General

All chemicals were used as delivered from Sigma-Aldrich.

Flash chromatography was done with an Isco Inc. CombiFlash Companion with silica gel from SdS (60, 40-63 μm, 550 m^2/g, pH 7). Eluents consisted of distilled technical grade ethyl acetate and hexane.

NMR spectra were recorded on a Bruker Avance DPX300 instrument at 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR at 25 ºC. Chemical shift (δ) is given in ppm relative to the solvent $CDCl_3$ (7.24 ppm for ^{1}H-NMR, 77.0 ppm for ^{13}C-NMR). ^{13}C-NMR spectra are decoupled. ^{1}H-, ^{13}C-NMR and DEPT135 spectra were recorded for all compounds. Peak assignment in ^{1}H- and ^{13}C-NMR is based on information obtained from DEPT135, HMQC, and/or COSY experiments, depending on what was necessary in each case.

MS spectra were recorded on a VG Prospec sector instrument from Fissions Instruments at 70eV.

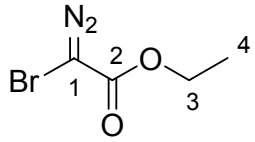
General procedure for experiments shown in Table 3:

NBS (1.3 mmol) was added to a solution of EDA (1.0 mmol) and DBU (1.4 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C, and the reaction mixture was stirred for 5 min. The crude reaction mixture was washed with cold $Na_2S_2O_3$ solution (aq, 20 %, 3 x 5 mL), dried with $MgSO_4$ at 0 °C and passed quickly through a silica column using cold CH_2Cl_2 as eluent. Toluene (10.0 mL) was added, and the CH_2Cl_2 was removed *in vacuo* at 0 °C. Alkene (2.0 mmol) was then added at 0 °C, and the temperature was slowly increased to r. t. A solution of $Rh_2(esp)_2$ (0.01 mmol) in toluene (2.0 mL) was added, and the reaction mixture was stirred for 15 min at r. t. The solvent was evaporated *in vacuo*, and the crude product was purified by flash chromatography.

Experimental data

For all cyclopropanes, NMR data are reported for the major diastereomer, and MS data are reported for the mixture of the two diastereomers.

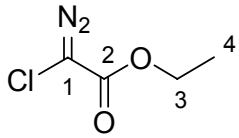
Ethyl diazobromoacetate (1)



^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.22-1.29 (t, 3H, *J*=7.1 Hz, H4), 4.18-4.29 (q, 2H, *J*=7.1 Hz, H3).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.3 (C4), 62.5 (C3), 162.9 (C2).

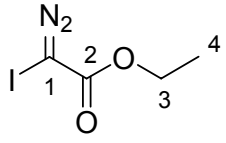
Ethyl diazochloroacetate (2)



^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.17-1.25 (t, 3H, *J*=7.1 Hz, H4), 4.15-4.26 (q, 2H, *J*=7.1 Hz, H3).

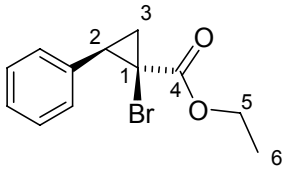
^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.2 (C4), 62.2 (C3), 162.8 (C2).

Ethyl diazoiodoacetate (3)



^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.24-1.29 (t, 3H, *J*=7.1 Hz, H4), 4.20-4.27 (q, 2H, *J*=7.1 Hz, H3).

