Supporting Information

Terminal Heck Vinylations of Chelating Vinyl Ethers

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Characterization data for new compounds

***(S)-N*-methyl-2-vinyloxymethylpyrrolidine (1c)** ($C_8H_{15}NO$, MW = 141.2): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.57-1.98 (m, 4H), 2.38 (s, 3H), 2.42-2.50 (m, 2H), 3.03-3.05 (m, 1H), 3.56-3.67 (m, 2H), 3.95-3.98 (d, *J* = 6.0 Hz, 1H), 4.15 (d, *J* = 7.5 Hz, 1H), 6.45-6.53 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 22.8, 28.4, 41.3, 57.6, 64.1, 70.0, 86.1, 151.9; GC/MS *m/z* (relative intensity) 142 (M^++1, 5), 98 (11), 84 (100); LC/MS (relative intensity) 142 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_8H_{16}NO$ (M^++H): 142.1232, found: 142.1233.

***N*-benzyl-1,2,3,6-tetrahydro-pyridine-4-triflate (2e)** ($C_{13}H_{14}F_3NO_3S$, MW = 321.3): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.38 (m, 2H), 2.64 (m, 2H), 3.06 (m, 2H), 3.55 (s, 2H), 5.65 (m, 1H), 7.22-7.26 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 14.1, 28.2, 50.0, 50.4, 61.2, 116.1, 123.9, 127.4, 128.4, 129.0, 129.5, 137.9, 147.2; GC/MS *m/z* (relative intensity) 322 (M^++1, 51), 188 (100); LC/MS (relative intensity) 322 (M^++1, 100);

High resolution MS (FAB+) calcd. for $C_{13}H_{15}F_3NO_3S$ (M^++H): 322.0724, found: 322.0724; Anal. calcd. C 48.59, H 4.39, N 4.36, found: C 48.70, H 4.43, N 4.45.

***(E)*-{2-[2-(Cyclohex-1-enyl)-vinyloxy]-ethyl}-dimethylamine (3a)** ($C_{12}H_{21}NO$, MW = 195.3, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.54-1.61 (m, 4H), 2.00 (m, 4H), 2.24 (s, 6H), 2.54 (t, *J* = 3.0 Hz, 2H), 3.75 (t, *J* = 3.0 Hz, 2H), 5.48 (m, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 6.42 (d, *J* = 12.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 22.4, 22.6, 24.7, 25.6, 45.7, 46.0, 58.2, 66.9, 109.8, 123.8, 132.6, 144.8; GC/MS *m/z* (relative intensity) 196 (M^++1, 18) 195 (19), 72 (100); LC/MS (relative intensity) 196 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{12}H_{22}NO$ (M^++H): 196.1701, found: 196.1709; Anal. calcd. C 73.80, H 10.84, N 7.17; found: C 73.55, H 10.66, N 7.15.

{2-[2-(4-*t*-Butyl-cyclohex-1-enyl)-vinyloxy]-ethyl}-dimethylamine (3b) ($C_{16}H_{29}NO$, MW = 251.4, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.89 (s, 9H), 1.19-1.25 (m, 3H), 1.82-1.90 (m, 2H), 2.04-2.13 (m, 2H), 2.27 (s, 6H), 2.57 (t, *J* = 3.0 Hz, 2H), 3.78 (t, *J* = 3.0 Hz, 2H), 5.49 (m, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 6.45 (d, *J* = 12.5 Hz, 1H) [vinyl protons: 4.73 (d, *J* = 7.0 Hz, 1H), 5.78 (m, 1H), 5.81 (d, *J* = 7.0 Hz, 1H) for cis-isomer]; ^{13}C-NMR ($CDCl_3$) δ (ppm) 23.8, 26.1, 27.2, 32.1, 44.2, 45.7, 52.8, 67.0, 109.4, 124.1, 131.9, 132.6, 145.0; GC/MS *m/z* (relative intensity) 251 (M^+, 8), 72 (100), 58 (64); LC/MS (relative intensity) 252 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{16}H_{30}NO$ (M^++H): 252.2327, found: 252.2330.

