Ni-catalyzed β-alkylation of cyclopropanol-derived homoenolates

L. Reginald Mills, Cuihan Zhou, Emily Fung, and Sophie A. L. Rousseaux*

*sophie.rousseaux@utoronto.ca

Davenport Research Laboratories, Department of Chemistry, University of Toronto
80 St. George St., Toronto, ON, M5S 3H6

Supporting Information 1: Experimental Data

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A. General information

Unless otherwise noted, all reactions were set up on the benchtop and run under an atmosphere of Ar or N_2 using flame-dried glassware and anhydrous solvents. CH_2Cl_2, Et_2O, MeCN, PhMe, and THF were purchased as HPLC-grade (inhibitor-free) from Caledon or Sigma–Aldrich, and were dried using a PureSolv MD 5 solvent purification system and used without further manipulation. DMA and DMF were purchased from Acros as Extra Dry over molecular sieves and were used as received. DMSO was purchased as reagent-grade and was dried over 3 Å molecular sieves for 3 days. $NiCl_2$(phen) was prepared from $NiCl_2$•$6H_2O$ and 1,10-phenanthroline and was stored in a desiccator open to air (see section C for details). $NiCl_2$(dtbbpy) was prepared from $NiCl_2$(dme) and dtbbbpy and was stored in a glovebox (see section C). $NiCl_2$(Bphen)•2DMF was prepared from $NiCl_2$•$6H_2O$ and bathophenanthroline.[1] $NiCl_2$(dme) was purchased from Sigma–Aldrich and was stored in a desiccator open to air and weighed on the benchtop. 2,6-Di(1*H*-pyrazol-1-yl)pyridine (bpp) was prepared from pyrazole and 2,6-dibromopyridine.[2] Zn(II) and Mg(II) salts were purchased as anhydrous-grade and were stored and weighed in a glovebox. $Zn(OMe)_2$ was prepared from Et_2Zn and MeOH.[3] All other commercial reagents were used as received. *trans*-2-Benzylcyclopropanol was prepared as previously described.[4] Compounds were purified by flash column chromatography using SiliCycle SilicaFlash P60 silica gel.

β-Alkylketone products were generally bench-stable and were stored on benchtop. NHPI ester starting materials were stored on benchtop and were repurified once a month to remove decomposition products resulting from hydrolysis. Cyclopropanols with 1-alkyl substituents were stored on benchtop; cyclopropanols with 1-aryl substitutents were stored at −20 ºC.

GC-MS data was obtained on a Shimadzu GCMS-QP2010 SE; yields represent peak areas calibrated against each compound's response factor relative to *n*-dodecane internal standard. ^{1}H and ^{13}C NMR spectra were recorded on Varian MercuryPlus 400 MHz, Agilent DD2 500 MHz, or Bruker AvanceIII 400 MHz spectrometers. TLC samples were run on EMD Millipore TLC Silica gel 60 F_{254} plates and were visualized by UV or by staining with standard $KMnO_4$, phosphomolybdic acid (PMA), or *p*-anisaldehyde stains. IR spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond/ZnSe ATR accessory as solids or thin films. Melting points were obtained on a Fisher-Johns Melting Point Apparatus. High-resolution mass spectra (HRMS) were recorded on a JEOL AccuTOF JMS-T1000LV mass spectrometer equipped with a Direct Analysis in Real Time (DART) ion source, or by electrospray ionization (ESI) on an Agilent 6538 UHD mass spectrometer. Chiral HPLC analysis was performed on a Shimadzu 20A series system using a Daicel Chiralpak column (IG). The 8- and 16-mL culture tubes used for reactions were purchased from Fisher (catalogue nos. 14-957-76A and 14-959-35A).

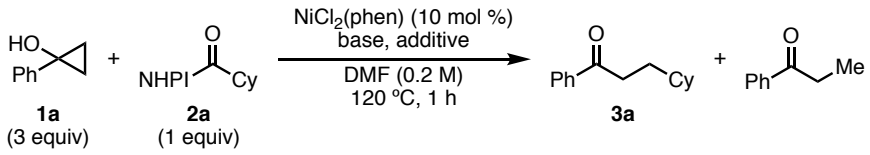
The following non-standard abbreviations are used in this SI:
"DCM" = CH_2Cl_2, dichloromethane.

B. Optimization details

Procedure for Tables S1–S5: Performed according to General Procedure A (see Section D) on 0.10 mmol scale.

Note: All reactions at 120 ºC gave full conversion of **1a** and **2a** after 1 h. The remaining mass balance of **1a** predominantly went to ring-opened isomer propiophenone, and the remaining mass balance of **2a** generally went to volatile side-products which were undetectable by GC-MS.

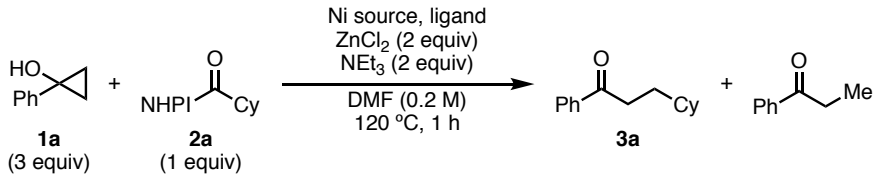
Table S1. Evaluation of bases and additives



Entry	base (equiv)	additive (equiv)	Yield **3a** (%)[a]
1	NEt_3 (2)	$ZnCl_2$ (2)	85[b]
2	DIPEA (2)	$ZnCl_2$ (2)	31
3	DBU (2)	$ZnCl_2$ (2)	17
4	pyridine (2)	$ZnCl_2$ (2)	8
5	DABCO (2)	$ZnCl_2$ (2)	32
6	TMP (2)	$ZnCl_2$ (2)	42
7	imidazole (2)	$ZnCl_2$ (2)	0
8	K_2CO_3 (2)	$ZnCl_2$ (2)	9
9	Cs_2CO_3 (2)	$ZnCl_2$ (2)	13
10	K_3PO_4	$ZnCl_2$ (2)	10
11	$NaHCO_3$ (2)	$ZnCl_2$ (2)	11
12	KO*t*-Bu (2)	$ZnCl_2$ (2)	0
13	NaOH (2)	$ZnCl_2$ (2)	9
14	NaH[c] (3) (pre-stir)	$ZnCl_2$ (2)	0
15	Et_2Zn[d] (1.5) (pre-stir)	$ZnCl_2$ (2)	20
16	none	$ZnCl_2$ (2)	3
17	NEt_3 (2)	$ZnBr_2$ (2)	51
18	NEt_3 (2)	ZnI_2 (2)	37
19	NEt_3 (2)	ZnF_2 (2)	38
20	NEt_3 (2)	$Zn(OAc)_2$ (2)	3
21	NEt_3 (2)	$Zn(OMe)_2$ (2)	14
22	NEt_3 (2)	$MgCl_2$ (2)	12
23	NEt_3 (2)	$MgBr_2$ (2)	11
24	NEt_3 (2)	$MnCl_2$ (2)	2
25	NEt_3 (2)	KCl (2)	47
26	NEt_3 (2)	LiCl (2)	12
27	NEt_3 (2)	none	40
28	NEt_3 (3)	$ZnCl_2$ (2)	77
29	NEt_3 (1)	$ZnCl_2$ (2)	57
30	NEt_3 (0.5)	$ZnCl_2$ (2)	35
31	NEt_3 (0.2)	$ZnCl_2$ (2)	23
32	NEt_3 (0.1)	$ZnCl_2$ (2)	17
33	NEt_3 (2)	$ZnCl_2$ (1)	55

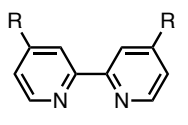
[a]GC-MS yield based on *n*-dodecane as internal standard; [b]Average of three runs; [c]60% w/w dispersion in mineral oil; [d]1.0 M solution in hexanes. phen = 1,10-phenanthroline.

Table S2. Evaluation of Ni sources and ligands

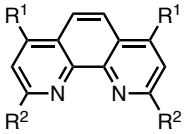


Entry	Ni source (mol %)	ligand (mol %)	Yield **3a** (%)[a]
1	$NiCl_2$(phen) (10)	none	85
2	$NiCl_2$(phen) (5)	none	46
3	$NiCl_2$(dme) (10)	bpy (12)	71
4	$NiCl_2$(dme) (10)	phen (12)	45
5	$NiCl_2$(dme) (10)	Bphen (12)	82
6	$NiCl_2$(dme) (10)	dtbbbpy (12)	65
7	$NiCl_2$(dme) (10)	dOMebpy (12)	31
8	$NiCl_2$(dme) (10)	neoc (12)	48
9	$NiCl_2$(dme) (10)	terpy (12)	57
10	$NiCl_2$(dme) (10)	bpp (12)	85
11	$NiCl_2$(Bphen)•2DMF (10)	none	49
12	$NiCl_2$(dtbbpy) (10)	none	54
13	$NiCl_2$(bpy) (10)	none	81
14	$NiCl_2$(bpy) (20)	none	78
15	$NiCl_2$(dppe) (10)	none	66
16	$NiCl_2(PPh_3)_2$ (10)	none	60
17	$NiBr_2$(bpy) (10)	none	86
18	$NiBr_2(bpy)_3$ (10)	none	70
19	$NiBr_2$(dme) (10)	bpy (12)	51
20	$NiBr_2$(dme) (10)	Bphen (12)	56
21	$NiCl_2•6H_2O$ (10)	Bphen (12)	56
22	$Ni(acac)_2$ (10)	Bphen (12)	32
23	$Ni(OAc)_2•4H_2O$ (10)	Bphen (12)	53
24	$Ni(cod)_2$ (10)	Bphen (12)	43
25	NiI_2 (10)	Bphen (12)	45
26	$NiCl_2$(dme) (10)	none	55
27	$NiBr_2$(dme) (10)	none	56

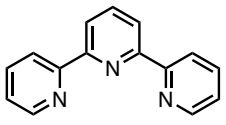
Reactions performed on 0.10 mmol scale.
[a]GC-MS yield based on *n*-dodecane as internal standard.
bpy = 2,2'-bipyridine; Bphen = bathophenanthroline; dtbbpy = 4,4'-di-tert-butyl-2,2'-dipyridyl; dOMebpy = 4,4'-dimethoxy-2,2'-bipyridine; neoc = neocuproine; phen = 1,10-phenanthroline; terpy = 2,2';6',2"-terpyridine; bpp = 2,6-di(1*H*-pyrazol-1-yl)pyridine.



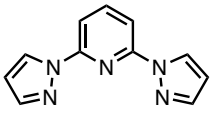
R = H, bpy
R = *t*-Bu, dtbbpy
R = OMe, dOMebpy



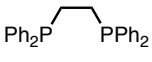
$R^1 = R^2 = H$, phen
R^1 = Ph, R^2 = H, Bphen
R^1 = H, R^2 = Me, neoc



terpy



bpp

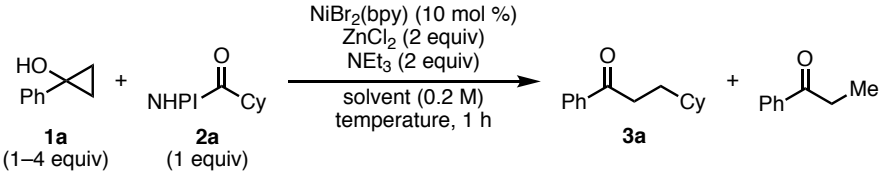


dppe

Procedure for Table S2 when precatalyst and ligand are added separately (entries 3–10, 19–25): The reaction was prepared in a two-vessel setup consisting of a 1-dram vial and a 8-mL culture tube. To a flame-dried 1-dram vial with a stir bar were added the Ni source and ligand and the vial was sealed and evacuated and backfilled with N_2 (×2). To a flame-dried 8-mL culture tube

with a stir bar was added NHPI ester **2a** (27 mg, 0.10 mmol, 1.0 equiv) and the tube was sealed, evacuated and backfilled with N_2 (×3), and brought into a glovebox. $ZnCl_2$ (27 mg, 0.20 mmol, 2.0 equiv) was added. The tube was sealed and removed from the glovebox. Cyclopropanol **1a** was prepared as a 1.0 M stock solution in DMF. To the 1-dram vial containing Ni source and ligand was added DMF (0.20 mL) and the solution was stirred at r.t. for 5 min, and the solution was transferred by syringe to the 8-mL culture tube. Then, the solution of **1a** in DMF (0.30 mL of a 1.0 M solution in DMF, 0.30 mmol, 3.0 equiv) was added to the culture tube, followed by NEt_3 (28 μL, 0.20 mmol, 2.0 equiv). The reaction was stirred for 30 s at r.t., then was stirred in a pre-heated oil bath at 120 ºC for 1 h. The reaction was cooled to r.t., opened to air, and quenched with sat. aq. 1 M HCl. *N*-Dodecane (23 μL, 0.10 mmol, 1.0 equiv) was added as an internal standard for GC-MS analysis. The solution was extracted with EtOAc (×1) and the organic fraction was filtered over a plug of $MgSO_4$ and Celite. The filtrate was analyzed by GC-MS.

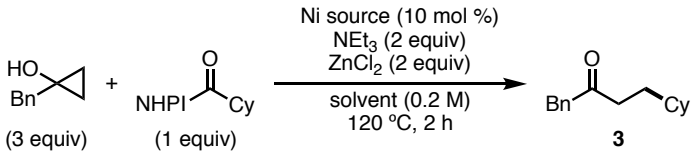
Table S3. Evaluation of solvent, temperature, and cyclopropanol stoichiometry



Entry	equiv **1a**	Solvent	Temp. (ºC)	Yield **3a** (%)[a]
1	3	DMF	120	86
2	1	DMF	120	35
3	1.5	DMF	120	44
4	2	DMF	120	58
5	2.5	DMF	120	81
6	4	DMF	120	80
7	2	DMF	130	69
8	2	DMF	100	43
9	2	DMF	80	30
10	2	DMF	60	13
11	2	DMF	r.t.	trace
12	2	DMA	120	52
13	2	1,4-dioxane	120	3
14	2	PhMe	120	3
15	2	MeCN	120	6
16	2	DMSO	120	35

Reactions performed on 0.10 mmol scale.
[a]GC-MS yield based on *n*-dodecane as internal standard.

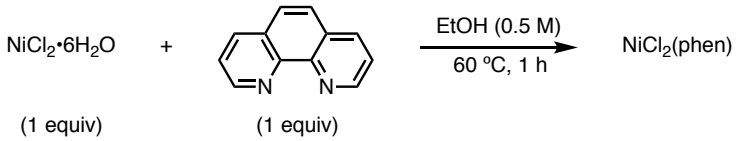
Table S4. Optimization of the reaction for 1-benzylcyclopropanol



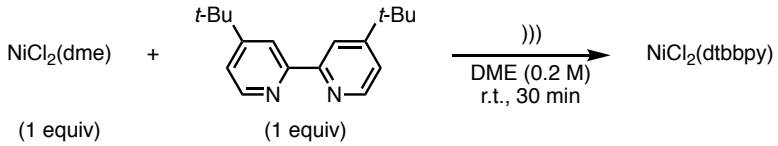
Entry	Ni source	Solvent	Yield (%)[a]
1	$NiCl_2$(phen)	DMA	92
2	$NiCl_2$(phen)	DMF	70
3	$NiCl_2$(phen)	NMP	15
4	$NiCl_2$(phen)	DMSO	20
5	$NiCl_2$(phen)	*n*-BuOH	0
6	$NiCl_2$(bpy)	DMA	74
7	$NiBr_2$(bpy)	DMA	89
8	$NiBr_2$(DPEphos)	DMA	21
9[b]	$NiCl_2$(phen)	DMA	6
10[b,c]	$NiCl_2$(phen)	DMA	5
11[b,d]	$NiCl_2$(phen)	DMA	0

[a]GC-MS yield based on *n*-dodecane as internal standard.
[b]Using TMS-protected cyclopropanol.
[c]Using CsF (3.6 equiv) instead of NEt_3.
[d]Using TBAF (1.2 equiv) instead of NEt_3.

C. Preparation of catalysts and reagents



$NiCl_2$(phen): To a 100-mL flask with a stir bar were added $NiCl_2$•$6H_2O$ (4.75 g, 20.0 mmol, 1.00 equiv) and EtOH (40 mL, 0.50 M), and the solution was stirred at r.t. until all $NiCl_2$•$6H_2O$ was dissolved (ca. 15 min). 1,10-Phenanthroline (3.60 g, 20.0 mmol, 1.00 equiv) was added at once, and the reaction was stirred at 60 ºC for 1 h. The solution was cooled to r.t. and the precipitate was collected in a fritted funnel, washed with EtOH (3×20 mL), and dried under high vacuum for 8 h to yield $NiCl_2$(phen) as a blue-green solid (4.1 g, 13 mmol, 65%). $NiCl_2$(phen) was stored in a desiccator open to air and was weighed on benchtop.



$NiCl_2$(dtbbpy):[5] To a flame-dried 25-mL flask were added $NiCl_2$(dme) (0.44 g, 2.0 mmol, 1.0 equiv) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.54 g, 2.0 mmol, 1.0 equiv), and the flask was sealed and evacuated and backfilled with N_2 (×3). DME (10 mL, 0.20 M) was added and the solution was sonicated at r.t. for 30 min. The reaction was opened to air and diluted with pentane (10 mL), filtered, and the precipitate was washed with pentane (×1) and dried under high vacuum for 8 h to yield $NiCl_2$(dtbbpy) as a pale blue solid (0.70 g, 1.8 mmol, 90%). $NiCl_2$(dtbbpy) was stored and weighed in a glovebox.

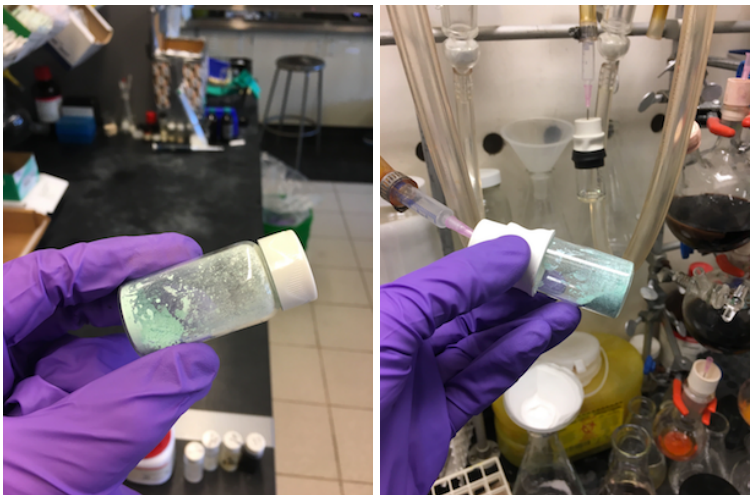
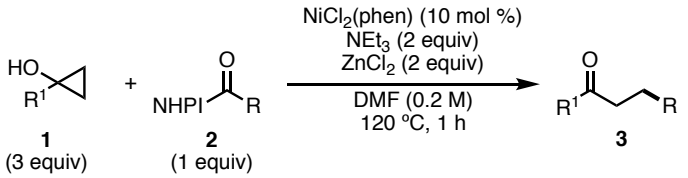


Figure S1. (Left) Appearance of $NiCl_2$(phen) precatalyst; (Right) Appearance of $NiCl_2$(dtbbpy) precatalyst.

