Electronic Supplementary Information

Enantioselective Addition of Terminal 1,3-Diynes to Aromatic Ketones
Triggered by Cu-Hydroxycamphorsulfonamide Complexes

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1. General information:

$^1$H, $^{13}$C and $^{19}$F were recorded on Varian Mercury Plus 400 instruments or Bruker AV 400 MHz at 400 MHz ($^1$H NMR), 100 MHz ($^{13}$C NMR), as well as 376 MHz ($^{19}$F NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal Me$_4$Si. MS were recorded on a VG-7070E or VG ZAB-HS spectrometer with the EI or ESI resource. Optical rotations were determined using an Autopol IV-T. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument. X-ray structural analyses was conducted on the XtaLAB mini (600 W, SHINE, CCD, 75mn, 0.1 electrons/pixel/sec).

Materials:

Tetrahydrofuran (THF), diethyl ether and toluene were distilled from sodium/benzophenone prior to use; CH$_2$Cl$_2$ (DCM) and ClCH$_2$CH$_2$Cl (DCE) were distilled from CaH$_2$. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. Ligands I–VI were synthesized by known method.¹ Substituted terminal 1,3-Diynes were synthesized by literature.² Dimethylzinc (1.2M solution in toluene) were purchased from ACROS Organics. Standard reagents and solvents were purified according to known procedures.

2. Preparation of Ligands:

Ligands I–VI were synthesized by known method.¹
N-(anthracen-9-ylmethyl)-1-(((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl)methanesulfonamide (IV): mp 167-169 °C; $[\alpha]_D^{20} = -34.5$ (c 1.0, CH$_2$Cl$_2$);

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 8.44 (1H, s), 8.29 (2H, d, $J = 8.9$ Hz), 8.00 (2H, d, $J = 8.4$ Hz), 7.60-7.56 (2H, m), 7.50-7.46 (2H, m), 5.29 (2H, d, $J = 5.6$ Hz), 4.95 (1H, t, $J = 5.5$ Hz), 3.98-3.94 (1H, m), 3.14 (2H, dd, $J = 26.3$ Hz, 8.7 Hz), 2.61 (1H, d, $J = 13.7$ Hz), 1.69-1.53 (5H, m), 1.02-0.95 (2H, m), 0.77 (3H, s), 0.47 (3H, s); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 131.5, 130.1, 129.4, 128.7, 127.1, 125.3, 123.4, 76.3, 52.9, 50.3, 48.5, 44.3, 39.4, 38.9, 30.3, 27.3, 20.2, 19.6; MS(ESI) m/z 446.2 (M+Na)$^+$; IR (neat) $\nu$ 3459, 3160, 3048, 2955, 2933, 2881, 1453, 1317, 1137, 1075, 1022, 878, 738, 568 cm$^{-1}$.

3. General procedure for the enantioselective addition of terminal 1,3-Diynes to aromatic ketones:

A CH$_2$Cl$_2$ solution (1.0 mL) of sulfonamide ligand III (7.46 mg, 0.02 mmol) and copper(II) triflate (7.22 mg, 0.02 mmol) was stirred at room temperature for 30 min to prepare the copper complex. Buta-1,3-diynylbenzene (65.5 mg, 0.52 mmol) and a 1.2M solution of dimethylzinc in toluene (0.5 mL, 0.6 mmol) were added to a dry flask at 0 °C under Ar$_2$ with stirring for 30 min. The copper complex was added to the flask containing ZnMe$_2$ and buta-1,3-diynylbenzene via a syringe and the homogeneous solution was stirred at 10 °C for 30 min, then acetophenone (23.5 μL, 0.2 mmol) was added. The mixture was allowed to stir at 10 °C for 48 h. The reaction
was quenched with 5% HCl solution. The product was extracted with ether (5 mL×3) washed with brine and dried over Na₂SO₄. The compound was purified via flash chromatography (silica gel) using 5% ethyl acetate in petroleum ether as eluent. The enantiomeric excess was determined by HPLC analysis on a Chiralcel OD-H IA or IB column.

