Supplementary Material (ESI) for Chemical Communications

Facile formation of iodocyclobutenes by a ruthenium-catalyzed enyne cycloisomerization

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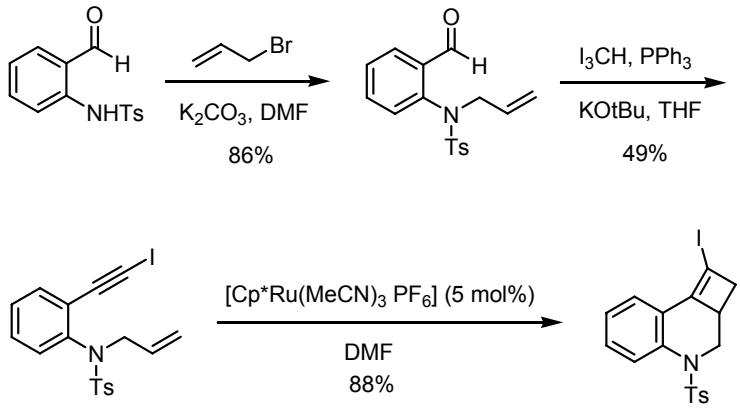
General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, Et_3N, hexane, pentane, toluene (Na/K), DMF (Desmodur 15, dibutyl tin dilaurat). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh), Alox (Aldrich, activated, neutral, Brockmann I, approx. 150 mesh, adjusted to grade IV by adding 10% of water), or Florisil (Aldrich, ~200 mesh), CombiFlash Companion (Teledyne Isco). NMR: Spectra were recorded on a Bruker DPX 300, AMX 300 or AV 400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv$ 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm; C_6D_6: $\delta_C \equiv 128.1$ ppm; residual C_6H_6 in C_6D_6: $\delta_H \equiv 7.26$ ppm; $[D]_8$-toluene: $\delta_C \equiv$ 137.9 ppm; residual toluene in $[D]_8$-toluene: $\delta_H \equiv 2.09$ ppm). *Where indicated, the signal assignments are unambiguous*; *the numbering scheme is arbitrary as shown in the inserts*. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ^1J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ^nJ(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms. IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.



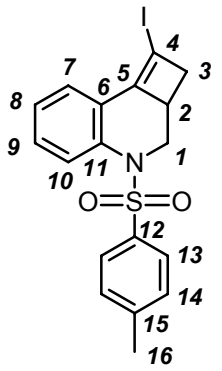
***N*-Allyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide.** Allyl bromide (0.35 mL, 4.1 mmol) was added to a suspension of 2-(tosylamido)benzaldehyde (0.75 g, 2.7 mmol)[1] and K_2CO_3 (1.1 g, 8.1 mmol) in DMF (20 mL) and the mixture was stirred at ambient temperature for 14 h. The solution was extracted with *tert*-butyl methyl ether and brine, the combined organic layers were dried over Na_2SO_4 and the solvent was evaporated to give the title compound as a yellow solid which was pure enough for use in the next step without further purification (0.73 g, 86%); m.p.: 109-110°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.39 (s, 1H), 8.00-7.98 (m, 1H), 7.50-7.41 (m, 4H), 7.29 (d, J = 8.0 Hz, 2H), 6.73-6.71 (m, 1H), 5.80-5.69 (m, 1H), 5.07-4.99 (m, 2H), 4.57 (bs, 1H), 3.85 (bs, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 144.2, 141.3, 136.0, 134.4, 134.0, 131.6, 129.7, 128.6, 128.4, 128.0, 127.9, 120.5, 54.4, 21.6 ppm; IR (KBr): $\tilde{\nu}$ = 3080, 2893, 1688, 1597, 1356, 1346, 1167, 1091, 1052, 868, 822, 728, 668, 578 cm^{-1}; MS (EI): *m/*z (%): 288 (<1), 160 (100), 132 (28), 91 (19), 77 (10); HRMS (ESI): calcd for $C_{17}H_{17}O_3NS$ $[M+Na]^+$: 338.0821, found: 338.0819.

***N*-Allyl-*N*-(2-(iodoethynyl)phenyl)-4-methylbenzenesulfonamide.** Iodoform (1.9 g, 4.7 mmol) and PPh_3 (1.0 g, 4.9 mmol) were dissolved in THF (25 mL). KO^{t}Bu (0.49 g, 4.4 mmol) was added followed after 1 min by a solution of *N*-allyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide (0.70 g, 2.2 mmol) in THF (15 mL). The reaction mixture was stirred at ambient temperature for 55 min before it was cooled to −70°C. KO^{t}Bu (1.2 g, 11.0 mmol) was added and stirring continued for 45 min. The reaction was quenched with brine and allowed to warm to ambient temperature, the mixture was filtered through Celite, the filtrate was extracted with *tert*-butyl methyl ether and brine, the combined organic layers were dried over Na_2SO_4, the solvents were evaporated and the residue was purified by flash chromatography (Companion, 0-25% *tert*-butyl methyl ether in hexanes) to give the title compound as a colorless solid (0.47 g, 49%). m.p.: 136-138°C; ^{1}H NMR (300 MHz, C_6D_6): δ = 7.67 (d, J = 7.7 Hz, 2H), 7.27 (dd, J = 8.0, 1.0 Hz, 1H), 7.09 (dd, J = 7.6, 1.6 Hz, 1H), 6.84 (dt, J = 7.9, 1.6 Hz, 1H), 6.78 (d, J = 8.1 Hz, 2H), 6.68 (dt, J = 7.6, 1.3 Hz, 1H), 5.87-5.73 (m, 1H), 4.90 (ddd, J = 17.2, 2.8, 1.3 Hz, 1H), 4.79 (ddd, J = 10.1, 2.5, 1.1 Hz, 1H), 4.34 (bd, J = 6.4 Hz, 2H), 1.94 (s, 3H) ppm; ^{13}C NMR (75 MHz, C_6D_6): δ = 142.8, 141.6, 138.0, 134.4, 133.8, 133.4, 129.8, 129.4, 127.9, 124.0, 118.5, 91.4, 53.6, 21.3, 12.4 ppm; IR (KBr): $\tilde{\nu}$ = 3068, 3027, 2921, 2166, 1642, 1598, 1480, 1340, 1166, 1089, 1069, 806, 767, 725, 662, 579, 544 cm^{-1}; MS (EI): *m/*z

[1] J.-Y. Goujon, F. Zammattio, J.-M. Chrétien and I. Beaudet, *Tetrahedron*, 2004, **60**, 4037.

