# **Supplementary Information**

# for

# Ni-Catalyzed Regioselective and Site-Divergent Reductive Arylalkylations of Allylic Amines

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# **I. General Information**

General remarks: Unless otherwise stated, reactions were performed under a nitrogen atmosphere using dried solvents. Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Jiangyou TLC silica gel plates HSG F254 and visualized using UV light or phosphomolybdic acid (PMA). Flash column chromatography was performed over silica gel (200-300 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, unless otherwise noted, on a Bruker AVANCE 600 MHz or a Bruker AVANCE 400 MHz spectrometer. Chemical shifts in <sup>1</sup>H NMR spectra were reported in parts per million (ppm) on the  $\delta$  scale from an internal standard of residual chloroform (7.26 ppm). Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift ( $\delta$  ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Data for <sup>13</sup>C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl<sub>3</sub> (77.16 ppm). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a Thermo Scientific Q Exactive mass spectrometer (mass analyzer type: Orbitrap).

**Methods and materials:** Unless otherwise noted, commercial reagents were purchased from Energy Chemical Limited, J&K, Adamas-beta®, Aladdin, Macklin Reagent, Bidepharm and used directly without further purification. DCM, DMA and MeCN were distilled over  $CaH_2$  and stored under nitrogen atmosphere.

# **II.** Synthesis and Characterization of Substrates



**General Procedure A:** To a solution of amine hydrochloride (10.0 mmol, 1.0 equiv) in  $CH_2Cl_2$  (0.5 M) at 0 °C was added  $Et_3N$  (35.0 mmol, 3.5 equiv). After stirring for 0.5 h, then acyl chloride (11.0 mmol, 1.1 equiv) was added dropwise to the above solution at 0 °C. The resulting solution was stirred at room temperature for 4 h. The mixture was diluted with  $CH_2Cl_2$  and washed with water and brine. The organic phase was dried with anhydrous  $Na_2SO_4$ , filtered, and purified by flash chromatography.<sup>1</sup>

$$\begin{array}{c} \mathsf{Ph} & \mathsf{H} \\ \mathsf{V} & \mathsf{N} \\ \mathsf{O} & \mathsf{1a} \end{array}$$

#### N-Allylbenzamide (1a)

Colorless oil. <sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 – 7.76 (m, 2H), 7.51 – 7.48 (m, 1H), 7.43 (dd, J = 8.4, 6.9 Hz, 2H), 6.29 (brs, 1H), 5.94 (ddt, J = 17.2, 10.2, 5.7 Hz, 1H), 5.26 (dd, J = 17.1, 1.6 Hz, 1H), 5.18 (dd, J = 10.2, 1.4 Hz, 1H), 4.09 (tt, J = 5.8, 1.6 Hz, 2H).



#### N-Allyl-4-(trifluoromethyl)benzamide (1b)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.91 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 6.31 (brs, 1H), 5.96 (ddt, J = 17.2, 10.2, 5.8 Hz, 1H), 5.30 (dd, J = 17.1, 1.5 Hz, 1H), 5.24 (dd, J = 10.2, 1.4 Hz, 1H), 4.15 – 4.11 (m, 2H).



#### N-Allyl-4-(*tert*-butyl)benzamide (1c)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.18 (brs, 1H), 5.94 (ddt, *J* = 17.1, 10.2, 5.6 Hz, 1H), 5.26 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.18 (dd, *J* = 10.2, 1.4 Hz, 1H), 4.09 (ddd, *J* = 5.7, 4.1, 1.6 Hz, 2H), 1.33 (s, 9H).



#### N-Allyl-4-(dimethylamino)benzamide (1d)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.69 (d, J = 8.9 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 6.10 (brs, 1H), 6.00 – 5.87 (m, 1H), 5.24 (dd, J = 17.1, 1.7 Hz, 1H), 5.15 (dd, J = 10.2, 1.6 Hz, 1H), 4.07 (td, J = 5.7, 2.8 Hz, 2H), 3.01 (s, 6H).



#### N-Allyl-3,5-dimethylbenzamide (1e)

Colorless oil. <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.38 (s, 1H), 7.12 (s, 1H), 6.25 (brs, 1H), 5.93 (ddt, J = 17.2, 10.2, 5.7 Hz, 1H), 5.25 (dq, J = 17.2, 1.6 Hz, 1H), 5.17 (dq, J = 10.3, 1.4 Hz, 1H), 4.07 (tt, J = 5.7, 1.6 Hz, 2H), 2.34 (s, 6H).



#### *N*-Allyl-2-methylbenzamide (1f)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.37 (d, J = 7.6 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.23 – 7.18 (m, 2H), 5.94 (ddt, J = 16.2, 10.7, 5.6 Hz, 1H), 5.83 (brs, 1H), 5.27 (dd, J = 17.2, 1.8 Hz, 1H), 5.19 (dd, J = 10.2, 1.6 Hz, 1H), 4.07 (t, J = 5.7 Hz, 2H), 2.45 (s, 3H).

# *N*-Allylfuran-2-carboxamide (1g)

Colorless oil. <sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.43 (dd, J = 1.8, 0.8 Hz, 1H), 7.12 (dd, J = 3.5, 0.8 Hz, 1H), 6.50 (dd, J = 3.5, 1.8 Hz, 1H), 6.43 (brs, 1H), 5.91 (ddt, J = 17.2, 10.3, 5.6 Hz, 1H), 5.26 (dq, J = 17.1, 1.6 Hz, 1H), 5.18 (dq, J = 10.2, 1.4 Hz, 1H), 4.05 (tt, J = 5.8, 1.6 Hz, 2H).

$$S \rightarrow 0$$
 1h

#### N-Allylthiophene-2-carboxamide (1h)

White solid. <sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.52 (dd, J = 3.7, 1.2 Hz, 1H), 7.47 (dd, J = 5.0, 1.2 Hz, 1H), 7.07 (dd, J = 5.0, 3.7 Hz, 1H), 6.10 (brs, 1H), 5.92 (ddt, J = 17.2, 10.2, 5.7 Hz, 1H), 5.26 (dd, J = 17.2, 1.6 Hz, 1H), 5.18 (dd, J = 10.2, 1.4 Hz, 1H), 4.06 (tt, J = 5.8, 1.6 Hz, 2H).



#### *N*-Allylpivalamide (1i)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.78 (ddt, J = 17.3, 10.3, 5.6 Hz, 1H), 5.67 (brs, 1H), 5.16 – 5.02 (m, 2H), 3.86 – 3.73 (m, 2H), 1.15 (s, 9H).

$$c_{y} \rightarrow N_{O}$$

## N-Allylcyclohexanecarboxamide (1j)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  5.77 (ddt, J = 17.2, 10.3, 5.6 Hz, 1H), 5.46 (brs, 1H), 5.16 – 5.01 (m, 2H), 3.84 – 3.78 (m, 2H), 2.03 (tt, J = 11.7, 3.5 Hz, 1H), 1.85 – 1.70 (m, 4H), 1.61 (ddt, J = 9.2, 5.0, 1.8 Hz, 1H), 1.38 (qd, J = 12.0, 3.0 Hz, 2H), 1.26 – 1.11 (m, 3H).



#### N-Allylcyclopropanecarboxamide (1k)

White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.85 (ddt, J = 17.2, 10.2, 5.7 Hz, 1H), 5.72 (brs, 1H), 5.20 (dd, J = 17.2, 1.6 Hz, 1H), 5.13 (dd, J = 10.2, 1.5 Hz, 1H), 3.80 – 4.00 (m, 2H), 1.35 (tt, J = 7.9, 4.5 Hz, 1H), 1.01 – 0.91 (m, 2H), 0.74 (dt, J = 7.9, 3.4 Hz, 2H).

Me 11

#### *N*-Allyl-*N*-methylbenzamide (11)

Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.35 (m, 5H), 5.92 – 5.69 (m, 1H), 5.34 – 5.17 (m, 2H), 4.21 – 3.76 (m, 2H), 3.12 – 2.65 (m, 3H)



**General Procedure B:** In a two-neck 200 mL flask, 10.0 mmol (2.0 equiv) of benzamide in MeCN (0.2 M) are introduced initially, potassium hydroxide (10.0 mmol, 2.0 equiv) are introduced with stirring. Tetrabutylammonium bromide (10.0 mmol, 2.0 equiv) are added and the mixture. 1-Bromohex-2-ene (5.0 mmol, 1.0 equiv) are then added dropwise with stirring. The mixture is stirred for another 24 h at 50 °C. Then filtered, and purified by flash chromatography.<sup>2</sup>

$$\stackrel{\mathsf{H}}{\xrightarrow{\mathsf{N}}}_{\mathsf{O}} \stackrel{\mathsf{H}}{\xrightarrow{\mathsf{Z-1m}}}_{\mathsf{C}_{6}\mathsf{H}_{13}}$$

# (Z)-N-(Non-2-en-1-yl)benzamide (Z-1m)

Colorless oil. <sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.78 – 7.71 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 6.06 (brs, 1H), 5.67 – 5.57 (m, 1H), 5.54 – 5.42 (m, 1H), 4.16 – 4.01 (m, 2H), 2.23 – 2.06 (m, 2H), 1.41 – 1.34 (m, 2H), 1.33 – 1.17 (m, 6H), 0.95 – 0.08 (m, 3H).

Ph H O **Z-1n** C<sub>7</sub>H<sub>15</sub>

# (Z)-N-(Dec-2-en-1-yl)benzamide (Z-1n)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 – 7.72 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 – 7.40 (m, 2H), 6.04 (brs, 1H), 5.62 (dddd, J = 10.9, 9.4, 3.3, 1.8 Hz, 1H), 5.54 – 5.45 (m, 1H), 4.10 (ddd, J = 6.8, 5.3, 1.4 Hz, 2H), 2.19 – 2.05 (m, 2H), 1.41 – 1.26 (m, 10H), 0.94 – 0.79 (m, 3H).

$$\overset{\mathsf{Ph}}{\underset{\mathsf{O}}{\overset{\mathsf{H}}{\underset{\mathsf{Z-10}}}}}_{\mathsf{Z-10}} \overset{\mathsf{H}}{\overset{\mathsf{C}_{3}\mathsf{H}_{7}}}$$

(Z)-N-(Hex-2-en-1-yl)benzamide (Z-1o)

White solid. <sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.84 – 7.70 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 6.06 (brs, 1H), 5.67 – 5.58 (m, 1H), 5.56 – 5.46 (m, 1H), 4.10 (t, *J* = 6.2 Hz, 2H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.42 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

$$\overset{\mathsf{Ph}}{\underset{\mathsf{O}}{\overset{\mathsf{H}}{\underset{\mathsf{E-10}}}}} C_3 \mathsf{H}_7$$

(E)-N-(Hex-2-en-1-yl)benzamide (E-10)

Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 – 7.69 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.33 (m, 2H), 6.08 (brs, 1H), 5.66 – 5.60 (m, 1H), 5.51 – 5.45 (m, 1H), 3.98 – 3.94 (m, 2H), 2.00 – 1.91 (m, 2H), 1.33 (h, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).

# **III. Optimization of Reaction Parameters**

Table S1. Optimization of ligand<sup>a</sup>



Entry	Ligand	RSM of <b>1a</b>	Yield of <b>4aa</b>	rr	ee of 4aa
1	No Ligand	27%	32%	5:1	/
2	L1	0%	85% (82%) <sup>b</sup>	>20:1	4%
3	L2	0%	61%	>20:1	2%
4	L3	55%	16%	>20:1	5%
5	L4	37%	39%	>20:1	4%
6	L5	58%	25%	>20:1	2%
7	L6	0%	43%	3:1	13%
8	PCy <sub>3</sub>	27%	34%	>20:1	/
9 <sup>c</sup>	L6	0%	28%	1:1.4	0%



<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. The ee value was determined by HPLC on a chiral stationary phase. 'rr' = Regiomeric ratio of **4aa/5aa**. <sup>b</sup> Isolated yield. <sup>c</sup> 50 °C.

Table S2. Evaluation of loading of Mn for 4aa<sup>a</sup>

BzHN	Br N	iBr₂•dme (10 mol%) L1 (12 mol%) Mn (x equiv)	PMP NHBz P	h
<b>1a</b> 0.10 mmol	Ph <b>2a 3a</b> 2.0 equiv 2.0 equiv	Nal (2.5 equiv) DMA (0.1 M) rt, 18 h	4aa Ph	5aa
Entry	Mn (x equiv)	RSM of <b>1a</b>	Yield of <b>4aa</b>	rr
1	2.5	0%	53%	>20:1
2	3.0	0%	71%	20:1
3	3.3	0%	76%	13:1
4	3.5	0%	83%	18:1
5	3.8	0%	81%	16:1
6	4.0	0%	83%	17:1
7	4.5	0%	77%	>20:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **4aa/5aa**.

# Table S3. Evaluation of loading of NaI for 4aa<sup>a</sup>

BzHN	+ PMP-I +	Br	liBr <sub>2</sub> •dme (10 mol%) <b>L1</b> (12 mol%) Mn (3.5 equiv)	PMP	NHBz Ph	1
<b>1a</b> 0.10 mmol	<b>2a</b> 2.0 equiv	Ph <b>3a</b> 2.0 equiv	Nal (x equiv) DMA (0.1 M) rt, 18 h	4aa	PMP 5a	NHBz Ia

Entry	NaI (x equiv)	RSM of <b>1a</b>	Yield of <b>4aa</b>	rr
1	0	0%	67%	5:1
2	1.0	0%	68%	10:1
3	2.3	0%	72%	10:1
4	2.5	0%	83%	15:1
5	3.0	0%	74%	18:1
6	3.5	0%	72%	11:1
7	4.0	0%	68%	12:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **4aa/5aa**.

Table S4. Evaluation of Solvent for 4aa<sup>a</sup>

BzHN	Br	iBr <sub>2</sub> •dme (10 mol%) L1 (12 mol%) Mn (3.5 equiv)	PMP NHBz PI	ı~
<b>1a</b> 0.10 mmol	Ph <b>2a 3a</b> 2.0 equiv 2.0 equiv	Nal (2.5 equiv) Solvent (0.1 M) rt, 18 h	4aa Ph	5aa
Entry	Solvent	RSM of <b>1a</b>	Yield of <b>4aa</b>	rr
1	DMA	0%	83%	18:1
2	NMP	0%	61%	>20:1
3	IPA	0%	52%	>20:1
4	<sup>i</sup> BuOH	67%	0%	/

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **4aa/5aa**.

	Table S5.	Evaluation	of loading	of <b>2a</b>	and <b>3a</b>	for 4aa <sup>*</sup>
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BzHN	+ PMP-I +	iBr <sub>2</sub> •dme (10 mol% L1 (12 mol%) Mn (3.5 equiv)	) PMP NHBz P	h
<b>1a</b> 0.10 mmol		Nai (2.5 equiv) DMA (0.1 M) rt, 18 h	4aa PMF	5aa
Entry	2a:3a = x:y	RSM of 1a	Yield of <b>4aa</b>	rr
1	1.5:1.5	0%	69%	>20:1
2	2.0:2.0	0%	85%	>20:1
3	2.5:2.5	0%	74%	>20:1
4	1.5:2.0	0%	66%	>20:1
5	1.5:2.5	0%	56%	>20:1
6	2.0:1.5	0%	70%	19:1
7	2.0:2.5	0%	72%	>20:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **4aa/5aa**.



BzHN	Ni(E 	3F <sub>4</sub> )₂•6H₂O (10 mo <b>L6</b> (12 mol%) Mn (3.0 equiv)	PMP NHBz Ph	$\sim$
<b>1a</b> 0.10 mmol	Ph 2a 3a 2.0 equiv 2.0 equiv	Nal (0.5 equiv) Solvent (0.1 M) 50 <sup>o</sup> C, 18 h	4aa PMP	NHBz 5aa
Entry	Solvent	RSM of 1a	Yield of 5aa	rr
1	DMA	56%	6%	>20:1
2	IPA	22%	49%	>20:1
3	MeOH	18%	28%	>20:1
4	IPA/MeOH (5/1)	0%	64%	>20:1
5	IPA/EtOH (5/1)	0%	67%	16:1
6	IPA/ <sup>n</sup> PrOH (5/1)	0%	50%	>20:1
7	<sup>n</sup> BuOH/MeOH (5/1)	5%	50%	>20:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa/4aa**.

# Table S7. Evaluation of loading of NaI for 5aa<sup>a</sup>



Entry	NaI (x equiv)	RSM of <b>1a</b>	Yield of <b>5aa</b>	rr
1	0	0%	26%	9:1
2	0.2	0%	63%	>20:1
3	0.4	0%	63%	>20:1
4	0.5	0%	66%	>20:1
5	0.6	0%	66%	>20:1
6	0.7	0%	64%	>20:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa/4aa**.

Table S8. Evaluation of iodine source for 5aa<sup>a</sup>

BzHN	Br + PMP-I +	i(BF <sub>4</sub> ) <sub>2</sub> •6H <sub>2</sub> O (10 mol%) <b>L6</b> (12 mol%) Mn (3.0 equiv)	NHBz Ph	$\sim$
<b>1a</b> 0.10 mmol	Ph <b>2a 3a</b> 2.0 equiv 2.0 equiv	MI (0.5 equiv) IPA/MeOH (0.1 M, 5/1) 50 °C, 18 h	4aa Ph	NHBz 5aa
Entry	MI	RSM of <b>1a</b>	Yield of <b>5aa</b>	rr
1	LiI	56%	6%	>20:1
2	NaI	0%	75%	18:1
3	KI	0%	61%	>20:1
4	RbI	0%	64%	>20:1
5	$CdI_2$	0%	66%	>20:1
6	CaI <sub>2</sub>	30%	17%	>20:1
7	TEAI	0%	58%	8:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa/4aa**.

# Table S9. Evaluation of loading of Mn for 5aa<sup>a</sup>



Entry	Mn (x equiv)	RSM of 1a	Yield of <b>5aa</b>	rr
1	1.5	0%	65%	>20:1
2	2.0	0%	69%	>20:1
3	2.5	0%	70%	>20:1
4	2.8	0%	71%	19:1
5	3.0	0%	75%	14:1
6	3.3	0%	70%	17:1
7	3.6	0%	72%	19:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa/4aa**.

Table S10. Evaluation of loading of 2a and 3a for 5aa<sup>a</sup>

BzHN 1a 0.10 mmol	+ PMP-I + 2a 3a x equiv x equiv	i(BF <sub>4</sub> )₂•6H₂O (10 mol%) <b>L6</b> (12 mol%) Mn (3.0 equiv) Nal (0.5 equiv) IPA/MeOH (0.1 M, 5/1) 50 °C, 18 h	NHBz Ph. PMP 4aa Ph	NHBz 5aa
Entry	2a:3a = x:y	RSM of <b>1a</b>	Yield of <b>5aa</b>	rr
1	1.5:1.5	0%	76% (72%) <sup>b</sup>	16:1
2	1.8:1.8	0%	70%	11:1
3	2.0:2.0	0%	70%	8:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa**/**4aa**. <sup>b</sup> Isolated yield.

# Table S11. Evaluation of catalyst for 5aa\*



Entry	[Ni]	RSM of <b>1a</b>	Yield of <b>5aa</b>	rr
1	NiCl <sub>2</sub> ·dme	0%	72%	12:1
2	NiBr <sub>2</sub> ·dme	0%	64%	9:1
3	NiI <sub>2</sub>	0%	66%	>20:1
4	NiBr <sub>2</sub>	80%	0%	/
5	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	5%	54%	7:1
6	NiBr <sub>2</sub> ·diglyme	0%	62%	12:1
7	Ni(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0%	75%	19:1

<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2a**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. 'rr' = Regiomeric ratio of **5aa**/**4aa**.