2,6-Diphenylhexa-3,5-diyn-2-ol (3a): 94% yield, 77% ee; [α]D²⁰ +9.9 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.65 (2H, d, J = 7.7 Hz), 7.49 (2H, d, J = 7.4 Hz), 7.39-7.31 (6H, m), 3.06 (1H, br s), 1.82 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 144.8, 132.6, 129.4, 128.5, 128.0, 124.9, 121.5, 85.5, 79.4, 73.3, 70.5, 69.6, 33.0; MS(EI) m/z 245.5; IR (neat) ν 3398, 3060, 3030, 2963, 2929, 2235, 1598, 1446, 1261, 1158, 1094, 1067, 1024, 800, 758, 694 cm⁻¹; HPLC (DAICEL Chiralpak OD-H, Hexane / i-PrOH = 90 / 10, 0.8 mL / min, 254 nm) t_R (major) = 12.5 min, t_R (minor) = 18.7 min.

2-(2-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3b): 92% yield, 90% ee; [α]D²⁰ +5.8 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.74 (1H, d, J = 7.5 Hz), 7.48 (2H, d, J = 7.7 Hz), 7.42 (1H, d, J = 7.6 Hz), 7.36-7.29 (5H, m), 3.14 (1H, s), 1.99 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 140.4, 132.6, 131.9, 131.4, 129.3, 128, 127.0, 126.6, 121.5, 84.1, 79.6, 73.3, 69.4, 69.3, 29.4; MS(EI) m/z 279.6 ; IR (neat) ν 3445, 3063, 2960, 2918, 2849, 2235, 1434, 1264, 1037, 755, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 10.7 min, t_R (minor) = 15.8 min.

(S)-2-(2-bromophenyl)-6-phenylhexa-3,5-diyn-2-ol (3c): 91% yield, 90% ee; [α]D²⁰
+3.6 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.76 (1H, d, J = 7.7 Hz), 7.63 (1H, d, J = 7.8 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.36-7.29 (4H, m), 7.18 (1H, t, J = 7.5 Hz), 3.22 (1H, s), 2.01 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 141.7, 134.9, 132.6, 129.5, 129.3, 128.4, 127.6, 126.9, 121.5, 121.1, 84.0, 79.6, 73.3, 70.2, 69.9, 29.5; MS(EI) m/z 323.7; IR (neat) ν 3401, 3061, 2962, 2929, 2235, 1489, 1443, 1260, 1093, 1027, 799, 755, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 85 / 15, 1.0 mL / min, 254 nm) tᵣ (major) = 5.9 min, tᵣ (minor) = 7.5 min.

2-(2-Fluorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3d): 88% yield, 79% ee; [α]D²⁰ +7.4 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.65 (1H, t, J = 7.9 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.36-7.30 (4H, m), 7.16 (1H, t, J = 7.6 Hz), 7.09 (1H, dd, J = 11.5 Hz, 8.4 Hz), 2.77 (1H, s), 1.94 (3H, s). ¹³C-NMR (CDCl₃, 100 MHz) δ 160.1 (d, ¹JF-C = 246.5 Hz), 132.6, 131.1 (d, ³JF-C = 10.5 Hz), 129.9 (d, ³JF-C = 8.6 Hz), 129.3, 128.4, 126.6 (d, ²JF-C = 22.1 Hz), 124.1 (d, ⁴JF-C = 3.4 Hz), 116.4 (d, ²JF-C = 22.1 Hz), 84.1, 79.6, 73.1, 69.0, 68.0, 30.2; ¹⁹F-NMR (CDCl₃, 376 MHz) δ -112.8 (1F, s); MS(EI) m/z 263.7; IR (neat) ν 3391, 3062, 3018, 2985, 2935, 2869, 2238, 1584, 1486, 1443, 1224, 1078, 754, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 95 / 5, 1.0 mL / min, 254 nm) tᵣ (major) = 11.3 min, tᵣ (minor) = 15.4 min.

