Electronic Supplementary Material (ESI) for ChemComm.

TABLE OF CONTENTS **Page**

1. General Information

Reaction setup: Air- and moisture-sensitive reactions were conducted in flame- or oven-dried glassware equipped with tightly fitted rubber septa and under a positive pressure of dry nitrogen. Reagents and solvents were handled by using standard syringe techniques. Unless stated otherwise, all the yields refer to isolated products after flash column chromatography.

NMR Spectroscopy: ^{1}H NMR spectra were acquired using a Bruker BioSpin 500MHz Avance III Digital NMR spectrometer and calibrated using the solvent signal ($CDCl_3$ 7.26 ppm). Multiplicities were determined using MNova software. ^{13}C NMR spectra were acquired using a Bruker BioSpin 126MHz Avance III Digital NMR spectrometer and calibrated using the solvent signal ($CDCl_3$ 77.16 ppm). ^{1}H NMR multiplicities are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

Infrared Spectroscopy: IR spectra were measured on Bruker Vertex 70 with an ATR accessory.

Mass Spectroscopy: High-Resolution mass spectra were acquired using an Agilent 6520 Q-TOF mass spectrometer.

Melting Points: All melting points were measured Barnstead Electrotherm 1001D/1001 Mel-Temp Capillary Melting Point apparatus and are uncorrected.

Optical Rotation: Optical rotations were acquired on a Jasco Digital Polarimeter with a 1 dm cell and a sodium lamp.

HPLC: Enantiomeric excess was determined by high performance liquid chromatography (HPLC) using Agilent 1260 equip with a diode array detector.

Solvents/chemicals: Ethyl acetate, hexanes, methanol, and chloroform were used as received. Acetonitrile and dimethyl sulfoxide were dried over 4Å molecular sieves prior to use. All other reagents were used directly as received from the manufacturer.

2. Sulfoxonium Ylides Synthesized

All sulfoxonium ylides were synthesized according to literature procedures. [1-5]

3. Chromenones and Quinolones Synthesized

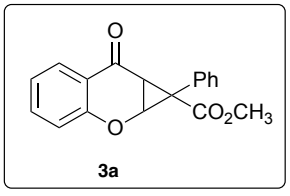
All chromenones were synthesized according to literature procedures.[6]

All quinolones were synthesized according to literature procedures.[7]

4. General Procedure for Cyclopropanation of Chromenones and Quinolones

To a 4mL reaction vial with a Teflon coated septum was added 0.1 mmol chromenone or *N*-protected quinolone, 0.2mL dry toluene (0.5M), and 30µL TIPSOTf (0.11 mmol, 1.1 equiv). The reaction was stirred at 60˚C for 1 hour before being brought back to room temperature. The reaction was further diluted with 0.3mL dry toluene (0.33M) followed by the addition of 0.12 mmol of sulfoxonium ylide (1.2 equiv). The reaction was stirred for 24-48 hours before being quenched with 0.2mL of 6M HCl and reacted at room temperature for a further 30 minutes. The reaction was quenched with 1mL H_2O and extracted with DCM (3 x 1mL). The crude product was concentrated under reduced pressure and purified by column chromatography in EtOAc /Hexanes.

Methyl 1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate

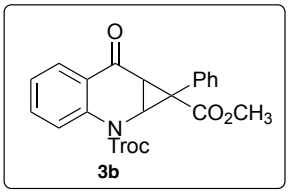


3a

(**3a**) White solid (26.4 mg, 90%). **Rf** = 0.41 (EtOAc/Hex, 1:4); **m.p.** 125°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (ddd, J = 7.9, 1.8, 0.5 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.49 (ddd, J = 8.5, 7.2, 1.8 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.09 – 7.00 (m, 2H), 4.79 (d,

J = 6.8 Hz, 1H), 3.28 (s, 3H), 2.80 (d, J = 6.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.85, 166.65, 158.49, 135.84, 135.64, 129.37, 129.23, 128.81, 126.41, 122.27, 120.10, 117.48, 77.41, 77.16, 76.91, 64.51, 52.79, 37.58, 34.55 ppm; **IR** (neat): ν (cm^{-1}) = 1723, 1674, 1608, 1579, 1464, 1333, 1297, 1221, 1195, 1168, 1132, 1105, 1076, 1049, 1026, 1014, 978, 935, 867, 821, 776, 751, 732, 697; **HRMS** (ESI): calcd for $C_{18}H_{14}O_4$ $[M+H^+]$: 295.0965; found: 295.0955.

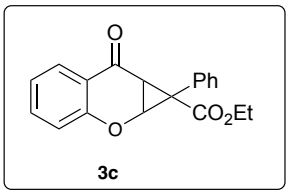
1-methyl 2-(2,2,2-trichloroethyl) 7-oxo-1-phenyl-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



3b

(**3b**) White solid (38.3 mg, 82%). **Rf** = 0.50 (EtOAc/Hex, 1:9); **m.p.** = 143˚C **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.7, 1.8 Hz, 2H), 7.72 (dd, J = 8.1, 1.5 Hz, 2H), 7.56 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.27 – 7.22 (m, 1H), 5.05 – 4.98 (m, 2H), 4.45 (d, J = 8.1 Hz, 1H), 3.41 (s, 3H), 2.85 (d, J = 8.1 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.48, 141.18, 136.49, 133.86, 130.19, 128.85, 128.64, 126.83, 124.88, 94.87, 77.41, 77.16, 76.91, 75.99, 53.03, 35.60 ppm; **IR** (neat): ν (cm^{-1}) =3027, 2954, 1741, 1715, 1685, 1601, 1483, 1462, 1437, 1390, 1328, 1312, 1237, 1198, 1180, 1151, 1090, 1058, 1032, 941, 919, 885, 808, 794, 757, 713, 700, 683; **HRMS** (ESI): calcd for $C_{21}H_{16}Cl_3NO_5$ $[M+H]^+$: 468.0167; found: 468.0159.

Ethyl 1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate

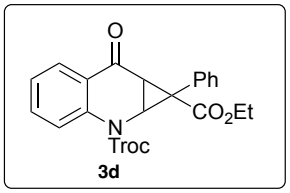


3c

(**3c**) White solid (25.3 mg, 82%). **Rf** = 0.38 (EtOAc/Hex, 1:4); **m.p.** = 79°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.9,

1.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.48 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.09 – 6.99 (m, 2H), 4.77 (d, J = 6.8 Hz, 1H), 3.79 – 3.66 (m, 2H), 2.78 (d, J = 6.8 Hz, 1H), 0.86 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.81, 166.14, 158.57, 135.87, 129.31, 129.21, 128.75, 126.55, 122.21, 117.58, 77.41, 77.16, 76.91, 64.51, 64.37, 62.11, 37.50, 34.39, 13.52 ppm; **IR** (neat): ν (cm^{-1}) = 2971, 1757, 1735, 1685, 1602, 1576, 1511, 1482, 1461, 1378, 1328, 1298, 1257, 1232, 1191, 1154, 1125, 1095, 1034, 1000, 945, 863, 819, 795, 756, 732, 711, 698, 684; **HRMS** (ESI): calcd for $C_{19}H_{16}O_4$ $[M+H]^+$: 309.1121; found: 309.1113.

