o-Dihaloarenes as Aryne Precursors for Nickel-Catalyzed Cycloaddition with Alkynes and Nitriles: a Novel Method to Polysubstituted Naphthalene, Phenanthridine and Triphenylene Derivatives

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Supporting Information

General. All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use. Substituted benzyne precursors were synthesized according to the literature procedures (see refs 1 and 2 in the main text). Other reagents were commercially available and used as purchased.

General procedure for the cyclotrimerization and reductive cyclization of diiodoarenes with acetylenes and nitrile:

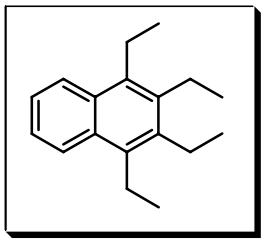
To a screw-capped sealed tube were added $NiBr_2$(dppe) (31 mg, 0.050 mmol), dppe (20 mg, 0.050 mmol) and zinc powder (96 mg, 1.5 mmol). The tube was sealed with septum and flushed several times with nitrogen. *o*-Diiodoarene[1,2] (0.5 mmol), alkyne[3] (3.0 mmol) (or diyne (1.5 mmol)) and acetonitrile (1.0 mL) were injected into the reaction system via a syringe (Solid diiodoarene and alkyne could be added to the tube immediately after the addition of catalyst.). The septum was removed, and the tube was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 100 °C for 48 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was

chromatographed on a silica gel column using a mixture of hexane and EA as the eluent to give the desired pure product.

Products **3a-p**, and **5a-m**, were prepared according to this procedure.

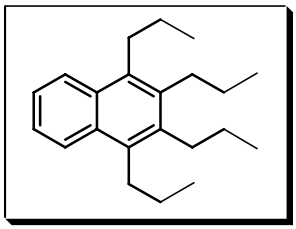
For the synthesis of phenanthridines **6a-e**, the procedure is similar to that described above except that no extra dppe was used and the amount of solvent acetonitrile used was 2.5 ml.

The synthesis of triphenylene derivatives **7a-c** also followed a similar procedure using THF (2 ml) as the solvent and $NiBr_2(PPh_3)_2$ as the catalyst. Spectral data for all of these compounds are listed below.



1,2,3,4-Tetraethylnaphthalene (3a):[4]

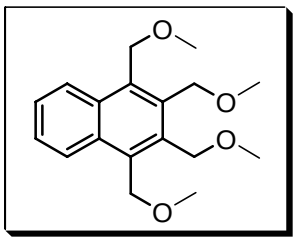
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, J = 6.5 Hz, 6 H), 1.30 (t, J = 6.5 Hz, 6 H), 2.84 (q, J = 6.5 Hz, 4 H), 3.11 (q, J = 4.5 Hz, 4 H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 8.03 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 15.8, 21.7, 22.8, 124.5, 124.5, 131.0, 135.4, 137.7; HRMS: $C_{18}H_{24}$ calculated 240.1878, found 240.1882. Registry Number: [**177327-40-1**]



1,2,3,4-Tetrapropylnaphthalene (3b):[5]

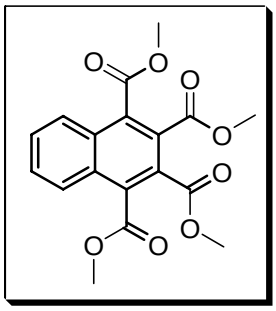
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (t, J = 7.0 Hz, 6 H), 1.10 (t, J =

7.0 Hz, 6 H), 1.58 (sixtet, J = 7.0 Hz, 4 H), 1.67 (sextet, J = 7.0 Hz, 2 H), 2.74 (t, J = 7.0 Hz, 4 H), 3.01 (t, J = 7.0 Hz, 4 H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.80 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.9, 15.1, 24.5, 24.8, 31.3, 32.6, 124.4, 124.5, 131.1, 134.1, 136.7; HRMS: $C_{22}H_{32}$ calculated 296.2504, found 296.2503. Registry Number: [**42101-99-5**]



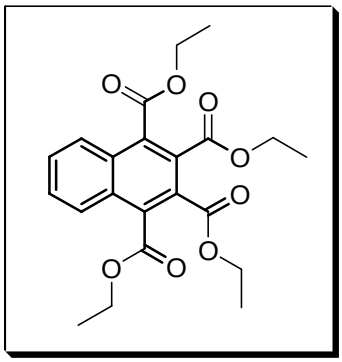
1,2,3,4-Tetrakis(methoxymethyl)naphthalene (3c):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.46 (s, 6 H), 3.47 (s, 6 H), 4.74 (s, 4 H), 4.97 (s, 4 H), 7.52 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 8.19 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 58.3, 58.5, 67.7, 68.3, 125.1, 126.5, 132.9, 134.1, 134.4; HRMS: $C_{18}H_{24}O_4$ calculated 304.1675, found 304.1678.