D. β-Functionalization reactions:

D.1. General procedure for the synthesis of β-alkylketones

General Procedure A: Synthesis of β-alkylketones from cyclopropanols (**1**) and NHPI esters (**2**)



An 8-mL culture tube with a stir bar was fitted with a size 19 rubber septum and was flame dried under high vacuum (30 s), backfilled with N_2, and cooled to r.t. To the tube were added NHPI ester (if solid) (0.30 mmol, 1.0 equiv) and $NiCl_2$(phen) (9.3 mg, 0.030 mmol, 0.10 equiv). The tube was refitted with the size 19 septum, sealed with electrical tape, and was evacuated and backfilled with N_2 (×3) and brought into a drybox. Zinc(II) chloride (82 mg, 0.60 mmol, 2.0 equiv) was added. The tube was resealed and brought out of the box. Cyclopropanol was prepared as a 0.60 M stock solution in DMF. Cyclopropanol (1.5 mL of a 0.60 M stock solution in DMF, 0.90 mmol, 3.0 equiv; concentration of DMF = 0.20 M with respect to limiting NHPI ester reagent) was added. If the NHPI ester was an oil, the ester was then added. Stirring was begun at r.t., and triethylamine (84 μL, 0.60 mmol, 2.0 equiv) was added immediately, being careful so that triethylamine was dropped into the reaction solution without hitting the sides of the tube. The solution was stirred at r.t. for 30 s, or until all organic starting materials were dissolved. The reaction was then placed in a preheated 120 ºC oil bath and was stirred for 1 h, during which time the oil bath temperature was not allowed to drop below 120 ºC (if the oil bath is found to drop by some ºC upon immersion of the room-temperature reaction tube, the oil bath can be preheated higher than 120 ºC). After 1 h at 120 ºC, the reaction was cooled to r.t., opened to air, and quenched with 1 M HCl (sat. aq. NH_4Cl or H_2O was used for acid-sensitive or Lewis basic substrates). The reaction was extracted with EtOAc (×3) and the organic fractions were combined, filtered over a plug of $MgSO_4$ and Celite, and concentrated. The crude residue was purified by flash column chromatography to yield the desired β-alkylketone.

D.2. Graphical guide for General Procedure A

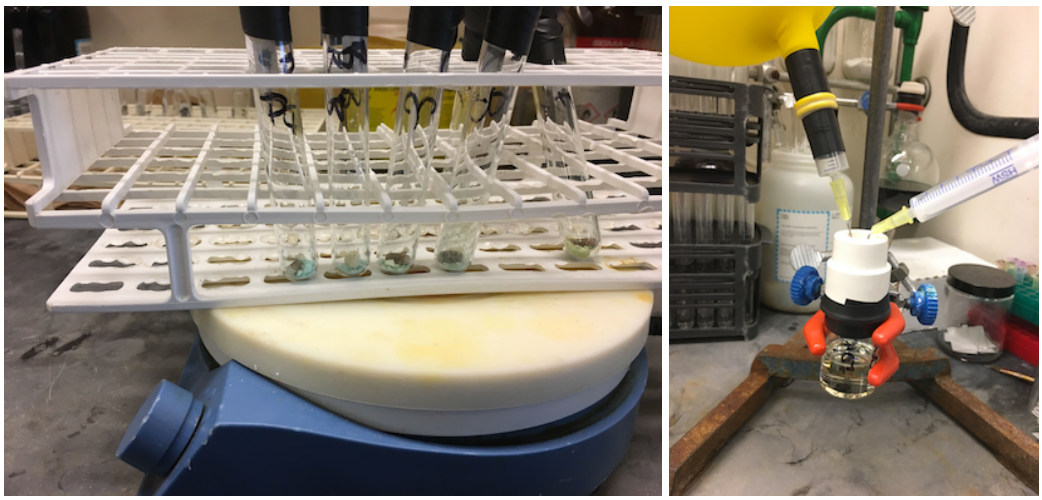


Figure S2. (Left) Appearance of the reaction vessels after adding all solids; (Right) 0.6 M stock solution of cyclopropanol in DMF.

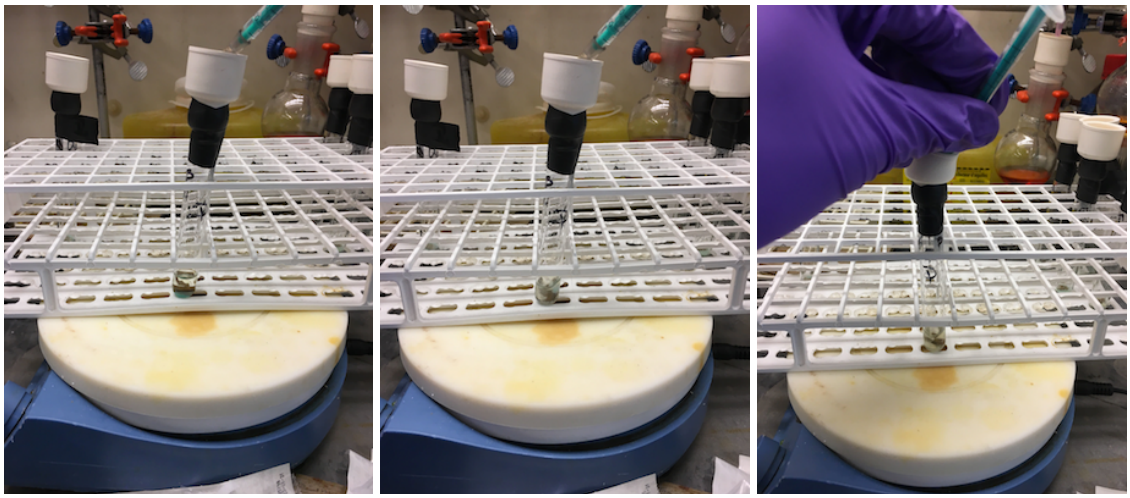


Figure S3. (Left) Appearance of the reaction after adding stock solution of cyclopropanol in DMF; (Centre) Stirring the solution before adding NEt_3; (Right) Appearance after adding NEt_3 while stirring.

N.B.: Decomposition of NHPI esters via hydrolysis over time affected β-functionalization reaction yields. The hydrolysis of NHPI esters was apparent after adding NEt_3 due to a characteristic red-orange colour, which was more pronounced with more decomposition (Figure S4).

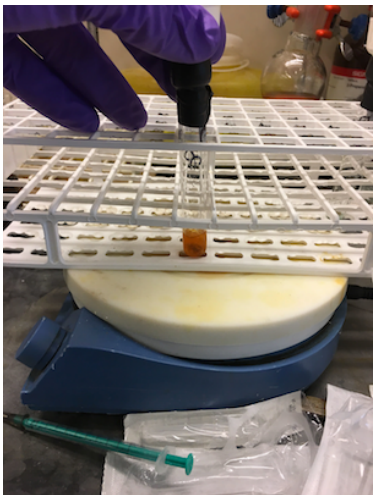


Figure S4. Appearance of the reaction after adding NEt_3 if NHPI ester starting material contains some hydrolyzed material.

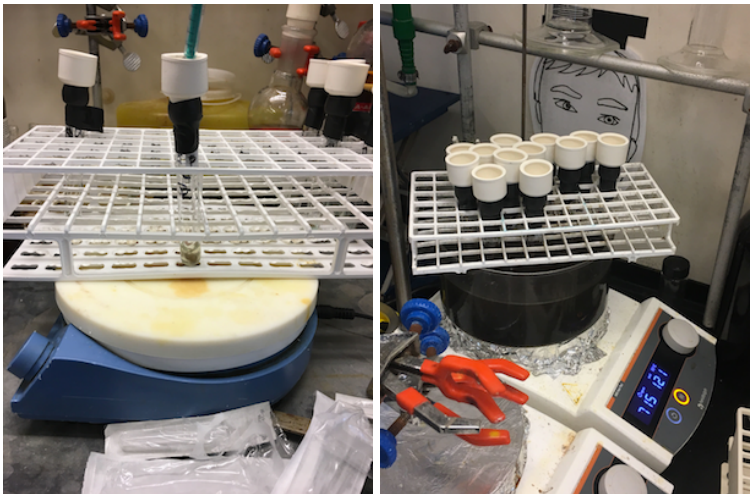


Figure S5. (Left) Appearance of solution after stirring for 30 s at r.t.; (Right) Submersion of reactions into a preheated 121 ºC oil bath.

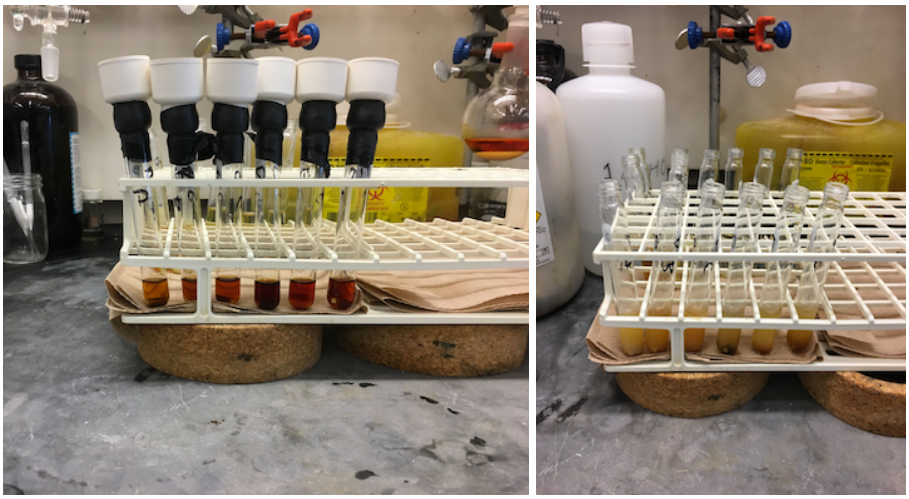
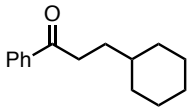


Figure S6. (Left) Appearance of reactions after stirring at 120 ºC for 1 h; (Right) After quenching with 1 M HCl.

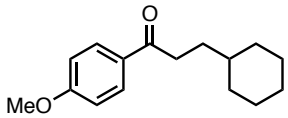
Figure S7. (Left) Plug of Celite (bottom layer) and $MgSO_4$ (top layer) used for filtration of organic fractions; (Centre) Plug during EtOAc extraction and filtration; (Right) After EtOAc (×3) extraction and filtration.

D.3. Preparation and characterization of β-alkylketone products

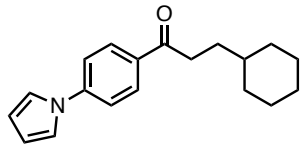


3-Cyclohexyl-1-phenylpropan-1-one (3a) (CAS: 28861-24-7): Prepared according to General Procedure A on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **3a** as a white solid (46 mg, 0.21 mmol, 71%). Analytical data:[6] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.92 (m, 2H), 7.58–7.51 (m, 1H), 7.49–7.42 (m, 2H), 3.01–2.94 (m, 2H), 1.80–1.59 (m, 7H), 1.37–1.09 (m, 4H), 1.02–0.79 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.9, 137.1, 132.8, 128.5, 128.1, 37.4, 36.2, 33.2, 31.8, 26.6, 26.3 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.66.

3a (1.0 mmol scale): Prepared according to General Procedure A on 1.0 mmol scale. The reaction was performed in a 16-mL culture tube and was quenched with 1 M HCl, extracted with EtOAc (×3), washed with brine (×1), and dried over $MgSO_4$. The crude residue was purified by flash column chromatograph (gradient of 0–5% EtOAc/hexanes) (0.11 g, 0.51 mmol, 51%). The analytical data matched the data for **3a** prepared on 0.30 mmol scale.

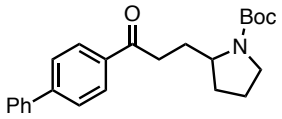


3-Cyclohexyl-1-(4-methoxyphenyl)propan-1-one (3b) (CAS: 31480-67): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% Et_2O/hexanes) to yield **3b** as a white solid (trial 1: 25 mg, 0.101 mmol, 51%; trial 2: 23 mg, 0.090 mmol, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.98–7.90 (m, 2H), 7.69–7.89 (m, 2H), 3.86 (s, 3H), 2.91 (t, J = 7.6 Hz, 2H), 1.77–1.57 (m, 7H), 1.35–1.09 (m, 4H), 1.00–0.88 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 199.7, 163.4, 130.5, 130.3, 113.8, 55.6, 37.6, 36.0, 33.4, 32.2, 26.7, 26.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{23}O_2$ (M+H): 247.1693; found: 247.1697; **IR** (neat): 2998, 2918, 2846, 1666, 1600, 1576, 1506, 1446, 1418, 1312, 1252, 1213, 1175, 1029, 958, 832, 770 cm^{-1}; **m.p.:** 57–58 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.54.

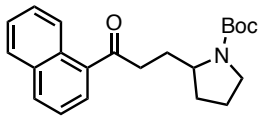


1-(4-(1*H*-Pyrrol-1-yl)phenyl)-3-cyclohexylpropan-1-one (3c): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% Et_2O/hexanes) to yield **3c** as a white solid (31 mg, 0.11 mmol, 55%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.07–8.01 (m, 2H), 7.49–7.43 (m, 2H), 7.19–7.14 (m, 2H), 6.42–6.37 (m, 2H), 3.00–2.94 (m, 2H), 1.82–1.56 (m, 7H), 1.38–1.11 (m, 4H), 1.02–0.90 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.0, 144.0, 134.1, 130.1, 119.5, 119.2, 111.7, 37.6, 36.2, 33.4, 32.0, 26.7, 26.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{19}H_{24}NO$ (M+H): 282.1852; found: 282.1851; **IR** (neat): 3146, 2920, 2849, 1677, 1603, 1523,

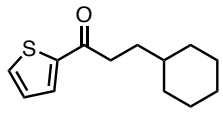
1475, 1330, 1193, 1183, 1127, 1066, 918, 822, 730, 723, 715 cm^{-1}; **m.p.:** 87–89 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.62.



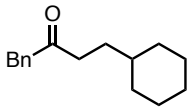
***tert*-Butyl 2-(3-([1,1'-biphenyl]-4-yl)-3-oxopropyl)pyrrolidine-1-carboxylate (3d):** Prepared according to General Procedure A on 0.20 mmol scale. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil, which was a 1:1 mixture of conformational isomers (52 mg, 0.14 mmol, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.07–7.99 (m, 2H), 7.71–7.57 (m, 4H), 7.50–7.34 (m, 3H), 4.06–3.81 (br m, 1H), 3.57–3.24 (br m, 2H), 3.20–2.91 (m, 2H), 2.20–1.77 (m, 5H), 1.77–1.61 (m, 1H), 1.44 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 199.8, 199.5, 155.0, 145.8, 140.0, 135.7, 134.4, 129.1, 128.8, 128.3, 127.4, 127.3, 123.7, 79.4, 79.1, 56.9, 46.5, 46.3, 36.0, 35.6, 31.1, 30.6, 29.5, 28.6, 23.9, 23.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{30}NO_3$ (M+H): 380.2220; found: 380.2224; **IR** (neat): 2974, 1963, 1678, 1390, 1364, 1280, 1173, 1110, 1095, 985, 836, 757, 694 cm^{-1}; **m.p.:** 93–94 ºC; $\mathbf{R_f}$ (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.36.



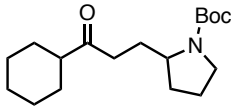
***tert*-Butyl 2-(3-(naphthalen-1-yl)-3-oxopropyl)pyrrolidine-1-carboxylate (3e):** Prepared according to General Procedure A on 0.20 mmol scale. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield **3e** as a colourless oil (33 mg, 0.093 mmol, 47%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.60–8.53 (m, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92–7.83 (m, 2H), 7.62–7.45 (m, 3H), 4.07–3.79 (br m, 1H), 3.56–3.26 (m, 2H), 3.24–2.97 (m, 2H), 2.22–2.06 (m, 1H), 2.05–1.55 (m, 5H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C 178.3, 175.7, 137.1, 136.2, 129.1, 128.7, 128.6, 128.1, 128.1, 127.9, 127.5, 126.8, 50.3, 47.9, 43.5, 39.7, 27.8, 26.3, 24.0, 23.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{28}NO_3$ (M+H): 354.2064; found: 354.2060; **IR** (neat): 2970, 2931, 2874, 1681, 1453, 1390, 1364, 1247, 1165, 1102, 946, 862, 801, 774 cm^{-1}; $\mathbf{R_f}$ (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.35.



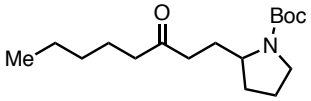
3-Cyclohexyl-1-(thiophen-2-yl)propan-1-one (3f) (CAS: 19740-01-3): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **3f** as a colourless oil (30 mg, 0.14 mmol, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.73–7.68 (m, 1H), 7.64–7.58 (m, 1H), 7.16–7.08 (m, 1H), 2.94–2.86 (m, 1H), 1.80–1.55 (m, 8H), 1.37–1.08 (m, 4H), 1.01–0.86 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 194.0, 144.6, 133.4, 131.7, 128.2, 37.5, 37.2, 33.3, 32.3, 26.7, 26.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{19}OS$ (M+H): 223.1151; found 223.1144; **IR** (neat): 3093, 2920, 2849, 1659, 1518, 1448, 1414, 1355, 1276, 1232, 1210, 1057, 852, 719 cm^{-1}; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/*p*-anisaldehyde): 0.67.



4-Cyclohexyl-1-phenylbutan-2-one (3g) (CAS: 175787-42-5): Prepared according to General Procedure A on 0.30 mmol scale using DMA instead of DMF. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (trial 1: 35 mg, 0.15 mmol, 51%; trial 2: 38 mg, 0.16 mmol, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.30 (m, 2H), 7.29–7.23 (m, 1H), 7.23–7.18 (m, 2H), 3.68 (s, 2H), 2.45 (t, J = 7.5 Hz, 2H), 1.72–1.57 (m, 4H), 1.49–1.40 (m, 2H), 1.35–1.03 (m, 5H), 0.91–0.76 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 209.0, 134.6, 129.5, 128.8, 127.1, 50.3, 39.7, 37.3, 33.2, 31.3, 26.7, 26.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{15}H_{21}O$ (M+H): 217.1587; found 217.1596; **IR** (neat): 2925, 2853, 1684, 1598, 1449, 1364, 1276, 1212, 1180, 1076, 1027, 762, 739, 696 cm^{-1}; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.36.