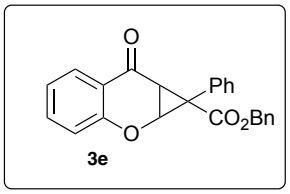
1-ethyl 2-(2,2,2-trichloroethyl) 7-oxo-1-phenyl-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



3d

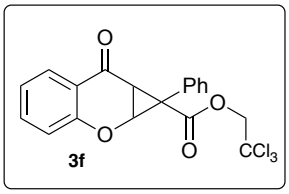
(**3d**) White solid (37.6 mg, 78%). **Rf** = 0.46 (EtOAc/Hex, 1:4); **m.p.** = 127˚C **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.71 (d, *J* = 6.7 Hz, 2H), 7.56 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.37 (dt, *J* = 13.3, 6.9 Hz, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 4.98 (s, 2H), 4.45 (d, *J* = 8.1 Hz, 1H), 3.88 (d, *J* = 7.1 Hz, 1H), 3.81 (dd, *J* = 10.8, 7.1 Hz, 1H), 2.84 (d, *J* = 8.1 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.40, 167.64, 141.24, 136.65, 133.92, 130.14, 128.82, 128.57, 126.87, 124.81, 123.08, 94.91, 77.42, 77.16, 76.91, 76.00, 62.22, 39.02, 35.30, 13.76 ppm; **IR** (neat): ν (cm^{-1}) = 2971, 1757, 1735, 1685, 1602, 1576, 1511, 1482, 1461, 1378, 1328, 1298, 1257, 1232, 1191, 1154, 1125, 1095, 1034, 1000, 945, 863, 819, 795, 756, 732, 711, 698, 684; **HRMS** (ESI): calcd for $C_{22}H_{18}Cl_3NO_5$ $[M+H]^+$: 482.0323; found: 482.0317.

Benzyl 7-oxo-1-phenyl-1-tetrahydrocyclopropa[b]chromene-1-carboxylate



(**3e**) White solid (30 mg, 81%). **Rf** = 0.40 (EtOAc/Hex, 1:4); **m.p.** = 76°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.9, 1.8 Hz, 1H), 7.58 (d, J = 6.8 Hz, 2H), 7.46 – 7.32 (m, 4H), 7.26 – 7.22 (m, 3H), 7.05 – 7.00 (m, 2H), 7.00 – 6.92 (m, 2H), 4.80 (d, J = 6.8 Hz, 1H), 4.75 (d, J = 12.5 Hz, 1H), 4.66 – 4.58 (m, 1H), 2.80 (d, J = 6.7 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.64, 166.01, 158.46, 135.82, 135.66, 134.84, 129.40, 129.23, 128.81, 128.56, 128.29, 128.08, 126.48, 122.23, 119.93, 117.43, 77.42, 77.16, 76.91, 67.62, 64.48, 37.53, 34.44 ppm; **IR** (neat): ν (cm^{-1}) = 2945, 1721, 1675, 1610, 1582, 1498, 1463, 1377, 1299, 1242, 1224, 1176, 1152, 1131, 1096, 1047, 975, 876, 823, 774, 756, 730, 700, 693, 676; **HRMS** (ESI): calcd for $C_{24}H_{18}O_4$ [M+H^+]: 371.1278; found: 371.1267.

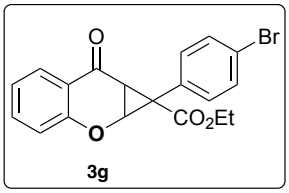
2,2,2-trichloroethyl 7-oxo-1-phenyl-tetrahydrocyclopropa[*b*]chromene-1-carboxylate



(**3f**) White solid (29 mg, 71%). **Rf** = 0.46 (EtOAc/Hex, 1:4); **m.p.** = 118°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.9, 1.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.49 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.07 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 7.01 (dd, J = 8.4, 1.0 Hz, 1H), 4.89 (d, J = 6.8 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.24 (d, J = 11.9 Hz, 1H), 2.86 (d, J = 6.7 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.34, 165.12, 159.03, 136.23, 135.23, 130.13, 129.49, 129.38, 129.35, 126.87, 122.67, 120.33, 117.74, 94.36, 77.67, 77.41, 77.16, 75.14, 65.26, 37.44, 34.65 ppm; **IR** (neat): ν (cm^{-1}) = 3073, 1748, 1670, 1610, 1498, 1463, 1368, 1330, 1313, 1276, 1244, 1220, 1166, 1149, 1126, 1104, 1070,

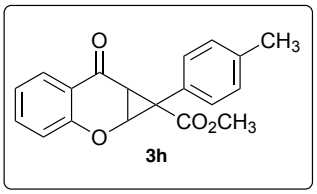
1047, 1024, 956, 910, 867, 830, 802, 746, 714, 700, 648; **HRMS** (ESI): calcd for $C_{19}H_{14}Cl_3O_4$ $[M+H]^+$: 410.9958; found: 410.9946.

Ethyl 1-(4-bromophenyl)-7-oxo-tetrahydrocyclopropa[b]chromene-1-carboxylate



(**3g**) White solid (29.6 mg, 78%). **Rf** = 0.39 (EtOAc/Hex, 1:4); **m.p.** = 117°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.9, 1.7 Hz, 1H), 7.55 – 7.43 (m, 5H), 7.06 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.01 (dd, J = 8.5, 1.1 Hz, 1H), 4.73 (d, J = 6.8 Hz, 1H), 3.80 – 3.67 (m, 2H), 2.73 (d, J = 6.8 Hz, 1H), 0.85 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.40, 165.79, 158.57, 135.94, 134.93, 132.38, 131.10, 126.51, 123.00, 122.31, 120.02, 117.52, 77.41, 77.16, 76.91, 64.32, 62.29, 36.96, 34.14, 13.52 ppm; **IR** (neat): ν (cm^{-1}) = 2968, 1720, 1669, 1609, 1463, 1368, 1333, 1301, 1244, 1225, 1182, 1134, 1095, 1058, 1026, 1009, 960, 868, 823, 788, 753, 712, 630; **HRMS** (ESI): calcd for $C_{19}H_{15}BrO_4$ $[M+H]^+$: 387.0226; found: 387.0221.

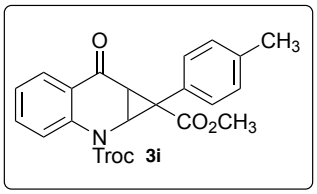
Methyl 7-oxo-1-(p-tolyl)- tetrahydrocyclopropa[b]chromene-1-carboxylate



(**3h**) White solid (26 mg, 85%). **Rf** = 0.41 (EtOAc/Hex, 1:4); **m.p.** 88°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.9, 1.8 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 (d, J = 1.9 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.01 – 6.91 (m, 2H), 4.69 (d, J = 6.7 Hz, 1H), 3.20 (s, 3H), 2.69 (d, J = 6.7 Hz, 1H), 2.27 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.84, 166.66, 158.35, 138.67, 135.66, 132.53, 129.77, 129.11, 126.26, 122.08, 119.99, 117.32, 77.29, 77.04, 76.78, 64.43, 53.33, 52.61, 37.16, 34.49, 21.16 ppm; **IR** (neat): ν (cm^{-1}) = 3074, 1723, 1671, 1608, 1581, 1511, 1476, 1462, 1429, 1330,

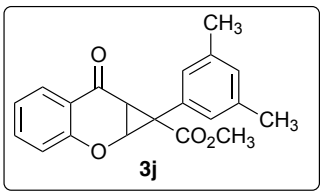
1300, 1229, 1194, 1167, 1134, 1106, 1055, 1020, 986, 938, 868, 822, 780, 754; **HRMS** (ESI): calcd for $C_{19}H_{16}O_4$ $[M+H]^+$: 309.1121; found: 309.1116.

