The cyclopropane ring as a reporter of radical leaving-group reactivity for Ni-catalyzed C(sp^3)–O arylation

L. Reginald Mills,[1] John J. Monteith,[1] Gabriel dos Passos Gomes,[1,2] Alán Aspuru-Guzik,[1,2,3,4] and Sophie A. L. Rousseaux[1]*

*sophie.rousseaux@utoronto.ca

[1]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON M5S 3H6, Canada
[3]Department of Computer Science, University of Toronto, 214 College St., Toronto, Ontario M5T 3A1, Canada
[4]Vector Institute for Artificial Intelligence, 661 University Ave. Suite 710, Toronto, Ontario M5G 1M1, Canada
[5]Lebovic Fellow, Canadian Institute for Advanced Research (CIFAR), 661 University Ave, Toronto, ON M5G 1M1, Canada

Supporting Information 1: Experimental Data

Table of Contents

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. DCM, 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. 1,4-Dioxane was purchased as anhydrous from Sigma–Aldrich in a Sure/Seal bottle and was degassed by sonicating under vacuum for 15 min prior to use. $Ni(acac)_2•xH_2O$ was purchased from Sigma–Aldrich as $Ni(acac)_2$ and was stored in a dessicator open to air, so was assumed to have a small amount of hydration and was denoted as "$Ni(acac)_2•xH_2O$". $Ni(acac)_2$ was purchased from Strem and was stored in a glovebox. Mg(II) and Zn(II) salts were purchased as anhydrous-grade and were stored and weighed in a glovebox. $Zn(OMe)_2$ for the formation of arylzinc reagents was prepared *in situ* from LiOMe and $ZnCl_2$ by stirring for 1 h in THF (see Section D).[1] All other commercial reagents were used as received. Compounds were purified by flash column chromatography using SiliCycle SilicaFlash P60 silica gel. The 8- and 16-mL threaded culture tubes used for reactions were purchased from Fisher (catalogue nos. 14-957-76A and 14-959-35A) and were sealed using size 19 rubber septa and electrical tape.

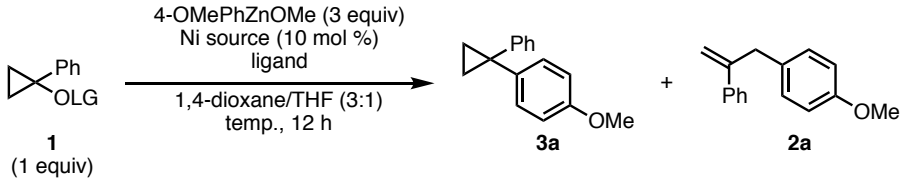
Thiocarbamate starting materials were stored at r.t. on the benchtop with no special precautions for air, moisture, or light. Arylzinc reagents were stored in culture tubes under N_2 at r.t. Electron-rich cyclopropanes are known to be unstable to air.[2] As a precaution, all crude residues were stored under N_2 at −20 ºC, and all electron-rich cyclopropane products were kept under N_2 at −20 ºC for long-term storage.

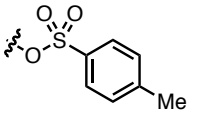
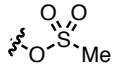
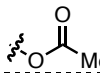
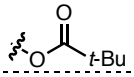
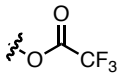
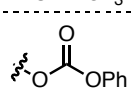
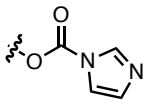
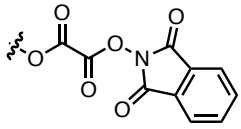
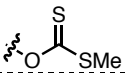
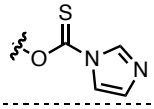
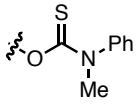
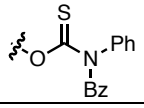
GC-MS data was obtained on a Shimadzu GCMS-QP2010 SE; yields represent peak areas calibrated against each compound's response factor relative to *n*-dodecane internal standard. ^1H and ^{13}C NMR spectra were recorded on Varian MercuryPlus 400 MHz, Agilent DD2 500 MHz, or Bruker AvanceIII 400 MHz spectrometers. 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), *p*-anisaldehyde, or vanillin 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. Chiral HPLC analysis was performed on a Shimadzu 20A series system using a Daicel Chiralpak column (IA).

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

B. Reaction optimization

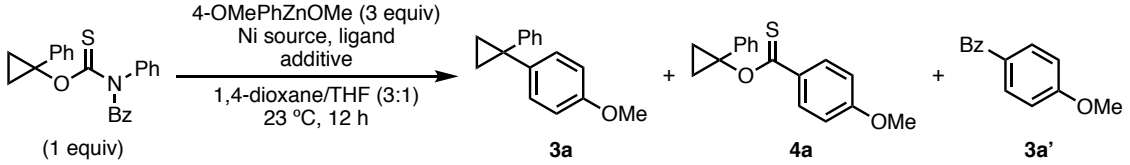
Table S1. Evaluation of cyclopropanol leaving group



Entry	–OLG (leaving group)		Ni source	ligand (mol %)	Temp (°C)	Yield **3a** (%)[a]	Yield **2a** (%)[a]
1		**(1a)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	9
2			$NiCl_2(PPh_3)_2$	none	110	0	96
3			$NiCl_2(PCy_3)_2$	none	110	0	41
4		**(1b)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	3
6			$NiCl_2(PPh_3)_2$	none	110	0	96
6			$NiCl_2(PCy_3)_2$	none	110	0	52
7		**(S6)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
8			$NiCl_2(PCy_3)_2$	none	110	0	0
9		**(1d)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
10			$NiCl_2(PCy_3)_2$	none	110	0	trace
11		**(1c)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
12			$NiCl_2(PCy_3)_2$	none	110	0	3
13		**(1f)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
14			$NiCl_2(PPh_3)_2$	none	110	0	trace
15			$NiCl_2(PCy_3)_2$	none	110	1	0.6
16		**(1g)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
17			$NiCl_2(PCy_3)_2$	none	23	0.3	0.2
18			$NiCl_2(PPh_3)_2$	none	110	trace	0
19			$NiCl_2(PCy_3)_2$	none	110	1	0.4
20		**(1e)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
21[b]			$NiCl_2(dme)$	dtbbpy (20)	23	1	0
22			$NiCl_2(PPh_3)_2$	none	110	0	0
23		**(1i)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	29	3
24			$NiCl_2(PCy_3)_2$	none	110	14	10
25		**(1j)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	54	0
26			$NiCl_2(PPh_3)_2$	none	110	40	6
27			$NiCl_2(PCy_3)_2$	none	110	37	5
28		**(1h)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	0	0
29			$NiCl_2(dme)$	bathocuproine (20)	23	0.5	0
30			$NiCl_2(dme)$	Bphen (20)	23	0.6	0
31			$NiCl_2(dme)$	neocuproine (20)	23	1	0
32			$NiCl_2(PCy_3)_2$	none	23	1	2
33			$NiCl_2(PPh_3)_2$	none	110	0	trace
34		**(1k)**	$Ni(acac)_2•xH_2O$	bathocuproine (20)	23	77	0
35			$NiCl_2(PPh_3)_2$	none	110	2	0

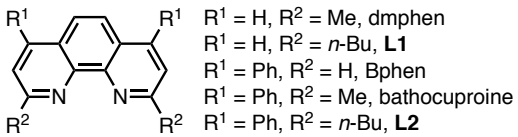
[a]GC-MS yield using *n*-dodecane as internal standard; [b]Using $Ru(bpy)_3(PF_6)_2$ (1 mol %), blue LEDs, ArZnCl (2 equiv) and acetone/THF (1:1).

Table S2. Evaluation of Ni sources and ligands

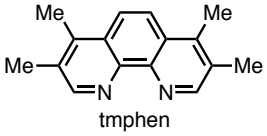


Entry	Ni source	Ligand (mol %)	Additive (equiv)	Yield **3a** (%)	Yield **4a** (%)	Yield **3a'** (%)
1	$Ni(acac)_2 \cdot xH_2O$	bathocuproine (20)	none	78	12	13
2	$Ni(acac)_2 \cdot xH_2O$	bpy (20)	$MgBr_2$ (2)	<1	29	43
3	$Ni(acac)_2 \cdot xH_2O$	dtbbpy (20)	$MgBr_2$ (2)	2	45	41
4	$Ni(acac)_2 \cdot xH_2O$	phen (20)	$MgBr_2$ (2)	0	7	71
5	$Ni(acac)_2 \cdot xH_2O$	Bphen (20)	$MgBr_2$ (2)	0	21	49
6	$Ni(acac)_2 \cdot xH_2O$	2,9-dmphen (20)	$MgBr_2$ (2)	3	40	23
7	$Ni(acac)_2 \cdot xH_2O$	tmphen (20)	$MgBr_2$ (2)	<1	22	14
8	$Ni(acac)_2 \cdot xH_2O$	Bn-BIOX (20)	$MgBr_2$ (2)	<1	<1	61
9	$Ni(acac)_2 \cdot xH_2O$	terpy (20)	$MgBr_2$ (2)	<1	0	5
10	$Ni(acac)_2 \cdot xH_2O$	bpp (20)	$MgBr_2$ (2)	1	0	36
11	$Ni(acac)_2 \cdot xH_2O$	**L1** (20)	$MgBr_2$ (2)	10	55	17
12	$Ni(acac)_2 \cdot xH_2O$	**L2** (20)	$MgBr_2$ (2)	<1	41	10
13	$Ni(acac)_2$	none	none	2	0	44
14	$Ni(acac)_2$	bathocuproine (20)	none	46	21	9
15	$Ni(acac)_2$	bathocuproine (15)	none	42	26	10
16	$Ni(acac)_2$	bathocuproine (12)	none	37	45	8
17	$Ni(acac)_2$	bathocuproine (10)	none	33	38	14
18	$NiCl_2$(dme)	bathocuproine (20)	none	51	17	9
19	$NiBr_2$(dme)	bathocuproine (20)	none	39	38	11
20	$Ni(OAc)_2 \cdot 4H_2O$	bathocuproine (20)	none	14	29	27
21	$NiCl_2 \cdot 6H_2O$	bathocuproine (20)	none	29	50	11
22	$Ni(dpm)_2$	bathocuproine (20)	none	14	2	37
23	$Ni(acac)_2 \cdot xH_2O$	SIPr•HCl (12)	none	1	0	27
24	$Ni(acac)_2 \cdot xH_2O$	IPr•HCl (12)	none	1	0	32
25	$Ni(acac)_2 \cdot xH_2O$	IMes•HCl (12)	none	1	2	27
26	$Ni(acac)_2 \cdot xH_2O$	dppf (12)	none	0	3	5
27	$Ni(acac)_2 \cdot xH_2O$	CyJohnPhos (12)	none	1	0	17
28	$NiCl_2(PPh_3)_2$	none	none	0	0	3
29	$NiCl_2(PCy_3)_2$	none	none	<1	0	15
30	$NiCl_2$(dppe)	none	none	0	0	0
31	none	none	none	0	0	0

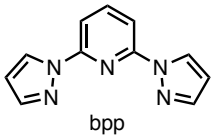
GC-MS yields using *n*-dodecane as internal standard.



R^1 = H, R^2 = Me, dmphen
R^1 = H, R^2 = *n*-Bu, **L1**
R^1 = Ph, R^2 = H, Bphen
R^1 = Ph, R^2 = Me, bathocuproine
R^1 = Ph, R^2 = *n*-Bu, **L2**

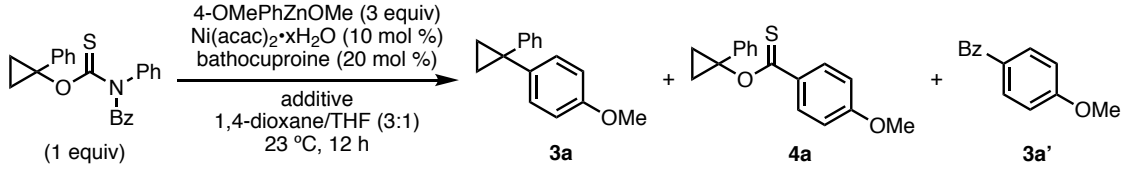


tmphen



bpp

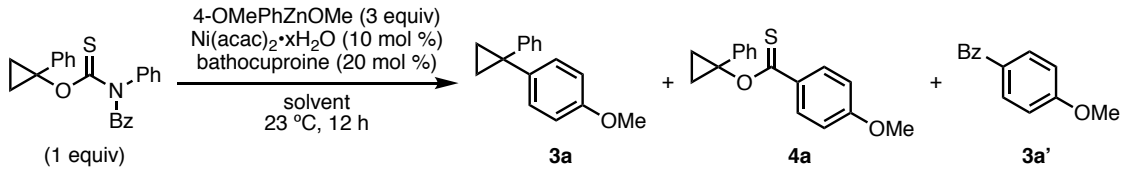
Table S3. Evaluation of additives



Entry	Additive	Yield **3a** (%)	Yield **4a** (%)	Yield **3a'** (%)
1	none	77	12	13
2	$MgCl_2$ (2)	73	12	5
3	$MgBr_2$ (2)	61	14	5
4	$MgBr_2$ (3)	57	7	12
5	MgI_2 (1)	0	0	0
6	LiCl (1)	50	9	12
7	LiBr (1)	50	10	11
8	LiOAc (1)	47	5	12
9	$ZnCl_2$ (1)	2	0	36
10	$ZnBr_2$ (1)	3	0	59
11	ZnI_2 (1)	2	0	50
12	$Zn(OAc)_2$ (1)	13	26	26
13	$Zn(OMe)_2$ (1)	30	0	14
14	$ZnCl_2$ (1) and $MgBr_2$ (1)	5	0	51

GC-MS yields using *n*-dodecane as an internal standard.

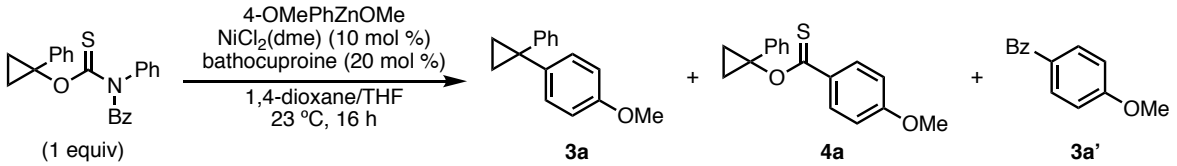
Table S4. Evaluation of solvent



Entry	solvent	Yield **3a** (%)	Yield **4a** (%)	Yield **3a'** (%)
1	1,4-dioxane/THF (3:1)	77	12	13
2	PhMe/THF (3:1)	21	16	36
3	THF	1	66	34
4	DME/THF (3:1)	3	17	49
5	CMPE/THF (3:1)	0	0	0
6	MTBE/THF (3:1)	36	24	21
7	DMF/THF (3:1)	0	0	4
8	MeCN/THF (3:1)	0	0	0
9	DCM/THF (3:1)	2	34	16
10	Et_2O/THF (3:1)	1	24	7

GC-MS yields using *n*-dodecane as an internal standard.

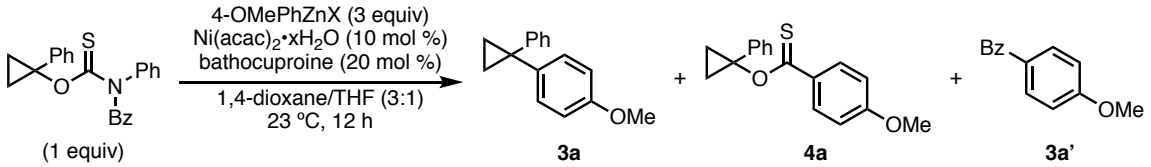
Table S5. Evaluation of arylzinc stoichiometry



Entry	Ratio 1,4-dioxane/THF	equiv ArZnOMe	Yield **3a** (%)[b]	Yield **4a** (%)[b]	Yield **3a'** (%)[b]
1	2.9:1	1.4	1	71	8
2	2.5:1	1.6	1	90	10
3	1.0:1	2.3	6	79	15
4	1.8:1	2.3	9	50	18
5	1.9:1	2.3	10	53	18
6	3.0:1	2.3	32	40	13
7	4.0:1	2.3	36	36	14
8	1.3:1	3.0	37	<5	13
9	1.5:1	3.0	40	<5	14
10	2.0:1	3.0	41	0	14
11	2.7:1	3.0	44	0	12
12	3.0:1	3.0	51	17	9
13	4.0:1	3.0	47	<5	13
14	1.2:1	3.4	38	0	15
15	1.0:1	4.0	33	0	17
16	2.0:1	4.0	43	0	14
17	0.9:1	4.4	37	0	28

The reaction concentration depended on the concentration of arylzinc, which was generally 0.30–0.40 M in THF.
[b]GC-MS yields using *n*-dodecane as an internal standard.

Table S6. Evaluation of arylzinc reagents

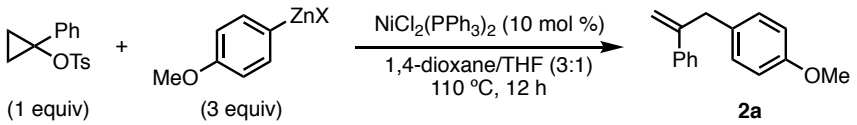


(1 equiv) **3a** **4a** **3a'**

Entry	–ZnX[a]	Yield **3a** (%)[b]	Yield **4a** (%)[b]	Yield **3a'** (%)[b]
1	–ZnOMe•MgX_2[c]	77	12	13
2	–ZnCl•MgX_2	68	5	11
3	–ZnBr•MgX_2	61	0	8
4	–ZnI•MgX_2	65	0	7
5	–ZnOAc•MgX_2[d]	0	0	0
6	Ar_2Zn (1.5 equiv)	35	2	15
7	Ar_2Zn (3 equiv)	7	0	10
8	–ZnCl•LiCl	57	2	9
9	–ZnOMe•LiCl[e]	trace	0	7
10[f]	–ZnOMe•LiCl[e]	trace	31	3
11	—MgBr[g]	0	0	8
12	–ZnO*t*-Bu•MgX_2	3	81	8
13	–ZnOPh•MgX_2	0	0	0
14	–ZnSPh•MgX_2	0	0	0

[a]For arylzinc reagents denoted as –ZnX•MgX_2, the reagent was prepared from the Grignard (ArMgBr•LiCl), which was made from 4-bromoanisole (1 equiv), Mg(0) turnings (2 equiv), and LiCl (1.2 equiv). For arylzinc reagents denoted as –ZnX•LiCl, the reagent was prepared from the aryllithium, which was made from 4-bromoanisole (1 equiv) and *n*-BuLi (1.1 equiv) via lithium-halogen exchange.
[b]GC-MS yields using *n*-dodecane as an internal standard.
[c]Using $Zn(OMe)_2$ prepared in situ from $ZnCl_2$ (1 equiv) and LiOMe (2 equiv).
[d]The arylzinc solution was heterogenerous.
[e]Using $Zn(OMe)_2$ prepared from MeOH and Et_2Zn.
[f]$MgCl_2$ (2 equiv) was added to the reaction.
[g]Using the corresponding Grignard reagent rather than the arylzinc reagent.

Table S7. Evaluation of arylzinc reagents for ring-opening of 1-phenylcyclopropyl tosylate



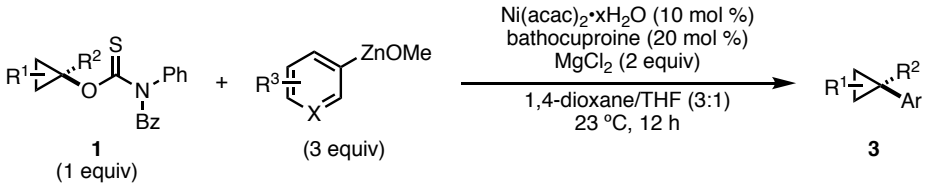
(1 equiv) (3 equiv) **2a**

Entry	–ZnX	Yield **2a** (%)[b]
1	–ZnOMe•MgX_2	96
2	–ZnCl•MgX_2	63
3	–ZnCl•LiX	11
4	–ZnOMe•LiX	3

GC-MS yields using *n*-dodecane as internal standard.

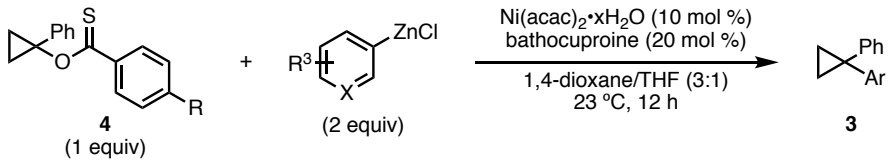
C. Preparation of cyclopropane products

General Procedure A: Synthesis of cyclopropanes



Representative procedure for 0.20-mmol scale reaction: A 16-mL threaded culture tube was equipped with a stir bar, sealed with a size 19 septum, and was flame-dried under vacuum and cooled under N_2. Thiocarbamate substrate (0.20 mmol, 1.0 equiv), bathocuproine (14 mg, 0.040 mmol, 20 mol %), and $Ni(acac)_2•xH_2O$ (5.1 mg, 0.020 mmol, 10 mol %) were added. The tube was sealed, evacuated and backfilled with N_2 (×3), and brought into a glovebox. Magnesium(II) chloride (38 mg, 0.40 mmol, 2.0 equiv) was added. The tube was re-sealed with a septum and electrical tape and was removed from the glovebox. 1,4-Dioxane (anhydrous, degassed; an amount to reach a 3:1 1,4-dioxane/THF ratio, according to the volume of titrated arylzinc(II) methoxide reagent required for 0.60 mmol) was added, and the solution was stirred at r.t. for 5 min. After 5 min at r.t., the solution turns pink-orange (Figure S1). While stirring, arylzinc solution (0.60 mmol of a solution in THF, 3.0 equiv) was added at once, and the reaction was stirred at r.t. (23 ºC) for 12 h. The reaction was opened to air and quenched with sat. aq. NH_4Cl. If analyzing by GC-MS, *n*-dodecane was added as internal GC-MS standard. The solution was extracted with EtOAc (×3) and the organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated. (The sulfur-containing aqueous waste was treated with bleach and disposed of appropriately.) If analyzing by ^1H NMR, dibromomethane was added as internal ^1H NMR standard. The crude residue was purified by flash column chromatography to yield the desired cyclopropane.

General Procedure B: Synthesis of cyclopropanes from thiobenzoates



Reactions using thiobenzoates (**4**) as starting materials were performed as described in General Procedure A with the following modifications: thiobenzoate (**4**) (1.0 equiv) instead of thiocarbamate substrate, arylzinc(II) chloride (2.0 equiv) instead of arylzinc(II) methoxide, and no $MgCl_2$ was added.

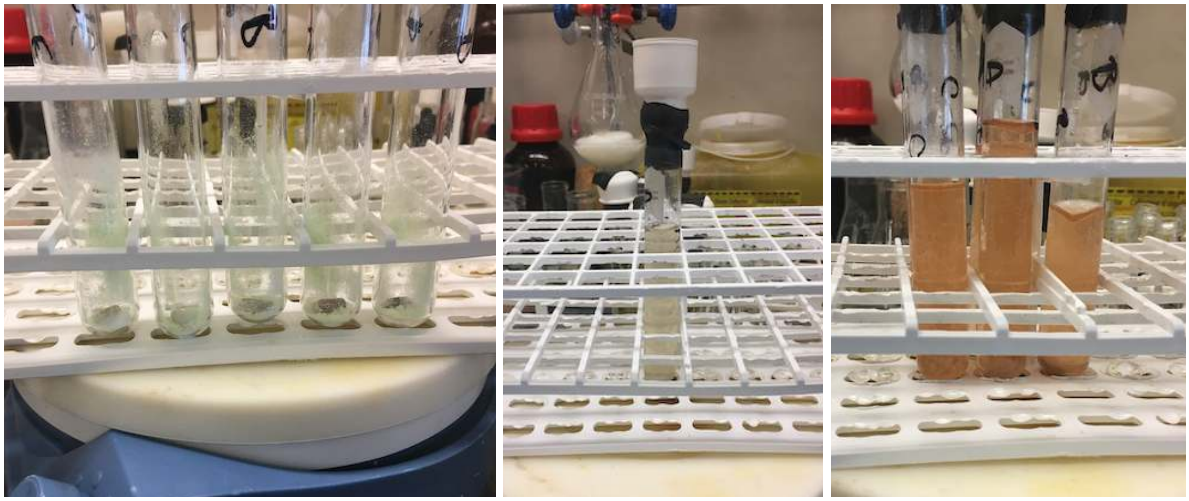


Figure S1. (Left) Appearance of reaction tubes with all solids; (Centre) Appearance of solution immediately after adding 1,4-dioxane; (Right) Appearance after stirring in 1,4-dioxane at r.t. for 5 min.