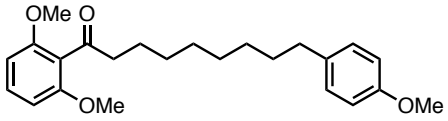


***tert*-Butyl 2-(3-cyclohexyl-3-oxopropyl)pyrrolidine-1-carboxylate (3h):** Prepared according to General Procedure A on 0.20 mmol scale using DMA instead of DMF. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil, which was a 1:1 mixture of conformational isomers (using $NiCl_2$(phen): 23 mg, 0.074 mmol, 37%; using $NiCl_2$(dtbbpy): trial 1: 23 mg, 0.074 mmol, 37%; trial 2: 23 mg, 0.074 mmol, 37%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 3.91–3.63 (m, 1H), 3.52–3.17 (m, 2H), 2.63–2.21 (m, 3H), 2.02–1.54 (m, 12H), 1.45 (s, 9H), 1.37–1.12 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 213.8, 155.0, 79.1, 77.4, 56.9, 50.9, 46.5, 46.3, 37.9, 37.5, 30.9, 30.4, 28.7, 26.0, 25.8, 23.8, 23.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{32}NO_3$ (M+H): 310.2377; found: 310.2370; **IR** (neat): 2969, 2928, 2855, 1689, 1450, 1390, 1365, 1252, 1166, 1104, 997, 865, 771 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.26.

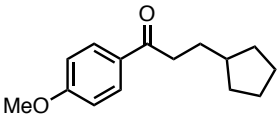


***tert*-Butyl 2-(3-oxooctyl)pyrrolidine-1-carboxylate (3i):** Prepared according to General Procedure A on 0.30 mmol scale using DMA instead of DMF. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil, which was a 1:1 mixture of conformational isomers (using $NiCl_2$(phen): 18 mg, 0.061 mmol, 20%; using $NiCl_2$(dtbbpy): trial 1: 54 mg, 0.18 mmol, 61%; trial 2 (0.20 mmol scale): 21 mg, 0.071 mmol, 36%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 3.90–3.66 (m, 1H), 3.50–3.20 (m, 2H), 2.56–2.25 (m, 4H), 1.99–1.74 (m, 4H), 1.72–1.51 (m, 4H), 1.45 (s, 9H), 1.35–1.20 (m, 4H), 0.87 (t, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 211.3, 210.9, 154.9 (br), 79.4, 791, 56.8, 46.5, 46.3, 42.9 (br), 40.0, 39.6, 31.5, 30.9, 30.4, 28.8 (br), 28.7, 23.8, 23.7, 23.1, 22.6, 14.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{32}NO_3$ (M+H): 298.2377; found 298.2373; **IR** (neat): 2959, 2932, 2874,

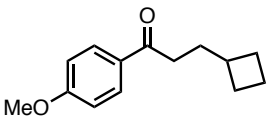
1689, 1454, 1390, 1365, 1252, 1166, 1104, 911, 863, 772 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.31.



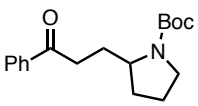
1-(2,6-Dimethoxyphenyl)-9-(4-methoxyphenyl)nonan-1-one (3j) (CAS: 114226-21-0): Prepared on 0.10 mmol scale according to General Procedure A. The product was purified by flash column chromatography (gradient of 0–30% Et_2O/hexanes) to yield **3j** as a colourless oil (8.8 mg, 0.023 mmol, 23%). Analytical data:[7] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.24 (t, *J* = 8.4 Hz, 1H), 7.11–7.05 (m, 2H), 6.84–6.79 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 6H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.56–2.50 (m, 2H), 1.60–1.53 (m, 4H), 1.34–1.28 (m, 8H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 205.7, 157.7, 156.8, 135.2, 130.5, 129.4, 120.9, 113.8, 104.1, 56.0, 55.4, 44.9, 35.2, 31.7, 29.5, 29.5, 29.4, 29.3, 23.6 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.26.



3-Cyclopentyl-1-(4-methoxyphenyl)propan-1-one (3k): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% Et_2O/hexanes) to yield the product as a colourless oil (31 mg, 0.13 mmol, 67%). Analytical data:[8] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.00–7.91 (m, 2H), 6.97–6.90 (m, 2H), 3.86 (s, 3H), 2.94–2.89 (m, 2H), 1.87–1.70 (m, 5H), 1.68–1.47 (m, 4H), 1.19–1.08 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 199.6, 163.4, 130.5, 130.3, 113.8, 55.6, 40.0, 37.8, 32.7, 31.1, 25.3 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.44.

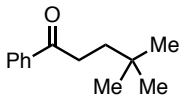


3-Cyclobutyl-1-(4-methoxyphenyl)propan-1-one (3l): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% Et_2O/hexanes) to yield the product as a colourless oil (trial 1: 15 mg, 0.069 mmol, 35%; trial 2: 16 mg, 0.073 mmol, 37%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.95–7.90 (m, 2H), 6.96–6.90 (m, 2H), 3.86 (s, 3H), 2.84–2.77 (m, 2H), 2.38–2.26 (m, 1H), 2.11–2.01 (m, 2H), 1.89–1.71 (m, 4H), 1.69–1.57 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 199.4, 163.4, 130.5, 130.3, 113.8, 55.6, 36.1, 35.8, 31.9, 28.2, 18.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{19}O_2$ (M+H): 219.1380; found: 219.1377; **IR** (neat): 2954, 2933, 2860, 1734, 1674, 1599, 1575, 1511, 1418, 1308, 1251, 1225, 1168, 1026, 973, 834, 810 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.42.

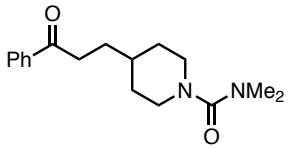


***tert*-Butyl 2-(3-oxo-3-phenylpropyl)pyrrolidine-1-carboxylate (3m):** Prepared according to General Procedure A on 0.30 mmol scale. The reaction was quenched with sat. aq. NH_4Cl. The

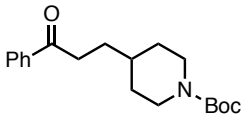
crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil, which was a 1:1 mixture of conformational isomers (61 mg, 0.20 mmol, 67%). Analytical data:[9] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.91 (m, 2H), 7.59–7.38 (br m, 3H), 3.91 (br m, 1H), 3.54–3.24 (br m, 2H), 3.18–2.86 (br m, 2H), 2.12–1.76 (m, 5H), 1.73–1.60 (br m, 1H), 1.42 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.2, 199.8, 155.0 (br), 137.1, 137.0, 133.2, 133.0, 128.7 (br), 128.1 (br), 79.4, 79.1, 56.9, 46.5, 46.2, 36.0, 35.5, 31.1, 30.5, 29.4, 28.6, 23.8, 23.1 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.23.



4,4-Dimethyl-1-phenylpentan-1-one (3n) (CAS: 37608-93-8): Prepared according to General Procedure A on 0.30 mmol scale. The product was purified by flash column chromatography (gradient of 0–5% Et_2O/hexanes) to yield **3n** as a colourless oil (41 mg, 0.22 mmol, 72%). Analytical data:[10] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.93 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.42 (m, 2H), 2.97–2.90 (m, 2H), 1.69–1.60 (m, 2H), 0.96 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K); δ_C 201.2, 137.2, 133.0, 128.7, 128.2, 38.3, 34.4, 30.3, 29.4 ppm; **R_f** (10% Et_2O/hexanes; UV/$KMnO_4$): 0.66.

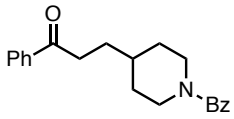


***N*,*N*-Dimethyl-4-(3-oxo-3-phenylpropyl)piperidine-1-carboxamide (3o):** Prepared according to General Procedure A on 0.30 mmol scale. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 30–70% EtOAc/hexanes) to yield the product as a colourless oil (36 mg, 0.13 mmol, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.86 (m, 2H), 7.57–7.48 (m, 1H), 7.47–7.38 (m, 2H), 3.69–3.56 (m, 2H), 3.02–2.89 (m, 2H), 2.85–2.59 (m, 8H), 1.77–1.58 (m, 4H), 1.55–1.38 (m, 1H), 1.29–1.10 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.2, 165.2, 137.0, 133.1, 128.7, 128.1, 47.1, 38.6, 36.0, 35.7, 32.1, 30.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{25}N_2O_2$ (M+H): 289.1911; found: 289.1917; **IR** (neat): 3486 (br), 2922, 2849, 1681, 1633, 1492, 1446, 1393, 1271, 1254, 1211, 1151, 945, 741, 691 cm^{-1}; **R_f** (6:4 hexanes/EtOAc; UV/$KMnO_4$): 0.21.

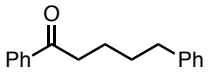


***tert*-Butyl 4-(3-oxo-3-phenylpropyl)piperidine-1-carboxylate (3p):** Prepared according to General Procedure A on 0.30 mmol scale. The reaction was quenched with sat. aq. NH_4Cl. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield **3p** as a colourless oil (trial 1: 35 mg, 0.11 mmol, 37%; trial 2: 40 mg, 0.13 mmol, 43%). Analytical data:[11] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.90 (m, 2H), 7.58–7.50 (m, 1H), 7.49–7.41 (m, 2H), 4.22–3.92 (br m, 2H), 3.06–2.92 (m, 2H), 2.77–2.56 (m, 2H), 1.91–1.62 (m, 4H), 1.54–1.34 (m, 10H), 1.20–1.05 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): 200.3, 155.0, 137.0, 133.1, 128.7, 128.1, 79.4, 44.0, 35.7, 35.7, 32.1, 30.8, 28.6 ppm; **HRMS** *m/z*

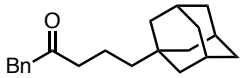
(DART): calcd for $C_{19}H_{28}NO_3$ (M+H): 318.2064; found: 318.2060; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.22.



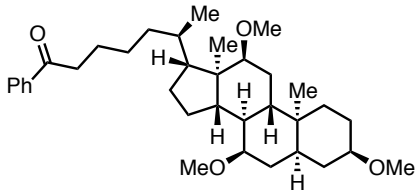
3-(1-Benzoylpiperidin-4-yl)-1-phenylpropan-1-one (3q): Prepared according to General Procedure A on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–60% EtOAc/hexanes) to yield **3q** as a colourless oil, which was a 1:1 mixture of conformational isomers (using $NiCl_2$(phen): 34 mg, 0.11 mmol, 35%; using $NiCl_2$(dtbbpy): trial 1: 57 mg, 0.18 mmol, 59%; trial 2: 38 mg, 0.12 mmol, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.91 (m, 2H), 7.60–7.52 (m, 1H), 7.50–7.42 (m, 2H), 7.41–7.31 (m, 5H), 4.90–4.55 (m, 1H), 3.89–3.61 (m, 1H), 3.13–2.63 (m, 4H), 1.97–1.54 (m, 5H), 1.38–1.06 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.0, 170.4, 136.9, 136.4, 133.1, 129.5, 128.7, 128.5, 128.0, 126.9, 48.0 (br), 42.4 (br), 35.8, 35.5, 32.9 (br), 31.8 (br), 30.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{24}NO_2$ (M+H): 322.1802; found: 322.1805; **IR** (neat): 3059, 2924, 2854, 1727, 1681, 1623, 1599, 1438, 1370, 1279, 1212, 1136, 965, 787, 734, 707, 691 cm^{-1}; **R_f** (6:4 hexanes/EtOAc; UV/$KMnO_4$): 0.35.



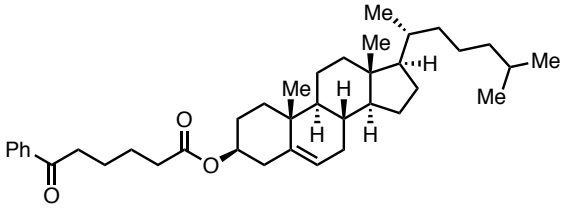
1,5-Diphenylpentan-1-one (3r): Prepared according to General Procedure A on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the product as a colourless oil (using $NiCl_2$(phen): 19 mg, 0.081 mmol, 27%; using $NiCl_2$(dtbbpy): trial 1: 30 mg, 0.13 mmol, 42%; trial 2: 32 mg, 0.13 mmol, 42%). Analytical data:[12] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.04–7.95 (m, 2H), 7.63–7.95 (m, 1H), 7.54–7.45 (m, 2H), 7.37–7.17 (m, 5H), 3.03 (t, J = 6.9 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 1.90–1.72 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.4, 142.4, 137.2, 133.1, 128.7, 128.5, 128.5, 128.2, 125.9, 38.6, 35.9, 31.2, 24.1 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.57.



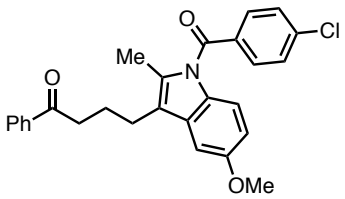
5-(Adamantan-1-yl)-1-phenylpentan-2-one (3s): Prepared according to General Procedure A on 0.10 mmol scale using DMA instead of DMF. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the product as a colourless oil (11 mg, 0.037 mmol, 37%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.39–7.16 (m, 5H), 3.67 (s, 2H), 2.39 (t, J = 7.4 Hz, 2H), 1.97–1.88 (m, 3H), 1.72–1.55 (m, 6H), 1.55–1.41 (m, 8H), 1.00–0.92 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 208.9, 134.6, 129.6, 128.8, 127.1, 50.3, 41.2, 43.1, 42.5, 37.4, 32.4, 28.9, 17.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{29}O$ (M+H): 297.2213; found: 297.2213; **IR** (neat): 2898, 2845, 1713, 1496, 1452, 1353, 1316, 1187, 1093, 1031, 810, 727, 697 cm^{-1}; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.39.



(*R*)-1-Phenyl-6-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)heptan-1-one (3t): Prepared according to General Procedure A on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless wax (53 mg, 0.098 mmol, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.00–7.91 (m, 2H), 7.58–7.51 (m, 1H), 7.49–7.41 (m, 2H), 3.39–3.35 (m, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.20 (s, 3H), 3.16–3.11 (m, 1H), 3.02–2.91 (m, 3H), 2.26–1.99 (m, 4H), 1.97–0.79 (m, 28H), 0.64 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.8, 137.3, 133.0, 128.7, 128.2, 82.2, 80.9, 77.2, 56.0, 55.8, 55.5, 46.7, 46.2, 42.8, 42.1, 39.8, 38.9, 35.8, 35.5, 35.4, 35.1, 34.6, 28.2, 27.9, 27.7, 26.9, 26.0, 25.0, 23.3, 23.0, 22.1, 17.9, 12.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{35}H_{58}NO_4$ (M+NH_4): 556.4360; found: 556.4369; **IR** (neat): 2930, 2866, 2819, 1685, 1581, 1452, 1369, 1185, 1099, 1091, 961, 750, 730, 691 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.38.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 6-oxo-6-phenylhexanoate (3u): Prepared according to General Procedure A on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white wax (33 mg, 0.057 mmol, 19%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.00–7.88 (m, 2H), 7.59–7.51 (m, 1H), 7.50–7.39 (m, 2H), 5.43–5.30 (m, 1H), 4.68–4.53 (m, 1H), 2.99 (t, J = 6.7 Hz, 2H), 2.66–2.53 (m, 1H), 2.43–2.20 (m, 4H), 2.06–0.79 (m, 41H), 0.68 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.0, 173.0, 139.0, 137.1, 133.1, 128.7, 128.2, 122.7, 74.0, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.3, 37.1, 36.7, 36.3, 35.9, 34.6, 32.0, 32.0, 28.4, 28.1, 27.9, 24.8, 24.4, 24.0, 23.8, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0 ppm; **HRMS** *m/z* (ESI): calcd for $C_{39}H_{59}O_3$ (M+H): 575.4459; found: 575.4455; **IR** (neat): 2940, 2867, 1736, 1687, 1599, 1461, 1371, 1259, 1174, 995, 801, 753, 724, 688 cm^{-1}; **R_f** (9:1 hexanes/Et_2O): 0.35.

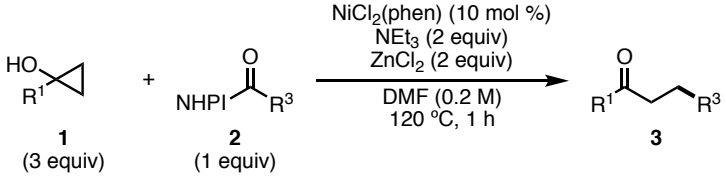


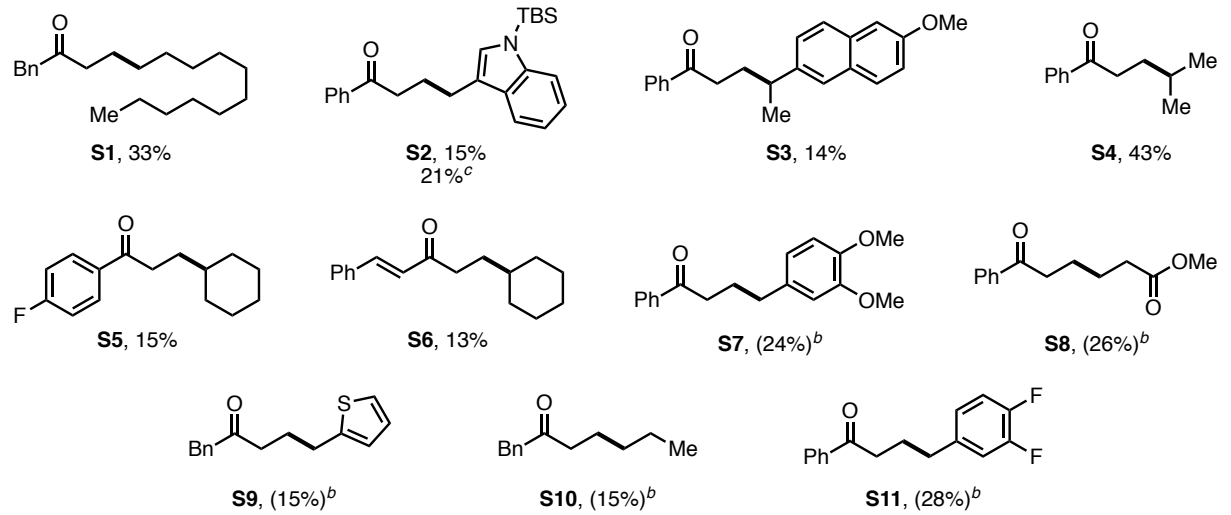
4-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3v): Prepared according to General Procedure A on 0.20 mmol scale. The crude residue was purified

by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a yellow oil (35 mg, 0.078 mmol, 39%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.94–7.90 (m, 2H), 7.65–7.61 (m, 2H), 7.58–7.53 (m, 1H), 7.47–7.42 (m, 4H), 6.98 (d, J = 2.6 Hz, 1H), 6.89 (d, J = 9.1 Hz, 1H), 6.65 (dd, J = 9.0, 2.6 Hz, 1H), 3.81 (s, 3H), 3.04 (t, J = 6.8 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.10 (app pent, J = 7.1 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.0, 168.4, 156.1, 139.1, 137.1, 134.4, 134.4, 133.2, 131.3, 131.2, 129.2, 128.7, 128.1, 126.3, 119.4, 115.1, 111.4, 101.5, 55.8, 37.7, 24.0, 23.3, 13.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{27}H_{25}NO_3Cl$ (M+H): 446.1518; found: 446.1517; **IR** (neat): 2956, 2931, 2871, 1737, 1681, 1596, 1477, 1452, 1371, 1358, 1318, 1237, 1220, 1143, 1088, 1043, 840, 753, 692 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.36.