Ethyl 1-bromo-2-phenylcyclopropanecarboxylate



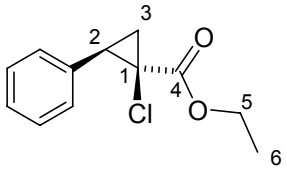
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.31-1.35 (t, 3H, *J*=7.1 Hz, H6), 1.77-1.82 (dd, 1H, *J*=8.7 Hz, *J*=6.0 Hz, H3β), 2.18-2.23 (dd, 1H, *J*=10.0 Hz, *J*=6.0 Hz, H3α), 2.93-2.99 (dd, 1H, *J*=10.0 Hz, *J*=8.7 Hz, H2), 4.22-4.30 (q, 2H, *J*=7.1 Hz, H5), 7.22-7.25 (m, 2H, Ar-H), 7.30-7.38 (m, 3H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.0 (C6), 23.7 (C3), 33.1 (C2), 35.2 (C1), 62.6 (C5), 127.4 (Ar-CH), 127.9 (Ar-CH), 129.3 (Ar-CH), 135.5 (Ar-C), 169.7 (C4).

MS (EI) m/z (relative intensity): 268/270 (3/3%, M^+), 188 (12), 143 (15), 131 (23), 115 (100), 84 (34).

HR-MS (ESI): Found 268.0083, calcd. for $C_{16}H_{15}{}^{79}BrO_2$: 268.0093 ppm (-3.9 ppm).

Ethyl 1-chloro-2-phenylcyclopropanecarboxylate



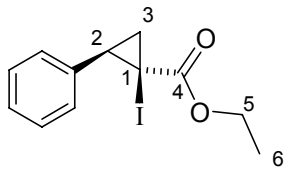
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.30-1.35 (t, 3H, *J*=7.1 Hz, H6), 1.71-1.76 (dd, 1H, *J*=8.7 Hz, *J*=6.0 Hz, H3β), 2.10-2.16 (dd, 1H, *J*=10.1 Hz, *J*=6.0 Hz, H3α), 3.03-3.09 (dd, 1H, *J*=10.1 Hz, *J*=8.7 Hz, H2), 4.23-4.30 (q, 2H, *J*=7.1 Hz, H5), 7.22-7.33 (m, 5H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.1 (C6), 23.4 (C3), 33.6 (C2), 44.8 (C1), 62.6 (C5), 127.5 (Ar-CH), 128.1 (Ar-CH), 129.4 (Ar-CH), 134.4 (Ar-C), 170.2 (C4).

MS (EI) m/z (relative intensity): 226/224 (12/37%), 198/196 (6/17), 159 (25), 131 (24), 115 (100).

HR-MS (ESI): Found 224.0602, calcd. for $C_{12}H_{13}{}^{35}ClO_2$: 224.0604 (1.1 ppm).

Ethyl 1-iodo-2-phenylcyclopropanecarboxylate



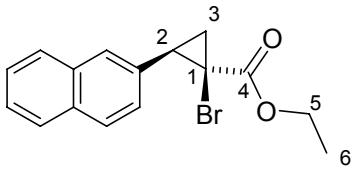
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.28-1.33 (t, 3H, *J*=7.1 Hz, H6), 1.70-1.74 (dd, 1H, *J*=8.7 Hz, *J*=6.0 Hz, H3β), 2.25-2.30 (dd, 1H, *J*=10.1 Hz, *J*=6.0 Hz, H3α), 2.53-2.58 (dd, 1H, *J*=10.1 Hz, *J*=8.7 Hz, H2), 4.18-4.25 (q, 2H, *J*=7.1 Hz, H5), 7.16-7.19 (m, 2H, Ar-H), 7.29-7.37 (m, 3H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 9.5 (C6), 14.1 (C3), 25.2 (C2), 33.1 (C1), 63.0 (C5), 127.6 (Ar-CH), 128.1 (Ar-CH), 129.3 (Ar-CH), 138.0 (Ar-C), 170.0 (C4).

MS (EI) m/z (relative intensity): 316 (75%), 270 (6), 160 (26), 133 (17), 115 (100).

HR-MS (ESI): Found 315.9926, calcd. for $C_{12}H_{13}IO_2$: 315.9960 (-0.7 ppm).