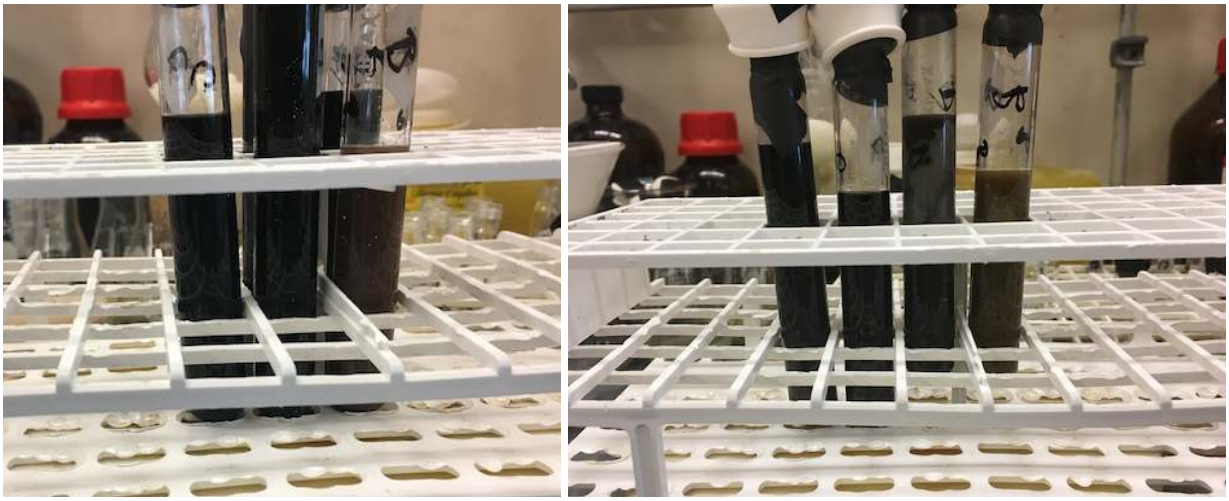
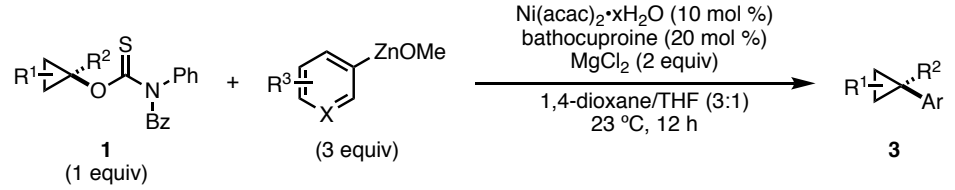
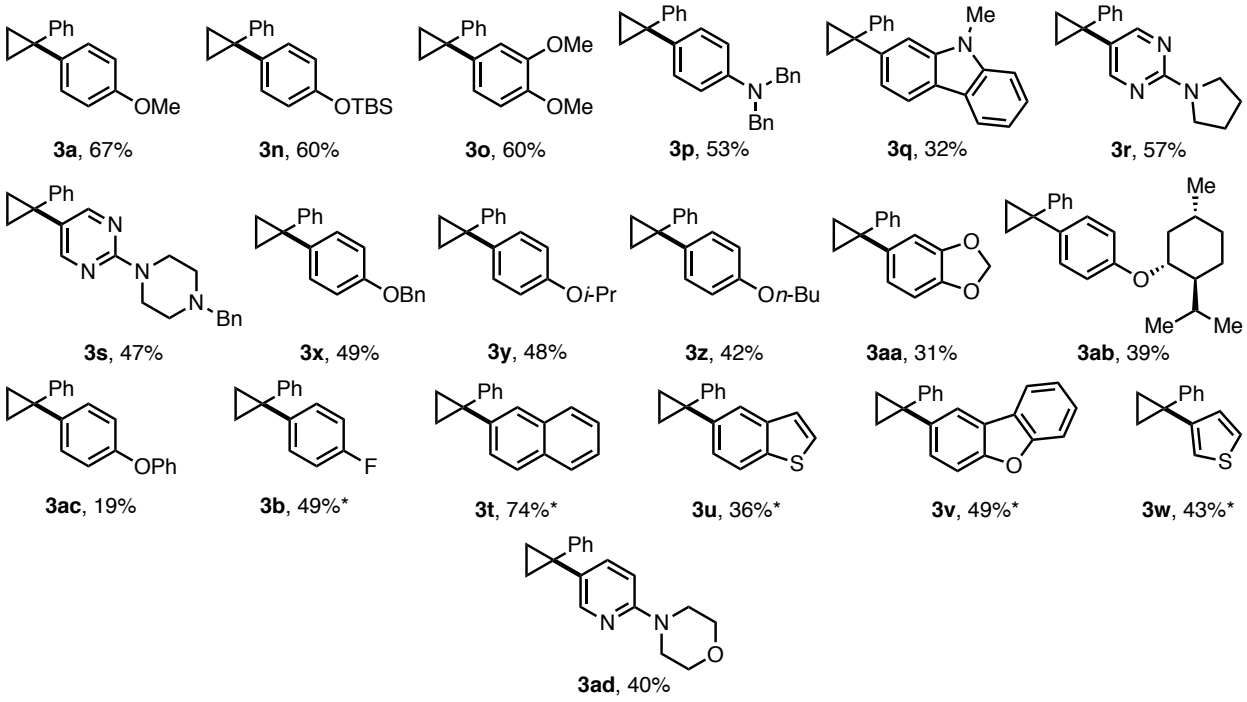
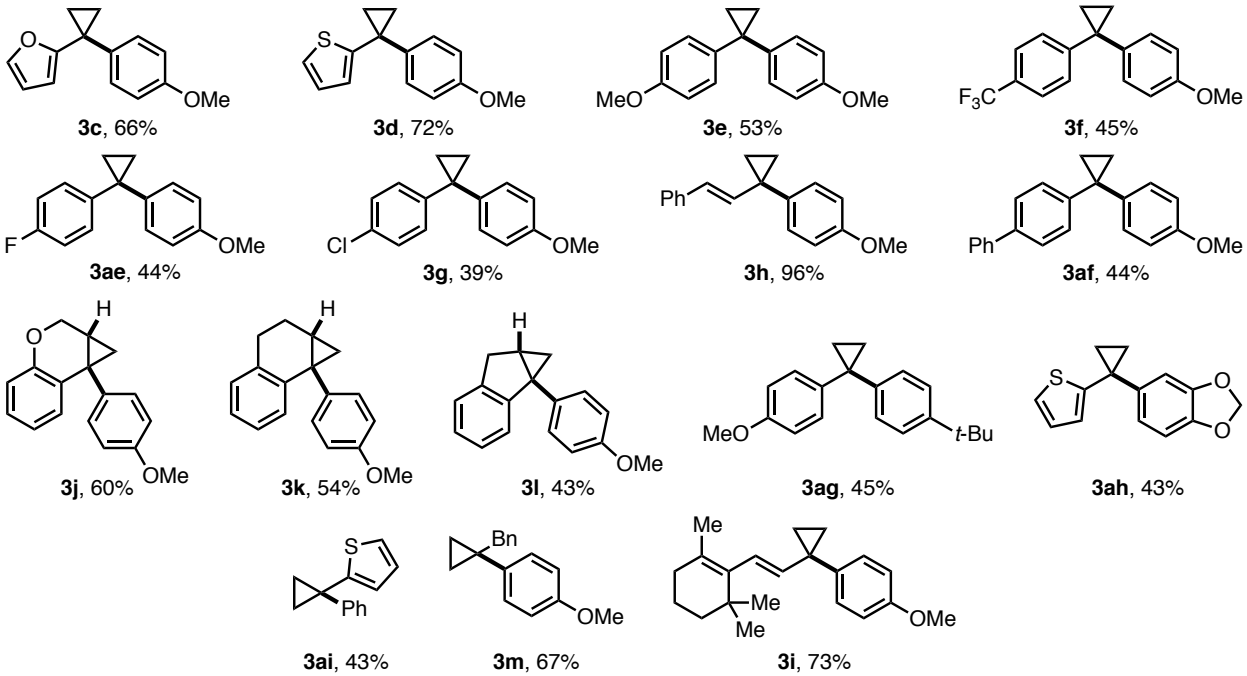


Figure S2. (Left) Appearance of reactions after stirring with arylzinc reagent for ca. 1 min; (Right) Appearance of reactions after stirring for 12 h.

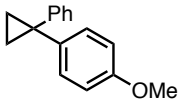
Table S8. Complete scope table



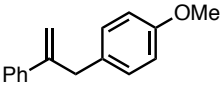




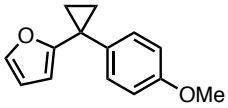
*Using 4-methoxyphenyl thiobenzoate ester **1a** instead of **1k**. See experimental data for details.



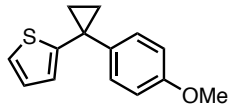
1-Methoxy-4-(1-phenylcyclopropyl)benzene (3a): Prepared on 0.30-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (44 mg, 0.200 mmol, 67%). Analytical data: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.31–7.13 (m, 7H), 6.88–6.80 (m, 2H), 3.80 (s, 3H), 1.34–1.20 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.9, 146.3, 137.8, 129.9, 128.2, 127.9, 125.7, 113.7, 55.3, 29.2, 16.3 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{20}NO$ (M+NH_4): 242.1539; found: 242.1542; **IR** (neat): 3081, 3003, 2835, 1604, 1511, 1496, 1458, 1243, 1173, 1028, 825, 756 cm^{-1}; **GC-MS** *m/z* (% relative intensity): 224[M^+] (86), 193 (66), 165 (43), 152 (45), 147 (26), 115 (100), 91 (26); **R_f** (50% PhMe/hexanes; UV/*p*-anisaldehyde): 0.51.



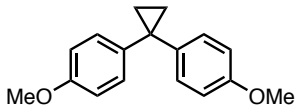
1-Methoxy-4-(2-phenylallyl)benzene (2a): The product was prepared on 0.10-mmol scale. To a 16-mL threaded culture tube with a stir bar was added **1a** (91 mg, 0.30 mmol, 1.0 equiv) and $NiCl_2(PPh_3)_2$ (20 mg, 0.030 mmol, 10 mol %), and the tube was sealed and evacuated and backfilled with N_2 (×3). 1,4-Dioxane (8.7 mL) was added and the reaction was stirred at r.t. for 5 min. 4-Methoxyphenylzinc(II) methoxide (2.9 mL of a 0.31 M solution in THF, 0.90 mmol, 3.0 equiv) was added and the reaction was stirred at 110 ºC for 16 h. The reaction was cooled to r.t., quenched with sat. aq. NH_4Cl, extracted with EtOAc (×2), and the organic fractions were combined, 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 (55 mg, 0.246 mmol, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.50–7.43 (m, 2H), 7.36–7.24 (m, 3H), 7.21–7.14 (m, 2H), 6.89–6.81 (m, 2H), 5.50 (app d, J = 1.4 Hz, 1H), 5.04 (app dd, J = 2.8, 1.4 Hz, 1H), 3.84–3.78 (m, 5H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 158.1, 147.5, 141.0, 131.7, 130.0, 128.4, 127.5, 126.3, 114.4, 113.9, 55.4, 40.9 ppm; **GC-MS** *m/z* (% relative intensity): 224[M^+] (44), 209 (10), 193 (12), 146 (9), 121 (100), 103 (13), 91 (11), 77 (22); **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.79.



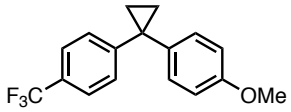
2-(1-(4-Methoxyphenyl)cyclopropyl)furan (3c): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (PhMe) to yield the product as a colourless oil (28 mg, 0.131 mmol, 66%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.30–7.26 (m, 2H), 7.25–7.23 (m, 1H), 6.88–6.82 (m, 2H), 6.25–6.20 (m, 1H), 5.81–5.76 (m, 1H), 3.80 (s, 3H), 1.39–1.35 (m, 2H), 1.20–1.16 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 159.4, 158.5, 140.8, 135.0, 130.4, 113.8, 110.3, 105.3, 55.4, 24.1, 14.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{15}O_2$ (M+H): 215.1067; found: 215.1067; **IR** (neat): 3002, 2836, 1611, 1581, 1512, 1462, 1293, 1243, 1159, 1032, 1007, 832, 802, 728, 582 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.59.



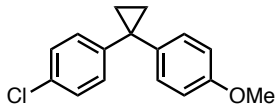
2-(1-(4-Methoxyphenyl)cyclopropyl)thiophene (3d): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (33 mg, 0.143 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.35–7.27 (m, 2H), 7.10–7.03 (m, 1H), 6.91–6.82 (m, 3H), 6.71–6.65 (m, 1H), 3.80 (s, 3H), 1.38–1.30 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.4, 152.6, 137.1, 130.2, 126.7, 123.7, 123.0, 113.8, 55.4, 25.8, 18.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{15}OS$ (M+H): 231.0838; found: 231.0842; **IR** (neat): 3004, 2943, 2834, 1161, 1511, 1441, 1242, 1176, 1032, 827, 691 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.61.



4,4'-(Cyclopropane-1,1-diyl)bis(methoxybenzene) (3e): Prepared on 0.074-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–80% PhMe/hexanes) to yield the product as a white solid (10 mg, 0.039 mmol, 53%). Analytical data:[2] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.17–7.13 (m, 4H), 6.82–6.78 (m, 4H), 3.78 (s, 6H), 1.21 (s, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 157.7, 138.3, 129.3, 113.6, 55.3, 28.5, 16.0 ppm; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.42.

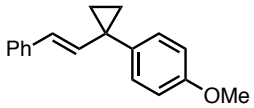


1-Methoxy-4-(1-(4-(trifluoromethyl)phenyl)cyclopropyl)benzene (3f): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (26 mg, 0.089 mmol, 45%). Analytical data:[2] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.56–7.48 (m, 2H), 7.32–7.20 (m, 4H), 6.92–6.85 (m, 2H), 3.83 (s, 3H), 1.43–1.25 (m, 4H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −62.3 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.4, 150.7 (q, J = 1.1 Hz), 136.7, 130.3, 127.9 (q, J = 32.2 Hz), 127.9, 125.3 (q, J = 15.2 Hz), 124.5 (q, J = 270.4 Hz), 114.0, 55.4, 29.3, 16.9 ppm; **IR** (neat): 3007, 2838, 1615, 1513, 1461, 1410, 1323, 1246, 1164, 1117, 1077, 828, 672 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.62.

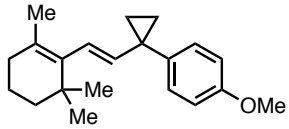


1-Chloro-4-(1-(4-methoxyphenyl)cyclopropyl)benzene (3g): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil that solidified upon standing to form a white solid (20 mg, 0.077 mmol, 39%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.23–7.15 (m, 4H), 7.14–7.09 (m, 2H), 6.85–6.80 (m, 2H), 3.79 (s, 3H), 1.30–1.20 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.2, 145.0, 137.3, 131.6, 129.9, 129.4, 128.4, 113.9, 55.4, 28.9, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{16}OCl$ (M+H): 259.0884; found: 259.0887; **IR**

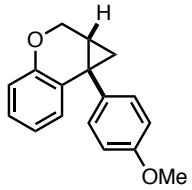
(neat): 3005, 2997, 2835, 1609, 1511, 1489, 1461, 1290, 1242, 1176, 1033, 1011, 818 cm^{-1}; **m.p.:** 33–36 ºC; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.67.



(*E*)-1-Methoxy-4-(1-styrylcyclopropyl)benzene (3h): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–60% PhMe/hexanes) to yield the product as a white solid (48 mg, 0.192 mmol, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.31–7.27 (m, 2H), 7.26–7.22 (m, 4H), 7.17–7.12 (m, 1H), 6.91–6.85 (m, 2H), 6.07 (d, *J* = 15.8 Hz, 1H), 5.92 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H), 1.18–1.13 (m, 2H), 1.09–1.04 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.3, 138.6, 137.7, 135.4, 131.3, 128.6, 127.8, 126.8, 125.9, 113.8, 55.4, 28.0, 15.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{19}O$ (M+H): 251.1430; found: 251.1434; **IR** (neat): 3085, 3029, 2998, 2953, 1642, 1611, 1511, 1494, 1444, 1291, 1237, 1169, 1029, 966, 932, 834, 747, 693 cm^{-1}; **m.p.:** 39–41 ºC; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.56.

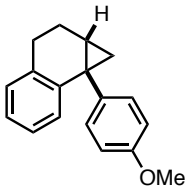


(*E*)-1-Methoxy-4-(1-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)cyclopropyl)benzene (3i): Prepared according to General Procedure A on 0.30-mmol scale. The crude residue was purified by flash column chromatography (gradient of 10–15% PhMe/hexanes) to yield the desired product as a clear colourless oil (64 mg, 0.22 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.25–7.21 (m, 2H), 6.88–6.78 (m, 2H), 5.47 (dtt, *J* = 15.8, 1.9, 1.0 Hz, 1H), 5.31 (d, *J* = 15.8 Hz, 1H), 3.80 (s, 3H), 1.97–1.89 (m, 2H), 1.62 (q, *J* = 1.0 Hz, 3H), 1.60–1.51 (m, 3H), 1.44–1.36 (m, 2H), 1.06–1.00 (m, 2H), 0.97–0.92 (m, 2H), 0.90 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.9, 140.6, 137.5, 136.2, 130.4, 127.4, 125.8, 113.5, 55.2, 39.4, 34.1, 32.6, 28.7, 27.4, 21.3, 19.3, 14.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{23}O$ (M+H): 207.1743; found: 207.1748; **IR** (neat): 3019, 3000, 2960, 2926, 2863, 2833, 1641, 1612, 1514, 1456, 1241, 1172, 1037, 830, 556 cm^{-1}; $\mathbf{R_f}$ (8:2 hexanes/toluene; UV, *p*-anisaldehyde): 0.60.

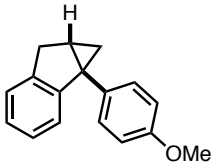


(*cis*)-7b-(4-Methoxyphenyl)-1,1a,2,7b-tetrahydrocyclopropachromene (3j): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (trial 1: 32 mg, 0.127 mmol, 64%; trial 2: 31 mg, 0.123 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.31 (m, 2H), 7.04 (ddd, *J* = 8.0, 7.0, 2.0 Hz, 1H), 6.94–6.90 (m, 2H), 6.85 (ddd, *J* = 8.0, 1.2, 0.4 Hz, 1H), 6.78 (ddd, *J* = 7.7, 7.0, 1.2 Hz, 1H), 6.75 (ddd, *J* = 7.7, 2.0, 0.4 Hz, 1H), 4.42 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.13–4.08 (m, 1H), 3.84 (s, 3H), 1.85 (ddt, *J* = 8.6, 5.7, 1.5 Hz, 1H), 1.53–1.45 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.7, 152.4, 135.0, 131.8, 130.8, 128.5, 126.3, 121.4, 117.2, 114.0, 62.8, 55.4, 26.9, 25.5, 16.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{17}O_2$

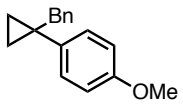
(M+H): 253.1223; found: 253.1220; **IR** (neat): 2958, 2838, 2005, 1610, 1578, 1513, 1484, 1451, 1241, 1210, 1036, 968, 820, 765 cm^{-1}; **m.p.:** 62–64 ºC; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.29.



(*cis*)-7b-(4-Methoxyphenyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropanaphthalene (3k): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–60% PhMe/hexanes) to yield the product as a colourless oil (trial 1: 26 mg, 0.104 mmol, 52%; trial 2: 28 mg, 0.112 mmol, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.33–7.28 (m, 2H), 7.09–6.87 (m, 3H), 6.92–6.87 (m, 2H), 6.80–6.76 (m, 1H), 3.84 (s, 3H), 2.79–2.71 (m, 1H), 2.68–2.58 (m, 1H), 2.23–2.14 (m, 1H), 2.06–1.97 (m, 1H), 1.74–1.68 (m, 1H), 1.38 (dd, J = 8.6, 5.0 Hz, 1H), 1.27–1.24 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.3, 142.2, 137.7, 134.2, 131.8, 128.6, 128.5, 126.0, 124.8, 113.8, 55.4, 27.7, 26.7, 24.1, 19.7, 15.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{19}O$ (M+H): 251.1430; found: 251.1430; **IR** (neat): 3066, 3005, 2925, 2854, 2834, 1746, 1610, 1512, 1489, 1460, 1286, 1242, 1174, 1033, 835, 758, 738 cm^{-1}; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/$KMnO_4$): 0.55.

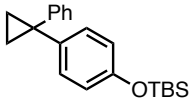


(*cis*)-1a-(4-Methoxyphenyl)-1,1a,6,6a-tetrahydrocyclopropaindene (3l): Prepared on 0.16-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a white solid (16 mg, 0.068 mmol, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.35–7.29 (m, 2H), 7.22–7.16 (m, 1H), 7.13–7.06 (m, 2H), 7.05–7.01 (m, 1H), 6.90–6.84 (m, 2H), 3.82 (s, 3H), 3.41–3.33 (m, 1H), 3.00 (dd, J = 17.0 Hz, 1H), 1.97–1.91 (m, 1H), 1.65 (dd, J = 8.3, 4.4 Hz, 1H), 0.52 (dd, J = 4.5, 4.5 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.4, 149.6, 141.9, 133.6, 130.5, 126.1, 125.7, 125.5, 123.8, 113.8, 55.4, 39.1, 35.7, 26.0, 21.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{17}O$ (M+H): 237.1274; found: 237.1277; **IR** (neat): 3037, 2995, 2907, 2836, 1611, 1513, 1476, 1459, 1440, 1243, 1176, 1031, 845, 757, 722 cm^{-1}; **m.p.:** 42–43 ºC; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/$KMnO_4$): 0.63.

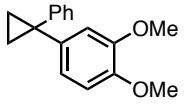


1-(1-Benzylcyclopropyl)-4-methoxybenzene (3m): Prepared on 0.20-mmol scale using General Procedure A with the modifications that 4 equiv 4-methoxyphenylzinc(II) chloride was used (1.8 mL, of a 0.44 M solution in THF, 0.80 mmol, 4.0 equiv), 20 mol % $Ni(acac)_2$•xH_2O was used (10 mg, 0.040 mmol, 0.20 equiv), and 40 mol % bathocuproine was used (29 mg, 0.080 mmol, 0.40 equiv). The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (16 mg, 0.066 mmol, 33%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.21–7.12 (m, 3H), 7.07–7.03 (m, 2H), 7.00–6.95 (m, 2H), 6.75–

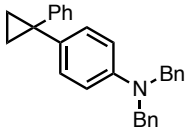
6.71 (m, 2H), 3.76 (s, 3H), 2.87 (s, 2H), 0.86–0.75 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 157.8, 140.0, 137.3, 130.4, 129.6, 128.0, 126.0, 113.4, 55.3, 46.2, 26.0, 12.7 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{22}NO$ (M+NH_4): 256.1696; found: 256.1697; **IR** (neat): 3029, 3001, 2912, 2836, 1611, 1514, 1454, 1293, 1242, 1174, 1035, 830, 745, 700 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/*p*-anisaldehyde): 0.55.



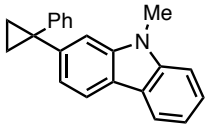
***tert*-Butyldimethyl(4-(1-phenylcyclopropyl)phenoxy)silane (3n):** Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% PhMe/hexanes) to yield the product as a colourless oil (39 mg, 0.120 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.30–7.22 (m, 2H), 7.22–7.13 (m, 3H), 7.13–7.07 (m, 2H), 6.78–6.71 (m, 2H), 1.30–1.21 (m, 4H), 0.98 (s, 9H), 0.18 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 153.9, 146.4, 138.4, 129.8, 128.3, 128.1, 125.8, 119.8, 29.3, 25.8, 18.3, 16.6, −4.3 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{29}OSi$ (M+H): 325.1982; found: 325.1990; **IR** (neat): 3026, 2956, 2930, 2858, 2006, 1606, 1510, 1472, 1462, 1255, 912, 833, 779, 697 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.77.



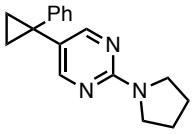
1,2-Dimethoxy-4-(1-phenylcyclopropyl)benzene (3o): Prepared on 0.10-mmol scale. The crude residue was purified by flash column chromatography on silica gel (gradient of 10–20% toluene/hexanes) to yield the desired product as a white solid (15 mg, 0.060 mmol, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.26–7.22 (m, 2H), 7.20–7.14 (m, 3H), 6.87–6.77 (m, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 1.29–1.25 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 148.8, 147.6, 146.3, 138.3, 128.3, 127.7, 125.8, 121.1, 112.6, 111.1, 56.0, 55.9, 29.7, 16.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{19}O_2$ (M+H): 255.1380; found: 255.1384; **IR** (neat): 3006, 2997, 2969, 2839, 1599, 1498, 1445, 1218, 1138, 1021, 871, 757, 697, 554 cm^{-1}; **m.p.:** = 43–45 °C; **R_f** (7:3 hexanes/EtOAc; UV, p-anisaldehyde): 0.67.



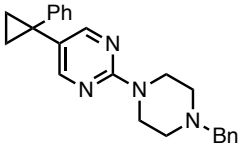
***N*,*N*-Dibenzyl-4-(1-phenylcyclopropyl)aniline (3p):** Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a white solid (41 mg, 0.105 mmol, 53%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.35–7.29 (m, 4H), 7.28–7.20 (m, 10H), 7.16–7.11 (m, 1H), 7.06–7.01 (m, 2H), 6.67–6.61 (m, 2H), 4.62 (s, 4H), 1.21 (app s, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.6, 146.7, 138.9, 133.9, 129.5, 128.7, 128.4, 128.3, 127.0, 126.8, 125.8, 112.4, 54.5, 29.2, 16.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{29}H_{28}N$ (M+H): 390.2216; found: 390.2214; **IR** (neat): 3080, 3023, 2863, 1614, 1602, 1520, 1493, 1386, 1351, 1197, 959, 805, 723 cm^{-1}; **m.p.:** 88–90 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde/$KMnO_4$): 0.53.



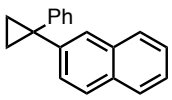
9-Methyl-2-(1-phenylcyclopropyl)-9*H*-carbazole (3q): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–60% PhMe/hexanes) to yield the product as a white solid (19 mg, 0.064 mmol, 32%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.08–8.04 (m, 1H), 8.03–7.98 (m, 1H), 7.52–7.40 (m, 1H), 7.35–7.31 (m, 1H), 7.30–7.15 (m, 7H), 3.91 (s, 3H), 1.50–1.37 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 146.6, 143.7, 141.5, 141.3, 128.3, 127.9, 125.8, 125.5, 122.8, 121.2, 120.5, 120.3, 120.2, 119.0, 109.1, 108.5, 30.7, 29.2, 17.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{20}N$ (M+H): 298.1590; found: 298.1590; **IR** (neat): 3050, 1599, 1495, 1466, 1448, 1422, 1322, 1245, 822, 744, 723, 702 cm^{-1}; **m.p.:** 111–113 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.43.



