{quat}). One CH and one C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 490 (100) [M^+], 460 (27), 77 (51). – HRMS (EI) calcd for $C_{37}H_{30}O$: 490.2297; found: 490.2298.

5-Methoxy-7,8-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3ua**): a colorless crystal (from CH_2Cl_2/ MeOH), m. p. 200 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.76 (s, 3 H), 2.36 (s, 3 H), 3.34 (s, 3 H), 6.65–6.72 (m, 5 H), 6.78–6.83 (m, 6 H), 6.96–7.12 (m, 10 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 19.7, 21.7, 55.8, 110.8, 124.5, 124.77, 124.82, 125.6, 126.08, 126.14, 126.24, 127.0, 129.7, 131.37, 131.5 and 131.7 (all +), 124.3, 125.3, 134.4, 135.9, 136.3, 136.8, 138.1, 140.3, 140.7, 140.9, 143.5, 144.4 and 154.8 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 490 (100) [M^+], 460 (15), 83 (19), 77 (21). – HRMS (EI) calcd for $C_{37}H_{30}O$: 490.2297; found: 490.2296.

6-Methoxy-5,7-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3va**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 269 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.88 (s, 3 H), 2.34 (s, 3 H), 3.71 (s, 3 H), 6.71–6.83 (m, 10 H), 7.08–7.25 (m, 10 H), 7.33 (s, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 15.9, 17.3, 60.1, 124.9, 125.1, 125.9, 126.2, 126.4, 126.9, 127.0, 127.4, 131.1, 131.3, 131.4 and 131.6 (all +), 126.5, 130.6, 130.7, 131.2, 137.7, 137.8, 138.2, 140.0, 140.2, 140.76, 140.83, 143.1 and 156.9 (all C_{quat}). One CH cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 490 (100) [M^+], 372 (64), 328 (26), 265 (20), 105 (41), 77 (17). – HRMS (EI) calcd for $C_{37}H_{30}O$: 490.2297; found: 490.2300.

6-Bromo-5,7-dimethyl-1,2,3,4-tetraphenylnaphthalene (**3wa**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 262 °C. – ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.10 (s, 3 H), 2.47 (s, 3 H), 6.72–6.86 (m, 10 H), 7.03–7.23 (m, 10 H), 7.36 (s, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.2 and 25.6 (+, CH_3), 125.1, 125.3, 126.1, 126.2, 126.4, 126.5, 127.2, 127.5, 131.0, 131.30, 131.34 and 131.4 (all +), 130.7, 132.1, 135.2, 135.5, 137.4, 138.3, 138.8, 139.7, 140.3, 140.5 x 2 and 142.9 (all C_{quat}). One CH and one C_{quat} cannot be observed due to the signals overlap. – MS (70 eV), *m*/*z* (%): 538/539/540/541

(100/37/100/41) [M^+], 444 (34), 222 (23), 201 (30), 194 (39), 182 (27), 175 (35), 84 (23). – HRMS (EI) calcd for $C_{36}H_{27}Br$: 538.1296; found: 538.1300.

1,2,3,4-Tetra(4-*tert*-butylphenyl)-5,8-dimethylnaphthalene (**3ab**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 228−229 □. ^{1}H NMR (300 MHz, CDCl3, ppm): δ = 1.07 (s, 18 H), 1.22 (s, 18 H), 1.92 (s, 6 H), 6.52 (d, ^3J = 8.1 Hz, 4 H), 6.73 (d, ^3J = 8.1 Hz, 4 H), 6.95 (d, ^3J = 8.1 Hz, 4 H), 7.05–7.06 (m, 6 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.6, 31.2, 31.3, 122.6, 123.3, 129.4, 130.9 and 131.3 (all +), 34.0, 34.3, 132.8, 134.2, 138.0, 138.2, 140.0, 140.3, 147.0 and 148.6 (all C_{quat}). – EI MS (70 eV), *m/z* (%): 684 (100) [M^+], 459 (14).

