Supplementary Information for

Cu(I)-catalysed chemo-, regio-, and stereoselective radical 1,2carboalkynylation with two different terminal alkynes

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1. Supplementary figure for experiments



Supplementary Fig. 1 | The X-ray structure of 1b (CCDC 2403993, 50% probability ellipsoids).



Supplementary Fig. 2 | The crude ¹H NMR spectrum of deprotonation experiments of S1 with S16. Sample preparation: An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (9.6 mg, 0.05 mmol, 1.0 equiv.), L*8 (36.7 mg, 0.05 mmol, 1.0 equiv.) and Cs₂CO₃ (81.5 mg, 0.25 mmol, 5.0 equiv.). Then CDCl₃ (2.0 mL) was added. The resulting mixture was pre-stirred at r.t. under argon for 4 hours. Then, S1 (14.8 mg, 0.05 mmol, 1.0 equiv.) and S16 (10.3 mg, 0.05 mmol, 1.0 equiv.) was added to the above Cu^I/L*8 complex mixture and stirred for 2 hours. The amount of residual alkyne was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.



Supplementary Fig. 3 | The crude ¹H NMR spectrum of deprotonation experiments of S1 with S16. Sample preparation: An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (9.6 mg, 0.05 mmol, 1.0 equiv.), L*8 (36.7 mg, 0.05 mmol, 1.0 equiv.) and Cs₂CO₃ (81.5 mg, 0.25 mmol, 5.0 equiv.). Then CDCl₃ (2.0 mL) was added. The resulting mixture was pre-stirred at r.t. under argon for 4 hours. Then, S1 (14.8 mg, 0.05 mmol, 1.0 equiv.) and S16 (10.3 mg, 0.05 mmol, 1.0 equiv.) was added to the above Cu^I/L*8 complex mixture and stirred for 4 hours. The amount of residual alkyne was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.



Supplementary Fig. 4 | Results of other 2-substituted aryl alkynes.



Supplementary Fig. 5 | Other unsuccessful example of radical precursors.



Supplementary Fig. 6 | The TEMPO adducts captured by HRMS.

2. Supplementary tables for experiments

Supplementary Table 1 | Reaction condition optimization: screening of different copper salt^a

H O O O S1	$Br \downarrow O'Bu + H = $	[Cu] (10 mol%) L*8 (12 mol%) Cs ₂ CO ₃ (5.0 equiv.) Et ₂ O, r.t., Ar, 5 d		+ O'Bu
(2.0 equiv.)	(2.0 equiv.) (0.05 mmol, 1.0	equiv.)	1	1'
Entry	[Cu]	Yield of 1 (%)	E.e. of 1 (%)	1'
1	CuTc	75	89	n.d.
2	CuI	39	88	n.d.
3	$CuBr \cdot SMe_2$	48	89	n.d.
4	CuCN	36	90	n.d.
5	Cu ₂ O	n.d.	_	n.d.
6	CuMes	10	89	n.d.
7	CuOAc	49	89	n.d.
8	Cu(OTf) ₂	46	89	n.d.
9	Cu(CH ₃ CN) ₄ PF ₆	57	89	n.d.

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), [Cu] (10 mol%), **L*8** (12 mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.

H O N [/] Pr ₂ + S1 (2.0 equiv.)	$Br + H = C_2$ C1 S16 (2.0 equiv.) (0.05 mmol, 1.0 eq	CuTc (10 mol%) L*8 (12 mol%) Cs ₂ CO ₃ (5.0 equiv.) solvent, r.t., Ar, 5 d	h o'Bu O'Bu O N'Pr2 +	
Entry	solvent	Yield of 1 (%)	E.e. of 1 (%)	1'
1	Et ₂ O	75	89	n.d.
2	THF	40	88	n.d.
3	1,4-dioxane	25	87	n.d.
4	MTBE	56	88	n.d.
5	^{<i>i</i>} Pr ₂ O	15	87	n.d.
6	DME	16	89	n.d.
7	EA	55	89	n.d.
8	DCM	12	87	n.d.
9	Toluene	46	87	n.d.
10	MeCN	13	86	n.d.

Supplementary Table 2 | Reaction condition optimization: screening of different solvent^a

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (10 mol%), L*8 (12 mol%) and Cs₂CO₃ (5.0 equiv.) in solvent (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.

H 0 0 0 0 0 0 0 0 0 0 0 0 0	Br O'Bu C1 (2.0 equiv.)	+ H	$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	+	+
Entry	Base	Equiv.	Yield of 1 (%)	E.e. of 1 (%)	1'
1	LiO ^t Bu	5	trace	_	n.d.
2	KOH	5	trace	_	n.d.
3	K_3PO_4	5	10	89	n.d.
4 ^b	K_2CO_3	5	13	89	n.d.
5	Rb_2CO_3	5	10	89	n.d.
6		3	60	89	n.d.
7	CarCOa	4	62	89	n.d.
8	CS2CO3	5	75	89	n.d.
9		6	75	89	n.d.

Supplementary Table 3 | Reaction condition optimization: screening of different base^a

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (10 mol%), **L*8** (12 mol%) and base (x equiv.) in Et₂O (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH_2Br_2 as an internal standard. E.e. values were based on chiral HPLC analysis. ^bBy-product **1''** was monitored in 16% yield.

$ \begin{array}{c} H \\ \downarrow \\ 0 \\ S1 \\ (x equiv.) \end{array} $	+ $Br = 0'Bu$ + $H = cz$ C1 S16 (y equiv.) (z equiv.)	CuTc (10 mol%) L*8 (12 mol%) Cs ₂ CO ₃ (5.0 equiv.) Et ₂ O, r.t., Ar, 5 d	Cz H O O'Bu O'Bu O'Bu O'Bu O'Bu O'Bu	0 N'Pr2 0 0'Bu 0 0'Bu 0'Bu
Entry	x:y:z	Yield of 1 (%)	E.e. of 1 (%)	1'
1	1:1:1	54	89	n.d.
2	2:2:1	75	89	n.d.
3	2:1:2	60	89	n.d.
4	1:2:2	57	89	n.d.
5	2:1:1	61	89	n.d.
6	1:2:1	50	89	n.d.
7	1:1:2	55	89	n.d.
8	1.5:1.5:1	56	89	n.d.
9	1:1.5:1.5	57	89	n.d.
10	1.5:1:1.5	63	89	n.d.
11	1.5:1:1	62	89	n.d.
12	1:1.5:1	52	89	n.d.
13	1:1:1.5	54	89	n.d.

Supplementary Table 4 | Reaction condition optimization: screening of substrate ratio^a

^aReaction conditions: **S1** (x equiv.), **C1** (y equiv.), **S16** (z equiv.), CuTc (10 mol%), **L*8** (12 mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.

H S1 (2.0 equiv.)	N ⁱ Pr ₂ + Br O'Bu + C1 (2.0 equiv.) (0	CuTe L^{*8} Cs ₂ CO, Cz Et ₂ O, S16 0.05 mmol, 1.0 equiv.)	c (x mol%) (y mol%) a (5.0 equiv.) r.t., Ar, 5 d 1	O'Bu N'Pr2 +	
Entry	CuTc (x mol %)	L*8 (y mol %)) Yield of 1 (%)	E.e. of 1 (%)	1'
1	5	6	43	89	n.d.
2	10	10	69	89	n.d.
3	10	12	75	89	n.d.
4	10	15	75	89	n.d.
5	15	20	76	89	n.d.
6	12	10	62	89	n.d.

Supplementary Table 5 | Reaction condition optimization: screening the ratio of CuTc and L*8 $^{\rm a}$

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (x mol%), L*8 (y mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.

(2.0 equiv.)	Br O'Bu + H	$\begin{array}{c} \text{CuTc (10 mol\%)}\\ \textbf{L*8 (12 mol\%)}\\ \hline \textbf{Cs}_2\text{CO}_3 (5.0 \text{ equiv.})\\ \hline \textbf{Et}_2\text{O}, \text{T/°C}, \text{Ar, 5 d}\\ \end{array}$	Cz H O'Bu O'Bu O N'Pr ₂ +	O N'Pr2 O O'BU O'BU O'BU O'BU
Entry	T (°C)	Yield of 1 (%)	E.e. of 1 (%)	1'
1	40	32	85	n.d.
2	r.t.	75	89	n.d.
3	10	72	93	n.d.
4	0	53	95	n.d.

Supplementary Table 6 | Reaction condition optimization: screening of reaction temperature^a

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (10 mol%), **L*8** (12 mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (1.0 mL) at T (°C) for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.

	+ Br O'Bu	+ HCz	CuTc (10 mol%) L*8 (12 mol%) Cs ₂ CO ₃ (5.0 equiv.) Et ₂ O, 10 °C, Ar	
(2.0 equiv.)	(2.0 equiv.)	(1.0 equiv.)		1
Entry	Time (d)	Et ₂ O (mL)	Yield of 1 (%)	E.e. of 1 (%)
1	5	4	70	93
2	3	4	55	93
3	1	4	32	93
4	3	2	60	93
5	3	1	64	93
6 ^b	3	4	76	93

Supplementary Table 7 | Reaction condition optimization for time^a

^aReaction conditions: **S1** (0.40 mmol), **C1** (0.40 mmol), **S16** (0.20 mmol), CuTc (10 mol%), **L*8** (12 mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (X mL) at 10 °C under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis. ^b20 mol% CuTc, 24 mol% **L*8**. The optimized reaction time of 5 d with CuTc (10 mol%) and **L*8** (12 mol%) was chosen as a balance between reaction efficiency and catalyst loading.

H H N O S15 (2.0 equiv.)	Bu + Br O'Bu O C1 (2.0 equiv.)	+ HCz S16 (0.05 mmol, 1.0 equiv.)	CuTc (10 mol%) L*(12 mol%) Cs ₂ CO ₃ (5.0 equiv.) Et ₂ O, r.t., Ar, 5 d	H O'Bu H O'Bu O'Bu 15
O NH NMe ₂ PAr ₂ L*8, Ar = 3,5-Ph ₂ C ₆ H ₃	H^{*}	OMe H, N N N H PPh ₂ L*5	OMe H, N NH PAr ₂ N O L*10, Ar = 3,5-Ph ₂ C ₆ H	$h = 2^{-i} PrC_6H_4$
Entry	L*	Yi	eld of 15 (%)	E.e. of 15 (%)
1	L*8	}	69	62
2	L*9)	n.d.	_
3	L*5	5	36	-7
4	L*1	0	79	26
5	L*1	1	70	-86

Supplementary Table 8 | Reaction condition optimization with S15, C1 and S16^a

^aReaction conditions: **S15** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (10 mol%), **L*** (12 mol%) and Cs₂CO₃ (5.0 equiv.) in Et₂O (1.0 mL) at r.t. for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. E.e. values were based on chiral HPLC analysis.



Supplementary Table 9 | Racemization experiments of 1^a

^aReaction conditions: **1** (16.1 mg, 0.025 mmol) in dry toluene (1.0 mL) at 70 °C under argon. E.e. values were based on chiral HPLC analysis.



Supplementary Table 10 | Racemization experiments of 34^a

^aReaction conditions: **34** (14.7 mg, 0.025 mmol) in dry toluene (1.0 mL) at 80 °C under argon. E.e. values were based on chiral HPLC analysis.

H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	+ Br O'Bu + H	CuTc (10 mol%) L*8 (12 mol%) Cs ₂ CO ₃ (5.0 equiv.) Et ₂ O, 10 °C, Ar, 5 d		
Entry	Variation	Yield of 1 (%)	E.e. of 1 (%)	1'
1	standard condition	72	93	n.d.
2	w/o L*	n.d.	_	n.d.
3	w/o Cu&L*	n.d.	_	n.d.
4	w/o Cs ₂ CO ₃	n.d.	_	n.d.

Supplementary Table 11 | Control experiment of S1^a

^aReaction conditions: **S1** (0.10 mmol), **C1** (0.10 mmol), **S16** (0.05 mmol), CuTc (10 mol%), **L*8** (12 mol%) and Cs_2CO_3 (5.0 equiv.) in Et₂O (1.0 mL) at 10 °C for 5 d under argon. Yield was based on ¹H NMR analysis of the crude product using CH_2Br_2 as an internal standard. E.e. values were based on chiral HPLC analysis.

