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# Supporting Information

## Ni-Catalysed Reductive Arylalkylation of Unactivated Alkenes

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#### **General Methods and Materials**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in CDCl<sub>3</sub> at 400 and 101 MHz. The chemical shifts are given in ppm relative to tetramethylsilane [<sup>1</sup>H:  $\delta$ = (SiMe<sub>4</sub>)= 0.00 ppm] as an internal standard or relative to the resonance of the solvent [<sup>1</sup>H:  $\delta$ =(CDCl<sub>3</sub>)= 7.26, <sup>13</sup>C:  $\delta$ = (CDCl<sub>3</sub>)= 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Alkenes 1,<sup>1</sup> Alkyl bromides 2,<sup>2</sup> and Ligands L1, L3 and L5<sup>3</sup> were prepared according to literature procedures. All other reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification.

#### General Procedure for the Ni-Catalyzed Reductive Arylalkylation of Unactivated Olefins



A sealed test tube charged with NiBr<sub>2</sub> (13.2 mg, 0.06 mmol, 15 mol%), ligand **L1** (9.0 mg, 0.06 mmol, 15 mol%), Zn-powder (104 mg, 1.6 mmol, 4.0 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles) before adding DMA (1.0 mL) under nitrogen atmosphere. Then the reaction mixture was stirred at 55  $^{\circ}$ C or 70  $^{\circ}$ C<sup>[a]</sup> for 15 minutes. Next, alkyl bromides **2** (0.8 mmol, 2.0 equiv) and alkenes **1** (0.4 mmol, 1.0 equiv.) were added and the resulting mixture was stirred at 55  $^{\circ}$ C or 70  $^{\circ}$ C<sup>[a]</sup> for 10 hours. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the corresponding products.

<sup>[a]</sup> 70 °C for 3i, 3j, 3m-o and 3q, 55 °C for the other products.

#### **Reaction on 5 mmol scale**



NiBr<sub>2</sub> (54.6 mg, 5 mol%), ligand L1 (36.3 mg, 5 mol%), and Zn (1.3 g, 4.0 equiv.) were placed in a flask equipped with a stir bar, which was evacuated and filled with nitrogen (three cycles). Then DMA (12.5 mL) were added and the resulting mixture was stirred at 65  $^{\circ}$ C for 30 minutes. Next, 4-bromobutyl acetate (2a) (10 mmol, 1.95 g, 2.0 equiv) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (1a) (5 mmol, 1.12 g, 1.0 equiv.) were added and stirred at 65  $^{\circ}$ C for 10 hours under nitrogen

atmosphere. The mixture was then filtered through a pad of Celite and treated with water. The aqueous phase was extracted with EtOAc (3x30ml) and the combined organic phases were washed with water and aqueous saturated NaCl solution, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) to give the 5-(1-methyl-2,3-dihydro-1*H*-inden-1-yl)pentyl acetate **3a** (0.85g, 65% yield ) as a yellow oil.

#### Control experiments for the Ni-catalyzed reductive arylalkylation



To a sealed test tube containing Zn (52 mg, 0.8 mmol, 4.0 equiv) were sequentially added DMA (0.5 mL) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (**1a**) (45 mg, 0.2 mmol, 1.0 equiv). The mixture was stirred at 55  $^{\circ}$ C for 10 h and then quenched with H<sub>2</sub>O and the aqueous phase was then extracted with DCM (3 x 20 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 20 mL), dried over MgSO4 and concentrated in vacuum. The residue was then subjected to GC analysis.



To a sealed test tube containing Zn (52 mg, 0.8 mmol, 4.0 equiv) were sequentially added DMA (0.5 mL) and 4-bromobutyl acetate (**2a**) (78 mg, 0.4 mmol, 2.0 equiv). The mixture was stirred at 55  $^{\circ}$ C for 10 h and then quenched with H<sub>2</sub>O and the aqueous phase was then extracted with DCM (3 x 20 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 20 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. The residue was then subjected to GC analysis.



To a sealed test tube containing Ni(COD)<sub>2</sub> (55 mg ,0.2 mmol, 1.0 equiv.), L1 (29.2 mg, 0.2 mmol, 1.0 equiv) were sequentially added DMA (0.5 mL) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (1a) (44.8mg, 0.2 mmol, 1.0 equiv). The mixture was stirred at 55 °C for 10 h and was then quenched with 3 mL H<sub>2</sub>O. The aqueous phase was then extracted with DCM (3 x 5 mL), and the combined organic layers were washed with H<sub>2</sub>O (3 x 5 mL), dried over MgSO4, filtered and concentrated in vacuum. The residue was then subjected to GC analysis.



To a sealed test tube containing Ni(COD)<sub>2</sub> (55 mg ,0.2 mmol, 1.0 equiv), L1 (29.2 mg, 0.2 mmol, 1.0 equiv) were sequentially added DMA (0.5 mL) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (1a) (44.8mg, 0.2 mmol, 1.0 equiv). The mixture was stirred at 55  $^{\circ}$ C for 10 h, before 4-bromobutyl acetate (2a) (78mg, 0.4mmol, 2.0 equiv.) was added. After stirring at this temperature for another 10 h the reaction was quenched with 3 mL H<sub>2</sub>O and the aqueous phase was then extracted with DCM (3 x 5 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. The residue was then subjected to GC analysis.



To a sealed test tube containing Ni(COD)<sub>2</sub> (55 mg ,0.2 mmol, 1.0 equiv), L1 (29.2 mg, 0.2 mmol, 1.0 equiv) were sequentially added DMA (0.5 mL) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (1a) (44.8 mg, 0.2 mmol, 1.0 equiv). The mixture was stirred at 55  $^{\circ}$ C for 2 h, before 4-bromobutyl acetate (2a) (78mg, 0.4mmol, 2.0 equiv.) was added. After stirring at this temperature for another 10 h the reaction was quenched with 3 mL H<sub>2</sub>O and the aqueous phase was then extracted with DCM (3 x 5 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. The residue was then subjected to GC analysis.



