

Supplementary material

cis-(1*S*,2*S*)-**3b** and *cis*-(1*R*,2*R*)-1,2-Dihydroxy-3-bromocyclohex-3-ene-**3b'**.

Enantiomer **3b**, white crystalline solid (0.82 g, 85%); mp 105-107 °C (CH₂Cl₂); [α]_D -114 (*c* 1.15, MeOH); (Found: C, 37.3; H, 4.6. C₆H₉O₂Br requires C 37.3; H, 4.7%); δ_{H} (500 MHz, CDCl₃) 1.80 (2 H, m, 6-H, 6'-H), 2.09 (1 H, m, 5-H), 2.24 (1 H, m, 5'-H), 3.95 (1 H, m, 1-H), 4.21 (1 H, d, $J_{2,1}$ 3.9, 2-H), 6.23 (1 H, dd, $J_{4,5'} = J_{4,5} = 4.1$, 4-H); *m/z* (EI) 194 (M⁺, 3%), 192 (M⁺, 3), 150 (98), 148 (100), 113 (17), 95 (10), 69 (18). Enantiomer **3b'**: [α]_D +106 (*c* 1.33, MeOH).

cis-(1*S*,2*S*)-**3c** and *cis*-(1*R*,2*R*)-1,2-Dihydroxy-3-iodocyclohex-3-ene-**3c'**.

Enantiomer **3c**, white crystalline solid (0.60 g, 50%); mp 109-111 °C (CHCl₃/hexane); [α]_D -84 (*c* 1.14, MeOH); (Found: C, 29.9; H, 3.6. C₆H₉O₂I requires C 30.0; H, 3.8%); δ_{H} (500 MHz, CDCl₃) 1.84 (2 H, m, 6-H, 6'-H), 2.09 (1 H, m, 5-H), 2.28 (1 H, m, 5'-H), 3.96 (1 H, m, 1-H), 4.20 (1 H, d, $J_{2,1}$ 4.0, 2-H), 6.51 (1 H, dd, $J_{4,5} = J_{4,5'} = 4.0$, 4-H); *m/z* (EI) 240 (M⁺, 21%), 222 (9), 196 (100), 127 (7), 113 (38), 95 (15), 69 (47). Enantiomer **3c'**: [α]_D +79 (*c* 1.20, MeOH).

cis-(1*S*,2*R*)-1,2-Dihydroxy-3-(trifluoromethyl)cyclohex-3-ene **3d**.

Enantiomer **3d**, white crystalline solid (0.82 g, 90%); mp 105-107 °C (CHCl₃/hexane); [α]_D -129 (*c* 0.24, MeOH); (Found: M⁺, 182.0550. C₇H₉O₂F₃ requires 182.0555); δ_{H} (500 MHz, CDCl₃) 1.71-1.79 (2 H, m, 6-H, 6'-H), 2.18 (1 H, m, 5-H), 2.33 (1 H, m, 5'-H), 3.71 (1 H, m, $J_{1,2}$ 3.5, 1-H), 4.27 (1 H, dd, $J_{2,1}$ 3.5, 2-H), 6.48 (1 H, m, $J_{4,2}$ 1.5, 4-H); *m/z* (EI) 182 (M⁺, 8%), 164 (25), 90 (100).

trans-(1*S*,2*R*)-**5b** and *trans*-(1*R*,2*S*)-1,2-Dihydroxy-3-bromocyclohex-3-ene-**5b'**.

Enantiomer **5b**, white crystals (0.70 g, 66%); mp 89-91 °C (CHCl₃ / hexane), [α]_D +76 (*c* 1.09, MeOH); (Found: C, 37.5; H, 4.5. C₆H₉O₂Br requires C 37.3; H, 4.7%); δ_{H} (500 MHz, CDCl₃) 1.76 (1 H, m, 6-H), 1.97 (1 H, m, 6'-H), 2.19 (2 H, m, 5-H, 5'-H), 3.86 (1 H, m, 1-H), 4.08 (1 H, d, $J_{2,1}$ 6.4, 2-H), 6.16 (1 H, dd, $J_{4,5} = J_{4,5'} = 3.7$, 4-H); *m/z* (EI) 194 (M⁺, 2%), 192 (2), 176 (1), 174 (1), 150 (98), 148 (100), 113 (10), 95 (9), 69 (20). Enantiomer **5b'**: [α]_D -74 (*c* 1.05, MeOH).