Table S12. Evaluation of reductant<sup>a</sup>

B7HN	+ PMP-I	Br Cor +	nditions A conditions B	IP NHBz	Ph
1a	2a	₽h 3a		4aa <sub>Ph</sub> Pi	MP NHBz 5aa
Entry	Reductant	Conditions	RSM of 1a	Yield of 4aa	Yield of <b>5aa</b>
1	Zn	Conditions A	47%	8%	0%
2	Fe	Conditions A	95%	0%	0%
3	Zn	Conditions B	0%	0%	7%
4	Fe	Conditions B	99%	0%	0%

<sup>a</sup> Reaction was run in 0.1 mmol scale. Conditions A: **1a** (0.10 mmol), **2a** (0.20 mmol), **3a** (0.20 mmol), NiBr<sub>2</sub>·dme (10 mol%), **L1** (12 mol%), Mn (3.5 equiv), NaI (2.5 equiv), DMA (0.1 M) under rt for 18 h). Conditions B: **1a** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.15 mmol) Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (10 mol%), **L6** (12 mol%), Mn (3.0 equiv), NaI (0.5 equiv), IPA/MeOH (5/1, 0.1 M) under 50 °C for 18 h). Yield was determined by GC analysis using *n*-dodecane as internal standard.

Table S13. Evaluation	of ligand for	or non-terminal	alkene
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<sup>a</sup> Reaction was run using 0.1 mmol of **1a**, 0.2 mmol of **2b**, and 0.2 mmol of **3a** under indicated conditions for 18 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. <sup>b</sup> 'rr' = Regiomeric ratio of **4am/5am**. <sup>c</sup> Isolated yield.

# IV. General Procedures for Ni-Catalyzed Regiodivergent

# **Arylalkylations of Allylic Amines**

General procedure for Ni-catalyzed 1,2-arylalkylations of allylic amines



**General Procedure C:** In a nitrogen-filled glovebox, NiBr<sub>2</sub>·dme (6.2 mg, 0.02 mmol, 10 mol%), **L1** (11.6 mg, 0.024 mmol, 12 mol%), aryl iodide **2** (0.40 mmol, 2.0 equiv, if **2** was solid), Mn (38.6 mg, 0.70 mmol, 3.5 equiv), NaI (75.0 mg, 0.50 mmol, 2.5 equiv) and DMA (2.0 mL) were added to a 10.0 mL vial equipped with a stirring bar. Then, **1** (0.20 mmol, 1.0 equiv), aryl iodide **2** (0.40 mmol, 2.0 equiv, if **2** was oil), and alkyl bromide **3** (0.40 mmol, 2.0 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated. The residue was purified by flash chromatography to afford **4**.

General procedure for Ni-catalyzed 1,3-arylalkylations of allylic amines



**General Procedure D:** In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.8 mg, 0.02 mmol, 10 mol%), **L6** (11.6 mg, 0.024 mmol, 12 mol%), aryl iodide **2** (0.30 mmol, 1.5 equiv, if **2** was solid), Mn (33.0 mg, 0.60 mmol, 3.0 equiv), NaI (15.0 mg, 0.10 mmol, 0.5 equiv), IPA (1.65 mL) and MeOH (0.35 mL) were added to a 10.0 mL vial equipped with a stirring bar. Then, **1** (0.20 mmol, 1.0 equiv), aryl iodide **2** (0.30 mmol, 1.5 equiv, if **2** was oil), and alkyl bromide **3** (0.30 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated. The residue was purified by flash chromatography to afford **5**.

# **V. Characterization of Products**



#### *N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)benzamide (4aa)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4aa** (63.1 mg, 82% yield, >20:1 rr, 4% ee) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (dd, J = 8.2, 1.5 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.34 (dd, J = 8.2, 6.9 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.13 (m, 3H), 7.08 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.95 – 5.86 (m, 1H), 3.76 (s, 3H), 3.52 (ddd, J = 13.7, 6.6, 5.4 Hz, 1H), 3.25 (ddd, J = 13.5, 7.1, 5.2 Hz, 1H), 2.70 (dd, J = 13.9, 5.9 Hz, 1H), 2.60 (t, J = 7.5 Hz, 2H), 2.49 (dd, J = 13.9, 8.2 Hz, 1H), 1.94 (dt, J = 13.2, 6.7 Hz, 1H), 1.73 (ddt, J = 10.4, 8.7, 3.2 Hz, 2H), 1.40 (dt, J = 9.5, 6.1 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 142.4, 134.7, 132.6, 131.4, 130.1, 128.55, 128.51, 128.4, 126.8, 125.9, 114.2, 55.4, 43.8, 40.6, 38.9, 36.1, 31.9, 28.6.

HR-MS (ESI) m/z calcd for  $C_{26}H_{30}NO_2^+$  [M+H<sup>+</sup>]: 388.2271, found 388.2269.

**HPLC** (CHIRALCEL OD-H, 80:20 hexane:isopropanol, 1.0 mL/min, 254 nm) retention time = 15.9 min (minor) and 20.8 min (major).



### *N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)benzamide (5aa)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5aa** (56.0 mg, 72% yield, 14:1 rr, 10% ee) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.64 – 7.53 (m, 2H), 7.46 – 7.39 (m, 1H), 7.37 – 7.28 (m, 2H), 7.23 – 7.15 (m, 2H), 7.13 – 7.04 (m, 3H), 7.04 – 6.97 (m, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 9.3 Hz, 1H), 4.17 (dh, *J* = 8.6, 4.3 Hz, 1H), 3.68 (s, 3H), 2.64 – 2.46 (m, 4H), 1.88 – 1.76 (m, 1H), 1.72 – 1.66 (m, 2H), 1.61 – 1.55 (m, 2H), 1.52 – 1.42 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 157.9, 142.2, 134.9, 134.0, 131.5, 129.4, 128.64, 128.57, 128.4, 126.9, 125.9, 114.0, 55.4, 49.6, 37.3, 35.8, 35.0, 31.6, 27.9. **HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 388.2271, found 388.2267.

**HPLC** (CHIRALCEL OD-H, 80:20 hexane:isopropanol, 1.0 mL/min, 230 nm) retention time = 12.1 min (minor) and 14.7 min (major).



#### *N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (4ab)

Following General Procedure C, *N*-allyl-4-(trifluoromethyl)benzamide (45.8 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ab** (71.8 mg, 79% yield, 17:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.49 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.12 – 7.06 (m, 3H), 7.01 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 5.81 (t, J = 5.9 Hz, 1H), 3.67 (s, 3H), 3.48 (ddd, J = 13.6, 6.7, 5.1 Hz, 1H), 3.15 (ddd, J = 13.6, 7.4, 5.0 Hz, 1H), 2.67 (dd, J = 13.9, 5.5 Hz, 1H), 2.54 (t, J = 7.5 Hz, 2H), 2.38 (dd, J = 13.9, 8.6 Hz, 1H), 1.88 (ddd, J = 13.5, 7.5, 5.5 Hz, 1H), 1.67 (ddt, J = 12.5, 10.3, 7.0 Hz, 2H), 1.36 – 1.26 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 158.2, 142.3, 137.9, 132.5, 130.0, 128.5, 128.4, 127.3, 125.9, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 114.2, 55.3, 44.2, 40.5, 39.1, 36.0, 32.1, 28.6.

<sup>19</sup>F NMR (**376** MHz, CDCl<sub>3</sub>) δ -62.88.

HR-MS (ESI) m/z calcd for C<sub>27</sub>H<sub>29</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 456.2145, found 456.2142.



# *N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)-4-(trifluoromethyl)benzamide (5ab)

Following General Procedure D, *N*-allyl-4-(trifluoromethyl)benzamide (45.8 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ab** (66.2 mg, 73% yield, 12:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.36 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 7.11 – 7.01 (m, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.93 (d, J = 8.8 Hz, 1H), 4.26 (dt, J = 8.6, 4.4 Hz, 1H), 3.75 (s, 3H), 2.72 – 2.57 (m, 4H), 1.92 (ddt, J = 13.9, 7.9, 3.9 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.72 – 1.61 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 158.0, 142.1, 138.2, 133.8, 129.4, 128.6, 128.5, 127.4, 126.0, 125.7 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 114.1, 55.3, 50.0, 36.9, 35.7, 34.8, 31.5, 27.9.

<sup>19</sup>**F NMR (376 MHz, CDCl<sub>3</sub>)** δ -62.91. **HR-MS** (ESI) m/z calcd for C<sub>27</sub>H<sub>29</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 456.2145, found 456.2144.



#### 4-(*tert*-Butyl)-N-(2-(4-methoxybenzyl)-5-phenylpentyl)benzamide (4ac)

Following General Procedure C, *N*-allyl-4-(*tert*-butyl)benzamide (43.4 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 3:1) to give the product **4ac** (58.2 mg, 66% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.41 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.17 (ddd, *J* = 7.2, 5.6, 1.5 Hz, 2H), 7.12 – 7.04 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.83 (t, *J* = 5.9 Hz, 1H), 3.68 (s, 3H), 3.44 (ddd, *J* = 13.6, 6.6, 5.4 Hz, 1H), 3.22 – 3.12 (m, 1H), 2.60 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.51 (t, *J* = 7.6 Hz, 2H), 2.42 (dd, *J* = 13.9, 8.0 Hz, 1H), 1.86 (p, *J* = 6.5 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.37 – 1.27 (m, 2H), 1.24 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 158.1, 154.8, 142.4, 132.6, 131.8, 130.0, 128.5, 128.4, 126.7, 125.8, 125.4, 114.1, 55.3, 43.6, 40.5, 38.8, 36.1, 34.9, 31.8, 31.3, 28.6. HR-MS (ESI) m/z calcd for C<sub>30</sub>H<sub>38</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 444.2897, found 444.2894.



#### 4-(*tert*-Butyl)-*N*-(1-(4-methoxyphenyl)-6-phenylhexan-3-yl)benzamide (5ac)

Following General Procedure D, *N*-allyl-4-(*tert*-butyl)benzamide (43.4 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **5ac** (80.6 mg, 91% yield, 11:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.07 (m, 3H), 7.03 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 5.75 (d, J = 9.2 Hz, 1H), 4.20 (dq, J = 8.6, 4.3 Hz, 1H), 3.71 (s, 3H), 2.58 (qd, J = 6.9, 3.9 Hz, 4H), 1.87 – 1.81 (m, 1H), 1.75 – 1.68 (m, 2H), 1.61 – 1.54 (m, 2H), 1.52 – 1.45 (m, 1H), 1.29 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 157.9, 154.9, 142.3, 134.0, 132.1, 129.4, 128.6, 128.4, 126.8, 125.9, 125.6, 114.0, 55.3, 49.5, 37.4, 35.8, 35.1, 35.0, 31.6, 31.3, 27.8. HR-MS (ESI) m/z calcd for C<sub>30</sub>H<sub>38</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 444.2897, found 444.2898.



**4-(Dimethylamino)-***N***-(2-(4-methoxybenzyl)-5-phenylpentyl)benzamide (4ad)** Following General Procedure C, *N*-allyl-4-(dimethylamino)benzamide (40.8 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 3:1) to give the product **4ad** (67.4 mg, 78% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.32 (m, 2H), 7.20 – 7.13 (m, 2H), 7.07 (ddd, *J* = 8.1, 6.9, 1.7 Hz, 2H), 7.02 – 6.95 (m, 2H), 6.90 (d, *J* = 21.7 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 9.0 Hz, 2H), 5.75 (t, *J* = 5.8 Hz, 1H), 3.68 (s, 3H), 3.45 – 3.37 (m, 1H), 3.15 (ddd, *J* = 13.6, 7.1, 5.2 Hz, 1H), 2.90 (s, 6H), 2.61 – 2.35 (m, 4H), 1.85 (d, *J* = 6.7 Hz, 1H), 1.64 (pd, *J* = 7.0, 2.2 Hz, 2H), 1.30 (dt, *J* = 8.9, 5.8 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.0, 152.4, 142.5, 132.7, 130.0, 128.5, 128.35, 128.30, 125.7, 121.5, 114.0, 111.0, 55.3, 43.5, 40.6, 40.2, 38.7, 36.1, 31.8, 28.6.

**HR-MS** (ESI) m/z calcd for  $C_{28}H_{35}N_2O_2^+$  [M+H<sup>+</sup>]: 431.2693, found 431.2692.



# 4-(Dimethylamino)-*N*-(1-(4-methoxyphenyl)-6-phenylhexan-3-yl)benzamide (5ad)

Following General Procedure D, *N*-allyl-4-(dimethylamino)benzamide (40.8 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **5ad** (72.6 mg, 84% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (d, J = 8.9 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.12 – 7.01 (m, 3H), 6.99 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 5.67 (d, J = 9.2 Hz, 1H), 4.15 (qt, J = 8.8, 4.8 Hz, 1H), 3.67 (s, 3H), 2.91 (s, 6H), 2.61 – 2.44 (m, 4H), 1.83 – 1.75 (m, 1H), 1.68 – 1.48 (m, 4H), 1.45 – 1.32 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 157.8, 152.5, 142.4, 134.2, 129.4, 128.6, 128.4, 125.8, 121.7, 113.9, 111.2, 55.3, 49.2, 40.2, 37.5, 35.8, 35.1, 31.6, 27.8. HR-MS (ESI) m/z calcd for C<sub>28</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 431.2693, found 431.2637.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-3,5-dimethylbenzamide (4ae)

Following General Procedure C, *N*-allyl-3,5-dimethylbenzamide (37.8 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ae** (60.4 mg, 73% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 – 7.14 (m, 2H), 7.11 – 7.05 (m, 3H), 7.01 (d, J = 8.7 Hz, 5H), 6.74 (d, J = 8.6 Hz, 2H), 5.78 (t, J = 5.9 Hz, 1H), 3.67 (s, 3H), 3.46 (ddd, J = 13.7, 6.6, 5.1 Hz, 1H), 3.15 (ddd, J = 13.6, 7.3, 5.1 Hz, 1H), 2.62 (dd, J = 13.9, 5.8 Hz, 1H), 2.52 (t, J = 7.6 Hz, 2H), 2.41 (dd, J = 13.8, 8.2 Hz, 1H), 2.22 (s, 6H), 1.86 (p, J = 6.8 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.32 (dt, J = 9.9, 6.4 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.6, 158.1, 142.4, 138.2, 134.6, 132.9, 132.6, 130.0, 128.5, 128.4, 125.8, 124.6, 114.1, 55.2, 43.9, 40.5, 39.0, 36.1, 32.1, 28.6, 21.2. HR-MS (ESI) m/z calcd for C<sub>28</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 416.2584, found 416.2580.



*N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)-3,5-dimethylbenzamide (5ae)

Following General Procedure D, *N*-allyl-3,5-dimethylbenzamide (37.8 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ae** (67.3 mg, 81% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.15 (m, 5H), 7.13 – 7.07 (m, 3H), 7.05 – 6.98 (m, 3H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.65 (d, *J* = 9.2 Hz, 1H), 4.18 (tq, *J* = 8.7, 4.5 Hz, 1H), 3.68 (s, 3H), 2.62 – 2.49 (m, 4H), 2.27 (s, 6H), 1.80 (d, *J* = 6.6 Hz, 1H), 1.71 – 1.61 (m, 3H), 1.46 (ddd, *J* = 12.9, 7.5, 5.6 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.5, 157.9, 142.3, 138.4, 134.9, 134.0, 133.0, 129.4, 128.6, 128.4, 125.9, 124.7, 114.0, 55.3, 49.5, 37.3, 35.8, 35.1, 31.6, 27.8, 21.4. HR-MS (ESI) m/z calcd for C<sub>28</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 416.2584, found 416.2581.



N-(2-(4-Methoxybenzyl)-5-phenylpentyl)-2-methylbenzamide (4af)

Following General Procedure C, *N*-allyl-2-methylbenzamide (35.0 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4af** (52.1 mg, 65% yield, 9:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.22 – 7.14 (m, 3H), 7.11 – 7.05 (m, 5H), 7.04 – 7.02 (m, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 5.50 (t, *J* = 5.9 Hz, 1H), 3.68 (s, 3H), 3.36 (dt, *J* = 13.5, 6.2 Hz, 1H), 3.19 (ddd, *J* = 13.6, 6.5, 5.5 Hz, 1H), 2.57 – 2.38 (m, 4H), 2.31 (s, 3H), 1.87 – 1.75 (m, 1H), 1.71 – 1.58 (m, 2H), 1.36 – 1.24 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.1, 158.1, 142.3, 136.7, 136.1, 132.3, 131.0, 130.0, 129.8, 128.5, 128.4, 126.6, 125.8, 125.7, 114.0, 55.3, 43.0, 40.5, 38.3, 36.1, 31.4, 28.5, 19.9.

**HR-MS** (ESI) m/z calcd for C<sub>27</sub>H<sub>32</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 402.2428, found 402.2425.





Following General Procedure D, *N*-allyl-2-methylbenzamide (35.0 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5af** (57.6 mg, 72% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.24 – 7.16 (m, 5H), 7.13 – 7.07 (m, 4H), 7.02 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 5.41 (d, J = 9.4 Hz, 1H), 4.14 (tt, J = 8.8, 4.2 Hz, 1H), 3.69 (s, 3H), 2.56 (ddt, J = 16.2, 9.0, 4.6 Hz, 4H), 2.37 (s, 3H), 1.77 (tdd, J = 11.7, 6.0, 3.4 Hz, 1H), 1.62 – 1.53 (m, 4H), 1.48 – 1.38 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.9, 158.0, 142.2, 137.1, 136.0, 133.9, 131.1, 129.8, 129.4, 128.55, 128.45, 126.5, 125.9, 125.8, 114.0, 55.4, 49.2, 37.6, 35.7, 35.0, 31.7, 27.9, 19.9.

**HR-MS** (ESI) m/z calcd for C<sub>27</sub>H<sub>32</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 402.2428, found 402.2415.





Following General Procedure C, *N*-allylfuran-2-carboxamide (30.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ag** (40.9 mg, 54% yield, 7:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (dd, J = 1.7, 0.9 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.16 (ddd, J = 8.1, 6.9, 1.6 Hz, 3H), 7.09 – 7.00 (m, 3H), 6.86 – 6.77 (m, 2H), 6.47 (dd, J = 3.5, 1.8 Hz, 1H), 6.14 (s, 1H), 3.78 (s, 3H), 3.48 – 3.37 (m, 1H), 3.27 (ddd, J = 13.7, 6.6, 5.7 Hz, 1H), 2.69 – 2.57 (m, 3H), 2.51 (dd, J = 13.9, 7.8 Hz, 1H), 1.92 (p, J = 6.3 Hz, 1H), 1.75 – 1.66 (m, 2H), 1.39 (dt, J = 9.3, 6.5 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.5, 158.1, 148.2, 143.7, 142.4, 132.3, 130.0, 128.5, 128.4, 125.8, 114.04, 114.98, 112.2, 55.4, 42.4, 40.5, 38.3, 36.1, 31.5, 28.6.

**HR-MS** (ESI) m/z calcd for C<sub>24</sub>H<sub>28</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 378.2064, found 378.2061.



