Supplementary Material

General Procedure of the coupling reaction of vinyl chlorides 1a-d with 2-ethynylbenzonitrile. (**method A**) A degassed solution of vinyl chloride (12 mmol) in dry ether (30 mL) containing $Pd(PPh_3)_4$ (0.8 mmol) and CuI (3.2 mmol) was added to a solution of 2-ethynylbenzonitrile (24 mmol) containing n-butylamine (34 mmol). The resulting solution was stirred for 6 h at 25 °C, quenched with saturated aqueous NH_4Cl and Na_2CO_3 solutions and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography to give the products.

2-(7-(Tetrahydropyranyloxy)-3(Z)-hexen-1,5-diynyl)benzonitrile (1a). obtained in 52% yield as a pale-yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.66 (m, 2H), 7.54 (td, 1H, J = 7.5, 1.3 Hz), 7.41 (td, 1H, J = 7.5, 1.3 Hz), 6.10 (d, 1H, J = 10.8 Hz), 6.02 (td, 1H, J = 10.8, 2.0 Hz), 4.87 (t, 1H, J = 3.5 Hz), 4.56 (dd, 1H, J = 6.3, 1.9 Hz), 4.49 (dd, 1H, J = 6.3, 1.9 Hz), 3.82-3.88 (m, 1H), 3.50-3.55 (m, 1H), 1.50-1.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.8, 132.7, 132.2, 128.6, 128.5, 121.7, 121.3, 118.6, 96.8, 94.8, 92.7, 92.5, 82.9, 61.9, 55.0, 51.0, 30.2, 25.3, 18.9; MS(EI) relative intensity: 291 (M^+, 1.8), 190 (100), 85 (45); HRMS calcd for $C_{19}H_{17}NO_2$ 291.1260, found 291.1255.

2-(3(Z)-Undecen-1,5-diynyl)benzonitrile (1b). obtained in 22% yield as a pale-yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (dd, 1H, J = 7.2, 1.1 Hz), 7.57-7.53 (m, 2H), 7.49-7.36 (m, 1H), 6.06-5.99 (m, 2H), 2.47 (td, 2H, J = 6.9, 1.5 Hz), 1.64-1.25 (m, 6H), 0.85 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7, 132.6, 132.2, 128.3, 127.1, 122.7, 117.3, 116.9, 115.0, 101.3, 93.3, 91.4, 78.1, 31.0, 28.2, 22.2, 19.9, 13.9; MS(EI) relative intensity: 247 (M^+, 14), 217 (49), 204 (100), 190 (68); HRMS calcd for $C_{18}H_{17}N$ 247.1362, found 247.1357.

2-(3(Z)-Dodecen-1,5-diynyl)benzonitrile (1c). obtained in 17% yield as a pale-yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (dd, 1H, J = 7.8, 1.0 Hz), 7.59-7.49 (m, 2H), 7.43-7.35 (m, 1H), 6.03-5.98 (m, 2H), 2.47 (td, 2H, J = 6.8, 1.5 Hz), 1.61-1.39 (m, 4H), 0.89 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7,

132.6, 132.2, 128.3, 127.1, 122.7, 117.3, 116.9, 115.0, 101.2, 93.3, 91.4, 78.1, 30.6, 21.9, 19.6, 13.6; MS(EI) relative intensity: 233 (M^+, 22), 218 (55), 204 (100), 190 (73), 164 (36); HRMS calcd for $C_{17}H_{15}N$ 233.1205, found 233.1210.

