Supporting Information

Ni-catalyzed regioselective hydrobenzylation of alkenes to afford C(sp³)-C(sp³)

bonds using BH₃ as reductant

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I. Experimental Section

Part 1. General Information

1. Chemical and Reagents

Unless otherwise mentioned, all reactions were performed under an atmosphere of nitrogen using anhydrous solvents in flame-dried tubes. Extra dry DMA, CH_3CN , Propylenecarbonate (99%, with molecular sieves, water ≤ 50 ppm (by K.F.)) was purchased from Energy Chemical, China. Deuterated solvents were used as received (CDCl₃ from J&K Co., China). Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

2. Physical Method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on JNM-ECZ400s/L or a Bruker Avance 600 MHz spectrometer at STP. NMR spectra are internally referenced to residual proton solvent signals (note: CDCl₃ referenced at 7.26 for ¹H NMR and 77.0 ppm for ¹³C NMR). Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ¹³C NMR spectra were recorded at 151 MHz or 101 MHz. Coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); br (broad). High-resolution mass spectra (HRMS) were obtained using Thermo Fisher Scientific Ultimate 3000-Q Exactive Focus Quadrupole-Orbitrap and Thermo Fisher Scientific LTQ FTICR-MS. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China)

Part 2. Optimization of the reaction conditions

~~ 1,	+ , 0.15 mmol	MeO ₂ C 2 , 2.0 equ	Nil ₂ (10 6,6'-dmi EtOLi (1 BH ₃ •Me; DMA, 0	M mp (10 mol%) 00 mol%) ₂S (100 mol%) °C, 4 h		CO ₂ Me
	N Me Me	N Me	N N R	R N tBu	tE N	tBu
	L1	L2	L3	R = <i>t</i> Bu, L4 R = OMe, L5	L6	
Entry	Cat.(10 mol%)	Ligand (10 mol%)	Base (100mol%)	Solvent (2.5 mL)	T ⁰C	Yield $(3a/3b)^a$
1	NiI ₂	L1	EtOLi	DMA	0	$80\%[78\%]^b(8/1)$
2	NiBr ₂	L1	EtOLi	DMA	0	56%(4/1)
3	NiCl ₂	L1	EtOLi	DMA	0	59%(4/1)
4	$N_1(COD)_2$	Ll	EtOL1	DMA	0	67%(5/1)
5	NIBr ₂ •DME		EtOLi	DMA	0	80%(3/1)
6	$N1(acac)_2$		EtOL1	DMA	0	32%(2/1)
/	N11 ₂		EtOLi	DMA	0	28%(3/1)
8	NII2		EtOL1		0	39%(2/1)
9	NII ₂	L4 15	EtOL1	DMA	0	44%(1.2/1)
10			EIOLI EtOL		0	43%(1.3/1)
11		L0 I 1	EIOLI EtOL	DMA	0	679/(4/1)
12	NiL	I I	EtOLI EtOLi	DIVIT	0	0770(4/1)
13	Nila	LI L1	EtOLi EtOL i	DCE	0	trace
15	Nila	L1	EtOLi EtOL i	DME	0	16%(7/1)
16	Nila	L1	EtOLi	CH ₂ CN	0	76%(1.2/1)
17	Nila	L1	EtOLi	THF	Ő	trace
18	NiI ₂	L1	EtOLi	Toluene	0	trace
19	NiI ₂	L1	MeOLi	DMA	0	76%(8/1)
20	NiI_2	L1	MeONa	DMA	0	29%(5/1)
21	NiI ₂	L1	NaF	DMA	0	15%(10/1)
22	NiI ₂	L1	KF	DMA	0	35%(10/1)
23	NiI ₂	L1	CsF	DMA	0	trace
24	NiI ₂	L1	Na ₂ CO ₃	DMA	0	53%(8/1)
25	NiI ₂	L1	<i>t</i> BuOK	DMA	0	35%(3/1)
26	NiI ₂	L1	tBuOLi	DMA	0	50%(5/1)
27	NiI ₂	L1	EtOLi	DMA(2 mL)	0	78%(8/1)
28	NiI ₂	L1	EtOLi	DMA (3 mL)	0	73%(8/1)
29	NiI ₂	L1	EtOLi	DMA	-10	80%(7/1)
30	NiI ₂	L1	EtOLi	DMA	10	74%(6.5/1)

^a NMR yields ^{, b} Isolated yield.

Part 3. Experimental Procedures and Characterization Data

General procedure: To an oven-dried Schlenk tube (10 mL) were charged with methyl 4-

(bromomethyl)benzoate (2, 0.3 mmol, 200 mol%), L1 (0.015 mmol, 10 mol%), EtOLi (0.15 mmol, 100 mol%) and NiI₂ (0.015 mmol, 10 mol%). After the mixture was evacuated and backfilled nitrogen three times, oct-1-ene (1, 0.15 mmol, 100 mol%), DMA (2.5 mL) and BH₃•SMe₂ (0.15 mmol, 100 mol%, Note: added last.). The reaction mixture was allowed to stir for ~4 h under a N₂ atmosphere at 0 °C, and was directly loaded onto a silica column without work-up. The residue was rinsed with small amount of DCM or the eluent, and the mixture was loaded onto the same silica column. Flash column chromatography afforded the product containing **3a** and **3b** as a colorless liquid (30.6 mg, 78% yield, L/B = 8:1). (Note: The ratio of **a** and **b** isomers were determined by ¹H NMR spectroscopic analysis of the characteristic peaks of the purified product after flash column chromatography.)

Methyl 4-nonylbenzoate (3)



 $\frac{1 \text{H NMR (600 MHz, CDCl_3)}}{8 7.94 \text{ (d, } J = 8.2 \text{ Hz, 2H}\text{)}, 7.24 \text{ (d, } J = 8.1 \text{ Hz, 2H}\text{)}, 3.90 \text{ (s, 3H)}, 2.66 - 2.63 \text{ (m, 2H)}, 1.64 - 1.54 \text{ (m, 2H)}, 1.34 - 1.25 \text{ (m, 12H)}, 0.87 \text{ (t, } J = 7.0 \text{ Hz, 3H}\text{)}.$

Me M_5 <u>13C NMR (151 MHz, CDCl_3)</u> δ 167.2, 148.5, 129.6, 128.4, 127.6, 51.9, 36.0, 31.9, 31.1, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₁₇H₂₇O₂⁺: 263.2006. Found: 263.2008.

Methyl 4-hexylbenzoate (4)



Following the general procedure: using pent-1-ene (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **4** as a colorless oil (17.5 mg,

53% yield, L/B = 8:1)

<u>**1H NMR (400 MHz, CDCl_3)</u></u> \delta 7.95 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H), 2.67 - 2.63 (m, 2H), 1.65 - 1.58 (m, 2H), 1.39 - 1.23 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H).</u>**

<u>¹³C NMR (101 MHz, CDCl₃)</u> δ 167.2, 148.5, 129.6, 128.4, 127.5, 51.9, 36.0, 31.6, 31.1, 28.9, 22.5, 14.0.

