Highly Enantio- and Diastereoselective Organocatalytic Domino Michael-Aldol Reactions of β-Diketone and β-Ketosulfone Nucleophiles with α,β-Unsaturated Ketones

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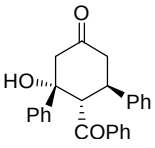
Supporting Information

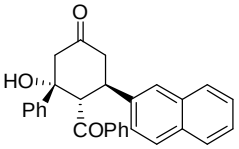
General Methods. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm relative to $CHCl_3$ (δ = 7.26) for ^{1}H and relative to the central $CDCl_3$ resonance (δ = 77.0) or $(CD_3)_2SO$ (δ = 39.52) for ^{13}C NMR. Flash chromatography (FC) was carried out using Merck silica gel 60 (230-400 mesh). Optical rotations were measured on Perkin-Elmer 241 polarimeter. All diastereoselectivities were measured by ^{1}H-NMR on crude reaction mixtures and confirmed by HPLC analysis. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC using the columns and eluents indicated in the respective entries.

Materials. Benzylideneacetone **2a**, 4-chlorobenzylideneacetone **2c**, furfurylideneacetone (*cis*-*trans* mixture) **2e**, *trans*-4-(2-thienyl)-3-butene-2-one **2h**, 4-hydroxybenzylideneacetone **2i**, dibenzoylmethane **3** and 2-phenylsulfonylacetophenone **4** were purchased commercially and used as received.
4-Benzyl-1-methyl-imidazolidine-2-carboxylic acid (*S*)-**1**,[1] 2-naphthylideneacetone[2] **2b**, 4-nitro-benzylideneacetone[3] **2d**, 1-phenyl-pent-1-en-3-one[4] **2f**, 4-methoxy-benzylideneacetone[5] **2g** were prepared according to literature procedures.

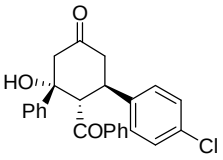
General procedure for the organocatalytic asymmetric domino Michael-aldol reaction of dibenzoylmethane 3 with a,b**-unsaturated ketones.**
To a solution of 0.5 mmol of α,β-unsaturated ketone **2** in 1.0 mL of $CHCl_3$ in a disposable glass test tube equipped with a magnetic stirring bar, is added 1.0 mmol of dibenzoylmethane **3**, 0.05 mmol of catalyst and the mixture was stirred at ambient temperature for the time indicated in the table. The reaction mixture was diluted with Et_2O (2 mL), filtered by suction and the precipitate washed with 2 mL of Et_2O.



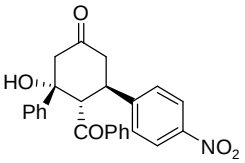
4-Benzoyl-3-hydroxy-3,5-diphenyl-cyclohexanone (5a). Isolated as a colorless solid, mp. 208-210 ^{o}C. The enantiomers were separated by HPLC using a Daicel Chiralcel OD-R chiral stationary phase in MeOH/MeCN 95/5; $[\alpha]^{rt}_{D}$ = -16.0^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 91% ee); ^{1}H NMR ($CDCl_3$) δ 2.71 (dd, *J* = 14.8, 2.3 Hz, 1H, CH**H**CO), 2.80 (dddd, *J* = 14.8, 4.7, 2 Hz, 1H, C**H**HCO), 2.89-2.98 (m, 2H, CH_2CO), 3.94 (td, *J* = 12.5, 4.7 Hz, 1H, PhC*H), 4.53 (d, *J* = 11.3, 1H, PhCOC*H), 5.11 (s, 1H, OH), 6.97-7.40 (m, 15H, ArH); ^{13}C NMR ($CDCl_3$) δ 44.7, 47.0, 53.9, 56.8, 78.5, 124.6, 127.3, 127.5, 127.6, 127.7, 127.8, 128.4, 128.7, 133.1, 137.6, 139.9, 143.9, 206.5, 206.7; HRMS m/z ($M+Na^+$) 393.1472, calc. for $C_{25}H_{22}O_3Na^+$ 393.1467.



