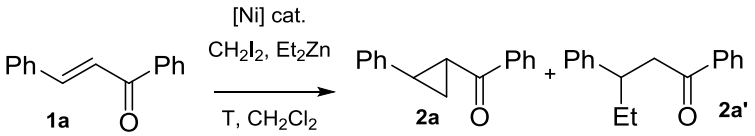
Supporting Information

General information. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF was dried over alumina under N_2 using a Grubbs-type solvent purification system. All α,β-unsaturated carbonyls were prepared according to the literature procedures. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by Agilent GC Series 6890N and GCMS 7890A. Merck silica gel plates (60F-254) using UV light as visualizing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-400 calibrated using residual deuterated solvent ($CDCl_3$: δH = 7.26 ppm, δC = 77.10 ppm) as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Perkin−Elmer Spectrum 100 FT-IR spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using EI (electron ionization) or ESI (electrospray ionization).

Optimizations for the Nickel-Catalysed Cyclopropanation of Chalcone 1a:



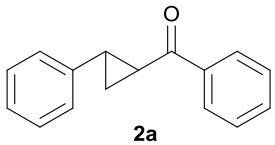
Entry	Ni catalyst (20 mol%)	CH_2I_2 (equiv.)	Et_2Zn (equiv.)	Ligand	Solvent	T (^oC)	Conv. (%)[b]	**2a** (%)[b]
1	None	4	2	none	DCM	0	25	7
2	$NiCl_2$	4	2	none	DCM	0	79	58
3	$NiCl_2$	4	2	none	DCE	0	84	57
4	$NiCl_2$	4	2	none	PhMe	0	61	34
5	$NiCl_2$	4	2	none	THF	0	93	25
6	$NiCl_2$	4	2	none	Et_2O	0	>99	8
7	$NiCl_2$	4	2	20 mol% Bipy[b]	DCM	0	88	32
8	$NiCl_2$	4	2	20 mol% PPh_3[b]	DCM	0	79	26
9	$NiCl_2$	4	2	20 mol% Dppf[b]	DCM	0	92	63
10	$NiCl_2$	4	2	none	DCM	rt	84	71
11	$NiCl_2$	4	2	none	DCM	40	>99	96
12	$NiBr_2$	4	2	none	DCM	40	>99	96
13	NiI_2	4	2	none	DCM	40	>99	97
14	$Ni(acac)_2$	4	2	none	DCM	40	>99	41 (27)[d]
15	$Ni(COD)_2$	4	2	none	DCM	40	67	41
16[c]	$NiCl_2$	4	2	none	DCM	40	100	0 (98)[d]
17	$NiCl_2$	4	1.2	none	DCM	40	56	38
18	$NiCl_2$	2	2	none	DCM	40	91	71 (9)[d]
19[e]	$NiCl_2$	4	2	none	DCM	40	94	94
20[f]	$NiCl_2$	4	2	none	DCM	40	98	96
21	none	4	2	none	DCM	40	30	7

[a] A solution of Et_2Zn in hexane was added slowly to a mixture of 1a, and Ni catalyst in CH_2Cl_2. [b] Determined by GC analysis using dodecane as an internal standard. [c] CH_2Br_2 was used instead of CH_2I_2. [d] Yield of **2a'**. [e] 10 mol% $NiCl_2$ was employed. [f] 2 mol% $NiCl_2$ was employed.

General Procedure A for Ni-catalysed Cyclopropanation of Ketones:

To a mixture of 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.) and 104 mg chalcone **1a** (0.5 mmol) in 2mL DCM at 40 ^oC was added slowly 1mL solution of Et_2Zn in hexane (1M, 1 mmol, 2 equiv.) over 20 min under nitrogen. After the addition, the reaction was stirred for a further 10 min before diluted with EtOAc and quenched with saturated aqueous NH_4Cl solution. Purification by silica gel column chromatography afforded the pure cyclopropane product.