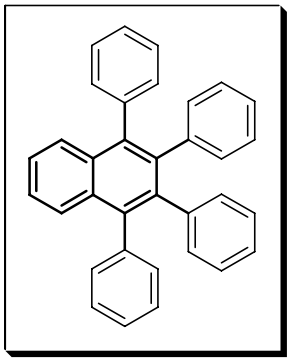
Tetramethyl naphthalene-1,2,3,4-tetracarboxylate (3d):[6]

Yellow solid, mp: 129-131 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.90 (s, 6 H), 4.99 (s, 6 H), 7.69 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 8.06 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.2, 53.2, 126.2, 128.2, 129.7, 130.0, 133.9, 166.7, 167.2; HRMS: $C_{18}H_{16}O_8$ calculated 360.0845, found 360.0842. Registry Number: [**36063-07-7**]



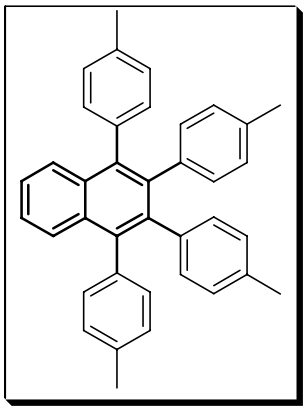
Tetraethyl naphthalene-1,2,3,4-tetracarboxylate (3e):[7]

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (t, J = 7.0 Hz, 6 H), 1.40 (t, J = 7.0 Hz, 6 H), 4.34 (q, J = 7.0 Hz, 4 H), 4.48 (q, J = 7.0 Hz, 4 H), 7.68 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 8.06 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 14.0, 62.3, 62.3, 126.1, 127.6, 129.5, 129.9, 133.9, 166.3, 166.8; HRMS: $C_{22}H_{24}O_8$ calculated 416.1471, found 416.1475. Registry Number: [**107002-74-4**]



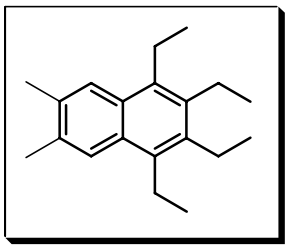
1,2,3,4-Tetraphenylnaphthalene (3f):[6]

White solid, mp: 157-159 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83-6.87 (m, 10 H), 7.20-7.27 (m, 10 H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.66 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.3, 125.8, 126.4, 126.5, 126.9, 127.5, 131.3, 132.0, 138.4, 138.8, 139.5, 140.5; HRMS: $C_{32}H_{24}$ calculated 432.1878, found 432.1881. Registry Number: [**751-38-2**]



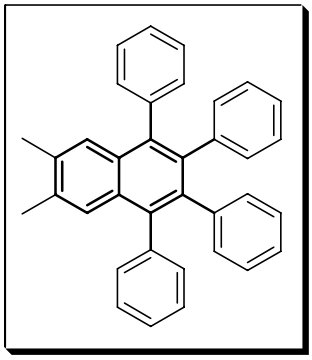
1,2,3,4-Tetra*p*-tolylnaphthalene (3g):[8]

Yellow solid, mp: 117-119 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.09 (s, 6 H), 2.31 (s, 6 H), 6.65 (d, J = 7.5 Hz, 4 H), 6.71 (d, J = 7.5 Hz, 4 H), 7.04 (d, J = 7.5 Hz, 4 H), 7.08 (d, J = 7.5 Hz, 4 H), 7.35 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 21.2, 125.5, 126.9, 127.2, 128.2, 131.1, 132.2, 134.3, 135.6, 136.8, 137.8, 138.3, 139.1; HRMS: $C_{38}H_{32}$ calculated 488.2504, found 488.2504. Registry Number: [**1003853-52-8**]



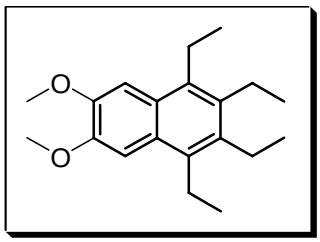
1,2,3,4-Tetraethyl-6,7-dimethylnaphthalene (3h):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (t, J = 6.5 Hz, 6 H), 1.28 (t, J = 6.5 Hz, 6 H), 2.42 (s, 6 H), 2.81 (q, J = 6.5 Hz, 4 H), 3.06 (q, J = 6.5 Hz, 4 H), 7.74 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.6, 15.7, 21.6, 22.7, 23.5, 124.2, 127.3, 128.8, 131.2, 137.4; HRMS: $C_{20}H_{28}$ calculated 268.2191, found 268.2192.



