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Supporting Information

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Biomimetic Fe-catalyzed Asymmetric Epoxidation of Aromatic Alkenes using Hydrogen Peroxide

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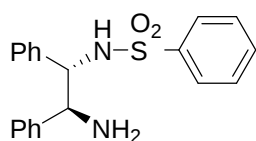
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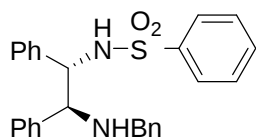
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Supporting Information



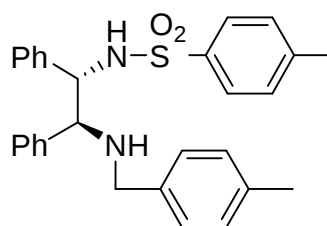
***N*-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)benzenesulfonamide:**^[33] Yield: 81%; R_f = 0.29 (*n*-hexane/ethylacetate 1:2, 1% NEt_3); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.56 (br., 2H, NH_2), 4.15 (d, J = 5.31 Hz, 1H, PhCHN), 4.43 (d, J = 5.31 Hz, 1H, PhCHN), 7.1-7.22 (m, 12H, H_{Ar}), 7.36 (tt, J = 7.47, 1.29 Hz, 1H, H_{Ar}), 7.44 (m, 2H, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 60.54 (PhCHN), 63.32 (PhCHN), 126.55, 126.85, 127.01, 127.48, 127.65, 128.31, 128.49, 128.55, 131.91, 139.15, 140.19, 141.45 ppm; IR (KBR): ν_{bar} = 3365, 3298,

3319 (s), 3030 (s), 2832, 1616, 1491, 1447, 1420, 1326 (s), 1157 (s), 1087, 1056, 918, 700, 592, 552 cm^{-1} ; HRMS (CI, isobutane, positive): m/z (%): calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$: 353.13183; found: 353.130539 (64), $[\text{M}+1]^+$; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C 68.16, H 5.72, N 7.95, S 9.10; found: C 68.21, H 5.98, N 7.77, S 9.00.



***N*-((1*S*,2*S*)-2-(benzylamino)-1,2-diphenylethyl)benzenesulfonamide:**^[33] Yield: 91%, R_f = 0.51 (*n*-hexane/ethylacetate 1:2, 6.6% NEt_3); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.72 (br., 1H, BnNH), 3.44 (d, J = 13.20 Hz, 1H, CH_2), 3.65 (d, J = 13.20 Hz, 1H, CH_2), 3.71 (d, J = 7.86 Hz, 1H, PhCHN), 4.37 (d, J = 7.77 Hz, 1H, PhCHN), 6.26 (br., 1H, SO_2NH), 6.89-7.1 (m, 7H, H_{Ar}), 7.16-7.4 (m, 11H, H_{Ar}), 7.49 (m, 2H, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 50.90, 63.17, 66.78, 127.09, 127.23, 127.44, 127.54, 127.57, 127.75, 128.01, 128.09,

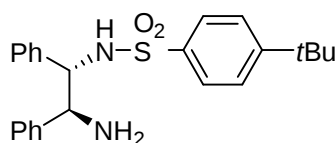
128.49, 128.52, 132.07, 138.02, 138.86, 139.38, 140.02 ppm; IR (KBR): ν_{bar} = 3439 (br), 3341, 3278 (s), 3030, 1453, 1449, 1433, 1324, 1162 (s), 700, 597, 551 cm^{-1} ; HRMS (CI, isobutane, positive): m/z (%): calcd for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$: 443.17878; found: 443.177743 (100), $[\text{M}+1]^+$; elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$: C 73.27, H 5.92, N 6.33, S 7.25; found: C 73.31, H 6.07, N 6.14, S 7.39.



4-Methyl-*N*-((1*S*,2*S*)-2-(4-methylbenzylamino)-1,2-diphenylethyl)benzenesulfonamide:

Yield: 87%; R_f = 0.67 (*n*-hexane/ethylacetate 2:1); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.66 (br, 1H, NH), 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.38 (d, J = 13.02 Hz, 1H, CH_2), 3.59 (d, J = 13.05 Hz, 1H, CH_2), 3.69 (d, J = 7.77 Hz, 1H, PhCHN), 4.31 (d, J = 7.65 Hz, 1H, PhCHN), 6.19 (br, 1H, NH), 6.91-7.19 (m, 16H, H_{Ar}), 7.37 (m, 2H, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 21.16 (CH_3), 21.47 (CH_3), 50.59 (CH_2), 63.12 (PhCHN), 66.76 (PhCHN), 127.13, 127.32, 127.55, 127.59, 127.96, 128.01, 128.43,

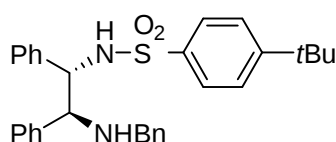
129.13, 129.17, 136.33, 136.80, 137.01, 138.32, 138.98, 142.73 ppm; IR (KBR): ν_{bar} = 3451 (br), 3345, 3063, 3028, 2928, 2852, 1454, 1437, 1334, 1327, 1160, 1096, 917, 800, 757, 700, 671, 576 cm^{-1} ; HRMS (CI, isobutane, negative): m/z (%): calcd for $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$: 469.19552; found: 469.194808 (100), $[\text{M}-1]^+$; elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_2\text{S}$: C 74.01, H 6.43, N 5.95, S 6.81; found: C 73.54, H 6.49, N 5.89, S 6.40.