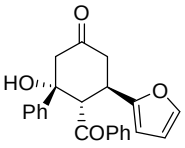
4-Benzoyl-3-hydroxy-5-naphthalen-2-yl-3-phenyl-cyclohexanone (5b). Isolated as a colorless solid, mp. 205-208 ^{o}C. The enantiomers were separated by HPLC using a Chiralpak AS chiral stationary phase in hexane/EtOH 50/50 containing 0.15% TFA; $[\alpha]^{rt}_{D}$ = -22.0^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 81% ee); ^{1}H NMR ($CDCl_3$) δ 2.76 (dd, *J* = 14.4, 1.9 Hz, 1H, CH**H**CO), 2.86 (ddd, *J* = 14.8, 4.7, 1.9 Hz, 1H, C**H**HCO), 3.00-3.06 (m, 2H, CH_2CO), 4.13 (td, *J* = 12.9, 4.7 Hz, 1H, 1-Np-C*H), 4.67 (d, *J* = 11.7 Hz, PhCOC*H), 5.12 (s, 1H, OH), 6.90-6.92 (m, 2H, ArH), 7.01-7.20 (m, 6H, ArH), 7.32-7.40 (m, 5H, ArH), 7.42-7.66 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 44.8, 47.2, 53.9, 56.6, 78.6, 124.6, 125.0, 125.9, 126.2, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.4, 128.6, 132.5, 133.0, 133.2, 137.2, 137.5, 143.9, 206.3, 206.7; HRMS m/z ($M+Na^+$) 443.1622, calc. for $C_{29}H_{24}O_3Na^+$ 443.1623.



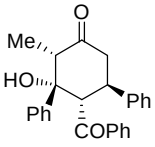
4-Benzoyl-5-(4-chloro-phenyl)-3-hydroxy-3-phenyl-cyclohexanone (5c). Isolated as a colorless solid, mp. 203-205 ^{o}C. The enantiomers were separated by HPLC using a Daicel Chiralcel OD-R chiral stationary phase in MeOH/MeCN 95/5; $[\alpha]^{rt}_{D}$ = -26.0^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 80% ee); ^{1}H NMR ($CDCl_3$) δ 2.65-2.93 (m, 4H, CH_2COCH_2), 3.88 (td, *J* = 11.7, 4.4 Hz, 1H, 4-Cl-Ph-C*H), 4.50 (d, *J* = 11.7, 1H, PhCOC*H), 5.03 (s, 1H, OH), 7.03-7.38 (m, 14H, ArH); ^{13}C NMR ($CDCl_3$) δ 44.0, 47.0, 53.8, 56.6, 78.4, 124.5, 127.4, 127.7, 128.0, 128.4, 128.8, 129.0, 129.1, 133.2, 133.4, 137.4, 138.5, 143.7, 205.9, 206.4; HRMS m/z ($M+Na^+$) 427.1098, calc. for $C_{25}H_{21}ClO_3Na^+$ 427.1077.



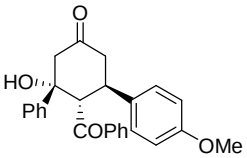
4-Benzoyl-3-hydroxy-5-(4-nitro-phenyl)-3-phenyl-cyclohexanone (5d). Isolated as a colorless solid, mp. 155-158 ^{o}C. The enantiomers were separated by HPLC using a Daicel Chiralcel OD-R chiral stationary phase in MeOH/MeCN 95/5; $[\alpha]^{rt}_{D}$ = -36^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 87% ee); ^{1}H NMR ($CDCl_3$) δ 2.74-2.82 (m, 2H, CH_2CO), 2.87 (dd, *J* = 14.8 12.9 Hz, 1H, C**H**HCO), 3.00 (dd, *J* = 14.8, 2.7 Hz, 1H, CH**H**CO), 4.09 (td, *J* = 12.5, 4.7 Hz, 1H, 4-NO_2-PhC*H), 4.57 (d, *J* = 11.7 Hz,1H, PhCOC*H), 4.97 (d, *J* = 3.1 Hz, 1H, OH), 7.03-7.10 (m, 2H, ArH), 7.14-7.18 (m, 2H, ArH), 7.25-7.37 (m, 4H, ArH), 7.38-7.40 (m, 4H, ArH), 7.96-7.98 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 44.3, 46.5, 53.8, 56.1, 78.5, 123.9, 124.5, 127.6, 127.7, 128.2, 128.5, 128.7, 133.8, 137.0, 143.4, 147.0, 147.4, 205.0, 205.5; HRMS m/z ($M+Na^+$) 438.1320, calc. for $C_{25}H_{21}NO_5Na^+$ 438.1317.