<u>HRMS</u> (DART) m/z ($[M+H]^+$) calcd for C₁₄H₂₁O₂⁺: 221.1536. Found: 221.1537.

Methyl 4-(7-(benzoyloxy)heptyl)benzoate (5)



Following the general procedure: using hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **5** as a colorless oil (45.1 mg, 85% yield, L/B = 8:1)

¹H NMR (600 MHz, CDCl₃) δ 8.04 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.56 - 7.53 (m,

1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.90 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.78 - 1.73 (m, 2H), 1.66 - 1.61 (m, 2H), 1.46 - 1.34 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 166.7, 148.3, 132.8, 130.5, 129.6, 129.5, 128.4, 128.3, 127.6, 65.0, 51.9, 35.9, 31.0, 29.1, 29.0, 28.6, 25.9.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₂₆O₄Na⁺: 377.1723. Found: 377.1726.

Methyl 4-(5-(benzoyloxy)pentyl)benzoate (6)

 CO_2Me Following the general procedure: using but-3-en-1-yl benzoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **6** as a colorless oil (40.0 mg, 82% yield, **L/B** = 1.7:1)

 $\frac{1 \text{H NMR (600 MHz, CDCl}_3)}{1.32 \text{ (m, 2H)}, 7.24 \text{ (dd, } J = 8.1, 5.7 \text{ Hz}, 2\text{H}), 4.31 \text{ (t, } J = 6.6 \text{ Hz}, 2\text{H}), 3.90 \text{ (s, 3H)}, 2.69 \text{ (t, } J = 7.7 \text{ Hz}, 2\text{H}), 1.82 - 1.76 \text{ (m, 2H)}, 1.75 - 1.67 \text{ (m, 2H)}, 1.53 - 1.45 \text{ (m, 2H)}.$

<u>1³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 166.6, 147.9, 132.8, 130.4, 129.6, 129.5, 128.4, 128.3, 127.7, 64.8, 51.9, 35.7, 30.6, 28.5, 25.5.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₀H₂₂O₄Na⁺: 349.1410. Found: 349.1408.

Dimethyl 2-(5-(4-(methoxycarbonyl)phenyl)pentyl)malonate (7)



CO₂Me Following the general procedure: using dimethyl 2allylmalonate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to

afford compound 7 as a colorless oil (25.6 mg, 53% yield, L/B = 1.7:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.72 (s, 6H), 3.34 (t, *J* = 7.5 Hz, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.69 – 1.61 (m, 2H), 1.39 – 1.30 (m, 2H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 169.8, 167.1, 147.7, 129.7, 129.1, 128.4, 52.5, 51.9, 51.5, 35.5, 30.6, 28.6, 26.8.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₁₇H₂₂O₆Na⁺: 345.1309. Found: 345.1302.

Dimethyl 2-(9-(4-(methoxycarbonyl)phenyl)nonyl)malonate (8)



Following the general procedure: using dimethyl 2-(oct-7en-1-yl)malonate (0.15 mmol, 100 mol%) and methyl 4(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **8** as a colorless oil (50.0 mg, 85% yield, L/B = 9.6:1)

<u>**H NMR (600 MHz, CDCl3)</u></u> \delta 7.93 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 3.89 (s, 3H), 3.72 (s, 6H), 3.34 (t, J = 7.6 Hz, 1H), 2.65 - 2.62 (m, 2H), 1.90 - 1.86 (m, 2H), 1.63 - 1.58 (m, 2H), 1.28 - 1.25 (m, 12H).</u>**

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 169.9, 167.2, 148.4, 129.6, 128.4, 127.6, 52.4, 51.9, 51.7, 35.9, 31.1, 29.3, 29.19, 29.15, 29.1, 28.8, 27.3.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₃₂O₆Na⁺: 415.2091. Found: 415.2087.

Methyl 4-(9-(phenylsulfonyl)nonyl)benzoate (9)



Following the general procedure: using (oct-7-en-1-ylsulfonyl)benzene (0.15 mmol, 100 mol%) and methyl 4- (bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound 9 as a colorless oil (52.4 mg, 87% yield,

L/B = 12.5:1)

<u>**1H NMR (600 MHz, CDCl_3)</u>** δ 7.93 (d, J = 8.2 Hz, 2H), 7.90 - 7.89 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 3.88 (s, 3H), 3.07 - 3.05 (m, 2H), 2.63 - 2.61 (m, 2H), 1.71 - 1.75 (m, 4H), 1.33 - 1.22 (m, 10H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 148.3, 139.1, 133.5, 129.5, 129.2, 128.3, 128.0, 127.6, 56.2, 51.9, 35.9, 31.0, 29.2, 29.0, 28.9, 28.1, 22.5.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₃H₃₀O₄SNa⁺: 425.1757. Found: 425.1744.

Methyl 4-(7-(tosyloxy)heptyl)benzoate (10)



Following the general procedure: using hex-5-en-1-yl 4methylbenzenesulfonate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **10** as a colorless oil (31.5 mg, 52% yield, L/B =

8.5:1)

<u>**1H NMR (600 MHz, CDCl_3)</u></u> \delta 7.94 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.89 (s, 3H), 2.63 - 2.61 (m, 2H), 2.43 (s, 3H), 1.64 - 1.55 (m, 4H), 1.31 - 1.23 (m, 6H).</u>**

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 148.2, 144.6, 133.2, 129.8, 129.6, 128.4, 127.8, 70.5, 51.9, 35.8, 30.9, 28.9, 28.73, 28.68, 25.2, 21.6.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₂₈O₅SNa⁺: 427.1550. Found: 427.1540.

Methyl 4-(9-((5,7-dichloroquinolin-8-yl)oxy)nonyl)benzoate (11)



Following the general procedure: using 5,7-dichloro-8-(oct-7-en-1-yloxy)quinoline (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **11** as a light-yellow oil (48.2 mg, 68% yield, L/B = 10:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.97 - 8.96 (m, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.51 - 7.49 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 2.65 - 2.62 (m, 2H), 1.94 - 1.89 (m, 2H), 1.66 - 1.50 (m, 4H), 1.40 - 1.32 (m, 8H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 151.0, 150.7, 148.5, 143.9, 133.2, 129.6, 128.4, 127.9, 127.5, 126.7, 126.2, 125.8, 121.9, 75.5, 51.9, 36.0, 31.1, 30.2, 29.4, 29.34, 29.33, 29.2, 25.8.

<u>**HRMS**</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₆H₃₀Cl₂NO₃⁺: 474.1597. Found: 474.1571.