N-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-4-*tert*-butylbenzenesulfonamide:

Yield: 81%; R_f = 0.44 (ethylacetate/dichloromethane 5:1); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.29 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.51 (br, 2H, NH_2), 4.14 (d, J = 5.31 Hz, 1H, PhCHN), 4.41 (d, J = 5.28 Hz, 1H, PhCHN), 6.14 (br, 1H, NH), 7.07-7.19 (m, 12H, H_{Ar}), 7.33-7.37 (m, 2H, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 31.10 ($\text{C}(\text{CH}_3)_3$), 34.94 ($\text{C}(\text{CH}_3)_3$), 60.54 (PhCHN), 63.25 (PhCHN), 125.46, 126.61, 126.75,

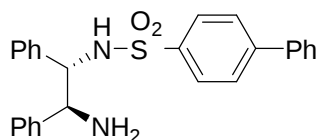
127.36, 127.03, 127.58, 128.23, 128.41, 137.04, 139.18, 141.52, 155.42 ppm; IR (KBR): ν_{bar} = 3356 (s), 3298, 3165 (br), 2962 (s), 2867, 1600, 1495, 1477, 1453, 1400, 1342, 1324 (s), 1159 (s), 1113, 1088, 1057, 1008, 895, 828, 769 (s), 699 (s), 626, 564 cm^{-1} ; HRMS (CI, isobutane, negative): m/z (%): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$: 407.17987; found: 407.178894 (100), $[\text{M}-1]^+$; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$: C 70.55, H 6.91, N 6.86, S 7.85; found: C 70.61, H 7.01, N 6.76, S 7.92.



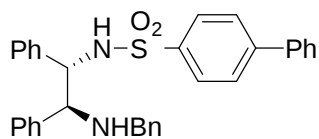
N-((1*S*,2*S*)-2-(benzylamino)-1,2-diphenylethyl)-4-*tert*-butylbenzenesulfonamide:

Yield: 85%; R_f = 0.26 (*n*-hexane/ethylacetate 4:1); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.79 (br, 1H, NH), 3.47 (d, J = 13.18 Hz, 1H, CH_2), 3.69 (d, J = 13.20 Hz, 1H, CH_2), 3.75 (d, J = 7.74 Hz, 1H, PhCHN), 4.41 (d, J = 7.61 Hz, 1H, PhCHN), 6.21 (br, 1H, NH), 6.93 (m, 2H, H_{Ar}), 6.99-7.10 (m, 5H, H_{Ar}), 7.19-7.25 (m, 7H, H_{Ar}), 7.28-7.39 (m, 3H, H_{Ar}), 7.40-7.45 (m, 2H, H_{Ar}), ppm; ^{13}C NMR (75.47

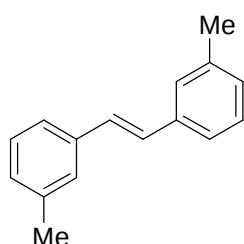
MHz, CDCl_3 , 25°C): δ = 31.08 ($\text{C}(\text{CH}_3)_3$), 34.96 ($\text{C}(\text{CH}_3)_3$), 50.90 (CH_2), 63.11 (PhCHN), 66.78 (PhCHN), 125.41, 127.01, 127.30, 127.54, 127.61, 127.68, 127.92, 128.09, 128.43, 128.51, 136.85, 138.09, 138.98, 139.43, 155.64 ppm; IR (KBR): ν_{bar} = 3441 (br), 3313, 3031, 2966 (s), 1595, 1494, 1455, 1351, 1332, 1163 (s), 1113 (s), 1087, 1027, 912, 830, 754 (s), 700 (s), 655, 567 cm^{-1} ; HRMS (CI, isobutane, negative): m/z (%): calcd for $\text{C}_{31}\text{H}_{33}\text{N}_2\text{O}_2\text{S}$: 497.22682; found: 497.225828 (32), $[\text{M}-1]^+$; elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2\text{S}$: C 74.66, H 6.87, N 5.62, S 6.43; found: C 74.66, H 7.27, N 5.55, S 6.46.



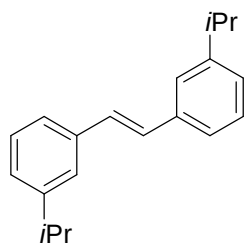
N-((1S,2S)-2-amino-1,2-diphenylethyl)biphenyl-4-sulfonamide: Yield: 88%; IR (KBR): $\bar{\nu}$ = 3440 (br), 3352, 3295, 2872, 1596, 1452, 1323, 1158 (s), 1097, 1061, 761, 699, 598 cm^{-1} ; HRMS (CI, isobutane, negative): m/z (%): calcd for $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$: 427.14857; found: 427.146865 (5), $[\text{M}-1]^+$.



