Chiral Cobalt(II) Complex-Promoted Asymmetric *para*-Claisen Rearrangement of Allyl α-Naphthol Ethers

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1. General Information

Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored with thin-layer chromatography (TLC) using 254 nm UV light. NMR characterization data were collected on bruker ASCENDTM operating at 400 MHz and 600 MHz for 1H NMR, 101 MHz and 151 MHz for ¹³C{1H} NMR (with complete proton decoupling), and 376 MHz and 565 MHz for 19 F{1H} NMR (with complete proton decoupling). 1H NMR and 13 C{1H} NMR: chemical shifts δ were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for ¹H NMR: $CDC_{13} = 7.26$ ppm, $(CD_3)_2CO = 2.05$ ppm; for ¹³C NMR: $CDC_{13} = 77.0$ ppm, $(CD_3)_2CO = 206.3$ ppm). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt =doublet of triplets, dd = doublet of doublets, m = multiplet, hept = heptet)), coupling constants (Hz), integration and assignment. High-resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Enantiomeric excesses (ee) were determined by HPLC or supercritical fluid chromatography (SFC) analysis using the corresponding commercial chiral column as stated in the experimental procedures at 25 °C with PDA detector. Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]^{T}_{D}$ (c g/100 mL, in solvent). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (v, cm⁻¹). All catalytic reactions were run under air conditions. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. 1,1,2,2-TCE, Ethyl acetate (EtOAc), dichloromethane (DCM), and chloroform (CHCl₃) were distilled over CaH₂. Co(BF₄)₂·6H₂O was purchased from Sigma-Aldrich. The N,N-dioxides,¹ C4-substituted 1-naphthols,² were prepared according to the methods reported in the literature were prepared according to the methods reported in the literature.

2. General Procedure for the Synthesis of L₃-TQCp



To a solution of (*S*)-Boc-tetrahydroisoquinoline-3-carboxylic acid (5.54 g, 20.0 mmol) in DCM (40 mL) was added Et₃N (2.43 g, 24.0 mmol), isobutyl carbonochloridate (3.28 g, 24.0 mmol) at 0 °C under stirring. After 15 min, cyclopropylamine (1.37 g, 24.0 mmol) was added. The reaction was allowed to warm to room temperature and detected by TLC. After 48 h, the mixture was washed with 1 M KHSO₄ solution, saturated NaHCO₃ solution, brine, dried over anhydrous Na₂SO₄. After filtration, the mixture was concentrated, and the residue was used in the next step without purification.

The residue in CH_2Cl_2 (10 mL) was added TFA (20 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was diluted with CH_2Cl_2 (20 mL). The pH value of the mixture was brought into the range of 10–12 by the addition of 2 M NaOH solution at 0 °C. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄ and evaporated in vacuo. The residue was subjected to flash column chromatography on silica gel and eluted with EtOAc to afford the product C (3.05 g, 14.13mmol) as a white solid.

To a solution of compound C (3.05 g, 14.13 mmol) in CH₃CN (8 mL) was added K₂CO₃ (5.85 g, 42.4 mmol) and 1,3-dibromopropane (1.43 g, 7.07 mmol). It was kept refluxing for 12 h. Then, K₂CO₃ was removed by filtration and washed by CH₂Cl₂. The filtrate was concentrated and was subjected to flash column chromatography on silica gel and eluted with Pet/EtOAc (1:1 – 1:4, v/v) to give the product **D** (3.08 g, 6.53 mmol) as a white solid.

To a solution of compound **D** (0.94 g, 2.0 mmol) in CH₂Cl₂ (30 mL) was slowly added mixed solid of *m*-CPBA (0.862 g, 5 mmol) at -20 °C. The reaction mixture was stirred at -20 °C for 1 h. Then the reaction was concentrated and was subjected to flash column chromatography on silica gel and eluted with EtOAc/MeOH (10:1 – 1:2, v/v) to afford L₃-TQCp (0.61 g, 1.21 mmol) as a white solid.

3. Typical Procedure for the Synthesis of Substrates



To a solution of naphthol (1.0 equiv), propargyl alcohol (1.2 equiv) and PPh₃ (1.5 equiv) in dry THF (4.0 mL/mmol of naphthol) at 0 °C, diethyl azodicarboxylate (1.5 equiv) was added dropwise. The reaction mixture was stirred at room temperature and detected by TLC. After removing the solvent under vacuo, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1 - 10:1, v/v) to afford the product **B**.

A round-bottomed flask was charged with product **B**, followed by the addition of 1,1,2,2-TCE (0.2 M). The reaction mixture was stirred at 140 °C for 16 h. After removing the solvent under vacuo, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1 – 10:1, v/v) to give the crude product, then wash with petroleum ether to afford product **C**.



A round-bottomed flask was charged with ethyl benzoylacetate (10 mmol, 1.92 g, 1.0 equiv), alkyne (20 mmol, 2.0 equiv), N-bromophthalimide (NBP, 2 mmol, 0.45 g, 0.2 equiv), 2-bromoethylamine hydrobromide (BEA, 3 mmol, 0.62 g, 0.3 equiv) and 1-butyl hydroperoxide (TBHP, 35 mmol, 3.5 equiv), followed by the addition of 1,4-dioxane (20 ml) and EtOH (20ml). The reaction mixture was stirred at 90 °C for 16 h. After removing the solvent under vacuo, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1 - 10:1, v/v) to give the corresponding naphthol products.



To a solution of naphthol (1.0 equiv), allyl alcohol (1.2 equiv) and PPh₃ (1.5 equiv) in dry THF (4.0 mL/mmol of naphthol) at 0 °C, diethyl azodicarboxylate (1.5 equiv) was added dropwise. The reaction mixture was stirred at room temperature and detected by TLC. After removing the solvent under vacuo, the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1 - 10:1, v/v) to afford the product.

4. General Procedure for Preparation of the Racemic Product



A dry reaction tube was charged with *race*- L_3 -PiPr₂ (4.8 mg, 10 mol%) and Zn(OTf)₂ (3.6 mg, 10 mol%) followed by the addition of 1,1,2,2-TCE (1.0 mL). The mixture was stirred at 35 °C for 30 min followed by addition of the substrate A (0.1 mmol). The reaction mixture was stirred at 35 °C and detected by TLC. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the desired racemic products **B**.

5. Representative Experimental Procedure for Asymmetric Catalytic Reactions



A dry reaction tube was charged with L₃-TQCp (5.0 mg, 10 mol%) and Co(BF₄)₂·6H₂O (3.4 mg, 10 mol%) followed by the addition of 1,1,2,2-TCE (1.0 mL). The mixture was stirred at 35 °C for 60 min followed by addition of the substrate **A** (0.1 mmol). The reaction mixture was stirred at 10 °C for 48 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the corresponding products **B**.

6. Optimization of Reaction Conditions

Table S1: Screening of metal salts^[a].

Ph A	Ph L ₃ -PrPr ₂ (10 CO ₂ Et Metal salts (1 1,1,2,2-TCE 16h, 35	0 mol%) 0 mol%) (0.1M) °C Ph	CO ₂ Et
Entry ^[a]	Metal salts	Yield [%] ^[b]	ee [%] ^[c]
1	Zn(OTf) ₂	48	9
2	Mg(OTf) ₂	47	39
3	Co(OTf) ₂	45	50
4	Ni(OTf) ₂	31	39
5	Co(BF ₄) ₂ ·6H ₂ O	47	56
6	Co(ClO ₄) ₂ ·8H ₂ O	64	40

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), L_3 -PrPr₂/metal salts (1:1, 10 mol %) in 1,1,2,2-TCE (0.1 M) at 35 °C for 16 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane.

Table S2: Screening of solvents^[a].

Ph	Ph L3-PrPr2 (1 CO2Et Co(BF4)26H2C Solvents 16h, 35	0 mol%) D(10 mol%) (0.1M) 5 °C Ph	CO ₂ Et
Entrv ^[a]	Solvents	Yield [%] ^[b]	ee [%] ^[c]
1	1,1,2,2-TCE	47	56
2	DCM	32	51
3	DCE	41	55
4	CHCl ₃	50	45
5	EA	18	7
6	Toluene	11	30
7	THF	Trace	ND
8	CH ₃ CN	12	13

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), L_3 -PrPr₂/Co(BF₄)₂·6H₂O (1:1, 10 mol %) in solvent (0.1 M) at 35 °C for 16 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane, DCM = Dichloromethane, DCE = 1,2-Dichloroethane, EA = Ethyl acetate, THF = Tetrahydrofuran, ND = not detected.

Table S3: Screening of ligands^[a].

	Ph		
Ph	Ligand (10 CO ₂ Et Co(BF ₄) <u>2</u> 6H ₂ C 1,1,2,2-TCI 16h, 38	0 mol%) 0 (10 mol%) E (0.1M) 5 °C Ph	CO ₂ Et
A1			B1
$\begin{array}{c} & & & \\ & & & \\ & & & \\$	$=2.6 \cdot \Pr_2 C_0 H_3 \qquad L_3 \cdot \Pr_2 C_1 = 2 \cdot 6 \cdot \Pr_2 C_0 H_3 \qquad L_3 \cdot \Pr_2 C_1 = 2 \cdot 6 \cdot \Pr_2 C_1 + 2 \cdot 6 \cdot \Pr_2 C_1 + 2 \cdot 6 \cdot \Pr_2 C_2 + 2 \cdot 6 \cdot \Pr_2 C_2 + 2 \cdot 6 \cdot \Pr_2 C_1 + 2 \cdot 6 \cdot \Pr_2 C_2 + 2 \cdot \Pr_2 C_2 + 2$		-0 H-N R 6-Pr ₂ C ₂ H ₃
0	от о	$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$	
Entry ^[a]	Ligand	Yield [%] ^[b]	ee [%] ^[c]
1	L ₃ -PrPr ₂	47	56
2	L ₃ -PiPr ₂	56	35
3	L ₃ -RaPr ₂	17	37
4	L3-TQPh	50	45
5	L ₃ -TQCy	Decomposed	
6	L3-TQ ⁱ Pr	Decomposed	
7	L ₃ -TQCp	Decomposed	

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), ligand/Co(BF_4)₂·6H₂O (1:1, 10 mol %) in 1,1,2,2-TCE (0.1 M) at 35 °C for 16 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane.

Table S4.	Screening	of ligands ^[a]
1 abic 57.	Screening	of figands .

	Ph CO ₂ Et Co(BF ₄) ₂ 6h 1.1.2.2-1 48h	(10 mol%) H₂O(10 mol%) → TCE (0.1M) 10 °C Ph	CO ₂ Et
Ph	1		B1
Entry ^[a]	Ligand	Yield [%] ^[b]	ee [%] ^[c]
1	L ₃ -PrPr ₂	<5	63
2	L ₃ -PiPr ₂	13	57
3	L ₃ -RaPr ₂	<5	55
4	L ₃ -TQPh	73	74
5	L ₃ -TQCy	78	82
6	L ₃ -TQ ⁱ Pr	87	85
7	L ₃ -TQCp	86	92
8 ^[d]	L ₃ -TQCp	85	88

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), ligand/Co(BF₄)₂·6H₂O (1:1, 10 mol %) in 1,1,2,2-TCE (0.1 M) at 10 °C for 48 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Reaction was performed at 20 °C for 16 h. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane.

Table S5: Screening of solvents^[a].

Ph	CO ₂ Et Co(BF ₄) ₂ 6H ₂ C Solvent (48h, 10	0 mol%) 0(10 mol%) 0.1M) 0°C Ph	CO ₂ Et
A	<u>Calaranta</u>	V: 11 [0/ 1 [b]	B1
Entry	Solvents		ee [%] ^[e]
1	1,1,2,2-TCE	86	92
2	DCM	83	69
3	DCE	87	77
4	CHCl ₃	82	88
5	EA	Trace	ND
6	Toluene	NR	
7	THF	NR	
8	CH ₃ CN	60	11

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), L_3 -TQCp/Co(BF₄₎₂·6H₂O (1:1, 10 mol %) in solvent (0.1 M) at 10 °C for 48 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane, DCM = Dichloromethane, DCE = 1,2-Dichloroethane, EA = Ethyl acetate, THF = Tetrahydrofuran, ND = not detected, ND = not detected, NR = no reaction.

Table S6: Screening of metal salts^[a].

Ph	Ph CO ₂ Et L ₃ -TQCP (11 Metal salts (1 1,1,2,2-TCE 48h, 10	^{0 mol%)} ^{0 mol%)} [≤] (0.1M) [°] C Ph	CO2Et
£	x1		B1
Entry ^[a]	Metal salts	Yield [%] ^[b]	ee [%] ^[c]
1	Co(BF ₄) ₂ ·6H ₂ O	86	92
2	Co(ClO ₄) ₂ ·8H ₂ O	82	91
3	Co(OTf) ₂	83	86
4	CoCl ₂	Trace	ND
5	Zn(OTf) ₂	89	85
6	Mg(OTf) ₂	90	89
7	Ni(OTf) ₂	91	89

[a] Unless otherwise noted, all reactions were carried out with A1 (0.05 mmol), L_3 -TQCp//metal salts (1:1, 10 mol %) in 1,1,2,2-TCE (0.1 M) at 10 °C for 48 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane, ND = not detected.

7. Gram-Scale Synthesis of the Product B1



An oven dried round-bottom flask (100 mL) was charged with L₃-TQCp (153.5 mg, 10 mol%) and $Co(BF_4)_2 \cdot 6H_2O$ (102.0 mg, 10 mol%) followed by the addition of 1,1,2,2-TCE (30.0 mL). The mixture was stirred at 35 °C for 60 min followed by addition of the substrate A1 (1.338 g, 3 mmol). The reaction mixture was stirred at 10 °C for 48 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the corresponding products B1, in 93% yield (1.247 g) with 91% ee.

8. Synthetic Transformation



To a solution of Copper(I) thiophene-2-carboxylate (2.1 mg, 0.011 mmol) and **B5** (40.7 mg, 0.11 mmol) in toluene (1.1 mL) was added *p*-toluenesulfonyl azide (25.6 mg, 0.13 mmol), and the reaction was stirred at 35 °C for 4 h. The residue was subjected to flash column chromatography on silica gel and eluted with Pet/EtOAc (2:1, v/v) to yield the product **B46** (59.4 mg, 95% yield, 95% *ee*).



9. Non-effect Study



[a] Unless otherwise noted, all reactions were carried out with A1 (0.1 mmol), L_3 -TQCp/Co(BF₄)₂·6H₂O (1:1, 10 mol %) in 1,1,2,2-TCE (0.1 M) at 10 °C for 48 h. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. 1,1,2,2-TCE = 1,1,2,2-Tetrachloroethane.

10. Kinetic Studies

Procedure of react IR experiment for kinetic studies of A1 and L₃-TQCp/Co(BF_4)₂·6H₂O catalyst. Kinetic analysis was performed using in situ attenuated total reflectance Fouriertransform infrared (ATR FTIR) spectroscopy to track the generation of the reactant B1 under synthetically relevant conditions. A Mettler Toledo SW License iC IR 701L instrument was treated as main experiment equipment. All the kinetic experiments on each plot were performed using a single batch of reagents.



First, the infrared absorption spectra of each reactant A1 and product B1 in 1,1,2,2-TCE (1.0 mL) were collected. The following figure shows the absorption of each participant minus the absorption of solvent. Peak at 1663 cm⁻¹ was identified as the characteristic absorption of product B1. Then L₃-TQCp and Co(BF₄)₂·6H₂O were added to the test tube and dissolved in 1,1,2,2-TCE (3.0 mL), the mixture was stirred at 35 °C for 60 min. Finally, A1 (dissolved in 1,1,2,2-TCE (2.0 mL)) was added to the test tube. The reaction mixture was allowed to stir at 20 °C. Reaction progression was monitored by the increasing absorbance of B1 at 1663 cm⁻¹.



Figure S1. Absorption spectra of A1 (0.1 mmol) and B1 (0.1 mmol) in 1,1,2,2-TCE (1.0 mL)



Figure S2. 3D ATR-FTIR profile of the catalytic asymmetric reaction B1.

10.1 Dependence of the reaction rate on concentration of L₃-TQCp/Co(BF₄)₂·6H₂O catalyst.



Kinetic profiles of different initial concentration of L₃-TQCp/Co(BF₄)₂·6H₂O (from 0.005 M to 0.015 M), The plot of k_{obs} vs L₃-TQCp/Co(BF₄)₂·6H₂O displayed a liner relationship, which indicates a first-order kinetic dependence in L₃-TQCp/Co(BF₄)₂·6H₂O.







10.2 Dependence of the reaction rate on concentration of A1.



Kinetic profiles of different initial concentration of A1 (from 0.08 M to 0.14 M), The plot of k_{obs} vs A1 displayed a liner relationship, which indicates a first-order kinetic dependence in A1.



A1/M	reaction rate/(A.U./h)
0.080	0.5677
0.010	0.7353
0.012	0.7724
0.014	0.9574



11. Unsuccessful substrates



12. X-ray Crystal Data

The structure of product **B1** was determined by X-ray chromatography analysis. A single crystal of **B1** was obtained by recrystallization in dichloromethane and petroleum ether at room temperature. The crystal data and further details are listed in **Table S7**. CCDC 2289879 (**B1**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless crystal in flake-shape, with approximate dimensions of $0.100 \times 0.299 \times 0.391 \text{ mm}^3$, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K_{\alpha} = 1.54178\text{ Å}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{a, b, c, d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.



Formula	$C_{31}H_{26}O_3$ (B1)
Formula mass (amu)	446.52
Space group	P 21 21 21
<i>a</i> (Å)	7.8307(1)
b (Å)	15.5594(3)
<i>c</i> (Å)	21.1844(4)
α (deg)	90
β (deg)	90
γ (deg)	90
$V(Å^3)$	2581.13(8)
Ζ	4
λ (Å)	1.54178
<i>T</i> (K)	173 K
$ ho_{ m calcd} ({ m g \ cm^{-3}})$	1.149
μ (mm ⁻¹)	0.576
Transmission factors	0.635, 1.000
$2\theta_{\max}(\deg)$	68.274
No. of unique data, including $F_0^2 < 0$	3056
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2770
No. of variables	237
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0467
$R_{\rm w}(F_{\rm o}{}^2)$ ^b	0.1760
Goodness of fit	1.180

Table S7. Crystallographic Data for C₃₁H₂₆O₃ (**B1**).

^{*a*} $R(F) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b $R_{\rm w}(F_{\rm o}^2) = \left[\sum [w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \sum wF_{\rm o}^4]^{1/2}; w^{-1} = [\sigma^2(F_{\rm o}^2) + (Ap)^2 + Bp], \text{ where } p = \left[\max(F_{\rm o}^2, 0) + 2F_{\rm c}^2\right] / 3.$

The structure of product **B35** was determined by X-ray chromatography analysis. A single crystal of **B35** was obtained by recrystallization in dichloromethane and petroleum ether at room temperature. The crystal data and further details are listed in **Table S8**. CCDC 2235350 (**B35**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless crystal in block-shape, with approximate dimensions of $0.136 \times 0.139 \times 0.256 \text{ mm}^3$, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K_{\alpha} = 1.54178\text{ Å}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{a, b, c, d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.



Table S8. Crystallographic Data for C₂₆H₂₄O₃ (B35).

Formula	C ₂₆ H ₂₄ O ₃ (B35)
Formula mass (amu)	384.45
Space group	P 21 21 21
<i>a</i> (Å)	7.9089(2)
<i>b</i> (Å)	15.0721(3)
<i>c</i> (Å)	17.4446(4)
α (deg)	90
β (deg)	90
γ (deg)	90
$V(Å^3)$	2079.46(8)
Ζ	4
λ (Å)	1.54178
<i>T</i> (K)	173 K
$ ho_{\text{calcd}} (\text{g cm}^{-3})$	1.228
$\mu (\mathrm{mm}^{-1})$	0.628
Transmission factors	0.820, 1.000
$2\theta_{\max}(\deg)$	79.379
No. of unique data, including $F_0^2 < 0$	4362
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4170
No. of variables	264
$R(F)$ for $F_{o}^{2} > 2\sigma(F_{o}^{2})^{a}$	0.0321
$R_{\rm w}(F_{\rm o}{}^2)$ ^b	0.0775
Goodness of fit	1.060

 $^{a}R(F) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b $R_w(F_o^2) = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\right]^{1/2}; w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp], \text{ where } p = \left[\max(F_o^2, 0) + 2F_c^2\right] / 3.$

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^a Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122.

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^d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. J. Appl. Cryst. 2009,

42, 339-341.

^e Spek, A. L. J. Appl. Cryst. 2003, 36, 7-13

13. DFT Calculation of Reaction Mechanism

13.1 Computational Methods

All calculations were performed using Gaussian 09 program package,^[1] employing the B3LYP-D3 density functional with the 6-31G(d,p) basis set. Geometries were optimized in 1,1,2,2-TCE solvent and characterized by frequency analysis at 298 K. The self-consistent reaction field (SCRF) method based on the universal solvation model SMD^[2] was adopted to evaluate the effect of solvent. Grimme's DFT-D3 approach for the treatment of London-dispersion interactions were used in structural optimization. ^[3-4] The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.^[5]



Figure S3. Energy profile for the rearrangement reaction of B1 catalyzed by Zn(OTf)₂.



Figure S4. Energy profile for the rearrangement reaction of B34 catalyzed by Zn(OTf)₂.



Figure S5. Evaluation of energy barrier associated with the formation of ion-pair by C₁-O bond relaxed scan.



Figure S6. Optimized geometries of intermediates and transition states. Relative Gibbs free energy in parenthesis was in kcal mol⁻¹.









IM3-Ph (5.3)









TS2-Ph-a (7.9)

IM4-Me (-3.0)

Figure S7. Optimized geometries of intermediates and transition states. Relative Gibbs free energy in parenthesis was in kcal mol⁻¹.

Structures	^a ZPE	^b <i>H</i> _c	$^{c}G_{c}$	E_z	Н	G
IM1-Me	0.49251	0.53566	0.41168	-4932.60362	-4932.56046	-4932.68444
TS1-Me	0.48937	0.53259	0.40680	-4932.58151	-4932.53829	-4932.66408
IM2-Me	0.49222	0.53512	0.41248	-4932.59220	-4932.54929	-4932.67193
TS2-Me	0.49032	0.53300	0.41120	-4932.58236	-4932.54057	-4932.66148
IM3-Me	0.49256	0.53544	0.41393	-4932.61181	-4932.56893	-4932.69044
IM1-Ph	0.54639	0.59199	0.46240	-5124.31128	-5124.26568	-5124.39527
TS1-Ph	0.54416	0.58959	0.46076	-5124.29843	-5124.25299	-5124.38182
IM2-Ph	0.54382	0.59016	0.45936	-5124.29773	-5124.25139	-5124.38219
IM3-Ph	0.54378	0.58986	0.46133	-5124.30443	-5124.25834	-5124.38688
TS2-Ph	0.54411	0.58935	0.46291	-5124.30349	-5124.25826	-5124.38469
IM4-Ph	0.54608	0.59161	0.46330	-5124.31734	-5124.27181	-5124.40012
TS1-Me-a	0.54355	0.59344	0.45423	-5124.29333	-5124.24345	-5124.38266

Table S9. The correct electronic energies (E_Z) , enthalpies (H), and Gibbs free energies (G) for all stationary points (in Hartree), obtained at the B3LYP-D3/6-31G(d,p) (SMD, CCl₄) level of theory.

