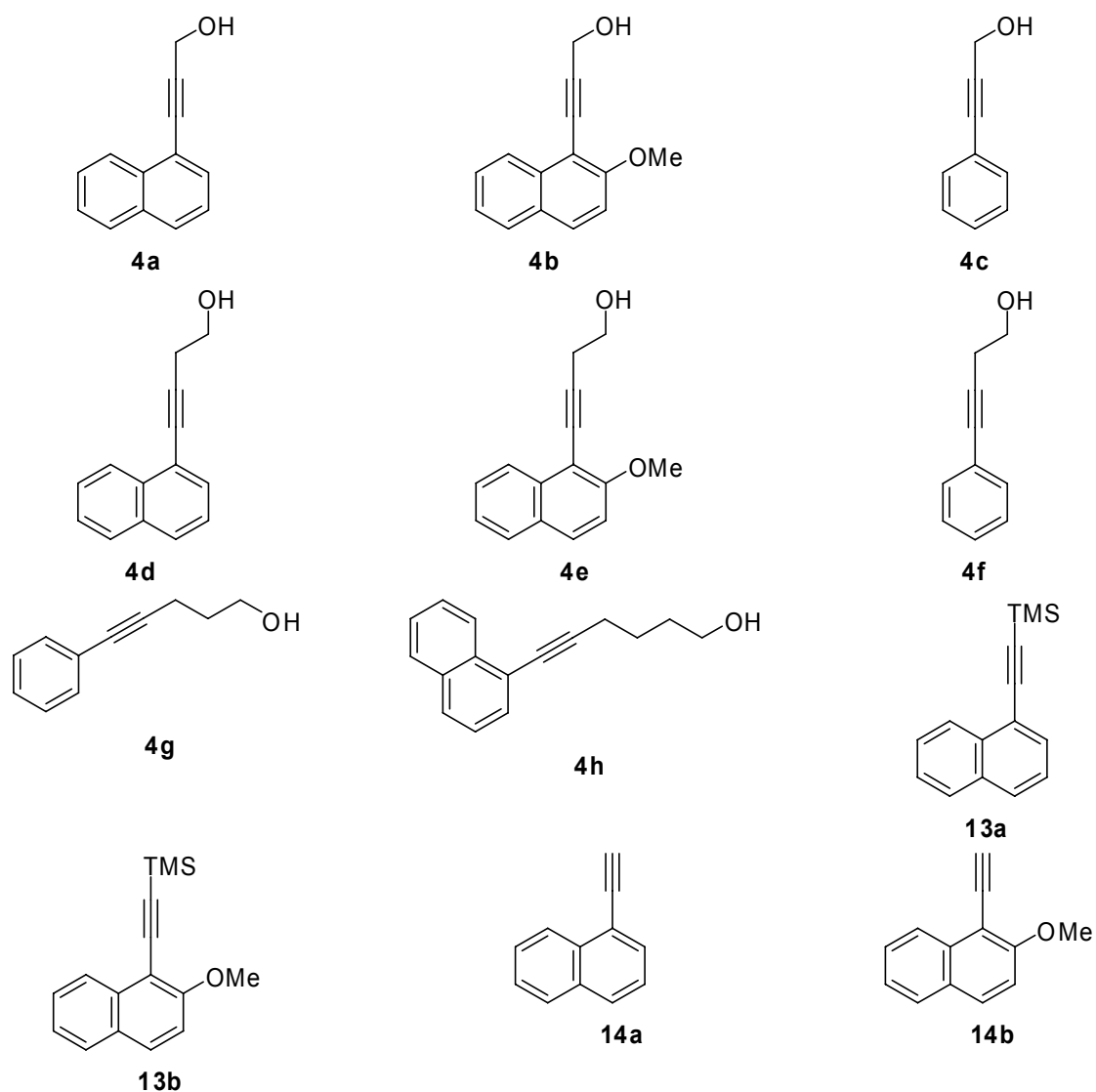


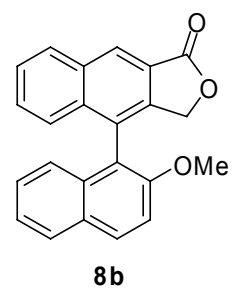
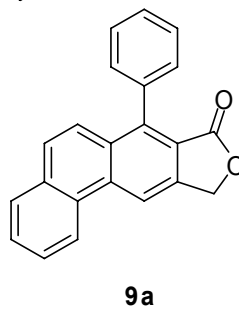
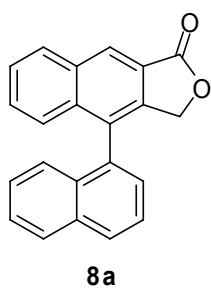
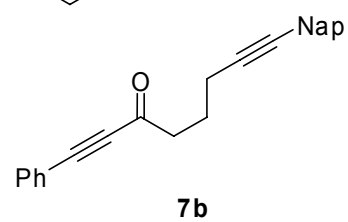
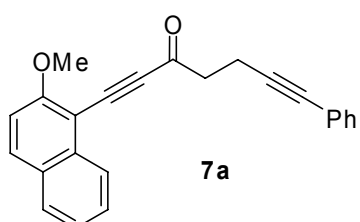
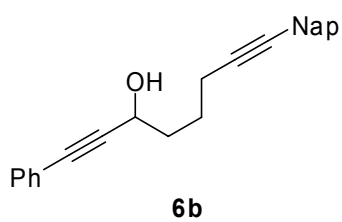
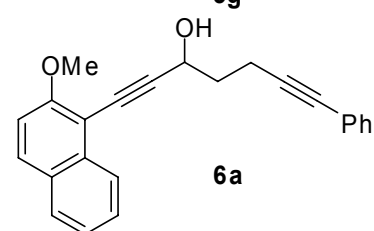
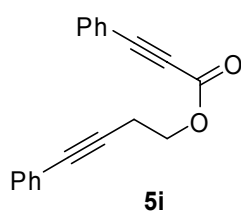
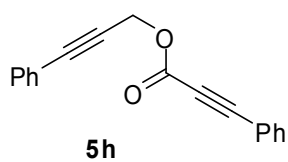
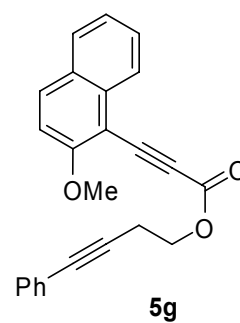
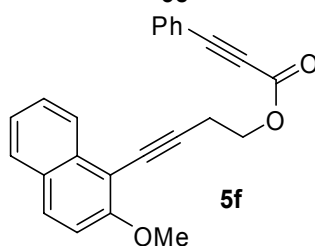
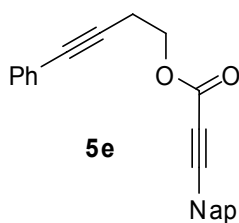
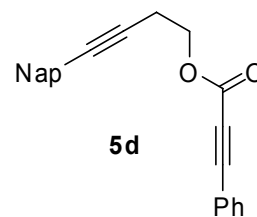
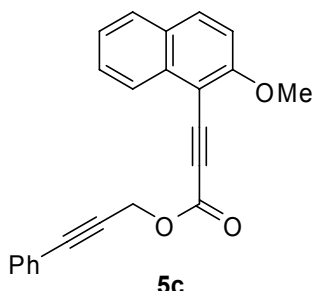
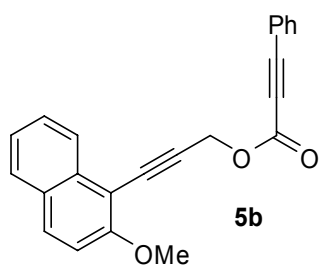
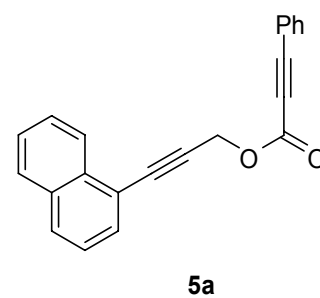
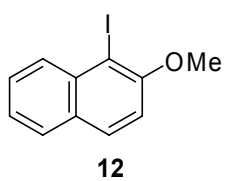
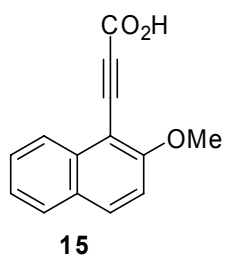
Synthesis of 1,1'-Binaphthyls by *Photo-Dehydro-Diels-Alder* reaction