D.4. Preparation and characterization of supplemental β-alkylketone products

Table S5. Supplemental scope of lower-yielding products[a]

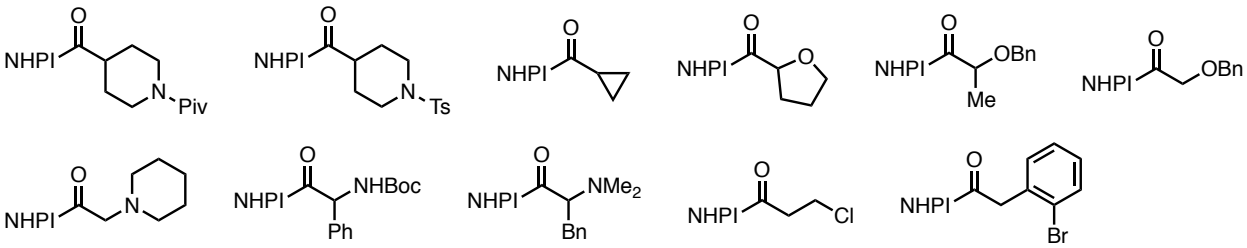




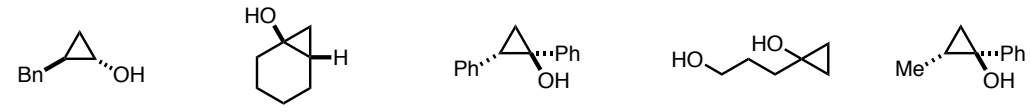
[a]Isolated yields (0.10–0.30 mmol scale); [b]Numbers in brackets represent *uncalibrated* GC-MS yields—data is shown purely for qualitative purposes; [c]Using $NiCl_2$(dtbbpy) (10 mol %).

Table S6. Table of unsuccessful starting materials (<10% yield)

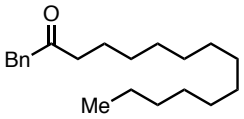
NHPI Esters



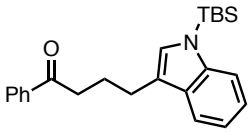
Cyclopropanols



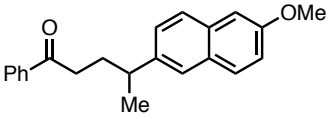
transesterification with NHPI ester	low conversion	rapid isomerization to ring-opened	transesterification	low yield



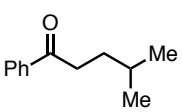
1-Phenylpentadecan-2-one (S1): Prepared on 0.10 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **S1** as a colourless oil (10 mg, 0.033 mmol, 33%). Analytical data:[13] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.37–7.29 (m, 2H), 7.29–7.23 (m, 1H), 7.23–7.17 (m, 2H), 3.68 (s, 2H), 2.43 (t, J = 7.4 Hz, 2H), 1.61–1.45 (m, 2H), 1.35–1.14 (m, 20H), 0.88 (t, J = 6.6 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 208.8, 134.6, 129.6, 128.8, 127.1, 50.3, 42.2, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.3, 23.9, 22.8, 14.3 ppm; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.43.



4-(1-(*tert*-Butyldimethylsilyl)-1*H*-indol-3-yl)-1-phenylbutan-1-one (S2): Prepared on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield **S2** as a colourless oil (17 mg, 0.045 mmol, mmol, 15%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.97–7.84 (m, 2H), 7.64–7.38 (m, 3H), 7.38–7.21 (m, 2H), 7.19–7.06 (m, 2H), 6.96 (s, 1H), 3.07–2.98 (m, 2H), 2.91–2.82 (m, 2H), 2.26–2.21 (m, 2H), 0.92 (s, 9H), 0.56 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 200.6, 137.2, 133.0, 131.1, 128.6, 128.3, 128.2, 121.5, 119.4, 119.0, 117.8, 114.0, 108.6, 38.2, 26.5, 24.7, 24.6, 20.0, −3.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{32}NOSi$ (M+H): 378.2248; found: 378.2253; **IR** (neat): 2952, 2930, 2858, 1684, 1598, 1451, 1361, 1304, 1257, 1218, 1136, 1002, 969, 952, 837, 821, 809, 788, 740, 687 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.64.

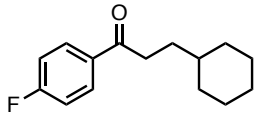


4-(6-Methoxynaphthalen-2-yl)-1-phenylpentan-1-one (S3): Prepared on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a white solid (13 mg, 0.041 mmol, 14%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.87–7.79 (m, 2H), 7.75–7.64 (m, 2H), 7.60–7.46 (m, 2H), 7.43–7.30 (m, 3H), 7.18–7.08 (m, 2H), 3.92 (s, 3H), 3.01–2.75 (m, 3H), 2.23–2.01 (m, 2H), 1.38 (d, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.6, 157.4, 141.8, 137.1, 133.4, 133.0, 129.2, 129.2, 128.6, 128.1, 127.2, 126.2, 125.4, 118.9, 105.8, 55.5, 39.6, 36.9, 32.5, 22.9 ppm; **HRMS** *m/z* (DART): calcd $C_{22}H_{23}O_2$ (M+H): 319.1693; found: 319.1700; **IR** (neat): 3355, 3053, 3023, 2954, 2924, 2866, 1737, 682, 1603, 1484, 1449, 1370, 1315, 1267, 1231, 1192, 1158, 1021, 902, 854, 828, 738, 688 cm^{-1}; **m.p.:** 84–86 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.51.

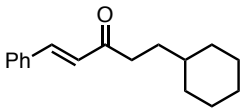


4-Methyl-1-phenylpentan-1-one (S4): Prepared on 0.30 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–4% Et_2O/hexanes) to yield the product as a colourless oil (24 mg, 0.14 mmol, 45%). Analytical data:[11] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.98–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.48–7.44 (m, 2H), 2.98–2.95 (m, 2H), 1.67–1.60

(m, 3H), 0.95 (d, J = 6.4 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$, 25 °C): δ_C 200.9, 137.2, 133.0, 128.7, 128.2, 36.8, 33.4, 28.0, 22.6 ppm; **R_f** (19:1 hexanes/Et_2O; UV/$KMnO_4$): 0.47.



3-Cyclohexyl-1-(4-fluorophenyl)propan-1-one (S5): Prepared on 0.20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the product as a colourless oil (7.0 mg, 0.030 mmol, 15%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.03–7.90 (m, 2H), 7.18–7.05 (m, 2H), 3.00–2.88 (m, 2H), 1.82–1.54 (m, 6H), 1.38–1.08 (m, 5H), 1.02–0.77 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 199.3, 165.7 (d, J = 52.5 Hz), 133.6 (d, J = 2.9 Hz), 130.8 (d, J = 9.2 Hz), 115.7 (d, J = 21.8 Hz), 37.6, 36.2, 33.3, 31.9, 26.7, 26.4 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −105.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{15}H_{20}OF$ (M+H): 235.1493; found: 235.1493; **IR** (neat): 2921, 2851, 1685, 1597, 1506, 1449, 1410, 1366, 1275, 1229, 1209, 1155, 939, 962, 837 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.79.

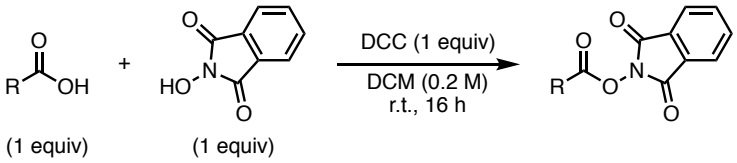


(*E*)-5-Cyclohexyl-1-phenylpent-1-en-3-one (S6): Prepared on 0.20 mmol scale. The product was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **S6** as a colourless oil (6.4 mg, 0.026 mmol, 13%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.58–7.48 (m, 3H), 7.42–7.33 (m, 3H), 6.74 (d, J = 16.3 ppm, 1H), 2.71–2.61 (m, 2H), 1.83–1.49 (m, 7H), 1.33–1.03 (m, 4H), 0.99–0.83 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 201.1, 142.4, 134.7, 130.5, 129.1, 128.4, 126.4, 38.7, 37.5, 33.3, 31.9, 26.7, 26.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{23}O$ (M+H): 243.1743; found: 243.1745; **IR** (neat): 3030, 2920, 2850, 1690, 1661, 1610, 1577, 1448, 1329, 1178, 1071, 977, 748, 690 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.62.

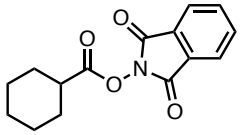
E. Preparation of N-hydroxyphthalimide (NHPI) ester starting materials

E.1. Preparation of N-hydroxyphthalimide (NHPI) esters

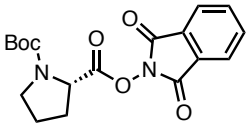
General Procedure B: Synthesis of NHPI esters using DCC



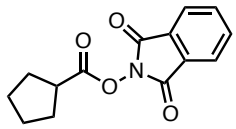
To a round-bottom flask with a stir bar were added carboxylic acid (if solid) (1 equiv), *N*-hydroxyphthalimide (1 equiv), *N*,*N'*-dicyclohexylcarbodiimide (1 equiv), and DCM (0.20 M). If the carboxylic acid was an oil the carboxylic acid was then added (1 equiv). The reaction was stirred at r.t. for 16 h. The solution was filtered using filter paper and the filtrate was concentrated and purified by flash column chromatography to yield the desired *N*-hydroxyphthalimide ester. If solid, NHPI esters were sufficiently ground up before use to ensure rapid dissolution in the reaction solvent. NHPI esters were stored on benchtop at r.t., and were repurified once a month to remove decomposition products resulting from hydrolysis.



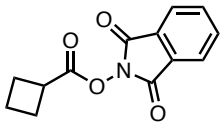
1,3-Dioxoisoindolin-2-yl cyclohexanecarboxylate (2a): The ester was prepared following General Procedure B on 20 mmol scale. The crude residue was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield **2a** as a white solid (4.7 g, 17 mmol, 85%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.83–7.76 (m, 2H), 2.80–2.69 (m, 1H), 2.18–2.06 (m, 2H), 1.91–1.78 (m, 2H), 1.75–1.60 (m, 3H), 1.48–1.23 (m, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 171.8, 162.1, 134.7, 129.1, 123.9, 40.5, 28.8, 25.5, 25.0 ppm; **R_f** (9:1 hexanes/EtOAc; UV): 0.32.



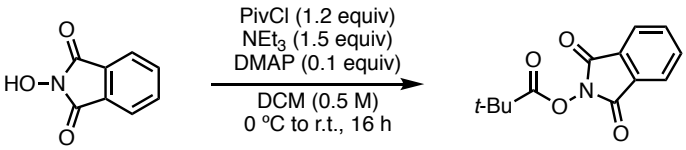
1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) (*S*)-pyrrolidine-1,2-dicarboxylate (S12): The ester was prepared following General Procedure B on 4.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a white solid (0.95 g, 2.6 mmol, 65%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.97–7.68 (m, 4H), 4.76–4.55 (m, 1H), 3.71–3.34 (m, 2H), 2.52–2.28 (m, 2H), 2.17–1.88 (m, 2H), 1.51 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 169.8, 161.8, 153.6, 134.9, 129.0, 124.1, 81.2, 57.3, 46.4, 31.5, 28.2, 23.6 ppm; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.08.



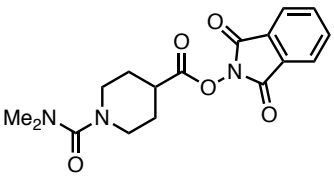
1,3-Dioxoisoindolin-2-yl cyclopentanecarboxylate (S13): The ester was prepared following General Procedure B on 5.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (1.2 g, 4.6 mmol, 92%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.93–7.82 (m, 2H), 7.81–7.70 (m, 2H), 3.18–3.02 (m, 1H), 2.22–1.94 (m, 4H), 1.89–1.54 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 173.0, 162.2, 134.8, 129.1, 124.0, 40.8, 30.3, 26.0 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.22.



1,3-Dioxoisoindolin-2-yl cyclobutanecarboxylate (S14): The ester was prepared following General Procedure B on 5.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (1.2 g, 4.9 mmol, 98%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.82–7.76 (m, 2H), 3.58–3.44 (m, 1H), 2.60–2.32 (m, 4H), 2.18–1.99 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 171.6, 162.2, 134.8, 129.2, 124.1, 35.2, 25.5, 18.9 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.20.

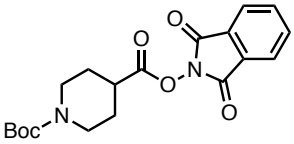


1,3-Dioxoisoindolin-2-yl pivalate (S15) (CAS: 84379-72-6): To a 50-mL flask with a stir bar were added *N*-hydroxyphthalimide (2.0 g, 12 mmol, 1.0 equiv) and DCM (24 mL, 0.50 M), and the solution was cooled to 0 ºC. DMAP (0.15 g, 1.2 mmol, 0.10 equiv) was added, followed by pivaloyl chloride (1.7 mL, 14 mmol, 1.2 equiv) and triethylamine (2.5 mL, 18 mmol, 1.5 equiv). The reaction was stirred at r.t. for 16 h. The reaction was concentrated and the concentrate was purified by flash column chromatography (gradient of 0–50% EtOAc/hexanes) to yield the product as a white solid (2.6 g, 10.5 mmol, 88%). Analytical data:[15] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 7.95–7.85 (m, 2H), 7.84–7.73 (m, 2H), 1.45 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 174.5, 162.2, 134.8, 129.2, 124.0, 38.5, 27.1 ppm.

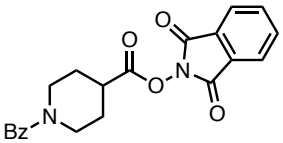


1,3-Dioxoisoindolin-2-yl 1-(dimethylcarbamoyl)piperidine-4-carboxylate (S16): The ester was prepared following General Procedure B on 2.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0/0/100–10/1/89 MeOH/NEt_3/DCM) to yield the product as an off-white solid. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.85 (m, 2H), 7.82–7.76 (m, 2H), 3.72–3.58 (m, 2H), 2.98–2.75 (m, 8H), 2.17–2.05 (m, 2H), 1.99–1.64 (m, 3H)

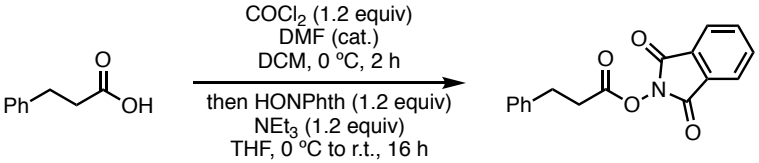
ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 170.8, 165.0, 162.0, 134.9, 129.1, 124.1, 46.1, 39.0, 38.6, 27.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{20}N_3O_5$ (M+H): 346.1398; found: 346.1406; **IR** (neat): 3325, 2928, 2855, 1783, 1736, 1628, 1495, 1364, 1184, 1117, 1025, 978, 877, 790, 696 cm^{-1}; **m.p.:** 79–81 ºC; **R_f** (10% MeOH/DCM; UV/$KMnO_4$): 0.61.



1-(*tert*-Butyl) 4-(1,3-dioxoisoindolin-2-yl) piperidine-1,4-dicarboxylate (S17): The ester was prepared following General Procedure B on 6.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–50% EtOAc/hexanes) to yield the product as a white solid (1.7 g, 4.5 mmol, 75%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.83–7.76 (m, 2H), 4.15–4.14 (m, 2H), 3.09–2.85 (m, 3H), 2.13–1.99 (m, 2H), 1.93–1.77 (m, 2H), 1.46 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 170.8, 162.1, 154.7, 134.9, 129.1, 123.1, 80.0, 42.6, 38.7, 28.6, 27.9 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.06.

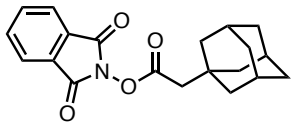


1,3-Dioxoisoindolin-2-yl 1-benzoylpiperidine-4-carboxylate (S18): The ester was prepared following General Procedure B on 7.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–60% EtOAc/hexanes) to yield the product as a white solid (4.2 g, 4.2 mmol, 60%). Analytical data:[16] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.83–7.77 (m, 2H), 7.47–7.37 (m, 5H), 4.48 (br s, 1H), 3.80 (br s, 1H), 3.31–3.18 (m, 2H), 3.19–2.99 (m, 1H), 2.30–1.54 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 170.5, 170.3, 161.9, 135.7, 134.9, 129.8, 128.9, 128.6, 126.9, 124.0, 46.4 (br), 40.9 (br), 38.5, 28.4 (br), 27.6 (br) ppm; **R_f** (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.10.