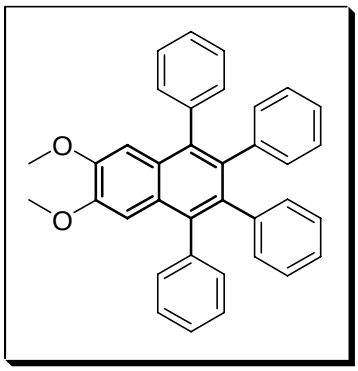
6,7-Dimethyl-1,2,3,4-tetraphenylnaphthalene (3i):[9]

Yellow solid, mp: 266-268 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 6 H), 6.81-6.84 (m, 10 H), 7.18-7.25 (m, 10 H), 7.38 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 125.1, 126.2, 126.4, 126.4, 127.4, 130.8, 131.3, 131.4, 135.6, 137.5, 138.0, 139.8, 140.8; HRMS: $C_{36}H_{28}$ calculated 460.2191, found 460.2193. Registry Number: [**76054-73-4**]



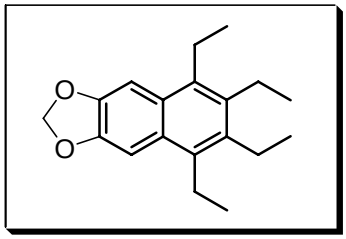
1,2,3,4-Tetraethyl-6,7-dimethoxynaphthalene (3j):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 6 H), 1.30 (t, J = 7.0 Hz, 6 H), 2.80 (q, J = 7.0 Hz, 4 H), 3.04 (q, J = 7.0 Hz, 4 H), 3.99 (s, 6 H), 7.28 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.1, 16.0, 22.1, 22.7, 55.7, 103.8, 126.5, 134.0, 136.2, 148.3; HRMS: $C_{20}H_{28}O_2$ calculated 300.3089, found 300.2092.



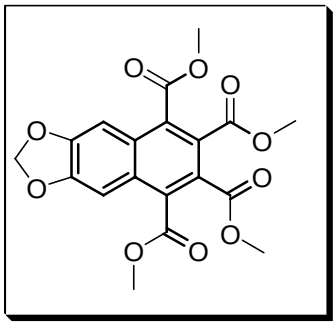
6,7-Dimethoxy-1,2,3,4-tetraphenylnaphthalene (3k):[10]

Yellow solid, mp: 305-307 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (s, 6 H), 6.84 (m, 10 H), 6.94 (s, 2 H), 7.21-7.24 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.6, 105.7, 125.1, 126.4, 127.6, 127.8, 131.1, 131.4, 137.0, 137.3, 139.9, 140.8, 149.2; HRMS: $C_{36}H_{28}O_2$ calculated 492.2089, found 492.2090. Registry Number: [**26002-78-8**]



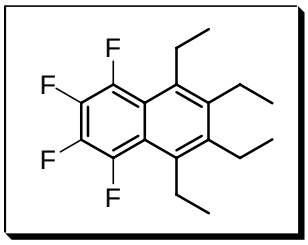
5,6,7,8-Tetraethylnaphtho[2,3-*d*][1,3]dioxole (3l):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (t, J = 7.0 Hz, 6 H), 1.26 (t, J = 7.0 Hz, 6 H), 2.78 (q, J = 7.0 Hz, 4 H), 2.98 (q, J = 7.0 Hz, 4 H), 5.99 (s, 2 H), 7.32 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.2, 15.9, 22.2, 22.7, 100.7, 101.1, 127.8, 134.7, 136.4, 146.6; HRMS: $C_{19}H_{24}O_2$ calculated 284.1776, found 284.1779.



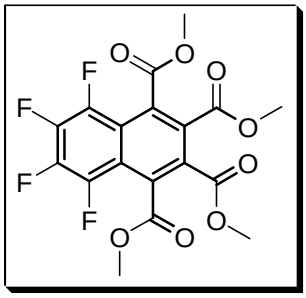
Tetramethyl naphtho[2,3-*d*][1,3]dioxole-5,6,7,8-tetracarboxylate (3m):

Yellow solid, mp: 120-122 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 6 H), 3.96 (s, 6 H), 6.12 (s, 2 H), 7.35 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.0, 53.1, 102.4, 102.4, 126.4, 128.3, 134.2, 150.7, 166.9, 167.5; HRMS: $C_{19}H_{16}O_{10}$ calculated 404.0743, found 404.0745.