***trans*-(1*S*,2*R*)-5c and *trans*-(1*R*,2*S*)-1,2-Dihydroxy-3-iodocyclohex-3-ene-5c'.**

Enantiomer **5c**, white crystals (0.77 g, 58%); mp 111-112 °C (CHCl₃ / hexane); [α]_D +46 (*c* 1.43, MeOH); (Found: C, 29.9; H, 3.7. C₆H₉O₂I requires C 30.0; H, 3.8%); δ _H (500 MHz, CDCl₃) 1.78 (1 H, m, 6-H), 2.00 (1 H, m, 6'-H), 2.19 (2 H, m, 5-H, 5'-H), 3.85 (1 H, m, 1-H), 4.03 (1 H, d, *J*_{2,1} 6.6, 2-H), 6.43 (1 H, dd, *J*_{4,5} = *J*_{4,5'} 3.9, 4-H); *m/z* (EI) 240 (M⁺, 24%), 196 (100), 127 (8), 113 (20), 95 (10), 69 (37), 65 (27), 41 (50). Enantiomer **5c'**: [α]_D -49 (*c* 1.5, MeOH).

***trans*-(1*S*,2*S*)-1,2-Dihydroxy-3-(trifluoromethyl)cyclohex-3-ene 5d.**

Enantiomer **5d**, light yellow oil (0.67 g, 67%); [α]_D +120 (*c* 0.4, CHCl₃); (Found: M⁺, 182.0546 C₇H₉F₃O₂ requires 182.0555); δ _H (500 MHz, CDCl₃) 1.74 (1 H, m, 6-H), 1.96 (1 H, m, 6'-H), 2.30 (2 H, m, 5-H, 5'-H), 3.88 (1 H, m, 1-H), 4.24 (1 H, d, *J*_{2,1} 6.6, 2-H), 6.55 (1 H, dd, *J*_{4,5} = *J*_{4,5'} 3.0, 4-H); *m/z* (EI) 182 (M⁺, 8%), 164 (25), 90 (100).

***trans*-(1*S*,2*R*)-6b and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-bromocyclohex-3-ene -6b'.**

Enantiomer **6b**, white crystals (0.92 g, 95%); mp 37-39 °C (CHCl₃ / hexane), [α]_D +111 (*c* 1.53, CHCl₃); (Found: C, 43.3; H, 4.55. C₁₀H₁₃O₄Br requires C 43.3; H, 4.7%); δ _H (300 MHz, CDCl₃) 1.78 (2 H, m, 6-H,), 2.00 (2 H, m, 6'-H), 2.07 (3 H, s, OCOMe), 2.13 (3 H, s, OCOMe), 2.19 (2 H, m, 5-H, 5'-H), 3.85 (1 H, m, 1-H), 4.03 (1 H, d, *J*_{2,1} 6.6, 2-H), 6.43 (1 H, d, *J*_{4,5} 3.9, 4-H); *m/z* (EI) 279 (M+1⁺, 1%), 197 (2), 176 (65), 174 (66), 155 (36), 113 (24), 95 (83), 77 (22), 43 (100). Enantiomer **6b'**: [α]_D -106 (*c* 1.33, CHCl₃).

***trans*-(1*S*,2*R*)-6c and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-iodocyclohex-3-ene-6c'.**

Enantiomer **6c**, white crystals (1.08 g, 95%); mp 32-34 °C (CHCl₃ / hexane), [α]_D +145 (*c* 1.09, MeOH); (Found: C, 37.0; H, 4.0. C₁₀H₁₃O₄I requires C 37.1; H, 4.0 %); δ _H (500 MHz, CDCl₃) 1.94 (2 H, m, 6-H, 6'-H), 2.06 (3 H, s, OCOMe), 2.14 (3 H, s, OCOMe), 2.22 (2 H, m, 5-H, 5'-H), 5.02 (1 H, m, H-1), 5.47 (1 H, d, *J*_{2,1} 4.7, 2-H), 6.14 (1 H, m, 4-H); *m/z* (EI) 323 (M-1⁺, 4), 264 (46), 239 (48), 222 (53), 197 (34), 155 (39), 113 (38), 95 (84), 77 (16), 43 (100). Enantiomer **6c'**: [α]_D -138 (*c* 1.23, CHCl₃).