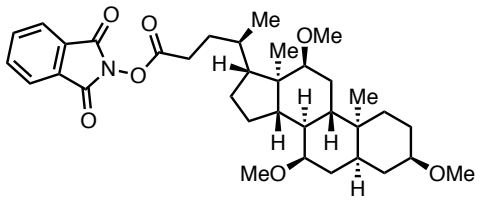


1,3-Dioxoisoindolin-2-yl 3-phenylpropanoate (S19) (CAS: 84379-71-5): To a flame-dried 100-mL flask with a stir bar were added hydrocinnamic acid (3.0 g, 20 mmol, 1.0 equiv) and DCM (50 mL, 0.40 M) and the solution was cooled to 0 ºC. Oxalyl chloride (2.0 mL, 24 mmol, 1.2 equiv) was added, followed by (DMF (2–3 drops), and the reaction was stirred at 0 ºC for 2 h. The solution was concentrated under reduced pressure, and was then dissolved in THF (50 mL, 0.40 M) and cooled to 0 ºC. *N*-Hydroxyphthalimide (3.9 g, 24 mmol, 1.2 equiv) was added, followed by dropwise addition of triethylamine (3.3 mL, 24 mmol, 1.2 equiv). The reaction was stirred at r.t. for 16 h. The reaction was quenched with 1M HCl and extracted with EtOAc (×2), and the organic fractions were combined, washed brine (×1), and concentrated. The crude material was suspended in $CHCl_3$, passed through a plug of Celite and further purified by recrystallization (EtOAc/hexanes) to yield the product as a white solid (5.7 g, 19 mmol, 95%).

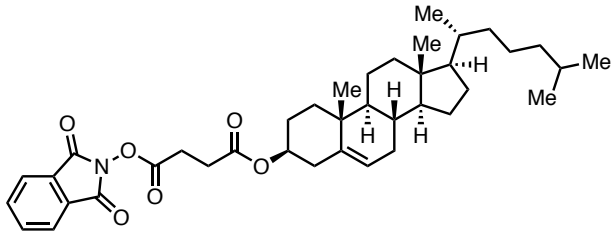
Analytical data:[17] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.93–7.87 (m, 2H), 7.82–7.76 (m, 2H), 7.37–7.30 (m, 2H), 7.29–7.22 (m, 3H), 3.15–3.07 (m, 2H), 3.03–2.95 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 169.0, 162.0, 139.3, 134.9, 129.1, 128.9, 128.4, 126.9, 124.1, 32.9, 30.7 ppm.



1,3-Dioxoisoindolin-2-yl 2-(adamantan-1-yl)acetate (S20): The ester was prepared according to General Procedure B on 10 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (2.3 g, 6.8 mmol, 68%). Analytical data:[18] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.82–7.75 (m, 2H), 2.40 (s, 2H), 2.07–2.00 (m, 3H), 1.80–1.64 (m, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 167.4, 162.2, 134.8, 129.2, 124.1, 45.6, 42.2, 36.7, 33.4, 28.8 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.31.

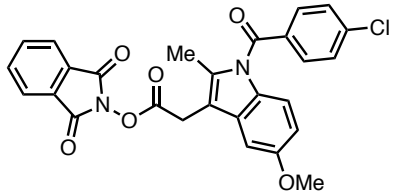


1,3-Dioxoisoindolin-2-yl (*R*)-4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (S21): The product was prepared according to General Procedure B on 8.2 mmol scale. The crude residue was purified by flash column chromatography (gradient of 15–40% EtOAc/hexanes) to yield the product as a white solid (2.9 g, 4.9 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.85 (m, 2H), 7.80–7.75 (m, 2H), 3.38 (t, J = 2.9 Hz, 1H), 3.33 (s, 3H), 3.27 (s, 3H), 3.21 (s, 3H), 3.14 (q, J = 3.1 Hz, 1H), 3.04–2.95 (m, 1H), 2.76–2.67 (m, 1H), 2.64–2.55 (m, 1H), 2.24–2.04 (m, 2H), 2.01–1.43 (m, 15H), 1.37–1.15 (m, 4H), 1.09–0.87 (m, 7H), 0.68 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 170.3, 162.2, 134.8, 129.1, 124.1, 82.1, 80.9, 77.1, 56.0, 55.8, 55.5, 46.4, 46.3, 42.8, 42.1, 39.8, 35.4, 35.1, 35.0, 34.6, 30.8, 28.1, 28.1, 27.9, 27.5, 26.9, 23.3, 23.0, 22.1, 17.5, 12.6 ppm; **HRMS** *m/z* (ESI): calcd for $C_{35}H_{53}N_2O_7$ (M+NH_4): 613.3847; found 613.3840; **IR** (neat): 2928, 2873, 2819, 1786, 1744, 1457, 1368, 1188, 1097, 1082, 965, 877, 860, 695 cm^{-1}; **m.p.:** 161–162 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.10.

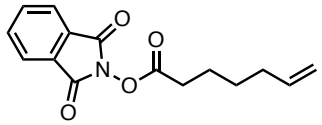


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (1,3-dioxoisoindolin-2-yl) succinate (S22): Prepared on 4.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the

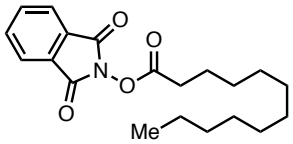
product as a white solid (1.9 g, 3.0 mmol, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.84 (m, 2H), 7.81–7.75 (m, 2H), 5.42–5.31 (m, 1H), 4.73–4.57 (m, 1H), 3.00 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.0 Hz, 2H), 2.70–2.53 (m, 1H), 2.39–2.26 (m, 2H), 2.06–1.75 (m, 4H), 1.68–0.80 (m, 33H), 0.67 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 170.5, 168.8, 161.8, 139.7, 134.9, 129.0, 124.1, 122.9, 75.0, 56.8, 56.3, 50.1, 42.4, 39.9, 39.6, 38.1, 37.1, 36.7, 36.3, 35.9, 32.0, 32.0, 29.3, 28.4, 28.1, 28.8, 26.5, 24.4, 24.0, 22.9, 22.7, 21.2, 19.4, 18.8, 12.0 ppm; **HRMS** *m/z* (ESI): calcd for $C_{39}H_{57}N_2O_6$ (M+NH_4): 649.4221; found 649.4212; **IR** (neat): 2938, 2864, 1821, 1791, 1746, 1730, 1468, 1371, 1314, 1190, 1138, 1088, 1059, 1000, 969, 877, 780, 695 cm^{-1}; **m.p.:** 111–115 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.13.



1,3-Dioxoisoindolin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (S23): The product was prepared according to General Procedure B on 2.0-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–50% EtOAc/hexanes) to yield the product as an off-white solid (0.15 g, 0.13 mmol, 7%). Analytical data:[19] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.84 (m, 2H), 7.82–7.76 (m, 2H), 7.71–7.66 (m, 2H), 7.50–7.44 (m, 2H), 7.03 (d, J = 2.5 Hz, 1H), 6.93 (dd, J = 9.0, 0.5 Hz, 1H), 6.71 (dd, J = 9.0, 2.5 Hz, 1H), 4.04 (s, 2H), 3.89 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 168.4, 167.2, 161.9, 156.4, 139.6, 136.6, 135.0, 133.8, 131.4, 130.9, 130.1, 129.3, 129.0, 124.2, 115.2, 112.6, 110.3, 110.8, 55.9, 27.3, 13.6 ppm; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.47.

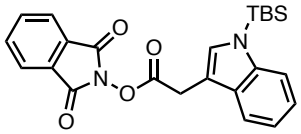


1,3-Dioxoisoindolin-2-yl hept-6-enoate (4): Prepared according to General Procedure B on 2.5 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield **4** as a colourless oil (0.33 g, 1.2 mmol, 48%). Analytical data:[20] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.95–7.84 (m, 2H), 7.83–7.73 (m, 2H), 5.88–5.74 (m, 1H), 5.10–4.93 (m, 2H), 2.67 (td, J = 4.6, 1.2 Hz, 2H), 2.17–2.07 (m, 2H), 1.86–1.75 (m, 2H), 1.62–1.50 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 169.7, 162.1, 138.2, 134.9, 129.1, 124.1, 115.2, 33.3, 31.0, 28.1, 24.1 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.15.

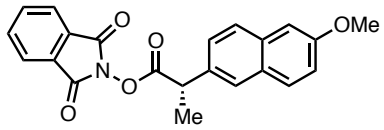


1,3-Dioxoisoindolin-2-yl dodecanoate (S24): Prepared according to General Procedure B on 15 mmol scale. The crude residue was purified by flash column chromatography (gradient of 5–10% EtOAc/hexanes) to yield the product as a white solid (3.7 g, 11 mmol, 73%). Analytical data:[21] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.86 (m, 2H), 7.82–7.76 (m, 2H), 2.66 (t, J = 7.5 Hz, 2H), 1.84–1.73 (m, 2H), 1.49–1.39 (m, 2H), 1.39–1.19 (m, 14H), 0.92–0.84 (m, 3H) ppm;

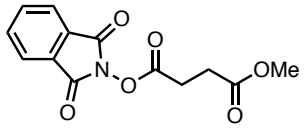
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C 169.8, 162.1, 134.8, 129.1, 124.0, 32.0, 31.1, 29.7, 29.7, 29.5, 29.4, 29.2, 28.9, 24.8, 22.8, 14.2 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.39.



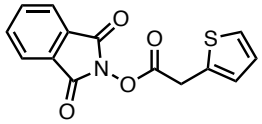
1,3-Dioxoisoindolin-2-yl 2-(1-(*tert*-butyldimethylsilyl)-1*H*-indol-3-yl)acetate (S25): Prepared according to General Procedure B on 4.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as an orange solid (0.48 g, 1.1 mmol, 28%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.84 (m, 2H), 7.80–7.72 (m, 2H), 7.68–7.60 (m, 1H), 7.56–7.48 (m, 1H), 7.35–7.30 (m, 1H), 7.23–7.14 (m, 2H), 4.15 (s, 2H), 0.95 (s, 9H), 0.63 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 163.0, 162.0, 141.4, 134.8, 130.4, 130.3, 129.1, 124.1, 122.0, 120.1, 118.6, 114.2, 108.0, 28.3, 26.4, 19.6, −3.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{27}N_2O_4Si$ (M+H): 435.1735; found 435.1734; **IR** (neat): 3072, 2956, 2927, 2856, 1812, 1784, 1740, 1611, 1456, 1421, 1371, 1258, 1217, 1185, 1137, 1101, 1081, 970, 809, 740, 692 cm^{-1}; **m.p.:** 77–78 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.23.



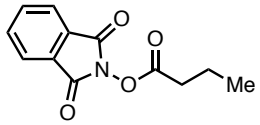
1,3-Dioxoisoindolin-2-yl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (S26) (CAS: 646510-95-4): Prepared on 3.0 mmol scale according to General Procedure B. The crude residue was purified by flash column chromatography (20% EtOAc/hexanes) to yield the product as an off-white solid (0.58 g, 1.6 mmol, 53%). Analytical data:[22] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.89–7.72 (m, 7H), 7.48 (dd, J = 8.6 Hz, 1H), 7.20–7.11 (m, 2H), 4.26 (q, J = 7.2 Hz, 1H), 3.92 (s, 3H), 1.75 (d, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 171.1, 162.0, 158.0, 134.8, 134.1, 133.6, 129.6, 129.1, 129.1, 127.7, 126.5, 126.0, 124.0, 119.3, 105.8, 55.5, 43.1, 19.1 ppm; **R_f** (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.21.



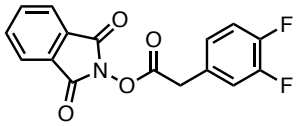
1,3-Dioxoisoindolin-2-yl methyl succinate (S28): Prepared on 5.0 mmol scale according to General Procedure B. The crude residue was purified by flash column chromatography (30% EtOAc/hexanes) to yield the product as a white solid (0.20 g, 0.72 mmol, 14%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.86 (m, 2H), 7.81–7.77 (m, 2H), 3.74 (s, 3H), 3.02 (td, J = 7.0, 0.6 Hz, 2H), 2.79 (t, J = 6.9 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 171.6, 168.8, 161.9, 134.9, 129.0, 124.2, 52.3, 28.8, 26.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{15}N_2O_6$ (M+NH_4): 295.0925; found 295.0920; **IR** (neat): 2939, 2853, 1813, 1784, 1730, 1466, 1441, 1399, 1376, 1355, 1236, 1211, 1183, 1129, 1081, 1054, 978, 879, 785, 967 cm^{-1}; **m.p.:** 104–108 ºC; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.43.



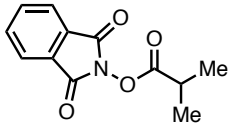
1,3-Dioxoisoindolin-2-yl 2-(thiophen-2-yl)acetate (S29): Prepared on 3.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 10–30% EtOAc/hexanes) to yield the product as an off-white solid (0.69 g, 2.4 mmol, 80%). Analytical data:[23] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.88–7.82 (m, 2H), 7.79–7.72 (m, 2H), 7.27–7.18 (m, 1H), 7.10–7.04 (m, 1H), 7.00–6.13 (m, 1H), 4.21–4.15 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 166.8, 161.9, 135.0, 132.1, 129.0, 128.0, 127.3, 125.9, 124.2, 32.2 ppm; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.19.



1,3-Dioxoisoindolin-2-yl butyrate (S30): Prepared on 5.0 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (0.77 g, 3.3 mmol, 66%). Analytical data:[24] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.84 (m, 2H), 7.82–7.73 (m, 2H), 2.70–2.59 (m, 2H), 1.89–1.75 (m, 2H), 1.13–1.02 (m, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 169.6, 162.1, 134.9, 129.1, 124.1, 32.9, 18.5, 13.5 ppm; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.27.



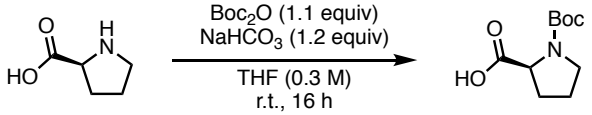
1,3-Dioxoisoindolin-2-yl 2-(3,4-difluorophenyl)acetate (S31): Prepared on 4.0-mmol scale according to General Procedure B. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (0.72 g, 2.3 mmol, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.95–7.72 (m, 4H), 7.29–7.04 (m, 3H), 3.95 (s, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −136.7–−136.9 (m), −138.7–−138.9 (m) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 167.2 (d, J = 1.4 Hz), 161.8, 151.8–141.8 (m, 2C), 135.0, 128.9, 128.4 (dd, J = 6.0, 4.0 Hz), 125.6 (dd, J = 6.3, 3.7 Hz), 124.2, 118.6 (d, J = 17.9 Hz), 117.7 (d, J = 17.1 Hz), 36.9 (d, J = 1.5 Hz) ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{10}NO_4F$ (M+H): 318.0572; found 318.0577; **IR** (neat): 3515, 3061, 2936, 1814, 1783, 1731, 1608, 1515, 1469, 1439, 1360, 1339, 1281, 1183, 1139, 1117, 1066, 966, 899, 867, 830, 760, 693 cm^{-1}; **m.p.:** 105–109 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.16.



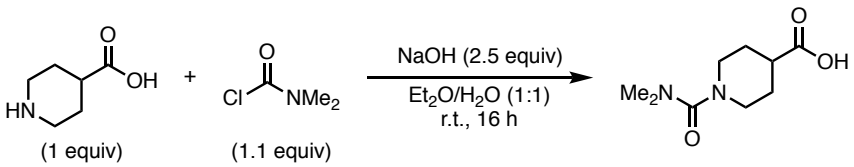
1,3-Dioxoisoindolin-2-yl isobutyrate (S32): The ester was prepared according to General Procedure B on 10 mmol scale. The crude residue was purified by flash column chromatography (15% EtOAc/hexanes) to yield the product as an off-white solid (1.7 g, 7.3 mmol, 73%). Analytical data:[14] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.90–7.85 (m, 2H), 7.80–7.75 (m, 2H), 2.95 (hept, J = 7.0 Hz, 1H), 1.70 (d, J = 7.0 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$,

298 K): δ_C 173.2, 162.1, 134.8, 129.1, 124.0, 31.9, 19.0 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.24.

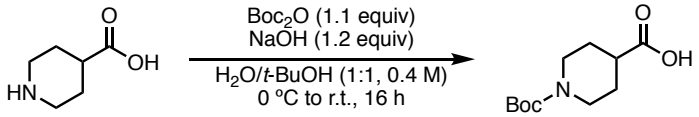
E.2. Preparation of noncommercial carboxylic acids



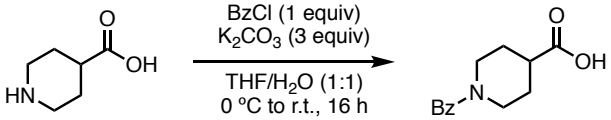
(*tert*-Butoxycarbonyl)-*L*-proline (S33): To a 50-mL flask with a stir bar were added L-proline (0.58 g, 5.0 mmol, 1.0 equiv), sodium bicarbonate (0.50 g, 6.0 mmol, 1.2 equiv), THF (15 mL, 0.30 M), and Boc_2O (1.3 mL, 5.5 mmol, 1.1 equiv). The reaction was stirred at r.t. for 16 h. The reaction was poured into H_2O (100 mL) and the solution was acidified with 1 M HCl to pH 2–3, and extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The concentrate was triturated with hexanes to yield the product as a white solid (0.96 g, 4.5 mmol, 90%). The NMR data was consistent with literature reports.[25]



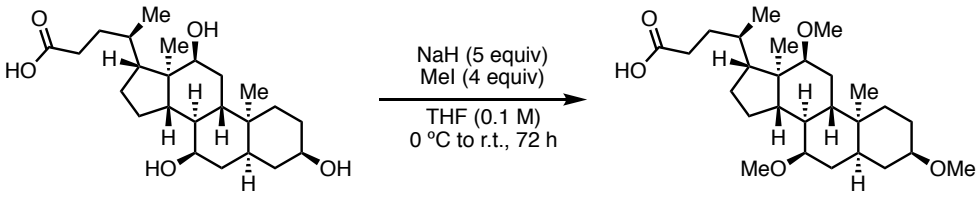
1-(Dimethylcarbamoyl)piperidine-4-carboxylic acid (S34): To a 100-mL flask with a stir bar were added isonipecotic acid (1.3 g, 10 mmol, 1.0 equiv), sodium hydroxide (1.0 g, 25 mmol, 2.5 equiv), Et_2O (10 mL), and H_2O (10 mL), and the solution was stirred at r.t. until all solids were dissolved (ca. 15 min). The solution was cooled to 5 ºC and dimethylcarbamoyl chloride (1.0 mL, 11 mmol, 1.1 equiv) was added. The reaction was warmed to r.t. and stirred for 16 h. The reaction was concentrated, diluted with H_2O (20 mL), and acidified to pH 2–3 with 1 M HCl. The solution was extracted with EtOAc (×3) and the organic fractions were combined, washed with brine (×1), and dried over $MgSO_4$ to yield the product as a white solid (0.54 g, 2.7 mmol, 27%). Analytical data:[26] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 3.70–3.53 (m, 2H), 2.93–2.73 (m, 8H), 2.54–2.41 (m, 1H), 2.00–1.84 (m, 2H), 1.79–1.64 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 179.3, 165.3, 46.4, 41.2, 38.7, 27.9 ppm.