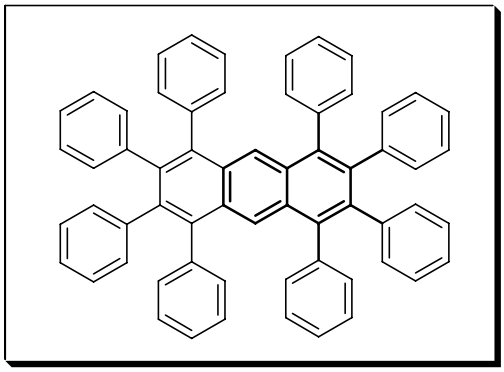
1,2,3,4-Tetraethyl-5,6,7,8-tetrafluoronaphthalene (3n):[11]

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 6 H), 1.28 (t, J = 7.0 Hz, 6 H), 2.84 (q, J = 7.0 Hz, 4 H), 3.12 (broad, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 15.7, 22.1, 22.3, 118.9, 133.9, 137.8, 140.7 (d, J = 240.0 Hz), 143.8 (d, J = 240.0 Hz); HRMS: $C_{18}H_{20}F_4$ calculated 312.1501, found 312.1502. Registry Number: [**900167-12-6**]



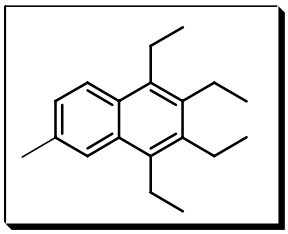
Tetramethyl 5,6,7,8-tetrafluoronaphthalene-1,2,3,4-tetracarboxylate (3o):

White solid, mp: 174-176 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 6 H), 3.99 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.5, 54.3, 116.7, 129.1, 129.9, 138.4 (d, J = 245.0 Hz), 142.7 (d, J = 245.0 Hz), 165.2, 166.4, 143.8; HRMS: $C_{18}H_{12}F_4O_8$ calculated 432.0468, found 432.0466.



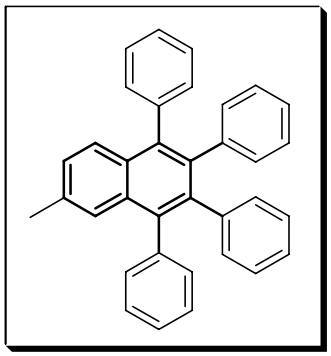
1,2,3,4,5,6,7,8-Octaphenylanthracene (3p):[12]

Yellow solid, mp: 766-768 ^{o}C;(very low solubility) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.79-6.83 (m, 20 H), 6.96-7.03 (m, 20 H), 7.89 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.3, 126.0, 126.5, 127.2, 130.8, 131.0, 131.1, 131.2, 131.3, 138.3, 139.2, 140.6; HRMS: $C_{62}H_{42}$ calculated 786.3287, found 786.3283. Registry Number: [**100367-30-4**]



1,2,3,4-Tetraethyl-6-methylnaphthalene (3q):

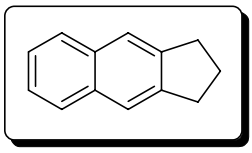
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 6 H), 1.30 (t, J = 7.0 Hz, 6 H), 2.51 (s, 3 H), 2.83 (q, J = 7.0 Hz, 4 H), 3.09 (q, J = 7.0 Hz, 4 H), 7.25 (d, J = 9.0 Hz, 1 H), 7.78 (s, 1 H), 7.92 (d, J = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 15.6, 15.8, 15.8, 21.6, 21.7, 22.1, 22.7, 22.8, 123.6, 124.4, 126.6, 129.1, 131.1, 133.8, 134.7, 135.2, 136.7, 137.8; HRMS: $C_{19}H_{26}$ calculated 254.2035, found 254.2037.



6-Methyl-1,2,3,4-tetraphenylnaphthalene (3r):[13]

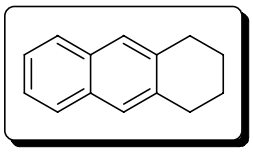
White solid, mp: 195-197 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3 H), 6.81-6.87 (m, 10 H), 7.18-7.26 (m, 11 H), 7.41 (s, 1 H), 7.55 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 125.2, 125.8, 126.3, 126.5, 126.9, 127.5, 128.1, 130.2, 131.2, 131.3, 131.3, 131.3, 132.1, 135.6, 137.7, 137.9, 138.2, 138.9, 139.7,

140.6, 140.7; HRMS: $C_{35}H_{26}$ calculated 446.2034, found 446.2034. Registry Number: [**21991-42-4**]



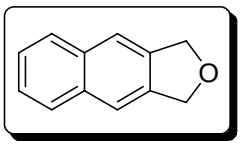
2,3-Dihydro-1*H*-cyclopenta[*b*]naphthalene (5a):[14]