***trans*-(1*S*,2*R*)-1,2-Diacetoxy-3-(trifluoromethyl)cyclohex-3-ene 6d.**

Enantiomer **6d**, yellow oil (0.87 g, 93%); $[\alpha]_D + 105$ (c 0.75, CHCl_3); (Found: M^+ - MeCO_2 , 207.0637 $\text{C}_9\text{H}_{10}\text{O}_2\text{F}$ requires 207.0633); δ_{H} (500 MHz, CDCl_3) 1.89 (1 H, m, 6-H), 2.00 (1 H, m, H-6'), 2.05 (3 H, s, OCOMe), 2.07 (3 H, s, OCOMe), 2.31 (2 H, m, 5-H, 5'-H), 5.06 (1 H, m, 1-H), 5.53 (1 H, d, $J_{2,1}$ 3.6, 2-H), 6.74 (1 H, m, 4-H); m/z (EI) 323 (M^+ - MeCO_2 , 100%), 148 (27).

***trans*-(1*S*,2*R*)-7b and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-bromo-5-bromocyclohex-3-ene 7b'.**

Enantiomers **7b** and **7b'** light yellow oil (1.16 g, 95%); δ_{H} (500 MHz, CDCl_3): 2.07 (3 H, s, OCOMe), 2.13 (3 H, s, OCOMe), 2.41 (1 H, m, 6-H), 2.52 (1 H, m, 6'-H), 4.71 (1 H, m, 5-H), 5.04 (1 H, m, 1-H), 5.60 (1 H, m, 2-H), 6.53 (1 H, m, 4-H).

***trans*-(1*S*,2*R*)-7c and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-iodo-5-bromocyclohex-3-ene-7c'.**

Enantiomers **7c** and **7c'** light yellow oil (1.3 g, 95%); δ_{H} (500 MHz, CDCl_3) 2.06 (3 H, s, OCOMe), 2.16 (3 H, s, OCOMe), 2.43 (1 H, m, 6-H), 2.52 (1 H, m, 6'-H), 4.66 (1 H, m, 5-H), 5.34 (1 H, m, 1-H), 5.61 (1 H, m, 2-H), 6.57 (1 H, m, 4-H).

***trans*-(1*S*,2*S*)-1,2-Diacetoxy-3-(trifluoromethyl)-5-bromocyclohex-3-ene 7d.**

Light yellow oil (1.08 g, 92%); δ_{H} (500 MHz, CDCl_3) 2.05 (3 H, s, OCOMe), 2.08 (3 H, s, OCOMe), 2.51 (1 H, m, 6-H), 2.66 (1 H, m, 6'-H), 4.87 (1 H, m, 5-H), 5.09 (1 H, m, 1-H), 5.65 (1 H, m, H-2), 6.78 (1 H, m, H-4).

***trans*-(1*S*,2*R*)-8b and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-bromocyclohexa-3,5-diene-8b'.**

Enantiomer **8b**, white crystals (0.73 g, 91%); mp 42-44 °C, (CHCl_3 / hexane); $[\alpha]_D + 363$ (c 2.13, CHCl_3); (Found: C, 43.5; H, 3.9 $\text{C}_{10}\text{H}_{11}\text{O}_4\text{Br}$ requires C 43.7; H, 4.0 %); δ_{H} (500 MHz, CDCl_3) 2.09 (3 H, s, OCOMe), 2.15 (3 H, s, OCOMe), 5.42 (1 H, dd, $J_{1,2}$ 4.4, $J_{1,6}$ 3.7, 1-H), 5.74 (1 H, d, $J_{2,1}$ 4.0, 2-H), 5.94 (1 H, m, 6-H), 6.02 (1 H, dd, $J_{5,4}$ 6.2, $J_{5,6}$ 9.5, 5-H), 6.53 (1 H, d, $J_{4,5}$ 6.2, 4-H); m/z (EI) 276 (M^+ , 6%), 230 (7), 274 (6), 195 (16), 174 (55), 172 (53), 43 (100). Enantiomer **8b'**: $[\alpha]_D - 351$ (c 1.62, CHCl_3).

***trans*-(1*S*,2*R*)-8c and *trans*-(1*R*,2*S*)-1,2-Diacetoxy-3-iodocyclohexa-3,5-diene -8c'.**

Enantiomer **8c**, white crystals (0.69 g, 74%); mp 45-46 °C, (CHCl₃/ hexane); [α]_D +235 (*c* 1.09, CHCl₃); (Found: C, 37.2; H, 3.3 C₁₀H₁₁O₄BI requires C 37.3; H, 3.4 %); δ_{H} (500 MHz, CDCl₃) 2.10 (3 H, s, OCOMe), 2.14 (3 H, s, OCOMe), 5.59 (1 H, m, 1-H), 5.78 (1 H, m, 2-H), 6.36(1 H, m, 6-H), 6.45 (1 H, m, 5-H), 6.56 (1 H, m, 4-H); *m/z* (EI) 322 (M⁺, 9%), 195 (22), 220 (68), 43 (100). Enantiomer **8c'**: [α]_D -223 (*c* 1.62, CHCl₃).