***(E)*-2-[2-(3,4,-Dihydronaphthalen-1-yl)-vinyloxy]-ethyl}-dimethylamine (*trans*-3c)** ($C_{16}H_{21}NO$, MW = 243.3, light yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.31 (m, 2H), 2.40 (s, 6H), 2.72 (t, *J* = 5.5 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 3.98 (t, *J* = 5.5 Hz, 2H), 5.76 (d, *J* = 12.5 Hz, 1H), 6.06 (t, *J* = 4.5 Hz, 1H), 6.82 (d, *J* = 12.5 Hz, 1H), 7.21-7.37 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 23.1, 28.2, 45.8, 58.3, 67.1, 103.8, 123.3, 123.8, 126.3, 126.9, 127.5, 133.3, 136.5 (arom.), 147.9; GC/MS *m/z* (relative intensity) 243 (M^+, 46), 99 (32), 72 (100); LC/MS (relative intensity) 244 (M^++1, 100), 242 (80); High resolution MS (FAB+) calcd. for $C_{16}H_{22}NO$ (M^++H): 244.1701, found: 244.1709.

***(Z)*-2-[2-(3,4-Dihydronaphthalen-1-yl)-vinyloxy]-ethyl}-dimethylamine (*cis*-3c)** ($C_{16}H_{21}NO$, MW = 243.3, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.29-2.35 (m, 8H), 2.62 (t, *J* = 5.5 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 5.5 Hz, 2H), 5.13 (d, *J* = 12.5 Hz, 1H), 6.25 (d, *J* = 12.5 Hz, 1H), 6.63 (t, *J* = 8.5 Hz, 1H), 7.11-7.30 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 23.2, 28.2, 45.6, 58.4, 67.6, 103.9, 123.2, 123.8, 126.4, 127.0, 127.7, 133.2, 135.1 (arom.), 148.0; GC/MS *m/z* (relative intensity) 243 (M^+, 43), 99 (22), 72 (100); LC/MS (relative intensity) 244 (M^++1, 100), 242 (50); High resolution MS (FAB+) calcd. for $C_{16}H_{22}NO$ (M^++H): 244.1701, found: 244.1692.
Separation of the geometrical isomers was achieved by FCC using ethylacetate/hexane (1:4 + 2% triethylamine) as eluent, with the *trans*-isomer eluted first (R_f = 0.65, TLC) and the *cis*-isomer eluted second (R_f = 0.52, TLC).

***(E)*-2-[2-(6-Methoxy-3,4,-dihydronaphthalen-1-yl)-vinyloxy]-ethyl}-dimethyl-amine (*trans*-3d)** ($C_{17}H_{23}NO_2$, MW = 273.4, dark yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.23-2.28 (m, 2H), 2.31 (s, 6H), 2.63 (t, *J* = 5.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 3.79 (s, 3H), 3.89 (t, *J* = 5.5 Hz, 2H), 5.65 (d, *J* = 12.5 Hz, 1H), 5.83 (t, *J* = 4.5 Hz, 1H), 6.69-6.73 (m, 3H), 7.20-7.25 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 23.0, 28.7, 45.7, 55.1, 58.1, 67.0, 103.9, 110.7, 113.6, 120.8, 124.9, 128.0, 132.7, 138.3 (arom.), 147.7, 158.4; GC/MS *m/z* (relative intensity) 273 (M^+, 19), 99 (12), 72 (100); LC/MS (relative intensity) 274 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{17}H_{24}NO_2$ (M^++H): 274.1807, found: 274.1822.
While purifying by FCC using ethylacetate/hexane (1:4 + 2% triethylamine) the *cis*-isomer disappeared, probably converted into the *trans*-isomer, which was the single product to be recovered after elution.

***(E)*-{2-[2-(*N*-Benzyl-1,2,3,6-tetrahydropyridin-4-yl)-vinyloxy]-ethyl}-dimethylamine (3e)** ($C_{18}H_{26}N_2O$, MW = 286.4, dark orange oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.19-2.25 (m, 2H), 2.27 (s, 6H), 2.57-2.61 (m, 4H), 3.03 (m, 2H), 3.57 (d, *J* = 4.0 Hz, 2H), 3.79 (t, *J* = 5.0 Hz, 2H), 5.43 (m, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 6.46 (d, *J* = 12.5 Hz, 1H), 7.25-7.33 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 25.7, 45.6, 49.5, 53.1, 58.1, 62.7, 67.0, 108.5, 120.6, 127.0, 128.2, 129.1 (arom.), 138.3, 145.6; GC/MS *m/z* (relative intensity) 287 (M^++1, 52), 198 (65), 185 (52), 72 (100); LC/MS (relative

intensity) 287 (M^++1, 40), 164 (100), 144 (96); High resolution MS (FAB+) calcd. for $C_{18}H_{27}N_2O$ (M^++H): 287.2123, found: 287.2120.