4-Benzoyl-5-furan-2-yl-3-hydroxy-3-phenyl-cyclohexanone (5e). Isolated as a colorless solid, mp. 180-183 ^{o}C. The enantiomers were separated by HPLC using a Daicel Chiralcel OD-R chiral stationary phase in MeOH/MeCN 95/5; $[\alpha]^{rt}_{D}$ = -9^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 85% ee); ^{1}H NMR ($CDCl_3$) δ 2.63 (dd, *J* = 14.8 1.9 Hz, 1H, C**H**HCO), 2.72 (dddd, *J* = 14.8 4.7, 1.9 Hz, 1H, CH**H**CO), 2.83 (d, *J* = 14.8 Hz, 1H, CH**H**CO), 2.96 (dd, *J* = 14.8, 13.2 Hz, 1H, C**H**HCO), 3.99 (td, *J* = 12.5, 4.7 Hz, 1H, 2-furyl-C***H**), 4.63 (d, *J* = 11.7 Hz, PhCOC*H), 5.02 (s, 1H, OH), 5.85-5.92 (m, 2H, ArH), 6.97-7.37 (m, 11H, ArH); ^{13}C NMR ($CDCl_3$) δ 38.1, 44.5, 53.9, 54.2, 78.1, 107.0, 110.3, 124.5, 127.3, 127.7, 128.1, 128.3, 133.3, 137.1, 141.8, 143.9, 152.7, 205.8, 206.4; HRMS m/z ($M+Na^+$) 383.1253, calc. for $C_{23}H_{20}O_4Na^+$ 383.1259.



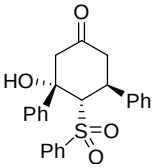
4-Benzoyl-3-hydroxy-2-methyl-3,5-diphenyl-cyclohexanone (5f). Isolated as a colorless solid, mp. 176-179 ^{o}C. The enantiomers were separated by HPLC using a Chiralpak AS chiral stationary phase in hexane/EtOH 50/50 containing 0.15% TFA; $[\alpha]^{rt}_{D}$ = -11.0^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 67% ee); ^{1}H NMR ($CDCl_3$) δ 0.84 (d, *J* = 6.6 Hz, 3H, CH_3), 2.82 (dd, *J* = 14.0, 4.7 Hz, 1H, CH**H**CO), 2.89-3.08 (m, 2H, C**H**HCOC***H**Me), 3.91 (td, *J* = 12.9, 4.3 Hz, 1H, PhC*H), 4.56 (d, *J* = 11.7 Hz, 1H, PhCOC*H), 4.97 (s, 1H, OH), 6.97-7.33 (m, 15H, ArH); ^{13}C NMR ($CDCl_3$) δ 7.5, 44.8, 47.2, 53.8, 58.8, 81.1, 127.0, 127.4, 127.6, 127.65, 127.7, 128.2, 128.7, 132.9, 137.6, 140.0, 142.9, 206.7, 208.0; HRMS m/z ($M+Na^+$) 407.1624, calc. for $C_{26}H_{24}O_3Na^+$ 407.1623.



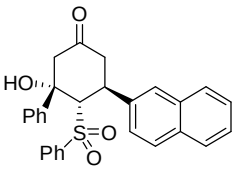
4-Benzoyl-3-hydroxy-5-(4-methoxy-phenyl)-3-phenyl-cyclohexanone (5g). Isolated as a colorless solid, mp. 178-180 ^{o}C. The enantiomers were separated by HPLC using a Daicel Chiralcel OD-R chiral stationary phase in MeOH/MeCN 95/5; $[\alpha]^{rt}_{D}$ = -14.0^{o} (*c* = 1.0 g/100 mL, $CHCl_3$, 64% ee); ^{1}H NMR ($CDCl_3$) δ 2.64 (dd, *J* = 14.4, 1.9 Hz, 1H, CH**H**CO), 2.73 (ddd, *J* = 14.4, 4.7, 1.9 Hz, 1H, C**H**HCO), 2.83-2.92 (m, 2H, CH_2CO), 3.57 (s, 3H, CH_3O), 3.86 (td, *J* = 12.5, 4.7 Hz, 1H, 4-MeO-Ph-C*H), 4.44 (d, *J* = 11.3, 1H, PhCOC*H), 5.11 (d, *J* = 2.7 Hz, 1H, OH), 6.57 (d, *J* = 12.1 Hz, 2H, ArH), 6.96-7.34 (m, 12H, ArH); ^{13}C NMR ($CDCl_3$) δ 43.8, 47.3, 53.9, 55.2, 57.1, 78.4, 114.0, 124.6, 127.3, 127.7, 127.9, 128.3, 128.6, 132.0, 133.0, 137.7, 144.0, 158.7, 206.5, 206.9; HRMS m/z ($M+Na^+$) 423.1571, calc. for $C_{26}H_{24}O_4Na^+$ 423.1572.

