Supporting Information-I

Direct Catalytic Asymmetric Synthesis of Highly Functionalized (2-Ethynylphenyl)alcohols via Barbas-List Aldol Reaction: Scope and Synthetic Applications

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General Methods: The $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for $^1$H NMR and relative to the central CDCl$_3$ resonance ($\delta = 77.0$) for $^{13}$C NMR. In the $^{13}$C NMR spectra, the nature of the carbons (C, CH, CH$_2$ or CH$_3$) was determined by recording the DEPT-135 experiment, and is given in parentheses. The coupling constants $J$ are given in Hz. Column chromatography was performed using Acme’s silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254

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were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of \( p \)-anisaldehyde (23 mL), conc. \( \text{H}_2\text{SO}_4 \) (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (\( ee \)) of the BLA products was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H, Chiralcel OJ-H, Chiralpak AD-H, Chiralpak AS-H or Lux 5u Amylose-2 columns and hexane/2-propanol as the eluent. Retention times and solvent ratios are indicated in the respective entries.

**Materials:** All solvents and commercially available chemicals were used as received.

**General Experimental Procedures for the Asymmetric BLA Reactions:**

**Prolinamide 3 catalyzed BLA reaction of 2-alkynylbenzaldehydes 1 with ketone 2** *(Method A)*: In a 10 mL round bottomed flask equipped with a magnetic stirring bar, to the prolinamide catalyst 3h or 3i (10 mol\%) was added PhCO\( _2 \text{H} \) (10 mol\%). The flask was cooled to \( -35^\circ \text{C} \) and then ketone 2 (1 mL, 0.3 M) was added to it. After stirring the reaction mixture at \( -35^\circ \text{C} \) for 0.5 h, 2-ethynylbenzaldehyde 1 (0.3 mmol) was added to it and stirring was continued at the same temperature for 24–60 h. The crude reaction mixture was worked up with aqueous NH\( _4 \text{Cl} \) solution and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na\( _2 \text{SO}_4 \)), filtered and concentrated. Pure BLA products 5 and double-aldol addition products 6 were obtained by column chromatography (silica gel, mixture of hexane/ethylacetate).

**trans-4-OH-L-Proline catalyzed BLA reaction of 2-alkynylbenzaldehydes with ketones** *(Method B)*: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 2-ethynylbenzaldehyde 1 was added 2.4 mL of solvent, followed by the addition of the catalyst \( \text{trans-4-OH-L-proline} \) 3d (0.06 mmol, 20 mol\%, 6.9 mg). After stirring the reaction mixture at 25 \( ^\circ \text{C} \) for 2–3 min, ketone 2 was added and the reaction mixture was allowed to stir at the same temperature for 24–72 h. The crude reaction mixture was worked up with aqueous NH\( _4 \text{Cl} \) solution and the aqueous layer was
extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure BLA products 5 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**CuSO₄/Na-(-)-Ascorbate-Catalyzed Click Reaction (Method C):** Compound 5aa (0.3 mmol) and aryl azide 7 (0.5 equiv.) was dissolved in t-BuOH/H₂O (2 mL, 1:1 ratio) in a 10 mL round bottomed flask equipped with a magnetic stirring bar, to that 40 mol% of CuSO₄, 20 mol% of Na-(-)-Ascorbate were added and the reaction mixture was stirred at the room temperature for 8-12 h. The crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure click products 10 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**CuSO₄/Cu-Catalyzed Click Reaction (Method D):** Compound 6aa (0.3 mmol) and aryl azide 7b (0.6 mmol) was dissolved in EtOH (2 mL) in a 10 mL round bottomed flask equipped with a magnetic stirring bar, to that 1.0 equiv. of CuSO₄, 5 mol% of Cu powder were added and the reaction mixture was stirred at the room temperature for 12 h. The crude reaction mixture was worked up with H₂O and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure cyclic click product 9aab was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**General Procedure for the Reduction of BLA Products 5 (Method E):** In a 10 mL round bottomed flask equipped with a magnetic stirring bar, compound 5aa-5bf (0.2 mmol) was dissolved in dry MeOH (0.25 M) and then cooled to ice salt temperature, NaBH₄ (2 equiv.) was added to it under nitrogen atmosphere. After stirring the reaction mixture at same temperature for 0.5 h, the crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure products 10 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).
Lewis acid Mediated *syn*-Selective *Reduction of BLA Products* 5 (**Method F**): In a 10 mL round bottomed flask equipped with a magnetic stirring bar, compound *5aa*-*5bf* (0.2 mmol) was dissolved in dry THF : MeOH (4:1, 0.2 M) and then cooled to −75 °C temperature, BEt₂(OMe) (1.1 equiv.), and NaBH₄ (1.1 equiv.) was added to it under nitrogen atmosphere. After stirring the reaction mixture at same temperature for 4 h, the crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure products *syn-10* was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Double Protection of BLA-Reduction Product syn-10af** (**Method G**): In a 10 mL round bottomed flask compound *syn-10af* (189 mg, 0.3 mmol) was dissolved in 1 mL of dry DCM, to that 2.0 equiv. of 3,5-dinitrobenzoyl chloride and 2.0 equiv. of DMAP were added. After stirring the reaction mixture at 25 °C for 12 h, the crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure product *11af* was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Scheme S1**: Double protection on BLA-reduction product *syn-10af*. 

![](image)
(R)-4-(2-Ethynylphenyl)-4-hydroxy-butan-2-one (5aa): Prepared following the Method-A; and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ= 254 nm), \( t_R = 8.56 \text{ min} \) (minor), \( t_R = 9.71 \text{ min} \) (major). \([\alpha]_D^{25} = +62.1^\circ \) \( (c = 0.27 \text{ g/100 mL}, \text{CHCl}_3, 93\% \text{ ee}) \); IR (Neat): \( \nu_{\text{max}} 3448, 3286 \text{ (O-H)}, 2925, 1709 \text{ (C=O)}, 1447, 1362, 1264, 1165, 1065, 763, 666, 651 \text{ and } 625 \text{ cm}^{-1}; \) \(^{1}\text{H} \text{NMR (CDCl}_3) \delta 7.58 (1H, d, \( J = 8.0 \text{ Hz} \)), 7.46 (1H, dd, \( J = 7.6, 1.2 \text{ Hz} \)), 7.37 (1H, dt, \( J = 7.6, 1.2 \text{ Hz} \)), 7.22 (1H, dt, \( J = 7.6, 1.2 \text{ Hz} \))[Ar-H]; 5.57 (1H, dd, \( J = 9.6, 2.0 \text{ Hz}, \text{C}H\text{OH})), 3.61 (1H, br s, O\text{H}), 3.34 (1H, s, C\text{=}C\text{H}), 3.00 (1H, dd, \( J = 17.2, 2.4 \text{ Hz}, \text{COCH}_2)), 2.72 (1H, dd, \( J =17.6, 9.6 \text{ Hz}, \text{COCH}_2)), 2.19 (3H, s, \text{COCH}_3); \(^{13}\text{C} \text{NMR (CDCl}_3, \text{DEPT-135) } \delta 209.1 \text{ (C, C}=\text{O}), 145.1 \text{ (C), 132.7 (CH), 129.3 (CH), 127.1 (CH), 125.2 (CH), 118.8 (C), 82.6 (CH, Ar-C}=\text{CH}), 81.0 \text{ (C, Ar-C}=\text{CH}), 67.6 \text{ (CH, CHO)}, 50.8 \text{ (CH}_2, \text{COCH}_2), 30.4 \text{ (CH}_3, \text{COCH}_3); \) LRMS m/z 189.10 (M+1), calcd. for C\textsubscript{12}H\textsubscript{12}O\textsubscript{2} 188.0837; Anal. calcd. for C\textsubscript{12}H\textsubscript{12}O\textsubscript{2} (188.0837); C, 76.57; H, 6.43. Found: C, 76.48; H, 6.51%.