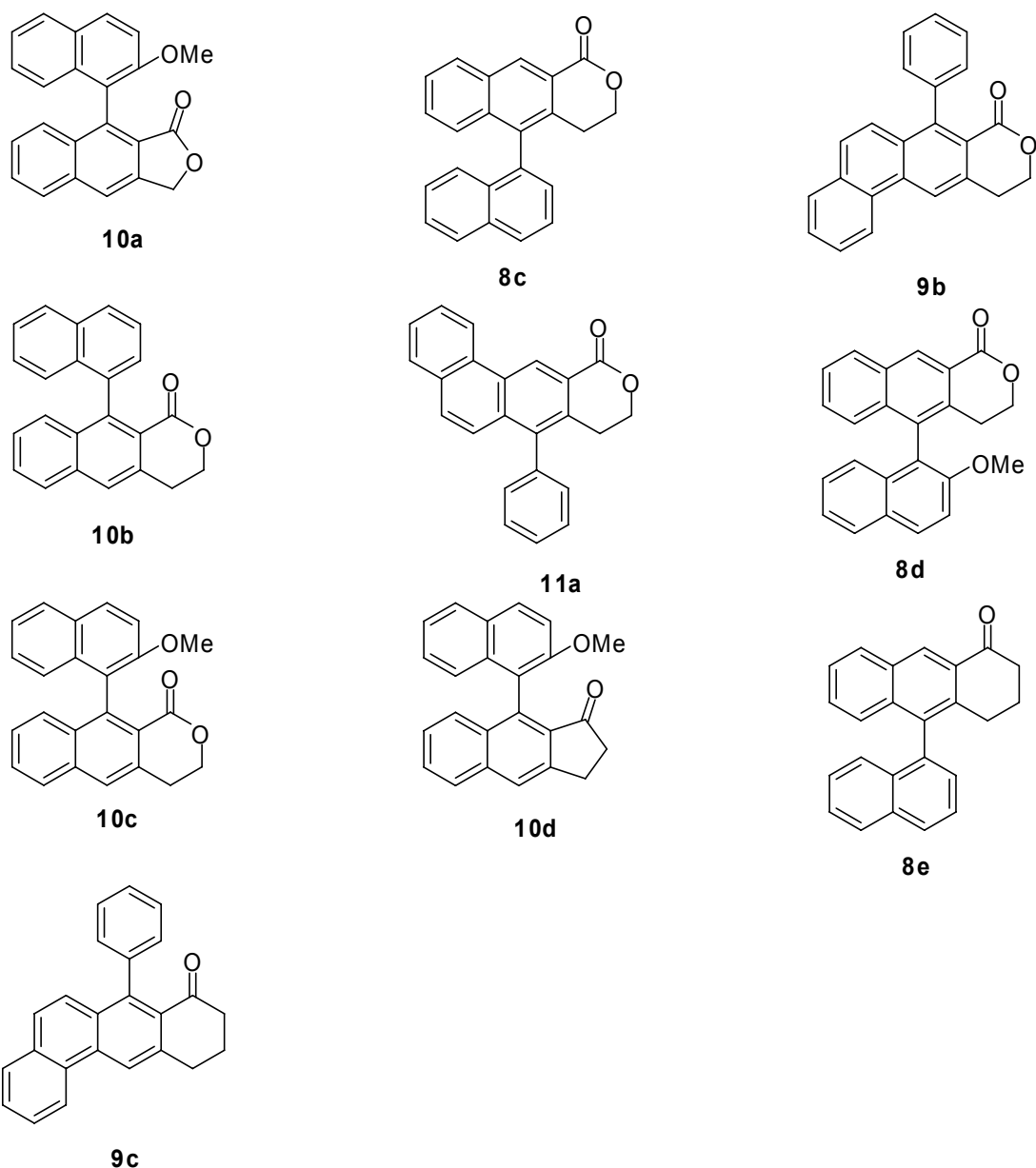
Pablo Wessig^{*a} and Gunnar Mueller^a

Supporting Information

Formula Overview







General. The following reagents were prepared according to literature procedures: 3-(naphthalene-1-yl)prop-2-yn-1-ol **4a**ⁱ, 3-phenylprop-2-yn-1-ol **4c**ⁱⁱ, 4-(naphthalene-1-yl)but-3-yn-1-ol **4d**ⁱⁱ, 4-phenylbut-3-yn-1-ol **4f**ⁱⁱⁱ, 5-phenylpent-4-yn-1-ol **4g**^{iv}, 1-iodo-2-methoxymethylnaphthalene **12**^v, trimethyl(naphthalen-1-ylethynyl)silane **13a**^{vi} and 1-ethynylnaphthalene **14a**^{vii}. THF and Et₂O were dried over Na metal in the presence of benzophenone as an indicator of dryness and distilled under a nitrogen atmosphere at atmospheric pressure. CH₂Cl₂ was dried by heating to reflux over P₄O₁₀ and distilled at atmospheric pressure. Methanol was dried by heating to reflux over Mg and distilled at atmospheric pressure. All moisture-sensitive reagents were transferred via syringe under N₂ atmosphere; moisture-sensitive reactions were carried out under N₂ atmosphere. Flash column

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chromatography: silica gel, 230-400 mesh (*Fluka*). Anal. TLC: *Merck* silica gel 60 F₂₅₄ plates; detection by UV light. Mp.: *Büchi* 530, uncorrected. NMR: CDCl₃ solutions; *Bruker DPX300* equipment; calibration: CDCl₃ (¹H: 7.26 ppm = HCCl₃ and 0.00 ppm = Me₄Si respectively; ¹³C: 77.0 ppm); IR: *Perkin-Elmer-881*, solids as KBr pastilles, liquids and oils on NaCl crystals as film. EI-MS: *Hewlett-Packard 5995 A*, 70eV at 293-593 K, m/z (%). HR-EIMS: *MSI Concept IH*. Photochemistry: prep. irradiations with a 150-W high pressure Hg-arc lamp (*Hanau*); anal. irradiations with a 500-W high pressure Hg-arc lamp (*OSRAM HBO-500*), UV cuvet 1 x 1 cm, filter *WG 295* (*Schott*).

General Procedure A. Sonogashira-coupling of 1-iodo-2-methoxynaphthalene 12. To a stirred suspension of 1 eq. 1-iodo-2-methoxynaphthalene **12** and PdCl₂(PPh₃)₂ (5 mol%) under a nitrogen atmosphere in dried TEA were added CuI (10 mol%) and then 1.5 eq. acetylene and heated to 80 °C. The course of the reaction was monitored by TLC. After completion of the conversion the mixture was allowed to come to r. t., after the addition of MTBE the organic phase was washed thrice with water. The aqueous phase was re-extracted once with MTBE, the combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure and the residue was purified by flash-chromatography.

3-(Methoxynaphthalen-1-yl)prop-2yn-1-ol 4b. From **12** (200 mg, 0.704 mmol) in 10 ml Et₃N in the presence of PdCl₂(PPh₃)₂ (25 mg, 0.035 mmol), CuI (13 mg, 0.070 mmol) and prop-2-yn-1-ol (59 mg, 1.056 mmol) according to general procedure A in 5 h to afford after flash-chromatography (CH₂Cl₂/MeOH : 100/1) a brownish solid (54 mg, 36 %).

Mp 77 °C

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.24 (1 H, dd, ³J = 8.3 Hz, ⁴J = 1.0 Hz), 7.82 (1 H, d, ³J = 9.1 Hz), 7.77 (1 H, d, ³J = 8.1 Hz), 7.52 (1 H, td, ³J = 8.3 Hz, ⁴J = 1.3 Hz), 7.37 (1 H, td, ³J = 8.1 Hz, ⁴J = 1.1 Hz), 7.23 (1 H, d, ³J = 9.1 Hz), 4.71 (2 H, s), 4.02 (3 H, s), 2.22 (1 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 159.0 (C_q), 134.5 (C_q), 130.4 (CH), 128.4 (C_q), 128.0 (CH), 127.4 (CH), 125.1 (CH), 124.2 (CH), 112.4 (CH), 105.4 (C_q), 96.9 (C_q), 80.0 (C_q), 56.5 (CH₃), 52.1 (CH₂);

HRMS (ESI) C₁₄H₁₃O₂ [M+H]⁺ 213.0910, found: 213.0912;

IR (KBr) ν (cm⁻¹) 1506, 1256, 1060, 807;

MS (ESI) 213 [M+H]⁺, 235 [M+Na]⁺, 447 [2M+Na]⁺.

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4-(2-Methoxynaphthalen-1-yl)but-3-yn-1-ol 4e. From **12** (200 mg, 0.704 mmol) in 10 ml TEA in the presence of PdCl₂(PPh₃)₂ (25 mg, 0.035 mmol), CuI (13 mg, 0.070 mmol) and but-3-yn-1-ol (74 mg, 1.056 mmol) according to general procedure A in 5 h to afford **4e** as a brownish oil (66 mg, 41 %) after flash-chromatography (CH₂Cl₂).

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.22 (1 H, d, ³J = 8.5 Hz), 7.81 (2 H, m), 7.53 (1 H, td, ³J = 8.4 Hz, ⁴J = 1.3 Hz), 7.37 (1 H, td, ³J = 8.1 Hz, ⁴J = 1.3 Hz), 7.24 (1 H, d, ³J = 9.1 Hz), 4.02 (3 H, s), 3.92 (2 H, t, ³J = 6.1 Hz), 2.91 (2 H, t, ³J = 6.1 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 158.8 (C_q), 134.5 (C_q), 129.6 (CH), 128.5 (C_q), 128.0 (CH), 127.2 (CH), 125.2 (CH), 124.1 (CH), 112.4 (CH), 106.3 (C_q), 96.2 (C_q), 77.2 (C_q), 61.2 (CH₂), 56.5 (CH₃), 24.6 (CH₂);

HRMS (EI) C₁₅H₁₄O₂ [M]⁺ 226.0994, found: 226.0994;

IR (KBr) ν (cm⁻¹) 1508, 1271, 1254, 1044, 807, 748;

MS (EI, 70 eV) *m/z* (%) 226 (100) [M]⁺, 195 (59) [M-CH₂OH]⁺, 181 (10) [M-C₂H₄OH]⁺.