White solid, mp: 84-86 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.13 (quintet, J = 10 Hz, 2 H), 3.05 (t, J = 7.5 Hz, 4 H), 7.37 (q, J = 6.5 Hz, 2 H), 7.65 (s, 2 H), 7.75 (q, J = 6.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.2, 32.6, 122.1, 124.8, 127.4, 132.6, 143.4; HRMS: $C_{13}H_{12}$ calculated 168.0939, found 168.0937. Registry Number: [**1624-26-6**]



1,2,3,4-Tetrahydroanthracene (5b):[14]

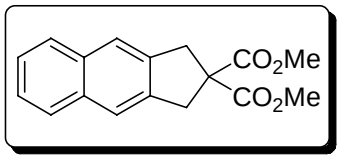
White solid, mp: 92-94 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.85 (quintet, J = 10 Hz, 4 H), 2.96 (t, J = 7.5 Hz, 4 H), 7.34 (q, J = 6.5 Hz, 2 H), 7.52 (s, 2 H), 7.59 (q, J = 6.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.4, 29.8, 124.9, 126.6, 126.9, 132.1, 136.2; HRMS: $C_{14}H_{14}$ calculated 182.1096, found 182.1095. Registry Number: [**2141-42-6**]



1,3-Dihydronaphtho-[2,3-*c*] furan (5c):[14]

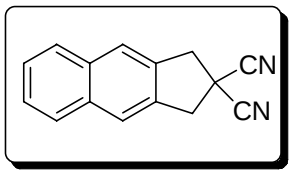
Yellow solid, mp: 153-155 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.12 (s, 4 H), 7.43 (q, J = 6.5 Hz, 2 H), 7.66 (s, 2 H), 7.80 (q, J = 6.5Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 72.8, 119.2, 125.7, 127.9, 133.1, 138.2; HRMS: $C_{12}H_{10}O$ calculated 170.0732,

found 170.0730. Registry Number: [**7193-16-0**]



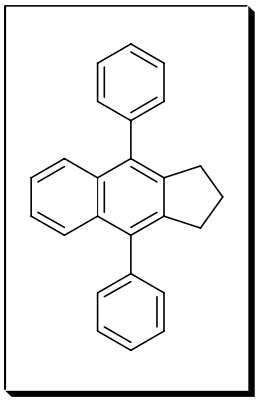
1,3-Dihydrocyclopenta[*c*]naphthalene-2,2-dicarboxylic acid dimethyl ester (5d):[14]

Yellow solid, mp: 120-122 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.71 (s, 4 H), 3.74 (s, 6 H), 7.38 (q, J = 6.5 Hz, 2 H), 7.63 (s, 2 H), 7.74 (q, J = 6.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2, 53.0, 60.9, 122.5, 125.3, 127.6, 133.1, 138.8, 171.9; HRMS: $C_{17}H_{16}O_4$ calculated 284.1049, found 284.1050. Registry Number: [**856897-90-0**]



1,3-Dihydrocyclopenta[*b*]naphthalene-2,2-dicarbonitrile (5e):[14]

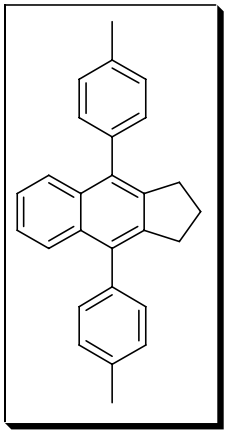
Yellow solid, mp: 161-163 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 4 H), 7.49 (q, J = 6 Hz, 2 H), 7.75 (s, 2 H), 7.80 (q, J = 6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 34.3, 44.2, 116.1, 123.8, 126.6, 127.9, 133.4, 134.1; HRMS: $C_{15}H_{10}N_2$ calculated 218.0844, found 218.0842. Registry Number: [**856897-91-1**]



2,3-Dihydro-4,9-diphenyl-1*H*-cyclopenta[*b*]naphthalene (5f):[15]

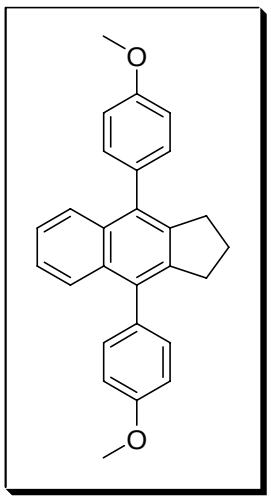
White solid, mp: 169-171 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.00 (quintet, J = 8.0 Hz, 2 H), 2.88 (t, J = 8.0 Hz, 4 H), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.40 (d, J