N-((1S,2S)-2-(benzylamino)-1,2-diphenylethyl)biphenyl-4-sulfonamide: Yield: 84%; R_f = 0.71 (*n*-hexane:ethylacetate 2:1); ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.70 (br, 1H, NH), 3.43 (d, J = 13.2, 1H, CH_2), 3.65 (d, J = 13.2, 1H, CH_2), 3.73 (d, J = 7.59, 1H, PhCHN), 4.41 (d, J = 7.59, 1H, PhCHN), 6.25 (br, 1H, NH), 6.93-7.54 (m, 24, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 50.91 (CH_2), 63.19, 66.75, 127.14, 127.23, 127.28, 127.41, 127.57, 127.59, 127.70, 128.05, 128.09, 128.34, 128.50, 128.53, 129.02, 138.13, 138.61, 138.88, 139.37, 139.60, 144.88 ppm; IR (KBR): $\bar{\nu}$ = 3448 (br), 3308 (s), 3060, 3031, 2839, 1594, 1480, 1453, 1426, 1350, 1334, 1159 (s), 759 (s), 700(s), 676, 602, 556 cm^{-1} ; HRMS (CI, isobutane, negative): m/z (%): calcd for $\text{C}_{33}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$: 517.19552; found: 517.19391 (32), $[\text{M}-1]^+$; elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_2\text{S}$: C 76.42, H 5.83, N 5.40, S 6.18; found: C 74.88, H 5.76, N 5.25, S 6.25.

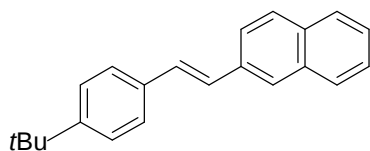


(E)-1,2-dim-tolyethene: Yield: 85%, m.p.: 63.8°C; ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 2.40 (s, 6H, CH_3), 7.10 (s, 2H, $\text{CH}=\text{CH}$), 7.10 (br, d', J = 7.02, 2H, H_{Ar}), 7.25-7.36 (m, 6H, H_{Ar}), ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 21.51 (CH_3), 123.73, 127.23, 128.43, 128.62, 137.40 (Ci), 138.25 (Ci) ppm; HRMS (EI): m/z (%): calcd for $\text{C}_{20}\text{H}_{24}$: 264.1873 $[\text{M}]^+$; found: 264.1873 (100).

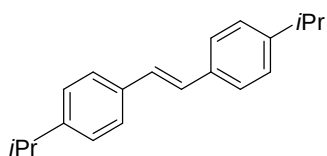


(E)-1,2-bis(3-isopropylphenyl)ethene:

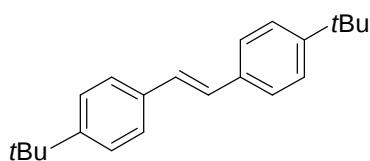
Yield: 88%; ^1H NMR (400.13 MHz, CDCl_3 , 25°C): δ = 1.30 (d, J = 6.96, 12H, CH_3), 2.94 (sept, J = 6.92, 2H, $(\text{CH}_3)_2\text{CH}$), 7.12 (s, 2H, olef), 7.14 (dt, J = 7.48, 1.2 Hz, 2H, H_{Ar}), 7.29 (t, J = 7.56 Hz, 2H, H_{Ar}), 7.35-7.38 (m, 4H, H_{Ar}) ppm; ^{13}C NMR (100.61 MHz, CDCl_3 , 25°C): δ = 24.07 (CH_3), 34.23 ($(\text{CH}_3)_2\text{C}$), 124.03, 124.81, 125.84, 128.70, 128.80, 137.49, 149.28 ppm; IR (KBR): $\bar{\nu}$ = 3024, 2959, 2926, 2869 cm^{-1} ; HRMS (EI): m/z (%): calcd for $\text{C}_{20}\text{H}_{24}$: 264.1873 $[\text{M}]^+$; found: 264.1873 (100).



(E)-2-(4-tert-butylstyryl)naphthalene: Yield: 35%; m.p.: 134°C; IR (KBR): $\bar{\nu}$ = 3853 (w), 3448 (br), 3051, 2961(sh), 2902, 2865; ^1H NMR (300.13 MHz, CDCl_3 , 25°C): δ = 1.27 (s, 9H, $2 \times \text{C}(\text{CH}_3)_3$), 7.15 (br. s, 2H, H_{olef}), 7.30-7.44 (m, 6H, H_{Ar}), 7.64-7.76 (m, 5H) ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 31.37, 34.72, 123.58, 125.73, 125.85, 126.35, 126.48, 127.75, 128.01, 128.06, 128.31, 128.90, 133.01, 133.79, 134.65, 135.09, 150.93 ppm; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{22}$: C 92.26, H 7.74; found: C 92.29, H 7.58; HRMS (EI): m/z (%): calcd for $\text{C}_{22}\text{H}_{22}$: 286.1716 $[\text{M}]^+$; found: 286.1713 (15.4).