3. General information

Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuTc was purchased from Adamas. Cs₂CO₃ was purchased from Bide Pharmatech Ltd., which was directly used without further treatment. Other reagents were purchased from J&K, Energy, etc. Anhydrous diethyl ether (Et₂O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was directly used without further treatment. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). As the eluent, the petroleum ether (PE), hexane, ethyl acetate (EtOAc), dichloromethane (CH₂Cl₂) and methanol were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic KMnO4 indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ¹H NMR and 100 or 151 MHz for ¹³C NMR, respectively, in CDCl₃ with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd = doublet of doublets; dt = doublet of triplet; ddd = doublet of doublet of doublets; t, triplet; g, quartet; m, multiplet), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm), multiplicity (d, doublet; q, quarter), coupling constant (Hz), integration. High-resolution mass spectroscopy (HRMS) was obtained on Thermo Scientific Q Exactive mass spectrometer using ESI ion source. Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector. Column conditions were reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu-Ka radiation.

4. The preparation of the substrates





S1-S15, **S28**, **S29**¹ were synthesized according to the literature. All the characterization data are consistent with those in the reported literature. **S16-S27** were purchased from commercial sources.

The synthesis of alkyne S30



To a solution of **S30-1** (1.0 equiv.) and 4-(*N*,*N*-dimethylamino)pyridine (4-DMAP, 2.0 equiv.) in CH₂Cl₂ (0.25 M), trifluoromethanesulfonic anhydride (1.2 equiv.) was slowly added at 0 °C under N₂ atmosphere. The mixture was then warmed to room temperature and stir for 4 h. The reaction was quenched by water, extracted with EtOAc. The combined organic layer was washed with 1.0 M HCl and brine, dried over anhydrous

Na₂SO₄, filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford compound **S30-2**.

To a solution of **S30-2** (1.0 equiv.) and ethylene glycol (3.0 equiv.) in anhydrous toluene (0.5 M) was added pyridinium *p*-toluenesulfonate (PPTS, 5 mol%). The mixture was refluxed for 10 h with a Dean-Stark apparatus. The reaction was removed to room temperature and quenched by saturated NaHCO₃, extracted with EtOAc. The combined organic layers was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford the compound **S30-3**.

A solution of $Pd(OAc)_2$ (10 mol%), dppp (10 mol%) in DMSO (0.25 M) was vigorously stirred at room temperature for 30 min under N₂ atmosphere. Then **S30-3** (1.0 equiv.), DIPEA (5.0 equiv.) and diphenylphosphine oxide (4.0 equiv.) were added sequentially before heating at 100 °C for 48 h. The reaction was removed to room temperature and quenched by water, extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude residue was purified by column chromatography to afford compound **S30-4**.

To a solution of **S30-4** (1.0 equiv.) in acetone (0.2 M) was added TsOH·H₂O (1.5 equiv.) in one portion, which was refluxed for 4 h. The reaction was removed to room temperature and quenched by water, extracted with EtOAc. The combined organic layers was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford compound **S30-5**.

To a solution of **S30-5** (178.0 mg, 0.5 mmol, 1.0 equiv.) and K_2CO_3 (207.3 mg, 1.5 mmol, 3.0 equiv.) in anhydrous MeOH (2.5 mL) was added dimethyl (1-diazo-2-oxopropyl)phosphonate (144.1 mg, 0.75 mmol, 1.5 equiv.). The mixture was stirred at room temperature for 12 h under argon. Upon completion of the reaction, the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product **S30**.

(1-Ethynylnaphthalen-2-yl)diphenylphosphine oxide (S30)



The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **S30** as a white solid (141.3 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.41 (m, 1H), 7.94 – 7.84 (m, 2H), 7.84 – 7.70 (m, 5H), 7.64 – 7.57 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.40 (m, 4H), 3.45 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 134.5, 134.2, 134.1 (d, *J* = 5.7 Hz), 133.1(4), 133.0(6), 132.4, 132.3, 132.1, 132.0 (d, J = 2.8 Hz), 128.8 (d, J = 11.6 Hz), 128.6, 128.5(4), 128.5(1), 128.4(4), 128.4(1), 128.0, 126.9, 124.7 (d, J = 6.4 Hz), 91.7, 79.6 (d, J = 7.1 Hz).

³¹P NMR (162 MHz, CDCl₃) δ 29.15.

HRMS (ESI) m/z calcd. for C₂₄H₁₇NaOP⁺ [M + Na]⁺ 375.0909, found 375.0907.

The synthesis of radical precursors



C1-C3, C6, C9-C13 were purchased from commercial sources.

C4-C5², C7³, C8⁴ were synthesized according to the literature. All the characterization data are consistent with those in the reported literature.

5. General procedure for the synthesis of axially chiral 1,3-enynes



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 2-substituted aryl alkynes (0.40 mmol, 2.0 equiv.), alkyne nucleophiles (0.20 mmol, 1.0 equiv.), CuTc (3.8 mg, 0.02 mmol, 10 mol%), L*8 (17.6 mg, 0.024 mmol, 12 mol%), and anhydrous Cs₂CO₃ (325.8 mg, 1.00 mmol, 5.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (4.0 mL) was added by syringe under argon atmosphere. Finally, radical precursor (0.40 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products (\pm) -1-33



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 2-substituted aryl alkynes (0.20 mmol, 2.0 equiv.), alkyne nucleophiles (0.10 mmol, 1.0 equiv.), CuTc (1.9 mg, 0.01 mmol, 10 mol%), **L-rac** (4.5 mg, 0.012 mmol, 12 mol%), and anhydrous Cs_2CO_3 (162.9 mg, 0.50 mmol, 5.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et_2O (2.0 mL) was added by syringe under argon atmosphere. Finally, radical precursor (0.20 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at r.t. for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (1)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **1** as a pale-yellow oil (96.4 mg, 75% yield, 93% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.96 – 7.90 (m, 1H), 7.84 – 7.75 (m, 2H), 7.51 – 7.41 (m, 2H), 7.41 – 7.35 (m, 4H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.50 (s, 1H), 5.10 – 4.91 (m, 2H), 3.95 – 3.73 (m, 2H), 1.38 (s, 9H), 1.18 (d, *J* = 6.7 Hz, 6H), 1.02 (s, 3H), 1.01 – 0.91 (m, 6H), 0.71 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.0, 146.2, 145.8, 140.0, 132.5, 131.0, 128.7,

128.1, 126.6, 125.9, 125.8, 125.5, 125.4, 123.1, 122.7, 120.3, 119.3, 115.8, 109.1, 85.8, 81.0, 80.8, 46.6(4), 46.5(6), 33.3, 28.0, 26.1, 22.9, 21.1, 21.0, 20.5.

HRMS (ESI) m/z calcd. for C₄₂H₄₇N₂O₄⁺ [M + H]⁺ 643.3530, found 643.3533.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 10.02 min, t_R (minor) = 18.61 min.

tert-Butyl (Z)-4,6-bis(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethylhex-3-en-5-ynoate (1')



¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.02 (m, 2H), 7.86 – 7.80 (m, 2H), 7.78 – 7.69 (m, 2H), 7.49 – 7.36 (m, 5H), 7.24 (d, *J* = 9.0 Hz, 1H), 6.79 (s, 1H), 4.23 – 3.74 (m, 4H), 1.46 (s, 9H), 1.32 – 1.13 (m, 27H), 0.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.4, 153.0, 150.5, 146.4, 145.3, 134.3, 132.8, 131.1, 130.9, 129.0, 128.6, 128.0, 127.9, 127.0, 126.6, 126.3, 126.2, 125.7, 125.5, 125.3, 122.7, 121.9, 117.2, 113.2, 100.9, 81.5, 80.8, 47.0, 46.7, 28.1, 26.3, 23.0, 21.5, 20.6. HRMS (ESI) *m/z* calcd. for C₄₆H₅₇N₂O₆⁺ [M + H]⁺ 733.4211, found 733.4208.

tert-Butyl (*E*)-4-bromo-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethylbut-3-enoate (1'')



¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.42 (m, 1H), 7.38 (d, J = 9.0 Hz, 1H), 6.75 (s, 1H), 4.44 – 3.83 (m, 2H), 1.48 – 1.37 (m, 15H), 1.34 (d, J = 6.7 Hz, 6H), 1.11 (s, 3H), 0.79 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.6, 152.7, 146.2, 140.6, 131.4, 131.0, 129.8, 128.2, 127.5, 127.1, 125.7, 125.5, 122.7, 114.3, 80.9, 47.7, 47.0, 46.8, 28.0, 25.8, 22.9, 21.5, 20.7, 20.6.

HRMS (ESI) m/z calcd. for C₂₇H₃₇BrNO₄⁺ [M + H]⁺ 518.1900, found 518.1903.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-6methylnaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (2)



According to the **general procedure** with **S2** (123.8 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **2** as a pale-yellow oil (85.4 mg, 65% yield, 93% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.05 (m, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.61 (s, 1H), 7.44 – 7.38 (m, 4H), 7.35 – 7.29 (m, 2H), 7.26-7.21 (m, 2H), 6.50 (s, 1H), 5.11 – 4.94 (m, 2H), 3.98 – 3.74 (m, 2H), 2.52 (s, 3H), 1.41 (s, 9H), 1.21 (d, *J* = 6.8 Hz, 6H), 1.04 (s, 3H), 1.03 – 0.91 (m, 6H), 0.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.1, 145.7, 145.5, 140.1, 135.0, 131.3, 130.6, 128.9, 128.0, 127.2, 125.8(1), 125.7(8), 125.4, 123.1, 122.7, 120.3, 119.3, 115.9, 109.1, 85.9, 80.9, 80.7, 46.7, 46.5, 33.4, 28.0, 26.0, 22.9, 21.7, 21.1, 21.0, 20.6.

HRMS (ESI) m/z calcd. for C₄₃H₄₉N₂O₄⁺ [M + H]⁺ 657.3687, found 657.3685.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 11.47 min, t_R (minor) = 26.22 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-6-phenylnaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (3)



According to the **general procedure** with **S3** (148.6 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **3** as a pale-yellow oil (60.4 mg, 42% yield, 90% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.06 (m, 2H), 8.05 (d, J = 1.8 Hz, 1H), 8.01 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.77 – 7.71 (m, 3H), 7.55 – 7.47 (m, 2H), 7.44 – 7.36 (m, 6H), 7.26 – 7.21 (m, 2H), 6.54 (s, 1H), 5.13 – 4.98 (m, 2H), 4.04 – 3.70 (m, 2H), 1.41 (s, 9H), 1.21 (d, J = 6.8 Hz, 6H), 1.06 (s, 3H), 1.05 – 0.95 (m, 6H), 0.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.0, 146.3, 145.9, 141.0, 140.1, 138.1, 131.7, 131.3, 129.0, 127.5, 126.5, 126.3, 126.0, 125.8, 125.5, 123.1(8), 123.1(6), 120.3, 119.3, 115.8, 109.1, 85.8, 81.1, 80.8, 46.7, 46.6, 33.4, 28.0, 26.1, 23.0, 21.1, 21.0, 20.6. HRMS (ESI) *m/z* calcd. for C₄₈H₅₁N₂O₄⁺ [M + H]⁺ 719.3843, found 719.3843. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254

nm, $t_{\rm R}$ (major) = 13.67 min, $t_{\rm R}$ (minor) = 37.77 min.

tert-Butyl (*Ra,Z*)-4-(6-bromo-2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-7-(9*H*-carbazol-9-yl)-2,2-dimethylhept-3-en-5-ynoate (4)



According to the **general procedure** with S4 (149.7 mg, 0.40 mmol, 2.0 equiv.), C1 (74.6 μ L, 0.40 mmol, 2.0 equiv.) and S16 (41.1 mg, 0.20 mmol, 1.0 equiv.) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product 4 as a pale-yellow oil (57.7 mg, 40% yield, 90% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 2.0 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.52 (dd, J = 8.9, 2.0 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.26 – 7.21 (m, 2H), 6.50 (s, 1H), 5.09 – 4.98 (m, 2H), 3.97 – 3.74 (m, 2H), 1.39 (s, 9H), 1.20 (d, J = 6.7 Hz, 6H), 1.06 – 0.94 (m, 9H), 0.70 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 152.8, 146.5, 146.2, 140.1, 132.2, 131.0, 130.1, 130.0, 127.8(1), 127.7(7), 125.9, 125.8, 124.0, 123.2, 120.4, 119.5, 119.4, 115.3, 109.0, 85.6, 81.5, 80.9, 46.7, 33.4, 28.0, 26.1, 23.0, 21.1, 21.0, 20.6.