(%): 437 (11) $[M]^+$, 410 (44), 282 (40), 154 (100), 127 (21), 101 (12), 91 (35); HRMS (ESI): calcd for $C_{18}H_{16}O_2NSI$ $[M+Na]^+$: 458.9839, found: 459.9835; elemental analysis calcd (%) for $C_{18}H_{16}O_2NSI$ (437.30): C 49.44, H 3.69, N 3.20, found: C 49.52, H 3.57, N 3.12.

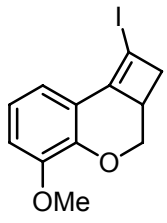
Representative Procedure for the Cycloisomerization: Preparation of 1-Iodo-4-tosyl-2,2a,3,4-tetrahydrocyclobuta[*c*]quinoline (15). $[Cp^*Ru(MeCN)_3\ PF_6]$ (**4**) (29.8 mg, 0.06 mmol) was added to a solution of *N*-allyl-*N*-(2-(iodoethynyl)phenyl)-4-methylbenzenesulfonamide (520 mg, 1.2 mmol) in DMF (6 mL) and the resulting mixture was stirred for 5 min. For work up, the reaction was quenched with brine (10 mL) and extracted with EtOAc (3x10 mL), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (neutral Alox, pentane/Et_2O, 4:1) to give iodocyclobutene **15** as a colorless oil (460 mg, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.81 (dd, J = 8.3, 0.9 Hz, 1H, H-10), 7.68 (dd, J = 7.6, 1.6 Hz, 1H, H-7), 7.49 (d, J = 8.4 Hz, 2H, H-13), 7.33 (t, J = 8.4 Hz, 1H, H-9), 7.25-7.20 (m, 3H, H-8, H-14), 4.64 (dd, J = 13.6, 4.8 Hz, 1H, H-1a), 3.20 (dd, J = 13.4, 12.5 Hz, 1H, H-1b), 3.06 (dd, 14.2, 4.3 Hz, 1H, H-3a), 2.65-2.58 (m, 2H, H-3b, H-2), 2.38 (s, 3H, H-16) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 150.2 (C-5), 144.6 (C-15), 137.5 (C-12), 136.1 (C-11), 130.2 (C-14), 129.1 (C-9), 127.3 (C-13), 126.0 (C-10), 125.6 (C-8), 123.5 (C-6), 122.4 (C-7), 81.4 (C-4), 52.6 (C-1), 42.9 (C-3), 38.7 (C-2), 21.7 (C-16) ppm; IR (film): $\tilde{\nu}$ = 3063, 2921, 2872, 1629, 1597, 1493, 1469, 1352, 1317, 1167, 1090, 1024, 852, 805, 760, 675, 574 cm^{-1}; MS (EI): *m/*z (%): 437 (27) $[M]^+$, 310 (16), 282 (18), 154 (100), 127 (16), 91 (15); HRMS (EI): calcd for $C_{18}H_{16}NO_2SI$ $[M+Na]^+$: 459.9837, found: 459.9840; elemental analysis calcd (%) for $C_{18}H_{16}NO_2SI$ (437.29): C 49.44, H 3.69, N 3.20, found: C 49.53, H 3.71, N 3.12.



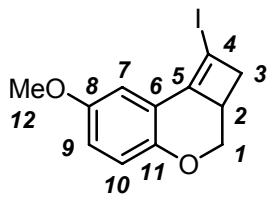
(arbitrary numbering)

The following compounds were prepared analogously:

1-Iodo-5-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (5). Colorless solid (82 mg, 94%); m.p.: 93-95°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.17 (dd, J = 7.6, 1.5 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 6.9 (dd, J = 8.1, 1.4 Hz, 1H), 4.66 (dd, J = 10.2, 5.3 Hz, 1H), 3.89 (dd, J = 11.8, 10.2 Hz, 1H), 3.82 (s, 3H), 3.27 (dd, J = 13.7, 4.3 Hz, 1H), 3.24-3.18 (m, 1H), 2.71 (dd, J = 13.7, 1.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 149.1, 149.0, 144.3, 120.7, 118.9, 114.6, 112.6, 78.8, 72.8, 56.2, 42.4, 39.2 ppm; IR (film): $\tilde{\nu}$ = 3078, 2998, 2956, 2910, 2862, 2834, 1642, 1572, 1483, 1442, 1288, 1262, 1218, 1108, 994, 921, 854, 778, 761, 730 cm^{-1}; MS (EI): *m/*z (%): 314 (98) $[M]^+$, 187 (100), 159 (14), 144 (54), 127 (23), 115 (38); HRMS (EI): calcd for $C_{12}H_{11}O_2I$ $[M+Na]^+$: 336.9696, found: 336.9695.



1-Iodo-7-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (6). Pale yellow oil (470 mg, 81%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.07-7.06 (m, 1H, H-7), 6.81-6.80 (m, 2H, H-9, H-10), 4.51 (dd, J = 10.2, 5.3 Hz, 1H, H-1a), 3.83 (dd, J = 11.8, 10.2 Hz, 1H, H-1b), 3.78 (s, 3H, H-12), 3.26 (dd, J = 13.7, 4.3 Hz, 1H, H-3a), 3.23-3.17 (m, 1H, H-2), 2.70 (dd, J = 13.7, 1.6 Hz, 1H, H-3b) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.9 (C-8), 149.4 (C-5), 149.1 (C-11), 118.6 (C-6), 118.3 (C-10), 116.8 (C-9), 106.4 (C-7), 78.7 (C-4), 72.6 (C-1), 56.1 (C-12), 42.4 (C-3), 39.6 (C-2) ppm; IR (film): $\tilde{\nu}$ = 2953, 2916, 2830, 1610, 1571, 1482, 1441, 1428, 1281, 1195, 1167, 1036, 987, 852, 807, 743, 686 cm^{-1}; MS (EI): *m/*z (%):



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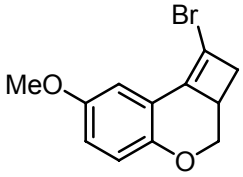
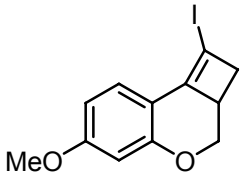
314 (100) $[M]^+$, 187 (86), 159 (19), 144 (61), 127 (27), 115 (39), 89 (13), 63 (14); HRMS (EI): calcd for $C_{12}H_{11}O_2I$ $[M]^+$: 313.9804, found: 313.9807; elemental analysis calcd (%) for $C_{12}H_{11}O_2I$ (314.12): C 45.88, H 3.53, found: C 45.87, H 3.64.