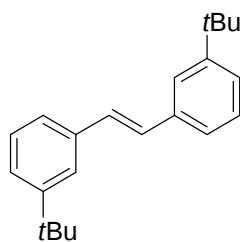


(E)-1,2-bis(4-isopropylphenyl)ethene: Yield: 95%; IR (KBR): $\bar{\nu}$ = 3448 (br), 3022, 2958 (sh); 2930, 2867, 1517, 1454, 1423, 1381, 1361, 1051 (sh), 973 (sh), 834 (sh), 564; ^1H NMR (400.13 MHz, CDCl_3 , 25°C): δ = 1.29 (d, J = 6.84 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.94 (q, J = 6.84 Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 7.08 (s, 2H, H_{olef}), 7.24 (m, 4H, H_{Ar}), 7.470 (m, 4H, H_{Ar}) ppm; ^{13}C NMR (100.61 MHz, CDCl_3 , 25°C): δ = 24.00 ($\text{CH}(\text{CH}_3)_2$), 33.95 ($\text{CH}(\text{CH}_3)_2$), 126.46, 126.78, 127.81, 135.25, 148.37 ppm; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{24}$: C 90.85, H 9.15; found: C 89.86, H 9.15; HRMS (EI): m/z (%): calcd for $\text{C}_{20}\text{H}_{24}$: 264.18660 $[\text{M}]^+$; found: 264.18725.

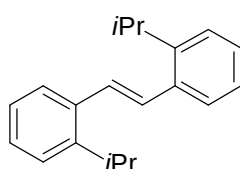


(E)-1,2-bis(4-tert-butylphenyl)ethene: Yield: 84%; ^1H NMR (400.13 MHz, CDCl_3): δ = 1.37 (s, 18H, $2 \times \text{C}(\text{CH}_3)_3$), 7.09 (s, 2H, H_{olef}), 7.39-7.43 (m, 4H, H_{Ar}), 7.46-7.50 (m, 4H, H_{Ar}) ppm; ^{13}C NMR (100.61 MHz, CDCl_3 , 25°C): δ = 31.36 ($2 \times \text{C}(\text{CH}_3)_3$), 34.66 ($(\text{CH}_3)_3\text{C}$), 125.63, 126.21, 127.79, 134.84, 150.62 ppm; IR (KBR): $\bar{\nu}$ = 3442 (br), 3087, 3028, 2951 (sh), 2903, 2866, 1520, 1511, 1463, 1365, 1269, 1115, 969, 835, 826, 567 cm^{-1} ; GC-MS (EI): m/z (%): calcd for $\text{C}_{22}\text{H}_{28}$:

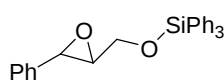
292.22 [M]⁺; found: 292.20 [M]⁺, 277.20 [M-CH₃]⁺; elemental analysis calcd (%) for C₂₂H₂₈: C 90.35, H 9.65; found: C 89.62, H 9.83.



(E)-1,2-bis(3-tert-butylphenyl)ethene: Yield: 85%; m.p.: 122.4°C; ¹H NMR (400.13 MHz, CDCl₃, 25°C): δ = 1.38 (s, 18H, 2×C(CH₃)₃), 7.15 (s, 2H, H_{olef}), 7.31-7.35 (m, 4H, H_{Ar}), 7.36-7.42 (m, 2H, H_{Ar}), 7.54-7.5 (br. m, 2H, H_{Ar}), ppm; ¹³C NMR (100.61 MHz, CDCl₃, 25°C): δ = 31.41 (2×C(CH₃)₃), 31.75 (2×(CH₃)₂C), 123.47, 123.84, 124.73, 128.42, 128.96, 137.18, 151.51 ppm; IR (KBR): ν_{bar} = 3886, 3443 (br), 3058, 3027, 2962(sh); 2900, 2867; 1598, 1581, 1360, 1216, 961, 889 796, 697 cm⁻¹; HRMS (EI): *m/z* (%): calcd for C₂₂H₂₈: 292.21848 [M]⁺; found: 292.21855 (100); elemental analysis calcd (%) for C₂₂H₂₈: C 90.35, H 9.65; found: C 89.89, H 9.72.

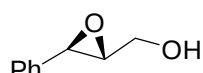


(E)-1,2-bis(2-isopropylphenyl)ethene: Yield: 91%; ¹H NMR (300.13 MHz, CDCl₃, 25°C): δ = 1.27 (d, *J* = 9.2 Hz, 12H, CH₃), 3.34 (m, 2H, (CH₃)₂CH), 7.55 (m, 2H, Ar), 6.83-7.33 (m, 8H, H_{Ar}+H_{olef}) ppm; ¹³C NMR (75.46 MHz, CDCl₃, 25°C): δ = 23.48 (CH₃), 29.33 (CH₃)₂C, 125.05, 125.98, 126.44, 127.90, 128.80, 136.18, 146.25 ppm; IR (KBR): ν_{bar} = 3406, 3062, 2962, 2927, 2869, 1599, 1487, 1448, 1383, 1363, 1080, 1035, 963, 755, 526 cm⁻¹; HRMS (EI): *m/z* (%): calcd for C₂₀H₂₄O: 264.1873 [M]⁺; found: 264.1875 (100).