Ethyl 1-bromo-2-(naphthalen-3-yl)cyclopropanecarboxylate



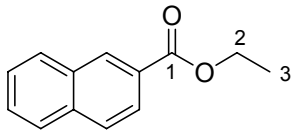
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.35-1.40 (t, 3H, *J*=7.1 Hz, H6), 1.94-1.99 (dd, 1H, *J*=8.7 Hz, *J*=6.1 Hz, H3β), 2.29-2.34 (dd, 1H, *J*=10.0 Hz, *J*=6.1 Hz, H3α), 3.13-3.19 (dd, 1H, *J*=10.0 Hz, *J*=8.7 Hz, H2), 4.28-4.35 (q, 2H, *J*=7.1 Hz, H5), 7.39-7.43 (dd, 1H, *J*=1.7 Hz, *J*=8.5 Hz, Ar-H), 7.49-7.52 (m, 2H, Ar-H), 7.72 (br s, 1H, Ar-H), 7.83-7.87 (m, 3H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.0 (C6), 23.8 (C3), 33.3 (C2), 35.3 (C1), 62.6 (C5), 125.8 (Ar-CH), 126.0 (Ar-CH), 127.3 (Ar-CH), 127.5 (Ar-CH), 127.5 (Ar-CH), 127.6 (Ar-CH), 128.0 (Ar-CH), 132.6 (Ar-C), 132.9 (Ar-C), 133.1 (Ar-C), 169.6 (C4).

MS (EI) m/z (relative intensity): 320/318 (10/10%, M^+), 238 (16), 209 (15), 193 (22), 165 (100).

HR-MS (ESI): Found 318.0252, calcd. for $C_{16}H_{15}{}^{79}BrO_2$: 318.0255 ppm (1.1 ppm).

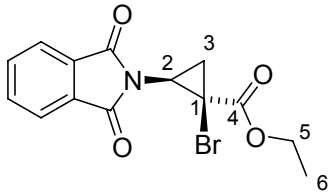
Ethyl 2-naphthoate[1]



^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.41-1.46 (t, 3H, *J*=7.1 Hz, H3), 4.40-4.47 (q, 2H, *J*=7.1 Hz, H2), 7.50-7.60 (m, 2H, Ar-H), 7.85-7.87 (d, 2H, J=8.7 Hz, Ar-H), 7.93-7.96 (dd, 1H, J=7.8 Hz, J=1.2 Hz, Ar-H), 8.04-8.08 (dd, 1H, J=8.7 Hz, J=1.7 Hz, Ar-H), 8.60 (br s, 1H, Ar-H).

MS (EI) m/z (relative intensity): 200 (74%, M^+), 172 (22), 155 (100), 127 (65).

Ethyl 1-bromo-2-(1,3-dioxoisoindolin-2-yl)cyclopropanecarboxylate



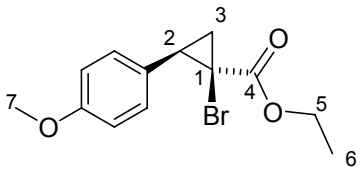
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.24-1.29 (t, 3H, *J*=7.1 Hz, H6), 2.29-2.35 (dd, 1H, *J*=9.6 Hz, *J*=7.6 Hz, H3β), 2.56-2.60 (dd, 1H, *J*=7.6 Hz, *J*=6.9 Hz, H3α), 3.40-3.46 (dd, 1H, *J*=9.6 Hz, *J*=6.9 Hz, H2), 4.17-4.24 (q, 2H, *J*=7.1 Hz, H5), 7.68-7.72 (m, 2H, Ar-H), 7.77-7.81 (m, 2H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 13.9 (C6), 23.3 (C3), 31.9 (C2), 35.4 (C1), 62.9 (C5), 123.4 (Ar-CH), 131.2 (Ar-C), 134.3 (Ar-CH), 168.2 (C4).

MS (EI) m/z (relative intensity): (339/337, 13/13%, M^+), 293/291 (94/94), 258 (57), 184 (77), 104 (91), 76 (100).

