

## Electronic Supplementary Information

### Chiral *N,N'*-Dioxide/Sc(OTf)<sub>3</sub> Complex Catalyzed Asymmetric

### Dearomatization of $\beta$ -Naphthols

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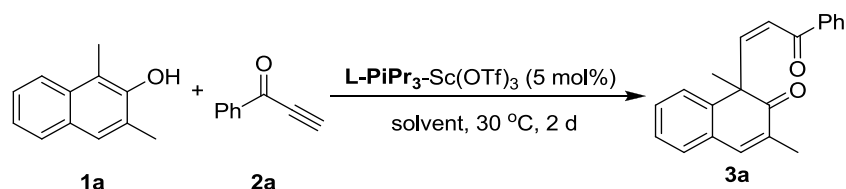
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## 1. General remarks

Reactions were carried out using commercially available reagents in oven-dried apparatus. DCE was dried over  $\text{Na}_2\text{SO}_4$  and distilled just before use. Enantiomeric excess (ee) were determined by HPLC analysis using the corresponding commercially chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 nm. Optical rotations were reported as follows:  $[\alpha]_{\text{D}}^{\text{T}}$  (c g/100 ml, in solvent).  $^1\text{H}$  NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Spectra were reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.  $^{13}\text{C}$  NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard.

## 2. Optimization of reaction conditions

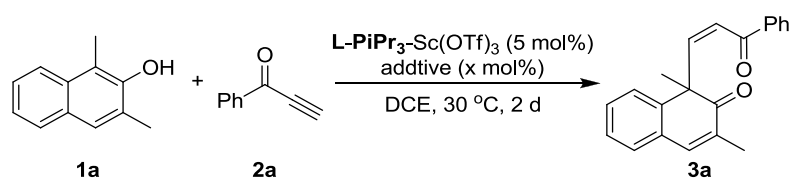
**Table 1. Optimization of condition for solvent.**



Entry <sup>a</sup>	Solvent	Conversion (%) <sup>b</sup>	Z/E <sup>b</sup>	ee (%) <sup>c</sup>
1	CH <sub>2</sub> Cl <sub>2</sub> (DCM)	94	4.5:1	85
2	ClCH <sub>2</sub> CH <sub>2</sub> Cl (DCE)	98	7.3:1	90
3	CCl <sub>3</sub> CH <sub>3</sub>	82	5.1:1	82
4	Cl <sub>2</sub> CHCHCl <sub>2</sub>	81	1.8:1	71
5	ethyl acetate	72	2.8:1	51
6	THF	65	1.4:1	34
7	Toluene	76	2.3:1	72

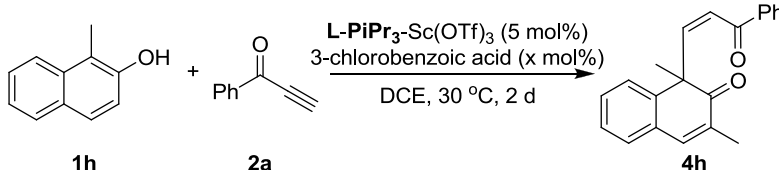
<sup>a</sup> Unless otherwise noted, all reactions were performed with **L-PiPr<sub>3</sub>-Sc(OTf)<sub>3</sub>** (5 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.10 mmol) in solvent (1.5 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture. <sup>c</sup> ee value of major isomer was analyzed by HPLC.

**Table 2. The effect of additive.**



Entry <sup>a</sup>	additive	x	conversion [%] <sup>b</sup>	Z/E <sup>b</sup>	ee [%] <sup>c</sup>
1	-	-	98	7.3:1	90
2	benzoic acid	5	98	>20:1	94
3	benzyl alcohol	5	99	>20:1	93
4	acetic acid	5	99	>20:1	90
5	HCl	5	65	>20:1	96
6	3-chorobenzoic acid	5	85 <sup>d</sup>	>20:1	97
7	3-chorobenzoic acid	2.5	90 <sup>d</sup>	>20:1	97
8	3-chorobenzoic acid	1.25	93 <sup>d</sup>	>20:1	96

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L-PiPr<sub>3</sub>-Sc(OTf)<sub>3</sub>** (5 mol%, 1:1), **1a** (0.10 mmol), **2a** (0.10 mmol) in DCE (1.5 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture. <sup>c</sup> ee value of Z isomer was analyzed by HPLC. <sup>d</sup> Yield of the isolated of Z adduct.

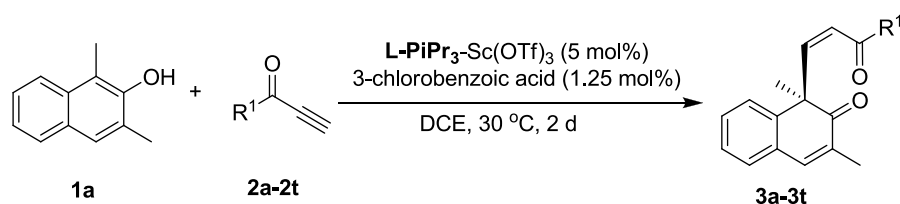
**Table 3. The effect of additive in the dearomatization of 1-methyl-2-naphthol.**

Entry <sup>a</sup>	x	conversion [%] <sup>b</sup>	Z/E <sup>b</sup>	ee [%] <sup>c</sup>
1	1.25	64	75/25	53
2	2.5	54	82/18	66
3	5	32	82/18	65

<sup>a</sup> Unless otherwise noted, all reactions were performed with **L-PiPr<sub>3</sub>-Sc(OTf)<sub>3</sub>** (5 mol%, 1:1), **1h** (0.10 mmol), **2a** (0.10 mmol) in DCE (1.5 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture. <sup>c</sup> ee value of Z isomer was analyzed by HPLC.

### 3. Experimental Section

#### 3.1 General procedures for the preparation of products 3a-3t



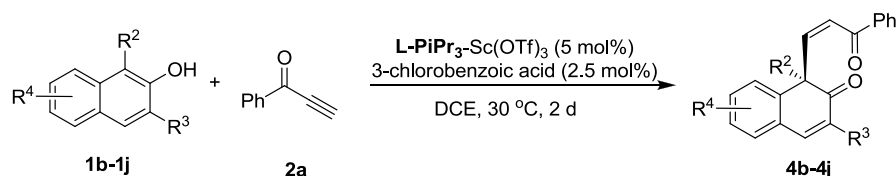
Preparation of products **3a-3p**: A dry reaction tube was charged with **L-PiPr<sub>3</sub>** (0.005 mmol), Sc(OTf)<sub>3</sub> (0.005 mmol) and alkyne (0.10 mmol) under N<sub>2</sub> atmosphere. 3-chlorobenzoic acid (0.00125 mol) in DCE (1 mL) was added and the mixture was stirred at 30 °C for 0.5 h. Then, **1a** (0.10 mmol) in DCE (0.5 mL) was added under stirring. The reaction mixture was stirred at the same temperature for 2 d. Finally, the residue was directly purified by flash chromatography on silica gel (PE/EA = 10/1) to afford the desired products **3a-3p**.

Preparation of products **3q**: A dry reaction tube was charged with **L-PiPr<sub>3</sub>** (0.005 mmol), Sc(OTf)<sub>3</sub> (0.005 mmol) and **2q** (0.10 mmol) under N<sub>2</sub> atmosphere. 3-chlorobenzoic acid (0.00125 mol) in DCE (1 mL) was added and the mixture was stirred at 30 °C for 0.5 h. Then, **1a** (0.10 mmol) in DCE (0.5 mL) was added under stirring. The reaction mixture was stirred at 50 °C for 4 d. Finally, the residue was directly purified by flash chromatography on silica gel (PE/EA = 10/1) to afford the desired products **3q**.

Preparation of products **3r-3t**: A dry reaction tube was charged with **L-PiPr<sub>3</sub>** (0.005 mmol), Sc(OTf)<sub>3</sub> (0.005 mmol) and **2r-2t** (0.10 mmol) under N<sub>2</sub> atmosphere. 3-chlorobenzoic acid (0.00125 mol) in DCE (1 mL) was added and the mixture was stirred at 30 °C for 0.5 h. Then, **1a** (0.10 mmol) in DCE (0.5 mL) was added under stirring. The reaction mixture was stirred at the same temperature for 1 d. Finally, the residue was directly purified by flash chromatography on

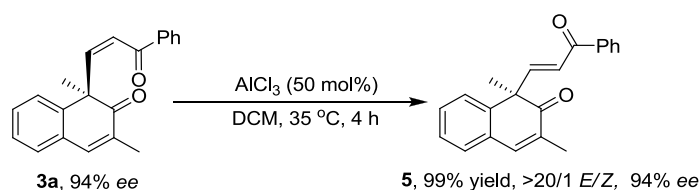
silica gel (PE/EA = 10/1) to afford the desired products **3r-3t**.

### 3.2 General procedures for the preparation of product **4b-4j**



A dry reaction tube was charged with **L-PiPr<sub>3</sub>** (0.005 mmol), Sc(OTf)<sub>3</sub> (0.005 mmol) and alkynone **2a** (0.10 mmol) under N<sub>2</sub> atmosphere. 3-chlorobenzoic acid (0.0025 mol) in DCE (1 mL) was added and the mixture was stirred at 30 °C for 0.5 h. Then, **1b-1j** (0.10 mmol) in DCE (0.5 mL) were added under stirring. The reaction mixture was stirred at the same temperature for 2 d. Finally, the residue was directly purified by flash chromatography on silica gel (PE/EA = 10/1) to afford the desired products **4b-4j**.

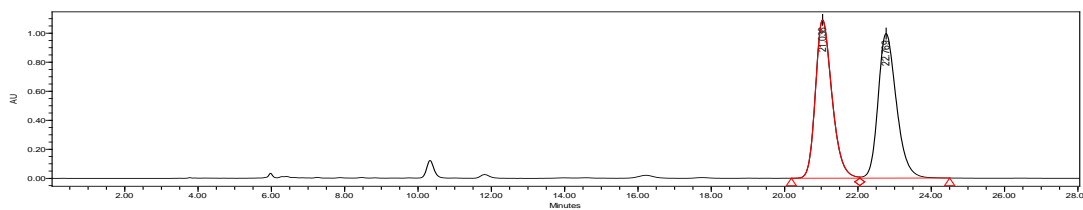
## 4. The transformations for the chiral product **3a**.



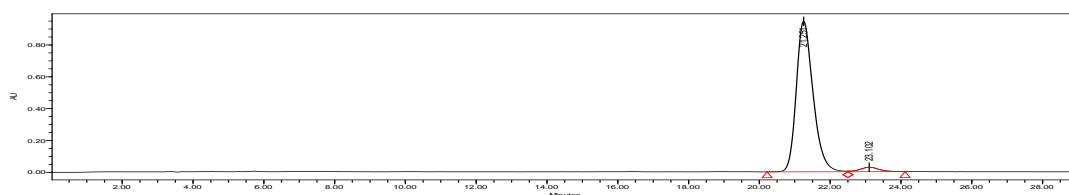
To a stirred solution of **Z-3a** (59.0 mg, 0.195 mmol) in DCM (2.0 mL), AlCl<sub>3</sub> (13.3 mg, 0.1 mmol, 0.5 eq.) was added for 2 times in 30 min at room temperature and the reaction mixture was stirred for 4 h at this temperature. Then the reaction was treated with water and extracted with DCM for three times. The residue obtained was dried over Na<sub>2</sub>SO<sub>4</sub> and purified by a Silica-gel column chromatography (PE/EA = 20/1) to afford the product **5**: Colorless oil. 99% yield; *Z/E* < 20:1; 93% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (major) = 21.25 min, *t<sub>r</sub>* (minor) = 23.10 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.82 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.27 (m, 5H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 190.8, 150.7, 142.7, 142.0, 137.8, 132.9, 132.2, 129.7, 129.4, 129.1, 128.7, 128.6, 127.8, 127.8, 125.8, 54.2, 25.0, 16.2.

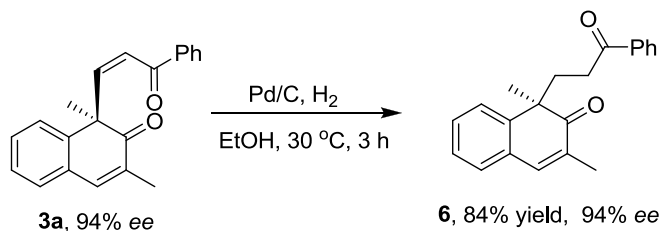
[α]<sub>D</sub><sup>18</sup> = +61.0 (*c* = 1.16, in CH<sub>2</sub>Cl<sub>2</sub>).



	Retention Time	Area	% Area
1	21.036	34218887	49.78
2	22.769	34519236	50.22



	Retention Time	Area	% Area
1	21.251	31104804	96.75
2	23.102	1046172	3.25

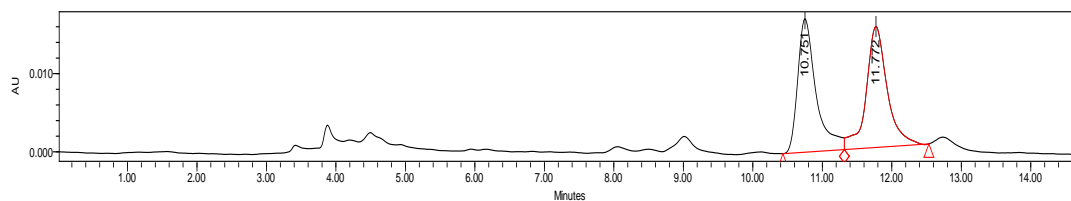


To a stirred solution of **3a** (70 mg, 94% *ee*, 0.2 mmol) in EtOH (2 mL), Pd/C (10%, 50mg) was added at room temperature and the reaction mixture was stirred for overnight under H<sub>2</sub> atmosphere. Subsequently, it was filtered to remove Pd/C and the solvent was evaporated in vacuo. The residue obtained was purified by a Silica-gel column chromatography to afford the product **6** (58.9 mg): Colorless oil. 84% yield; 94% *ee*. HPLC (Chiral IA column), *i*-PrOH/ *n*-Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) = 10.75 min, *tr* (major) = 11.77 min.