A sealed test tube charged with NiBr<sub>2</sub> (6.6 mg, 0.03 mmol, 15mol%), ligand L1 (4.5 mg, 0.03 mmol, 15 mol%), TEMPO (31.2 mg, 0.2 mmol, 1.0 equiv), Zn-powder (52 mg, 0.8 mmol, 4.0 equiv.) and a stir bar was evacuated and filled with nitrogen (three cycles) before adding DMA (0.5ml) under nitrogen atmosphere. Then the reaction mixture was stirred at 55  $\$  for 15 minutes. Next, 4-bromobutyl acetate (**2a**) (78 mg, 0.4 mmol, 2.0 equiv) and 1-bromo-2-(3-methylbut-3-en-1-yl)benzene (**1a**) (44.8 mg, 0.2 mmol, 1.0 equiv) were added and the resulting mixture was stirred at 55  $\$  for 10 hours, before it was quenched with H<sub>2</sub>O. The aqueous phase was then extracted with DCM (3 x 5 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. The residue was then subjected to GC analysis.



A sealed test tube charged with NiBr<sub>2</sub> (6.6 mg, 0.03 mmol, 15mol%), ligand L1 (4.5 mg, 0.03 mmol, 15 mol%), Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles) before adding DMA (0.5ml) under nitrogen atmosphere. Then the reaction mixture was stirred at 55 °C for 15 minutes. Next, 4-bromobutyl acetate (2a) (78 mg, 0.4 mmol, 2.0 equiv) and 1-bromo-2-(4-cyclopropyl-3-methylbut-3-en-1-yl)benzene (52.8 mg, 0.2 mmol, 1.0 equiv)were added and the resulting mixture was stirred at 55 °C for 10 hours, before it was quenched with H<sub>2</sub>O. The aqueous phase was then extracted with DCM (3 x 5 mL). The combined organic layers were washed with H<sub>2</sub>O (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated in vacuum. The residue was purified by silica gel column chromatography with eluent of

petroleum ether to the mixture of ethyl acetate and petroleum ether (20:1) to afford the product **3aj** (19 mg, 32% yield) as a yellow oil.

#### **Analytical Data for the Products**



5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3a**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (69 mg, 67%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.23-7.00 (m, 4H), 4.02 (t, *J* = 6.7 Hz, 2H), 2.96-2.79 (m, 2H), 2.10-1.94 (m, 1H), 2.03(s, 3H),1.87-1.76 (m, 1H), 1.66-1.54 (m, 3H), 1.53-1.42 (m, 1H), 1.39-1.15 (m, 1H), 1.23(s, 3H) ppm. <sup>13</sup>C NMR (101

MHz, Chloroform-*d*):  $\delta$ = 171.3, 151.5, 143.2, 126.2, 126.1, 124.5, 122.6, 64.7, 47.3, 41.3, 38.6, 30.3, 28.6, 26.8, 26.7, 24.6, 21.0 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>:283.1669, found: 283.1671.



*1,2-Bis*(*1-methyl-2,3-dihydro-1H-inden-1-yl)ethane* (**3a-1**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil. <sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.19-7.08 (m, 6H), 7.07-7.01 (m, 2H), 2.91-2.75 (m, 4H), 2.03-1.92 (m, 2H), 1.72-1.83 (m, 2H), 1.68-1.53 (m, 2H), 1.52-1.37 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-d): δ (mixture of two diastereomers)= 151.8, 151.7, 143.2, 143.1,

126.24, 126.21, 126.20, 126.18, 124.5 (2C), 122.61, 122.59, 47.24, 47.15, 38.2, 38.1, 36.01, 35.96, 30.3 (2C), 27.0, 26.9 ppm. HRMS (EI): calcd. for C<sub>22</sub>H<sub>26</sub> [M]: 290.2035, found: 290.2030.



5-(1-Ethyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3b**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (67 mg, 61%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.21-7.09 (m, 3H), 7.08-7.00 (m, 1H), 4.01 (t, *J* = 6.8 Hz, 2H), 2.95-2.80 (m, 2H), 2.02 (s, 3H), 1.96-1.87 (m, 2H), 1.71-1.46 (m, 6H), 1.34 – 1.23 (m, 3H), 1.19-1.05 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 149.7, 143.9, 126.2, 125.8, 124.5, 123.5, 64.7, 51.1, 38.9, 35.9, 31.7, 30.6, 28.6, 26.8, 24.1, 21.0, 8.9 ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>26</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 297.1825, found: 297.1828.



5-(1-Propyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3c**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (63 mg, 55%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.20-7.08 (m, 3H), 7.08-7.00 (m, 1H), 4.01 (t, *J* = 6.8 Hz, 2H), 2.93-2.78 (m, 2H), 2.01 (s, 3H), 1.92 (t, *J* = 7.2 Hz, 2H), 1.68-1.53 (m, 4H), 1.52-1.41 (m, 2H), 1.33-1.21 (m, 4H), 1.20-1.07 (m, 2H), 0.85 (t,

J = 7.3 Hz, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta = 171.2$ , 150.0, 143.8, 126.2, 125.8, 124.5, 123.4, 64.7, 50.9, 42.1, 39.5, 36.5, 30.6, 28.6, 26.8, 24.2, 21.0, 17.7, 14.9 ppm. HRMS (ESI): calcd. for C<sub>19</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 311.1982, found: 311.1986.