7-(4-(methoxycarbonyl)phenyl)heptyl furan-2-carboxylate (12)



Following the general procedure: using hex-5-en-1-yl furan-2-carboxylate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **12** as a colorless oil (38.7 mg, 75% yield,

L/B = 5.5:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.93 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 3.4 Hz, 1H), 6.49 (s, 1H), 4.28 (t, J = 6.6 Hz, 2H), 3.88 (s, 3H), 2.64 (t, J = 7.7 Hz, 2H), 1.76 - 1.59 (m, 4H), 1.39 - 1.33 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 158.8, 148.2, 146.1, 144.8, 129.6, 128.4, 127.6, 117.7, 111.7, 64.9, 51.9, 35.9, 30.9, 28.98, 28.95, 28.6, 25.7.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₀H₂₄O₅Na⁺: 367.1516. Found: 367.1518.

7-(4-(methoxycarbonyl)phenyl)heptyl thiophene-2-carboxylate (13)



Following the general procedure: using hex-5-en-1-yl thiophene-2-carboxylate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **13** as a colorless oil (33.4 mg, 62% yield,

L/B = 7:1)

<u>**1H NMR (600 MHz, CDCl_3)</u>** δ 7.94 (d, J = 8.3 Hz, 2H), 7.79 - 7.78 (m, 1H), 7.54 - 7.53 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 7.10 - 7.08 (m, 1H), 4.28 (t, J = 6.7 Hz, 2H), 3.89 (s, 3H), 2.66 - 2.64 (m,</u>

2H), 1.75 - 1.70 (m, 2H), 1.66 - 1.61 (m, 2H), 1.46 - 1.32 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 162.3, 148.3, 133.2, 132.1, 129.6, 128.4, 127.7, 65.1, 51.9, 35.9, 30.9, 29.02, 28.97, 28.6, 25.8.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₀H₂₄O₄SNa: 383.1288. Found: 383.1273.

7-(4-(methoxycarbonyl)phenyl)heptyl 1-methyl-1H-indole-2-carboxylate (14)



Following the general procedure: using hex-5-en-1-yl 1methyl-1H-indole-2-carboxylate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **14** as a colorless oil

(40.9 mg, 67% yield, L/B = 7:1)

<u>**1H NMR (600 MHz, CDCl_3)</u></u> \delta 7.95 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.40 - 7.34 (m, 2H), 7.30 (s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 4.31 (t, J = 6.6 Hz, 2H), 4.08 (s, 3H), 3.90 (s, 3H), 2.68 - 2.65 (m, 2H), 1.80 - 1.75 (m, 2H), 1.67 - 1.63 (m, 2H), 1.49 - 1.36 (m, 6H).</u>**

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 162.3, 148.3, 139.6, 129.6, 128.2, 127.6, 125.8, 124.9, 122.5, 120.5, 110.2, 110.0, 64.5, 51.9, 35.9, 31.6, 31.0, 29.1, 29.0, 28.7, 25.9.

<u>**HRMS**</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₅H₃₀NO₄⁺: 408.2169. Found: 408.2163.

Methyl 4-(7-(1,3-dioxoisoindolin-2-yl)heptyl)benzoate (15)



Following the general procedure: using 2-(hex-5-en-1yl)isoindoline-1,3-dione (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **15** as a white solid (35.8 mg, 63% yield, L/B = 7:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.83 - 7.82 (m, 2H), 7.70 - 7.69 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 3.66 (t, *J* = 7.3 Hz, 2H), 2.64 - 2.61 (m, 2H), 1.68 - 1.58 (m, 4H), 1.38 - 1.30 (m, 6H).

<u>1³C NMR (151 MHz, CDCl₃)</u> δ 168.4, 167.2, 148.3, 133.8, 132.1, 129.6, 128.4, 123.1, 51.9, 37.9, 35.9, 30.9, 29.0, 28.9, 28.5, 26.7.

<u>HRMS</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₃H₂₅NO₄Na⁺: 402.1676. Found: 402.1657.

Methyl 4-(12-(ethyl(phenyl)amino)-12-oxododecyl)benzoate (16)

Following the general procedure: using N-ethyl-N-



phenylundec-10-enamide (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **16** as a colorless oil (51.1 mg, 78% yield, L/B = 11:1)

<u>**H NMR (600 MHz, CDCl_3)**</u> δ 7.93 (d, J = 8.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 3.88 (s, 3H), 3.73 (q, J = 7.1 Hz, 2H), 2.64 - 2.61 (m, 2H), 1.98 (t, J = 7.6 Hz, 2H), 1.62 - 1.52 (m, 4H), 1.31 - 1.15 (m, 14H), 1.09 (t, J = 7.1 Hz, 3H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 172.6, 167.1, 148.4, 142.5, 129.54, 129.51, 128.38, 128.35, 127.7, 127.5, 51.9, 43.9, 35.9, 34.4, 31.1, 29.46, 29.42, 29.35, 29.3, 29.23, 29.16, 13.0.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₈H₄₀NO₃⁺: 438.3003. Found: 438.2993.

Methyl 4-(4-(2-(benzoyloxy)ethoxy)butyl)benzoate (17)



Following the general procedure: using 2-(allyloxy)ethyl benzoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column

chromatograph to afford compound 17 as a colorless oil (21.4 mg, 40% yield, L/B > 20:1)

<u>**1H NMR (600 MHz, CDCl_3)</u></u> \delta 8.04 (d, J = 7.3 Hz, 2H), 7.92 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.47 - 4.45 (m, 2H), 3.89 (s, 3H), 3.75 - 3.74 (m, 2H), 3.53 (t, J = 6.3 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 1.72 - 1.61 (m, 4H).</u>**

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 166.5, 147.9, 132.9, 130.1, 129.6, 128.4, 128.3, 127.7, 71.0, 68.7, 64.1, 51.9, 35.6, 29.2, 27.6.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₄O₅Na⁺: 379.1516. Found: 379.1516.

Methyl 4-(12-oxododecyl)benzoate (18)



Following the general procedure: using undec-10-enal (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **18** as a colorless oil

(19.1 mg, 40% yield, L/B = 9.5:1)

<u>¹H NMR (400 MHz, CDCl₃)</u> δ 9.76 (t, *J* = 1.9 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.67 - 2.63 (m, 2H), 2.44 - 2.39 (m, 2H), 1.67 - 1.60 (m, 2H), 1.29 - 1.25 (m, 16H).

<u>¹³C NMR (101 MHz, CDCl₃)</u> δ 203.0, 167.2, 148.5, 129.6, 128.4, 127.6, 52.0, 43.9, 36.0, 31.1, 29.5, 29.41, 29.37, 29.3, 29.2, 29.1, 22.1.

<u>**HRMS**</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₀H₃₀O₃Na⁺: 341.2087. Found: 341.2072.