HRMS (ESI) m/z calcd. for C₄₂H₄₆BrN₂O₄⁺ [M + H]⁺ 721.2635, found 721.2636.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 7.69 min, $t_{\rm R}$ (minor) = 20.87 min.

Methyl (*Ra*,*Z*)-5-(7-(*tert*-butoxy)-1-(9*H*-carbazol-9-yl)-6,6-dimethyl-7-oxohept-4en-2-yn-4-yl)-6-((diisopropylcarbamoyl)oxy)-2-naphthoate (5)



According to the **general procedure** with **S5** (141.4 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **5** as a pale-yellow oil (84.1 mg, 60% yield, 94% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, J = 1.8 Hz, 1H), 8.10 – 8.03 (m, 3H), 7.97 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.25 – 7.20 (m, 2H), 6.52 (s, 1H), 5.11 – 4.98 (m, 2H), 4.00 (s, 3H), 3.95 – 3.74 (m, 2H), 1.39 (s, 9H), 1.20 (d, J = 6.7 Hz, 6H), 1.04 – 0.93 (m, 9H), 0.69 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 167.2, 152.6, 148.0, 146.1, 139.9, 134.7, 131.1, 130.0, 126.9, 126.1, 126.0, 125.7(3), 125.7(0), 123.5, 123.1, 120.2, 119.3, 115.2, 108.9, 85.4, 81.3, 80.8, 52.3, 46.6, 46.5, 33.2, 27.9, 25.9, 22.9, 21.0, 20.9, 20.4.

HRMS (ESI) m/z calcd. for C₄₄H₄₉N₂O₆⁺ [M + H]⁺ 701.3585, found 701.3587.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 9.82 min, $t_{\rm R}$ (minor) = 22.93 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-7-phenylnaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (6)



According to the **general procedure** with **S6** (148.6 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **6** as a pale-yellow oil (14.4 mg, 10% yield, 88% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.04 (m, 3H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.47 – 7.32 (m, 8H), 7.24 – 7.16 (m, 2H), 6.56 (s, 1H), 5.13 – 4.96 (m, 2H), 3.97 – 3.77 (m, 2H), 1.24 (s, 9H), 1.21 (d, *J* = 5.7 Hz, 6H), 1.06 – 0.94 (m, 9H), 0.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.0, 146.6, 146.1, 141.4, 140.1, 139.5, 132.8, 130.3, 128.9, 128.6, 128.5, 127.8, 127.5, 125.9, 125.8, 125.2, 123.9, 123.2, 122.7, 120.3, 119.3, 115.9, 109.1, 85.8, 81.2, 80.8, 46.7, 46.6, 33.4, 27.8, 26.1, 23.2, 21.1, 21.0, 20.6. HRMS (ESI) *m/z* calcd. For C₄₈H₅₁N₂O₄⁺ [M + H]⁺ 719.3843, found 719.3844.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 12.00 min, t_R (minor) = 24.56 min.

Methyl (*Ra*,*Z*)-5-(7-(*tert*-butoxy)-1-(9*H*-carbazol-9-yl)-6,6-dimethyl-7-oxohept-4en-2-yn-4-yl)-6-((diisopropylcarbamoyl)oxy)-1-naphthoate (7)



According to the **general procedure** with **S7** (141.4 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **7** as a pale-yellow oil (86.9 mg, 62% yield, 92% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.99 – 8.86 (m, 1H), 8.23 – 8.02 (m, 4H), 7.58 – 7.33 (m, 6H), 7.31 – 7.17 (m, 2H), 6.57 – 6.47 (m, 1H), 5.03 (s, 2H), 4.10 – 3.97 (m, 3H), 3.96 – 3.73 (m, 2H), 1.47 – 1.34 (m, 9H), 1.28 – 1.13 (m, 6H), 1.11 – 0.92 (m, 9H), 0.67 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 168.1, 152.8, 146.5, 146.1, 140.0, 133.1, 131.1, 129.6, 129.0, 127.5, 126.8, 125.9, 125.8, 125.4, 124.4, 123.2, 120.3, 119.4, 115.7, 109.0, 85.6, 81.6, 80.9, 52.4, 46.7, 46.6, 33.3, 28.0, 26.1, 22.9, 21.2, 21.1, 20.6.

HRMS (ESI) m/z calcd. For C₄₄H₄₉N₂O₆⁺ [M + H]⁺ 701.3585, found 701.3587. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, $\lambda = 254$

nm, $t_{\rm R}$ (major) = 8.30 min, $t_{\rm R}$ (minor) = 12.73 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-4phenylnaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (8)



According to the **general procedure** with **S8** (148.6 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **8** as a pale-yellow oil (93.5 mg, 65% yield, 91% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.04 (m, 2H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.51 – 7.45 (m, 3H), 7.44 – 7.37 (m, 6H), 7.31 (s, 1H), 7.24 – 7.20 (m, 2H), 6.53 (s, 1H), 5.12 – 4.98 (m, 2H), 3.97 – 3.75 (m, 2H), 1.39 (s, 9H), 1.21 – 1.15 (m, 6H), 1.07 (s, 3H), 1.05 – 0.94 (m, 6H), 0.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.0, 146.1, 145.6, 141.2, 140.1, 140.0, 132.9, 130.4, 129.5, 128.3, 127.6, 126.6, 126.4, 126.3, 125.8, 125.4, 124.9, 123.6, 123.2, 120.3, 119.3, 115.9, 109.1, 85.9, 81.0, 80.8, 46.7, 46.6, 46.5, 33.5, 28.0, 26.2, 23.1, 21.2, 21.1, 20.6.

HRMS (ESI) m/z calcd. For C₄₈H₅₁N₂O₄⁺ [M + H]⁺ 719.3843, found 719.3843. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.6 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 12.56 min, $t_{\rm R}$ (minor) = 15.05 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-4methylnaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (9)



According to the **general procedure** with **S9** (123.8 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **9** as a pale-yellow oil (92.0 mg, 70% yield, 91% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.05 (m, 2H), 8.01 – 7.94 (m, 2H), 7.53 – 7.48 (m, 2H), 7.43 – 7.38 (m, 4H), 7.25 – 7.20 (m, 3H), 6.51 (s, 1H), 5.10 – 4.95 (m, 2H), 3.99 – 3.76 (m, 2H), 2.71 (s, 3H), 1.40 (s, 9H), 1.21 (d, *J* = 6.7 Hz, 6H), 1.04 (s, 3H), 1.03 – 0.95 (m, 6H), 0.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.1, 145.8, 145.7, 140.1, 135.6, 132.6, 130.5, 126.6, 126.4, 125.8, 125.2, 124.4, 123.8, 123.2, 123.1, 120.3, 119.3, 116.0, 109.1, 86.0, 80.8, 80.7, 46.7, 46.6, 46.5, 33.4, 28.0, 26.1, 22.9, 21.1, 21.0, 20.6, 19.7.

HRMS (ESI) m/z calcd. For C₄₃H₄₉N₂O₄⁺ [M + H]⁺ 657.3687, found 657.3690.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.6 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 15.22 min, $t_{\rm R}$ (minor) = 29.00 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-5,6,7,8-tetrahydronaphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (10)



According to the **general procedure** with **S10** (119.8 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **10** as a pale-yellow oil (107.5 mg, 83% yield, 94% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.7 Hz, 2H), 7.49 – 7.37 (m, 4H), 7.27 – 7.20 (m, 2H), 7.02 (d, J = 8.3 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.17 (s, 1H), 5.07 (s, 2H), 3.93 – 3.78 (m, 2H), 2.80 – 2.71 (m, 2H), 2.71 – 2.56 (m, 2H), 1.80 – 1.65 (m, 4H), 1.38 (s, 9H), 1.24 – 1.11 (m, 6H), 1.07 (s, 3H), 1.05 – 0.94 (m, 6H), 0.83 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.2, 146.3, 143.7, 140.1, 136.3, 133.8, 129.2(3), 129.1(7), 125.8, 123.2, 120.3, 120.1, 119.3, 117.0, 109.1, 85.5, 80.8, 80.4, 46.7, 46.4, 33.5, 29.5, 28.0, 27.1, 26.6, 22.9(9), 22.9(6), 22.5, 21.1, 20.6. HRMS (ESI) *m/z* calcd. For C₄₂H₅₁N₂O₄⁺ [M + H]⁺ 647.3843, found 647.3847. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.6 mL/min, $\lambda = 254$

nm, t_R (major) = 14.53 min, t_R (minor) = 25.95 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-6methylphenyl)-2,2-dimethylhept-3-en-5-ynoate (11)



According to the **general procedure** with **S11** (103.7 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **11** as a pale-yellow oil (97.1 mg, 80% yield, 95% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.8 Hz, 2H), 7.46 – 7.39 (m, 4H), 7.27 – 7.16 (m, 3H), 6.99 (dd, J = 7.9, 2.9 Hz, 2H), 6.22 (s, 1H), 5.07 (s, 2H), 3.92 – 3.76 (m, 2H), 2.26 (s, 3H), 1.39 (s, 9H), 1.19 (d, J = 5.1 Hz, 6H), 1.07 (s, 3H), 1.04 – 0.92(m, 6H), 0.84 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 152.9, 148.7, 144.0, 140.1, 137.7, 129.9, 128.1, 126.2, 125.8, 123.2, 120.5, 120.3, 119.3, 117.1, 109.1, 85.4, 80.8, 80.7, 46.6, 46.5(2), 46.4(6), 33.4, 28.0, 26.5, 22.6, 21.1, 21.0, 20.6, 19.8.

HRMS (ESI) m/z calcd. For C₃₉H₄₇N₂O₄⁺ [M + H]⁺ 607.3530, found 607.3534.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 9.54 min, $t_{\rm R}$ (minor) = 12.85 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)-4,6dimethylphenyl)-2,2-dimethylhept-3-en-5-ynoate (12)



According to the general procedure with S12 (109.4 mg, 0.40 mmol, 2.0 equiv.), C1

(74.6 µL, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **12** as a pale-yellow oil (108.0 mg, 87% yield, 91% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.03 (m, 2H), 7.47 – 7.38 (m, 4H), 7.25 – 7.20 (m, 2H), 6.82 (d, *J* = 2.4 Hz, 2H), 6.20 (s, 1H), 5.06 (s, 2H), 3.93 – 3.74 (m, 2H), 2.31 (s, 3H), 2.22 (s, 3H), 1.38 (s, 9H), 1.18 (d, *J* = 6.7 Hz, 6H), 1.07 (s, 3H), 1.04 – 0.92

(m, 6H) 0.85 (s, 3H). 1.38 (s, 9H), 1.18 (d, 3)

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.0, 148.5, 144.1, 140.1, 138.2, 137.2, 127.3, 126.9, 125.8, 123.2, 121.0, 120.3, 119.3, 117.2, 109.1, 85.6, 80.8, 80.5, 46.6, 46.4, 33.4, 28.0, 26.5, 22.6, 21.3, 21.1, 21.0, 20.6, 19.7.

HRMS (ESI) *m/z* calcd. For C₄₀H₄₉N₂O₄⁺ [M + H]⁺ 621.3687, found 621.3690. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.6 mL/min, λ = 254 nm, *t*_R (major) = 10.94 min, *t*_R (minor) = 15.07 min.