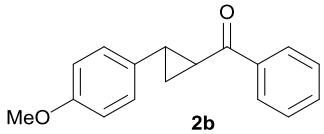
Phenyl(2-phenylcyclopropyl)methanone[1]



2a

Purification by silica gel column chromatography (2-5% Et_2O/petroleum ether) afforded **2a** as a white solid (96 mg, 86%). 1H NMR (400 MHz, CDCl3) δ 7.99 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.46 (s, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.17 (m, 3H), 2.93 – 2.88 (m, 1H), 2.74 – 2.68 (m, 1H), 1.96 – 1.90 (m, 1H), 1.59 – 1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 140.5, 137.8, 132.9, 128.5 (4C), 128.1 (2C), 126.6, 126.2 (2C), 30.0, 29.3, 19.2.

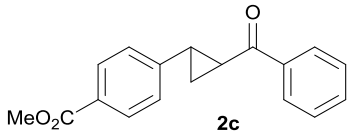
(2-(4-Methoxyphenyl)cyclopropyl)(phenyl)methanone[2]



2b

A similar procedure was used for 119 mg **1b** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1.5 mL solution Et_2Zn in hexane (1 M, 1.5 mmol, 3 equiv., added over 30 min). Purification by silica gel column chromatography (5-10% Et_2O/petroleum ether) afforded **2b** as a white solid (93 mg, 74%). ^1H NMR (400 MHz, Acetone-d_6) δ 8.05 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.54 – 7.49 (m, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.03 (ddd, *J* = 26.4, 4.1, 2.8 Hz, 1H), 2.55 (ddd, *J* = 8.9, 6.6, 4.0 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.52 (dd, *J* = 3.8, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 197.4, 158.6, 137.8, 132.7, 132.4, 128.6 (2C), 127.9 (2C), 127.3 (2C), 113.9 (2C), 54.6, 28.9, 28.4, 18.3.

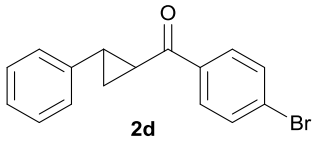
Methyl 4-(2-benzoylcyclopropyl)benzoate



2c

A similar procedure was used for 133 mg **1c** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (10% Et_2O/petroleum ether) afforded **2c** as a white solid (117 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 4H), 7.60 – 7.54 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 2.98 – 2.92 (m, 1H), 2.77 – 2.71 (m, 1H), 2.00 – 1.94 (m, 1H), 1.62 – 1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 166.8, 146.0, 137.5, 133.1, 129.9 (2C), 128.6 (2C), 128.5, 128.1 (2C), 126.0 (2C), 52.0, 29.6, 29.5, 19.6. IR (neat, cm^{-1}) 2955 (w), 2927 (w), 1715 (s), 1708 (s), 1658 (m), 1439 (w), 1277 (s), 1226 (m), 1114 (m), 987 (w), 765 (m), 704 (s). HRMS (ESI-TOF) *m/z*: calc. for $C_{18}H_{16}O_3Na$ $[M+Na]^+$: 303.0987, found 303.0992.

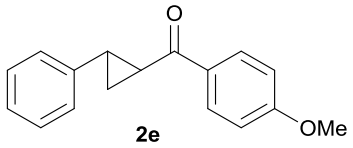
(4-Bromophenyl)(2-phenylcyclopropyl)methanone[3]



2d

A similar procedure was used for 144 mg **1d** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-15% Et_2O/petroleum ether) afforded **2d** as a white solid (116 mg, 77%). ^1H NMR (400 MHz, CDCl3) δ 7.86 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.25 (d, J = 7.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 2.86 – 2.80 (m, 1H), 2.71 (ddd, J = 9.1, 6.6, 4.0 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.61 – 1.55 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 197.4, 140.2, 136.5, 131.9, 129.6 (2C), 128.6 (2C), 128.1 (2C), 126.7, 126.2 (2C), 30.2, 29.2, 19.3.