(S)-4-(2-Ethynylphenyl)-4-hydroxy-butan-2-one (5aa): Prepared following the Method-A; and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ= 254 nm), \( t_R = 8.56 \text{ min} \) (major), \( t_R = 9.71 \text{ min} \) (minor). \([\alpha]_D^{25} = -56.2^\circ \) \( (c = 0.42 \text{ g/100 mL}, \text{CHCl}_3, 95\% \text{ ee}) \); IR (Neat): \( \nu_{\text{max}} 3448, 3286 \text{ (O-H)}, 2925, 1709 \text{ (C=O)}, 1447, 1362, 1264, 1165, 1065, 763, 666, 651 \text{ and } 625 \text{ cm}^{-1}.\)

(R,R)-1,5-Bis-(2-ethynylphenyl)-1,5-dihydroxy-pentan-3-one (6aa): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as gummy liquid. The enantiomeric excess (ee) was
determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 20.10 \) min (major), \( t_R = 22.95 \) min (major). \([\alpha]_D^{25} = +122.0^\circ \) (c = 0.81 g/100 mL, CHCl₃, >99% ee); IR (Neat): \( \nu_{\text{max}} \) 3285 (O-H), 1708 (C=O), 1479, 1363, 1316, 1204, 1105, 1059, 763, 685, 650 and 612 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \( \delta \) 7.59 (2H, d, \( J = 8.0 \) Hz), 7.47 (2H, d, \( J = 7.2 \) Hz), 7.39 (2H, t, \( J = 7.6 \) Hz), 7.24 (2H, t, \( J = 7.6 \) Hz)(Ar-H); 5.64 (2H, d, \( J = 9.2 \) Hz, 2 x CHOH), 3.42 (2H, br s, 2 x OH), 3.34 (2H, s, 2 x C≡CH), 3.02 (2H, dd, \( J = 16.8, 2.0 \) Hz, 2 x COC₂H₂), 2.82 (2H, dd, \( J = 17.2, 10.0 \) Hz, 2 x COCH₂); \(^{13}\)C NMR (CDCl₃, DEPT-135) \( \delta \) 211.0 (C, C=O), 145.0 (2 x C), 132.9 (2 x CH), 129.4 (2 x CH), 127.3 (2 x CH), 125.2 (2 x CH), 118.9 (2 x C), 82.9 (2 x CH, 2 x Ar-C≡CH), 81.0 (2 x C, 2 x Ar-C≡CH), 67.8 (2 x CH, 2 x CHOH), 50.6 (2 x CH₂, 2 x COCH₂); LRMS m/z 317.00 (M⁺-1), calcd for C₂₁H₁₈O₃ 318.1256; Anal. calcd. for C₂₁H₁₈O₃ (318.1256); C, 79.22; H, 5.70. Found: C, 79.32; H, 5.65%.

\( (S,S)-1,5\)-Bis-(2-ethylphenyl)-1,5-dihydroxy-pentan-3-one (6aa): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as gummy liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 20.10 \) min (major), \( t_R = 22.95 \) min (minor). \([\alpha]_D^{25} = -112.4^\circ \) (c = 0.27 g/100 mL, CHCl₃, >99% ee); IR (Neat): \( \nu_{\text{max}} \) 3285 (O-H), 1708 (C=O), 1479, 1363, 1316, 1204, 1105, 1059, 763, 685, 650 and 612 cm\(^{-1}\).

\( (R)-1-(2\)-Ethynylphenyl\)-1-hydroxy-pentan-3-one (5ab): Prepared following the Method-A; purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 9.22 \) min (major), \( t_R = 10.44 \) min (minor). \([\alpha]_D^{25} = +109.7^\circ \) (c = 0.43 g/100 mL,
CHCl₃, 99% ee); IR (Neat): \( \nu_{\text{max}} \) 3449, 3291 (O-H), 3069, 2978, 2939, 2102, 1712 (C=O), 1448, 1408, 1373, 1311, 1203, 1113, 1070 and 761 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \( \delta \) 7.59 (1H, br dd, \( J = 8.0, 0.5 \text{ Hz} \)), 7.47 (1H, dd, \( J = 7.6, 1.2 \text{ Hz} \)), 7.39 (1H, dt, \( J = 7.6, 1.3 \text{ Hz} \)), 7.23 (1H, dt, \( J = 7.5, 1.3 \text{ Hz} \))[Ar-H]; 5.58 (1H, d, \( J = 9.2 \text{ Hz} \), CHO), 3.63 (1H, br s, OH), 3.33 (1H, s, Ar-C=CH), 3.00 (1H, dd, \( J = 17.4, 2.0 \text{ Hz} \), COCH₂), 2.69 (1H, dd, \( J = 17.6, 10.0 \text{ Hz} \), COCH₂), 2.56–2.40 (2H, m, COCH₂CH₃), 1.08 (3H, t, \( J = 7.3 \text{ Hz} \), COCH₂CH₃); \(^{13}\)C NMR (CDCl₃, DEPT-135) \( \delta \) 212.2 (C, C=O), 145.2 (C), 132.8 (CH), 129.4 (CH), 127.1 (CH), 125.2 (CH), 118.8 (C), 82.6 (CH, Ar-C=CH), 81.1 (C, Ar-C=CH), 67.9 (CH, CHO), 49.4 (CH₂, COCH₂), 36.6 (CH₂, COCH₂CH₃), 7.5 (CH₃, COCH₂CH₃); LRMS m/z 203.0 (M+1), calcd. for C₁₃H₁₄O₂ 202.0994; Anal. calcd. for C₁₃H₁₄O₂ (202.0994); C, 77.20, H, 6.98; Found: C, 77.38; H, 6.05%.

(5′ab)-4-(2-Ethynylphenyl)-4-hydroxy-3-methyl-butan-2-one (5′ab): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \)), \( t_R = 9.10 \text{ min} \) (major), \( t_R = 12.43 \text{ min} \) (minor). \([\alpha]_D^{25} = +30.9^\circ \) (c = 0.13 g/100 mL, CHCl₃, >99% ee and >99% de); IR (Neat): \( \nu_{\text{max}} \) 3430, 3295 (O-H), 3065, 2975, 2934, 2104, 1707 (C=O), 1481, 1456, 1360, 1242, 1170, 1100, 1051, 1019, 955, 912, 833 and 764 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \( \delta \) 7.49 (1H, dd, \( J = 8.0, 1.2 \text{ Hz} \)), 7.47–7.45 (1H, m), 7.39 (1H, dt, \( J = 8.0, 1.2 \text{ Hz} \)), 7.25 (1H, dt, \( J = 7.6, 1.2 \text{ Hz} \))[Ar-H]; 5.29 (1H, dd, \( J = 7.2, 3.4 \text{ Hz} \), CHO), 3.35 (1H, s, Ar-C=CH), 3.30 (1H, br s, OH), 3.09 (1H, quintet, \( J = 7.6 \text{ Hz} \), COCHCH₃), 2.16 (3H, s, COCH₃), 1.06 (3H, d, \( J = 7.2 \text{ Hz} \), COCHCH₃); \(^{13}\)C NMR (CDCl₃, DEPT-135) \( \delta \) 213.6 (C, C=O), 144.4 (C), 132.9 (CH), 129.3 (CH), 127.5 (CH), 126.2 (CH), 120.3 (C), 82.4 (CH, Ar-C=CH), 81.5 (C, Ar-C=CH), 73.7 (CH, CHO), 53.0 (CH, COCHCH₃), 30.0 (CH₃, COCH₃), 14.0 (CH₃, COCHCH₃); LRMS m/z 203.05 (M+1), calcd. for C₁₃H₁₄O₂ 202.0994; Anal. calcd. for C₁₃H₁₄O₂ (202.0994); C, 77.20, H, 6.98; Found: C, 77.38; H, 6.05%.
(3S,4R)-4-(2-Ethynylphenyl)-3,4-dihydroxy-butan-2-one (5′ac):
Prepared following Method-B, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ = 254 nm),
t_R(syn) = 18.46 min (major), t_R(syn) = 23.66 min (minor); t_R(anti) = 26.86 min (major),
t_R(anti) = 29.22 min (minor). [α]D²⁵ = +72.1° (c = 0.47 g/100 mL, CHCl₃, 93% ee for major anti-isomer and 26% ee for minor syn-isomer; and 50% de); IR (Neat): ν_max 3418, 3283 (O-H), 3067, 2926, 2099, 1960, 1715 (C=O), 1622, 1399, 1360, 1254, 1096, 1053 and 762 cm⁻¹; ¹H NMR (CDCl₃, 3:1 mixture of anti:syn diastereomers) δ 7.59 (1H, d, J = 8.0 Hz), 7.54–7.50 (3H, m), 7.44–7.38 (2H, m), 7.31–7.26 (2H, m)[Ar-H]; 5.60 (1H, s, ArCHOH), 5.42 (1H, d, J = 4.0 Hz, ArCHOH), 4.75 (1H, d, J = 3.2 Hz, COCHOH), 4.52 (1H, s, COCHOH), 3.89 (1H, br s, OH), 3.74 (1H, br. s, OH), 3.45 (1H, s, Ar-C=CH), 3.42 (1H, s, Ar-C=CH), 3.16 (1H, br s, OH), 3.00 (1H, br s, OH), 2.37 (3H, s, COCH₃), 1.88 (3H, s, COCH₃); ¹³C NMR (CDCl₃, DEPT-135, 3:1 mixture of anti:syn diastereomers) δ 208.1 (C, C=O), 207.4 (C, C=O), 142.8 (C), 141.3 (C), 133.2 (CH), 132.9 (CH), 129.3 (2 x CH), 127.9 (CH), 127.6 (CH), 126.3 (CH), 126.0 (CH), 119.9 (C), 119.0 (C), 83.3 (CH, Ar-C=CH), 83.2 (CH, Ar-C=CH), 81.5 (C, Ar-C=CH), 81.1 (C, Ar-C=CH), 79.7 (CH, ArCHOH), 79.4 (CH, ArCHOH), 73.2 (CH, COCHOH), 71.1 (CH, COCHOH), 27.9 (CH₃, COCH₃), 25.3 (CH₃, COCH₃); LRMS m/z 205.20 (M+1), calcd. for C₁₂H₁₂O₃ 204.0786; Anal. calcd. for C₁₂H₁₂O₃ (204.0786); C, 70.57, H, 5.92; Found: C, 70.42; H, 5.85%.