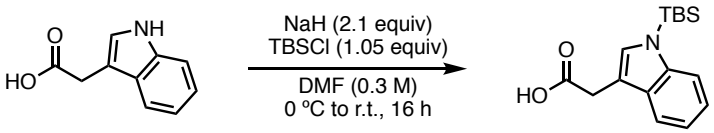
1-(*tert*-Butoxycarbonyl)piperidine-4-carboxylic acid (S35): To a 100-mL flask with a stir bar were added isonipecotic acid (2.6 g, 20 mmol, 1.0 equiv), sodium hydroxide (0.96 g, 24 mmol, 1.2 equiv), H_2O (20 mL), and *t*-BuOH (20 mL) (total reaction solvent = 40 mL of a 1:1 H_2O/*t*-BuOH mixture, 0.40 M), and the solution was cooled to 0 ºC. Boc_2O (5.1 mL, 22 mmol, 1.1 equiv) was added portionwise over 30 min, and the reaction was warmed to r.t. and stirred for 16 h. The reaction was concentrated under reduced pressure and the concentrate was diluted with H_2O (20 mL), acidified with 1 M HCl to pH 5–6, and extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated to yield the product as a white solid (4.5 g, 20 mmol, 98%). The NMR data was consistent with literature reports.[27]



1-Benzoylpiperidine-4-carboxylic acid (S36): To a 50-mL flask with a stir bar were added isonipecotic acid (1.3 g, 10 mmol, 1.0 equiv), potassium carbonate (4.1 g, 30 mmol, 3.0 equiv), THF (10 mL), and H_2O (10 mL), and the solution was cooled to 0 ºC. Benzoyl chloride (1.2 mL, 10 mmol, 1.0 equiv) was added and the solution was warmed to r.t. and stirred for 16 h. The reaction was diluted with H_2O (50 mL) and the aqueous layer was washed with EtOAc (×1), and the organic layer was discarded. The aqueous layer was acidified with 1 M HCl to pH 2–3 and the solution was extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated to yield the product as a white solid (2.1 g, 9.0 mmol, 90%). The NMR data was consistent with literature reports.[28]

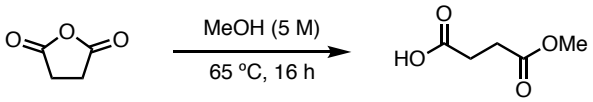


(*R*)-4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-Trimethoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (S37): To a flame-dried 250-mL flask with a stir bar were added cholic acid (4.1 g, 10 mmol, 1.0 equiv) and THF (100 mL, 0.10 M), and the solution was cooled to 0 ºC. Sodium hydride (2.0 g of a 60% w/w dispersion in mineral oil, 50 mmol, 5.0 equiv) was added portionwise over 30 min. Then, iodomethane (2.5 mL, 40 mmol, 4.0 equiv) was added dropwise over 15 min. The reaction was allowed to warm to r.t. and was stirred for 72 h. The reaction was quenched with 1 M HCl and extracted with EtOAc (×3). The organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 20–80% EtOAc/hexanes) to yield the product as a white solid (3.7 g, 8.2 mmol, 82%). Analytical data:[29] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 3.42–3.30 (m, 4H), 3.25 (s, 3H), 3.21 (s, 3H), 3.17–3.11 (m, 1H), 3.06–2.94 (m, 1H), 2.46–2.35 (m, 1H), 2.31–0.81 (m, 29H), 0.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ_C 179.7, 82.1, 80.9, 77.1, 56.0, 55.8, 55.5, 46.4, 46.3, 42.8, 42.1, 39.8, 35.4, 35.2, 35.1, 34.6, 31.0, 30.9, 28.1, 27.9, 27.5, 26.8, 23.3, 23.0, 22.1, 17.5, 12.6 ppm; **R_f** (7:3 hexanes/EtOAc; $KMnO_4$): 0.21.

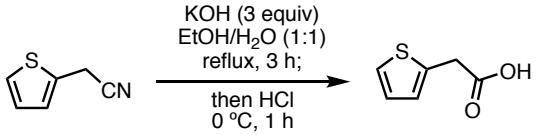


2-(1-(*tert*-Butyldimethylsilyl)-1H-indol-3-yl)acetic acid (S38) (CAS: 480437-10-3): To a 100-mL flask with a stir bar were added 3-indolylacetic acid (2.1 g, 12 mmol, 1.0 equiv), and DMF (40 mL, 0.30 M), and the solution was cooled to 0 ºC. Sodium hydride (1.0 g, 25 mmol, 2.1 equiv) was added and the reaction was stirred at r.t. for 1 h. TBSCl (2.0 g, 13 mmol, 1.05 equiv) was added and the reaction was stirred at r.t. for 16 h. The reaction was diluted with H_2O (100 mL) and acidified to pH 2–3 with 1 M HCl. The solution was cooled to 0 ºC and allowed to stand for 15 min. The precipitate was then collected in a fritted funnel, washed with pentane (×1), and dried under high vacuum for 4 h to yield the product as a red solid (3.0 g, 10 mmol,

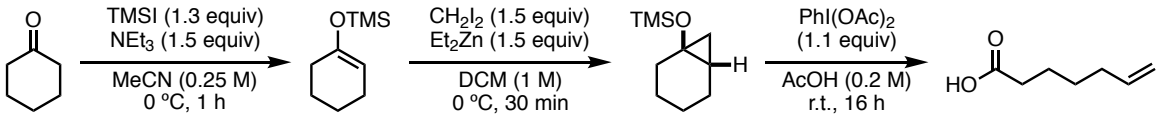
83%). Analytical data:[30] **^{1}H NMR** (500 MHz, DMSO-δ_6, 298 K): δ_H 7.52–7.45 (m, 2H), 7.22 (s, 1H), 7.13–7.09 (m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 3.65 (s, 2H), 0.86 (s, 9H), 0.57 (s, 6H) ppm; **^{13}C NMR** (125 MHz, DMSO-δ_6, 298 K): δ_C 173.2, 141.0, 130.7, 130.2, 121.6, 119.5, 119.1, 113.9, 111.2, 31.1, 26.3, 19.3, −4.0 ppm.



4-Methoxy-4-oxobutanoic acid (S39) (CAS: 3878-55-5): To a flame-dried 100-mL round-bottom flask was added succinic anhydride (10 g, 100 mmol, 1.0 equiv) and MeOH (20 mL, 5.0 M). The reaction was sealed with a septum and was stirred at 65 ºC for 16 h. The reaction was cooled to r.t. and concentrated. The concentrate was treated with pentane to induce precipitation. The precipitate was collected using a fritted funnel and was washed with pentane (×2) and dried under high vacuum to yield the product as a white solid (13 g, 98 mmol, 98%). Analytical data: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 3.70 (s, 3H), 2.73–2.58 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 177.7, 172.6, 52.0, 28.9, 28.7 ppm.



2-(Thiophen-2-yl)acetic acid (S40): To a 100-mL flask with a stir bar were added 2-thiophenylacetonitrile (0.95 mL, 8.0 mmol, 1.0 equiv), EtOH (16 mL), H_2O (16 mL), and potassium hydroxide (1.3 g, 24 mmol, 3.0 equiv), and the mixture was stirred at reflux for 3 h. The reaction was cooled to r.t. and acidified with 1 M HCl to pH 2–3. The reaction was extracted with DCM (×3) and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated to yield the product as a colourless oil (0.84 g, 5.9 mmol, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.69 (br s, 1H), 7.32–7.17 (m, 1H), 7.05–6.86 (m, 2H), 3.98 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 176.7, 134.2, 137.4, 137.1, 125.5, 35.2 ppm.



((*trans*-Bicyclo[4.1.0]heptan-1-yl)oxy)trimethylsilane: The TMS-protected cyclopropanol was prepared following General Procedure D (see Section F.2).

Step 1: **(Cyclohex-1-en-1-yloxy)trimethylsilane (S41):** Performed using cyclohexanone (2.1 mL, 20 mmol, 1.0 equiv), TMSCl (3.3 mL, 26 mmol, 1.3 equiv), sodium iodide (4.2 g, 28 mmol, 1.4 equiv), triethylamine (4.2 mL, 30 mmol, 1.5 equiv), and MeCN (80 mL, 0.25 M). The crude material was a colourless oil (3.2 g, 19 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 4.91–4.80 (m, 1H), 2.05–1.91 (m, 4H), 1.72–1.59 (m, 2H), 1.56–1.44 (m, 2H), 0.18 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 150.4, 104.4, 30.1, 24.0, 23.3, 24.5, 0.5 ppm; **R_f** (hexanes; $KMnO_4$/*p*-anisaldehyde): 0.44.

Step 2: **((*trans*-Bicyclo[4.1.0]heptan-1-yl)oxy)trimethylsilane (S42):**[31] Performed using **S41** (0.60 g, 3.5 mmol, 1.0 equiv), DCM (3.5 mL, 1.0 M), diiodomethane (0.43 mL, 5.3 mmol, 1.5

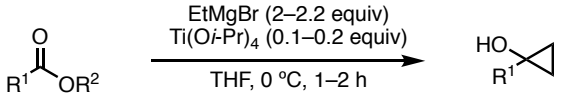
equiv), and diethylzinc (5.3 mL of a 1.0 M solution in hexanes, 5.3 mmol, 1.5 equiv). The reaction was stopped after 30 min. The crude residue was a colourless oil (0.58 g, 3.2 mmol, 91%). **S42** was used in the next step without further purification. $\mathbf{R_f}$ (5% EtOAc/hexanes; *p*-anisaldehyde): 0.26.

Step 3: **Hept-6-enoic acid (S43):**[32] To a 20-mL scintillation vial with a stir bar was transferred **S45** (0.58 g, 3.2 mmol, 1.0 equiv). AcOH (16 mL, 0.20 M) was added, then (diacetoxyiodo)benzene (1.1 g, 3.5 mmol, 1.1 equiv) was added at once. The reaction was stirred at r.t. for 16 h. The reaction was quenched with H_2O and extracted with DCM (×3), and the organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (0.32 g, 2.5 mmol, 78%). Analytical data:[33] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 10.79 (br s, 1H), 5.86–5.71 (m, 1H), 5.07–4.91 (m, 2H), 2.36 (td, J = 7.6, 0.7 Hz, 2H), 2.14–2.04 (m, 2H), 1.74–1.60 (m, 2H), 1.52–1.40 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 169.6, 138.4, 114.9, 34.0, 33.5, 28.4, 24.2 ppm; $\mathbf{R_f}$ (7:3 hexanes/EtOAc; $KMnO_4$): 0.69.

F. Preparation of cyclopropanol starting materials

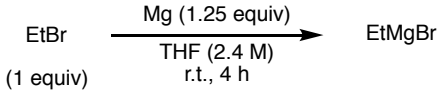
F.1. Preparation of cyclopropanols via Kulinkovich Reaction

General Procedure C: Kulinkovich Reaction[34]



(1 equiv)

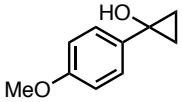
To a flame-dried round-bottom flask with a stir bar was added THF, and the solution was cooled to 0 ºC. To the flask were added the ester (1.0 equiv) and titanium(IV) isopropoxide (0.10–0.20 equiv) and the solution was stirred at 0 ºC for 10 min. Ethylmagnesium bromide (2.0–2.2 equiv of a solution in THF) was added in 6 portions over 1–2 h. The reaction was then quenched with 10% H_2SO_4 and extracted with Et_2O (×3). The organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash column chromatography to yield the desired cyclopropanol.



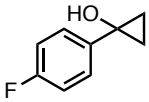
(1 equiv)

Ethylmagnesium bromide (typical procedure): To a flame-dried 1-L teardrop-shaped flask with a stir bar was added magnesium(0) turnings (36 g, 1.5 mol, 1.25 equiv) and the flask was flame-dried and cooled under vacuum. The flask was backfilled with N_2, THF (500 mL) was added and the magnesium turnings were activated with 1,2-dibromoethane (ca. 0.50 mL, 5.8 mmol, 0.0048 equiv). The flask was equipped with a reflux condenser and two syringes of bromoethane (2×45 mL; 90 mL total, 1.2 mol, 1.0 equiv) were inserted. Bromoethane was added dropwise until initiation occurred, then was added portionwise over 4 h. The solution was kept at r.t. using a cooling bath as necessary. After all the bromoethane was added the solution was diluted with THF (400 mL; total solution volume = 900 mL) and the solution was stirred for an additional 2 h at r.t. The solution was allowed to stand at r.t. for 4 h. The solution was titrated with I_2 using Knochel's protocol[35] and was found to have a concentration of 1.1 M (0.99 mol, 83%).

1-Phenylcyclopropanol (1a): The product was prepared according to General Procedure C with the following details: methyl benzoate (7.5 mL, 60 mmol, 1.0 equiv), THF (60 mL, 1.0 M), titanium(IV) isopropoxide (3.6 mL, 12 mmol, 0.20 equiv), and ethylmagnesium bromide (220 mL of a 0.60 M solution in THF, 132 mmol, 2.2 equiv) added portionwise over 1 h. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield **1a** as a colourless oil (4.2 g, 31 mmol, 52%). **1a** was stored at −20 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.44–7.21 (m, 5H), 2.53 (br s, 1H), 1.34–1.26 (m, 2H), 1.13–1.04 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 144.4, 128.5, 126.5, 124.6, 56.8, 18.0 ppm.

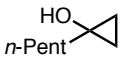


1-(4-Methoxyphenyl)cyclopropan-1-ol (S44): Prepared according to general procedure C with the following details: ethyl 4-methoxybenzoate (3.3 mL, 20 mmol, 1.0 equiv), THF (20 mL, 1.0 M), titanium(IV) isopropoxide (8.9 mL, 30 mmol, 3.0 equiv), and ethylmagnesium bromide (130 mL of a 0.46 M solution in THF, 60 mmol, 3.0 equiv) added portionwise over 1 h. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil, which was inseparable from 1-(4-methoxyphenyl)propan-1-ol (ratio of **S44**:side-product = 2.1:1; yield of **S44** = 1.4 g, 8.5 mmol, 43%). Analytical data:[36] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.33–7.22 (m, 2H), 6.91–6.84 (m, 2H), 3.80 (s, 3H), 2.30 (br s, 1H), 1.23–1.15 (m, 2H), 1.01–0.94 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.6, 136.3, 126.5, 113.9, 56.8, 55.5, 16.9 ppm.



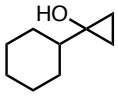
1-(4-Fluorophenyl)cyclopropan-1-ol (S45): Prepared according to General Procedure C with the following details: ethyl 4-fluorobenzoate (1.5 mL, 10 mmol, 1.0 equiv), THF (10 mL, 1.0 M), titanium(IV) isopropoxide (4.4 mL, 15 mmol, 1.5 equiv), and ethylmagnesium bromide (65 mL of a 0.46 M solution in THF, 30 mmol, 3.0 equiv) added portionwise over 1 h. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil, which was inseparable from side-product 1-(4-fluorophenyl)propan-1-ol (ratio of **S45**:side product = 1.6:1; yield of **S45** = 0.63 g, 4.1 mmol, 41%). Analytical data: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.22 (m, 2H), 7.08–6.95 (m, 2H), 2.33 (br s, 1H), 1.28–1.19 (m, 2H), 1.02–0.96 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 160.8 (d, J = 51 Hz), 140.0, 126.6 (d, J = 8.0 Hz), 115.2 (d, J = 7.6 Hz), 56.5, 17.5 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.16.

1-Benzylcyclopropanol (S46): The product was prepared according to General Procedure C with the following details: methyl 2-phenylacetate (2.1 mL, 15 mmol, 1.0 equiv), THF (50 mL, 0.30 M), titanium(IV) isopropoxide (0.44 mL, 1.5 mmol, 0.10 equiv), and ethylmagnesium bromide (28 mL of a 1.2 mL solution in THF, 33 mmol, 2.2 equiv) added portionwise over 1 h. The crude residue was purified by flash column chromatography (9:1 hexanes/EtOAc) to yield the product as a colourless oil (1.8 g, 12 mmol, 80%). Analytical data:[37] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.43–7.23 (m, 5H), 2.92 (s, 2H), 1.99 (br s, 1H), 0.88–0.83 (m, 2H), 0.71–0.65 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 138.6, 129.4, 128.5, 126.7, 56.2, 44.1, 13.3 ppm.



1-Pentylcyclopropan-1-ol (S47): The product was prepared according to General Procedure C with the following details: ethyl hexanoate (5.0 mL, 30 mmol, 1.0 equiv), THF (30 mL, 1.0 M), titanium(IV) isopropoxide (0.89 mL, 3.0 mmol, 0.10 equiv), and ethylmagnesium bromide (60 mL of a 1.0 M solution in THF, 60 mmol, 2.0 equiv) added portionwise over 2 h. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to

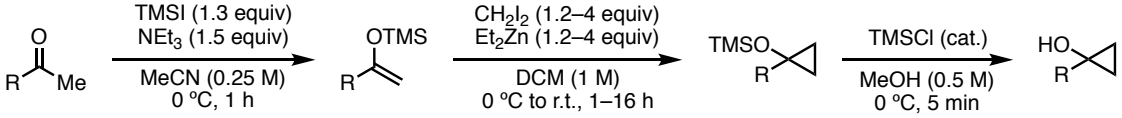
yield the product as a colourless oil (2.2 g, 17 mmol, 57%). Analytical data:[38] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 2.16–1.68 (br m, 1H), 1.63–1.23 (m, 8H), 1.03–0.83 (m, 3H), 0.81–0.67 (m, 2H), 0.55–0.38 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 56.0, 38.4, 32.0, 25.7, 22.8, 14.2, 13.6 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.55.



1-Cyclohexylcyclopropan-1-ol (S48): The product was prepared according to General Procedure C with the following details: methyl cyclohexanoate (2.1 mL, 15 mmol, 1.0 equiv), THF (30 mL, 0.50 M), titanium(IV) isopropoxide (0.44 mL, 1.5 mmol, 0.10 equiv), and ethylmagnesium bromide (48 mL of a 0.62 M solution in THF, 30 mmol, 2.0 equiv) added portionwise over 2 h. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (0.94 g, 6.7 mmol, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 1.87–1.58 (m, 7H), 1.31–1.08 (m, 4H), 1.00–0.97 (m, 1H), 1.73–0.64 (m, 2H), 0.47–0.39 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 59.7, 45.1, 29.0, 26.6, 26.6, 12.8 ppm.