1-methyl 2-(2,2,2-trichloroethyl) 7-oxo-1-(p-tolyl)-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



(**3i**) White solid (38 mg, 79%). **Rf** = 0.42 (EtOAc/Hex, 1:4); **m.p.** = 143˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.8, 1.7 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.56 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.18 (m, 2H), 5.06 – 4.96 (m, 2H), 4.43 (d, J = 8.0 Hz, 1H), 3.40 (s, 3H), 2.83 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) 187.68, 168.46, 153.56, 141.28, 138.68, 133.93, 133.67, 130.15, 129.66, 126.93, 124.96, 123.29, 94.99, 76.09, 53.12, 38.85, 35.82, 21.45 ppm; **IR** (neat): ν (cm^{-1}) = 2955, 1732, 1681, 1602, 1576, 1511, 1480, 1462, 1438, 1376, 1327, 1296, 1230, 1194, 1152, 1130, 1094, 1033, 974, 936, 869, 811, 756, 732, 708; **HRMS** (ESI): calcd for $C_{22}H_{18}Cl_3NO_5$ $[M+H]^+$: 482.0323; found: 482.0319.

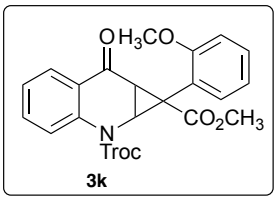
Methyl 1-(3,5-dimethylphenyl)-7-oxo-1-tetrahydrocyclopropa[b]chromene-1-carboxylate



(**3j**) White solid (24.5 mg, 76%). **Rf** = 0.40 (EtOAc/Hex, 1:4); **m.p. =** 139°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.9, 1.7 Hz, 1H), 7.48 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.19 (d, J = 1.7 Hz, 2H), 7.09 – 6.95 (m, 3H), 4.76 (d, J = 6.7 Hz, 1H), 3.27 (s, 3H), 2.77 (d, J = 6.7 Hz, 1H), 2.32 (s, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.12, 166.77, 158.43, 138.96, 135.82, 135.33, 130.49, 126.42, 122.21,

120.05, 117.51, 77.41, 77.16, 76.91, 64.50, 64.37, 52.74, 37.53, 34.57, 21.32 ppm; **IR** (neat): ν (cm^{-1}) = 2959, 1731, 1670, 1628, 1604, 1576, 1511, 1463, 1439, 1378, 1329, 1303, 1276, 1221, 1194, 1165, 1151, 1130, 1107, 1048, 1026, 976, 869, 852, 820, 761, 732, 707, 667; **HRMS** (ESI): calcd for $C_{20}H_{18}O_4$ $[M+H]^+$: 323.1278; found: 323.1272.

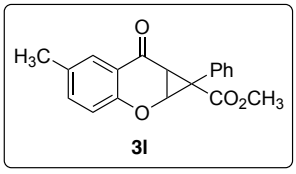
1-methyl 2-(2,2,2-trichloroethyl) 1-(2-methoxyphenyl)-7-oxo-1,1a,7,7a-tetrahydro-2*H*-cyclopropa[*b*]quinoline-1,2-dicarboxylate



3k

(**3k**) White solid (14.9 mg, 30%). **Rf** = 0.42 (EtOAc/Hex, 1:4); **m.p** = 142˚C **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.78 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.99 – 6.90 (m, 2H), 4.99 (s, 2H), 4.50 (d, *J* = 7.9 Hz, 1H), 3.94 (s, 3H), 3.46 (s, 3H), 2.52 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.18, 168.87, 158.89, 141.65, 133.43, 130.17, 130.05, 126.63, 125.26, 124.77, 123.01, 120.37, 111.02, 77.42, 77.16, 76.91, 75.95, 55.92, 53.00, 35.71, 35.46 ppm; **IR** (neat): ν (cm-1) = 3011, 1736, 1714, 1686, 1598, 1497, 1479, 1459, 1437, 1388, 1326, 1285, 1254, 1229, 1201, 1180, 1152, 1126, 1098, 1086, 1052, 1031, 951, 885, 807, 796, 757, 714, 699, 682; **HRMS** (ESI): calcd for $C_{22}H_{13}Cl_3NO_6$ $[M+H]^+$: 498.0278; found: 498.0274.

Methyl 5-methyl-7-oxo-1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate

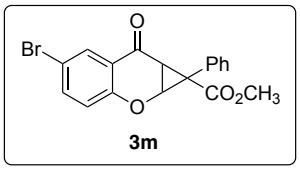


3l

(**3l**) White solid (20.2 mg, 65%). **Rf** = 0.43 (EtOAc/Hex, 1:4); **m.p.** = 120˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ δ 7.74 – 7.70 (m, 1H), 7.63 – 7.56 (m, 1H), 7.56 – 7.52 (m, 1H), 7.41 – 7.28 (m, 4H), 6.92 (d, J = 8.5 Hz, 1H), 4.76 (d, J = 6.8 Hz, 1H), 3.30 (s, 3H), 2.78 (d, J = 6.8 Hz,

1H), 2.32 (d, J = 0.7 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.06, 166.71, 156.56, 136.97, 135.75, 131.77, 129.37, 129.20, 128.75, 125.91, 119.68, 117.24, 77.42, 77.16, 76.91, 64.50, 52.79, 37.51, 34.57, 20.61 ppm; **IR** (neat): ν (cm^{-1}) = 2952, 1726, 1699, 1618, 1579, 1488, 1463, 1295, 1223, 1193, 1169, 1133, 1105, 1048, 937, 865, 815, 777, 751, 734; **HRMS** (ESI): calcd for $C_{19}H_{16}O_4$ $[M+H]^+$: 309.1121; found: 309.1117.

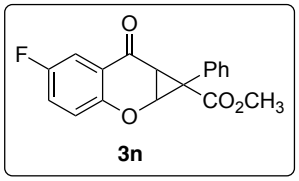
Methyl 5-bromo-1-phenyl-tetrahydrocyclopropa[*b*]chromene-1-carboxylate



3m

(**3m**) Off-white solid (33.5 mg, 90%). **Rf** = 0.45 (EtOAc/Hex, 1:4); **m.p.** = 130˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 2.5 Hz, 1H), 7.55 (ddd, J = 8.0, 3.7, 1.9 Hz, 3H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 6.92 (d, J = 8.8 Hz, 1H), 4.81 (d, J = 6.8 Hz, 1H), 3.36 (s, 3H), 2.78 (d, J = 6.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.58, 166.63, 157.62, 138.42, 135.41, 129.44, 129.27, 128.93, 128.81, 121.47, 119.43, 114.90, 77.42, 77.16, 76.91, 64.99, 53.05, 37.86, 34.08 ppm; **IR** (neat): ν (cm^{-1}) = 2955, 1725, 1668, 1600, 1470, 1438, 1420, 1287, 1241, 1216, 1195, 1176, 1135, 1099, 1041, 968, 939, 883, 819, 777, 765, 742, 698, 646; **HRMS** (ESI): calcd for $C_{18}H_{13}BrO_4$ $[M+H]^+$: 373.0070; found: 373.0068.

Methyl 5-fluoro-7-oxo-1-phenyl-tetrahydrocyclopropa[*b*]chromene-1-carboxylate

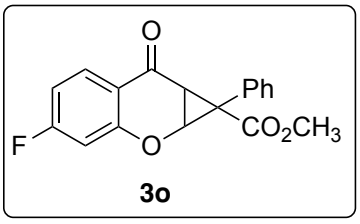


3n

(**3n**) White solid (24.6 mg, 79%). **Rf** = 0.39 (EtOAc/Hex, 1:4); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 3H), 7.43 – 7.33 (m, 3H), 7.21 (ddd, J = 9.1, 7.6, 3.2 Hz, 1H), 7.04 – 6.98 (m, 1H), 4.80 (d, J = 6.8 Hz, 1H), 3.34 (s, 3H), 2.78 (d, J = 6.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.11, 166.61, 158.59, 156.66,

154.69, 135.45, 130.27, 129.39, 129.26, 128.89, 128.82, 128.57, 126.82, 124.82, 123.49, 123.30, 119.20, 119.14, 111.51, 111.33, 77.42, 77.16, 76.91, 67.49, 64.83, 64.59, 52.93, 37.64, 35.44, 34.09 ppm; **IR** (neat): ν (cm^{-1}) = 1965, 1713, 1673, 1614, 1591, 1493, 1443, 1382, 1336, 1303, 1249, 1204, 1183, 1142, 1098, 1080, 1042, 979, 943, 884, 852, 811, 778, 764, 735, 706, 666, 650; **HRMS** (ESI): calcd for $C_{18}H_{13}FO_4$ [$M+H^+$]: 313.0871; found: 313.0865.