= 8.0 Hz, 4 H), 7.42 (t, J = 8.0 Hz, 2 H), 7.50 (t, J = 8.0 Hz, 4 H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 33.0, 124.7, 125.8, 127.0, 128.3, 130.1, 131.9, 134.1, 139.6, 141.1; HRMS: $C_{25}H_{20}$ calculated 320.1565, found 320.1566. Registry Number: [**1167-64-2**]



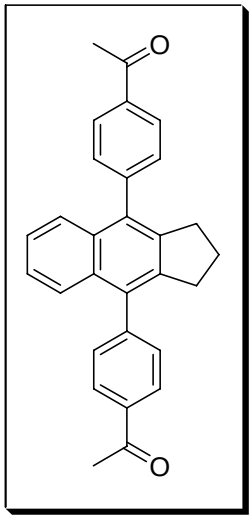
2,3-Dihydro-4,9-bis(4-methylphenyl)-1*H*-cyclopenta[*b*]naphthalene (5g):

White solid, mp: 169-171 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.00 (quintet, J = 8.0 Hz, 2 H), 2.88 (t, J = 8.0 Hz, 4 H), 2.31 (s, 6 H), 7.05 (d, J = 8.0 Hz, 4 H), 7.10 (d, J = 8.0 Hz, 4 H), 7.27 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.64 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 25.7, 33.1, 55.3, 124.6, 125.9, 128.2, 131.1 131.2, 132.1, 134.1, 139.6, 141.3; HRMS: $C_{27}H_{24}$ calculated 348.1878, found 348.1881.



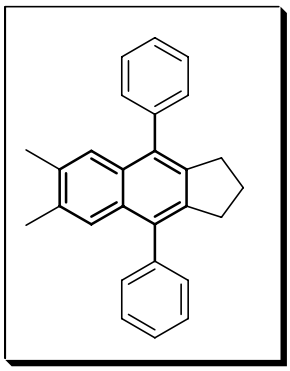
2,3-Dihydro-4,9-bis(4-methoxyphenyl)-1*H*-cyclopenta[*b*]naphthalene (5h):

White solid, mp: 204-206 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.00 (quintet, J = 8.0 Hz, 2 H), 2.87 (t, J = 8.0 Hz, 4 H), 3.89 (s, 6 H), 7.03 (d, J = 8.0 Hz, 4 H), 7.27 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 4 H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 33.1, 55.3, 113.7, 124.6, 125.9, 131.2, 131.9, 132.2, 133.6, 141.3, 158.6; HRMS: $C_{27}H_{24}O_2$ calculated 380.1776, found 380.1778.



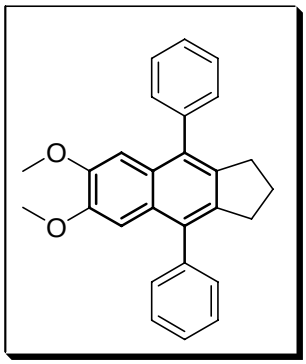
2,3-Dihydro-4,9-bis(4-acetonphenone)-1*H*-cyclopenta[*b*]naphthalene (5i):

White solid, mp: 265-267 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.02 (quintet, J = 8.0 Hz, 2 H), 2.67 (s, 6 H), 2.85 (t, J = 8.0 Hz, 4 H), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 7.50 (d, J = 8.0 Hz, 4 H), 7.55 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2 H), 8.10 (d, J = 8.0 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 26.7, 32.8, 125.3, 125.6, 128.5, 130.4, 131.5, 132.0, 133.5, 141.1, 144.7, 197.9; HRMS: $C_{29}H_{24}O_2$ calculated 404.1776, found 404.1778.



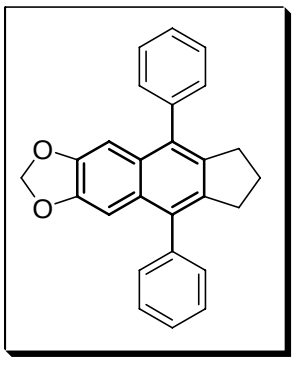
2,3-Dihydro-6,7-dimethyl-4,9-diphenyl-1*H*-cyclopenta[*b*]naphthalene (5j):

White solid, mp: 192-194 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (quintet, J = 8.0 Hz, 2 H), 2.27 (s, 6 H), 2.84 (t, J = 8.0 Hz, 4 H), 7.37 (s, 2 H), 7.40 (d, J = 8.0 Hz, 4 H), 7.42 (t, J = 8.0 Hz, 2 H), 7.51 (t, J = 8.0 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.1, 25.7, 32.9, 125.4, 126.8, 128.2, 130.1, 130.7, 133.3, 134.2, 140.0, 140.1; HRMS: $C_{27}H_{24}$ calculated 348.1878, found 348.1879.