***(E)*-2-[(4-Ethyl-hexa-1,3-dienyl)-oxy]-ethyl}-dimethylamine (3f)** ($C_{12}H_{23}NO$, MW = 197.3, orange oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.89-0.95 (m, 6H), 2.01-2.06 (m, 4H), 2.19 (s, 6H), 2.51-2.55 (m, 2H), 3.80 (t, *J* = 6.5 Hz, 2H), 5.58 (d, *J* = 12.5 Hz, 1H), 5.85 (m, 1H), 6.48 (d, *J* = 12.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 12.7, 23.5, 29.4, 45.6, 58.1, 67.2, 103.9, 115.0, 144.3, 148.6; GC/MS *m/z* (relative intensity) 198 (M^++1, 13), 72 (100), 58 (52); LC/MS (relative intensity) 198 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{12}H_{23}NO$ (M^+): 197.1780, found: 197.1790.

***(E)*-{2-[2-(Cyclohex-1-enyl)-vinyloxy]-ethyl}-diethylamine (3g)** ($C_{14}H_{25}NO$, MW = 223.3, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.03 (t, *J* = 7.0 Hz, 6H,), 1.60-1.65 (m, 4H), 2.05 (m, 4H), 2.58 (q, *J* = 7.0 Hz, 4H), 2.72 (t, *J* = 5.5 Hz, 2H), 3.78 (t, *J* = 6.0 Hz 2H), 5.50 (m, 1H), 5.53 (d, *J* = 12.5 Hz, 1H), 6.45 (d, *J* = 12.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 11.7 (2C), 22.6, 22.8, 24.8, 25.5, 47.5 (2C), 51.7, 67.8, 109.6, 123.8, 144.9 (2C); GC/MS *m/z* (relative intensity) 224 (M^++1, 4), 100 (43), 86 (100); LC/MS (relative intensity) 224 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{14}H_{26}NO$ (M^++H): 224.2014, found: 224.2017.

{2-[2-(4-*t*-Butyl-cyclohex-1-enyl)-vinyloxy]-ethyl}-diethylamine (3h) ($C_{18}H_{33}NO$, MW = 279.4, light yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.86 (s, 9H), 1.03 (t, *J* = 7.0 Hz, 6H), 1.20-1.25 (m, 2H), 1.78-1.88 (m, 3H), 2.06-2.14 (m, 2H), 2.56 (q, *J* = 7.0 Hz, 4H), 2.72 (t, *J* = 6.0 Hz, 2H), 3.78 (t, *J* = 6.0 Hz, 2H), 5.51 (m, 1H), 5.54 (d, *J* = 12.5 Hz, 1H), 6.44 (d, *J* = 12.5 Hz, 1H) [vinyl protons: 4.71 (d, *J* = 7.0 Hz, 1H), 5.78 (m, 1H), 5.81 (d, *J* = 7.0 Hz, 1H) for cis-isomer]; ^{13}C-NMR ($CDCl_3$) δ (ppm) 11.7, 23.8, 26.2, 27.2, 32.4, 44.3, 47.5, 51.8, 67.7, 109.4, 124.0, 132.5, 145.2; GC/MS *m/z* (relative intensity) 280 (M^++1, 10), 127 (12), 100 (93), 86 (100); LC/MS (relative intensity) 280 (M^++1 ,100); High resolution MS (FAB+) calcd. for $C_{18}H_{34}NO$ (M^++H): 280.2640, found: 280.2635; Anal. calcd. C 77.36, H 11.90, N 5.01, found: C 77.16, H 11.80, N 5.16.