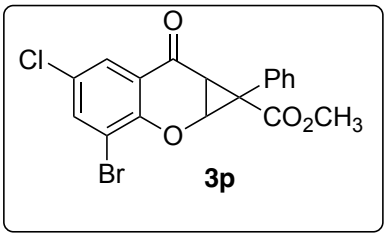
Methyl 6-fluoro-7-oxo-1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate



3o

(**3o**) White solid (22.1 mg, 71%). **Rf** = 0.42 (EtOAc/Hex, 1:4); **m.p.** = 134˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.8, 6.5 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.42 – 7.33 (m, 2H), 6.78 (ddd, J = 8.8, 8.0, 2.4 Hz, 1H), 6.71 (dd, J = 9.7, 2.4 Hz, 1H), 4.81 (d, J = 6.8 Hz, 1H), 3.34 (s, 3H), 2.77 (d, J = 6.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.42, 168.34, 166.56, 166.30, 160.26, 160.15, 135.42, 129.36, 129.24, 128.99, 128.90, 128.87, 110.76, 110.58, 104.33, 104.14, 77.41, 77.16, 76.90, 65.13, 64.93, 53.52, 52.92, 37.69, 34.02 ppm; **IR** (neat): ν (cm^{-1}) = 1965, 1713, 1673, 1614, 1591, 1493, 1443, 1382, 1336, 1303, 1249, 1204, 1183, 1142, 1098, 1080, 1042, 979, 943, 884, 852, 811, 778, 764, 735, 706, 666, 650; **HRMS** (ESI): calcd for $C_{18}H_{13}FO_4$ [$M+H^+$]: 313.0871; found: 313.0865.

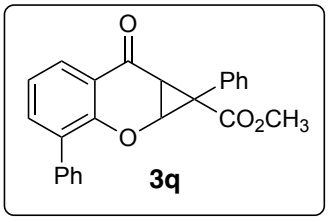
Methyl 3-bromo-5-chloro-7-oxo-1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate



3p

(**3p**) White solid (26.4 mg, 65%). **Rf** = 0.54; **m.p** = 140-141˚C **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, J = 2.6 Hz, 1H), 7.71 (d, J = 2.6 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.43 – 7.35 (m, 3H), 4.96 (d, J = 6.7 Hz, 1H), 3.40 (s, 3H), 2.78 (d, J = 6.7 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.24, 166.57, 154.01, 138.20, 135.15, 129.55, 129.27, 129.02, 127.86, 125.11, 122.03, 111.73, 77.41, 77.16, 76.90, 65.60, 53.18, 38.43, 33.70, 17.85, 12.43 ppm; **IR** (neat): ν (cm^{-1}) = 3063, 1733, 1683, 1592, 1446, 1277, 1224, 1198, 1164, 1130, 1108, 1050, 989, 936, 872, 818, 799, 772, 731, 693, 673; **HRMS** (ESI): calcd for $C_{18}H_{12}BrClO_4$ $[M+H]^+$: 406.9680; found: 406.9678.

Methyl 7-oxo-1,3-diphenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate

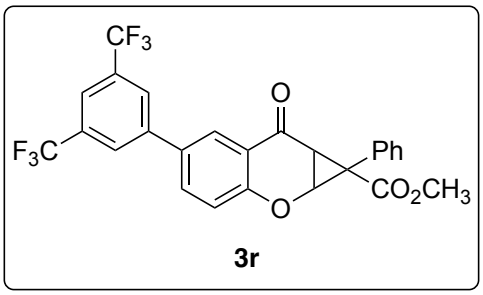


3q

(**3q**) Clear, colorless oil (17.7 mg, 48%). **Rf** = 0.39 (EtOAc/Hex, 1:4); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.9, 1.8 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.58 – 7.55 (m, 2H), 7.53 – 7.47 (m, 3H), 7.42 – 7.34 (m, 4H), 7.17 – 7.10 (m, 1H), 4.78 (d, J = 6.7 Hz, 1H), 3.31 (s, 3H), 2.84 (d, J = 6.7 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.20, 166.65, 154.93, 136.94, 136.91, 135.51, 131.06, 129.85, 129.56, 129.24, 128.82, 128.52, 128.46, 128.25, 127.83, 126.90, 125.86, 122.17, 120.54, 77.42, 77.16, 76.91, 64.19, 52.86, 52.79, 37.64, 34.83 ppm; **IR** (neat): ν (cm^{-1}) = 2951, 1732, 1676, 1589, 1498, 1471, 1454, 1430, 1384, 1303, 1221, 1195, 1169, 1114, 1085,

1047, 1026, 940, 910, 865, 806, 756, 731, 697, 662; **HRMS** (ESI): calcd for $C_{24}H_{18}O_4$ $[M+H]^+$: 371.1278; found: 371.1267.

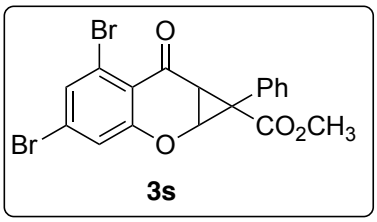
Methyl 5-(3,5-bis(trifluoromethyl)phenyl)-7-oxo-1-phenyl-tetrahydrocyclopropa[*b*]chromene-1-carboxylate



3r

(**3r**) White solid (40 mg, 79%). **Rf** = 0.36 (EtOAc/Hex, 1:4); **m.p.** = 158°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 1H), 8.01 (s, 2H), 7.86 (s, 1H), 7.76 (dd, J = 8.7, 2.5 Hz, 1H), 7.59 (dd, J = 8.2, 1.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.38 (d, J = 7.2 Hz, 1H), 7.18 (dd, J = 8.6, 0.4 Hz, 1H), 4.88 (d, J = 6.8 Hz, 1H), 3.38 (s, 3H), 2.85 (d, J = 6.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.48, 166.88, 159.34, 135.57, 134.23, 132.70, 132.44, 129.60, 129.39, 129.05, 129.03, 127.05, 127.02, 124.87, 122.45, 121.30, 120.73, 118.76, 77.51, 77.26, 77.01, 65.32, 65.09, 53.18, 53.15, 38.15, 34.35, 34.18 ppm; **IR** (neat): ν (cm^{-1}) = 1726, 1678, 1611, 1579, 1502, 1462, 1438, 1413, 1379, 1330, 1301, 1273, 1128, 1077, 1077, 1057, 1043, 980, 955, 891, 867, 837, 771, 738, 701, 681, 642, 624; **HRMS** (ESI): calcd for $C_{26}H_{16}F_6O_4$ $[M+H]^+$: 507.1026; found: 507.1021.