(*Ra,Z*)-1-(7-(*tert*-Butoxy)-1-(9*H*-carbazol-9-yl)-6,6-dimethyl-7-oxohept-4-en-2-yn-4-yl)naphthalen-2-yl 4-methylbenzoate (13)



According to the **general procedure** with **S13** (114.5 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **13** as a pale-yellow wax (69.7 mg, 55% yield, 80% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.7 Hz, 2H), 8.00 – 7.83 (m, 5H), 7.55 – 7.46 (m, 2H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.39 – 7.30 (m, 4H), 7.24 – 7.19 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.44 (s, 1H), 5.08 – 4.88 (m, 2H), 2.39 (s, 3H), 1.32 (s, 9H), 0.97 (s, 3H), 0.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 165.0, 146.0, 145.8, 144.3, 140.1, 132.6, 131.5, 130.3, 129.3(4), 129.2(6), 128.2, 127.0, 126.7, 126.2, 126.1, 125.9, 123.2, 122.0, 120.3, 119.3, 115.0, 109.1, 85.4, 81.5, 80.9, 46.6, 33.4, 27.9, 25.9, 23.5, 21.9.

HRMS (ESI) m/z calcd. For C₄₃H₃₉NNaO₄⁺ [M + Na]⁺ 656.2771, found 656.2773.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 9.90 min, $t_{\rm R}$ (minor) = 16.74 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-(2-(pivaloyloxy)naphthalen-1-yl)hept-3-en-5-ynoate (14)



According to the **general procedure** with **S14** (100.9 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **14** as a pale-yellow oil (48.0 mg, 40% yield, 89% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.95 – 7.88 (m, 1H), 7.87 – 7.79 (m, 2H), 7.53 – 7.37 (m, 6H), 7.27 – 7.18 (m, 3H), 6.48 (s, 1H), 5.02 (s, 2H), 1.36 (s, 9H), 1.17 (s, 9H), 1.00 (s, 3H), 0.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.7, 174.8, 146.0, 145.6, 140.1, 132.5, 131.5, 129.2, 128.2, 126.9, 126.0(1), 125.9(9), 125.9, 125.8, 123.2, 121.9, 120.3, 119.4, 115.1, 109.1, 85.3, 81.5, 80.9, 46.6, 39.1, 33.3, 28.0, 27.1, 25.8, 23.5.

HRMS (ESI) *m/z* calcd. For C₄₀H₄₁NNaO₄⁺ [M + Na]⁺ 622.2928, found 622.2933. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, *t*_R (major) = 8.25 min, *t*_R (minor) = 13.42 min.

tert-Butyl (*Sa,Z*)-7-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-(2-pivalamidonaphthalen-1-yl)hept-3-en-5-ynoate (15)



According to the **general procedure** with **S15** (100.5 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.) and L*11 (16.7 mg, 0.024 mmol, 12 mol%) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **15** as a pale-yellow wax (83.8 mg, 70% yield, -86% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 9.0 Hz, 1H), 8.11 – 8.02 (m, 3H), 7.84 – 7.75 (m, 3H), 7.48 – 7.31 (m, 6H), 7.27 – 7.20 (m, 2H), 6.54 (s, 1H), 5.07 – 4.91 (m, 2H), 1.30 (s, 9H), 1.13 (s, 9H), 0.95 (s, 3H), 0.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 177.1, 175.1, 147.9, 139.9, 133.5, 131.7, 130.7, 128.7, 128.2, 126.6, 126.0, 125.5, 125.0, 123.2(3), 123.1(8), 121.8, 120.4, 119.5, 117.2, 108.9, 84.4, 82.0, 81.4, 46.5, 39.8, 33.2, 27.9, 27.4, 25.8, 24.5.

HRMS (ESI) m/z calcd. For C₄₀H₄₃N₂O₃⁺ [M + H]⁺ 599.3268, found 599.3274.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, t_R (minor) = 14.29 min, t_R (major) = 30.65 min.

Ethyl (Ra,Z)-7-(9H-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (16)



According to the general procedure with S1 (118.2 mg, 0.40 mmol, 2.0 equiv.), C2 (58.7 µL, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **16** as a pale-yellow oil (103.3 mg, 84% yield, 91% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 7.7 Hz, 2H), 7.94 – 7.86 (m, 1H), 7.86 – 7.77 (m, 2H), 7.53 – 7.32 (m, 7H), 7.27 – 7.18 (m, 2H), 6.46 (s, 1H), 5.08 – 4.94 (m, 2H), 3.98 - 3.69 (m, 4H), 1.21 (d, J = 6.8 Hz, 6H), 1.13 - 0.98 (m, 12H), 0.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.4, 152.9, 146.3, 145.8, 140.0, 132.3, 131.1, 128.9, 128.1, 126.6, 125.8, 125.4, 125.0, 123.1, 122.7, 120.3, 119.3, 116.4, 109.1, 85.5, 81.4, 60.8, 46.6, 46.5, 45.6, 33.3, 26.2, 23.8, 21.1, 21.0, 20.6, 14.0. HRMS (ESI) m/z calcd. for C₄₀H₄₃N₂O₄⁺ [M + H]⁺ 615.3217, found 615.3221.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, $\lambda = 254$ nm, t_R (major) = 13.62 min, t_R (minor) = 31.22 min.

Cyclopentyl

(Ra,Z)-7-(9H-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (17)



According to the general procedure with S1 (118.2 mg, 0.40 mmol, 2.0 equiv.), C3 (94.0 mg, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product 17 as a pale-yellow oil (99.6 mg, 76% yield, 93% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 7.7 Hz, 2H), 7.98 – 7.92 (m, 1H), 7.90 – 7.81 (m, 2H), 7.58 – 7.36 (m, 7H), 7.31 – 7.24 (m, 2H), 6.52 (s, 1H), 5.12 – 5.00 (m, 2H), 4.98 – 4.92 (m, 1H), 4.00 – 3.80 (m, 2H), 1.86 – 1.73 (m, 2H), 1.72 – 1.63 (m, 2H), 1.63 - 1.52 (m, 4H), 1.24 (d, J = 6.7 Hz, 6H), 1.13 - 0.98 (m, 9H), 0.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.3, 153.0, 146.2, 145.7, 140.0, 132.4, 131.1, 128.8, 128.1, 126.6, 125.8(3), 125.8(0), 125.4, 125.3, 123.1, 122.7, 120.3, 119.3, 116.2, 109.1, 85.6, 81.3, 77.6, 46.6, 45.8, 33.3, 32.6(5), 32.5(7), 26.0, 23.8(3), 23.8(1), 23.2, 21.1, 21.0, 20.6.

HRMS (ESI) m/z calcd. for C₄₃H₄₇N₂O₄⁺ [M + H]⁺ 655.3530, found 655.3531. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, $\lambda = 254$ nm, t_R (major) = 13.36 min, t_R (minor) = 28.53 min.

4-Methoxybenzyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (18)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C4** (114.9 mg, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **18** as a pale-yellow oil (90.5 mg, 64% yield, 92% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 7.7 Hz, 2H), 7.92 – 7.81 (m, 3H), 7.51 – 7.38 (m, 7H), 7.31 – 7.24 (m, 2H), 7.19 – 7.11 (m, 2H), 6.89 – 6.81 (m, 2H), 6.52 (s, 1H), 5.12 – 4.99 (m, 2H), 4.86 – 4.68 (m, 2H), 4.00 – 3.86 (m, 2H), 3.82 (s, 3H), 1.29 – 1.19 (m, 6H), 1.12 (s, 3H), 1.11 – 0.99 (m, 6H), 0.91 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.2, 159.5, 152.9, 146.3, 145.6, 140.1, 132.3, 131.1, 129.7, 128.9, 128.2, 128.1, 126.7, 125.9, 125.8, 125.4, 125.0, 123.2, 122.7, 120.3, 119.4, 116.6, 113.9, 109.1, 85.5, 81.5, 66.2, 55.4, 46.7, 46.5, 45.7, 33.4, 26.2, 23.7, 21.1, 20.6. HRMS (ESI) *m/z* calcd. for C₄₆H₄₇N₂O₅⁺ [M + H]⁺ 707.3479, found 707.3483.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 15.57 min, t_R (minor) = 30.29 min.

p-Tolyl (*Ra*,*Z*)-7-(9*H*-carbazol-9-yl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (19)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C5** (102.9 mg, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **19** as a pale-yellow oil (88.2 mg, 65% yield, 96% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 7.7 Hz, 2H), 7.99 – 7.92 (m, 1H), 7.86 – 7.79 (m, 2H), 7.51 – 7.33 (m, 7H), 7.27 – 7.17 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.62 (s, 1H), 5.11 – 4.94 (m, 2H), 3.97 – 3.73 (m, 2H), 2.31 (s, 3H), 1.24 – 1.08 (m, 9H), 1.05 – 0.88 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 174.4, 153.0, 148.7, 146.3, 144.6, 140.0, 135.4, 132.4,

131.1, 129.8, 129.0, 128.2, 126.8, 125.9, 125.8, 125.5, 125.2, 123.2, 122.7, 121.1, 120.3, 119.4, 117.2, 109.1, 85.5, 81.8, 46.6, 46.1, 33.3, 25.8, 23.7, 21.1, 21.0, 20.6, 20.5. HRMS (ESI) *m/z* calcd. for C₄₅H₄₅N₂O₄⁺ [M + H]⁺ 677.3374, found 677.3376. HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), *t*_R (major) = 14.14 min, *t*_R (minor) = 30.91 min.

Ethyl (*Ra,Z*)-1-(5-(9*H*-carbazol-9-yl)-2-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)pent-1-en-3-yn-1-yl)cyclopentane-1carboxylate (20)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C6** (62.2 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **20** as a pale-yellow oil (64.1 mg, 50% yield, 92% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.88 – 7.76 (m, 3H), 7.48 – 7.34 (m, 7H), 7.27 – 7.18 (m, 2H), 6.48 (s, 1H), 5.02 (s, 2H), 4.12 – 3.69 (m, 2H), 3.64 – 3.36 (m, 2H), 2.13 – 1.98 (m, 1H), 1.75 – 1.62 (m, 1H), 1.56 – 1.47 (m, 1H), 1.46 – 1.29 (m, 5H), 1.27 – 1.00 (m, 12H), 0.95 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.0, 152.7, 146.5, 145.4, 140.1, 132.1, 131.1, 129.0, 128.0, 126.3, 125.9, 125.8, 125.4, 124.8, 123.2, 122.6, 120.3, 119.4, 117.0, 109.1, 85.3, 81.6, 60.5, 56.6, 46.8, 46.3, 38.8, 34.4, 33.4, 24.3, 23.3, 21.0, 20.6, 13.9.

HRMS (ESI) m/z calcd. for C₄₂H₄₅N₂O₄⁺ [M + H]⁺ 641.3374, found 641.3377.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, $\lambda = 254$ nm, t_R (major) = 14.40 min, t_R (minor) = 37.21 min.

(*Ra,Z*)-1-(1-(9*H*-Carbazol-9-yl)-6,6-dimethyl-7-oxo-7-(*p*-tolylamino)hept-4-en-2yn-4-yl)naphthalen-2-yl diisopropylcarbamate (21)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C7** (102.5 mg, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **21** as a pale-yellow oil (105.4 mg, 78% yield, 99% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 8.3 Hz, 1H), 7.81
(d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.66 (s, 1H), 7.58 – 7.35 (m, 6H), 7.26 – 7.12 (m, 5H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.47 (s, 1H), 5.13 – 4.98 (m, 2H), 4.15 – 3.91 (m, 1H), 3.65 – 3.43 (m, 1H), 2.28 (s, 3H), 1.21 – 1.07 (m, 6H), 1.05 – 0.96 (m, 6H), 0.96 – 0.87 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 172.7, 154.4, 146.4, 140.0, 135.6, 133.5, 132.6, 131.2, 129.6, 129.3, 129.0, 128.4, 127.1, 125.9, 125.6(4), 125.5(6), 125.4, 123.2, 121.9, 120.4, 120.3, 119.4, 116.1, 109.0, 85.4, 82.0, 47.4, 33.3, 25.1, 24.4, 20.9.

HRMS (ESI) m/z calcd. for C₄₅H₄₆N₃O₃⁺ [M + H]⁺ 676.3534, found 676.3536.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 14.21 min, t_R (minor) = 33.48 min.