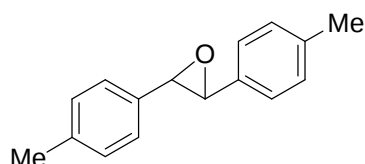
((trans-3-phenyloxiran-2-yl)methoxy)triphenylsilane: Yield: 82%; m.p.: 57.8°C; ¹H NMR (300.13 MHz, CDCl₃, 25°C): δ = 3.22 (m, 1H, CH₂CHO), 3.76 (d, *J* = 2.1 Hz, 1H, PhCHO), 3.99 (dd, *J* = 11.8, 4.3 Hz, 1H, CHOSi), 4.05 (dd, *J* = 11.8, 3.6 Hz, 1H, CHOSi), 7.19-7.48 (m, 15H, Ph), 7.61-7.67 (m, 5H, Ph) ppm. ¹³C NMR (75.47 MHz, CDCl₃, 25°C): δ = 56.26 (CHO), 62.40 (CHO), 63.78 (CH₂), 125.76, 128.04, 128.21, 128.48, 128.59, 130.28, 133.68, 135.04, 135.48, 137.08 ppm; IR (KBR): ν_{bar} = 3431(br), 3064, 3006, 2975, 2899, 2861, 1969(w), 1899(w), 1588, 1428 (sh), 1134, 1118 (sh), 962, 712, 699, 515 cm⁻¹; MS (CI, isobutene, positive): *m/z* (%): calcd for C₂₇H₂₄O₂Si+H: 409.15 [M+H]⁺; found: 409.20. HPLC (Reposil 100: *n*-hexane: EtOH: 98:2 (v/v), flow: 1.0 mL/min): *t*_R 8.86 min, 13.22 min.

(+)-((2R,3R)-trans-3-phenyloxiran-2-yl)triphenylsilane:^[33] Yield: 67%; [α]_D²⁵ = +16.4 (*c* = 0.518 in CH₂Cl₂); ee 35%; ¹H NMR, ¹³C NMR: as above.



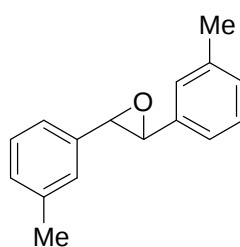
(+)-((2R,3R)-trans-3-phenyloxiran-2-yl)methanol:

This product was obtained after desilylation of (+)-((2R,3R)-3-phenyloxiran-2-yl)triphenylsilane of 35% ee with tetrabutyl ammonium fluoride in THF at 0°C: Yield: 84%; [α]_D²⁵ = +21.2 (*c* = 0.89 in CH₂Cl₂); ¹H NMR, ¹³C NMR: As reported.^[34]



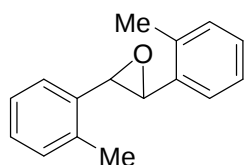
trans-2,3-Dip-tolyloxirane: Yield: 71%; ¹H NMR (300.13 MHz, CD₂Cl₂, 25°C): δ 2.36 (s, 6H, 2×CH₃), 3.83 (s, 2H, OCH), 7.18-7.25 (m, 8H, H_{Ar}). ¹³C NMR (75.47 MHz, CD₂Cl₂, 25°C): δ = 21.31, 62.98, 125.82, 129.55, 134.75, 138.57 ppm; HRMS (EI): *m/z* (%): calcd for C₁₆H₁₆O: 224.11957 [M]⁺; found: 224.11954 (7). HPLC (Reposil 100: *n*-hexane: EtOH: 98:2 (v/v), flow: 1.0 mL/min): *t*_R 6.48 min, 16.55 min.

(+)-((2R,3R)-trans-2,3-dip-tolyloxirane:^[33] Yield: 92%; m.p.: 111.5°C; [α]_D²⁵ = +182 (*c* = 0.45 in CH₂Cl₂), ee 64%; ¹H NMR, ¹³C NMR, HRMS: as above.



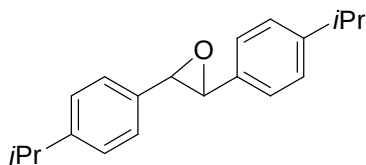
trans-2,3-Dim-tolyloxirane: Yield: 96%; ¹H NMR, ¹³C NMR: as reported;^[35] IR (KBR): ν_{bar} = 3424, 3029, 2981, 2921, 1726, 1609, 1592, 1490, 1459, 1379, 1334, 1281, 863, 784, 764, 698, 625, 442cm⁻¹; HRMS (EI): *m/z* (%): calcd for C₁₆H₁₆O: 224.1196 [M]⁺; found: 224.1197 (100). HPLC (Reposil 100: *n*-hexane/ EtOH 98:2, flow: 1.0 mL/min): *t*_R 6.06 min, 13.70 min.

(+)-trans-2,3-Dim-tolyloxirane:^[33] Yield: 88%; [α]_D²⁵ = +71 (*c* = 0.53 in CH₂Cl₂); ee 27%; ¹H NMR, ¹³C NMR: as reported.^[35]



trans-2,3-Dio-tolyloxirane: Yield: 74%; ^1H NMR, ^{13}C NMR: as reported;^[35] IR (KBR): $\nu_{\text{bar}} = 3440$ (br), 3102, 3065, 3028, 2945, 1955, 1920, 1488, 1457, 1436, 1387, 1338, 1284, 1108, 1040, 942, 888, 868, 752, 723, 618, 550, 451 cm^{-1} ; HPLC (Reposil 100: *n*-hexane/ EtOH 98:2), flow: 1.0 mL/ min): t_{R} 5.02 min, 7.47 min.