^a Zero-point correction energy;

^b Thermal correction to enthalpy;

^c Thermal correction to Gibbs free energy.

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INIT-Me			
С	2.50145000	1.97114000	1.81214100
С	2.97649200	2.89782500	0.74939100
С	2.49575700	4.13662400	0.59016100
С	2.87935300	5.07438000	-0.51096200
Н	3.63300200	4.64006800	-1.17439000
Н	1.99652100	5.33594100	-1.10838700
Н	3.28259300	1.32260200	2.20703700
Н	3.70680500	2.49665200	0.04870600
Н	1.75735000	4.50610500	1.30301200
Н	1.98317600	2.48133100	2.62638300
Н	3.27443200	6.01526100	-0.10885300
С	-2.45213200	0.85862500	4.30776600
С	-1.10885200	0.43445000	4.42775600
С	-0.22813400	0.62787900	3.38902000
С	-0.66125300	1.26313500	2.19501000
С	-2.89962200	1.46751200	3.15504900
С	-2.02229600	1.69593400	2.06309300
Н	-3.14263400	0.68922300	5.12825500
Н	-0.77775600	-0.06073400	5.33497400
Н	0.79427500	0.27423000	3.45400600
Н	-3.94127300	1.75395000	3.07409000
С	-2.44580700	2.31822700	0.84242600
С	0.21817800	1.43410400	1.09637400
С	-0.20792200	2.02003500	-0.08648700
С	-1.55215500	2.47216400	-0.18789600
0	1.52328200	0.98092800	1.24091900
С	-3.89453400	2.74120000	0.63797200
Н	-3.94922600	3.42520100	-0.21721100
С	-4.75942300	1.58251200	0.40210300
С	-5.40891800	0.57714100	0.20813400
Н	-4.25465000	3.31113900	1.50383900
С	-6.17068400	-0.61001900	-0.02405400
С	-5.55248400	-1.75246700	-0.56859700
С	-7.54260800	-0.65624800	0.29040900
С	-6.29352000	-2.91043100	-0.79003900
Н	-4.49744200	-1.72100300	-0.81310000
С	-8.27489100	-1.81915700	0.06435200
Н	-8.02166300	0.22265000	0.71027800
С	-7.65417200	-2.94871600	-0.47512800

13.2	Cartesian	coordinates	of all	stationary	points in	this	work
IM1	Mo						

Н	-5.80553000	-3.78557900	-1.20880100
Н	-9.33250300	-1.84429200	0.31041800
Н	-8.22790500	-3.85428900	-0.64899900
С	0.65922600	2.06256500	-1.27859300
0	1.56383500	1.24144900	-1.53079200
0	0.37602700	3.03048500	-2.12128200
С	1.11761800	3.06506200	-3.38820100
С	0.56459500	4.22050800	-4.18925400
Н	2.17803200	3.18355800	-3.15188700
Н	0.97777900	2.10181300	-3.88557600
Н	0.70246400	5.16928100	-3.66277000
Н	1.09287700	4.27758800	-5.14569800
Н	-0.50107200	4.08207400	-4.39257000
Н	-1.87510700	2.91015800	-1.12504900
Zn	2.02139300	-0.26791000	-0.32030000
0	3.88566400	-0.60344300	-0.54298200
S	4.63519500	-1.20483900	0.66756700
С	4.42736100	-3.02572600	0.32677700
0	6.06595800	-0.92225400	0.62233900
F	3.12084100	-3.31509400	0.25470600
F	5.01096700	-3.34859100	-0.82801500
F	4.97824200	-3.73435900	1.31478600
0	3.88064700	-0.95674600	1.91026500
0	0.58365000	-1.48644100	0.05580500
S	-0.02191400	-2.21560200	-1.15659400
С	-1.54694000	-1.17091300	-1.45814200
0	-0.52238300	-3.54474600	-0.82489100
F	-2.15456200	-0.86978200	-0.30583700
F	-2.40396400	-1.83412200	-2.24114900
0	0.82158300	-2.01511100	-2.34675400
F	-1.20875300	-0.02311600	-2.07546400
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С	-1.36405000	-1.93343500	-0.92537900
С	-3.59962400	-2.86942000	-1.13309500
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Н	-1.81788600	-3.34593600	-3.99619200
Н	-0.10681200	-2.13211900	-2.65593500
Н	-4.58777800	-3.06001600	-0.73210200

-2.91469800

С

-1.73792300

1.00170500

С	-0.32684500	-1.23798300	-0.17136800
С	-0.60148300	-0.92445400	1.20620100
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Н	-4.23778400	-1.66554800	2.68733900
С	-5.33202500	-1.14369300	0.96902400
С	-6.16395200	-0.48549600	0.38220000
Н	-4.56185500	-2.99904600	1.59556000
С	-7.13200200	0.28574300	-0.33244700
С	-6.91700000	0.60578700	-1.68734200
С	-8.30801800	0.73318300	0.29932800
С	-7.85814400	1.35545100	-2.38830300
Н	-6.01026400	0.26247700	-2.17537300
С	-9.24363900	1.48187700	-0.41059500
Н	-8.47630100	0.48905200	1.34342300
С	-9.02288500	1.79524100	-1.75405600
Н	-7.68171000	1.59814100	-3.43207000
Н	-10.14722400	1.82260700	0.08637000
Н	-9.75436800	2.38009000	-2.30379200
С	0.34171800	-0.10236700	1.98487400
0	1.51074000	0.15670500	1.65898300
0	-0.14186800	0.33283100	3.13574300
С	0.71505100	1.23508700	3.91621700
С	-0.11550000	1.72177500	5.08124200
Н	1.59685400	0.67223500	4.23513200
Н	1.04019300	2.04076900	3.25456700
Н	-0.44173800	0.88958900	5.71264000
Н	0.48624300	2.40218600	5.69139000
Н	-0.99771700	2.26488700	4.73062800
Н	-2.14370000	-0.76299200	2.71538300
Zn	2.25803100	0.16327700	-0.20520900
0	4.07472400	-0.49857800	0.50589200
S	4.61850700	-1.05656800	-0.79953700
С	6.00099900	0.11292000	-1.23132300
0	5.20972400	-2.39325000	-0.72003600
F	5.52856000	1.35824300	-1.29582800
F	6.95210200	0.04757800	-0.29611700
F	6.52009100	-0.22695300	-2.41357800
0	3.55913100	-0.82341900	-1.82903000
0	2.21200800	1.94768500	-0.94568900
S	1.68082900	3.19709600	-0.23120700
С	-0.15002500	2.99949400	-0.51829600
0	2.05650500	4.42450100	-0.92844600

F	-0.42903400	2.92703400	-1.82165400
F	-0.81921300	4.02354000	0.01807200
0	1.83068200	3.12435300	1.22845500
F	-0.58451400	1.85946500	0.06800600
С	1.90392000	-3.33815100	-0.05190500
С	1.74037600	-3.00107300	1.25951600
С	0.47616000	-3.05301300	1.88381000
С	0.31958100	-2.93426300	3.35868300
Н	1.06423800	-2.27017100	3.80493900
Н	-0.68564300	-2.61712200	3.64285000
Н	2.87923200	-3.31631200	-0.52562100
Н	2.59009600	-2.62816300	1.82524500
Н	-0.34292400	-3.51498100	1.33873600
Н	1.07283700	-3.69788500	-0.64995400
Н	0.47395300	-3.93614800	3.78794800
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0	4.18764700	-0.36079900	0.83189300
S	4.83717100	-0.55057700	-0.52716000
С	6.01328400	0.88723000	-0.66566900
0	5.63178200	-1.76003900	-0.71908100
F	5.33836200	2.02672900	-0.49948100
F	6.95564700	0.78954200	0.27425200
F	6.58538600	0.88163800	-1.87054600
0	3.74996100	-0.24895100	-1.52556200
С	2.55683200	-3.43422800	-0.40508200
С	2.04210800	-2.99061600	0.74348700
С	0.59948400	-3.15565900	1.13589300
С	0.49595300	-3.70411000	2.56744300
Н	0.90827700	-3.00149700	3.30009900
Н	-0.53301100	-3.93740800	2.84917100
Н	3.61325600	-3.32806000	-0.62989600
Н	2.69101100	-2.50054900	1.46554700
Н	0.11625000	-3.85458100	0.44601100
Н	1.94008000	-3.91660300	-1.16055700
Н	1.07969300	-4.62620300	2.63595600
С	-3.05927300	-2.38311900	-3.35924700
С	-1.81806400	-1.88177800	-3.76860100
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С	-1.14548400	-1.73714700	-1.44617700
С	-3.35156700	-2.55352900	-2.00782000
С	-2.40458800	-2.23668300	-1.02229300
Н	-3.81113300	-2.63654000	-4.10055100
Н	-1.60084300	-1.74618400	-4.82282300

Н	0.09674900	-1.14941100	-3.09836100
Н	-4.33206000	-2.91556200	-1.72480800
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С	-1.72294300	-2.13709400	1.32070500
0	0.90643000	-0.79072600	-0.86883000
С	-4.08330600	-2.75686400	0.87645900
Н	-4.06694600	-2.93226000	1.95769400
С	-5.07005900	-1.72378200	0.55374500
С	-5.83158500	-0.83373800	0.24147900
Н	-4.37870900	-3.71153500	0.41875700
С	-6.70278600	0.22640400	-0.15781200
С	-6.37162000	1.02072400	-1.27335100
С	-7.89077700	0.49576600	0.54793700
С	-7.21149100	2.05841300	-1.66888600
Н	-5.45477400	0.81486800	-1.81693100
С	-8.72437500	1.53617500	0.14413700
Н	-8.14843800	-0.11368300	1.40836100
С	-8.38877400	2.31958500	-0.96296200
Н	-6.94570700	2.66568000	-2.52911200
Н	-9.63836500	1.73689000	0.69545800
Н	-9.04075200	3.13049300	-1.27389700
С	0.27802300	-0.74371500	1.92525500
0	1.41835200	-0.28753600	1.81327300
0	-0.52978100	-0.38936400	2.89565500
С	-0.10328000	0.68759900	3.80405500
С	-1.36010300	1.37521000	4.28430700
Н	0.46325500	0.21482500	4.61073200
Н	0.55376900	1.36204400	3.25546800
Н	-2.02721100	0.67803300	4.79872800
Н	-1.08653700	2.17299700	4.98148700
Н	-1.89245800	1.82315200	3.44167800
Н	-1.95246400	-2.22636100	2.37431400
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0	1.99523400	2.12329600	0.18466400
S	0.94139800	2.85922400	-0.65508200
С	-0.56554400	2.65358600	0.42982900
0	0.60492800	2.13594000	-1.88590000
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F	-1.59906300	3.32613700	-0.07555400
0	1.18084800	4.29929700	-0.69514300
F	-0.33004300	3.08963300	1.67697600

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С	2.55334400	3.37269300	-1.95506600
С	1.84332100	2.75251800	-0.90969200
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Н	-0.92453400	1.82448100	-2.70556300
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С	0.31132700	1.51663100	1.18503900
С	1.64409700	2.01649000	1.40850900
0	-1.24258900	0.86989100	-0.53912900
С	3.81095200	3.04380400	0.75032700
Н	3.92391100	3.19951600	1.82958700
С	4.68318700	1.95548200	0.30066600
С	5.21663700	0.93717600	-0.08600900
Н	4.07594400	3.99482500	0.27536700
С	5.69467800	-0.33753000	-0.51963000
С	4.81335800	-1.43469000	-0.44503200
С	6.99287900	-0.53154000	-1.02275100
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Н	7.67573900	0.31012900	-1.08127200
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С	-0.22981400	0.57853400	2.19732200
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0	0.33637800	0.70471800	3.38278100
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С	0.71252500	-1.55698900	4.25154100
Н	0.25143100	0.26735400	5.35257900
Н	-1.11806600	-0.38743200	4.41629100
Н	1.79292500	-1.38546500	4.23660800
Н	0.48083700	-2.22035900	5.09107300
Н	0.40971500	-2.05921500	3.33025700
Н	2.06416100	1.89668300	2.39943000
Zn	-2.02670000	-0.70518700	0.29612000

0	-3.92222700	-0.84186700	0.53195700
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С	-4.69622600	-0.61195700	-1.96300700
0	-6.31295300	-0.30413100	0.14559700
F	-3.39642700	-0.46961000	-2.30375400
F	-5.01765200	-1.90277200	-2.04774000
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S	-0.40582700	-3.27409300	0.12484300
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F	2.20638700	-3.22875700	0.57072900
0	-0.65915800	-3.26614400	1.57262600
F	1.28206200	-1.25924800	0.50100500
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С	-0.98160100	3.24123900	1.77760000
С	-2.38259400	2.76469300	1.60145900
Н	-2.64168800	2.56672000	0.55962100
Н	-2.61108000	1.87904900	2.19586000
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Н	-0.98343700	4.52493600	0.03661100
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С	1.37018500	3.17508400	-3.54432300
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С	1.02699900	1.21790100	0.95250300
С	2.29988800	1.70036600	1.22520900
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С	4.80609400	-1.85634600	-0.47454700
С	7.18185900	-1.36221600	-0.60142100
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Н	3.79108600	-1.52374000	-0.29027400
С	7.42904200	-2.69048500	-0.94312800
Н	7.99927300	-0.65303300	-0.51812300
С	6.37467800	-3.60132100	-1.05010000
Н	4.23529000	-3.87834200	-0.89663000
Н	8.44874700	-3.01594000	-1.12708500
Н	6.57459400	-4.63492800	-1.31651500
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0	-0.77837900	-0.12908100	1.82629100
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С	0.42685700	-0.54157100	4.16179100
С	0.75796300	-1.98655200	3.84162300
Н	0.92211900	-0.19512100	5.07019300
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F	1.80733500	-2.96324100	-1.22520900
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С	-3.97534700	2.72868000	-0.33847400
Н	-1.98351500	3.17203100	2.95501400
Н	-4.37835200	2.55379000	3.03658200
Н	-5.64207100	2.21485300	0.91653300
Н	-4.52636000	2.56939500	-1.25816300
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С	3.18619400	2.40676600	-3.70636500
С	1.91382200	1.95338500	-4.08266500
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С	1.28421200	1.85918600	-1.74420900
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С	5.64278500	0.54860900	0.27800700
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С	6.09296200	-0.80270400	0.16825000
С	5.14298700	-1.82965500	0.33526900
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С	5.52003600	-3.16333400	0.22124200
Н	4.11793100	-1.56048600	0.55542300
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С	6.85016300	-3.49187700	-0.05583000
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Н	-1.37671200	0.46604900	3.90150000
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F	-5.45646200	-2.56046500	-2.22968000
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0	-0.90491300	-2.06924300	-0.77554500
S	-0.25765000	-3.04937800	0.20527600
С	1.48686100	-2.38773800	0.23435200
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F

Н

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С	-0.58488200	4.33899000	-2.06037800
С	-0.40526300	3.28244400	-1.16089300
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С	-0.03765100	1.05594500	0.64791700
С	-0.48962100	2.23638700	1.12062700
0	0.72351800	-0.16384600	-1.26205800
С	0.31925100	4.54229600	0.91117000
Н	0.03576200	4.74097900	1.95246000
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С	2.77880300	3.52996600	0.75627700
Н	0.18477400	5.48099300	0.36300500
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С	4.06307800	1.44455000	0.85410300
С	5.22522200	3.53101000	0.40460200
С	5.27036400	0.75762300	0.77066900
Н	3.14945600	0.89839400	1.05929900
С	6.42859900	2.83432600	0.32257500
Н	5.20025000	4.60689800	0.26298800
С	6.45478300	1.44892900	0.50405200
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0	0.44851900	0.28362800	2.80778400
С	0.73524800	-0.78851300	3.77601200
С	1.19527000	-0.11394700	5.04676800
Н	-0.17944500	-1.37196100	3.91027200
Н	1.50261500	-1.42593400	3.33065600
Н	0.41699700	0.53687900	5.45583700
Н	1.43054800	-0.87991200	5.79180100

2.09624100

4.86780400

0.47937400

Н	-0.71224200	2.32395600	2.18042900
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F	-2.36672000	-2.92639700	1.18829200
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0	-3.50180500	-1.90812400	-2.30293800
0	1.78341800	-3.19926600	-0.43723100
S	3.09090500	-2.85141100	0.29648600
С	4.15309900	-2.34949500	-1.15051000
0	3.72019900	-4.02924800	0.88578200
F	4.18029600	-3.31815400	-2.06813100
F	5.40407700	-2.10766800	-0.73639400
0	2.96117800	-1.62709500	1.10858300
F	3.65756800	-1.23544100	-1.70597000
С	-2.15265800	3.97966000	0.56456100
С	-3.19058800	2.97233400	0.15763200
С	-4.13148800	2.49811700	0.98786800
Н	-2.28000300	4.91703800	0.00948700
Н	-3.14229600	2.62709900	-0.87249500
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С	-6.20380600	1.29836100	1.61697600
С	-6.17693400	-0.20480500	-0.72533900
Н	-4.36730900	0.82793800	-1.20766300
С	-7.21126400	0.36379000	1.38094800
Н	-6.21385300	1.88016700	2.53569500
С	-7.20211600	-0.39112000	0.20714800
Н	-6.13728400	-0.80969500	-1.62570100
Н	-7.99915900	0.22296900	2.11547500
Н	-7.97922600	-1.12768800	0.02491600

14. Spectral Characterization Data for the Substrates

Ethyl 1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A1)

White solid, Mp: 109-111 °C, 75% yield.



¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (dd, J = 8.4, 1.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 7.69 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.61 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.36 (td, J = 7.1, 6.1, 1.3 Hz, 2H), 7.30 (dq, J = 6.3, 3.0 Hz, 4H), 6.82 (d, J = 15.8 Hz, 1H), 6.61 (dt, J = 16.0, 6.1 Hz, 1H), 4.84 (dd, J = 6.1, 1.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.44 (t, J = 7.2 Hz, 3H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 166.2, 156.2, 136.5, 134.6, 133.1, 131.6, 129.2, 128.6, 128.5, 128.2, 127.9, 126.6, 126.5, 126.4, 124.8, 124.5, 123.8, 123.5, 119.5, 86.8, 83.7, 76.6, 61.2, 23.5, 14.4.

HRMS (ESI) Calculated for $C_{31}H_{26}O_3$ ([M]+Na⁺) = 469.1774, Found 469.1781.

IR (neat) 2980, 1718, 1620, 1599, 1571, 1491, 1446, 1416, 1393, 1355, 1305, 1274, 1224, 1204, 1152, 1082, 1022, 961, 802, 754, 690, 639, 556, 529, 495, 432 cm⁻¹.

Methyl 1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A2)

Colorless oil, 48% yield.



¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.44 – 8.39 (m, 1H), 8.14 (dt, *J* = 8.5, 0.9 Hz, 1H), 8.11 (s, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.49 – 7.44 (m, 4H), 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 6.83 (d, *J* = 15.8 Hz, 1H), 6.62 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.84 (dd, *J* = 6.1, 1.4 Hz, 2H), 4.19 (s, 2H), 3.99 (s, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 166.6, 156.3, 136.5, 134.6, 133.3, 131.6, 129.2, 128.6, 128.6, 128.5, 128.2, 127.9, 127.9, 126.6, 126.5, 126.4, 124.7, 124.5, 123.8, 123.5, 119.1, 86.8, 83.6, 76.7, 52.3, 23.5.

HRMS (ESI) Calculated for $C_{30}H_{24}O_3$ ([M]+Na⁺) = 455.1618, Found 455.1620.

IR (neat) 3026, 2948, 1722, 1620, 1600, 1571, 1492, 1436, 1388, 1359, 1307, 1276, 1229, 1208, 1153, 1084, 1027, 965, 692, 529, 495 cm⁻¹.

Isopropyl 1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A3)



White solid, Mp: 77-80 °C, 63% yield.

¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, J = 8.4 Hz, 1H), 8.14 – 8.08 (m, 2H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.46 (dt, J = 5.9, 2.3 Hz, 4H), 7.37 – 7.33 (m, 2H), 7.29 (p, J = 3.8, 3.1 Hz, 4H), 6.83 (d, J = 15.9 Hz, 1H), 6.61 (dt, J = 15.9, 6.0 Hz, 1H), 5.35 (hept, J = 6.1 Hz, 1H), 4.84 (dd, J = 6.0, 1.5 Hz, 2H), 4.19 (s, 2H), 1.42 (d, J = 6.2 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.7, 156.0, 136.6, 134.5, 133.0, 131.6, 129.2, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 126.6, 126.5, 126.4, 124.9, 124.5, 123.8, 123.5, 119.9, 86.8, 83.7, 76.5, 68.6, 23.5, 22.0.

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1948.

IR (neat) 3027, 2979, 2934, 1715, 1620, 1600, 1572, 1492, 1448, 1416, 1388, 1362, 1306, 1275, 1227, 1206, 1154, 1107, 1082, 1027, 963, 835, 691, 529, 496, 425 cm⁻¹.

Phenyl 1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A4)

White solid, Mp: 96–99 °C, 60% yield.



¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.46 (t, J = 6.5 Hz, 1H), 8.32 (q, J = 3.0 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.46 (h, J = 3.2 Hz, 4H), 7.42 (t, J = 5.8 Hz, 2H), 7.39 – 7.27 (m, 9H), 6.81 (dd, J = 15.9, 4.6 Hz, 1H), 6.67 – 6.60 (m, 1H), 4.93 (d, J = 5.4 Hz, 2H), 4.24 (s, 2H). ¹³C{¹H} **NMR** (151 MHz, Chloroform-*d*) δ 164.3 , 157.4 , 150.9 , 136.4 , 135.0 , 133.6 , 131.6 , 129.5 , 129.0 , 128.8 , 128.5 , 128.2 , 127.9 , 126.7 , 126.6 , 126.5 , 125.9 , 124.7 , 124.6 , 123.9 , 123.4 , 121.8 , 118.4 , 86.7 , 83.9 , 77.0 , 23.6 . **HRMS** (ESI) Calculated for C₃₅H₂₆O₃ ([M]+Na⁺) = 517.1774, Found 517.1780.

IR (neat) 3059, 1738, 1620, 1595, 1571, 1491, 1452, 1415, 1388, 1358, 1306, 1274, 1191, 1160, 1140, 1069, 1025, 961, 897, 837, 756, 735, 689, 528, 499, 434 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-(prop-2-yn-1-yl)-2-naphthoate (A5)



White solid, Mp: 81-84 °C, 82% yield.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (dd, J = 8.3, 1.3 Hz, 1H), 8.04 (dt, J = 8.6, 0.9 Hz, 1H), 8.02 (s, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.60 (dt, J = 15.9, 6.1 Hz, 1H), 4.82 (dd, J = 6.1, 1.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 3.97 (dd, J = 2.7, 0.9 Hz, 2H), 2.28 (t, J = 2.7 Hz, 1H), 1.44 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.2 , 156.2 , 136.5 , 134.4 , 133.1 , 128.6 , 128.6 , 127.9 , 127.8 , 126.6 , 126.5 , 124.8 , 124.6 , 123.7 , 119.5 , 81.22 , 76.6 , 71.5 , 61.2 , 22.5 , 14.4 .