6-Phenyl-2-(o-tolyl)hexa-3,5-diyn-2-ol (3e): 60% yield, 71% ee; [α]D²⁰ +3.2 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.68-7.66 (1H, m), 7.48 (2H, d, J = 6.9 Hz), 7.35-7.29 (3H, m), 7.24-7.20 (3H, m), 2.83 (1H, s), 2.65 (3H, s), 1.90 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 141.3, 135.8, 132.6, 132.4, 129.3, 128.4, 128.0, 125.9, 121.6, 85.5, 79.5, 73.3, 70.2, 69.5, 30.7, 21.2; MS(EI) m/z 259.7; IR (neat) ν 3397, 3062, 3018, 2985, 2931, 2235, 1488, 1442, 1159, 1079, 1058, 912, 755, 726, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 80 / 20, 1.0 mL / min, 254 nm) tᵣ
6-Phenyl-2-(p-tolyl)hexa-3,5-diyn-2-ol (3f): 67% yield, 71% ee; \([\alpha]_D^{20} +11.7 (c 1.0, \text{CH}_2\text{Cl}_2)\); \(^1\text{H}-\text{NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.54 (2\text{H}, d, J = 7.7 \text{ Hz}), 7.49 (2\text{H}, d, J = 7.2 \text{ Hz}), 7.36-7.29 (3\text{H}, m), 7.18 (2\text{H}, d, J = 7.7 \text{ Hz}), 2.67 (1\text{H}, s), 2.35 (3\text{H}, s), 1.82 (3\text{H}, s); \(^{13}\text{C}-\text{NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 142.0, 137.7, 132.6, 129.3, 129.1, 128.4, 124.9, 121.6, 85.8, 79.2, 73.4, 70.3, 69.3, 32.9, 21.1; \text{MS}(\text{EI}) \text{ m/z} 259.8; \text{IR} (\text{neat}) \nu 3382, 3056, 3028, 2983, 2236, 1596, 1442, 1158, 1091, 917, 818, 755, 688, 578, 526 \text{ cm}^{-1}; \text{HPLC} (\text{DAICEL Chiralpak OD-H, Hexane / i-PrOH} = 95 / 5, 0.8 \text{ mL / min, 254 nm}) t_R (\text{major}) = 20.2 \text{ min}, t_R (\text{minor}) = 31.4 \text{ min}.

2-(4-Fluorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3g): 83% yield, 71% ee; \([\alpha]_D^{20} +17.8 (c 1.0, \text{CH}_2\text{Cl}_2); \(^1\text{H}-\text{NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.65-7.62 (2\text{H}, m), 7.50 (2\text{H}, d, J = 6.9 \text{ Hz}), 7.36-7.31 (3\text{H}, m), 7.06 (2\text{H}, t, J = 8.6 \text{ Hz}), 2.41 (1\text{H}, s), 1.82 (3\text{H}, s); \(^{13}\text{C}-\text{NMR} (\text{CDCl}_3, 100 \text{ MHz}) \delta 159.8 (d, ^{3}J_{\text{F-C}} = 236.5 \text{ Hz}), 140.5 (d, ^{4}J_{\text{F-C}} = 3.4 \text{ Hz}), 132.6, 129.4, 128.5, 126.8 (d, ^{3}J_{\text{F-C}} = 8.1 \text{ Hz}), 121.4, 115.2 (d, ^{2}J_{\text{F-C}} = 22.1 \text{ Hz}), 84.8, 79.7, 73.0, 70.1, 69.9, 33.1; \(^{19}\text{F}-\text{NMR} (\text{CDCl}_3, 376 \text{ MHz}) \delta -114.6 (1\text{F}, s); \text{MS}(\text{EI}) \text{ m/z} 263.7; \text{IR} (\text{neat}) \nu 3380, 3063, 2986, 2929, 2856, 2237, 1602, 1506, 1226, 1159, 1087, 836, 755, 688, 575, 525 \text{ cm}^{-1}; \text{HPLC} (\text{DAICEL Chiralpak IB, Hexane / i-PrOH} = 95 / 5, 1.0 \text{ mL / min, 254 nm}) t_R (\text{major}) = 12.0 \text{ min}, t_R (\text{minor}) = 16.2 \text{ min}.