(R)-4-(2-Ethynylphenyl)-1,4-dihydroxy-butan-2-one (5ac):
Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.11 min (major), t_R = 19.56 min (minor). [α]D²⁵ = +35.2° (c = 0.18 g/100 mL, CHCl₃, 90% ee); IR (Neat): ν_max 3397 (O-H), 3283, 3073, 2926, 2859, 1715
(C=O), 1622, 1449, 1389, 1263, 1161, 1069 and 762 cm⁻¹; ¹H NMR (CDCl₃) δ 7.56 (1H, d, J = 7.6 Hz), 7.47 (1H, d, J = 7.6 Hz), 7.40 (1H, t, J = 7.6 Hz), 7.24 (1H, t, J = 7.6 Hz) [Ar-H]; 5.62 (1H, dd, J = 9.6, 2.4 Hz), 4.28 (2H, ABq, J = 19.2 Hz), 3.38 (1H, s, Ar-C≡CH), 3.40-3.20 (2H, br s, 2 x OH), 2.90 (1H, dd, J = 16.4, 2.8 Hz), 2.76 (1H, dd, J = 16.4, 9.6 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 209.3 (C, C=O), 144.9 (C), 133.0 (CH), 129.5 (CH), 127.5 (CH), 125.1 (CH), 118.9 (C), 83.1 (CH, Ar-C=CH), 80.9 (C, Ar-C≡CH), 68.8 (CH₂, COCH₂OH), 67.9 (CH, ArCHOH), 46.2 (CH₂, COCH₂); LRMS m/z 205.20 (M+1), calcd. for C₁₂H₁₂O₃ 204.0786; Anal. calcd. for C₁₂H₁₂O₃ (204.0786); C, 70.57, H, 5.92; Found: C, 70.45; H, 5.86%.

(2S,1’R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-cyclohexanone (anti–5ad): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 8.42 min (major), tᵣ = 9.87 min (minor). [α]D²⁵ = +41.6° (c = 0.14 g/100 mL, CHCl₃, 96% ee); IR (Neat): νmax 3520, 3442, 3285 (O-H), 2940, 2868, 1694 (C=O), 1445, 1409, 1311, 1230, 1128, 1037, 1017, 763, 652 and 625 cm⁻¹; ¹H NMR (CDCl₃) δ 7.52 (1H, d, J = 8.0 Hz), 7.47 (1H, d, J = 8.0 Hz), 7.39 (1H, t, J = 7.6 Hz), 7.24 (1H, t, J = 7.6 Hz)[Ar-H]; 5.39 (1H, d, J = 8.4 Hz, CHOH), 4.04 (1H, br s, OH ), 3.27 (1H, s, Ar-C≡CH), 2.73–2.66 (1H, m), 2.46 (1H, d, J = 13.2 Hz), 2.34 (1H, dt, J = 13.2, 6.0 Hz), 2.09–2.04 (1H, m), 1.82–1.79 (1H, m), 1.74–1.66 (1H, m), 1.61–1.51 (3H, m); ¹³C NMR (CDCl₃, DEPT-135) δ 215.4 (C, C=O), 143.7 (C), 132.5 (CH), 129.3 (CH), 127.3 (CH), 126.4 (CH), 120.9 (C), 81.8 (CH, Ar-C=CH), 81.7 (C, Ar-C=CH), 71.6 (CH, CHOH), 57.7 (CH, COCH-), 42.6 (CH₂), 30.4 (CH₂), 27.7 (CH₂), 24.8 (CH₂); LRMS m/z 228.20 (M⁺), calcd. for C₁₅H₁₆O₂ 228.1150; Anal. calcd. for C₁₅H₁₆O₂ (228.1150); C, 78.92, H, 7.06; Found: C, 78.81; H, 7.15%. 

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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(2R,1’R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-cyclohexanone (syn-5ad): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ = 254 nm), trR = 10.65 min (minor), trR = 11.98 min (major). [α]D 25 = +108.8° (c = 0.06 g/100 mL, CHCl3, 91% ee); IR (Neat): νmax 3459, 3291 (O-H), 3061, 2940, 2866, 1703 (C=O), 1605, 1449, 1308, 1235, 1130, 1065, 1032, 978, 887 and 762 cm⁻¹; 1H NMR (CDCl3) δ 7.55 (1H, d, J = 7.8 Hz), 7.46 (1H, d, J = 7.6 Hz), 7.37 (1H, t, J = 7.6 Hz), 7.22 (1H, t, J = 7.5 Hz)[Ar-H]; 5.80 (1H, br s, CHOHOH), 3.29 (1H, s, Ar-C≡CH), 3.19 (1H, br s, OH), 2.88 (1H, dd, J = 12.6, 5.2 Hz), 2.47–2.35 (2H, m), 2.10–2.04 (1H, m), 1.84–1.49 (5H, m); 13C NMR (CDCl3, DEPT-135) δ 214.8 (C, C=O), 143.8 (C), 132.7 (CH), 128.7 (CH), 126.7 (CH), 126.5 (CH), 118.5 (C), 82.6 (CH, Ar-C≡CH), 81.2 (C, Ar-C≡CH), 68.7 (CH, CHOHOH), 54.6 (CH, COCH), 42.5 (CH2), 27.9 (CH2), 25.9 (CH2), 24.8 (CH2); LRMS m/z 228.70 (M+1), calcd. for C15H16O2 228.1150; Anal. calcd. for C13H16O2 (228.1150): C, 78.92, H, 7.06; Found: C, 78.82; H, 6.95%.