((2-Methoxynaphthalen-1-yl)ethynyl)trimethylsilane 13b. From **12** (0.57 g, 1.99 mmol) in 40 ml TEA in the presence of PdCl₂(PPh₃)₂ (70 mg, 0.010 mmol), CuI (38 mg, 0.199 mmol) and ethynyltrimethylsilane (0.29 g, 2.99 mmol) according to general procedure A in 5 h to afford **13b** as a yellow oil (0.46 g, 91 %) after flash-chromatography (PE/EtOAc : 10/1).

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.26 (1 H, dd, ³J = 8.5 Hz, ⁴J = 1.1 Hz), 7.81 (1 H, d, ³J = 9.1 Hz), 7.78-7.76 (1 H, m), 7.55 (1 H, td, ³J = 8.3 Hz, ⁴J = 1.3 Hz), 7.38 (1 H, td, ³J = 8.1 Hz, ⁴J = 1.1 Hz), 7.22 (1 H, d, ³J = 9.1 Hz), 4.03 (3 H, s), 0.36 (9 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 159.4 (C_q), 134.8 (C_q), 130.4 (CH), 128.4 (C_q), 128.0 (CH), 127.4 (CH), 125.2 (CH), 124.1 (CH), 112.7 (CH), 106.1 (C_q), 104.4 (C_q), 99.3 (C_q), 56.6 (CH₃), 0.3 (CH₃);

HRMS (EI) C₁₆H₁₈OSi [M]⁺ 254.1127, found: 254.1127;

IR (Film) ν (cm⁻¹) 1506, 1273, 1255, 1091, 873, 777;

MS (EI, 70 eV) *m/z* (%) 254 (100) [M]⁺, 239 (62) [M-CH₃]⁺, 224 (33) [M-2(CH₃)]⁺, 209 (32) [M-3(CH₃)]⁺.

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6-(Naphthalen-1-yl)hex-5-yn-1-ol 4h. To a stirred suspension of 1-iodonaphthalene (1.31 g, 5.14 mmol) and PdCl₂(PPh₃)₂ (72 mg, 0.103 mmol) under a nitrogen atmosphere hex-5-yn-1-ol (0.61 g, 6.18 mmol) was added and stirred for 5 min. Now CuI (10 mg, 0.051 mmol) was added and the resulting suspension was heated to 50 °C for 2 h. After cooling to r. t. the mixture was filtered over celite, washed with MTBE and concentrated under reduced pressure. Purification by flash-chromatography afforded the alcohol (1.20 g, 96 %) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.33 (1 H, d, ³J = 8.29 Hz), 7.85-7.77 (2 H, m), 7.63-7.61 (1 H, m), 7.58-7.47 (2 H, m), 7.42-7.37 (1 H, m), 3.76 (2 H, t, ³J = 6.03 Hz), 2.62 (2 H, t, ³J = 6.59 Hz), 1.86-1.78 (4 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 133.4 (C_q), 133.2 (C_q), 130.0 (CH), 128.2 (CH), 128.0 (CH), 126.5 (CH), 126.2 (CH), 125.2 (CH), 121.5 (C_q), 94.9 (C_q), 78.9 (C_q), 62.5 (CH₂), 32.0 (CH₂), 25.2 (CH₂).

HRMS (EI) C₁₆H₁₆O [M]⁺ 224.1201, found: 224.1201;

IR (KBr) ν (cm⁻¹) 2225, 1503, 1394, 1061, 799, 773;

MS (EI, 70 eV) *m/z* (%) 224 (100) [M]⁺, 206 (8) [M-H₂O]⁺, 193 (13) [M-CH₂OH]⁺, 179 (47) [NapCCCH₂CH₂]⁺, 151 (12) [NapCC]⁺.

1-Ethynyl-2-methoxynaphthalene 14b. A suspension of **13b** (0.45 g, 1.77 mmol) and K₂CO₃ (34 mg, 0.248 mmol) in dried methanol under nitrogen atmosphere was stirred for 5 h. After that the solvent was removed under reduced pressure and the residue was taken up with sat. NaHCO₃ and extracted thrice with CH₂Cl₂. The combined organic layers were dried over MgSO₄ and concentrated in vacuo to give **14b** (0.24 g, 74 %) as a red-brown solid.

Mp 105 °C

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.28 (1 H, dd, ³J = 8.5 Hz, ³J = 8.5 Hz), 7.85 (1 H, d, ³J = 9.1 Hz), 7.79 (1 H, d, ³J = 8.1 Hz), 7.56 (1 H, td, ³J = 8.5 Hz, ⁴J = 1.3 Hz), 7.39 (1 H, td, ³J = 8.1 Hz, ⁴J = 1.3 Hz), 2.26 (1 H, d, ³J = 9.1 Hz), 4.05 (3 H, s), 3.76 (1 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 159.8 (C_q), 134.8 (C_q), 130.7 (CH), 128.4 (C_q), 128.1 (CH), 127.5 (CH), 125.1 (CH), 124.2 (CH), 112.4 (CH), 86.5 (CH), 78.2 (C_q), 56.6 (CH₃);

HRMS (ESI) C₁₃H₁₁O [M + H]⁺ 183.0810, found: 183.0810;

IR (KBr) ν (cm⁻¹) 1618, 1507, 1273, 1081, 809;

MS (ESI) 183 [M+H]⁺, 200 [M+NH₄]⁺, 205 [M+Na]⁺.

3-(2-Methoxynaphthalen-1-yl)propionic acid 15. To a stirred solution of **14b** (1.65 g, 9.06 mmol) in dried THF under a nitrogen atmosphere at -78 °C *n*-BuLi (6.2 ml, 9.96 mmol, 1.6 M in hexane) was added and stirred for further 45 min. Via cannula CO₂ was gassed to this lithium acetylide solution from a second flask by warming up dry ice from -78 °C to r. t.. After a further stirring for 12 h, the resulting mixture was quenched with water. The aqueous phase was washed twice with MTBE, subsequently acidified with semi concentrated aqueous HCl and extracted thrice with MTBE to afford the pure acid **15** (2.05 g, > 99.9 %) as a reddish white solid.

Mp 197-198 °C;

¹H-NMR (300 MHz, DMSO-d⁶) δ [ppm] 8.13 (1 H, d, ³*J* = 9.2 Hz), 8.08 (1 H, dd, ³*J* = 8.5 Hz, ⁴*J* = 0.6 Hz), 7.96 (1 H, d, ³*J* = 8.1 Hz), 7.66 (1 H, ddd, ³*J* = 8.5 Hz, ³*J* = 8.1 Hz, ⁴*J* = 1.1 Hz), 7.53 (1 H, d, ³*J* = 9.2 Hz), 7.49 (1 H, ddd, ³*J* = 8.1 Hz, ³*J* = 8.1 Hz, ⁴*J* = 1.1 Hz), 4.01 (3 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 161.7 (C_q), 155.0 (C_q), 134.4 (C_q), 133.7 (CH), 129.0 (CH), 128.8 (CH), 128.1 (C_q), 124.9 (CH), 123.9 (CH), 113.4 (C_q), 91.2 (C_q), 80.5 (C_q), 56.8 (CH₃);

HRMS (EI) C₁₄H₁₀O₃ [M]⁺ 226.0630, found: 226.0630;

IR (KBr) ν (cm⁻¹) 2197, 1665, 1419, 1293, 1249, 1187, 809;

MS (EI, 70 eV) *m/z* (%) 226 (57) [M]⁺, 182 (90) [M-CO₂]⁺.

General Procedure B. Preparation of esters 5 by coupling with DCC. ^{viii} To a solution of the appropriate alcohol (1 eq.) and acid (1 eq.) in dried CH₂Cl₂ (0.1 M) under a nitrogen atmosphere DMAP (6 mol%) was added and cooled to 0 °C. To the resulting solution a solution of DCC in dried CH₂Cl₂ (0.1 M) was dropped in slowly. After this the mixture was allowed to come to r. t. and stirred for further 12 h. The resulting suspension was filtered over celite. The organic layer was washed thrice with 0.25 N aqueous HCl-, once with sat. aqueous NaHCO₃-solution, dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by flash-chromatography (PE/EtOAc 20/1).

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3-(Naphthalen-1-yl)prop-2-ynyl 3-phenylpropiolate 5a. From **4a** (0.30 g, 1.65 mmol) and 3-phenylpropiolic acid (0.24 g, 1.65 mmol) in the presence of DMAP (12 mg, 0.099 mmol) and DCC (0.37 g, 1.81 mmol) according to general procedure B to afford **5a** (0.49 g, 96 %) as an orange oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.33 (1 H, dd, ³J = 8.3 Hz, ⁵J = 0.8 Hz), 7.87-7.85 (2 H, m), 7.73 (1 H, dd, ³J = 8.3 Hz, ⁴J = 1.1 Hz), 7.64-7.36 (8 H, m), 5.22 (2 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 153.4 (C_q), 133.3 (C_q), 133.1 (CH), 133.0 (C_q), 131.1 (CH), 130.8 (CH), 129.5 (CH), 128.6 (CH), 128.3 (CH), 127.0 (CH), 126.5 (CH), 126.0 (CH), 125.1 (CH), 119.5 (C_q), 119.3 (C_q), 87.5 (C_q), 86.7 (C_q), 85.5 (C_q), 80.0 (C_q), 54.3 (CH₂);

HRMS (EI) C₂₂H₁₄O₂ [M]⁺ 310.0994, found: 310.0994;

IR (KBr) ν (cm⁻¹) 2224, 1712, 1281, 1164, 800, 756;

MS (EI, 70 eV) *m/z* (%) 310 (20) [M]⁺, 181 (18) [NapCCCH₂O]⁺, 129 (53) [PhCCCO]⁺, 165 (78) [NapCCCH₂]⁺, 151 (18) [NapCC]⁺, 101 (12) [PhCC]⁺.