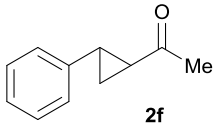
(4-Methoxyphenyl)(2-phenylcyclopropyl)methanone[4]



2e

A similar procedure was used for 60 mg **1e** (0.25 mmol), 6.5 mg $NiCl_2$ (0.05 mmol, 20 mol%), 268 mg CH_2I_2 (1 mmol, 4 equiv), 1 mL DCM at 40 ^oC and 0.5 mL solution Et_2Zn in hexane (1 M, 0.5 mmol, 2 equiv., added over 10 min). Purification by silica gel column chromatography (5% Et_2O/petroleum ether) afforded **2e** as a white solid (47 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.88 – 2.82 (m, 1H), 2.71 – 2.64 (m, 1H), 1.92 – 1.86 (m, 1H), 1.54 – 1.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.4, 140.7, 130.8, 130.3 (2C), 128.5 (2C), 126.5, 126.2 (2C), 113.7 (2C), 55.5, 29.4, 28.8, 18.8.

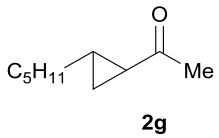
1-(2-Phenylcyclopropyl)ethan-1-one[5]



2f

A similar procedure was used for 74 mg **1f** (0.5 mmol), 6.5 mg $NiCl_2$ (0.05 mmol, 10 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-10% Et_2O/petroleum ether) afforded **2f** as a colourless gum (49 mg, 61%). ^1H NMR (400 MHz, CDCl3) δ 7.31 – 7.25 (m, 3H), 7.21 (d, J = 7.4 Hz, 1H), 7.12 – 7.07 (m, 2H), 2.56 – 2.49 (m, 1H), 2.30 (s, 3H), 2.24 – 2.18 (m, 1H), 1.70 – 1.64 (m, 1H), 1.41 – 1.34 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 206.7, 140.3, 128.5 (2C), 126.5, 126.0 (2C), 32.8, 30.8, 29.0, 19.0.

1-(2-Pentylcyclopropyl)ethan-1-one

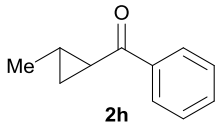


2g

A similar procedure was used for 70 mg **1g** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-5%

Et_2O/petroleum ether) afforded **2g** as a colourless oil (39 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 1.68 (dt, *J* = 8.1, 4.1 Hz, 1H), 1.45 – 1.17 (m, 10H), 0.88 (d, *J* = 7.5 Hz, 3H), 0.73 (ddd, *J* = 7.9, 6.3, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 33.2, 31.5, 30.1, 29.3, 28.8, 26.0, 22.6, 18.0, 14.0. IR (neat, cm^{-1}) 2960 (m), 2929 (s), 2858 (m), 1700 (s), 1402 (m), 1358 (m), 1173 (s), 1025 (w), 960 (w), 861 (w). HRMS (ESI-TOF) *m/z*: calc. for $C_{10}H_{19}O$ $[M+H]^+$: 155.1430, found 155.1428.

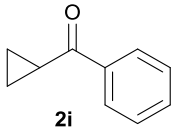
(2-Methylcyclopropyl)(phenyl)methanone[6]



2h

A similar procedure was used for 74 mg **1h** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^{o}C and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (20-40% DCM/petroleum ether) afforded **2h** as a colourless oil (52 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 2.35 – 2.29 (m, 1H), 1.58 – 1.49 (m, 2H), 1.45 – 1.39 (m, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.85 – 0.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 137.2, 131.5, 127.4 (2C), 126.9 (2C), 25.4, 20.2, 19.1, 17.3.

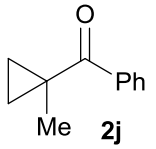
Cyclopropyl(phenyl)methanone[7]



2i

A similar procedure was used for 66 mg **1i** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^{o}C and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (1% Et_2O/pentane) afforded **2i** as a colourless oil (39 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.41 (dd, *J* = 8.0, 7.3 Hz, 2H), 2.65 – 2.57 (m, 1H), 1.21 – 1.16 (m, 2H), 1.01 – 0.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 138.1, 132.7, 128.5 (2C), 128.0 (2C), 17.1, 11.6 (2C).