(2S,1’R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-cyclopentanone (anti-5ae): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), trR = 10.51 min (major), trR = 12.42 min (minor). [α]D 25 = -23.8° (c = 0.71g/100 mL, CHCl3, 95% ee); IR (Neat): νmax 3281 (O-H), 3061, 2927, 2882, 2102, 1937, 1728 (C=O), 1622, 1402, 1159, 1026, 841 and 766 cm⁻¹; 1H NMR (CDCl3) δ 7.56 (1H, dd, J = 8.0, 0.8 Hz), 7.48 (1H, dd, J = 8.0, 1.2 Hz), 7.41 (1H, dt, J = 8.0, 1.2 Hz), 7.25 (1H, dt, J = 7.6, 1.2 Hz)[Ar-H]; 5.33 (1H, d, J = 9.6 Hz, CHOH), 4.58 (1H, br s, OH), 3.27 (1H, s, Ar-C≡CH), 2.50–2.40 (2H, m), 2.36–2.26 (1H, m), 2.05–1.95 (1H, m), 1.80–1.65 (3H, m); 13C NMR (CDCl3, DEPT-135) δ 223.2 (C, C=O), 143.8 (C),
132.8 (CH), 129.5 (CH), 127.6 (CH), 126.5 (CH), 120.4 (C), 81.9 (C, Ar-C=CH), 81.8 (CH, Ar-C=CH), 71.8 (CH, CHOH), 55.7 (CH), 38.7 (CH₂), 26.4 (CH₂), 20.5 (CH₂); LRMS m/z 213.10 (M-1), calcd. for C₁₄H₁₄O₂ 214.0994; Anal. calcd. for C₁₄H₁₄O₂ (214.0994); C, 78.48, H, 6.59; Found: C, 78.32; H, 6.65%.

(2R,1’R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-cyclopentanone (syn-5ae): Prepared following Method-B, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 11.52 min., tᵣ = 14.61 min., 0% ee; IR (Neat): νmax 3443, 3291 (O-H), 3065, 2965, 2882, 1736 (C=O), 1622, 1478, 1449, 1402, 1337, 1269, 1204, 1157, 1107, 1026, 968, 883, 841 and 762 cm⁻¹; ¹H NMR (CDCl₃) δ 7.57 (1H, d, J = 7.6 Hz), 7.47 (1H, dd, J = 7.6, 1.2 Hz), 7.39 (1H, dt, J = 7.6, 0.8 Hz), 7.24 (1H, dt, J = 7.6, 1.2 Hz)[Ar-H]; 5.78 (1H, s, CH=O), 3.36 (1H, s, Ar-C≡C), 2.77–2.72 (1H, m), 2.41–2.33 (2H, m), 2.20–2.10 (1H, m), 2.03–1.95 (2H, m), 1.76–1.65 (2H, m); ¹³C NMR (CDCl₃, DEPT-135) δ 220.1 (C, C=O), 145.0 (C), 132.7 (CH), 129.0 (CH), 127.0 (CH), 125.5 (CH), 118.8 (C), 83.0 (CH, Ar-C≡CH), 80.9 (C, Ar-C≡CH), 69.2 (CH, CHOH), 54.3 (CH), 39.0 (CH₂), 22.6 (CH₂), 20.3 (CH₂); LRMS m/z 213.10 (M-1), calcd. for C₁₄H₁₄O₂ 214.0994; Anal. calcd. for C₁₄H₁₄O₂ (214.0994); C, 78.48, H, 6.59; Found: C, 78.36; H, 6.51%.

(2S,4S,1’R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-4-methyl-cyclohexanone [(2S,4S,1’R)-5af]: Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as a yellow liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 96:4, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 17.37 min (minor), tᵣ = 18.55 min (major). [α]D²⁵ = −8.1° (c = 0.15 g/100 mL, CHCl₃, >99% de and 96% ee); IR (Neat): νmax 3443, 3267 (O-H), 2961, 2876, 2830, 1708 (C=O),
1452, 1379, 1327, 1187, 1125, 1099, 1038, 951 and 763 cm\(^{-1}\);

\(^1\)H NMR (CDCl\(_3\)) \(\delta\)

7.51–7.47 (2H, m), 7.39 (1H, t, \(J = 7.6\) Hz), 7.27–7.23 (1H, m)[Ar-H];

5.40 (1H, d, \(J = 8.4\) Hz, CHOH), 3.71 (1H, br s, OH), 3.30 (1H, s, Ar-C≡CH),

2.86 (1H, dd, \(J = 8.8, 2.8\) Hz), 2.53–2.40 (2H, m), 2.17–2.10 (1H, m),

2.00–1.92 (1H, m), 1.76–1.64 (2H, m), 1.40–1.34 (1H, m), 1.01 (3H, d, \(J = 6.8\) Hz, CH\(_3\));

\(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\)

215.3 (C, C=O), 144.0 (C), 132.7 (CH), 129.4 (CH), 127.5 (CH), 126.4 (CH), 120.7 (C),

81.9 (CH, Ar-C≡CH), 81.7 (C, Ar-C≡CH), 72.0 (CH, CHOH), 54.0 (CH), 38.4 (CH\(_2\)),

36.1 (CH\(_2\)), 33.6 (CH\(_2\)), 26.9 (CH), 18.7 (CH\(_3\));

LRMS m/z 243.10 (M+1), calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) 242.1307; Anal. calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) (242.1307);

C, 79.31, H, 7.49; Found: C, 79.45; H, 7.41%.

(2\(R\),4\(R\))-2-((2-ethynylphenyl)(hydroxy)methyl)-4-methylcyclohexanone (5af):

Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak OJ-H column (hexane/2-propanol = 96:4, flow rate 1.0 mL/min, \(\lambda = 254\) nm),

\(t_R = 15.38\) min (major), \(t_R = 16.96\) min (minor). \([\alpha]_D^{25} = +3.3^\circ\) (c = 0.67 g/100 mL, CHCl\(_3\), >99% de and 96% ee);

IR (Neat): \(\lambda_{\text{max}}\) 3499 (O-H), 2951, 1707 (C=O), 1493, 1443, 1035, 757, 664 and 647 cm\(^{-1}\);

\(^1\)H NMR (CDCl\(_3\)) \(\delta\)

7.47 (1H, d, \(J = 7.6\) Hz), 7.46 (1H, d, \(J = 7.2\) Hz), 7.36 (1H, t, \(J = 7.6\) Hz),

7.22 (1H, t, \(J = 7.6\) Hz), 5.40 (1H, d, \(J = 8.8\) Hz), 3.76 (1H, br s), 3.30 (1H, s, Ar-C≡CH),

2.84 (1H, q, \(J = 8.8\) Hz), 2.47–2.42 (2H, m), 2.15–2.12 (1H, m), 1.97–1.91 (1H, m),

1.73–1.62 (2H, m), 1.37–1.31 (1H, m), 1.00 (3H, d, \(J = 6.8\) Hz, CH\(_3\));

\(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\)

215.2 (C, C=O), 144.0 (C), 132.7 (CH), 129.4 (CH), 127.4 (CH),

126.3 (CH), 120.7 (C), 81.9 (CH, Ar-C≡CH), 81.6 (C, Ar-C≡CH), 71.9 (CH, CHOH),

54.1 (CH), 38.4 (CH\(_2\)), 36.1 (CH\(_2\)), 26.9 (CH), 18.7 (CH\(_3\));

LRMS m/z 243.10 (M+1), calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) 242.1307; Anal. calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) (242.1307);

C, 79.31, H, 7.49; Found: C, 79.26; H, 7.55%.
(2S,4R,1'R)-2-[(2-Ethynylphenyl)-hydroxymethyl]-4-methyl-cyclohexanone