***trans*-(1*S*,2*R*)-1,2-Diacetoxy-3-(trifluoromethyl)-cyclohexa-3,5-diene 8d.**

Colourless oil (0.72 g, 94%); [α]_D +292 (*c* 0.50, CHCl₃); (Found: M⁺, 264.0609 C₁₁H₁₁O₄F₃ requires 264.0609); δ_{H} (500 MHz, CDCl₃) 2.07 (3 H, s, OCOMe), 2.08 (3 H, s, OCOMe), 5.31 (1 H, dd, *J*_{1,2} 4.8, *J*_{1,6} 3.9, 1-H), 5.78 (1 H, d, *J*_{2,1} 4.8, 2-H), 6.22(1 H, dd, *J*_{6,1} 3.9, *J*_{6,5} 5.2, 6-H), 6.31 (1 H, dd, *J*_{5,4} 5.8, *J*_{5,6} 5.2, 5-H), 6.77 (1 H, d, *J*_{4,5} 5.8, 4-H); *m/z*(EI) 264 (M⁺, 1), 223 (3), 207 (3), 43 (100).

***trans*-(1*S*,2*R*)-9b and *trans*-(1*R*,2*S*)-1,2-Dihydroxy-3-bromocyclohexa-3,5-diene-9b'.**

Enantiomer **9b**, white crystals (0.50 g, 98%); mp 107-109 °C (CHCl₃); [α]_D +458 (*c* 0.53, MeOH); (Found: M⁺, 189.9627. C₆H₇BrO₂ requires 189.9629); δ_{H} (500 MHz, CDCl₃) 4.47 (1 H, d, *J*_{2,1} 9.5, 2-H), 4.52 (1 H, ddd, *J*_{1,2} 9.5, *J*_{1,5} 1.7, *J*_{1,6} 3.0, 1-H), 5.82 (2 H,m, 5-H), 5.98 (1 H, dd, *J*_{6,5} 9.5, *J*_{6,1} 3.0, 6-H), 6.36 (1 H, d *J*_{4,5} 6.0, 4-H); *m/z* (EI) 190 (M⁺, 35%), 174(10), 172(10), 146 (32), 144(29), 111 (29), 93 (19), 81 (48), 65 (100), 55 (39). Enantiomer **9b'**: [α]_D -443 (*c* 0.48, MeOH).

***trans*-(1*S*,2*R*)-9c and *trans*-(1*R*,2*S*)-1,2-Dihydroxy-3-iodocyclohexa-3,5-diene-9c'.**

Enantiomer **9c**, white crystals (0.59 g, 94%); mp 94-96 °C (CHCl₃); [α]_D +256 (*c* 0.85, MeOH); (Found: M⁺, 237.9489. C₆H₇O₂ I requires 237.9490); δ_{H} (500 MHz, CDCl₃) 4.39 (1 H, d, *J*_{2,1} 10.7, 2-H), 4.50 (1 H, m, 1-H), 5.66 (1 H,dd, *J*_{5,4} 6.1, *J*_{5,6} 9.6, 5-H), 6.00 (1 H, dd, *J*_{6,5} 9.5, *J*_{6,1} 3.0, 6-H), 6.66 (1 H, d *J*_{4,5} 6.1, 4-H); *m/z* (EI) 238 (M⁺, 59%), 220 (13), 196 (47), 192 (13), 127 (10), 111 (74), 93 (25), 83 (32), 65 (100), 55 (39). Enantiomer **9c'**: [α]_D -243 (*c* 0.77, MeOH).