General procedure for the organocatalytic asymmetric domino Michael-aldol reaction of phenylsulfonylacetophenone 4 with a,b-unsaturated ketones.

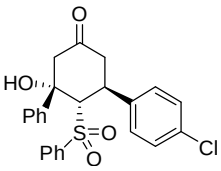
To a solution of 0.5 mmol phenylsulfonylacetophenone **4** in 1.0 mL of CH_2Cl_2 in a disposable glass test tube equipped with a magnetic stirring bar, is added 1.0 mmol of α,β-unsaturated ketone **2**, 0.05 mmol of catalyst and the mixture was stirred at ambient temperature for the time indicated in the table. The CH_2Cl_2 was evaporated and Et_2O (2 mL) was added and the precipitate was isolated by suction filtration and washed with Et_2O.



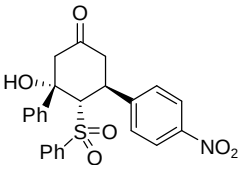
4-Benzenesulfonyl-3-hydroxy-3,5-diphenylcyclohexanone 5h. Isolated as a colorless solid, mp = 229-230 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 80/20 containing 0.3% TFA; $[\alpha]^{rt}_D$ = -22.2° (c = 1.0 g/100 mL, acetone, 96% ee); ^{1}H NMR ($CDCl_3$) δ 2.56 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.60 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.67 (dd, *J* = 16.0, 3.2 Hz, 1H), 3.16 (ddd, *J* = 15.6, 6.8, 1.6 Hz, 1H), 4.31 (ddd, *J* = 8.8, 7.6, 6.8 Hz, 1H), 4.45 (d, *J* = 8.8 Hz, 1H), 4.93 (d, *J* = 3.0 Hz, 1H, OH), 6.89 (m, 2 H), 7.06-7.11 (m, 4H), 7.16-7.13 (m, 2H), 7.24-7.19 (m, 3 H), 7.32-7.23 (m, 4 H); ^{13}C NMR ($(CD_3)_2SO$) δ 43.2, 49.3, 57.8, 73.0, 79.9, 125.1, 126.7, 127.1, 127.2, 128.2, 128.5, 128.9, 129.3, 132.7, 142.4, 143.1, 147.9, 206.2; HRMS m/z 429.1133 ($M + Na^+$), calc. for $C_{24}H_{22}O_4SNa^+$ 429.1137.



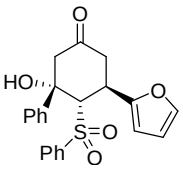
4-Benzenesulfonyl-3-hydroxy-5-naphthalen-2-yl-3-phenylcyclohexanone 5i. Isolated as a colorless solid, mp = 187-189 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 70/30 containing 0.3% TFA; $[\alpha]^{rt}_D$ = +3.2° (c = 1.0 g/100ml, acetone, 99% ee); ^{1}H NMR ($CDCl_3$) δ 2.38 (dd, *J* = 14.6, 2.4 Hz, 1H), 2.72 (ddd, *J* = 15.0, 5.6, 2.8 Hz, 1H), 2.88 (dd, *J* = 15.0, 11.2, 1H), 3.13 (dd, *J* = 14.6, 0.8 Hz, 1 H), 4.32 (ddd, *J* = 11.2, 11.2, 5.6 Hz, 1 H), 5.06 (d, *J* =11.2, 1 H), 5.45 (s, 1H, OH), 6.87 (m, 2H), 7.01 (m, 2 H), 7.32-7.22 (m, 4H), 7.58-7.49 (m, 4 H), 7.80-7.75 (m, 3H), 7.88-7.84 (m, 2 H); ^{13}C NMR ($(CD_3)_2SO$) δ 43.3 (d), 49.2, 57.9 (2 t), 72.9 (d), 79.9 (s), 125.1, 125.1, 126.4, 126.5, 126.7, 127.1, 127.3, 128.0, 128.2, 128.2, 128.2, 128.5, 132.6 (13 d), 132.6, 133.4, 139.9, 142.9, 147.7, 206.1 (6 s); HRMS m/z 479.1291 ($M + Na^+$), calc. for $C_{28}H_{24}O_4SNa^+$ 479.1293.