*N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)furan-2-carboxamide (5ag)

Following General Procedure D, *N*-allylfuran-2-carboxamide (30.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ag** (46.4 mg, 61% yield, 5:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (ddd, J = 5.1, 1.8, 0.9 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.12 – 7.06 (m, 3H), 7.03 – 6.96 (m, 3H), 6.72 (d, J = 8.6 Hz, 2H), 6.42 (dd, J = 3.5, 1.7 Hz, 1H), 5.98 (d, J = 9.3 Hz, 1H), 4.11 (tt, J = 8.8, 4.3 Hz, 1H), 3.69 (s, 3H), 2.63 – 2.44 (m, 4H), 1.84 – 1.76 (m, 1H), 1.64 – 1.51 (m, 3H), 1.48 – 1.40 (m, 1H), 1.21 (t, J = 7.8 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.9, 148.2, 143.7, 142.2, 133.9, 129.4, 128.6, 128.4, 125.9, 114.2, 113.9, 112.3, 55.3, 48.8, 37.5, 35.7, 35.1, 31.5, 27.8.

**HR-MS** (ESI) m/z calcd for C<sub>24</sub>H<sub>27</sub>NO<sub>3</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 400.1883, found 400.1882.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)thiophene-2-carboxamide (4ah)

Following General Procedure C, *N*-allylthiophene-2-carboxamide (33.4 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ah** (51.8 mg, 66% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (dd, J = 5.0, 1.2 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.12 – 7.06 (m, 4H), 7.01 (d, J = 8.6 Hz, 2H), 6.93 (dd, J = 5.0, 3.7 Hz, 1H), 6.75 (d, J = 8.6 Hz, 2H), 5.64 (t, J = 5.8 Hz, 1H), 3.70 (s, 3H), 3.42 (ddd, J = 13.6, 6.6, 5.3 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.62 (dd, J = 13.9, 5.9 Hz, 1H), 2.53 (t, J = 7.6 Hz, 2H), 2.41 (dd, J = 13.9, 8.2 Hz, 1H), 1.86 (p, J = 6.5 Hz, 1H), 1.66 (td, J = 7.6, 4.0 Hz, 2H), 1.32 (dt, J = 9.0, 6.0 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.8, 158.2, 142.4, 139.3, 132.5, 130.0, 129.8, 128.6, 128.4, 127.7, 127.5, 125.9, 114.2, 55.4, 43.7, 40.6, 38.8, 36.1, 31.9, 28.6. HR-MS (ESI) m/z calcd for C<sub>24</sub>H<sub>28</sub>NO<sub>2</sub>S<sup>+</sup> [M+H<sup>+</sup>]: 394.1835, found 394.1834.



#### *N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)thiophene-2-carboxamide (5ah)

Following General Procedure D, *N*-allylthiophene-2-carboxamide (33.4 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ah** (57.2 mg, 73% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (dd, J = 5.0, 1.1 Hz, 1H), 7.30 (dd, J = 3.7, 1.2 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.12 – 7.05 (m, 3H), 7.02 – 6.93 (m, 3H), 6.72 (d, J = 8.6 Hz, 2H), 5.56 (d, J = 9.1 Hz, 1H), 4.12 (tt, J = 8.7, 4.0 Hz, 1H), 3.69 (s, 3H), 2.62 – 2.45 (m, 4H), 1.87 – 1.77 (m, 1H), 1.72 – 1.53 (m, 4H), 1.51 – 1.40 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 161.6, 158.0, 142.2, 139.4, 133.9, 129.8, 129.4, 128.6, 128.5, 127.8, 127.7, 125.9, 114.0, 55.4, 49.7, 37.3, 35.7, 35.0, 31.6, 27.8.

HR-MS (ESI) m/z calcd for C<sub>24</sub>H<sub>28</sub>NO<sub>2</sub>S<sup>+</sup> [M+H<sup>+</sup>]: 394.1835, found 394.1834.



#### N-(2-(4-Methoxybenzyl)-5-phenylpentyl)pivalamide (4ai)

Following General Procedure C, *N*-allylpivalamide (28.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ai** (60.1 mg, 82% yield, 10:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.31 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 7.07 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.41 (t, J = 5.9 Hz, 1H), 3.79 (s, 3H), 3.32 (ddd, J = 13.6, 6.4, 5.4 Hz, 1H), 3.07 (ddd, J = 13.6, 6.9, 5.2 Hz, 1H), 2.68 – 2.58 (m, 3H), 2.43 (dd, J = 13.8, 8.0 Hz, 1H), 1.83 (p, J = 6.6 Hz, 1H), 1.78 – 1.66 (m, 2H), 1.40 – 1.29 (m, 2H), 1.07 (s, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 178.3, 158.2, 142.4, 132.6, 130.0, 128.5, 128.4, 125.8, 114.1, 55.4, 43.2, 40.5, 38.7, 38.7, 36.1, 31.8, 28.6, 27.6.

**HR-MS** (ESI) m/z calcd for C<sub>24</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 368.2584, found 368.2581.



*N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)pivalamide (5ai)

Following General Procedure D, *N*-allylpivalamide (28.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ai** (62.6 mg, 85% yield, 14:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.25 (m, 3H), 7.17 (dd, J = 7.6, 6.0 Hz, 2H), 7.08 (dd, J = 8.5, 3.9 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.35 – 5.29 (m, 1H), 4.04 (qt, J = 8.8, 4.8 Hz, 1H), 3.78 (s, 3H), 2.67 – 2.49 (m, 4H), 1.82 – 1.74 (m, 1H), 1.69 – 1.60 (m, 3H), 1.59 – 1.50 (m, 1H), 1.47 – 1.36 (m, 1H), 1.19 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.0, 157.9, 142.3, 134.0, 129.3, 128.5, 128.4, 125.8, 114.0, 55.3, 48.6, 38.8, 37.5, 35.7, 34.8, 31.5, 27.75, 27.72.

**HR-MS** (ESI) m/z calcd for C<sub>24</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 368.2584, found 368.2583.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)cyclohexanecarboxamide (4aj)

Following General Procedure C, *N*-allylcyclohexanecarboxamide (33.4 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4aj** (69.0 mg, 88% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 7.04 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 5.23 (t, J = 5.9 Hz, 1H), 3.78 (s, 3H), 3.27 (dt, J = 13.5, 6.1 Hz, 1H), 3.06 (ddd, J = 13.6, 6.8, 5.4 Hz, 1H), 2.63 – 2.52 (m, 3H), 2.43 (dd, J = 13.9, 7.8 Hz, 1H), 1.89 (tt, J = 8.2, 3.3 Hz, 1H), 1.80 – 1.60 (m, 7H), 1.33 – 1.18 (m, 8H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.0, 158.1, 142.4, 132.5, 130.0, 128.6, 128.4, 125.8, 114.0, 55.4, 45.7, 42.7, 40.4, 38.5, 36.1, 31.4, 29.8, 28.5, 25.9, 25.8.

**HR-MS** (ESI) m/z calcd for  $C_{26}H_{36}NO_2^+$  [M+H<sup>+</sup>]: 394.2741, found 394.2738.



*N*-(**1**-(**4**-**Methoxyphenyl**)-**6**-**phenylhexan-3**-**yl**)**cyclohexanecarboxamide** (**5aj**) Following General Procedure D, *N*-allylcyclohexanecarboxamide (33.4 mg, 0.2

mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5aj** (54.4 mg, 69% yield, 12:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.35 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 7.08 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.19 (d, J = 9.3 Hz, 1H), 4.04 (qt, J = 9.0, 4.8 Hz, 1H), 3.78 (s, 3H), 2.69 – 2.49 (m, 4H), 2.08 – 2.00 (m, 1H), 1.83 – 1.74 (m, 5H), 1.65 (ddd, J = 14.5, 8.6, 6.6 Hz, 3H), 1.58 – 1.50 (m, 1H), 1.46 – 1.38 (m, 3H), 1.31 – 1.18 (m, 4H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.8, 157.9, 142.3, 134.1, 129.3, 128.5, 128.4, 125.8, 113.9, 55.3, 48.4, 45.9, 37.5, 35.7, 34.9, 31.5, 30.0, 29.9, 27.7, 25.9.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>36</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 394.2741, found 394.2738.



#### *N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)cyclopropanecarboxamide (4ak)

Following General Procedure C, *N*-allylcyclopropanecarboxamide (25.0 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ak** (43.5 mg, 62% yield, 9:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.23 – 7.14 (m, 2H), 7.12 – 7.03 (m, 3H), 6.96 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 5.48 (t, J = 6.0 Hz, 1H), 3.69 (s, 3H), 3.18 (dt, J = 12.8, 6.1 Hz, 1H), 3.03 (dd, J = 13.4, 6.3 Hz, 1H), 2.48 (q, J = 6.7, 5.9 Hz, 3H), 2.39 (dd, J = 13.9, 7.4 Hz, 1H), 1.73 (p, J = 6.5 Hz, 1H), 1.60 (tq, J = 12.2, 5.4, 3.9 Hz, 2H), 1.30 – 1.17 (m, 2H), 1.10 (tt, J = 8.0, 4.5 Hz, 1H), 0.82 (dt, J = 6.6, 3.4 Hz, 2H), 0.58 (dq, J = 7.1, 3.9 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.0, 142.4, 132.5, 130.0, 128.5, 128.3, 125.8, 113.9, 55.3, 43.0, 40.3, 38.1, 36.0, 31.2, 28.4, 14.7, 7.0.

HR-MS (ESI) m/z calcd for C<sub>23</sub>H<sub>30</sub>NO<sub>2</sub>S<sup>+</sup> [M+H<sup>+</sup>]: 352.2271, found 352.2268.





<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 – 7.18 (m, 2H), 7.11 – 7.07 (m, 3H), 7.00 (d, J =

8.5 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.24 (d, *J* = 9.2 Hz, 1H), 3.96 (tt, *J* = 8.7, 3.9 Hz, 1H), 3.70 (s, 3H), 2.51 (dddd, *J* = 20.8, 17.2, 13.4, 7.1 Hz, 4H), 1.73 – 1.66 (m, 1H), 1.60 – 1.54 (m, 3H), 1.51 – 1.42 (m, 1H), 1.38 – 1.32 (m, 1H), 1.23 – 1.11 (m, 1H), 0.89 (tt, *J* = 4.5, 2.7 Hz, 2H), 0.68 – 0.57 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 173.2, 157.9, 142.4, 134.1, 129.4, 128.6, 128.4, 125.9, 113.9, 55.4, 49.1, 37.6, 35.8, 35.1, 31.6, 27.8, 15.0, 7.14, 7.12.

HR-MS (ESI) m/z calcd for C<sub>23</sub>H<sub>29</sub>NO<sub>2</sub>SNa<sup>+</sup> [M+Na<sup>+</sup>]: 374.2091, found 374.2088.



*N*-(-(2-(4-Methoxybenzyl)-5-phenylpentyl)-*N*-methylbenzamide (4al)

Following General Procedure C, *N*-allyl-*N*-methylbenzamide (35.0 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4al** (54.5 mg, 68% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.40 – 7.32 (m, 4H), 7.28 – 7.23 (m, 3H), 7.21 – 7.04 (m, 4H), 6.92 – 6.75 (m, 3H), 3.79 (s, 3H), 3.64 – 3.35 (m, 1H), 3.28 – 3.09 (m, 1H), 3.04 – 2.71 (m, 3H), 2.65 – 2.44 (m, 3H), 2.35 – 2.10 (m, 1H), 1.93 – 1.61 (m, 2H), 1.41 (s, 2H), 1.26 – 1.07 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.0, 136.9, 130.0, 129.9, 129.8, 129.4, 128.6, 128.4, 127.1, 127.0, 125.8, 113.9, 55.4, 55.2, 51.3, 38.0, 37.8, 36.2, 31.1, 28.4.

**HR-MS** (ESI) m/z calcd for  $C_{27}H_{32}NO_2^+$  [M+H<sup>+</sup>]: 402.2428, found 402.2422.



## *N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)-*N*-methylbenzamide (5al)

Following General Procedure D, *N*-allyl-*N*-methylbenzamide (35.0 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5al** (34.5 mg, 43% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.33 (m, 4H), 7.30 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 7.14 – 7.07 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 18.0, 8.6 Hz, 2H), 3.78 (s, 3H), 3.70 – 3.49 (m, 1H), 2.90 (s, 1H), 2.67 (s, 2H), 2.62 – 2.50 (m, 2H), 2.41 (td, *J* = 9.2, 6.7 Hz, 1H), 1.87 – 1.68 (m, 2H), 1.64 (s, 1H), 1.57 – 1.44 (m, 3H), 1.32 – 1.21 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 158.2, 134.8, 132.8, 131.7, 131.4, 130.9, 130.1, 128.5, 126.8, 124.8, 123.8, 114.2, 55.4, 44.0, 40.8, 39.1, 32.7, 29.2, 26.9, 18.1, 12.9. HR-MS (ESI) m/z calcd for C<sub>27</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+NH<sub>4</sub><sup>+</sup>]: 419.2693, found 419.2747.



# *N*-2-(3-Phenylpropyl)-3-(*p*-tolyl)nonyl)benzamide (4am)

Following General Procedure C, NiBr<sub>2</sub>·dme (3.1 mg, 0.01 mmol, 10 mol%), L7 (4.3 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(non-2-en-1-yl)benzamide (24.5 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 39.6 mg, 0.2 mmol), Mn (19.3 mg, 0.35 mmol), NaI (37.5 mg, 0.50 mmol) and DMA (1.0 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4am** (22.8 mg, 50% yield, >20:1 dr, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.31 (m, 3H), 7.30 – 7.23 (m, 2H), 7.17 (d, J = 6.4 Hz, 2H), 7.12 – 7.08 (m, 3H), 7.04 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 5.36 (t, J = 5.9 Hz, 1H), 3.26 (t, J = 5.8 Hz, 2H), 2.56 (td, J = 7.4, 2.1 Hz, 2H), 2.41 (ddd, J = 11.4, 7.7, 4.2 Hz, 1H), 2.25 (s, 3H), 1.78 – 1.60 (m, 5H), 1.49 – 1.43 (m, 1H), 1.40 – 1.31 (m, 1H), 1.17 – 1.06 (m, 6H), 1.02 – 0.94 (m, 2H), 0.77 (t, J = 7.0 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.0, 142.5, 140.7, 136.1, 134.7, 131.2, 129.5, 128.6, 128.44, 128.42, 126.8, 125.8, 48.1, 44.2, 41.8, 36.2, 33.2, 31.8, 30.0, 29.5, 28.3, 27.8, 22.8, 21.1, 14.2.

**HR-MS** (ESI) m/z calcd for C<sub>32</sub>H<sub>41</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 478.3080, found 478.3080.



#### *N*-(1-Phenyl-6-(*p*-tolyl)dodecan-4-yl)benzamide (5am)

Following General Procedure D, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.8 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(non-2-en-1-yl)benzamide (24.5 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol), Mn (16.5 mg, 0.3 mmol), NaI (7.5 mg, 0.05 mmol), MeOH (0.17 mL) and IPA (0.83 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5am** (25.6 mg, 56% yield, >20:1 dr, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (dd, J = 11.5, 7.2 Hz, 2H), 7.34 (d, J = 15.4 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.15 (dd, J = 14.1, 7.1 Hz, 3H), 7.06 – 6.96 (m, 4H), 5.49 (d, J = 8.7 Hz, 1H), 4.14 (ddt, J = 15.9, 11.3, 5.6 Hz, 1H), 2.64 – 2.48 (m, 3H), 2.23 (s, 3H), 1.86 (dt, J = 14.1, 5.3 Hz, 1H), 1.78 (dt, J = 14.2, 8.8 Hz, 1H), 1.64 (tdd, J = 10.2, 6.0, 3.5 Hz, 4H), 1.48 (tt, J = 8.3, 3.6 Hz, 2H), 1.29 – 1.24 (m, 2H), 1.21 (q, J = 6.6 Hz, 2H), 1.15 (d, J = 8.5 Hz, 2H), 1.10 – 1.02 (m, 2H), 0.82 (t, J = 7.1 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.9, 142.9, 142.4, 135.6, 134.9, 131.2, 129.4, 128.6, 128.44, 128.42, 127.4, 126.8, 125.9, 49.3, 43.4, 42.2, 37.7, 35.9, 35.4, 31.9, 29.4, 27.6,

27.4, 22.8, 21.1, 14.2. **HR-MS** (ESI) m/z calcd for C<sub>32</sub>H<sub>41</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 478.3080, found 478.3079.



# *N*-2-(3-Phenylpropyl)-3-(*p*-tolyl)decyl)benzamide (4an)

Following General Procedure C, NiBr<sub>2</sub>·dme (3.1 mg, 0.01 mmol, 10 mol%), **L8** (4.6 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(dec-2-en-1-yl)benzamide (25.9 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol), Mn (19.3 mg, 0.35 mmol), NaI (37.5 mg, 0.25 mmol) and DMA (1.0 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4an** (23.9 mg, 51% yield, >20:1 dr, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.45 – 7.39 (m, 3H), 7.37 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 – 7.15 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.44 (d, *J* = 6.7 Hz, 1H), 3.33 (t, *J* = 5.8 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.48 (ddd, *J* = 11.4, 7.5, 4.2 Hz, 1H), 2.32 (s, 3H), 1.84 – 1.78 (m, 2H), 1.77 – 1.68 (m, 3H), 1.63 (dd, *J* = 10.7, 7.0 Hz, 1H), 1.57 – 1.49 (m, 1H), 1.47 – 1.40 (m, 1H), 1.30 – 1.14 (m, 7H), 1.11 – 1.03 (m, 2H), 0.86 – 0.79 (m, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.0, 142.5, 140.7, 136.1, 134.8, 131.2, 129.5, 128.6, 128.44, 128.43, 126.8, 125.8, 48.1, 44.2, 41.8, 36.2, 33.2, 32.0, 30.0, 29.0, 28.3, 27.5, 22.7, 21.1, 14.2.

HR-MS (ESI) m/z calcd for C<sub>33</sub>H<sub>44</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 470.3417, found 470.3412.



# *N*-1-Phenyl-6-(*p*-tolyl)tridecan-4-yl)benzamide (5an)

Following General Procedure D, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.8 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(dec-2-en-1-yl)benzamide (25.9 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol), Mn (16.5 mg, 0.3 mmol), NaI (7.5 mg, 0.05 mmol), MeOH (0.17 mL) and IPA (0.83 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5an** (25.5 mg, 54% yield, >20:1 dr, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.52 – 7.43 (m, 2H), 7.38 – 7.29 (m, 2H), 7.25 (d, J = 8.0 Hz, 3H), 7.20 – 7.11 (m, 3H), 7.04 – 6.96 (m, 4H), 5.49 (d, J = 8.7 Hz, 1H), 4.16 (dq, J = 9.8, 5.4, 4.7 Hz, 1H), 2.58 (dq, J = 14.0, 8.1, 7.4 Hz, 3H), 2.23 (s, 3H), 1.90 – 1.76 (m, 2H), 1.69 – 1.60 (m, 5H), 1.49 (td, J = 8.7, 4.9 Hz, 2H), 1.31 – 1.04 (m, 9H), 0.85 – 0.73 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.9, 142.9, 142.4, 135.6, 134.9, 131.2, 129.4, 128.6,

128.43, 128.42, 127.4, 126.8, 125.9, 49.3, 43.4, 42.2, 37.6, 35.9, 35.4, 32.0, 27.6, 27.1, 22.7, 21.1, 14.2.

HR-MS (ESI) m/z calcd for C<sub>33</sub>H<sub>43</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 492.3237, found 492.3243.