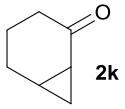
(1-Methylcyclopropyl)(phenyl)methanone[5b]



2j

A similar procedure was used for 74 mg **1j** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (1% Et_2O/pentane) afforded **2j** as a colourless oil (48 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 1.44 (s, 3H), 1.28 (dd, *J* = 6.5, 4.0 Hz, 2H), 0.79 (dd, *J* = 6.5, 4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 137.7, 131.6 (2C), 128.2 (3C), 128.2, 25.5, 21.9, 15.2 (2C).

Bicyclo[4.1.0]heptan-2-one[8]



2k

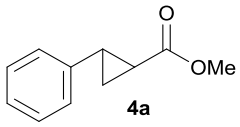
A similar procedure was used for 48 mg **1j** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 536 mg CH_2I_2 (2 mmol, 4 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (10-15% Et_2O/petroleum ether) afforded **2k** as a colourless oil (24 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 – 2.23 (m, 1H), 2.11 – 1.85 (m, 3H), 1.79 – 1.55 (m, 4H), 1.25 – 1.15 (m, 1H), 1.12 – 1.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 36.7, 25.8, 21.3, 17.8, 17.4, 10.2.

General Procedure A for Ni-catalysed Cyclopropanation of Esters and Amides:

A mixture of 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv) and 82 mg ester **2a** (0.5 mmol) in 2mL DCM was stirred at 40 ^oC for 30 min. 268 mg CH_2I_2 (1 mmol, 2 equiv.) was added followed by a slow addition of 1 ml solution of Et_2Zn in hexane (1M, 1 mmol, 2 equiv.) over 20 min under nitrogen. After the addition, the reaction was stirred for a further 10 min before diluted with EtOAc and quenched with saturated aqueous NH_4Cl solution. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The residual oil was dissolved in 1mL $CHCl_3$, and was treated with a few drops of Br_2 for 10 min to

remove residual **2a** left. Purification by silica gel column chromatography afforded the pure product.

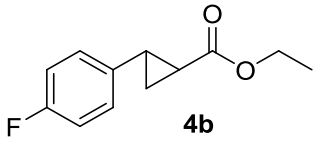
Methyl 2-phenylcyclopropane-1-carboxylate[9]



4a

Purification by silica gel column chromatography (20-40% DCM/petroleum ether) afforded **4a** as a colourless oil (80 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 2.86 – 2.80 (m, 1H), 2.71 (ddd, *J* = 9.1, 6.6, 4.0 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.61 – 1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 140.2, 136.5, 131.9, 129.6 (2C), 128.6 (2C), 128.1 (2C), 126.7, 126.2 (2C), 30.2, 29.2, 19.3.

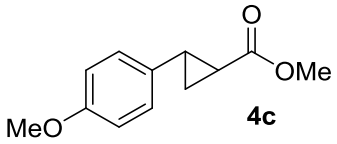
Ethyl 2-(4-fluorophenyl)cyclopropane-1-carboxylate[10]



4b

A similar procedure was used for 97 mg **3b** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv), 268 mg CH_2I_2 (1 mmol, 2 equiv.), 2 mL DCM at 40 ^{o}C and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-10% Et_2O/petroleum ether) afforded **4b** as a colourless oil (79 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 8.6, 5.3 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.50 (ddd, *J* = 9.4, 6.5, 4.2 Hz, 1H), 1.84 (ddd, *J* = 8.5, 5.3, 4.2 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.27 – 1.23 (m, 1H, overlapped). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 161.6 (d, *J* = 244.8 Hz), 135.7 (d, *J* = 3.2 Hz), 127.8 (d, *J* = 8.0 Hz, 2C), 115.2 (d, *J* = 21.5 Hz, 2C), 60.7, 25.4, 23.9, 16.8, 14.2.