2,3-Dihydro-6,7-dimethoxy-4,9-diphenyl-1*H*-cyclopenta[*b*]naphthalene (5k):

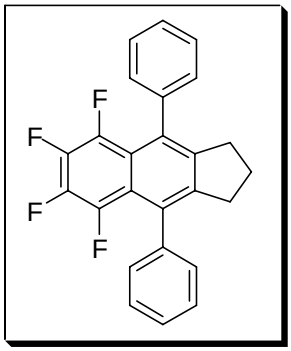
White solid, mp: 150-152 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (quintet, J = 8.0 Hz, 2 H), 2.84 (t, J = 8.0 Hz, 4 H), 3.73 (s, 6 H), 6.96 (s, 2 H), 7.40 (d, J = 8.0 Hz, 4 H), 7.42 (t, J = 8.0 Hz, 2 H), 7.52 (t, J = 8.0 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 33.0, 55.5, 104.9, 127.0, 127.4, 128.4, 129.9, 133.0, 139.4, 139.9, 148.4; HRMS: $C_{27}H_{24}O_2$ calculated 380.1776, found 380.1778.



2,3-Dihydro-4,9-diphenyl-1*H*-cyclopentanaphtho[2,3-*d*][1,3]dioxole (5l):

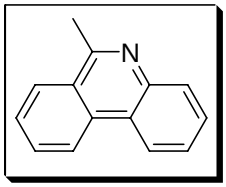
White solid, mp: 141-143 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (quintet, J = 8.0 Hz, 2 H), 2.84 (t, J = 8.0 Hz, 4 H), 5.76 (s, 6 H), 6.99 (s, 2 H), 7.40 (d, J = 8.0 Hz, 4

H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.52 (t, *J* = 8.0 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.8, 33.5, 101.0, 102.2, 127.0, 127.8, 128.4, 130.0, 133.0, 140.1, 140.5, 146.7; HRMS: $C_{26}H_{20}O_2$ calculated 364.1463, found 364.1462.



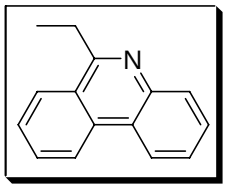
2,3-Dihydro-5,6,7,8-tetrafluoro-4,9-diphenyl-1*H*-cyclopenta[*b*]naphthalene (5m):

White solid, mp: 203-205 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.00 (quintet, *J* = 8.0 Hz, 2 H), 2.88 (t, *J* = 8.0 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 33.0, 119.1, 125.8, 127.0, 128.3, 130.1, 137.9, 143.1(d, *J* = 240.0 Hz), 145.2, 149.1(d, *J* = 240.0 Hz); HRMS: $C_{25}H_{16}F_4$ calculated 392.1188, found 392.1190.



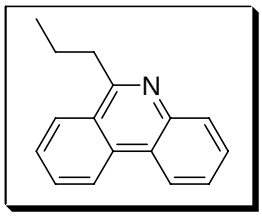
6-Methylphenanthridine (6a):[16]

Yellow solid, mp: 81-83 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.03 (s, 3 H), 7.61 (t, *J* = 7.0 Hz, 1 H), 7.67-7.71 (m, 2 H), 7.83 (t, *J* = 8.0 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 8.52 (d, *J* = 8.0 Hz, 1 H), 8.62 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.4, 121.9, 122.3, 123.8, 125.9, 126.3, 126.6, 127.3, 128.6, 129.3, 130.5, 132.6, 143.7, 158.9; HRMS: $C_{14}H_{11}N$ calculated 193.0891, found 193.0890. Registry Number: [**3955-65-5**]



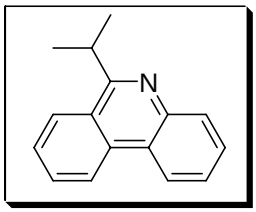
6-Ethylphenanthridine (6b):[17]

Yellow solid, mp: 55-57 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50 (t, J = 7.5 Hz, 3 H), 3.40 (q, J = 7.5 Hz, 2 H), 7.61 (t, J = 7.0 Hz, 1 H), 7.67-7.71 (m, 2 H), 7.82 (t, J = 8.0 Hz, 1 H), 8.10 (d, J = 8.0 Hz, 1 H), 8.25 (d, J = 8.0 Hz, 1 H), 8.53 (d, J = 8.0 Hz, 1 H), 8.63 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.6, 29.4, 121.9, 122.5, 123.7, 125.0, 126.3, 126.3, 127.2, 128.6, 129.5, 130.3, 132.9, 143.7, 163.3; HRMS: $C_{15}H_{13}N$ calculated 207.1048, found 207.1051. Registry Number: [**13362-58-8**]