2-(4-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3h): 86% yield, 72% ee; \([\alpha]_D^{20} +11.7 (c 1.0, \text{CH}_2\text{Cl}_2); \(^1\text{H}-\text{NMR} (\text{CDCl}_3, 400 \text{ MHz}) \delta 7.59 (2\text{H}, d, J = 8.4 \text{ Hz}), 7.50 (2\text{H}, d, J = 7.1 \text{ Hz}), 7.38-7.31 (5\text{H}, m), 2.42 (1\text{H}, s), 1.81 (3\text{H}, s); \(^{13}\text{C}-\text{NMR} (\text{CDCl}_3,
100 MHz) δ 143.2, 133.9, 132.6, 129.5, 128.6, 128.5, 126.4, 121.3, 84.6, 79.8, 72.9, 70.1, 70.0, 33.0; MS(EI) m/z 279.8; IR (neat) ν 3552, 3357, 3296, 3057, 2984, 2929, 2856, 2236, 1489, 1092, 1013, 829, 755, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 16.7 min, t_R (minor) = 18.1 min.

2-(4-Bromophenyl)-6-phenylhexa-3,5-diyn-2-ol (3i): 80% yield, 65% ee; [α]_D^{20} +20.2 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.54-7.49 (6H, m), 7.38-7.31 (3H, m), 2.45 (1H, s), 1.81 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 143.8, 132.6, 131.5, 129.5, 128.5, 126.8, 122.0, 121.3, 84.5, 79.8, 72.9, 70.2, 70.0, 33.0; MS(EI) m/z 324.4; IR (neat) ν 3331, 3059, 2985, 2926, 2850, 2235, 1590, 1486, 1087, 1009, 823, 754, 688 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 80 / 20, 0.8 mL / min, 254 nm) t_R (major) = 7.2 min, t_R (minor) = 8.1 min.

2-(4-Iodophenyl)-6-phenylhexa-3,5-diyn-2-ol (3j): 95% yield, 81% ee; [α]_D^{20} +10.5 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.71 (2H, d, J = 8.6 Hz), 7.50 (2H, d, J = 6.7 Hz), 7.41-7.31 (5H, m), 2.43 (1H, s), 1.80 (3H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 144.5, 137.5, 132.6, 129.4, 128.5, 127.0, 121.3, 93.6, 84.5, 79.8, 72.9, 70.2, 70.0, 32.9; MS(ESI) m/z 355.0 (M-OH)⁺; IR (neat) ν 3411, 3054, 2985, 2918, 2849, 2235, 1484, 1391, 1264, 1087, 1005, 820, 754, 739, 688 cm⁻¹; HPLC (DAICEL Chiralpak OD-H, Hexane / i-PrOH = 80 / 20, 0.8 mL / min, 254 nm) t_R (major) = 11.5 min, t_R (minor) = 24.0 min.

2-(3-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3k): 92% yield, 70% ee; [α]_D^{20} +9.0 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.65 (1H, s), 7.53 (1H, d, J = 7.0
Hz), 7.50 (2H, d, \( J = 7.1 \) Hz), 7.37-7.28 (5H, m), 3.68 (1H, br s), 1.81 (3H, s);
\(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 147.0, 134.4, 132.6, 129.7, 129.4, 128.5, 128.0, 125.3, 123.2, 121.4, 84.8, 79.6, 73.1, 69.9, 69.8, 33.1; MS(EI) m/z 279.9; IR (neat) \( \nu \) 3295, 3060, 2918, 2849, 2236, 1433, 1264, 1037, 755, 688 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \( i-\)PrOH = 70 / 30, 0.8 mL / min, 254 nm) \( t_R \) (major) = 5.1 min, \( t_R \) (minor) = 6.0 min.