(2S,4R,1'R)-5af: Prepared following Method-B, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R = 8.67 \) min (minor), \( t_R = 11.43 \) min (major). \([\alpha]_D^{25} = -172.7^\circ \ (c = 0.14 \ g/100 \ mL, \ CHCl_3, 77\% \ ee)\); IR (Neat): \( \nu_{max} \) 3415, 3298 (O-H), 3279, 2955, 2874, 1704 (C=O), 1451, 1306, 1258, 1220, 1198, 1121 1077, 1021 and 763 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.53 (1H, d, \( J = 7.6 \) Hz), 7.47 (1H, dd, \( J = 7.6, 1.2 \) Hz), 7.38 (1H, dt, \( J = 7.6, 1.2 \) Hz), 7.23 (1H, dt, \( J = 7.6, 1.2 \) Hz)[Ar-H]; 5.79 (1H, s, C\( \equiv \)OH), 3.31 (1H, s, Ar-C≡CH), 3.14–3.09 (1H, m), 3.03 (1H, d, \( J = 2.4 \) Hz), 2.59–2.51 (1H, m), 2.38–2.31 (1H, m), 2.13–2.01 (2H, m), 1.95–1.88 (1H, m), 1.79–1.74 (1H, m), 1.35–1.29 (1H, m), 1.03 (3H, d, \( J = 6.8 \) Hz, \( CH_3 \)); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 215.3 (C, C\=O), 143.7 (C), 132.9 (CH), 128.9 (CH), 126.8 (CH), 126.6 (CH), 118.6 (C), 82.6 (CH, Ar-C≡CH), 81.3 (C, Ar-C=CH), 69.2 (CH, CHOH), 50.2 (CH), 38.3 (CH\(_2\)), 33.1 (CH\(_2\)), 31.7 (CH\(_2\)), 26.7 (CH), 18.3 (CH\(_3\)); LRMS m/z 243.10 (M+1), calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) 242.1307; Anal. calcd. for C\(_{16}\)H\(_{18}\)O\(_2\) (242.1307); C, 79.31, H, 7.49; Found: C, 79.45; H, 7.53%.

(2R, 4R)-2-[(S)-Hydroxy-(2-(phenylethynyl)phenyl)methyl]-4-methylcyclohexanone

(5bf): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R = 18.33 \) min (major), \( t_R = 22.77 \) min (minor). \([\alpha]_D^{25} = +109.2^\circ \ (c = 0.26 \ g/100 \ mL, \ CHCl_3, \ >99\% \ de \ and \ 90\% \ ee)\); IR (Neat): \( \lambda_{max} \) 3353 (O-H), 2929, 1711 (C=O), 1493, 1038, 757, 686 and 633 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.56–7.54 (4H, m), 7.41–7.38 (4H, m), 7.29 (1H, t, \( J = 6.0 \) Hz), 5.53–5.51 (1H, m), 2.96 (1H, q, \( J = 6.4 \) Hz), 2.50 (2H, t, \( J = 5.2 \) Hz), 2.22–2.18 (1H, m), 1.98–1.95 (1H, m), 1.81–1.76 (1H, m), 1.68–1.66 (1H, m), 1.47-
1.45 (1H, m) 1.00-0.98 (3H, br s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 215.1 (C, C=O), 143.6 (C), 132.2 (CH), 131.5 (2 x CH), 129.0 (CH), 128.5 (CH), 128.5 (2 x CH), 127.6 (CH), 126.6 (CH), 123.0 (C), 121.8 (C), 94.1 (CH, Ar-C≡CH), 87.5 (C, Ar-C≡CH), 72.4 (CH, CHO), 54.4 (CH), 38.6 (CH₂), 36.6 (CH₂), 33.9 (CH₂), 27.1 (CH), 19.0 (CH₃); LRMS m/z 319.20 (M⁺1), calcd. for C₂₂H₂₂O₂ 318.1620; Anal. calcd. for C₂₂H₂₂O₂ (318.1620): C, 82.99, H, 6.96; Found: C, 82.85; H, 6.88%.

(2S,4S)-2-[(R)-Hydroxy-(2-(phenylethynyl)phenyl)methyl]-4-methylcyclohexanone (5bf): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ= 254 nm), tᵣ = 18.33 min (minor), tᵣ = 22.77 min (major). [α]D²⁵ = -89.2° (c = 0.37 g/100 mL, CHCl₃, >99% de and 86% ee); IR (Neat): λmax 3353 (O-H), 2929, 1711 (C=O), 1493, 1038, 757, 686 and 633 cm⁻¹.

(2S, 4S, 1'R)-5bf

(S)-3-[(R)-(2-ethynylphenyl)(hydroxymethyl)dihydro-2H-pyran-4(3H)-one (5ag):
Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ= 254 nm), tᵣ(syn) = 9.31 min (major), tᵣ(syn) = 10.84 min (minor); tᵣ(anti) = 13.79 min (minor), tᵣ(anti) = 15.17 min (major). [α]D²⁵ = +206.3° (c = 0.06 g/100 mL, CHCl₃, 93% ee); IR (Neat): λmax 3423 (O-H), 1708 (C=O), 1208, 760, 684, 666, 648 and 635 cm⁻¹; ¹H NMR (CDCl₃, 8.2:1 mixture of anti:syn diastereomers) δ 7.54 (1H, d, J = 8.0 Hz), 7.50 (1H, d, J = 7.6 Hz), 7.47 (2H, d, J = 7.6 Hz), 7.42-7.35 (2H, m), 7.27-7.21 (2H, m) [Ar-H], 5.84 (1H, br s), 5.39 (1H, br d, J = 7.2 Hz), 4.22-4.16 (2H, m), 3.91 (1H, br s), 3.82 (2H, d, J = 8.4 Hz), 3.79-3.68 (3H, m), 3.60 (1H, dd, J = 11.2, 10.0 Hz), 3.33 (1H, s, Ar-C≡CH), 3.32 (1H, s, Ar-C≡CH), 3.19-3.14 (1H, m), 3.04–2.99 (2H, m), 2.71–2.62 (2H, m), 2.48 (2H, tt, J = 15.2, 3.2 Hz); ¹³C NMR (CDCl₃,
DEPT-135, 8.2:1 mixture of anti:syn diastereomers) δ 210.1 (C, C=O), 209.0 (C), 142.9 (C), 142.8 (C), 133.0 (CH), 132.9 (CH), 129.6 (CH), 129.1 (CH), 127.8 (CH), 127.2 (CH), 126.5 (CH), 125.9 (CH), 120.2 (C), 118.8 (C), 83.1 (CH, Ar-C≡C), 82.5 (C, Ar-C≡C), 81.3 (C, Ar-C≡C), 81.0 (C, Ar-C≡C), 70.0 (CH2), 69.4 (CH), 68.4 (CH2), 67.9 (CH2), 67.8 (CH), 58.2 (CH), 55.3 (CH), 45.0 (CH2), 43.1 (CH2), 43.0 (CH2); LRMS m/z 231.10 (M+1), calcd. for C14H14O3 230.0943; Anal. calcd. for C14H14O3 (230.0943); C, 73.03, H, 6.13; Found: C, 73.21; H, 6.18%.

(S)-3-((R)-(2-ethynylphenyl)(hydroxy)methyl)dihydro-2H-thiopyran-4(3H)-one (5ah): Prepared following method A in THF, purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ= 254 nm), t_R = 14.74 min (minor), t_R = 16.44 min (major); [\alpha]_D^{25} = +26.2° (c = 0.16 g/100 mL, CHCl3, 99% de, 88% ee); IR (Neat): \lambda_{max} 3428 (O-H), 2924, 1703 (C=O), 1425, 1287, 1107, 1018 and 762 cm⁻¹; ¹H NMR (CDCl3) δ 7.54 (1H, d, J = 7.5 Hz), 7.49 (1H, d, J = 8.0 Hz), 7.41 (1H, t, J = 7.5 Hz), 7.27 (1H, t, J = 7.5 Hz) [Ar-H]; 5.48 (1H, dd, J = 8.0, 3.5 Hz), 3.75-3.71 (1H, m, OH), 3.32 (1H, s, Ar-C≡C), 3.12-3.08 (1H, m), 3.02-2.94 (2H, m), 2.85-2.78 (3H, m), 2.53-2.49 (1H, m); ¹³C NMR (CDCl3, DEPT-135) δ 212.0 (C, C=O), 142.8 (C), 132.8 (CH), 129.6 (CH), 127.8 (CH), 126.6 (CH), 120.7 (C), 82.5 (CH, Ar-C≡C), 81.5 (C, Ar-C≡C), 71.3 (CH), 59.9 (CH), 45.0 (CH2), 32.8 (CH2), 30.9 (CH2); LRMS m/z 247.20 (M+1), calcd. for C14H14O2S 246.0715; Anal. calcd. for C14H14O2S (246.0715); C, 68.26, H, 5.73; Found: C, 68.15; H, 5.78%.