1-Bromo-7-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (7). Colorless oil (44 mg, 78%);



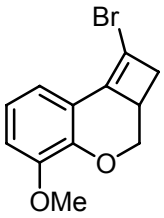
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.98 (d, J = 2.8 Hz, 1H), 6.84-6.77 (m, 2H), 4.56 (dd, J = 10.2, 5.3 Hz, 1H), 3.80 (dd, J = 11.8, 10.3 Hz, 1H), 3.78 (s, 3H), 3.21 (dd, J = 13.9, 4.3 Hz, 1H), 3.01-2.95 (m, 1H), 2.68 (dd, J = 13.9, 1.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2C_2): δ = 154.2, 149.2, 141.4, 118.2, 117.8, 116.7, 108.3, 106.5, 72.4, 56.1, 41.0, 35.5 ppm; IR (film): $\tilde{\nu}$ = 2951, 2918, 2864, 2831, 1660, 1611, 1572, 1480, 1427, 1279, 1191, 1167, 1033, 986, 809 cm^{-1}; MS (EI): *m/*z (%): 266 (36) $[M]^+$, 187 (100), 161 (20), 144 (39), 127 (17), 115 (32), 89 (11), 63 (11); HRMS (EI): calcd for $C_{12}H_{11}O_2Br$ $[M]^+$: 265.9943, found: 265.9940; elemental analysis calcd (%) for $C_{12}H_{11}O_2Br$ (267.12): C 53.96 H 4.15, found: C 53.90, H 4.09.

1-Iodo-6-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (9). Colorless oil (20 mg, 45%); ^{1}H



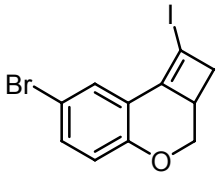
NMR (400 MHz, CD_2Cl_2): δ = 7.45 (d, J = 8.5 Hz, 1H), 6.55 (dd, J = 8.5, 2.5 Hz, 1H), 6.44 (d, J = 2.5 Hz, 1H), 4.54 (dd, J = 10.1, 5.4 Hz, 1H), 3.89 (dd, J = 11.7, 10.3 Hz, 1H), 3.77 (s, 3H), 3.23 (dd, J = 13.3, 4.3 Hz, 1H), 3.21-3.15 (m, 1H), 2.70 (dd, J = 13.3, 1.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 161.6, 156.3, 148.8, 123.7, 111.6, 108.1, 102.3, 74.9, 72.8, 55.7, 42.1, 39.4 ppm; IR (film): $\tilde{\nu}$ = 2958, 2914, 2834, 1648, 1609, 1490, 1261, 1196, 1154, 1082, 870, 830, 806, 585 cm^{-1}; MS (EI): *m/*z (%): 314 (100) $[M]^+$, 187 (86), 171 (25), 159 (23), 144 (38), 127 (19), 115 (36); HRMS (EI): calcd for $C_{12}H_{11}O_2I$ $[M+Na]^+$: 336.9696, found: 336.9699.

1-Bromo-5-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (10). Colorless oil (20 mg, 43%);



^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.08 (dd, J = 7.5, 1.6 Hz, 1H), 6.93-6.88 (m, 1H), 6.84 (dd, J = 8.1, 1.6 Hz, 1H), 4.71 (dd, J = 10.3, 5.4 Hz, 1H), 3.86 (dd, J = 11.9, 10.3 Hz, 1H), 3.82 (s, 3H), 3.22 (dd, J = 13.9, 4.3 Hz, 1H), 3.03-2.95 (m, 1H), 2.69 (dd, J = 13.9, 1.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 149.1, 144.4, 140.8, 120.9, 118.1, 116.4, 112.4, 106.6, 72.7, 56.2, 41.1, 35.0 ppm; IR (film): $\tilde{\nu}$ = 2951, 2923, 2835, 1659, 1573, 1483, 1439, 1287, 1261, 1216, 1110, 996, 928, 763, 730 cm^{-1}; MS (EI): *m/*z (%): 266 (40) $[M]^+$, 187 (100), 161 (13), 144 (39), 127 (17), 115 (35), 63 (10); HRMS (EI): calcd for $C_{12}H_{11}O_2Br$ $[M]^+$: 265.9943, found: 265.9940; elemental analysis calcd (%) for $C_{12}H_{11}O_2Br$ (267.12): C 53.96 H 4.15, found: C 53.79, H 4.22.

7-Bromo-1-iodo-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (11). Colorless oil (82 mg, 90%); ^{1}H



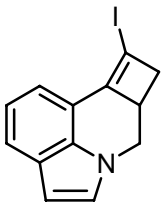
NMR (300 MHz, CD_2Cl_2): δ = 7.65 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 8.8, 2.5 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 4.57 (dd, J = 10.3, 5.4 Hz, 1H), 3.88 (dd, J = 11.8, 10.4 Hz, 1H), 3.29 (dd, J = 13.9, 4.3 Hz, 1H), 3.23-3.15 (m, 1H), 2.72 (dd, J = 14.0, 1.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 154.0, 147.9, 132.8, 125.1, 120.1, 119.4, 113.1, 80.6, 72.7, 42.6, 39.2 ppm; IR (film): $\tilde{\nu}$ = 3057, 2967, 2918, 2867, 2829, 1643, 1592, 1466, 1454, 1311, 1269, 1218, 1120, 1058, 994, 979, 889, 815, 780, 608 cm^{-1}; MS (EI): *m/*z (%): 362 (44) $[M]^+$, 235 (28), 156 (100), 128 (88), 102 (15), 75 (12), 63 (12), 51 (14); HRMS (EI): calcd for $C_{11}H_8OBrI$ $[M]^+$: 361.8803, found: 361.8807.

1,7-Dibromo-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (12). Yellow oil (35 mg, 89%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.57 (d, J = 2.3 Hz, 1H), 7.29 (dd, J = 8.8, 2.3 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 4.62 (dd, J = 10.3, 5.4 Hz, 1H), 3.85 (t, J = 11.0 Hz, 1H), 3.23 (dd, J = 14.1, 4.3 Hz, 1H), 3.00-2.94 (m, 1H), 2.70 (d, J = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 154.0, 139.7, 132.6, 126.9, 119.3, 119.3, 113.2, 108.3, 72.6, 41.2, 34.9 ppm; IR (film): $\tilde{\nu}$ = 3059, 2967, 2921, 2868, 1660, 1594, 1468, 1456, 1413, 1315, 1269, 1221, 1121, 1068, 996, 980, 899, 816, 784, 608 cm^{-1}; MS (EI): *m/*z (%): 316 (66) [M]$^+$, 235 (68), 209 (39), 156 (100), 128 (100), 102 (19), 75 (17), 63 (23), 51 (20); HRMS (EI): calcd for $C_{11}H_8OBr_2$ [M]$^+$: 313.8942, found: 313.8944.