5-(1-Isopropyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3d**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (53 mg, 46%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.21-7.07 (m, 3H), 7.07-6.98 (m, 1H), 3.98 (t, *J* = 6.7 Hz, 2H), 2.91-2.78 (m, 2H), 2.08-1.95 (m, 2H), 2.01 (s, 3H), 1.78-1.68 (m, 1H), 1.66-1.60 (m, 1H), 1.59-1.48 (m, 3H), 1.33-1.12 (m, 3H), 1.10-0.98 (m,

1H), 0.89 (d, J = 6.7 Hz, 3H), 0.69 (d, J = 6.8 Hz, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta = 171.2$ , 148.7, 144.3, 126.1, 125.7, 124.3, 123.9, 64.7, 54.7, 38.9, 34.6, 31.4, 31.1, 28.6, 26.8, 23.9, 21.0, 18.3, 17.7 ppm. HRMS (ESI): calcd. for C<sub>19</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 311.1982, found: 311.1990.



5-(1-Cyclohexyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3e**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (76 mg, 58%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.12-7.00 (m, 3H), 6.98-6.91 (m, 1H), 3.91 (t, *J* = 6.7 Hz, 2H), 2.82-2.72 (m, 2H), 2.04-1.96 (m, 1H), 1.94 (s, 3H), 1.80-1.62 (m, 3H), 1.61-1.41 (m, 7H), 1.31-0.93 (m, 8H), 0.91-0.75 (m, 2H).<sup>13</sup>C NMR

(101 MHz, Chloroform-*d*): δ= 171.2, 148.6, 144.3, 126.1, 125.6, 124.3, 124.1, 64.7, 54.5, 45.4, 38.6, 32.6, 31.3, 28.6, 27.9, 27.6, 27.1, 26.9, 26.8, 26.7, 23.8, 21.0 ppm. HRMS (ESI): calcd. for C<sub>22</sub>H<sub>32</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>:351.2295, found: 351.2292.



5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)hexyl acetate (**3f**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (64 mg, 58%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.14-6.99 (m, 4H), 3.95 (t, *J* = 6.7 Hz, 2H), 2.86-2.73 (m, 2H), 1.98-1.88 (m, 1H), 1.96 (s, 3H), 1.81-1.69 (m, 1H), 1.58-1.46 (m, 3H), 1.46-1.37 (m, 1H), 1.27-1.09 (m, 6H), 1.15 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 151.6, 143.2, 126.2, 126.1, 124.5, 122.6, 64.6, 47.3, 41.3, 38.6,

 $30.3,\,30.0,\,28.6,\,26.8,\,25.9,\,24.8,\,21.0 \text{ ppm. HRMS (ESI): calcd. for } C_{18}H_{26}NaO_2 \text{ [M+Na]}^+: 297.1825,\,found:\,297.1827.$ 



5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)heptyl acetate (**3g**) was isolated through column chromatography on with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (58 mg, 50%).<sup>1</sup>H NMR: (400 MHz, Chloroform-d)  $\delta$ = 7.14-6.97 (m, 4H), 3.96 (t, *J* = 6.8 Hz, 2H), 2.85-2.72 (m, 2H), 1.99-1.88 (m, 1H), 1.96 (s, 3H), 1.80-1.67 (m, 1H), 1.60-1.35 (m, 4H), 1.28-1.06 (m, 8H), 1.15 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ =

171.3, 151.7, 143.2, 126.2, 126.1, 124.5, 122.6, 64.6, 47.3, 41.4, 38.6, 30.3 (2C), 29.2, 28.6, 26.8, 25.9, 24.9, 21.1 ppm. HRMS (ESI): calcd. for C<sub>19</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 311.1982, found: 311.1985.



5-(4-Chloro-1-methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3h**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (76 mg, 65%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.16-7.06 (m, 2H), 6.99-6.94 (m, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 2.97-2.86 (m, 2H),2.08-1.98 (m, 1H), 2.03 (s, 3H), 1.89-1.79 (m, 1H), 1.63-1.55 (m, 3H), 1.54-1.45 (m, 1H), 1.37-1.25 (m, 3H), 1.23 (s,

3H), 1.20-1.11 (m, 1H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.2, 153.6, 141.3, 130.6, 127.9, 126.3, 120.9, 64.6, 48.6, 41.4, 37.7, 29.6, 28.6, 27.0, 26.6, 24.6, 21.0 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>23</sub>ClNaO<sub>2</sub> [M+H]<sup>+</sup>: 317.1279, found: 317.1278.



5-(5-Methoxy-1-methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3i**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (60 mg, 52%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 6.98 (d, *J* = 8.1 Hz, 1H), 6.77-6.67 (m, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 2.89-2.79 (m, 2H), 2.09-1.94 (m, 1H), 2.03 (s, 3H), 1.88-1.78 (m, 1H), 1.68-1.42 (m,

4H), 1.36-1.24 (m, 4H), 1.20 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 158.6, 144.7, 143.7, 123.1, 112.0, 109.8, 64.7, 55.4, 46.6, 41.5, 39.0, 30.4, 28.6, 27.0, 26.7, 24.7, 21.0 ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>26</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>:313.1774, found: 313.1780.



5-(6-Fluoro-1-methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (3**j**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (59 mg, 53%).<sup>1</sup>H NMR: (400 MHz, Chloroform-d)  $\delta$ = 6.99 (m, 1H), 6.91-6.74 (m, 2H), 4.02 (t, *J* = 6.7 Hz, 3H), 2.90-2.72 (m, 2H), 2.09-1.94 (m, 1H), 2.03 (s, 3H), 1.89-1.79 (m, 1H), 1.66-1.51 (m, 3H), 1.53-1.41 (m, 1H), 1.35-1.25 (m, 3H), 1.21 (s,

3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-d):  $\delta$ = 171.2, 161.9 (d, *J* = 242.3 Hz), 146.9 (d, *J* = 2.3 Hz), 145.2 (d, *J* = 7.9 Hz), 123.4 (d, *J* = 8.9 Hz), 112.9 (d, *J* = 22.3 Hz), 111.3 (d, *J* = 21.5 Hz), 64.6, 46.7, 41.4, 38.9, 30.6, 30.2, 28.6, 27.0, 26.7, 24.6, 21.0 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>24</sub>FO<sub>2</sub> [M+H]<sup>+</sup>: 279.1755, found: 279.1758.