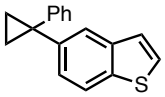
5-(1-Phenylcyclopropyl)-2-(pyrrolidin-1-yl)pyrimidine (3r): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–100% EtOAc/hexanes) to yield the product as a tan solid (30 mg, 0.113 mmol, 57%), which was inseparable from the homodimer side-product. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.28 (s, 2H), 7.27–7.22 (m, 2H), 7.19–7.13 (m, 3H), 3.58–3.52 (m, 4H), 2.01–1.94 (m, 4H), 1.29–1.25 (m, 2H), 1.20–1.17 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 160.9, 158.9, 145.4, 129.5, 127.5, 126.1, 125.5, 46.8, 25.7, 25.1, 15.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{20}N_3$ (M+H): 266.1652; found: 266.1651; **IR** (neat): 2969, 2868, 1594, 1524, 1514, 1480, 1281, 1018, 797, 700 cm^{-1}; **m.p.:** 83–85 ºC; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.42.



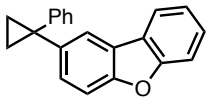
2-(4-Benzylpiperazin-1-yl)-5-(1-phenylcyclopropyl)pyrimidine (3s): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–100% EtOAc/hexanes) to yield the product as a white solid (35 mg, 0.094 mmol, 47%), which was inseparable from the homodimer side-product. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.25 (s, 2H), 7.37–7.31 (m, 4H), 7.29–7.23 (m, 3H), 7.19–7.14 (m, 3H), 3.88–3.74 (br m, 4H), 3.56 (br s, 2H), 2.58–2.44 (br m, 4H), 1.31–1.25 (m, 2H), 1.20–1.16 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 160.6, 158.7, 145.1, 137.8, 129.4, 128.6, 128.5, 127.7, 127.4, 126.6, 126.2, 63.3, 53.1, 43.9, 25.1, 15.3 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{27}N_4$ (M+H): 371.2230; found: 371.2236; **IR** (neat): 3072, 3026, 3000, 2835, 2824, 1598, 1530, 1486, 1451, 1444, 1355, 1253, 1239, 1006, 960, 931, 797, 734 cm^{-1}; **m.p.:** 94–96 ºC; **R_f** (7:3 hexanes/EtOAc; UV/$KMnO_4$): 0.28.



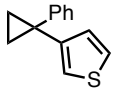
2-(1-Phenylcyclopropyl)naphthalene (3t): Prepared on 0.10-mmol scale according to General Procedure B using **6a** (0.10 mmol). The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil that slowly solidified upon standing (18 mg, 0.074 mmol, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.81–7.73 (m, 3H), 7.70–7.63 (m, 1H), 7.47–7.37 (m, 3H), 7.30–7.24 (m, 4H), 7.21–7.16 (m, 1H), 1.45–1.35 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 145.8, 143.2, 133.5, 132.2, 128.4, 128.4, 128.0, 127.8, 127.7, 127.5, 127.0, 126.1, 126.1, 125.6, 30.2, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{19}H_{17}$ (M+H): 245.1325; found: 245.1321; **IR** (neat): 3077, 3055, 3004, 1598, 1497, 1425, 1267, 1197, 1136, 1025, 863, 822, 756, 741, 696 cm^{-1}; **m.p.:** 40–42 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.66.



5-(1-Phenylcyclopropyl)benzothiophene (3u): Prepared on 0.20-mmol scale according to General Procedure B using **6a** (0.20 mmol). The crude residue was purified by flash column chromatography (gradient of 0–20% Et_2O/hexanes) to yield the product as a colourless semisolid (18 mg, 0.072 mmol, 36%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.78 (app d, J = 8.5 Hz, 1H), 7.72 (app d, J = 1.9 Hz, 1H), 7.41 (d, J = 5.4 Hz, 1H), 7.32–7.20 (m, 6H), 7.19–7.15 (m, 1H), 1.39–1.32 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 146.2, 142.1, 139.9, 137.7, 128.4, 128.2, 126.8, 126.0, 125.9, 123.9, 123.7, 122.4, 30.1, 16.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{15}S$ (M+H): 251.0889; found: 251.0891; **IR** (neat): 3077, 2924, 1599, 1494, 1435, 1189, 1044, 1023, 900, 754, 695 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/$KMnO_4$): 0.63.

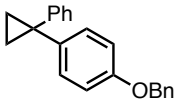


2-(1-Phenylcyclopropyl)dibenzofuran (3v): Prepared on 0.20-mmol scale according to General Procedure B using **6a** (0.20 mmol). The crude residue was purified by flash column chromatography (gradient of 0–20% Et_2O/hexanes) to yield the product as a white solid (28 mg, 0.098 mmol, 49%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.93–7.88 (m, 2H), 7.55 (app dt, J = 8.3, 0.8 Hz, 1H), 7.47 (dd, J = 8.6, 0.7 Hz, 1H), 7.46–7.40 (m, 2H), 7.32 (app td, J = 7.5, 1.0 Hz, 1H), 7.29–7.20 (m, 4H), 7.19–7.14 (m, 1H), 1.43–1.35 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 156.6, 154.8, 146.3, 140.2, 128.6, 128.3, 127.7, 127.0, 125.8, 124.2, 124.2, 122.6, 121.0, 120.6, 111.6, 111.3, 30.0, 16.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{17}O$ (M+H): 285.1274; found: 285.1275; **IR** (neat): 3055, 2925, 1601, 1495, 1479, 1448, 1344, 1194, 1116, 1022, 823, 810, 746, 697 cm^{-1}; **m.p.:** 50–53 ºC; **R_f** (40% PhMe/hexanes; UV; *p*-anisaldehyde): 0.68.

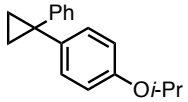


3-(1-Phenylcyclopropyl)thiophene (3w): Prepared on 0.20-mmol scale according to General Procedure B using **6a** (0.20 mmol). The crude residue was purified by flash column chromatography (gradient of 0–20% Et_2O/hexanes) to yield the product as a colourless oil (17 mg, 0.085 mmol, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.33–7.27 (m, 4H), 7.24–7.19 (m, 2H), 6.83 (dd, J = 5.0, 1.4 Hz, 1H), 6.76 (dd, J = 3.0, 1.4 Hz, 1H), 1.31–1.24 (m, 4H) ppm;

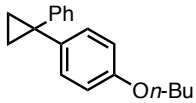
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ_C 147.8, 145.2, 129.0, 128.4, 127.1, 126.4, 125.5, 120.5, 26.5, 16.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{13}S$ (M+H): 201.0733; found: 201.0733; **IR** (neat): 3082, 3004, 1601, 1495, 1445, 1203, 1023, 949, 849, 775, 758, 698 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.67.



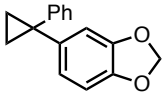
1-(Benzyloxy)-4-(1-phenylcyclopropyl)benzene (3x): Prepared on 0.30-mmol scale. The crude residue was purified by flash column chromatography on silica gel (gradient of 10–20% PhMe/hexanes) to yield the product as a pale yellow solid (44 mg, 0.147 mmol, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.45–7.29 (m, 5H), 7.29–7.23 (m, 2H), 7.23–7.12 (m, 5H), 6.94–6.86 (m, 2H), 5.04 (s, 2H), 1.26 (m, 4H) ppm;**^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.2, 146.3, 138.2, 137.3, 129.9, 128.7, 128.3, 128.1, 128.0, 127.6, 125.8, 114.7, 70.2, 29.3, 16.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{24}NO$ (M+NH_4): 318.1852; found: 318.1851; **IR** (neat): 3075, 3024, 2920, 1605, 1510, 1496, 1455, 1387, 1237, 1174, 1012, 1919, 819, 756, 747 cm^{-1}; **m.p.:** 59–61 ºC; **R_f** (7:3 hexanes/toluene; UV, p-anisaldehyde): 0.48.



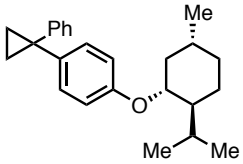
1-Isopropoxy-4-(1-phenylcyclopropyl)benzene (3y): Prepared on 0.40-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–50% PhMe/hexanes) to yield the product as a colourless oil (48 mg, 0.190 mmol, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.42–7.14 (m, 7H), 6.92–6.80 (m, 2H), 4.60–4.48 (m, 1H), 1.48–1.25 (m, 10H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 156.3, 146,4, 137.7, 129.9, 128.3, 128.1, 125.8 , 115.7, 70.0, 29.3, 22.3, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{21}O$ (M+H): 253.1587; found: 253.1595; **IR** (neat): 3082, 2977, 1606, 1509, 1497, 1371, 1238, 1115, 953, 756, 697 cm^{-1}; **R_f** (20% PhMe/hexanes; UV/$KMnO_4$): 0.50.



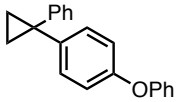
1-Butoxy-4-(1-phenylcyclopropyl)benzene (3z): Prepared on 0.30-mmol scale. The crude residue was purified by flash column chromatography (gradient of 10–15% PhMe/hexanes) to yield the product as a pale yellow solid (33 mg, 0.13 mmol, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.31–7.22 (m, 2H), 7.22–7.12 (m, 5H), 6.85–6.75 (m, 2H), 3.94 (t, J = 6.5 Hz, 2H), 1.80–1.71 (m, 2H), 1.56–1.43 (m, 3H), 0.97 (t, J = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.6, 146.4, 137.6, 129.9, 128.3, 128.0, 125.8, 114.3, 67.8, 31.5, 29.8, 29.3, 19.4, 16.4, 13.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{19}H_{23}O$ (M+H): 267.1743; found: 267.1744; **IR** (neat): 3081, 2958, 2933, 2914, 2872, 2861, 1610, 1516, 1497, 1454, 1288, 1241, 1177, 1070, 1021, 969, 921, 838, 816, 754, 696 cm^{-1}; **m.p.:** 30–32 ºC; **R_f** (7:3 hexanes/toluene; UV, p-anisaldehyde): 0.62.



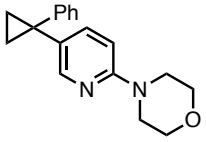
5-(1-Phenylcyclopropyl)benzo[1,3]dioxole (3aa): Prepared on 0.30-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (22 mg, 0.092 mmol, 31%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.29–7.24 (m, 2H), 7.23–7.14 (m, 3H), 6.81–6.85 (m, 2H), 7.74–7.70 (m, 1H), 5.92 (s, 2H), 1.32–1.21 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.6, 146.2, 145.9, 139.8, 128.4, 128.0, 126.0, 122.0, 109.7, 108.1, 101.0, 30.0, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{15}O_2$ (M+H): 239.1067; found: 239.1073; **IR** (neat): 3081, 3006, 2890, 1742, 1602, 1503, 1484, 1433, 1251, 1225, 1033, 934, 808, 756, 697, 560 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde/$KMnO_4$): 0.45.



1-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-4-(1-phenylcyclopropyl)benzene (3ab): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% PhMe/hexanes) to yield the product as a colourless oil (27 mg, 0.077 mmol, 39%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.29–7.11 (m, 7H), 6.83–6.77 (m, 2H), 3.98 (td, *J* = 10.6, 4.2 Hz, 1H), 2.26–2.09 (m, 2H), 1.77–1.66 (m, 2H), 1.58–1.37 (m, 2H), 1.33–1.19 (m, 4H), 1.14–1.02 (m, 1H), 1.02–0.85 (m, 8H), 0.77 (d, *J* = 6.9 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 156.7, 146.5, 137.6, 129.8, 128.3, 128.2, 125.9, 115.7, 77.5, 48.2, 40.4, 34.7, 31.6, 26.1, 23.8, 22.3, 20.9, 16.7, 16.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{25}H_{33}O$ (M+H): 349.2526; found: 349.2524; **IR** (neat): 2954, 2924, 2869, 1600, 1508, 1456, 1270, 1241, 1166, 1013, 993, 823, 755, 697 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.68.

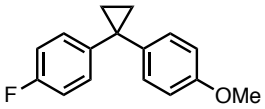


1-Phenoxy-4-(1-phenylcyclopropyl)benzene (3ac): Prepared on 0.40-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a white solid (22 mg, 0.077 mmol, 19%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.39–7.19 (m, 9H), 7.15–7.09 (m, 1H), 7.07–7.01 (m, 2H), 6.98–6.93 (m, 2H), 1.36–1.28 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.5, 155.5, 146.0, 140.8, 130.0, 129.8, 128.4, 128.4, 126.1, 123.2, 118.9, 118.8, 29.5, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{19}O$ (M+H): 287.1430; found: 287.1434; **IR** (neat): 3077, 3003, 1581, 1492, 1477, 1291, 1162, 1015, 857, 769, 752, 704 cm^{-1}; **m.p.:** 83–85 ºC; **R_f** (20% PhMe/hexanes; UV/*p*-anisaldehyde): 0.56.

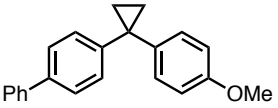


4-(5-(1-Phenylcyclopropyl)pyridin-2-yl)morpholine (3ad): Prepared according to General Procedure A on 0.20-mmol scale. The crude residue was purified by flash column

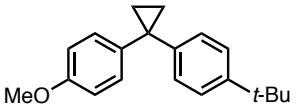
chromatography (gradient of 5–15% toluene/hexanes) to yield the desired product as a pale yellow solid (22 mg, 0.079 mmol, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.15 (dd, J = 2.5, 0.8 Hz, 1H), 7.43 (dd, J = 8.7, 2.5 Hz, 1H), 7.27–7.22 (m, 2H), 7.20–7.13 (m, 3H), 6.58 (dd, J = 8.8, 0.8 Hz, 1H), 3.87–3.76 (m, 4H), 3.54–3.41 (m, 4H), 1.29–1.25 (m, 2H), 1.24–1.21 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 158.1, 148.2, 145.6, 138.6, 130.8, 128.3, 127.7, 125.9, 106.6, 66.8, 45.8, 27.0, 15.7 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{21}N_2O$ (M+H): 281.1648; found: 281.1644; **IR** (neat): 3021, 2966, 2886, 2844, 1600, 1556, 1494, 1445, 1391, 1239, 1116, 943, 808, 757, 559, cm^{-1}; **m.p.:** 59–61°C; **R_f** (7:3 hexanes/EtOAc; UV, $KMnO_4$): 0.40.



1-Fluoro-4-(1-(4-methoxyphenyl)cyclopropyl)benzene (3ae): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil (21 mg, 0.087 mmol, 44%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.24–7.15 (m, 4H), 7.01–6.93 (m, 2H), 6.88–6.82 (m, 2H), 3.81 (s, 3H), 1.34–1.20 (m, 4H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −117.5; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 161.1 (d, J = 242.8 Hz), 157.9, 141.9, 137.7, 129.7 (d, J = 7.9 Hz), 129.5, 114.9 (d, J = 21.1 Hz), 113.7, 55.3, 28.7, 16.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{16}OF$ (M+H): 243.1180; found: 243.1184; **IR** (neat): 3079, 3004, 2947, 2836, 2005, 1606, 1509, 1460, 1243, 1218, 1030, 822, 554 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.58.

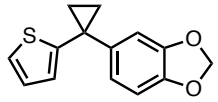


4-(1-(4-Methoxyphenyl)cyclopropyl)-1,1'-biphenyl (3af): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a white solid (26 mg, 0.087 mmol, 44%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.58–7.53 (m, 2H), 7.50–7.45 (m, 2H), 7.44–7.38 (m, 2H), 7.34–7.29 (m, 1H), 7.26–7.22 (m, 4H), 6.87–6.82 (m, 2H), 3.80 (s, 3H), 1.33–1.27 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.1, 145.7, 141.1, 138.8, 137.7, 130.2, 128.8, 128.3, 127.2, 127.1, 127.1, 113.9, 55.4, 29.1, 16.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{24}NO$ (M+NH_4): 318.1852; found: 318.1855; **IR** (neat): 3031, 2951, 2931, 2005, 1611, 1511, 1486, 1451, 1242, 1181, 1174, 1037, 827, 761 cm^{-1}; **m.p.:** 48–50 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.55.

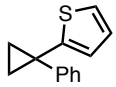


1-(*tert*-Butyl)-4-(1-(4-methoxyphenyl)cyclopropyl)benzene (3ag): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–60% PhMe/hexanes) to yield the product as a white solid (25 mg, 0.089 mmol, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.30–7.26 (m, 2H), 7.25–7.21 (m, 2H), 7.13–7.09 (m, 2H), 6.86–8.81 (m, 2H), 3.80 (s, 3H), 1.30 (s, 9H), 1.28–1.23 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.0, 148.6, 143.4, 138.1, 130.2, 127.4, 125.2, 113.8, 55.4, 34.4, 31.5, 28.8, 16.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{20}H_{28}NO$ (M+NH_4): 298.2165; found: 298.2163; **IR** (neat):

2959, 2903, 1608, 1511, 1440, 1290, 1242, 1169, 1025, 1017, 832, 816, 577 cm^{-1}; **m.p.:** 75–77 ºC; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/$KMnO_4$): 0.60.



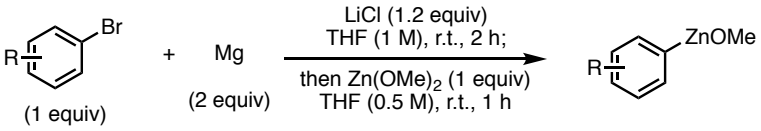
5-(1-(Thiophen-2-yl)cyclopropyl)benzo[1,3]dioxole (3ah): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (16 mg, 0.066 mmol, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.06 (dd, J = 5.2, 1.3 Hz, 1H), 6.88–6.83 (m, 3H), 6.76–6.72 (m, 1H), 6.69 (d, J = 3.5, 1.2 Hz, 1H), 5.93 (s, 2H), 1.34–1.29 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 152.3, 147.6, 146.3, 139.0, 126.7, 123.8, 123.2, 122.2, 109.9, 108.1, 101.1, 26.4, 18.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{13}O_2S$: 245.0631; found: 245.0638; **IR** (neat): 3077, 3004, 2887, 1503, 1485, 1435, 1226, 1035, 932, 809, 692 cm^{-1}; $\mathbf{R_f}$ (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.53.



2-(1-Phenylcyclopropyl)thiophene (3ai): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 0–20% PhMe/hexanes) to yield the product as a colourless oil (17 mg, 0.085 mmol, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.32 (m, 2H), 7.32–7.27 (m, 2H), 7.24–7.19 (m, 1H), 7.08 (dd, J = 5.2, 1.3 Hz, 1H), 6.86 (dd, J = 5.2, 3.5 Hz, 1H), 6.72 (dd, J = 3.6, 1.3 Hz, 1H), 1.39–1.35 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 151.8, 145.0, 128.7, 128.5, 126.7, 126.6, 124.4, 123.3, 26.2, 18.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{13}S$ (M+H): 201.0733; found: 201.0738; **IR** (neat): 3084, 3030, 1599, 1494, 1444, 1221, 1029, 850, 738 cm^{-1}.

D. Preparation of arylzinc reagents

D.1. Procedure for preparation of arylzinc reagents



General Procedure C: Preparation of arylzinc reagents

Preparation of the Grignard reagent (representative procedure on 6.0-mmol scale): To a flame-dried 16-mL culture tube with stir bar was added magnesium(0) turnings (0.29 g, 12 mmol, 2.0 equiv) and lithium chloride (0.30 g, 7.2 mmol, 1.2 equiv). The tube was sealed with a size 19 septum and electrical tape and was flame-dried under vacuum and cooled under N_2. THF (6.0 mL, 1.0 M) was added. The tube was equipped with syringes containing 1,2-dibromoethane (ca. 0.010 mL, 0.12 mmol, 0.020 equiv) and the desired aryl bromide (6.0 mmol, 1.0 equiv). (If the aryl bromide was solid, the substrate was prepared as a stock solution in 2.0 mL of THF and 4.0 mL of THF as reaction solvent was used instead of 6.0 mL.) The magnesium was activated with 1,2-dibromoethane and the aryl bromide was added portionwise over 1 h at r.t. The reaction was stirred for an additional 1 h at r.t. to yield the Grignard reagent as a grey-black solution.

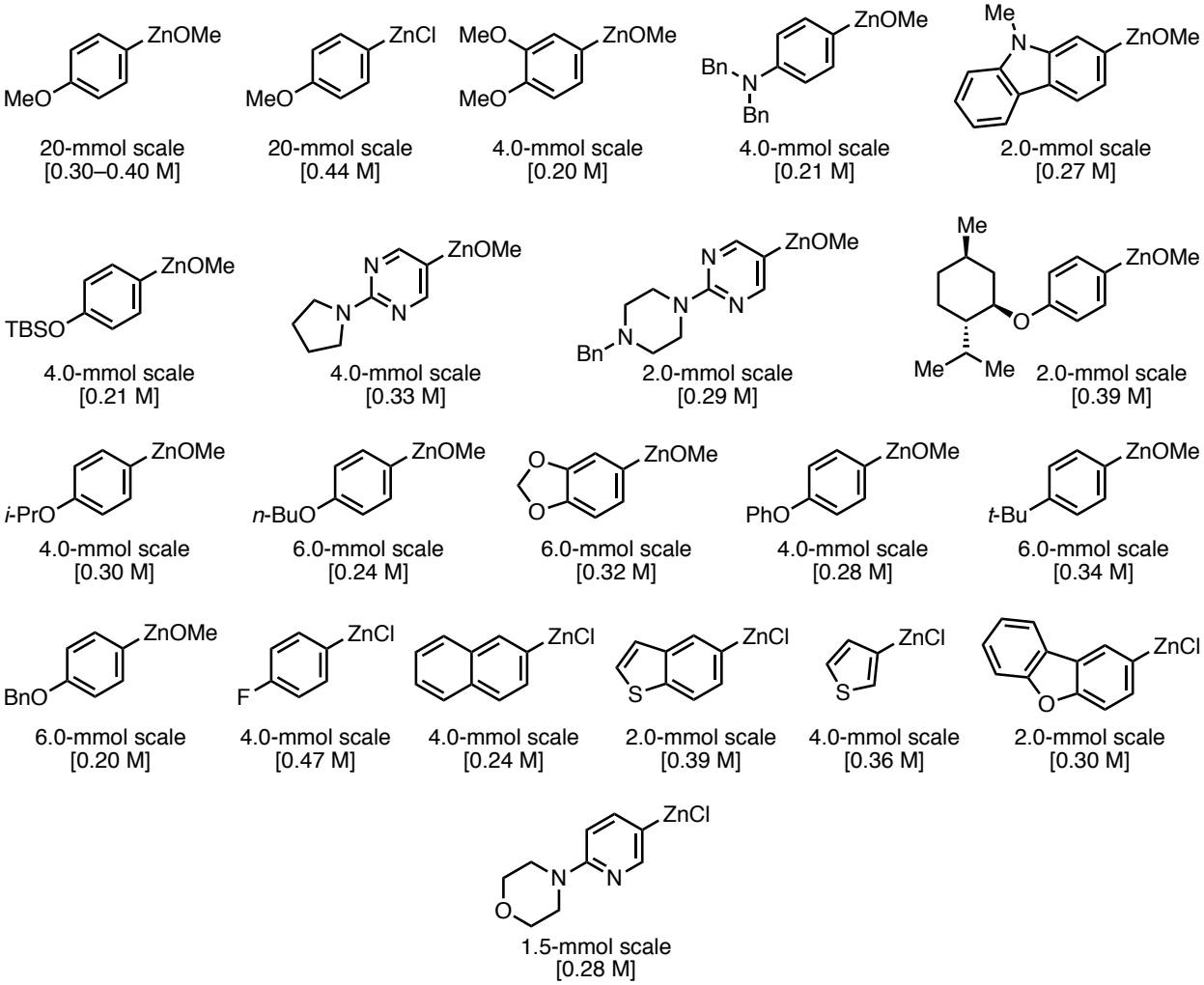
Preparation of $Zn(OMe)_2$:[1] A flame-dried 16-mL culture tube (or appropriately sized flask) with a stir bar was sealed with a size-19 septum and brought into a glovebox. Zinc(II) chloride (0.82 g, 6.0 mmol, 1.0 equiv) and lithium methoxide (0.46 g, 12 mmol, 2.0 equiv) were added and the tube was again sealed with the size-19 septum and electrical tape and was removed from the glovebox. THF (6.0 mL, 1 M) was added and the reaction was stirred at r.t. for 1 h (sonication or shaking may initially be necessary) to yield a 1 M solution of $Zn(OMe)_2$ in THF as a cloudy-grey solution.

Preparation of the arylzinc reagent: While stirring the solution of $Zn(OMe)_2$ in THF at r.t., the solution of Grignard reagent was transferred to the solution of $Zn(OMe)_2$ using a syringe. After addition, the solution was stirred for 1 h at r.t. to yield the arylzinc reagent as a grey solution. The reagent was stored at r.t. under N_2. *For best reproducibility, the reagent was aged before use for 72 h at r.t. under N_2 to allow precipitate to settle to the bottom of the flask (Figure S3).*

Arylzinc reagents with other counterions (Table S6) were prepared using the same protocol and by transmetallating with the appropriate Zn(II) source.

Titration of arylzinc reagents using I_2:[3] To an 8-mL threaded culture tube with a stir bar was added LiCl (ca. 21 mg, 0.50 mmol) and the tube was flame-dried under vacuum and cooled under N_2. The tube was briefly opened to air and I_2 (ca. 25–50 mg, 0.10–0.20 mmol) was added. The exact amount of I_2 was recorded. The tube was evacuated and backfilled with N_2 (×3) and THF (2.0 mL) was added. The solution was cooled to 0 ºC and arylzinc reagent was added dropwise to the solution. The volume of arylzinc reagent required to turn the solution colourless was used to calculate the titre of the arylzinc reagent, which was generally 0.30–0.40 M.