(R)-4-Hydroxy-4-(2-phenylethynylphenyl)-butan-2-one (5ba): Prepared following Method-B, purified by column chromatography using EtOAc/hexane and isolated as white solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel AD-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ= 254 nm), t_R = 13.52 min (major), t_R = 15.56 min (minor). [\alpha]_D^{25} = +52.2° (c = 0.54
(R,R)-1,5-Dihydroxy-1,5-bis-(2-phenylethynylphenyl)-pentan-3-one (6ba): Prepared following Method-A, purified by column chromatography using EtOAc/hexane/isopropanol = 94:6, flow rate 1.0 mL/min, λ = 254 nm), t_R = 56.27 min (minor), t_R = 61.58 min (major), >99.9% ee. IR (Neat): ν_max 3410 (O-H), 3059, 2926, 2216, 1960, 1713 (C=O), 1597, 1493, 1447, 1389, 1267, 1063, 756 and 691 cm⁻¹; ¹H NMR (CDCl_3) δ 7.58 (4H, d, J = 7.0 Hz), 7.51–7.48 (8H, m), 7.34–7.32 (6H, m)[Ar-H]; 5.78 (2H, dd, J = 9.9, 2.1 Hz, 2 x CHO), 3.20 (2H, br s, OH), 3.09 (2H, dd, J = 16.8, 2.4 Hz, COCH_2), 2.86 (2H, dd, J = 16.8, 9.8 Hz, COCH_2); ¹³C NMR (CDCl_3, DEPT-135) δ 210.8 (C, C=O), 144.4 (2 x C), 132.1 (2 x CH), 131.5 (4 x CH), 128.9 (2 x CH), 128.6 (2 x CH), 128.5 (4 x CH), 127.3 (2 x CH), 125.1 (2 x CH), 122.8 (2 x C), 120.0 (2 x C), 95.2 (2 x C, 2 x Ar-C=CPh), 86.5 (2 x C, 2 x Ar-C=CPh), 68.1 (2 x CH, 2 x CHO), 51.1 (2 x CH_2, 2 x COCH_2); LRMS m/z 471.30 (M⁺+1), calcd. for C_{33}H_{26}O_{3} 470.1882; Anal. calcd. for C_{33}H_{26}O_{3} (470.1882); C, 84.23; H, 5.57. Found: C, 84.15; H, 5.63%.
(R,R)-4-Hydroxy-4-(2-{4-[2-(1-hydroxy-3-oxobutyl)phenyl]buta-1,3-diynyl}-phenyl)butan-2-one (5ca, major) and (R,S)-4-Hydroxy-4-(2-{4-[2-(1-hydroxy-3-oxobutyl)phenyl]buta-1,3-diynyl}-phenyl)butan-2-one (5ca, minor): Prepared following Method-A, purified by column chromatography using EtOAc/hexane and isolated as yellow liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 94:6, flow rate 1.0 mL/min, λ= 254 nm), tR = 44.46 min (minor), tR = 57.34 min (major). [α]D^25 = +69.5° (c = 0.27 g/100 mL, CHCl₃, 21:1 dr and >99% ee); IR (Neat): νmax 3432 (O-H), 3065, 2920, 2213, 2143, 1715 (C=O), 1711 (C=O), 1476, 1447, 1362, 1233, 1163, 1107, 1067, 955, 887, 818 and 762 cm⁻¹; ¹H NMR (CDCl₃, major isomer) δ 7.61 (2H, d, J = 7.8 Hz), 7.51 (2H, d, J = 7.2 Hz), 7.41 (2H, dt, J = 7.6, 1.0 Hz), 7.25 (2H, dt, J = 7.6, 1.2 Hz)[Ar-H]; 5.56 (2H, dd, J = 9.6, 2.0 Hz, 2 x CHO), 3.69 (2H, br s, 2 x OH), 2.99 (2H, dd, J = 17.4, 2.4 Hz, COCH₂), 2.76 (2H, dd, J =17.4, 9.6 Hz, COCH₂), 2.24 (6H, s, 2 x COCH₃); ¹³C NMR (CDCl₃, DEPT-135, major isomer) δ 209.15 (2 x C, 2 x C=O), 146.0 (2 x C), 133.23 (2 x CH), 129.9 (2 x CH), 127.3 (2 x CH), 125.5 (2 x CH), 118.42 (2 x C), 80.2 (2 x C), 78.5 (2 x C), 67.8 (2 x CH, 2 x CHOH), 50.9 (2 x CH₂, 2 x COCH₂), 30.6 (2 x CH₃, 2 x COCH₃); LRMS m/z 375.30 (M+1), calcd. for C₂₄H₂₂O₄ 374.1518; Anal. calcd. for C₂₄H₂₂O₄ (374.1518); C, 76.99; H, 5.92. Found: C, 76.85; H, 5.98%.

(4R,4'R)-4,4'-(1,1'-(1,2-phenylenebis(methylene))bis(1H-1,2,3-triazole-4,1-diyl))bis(2,1-phenylene)bis(4-hydroxybutan-2-one) (8aaa): Prepared following Method-C, purified by column chromatography using EtOAc/hexane and isolated as liquid. [α]D^25 = +60.5° (c = 0.385 g/100 mL, CHCl₃, 95% ee); IR (Neat): λmax 3464 (O-H), 2359, 1708 (C=O), 1361, 1075, 911, 733, 681 and 673 cm⁻¹; ¹H NMR (CDCl₃) δ 7.72 (1H, s),
7.53 (1H, d, J = 7.6 Hz), 7.41-7.38 (1H, m), 7.34-7.29 (3H, m), 7.19 (1H, t, J = 7.6 Hz), 5.68 (2H, ABq, J = 15.2 Hz, NCH$_2$Ar), 5.31 (1H, t, J = 5.6 Hz, CHOH), 2.89 (2H, d, J = 6.0 Hz), 2.11 (3H, s, CH$_3$CO); $^{13}$C NMR (CDCl$_3$, DEPT-135) δ 208.7 (C, C=O), 147.3 (C), 140.8 (C), 133.1 (C), 130.6 (CH), 129.9 (CH), 129.4 (CH), 128.8 (CH), 127.9 (C), 127.6 (CH), 126.6 (CH), 122.4 (CH), 67.2 (CH), 51.2 (CH$_2$), 50.3 (CH$_2$), 30.6 (CH$_3$); HRMS m/z 587.2383 (M+Na), calcd. for C$_{32}$H$_{32}$N$_6$O$_4$Na 587.2383; Anal. calcd. for C$_{32}$H$_{32}$N$_6$O$_4$ (564.2485); C, 68.07; H, 5.71; N, 14.88; Found: C, 67.95; H, 5.69; N, 14.92%.

(4R,4'R)-4,4'-(1,1'-(1,3-phenylenebis(methylene))bis(1H-1,2,3-triazole-4,1-diyl))bis(2,1-phenylene)bis(4-hydroxybutan-2-one) (8aab): Prepared following Method-C, purified by column chromatography using EtOAc/hexane and isolated as solid. [α]$_D^{25}$ = +48.5° ($c$ = 1.714 g/100 mL, CHCl$_3$, 95% ee); IR (Neat): $\lambda_{\text{max}}$ 3446 (O-H), 2929, 1709 (C=O), 1357, 1218, 1075, 760, 659 and 652 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.78 (1H, s), 7.52 (1H, d, J = 7.2 Hz), 7.35-7.30 (2H, m), 7.28-7.25 (2H, m), 7.20-7.19 (2H, m), 5.51 (2H, s, NCH$_2$Ar), 5.32-5.30 (1H, m, CHOH), 4.80 (1H, br s, OH), 2.89-2.87 (2H, m), 2.10 (3H, s, COCH$_3$); $^{13}$C NMR (CDCl$_3$, DEPT-135) δ 208.7 (C, C=O), 147.2 (C), 140.8 (C), 135.6 (C), 129.7 (CH), 129.3 (CH), 128.7 (CH), 128.1 (CH), 128.0 (C), 127.5 (CH), 127.2 (CH), 126.5 (CH), 122.3 (CH), 67.1 (CH), 53.5 (CH$_2$), 50.3 (CH$_2$), 30.6 (CH$_3$); HRMS m/z 587.2383 (M+Na), calcd. for C$_{32}$H$_{32}$N$_6$O$_4$Na 587.2383; Anal. calcd. for C$_{32}$H$_{32}$N$_6$O$_4$ (564.2485); C, 68.07; H, 5.71; N, 14.88; Found: C, 68.12; H, 5.75; N, 14.78%.