HR-MS (ESI): Found 336.9952, calcd. for $C_{14}H_{12}{}^{79}BrNO_2$: 336.9950 ppm (-0.6 ppm).

Ethyl 1-bromo-2-(4-methoxyphenyl)cyclopropanecarboxylate



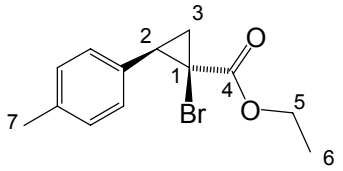
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.28-1.33 (t, 3H, *J*=7.1 Hz, H6), 1.69-1.74 (dd, 1H, *J*=8.7 Hz, *J*=6.0 Hz, H3β), 2.14-2.19 (dd, 1H, *J*=10.1 Hz, *J*=6.0 Hz, H3α), 2.84-2.90 (dd, 1H, *J*=10.1 Hz, *J*=8.7 Hz, H2), 3.77 (s, 3H, H7), 4.19-4.27 (q, 2H, *J*=7.1 Hz, H5), 6.84-6.88 (m, 2H, Ar-H), 7.11-7.16 (m, 2H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.0 (C6), 23.9 (C3), 32.6 (C2), 35.7 (C1), 66.0 (C7), 62.5 (C5), 113.4 (Ar-CH), 127.6 (Ar-C), 130.3 (Ar-CH), 158.9 (Ar-C), 169.7 (C4).

MS (EI) m/z (relative intensity): 300/298 (21/21%, M^+), 271/269 (12/12), 219 (100), 189 (30), 145 (93).

HR-MS (ESI): Found 298.0196, calcd. for $C_{13}H_{15}{}^{79}BrO_3$: 298.0205 ppm (2.9 ppm).

Ethyl 1-bromo-2-*p*-tolylcyclopropanecarboxylate



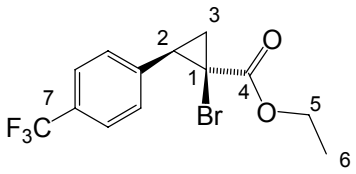
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.31-1.36 (t, 3H, *J*=7.1 Hz, H6), 1.75-1.79 (dd, 1H, *J*=8.7 Hz, *J*=6.0 Hz, H3β), 2.17-2.22 (dd, 1H, *J*=10.0 Hz, *J*=6.0 Hz, H3α), 2.36 (s, 3H, H7), 2.89-2.95 (dd, 1H, *J*=10.0 Hz, *J*=8.7 Hz, H2), 4.23-4.30 (q, 2H, *J*=7.1 Hz, H5), 7.11-7.18 (m, 4H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.0 (C6), 21.0 (C7), 23.7 (C3), 32.9 (C2), 35.4 (C1), 62.6 (C5), 128.7 (Ar-CH), 129.1 (Ar-CH), 132.5 (Ar-C), 137.1 (Ar-C), 169.7 (C4).

MS (EI) m/z (relative intensity): 284/282 (45/46%, M^+), 203 (20), 173 (42), 129 (100), 115 (45).

HR-MS (ESI): Found 282.0262, calcd. for $C_{13}H_{15}{}^{79}BrO_2$: 282.0255 ppm (-0.7 ppm).

Ethyl 1-bromo-2-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylat



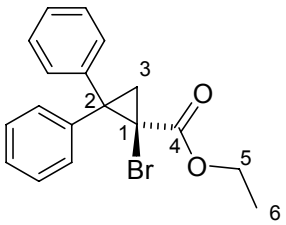
^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.30-1.35 (t, 3H, *J*=7.1 Hz, H6), 1.77-1.81 (dd, 1H, *J*=8.4 Hz, *J*=6.2 Hz, H3β), 2.21-2.26 (dd, 1H, *J*=10.1 Hz, *J*=6.2 Hz, H3α), 2.94-3.00 (m, 1H, H2), 4.23-4.29 (q, 2H, *J*=7.1 Hz, H5), 7.32-7.34 (m, 2H, Ar-H), 7.57-7.60 (m, 2H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.1 (C6), 24.0 (C3), 32.6 (C2), 34.7 (C1), 63.0 (C5), 125.0 (q, *J*=3.8 Hz, Ar-CH), 129.2 (Ar-C), 129.8 (Ar-CH), 139.7 (Ar-C), 169.4 (C4).