Methyl 4-(5-phenylpentyl)benzoate (19)



Following the general procedure: using but-3-en-1ylbenzene (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **19** as a colorless

oil (35.9 mg, 85% yield, C1:C2:C4=14:1:2.5)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.28 - 7.25 (m, 7H), 3.89 (s, 3H), 2.65 - 2.58 (m, 4H), 1.68 - 1.61 (m, 4H), 1.40 - 1.34 (m, 2H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 148.3, 142.6, 129.6, 128.4, 128.3, 128.2, 125.6, 51.9, 35.9, 35.8, 31.2, 30.9, 28.8.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₁₉H₂₂O₂Na⁺: 305.1512. Found: 305.1510.

Methyl 4-(5-(benzo[d][1,3]dioxol-5-yl)-4-methylpentyl)benzoate (20)



Following the general procedure: using 5-(2methylbut-3-en-1-yl)benzo[d][1,3]dioxole (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by

flash column chromatograph to afford compound 20 as a colorless oil (45.9 mg, 90% yield)

<u>**H NMR (600 MHz, CDCl_3)</u></u> \delta 7.95 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 7.9 Hz, 1H), 6.61 (d, J = 1.5 Hz, 1H), 6.57 - 6.55 (m, 1H), 5.92 (s, 2H), 3.90 (s, 3H), 2.66 - 2.57 (m, 2H), 2.55 - 2.50 (m, 1H), 2.31 - 2.28 (m, 1H), 1.70 - 1.59 (m, 3H), 1.41 - 1.35 (m, 1H), 1.22 - 1.14 (m, 1H), 0.85 (d, J = 6.6 Hz, 3H).</u>**

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 148.2, 147.3, 145.4, 135.1, 129.6, 128.4, 127.6, 121.8, 109.4, 107.9, 100.7, 51.9, 43.3, 36.1, 35.9, 35.0, 28.6, 19.3.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₄O₄Na⁺: 363.1567. Found: 363.1565.

Methyl 4-(4-(benzoyloxy)hexyl)benzoate (21)



Following the general procedure: using pent-1-en-3-yl benzoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **21** as a colorless oil

(21.4 mg, 42% yield)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.05 - 8.03 (m, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.4 Hz,

1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.13 - 5.10 (m, 1H), 3.89 (s, 3H), 2.73 - 2.64 (m, 2H), 1.76 - 1.68 (m, 6H), 0.93 (t, *J* = 7.4 Hz, 3H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 166.4, 147.6, 132.8, 130.6, 129.7, 129.5, 128.4, 128.3, 127.8, 75.7, 52.0, 35.7 33.2, 27.1, 26.7, 9.6.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₄O₄Na⁺: 363.1567. Found: 363.1566.

Tert-butyl 3-(3-(4-(methoxycarbonyl)phenyl)propyl)piperidine-1-carboxylate (22)



Following the general procedure: using *tert*-butyl 3vinylpiperidine-1-carboxylate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to

afford compound 22 as a light-yellow oil (49.8 mg, 92% yield)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.02 - 3.75 (m, 5H), 2.73 - 2.62 (m, 3H), 1.80 - 1.77 (m, 1H), 1.68 - 1.56 (m, 3H), 1.45 - 1.38 (m, 12H), 1.27 - 1.03 (m, 3H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 154.8, 147.9, 129.6, 128.3, 127.7, 79.1, 51.9, 36.0, 35.7, 30.9, 28.4, 28.1.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₃₁NO₄Na⁺: 384.2145. Found: 384.2141.

Methyl 4-(6-methoxy-4,4-dimethyl-6-oxohexyl)benzoate (23)



Following the general procedure: using methyl 3,3dimethylpent-4-enoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph

to afford compound 23 as a colorless oil (28.4 mg, 65% yield)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.61 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.18 (s, 2H), 1.64 - 1.59 (m, 2H), 1.35 - 1.32 (m, 2H), 0.96 (s, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 172.7, 167.1, 148.1, 129.6, 128.4, 127.7, 51.9, 51.1, 45.7, 41.6, 36.5, 33.2, 27.2, 25.7.

HRMS (ESI) m/z ([M+Na]⁺) calcd for C₁₇H₂₄O₄Na⁺: 315.1567. Found: 315.1556.

Methyl 4-(2-(4-methoxyphenyl)propyl)benzoate (24)



Following the general procedure: using 1-methoxy-4vinylbenzene (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford S10 compound 24 as a colorless oil (25.5 mg, 60% yield, L/B = 1:7.5)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.89 (d, *J* = 8.2 Hz, 2H)), 7.11 - 7.06 (m, 4H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 3.01 - 2.81 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H).

<u>1³C NMR (151 MHz, CDCl₃)</u> δ 167.2, 157.9, 146.4, 138.3, 129.4, 129.2, 127.8, 113.7, 55.2, 51.9, 45.2, 40.8, 21.5.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₁₈H₂₀O₃Na⁺: 307.1305. Found: 307.1286.

Methyl-4-(6-(((3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)hexyl)benzoate (25)



Following the general procedure: using (3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(pent-4-en-1-

yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford

compound 25 as a colorless oil (51.6 mg, 72% yield, L/B = 10:1)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 7.93 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 5.85 (d, J = 3.7 Hz, 1H), 4.50 (d, J = 3.7 Hz, 1H), 4.30 - 4.26 (m, 1H), 4.12 - 4.05 (m, 2H), 3.98 - 3.96 (m, 1H), 3.88 (s, 3H), 3.83 (d, J = 3.0 Hz, 1H), 3.58 - 3.47 (m, 2H), 2.65 - 2.63 (m, 2H), 1.64 - 1.59 (m, 2H), 1.56 - 1.52 (m, 2H), 1.48 (s, 3H), 1.41 (s, 3H), 1.38 - 1.30 (m, 10H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 148.2, 129.6, 128.4, 127.6, 111.7, 108.8, 105.2, 82.5, 82.05, 81.12, 72.5, 70.5, 67.2, 51.9, 35.9, 31.0, 29.6, 28.9, 26.8, 26.7, 26.2, 25.9, 25.4.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₆H₃₉O₈⁺: 479.2640. Found: 479.2630.

Methyl-4-(9-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5b:4',5'-d]pyran-5-yl)methoxy)nonyl)benzoate (26)



Following the general procedure: using (3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyl-5-((oct-7-en-1-vloxy)methyl)tetrahydro-5*H*-

bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound

26 as a colorless oil (60.8 mg, 78% yield, L/B = 13:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.54 (d, *J* = 5.0

Hz, 1H), 4.60 - 4.59 (m, 1H), 4.31 - 4.25 (m, 2H), 3.96 (t, *J* = 6.2 Hz, 1H), 3.89 (s, 3H), 3.65 - 3.56 (m, 2H), 3.52 - 3.43 (m, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.64 - 1.54 (m, 7H), 1.45 (s, 3H), 1.34 - 1.28 (m, 16H).