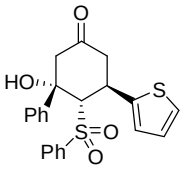
4-Benzenesulfonyl-5-(4-chlorophenyl)-3-hydroxy-3-phenylcyclohexanone 5j. Isolated as a colorless solid, mp = 218-220 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 70/30 containing 0.2% TFA; $[\alpha]^{rt}_D$ = -2.1° (c = 1.0 g/100mL, acetone, 94% ee); ^{1}H NMR ($CDCl_3$) δ 2.54 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.57 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.62 (dd, *J* = 16.0, 2.8, 1H), 3.12 (d, *J* = 15.4, 1.4 Hz, 1 H), 4.30 (ddd, *J* = 9.2, 7.2, 1.4 Hz, 1 H), 4.37 (d, *J* = 9.2 Hz, 1H), 4.91 (d, *J* = 2.8, 1H, OH), 6.94 (m, 2H), 7.16-7.13 (m, 4H), 7.21-7.18 (m, 3H), 7.24 (m, 2H), 7.33 (m, 2H), 7.40 (m, 1H); ^{13}C NMR (DMSO) δ 42.0, 48.3, 57.2, 72.1, 79.2, 124.4, 126.0, 126.3, 127.5, 127.7, 128.3, 130.6, 131.3, 132.0, 140.7, 142.3, 147.0, 205.3; HRMS m/z 463.0755 (M + Na^+), calc. for $C_{24}H_{21}ClO_4SNa^+$ 463.0747.



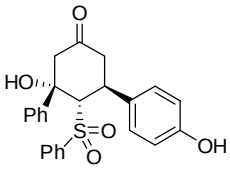
4-Benzenesulfonyl-3-hydroxy-5-(4-nitro-phenyl)-3-phenylcyclohexanone 5k. Isolated as a pale brown solid, mp = 193-196 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 70/30 containing 0.2% TFA; $[\alpha]^{rt}_D$ = +1.2° (*c* = 1.0 g/100mL, $CHCl_3$, 90%ee); ^{1}H NMR ($CDCl_3$) δ 2.54 (dd, J = 16.4, 7 Hz, 1H), 2.59 (dd, J = 16.0, 2 Hz, 1H), 2.68 (dd, J = 16.0, 3.2 Hz, 1H), 3.08 (dd, J = 16.4, 2.0 Hz, 1H), 4.43 (m, 2H), 5.01 (d, J = 3.2 Hz, 1H), 6.82 (d, J = 8 Hz, 2H), 7.02-7.12 (m, 7H), 7.33 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H); ^{13}C NMR (DMSO) δ 43.1, 48.5, 57.8, 72.3, 79.9, 123.6, 125.2, 126.8, 127.1, 128.2, 129.1, 130.7, 133.0, 142.7, 146.7, 147.3, 150.5, 205.6; HRMS m/z (M+Na^+) 474.0996, calc. for $C_{24}H_{21}NO_6SNa^+$ 474.0988.



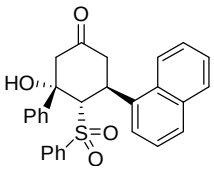
4-Benzenesulfonyl-5-furan-2-yl-3-hydroxy-3-phenylcyclohexanone 5l. Isolated as a colorless solid, mp = 213-215 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 50/50 containing 0.15 % TFA; $[\alpha]^{rt}_D$ = -5.6° (c = 1.0 g/100mL, acetone, 94 % ee); ^{1}H NMR ($CDCl_3$) δ 2.50 (d, *J* = 16.4, 1H), 2.63 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.70 (m, 1H), 3.27 (m, 1H), 4.45 (m, 2H), 4.92 (d, *J* = 2.8 Hz, 1H, OH), 6.09 (d, *J* = 3.2 Hz, 1H), 6.28 (dd, *J* = 3.2, 2.0, Hz, 1H), 7.16-7.04 (m, 5H), 7.18-7.15 (m, 4H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.36 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 32.6, 42.8, 54.1, 70.2, 77.5, 106.4, 111.2, 124.9, 127.7, 127.8, 128.6, 129.1, 133.4, 140.3, 142.2, 143.3, 155.5, 206.1; HRMS m/z 419.0932 (M + Na^+), calc. for $C_{22}H_{20}O_5SNa^+$ 419.0929.