(4R,4'R)-4,4'-(1,1'-(1,4-phenylenebis(methylene))bis(1H-1,2,3-triazole-4,1-diyl))bis(2,1-phenylene)bis(4-hydroxybutan-2-one) (8aac): Prepared following Method-C, purified by column chromatography using EtOAc/hexane and isolated as liquid. [α]$_D^{25}$ = +47.4° ($c$ = 0.80 g/100 mL, CHCl$_3$, 95% ee); IR (Neat): $\lambda_{\text{max}}$ 3421 (O-H), 2928, 1710 (C=O),
1356, 1109, 1077, 764, 642 and 611 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.74 (1H, s), 7.52 (1H, d, \(J = 8.0\) Hz), 7.36-7.30 (2H, m), 7.28 (2H, m), 7.21 (1H, t, \(J = 7.2\) Hz), 5.51 (2H, s, NCH\(_2\)Ar), 5.31 (1H, t, \(J = 6.4\) Hz, CHOH), 2.91 (2H, d, \(J = 6.4\) Hz), 2.11 (3H, s, COCH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\) 208.7 (C, C=O), 147.4 (C), 140.8 (C), 135.1 (C), 129.3 (CH), 128.7 (3 x CH), 128.0 (C), 127.5 (CH), 126.5 (CH), 122.1 (CH), 67.2 (CH), 53.5 (CH\(_2\)), 50.1 (CH\(_2\)), 2.91 (2H, d, \(J = 6.4\) Hz), 2.11 (3H, s, COCH\(_3\)); HRMS m/z 587.2383 (M+Na), calcd. for C\(_{32}\)H\(_{32}\)N\(_6\)O\(_4\)Na 587.2383; Anal. calcd. for C\(_{32}\)H\(_{32}\)N\(_6\)O\(_4\)Na (564.2485); C, 68.07; H, 5.71; N, 14.88; Found: C, 68.15; H, 5.75; N, 14.76%.

(R, R)-Cyclic double click product (9aab): Prepared following Method-\(D\), purified by column chromatography using EtOAc/hexane and isolated as white solid. [\(\alpha\)]\(_D\)\(^{25}\) = +3.0° (\(c = 0.42\) g/100 mL, CHCl\(_3\), 99% ee); IR (Neat): \(\nu_{\text{max}}\) 3430, 2360, 1654 (C=O), 907, 731, 659 and 650 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.78 (1H, s), 7.63 (1H, d, \(J = 7.6\) Hz), 7.51 (1H, d, \(J = 7.2\) Hz), 7.49-7.38 (2H, m), 7.32 (1H, t, \(J = 7.2\) Hz), 7.28 (1H, s), 6.45-5.51 (2H, m), 5.37-5.29 (1H, m), 4.86 (1H, brs), 3.09-2.89 (2H, m); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\) 210.2 (C, C=O), 147.4 (C), 141.6 (C), 136.0 (C), 129.7 (CH), 129.5 (CH), 129.1 (CH), 128.2 (CH), 127.7 (CH), 127.4 (CH), 127.4 (CH), 126.0 (CH), 122.4 (CH), 68.8 (CH), 53.7 (CH\(_2\)), 51.8 (CH\(_2\)); HRMS m/z 529.1957 (M+Na), calcd. for C\(_{29}\)H\(_{26}\)O\(_3\)Na 529.1964.

(R,S)-1-(2-Ethynylphenyl)-butane-1,3-diol (anti–10aa): Prepared following Method-\(E\), purified by column chromatography using EtOAc/hexane and isolated as liquid. [\(\alpha\)]\(_D\)\(^{25}\) = +58.6° (\(c = 0.27\) g/100 mL, CHCl\(_3\), 93% ee); IR (Neat): \(\nu_{\text{max}}\) 3293 (O-H), 3063, 2973, 2903, 2103, 1698, 1447, 1373, 1318, 1208, 1130, 1069, 932, 847 and 763 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.57 (1H, d, \(J = 8.4\) Hz), 7.46 (1H, d, \(J = 7.2\) Hz), 7.38 (1H, t, \(J = 7.2\) Hz), 7.22 (1H, t, \(J = 7.2\) Hz)[Ar-H]; 5.38 (1H, d, \(J = 10.0\) Hz, CHOH), 4.21–4.11 (1H, m), 3.79 (1H, br s, OH), 3.43 (1H, br s, OH), 3.32 (1H, s, Ar-C=CH), 1.92–1.85 (1H, m), 1.76–1.70 (1H, m), 1.21 (3H, d, \(J = 6.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\) 146.8 (C), 132.7 (CH), 129.4 (CH), 127.0 (CH), 125.2 (CH), 118.9 (C), 82.2 (CH, Ar-C=CH), 81.3
(C, Ar-C≡CH), 72.7 (CH, CHOH), 69.0 (CH, CHOH), 45.9 (CH₂), 23.9 (CH₃); LRMS m/z 188.95 (M-1), calcd. for C₁₂H₁₄O₂ 190.0994; Anal. calcd. for C₁₂H₁₄O₂ (190.0994); C, 76.57; H, 6.43. Found: C, 75.68; H, 7.51%.

(R,R)-1-(2-Ethynylphenyl)-butane-1,3-diol (syn–10aa): Prepared following Method-F, purified by column chromatography using EtOAc/hexane and isolated as liquid. [α]D²⁵ = –43.2° (c = 0.21 g/100 mL, CHCl₃, 95% ee); IR (Neat): νmax 3293 (O–H), 3055, 2971, 2917, 1644, 1447, 1420, 1377, 1335, 1109, 1071, 974, 937, 866, 814 and 760 cm⁻¹; ¹H NMR (CDCl₃) δ 7.61 (1H, d, J = 7.2 Hz), 7.47 (1H, d, J = 7.6 Hz), 7.39 (1H, t, J = 7.2 Hz), 7.23 (1H, t, J = 7.2 Hz)[Ar-H]; 5.52 (1H, s, C≡CH₂), 4.07 (1H, s), 3.43 (1H, br s, OHO), 3.33 (1H, s, Ar-C≡CH), 2.53 (1H, br. s, OH), 2.00–1.90 (2H, m), 1.27 (3H, d, J = 6.0 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 146.8 (C), 132.9 (CH), 129.2 (CH), 126.9 (CH), 125.4 (CH), 118.9 (C), 82.4 (CH, Ar-C≡CH), 81.3 (C, Ar-C≡CH), 69.9 (CH, CHOH), 65.9 (CH, CHOH), 44.2 (CH₂), 23.3 (CH₃); LRMS m/z 191.15 (M+1), calcd. for C₁₂H₁₄O₂ (190.0994); C, 76.57; H, 6.43. Found: C, 75.61; H, 7.52%.