3-(2-Methoxynaphthalen-1-yl)prop-2-ynyl 3-phenylpropiolate 5b. From **4b** (218 mg, 1.026 mmol) and 3-phenylpropiolic acid (150 mg, 1.026 mmol) in the presence of DMAP (8 mg, 0.062 mmol) and DCC (233 mg, 1.129 mmol) according to general procedure B to afford **5b** (140 mg, 40 %) as a red brownish solid.

Mp 69-71 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.25 (1 H, dd, ³J = 8.5 Hz, ⁴J = 0.9 Hz), 7.85 (1 H, d, ³J = 9.1 Hz), 7.78 (1 H, d, ³J = 8.1 Hz), 7.63-7.54 (3 H, m), 7.47-7.35 (4 H, m), 7.25 (1 H, d, ³J = 8.5 Hz), 5.28 (2 H, s), 4.04 (3 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 159.6 (C_q), 153.4 (C_q), 134.7 (C_q), 133.1 (CH), 131.0 (CH), 130.8 (CH), 128.6 (CH), 128.4 (C_q), 128.1 (CH), 127.6 (CH), 125.1 (CH), 124.3 (CH), 119.4 (C_q), 112.4 (CH), 104.8 (C_q), 91.3 (C_q), 87.3 (C_q), 81.9 (C_q), 80.2 (C_q), 56.6 (CH₃), 54.7 (CH₂);

HRMS (EI) C₂₃H₁₆O₃ [M]⁺ 340.1094, found: 340.1100;

IR (Film) ν (cm⁻¹) 2215, 1703, 1507, 1259, 1181, 807, 690;

MS (EI, 70 eV) *m/z* (%) 340 (100) [M]⁺, 325 (5) [M-CH₃]⁺, 239 (30) [M-PhC₂]⁺, 129 (18) [M-PhC₂CO]⁺.

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3-Phenylprop-2-ynyl 3-(2-methoxynaphthalen-1-yl)propiolate 5c. From **4c** (58 mg, 0.442 mmol) and 3-(2-methoxynaphthalen-1-yl)propiolic acid (100 mg, 0.442 mmol) in the presence of DMAP (3 mg, 0.027 mmol) and DCC (100 mg, 0.486 mmol) according to general procedure B to afford **5c** (150 mg, 99 %) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.25 (1 H, dd, ³J = 8.3 Hz, ⁴J = 0.9 Hz), 7.94 (1 H, d, ³J = 9.1 Hz), 7.80 (1 H, d, ³J = 7.6 Hz), 7.60 (1 H, ddd, ³J = 8.3 Hz, ³J = 8.3 Hz, ⁴J = 1.3 Hz), 7.51-7.48 (2 H, m), 7.44-7.41 (1 H, m), 7.35-7.30 (3 H, m), 7.24 (1 H, d, ³J = 9.1 Hz), 5.11 (2 H, s), 4.05 (3 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 161.9 (C_q), 153.6 (C_q), 135.0 (C_q), 133.3 (CH), 133.0 (CH), 132.0 (CH), 131.7 (CH), 128.8 (CH), 128.4 (CH), 128.29 (CH), 128.25 (CH), 128.1 (C_q), 124.8 (CH), 124.6 (CH), 122.0 (C_q), 112.1 (CH), 89.3 (C_q), 87.1 (C_q), 83.3 (C_q), 82.3 (C_q), 56.5 (CH₃), 54.0 (CH₂);

HRMS (EI) C₂₃H₁₆O₃ [M]⁺ 340.1094, found: 340.1098;

IR (Film) ν (cm⁻¹) 2203, 1706, 1506, 1148, 810, 756;

MS (EI, 70 eV) *m/z* (%) 340 (4) [M]⁺, 209 (24) [MeONapC₂CO]⁺, 182 (100) [MeONapC₂H]⁺, 115 (8) [PhC₂CH₂]⁺.

4-(Naphthalen-1-yl)but-3-ynyl 3-phenylpropiolate 5d. From **4d** (0.50 g, 2.55 mmol) and 3-phenylpropiolic acid (0.37 g, 2.55 mmol) in the presence of DMAP (19 mg, 0.153 mmol) and DCC (0.58 g, 2.83 mmol) according to general procedure B to afford **5d** (0.81 g, 98 %) as a light yellow solid.

Mp 79 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.35 (1 H, d, ³J = 8.3 Hz), 7.82 (2 H, dd, ³J = 8.3 Hz, ³J = 8.7 Hz), 7.67-7.35 (9 H, m), 4.53 (2 H, t, ³J = 6.8 Hz), 3.02 (2 H, t, ³J = 6.8 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 153.8 (C_q), 133.4 (C_q), 133.10 (C_q), 133.05 (CH), 130.7 (CH), 130.3 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 126.7 (CH), 126.3 (CH), 126.2 (CH), 125.2 (CH), 120.8 (C_q), 119.4 (C_q), 89.7 (C_q), 86.9 (C_q), 80.5 (C_q), 80.4 (C_q), 63.8 (CH₂), 20.1 (CH₂);

HRMS (EI) C₂₃H₁₆O₂ [M]⁺ 324.1150, found: 324.1152;

IR (KBr) ν (cm⁻¹) 2226, 1710, 1281, 1169, 801, 762;

MS (EI, 70 eV) *m/z* (%) 324 (29) [M]⁺, 179 (20) [NapCCC₂H₄]⁺, 165 (28) [NapCCCH₂]⁺, 129 (61) [PhC₂CO]⁺, 101 (7) [PhCC]⁺.

4-(2-Methoxynaphthalen-1-yl)but-3-ynyl 3-phenylpropiolate 5f. From **4e** (105 mg, 0.464 mmol) and 3-phenylpropionic acid (68 mg, 0.464 mmol) in the presence of DMAP (3 mg, 0.028 mmol) and DCC (105 mg, 0.510 mmol) according to general procedure B to afford **5f** (149 mg, 91 %) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.31 (1 H, d, ³J = 8.5 Hz, ⁵J = 1.0 Hz), 7.82 (2 H, t, ³J = 9.4 Hz), 7.65 (2 H, m), 7.57-7.47 (2 H, m), 7.44-7.36 (3 H, m), 7.30-7.29 (1 H, m), 4.59 (2 H, t, ³J = 6.9 Hz), 4.06 (3 H, s), 3.12 (2 H, t, ³J = 6.9 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 158.8 (C_q), 153.9 (C_q), 134.8 (C_q), 133.0 (CH), 130.7 (CH), 129.8 (CH), 128.6 (CH), 128.5 (C_q), 128.0 (CH), 127.3 (CH), 125.3 (CH), 124.1 (CH), 119.5 (C_q), 112.6 (CH), 106.2 (C_q), 94.4 (C_q), 86.8 (C_q), 80.5 (C_q), 76.7 (C_q), 64.0 (CH₂), 56.6 (CH₃), 20.5 (CH₂);

HRMS (EI) C₂₄H₁₈O₃ [M]⁺ 354.1256, found: 354.1256;

IR (Film) ν (cm⁻¹) 2368, 1707, 1506, 1274, 1184, 756;

MS (EI, 70 eV) *m/z* (%) 354 (40) [M]⁺, 339 (1) [M-Me]⁺, 323 (4) [M-OMe]⁺, 208 (100) [M-PhC₂COO₂H]⁺, 195 (6) [MeO-Nap-C₂CH₂]⁺.

3-Phenylprop-2-ynyl 3-phenylpropiolate 5h. ^{ix} From **4c** (0.60 g, 4.54 mmol) and 3-phenylpropionic acid (0.66 g, 4.54 mmol) in the presence of DMAP (33 mg, 0.272 mmol) and DCC (1.03 g, 4.99 mmol) according to general procedure B to afford **5h** (1.06 g, 90 %) as a light yellow solid.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 7.62-7.59 (2 H, m), 7.49-7.43 (3 H, m), 7.41-7.32 (5 H, m), 5.07 (2 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 153.3 (C_q), 133.1 (CH), 131.9 (CH), 130.8 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 121.9 (C_q), 119.3 (C_q), 87.5 (C_q), 87.3 (C_q), 81.9 (C_q), 80.0 (C_q), 54.2 (CH₂);

HRMS (EI) C₁₈H₁₂O₂ [M]⁺ 260.0837, found: 260.0837.

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4-Phenylbut-3-ynyl 3-phenylpropiolate 5i. From **4f** (0.39 g, 2.68 mmol) and 3-phenylpropiolic acid (0.39 g, 2.68 mmol) in the presence of DMAP (20 mg, 0.161 mmol) and DCC (0.61 g, 2.95 mmol) according to general procedure B to afford **5i** (0.64 g, 88 %) as a light yellow solid.

Mp 71 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 7.62-7.59 (2 H, m), 7.49-7.35 (5 H, m), 7.32-7.27 (3 H, m), 4.43 (2 H, t, ³J = 6.8 Hz), 2.85 (2 H, t, ³J = 6.8 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 153.8 (C_q), 133.0 (CH), 131.7 (CH), 130.7 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 123.2 (C_q), 119.5 (C_q), 86.8 (C_q), 84.8 (C_q), 82.3 (C_q), 80.4 (C_q), 63.7 (CH₂), 19.8 (CH₂);

HRMS (EI) C₁₉H₁₄O₂ [M]⁺ 274.0994, found: 274.0992;

IR (KBr) ν (cm⁻¹) 2235, 1710, 1487, 1302, 1186, 760;

MS (EI, 70 eV) *m/z* (%) 274 (12) [M]⁺, 129 (32) [PhC₂CO]⁺, 115 (13) [PhC₂CH₂]⁺, 101 (7) [PhCC]⁺.