5-(1-Methyl-5-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3k**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (80 mg, 61%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.49-7.39 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 4.04 (t, *J* = 6.7 Hz, 2H), 3.00-2.87

(m, 2H), 2.16-1.99 (m, 1H), 2.04 (s, 3H), 1.95-1.81 (m, 1H), 1.69-1.46 (m, 4H), 1.38-1.30 (m, 3H), 1.28-1.18 (m, 1H), 1.26 (s, 3H) ppm.  $^{13}$ C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 155.6, 143.9, 128.6 (q, *J* = 31.3 Hz), 123.4 (q, *J* = 273.7 Hz), 123.5 (q, *J* = 4.2 Hz), 122.8, 121.4 (q, *J* = 4.2 Hz), 64.6, 47.4, 41.0, 38.5, 30.1, 28.5, 26.7, 26.6, 24.5, 21.0 ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>24</sub>F<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 329.1723, found: 329.1722.



5-(5-Fluoro-1-methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3**I) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (64 mg, 58%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.02 (dd, *J* = 8.2, 5.3 Hz, 1H), 6.79-6.62 (m, 2H), 3.95 (t, *J* = 6.7 Hz, 2H), 2.82-2.65 (m, 2H), 2.01-1.91 (m, 1H), 1.96 (s, 3H), 1.85-1.71 (m, 1H), 1.58-1.37 (m, 4H), 1.31-1.16 (m, 4H), 1.14 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 162.1 (d, *J*= 243.4 Hz), 153.8 (d, *J*= 7.1 Hz), 138.3 (d, *J*= 2.0 Hz), 125.2 (d, *J*= 8.1 Hz), 112.9 (d, *J*= 22.2Hz), 109.6 (d, *J*= 22.2Hz), 64.6, 47.6, 41.2, 39.0, 29.6, 28.6, 26.72, 26.66, 24.5, 21.0 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>24</sub>FO<sub>2</sub> [M+H]<sup>+</sup>: 279.1755, found: 279.1757.



5-(1-Methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-yl)pentyl acetate (**3m**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (50 mg, 40%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 8.10 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.87-7.81 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.49-7.35 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 3.96 (t, *J* = 6.7 Hz, 2H), 3.05-2.90 (m, 2H), 2.29-2.15 (m, 1H), 2.10-2.02

(m, 1H), 1.99 (s, 3H), 1.97-1.79 (m, 2H), 1.57-1.47 (m, 2H), 1.54 (s, 3H), 1.36-1.24 (m, 3H), 1.12-1.00 (m, 1H) ppm. <sup>13</sup>C

NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 143.9, 141.2, 133.6, 130.4, 129.2, 127.6, 125.5, 124.2, 123.6, 123.6, 64.7, 49.9, 41.5, 39.3, 31.1, 28.5, 27.9, 26.7, 24.8, 21.0 ppm. HRMS (ESI): calcd. for C<sub>21</sub>H<sub>26</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>:333.1825, found: 333.1833.



5-(1,3-Dimethylindolin-3-yl)pentyl acetate (**3n**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (67 mg, 61%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.09 (td, *J* = 7.6, 1.3 Hz, 1H), 6.96 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.18 (d, *J* = 8.6 Hz, 1H), 2.97 (d, *J* = 8.7 Hz, 1H), 2.74 (s, 3H), 2.02 (s, 3H), 1.67-1.50

(m, 3H), 1.44-1.16 (m, 5H), 1.27 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.2, 152.3, 138.1, 127.5, 122.1, 117.6, 107.2, 68.3, 64.6, 43.6, 40.3, 35.9, 28.5, 26.6, 25.4, 24.4, 21.0 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>25</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>: 298.1778, found: 298.1786.



5-(3-Methyl-1-(2-methylallyl)indolin-3-yl)pentyl acetate (**30**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (57 mg, 57%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.05 (td, *J* = 7.7, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.65 (td, *J* = 7.3, 1.0 Hz, 1H), 6.44 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.01-4.79 (m, 2H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.68-3.47 (m, 2H), 3.19 (d, *J* = 8.8

Hz, 1H), 2.99 (d, J = 8.9 Hz, 1H), 2.02 (s, 3H), 1.76 (s, 3H), 1.65-1.49 (m, 3H), 1.44-1.10 (m, 5H), 1.27 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta = 171.3$ , 151.6, 142.4, 137.5, 127.4, 122.3, 117.1, 111.9, 106.6, 65.7, 64.6, 55.4, 43.4, 40.7, 28.6, 26.6, 25.9, 24.5, 21.0, 20.4 ppm. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>30</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:316.2271, found: 316.2271.



5-(1-Benzyl-3-methylindolin-3-yl)pentyl acetate (**3p**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (70 mg, 50%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.43-7.35 (m, 2H), 7.36-7.28 (m, 2H), 7.30-7.20 (m, 2H), 7.21-7.12 (m, 1H), 7.13-7.04 (m, 1H), 7.01-6.93 (m, 1H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.74-3.46 (m, 4H), 2.66-2.52 (m, 1H), 2.37-2.22 (m, 1H),

2.03 (s, 3H), 1.84-1.71 (m, 1H), 1.58-1.47 (m, 3H), 1.30-1.16 (m, 2H), 1.21 (s, 3H) ppm.  $^{13}$ C NMR (101 MHz, Chloroformd):  $\delta$ = 171.3, 143.5, 138.9, 134.5, 128.9 (2C), 128.2, 127.0, 126.3 (2C), 126.1, 125.4, 64.7, 62.9, 61.3, 57.7, 41.9, 38.2, 28.6, 27.1, 26.7, 24.0, 21.1 ppm. HRMS (ESI): calcd. for C<sub>23</sub>H<sub>30</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:352.2271, found: 352.2274.