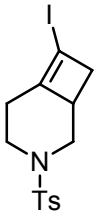
1-Iodo-7-phenyl-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (13). Colorless oil (49 mg, 86%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.79 (d, J = 2.3 Hz, 1H), 7.60-7.57 (m, 2H), 7.50-7.42 (m, 3H), 7.33 (dt, J = 7.4, 1.9 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 4.61 (dd, J = 10.3, 5.4 Hz, 1H), 3.94 (dd, J = 11.7, 10.3 Hz, 1H), 3.33-3.23 (m, 2H), 2.74 (dd, J = 13.5, 1.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 154.4, 149.0, 140.7, 134.1, 129.1, 128.9, 127.3, 127.0, 120.9, 118.7, 117.8, 79.0, 72.8, 42.5, 39.5 ppm; IR (film): $\tilde{\nu}$ = 3059, 3030, 2916, 1608, 1473, 1456, 1265, 1215, 995, 977, 889, 827, 793, 762, 698 cm^{-1}; MS (EI): *m/*z (%): 360 (100) [M]$^+$, 233 (56), 215 (11), 205 (35), 190 (18), 178 (13), 165 (14), 127 (12), 89 (10); HRMS (ESI): calcd for $C_{17}H_{13}IO$ [M]$^+$: 360.0011, found: 360.0009.

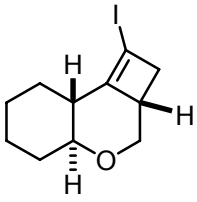
1-Iodo-2,2a,3,4-tetrahydrocyclobuta[*a*]naphthalene (14). Pale yellow oil (60 mg, 82%); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.73-7.68 (m, 1H), 7.28-7.15 (m, 3H), 3.18-3.06 (m, 2H), 2.88 (d, J = 3.4 Hz, 1H), 2.86-2.84 (m, 1H), 2.71-2.65 (m, 1H), 2.23-2.15 (m, 1H), 1.70-1.56 (m, 1H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 155.3, 137.9, 130.1, 129.5, 128.6, 126.3, 122.0, 77.0, 45.0, 44.4, 29.6, 29.4 ppm; IR (film): $\tilde{\nu}$ = 3062, 3011, 2918, 1630, 1473, 1429, 1307, 1231, 1059, 874, 760, 752, 726, 677 cm^{-1}; MS (EI): *m/*z (%): 282 (24) [M]$^+$, 155 (100), 128 (15), 115 (13); HRMS (EI): calcd for $C_{12}H_{11}I$ [M]$^+$: 281.9905, found: 281.9904; elemental analysis calcd (%) for $C_{12}H_{11}I$ (281.99): C 51.09, H 3.93, found: C 50.96, H 3.91.

1-(1-Iodo-2a,3-dihydrocyclobuta[*c*]quinolin-4(2*H*)-yl)ethanone (16). Colorless solid (91 mg, 74%); m.p.: 146-147°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.80 (bd, J = 7.5 Hz, 1H), 7.34 (bs, 1H), 7.33-7.28 (m, 1H), 7.25-7.21 (m, 1H), 4.91 (bs, 1H), 3.25-3.15 (m, 2H), 2.90 (bt, J = 10.1 Hz, 1H), 2.76 (dd, J = 13.5, 1.3 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.5, 151.7, 138.6, 128.5, 126.2, 125.5, 123.7, 122.3, 81.1, 49.7 (b), 43.0, 42.5, 23.6 ppm; IR (film): $\tilde{\nu}$ = 3062, 3004, 2918, 1723, 1661, 1597, 1567, 1471, 1372, 1345, 1227, 1217, 1055, 865, 758 cm^{-1}; MS (EI): *m/*z (%): 325 (59) [M]$^+$, 282 (11), 198 (53), 156 (100), 129 (22), 43 (25); HRMS (EI): calcd for $C_{13}H_{12}NOI$ [M+Na]$^+$: 347.9856, found: 347.9858.

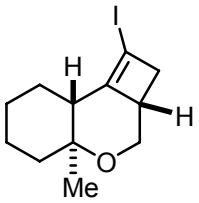
9-Iodo-7a,8-dihydro-7*H*-cyclobuta[*c*]pyrrolo[3,2,1-*ij*]quinoline (17). Colorless oil (31 mg, 63%);  ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.57 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.13-7.10 (m, 2H), 6.48 (d, J = 3.1 Hz, 1H), 4.47 (dd, J = 11.6, 6.4 Hz, 1H), 3.91 (t, J = 11.4 Hz, 1H), 3.49-3.43 (m, 1H), 3.34 (dd, J = 13.5, 4.4 Hz, 1H), 2.82 (dd, J = 13.5, 1.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 149.7, 134.3, 128.0, 127.0, 121.6, 120.2, 116.2, 114.0, 101.8, 78.9, 49.7, 43.1, 40.8 ppm; IR (film): $\tilde{\nu}$ = 3054, 2917, 2856, 1500, 1441, 1346, 1300, 1185, 1057, 872, 793, 771, 722 cm^{-1}; MS (EI): *m/*z (%): 307 (43) $[M]^+$, 180 (100), 152 (9), 127 (3), 89 (9), 77 (7), 63 (4); HRMS (EI): calcd for $C_{13}H_{10}NI$ $[M]^+$: 306.9858, found: 306.9855; elemental analysis calcd (%) for $C_{13}H_{10}NI$ (306.99): C 50.84, H 3.28, N 4.56, found: C 50.72, H 3.35, N 4.50.

7-Iodo-3-oxabicyclo[4.2.0]oct-6-ene (18). Pale yellow oil (25 mg, 63%);  ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.21 (dd, J = 10.5, 5.7 Hz, 1H), 4.04 (dd, J = 10.9, 6.6 Hz, 1H), 3.20 (ddd, J = 11.6, 11.0, 3.3 Hz, 1H), 3.13 (t, J = 10.4 Hz, 1H), 3.05-3.00 (m, 1H), 2.96 (dt, J = 13.0, 3.7 Hz, 1H), 2.50 (ddd, J = 12.9, 2.8, 1.1 Hz, 1H), 2.31-2.21 (m, 1H), 2.06 (dd, J = 13.6, 2.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.0, 78.2, 75.2, 67.7, 45.0, 42.7, 29.1 ppm; IR (film): $\tilde{\nu}$ = 2955, 2921, 2842, 1654, 1458, 1426, 1366, 1218, 1200, 1071, 1049, 892 cm^{-1}; MS (EI): *m/*z (%): 236 (65) $[M]^+$, 109 (73), 77 (100), 53 (41), 39 (24); HRMS (EI): calcd for C_7H_9OI $[M]^+$: 235.9698, found: 235.9700.