Table S9. Scale and concentration of arylzinc reagents prepared for this study



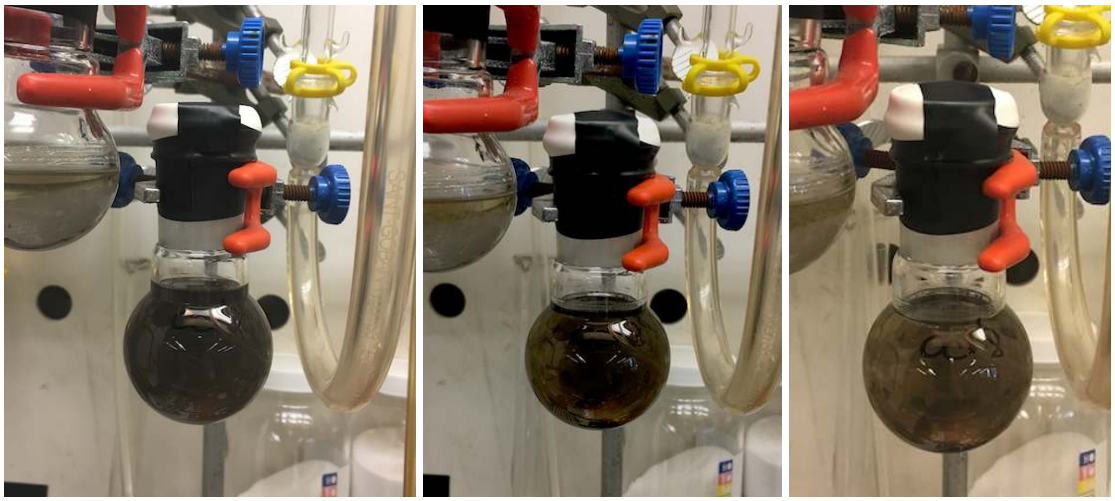


Figure S3. (Left) Appearance of 4-methoxyphenylzinc(II) methoxide reagent after standing for 1 h at r.t.; (Centre) Appearance after 24 h; (Right) Appearance after 72 h.

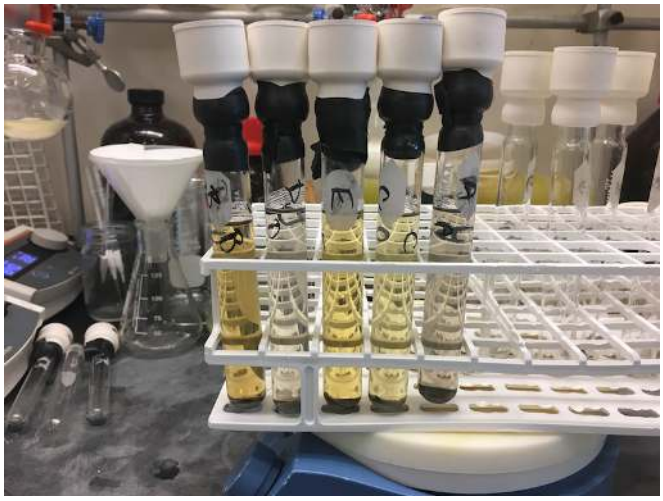
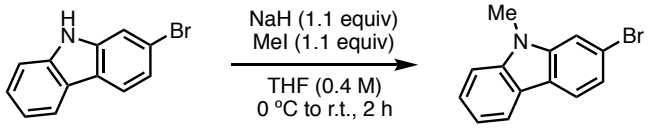


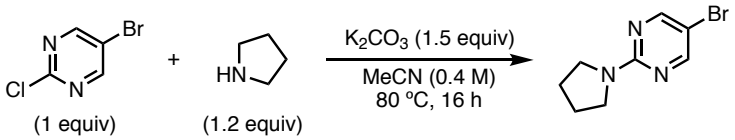
Figure S4. Typical appearance of arylzinc reagents after standing for 72 h at r.t.

D.2. Preparation of aryl bromide starting materials

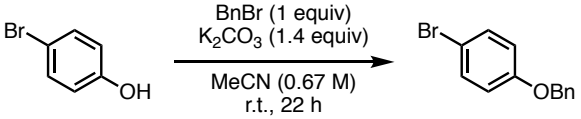
The following aryl bromides were prepared as previously described:[4] 1-bromo-4-isopropoxybenzene, 1-bromo-4-phenoxybenzene, 1-bromo-4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)benzene, *N*,*N*-dibenzyl-4-bromoaniline, (4-bromophenoxy)(*tert*-butyl)dimethylsilane, 2-(4-benzylpiperazin-1-yl)-5-bromopyrimidine, 2-bromodibenzofuran.



2-Bromo-9-methyl-9*H*-carbazole (S1): To a 50-mL flask with a stir bar were added 2-bromocarbazole (1.2 g, 5.0 mmol, 1.0 equiv) and THF (12 mL, 0.40 M), and the solution was cooled to 0 ºC. Sodium hydride (0.22 g, 5.5 mmol, 1.1 equiv) was added at once and the reaction was stirred at r.t. for 30 min. Iodomethane (0.34 mL, 5.5 mmol, 1.1 equiv) was added and the reaction was stirred at r.t. for 2 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (×3), and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The solid concentrate was washed with hexanes (5.0 mL) to yield the product as an off-white solid (1.2 g, 4.6 mmol, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.08–8.03 (m, 1H), 7.94–7.91 (m, 1H), 7.56–7.48 (m, 2H), 7.39 (dt, J = 8.2, 0.9 Hz, 1H), 7.34 (dd, J = 8.2, 1.7 Hz, 1H), 7.26 (td, J = 7.7, 1.0 Hz, 1H), 3.80 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 141.9, 141.2, 126.3, 122.4, 122.1, 121.9, 121.5, 120.4, 119.6, 119.4, 111.7, 108.8, 29.3 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{11}NBr$ (M+H): 260.0069; found: 260.0070; **IR** (neat): 2926, 2853, 1590, 1476, 1448, 1320, 1245, 1127, 1054, 842, 797, 742, 720 cm^{-1}; **m.p.:** 74–75 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.59.

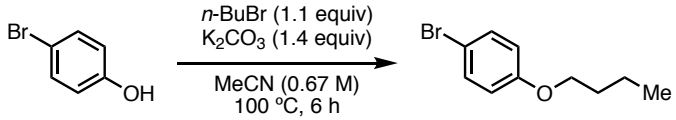


5-Bromo-2-(pyrrolidin-1-yl)pyrimidine (S2): To a 50-mL flask with a stir bar were added 5-bromo-2-chloropyrimidine (1.9 g, 10 mmol, 1.0 equiv), potassium carbonate (2.1 g, 15 mmol, 1.5 equiv), MeCN (25 mL, 0.40 M), and piperidine (1.0 mL, 12 mmol, 1.2 equiv), and the reaction was stirred at 80 ºC for 16 h. The reaction was cooled to r.t., quenched with H_2O, and extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The solid concentrate was washed with hexanes (5.0 mL) to yield the product as an off-white solid (2.0 g, 8.8 mmol, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.28 (s, 2H), 3.57–3.46 (m, 4H), 2.04–1.93 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 158.6, 158.0, 105.0, 47.0, 25.7 ppm; **HRMS** *m/z* (DART): calcd for $C_8H_{11}N_3Br$ (M+H): 228.0131; found: 228.0135; **IR** (neat): 2971, 2872, 1578, 1516, 1450, 1283, 1153, 1115, 939, 782, 639 cm^{-1}; **m.p.:** 89–91 ºC; **R_f** (6:4 hexanes/EtOAc; UV): 0.81.

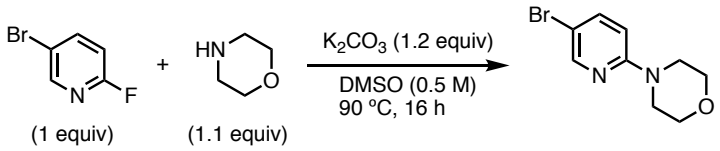


1-(Benzyloxy)-4-bromobenzene (S3): To a flame-dried 100-mL flask with a stir bar was added 1-Bromo-4-iodobenzene (5.2 g, 30 mmol, 1.0 equiv). The flask was evacuated and backfilled

with N_2 (×3) and MeCN (75 mL, 0.40 M) was added. Potassium bicarbonate (5.8 g, 42 mmol, 1.4 equiv) was added and the solution was stirred at r.t. for 15 minutes. Benzyl bromide (3.6 mL, 30 mmol, 1.0 equiv) was added and the reaction was stirred at r.t. for 22 hours. The reaction was then opened to air and filtered through celite. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel (gradient of 0–5% EtOAc/hexanes). The fractions containing desired product were collected, combined, and concentrated to yield the desired product as a white solid (7.4 g, 28 mmol, 94%). Analytical data:[4] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.43–7.39 (m, 3H), 7.39–7.36 (m, 3 H), 7.35–7.30 (m, 1H), 6.89–6.82 (m, 2H), 5.04 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 157.9, 136.6, 132.3, 128.7, 128.1, 127.4, 116.7, 113.1, 70.3 ppm; **R_f** (95:5 hexanes/EtOAc; vanillin): 0.73.



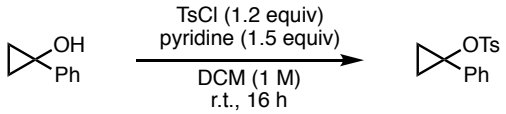
1-Bromo-4-butoxybenzene (S4): To a flame-dried 100-mL flask with a stir bar was added 4-bromophenol (6.9 g, 40 mmol, 1.0 equiv). The flask was set up with a reflux condenser, was evacuated and backfilled with N_2 (×3) and MeCN (60 mL, 0.67 M) was added. Potassium bicarbonate (7.7 g, 56 mmol, 1.4 equiv) was added and the solution was stirred at r.t. for 10 minutes. 1-Bromobutane (4.7 mL, 44 mmol, 1.1 equiv) was added and the reaction was stirred at 100 °C for 6 hours. The reaction was allowed to cool to r.t., opened to air and then filtered. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel (gradient of 0–5% EtOAc/hexanes). The fractions containing desired product were collected, combined, and concentrated to yield the desired product as a colourless oil (7.8 g, 34 mmol, 85%). Analytical data:[6] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.40-7.31 (m, 2H), 6.81-6.73 (m, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.75 (ddt, J = 8.9, 7.8, 6.3 Hz, 2H), 1.54-1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 158.4, 132.3, 116.5, 112.7, 68.1, 31.4, 19.3, 14.0 ppm; **R_f** (9:1 hexanes/EtOAc; $KMnO_4$): 0.87.



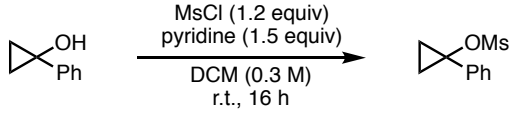
4-(5-Bromopyridin-2-yl)morpholine (S5): To a 25-mL flask with a stir bar were added potassium carbonate (0.83 g, 6.0 mmol, 1.2 equiv), DMSO (10 mL, 0.50 M), 5-bromo-2-fluoropyridine (0.51 mL, 5.0 mmol, 1.0 equiv), and morpholine (0.48 mL, 5.5 mmol, 1.1 equiv), and the reaction was stirred at 90 ºC for 16 h. The reaction was cooled to r.t., quenched with sat. aq. NH_4Cl, and extracted with EtOAc (×3), and the organic fractions were washed with brine (×1), dried over $MgSO_4$, and concentrated. The concentrate was triturated with hexanes and dried under high vacuum to yield the product as an off-white solid (1.0 g, 4.1 mmol, 82%). The analytical data was consistent with literature.[5]

E. Preparation of cyclopropanol starting materials

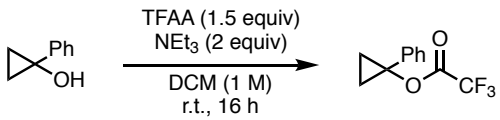
E.1. Preparation of cyclopropanols with alternate leaving groups



1-Phenylcyclopropyl 4-methylbenzenesulfonate (1a): To a 100-mL round-bottom flask with a stir bar were sequentially added 1-phenylcyclopropanol (3.1 g, 23 mmol, 1.0 equiv), DCM (23 mL, 1.0 M), pyridine (2.8 mL, 35 mmol, 1.5 equiv), and tosyl chloride (5.3 g, 28 mmol, 1.2 equiv). 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 brine (×1), dried over $MgSO_4$, and concentrated. The concentrate was dried under high vacuum at 0 ºC to induce solidification of the crude residue. The product was reprecipitated (pyridine/H_2O) and the precipitate was washed with hexanes (3 × 20 mL) and dried under high vacuum to yield the product as a white solid (3.2 g, 11 mmol, 48%). Analytical data:[6] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.52–7.44 (m, 2H), 7.33–7.26 (m, 2H), 7.22–7.15 (m, 3H), 7.13–7.07 (m, 2H), 2.36 (s, 3H), 1.66–1.56 (m, 2H), 1.18–1.11 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 144.2, 137.8, 135.2, 129.4, 128.2, 128.2, 128.2, 127.8, 67.2, 21.7, 13.7 ppm; **R_f** (5% EtOAc/hexanes; UV): 0.40.

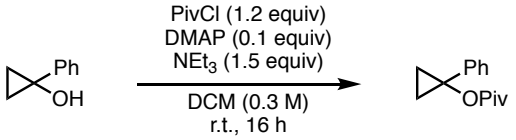


1-Phenylcyclopropyl methanesulfonate (1b): To a 25-mL flask with a stir bar were added 1-phenylcyclopropanol (0.40 g, 3.0 mmol, 1.0 equiv), DCM (10 mL, 0.30 M), pyridine (0.36 mL, 4.5 mmol, 1.5 equiv), and mesyl chloride (0.28 mL, 3.6 mmol, 1.2 equiv), and the reaction was stirred at r.t. for 16 h. The reaction was concentrated and purified by flash column chromatography (gradient of 10–40% EtOAc/hexanes) to yield the product as a colourless oil (0.47 g, 2.2 mmol, 73%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.59–7.55 (m, 2H), 7.42–7.34 (m, 3H), 2.54 (s, 3H), 1.69–1.64 (m, 2H), 1.24–1.18 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 137.4, 129.2, 129.1, 128.9, 67.5, 39.8, 13.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{10}H_{16}NO_3S$ ($M+NH_4$): 230.0845; found: 230.0849; **IR** (neat): 3031, 1353, 1213, 1166, 1027, 971, 884, 804, 698 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/*p*-anisaldehyde): 0.17.

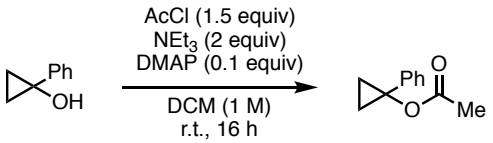


1-Phenylcyclopropyl 2,2,2-trifluoroacetate (1c): To a 50-mL flask with a stir bar were sequentially added 1-phenylcyclopropanol (1.3 g, 10 mmol, 1.0 equiv), DCM (10 mL, 1.0 M), triethylamine (2.8 mL, 20 mmol, 1.0 equiv), and trifluoroacetic anhydride (2.1 mL, 15 mmol, 1.5 equiv), and the reaction was stirred at r.t. for 16 h. The reaction was concentrated and purified by flash column chromatography (gradient of 0–4% EtOAc/hexanes) to yield the product as a colourless oil (1.2 g, 5.0 mmol, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.45–7.28 (m, 5H), 1.48–1.29 (m, 4H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −75.4 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 157.1 (q, J = 41.9 Hz), 137.2, 128.8, 128.6, 127.3, 114.4 (q, J =

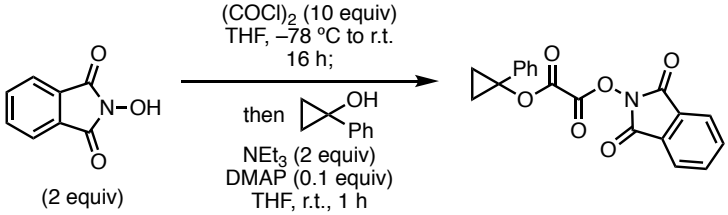
284.7 Hz), 64.4, 14.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{11}H_{13}NO_2F_3$ (M+NH_4): 248.0893; found: 248.08955; **IR** (neat): 1791, 1361, 1219, 1138, 1100, 1028, 848, 775, 753, 695 cm^{-1}; $\mathbf{R_f}$ (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.48.



1-Phenylcyclopropyl pivalate (1d): To a 25-mL flask with a stir bar were added 1-phenylcyclopropanol (0.40 g, 3.0 mmol, 1.0 equiv), DCM (10 mL, 0.30 M), triethylamine (0.63 mL, 4.5 mmol, 1.5 equiv), pivaloyl chloride (0.44 mL, 3.6 mmol, 1.2 equiv), and DMAP (37 mg, 0.30 mmol, 0.10 equiv), and the reaction was stirred at r.t. for 16 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with DCM (×3), and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrate. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (0.48 g, 2.2 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.35–7.18 (m, 5H), 1.25–1.21 (m, 4H), 1.19 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 178.1, 140.5, 128.4, 127.1, 125.8, 59.8, 38.7, 27.1, 15.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{19}O_2$ (M+H): 219.1380; found: 219.1377; **IR** (neat): 2975, 1743, 1480, 1456, 1280, 1222, 1136, 1028, 1001, 753, 695 cm^{-1}; $\mathbf{R_f}$ (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.43.

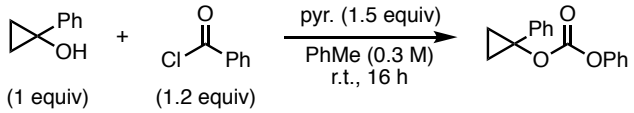


1-Phenylcyclopropyl acetate (S6): To a 25-mL flask with a stir bar were sequentially added 1-phenylcyclopropanol (0.27 g, 2.0 mmol, 1.0 equiv), DCM (2.0 mL, 1.0 M), acetyl chloride (0.21 mL, 3.0 mmol, 1.5 equiv), triethylamine (0.56 mL, 4.0 mmol, 2.0 equiv), and DMAP (22 mg, 0.20 mmol, 0.10 equiv), and the reaction was stirred at r.t. for 16 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with DCM (×3), and the organic fractions were combined, dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 5–10% EtOAc/hexanes) to yield the product as a colourless oil (0.17 g, 0.96 mmol, 48%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.34–7.29 (m, 4H), 7.25–7.21 (m, 1H), 2.04 (s, 3H), 1.31–1.19 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 170.7, 140.2, 128.4, 127.3, 126.3, 60.1, 21.4, 15.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{11}H_{16}NO_2$ (M+NH_4): 194.1176; found: 194.1177; **IR** (neat): 1753, 1499, 1455, 1369, 1244, 1202, 1101, 1026, 985, 754, 695 cm^{-1}; $\mathbf{R_f}$ (5% EtOAc/hexanes; UV/*p*-anisaldehyde): 0.23.



1,3-Dioxoisoindolin-2-yl (1-phenylcyclopropyl) oxalate (1e):[7] To a flame-dried 500-mL round-bottom flask was added *N*-hydroxyphthalimide (2.0 g, 12 mmol, 2.0 equiv). The flask was evacuated and backfilled with N_2 (×3) and THF (200 mL) was added. The solution was cooled to

−78 ºC and oxalyl chloride (5.1 mL, 60 mmol, 10 equiv) was added dropwise. After addition, the flask was removed from the cooling bath and was allowed to warm to r.t. while stirring for 16 h. The solution was concentrated and dried under high vacuum for 1 h to yield an off-white solid, which was dissolved in THF (200 mL). To a separate flame-dried 500-mL round-bottom flask with a stir bar were added 1-phenylcyclopropanol (0.80 g, 6.0 mmol, 1.0 equiv), triethylamine (1.7 mL, 12 mmol, 2.0 equiv), and DMAP (73 mg, 0.60 mmol, 0.10 equiv). While stirring, the THF solution was added by syringe, and the reaction was stirred at r.t. for 1 h. The reaction was concentrated. The concentrate was dissolved in DCM (30 mL), and the solution was poured into hexanes (1 L). The precipitate was collected by filtration and was washed with hexanes (×1), and the filtrate was discarded. The precipitate was extracted with EtOAc (3 × 50 mL), and the organic fractions were combined and concentrated. The concentrate was recrystallized (DCM/pentane) to yield the product as a brown solid (1.2 g, 3.4 mmol, 57%). **1e** was not characterized due to poor solubility in most solvents. However, similar products bearing other substituents have been characterized.[7]



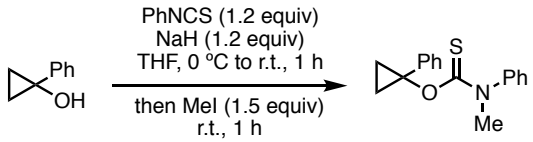
(1 equiv) (1.2 equiv)

Phenyl (1-phenylcyclopropyl) carbonate (1f): To a flame-dried 50-mL flask with stir bar was added 1-phenylcyclopropanol (0.80 g, 6.0 mmol, 1.0 equiv). The flask was sealed and evacuated and backfilled with N_2 (×3) and PhMe (20 mL, 0.30 M) was added. Pyridine (0.73 mL, 9.0 mmol, 1.5 equiv) was added, then phenyl chloroformate (0.90 mL, 7.2 mmol, 1.2 equiv) was added dropwise. The reaction was stirred at r.t. under N_2 for 16 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–4% EtOAc/hexanes) to yield the product as a white solid (1.3 g, 5.1 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.49–7.44 (m, 2H), 7.40–7.27 (m, 5H), 7.23–7.17 (m, 1H), 7.16–7.11 (m, 2H), 1.52–1.44 (m, 2H), 1.34–1.23 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 153.2, 151.1, 138.9, 129.5, 128.6, 128.0, 127.2, 126.1, 121.1, 63.7, 14.6; **HRMS** *m/z* (DART): calcd for $C_{16}H_{18}NO_3$ (M+NH_4): 272.1281; found: 272.1288; **IR** (neat): 1769, 1593, 1498, 1452, 1247, 1192, 1177, 1098, 1029, 927, 753, 722, 685 cm^{-1}; **m.p.:** 43–44 ºC; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.53.

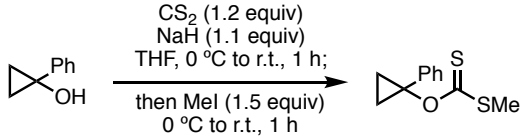
(1 equiv) (1.1 equiv)

1-Phenylcyclopropyl 1*H*-imidazole-1-carboxylate (1g): To a flame-dried 25-mL flask with stir bar was added 1-phenylcyclopropanol (0.54 g, 4.0 mmol, 1.0 equiv). The flask was sealed, evacuated and backfilled with N_2 (×3), and DCM (13 mL, 0.30 M) was added. The flask was briefly opened to air and 1,1'-carbonyldiimidazole (0.71 g, 4.4 mmol, 1.1 equiv) was added. The reaction was stirred at r.t. under N_2 for 16 h. The reaction was opened to air, dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 30–40% EtOAc/hexsnes) to yield the product as a white solid (0.52 g, 2.3 mmol, 58%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): 8.16–8.08 (m, 1H), 7.47–7.43 (m, 2H), 7.41–7.38 (m, 1H), 7.38–7.34 (m, 2H), 7.33–7.28 (m, 1H), 7.09–7.02 (m, 1H), 1.55–1.46 (m, 2H), 1.40–1.32 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 148.2, 138.0, 137.2, 130.8, 128.7, 128.5, 127.4, 117.3, 64.2,

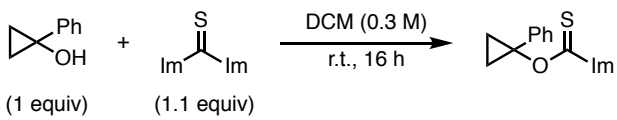
14.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{13}N_2O$ (M+H): 229.0972; found: 229.0969; **IR** (neat): 3151, 3127, 1768, 1471, 1385, 1297, 1285, 1220, 1158, 1004, 820, 760, 700, 644 cm^{-1}; **m.p.:** 56–57 ºC; **R_f** (7:3 hexanes/EtOAc; $KMnO_4$): 0.16.



***O*-(1-Phenylcyclopropyl) methyl(phenyl)carbamothioate (1h):** To a flame-dried 100-mL flask with a stir bar were added 1-phenylcyclopropanol (1.6 g, 12 mmol, 1.0 equiv) and THF (40 mL, 0.30 M), and the solution was cooled to 0 ºC. Phenyl isothiocyanate (1.5 mL, 14 mmol, 1.2 equiv) was added, followed by sodium hydride (0.56 g of a 60% w/w dispersion in mineral oil, 14 mmol, 1.2 equiv) (gas evolves), and the reaction was stirred at r.t. for 1 h. Iodomethane (1.1 mL, 18 mmol, 1.5 equiv) was added and the reaction was stirred at r.t. for an additional 1 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (×3). The organic fractions were combined, washed with 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 white solid (2.4 g, 8.5 mmol, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.39–7.30 (m, 4H), 7.28–7.18 (m, 3H), 7.04–6.98 (m, 1H), 6.74–6.65 (m, 2H), 2.38 (s, 3H), 1.54–1.48 (m, 2H), 1.33–1.26 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 156.4, 147.7, 140.4, 128.9, 128.2, 126.9, 126.1, 123.6, 121.4, 63.4, 16.1, 14.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{18}NOS$ (M+H): 284.1104; found: 284.1107; **IR** (neat): 3054, 2935, 1634, 1591, 1486, 1151, 1024, 969, 876, 755, 726, 692 cm^{-1}; **m.p.:** 53–54 ºC; **R_f** (5% EtOAc/hexanes; UV): 0.59.



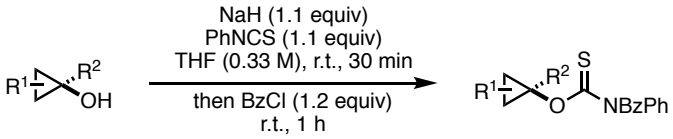
***S*-Methyl *O*-(1-phenylcyclopropyl) carbonodithioate (1i):** To a flame-dried 50-mL flask with a stir bar were added 1-phenylcyclopropanol (0.67 g, 5.0 mmol, 1.0 equiv) and THF (15 mL, 0.33 M), and the solution was cooled to 0 ºC. CS_2 (0.36 mL, 6.0 mmol, 1.2 equiv) was added, followed by sodium hydride (0.22 g of a 60% w/w dispersion in mineral oil, 5.5 mmol, 1.1 equiv), and the reaction was stirred at r.t. for 1 h. The reaction was cooled to 0 ºC and iodomethane (0.47 mL, 7.5 mmol, 1.5 equiv) was added. The reaction was stirred at r.t. for 1 h. The reaction was diluted with Et_2O and was quenched with sat. aq. NH_4Cl and extracted with Et_2O (×2). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the product as a yellow oil (0.93 g, 4.1 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.29 (m, 2H), 7.27–7.20 (m, 3H), 2.53 (s, 3H), 1.58–1.52 (m, 2H), 1.40–1.35 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 214.2, 139.5, 128.4, 127.1, 125.6, 67.4, 19.6, 16.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{11}H_{13}OS_2$ (M+H): 225.0402; found: 225.0400; **IR** (neat): 2921, 1453, 1415, 1224, 1182, 1056, 963, 751, 694 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV/*p*-anisaldehyde): 0.73.



