Expanded Chiral Surfaces for Asymmetric Anion-π Catalysis

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Supplementary Information

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1. Material and Methods

As in reference S1–S4. Reagents for synthesis were purchased from Sigma-Aldrich, Fluka, Acros, Apollo Scientific and Bachem. All reactions were performed under N\textsubscript{2} or Ar atmosphere. Unless stated otherwise, column chromatography was carried out on silica gel 60 (SiliaFlash P60, 40-63 µm). Analytical (TLC) and preparative thin layer chromatography (PTLC) were performed on silica gel 60 (Merck, 0.2 mm) and silica gel GF (SiliCycle, 1 mm), respectively. Chiral HPLC were performed on a LC-4000 from JASCO. Melting points (Mp) were measured on a Melting Point M-565 (BUCHI). \([\alpha]^{20}_D\) values were recorded on a Jasco P-1030 Polarimeter. Circular dichroism spectra were obtained using JASCO J-815 spectropolarimeter and are reported as extremum wavelength \(\lambda\) in nm (\(\Delta\varepsilon\) in M\(^{-1}\)cm\(^{-1}\)). IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumbers \(n\) in cm\(^{-1}\) with band intensities indicated as s (strong), m (medium), w (weak). \(^1\)H and \(^{13}\)C spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (d) in ppm relative to TMS \((\delta = 0)\). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t) and quartet (q) with coupling constants \((J)\) given in Hz, or multiplet (m). Broad peaks are marked as br. \(^1\)H and \(^{13}\)C resonances were assigned with the aid of additional information from 1D and 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). ESI-MS were performed on a ESI API 150EX and are reported as \(m/z\) (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar mass spectrometer. A microwave reaction was performed on a Biotage Initiator+ Microwave System w. Robot Sixty.

**Abbreviations.** DMF: \(N,N\)-Dimethylformamide; mCPBA: 3-Chloroperbenzoic acid; rt: Room temperature; TEA: Triethylamine; TFA: Trifluoroacetic acid.
2. Catalyst Synthesis

2.1. NDI Catalyst with Sulfide Core Substituent

Scheme S1. Reagents and conditions: (a) thiophenol, K₂CO₃, CHCl₃, 85 °C, 12 h, 96%; (b) 1. KOH, i-PrOH/water, 85 °C, overnight, 2. AcOH, 85 °C, overnight (2 steps 86%); (c) TEA, DMF, µW, 145 °C, 30 min, 32%; (d) TFA, CH₂Cl₂, rt, 2 h, quantitative.

**Compound 10.** This compound was prepared following the literature procedure.⁵⁵

**Compound 11.** This compound was prepared following the literature procedure.⁵⁶

**Compound 12.** This compound was prepared following the literature procedure.⁵³

**Compound 13.** To a solution of 10 (0.574 g, 1.00 mmol) in CHCl₃ (26 mL), potassium carbonate (2.5 g, 18 mmol), thiophenol (3.85 g, 35.0 mmol) and catalytic amount of 18-crown-6-ether were added. The mixture was then stirred for 12 h at 85 °C in a pressure-tight vessel. The resulting mixture was subjected to liquid/liquid extraction with saturated NaHCO₃ aqueous solution (30 mL), dried over anhydrous Na₂SO₄, and
then the solvent was removed under reduced pressure. Silica gel column chromatography of the residue (pentane/EtOAc 9:1 then to 6:1; $R_f$ (pentane/EtOAc 9:1): 0.18) gave 13 (0.606 g, 96%) as a yellow solid. Mp: 164 – 165 °C; IR (neat): 2982 (m), 1714 (s), 1554 (m), 1466 (m), 1439 (m), 1401 (m), 1382 (m), 1322 (w), 1270 (m), 1244 (s), 1177 (s), 1161 (s), 1139 (s), 1023 (m), 912 (m), 884 (m), 854 (m), 804 (m), 772 (m), 747 (m), 687 (m), 652 (m), 600 (m), 576 (m); $^1$H NMR (400 MHz, CDCl$_3$): 7.52 – 7.45 (m, 6H), 7.42 – 7.36 (m, 6H), 4.34 (q, $^3J$ (H,H) = 7.2 Hz, 4H), 4.20 (q, $^3J$ (H,H) = 7.2 Hz, 4H), 1.38 (t, $^3J$ (H,H) = 7.2 Hz, 6H), 1.20 (t, $^3J$ (H,H) = 7.2 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): 167.3 (C), 166.9 (C), 138.3 (C), 134.2 (CH), 132.8 (C), 131.9 (C), 130.9 (CH), 130.6 (C), 129.8 (CH), 129.0 (CH), 127.4 (C), 61.9 (CH$_2$), 61.6 (CH$_2$), 14.0 (CH$_3$), 13.9 (CH$_3$); MS (ESI, CH$_2$Cl$_2$/MeOH 1:1): 587 (100, [M-OC$_2$H$_5$]+); HRMS (ESI, +ve) calcd for C$_{34}$H$_{32}$O$_8$S$_2$ ([M-OC$_2$H$_5$]+): 587.1193, found: 587.1192.