***(E)*-{2-[2-(3,4-Dihydronaphthalen-1-yl)-vinyloxy]-ethyl}-dimethylamine (3i)** ($C_{18}H_{25}NO$, MW = 271.4, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.09 (t, *J* = 7.0 Hz, 6H), 1.26-1.29 (m, 4H), 2.61 (q, *J* = 7.0 Hz, 4H), 2.75-2.78 (m, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 5.64 (d, *J* = 12.5 Hz, 1H), 5.98 (t, 1H), 6.73 (d, *J* = 12.5 Hz, 1H), 7.13-7.29 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 14.1, 23.0, 28.2, 47.6, 51.7, 60.3, 103.7, 115.3, 121.2, 123.1, 123.7, 126.8, 127.4 (arom.), 147.9; GC/MS *m/z* (relative intensity) 271 (M^+, 6), 127 (20), 100 (37), 86 (100); LC/MS (relative intensity) 272 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{18}H_{26}NO$ (M^++H): 272.2014, found: 272.2008.

***(E)*-2-[2-(6-Methoxy-3,4-dihydronaphthalen-1-yl)-vinyloxy]-ethyl}-diethylamine (3j)** ($C_{19}H_{27}NO_2$, MW = 301.4, orange oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.06 (t, *J* = 7.0 Hz, 6H), 1.59 (m, 2H), 2.23-2.28 (m, 2H), 2.60 (q, *J* = 7.0 Hz, 4H), 2.78 (m, 2H), 3.80 (s, 3H), 3.88 (m, 2H), 5.64 (d, *J* = 12.5 Hz, 1H), 5.83 (t, *J* = 3.5 Hz, 1H), 6.71-6.76 (m, 3H), 7.21-7.24 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 11.6, 23.0, 28.9 47.5, 53.4, 55.1, 67.8, 103.9, 110.6, 113.6, 120.7, 124.9, 132.8, 138.5 (arom.), 147.8, 151.7 158.2; GC/MS *m/z* (relative intensity) 301 (M^+, 22), 127 (51), 100 (60), 86 (100); LC/MS (relative intensity) 302 (M^++1, 100), 300 (22); High resolution MS (FAB+) calcd. for $C_{19}H_{28}NO_2$ (M^++H): 302.2120, found: 302.2121.

***(E)*-{2-[2-(*N*-Benzyl-1,2,3,6-tetrahydropyridin-4-yl)-vinyloxy]-ethyl}-diethylamine (3k)** ($C_{20}H_{30}N_2O$, MW = 314.4, light yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.96-1.01 (m, 6H), 2.15 (m, 2H), 2.49-2.57 (m, 6H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.99 (d, *J* = 2.5 Hz, 2H), 3.53 (s, 2H), 3.74 (m, 2H), 5.39 (m, 1H), 5.50 (d, *J* = 12.5 Hz, 1H), 6.41 (d, *J* = 12.5 Hz, 1H), 7.22-7.29 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 11.7, 25.7, 47.5, 49.6, 51.7, 53.2, 62.8, 67.8, 108.5, 120.6, 127.0, 128.2, 129.1, 131.5, 138.4 (arom.), 145.9; GC/MS *m/z* (relative intensity) 314 (M^+, 7), 185 (30), 91 (100), 86 (88); LC/MS (relative intensity) 315 (M^++1, 5), 178 (5), 158 (100); High resolution MS (FAB+) calcd. for $C_{20}H_{31}N_2O$ (M^++H): 315.2436, found: 315.2440.

***(E)*-{2-[(4-Ethyl-hexa-1,3-dienyl)-oxy]-ethyl}-diethylamine (3l)** ($C_{14}H_{27}NO$, MW = 225.3): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.01-1.06 (m, 12H), 2.10 (m, 4H), 2.57-2.61 (m, 4H), 2.70-2.73 (m, 2H), 3.74-3.80 (m, 2H), 5.94 (d, *J* = 12.5 Hz, 1H), 6.08 (m, 1H),

6.48 (d, J = 12.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 11.6, 11.8, 12.8, 13.2, 23.6, 29.0, 47.5, 47.8, 53.4, 66.0, 103.3, 115.0, 144.5, 149.0; GC/MS *m/z* (relative intensity) 225 (M^+, 5), 100 (95), 86 (100); LC/MS (relative intensity) 226 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{14}H_{28}NO$ (M^++H): 226.2171, found: 226.2165.