(1S,2S,4R)-2-((S)-(2-ethynylphenyl)(hydroxy)methyl)-4-methylecyclohexanol (10af):

Prepared following Method-F and purified by column chromatography using EtOAc/hexane and isolated as liquid. [α]D²⁵ = +29.6° (c = 0.071 g/100 mL, CHCl₃, 96% ee and >99% de); IR (Neat): λmax 3300 (O–H), 2929, 1084, 756, 613, 566 and 538 cm⁻¹; ¹H NMR (CDCl₃) δ 7.48 (2H, d, J = 7.2 Hz), 7.24 (1H, t, J = 7.2 Hz), 5.18 (1H, d, J = 9.2 Hz, CHOH), 4.00-3.80 (2H, br s, OH), 3.80-3.72 (1H, m, CHOH), 3.29 (1H, s, Ar-C≡CH), 2.03–1.99 (1H, m), 1.84–1.76 (2H, m), 1.68–1.49 (3H, m), 1.25–1.15 (1H, m), 0.90–0.80 (1H, m), 0.84 (3H, d, J = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 145.0 (C), 132.8 (CH), 129.6 (CH), 127.5 (CH), 126.8 (CH), 120.8 (C), 81.9 (C, Ar-C≡CH), 81.8 (CH, Ar-C≡CH), 78.3 (CH, CHOH), 76.6 (CH, CHOH), 44.7 (CH), 32.4 (CH₂), 29.7 (CH₂), 29.3 (CH₂), 26.4 (CH), 17.7 (CH₃); LRMS m/z 245.25 (M+1), calcd. for C₁₆H₂₀O₂ 244.1463.
(1S,2S,4R)-2-((S)-(2-ethynylphenyl)(hydroxy)methyl)-4-methylcyclohexanol (10af): Prepared following Method-E, purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +2.2^\circ \ (c = 0.67 \text{ g/100 mL, CHCl}_3, 96\% \text{ ee and 90}\% \text{ de});$ IR (Neat): $\lambda_{\text{max}}$ 3415 (O-H), 1395, 1324, 1135, 755, 703, 658 and 646 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.47 (1H, d, $J = 6.8 \text{ Hz})$, 7.45 (1H, d, $J = 6.8 \text{ Hz})$, 7.38 (1H, t, $J = 7.6 \text{ Hz})$, 7.22 (1H, t, $J = 7.6 \text{ Hz})$, 5.16 (1H, d, $J = 9.2 \text{ Hz, CHOH})$, 4.38 (1H, br s, OH), 4.20 (1H, br s, OH), 3.71-3.68 (1H, m, CHOH), 3.28 (1H, s, Ar-C=CH), 1.97–1.93 (1H, m), 1.89–1.80 (1H, m), 1.75–1.72 (1H, m), 1.58–1.46 (3H, m), 1.22–1.15 (1H, m), 0.90–0.80 (1H, m), 0.82 (3H, d, $J = 7.2 \text{ Hz})$; $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 145.2 (C), 132.7 (CH), 129.6 (CH), 127.4 (CH), 126.8 (CH), 120.9 (C), 82.0 (C, Ar-C=CH), 81.7 (CH, Ar-C=CH), 78.1 (CH, CHOH), 76.5 (CH, CHOH), 44.7 (CH), 32.4 (CH$_2$), 29.7 (CH$_2$), 29.3 (CH$_2$), 26.5 (CH), 17.7 (CH$_3$); LRMS m/z 245.25 (M+1), calcd. for C$_{16}$H$_{20}$O$_2$ 244.1463; Anal. calcd. for C$_{16}$H$_{20}$O$_2$ (244.1463); C, 78.65, H, 8.25; Found: C, 78.53; H, 8.16%.

(1R,2R,4S)-2-((R)-hydroxy(2-(phenylethynyl)phenyl)methyl)-4-methylcyclohexanol (10bf): Prepared following Method-E, purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = -98.2^\circ \ (c = 0.26 \text{ g/100 mL, CHCl}_3, 86\% \text{ ee and 80}\% \text{ de});$ IR (Neat): $\nu_{\text{max}}$ 3401 (O-H), 2970, 1458, 1383, 1307, 910, 881, 763, 748 and 645 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.47-7.42 (4H, m), 7.32-7.29 (4H, m), 7.19 (1H, t, $J = 8.0 \text{ Hz})$, 5.18 (1H, d, $J = 9.2 \text{ Hz, CHOH})$, 4.60-4.00 (2H, br s, OH), 3.72-3.63 (1H, m, CHOH), 2.04-1.95 (1H, m), 1.84-1.64 (2H, m), 1.57-1.31 (3H, m), 1.20–1.06 (1H, m), 0.82–0.78 (1H, m), 0.75 (3H, d, $J = 10.0 \text{ Hz})$; $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 144.5 (C), 132.1 (CH), 131.4 (2 x CH), 129.1 (CH), 128.5 (3 x CH), 127.5 (CH), 126.9 (CH), 123.1 (C), 121.9 (C), 93.9 (C), 87.6 (C), 78.6 (CH, CHOH), 76.5 (CH, CHOH), 44.8 (CH), 32.6 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 26.5 (CH), 17.8 (CH$_3$); LRMS m/z 321.25 (M+1), calcd. for
C_{22}H_{24}O_{2} 320.1776; Anal. calcd. for C_{22}H_{24}O_{2} (320.1776); C, 82.46, H, 7.55; Found: C, 82.15; H, 7.49%.

(1S,2S,4R)-2-((S)-(3,5-dinitrobenzoyl)oxy)(2-ethynylphenyl)methyl)-4-methylocyclohexyl 3,5-dinitrobenzoate (11af): Prepared following Method-G, purified by column chromatography using EtOAc/hexane and isolated as solid. \([\alpha]_{D}^{25} = +1.9^\circ (c = 0.38 \text{ g/100 mL, CHCl}_{3}, 96\% \text{ ee and 90\% de});\) IR (Neat): \(\lambda_{\text{max}}\) 2955, 1728 (C=O), 1543 (NO\(_2\)), 1343 (NO\(_2\)), 1275, 1167, 730, 719 and 661 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.28-9.27 (2H, m), 9.24-9.23 (1H, m), 9.21-9.19 (1H, m), 9.02-9.01 (2H, m), 7.59-7.57 (1H, m), 7.37-7.34 (1H, m), 7.25-7.22 (2H, m), 6.58 (1H, d, \(J = 8.8\) Hz, CHO\(_{Bz}\)), 5.57 (1H, q, \(J = 4.4\) Hz, CHO\(_{Bz}\)), 3.54 (1H, s, Ar-C≡CH), 3.08 (1H, m), 1.76-1.72 (1H, m), 1.58-1.50 (1H, m), 1.48-1.42 (1H, m), 1.35–1.24 (2H, m), 0.98 (3H, d, \(J = 6.4\) Hz), 0.90-0.80 (1H, m); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \(\delta\) 161.8 (C), 161.7 (C), 148.8 (2 x C), 148.6 (2 x C), 140.3 (C), 134.1 (C), 134.0 (CH), 133.5 (C), 129.7 (2 x CH), 129.3 (3 x CH), 128.4 (CH), 126.4 (CH), 122.6 (CH), 122.4 (CH), 121.2 (C), 83.1 (CH, Ar-C≡CH), 81.3 (C, Ar-C≡CH), 77.3 (CH), 73.7 (CH), 42.0 (CH), 32.4 (CH\(_2\)), 29.2 (CH\(_2\)), 27.0 (CH), 26.4 (CH\(_2\)), 20.8 (CH\(_3\)); LRMS m/z 632.55 (M+1), calcd. for C\(_{30}\)H\(_{24}\)N\(_4\)O\(_{12}\) 632.1391; Anal. calcd. for C\(_{30}\)H\(_{24}\)N\(_4\)O\(_{12}\) (632.1391); C, 56.96, H, 3.82, N, 8.86; Found: C, 56.85; H, 3.76; N, 8.45%.
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<td>(\theta_{\text{max}})</td>
<td>26.050</td>
<td></td>
</tr>
<tr>
<td>(R(\text{reflections}))</td>
<td>0.0556(2978)</td>
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<tr>
<td>(wR^2(\text{reflections}))</td>
<td>0.1295(3480)</td>
<td></td>
</tr>
<tr>
<td>(S)</td>
<td>1.116</td>
<td>Npar=223</td>
</tr>
</tbody>
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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**Datablock (R,R)-(+)-6aa - ellipsoid plot**

![Ellipsoid plot of Datablock (R,R)-(+)-6aa](image-url)