4-Benzenesulfonyl-3-hydroxy-3-phenyl-5-thiophen-2-yl-cyclohexanone 5m. Isolated as a colorless solid, mp = 205-207 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 50/50 containing 0.3% TFA; $[\alpha]^{rt}_D$ = -9.8° (c = 1.0 g/100mL, acetone, 99% ee); ^{1}H NMR ($CDCl_3$) δ 2.53 (d, *J* = 17.2, 1H), 2.59 (dd, *J* = 17.2, 3.2 Hz, 1H), 2.81 (dd, *J* = 16.4, 4.4 Hz, 1H), 3.50 (dd, *J* = 16.4, 6.8 Hz, 1H), 4.32 (d, *J* = 6.0 Hz, 1H), 4.45 (ddd, *J* = 6.8, 6.0, 4.4 Hz, 1 H), 4.97 (d, *J* = 2.8 Hz, 1H, OH), 6.84 (d, *J* = 3.6 Hz, 1H), 6.88 (dd, *J* = 5.2, 3.6, Hz, 1H), 7.10-7.03 (m, 5H), 7.20-7.14 (m, 5H), 7.36 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.7, 44.9, 53.9, 74.5, 77.5, 124.7, 124.9, 124.9, 127.5, 127.8, 127.8, 128.7, 129.2, 133.5, 140.1, 143.2, 148.5, 206.6; HRMS m/z 435.0692 (M + Na^+), calc. for $C_{22}H_{20}O_4S_2Na^+$ 435.0701.



4-Benzenesulfonyl-3-hydroxy-5-(4-hydroxyphenyl)-3-phenylcyclohexanone 5n. Isolated as a pale brown solid, mp = 225-227 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 80/20 containing 0.2 % TFA; $[\alpha]^{rt}_D$ = -12.9° (c = 1.0 g/100mL, acetone, 98% ee); ^{1}H NMR (CD_3CN) δ 2.30 (dd, *J* = 15.0, 2.4 Hz, 1H), 2.56 (ddd, *J* = 17.2, 5.6, 2.4 Hz, 1H), 2.71 (ddd, *J* = 17.2, 11.6, 1H), 3.02 (d, *J* = 15.0 Hz, 1 H), 4.03 (ddd, *J* = 11.6, 10.8, 5.6 Hz, 1 H), 4.56 (br s, 1H, OH), 4.81 (d, *J* = 10.8 Hz, 1H), 6.07 (m, 2H), 6.95-6.92 (m, 2H), 7.12 (m, 2H), 7.24-7.19 (m, 3H), 7.31-7.26 (m, 2H), 7.43 (m, 1H), 7.52-7.47 (m, 2H); ^{13}C NMR (CD_3CN) δ 41.6, 49.1, 56.6, 72.8, 79.6, 115.4, 124.7, 127.1, 127.2, 128.4, 128.9, 129.3, 132.8, 134.0, 142.0, 145.9, 156.0, 205.1; HRMS m/z 445.1097 (M + Na^+), calc. for $C_{24}H_{22}O_5SNa^+$ 445.1086.



4-Benzenesulfonyl-3-hydroxy-5-naphthalen-1-yl-3-phenylcyclohexanone 5o. Isolated as a colorless solid, mp = 220-222 °C. The enantiomers were separated by HPLC using a Daicel Chiralpak AS chiral stationary phase in hexane/EtOH 80/20 containing 0.2% TFA; $[\alpha]^{rt}_D$ = +24.8° (c = 1.0 g/100mL, acetone, >99% ee); ^{1}H NMR ($CDCl_3$) δ 2.55 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.69 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.84 (dd, *J* = 15.6, 3.2, 1H), 3.09 (dd, *J* = 14.0, 1.2 Hz, 1 H), 4.93 (d, *J* =10.8, 1 H), 4.96 (d, *J* = 2.8, 1H, OH), 5.05 (ddd, *J* = 10.8, 9.6, 1.2 Hz, 1 H), 6.78 (m, 2H), 6.92 (m, 2 H), 7.12 (m, 1H), 7.24-7.16 (m, 3H), 7.40-7.32 (m, 4 H), 7.44 (m, 1H), 7.49 (m, 1H), 7.68 (dd, *J* = 6.8, 2.2 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($(CD_3)_2SO$) δ 35.8, 48.7, 57.3, 72.4, 79.2, 123.0, 124.6, 125.0, 125.5, 126.0, 126.1, 126.5, 127.0, 127.6, 127.6, 128.1, 128.6, 130.6, 132.1, 133.3, 138.0, 142.2, 147.0, 205.4; HRMS m/z 479.1304 (M + Na^+), calc. for $C_{28}H_{24}O_4SNa^+$ 479.1293.

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