#### *N*-2-(3-Phenylpropyl)-3-(*p*-tolyl)hexyl)benzamide (4ao)

Following General Procedure C, NiBr<sub>2</sub>·dme (3.1 mg, 0.01 mmol, 10 mol%), L7 (4.3 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(hex-2-en-1-yl)benzamide (20.3 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol), Mn (19.3 mg, 0.35 mmol), NaI (37.5 mg, 0.25 mmol) and DMA (1.0 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4ao** (21.3 mg, 52% yield, >20:1 dr, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.46 – 7.39 (m, 3H), 7.38 – 7.32 (m, 2H), 7.25 (d, J = 7.0 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.11 (d, J = 7.9 Hz, 2H), 7.08 – 7.01 (m, 2H), 5.44 (d, J = 6.2 Hz, 1H), 3.41 – 3.26 (m, 2H), 2.64 (td, J = 7.5, 2.2 Hz, 2H), 2.51 (ddd, J = 10.6, 7.7, 4.4 Hz, 1H), 2.32 (s, 3H), 1.84 – 1.67 (m, 5H), 1.55 (td, J = 5.3, 3.4 Hz, 1H), 1.48 – 1.41 (m, 1H), 1.16 – 1.01 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.0, 142.5, 140.7, 136.2, 134.8, 131.2, 129.5, 128.6, 128.44, 128.43, 126.8, 125.8, 47.8, 44.1, 41.8, 36.2, 35.4, 30.0, 28.3, 21.1, 20.9, 14.2. HR-MS (ESI) m/z calcd for C<sub>29</sub>H<sub>35</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 436.2611, found 436.2611.



# *N*-1-Phenyl-6-(*p*-tolyl)nonan-4-yl)benzamide (5ao)

Following General Procedure D, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.8 mg, 0.012 mmol, 12 mol%), (*Z*)-*N*-(hex-2-en-1-yl)benzamide (20.3 mg, 0.1 mmol), 4-iodotoluene (43.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol), Mn (16.5 mg, 0.3 mmol), NaI (0.75 mg, 0.05 mmol), MeOH (0.17 mL) and IPA (0.83 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5ao** (23.5 mg, 57% yield, >20:1 dr, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 – 7.41 (m, 3H), 7.34 (dd, J = 8.2, 6.8 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 – 7.11 (m, 4H), 7.04 – 6.96 (m, 4H), 5.53 (d, J = 8.7 Hz, 1H), 4.22 – 4.11 (m, 1H), 2.65 – 2.53 (m, 3H), 2.24 (s, 3H), 1.89 – 1.78 (m, 2H), 1.64 (dtd, J = 18.7, 10.1, 4.1 Hz, 4H), 1.54 – 1.42 (m, 2H), 1.16 – 1.04 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.9, 142.8, 142.4, 135.6, 134.9, 131.2, 129.4, 128.6, 128.42, 128.40, 127.4, 126.8, 125.9, 49.3, 43.1, 42.2, 39.8, 35.9, 35.4, 27.6, 21.1, 20.5,





# 4-(*N*,*N*-Dipropylsulfamoyl)-*N*-(2-(4-methoxybenzyl)-5-phenylpentyl)benzamide (4ap)

Following General Procedure C, NiBr<sub>2</sub>·dme (3.1 mg, 0.01 mmol, 10 mol%), **L1** (5.8 mg, 0.012 mmol, 12 mol%), *N*-allyl-4-(*N*,*N*-dipropylsulfamoyl)benzamide (32.4 mg, 0.1 mmol), 4-iodoanisole (46.8 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol), , Mn (19.3 mg, 0.35 mmol), NaI (37.5 mg, 0.25 mmol) and DMA (1.0 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 3:1) to give the product **4ap** (43.2 mg, 79% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.25 (dd, J = 8.1, 1.5 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.09 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.99 (t, J = 5.8 Hz, 1H), 3.77 (s, 3H), 3.55 (ddd, J = 13.6, 6.6, 5.2 Hz, 1H), 3.25 (ddd, J = 13.6, 7.4, 5.0 Hz, 1H), 3.11 – 3.03 (m, 4H), 2.74 (dd, J = 13.9, 5.7 Hz, 1H), 2.62 (t, J = 7.5 Hz, 2H), 2.49 (dd, J = 13.9, 8.4 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.75 (dt, J = 15.0, 7.5 Hz, 2H), 1.61 – 1.48 (m, 4H), 1.41 (dd, J = 15.9, 6.3 Hz, 2H), 0.86 (t, J = 7.4 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 158.2, 142.7, 142.3, 138.2, 132.5, 130.0, 128.5, 128.4, 127.6, 127.1, 125.9, 114.2, 55.4, 50.1, 44.1, 40.4, 39.0, 36.0, 32.0, 28.5, 22.0, 11.3.

HR-MS (ESI) m/z calcd for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>SNa<sup>+</sup> [M+Na<sup>+</sup>]: 573.2757, found 573.2756.



# 4-(*N*,*N*-Dipropylsulfamoyl)-*N*-(1-(4-methoxyphenyl)-6-phenylhexan-3-yl)benzam ide (5ap)

Following General Procedure D, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.8 mg, 0.012 mmol, 12 mol%), *N*-allyl-4-(*N*,*N*-dipropylsulfamoyl)benzamide (32.4 mg, 0.1 mmol), 4-iodoanisole (35.1 mg, 0.15 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol), Mn (16.5 mg, 0.3 mmol), NaI (7.5 mg, 0.05 mmol), MeOH (0.17 mL) and IPA (0.83 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **5ap** (40.2 mg, 73% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.86 – 7.78 (m, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 7.11 – 7.04 (m, 2H), 6.85 – 6.72 (m, 2H), 5.79 (d,

*J* = 9.0 Hz, 1H), 4.24 (dt, *J* = 8.8, 4.4 Hz, 1H), 3.76 (s, 3H), 3.18 – 2.98 (m, 4H), 2.70 – 2.52 (m, 4H), 1.96 – 1.76 (m, 2H), 1.70 (q, *J* = 6.3, 5.8 Hz, 2H), 1.62 – 1.51 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.0, 158.0, 142.6, 142.2, 138.6, 133.8, 129.4, 128.53, 128.46, 127.7, 127.2, 126.0, 114.1, 55.4, 50.1, 50.0, 37.0, 35.7, 34.8, 31.6, 27.9, 22.1, 11.3.

**HR-MS** (ESI) m/z calcd for C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>SNa<sup>+</sup> [M+Na<sup>+</sup>]: 573.2757, found 573.2758.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxep in-1-yl)acetamide (4aq)

Following General Procedure C, NiBr<sub>2</sub>-dme (3.1 mg, 0.01 mmol, 10 mol%), L1 (5.8 mg, 0.012 mmol, 12 mol%), N-allyl-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-1-yl)acetamide (30.7 mg, 0.1 mmol), 4-iodoanisole (46.8 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4aq** (40.5 mg, 76% yield, 10:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, J = 2.4 Hz, 1H), 7.88 (dd, J = 7.8, 1.4 Hz, 1H), 7.56 (dd, J = 7.4, 1.4 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.35 (ddd, J = 10.8, 8.0, 1.8 Hz, 2H), 7.25 (ddd, J = 7.6, 6.2, 1.4 Hz, 2H), 7.20 – 7.09 (m, 3H), 7.02 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 5.24 (t, J = 5.9 Hz, 1H), 5.18 (s, 2H), 3.76 (s, 3H), 3.45 (s, 2H), 3.20 (dt, J = 13.6, 6.1 Hz, 1H), 3.09 (dt, J = 13.5, 6.0 Hz, 1H), 2.51 (dt, J = 12.0, 6.9 Hz, 3H), 2.34 (dd, J = 13.9, 7.6 Hz, 1H), 1.76 (q, J = 6.6 Hz, 1H), 1.65 – 1.55 (m, 2H), 1.30 – 1.20 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 170.6, 160.7, 158.0, 142.4, 140.5, 136.5, 135.6, 133.0, 132.4, 132.2, 130.0, 129.6, 129.5, 129.0, 128.6, 128.4, 128.0, 125.9, 125.4, 121.6, 114.0, 73.8, 55.4, 42.9, 40.3, 38.1, 36.1, 31.4, 28.5.

**HR-MS** (ESI) m/z calcd for  $C_{35}H_{36}NO_4^+$  [M+H<sup>+</sup>]: 534.2639, found 534.2630.



*N*-(1-(4-Methoxyphenyl)-6-phenylhexan-3-yl)-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*] oxepin-1-yl)acetamide (5aq)

Following General Procedure D, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.8 mg, 0.012 mmol, 12 mol%), N-allyl-2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-1-yl)acetamide (30.7 mg, 0.1 mmol), 4-iodoanisole (35.1 mg, 0.15 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol), Mn (16.5 mg, 0.3 mmol), NaI (7.5 mg, 0.05 mmol), MeOH (0.17 mL) and IPA (0.83 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5aq** (39.1 mg, 73% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 2.5 Hz, 1H), 7.79 (dd, J = 7.7, 1.4 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.42 – 7.33 (m, 2H), 7.29 (dd, J = 7.5, 1.2 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.07 (d, J = 7.4 Hz, 1H), 7.03 – 6.98 (m, 2H), 6.97 – 6.89 (m, 3H), 6.73 – 6.67 (m, 2H), 5.16 – 4.99 (m, 3H), 3.92 (tt, J = 8.7, 4.2 Hz, 1H), 3.68 (s, 3H), 3.45 (s, 2H), 2.52 – 2.36 (m, 4H), 1.64 (ddt, J = 16.3, 8.4, 4.1 Hz, 1H), 1.52 – 1.39 (m, 3H), 1.30 – 1.15 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 170.4, 160.7, 157.9, 142.2, 140.5, 136.4, 135.6, 133.9, 133.0, 132.3, 129.6, 129.4, 129.3, 129.2, 128.5, 128.4, 128.0, 125.9, 125.4, 121.7, 113.9, 73.8, 55.4, 49.2, 43.1, 37.4, 35.7, 34.8, 31.5, 27.7.

**HR-MS** (ESI) m/z calcd for C<sub>35</sub>H<sub>36</sub>NO<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 534.2639, found 534.2629.





Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), iodobenzene (44.0  $\mu$ L, 81.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol), were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4ba** (35.3 mg, 49% yield, 12:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.54 – 7.50 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.34 – 7.28 (m, 3H), 7.28 – 7.26 (m, 1H), 7.20 (dd, *J* = 9.2, 7.1 Hz, 6H),

5.91 (t, J = 6.0 Hz, 1H), 3.58 (ddd, J = 13.6, 6.6, 5.4 Hz, 1H), 3.31 (ddd, J = 13.6, 7.0, 5.3 Hz, 1H), 2.79 (dd, J = 13.8, 6.0 Hz, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.61 – 2.55 (m, 1H), 2.12 – 2.00 (m, 1H), 1.82 – 1.68 (m, 2H), 1.52 – 1.42 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.4, 142.4, 140.7, 134.7, 131.4, 129.2, 128.8, 128.58, 128.56, 128.5, 126.9, 126.3, 125.9, 43.8, 40.5, 39.8, 36.1, 32.0, 28.6.

**HR-MS** (ESI) m/z calcd for C<sub>25</sub>H<sub>28</sub>NO<sup>+</sup> [M+H<sup>+</sup>]: 358.2165, found 358.2164.



*N*-(1,6-Diphenylhexan-3-yl)benzamide (5ba)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), iodobenzene (33.0  $\mu$ L, 61.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5ba** (61.1 mg, 86% yield, 12:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (dd, J = 8.3, 1.3 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 (dd, J = 8.2, 6.9 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.19 – 7.13 (m, 6H), 5.77 (d, J = 9.1 Hz, 1H), 4.27 (tt, J = 8.6, 4.1 Hz, 1H), 2.74 – 2.68 (m, 2H), 2.67 – 2.58 (m, 2H), 1.93 (dddd, J = 13.8, 9.1, 7.1, 4.7 Hz, 1H), 1.80 (dtd, J = 13.9, 8.8, 6.5 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.59 – 1.53 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 142.2, 142.0, 135.0, 131.5, 128.7, 128.64, 128.59, 128.49, 128.47, 126.9, 126.1, 125.9, 49.7, 37.2, 35.8, 35.0, 32.5, 27.9. HR-MS (ESI) m/z calcd for C<sub>25</sub>H<sub>28</sub>NO<sup>+</sup> [M+H<sup>+</sup>]: 358.2165, found 358.2152.



# N-(2-(4-Chlorobenzyl)-5-phenylpentyl)benzamide (4bb)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-chloro-4-iodobenzene (95.2 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4bb** (39.9 mg, 51% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.48 – 7.43 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.28 (m, 2H), 7.20 (d, *J* = 5.5 Hz, 1H), 7.18 – 7.14 (m, 3H), 7.11 (d, *J* = 6.7 Hz, 1H), 7.09 – 7.05 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.83 (t, *J* = 5.7 Hz, 1H), 3.47 – 3.36 (m, 1H), 3.21 (dd, *J* = 20.2, 5.9 Hz, 1H), 2.64 – 2.41 (m, 4H), 1.90 (p, *J* = 6.6 Hz, 1H), 1.64 (d, *J* = 6.6 Hz, 2H), 1.38 – 1.28 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.5, 142.2, 139.1, 134.6, 132.1, 131.5, 130.5, 128.8, 128.7, 128.54, 128.47, 126.8, 125.9, 43.6, 40.4, 38.9, 36.0, 31.5, 28.5.

**HR-MS** (ESI) m/z calcd for C<sub>25</sub>H<sub>27</sub>ClNO<sup>+</sup> [M+H<sup>+</sup>]: 392.1776, found 392.1774.



# *N*-(1-(4-Chlorophenyl)-6-phenylhexan-3-yl)benzamide (5bb)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-chloro-4-iodobenzene (71.4 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5bb** (56.9 mg, 73% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, J = 7.2 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.37 (dd, J = 8.3, 6.8 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.13 (m, 2H), 7.11 (dd, J = 8.6, 7.0 Hz, 3H), 7.04 (d, J = 8.3 Hz, 2H), 5.79 (d, J = 9.2 Hz, 1H), 4.19 (qt, J = 8.8, 4.8 Hz, 1H), 2.59 (ddd, J = 14.3, 9.8, 6.5 Hz, 4H), 1.90 – 1.79 (m, 1H), 1.74 – 1.57 (m, 4H), 1.54 – 1.45 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 142.1, 140.4, 134.8, 131.8, 131.6, 129.8, 128.70, 128.66, 128.6, 128.5, 126.9, 126.0, 49.5, 37.2, 35.7, 35.0, 31.9, 27.8. HR-MS (ESI) m/z calcd for C<sub>25</sub>H<sub>27</sub>ClNO<sup>+</sup> [M+H<sup>+</sup>]: 392.1776, found 392.1778.



*N*-(5-Phenyl-2-(4-(trifluoromethoxy)benzyl)pentyl)benzamide (4bc)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-4-(trifluoromethoxy)benzene (62.6  $\mu$ L, 115.2 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4bc** (43.0 mg, 49% yield, 10:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.61 – 7.54 (m, 2H), 7.51 – 7.45 (m, 1H), 7.42 – 7.35 (m, 2H), 7.29 – 7.22 (m, 1H), 7.20 – 7.15 (m, 5H), 7.14 – 7.07 (m, 3H), 5.95 (q, *J* = 6.2 Hz, 1H), 3.53 – 3.45 (m, 1H), 3.37 – 3.27 (m, 1H), 2.69 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.65 – 2.54 (m, 3H), 2.00 (p, *J* = 6.5 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.46 – 1.37 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.6, 147.8, 142.2, 139.3, 134.7, 131.6, 130.4, 128.7, 128.6, 128.5, 126.9, 126.0, 120.6 (q, *J* = 254.9 Hz), 121.1, 43.5, 40.4, 38.7, 36.0, 31.4, 28.4.

<sup>19</sup>F NMR (**376** MHz, CDCl<sub>3</sub>) δ -57.87.

**HR-MS** (ESI) m/z calcd for  $C_{26}H_{27}F_3NO_2^+$  [M+H<sup>+</sup>]: 442.1988, found 442.1990.



*N*-(6-Phenyl-1-(4-(trifluoromethoxy)phenyl)hexan-3-yl)benzamide (5bc)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-4-(trifluoromethoxy)benzene (58.0  $\mu$ L, 86.4 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5bc** (63.3 mg, 72% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.59 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17 – 7.09 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 5H), 6.96 (d, *J* = 8.3 Hz, 2H), 5.86 (d, *J* = 9.2 Hz, 1H), 4.12 (qt, *J* = 8.8, 4.7 Hz, 1H), 2.62 – 2.41 (m, 4H), 1.76 (dq, *J* = 12.0, 3.8, 3.4 Hz, 2H), 1.68 – 1.62 (m, 1H), 1.63 – 1.54 (m, 1H), 1.53 – 1.47 (m, 1H), 1.41 (dq, *J* = 14.5, 8.0, 7.6 Hz, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.4, 147.5, 142.1, 140.7, 134.8, 131.6, 129.7, 128.7, 128.5, 128.4, 126.9, 125.9, 121.1, 119.3 (q, *J* = 253.3 Hz), 49.5, 37.2, 35.7, 35.0, 31.9, 27.8.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ-57.87.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>27</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 442.1988, found 442.1986.



#### Methyl-4-(2-(benzamidomethyl)-5-phenylpentyl)benzoate (4bd)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), methyl 4-iodobenzoate (104.8 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4bd** (48.2 mg, 58% yield, 10:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.85 (d, J = 8.3 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.34 (m, 1H), 7.28 (dd, J = 8.3, 6.9 Hz, 2H), 7.20 – 7.13 (m, 5H), 7.10 – 7.01 (m, 2H), 5.93 (t, J = 6.0 Hz, 1H), 3.82 (s, 3H), 3.40 (dt, J = 13.6, 6.1 Hz, 1H), 3.22 (ddd, J = 13.7, 6.8, 5.6 Hz, 1H), 2.65 (dd, J = 13.7, 6.7 Hz, 1H), 2.60 – 2.47 (m, 3H), 1.96 (p, J = 6.6 Hz, 1H), 1.64 (dtd, J = 14.9, 8.0, 7.0, 3.2 Hz, 2H), 1.37 – 1.26 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.6, 167.1, 146.2, 142.2, 134.6, 131.5, 130.0, 129.2, 128.6, 128.54, 128.48, 128.3, 126.8, 125.9, 52.2, 43.6, 40.4, 39.5, 36.0, 31.5, 28.4. HR-MS (ESI) m/z calcd for C<sub>27</sub>H<sub>30</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 416.2220, found 416.2219.



Methyl-4-(3-benzamido-6-phenylhexyl)benzoate (5bd)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), methyl 4-iodobenzoate (78.6 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5bd** (47.6 mg, 57% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 8.3 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.44 – 7.38 (m, 1H), 7.33 (dd, J = 8.2, 6.7 Hz, 2H), 7.20 – 7.13 (m, 4H), 7.11 – 7.03 (m, 3H), 5.79 (d, J = 9.2 Hz, 1H), 4.18 (qt, J = 8.7, 4.8 Hz, 1H), 3.80 (s, 3H), 2.66 (dd, J = 8.9, 7.0 Hz, 2H), 2.60 – 2.47 (m, 2H), 1.91 – 1.80 (m, 1H), 1.77 – 1.70 (m, 1H), 1.63 (q, J = 6.7, 6.2 Hz, 2H), 1.59 – 1.53 (m, 1H), 1.52 – 1.41 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 167.2, 147.5, 142.1, 134.8, 131.5, 129.9, 128.7, 128.55, 128.49, 128.47, 128.0, 126.9, 126.0, 52.1, 49.6, 37.0, 35.7, 35.0, 32.7, 27.8. HR-MS (ESI) m/z calcd for C<sub>27</sub>H<sub>30</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 416.2220, found 416.2222.