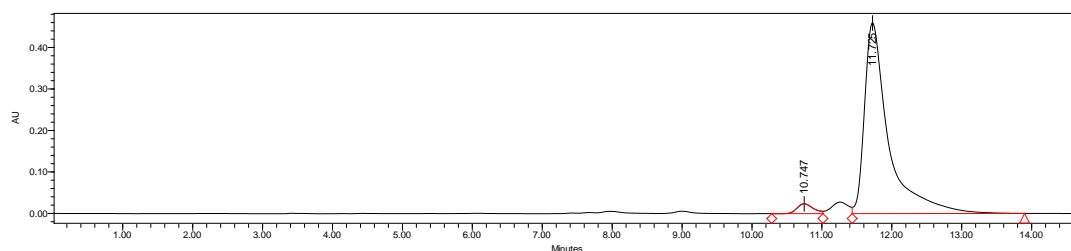
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.72 (m, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.31 (m, 5H), 7.30 – 7.26 (m, 2H), 2.75 – 2.53 (m, 2H), 2.40 – 2.28 (m, 2H), 2.04 (d, *J* = 1.2 Hz, 3H), 1.47 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 204.1, 199.6, 144.9, 142.0, 136.7, 133.1, 132.7, 130.3, 129.5, 128.9, 128.6, 128.1, 127.1, 126.2, 50.8, 35.7, 34.3, 29.1, 16.1.

[α]<sub>D</sub><sup>18</sup> = +27.0 (*c* = 0.50, in CH<sub>2</sub>Cl<sub>2</sub>).

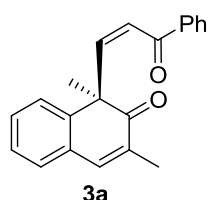


	Retention Time	Area	% Area
1	10.751	314408	48.89
2	11.772	328677	51.11



	Retention Time	Area	% Area
1	10.747	383365	3.37
2	11.725	10985929	96.63

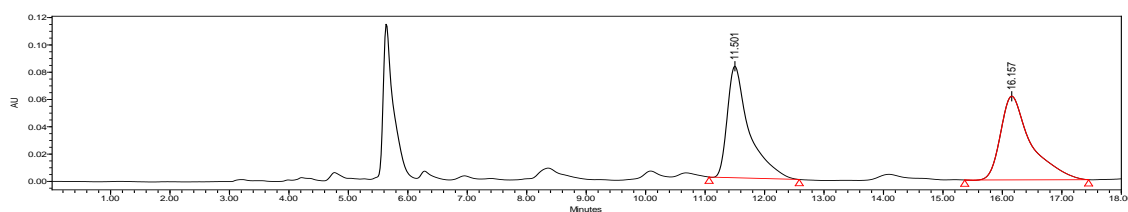
## 5. Characterization of the products.



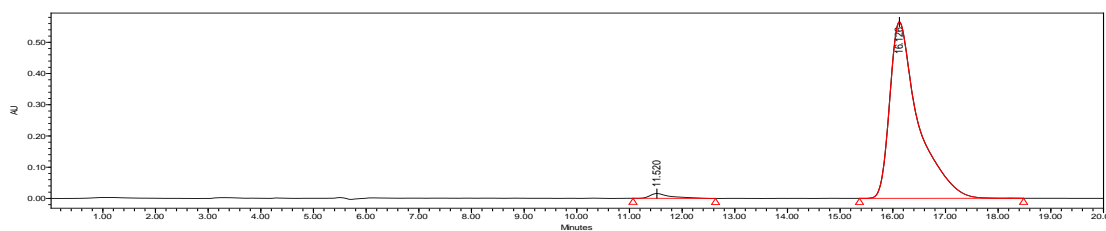
**1,3-dimethyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 3a:**  
 Colorless oil. 95% yield; *Z/E* > 20:1; 96% ee. HPLC (Chiral IC column),  
*i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) =  
 11.52 min, *tr* (major) = 16.13 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.25 (m, 1H), 7.18 – 7.08 (m, 3H), 7.02 (d, *J* = 11.6 Hz, 1H), 6.80 (d, *J* = 11.2 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 190.3, 152.0, 146.2, 140.5, 137.8, 132.8, 132.6, 130.2, 128.6, 128.6, 128.3, 126.6, 125.6, 125.3, 52.9, 33.1, 16.2.

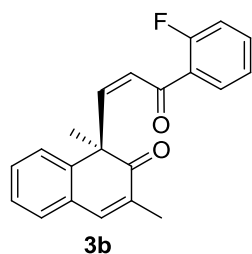
[α]<sub>D</sub><sup>26</sup> = +242.3 (c = 0.57, in CH<sub>2</sub>Cl<sub>2</sub>)



	Retention Time	Area	% Area
1	11.501	2082195	48.89
2	16.157	2176786	51.11



	Retention Time	Area	% Area
1	11.520	421545	1.96
2	16.126	21130402	98.04



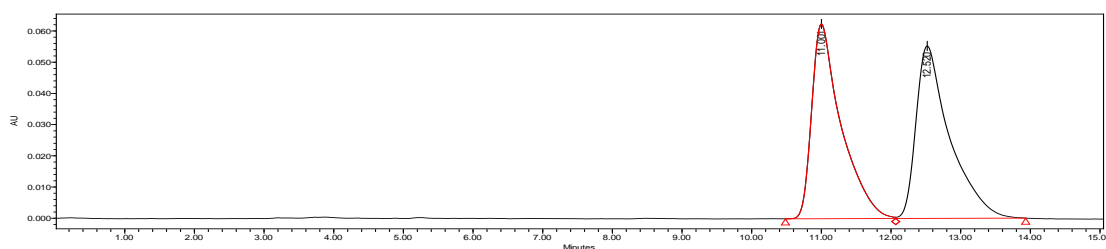
**1-(3-(2-fluorophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one **3b**:**

Colorless oil. 98% yield; *Z/E* > 20:1; 97% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 11.05 min, *t<sub>r</sub>* (major) = 12.56 min.

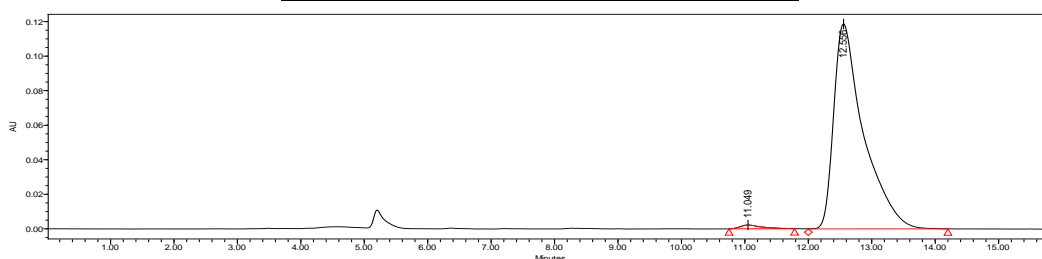
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.34 (m, 3H), 7.28 – 7.25 (m, 1H), 7.19 – 7.09 (m, 3H), 7.08 – 6.94 (m, 3H), 6.78 (d, *J* = 11.2 Hz, 1H), 2.08 (s, 3H), 1.59 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 187.9 (d, *J* = 3.0 Hz), 161.2 (d, *J* = 252.5 Hz), 152.5, 146.3, 140.5, 134.1 (d, *J* = 8.8

Hz), 132.6, 131.1 (d, *J* = 2.5 Hz), 130.4, 128.6, 128.9 (d, *J* = 6.8 Hz), 128.2, 126.7 (d, *J* = 12.8 Hz), 126.6, 125.4, 124.3 (d, *J* = 3.5 Hz), 116.4 (d, *J* = 23.1 Hz), 53.1, 33.3, 16.2.

[α]<sub>D</sub><sup>27</sup> = +210.2 (c = 0.62, in CH<sub>2</sub>Cl<sub>2</sub>).



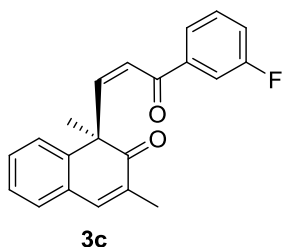
	Retention Time	Area	% Area
1	11.001	1829135	49.69
2	12.520	1851877	50.31





	Retention Time	Area	% Area
1	11.049	50988	1.30
2	12.556	3864580	98.70

**1-(3-(3-fluorophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3c:** Colorless oil.



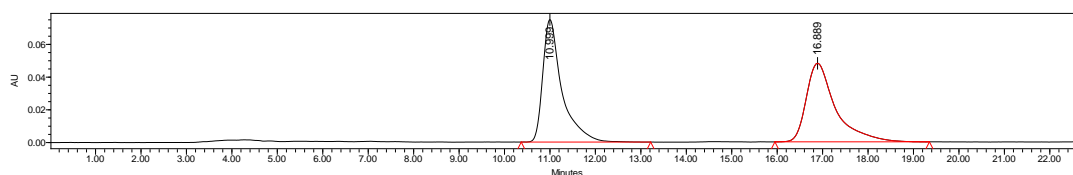
Prepared according to the general procedure A. 87% yield; *Z/E* = 8.7/1.0; 93% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 11.04 min, *t<sub>r</sub>* (major) = 16.76 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.37 – 7.23 (m, 4H), 7.20 – 7.06 (m, 4H), 6.97 (d, *J* = 11.6 Hz, 1H), 6.84 (d, *J* = 11.6 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

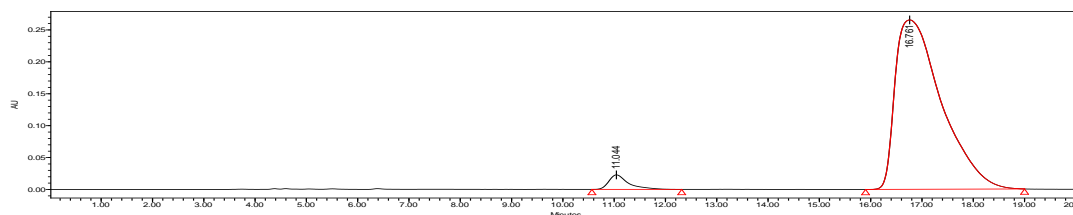
δ 201.0, 188.9(d, *J* = 2.2 Hz), 164.0, 161.5, 153.0, 146.0, 145.0(d, *J* = 22.3 Hz), 140.6, 139.9(d, *J* = 6.3 Hz), 132.7, 130.2, 130.1, 128.5 (d, *J* = 31.1 Hz), 126.7, 125.6, 124.8, 124.0 (d, *J* = 3.0 Hz), 119.8 (d, *J* = 21.4 Hz), 53.0, 33.1, 16.2.

[α]<sub>D</sub><sup>27</sup> = +194.6 (*c* = 0.56, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>17</sub>FN<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>+Na<sup>+</sup>) = 343.1110, Found 343.1110.

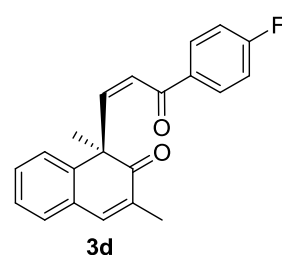


	Retention Time	Area	% Area
1	10.999	2183407	50.50
2	16.889	2139770	49.50



	Retention Time	Area	% Area
1	11.044	604106	3.50
2	16.761	16654208	96.50

**1-(3-(4-fluorophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3d:** Colorless oil.

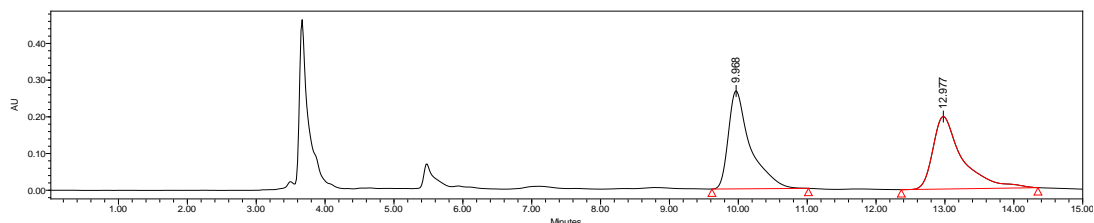


92% yield; *Z/E* > 20:1; 96% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 9.83 min, *t<sub>r</sub>* (major) = 12.74 min.