***trans*-(1*S*,2*S*)-1,2-Dihydroxy-3-(trifluoromethyl)cyclohexa-3,5-diene 9d.**

Colourless semi-solid (0.85 g, 93%); $[\alpha]_D^{25} +337$ (c 0.56, CHCl_3); (Found: M^+ , 182.0551. $\text{C}_7\text{H}_9\text{F}_3\text{O}_2$ requires 182.0555); δ_{H} (500 MHz, CDCl_3) 4.41 (1 H, dd, $J_{1,2}$ 7.1, $J_{1,6}$ 5.9, H-1), 4.52 (1 H, d, $J_{2,1}$ 7.1, H-1), 6.11 (1 H, dd, $J_{5,4}$ 5.5, $J_{5,6}$ 3.9, H-5), 6.20 (1 H, dd, $J_{6,1}$ 5.9, $J_{6,5}$ 3.9, H-6), 6.55 (1 H, d, $J_{4,5}$ 5.5, H-4); m/z (EI) 182 (M^+ , 1%), 164 ($M-\text{H}_2\text{O}$, 12), 30 (100).

**(1*S*,2*R*)-Di-[(*S*)-2-methoxy-2-phenyl-2-trifluoroacetoxy]-3-bromocyclohex-3-ene
21b.**

White crystalline solid, mp 126-126 °C; (Found: M^+ , 624.0587. $\text{C}_{26}\text{H}_{23}\text{O}_6^{79}\text{BrF}_6$ requires 624.0581); $[\alpha]_D^{25} +67$ (c 0.77, CHCl_3); δ_{H} (500 MHz, CDCl_3) 1.68 (1 H, m, 6-H), 1.95 (1 H, m, 6'-H), 2.14 (2 H, m, 5-H, 5'-H), 3.51 (3 H, s, OMe), 3.62 (3 H, s, OMe), 5.23 (1 H, m, 1-H), 5.53 (1 H, d, $J_{2,1}$ 2.2, 2-H), 6.41 (1 H, d, $J_{4,5}$ 4.0, 4-H), 7.41-7.61 (10 H, m, Ar-H).

**(1*R*,2*S*)-Di-[(*S*)-2-methoxy-2-phenyl-2-trifluoroacetoxy]-3-bromocyclohex-3-ene
21b'.**

White solid, mp 131-133 °C; (Found: M^+ , 624.0591. $\text{C}_{26}\text{H}_{23}\text{O}_6^{79}\text{BrF}_6$ requires 624.0581); $[\alpha]_D^{25} -136$ (c 1.45, CHCl_3); δ_{H} (500 MHz, CDCl_3) 2.00 (2 H, m, 5-H, 5'-H, 6-H, 6'-H), 3.54 (3 H, s, OMe), 3.57 (3 H, s, OMe), 5.35 (1 H, m, 1-H), 5.64 (1 H, d, $J_{2,1}$ 3.3, 2-H), 6.36 (1 H, m, 4-H), 7.40-7.61 (10 H, m, Ar-H).

**(1*S*,2*R*)-Di-[(*S*)-2-methoxy-2-phenyl-2-trifluoroacetoxy]-3-iodocyclohex-3-ene
21c.**

White crystalline solid, mp 132-134 °C; (Found: M^+ , 672.0428. $\text{C}_{26}\text{H}_{23}\text{O}_6\text{IF}_6$ requires 672.0447); $[\alpha]_D^{25} +113$ (c 1.62, CHCl_3); δ_{H} (500 MHz, CDCl_3) 1.60 (1 H, m, 6-H), 1.94 (1 H, m, 6'-H), 2.10 (2 H, m, 5-H, 5'-H), 3.51 (3 H, s, OMe), 3.64 (3 H, s, OMe), 5.17 (1 H, m, 1-H), 5.53 (1 H, m, 2-H), 6.69 (1 H, d, $J_{4,5}$ 3.6, 4-H), 7.41-7.63 (10 H, m, Ar-H).

**(1*R*,2*S*)-Di-[(*S*)-2-Methoxy-2-phenyl-2-trifluoroacetoxy]-3-iodocyclohex-3-ene
21c'.**

White crystalline solid, mp 125-127 °C; (Found: M^+ , 672.0447. $\text{C}_{26}\text{H}_{23}\text{O}_6\text{IF}_6$ requires 672.0443); $[\alpha]_D^{25} -89$ (c 0.95, CHCl_3); δ_{H} (500 MHz, CDCl_3) 1.95 (1 H, m, 6-H), 2.06

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(3 H, m, 5-H, 5'-H, 6'-H), 3.55 (3 H, s, OMe), 3.59 (3 H, s, OMe), 5.30 (1 H, m, 1-H),
5.62 (1 H, m, 2-H), 6.68 (1 H, d, $J_{4,5}$ 3.4, 4-H), 7.41-7.63 (10 H, m, Ar-H).