HRMS (ESI) Calculated for $C_{25}H_{22}O_3$ ([M]+Na⁺) = 393.1461, Found 393.1465.

IR (neat) 3295, 2981, 1719, 1621, 1602, 1572, 1508, 1450, 1416, 1394, 1356, 1302, 1277, 1206, 1155, 1084, 1021, 965, 890, 765, 693, 645, 496 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-(ethoxymethyl)-2-naphthoate (A6)

White solid, Mp: 39–42 °C, 55% yield.



¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.38 – 8.33 (m, 1H), 8.16 – 8.11 (m, 1H), 7.91 (s, 1H), 7.64 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.57 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 6.80 (d, J = 15.8 Hz, 1H), 6.58 (dt, J = 15.9, 6.1 Hz, 1H), 4.90 (s, 2H), 4.81 (dd, J = 6.1, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 3.63 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.2 , 156.9 , 136.5 , 135.0 , 133.1 , 129.9 , 129.2 , 128.5 , 127.9 , 127.4 , 126.6 , 126.4 , 124.7 , 124.4 , 124.2 , 119.1 , 76.6 ,

70.9,65.9,61.2,15.2,14.3.

HRMS (ESI) Calculated for $C_{25}H_{26}O_4$ ([M]+Na⁺) = 413.1723, Found 413.1724.

IR (neat) 2975, 2864, 1719, 1620, 1571, 1507, 1449, 1419, 1394, 1353, 1277, 1220, 1154, 1087, 1021, 963, 765, 692, 496, 435 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-2-naphthoate (A7)

Colorless oil, 91% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.37 (dd, J = 6.3, 3.6 Hz, 1H), 7.95 (dt, J = 6.9, 3.4 Hz, 1H), 7.77 (s, 1H), 7.54 (dt, J = 6.5, 2.9 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.20 (d, J = 7.4 Hz, 3H), 6.82 (d, J = 15.8 Hz, 1H), 6.61 (dt, J = 15.9, 6.0 Hz, 1H), 4.84 (dd, J = 6.0, 1.4 Hz, 2H), 4.47 – 4.40 (m, 4H), 1.44 (d, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.4 , 155.7 , 140.2 , 136.5 , 135.3 , 133.0 , 132.4 , 129.3 , 128.6 , 128.5 , 128.5 , 128.3 , 127.9 , 127.9 , 126.6 , 126.2 , 126.1 , 124.9 , 124.7 , 124.4 , 119.5 , 76.5 , 61.2 , 38.8 , 14.34 .

HRMS (ESI) Calculated for $C_{29}H_{26}O_3$ ([M]+Na⁺) = 445.1774, Found 445.1775.

IR (neat) 3026, 2979, 1718, 1619, 1600, 1571, 1494, 1450, 1416, 1393, 1355, 1276, 1225, 1205, 1152, 1081, 1022, 962, 866, 802, 765, 730, 694, 559, 495, 459 cm⁻¹.

Ethyl 4-chloro-1-(cinnamyloxy)-2-naphthoate (A8)

White solid, Mp: 66–69 °C, 84% yield.



¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (dt, J = 8.3, 1.1 Hz, 1H), 8.26 (dt, J = 8.4, 0.9 Hz, 1H), 8.02 (s, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.46 – 7.43 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 6.80 (d, J = 15.9 Hz, 1H), 6.58 (dt, J = 15.9, 6.1 Hz, 1H), 4.83 (dd, J = 6.1, 1.4 Hz, 2H), 4.47 – 4.42 (m, 2H), 1.44 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 165.1, 155.8, 136.4, 133.6, 133.5, 130.0, 129.4, 128.6, 128.0, 127.3, 127.1, 126.7, 126.5, 124.7, 124.4, 124.3, 120.1, 76.8, 61.5, 14.3.

HRMS (ESI) Calculated for $C_{22}H_{219}ClO_3$ ([M]+Na⁺) = 389.0915, Found 389.0913.

IR (neat) 2981, 1724, 1619, 1591, 1497, 1449, 1415, 1350, 1329, 1269, 1223, 1203, 1149, 1084, 1021, 966, 925, 801, 766, 732, 693, 532, 496 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-propyl-2-naphthoate (A9)

White solid, Mp: 31–34 °C, 66% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.37 (dd, J = 8.3, 1.4 Hz, 1H), 8.04 (dd, J = 8.5, 1.6 Hz, 1H), 7.73 (s, 1H), 7.64 – 7.54 (m, 2H), 7.48 – 7.44 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 6.82 (d, J = 14.3 Hz, 1H), 6.61 (dt, J = 15.9, 6.0 Hz, 1H), 4.81 (dd, J = 6.0, 1.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 3.06 – 3.00 (m, 2H), 1.84 – 1.75 (m, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.3 Hz, 3H). ¹³C{¹H} **NMR** (101 MHz, Chloroform-d) δ 166.6, 155.0, 136.6, 135.1, 134.7, 132.9, 129.1, 128.6, 128.0, 127.8, 126.6, 126.2, 126.0, 125.0, 124.4, 124.2, 119.4, 76.4, 61.1, 34.8, 23.8, 14.4, 14.2.

HRMS (ESI) Calculated for $C_{25}H_{26}O_3$ ([M]+Na⁺) = 397.1774, Found 397.1773.

IR (neat) 2959, 2932, 2870, 1619, 1600, 1572, 1495, 1451, 1416, 1394, 1357, 1273, 1208, 1153, 1024, 964, 766, 693, 496, 434 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-cyclopropyl-2-naphthoate (A10)

Colorless oil, 84% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.43 (dt, J = 8.5, 0.9 Hz, 1H), 8.39 – 8.34 (m, 1H), 7.72 – 7.69 (m, 1H), 7.69 – 7.64 (m, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 6.83 (d, J = 15.9 Hz, 1H), 6.61 (dt, J = 15.9, 6.0 Hz, 1H), 4.82 (dd, J = 6.0, 1.4 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 2.29 (dddd, J = 8.4, 7.3, 4.2, 2.7 Hz, 1H), 1.45 (t, J = 7.1 Hz, 3H), 1.12 – 1.06 (m, 2H), 0.85 – 0.79 (m, 2H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.6 , 155.2 , 136.6 , 136.5 , 135.00 , 132.9 , 128.7 , 128.5 , 128.1 , 127.8 , 126.6 , 126.2 , 124.9 , 124.6 , 124.6 , 124.2 ,

119.4 , 76.4 , 61.1 , 14.4 , 13.0 , 6.2.

HRMS (ESI) Calculated for $C_{25}H_{24}O_3$ ([M]+Na⁺) = 395.1618, Found 395.1617.

IR (neat) 2980, 1702, 1599, 1571, 1496, 1448, 1404, 1372, 1332, 1268, 1225, 1205, 1151, 1081, 1021, 961, 896, 874, 801, 766, 750, 691, 634, 590, 495, 437 cm⁻¹.

3-ethyl 1-methyl 4-(cinnamyloxy)naphthalene-1,3-dicarboxylate (A11)

White solid, Mp: 73-76 °C, 36% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 9.00 (d, J = 8.5 Hz, 1H), 8.66 (s, 1H), 8.43 - 8.38 (m, 1H), 7.72 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.61 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.46 - 7.42 (m, 2H), 7.38 - 7.32 (m, 2H), 7.31 - 7.26 (m, 1H), 6.79 (d, J = 15.9 Hz, 1H), 6.56 (dt, J = 15.9, 6.1 Hz, 1H), 4.87 (dd, J = 6.2, 1.4 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 167.1, 165.6, 160.3, 136.3, 134.5, 133.8, 132.1, 130.0, 129.4, 128.6, 128.1, 126.9, 126.7, 126.1, 124.2, 124.1, 122.7, 118.7, 77.0, 61.5, 52.2, 14.4.

HRMS (ESI) Calculated for $C_{22}H_{24}O_5$ ([M]+Na⁺) = 413.1359, Found 413.1362.

IR (neat) 2951, 1617, 1567, 1505, 1448, 1416, 1356, 1283, 1236, 1147, 1086, 1025, 963, 793, 770, 749, 693 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-ethoxy-2-naphthoate (A12)

White solid, Mp: 92-94 °C, 76% yield.



¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.33 – 8.29 (m, 1H), 8.27 (dd, *J* = 7.0, 2.7 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (m, 1H), 7.19 (s, 1H), 6.82 (d, *J* = 15.9 Hz, 1H), 6.60 (m, 1H), 4.78 (d, *J* = 5.6 Hz, 2H), 4.46 (q, *J* = 7.0 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.56 (t, *J* = 7.0 Hz, 3H), 1.45 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 166.6 , 150.8 , 150.1 , 136.6 , 132.7 , 129.4 , 128.8 , 128.6 , 127.8 , 127.6 , 127.0 , 126.6 , 125.1 , 123.5 , 122.4 , 119.6 , 104.4 ,

76.3, 64.0, 61.2, 14.8, 14.4.

HRMS (ESI) Calculated for $C_{24}H_{24}O_4$ ([M]+Na⁺) = 399.1567, Found 399.1570.

IR (neat) 2981, 1701, 1595, 1453, 1349, 1272, 1228, 1157, 1101, 965, 863, 765, 693, 498 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-6-methyl-2-naphthoate (A13)

White solid, Mp: 60–63°C, 67% yield.



¹**H** NMR (400 MHz, Chloroform-d) δ 8.27 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 2.5 Hz, 2H), 7.46 (d, J = 7.1 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.28 (ddd, J = 9.0, 6.0, 2.2 Hz, 3H), 7.21 (d, J = 7.5 Hz, 3H), 6.82 (d, J = 15.9 Hz, 1H), 6.61 (dt, J = 15.9, 6.0 Hz, 1H), 4.82 (dd, J = 6.0, 1.4 Hz, 2H), 4.43 (dd, J = 14.1, 6.9 Hz, 4H), 2.48 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.5, 155.8, 140.3, 138.5, 136.6, 135.6, 130.0, 131.7, 128.6, 128.5, 128.4, 128.4, 128.1, 127.8, 127.4, 126.6, 126.1, 125.0, 124.3, 123.8, 118.5, 76.5, 61.1, 38.6, 22.1, 14.4.

HRMS (ESI) Calculated for $C_{30}H_{28}O_3$ ([M]+Na⁺) = 459.1931, Found 459.1930.

IR (neat) 3026, 2979, 1718, 1624, 1602, 1573, 1495, 1449, 1412, 1369, 1351, 1280, 1199, 1154, 1086, 1026, 964, 829, 797, 733, 695, 589, 558, 509, 434 cm⁻¹.

Ethyl 4-benzyl-6-(tert-butyl)-1-(cinnamyloxy)-2-naphthoate (A14)

Colorless oil, 85% yield.



¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.78 (s, 1H), 7.60 (dd, J = 8.9, 1.9 Hz, 1H), 7.45 (d, J = 6.8 Hz, 2H), 7.34 (m, 2H), 7.26 (m, 5H), 7.17 (m, 1H), 6.81 (d, J = 15.8 Hz, 1H), 6.60 (dt, J = 15.9, 6.0 Hz, 1H), 4.81 (d, J = 4.9 Hz, 2H), 4.46 – 4.37 (m, 4H), 1.42 (t, J = 7.1 Hz, 3H), 1.32 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.5 , 155.8 , 151.1 , 140.5 , 136.6 , 135.2 , 132.9 , 132.6 , 128.6 , 128.6 , 128.4 , 127.9 , 127.8 , 127.4 , 126.6 , 126.1 , 125.0 , 125.0 , 124.1 , 120.2 , 118.6 , 61.1 , 39.3 , 35.2 , 31.1 , 14.4 .

HRMS (ESI) Calculated for $C_{31}H_{26}O_3$ ([M]+Na⁺) = 501.2400, Found 501.2401.

IR (neat) 3028, 2960, 1715, 1622, 1573, 1491, 1452, 1405, 1358, 1286, 1221, 1116, 1080, 1024, 964, 838, 803, 732, 695, 618, 536, 497 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-6-phenyl-2-naphthoate (A15)



Colorless oil, 82% yield.

¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.42 (d, J = 8.6 Hz, 1H), 8.15 (s, 1H), 7.80 – 7.77 (m, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.46 (m, 4H), 7.39 – 7.33 (m, 3H), 7.26 (m, 5H), 7.20 (t, J = 6.9 Hz, 1H), 6.83 (d, J = 15.9 Hz, 1H), 6.62 (m, 1H), 4.85 (d, J = 6.0 Hz, 2H), 4.45 (d, J = 15.1 Hz, 4H), 1.43 (t, J = 7.0 Hz, 3H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 166.4 , 155.8 , 140.9 , 140.7 , 140.3 , 136.6 , 135.6 , 133.1 , 132.7 , 128.9 , 128.6 , 128.6 , 128.5 , 128.4 , 128.4 , 127.9 , 127.8 , 127.5 , 126.7 , 126.2 , 125.9 , 125.1 , 124.9 , 122.8 , 119.3 , 76.6 , 61.2 ,

39.0, 14.4.

HRMS (ESI) Calculated for $C_{31}H_{26}O_3$ ([M]+Na⁺) = 521.2087, Found 521.2097.

IR (neat) 3028, 2981, 1716, 1618, 1571, 1492, 1452, 1407, 1351, 1284, 1230, 1196, 1091, 1024, 964, 839, 803, 760, 737, 697, 558 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-6-methoxy-2-naphthoate (A16)

White solid, Mp: 85–87 °C, 54% yield.



¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (m, 3H), 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.61 (m, 1H), 4.83 (d, *J* = 5.3 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.37 (s, 2H), 3.79 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 166.4 , 159.5 , 156.2 , 140.2 , 137.0 , 136.5 , 133.0 , 131.0 , 128.9 , 128.6 , 128.5 , 128.5 , 127.8 , 126.6 , 126.2 , 126.2 ,

 $124.9\ , 124.4\ , 118.4\ , 117.0\ , 103.7\ , 76.5\ , 61.0\ , 55.2\ , 39.3\ , 14.4\ .$

HRMS (ESI) Calculated for $C_{30}H_{25}O_4$ ([M]+Na⁺) = 475.1880, Found 475.1890.

IR (neat) 2979, 1714, 1619, 1577, 1500, 1468, 1420, 1350, 1274, 1231, 1200, 1089, 1025, 965, 743, 699, 493 cm⁻¹.

Ethyl 4-benzyl-6-chloro-1-(cinnamyloxy)-2-naphthoate (A17)

White solid, Mp: 69–72 °C, 70% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.31 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 2.1 Hz, 1H), 7.78 (s, 1H), 7.49 – 7.43 (m, 3H), 7.36 (dd, J = 8.3, 6.5 Hz, 2H), 7.30 (dd, J = 7.3, 2.3 Hz, 3H), 7.25 – 7.19 (m, 3H), 6.80 (d, J = 15.7 Hz, 1H), 6.58 (dt, J = 15.9, 6.1 Hz, 1H), 4.82 (dd, J = 6.1, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.37 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.1, 155.6, 139.6, 136.4, 136.0, 134.8, 133.4, 131.7, 129.2, 128.6, 128.5, 128.0, 127.7, 127.1, 126.6, 126.4, 119.6, 76.7, 61.3, 38.5, 14.3

126.2 , 124.5 , 123.8 , 119.6 , 76.7 , 61.3 , 38.5 , 14.3 .

HRMS (ESI) Calculated for $C_{29}H_{25}ClO_3$ ([M]+Na⁺) = 479.1384, Found 479.1389.

IR (neat) 3026, 2980, 1718, 1613, 1568, 1492, 1448, 1408, 1368, 1346, 1270, 1227, 1202, 1150, 1078, 1024, 961, 856, 829, 793, 730, 694, 621, 592, 555, 497, 459, 430 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-6-cyano-2-naphthoate (A18)



White solid, Mp: 84-86 °C, 73% yield.

¹**H NMR** (600 MHz, Chloroform-*d*) δ 8.46 (d, J = 8.7 Hz, 1H), 8.33 (s, 1H), 7.85 (s, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.30 (m, 3H), 7.23 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 6.79 (d, J = 15.9 Hz, 1H), 6.55 (m, 1H), 4.83 (d, J = 6.2 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 4.42 (s, 2H), 1.44 (t, J = 7.2 Hz, 3H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 165.8 , 155.0 , 139.1 , 136.2 , 134.1 , 133.8 , 133.0 , 131.1 , 130.6 , 129.7 , 128.7 , 128.6 , 128.4 , 128.1 , 126.8 , 126.6 ,

125.8, 124.1, 122.4, 118.9, 111.7, 76.9, 61.6, 38.5, 14.3.

HRMS (ESI) Calculated for $C_{30}H_{25}NO_3$ ([M]+Na⁺) = 470.1727, Found 470.1734.

IR (neat) 3029, 2982, 2229, 1717, 1598, 1572, 1498, 1451, 1410, 1350, 1275, 1233, 1200, 1086, 1022, 963, 897, 838, 801, 738, 698, 540 cm⁻¹.

Ethyl 4-benzyl-1-(cinnamyloxy)-8-methyl-2-naphthoate (A19)

Colorless oil, 40% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 7.81 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.33 (m, 3H), 7.31 – 7.26 (m, 3H), 7.25 (s, 1H), 7.21 – 7.17 (m, 3H), 6.78 (d, J = 16.0 Hz, 1H), 6.55 (dt, J = 15.9, 5.9 Hz, 1H), 4.66 (dd, J = 5.9, 1.5 Hz, 2H), 4.46 – 4.39 (m, 4H), 2.98 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H). ¹³C{¹H} **NMR** (101 MHz, Chloroform-d) δ 167.0, 157.3, 140.3, 136.5, 132.9, 132.6, 129.9, 128.7, 128.6, 128.5, 128.4, 128.1, 127.8, 127.7, 126.6, 126.1, 124.7, 123.1, 120.8, 77.3, 61.2, 39.5, 24.8, 14.3.

HRMS (ESI) Calculated for $C_{30}H_{28}O_3$ ([M]+Na⁺) = 459.1931, Found 459.1929. **IR** (neat) 3026, 2978, 1719, 1605, 1570, 1494, 1451, 1413, 1370, 1351, 1264, 1236, 1205, 1135, 1111, 1069, 1024, 963, 821, 762, 731, 694, 620, 576, 554, 521, 494, 458 cm⁻¹.

Ethyl (E)-1-((3-(4-nitrophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A20)

White solid, Mp: 125-128 °C, 55% yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 – 8.33 (m, 1H), 8.25 – 8.18 (m, 2H), 8.16 – 8.10 (m, 2H), 7.73 – 7.67 (m, 1H), 7.61 (dd, *J* = 15.1, 8.1 Hz, 3H), 7.45 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.32 – 7.26 (m, 3H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.77 (dt, *J* = 16.0, 5.5 Hz, 1H), 4.88 (dd, *J* = 5.4, 1.5 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.19 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 165.9 , 155.9 , 147.1 , 143.1 , 134.6 , 131.6 , 130.1 , 129.9 , 129.0 , 128.8 , 128.7 , 128.2 , 128.0 , 127.1 , 126.6 , 126.4 , 124.2 , 124.0 , 123.9 , 123.4 , 119.4 , 86.7 , 83.8 , 75.6 , 61.2 , 23.5 , 14.4 .

HRMS (ESI) Calculated for $C_{31}H_{25}NO_5$ ([M]+Na⁺) = 514.1625, Found 514.1633.

IR (neat) 2981, 1719, 1620, 1598, 1572, 1515, 1491, 1444, 1394, 1341, 1275, 1227, 1154, 1087, 1023, 970, 861, 759, 528 cm⁻¹.

Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)-2-naphthoate (A21)



White solid, Mp: 129–132 °C, 66% yield.

¹**H** NMR (400 MHz, Chloroform-d) δ 8.38 (dd, J = 8.4, 1.3 Hz, 1H), 8.13 (d, J = 7.8 Hz, 2H), 7.69 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.66 – 7.58 (m, 3H), 7.55 (d, J = 8.2 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.30 (qd, J = 4.0, 2.3 Hz, 3H), 6.88 (d, J = 15.8 Hz, 1H), 6.70 (dt, J = 15.9, 5.7 Hz, 1H), 4.86 (dd, J = 5.7, 1.5 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.0, 156.0, 140.1, 134.6, 131.6, 131.2, 129.7, 129.4, 129.1, 128.7, 128.6, 128.2, 127.9, 127.6, 126.8, 126.5, 126.5, 125.6, 125.6, 125.5, 125.5, 124.3, 123.9, 123.4, 122.8, 119.5, 86.7,

83.8, 76.0, 61.2, 23.5, 14.3.

HRMS (ESI) Calculated for $C_{32}H_{25}F_{3}O_{3}$ ([M]+Na⁺) = 537.1648, Found 537.1653.

¹⁹**F NMR** (377 MHz, Chloroform-d) δ -62.48.

IR (neat) 2982, 1719, 1618, 1572, 1491, 1445, 1416, 1394, 1358, 1325, 1275, 1228, 1161, 1120, 1087, 1067, 1018, 969, 858, 758, 692, 597 cm⁻¹.

Ethyl (E)-1-((3-(4-fluorophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A22)

White solid, Mp: 80–83 °C, 28% yield.



 $\label{eq:hardenergy} \begin{array}{l} ^{1}\textbf{H} \ \textbf{NMR} \ (400 \ \text{MHz}, \ \text{Chloroform-d}) \ \delta \ 8.39 \ (dd, \ J=8.4, \ 1.3 \ \text{Hz}, \ 1\text{H}), \ 8.12 \ (d, \ J=9.5 \ \text{Hz}, \ 2\text{H}), \ 7.69 \ (dd, \ J=8.3, \ 6.8, \ 1.4 \ \text{Hz}, \ 1\text{H}), \ 7.61 \ (ddd, \ J=8.1, \ 6.8, \ 1.2 \ \text{Hz}, \ 1\text{H}), \ 7.43 \ (dtd, \ J=14.2, \ 5.3, \ 3.0 \ \text{Hz}, \ 4\text{H}), \ 7.30 \ (q, \ J=2.8 \ \text{Hz}, \ 3\text{H}), \ 7.04 \ (t, \ J=8.7 \ \text{Hz}, \ 2\text{H}), \ 6.78 \ (d, \ J=15.9 \ \text{Hz}, \ 1\text{H}), \ 6.52 \ (dt, \ J=15.9, \ 6.1 \ \text{Hz}, \ 1\text{H}), \ 4.82 \ (dd, \ J=6.1, \ 1.4 \ \text{Hz}, \ 2\text{H}), \ 4.45 \ (q, \ J=7.1 \ \text{Hz}, \ 2\text{H}), \ 4.19 \ (s, \ 2\text{H}), \ 1.44 \ (t, \ J=7.1 \ \text{Hz}, \ 3\text{H}). \ \ 1^3 C\{^1 \textbf{H}\} \ \textbf{NMR} \ (101 \ \text{MHz}, \ \text{Chloroform-d}) \ \delta \ 166.1 \ , \ 162.5 \ (d, \ ^1 J_{FC}=247.0 \ \text{Hz}) \ , \ 156.1 \ , \ 134.6 \ , \ 132.7 \ , \ 132.0 \ , \ 131.6 \ , \ 129.2 \ , \ 128.6 \ , \ 128.5 \ , \ 128.2 \ (d, \ ^3 J_{FC}=6.7 \ \text{Hz}) \ , \ 127.9 \ , \ 126.5 \ , \ 126.4 \ , \ 124.6 \ (d, \ ^4 J_{FC}=2.2 \ \text{Hz}), \ 124.5 \ , \ 123.8 \ , \ 123.5 \ , \ 119.5 \$

115.5 (d, $^2J_{FC}$ = 21.7 Hz) , 86.8 , 83.7 , 76.5 , 61.2 , 23.5 , 14.3 .