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\begin{align*}
\text{2-(Naphthalen-2-yl)-6-phenylhexa-3,5-diyn-2-ol (3l):} & \quad 71\% \text{ yield, 68\% ee; } [\alpha]_D^{20} +2.5 (c 1.0, \text{CH}_2\text{Cl}_2); \quad ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta 8.12 (1H, s), 7.90-7.83 (3H, m), 7.74 (1H, d, \( J = 8.6 \) Hz), 7.52-7.49 (4H, m), 7.38-7.31 (3H, m), 2.58 (1H, s), 1.92 (3H, s); \quad ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta 141.9, 133.1, 133.0, 132.6, 129.4, 128.5, 128.4, 128.4, 127.6, 126.4, 126.3, 123.5, 123.2, 121.5, 85.2, 79.6, 73.2, 70.7, 69.9, 32.8; \quad \text{MS(ESI) m/z 279.1 (M-OH)$^+$; IR (neat) } \nu 3538, 3384, 3057, 2984, 2928, 2859, 2236, 1598, 1489, 1442, 1187, 1127, 1084, 858, 818, 752, 688, 526, 477 \text{ cm}^{-1}; \quad \text{HPLC (DAICEL Chiralpak IB, Hexane / } i-\text{PrOH = 80 / 20, 1.0 mL / min, 254 nm) } t_R \text{ (minor) } = 7.7 \text{ min, } t_R \text{ (major) } = 21.1 \text{ min.}
\end{align*}
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\begin{align*}
\text{3,7-Diphenylepta-4,6-diyn-3-ol (3m):} & \quad 91\% \text{ yield, 62\% ee; } [\alpha]_D^{20} +11.0 (c 1.0, \text{CH}_2\text{Cl}_2); \quad ^1\text{H-NMR (CDCl}_3, 400 MHz) \delta 7.62 (1H, d, \( J = 7.4 \) Hz), 7.51 (1H, d, \( J = 7.0 \) Hz), 7.39-7.31 (6H, m), 2.08-1.95 (2H, m), 0.99 (3H, t, \( J = 7.3 \) Hz); \quad ^{13}\text{C-NMR (CDCl}_3, 100 MHz) \delta 143.7, 132.6, 129.4, 128.5, 128.3, 127.9, 125.5, 121.5, 84.6, 79.0, 74.5, 73.3, 70.6, 38.3, 9.1; \quad \text{MS(EI) m/z 259.6; IR (neat) } \nu 3396, 3384, 3057, 2984, 2928, 2859, 2236, 1598, 1489, 1442, 1187, 1127, 1084, 858, 818, 752, 688, 526, 477 \text{ cm}^{-1}; \quad \text{HPLC (DAICEL Chiralpak IB, Hexane / } i-\text{PrOH = 80 / 20, 1.0 mL / min, 254 nm) } t_R \text{ (minor) } = 4.3 \text{ min, } t_R \text{ (major) } = 4.7 \text{ min.}
\end{align*}
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6-(4-Methoxyphenyl)-2-phenylhexa-3,5-diyn-2-ol (3n): 90% yield, 80% ee; [\(\alpha\)]\(_D\)\(^{20}\) +22.4 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.66 (2H, d, J = 7.6 Hz), 7.44 (2H, d, J = 8.7 Hz), 7.38 (2H, t, J = 7.5 Hz), 7.31 (1H, t, J = 7.2 Hz), 6.84 (2H, d, J = 8.7 Hz), 3.81 (3H, s), 2.50 (1H, s), 1.83 (3H, s); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 160.5, 144.8, 134.2, 128.4, 128.0, 124.9, 114.2, 113.4, 84.7, 79.9, 72.1, 70.6, 69.9, 55.3, 33.0; MS(EI) m/z 275.7; IR (neat) ν 3418, 3060, 2984, 2933, 2838, 2233, 1603, 1509, 1252, 1174, 1030, 831, 763, 699 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \(i\)-PrOH = 90 / 10, 1.0 mL / min, 254 nm) \(t_R\) (major) = 10.2 min, \(t_R\) (minor) = 12.2 min.