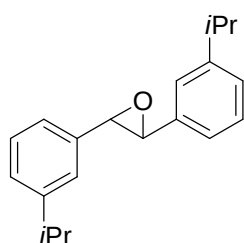
(-)-trans-2,3-dio-tolyloxirane:^[33] Yield: 57% (NMR, int. standard: *cis*-stilbene); ee 54%; ^1H NMR, ^{13}C NMR: as reported.^[33]



trans-2,3-bis(4-isopropylphenyl)oxirane: Yield: 91%; ^1H NMR (300.13 MHz, CDCl_3 , 25°C): $\delta = 1.18$ (d, $J = 6.90$ Hz, 12H, $2 \times \text{CH}(\text{CH}_3)_2$), 2.85 (q, $J = 6.90$ Hz, 2H, $2 \times \text{CH}(\text{CH}_3)_2$), 3.77 (s, 2H, OCH), 7.14-7.21 (m, 8H, H_{Ar}) ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): $\delta = 24.03$, 33.97, 62.80, 125.00, 125.55, 134.71, 149.17 ppm; IR (KBR): $\nu_{\text{bar}} = 3443$, 2954, 2868, 1913, 1515, 1458, 1439, 1418, 1055, 1018, 851, 841, 820, 708, 590 cm^{-1} ; HRMS (EI): m/z (%): calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: 280.18217 $[\text{M}]^+$; found: 280.18215 (20); HPLC (Reposil 100: *n*-hexane/EtOH 98:2,

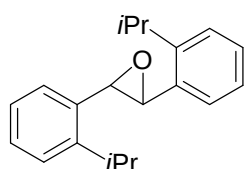
flow: 1.0 mL/ min): t_{R} 5.52 min, 14.16 min.

(+)-(2R,3R)-trans-2,3-bis(4-isopropylphenyl)oxirane:^[33] Yield: 90%; ee 71%; ^1H NMR, ^{13}C NMR, HRMS: as above.

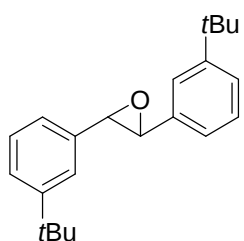


trans-2,3-bis(3-isopropylphenyl)oxirane: Yield: 90%; HRMS (EI): m/z (%): calcd. for $\text{C}_{20}\text{H}_{24}\text{O}$: 280.18199 $[\text{M}]^+$; found: 280.18217; IR (KBR): $\nu_{\text{bar}} = 3407$, 2960, 2926, 2869, 1728, 1608, 1488, 1464, 1383, 1363, 1372, 864, 792, 703 cm^{-1} ; HPLC (ChiralPak AD-H: *n*-hexane/EtOH 98:2, flow: 1.0 mL/ min): t_{R} 3.90 min, 7.51 min.

(+)-trans-2,3-bis(3-isopropylphenyl)oxirane:^[33] Yield: 87%, $[\alpha]_{\text{D}}^{25} = +31$ ($c = 0.675$ in CH_2Cl_2), ee 12%; ^1H NMR, ^{13}C NMR, HRMS: data as above.

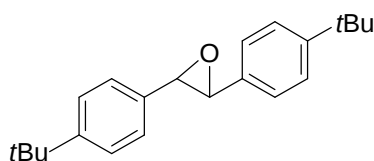


trans-2,3-bis(2-isopropylphenyl)oxirane: Yield: 92%; IR (KBR): $\nu_{\text{bar}} = 3445$ (br), 3061, 2963, 2925, 2867 (w), 1488, 1448, 1383, 1363, 1035, 890, 867, 766 (sh), 732, 617 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{24}\text{O}$: C 85.67, H 8.63; found: C 85.36, H 7.92; HRMS (EI): m/z (%): calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: 280.18211 $[\text{M}]^+$; found: 280.18217.



trans-2,3-bis(3-tert-butylphenyl)oxirane: Yield: 76%; ^1H NMR (300.13 MHz, CD_2Cl_2 , 25°C): $\delta = 1.25$ (s, 18H, $2 \times (\text{CH}_3)_3$), 3.78 (s, 2H, $2 \times \text{OCH}$), 7.07 (dt, $J = 7.36$, 1.54 Hz, 2H, H_{Ar}), 7.20-7.30 (m, 6H, H_{Ar}) ppm; ^{13}C NMR (75.46 MHz, CDCl_3 , 25°C): $\delta = 31.44$ ($2 \times (\text{CH}_3)_3$), 35.00 ($2 \times (\text{CH}_3)_2\text{C}$), 63.42, 122.83, 122.98, 125.72, 128.63, 137.36, 152.00 ppm; IR (KBR): $\nu_{\text{bar}} = 3435$ (br), 3062, 2963, 2868, 1948 (w), 1727, 1606, 1489, 1365, 798, 704 cm^{-1} ; HRMS (EI): m/z (%): calcd for $\text{C}_{22}\text{H}_{28}\text{O}$: 308.2125 $[\text{M}]^+$; found: 308.2134 $[\text{M}]^+$; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{28}\text{O}$: C 85.66, H 9.15; found: C 85.15, H 10.10; HPLC (Reposil 100: *n*-hexane/EtOH 98:2, flow: 1.0 mL/ min): t_{R} 7.20 min, 17.36 min.