1,2,3,4-Tetra(4-tolyl)-5,8-dimethylnaphthalene (**3ac**): a colorless crystal (from CH_2Cl_2/ MeOH), m. p. 226–227 □. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.83 (s, 6 H), 2.07 (s, 6 H), 2.24 (s, 6 H), 6.52–6.61 (m, 8 H), 6.85–6.93 (m, 8 H), 7.04 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 21.0, 21.2, 25.1, 126.9, 127.5, 129.4, 131.1 and 131.6 (all +), 133.2, 133.8, 134.0, 135.2, 137.9, 138.0, 139.5 and 140.3 (all C_{quat}). – EI MS (70 eV), *m/z* (%): 516 (100) [M^+], 97 (19), 91 (22), 83 (25). – Elemental analysis calcd (%) for $C_{40}H_{36}$ (516.7): C 92.98, H 7.02; found: C 92.72, H 7.02. – HRMS (EI) calcd for $C_{40}H_{36}$: 516.2817; found: 516.2820.

5,8-Dimethyl-1,2,3,4-tetra(4-fluorophenyl)naphthalene (**3ad**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 242 □. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.88 (s, 6 H), 6.52–6.73 (m, 8 H), 6.78–6.87 (m, 4 H), 6.96–7.04 (m, 4 H), 7.14 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.4, 113.7 (d, $^2J_{C\text{-}F}$ = 30.0 Hz), 114.1 (d, $^2J_{C\text{-}F}$ = 30.0 Hz), 130.3, 132.4 (d, $^3J_{C\text{-}F}$ = 7.9 Hz) and 132.8 (d, $^3J_{C\text{-}F}$ = 7.9 Hz) [all +], 133.2, 133.9, 136.4 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 137.6, 138.6, 138.8 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 160.5 (d, $^1J_{C\text{-}F}$ = 245.2 Hz) and 161.4 (d, $^1J_{C\text{-}F}$ = 246.3 Hz) [all C_{quat}]. – MS (70 eV), *m/z* (%): 532 (100) [M^+], 96 (48). – HRMS (EI) calcd for $C_{38}H_{24}F_4$: 532.1814; found: 532.1816.

5,8-Dimethyl-1,2,3,4-tetra(4-anisyl)naphthalene (**3ae**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 272 □. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.86 (s, 6 H), 3.62 (s, 6 H), 3.76 (s, 6 H), 6.39 (d, ^3J = 8.4 Hz, 4 H), 6.56 (d, ^3J = 8.4 Hz, 4 H), 6.65 (d, ^3J = 8.3 Hz, 4 H), 6.94 (d, ^3J = 8.3 Hz, 4 H), 7.07 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 25.2, 54.9, 55.1, 111.9, 112.3, 129.5, 132.2 and 132.6, (all +), 133.48, 133.50,

134.0, 135.8, 137.9, 139.5, 156.6 and 157.7 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 580 (100) [M^+]. – HRMS (EI) calcd for $C_{40}H_{36}O_4$: 580.2613; found: 580.2618.

Tetramethyl 5,8-dimethylnaphthalene-1,2,3,4-tetracarboxylate (**3af**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 134 □. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.54 (s, 6 H), 3.87 (s, 6 H), 3.93 (s, 6 H), 7.32 (s, 2 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm): δ = 21.5, 52.3, 53.1 and 132.3 (all +), 127.3, 130.4, 133.2, 133.4, 167.1 and 169.2 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 388 (26) [M^+], 357 (72), 324 (100), 309 (91), 266 (29), 208 (48), 152 (22), 139 (24), 133 (20), 105 (31), 59 (17). – HRMS (EI) calcd for $C_{20}H_{20}O_8$: 388.1158; found: 388.1162.