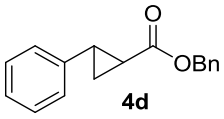
Ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate[11]



4c

A similar procedure was used for 96 mg **3c** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv), 268 mg CH_2I_2 (1 mmol, 2 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-10% Et_2O/petroleum ether) afforded **4c** as a white solid (61 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 2.49 (ddd, *J* = 9.2, 6.5, 4.1 Hz, 1H), 1.83 (ddd, *J* = 8.3, 5.2, 4.1 Hz, 1H), 1.58 – 1.53 (m, 1H), 1.26 (ddd, *J* = 8.3, 6.5, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 158.4, 131.9, 127.4, 113.9, 55.3, 51.8, 25.7, 23.6, 16.6.

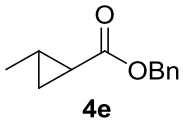
Benzyl 2-phenylcyclopropane-1-carboxylate[12]



4d

A similar procedure was used for 119 mg **3d** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv), 268 mg CH_2I_2 (1 mmol, 2 equiv.), 2 mL DCM at 40 ^oC and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-10% Et_2O/petroleum ether) afforded **4d** as a colourless gum (104 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 7H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.02 – 6.97 (m, 2H), 5.07 (d, *J* = 12.4 Hz, 1H, Germinal coupling), 5.04 (d, *J* = 12.4 Hz, 1H, Germinal coupling), 2.49 – 2.43 (m, 1H), 1.89 – 1.84 (m, 0H), 1.56 – 1.50 (m, 1H), 1.26 – 1.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 139.9, 136.0, 128.6 (2C), 128.5 (2C), 128.2 (2C), 126.5 (2C), 126.2 (2C), 66.6, 26.4, 24.1, 17.2.

Benzyl 2-methylcyclopropane-1-carboxylate[13]

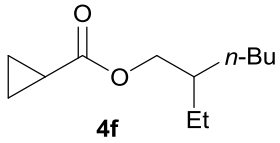


4e

A similar procedure was used for 86 mg **3e** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv), 268 mg CH_2I_2 (1 mmol, 2 equiv.), 2 mL DCE at 70 ^oC and 1 mL

solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (0-10% Et_2O/petroleum ether) afforded **4e** as a colourless oil (34 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.11 (s, 2H), 1.47 – 1.36 (m, 2H), 1.24 – 1.18 (m, 1H), 1.11 (d, *J* = 5.9 Hz, 3H), 0.73 – 0.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 136.2, 128.5 (2C), 128.13 (2C), 128.10, 66.2, 21.3, 17.8, 17.4, 16.9.

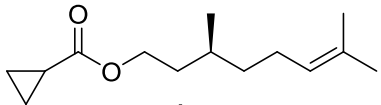
2-Ethylhexyl cyclopropanecarboxylate



4f

A similar procedure was used for 92 mg **3f** (0.5 mmol), 1.3 mg $NiCl_2$ (0.01 mmol, 2 mol%), 68 mg $ZnCl_2$ (0.5 mmol, 1 equiv.), 268 mg CH_2I_2 (1 mmol, 2 equiv.), 2 mL DCM at 40 ^{o}C and 1 mL solution Et_2Zn in hexane (1 M, 1 mmol, 2 equiv., added over 20 min). Purification by silica gel column chromatography (2% Et_2O/petroleum ether) afforded **4f** as a colourless oil (81 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (d, *J* = 2.2 Hz, 1H), 3.98 (d, *J* = 2.2 Hz, 1H), 1.55 (s, 2H), 1.41 – 1.24 (m, 10H), 1.02 – 0.96 (m, 2H), 0.93 – 0.80 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 66.9, 38.8, 30.4, 28.9, 23.8, 22.9, 14.0, 12.9, 11.0, 8.2 (2C). IR (neat, cm^{-1}) 2962 (m), 2933 (m), 2865 (w), 1732 (s), 1461 (w), 1402 (m), 1175 (s), 1073 (m), 1030 (w), 917 (w), 824 (w). HRMS (ESI-TOF) *m/z*: calc. for $C_{12}H_{22}O_2Na$ $[M+Na]^+$: 222.1512, found 221.1507.