¹⁹**F NMR** (377 MHz, Chloroform-d) δ -113.98.

HRMS (ESI) Calculated for $C_{31}H_{25}FO_3$ ([M]+Na⁺) = 487.1680, Found 487.1684.

IR (neat) 2982, 1720, 1621, 1600, 1571, 1508, 1445, 1394, 1356, 1306, 1275, 1155, 1085, 1023, 965, 847, 758, 692, 525 cm⁻¹.

Ethyl (E)-1-((3-(4-bromophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A23)

White solid, Mp: 123–126 °C, 31% yield.



.CO₂Et

¹**H NMR** (400 MHz, Chloroform-d) δ 8.37 (dd, J = 8.4, 1.3 Hz, 1H), 8.17 – 8.06 (m, 2H), 7.69 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.50 – 7.42 (m, 4H), 7.34 – 7.27 (m, 5H), 6.77 (d, J = 15.9 Hz, 1H), 6.59 (dt, J = 15.9, 5.9 Hz, 1H), 4.82 (dd, J = 5.9, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.1, 156.1, 135.5, 134.6, 131.8, 131.7, 131.6, 129.1, 128.6, 128.6, 128.2, 128.2, 127.9, 126.5, 125.7, 124.4, 123.9, 123.5, 121.7, 119.5, 86.8, 83.8, 76.3, 61.2, 23.5, 14.4.

HRMS (ESI) Calculated for $C_{31}H_{25}BrO_3$ ([M]+Na⁺) = 547.0879, Found 547.0887.

HRMS (ESI) Calculated for $C_{31}H_{25}^{81}BrO_3$ ([M]+Na⁺) = 549.0859, Found 549.0865.

IR (neat) 2980, 1620, 1600, 1571, 1508, 1488, 1444, 1394, 1356, 1306, 1275, 1226, 1153, 1084, 1009, 965, 835, 758, 692, 528, 499 cm⁻¹.

Ethyl (E)-1-((3-(4-chlorophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A24)

White solid, Mp: 119–122 °C, 39% yield.

¹**H NMR** (400 MHz, Chloroform-d) δ 8.38 (dd, J = 8.4, 1.3 Hz, 1H), 8.12 (d, J = 9.2 Hz, 2H), 7.72 – 7.66 (m, 1H), 7.61 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.34 – 7.27 (m, 5H), 6.78 (d, J = 15.9 Hz, 1H), 6.58 (dt, J = 15.9, 6.0 Hz, 1H), 4.82 (dd, J = 5.9, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.1, 156.1, 135.1, 134.6, 133.5, 131.8, 131.6, 129.1, 128.8, 128.6, 128.6, 128.2, 127.9, 127.8, 126.5, 125.5, 124.4, 123.8, 123.5, 119.5, 86.8, 83.8, 76.3, 61.2, 23.5, 14.3.

HRMS (ESI) Calculated for $C_{31}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1389.

IR (neat) 2980, 1620, 1600, 1571, 1490, 1444, 1394, 1358, 1306, 1275, 1226, 1153, 1087, 1016, 965, 851, 692, 528, 504 cm⁻¹.

Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(p-tolyl)allyl)oxy)-2-naphthoate (A25)

White solid, Mp: 90–93 °C, 30% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.40 (dd, J = 8.4, 1.4 Hz, 1H), 8.15 – 8.08 (m, 2H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.45 (dd, J = 6.6, 3.0 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 15.9 Hz, 1H), 6.55 (dt, J = 15.9, 6.2 Hz, 1H), 4.82 (dd, J = 6.2, 1.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 2.36 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.2, 156.2, 137.8, 134.6, 133.7, 133.3, 131.6, 129.3, 129.2, 128.6, 128.4, 128.2, 127.9, 126.6, 126.5, 126.4,

 $124.6\ , 123.8\ , 123.7\ , 123.5\ , 119.5\ , 86.8\ , 83.7\ , 76.8\ , 61.2\ , 23.5\ , 21.2\ , 14.4\ .$

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1934.

IR (neat) 2980, 1620, 1601, 1571, 1511, 1490, 1445, 1416, 1394, 1356, 1306, 1275, 1226, 1153, 1084, 1023, 966, 832, 756, 692, 525, 502 cm⁻¹.

Ethyl (E)-1-((3-(4-methoxyphenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A26)

White solid, Mp: 97–100 °C, 36% yield.



¹**H NMR** (600 MHz, Chloroform-d) δ 8.10 (dd, J = 7.8, 1.4 Hz, 1H), 7.65 (td, J = 7.5, 1.5 Hz, 1H), 7.54 (dd, J = 8.0, 1.0 Hz, 1H), 7.42 (td, J = 7.5, 1.1 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.23 (m, 3H), 7.08 – 7.03 (m, 2H), 6.69 – 6.63 (m, 2H), 6.42 – 6.34 (m, 2H), 5.87 (ddd, J = 15.4, 8.1, 7.0 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.76 – 3.67 (m, 5H), 3.09 – 3.00 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 196.2, 169.7, 158.8, 137.1, 134.7, 133.5, 131.5, 130.3, 129.9, 128.8, 129.2, 128.4, 128.2, 128.0, 127.5, 127.3, 124.0, 123.2, 121.3, 113.7, 85.6, 84.2, 61.9, 60.8, 55.2, 40.3, 23.7, 13.9.

HRMS (ESI) Calculated for $C_{32}H_{28}O_4$ ([M]+Na⁺) = 499.1880, Found 499.1880.

IR (neat) 2980, 2836, 1738, 1678, 1605, 1574, 1511, 1489, 1444, 1393, 1366, 1300, 1247, 1209, 1175, 1083, 1032, 967, 843, 802, 757, 692, 527 cm⁻¹.

Ethyl (E)-1-((3-(3-chlorophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A27)



White solid, Mp: 110–113 °C, 24% yield.

¹**H NMR** (400 MHz, Chloroform-d) δ 8.36 (dd, J = 8.4, 1.3 Hz, 1H), 8.12 (d, J = 10.6 Hz, 2H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.34 – 7.23 (m, 6H), 6.77 (d, J = 15.7 Hz, 1H), 6.60 (dt, J = 15.9, 5.8 Hz, 1H), 4.82 (dd, J = 5.9, 1.5 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.18 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.0 , 156.1 , 138.5 , 134.6 , 134.5 , 131.6 , 131.5 , 129.8 , 129.1 , 128.6 , 128.6 , 128.2 , 127.9 , 127.8 , 126.6 , 126.5 ,

 $126.5\ , 124.8\ , 124.4\ , 123.9\ , 123.5\ , 119.5\ , 86.8\ , 83.8\ , 76.1\ , 61.2\ , 23.5\ , 14.4\ .$

HRMS (ESI) Calculated for $C_{32}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1386.

IR (neat) 2980, 1621, 1596, 1569, 1508, 1490, 1475, 1418, 1394, 1356, 1307, 1275, 1227, 1207, 1154, 1085, 1023, 963, 888, 691, 527, 436 cm⁻¹.

Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(m-tolyl)allyl)oxy)-2-naphthoate (A28)

White solid, Mp: 92–95 °C, 68% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.39 (dd, J = 8.4, 1.3 Hz, 1H), 8.10 (t, J = 4.2 Hz, 2H), 7.66 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.59 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.32 – 7.21 (m, 6H), 7.08 (dd, J = 6.8, 1.9 Hz, 1H), 6.77 (d, J = 15.9 Hz, 1H), 6.58 (dt, J = 15.9, 6.1 Hz, 1H), 4.81 (dd, J = 6.0, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 2.35 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). $^{13}C{^{1}H}$ **NMR** (101 MHz, Chloroform-d) δ 166.2, 156.2, 138.1, 136.5, 134.6, 133.3, 131.6, 129.2, 128.7, 128.5, 128.5, 128.4, 128.2, 127.9, 127.4, 126.5,

126.4, 124.6, 124.5, 123.8, 123.5, 119.4, 86.8, 83.7, 76.7, 61.2, 23.5, 21.4, 14.3.

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1932.

IR (neat) 2980, 1719, 1620, 1601, 1571, 1508, 1489, 1444, 1416, 1393, 1354, 1307, 1275, 1224, 1153, 1084, 1023, 963, 691, 526, 435 cm⁻¹.

Ethyl (E)-1-((3-(2-chlorophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A29)





¹**H NMR** (400 MHz, Chloroform-d) δ 8.40 (dd, J = 8.3, 1.5 Hz, 1H), 8.17 – 8.03 (m, 2H), 7.67 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (dtd, J = 6.8, 3.5, 1.2 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.27 (tt, J = 5.5, 2.2 Hz, 3H), 7.26 – 7.16 (m, 3H), 6.58 (dt, J = 15.9, 6.1 Hz, 1H), 4.86 (dd, J = 6.0, 1.6 Hz, 2H), 4.45 (q, J = 7.2 Hz, 2H), 4.17 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.13, 156.11, 134.67, 134.58, 133.23, 131.58, 129.68, 129.24, 128.85, 128.57, 128.51, 128.18, 127.87, 127.73, 127.05, 126.86, 126.46, 124.51, 123.79, 123.46, 119.42, 86.79, 83.74, 76.39, 61.20, 23.46, 14.36.

HRMS (ESI) Calculated for $C_{31}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1386.

IR (neat) 2981, 1719, 1620, 1600, 1571, 1508, 1490, 1470, 1442, 1416, 1394, 1356, 1307, 1275, 1227, 1207, 1154, 1085, 1029, 964, 693, 527, 450 cm⁻¹.

Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(o-tolyl)allyl)oxy)-2-naphthoate (A30)

White solid, Mp: 95–98 °C, 55% yield.



¹**H** NMR (400 MHz, Chloroform-d) δ 8.42 (dd, J = 8.4, 1.3 Hz, 1H), 8.12 (d, J = 11.0 Hz, 2H), 7.69 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.61 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.45 (dd, J = 6.7, 2.9 Hz, 2H), 7.30 (q, J = 2.8 Hz, 3H), 7.23 – 7.13 (m, 3H), 6.99 (d, J = 15.5 Hz, 1H), 6.48 (dt, J = 15.7, 6.2 Hz, 1H), 4.86 (dd, J = 6.2, 1.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 2.36 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.2 , 156.2 , 135.7 , 134.6 , 131.6 , 131.3 , 130.3 , 129.3 , 128.6 , 128.4 , 128.2 , 127.9 , 127.8 , 126.5 , 126.4 , 126.1 , 126.1 , 125.9 , 124.6 , 123.8 , 123.5 , 119.5 , 86.8 , 83.7 , 76.9 , 61.2 , 23.5 , 19.8 , 14.4

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1934.

IR (neat) 2979, 1719, 1620, 1600, 1571, 1507, 1488, 1458, 1415, 1394, 1354, 1306, 1275, 1224, 1153, 1084, 1023, 964, 692, 527, 449 cm⁻¹.

Ethyl (E)-1-((3-(2-methoxyphenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A31)

White solid, Mp: 92–98 °C, 63% yield.



¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.42 (dd, J = 8.5, 1.3 Hz, 1H), 8.15 – 8.07 (m, 2H), 7.67 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.51 (dd, J = 7.6, 1.6 Hz, 1H), 7.44 (dd, J = 6.7, 2.9 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.24 (dd, J = 8.2, 0.9 Hz, 1H), 7.10 (d, J = 16.0 Hz, 1H), 6.95 (td, J = 7.5, 1.1 Hz, 1H), 6.88 (dd, J = 8.2, 1.0 Hz, 1H), 6.62 (dt, J = 16.0, 6.3 Hz, 1H), 4.84 (dd, J = 6.4, 1.4 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 4.18 (s, 2H), 3.85 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.3 , 156.9 , 156.3 , 134.6 , 131.6 , 129.3 , 129.0 , 128.5 , 128.4 , 128.3 , 128.2 , 127.9 , 127.2 , 126.5 , 126.3 , 125.5 , 125.4 , 124.7 , 123.7 , 123.5 , 120.6 , 119.4 , 110.8 , 86.9 , 83.7 , 61.2 , 55.4 , 23.5 , 14.3 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_4$ ([M]+Na⁺) = 499.1880, Found 499.1879.

IR (neat) 2979, 1720, 1620, 1598, 1573, 1489, 1461, 1416, 1394, 1355, 1305, 1275, 1242, 1155, 1084, 1027, 972, 692, 527 cm⁻¹.

Ethyl (E)-1-((3-(naphthalen-1-yl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A32)

White solid, Mp: 112–115 °C, 60% yield.



¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (dd, J = 8.3, 1.5 Hz, 1H), 8.20 – 8.05 (m, 3H), 7.86 (dd, J = 7.6, 2.0 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.58 – 7.44 (m, 6H), 7.30 (qd, J = 4.1, 2.2 Hz, 3H), 6.62 (dt, J = 15.5, 6.1 Hz, 1H), 4.96 (dd, J = 6.1, 1.6 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 4.20 (s, 2H), 1.44 (t, J = 7.2 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.2, 156.2, 134.6, 134.3, 133.6, 131.6, 131.1, 130.6, 129.3, 128.6, 128.5, 128.2, 128.0, 127.9, 126.5, 126.5,

126.1 , 125.8 , 125.6 , 124.6 , 124.1 , 123.8 , 123.8 , 123.5 , 119.5 , 86.8 , 83.7 , 61.2 , 23.5 , 14.4 .

HRMS (ESI) Calculated for $C_{35}H_{28}O_3$ ([M]+Na⁺) = 519.1931, Found 519.1936.

IR (neat) 3058, 2980, 1620, 1599, 1571, 1508, 1490, 1444, 1416, 1393, 1357, 1307, 1275, 1227, 1154, 1084, 1022, 961, 692, 527, 425 cm⁻¹.

Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(thiophen-2-yl)allyl)oxy)-2-naphthoate (A33)



White solid, Mp: 80-83 °C, 20% yield.

¹**H NMR** (400 MHz, Chloroform-d) δ 8.38 (dd, J = 8.4, 1.3 Hz, 1H), 8.12 (d, J = 7.0 Hz, 2H), 7.69 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.61 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.46 (dd, J = 6.5, 3.0 Hz, 2H), 7.30 (dq, J = 4.9, 2.8 Hz, 3H), 7.21 (d, J = 5.0 Hz, 1H), 7.06 – 6.93 (m, 3H), 6.44 (dt, J = 15.7, 6.1 Hz, 1H), 4.80 (dd, J = 6.1, 1.4 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.45 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.1, 156.1, 141.6, 134.6, 131.6, 129.1, 128.6, 128.5, 128.2, 127.9, 127.4, 126.5, 126.3, 124.7, 124.5, 124.3,

123.8 , 123.5 , 119.5 , 86.8 , 83.7 , 76.2 , 61.2 , 23.5 , 14.3 .

HRMS (ESI) Calculated for $C_{29}H_{24}O_3S$ ([M]+Na⁺) = 475.1338, Found 475.1339.

IR (neat) 2980, 1621, 1600, 1571, 1508, 1444, 1416, 1394, 1367, 1344, 1306, 1275, 1226, 1154, 1084, 1023, 954, 855, 758, 693, 528cm⁻¹.

Ethyl (E)-1-((4-ethoxy-4-oxobut-2-en-1-yl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A34)

White solid, Mp: 116–119 °C, 58% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.25 (dd, J = 8.4, 1.4 Hz, 1H), 8.14 – 8.09 (m, 2H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.60 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.32 – 7.26 (m, 3H), 7.22 (dt, J = 15.7, 4.2 Hz, 1H), 6.45 (dt, J = 15.7, 2.1 Hz, 1H), 4.83 (dd, J = 4.2, 2.1 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.3 , 165.8 , 155.5 , 142.7 , 134.6 , 131.6 , 129.0 , 128.7 , 128.7 , 128.2 , 127.9 , 126.7 , 126.4 , 124.0 , 123.9 , 123.4 , 121.7 , 119.5 , 86.6 , 83.8 , 73.8 , 61.2 , 60.5 , 23.5 , 14.3 , 14.2 .

HRMS (ESI) Calculated for $C_{28}H_{26}O_5$ ([M]+Na⁺) = 465.1672, Found 465.1682

IR (neat) 2981, 1717, 1665, 1620, 1600, 1571, 1508, 1491, 1444, 1394, 1367, 1303, 1274, 1228, 1177, 1093, 1036, 759, 692, 528 cm⁻¹.

Ethyl (E)-1-(but-2-en-1-yloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A35)

White solid, Mp: 65–68 °C, 17% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.35 (dd, J = 8.4, 1.3 Hz, 1H), 8.14 – 8.05 (m, 2H), 7.67 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.59 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.33 – 7.26 (m, 3H), 6.02 – 5.79 (m, 2H), 4.63 – 4.55 (m, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 1.79 (d, J = 4.5 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 166.2 , 156.3 , 134.5 , 131.6 , 130.9 , 129.3 , 128.5 , 128.2 , 127.9 , 126.6 , 126.5 , 126.3 , 124.6 , 123.7 , 123.5 , 119.4 , 86.8 , 83.7 , 76.8 , 61.1 , 23.4 , 17.9 , 14.3 .

HRMS (ESI) Calculated for $C_{26}H_{24}O_3$ ([M]+Na⁺) = 407.1618, Found 407.1616.

IR (neat) 2978, 1620, 1600, 1571, 1508, 1491, 1445, 1416, 1394, 1354, 1306, 1275, 1226, 1206, 1154, 1085, 1023, 965, 912, 758, 692, 528 cm⁻¹.

Ethyl (E)-1-(hex-2-en-1-yloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A36)

Colorless oil, Mp: 28-31 °C, 30% yield.



¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.67 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.29 (p, *J* = 3.5 Hz, 3H), 5.96 – 5.83 (m, 2H), 4.62 (d, *J* = 5.2 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 2.10 (dt, *J* = 7.9, 5.9 Hz, 2H), 1.44 (dt, *J* = 9.9, 7.2 Hz, 5H), 0.91 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.3 , 156.3 , 136.0 , 134.5 , 131.6 , 129.3 , 128.4 , 128.2 , 128.1 , 127.8 , 126.5 , 126.2 , 125.4 , 124.7 , 123.7 , 123.5 , 119.4 , 86.8 , 83.6 , 77.0 , 61.1 , 34.4 , 23.4 , 22.1 , 14.3 , 13.6 .

HRMS (ESI) Calculated for C₂₈H₂₈O₃ ([M]+Na⁺) = 435.1931, Found 435.1933.8 **IR** (neat) 2959, 2929, 2871, 1722, 1621, 1600, 1571, 1507, 1491, 1457, 1416, 1394, 1357, 1306, 1275, 1225, 1154, 1083, 1023, 972, 692, 527 cm⁻¹.

Ethyl (E)-1-((3-cyclohexylallyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A37)

White solid, Mp: 59–62 °C, 25% yield.



¹**H NMR** (600 MHz, Chloroform-d) δ 8.35 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.08 (s, 1H), 7.67 (ddd, J = 8.3, 6.7, 1.3 Hz, 1H), 7.59 (ddd, J = 8.1, 6.8, 1.0 Hz, 1H), 7.44 (dd, J = 6.7, 3.0 Hz, 2H), 7.31 – 7.27 (m, 3H), 5.85 – 5.76 (m, 2H), 4.60 (d, J = 5.9 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 2.03 (dtd, J = 11.1, 6.8, 3.0 Hz, 1H), 1.76 – 1.71 (m, 4H), 1.68 – 1.63 (m, 1H), 1.45 (t, J = 7.2 Hz, 3H), 1.27 (tt, J = 12.9, 3.5 Hz, 2H), 1.18 – 1.06 (m, 3H).

¹³C{¹H} NMR (151 MHz, Chloroform-d) δ 166.3 , 156.3 , 141.9 , 134.5 , 131.6 , 129.4 , 128.5 , 128.2 , 128.1 , 127.9 , 126.5 , 126.2 , 124.8 , 123.7 , 123.5 , 122.7 , 119.4 , 86.9 , 83.6 , 77.2 , 61.1 , 40.3 , 32.5 , 26.1 , 26.0 , 23.5 , 14.4 .

HRMS (ESI) Calculated for $C_{31}H_{32}O_3$ ([M]+Na⁺) = 475.2244, Found 475.2246.

IR (neat) 2923, 2850, 1721, 1620, 1600, 1571, 1508, 1490, 1447, 1416, 1394, 1368, 1351, 1306, 1275, 1225, 1153, 1083, 1024, 971, 692, 528 cm⁻¹.

Ethyl 4-((E)-3-(4-bromophenyl)allyl)-1-(cinnamyloxy)-2-naphthoate (A38)

White solid, Mp: 96–99 °C, 84% yield.



.CO₂Et

¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.78 (s, 1H), 7.60 (dddd, J = 20.2, 8.1, 6.8, 1.3 Hz, 2H), 7.45 (d, J = 7.3 Hz, 2H), 7.42 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.18 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 15.9 Hz, 1H), 6.59 (dt, J = 15.9, 6.0 Hz, 1H), 6.48 (dt, J = 15.9, 6.1 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 4.82 (dd, J = 6.0, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 3.95 (d, J = 6.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.6 , 155.8 , 136.7 , 136.4 , 135.3 , 133.3 , 132.0 , 131.7 , 130.5 , 129.5 , 129.4 , 128.8 , 128.6 , 128.1 , 127.8 ,

 $127.2\ ,\ 126.8\ ,\ 126.5\ ,\ 125.0\ ,\ 124.7\ ,\ 124.5\ ,\ 121.0\ ,\ 119.8\ ,\ 76.7\ ,\ 61.4\ ,\ 36.3\ ,\ 14.6\ .$

HRMS (ESI) Calculated for $C_{31}H_{27}^{79}BrO_3$ ([M]+Na⁺) = 549.1036, Found 549.1047.

HRMS (ESI) Calculated for $C_{31}H_{27}^{81}BrO_3$ ([M]+Na⁺) = 551.1015, Found 551.1022.

IR (neat) 3026, 2980, 2361, 1619, 1571, 1487, 1449, 1395, 1356, 1276, 1228, 1206, 1154, 1079, 1011, 965, 833, 765, 693, 498 cm⁻¹.