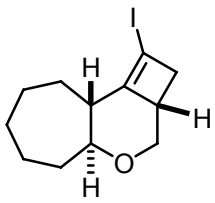
7-Iodo-3-tosyl-2-azabicyclo[4.2.0]oct-6-ene (19). Pale yellow oil (36 mg, 63%);  ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.62 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 4.13 (ddd, J = 10.2, 6.2, 1.3 Hz, 1H), 4.01-3.93 (m, 1H), 3.06-3.00 (m, 1H), 2.99-2.94 (m, 1H), 2.43-2.39 (m, 4H), 2.31-2.24 (m, 2H), 2.18-2.13 (m, 2H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 157.1, 144.2, 135.0, 130.1, 127.6, 79.7, 53.7, 46.5, 43.5, 42.6, 27.4, 21.6 ppm; IR (film): $\tilde{\nu}$ = 2922, 2845, 1724, 1656, 1597, 1458, 1349, 1337, 1306, 1163, 1093, 885, 677 cm^{-1}; MS (EI): *m/*z (%): 389 (9) $[M]^+$, 262 (100), 155 (34), 106 (21), 91 (48), 77 (14); HRMS (ESI): calcd for $C_{14}H_{16}INO_2S$ $[M+Na]^+$: 411.9839, found: 411.9841; elemental analysis calcd (%) for $C_{14}H_{16}INO_2S$ (389.25): C 43.20 H 4.14, found: C 43.32, H 4.10.

(2a*S*,4a*S*,8a*R*)-1-Iodo-2a,3,4a,5,6,7,8,8a-octahydro-2*H*-cyclobuta[*c*]chromene (20). Colorless oil (43 mg, 70%); the iodo-alkyne used as the strating material had an ee = 86%;  the optical purity of the resulting product **20** was determined as 83% *ee* (HPLC: 150 mm Chiralpak AD-RH, Ø 4.6 mm, MeOH/H_2O = 85/15, 0.5 mL/min, 4.4 MPa, 298 K, DAD, 220 nm)); $[\alpha]_D^{20}$ = –58.9 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6): δ = 3.94 (dd, J = 10.7, 6.2 Hz, 1H), 2.91 (t, J = 10.6 Hz, 1H), 2.65-2.59 (m, 2H), 2.51 (ddd, J = 12.9, 4.0, 3.2 Hz, 1H), 2.07 (ddd, J = 12.9, 2.6, 1.4 Hz, 1H), 1.97-1.85 (m, 2H), 1.78-1.72 (m, 1H), 1.52-1.43 (m, 3H), 1.38-1.28 (m, 1H), 1.12-0.85 (m, 2H) ppm; ^{13}C NMR (100 MHz, C_6D_6): δ = 159.1, 82.8, 74.3, 72.6, 46.5, 44.8, 41.5, 32.8, 25.2, 25.1, 24.4 ppm; IR (film): $\tilde{\nu}$ = 2929, 2857, 1648, 1448, 1362, 1215, 1151, 1073, 1058, 1028, 1003, 934, 738 cm^{-1}; MS (EI): *m/*z (%): 290 (92) $[M]^+$, 163 (44), 145 (23), 133 (12), 119 (26), 105 (33), 91 (100), 81 (28), 79 (54), 67 (44), 55 (25), 41 (42); HRMS (ESI): calcd for $C_{11}H_{15}OI$ $[M]^+$: 290.0168, found: 290.0171; elemental analysis calcd (%) for $C_{11}H_{15}IO$ (290.14): C 45.54, H 5.21, found: C 45.61, H 5.25.

1-Iodo-4a-methyl-2a,3,4a,5,6,7,8,8a-octahydro-2*H*-cyclobuta[*c*]chromene (21). Colorless oil (66 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (dd, *J* = 11.5, 7.0 Hz, 1H), 3.68 (dd, *J* = 11.5, 10.2 Hz, 1H), 3.01-2.95 (m, 1H), 2.90 (ddd, *J* = 12.8, 4.0, 2.8 Hz, 1H), 2.50 (ddd, *J* = 12.8, 2.6, 1.4 Hz, 1H), 2.26-2.21 (m, 1H), 1.83-1.75 (m, 2H), 1.74-1.64 (m, 2H), 1.60-1.42 (m, 3H), 1.35-1.23 (m, 1H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 76.7, 73.9, 67.5, 50.7, 44.9, 42.4, 38.9, 25.8, 23.7, 22.2, 15.8 ppm; IR (film): $\tilde{\nu}$ = 2931, 2863, 1655, 1445, 1373, 1210, 1098, 1059, 1047, 1022, 884, 740 cm^{-1}; MS (EI): *m/*z (%): 304 (61) $[M]^+$, 177 (14), 150 (82), 133 (34), 119 (59), 105 (21), 91 (100), 79 (31), 65 (16), 55 (11), 43 (100); HRMS (EI): calcd for $C_{12}H_{17}IO$ $[M]^+$: 304.0324, found: 304.0326; elemental analysis calcd (%) for $C_{12}H_{17}IO$ (304.17): C 47.38 H 5.63, found: C 47.30, H 5.60.

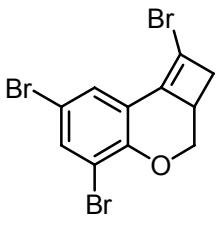


1-Iodo-2,2a,3,4a,5,6,7,8,9,9a-decahydrocyclobuta[*d*]cyclohepta[*b*]pyran (22). Colorless oil (34 mg, 80%). The two diastereomers of the product could be separated by preparative HPLC (150 mm YMC, Ø 20 mm, MeOH/H_2O = 90/10, 10.0 mL/min, 5.4 MPa, 308 K, UV, 220 nm). ***Major diastereomer*** (the stereochemical assignment is tentative as shown in the insert): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.95 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.82 (dd, *J* = 11.3, 8.0 Hz, 1H), 3.20-3.08 (m, 2H), 3.02 (dd, 12.4, 3.9 Hz, 1H), 2.54 (dt, *J* = 12.2, 1.5 Hz, 1H), 2.31 (bt, *J* = 10.2 Hz, 1H), 2.07-1.97 (m, 1H), 1.77-1.36 (m, 9H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.8, 79.4, 79.1, 70.4, 45.3, 44.5, 39.9, 34.8, 29.1, 28.4, 25.8, 25.1 ppm; IR (film): $\tilde{\nu}$ = 2921, 2853, 1656, 1454, 1355, 1239, 1085, 1056, 866 cm^{-1}; MS (EI): *m/*z (%): 304 (55) $[M]^+$, 177 (25), 159 (14), 133 (21), 117 (26), 105 (35), 91 (100), 79 (73), 67 (48), 55 (31), 41 (54), 29 (23); HRMS (ESI): calcd for $C_{12}H_{17}OI$ $[M+Na]^+$: 327.0216, found: 327.0216; elemental analysis calcd (%) for $C_{12}H_{17}IO$ (304.17): C 47.38 H 5.63, found: C 47.49, H 5.72. ***Minor diastereomer:*** ^{1}H NMR (400 MHz, CD_2Cl_2): 4.20 (dd, *J* = 10.6, 6.0 Hz, 1H), 3.16 (t, *J* = 10.6 Hz, 1H), 2.97-2.90 (m, 2H), 2.82 (ddd, *J* = 9.7, 4.0, 3.4 Hz, 1H), 2.36 (ddd, *J* = 13.0, 2.9, 1.4 Hz, 1H), 2.32-2.24 (m, 1H), 2.17-2.09 (m, 1H), 2.04-1.97 (m, 1H), 1.83, 1.74 (m, 1H), 1.70-1.43 (m, 7H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.9, 85.4, 74.7, 74.5, 46.9, 45.2, 41.7, 36.4, 27.3, 25.8, 24.1, 23.2 ppm; IR (film): $\tilde{\nu}$ = 2921, 2856, 1775, 1732, 1713, 1534, 1455, 1357, 1217, 1064, 1046, 906 cm^{-1}; MS (EI): *m/*z (%): 304 (94) $[M]^+$, 194 (13), 177 (49), 159 (13), 147 (12), 133 (21), 117 (25), 105 (36), 91 (100), 79 (68), 67 (49), 55 (30), 41 (49), 29 (19); HRMS (EI): calcd for $C_{12}H_{17}OI$ $[M]^+$: 304.0324, found: 304.0322.