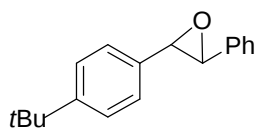
(-)-trans-2,3-bis(3-tert-butylphenyl)oxirane:^[33] Yield: 66%; $[\alpha]_{\text{D}}^{25} = -22.5$ ($c = 0.4$ in CH_2Cl_2), ee 10%; ^1H NMR, ^{13}C NMR, HRMS: as above.



trans-2,3-bis(4-tert-butylphenyl)oxirane: Yield: 91%; ^1H NMR (300.13 MHz, CDCl_3 , 25°C): $\delta = 1.33$ (s, 18H, $2 \times \text{C}(\text{CH}_3)_3$), 3.85 (s, 2H, OCH), 7.25-7.29 (m, 4H, H_{Ar}), 7.39-7.43 (m, 4H, H_{Ar}) ppm; ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): $\delta = 31.38$ ($2 \times \text{C}(\text{CH}_3)_3$), 34.68 ($2 \times \text{C}(\text{CH}_3)_3$), 62.83 (OCH), 125.29, 125.53, 134.35, 151.41 ppm; IR (KBR): $\nu_{\text{bar}} = 3441$ (br), 2961, 2902, 2866, 1911, 1615, 1516, 1474, 1460, 1364, 1268, 1202, 1110, 1017, 881, 859, 834, 818, 738, 682, 564 cm^{-1}

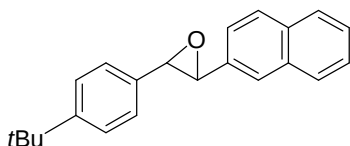
1 ; HRMS (EI): m/z (%): calcd for $\text{C}_{22}\text{H}_{28}\text{O}$: 308.2134 $[\text{M}]^+$; found: 308.2129 (100); HPLC (ChiralPak-AD-H: *n*-hexane/EtOH 98:2, flow: 1.0 mL/ min): t_{R} 2.56 min, 3.76 min.

(+)-(2R,3R)-trans-2,3-bis(4-tert-butylphenyl)oxirane:^[33] Yield: 82%; $[\alpha]_D^{25} = +172$ ($c = 0.715$ in CH_2Cl_2), ee 81%. ^1H NMR, ^{13}C NMR, HRMS: as above.



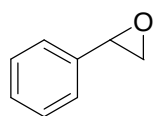
trans-2-(4-tert-butylphenyl)-3-phenyloxirane: Yield: 96%; ^1H NMR (400.13 MHz, CD_2Cl_2 , 25°C): δ 1.34 (s, 9H, $(\text{CH}_3)_3$), 3.85 (d, 1.88 Hz, 1H, OCH), 3.88 (d, 1.84 Hz, 1H, OCH), 7.27–7.44 (m, 9H, H_{Ar}). ^{13}C NMR (75.47 MHz, CDCl_3 , 25°C): δ = 31.39, 34.70, 62.77, 62.87, 125.34, 125.53, 125.57, 128.29, 128.60, 134.20, 137.33, 151.53 ppm; IR (KBR): ν_{bar} = 3853, 3063, 2963, 2360, 1604, 1519, 1459, 1429, 1364, 1269, 1107, 1070, 1027, 878, 837, 792, 699, 619, 563, 509 cm^{-1} ; HRMS (EI): m/z (%): calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: 252.1509 $[\text{M}]^+$; found: 252.1515 (100); HPLC (Whelk-O1-(S,S): hexane/EtOH 98:2, flow: 1.0 mL/min): t_R 2.70 min, 3.99 min.

(+)-(R,R)-trans-2-(4-tert-butylphenyl)-3-phenyloxirane: Yield: 91%; $[\alpha]_D^{25} = +134$ ($c = 0.58$ in CH_2Cl_2), ee 53%; ^1H NMR, ^{13}C NMR, HRMS: as above.

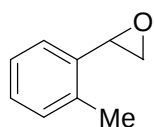


trans-2-(4-tert-butylphenyl)-3-(naphthalen-2-yl)oxirane: Yield: 92%; m.p.: 115.6°C ; ^1H NMR (300.13 MHz, CD_2Cl_2 , 25°C): δ = 1.34 (s, 9H, $(\text{CH}_3)_3$), 3.96 (d, 1.83 Hz, 1H, OCH), 4.05 (d, 1.83 Hz, 1H, OCH), 7.29–7.33 (m, 2H), 7.41–7.54 (m, 5H), 7.83–7.89 (m, 4H) ppm; ^{13}C NMR (75.47 MHz, CD_2Cl_2 , 25°C): δ = 31.45, 34.92, 63.13, 63.15, 123.26, 125.29, 125.68, 125.88, 126.48, 126.76, 128.09, 128.14, 128.67, 133.59, 133.72, 134.59, 135.31, 151.97 ppm; IR (KBR): ν_{bar} = 3433, 3055, 2965, 2903, 2866, 1515, 1461, 1360, 1268, 1223, 1108, 967, 897, 862, 830, 818, 750.577, 483 cm^{-1} ; HRMS (EI): m/z (%): calcd for $\text{C}_{22}\text{H}_{22}\text{O}$: 302.16652 $[\text{M}]^+$; found: 302.16739 (40); HPLC (Reposil 100, *n*-hexane/EtOH 98:2, flow: 1.0 mL/min): t_R 8.83 min, 25.28 min).