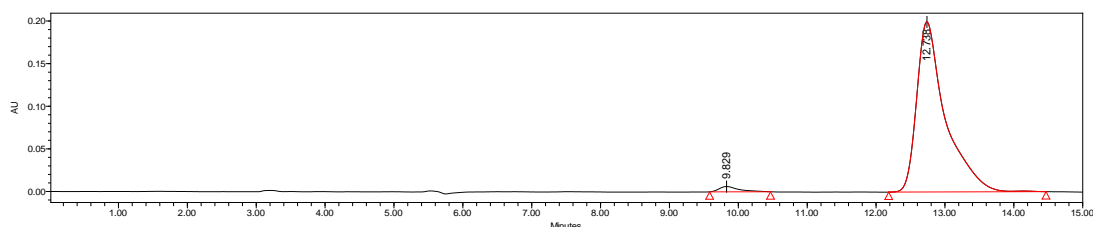
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (t, *J* = 6.4 Hz, 2H), 7.34 (s, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.19 – 7.06 (m, 3H), 7.03 – 6.92 (m, 3H), 6.80 (d, *J* = 11.6 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  201.1, 188.8, 166.8, 164.3, 152.1, 146.1, 140.5, 134.2 (d,  $J = 3.0$  Hz), 132.6, 130.9 (d,  $J = 9.2$  Hz), 130.1, 128.6, 128.3, 126.2 (d,  $J = 95.7$  Hz), 125.0, 115.6 (d,  $J = 21.7$  Hz), 52.9, 33.0, 16.2.

$[\alpha]_D^{29} = +259.6$  (c = 0.57, in CH<sub>2</sub>Cl<sub>2</sub>).

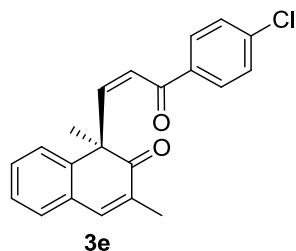


	Retention Time	Area	% Area
1	9.968	5899724	50.18
2	12.977	5858114	49.82



	Retention Time	Area	% Area
1	9.829	123959	2.11
2	12.738	5759418	97.89

**1-(3-(4-chlorophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3e:** Colorless oil.

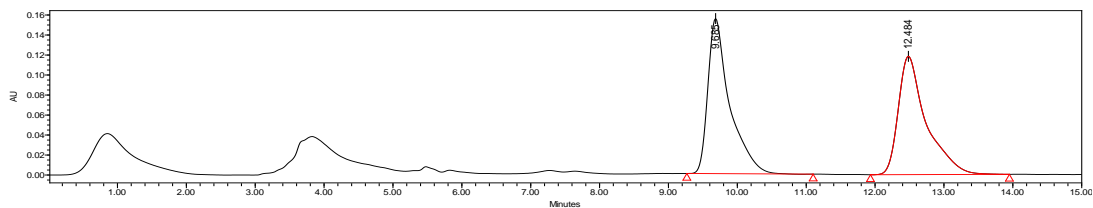


83% yield;  $Z/E > 20:1$ ; 96% ee. HPLC (Chiral IC column), i-PrOH/n-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 9.84 min, tr (major) = 12.70 min.

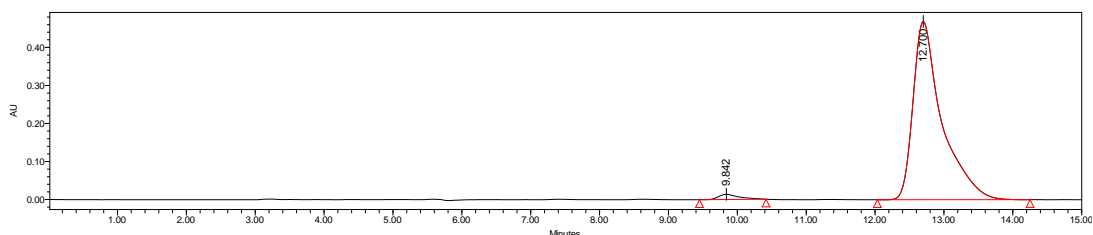
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (d,  $J = 8.0$  Hz, 2H), 7.37 – 7.23 (m, 4H), 7.12 – 7.05 (m, 3H), 6.96 (d,  $J = 11.2$  Hz, 1H), 6.82 (d,  $J = 11.6$  Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.1, 189.1, 152.6, 146.1, 140.5, 139.2, 136.1, 132.7, 130.1, 129.7,

128.8, 128.6, 128.3, 126.7, 125.7, 124.9, 53.0, 33.1, 16.2.

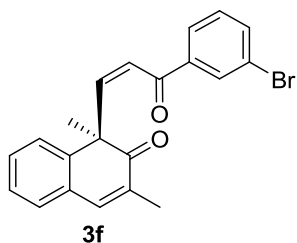
$[\alpha]_D^{26} = +237.9$  (c = 0.58, in CH<sub>2</sub>Cl<sub>2</sub>).



	Retention Time	Area	% Area
1	9.685	3407237	50.67
2	12.484	3317516	49.33



	Retention Time	Area	% Area
1	9.842	284694	2.05
2	12.700	13592297	97.95



**1-(3-(3-bromophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3f:** Colorless oil. 51% yield; *Z/E* > 20:1; 97% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 9.82 min, *t<sub>r</sub>* (major) = 13.41 min.

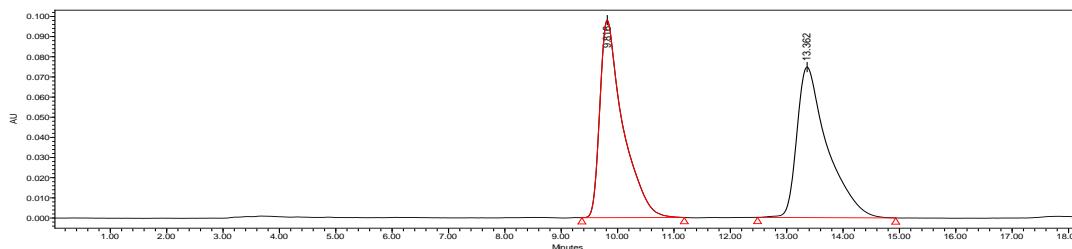
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (t, *J* = 1.8 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.34 (s, 1H), 7.28 – 7.06 (m, 5H), 6.95 (d, *J* = 11.6 Hz, 1H), 6.84 (d, *J* = 9.6 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>) δ 201.0, 188.9, 153.1, 145.9, 140.6, 139.5, 135.6, 132.7, 131.2, 130.1, 130.0, 128.6, 128.3, 126.8, 126.7, 125.7, 124.7, 122.9, 53.0, 33.1, 16.2.

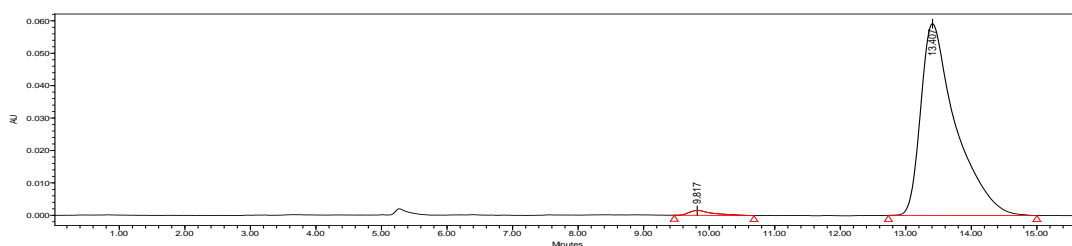
[α]<sub>D</sub><sup>27</sup> = +221.0 (*c* = 0.59, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>17</sub>Br<sup>78.9183</sup>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 403.0310, Found 403.0309.

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>17</sub>Br<sup>80.9163</sup>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 405.0289, Found 405.0294.

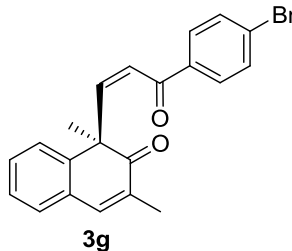


	Retention Time	Area	% Area
1	9.816	2761940	49.74
2	13.362	2790315	50.26



	Retention Time	Area	% Area
1	9.817	37727	1.70
2	13.407	2184598	98.30

**1-(3-(4-bromophenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(H)-one 3g:** Colorless oil.

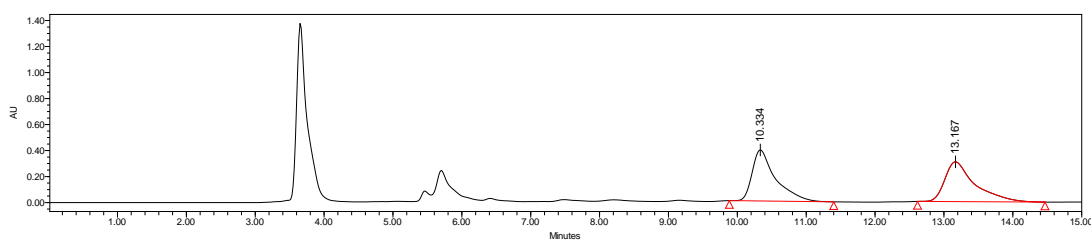


85% yield; *Z/E* > 20:1; 96% ee. HPLC (Chiral IC column), *i*-PrOH/*n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) = 10.42 min, *tr* (major) = 13.29 min.

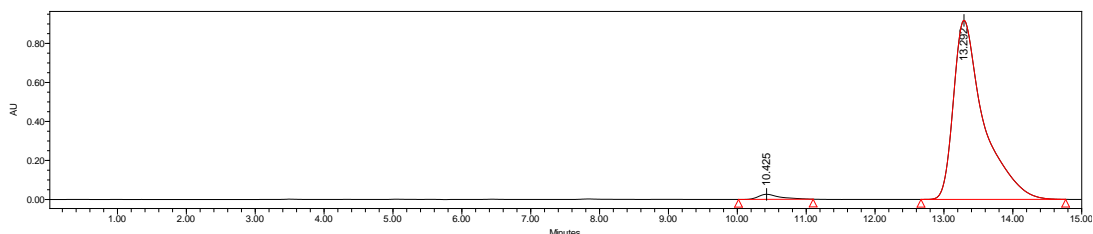
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.05 (m, 3H), 6.96 (d, *J* = 11.2 Hz, 1H), 6.82 (d, *J* = 11.6 Hz, 1H), 2.05 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 189.3, 152.7,

146.1, 140.5, 136.5, 132.6, 131.7, 130.1, 129.8, 128.6, 128.3, 128.0, 126.7, 125.6, 124.8, 53.0, 33.1, 16.2.

[α]<sub>D</sub><sup>26</sup> = +221.5 (*c* = 0.65, in CH<sub>2</sub>Cl<sub>2</sub>).

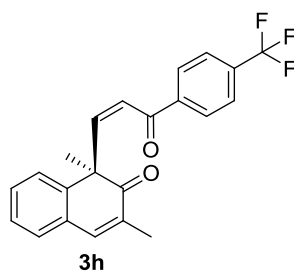


	Retention Time	Area	% Area
1	10.334	9231132	49.98
2	13.167	9238374	50.02



	Retention Time	Area	% Area
1	10.425	564644	1.99
2	13.292	27846971	98.01

**1,3-dimethyl-1-(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-enyl)naphthalen-2(1H)-one 3h:**



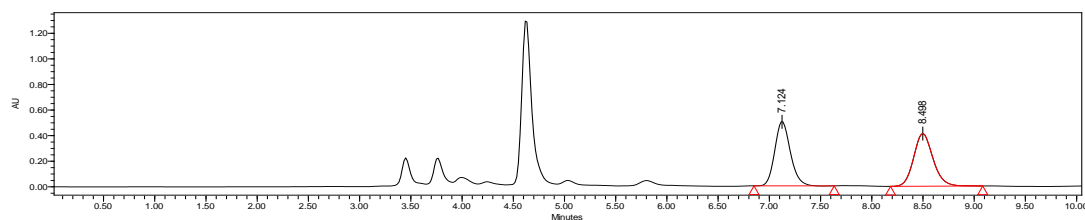
Colorless oil. 82% yield; *Z/E* = 5.5/1.0; 95% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) = 7.13 mn, *tr* (major) = 8.50 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.33 (s, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.20 – 7.06 (m, 3H), 6.99 (d, *J* = 11.6 Hz, 1H), 6.88 (d, *J* = 11.6 Hz, 1H), 2.04 (s, 3H), 1.59 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 189.4, 153.5,

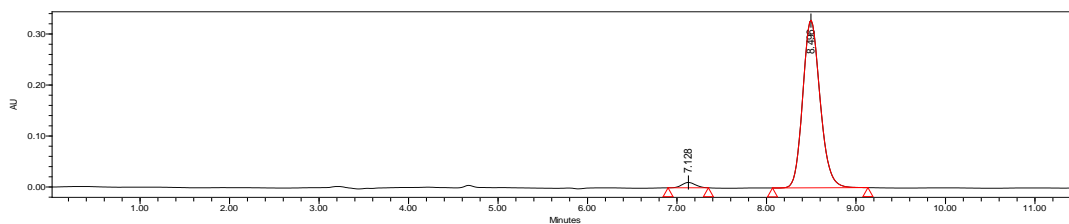
145.9, 140.6, 140.5, 134.0 (q, *J* = 32.2 Hz), 132.7, 130.2, 128.7, 128.6, 128.4, 126.8, 125.7, 125.6, 125.5 (q, *J* = 3.7 Hz), 124.8, 123.7 (q, *J* = 270.9 Hz), 100.1, 53.1, 33.1, 16.2.

[α]<sub>D</sub><sup>26</sup> = +221.1 (c = 0.60, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>17</sub>F<sub>3</sub>NaO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>+Na<sup>+</sup>) = 393.1078, Found 393.1078.