 $\frac{^{13}\text{C NMR (151 MHz, CDCl_3)}}{^{13}\text{C NMR (151 MHz, CDCl_3)}} \delta 167.1, 148.4, 129.5, 128.3, 127.5, 109.1, 108.4, 96.3, 71.5, 71.1, 70.6, 70.5, 69.3, 66.7, 51.9, 35.9, 31.0, 29.5, 29.4, 29.34, 29.30, 29.2, 26.00, 25.94, 25.9, 24.9, 24.4. HRMS (ESI) m/z ([M+Na]⁺) calcd for <math>C_{29}H_{44}O_8Na^+$: 543.2928. Found: 543.2917.

Methyl 4-(9-(((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5' -*d*]pyran-3a-yl)methoxy)nonyl)benzoate (27)



Following the general procedure: using (3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyl-3a-((oct-7-en-1-yloxy)methyl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The

crude mixture was purified by flash column chromatograph to afford compound **27** as a colorless oil (54.6 mg, 70% yield, L/B = 12:1)

<u>**'H NMR (600 MHz, CDCl_3)</u></u> \delta 7.93 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.59 - 4.57 (m, 1H), 4.39 (d, J = 2.6 Hz, 1H), 4.22 - 4.21 (m, 1H), 3.91 - 3.88 (m, 4H), 3.72 - 3.70 (m, 1H), 3.56 - 3.42 (m, 4H), 2.65 - 2.62 (m, 2H), 1.62 - 1.52 (m, 7H), 1.46 (s, 3H), 1.41 (s, 3H), 1.33 - 1.26 (m, 13H).</u>**

 $\frac{^{13}\text{C NMR (151 MHz, CDCl_3)}}{^{13}\text{C NMR (151 MHz, CDCl_3)}} \delta 167.1, 148.4, 129.6, 128.4, 127.6, 108.8, 108.4, 102.7, 72.0, 71.0, 70.2, 69.9, 60.9, 51.9, 35.9, 31.1, 29.5, 29.39, 29.36, 29.3, 29.2, 26.5, 26.0, 25.8, 25.3, 24.0.$ $\frac{\text{HRMS}}{\text{HRMS}} \text{(ESI) m/z ([M+Na]^+) calcd for C}_{29}\text{H}_{44}\text{O}_8\text{Na}^+\text{: 543.2928. Found: 543.2922.}$

Methyl-4-(7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6Hcyclopenta[*a*]phenanthren-2-yl)oxy)heptyl)benzoate (28)



Following the general procedure: using (8R,9S,13S,14S)-2-(hex-5-en-1-yloxy)-13methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (0.15 mmol, 100 mol%) and methyl 4-

(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **28** as a white solid (56.4 mg, 75% yield, L/B = 10:1)

<u>**1H NMR (600 MHz, CDCl_3)</u></u> \delta 7.95 (d, J = 8.2 Hz, 2H), 7.25 - 7.18 (m, 3H), 6.72 - 6.70 (m, 1H), 6.64 (d, J = 2.5 Hz, 1H), 3.93 - 3.90 (m, 5H), 2.91 - 2.88 (m, 2H), 2.67 - 2.65 (m, 2H), 2.52 - 2.48 (m, 1H), 2.43 - 2.36 (m, 1H), 2.29 - 2.23 (m, 1H), 2.17 - 1.94 (m, 4H), 1.78 - 1.73 (m, 2H), 1.67 - 1.35 (m, 2H), 2.67 - 2.65 (m, 2H), 2.67 - 2.65 (m, 2H), 2.52 - 2.48 (m, 2H), 2.43 - 2.36 (m, 1H), 2.29 - 2.23 (m, 2H), 2.17 - 1.94 (m, 4H), 1.78 - 1.73 (m, 2H), 1.67 - 1.35 (m, 2H), 2.43 - 2.48 (m, 2H), 2.43 - 2.48 (m, 2H), 2.43 - 2.48 (m, 2H), 2.44 - 2.48 (m, 2H), 2.4</u>**

14H), 0.91 (s, 3H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.1, 157.1, 148.3, 137.6, 131.8, 129.6, 128.4, 127.6, 126.2, 114.5, 112.0, 67.7, 51.9, 50.3, 47.9, 43.9, 38.3, 35.9, 35.8, 31.5, 31.0, 29.6, 29.09, 29.06, 26.5, 25.89, 25.85, 21.5, 13.8.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₃₃H₄₃O₄⁺: 503.3156. Found: 503.3137.

Methyl-4-(9-((2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoyl)oxy)nonyl)benzoate

(29)

Following the general procedure: using oct-7-en-1-yl 2-(10-oxo-10,11dihydrodibenzo[*b*,*f*]thiepin-2-yl)propanoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200

mol%). The crude mixture was purified by flash column chromatograph to afford compound **29** as a yellow oil (50.2 mg, 60% yield, L/B = 19:1)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 8.20 - 8.18 (m, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.42 - 7.38 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.15 - 7.13 (m, 1H), 4.34 (s, 2H), 4.03 (t, J = 6.7 Hz, 2H), 3.89 (s, 3H), 3.70 (q, J = 7.2 Hz, 1H), 2.65 - 2.62 (m, 2H), 1.62 - 1.53 (m, 4H), 1.47 (d, J = 7.2 Hz, 3H), 1.30 - 1.20 (m, 10H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 191.2, 173.9, 167.1, 148.4, 142.8, 140.2, 137.8, 136.1, 133.1, 132.4, 131.5, 131.3, 130.8, 129.6, 128.6, 128.4, 127.6, 126.8, 126.3, 65.0, 51.9, 51.0, 45.2, 35.9, 31.0, 29.3, 29.2, 29.1, 29.0, 28.4, 25.7, 18.3.

HRMS (ESI) m/z ([M+Na]⁺) calcd for C₃₄H₃₈O₅SNa⁺: 581.2332. Found: 581.2315.

Methyl (S)-4-(9-((tert-butoxycarbonyl)amino)-10-methoxy-10-oxodecyl)benzoate (30)



Following the general procedure: using methyl (S)-2-((*tert*-butoxycarbonyl)amino)non-8-enoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **30** as a colorless oil (49.5

mg, 76% yield, L/B = 13:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 7.93 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.01 (d, J = 8.0 Hz, 1H), 4.28 - 4.25 (m, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 2.64 - 2.61 (m, 2H), 1.80 - 1.71 (m, 1H), 1.64 - 1.53 (s, 3H), 1.43 (s, 9H), 1.32 - 1.26 (m, 10H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 173.5, 167.1, 155.3, 148.4, 129.6, 128.4, 127.6, 79.7, 53.4, 52.1, 51.9, 35.9, 32.7, 31.0, 29.22, 29.20, 29.09, 29.05, 28.3, 25.2.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₄H₃₇NO₆Na⁺: 458.2513. Found: 458.2507.

