Supporting Information for

Copper-Catalyzed Asymmetric Radical 1,2-Carboalkynylation of Alkenes with Alkyl Halides and Terminal Alkynes

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Figure S1. The X ray structure of 53.



Figure S2. Stacking of ³¹P NMR spectra. Red: L2, $\delta^{31}P = -10.8$ ppm; Blue: L2Cu(I), $\delta^{31}P = -8.4$ ppm.



Figure S3. The HRMS of L2Cu complex. The sample was prepared by mixing CuI and L2 in CH₃CN.

Scheme S1. Unsuccessful alkene substrates



Scheme S2. Alternative pathways for the C–C bond formation¹



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. CuI was purchased from Sigma-Aldrich. CuOAc was purchased from TCI. 1,4-Dioxane was purchased from Aladdin, which was redistilled with sodium and benzophenone under argon atmosphere. 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). 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, 100 or 150 MHz for ¹³C NMR, and 376 MHz for ¹⁹F NMR, respectively, in CDCl₃ with tetramethylsilane (TMS) as an internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ¹H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR were reported in terms of chemical shift (δ , ppm). EPR spectra were recorded on Bruker EMX^{plus}-10/12. Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at an appropriate wavelength). Column conditions were reported in the experimental section below.

The synthesis of substrates

Most of alkenes, alkynes, and radical precursors were purchased from commercial sources. The alkenes $1f^2$, $1j^3$, $1za-1zd^3$, $1r-1t^4$, $1y^4$, $1ze^4$, $1x^5$, $1z^6$, and $1zf^6$ were synthesized according to the reported literature. The radical precursors $3c^{7,8}$ and $3d^9$ were synthesized according to the reported literature. All the characterization data are consistent with those in the reported literature.



Synthesis of 1zh



ⁿBuLi (2.4 M in hexane, 23.0 ml, 55.0 mmol, 1.1 equiv.) was added dropwise into a solution of triisopropylsilacetylene (9.1 g, 50.0 mmol, 1.0 equiv.) in anhydrous THF (100.0 ml) at 0 °C. The mixture was stirred at room temperature for 30 min and cooled to 0 °C. DMF (4.0 g, 55.0 mmol, 1.1 equiv.) was added dropwise and refluxed for 1 h. After cooling down, the mixture was quenched by 5% aq. H₂SO₄ to a slightly acidic pH, then weakly basic by addition of a saturated aq. NaHCO₃. The mixture was extracted with Et₂O, washed by brine and dried over Na₂SO₄. The organic phase was concentrated in vacuum. The crude aldehyde was used without further purification. To a solution of methyltriphenylphosphonium bromide (21.4 g, 60 mmol, 1.2 equiv.) in THF (120.0 ml) at 0 °C, "BuLi (2.4 M in hexane, 25.0 ml, 60.0 mmol, 1.2 equiv.) was added dropwise. The mixture was stirred at room temperature for 1 h then cooled to -78 °C. A solution of aldehyde (10.5 g, 50.0 mmol, 1.0 equiv.) in THF (120.0 ml) was added dropwise and warm up to room temperature for another 18 h. After completion (monitored by TLC), the reaction was quenched by H₂O and extracted with Et₂O. The organic phase was washed by brine, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by column chromatography to afford the 1zh (3.6 g, 35% yield) as a red liquid.

¹**H NMR** (400 MHz, CDCl₃) δ 5.84 (dd, J = 17.6, 11.1 Hz, 1H), 5.67 (dd, J = 17.6, 2.4 Hz, 1H), 5.48 (dd, J = 11.1, 2.4 Hz, 1H), 1.10 – 1.06 (m, 21H). ¹³**C NMR** (100 MHz, CDCl₃) δ 127.5, 117.5, 105.7, 94.8, 91.3, 18.6, 11.3.

Asymmetric radical 1,2-carboalkynylation of alkenes with alkyl halides and terminal alkynes



General procedure A:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (1.84 mg, 0.015 mmol, 7.5 mol%), L1 (12.5 mg, 0.015 mmol, 7.5 mol%), Cs₂CO₃ (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous 1,4-dioxane (2.0 mL). Then, alkene (0.30 mmol, 1.5 equiv.), alkyl halide or other radical precursor (0.24 mmol, 1.2 equiv.), and alkyne (0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 12 to 48 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH₂Cl₂. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuOAc (2.45 mg, 0.020 mmol, 10 mol%), L1 (25 mg, 0.030 mmol, 15 mol%), Cs₂CO₃ (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous 1,4-dioxane (2.0 mL). Then, alkene (0.30 mmol, 1.5 equiv.), alkyl halide or other radical precursor (0.24 mmol, 1.2 equiv.), and alkyne (0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 6 to 48 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by CH₂Cl₂. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Note: Most of the products are unstable in neat state in air after purification, and should be stored in solvent (CH_2Cl_2 or Et_2O) at -10 °C. Their characterization by NMR, HPLC or HRMS should be done as soon as possible. Meanwhile, the reaction is sensitive to water and air, and thus, Schlenk tubes and the reagents must be dried prior to use. Especially, 1,4-dioxane must be redistilled.



The racemates of products were prepared following the same procedure as described above using CuOAc (2.45 mg, 0.020 mmol, 10 mol%) and L_{rac} (11.3 mg, 0.030 mmol, 15 mol%) as the catalyst and the ligand, respectively, at room temperature or 80 °C in anhydrous 1,4-dioxane (2.0 mL) for 24 to 72 h. Upon completion (monitored by TLC),

the precipitate was filtered off and washed with CH₂Cl₂. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford the desired product.

Substrates scope of alkene

(R)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (4)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 4 as a colorless oil (53.2 mg, 71% yield, 93% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), *t*_R (minor) = 12.74 min, *t*_R (major) = 13.66 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (ddd, J = 7.3, 3.9, 1.2 Hz, 1H), 3.92 (dd, J = 9.8, 4.3 Hz, 1H), 2.18 (dd, J = 13.9, 9.9 Hz, 1H), 2.05 (dd, J = 13.9, 4.3 Hz, 1H), 1.42 (s, 9H), 1.34 (s, 3H), 1.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 142.4, 132.1, 131.9, 128.8, 127.4, 127.0, 118.6, 111.1, 97.2, 82.2, 80.2, 48.3, 43.1, 35.4, 28.1, 26.2, 25.7.

HRMS (ESI) m/z calcd. for C₂₅H₂₈NO₂ [M + H]⁺ 374.2115, found 374.2108.

(*S*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(2-methoxyphenyl)-2,2-dimethylhex-5-ynoate (5)



According to General Procedure A with 1-methoxy-2-vinylbenzene **1b** (40.3 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **5** as a colorless oil (56.2 mg, 70% yield, 89% ee).

HPLC analysis: Chiralcel ASH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 19.85 min, t_R (major) = 23.45 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.63 – 7.53 (m, 3H), 7.54 – 7.47 (m, 2H), 7.26 (m, 1H), 7.10 – 6.96 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 4.46 (dd, *J* = 9.9, 4.3 Hz, 1H), 3.88 (s,

3H), 2.18 (dd, *J* = 13.8, 9.9 Hz, 1H), 1.97 (dd, *J* = 13.8, 4.4 Hz, 1H), 1.42 (s, 9H), 1.33 (s, 3H), 1.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 155.7, 132.1, 131.9, 130.6, 129.1, 128.5, 128.1, 120.9, 118.7, 110.9, 110.7, 97.9, 81.1, 79.9, 55.4, 46.2, 42.9, 28.2, 28.0, 26.1, 25.2. HRMS (ESI) *m/z* calcd. for C₂₆H₃₀NO₃ [M + H]⁺ 404.2220, found 404.2210

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(3-methoxyphenyl)-2,2-dimethylhex-5-ynoate (6)



According to General Procedure **A** with 1-methoxy-3-vinylbenzene 1c (40.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **6** as a colorless oil (51.1 mg, 63% yield, 95% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.65 min, t_R (major) = 7.26 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.27 (dd, J = 9.0, 6.7 Hz, 1H), 7.07 – 6.92 (m, 2H), 6.80 (dd, J = 8.0, 2.3 Hz, 1H), 3.89 (dd, J = 9.8, 4.2 Hz, 1H), 3.82 (s, 3H), 2.17 (dd, J = 13.9, 9.9 Hz, 1H), 2.05 (dd, J = 13.9, 4.3 Hz, 1H), 1.42 (s, 9H), 1.33 (s, 3H), 1.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 159.9, 144.0, 132.1, 131.9, 129.8, 128.8, 119.7, 118.6, 113.5, 112.0, 111.1, 97.1, 82.2, 80.2, 55.3, 48.2, 43.1, 35.4, 28.1, 26.2, 25.7. HRMS (ESI) *m/z* calcd. for C₂₆H₃₀NO₃ [M + H]⁺ 404.2220, found 404.2210.

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(4-methoxyphenyl)-2,2-dimethylhex-5-ynoate (7)



According to General Procedure A with 1-methoxy-4-vinylbenzene 1d (40.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the

product 7 as a colorless oil (57.9 mg, 72% yield, 91% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.68 min, t_R (minor) = 11.60 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.87 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.80 (s, 3H), 2.15 (dd, *J* = 13.7, 9.8 Hz, 1H), 2.03 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.42 (s, 9H), 1.32 (s, 3H), 1.23 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.5, 158.6, 134.5, 132.1, 131.9, 128.9, 128.3, 118.6, 114.1, 111.0, 97.6, 82.0, 80.2, 55.3, 48.4, 43.1, 34.6, 28.1, 26.2, 25.7.

HRMS (ESI) m/z calcd. for C₂₆H₃₀NO₃ [M + H]⁺ 404.2220, found 404.2210.

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(4-phenoxyphenyl)hex-5-ynoate (8)



According to General Procedure **A** with 1-phenoxy-4-vinylbenzene **1e** (58.9 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **8** as a colorless oil (71.6 mg, 77% yield, 94% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 20.61 min, t_R (major) = 24.14 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.44 – 7.32 (m, 4H), 7.19 – 7.09 (m, 1H), 7.08 – 6.94 (m, 4H), 3.94 (dd, J = 9.7, 4.2 Hz, 1H), 2.20 (dd, J = 13.9, 9.9 Hz, 1H), 2.09 (dd, J = 13.9, 4.2 Hz, 1H), 1.46 (s, 9H), 1.37 (s, 3H), 1.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 157.2, 156.3, 137.2, 132.1, 131.9, 129.8, 128.7, 128.7, 123.4, 119.02, 118.95, 118.6, 111.1, 97.2, 82.3, 80.3, 48.4, 43.1, 34.8, 28.1, 26.3, 25.7.

HRMS (ESI) m/z calcd. for C₃₁H₃₂NO₃ [M + H]⁺ 466.2377, found 466.2368.

(R)-tert-Butyl-4-(4-acetoxyphenyl)-2,2-dimethyl-6-phenylhex-5-ynoate (9)



According to General Procedure **A** with 4-vinylphenyl acetate **1f** (48.6 mg, 0.30 mmol, 1.5 equiv), ethynylbenzene **2b** (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **9** as a colorless oil (52.2 mg, 64% yield, 98% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 9.88 min, t_R (minor) = 11.84 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.57 (dd, J = 7.5, 1.9 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.30 – 7.25 (m, 4H), 7.24 – 7.20 (m, 1H), 7.07 (dd, J = 7.7, 1.1 Hz, 1H), 4.09 (dd, J = 10.1, 4.2 Hz, 1H), 2.34 (s, 3H), 2.18 (dd, J = 13.8, 10.1 Hz, 1H), 1.94 (dd, J = 13.8, 4.2 Hz, 1H), 1.40 (s, 9H), 1.34 (s, 3H), 1.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.6, 169.4, 147.7, 134.6, 131.5, 129.4, 128.2, 127.8, 127.8, 126.4, 123.7, 123.0, 91.3, 82.8, 80.0, 46.3, 42.9, 30.0, 28.0, 25.9, 25.8, 21.2.

HRMS (ESI) m/z calcd. for C₂₆H₃₀NaO₄ [M + Na]⁺ 429.2036, found 429.2035.

(S)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(o-tolyl)hex-5-ynoate (10)



According to General Procedure **A** with 1-methyl-2-vinylbenzene **1g** (35.5 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **10** as a colorless oil (52.5 mg, 68% yield, 86% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 13.16 min, t_R (major) = 14.03 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 8.6 Hz, 3H), 7.27 – 7.21 (m, 1H), 7.19 (d, *J* = 4.2 Hz, 2H), 4.16 (dd, *J* = 10.3, 4.1 Hz, 1H), 2.45 (s, 3H), 2.24 (dd, *J* = 13.9, 10.4 Hz, 1H), 1.95 (dd, *J* = 14.0, 4.1 Hz, 1H), 1.44 (s, 9H), 1.37 (s, 3H), 1.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 140.5, 134.7, 132.1, 131.9, 130.8, 128.9, 127.8, 127.0, 126.6, 118.6, 111.0, 97.4, 81.6, 80.2, 46.3, 43.0, 31.9, 28.0, 26.2, 25.7, 19.4. HRMS (ESI) *m/z* calcd. for C₂₆H₃₀NO₂ [M + H]⁺ 388.2271, found 388.2261.

(R)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(m-tolyl)hex-5-ynoate (11)



According to General Procedure A with 1-methyl-3-vinylbenzene 1h (35.5 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 11 as a colorless oil (55.3 mg, 71% yield, 90% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 13.97 min, t_R (major) = 15.29 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.22 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 1H), 3.88 (dd, *J* = 9.9, 4.1 Hz, 1H), 2.37 (s, 3H), 2.17 (dd, *J* = 13.8, 10.0 Hz, 1H), 2.03 (dd, *J* = 13.9, 3.9 Hz, 1H), 1.42 (s, 9H), 1.34 (s, 3H), 1.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 142.4, 138.4, 132.1, 131.9, 128.9, 128.7, 128.1, 127.8, 124.4, 118.6, 111.0, 97.4, 82.1, 80.2, 48.3, 43.1, 35.3, 28.1, 26.2, 25.7, 21.5. HRMS (ESI) *m/z* calcd. for C₂₆H₃₀NO₂ [M + H]⁺ 388.2271, found 388.2261.

(R)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(p-tolyl)hex-5-ynoate (12)



According to General Procedure A with 1-methyl-4-vinylbenzene 1i (35.4 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 12 as a colorless oil (56.1 mg, 72% yield, 92% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.97 min, t_R (minor) = 8.46 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.52 – 7.48 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 3.91 (dd, J = 9.8, 4.3 Hz, 1H), 2.37 (s, 3H), 2.19 (dd, J = 13.9, 9.8 Hz, 1H), 2.06 (dd, J = 13.9, 4.4 Hz, 1H), 1.45 (s, 9H), 1.36 (s, 3H), 1.26 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 139.5, 136.6, 132.1, 131.9, 129.4, 128.9, 127.2, 118.6, 111.0, 97.5, 82.0, 80.2, 48.4, 43.1, 35.0, 28.1, 26.2, 25.7, 21.1.

HRMS (ESI) m/z calcd. for C₂₆H₃₀NO₂ [M + H]⁺ 388.2271, found 388.2261.

(R)-tert-Butyl-4-(4-isobutylphenyl)-2,2-dimethyl-6-phenylhex-5-ynoate (13)



According to General Procedure **A** with **1j** 1-isobutyl-4-vinylbenzene (48.0 mg, 0.30 mmol, 1.5 equiv.), ethynylbenzene **2b** (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **13** as a colorless oil (76.9 mg, 95% yield, 96% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 11.96 min, t_R (minor) = 13.58 min.

¹**H NMR** (400 MHz, CDCl₃) 7.51 – 7.43 (m, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.16 (d, J = 7.6 Hz, 2H), 3.92 (dd, J = 9.6, 4.0 Hz, 1H), 2.51 (d, J = 7.1 Hz, 2H), 2.18 (dd, J = 13.3, 10.3 Hz, 1H), 2.10 (dd, J = 13.8, 4.2 Hz, 1H), 1.91 (dp, J = 13.4, 6.7 Hz, 1H), 1.49 (s, 9H), 1.42 (s, 3H), 1.29 (s, 3H), 0.96 (d, J = 6.6 Hz, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 176.8, 140.5, 140.1, 131.5, 129.4, 128.2, 127.7, 127.2, 124.0, 92.5, 83.5, 80.1, 48.9, 45.1, 43.3, 34.9, 30.3, 28.1, 26.6, 25.4, 22.5. **HRMS** (ESI) *m/z* calcd. for C₂₈H₃₇O₂ [M + H]⁺ 405.2788, found 405.2799.

(*R*)-*tert*-Butyl-4-(4-(*tert*-butyl)phenyl)-6-(4-cyanophenyl)-2,2-dimethylhex-5ynoate (14)



According to General Procedure **A** with 1-(*tert*-butyl)-4-vinylbenzene **1k** (48.1 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **14** as a colorless oil (60.6 mg, 71% yield, 95% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 10.03 min, t_R (minor) = 11.34 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.35 (q, J = 8.4 Hz, 4H), 3.89 (dd, J = 9.8, 4.3 Hz, 1H), 2.16 (dd, J = 13.9, 9.9 Hz, 1H), 2.06 (dd, J = 14.0, 4.3 Hz, 1H), 1.41 (s, 9H), 1.34 (s, 3H), 1.32 (s, 9H), 1.24 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 176.5, 149.9, 139.3, 132.1, 131.9, 128.9, 127.0, 125.7, 118.6, 111.0, 97.5, 82.1, 80.2, 48.3, 43.1, 34.9, 34.1, 31.4, 28.1, 26.3, 25.6. **HRMS** (ESI) m/z calcd. for C₂₉H₃₆NO₂ [M + H]⁺ 430.2741, found 430.2732.