General Procedure C. Preparation of esters 5 via chloroformates. To the appropriate alcohol (3 eq.) under a nitrogen atmosphere 9 eq. phosgene (2.0 M in toluol) were slowly dropped and stirred for 24 h. Subsequently, the solvent and not converted phosgene was removed under reduced pressure. The crude residue was dissolved in dried Et₂O under a nitrogen atmosphere and cooled to 0 °C. In a second flask the appropriate lithium acetylide was prepared by treating 1 eq. acetylene in dried Et₂O with *n*-BuLi (1.1 eq., 1.6 M in hexane) and further stirring for 45 min. The lithium acetylide was transferred to the chloroformate via cannula, the resulting mixture was allowed to stir for 45 min and then quenched with ice water. The aqueous phase was extracted thrice with MTBE, dried over MgSO₄, concentrated under reduced pressure and purified by flash-chromatography.

4-Phenylbut-3-ynyl 3-(naphthalen-1-yl)propiolate 5e. From **14a** (0.56 g, 3.68 mmol), **4f** (1.61 g, 11.04 mmol), phosgene (17.4 ml, 33.12 mmol) and *n*-BuLi (2.5 ml, 4.05 mmol) according to general procedure C to afford **5e** (0.55 g, 46 %) as a light brown solid after flash-chromatography (PE/EtOAc 100/3).

Mp 59 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.37-8.33 (1 H, m), 7.96 (1 H, d, ³J = 8.3 Hz), 7.90-7.86 (2 H, m), 7.66-7.54 (2 H, m), 7.48-7.43 (3 H, m), 7.31-7.29 (3 H, m), 4.49 (2 H, t, ³J = 7.2 Hz), 2.90 (2 H, t, ³J = 7.2 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 153.9 (C_q), 133.6 (C_q), 133.1 (CH), 133.0 (CH), 131.7 (CH), 131.4 (CH), 129.5 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 127.0 (CH), 125.7 (CH), 125.1 (CH), 123.2 (C_q), 121.0 (CH), 117.0 (C_q), 85.2 (C_q), 85.0 (C_q), 84.8 (C_q), 82.4 (C_q), 63.8 (CH₂), 19.9 (CH₂);

HRMS (EI) C₂₃H₁₆O₂ [M]⁺ 324.1150, found: 324.1150;

IR (KBr) ν (cm⁻¹) 2216, 1709, 1290, 1200, 802, 757;

MS (EI, 70 eV) *m/z* (%) 324 (35) [M]⁺, 196 (19) [NapC₂CO₂H]⁺, 179 (31) [NapC₂CO]⁺, 151 (18) [NapCC]⁺, 128 (100) [PhC₂CH₂CH]⁺, 77 (18) [Ph]⁺.

4-Phenylbut-3-ynyl 3-(2-methoxynaphthalen-1-yl)propiolate 5g. From **14b** (0.93 g, 5.09 mmol), **4f** (2.23 g, 15.25 mmol), phosgene (24.1 ml, 45.76 mmol) and *n*-BuLi (3.5 ml, 5.59 mmol) according to general procedure C to afford **5e** (0.98 g, 55 %) as a light brown solid after flash-chromatography (PE/EtOAc 10/1).

Mp 112-114 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.22 (1 H, d, ³J = 8.0 Hz), 7.91 (1 H, d, ³J = 9.0 Hz), 7.77 (1 H, d, ³J = 8.0 Hz), 7.56 (1 H, dt, ⁵J = 1.3 Hz, ³J = 7.7 Hz), 7.43-7.37 (3 H, m), 7.28-7.21 (3 H, m), 4.46 (2 H, t, ³J = 7.3 Hz), 4.02 (3 H, s), 2.88 (2 H, t, ³J = 7.3 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 161.7 (C_q), 154.1 (C_q), 134.9 (C_q), 133.2 (CH), 131.7 (CH), 128.32 (CH), 128.28 (CH), 128.21 (CH), 128.16 (C_q), 127.9 (CH), 124.8 (CH), 124.6 (CH), 123.2 (C_q), 112.1 (CH), 102.2 (C_q), 89.7 (C_q), 84.9 (C_q), 82.6 (C_q), 82.3 (C_q), 63.6 (CH₂), 56.5 (CH₃), 19.9 (CH₂);

HRMS (EI) C₂₄H₁₈O₃ [M]⁺ 354.1256, found: 354.1256;

IR (KBr) ν (cm⁻¹) 2205, 1704, 1239, 1170, 754;

MS (EI, 70 eV) *m/z* (%) 354 (100) [M]⁺, 226 (60) [M-PhC₂H₃]⁺, 209 (33) [M-PhC₄H₄O]⁺, 181 (50) [MeONapCC]⁺, 128 (79) [PhC₂CH₂CH]⁺, 115 (30) [PhC₂CH₂]⁺, 77 (15) [Ph]⁺.

General Procedure D. Preparation of alcohols 6. To a solution of 1 eq. alcohol **4** in dried CH_2Cl_2 under a nitrogen atmosphere 1.1 eq. DMP was added and stirred for 2 h. MTBE was added and the resulting mixture was washed five times with DMP washing solution (25 g $\text{Na}_2\text{S}_2\text{O}_3$ in 100 ml sat. aqueous NaHCO_3 solution), dried over MgSO_4 and concentrated in vacuo. The crude residue was dissolved in dried THF and dropped to a lithium acetylide solution - prepared by treating the appropriate acetylene (1 eq.) with *n*-BuLi (1.1 eq., 1.6 M in hexane) in dried THF at $-78\text{ }^\circ\text{C}$ and stirring for 45 min - at $-78\text{ }^\circ\text{C}$ and a further stirring for 3 h at the same temperature, followed by quenching with sat. aqueous NH_4Cl solution. After separation of the layers the aqueous phase was extracted thrice with MTBE, the combined organic layers were washed once with sat. aqueous NaHCO_3 solution and once with brine, dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified by flash-chromatography.

1-(2-methoxynaphthalen-1-yl)-7-phenylhepta-1,6-diyne-3-ol 6a. From **4g** (1.00 g, 5.49 mmol) and **14b** (0.88 g, 5.49 mmol) in the presence of DMP (2.56 g, 6.04 mmol) and *n*-BuLi (3.8 ml, 6.04 mmol) according to general procedure D to afford **6a** (1.28 g, 68 %) as a brownish oil after flash-chromatography (PE/EtOAc 20/1).

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm] 8.27 (1 H, dd, $^3J = 8.5\text{ Hz}$, $^4J = 0.9\text{ Hz}$), 7.86 (1 H, d, $^3J = 9.1\text{ Hz}$), 7.82 (1 H, d, $^3J = 8.1\text{ Hz}$), 7.57 (1 H, ddd, $^3J = 8.5\text{ Hz}$, $^3J = 7.0\text{ Hz}$, $^4J = 1.5\text{ Hz}$), 7.48-7.41 (3 H, m), 7.34-7.29 (4 H, m), 5.08 (1 H, t, $^3J = 7.2\text{ Hz}$), 4.06 (3 H, s), 2.92-2.75 (2 H, m), 2.29 (2 H, dd, $^3J = 7.2\text{ Hz}$, $^3J = 6.8\text{ Hz}$);

$^{13}\text{C-NMR}$ (70 MHz, CDCl_3) δ [ppm] 159.1 (C_q), 134.5 (C_q), 131.6 (CH), 130.4 (CH), 128.4 (C_q), 128.2 (CH), 128.2 (CH), 127.7 (CH), 127.4 (CH), 125.0 (CH), 124.2 (CH), 123.7 (C_q), 112.5 (CH), 105.4 (C_q), 99.0 (C_q), 89.1 (C_q), 81.3 (C_q), 79.8 (C_q), 62.3 (CH), 56.5 (CH_3), 36.8 (CH_2), 15.6 (CH_2);

HRMS (EI) $\text{C}_{24}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 340.1463, found: 340.1463;

IR (Film) ν (cm^{-1}) 1589, 1507, 1272, 1256, 1066, 807;

MS (EI, 70 eV) m/z (%) 340 (70) $[\text{M}]^+$, 339 (72) $[\text{M-H}]^+$, 325 (37) $[\text{M-CH}_3]^+$, 322 (35) $[\text{M-OH}_2]^+$, 307 (23), $[\text{M-CH}_3\text{OH}_2]^+$, 263 (100) $[\text{M-Ph}]^+$, 239 (13) $[\text{M-PhC}_2]^+$, 165 (40) $[\text{M-MeONapOH}_2]^+$, 115 (59) $[\text{PhC}_2\text{CH}_2]^+$, 77 (15) $[\text{Ph}]^+$.

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8-(naphthalen-1-yl)-1-phenylocta-1,7-diyn-3-ol 6b. From **4h** (0.60 g, 2.48 mmol) and ethynylbenzene (0.25 g, 2.48 mmol) in the presence of DMP (1.16 g, 2.73 mmol) and *n*BuLi (1.7 ml, 2.73 mmol) according to general procedure D to afford **6b** (0.41 g, 51 %) as a yellow oil after flash-chromatography (PE/EtOAc 20/1).