(*S*)-3,7-Dimethyloct-6-en-1-yl cyclopropanecarboxylate

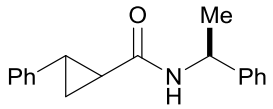


4g

A mixture of 6.5 mg $NiCl_2$ (0.05 mmol, 20 mol%), 34 mg $ZnCl_2$ (0.25 mmol, 1 equiv.) and 53 mg of (*S*)-3,7-dimethyloct-6-en-1-yl acrylate (0.25 mmol) in 1mL DCM was stirred at 40 ^{o}C for 10 min. 70 mg CH_2I_2 (0.26 mmol, 1.05 equiv.) was added followed by a slow addition of a solution of Et_2Zn (1M, 0.27 mL, 1.1 equiv.) in hexane over 40 min. After the addition, the reaction was stirred for a further 10 min before diluted with EtOAc and quenched with saturated aqueous NH_4Cl solution. Purification by silica gel column chromatography (0-3% Et_2O/petroleum ether) afforded **4g** as a colourless oil (38 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$)

δ 5.09 (d, *J* = 7.3 Hz, 1H), 4.17 – 4.05 (m, 2H), 2.07 – 1.89 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.71 – 1.51 (m, 2H, overlapped), 1.49 – 1.30 (m, 2H), 1.26 – 1.11 (m, 2H), 1.02 – 0.95 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.88 – 0.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 131.3, 124.6, 63.0, 37.0, 35.5, 29.5, 25.7, 25.4, 19.4, 17.6, 12.9, 8.2 (2C). IR (neat, cm^{-1}) 2960 (w), 2920 (w), 1729 (s), 1456 (w), 1404 (m), 1374 (m), 1173 (s), 1075 (w), 903 (w), 825 (w). HRMS (ESI-TOF) *m/z*: calc. for $C_{14}H_{25}O_2$ $[M+H]^+$: 225.1849, found 225.1844.

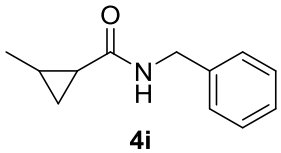
2-Phenyl-*N*-((S)-1-phenylethyl)cyclopropane-1-carboxamide[14]



4h

A similar procedure was used for 3.3 mg $NiCl_2$ (0.025 mmol, 10 mol%), 134 mg CH_2I_2 (0.5 mmol, 2 equiv), 63 mg **3h** (0.25 mmol) in 1mL DCE at 70 ^{o}C and 0.5 mL solution Et_2Zn in hexane (1 M, 0.5 mmol, 2 equiv, added over 30 min). Purification by silica gel column chromatography (0-25% EtOAc/petroleum ether) afforded **4h** as a white solid (40 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.03 (m, 10H), 5.81 (d, *J* = 7.2 Hz, 1H, NH), 5.22 – 5.12 (m, 1H), 1.67 – 1.55 (m, 2H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.28 – 1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): mixture of two diastereomers, δ 170.8 (2C), 143.3, 143.2, 140.9 (2C), 128.7 (3C), 128.4 (3C), 128.4 (2C), 127.4 (2C), 126.2 (6C), 126.0 (4C), 49.2 (2C), 26.9, 26.8, 25.0 (2C), 21.9, 21.8, 16.1, 16.0.

