Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Nickel-catalyzed cocylotrimerization of arynes with diynes; a novel method for synthesis of naphthalene derivatives

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Experimental section

General procedure for the [2 + 2 +2] cycloaddition of benzynes with diyne: $NiBr_2$(dppe) (31 mg, 0.050 mmol), Zn (9.6 mg, 0.15 mmol) and CsF (151 mg, 2.0 mmol) were placed in a screw-capped vial. The vial was sealed with a septum and flushed several times with nitrogen. Benzyne precursor (0.50 mmol), diyne (1.0 mmol), and acetonitrile (2.0 mL) were injected into the reaction mixture via a syringe. The septum was removed, and the vial was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 80 ^{o}C for 12 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was purified by chromatography on a silica gel column using hexane as the eluent to give the pure product.

Products **3a-p** were obtained according to this procedure. Spectral data for these compounds are listed below.

1,2,3,4-Tetrahydroanthracene (3a): white solid, mp: 92-94 ^{o}C; IR (KBr): 2900, 832, 719 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ1.85 (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, $CDCl_3$): δ23.4, 29.8, 124.9, 126.6, 126.9, 132.1, 136.2; HRMS: $C_{14}H_{14}$ calculated 182.1096, found 182.1095.

2,3-Dihydro-1*H*-cyclopenta[*c*]naphthalene (3b): white solid, mp: 84-86 ^{o}C; IR (KBr): 2955, 741, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.13 (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, $CDCl_3$): δ26.2, 32.6, 122.1, 124.8, 127.4, 132.6, 143.4; HRMS: $C_{13}H_{12}$ calculated 168.0939, found 168.0937.

7,8,9,10-Tetrahydro-6*H*-cyclohepta[*c*]naphthalene (3c): white solid, mp: 104-106 ^{o}C; IR (KBr): 2924, 946, 887, 831, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ1.68-1.73 (m, 4 H), 1.81-1.86 (m, 2 H), 2.92-2.94 (m, 4 H), 7.36 (q, J = 7 Hz, 2 H), 7.53 (s, 2 H), 7.71 (q, J = 7 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ29.2, 32.4, 36.8, 125.1, 126.7, 127.0, 132.4, 142.2; HRMS: $C_{15}H_{16}$ calculated 196.1252, found 196.1253.

1,3-Dihydro{naphtho-[2,3-c]}furan (3d): yellow solid, mp: 153-155 ^{o}C; IR (KBr): 2921, 1045 (s, ν_{C-O}), 870, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ5.12 (s, 4 H), 7.43 (q, J = 6.5 Hz, 2 H), 7.66 (s, 2 H), 7.80 (q, J = 6.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ72.8, 119.2, 125.7, 127.9, 133.1, 138.2; HRMS: $C_{12}H_{10}O$ calculated 170.0732, found 170.0730.

1,3-Dihydrocyclopenta[*c*]naphthalene-2,2-dicarboxylic acid dimethyl ester (3e): yellow solid, mp: 120-122 ^{o}C; IR (KBr): 1742 (s, $\nu_{C=O}$), 1271, 1252, 1198, 1052, 882, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ3.71 (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, $CDCl_3$): δ40.2,

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.

1,3-Dihydrocyclopenta[*c*]naphthalene-2,2-dicarbonitrile (3f): yellow solid, mp: 161-163 ^{o}C; IR (KBr): 2244 ($\nu_{C\equiv N}$), 752, 694 cm^{-1}; ^{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, $CDCl_3$): δ34.3, 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.

2-(4-Toluenesulfonyl)-2,3-dihydro-1*H*-benzo[*f*]isoindole (3g): brown solid, mp: 285-287 ^{o}C ; IR (KBr): 1162 ($\nu_{S=O}$), 747, 664 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3 H), 4.72 (s, 4 H), 7.29 (d, *J* = 8 Hz, 2 H), 7.41 (q, *J* = 6.5 Hz, 2 H), 7.60 (s, 2 H), 7.74 (q, *J* = 6.5 Hz, 2 H), 7.78 (q, *J* = 8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5, 53.1, 121.2, 126.1, 127.7, 127.7, 129.8, 133.0, 134.8, 138.8, 143.8; HRMS: $C_{19}H_{17}NO_2S$ calculated 323.0980, found 323.0983.