2-Phenyl-6-(p-tolyl)hexa-3,5-diyn-2-ol (3o): 82% yield, 70% ee; [\(\alpha\)]\(_D\)\(^{20}\) +17.7 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.65 (2H, d, J = 7.7 Hz), 7.40-7.36 (4H, m), 7.31 (1H, t, J = 7.2 Hz), 7.12 (2H, d, J = 7.8 Hz), 2.54 (1H, s), 2.35 (3H, s), 1.83 (3H, s); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 144.8, 139.8, 132.5, 129.2, 128.4, 128.0, 124.9, 118.4, 85.0, 79.7, 72.6, 70.6, 69.8, 33.0, 21.6; MS(EI) m/z 259.6; IR (neat) ν 3415, 3029, 2958, 2928, 2870, 2234, 1602, 1509, 1448, 1286, 1180, 815, 763, 699, 527 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \(i\)-PrOH = 80 / 20, 0.8 mL / min, 254 nm) \(t_R\) (major) = 5.8 min, \(t_R\) (minor) = 6.0 min.

6-(4-Fluorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3p): 77% yield, 62% ee; [\(\alpha\)]\(_D\)\(^{20}\) +12.1 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.65 (2H, d, J = 7.3 Hz), 7.48 (2H, m), 7.38 (2H, t, J = 7.5 Hz), 7.30 (1H, t, J = 7.2 Hz), 7.02 (2H, t, J = 8.6 Hz), 2.91 (1H, br s), 1.83 (3H, m); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 163.1 (d, \(J_{F-C} = 250.1\) Hz), 145.0, 134.6 (d, \(J_{F-C} = 8.6\) Hz), 128.4, 127.9, 124.9, 117.7 (d, \(4J_{F-C} = 3.4\) Hz),
115.9 (d, \( J_{F-C} = 22.1 \) Hz), 85.9, 78.1, 73.2, 70.3, 69.2, 33.1; \(^{19}\)F-NMR (CDCl\(_3\), 376 MHz) \( \delta \) -108.4 (1F, s); MS(EI) m/z 263.6; IR (neat) ν 3359, 3061, 3029, 2985, 2931, 2237, 1598, 1505, 1232, 1155, 835, 699, 529 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \( i\)-PrOH = 80 / 20, 1.0 mL / min, 254 nm) \( t_R \) (major) = 4.6 min, \( t_R \) (minor) = 5.0 min.

\[ \text{6-(4-Chlorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3q): 79\% yield, 66\% ee; } [\alpha]^{20}_D \]

+12.6 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.64 (2H, d, \( J = 7.5 \) Hz), 7.42-7.36 (4H, m), 7.32-7.28 (3H, m), 2.69 (1H, s), 1.82 (3H, s); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 144.8, 139.8, 132.5, 129.2, 128.4, 128.0, 124.9, 118.4, 85.0, 79.7, 72.6, 70.6, 69.8, 33.0, 21.6; MS(EI) m/z 279.6; IR (neat) ν 3554, 3375, 3060, 330, 2985, 2929, 2860, 2236, 1489, 1092, 1013, 826, 763, 699, 578, 524 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \( i\)-PrOH = 90 / 10, 1.0 mL / min, 254 nm) \( t_R \) (major) = 6.2 min, \( t_R \) (minor) = 7.0 min.

\[ \text{6-(2-Chlorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3r): 85\% yield, 67\% ee; } [\alpha]^{20}_D \]