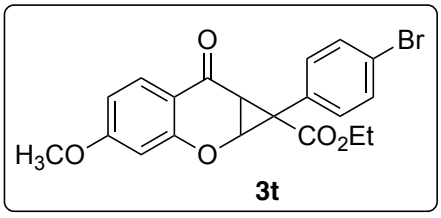
Methyl 4,6-dibromo-1-phenyl-tetrahydrocyclopropa[b]chromene-1-carboxylate



3s

(**3s**) white solid (34.3 mg, 76%). **Rf** = 0.44 (EtOAc/Hex, 1:4); **m.p.** = 137˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 3H), 7.41 – 7.33 (m, 2H), 7.21 (d, J = 1.8 Hz, 1H), 4.78 (d, J = 7.0 Hz, 1H), 3.40 (s, 3H), 2.88 (d, J = 6.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.07, 166.80, 160.04, 135.18, 132.07, 129.62, 129.58, 129.30, 128.74, 122.10, 120.78, 118.80, 77.67, 77.41, 77.16, 65.25, 53.38, 53.18, 38.80, 36.15 ppm; **IR** (neat): ν (cm^{-1}) = 2955, 1722, 1686, 1602, 1578, 1545, 1481, 1462, 1437, 1409, 1377, 1329, 1301, 1257, 1233, 1190, 1155, 1122, 1086, 1033, 976, 946, 883, 838, 821, 791, 757, 695, 684, 615; **HRMS** (ESI): calcd for $C_{18}H_{12}Br_2O_4$ $[M+H]^+$: 450.9175; found: 450.9172.

Ethyl 1-(4-bromophenyl)-6-methoxy-tetrahydrocyclopropa[b]chromene-1-carboxylate

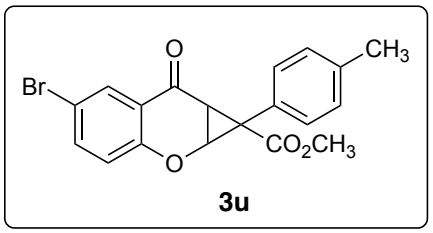


3t

(**3t**) White oil (27.5 mg, 66%). **Rf** = 0.23 (EtOAc/Hex, 1:4); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.08 (dd, J = 2.4, 1.0 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 6.73 (dd, J = 8.7, 2.3 Hz, 1H), 5.14 (d, J = 0.8 Hz, 1H), 4.21 (qd, J = 7.1, 3.2 Hz, 2H), 3.82 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.58, 156.92, 137.92, 137.26, 131.72, 130.32, 122.03, 121.35, 120.95, 119.80, 113.39, 109.99, 94.86, 77.41, 77.16, 76.90, 61.40, 55.80, 48.70, 14.30 ppm; **IR** (neat): ν (cm^{-1}) = 2979, 1727, 1714, 1661, 1610, 1578, 1487, 1438, 1392, 1333, 1295, 1260, 1235, 1212, 1187,

1151, 1131, 1091, 1071, 1051, 1024, 1008, 965, 914, 856, 833, 814, 781, 755, 718; **HRMS** (ESI): calcd for $C_{20}H_{18}BrO_5$ $[M+H]^+$: 417.0338.

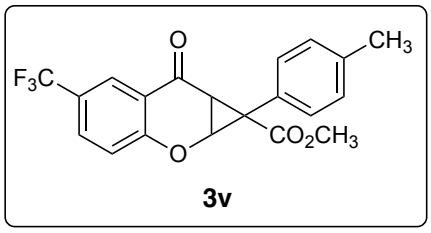
Methyl 5-bromo-7-oxo-1-(*p*-tolyl)-tetrahydrocyclopropa[*b*]chromene-1-carboxylate



3u

(**3u**) White solid (25.5 mg, 66%). **Rf** = 0.52 (EtOAc/Hex, 1:4); **m.p. =** 160°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, J = 2.5 Hz, 1H), 7.55 (dd, J = 8.9, 2.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.20 (dd, J = 7.8, 0.7 Hz, 2H), 6.92 (d, J = 8.8 Hz, 1H), 4.78 (d, J = 6.7 Hz, 1H), 3.35 (s, 3H), 2.75 (d, J = 6.8 Hz, 1H), 2.35 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.70, 166.77, 157.61, 138.95, 138.38, 132.43, 129.93, 129.30, 128.79, 121.49, 119.42, 114.84, 77.41, 77.16, 76.91, 65.06, 53.01, 37.57, 34.16, 21.30 ppm; **IR** (neat): ν (cm^{-1}) = 2956, 1762, 1724, 1672, 1599, 1470, 1438, 1419, 1287, 1215, 1195, 1136, 1096, 1043, 969, 938, 868, 818, 782, 765, 736, 700, 672, 647; **HRMS** (ESI): calcd for $C_{19}H_{15}BrO_4$ $[M+H]^+$: 387.0226; found: 387.0221.

Methyl 7-oxo-1-(p-tolyl)-5-(trifluoromethyl)-tetrahydrocyclopropa[b]chromene-1-carboxylate

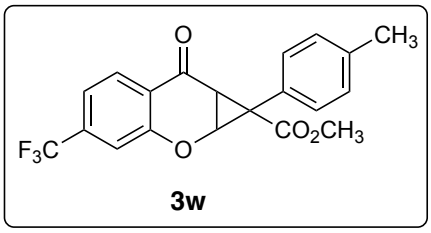


3v

(**3v**) White solid (18.7 mg, 52%). **Rf** = 0.49 (EtOAc/Hex, 1:4); **m.p** = 125˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (dd, J = 2.2, 0.9 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.12 (d, J = 8.7 Hz, 1H), 4.84 (d, J = 6.7 Hz, 1H), 3.34 (s, 3H), 2.79 (d, J = 6.7

Hz, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.68, 166.79, 160.81, 139.03, 132.28, 132.03, 132.00, 131.97, 131.95, 129.95, 129.33, 124.20, 124.17, 124.14, 120.05, 118.32, 77.41, 77.16, 76.90, 65.39, 53.02, 37.79, 34.13, 21.29 ppm; **IR** (neat): ν (cm^{-1}) = 2953, 1715, 1676, 1620, 1591, 1497, 1442, 1383, 1306, 1286, 1249, 1203, 1180, 1142, 1109, 1069, 1043, 970, 944, 884, 853, 833, 812, 779, 765, 736, 707, 686; **HRMS** (ESI): calcd for $C_{20}H_{15}F_3O_4$ [M+H$^+$]: 377.0995; found: 377.0986.

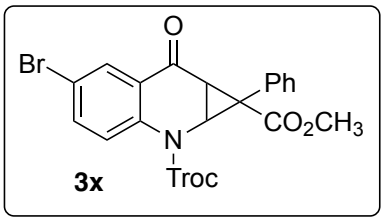
Methyl 7-oxo-1-(p-tolyl)-6-(trifluoromethyl)-tetrahydrocyclopropa[b]chromene-1-carboxylate



3w

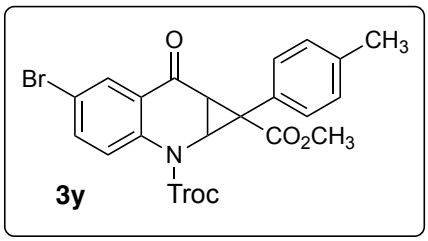
(**3w**) White solid (18.4mg, 51%). **Rf** = 0.51 (EtOAc/Hex, 1:4); **m.p** = 161˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.5, 0.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.29 (d, J = 7.5 Hz, 2H), 7.24 – 7.18 (m, 2H), 4.84 (d, J = 6.7 Hz, 1H), 3.35 (s, 3H), 2.78 (d, J = 6.8 Hz, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.00, 166.87, 158.61, 139.01, 132.36, 129.95, 129.37, 127.30, 124.31, 122.61, 118.61, 118.58, 118.55, 118.52, 115.05, 115.01, 114.98, 114.95, 77.41, 77.16, 76.90, 65.46, 53.02, 37.94, 34.30, 21.30 ppm; **IR** (neat): ν (cm^{-1}) = 2954, 1725, 1684, 1631, 1581, 1499, 1433, 1333, 1308, 1252, 1222, 1164, 1146, 1130, 1068, 1050, 1031, 984, 937, 890, 875, 842, 824, 804, 785, 765, 737, 714, 699, 655; **HRMS** (ESI): calcd for $C_{20}H_{15}F_3O_4$ [M+H$^+$]: 377.0995; found: 377.1003