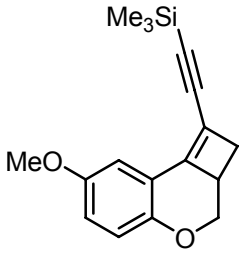
Further Transformations

1,5,7-Dibromo-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (2). A solution of bromoalkyne **1** (30.7 mg, 0.08 mmol) and AuCl (3.6 mg, 0.016 mmol) in toluene (2 mL) was stirred at 80°C for 5 min. For work up, the mixture was filtered through a short pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (3% *tert*-butyl methyl ether in hexanes) to give cyclobutene **2** as a pale yellow oil (26.7 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 2.3 Hz, 1H), 4.79 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.92



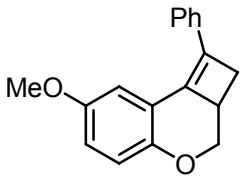
(dd, *J* = 11.8, 10.3 Hz, 1H), 3.26 (dd, *J* = 14.3, 4.3 Hz, 1H), 3.03-2.97 (m, 1H), 2.71 (dd, *J* = 14.3, 1.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 138.5, 135.0, 125.8, 119.6, 113.1, 112.0, 109.7, 73.0, 40.6, 34.4 ppm; IR (film): $\tilde{\nu}$ = 2921, 1658, 1541, 1462, 1432, 1257, 1226, 1166, 1097, 981, 750 cm^{-1}; MS (EI): *m/*z (%): 394 (55) $[M]^+$, 315 (100), 289 (22), 235 (55), 206 (21), 155 (85), 127 (61), 99 (14), 74 (21), 63 (33), 51 (15): HRMS (EI): calcd for $C_{11}H_7OBr_3$ $[M]^+$: 391.8047, found: 391.8050.

((7-Methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromen-1-yl)ethynyl)trimethylsilane (28).



Compound **6** (100 mg, 0.32 mmol) was added to a solution of CuI (12 mg, 0.06 mmol) and $(PPh_3)_2PdCl_2$ (23 mg, 0.03 mmol) in Et_3N (2.5 mL) at 0°C. After stirring for 10 min at that temperature, trimethylsilyl acetylene (0.05 mL, 0.35 mmol) was introduced and the resulting mixture allowed to reach ambient temperature. After stirring for another 2 h, the Et_3N was evaporated and the residue purified by flash chromatography (neutral Alox, 5% EtOAc in hexanes) to give product **28** as a yellow oil (70 mg, 77%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.97 (d, *J* = 2.9 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 9.0, 2.9 Hz, 1H), 4.56 (dd, *J* = 10.0, 5.9 Hz, 1H), 3.82 (dd, *J* = 12.1, 10.1 Hz, 1H), 3.77 (s, 3H), 2.98 (dd, *J* = 13.4, 4.7 Hz, 1H), 2.93-2.87 (m, 1H), 2.47 (dd, *J* = 13.4, 2.0 Hz, 1H), 0.24 (s, 9H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 154.1, 149.9, 147.2, 119.4, 118.3, 117.3, 116.3, 108.2, 100.6, 99.9, 72.8, 55.9, 36.1, 33.6, 0.0 ppm; IR (film): $\tilde{\nu}$ = 2957, 2915, 2833, 2131, 1682, 1484, 1250, 1204, 1038, 845, 760 cm^{-1}; MS (EI): *m/*z (%): 284 (100) $[M]^+$, 269 (41), 253 (11), 241 (27), 225 (15), 211 (13), 195 (17), 161 (19), 73 (45); HRMS (ESI): calcd for $C_{17}H_{20}O_2Si$ $[M]^+$: 284.1233, found: 284.1234; elemental analysis calcd (%) for $C_{17}H_{20}O_2Si$ (284.43): C 71.79, H 7.09, found: C 71.88, H 6.95.

7-Methoxy-1-phenyl-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (29). 9-MeO-9-BBN (0.06 mL, 0.44 mmol) was added to a solution of phenylmagnesium bromide (1 M in THF, 0.44 mmol) in THF (3.5 mL) and Et_2O (0.5 mL) at −78°C and the resulting mixture was stirred for 15 min before it was allowed to reach ambient temperature. After 60 min, a solution of iodide **6** (70 mg, 0.22 mmol) in DMF (3.5 mL) was introduced followed by $(dppf)PdCl_2$ (8 mg, 0.01 mmol) and $AsPh_3$ (6.7 mg, 0.02 mmol). The reaction mixture was stirred at 60°C for 4 h and for additional 3 h at 80°C. After cooling to ambient temperature, the mixture was filtered through a pad of Alox, the filtrate was extracted with EtOAc and brine, the combined organic layers were dried over Na_2SO_4, the solvents were evaporated, and the residue was purified by flash chromatography (neutral Alox, 3% EtOAc in hexanes) to give product **29** as a colorless solid (33 mg, 56%). m.p.: 107-108°; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.60-7.57 (m, 2H), 7.43-7.39 (m, 2H), 7.32-7.28 (m, 1H), 7.17 (d, *J* = 2.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.77 (dd, *J* = 8.9, 3.0 Hz, 1H), 4.66 (dd, *J* = 10.0, 5.7 Hz, 1H), 3.90 (dd, *J* = 12.0, 10.0 Hz, 1H), 3.79 (s, 3H), 3.14 (dd, *J* = 13.8, 4.6 Hz, 1H), 2.93-2.87 (m, 1H), 2.53 (dd, *J* = 13.8, 1.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.7, 149.7, 136.9, 135.8, 134.6, 128.9, 128.1, 126.2, 120.2, 118.0, 115.5, 110.4, 72.9, 56.1, 32.2, 31.5 ppm; IR (film): $\tilde{\nu}$ = 2935, 2904, 2830, 1572, 1480, 1196, 1042, 760, 692 cm^{-1}; MS (EI): *m/*z (%): 264 (100) $[M]^+$, 237 (17), 187 (14), 165 (11), 161 (19); HRMS (ESI): calcd for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150, found: 264.1151; elemental analysis calcd (%) for $C_{18}H_{16}O_2$ (264.32): C 81.79 H 6.10, found: C 81.72, H 6.02.