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(4-fluorophenyl)-2,2-dimethylhex-5-ynoate (15)



According to General Procedure **A** with 1-fluoro-4-vinylbenzene **11** (36.6 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **15** as a colorless oil (64.0 mg, 82% yield, 92% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 15.70 min, t_R (minor) = 17.02 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.59 (m, 2H), 7.50 (m, 2H), 7.39 (m, 2H), 7.05 (m, 2H), 3.93 (dd, J = 9.6, 4.3 Hz, 1H), 2.16 (dd, J = 13.8, 9.8 Hz, 1H), 2.05 (dd, J = 14.0, 4.2 Hz, 1H), 1.44 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.5, 161.8 (d, *J* = 245.4 Hz), 138.1 (d, *J* = 3.2 Hz), 132.0, 131.9, 128.9 (d, *J* = 8.0 Hz), 128.6, 118.6, 115.5 (d, *J* = 21.5 Hz), 111.2, 96.9, 82.4, 80.3, 48.4, 43.1, 34.7, 28.0, 26.3, 25.6.

¹⁹**F NMR** (376 MHz, CDCl₃) δ –114.47 – –116.70 (m, 1F).

HRMS (ESI) m/z calcd. for C₂₅H₂₇FNO₂ [M + H]⁺ 392.2020, found 392.2011.

(*R*)-*tert*-Butyl-4-(4-chlorophenyl)-6-(4-cyanophenyl)-2,2-dimethylhex-5-ynoate (16)



According to General Procedure A with 1-chloro-4-vinylbenzene 1m (41.6 mg, 0.30

mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 16 as a colorless oil (54.0 mg, 66% yield, 90% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 7.59 min, t_R (minor) = 8.85 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.61 – 7.58 (m, 2H), 7.51 – 7.47 (m, 2H), 7.39 – 7.30 (m, 4H), 3.92 (dd, J = 9.6, 4.4 Hz, 1H), 2.16 (dd, J = 13.9, 9.7 Hz, 1H), 2.04 (dd, J = 13.9, 4.4 Hz, 1H), 1.44 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.4, 140.9, 132.8, 132.1, 132.0, 128.9, 128.8, 128.5, 111.3, 96.5, 82.5, 80.3, 48.2, 43.1, 34.9, 28.0, 26.3, 25.6.

HRMS (ESI) *m/z* calcd. for C₂₅H₂₇ClNO₂ [M + H]⁺ 408.1725, found 408.1713.

(*S*)-*tert*-Butyl-4-(2-bromophenyl)-6-(4-cyanophenyl)-2,2-dimethylhex-5-ynoate (17)



According to General Procedure A with 1-bromo-2-vinylbenzene 1n (54.9 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 17 as a colorless oil (68.5 mg, 76% yield, 88% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.28 min, t_R (major) = 15.03 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 3H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.49 (dd, *J* = 10.2, 4.1 Hz, 1H), 2.35 – 2.12 (m, 1H), 2.04 – 1.91 (m, 1H), 1.41 (s, 9H), 1.36 (s, 3H), 1.33 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 141.4, 133.1, 132.1, 131.9, 129.5, 128.7, 128.6, 128.1, 122.92, 118.6, 111.2, 96.0, 82.2, 80.2, 45.7, 42.8, 34.8, 28.0, 26.9, 24.6. HRMS (ESI) *m/z* calcd. for C₂₅H₂₇BrNO₂ [M + H]⁺ 452.1220, found 452.1209.

(*R*)-*tert*-Butyl-4-(3-bromophenyl)-6-(4-cyanophenyl)-2,2-dimethylhex-5-ynoate (18)



According to General Procedure **A** with 1-bromo-3-vinylbenzene **10** (54.9 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **18** as a colorless oil (64.8 mg, 72% yield, 88% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.14 min, t_R (major) = 6.45 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.63 – 7.55 (m, 3H), 7.54 – 7.46 (m, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 3.91 (dd, *J* = 9.7, 4.3 Hz, 1H), 2.16 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.06 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.44 (s, 9H), 1.36 (s, 3H), 1.26 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.4, 144.7, 132.1, 132.0, 130.5, 130.3, 130.1, 128.4, 126.1, 122.7, 118.5, 111.3, 96.2, 82.7, 80.4, 48.1, 43.1, 35.1, 28.0, 26.3, 25.6. HRMS (ESI) *m/z* calcd. for C₂₅H₂₇BrNO₂ [M + H]⁺ 452.1220, found 452.1209.

(*R*)-*tert*-Butyl-4-(4-bromophenyl)-6-(4-cyanophenyl)-2,2-dimethylhex-5-ynoate (19)



According to General Procedure A with 1-bromo-4-vinylbenzene 1p (54.9 mg, 0.30 mmol, 1.5 equiv), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 19 as a colorless oil (65 mg, 72% yield, 92% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.04 min, t_R (minor) = 9.51 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 4H), 7.32 – 7.31 (m, 1H), 7.33 – 7.27 (m, 1H), 3.91 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.15 (dd, *J* = 13.9, 9.7 Hz, 1H), 2.04 (dd, *J* = 13.9, 4.4 Hz, 1H), 1.43 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.4, 141.4, 132.1, 132.0, 131.8, 129.2, 128.5, 120.8, 111.3, 96.4, 82.5, 80.3, 48.1, 43.1, 34.9, 28.0, 26.3, 25.6.

HRMS (ESI) m/z calcd. for C₂₅H₂₇BrNO₂ [M + H]⁺ 452.1220, found 452.1207.

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(3-(trifluoromethyl)phenyl)hex-5-ynoate (20)



According to General Procedure A with 1-(trifluoromethyl)-3-vinylbenzene 1q (51.6 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 20 as a colorless oil (63.7 mg, 72% yield, 86% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 16.91 min, t_R (minor) = 18.21 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.65 – 7.58 (m, 3H), 7.57 – 7.46 (m, 4H), 4.02 (dd, *J* = 9.8, 4.2 Hz, 1H), 2.19 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.08 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.44 (s, 9H), 1.38 (s, 3H), 1.27 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.4, 143.4, 132.1, 132.0, 131.1 (q, *J* = 32.2 Hz), 130.8, 129.3, 128.3, 124.2 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.5 Hz), 123.9 (q, *J* = 3.7 Hz), 118.5, 111.4, 95.9, 82.8, 80.5, 48.2, 43.1, 35.3, 28.0, 26.4, 25.6.

¹⁹F NMR (376 MHz, CDCl₃) δ –62.56 (s, 3F).

HRMS (ESI) m/z calcd. for C₂₆H₂₇F₃NO₂ [M + H]⁺ 442.1988, found 442.1979.

(R)-tert-Butyl-4-(3-cyanophenyl)-2,2-dimethyl-6-phenylhex-5-ynoate (21)



According to General Procedure A with 3-vinylbenzonitrile 1r (37.5 mg, 0.30 mmol, 1.5 equiv.), Phenylacetylene 2a (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 21 as a colorless oil (61.2 mg, 82% yield, 85% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.01 min, t_R (minor) = 17.43 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.37 – 7.29 (m, 3H), 3.97 (dd, *J* = 9.3, 4.5 Hz, 1H), 2.18 – 2.01 (m, 2H), 1.46 (s, 9H), 1.41 (s, 3H), 1.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 144.7, 132.1, 131.5, 131.1, 130.5, 129.4, 128.3, 128.2, 123.2, 118.9, 112.6, 90.5, 84.6, 80.4, 48.5, 43.2, 35.0, 28.1, 26.8, 25.2. HRMS (ESI) *m/z* calcd. for C₂₅H₂₈NO₂ [M + H]⁺ 374.2115, found 374.2104.

(*R*)-tert-Butyl-4-(3-formylphenyl)-2,2-dimethyl-6-phenylhex-5-ynoate (22)



According to General Procedure A with 3-vinylbenzaldehyde 1s (31.2 mg, 0.30 mmol, 1.5 equiv.), ethynylbenzene 2b (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 22 as a colorless oil (55.2 mg, 74% yield, 88% ee).

HPLC analysis: Chiralcel AY3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 18.24 min, t_R (major) = 21.72 min.

¹**H NMR** (400 MHz, CDCl₃) δ 10.06 (s, 1H), 8.00 (s, 1H), 7.78 (dd, J = 11.6, 7.8 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.49–7.39 (m, 2H), 7.36–7.26 (m, 3H), 4.03 (dd, J = 9.6, 4.2 Hz, 1H), 2.24–2.05 (m, 2H), 1.46 (s, 9H), 1.41 (s, 3H), 1.28 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ192.3, 176.6, 144.4, 136.8, 133.7, 131.5, 129.4, 128.6, 128.4, 128.2, 128.0, 123.5, 91.2, 84.2, 80.3, 48.5, 43.2, 35.1, 28.1, 26.6, 25.3. **HRMS** (ESI) m/z calcd. for C₂₅H₂₈NaO₃ [M + Na]⁺ 399.1931, found 399.1929.

(R)-tert-Butyl-4-(3-acetylphenyl)-2,2-dimethyl-6-phenylhex-5-ynoate (23)



According to General Procedure **A** with 1-(3-vinylphenyl)ethan-1-one **1t** (43.8 mg, 0.30 mmol, 1.5 equiv.), ethynylbenzene **2b** (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **23** as a colorless oil (66.7 mg, 85% yield, 95% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 19.05 min, t_R (minor) = 23.55 min.

¹**H NMR** (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.34 – 7.26 (m, 3H), 4.00 (dd, *J* = 9.7, 4.2 Hz, 1H), 2.64 (s, 3H), 2.18 (dd, *J* = 13.9, 9.7 Hz, 1H), 2.09 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.46 (s, 9H), 1.41 (s, 3H), 1.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 198.0, 176.6, 143.9, 137.5, 132.3, 131.5, 128.9, 128.2, 127.9, 127.3, 126.9, 123.6, 91.5, 84.1, 80.3, 48.5, 43.2, 35.3, 28.1, 26.7, 26.6, 25.4. HRMS (ESI) *m/z* calcd. for C₂₆H₃₁NaO₃ [M +Na]⁺ 413.2087, found 413.2075.

(*R*)-Methyl-3-(6-(*tert*-butoxy)-1-(4-cyanophenyl)-5,5-dimethyl-6-oxohex-1-yn-3-yl)benzoate (24)



According to General Procedure **A** with methyl 3-vinylbenzoate **1u** (48.7 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **24** as a colorless oil (45.1 mg, 52% yield, 89% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 18.84 min, t_R (minor) = 25.11 min.

¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 3.99 (dd, J = 9.8, 4.1 Hz, 1H), 3.95 – 3.88 (s, 3H), 2.19 (dd, J = 13.8, 10.0 Hz, 1H), 2.06 (dd, J = 14.0, 4.0 Hz, 1H), 1.54 – 1.38 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 176.4, 166.9, 142.9, 132.1, 132.0, 130.7, 128.9, 128.6,

128.5, 128.3, 118.6, 111.3, 96.4, 82.6, 80.4, 52.2, 48.1, 43.1, 35.3, 28.0, 26.3, 25.7. **HRMS** (ESI) m/z calcd. for C₂₇H₃₀NO₄ [M + H]⁺ 432.2169, found 432.2162.

(*S*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(2,5-dimethylphenyl)-2,2-dimethylhex-5ynoate (25)



According to General Procedure A with 1,4-dimethyl-2-vinylbenzene **1v** (39.7 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the

reaction mixture was purified by column chromatography on silica gel to yield the product **25** as a colorless oil (53.2 mg, 66% yield, 87% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 17.04 min, t_R (major) = 19.43 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H), 7.05 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 4.09 (dd, J = 10.3, 4.1 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 2.20 (dd, J = 13.9, 10.4 Hz, 1H), 1.90 (dd, J = 14.0, 4.1 Hz, 1H), 1.41 (s, 9H), 1.34 (s, 3H), 1.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 140.2, 136.0, 132.1, 131.9, 131.5, 130.7, 129.0, 128.5, 127.7, 118.7, 111.0, 97.6, 81.5, 80.2, 46.3, 43.0, 31.9, 28.0, 26.2, 25.7, 21.1, 19.0. HRMS (ESI) *m/z* calcd. for C₂₇H₃₂NO₂ [M + H]⁺ 402.2428, found 402.2417.

(*R*)-*tert*-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(naphthalen-2-yl)hex-5-ynoate (26)



According to General Procedure A with 2-vinylnaphthalene 1w (46.2 mg, 0.30 mmol, 1.5 equiv), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 26 as a colorless oil (56.0 mg, 66% yield, 86% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.99 min, t_R (minor) = 9.70 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.83 (t, J = 8.3 Hz, 4H), 7.57 – 7.52 (m, 3H), 7.50 – 7.42 (m, 4H), 4.09 (dd, J = 9.6, 4.4 Hz, 1H), 2.26 (dd, J = 13.9, 9.6 Hz, 1H), 2.15 (dd, J = 14.0, 4.5 Hz, 1H), 1.42 (s, 9H), 1.37 (s, 3H), 1.26 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 139.7, 133.5, 132.6, 132.1, 132.0, 128.8, 128.6, 127.8, 127.7, 126.3, 125.9, 125.81, 125.75, 118.6, 111.1, 97.2, 82.5, 80.3, 48.1, 43.2, 35.6, 28.1, 26.3, 25.7.

HRMS (ESI) m/z calcd. for C₂₉H₃₀NO₂ [M + H]⁺ 424.2271, found 424.2262.

(*R*)-*tert*-Butyl-4-(benzo[*d*][1,3]dioxol-5-yl)-6-(4-cyanophenyl)-2,2-dimethylhex-5ynoate (27)



According to General Procedure A with 5-vinylbenzo[d][1,3]dioxole 1x (44.4 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 27 as a colorless oil (70.8 mg, 85% yield, 87% ee).

HPLC analysis: Chiralcel IF (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), *t*_R (major) = 27.67 min, *t*_R (minor) = 30.69 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 1.5 Hz, 1H), 6.82 (d, J = 1.6 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 3.84 (dd, J = 9.6, 4.5 Hz, 1H), 2.14 (dd, J = 13.9, 9.7 Hz, 1H), 2.02 (dd, J = 13.9, 4.5 Hz, 1H), 1.42 (s, 9H), 1.32 (s, 3H), 1.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 147.9, 146.5, 136.3, 132.1, 131.9, 128.7, 120.4, 118.6, 111.1, 108.3, 107.9, 101.1, 97.2, 82.1, 80.2, 48.4, 43.0, 35.1, 28.0, 26.2, 25.7. HRMS (ESI) *m/z* calcd. for C₂₆H₂₈NO₄ [M + H]⁺ 418.2013, found 418.2002.

(*R*)-*tert*-Butyl-4-(4-(1*H*-pyrazol-1-yl)phenyl)-7-acetoxy-2,2-dimethylhept-5ynoate (28)



According to General Procedure A with 1-(4-vinylphenyl)-1*H*-pyrazole 1y (51.0 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-yl acetate 2za (19.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 28 as a colorless oil (37.7 mg, 46% yield, 90% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 22.61 min, t_R (minor) = 24.04 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 2.2 Hz, 1H), 7.73 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 6.55 – 6.40 (m, 1H), 4.72 (s, 2H), 3.83 – 3.69 (m, 1H), 2.09 (s, 3H), 2.08 – 1.91 (m, 2H), 1.47 (s, 9H), 1.30 (s, 3H), 1.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 170.3, 141.0, 140.9, 139.0, 128.4, 126.7, 119.4, 107.6, 89.0, 80.2, 52.7, 48.1, 43.1, 34.2, 28.0, 26.3, 25.4, 20.8. HRMS (ESI) *m/z* calcd. for C₂₄H₃₁N₂O₄ [M + H]⁺ 411.2278, found 411.2276.

(S)-tert-butyl -6-(4-cyanophenyl)-4-(furan-3-yl)-2,2-dimethylhex-5-ynoate (29)



According to General Procedure A with 3-vinylfuran 1z (28.0 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 29 as a colorless oil (43.4 mg, 60% yield, 85% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 24.03 min, t_R (minor) = 25.61 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.44– 7.39 (m, 2H), 6.45 (s, 1H), 3.86 (dd, *J* = 7.8, 6.0 Hz, 1H), 2.12 (d, *J* = 2.6 Hz, 1H), 2.11 (s, 1H), 1.43 (s, 9H), 1.34 (s, 3H), 1.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 143.3, 139.1, 132.1, 131.9, 128.6, 126.3, 118.6, 111.2, 109.8, 96.5, 80.9, 80.2, 46.4, 42.9, 28.0, 26.3, 26.0, 25.5.

HRMS (ESI) m/z calcd. for C₂₃H₂₆NO₃ [M + H]⁺ 364.1907, found 364.1899.

(*S*)-*tert*-Butyl-4-(benzofuran-3-yl)-6-(4-cyanophenyl)-2,2-dimethylhex-5-ynoate (30)



According to General Procedure A with 3-vinylbenzofuran 1za (43.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 30 as a colorless oil (53.0 mg, 64% yield, 96% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.96 min, t_R (major) = 11.35 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.85 – 7.75 (m, 1H), 7.63 – 7.52 (m, 3H), 7.52 – 7.41 (m, 3H), 7.36 – 7.24 (m, 2H), 4.17 (t, *J* = 7.1 Hz, 1H), 2.28 (d, *J* = 7.1 Hz, 2H), 1.38 (m, 12H), 1.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.4, 155.8, 141.4, 132.1, 132.0 128.5, 126.4, 124.6, 122.6, 121.0, 120.2, 118.6, 111.8, 111.3, 95.6, 81.4, 80.3, 45.0, 42.9, 28.0, 26.3, 25.7, 25.5.

HRMS (ESI) m/z calcd. for C₂₇H₂₈NO₃ [M + H]⁺ 414.2064, found 414.2061.

(S)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(thiophen-3-yl)hex-5-ynoate (31)



According to General Procedure A with 3-vinylthiophene **1zb** (33.0 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **31** as a colorless oil (53.3 mg, 70% yield, 92% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 23.88 min, t_R (minor) = 26.22 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.32 (dd, J = 5.0, 3.0 Hz, 1H), 7.22 (d, J = 2.9 Hz, 1H), 7.14 (dd, J = 5.0, 1.2 Hz, 1H), 4.04 (dd, J = 8.8, 5.1 Hz, 1H), 2.23 – 2.09 (m, 2H), 1.44 (s, 9H), 1.35 (s, 3H), 1.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.5, 142.4, 132.1, 131.9, 128.7, 126.9, 126.2, 120.9, 118.6, 111.2, 96.9, 81.7, 80.2, 47.2, 43.0, 30.7, 28.1, 26.2, 25.6.