1-methyl 2-(2,2,2-trichloroethyl) 5-bromo-7-oxo-1-phenyl-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



(**3x**) White solid (9.9 mg, 18%). **Rf** = 0.51 (EtOAc/Hex, 1:4); **m.p** = 165˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, J = 2.5 Hz, 1H), 7.91 (s, 1H), 7.73 – 7.68 (m, 2H), 7.64 (dd, J = 9.0, 2.5 Hz, 1H), 7.42 – 7.34 (m, 3H), 5.02 (s, 2H), 4.41 (d, J = 8.1 Hz, 1H), 3.45 (s, 3H), 2.84 (d, J = 8.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.17, 140.30, 136.44, 136.18, 130.19, 129.46, 128.90, 128.75, 124.91, 118.35, 94.73, 77.41, 77.16, 76.91, 76.09, 53.23, 39.22, 35.30, 17.85 ppm; **IR** (neat): ν (cm^{-1}) = 2964, 1744, 1717, 1691, 1589, 1472, 1440, 1416, 1385, 1310, 1282, 1242, 1224, 1177, 1156, 1087, 1054, 1026, 940, 880, 830, 811, 795, 783, 754, 713, 700, 662, 644; **HRMS** (ESI): calcd for $C_{21}H_{15}BrCl_3NO_5$ $[M+H]^+$: 549.9222; found: 549.9210

1-methyl 2-(2,2,2-trichloroethyl) 5-bromo-7-oxo-1-(p-tolyl)-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



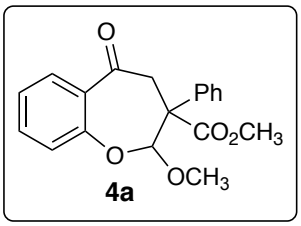
(**3y**) White solid (12.3 mg, 22%). **Rf** = 0.54 (EtOAc/Hex, 1:4); **m.p** = 149˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, J = 2.5 Hz, 1H), 7.95 – 7.85 (m, 1H), 7.64 (dd, J = 9.0, 2.5 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.22 – 7.17 (m, 2H), 5.01 (s, 1H), 4.39 (d, J = 8.0 Hz, 1H), 3.44 (s, 3H), 2.82 (d, J = 8.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.02, 140.04, 138.46, 136.16, 133.00, 130.12, 129.79, 129.53, 129.50, 129.34, 129.20, 129.13, 127.72, 124.64, 118.07,

94.50, 77.16, 76.91, 76.65, 75.83, 52.96, 52.58, 52.09, 35.16, 21.82, 21.22, 21.11 ppm; **IR** (neat): ν (cm^{-1}) = 2962, 1745, 1719, 1692, 1588, 1516, 1474, 1439, 1416, 1390, 1320, 1308, 1284, 1242, 1224, 1203, 1157, 1113, 1088, 1056, 1029, 938, 883, 828, 809, 794, 755, 714, 658, 608; **HRMS** (ESI): calcd for $C_{22}H_{17}BrCl_3NO$ [$M+H^+$]: 559.9428; found: 559.9420.

5. General Procedure for Heterocycle Ring Expansion

To a flame-dried 4mL reaction vial with a Tefloan coated septum was added 0.1 mmol of the cyclopropyl compound, 0.5mL dry toluene (0.2M), and 30µL TIPSOTf. The reaction was allowed to stir at 60˚C for 1 hour. The reaction was then cooled to room temperature before the addition of 0.2mL MeOH. The reaction was allowed to react at room temperature for 24 hours before being quenched with 0.2mL 6M HCl. The reaction was stirred for a further 30 minutes before being quenched with 1mL H_2O and the organic layer was extracted with DCM (3 x 1mL). The crude product was concentrated and purified via column chromatography in EtOAc /Hexanes.

Methyl 2-methoxy-5-oxo-3-phenyl-2,3,4,5-tetrahydrobenzo[b]oxepine-3-carboxylate

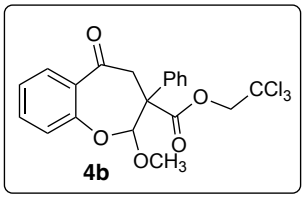


4a

(**4a**) Clear, sticky oil (29.0 mg, 89%). **Rf** = 0.35; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.8, 1.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.44 (ddd, J = 8.2, 7.2, 1.8 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.15 – 7.07 (m, 2H), 5.66 (s, 1H), 3.77 (d, J = 13.6 Hz, 1H), 3.73 (s, 3H), 3.43 (s, 3H), 3.37 (d, J = 13.6 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.11, 171.48, 154.97, 138.60, 134.09, 129.76, 129.15, 128.77, 127.82, 126.80, 123.17, 121.23, 107.65, 59.46, 57.38, 52.81, 52.65, 47.84 ppm;

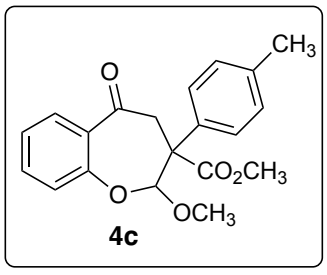
IR (neat): ν (cm^{-1}) = 2951, 1734, 1684, 1602, 1476, 1450, 1293, 1191, 1147, 1116, 1100, 1070, 1028, 967, 813, 759, 732, 697; **HRMS** (ESI): calcd for $C_{19}H_{18}O_5$ $[M+H]^+$: 327.1227; found: 327.1220.

2,2,2-trichloroethyl 2-methoxy-5-oxo-3-phenyl-2,3,4,5-tetrahydrobenzo[b]oxepine-3-carboxylate



(**4b**) Clear, colorless oil (27.6mg, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (ddd, J = 7.6, 1.8, 0.6 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.45 (ddd, J = 8.2, 7.2, 1.8 Hz, 1H), 7.36 (dd, J = 8.4, 6.9 Hz, 2H), 7.32 – 7.21 (m, 3H), 7.12 (td, J = 7.8, 1.0 Hz, 2H), 5.81 (s, 1H), 4.81 (d, J = 11.9 Hz, 1H), 4.68 (d, J = 11.9 Hz, 1H), 3.83 (d, J = 13.6 Hz, 1H), 3.47 (d, J = 13.6 Hz, 1H), 3.44 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.95, 169.49, 154.59, 137.70, 134.29, 130.01, 129.31, 128.97, 128.24, 127.07, 123.44, 121.47, 106.92, 74.89, 59.54, 57.54, 47.41 ppm; **HRMS** (ESI): calcd for $C_{20}H_{17}Cl_3O_5$ $[M+H]^+$: 443.0214; found: 443.0211.

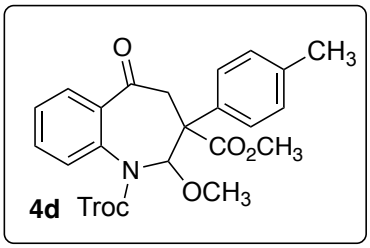
Methyl 2-methoxy-5-oxo-3-(p-tolyl)-tetrahydrobenzo[b]oxepine-3-carboxylate



(**4c**) White solid (30.7 mg, 90 %). **Rf** = 0.43 (EtOAc/Hex, 1:4); **m.p.** = 116°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (ddd, J = 7.9, 1.8, 0.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.07 (m, 2H), 5.64 (s, 1H), 3.76 (d, J = 13.6 Hz, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 3.37 (d, J = 13.6 Hz, 1H), 2.31 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.42,

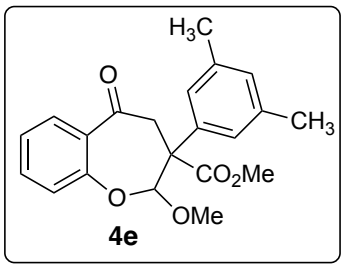
171.78, 155.14, 137.72, 135.67, 134.19, 129.92, 129.60, 129.33, 126.83, 123.27, 121.41, 107.87, 77.42, 77.16, 76.91, 59.14, 57.50, 52.93, 47.86, 21.12 ppm; **IR** (neat): ν (cm^{-1}) = 2955, 1981, 1748, 1686, 1603, 1516, 1475, 1451, 1432, 1385, 1313, 1284, 1264, 1240, 1211, 1188, 1152, 1116, 1102, 1069, 1033, 1023, 976, 927, 846, 829, 784, 752, 715, 652; **HRMS** (ESI): calcd for $C_{20}H_{21}O_5$ $[M+H]^+$: 341.1384; found: 341.1378.