Ethyl 1-(((E)-3-(4-bromophenyl)allyl)oxy)-4-cinnamyl-2-naphthoate (ent-A38)

Br White solid, Mp: 110–113 °C, 76% yield.

¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.80 (s, 1H), 7.57 (dddd, J = 19.4, 8.0, 6.8, 1.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.32 – 7.22 (m, 6H), 7.19 – 7.14 (m, 1H), 6.74 (d, J = 15.9 Hz, 1H), 6.57 (dt, J = 15.9, 5.9 Hz, 1H), 6.45 (d, J = 2.6 Hz, 2H), 4.80 (dd, J = 5.8, 1.4 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 4.02 – 3.87 (m, 2H), 1.41 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.4 , 155.6 , 137.4 , 135.6 , 135.3 , 132.4 , 131.8 , 131.8 , 131.6 , 129.3 , 128.6 , 128.5 , 128.2 , 127.3 , 127.0 , 126.4 , 126.2 , 125.8 , 124.5 , 124.4 , 121.8 , 119.7 , 76.3 , 61.3 , 36.3 , 14.5 .

HRMS (ESI) Calculated for $C_{31}H_{27}^{79}BrO_3$ ([M]+Na⁺) = 549.1036, Found 549.1047. **HRMS** (ESI) Calculated for $C_{31}H_{27}^{81}BrO_3$ ([M]+Na⁺) = 551.1015, Found 551.1024. **IR** (neat) 3026, 2980, 1619, 1599, 1571, 1487, 1448, 1417, 1393, 1357, 1277, 1227, 1207, 1152, 1073, 1009, 966, 847, 767, 741, 693, 498 cm⁻¹.

Ethyl 1-(cinnamyloxy)-4-((E)-3-(naphthalen-1-yl)allyl)-2-naphthoate (A39)

White solid, Mp: 74–77 °C, 71% yield.

CO₂Et

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.26 – 8.15 (m, 1H), 8.10 (s, 1H), 8.04 – 7.98 (m, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.79 (ddd, J = 26.9, 13.3, 7.1 Hz, 3H), 7.65 (d, J = 7.6 Hz, 4H), 7.60 – 7.51 (m, 3H), 7.46 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 15.7 Hz, 1H), 7.02 (d, J = 15.9 Hz, 1H), 6.81 (dt, J = 15.4, 5.8 Hz, 1H), 6.74 – 6.63 (dt, 1H), 5.04 (d, J = 6.1 Hz, 2H), 4.65 (q, J = 7.1 Hz, 2H), 4.28 (d, J = 6.4 Hz, 2H), 1.63 (t, J = 7.2 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.4 , 155.6 , 136.5 , 135.2 , 135.1 , 133.5 , 133.0 , 132.1 , 131.6 , 131.0 , 129.2 , 128.9 , 128.5 , 128.4 , 128.3 , 127.8 , 127.5 , 126.9 , 126.6 , 126.3 , 125.8 , 125.6 , 125.5 , 124.8 , 124.4 , 124.4 , 123.8 ,

123.7, 119.6, 76.5, 61.2, 36.5, 14.3.

HRMS (ESI) Calculated for $C_{35}H_{30}O_3$ ([M]+Na⁺) = 521.2087, Found 521.2094.

IR (neat) 3058, 2980, 1619, 1598, 1572, 1507, 1448, 1516, 1393, 1356, 1276, 1226, 1206, 1153, 1083, 1022, 965, 863, 768, 692, 561, 496, 424cm⁻¹.

Ethyl 4-cinnamyl-1-(((E)-3-(naphthalen-1-yl)allyl)oxy)-2-naphthoate (ent-A39)



White solid, Mp: 98–101 °C, 77% yield.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.51 – 8.37 (m, 1H), 8.09 (dd, *J* = 8.8, 4.3 Hz, 2H), 7.91 – 7.77 (m, 3H), 7.67 – 7.44 (m, 7H), 7.36 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.14 (m, 1H), 6.61 (dt, *J* = 15.5, 6.0 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 2H), 4.95 (dd, *J* = 6.1, 1.5 Hz, 2H), 4.46 (qd, *J* = 7.1, 1.5 Hz, 2H), 3.98 (d, *J* = 4.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.7, 155.7, 137.4, 135.3, 134.4, 133.7, 132.3, 131.6, 131.3, 130.6, 129.5, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 127.3, 127.1, 126.4, 126.3, 126.2, 126.0, 125.8, 124.7, 124.6, 124.2,

 $123.9\ , 119.8\ , 76.8\ , 61.4\ , 36.4\ , 14.6\ .$

HRMS (ESI) Calculated for C₃₅H₃₀O₃ ([M]+Na⁺) = 521.2087, Found 521.2092. **IR** (neat) 3057, 2980, 1619, 1597, 1571, 1505, 1448, 1416, 1392, 1360, 1277, 1228, 1205, 1154, 1084, 1021, 964, 866, 769, 738, 693, 493, 426 cm⁻¹.

Ethyl 4-((E)-but-2-en-1-yl)-1-(cinnamyloxy)-2-naphthoate (A40)

White solid, Mp: 40–43 °C, 75% yield.



¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.35 (dd, J = 7.8, 1.4 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.73 (s, 1H), 7.64 – 7.54 (m, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 6.85 – 6.77 (m, 1H), 6.59 (dt, J = 15.9, 6.0 Hz, 1H), 5.82 – 5.65 (m, 1H), 5.66 – 5.50 (m, 1H), 4.80 (dd, J = 6.0, 1.4 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 3.74 (dq, J = 6.3, 1.3 Hz, 2H), 1.68 (dt, J = 6.4, 1.5 Hz, 3H), 1.43 (t, J = 7.1 Hz, 3H).

 $^{13}\mathrm{C}$ NMR (101 MHz, Chloroform-d) δ 166.7 , 155.5 , 136.7 , 135.3 , 133.2 ,

133.1 , 129.3 , 129.2 , 128.7 , 128.3 , 128.0 , 127.2 , 126.8 , 126.6 , 126.3 , 125.1 , 124.6 , 124.5 , 119.7 , 76.6 , 61.3 , 36.0 , 18.1 , 14.5 .

HRMS (ESI) Calculated for $C_{26}H_{26}O_3$ ([M]+Na⁺) = 409.1774, Found 409.1775.

IR (neat) 2978, 2361, 1720, 1619, 1571, 1500, 1448, 1416, 1393, 1358, 1276, 1228, 1205, 1154, 1083, 1023, 965, 766, 693 cm⁻¹.

Ethyl 1-(((E)-but-2-en-1-yl)oxy)-4-cinnamyl-2-naphthoate (ent-A40)

White solid, Mp: 72–75 °C, 74% yield.



¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.33 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.06 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.77 (s, 1H), 7.58 (dddd, *J* = 20.8, 8.2, 6.8, 1.4 Hz, 2H), 7.33 (dt, *J* = 6.4, 1.4 Hz, 2H), 7.27 (d, *J* = 4.2 Hz, 2H), 7.23 – 7.15 (m, 1H), 6.48 (d, *J* = 3.5 Hz, 2H), 6.05 – 5.74 (m, 2H), 4.58 (d, *J* = 3.3 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 3.8 Hz, 2H), 1.79 (d, *J* = 4.3 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.7, 155.8, 137.5, 135.3, 132.0, 131.6, 131.0, 129.4, 128.7, 128.6, 128.4, 127.3, 127.1, 126.8, 126.3, 124.7, 124.5, 119.7, 76.9,

61.3, 36.4, 18.1, 14.5.

HRMS (ESI) Calculated for $C_{26}H_{26}O_3$ ([M]+Na⁺) = 409.1774, Found 409.1773.

IR (neat) 3025, 2978, 2361, 1619, 1600, 1571, 1500, 1448, 1416, 1393, 1356, 1277, 1228, 1205, 1154, 1085, 1024, 965, 767, 738, 693, 493 cm⁻¹.

1-chloro-4-(cinnamyloxy)naphthalene (A41)

Colorless oil, 91% yield.

¹**H** NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.44 – 7.41 (m, 2H), 7.34 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 6.78 (d, J = 15.7 Hz, 1H), 6.58 (dt, J = 15.9, 6.2 Hz, 1H), 4.80 (dd, J = 6.2, 1.4 Hz, 2H).

¹³**C NMR** (101 MHz, Chloroform-*d*) δ 150.6 , 136.4 , 133.5 , 133.4 , 129.3 , 128.6 , 127.9 , 127.5 , 126.7 , 126.6 , 126.4 , 124.9 , 124.5 , 122.1 , 74.6 .

HRMS (ESI) Calculated for $C_{19}H_{15}CIO$ ([M]+Na⁺) = 317.0704, Found 317.0706.

4-benzyl-1-(cinnamyloxy)-2-naphthonitrile (A43)



Colorless oil, 64% yield.

¹**H NMR** (600 MHz, Chloroform-d) δ 8.32 (d, J = 7.4 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.43 (m, 2H), 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 (d, J = 6.9 Hz, 2H), 6.76 (d, J = 15.8 Hz, 1H), 6.61 – 6.53 (m, 1H), 5.09 (d, J = 6.4 Hz, 2H), 4.36 (s, 2H).

¹³C NMR (151 MHz, Chloroform-d) δ 159.0 , 139.2 , 136.1 , 135.1 , 134.7 , 133.3 , 129.4 , 128.7 , 128.6 , 128.2 , 128.0 , 127.5 , 126.9 , 126.8 , 126.5 , 124.7 , 123.7 , 123.6 , 117.8 , 99.6 , 76.2 , 38.4 .

HRMS (ESI) Calculated for $C_{27}H_{21}NO([M]+Na^+) = 398.1515$, Found 398.1507.

4-chloro-1-(cinnamyloxy)-2-naphthaldehyde (A44)



¹**H NMR** (600 MHz, Chloroform-*d*) δ 10.56 (s, 1H), 8.32 (dd, *J* = 12.8, 8.4 Hz, 2H), 7.96 (s, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.54 – 6.49 (m, 1H), 4.88 (d, *J* = 6.1 Hz, 2H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 188.51, 159.71, 135.81, 135.06, 134.91, 130.41, 129.36, 128.72, 128.68, 128.42, 127.64, 126.74, 125.49, 125.42, 123.88, 122.90, 122.47, 79.02.

HRMS (ESI) Calculated for $C_{20}H_{15}ClO_2$ ([M]+Na⁺) = 345.0653, Found 345.0658.

IR (neat) 3027, 2886, 1678, 1618, 1587, 1496, 1449, 1411, 1349, 1259, 1218, 1185, 1095, 1030, 963, 921, 836, 746, 685, 615, 510 cm-1.

1-(1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)naphthalen-2-yl)ethan-1-one (A45)

Yellow solid, Mp: 107–110 °C, 28% yield.



¹**H NMR** (400 MHz, Chloroform-d) δ 8.34 (dd, J = 8.1, 1.6 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 4.1 Hz, 1H), 7.69 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.62 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.45 (h, J = 2.1 Hz, 4H), 7.40 – 7.34 (m, 2H), 7.30 (td, J = 5.2, 2.1 Hz, 4H), 6.82 (d, J = 15.8 Hz, 1H), 6.53 (dt, J = 15.8, 6.0 Hz, 1H), 4.74 (dd, J = 6.1, 1.4 Hz, 2H), 4.18 (s, 2H), 2.81 (s, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 200.4 , 155.2 , 136.2 , 134.7 , 133.6 , 131.6 , 129.1 , 128.7 , 128.7 , 128.6 , 128.2 , 128.1 , 128.1 , 127.9 , 126.7 ,

 $126.6\ , 125.3\ , 124.2\ , 124.1\ , 124.0\ , 123.4\ , 86.7\ , 83.7\ , 77.3\ , 31.0\ , 23.5.$

HRMS (ESI) Calculated for $C_{30}H_{24}O_2$ ([M]+Na⁺) = 439.1669, Found 439.1669.

IR (neat) 3057, 1670, 1619, 1599, 1570, 1491, 1446, 1412, 1386, 1360, 1305, 1272, 1225, 1186, 1153, 1070, 1025, 965, 611, 529, 504, 433 cm⁻¹.

15. Spectral Characterization Data for the Products

Ethyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B1)



White solid, Mp: 82–85 °C, 88% yield, 91% *ee*; $[\alpha]^{12.6} = -28.2$ (*c* = 1.79 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 12.68 min, $t_{R(major)}$ = 21.40 min.

¹**H NMR** (400 MHz, Acetone- d_6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.78 (s, 1H), 7.74 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.28 – 7.14 (m, 10H), 6.45 – 6.39 (m, 1H), 5.89 – 5.81 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.28 (s, 2H), 3.26 – 3.20 (m, 1H), 3.13 (ddd, J = 14.0, 7.5, 1.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-*d*₆) δ 181.2 , 165.6 , 157.2 , 145.7 , 137.9 , 134.99 , 135.2 ,135.0 , 134.0 , 134.0 , 133.9 , 132.2 , 129.4 , 129.3 , 129.0 , 128.4 , 128.3 , 127.5 , 127.3 , 127.0 , 124.9 , 124.1 , 86.2 , 84.7 , 61.7 , 46.7 , 44.1 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{31}H_{26}O_3$ ([M]+Na⁺) = 469.1774, Found 469.1786.

IR (neat) 3028, 2982, 1733, 1662, 1600, 1490, 1451, 1378, 1275, 1231, 1161, 1138, 1086, 1019, 967, 928, 862, 756, 692, 618, 527 cm⁻¹.



	Retention	Area	% Area
	Time		
1	12.684	7172585	4.50
2	21.399	152140239	95.50

Methyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B2)



Colorless oil, 72% yield, 81% *ee*; $[\alpha]^{12.3} = -24.3$ (*c* = 0.59 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 15.27 min, $t_{R(major)}$ = 24.53 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.19 – 8.06 (m, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.81 (s, 1H), 7.77 – 7.72 (m, 1H), 7.51 – 7.47 (m, 1H), 7.28 – 7.13 (m, 10H), 6.42 (d, J = 15.7 Hz, 1H), 5.89 – 5.81 (m, 1H), 3.79 (s, 3H), 3.28 (s, 2H), 3.26 – 3.11 (m, 2H).

¹³C{¹H} NMR (101 MHz, Acetone-*d*₆) δ 181.2 , 166.0 , 157.7 , 145.6 , 137.9 , 135.0 , 134.8 , 134.1 , 133.9 , 132.2 , 129.4 , 129.3 , 129.0 , 128.4 , 128.3 , 127.5 , 127.3 , 127.0 , 124.9 ,124.0 , 86.2 , 84.7 , 52.5 , 46.8 , 44.1 , 32.8

HRMS (ESI) Calculated for $C_{30}H_{24}O_3$ ([M]+Na⁺) = 455.1618, Found 455.1621.

IR (neat) 3028, 2950, 1738, 1663, 1600, 1491, 1437, 1380, 1279, 1234, 1188, 1161, 1137, 1086, 984, 873, 693, 619, 528 cm⁻¹.



Isopropyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2carboxylate (B3)



White solid, Mp: 50–53 °C, 78% yield, 97% *ee*; $[\alpha]^{12.6} = -30.7$ (*c* = 0.68 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 Ml/min, λ = 224 nm, $t_{R(minor)}$ = 9.95 min, $t_{R(major)}$ = 16.44 min.

¹**H NMR** (400 MHz, Acetone- d_6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.51 – 7.46 (m, 1H), 7.28 – 7.15 (m, 10H), 6.42 (d, J = 15.8 Hz, 1H), 5.89 – 5.81 (m, 1H), 5.14 (hept, J = 6.2 Hz, 1H), 3.28 (s, 2H), 3.24 – 3.10 (m, 2H), 1.29 (dd, J = 6.3, 2.6 Hz, 6H).

¹³C{¹H} NMR (101 MHz, Acetone-*d*₆) δ 181.3 , 165.3 , 156.6 , 145.7 , 138.0 , 135.6 , 135.0 , 134.0 133.9 , 132.3 , 129.4 , 129.3 , 129.0 , 128.4 , 128.3 , 127.5 , 127.3 , 127.0 , 124.9 , 124.1 , 86.3 , 84.7 , 69.3 , 46.7 , 44.1 , 32.8 , 22.1.

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1935.

IR (neat) 3028, 2981, 2934, 1730, 1663, 1600, 1491, 1452, 1378, 1277, 1234, 1181, 1142, 1105, 1085, 1027, 966, 942, 836, 692, 618, 527 cm⁻¹.



	Retention	Alca	70 Alca
	Time		
1	9.949	697318	1.32
2	16.437	51941290	98.68

Phenyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B4)



White solid, Mp: 46–49 °C, 87% yield, 97% *ee*; $[\alpha]^{13.0} = -43.0$ (*c* = 0.83 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 25.41 min, $t_{R(major)}$ = 45.28 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.17 (dd, J = 7.9, 1.5 Hz, 1H), 8.10 (s, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.51 (ddd, J = 8.1, 7.3, 1.1 Hz, 1H), 7.44 (ddd, J = 7.6, 6.4, 2.0 Hz, 2H), 7.30 – 7.13 (m, 13H), 6.47 (d, J = 15.8 Hz, 1H), 5.92 (dt, J = 15.4, 7.5 Hz, 1H), 3.34 (s, 2H), 3.31 – 3.17 (m, 2H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.1 , 164.0 , 159.1 , 152.0 , 145.6 , 137.9 , 135.1 , 134.2 ,134.2 ,133.8 ,132.2 ,130.4 ,129.4 ,129.3 ,129.0 ,128.5 ,128.3 ,127.5 ,127.0 ,127.0 ,126.9 , 124.8 ,124.0 ,122.7 ,86.2 ,84.8 ,47.1 ,44.1 ,32.8.

HRMS (ESI) Calculated for $C_{35}H_{26}O_3$ ([M]+Na⁺) = 517.1774, Found 517.1777.

IR (neat) 3028, 1752, 1665, 1598, 1490, 1454, 1379, 1267, 1215, 1189, 1161, 1129, 1072, 1025, 966, 928, 897, 838, 754, 691, 528, 499 cm⁻¹.



	Retention	Area	% Area
	Time		
1	25.413	410151	1.36
2	45.276	29657342	98.64

Ethyl (R)-4-cinnamyl-1-oxo-4-(prop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B5)



Colorless oil, 86% yield, 93% *ee*; $[\alpha]^{19.5} = 51.2$ (*c* = 0.52 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 9.59 min, $t_{R(major)}$ = 11.45 min.

¹**H NMR** (400 MHz, Acetone- d_6) δ 8.11 – 8.09 (m, 1H), 7.89 – 7.87 (m,

1H), 7.74 (d, *J* = 3.2 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 – 7.14 (m, 3H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.80 – 5.75 (m, 1H), 4.28 (d, *J* = 7.1 Hz, 2H), 3.11 – 3.08 (m, 4H), 2.37 (t, *J* = 2.6 Hz, 1H), 1.30 (s, 3H).

¹³C NMR (101 MHz, Acetone- d_6) δ 206.3, 181.1, 165.5, 157.1, 145.4, 137.9, 135.1, 134.9, 134.0, 133.8, 129.4, 128.4, 128.3, 127.4, 127.4, 127.0, 124.6, 80.3, 73.3, 61.7, 46.1, 44.4, 31.3, 14.6. HRMS (ESI) Calculated for C₂₅H₂₂O₃ ([M]+Na⁺) = 393.1461, Found 393.1463.

IR (neat) 3293, 3028, 2982, 1735, 1664, 1601, 1453, 1380, 1276, 1233, 1162, 1139, 1087, 1019, 967, 929, 862, 752, 647, 514 cm⁻¹



	Retention	Area	% Area
	Time		
1	9.593	647641	3.74
2	11.446	16671273	96.26

Ethyl (R)-4-cinnamyl-4-(ethoxymethyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B6)



Colorless oil, 42% yield, 93% *ee*; $[\alpha]^{13.5} = 69.8$ (*c* = 0.32 in CH₂Cl₂, $\lambda = 589$ nm). **HPLC**: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 9.90$ min, $t_{R(major)} = 11.34$ min.

¹**H** NMR (400 MHz, Acetone-d6) δ 8.09 (dd, J = 7.9, 1.5 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.76 (s, 1H), 7.71 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 7.48 (ddd, J = 8.2,

7.3, 1.2 Hz, 1H), 7.21 – 7.12 (m, 5H), 6.34 (d, J = 15.7 Hz, 1H), 5.75 (dd, J = 15.6, 7.6 Hz, 1H), 4.25 (t, J = 7.1 Hz, 2H), 3.98 – 3.87 (m, 2H), 3.48 – 3.38 (m, 2H), 3.02 (ddd, J = 7.6, 2.9, 1.3 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.0 Hz, 3H)

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 157.6 , 145.0 , 138.0 , 134.8 , 134.7 , 133.9 , 133.7 , 129.4 , 128.3 , 128.2 , 127.5 , 127.4 , 126.9 , 124.5 , 77.9 , 67.7 , 61.6 , 48.1 , 41.5 , 15.3 , 14.6. HRMS (ESI) Calculated for C₂₅H₂₆O₄ ([M]+Na⁺) = 413.1723, Found 413.1721.

IR (neat) 2978, 2869, 1736, 1663, 1601, 1453, 1378, 1277, 1230, 1110, 1020, 966, 929, 754, 695, 620, 514 cm⁻¹.



	Retention	Area	% Area
	Time		
1	9.898	879071	3.05
2	11.343	27900035	96.95

Ethyl (R)-4-benzyl-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B7)



Colorless oil, 55% yield, 94% *ee*; $[\alpha]^{13.2} = 13.2$ (*c* = 0.46 in CH₂Cl₂, $\lambda = 436$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 16.18$ min, $t_{R(major)} = 22.88$ min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.04 (dd, J = 8.0, 1.1 Hz, 1H), 7.91 (dd, J = 7.9, 1.5 Hz, 1H), 7.80 (s, 1H), 7.77 (ddd, J = 8.0, 7.3, 1.5 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.10 (m, 3H), 7.04 – 6.99 (m, 3H), 6.82 – 6.78 (m, 2H), 6.40 (d, J = 15.6 Hz, 1H), 5.82 (dt, J = 15.4, 7.4 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.54 – 3.44 (m, 2H), 3.33 – 3.07 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 180.8 , 165.4 , 158.7 , 145.8 , 138.0 , 137.0 , 134.7 , 134.5 , 134.0 , 133.6 , 130.9 , 129.4 , 128.4 , 128.2 , 128.1 , 128.1 , 127.4 , 127.2 , 127.0 , 125.2 , 61.5 , 48.6 , 48.4 , 45.3 , 14.6.

HRMS (ESI) Calculated for $C_{29}H_{26}O_3$ ([M]+Na⁺) = 445.1774, Found 445.1775.

IR (neat) 3029, 2982, 1736, 1662, 1601, 1494, 1452, 1380, 1276, 1230, 1159, 1138, 1087, 1020, 966, 929, 748, 699, 617 cm⁻¹.