HRMS (ESI) m/z calcd. for C₂₃H₂₆NO₂S [M + H]⁺ 380.1679, found 380.1670.

(S)-tert-Butyl-4-(benzo[b]thiophen-3-yl)-6-(4-cyanophenyl)-2,2-dimethylhex-5ynoate (32)



According to General Procedure A with 3-vinylbenzo[*b*]thiophene **1zc** (48.0 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **32** as a colorless oil (65.7 mg, 77% yield, 92% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 21.15 min, t_R (minor) = 26.49 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.58 – 7.51 (m, 2H), 7.48–7.45 (m, 1H), 7.45–7.43 (m, 1H), 7.43–7.40 (m, 1H), 7.39 (s, 1H),

7.39 – 7.33 (m, 1H), 4.37 (dd, *J* = 9.9, 4.5 Hz, 1H), 2.32 (dd, *J* = 14.0, 9.9 Hz, 1H), 2.22 (dd, *J* = 14.0, 4.6 Hz, 1H), 1.41 (s, 9H), 1.38 (s, 3H), 1.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 141.0, 137.2, 135.9, 132.1, 131.9, 128.6, 124.5, 124.1, 123.2, 122.9, 122.2, 118.6, 111.2, 96.0, 82.0, 80.4, 45.2, 42.9, 29.7, 28.1, 26.1, 26.0.

HRMS (ESI) m/z calcd. for C₂₇H₂₈NO₂S [M + H]⁺ 430.1835, found 430.1833.

(S)-tert-Butyl-7-acetoxy-2,2-dimethyl-4-(pyridin-3-yl)hept-5-ynoate (33)



According to General Procedure A with 3-vinylpyridine 1zd (31.6 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-yl acetate 2za (19.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 33 as a colorless oil (62.8 mg, 91% yield, 94% ee).

HPLC analysis: Chiralcel AZ3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 42.28 min, t_R (major) = 50.18 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 1.9 Hz, 1H), 8.50 – 8.42 (m, 1H), 7.75 – 7.60 (m, 1H), 7.23 (dd, J = 7.9, 4.8 Hz, 1H), 4.66 (d, J = 2.0 Hz, 2H), 3.77 – 67 (m, 1H), 2.05 (s, 3H), 2.04 – 1.90 (m, 2H), 1.42 (s, 9H), 1.27 (s, 3H), 1.16 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.3, 170.2, 149.0, 148.2, 138.0, 134.9, 123.5, 88.0, 80.3, 77.7, 52.5, 47.8, 43.0, 32.3, 28.0, 26.4, 25.2, 20.7.

HRMS (ESI) m/z calcd. for C₂₀H₂₈NO₄ [M + H]⁺ 346.2013, found 346.2005.

(S)-tert-Butyl-6-(4-cyanophenyl)-2,2-dimethyl-4-(quinolin-3-yl)hex-5-ynoate (34)



According to General Procedure A with 3-vinylquinoline **1ze** (46.5 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **34** as a colorless oil (55.5 mg, 65% yield, 85% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 26.20 min, t_R (major) = 29.21 min.

¹**H** NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.20 – 8.05 (m, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.58 (m, 3H), 7.51 (d, J = 8.3 Hz, 2H), 4.17 (dd, J = 9.5, 4.5 Hz, 1H), 2.28 (dd, J = 14.0, 9.6 Hz, 1H), 2.19 (dd, J = 14.0, 4.5 Hz, 1H), 1.41 (s, 9H), 1.40 (s, 3H), 1.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.3, 150.6, 147.3, 135.0, 133.7, 132.1, 132.0, 129.4, 129.2, 128.2, 127.9, 127.7, 127.0, 118.5, 111.5, 95.7, 82.3, 80.5, 47.8, 43.1, 33.3, 28.0, 26.4, 25.6.

HRMS (ESI) m/z calcd. for C₂₈H₂₉N₂O₂ [M + H]⁺ 425.2224, found 425.2214.

(S)-tert-Butyl-7-acetoxy-2,2-dimethyl-4-(thiazol-4-yl)hept-5-ynoate (35)



According to General Procedure A with 4-vinylthiazole 1zf (33.3 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-yl acetate 2za (19.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 35 as a colorless oil (36.2 mg, 52% yield, 83% ee).

HPLC analysis: Chiralcel AZ3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.75 min, t_R (minor) = 21.10 min.

¹**H NMR** (400 MHz, CDCl₃) 8.77 (s, 1H), 7.28 – 7.24 (m, 1H), 4.74 – 4.67 (m, 2H), 4.10 – 3.97 (m, 1H), 2.27 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.09 (s, 3H), 1.45 (s, 9H), 1.27 (s, 3H), 1.21 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 170.3, 157.5, 153.0, 114.3, 87.9, 80.1, 77.2, 52.8, 45.1, 42.7, 31.1, 28.0, 25.8, 25.4, 20.8.

HRMS (ESI) m/z calcd. for C₁₈H₂₆NO₄S [M + H]⁺ 352.1577, found 352.1575.

(*S*)-*tert*-Butyl-6-(4-cyanophenyl)-4-(diethylcarbamoyl)-2,2-dimethylhex-5-ynoate (36)



According to General Procedure A with *N*,*N*-diethylacrylamide **1zg** (101.6 mg, 0.80 mmol, 4.0 equiv), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **36** as a colorless oil (15.7 mg, 20% yield, 81% ee).

HPLC analysis: Chiralcel AZ3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 38.01 min, t_R (minor) = 50.23 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 3.73 (t, J = 6.1 Hz, 1H), 3.62 - 3.50 (m, 1H), 3.49 - 3.34 (m, 3H), 2.41 (dd, J = 14.2, 6.0 Hz, 1H), 2.17 (dd, J = 14.2, 6.3 Hz, 1H), 1.45 (s, 9H), 1.32 - 1.26 (m, 6H), 1.20 - 1.12 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 176.7, 168.3, 132.2, 131.9, 128.2, 118.5, 111.4, 93.1, 81.3, 80.3, 42.8, 42.3, 41.5, 41.1, 32.7, 28.0, 26.1, 25.0, 14.4, 12.7.

HRMS (ESI) m/z calcd. for C₂₄H₃₂N₂O₃ [M + H]⁺ 397.2486, found 397.2486.

(*S*)-*tert*-butyl-7-(9*H*-carbazol-9-yl)-2,2-dimethyl-4-((triisopropylsilyl)ethynyl)hept -5-ynoate (37)



According to General Procedure A with but-3-en-1-yn-1-yltriisopropylsilane 1zh (62.4 mg, 0.3 mmol, 1.5 equiv.), 9-(prop-2-yn-1-yl)-9*H*-carbazole 2v (41.0 mg, 0.2 mmol, 1.0 equiv.) and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.), after 18 h, the reaction mixture was purified by the column chromatography on silica gel to yield the product 37 as a yellow oil (73.3 mg, 66% yield, 65% ee).

HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 97/3, flow rate 0.2 mL/min, $\lambda = 254$ nm), t_R (minor) = 19.86 min, t_R (major) = 20.67 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.19 – 8.09 (m, 2H), 7.56 – 7.46 (m, 4H), 7.32 – 7.26 (m, 2H), 5.05 (d, J = 2.0 Hz, 2H), 3.46 – 3.34 (m, 1H), 2.06 (dd, J = 13.9, 6.4 Hz, 1H), 1.96 (dd, J = 13.9, 6.5 Hz, 1H), 1.41 (s, 9H), 1.19 (s, 3H), 1.16 (s, 3H), 1.10 – 1.02 (m, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 176.3, 140.0, 125.8, 123.2, 120.3, 119.3, 108.9, 106.7, 83.3, 81.7, 80.3, 75.0, 45.7, 42.9, 32.8, 27.9, 26.0, 24.8, 21.2, 18.6, 11.2. HRMS (ESI) m/z calcd. for C₃₆H₄₉NO₂Si [M + Na]⁺ 578.3425, found 578.3422.

(S)-9-(4-benzyl-6,6,6-trifluorohex-2-yn-1-yl)-9H-carbazole (38)



According to General Procedure **B** with allylbenzene **1zi** (35.4 mg, 0.3 mmol, 1.5 equiv.), 9-(prop-2-yn-1-yl)-9*H*-carbazole **2v** (41.0 mg, 0.2 mmol, 1.0 equiv.), and **3h** 1- (trifluoromethyl)- $1\lambda^3$ -benzo[*d*][1,2]iodaoxol-3(1*H*)-one (75.8 mg, 0.24 mmol, 1.2 equiv.), after 60 h, the reaction mixture was purified by the column chromatography on silica gel to yield the product **38** as a white solid (44.4 mg, 69% yield, 20% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.98 min, t_R (major) = 11.90 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.18 – 8.10 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.33 – 7.29 (m, 2H), 7.21 – 7.08 (m, 3H), 7.05 – 6.99 (m, 2H), 5.02 (d, J = 2.0 Hz, 2H), 2.95 (tt, J = 8.0, 6.3 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.32-2.10 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 137.5, 129.3, 128.3, 126.8, 126.1 (q, J = 276.0 Hz), 125.9, 123.2, 120.4, 119.4, 108.9, 84.0, 72.3, 40.6, 38.0 (q, J = 28.0 Hz), 32.5, 27.7 (q, J = 2.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ –63.93 (t, J = 10.5 Hz, 3F).

HRMS (ESI) m/z calcd. for $C_{25}H_{20}F_{3}N [M + H]^+$ 392.1621, found 392.1618.

Substrates scope of alkyne

(*R*)-*tert*-Butyl-2,2-dimethyl-4,6-diphenylhex-5-ynoate (39)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), ethynylbenzene 2b (20.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 39 as a colorless oil (57.1 mg, 82% yield, 96% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 6.24 min, t_R (minor) = 9.71 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.52 – 7.44 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.26 (m, 4H), 3.95 (dd, *J* = 9.6, 4.3 Hz, 1H), 2.19 (dd, *J* = 13.9, 9.7 Hz, 1H), 2.11 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.49 (s, 9H), 1.42 (s, 3H), 1.30 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.7, 143.3, 131.5, 128.6, 128.2, 127.8, 127.5, 126.7, 123.9, 92.2, 83.6, 80.1, 48.8, 43.3, 35.3, 28.1, 26.6, 25.4.

HRMS (ESI) m/z calcd. for C₂₄H₂₉O₂ [M + H]⁺ 349.2162, found 349.2159.

(R)-tert-Butyl-2,2-dimethyl-4-phenyl-6-(p-tolyl)hex-5-ynoate (40)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-4-methylbenzene 2c (23.2 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 40 as a colorless oil (49.8 mg, 69% yield, 96% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 4.45 min, *t*_R (minor) = 6.67 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 7.7 Hz, 2H), 7.37 (dd, J = 13.1, 7.3 Hz, 4H),

7.28 (t, *J* = 6.9 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.93 (dd, *J* = 9.5, 4.0 Hz, 1H), 2.37 (s, 3H), 2.18 (dd, *J* = 13.4, 10.8 Hz, 1H), 2.10 (dd, *J* = 13.8, 3.6 Hz, 1H), 1.48 (s, 9H), 1.41 (s, 3H), 1.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.4, 137.7, 131.4, 128.9, 128.6, 127.5, 126.7, 120.8, 91.4, 83.7, 80.1, 48.8, 43.3, 35.3, 28.1, 26.6, 25.4, 21.5.

HRMS (ESI) m/z calcd. for C₂₅H₃₀NaO₂ [M + Na]⁺ 385.2138, found 385.2136.

(R)-tert-Butyl-6-(2-methoxyphenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (41)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-2-methoxybenzene 2d (39.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 36 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 41 as a colorless oil (34.2 mg, 45% yield, 95% ee).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 8.60 min, t_R (minor) = 9.42 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.54 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 – 7.21 (m, 2H), 6.90 (dd, J = 16.5, 8.0 Hz, 2H), 3.97 (t, J = 6.8 Hz, 1H), 3.88 (s, 3H), 2.15 (d, J = 6.9 Hz, 2H), 1.47 (s, 9H), 1.43 (s, 3H), 1.28 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 176.9, 160.2, 143.4, 133.3, 129.1, 128.5, 127.6, 126.6, 120.3, 113.2, 110.7, 96.4, 80.04, 80.02, 55.7, 49.0, 43.3, 35.6, 28.1, 26.9, 24.9. **HRMS** (ESI) m/z calcd. for C₂₅H₃₀NaO₃ [M + Na]⁺ 401.2087, found 401.2086.

(R)-tert-Butyl-6-(3-methoxyphenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (42)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-3-methoxybenzene 2e (39.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 42 as a colorless oil (62.7 mg, 83% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 10.01 min, t_R (minor) = 14.21 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 7.9, 6.8 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.06 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.99 (d, *J* = 1.1 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.94 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.82 (s, 3H), 2.19 (dd, *J* = 13.9, 9.6 Hz, 1H), 2.11 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.48 (s, 9H),

1.41 (s, 3H), 1.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 159.3, 143.2, 129.2, 128.6, 127.5, 126.8, 124.9, 124.1, 116.4, 114.3, 92.1, 83.5, 80.1, 55.3, 48.7, 43.2, 35.3, 28.1, 26.6, 25.4. HRMS (ESI) *m/z* calcd. for C₂₅H₃₀NaO₃ [M + Na]⁺ 401.2087, found 401.2085.

(R)-tert-Butyl-6-(4-methoxyphenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (43)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-4-methoxybenzene 2f (39.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 43 as a colorless oil (62.1 mg, 82% yield, 95% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 99 /1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.09 min, t_R (minor) = 6.83 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.4 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.31 – 7.25 (m, 1H), 6.88 – 6.79 (m, 2H), 3.92 (dd, J = 9.7, 4.3 Hz, 1H), 3.82 (s, 3H), 2.17 (dd, J = 13.9, 9.7 Hz, 1H), 2.09 (dd, J = 13.9, 4.3 Hz, 1H), 1.48 (s, 9H), 1.41 (s, 3H), 1.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 159.2, 143.5, 132.9, 128.6, 127.5, 126.7, 116.1, 113.8, 90.6, 83.4, 80.1, 55.3, 48.8, 43.2, 35.3, 28.1, 26.5, 25.4.

HRMS (ESI) m/z calcd. for C₂₅H₃₀NaO₃ [M + Na]⁺ 401.2087, found 401.2086.

(R)-tert-Butyl-6-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-4-phenylhex-5-ynoate (44)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynyl-1,1'-biphenyl 2g (35.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 44 as a colorless oil (59.6 mg, 70% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 4.94 min, *t*_R (minor) = 6.59 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 – 7.46 (m, 10H), 7.45 – 7.37 (m, 3H), 7.34 – 7.26 (m, 1H), 4.00 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.23 (dd, *J* = 13.8, 9.8 Hz, 1H), 2.15 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.52 (s, 9H), 1.46 (s, 3H), 1.33 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.3, 140.5, 140.5, 132.0, 128.9, 128.7, 127.6, 127.5, 127.0, 126.9, 126.8, 122.9, 93.0, 83.5, 80.2, 48.8, 43.3, 35.5, 28.1, 26.6, 25.5.

HRMS (ESI) m/z calcd. for C₃₀H₃₂NaO₂ [M + Na]⁺ 447.2295, found 447.2293.

(R)-tert-Butyl-6-(4-fluorophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (45)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-4-fluorobenzene 2h (24 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 45 as a colorless oil (59.9 mg, 82% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 4.65 min, *t*_R (minor) = 5.80 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.50 – 7.34 (m, 6H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 8.4 Hz, 2H), 3.92 (dd, *J* = 9.8, 4.2 Hz, 1H), 2.19 (dd, *J* = 13.9, 9.9 Hz, 1H), 2.08 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.47 (s, 9H), 1.40 (s, 3H), 1.29 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.7, 162.2 (d, *J* = 248.4 Hz), 143.1, 133.3 (d, *J* = 8.2 Hz), 128.7, 127.4, 126.8, 119.9 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 22.0 Hz), 91.8, 82.5, 80.1, 48.6, 43.2, 35.3, 28.1, 26.4, 25.6.

¹⁹F NMR (376 MHz, CDCl₃) δ –111.86 – –112.06 (m, 1F).

HRMS (ESI) *m/z* calcd. for C₂₄H₂₇FNaO₂ [M + Na]⁺ 389.1887, found 389.1886.

(R)-tert-Butyl-6-(2-chlorophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (46)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-chloro-2-ethynylbenzene 2i (27.3 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 46 as a colorless oil (58.8 mg, 77% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 4.31 min, t_R (minor) = 6.19 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.38 – 7.31 (m, 3H), 7.26 – 7.13 (m, 3H), 3.93 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.16 (dd, *J* = 13.9, 9.6 Hz, 1H), 2.09 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.43 (s, 9H), 1.38 (s, 3H), 1.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.7, 142.9, 135.9, 133.3, 129.2, 128.7, 128.6, 127.5, 126.8, 126.3, 123.7, 97.7, 80.7, 80.1, 48.8, 43.3, 35.5, 28.0, 26.7, 25.3.

HRMS (ESI) m/z calcd. for C₂₄H₂₇ClNaO₂ [M + Na]⁺ 405.1592, found 405.1591.

(R)-tert-Butyl-6-(3-chlorophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (47)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-chloro-3-ethynylbenzene 2j (27.3 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 47 as a colorless oil (61.3 mg, 80% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 5.81 min, t_R (minor) = 8.20 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.48 – 7.43 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.21 (m, 4H), 3.93 (dd, *J* = 9.7, 4.2 Hz, 1H), 2.18 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.10 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.48 (s, 9H), 1.40 (s, 3H), 1.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 142.9, 134.0, 131.4, 129.7, 129.4, 128.7, 128.0, 127.4, 126.9, 125.6, 93.7, 82.3, 80.2, 48.6, 43.2, 35.3, 28.1, 26.5, 25.5.

HRMS (ESI) m/z calcd. for C₂₄H₂₇ClNaO₂ [M + Na]⁺ 405.1592, found 405.1591.