Following General Procedure C, *N*-allylbenzamide (16.1 mg, 0.1 mmol), 2-(4-iodophenyl)acetonitrile (48.6 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 3:1) to give the product **4be** (30.2 mg, 76% yield, 7:1 rr) as a white solid.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.51 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H), 7.32 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.21 – 7.13 (m, 4H), 7.08 (dd, *J* = 8.1, 6.4 Hz, 5H), 5.85 (t, *J* = 6.0 Hz, 1H), 3.60 (s, 2H), 3.40 (dt, *J* = 13.7, 6.1 Hz, 1H), 3.23 (dt, *J* = 13.3, 6.2 Hz, 1H), 2.63 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.51 (dt, *J* = 14.5, 7.8 Hz, 3H), 1.93 (p, *J* = 6.9 Hz, 1H), 1.66 (dq, *J* = 9.6, 7.1 Hz, 2H), 1.33 (ddd, *J* = 12.2, 7.3, 2.8 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.5, 142.3, 140.6, 134.6, 131.5, 129.9, 128.6, 128.54, 128.46, 128.2, 127.8, 126.8, 125.9, 118.1, 43.5, 40.3, 39.0, 36.0, 31.5, 28.5, 23.3.

**HR-MS** (ESI) m/z calcd for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sup>+</sup> [M+H<sup>+</sup>]: 397.2274, found 397.2275.



### *N*-(1-(4-(Cyanomethyl)phenyl)-6-phenylhexan-3-yl)benzamide (5be)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 2-(4-iodophenyl)acetonitrile (72.9 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **5be** (44.7 mg, 56% yield, >20:1 rr) as a white solid

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, J = 7.0 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.43 (dd, J = 8.3, 6.8 Hz, 2H), 7.28 (dd, J = 8.6, 6.2 Hz, 2H), 7.23 – 7.13 (m, 7H), 5.91 (d, J = 9.2 Hz, 1H), 4.26 (qt, J = 8.8, 4.7 Hz, 1H), 3.68 (s, 2H), 2.74 – 2.55 (m, 4H), 1.97 – 1.88 (m, 1H), 1.83 – 1.72 (m, 3H), 1.69 – 1.63 (m, 1H), 1.60 – 1.52 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.3, 142.1, 141.9, 134.8, 131.5, 129.2, 128.7, 128.5, 128.4, 128.1, 127.5, 126.9, 125.9, 118.1, 49.5, 37.1, 35.7, 35.0, 32.2, 27.8, 23.3.

**HR-MS** (ESI) m/z calcd for  $C_{27}H_{29}N_2O^+$  [M+H<sup>+</sup>]: 397.2274, found 397.2272.





Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-(*tert*-butyl)-4-iodobenzene (70.8  $\mu$ L, 104.0 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4bf** (64.1 mg, 78% yield, 14:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.49 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.36 – 7.32 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.18 – 7.13 (m, 3H), 7.11 (d, *J* = 8.3 Hz, 2H), 5.86 (t, *J* = 5.9 Hz, 1H), 3.56 (ddd, *J* = 13.6, 6.6, 5.1 Hz, 1H), 3.26 (ddd, *J* = 13.6, 7.2, 5.1 Hz, 1H), 2.75 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.50 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.81 – 1.70 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 149.2, 142.4, 137.5, 134.7, 131.3, 128.8, 128.54, 128.51, 128.4, 126.8, 125.8, 125.6, 44.0, 40.4, 39.5, 36.1, 34.5, 32.2, 31.5, 28.6.

**HR-MS** (ESI) m/z calcd for C<sub>29</sub>H<sub>35</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 436.2611, found 436.2608.



### N-(1-(4-(tert-Butyl)phenyl)-6-phenylhexan-3-yl)benzamide (5bf)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-(tert-butyl)-4-iodobenzene (57.0  $\mu$ L, 78.0 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction.

The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5bf** (58.4 mg, 71% yield, 11:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.63 – 7.55 (m, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.23 - 7.14 (m, 4H), 7.12 - 7.05 (m, 3H), 7.03 (d, J = 8.3 Hz, 2H), 5.73 $(d, J = 9.1 \text{ Hz}, 1\text{H}), 4.20 \text{ (ddt}, J = 12.9, 8.6, 4.0 \text{ Hz}, 1\text{H}), 2.63 - 2.52 \text{ (m, 4H)}, 1.89 - 2.52 \text{ ($  $1.79 \text{ (m, 1H)}, 1.76 - 1.70 \text{ (m, 1H)}, 1.65 \text{ (d, } J = 7.3 \text{ Hz}, 1\text{H}), 1.62 - 1.55 \text{ (m, 2H)}, 1.51 \text{ (m,$ - 1.43 (m, 1H), 1.21 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 148.8, 142.3, 138.8, 131.4, 128.7, 128.6, 128.5, 128.1, 126.9, 125.9, 125.5, 49.7, 36.9, 35.8, 35.0, 34.5, 31.9, 31.5, 27.8.

**HR-MS** (ESI) m/z calcd for C<sub>29</sub>H<sub>35</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 436.2611, found 436.2609.



## *N*-(2-(3-Methoxybenzyl)-5-phenylpentyl)benzamide (4bg)

Following General Procedure C, N-allylbenzamide (32.2 mg, 0.2 mmol), μL. 1-iodo-3-methoxybenzene (48.0)93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0 µL, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product 4bg (43.3 mg, 56% yield, 8:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.45 – 7.35 (m, 3H), 7.28 (dd, J = 8.2, 6.8 Hz, 2H), 7.22 - 7.14 (m, 3H), 7.09 (dd, J = 8.5, 6.5 Hz, 3H), 6.74 - 6.60 (m, 3H), 5.83 - 5.74(m, 1H), 3.68 (s, 3H), 3.48 (ddd, J = 13.6, 6.6, 5.3 Hz, 1H), 3.20 (ddd, J = 13.6, 7.2, 5.2 Hz, 1H), 2.67 (dd, J = 13.8, 5.9 Hz, 1H), 2.54 (t, J = 7.6 Hz, 2H), 2.45 (dd, J =13.8, 8.3 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.67 (dtd, J = 15.7, 7.9, 5.3 Hz, 2H), 1.35 (ddd, *J* = 11.4, 6.5, 2.9 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 160.0, 142.4, 142.4, 134.7, 131.4, 129.8, 128.6, 128.5, 128.4, 126.9, 125.9, 121.5, 114.9, 111.6, 55.3, 43.8, 40.4, 40.0, 36.1, 32.1, 28.6.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 410.2091, found 410.2088.





Following General Procedure D, N-allylbenzamide (32.2 mg, 0.2 mmol), mmol) 1-iodo-3-methoxybenzene (36.0 μL, 70.2 mg, 0.3 and 1-bromo-3-phenylpropane (45.0 µL, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5bg** (65.6 mg, 85% yield, >20:1 rr) as a
colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.52 (m, 2H), 7.40 – 7.34 (m, 1H), 7.28 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.08 – 6.98 (m, 4H), 6.67 – 6.63 (m, 1H), 6.60 (dd, *J* = 8.5, 1.9 Hz, 2H), 5.81 (d, *J* = 9.2 Hz, 1H), 4.20 (dq, *J* = 8.8, 4.3 Hz, 1H), 3.64 (s, 3H), 2.61 – 2.44 (m, 4H), 1.86 – 1.78 (m, 1H), 1.74 – 1.65 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 2H), 1.54 (d, *J* = 6.9 Hz, 1H), 1.44 (t, *J* = 7.1 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 159.8, 143.6, 142.2, 134.9, 131.4, 129.5, 128.6, 128.5, 128.4, 126.9, 125.9, 120.8, 114.2, 111.4, 55.2, 49.7, 36.9, 35.7, 35.0, 32.6, 27.8.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 410.2091, found 410.2088.



#### *N*-(2-(3-Methylbenzyl)-5-phenylpentyl)benzamide (4bh)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-3-methylbenzene (51.0  $\mu$ L, 87.2 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4bh** (52.2 mg, 70% yield, 14:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.42 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.18 (dd, *J* = 8.9, 6.2 Hz, 2H), 7.09 (dd, *J* = 7.4, 5.0 Hz, 4H), 6.97 – 6.82 (m, 3H), 5.81 – 5.73 (m, 1H), 3.50 (ddd, *J* = 13.7, 6.7, 5.2 Hz, 1H), 3.18 (ddd, *J* = 13.4, 7.2, 5.1 Hz, 1H), 2.68 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.42 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.21 (s, 3H), 1.92 (p, *J* = 6.4 Hz, 1H), 1.67 (ddd, *J* = 21.3, 10.9, 5.2 Hz, 2H), 1.35 (dt, *J* = 9.0, 5.5 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 142.4, 140.7, 138.4, 134.7, 131.3, 129.9, 128.7, 128.5, 128.43, 128.39, 127.0, 126.8, 126.1, 125.8, 43.9, 40.4, 39.9, 36.0, 32.1, 28.6, 21.5.

HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 394.2141, found 394.2142.





Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-3-methylbenzene (38.0  $\mu$ L, 65.4 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5bh** (45.2 mg, 61% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.64 – 7.58 (m, 2H), 7.46 – 7.40 (m, 1H), 7.35 (d, J = 14.9 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.07 (m, 4H), 6.96 – 6.89 (m, 3H), 5.80 (d,

J = 9.1 Hz, 1H), 4.28 - 4.16 (m, 1H), 2.60 (ddd, J = 12.8, 8.7, 6.6 Hz, 4H), 2.24 (s, 3H), 1.92 - 1.84 (m, 1H), 1.76 (d, J = 7.8 Hz, 1H), 1.66 (d, J = 7.0 Hz, 2H), 1.60 (ddd, J = 8.5, 6.9, 5.0 Hz, 1H), 1.55 - 1.47 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 142.2, 141.9, 138.2, 134.9, 131.4, 129.3, 128.62, 128.56, 128.5, 128.4, 126.9, 126.8, 125.9, 125.4, 49.8, 37.1, 35.8, 34.9, 32.4, 27.9, 21.5.

HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NONa<sup>+</sup> [M+Na<sup>+</sup>]: 394.2141, found 394.2140.



## *N*-(6-Phenyl-1-(*o*-tolyl)hexan-3-yl)benzamide (4bi)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-2-methylbenzene (51.0  $\mu$ L, 87.2 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **4bi** (44.2 mg, 60% yield, 20:1 rr) as a white solid.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.47 – 7.41 (m, 3H), 7.37 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.19 – 7.09 (m, 7H), 5.84 (t, *J* = 5.8 Hz, 1H), 3.63 (ddd, *J* = 13.5, 7.0, 5.2 Hz, 1H), 3.20 (ddd, *J* = 13.6, 7.3, 4.8 Hz, 1H), 2.77 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.66 – 2.49 (m, 3H), 2.29 (s, 3H), 2.07 – 1.92 (m, 1H), 1.76 (dddd, *J* = 15.2, 11.5, 7.3, 2.1 Hz, 2H), 1.45 (qd, *J* = 8.0, 7.4, 5.1 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 142.4, 139.0, 136.4, 134.6, 131.4, 130.8, 130.0, 128.55, 128.50, 128.4, 126.8, 126.5, 126.3, 125.9, 44.0, 39.2, 37.7, 36.1, 32.6, 28.6, 19.7.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>30</sub>NO<sup>+</sup> [M+H<sup>+</sup>]: 372.2322, found 372.2323.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (5bi)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-2-methylbenzene (38.0  $\mu$ L, 65.4 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 12:1) to give the product **5bi** (40.0 mg, 54% yield, 13:1 rr) as a white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.60 (m, 2H), 7.46 – 7.38 (m, 1H), 7.35 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.14 – 7.07 (m, 3H), 7.06 – 6.97 (m, 4H), 5.76 (d, *J* = 9.2 Hz, 1H), 4.22 (ddq, *J* = 13.2, 8.6, 4.8 Hz, 1H), 2.66 – 2.50 (m, 4H), 2.20 (s, 3H), 1.86 – 1.77 (m, 1H), 1.71 – 1.61 (m, 4H), 1.52 – 1.43 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.3, 142.2, 140.1, 135.9, 135.0, 131.5, 130.4, 128.8, 128.7, 128.6, 128.5, 126.9, 126.24, 126.21, 126.0, 50.0, 36.0, 35.8, 35.0, 29.9, 27.9,

19.4. **HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>30</sub>NO<sup>+</sup> [M+H<sup>+</sup>]: 372.2322, found 372.2320.



#### *N*-(2-(2-Methoxybenzyl)-5-phenylpentyl)benzamide (4bj)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-2-methoxybenzene (93.6 mg, 0.4 mmol) and 1-bromo-3-phenylpropane (60.0  $\mu$ L, 79.2 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4bj** (55.1 mg, 71% yield, 8:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.57 – 7.50 (m, 2H), 7.42 – 7.36 (m, 1H), 7.35 – 7.28 (m, 2H), 7.21 – 7.15 (m, 2H), 7.14 – 7.06 (m, 4H), 7.04 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.78 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.37 (t, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.25 (t, *J* = 5.7 Hz, 2H), 2.60 (dd, *J* = 6.9, 3.1 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.84 (m, 1H), 1.75 – 1.61 (m, 2H), 1.36 (dtd, *J* = 9.1, 6.6, 2.0 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.5, 157.4, 142.6, 135.2, 131.3, 131.1, 128.9, 128.6, 128.5, 128.4, 127.6, 126.9, 125.8, 121.1, 110.9, 55.6, 42.6, 39.6, 36.1, 33.0, 32.2, 28.8.

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 410.2091, found 410.2088.



#### *N*-(6-Phenyl-1-(*o*-tolyl)hexan-3-yl)benzamide (5bj)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-2-methoxybenzene (70.2 mg, 0.3 mmol) and 1-bromo-3-phenylpropane (45.0  $\mu$ L, 59.4 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5bj** (39.6 mg, 51% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.71 – 7.64 (m, 2H), 7.46 – 7.41 (m, 1H), 7.39 – 7.34 (m, 2H), 7.23 – 7.19 (m, 2H), 7.15 – 7.04 (m, 5H), 6.85 – 6.79 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.90 (d, *J* = 9.0 Hz, 1H), 4.20 (dp, *J* = 12.6, 4.3, 3.8 Hz, 1H), 3.71 (s, 3H), 2.70 (ddd, *J* = 14.7, 9.7, 5.4 Hz, 1H), 2.59 (q, *J* = 7.4 Hz, 3H), 1.87 (ddt, *J* = 11.7, 5.9, 3.0 Hz, 1H), 1.73 – 1.64 (m, 4H), 1.57 – 1.49 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 157.4, 142.4, 135.2, 131.4, 130.4, 130.0, 128.62, 128.56, 128.4, 127.3, 126.9, 125.9, 120.7, 110.5, 55.4, 49.9, 35.9, 35.2, 34.9, 27.9, 26.9.

HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 410.2091, found 410.2089.



*N*-(5-Phenyl-2-((9-phenyl-9*H*-carbazol-3-yl)methyl)pentyl)benzamide (4bk)

Following General Procedure C, *N*-allylbenzamide (16.1 mg, 0.1 mmol), 3-iodo-*N*-phenylcarbazole (73.8 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (30.0  $\mu$ L, 39.6 mg, 0.2 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 5:1) to give the product **4bk** (36.0 mg, 69% yield, >20:1 rr) as a white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 1.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 7.20 – 7.17 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.12 – 7.04 (m, 4H), 7.04 – 7.00 (m, 3H), 6.99 – 6.94 (m, 2H), 5.63 (t, J = 5.8 Hz, 1H), 3.49 (ddd, J = 13.7, 6.6, 4.9 Hz, 1H), 3.15 (ddd, J = 13.1, 7.4, 4.9 Hz, 1H), 2.85 (dd, J = 13.8, 5.6 Hz, 1H), 2.57 (dd, J = 13.9, 8.5 Hz, 1H), 2.48 (t, J = 7.6 Hz, 2H), 1.95 (p, J = 6.7 Hz, 1H), 1.71 – 1.60 (m, 2H), 1.34 (q, J = 7.5 Hz, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.2, 142.5, 141.2, 139.7, 137.8, 134.6, 132.2, 131.2, 130.0, 128.6, 128.4, 128.3, 127.5, 127.2, 127.0, 126.7, 126.2, 125.9, 123.9, 123.1, 120.5, 120.3, 120.1, 110.1, 109.9, 44.2, 41.2, 40.3, 36.2, 32.4, 28.8.

HR-MS (ESI) m/z calcd for C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O<sup>+</sup> [M+H<sup>+</sup>]: 523.2744, found 523.2745.



#### *N*-(6-Phenyl-1-(9-phenyl-9*H*-carbazol-2-yl)hexan-3-yl)benzamide (5bk)

Following General Procedure D, *N*-allylbenzamide (16.1 mg, 0.1 mmol), 3-iodo-*N*-phenylcarbazole (55.3 mg, 0.15 mmol) and 1-bromo-3-phenylpropane (22.5  $\mu$ L, 29.7 mg, 0.15 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 7:1) to give the product **5bk** (38.6 mg, 74% yield, >20:1 rr) as a white solid.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 1.7 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.65 – 7.57 (m, 4H), 7.53 – 7.49 (m, 2H), 7.47 – 7.38 (m, 4H), 7.35 – 7.28 (m, 3H), 7.26 – 7.21 (m, 3H), 7.20 – 7.14 (m, 3H), 5.79 (d, J = 9.0 Hz, 1H), 4.34 (tt, J = 8.6, 4.0 Hz, 1H), 2.96 – 2.87 (m, 2H), 2.66 (dh, J = 21.3, 7.2 Hz, 2H), 2.09 – 2.05 (m, 1H), 1.96 – 1.88 (m, 1H), 1.80 – 1.69 (m, 3H), 1.67 – 1.62 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 142.3, 141.2, 139.6, 137.9, 135.0, 133.6, 131.4, 130.0, 128.61, 128.59, 128.5, 127.4, 127.1, 126.9, 126.7, 126.0, 125.9, 123.7, 123.3, 120.4, 119.9, 119.7, 109.9, 109.8, 49.9, 37.8, 35.8, 35.0, 32.6, 27.9.

**HR-MS** (ESI) m/z calcd for C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O<sup>+</sup> [M+H<sup>+</sup>]: 523.2744, found 523.2748.



## *N*-(2-(4-Methoxybenzyl)hexyl)benzamide (4ca)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromobutane (43.0  $\mu$ L, 54.4 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ca** (39.7 mg, 61% yield, 12:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.55 – 7.50 (m, 2H), 7.47 – 7.40 (m, 1H), 7.38 – 7.32 (m, 2H), 7.16 – 7.08 (m, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.93 (t, J = 6.0 Hz, 1H), 3.77 (s, 3H), 3.57 (ddd, J = 13.6, 6.6, 5.0 Hz, 1H), 3.25 (ddd, J = 13.6, 7.4, 5.1 Hz, 1H), 2.74 (dd, J = 13.9, 5.8 Hz, 1H), 2.50 (dd, J = 13.9, 8.4 Hz, 1H), 1.92 (tdd, J = 12.6, 6.5, 2.9 Hz, 1H), 1.39 – 1.26 (m, 6H), 0.89 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 134.8, 132.8, 131.3, 130.1, 128.5, 126.8, 114.2, 55.3, 44.0, 40.7, 39.1, 32.4, 29.1, 23.0, 14.2.

**HR-MS** (ESI) m/z calcd for C<sub>21</sub>H<sub>28</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 326.2115, found 326.2112.



*N*-(1-(4-Methoxyphenyl)heptan-3-yl)benzamide (5ca)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromobutane (32.2  $\mu$ L, 40.8 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ca** (33.6 mg, 52% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.73 – 7.65 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.36 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.84 (d, *J* = 9.1 Hz, 1H), 4.26 – 4.13 (m, 1H), 3.76 (s, 3H), 2.67 (dd, *J* = 8.7, 7.0 Hz, 2H), 1.96 – 1.86 (m, 1H), 1.85 – 1.77 (m, 1H), 1.67 – 1.60 (m, 1H), 1.54 – 1.48 (m, 1H), 1.34 (qd, *J* = 8.4, 7.5, 3.8 Hz, 4H), 0.93 – 0.82 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 158.0, 135.1, 134.1, 131.4, 129.4, 128.6, 126.9, 114.0, 55.4, 49.8, 37.3, 35.2, 31.6, 28.2, 22.8, 14.2.