7-Methoxy-1-methyl-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (30). Iodide **6** (50 mg, 0.16 mmol) was added to a solution of $[(C_2H_4)_4Fe][Li(tmeda)]_2$ (7.3 mg, 0.018 mmol)[2] in THF (1 mL) at –20°C, causing an immediate color change of the mixture from green to red. Methylmagnesium bromide (3 M in Et_2O, 0.38 mmol) was added dropwise and stirring was continued at –20°C for 25 min. For work up, the reaction was quenched with aq. sat. NH_4Cl, the organic phase was washed with brine and dried over Na_2SO_4, the solvent was evaporated and the residue purified by flash chromatography (neutral Alox, 5% Et_2O in pentanes) to give product **30** as a colorless oil (17 mg, 55%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.77-6.75 (m, 2H), 6.66 (dd, J = 8.9, 3.0 Hz, 1H), 4.55 (dd, J = 9.9, 5.5 Hz, 1H), 3.76-3.10 (m, 4H), 2.83-2.78 (m, 1H), 2.75-2.68 (m, 1H), 2.15 (dt, J = 14.2, 1.5 Hz, 1H), 1.92 (dd, J = 1.9, 1.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.9, 148.9, 137.3, 134.3, 120.6, 117.7, 114.1, 109.3, 73.4, 56.0, 36.1, 32.3, 15.9 ppm; IR (film): $\tilde{\nu}$ = 2930, 2905, 2860, 2829, 1610, 1572, 1482, 1431, 1305, 1256, 1198, 1169, 1039, 977 cm^{-1}; MS (EI): *m/*z (%): 202 (92) $[M]^+$, 187 (100), 175 (22), 161 (32), 144 (16), 128 (14), 115 (19), 91 (13), 77 (10); HRMS (EI): calcd for $C_{13}H_{14}O_2$ $[M]^+$: 202.0994, found: 202.0996; elemental analysis calcd (%) for $C_{13}H_{14}O_2$ (202.25): C 77.20 H 6.98, found: C 77.29, H 7.08.

1-Hexyl-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (32a). Prepared as described above from iodide **6** (74 mg, 0.17 mmol) and hexylmagnesium bromide; colorless oil (37 mg, 51%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.77 (dd, J = 7.8, 1.4 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.26 (dd, J = 7.4, 1.8 Hz, 1H), 7.22 (d, J = 8.5 Hz, 2H), 7.20-7.22 (m, 2H), 4.68 (dd, J = 13.2, 5.2 Hz, 1H), 3.05 (dd, J = 13.1, 0.8 Hz, 1H), 2.61 (dd, J = 14.4, 4.2 Hz, 1H), 2.38 (s, 3H), 2.30-2.14 (m, 3H), 2.09 (bd, J = 14.5 Hz, 1H), 1.45-1.38 (m, 2H), 1.29-1.21 (m, 6H), 0.85 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 144.2, 144.1, 137.9, 135.7, 135.1, 130.0, 127.4, 126.9, 125.8, 125.6, 125.5, 125.1, 53.5, 34.6, 32.0, 31.3, 30.1, 29.5, 27.5, 22.9, 21.6, 14.2 ppm; IR (film): $\tilde{\nu}$ = 3065, 2928, 2855, 1655, 1598, 1459, 1353, 1165, 1091, 1024, 853, 814, 757, 659, 576 cm^{-1}; MS (EI): *m/*z (%): 395 (30) $[M]^+$, 240 (100), 168 (31), 155 (20), 130 (19), 91 (13); HRMS (EI): calcd for $C_{24}H_{29}NO_2S$ $[M]^+$: 395.1919, found: 395.1918.

1-Butyl-7-methoxy-2a,3-dihydro-2*H*-cyclobuta[*c*]chromene (31). *n*BuLi (1.6 M in hexane, 0.5 mmol) was slowly added to a solution of iodide **6** (138 mg, 0.4 mmol) in Et_2O (0.8 mL) and THF (0.4 mL) at –78°C. Once the addition was complete, the mixture was stirred at ambient temperature for 75 min until GC/MS showed full conversion. The reaction was quenched with water, the aqueous phase was extracted with Et_2O, the combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue purified by flash chromatography (neutral Alox, 3% Et_2O in pentanes) to give product **31** as a colorless oil (70 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (d, J = 8.9 Hz, 1H), 6.77 (d, J = 3.0 Hz, 1H), 6.68 (dd, J = 8.9, 3.0 Hz, 1H), 4.59 (dd, J = 9.8, 5.5 Hz, 1H), 3.78 (s, 3H), 3.76 (dd, J = 11.5, 9.9 Hz, 1H), 2.82-2.71 (m, 2H), 2.31-2.27 (m, 2H), 2.16 (dd, J = 13.9, 1.2 Hz, 1H), 1.54-1.47 (m, 2H), 1.42-1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 148.5, 141.3, 133.5, 120.2, 117.4, 113.7, 109.5, 73.2, 55.7, 33.8, 31.5, 29.7, 29.6, 22.6, 13.9

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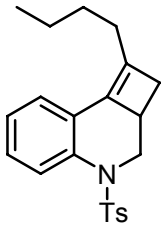
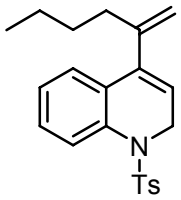
[2] (*a*) K. Jonas and L. Schieferstein, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 549. (*b*) K. Jonas, L. Schieferstein, C. Krüger and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 550.