MS (EI) m/z (relative intensity): 338/336 (39/40%, M^+), 310/308 (19/19), 201 (37), 183 (100), 115 (71).

HR-MS (ESI): Found 335.9976, calcd. for $C_{13}H_{12}{}^{79}BrF_3O_2$: 335.9973 ppm (-1.0 ppm).

Ethyl 1-bromo-2,2-diphenylcyclopropanecarboxylate



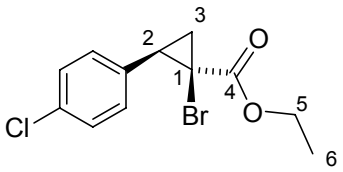
^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.94-0.98 (t, 3H, *J*=7.1 Hz, H6), 2.05-2.08 (dd, 1H, *J*=6.5 Hz, *J*=0.8 Hz, H3β), 2.80-2.82 (dd, 1H, *J*=6.5 Hz, *J*=0.8 Hz, H3α), 3.81-4.03 (m, 2H, H5), 7.14-7.53 (m, 10H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 13.6 (C6), 27.6 (C3), 39.0 (C2), 45.0 (C1), 62.2 (C5), 127.2 (Ar-CH), 127.3 (Ar-CH), 128.3 (Ar-CH), 128.5 (Ar-CH), 129.4 (Ar-CH), 140.5 (Ar-C), 141.5 (Ar-C), 167.7 (C4).

MS (EI) m/z (relative intensity): 346/344 (0.3/0.3%, M^+), 264 (32), 219 (44), 191 (100), 165 (27).

HR-MS (ESI): Found 344.0423, calcd. for $C_{18}H_{17}{}^{79}BrO_2$: 344.0412 ppm (-3.2 ppm).

Ethyl 1-bromo-2-(4-chlorophenyl)cyclopropanecarboxylate



^{1}H-NMR (300 MHz; $CDCl_3$): δ 1.29-1.35 (t, 3H, *J*=7.1 Hz, H6), 1.70-1.75 (dd, 1H, *J*=8.6 Hz, *J*=6.1 Hz, H3β), 2.16-2.22 (dd, 1H, *J*=10.0 Hz, *J*=6.1 Hz, H3α), 2.86-2.92 (dd, 1H, *J*=10.0S Hz, *J*=8.6 Hz, H2), 4.21-4.28 (q, 2H, *J*=7.1 Hz, H5), 7.13-7.16 (m, 2H, Ar-H), 7.28-7.31 (m, 2H, Ar-H).

^{13}C-NMR (75 MHz; $CDCl_3$): δ 14.1 (C6), 24.0 (C3), 32.5 (C2), 35.0 (C1), 62.9 (C5), 128.3 (Ar-CH), 130.2 (Ar-CH), 130.7 (Ar-CH), 133.4 (Ar-C), 134.2 (Ar-C), 169.6 (C4).

MS (EI) m/z (relative intensity): 306/304/302 (10/39/29%, M^+), 193 (28), 167 (26), 149 (73), 115 (100).

HR-MS (ESI): Found 301.9715, calcd. for $C_{12}H_{12}{}^{79}Br^{35}ClO_2$: 301.9709 ppm (-1.8 ppm).

[1] N. Asao, T. Nogami, S. Lee, and Y. Yamamoto, *Journal of the American Chemical Society*, 2003, **125**, 10921.