**HR-MS** (ESI) m/z calcd for C<sub>21</sub>H<sub>28</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 326.2115, found 326.2113.



*N*-((2-(4-Methoxybenzyl)-5-methylhexyl)benzamide (4cb)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-methylbutane (47.8  $\mu$ L, 60.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cb** (36.5 mg, 54% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.53 – 7.49 (m, 2H), 7.49 – 7.40 (m, 1H), 7.39 – 7.30 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.89 (s, 1H), 3.77 (s, 3H), 3.62 – 3.50 (m, 1H), 3.31 – 3.16 (m, 1H), 2.75 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.50 (dd, *J* = 13.9, 8.4 Hz, 1H), 1.90 (ddt, *J* = 10.5, 7.0, 3.9 Hz, 1H), 1.52 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.38 – 1.25 (m, 4H), 0.88 (d, *J* = 3.0 Hz, 3H), 0.87 (d, *J* = 2.9 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 134.8, 132.8, 131.4, 130.1, 128.5, 126.8, 114.2, 55.4, 44.1, 41.0, 39.2, 36.1, 30.5, 28.4, 22.8, 22.7.

**HR-MS** (ESI) m/z calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 340.2271, found 340.2270.





Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-methylbutane (36.0  $\mu$ L, 45.0 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cb** (47.2 mg, 69% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.66 – 7.56 (m, 2H), 7.44 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.74 (d, *J* = 9.1 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.69 (s, 3H), 2.59 (dd, *J* = 8.7, 7.0 Hz, 2H), 1.89 – 1.81 (m, 1H), 1.75 – 1.67 (m, 1H), 1.50 – 1.39 (m, 2H), 1.25 – 1.14 (m, 3H), 0.81 (d, *J* = 2.2 Hz, 3H), 0.80 (d, *J* = 2.2 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 158.0, 135.1, 134.1, 131.4, 129.4, 128.7, 126.9, 114.0, 55.4, 50.1, 37.3, 35.1, 33.3, 31.6, 28.2, 22.8, 22.7.

HR-MS (ESI) m/z calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 340.2271, found 340.2265.





Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3,3-dimethylbutane (57.0  $\mu$ L, 65.6 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cc** (39.1 mg, 55% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 7.29 (dd, J

= 8.2, 6.8 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 5.80 – 5.72 (m, 1H), 3.70 (s, 3H), 3.53 (ddd, J = 13.6, 6.7, 4.9 Hz, 1H), 3.17 (ddd, J = 13.6, 7.5, 4.9 Hz, 1H), 2.70 (dd, J = 13.9, 5.6 Hz, 1H), 2.43 (dd, J = 13.9, 8.5 Hz, 1H), 1.86 – 1.73 (m, 1H), 1.30 – 1.17 (m, 4H), 0.80 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 134.8, 132.8, 131.4, 130.1, 128.5, 126.8, 114.2, 55.4, 44.1, 41.4, 41.0, 39.2, 30.4, 29.5, 27.5.

**HR-MS** (ESI) m/z calcd for C<sub>23</sub>H<sub>32</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 354.2428, found 354.2420.



#### *N*-(1-(4-Methoxyphenyl)-6,6-dimethylheptan-3-yl)benzamide (5cc)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3,3-dimethylbutane (43.0  $\mu$ L, 49.2 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cc** (50.4 mg, 71% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.67 – 7.57 (m, 2H), 7.45 – 7.38 (m, 1H), 7.35 – 7.30 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.83 (d, *J* = 9.1 Hz, 1H), 4.10 (dq, *J* = 7.9, 3.7 Hz, 1H), 3.68 (s, 3H), 2.58 (dd, *J* = 8.9, 6.9 Hz, 2H), 1.87 – 1.81 (m, 1H), 1.74 – 1.65 (m, 1H), 1.56 – 1.48 (m, 1H), 1.44 – 1.37 (m, 1H), 1.18 (ddd, *J* = 10.6, 5.5, 4.0 Hz, 2H), 0.79 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 157.9, 135.1, 134.1, 131.4, 129.4, 128.6, 126.9, 114.0, 55.3, 50.4, 40.0, 37.2, 31.6, 30.4, 30.2, 29.4.

**HR-MS** (ESI) m/z calcd for C<sub>23</sub>H<sub>32</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 354.2428, found 354.2426.



*N*-(6-Chloro-2-(4-methoxybenzyl)hexyl)benzamide (4cd)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-4-chlorobutane (46.0  $\mu$ L, 68.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cd** (38.7 mg, 54% yield, 8:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 – 7.51 (m, 2H), 7.45 (d, J = 7.4 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.12 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.96 (t, J = 6.0 Hz, 1H), 3.77 (d, J = 1.9 Hz, 3H), 3.61 – 3.47 (m, 3H), 3.27 (ddd, J = 13.7, 7.2, 5.2 Hz, 1H), 2.72 (dd, J = 13.8, 6.1 Hz, 1H), 2.53 (dd, J = 14.0, 8.2 Hz, 1H), 1.95 (dt, J = 11.6, 6.8 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.63 – 1.51 (m, 2H), 1.39 (dd, J = 8.8, 6.6 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 158.2, 134.7, 132.4, 131.4, 130.0, 128.5, 126.8, 114.2, 55.4, 45.0, 43.8, 40.7, 38.9, 32.8, 31.7, 24.2. HR-MS (ESI) m/z calcd for C<sub>21</sub>H<sub>27</sub>ClNO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 360.1725, found 360.1723.



#### *N*-(7-Chloro-1-(4-methoxyphenyl)heptan-3-yl)benzamide (5cd)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-4-chlorobutane (34.5  $\mu$ L, 51.0 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cd** (41.0 mg, 57% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.70 – 7.65 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.37 (m, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.87 (d, *J* = 9.2 Hz, 1H), 4.21 (td, *J* = 8.2, 3.8 Hz, 1H), 3.76 (s, 3H), 3.52 (td, *J* = 6.6, 2.1 Hz, 2H), 2.67 (dd, *J* = 8.8, 6.7 Hz, 2H), 1.95 – 1.87 (m, 1H), 1.85 – 1.75 (m, 3H), 1.66 – 1.61 (m, 1H), 1.57 – 1.49 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.0, 134.9, 133.9, 131.5, 129.4, 128.7, 126.9, 114.1, 55.4, 49.6, 45.0, 37.2, 34.7, 32.4, 31.6, 23.3.

**HR-MS** (ESI) m/z calcd for C<sub>21</sub>H<sub>27</sub>ClNO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 360.1725, found 360.1726.



*N*-(8-(1,3-Dioxoisoindolin-2-yl)-2-(4-methoxybenzyl)octyl)benzamide (4ce)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 2-(6-bromohexyl)isoindoline-1,3-dione (124.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 3:1) to give the product **4ce** (69.6 mg, 70% yield, 7:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (dd, J = 5.5, 3.0 Hz, 2H), 7.69 (dd, J = 5.4, 3.0 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.46 – 7.40 (m, 1H), 7.38 – 7.32 (m, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.98 – 5.91 (m, 1H), 3.76 (s, 3H), 3.66 (t, J = 7.3 Hz, 2H), 3.53 (ddd, J = 13.8, 6.5, 5.0 Hz, 1H), 3.25 (ddd, J = 13.7, 7.2, 5.2 Hz, 1H), 2.71 (dd, J = 13.9, 5.8 Hz, 1H), 2.49 (dd, J = 13.9, 8.3 Hz, 1H), 1.89 (d, J = 6.4 Hz, 1H), 1.77 (d, J = 5.0 Hz, 1H), 1.69 – 1.64 (m, 3H), 1.41 – 1.29 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.6, 167.3, 158.2, 134.8, 134.0, 132.7, 132.3, 131.3, 130.1, 128.5, 126.9, 123.3, 114.2, 55.3, 43.9, 40.7, 39.0, 38.0, 32.5, 29.4, 28.6, 26.8, 26.7.

**HR-MS** (ESI) m/z calcd for  $C_{31}H_{35}N_2O_4^+$  [M+H<sup>+</sup>]: 499.2591, found 499.2591.



*N*-(9-(1,3-Dioxoisoindolin-2-yl)-1-(4-methoxyphenyl)nonan-3-yl)benzamide (5ce) Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 2-(6-bromohexyl)isoindoline-1,3-dione (93.0 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 6:1) to give the product **5ce** (53.8 mg, 54% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (dd, J = 5.4, 3.0 Hz, 2H), 7.71 – 7.66 (m, 4H), 7.49 – 7.44 (m, 1H), 7.41 – 7.34 (m, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 5.93 (d, J = 9.1 Hz, 1H), 4.19 (dt, J = 7.9, 4.3 Hz, 1H), 3.75 (s, 3H), 3.64 (t, J = 7.3 Hz, 2H), 2.64 (dd, J = 8.8, 7.0 Hz, 2H), 1.87 (td, J = 8.1, 4.7 Hz, 2H), 1.82 – 1.74 (m, 1H), 1.68 – 1.61 (m, 2H), 1.52 – 1.48 (m, 1H), 1.39 – 1.29 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 167.2, 157.9, 135.0, 134.0, 133.9, 132.2, 131.4, 129.3, 128.6, 126.9, 123.2, 114.0, 55.3, 49.8, 38.0, 37.3, 35.3, 31.6, 29.2, 28.5, 26.8, 25.9.

**HR-MS** (ESI) m/z calcd for  $C_{31}H_{35}N_2O_4^+$  [M+H<sup>+</sup>]: 499.2591, found 499.2572.



#### Benzyl-10-benzamido-9-(4-methoxybenzyl)decanoate (4cf)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and benzyl 8-bromooctanoate (124.8 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cf** (42.3 mg, 42% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  7.54 – 7.50 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.34 (m, 6H), 7.33 – 7.30 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.90 (t, *J* = 5.7 Hz, 1H), 5.11 (s, 2H), 3.77 (s, 3H), 3.56 (ddd, *J* = 13.6, 6.6, 5.0 Hz, 1H), 3.25 (ddd, *J* = 13.6, 7.3, 5.1 Hz, 1H), 2.73 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.50 (dd, *J* = 13.9, 8.3 Hz, 1H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.91 (dd, *J* = 9.8, 3.7 Hz, 1H), 1.62 (q, *J* = 7.2 Hz, 2H), 1.41 – 1.33 (m, 4H), 1.33 – 1.23 (m, 6H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 173.8, 167.3, 158.2, 136.3, 134.8, 132.7, 131.4, 130.1, 128.7, 128.5, 128.3, 126.8, 114.2, 66.2, 55.4, 44.0, 40.7, 39.1, 34.4, 32.7, 29.7, 29.25, 29.17, 26.8, 25.0.

**HR-MS** (ESI) m/z calcd for C<sub>32</sub>H<sub>40</sub>NO<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 502.2952, found 502.2950.



Benzyl-9-benzamido-11-(4-methoxyphenyl)undecanoate (5cf)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and benzyl 8-bromooctanoate (93.6 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cf** (52.1 mg, 52% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.57 (m, 2H), 7.45 – 7.39 (m, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 4H), 7.24 (d, *J* = 3.1 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.74 (d, *J* = 9.1 Hz, 1H), 5.03 (s, 2H), 4.13 (tt, *J* = 8.6, 3.7 Hz, 1H), 3.69 (s, 3H), 2.59 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.75 – 1.66 (m, 1H), 1.57 – 1.48 (m, 3H), 1.47 – 1.36 (m, 1H), 1.30 – 1.25 (m, 2H), 1.22 – 1.18 (m, 6H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 173.8, 167.2, 158.0, 136.3, 135.1, 134.1, 131.4, 129.4, 128.7, 128.6, 128.3, 126.9, 114.0, 66.2, 55.4, 49.8, 37.3, 35.5, 34.4, 31.6, 29.5, 29.2, 29.1, 26.0, 25.0.

HR-MS (ESI) m/z calcd for C<sub>32</sub>H<sub>40</sub>NO<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 502.2952, found 502.2949.



#### N-(2-(4-Methoxybenzyl)-4-phenylbutyl)benzamide (4cg)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and (2-bromoethyl)benzene (55.0  $\mu$ L, 73.6 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cg** (37.8 mg, 51% yield, 5:1 rr) as a white solid.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.55 – 7.50 (m, 2H), 7.48 – 7.44 (m, 1H), 7.37 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.90 (t, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.60 (ddd, *J* = 13.6, 6.5, 5.3 Hz, 1H), 3.35 (ddd, *J* = 13.6, 6.9, 5.2 Hz, 1H), 2.86 – 2.69 (m, 3H), 2.58 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.78 – 1.65 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 158.3, 142.3, 134.7, 132.4, 131.4, 130.1, 128.54, 128.52, 126.9, 126.0, 114.2, 55.4, 43.7, 40.2, 38.9, 34.3, 33.2.

HR-MS (ESI) m/z calcd for C<sub>25</sub>H<sub>27</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 396.1934, found 396.1926.



## N-(1-(4-Methoxyphenyl)-5-phenylpentan-3-yl)benzamide (5cg)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and (2-bromoethyl)benzene (41.0  $\mu$ L, 55.2 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cg** (58.3 mg, 78% yield, >20:1 rr) as a white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 – 7.55 (m, 2H), 7.46 – 7.41 (m, 1H), 7.39 – 7.33 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 3H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.83 (d, *J* = 9.1 Hz, 1H), 4.26 (tdd, *J* = 8.5, 4.7, 3.5 Hz, 1H), 3.72 (s, 3H), 2.65 (dt, *J* = 19.4, 7.9 Hz, 4H), 1.97 – 1.87 (m, 2H), 1.80 – 1.75 (m, 1H), 1.70 – 1.61 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 158.0, 141.9, 134.9, 133.9, 131.5, 129.4, 128.6, 128.5, 126.9, 126.8, 126.1, 114.0, 55.4, 49.8, 37.3, 37.2, 32.5, 31.6.

**HR-MS** (ESI) m/z calcd for C<sub>25</sub>H<sub>28</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 374.2115, found 374.2098.



*N*-(2-(4-Methoxybenzyl)-6-methylhept-5-en-1-yl)benzamide (4ch)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 5-bromo-2-methylpent-2-ene (54.0  $\mu$ L, 64.8 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ch** (44.9 mg, 64% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.56 – 7.50 (m, 2H), 7.48 – 7.43 (m, 1H), 7.36 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.17 – 7.10 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.94 – 5.86 (m, 1H), 5.09 (ddt, *J* = 8.6, 7.1, 1.5 Hz, 1H), 3.78 (s, 3H), 3.56 (ddd, *J* = 13.5, 6.5, 5.2 Hz, 1H), 3.30 (ddd, *J* = 13.5, 7.1, 5.1 Hz, 1H), 2.76 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.51 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.10 (q, *J* = 7.7 Hz, 2H), 1.95 (p, *J* = 6.7 Hz, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.47 – 1.36 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 134.8, 132.7, 132.1, 131.4, 130.1, 128.5, 126.8, 124.3, 114.2, 55.4, 43.9, 40.3, 39.0, 32.8, 25.9, 25.5, 17.9.

**HR-MS** (ESI) m/z calcd for C<sub>23</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 352.2271, found 352.2269.



#### *N*-(1-(4-Methoxyphenyl)-7-methyloct-6-en-3-yl)benzamide (5ch)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 5-bromo-2-methylpent-2-ene (40.0  $\mu$ L, 48.6 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ch** (35.1 mg, 50% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.68 – 7.64 (m, 2H), 7.47 – 7.41 (m, 1H), 7.36 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.89 (d, *J* = 9.0 Hz, 1H), 5.08 (tt, *J* = 7.0, 1.6 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.72 (s, 3H), 2.62 (t, *J* = 7.9 Hz, 2H), 2.04 (q, *J* = 8.1 Hz, 2H), 1.89 – 1.83 (m, 1H), 1.80 – 1.74 (m, 1H), 1.65 – 1.60 (m, 4H), 1.56 – 1.49 (m, 4H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.1, 157.9, 135.1, 134.1, 132.3, 131.4, 129.4, 128.6, 126.9, 123.9, 114.0, 55.3, 49.8, 37.3, 35.3, 31.6, 25.8, 24.7, 17.8.

**HR-MS** (ESI) m/z calcd for  $C_{23}H_{30}NO_2^+$  [M+H<sup>+</sup>]: 352.271, found 352.2269.



*N*-(2-(4-Methoxybenzyl)undec-10-en-1-yl)benzamide (4ci)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 9-bromonon-1-ene (74.3  $\mu$ L, 82.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ci** (31.0 mg, 39% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.52 (d, J = 7.7 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.33 (m, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.88 (t, J = 5.8 Hz, 1H), 5.53 – 5.28 (m, 3H), 3.77 (s, 3H), 3.57 (dt, J = 11.7, 4.4 Hz, 1H), 3.25 (dt, J = 13.4, 6.4 Hz, 1H), 2.74 (dd, J = 14.1, 5.8 Hz, 1H), 2.50 (dd, J = 14.0, 8.3 Hz, 1H), 1.98 (dt, J = 24.9, 10.0 Hz, 4H), 1.71 – 1.57 (m, 2H), 1.29 (dd, J = 9.9, 6.3 Hz, 7H), 0.92 – 0.79 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 158.2, 134.8, 132.8, 131.4, 130.1, 128.5, 126.8, 124.8, 123.8, 114.2, 55.4, 44.0, 40.7, 39.1, 32.7, 29.9, 29.6, 29.2, 26.9, 18.1, 14.1. HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>36</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 394.2741, found 394.2735.



## *N*-(1-(4-Methoxyphenyl)dodec-11-en-3-yl)benzamide (5ci)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 9-bromonon-1-ene (55.7  $\mu$ L, 61.5 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was

purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ci** (42.4 mg, 54% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** )  $\delta$  7.63 – 7.57 (m, 2H), 7.43 – 7.38 (m, 1H), 7.33 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.79 (d, *J* = 9.6 Hz, 1H), 5.76 – 5.66 (m, 1H), 4.90 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.86 – 4.79 (m, 1H), 4.12 (tt, *J* = 8.6, 3.6 Hz, 1H), 3.68 (s, 3H), 2.58 (dd, *J* = 8.8, 6.9 Hz, 2H), 1.98 – 1.91 (m, 2H), 1.87 – 1.79 (m, 1H), 1.74 – 1.65 (m, 1H), 1.58 – 1.51 (m, 2H), 1.44 – 1.38 (m, 1H), 1.23 – 1.14 (m, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 157.9, 139.3, 135.0, 134.1, 131.4, 129.4, 128.6, 126.9, 114.3, 114.0, 55.3, 49.9, 37.3, 35.5, 33.9, 31.6, 29.2, 29.0, 26.0, 22.8, 14.2. HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>36</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 394.2741, found 394.2733.



#### *N*-(5-Fluoro-2-(4-methoxybenzyl)pentyl)benzamide (4cj)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-3-fluoropropane (37.0  $\mu$ L, 56.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cj** (50.0 mg, 76% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 – 7.51 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 – 7.34 (m, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.01 – 5.97 (m, 1H), 4.50 – 4.44 (m, 1H), 4.43 – 4.36 (m, 1H), 3.77 (s, 3H), 3.55 (ddd, *J* = 13.7, 6.6, 5.3 Hz, 1H), 3.30 (ddd, *J* = 13.7, 7.0, 5.3 Hz, 1H), 2.73 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.54 (dd, *J* = 13.9, 8.2 Hz, 1H), 1.99 (dt, *J* = 13.2, 6.5 Hz, 1H), 1.86 – 1.78 (m, 2H), 1.52 – 1.46 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 158.3, 134.6, 132.3, 131.5, 130.0, 128.6, 126.9, 114.2, 84.3 (d, J = 164.8 Hz), 55.4, 43.6, 40.4, 39.0, 28.2 (d, J = 4.8 Hz), 27.8 (d, J = 19.4 Hz).