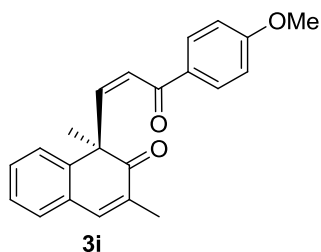


	Retention Time	Area	% Area
1	7.124	5325605	49.67
2	8.498	5397338	50.33



	Retention Time	Area	% Area
1	7.128	111058	2.45
2	8.496	4429980	97.55

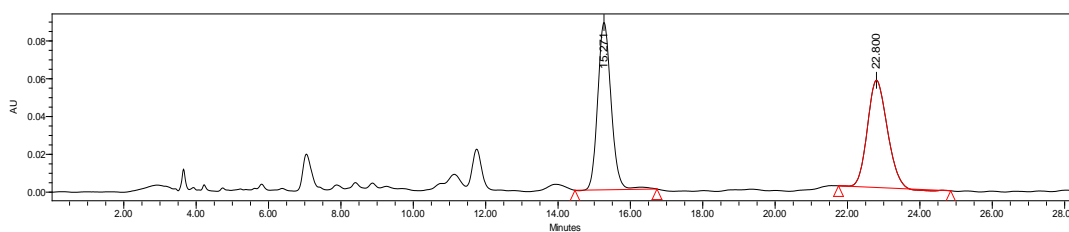
**1-(3-(4-methoxyphenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3i:** Colorless oil. 83% yield; *Z/E* > 20:1; 88% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 15.21 min, tr (major) = 22.56 min.



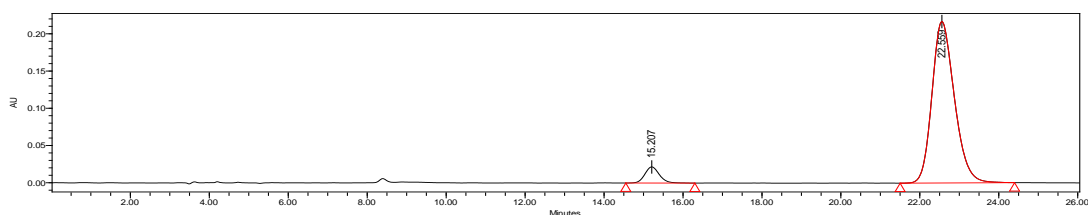
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.33 (s, 1H), 7.28 – 7.20 (m, 1H), 7.18 – 7.07 (m, 3H), 6.99 (d, *J* = 11.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 2.05 (s, 3H), 1.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 188.9, 163.3, 150.8, 146.3, 140.4, 132.6, 131.0, 130.6, 130.1, 128.5, 128.2, 126.5, 125.7, 125.4, 113.6, 55.5, 52.8, 33.0, 16.2.

[α]<sub>D</sub><sup>26</sup> = +261.6 (c = 0.50, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 355.1310, Found 355.1309.

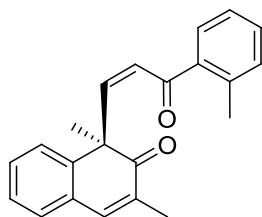


	Retention Time	Area	% Area
1	15.271	2282171	50.96
2	22.800	2196490	49.04



	Retention Time	Area	% Area
1	15.207	554972	6.09
2	22.559	8559626	93.91

**1,3-dimethyl-1-(3-oxo-3-o-tolylprop-1-enyl)naphthalen-2(1H)-one 3j:** Colorless oil. 73% yield; *Z/E* > 20:1; 93% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 9.87 min, tr (major) = 12.38 min.

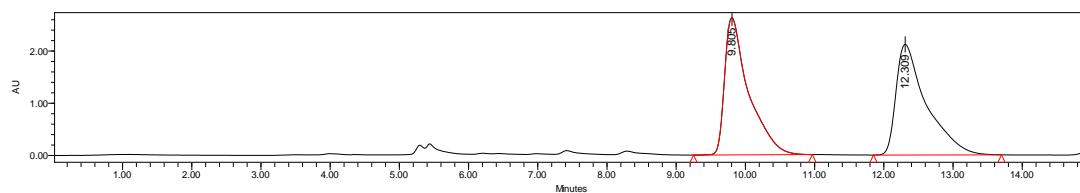


**3j**

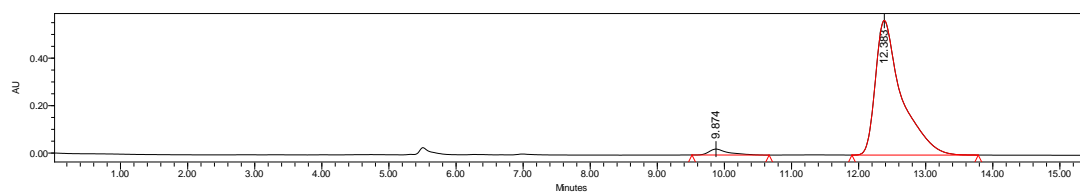
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.0$  Hz, 1H), 7.30 (s, 1H), 7.26 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 7.15 – 7.09 (m, 2H), 7.06 (d,  $J = 7.6$  Hz, 1H), 6.77 (d,  $J_1 = 11.2$  Hz, 1H), 6.72 (d,  $J_1 = 11.2$  Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.57 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 194.0, 151.2, 146.3, 140.4, 138.9, 137.6, 132.7, 131.4, 130.9, 130.4, 128.5, 128.5, 128.3, 128.2, 126.7, 125.7, 125.5, 52.8, 33.3, 20.2, 16.2.

$[\alpha]_D^{27} = +140.4$  ( $c = 0.45$ , in  $\text{CH}_2\text{Cl}_2$ ).

HRMS (ESI-TOF) calcd for  $\text{C}_{22}\text{H}_{20}\text{NaO}_2^+$  ( $[\text{M}] + \text{Na}^+$ ) = 339.1356, Found 339.1360.

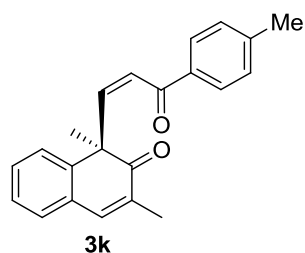


	Retention Time	Area	% Area
1	9.805	63010805	49.52
2	12.309	64227236	50.48



	Retention Time	Area	% Area
1	9.874	501038	3.17
2	12.383	15314675	96.83

**1,3-dimethyl-1-(3-oxo-3-p-tolylprop-1-enyl)naphthalen-2(1H)-one 3k:** Colorless oil. 57% yield;

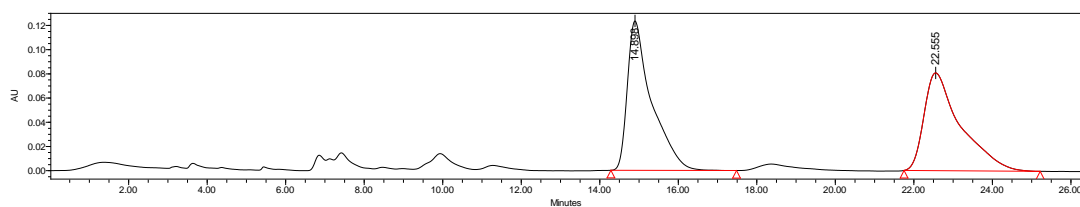


$Z/E > 20:1$ ; 92% ee. HPLC (Chiral IC column), i-PrOH/ n-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm,  $t_r$  (minor) = 14.59 min,  $t_r$  (major) = 21.72 min.

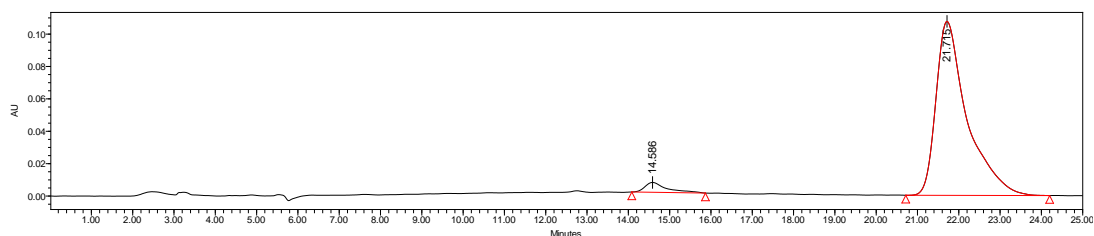
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.6$  Hz, 2H), 7.34 (s, 1H), 7.25 (d,  $J = 8.8$  Hz, 1H), 7.18 – 7.08 (m, 5H), 7.02 (d,  $J = 11.6$  Hz, 1H), 6.77 (d,  $J = 11.6$  Hz, 1H), 2.34 (s, 3H), 2.05 (s, 3H), 1.57 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 189.8, 151.6, 146.6,

143.6, 140.5, 135.4, 132.6, 130.2, 129.2, 128.6, 128.5, 128.3, 126.5, 125.6, 125.4, 52.9, 33.1, 21.7, 16.3.

$[\alpha]_D^{26} = +224.0$  ( $c = 0.33$ , in  $\text{CH}_2\text{Cl}_2$ ).

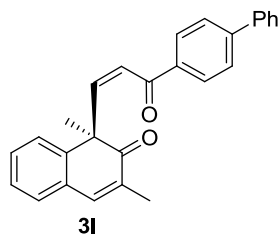


	Retention Time	Area	% Area
1	14.898	5287709	50.35
2	22.555	5214011	49.65



	Retention Time	Area	% Area
1	14.586	226468	3.89
2	21.715	5599628	96.11





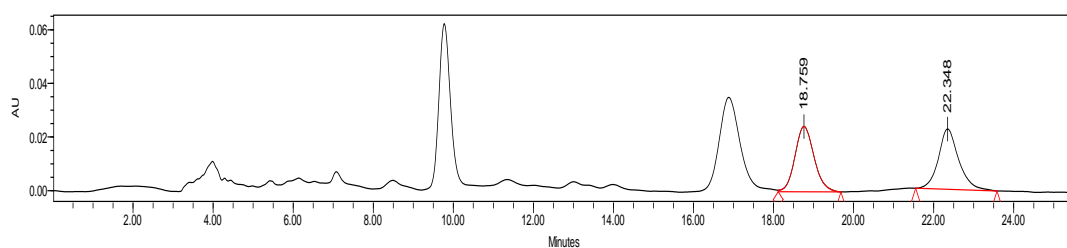
**1-(3-(biphenyl-4-yl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1**

**H)-one 3I:** White solid. 70% yield; *Z/E* > 20:1; 97% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 18.94 min, *t<sub>r</sub>* (major) = 22.49 min.

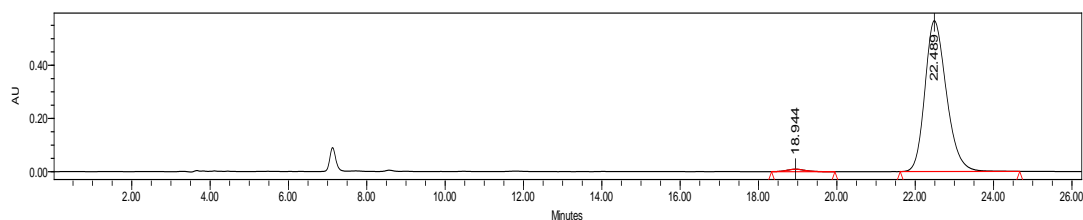
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 6.8 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.19 – 7.10 (m, 3H), 7.06 (d, *J* = 11.6 Hz, 1H), 6.81 (d, *J* = 11.6

Hz, 1H), 2.06 (s, 3H), 1.59 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 189.8, 151.9, 146.2, 145.4, 140.5, 140.0, 136.6, 132.6, 130.1, 129.0, 128.9, 128.6, 128.3, 128.3, 127.3, 127.1, 126.6, 125.7, 125.3, 53.0, 33.1, 16.3.

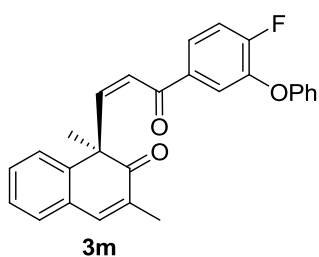
[α]<sub>D</sub><sup>27</sup> = +226.2 (c = 0.53, in CH<sub>2</sub>Cl<sub>2</sub>).