(R)-tert-Butyl-6-(4-chlorophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (48)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-chloro-4-ethynylbenzene 2k (27.3 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 48 as a colorless oil (58.9 mg, 77% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 5.88 min, *t*_R (minor) = 7.66 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 7.6 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.31 – 7.25 (m, 3H), 3.93 (dd, J = 9.8, 4.2 Hz, 1H), 2.19 (dd, J = 13.9, 9.9 Hz, 1H), 2.08 (dd, J = 13.9, 4.2 Hz, 1H), 1.47 (s, 9H), 1.39 (s, 3H), 1.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 143.0, 133.7, 132.8, 128.7, 128.5, 127.4, 126.8, 122.4, 93.3, 82.5, 80.1, 48.6, 43.2, 35.3, 28.1, 26.4, 25.6.

HRMS (ESI) m/z calcd. for C₂₄H₂₈ClO₂ [M + H]⁺ 383.1772, found 383.1771.

(*R*)-methyl-4-(6-(*tert*-butoxy)-5,5-dimethyl-6-oxo-3-phenylhex-1-yn-1-yl)benzoate (49)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), methyl 4-ethynylbenzoate 2l (25.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 49 as a colorless oil (52.9 mg, 65% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 10.27 min, *t*_R (minor) = 13.62 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.5 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 – 7.21 (m, 1H), 3.94 – 3.87 (m, 4H), 2.17 (dd, J = 13.9, 9.8 Hz, 1H), 2.06 (dd, J = 13.9, 4.3 Hz, 1H), 1.42 (s, 9H), 1.35 (s, 3H), 1.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 166.7, 142.8, 131.4, 129.4, 129.1, 128.7, 128.6, 127.4, 126.9, 95.6, 83.0, 80.2, 52.2, 48.5, 43.2, 35.4, 28.1, 26. 3, 25.6.

HRMS (ESI) m/z calcd. for C₂₆H₃₀NaO₄ [M + Na]⁺ 429.2036, found 429.2034.

(R)-tert-Butyl-6-(4-formylphenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (50)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzaldehyde 2m (26 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 50 as a colorless oil (53.5 mg, 71% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 280 nm), t_R (major) = 17.20 min, t_R (minor) = 22.91 min.

¹**H NMR** (600 MHz, CDCl₃) δ 9.98 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 3.93 (dd, *J* = 9.9, 4.1 Hz, 1H), 2.18 (dd, *J* = 13.9, 10.0 Hz, 1H), 2.06 (dd, *J* = 14.0, 4.1 Hz, 1H), 1.43 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 191.5, 176.6, 142.6, 135.1, 132.1, 130.2, 129.5, 128.7, 127.4, 126.9, 96.9, 82.9, 80.2, 48.4, 43.2, 35.5, 28.1, 26.3, 25.6.

HRMS (ESI) m/z calcd. for C₂₅H₂₉O₃ [M + H]⁺ 377.2111, found 377.2112.

(R)-tert-Butyl-2,2-dimethyl-6-(4-nitrophenyl)-4-phenylhex-5-ynoate (51)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynyl-4-nitrobenzene 2n (29.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 51 as a colorless oil (36.3 mg, 46% yield, 93% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 300 nm), *t*_R (major) = 12.58 min, *t*_R (minor) = 14.55 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 3.94 (dd, J = 9.8, 4.3 Hz, 1H), 2.20 (dd, J = 13.9, 9.9 Hz, 1H), 2.06 (dd, J = 14.0, 4.3 Hz, 1H), 1.43 (s, 9H), 1.35 (s, 3H), 1.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 146.8, 142.3, 132.3, 130.8, 128.8, 127.4, 127.1, 123.5, 98.2, 82.1, 80.3, 48.3, 43.1, 35.5, 28.1, 26.2, 25.8.

HRMS (ESI) m/z calcd. for C₂₄H₂₇NNaO₄ [M + Na]⁺ 416.1832, found 416.1833.

(*R*)-*tert*-Butyl-2,2-dimethyl-4-phenyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-5-ynoate (52)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 2o (45.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 52 as a colorless oil (65.7 mg, 69% yield, 96% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 6.90 min, *t*_R (minor) = 8.17 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.46 (dd, *J* = 12.1, 7.8 Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.24 (m, 1H), 3.94 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.19 (dd, *J* = 13.7, 9.9 Hz, 1H), 2.09 (dd, *J* = 13.8, 3.9 Hz, 1H), 1.47 (s, 9H), 1.40 (s, 3H), 1.37 (s, 12H), 1.28 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 176.7, 143.1, 134.5, 130.7, 128.7, 127.5, 126.8, 126.7, 93.7, 83.9, 83.8, 80.1, 48.7, 43.2, 35.4, 28.1, 26.5, 25.5, 24.9.

HRMS (ESI) *m/z* calcd. for C₃₀H₃₉BNaO₄ [M + Na]⁺ 497.2834, found 497.2835.

(*R*)-*tert*-Butyl-6-(6-methoxynaphthalen-2-yl)-2,2-dimethyl-4-phenylhex-5-ynoate (53)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 2-ethynyl-6-methoxynaphthalene 2p (36.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 53 as a colorless oil (62.9 mg, 74% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 6.63 min, t_R (minor) = 8.99 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.63 (dd, J = 11.3, 8.8 Hz, 2H), 7.51 – 7.40 (m, 3H), 7.34 (t, J = 7.6 Hz, 2H), 7.27 – 7.20 (m, 1H), 7.12 (dd, J = 8.9, 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 3.93 (dd, J = 9.7, 4.0 Hz, 1H), 3.87 (s, 3H), 2.18 (dd, J = 13.9, 9.8 Hz, 1H), 2.08 (dd, J = 13.9, 4.2 Hz, 1H), 1.43 (s, 9H), 1.39 (s, 3H), 1.27 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 176.8, 158.1, 143.4, 133.9, 130.9, 129.2, 128.7, 128.5, 127.5, 126.8, 126.7, 119.3, 118.9, 105.8, 91.8, 84.1, 80.1, 55.3, 48.8, 43.3, 35.5, 28.1,

26.5, 25.5.

HRMS (ESI) m/z calcd. for C₂₉H₃₂NaO₃ [M + Na]⁺ 451.2244, found 451.2243.

(R)-6-(tert-Butyl-2,2-dimethyl-4-phenylhex-5-ynoate)ferrocene (54)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 1-ethynylferrocene 2q (42 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 54 as a colorless oil (78.6 mg, 86% yield, 94% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 7.76 min, t_R (minor) = 8.18 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 4.43 (s, 2H), 4.24 (s, 5H), 4.19 (s, 2H), 3.83 (dd, *J* = 8.5, 5.0 Hz, 1H), 2.19 – 2.04 (m, 2H), 1.52 (s, 9H), 1.45 (s, 3H), 1.30 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.7, 128.6, 127.5, 126.6, 88.4, 81.7, 80.1, 71.2, 69.7, 68.3, 66.4, 49.0, 43.4, 35.5, 28.2, 27.1, 25.0.

HRMS (ESI) *m/z* calcd. for C₂₈H₃₂FeO₂ [M]⁺ 456.1746, found 456.1745.
(R)-tert-Butyl-2,2-dimethyl-4-phenyl-6-(pyridin-3-yl)hex-5-ynoate (55)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 3-ethynylpyridine 2r (20.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 55 as a colorless oil (36.8 mg, 53% yield, 96% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 25.53 min, *t*_R (minor) = 27.43 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 8.49 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 3.91 (dd, *J* = 9.8, 4.3 Hz, 1H), 2.17 (dd, *J* = 13.9, 9.8 Hz, 1H), 2.06 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.43 (s, 9H), 1.35 (s, 3H), 1.24 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 152.2, 148.1, 142.7, 138.5, 128.7, 127.4, 126.9, 123.0, 95.9, 80.3, 80.2, 48.4, 43.2, 35.4, 28.1, 26.3, 25.6.

HRMS (ESI) m/z calcd. for C₂₃H₂₈NO₂ [M + H]⁺ 350.2115, found 350.2113.

(R)-tert-Butyl-2,2-dimethyl-4-phenyl-6-(thiophen-2-yl)hex-5-ynoate (56)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 2-ethynylthiophene 2s (21.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 56 as a colorless oil (34.1 mg, 48% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 270 nm), *t*_R (major) = 7.90 min, *t*_R (minor) = 9.42 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.21 (dd, *J* = 5.2, 0.9 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.93 (dd, *J* = 9.5, 4.3 Hz, 1H), 2.16 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.09 (dd, *J* = 13.9, 4.4 Hz, 1H), 1.47 (s, 9H), 1.37 (s, 3H), 1.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 142.9, 131.2, 128.7, 127.4, 126.8, 126.8, 126.2, 123.9, 96.2, 80.2, 76.8, 48.5, 43.2, 35.5, 28.1, 26.6, 25.3.

HRMS (ESI) m/z calcd. for C₂₂H₂₇O₂S [M + H]⁺ 355.1726, found 355.1726.

(*R*)-*tert*-Butyl-6-(imidazo[1,2-*b*]pyridazin-3-yl)-2,2-dimethyl-4-phenylhex-5-ynoate (57)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 3-ethynylimidazo[1,2-*b*]pyridazine 2t (28.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 57 as a colorless oil (52.8 mg, 68% yield, 93% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 8.28 min, t_R (minor) = 10.19 min.

¹**H NMR** (400 MHz, CDCl₃) δ 8.41 (d, J = 4.2 Hz, 1H), 7.93 (d, J = 9.8 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.05 (dd, J = 9.1, 4.4 Hz, 1H), 4.07 (dd, J = 9.4, 4.3 Hz, 1H), 2.24 (dd, J = 13.9, 9.4 Hz, 1H), 2.16 (dd, J = 14.0, 4.3 Hz, 1H), 1.44 (s, 9H), 1.40 (s, 3H), 1.26 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 143.6, 142.5, 137.7, 128.7, 127.5, 126.9, 125.7, 117.2, 102.2, 80.2, 70.4, 48.6, 43.3, 35.8, 28.2, 26.7, 25.2.

HRMS (ESI) m/z calcd. for C₂₄H₂₈N₃O₂ [M + H]⁺ 390.2176, found 390.2175.

(R)-tert-Butyl-8-cyano-2,2-dimethyl-4,8,8-triphenyloct-5-ynoate (58)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 2,2-diphenylpent-4-ynenitrile 2u (46.2 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 58 as a colorless oil (86.0 mg, 90% yield, 89% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 7.15 min, t_R (major) = 8.07 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.47 – 7.42 (m, 4H), 7.42 – 7.33 (m, 6H), 7.30 – 7.25 (m, 2H), 7.22 (t, *J* = 6.2 Hz, 3H), 3.59 (dd, *J* = 9.1, 1.8 Hz, 1H), 3.32 (d, *J* = 1.8 Hz, 2H), 1.98 (dd, *J* = 13.9, 4.0 Hz, 1H), 1.90 (dd, *J* = 13.8, 9.4 Hz, 1H), 1.48 (s, 9H), 1.22 (s, 3H), 1.12 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.1, 139.3, 139.2, 128.9, 128.8, 128.5, 128.2, 128.2, 127.4, 127.3, 127.2, 126.5, 122.0, 87.8, 80.0, 77.6, 51.7, 48.5, 43.2, 34.6, 31.5, 28.1, 26.8, 24.7.

HRMS (ESI) m/z calcd. for C₃₃H₃₅NNaO₂ [M + Na]⁺ 500.2560, found 500.2561.



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 9-(prop-2-yn-1-yl)-9*H*-carbazole 2v (41.0 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 59 as a colorless oil (76.7 mg, 85% yield, 96% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.11 min, t_R (major) = 6.28 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 7.6 Hz, 2H), 7.62 – 7.47 (m, 4H), 7.38 – 7.39 (m, 6H), 7.29 – 7.22(m, 1H), 5.10 (d, J = 1.8 Hz, 2H), 3.73 – 3.64 (m, 1H), 2.01 (d, J = 5.3 Hz, 2H), 1.49 (s, 9H), 1.23 (s, 3H), 1.16 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.7, 142.8, 140.1, 128.6, 127.4, 126.8, 125.8, 123.3, 120.4, 119.4, 109.1, 86.8, 80.1, 48.3, 43.1, 34.7, 33.0, 28.1, 26.4, 25.2.

HRMS (ESI) m/z calcd. for C₃₁H₃₄NO₂ [M + H]⁺ 452.2584, found 452.2584.

(*R*)-*tert*-Butyl-7-((*tert*-butoxycarbonyl)amino)-2,2-dimethyl-4-phenylhept-5ynoate (60)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), *tert*-butyl prop-2-yn-1-ylcarbamate 2w (31 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **60** as a colorless oil (76.1 mg, 95% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 214 nm), *t*_R (minor) = 19.18 min, *t*_R (major) = 21.33 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 1H), 4.81 (s, 1H), 3.92 (s, 2H), 3.71 – 3.63 (m, 1H), 2.08 (dd, *J* = 13.9, 9.9 Hz, 1H), 1.93 (dd, *J* = 13.9, 4.4 Hz, 1H), 1.47 (s, 9H), 1.46 (s, 9H), 1.28 (s, 3H), 1.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 155.4, 142.9, 128.6, 127.3, 126.7, 85.5, 80.1, 79.7, 79.1, 48.2, 43.0, 34.7, 31.0, 28.4, 28.0, 25.91, 25.85.

HRMS (ESI) *m/z* calcd. for C₂₄H₃₅NNaO₄ [M + Na]⁺ 424.2458, found 424.2458.

(*R*)-*tert*-Butyl-7,7-diethoxy-2,2-dimethyl-4-phenylhept-5-ynoate (61)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 3,3-diethoxyprop-1-yne 2x (25.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 61 as a colorless oil (57.7 mg, 77% yield, 96% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 99.3/0.7 flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 5.82 min, t_R (minor) = 6.57 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 7.1 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 5.28 (d, J = 1.3 Hz, 1H), 3.77 – 3.67 (m, 3H), 3.61 – 3.52 (m, 2H), 2.13 – 1.96 (m, 2H), 1.43 (s, 9H), 1.30 (s, 3H), 1.21 (t, J = 7.1 Hz, 6H), 1.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.5, 142.6, 128.6, 127.5, 126.6, 91.6, 88.3, 80.1, 78.8, 60.73, 60.67, 48.2, 43.1, 34.6, 28.1, 26.7, 25.0, 15.1.

HRMS (ESI) m/z calcd. for C₂₃H₃₄NaO₄ [M + Na]⁺ 397.2349, found 397.2348.

(*R*)-*tert*-Butyl-7-cyclohexyl-2,2-dimethyl-4-phenylhept-5-ynoate (62)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-ylcyclon-hexane 2y (24.4 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 62 as a colorless oil (53.1 mg, 72% yield, 95% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 4.57 min, t_R (minor) = 5.21 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.29 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 3.60 – 3.50 (m, 1H), 2.00 (d, J = 2.1 Hz, 1H), 1.99 (d, J = 2.1 Hz, 1H), 1.96 – 1.84 (m, 2H), 1.71 (d, J = 11.1 Hz, 2H), 1.67 – 1.51 (m, 3H), 1.42 – 1.31 (m, 10H), 1.22 (s, 3H), 1.20 – 1.12 (m, 2H), 1.10 (s, 3H), 1.09 – 0.98 (m, 1H), 0.97 – 0.84 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 144.2, 128.4, 127.4, 126.4, 83.1, 82.4, 79.9, 49.0, 43.2, 37.6, 34.8, 32.8, 28.1, 26.9, 26.5, 26.4, 26.2, 25.3.

HRMS (ESI) m/z calcd. for C₂₅H₃₆NaO₂ [M + Na]⁺ 391.2608, found 391.2605.

(R)-tert-Butyl-2,2-dimethyl-4,7-diphenylhept-5-ynoate (63)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-ylbenzene 2z (23.2 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 63 as a colorless oil (41.4 mg, 57% yield, 95% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 99.3/0.7 flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 6.00 min, t_R (major) = 6.49min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, J = 7.4 Hz, 2H), 7.39 – 7.31 (m, 6H), 7.25 (t, J = 7.3 Hz, 2H), 3.78 – 3.71 (m, 1H), 3.65 (d, J = 1.8 Hz, 2H), 2.10 (d, J = 9.6 Hz, 1H), 2.01 (dd, J = 13.9, 4.3 Hz, 1H), 1.48 (s, 9H), 1.33 (s, 3H), 1.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.8, 137.3, 128.5, 128.4, 127.9, 127.4, 126.6, 126.4, 84.7, 80.8, 80.0, 48.7, 43.1, 34.9, 28.1, 26.3, 25.6, 25.4.

HRMS (ESI) m/z calcd. for C₂₅H₃₀NaO₂ [M + Na]⁺ 385.2138, found 385.2137.

(R)-tert-Butyl-7-acetoxy-2,2-dimethyl-4-phenylhept-5-ynoate (64)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-yl acetate 2za (19.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 64 as a colorless oil (67.9 mg, 99% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), *t*_R (minor) = 7.28 min, *t*_R (major) = 7.77 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.39 – 7.30 (m, 4H), 7.24 (ddd, J = 8.4, 3.2, 1.6 Hz, 1H), 4.71 (d, J = 2.1 Hz, 2H), 3.73 (dtd, J = 6.3, 4.1, 1.9 Hz, 1H), 2.13 – 2.05 (m, 4H), 1.99 (dd, J = 13.9, 4.4 Hz, 1H), 1.47 (s, 9H), 1.30 (s, 3H), 1.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 170.3, 142.6, 128.6, 127.4, 126.8, 89.4, 80.1, 77.0, 52.8, 48.2, 43.1, 34.7, 28.0, 26.3, 25.4, 20.8.

HRMS (ESI) m/z calcd. for C₂₁H₂₈NaO₄ [M + Na]⁺ 367.1880, found 367.1879.

(R)-tert-Butyl-8-hydroxy-2,2-dimethyl-4-phenyloct-5-ynoate (65)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.),

but-3-yn-1-ol **2zb** (14 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **65** as a colorless oil (56.9 mg, 90% yield, 97% ee).