4-Methyl-1,3-dihydronaphtho[2,3-c]furan (3h): yellow oil; IR (KBr): 2918, 1211 (s, $\nu_{C\text{-}O}$), 1040, 755, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ2.54 (s, 3 H), 5.23 (s, 2 H), 5.24 (s, 2 H), 7.40-7.48 (m, 2 H), 7.52 (s, 1 H), 7.79 (d, *J* = 8 Hz, 1 H), 7.97 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ15.4, 72.8, 73.5, 120.5, 122.8, 125.3, 125.5, 128.5, 131.1, 131.7, 133.4, 137.3, 138.1; HRMS: $C_{13}H_{12}O$ calculated 184.0888, found 184.0890.

4-Phenyl-1,3-dihydronaphtho[2,3-c]furan (3i): brown solid, mp: 122-124 ^{o}C; IR (KBr): 2925, 1051, 1025 (s, $\nu_{C\text{-}O}$), 751, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ5.00 (s, 2 H), 5.28 (s, 2 H), 7.31-7.50 (m, 7 H), 7.66 (d, *J* = 8.5 Hz, 1 H), 7.68 (s, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ72.9, 73.4, 118.8, 125.6, 125.7, 125.7, 127.6, 128.0, 128.6, 129.3, 29.4, 131.8,133.6, 136.8, 137.6, 138.1; HRMS: $C_{18}H_{14}O$ calculated 246.1045, found 246.1047.

5,10-Dimethyl-1,2,3,4-tetrahydroanthracene (3j): colorless oil; IR (KBr): 2929, 838, 781, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.83-188 (m, 4 H), 2.54 (s, 6 H), 2.79 (t, *J* = 7.5 Hz, 4 H), 7.40 (q, *J* = 6 Hz, 2 H), 7.97(q, *J* = 6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ14.0, 23.2, 28.9, 123.1, 124.2, 131.0, 133.6, 137.1; HRMS: $C_{16}H_{18}$ calculated 210.1409, found 210.1411.

7-Methyl-1,2,3,4-tetrahydroanthracene (3k): yellow solid, mp: 72-74 ^oC ; IR (KBr): 1501, 922, 876, 797 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.82-185 (m, 4 H), 2.45 (s, 3 H), 2.93 (t, *J* = 7.5 Hz, 4 H), 7.17 (d, *J* = 8 Hz, 1 H), 7.42 (s, 1H), 7.45 (s,1 H), 7.46 (s, 1 H), 7.58 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ21.7, 23.4 (2C), 29.7, 29.8, 125.8, 126.0, 126.4, 126.8, 127.2, 130.3, 132.3, 134.3, 135.2, 136.2; HRMS: $C_{15}H_{16}$ calculated 196.1252, found 196.1248.

6-Methyl-2,3-dihydro-1*H*-cyclopenta[*c*]naphthalene (3l): yellow solid, mp: 102-104 ^oC; IR (KBr): 2921, 880, 797, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.09-2.13 (m, 2 H), 2.46 (s, 3 H), 3.01 (t, *J* = 7.5 Hz , 4 H), 7.20 (d, *J* = 8 Hz, 1 H), 7.50 (s, 1 H), 7.54 (s, 1 H), 7.58 (s, 1 H), 7.62 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ21.2, 26.2, 32.5, 32.6, 126.0, 126.5, 126.7, 127.1, 127.9, 134.3, 137.0, 137.7, 142.5, 143.4; HRMS: $C_{14}H_{14}$ calculated 182.1096, found 182.1098.