	Retention Time	Area	% Area
1	18.759	808024	50.41
2	22.348	794923	49.59



	Retention Time	Area	% Area
1	18.944	298200	1.36
2	22.489	21549501	98.64

**1-(3-(4-fluoro-3-phenoxyphenyl)-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one 3m:**

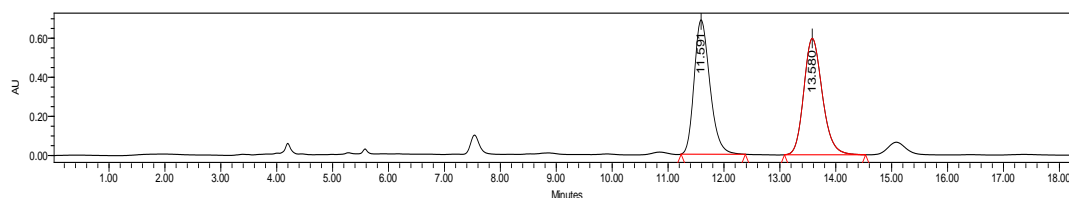
Colorless oil. 68% yield; *Z/E* > 20:1; 96% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t*<sub>r</sub> (minor) = 11.56 min, *t*<sub>r</sub> (major) = 13.47 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.46 (m, 1H), 7.39 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.26 – 7.23 (m, 1H), 7.17 – 7.04 (m, 5H), 6.95 – 6.87 (m, 3H), 6.78 (d, *J* = 11.2 Hz, 1H), 2.03 (s, 3H), 1.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 188.1, 158.6, 156.9,

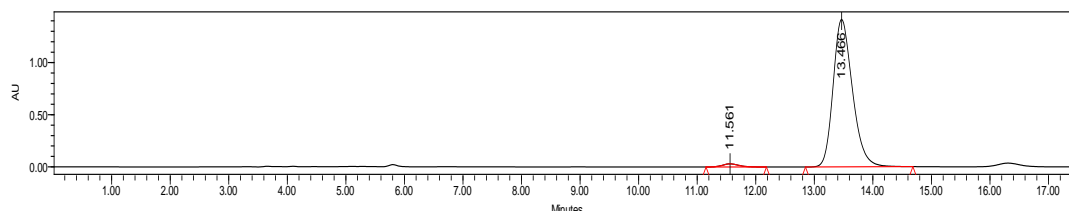
156.0, 152.6, 146.0, 144.1 (d, *J* = 1.8 Hz), 140.5, 134.9 (d, *J* = 3.3 Hz), 132.7, 130.1, 130.0, 129.0, 128.4 (d, *J* = 28.6 Hz), 126.7, 125.7, 125.4 (d, *J* = 8.0 Hz), 124.7, 123.7, 121.7 (d, *J* = 2.6 Hz), 117.5 (d, *J* = 60.0 Hz), 52.9, 33.1, 16.2.

[α]<sub>D</sub><sup>27</sup> = +190.4 (c = 0.56, in CH<sub>2</sub>Cl<sub>2</sub>).

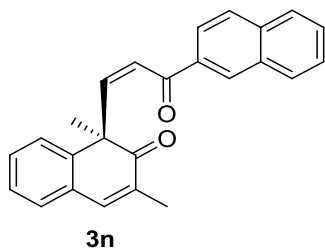
HRMS (ESI-TOF) calcd for C<sub>27</sub>H<sub>21</sub>FNaO<sub>3</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 435.1372, Found 435.1368.



	Retention Time	Area	% Area
1	11.591	13435376	49.51
2	13.580	13701079	50.49



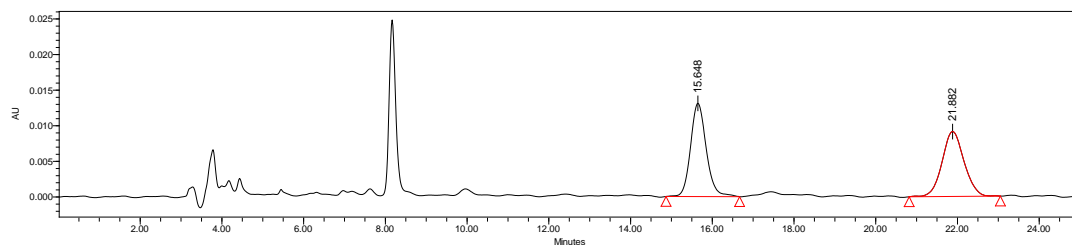
	Retention Time	Area	% Area
1	11.561	592481	1.79
2	13.466	32420681	98.21

**1,3-dimethyl-1-(3-(naphthalen-2-yl)-3-oxoprop-1-enyl)naphthalen-2(1H)-one 3n:**

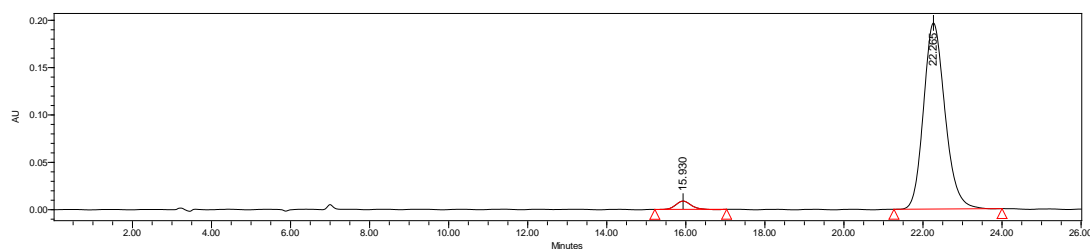
Colorless oil. 91% yield; *Z/E* > 20:1; 94% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t*<sub>r</sub> (minor) = 15.93 min, *t*<sub>r</sub> (major) = 22.27 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.44 (m, 2H), 7.30 – 7.07

(m, 6H), 6.84 (d,  $J = 11.6$  Hz, 1H), 2.02 (s, 3H), 1.59 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 190.5, 151.6, 146.2, 140.5, 135.4, 135.2, 132.6, 132.5, 130.1, 130.1, 129.6, 128.6, 128.4, 128.3, 128.3, 127.8, 126.7, 126.6, 125.8, 125.6, 124.0, 53.0, 33.2, 16.2.  $[\alpha]_{\text{D}}^{27} = +175.5$  ( $c = 0.64$ , in  $\text{CH}_2\text{Cl}_2$ ).

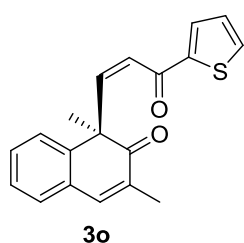


	Retention Time	Area	% Area
1	15.648	349046	50.63
2	21.882	340378	49.37



	Retention Time	Area	% Area
1	15.930	236668	3.10
2	22.265	7387837	96.90

**1,3-dimethyl-1-(3-oxo-3-(thiophen-2-yl)prop-1-enyl)naphthalen-2(1H)-one 3o**: Colorless oil.

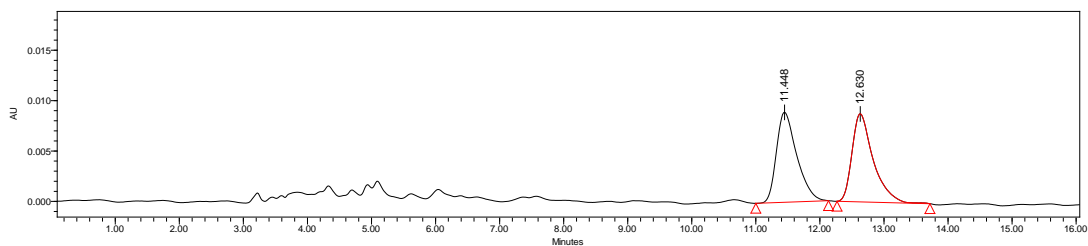


Prepared according to the general procedure A. 65% yield;  $Z/E > 20:1$ ; 93% ee. HPLC (Chiral IC column),  $i\text{-PrOH}/n\text{-Hexane} = 20/80$ , Flow rate: 1.0 mL/min, 254 nm,  $t_r$  (minor) = 11.61 min,  $t_r$  (major) = 12.67 min.

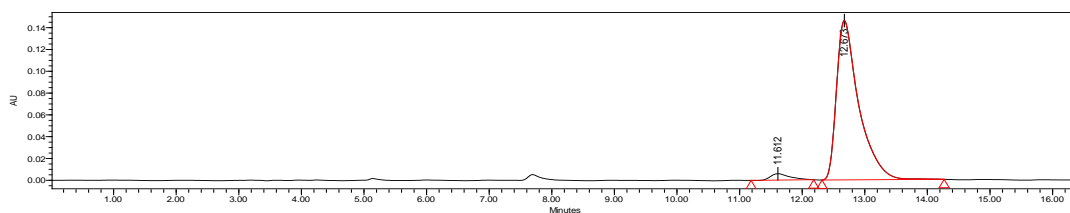
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.57 (m, 1H), 7.51 (d,  $J = 4.8$  Hz, 1H), 7.36 (s, 1H), 7.27 (d,  $J = 8.4$  Hz, 1H), 7.21 – 7.11 (m, 2H), 7.08 (d,  $J = 6.8$  Hz, 1H), 7.05 – 7.00 (m, 1H), 6.96 (d,  $J = 11.2$  Hz, 1H), 6.78 (d,  $J = 11.6$  Hz, 1H), 2.05 (s, 3H), 1.57 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$

200.8, 181.5, 152.5, 146.4, 145.3, 140.4, 133.9, 132.7, 132.0, 130.1, 128.6, 128.3, 128.1, 126.6, 125.4, 124.8, 53.0, 33.3, 16.3.

$[\alpha]_{\text{D}}^{26} = +303.3$  ( $c = 0.39$ , in  $\text{CH}_2\text{Cl}_2$ ).

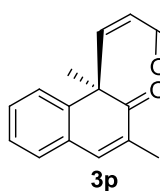


	Retention Time	Area	% Area
1	11.448	197264	49.57
2	12.630	200668	50.43



	Retention Time	Area	% Area
1	11.612	124813	3.34
2	12.673	3611393	96.66

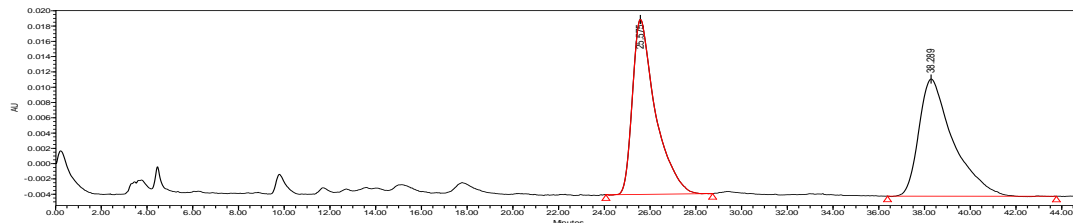
**1,3-dimethyl-1-((1Z,4E)-3-oxo-5-phenylpenta-1,4-dienyl)naphthalen-2(1H)-one 3p:** Colorless



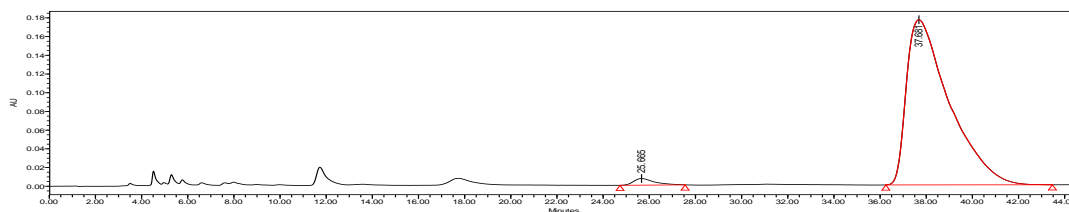
oil. 77% yield; *Z/E* > 20:1; 96% ee. HPLC (Chiral IC column), *i*-PrOH/*n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 25.67 min, *t<sub>r</sub>* (major) = 37.68 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.37 (m, 2H), 7.36 – 7.29 (m, 5H), 7.29 – 7.23 (m, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 6.76 – 6.65 (m, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 2.05 (d, *J* = 0.8 Hz, 3H), 1.55 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 188.7, 152.0, 146.4, 143.4, 140.3, 134.6, 132.9, 130.5, 130.2, 128.9, 128.6, 128.3, 128.2, 127.1, 126.6, 126.6, 125.4, 53.0, 33.2, 16.2.

[α]<sub>D</sub><sup>27</sup> = +284.8 (c = 0.50, in CH<sub>2</sub>Cl<sub>2</sub>).

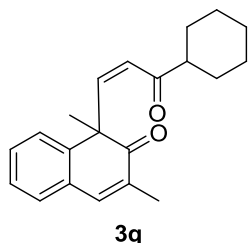


	Retention Time	Area	% Area
1	25.575	1592455	49.99
2	38.289	1592826	50.01



	Retention Time	Area	% Area
1	25.665	444336	1.91
2	37.681	22772421	98.09

**1-(3-cyclohexyl-3-oxoprop-1-enyl)-1,3-dimethylnaphthalen-2(1H)-one:** Colorless oil. 60% yield; *Z/E* > 20:1; 95% ee. HPLC (Chiral IC column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 9.09 min, *t<sub>r</sub>* (major) = 10.71 min.

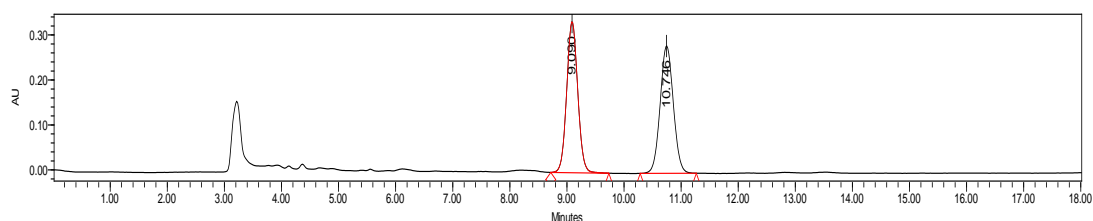


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (s, 1H), 7.28 – 7.22 (m, 1H), 7.22 – 7.12 (m, 2H), 7.06 – 6.97 (m, 1H), 6.58 (d, *J* = 11.4 Hz, 1H), 6.43 (d, *J* = 11.4 Hz, 1H), 2.20 – 2.07 (m, 1H), 2.04 (s, 3H), 1.60 – 1.40 (m, 8H), 1.20 – 1.00 (m, 4H), 0.97 – 0.85 (m, 1H).