	Retention	Area	% Area
	Time		
1	16.179	863343	3.24
2	22.875	25757539	96.76

Ethyl (R)-4-chloro-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B8)



Colorless oil, 83% yield, 93% *ee*; $[\alpha]^{13.5} = 24.3$ (*c* = 0.59 in CH₂Cl₂, $\lambda = 589$ nm). **HPLC**: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 11.44$ min, $t_{R(major)} = 10.02$ min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.05 (ddd, J = 9.6, 8.0, 1.3 Hz, 2H), 7.84 (td, J = 7.7, 1.5 Hz, 1H), 7.72 (s, 1H), 7.60 (td, J = 7.6, 1.2 Hz, 1H), 7.21 (qd, J = 7.0, 2.4 Hz, 5H), 6.49 (d, J = 15.8 Hz, 1H), 5.87 (dd, J = 15.6, 7.6 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.53 – 3.43 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 180.1 , 164.7 , 151.4 , 143.3 , 137.6 , 137.0 , 134.9 , 132.6 , 131.0 , 130.3 , 129.5 , 129.3 , 128.8 , 127.3 , 127.2 , 122.5 , 65.1 , 62.2 , 48.6 , 14.5.

HRMS (ESI) Calculated for $C_{22}H_{19}ClO_3$ ([M]+Na⁺) = 389.0915, Found 389.0912.

IR (neat) 2982, 1740, 1670, 1600, 1453, 1375, 1278, 1230, 1138, 1087, 968, 930, 757, 694, 511 cm⁻¹.



	Retention	Area	% Area
	Time		
1	10.020	30429365	96.48
2	11.438	1109263	3.52

Ethyl (S)-4-cinnamyl-1-oxo-4-propyl-1,4-dihydronaphthalene-2-carboxylate (B9)



Colorless oil, 62% yield, 93% *ee*; $[\alpha]^{13.5} = 100.2$ (*c* = 0.47 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{\text{R(minor)}} = 16.37 \text{ min}, t_{\text{R(major)}} = 15.02 \text{ min}.$

¹**H** NMR (400 MHz, Acetone-d6) δ 8.09 (dd, J = 7.9, 1.5 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.62 (s, 1H), 7.48 – 7.44 (m, 1H), 7.22 – 7.17 (m, 2H), 7.13 (td, J = 5.6, 1.5 Hz, 3H), 6.31 (d, J = 15.7 Hz, 1H), 5.75 (dd, J = 15.6, 7.7 Hz, 1H), 4.25 (t, J = 7.1 Hz, 2H), 3.05 – 2.91 (m, 2H), 2.31 – 2.07 (m, 2H), 1.02 (dq, J = 12.8, 6.7, 6.0 Hz, 1H), 0.80 – 0.74 (m, 4H). ¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.7 , 159.3 , 146.6 , 138.1 , 134.9 , 134.7 , 134.1 , 133.9 , 129.4 , 128.2 , 128.0 , 127.4 , 127.4 , 126.9 , 125.0 , 61.6 , 47.4 , 46.3 , 44.1 , 18.9 , 14.6 , 14.5 . **HRMS** (ESI) Calculated for $C_{25}H_{26}O_3$ ([M]+Na⁺) = 397.1774, Found 397.1772.

IR (neat) 3028, 2959, 2932, 2872, 1737, 1661, 1601, 1452, 1380, 1274, 1231, 1141, 1087, 1022, 966, 927, 748, 695, 619, 513 cm⁻¹.



	Retention	Area	% Area
	Time		
1	15.024	43097389	96.75
2	16.366	1448819	3.25

Ethyl (R)-4-cinnamyl-4-cyclopropyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B10)



Colorless oil, 34% yield, 78% *ee*; $[\alpha]^{13.4} = 74.0$ (*c* = 0.19 in CH₂Cl₂, $\lambda = 589$ nm). **HPLC**: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 17.64$ min, $t_{R(major)} = 18.51$ min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.07 (dd, J = 7.9, 1.5 Hz, 1H), 7.90 (dd, J = 8.1, 1.1 Hz, 1H), 7.73 (ddd, J = 8.0, 7.2, 1.5 Hz, 1H), 7.55 (s, 1H), 7.47 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.14 – 7.11 (m, 3H), 6.37 (d, J = 15.8 Hz, 1H), 5.82 – 5.74 (m, 1H), 4.27 – 4.21 (m, 2H), 3.15 – 2.91 (m, 2H), 1.48 (tt, J = 8.1, 5.8 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.61 – 0.56 (m, 2H), 0.46 – 0.41 (m, 1H), 0.28 – 0.23 (m, 1H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.1 , 165.6 , 157.0 , 147.2 , 138.1 , 134.6 , 134.6 , 133.8 ,133.0 , 129.4 , 128.2 , 128.1 , 127.3 , 126.9 , 125.2 , 61.7 , 45.2 , 42.9 , 23.0 , 14.6 , 14.2.

HRMS (ESI) Calculated for $C_{25}H_{24}O_3$ ([M]+Na⁺) = 395.1618, Found 395.1616.

IR (neat) 2983, 1737, 1664, 1601, 1453, 1380, 1278, 1230, 1136, 1086, 1022, 966, 928, 761, 695 cm⁻¹.



	Retention	Area	% Area
	Time		
1	17.641	6147421	11.00
2	18.513	49758753	89.00

3-ethyl 1-methyl (R)-1-cinnamyl-4-oxo-1,4-dihydronaphthalene-1,3-dicarboxylate (B11)



Colorless oil, 36% yield, 80% *ee*; $[\alpha]^{13.8} = 115.0$ (*c* = 0.22 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{\text{R(minor)}}$ = 14.55 min, $t_{\text{R(major)}}$ = 15.94 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.11 (dt, J = 7.6, 1.1 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.56 (ddd, J = 8.2, 6.0, 2.4 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.16 (dq, J = 5.6, 1.9, 1.4 Hz, 3H), 6.38 (d, J = 15.8 Hz, 1H), 5.81 – 5.73 (m, 1H), 4.30 – 4.24 (m, 2H), 3.70 (s, 3H), 3.30 (ddd, J = 7.7, 6.7, 1.3 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 180.6 , 171.6 , 165.3 , 151.6 , 141.3 , 137.8 , 136.0 , 134.5 , 134.3 , 132.8 , 129.4 , 129.3 , 128.4 , 128.0 , 127.6 , 127.0 , 123.4 , 61.9 , 53.9 , 53.5 , 43.2 , 14.6 .

HRMS (ESI) Calculated for $C_{24}H_{22}O_5$ ([M]+Na⁺) = 413.1359, Found 413.1358.

IR (neat) 2955, 1668, 1600, 1452, 1379, 1280, 1230, 1137, 1086, 1020, 969, 927, 754, 695 cm⁻¹.



	Retention	Area	% Area
	Time		
1	14.550	1865585	10.03
2	15.941	16733800	89.97

Ethyl (R)-4-cinnamyl-4-ethoxy-1-oxo-1,4-dihydronaphthalene-2-carboxylate (A12)



Colorless oil, 30% yield, 5% ee.

HPLC: Daicel chiralcel IC *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 13.45 min, $t_{R(major)}$ = 16.07 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.04 (d, J = 7.9 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.61 (s, 1H), 7.55 (m, 1H), 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 6.26 (d, J = 15.9 Hz, 1H), 5.82 (dt, J = 15.6, 7.6 Hz, 1H), 4.26 (t, J = 7.2 Hz, 2H), 3.40 – 3.34 (m, 1H), 3.20 – 3.14 (m, 1H), 2.97 – 2.92 (m, 1H), 2.88 – 2.82 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 180.5, 164.9, 155.4, 144.2, 138.1, 136.1, 135.8, 134.4, 133.1, 129.4, 129.4, 128.3, 127.3, 127.1, 127.0, 123.3, 77.6, 61.9, 61.7, 47.5, 16.1, 14.5.

HRMS (ESI) Calculated for $C_{24}H_{24}O_4$ ([M]+Na⁺) = 399.1567, Found 399.1568.

IR (neat) 2978, 2931, 1738, 1672, 1600, 1451, 1368, 1276, 1073, 1019, 970, 922, 757, 697, 579, 450 cm⁻¹.



	Retention	Area	% Area
	Time		
1	13.451	331169	47.38
2	16.067	367779	52.62

Ethyl (R)-4-benzyl-4-cinnamyl-6-methyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B13)



Colorless oil, 59% yield, 92% *ee*; $[\alpha]^{13.7} = 23.2$ (*c* = 0.50 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 13.64$ min, $t_{R(major)} = 18.18$ min.

¹**H NMR** (400 MHz, Acetone-d6) δ 7.87 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.25 – 7.12 (m, 6H), 7.05 – 6.99 (m, 3H), 6.84 – 6.80 (m, 2H), 6.41 (d, J = 15.7 Hz, 1H), 5.81 (dt, J = 15.4, 7.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.53 – 3.40 (m, 2H), 3.31 – 3.04 (m, 2H), 2.52 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 180.6, 165.6, 158.4, 145.9, 144.3, 138.1, 137.1, 134.6, 134.5, 131.7, 131.0, 129.4, 129.1, 128.4, 128.4, 128.2, 127.4, 127.3, 126.9, 125.3, 61.4, 48.4, 48.3, 45.3, 22.0, 14.6.

HRMS (ESI) Calculated for $C_{30}H_{28}O_3$ ([M]+Na⁺) = 459.1931, Found 459.1927.

IR (neat) 3028, 2981, 1736, 1661, 1608, 1494, 1450, 1381, 1275, 1232, 1160, 1085, 1021, 966, 931, 842, 799, 738, 699, 529, 480 cm⁻¹.



	Retention	Alta	70 Alea
	Time		
1	13.640	2642178	3.85
2	18.187	65970340	96.15

Ethyl (R)-4-benzyl-6-(tert-butyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B14)



Colorless oil, 52% yield, 91% *ee*; $[\alpha]^{18.6} = 14.6$ (*c* = 0.46 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 12.03 min, $t_{R(major)}$ = 13.82 min.

¹**H NMR** (400 MHz, Acetone- d_6) δ 8.00 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.79 (s, 1H), 7.45 (dd, J = 8.4, 1.9 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.14 (m, 3H), 7.02 (m, 3H), 6.82 (dd, J = 7.1, 2.4 Hz, 2H), 6.38 (d, J = 15.6 Hz, 1H), 5.85 (dt, J = 15.4, 7.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.60 – 3.41 (m, 2H), 3.37 – 3.05 (m, 2H), 1.45 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 180.6, 165.6, 158.7, 156.9, 145.3, 138.1, 137.2, 134.7, 134.5, 131.6, 131.0, 129.4, 128.4, 128.2, 127.4, 127.2, 126.9, 125.4, 125.2, 125.1, 61.4, 48.7, 48.3, 45.3, 36.0, 31.5, 14.6.

HRMS (ESI) Calculated for $C_{31}H_{26}O_3$ ([M]+Na⁺) = 501.2400, Found 502.2381.

IR (neat) 3028, 2962, 1736, 1663, 1605, 1490, 1451, 1417, 1381, 1270, 1238, 1171, 1022, 966, 930, 850, 806, 744, 699, 597, 491 cm⁻¹.



	Retention	Area	% Area
	Time		
1	12.007	9714877	50.47
2	13.882	9533159	49.53



	Retention	Area	% Area
	Time		
1	12.031	118827	2.50
2	13.823	4626142	97.50
Ethyl (R)-4-benzyl-4-cinnamyl-1-oxo-6-phenyl-1,4-dihydronaphthalene-2-carboxylate (B15)



Colorless oil, 45% yield, 94% *ee*; $[\alpha]^{18.6} = 87.7$ (*c* = 0.34 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 23.31$ min, $t_{R(major)} = 29.21$ min.

¹**H NMR** (400 MHz, Acetone-*d*₆) δ 8.31 (d, J = 1.9 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.84 (s, 1H), 7.72 (dd, J = 8.2, 1.8 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.21 – 7.10 (m, 5H), 7.04 (m, 3H), 6.88 (dd, J = 6.4, 3.2 Hz, 2H), 6.45 (d, J = 15.8 Hz, 1H), 5.91 (dt, J = 15.4, 7.5 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.60 (dd, J = 73.5, 13.4 Hz, 2H), 3.49 – 3.11 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 180.5, 165.5, 158.9, 146.4, 145.9, 140.9, 138.0, 137.2, 134.7, 134.5, 132.8, 131.0, 130.0, 129.4, 129.3, 128.5, 128.4, 128.2, 128.0, 127.4, 127.0, 126.8, 126.5, 125.4, 61.5, 48.8, 48.3, 45.2, 14.6.

HRMS (ESI) Calculated for $C_{35}H_{34}O_3$ ([M]+Na⁺) = 501.2400, Found 501.2381.

IR (neat) 3029, 2982, 2927, 1734, 1661, 1603, 1492, 1449, 1409, 1381, 1268, 1235, 1166, 1090, 1022, 967, 927, 849, 806, 760, 698, 487 cm⁻¹.



	Retention	Area	% Area
	Time		
1	23.313	1603846	3.07
2	29.206	50565777	96.93

Ethyl (R)-4-benzyl-4-cinnamyl-6-methoxy-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B16)



Colorless oil, 61% yield, 93% *ee*; $[\alpha]^{18.6} = 21.0$ (*c* = 0.53 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralce ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 16.59 min, $t_{R(major)}$ = 19.78 min.

¹**H NMR** (400 MHz, Acetone- d_6) δ 7.87 (d, J = 8.8 Hz, 1H), 7.70 (s, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.21 – 7.11 (m, 5H), 7.04 (m, 3H), 6.98 (dd, J = 8.8, 2.5 Hz, 1H), 6.87 (dd, J = 6.5, 3.1 Hz, 2H), 6.42 (d, J = 15.7 Hz, 1H), 5.84 (dt, J = 15.4, 7.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.00 (s, 3H), 3.55 – 3.40 (m, 2H), 3.33 – 3.03 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 179.9, 165.7, 164.3, 157.8, 148.2, 138.1, 137.1, 134.5, 134.5, 130.9, 129.6, 129.4, 128.4, 128.2, 127.5, 127.4, 126.9, 125.3, 115.2, 111.8, 61.3, 56.2, 48.6, 48.4, 45.4, 14.6.

HRMS (ESI) Calculated for $C_{30}H_{28}O_4([M]+Na^+) = 475.1880$, Found 475.1886.

IR (neat) 3028, 2360, 2242, 1734, 1659, 1600, 1492, 1450, 1381, 1275, 1233, 1085, 1022, 968, 931, 801, 744, 699, 576, 489 cm⁻¹.



	Retention	Area	% Area
	Time		
1	15.667	5949304	50.02
2	19.173	5944016	49.98



	Retention	Area	% Area
	Time		
1	16.587	3214549	3.47
2	19.784	89548507	96.53

Ethyl (R)-4-benzyl-6-chloro-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B17)



Colorless oil, 51% yield, 88% *ee*; $[\alpha]^{13.4} = -11.9$ (*c* = 0.37 in CH₂Cl₂, $\lambda = 436$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 14.40 min, $t_{R(major)}$ = 18.49 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.12 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.84 (s, 1H), 7.45 (dd, J = 8.5, 2.0 Hz, 1H), 7.22 – 7.13 (m, 5H), 7.07 – 7.03 (m, 3H), 6.86 – 6.82 (m, 2H), 6.43 (d, J = 15.7 Hz, 1H), 5.86 (dt, J = 15.4, 7.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.58 – 3.47 (m, 2H), 3.38 – 3.10 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 179.9, 165.1, 158.8, 147.9, 139.8, 137.9, 136.8, 135.0, 134.3, 132.6, 130.9, 129.4, 129.3, 128.6, 128.6, 128.3, 128.2, 127.6, 127.00, 124.9, 61.6, 48.8, 48.2, 45.0, 14.6, 14.5.

HRMS (ESI) Calculated for $C_{29}H_{25}ClO_3$ ([M]+Na⁺) = 479.1384, Found 479.1384.

IR (neat) 3028, 2982, 1736, 1665, 1599, 1491, 1442, 1379, 1276, 1232, 1162, 1138, 1086, 1020, 967, 928, 799, 756, 693, 619, 546, 509 cm⁻¹.



	Time		
1	14.395	1291349	5.96
2	18.487	20371987	94.04

Ethyl (R)-4-benzyl-4-cinnamyl-6-cyano-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B18)



Colorless oil, 35% yield, 80% *ee*; $[\alpha]^{18.6} = 46.0$ (*c* = 0.28 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 26.28$ min, $t_{R(major)} = 34.73$ min.

¹**H NMR** (400 MHz, Acetone-*d*₆) δ 8.57 (d, J = 1.5 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.97 (s, 1H), 7.80 (dd, J = 8.1, 1.5 Hz, 1H), 7.21 – 7.12 (m, 5H), 7.04 (m, 3H), 6.83 (dd, J = 6.4, 3.1 Hz, 2H), 6.45 (d, J = 15.7 Hz, 1H), 5.88 (dt, J = 15.5, 7.5 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.65 – 3.52 (m, 2H), 3.32 (ddd, J = 97.4, 14.5, 8.0 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 179.6, 164.8, 159.7, 146.7, 137.8, 136.7, 136.5, 135.2, 134.3, 132.9, 131.3, 131.0, 129.4, 128.6, 128.3, 128.1, 127.6, 127.0, 124.7, 119.0, 116.9, 61.7, 49.0, 48.1, 44.8, 14.6.

HRMS (ESI) Calculated for $C_{30}H_{25}NO_3$ ([M]+Na⁺) = 470.1727, Found 470.1731.

IR (neat) 3030, 2927, 2233, 1734, 1667, 1605, 1494, 1449, 1416, 1382, 1273, 1230, 1154, 1082, 1020, 969, 930, 853, 804, 742, 699, 587, 495 cm⁻¹.



	Retention	Area	% Area
	Time		
1	26.278	2719661	10.03

Ethyl (R)-4-benzyl-4-cinnamyl-8-methyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B19)



Colorless oil, 62% yield, 60% *ee*; $[\alpha]^{13.3} = -25.9$ (*c* = 0.51 in CH₂Cl₂, $\lambda = 436$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 8.04min, $t_{R(major)}$ = 10.62 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 7.87 (d, J = 7.9 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.26 – 7.08 (m, 6H), 7.07 – 6.98 (m, 3H), 6.86 – 6.77 (m, 2H), 6.41 (d, J = 15.8 Hz, 1H), 5.83 (dt, J = 15.4, 7.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.42 (q, J = 13.3 Hz, 2H), 3.31 – 3.01 (m, 2H), 2.52 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 183.3 , 165.7 , 155.5 , 147.2 , 141.2 , 138.1 , 137.1 , 136.2 , 134.5 , 132.7 , 132.4 , 131.8 , 131.1 , 129.4 , 128.4 , 128.2 , 127.4 , 127.0 , 126.4 , 125.4 , 61.4 , 49.1 , 48.6 , 45.7 , 23.7 , 14.6 .

HRMS (ESI) Calculated for $C_{30}H_{28}O_3$ ([M]+Na⁺) = 459.1931, Found 459.1926.

2

10.615

IR (neat) 3028, 2980, 2928, 1735, 1665, 1593, 1494, 1469, 1450, 1422, 1376, 1269, 1229, 1126, 1088, 1021, 966, 928, 792, 749, 699, 476 cm⁻¹.



18222112

79.83

Ethyl (R,E)-4-(3-(4-nitrophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B20)



in CH₂Cl₂, $\lambda = 589$ nm). White solid, Mp: 37–40 °C, 76% yield, 90% *ee*; $[\alpha]^{14.0} = -22.3$ (*c* = 0.72

SFC Chiralcel BYPASS, CO₂/MeOH = 80/20, 1.5 mL/min, λ = 224 nm, $t_{R(minor)}$ = 10.34 min, $t_{R(major)}$ = 12.95 min

¹H NMR (400 MHz, Acetone-d6) δ 8.16 – 8.03 (m, 3H), 7.95 (d, J =

7.9 Hz, 1H), 7.80 (s, 1H), 7.75 (ddd, J = 8.0, 7.2, 1.5 Hz, 1H), 7.50 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.30 – 7.22 (m, 3H), 7.21 – 7.16 (m, 2H), 6.61 – 6.55 (m, 1H), 6.19 – 6.11 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.35 – 3.20 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.1, 165.6, 156.8, 147.8, 145.4, 144.4, 135.3, 134.1, 133.8, 133.1, 132.2, 130.5, 129.3, 129.0, 128.5, 127.8, 127.5, 127.4, 124.7, 124.0, 86.1, 84.8, 61.7, 46.6, 44.1, 32.9, 14.6, 14.4.

HRMS (ESI) Calculated for $C_{31}H_{25}NO_5$ ([M]+Na⁺) = 514.1625, Found 514.1626.

IR (neat) 2982, 1734, 1662, 1597, 1514, 1490, 1453, 1379, 1340, 1276, 1232, 1181, 1138, 1109, 1087, 1018, 971, 928, 860, 831, 758, 692, 636, 528 cm⁻¹.



	Time		
1	10.338	1007441	4.91
2	12.950	19497495	95.09

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(4-(trifluoromethyl)phenyl)allyl)-1,4dihydronaphthalene-2-carboxylate (B21)



White solid, Mp: 34–37 °C, 54% yield, 92% *ee*; $[\alpha]^{14.0} = -30.3$ (*c* = 0.52 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 28.80 min, $t_{R(major)}$ = 30.98 min.

¹**H** NMR (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.8, 1.5 Hz, 1H), 7.94 (dd, J = 8.0, 1.0 Hz, 1H), 7.79 (s, 1H), 7.75 (td, J = 7.7, 1.5 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.49 (td, J = 7.6, 1.0 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.26 (qd, J = 4.7, 1.6 Hz, 3H), 7.21 – 7.16 (m, 2H), 6.52 (d, J = 15.7 Hz, 1H), 6.04 (dt, J = 15.4, 7.4 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.32 – 3.16 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 156.9 , 145.5 , 141.9 , 135.3 , 134.1 , 133.9 , 133.6 , 132.3 , 129.3 , 129.0 , 128.5 , 128.4 , 127.5 , 127.5 , 127.4 , 126.4 , 126.4 , 126.3 , 126.3 , 124.1 , 86.1 , 84.8 , 61.7 , 46.6 , 44.0 , 32.9 , 14.6 .

 ^{19}F NMR (377 MHz, Acetone-d6) δ -63.0 .

HRMS (ESI) Calculated for $C_{32}H_{25}F_3O_3$ ([M]+Na⁺) = 537.1648, Found 537.1651.

IR (neat) 2984, 1736, 1665, 1602, 1490, 1454, 1380, 1325, 1277, 1233, 1164, 1120, 1067, 1017, 970, 929, 860, 759, 596, 526 cm⁻¹.