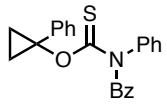
***O*-(1-Phenylcyclopropyl) 1*H*-imidazole-1-carbothioate (1j):** To a flame-dried 25-mL flask with stir bar was added 1-phenylcyclopropanol (0.54 g, 4.0 mmol, 1.0 equiv). The flask was sealed, evacuated and backfilled with N_2 (×3), and DCM (13 mL, 0.30 M) was added. The flask was briefly opened to air and 1,1'-thiocarbonyldiimidazole (0.71 g, 4.4 mmol, 1.1 equiv) was added. The reaction was stirred at r.t. under N_2 for 16 h. The reaction was opened to air and concentrated. The crude residue was purified by flash column chromatography (gradient of 30–40% EtOAc/hexanes) to yield *O*-(1-phenylcyclopropyl) 1*H*-imidazole-1-carbothioate as a yellow solid (0.41 g, 1.7 mmol, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.40–8.32 (m, 1H), 7.69–7.61 (m, 1H), 7.42–7.30 (m, 4H), 7.30–7.21 (m, 1H), 7.08–7.00 (m, 1H), 1.66–1.58 (m, 2H), 1.52–1.43 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 182.2, 137.8, 136.5, 130.7, 128.4, 127.6, 126.1, 117.9, 67.1, 16.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{13}H_{13}N_2OS$ (M+H): 245.0743; found: 245.0745; **IR** (neat): 3151, 3127, 1528, 1475, 1459, 1383, 1332, 1280, 1231, 1204, 1110, 1043, 979, 951, 818, 697, 651 cm^{-1}; **m.p.:** 50–52 ºC; **R_f** (7:3 hexanes/EtOAc; $KMnO_4$): 0.21.

E.2. Preparation of standard thiocarbamate substrates

General Procedure D: Preparation of thiocarbamate starting materials

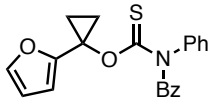


To a flame-dried 50-mL flask with stir bar was added cyclopropanol (1.0 equiv). The flask was evacuated and backfilled with N_2 and THF (0.33 M) was added. Phenyl isothiocyanate (1.1 equiv) was added, followed by sodium hydride (60% dispersion in mineral oil, 1.1 equiv), and the reaction was stirred at r.t. for 0.50–16 h. Then, benzoyl chloride (1.2 equiv) was added, and the reaction was stirred at r.t. for 1–16 h. The reaction was opened to air, quenched with sat. aq. NH_4Cl, and extracted with EtOAc (×3). The organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography and the fractions containing desired product were collected, combined, and concentrated. If the concentrate solidified, it was recrystallized (DCM/hexanes) or washed (hexanes or Et_2O) to yield the desired product. If the concentrate was a foam, it was stripped of solvent (hexanes or Et_2O) and/or triturated (hexanes) to yield the desired product.

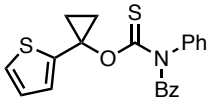


***O*-(1-Phenylcyclopropyl) benzoyl(phenyl)carbamothioate (1k):** Prepared according to General Procedure D by stirring for 30 min after the addition of NaH and PhNCS and for 1 h after the addition of BzCl. The crude material was triturated (hexanes), then recrystallized (DCM/pentane, 3 crops) to yield the product as a pale yellow solid (Figure S5). The product was prepared on 21-mmol scale (3.5 g isolated, 9.4 mmol, 45%) and on 4.0-mmol scale (0.97 g, isolated, 2.6 mmol, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.86–7.82 (m, 2H), 7.61–7.57 (m, 1H), 7.59–7.45 (m, 2H), 7.44–7.39 (m, 2H), 7.37–7.33 (m, 1H), 7.32–7.36 (m, 4H), 7.24–7.20 (m, 1H), 7.20–7.16 (m, 2H), 1.19–1.08 (m, 2H), 0.97–0.86 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.8, 172.3, 141.7, 139.1, 136.0, 132.9, 129.6, 128.9, 128.8, 128.4, 128.4, 128.3, 127.2, 126.2, 66.0, 16.3 ppm; **HRMS** *m/z* (DART): calcd for $C_{23}H_{20}NO_2S$ (M+H): 374.1209; found: 374.1203; **IR** (neat): 3053, 3009, 1686, 1591, 1489, 1449, 1294, 1271, 1232, 1176, 1070, 1028, 999, 755, 690 cm^{-1}; **m.p.:** 97–99 ºC; **R_f** (5% EtOAc/hexanes; UV): 0.31.

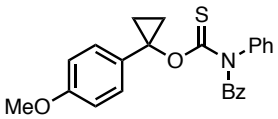
Figure S5. Appearance of thiocarbamate substrate **1k**.



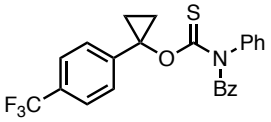
***O*-(1-(Furan-2-yl)cyclopropyl) benzoyl(phenyl)carbamothioate (S7):** Prepared on 2.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then washed with hexanes to yield the product as a pale yellow solid (0.29 g, 0.80 mmol, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.83–7.78 (m, 2H), 7.60–7.55 (m, 1H), 7.47–7.39 (m, 4H), 7.37–7.33 (m, 1H), 7.31–7.26 (m, 3H), 6.35 (dd, *J* = 3.3, 0.9 Hz, 1H), 6.30 (dd, *J* = 3.3, 1.8 Hz, 1H), 1.18–1.13 (m, 2H), 0.91–0.86 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.6, 172.1, 151.8, 141.8, 141.7, 135.9, 132.8, 129.6, 128.8, 128.7, 128.4, 128.3, 110.5, 109.5, 59.9, 14.7 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{18}NO_3S$ (M+H): 364.1002; found: 364.1001; **IR** (neat): 1686, 1595, 1489, 1448, 1295, 1271, 1244, 1186, 1167, 1006, 732, 698, 690 cm^{-1}; **m.p.:** 71–72 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.29.



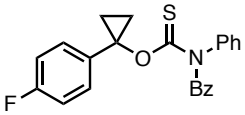
***O*-(1-(Thiophen-2-yl)cyclopropyl) benzoyl(phenyl)carbamothioate (S8):** Prepared on 3.1-mmol scale scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then triturated with hexanes to yield the product as a pale yellow solid (0.79 g, 2.1 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.84–7.80 (m, 2H), 7.59–7.53 (m, 1H), 7.47–7.38 (m, 4H), 7.38–7.32 (m, 1H), 7.31–7.26 (m, 2H), 7.21 (dd, *J* = 5.2, 1.4 Hz, 1H), 6.97 (dd, *J* = 3.6, 1.4 Hz, 1H), 6.89 (dd, *J* = 5.2, 3.7 Hz, 1H), 1.21–1.14 (m, 2H), 1.03–0.98 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.5, 172.1, 142.6, 141.7, 135.8, 132.8, 129.6, 128.8, 128.7, 128.4, 128.3, 127.2, 126.3, 125.8, 61.9, 16.7 ppm; **HRMS** *m/z* (DART): calcd for $C_{21}H_{18}NO_2S_2$ (M+H): 380.0774; found: 380.0775; **IR** (neat): 3052, 1682, 1491, 1448, 1293, 1270, 1171, 1006, 697, 690 cm^{-1}; **m.p.:** 80–82 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.19.



***O*-(1-(4-methoxyphenyl)cyclopropyl) benzoyl(phenyl)carbamothioate (S9):** Prepared on 6.1-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 1 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes), then washed with hexanes to yield the product as a white solid (1.8 g, 4.8 mmol, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.84–7.79 (m, 2H), 7.61–7.55 (m, 1H), 7.49–7.43 (m, 2H), 7.43–7.37 (m, 2H), 7.37–7.31 (m, 1H), 7.29–7.24 (m, 2H), 7.21–7.16 (m, 2H), 6.83–6.77 (m, 2H), 3.79 (s, 3H), 1.10–1.00 (m, 2H), 0.94–0.84 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.8, 172.3, 159.0, 141.7, 136.1, 132.8, 130.8, 129.6, 129.1, 128.9, 128.7, 128.4, 128.3, 113.5, 66.1, 55.4, 15.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{22}NO_3S$ (M+H): 404.1315; found: 404.1316; **IR** (neat): 3007, 2835, 1689, 1613, 1516, 1448, 1316, 1276, 1251, 1192, 1170, 1024, 825, 695 cm^{-1}; **m.p.:** 77–80 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.23.

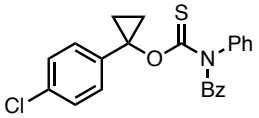


***O*-(1-(4-(Trifluoromethyl)phenyl)cyclopropyl) benzoyl(phenyl)carbamothioate (S10):** Prepared on 1.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then washed with hexanes to yield the product as a white solid (0.26 g, 0.59 mmol, 59%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.87–7.81 (m, 2H), 7.64–7.57 (m, 1H), 7.57–7.51 (m, 2H), 7.51–7.45 (m, 2H), 7.45–7.40 (m, 2H), 7.38–7.33 (m, 1H), 7.33–7.29 (m, 2H), 7.28–7.23 (m, 2H), 1.23–1.15 (m, 2H), 1.04–0.97 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −62.4 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.6, 172.1, 143.5 (q, J = 1.3 Hz), 141.6, 135.8, 133.1, 129.7, 129.2 (q, J = 32.4 Hz), 129.0, 128.9, 128.6, 128.4, 126.0, 125.4 (q, J = 3.8 Hz), 65.3, 17.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{19}NO_2F_3S$ (M+H): 442.1083; found: 442.1082; **IR** (neat): 3180, 3034, 1689, 1683, 1600, 1553, 1451, 1323, 1278, 1166, 1115, 1098, 1067, 1011, 830 cm^{-1}; **m.p.:** 78–80 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.50.

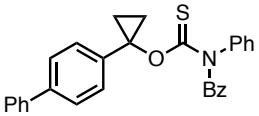


***O*-(1-(4-Fluorophenyl)cyclopropyl) benzoyl(phenyl)carbamothioate (S11):** Prepared on 3.9-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then triturated with hexanes to yield the product as an off-white solid (0.60 g, 1.5 mmol, 38%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.90–7.81 (m, 2H), 7.65–7.59 (m, 1H), 7.54–7.19 (m, 9H), 7.04–6.95 (m, 2H), 1.16–1.08 (m, 2H), 1.02–0.94 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −114.7 ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 190.7, 172.2, 162.0 (d, J = 244.7), 141.6, 135.9, 132.9, 129.6, 129.2, 129.1, 128.9, 128.8, 128.4, 128.4, 115.1 (d, J = 21.5 Hz), 65.7, 15.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{23}H_{19}NO_2FS$

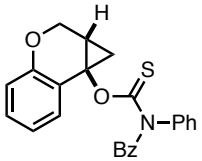
(M+H): 392.1115; found: 392.1111; **IR** (neat): 3199, 3032, 1683, 1596, 1512, 1449, 1315, 1271, 1189, 1173, 1022, 832, 694 cm^{-1}; **m.p.:** 101–103 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.52.



***O*-(1-(4-Chlorophenyl)cyclopropyl) benzoyl(phenyl)carbamothioate (S12):** Prepared on 2.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then washed with hexanes to yield the product as a white solid (0.51 g, 1.3 mmol, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.85–7.79 (m, 2H), 7.62–7.57 (m, 1H), 7.49–7.44 (m, 2H), 7.44–7.39 (m, 2H), 7.37–7.32 (m, 1H), 7.30–7.22 (m, 4H), 7.15–7.10 (m, 2H), 1.15–1.07 (m, 2H), 0.98–0.91 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 190.7, 172.2, 141.6, 137.6, 135.9, 133.1, 133.0, 129.6, 128.9, 128.8, 128.5, 128.4, 128.4, 128.1, 65.5, 16.1; **HRMS** *m/z* (DART): calcd for $C_{23}H_{19}NO_2SCl$ (M+H): 408.0820; found: 408.0813; **IR** (neat): 1686, 1595, 1494, 1450, 1317, 1296, 1269, 1232, 1191, 1171, 1095, 1014, 825, 694 cm^{-1}; **m.p.:** 111–112 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.41.

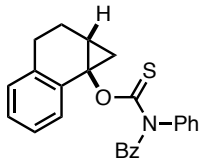


***O*-(1-([1,1'-biphenyl]-4-yl)cyclopropyl) benzoyl(phenyl)carbamothioate (S13):** Prepared on 3.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then triturated with hexanes to yield the product as a tan solid (0.58 g, 1.3 mmol, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.88–7.83 (m, 2H), 7.62–7.54 (m, 4H), 7.53–7.46 (m, 3H), 7.45–7.40 (m, 4H), 7.39–7.30 (m, 4H), 7.26–7.23 (m, 2H), 1.20–1.15 (m, 2H), 0.98–0.93 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.7, 172.1, 141.6, 140.6, 140.0, 138.0, 135.9, 132.8, 129.5, 128.8, 128.7, 128.7, 128.6, 128.3, 127.3, 127.0, 126.9, 126.5, 65.7, 16.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{29}H_{24}NO_2S$ (M+H): 450.1522; found: 450.1525; **IR** (neat): 3031, 1699, 1547, 1488, 1279, 1175, 1064, 831, 764, 699 cm^{-1}; **m.p.:** 88–90 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.53.

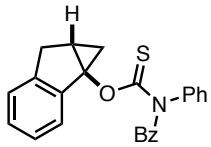


***O*-((*trans*)-1a,2-Dihydrocyclopropa[c]chromen-7b(1*H*)-yl) benzoyl(phenyl)carbamothioate (S14):** Prepared on 3.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then stripped with Et_2O/hexanes and washed with hexanes to yield the product as a white solid (0.56 g, 1.4 mmol, 47%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.86 (m, 2H), 7.63–7.58 (m, 1H), 7.53–7.42 (m, 4H), 7.40–7.35 (m, 3H), 7.30 (dd, J = 7.7, 1.8 Hz, 1H), 7.10 (ddd, J = 8.1, 7.5, 1.7 Hz, 1H), 6.97 (td, J = 7.6, 1.2 Hz, 1H), 6.81 (dd, J = 8.1, 1.2 Hz, 1H), 4.18 (dd, J = 10.5, 1.5 Hz, 1H), 4.11–4.07 (m,

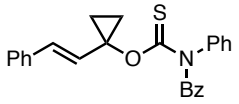
1H), 1.89 (ddt, J = 10.1, 7.0, 1.6 Hz, 1H), 1.16 (tdd, J = 7.0, 0.9, 0.7 Hz, 1H), 0.74 (dd, J = 10.3, 6.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.9, 172.1, 150.6, 141.5, 135.8, 133.1, 129.7, 129.0, 128.9, 128.6, 128.3, 127.4, 125.5, 124.3, 121.7, 117.5, 61.7, 60.5, 27.8, 17.6 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{20}NO_3S$ (M+H): 402.1158; found: 402.1162; **IR** (neat): 3056, 3034, 1692, 1584, 1490, 1460, 1263, 1186, 1177, 1066, 1034, 750, 697 cm^{-1}; **m.p.:** 118–119 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.39.



O-((*trans*)-1,1a,2,3-Tetrahydro-7bH-cyclopropa[a]naphthalen-7b-yl) benzoyl(phenyl)carbamothioate (S15): Prepared on 4.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then stripped with Et_2O/hexanes and washed with hexanes to yield the product as a white solid (1.1 g, 2.8 mmol, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.86 (m, 2H), 7.62–7.57 (m, 1H), 7.57–7.41 (m, 4H), 7.39–7.32 (m, 4H), 7.21 (tt, J = 7.5, 1.1 Hz, 1H), 7.10 (td, J = 7.5, 1.4 Hz, 1H), 7.03 (dt, J = 7.5, 1.3 Hz, 1H), 2.68–2.61 (m, 1H), 2.35–2.25 (m, 1H), 2.02–1.90 (m, 2H), 1.72–1.65 (m, 1H), 0.94 (t, J = 6.8 Hz, 1H), 0.50 (dd, J = 10.3, 6.3 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 191.2, 172.3, 141.8, 136.2, 136.1, 132.9, 132.1, 129.7, 128.9, 128.8, 128.8, 128.4, 128.4, 126.2, 126.0, 124.0, 64.0, 25.8, 24.8, 18.1, 16.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{25}H_{22}NO_2S$ (M+H): 400.1366; found: 400.1374; **IR** (neat): 3037, 2932, 2915, 1694, 1596, 1491, 1449, 1312, 1269, 1192, 1174, 1060, 854, 751, 719, 695 cm^{-1}; **m.p.:** 110–112 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.32.

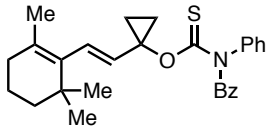


O-((*trans*)-6,6a-dihydrocyclopropa[a]inden-1a(1*H*)-yl) benzoyl(phenyl)carbamothioate (S16): Prepared on 3.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then stripped with hexanes and washed with Et_2O to yield the product as an off-white solid (0.72 g, 1.9 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.89–7.84 (m, 2H), 7.62–7.58 (m, 1H), 7.51–7.42 (m, 4H), 7.40–7.33 (m, 4H), 7.19–7.12 (m, 2H), 7.11–7.07 (m, 1H), 3.27–3.21 (m, 1H), 2.67 (d, J = 17.1 Hz, 1H), 1.79–1.74 (m, 1H), 1.01 (ddd, J = 9.7, 5.8, 0.5 Hz, 1H), 0.55 (dd, J = 5.6, 5.6 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 191.6, 172.2, 142.5, 141.8, 139.8, 136.0, 132.9, 129.7, 128.9, 128.8, 128.4, 128.3, 127.3, 126.3, 125.7, 122.7, 73.9, 34.3, 24.2, 22.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{20}NO_2S$ (M+H): 386.1209; found: 386.1214; **IR** (neat): 3043, 1693, 1598, 1494, 1450, 1319, 1270, 1194, 1175, 1065, 854, 694 cm^{-1}; **m.p.:** 117–119 ºC; **R_f** (9:1 hexanes/EtOAc; UV): 0.45.



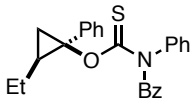
(*E*)-*O*-(1-Styrylcyclopropyl) benzoyl(phenyl)carbamothioate (S17): Prepared on 2.2-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then triturated with hexanes to yield the product as an off-white solid (0.15 g, 0.38 mmol, 17%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.87–7.82 (m, 2H), 7.61–7.56 (m, 1H), 7.50–7.42 (m, 4H), 7.40–7.27 (m, 7H), 7.25–7.20 (m, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 6.25 (d, *J* = 16.1 Hz, 1H), 1.04–0.94 (m, 2H), 0.84–0.74 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 191.0, 172.2, 141.8, 136.5, 136.1, 132.9, 129.7, 129.4, 128.9, 128.7, 128.7, 128.5, 128.4, 127.8, 127.7, 126.5, 65.1, 15.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{25}H_{22}NO_2S$ (M+H): 400.1366; found: 400.1367; **IR** (neat): 3028, 1691, 1597, 1495, 1448, 1298, 1283, 1258, 1191, 1174, 1062, 853, 742, 692 cm^{-1}; **m.p.:** 145–147 ºC; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.41.

***O*-(1-benzylcyclopropyl) benzoyl(phenyl)carbamothioate (S18):** Prepared according to General Procedure D on 4.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 1 h after the addition of BzCl. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes), then recrystallized (DCM/hexanes) to yield the product as a white solid (1.2 g, 3.1 mmol, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.74–7.85 (m, 2H), 7.62–7.54 (m, 1H), 7.51–7.16 (m, 12H), 3.38 (s, 2H), 0.69–0.49 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 191.1, 172.0, 141.4, 137.3, 135.8, 132.8, 129.7, 129.6, 128.8, 128.7, 128.4, 128.3, 128.3, 126.8, 66.1, 38.9, 12.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{24}H_{22}NO_2S$ (M+H): 388.1366; found: 388.1375; **IR** (neat); 3020, 1695, 1490, 1449, 1300, 1270, 1244, 1191, 1173, 1154, 1064, 980, 856, 695, 688 cm^{-1}; **m.p.:** 76–78 ºC; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.33.

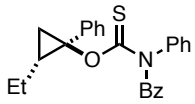


(*E*)-O-(1-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)cyclopropyl) benzoyl(phenyl)carbamothioate (S19): Prepared according to General Proceduer D on 1.9-mmol scale by stirring for 1 h after the addition of NaH and PhNCS and for 1 h after the addition of BzCl. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the desired product as a yellow solid (0.34 g, 0.78 mmol, 41%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.85–7.80 (m, 2H), 7.60–55 (m, 1H), 7.49–7.41 (m, 4H), 7.39–7.34 (m, 1H), 7.34–7.29 (m, 2H), 5.94–5.88 (m, 1H), 5.41 (d, *J* = 16.1 Hz, 1H), 1.98–1.93 (m, 2H), 1.65–1.62 (m, 3H), 1.62–1.56 (m, 2H), 1.46–1.41 (m, 2H), 0.97 (s, 6H), 0.90–0.84 (m, 2H), 0.70–0.66 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 191.0, 172.1, 141.8, 136.6, 136.0, 132.6, 130.9, 129.5, 128.9, 128.7, 128.5, 128.2, 128.2, 127.8, 64.9, 39.3, 34.1, 32.7, 28.7, 21.4, 19.3, 15.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{28}H_{32}NO_2S$ (M+H): 446.2148; found: 446.2157; **IR** (neat): 3038, 2955, 2927, 2862, 2823, 1688, 1598, 1494, 1450, 1318, 1267,

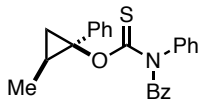
1164, 1072, 975, 695, 659cm^{-1}; **m.p.:** = 76–78°C; $\mathbf{R_f}$ (8:2 hexanes/toluene; UV/*p*-anisaldehyde): 0.30.



***O*-((*cis*)-2-Ethyl-1-phenylcyclopropyl) benzoyl(phenyl)carbamothioate (*cis*-17):** Prepared on 4.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then stripped with hexanes and washed with hexanes to yield the product as a pale yellow solid (1.4 g, 3.5 mmol, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.92–7.85 (m, 2H), 7.59–7.52 (m, 1H), 7.46–7.38 (m, 4H), 7.36–7.25 (m, 5H), 7.24–7.18 (m, 1H), 7.17–7.11 (m, 2H), 1.80–1.69 (m, 1H), 1.31–1.17 (m, 1H), 1.16–1.05 (m, 1H), 1.05–0.94 (m, 2H), 0.82–0.76 (m, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.8, 172.2, 141.1, 140.2, 135.0, 133.1, 129.7, 129.5, 128.9, 128.4, 128.3, 128.2, 127.0, 126.4, 69.3, 30.6, 22.0, 20.5, 13.8; **HRMS** *m/z* (DART): calcd for $C_{25}H_{24}NO_2S$ (M+H): 402.1522; found: 402.1536; **IR** (neat): 2970, 1686, 1494, 1449, 1318, 1274, 1175, 1017, 755, 694 cm^{-1}; **m.p.:** 71–73 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.45.

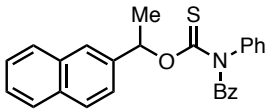


***O*-(*trans*-2-Ethyl-1-phenylcyclopropyl) benzoyl(phenyl)carbamothioate (*trans*-17):** Prepared on 1.4-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude residue was purified by flash column chromatography (gradient of 0–30% Et_2O/hexanes) and the fractions containing product were collected, concentrated, stripped with hexanes and recrystallized (hexanes) to yield the product as a white solid (0.35 g, 0.87 mmol, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.83–7.78 (m, 2H), 7.60–7.55 (m, 1H), 7.47–7.41 (m, 2H), 7.41–7.35 (m, 2H), 7.35–7.30 (m, 1H), 7.29–7.20 (m, 7H), 1.24–1.16 (m, 2H), 1.07–0.96 (m, 1H), 0.87–0.76 (m, 1H), 0.74–0.61 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 190.8, 172.4, 141.7, 136.1, 135.8, 132.7, 129.5, 129.5, 128.9, 128.8, 128.4, 128.2, 127.9, 127.8, 70.6, 27.6, 22.2, 18.0, 13.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{25}H_{24}NO_2S$ (M+H): 402.1522; found: 402.1527; **IR** (neat): 3062, 2980, 1705, 1683, 1595, 1491, 1450, 1317, 1271, 1204, 1174, 1059, 1022, 856, 752, 694 cm^{-1}; **m.p.:** 119–120 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.41.