***(E)*-2-[2-(4-*t*-Butyl-cyclohex-1-enyl)-vinyloxymethyl]-1-methyl-pyrrolidine (3m)** ($C_{18}H_{31}NO$, MW = 277.4, slight yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.86 (s, 9H), 1.20-1.25 (m, 2H), 1.65-1.90 (m, 6H), 2.04-2.28 (m, 4H), 2.40 (s, 3H), 2.48-2.51 (m, 1H), 3.04-3.09 (m, 1H), 3.65-3.72 (m, 2H), 5.51 (m, 1H), 5.55 (d, J = 12.5 Hz, 1H), 6.46 (d, J = 12.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 22.7, 23.8, 26.1, 27.1, 28.4, 32.1, 41.4, 44.3, 57.6, 64.3, 71.7, 109.3, 124.0, 145.3; GC/MS *m/z* (relative intensity) 277 (M^+, 12), 98 (65), 84 (100); LC/MS (relative intensity) 278 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{18}H_{32}NO$ (M^++H): 278.2484, found: 278.2481.

***(E)*-2-[2-(3,4-Dihydronaphthalen-1-yl)-vinyloxymethyl]-1-methyl-pyrrolidine (3n)** ($C_{18}H_{23}NO$, MW = 269.4, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.65-1.90 (m, 6H), 2.04-2.28 (m, 4H), 2.42 (s, 3H), 3.04-3.09 (m, 1H), 3.65-3.72 (m, 2H), 5.51 (m, 1H), 5.55 (d, J = 12.5 Hz, 1H), 6.46 (d, J = 12.5 Hz, 1H), 7.12-7.25 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 22.9, 23.0, 27.8, 29.2, 41.7, 57.7, 64.0, 70.9, 115.1, 123.7, 125.3, 126.0, 126.8, 127.3, 135.4, 136.9, 137.4 (arom.), 149.1; GC/MS *m/z* (relative intensity) 269 (M^+, 12), 98 (50), 84 (100); LC/MS (relative intensity) 270 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{18}H_{24}NO$ (M^++H): 270.1858, found: 270.1865.

***(E)*-2-[2-(6-Methoxy-3,4-dihydronaphthalen-1-yl)-vinyloxymethyl]-1-methyl-pyrrolidine (3o)** ($C_{19}H_{25}NO_2$, MW = 299.4, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.70-1.88 (m, 6H), 2.12-2.25 (m, 4H), 2.42 (s, 3H), 3.02-3.07 (m, 1H), 3.64-3.70 (m, 2H), 3.86 (s, 3H), 5.52 (m, 1H), 5.56 (d, J = 12.5 Hz, 1H), 6.47 (d, J = 12.5 Hz, 1H), 7.15-7.21 (m, 3H); GC/MS *m/z* (relative intensity) 299 (M^+, 28), 98 (40), 84 (100); LC/MS (relative intensity) 300 (M^++1, 100); High resolution MS (FAB+) calcd. for $C_{19}H_{26}NO_2$ (M^++H): 300.1963, found: 300.1962.

5,6,7,8-Tetrahydronaphthalene-1,2-dicarboxylic acid methylester (5a) ($C_{14}H_{16}O_4$, MW = 248.3, yellow oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.79-1.90 (m, 4H), 2.72-2.82 (m, 4H), 3.88 (s, 3H), 3.95 (s, 3H), 7.15-7.18 (m, 1H,), 7.72-7.75 (m, 1H,); ^{13}C-NMR ($CDCl_3$) δ (ppm) 22.1, 23.3, 25.9, 29.9, 52.2, 52.4, 125.4, 126.7, 126.8, 129.9 (arom.), 143.22; GC/MS *m/z* (relative intensity) 249 (M^++1, 3), 216 (100), 158 (55), 129 (35); LC/MS (relative intensity) 249 (M^++1, 75), 497 (dimer, 100); High resolution MS (FAB+) calcd. for $C_{14}H_{17}O_4$ (M^++H): 249.1127, found: 249.1151.

7-*t*-Butyl-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylic acid methylester (5b) ($C_{18}H_{24}O_4$, MW = 304.3, colorless oil): ^{1}H-NMR ($CDCl_3$) δ (ppm) 0.93 (s, 9H), 2.01-2.07 (m, 4H), 2.30-2.54(m, 1H), 2.70-3.01 (m, 2H), 3.87, (s, 3H), 3.97 (s, 3H), 7.14-7.31 (m, 1H), 7.70-7.80 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 23.6, 27.0, 27.5, 31.0, 32.4, 34.5, 44.1, 52.3, 52.4, 126.9, 129.4 (arom.), 143.50, 169.5; GC/MS *m/z* (relative intensity) 304 (M^+, 2), 272 (17), 215 (100), 158 (10); LC/MS (relative intensity) 305 (M^++1, 65), 609 (dimer, 100); High resolution MS (FAB+) calcd. for $C_{18}H_{24}O_4Na$ (M^++Na): 327.1572, found: 327.1582.