2-(9-(Tetrahydropyranyloxy)-3(Z)-nonen-1,5-diynyl)benzonitrile (1d). obtained in 33% yield as a pale-yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.63 (m, 2H), 7.58-7.50 (m, 2H), 7.43-7.35 (m, 2H), 6.03 (d, 1H, J = 10.9 Hz), 5.96 (dt, 1H, J = 10.9, 1.7 Hz), 4.58 (t, 1H, J = 3.8 Hz), 3.90-3.76 (m, 2H), 3.57-3.46 (m, 2H), 2.60 (td, 2H, J = 7.3, 1.7 Hz), 1.95-1.48 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.8, 132.7, 132.6, 132.4, 132.2, 128.4, 122.5, 117.1, 115.0, 100.4, 98.7, 93.2, 91.7, 78.3, 66.0, 62.1, 30.6, 28.7, 25.4, 19.5, 16.8; MS(EI) relative intensity: 319 (M^+, 11), 235 (68), 216 (100), 203 (38), 190 (71); HRMS calcd for $C_{21}H_{21}NO_2$ 319.1573, found 319.1576.

General Procedure of methanolysis of 1a-d. (method B) To a solution of 3-henxen-1,5-diynylbenzonitrile (1.1 mmol) in 25 ml of methanol was added freshly cut sodium metal (5.5 mmol-atom). The resulting solution was heated to reflux and stirred at this temperature for 12 h. After cooling to room temperature, the methanol was removed *in vacuo*. Water was added to the residue and it was extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by flash chromatography on silica gel to give the products.

1-(2-Tetrahydropyranyloxymethyl)-6-methoxyphenanthridine (4a) and 1-(2-Tetrahydropyranyloxymethyl)-6-phenanthridone (5a). Methanolysis of **1a** according to method B gave **4a** in 4% yield as an oil and **5a** in 7% yield as a white solid. Spectra data of **4a**: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.80 (d, 1H, J = 8.4 Hz), 8.43 (dd, 1H, J = 8.4, 1.3 Hz), 7.96 (dd, 1H, J = 8.0, 1.6 Hz), 7.83 (td, 1H, J = 7.1, 1.6 Hz), 7.69-7.58 (m, 3H), 5.40 (d, 1H, J = 12.1 Hz), 5.08 (d, 1H, J = 12.1 Hz), 4.93 (t, 1H, J = 3.6 Hz), 4.23 (s, 3H), 4.03-4.00 (m, 1H), 3.64-3.62 (m, 1H), 1.78-1.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.8, 144.7, 134.8, 134.1, 130.5, 128.5, 128.1, 127.7, 127.2, 126.9, 124.7, 122.5, 120.9, 97.7, 69.6, 62.4, 53.5,

30.7, 25.5, 19.4; MS(EI) relative intensity: 323 (M^+, 13), 239 (12), 223 (100), 222 (64); HRMS calcd for $C_{20}H_{21}NO_3$ 323.1522, found 323.1526. Spectra data of **5a**: mp 164-165 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 10.55 (bs, 1H), 8.66 (dd, 1H, J = 7.6, 1.3 Hz), 8.59 (d, 1H, J = 8.1 Hz), 7.84 (td, 1H, J = 7.2, 1.4 Hz), 7.65 (td, 1H, J = 8.0, 1.0 Hz), 7.49 (d, 2H, J = 0.7 Hz), 7.49-7.33 (m, 1H), 5.29 (d, 1H, J = 12.1 Hz), 4.97 (d, 1H, J = 12.1 Hz), 4.91 (t, 1H, J = 3.7 Hz), 4.10-3.94 (m, 1H), 3.68-3.48 (m, 1H), 1.95-1.54 (m, 6H); ^{13}C NMR ($CDCl_3$, 49.9 MHz) δ 162.2, 136.8, 135.5, 135.0, 132.6, 128.6, 128.2, 127.6, 127.5, 126.6, 126.5, 118.6, 116.9, 97.8, 69.1, 62.5, 30.6, 25.4, 19.4; MS(EI) relative intensity: 309 (M^+, 9), 225 (20), 209 (100), 190 (22), 180 (22), 165 (35); HRMS calcd for $C_{19}H_{19}NO_3$ 309.1366, found 309.1365.