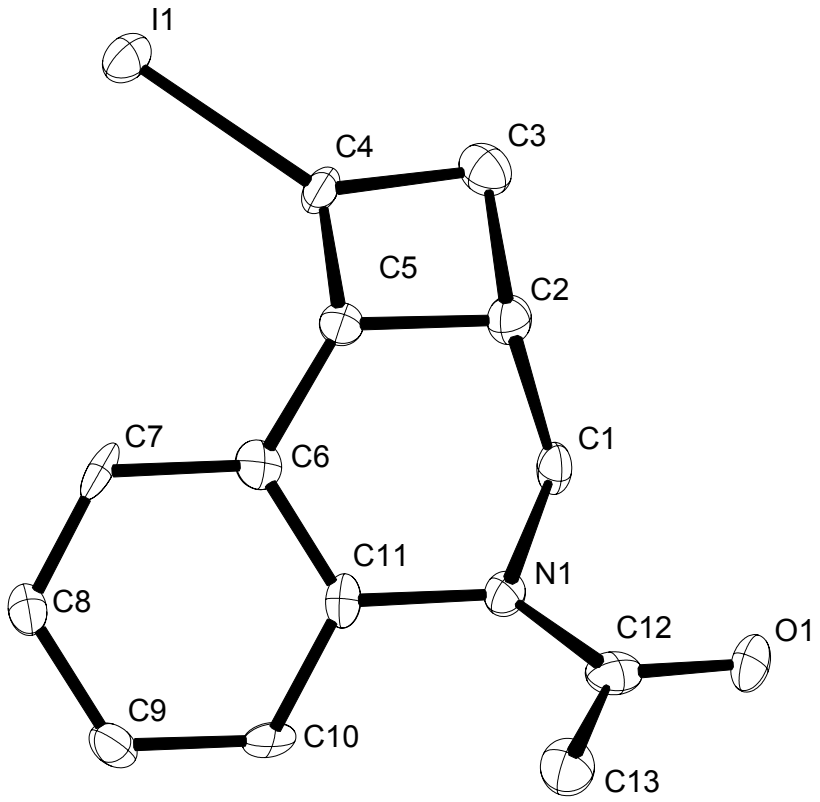
ppm; IR (film): $\tilde{\nu}$ = 2956, 2928, 2859, 2830, 1611, 1573, 1482, 1432, 1295, 1258, 1197, 1169, 1040, 990, 814 cm^{-1}; MS (EI): *m/*z (%): 244 (62) [M]$^{+}$, 201 (100), 187 (82), 161 (15), 115 (12); HRMS (ESI): calcd for $C_{16}H_{20}O_2$ [M]$^{+}$: 244.1463, found: 244.1462.

1-Butyl-4-tosyl-2,2a,3,4-tetrahydrocyclobuta[*c*]quinoline (32b). Prepared as described above; yellow solid (90 mg, 31%); m.p.: 45-48°C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.77 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20-7.11 (m, 2H), 4.68 (dd, *J* = 13.1, 5.2 Hz, 1H), 3.05 (dd, *J* = 13.1, 12.2 Hz, 1H), 2.64-2.59 (m, 1H), 2.38 (s, 3H), 2.24-2.15 (m, 3H), 2.09-2.05 (m, 1H), 1.45-1.37 (m, 2H), 1.35-1.25 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 144.2, 138.0, 135.8, 135.2, 130.0, 127.4, 127.0, 125.8, 125.6, 125.1, 53.5, 34.6, 31.4, 29.8, 29.8, 23.0, 21.6, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3063, 3027, 2927, 2871, 1654, 1598, 1458, 1349, 1160, 1090, 1023, 852, 813, 755, 729, 672, 658 cm^{-1}; MS (EI): *m/*z (%): 367 (34) [M]$^{+}$, 212 (100), 168 (37), 155 (25), 130 (20). 91 (9); HRMS (ESI): calcd for $C_{22}H_{25}NO_2S$ [M+Na]$^{+}$: 390.1498, found: 390.1504; elemental analysis calcd (%) for $C_{22}H_{25}NO_2S$ (367.50): C 71.90 H 6.86, found: C 71.78, H 6.81.



4-(Hex-1-en-2-yl)-1-tosyl-1,2-dihydroquinoline (33). A solution of cyclobutene **32b** (30 mg, 0.08 mmol) in toluene was refluxed for 6 h. The mixture was adsorped on silica and the product purified by flash chromatography (10% Et_2O in pentanes) to give product **33** as a pale yellow oil (26 mg, 88%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.72 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.35-7.32 (m, 2H), 7.29 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.19 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.11-7.08 (m, 3H), 5.49 (t, *J* = 4.4 Hz, 1H), 4.94 (dd, *J* = 3.4, 1.5 Hz, 1H), 4.61-4.60 (m, 1H), 4.43 (d, *J* = 4.4 Hz, 2H), 2.31 (s, 3H), 1.73-1.69 (m, 2H), 1.24-1.11 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 147.2, 143.9, 140.1, 137.2, 135.9, 130.5, 129.6, 128.2, 127.7, 127.4, 126.7, 126.1, 120.4, 114.4, 45.7, 35.3, 30.1, 22.7, 21.6, 14.1 ppm; IR (film): $\tilde{\nu}$ = 3063, 3032, 2957, 2930, 2859, 1629, 1598, 1480, 1451, 1354, 1163, 1090, 813, 768, 682 cm^{-1}; MS (EI): *m/*z (%): 367 (28) [M]$^{+}$, 212 (100), 168 (31), 155 (23), 130 (17); HRMS (ESI): calcd for $C_{22}H_{25}NO_2S$ [M+Na]$^{+}$: 390.1498, found: 390.1496.





Crystal data for compound 16: [$C_{13}H_{12}INO$], M_r = 325.14, colourless, crystal size: 0.03×0.05×0.07 mm^3; a = 24.4838(8), b = 8.0709(3), c = 12.1166(4) Å, β = 104.469(2)°, U = 2318.4(1) Å^3, T = 100 K, monoclinic, space group Cc (No. 9), Z = 8, ρ_{calcd} = 1.86 g cm^{-3}, $F(000)$ = 1264, Bruker-AXS X8-Proteum diffractometer, λ(Cu-K$_\alpha$) = 1.54178 Å, μ = 21.52 mm^{-1}, 9921 measured and 2821 independent reflections (R_{int} = 0.037), 2474 with $I > 2\sigma(I)$, θ_{max} = 63.26°, apparent $T_{min/max}$ = 0.4362 (*SADABS*), direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL-97*) on F_o^2 , programs from G. Sheldrick, University of Göttingen, 1997. Two crystallographically independent molecules. Chebyshev type weights, 290 parameters, R_1 = 0.032 ($I > 2\sigma(I)$), wR_2 = 0.081 (all data), $\Delta\rho_{max/min}$ = 1.5 / -0.7 eÅ^{-3} (1.0 Å from I2/ 0.95 Å from I1).