+12.1 (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.65 (2H, d, \( J = 6.9 \) Hz), 7.52 (1H, d, \( J = 6.9 \) Hz), 7.39-7.38 (3H, m), 7.33-7.26 (2H, m), 7.21 (1H, t, \( J = 6.4 \) Hz), 2.61 (1H, s), 1.84 (3H, s); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 144.5, 137.0, 134.4, 130.3, 129.6, 128.5, 128.1, 126.6, 124.9, 121.7, 86.8, 78.0, 75.9, 70.6, 69.4, 32.9; MS(EI) m/z 279.6; IR (neat) ν 3911, 3063, 2983, 2963, 2917, 2849, 2235, 1435, 1093, 1067, 754, 698 cm\(^{-1}\); HPLC (DAICEL Chiralpak IB, Hexane / \( i\)-PrOH = 90 / 10, 1.0 mL / min, 254 nm) \( t_R \) (major) = 6.3 min, \( t_R \) (minor) = 7.7 min.
6-(Cyclohex-1-en-1-yl)-2-phenylhexa-3,5-diyn-2-ol (3s): 85% yield, 79% ee; [α]_D^{20} +16.5 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.62 (2H, d, J = 7.5 Hz), 7.35 (2H, t, J = 7.3 Hz), 7.29 (1H, d, J = 7.1 Hz), 6.29 (1H, m), 2.94 (1H, s), 2.14-2.09 (4H, m), 1.78 (3H, s), 1.63-1.56 (4H, m); ¹³C-NMR (CDCl₃, 100 MHz) δ 144.9, 139.2, 128.4, 127.9, 124.9, 119.5, 84.4, 81.5, 70.7, 70.5, 69.9, 33.0, 28.6, 25.9, 22.1, 21.3; MS(EI) m/z 249.7; IR (neat) ν 3384, 3061, 3027, 2984, 2932, 2860, 2228, 1448, 1146, 1092, 1055, 919, 763, 699, 578 cm⁻¹; HPLC (DAICEL Chiralpak IB, Hexane / i-PrOH = 90 / 10, 1.0 mL / min, 254 nm) tᵣ (major) = 5.2 min, tᵣ (minor) = 5.5 min.

2-Phenyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (3t): 71% yield, 72% ee, [α]_D^{20} +6.1 (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃, 400 MHz) δ 7.62 (2H, d, J = 7.5 Hz), 7.37 (2H, t, J = 7.5 Hz), 7.30 (1H, d, J = 7.2 Hz), 2.53 (1H, s), 1.79 (3H, s), 1.09 (21H, s); ¹³C-NMR (CDCl₃, 100 MHz) δ 144.6, 128.4, 128.0, 124.9, 88.9, 85.6, 79.2, 70.4, 70.2, 32.9, 18.5, 11.3; MS(EI) m/z 283.1 (M⁻Pr); IR (neat) ν 3325, 2944, 2891, 2866, 2211, 2102, 1462, 1367, 1239, 1065, 921, 882, 763, 697, 678, 579 cm⁻¹; HPLC (DAICEL Chiralpak IA, Hexane / i-PrOH = 95 / 5, 1.0 mL / min, 254 nm) tᵣ (minor) = 4.7 min, tᵣ (major) = 5.0 min.

4. A large-scale addition, Further transformation, and X-ray Analysis:
A CH₂Cl₂ solution (15.0 mL) of sulfonamide ligand III (112.0 mg, 0.3 mmol) and copper(II) triflate (108.3 mg, 0.3 mmol) was stirred at room temperature for 30 min to prepare the copper complex. Buta-1,3-diynylbenzene 2a (982.5 mg, 7.8 mmol) and a 1.2M solution of dimethylzinc in toluene (7.5 mL, 9 mmol) were added to a dry flask at 0 °C under Ar with stirring for 30 min. The copper complex was added to the flask containing ZnMe₂ and buta-1,3-diynylbenzene via a syringe and the homogeneous solution was stirred at 10 °C for 30 min, then 1-(2-bromophenyl)ethanone 1a (593.9 mg, 3 mmol) was added. The mixture was allowed to stir at 10 °C for 48 h. The reaction was quenched with 5% HCl solution and extracted with ether (25 mL×3). The organic layer was washed with brine and dried over Na₂SO₄. The crude was purified via flash chromatography (silica gel) using ethyl acetate in petroleum ether (0–5%, v/v) as eluent to recover the buta-1,3-diynylbenzene (562.3 mg, 93%) and to afford the light yellow oil 3c (923.5 mg, 95% yield and 90% ee).