	Retention	Area	% Area
	Time		
1	28.800	945659	3.90
2	30.978	23273402	96.10

Ethyl (R,E)-4-(3-(4-fluorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B22)



Colorless oil, 84% yield, 94% *ee*; $[\alpha]^{14.2} = -26.5$ (*c* = 0.75 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 254 \text{ nm}, t_{\text{R(minor)}} = 19.73 \text{ min}, t_{\text{R(major)}} = 23.53 \text{ min}.$

¹H NMR (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.92 (dd, J = 8.0, 1.1 Hz, 1H), 7.77 (s, 1H), 7.76 – 7.72 (m, 1H), 7.51 – 7.46 (m, 1H), 7.26 (pd, J = 4.3, 1.8 Hz, 3H), 7.23 – 7.17 (m, 4H), 7.00 – 6.94 (m, 2H), 6.41 (d, J = 15.7 Hz, 1H), 5.80 (dt, J = 15.4, 7.4 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.28 (s, 2H), 3.25 – 3.10 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

$$\label{eq:stars} \begin{split} ^{13}C\{^1H\} \ \text{NMR} \ (101 \ \text{MHz}, \ \text{Acetone-d6}) \ \delta \ 181.2 \ , \ 165.6 \ , \ 163.0 \ (d, \ ^1J_{FC} = 244.8 \ \text{Hz}), \ 157.1 \ , \ 145.6 \ , \\ 135.2 \ , \ 134.4 \ , \ 133.9 \ , \ 133.7 \ , \ 132.2 \ , \ 129.0 \ , \ 129.0 \ , \ 128.8 \ (d, \ ^3J_{FC} = 8.1 \ \text{Hz}) \ , \ 128.4 \ , \ 127.4 \ , \ 127.3 \ , \\ 124.9 \ (d, \ ^4J_{FC} = 2.5 \ \text{Hz}) \ , \ 124.1 \ , \ 116.1 \ (d, \ ^2J_{FC} = 21.7 \ \text{Hz}) \ , \ 86.2 \ , \ 84.7 \ , \ 61.7 \ , \ 46.7 \ , \ 44.1 \ , \ 32.8 \ , \ 14.6 \ . \\ \ ^{19}F \ \text{NMR} \ (377 \ \text{MHz}, \ \text{Acetone-d6}) \ \delta \ -116 \ . \end{split}$$

HRMS (ESI) Calculated for $C_{31}H_{25}FO_3$ ([M]+Na⁺) = 487.1680, Found 487.1678.

2

23.525

IR (neat) 2983, 1734, 1663, 1600, 1508, 1490, 1454, 1379, 1276, 1228, 1159, 1138, 1088, 1017, 967, 930, 847, 816, 759, 692, 640, 572, 523 cm⁻¹.



158938968

96.73

Ethyl (R,E)-4-(3-(4-bromophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B23)



White solid, Mp: 42–45 °C, 85% yield, 91% *ee*; $[\alpha]^{14.0} = -16.6$ (*c* = 0.78 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 26.07 min, $t_{R(major)}$ = 28.11 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.92 (dd, J = 8.0, 1.1 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.48 (td, J = 7.6, 1.1 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.29 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.14 – 7.11 (m, 2H), 6.40 (d, J = 15.7 Hz, 1H), 5.90 (dt, J = 15.4, 7.5 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.27 (s, 2H), 3.24 – 3.10 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 157.0 , 145.6 , 137.2 , 135.2 , 134.1 , 133.9 , 133.7 , 132.4 , 132.2 , 129.3 , 129.0 , 128.9 , 128.5 , 127.4 , 127.3 , 126.1 , 124.0 , 121.5 , 86.2 , 84.7 , 61.7 , 55.1 , 46.6 , 44.1 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{31}H_{25}^{79}BrO_3$ ([M]+Na⁺) = 547.0879, Found 547.0879.

HRMS (ESI) Calculated for $C_{31}H_{25}^{81}BrO_3$ ([M]+Na⁺) = 549.0859, Found 549.0861.

IR (neat) 2982, 2926, 1735, 1663, 1601, 1487, 1454, 1379, 1276, 1232, 1162, 1138, 1087, 1073, 1010, 967, 929, 853, 814, 759, 692, 636, 525 cm⁻¹.



	Retention	Area	% Area
	Time		
1	26.073	7787519	4.50
2	28.114	165290709	95.50

Ethyl (R,E)-4-(3-(4-chlorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B24)



White solid, Mp: 43–46 °C, 81% yield, 92% *ee*; $[\alpha]^{14.0} = -20.9$ (*c* = 0.72 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 24.06 min, $t_{R(major)}$ = 26.78 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.8, 1.4 Hz, 1H), 7.92 (dd, J = 8.1, 1.2 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.48 (td, J = 8.1, 1.2 Hz, 1H), 7.28 – 7.16 (m, 9H), 6.41 (d, J = 15.8 Hz, 1H), 5.88 (dt, J = 15.5, 7.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.28 (s, 2H), 3.25 – 3.10 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 157.0 , 145.6 , 136.8 , 135.2 , 134.1 , 133.9 , 133.7 , 133.4 , 132.2 , 129.5 , 129.3 , 129.0 , 128.6 , 128.5 , 127.4 , 127.3 , 126.0 , 124.1 , 86.2 , 84.7 , 61.7 , 46.6 , 44.0 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{31}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1386.

IR (neat) 2982, 1736, 1665, 1600, 1490, 1454, 1379, 1277, 1232, 1162, 1138, 1090, 1014, 968, 929, 816, 759, 692, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	24.062	439704	3.95
2	26.775	10689853	96.05

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(p-tolyl)allyl)-1,4-dihydronaphthalene-2-carboxylate (B25)



White solid, Mp: 40–43 °C, 81% yield, 81% *ee*; $[\alpha]^{14.0} = -16.4$ (*c* = 0.72 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 21.50 min, $t_{R(major)}$ = 22.61 min.

¹H NMR (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.91 (dd, J = 8.1, 1.1 Hz, 1H), 7.77 (s, 1H), 7.74 (td, J = 7.7, 1.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.29 –

7.23 (m, 3H), 7.20 – 7.16 (m, 2H), 7.07 – 7.00 (m, 4H), 6.37 (d, J = 15.7 Hz, 1H), 5.78 (dt, J = 15.4, 7.4 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.28 – 3.25 (m, 2H), 3.23 – 3.08 (m, 2H), 2.22 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 157.2 , 145.7 , 138.0 , 135.2 , 135.1 , 134.9 , 134.0 , 133.9 , 132.2 , 130.0 , 129.3 , 129.0 , 128.4 , 127.4 , 127.3 , 126.9 , 124.1 , 123.7 , 86.3 , 84.7 , 61.7 , 46.7 , 44.2 , 32.8 , 32.4 , 21.2 , 14.6 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1930.

IR (neat) 2981, 1735, 1665, 1601, 1512, 1490, 1454, 1379, 1276, 1232, 1162, 1138, 1087, 1020, 968, 929, 803, 759, 692, 641, 526 cm⁻¹.



	Retention	Area	% Area
	Time		
1	21.503	4727308	9.42
2	22.607	45467170	90.58

Ethyl (R,E)-4-(3-(4-methoxyphenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B26)



Colorless oil, 45% yield, 39% *ee*; $[\alpha]^{14.1} = -3.8$ (*c* = 0.39 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 30.85$ min, $t_{R(major)} = 23.84$ min.

 ^1H NMR 1H NMR (400 MHz, Acetone-d6) δ 8.11 (ddd, J = 7.9, 1.4,

0.6 Hz, 1H), 7.91 (dt, J = 7.9, 0.9 Hz, 1H), 7.76 (s, 1H), 7.76 – 7.72 (m, 1H), 7.48 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.12 – 7.08 (m, 2H), 6.79 – 6.75 (m, 2H), 6.35 (d, J = 15.8 Hz, 1H), 5.73 – 5.65 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 3.27 (s, 2H), 3.22 – 3.07 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.6 , 160.3 , 157.3 , 145.8 , 135.1 , 134.5 , 134.0 , 133.9 , 132.3 , 130.6 , 129.3 , 129.0 , 128.4 , 128.2 , 127.5 , 127.3 , 124.1 , 122.4 , 114.8 , 86.3 , 84.7 , 61.7 , 55.6 , 46.8 , 44.2 , 32.7 , 14.6 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_4$ ([M]+Na⁺) = 499.1880, Found 499.1879.

IR (neat) 2933, 1736, 1665, 1605, 1511, 1490, 1456, 1379, 1277, 1249, 1176, 1138, 1087, 1030, 967, 930, 840, 759, 693, 527 cm⁻¹.



	Retention	Area	% Area
	Time		
1	23.841	45483502	69.48
2	30.852	19978327	30.52

Ethyl (R,E)-4-(3-(3-chlorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B27)



White solid, Mp: 102–105 °C, 84% yield, 95% *ee*; $[\alpha]^{13.8} = -28.5$ (*c* = 0.66 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 12.05 min, $t_{R(major)}$ = 23.07 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.93 (dd, J = 8.0, 1.1 Hz, 1H), 7.78 (s, 1H), 7.77 – 7.72 (m, 1H), 7.49 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.23 – 7.20 (m, 2H), 7.18 (ddd, J = 6.6, 3.5, 1.8 Hz, 3H), 7.12 (dt, J = 7.6, 1.5 Hz, 1H),

6.41 (d, J = 15.7 Hz, 1H), 5.95 (dd, J = 15.6, 7.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.28 (d, J = 2.2 Hz, 2H), 3.26 – 3.12 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.2 , 165.6 , 156.9 , 145.5 , 140.2 , 135.2 , 134.9 , 134.1 , 133.9 , 133.6 , 132.2 , 131.1 , 129.3 , 129.0 , 128.5 , 128.1 , 127.5 , 127.4 , 127.0 , 126.8 , 125.5 , 124.1 , 86.2 , 84.7 , 61.7 , 46.6 , 44.0 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{31}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1383.

IR (neat) 2982, 1736, 1665, 1598, 1567, 1489, 1454, 1380, 1277, 1232, 1162, 1138, 1086, 1020, 966, 928, 759, 692, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	12.052	2860647	2.58
2	23.066	108056165	97.42

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(m-tolyl)allyl)-1,4-dihydronaphthalene-2carboxylate (B28)



White solid, Mp: 93–96 °C, 89% yield, 90% *ee*; $[\alpha]^{13.8} = -20.0$ (*c* = 0.74 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 11.85 min, $t_{R(major)}$ = 16.93 min.

¹**H** NMR (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.92 (dd, J = 7.9, 1.1 Hz, 1H), 7.78 (s, 1H), 7.76 – 7.72 (m, 1H), 7.48 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 7.08 (t, J = 7.5 Hz, 1H), 7.00 – 6.94 (m, 3H), 6.38 (d, J = 15.8 Hz, 1H), 5.85 (dd, J = 15.5, 7.7 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.27 (s, 2H), 3.25 – 3.10 (m, 2H), 2.21 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.6 , 157.2 , 145.7 , 138.8 , 137.9 , 135.2 , 135.1 , 134.0 , 133.9 , 132.2 , 129.3 , 129.3 , 129.0 , 129.0 , 128.4 , 127.7 , 127.5 , 127.3 , 124.6 , 124.2 , 124.1 , 86.2 , 84.7 , 61.7 , 46.7 , 44.2 , 32.9 , 21.4 , 14.6 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1929.

IR (neat) 2982, 2361, 2160, 1736, 1666, 1601, 1489, 1454, 1379, 1276, 1232, 1162, 1138, 1087, 1019, 967, 927, 759, 692, 528 cm⁻¹.



	11010111011	11104	/ 0 1 11 0 00
	Time		
1	11.846	5650913	5.17
2	16.930	103617955	94.83

Ethyl (R,E)-4-(3-(2-chlorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B29)



White solid, Mp: 31–34 °C, 40% yield, 96% *ee*; $[\alpha]^{14.0} = -29.2$ (*c* = 0.37 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 11.89 min, $t_{R(major)}$ = 16.52 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.96 (dd, J = 8.0, 1.1 Hz, 1H), 7.80 (s, 1H), 7.75 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.49 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.31 – 7.24 (m, 5H), 7.20 – 7.15 (m, 4H), 6.71 (d, J = 15.7 Hz, 1H), 5.89 – 5.82 (m, 1H), 4.26 (t, J = 7.1 Hz, 2H), 3.32 – 3.19 (m, 4H), 1.29 (d, J = 7.1 Hz, 3H).

¹³C{¹H} NMR 13C NMR (101 MHz, Acetone-d6) δ 181.3 , 165.5 , 157.1 , 145.5 , 136.0 , 135.2 , 134.1 , 133.9 , 133.1 , 132.3 , 131.0 , 130.3 , 129.8 , 129.3 , 129.0 , 128.5 , 128.5 , 128.1 , 127.9 , 127.5 , 127.4 , 124.1 , 86.2 , 84.8 , 61.7 , 46.7 , 44.0 , 32.9 , 14.6 .

HRMS (ESI) Calculated for $C_{31}H_{25}ClO_3$ ([M]+Na⁺) = 503.1384, Found 503.1382.

IR (neat) 2982, 1736, 1665, 1601, 1490, 1470, 1441, 1379, 1276, 1232, 1162, 1138, 1087, 1021, 967, 929, 693, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	11.887	566875	2.00
2	16.518	27803693	98.00

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(o-tolyl)allyl)-1,4-dihydronaphthalene-2-carboxylate (B30)



White solid, Mp: 33–36 °C, 72% yield, 93% *ee*; $[\alpha]^{14.2} = -26.6$ (*c* = 0.56 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 11.01 min, $t_{R(major)}$ = 14.94 min.

^{Me} ¹**H NMR** (400 MHz, Acetone-d6) δ 8.10 (dd, J = 7.9, 1.5 Hz, 1H), 7.95 (dd, J = 8.0, 1.1 Hz, 1H), 7.80 (s, 1H), 7.78 – 7.73 (m, 1H), 7.48 (ddd, J = 8.1, 7.3, 1.1 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 7.10 – 7.07 (m, 1H), 7.05 – 6.98 (m, 3H), 6.58 (d, J = 15.6 Hz, 1H), 5.67 – 5.60 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.29 (s, 2H), 3.27 – 3.12 (m, 2H), 2.11 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.6 , 157.3 , 145.7 , 137.3 , 135.9 , 135.2 , 134.0 , 134.0 , 133.4 , 132.3 , 130.9 , 129.3 , 129.0 , 128.4 , 128.2 , 127.5 , 127.3 , 126.9 , 126.5 , 126.4 , 124.1 , 86.2 , 84.7 , 61.7 , 46.9 , 44.3 , 32.8 , 19.8 , 14.6 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_3$ ([M]+Na⁺) = 483.1931, Found 483.1929.

IR (neat) 2981, 1736, 1665, 1601, 1488, 1455, 1379, 1277, 1232, 1162, 1138, 1087, 1020, 967, 929, 756, 692, 528 cm⁻¹.



	Ketention	Alea	70 Alea
	Time		
1	11.011	4526312	3.36
2	14.937	130116361	96.64

Ethyl (R,E)-4-(3-(2-methoxyphenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B31)



White solid, Mp: 36–39 °C, 78% yield, 92% *ee*; $[\alpha]^{14.2} = -19.5$ (*c* = 0.70 in CH₂Cl₂, $\lambda = 589$ nm).

SFC Chiralcel BYPASS, CO₂/MeOH = 90/10, 1.5 mL/min, λ = 224 nm, $t_{\text{R(minor)}}$ = 15.68 min, $t_{\text{R(major)}}$ = 17.46 min

¹**H NMR** (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.92 (dd, J = 8.0, 1.1 Hz, 1H), 7.78 (s, 1H), 7.74 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.48 (ddd, J = 8.2, 7.4, 1.1 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 7.15 – 7.10 (m, 2H), 6.87 (d, J = 8.1 Hz, 1H), 6.77 (td, J = 7.4, 1.1 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 5.87 – 5.79 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 3.28 (s, 2H), 3.24 – 3.10 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.6 , 157.5 , 157.3 , 145.8 , 135.1 , 134.0 , 133.9 , 132.2 , 129.8 , 129.5 , 129.3 , 129.0 , 128.4 , 127.5 , 127.4 , 127.3 , 126.7 , 125.4 , 124.1 , 121.4 , 112.0 , 86.3 , 84.7 , 61.7 , 55.8 , 46.8 , 44.6 , 32.7 , 14.6 .

HRMS (ESI) Calculated for $C_{32}H_{28}O_4$ ([M]+Na⁺) = 499.1880, Found 499.1877.

IR (neat) 2936, 2837, 1736, 1665, 1599, 1489, 1459, 1379, 1276, 1244, 1180, 1162, 1138, 1087, 1049, 1025, 972, 929, 693, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	15.677	1941932	3.74
2	17.456	50042543	96.26

Ethyl (R,E)-4-(3-(naphthalen-1-yl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B32)



Colorless oil, 94% yield, 95% *ee*; $[\alpha]^{14.1} = -32.0$ (*c* = 0.82 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 20.31 min, $t_{R(major)}$ = 42.88 min.

¹**H NMR** 1H NMR (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 8.01 (dd, J = 8.0, 1.1 Hz, 1H), 7.88 (s, 1H), 7.85 – 7.72 (m, 4H), 7.52 – 7.43 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.21 (dq, J = 4.5, 2.6 Hz, 2H), 7.12 (d, J = 15.5 Hz, 1H), 5.79 (dt, J = 15.3, 7.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.39 – 3.24 (m, 4H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.3 , 165.6 , 157.3 , 145.7 , 135.9 , 135.3 , 134.5 , 134.1 , 134.0 , 132.8 , 132.3 , 131.9 , 129.3 , 129.2 , 129.0 , 128.6 , 128.4 , 128.4 , 127.6 , 127.4 , 126.9 , 126.7 , 126.5 , 124.8 , 124.6 , 124.1 , 86.2 , 84.8 , 61.7 , 55.1 , 46.9 , 44.3 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{35}H_{28}O_3$ ([M]+Na⁺) = 519.1931, Found 519.1933.

IR (neat) 3060, 2982, 1735, 1664, 1601, 1490, 1454, 1379, 1277, 1232, 1162, 1138, 1087, 968, 928, 862, 759, 692, 528 cm⁻¹.



	Retention	Area	70 Area
	Time		
1	20.307	2789580	2.74
2	42.877	99126450	97.26

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(thiophen-2-yl)allyl)-1,4-dihydronaphthalene-2-carboxylate (B33)



Colorless oil, 45% yield, 43% *ee*; $[\alpha]^{13.9} = -13.6$ (*c* = 0.39 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 14.25 min, $t_{R(major)}$ = 18.18 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.11 (dd, J = 7.9, 1.6 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.76 – 7.72 (m, 2H), 7.51 – 7.47 (m, 1H), 7.28 – 7.24 (m, 3H), 7.21 – 7.15 (m, 3H), 6.88 (dd, J = 5.1, 3.5 Hz, 1H), 6.84 – 6.81 (m, 1H), 6.56 (d, J = 15.5 Hz, 1H), 5.62 (dt, J = 15.3, 7.5 Hz, 1H), 4.27 (d, J = 7.1 Hz, 2H), 3.26 (s, 2H), 3.21 (td, J = 7.5, 7.0, 1.3 Hz, 1H), 3.14 – 3.07 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.2 , 165.6 , 157.0 , 145.5 , 142.7 , 134.1 , 133.9 , 132.2 , 129.3 , 129.0 , 128.5 , 128.3 , 128.1 , 127.4 , 127.4 , 126.4 , 125.1 , 124.4 , 124.1 , 86.2 , 84.7 , 61.7 , 46.7 , 43.9 , 32.8 , 14.6 .

HRMS (ESI) Calculated for $C_{29}H_{24}O_3S$ ([M]+Na⁺) = 475.1338, Found 475.1338.

IR (neat) 2984, 1735, 1665, 1601, 1490, 1454, 1380, 1277, 1232, 1161, 1138, 1087, 1019, 957, 929, 854, 759, 693, 528 cm⁻¹.



Retention	Area	% Area
Time		
14.246	10156754	28.42
18.177	25585604	71.58
	Time 14.246 18.177	Retention Area Time 10156754 18.177 25585604

Ethyl (R,E)-4-(4-ethoxy-4-oxobut-2-en-1-yl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B34)



Colorless oil, 51% yield, 85% *ee*; $[\alpha]^{14.1} = -57.9$ (*c* = 0.43 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 122.40 min, $t_{R(major)}$ = 140.72min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.14 (dd, J = 7.9, 1.2 Hz, 1H), 7.91 (dt, J = 8.0, 0.9 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.73 (s, 1H), 7.52 (ddd, J = 7.9, 7.1, 1.0 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 6.44 (dt, J = 15.4, 7.6 Hz, 1H), 5.84 (dt, J = 15.5, 1.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.01 (qd, J = 7.1, 0.7 Hz, 2H), 3.36 (ddd, J = 14.4, 7.7, 1.4 Hz, 1H), 3.26 (s, 2H), 3.22 – 3.17 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.0, 165.9, 165.5, 156.2, 144.9, 143.2, 135.6, 134.2, 133.8, 132.2, 129.3, 129.0, 128.7, 127.5, 127.4, 125.8, 124.0, 85.8, 85.0, 61.8, 60.7, 46.1, 42.5, 33.5, 14.6, 14.5.

HRMS (ESI) Calculated for $C_{28}H_{26}O_5$ ([M]+Na⁺) = 465.1672, Found 465.1671.

IR (neat) 2983, 1716, 1661, 1601, 1490, 1453, 1379, 1275, 1232, 1207, 1168, 1139, 1114, 1088, 1026, 982, 928, 861, 758, 693, 529 cm⁻¹.



5814645

7.43

146.593

Ethyl (R,E)-4-(but-2-en-1-yl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B35)



White solid, Mp: 101–104 °C, 70% yield, 99% *ee*; $[\alpha]^{14.2} = -65.3$ (*c* = 0.41 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 15.51$ min, $t_{R(major)} = 16.84$ min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.83 (dd, J = 8.0, 1.1 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (s, 1H), 7.48 (ddd, J = 8.1, 7.2, 1.2 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.18 – 7.14 (m, 2H), 5.48 – 5.39 (m, 1H), 5.02 (ddd, J = 15.1, 7.5, 1.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.18 (s, 2H), 3.01 – 2.84 (m, 2H), 1.45 – 1.42 (m, 3H), 1.31 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.4 , 165.7 , 157.4 , 145.8 , 135.1 , 134.0 , 133.9 , 132.2 , 130.5 , 129.3 , 129.0 , 128.3 , 127.4 , 127.2 , 125.82 , 124.1 , 86.3 , 84.6 , 61.7 , 46.6 , 43.9 , 32.7 , 18.1 , 14.6 .

HRMS (ESI) Calculated for $C_{26}H_{24}O_3$ ([M]+Na⁺) = 407.1618, Found 407.1615.

IR (neat) 2980, 1736, 1664, 1601, 1490, 1452, 1379, 1276, 1231, 1186, 1162, 1139, 1085, 1019, 967, 928, 861, 692, 638, 529 cm⁻¹.