5-(2,4-Dimethyl-1,2,3,4-tetrahydroisoquinolin-4-yl)pentyl acetate (**3q**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (75 mg, 65%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 7.09 (td, *J* = 7.3, 1.4 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.67-3.32 (m, 2H), 2.52 (d, *J* = 11.3 Hz, 1H), 2.39 (s, 3H), 2.29 (d, *J* = 11.3 Hz, 1H), 2.02 (s, 3H), 1.78-1.67 (m, 1H), 1.65-1.47 (m, 3H), 1.37-1.24 (m, 3H), 1.26 (s, 3H),

1.22-1.11 (m, 1H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 142.7, 134.4, 126.3, 126.2, 126.1, 125.4, 64.63, 64.59, 59.3, 46.6, 42.1, 38.0, 28.6, 27.8, 26.7, 24.1, 21.0 ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>27</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>:312.1934, found: 312.1942.



5-(4-Methyl-2-(2-methylallyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)pentyl acetate (**3r**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (99 mg, 70%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.24 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.16 (td, *J* = 7.4, 1.5 Hz, 1H), 7.09 (td, *J* = 7.4, 1.4 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.01-4.83 (m, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 3.64-3.40 (m, 2H), 3.08-2.87 (m, 2H), 2.62-2.46 (m, 1H), 2.32-2.18 (m, 1H), 2.02 (s, 3H), 1.82-1.70 (m, 4H), 1.64-1.51 (m, 3H), 1.33-

1.24 (m, 3H), 1.25 (s, 3H), 1.20-1.08 (m, 1H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.2, 143.4, 143.1, 134.7, 126.3, 126.2, 126.1, 125.3, 113.1, 65.5, 64.7, 61.5, 57.7, 42.0, 38.1, 28.6, 27.5, 26.7, 24.1, 21.0, 20.8 ppm. HRMS (ESI): calcd. for C<sub>21</sub>H<sub>31</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>:352.2247, found: 352.2255.



5-(2-Benzyl-4-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)pentyl acetate (**3s**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (74 mg, 51%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.42-7.36 (m, 2H), 7.36-7.29 (m, 2H), 7.29-7.21 (m, 2H), 7.19-7.13 (m, 1H), 7.11-7.05 (m, 1H), 7.01-6.93 (m, 1H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.71-3.62 (m, 2H), 3.61-3.51 (m, 2H), 2.59 (d, *J* = 11.3 Hz, 1H), 2.27 (d, *J* = 11.3 Hz, 1H), 2.03 (s, 3H), 1.83-1.72 (m, 1H), 1.59-1.44 (m, 3H), 1.31-1.15 (m, 3H),

1.21(s, 3H), 1.04-0.89 (m, 1H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 171.3, 143.5, 138.9, 134.5, 128.9 (2C), 128.2 (2C), 127.0, 126.3 (2C), 126.1, 125.4, 64.7, 62.9, 61.3, 57.7, 41.9, 38.2, 28.6, 27.1, 26.7, 24.0, 21.1 ppm. HRMS (ESI): calcd. for C<sub>24</sub>H<sub>31</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>:388.2247, found: 388.2254.



5-(4-Methyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-4-yl)pentyl acetate (**3t**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (105 mg, 61%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.80-7.68 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27-7.08 (m, 3H), 7.00 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.47-3.86 (m, 4H), 3.34 (d, *J* = 11.5 Hz, 1H), 2.73 (d, *J* = 11.5 Hz, 1H), 2.43 (s, 3H), 2.03 (s, 3H), 1.83-1.71 (m, 1H), 1.66-1.54 (m, 3H), 1.36-1.18 (m, 4H), 1.27 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):

 $\delta$ = 174.7, 147.1, 145.4, 136.3, 134.2, 133.2 (2C), 131.2 (2C), 130.4, 129.7, 129.5 (2C), 68.0, 56.7, 51.8, 44.5, 41.5, 31.9, 29.9, 29.1, 27.2, 24.9, 24.5 ppm. HRMS (ESI): calcd. for C<sub>24</sub>H<sub>31</sub>NNaO4S [M+Na]<sup>+</sup>:452.1866, found: 452.1873.

Me ( )

4-(6-Fluorohexyl)-4-methylisochromane (**3u**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (62 mg, 62%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.29-7.24 (m, 1H), 7.23-7.17 (m, 1H), 7.13 (td, *J* = 7.4, 1.5 Hz, 1H), 6.99-6.90 (m, 1H), 4.77 (s, 2H), 4.52-4.40 (m, 1H), 4.38-4.27 (m, 1H), 3.80 (d, *J* = 11.2 Hz, 1H), 3.54 (d, *J* = 11.3 Hz, 1H), 1.77-1.49 (m, 4H), 1.42-1.10 (m, 6H), 1.21 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz,

Chloroform-*d*):  $\delta$ = 142.0, 133.9, 126.6, 125.9, 125.7, 124.0, 84.9, 83.4, 74.6, 68.9, 40.8, 36.4 (d, *J* = 20.2Hz), 30.3, 29.9, 25.1 (d, *J* = 5.1Hz), 24.6 (d, *J* = 56 Hz) ppm. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>24</sub>FO [M+H]<sup>+</sup>:251.1806, found: 251.1805.



3u

*1-Methyl-1-nonyl-2,3-dihydro-1H-indene* (**3v**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (75 mg, 73%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.22-7.06 (m, 4H), 2.91-2.77 (m, 2H), 2.10-1.94 (m, 1H), 1.87-1.75 (m, 1H), 1.62-1.42 (m, 2H), 1.38-1.12 (m, 13H), 1.22 (s, 3H), 0.93-0.77 (m, 4H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 151.8, 143.2, 126.13,126.10, 124.5, 122.7, 47.4, 41.5, 38.6, 31.9, 30.5, 30.3, 29.7(2C), 29.4, 26.8, 24.9, 22.7, 14.2

ppm. HRMS (ESI): calcd. for  $C_{19}H_{31}$  [M+H]<sup>+</sup>:259.2420, found: 259.2426.