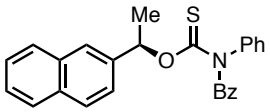


***O*-((*cis*)-2-methyl-1-phenylcyclopropyl) benzoyl(phenyl)carbamothioate (*cis*-18):** Prepared on 4.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then washed with hexanes to yield the product as a white solid (1.5 g, 3.9 mmol, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.91–7.86 (m, 2H), 7.58–7.52 (m, 1H), 7.46–7.37 (m, 4H), 7.46–7.31 (m, 3H), 7.30–7.25 (m, 2H), 7.23–7.18 (m, 1H), 7.15–7.10 (m, 2H), 1.63 (dd, *J* = 9.6, 6.9 Hz, 1H), 1.29–1.18 (m, 1H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.94 (dd, *J* = 7.9, 6.9 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 191.0, 172.2, 141.2, 140.2,

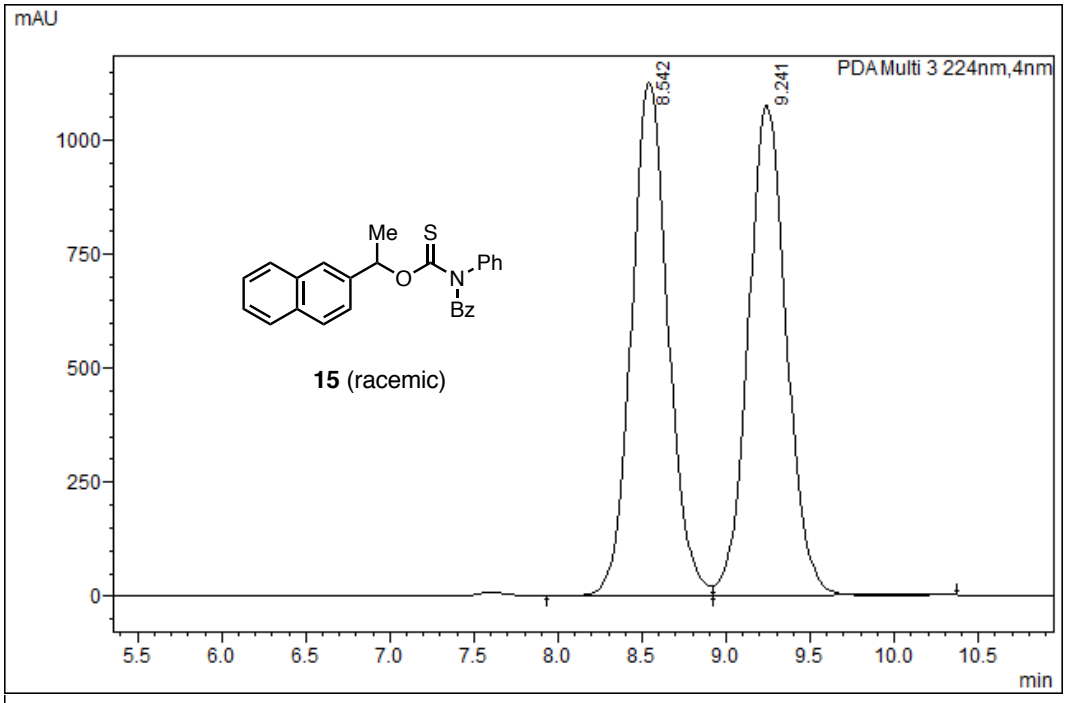
135.2, 133.0, 129.6, 129.5, 128.9, 128.4, 128.4, 128.2, 126.9, 126.2, 69.3, 23.0, 21.8, 13.1; **HRMS** *m/z* (DART): calcd for $C_{24}H_{22}NO_2S$ (M+H): 388.1366; found: 388.1371; **IR** (neat): 3163, 3035, 2926, 1694, 1678, 1595, 1493, 1274, 1238, 1172, 1074, 1004, 853, 743, 691 cm^{-1}; **m.p.:** 90–91 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.46.



***O*-(1-(Naphthalen-2-yl)ethyl) benzoyl(phenyl)carbamothioate (racemic) (*rac*-15):** Prepared on 5.0-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then concentrated and washed with Et_2O to yield the product as a white solid (1.1 g, 2.7 mmol, 54%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.87–7.83 (m, 2H), 7.82–7.78 (m, 1H), 7.76–7.72 (m, 1H), 7.70 (app d, *J* = 8.5 Hz, 1H), 7.50–7.46 (m, 3H), 7.45–7.30 (m, 8H), 7.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.48 (q, *J* = 6.6 Hz, 1H), 1.39 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 191.0, 172.3, 141.6, 137.3, 135.6, 133.2, 133.1, 132.9, 129.6, 129.0, 128.8, 128.5, 128.5, 128.4, 128.2, 127.8, 126.4, 126.4, 125.7, 124.2, 81.5, 21.5 ppm; **HRMS** *m/z* (DART): calcd for $C_{26}H_{22}NO_2S$ (M+H): 412.1366; found: 412.1367; **IR** (neat): 2983, 1683, 1601, 1486, 1451, 1341, 1301, 1267, 1213, 1044, 1006, 853, 821, 749, 691 cm^{-1}; **m.p.:** 100–102 ºC; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV): 0.43.

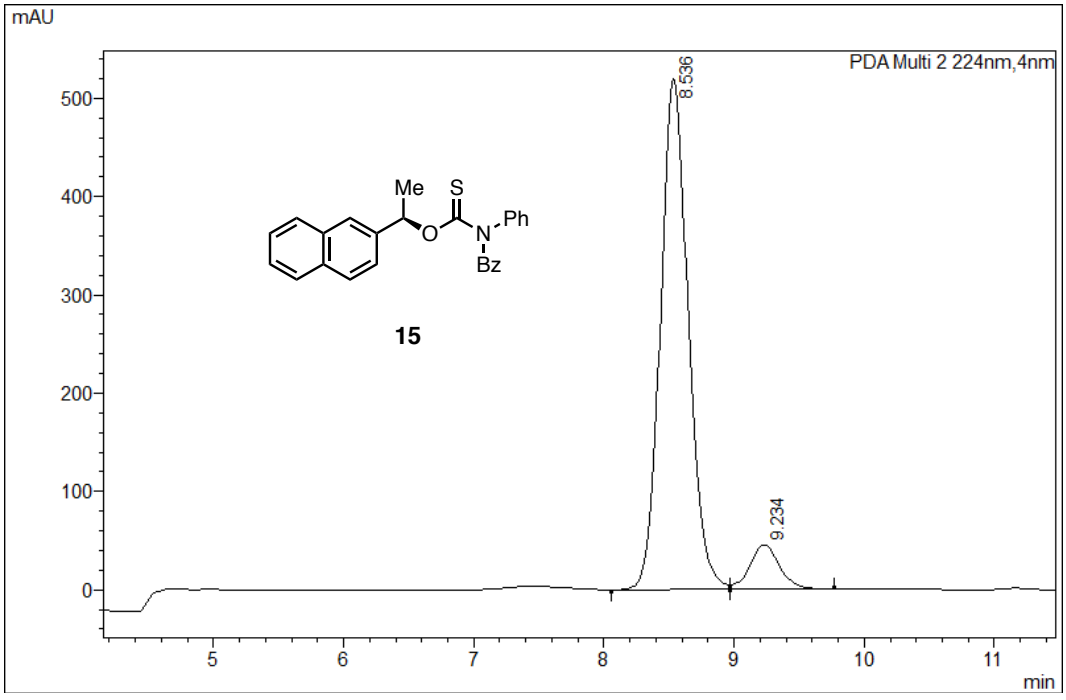


***O*-(1-(Naphthalen-2-yl)ethyl) benzoyl(phenyl)carbamothioate (enantioenriched) (15):** Prepared on 0.41-mmol scale by stirring for 30 min after the addition of NaH and PhNCS and for 16 h after the addition of BzCl. The crude material was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes), then concentrated and washed with hexanes to yield the product as a white solid (0.11 g, 0.27 mmol, 66%). The analytical data was identical to that of the racemic product. **Chiral HPLC** (Chiralpak IA, 0.3% *i*-PrOH/hexanes, 1.0 mL/min, λ = 224 nm): t_R (major): 8.54 min; t_R (minor): 9.23 min; 83% e.e.



PDA Ch3 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.542	17023734	1124822	0.000			
2	9.241	16932549	1075241	0.000		V M	
Total		33956282	2200063				



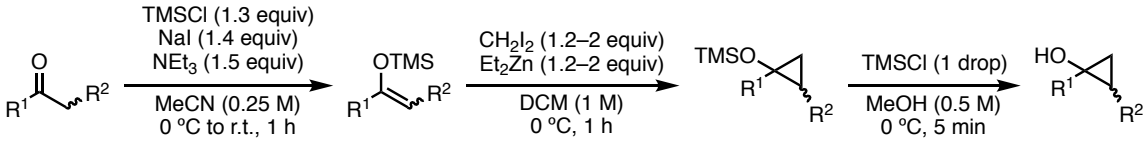
PDA Ch2 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.536	7713344	519990	0.000			
2	9.234	704675	44967	0.000		V M	
Total		8418019	564957				

E.3. Preparation of alcohols

The following cyclopropanols were prepared as previously described:[8] 1-phenylcyclopropanol, 1-(4-fluorophenyl)cyclopropan-1-ol, 1-benzylcyclopropanol, 1-([1,1'-biphenyl]-4-yl)cyclopropan-1-ol, 1-(thiophen-2-yl)cyclopropan-1-ol, (*E*)-1-styrylcyclopropan-1-ol, 6,6a-dihydrocyclopropa[a]inden-1a(1*H*)-ol, 1-benzylcyclopropanol.

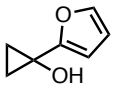
General Procedure E: Simmons–Smith sequence for the synthesis of cyclopropanols



Silyl enol ether (Step 1): To an appropriately sized 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 ketone substrate (1.0 equiv). The solution was cooled to 0 ºC and stirred, and chlorotrimethylsilane (1.3 equiv) and triethylamine (1.5 equiv) were sequentially added. The reaction was stirred at r.t. for 1 h. The reaction was concentrated under vacuum and the solid concentrate was extracted with hexanes (×3) (for more polar substrates Et_2O can be used). The organic extracts were combined and concentrated to yield the crude silyl enol ether, which was used in the next step without further purification.

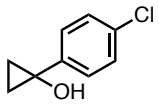
TMS-protected cyclopropanol (Step 2): The crude material was transferred to an appropriately sized flame-dried round-bottom flask and a stir bar was added. The flask was evacuated and backfilled with N_2 (×3) and DCM (1.0 M) was added. The solution was cooled to 0 ºC and diiodomethane (1.2–2.0 equiv) was added. Over 10 min, diethylzinc (1.0 M solution in hexanes, 1.2–2.0 equiv) was added down the side of the flask. The reaction was stirred at 0 ºC for 1 h. The reaction was slowly quenched with sat. aq. $NaHCO_3$ (gas evolves). The mixture was extracted with DCM (×3) and the organic fractions were combined, washed with H_2O (×1) and brine (×1), dried over $MgSO_4$, and concentrated to yield the crude material, which was used in the next step without further purification. If incomplete conversion of the silyl enol ether was determined by ^1H NMR, the crude material can be re-exposed to Simmons–Smith conditions.

Cyclopropanol (Step 3): The crude material from the previous step was dissolved in MeOH (0.5 M) (note: anhydrous MeOH is necessary) and the solution was cooled to 0 ºC. TMSCl (1 drop) was added and the solution was stirred at 0 ºC for 5 min. The solution was concentrated and the crude concentrate was purified by flash column chromatography to yield the cyclopropanol. As a precaution, all cyclopropanols were stored at −20 ºC.

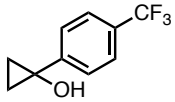


1-(Furan-2-yl)cyclopropan-1-ol (S20): Prepared according to General Procedure E on 8.0-mmol scale from 1-(furan-2-yl)ethan-1-one (0.88 g, 8.0 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (1.3 mL, 16 mmol, 2.0 equiv) and diethylzinc (16 mL, 16 mmol). The cyclopropanol was purified by flash column chromatography (gradient of 0–

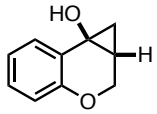
30% EtOAc/hexanes) to yield the product as a pale yellow oil (0.39 g, 3.1 mmol, 39% over three steps). Analytical data:[9] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.33–7.29 (m, 1H), 6.34–6.19 (m, 1H), 6.23–6.19 (m, 1H), 2.82 (br s, 1H), 1.18–1.11 (m, 2H), 1.10–1.02 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 156.7, 141.5, 110.5, 104.9, 52.4, 15.3 ppm; **R_f** (9:1 hexanes/EtOAc; $KMnO_4$): 0.17.



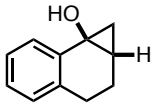
1-(4-Chlorophenyl)cyclopropan-1-ol (S21): Prepared according to General Procedure E on 8.0-mmol scale from 4-chloroacetophenone (1.0 mL, 8.0 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (0.96 mL, 12 mmol, 1.5 equiv) and diethylzinc (12 mL, 12 mmol, 1.5 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a white solid (0.44 g, 2.6 mmol, 33% over three steps). Analytical data:[10] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.32–7.26 (m, 2H), 7.25–7.20 (m, 2H), 2.39 (br s, 1H), 1.34–1.20 (m, 2H), 1.08–0.95 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 143.0, 132.3, 128.6, 126.0, 56.4, 18.2 ppm; **R_f** (8:2 hexanes/EtOAc; UV/$KMnO_4$): 0.53.



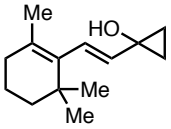
1-(4-(Trifluoromethyl)phenyl)cyclopropan-1-ol (S22): Prepared according to General Procedure E on 8.0-mmol scale using 1-(4-(trifluoromethyl)phenyl)ethan-1-one (1.3 mL, 8.0 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (0.77 mL, 9.6 mmol, 1.2 equiv) and diethylzinc (9.6 mL, 9.6 mmol, 1.2 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 5–30% EtOAc/hexanes) to yield the product as a white solid (0.36 g, 1.8 mmol, 23% over three steps). Analytical data:[11] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.60–7.53 (m, 2H), 7.40–7.33 (m, 2H), 2.60 (br s, 1H), 1.38–1.30 (m, 2H), 1.13–1.06 (m, 2H) ppm; **^{19}F NMR** (377 MHz, $CDCl_3$, 298 K): δ_F −62.4 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 148.8 (q, J = 1.4 Hz), 128.6 (q, J = 32.2 Hz), 125.4 (q, J = 3.8 Hz), 124.4 (q, J = 261.5 Hz), 124.3, 56.3, 19.1 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.33.



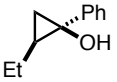
(*trans*)-1a,2-Dihydrocyclopropa[*c*]chromen-7b(1*H*)-ol (S23): Prepared according to General Procedure E on 8.0-mmol scale from 4-chromanone (1.2 g, 8.0 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (0.77 mL, 9.6 mmol, 1.2 equiv) and diethylzinc (9.6 mL, 9.6 mmol, 1.2 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a colourless oil (0.75 g, 4.6 mmol, 58% over three steps). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.64–7.58 (m, 1H), 7.13 (app td, J = 7.8, 1.8 Hz, 1H), 7.02 (app tt, J = 7.5, 1.4 Hz, 1H), 6.84 (dd, J = 8.0, 1.2 Hz, 1H), 4.23–4.18 (m, 1H), 3.91–3.85 (m, 1H), 2.50 (br s, 1H), 1.95–1.85 (m, 1H), 1.44–1.35 (m, 1H), 1.26–1.19 (m, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 151.1, 129.7, 127.2, 124.5, 121.9, 117.1, 62.4, 52.0, 27.4, 18.3 ppm.



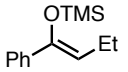
(*trans*)-1,1a,2,3-Tetrahydro-7b*H*-cyclopropa[*a*]naphthalen-7b-ol (S24): Prepared according to General Procedure E on 8.0-mmol scale from tetralone (1.1 mL, 8.0 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (0.96 mL, 12 mmol, 1.5 equiv) and diethylzinc (12 mL, 12 mmol, 1.5 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 0–30% EtOAc/hexanes) to yield the product as a white solid (0.88 g, 5.5 mmol, 69% over three steps). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.75 (dd, J = 7.7, 1.4 Hz, 1H), 7.30 (app tt, J = 7.4, 1.3 Hz, 1H), 7.17 (app td, J = 7.4, 1.4 Hz, 1H), 7.12–7.07 (m, 1H), 2.72–2.61 (m, 1H), 2.55–2.32 (m, 2H), 2.09–1.98 (m, 1H), 1.85–1.72 (m, 2H), 1.26 (dd, J = 9.8, 5.7 Hz, 1H), 1.11 (dd, J = 5.8, 5.8 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 140.6, 132.8, 128.2, 126.3, 125.6, 124.1, 54.6, 26.1, 24.6, 18.4, 16.4 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.22.



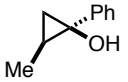
(*E*)-1-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)cyclopropan-1-ol (S25): Prepared according to General Procedure E on 15-mmol scale from β-ionone (3.1 mL, 15 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (1.7 mL, 21 mmol, 1.4 equiv) and diethylzinc (21 mL of a 1.0 M solution in hexanes, 21 mmol, 1.4 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 0–5% EtOAc/hexanes) to yield the desired product as a yellow solid (0.98 g, 4.7 mmol, 32% over three steps). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 6.10 (dtd, J = 15.9, 2.0, 1.0 Hz, 1H), 5.24 (d, J = 16.0 Hz, 1H), 2.00–1.95 (m, 2H), 1.67 (q, J = 1.0 Hz, 3H), 1.60 (ddt, J = 9.9, 6.4, 3.4 Hz, 2H), 1.47–1.43 (m, 2H), 1.07–1.03 (m, 2H), 1.00 (s, 6H), 0.78–0.70 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 137.1, 137.0, 128.2, 123.9, 55.8, 39.5, 34.1, 32.8, 28.7, 21.4, 19.3, 15.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{14}H_{23}O$ (M+H): 207.1743; found: 207.1748; **IR** (neat): 3236 (broad), 3089, 2982, 2965, 2925, 2905, 2863, 1357, 1290, 1018, 979, 965, 919, 886, 679 cm^{-1}; **m.p.:** 50–53°C; **R_f (**19:1 hexanes/EtOAc; *p*-anisaldehyde): 0.30.



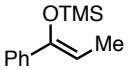
(*cis*)-2-Ethyl-1-phenylcyclopropan-1-ol (>20:1 d.r.) (S26): Prepared according to General Procedure E on 12-mmol scale using butyrophenone (1.7 mL, 12 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (1.1 mL, 14 mmol, 1.2 equiv) and diethylzinc (14 mL, 14 mmol, 1.2 equiv). The crude cyclopropanol was a colourless oil, which was sufficiently clean to use without further purification (1.3 g, 8.0 mmol, 67% over three steps). The relative configuration was determined by the configuration of the silyl enol ether precursor (see below). Analytical data:[12] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.37–7.27 (m, 4H), 7.24–7.18 (m, 1H), 2.07 (br s, 1H), 1.75–1.59 (m, 2H), 1.23–1.12 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H), 0.88–0.83 (m, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 145.6, 128.4, 126.3, 124.3, 59.7, 30.8, 22.9, 21.4, 14.4 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.35.



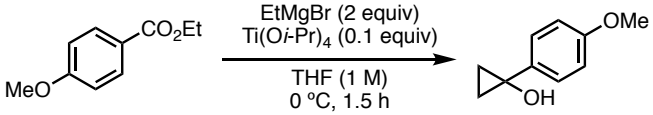
(*Z*)-Trimethyl((1-phenylbut-1-en-1-yl)oxy)silane (>20:1 isomer ratio) (S27):[13] Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.50–7.43 (m, 2H), 7.33–7.18 (m, 3H), 7.24 (t, J = 7.1 Hz, 1H), 2.22 (pent, J = 7.4 Hz, 2H), 1.04 (td, J = 7.6, 0.5 Hz, 3H), 0.13 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 148.5, 139.4, 128.1, 127.4, 125.5, 113.5, 19.7, 14.4, 0.7 ppm; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.78.



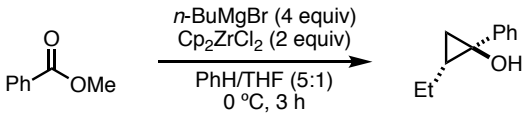
(*cis*)-2-Methyl-1-phenylcyclopropan-1-ol (>20:1 d.r.) (S28): Prepared according to General Procedure E on 10-mmol scale using propiophenone (1.3 mL, 10 mmol, 1.0 equiv). The Simmons–Smith reaction was performed using diiodomethane (0.96 mL, 12 mmol, 1.2 equiv) and diethylzinc (12 mL, 12 mmol, 1.2 equiv). The cyclopropanol was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil which solidified over time to form a white solid (0.95 g, 6.4 mmol, 64% over three steps). The relative configuration was determined by the configuration of the silyl enol ether precursor (see below). Analytical data:[9] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.36–7.31 (m, 2H), 7.30–7.26 (m, 2H), 7.24–7.19 (m, 1H), 2.28 (br s, 1H), 1.35–1.31 (m, 3H), 1.29–1.20 (m, 2H), 0.85–0.82 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 145.6, 128.4, 126.2, 124.0, 59.2, 24.3, 23.3, 12.7 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.28.



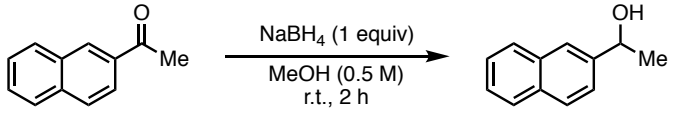
(*Z*)-Trimethyl((1-phenylprop-1-en-1-yl)oxy)silane (>20:1 isomer ratio) (S29):[14] Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.49–7.42 (m, 2H), 7.33–7.18 (m, 3H), 5.33 (q, J = 6.8 Hz, 1H), 1.74 (d, J = 6.8 Hz, 3H), 0.14 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 150.0, 139.3, 128.2, 127.4, 125.3, 105.5, 11.8, 0.7 ppm; **R_f** (5% EtOAc/hexanes; UV/$KMnO_4$): 0.58.



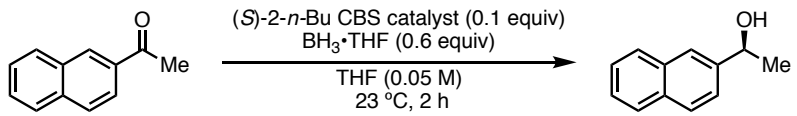
1-(4-Methoxyphenyl)cyclopropan-1-ol (S30): To a flame-dried 250-mL flask with a stir bar were added THF (40 mL, 1.0 M), ethyl 4-methoxybenzoate (6.5 mL, 40 mmol, 1.0 equiv), and titanium(IV) isopropoxide (1.2 mL, 4.0 mmol, 0.10 equiv), and the solution was stirred and cooled to 0 ºC. Over 1.5 h, ethylmagnesium bromide (84 mL of a 0.95 M solution in THF, 80 mmol, 2.0 equiv) was added portionwise (6 portions) down the side of the flask. The reaction was quenched with 10% H_2SO_4 and extracted with Et_2O (×3), and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) and the fractions containing product were combined and concentrated. The concentrate was triturated with hexanes to yield the product as a white solid (2.5 g, 15 mmol, 38%). Analytical data:[8] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.35–7.26 (m, 2H), 6.94–6.87 (m, 2H), 3.83 (s, 3H), 2.41 (br s, 1H), 1.28–1.19 (m, 2H), 1.05–0.95 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 158.6, 136.3, 126.5, 113.9, 56.8, 55.5, 16.9ppm.



(*trans*)-2-Ethyl-1-phenylcyclopropan-1-ol (S31):[15] A flame-dried 100-mL flask with a stir bar was brought into a glovebox and bis(cyclopentadienyl)zirconium(IV) dichloride (0.58 g, 2.0 mmol, 2.0 equiv) was added. The flask was sealed and removed from the glovebox, equipped with a N_2 balloon, and PhH (31 mL) was added. The solution was cooled to 0 ºC. Butylmagnesium bromide (6.1 mL of a 0.66 M solution in THF, 4.0 mmol, 4.0 equiv) was added down the side of the flask (total reaction volume = 37 mL of a 5:1 PhH/THF mixture). The reaction was stirred at 0 ºC for 30 min. Then, methyl benzoate (0.12 mL, 1.0 mmol, 1.0 equiv) was added dropwise, and the reaction was stirred at 0 ºC for 3 h. The reaction was quenched with 1 M HCl and extracted with Et_2O (×3), and the organic fractions were combined, washed with 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 43 mg of (*trans*)-2-ethyl-1-phenylcyclopropan-1-ol (0.27 mmol, 27%) and 11 mg of (*cis*)-2-ethyl-1-phenylcyclopropan-1-ol (0.068 mmol, 7%). The same procedure was repeated on 3.0-mmol scale to yield 0.23 g of the desired *trans* product (1.4 mmol, 47%). The analytical data for (*cis*)-2-ethyl-1-phenylcyclopropan-1-ol was identical to the previously prepared sample. The analytical data for (*trans*)-2-ethyl-1-phenylcyclopropan-1-ol was consistent with literature:[15] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.45–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.30–7.25 (m, 1H), 1.45–1.34 (m, 1H), 1.18–1.06 (m, 2H), 0.92 (dd, J = 6.7, 5.6 Hz, 1H), 0.87–0.78 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 140.6, 128.3, 128.2, 127.5, 62.0, 29.3, 22.9, 18.3, 13.5 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.20.



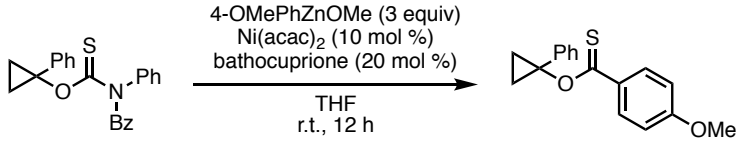
1-(Naphthalen-2-yl)ethan-1-ol (racemic) (S32): To a 100-mL flask with a stir bar were sequentially added 2-naphthyl methyl ketone (1.7 g, 10 mmol, 1.0 equiv), MeOH (20 mL, 0.50 M), and sodium borohydride (0.38 g, 10 mmol, 1.0 equiv), and the reaction was stirred at r.t. for 2 h. The reaction was quenched 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 to yield the product as a white solid (1.7 g, 9.9 mmol, 99%). Analytical data:[16] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.99–7.70 (m, 4H), 7.60–7.36 (m, 3H), 5.07 (br q, J = 6.9 Hz, 1H), 1.99 (br s, 1H), 1.59 (d, J = 6.5 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 143.3, 133.5, 133.1, 128.5, 128.1, 127.8, 126.3, 125.9, 124.0, 123.9, 70.7, 25.3 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.17.



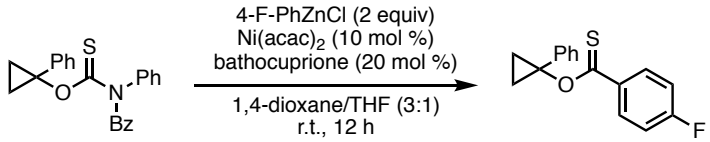
1-(Naphthalen-2-yl)ethan-1-ol (enantioenriched) (S33): To a 100-mL flask was added 2-naphthyl methyl ketone (0.17 g, 1.0 mmol, 1.0 equiv) and THF (18 mL), and the solution was submerged in a 23 ºC water bath. BH_3–THF (0.60 mL of a 1.0 mL solution in THF, 0.60 mmol, 0.60 equiv) was added to the reaction, followed by a stock solution of (*S*)-(-)-2-Butyl-CBS-

oxazaborolidine catalyst (0.10 mL of a 1.0 M solution of catalyst in PhMe diluted with 2.0 mL THF, 0.10 mmol, 0.10 equiv), and the reaction was stirred at 23 ºC for 2 h. The reaction was quenched with H_2O and extracted with Et_2O, and the organic fractions were combined, washed with brine (×1), dried over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (gradient of 0–40% EtOAc/hexanes) to yield the product as a white solid (71 mg, 0.41 mmol, 41%). The analytical data was identical to that of the racemic product. The e.e. of the material was determined in the next step (compound **6**).