A inseparable mixture of **5,6-dimethyl-1,2,3,4-tetra(4-*tert*-butylphenyl)naphthalene** (**3kb-a**) and **6,7-dimethyl-1,2,3,4-tetra(4-*tert*-butylphenyl)naphthalene** (**3kb-b**): a colorless crystal (from CH_2Cl_2/MeOH). **3kb-a**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.06 (s, 9 H), 1.08 (s, 9 H), 1.23 (s, 9 H), 1.25 (s, 9 H), 1.90 (s, 3 H), 2.36 (s, 3 H), 6.54–6.63 (m, 4 H), 6.74–6.78 (m, 4 H), 6.94–6.97 (m, 2 H), 7.04–7.10 (m, 4 H), 7.16–7.24 (m, 3 H), 7.50 (m, 1 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm) δ = 20.3, 21.5, 31.1×2, 31.2, 31.3, 122.6, 122.8, 123.4, 123.9, 125.1, 128.5, 130.7 and 131.0×3 (all +), 33.9×2, 34.2, 34.3, 131.7, 132.0, 133.0, 135.2, 137.3×2, 137.9, 138.0×2, 138.5, 140.7, 140.8, 147.0, 147.2, 148.3 and 148.6 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 684 (100) [M^+].

Dimethyl 5,8-dimethyl-1,3-diphenylnaphthalene-2,4-dicarboxylate (**3ai**) and **Dimethyl 5,8-dimethyl-1,4-diphenylnaphthalene-2,3-dicarboxylate** (**3'ai**). **3ai**: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.91 (s, 3 H), 2.65 (s, 3 H), 3.10 (s, 3 H), 3.49 (s, 3 H), 7.18 (d, ^3J = 7.3 Hz, 1 H), 7.31 (d, ^3J = 7.3 Hz, 1 H), 7.36 (br. s, 10 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm) δ = 21.7, 25.3, 51.4, 51.8, 127.4, 127.5, 127.7, 127.8, 129.8, 130.3, 130.93 and 130.97 (all +), 130.1, 131.3, 131.4, 132.1, 134.1, 134.3, 135.0, 137.3, 138.5, 141.0, 168.7 and 170.9 (all C_{quat}). – MS (70 eV), *m*/*z* (%): 684 (100) [M^+]. – MS (70 eV), *m*/*z* (%): 424 (100) [M^+], 393 (48), 361 (62), 290 (22), 144 (63), 105 (92), 77 (28), 55 (26). – HRMS (EI) calcd for $C_{28}H_{24}O_4$: 424.1675; found: 424.1672.

3'ai: a colorless crystal (from CH_2Cl_2/MeOH), m. p. 224–225 ºC. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.87 (s, 6 H), 3.41 (s, 6 H), 7.15 (s, 2 H), 7.33–7.39 (m, 10 H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm) δ = 25.0, 52.1, 127.6, 130.2 and 131.2 (all +), 129.5, 133.4, 134.8, 138.0, 141.2 and 169.3 (all C_{quat}). One CH cannot be observed due to the signals

overlap. – MS (70 eV), *m*/*z* (%): 424 (47) [M^+], 336 (19), 289 (18), 189 (14), 105 (100), 77 (26). – HRMS (EI) calcd for $C_{28}H_{24}O_4$: 424.1675; found: 424.1678.

1,2,3,4-Tetraphenyltriphenylene (**11**): a colorless crystal (from CH_2Cl_2/MeOH), m. p. 300 ºC. ^{1}H-NMR spectrum is identical to the reference.[S2] – ^{13}C NMR (75.5 MHz, $CDCl_3$, plus DEPT, ppm) δ = 123.1, 125.2, 125.4, 126.1, 126.3, 126.6, 127.9, 129.9, 131.5 and 132.1 (all +), 130.7, 131.2, 137.1, 140.33, 140.35 x 2, and 142.8 (all C_{quat}).

Reference:

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[S2] R. A. Pascal, Jr., D. van Engen, B. Kahr, W. D. McMillan *J. Org. Chem.* **1988**, *53*, 1687.