1-Pentyl-6-methoxyphenanthridine (4b), 1-pentyl-6-phenanthridone (5b) and 2-(2-pentyl-6-methoxyphenyl)benzonitrile (6b). Methanolysis of **1b** according to method B gave **4b** in 12% yield as an oil, **5b** in 6% yield as a white solid and **6c** in 4% yield as an oil. Spectra data of **4b**: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, 1H, J = 8.4 Hz), 8.43 (dd, 1H, J = 8.1, 1.5 Hz), 7.81 (td, 1H, J = 7.1, 1.6 Hz), 7.64 (td, 1H, J = 8.1, 1.1 Hz), 7.50 (t, 1H, J = 7.3 Hz), 7.33 (dd, 1H, J = 7.5, 1.5 Hz), 7.27-7.21 (m, 1H), 4.24 (s, 3H), 3.36 (t, 2H, J = 7.8 Hz), 1.87-1.25 (m, 6H), 0.96 (t, 3H, J = 7.3 Hz); MS(EI) relative intensity: 279 (M^+, 13), 250 (53), 222 (16), 207 (15), 190 (11); HRMS calcd for $C_{19}H_{21}NO$ 279.1624, found 279.1620. Spectra data of **5b**: mp 177-178 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.23 (bs, 1H), 8.62 (dd, 1H, J = 7.7, 1.3 Hz), 8.40 (d, 1H, J = 8.4 Hz), 7.79 (td, 1H, J = 8.6, 1.7 Hz), 7.61 (t, 1H, J = 7.9 Hz), 7.37 (t, 1H, J = 7.7 Hz), 7.16 (d, 1H, J = 7.4 Hz), 7.06 (d, 1H, J = 8.0 Hz), 3.24 (t, 2H, J = 8.0 Hz), 1.85-1.20 (m, 6H), 0.95 (t, 3H, J = 7.1 Hz); MS(EI) relative intensity: 265 (M^+, 53), 209 (100), 180 (55), 165 (75); HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1472. Spectra data of **5b**: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (ddd, 1H, J = 7.7, 1.3, 0.4 Hz), 7.62 (td, 1H, J = 7.7, 1.3 Hz), 7.43 (td, 1H, J = 7.5, 1.1 Hz), 7.34-7.31 (m, 2H), 6.94 (td, 1H, J = 7.7, 0.6 Hz), 6.84 (d, 1H, J = 8.2 Hz), 3.73 (s, 3H), 2.41-2.24 (m, 2H), 1.41-1.38 (m, 2H), 1.16-1.11 (m,

4H), 0.77 (t, 3H, J = 7.9 Hz); MS(EI) relative intensity: 279 (M^+, 38), 222 (100), 190 (56), 165 (25); HRMS calcd for $C_{19}H_{21}NO$ 279.1624, found 279.1623.