E.4. Preparation of thiobenzoates



***O*-(1-Phenylcyclopropyl) 4-methoxybenzothioate (4a):** The product was prepared according to General Procedure A with the modifications that THF was used instead of 1,4-dioxane and that no magnesium(II) chloride was added. The crude residue was purified by flash column chromatography (gradient of 0–60% PhMe/hexanes) to yield the product as a yellow oil which slowly solidified upon standing. The product was prepared on 0.20-mmol scale (33 mg isolated, 0.116 mmol, 58%) and on 1.0-mmol scale (81 mg isolated, 0.285 mmol, 29%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.24–8.18 (m, 2H), 7.31–7.27 (m, 2H), 7.27–7.23 (m, 2H), 7.22–7.17 (m, 1H), 6.89–6.85 (m, 2H), 3.87 (s, 3H), 1.62–1.56 (m, 2H), 1.49–1.43 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 208.6, 163.8, 140.0, 131.9, 131.1, 128.4, 126.8, 125.2, 113.4, 65.3, 55.7, 17.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{17}O_2S$ (M+H): 285.0944; found: 285.0951; **IR** (neat): 3077, 3018, 2974, 2929, 2836, 1727, 1596, 1498, 1453, 1421, 1328, 1277, 1249, 1195, 1169, 1112, 1097, 1023, 837 cm^{-1}; **m.p.:** 52–55 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.31.

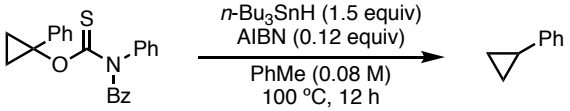


***O*-(1-Phenylcyclopropyl) 4-fluorobenzothioate (4b):** The product was prepared according to General Procedure A on 0.20-mmol scale with the modifications that 4-fluorophenylzinc chloride (2.0 equiv) was used and that no magnesium(II) chloride was added. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a yellow solid (31 mg, 0.114 mmol, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): 8.26–8.21 (m, 2H), 7.33–7.24 (m, 4H), 7.24–7.19 (m, 1H), 7.09–7.03 (m, 2H), 1.61–1.56 (m, 2H), 1.50–1.45 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −106.3 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 207.8, 166.0 (d, J = 253.7 Hz), 139.5, 135.1 (d, J = 2.8 Hz), 131.3 (d, J = 9.1 Hz), 128.4, 127.0, 125.5, 115.3 (d, J = 21.9 Hz), 65.9, 17.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{14}OFS$ (M+H): 273.0744; found: 273.0747; **IR** (neat): 2924, 2854, 1599, 1503, 1455, 1412, 1269, 1231, 1196, 1155, 1097, 1041, 843, 830, 696 cm^{-1}; **m.p.:** 42–44 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde) 0.60.

F. Mechanistic experiments

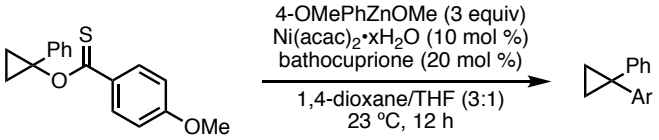
*F.1. Barton–McCombie deoxygenation of **1k***

Equation S1. Barton–McCombie deoxygenation of **1k**



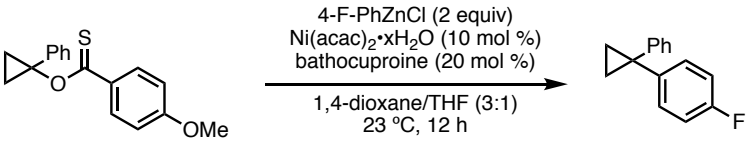
Cyclopropylbenzene (S34): To a 16-mL threaded culture tube with a stir bar was added **1k** (75 mg, 0.20 mmol, 1.0 equiv) and the tube was sealed and evacuated and backfilled with N_2 (×3). PhMe (degassed, 1.5 mL) was added, followed by tributyltin hydride (81 µL, 0.30 mmol, 1.5 equiv), and AIBN (3.9 mg as a stock solution in 1.0 mL PhMe, 0.024 mmol, 0.12 equiv). The reaction was heated at 100 ºC for 12 h. The reaction was cooled to r.t., quenched with H_2O, and extracted with Et_2O (×3). The organic fractions were combined, washed with 1 M aq. TBAF, dried over $MgSO_4$, and concentrated. Dibromomethane (14 µL, 0.20 mmol, 1.0 equiv) was added as internal ^{1}H NMR standard. The yield was determined to be 65% by ^{1}H NMR. The spectral data for the cyclopropylbenzene product matched literature data.[17]

*F.2. Reaction using **4a***



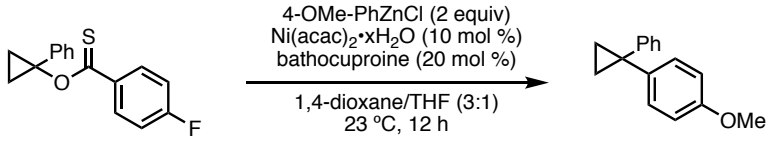
The reaction was performed on 0.10-mmol scale according to General Procedure B. The yield was determined to be 82% by GC-MS using dodecane as an internal standard. The analytical data was identical to that of **3a** prepared in the standard reaction.

F.3. Crossover experiments



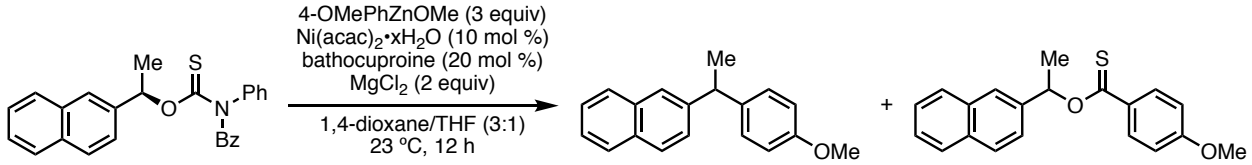
1-Fluoro-4-(1-phenylcyclopropyl)benzene (3b): Prepared according to General Procedure B on 0.10-mmol scale from **4a** (28 mg as a stock solution in 1.3 mL of 1,4-dioxane, 0.10 mmol, 1.0 equiv) and 4-fluorophenylzinc chloride (1.3 mL of a 0.46 M solution in THF, 0.20 mmol, 2.0 equiv). The crude residue was purified by flash column chromatography (gradient of 0–10% PhMe/hexanes). Cyclopropane **3b** was inseparable from homodimer side-product, 4,4'-difluoro-1,1'-biphenyl. A 15 mg sample was obtained which was a 1:1 mixture of **3b** to homodimer as determined by ^{19}F NMR (desired: 0.049 mmol, 49%; homodimer: 0.025 mmol, 25%). 4,4'-Difluoro-1,1'-biphenyl is a known compound.[18] Characterization for **3b**: **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.30–7.15 (m, 7H), 6.91–6.90 (m, 2H), 1.32–1.28 (m, 4H) ppm; **^{19}F NMR**

(376 MHz, $CDCl_3$, 298 K): δ_F −117.1 ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 161.0 (d, J = 148.0 Hz), 145.8, 141.5 (d, J = 3.1 Hz), 130.3 (d, J = 7.9 Hz), 128.5, 128.2, 126.1, 115.1 (d, J = 21.2 Hz), 29.9, 16.5 ppm; **R_f** (40% PhMe/hexanes; UV): 0.58.

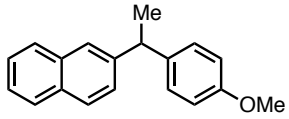


Reaction using O-(1-phenylcyclopropyl) 4-fluorobenzothioate (4b): Performed according to General Procedure B on 0.088-mmol scale using **4b** (24 mg as a solution in 1.7 mL 1,4-dioxane, 0.088 mmol, 1.0 equiv) and 4-methoxyphenylzinc chloride (0.55 mL of a 0.33 M solution in THF, 0.18 mmol, 2.0 equiv). At the end of the reaction, *n*-dodecane was added as GC-MS standard. The yield of cyclopropane **3a** was determined to be 5% by GC-MS. There was no detectable amount of **3b** by GC-MS.

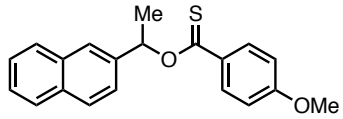
F.4. Loss of enantiomeric excess



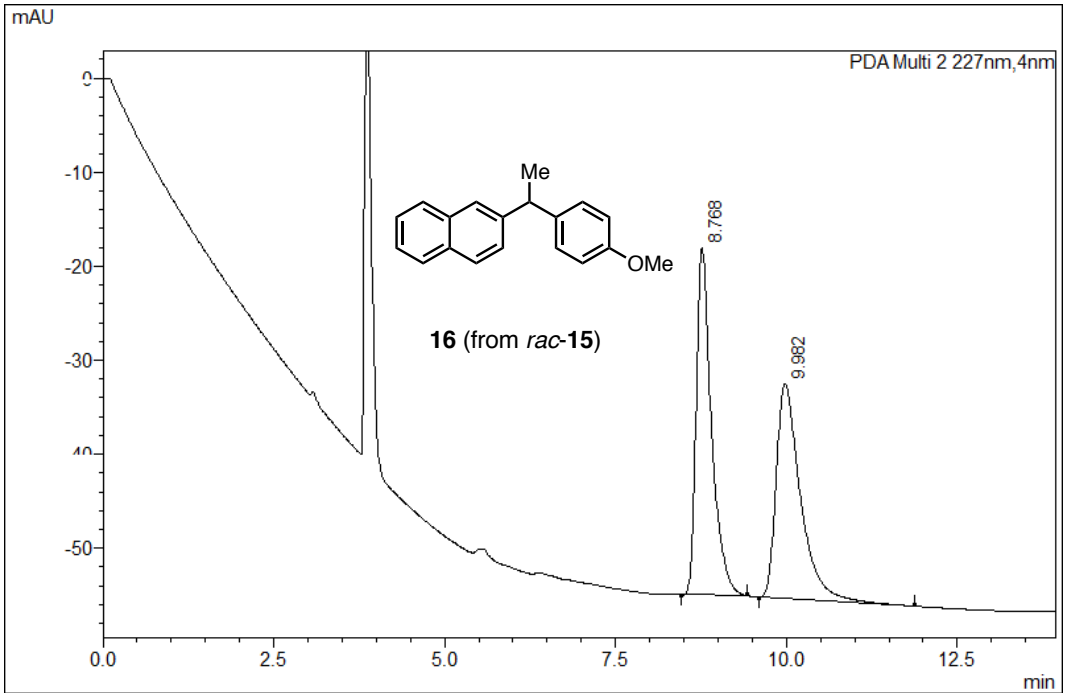
2-(1-(4-Methoxyphenyl)ethyl)naphthalene (16): Performed on 0.10-mmol scale according to General Procedure A using **6** (83% e.e.). The crude residue was purified by flash column chromatography (gradient of 0–20% Et_2O/hexanes) to yield 2-(1-(4-methoxyphenyl)ethyl)naphthalene **(7)** (1.7 mg, 0.0065 mmol, 7%) and thiobenzoate side-product *O*-(1-(naphthalen-2-yl)ethyl) 4-methoxybenzothioate (3.8 mg, 0.012 mmol, 12%). The reaction was repeated using *rac*-**7** and 4,4'-dimethoxybipyridyl (20 mol %) to obtain a racemic sample of **8** (8.1 mg isolated, 0.031 mmol, 31%).



2-(1-(4-Methoxyphenyl)ethyl)naphthalene (16): White solid. The NMR data was consistent with literature.[19] **Chiral HPLC** (Chiralpak IA, 0.2% *i*-PrOH/hexanes, 1.0 mL/min, λ = 227 nm): t_R (major): 8.39 min; t_R (minor): 9.45 min; 9% e.e.

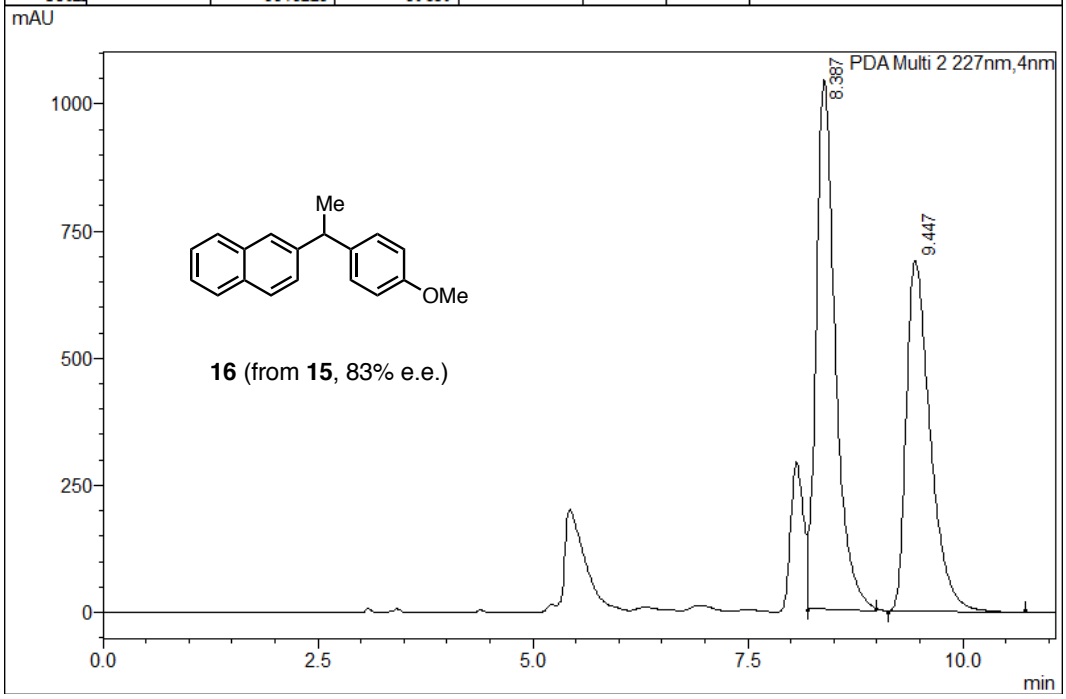


***O*-(1-(Naphthalen-2-yl)ethyl) 4-methoxybenzothioate (S35):** Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.26–8.21 (m, 2H), 7.90–7.81 (m, 4H), 7.57 (dd, *J* = 8.5, 1.8 HZ, 1H), 7.51–7.45 (m, 2H), 6.93 (q, *J* = 6.5 Hz, 1H), 6.90–6.86 (m, 2H), 3.87 (s, 3H), 1.84 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 209.3, 163.8, 138.8, 133.3, 133.2, 132.1, 131.4, 128.6, 128.2, 127.8, 126.4, 126.3, 125.5, 124.4, 113.4, 79.5, 55.7, 22.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{20}H_{19}O_2S$ (M+H): 323.1100; found: 323.1098; **IR** (neat): 2971, 2921, 2850, 1597, 1505, 1454, 1316, 1253, 1218, 1169, 1110, 1055, 1024, 839, 828, 747, 639 cm^{-1}; **m.p.:** 78–80 ºC; **R_f** (9:1 hexanes/EtOAc; UV/*p*-anisaldehyde): 0.47.



PDA Ch2 227nm

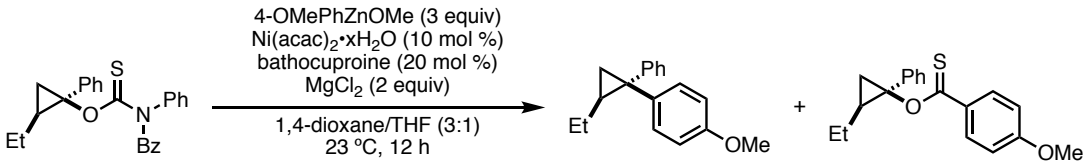
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.768	575149	37001	0.000		M	
2	9.982	566076	22838	0.000		M	
Total		1141225	59839				



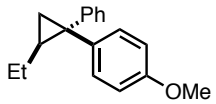
PDA Ch2 227nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.387	16136263	1041944	0.000		M	
2	9.447	13365471	689875	0.000		M	
Total		29501734	1731819				

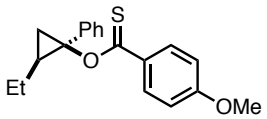
F.5. Maintenance of stereochemistry



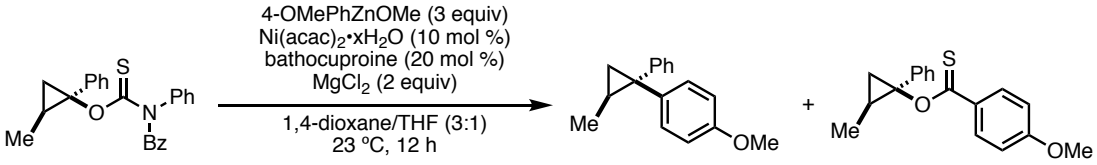
Reaction using *cis*-**17**: The reaction was performed on 0.20-mmol scale according to General Procedure A. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield cyclopropane 1-((*cis*)-2-ethyl-1-phenylcyclopropyl)-4-methoxybenzene (*cis*-**19**) (9.1 mg, 0.036 mmol, 18%) and thioester side-product *O*-((*cis*)-2-ethyl-1-phenylcyclopropyl) 4-methoxybenzothioate (12 mg, 0.038 mmol, 19%). The crude material was analyzed by GC-MS to determine the d.r. of the cyclopropane product to be >20:1 *cis/trans*, which was confirmed by ^{1}H NMR of the crude material.



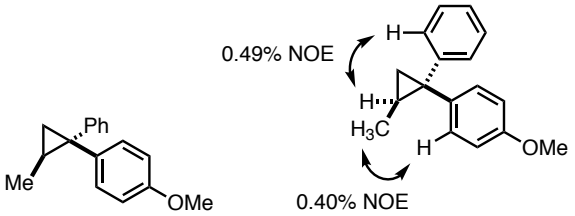
1-((*cis*)-2-Ethyl-1-phenylcyclopropyl)-4-methoxybenzene (*cis*-19): Colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.26–7.18 (m, 4H), 7.17–7.13 (m, 2H), 7.12–7.08 (m, 1H), 6.86–6.81 (m, 2H), 3.79 (s, 3H), 1.55–1.49 (m, 1H), 1.46–1.36 (m, 1H), 1.19 (ddd, J = 8.7, 4.6, 0.6 Hz, 1H), 1.12 (dd, J = 6.0, 4.6 Hz, 1H), 0.98 (t, J = 7.4 Hz, 3H), 0.91–0.79 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.1, 148.1, 134.2, 131.7, 128.2, 127.6, 125.5, 113.6, 55.3, 34.8, 28.7, 24.3, 21.0, 13.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{21}O$ (M+H): 253.1587; found: 253.1584; **IR** (neat): 2957, 2926, 2854, 1609, 1512, 1455, 1246, 1177, 1036, 699 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.66.



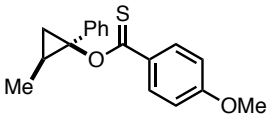
***O*-((*cis*)-2-Ethyl-1-phenylcyclopropyl) 4-methoxybenzothioate (S36):** Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.25–8.21 (m, 2H), 7.31–7.25 (m, 2H), 7.23–7.14 (m, 3H), 6.91–6.86 (m, 2H), 3.87 (s, 3H), 1.88 (dd, J = 9.6, 7.1 Hz, 1H), 1.85–1.75 (m, 1H), 1.68–1.59 (m, 1H), 1.39–1.30 (m, 1H), 1.20–1.14 (m, 4H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 208.8, 163.8, 141.1, 132.0, 131.0, 128.4, 126.5, 124.9, 113.5, 68.3, 55.7, 32.0, 22.5, 21.9, 14.1 ppm; **HRMS** *m/z* (DART) calcd for $C_{19}H_{21}O_2S$ (M+H): 313.1257; found: 313.1255; **IR** (neat): 2960, 2927, 2839, 1596, 1573, 1502, 1452, 1330, 1277, 1253, 1204, 1161, 1111, 1020, 838, 742, 695 cm^{-1}; **m.p.:** 82–92 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.59.



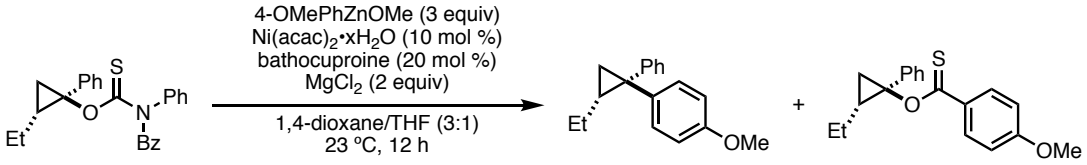
Reaction using *cis*-**18**: The reaction was performed on 0.20-mmol scale according to General Procedure A. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield cyclopropane 1-methoxy-4-((*cis*)-2-methyl-1-phenylcyclopropyl)benzene (*cis*-**20**) (9.3 mg, 0.039 mmol, 20%) and thioester side-product *O*-((*cis*)-2-methyl-1-phenylcyclopropyl) 4-methoxybenzothioate (38 mg, 0.127 mmol, 64%). The crude material was analyzed by GC-MS to determine the d.r. of the cyclopropane product to be >20:1 *cis/trans*, which was confirmed by ^{1}H NMR of the crude material.



1-Methoxy-4-((*cis*)-2-methyl-1-phenylcyclopropyl)benzene (*cis*-20): Colourless oil. The relative configuration was determined by NOE analysis. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.26–7.17 (m, 4H), 7.14–7.07 (m, 3H), 6.88–6.83 (m, 2H), 3.80 (s, 3H), 1.66–1.57 (m, 1H), 1.25 (ddd, J = 8.7, 4.6, 1.0 Hz, 1H), 1.08 (ddd, J = 5.7, 4.5, 1.0 Hz, 1H), 0.94 (d, J = 6.2 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.1, 148.2, 133.9, 132.0, 128.2, 127.3, 125.5, 113.7, 55.3, 34.3, 22.9, 21.0, 16.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{22}NO$ (M+NH_4): 256.1696; found: 256.1699; **IR** (neat): 3061, 3000, 2946, 2835, 1608, 1511, 1496, 1443, 1290, 1242, 1176, 1032, 822, 745, 697 cm^{-1}; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.64.

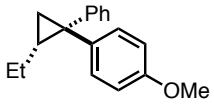


***O*-((*cis*)-2-Methyl-1-phenylcyclopropyl) 4-methoxybenzothioate (S37):** Yellow oil which slowly solidified upon standing. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.28–8.23 (m, 2H), 7.30–7.25 (m, 2H), 7.21–7.15 (m, 3H), 6.91–6.87 (m, 2H), 3.88 (s, 3H), 1.80 (dd, J = 9.6, 7.0 Hz, 1H), 1.56–1.47 (m, 1H), 1.39 (d, J = 6.2 Hz, 3H), 1.16 (dd, J = 7.7, 7.0 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 208.9, 163.8, 141.1, 132.0, 131.1, 128.3, 126.4, 124.7, 113.5, 68.1, 55.7, 24.3, 23.3, 13.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{19}O_2S$ (M+H): 299.1100; found: 299.1093; **IR** (neat): 3005, 2960, 2929, 2839, 1592, 1500, 1450, 1330, 1278, 1250, 1171, 1110, 1021, 834, 749, 694 cm^{-1}; **m.p.:** 99–101 ºC; **R_f** (40% PhMe/hexanes; UV/*p*-anisaldehyde): 0.58.

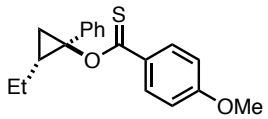


Reaction using *trans*-**17**: The reaction was performed on 0.10-mmol scale according to General Procedure A. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield cyclopropane product 1-((*trans*)-2-ethyl-1-phenylcyclopropyl)-4-methoxybenzene (*trans*-**19**) (3.5 mg, 0.014 mmol, 14%) and thioester side-product *O*-((*trans*)-2-ethyl-1-phenylcyclopropyl) 4-methoxybenzothioate (17 mg, 0.054 mmol, 54%). The crude material was analyzed by GC-MS to determine the d.r. of the cyclopropane product to be >20:1 *trans/cis*, which was confirmed by ^{1}H NMR of the crude material.

The reaction was repeated on 0.40-mmol scale using 4.0 equiv of arylzinc reagent, 20 mol % $Ni(acac)_2$•xH_2O, and 40 mol % bathocuproine to yield 28 mg of *trans*-**19** (0.111 mmol, 28%) and 18 mg of thioester side-product *O*-((*trans*)-2-ethyl-1-phenylcyclopropyl) 4-methoxybenzothioate (0.058 mmol, 15%). The d.r. of the crude material was >20:1.



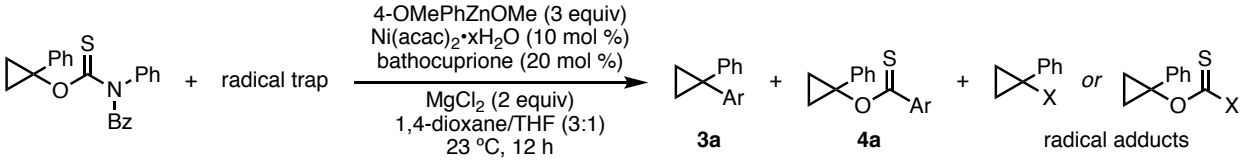
1-((*trans*)-2-Ethyl-1-phenylcyclopropyl)-4-methoxybenzene (*trans*-19): Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.35–7,.24 (m, 4H), 7.22–7.11 (m, 3H), 6.81–6.74 (m, 2H), 3.76 (s, 3H), 1.57–1.50 (m, 1H), 1.45–1.33 (m, 1H), 1.18–1.12 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H), 0.93–0.77 (m, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): 157.7, 142.6, 140.1, 130.5, 129.1, 128.2, 126.1, 113.7, 55.4, 35.1, 28.1, 24.2, 20.1, 13.9 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{21}O$ (M+H): 253.1587; found: 253.1590; **IR** (neat): 3063, 2999, 2958, 2872, 2834, 1613, 1496, 1462, 1446, 1288, 1243, 1178, 806, 828, 785, 699 cm^{-1}; **R_f** (9:1 hexanes/EtOAc; UV): 0.50.