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.36-8.33 (1 H, m), 7.85-7.77 (2 H, m), 7.63 (1 H, dd, ³*J* = 7.2 Hz, ⁴*J* = 1.1 Hz), 7.56-7.37 (5 H, m), 7.32-7.29 (3 H, m), 4.73 (1 H, t, ³*J* = 6.1 Hz), 2.68 (2 H, t, ³*J* = 7.2 Hz), 2.12-1.92 (4 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 133.4 (C_q), 133.2 (C_q), 131.7 (CH), 130.1 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 126.5 (CH), 126.2 (CH), 125.2 (CH), 122.5 (C_q), 121.5 (C_q), 94.6 (C_q), 89.8 (C_q), 85.2 (C_q), 79.1 (C_q), 62.6 (CH), 37.1 (CH₂), 24.6 (CH₂), 19.5 (CH₂);

HRMS (EI) C₂₄H₂₀O [M]⁺ 324.1514, found: 324.1514;

IR (Film) ν (cm⁻¹) 1588, 1507, 1271, 1254, 1045, 807;

MS (EI, 70 eV) *m/z* (%) 324 (23) [M]⁺, 306 (31) [M-H₂O]⁺, 247 (15) [M-Ph]⁺, 205 (19) [M-PhC₂CH₂OH]⁺, 77 (28) [Ph]⁺.

General Procedure E. Preparation of ketones 7 by oxidation with DMP. To a solution of 1 eq. alcohol **6** in dried CH₂Cl₂ under a nitrogen atmosphere 1.1 eq. DMP was added and stirred for 2 h. MTBE was added and the resulting mixture was washed five times with DMP washing solution (25 g NaS₂O₃ in 100 ml sat. aqueous NaHCO₃ solution), dried over MgSO₄ and concentrated in vacuo. The crude residue was purified by flash-chromatography (PE/EtOAc 20/1).

1-(2-Methoxynaphthalen-1-yl)-7-phenylhepta-1,6-diyn-3-one 7a. From **6a** (1.24 g, 3.64 mmol) in the presence of DMP (1.70 g, 4.01 mmol) according to general procedure E to afford **7a** (0.64 g, 52 %) as a brownish solid.

Mp 86-88 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.25 (1 H, dd, ³*J* = 8.3 Hz, ⁵*J* = 0.9 Hz), 7.97 (1 H, d, ³*J* = 9.1 Hz), 7.82 (1 H, d, ³*J* = 8.3 Hz), 7.61 (1 H, ddd, ³*J* = 7.0 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.3 Hz), 7.46-7.41 (3 H, m), 7.32-7.27 (4 H, m), 4.08 (3 H, s), 2.95 (2 H, dd, ³*J* = 6.0 Hz, ³*J* = 8.3 Hz), 3.14 (2 H, dd, ³*J* = 6.0 Hz, ³*J* = 8.3 Hz);

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¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 185.5 (C_q), 161.8 (C_q), 134.8 (C_q), 133.5 (CH), 131.6 (CH), 128.4 (CH), 128.3 (CH), 128.20 (CH), 128.15 (CH), 124.7 (CH), 124.6 (CH), 123.5 (C_q), 112.1 (CH), 102.5 (C_q), 97.1 (C_q), 88.1 (C_q), 87.8 (C_q), 81.4 (C_q), 56.5 (CH₃), 44.4 (CH₂), 14.6 (CH₂);

HRMS (EI) C₂₄H₁₈O₂ [M]⁺ 338.1307, found: 338.1305;

IR (KBr) ν (cm⁻¹) 2181, 1664, 1505, 1274, 1260, 1121, 813, 753;

MS (EI, 70 eV) *m/z* (%) 338 (100) [M]⁺, 323 [M-CH₃]⁺, 209 (10) [MeONapC₂CO]⁺, 181 (11) [MeONapC₂]⁺, 115 (30) [PhC₂CH₂]⁺, 77 (23) [Ph]⁺.

8-(Naphthalen-1-yl)-1-phenylocta-1,7-diyn-3-one 7b. From **6b** (0.38 g, 1.17 mmol) in the presence of DMP (0.55 g, 1.29 mmol) according to general procedure E to afford **7b** (0.23 g, 61 %) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.35-8.32 (1 H, m), 7.85-7.78 (2 H, m), 7.64 (1 H, dd, ³*J* = 7.2 Hz, ⁴*J* = 1.1 Hz), 7.58-7.34 (8 H, m), 2.97 (2 H, t, ³*J* = 7.3 Hz), 2.70 (2 H, t, ³*J* = 6.9 Hz), 2.17 (2 H, tt, ³*J* = 7.3 Hz, ³*J* = 6.9 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 187.2 (C_q), 133.4 (C_q), 133.1 (C_q), 133.0 (CH), 130.7 (CH), 130.2 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 126.6 (CH), 126.23 (CH), 126.16 (CH), 125.2 (CH), 121.3 (C_q), 119.9 (C_q), 93.8 (C_q), 91.0 (C_q), 87.8 (C_q), 79.7 (C_q), 44.4 (CH₂), 23.2 (CH₂), 19.1 (CH₂);

HRMS (EI) C₂₄H₁₈O [M]⁺ 322.1358, found: 322.1358;

IR (Film) ν (cm⁻¹) 2200, 1667, 1487, 1094, 799, 774, 688;

MS (EI, 70 eV) *m/z* (%) 322 (80) [M]⁺, 178 (100) [NapC₂CHCH₂]⁺, 165 (23) [NapC₂CH₂]⁺, 129 (32) [PhC₂CO]⁺.

General procedure F. Photolysis of diacetylenes 5 and 7. The irradiation of esters **5** was performed in acetone and of ketones **7** in methanol at concentrations of 0.01 mmol/ml using a high pressure mercury arc lamp (150 W). Light of wavelength below 300 nm was absorbed using a PyrexTM glass jacket between the lamp and the reaction vessel. The reaction was monitored by TLC and determined when the reactant had completely disappeared (1-6 h). The solution was concentrated under reduced pressure and purified by flash-chromatography to give the pure photoproducts.

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Photolysis of 5a. Irradiation of **5a** (232 mg, 0.748 mmol) according to general procedure F afforded 4-(naphthalen-1-yl)naphtho[2,3-c]furan-1(3H)-one **8a** (85 mg, 37 %) as a white solid and 7-phenylphenanthro[3,2-c]furan-8(10H)-one **9a** (97 mg, 42 %) as a light yellow solid.

8a:

Mp 202 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.63 (1 H, s), 8.16 (1 H, d, ³J = 8.3 Hz), 8.05-7.96 (2 H, m), 7.67-7.45 (6 H, m), 7.34 (1 H, ddd, ³J = 7.2 Hz, ³J = 6.8 Hz, ⁴J = 1.3 Hz), 7.21 (1 H, dd, ³J = 8.5 Hz, ⁴J = 0.9 Hz), 5.17 (1 H, d, ²J = 15.3 Hz), 4.97 (1 H, d, ²J = 15.3 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 171.2 (C_q), 135.8 (C_q), 133.9 (C_q), 133.6 (C_q), 133.2 (C_q), 131.6 (C_q), 130.2 (CH), 129.1 (CH), 128.7 (CH), 127.6 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 125.2 (CH), 123.1 (C_q), 69.5 (CH₂);

HRMS (EI) C₂₂H₁₄O₂ [M]⁺ 310.0994, found: 310.0995;

IR (KBr) ν (cm⁻¹) 1769, 1630, 1342, 1117, 1017, 774;

MS (EI, 70 eV) *m/z* (%) 310 (100) [M]⁺, 281 (68) [M-COH]⁺, 252 (77) [M-CO₂CH₂]⁺.

9a:

Mp 265-267 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.80-8.75 (2 H, m), 7.94-7.91 (1 H, m), 7.75-7.69 (4 H, m), 7.57-7.54 (3 H, m), 7.43-7.39 (2 H, m), 5.54 (2 H, d, ⁴J = 0.9 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 169.6 (C_q), 142.1 (C_q), 141.7 (C_q), 134.8 (C_q), 134.6 (C_q), 132.7 (C_q), 131.4 (C_q), 130.1 (CH), 129.5 (C_q), 128.8 (CH), 128.35 (CH), 128.27 (CH), 128.1 (CH), 127.8 (CH), 127.2 (CH), 124.9 (CH), 123.6 (CH), 120.6 (C_q), 115.2 (CH), 68.5 (CH₂);

HRMS (EI) C₂₂H₁₄O₂ [M]⁺ 310.0994, found: 310.0994;

IR (KBr) ν (cm⁻¹) 1759, 1619, 1364, 1065, 1018, 749;

MS (EI, 70 eV) *m/z* (%) 310 (98) [M]⁺, 265 (32) [M-CO₂H]⁺, 252 (48) [M-CH₂CO₂]⁺.

Photolysis of 5b. Irradiation of **5b** (200 mg, 0.588 mmol) according to general procedure F afforded 4-(2-methoxynaphthalen-1-yl)naphtho[2,3-c]furan-1(3H)-one **8b** (87 mg, 46 %) as a white solid.