1-Butyl-6-methoxyphenanthridine (4c), 1-butyl-6-phenanthridone (5b) and 2-(2-butyl-6-methoxyphenyl)benzonitrile (6c). Methanolysis of **1c** according to method B gave **4c** in 1% yield as an oil, **5c** in 17% yield as a white solid and **6c** in 9% yield as an oil. Spectra data of **4c**: ^1H NMR ($CDCl_3$, 200 MHz) δ 8.62 (dd, 1H, J = 7.9, 1.6 Hz), 8.29 (d, 1H, J = 8.5 Hz), 7.73 (td, 1H, J = 8.3, 1.5 Hz), 7.58 (td, 1H, J = 8.0, 1.2 Hz), 7.45 (t, 1H, J = 8.3 Hz), 7.31 (dd, 1H, J = 8.3, 1.2 Hz), 7.21 (dd, 1H, J = 7.3, 1.4 Hz), 3.80 (s, 3H), 3.24 (t, 2H, J = 7.7 Hz), 1.88-1.70 (m, 2H), 1.58-1.47 (m, 2H), 1.01 (t, 3H, J = 7.2 Hz); MS(EI) relative intensity: 265 (M^+, 100), 223 (94), 222 (91), 192 (20), 165 (46); HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1467. Spectra data of **5c**: mp 160-161 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.83 (bs, 1H), 8.67 (dd, 1H, J = 8.1, 1.6 Hz), 8.43 (d, 1H, J = 8.4 Hz), 7.81 (td, 1H, J = 7.1, 1.5 Hz), 7.28 (dd, 1H, J = 8.0, 1.3 Hz), 7.17 (dd, 1H, J = 7.5, 1.3 Hz), 3.26 (t, 2H, J = 7.8 Hz), 1.80-1.78 (m, 2H), 1.57-1.51 (m, 2H), 1.02 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 162.1, 141.1, 136.8, 135.7, 13.3, 128.6, 128.4, 127.1, 126.9, 126.5, 117.7, 115.3, 37.0, 32.4, 22.8, 13.9; MS(EI) relative intensity: 251 (M^+, 73), 209 (100), 208 (60), 190 (30), 165 (40), 152 (24); HRMS calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1316. Spectra data of **6c**: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.74 (dd, 1H, J = 7.7, 1.2 Hz), 7.62 (td, 1H, J = 7.6, 1.4 Hz), 7.47-7.39 (m, 1H), 7.37-7.29 (m, 2H), 6.94 (d, 1H, J = 7.6 Hz), 6.84 (d, 1H, J = 8.3 Hz), 3.73 (s, 3H), 2.45-2.23 (m, 2H), 1.42-1.31 (m, 2H), 1.25-1.14 (m, 2H), 0.74 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 49.9 MHz) δ 156.7, 142.2, 141.9, 132.5, 132.1, 131.2, 129.5, 127.2, 126.6, 121.7, 118.2, 114.4, 108.4, 55.7, 33.0, 32.7, 22.3, 13.7; MS(EI) relative intensity: 265 (M^+, 58), 223 (100), 190 (24), 180 (15); HRMS calcd for $C_{18}H_{19}NO$ 265.1468, found 265.1474.

1-(3-(2-Tetrahydropyranyloxy)propyl)-6-methoxyphenanthridine (4d) and 3-(7-(2-Tetrahydropyranyloxy)-1-hepten-3-ynyl)-1-methoxyisoquinoline (7d). Methanolysis of **1d** according to method B gave **4d** in

26% yield as an oil and **7d** in 12% yield as an oil. Spectra data of **4d**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (d, 1H, J = 7.6 Hz), 8.43 (dd, 1H, J = 8.1, 1.7 Hz), 7.82-7.75 (m, 2H), 7.63 (td, J = 8.0, 1.1 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.34 (td, 1H, J = 8.3, 1.4 Hz), 4.67 (t, 1H, J = 3.4 Hz), 4.22 (s, 3H), 3.96-3.89 (m, 2H), 3.58-3.46 (m, 4H), 2.18-2.15 (m, 2H), 1.94-1.51 (m, 6H); MS(EI) relative intensity: 351 (M^+, 15), 249 (31), 222 (56), 208 (79), 165 (32), 85 (61), 41 (100); HRMS calcd for $C_{22}H_{25}NO_3$ 351.1835, found 351.1840. Spectra data of **7d**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (dd, 1H, J = 7.3, 1.4 Hz), 7.98 (s, 1H), 7.72 (d, 1H, J = 7.3 Hz), 7.62 (td, 1H, J = 6.8, 1.4 Hz), 7.50 (td, 1H, J = 6.8, 1.4 Hz), 6.73 (d, 1H, J = 12.0 Hz), 5.84 (dt, 1H, J = 12.0, 2.5 Hz), 4.60 (t, 1H, J = 3.0 Hz), 4.16 (s, 3H), 3.95-3.84 (m, 2H), 3.61-3.47 (m, 2H), 2.62 (td, 2H, J = 7.1, 2.5 Hz), 2.00-1.49 (m, 8H); MS(EI) relative intensity: 351 (M^+, 28), 249 (47), 222 (66), 208 (100), 195 (25), 85 (51), 41 (56); HRMS calcd for $C_{22}H_{25}NO_3$ 351.1835, found 351.1827.