3-methyl 1-(2,2,2-trichloroethyl) 2-methoxy-5-oxo-3-(*p*-tolyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-1,3-dicarboxylate



(**4d**) Clear, colorless oil (41.1 mg, 80%). **Rf** = 0.35 (EtOAc/Hex, 1:4) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.8, 1.6 Hz, 1H), 7.50 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.41 – 7.29 (m, 2H), 7.15 – 7.10 (m, 2H), 6.35 (s, 1H), 4.65 (s, 2H), 3.57 (s, 3H), 3.53 (s, 2H), 3.41 (s, 3H), 2.30 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.31, 171.52, 138.20, 136.57, 134.21, 132.56, 129.42, 129.28, 127.91, 127.72, 95.16, 91.74, 75.02, 57.70, 52.76, 46.09, 21.16 ppm; **IR** (neat): ν (cm^{-1}) = 2955, 1766, 1736, 1725, 1696, 1682, 1599, 1577, 1487, 1467, 1435, 1388, 1343, 1288, 1266, 1242, 1210, 1134, 1095, 1072, 1037, 1022, 1001, 984, 927, 902, 820, 789, 754, 744, 729, 699, 665; **HRMS** (ESI): calcd for $C_{23}H_{22}Cl_3NO_6$ $[M+Na]^+$: 536.0405; found: 536.0387.

Methyl 3-(3,5-dimethylphenyl)-2-methoxy-5-oxo-tetrahydrobenzo[b]oxepine-3-carboxylate

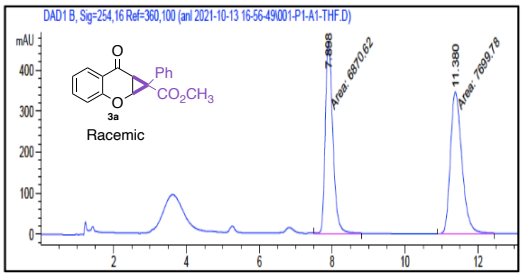


4e

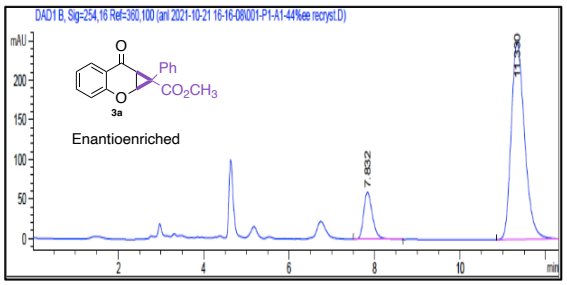
(**4e**) Clear, sticky oil (20.2 mg, 57%). **Rf** = 0.68 (EtOAc/Hex, 1:4); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 6.90 (dd, J = 10.1, 1.6 Hz, 3H), 4.92 (s, 1H), 3.74 (d, J = 1.5 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 2.30 – 2.28 (m, 1H), 2.28 (d, J = 0.8 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.53, 138.83, 138.35, 137.09, 136.05, 129.50, 129.23, 129.19, 128.70, 127.48, 126.93, 126.50, 126.44, 56.81, 52.49, 21.58, 21.29 ppm; **IR** (neat): ν (cm^{-1}) = 2920, 1980, 1740, 1684, 1602, 1514, 1472, 1433, 1375, 1311, 1283, 1260, 1193, 1149, 1039, 975, 928, 820, 739, 692, 651; **HRMS** (ESI): calcd for $C_{21}H_{22}O_5$ [$M+H^+$]: 355.1540.

6. Enantioselective Cyclopropanation of Benzopyrylium Triflates

To a flame dried 4 mL reaction vial with a Teflon coated septum screw-top was added 0.12 mmol of sulfoxonium ylide (1.2 equiv.) and 0.02 mmol organocatalyst (0.2 equiv.) The vial was then placed under vacuum and backfilled with nitrogen. 0.85 mL of dry toluene was added to the vial and the reaction was stirred at room temperature. After twenty minutes, a solution of 0.1 mmol of chromone (1 equiv.) in 0.85mL of MTBE was added to the reaction via syringe. Freshly distilled triisopropyl trifluoromethanesulfonate (30µL, 0.11 mmol, 1.1 equiv.) was added to the reaction via microliter syringe. The reaction was then reacted at room temperature over night. The reaction was then quenched with 200 µL of 6M HCl and stirred at room temperature for an additional 30 minutes. Then, the crude reaction was diluted with water and extracted with CH_2Cl_2 (3 x 2 mL), dried over sodium sulfate, and concentrated under reduced pressure. The product was purified by flash column chromatography in EtOAc/Hexanes. The *ee* value was determined by chiral HPLC analysis of the purified product.