***N*-benzyl-2-methylcyclopropane-1-carboxamide[15]**

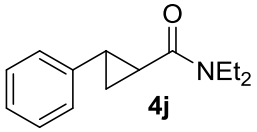


4i

A similar procedure was used for 3.3 mg $NiCl_2$ (0.1 mmol, 10 mol%), 134 mg CH_2I_2 (0.5 mmol, 2 equiv), 44 mg **3i** (0.25 mmol) in 1mL DCE at 70 ^{o}C and 0.5 mL solution Et_2Zn in hexane (1 M, 0.5 mmol, 2 equiv, added over 30 min). Purification by silica gel column chromatography (0-25% EtOAc/petroleum ether) afforded **4i** as a colourless gum (17 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 5.80 (br s, 1H, NH), 4.45 (d, *J* = 2.2 Hz, 1H), 4.44 (d, *J* = 2.2 Hz,

1H), 1.46 – 1.35 (m, 1H), 1.23 – 1.15 (m, 1H), 1.09 (d, *J* = 6.0 Hz, 3H), 1.08 – 1.02 (m, 1H), 0.61 – 0.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 138.5, 128.7 (2C), 127.9 (2C), 127.5, 43.9, 23.6, 17.9, 15.7, 15.7.

***N,N*-diethyl-2-phenylcyclopropane-1-carboxamide[16]**



4j

A similar procedure was used for 3.3 mg $NiCl_2$ (0.1 mmol, 10 mol%), 134 mg CH_2I_2 (0.5 mmol, 2 equiv), 51 mg **3j** (0.25 mmol) in 1mL DCE at 70 ^oC and 0.5 mL solution Et_2Zn in hexane (1 M, 0.5 mmol, 2 equiv, added over 30 min). Purification by silica gel column chromatography (0-30% Et_2O /petroleum ether) afforded **4j** as a colourless gum (39 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 (dd, *J* = 8.7, 0.7 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 2.51 – 2.45 (m, 1H), 1.96 – 1.90 (m, 1H), 1.68 – 1.62 (m, 1H), 1.27 – 1.22 (m, 1H), 1.16 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 141.2, 128.4 (2C), 126.1 (3C), 42.1, 41.0, 25.5, 23.2, 16.2, 14.9, 13.3.

$Ni(COD)_2$-Catalyzed Cyclopropanation of chalcone 1a with $Zn(CH_2I)_2$[17] (Scheme 3b):

To a solution of Et_2Zn (0.5 mmol) in DCM (1ml) at -78 ^oC was added 268 mg CH_2I_2 (1.0 mmol) dropwise. The mixture was stirred at -15 ^oC for 30 min followed by addition of **1a** (52mg, 0.25 mmol) and $Ni(COD)_2$ (13.5 mg, 0.049 mmol, 20 mol%). The reaction mixture was stirred at 0 ^oC for 1h. GC analysis using dodecane as an internal standard indicated the formation of **2a** in 79% yield with 2% of **1a** remaining.

$Ni(COD)_2$-Catalyzed Cyclopropanation of chalcone 1a with $EtZnCH_2I$[18] (Scheme 3b):

To a solution of Et_2Zn (0.5 mmol) in DCM (1ml) at -78 ^oC was added 134 mg CH_2I_2 (0.5 mmol) dropwise. The mixture was stirred at 0 ^oC for 5 min followed by addition of **1a** (52mg, 0.25 mmol) and $Ni(COD)_2$ (13.5 mg, 0.049 mmol, 20 mol%). The reaction mixture was stirred at 0 ^oC for 1h. GC analysis using dodecane as an internal standard indicated the formation of **2a** in 8% yield with 64% of **1a** remaining.

$Ni(COD)_2$-Catalyzed Cyclopropanation of chalcone 1a with $IZnCH_2I$[18] (Scheme 3b):

To a solution of I_2 (0.5 mmol) in DCM (1 ml) at 0 ^oC was added 0.5 mL solution of Et_2Zn in hexane (1 M, 0.5 mmol). After stirring for 5 min, 134 mg CH_2I_2 (0.5 mmol) was added dropwise. The mixture was stirred at 0 ^oC for 5 min followed by addition of **1a** (52mg, 0.25 mmol) and $Ni(COD)_2$ (13.5 mg, 0.049 mmol, 20 mol%). The reaction mixture was stirred at 0 ^oC for 1h. GC analysis using dodecane as an internal standard indicated the formation of **2a** in 59% yield with 36% of **1a** remaining.

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