To a solution of 3c (0.37 mmol, 120 mg) in CH₂Cl₂ (4 mL) was directly dropped a mixture of 4-nitrobenzoyl chloride (74 mg, 0.4 mmol, 1.1 equiv) and Et₃N (103 μL, 0.74 mmol, 2 equiv) in CH₂Cl₂ (2 mL) at 0 °C, then stirring was maintained for 48 h at room temperature. The resulting mixture was poured into water and extracted with CH₂Cl₂. The organic extracts were dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel to afford the product. Recrystallization of this product from CH₂Cl₂/hexane furnished acicular crystal.
(S)-2-(2-bromophenyl)-6-phenylhexa-3,5-diyn-2-yl 4-nitrobenzoate (4): 133 mg, 76% yield, >99.99% ee; mp 164-165 °C; [α]D20 -29.7 (c 1.0, CH2Cl2); 1H-NMR (CDCl3, 400 MHz) δ 8.30-8.25 (4H, m), 8.05 (1H, d, J = 7.9 Hz), 7.59 (1H, d, J = 7.9 Hz), 7.51 (2H, d, J = 6.8 Hz), 7.43-7.32 (4H, m), 7.20 (1H, t, J = 7.6 Hz), 2.30 (3H, s); 13C-NMR (CDCl3, 100 MHz) δ 162.2, 150.7, 138.1, 135.6, 135.3, 132.6, 131.2, 130.0, 129.6, 128.5, 127.6, 123.5, 121.2, 119.3, 80.8, 79.8, 78.3, 73.3, 72.9, 28.5; MS(ESI) m/z 473.0 (M)+; IR (neat) ν 3442, 2918, 2850, 2242, 1729, 1523, 1348, 1266, 1091, 1055, 841, 762, 719 cm⁻¹.

5. References

6. NMR Spectra and HPLC Charts for the Addition Adducts:
Electronic Supplementary Material (ESI) for Chemical Communications
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S23
**Electronic Supplementary Material (ESI) for Chemical Communications**

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**Signal 1:** UV-Vis, Wavelength=254 nm

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**Signal 2:** UV-Vis, Wavelength=254 nm

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**Sample Info:**
- **254 nm**
- **1-PrOH**
- **Nexansite:** 20.80 L, 1.0 mL/min

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S40
Sample Info : 254 nm, 1, i-PrOH : Hexane = 5:95, 1.0 mL/min

**Signal 1: UV/vis, Wavelength=254 nm**

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**Signal 2: UV/vis, Wavelength=254 nm**

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Signal 1: UV/Vis, Wavelength=254 nm

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Signal 1: UV/Vis, Wavelength=284 nm

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**Signal 1: VWD A, Wavelength=254 nm**

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**Signal 2: VWD A, Wavelength=254 nm**

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**Signal 1:** UV-Vis, Wavelength=254 nm

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**Signal 2:** UV-Vis, Wavelength=254 nm

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**Signal 1**: WCL A, Wavelength=254 nm

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7. Basic crystal data for the product 4

CCDC 830329 contains the supplementary crystallographic data for the product 4. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

checkCIF/PLATON report

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No syntax errors found. CIF dictionary Interpreting this report

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Bond precision: C-C = 0.0055 Å  Wavelength=0.71073

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Temperature: 294 K

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Hall group P 2ac 2ab  ?
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- Alert level C