Methyl 4-(6-(benzoyloxy)hexyl)benzoate (31)



Following the general procedure: using (*E*)-hex-4-en- 1yl benzoate (0.15 mmol, 100 mol%) and methyl 4-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column

chromatograph to afford compound **31** as a colorless oil (29.2 mg, 55% yield, C1/C2/Cx = 9:3:1, Cx: It's uncertain the position of Cx in the carbon chain.)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.08 – 8.01 (m, 2H), 7.94 (dd, J = 8.4, 2.3 Hz, 2H), 7.55 (td, J = 7.3, 1.4 Hz, 1H), 7.47 – 7.39 (m 2H), 7.23 (d, J = 8.2 Hz, 2H), 4.31 (t, J = 6.6 Hz, 2H), 3.90 (s, 3H), 2.65 (t, J = 7.8, 2H), 1.81 – 1.71 (m, 2H), 1.67 – 1.59 (m, 2H), 1.48 – 1.30 (m, 4H).

<u>13C NMR (151 MHz, CDCl₃)</u> δ 167.2, 166.6, 148.3, 132.8, 130.5, 129.6, 129.5, 129.1, 128.4, 128.3, 65.0, 51.9, 35.9, 31.0, 29.0, 29.0, 28.6, 25.9.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₂₆O₄Na⁺: 377.1723. Found: 377.1718.

7-phenylheptyl benzoate (32)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and (bromomethyl)benzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to

afford compound **32** as a colorless oil (31.1 mg, 70% yield, L/B = 11:1)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 8.07 - 8.05 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 - 7.44 (m, 2H), 7.30 - 7.27 (m, 2H), 7.20 - 7.15 (m, 3H), 4.33 (t, J = 6.7 Hz, 2H), 2.63 - 2.61 (m, 2H), 1.80 - 1.74 (m, 2H), 1.67 - 1.62 (m, 2H), 1.47 - 1.37 (m, 6H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.7, 142.7, 132.8, 130.5, 129.5, 128.4, 128.3, 128.2, 125.6, 65.1, 35.9, 31.4, 29.13, 29.11, 28.7, 25.9.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₀H₂₄O₂⁺: 297.1849. Found: 297.1834.

7-(*p*-tolyl)heptyl benzoate (33)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(bromomethyl)-4- methylbenzene (0.3 mmol, 200 mol%). The crude mixture was

purified by flash column chromatograph to afford compound **33** as a colorless oil (36.2 mg, 78% yield, L/B = 12:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.07 - 8.05 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.11 - 7.07 (m, 4H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.59 - 2.57 (m, 2H), 2.33 (s, 3H), 1.80 - 1.75 (m, 2H), 1.64 - 1.59 (m, 2H), 1.47 - 1.36 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.7, 139.6, 135.0, 132.8, 130.5, 129.5, 128.9, 128.3, 128.2, 65.1, 35.4, 31.5, 29.13, 29.12, 28.7, 26.0, 21.0.

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₆O₂Na⁺: 333.1825. Found: 333.1826.

7-(4-(tert-butyl)phenyl)heptyl benzoate (34)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(bromomethyl)-4-(*tert*-butyl)benzene (0.3 mmol, 200 mol%). The crude mixture was

purified by flash column chromatograph to afford compound **34** as a colorless oil (45.4 mg, 86% yield, L/B = 10:1)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 8.08 - 8.07 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 - 7.44 (m, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 4.34 (t, J = 6.7 Hz, 2H), 2.62 - 2.59 (m, 2H), 1.82 -1.77 (m, 2H), 1.68 - 1.62 (m, 2H), 1.50 - 1.41 (m, 6H), 1.34 (s, 9H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.6, 148.3, 139.6, 132.7, 130.5, 129.5, 128.3, 128.0, 125.1, 65.1, 35.3, 34.3, 31.4, 31.3, 29.2, 29.1, 28.7, 26.0.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₄H₃₃O₂⁺: 353.2475. Found: 353.2476.

7-(4-methoxyphenyl)heptyl benzoate (35)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(bromomethyl)-4- methoxybenzene (0.3 mmol, 200 mol%). The crude mixture was

purified by flash column chromatograph to afford compound **35** as a colorless oil (33.2 mg, 68% yield, L/B = 26.5:1)

<u>**1H NMR (400 MHz, CDCl_3)**</u> δ 8.08 - 8.06 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.33 (t, J = 6.7 Hz, 2H), 3.80 (s, 3H), 2.59 - 2.55 (m, 2H), 1.81 - 1.75 (m, 2H), 1.65 - 1.58 (m, 2H), 1.50 - 1.33 (m, 6H).

<u>¹³C NMR (101 MHz, CDCl₃)</u> δ 166.6, 157.5, 134.8, 132.7, 130.4, 129.5, 129.16, 128.3, 113.6, 65.0, 55.1, 34.9, 31.6, 29.1, 29.0, 28.6, 25.9.

<u>**HRMS**</u> (DART) m/z ($[M+H]^+$) calcd for C₂₁H₂₇O₃⁺: 327.1955. Found: 327.1956.

7-(4-chlorophenyl)heptyl benzoate (36)

CI Following the general procedure: using methyl hex-5-en-1-yl benzoate

(0.15 mmol, 100 mol%) and 1-(bromomethyl)-4-chlorobenzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **36** as a colorless oil (35.6 mg, 72% yield, L/B = 12:1)

<u>**1H NMR (600 MHz, CDCl_3)</u>** δ 8.06 - 8.04 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 2.59 - 2.56 (m, 2H), 1.79 - 1.74 (m, 2H), 1.63 - 1.58 (m, 2H), 1.46 - 1.33 (m, 6H).</u>

<u>1³C NMR (151 MHz, CDCl₃)</u> δ 166.7, 141.1, 132.8, 131.2, 130.5, 129.7, 129.5, 128.29, 128.28, 65.0, 35.2, 31.2, 29.04, 28.99, 28.7, 25.9.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₀H₂₄ClO₂⁺: 331.1459. Found: 331.1459.

7-(4-bromophenyl)heptyl benzoate (37)

Br Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-bromo-4-(bromomethyl)benzene (0.3 mmol, 200 mol%). The crude mixture

was purified by flash column chromatograph to afford compound **37** as a colorless oil (46.0 mg, 82% yield, L/B = 10.5:1)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 8.05 - 8.04 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 2.57 - 2.54 (m, 2H), 1.79 - 1.74 (m, 2H), 1.61 - 1.57 (m, 2H), 1.46 - 1.34 (m, 6H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.6, 141.6, 132.8, 131.2, 131.1, 130.5, 130.1, 129.5, 128.3, 119.3, 65.0, 35.2, 31.2, 29.04, 28.98, 28.7, 25.9.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₀H₂₃BrO₂Na⁺: 397.0774. Found: 397.0773.