(*Ra,Z*)-1-(1-(9*H*-carbazol-9-yl)-7-(methoxy(methyl)amino)-6,6-dimethyl-7oxohept-4-en-2-yn-4-yl)naphthalen-2-yl diisopropylcarbamate (22)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C8** (83.6 mg, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **22** as a pale-yellow oil (37.8 mg, 30% yield, 92% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 7.8 Hz, 2H), 7.90 – 7.78 (m, 3H), 7.50 – 7.36 (m, 7H), 7.26 – 7.21 (m, 2H), 6.47 (s, 1H), 5.03 (s, 2H), 4.06 – 3.81 (m, 2H), 3.50 (s, 3H), 3.05 (s, 3H), 1.30 – 1.20 (m, 6H), 1.14 (s, 3H), 1.12 – 1.00 (m, 6H), 0.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.4, 152.9, 146.8, 146.3, 140.0, 132.4, 131.1, 128.9, 128.2, 126.3, 125.9, 125.8, 125.4, 124.9, 123.2, 122.7, 120.3, 119.4, 114.9, 109.1, 85.9, 81.1, 60.6, 46.8, 46.5, 45.6, 33.6, 33.4, 26.0, 22.8, 21.1, 20.6.

HRMS (ESI) *m/z* calcd. for C₄₀H₄₃N₃NaO₄⁺ [M + Na]⁺ 652.3146, found 652.3145. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm, *t*_R (major) = 15.38 min, *t*_R (minor) = 24.64 min.

tert-Butyl (*Ra,Z*)-7-acetoxy-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (23)



According to the **general procedure** with S1 (118.2 mg, 0.40 mmol, 2.0 equiv.), C1 (74.6 μ L, 0.40 mmol, 2.0 equiv.) and S17 (19.8 μ L, 0.20 mmol, 1.0 equiv.), the reaction

mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **23** as a pale-yellow oil (64.3 mg, 60% yield, 84% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.52 – 7.41 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.65 (s, 1H), 4.68 (s, 2H), 4.25 – 3.90 (m, 2H), 2.03 (s, 3H), 1.43 (s, 9H), 1.41 – 1.28 (m, 12H), 1.09 (s, 3H), 0.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.8, 170.2, 152.9, 146.2, 132.4, 131.0, 128.7, 128.0

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 170.2, 152.9, 146.2, 132.4, 131.0, 128.7, 128.0, 126.6, 125.8, 125.3, 125.2, 122.6, 115.7, 88.0, 80.8, 80.4, 53.0, 46.6, 27.9, 26.1, 22.9, 21.4, 20.8, 20.6, 20.5.

HRMS (ESI) m/z calcd. for C₃₂H₄₂NO₆⁺ [M + H]⁺ 536.3007, found 536.3009. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 8.23 min, $t_{\rm R}$ (minor) = 17.88 min.

tert-Butyl (*Ra,Z*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethyl-7-phenoxyhept-3-en-5-ynoate (24)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S18** (25.7 μ L, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **24** as a pale-yellow oil (86.6 mg, 76% yield, 87% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.8 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.51 – 7.40 (m, 2H), 7.37 (d, J = 8.9 Hz, 1H), 7.27 – 7.16 (m, 2H), 6.96 – 6.84 (m, 3H), 6.63 (s, 1H), 4.73 – 4.60 (m, 2H), 4.18 – 3.90 (m, 2H), 1.42 (s, 9H), 1.34 – 1.24 (m, 12H), 1.09 (s, 3H), 0.75 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 157.9, 153.0, 146.2, 146.0, 132.5, 131.1, 129.4, 128.8, 128.1, 126.6, 125.9, 125.4(4), 125.3(9), 122.7, 121.2, 115.9, 115.0, 88.7, 81.8, 80.8, 56.8, 46.7, 28.0, 26.1, 23.0, 21.4(2), 21.3(9), 20.6(3), 20.6(0).

HRMS (ESI) m/z calcd. for C₃₆H₄₄NO₅⁺ [M + H]⁺ 570.3214, found 570.3217.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 7.13 min, $t_{\rm R}$ (minor) = 12.63 min.

tert-Butyl (*Ra,Z*)-7-(benzyloxy)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (25)



According to the general procedure with S1 (118.2 mg, 0.40 mmol, 2.0 equiv.), C1

(74.6 µL, 0.40 mmol, 2.0 equiv.) and **S19** (28.9 µL, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **25** as a pale-yellow oil (47.9 mg, 41% yield, 86% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.52 – 7.41 (m, 2H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.30 – 7.19 (m, 5H), 6.64 (s, 1H), 4.48 (s, 2H), 4.18 (s, 2H), 4.16 – 3.93 (m, 2H), 1.43 (s, 9H), 1.41 – 1.24 (m, 12H), 1.11 (s, 3H), 0.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.1, 146.2, 145.4, 137.6, 132.5, 131.1, 128.7, 128.4, 128.2, 128.1, 127.8, 126.6, 126.0, 125.7, 125.4, 122.7, 116.1, 88.3, 82.9, 80.8, 71.4, 58.0, 46.7, 28.1, 26.2, 23.0, 21.6, 20.7.

HRMS (ESI) m/z calcd. for C₃₇H₄₆NO₅⁺ [M + H]⁺ 584.3371, found 584.3373.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 7.79 min, $t_{\rm R}$ (minor) = 13.37 min.

tert-Butyl (*Ra,Z*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethyl-8-(tosyloxy)oct-3-en-5-ynoate (26)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S20** (35.3 μ L, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **26** as a pale-yellow oil (55.6 mg, 42% yield, 91% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.87 (m, 1H), 7.84 – 7.75 (m, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.34 (d, J = 8.9 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 6.52 (s, 1H), 4.18 – 3.91 (m, 4H), 2.56 (t, J = 7.5 Hz, 2H), 2.41 (s, 3H), 1.42 (s, 9H), 1.39 – 1.24 (m, 12H), 1.08 (s, 3H), 0.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.1, 146.1, 144.9(8), 144.9(5), 133.0, 132.5, 131.1, 130.0, 128.7, 128.1, 128.0, 126.6, 125.9(3), 125.9(2), 125.4, 122.8, 116.2, 84.5, 81.2, 80.8, 67.7, 46.7, 46.5, 28.1, 26.3, 23.0, 21.7, 21.5, 20.7, 20.4.

HRMS (ESI) m/z calcd. for C₃₈H₄₈NO₇S⁺ [M + H]⁺ 662.3146, found 662.3145. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 8.82 min, $t_{\rm R}$ (minor) = 23.90 min.

tert-Butyl (*Ra,Z*)-7-((*tert*-butoxycarbonyl)amino)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhept-3-en-5-ynoate (27)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 µL, 0.40 mmol, 2.0 equiv.) and **S21** (31.4 µL, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **27** as a pale-yellow oil (54.5 mg, 46% yield, 90% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 1H), 7.88 – 7.80 (m, 2H), 7.54 – 7.43 (m, 2H), 7.34 (d, *J* = 8.9 Hz, 1H), 6.59 (s, 1H), 4.90 (s, 1H), 4.29 – 4.00 (m, 2H), 3.93 (d, *J* = 3.7 Hz, 2H), 1.46 (s, 9H), 1.44 – 1.38 (m, 15H), 1.35 – 1.29 (m, 6H), 1.12 (s, 3H), 0.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.9, 155.4, 153.7, 146.2, 144.9, 132.5, 131.2, 128.9, 128.1, 126.7, 126.2, 125.9, 125.5, 122.7, 116.2, 85.2, 83.0, 80.9, 79.6, 47.0, 46.5, 46.4, 31.5, 28.5, 28.1, 26.4, 23.1, 21.6(8), 21.6(6), 20.7, 20.6. HRMS (ESI) *m/z* calcd. for C₃₅H₄₉N₂O₆⁺ [M + H]⁺ 593.3585, found 593.3588. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, *t*_R (major) = 7.81 min, *t*_R (minor) = 15.24 min.

tert-Butyl (*Ra,Z*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethyl-7-(phenylamino)hept-3-en-5-ynoate (28)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S22** (25.9 μ L, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **28** as a pale-yellow oil (79.6 mg, 70% yield, 92% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.91 (m, 1H), 7.85 – 7.77 (m, 2H), 7.51 – 7.41 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.74 – 6.67 (m, 1H), 6.60 – 6.53 (m, 3H), 4.12 – 4.00 (m, 2H), 3.89 (s, 2H), 1.43 (s, 9H), 1.38 – 1.24 (m, 12H), 1.09 (s, 3H), 0.76 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.4, 147.5, 146.2, 144.8, 132.5, 131.2, 129.2, 128.8, 128.1, 126.7, 126.1, 126.0, 125.4, 122.7, 118.1, 116.4, 113.3, 85.2, 84.2, 80.8, 46.5, 34.8, 28.1, 26.3, 23.2, 21.6, 20.6.

HRMS (ESI) m/z calcd. for C₃₆H₄₅N₂O₄⁺ [M + H]⁺ 569.3374, found 569.3376.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 7.88 min, $t_{\rm R}$ (minor) = 18.36 min.

tert-Butyl (*Ra,Z*)-6-(4-chlorophenyl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethylhex-3-en-5-ynoate (29)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S23** (27.3 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **29** as a pale-yellow oil (59.7 mg, 52% yield, 81% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.53 – 7.42 (m, 2H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.21 – 7.15 (m, 2H), 6.70 (s, 1H), 4.20 – 3.90 (m, 2H), 1.44 (s, 9H), 1.41- 1.31 (m, 6H), 1.27 – 1.17 (m, 6H), 1.13 (s, 3H), 0.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 153.2, 146.4, 145.4, 133.9, 132.9, 132.6, 131.2, 128.8, 128.5, 128.1, 126.7, 126.0, 125.8, 125.4, 122.8, 122.2, 116.7, 92.3, 86.2, 80.9, 46.8, 46.7, 46.6, 28.1, 26.5, 23.1, 21.6, 20.6.

HRMS (ESI) m/z calcd. for C₃₅H₄₁ClNO₄⁺ [M + H]⁺ 574.2719, found 574.2719. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 6.99 min, $t_{\rm R}$ (minor) = 20.36 min.

Methyl (*Ra*,*Z*)-4-(6-(*tert*-butoxy)-3-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-5,5-dimethyl-6-oxohex-3-en-1-yn-1-yl)benzoate (30)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S24** (32.0 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **30** as a pale-yellow oil (50.2 mg, 42% yield, 80% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.98 (m, 1H), 7.92 – 7.81 (m, 4H), 7.53 – 7.43 (m, 2H), 7.43 – 7.37 (m, 3H), 6.75 (s, 1H), 4.17 – 3.95 (m, 2H), 3.88 (s, 3H), 1.45 (s, 9H), 1.41 – 1.31 (m, 6H), 1.26 – 1.17 (m, 6H), 1.14 (s, 3H), 0.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 166.7, 153.2, 146.4, 146.2, 132.6, 131.6, 131.2, 129.3, 129.1, 128.9, 128.4, 128.2, 126.7, 125.9, 125.6, 125.5, 122.8, 116.6, 94.4, 86.5, 80.9, 52.3, 46.8, 46.6, 28.1, 26.4, 23.1, 21.6, 20.6.

HRMS (ESI) m/z calcd. for C₃₇H₄₄NO₆⁺ [M + H]⁺ 598.3163, found 598.3165.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, $\lambda = 254$ nm, t_R (major) = 7.68 min, t_R (minor) = 21.64 min.

tert-Butyl (*Ra,Z*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethyl-6-(4-(trifluoromethyl)phenyl)hex-3-en-5-ynoate (31)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S25** (32.6 μ L, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **31** as a pale-yellow oil (70.5 mg, 58% yield, 83% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.97 (m, 1H), 7.88 – 7.81 (m, 2H), 7.55 – 7.37 (m, 7H), 6.76 (s, 1H), 4.18 – 3.94 (m, 2H), 1.45 (s, 9H), 1.42 – 1.32 (m, 6H), 1.26 – 1.17 (m, 6H), 1.15 (s, 3H), 0.80 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 175.0, 153.2, 146.4, 146.3, 132.6, 131.9, 131.2, 129.6 (q, J = 32.6 Hz), 129.0, 128.2, 127.5(4) – 124.4(7) (m), 126.7, 125.9, 125.6, 125.5, 125.1 (q, J = 3.7 Hz), 124.1 (q, J = 272.0 Hz), 122.8, 116.5, 93.7, 85.9, 81.0, 46.8, 46.6, 28.1, 26.4, 23.1, 21.6, 20.6(2), 20.5(9).