HPLC analysis: Chiralcel IB (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 12.70 min, t_R (minor) = 15.55 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.40 – 7.30 (m, 4H), 7.27 – 7.19 (m, 1H), 3.76 – 3.67 (m, 3H), 2.46 (td, J = 6.2, 2.2 Hz, 3H), 2.10 (dd, J = 13.9, 10.2 Hz, 1H), 1.90 (dd, J = 13.9, 4.5 Hz, 1H), 1.49 (s, 9H), 1.30 (s, 3H), 1.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 177.0, 143.5, 128.6, 127.3, 126.7, 84.1, 80.2, 80.2, 61.3, 48.4, 43.0, 34.8, 28.1, 26.3, 25.7, 23.5.

HRMS (ESI) m/z calcd. for C₂₀H₂₈NaO₃ [M + Na]⁺ 339.1931, found 339.1931.

(R)-tert-Butyl-10-chloro-2,2-dimethyl-4-phenyldec-5-ynoate (66)



According to General Procedure A with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 6-chlorohex-1-yne **2zc** (23.3 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.) after 36 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **66** as a colorless oil (50.6 mg, 70% yield, 94% ee).

HPLC analysis: Chiralcel OZ3 (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 8.35 min, t_R (minor) = 8.90 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.31 (m, 4H), 7.26 – 7.21 (m, 1H), 3.66 (dtd, J = 6.4, 4.2, 2.0 Hz, 1H), 3.58 (t, J = 6.6 Hz, 2H), 2.26 (td, J = 7.0, 2.2 Hz, 2H), 2.04 (dd, J = 13.8, 9.6 Hz, 1H), 1.96 (dd, J = 13.8, 4.4 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.74 – 1.66 (m, 2H), 1.48 (s, 9H), 1.32 (s, 3H), 1.21 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.9, 128.5, 127.3, 126.5, 83.1, 82.5, 79.9, 48.7, 44.6, 43.1, 34.8, 31.7, 28.1, 26.3, 26.0, 25.5, 18.3.

HRMS (ESI) m/z calcd. for C₂₂H₃₁ClNaO₂ [M + Na]⁺ 385.1905, found 385.1904.

(R)-tert-Butyl-2,2-dimethyl-4-phenylhept-5-ynoate (67)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), prop-1-yne 2zd (0.2 mL, 1 mol/L in THF, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 67 as a colorless oil (37.9 mg, 66% yield, 95% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 1.0 mL/min, λ

= 214 nm), t_R (major) = 5.55 min, t_R (minor) = 6.48 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 3.65 (dtd, J = 9.0, 4.5, 2.2 Hz, 1H), 2.10 (dd, J = 13.8, 10.0 Hz, 1H), 1.90 (dd, J = 13.8, 4.4 Hz, 1H), 1.83 (d, J = 2.4 Hz, 3H), 1.48 (s, 9H), 1.29 (s, 3H), 1.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 143.9, 128.5, 127.4, 126.5, 81.2, 79.9, 78.8, 48.5, 43.0, 34.8, 28.1, 26.0, 25.7, 3.8.

HRMS (ESI) m/z calcd. for C₁₉H₂₆NaO₂ [M + Na]⁺ 309.1825, found 309.1824.

(R)-tert-Butyl-2,2-dimethyl-4-phenyl-6-(trimethylsilyl)hex-5-ynoate (68)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), ethynyltrimethylsilane 2ze (19.6 mg, 0.20 mmol, 1.0 equiv.), and *tert*-butyl 2-bromo-2-methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 68 as a colorless oil (62.1 mg, 90% yield, 96% ee).

HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 11.06 min, t_R (minor) = 12.14 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.08 – 7.02 (m, 1H), 3.52 (dd, *J* = 9.4, 4.0 Hz, 1H), 1.88 (dd, *J* = 13.9, 4.0 Hz, 1H), 1.79 (dd, *J* = 13.9, 9.5 Hz, 1H), 1.29 (s, 9H), 1.18 (s, 3H), 1.02 (s, 3H), 0.00 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 176.7, 143.0, 128.5, 127.4, 126.6, 109.3, 87.6, 80.1, 48.9, 43.4, 35.6, 28.1, 27.3, 24.5, 0.0.

HRMS (ESI) m/z calcd. for C₂₁H₃₂NaO₂Si [M + Na]⁺ 367.2064, found 367.2063.

Substrates scope of other radical precursors

(R)-Ethyl-6-(4-cyanophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (69)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and ethyl 2-bromo-2methylpropanoate 3b (46.8 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 69 as a colorless oil (53.9 mg, 78% yield, 93% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 17.75 min, *t*_R (minor) = 21.01 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 4.03 – 3.89 (m, 3H), 2.30 (dd, *J* = 13.8, 10.1 Hz,

1H), 2.00 (dd, J = 13.9, 4.7 Hz, 1H), 1.32 (d, J = 5.8 Hz, 6H), 1.19 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 141.9, 132.1, 131.9, 128.8, 128.6, 127.4, 127.1, 118.6, 111.2, 96.4, 82.2, 60.5, 48.4, 42.1, 35.3, 26.5, 25.2, 14.1. HRMS (ESI) *m/z* calcd. for C₂₃H₂₄NO₂ [M + H]⁺ 346.1802, found 346.1802.

(*R*)-Methyl-6-(4-cyanophenyl)-2,2-dimethyl-4-phenylhex-5-ynoate (70)



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), and methyl 2-chloro-2methylpropanoate 3c (32.8 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product 70 as a colorless oil (33.9 mg, 51% yield, 93% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 21.64 min, *t*_R (minor) = 24.86 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.60 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.31 – 7.25 (m, 1H), 3.95 (dd, J = 10.0, 4.8 Hz, 1H), 3.55 (s, 3H), 2.34 (dd, J = 13.9, 10.1 Hz, 1H), 2.01 (dd, J = 13.9, 4.8 Hz, 1H), 1.35 (d, J = 1.0 Hz, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 177.7, 141.8, 132.1, 132.0, 128.8, 128.6, 127.4, 127.1, 118.6, 111.2, 96.2, 82.2, 51.8, 48.5, 42.1, 35.3, 26.7, 25.0. **HRMS** (ESI) *m/z* calcd. for C₂₂H₂₂NO₂ [M + H]⁺ 332.1645, found 332.1645.

(R)-6-(4-Cyanophenyl)-N-methoxy-N,2,2-trimethyl-4-phenylhex-5-ynamide (71)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and 2-bromo-*N*-methoxy-N,2-dimethylpropanamide **3d** (50.4 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **71** as a colorless oil (53.1 mg, 74% yield, 94% ee).

HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t*_R (major) = 16.06 min, *t*_R (minor) = 32.47 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.30 – 7.24 (m, 1H), 3.98 (dd, J = 9.8, 4.4 Hz, 1H), 3.69 (s, 3H), 3.07 (s, 3H), 2.41 (dd, J = 13.9, 9.8 Hz, 1H), 2.13 (dd, J = 13.9, 4.4 Hz, 1H), 1.43 (s, 3H), 1.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 177.5, 142.3, 132.1, 131.9, 128.9, 128.7, 127.5, 127.0, 118.6, 111.0, 97.2, 82.1, 60.5, 48.0, 43.1, 35.2, 33.8, 26.2, 26.1.

HRMS (ESI) m/z calcd. for C₂₃H₂₅N₂O₂ [M + H]⁺ 361.1911, found 361.1910.

(*R*)-Ethyl-6-(4-cyanophenyl)-2,2-difluoro-4-phenylhex-5-ynoate (72)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and ethyl 2-bromo-2,2difluoroacetate **3e** (48.7 mg, 0.24 mmol, 1.2 equiv.) after 48 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **72** as a colorless oil (18.8 mg, 53% yield based on recovered **2a**, 92% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 36.34 min, t_R (major) = 47.91 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 4.28 – 4.12 (m, 3H), 2.80 (dtd, *J* = 16.9, 14.6, 9.4 Hz, 1H), 2.62 (qd, *J* = 14.9, 5.3 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 163.6 (t, *J* = 32.3 Hz), 139.4, 132.2, 132.0, 129.0, 128.0, 127.8, 127.4, 118.5, 114.8 (dd, *J* = 252.3, 251.1 Hz), 111.6, 93.9, 82.6, 63.1, 42.4 (t, *J* = 23.2 Hz), 32.2 (t, *J* = 5.2 Hz), 13.9.

¹⁹**F NMR** (376 MHz, CDCl₃) δ –103.47 (dt, *J* = 265.1, 14.7 Hz, 1F), –105.26 (dt, *J* = 265.1, 16.2 Hz, 1F).

HRMS (ESI) m/z calcd. for C₂₁H₁₇F₂NNaO₂ [M + Na]⁺ 376.1120, found 376.1119.

4-((3R)-5-Cyano-3-phenylhex-1-yn-1-yl)benzonitrile (73)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and 2-chloropropanenitrile **3f** (21.5 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **73** as a colorless oil (diastereomeric mixture, 22.8 mg, 40% yield, 1.3:1.0 dr, 91% ee₁, 94% ee₂).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor₁) = 26.40 min, t_R (minor₂) = 27.86 min, t_R (major₁) = 32.55 min, t_R (major₂) = 73.71 min.

¹**H NMR** (400 MHz, CDCl₃) (diastereomeric mixture) δ 7.63 (dd, J = 8.1, 5.6 Hz, 2H), 7.55 (dd, J = 11.3, 8.3 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 4.19 (dd, J = 10.9, 4.7 Hz, 0.58H), 4.06 (dd, J = 8.6, 7.1 Hz, 0.42H), 3.10 – 2.97 (m, 0.63H), 2.65 – 2.52 (m, 0.45H), 2.34 (ddd, J = 13.6, 9.2, 7.0 Hz, 0.49H), 2.18 – 2.08 (m, 0.74H), 2.06 – 1.94 (m, 1H), 1.44 (s, 0.86H), 1.42 (s, 0.86H), 1.40 (s, 0.65H), 1.38 (s, 0.65H).

¹³C NMR (100 MHz, CDCl₃) (diastereomeric mixture) δ 139.7, 139.2, 132.30, 132.2, 132.0, 132.0, 129.1, 129.0, 128.0, 127.9, 127.8, 127.6, 127.5, 127.2, 122.2, 118.4, 111.7, 111.6, 94.5, 93.7, 83.4, 82.3, 42.6, 41.9, 36.9, 36.4, 24.4, 23.6, 18.3, 17.9. **HRMS** (ESI) *m/z* calcd. for C₂₀H₁₇N₂ [M + H]⁺ 285.1386, found 285.1387.

(R)-4-(5-Cyano-3-phenylpent-1-yn-1-yl)benzonitrile (74)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and 2-bromoacetonitrile **3g** (28.8 mg, 0.24 mmol, 1.2 equiv.) after 48 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **74** as a colorless oil (18.8 mg, 70% yield based on recovered **2a**, 95% ee).

HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 49.59 min, t_R (minor) = 61.27 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.64 – 7.58 (m, 2H), 7.57 – 7.50 (m, 2H), 7.43 – 7.36 (m, 4H), 7.34 – 7.31 (m, 1H), 4.07 (t, *J* = 7.2 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.44 (dt, *J* = 16.9, 6.9 Hz, 1H), 2.24 – 2.16 (m, 2H).

¹³**C NMR** (100 MHz, CDCl₃) δ 138.9, 132.3, 132.1, 129.1, 127.8, 127.4, 119.0, 118.4, 111.7, 93.6, 83.3, 37.3, 33.4, 15.2.

HRMS (ESI) m/z calcd. for C₁₉H₁₅N₂ [M + H]⁺ 271.1230, found 271.1228.

(R)-4-(5,5,5-Trifluoro-3-phenylpent-1-yn-1-yl)benzonitrile (75)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), and 1-(trifluoromethyl)- $1\lambda^3$ benzo[*d*][1,2]iodaoxol-3(1*H*)-one **3h** (75.8 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **75** as a colorless oil (42.3 mg, 71% yield, 96% ee).

HPLC analysis: Chiralcel AD3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 19.92 min, t_R (major) = 26.54 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.39 – 7.32 (m, 1H), 4.26 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.85 – 2.69 (m, 1H), 2.70 – 2.55 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 139.0, 132.2, 132.0, 129.1, 127.93, 127.91, 127.3, 125.6 (q, J = 277.9 Hz), 118.5, 111.7, 93.2, 82.72, 41.9 (q, J = 27.8 Hz), 32.6 (q, J = 3.2 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ –64.37 (t, J = 10.2 Hz, 3F). **HRMS** (ESI) m/z calcd. for C₁₈H₁₃F₃N [M + H]⁺ 300.0995, found 300.0994.

(*R*)-(5,5,5-Trifluoropent-1-yne-1,3-diyl)dibenzene (76)



According to General Procedure **B** with styrene **1a** (31.2 mg, 0.30 mmol, 1.5 equiv.), ethynylbenzene **2a** (20.4 mg, 0.20 mmol, 1.0 equiv.), and 1-(trifluoromethyl)- $1\lambda^3$ -benzo[*d*][1,2]iodaoxol-3(1*H*)-one **3h** (75.8 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was purified by column chromatography on silica gel to yield the product **76** as a colorless oil (37.8 mg, 69% yield, 98% ee).

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, λ = 240 nm), t_R (minor) = 14.38 min, t_R (major) = 16.09 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.55 – 7.45 (m, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 – 7.30 (m, 4H), 4.25 (dd, J = 9.0, 5.4 Hz, 1H), 2.85 – 2.70 (m, 1H), 2.69 – 2.54 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 138.7, 130.6, 127.9, 127.23, 127.17, 126.6, 126.3, 124.6 (q, J = 277.8 Hz), 122.0, 87.4, 83.1, 41.2 (q, J = 27.6 Hz), 31.5 (q, J = 3.0 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ –64.30 (t, J = 10.2 Hz, 3F).

HRMS (ESI) m/z calcd. for C₁₇H₁₄F₃ [M + H]⁺ 275.1042, found 275.1040.

Transformations

Synthesis of 77



To a mixture of Pd/C (10.0 mg, 10% w/w Pd on carbon) in THF (2.0 mL) was added **59** (90.2 mg, 0.20 mmol, 1.0 equiv., 96% ee) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 2 h. After completion, the reaction mixture was filtered and rinsed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **77** as a colorless oil (72.9 mg, 80% yield, 96% ee).

(R)-tert-Butyl-7-(9H-carbazol-9-yl)-2,2-dimethyl-4-phenylheptanoate (77)



HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 18.42 min, t_R (major) = 20.46 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 7.7 Hz, 2H), 7.52 – 7.43 (m, 2H), 7.36 – 7.12 (m, 9H), 4.30 – 4.14 (m, 2H), 2.63 (tt, J = 8.9, 4.5 Hz, 1H), 1.97 (dd, J = 14.1, 8.2 Hz, 1H), 1.91 (dd, J = 14.1, 4.3 Hz, 1H), 1.84 – 1.58 (m, 4H), 1.35 (s, 9H), 1.09 (s, 3H), 0.97 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 177.1, 145.7, 140.3, 128.5, 128.0, 126.3, 125.6, 122.8, 120.3, 118.7, 108.7, 79.8, 47.3, 43.01, 42.97, 36.3, 27.9, 26.8, 25.4.

HRMS (ESI) m/z calcd. for C₃₁H₃₈NO₂ [M + H]⁺ 456.2897, found 456.2896.

Synthesis of 78



To a flamed Schlenk tube charged with a stir bar were added NaO'Bu (38.4 mg, 0.40 mmol, 2.0 equiv.), **59** (90.2 mg, 0.20 mmol, 1.0 equiv., 96% ee), Pd(OAc)₂ (2.24 mg, 0.010 mmol, 5.0 mol%), L (7.6 mg, 0.020 mmol, 10 mol%), IPrCuCl (9.76 mg, 0.020 mmol, 10 mol%), TMDSO (1,1,3,3-tetramethyldisiloxane) (53.6 mg, 0.40 mmol, 2.0

equiv.), MeOH (32.0 mg, 1.0 mmol, 5.0 equiv.), and toluene (2.0 mL). The reaction mixture was stirred at 60 °C for 4 h. Upon completion, the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc (3 mL) and purified by column chromatography to afford **78** as a slight yellow oil (74.1 mg, 82% yield, 96% ee).

(S, Z)-tert-Butyl-7-(9H-carbazol-9-yl)-2,2-dimethyl-4-phenylhept-5-enoate (78)



HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.85 min, t_R (major) = 25.26 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 7.1 Hz, 2H), 7.52 – 7.32 (m, 7H), 7.32 – 7.11 (m, 4H), 5.99 – 5.81 (m, 1H), 5.47 (dt, J = 10.9, 5.6 Hz, 1H), 5.11 (dd, J = 16.9, 5.0 Hz, 1H), 4.97 (dd, J = 16.9, 6.7 Hz, 1H), 4.01 (dd, J = 13.6, 8.7 Hz, 1H), 2.23 (dd, J = 13.9, 8.5 Hz, 1H), 2.11 (dd, J = 13.9, 4.9 Hz, 1H), 1.54 (s, 9H), 1.32 (s, 3H), 1.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.9, 145.4, 140.3, 136.7, 128.9, 127.5, 126.5, 125.7, 125.5, 123.0, 120.3, 119.0, 108.9, 80.2, 48.2, 43.0, 41.5, 40.6, 28.2, 27.0, 25.8. HRMS (ESI) *m/z* calcd. for C₃₁H₃₆NO₂ [M + H]⁺ 454.2741, found 454.2742.

Synthesis of 79



To a solution of **68** (69 mg, 0.20 mmol, 1.0 equiv., 96% ee) in MeOH (2.0 mL) was added K_2CO_3 (55.2 mg, 0.40 mmol, 2.0 equiv.) and the resulting mixture was stirred at room temperature for 1 h. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography to yield **68-1** as a colorless oil (41.4 mg, 76% yield, 96% ee).