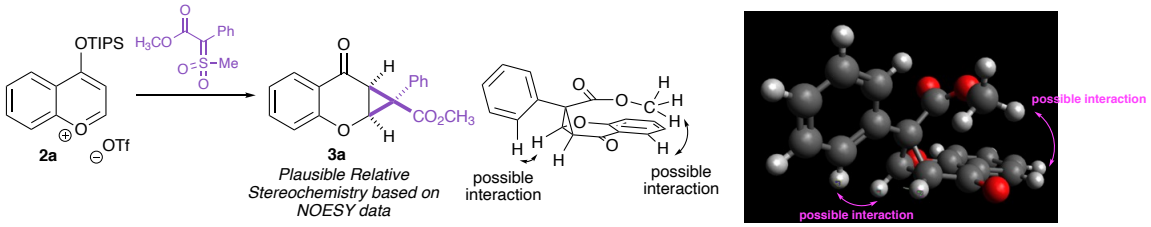


Ret. Time (min)	Area %
7.89	47.2
11.38	52.8

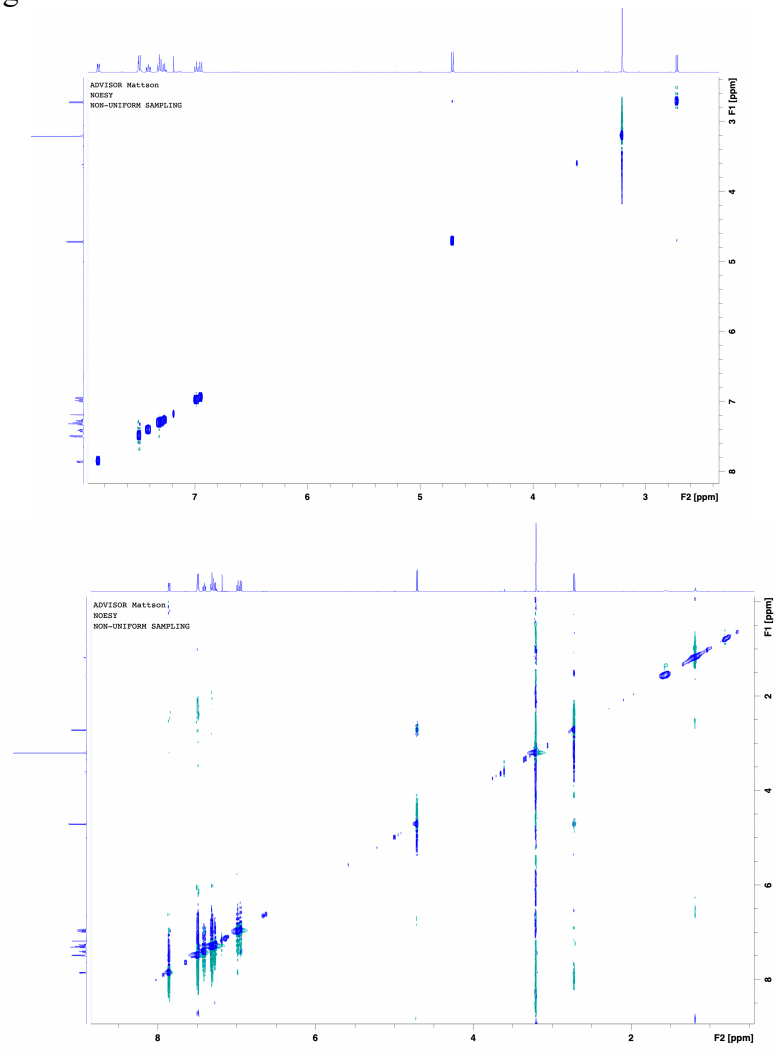


Ret. Time (min)	Area %
7.83	13.7
11.33	86.3

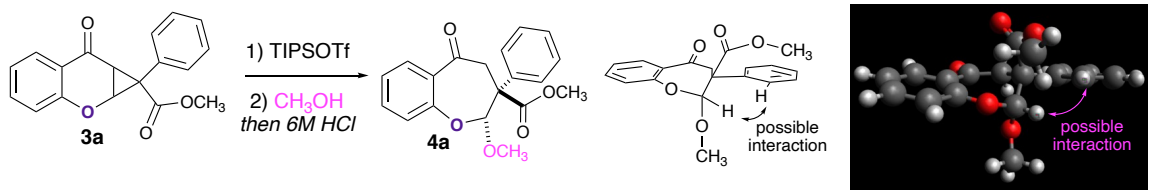
7. NOESY Data for 3a.



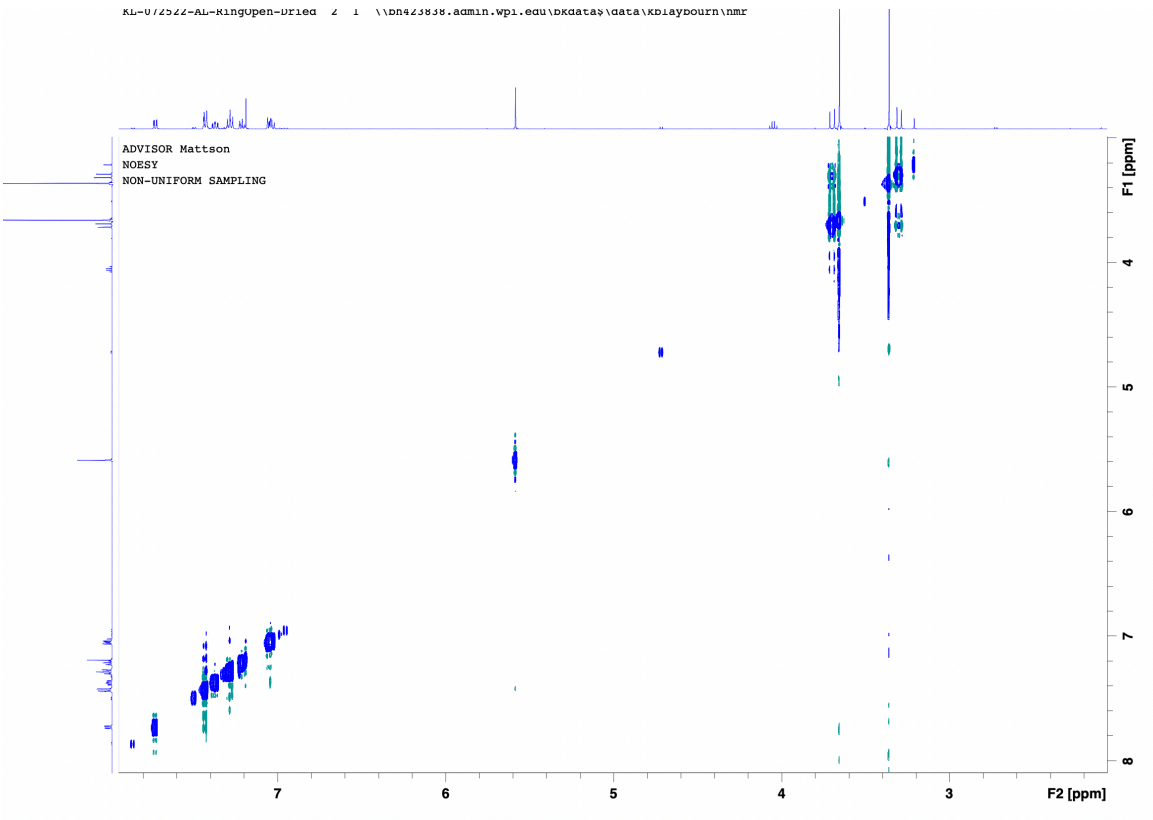
A NOESY experiment on **3a** was used to help collect information to reveal its relative stereochemistry. We analyzed the 3 dimensional structure (right) and we were able to draw the following conclusions. There is a clear correlation between the two hydrogens on the cyclopropane (1 and 2). Upon zooming in there also appears to be a weak correlation between hydrogen 3 on the phenyl ring and one of the cyclopropyl hydrogen. A weak interaction between the ester methyl group and the doublet signal around 8ppm may also be observed. These interactions lead us to suspect the phenyl ring is on the same face as the cyclopropyl hydrogens while the methyl ester is above the chromanone. Further investigations are needed to confirm this.



8. NOESY Data for 4a.



A NOESY experiment was conducted on **4a** to help collect information about its relative configuration. To help us interpret the data, the 3D structures of **4a** were studied (right). The molecule adopts a confirmation where the 7-membered ring is a bit twisted and it appears as though there may be a correlation between the hydrogen alpha to the ring oxygen (singlet at 5.6 ppm) and the ortho hydrogen on the phenyl ring substituent. At this time, our data suggests that the phenyl ring and the methoxy substituents may both be down. Further investigations will help to confirm this hypothesis and will be reported in a forthcoming full article.



9. References

1. Dias, R. M. P.; Burtoloso, A. C. B. *Org. Lett*. **2016**, *18*, 3034–3037.
2. Janot, C.; Palamini, P.; Dobson, B. C.; Muir, J.; Aissa, C. *Org. Lett*. **2019**, *211*, 296-299.
3. Momo, P. B.; Leveille, A. N.; Farrar, E. H. E.; Grayson, M. N.; Mattson, A. E.; Burtoloso, A. C. B. *Angew. Chem. Int. Ed*. **2020**, *59*, 15554 –15559.
4. Leveille, A. N.; Echemendia, R.; Mattson, A. E.; Burtoloso, A. C. B. *Org. Lett.* **2021**, *23*, 9446-9450.
5. Furniel, L. G.; Echemendía, R.; Burtoloso, A. C. B. *Chem. Sci.* **2021**, *12,* 7453-7459.
6. Hardman-Baldwin, A. M.; Visco, M. D.; Wieting, J. M.; Stern, C.; Kondo, S. I.; Mattson, A. E. *Org. Lett.* **2016,** *18*, 3766-3769.