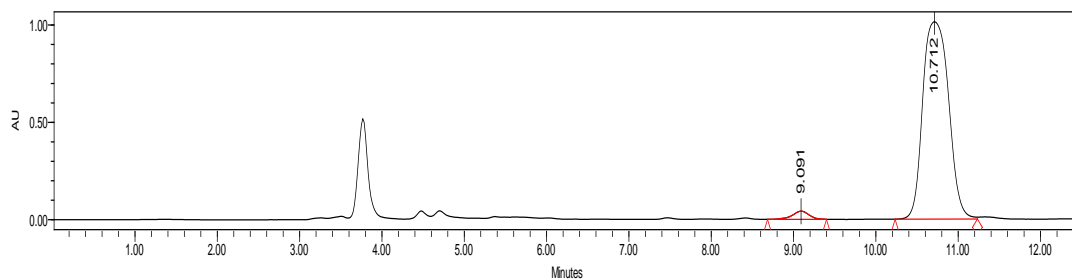
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.5, 201.1, 151.1, 146.6, 140.2, 132.7, 130.3, 128.3, 128.2, 127.1, 126.4, 125.2, 52.6, 50.9, 33.3, 28.0, 27.7, 25.9, 25.7, 25.5, 16.3.

[α]<sub>D</sub><sup>27</sup> = +226 (c = 0.41, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>24</sub>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 331.1669, Found 331.1664.

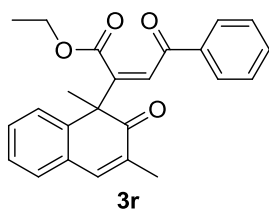


	Retention Time	Area	% Area
1	9.090	4512735	49.85
2	10.746	4539371	50.15



	Retention Time	Area	% Area
1	9.091	597404	2.63
2	10.712	22148238	97.37

**Ethyl 2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-oxo-4-phenylbut-2-enoate:**

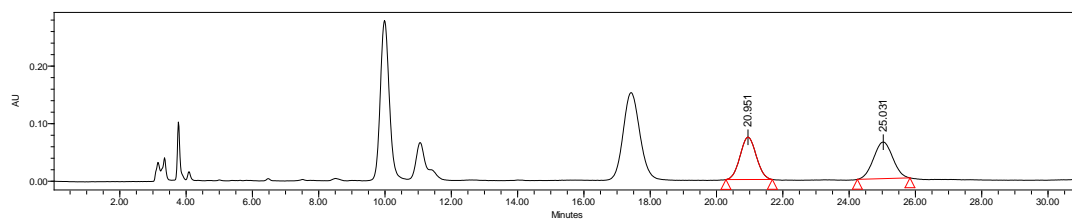


Colorless oil. 72% yield; 98% ee. HPLC (Chiral IC column), i-PrOH/n-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 21.21 min, tr (major) = 25.31 min.

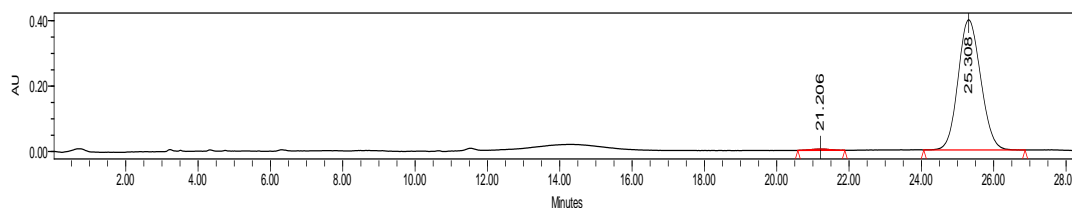
$^1\text{H NMR}$  (400 MHz,  $\text{DCl}_3$ )  $\delta$  8.16 (d,  $J = 7.8$  Hz, 2H), 7.58 (t,  $J = 6.8$  Hz, 1H), 7.51 (t,  $J = 7.6$  Hz, 2H), 7.36 (s, 1H), 7.34 – 7.19 (m, 4H), 7.01 (s, 1H), 3.70 – 3.50 (m, 2H), 2.11 (s, 3H), 1.55 (s, 3H), 0.60 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.9, 194.8, 164.6, 144.4, 141.5, 140.9, 137.5, 136.4, 133.6, 131.8, 129.4, 129.4, 129.2, 129.1, 129.0, 127.4, 126.0, 61.5, 54.9, 27.8, 16.3, 13.0.

$[\alpha]_D^{25} = +212$  ( $c = 0.77$ , in  $\text{CH}_2\text{Cl}_2$ ).

HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{22}\text{NaO}_4^+$  ( $[\text{M}]+\text{Na}^+$ ) = 397.1416, Found 397.1405.



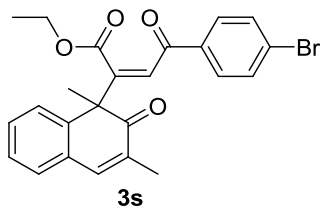
	Retention Time	Area	% Area
1	20.951	2494065	49.40
2	25.031	2555014	50.60



	Retention Time	Area	% Area
1	21.206	142067	0.82
2	25.308	17274093	99.18

**Ethyl 4-(4-bromophenyl)-2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-oxobut-2-enoate**

Colorless oil. 79% yield; 98% ee. HPLC (Chiral IC column), i-PrOH/ n-Hexane = 30/70, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 10.85 min, tr (major) = 16.93 min.

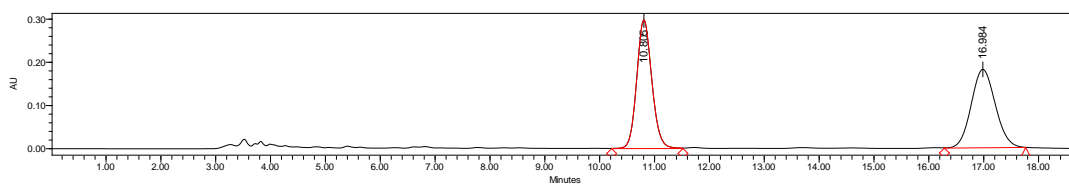


$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.2$  Hz, 2H), 7.66 (d,  $J = 8.4$  Hz, 2H), 7.36 (s, 1H), 7.34 – 7.23 (m, 3H), 7.19 (d,  $J = 6.8$  Hz, 1H), 6.96 (s, 1H), 3.73 – 3.49 (m, 2H), 2.10 (s, 3H), 1.54 (s, 3H), 0.63

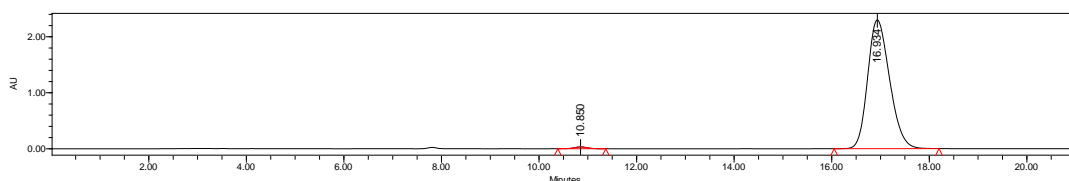
(t,  $J = 7.2$  Hz, 3H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 193.9, 164.4, 144.3, 141.6, 141.3, 137.1, 135.2, 132.3, 131.7, 130.7, 129.4, 129.4, 129.1, 128.9, 127.4, 125.9, 61.6, 54.9, 27.8, 16.3, 13.1.  $[\alpha]_D^{24} = +211$  ( $c = 0.72$ , in  $\text{CH}_2\text{Cl}_2$ ).

HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{21}\text{Br}^{78.9183}\text{NaO}_4^+$  ( $[\text{M}]+\text{Na}^+$ ) = 475.0521, Found 475.0508.

HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{21}\text{Br}^{80.9163}\text{NaO}_4^+$  ( $[\text{M}]+\text{Na}^+$ ) = 477.0500, Found 475.0485.

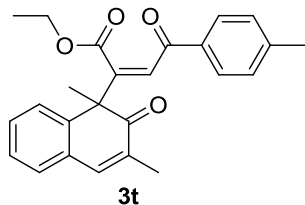


	Retention Time	Area	% Area
1	10.805	5707672	49.79
2	16.984	5756319	50.21



	Retention Time	Area	% Area
1	10.850	598696	0.83
2	16.934	71704534	99.17

**Ethyl 2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-oxo-4-p-tolylbut-2-enoate**



**3t**

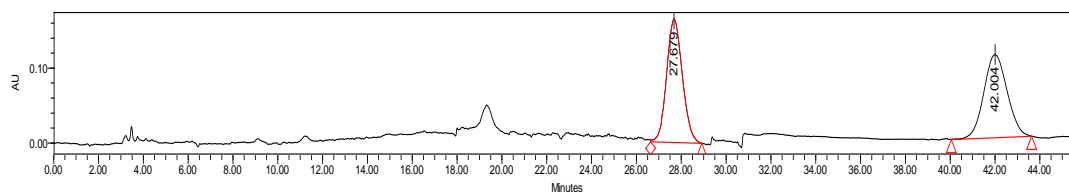
Colorless oil. 73% yield; 98% ee. HPLC (Chiral IC column), i-PrOH/ n-Hexane = 30/70, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 27.27 min, tr (major) = 41.22 min.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 6.8$  Hz, 2H), 7.44 – 7.17 (m, 7H), 6.99 (s, 1H), 3.75 – 3.50 (m, 2H), 2.41 (s, 3H), 2.10 (s, 3H), 1.54 (s, 3H), 0.62 (t,  $J = 6.0$  Hz, 3H).

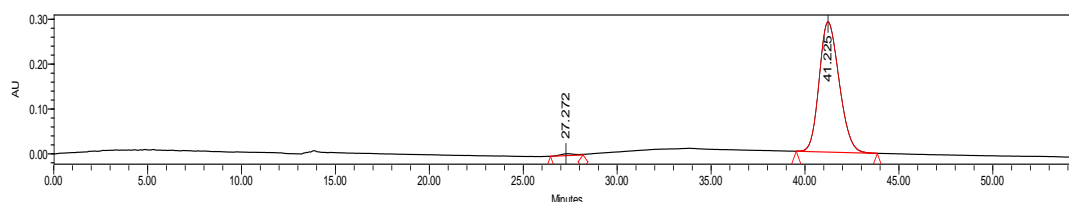
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 194.5, 164.6, 144.4, 144.4, 141.4, 140.6, 137.6, 134.0, 131.8, 129.6, 129.4, 129.3, 129.0, 127.3, 126.0, 61.4, 54.8, 27.7, 21.9, 16.3, 13.1.

$[\alpha]_D^{25} = +163$  ( $c = 0.57$ , in  $\text{CH}_2\text{Cl}_2$ ).

HRMS (ESI-TOF) calcd for  $\text{C}_{25}\text{H}_{24}\text{NaO}_4^+$  ( $[\text{M}] + \text{Na}^+$ ) = 411.1572, Found 411.1562.

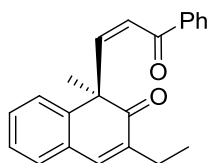


	Retention Time	Area	% Area
1	27.679	8050995	50.07
2	42.004	8029442	49.93



	Retention Time	Area	% Area
1	27.272	211155	0.98
2	41.225	21444783	99.02

**3-ethyl-1-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4b:** Colorless oil. 80% yield;  $Z/E > 20:1$ ; 98% ee. HPLC (Chiral ID column), i-PrOH/ n-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, tr (minor) = 7.57 min, tr (major) = 8.55 min.

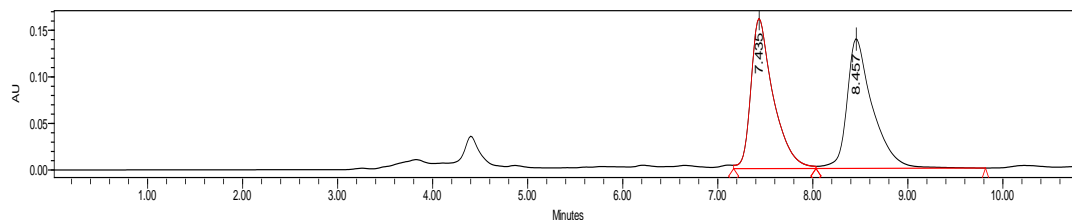


**4b**

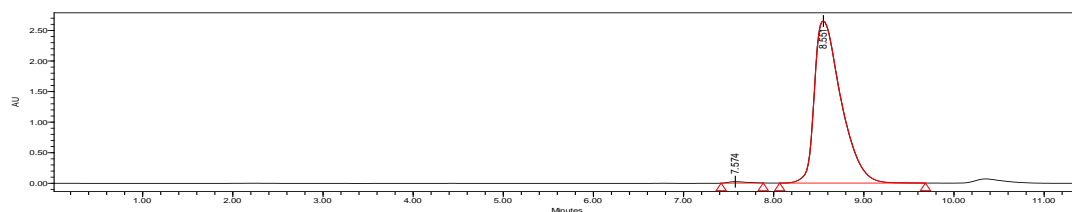
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.61 (m, 2H), 7.47 – 7.39 (m, 1H), 7.35 – 7.24 (m, 4H), 7.19 – 7.09 (m, 3H), 7.01 (d,  $J = 11.6$  Hz, 1H), 6.78 (d,  $J =$



11.6 Hz, 1H), 2.55 – 2.36 (m, 2H), 1.56 (s, 3H), 1.17 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.6, 190.2, 151.9, 146.1, 138.7, 138.1, 137.9, 132.7, 130.2, 128.6, 128.5, 128.4, 128.3, 126.6, 125.6, 125.3, 53.1, 32.9, 22.6, 12.8.  
 $[\alpha]_{\text{D}}^{28} = +262.1$  ( $c = 0.50$ , in  $\text{CH}_2\text{Cl}_2$ ).