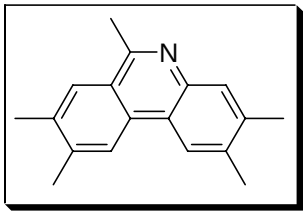
6-Propylphenanthridine (6c):[17]

Yellow oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (t, J = 7.5 Hz, 3 H), 1.96 (quintet, J = 7.5 Hz, 2 H), 3.34 (t, J = 7.5 Hz, 2 H), 7.61 (t, J = 8.0 Hz, 1 H), 7.66-7.71 (m, 2 H), 7.81 (t, J = 8.0 Hz, 1 H), 8.10 (d, J = 8.0 Hz, 1 H), 8.25 (d, J = 8.0 Hz, 1 H), 8.53 (d, J = 8.0 Hz, 1 H), 8.63 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 23.0, 38.4, 121.9, 122.5, 123.7, 125.3, 126.3, 127.2, 128.6, 129.5, 130.3, 132.9, 143.7, 162.3; HRMS: $C_{16}H_{15}N$ calculated 221.1204, found 221.1206. Registry Number: [**31150-40-0**]



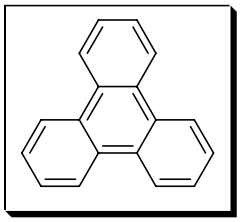
6-Isopropylphenanthridine (6d):[16]

Yellow oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50 (s, s, 6 H), 3.99 (quintet, J = 6.5 Hz, 1 H), 7.58 (t, J = 7.0 Hz, 1 H), 7.67-7.70 (m, 2 H), 7.80 (t, J = 8.0 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 8.30 (d, J = 8.0 Hz, 1 H), 8.53 (d, J = 8.0 Hz, 1 H), 8.64 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.9, 31.5, 121.8, 122.6, 123.4, 124.7, 125.7, 126.2, 127.1, 128.4, 129.9, 129.9, 133.0, 143.8, 165.9; HRMS: $C_{16}H_{15}N$ calculated 221.1204, found 221.1206. Registry Number: [**16573-52-7**]



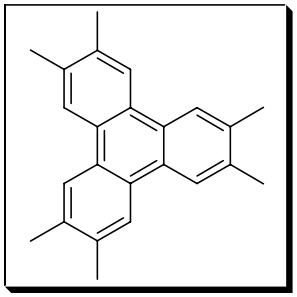
2,3,6,8,9-pentamethylphenanthridine (6e):

White solid, mp: 157-159 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3 H), 2.48 (s, 6 H), 2.53 (s, 3 H), 2.96 (s, 3 H), 7.82 (s, 1 H), 7.90 (s, 1 H), 8.22 (s, 1 H), 8.31 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.1, 20.3 (2 C), 20.7, 23.1, 121.7, 121.9 (2 C), 122.3, 124.3, 124.7, 126.6, 127.8, 129.0, 130.8, 136.1, 137.6, 157.3; HRMS: $C_{18}H_{19}N$ calculated 249.1517, found 249.1517.



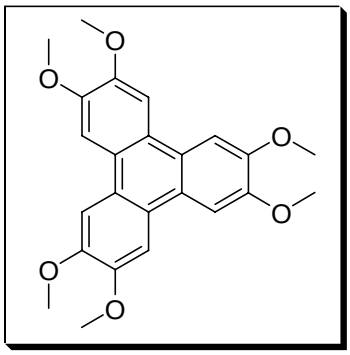
Triphenylene (7a):[18]

White solid, mp: 197-199 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (dd, J_1 = 7.0 Hz, J_2 = 3.0 Hz, 6 H), 8.65 (dd, J_1 = 7.0 Hz, J_2 = 3.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.2, 127.1, 129.7; HRMS: $C_{18}H_{12}$ calculated 228.0939, found 228.0942. Registry Number: [**217-59-4**]



2,3,6,7,10,11-Hexamethyltriphenylene (7b):[19]

White solid, mp: 277-279 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.49 (s, 18 H), 8.32 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 123.6, 127.6, 135.3; HRMS: $C_{24}H_{24}$ calculated 312.1878, found 312.1879. Registry Number: [**26146-81-6**]



2,3,6,7,10,11-Hexamethoxytriphenylene (7c):[20]

White solid, mp: 330-332 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (s, 18 H), 7.79 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.1, 104.3, 123.2, 148.8; HRMS: $C_{24}H_{24}O_6$ calculated 408.1573, found 408.1571. Registry Number: [**808-57-1**]

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