9,10-Dihydrophenanthrene-1,2-dicarboxylic acid methylester (5c) ($C_{18}H_{16}O_4$, MW = 296.3, pale yellow powder): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.02-2.07 (m, 4H), 3.85-3.99 (m, 6H), 7.20-7.49 (m, 3H), 7.70-7.94 (m, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 25.5, 28.2, 52.4, 52.6, 124.4, 124.5, 125.8, 127.2, 128.1, 128.6, 129.9, 132.9, 134.2, 134.5, 137.7, 139.4 (arom.), 169.8, 169.9; GC/MS *m/z* (relative intensity) 296 (M^+, 8), 264 (100), 205 (55), 178 (40); LC/MS (relative intensity) 297 (M^++1, 54), 593 (dimer, 100); High resolution MS (FAB+) calcd. for $C_{18}H_{16}O_4$ (M^+): 296.1049, found: 296.1052; Anal. calcd. C 72.96, H 5.44, found: C 72.71, 5.60.

7-Methoxy-9,10-dihydrophenanthrene-1,2-dicarboxylic acid methylester (5d) ($C_{19}H_{18}O_5$, MW = 326.3, yellow solid): ^{1}H-NMR ($CDCl_3$) δ (ppm) 2.82 (m, 4H), 3.85 (s, 3H), 3.87 (s, 3H), 3.98 (s, 3H), 6.78-7.91 (m, 5H), ^{13}C-NMR ($CDCl_3$) δ (ppm) 25.5, 28.6, 52.3, 52.6, 55.3, 112.8, 113.2, 123.6, 126.0, 128.6, 133.6, 134.2, 139.5 (arom.), 159.0; GC/MS *m/z* (relative intensity) 326 (98), 294 (100), 235 (35), 165 (30); LC/MS (relative intensity) 327 (M^++1, 75), 653 (dimer, 100); High resolution

MS (FAB+) calcd. for $C_{19}H_{18}O_5$ (M^+): 326.1154, found: 326.1159; Anal. calcd. C 69.93, H 5.56, found: C 70.07, H 5.60.

Phenanthrene-1,2-dicarboxylic acid methylester (6c) ($C_{18}H_{14}O_4$, MW = 294.3, colorless crystals, mp = 128 °C): ^{1}H-NMR ($CDCl_3$) δ (ppm) 3.87 (s, 3H), 3.95 (s, 3H), 7.35-7.98 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 52.6, 52.9, 123.3, 123.9, 125.1, 126.3, 127.4, 128.2, 128.7, 129.0, 129.4, 132.4, 133.3 (arom.), 169.5; GC/MS *m/z* (relative intensity) 294 (M^+, 100), 264 (30), 177 (40); LC/MS (relative intensity) 295 (M^++1, 100), 589 (dimer, 96); High resolution MS (FAB+) calcd. for $C_{18}H_{14}O_4$ (M^+): 294.0892, found: 294.0890; Anal. calcd. C 73.46, H 4.79, found: C 72.43, H 4.86.

7-Methoxy-phenanthrene-1,2-dicarboxylic acid methylester (6d) ($C_{19}H_{16}O_5$, MW = 324.3, pale yellow crystals, mp = 135 °C): ^{1}H-NMR ($CDCl_3$) δ (ppm) 3.95 (s, 6H), 4.12 (s, 3H), 7.26-7.31 (m, 2H), 7.71-7.79 (m, 2H), 8.17-8.20 (d, 1H), 8.60-8.68 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm) 52.5, 52.9, 55.4, 108.4, 117.9, 123.3, 123.6, 123.9, 125.0, 125.9, 126.2, 128.5, 133.4, 134.1 (arom.), 159.5; GC/MS *m/z* (relative intensity) 324 (M^+, 100), 294 (76); LC/MS (relative intensity) 325 (M^++1, 100), 649 (dimer, 96); High resolution MS (FAB+) calcd. for $C_{19}H_{16}O_5$ (M^+): 324.0998, found: 324.1002.