**HR-MS** (ESI) m/z calcd for  $C_{20}H_{25}FNO_2^+$  [M+H<sup>+</sup>]: 330.1864, found 330.1856.





Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-3-fluoropropane (28.0  $\mu$ L, 42.0 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cj** (48.4 mg, 74% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.63 – 7.59 (m, 2H), 7.40 (dd, J = 8.3, 6.7 Hz, 1H),

7.35 – 7.26 (m, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 5.95 (d, J = 9.1 Hz, 1H), 4.44 – 4.37 (m, 1H), 4.32 (dtd, J = 9.1, 4.5, 2.6 Hz, 1H), 4.16 (tt, J = 8.9, 4.5 Hz, 1H), 3.67 (s, 3H), 2.65 – 2.54 (m, 2H), 1.86 – 1.79 (m, 1H), 1.73 – 1.63 (m, 4H), 1.57 – 1.49 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.3, 158.0, 134.8, 133.8, 131.5, 129.3, 128.6, 126.9, 114.0, 83.9 (d, *J* = 164.6 Hz), 55.3, 49.4, 37.3, 31.6, 31.3 (d, *J* = 4.3 Hz), 27.2 (d, *J* = 19.8 Hz).

<sup>19</sup>F NMR (**376** MHz, CDCl<sub>3</sub>) δ -220.7 - -213.1 (m).

**HR-MS** (ESI) m/z calcd for  $C_{20}H_{25}FNO_2^+$  [M+H<sup>+</sup>]: 330.1864, found 330.1855.



## *N*-(6,6,6-Trifluoro-2-(4-methoxybenzyl)hexyl)benzamide (4ck)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 4-bromo-1,1,1-trifluorobutane (49.0  $\mu$ L, 76.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4ck** (52.3mg, 69% yield, 4:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.56 – 7.50 (m, 2H), 7.48 – 7.45 (m, 1H), 7.40 – 7.33 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.95 (t, *J* = 6.1 Hz, 1H), 3.78 (s, 3H), 3.56 (ddd, *J* = 13.7, 6.7, 5.1 Hz, 1H), 3.28 (ddd, *J* = 13.7, 7.2, 5.3 Hz, 1H), 2.72 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.54 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.11 – 2.02 (m, 2H), 2.00 – 1.90 (m, 1H), 1.68 (q, *J* = 7.5 Hz, 2H), 1.49 – 1.38 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 158.4, 134.6, 132.1, 131.5, 130.0, 128.6, 127.2 (q, *J* = 283.3 Hz), 126.9, 114.3, 55.4, 43.6, 40.6, 38.8, 34.0 (q, *J* = 28.5 Hz), 31.6, 19.5 (q, *J* = 3.1 Hz).

<sup>19</sup>**F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -63.19 – -66.95 (m)

**HR-MS** (ESI) m/z calcd for  $C_{21}H_{25}F_3NO_2^+$  [M+H<sup>+</sup>]: 380.1832, found 380.1831.



#### *N*-(1-(4-Methoxyphenyl)heptan-3-yl)benzamide (5ck)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 4-bromo-1,1,1-trifluorobutane (37.0  $\mu$ L, 57.0 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5ck** (41.1 mg, 54% yield, >20:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.74 – 7.67 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.40 (m, 2H), 7.12 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.09 (d, J = 9.1 Hz, 1H),

4.23 (tt, *J* = 8.7, 4.1 Hz, 1H), 3.78 (s, 3H), 2.69 (dt, *J* = 10.1, 4.7 Hz, 2H), 2.20 – 2.08 (m, 2H), 1.97 – 1.81 (m, 2H), 1.72 – 1.60 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 158.1, 134.7, 133.6, 131.6, 129.4, 128.7, 126.9, 125.8 (q, *J* = 276.2 Hz), 114.1, 55.4, 49.3, 37.1, 34.6, 33.5 (d, *J* = 28.5 Hz), 31.6, 18.7 (d, *J* = 3.0 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -64.61 – -68.65 (m)

**HR-MS** (ESI) m/z calcd for C<sub>21</sub>H<sub>25</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 380.1832, found 380.1830.



#### *N*-(6-Methoxy-2-(4-methoxybenzyl)hexyl)benzamide (4cl)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 1-bromo-4-methoxybutane (51.0  $\mu$ L, 66.4 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cl** (49.0 mg, 69% yield, 5:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.50 – 7.44 (m, 2H), 7.41 – 7.34 (m, 1H), 7.32 – 7.26 (m, 2H), 7.06 – 7.00 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.90 (s, 1H), 3.69 (s, 3H), 3.48 (dt, *J* = 12.2, 6.0 Hz, 1H), 3.29 (t, *J* = 6.2 Hz, 2H), 3.23 (s, 3H), 3.19 – 3.14 (m, 1H), 2.69 – 2.55 (m, 1H), 2.49 – 2.41 (m, 1H), 1.89 – 1.75 (m, 1H), 1.53 – 1.47 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.28 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 134.7, 132.6, 131.4, 130.1, 128.5, 126.9, 114.2, 72.7, 58.7, 55.3, 43.8, 40.7, 38.9, 32.3, 29.9, 23.5.

HR-MS (ESI) m/z calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 356.2220, found 356.2218.



#### *N*-(7-Methoxy-1-(4-methoxyphenyl)heptan-3-yl)benzamide (5cl)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 1-bromo-4-methoxybutane (38.0  $\mu$ L, 49.8 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cl** (43.2 mg, 61% yield, 20:1 rr) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 – 7.67 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.97 (d, *J* = 9.0 Hz, 1H), 4.25 – 4.17 (m, 1H), 3.75 (s, 3H), 3.35 (td, *J* = 6.4, 1.6 Hz, 2H), 3.30 (s, 3H), 2.66 (dd, *J* = 8.7, 7.0 Hz, 2H), 1.96 – 1.87 (m, 1H), 1.85 – 1.75 (m, 1H), 1.65 – 1.52 (m, 4H), 1.49 – 1.38 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 157.9, 135.0, 134.0, 131.4, 129.3, 128.6, 126.9, 114.0, 72.7, 58.6, 55.3, 49.8, 37.2, 35.2, 31.6, 29.6, 22.7.

**HR-MS** (ESI) m/z calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 356.2220, found 356.2217.



*N*-(2-(4-Methoxybenzyl)-8-oxo-8-phenyloctyl)benzamide (4cm)

Following General Procedure C, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (93.6 mg, 0.4 mmol) and 6-bromo-1-phenylbexan-1-one (102.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product **4cm** (60.2 mg, 68% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.00 – 7.92 (m, 2H), 7.58 – 7.49 (m, 3H), 7.49 – 7.42 (m, 3H), 7.36 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.95 – 5.87 (m, 1H), 3.77 (s, 3H), 3.57 (ddd, *J* = 13.6, 6.6, 5.1 Hz, 1H), 3.27 (ddd, *J* = 13.6, 7.2, 5.1 Hz, 1H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.73 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.51 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.94 (p, *J* = 6.5 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.50 – 1.43 (m, 2H), 1.41 – 1.37 (m, 3H), 1.31 – 1.23 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.6, 167.3, 158.2, 137.2, 134.8, 133.1, 132.7, 131.4, 130.1, 128.7, 128.5, 128.2, 126.9, 114.2, 55.4, 43.9, 40.7, 39.1, 38.6, 32.5, 29.6, 26.8, 24.2.

**HR-MS** (ESI) m/z calcd for  $C_{29}H_{34}NO_3^+$  [M+H<sup>+</sup>]: 444.2533, found 44.2532.





Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 4-iodoanisole (70.2 mg, 0.3 mmol) and 6-bromo-1-phenylhexan-1-one (76.5 mg, 0.3 mmol), Mn (22.0 mg, 0.4 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cm** (51.8 mg, 58% yield, 6:1 rr) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.96 – 7.88 (m, 2H), 7.72 – 7.65 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.36 (m, 5H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.94 (d, *J* = 9.2 Hz, 1H), 4.21 (dt, *J* = 9.3, 4.6 Hz, 1H), 3.75 (s, 3H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.93 – 1.86 (m, 1H), 1.83 – 1.78 (m, 1H), 1.72 (t, *J* = 7.0 Hz, 2H), 1.67 – 1.58 (m, 2H), 1.49 – 1.36 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.6, 167.2, 157.9, 137.1, 135.0, 134.0, 133.0, 131.4, 129.4, 128.7, 128.6, 128.1, 126.9, 114.0, 55.3, 49.7, 38.5, 37.3, 35.3, 31.6, 29.3, 25.9, 24.2.

**HR-MS** (ESI) m/z calcd for C<sub>29</sub>H<sub>34</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 444.2533, found 444.2433.



*N*-(3-(4-Methoxyphenyl)-2-(tetrahydro-2*H*-pyran-4-yl)propyl)benzamide (4cn) Following General Procedure C, *N*-allylbenzamide (1a, 32.2 mg, 0.2 mmol), 1-(*tert*-butyl)-4-iodobenzene (2g, 104.0 mg, 0.4 mmol) and 4-iodotetrahydro-2*H*-pyran (3o, 63.6 mg, 0.3 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 4:1) to give the product 4cn (41.7 mg, 55% yield, 10:1 rr) as a white solid.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.42 (d, *J* = 7.3 Hz, 3H), 7.35 – 7.31 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.73 (t, *J* = 6.0 Hz, 1H), 4.05 – 3.98 (m, 2H), 3.74 (ddd, *J* = 13.7, 6.9, 4.3 Hz, 1H), 3.38 (td, *J* = 11.6, 2.1 Hz, 2H), 3.25 – 3.18 (m, 1H), 2.93 – 2.88 (m, 1H), 2.46 (dd, *J* = 13.8, 10.0 Hz, 1H), 1.86 (ddd, *J* = 9.6, 7.7, 4.4 Hz, 1H), 1.71 – 1.65 (m, 3H), 1.60 (qd, *J* = 12.1, 4.5 Hz, 2H), 1.30 (s, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.0, 149.4, 137.8, 134.5, 131.3, 128.7, 128.5, 126.7, 125.9, 68.5, 68.4, 45.9, 42.0, 38.0, 36.6, 34.5, 31.5, 30.3, 29.8.

HR-MS (ESI) m/z calcd for C<sub>25</sub>H<sub>34</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 380.2584, found 380.2576.



*N*-(1-(Tetrahydro-2*H*-pyran-4-yl)-3-(4-(trifluoromethyl)phenyl)propyl)benzamid e (5cn)

Following General Procedure D, *N*-allylbenzamide (32.2 mg, 0.2 mmol), 1-iodo-4-(trifluoromethyl)benzene (**2n**, 108.8 mg, 0.4 mmol), 4-iodotetrahydro-2*H*-pyran (34.5  $\mu$ L, 63.6 mg, 0.3 mmol), NaBr (82.4 mg, 0.8 mmol), IPA (1.65 mL) and 3-methyl-1-butanol (0.35 mL) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5cn** (30.4 mg, 39% yield, >20:1 rr) as a white solid.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  7.75 – 7.65 (m, 2H), 7.53 – 7.49 (m, 3H), 7.44 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.80 (d, *J* = 9.7 Hz, 1H), 4.16 (tdd, *J* = 9.7, 6.0, 3.5 Hz, 1H), 4.05 – 3.96 (m, 2H), 3.36 (tdd, *J* = 11.8, 3.8, 2.3 Hz, 2H), 2.82 – 2.72 (m, 2H), 2.06 – 1.94 (m, 1H), 1.85 – 1.72 (m, 2H), 1.68 – 1.61 (m, 2H), 1.52 – 1.40 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 145.9, 134.6, 131.8, 128.84, 128.81, 127.8 (q, J = 262.9 Hz), 126.9, 125.6 (q, J = 3.7 Hz), 68.0, 67.9, 53.5, 40.2, 33.9, 32.7, 29.9, 28.6.

<sup>19</sup>F NMR (**376** MHz, CDCl<sub>3</sub>) δ -62.3.

## **VI.** Mechanistic Experiments

6.1 Scale-up reactions of three-component arylalkylations of allylic amines



In a nitrogen-filled glovebox, NiBr<sub>2</sub>·dme (62.0 mg, 0.2 mmol, 10 mol%), L1 (116.0 mg, 0.24 mmol, 12 mol%), 4-iodoanisole 2a (936.1 mg, 4.0 mmol, 2.0 equiv), Mn (386.0 mg, 7.0 mmol, 3.5 equiv), NaI (750.0 mg, 5.0 mmol, 2.5 equiv) and DMA (20.0 mL) were added to a 100-mL vial equipped with a stirring bar. Then, 1a (322.0 mg, 2.0 mmol, 1.0 equiv) and 1-bromo-3-phenylpropane 3a (792.0 mg, 4.0 mmol, 2.0 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford 4aa (light yellow solid, 656.0 mg, 84% yield, 9:1 rr).



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (68.0 mg, 0.2 mmol, 10 mol%), **L6** (116.0 mg, 0.24 mmol, 12 mol%), 4-iodoanisole **2a** (702.1 mg, 3.0 mmol, 1.5 equiv), Mn (330.0 mg, 6.0 mmol, 3.0 equiv), NaI (150.0 mg, 1.0 mmol, 0.5 equiv), IPA (16.5 mL) and MeOH (3.5 mL) were added to a 100-mL vial equipped with a stirring bar. Then, **1a** (322.0 mg, 2.0 mmol, 1.0 equiv), and 1-bromo-3-phenylpropane **3a** (594.0 mg, 3.0 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **5aa** (light yellow solid, 606.2 mg, 78% yield, 10:1 rr).

#### 6.2 Intermolecular cross-over reaction



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.8 mg, 0.02 mmol, 10 mol%), **L6** (11.6 mg, 0.024 mmol, 12 mol%), 4-iodoanisole **2a** (70.2 mg, 0.3 mmol, 1.5 equiv), Mn (33.0 mg, 0.6 mmol, 3.0 equiv), NaI (15.0 mg, 0.1 mmol, 0.5 equiv), IPA (1.65 mL) and MeOH (0.35 mL) were added to a 10-mL vial equipped with a stirring bar. Then, **1a** (16.1 mg, 0.1 mmol, 0.5 equiv), **1k'** (12.5 mg, 0.1 mmol, 0.5 equiv), and 1-bromo-3-phenylpropane **3a** (59.4 mg, 0.3 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **5aa** (light yellow solid, 29.4 mg, 38% yield, >20:1 rr).

**6.3 Radical clock reactions** 



In a nitrogen-filled glovebox, NiBr<sub>2</sub>·dme (6.2 mg, 0.02 mmol, 10 mol%), L1 (11.6 mg, 0.024 mmol, 12 mol%), 4-iodoanisole 2a (93.6 mg, 0.40 mmol, 2.0 equiv), Mn (38.6 mg, 0.70 mmol, 3.5 equiv), NaI (75.0 mg, 0.50 mmol, 2.5 equiv) and DMA (2.0 mL) were added to a 10-mL vial equipped with a stirring bar. Then, 1a (32.2 mg, 0.20 mmol, 1.0 equiv), and 1-(bromomethyl)cyclopropane 3 (39.0  $\mu$ L, 54.0 mg, 0.40 mmol, 2.0 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford 6 (32.2 mg, 50% yield, 12:1 rr) as a colorless oil.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (6) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.47 - 7.41 (m, 1H),

7.39 – 7.31 (m, 2H), 7.12 (d, J = 8.6 Hz, 2H), 6.87 – 6.77 (m, 2H), 5.95 (t, J = 5.7 Hz, 1H), 5.79 (ddt, J = 16.9, 10.3, 6.6 Hz, 1H), 5.04 (dd, J = 17.1, 1.8 Hz, 1H), 4.97 (dd, J = 10.3, 1.8 Hz, 1H), 3.77 (s, 3H), 3.56 (ddd, J = 13.6, 6.5, 5.1 Hz, 1H), 3.28 (ddd, J = 13.6, 7.2, 5.2 Hz, 1H), 2.75 (dd, J = 13.9, 5.8 Hz, 1H), 2.51 (dd, J = 13.9, 8.4 Hz, 1H), 2.23 – 2.12 (m, 2H), 2.03 – 1.91 (m, 1H), 1.53 – 1.41 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 138.5, 134.7, 132.5, 131.4, 130.1, 128.5, 126.8, 115.0, 114.2, 55.3, 43.8, 40.1, 38.9, 31.7, 31.1.

**HR-MS** (ESI) m/z calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 324.1958, found 324.1957.



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.8 mg, 0.02 mmol, 10 mol%), **L6** (11.6 mg, 0.024 mmol, 12 mol%), 4-iodoanisole **2** (70.2 mg, 0.30 mmol, 1.5 equiv), Mn (33.0 mg, 0.60 mmol, 3.0 equiv), NaI (15.0 mg, 0.10 mmol, 0.5 equiv), IPA (1.65 mL) and MeOH (0.35 mL) were added to a 10-mL vial equipped with a stirring bar. Then, **1a** (32.2 mg, 0.20 mmol, 1.0 equiv), and 1-(bromomethyl)cyclopropane **3** (29.0  $\mu$ L, 40.5 mg, 0.30 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **7** (42.1 mg, 65% yield, 4:1 rr) as a colorless oil.



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (7) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.74 – 7.64 (m, 2H), 7.52 – 7.40 (m, 3H), 7.11 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.83 (dtd, J = 13.4, 10.2, 6.6 Hz, 2H), 5.03 (dd, J = 17.1, 1.7 Hz, 1H), 4.97 (dd, J = 10.2, 1.7 Hz, 1H), 4.26 (ddt, J = 12.9, 8.5, 4.3 Hz, 1H), 3.77 (s, 3H), 2.67 (dd, J = 8.7, 7.0 Hz, 2H), 2.16 (dddd, J = 7.7, 6.4, 5.2, 1.4 Hz, 2H), 1.96 – 1.89 (m, 1H), 1.82 – 1.72 (m, 1H), 1.69 – 1.59 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.2, 158.0, 138.2, 135.0, 134.0, 131.5, 129.4, 128.7, 126.9, 115.2, 114.1, 55.4, 49.6, 37.3, 34.7, 31.6, 30.4. HR-MS (ESI) m/z calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 324.1958, found 324.1955.

6.4 Deuterium-labeling experiments



In a nitrogen-filled glovebox, NiBr<sub>2</sub>-dme (3.1 mg, 0.02 mmol, 10 mol%), **L1** (5.9 mg, 0.012 mmol, 12 mol%), 4-iodoanisole **2a** (46.8 mg, 0.20 mmol, 2.0 equiv), Mn (19.3 mg, 0.35 mmol, 3.5 equiv), NaI (37.5 mg, 0.25 mmol, 2.5 equiv) and DMA (1.0 mL) were added to a 10-mL vial equipped with a stirring bar. Then, **1a** (16.1 mg, 0.10 mmol, 1.0 equiv), and alkyl bromide **3a'** (40.0 mg, 0.20 mmol, 2.0 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **8** as colorless oil (24.4 mg, 63% yield, 10:1 rr, 160% D).