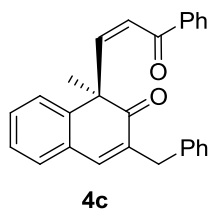


	Retention Time	Area	% Area
1	7.435	2626046	50.31
2	8.457	2593849	49.69



	Retention Time	Area	% Area
1	7.574	511369	0.92
2	8.551	54871936	99.08

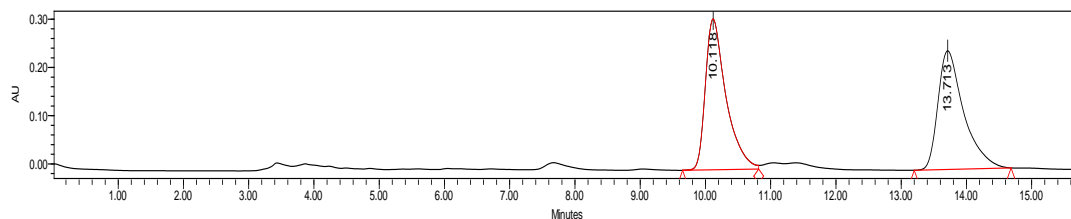
**3-benzyl-1-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4c:** Colorless oil. 77% yield;  $Z/E > 20:1$ ; 97% ee. HPLC (Chiral ID column),  $i\text{-PrOH}/n\text{-Hexane} = 20/80$ , Flow rate: 1.0 mL/min, 254 nm,  $t_r$  (minor) = 9.61 min,  $t_r$  (major) = 13.12 min.



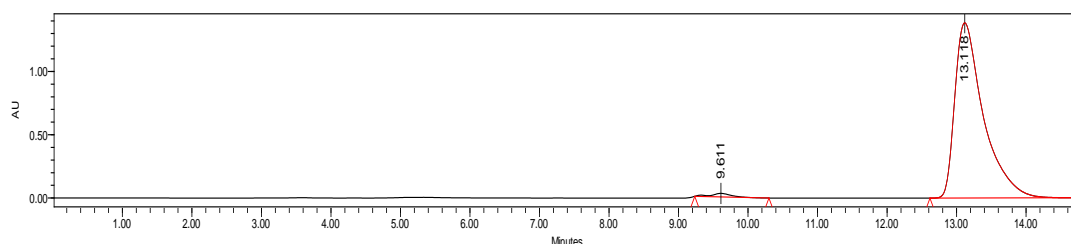
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 7.6$  Hz, 2H), 7.46 (t,  $J = 7.2$  Hz, 1H), 7.38 – 7.28 (m, 6H), 7.24 – 7.18 (m, 2H), 7.18 – 7.09 (m, 4H), 7.05 (d,  $J = 11.6$  Hz, 1H), 6.79 (d,  $J = 11.6$  Hz, 1H), 3.86 (d,  $J = 15.6$  Hz, 1H), 3.71 (d,  $J = 16.0$  Hz, 1H), 1.54 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 190.0, 152.0, 146.3, 140.9, 139.7, 137.8, 136.1, 132.8, 130.0, 129.4, 128.9, 128.8, 128.5, 128.5, 128.3, 126.6, 126.2, 125.5, 125.2, 53.2, 35.5, 32.9.

$[\alpha]_{\text{D}}^{27} = +100.9$  ( $c = 0.57$ , in  $\text{CH}_2\text{Cl}_2$ ).

HRMS (ESI-TOF) calcd for  $\text{C}_{27}\text{H}_{22}\text{NaO}_2^+$  ( $[\text{M}] + \text{Na}^+$ ) = 401.1512, Found 401.1512.

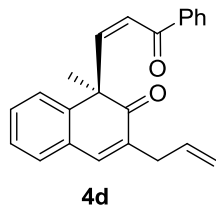


	Retention Time	Area	% Area
1	10.118	6866848	50.51
2	13.713	6727638	49.49



	Retention Time	Area	% Area
1	9.611	565217	1.41
2	13.118	39420809	98.59

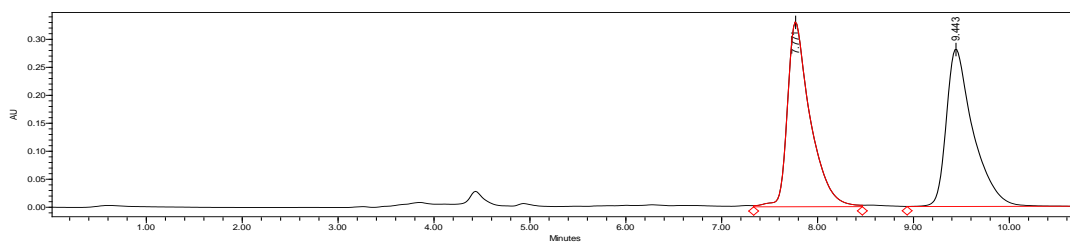
**3-allyl-1-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4d:** Colorless oil. 77% yield; *Z/E* > 20:1; 98% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 7.79 min, *t<sub>r</sub>* (major) = 9.45 min.



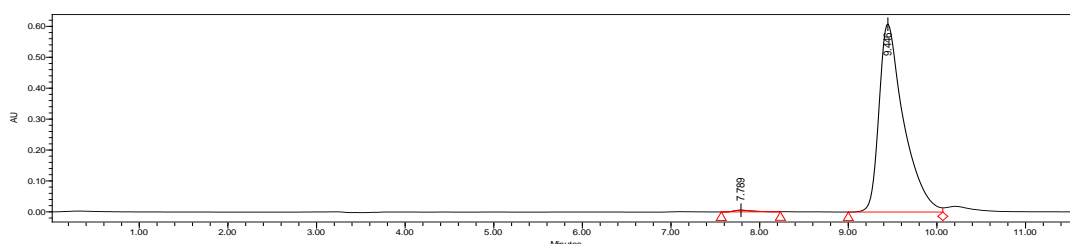
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.63 (m, 2H), 7.45 (tt, *J* = 6.4, 1.2 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.20 – 7.10 (m, 3H), 7.03 (d, *J* = 11.2 Hz, 1H), 6.79 (d, *J* = 11.2 Hz, 1H), 6.05 – 5.90 (m, 1H), 5.24 – 5.10 (m, 2H), 3.32 – 3.10 (m, 2H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 190.2, 151.9, 146.2, 140.3, 137.9, 135.7, 134.7, 132.8, 130.0, 128.8, 128.7, 128.5, 128.3, 126.6, 125.6, 125.3, 123.7, 116.9, 53.2, 33.5, 33.0.

[α]<sub>D</sub><sup>28</sup> = +199.7 (*c* = 0.39, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>20</sub>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 351.1361, Found 351.1358.

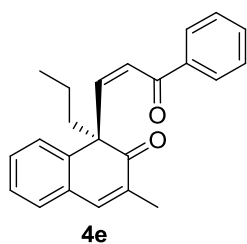


	Retention Time	Area	% Area
1	7.771	5458523	50.11
2	9.443	5435400	49.89



	Retention Time	Area	% Area
1	7.789	78510	0.67
2	9.446	11714913	99.33

**3-methyl-1-(3-oxo-3-phenylprop-1-enyl)-1-propylnaphthalen-2(1H)-one 4e:** Colorless oil.

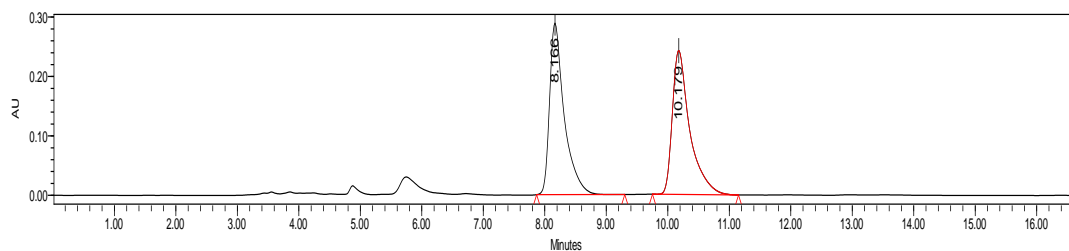


Prepared according to the general procedure B. 70% yield; *Z/E* > 20:1; 89% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t*<sub>r</sub> (minor) = 8.13 min, *t*<sub>r</sub> (major) = 10.06 min.

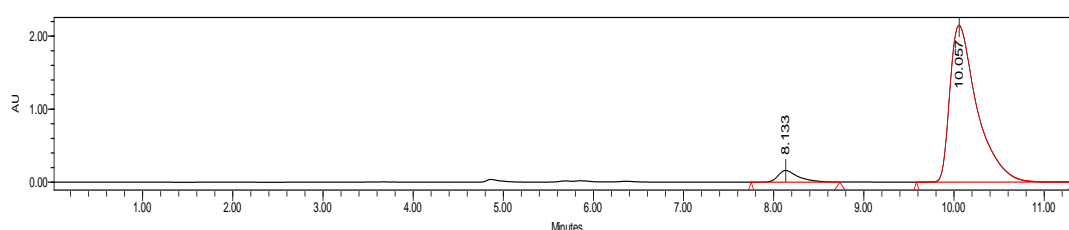
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.59 (m, 2H), 7.47 – 7.35 (m, 1H), 7.37 – 7.23 (m, 3H), 7.23 – 7.17 (m, 1H), 7.16 – 7.03 (m, 3H), 6.94 (d, *J* = 11.6 Hz, 1H), 6.76 (d, *J* = 11.6 Hz, 1H), 2.14 (td, *J* = 12.8, 3.6 Hz, 1H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.87 (td, *J* = 12.6, 3.6 Hz, 1H), 1.16 – 1.01 (m, 1H), 0.99 – 0.85 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.2, 190.6, 151.4, 144.4, 140.7, 137.8, 134.0, 132.7, 131.6, 128.4, 128.3, 128.3, 127.9, 126.6, 126.3, 125.4, 56.6, 49.8, 17.2, 16.0, 14.4.

[α]<sub>D</sub><sup>27</sup> = +275.5 (c = 0.30, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>22</sub>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 353.1517, Found 353.1519.

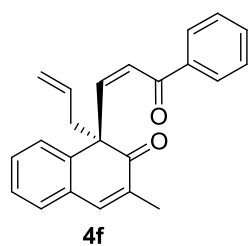


	Retention Time	Area	% Area
1	8.166	4766718	50.04
2	10.179	4758520	49.96



	Retention Time	Area	% Area
1	8.133	2524699	5.35
2	10.057	44704900	94.65

**1-allyl-3-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4f:** Colorless oil.

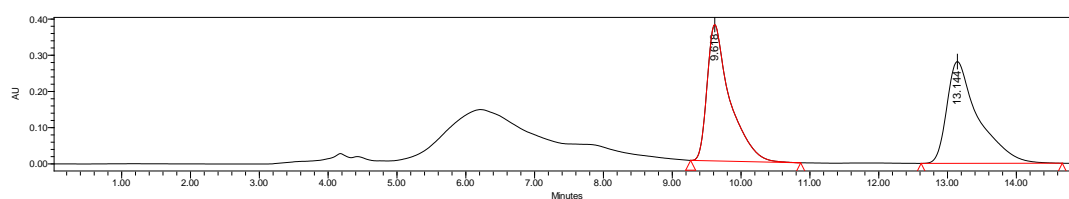


Prepared according to the general procedure B. 68% yield; *Z/E* > 20/1; 97% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) = 9.64 min, *tr* (major) = 13.11 min.

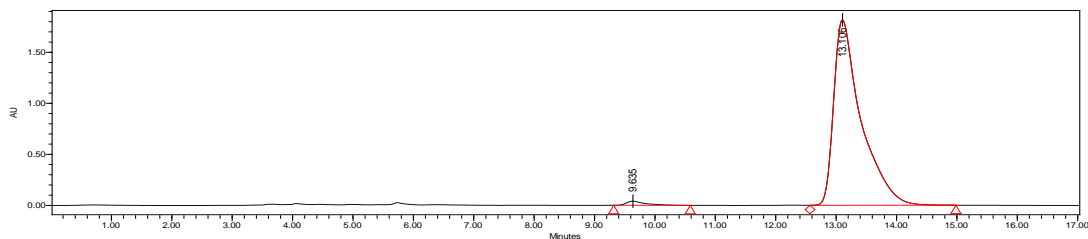
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.61 (m, 2H), 7.44 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.08 – 6.98 (m, 2H), 6.81 (d, *J* = 11.6 Hz, 1H), 5.52 – 5.31 (m, 1H), 5.02 – 4.85 (m, 2H), 2.67 (ddd, *J* = 44.8, 13.2, 7.4 Hz, 2H), 2.02 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 190.3, 150.3, 143.8, 140.6, 137.8, 133.7, 132.7, 132.0, 131.3, 128.4, 128.3, 128.2, 128.1, 126.7, 126.4, 125.5, 119.3, 56.7, 50.1, 16.0.

[α]<sub>D</sub><sup>27</sup> = +230.0 (*c* = 0.33, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>20</sub>NaO<sub>2</sub><sup>+</sup> ([M]+Na<sup>+</sup>) = 351.1356, Found 351.1356.