Mp 198 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.61 (1 H, s), 8.14 (1 H, d, ³J = 8.3 Hz), 8.06 (1 H, d, ³J = 9.2 Hz), 7.92 (1 H, d, ³J = 8.1 Hz), 7.58 (1 H, ddd, ³J = 8.1 Hz, ³J = 8.1 Hz, ⁴J = 1.7 Hz), 7.48 (1 H, d, ³J = 9.2 Hz), 7.48-7.42 (2 H, m), 7.36 (1 H, ddd, ³J = 7.9 Hz, ³J = 8.1 Hz, ⁴J = 1.3 Hz), 7.26 (1 H, ddd, ³J = 8.3 Hz, ³J = 8.3 Hz, ⁴J = 1.3 Hz), 7.00-6.96 (1 H, m), 5.13 (1 H, d, ²J = 14.5 Hz), 4.95 (1 H, d, ²J = 14.5 Hz), 3.79 (3 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 171.5 (C_q), 154.5 (C_q), 140.5 (C_q), 135.8 (C_q), 133.6 (C_q), 132.9 (C_q), 130.8 (CH), 130.3 (CH), 129.0 (C_q), 128.9 (CH), 128.8 (C_q), 128.3 (CH), 127.3 (CH), 126.7 (CH), 126.0 (CH), 124.2 (CH), 124.0 (CH), 123.2 (C_q), 117.3 (C_q), 69.9 (CH₂), 56.4 (CH₃);

HRMS (EI) C₂₃H₁₆O₃ [M]⁺ 340.1099, found: 340.1100;

IR (KBr) ν (cm⁻¹) 1766, 1507, 1265, 1119, 1020, 662;

MS (EI, 70 eV) *m/z* (%) 340 (12) [M]⁺, 127 (22) [Naphthyl]⁺.

Photolysis of 5c. Irradiation of **5c** (64 mg, 0.188 mmol) according to general procedure F afforded 9-(2-methoxynaphthalen-1-yl)naphtho[2,3-*c*]furan-1(3H)-one **10a** (23 mg, 36 %) as a light yellow solid.

Mp 239-242 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.05 (1 H, d, ³J = 9.1 Hz), 8.01 (1 H, d, ³J = 8.5 Hz), 7.99 (1 H, s), 7.88 (1 H, d, ³J = 8.1 Hz), 7.62 (1 H, ddd, ³J = 7.0 Hz, ³J = 7.0 Hz, ⁴J = 1.1 Hz), 7.51 (1 H, d, ³J = 8.1 Hz), 7.48 (1 H, d, ³J = 9.1 Hz), 7.38 (2 H, m), 7.17 (1 H, ddd, ³J = 7.0 Hz, ³J = 7.0 Hz, ⁴J = 1.3 Hz), 6.85 (1 H, d, ³J = 7.9 Hz), 5.49 (2 H, d, ⁴J = 0.9 Hz), 3.78 (3 H, s);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 169.3 (C_q), 154.8 (C_q), 140.4 (C_q), 137.1 (C_q), 136.3 (C_q), 133.6 (C_q), 133.3 (C_q), 130.5 (CH), 128.9 (C_q), 128.7 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 126.8 (CH), 126.6 (CH), 124.5 (CH), 123.5 (CH), 121.9 (C_q), 120.5 (CH), 117.2 (C_q), 113.4 (CH), 68.4 (CH₂), 56.6 (CH₃);

HRMS (EI) C₂₃H₁₆O₃ [M]⁺ 340.1099, found: 340.1100;

IR (KBr) ν (cm⁻¹) 1762, 1653, 1265, 1116, 767;

MS (EI, 70 eV) *m/z* (%) 340 (100) [M]⁺, 295 (13) [M-CO₂H]⁺, 281 (21) [M-CH₂CO₂H]⁺.

Photolysis of 5d. Irradiation of **5d** (205 mg, 0.632 mmol) according to general procedure F afforded 5-(naphthalen-1-yl)-3,4-dihydro-1H-benzo[g]isochromen-1-one **8c** (84 mg, 41 %) as a yellow oil and 7-phenyl-10,11-dihydro-8H-naphtho[1,2-g]isochromen-8-one **9b** (62 mg, 30 %) as a yellow solid.

8c:

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.89 (1 H, s), 8.06 (1 H, d, ³J = 7.9 Hz), 8.01 (1 H, d, ³J = 7.9 Hz), 7.99 (1 H, d, ³J = 7.6 Hz), 7.54-7.48 (2 H, m), 7.42-7.24 (6 H, m), 4.49 (2 H, m), 2.87-2.77 (1 H, m), 2.68-2.59 (1 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 165.9 (C_q), 135.5 (C_q), 135.4 (C_q), 134.9 (C_q), 133.7 (C_q), 133.4 (C_q), 132.4 (CH), 132.2 (C_q), 132.1 (CH), 132.0 (C_q), 129.7 (CH), 129.1 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.9 (CH), 126.7 (CH), 126.2 (CH), 125.6 (CH), 125.3 (CH), 122.9 (C_q), 67.4 (CH₂), 26.5 (CH₂);

HRMS (ESI) C₂₃H₁₇O₂ [M+H]⁺ 325.1229, found: 325.1228;

IR (KBr) ν (cm⁻¹) 1722, 1296, 1185, 774;

MS (ESI) 325 [M+H]⁺, 342 [M+NH₄]⁺, 347 [M+Na]⁺, 648 [2M+H]⁺, 666 [2M+NH₄]⁺, 671 [M+Na]⁺.

9b:

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.72 (1 H, d, ³J = 7.5 Hz), 8.58 (1 H, s), 7.89-7.86 (1 H, m), 7.72-7.42 (7 H, m), 7.33-7.30 (2 H, m), 4.59 (2 H, t, ³J = 5.7 Hz), 3.34 (2 H, t, ³J = 5.7 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 163.5 (C_q), 145.0 (C_q), 139.2 (C_q), 136.4 (C_q), 132.9 (C_q), 132.5 (C_q), 132.0 (C_q), 130.9 (C_q), 129.2 (CH), 129.0 (C_q), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 127.1 (CH), 127.0 (CH), 125.3 (CH), 123.4 (CH), 122.1 (C_q), 120.5 (CH), 66.9 (CH₂), 30.0 (CH₂);

HRMS (ESI) C₂₃H₁₇O₂ [M+H]⁺ 325.1229, found: 325.1230;

IR (KBr) ν (cm⁻¹) 1717, 1618, 1386, 1259, 1092, 741;

MS (ESI) 325 [M+H]⁺, 347 [M+Na]⁺, 666 [2M+NH₄]⁺, 671 [M+Na]⁺.

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Photolysis of 5e. Irradiation of **5e** (160 mg, 0.493 mmol) according to general procedure F afforded 10-(naphthalen-1-yl)-3,4-dihydro-1H-benzo[g]isochromen-1-one **10b** (58 mg, 36 %) as a yellow solid and 7-phenyl-8H-naphtho[2,1-g]isochromen-11(9H)-one **11a** (37 mg, 23 %) as a yellow oil.

10b:

Mp 87 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 7.98 (1 H, d, ³J = 7.2 Hz), 7.95 (1 H, d, ³J = 7.3 Hz), 7.90 (1 H, d, ³J = 8.3 Hz), 7.83 (1 H, s), 7.62-7.54 (2 H, m), 7.45 (1 H, ddd, ³J = 6.9 Hz, ³J = 6.9 Hz, ⁴J = 1.3 Hz), 7.33 (1 H, d, ³J = 6.9 Hz), 7.28-7.23 (3 H, m), 7.15 (1 H, d, ³J = 8.3 Hz), 4.61 (2 H, m), 3.41-3.31 (1 H, m), 3.23 (1 H, dt, ²J = 16.1 Hz, ³J = 4.7 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 163.1 (C_q), 143.8 (C_q), 136.8 (C_q), 135.1 (C_q), 134.9 (C_q), 133.3 (C_q), 133.0 (C_q), 132.7 (C_q), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.2 (CH), 126.40 (CH), 126.36 (CH), 126.0 (CH), 125.7 (CH), 125.6 (CH), 125.2 (CH), 122.8 (C_q), 70.0 (CH₂), 29.7 (CH₂);

HRMS (EI) C₂₃H₁₆O₂ [M]⁺ 324.1150, found: 324.1143;

IR (KBr) ν (cm⁻¹) 1725, 1386, 1252, 1132, 771;

MS (EI) 324 (10) [M]⁺, 279 (23) [M-CO₂H]⁺.

11a:

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 9.62 (1 H, s), 8.88 (1 H, d, ³J = 8.3 Hz), 7.91 (1 H, m), 7.75 (1 H, d, ³J = 9.5 Hz), 7.70-7.47 (3 H, m), 7.43 (1 H, dd, ³J = 9.5 Hz, ⁵J = 0.6 Hz), 7.34-7.26 (2 H, m), 4.55 (2 H, t, ³J = 6.0 Hz), 2.94 (2 H, t, ³J = 6.0 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 166.0 (C_q), 138.2 (C_q), 137.7 (C_q), 134.03 (C_q), 133.99 (C_q), 131.7 (CH), 131.5 (CH), 131.4 (C_q), 130.4 (C_q), 130.0 (CH), 129.3 (C_q), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 122.8 (C_q), 67.4 (CH₂), 26.8 (CH₂);

HRMS (EI) C₂₃H₁₆O₂ [M]⁺ 324.1150, found: 324.1152;

IR (KBr) ν (cm⁻¹) 1720, 1401, 1175, 1087, 753;

MS (EI, 70 eV) *m/z* (%) 324 (100) [M]⁺, 265 (50) [M-CO₂CH₃]⁺, 252 (7) [M-CO₂CH₂CH₂]⁺, 77 (8) [Ph]⁺.