7-(4-cyanophenyl)heptyl benzoate (38)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 4-(bromomethyl)benzonitrile (0.3 mmol, 200 mol%). The crude mixture was purified by flash

column chromatograph to afford compound **38** as a colorless oil (34.1 mg, 71% yield, L/B = 5:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.05 - 8.03 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.67 - 2.64 (m, 2H), 1.78 - 1.74 (m, 2H), 1.65 - 1.60 (m, 2H), 1.47 - 1.32 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.6, 148.4, 132.8, 132.1, 130.4, 129.5, 129.1, 128.3, 119.1, 109.5, 64.9, 36.0, 30.8, 28.96, 28.95, 28.6, 25.8.

<u>HRMS</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₁H₂₃NO₂Na⁺: 344.1621. Found: 344.1612.

7-(4-formylphenyl)heptyl benzoate (39)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 4- (bromomethyl)benzaldehyde (0.3 mmol, 200 mol%). The crude

mixture was purified by flash column chromatograph to afford compound **39** as a colorless oil (29.1 mg, 60% yield, L/B = 15:1)

<u>**H NMR (400 MHz, CDCl_3)</u>** δ 11.84 (s, 1H), 8.05 - 8.02 (m, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 - 7.41 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.31 (t, J = 6.6 Hz, 2H), 2.70 - 2.67 (m, 2H), 1.80 - 1.73 (m, 2H), 1.67 - 1.62 (m, 2H), 1.46 - 1.35 (m, 6H).</u>

<u>¹³C NMR (101 MHz, CDCl₃)</u> δ 192.0, 166.7, 150.3, 134.4, 132.8, 130.4, 129.9, 129.5, 129.0, 128.3, 65.0, 36.1, 30.9, 29.1, 29.0, 28.6, 25.9.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₁H₂₅O₃⁺: 325.1798. Found: 325.1794.

7-(4-acetylphenyl)heptyl benzoate (40)

BzO (bromomethyl)phenyl)ethan-1-one (0.3 mmol, 200 mol%). The

crude mixture was purified by flash column chromatograph to afford compound **40** as a colorless oil (41.7 mg, 82% yield, L/B = 14:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.04 - 8.03 (m, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.56 - 7.54 (m, 1H), 7.44 - 7.42 (m, 2H), 7.26 - 7.24 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 2.67 - 2.64 (m, 2H), 2.57 (s, 3H), 1.79 - 1.73 (m, 2H), 1.66 - 1.61 (m, 2H), 1.46 - 1.32 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 197.8, 166.6, 148.6, 134.9, 132.8, 130.4, 129.5, 128.5, 128.4, 128.3, 64.9, 35.9, 30.9, 29.02, 29.00, 28.6, 26.5, 25.9.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₂₆O₃Na⁺: 361.1774. Found: 361.1758.

Methyl 3-(7-(benzoyloxy)heptyl)benzoate (41)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and methyl 3- (bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford

compound 41 as a colorless oil (41.4 mg, 78% yield, L/B = 11.5:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.05 - 8.03 (m, 2H), 7.86 - 7.83 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.37 - 7.32 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 3.90 (s, 3H), 2.66 - 2.64 (m, 2H), 1.78 - 1.73 (m, 2H), 1.67 - 1.62 (m, 2H), 1.47 - 1.34 (m, 6H). <u>¹³C NMR (151 MHz, CDCl₃)</u> δ 167.3, 166.6, 143.0, 133.0, 132.8, 130.4, 130.1, 129.5, 129.4, 128.3, 128.2, 126.9, 65.0, 52.0, 35.6, 31.2, 29.1, 29.0, 28.6, 25.9.

<u>**HRMS**</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₂H₂₆O₄Na⁺: 377.1723. Found: 377.1727.

Methyl 2-(7-(benzoyloxy)heptyl)benzoate (42)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and methyl 2-(bromomethyl)benzoate (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **42** as a colorless oil (37.1 mg, 70%)

yield, **L/B** = 11:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.05 - 8.03 (m, 2H), 7.86 - 7.85 (m, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 - 7.39 (m, 3H), 7.24 (d, J = 7.6 Hz, 2H), 4.31 (t, J = 6.7 Hz, 2H), 3.88 (s, 3H), 2.96 - 2.93 (m, 2H), 1.79 - 1.74 (m, 2H), 1.62 - 1.58 (m, 2H), 1.46 - 1.40 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 168.2, 166.7, 144.6, 132.8, 131.8, 130.9, 130.54, 130.50, 129.5, 129.4, 128.3, 125.7, 65.1, 51.9, 34.4, 31.7, 29.6, 29.1, 28.7, 26.0.

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₂H₂₆O₄Na⁺: 377.1723. Found: 377.1731.

7-(3-nitrophenyl)heptyl benzoate (43)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(bromomethyl)-3-nitrobenzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **43** as a light-yellow oil (25.5 mg, 50%)

yield, L/B = 27:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.05 - 8.03 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 - 7.49 (m, 1H), 7.45 - 7.42 (m, 3H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.73 - 2.70 (m, 2H), 1.79 - 1.74 (m, 2H), 1.69 - 1.64 (m, 2H), 1.47 - 1.35 (m, 6H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.7, 148.3, 144.6, 134.7, 132.8, 130.4, 129.5, 129.1, 128.3, 123.2, 120.9, 65.0, 35.5, 31.0, 29.02, 28.98, 28.7, 25.9.

HRMS (ESI) m/z ([M+Na]⁺) calcd for C₂₀H₂₃NO₄Na⁺: 364.1519. Found: 364.1521.

7-(4-fluoro-3-methoxyphenyl)heptyl benzoate (44)



colorless oil (41.2 mg, 80% yield, L/B = 11.5:1)

1H NMR (600 MHz, CDCl₃) δ 8.05 - 8.04 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz,

2H), 6.98 - 6.94 (m, 1H), 6.77 - 6.66 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 2.58 - 2.55 (m, 2H), 1.79 - 1.74 (m, 2H), 1.63 - 1.58 (m, 2H), 1.48 - 1.34 (m, 6H).

 $\frac{{}^{13}\text{C NMR} (151 \text{ MHz, CDCl}_3)}{132.79, 130.4, 129.5, 128.3, 120.3 (J_{C-F} = 6.0 \text{ Hz}), 115.6 (J_{C-F} = 18.1 \text{ Hz}), 113.5, 65.0, 56.1, 35.6, 31.4, 29.1 (J_{C-F} = 1.5 \text{ Hz}), 28.7, 25.92.$

<u>HRMS</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₅FO₃Na⁺: 367.1680. Found: 367.1667.