5-Methoxy-1-methyl-1-(5-phenylpentyl)-2,3-dihydro-1H-indene (**3w**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (80 mg, 65%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.20-7.15 (m, 2H), 7.13-7.03 (m, 3H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.69-6.59 (m, 2H), 3.70 (s, 3H), 2.79-2.72 (m, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 1.98-1.88 (m, 1H), 1.79-1.69 (m, 1H), 1.56-1.44 (m,

3H), 1.42-1.33 (m, 1H), 1.28-1.17 (m, 4H), 1.12 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 158.5, 144.7, 143.9, 142.9, 128.4 (2C), 128.2 (2C), 125.6, 123.1, 112.0, 109.8, 55.4, 46.6, 41.6, 39.0, 36.0, 31.5, 30.4, 30.1, 27.0, 24.8 ppm. HRMS (ESI): calcd. for C<sub>22</sub>H<sub>29</sub>O [M+H]<sup>+</sup>:309.2213, found: 309.2221.



*1-(3-Ethylheptyl)-1-methyl-2,3-dihydro-1H-indene* (**3x**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (73 mg, 71%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.22-7.04 (m, 4H), 2.93-2.80 (m, 2H), 2.07-1.95 (m, 1H), 1.87-1.74 (m, 1H), 1.62-1.40 (m, 2H), 1.32-1.10 (m, 14H), 0.92-0.83 (m, 3H), 0.84-0.74 (m, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 151.9, 143.1, 126.1(2C), 124.5, 122.6, 47.34, 39.40(39.36),

38.30(38.27), 38.00(37.98), 32.90(32.82), 30.3, 29.1(28.98), 27.84(27.80), 26.83(26.80), 25.89(25.77), 23.17, 14.22, 10.99(10.86) ppm. Inside the brackets are the chemical shifts of another diastereomer. HRMS (ESI): calcd. for  $C_{19}H_{31}$  [M+H]<sup>+</sup>:259.2420, found: 259.2426.



4-(1-Methyl-2,3-dihydro-1H-inden-1-yl)butan-1-ol (**3y**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 10:1) as a colorless oil (42 mg, 51%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.23-7.05 (m, 4H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.92-2.81 (m, 2H), 2.06-1.96 (m, 1H), 1.89-1.76 (m, 1H), 1.67-1.57 (m, 1H), 1.57-1.47 (m, 3H), 1.44-1.32 (m, 1H), 1.31-1.19 (m, 2H), 1.24(s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-d):  $\delta$ = 151.5, 143.2, 126.2,

126.2, 124.5, 122.6, 62.9, 47.3, 41.2, 38.6, 33.5, 30.3, 26.8, 21.2 ppm. HRMS (ESI): calcd. for  $C_{14}H_{20}NaO^+$  [M+Na]:227.1406, found: 227.1405.



4,4,5,5-*Tetramethyl*-2-(4-(1-*methyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*butyl*)-1,3,2-*dioxaborolane* (**3z**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (53 mg, 42%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.21-7.04 (m, 4H), 2.92-2.80 (m, 2H), 2.06-1.91 (m, 1H), 1.86-1.74 (m, 1H), 1.64-1.56 (m, 1H), 1.54-1.44 (m, 1H), 1.41-1.24 (m, 5H), 1.23-1.19(m, 2H), 1.21 (s, 12H), 0.80-0.70 (m, 2H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):

 $\delta$ = 151.8, 143.2, 126.07, 126.06, 124.4, 122.7, 82.9, 47.3, 41.2, 38.6, 30.3, 27.6, 26.9, 24.8 (7C) ppm. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>32</sub>BO<sub>2</sub> [M+H]<sup>+</sup>:315.2490, found: 315.2492.



5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3aa**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (69 mg, 67%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.23-7.05 (m, 4H), 4.81 (t, *J* = 4.8 Hz, 1H), 3.99-3.89 (m, 2H), 3.87-3.78 (m, 2H), 2.94-2.79 (m, 2H), 2.07-1.95 (m, 1H), 1.86-1.76 (m, 1H), 1.68-1.56 (m, 3H), 1.55-1.46 (m, 1H), 1.42-1.31 (m,

3H), 1.28-1.16 (m, 1H), 1.22 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 151.6, 143.2, 126.2, 126.1, 124.5, 122.6, 104.6, 64.8 (2C), 47.3, 41.3, 38.5, 33.9, 30.3, 26.8, 24.9, 24.8 ppm. HRMS (ESI): calcd. for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub> [M+H]<sup>+</sup>:261.1849, found: 240.261.1850.



3ab

*1-(5-Methoxypentyl)-1-methyl-2,3-dihydro-1H-indene* (**3ab**) was isolated through column chromatography on silica gel to the mixture eluent of ethyl acetate and petroleum ether (50:1) as a colorless oil (53 mg, 57%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.22-7.05 (m, 4H), 3.38-3.28 (m, 2H), 3.31(s, 3H), 2.92-2.81 (m, 2H), 2.06-1.95 (m, 1H), 1.88-1.74 (m, 1H), 1.61-1.44 (m, 4H), 1.36-1.26 (m, 3H), 1.24-1.13 (m, 1H), 1.22(s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ =

151.6, 143.2, 126.2, 126.1, 124.5, 122.6, 72.9, 58. 5, 47.3, 41.4, 38.6, 30.3, 29.6, 26.9, 26.8, 24.8 ppm. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>25</sub>O [M+H]<sup>+</sup>:233.1900, found: 233.1899.