F.2. Preparation of cyclopropanols via Simmons–Smith

General Procedure D: Simmons–Smith Sequence

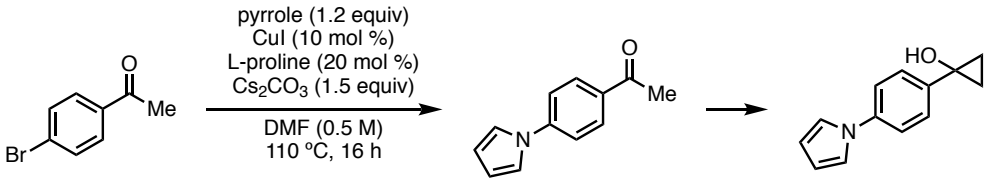


Step 1: To an appropriate-sized round-bottom flask with a stir bar was added sodium iodide (1.4 equiv) and the flask was flame-dried and cooled under vacuum. The flask was backfilled with N_2 and MeCN (0.25 M) was added, followed by the desired ketone (1.0 equiv). The solution was cooled to 0 ºC and TMSCl (1.3 equiv) was added, followed by triethylamine (1.5 equiv). The reaction was stirred at 0 ºC for 1 h under N_2. The reaction was concentrated and the concentrate was extracted with hexanes (×3) (Et_2O was used for more polar products). The organic extracts were combined and concentrated to yield the crude silyl enol ether.

Step 2: To an appropriate-sized flame-dried round-bottom flask with a stir bar was transferred the crude silyl enol ether (1.0 equiv). The flask was evacuated and backfilled with N_2 (×3) and DCM (1.0 M) was added. The solution was cooled to 0 ºC. Diiodomethane (1.2–4.0 equiv) was added. Diethylzinc (1.2–4.0 equiv of a 1.0 M stock solution in hexanes) was added dropwise over 10 min. The reaction was stirred at 0 ºC for 1 h, then at r.t. until full conversion of the silyl enol ether was achieved as determined by TLC. The reaction was opened to air, quenched with sat. aq. $NaHCO_3$, and extracted with DCM (×3). The organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated to yield the crude trimethylsilyl cyclopropanol.

Step 3:[39] To an appropriate-sized round-bottom flask with a stir bar was transferred the crude trimethylsilyl cyclopropanol, and MeOH (0.50 M) was added. The solution was cooled to 0 ºC and TMSCl (1 drop from a 1-mL syringe fitted with a 22-gauge needle) was added. The reaction

was stirred at 0 ºC for 5 min. The reaction was concentrated and the concentrate was purified by flash column chromatography to yield the desired cyclopropanol.



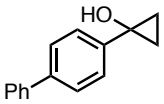
1-(4-(1*H*-Pyrrol-1-yl)phenyl)ethan-1-one (S49): To a 100-mL flask with a stir bar were added 4'-bromoacetophenone (3.0 g, 15 mmol, 1.0 equiv), copper(I) iodide (0.29 g, 1.5 mmol, 0.10 equiv), L-proline (0.35 g, 3.0 mmol, 0.20 equiv), cesium carbonate (7.5 g, 23 mmol, 1.5 equiv), and DMF (30 mL, 0.50 M), and the reaction mixture was stirred at 110 ºC for 16 h. The reaction was cooled to r.t., quenched with sat. aq. NH_4Cl, and extracted with EtOAc (×3). The organic extracts were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as an off-white solid (0.90 g, 4.9 mmol, 33%). Analytical data:[40] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.07–7.99 (m, 2H), 7.51–7.43 (m, 2H), 7.17 (t, J = 2.2 Hz, 2H), 6.39 (t, J = 2.2 Hz, 2H), 2.62 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 196.9, 144.2, 134.2, 130.3, 119.5, 119.2, 111.8, 26.7 ppm; **R_f** (9:1 hexanes/EtOAc; UV): 0.25.

1-(4-(1*H*-Pyrrol-1-yl)phenyl)cyclopropan-1-ol: The product was prepared following General Procedure D.

Step 1: **1-(4-(1-((Trimethylsilyl)oxy)vinyl)phenyl)-1*H*-pyrrole (S50):** Performed using 1-(4-(1*H*-pyrrol-1-yl)phenyl)ethan-1-one (0.90 g, 4.9 mmol, 1.0 equiv), MeCN (20 mL, 0.25 M), TMSCl (0.81 mL, 6.4 mmol, 1.3 equiv), sodium iodide (1.0 g, 6.9 mmol, 1.4 equiv), and triethylamine (1.0 mL, 7.4 mmol, 1.5 equiv). The concentrate was extracted with Et_2O. The crude product was a brown oil, which was used in the next step without further purification (1.2 g, 4.7 mmol, 96% crude yield). **R_f** (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.73.

Step 2: **1-(4-(1-((Trimethylsilyl)oxy)cyclopropyl)phenyl)-1*H*-pyrrole (S51):** Performed using DCM (4.7 mL, 1.0 M), diiodomethane (0.90 mL, 11 mmol, 2.4 equiv), and diethylzinc (11 mL of a 1.0 M solution in hexanes, 11 mmol, 2.4 equiv). The reaction was stopped after 16 h. The crude material was used in the next step without further purification.

Step 3: **1-(4-(1*H*-Pyrrol-1-yl)phenyl)cyclopropan-1-ol (S52):** Performed using MeOH (9.4 mL, 0.50 M) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as an off-white solid (0.23 g, 1.2 mmol, 24% over three steps). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.36 (app s, 4H), 7.08 (t, J = 1.8 Hz, 2H), 6.36–6.33 (m, 2H), 2.38 (br s, 1H), 1.32–1.27 (m, 2H), 1.09–1.04 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 141.9, 139.4, 125.8, 120.6, 119.5, 110.5, 56.5, 18.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{14}NO$ (M+H): 200.1070; found: 200.1070; **IR** (neat): 3246 (br), 1614, 1524, 1326, 1256, 1233, 1069, 1016, 922, 870, 821, 725, 716 cm^{-1}; **m.p.:** 135–137 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.17.

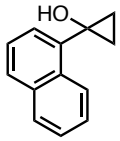


1-([1,1'-Biphenyl]-4-yl)cyclopropan-1-ol: The product was prepared following General Procedure D.

Step 1: **((1-([1,1'-Biphenyl]-4-yl)vinyl)oxy)trimethylsilane (S53):** Performed using 4-acetylbiphenyl (2.4 g, 12 mmol, 1.0 equiv), MeCN (48 mL, 0.25 M), TMSCl (2.0 mL, 16 mmol, 1.3 equiv), sodium iodide (2.5 g, 17 mmol, 1.4 equiv), and triethylamine (2.5 mL, 18 mmol, 1.5 equiv). The crude product was an orange solid, which was used in the next step without further purification (3.3 g, 12 mmol, 99% crude yield). $\mathbf{R_f}$ (5% EtOAc/hexanes; UV): 0.56.

Step 2: **(1-([1,1'-Biphenyl]-4-yl)cyclopropoxy)trimethylsilane (S54):** Performed using DCM (12 mL, 1.0 M), diiodomethane (1.1 mL, 14 mmol, 1.2 equiv), and diethylzinc (14 mL of a 1.0 M solution in hexanes, 14 mmol, 1.2 equiv). The reaction was stopped after 4 h. The crude material was used in the next step without further purification.

Step 3: **1-([1,1'-Biphenyl]-4-yl)cyclopropan-1-ol (S55):** Performed using MeOH (24 mL, 0.50 M) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as an off-white solid, which was inseparable from starting material 4-acetylbiphenyl (ratio of **S55**:starting material = 7.1:1; yield of **S55** = 1.4 g, 6.7 mmol, 56% over three steps). Analytical data:[41] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.65–7.52 (m, 4H), 7.51–7.30 (m, 5H), 1.60 (br s, 1H), 1.35–1.26 (m, 2H), 1.16–1.04 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 140.9, 128.9, 127.3, 127.2, 127.2, 127.2, 127.1, 125.0, 56.6, 18.2 ppm; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.19.



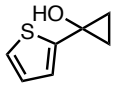
1-(Naphthalen-1-yl)cyclopropan-1-ol: Prepared following General Procedure D.

Step 1: **Trimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane (S56):** Performed using 1-acetylnaphthalene (1.8 mL, 12 mmol, 1.0 equiv), MeCN (48 mL, 0.25 M), TMSCl (2.0 mL, 16 mmol, 1.3 equiv), sodium iodide (2.5 g, 17 mmol, 1.4 equiv), and triethylamine (2.5 mL, 18 mmol, 1.5 equiv). The crude product was a yellow oil, which was used in the next step without further purification (2.9 g, 12 mmol, 99% crude yield). $\mathbf{R_f}$ (5% EtOAc/hexanes; UV): 0.71.

Step 2: **Trimethyl(1-(naphthalen-1-yl)cyclopropoxy)silane (S57):** Performed using DCM (12 mL, 1.0 M), diiodomethane (1.1 mL, 14 mmol, 1.2 equiv), and diethylzinc (14 mL of a 1.0 M solution in hexanes, 14 mmol, 1.2 equiv). The reaction was stopped after 4 h. The crude material was used in the next step without further purification.

Step 3: **1-(Naphthalen-1-yl)cyclopropan-1-ol (S58):** Performed using MeOH (24 mL, 0.50 M) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (1.8 g, 9.8 mmol, 82%). Analytical data:[42] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.59 (d, J = 8.8 Hz, 1H), 7.93–7.76

(m, 2H), 7.64–7.48 (m, 3H), 7.45–7.37 (m, 1H), 2.55–2.31 (m, 1H), 1.45–1.30 (m, 2H), 1.17–1.01 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 138.1, 134.2, 132.5, 129.0, 128.7, 126.4, 126.0, 125.8, 125.4, 125.3, 57.0, 13.9 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.39.

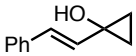


1-(Thiophen-2-yl)cyclopropan-1-ol: Prepared following General Procedure D.

Step *1:* **Trimethyl((1-(thiophen-2-yl)vinyl)oxy)silane (S59):** Performed using 2-acetylthiophene (1.3 mL, 12 mmol, 1.0 equiv), MeCN (48 mL, 0.25 M), TMSCl (1.8 mL, 16 mmol, 1.3 equiv), sodium iodide (2.5 g, 17 mmol, 1.4 equiv), and triethylamine (2.5 mL, 18 mmol, 1.5 equiv). The crude product was an orange oil, which was used in the next step without further purification (2.0 g, 10 mmol, 83% crude yield). **R_f** (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.73.

Step 2: **Trimethyl(1-(thiophen-2-yl)cyclopropoxy)silane (S60):** Performed using DCM (10 mL, 1.0 M), diiodomethane (1.9 mL, 24 mmol, 2.4 equiv), and diethylzinc (24 mL of a 1.0 M solution in hexanes, 24 mmol, 2.4 equiv). The reaction was stirred for 2 h. The crude material was used in the next step without further purification.

Step 3: **1-(Thiophen-2-yl)cyclopropan-1-ol (S61):** Performed using MeOH (20 mL, 0.50 M) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (0.37 g, 2.6 mmol, 26% over three steps). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): 7.18 (dd, J = 5.0, 1.2 Hz, 1H), 6.93 (dd, J = 6.1, 3.4 Hz, 1H), 6.87 (dd, J = 3.6, 1.2 Hz, 1H), 2.61 (br s, 1H), 1.34–1.26 (m, 2H), 1.11–1.03 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): 149.4, 127.0, 124.0, 122.3, 54.5, 18.6 ppm; **HRMS** *m/z* (DART): calcd for C_7H_9OS (M+H): 141.0369; found 141.0369; **IR** (neat): 3302, 3091, 3006, 1713, 1443, 1413, 1354, 1290, 1245, 1212, 1038, 1010, 964, 856, 845, 923, 690 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; $KMnO_4$/*p*-anisaldehyde): 0.31.

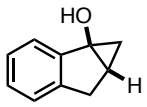


(*E*)-1-Styrylcyclopropan-1-ol: Prepared according to General Procedure D.

Step 1: **(*E*)-Trimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane (S62):** Performed using 4-phenylbut-3-en-2-one (1.8 g, 12 mmol, 1.0 equiv), TMSCl (2.0 mL, 16 mmol, 1.3 equiv), sodium iodide (2.5 g, 17 mmol, 1.4 equiv), triethylamine (2.5 mL, 18 mmol, 1.5 equiv), and MeCN (48 mL, 0.25 M). The crude residue was an orange oil (2.7 g, 12 mmol, >99% crude yield). **R_f** (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.70.

Step 2: **(*E*)-Trimethyl(1-styrylcyclopropoxy)silane (S63):** Performed using diiodomethane (2.1 mL, 26 mmol, 2.2 equiv), diethylzinc (26 mL of a 1.0 M solution in hexanes, 26 mmol, 2.2 equiv), and DCM (12 mL, 1.0 M). The crude residue was used in the next step without further purification.

Step 3: **(*E*)-1-Styrylcyclopropan-1-ol (S64):** Performed using MeOH (24 mL) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as an orange oil (0.74 g, 4.6 mmol, 38% over three steps). The NMR data was consistent with literature reports.[41] $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.23.



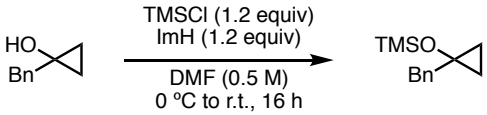
6,6a-Dihydrocyclopropa[*a*]inden-1a(1*H*)-ol (1b): Prepared following General Procedure D.

Step 1: **((1*H*-Inden-3-yl)oxy)trimethylsilane (S65):** Performed using indanone (1.3 g, 10 mmol, 1.0 equiv), TMSCl (1.6 mL, 13 mmol, 1.3 equiv), sodium iodide (2.1 g, 14 mmol, 1.4 equiv), triethylamine (2.1 mL, 15 mmol, 1.5 equiv), and MeCN (40 mL, 0.25 M). The crude residue was used in the next step without further purification (1.9 g, 9.3 mmol, 93% crude yield). $\mathbf{R_f}$ (5% EtOAc/hexanes; UV/$KMnO_4$): 0.69.

Step 2: **((*trans*-6,6a-Dihydrocyclopropa[*a*]inden-1a(1*H*)-yl)oxy)trimethylsilane (S66):** Performed using diiodomethane (0.89 mL, 11 mmol, 1.2 equiv), diethylzinc (11 mL of a 1.0 M solution in hexanes, 11 mmol, 1.2 equiv), and DCM (9.3 mL, 1.0 M). The crude residue was used in the next step without further purification.

Step 3: **6,6a-Dihydrocyclopropa[*a*]inden-1a(1*H*)-ol (1b):** Prepared using MeOH (19 mL, 0.50 M) and TMSCl (1 drop). The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield **1b** as a colourless oil (0.67 g, 4.6 mmol, 46% over three steps). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.49–7.43 (m, 1H), 7.26–7.20 (m, 1H), 7.20–7.10 (m, 2H), 3.21 (dd, J = 17.2, 6.5 Hz, 1H), 2.76 (br s, 1H), 2.68 (d, J = 17.2 Hz, 1H), 2.03–1.96 (m, 1H), 1.54 (dd, J = 9.4, 5.1 Hz, 1H), 0.46 (t, J = 4.8 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 146.0, 139.9, 126.7, 126.3, 125.5, 122.0, 67.6, 34.4, 24.9, 23.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{10}H_{10}O$ (M+H): 147.0804; found 147.0809; **IR** (neat): 3275 (br), 3068, 2910, 2838, 1674, 1602, 1477, 1436, 1334, 1284, 1233, 1213, 1184, 1074, 1049, 1023, 903, 834, 756, 721, 697 cm^{-1}; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.26.

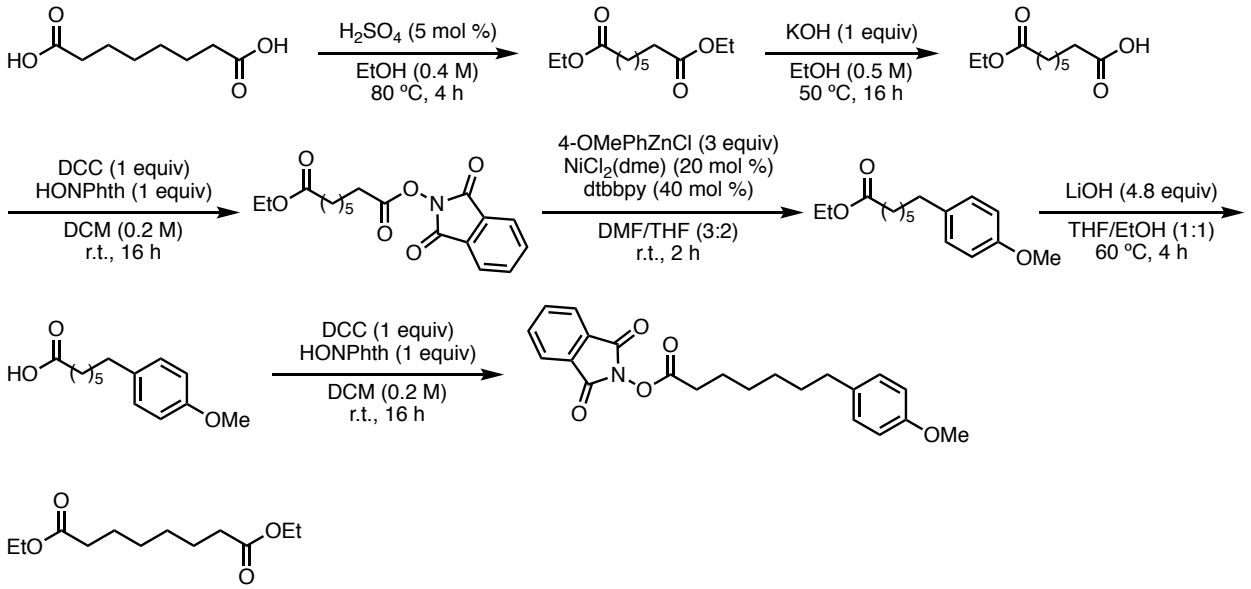
F.3. Preparation of TMS-protected 1-benzylcycopropanol



(1-Benzylcyclopropoxy)trimethylsilane (S67): To a 50-mL flask with a stir bar were added 1-benzylcyclopropanol (0.74 g, 5.0 mmol, 1.0 equiv) and DMF (10 mL, 0.50 M), and the solution was cooled to 0 ºC. Imidazole (0.41 g, 6.0 mmol, 1.2 equiv) and TMSCl (0.76 mL, 6.0 mmol, 1.2 equiv) were added. The reaction was warmed to r.t. and stirred for 16 h. The solution was extracted with pentane (×2) and the organic layers were combined, dried over $MgSO_4$, and concentrated. The crude residue was a colourless oil which was used without further purification (0.63 g, 2.9 mmol, 58% crude yield). $\mathbf{R_f}$ (8:2 hexanes/EtOAc): 0.88.