¹⁹F NMR (376 MHz, CDCl₃) δ –62.76.

HRMS (ESI) *m/z* calcd. for C₃₆H₄₁F₃NO₄⁺ [M + H]⁺ 608.2982, found 608.2985. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, *t*_R (major) = 5.97 min, *t*_R (minor) = 13.54 min.

tert-Butyl (*Ra,Z*)-6-(4-cyanophenyl)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2.2-dimethylhex-3-en-5-ynoate (32)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S26** (25.4 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **32** as a pale-yellow oil (45.2 mg, 40% yield, 83% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.9 Hz, 2H), 7.53 – 7.35 (m, 7H), 6.78 (s, 1H), 4.19 – 3.92 (m, 2H), 1.45 (s, 9H), 1.40 – 1.31 (m, 6H), 1.24 – 1.16 (m, 6H), 1.15 (s, 3H), 0.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 153.2, 146.9, 146.4, 132.6, 132.1, 131.9, 131.2, 129.1, 128.6, 128.2, 126.8, 125.8, 125.5, 125.3, 122.8, 118.7, 116.4, 111.1, 95.7, 85.7,

81.0, 46.8, 46.5, 28.1, 26.4, 23.1, 21.6, 20.6. HRMS (ESI) *m/z* calcd. for $C_{36}H_{41}N_2O_4^+$ [M + H]⁺ 565.3061, found 565.3061. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 290 nm, *t*_R (major) = 13.12 min, *t*_R (minor) = 38.32 min.

tert-Butyl (*Ra,Z*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2dimethyl-6-(pyridin-3-yl)hex-3-en-5-ynoate (33)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S27** (20.6 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **33** as a pale-yellow oil (43.3 mg, 40% yield, 84% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.60 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.14 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.75 (s, 1H), 4.23 – 3.89 (m, 2H), 1.45 (s, 9H), 1.42 – 1.32 (m, 6H), 1.27 – 1.17 (m, 6H), 1.14 (s, 3H), 0.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.0, 153.2, 152.2, 148.2, 146.4, 146.2, 138.6, 132.6, 131.2, 129.0, 128.2, 126.8, 125.9, 125.5, 122.9, 122.8, 116.4, 94.5, 83.8, 81.0, 46.8, 46.6, 28.1, 26.4, 23.1, 21.6, 20.6.

HRMS (ESI) m/z calcd. for C₃₄H₄₁N₂O₄⁺ [M + H]⁺ 541.3061, found 541.3061. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 9.88 min, $t_{\rm R}$ (minor) = 28.39 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-(2-phenylnaphthalen-1-yl)hept-3-en-5-ynoate (P1)



According to the **general procedure** with **S28** (91.3 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to yield the product **P1** as a pale-yellow oil (24.2 mg, 21% yield, 25% e.e.). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.8 Hz, 2H), 8.08 – 8.04 (m, 1H), 7.89 – 7.83 (m, 2H), 7.54 – 7.47 (m, 4H), 7.46 – 7.40 (m, 5H), 7.28 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.12 (m, 3H), 6.17 (s, 1H), 5.10 (s, 2H), 1.23 (s, 9H), 0.54 (d, *J* =

9.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 144.9, 141.6, 140.1, 138.1, 132.7, 132.6, 132.1, 129.8, 128.3(8), 128.3(5), 128.0, 127.1, 127.0, 126.7, 126.0, 125.9, 123.3, 120.4, 119.4, 118.6, 109.1, 88.0, 82.1, 80.6, 46.6, 33.5, 27.9, 24.4, 23.3.

HRMS (ESI) m/z calcd. for C₄₁H₃₇NNaO₂⁺ [M + Na]⁺ 598.2717, found598.2718. HPLC analysis: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (minor) = 19.58 min, $t_{\rm R}$ (major) = 21.57 min.

tert-Butyl (*Ra,Z*)-7-(9*H*-carbazol-9-yl)-4-(2-isopropylnaphthalen-1-yl)-2,2dimethylhept-3-en-5-ynoate (P2)



According to the **general procedure** with **S29** (77.7 mg, 0.40 mmol, 2.0 equiv.), **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to yield the product **P2** as a pale-yellow oil (47.7 mg, 44% yield, 56% e.e.).

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 7.8 Hz, 2H), 7.94 – 7.89 (m, 1H), 7.80 – 7.74 (m, 2H), 7.48 – 7.35 (m, 7H), 7.25 – 7.19 (m, 2H), 6.44 (s, 1H), 5.02 (s, 2H), 3.38 – 3.27 (m, 1H), 1.38 (s, 9H), 1.26 (d, J = 6.9 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.5 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 144.6, 143.2, 140.1, 132.0, 131.8, 131.7, 128.4, 128.0, 126.5, 126.3, 125.8, 125.2, 123.8, 123.2, 120.4, 119.4, 118.7, 109.1, 86.6, 81.4, 80.9, 46.7, 33.4, 30.8, 28.0, 24.7, 24.6, 24.5, 22.4.

HRMS (ESI) m/z calcd. for C₃₈H₃₉NNaO₂⁺ [M + Na]⁺ 564.2873, found 564.2875. HPLC analysis: Chiralcel OD-H, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 13.57 min, t_R (minor) = 15.69 min.

(*E*)-1-(1-Bromo-3,3-dimethyl-4-oxo-4-phenylbut-1-en-1-yl)naphthalen-2-yl diisopropylcarbamate (P4-Br)



According to the **general procedure** with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **C9** (67.3 μ L, 0.40 mmol, 2.0 equiv.) and **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the side product **P4-Br** as a white solid (70.1 mg, 67% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.97 – 7.85 (m, 2H), 7.78 (d, *J* = 8.3, 1H), 7.52 – 7.21 (m, 6H), 6.77 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.17 (s, 1H), 3.95

- 3.59 (m, 2H), 1.47 (s, 3H), 1.38 (s, 3H), 1.12 (dd, *J* = 22.1, 6.8 Hz, 6H), 0.93 (dd, *J* = 63.7, 6.8 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 203.8, 153.4, 146.9, 142.5, 138.9, 134.6, 133.6, 131.7, 129.1, 128.8, 128.3, 128.0, 127.9, 127.3, 127.0, 126.7, 126.6, 125.5, 125.3, 122.8, 46.7, 46.2, 45.6, 26.7, 25.4, 21.3, 21.0, 20.5, 20.4.

HRMS (ESI) m/z calcd. for C₂₉H₃₂BrNNaO₃⁺ [M + Na]⁺ 544.1458, found 544.1456.

6. Gram-scale reaction



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S1** (2.95 g, 10.0 mmol, 2.0 equiv.), **S16** (1.03 g, 5.0 mmol, 1.0 equiv.), CuTc (95.4 mg, 0.50 mmol, 10 mol%), **L*8** (441.0 mg, 0.60 mmol, 12 mol%) and anhydrous Cs₂CO₃ (8.15 g, 25.0 mmol, 5.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (100.0 mL) was added by syringe under argon atmosphere. Finally, **C1** (1.87 mL, 0.40 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to afford the product **1** as a white wax (1.96 g, 61% yield, 92% e.e.).

7. Transformation



Procedure (a): the synthesis of 1a



To a solution of **1** (1.96 g, 3.0 mmol, 1.0 equiv., 92% e.e.) in THF (20.0 mL) was slowly added LiAlH₄ (227.7 mg, 6.0 mmol, 2.0 equiv.) at 0 °C under argon. The reaction mixture was stirred at 0 °C for 4 h. Upon completion of the reaction (monitored by TLC), the reaction was quenched with water and extracted with EtOAc (20 mL \times 3). The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the desired product **1a** as a white wax (1.37 g, 80% yield, 92% e.e.).

(*Ra*,*Z*)-1-(1-(9*H*-Carbazol-9-yl)-7-hydroxy-6,6-dimethylhept-4-en-2-yn-4-yl)naphthalen-2-yl diisopropylcarbamate (1a)



¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 7.7 Hz, 2H), 7.94 (d, J = 8.1 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.56 – 7.45 (m, 2H), 7.44 – 7.37 (m, 4H), 7.34 (d, J = 8.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 6.30 (s, 1H), 5.10 – 4.96 (m, 2H), 4.04 – 3.73 (m, 2H), 3.23 – 3.08 (m, 2H), 1.27 – 0.95 (m, 12H), 0.72 (s, 3H), 0.67 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.4, 149.5, 146.2, 140.1, 132.7, 131.1, 128.8, 128.2, 126.7, 125.8(4), 125.7(6), 125.4, 123.2, 122.6, 120.3, 119.4, 115.9, 109.0, 85.9, 80.7, 72.0, 46.8, 46.5, 40.7, 33.3, 23.9, 23.5, 21.0, 20.6.

HRMS (ESI) m/z calcd. for C₃₈H₄₁N₂O₃⁺ [M + H]⁺ 573.3112, found 573.3113.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 9.05 min, $t_{\rm R}$ (minor) = 13.65 min.

Procedure (b): the synthesis of 1b



To a solution of **1a** (1.37 g, 2.4 mmol, 1.0 equiv., 92% e.e.) in THF (20.0 mL) was slowly added NaH (288.0 mg, 7.2 mmol, 3.0 equiv.) at 0 °C under argon and stirred for 30 min. Then CH₃I (747.1 μ L, 12.0 mmol, 5.0 equiv.) was added into the mixture and the reaction mixture was stirred at 0 °C for 4 h. Upon completion of the reaction (monitored by TLC), the reaction was quenched with water and extracted with EtOAc (20 mL × 3). The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product **1b** as a white solid (1.21 g, 86% yield, 92% e.e.).

(*Ra,Z*)-1-(1-(9*H*-Carbazol-9-yl)-7-methoxy-6,6-dimethylhept-4-en-2-yn-4-yl)naphthalen-2-yl diisopropylcarbamate (1b)



¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.77 (m, 2H), 7.55 – 7.44 (m, 2H), 7.44 – 7.36 (m, 5H), 7.26 – 7.22 (m, 2H), 6.38 (s, 1H), 5.11 – 4.94 (m, 2H), 4.02 – 3.79 (m, 2H), 3.15 (s, 3H), 2.96 – 2.88 (m, 2H), 1.28 – 1.18 (m, 6H), 1.12 – 0.98 (m, 6H), 0.75 (s, 3H), 0.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.0, 149.6, 146.1, 140.1, 132.6, 131.1, 128.5, 128.0, 126.4, 126.2, 126.0, 125.8, 125.3, 123.2, 122.7, 120.3, 119.3, 115.2, 109.1, 86.1, 82.0, 80.4, 59.2, 46.6, 39.4, 33.4, 24.6, 23.7, 21.1(4), 21.0(7), 20.6.

HRMS (ESI) m/z calcd. for C₃₉H₄₃N₂O₃⁺ [M + H]⁺ 587.3268, found 587.3272.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 14.52 min, t_R (minor) = 28.70 min.

Procedure (c): the synthesis of 1c



To a solution of **1b** (1.21 g, 2.1 mmol, 1.0 equiv., 92% e.e.) in DCM (50.0 mL) was slowly added DIBAL-H (1 M in hexane, 8.4 mL, 8.4 mmol, 4.0 equiv.) at -78 °C under argon and slowly warmed to room temperature. The reaction mixture was stirred for 4 h. Upon completion of the reaction (monitored by TLC), the reaction was quenched with water and extracted with EtOAc (20 mL × 3). The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product **1c** as a pale-yellow wax (723.9 mg, 75% yield, 92% e.e.).