2-(5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)pentyl)isoindoline-1,3-dione (**3ac**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (10:1) as a colorless oil (69 mg, 50%).<sup>1</sup>H NMR: (400 MHz, Chloroformd)  $\delta$ = 7.76 (dd, J = 5.4, 3.1 Hz, 2H), 7.63 (dd, J = 5.5, 3.0 Hz, 2H), 7.13-6.93 (m, 4H), 3.58 (t, J = 7.3 Hz, 2H), 2.85-2.71 (m, 2H), 2.00-1.85 (m, 1H), 1.78-1.68 (m, 1H), 1.62-1.55 (m, 2H), 1.52-1.34

(m, 2H), 1.30-1.17 (m, 4H), 1.14 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 168.5 (2C), 151.5, 143.1, 133.9 (3C), 132.2, 126.2, 126.1, 124.5, 123.2 (2C), 122.6, 47.3, 41.2, 38.5, 38.1, 30.3, 28.6, 27.6, 26.8, 24.5 ppm. HRMS (ESI): calcd. for C<sub>23</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:348.1958, found: 348.1955.



6-(1-Methyl-2,3-dihydro-1H-inden-1-yl)hexanenitrile (**3ad**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a colorless oil (55 mg, 60%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.16-7.04 (m, 3H), 7.05-6.98 (m, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.27-2.17 (m, 2H), 1.98-1.87 (m, 1H), 1.81-1.70 (m, 1H), 1.60-1.49 (m, 3H), 1.48-1.39 (m, 1H), 1.38-1.29 (m, 2H), 1.29-1.21 (m, 1H), 1.20-1.09

(m, 1H), 1.16(s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 143.2, 126.3, 126.2, 124.6 (2C), 122.6, 47.2, 41.1, 38.5, 30.3, 29.4 (2C), 26.9, 25.3, 24.2, 17.1 ppm. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>22</sub>N [M+H]<sup>+</sup>:228.1747, found: 228.1736.



*Methyl-1-(5-(1,3-dioxoisoindolin-2-yl)pentyl)-1-methyl-2,3-dihydro-1H-indene-5carboxylate* (**3ae**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (10:1) as a yellow oil (92 mg, 57%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.87-7.78 (m, 3H), 7.76-7.66 (m, 3H), 7.24-

7.18 (m, 1H), 3.90 (s, 3H), 3.65 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.3 Hz, 2H), 2.09-1.97 (m, 1H), 1.90-1.80 (m, 1H), 1.79-1.55 (m, 4H), 1.55-1.43 (m, 1H), 1.38-1.12 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta = 168.4$  (2C), 167.5, 151.9, 149.0, 133.8 (2C), 132.1(2C), 128.4, 128.1, 124.4, 123.8, 123.1 (2C), 51.9, 47.2, 41.2, 38.4, 37.9, 30.5, 28.5, 27.5, 26.8, 24.5 ppm. HRMS (ESI): calcd. for C<sub>25</sub>H<sub>28</sub>NO<sub>4</sub> [M+H]<sup>+</sup>:406.2013, found: 406.2020.



*Ethyl 7-(1-methyl-2,3-dihydro-1H-inden-1-yl)heptanoate* (**3af**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (73 mg, 63%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.15-6.98 (m, 4H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.87-2.74 (m, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.98-1.87 (m, 1H), 1.78-1.68 (m, 1H), 1.56-1.46 (m, 3H), 1.45-1.35 (m, 1H), 1.27-1.08 (m, 9H), 1.15(s, 3H)

ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$ = 173.9, 151.7, 143.2, 126.2, 126.1, 124.5, 122.6, 60.2, 47.3, 41.4, 38.6, 34.4, 30.3, 30.1, 29.2, 26.8, 25.0, 24.8, 14.3 ppm. HRMS (ESI): calcd. for C<sub>19</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>:311.1982, found: 311.1989.



5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)pentyl acetate (**3ag**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (74 mg, 53%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 10.51 (d, *J* = 0.8 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.56-7.47 (m, 1H), 7.22-7.06 (m, 4H), 7.04-6.92 (m, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 2.93-2.80 (m, 2H), 2.07-1.95 (m, 1H), 1.88-1.76 (m,

3H), 1.68-1.39 (m, 5H), 1.40-1.23 (m, 5H), 1.23 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*): δ= 189.9, 161.6, 151.7, 143.2, 135.9, 128.2, 126.2, 126.1, 124.9, 124.5, 122.6, 120.5, 112.5, 68.5, 47.3, 41.4, 38.6, 30.32, 30.30, 29.3, 29.1, 26.8, 26.1, 24.9 ppm. HRMS (ESI): calcd. for C<sub>24</sub>H<sub>30</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>:373.2138, found: 373.2143.



(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 7-(1,3-dimethylindolin-3-yl)heptanoate (**3ah**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (104 mg, 63%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.01 (td, *J* = 7.7, 1.3 Hz, 1H), 6.89 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.61 (td, *J* = 7.3, 1.0 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 4.60 (td, *J* = 10.9, 4.3 Hz, 1H), 3.10 (d, *J* = 8.6 Hz, 1H), 2.90 (d, *J* = 8.6 Hz, 1H), 2.67 (s, 3H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.94-1.87 (m, 1H),

1.85-1.71 (m, 1H), 1.66-1.40 (m, 6H), 1.34-1.08 (m, 10H), 1.03-0.85 (m, 2H), 0.84-0.78 (m, 8H), 0.67 (d, J = 7.0 Hz, 3H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta = 173.5$ , 152.3, 138.3, 127.4, 122.2, 117.6, 107.2, 73.9, 68.3, 47.0, 43.6, 40.9, 40.3, 36.0, 34.7, 34.3, 31.4, 29.9, 29.1, 26.2, 25.4, 25.1, 24.6, 23.4, 22.1, 20.8, 16.3 ppm. HRMS (ESI): calcd. for C<sub>27</sub>H<sub>44</sub>NO<sub>2</sub> [M+H]<sup>+</sup>:414.3367, found: 414.3373.