To a solution of the thus-obtained **68-1** in toluene (2.0 mL) were added 4-acetamidobenzenesulfonyl azide (36 mg, 0.15 mmol, 1.0 equiv.) and copper thiophene-2-carboxylate (1.42 mg, 0.0075 mmol, 5.0 mol%) under argon atmosphere. The reaction mixture was stirred under the same conditions for 4 h, and then, was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the product **79** as a yellow oil (69.3 mg, 90% yield, 96% ee).

(S)-tert-Butyl-2,2-dimethyl-4-phenylhex-5-ynoate (68-1)



HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 214 nm), t_R (major) = 11.20 min, t_R (major) = 13.76 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 7.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.17 – 7.11 (m, 1H), 3.59 (ddd, J = 9.8, 4.1, 2.7 Hz, 1H), 2.15 (d, J = 2.5 Hz, 1H), 2.06 (dd, J = 13.9, 9.9 Hz, 1H), 1.84 (dd, J = 13.9, 4.3 Hz, 1H), 1.37 (s, 9H), 1.20 (s, 3H), 1.12 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.6, 142.7, 128.6, 127.4, 126.8, 86.4, 80.1, 71.7, 48.1, 43.0, 34.5, 28.0, 26.0, 25.8.

HRMS (ESI) m/z calcd. for C₁₈H₂₄NaO₂ [M + Na]⁺ 295.1669, found 295.1669.

(*R*)-*tert*-Butyl-4-(1-((4-acetamidophenyl)sulfonyl)-1*H*-1,2,3-triazol-4-yl)-2,2-dimethyl-4-phenylbutanoate (79)



HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 280 nm), t_R (minor) = 14.18 min, t_R (major) = 17.62 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.89 (d, J = 8.9 Hz, 2H), 7.77 (s, 1H), 7.65 (d, J = 8.9 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 4.22 – 4.12 (m, 1H), 2.52 (dd, J = 14.2, 5.8 Hz, 1H), 2.31 (dd, J = 14.1, 7.5 Hz, 1H), 2.18 (s, 3H), 1.31 (s, 9H), 1.03 (s, 3H), 1.01 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.5, 169.3, 152.2, 145.1, 142.8, 130.1, 129.3, 128.9, 128.0, 127.1, 120.8, 119.5, 80.3, 45.5, 43.0, 40.2, 27.9, 26.1, 26.0, 24.7.

HRMS (ESI) m/z calcd. for C₂₆H₃₃N₄O₅S [M + H]⁺ 513.2166, found 513.2169.

Synthesis of 80



To a mixture of RuCl₃ (1.5 mg, 0.010 mmol, 5.0 mol%) and sodium periodate (171.0 mg, 0.80 mmol, 4.0 equiv.) in a mixed solvent of CCl₄ (0.4 mL) and water (0.6 mL) was added a solution of **68** (68.8 mg, 0.20 mmol, 1.0 equiv.) in MeCN (0.4 mL) in one portion. The reaction mixture was stirred at room temperature for 2 h, and then, was concentrated. The residue was purified by column chromatography on silica gel to afford the product **68-2** as a white solid (30.4 mg, 52% yield).

To a solution of 68-2 in anhydrous THF was added LiAlH4 (15.2 mg, 0.40 mmol, 4.0

equiv.) powder slowly at 0 °C. Then it was stirred at room temperature for 4 h. Upon completion (monitored by TLC), the reaction was quenched with wet Na₂SO₄ (0.2 mL water per gram) and filtered, and the solid was washed with THF. The organic phase was concentered and purified with by column chromatography on silica gel to afford the product **80** as a colorless oil (18.7 mg, 90% yield, 96% ee).

(R)-5-(tert-Butoxy)-4,4-dimethyl-5-oxo-2-phenylpentanoic acid (68-2)



¹**H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.14 (m, 5H), 3.63 (dd, *J* = 8.0, 4.3 Hz, 1H), 2.50 (dd, *J* = 14.2, 8.1 Hz, 1H), 2.00 (dd, *J* = 14.2, 4.3 Hz, 1H), 1.41 (s, 9H), 1.17 (s, 3H), 1.11 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 180.1, 176.5, 139.7, 128.7, 128.0, 127.4, 80.4, 48.5, 43.1, 43.0, 27.9, 26.0, 24.8.

HRMS (ESI) m/z calcd. for C₁₇H₂₄NaO₄ [M + Na]⁺ 315.1567, found 315.1566.

(*R*)-2,2-dimethyl-4-phenylpentane-1,5-diol (80)



HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 10.60 min, t_R (minor) = 11.51 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.35 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 3.65 (dd, J = 7.2, 1.1 Hz, 2H), 3.29 (d, J = 11.0 Hz, 1H), 3.16 (d, J = 11.0 Hz, 1H), 2.95 – 2.81 (m, 1H), 1.75 (brs, 2H), 1.73 (s, 1H), 1.71 (d, J = 1.9 Hz, 1H), 0.82 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 144.1, 128.8, 128.1, 126.8, 71.0, 69.0, 44.4, 40.4, 35.9, 25.1, 24.6.

HRMS (ESI) m/z calcd. for C₁₃H₂₀NaO₂ [M + Na]⁺ 231.1356, found 231.1355.

Synthesis of 81



To a solution of **76** (38 mg, 0.14 mmol, 1.0 equiv.) in CF₃CH₂OH (0.5 mL) were added CF₃SO₃H (4.2 mg, 0.028 mmol, 0.2 equiv.) and H₂O (5.0 mg, 0.28 mmol, 2.0 equiv.). And the reaction mixture was stirred at 80 °C for 16 h. After evaporation under reduced pressure, the residue was purified with column chromatography on silica gel to yield the product **81** as a colorless oil (31.9 mg, 78% yield, 97% ee).

(R)-5,5,5-Trifluoro-1,3-diphenylpentan-1-one (81)



HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 17.32 min, t_R (minor) = 25.63 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.22 (m, 5H), 3.86 – 3.74 (m, 1H), 3.51 – 3.21 (m, 2H), 2.76 – 2.60 (m, 1H), 2.60 – 2.43 (m, 1H).

¹³**C NMR** (100 MHz, CDCl₃) δ 197.5, 142.6, 136.7, 133.3, 128.8, 128.7, 128.0, 127.3, 127.1, 126.4 (q, *J* = 277.7 Hz), 44.7, 39.6 (q, *J* = 27.4 Hz), 35.2 (q, *J* = 2.5 Hz).

¹⁹**F NMR** (376 MHz, CDCl₃) δ –63.49 (t, J = 10.7 Hz, 3F).

HRMS (ESI) m/z calcd. for C₁₇H₁₆F₃O [M + H]⁺ 293.1148, found 293.1147.

Mechanistic study

Analysis of NMR spectroscopy of ligand L2 and L2Cu^I

Experiment for taking the NMR spectroscopy of ligand L2 and L2Cu^I

L2 (24.4 mg, 0.04 mmol) was dissolved in CDCl₃ (0.5 mL) in an NMR tube to record the ¹H NMR, ¹³C NMR, COSY, HSQC, HMBC of the ligand L2.



In an oven-dried vial was added CuI (7.6 mg, 0.04 mmol), L2 (24.4 mg, 0.04 mmol) and CDCl₃ (0.5 mL). The reaction mixture was stirred for 10 min and transferred into an NMR tube to record the ¹H NMR, ¹³C NMR, COSY, HSQC, HMBC of the complex $L2Cu^{I}$.



5.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Figure S4. Stacking ¹H NMR spectrum of L2 and L2Cu^I. (red color: L2; blue color: $L2Cu^{I}$



Figure S5. Stacking ³¹P NMR spectrum of L2 and L2Cu^I. (red color: L2; blue color: L2Cu^I)

	H-2	H-3a	H-3b	H-4	H-5	H-6a	H-6b	H-7a
$\delta_{\rm H} L2$	3.02	1.41	0.87	1.62	2.24	3.12	2.54	3.17
$\delta_{\rm H} L2 C u^{\rm I}$	4.61	1.87	0.83	1.80	2.51	3.63	3.60	3.80
$\Delta\delta_{ m H}$	1.59	0.46	-0.04	0.18	0.27	0.51	1.06	0.63
	H-7b	H-8	H-9	H-10	H-11	H-13	H-14	H-16
$\delta_{\rm H} L2$	2.62	1.55	5.70	4.95	5.50	~7.30	8.63	8.00
$\delta_{\rm H} L2 C u^{\rm I}$	2.99	~1.70	5.87	5.15	6.19	7.60	8.79	8.08
$\Delta\delta_{ m H}$	0.37	0.15	0.17	0.20	0.69	0.30	0.16	0.08
	H-17	H-19	H-22	H-23	H-27	H-28	H-29	H-30
$\delta_{\rm H} L2$	~7.4	7.70	3.95	ND	7.64	~7.30	~7.20	6.90
$\delta_{\rm H} L2 C u^{\rm I}$	~7.4	7.66	3.95	7.22	6.83	~7.30	~7.20	7.04
$\Delta \delta_{\mathrm{H}}$	0	-0.04	0	NA	-0.81	0	0	0.14

Table S1. The NMR comparison of L2 and L2Cu^I complex.

Cyclic voltammogram (CV) experiments

Cyclic Voltammetry experiments were performed using a CH Instruments Electrochemical Workstation model CHI620E, scan rate = 0.1V/s, 2 sweep segments, sample interval = 0.001 V. The electrochemical cell was equipped with a glassy carbon disk working electrode (3mm diameter) and a Pt wire counter electrode and the potentials were calibrated with Fc as an internal standard. The samples(0.01M) were prepared under the protection of the N₂ by dissolving them in degassed CH₃CN (0.1 M

Bu₄NPF₆) directly and stirred for 1min, the air sensitive mixture should be tested quickly to avoid forming precipitates or being oxidized.



Figure S6. CV of CuBr, calibrated with Fc as an internal standard.



Figure S7. CV of L2, calibrated with Fc as an internal standard.



Figure S8. CV of a mixture of L2 and CuBr in a 1:1 ratio, calibrated with Fc as an internal standard.



Figure S9. CV of a mixture of L2, CuBr and base (Cs₂CO₃) in a 1:1:1 ratio, calibrated with Fc as an internal standard.



Figure S10. CV of the L2Cu from a mixture of L2, CuBr and base (Cs₂CO₃) in a 1:1:1 ratio calibrated with Fc as an internal standard.



Figure S11. CVs of CuBr and the L2CuBr complex, calibrated with Fc as an internal standard.

EPR experiments for detection of the Cu^{II} Species

EPR Experiments for detection of the Cu^{II} intermediate during the reaction.

An oven-dried Schlenk tube was sequentially charged with CuOAc (1.83 mg, 0.015 mmol), L2 (9.2 mg, 0.015 mmol), Cs₂CO₃ (65 mg, 0.20 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (4.0 mL) was added and the reaction mixture was stirred for 10 min at 28 °C. Substrates 11 (15 mg, 0.12 mmol), 3a (34 mg, 0.15 mmol) and alkyne 2a (12.7 mg, 0.10 mmol) were added and the reaction mixture was stirred at that temperature for 30 min. An aliquot of the reaction mixture (0.50 mL) was transferred to an EPR tube under an argon atmosphere for X-band EPR measurement at 100 K.

Experiment for independent synthesis of the Cu^{II} intermediate.

An oven-dried round bottom flask was charged with $Cu(OAc)_2$ (1 mg, 0.005 mmol), L2 (3 mg, 0.005 mmol) and 2a (1.3 mg, 0.010 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (1.0 mL) was added and the

reaction mixture was stirred for 30 min at 28 °C. An aliquot of the reaction mixture (0.50 mL) was transferred to an EPR tube for X-band EPR measurement at 100 K.



Figure S12. X-band EPR spectrum (9.26 GHz, 100K). black: a mixture of Cu(OAc)₂, **L2** and **2a**. red: a reaction component of the standard carboalkynylation reaction.

Control experiments Control experiment with copper phenylacetylide



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with styrene **1a** (15.6 mg, 0.15 mmol, 1.5 equiv.), copper phenylacetylide (16.5 mg, 0.10 mmol, 1.0 equiv.), *tert*-butyl 2-bromo-2-methylpropanoate **3a** (26.8 mg, 0.12 mmol, 1.2 equiv.), **L1** (83.6 mg, 0.10 mmol, 1.0 equiv.), and anhydrous 1,4-dioxane (1.0 mL). The resulting reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered and washed by CH₂Cl₂. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **39** (27.9 mg, 80% yield, 96% ee).

The procedure for the reaction without L1 was the same with that described above except that L1 was not added. No desired product 37 was observed.

Control experiment with a clock substrate



The substrate **82** was synthesized according to the reported procedure.¹⁰ Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with (1-(2-phenylcyclopropyl)vinyl)benzene **82** (66 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **2a** (25.4 mg, 0.20 mmol, 1.0 equiv.), *tert*butyl 2-bromo-2-methylpropanoate **3a** (53.5 mg, 0.24 mmol, 1.2 equiv.), **L1** (12.5 mg, 0.015 mmol, 7.5 mol%), and anhydrous 1,4-dioxane (2.0 mL). The resulting reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered and washed by CH₂Cl₂. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **83** (62.8 mg, 64% yield, *Z*:*E* = 1:5, 88% ee_{major}).

(*R*)-*tert*-Butyl-9-(4-cyanophenyl)-2,2-dimethyl-4,7-diphenylnon-4-en-8-ynoate (83)



HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.71 min, t_R (minor) = 21.39 min.

¹**H** NMR (400 MHz, CDCl₃) (*Z* and *E* mixture) δ 7.67 – 7.58 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.48 – 7.36 (m, 3H), 7.35 – 7.20 (m, 6.61H), 7.10 – 7.02 (m, 0.36H), 5.78 (t, *J* = 7.3 Hz, 0.83H), 5.63 (t, *J* = 7.3 Hz, 0.17H), 4.01 (t, *J* = 7.1 Hz, 0.81H), 3.89 (t, *J* = 7.0 Hz, 0.16H), 2.86 – 2.44 (m, 4H), 1.30 (s, 7.41H), 1.27 (s, 1.56H), 1.03 (d, *J* = 0.8 Hz, 1.05H), 0.99 (s, 4.91H).

¹³**C NMR** (100 MHz, CDCl₃) (*Z* and *E* mixture) δ 176.9, 176.6, 144.8, 141.0, 140.7, 140.6, 140.5, 140.3, 132.2, 132.0, 129.5, 128.7, 128.62, 128.59, 128.2, 128.0, 127.57, 127.52, 127.4, 127.2, 127.1, 127.0, 126.8, 126.7, 118.6, 111.2, 111.2, 96.4, 96.2, 82.30, 82.25, 79.9, 79.6, 49.2, 43.6, 43.2, 38.84, 38.77, 38.1, 37.4, 27.79, 27.77, 25.85, 25.82, 25.6.

HRMS (ESI) m/z calcd. for C₃₄H₃₆NO₂ [M + H]⁺ 490.2741, found 490.2741.

Control experiment with TEMPO



According to General Procedure A with styrene 1a (31.2 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile 2a (25.4 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyl 2-bromo-2methylpropanoate 3a (53.5 mg, 0.24 mmol, 1.2 equiv.), and 2,2,6,6tetramethylpiperidinyloxy (TEMPO) (37.4 mg, 0.24 mmol, 1.2 equiv.) after 12 h, the reaction mixture was monitored by TLC. There was no product observed.

Kinetic Studies

Experiment for determining the dependence of reaction rate on the concentration of alkene 11



A stock solution of 4-bromofluorobenzene (35 mg, 0.20 mmol) in CDCl₃ (2 mL) was prepared as the internal standard.

An oven-dried Schlenk tube was sequentially charged with CuOAc (1.83 mg, 0.015 mmol), L2 (9.2 mg, 0.015 mmol), Cs₂CO₃ (65 mg, 0.20 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (4.0 mL) was added and the reaction mixture was stirred for 10 min at 28 °C. Substrates 11 (0.05–0.25 mmol), 3a (0.30 mL, 1.6 mmol) and alkyne 2a (127 mg, 1.0 mmol) were added and the reaction mixture was stirred at that temperature. An aliquot of the reaction mixture (0.20 mL) was taken out at a proper time interval. The reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was concentrated and vacuumed to afford the crude residue. The internal standard (100 µL) was added and the sample was analyzed by ¹⁹F NMR spectroscopy.

Table S2. The molar concentrations of product 15 ([15]/M) with different initial concentrations of alkene ([11]/M) at different time intervals

Time	0.0125 M	0.0250 M	0.0375 M	0.0500 M	0.0625 M
(h)	[11]	[11]	[11]	[11]	[11]
0.167		0.00003	0.00004	0.00018	0.00019
0.333	0.00017	0.00041	0.00056	0.00116	0.00116
0.500		0.00110	0.00124	0.00219	0.00180
0.667	0.00078	0.00176	0.00143	0.00319	0.00322
0.833		0.00220	0.00235	0.00489	0.00481
1.000	0.00171	0.00255	0.00271	0.00495	0.00500
1.333	0.00181				
2.0	0.00230				

[11] (M)	0.0125	0.0250	0.0375	0.0500	0.0625
$k_{\rm in}({\rm Mh}^{-1})$	0.0013	0.0032	0.0033	0.0062	0.0068

Table S3. The k_{in} values at different initial concentrations of alkene (11)



Figure S13. Plot of *k*_{in} versus [11] from the reactions with 0.0125 M, 0.025 M, 0.0375 M, 0.050 and 0.0625 M of alkene 11.

Experiment for determining the dependence of reaction rate on the concentration of alkyne 2a



A stock solution of 4-bromofluorobenzene (35 mg, 0.20 mmol) in CDCl₃ (2 mL) was prepared as the internal standard.

An oven-dried Schlenk tube was sequentially charged with CuOAc (1.83 mg, 0.015 mmol), L2 (9.2 mg, 0.015 mmol), Cs₂CO₃ (65 mg, 0.20 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (4.0 mL) was added and the reaction mixture was stirred for 10 min at 28 °C. Substrates 11 (0.20 mL, 1.4 mmol), 3a (0.30 mL, 1.6 mmol) and alkyne 2a (0.05–0.30 mmol) were added and the reaction mixture was stirred at that temperature. An aliquot of the reaction mixture (0.3 mL) was

taken out at a proper time interval. The reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was concentrated and vacuumed to afford the crude residue. The internal standard (0.15 mL) was added and the sample was analyzed by ¹⁹F NMR spectroscopy.