(*Ra*,*Z*)-1-(1-(9*H*-Carbazol-9-yl)-7-methoxy-6,6-dimethylhept-4-en-2-yn-4-yl)naphthalen-2-ol (1c)



¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.8 Hz, 2H), 7.79 – 7.68 (m, 3H), 7.45 – 7.31 (m, 6H), 7.26 – 7.15 (m, 4H), 6.28 (s, 1H), 5.08 – 4.87 (m, 2H), 3.34 (s, 3H), 3.17 (d, J = 8.5 Hz, 1H), 2.99 (d, J = 8.5 Hz, 1H), 0.87 (s, 3H), 0.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.0, 150.6, 140.1, 132.7, 129.7, 129.1, 128.1, 126.7, 125.9, 124.9, 123.5, 123.2, 120.4, 119.4, 119.1, 118.0, 116.0, 109.2, 86.0, 82.2, 80.4, 59.3, 40.0, 33.4, 26.9, 21.7.

HRMS (ESI) m/z calcd. for C₃₂H₃₀NO₂⁺ [M + H]⁺ 460.2271, found 460.2272. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 95/05, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (minor) = 9.73 min, $t_{\rm R}$ (major) = 13.45 min.

Procedure (d): the synthesis of 34



To a solution of **1c** (723.9 mg, 1.6 mmol, 1.0 equiv., 92% e.e.) in DCM (10.0 mL) was slowly added pyridine (258.8 μ L, 3.2 mmol, 2.0 equiv.) then Tf₂O (319.7 μ L, 1.9 mmol,

1.2 equiv.) at 0 °C. The reaction mixture was slowly warmed to r.t. and stirred for 4 h. Upon completion of the reaction (monitored by TLC), the reaction was quenched with 1 N HCl and extracted with EtOAc (20 mL \times 3). The organic phase was concentrated in vacuum and purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product **34** as a pale-yellow wax (743.1 mg, 80% yield, 92% e.e.).

(*Ra*,*Z*)-1-(1-(9*H*-Carbazol-9-yl)-7-methoxy-6,6-dimethylhept-4-en-2-yn-4-yl)naphthalen-2-yl trifluoromethanesulfonate (34)



¹H NMR (600 MHz, CDCl₃) δ 8.07 (d, J = 7.7 Hz, 2H), 7.96 (d, J = 8.4 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.58 – 7.53 (m, 1H), 7.53 – 7.48 (m, 1H), 7.45 – 7.37 (m, 5H), 7.25 – 7.20 (m, 2H), 6.44 (s, 1H), 5.19 – 4.93 (m, 2H), 3.08 (s, 3H), 2.95 (d, J = 8.6 Hz, 1H), 2.88 (d, J = 8.7 Hz, 1H), 0.74 (s, 3H), 0.63 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 151.3, 143.8, 140.1, 132.6, 132.3, 130.5, 128.4, 128.1, 127.8, 127.2, 127.0, 125.8, 123.2, 120.3, 119.4, 119.0, 118.6 (q, *J* = 320.1 Hz), 112.7, 109.1, 85.1, 82.2, 81.7, 59.1, 39.5, 33.3, 24.1, 23.7.

¹⁹F NMR (565 MHz, CDCl₃) δ –74.13.

HRMS (ESI) m/z calcd. for C₃₃H₂₉F₃NO₄S⁺ [M + H]⁺ 592.1764, found 592.1767. HPLC analysis: Chiralcel IE + IG, hexane/*i*-PrOH = 99/01, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 17.34 min, t_R (minor) = 20.17 min.

Procedure (e): Ni-catalysed coupling of 34 with Ph₂PH⁵



To a mixture of chiral triflate-containing styrene **34** (59.1 mg, 0.10 mmol, 1.0 equiv., 92% e.e.), diphenylphosphane (27.9 mg, 0.15 mmol, 1.50 equiv.), Ni(COD)₂ (5.50 mg, 0.020 mmol, 20 mol%), dppf (11.08 mg, 0.020 mmol, 20 mol%) and Na₂CO₃ (31.8 mg, 0.30 mmol, 3.0 equiv.) was added dry 1,4-dioxane (2.0 mL) under argon. Then, the reaction was stirred at 80 °C for 72 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na₂SO₄ and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography (petroleum ether/EtOAc = 15/1) to yield the desired product **35** as a colorless wax (40.7 mg, 65% yield, 91% e.e.).

(*Ra*,*Z*)-9-(4-(2-(Diphenylphosphaneyl)naphthalen-1-yl)-7-methoxy-6,6dimethylhept-4-en-2-yn-1-yl)-9*H*-carbazole (35)



¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 9.4 Hz, 1H), 7.94 – 7.81 (m, 4H), 7.77 – 7.70 (t, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 9.1 Hz, 1H), 7.23 – 6.98 (m, 13H), 6.76 (d, J = 7.9 Hz, 2H), 6.13 (d, J = 5.5 Hz, 1H), 6.10 (s, 1H), 4.95 (ddd, J = 17.2, 5.6, 2.1 Hz, 1H), 4.42 (ddd, J = 17.2, 6.2, 2.2 Hz, 1H), 3.15 (s, 3H), 3.09 – 2.95 (m, 2H), 0.82 (s, 3H), 0.69 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 147.5, 144.2, 141.2, 140.0, 139.0 (d, J = 22.1 Hz), 135.0, 134.4 (d, J = 6.1 Hz), 134.2 (d, J = 5.9 Hz), 133.7, 132.1, 130.7, 130.4, 128.8, 128.6, 128.4, 128.3 (d, J = 3.3 Hz), 128.2, 128.0, 127.5 (d, J = 16.0 Hz), 125.2, 122.8, 119.8, 119.1, 118.8, 109.5 (d, J = 2.3 Hz), 82.4, 59.3, 44.6, 44.4, 39.6, 29.9, 24.6, 23.8. ³¹P NMR (162 MHz, CDCl₃) δ –5.35.

HRMS (ESI) *m/z* calcd. for C₄₄H₃₉NOP⁺ [M + H]⁺ 628.2764, found 628.2765. HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, *t*_R (minor) = 12.29 min, *t*_R (major) = 14.82 min.

Procedure (f): Pd-catalysed coupling of **34** with $Ph_2P(O)H^6$



To a mixture of chiral triflate-containing styrene **34** (59.1 mg, 0.10 mmol, 1.0 equiv., 92% e.e.), diphenylphosphine oxide (80.8 mg, 0.40 mmol, 4.0 equiv.), Pd(OAc)₂ (4.48 mg, 0.020 mmol, 20 mol%), dppb (17.0 mg, 0.040 mmol, 40 mol%) and N,N-diisopropylethylamine (88.0 μ L, 0.50 mmol, 5.0 equiv.) was added dry DMSO (2.0 mL) under argon. Then, the reaction was stirred at 80 °C for 72 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na₂SO₄ and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography (petroleum ether/EtOAc = 2/1) to afford the desired product **36** as a colorless wax (28.9 mg, 45% yield, 90% e.e.).

(*Ra*,*Z*)-(1-(1-(9*H*-Carbazol-9-yl)-7-methoxy-6,6-dimethylhept-4-en-2-yn-4-yl)naphthalen-2-yl)diphenylphosphine oxide (36)



¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 8.1 Hz, 1H), 7.76 – 7.37 (m, 10H), 7.32 – 7.23 (m, 4H), 7.22 – 7.10 (m, 6H), 6.32 (s, 1H), 4.55 (q, J = 18.2 Hz, 2H), 3.18 (s, 3H), 3.12 (d, J = 8.7 Hz, 1H), 2.96 (d, J = 8.7 Hz, 1H), 0.78 (s, 3H), 0.69 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 150.1, 142.6, 139.9, 135.1, 134.6, 133.9 (d, *J* = 31.8 Hz), 132.5 (d, *J* = 9.8 Hz), 132.3 (d, *J* = 9.4 Hz), 131.7 (d, *J* = 2.7 Hz), 131.5, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.7, 127.1, 125.6, 123.0, 120.2, 119.2, 115.8 (d, *J* = 5.1 Hz), 109.2, 82.1, 81.6, 59.2, 40.2, 33.2, 24.1, 23.8.

³¹P NMR (162 MHz, CDCl₃) δ 28.73.

HRMS (ESI) *m/z* calcd. for C₄₄H₃₉NO₂P⁺ [M + H]⁺ 644.2713, found 644.2713. HPLC analysis: Chiralcel OD-H, hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm, *t*_R (major) = 14.45 min, *t*_R (minor) = 19.11 min.

Application of chiral styrene monophosphine ligand in the Pd-catalysed asymmetric Suzuki–Miyaura cross-coupling reactions⁷



To a mixture of 1-bromo-2-methylnaphthalene **37** (22.1 mg, 0.10 mmol, 1.0 equiv.), (2methylnaphthalen-1-yl)boronic acid **38** (46.7 mg, 0.25 mmol, 2.5 equiv.), Pd(OAc)₂ (1.12 mg, 0.005 mmol, 5.0 mol%), L* (0.01 mmol, 10 mol%) and K₃PO₄ (106.1, 0.50 mmol, 5.0 equiv.) was added dry THF (1.0 mL) under argon. Then, the reaction was stirred at 65 °C for 48 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na₂SO₄ and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography (petroleum ether/EtOAc = 50/1) to afford the desired product **39** as a colorless oil (11.3 mg, 40% yield, 52% e.e.).

(S)-2,2'-Dimethyl-1,1'-binaphthalene (39)



¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.81 (m, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 2.03 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 135.2, 134.4, 132.9, 132.3, 128.9, 128.1, 127.6, 126.2, 125.8, 125.0, 20.2.

HPLC analysis: Chiralcel OD-H, hexane/*i*-PrOH = 100/0, flow rate 0.8 mL/min, λ = 254 nm, t_R (major) = 9.36 min, t_R (minor) = 13.10 min.

8. Mechanistic investigation

A. Radical inhibition experiments



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.8 mg, 0.02 mmol, 10 mol%), **L*8** (17.6 mg, 0.024 mmol, 12 mol%), anhydrous Cs₂CO₃ (325.8 mg, 1.00 mmol, 5.0 equiv.), and TEMPO (93.8 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (4.0 mL) was added by syringe under argon atmosphere. Finally, **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated. **1** was not detected by either TLC or NMR.



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S1** (118.2 mg, 0.40 mmol, 2.0 equiv.), **S16** (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.8 mg, 0.02 mmol, 10 mol%), **L*8** (17.6 mg, 0.024 mmol, 12 mol%), anhydrous Cs₂CO₃ (325.8 mg, 1.00 mmol, 5.0 equiv.), and BHT (132.2 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (4.0 mL) was added by syringe under argon atmosphere. Finally, **C1** (74.6 μ L, 0.40 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated. **1** was not detected by either TLC or NMR. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to afford the radical trapped product **40** as a pale-yellow oil (55.8 mg, 77% yield).

tert-Butyl dimethylpropanoate (40)



3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-yl)-2,2-

¹H NMR (400 MHz, CDCl₃) δ 6.58 (s, 2H), 1.48 (s, 9H), 1.43 – 1.40 (m, 2H), 1.25 – 1.22 (m, 19H), 1.08 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 186.5, 174.8, 147.0, 144.1, 81.1, 49.3, 43.2, 35.1, 29.7, 28.3, 22.2, 22.0.

HRMS (ESI) m/z calcd. for C₂₃H₃₉O₃⁺ [M + H]⁺ 363.2894, found 363.2894.