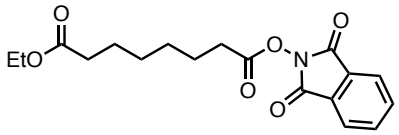
G. Preparation of starting materials for malabaricone B intermediate

G.1. Preparation of NHPI ester starting material

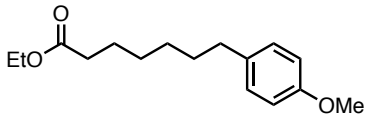


Diethyl octanedioate (S68): To a 250-mL flask with a stir bar were added suberic acid (5.2 g, 30 mmol, 1.0 equiv), EtOH (75 mL, 0.40 M), and conc. sulfuric acid (80 µL, 1.5 mmol, 0.050 equiv), and the reaction was stirred at 80 ºC for 4 h. The reaction was cooled to r.t. and concentrated. The concentrate was dissolved in EtOAc (150 mL), and the organic fraction was washed with sat. aq. $NaHCO_3$ (×1), water (×1), and brine (×1), dried over $MgSO_4$, and concentrated to yield the product as a colourless oil (6.0 g, 26 mmol, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 4.17–4.05 (m, 4H), 2.31–2.22 (m, 4H), 1.69–1.54 (m, 4H), 1.38–1.28 (m, 4H), 1.27–1.20 (m, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 173.9, 60.3, 34.4, 28.9, 24.9, 14.4 ppm; **R_f** (8:2 hexanes/EtOAc; $KMnO_4$): 0.66.

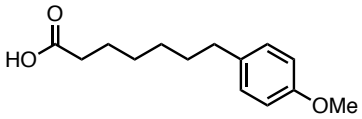
8-Ethoxy-8-oxooctanoic acid (S69): To a 100-mL flask with a stir bar were added EtOH (40 mL, 0.50 M) and potassium hydroxide (1.1 g, 20 mmol, 1.0 equiv), and the reaction was stirred until all solid was dissolved. **S68** (4.7 mL, 20 mmol, 1.0 equiv) was added and the reaction was stirred at 50 ºC for 16 h. The reaction was cooled to r.t., quenched with 1 M HCl (50 mL), and extracted with EtOAc (×3), and the organic fractions were combined, washed with H_2O (×3) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 20–40% EtOAc/hexanes) to yield **S69** as a colourless oil (2.1 g, 10.3 mmol, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 10.4 (br s, 1H), 4.31–3.97 (m, 2H), 2.42–2.20 (m, 4H), 1.71–1.53 (m, 4H), 1.43–1.28 (m, 4H), 1.28–1.14 (m, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 180.0, 174.0, 60.4, 34.4, 34.1, 28.8, 28.8, 24.8, 24.6, 14.3 ppm; **R_f** (8:2 hexanes/EtOAc; $KMnO_4$): 0.17.



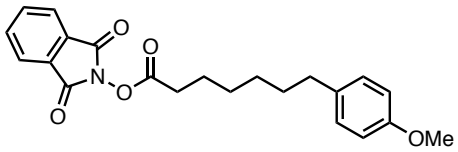
1-(1,3-Dioxoisoindolin-2-yl) 8-ethyl octanedioate (S70): Prepared according to General Procedure B on 8.0-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a colourless oil (2.6 g, 7.5 mmol, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.81–7.75 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 1.79 (pent, J = 7.4 Hz, 2H), 1.66 (pent, J = 6.0 Hz, 2H), 1.51–1.34 (m, 4H), 1.25 (td, J = 7.0, 0.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz $CDCl_3$, 298 K): δ_C 173.8, 169.7, 162.1, 134.9, 129.1, 124.1, 60.4, 34.4, 31.0, 28.7, 28.6, 24.8, 24.6, 14.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{22}NO_6$ (M+H): 348.1442; found: 348.1450; **IR** (neat): 2984, 2937, 2864, 1816, 1788, 1734, 1467, 1366, 1185, 1137, 1081, 1062, 966, 877, 696 cm^{-1}; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.52.



Ethyl 7-(4-methoxyphenyl)heptanoate (S71):[43] To a flame-dried 250-mL flask with a stir bar were added $NiCl_2$(dme) (0.11 g, 0.50 mmol, 0.20 equiv), dtbbpy (0.27 g, 1.0 mmol, 0.40 equiv), DMF (36 mL), and **S70** (0.87 g in 5.0 mL of DMF, 2.5 mmol, 1.0 equiv), and the solution was stirred at r.t. for 2 min under N_2. (4-Methoxyphenyl)zinc(II) chloride[43] (27 mL of a 0.28 M solution in THF, 7.5 mmol, 3.0 equiv) (total reaction volume = 68 mL of a 3:2 DMF/THF mixture, 0.037 M) was added down the side of the flask. The reaction was stirred at r.t. for 2 h under N_2. The reaction was quenched with 1 M HCl and extracted with EtOAc (×3). The organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–100% PhMe/hexanes) and the fractions containing product were collected and concentrated. **S71** was inseparable from homodimer side-product 4,4'-dimethoxy-1,1'-biphenyl and the material was used in the next step without further purification (ca. 0.55 g, 2.1 mmol, 84% crude yield). **R_f** (20% PhMe/hexanes; UV/$KMnO_4$): 0.21.

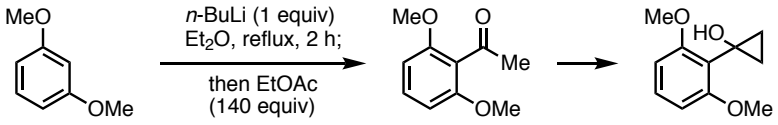


7-(4-Methoxyphenyl)heptanoic acid (S72): To a 50-mL flask with a stir bar were added **S71** (ca. 2.1 mmol, 1.0 equiv), lithium hydroxide (0.24 g, 10 mmol, 4.8 equiv), THF (10 mL), and H_2O (10 mL), and the reaction was stirred at 60 ºC for 4 h. The reaction was cooled to r.t. and acidified with 1 M HCl to pH 2–3. The solution was extracted with Et_2O (×3) and the organic fractions were washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 10–50% EtOAc/hexanes) and the fractions containing product were combined and concentrated (the sample contained some remaining homodimer side-product 4,4'-dimethoxy-1,1'-biphenyl from the synthesis of **S71**). The material was used in the next step without further purification (ca. 0.33 g, 0.89 mmol, 42% crude yield). **R_f** (9:1 hexanes/EtOAc): 0.06.



1,3-Dioxoisoindolin-2-yl 7-(4-methoxyphenyl)heptanoate (S73): The product was prepared according to General Procedure B on 0.89 mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (0.23 g, 0.60 mmol, 24% over three steps). **^{1}H NMR** (7.92–7.85 (m, 2H), 7.82–7.75 (m, 2H), 7.13–7.05 (m, 2H), 6.85–6.79 (m, 2H), 3.79 (s, 3H), 2.65 (t, J = 7.5 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 1.82–1.74 (m, 2H), 1.66–1.57 (m, 2H), 1.52–1.43 (m, 2H), 1.42–1.34 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 169.8, 162.2, 157.8, 134.9, 134.8, 129.4, 129.1, 124.1, 113.8, 55.4, 35.0, 31.5, 31.1, 28.8, 28.8, 24.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{24}NO_5$ (M+H): 382.1649; found: 382.1655; **IR** (neat): 2932, 2842, 1811, 1784, 1734, 1614, 1513, 1466, 1357, 1237, 1181, 1091, 1067, 1049, 1033, 963, 875, 819, 696 cm^{-1}; **m.p.:** 86–87 ºC; **R_f** (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.26.

G.2. Preparation of cyclopropanol starting material



1-(2,6-Dimethoxyphenyl)ethan-1-one (S74):[44] To a flame-dried 250-mL two-neck flask with a stir bar and reflux condenser were added Et_2O (30 mL, 0.50 M) and *n*-butyllithium (9.4 mL of a 1.6 M solution in hexanes, 15 mmol). 1,3-Dimethoxybenzene (2.0 mL, 15 mmol, 1.0 equiv) was added dropwise. The solution was heated at reflux for 2 h, then was cooled to r.t. Under inert atmosphere, the solution was poured into a 500-mL flask containing EtOAc (200 mL, ca. 140 equiv) and a stir bar. The reaction was opened to air and the solution was washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (0.35 g, 1.9 mmol, 13%). Analytical data:[45] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.26 (t, J = 8.4 Hz, 1H), 6.55 (s, J = 8.4 Hz, 2H), 3.80 (s, 6H), 2.48 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 203.0, 156.9, 130.8, 120.7, 104.1, 56.0, 32.5 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.16.

1-(2,6-Dimethoxyphenyl)cyclopropan-1-ol: The product was prepared according to General Procedure D.

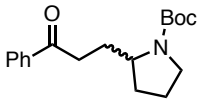
Step 1: **((1-(2,6-Dimethoxyphenyl)vinyl)oxy)trimethylsilane (S75):** Prepared using 1-(2,6-dimethoxyphenyl)ethan-1-one (0.35 g, 1.9 mmol, 1.0 equiv), MeCN (10 mL, 0.19 M), sodium iodide (0.40 g, 2.7 mmol, 1.4 equiv), TMSCl (0.32 mL, 2.5 mmol, 1.3 equiv), and triethylamine (0.40 mL, 2.9 mmol, 1.5 equiv). The crude residue was used in the next step without further purification (0.21 g, 0.83 mmol, 44% crude yield).

Step 2: **(1-(2,6-Dimethoxyphenyl)cyclopropoxy)trimethylsilane (S76):** Prepared using DCM (1.0 mL, 0.83 M), diiodomethane (0.24 mL, 3.0 mmol, 3.6 equiv), and diethylzinc (3.0 mL of a 1.0 M solution in hexanes, 3.0 mmol, 3.6 equiv). The crude residue was used in the next step without further purification. **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.61.

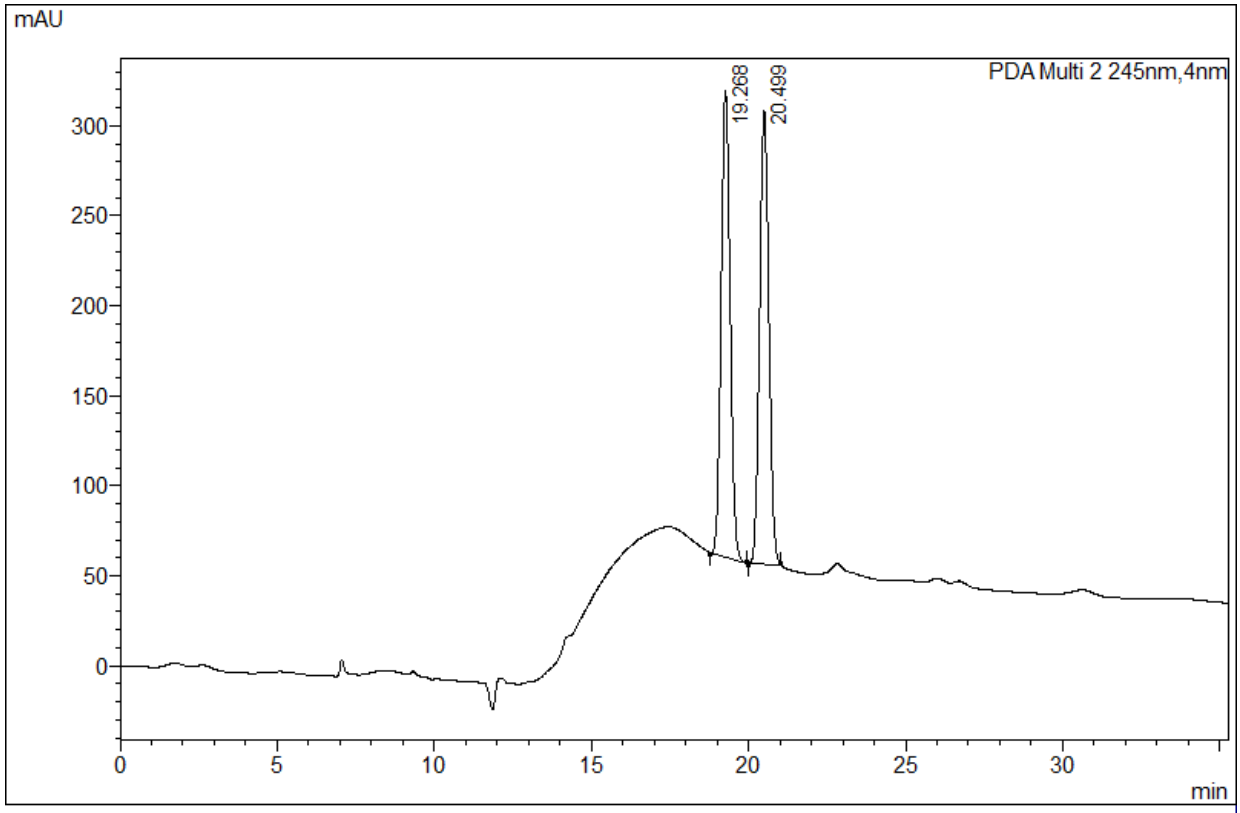
Step 3: **1-(2,6-Dimethoxyphenyl)cyclopropan-1-ol (S77):** Prepared using MeOH (2.0 mL, 0.41 M) and TMSCl (1 drop). The product was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as white-yellow solid (0.10 g, 0.51 mmol, 27% over three steps). The product was unstable on benchtop and was stored at −20 ºC under N_2. Analytical data: **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.21 (t, J = 8.4 Hz, 1H), 6.56 (d, J = 8.4 Hz, 2H), 3.86 (s, 6H), 2.93 (s, 1H), 1.17–1.12 (m, 2H), 0.94–0.90 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): 159.5, 129.3, 118.3, 104.3, 56.0, 49.6, 15.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{11}H_{18}NO_3$ (M+NH_4): 212.1281; found: 212.1279; **IR** (neat): 3527, 3110, 3006, 2950, 2843, 1588, 1472, 1457, 1435, 1360, 1246, 1218, 1098, 1072, 1017, 959, 926, 870, 776, 727 cm^{-1}; **m.p.:** 61–63 ºC; **R_f** (9:1 hexanes/EtOAc): 0.14.

H. Mechanistic experiments

H.1. Loss of stereoinformation



An isolated sample of **3m** from a standard reaction (see Section D) was analyzed by chiral HPLC, and was determined to be racemic: **Chiral HPLC** (Chiralpak IG, 25% *i*-PrOH/hexanes, 0.40 mL/min, λ = 245 nm): t_R (major): 20.50 min; t_R (minor): 19.27 min; 0% ee.

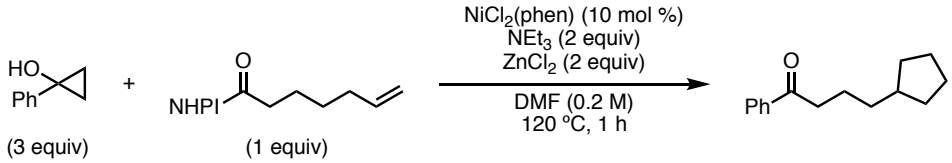


Peak Table

PDA Ch2 245nm

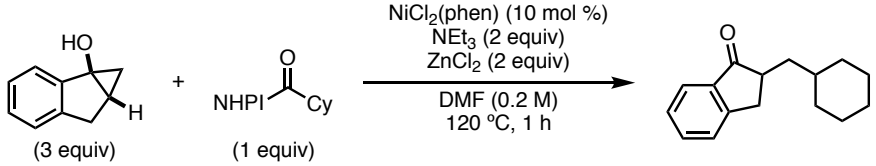
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.268	5171236	259289	0.000		M	
2	20.499	5177984	251784	0.000		M	
Total		10349220	511073				

H.2. 5-exo-trig cyclization



4-Cyclopentyl-1-phenylbutan-1-one (5): Prepared according to General Procedure A on 0.30 mmol scale. The crude sample was analyzed by GC-MS and ^{1}H NMR using dibromomethane (0.30 mmol, 1.0 equiv) as internal standard. The ring-closed:ring-opened selectivity was determined to be >20:1 by ^{1}H NMR and 96:1 (uncalibrated) by GC-MS, and the yield was determined to be 35% by ^{1}H NMR. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **5** as a colourless oil. Analytical data:[46] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.98–7.93 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.43 (m, 2H), 2.99–2.93 (m, 2H), 1.84–1.70 (m, 5H), 1.66–1.46 (m, 4H), 1.43–1.35 (m, 2H), 1.15–1.03 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 200.8, 137.2, 133.0, 128.7, 128.2, 40.1, 39.0, 36.0, 32.8, 25.3, 23.7 ppm; R_f (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.74.

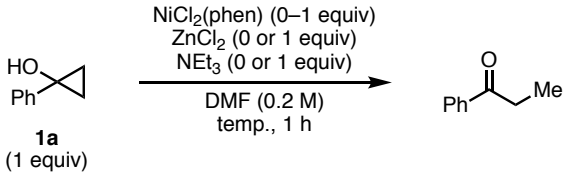
H.3. Polar (2e) β-carbon elimination



2-(Cyclohexylmethyl)-2,3-dihydro-1*H*-inden-1-one (3w): Prepared according to General Procedure A on 0.20 mmol scale. The crude sample was analyzed by GC-MS and only one isomer of the β-alkylated product (**3w**) was detected, with the remaining mass going towards ring-opened side-product 2-methyl-2,3-dihydro-1*H*-inden-1-one. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield **3w** as a colourless oil (6.0 mg, 0.026 mmol, 13%). Analytical data:[47] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.78–7.72 (m, 1H), 7.57 (td, J = 7.4 Hz, 1H), 7.48–7.41 (m, 1H), 7.39–7.32 (m, 1H), 3.33 (dd, J = 16.9, 7.6 Hz, 1H), 2.85–2.68 (m, 2H), 1.92–1.56 (m, 6H), 1.54–1.40 (m, 1H), 1.35–1.11 (m, 4H), 1.08–0.88 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 209.7, 153.9, 136.9, 134.7, 127.4, 126.7, 124.0, 45.5, 39.4, 36.3, 34.4, 33.6, 32.6, 26.7, 26.5, 26.4 ppm.

*H.4. Isomerization of cyclopropanol **1a***

Table S7. Isomerization of cyclopropanol **1a**



Entry	Temp. (ºC)	Equiv $ZnCl_2$	Equiv NEt_3	Equiv Ni	Remaining **1a** (%)[a]	Yield ketone (%)[a]
1	120	1	1	0.1	0	50
2	90	1	1	0.1	16	34
3	60	1	1	0.1	33	20
4	r.t.	1	1	0.1	61	17
5	120	1	1	0	0	74
6	120	1	0	0	0	67
7	120	0	1	0	45	21
8	120	0	0	0.1	17	43
9	120	0	0	1	42	21
10[b]	120	0	0	0	46	16

[a]GC-MS yield based on *n*-dodecane as internal standard.
[b]NEt_3•HCl (1 equiv) was added.

H. References

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