Time	0.0125 M	0.0250 M	0.0375 M	0.0500 M	0.0625 M	0.0750 M
(h)	[2a]	[2a]	[2a]	[2 a]	[2a]	[2 a]
0.167		0.00047	0.00043	0.00043	0.00062	
0.333	0.00041	0.00111	0.00139	0.00173	0.00173	0.00167
0.500		0.00220	0.00242	0.00322	0.00324	
0.667	0.00112	0.00300	0.00347	0.00458	0.00470	0.00432
1.000	0.00176					0.00477
1.333	0.00183					0.00936

Table S4. The molar concentrations of product 15 ([15]/M) with different initial concentrations of alkyne ([2a]/M) at different time intervals

Table S5. The k_{in} values at different initial concentrations of alkyne (2a)

[2a] (M)	0.0125	0.0250	0.0375	0.0500	0.0625	0.0750
$k_{\rm in}({\rm Mh}^{-1})$	0.0020	0.0047	0.0061	0.0078	0.0082	0.0077



Figure S14. Plot of *k*_{in} versus [**2a**] from the reactions with 0.0125 M, 0.025 M, 0.0375 M, 0.050 M, 0.0625 M and 0.075 M of alkyne **2a**.

Experiment for determining the dependence of reaction rate on the concentration of the radical precursor 3a



A stock solution of 4-bromofluorobenzene (35 mg, 0.20 mmol) in CDCl₃ (2 mL) was prepared as the internal standard.

An oven-dried Schlenk tube was sequentially charged with CuOAc (1.83 mg, 0.015 mmol), L2 (9.2 mg, 0.015 mmol), Cs₂CO₃ (65 mg, 0.20 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (4.0 mL) was added and the reaction mixture was stirred for 10 min at 28 °C. Substrates 11 (0.20 mL, 1.4 mmol), 3a (0.05–0.25 mmol) and alkyne 2a (127 mg, 1.0 mmol) were added and the reaction mixture was stirred at that temperature. An aliquot of the reaction mixture (0.20 mL) was taken out at a proper time interval. The reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was concentrated and vacuumed to afford the crude residue. The internal standard (100 µL) was added and the sample was analyzed by ¹⁹F NMR spectroscopy.

Table S6. The molar concentrations of product 15 ([15]/M) with different initial concentrations of alkene ([3a]/M) at different time intervals

Time (h)	0.0125 M [3 a]
0.133	0.0002675
0.200	0.0009150
0.267	0.0011925
0.333	0.0022575
0.400	0.002850

Time (h)	0.0250 M [3a]	0.0375 M [3a]	0.0500 M [3a]	0.0625 M [3 a]
0.167	0.00083	0.00056	0.00062	0.00086
0.333	0.00261	0.00251	0.00225	0.00274
0.500	0.00471	0.00582	0.00478	0.00459
0.667	0.00753	0.01030	0.00775	0.00705
0.833	0.01006	0.01018	0.01064	0.01105
1.000	0.01179	0.01144	0.01093	0.01252

Table S7. The k_{in} values at different initial concentrations of radical precursor (3a)

[3a] (M)	0.0125	0.0250	0.0375	0.0500	0.0625
$k_{\rm in}({\rm Mh}^{-1})$	0.0098	0.0137	0.0140	0.0134	0.0147



Figure S15. Plot of k_{in} versus [3a] from the reactions with 0.0125 M, 0.025 M, 0.0375 M, 0.050 M and 0.0625 M of radical precursor 3a.

Experiment for determining the dependence of reaction rate on the concentration of catalyst



A stock solution of 4-bromofluorobenzene (35 mg, 0.20 mmol) in CDCl₃ (2 mL) was prepared as the internal standard.

An oven-dried Schlenk tube was sequentially charged with CuOAc, L2 and Cs₂CO₃ (65 mg, 0.20 mmol). The tube was evacuated and back-filled with argon three times. Then, 1,4-dioxane (4.0 mL) was added and the reaction mixture was stirred for 10 min at 28 °C. Substrates 11 (0.20 mL, 1.4 mmol), 3a (22 mg, 0.10 mmol) and alkyne 2a (127 mg, 1.0 mmol) were added and the reaction mixture was stirred at that temperature. An aliquot of the reaction mixture (0.20 mL) was taken out at a proper time interval. The reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was concentrated and vacuumed to afford the crude residue. The internal standard (100 μ L) was added and the sample was analyzed by ¹⁹F NMR spectroscopy.

Table S8. The molar concentrations of product 15 ([15]/M) with different initial concentrations of catalyst (ratio of CuOAc and L2 is 1:1) at different time intervals

Time (h)	0.00125 M	0.00250 M	0.00375 M
0.167	0.00028	0.00040	0.00083
0.333	0.00078	0.00124	0.00261
0.500	0.00107	0.00304	0.00471
0.667	0.00208	0.00420	0.00753
0.833	0.00241	0.00677	0.01006
1.000	0.00270	0.00717	0.01179

Time (h)	0.00500 M	0.00625 M
0.067	0.00023	0.00047
0.133	0.00112	0.00146
0.200	0.00258	0.00287
0.267	0.00348	0.00426
0.333	0.00434	0.00613
0.400	0.00613	0.00800

Table S9. The k_{in} values at different initial concentrations of catalyst

catalyst (M)	0.00125	0.00250	0.00375	0.00500	0.00625
$k_{\rm in}({\rm Mh}^{-1})$	0.0031	0.0088	0.0137	0.0172	0.0227



Figure S16. Plot of k_{in} versus catalyst from the reactions with 0.00125 M, 0.0025 M, 0.00375 M, 0.00500 M and 0.00625 M of catalyst.

NMR spectra

















00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -: f1 (ppm)



00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)


















S79

























S87











S90































S101
































S117













S123











S128











S133



S134




























S146



































.50 -2 130 110 90 -50 f1 (ppm) -150 -170 -190 -210 -230 70 50 30 10 70 -110 -130 30





5.5 5.0

4.5 4.0 f2 (ppm) 15

3.5

29

0.5 0.0 -0.5

L2 3.0 2.5 2.0 1.5 1.0 170

. 35¹⁸⁰ - 190 - 200

210

24-

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0



HPLC spectra



Peak #	RetTime [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.703	BV	0.2645	9986.22168	564.14404	49.9968
2	13.641	VB	0.2829	9987.49707	527.41492	50.0032



1.99737e4 1091.55896



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.735	BV	0.2786	1418.15674	74.99559	3.4004
2	13.658	VB	0.3006	4.02873e4	2038.65625	96.5996

Totals : 4.17055e4 2113.65184



Peak RetTime Type Width Height Area Area % # [min] [min] [mAU*s] [mAU] 1 20.208 BB 1.0124 1.79216e4 269.99878 50.0190 2 24.082 BB 1.1379 1.79081e4 237.45607 49.9810







Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.845	BB	0.9499	2078.49048	32.33758	5.3062
2	23.445	BB	1.1306	3.70929e4	505.21445	94.6938
Tota]	s :			3.91713e4	537.55202	



Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 6.643 VV 0.1498 8376.49707 829.37665 49.9982 1 7.258 VB 2 0.1640 8377.09570 763.55206 50.0018

Totals :

1.67536e4 1592.92871



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area % [min] [min] [mAU*s] [mAU] # 6.646 BV 0.1509 395.26715 38.77490 2.4214 1 2 7.256 VV 0.1638 1.59284e4 1453.59912 97.5786

```
Totals: 1.63237e4 1492.37402
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.686	BB	0.2025	4138.18701	316.54446	50.1024
2	11.582	BB	0.2483	4121.27344	258.11472	49.8976



8259.46045 574.65918



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area [mAU*s] [min] [min] [mAU] % # 0.1984 3755.22925 291.31894 1 9.683 BB 95.6361 2 11.600 BB 0.2372 171.35039 10.91465 4.3639 Totals : 3926.57964 302.23359



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.746	BB	0.3817	3536.30249	143.38103	50.0250
2	24.413	BB	0.4528	3532.76709	120.92850	49.9750



7069.06958 264.30952



```
Signal 2: DAD1 B, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.605	BB	0.3844	652.34644	26.20405	3.0455
2	24.142	BB	0.4589	2.07676e4	702.42078	96.9545
Tota]	ls :			2.14200e4	728,62482	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.071	BB	0.4314	4735.99756	167.71832	50.9421
2	12.164	VV	0.4960	4560.82959	136.42535	49.0579
T - + - 1				0206 02715	204 14260	



9296.82715 304.14368



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Height Area Area [min] [mAU*s] [mAU] % # [min] 0.3203 3.35888e4 1449.56494 9.879 BV 99.1978 1 2 11.844 BV 0.2986 271.61356 12.35120 0.8022 Totals : 3.38604e4 1461.91614



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.123	BV	0.2609	9627.07520	564.75964	49.5727
2	13.999	VB	0.2796	9793.02051	539.91400	50.4273



1.94201e4 1104.67365



Totals : 5.79459e4 2759.04672



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.767	BB	0.3052	3073.79346	156.45981	49.9899
2	15.086	BB	0.3141	3075.03418	151.94891	50.0101



6148.82764 308.40872







Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.119	BB	0.1504	2534.43359	258.52734	50.4786
2	8.738	BB	0.1914	2486.37427	202.34375	49.5214



5020.80786 460.87109



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type Width Height Area Area [min] [min] [mAU*s] [mAU] % # 1 6.974 VB 0.1458 1.87221e4 1989.22314 95.8932 2 8.464 BB 0.1694 801.80139 73.41045 4.1068





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.513	BB	0.2097	6821.94531	504.73380	50.2615
2	13.123	BB	0.2615	6750.94580	402.82224	49.7385



1.35729e4 907.55603



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.958	BB	0.2044	9897.90039	748.00787	98.0719
2	13.579	BB	0.2303	194.58932	13.02612	1.9281
Total	ls :			1.00925e4	761.03399	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.008	BV	0.3045	2998.67676	155.84207	50.1583
2	11.338	VB	0.3422	2979.74731	138.91982	49.8417

```
Totals :
```

2

11.337 VB

5978.42407 294.76189

11.25737

2.3185



Totals :	1.03215e4	526.84129

0.3320 239.30016



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.723	VB	0.3031	6448.95654	328.45575	49.9606
2	17.028	BB	0.3256	6459.11670	306.82410	50.0394
Total	ls :			1.29081e4	635.27985	



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.703	VV	0.3204	2.43501e4	1181.84229	96.0009
2	17.019	VB	0.3464	1014.34229	45.79979	3.9991

Totals : 2.53644e4 1227.64207



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.629	BB	0.1581	1228.37537	119.35578	49.9708
2	8.871	BB	0.1854	1229.81091	102.91573	50.0292
Total	s :			2458.18628	222.27151	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.591	BB	0.1646	2.72255e4	2591.50342	95.2287
2	8.850	BV	0.1787	1364.10217	118.18421	4.7713
Total	s :			2.85896e4	2709.68763	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.283	BV	0.2827	4584.15869	249.13396	50.2477
2	15.069	VB	0.2945	4538.95898	238.03766	49.7523



9123.11768 487.17162



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
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RetTime	Туре	Width	Area	Height	Area
[min]		[min]	[mAU*s]	[mAU]	%
14.283	BV	0.3535	3633.41821	158.46327	5.9227
15.032	VB	0.3446	5.77138e4	2644.47632	94.0773
	RetTime [min] 14.283 15.032	RetTime Type [min] 14.283 BV 15.032 VB	RetTime Type Width [min] [min] 14.283 BV 0.3535 15.032 VB 0.3446	RetTime Type Width Area [min] [min] [mAU*s] 14.283 BV 0.3535 3633.41821 15.032 VB 0.3446 5.77138e4	RetTime Type Width Area Height [min] [min] [mAU*s] [mAU] 14.283 BV 0.3535 3633.41821 158.46327 15.032 VB 0.3446 5.77138e4 2644.47632

Totals : 6.13472e4 2802.93959



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

ea
%
7119
2881







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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.144	BV	0.1203	716.04517	92.50546	5.9480
2	6.453	VB	0.1298	1.13223e4	1350.60046	94.0520
Total	s :			1.20383e4	1443.10592	



Area Peak RetTime Type Width Height Area [mAU*s] [min] [min] [mAU] % # 8.036 BB 0.1700 2476.59131 225.69868 49.9545 1 2 9.488 BB 0.2019 2481.09985 190.61894 50.0455 Totals : 4957.69116 416.31763



1	8.041	BB	0.1622	3383.14795	323.10596	95.8819
2	9.513	BB	0.1969	145.30525	11.53650	4.1181
Totals	:			3528.45320	334.64245	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.750	BV	0.3327	1.67234e4	772.07825	49.1200
2	17.877	VV	0.3816	1.73226e4	693.12799	50.8800



3.40461e4 1465.20624



Peak	RetTime	Туре	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
1	16.907	BV	0.4204	8.21386e4	3067.67017	93.2215	
2	18.214	VV	0.4606	5972.62012	192.14595	6.7785	

Totals : 8.81112e4 3259.81612



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.756	BB	0.3816	1437.55469	56.74049	50.4282
2	17.127	BB	0.4383	1413.14209	48.44251	49.5718

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Totals :
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2850.69678 105.18300



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.005	BV	0.4017	2.36423e4	902.31360	92.3043
2	17.427	VV	0.4524	1971.13513	65.24872	7.6957
Tota]	ls :			2.56134e4	967.56232	



Peak	RetTime	Туре	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
1	18.774	VB	0.8259	3899.42847	70.00223	50.0651	
2	22.029	BB	0.9093	3889.28955	63.79278	49.9349	



7788.71802 133.79501





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.948	BB	0.4883	2686.54883	82.41031	49.4788
2	23.430	BB	0.5918	2743.15259	68.11906	50.5212



5429.70142 150.52937



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
		·				
1	19.050	BV	0.4962	4.03757e4	1213.56494	97.5707
2	23.549	VB	0.5735	1005.28259	25.86107	2.4293




Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.271	BB	0.5821	5062.56592	130.63191	49.9272
2	26.488	MM	1.0906	5077.33789	77.58896	50.0728



1.01399e4 208.22087





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.329	BB	0.3291	2249.07300	104.51752	50.2584
2	19.889	BB	0.4391	2225.94849	77.48733	49.7416



4475.02148 182.00484



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.037	BB	0.3605	781.04919	33.44235	6.5012
2	19.434	BV	0.4509	1.12328e4	379.99142	93.4988
Tota	ls :			1.20139e4	413.43377	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.914	BV	0.1855	714.00421	58.87333	49.9179
2	9.629	VB	0.2049	716.35333	53.94331	50.0821
Total	s :			1430.35754	112.81664	



а
701
299
7 2







1.76026e4 487.27794



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.674	VV	0.5491	8.79661e4	2448.83740	93.5656
2	30.691	VB	0.5886	6049.37012	155.23265	6.4344

```
Totals : 9.40155e4 2604.07005
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.802	BV	0.4693	1405.36633	46.41291	49.2446
2	24.040	VB	0.5282	1448.48438	41.60647	50.7554
Tota]	s:			2853.85071	88,01938	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.612	BV	0.5030	2.20600e4	678.99518	95.2638
2	24.037	VB	0.6017	1096.75525	27.24277	4.7362
Tota]	ls :			2.31567e4	706.23795	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.119	BV	0.4758	2919.05786	94.12176	49.3627
2	25.645	VB	0.5074	2994.42627	89.72096	50.6373



5913.48413 183.84272







Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.853	VV	0.1951	4543.17920	350.85968	47.2434
2	11.245	VB	0.2132	5073.34863	349.86975	52.7566



9616.52783 700.72943



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.964	BV	0.1747	718.91083	63.18927	2.0244
2	11.345	VB	0.2150	3.47939e4	2430.25317	97.9756
Tota]	ls :			3.55128e4	2493.44244	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.280	BV	0.4637	5269.39990	174.79636	50.5791
2	26.553	VB	0.5285	5148.74512	148.48883	49.4209







Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.879	BV	0.4874	6.04618e4	1889.11804	95.8671
2	26.217	VB	0.6547	2606.57178	57.95861	4.1329

```
Totals : 6.30684e4 1947.07665
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.419	BV	0.5267	1.02680e4	303.47620	48.4640
2	27.588	VB	0.5915	1.09188e4	280.89456	51.5360
Tota]	ls:			2.11868e4	584.37076	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	25.145	BV	0.5716	1.17148e5	3166.87402	95.7628
2	26.486	VB	0.7031	5183.43701	101.96001	4.2372





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	42.385	BB	1.1541	7750.16748	101.81424	50.0284
2	51.588	BB	1.4446	7741.35840	80.74204	49.9716
Tota]	ls :			1.54915e4	182.55628	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	42.280	BB	0.9957	1244.65991	18.91478	2.7489
2	50.180	BB	1.7131	4.40335e4	367.19342	97.2511
Total	ls:			4.52782e4	386,10820	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.186	BV	0.6618	1.17463e4	258.66711	49.8264
2	29.213	VB	0.7454	1.18281e4	230.97859	50.1736
Tota]	ls:			2.35744e4	489.64571	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.197	BB	0.6596	669.47949	14.91753	7.6668
2	29.210	BB	0.7473	8062.67285	157.49063	92.3332

```
Totals : 8732.15234 172.40817
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.784	BB	0.6778	941.92542	19.42363	50.0661
2	21.084	BB	0.6979	939.43787	18.83613	49.9339
Tota]	ls:			1881.36328	38.25976	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.754	BB	0.5322	2097.30005	61.45028	91.6463
2	21.101	BB	0.5417	191.17317	5.18992	8.3537
Tota]	ls:			2288.47322	66.64020	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	37.981	BB	1.0860	1.48438e4	204.69620	50.1848
2	50.019	BB	1.3935	1.47345e4	156.91739	49.8152
Tota]	ls :			2.95783e4	361.61359	



1	38.012	VB	1.1155	9.37797e4	1275.88586	90.4148
2	50.232	BB	1.3903	9941.93848	106.18739	9.5852