## *N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (8)

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 – 7.48 (m, 2H), 7.45 (d, J = 7.3 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 7.10 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.81 (d, J = 6.0 Hz, 1H), 3.78 (s, 3H), 3.55 (dt, J = 13.7, 5.9 Hz, 1H), 3.26 (ddd, J = 13.1, 7.1, 5.2 Hz, 1H), 2.72 (dd, J = 13.9, 5.8 Hz, 1H), 2.60 (s, 2H), 2.50 (dd, J = 13.9, 8.3 Hz, 1H), 1.96 (p, J = 6.4 Hz, 1H), 1.80 – 1.71 (m, 0.4H), 1.40 (d, J = 6.6 Hz, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.3, 158.2, 142.4, 134.8, 132.6, 131.4, 130.1, 128.6, 128.53, 128.45, 126.9, 125.9, 114.2, 55.4, 43.8, 40.6, 39.0, 35.9, 31.8, 28.2 – 27.5 (m).

**HR-MS** (ESI) m/z calcd for C<sub>26</sub>H<sub>27</sub>D<sub>2</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 421.2212, found 412.2213.



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.9 mg, 0.012 mmol, 12 mol%), 4-iodoanisole **2a** (35.1 mg, 0.15 mmol, 1.5 equiv), Mn (16.5 mg, 0.30 mmol, 3.0 equiv), NaI (7.5 mg, 0.05 mmol, 0.5 equiv), IPA (0.83 mL) and MeOH (0.17 mL) were added to a 10-mL vial equipped with a stirring bar. Then,

**1a** (16.1 mg, 0.10 mmol, 1.0 equiv), and alkyl bromide **3a'** (30.0 mg, 0.30 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **9** (colorless oil, 22.8 mg, 59% yield, >20:1 rr, 160% D).



*N*-(2-(4-Methoxybenzyl)-5-phenylpentyl)-4-(trifluoromethyl)benzamide (9) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 – 7.64 (m, 2H), 7.51 – 7.46 (m, 1H), 7.41 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 7.10 – 7.06 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.77 (d, *J* = 9.2 Hz, 1H), 4.30 – 4.23 (m, 1H), 3.76 (s, 3H), 2.69 – 2.56 (m, 4H), 1.90 (dddd, *J* = 13.5, 8.8, 7.3, 4.6 Hz, 1H), 1.77 (dtd, *J* = 13.7, 8.6, 6.5 Hz, 1H), 1.72 – 1.69 (m, 0.4H), 1.67 – 1.60 (m, 1H), 1.54 (dd, *J* = 13.8, 8.2 Hz, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 158.0, 142.2, 135.0, 134.0, 131.5, 129.4, 128.7, 128.6, 128.5, 126.9, 125.9, 114.1, 55.4, 49.6, 37.3, 35.6, 34.8, 31.6, 28.0 – 26.7 (m). HR-MS (ESI) m/z calcd for C<sub>26</sub>H<sub>27</sub>D<sub>2</sub>NO<sub>2</sub>Na<sup>+</sup> [M+Na<sup>+</sup>]: 421.2212, found 412.2214. **6.5 Reaction with** *E*-alkene or *Z*-alkenes:



In a nitrogen-filled glovebox, NiBr<sub>2</sub>-dme (3.1 mg, 0.02 mmol, 10 mol%), **L8** (4.3 mg, 0.012 mmol, 12 mol%), 4-iodotoluene **2b** (43.6 mg, 0.20 mmol, 2.0 equiv), Mn (19.3 mg, 0.35 mmol, 3.5 equiv), NaI (37.5 mg, 0.25 mmol, 2.5 equiv) and DMA (1.0 mL) were added to a 10-mL vial equipped with a stirring bar. Then, *E*-10 (20.3 mg, 0.10 mmol, 1.0 equiv), and 1-bromo-3-phenylpropane **3a** (30.0  $\mu$ L, 39.6 mg, 0.20 mmol, 2.0 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **4ao'** as colorless oil (5.0 mg, 12% yield, 8:1 rr, >20:1 dr).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.42 (m, 3H), 7.39 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 5H), 7.07 (d, J = 8.1 Hz, 2H), 5.63 (s, 1H), 3.62 – 3.53 (m, 1H), 3.43 (dt, J = 13.8, 5.2 Hz, 1H), 2.69 (dt, J = 10.4, 5.2 Hz, 1H), 2.56 (h, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.91 (dt, J = 9.5, 5.1 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 2.69 (dt, J = 10.4, 5.2 Hz, 1H), 2.56 (h, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.91 (dt, J = 9.5, 5.1 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 5.2 Hz, 1H), 1.77 – 1.63 (m, 5H), 1.47 (tt, J = 10.4, 1.47 (tt, J = 10.4

10.3, 5.2 Hz, 1H), 1.18 – 1.06 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 142.4, 140.5, 136.0, 134.8, 131.3, 129.4, 128.6, 128.5, 128.4, 126.9, 125.8, 60.5, 47.6, 43.9, 41.2, 36.1, 34.0, 28.9, 28.4, 21.09, 14.3. HR-MS (ESI) m/z calcd for C<sub>29</sub>H<sub>36</sub>NO<sub>2</sub><sup>+</sup> [M+H<sup>+</sup>]: 414.2791, found 414.2784.



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.9 mg, 0.012 mmol, 12 mol%), methyl 4-iodo-benzoate (**2f**, 52.4 mg, 0.20 mmol, 2.0 equiv), Mn (16.5 mg, 0.30 mmol, 3.0 equiv), NaI (7.5 mg, 0.05 mmol, 0.5 equiv), IPA (0.83 mL) and MeOH (0.17 mL) were added to a 10-mL vial equipped with a stirring bar. Then, **Z-10** (20.3 mg, 0.10 mmol, 1.0 equiv), and 1-bromo-3-phenylpropane **3a** (22.5  $\mu$ L, 29.7 mg, 0.30 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and purified by flash chromatography to afford **10** (white solid, 23.8 mg, 52% yield, >20:1 rr, >20:1 dr).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 8.3 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.33 (dd, J = 8.1, 6.8 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.20 – 7.11 (m, 5H), 5.48 (d, J = 9.0 Hz, 1H), 4.16 (ddt, J = 12.1, 7.5, 3.9 Hz, 1H), 3.87 (s, 3H), 2.74 – 2.66 (m, 1H), 2.59 (dd, J = 9.3, 7.0 Hz, 2H), 1.92 – 1.79 (m, 2H), 1.70 – 1.62 (m, 4H), 1.53 – 1.40 (m, 2H), 1.09 (dtd, J = 15.4, 9.0, 4.3 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 166.9, 151.5, 142.2, 134.7, 131.4, 130.1, 128.6, 128.52, 128.48, 128.2, 127.6, 126.8, 126.0, 52.1, 49.0, 43.6, 42.3, 39.5, 35.8, 35.3, 27.6, 20.5, 14.1.

**HR-MS** (ESI) m/z calcd for C<sub>30</sub>H<sub>36</sub>NO<sub>3</sub><sup>+</sup> [M+H<sup>+</sup>]: 458.2690, found 458.2681.



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.4 mg, 0.01 mmol, 10 mol%), **L6** (5.9 mg, 0.012 mmol, 12 mol%), methyl 4-iodo-benzoate **2f** (52.4 mg, 0.20 mmol, 2.0 equiv), Mn (16.5 mg, 0.30 mmol, 3.0 equiv), NaI (7.5 mg, 0.05 mmol, 0.5 equiv), IPA (0.83 mL) and MeOH (0.17 mL) were added to a 10-mL vial equipped with a stirring bar. Then, *E*-10 (20.3 mg, 0.10 mmol, 1.0 equiv), and 1-bromo-3-phenylpropane **3a** (29.7 mg, 0.30 mmol, 1.5 equiv) were added. The reaction mixture was transferred out of the glovebox and stirred at 50 °C for 18 h. The mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried with anhydrous

Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under vacuum. Conversion of *E*-10 was determined to be 69% based on the <sup>1</sup>H NMR of the crude mixture using mesitylene as internal standard. Purification by flash chromatography afforded 11 (white solid, 7.8 mg, 17% yield, >20:1 rr, >20:1 dr).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 8.3 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.36 (m, 4H), 7.30 (d, J = 2.9 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.11 – 7.08 (m, 2H), 5.56 (d, J = 8.9 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.90 (s, 3H), 2.73 (td, J = 11.9, 11.3, 7.7 Hz, 1H), 2.60 – 2.48 (m, 2H), 2.03 (q, J = 7.0 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.65 – 1.59 (m, 2H), 1.53 – 1.47 (m, 2H), 1.41 (q, J = 7.4 Hz, 1H), 1.16 – 1.03 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.2, 166.8, 151.1, 142.2, 134.9, 134.3, 131.5, 130.1, 128.63, 128.58, 128.4, 128.0, 126.8, 125.9, 52.1, 48.2, 42.5, 42.3, 39.4, 35.6, 34.9, 27.8, 20.7, 14.1.

**HR-MS** (ESI) m/z calcd for  $C_{30}H_{36}NO_3^+$  [M+H<sup>+</sup>]: 458.2690, found 458.2681. **6.5 Unsuccessful substrates** 





*N*-(1-(Benzo[d][1,3]dioxol-5-yl)-6-phenylhexan-3-yl)benzamide (5bl)

Following General Procedure D, *N*-allylbenzamide (16.1 mg, 0.1 mmol), 1-iodo-3,4-methylenedioxybenzene (19.5  $\mu$ L, 37.2 mg, 0.15 mmol) and 1-bromo-3-phenylpropane (23.0  $\mu$ L, 29.7 mg, 0.15 mmol) were used for the reaction. The crude mixture was purified by flash chromatography on silica gel (eluted with hexanes/EtOAc = 8:1) to give the product **5bl** (22.6 mg, 56% yield, 20:1 rr) as a white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 – 7.65 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 – 7.11 (m, 3H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.87 (dd, *J* = 12.0, 1.5 Hz, 2H), 5.83 (d, *J* = 9.1 Hz, 1H), 4.24 (qt, *J* = 8.8, 4.8 Hz, 1H), 2.68 – 2.54 (m, 4H), 1.91 – 1.83 (m, 1H), 1.76 – 1.68 (m, 3H), 1.68 – 1.61 (m, 1H), 1.57 – 1.49 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.2, 147.8, 145.8, 142.2, 135.8, 134.9, 131.5, 128.65, 128.56, 128.5, 126.9, 125.9, 121.2, 108.9, 108.3, 100.9, 49.6, 37.4, 35.8, 35.0, 32.3, 27.8.

**HR-MS** (ESI) m/z calcd for  $C_{26}H_{28}NO_3^+$  [M+H<sup>+</sup>]: 402.2064, found 402.2062. **6.6 Kinetic analysis of the reaction** 



added internal standard: 0.2 mmol n-dedocane

In a nitrogen-filled glovebox, NiBr<sub>2</sub>·dme, L1, 4-iodoanisole 2a, Mn, NaI (75.0 mg, 0.5 mmol, 2.5 equiv) and DMA (0.1 M) were added to a 10-mL vial equipped with a stirring bar. Then, 1a, 1-bromo-3-phenylpropane 3a and internal standard (0.2 mmol *n*-dedocane) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature. The aliquot (20.0  $\mu$ L) of the reaction mixture were taken each time, and immediately placed to H<sub>2</sub>O (200  $\mu$ L) to quench. The composition of mixture was analyzed by GC.

The rate on the concentration of NiBr<sub>2</sub>·dme&L1



added internal standard: 0.2 mmol n-dedocane



Figure S1. Rate on the concentration of NiBr<sub>2</sub>·dme & L1 from the reaction of 1a (0.10 M), 2a (0.20 M), 3a (0.20 M), Mn (0.35 M), NaI (0.25 M) with 0.006 M, 0.01 M, 0.014 M, 0.018 M of NiBr<sub>2</sub>·dme & L1.

#### The rate dependence on the concentration of Mn





Figure S2. Rate on the concentration of Mn from the reaction of **1a** (0.10 M), **2a** (0.20 M), **3a** (0.20 M), NiBr<sub>2</sub>·dme (0.01 M), **L1** (0.012 M), NaI (0.25 M) with 0.2 M, 0.25 M, 0.30 M, 0.35 M of Mn.







Figure S3. Rate on the concentration of **1a** from the reaction of **2a** (0.20 M), **3a** (0.20 M), NiBr<sub>2</sub>·dme (0.01 M), **L1** (0.012 M), Mn (0.36 M), NaI (0.25 M) with 0.075 M, 0.10 M, 0.12 M, 0.14 M of **1a**.

The rate dependence on the concentration of 2a



Figure S4. Rate on the concentration of **2a** from the reaction of **1a** (0.10 M), **3a** (0.20 M), NiBr<sub>2</sub>·dme (0.01 M), **L1** (0.012 M), Mn (0.35 M), NaI (0.25 M) with 0.10 M, 0.14 M, 0.18 M of **2a**.

#### The rate dependence on the concentration of 3a





Figure S5. Rate on the concentration of **3a** from the reaction of **1a** (0.10 M), **2a** (0.20 M), NiBr<sub>2</sub>·dme (0.01 M), **L1** (0.012 M), Mn (0.35 M), NaI (0.25 M) with 0.10 M, 0.14 M, 0.18 M, 0.20 M of **3a**.



In a nitrogen-filled glovebox, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, **L6**, 4-iodoanisole **2a**, Mn, NaI (15.0 mg, 0.1 mmol, 0.5 equiv) and IPA/MeOH (0.1 M, 5/1) were added to a 10-mL vial equipped with a stirring bar. Then, **1a**, 1-bromo-3-phenylpropane **3a** and internal standard (0.2 mmol *n*-dodecane) were added. The reaction mixture was transferred out of the glovebox and stirred at room temperature. The aliquot (20.0  $\mu$ L) of the reaction mixture were taken each time, and immediately placed to H<sub>2</sub>O (200  $\mu$ L) to quench. The composition of mixture was analyzed by GC.

The rate dependence on the concentration of Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O&L6





Figure S6. Rate on the concentration of Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O & **L6** from the reaction of **1a** (0.10 M), **2a** (0.15 M), **3a** (0.15 M), Mn (0.35 M), NaI (0.25 M) with 0.06 M, 0.01 M, 0.014 M, 0.018 M of Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O & **L6**.

#### The rate dependence on the concentration of Mn





Figure S7. Rate on the concentration of Mn from the reaction of **1a** (0.10 M), **2a** (0.15 M), **3a** (0.15 M), Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.01 M), **L6** (0.012 M), NaI (0.05 M) with 0.15 M, 0.20 M, 0.25 M, 0.30 M of Mn.







Figure S8. Rate on the concentration of **1a** from the reaction of **2a** (0.15 M), **3a** (0.15 M), Ni(BF<sub>4</sub>)<sub>2</sub>· $^{6}$ H<sub>2</sub>O (0.01 M), **L6** (0.012 M), NaI (0.05 M) with 0.075 M, 0.10 M, 0.12 M, 0.14 M of **1a**.

The rate dependence on the concentration of 2a



Figure S9. Rate on the concentration of **2a** from the reaction of **1a** (0.10 M), **3a** (0.15 M), Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.01 M), **L6** (0.012 M), NaI (0.05 M) with 0.10 M, 0.12 M, 0.14 M, 0.15 M of **2a**.

#### The rate dependence on the concentration of 3a



Figure S10. Rate on the concentration of **3a** from the reaction of **1a** (0.10 M), **2a** (0.15 M), Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.01 M), **L6** (0.012 M), NaI (0.05 M) with 0.08 M, 0.10 M, 0.13 M, 0.15 M of **3a**.

## VII. X-Ray Diffraction Data of 4af and 5be

X-Ray Diffraction Data of 4af (CCDC 2361506)



# Table S14 Crystal data and structure refinement for 4af (MH2023112301\_0m).

Identification code	MH2023112301_0m
Empirical formula	$C_{27}H_{31}NO_2$
Formula weight	401.53
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	12.5383(6)
b/Å	9.5231(4)
c/Å	18.6900(10)
$\alpha/^{\circ}$	90
β/°	97.104(2)
γ/°	90
Volume/Å <sup>3</sup>	2214.52(18)
Z	4
$\rho_{calc}g/cm^3$	1.204
µ/mm <sup>-1</sup>	0.583
F(000)	864.0
Crystal size/mm <sup>3</sup>	$0.03 \times 0.02 \times 0.02$
Radiation	$CuK\alpha$ ( $\lambda = 1.54178$ )
2@ range for data collection/°	8.052 to 144.514
Index ranges	$-15 \le h \le 15,  -11 \le k \le 11,  -23 \le l \le 22$
Reflections collected	22110
Independent reflections	$4341 \ [R_{int} = 0.1052, R_{sigma} = 0.0802]$
Data/restraints/parameters	4341/0/278
Goodness-of-fit on F <sup>2</sup>	1.053
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0837, wR_2 = 0.2105$
Final R indexes [all data]	$R_1 = 0.0910, wR_2 = 0.2218$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.54/-0.57

# X-Ray Diffraction Data of 5be (CCDC 2361509)



## Table S15 Crystal data and structure refinement for 5be (MH2023112002\_0m).

Identification code	MH2023112002_0m
Empirical formula	$C_{27}H_{27}N_2O$
Formula weight	395.528
Temperature/K	227.00
Crystal system	monoclinic
Space group	Cc
a/Å	13.8063(6)
b/Å	17.9373(8)
c/Å	9.9554(5)
$\alpha/^{\circ}$	90
β/°	113.319(2)
$\gamma/^{\circ}$	90
Volume/Å <sup>3</sup>	2264.04(18)
Z	4
$\rho_{calc}g/cm^3$	1.160
µ/mm <sup>-1</sup>	0.547
F(000)	846.4
Crystal size/mm <sup>3</sup>	$0.02\times0.01\times0.01$
Radiation	Cu Ka ( $\lambda = 1.54178$ )
$2\Theta$ range for data collection/°	8.54 to 144.06
Index ranges	$-16 \le h \le 16, -22 \le k \le 19, -12 \le l \le 12$
Reflections collected	12925
Independent reflections	4152 [ $R_{int} = 0.0566$ , $R_{sigma} = 0.0606$ ]
Data/restraints/parameters	4152/2/271
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0561, wR_2 = 0.1503$
Final R indexes [all data]	$R_1\!=\!0.0615,wR_2\!=\!0.1552$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.19
Flack parameter	0.5(4)

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# **VIII. References**

1. Yang, P.-F.; Shu, W. Angew. Chem. Int. Ed. 2022, 61, e202208018.

2. Hibbard, J. P.; Yam, J. G.; Alsalek, E. B.; Bahamonde, A. J. Org. Chem. 2022, 87, 12036-12040.
## IX. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra Data













































































S99











S104




































zo 10 0 -10 -20 -30 -40 -50 -70 -50 -90 -100 -110 -120 -130 -140 -150 -160 -170 -150 -190 -200 -210 -2 fl (ppm)































<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



## Constant of the second se



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)










































mh-10-211c-f.1.fid

218.15 218.15 218.21 218.22 218.22 218.23 218.23 218.28 218.35 218.35 218.35 218.35 218.35





209.0 -209.5 -210.0 -210.5 -211.0 -211.5 -212.0 -212.5 -213.0 -213.5 -214.0 -214.5 -215.0 -215.5 -216.0 -216.5 -217.0 -217.5 -218.0 -218.5 -218.0 -218.5 -219.0 -219.5 -220.0 f1 (ppm)







mh-10-211b-f.1.fid

 $\underbrace{ \begin{smallmatrix} -66.16 \\ -66.19 \\ -66.22 \\ -66.36 \\ -66.36 \\ \end{smallmatrix} }$ 

NHBz MeC CFa 4ck 19F NMR (376 MHz, CDCI3)

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)





























## **X. HPLC Traces**



HPLC data using rac-L1