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **S1** (236.4 mg, 0.80 mmol, 2.0 equiv.), **S16** (82.2 mg, 0.40 mmol, 1.0 equiv.), CuTc (7.6 mg, 0.04 mmol, 10 mol%), **L*8** (35.2 mg, 0.048 mmol, 12 mol%), anhydrous Cs₂CO₃ (651.6 mg, 2.00 mmol, 5.0 equiv.), and Ph–Se–Se–Ph (25.0 mg, 0.08 mmol, 0.2 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (8.0 mL) was added by syringe under argon atmosphere. Finally, **C1** (149.2 μ L, 0.80 mmol, 2.0 equiv.) was added into the mixture and the reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford **1** as a pale-yellow oil (54.0 mg, 21% yield, 92% e.e.) and **41** as a pale-yellow oil (47.1 mg, 99% yield, 0% e.e.). (Yield of **41** was calculated based on the amount of Ph–Se–Se–Ph)

tert-Butyl (*E*)-4-(2-((diisopropylcarbamoyl)oxy)naphthalen-1-yl)-2,2-dimethyl-4-(phenylselanyl)but-3-enoate (41)



¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.89 (m, 1H), 7.78 – 7.69 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.17 – 7.08 (m, 2H), 6.10 (s, 1H), 4.31 – 3.90 (m, 2H), 1.45 – 1.31 (m, 21H), 1.05 (s, 3H), 0.74 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 175.3, 153.0, 145.9, 137.1, 135.2, 132.2, 130.8, 128.9, 128.7, 128.6(3), 128.6(1), 127.8, 126.9, 126.4, 126.3, 125.3, 122.7, 80.4, 47.6, 46.9, 46.6, 28.1, 26.1, 23.0, 21.6, 20.8, 20.7.

HRMS (ESI) m/z calcd. for C₃₃H₄₂NO₄Se⁺ [M + H]⁺ 596.2274, found 596.2274.

HPLC analysis: Chiralcel IF, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm, $t_{\rm R}$ (major) = 6.64 min, $t_{\rm R}$ (minor) = 8.63 min.

B. Reaction of 1"



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 1" (103.7 mg, 0.20 mmol, 1.0 equiv.), S16 (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.8 mg, 0.02 mmol, 10 mol%), L*8 (17.6 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (325.8 mg, 1.00 mmol, 5.0 equiv.). The tube was evacuated and backfilled with argon three times. Then Et₂O (4.0 mL) was added by syringe under argon atmosphere. The reaction mixture was stirred at 10 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated. 1 was not detected by either TLC or NMR.

9. NMR spectra





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S67







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S71












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Parameter	Value	
Solvent	CDC13	
Temperature	298.1 K	
Spectrometer	Frequency	400.13 Hz











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$\begin{array}{c} 1.22 \\ 1.21 \\ 1.06 \\ 1.03 \\ 1.01 \\ 0.72 \\ 0.67 \end{array}$



Value Parameter CDC13 Solvent Temperature 297.0 K Spectrometer Frequency

400.13 Hz



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- 46.83 - 46.55 - 40.72 $\frac{-33.33}{\int 23.90} \frac{23.90}{23.48} \\ \sum \frac{21.05}{20.57}$



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⁷ 7.45
⁷ 7.72
⁸ 7.72</p





Parameter	Value	
Solvent	CDC13	
Temperature	300.8 K	
Spectrometer	Frequency	400.13 Hz









00 190 180 170 160 150 100 90 f1 (ppm) -10



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



8.25 7.900 7.910 7.888 7.888 7.888 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.885 7.712 7.112 7





8.17 8.8.14 8.8.14 8.8.01 8.8.01 8.8.01 7.7.84 7.7.7 7.7.7 7.7.7 7.7.60 7.7.60 7.7.60 7.7.60 7.7.60 7.7.60 7.7.60 7.7.60 7.7.60 7.7.7 7.7.60 7.7.7.7 7.7.7.7 7.7.7



150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25 fl (ppm)







00 190 180

170

Parameter	Value	
Solvent	CDC13	
Temperature	294.0 K	
Spectrometer	Frequency	400.13 Hz

40

50

20

10

30

0

-



160 150 140 130 120 110 100 90 80 70 60 fl (ppm)

10.HPLC spectra





Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	10.040	1660172	50.173
2	18.568	1648725	49.827





PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	10.018	3457256	96.330
2	18.614	131730	3.670



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	11.512	17454061	49.784
2	26.083	17605388	50.216



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	11.468	26826446	96.685
2	26.223	919902	3.315



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	13.542	5180331	50.268
2	36.883	5125148	49.732





P	DA Ch	1 254nm		
Ρ	eak#	Ret. Time	Area	Area%
	1	13.666	14317091	95.044
	2	37.774	746531	4.956



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	7.661	5810060	50.874
2	20.701	5610354	49.126



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	7.686	15050870	94.831
2	20.874	820431	5.169

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PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	9.794	2615743	50.352
2	22.849	2579141	49.648



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	0 822	3700366	07 065

I	9.822	3700366	97.065
2	22.926	111903	2.935



Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	11.914	6055786	50.274	
2	24.350	5989685	49.726	



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	11.999	3193907	93.885
2	24.562	208041	6.115



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	8.340	14120139	50.131	
2	12.740	14046063	49.869	



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	8.298	7682791	95.984
2	12.728	321446	4.016



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	12.631	6755013	50.142
2	14.992	6716782	49.858



ļ	PDA Ch1 254nm				
ſ	Peak#	Ret. Time	Area	Area%	
ĺ	1	12.563	3087938	95.740	
ĺ	2	15.046	137415	4.260	





PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	15.147	894158	50.759
2	28.511	867419	49.241



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	15.221	1495254	95.512
2	29.001	70261	4,488



Peak Table

PDA Ch1 254nm			
Peak#	Ret. Time	Area	Area%
1	14.541	2570545	50.478
2	25.977	2521816	49.522



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.528	2642994	97.090
2	25,949	79213	2,910



Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	9.542	953225	50.996	
2	12.823	915990	49.004	



Peak Table

PDA Ch	1 254nm	
Peak#	Ret. Time	Area

Peak#	Ret. Time	Area	Area%
1	9.544	1029912	97.331
2	12.853	28247	2.669





PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	10.954	3086189	50.153	
2	15.091	3067412	49.847	



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	10.942	8000188	95.510
2	15.073	376063	4.490





Detector A Ch2 254nm					
Peak#	Ret. Time	Area	Area%		
1	9.889	6868523	50.056		
2	16.582	6853108	49.944		



Detector A Ch2 254nm					
Peak#	Ret. Time	Area	Area%		
1	9.897	6114668	90.053		
2	16.736	675395	9.947		



Detector A Ch2 254nm					
Peak#	Ret. Time	Area	Area%		
1	8.278	2778566	49.660		
2	13.418	2816614	50.340		



Detector A Ch2 254nm					
Peak#	Ret. Time	Area	Area%		
1	8.247	2991650	94.543		
2	13.422	172675	5.457		



Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	14.170	36745867	49.484	
2	30.723	37511804	50.516	

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Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.290	1218653	7.209
2	30.645	15684784	92.791





PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	13.675	4632848	49.819	
2	31.034	4666477	50.181	



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	13.615	12295312	95.290	
2	31.220	607783	4.710	





PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	13.406	4762670	50.086	
2	28.466	4746336	49.914	



PDA Ch1 254nm				
	Peak#	Ret. Time	Area	Area%
	1	13.360	5862835	96.416
	2	28,526	217929	3.584





PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	15.535	10105036	50.442	
2	29.859	9928039	49.558	



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	15.573	17094925	96.043
2	30.294	704287	3.957



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.084	8202689	50.121
2	30.117	8162999	49.879



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.135	18888423	97.802
2	30.911	424451	2.198



Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	14.638	2955347	50.915	
2	36.927	2849144	49.085	



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.403	49525255	95.803
2	37.212	2169601	4.197



Peak Table

Detector A Ch2 254nm				
Peak#	Ret. Time	Area	Area%	
1	14.289	1565553	49.934	
2	33.508	1569663	50.066	



Peak Table

Detect	or A Ch2 2	254nm	
Peak#	Ret. Time	Area	Area%
1	14.210	10130444	99.314
2	33.477	69959	0.686



Peak Table

Detector A Ch2 254nm			
Peak#	Ret. Time	Area	Area%
1	15.558	372600	48.264
2	24.862	399409	51.736



Peak	Table	

Detect	or A Ch2 2	254nm	
Peak#	Ret. Time	Area	Area%
1	15.379	5803018	95.817
2	24.643	253310	4.183





Detector A Ch2 254nm				
Peak#	Ret. Time	Area	Area%	
1	8.267	509298	50.028	
2	18.134	508738	49.972	



Detector A Ch2 254nm					
Peak#	Ret. Time	Area	Area%		
1	8.230	333387	91.923		
2	17.877	29292	8.077		





Peak Table

Detector A Ch2 254nm				
Peak#	Ret. Time	Area	Area%	
1	7.162	677683	49.836	
2	12.755	682134	50.164	



Peak#	Ret. Time	Area	Area%
1	7.127	1326551	93.431
2	12.633	93261	6.569



Peak Table

PDA Ch1 254nm			
Peak#	Ret. Time	Area	Area%
1	7.644	981982	51.217
2	12.967	935322	48.783



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	7.787	1021081	92.778	
2	13.371	79480	7.222	



PDA Ch1 254nm			
Peak#	Ret. Time	Area	Area%
1	8.940	261903	50.666
2	24.376	255013	49.334



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	8.820	1250801	95.480
2	23.903	59207	4.520



Peak Table

PDA Ch1 254nm			
Peak#	Ret. Time	Area	Area%
1	7.967	210063	51.683
2	15.634	196379	48.317



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	7.811	1759985	95.159	
2	15 243	89535	4 841	





Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	7.877	1117225	49.658	
2	18.296	1132614	50.342	



PDA	Ch1	254nm
-		

Peak#	Ret. Time	Area	Area%
1	7.879	922612	95.854
2	18.361	39908	4.146



Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	6.980	3404722	50.030	
2	20.275	3400652	49.970	



PDA	Ch1	254nm
	OIL L	

Peak#	Ret. Time	Area	Area%
1	6.993	4847405	90.476
2	20.355	510256	9.524



PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	7.682	3940240	49.856		
2	21.505	3962998	50.144		



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.683	2927085	90.042
2	21.641	323732	9.958



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	5.962	7108325	49.695
2	13.490	7195662	50.305



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.966	1129020	91.303
2	13.539	107539	8.697



Peak Table

PDA Ch2 290nm				
Peak#	Ret. Tim	e Area	Area%	
1	13.098	63999475	49.542	
2	37.865	65182166	50.458	



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PDA Ch3 290nm				
Peak#	Ret. Time	Area	Area%	
1	13.116	34755569	91.281	
2	38.317	3319674	8.719	





PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	9.846	2936620	49.548	
2	28.232	2990157	50.452	



Peak Table

PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	9.875	1815633	92.033
2	28.387	157167	7.967



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	19.567	9988843	50.176	
2	22.868	9918817	49.824	



PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	19.576	4606358	37.711		
2	21.568	7608399	62.289		



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	13.480	4816690	50.781	
2	15.339	4668504	49.219	



PDA Ch1 254nm				
	Peak#	Ret. Time	Area	Area%
	1	13.569	3460208	78.211
	2	15.686	963972	21.789


Peak Table

Detector A Ch2 254nm				
Peak#	Ret. Time	Area	Area%	
1	9.054	6952184	49.916	
2	13.625	6975609	50.084	



Peak Table

Detect	or A Ch2 2	254nm	
Peak#	Ret. Time	Area	Area%
1	9.048	8456564	95.827
2	13.654	368287	4.173



Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	14.483	15674211	48.810		
2	28.901	16438405	51.190		



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.523	1232676	96.316
2	28.704	47152	3.684



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	9.590	20912019	49.346
2	13.526	21466727	50.654



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	9.734	2682059	4.193
2	13.445	61283350	95, 807





PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	17.867	6039195	49.999
2	20.751	6039322	50.001



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	17.338	23867227	95.882
2	20.165	1025185	4,118





PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	12.391	1329199	49.465		
2	15.007	1357937	50.535		





PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	12.288	143515	4.713
2	14.815	2901278	95.287

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Peak Table

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	14.681	9762391	49.779	
2	19.205	9849095	50.221	

mAU



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	14.450	29506520	95.111
2	19.114	1516764	4.889



PDA Ch1 254nm						
Peak#	Ret. Time	Area	Area%			
1	10.333	2563266	49.586			
2	13.531	2606030	50.414			



PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	9.363	10587756	75.706		
2	13.104	3397590	24.294		



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	6.637	7675219	49.512	
2	8.637	7826624	50.488	

mAU



Peak Table

PDA Ch1 254nm

I DA UI			
Peak#	Ret. Time	Area	Area%
1	6.642	4058799	50.557
2	8.629	3969311	49.443

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