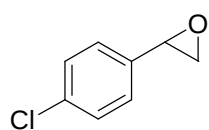
(+)-(2R,3R)-trans-2-(4-tert-butylphenyl)-3-(naphthalen-2-yl)oxirane:^[33] Method 1 (rt): yield: 46%; ee 91%. Method 2 (10°C): yield: 40%; $[\alpha]_D^{25} = +275$ ($c = 0.209$ in CH_2Cl_2); ee 97%; ^1H NMR, ^{13}C NMR, HRMS: as above.



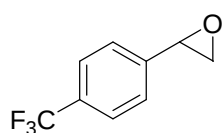
Phenyloxirane: ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 2.72 (dd, $J = 5.6, 2.6$ Hz, 1H), 3.06 (dd, $J = 5.6, 4.2$ Hz, 1H), 3.78 (dd, $J = 4.2, 2.6$ Hz, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 51.3, 52.5, 125.6, 128.3, 128.6, 137.7; MS (70 eV): m/z (%): 120 (M^+ , 41), 119 (65), 92 (37), 91 (100), 90 (64), 89 (79); HPLC (Chiralcel OD-H, hexane/EtOH 99.95:0.05, flow: 0.5 mL/min): t_R 6.27 min, 7.13 min.



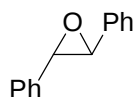
2-Tolyloxirane: ^1H NMR (400 MHz, CD_2Cl_2 , 25°C): δ = 7.14–7.22 (m, 4H), 3.98 (dd, $J = 3.97, 2.58$ Hz, 1H), 3.13 (dd, $J = 5.75, 3.97$ Hz, 1H), 2.65 (dd, $J = 5.75, 2.58$ Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25°C): δ = 136.4, 136.2, 129.8, 127.6, 126, 124, 50.3, 50.1; MS (70 eV): m/z (%): 134 (M^+ , 53), 119 (44), 118 (42), 117 (64), 105 (100), 103 (48), 91 (52), 78 (33), 77 (35); HPLC (Chiralpak AD-H, hexane/EtOH, 99.95:0.05, flow: 1.5 mL/min): t_R 16.70 min, 19.84 min.



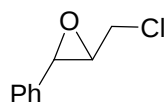
4-Chlorophenyloxirane: ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 2.68 (dd, $J = 5.6, 2.6$ Hz, 1H), 3.07 (dd, $J = 5.6, 4.0$ Hz, 1H), 3.76 (dd, $J = 4.0, 2.6$ Hz, 1H), 7.12–7.26 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25°C): δ = 51.4, 51.9, 127.0, 128.8, 134.1, 136.3; MS (70 eV): m/z (%): 156 ($\text{M}^+ + 2$, 9), 155 ($\text{M}^+ + 1$, 10), 154 (M^+ , 28), 153 ($\text{M}^+ - 1$, 23), 125 (53), 119 (74), 89 (106); HPLC (Chiralcel OB-H, hexane, flow: 1.0 mL/min): t_R 14.47 min, 17.18 min.



4-Trifluoromethylphenyloxirane: ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 2.77 (dd, $J = 5.6, 2.6$ Hz, 1H), 3.19 (dd, $J = 5.6, 4.0$ Hz, 1H), 3.92 (dd, $J = 4.0, 2.6$ Hz, 1H), 7.4 (d, $J = 8.1$ Hz, 2H), 7.6 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 51.4, 51.6, 125.4 (q, $J = 3.8$), 125.9, 141.9; MS (70 eV): m/z (%): 188 (M^+ , 14), 187 (20), 159 (49), 158 (48), 119 (100), 91 (37); HPLC (Chiralcel AD-151, hexane, flow: 0.5 mL/min): t_R 12.30 min, 13.40 min.



trans-2,3-Diphenyloxirane: ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.24–7.31 (m, 10H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 137.1, 128.6, 128.6, 125.5, 62.8; MS (70 eV): m/z (%): 197 ($\text{M}^+ + 1$, 18), 196 (M^+ , 100), 195 (72), 178 (28), 167 (85), 90 (66), 89 (65); HPLC (Chiralcel OD-H, hexane/EtOH, 98:2, flow: 0.5 mL/min): t_R 14.10 min, 4.79 min.



trans-2-Chloromethyl-3-phenyloxirane: ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 3.28 (ddd, $J = 5.8, 4.8, 1.9$ Hz, 1H), 3.66 (dd, $J = 11.8, 5.8$ Hz, 1H), 3.72 (dd, $J = 11.8, 4.8$ Hz, 1H), 3.82 (d, $J = 1.9$ Hz, 1H), 7.26–7.38 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 44.3, 58.5, 60.9, 116.6, 125.6, 128.6, 135.9; GC-MS (70 eV): m/z (%): 168 (M^+); HPLC (Chiralpak AD-H, hexane/EtOH, 95:5, flow: 1.0 mL/min): t_R 7.62 min, 9.09 min.

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- [33] For additional information on synthesis, asymmetric epoxidation conditions and/or results see ref. [17].
- [34] S. K. Cherian, P. Kumar *Tetrahedron: Asymmetry* **2007**, *18*, 982–987.
- [35] S. Florio; V. Aggarwal; A. Salomone *Org. Lett.* **2004**, *23*, 4191–4194.