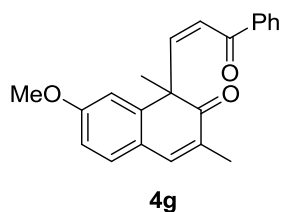


	Retention Time	Area	% Area
1	9.618	8607839	49.22
2	13.144	8879111	50.78



	Retention Time	Area	% Area
1	9.635	876472	1.51
2	13.106	57073475	98.49

### 7-methoxy-1,3-dimethyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one



Colorless oil. 82% yield; >20:1 *Z/E*; 97% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 30/70, Flow rate: 1.0 mL/min, 254 nm, *tr* (minor) = 10.25 min, *tr* (major) = 11.50 min.

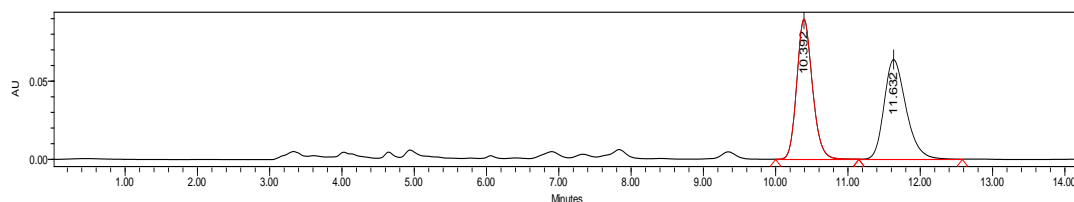
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.24 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 11.6 Hz, 1H), 6.76 (d, *J* = 11.6 Hz, 1H), 6.70 – 6.65 (m, 2H), 3.69 (s, 3H), 2.02 (s,

3H), 1.57 (s, 3H).

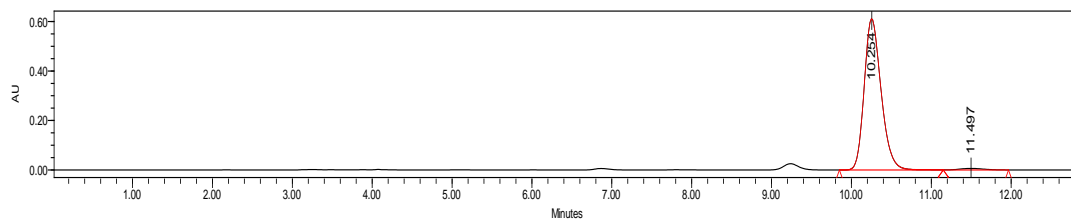
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 190.4, 160.1, 151.6, 148.1, 140.5, 137.8, 132.8, 130.0, 129.7, 128.4, 128.3, 125.5, 123.7, 112.4, 111.5, 55.3, 55.3, 53.2, 33.3, 16.1.

[α]<sub>D</sub><sup>27</sup> = +424.7 (c = 0.21, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>+Na<sup>+</sup>) = 355.1310, Found 355.1301

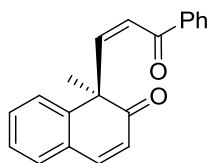


	Retention Time	Area	% Area
1	10.392	1357314	50.04
2	11.632	1355073	49.96



	Retention Time	Area	% Area
1	10.254	8968102	98.61
2	11.497	126641	1.39

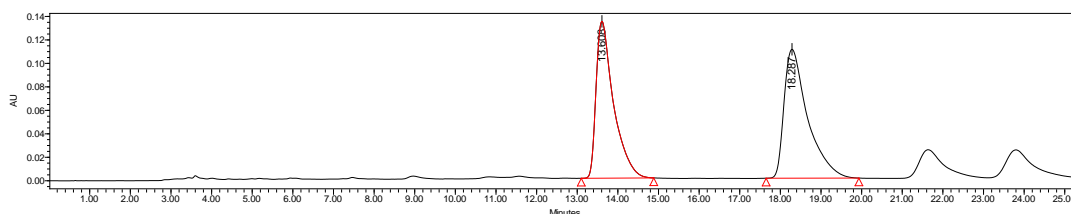
**1-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4h:** Colorless oil. 39% yield; *Z/E* = 4.5:1; 66% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 13.63 min, *t<sub>r</sub>* (major) = 17.89 min.



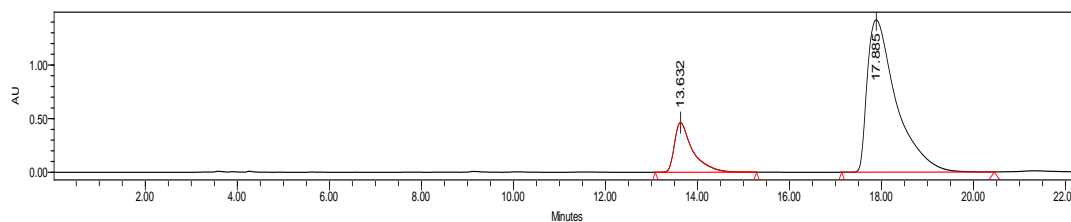
**4h**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 – 7.62 (m, 2H), 7.54 (d, *J* = 9.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.23 – 7.12 (m, 3H), 7.08 (d, *J* = 11.6 Hz, 1H), 6.81 (d, *J* = 11.6 Hz, 1H), 6.29 (d, *J* = 9.6 Hz, 1H), 1.62 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.9, 189.9, 152.0, 147.0, 144.1, 137.8, 132.9, 129.7, 129.6, 129.2, 128.5, 128.3, 126.7, 125.8, 125.6, 125.3, 53.3, 33.0.

[α]<sub>D</sub><sup>27</sup> = +171.2 (c = 0.22, in CH<sub>2</sub>Cl<sub>2</sub>).

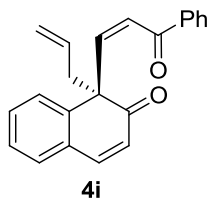


	Retention Time	Area	% Area
1	13.608	3974464	47.37
2	18.287	4415490	52.63



	Retention Time	Area	% Area
1	13.632	12657716	16.98
2	17.885	61878784	83.02

**1-allyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one 4i:** Colorless oil. 33% yield; *Z/E* >



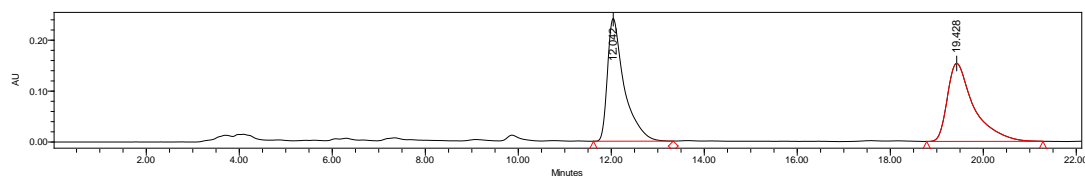
20:1; 89% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 20/80, Flow rate: 1.0 mL/min, 254 nm, *t<sub>r</sub>* (minor) = 12.01 min, *t<sub>r</sub>* (major) = 19.27 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.41 (m, 2H), 7.27 – 7.41 (m, 3H), 7.24 – 7.13 (m, 2H), 7.14 – 7.03 (m, 2H), 6.84 (d, *J* = 11.6 Hz, 1H), 6.28 (d, *J* = 9.6 Hz, 1H), 5.63 – 5.45 (m, 1H), 5.12 – 4.92 (m, 2H), 2.68 (ddd, *J* = 44.6, 13.2, 7.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

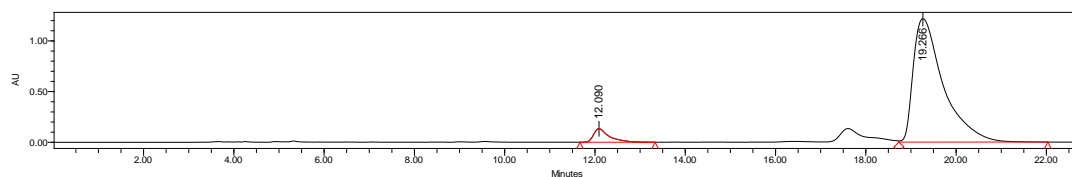
200.0, 189.9, 150.1, 144.7, 144.2, 137.8, 132.8, 131.8, 130.6, 129.3, 129.0, 128.5, 128.3, 126.8, 126.6, 126.5, 125.6, 119.7, 57.1, 49.7.

[α]<sub>D</sub><sup>27</sup> = +316.2 (*c* = 0.21, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>18</sub>NaO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>+Na<sup>+</sup>) = 337.1204, Found 337.1201

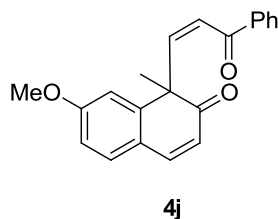


	Retention Time	Area	% Area
1	12.042	5992391	49.91
2	19.428	6014012	50.09



	Retention Time	Area	% Area
1	12.090	3172070	5.33
2	19.266	56356339	94.67

### 7-methoxy-1-methyl-1-(3-oxo-3-phenylprop-1-enyl)naphthalen-2(1H)-one



Colorless oil. 61% yield; *Z/E* > 20:1; 71% ee. HPLC (Chiral ID column), *i*-PrOH/ *n*-Hexane = 30/70, Flow rate: 1.0 mL/min, 254 nm, *t*<sub>r</sub> (minor) = 14.77 min, *t*<sub>r</sub> (major) = 17.73 min.

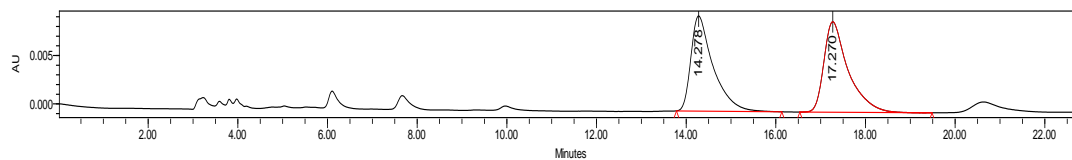
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.40 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 11.4 Hz, 1H), 6.78 (d, *J* = 11.4 Hz, 1H), 6.70 (d, *J* = 14.4 Hz, 2H), 6.17 (d, *J*

= 9.6 Hz, 1H), 3.72 (s, 3H), 1.61 (s, 3H).

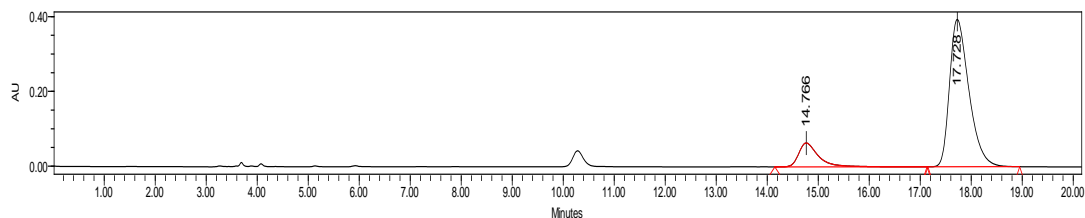
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 190.0, 161.0, 151.7, 149.1, 144.1, 137.8, 132.9, 130.8, 128.5, 128.3, 125.5, 123.2, 123.1, 112.6, 111.4, 55.4, 53.6, 33.2

[α]<sub>D</sub><sup>24</sup> = +226.1 (*c* = 0.39, in CH<sub>2</sub>Cl<sub>2</sub>).

HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>+Na<sup>+</sup>) = 341.1154, Found 341.1143



	Retention Time	Area	% Area
1	14.278	337576	49.03
2	17.270	350945	50.97

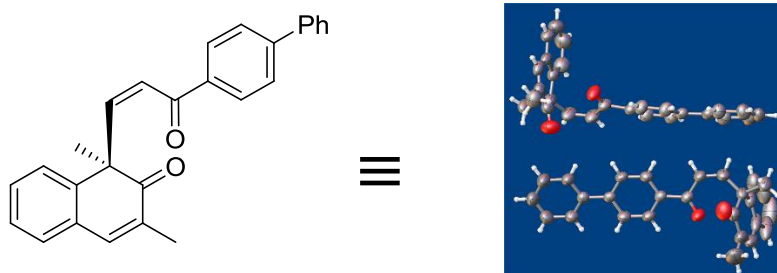


	Retention Time	Area	% Area
1	14.766	1734948	14.28
2	17.728	10417990	85.72



## 6. Determination of the absolute stereochemistry

The absolute configuration of **31** was determined by X-ray diffraction. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 1539229).



**Table 1. Crystal data and structure refinement for 31**

Identification code	fxm-c-na-k18
Empirical formula	C <sub>54</sub> H <sub>44</sub> O <sub>4</sub>
Formula weight	756.89
Temperature/K	297.0(5)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	6.7287(3)
b/Å	36.9509(16)
c/Å	8.6433(5)
α/°	90
β/°	105.177(6)
γ/°	90
Volume/Å <sup>3</sup>	2074.05(19)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.212
μ/mm <sup>-1</sup>	0.588
F(000)	800.0
Crystal size/mm <sup>3</sup>	0.8 × 0.7 × 0.6
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.574 to 145.138
Index ranges	-7 ≤ h ≤ 8, -45 ≤ k ≤ 44, -10 ≤ l ≤ 10
Reflections collected	22516
Independent reflections	7821 [R <sub>int</sub> = 0.0485, R <sub>sigma</sub> = 0.0364]
Data/restraints/parameters	7821/1/527
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0599, wR <sub>2</sub> = 0.1578

Final R indexes [all data]  $R_1 = 0.0647$ ,  $wR_2 = 0.1653$   
Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  0.25/-0.26  
Flack parameter 0.08(15)

## 6. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for the products.