6-Methyl-1,3-dihydrocyclopenta[*b*]naphthalene-2,2-dicarboxylic acid dimethyl ester (3m): yellow solid, mp: 117-119 ^oC ; IR (KBr): 1732 (s, $\nu_{C=O}$), 1248 (s, ν_{C-O}), 1199, 1150, 1070, 884, 797 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ2.46 (s, 3 H), 3.71 (s, 4 H), 3.74 (s, 6 H), 7.21 (d, *J* = 8 Hz, 1 H),7.50 (s, 1 H), 7.53 (s, 1 H), 7.57 (s, 1 H), 7.62 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ21.6, 40.1, 40.2, 53.0, 60.9, 121.8, 122.2, 126.6, 127.3, 127.6, 131.6, 133.9, 134.9, 137.8, 138.8, 172.0; HRMS: $C_{18}H_{18}O_4$ calculated 298.1205, found 298.1203.

7,8-Dimethyl-1,2,3,4-tetrahydroanthracene (3n) : white solid, mp: 125-127 ^oC; IR

(KBr): 2928, 1028, 920, 887 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.83 (quintet, *J* = 6.5 Hz, 4 H), 2.36 (s, 6 H), 2.91 (t, *J* = 6.5 Hz, 4 H), 7.38 (s, 2 H), 7.42 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ20.2, 23.5, 29.7, 125.6, 126.4, 131.1, 134.4, 135.1; HRMS: $C_{16}H_{18}$ calculated 210.1409, found 210.1404.

8,9,10,11-Tetrahydro-benzo[*a*]anthracene (3o): brown solid, mp: 90-92 ^oC; IR (KBr): 890, 908, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ1.87-2.08 (m, 4 H), 2.98 (t, *J* = 10 Hz, 2 H), 3.06 (t, *J* = 10 Hz, 2 H), 7.52-7.60 (m, 5 H), 7.82 (d, *J* = 8 Hz, 1 H), 8.35 (s, 1 H), 8.61 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ23.4, 23.4, 29.5, 30.1, 122.4, 122.4, 125.9, 126.0, 126.2 (2C), 126.5, 127.9, 128.4, 128.5, 130.1 (2C), 136.44, 136.6; HRMS: $C_{18}H_{16}$ calculated 232.1252, found 232.1253.

4-(Phenanthren-9-yl)butyronitrile (3p): orange solid, mp: 91-93 ^oC ; IR (KBr): 2918, 2366 ($\nu_{C\equiv N}$), 884, 797 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ2.14-2.20 (m, 2 H), 2.39 (t, *J* = 7 Hz, 2 H), 3.29 (t, *J* = 7 Hz, 2 H), 7.57-7.68 (m, 5 H), 7.83 (d, *J* = 8 Hz, 1 H), 8.04 (d, *J* = 7.5 Hz, 1 H), 8.65 (d, *J* = 8.5 Hz, 1 H), 8.74 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ16.8, 25.6, 32.0, 119.6, 122.5, 124.0, 124.4, 126.4, 126.5, 126.8, 127.0, 128.2, 129.2, 129.9, 130.6, 130.9, 131.5, 133.7; HRMS: $C_{18}H_{15}N$ calculated 245.1204, found 245.1203.

2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (3p'): yellow oil; IR (KBr): 2926, 2242 ($\nu_{C=N}$), 782, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ2.09-2.18 (m, 2 H), 2.97 (t, *J* = 7.5 Hz, 2 H), 3.28 (t, *J* = 7.5 Hz, 2 H), 7.55 (q, *J* = 6.5 Hz, 2 H), 7.61 (s, 1 H), 7.87 (q, *J* = 6 Hz, 1 H), 8.01 (q, *J* = 6.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ26.5, 31.6, 34.4, 127.1, 127.9, 128.5, 130.3, 132.3, 136.0, 138.7, 152.1, 167.2; HRMS: $C_{12}H_{11}N$ calculated 169.0891, found 160.0890.