```
Totals : 1.03722e5 1382.07326
```

DAD1 A, Sig=254,4 Ref=360,100 (ZYF\ZYF-766B-IF 2020-03-08 14-31-02\ZYF-766B-RAC-IF970302.D)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.838	BV	0.3619	694.75287	29.38045	49.2771
2	20.662	MF R	0.4203	715.13733	28.36056	50.7229
Total	ls :			1409.89020	57.74101	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area # [min] % [min] [mAU*s] [mAU] 1 19.863 BV 0.4273 1191.67480 43.27234 17.4276 2 20.671 MF R 0.4519 5646.16846 208.21959 82.5724

```
Totals: 6837.84326 251.49193
```

DAD1 A, Sig=254,4 Ref=360,100 (ZYF\ZYF-752-748Q-IA 2020-03-06 19-41-32\ZYF-766D-RAC-AD3-9901102.D)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Area
%
9.5967
0.4033

```
Totals :
```

3735.59473 172.01463





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area [mAU*s] [mAU] # [min] [min] % 1 9.983 MM R 0.3927 4753.51270 201.73419 40.2100 2 11.902 BB 0.4165 7068.21826 265.55365 59.7900 Totals : 1.18217e4 467.28784



Peak RetTime Type Width Area Height Area [min] [mAU*s] [min] [mAU] % # 0.2353 3149.34180 6.202 BV 188.10683 50.0656 1 9.504 BV 2 0.8073 3141.08862 61.14469 49.9344



6290.43042 249.25151



```
Signal 2: DAD1 B, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.239	VB	0.2827	1.10752e4	560.16913	97.9189
2	9.710	MM R	0.5955	235.38094	6.58729	2.0811
Total	s :			1.13106e4	566.75642	



Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 4.372 MM R 0.0848 4914.72217 966.10699 50.5425 1 6.534 MM R 0.3188 4809.20996 49.4575 2 251.38422

Totals :

9723.93213 1217.49121



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area [min] [mAU*s] % # [min] [mAU] 1 4.450 VB 0.1178 4490.42578 625.29132 97.9407 6.666 BB 2 0.1958 94.41592 7.35489 2.0593

Totals : 4584.84171 632.64621



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.597	VB	0.1857	1266.12915	102.80067	50.0310
2	9.414	BB	0.2065	1264.56030	93.09380	49.9690
Total	s :			2530.68945	195.89446	



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Height Area Area % [min] [mAU*s] [min] [mAU] # 8.599 VV 0.1794 7514.17139 637.98065 1 97.2802 9.418 VB 2 0.2113 210.08444 14.64723 2.7198 Totals : 7724.25583 652.62788



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.427	PM R	0.5393	1340.15222	41.41570	50.0724
2	13.593	VB	0.5357	1336.27417	36.79116	49.9276
Total	ls :			2676.42639	78.20685	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.009	BV	0.2950	8705.35645	432.26004	97.7066
2	14.206	BB	0.3949	204.33649	7.66687	2.2934

```
Totals : 8909.69293 439.92692
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.029	VB	0.1267	3149.25854	388.15182	50.1868
2	6.765	BV	0.1355	3125.81274	359.19843	49.8132

```
Totals :
```

6275.07129 747.35025



I Cult I	CCCT IIIC	'ypc	MIGCH	Alcu	nergne	Alcu
#	[min]		[min]	[mAU*s]	[mAU]	%
-						
1	6.087	BV	0.1198	1.41919e4	1844.25476	97.7097
2	6.827	VV	0.1404	332.66104	36.47655	2.2903
Totals	:			1.45246e4	1880.73131	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.483	BB	0.3078	756.79382	37.12859	49.5876
2	6.400	BB	0.4100	769.38037	27.19870	50.4124
Total	s :			1526.17419	64.32729	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.936	BB	0.1827	3038.54712	255.65346	97.7201
2	6.593	BB	0.1787	70.89193	6.13808	2.2799
Total	s :			3109.43905	261.79154	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.351	BV	0.0916	1188.51404	199.28923	49.7512
2	5.074	BB	0.0853	1200.40137	214.38448	50.2488



2388.91541 413.67371





Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU] % 4.211 BB 0.0934 2319.35669 401.22198 50.2858 1 2 5.959 BB 0.3145 2292.99512 118.08895 49.7142



4612.35181 519.31094



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area [mAU*s] [mAU] % [min] [min] # 4.308 BB 0.1052 1849.19604 265.68259 96.7999 1 2 6.186 BB 0.1732 61.13306 5.43506 3.2001 Totals : 1910.32911 271.11764



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.711	BB	0.1605	2029.38220	196.44568	49.9257
2	7.848	BB	0.2327	2035.42004	137.52225	50.0743



4064.80225 333.96793



Peak RetTime Type Width Area Height Area [min] [mAU*s] [mAU] % # [min] 5.806 BV 0.1652 7861.32471 732.59369 97.0239 1 2 8.200 BB 0.2364 241.13655 15.76774 2.9761 Totals : 8102.46126 748.36143



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

77
23



4195.56348 332.79462





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.515	BB	0.3836	1586.25696	63.89269	50.0502
2	14.268	BB	0.5457	1583.07239	45.30571	49.9498

```
Totals :
```

3169.32935 109.19839



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.273	VB	0.3281	2.78173e4	1329.43298	97.2112
2	13.623	BB	0.3885	798.02722	30.57106	2.7888

```
Totals : 2.86153e4 1360.00405
```



Signal 5: DAD1 E, Sig=280,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.206	BB	0.4557	1890.50024	62.71809	50.4911
2	22.785	BB	0.6365	1853.72375	40.77003	49.5089



3744.22400 103.48812



```
Signal 5: DAD1 E, Sig=280,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.197	BB	0.4759	2.63299e4	844.07996	97.3311
2	22.913	BB	0.5470	721.99683	15.86399	2.6689
Total	ls ·			2.70519e4	859 94394	







Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.877	MF R	0.2693	385.24509	23.84423	49.9686
2	7.868	FM R	0.1151	385.72952	55.86004	50.0314
Total	c •			770 97461	79 70428	



Peak RetTime Type Width Height Area Area [min] [min] [mAU*s] [mAU] % # 6.900 MM R 0.3778 6059.02344 267.26840 97.8012 1 2 8.170 MM R 0.1175 136.21985 19.31556 2.1988

Totals : 6195.24329 286.58396



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.848	BB	0.3444	5882.30078	271.88184	50.0957
2	9.647	BB	0.4000	5859.83740	230.99181	49.9043
Total	s :			1.17421e4	502.87364	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.628	BB	0.2536	2.84421e4	1787.75195	96.8677
2	8.993	BB	0.2869	919.70154	49.02748	3.1323

```
Totals : 2.93618e4 1836.77943
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.765	BV	0.1401	1881.16785	206.88243	49.5946
2	8.179	VB	0.1435	1911.92310	203.71669	50.4054



3793.09094 410.59912





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.364	BV	0.7152	3192.59692	67.33228	49.7844
2	28.221	VB	0.7399	3220.24268	61.19516	50.2156

Totals :

6412.83960 128.52745



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area [mAU*s] % # [min] [min] [mAU] 0.6580 4539.26367 105.92168 1 25.530 BB 98.2285 2 27.427 MM R 0.6356 81.86126 2.14651 1.7715

```
Totals : 4621.12493 108.06819
```



Signal 7: DAD1 G, Sig=270,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.878	BV	0.3206	3138.85400	152.20680	49.9336
2	9.392	VB	0.3456	3147.20752	140.37834	50.0664
Total	s :			6286.06152	292,58514	



```
Signal 7: DAD1 G, Sig=270,4 Ref=360,100
```

Peak RetTime Type Width Height Area Area [mAU*s] % # [min] [min] [mAU] 7.899 MM R 0.3619 5.67590e4 2613.85107 97.6587 1 2 9.419 MM R 0.3478 1360.75684 65.20293 2.3413

```
Totals : 5.81197e4 2679.05401
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.290	BB	0.2714	347.67838	18.48835	50.7262
2	10.138	BB	0.3196	337.72354	15.53461	49.2738
Tota]	ls :			685.40192	34.02296	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.279	BV	0.2387	4.04618e4	2527.73828	96.4793
2	10.186	BB	0.2707	1476.53137	81.00645	3.5207

```
Totals : 4.19383e4 2608.74474
```



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.244	BB	0.1553	655.55847	65.20034	51.3881
2	8.217	BB	0.1717	620.14203	55.78038	48.6119
Total	s :			1275.70050	120.98072	





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.062	BV	0.0981	2008.43689	316.12735	50.3937
2	6.192	BV	0.1211	1977.05383	253.16180	49.6063



3985.49072 569.28915



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area [mAU*s] % # [min] [min] [mAU] 1 5.106 VV 0.0961 80.43413 13.02098 2.0035 2 6.267 BV 0.1220 3934.30713 499.01938 97.9965

```
Totals : 4014.74126 512.04036
```


Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.646	BB	0.5680	1554.61609	42.57450	49.4216
2	20.888	BB	0.6220	1591.00269	38.83545	50.5784
Tota]	ls :			3145.61877	81.40995	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.184	BB	0.4812	206.54774	6.19099	2.8117
2	21.330	BB	0.6198	7139.35107	178.83075	97.1883
Tota]	ls :			7345.89882	185.02174	



Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.213	MM R	0.0731	1083.55103	247.09938	50.5407
2	6.424	BB	0.7832	1060.36792	19.17383	49.4593



2143.91895 266.27321



Peak RetTime Type Width Height Area Area [mAU*s] [mAU] % # [min] [min] 5.818 MM R 0.1204 9809.58203 1357.92017 98.0296 1 2 6.565 MM R 0.2633 197.17323 12.47970 1.9704





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	4.751	MM R	0.1201	345.87381	47.98752	48.7034
2	5.358	MM R	0.1420	364.28961	42.74282	51.2966
Total	s :			710.16342	90.73034	



```
Signal 1: DAD1 A, Sig=214,4 Ref=360,100
```

Peak RetTime Type Width Height Area Area [min] [mAU*s] [mAU] % [min] # 0.1131 6794.41016 870.11493 1 4.573 BV 97.5879 5.205 VV 2 0.1216 167.94067 20.06841 2.4121

```
Totals : 6962.35083 890.18334
```



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.015	BB	0.1134	913.40027	124.72250	49.3037
2	6.451	MM R	0.0688	939.20123	227.45976	50.6963



1852.60150 352.18226



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.003	MM R	0.1244	43.97273	5.89007	2.3082
2	6.494	BB	0.0836	1861.09436	352.44507	97.6918





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.282	BV	0.1942	1980.71033	158.10667	50.0126
2	7.780	VB	0.2101	1979.71606	146.04352	49.9874



3960.42639 304.15019



```
Signal 1: DAD1 A, Sig=214,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.284	BV	0.1908	288.00461	23.20487	2.8062
2	7.773	VB	0.2140	9975.31543	727.34558	97.1938
Total	s :			1.02633e4	750.55045	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
		·				
1	12.874	BB	0.3205	945.29657	44.37400	49.5588
2	15.653	MM R	0.4689	962.12701	34.20055	50.4412
Tota]	ls :			1907.42358	78.57455	





Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.370	MM R	0.1164	2567.30859	367.73059	49.7400
2	8.869	VB	0.1165	2594.14429	342.09372	50.2600



5161.45288 709.82431



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.349	BV	0.1139	6697.67578	909.37958	97.2002
2	8.900	VB	0.1291	192.92085	22.26547	2.7998
Total	s :			6890.59663	931.64505	



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.825	VB	0.1350	671.90717	71.92393	50.5346
2	6.945	BB	0.1681	657.69202	57.21733	49.4654
Total	s :			1329.59918	129.14126	



Peak RetTime Type Width Area Height Area [min] [min] [mAU*s] [mAU] % # 5.545 BB 0.1386 6701.07666 706.94299 1 97.4670 6.478 BB 0.1396 174.14894 2 18.53441 2.5330



6875.22560 725.47740



Peak	RetTime	Туре	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
1	11.085	BV	0.2523	5272.16260	301.03622	49.6566	
2	11.937	VV	0.3523	5345.07666	217.82977	50.3434	



1.06172e4 518.86600



```
Signal 3: DAD1 C, Sig=214,4 Ref=360,100
```

Peak RetTime Type Width Area Height Area [mAU*s] [mAU] % [min] [min] # 1 11.061 BV 0.2739 1.38336e4 727.25342 97.8746 2 12.137 VV 0.2664 14.70348 300.40100 2.1254







3.29733e4 1793.94177



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.200	BB	0.2572	1.14470e4	684.04071	98.0414
2	13.763	BB	0.3176	228.67451	11.23076	1.9586
Tota]	ls :			1.16757e4	695.27147	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.837	BB	0.4457	2098.60278	72.07382	50.0566
2	21.046	BB	0.5154	2093.85718	62.09042	49.9434



4192.45996 134.16424



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.746	BB	0.4564	1.09902e4	372.29544	96.6405
2	21.008	BB	0.4573	382.05267	11.33355	3.3595
Tota]	ls :			1.13723e4	383.62899	



```
Peak RetTime Type Width Area Height
```

#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.451	MM R	0.5434	1159.58057	35.56630	50.1926
2	24.779	MM R	0.9105	1150.68372	21.06347	49.8074



2310.26428 56.62976

Area



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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.641	BB	0.5604	1.47110e4	372.77234	96.3564
2	24.860	BB	0.7647	556.28619	10.76901	3.6436
Tota]	ls :			1.52673e4	383,54134	



Peak RetTime Type Width Area Height Area [mAU*s] % # [min] [min] [mAU] 16.139 BB 0.9433 4851.99951 77.83559 1 49.9747 2 32.344 MM R 2.7534 4856.91992 29.39925 50.0253

Totals :

9708.91943 107.23483





Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.090	MM R	0.7895	2715.98438	57.33488	50.5562
2	47.345	BB	0.9143	2656.22070	43.75444	49.4438

```
Totals :
```

5372.20508 101.08932



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Signal 2: DAD1 B, Sig=254,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.343	BB	0.7382	731.45221	14.80937	3.8413
2	47.912	BB	0.8706	1.83105e4	316.67783	96.1587
Total	ls :			1.90420e4	331,48719	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.442	MF R	0.7498	3972.74390	88.30556	22.5920
2	27.965	FM R	0.8227	4820.98682	97.66157	27.4158
3	32.622	BB	0.9617	3949.62598	64.74719	22.4606
4	72.701	MM R	3.6939	4841.35400	21.84377	27.5316

Totals :

1.75847e4 272.55810



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.399	MM R	0.8570	83.60978	1.62611	2.4258
2	27.855	MM R	0.9583	46.63989	8.11171e-1	1.3532
3	32.549	BB	0.9589	1821.65247	29.64622	52.8518
4	73.711	MM R	3.6009	1494.81494	6.91866	43.3692
Total	s:			3446.71708	39,00216	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	49.762	BB	1.4710	3122.11987	30.63352	50.1574
2	60.365	BB	1.7396	3102.52734	25.82574	49.8426
Tota]	ls:			6224.64722	56.45926	



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime T	ype l	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
	-	-				
1	49.588 B	В	1.5729	8136.13623	77.49374	97.6809
2	61.270 M	MR	1.9579	193.16867	1.64433	2.3191
Tota]	ls :			8329,30490	79.13808	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.062	BB	0.6608	2472.86621	55.18290	49.3537
2	26.628	BB	0.9212	2537.63110	40.71278	50.6463
Total	ls :			5010.49731	95.89569	





```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.924	BB	0.6588	1228.36011	27.83800	2.2159
2	26.539	MM R	1.1075	5.42060e4	815.72455	97.7841
Total	ls :			5.54343e4	843,56255	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.369	MM R	0.5201	4320.77100	138.46153	50.1018
2	16.382	MM R	0.7889	4303.21582	90.91515	49.8982



8623.98682 229.37668











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Signal 1: DAD1 A, Sig=254,4 Ref=360,100
```

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.419	VB	0.4290	528.89917	19.22113	1.8773
2	20.464	BB	0.5423	2.76447e4	778.51514	98.1227
Tota]	ls :			2.81736e4	797.73627	



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.161	VB	0.3563	3997.34106	173.79562	50.0666
2	26.189	BB	0.6617	3986.71338	92.70757	49.9334



7984.05444 266.50319



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.846	VB	0.3518	391.41522	17.05072	1.9788
2	25.255	BB	0.6989	1.93891e4	426.04935	98.0212
Tota]	ls :			1.97805e4	443.10006	



Signal 6: DAD1 F, Sig=280,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.637	BB	0.9903	5895.09082	93.66658	48.6286
2	17.620	MM R	0.7128	6227.59229	145.62328	51.3714

1.21227e4 239.28986



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.175	BB	0.5286	141.67476	4.14668	2.0060
2	17.618	MM R	0.7568	6920.94727	152.40685	97.9940

Totals : 7062.62202 156.55353



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.588	BB	0.1961	3457.52783	272.33218	49.8547
2	11.492	BB	0.2136	3477.67480	251.00453	50.1453



6935.20264 523.33672



```
Signal 1: DAD1 A, Sig=214,4 Ref=360,100
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Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.599	BB	0.1955	3697.45703	288.56125	98.0243
2	11.514	BB	0.2088	74.52402	5.33948	1.9757
Tota]	ls :			3771.98105	293.90073	





Peak RetTime Type Width Area Height Area % # [min] [min] [mAU*s] [mAU] 1 17.772 BV 0.3124 2820.82251 138.06364 50.3584 2 26.293 BV 0.4474 2780.67456 95.02544 49.6416



5601.49707 233.08909



DAD1 B, Sig=254,4 Ref=360,100 (D:\CHEM\1\DATA\DONGXY\D-7-103 RAC-ODH-980205-1.D)



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.815	MM R	0.5350	7354.45313	229.11613	49.9248
2	21.307	MM R	0.6960	7376.61523	176.63210	50.0752

1.47311e4 405.74823



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.713	BV	0.4837	5418.10693	170.07100	93.7927
2	21.390	VB	0.7526	358.57712	7.01265	6.2073



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