	Time		
1	15.506	10563	0.24
2	16.840	4326482	99.76

Ethyl (R,E)-4-(hex-2-en-1-yl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B36)



Colorless oil, 35% yield, 99% *ee*; $[\alpha]^{14.1} = -66.2$ (*c* = 0.27 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 13.57 min, $t_{R(major)}$ = 15.24 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.84 (dd, J = 8.1, 1.2 Hz, 1H), 7.72 (td, J = 8.5, 7.9, 1.5 Hz, 1H), 7.66 (s, 1H), 7.48 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.19 – 7.12 (m, 2H), 5.44 – 5.36 (m, 1H), 4.97 (dddd, J = 15.0, 7.4, 5.9, 1.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.19 (s, 2H), 3.02 – 2.85 (m, 2H), 1.78 – 1.72 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.14 (q, J = 7.3 Hz, 2H), 0.67 (t, J = 7.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.4 , 165.6 , 157.5 , 145.8 , 136.1 , 135.1 , 134.0 , 133.9 , 132.2 , 129.3 , 129.0 , 128.3 , 127.4 , 127.2 , 124.9 , 124.1 , 86.3 , 84.6 , 61.6 , 46.7 , 43.9 , 35.2 , 32.7 , 23.1 , 14.6 , 13.7 .

HRMS (ESI) Calculated for $C_{28}H_{28}O_3$ ([M]+Na⁺) = 435.1931, Found 435.1928.

IR (neat) 2959, 2928, 2870, 1737, 1666, 1601, 1490, 1454, 1379, 1275, 1231, 1162, 1139, 1086, 1020, 969, 928, 759, 692, 640, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	13.570	212990	0.52
2	15.240	40871541	99.48

Ethyl (R,E)-4-(3-cyclohexylallyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B37)



Colorless oil, 55% yield, 95% *ee*; $[\alpha]^{14.2} = -42.4$ (*c* = 0.47 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 12.44 min, $t_{R(major)}$ = 15.15 min.

¹**H** NMR 1H NMR (400 MHz, Acetone-d6) δ 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.84 (dd, J = 8.1, 1.1 Hz, 1H), 7.72 (td, J = 7.7, 1.5 Hz, 1H), 7.64 (s, 1H), 7.48 (ddd, J = 8.1, 7.2, 1.1 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 – 7.14 (m, 2H), 5.31 (dd, J = 15.3, 7.1 Hz, 1H), 4.95 – 4.87 (m, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.21 (s, 2H), 2.97 – 2.81 (m, 2H), 1.68 (dp, J = 11.1, 3.6 Hz, 1H), 1.58 – 1.38 (m, 5H), 1.31 (t, J = 7.1 Hz, 3H), 1.16 – 1.02 (m, 3H), 0.84 (tq, J = 12.2, 3.8 Hz, 2H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 181.4 , 165.7 , 157.4 , 145.9 , 142.3 , 135.1 , 134.0 , 133.9 , 132.2 , 129.3 , 129.0 , 128.2 , 127.4 , 127.2 , 124.1 , 122.0 , 86.4 , 84.5 , 61.6 , 46.8 , 44.0 , 41.4 , 33.6 , 33.6 , 32.4 , 26.8 , 26.5 , 14.7 .

HRMS (ESI) Calculated for $C_{31}H_{32}O_3$ ([M]+Na⁺) = 475.2244, Found 475.2243.

IR (neat) 2923, 2850, 1737, 1667, 1601, 1490, 1448, 1379, 1276, 1231, 1138, 1087, 1021, 970, 928, 759, 692, 528 cm⁻¹.



	Retention	Area	% Area
	Time		
1	12.435	775597	2.31
2	15.149	32799082	97.69

Ethyl (R)-4-((E)-3-(4-bromophenyl)allyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B38)



White solid, Mp: 37–40 °C, 62% yield, 90% *ee*; $[\alpha]^{23.0} = -9.0$ (*c* = 0.65 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 34.84 min, $t_{R(major)}$ = 39.85 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.06 (dd, J = 7.9, 1.5 Hz, 1H), 7.90 (dd, J = 8.1, 1.1 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.48 – 7.43 (m,

1H), 7.40 – 7.35 (m, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.09 (m, 5H), 6.35 (dd, *J* = 15.8, 7.8 Hz, 2H), 5.89 – 5.77 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.15 (ddt, *J* = 13.9, 7.4, 1.6 Hz, 2H), 3.04 (ddd, *J* = 13.9, 7.6, 1.3 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.1, 165.6, 158.6, 146.1, 138.0, 137.3, 134.9, 134.8, 134.0, 133.7, 133.6, 132.4, 129.4, 128.8, 128.2, 128.2, 127.7, 127.4, 127.0, 126.2, 124.9, 121.5, 61.6, 47.5, 45.3, 45.2, 14.6.

HRMS (ESI) Calculated for $C_{31}H_{27}^{79}BrO_3$ ([M]+Na⁺) = 549.1036, Found 549.1044.

HRMS (ESI) Calculated for $C_{31}H_{27}^{81}BrO_3$ ([M]+Na⁺) = 551.1015, Found 551.1019.

IR (neat) 3027, 2982, 2361, 1734, 1660, 1600, 1486, 1450, 1379, 1269, 1229, 1161, 1137, 1073, 1011, 966, 929, 805, 739, 695, 626, 515 cm⁻¹.



	Retention	Area	% Area
	Time		
1	34.843	1232104	5.01
2	39.846	23348137	94.99

Ethyl (S)-4-((E)-3-(4-bromophenyl)allyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B38)



White solid, Mp: 37–40 °C, 55% yield, 93% *ee*; $[\alpha]^{23.9} = 9.5$ (*c* = 0.58 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 39.96 min, $t_{R(major)}$ = 34.67 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.06 (dd, J = 7.9, 1.4 Hz, 1H), 7.90 (dd, J = 8.0, 1.1 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.48 – 7.43 (m,

1H), 7.40 – 7.35 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 – 7.09 (m, 5H), 6.35 (dd, *J* = 15.8, 7.5 Hz, 2H), 5.89 – 5.77 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.15 (ddt, *J* = 13.9, 7.4, 1.6 Hz, 2H), 3.04 (ddd, *J* = 13.8, 7.6, 1.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.1, 165.6, 158.6, 146.1, 138.0, 137.3, 134.9, 134.8, 134.0, 133.8, 133.6, 132.4, 129.4, 128.8, 128.2, 128.2, 127.7, 127.4, 127.0, 126.2, 124.9, 121.5, 61.6, 47.5, 45.3, 45.2, 14.6.

HRMS (ESI) Calculated for $C_{31}H_{27}^{79}BrO_3$ ([M]+Na⁺) = 549.1036, Found 549.1046.

HRMS (ESI) Calculated for $C_{31}H_{27}^{81}BrO_3$ ([M]+Na⁺) = 551.1015, Found 551.1020.

IR (neat) 3027, 2982, 2361, 1734, 1660, 1600, 1486, 1450, 1379, 1269, 1229, 1161, 1137, 1073, 1011, 966, 929, 805, 739, 695, 626, 515 cm⁻¹.



	Time		
1	34.670	49735969	96.45
2	39.963	1830803	3.55

Ethyl (R)-4-cinnamyl-4-((E)-3-(naphthalen-1-yl)allyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B39)



White solid, Mp: 52–55 °C, 76% yield, 97% *ee*; $[\alpha]^{24.5} = 15.2$ (*c* = 0.66 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 25.80 min, $t_{R(major)}$ = 20.23 min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.06 (dd, J = 7.8, 1.5 Hz, 1H), 7.98 (dd, J = 8.0, 1.1 Hz, 1H), 7.85 (s, 1H), 7.84 – 7.76 (m, 3H), 7.73 (d, J =

8.1 Hz, 1H), 7.49 - 7.42 (m, 3H), 7.35 - 7.30 (m, 1H), 7.26 - 7.14 (m, 6H), 7.07 (d, J = 15.5 Hz, 1H), 6.40 (d, J = 15.7 Hz, 1H), 5.90 - 5.82 (m, 1H), 5.74 (dt, J = 15.3, 7.6 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.29 (ddd, J = 13.6, 7.6, 1.3 Hz, 1H), 3.22 - 3.14 (m, 2H), 3.08 (ddd, J = 13.9, 7.6, 1.3 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.2 , 165.6 , 158.9 , 146.3 , 138.1 , 136.0 , 134.8 , 134.6 , 134.0 , 133.9 , 132.6 , 132.0 , 129.4 , 129.3 , 128.6 , 128.5 , 128.3 , 128.2 , 127.8 , 127.5 , 127.0 , 126.9 , 126.7 , 126.5 , 125.0 , 124.8 , 124.6 , 61.6 , 47.8 , 45.5 , 45.4 , 14.6 .

HRMS (ESI) Calculated for $C_{35}H_{30}O_3$ ([M]+Na⁺) = 521.2087, Found 521.2093.

IR (neat) 3029, 2983, 2361, 1734, 1661, 1600, 1450, 1380, 1268, 1230, 1162, 1138, 1087, 1019, 966, 928, 863, 775, 695, 618, 553, 515 cm⁻¹.



	Retention	Area	% Area
	Time		
1	20.230	46162220	98.44
2	25.799	733541	1.56

Ethyl (S)-4-cinnamyl-4-((E)-3-(naphthalen-1-yl)allyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B39)



White solid, Mp: 52–55 °C, 67% yield, 96% *ee*; $[\alpha]^{24.7} = -14.6$ (*c* = 0.47 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 224 \text{ nm}, t_{R(\text{minor})} = 20.95 \text{ min}, t_{R(\text{major})} = 24.64 \text{ min}.$

¹**H NMR** (400 MHz, Acetone- d_6) δ 8.06 (dd, J = 7.9, 1.5 Hz, 1H), 7.98 (dd, J = 8.0, 1.1 Hz, 1H), 7.85 (s, 1H), 7.84 – 7.77 (m, 3H), 7.73 (d, J =

8.1 Hz, 1H), 7.49 - 7.43 (m, 3H), 7.35 - 7.30 (m, 1H), 7.26 - 7.14 (m, 6H), 7.06 (d, J = 15.5 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 5.90 - 5.82 (m, 1H), 5.74 (dt, J = 15.3, 7.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.28 (ddd, J = 13.7, 7.5, 1.3 Hz, 1H), 3.22 - 3.14 (m, 2H), 3.08 (ddd, J = 13.9, 7.6, 1.3 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.2 , 165.6 , 158.8 , 146.3 , 138.0 , 136.0 , 134.8 , 134.6 , 134.0 , 133.9 , 132.6 , 131.9 , 129.4 , 129.2 , 128.6 , 128.5 , 128.2 , 128.2 , 127.8 , 127.5 , 127.0 , 126.8 , 126.7 , 126.5 , 125.0 , 124.8 , 124.6 , 61.6 , 47.8 , 45.5 , 45.4 , 14.6 .

HRMS (ESI) Calculated for $C_{35}H_{30}O_3$ ([M]+Na⁺) = 521.2087, Found 521.2088.

IR (neat) 3029, 2982, 2361, 1735, 1662, 1600, 1450, 1380, 1270, 1230, 1161, 1138, 1087, 1019, 966, 928, 863, 775, 695, 618, 552, 514 cm⁻¹.



	Retention	Area	% Area
	Time		
1	20.949	995406	1.92
2	24.639	50789067	98.08

Ethyl (S)-4-((E)-but-2-en-1-yl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B40)



White solid, Mp: 79–82 °C, 64% yield, 89% *ee*; $[\alpha]^{21.8} = 41.7$ (*c* = 0.50 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 16.07$ min, $t_{R(major)} = 17.17$ min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.07 (dd, J = 7.9, 1.5 Hz, 1H), 7.81 (dd, J = 8.0, 1.2 Hz, 1H), 7.72 (td, J = 7.6, 1.5 Hz, 1H), 7.64 (s, 1H), 7.45 (ddd, J = 1.0 M s = 3.0, 1.2 Hz, 1H), 7.72 (td, J = 7.6, 1.5 Hz, 1H), 7.64 (s, 1H), 7.45 (ddd, J = 1.0 M s = 3.0 M s = 3.

8.1, 7.1, 1.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 3H), 6.33 (d, J = 15.8 Hz, 1H), 5.77 (dd, J = 15.5, 7.8 Hz, 1H), 5.42 – 5.34 (m, 1H), 4.97 (dtq, J = 15.0, 7.4, 1.7 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.09 – 3.03 (m, 1H), 2.97 – 2.88 (m, 2H), 2.81 – 2.75 (m, 1H), 1.42 (d, J = 6.3 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.3 , 165.6 , 159.0 , 146.4 , 138.1 , 134.7 , 134.6 , 133.9 , 130.2 , 129.4 , 128.2 , 128.0 , 127.6 , 127.3 , 126.9 , 125.8 , 125.1 , 61.6 , 47.4 , 45.3 , 45.1 , 18.1 , 14.6 .

HRMS (ESI) Calculated for $C_{26}H_{26}O_3$ ([M]+Na⁺) = 409.1774, Found 409.1772.

IR (neat) 3027, 2980, 2361, 1736, 1663, 1601, 1450, 1380, 1273, 1230, 1138, 1087, 1020, 967, 929, 757, 695, 618 cm⁻¹.



1	A	A
I	U	U

6232654

94.47

17.174

Ethyl (R)-4-((E)-but-2-en-1-yl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B40)



White solid, Mp: 79–82 °C, 57% yield, 95% *ee*; $[\alpha]^{25.2} = -45.7$ (*c* = 0.30 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 224$ nm, $t_{R(minor)} = 17.22$ min, $t_{R(major)} = 15.96$ min.

¹**H** NMR (400 MHz, Acetone- d_6) δ 8.07 (dd, J = 7.9, 1.4 Hz, 1H), 7.82 (dd, J = 8.1, 1.1 Hz, 1H), 7.72 (td, J = 7.6, 1.5 Hz, 1H), 7.64 (s, 1H), 7.45 (ddd, J

= 8.2, 7.2, 1.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 3H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.76 (dd, *J* = 15.5, 7.8 Hz, 1H), 5.42 – 5.34 (m, 1H), 4.97 (dtq, *J* = 15.0, 7.4, 1.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.09 – 3.03 (m, 1H), 2.97 – 2.88 (m, 2H), 2.81 – 2.75 (m, 1H), 1.42 (d, *J* = 6.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 181.3 , 165.6 , 159.0 , 146.4 , 138.1 , 134.7 , 134.6 , 133.9 , 130.2 , 129.4 , 128.2 , 128.0 , 127.6 , 127.3 , 126.9 , 125.8 , 125.1 , 61.6 , 47.4 , 45.3 , 45.1 , 18.1 , 14.6 .

HRMS (ESI) Calculated for $C_{26}H_{26}O_3$ ([M]+Na⁺) = 409.1774, Found 409.1775.

IR (neat) 3027, 2980, 2361, 1736, 1662, 1601, 1450, 1380, 1272, 1230, 1138, 1087, 1020, 966, 929, 757, 695, 618 cm⁻¹.



(R)-2-acetyl-4-cinnamyl-4-(3-phenylprop-2-yn-1-yl)naphthalen-1(4H)-one (B45)



White solid, Mp: 101–104 °C, 84% yield, 17% *ee*; $[\alpha]^{13.0} = -2.2$ (*c* = 0.69 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 11.32 min, $t_{R(major)}$ = 17.31 min.

¹**H NMR** (400 MHz, Acetone-d6) δ 8.17 (dd, J = 7.9, 1.5 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.52 – 7.48 (m, 1H), 7.28 – 7.13 (m, 10H), 6.41 (dd, J = 15.8, 1.4 Hz, 1H), 5.87 – 5.80 (m, 1H), 3.28 (d, J = 5.5 Hz, 2H), 3.25 - 3.12 (m, 2H), 2.49 (s, 3H).

¹³C{¹H} NMR (101 MHz, Acetone-d6) δ 198.4 , 183.5 , 158.0 , 145.9 , 141.0 , 137.9 , 134.9 , 134.1 , 134.1 , 132.2 , 129.4 , 129.3 , 129.0 , 128.4 , 128.3 , 127.4 , 127.4 , 127.0 , 124.9 , 124.0 , 86.3 ,84.6 , 46.9 , 44.1 , 32.8 , 31.1.

HRMS (ESI) Calculated for $C_{30}H_{24}O_2$ ([M]+Na⁺) = 439.1669, Found 439.1667.

IR (neat) 3028, 1693, 1658, 1600, 1491, 1453, 1372, 1260, 1160, 1131, 1071, 966, 864, 758, 717, 692, 623, 528 cm⁻¹.



Ethyl (R)-4-cinnamyl-1-oxo-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)-1,4-dihydronaphthalene-2-carboxylate (B46)



White solid, Mp: 50–53 °C, 95% yield, 95% *ee*; $[\alpha]^{19.2} = 49.6$ (*c* = 1.04 in CH₂Cl₂, $\lambda = 589$ nm).

HPLC: Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 224 nm, $t_{R(minor)}$ = 34.18 min, $t_{R(major)}$ = 48.34 min.

¹**H NMR** (400 MHz, Acetone-*d*₆) δ 7.94 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.75 (d, *J* = 6.1 Hz, 2H), 7.70 (dt, *J* = 7.2, 2.2

Hz, 3H), 7.46 (d, J = 8.1 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.21 – 7.13 (m, 5H), 6.38 (d, J = 15.7 Hz, 1H), 5.83 (dd, J = 15.5, 7.7 Hz, 1H), 4.26 (t, J = 7.1 Hz, 2H), 3.74 (d, J = 14.6 Hz, 1H), 3.58 (d, J = 14.5 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.11 (ddd, J = 13.8, 7.6, 1.3 Hz, 1H), 2.46 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Acetone- d_6) δ 180.6, 165.4, 157.3, 148.3, 145.0, 144.1, 137.9, 135.1, 135.0, 134.1, 134.0, 133.4, 131.6, 129.4, 128.7, 128.3, 128.3, 127.9, 127.2, 127.0, 124.6, 123.5, 61.7, 47.4, 45.2, 37.2, 21.8, 14.6.

HRMS (ESI) Calculated for $C_{32}H_{29}N_3O_5S$ ([M]+Na⁺) = 590.1720, Found 590.1732.

2

48.335

IR (neat) 3028, 2950, 2827, 1741, 1670, 1600,1495, 1452, 1435, 1365, 1277, 1247, 1157, 1133, 1081, 970, 874, 754, 695, 610, 496 cm⁻¹.



17081735

97.55

16. Copies of NMR Spectra for the Reaction Products

Ethyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B1)



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)



Methyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B2)

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

Isopropyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B3)



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)



Phenyl (R)-4-cinnamyl-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B4)

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



Ethyl (R)-4-cinnamyl-1-oxo-4-(prop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B5)

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


Ethyl (R)-4-cinnamyl-4-(ethoxymethyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B6)





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



Ethyl (S)-4-cinnamyl-1-oxo-4-propyl-1,4-dihydronaphthalene-2-carboxylate (B9)

210 200 190 180 170 160 150 140 130 120 110 100 90 10 (f1 (ppm)



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)







Ethyl (R)-4-benzyl-4-cinnamyl-6-methyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B13)



Ethyl (R)-4-benzyl-6-(tert-butyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B14)

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)



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)



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)



f1 (ppm)













Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(4-(trifluoromethyl)phenyl)allyl)-1,4dihydronaphthalene-2-carboxylate (B21)



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





Ethyl (R,E)-4-(3-(4-fluorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene -2-carboxylate (B22)



Ethyl (R,E)-4-(3-(4-bromophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene -2-carboxylate (B23)



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)

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Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(p-tolyl)allyl)-1,4-dihydronaphthalene-2carboxylate (B25)



Ethyl (R,E)-4-(3-(4-methoxyphenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B26)



Ethyl (R,E)-4-(3-(3-chlorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4 -dihydronaphthalene-2-carboxylate (B27)



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

Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(m-tolyl)allyl)-1,4-dihydronaphthalene-2carboxylate (B28)



Ethyl (R,E)-4-(3-(2-chlorophenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B29)



Ethyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(o-tolyl)allyl)-1,4-dihydronaphthalene-2-carboxylate (B30)



Ethyl (R,E)-4-(3-(2-methoxyphenyl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B31)



Ethyl (R,E)-4-(3-(naphthalen-1-yl)allyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B32)



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

Ehyl (R,E)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-4-(3-(thiophen-2-yl)allyl)-1,4-dihydronaphthalene-2-carboxylate (B33)



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)

Ehyl (R,E)-4-(4-ethoxy-4-oxobut-2-en-1-yl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4dihydronaphthalene-2-carboxylate (B34)







Ehyl (R,E)-4-(hex-2-en-1-yl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B36)



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

Ehyl (R,E)-4-(3-cyclohexylallyl)-1-oxo-4-(3-phenylprop-2-yn-1-yl)-1,4-dihydronaphthalene-2-carboxylate (B37)



Ethyl (R)-4-((E)-3-(4-bromophenyl)allyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2carboxylate (B38)



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

Ethyl (S)-4-((E)-3-(4-bromophenyl)allyl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B38)



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)
Ethyl (R)-4-cinnamyl-4-((E)-3-(naphthalen-1-yl)allyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (B39)



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

Ethyl (S)-4-cinnamyl-4-((E)-3-(naphthalen-1-yl)allyl)-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B39)



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



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

Ethyl (R)-4-((E)-but-2-en-1-yl)-4-cinnamyl-1-oxo-1,4-dihydronaphthalene-2-carboxylate (*ent*-B40)



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

Ethyl (R)-4-cinnamyl-1-oxo-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)-1,4-dihydronaphthalene-2-Carboxylate



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)



f1 (ppm)

17. Copies of NMR Spectra for the Reaction Substrates Ethyl 1-(cinnamyloxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A1)

























Ethyl 4-chloro-1-(cinnamyloxy)-2-naphthoate (A8)















Ethyl 4-benzyl-1-(cinnamyloxy)-6-methyl-2-naphthoate (A13)



















Ethyl 4-benzyl-6-chloro-1-(cinnamyloxy)-2-naphthoate (A17)

Ethyl 4-benzyl-1-(cinnamyloxy)-6-cyano-2-naphthoate (A18)







f1 (ppm)





Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)-2-naphthoate (A21)





Ethyl (E)-1-((3-(4-fluorophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A22)



-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -14 f1 (ppm)



Ethyl (E)-1-((3-(4-bromophenyl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A23)


















Ethyl (E)-4-(3-phenylprop-2-yn-1-yl)-1-((3-(o-tolyl)allyl)oxy)-2-naphthoate (A31)



Ethyl (E)-1-((3-(naphthalen-1-yl)allyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A32)







Ethyl (E)-1-((4-ethoxy-4-oxobut-2-en-1-yl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A34)







Ethyl (E)-1-((3-cyclohexylallyl)oxy)-4-(3-phenylprop-2-yn-1-yl)-2-naphthoate (A37)



Ethyl 4-((E)-3-(4-bromophenyl)allyl)-1-(cinnamyloxy)-2-naphthoate (A38)



Ethyl 1-(((E)-3-(4-bromophenyl)allyl)oxy)-4-cinnamyl-2-naphthoate (ent-A38)



Ethyl 1-(cinnamyloxy)-4-((E)-3-(naphthalen-1-yl)allyl)-2-naphthoate (A39)







f1 (ppm)





1-chloro-4-(cinnamyloxy)naphthalene (A41)













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

18. Reference

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