(8R,9S,13S,14S)-13-Methyl-3-((7-(1-methyl-2,3-dihydro-1H-inden-1-yl)heptyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3ai**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (100 mg, 55%).<sup>1</sup>H NMR: (400 MHz, Chloroform-d)  $\delta$ = 7.22-7.04 (m, 5H), 6.70 (dd, J = 8.6, 2.8 Hz, 1H), 6.63 (d,

 $J = 2.7 \text{ Hz}, 1\text{H}, 3.90 \text{ (t}, J = 6.6 \text{ Hz}, 2\text{H}, 2.94-2.81 \text{ (m}, 4\text{H}), 2.56-2.44 \text{ (m}, 1\text{H}), 2.43-2.35 \text{ (m}, 1\text{H}), 2.30-2.19 \text{ (m}, 1\text{H}), 2.21-2.09 \text{ (m}, 1\text{H}), 2.11-1.91 \text{ (m}, 3\text{H}), 1.87-1.77 \text{ (m}, 1\text{H}), 1.77-1.68 \text{ (m}, 2\text{H}), 1.68-1.50 \text{ (m}, 5\text{H}), 1.54-1.36 \text{ (m}, 6\text{H}), 1.36-1.24 \text{ (m}, 6\text{H}), 1.22 \text{ (s}, 3\text{H}), 0.90 \text{ (s}, 3\text{H}) \text{ ppm}. {}^{13}\text{C} \text{ NMR} \text{ (101 MHz}, \text{Chloroform-}d): \delta = 157.1, 151.7, 143.2, 137.7, 131.8, 126.3, 126.13, 126.09, 124.5, 122.6, 114.5, 112.1, 67.9, 50.4, 48.1, 47.3, 43.9, 41.4, 38.5, 38.4, 35.9, 31.6, 30.4, 30.3, 29.7 \text{ (2C)}, 29.4, 29.3, 26.8, 26.6, 26.1, 25.9, 24.9, 21.6, 13.9 \text{ ppm}. \text{HRMS} \text{ (ESI): calcd. for } C_{35}\text{H}_47\text{O}_2 \text{ [M+H]}^+:499.3571, \text{ found: } 499.3578.$ 



8-(1-methyl-2,3-dihydro-1H-inden-1-yl)oct-7-en-1-yl acetate (**3aj**) were isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of ethyl acetate and petroleum ether (20:1) as a yellow oil (19 mg, 32%).<sup>1</sup>H NMR: (400 MHz, Chloroform-*d*)  $\delta$ = 7.17-7.04 (m, 3H), 7.03-6.96 (m, 1H), 5.57-5.39 (m, 1H), 5.27-4.92 (m, 1H), 4.02-3.89 (m, 2H), 2.85-2.75 (m, 2H), 2.06-1.90 (m, 2H), 2.03 (s, 3H), 1.88-1.78 (m,

1H), 1.59-1.45 (m, 2H), 1.33-1.09 (m, 8H), 0.91-0.84 (m, 2H) ppm. <sup>13</sup>C NMR (101 MHz, Chloroform-*d*):  $\delta$  (major isomer)= 171.2, 150.52, 143.21, 138.1, 136.52, 132.8, 126.22, 124.5, 123.27, 64.6, 49.35, 40.9, 36.64, 32.4, 30.1, 29.4, 28.62, 25.88, 23.74, 21.00 ppm;  $\delta$  (minor isomer)= 171.2, 150.47, 143.19, 138.1, 136.64, 132.8, 126.33, 124.5, 123.25, 64.6, 49.43, 40.94, 36.72, 32.4, 30.1, 29.4, 28.70, 25.73, 23.61, 21.07 ppm. HRMS (ESI): calcd. for C<sub>20</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 323.1982, found: 323.1984.

### **Unsuccessful Substrates:**



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### <sup>1</sup>H and <sup>13</sup>C NMR Spectra



![](_page_15_Figure_0.jpeg)

![](_page_16_Figure_0.jpeg)

![](_page_17_Figure_0.jpeg)

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

![](_page_18_Figure_0.jpeg)

3b

![](_page_18_Figure_2.jpeg)

![](_page_19_Figure_0.jpeg)

110 100 f1 (ppm) 50 -10 

![](_page_20_Figure_0.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

110 100 f1 (ppm) 50 -10

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_23_Figure_1.jpeg)

![](_page_24_Figure_0.jpeg)

![](_page_25_Figure_0.jpeg)

![](_page_25_Figure_1.jpeg)

![](_page_26_Figure_0.jpeg)

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![](_page_32_Figure_0.jpeg)

![](_page_33_Figure_0.jpeg)

![](_page_34_Figure_0.jpeg)

![](_page_35_Figure_0.jpeg)




110 100 f1 (ppm) -10 



































3r



















3u







110 100 90 f1 (ppm) -10 





|          |     |     |     |     | · · · | 1 1 | 1 1 | - I - I |     |     |     |    |    |    | 1  |    |    |    |    | 1  |   |     | - |
|----------|-----|-----|-----|-----|-------|-----|-----|---------|-----|-----|-----|----|----|----|----|----|----|----|----|----|---|-----|---|
| 210      | 200 | 190 | 180 | 170 | 160   | 150 | 140 | 130     | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 | -10 |   |
| f1 (ppm) |     |     |     |     |       |     |     |         |     |     |     |    |    |    |    |    |    |    |    |    |   |     |   |







110 100 90 f1 (ppm) 160 150 130 120 -10 210 200 







110 100 90 f1 (ppm)  $\frac{1}{70}$ -10 







130 120 110 100 90 80 f1 (ppm) -10 





110 100 90 f1 (ppm) 130 120  $\frac{1}{70}$ -10 



3ab







3ab



110 100 90 f1 (ppm) 130 120 -10


3ac















130 120 110 100 90 80 f1 (ppm) -10 









110 100 90 f1 (ppm) -10 





















HPLC (Chiralpak IB): t<sub>R</sub>= 11.8 (major), 13.5 (minor) Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



HPLC (Chiralpak IB): t<sub>R</sub>= 18.3, 20.4

Condition: 96:4 n-Hexane: i-PrOH, flow rate 0.5 mL/min, 25 °C.



HPLC (Chiralpak IF):  $t_R$ = 14.1, 15.6 Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.