Photolysis of 5f. Irradiation of **5f** (104 mg, 0.293 mmol) according to general procedure F afforded 5-(2-methoxynaphthalen-1-yl)-3,4-dihydro-1H-benzo[g]isochromen-1-one **8d** (39 mg, 38 %) as a white solid.

Mp 202-204 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.86 (1 H, s), 8.05 (1 H, d, ³J = 7.8 Hz), 8.03 (1 H, d, ³J = 9.1 Hz), 7.91 (1 H, d, ³J = 8.1 Hz), 7.50 (1 H, ddd, ³J = 8.1 Hz, ³J = 7.8 Hz, ⁴J = 1.3 Hz), 7.47 (1 H, d, ³J = 9.1 Hz), 7.40-7.33 (2 H, m), 7.28-7.18 (2 H, m), 6.97-6.94 (1 H, m), 4.51-4.38 (2 H, m), 3.77 (3 H, s), 2.80 (1 H, ddd, ²J = 16.9 Hz, ³J = 7.2 Hz, ³J = 7.0 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 166.1 (C_q), 154.6 (C_q), 140.2 (C_q), 134.1 (C_q), 133.4 (C_q), 132.3 (CH), 132.1 (C_q), 131.9 (C_q), 130.3 (CH), 129.9 (CH), 129.0 (CH), 128.2 (CH), 127.1 (CH), 126.3 (CH), 126.1 (CH), 124.4 (CH), 123.9 (CH), 123.2 (C_q), 113.3 (CH), 67.5 (CH₂), 56.4 (CH₃), 26.3 (CH₂);

HRMS (EI) C₂₄H₁₈O₃ [M]⁺ 354.1256, found: 354.1256;

IR (KBr) ν (cm⁻¹) 1723, 1618, 1505, 1266, 1171, 1058, 746;

MS (EI, 70 eV) *m/z* (%) 354 (100) [M]⁺, 126 (8) [Naphthyl]⁺.

Photolysis of 5g. Irradiation of **5g** (120 mg, 0.339 mmol) according to general procedure F afforded 10-(2-methoxynaphthalen-1-yl)-3,4-dihydro-1H-benzo[g]isochromen-1-one **10c** (33 mg, 28 %) as a red solid.

Mp 223 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 7.99 (1 H, d, ³J = 9.1 Hz), 7.87 (2 H, dd, ³J = 8.1 Hz, ³J = 7.4 Hz), 7.81 (1 H, s), 7.58-7.51 (2 H, m), 7.44 (1 H, d, ³J = 9.1 Hz), 7.29-7.25 (2 H, m), 7.16 (1 H, ddd, ³J = 8.3 Hz, ³J = 8.3 Hz, ⁴J = 1.3 Hz), 6.88 (1 H, d, ³J = 8.5 Hz), 4.53 (2 H, t, ³J = 5.8 Hz), 3.76 (3 H, s), 3.29 (2 H, t, ³J = 5.8 Hz);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 163.2 (C_q), 153.8 (C_q), 140.5 (C_q), 135.24 (C_q), 135.15 (C_q), 133.5 (C_q), 132.7 (C_q), 131.5 (C_q), 130.9 (CH), 129.5 (CH), 129.0 (C_q), 128.8 (CH), 128.5 (CH), 127.9 (CH), 127.4 (CH), 126.4 (CH), 125.5 (CH), 124.4 (CH), 123.3 (CH), 121.6 (C_q), 113.6 (CH), 67.1 (CH₂), 56.7 (CH₃), 29.1 (CH₂);

HRMS (EI) C₂₄H₁₈O₃ [M]⁺ 354.1256, found: 354.1255;

IR (KBr) ν (cm⁻¹) 1721, 1507, 1266, 1081, 804;

MS (EI, 70 eV) *m/z* (%) 354 (28) [M]⁺, 323 (8) [M-OMe]⁺.

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Photolysis of 7a. Irradiation of **7a** (132 mg, 0.390 mmol) according to general procedure F afforded 9-(2-methoxynaphthalen-1-yl)-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-one **10d** (24 mg, 18 %) as a light yellow solid.

Mp 188-191 °C;

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.02 (1 H, d, ³J = 9.1 Hz), 7.99 (1 H, s), 7.93 (1 H, d, ³J = 8.3 Hz), 7.88 (1 H, d, ³J = 8.1 Hz), 7.55 (1 H, ddd, ³J = 8.1 Hz, ³J = 7.9 Hz, ⁴J = 1.3 Hz), 7.48-7.42 (2 H, m), 7.31-7.24 (2 H, m), 7.14 (1 H, ddd, ³J = 8.3 Hz, ³J = 8.5 Hz, ⁴J = 1.3 Hz), 6.85 (1 H, d, ³J = 8.5 Hz), 3.74 (3 H, s), 3.36 (2 H, t, ³J = 6.3 Hz), 2.69 (2 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 205.6 (C_q), 154.5 (C_q), 148.3 (C_q), 136.9 (C_q), 134.6 (C_q), 133.7 (C_q), 132.6 (C_q), 132.4 (C_q), 129.8 (CH), 129.0 (C_q), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 126.3 (CH), 126.0 (CH), 124.7 (CH), 124.5 (CH), 123.3 (CH), 119.2 (C_q), 113.5 (CH), 56.6 (CH₃), 37.2 (CH₂), 24.9 (CH₂);

HRMS (EI) C₂₄H₁₈O₂ [M]⁺ 338.1307, found: 338.1307;

IR (KBr) ν (cm⁻¹) 1711, 1618, 1264, 1077, 806;

MS (EI, 70 eV) *m/z* (%) 338 (100) [M]⁺, 307 (28) [M-CH₃O]⁺, 281 (18) [M-HCOCH₂CH₂]⁺.

Photolysis of 7b. Irradiation of **7b** (200 mg, 0.620 mmol) according to general procedure F afforded 10-(naphthalen-1-yl)-3,4-dihydroanthracen-1(2H)-one **8e** (35 mg, 18 %) as a yellow oil and 7-phenyl-10,11-dihydro-8H-naphtho[1,2-g]isochromen-8-one **9c** (25 mg, 13 %) as a yellow oil.

8e:

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.81 (1 H, s), 8.05 (1 H, d, ³J = 8.1 Hz), 8.00 (1 H, d, ³J = 8.3 Hz), 7.98 (1 H, d, ³J = 8.3 Hz), 7.67-7.28 (6 H, m), 7.20 (1 H, d, ³J = 8.5 Hz), 7.16 (1 H, dd, ³J = 8.5 Hz, ⁴J = 0.8 Hz), 2.76 (4 H, m), 2.07-1.96 (2 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 199.1 (C_q), 137.9 (C_q), 136.3 (C_q), 136.2 (C_q), 135.7 (C_q), 133.7 (C_q), 133.1 (CH), 132.2 (C_q), 131.5 (C_q), 130.6 (C_q), 130.1 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 126.4 (CH), 126.3 (CH), 125.9 (CH), 125.7 (CH), 125.5 (CH), 125.2 (C_q), 39.4 (CH₂), 28.0 (CH₂), 23.0 (CH₂);

HRMS (EI) C₂₄H₁₈O [M]⁺ 322.1358, found: 322.1358;

IR (Film) ν (cm⁻¹) 1683, 1504, 1291, 1173, 797;

MS (EI, 70 eV) *m/z* (%) 322 (100) [M]⁺, 293 (12) [M-CHO]⁺, 279 (12) [M-CHOCH₂]⁺, 265 (34) [M-CHOCH₂CH₂]⁺.

9c:

¹H-NMR (300 MHz, CDCl₃) δ [ppm] 8.74 (1 H, d, ³J = 7.4 Hz), 8.62 (1 H, s), 7.86-83 (1 H, m), 7.69-7.64 (1 H, m), 7.54 (1 H, d, ³J = 9.3 Hz), 7.50-745 (3 H, m), 7.35 (1 H, d, ³J = 8.7 Hz), 7.23-7.20 (3 H, m), 3.30 (2 H, t, ³J = 6.0 Hz), 2.68 (2 H, t, ³J = 6.5 Hz), 2.28-2.17 (2 H, m);

¹³C-NMR (70 MHz, CDCl₃) δ [ppm] 198.8 (C_q), 142.6 (C_q), 142.1 (C_q), 141.2 (C_q), 140.7 (C_q), 132.9 (C_q), 132.6 (C_q), 130.5 (C_q), 129.2 (C_q), 128.9 (CH), 128.5 (CH), 128.0 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 125.6 (CH), 123.5 (CH), 122.0 (CH), 41.0 (CH₂), 31.6 (CH₂), 23.1 (CH₂);

HRMS (EI) C₂₄H₁₈O [M]⁺ 322.1358, found: 322.1358;

IR (Film) ν (cm⁻¹) 1688, 1583, 1291, 939, 761, 699;

MS (EI, 70 eV) *m/z* (%) 322 (61) [M]⁺, 294 (21) [M-CO]⁺, 265 [M-CHOCH₂CH₂]⁺, 43 (100) [CHOCH₂]⁺.

DCC	N,N'-methanediyliidenedicyclohexanamine
DMAP	N,N-dimethyl-4-aminopyridine
DMP	<i>Dess-Martin</i> -Periodinane
eq.	equivalent
mp	melting point
MTBE	methyl- <i>t</i> -butyl-ether
r. t.	room temperature
TEA	triethylamin
TLC	thin layer chromatography
sat.	saturated

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