***O*-((*trans*)-2-Ethyl-1-phenylcyclopropyl) 4-methoxybenzothioate (S38):** Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.18–8.13 (m, 2H), 7.48–7.43 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.20 (m, 1H), 7.87–8.81 (m, 2H), 3.85 (s, 3H), 1.75–1.67 (m, 1H), 1.55–1.46 (m, 2H), 1.30–1.21 (m, 1H), 1.02–0.92 (m, 1H), 0.90 (t, J = 6.9 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 208.4, 163.6, 136.7, 132.2, 131.0, 128.9, 127.9, 127.4, 113.3, 70.0, 55.6, 28.4, 22.3, 18.5, 13.2 ppm; **HRMS** *m/z* (DART): calcd for $C_{19}H_{21}O_2S$: 313.1257; found: 313.1261; **IR** (neat): 2961, 2931, 2870, 1596, 1574, 1506, 1450, 1422, 1275, 1256, 1162, 1112, 1016, 837, 747, 698 cm^{-1}; **m.p.:** 87–89 ºC.

F.6. Other experiments

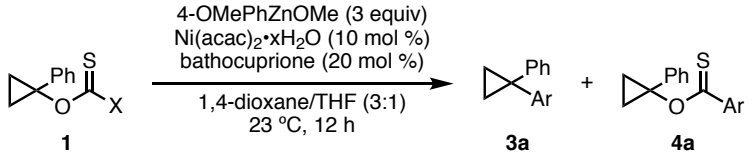
Table S10. Reactions with radical traps



Entry	radical trap (equiv)	Yield **3a** (%)	Yield **4a** (%)	Yield adduct
1	none	73	12	N/A
2	TEMPO (1)	0	0	n.d.
3	styrene (1)	63	13	n.d.
4	benzyl acrylate (1)	51	14	n.d.

GC-MS yields using *n*-dodecane as internal standard.

Table S11. Yield of cyclopropane and thioester with other leaving groups



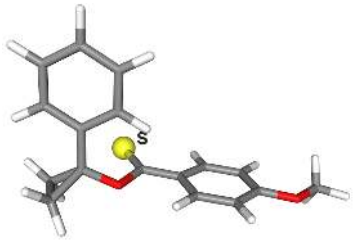
Entry	X	Yield **3a** (%)	Yield **4a** (%)
1	NBzPh	78	12
2	1-imidazolyl	54	4
3	SMe	29	67

GC-MS yields using *n*-dodecane as internal standard.

G. Computational Details

All DFT calculations were carried out with the *Gaussian 16* software package.[20] Initial geometries were generated with *openbabel*[21] from their SMILES strings, and pre-optimized with Grimme's *xtb 6.2.3*.[22] The initial *xtb*-optimized geometries were used for a thorough conformer search with Grimme's *crest*.[23] Further geometry optimizations were performed with (SMD[24]=1,4-dioxane) for solvation corrections and the unrestricted ωB97X DFT functional[25] (with an integration grid of pruned 175,974 for first-row atoms and 250,974 for atoms in the second and later rows) with the 6-311++G(2d,p) basis set for all atoms. Grimme's D2 version for empirical dispersion[26] was also included. Frequency calculations were performed to confirm if a structure is a ground or transition state. Paton's *GoodVibes*[27] was used for quasi-harmonic corrections to Gibbs Free Energies (via quasi-harmonic corrections to both entropy and enthalpy, defaulting to the Grimme method for entropy and the Head-Gordon enthalpy correction). Intermediates with their highest Boltzmann weights and their respective transition states were selected for the barriers herein reported. For those structures, Natural Bond Orbital[28] (NBO) analysis were performed with *NBO6* linked to *Gaussian 16.* NBO analyses were used to gauge the magnitude of the hyperconjugative interactions in the presented systems.

NBO analysis transforms the canonical delocalized molecular orbitals from DFT calculations into localized orbitals that are closely tied to the chemical bonding concepts. Each of the localized NBO sets is complete and orthonormal. The filled NBOs describe the hypothetical, strictly localized Lewis structure. The interactions between filled and antibonding orbitals represent the deviation from the Lewis structure and can be used to measure delocalization. For example, delocalizing interaction can be treated via the 2nd order perturbation energy approach as $E(2) = n_i\left|F_{ij}\right|^2/\Delta E$, where n_i is the population of a donor orbitals, F_{ij} is the Fock matrix element for the interacting orbitals i and j, and ΔE is the energy gap between these orbitals**.** CYLView[29] was used to render the molecules. Structures and energies for this SI were prepared with ESIgen.[30]



Charge -1
Multiplicity 2
Stoichiometry C17H16O2S(-1)
Electronic Energy (Eh) -1206.0701116
Number of Imaginary Frequencies 0
Mean of alpha and beta Electrons 75.5

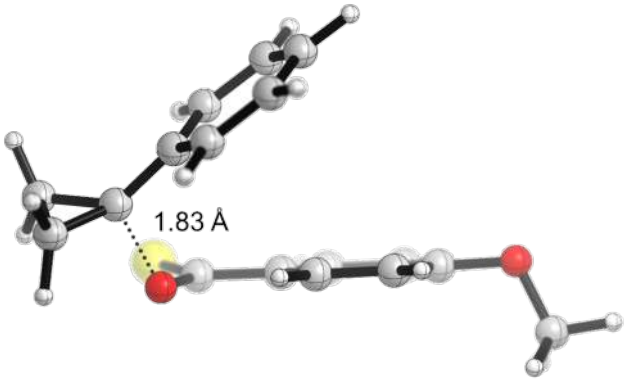
Molecular Geometry in Cartesian Coordinates

C	1.705517	0.040366	-1.160821
C	2.971935	-0.450923	-1.390762
C	3.949416	-0.409355	-0.395727
C	3.622830	0.139937	0.842725
C	2.350834	0.633306	1.078605
C	1.334819	0.601230	0.093699
C	0.023328	1.091857	0.348180
S	-0.547241	1.725061	1.828720
O	-0.760262	1.058666	-0.811440
C	-2.143979	0.959381	-0.719613
C	-2.667778	-0.355838	-0.232899

C	-1.805814	-1.442255	-0.096813
C	-2.281947	-2.680357	0.309341
C	-3.629264	-2.862219	0.583911
C	-4.497043	-1.787551	0.448964
C	-4.020227	-0.549214	0.047469
H	-4.719117	0.274597	-0.043589
H	-5.553114	-1.910136	0.663972
H	-3.999406	-3.829370	0.905126
H	-1.588357	-3.507070	0.416136
H	-0.751026	-1.315077	-0.302903
C	-2.849362	1.615045	-1.883786
C	-2.903724	2.235704	-0.515964
H	-3.825873	2.208409	0.050616
H	-2.286676	3.103841	-0.334272
H	-3.731313	1.116975	-2.268546
H	-2.214084	2.079835	-2.627702
H	2.110473	1.055032	2.046226
H	4.354151	0.192429	1.640008
O	5.179189	-0.924548	-0.726369
C	6.178498	-0.882410	0.257848
H	7.069083	-1.327555	-0.186808
H	6.410722	0.145889	0.560524
H	5.900905	-1.460946	1.147349
H	3.228526	-0.877249	-2.355108
H	0.971319	-0.003756	-1.954220

Frequencies (Top 10 out of 102)

1. 34.3003 cm-1 (Symmetry: A)
2. 58.9754 cm-1 (Symmetry: A)
3. 70.1488 cm-1 (Symmetry: A)
4. 77.8943 cm-1 (Symmetry: A)
5. 101.4368 cm-1 (Symmetry: A)
6. 116.9462 cm-1 (Symmetry: A)
7. 130.3683 cm-1 (Symmetry: A)
8. 160.7246 cm-1 (Symmetry: A)
9. 201.1257 cm-1 (Symmetry: A)
10. 211.0946 cm-1 (Symmetry: A)



Charge -1
Multiplicity 2
Stoichiometry C17H16O2S(-1)
Electronic Energy (Eh) -1206.03945823

Number of Imaginary Frequencies 1
Mean of alpha and beta Electrons 75.5

Molecular Geometry in Cartesian Coordinates

C	-1.011543	-0.001316	-0.931645
C	-2.265544	0.581054	-0.881135
C	-3.241340	0.051644	-0.047896
C	-2.951335	-1.057001	0.734542
C	-1.690357	-1.628622	0.688549
C	-0.689178	-1.115081	-0.144643
C	0.674076	-1.697286	-0.215569
S	1.190910	-2.926878	0.869039
O	1.444976	-1.203978	-1.120618
C	2.712591	0.001212	-0.577390
C	2.051096	1.104782	0.052763
C	1.771269	2.291306	-0.646318
C	1.006049	3.286694	-0.070318
C	0.486787	3.121114	1.212918
C	0.764554	1.957420	1.918957
C	1.540656	0.959502	1.352968
H	1.738271	0.040591	1.893720
H	0.357556	1.818502	2.914574
H	-0.130317	3.894743	1.655709
H	0.797384	4.195678	-0.624852
H	2.151513	2.409508	-1.655819
C	3.792528	-0.047412	-1.569833
C	3.919418	-0.752780	-0.219741
H	4.585866	-0.322445	0.522440
H	3.848242	-1.833683	-0.210388
H	4.381341	0.848371	-1.744747
H	3.639636	-0.677382	-2.440219
H	-1.454792	-2.483982	1.309278
H	-3.717680	-1.459599	1.388579
H	-2.493127	1.457346	-1.478691
H	-0.249938	0.413594	-1.578005
O	-4.487112	0.642311	0.021773
C	-5.403891	0.119687	-0.919230
H	-6.345247	0.654130	-0.782095
H	-5.050115	0.270583	-1.946073
H	-5.571087	-0.952069	-0.759137

Frequencies (Top 10 out of 102)

1. -782.4990 cm-1 (Symmetry: A) *
2. 24.2976 cm-1 (Symmetry: A)
3. 30.3713 cm-1 (Symmetry: A)
4. 50.0140 cm-1 (Symmetry: A)
5. 70.5248 cm-1 (Symmetry: A)
6. 75.8368 cm-1 (Symmetry: A)
7. 95.2858 cm-1 (Symmetry: A)
8. 98.0492 cm-1 (Symmetry: A)
9. 145.0029 cm-1 (Symmetry: A)
10. 163.1225 cm-1 (Symmetry: A)

Charge -1
Multiplicity 1
Stoichiometry C8H7O2S(-1)
Electronic Energy (Eh) -857.798235944
Number of Imaginary Frequencies 0
Mean of alpha and beta Electrons 44
Molecular Geometry in Cartesian Coordinates

C	0.076357	1.455565	0.000004
C	-1.304405	1.452348	0.000058
C	-1.998247	0.243733	0.000047
C	-1.289569	-0.952330	0.000001
C	0.100885	-0.926189	-0.000030
C	0.808944	0.266641	-0.000022
C	2.330551	0.345641	-0.000034
S	3.237904	-1.128751	0.000048
O	2.821458	1.471859	-0.000091
H	0.660915	-1.853468	-0.000049
H	-1.798712	-1.907165	-0.000010
O	-3.356833	0.333892	0.000083
C	-4.093836	-0.866314	-0.000084
H	-5.144628	-0.577965	-0.000093
H	-3.889333	-1.466260	-0.893543
H	-3.889409	-1.466472	0.893250
H	-1.867354	2.378937	0.000093
H	0.620974	2.391840	-0.000002

Frequencies (Top 10 out of 48)

1. 78.4831 cm-1 (Symmetry: A)
2. 99.2623 cm-1 (Symmetry: A)
3. 137.5786 cm-1 (Symmetry: A)
4. 163.4692 cm-1 (Symmetry: A)
5. 246.2173 cm-1 (Symmetry: A)
6. 280.8262 cm-1 (Symmetry: A)
7. 297.8859 cm-1 (Symmetry: A)
8. 311.4702 cm-1 (Symmetry: A)
9. 416.6012 cm-1 (Symmetry: A)
10. 442.7687 cm-1 (Symmetry: A)

Charge 0
Multiplicity 2
Stoichiometry C9H9
Electronic Energy (Eh) -348.26598436
Number of Imaginary Frequencies 0
Mean of alpha and beta Electrons 31.5
Molecular Geometry in Cartesian Coordinates

C	1.533260	0.000003	-0.000049

C	0.142958	0.000002	-0.000022
C	-0.588349	-1.214638	-0.000009
C	-1.966880	-1.205614	0.000003
C	-2.667872	-0.000001	0.000012
C	-1.966883	1.205612	0.000003
C	-0.588352	1.214640	-0.000009
H	-0.044323	2.152506	-0.000018
H	-2.509826	2.144093	0.000013
H	-3.751329	-0.000003	0.000029
H	-2.509821	-2.144096	0.000013
H	-0.044318	-2.152503	-0.000019
C	2.764221	-0.770782	0.000022
C	2.764226	0.770780	0.000021
H	3.075503	1.273568	-0.912578
H	3.075326	1.273626	0.912649
H	3.075496	-1.273572	-0.912576
H	3.075318	-1.273628	0.912651

Frequencies (Top 10 out of 48)

1. 48.8021 cm-1 (Symmetry: A)
2. 137.4509 cm-1 (Symmetry: A)
3. 140.1076 cm-1 (Symmetry: A)
4. 206.9422 cm-1 (Symmetry: A)
5. 392.4851 cm-1 (Symmetry: A)
6. 416.8840 cm-1 (Symmetry: A)
7. 483.0980 cm-1 (Symmetry: A)
8. 484.9088 cm-1 (Symmetry: A)
9. 629.9552 cm-1 (Symmetry: A)
10. 694.3463 cm-1 (Symmetry: A)

Charge -1
Multiplicity 2
Stoichiometry C16H13FOS(-1)
Electronic Energy (Eh) -1190.7957172
Number of Imaginary Frequencies 0
Mean of alpha and beta Electrons 71.5

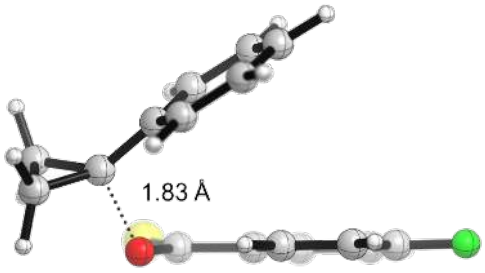
Molecular Geometry in Cartesian Coordinates

C	2.113758	-0.105316	-1.112571
C	3.368299	-0.645405	-1.328613
C	4.280090	-0.671925	-0.290195
C	3.965820	-0.171467	0.963261
C	2.714704	0.365806	1.181873
C	1.734410	0.422765	0.153672
C	0.443075	0.971467	0.384041
S	-0.145580	1.585922	1.860654
O	-0.307581	1.000430	-0.793879
C	-1.697142	1.014852	-0.733736

C	-2.331915	-0.256315	-0.263258
C	-1.560808	-1.407482	-0.114721
C	-2.140919	-2.605147	0.276708
C	-3.503646	-2.681106	0.523571
C	-4.281431	-1.541326	0.375449
C	-3.700828	-0.343294	-0.011628
H	-4.330731	0.533262	-0.113001
H	-5.347953	-1.581091	0.568824
H	-3.954861	-3.616998	0.833458
H	-1.516839	-3.484147	0.394167
H	-0.495117	-1.363729	-0.298384
C	-2.320117	1.729430	-1.909685
C	-2.355329	2.347435	-0.540005
H	-3.289238	2.389561	0.005991
H	-1.677472	3.164874	-0.340104
H	-3.230028	1.305107	-2.316891
H	-1.632634	2.144840	-2.636148
H	2.457754	0.756301	2.158069
H	4.702521	-0.207953	1.757813
F	5.521081	-1.203007	-0.503661
H	3.643625	-1.045530	-2.298063
H	1.403067	-0.083461	-1.927181

Frequencies (Top 10 out of 90)

1. 24.8157 cm-1 (Symmetry: A)
2. 56.3199 cm-1 (Symmetry: A)
3. 73.1143 cm-1 (Symmetry: A)
4. 92.9923 cm-1 (Symmetry: A)
5. 103.1879 cm-1 (Symmetry: A)
6. 118.9110 cm-1 (Symmetry: A)
7. 156.9054 cm-1 (Symmetry: A)
8. 172.5633 cm-1 (Symmetry: A)
9. 213.1404 cm-1 (Symmetry: A)
10. 245.5052 cm-1 (Symmetry: A)



Charge -1
Multiplicity 2
Stoichiometry C16H13FOS(-1)
Electronic Energy (Eh) -1190.76689813
Number of Imaginary Frequencies 1
Mean of alpha and beta Electrons 71.5

Molecular Geometry in Cartesian Coordinates

C	-1.219313	-0.000260	-1.096274
C	-2.480851	0.567998	-1.130814
C	-3.483215	-0.006755	-0.375733
C	-3.263829	-1.121764	0.406423

C	-1.992478	-1.672477	0.437481
C	-0.940590	-1.124184	-0.306479
C	0.433027	-1.684915	-0.276759
S	0.867995	-2.944069	0.808901
O	1.274063	-1.149278	-1.090668
C	2.452712	0.065114	-0.393406
C	1.694523	1.148523	0.155815
C	1.439027	2.312706	-0.588902
C	0.561033	3.271338	-0.122706
C	-0.096090	3.090085	1.093678
C	0.162330	1.953032	1.848971
C	1.052460	0.994186	1.395734
H	1.236305	0.096218	1.974407
H	-0.347769	1.805225	2.794521
H	-0.802953	3.832087	1.447461
H	0.370252	4.161285	-0.713356
H	1.924531	2.437898	-1.551277
C	3.638778	0.035804	-1.256380
C	3.620128	-0.675336	0.097081
H	4.192261	-0.240589	0.911876
H	3.558884	-1.757088	0.095446
H	4.231608	0.940018	-1.359335
H	3.593259	-0.591346	-2.140971
H	-1.789183	-2.540341	1.052057
H	-4.076387	-1.545622	0.984552
F	-4.725713	0.544415	-0.403691
H	-2.687560	1.447191	-1.729117
H	-0.418170	0.436079	-1.676509

Frequencies (Top 10 out of 90)

1. -790.9853 cm-1 (Symmetry: A) *
2. 63.4610 cm-1 (Symmetry: A)
3. 72.1982 cm-1 (Symmetry: A)
4. 92.0594 cm-1 (Symmetry: A)
5. 105.4938 cm-1 (Symmetry: A)
6. 111.9516 cm-1 (Symmetry: A)
7. 152.9136 cm-1 (Symmetry: A)
8. 180.1198 cm-1 (Symmetry: A)
9. 183.4795 cm-1 (Symmetry: A)
10. 213.4082 cm-1 (Symmetry: A)

Charge -1
Multiplicity 1
Stoichiometry C7H4FOS(-1)
Electronic Energy (Eh) -842.521121919
Number of Imaginary Frequencies 0
Mean of alpha and beta Electrons 40

Molecular Geometry in Cartesian Coordinates

C	-0.513182	1.300177	-0.000004
C	-1.890926	1.141735	-0.000003

C	-2.398373	-0.140803	0.000000
C	-1.587508	-1.256633	0.000002
C	-0.212359	-1.072838	0.000002
C	0.344762	0.202628	-0.000002
C	1.850793	0.463065	0.000001
S	2.922470	-0.891758	-0.000002
O	2.198017	1.641190	0.000006
H	0.457216	-1.924119	0.000002
H	-2.028482	-2.246109	0.000004
F	-3.743843	-0.310696	0.000001
H	-2.563211	1.991227	-0.000004
H	-0.073828	2.289895	-0.000003

Frequencies (Top 10 out of 36)

1. 75.9492 cm-1 (Symmetry: A)
2. 120.8453 cm-1 (Symmetry: A)
3. 191.7927 cm-1 (Symmetry: A)
4. 303.4773 cm-1 (Symmetry: A)
5. 310.9199 cm-1 (Symmetry: A)
6. 398.9774 cm-1 (Symmetry: A)
7. 441.8967 cm-1 (Symmetry: A)
8. 463.3094 cm-1 (Symmetry: A)
9. 510.2775 cm-1 (Symmetry: A)
10. 529.2753 cm-1 (Symmetry: A)

H. References

[1] Côté, A.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 2771–2773.
[2] Hixson, S. S.; Franke, L. A. *J. Org. Chem.* **1988**, *53*, 2706–2711.
[3] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890–891.
[4] Mills, L. R.; Graham, J. M.; Patel, P.; Rousseaux, S. A. L. *J. Am. Chem. Soc.* **2019**, *141*, 19257–19262.
[5] Keylor, M. H.; Niemeyer, Z. L.; Sigman, M. S.; Tan, Kian. L. *J. Am. Chem. Soc.* **2017**, *139*, 10613–10616.
[6] Salaun, J. *J. Org. Chem.* **1978**, *43*, 2809–2815.
[7] Lackner, G. L.; Quasdorf, K. W.; Overman, L. E. *J. Am. Chem. Soc.* **2013**, *41*, 15342–15345.
[8] Mills, L. R.; Zhou, C.; Fung, E.; Rousseaux, S. A. L. *Org. Lett.* **2019**, *21*, 8805–8809.
[9] Nomura, K.; Matsubara, S. *Chem. Lett.* **2007**, *36*, 164–165.
[10] Jia, K.; Zhang, F.; Huang, H.; Chen, Y. *J. Am. Chem. Soc.* **2016**, *138*, 1514–1517.
[11] Nomura, K.; Matsubara, S. *Chem. Asian J.* **2010**, *5*, 147–152.
[12] Jiao, J.; Nguyen, L. X.; Patterson, D. R.; Floewrs, R. A. *Org. Lett.* **2007**, *9*, 1323–1326.
[13] Pramanik, S.; Rej, S.; Kando, S.; Tsurugi, H.; Mashima, K. *J. Org. Chem.* **2018**, *83*, 2409–2417.
[14] Vita, M. V.; Waser, J. *Org. Lett.* **2013**, *15*, 3246–3249.
[15] Fujita, K.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 12115–12116.
[16] Wei, Y.; Xue, D.; Lei, Q.; Wang, C.; Xiao, J. *Green Chem.* **2013**, *15*, 629–634.
[17] Li, H.; Breen, C. P.; Seo, H.; Jamison, T. F.; Fang, Y.-Q.; Bio, M. M. *Org. Lett.* **2018**, *20*, 1338–1341.
[18] Puthiaraj, P.; Suresh, P.; Pitchumani, K. *Green Chem.* **2014**, *16*, 2865–2875.
[19] Noji, M.; Ohno, T.; Fuji, K.; Futaba, N.; Tajima, H.; Ishii, K. *J. Org. Chem.* **2003**, *68*, 9340–9347.
[20] *Gaussian '16*, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
[21] (a) O'Boyle, N. M.; Banck, M.; James, C. A.; Morley, C.; Vandermeersch, T.; Hutchison, G. R. "Open Babel: An open chemical toolbox." *J. Cheminf.*, **2011**, *3*, 33. (b) The Open Babel Package, version 2.3.1 http://openbabel.org (accessed Feb 2019).
[22] *xtb* can be freely obtained at**:** https://github.com/grimme-lab/xtb**.** Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB—An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652.

[23] Grimme, S. Exploration of Chemical Compound, Conformer, and Reaction Space with Meta-Dynamics Simulations Based on Tight-Binding Quantum Chemical Calculations. *J. Chem. Theory Comput.* **2019**, *15* (5), 2847.
[24] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. "Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions," *J. Phys. Chem. B*, **2009**, *113*, 6378.
[25] Chai, J.-D.; Head-Gordon, M. "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections," *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615.
[26] (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.,* **2010**, *132*, 154104. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem.*, **2011**, *32*, 1456.
[27] *GoodVibes* can be freely obtained at: https://github.com/bobbypaton/GoodVibes. Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000Research*, **2020**, *9*, 291.
[28] (a) Weinhold, F.; Landis, C. R.; Glendening, E. D. *International Reviews in Physical Chemistry* **2016**, *35*, 1. Reed, A. E.; Weinhold, F. J. *Chem. Phys.,* **1985**, *83*, 1736. (b) Reed, A. E.; Weinhold, F. *Isr. J. Chem.*, **1991**, *31*, 277. (c) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.,* **1988**, *88*, 899. (d) Weinhold F. in Schleyer P.v.R. *Encyclopedia of Computational Chemistry*: Wiley: New-York, **1998**, *3*, 1792. Selected recent applications of NBO analysis towards analysis of organic structure and reactivity: a) Podlech, J. *J. Phys. Chem. A* **2010**, *114*, 8480. b) Freitas, M. P. *J. Org. Chem.* **2012**, *77*, 7607. c) Greenway, K. T.; Bischoff, A. G.; Pinto, B. M. *J. Org. Chem.* **2012**, *77*, 9221. d) Juaristi, E.; Notario, R. *J. Org. Chem.* **2015**, *80*, 2879. e) Gomes, G. P.; Vil', V.; Terent'ev, A.; Alabugin, I. V. *Chem. Sci.* **2015**, **6**, 6783. f) Vidhani, D.; Krafft, M.; Alabugin, I. V. *J. Am. Chem. Soc*., **2016**, *138*, 2769. g) V. A. Vil', G. dos Passos Gomes, O. V. Bityukov, K. A. Lyssenko, G. I. Nikishin, I. V. Alabugin, A. O. Terent'ev, *Angew. Chem. Int. Ed.,* **2018**, *57,* 3372.
[29] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)
[30] ESIgen can be freely obtained at: https://github.com/insilichem/esigen. *J. Chem. Inf. Model.*, **2018**, *58* (3), 561.