7-(3-cyano-4-fluorophenyl)heptyl benzoate (45)

Bzo ()4

Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 5-(bromomethyl)-2-fluorobenzonitrile (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **45** as a colorless oil (30.5

mg, 60% yield, L/B = 21:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.04 - 8.03 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.40 - 7.36 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.61 - 2.59 (m, 2H), 1.78 - 1.74 (m, 2H), 1.62 - 1.57 (m, 2H), 1.46 - 1.32 (m, 6H).

 $\frac{^{13}\text{C NMR (151 MHz, CDCl_3)}}{^{13}\text{C NMR (151 MHz, CDCl_3)}} \delta \ 166.6, \ 162.3, \ 160.6, \ 139.6(J_{C-F} = 3.0 \text{ Hz}), \ 135.0(J_{C-F} = 9.1 \text{ Hz}), \ 132.8(J_{C-F} = 7.6 \text{ Hz}), \ 130.4, \ 129.5, \ 128.3, \ 116.2(J_{C-F} = 19.6 \text{ Hz}), \ 114.2, \ 101.1(J_{C-F} = 16.6 \text{ Hz}), \ 64.9, \ 34.6, \ 31.0, \ 29.0, \ 28.9, \ 28.6, \ 25.9.$

<u>**HRMS**</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₁H₂₂FNO₂Na⁺: 362.1527. Found: 362.1525.

7-(4-fluoro-3-methylphenyl)heptyl benzoate (46)

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Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 4-(bromomethyl)-1-fluoro-2-methylbenzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **46** as a colorless

oil (38.3 mg, 78% yield, L/B = 15.5:1)

<u>**H NMR (600 MHz, CDCl_3)**</u> δ 8.06 - 8.05 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 6.97 - 6.88 (m, 3H), 4.32 (t, J = 6.7 Hz, 2H), 2.55 - 2.52 (m, 2H), 2.25 (s, 3H), 1.79 - 1.75 (m, 2H), 1.62 - 1.57 (m, 2H), 1.47 - 1.34 (m, 6H).

 $\frac{^{13}\text{C NMR (151 MHz, CDCl_3)}}{^{13}\text{C NMR (151 MHz, CDCl_3)}} \delta 166.7, 160.4, 158.8, 138.0 (J_{C-F} = 4.5 \text{ Hz}), 132.8, 131.2 (J_{C-F} = 4.5 \text{ Hz}), 130.5, 129.5, 128.3, 126.9 (J_{C-F} = 7.6 \text{ Hz}), 124.3 (J_{C-F} = 18.1 \text{ Hz}), 114.6 (J_{C-F} = 22.7 \text{ Hz}), 65.0, 35.0, 31.5, 29.1 (J_{C-F} = 4.5 \text{ Hz}), 28.7, 25.9, 14.5, 14.5.$

<u>**HRMS**</u> (ESI) m/z ($[M+Na]^+$) calcd for C₂₁H₂₅FO₂Na: 351.1731. Found: 351.1714.

7-(naphthalen-1-yl)heptyl benzoate (47)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(bromomethyl)naphthalene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **47** as a colorless oil (33.7 mg, 65% yield, L/B = 13:1)

<u>**1H NMR (600 MHz, CDCl_3)</u>** δ 8.06 - 8.04 (m, 3H), 7.86 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.56 (t, J = 6.8 Hz, 1H), 7.52 - 7.39 (m, 5H), 7.33 - 7.32 (m, 1H), 4.33 (t, J = 6.6 Hz, 2H), 3.09 - 3.07 (m, 2H), 1.82 - 1.75 (m, 4H), 1.51 - 1.44 (m, 6H).</u>

<u>13C NMR (151 MHz, CDCl₃)</u> δ 166.7, 138.8, 133.6 132.8, 131.9, 130.5, 129.5, 128.7, 128.3, 128.3, 126.4, 125.8, 125.6, 125.5, 125.3, 123.8, 65.1, 33.0, 30.2, 29.7, 29.2, 28.7, 26.0.

<u>**HRMS**</u> (ESI) m/z ([M+Na]⁺) calcd for C₂₄H₂₆O₂Na⁺: 369.1825. Found: 369.1806.

7-phenyloctyl benzoate (48)

Following the general procedure: using methyl hex-5-en-1-yl benzoate BzO//4 Me Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and (1-chloroethyl)benzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **48** as a colorless oil (32.5 mg, 70% yield, **L/B** = 7:1)

<u>¹H NMR (600 MHz, CDCl₃)</u> δ 8.07 - 8.05 (m, 2H), 7.58 - 7.55 (m, 1H), 7.47 - 7.44 (m, 2H), 7.31 - 7.27 (m, 2H), 7.20 - 7.16 (m, 3H), 4.36 - 4.25 (m, 2H), 2.72 - 2.66 (m, 1H), 1.80 - 1.69 (m, 2H), 1.63 - 1.53 (m, 2H), 1.43 - 1.19 (m, 9H).

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.6, 147.8, 132.8, 130.5, 129.5, 128.3, 128.2, 126.9, 125.7, 65.0, 39.9, 38.3, 29.3, 28.7, 27.5, 25.9, 22.3.

<u>HRMS</u> (ESI) m/z ($[M+H]^+$) calcd for C₂₁H₂₇O₂⁺: 311.2006. Found: 311.2001.

7-(2,3-dimethylphenyl)octyl benzoate (49)



Following the general procedure: using methyl hex-5-en-1-yl benzoate (0.15 mmol, 100 mol%) and 1-(1-chloroethyl)-2,3-dimethylbenzene (0.3 mmol, 200 mol%). The crude mixture was purified by flash column chromatograph to afford compound **49** as a colorless oil (28.8 mg, 57%)

<u>**H NMR (600 MHz, CDCl_3)</u>** δ 8.05 - 8.04 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.10 - 7.06 (m, 2H), 7.00 - 6.99 (m, 1H), 4.30 (t, J = 6.7 Hz, 2H), 3.07 - 3.01 (m, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 1.77 - 1.72 (m, 2H), 1.66 - 1.60 (m, 1H), 1.57 - 1.49 (m, 1H), 1.45 - 1.40 (m, 2H), 1.38 - 1.32 (m, 3H), 1.27 - 1.22 (m, 1H), 1.19 (d, J = 6.9 Hz, 3H).</u>

<u>¹³C NMR (151 MHz, CDCl₃)</u> δ 166.7, 145.7, 136.5, 133.9, 132.8, 130.5, 129.5, 128.3, 127.2, 125.5, 123.0, 65.1, 37.8, 34.5, 29.7, 29.5, 28.7, 27.6, 26.0, 21.7, 21.1, 14.7.

<u>**HRMS**</u> (ESI) m/z ([M+Na]⁺) calcd for $C_{23}H_{30}O_2Na^+$: 361.2138. Found: 361.2138.

Part 4. Result of a 1,1-disubstituted alkene





II. Copies of NMR Data







































































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