**Compound 14.** To a solution of 13 (0.316 g, 0.499 mmol) in isopropanol (20 mL) and water (20 mL), potassium hydroxide (0.84 g, 15 mmol) was added. The mixture was then stirred for 16 h at 85 °C. The resulting mixture was concentrated in vacuo, and then glacial acetic acid (20 mL) was added. The mixture was stirred for 20 h at 85 °C. A formed precipitate was filtrated, and then washed with the glacial acetic (60 mL) and water (60 mL), and red solid was obtained (0.209 g, 86%). The product was insoluble in common organic solvents. It was used in the next step without further purification. IR (neat): 2987 (w), 1766 (m), 1723 (s), 1557 (m), 1472 (m), 1441 (m), 1411 (m), 1383 (m), 1327 (w), 1268 (s), 1180 (s), 1139 (s), 1091 (m), 1054 (m), 1034 (m), 981 (m), 914 (w), 897 (w), 857 (w), 774 (m), 748 (s), 688 (m), 647 (w), 623 (w), 585 (w), 553 (w), 568 (w).

**Compound 15.** To a solution of 14 (0.540 g, 1.11 mmol) in DMF (45 mL), 11 (0.270 g, 0.945 mmol) was added. The mixture was then heated for 5 min at 45 °C, and then for 15 min at 145 °C with a microwave reactor. Then, 12 (0.346 g, 1.11 mmol) and triethylamine (0.78 mL, 5.6 mmol) were added to the reaction mixture, and then the mixture was heated for 15 min at 145 °C with the microwave reactor. The solvent was removed under reduced pressure. Silica gel column chromatography of the residue (CH$_2$Cl$_2$/EtOAc 6:1; $R_f$ (CH$_2$Cl$_2$/EtOAc 6:1): 0.30) gave 15 (0.377 g, 32%) as a red solid. Mp: 130 – 131 °C; IR (neat): 3408 (w), 2929 (m), 2861 (m), 1693 (s), 1650 (s), 1615 (s), 1571 (s), 1471 (m), 1455 (s), 1399 (s), 1340 (m), 1298 (m), 1272 (s), 1198 (s), 1167 (s), 1097 (m), 1034 (m), 764 (m), 721 (m), 684 (m), 647 (m).
1548 (m), 1518 (m), 1475 (m), 1438 (m), 1389 (m), 1367 (m), 1311 (m), 1275 (w),
1236 (s), 1214 (s), 1157 (s), 1123 (w), 1023 (w), 1001 (w), 949 (w), 917 (w), 855 (w),
790 (w), 747 (m), 732 (w), 690 (w), 653 (w), 629 (w), 616 (w), 589 (w), 556 (w);
$^1$H NMR (400 MHz, CDCl$_3$): 8.26 – 7.99 (m, 2H), 7.76 – 7.51 (m, 10H), 6.10 (t, $^3$$J$
(H,H) = 5.4 Hz, 1H), 5.68 – 5.55 (m, 1H), 5.00 – 4.66 (m, 2H), 4.04 – 3.87 (m, 1H),
3.39 – 3.16 (m, 3H), 2.99 – 2.72 (m, 1H), 2.61 – 2.44 (m, 1H), 2.29 – 2.24 (m, 1H),
2.19 – 2.01 (m, 1H), 1.97 – 1.73 (m, 3H), 1.66 – 1.57 (m, 2H), 1.56 – 1.45 (m, 4H), 1.43
– 1.34 (m, 18H), 1.33 – 1.23 (m, 10H), 0.86 (t, $^3$$J$(H,H) = 6.2 Hz, 3H); $^{13}$C NMR (101
MHz, CDCl$_3$): 172.1 (C), 168.2 (C), 164.9 (C), 163.7 (C), 163.6 (C), 163.5 (C), 163.3
(C), 162.1 (C), 150.4 (C), 163.8 (CH), 135.9 (CH), 130.7 (CH), 130.6 (CH), 130.4
(CH), 130.2 (CH), 130.0 (CH), 129.8 (CH), 129.6 (CH), 125.4 (C), 125.3 (C), 123.7 (C), 123.3 (C), 117.6 (C), 81.0 (C), 80.4 (C), 58.2 (CH), 57.6 (CH), 54.8 (CH), 48.2 (CH), 48.0 (CH), 47.0 (CH$_2$), 46.8 (CH$_2$), 40.0 (CH$_2$), 33.5 (CH$_2$), 32.6
(CH$_2$), 31.5 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 28.3 (CH$_3$), 28.0 (CH$_3$), 27.9 (CH$_2$), 26.5
(CH$_2$), 24.5 (CH$_2$), 24.0 (CH$_2$), 22.5 (CH$_2$), 14.0 (CH$_3$); MS (ESI, CH$_2$Cl$_2$/MeOH 1:1):
1046 (58, [M+H]+), 946 (100, [M-Boc+H]+); HRMS (ESI, +ve) calcd for
C$_{57}$H$_{67}$N$_5$O$_{10}$S$_2$ ([M+H]+): 1046.4402, found: 1046.4402.

Compound 7. A solution of 15 (20 mg, 0.019 mmol) in TFA (1 mL) and
CH$_2$Cl$_2$ (1 mL) was stirred for 2 h at rt. The mixture was concentrated and dried in
vacuo to afford pure 7 (TFA salt, quantitative) as a red solid. Mp: decomp. >190 °C; IR
(neat): 3070 (m), 2932 (m), 2860 (m), 1651 (s), 1549 (s), 1437 (s), 1376 (s), 1311 (s),
1235 (s), 1202 (s), 1129 (s), 1023 (w), 1000 (w), 918 (w), 893 (w), 832 (w), 791 (m),
750 (m), 721 (m), 703 (m), 691 (m), 648 (w), 630 (w), 566 (w); $^1$H NMR (400 MHz,
CD$_3$OD): 8.05 (s, 2H), 7.68 – 7.58 (m, 10H), 5.57 (dd, $^3$$J$(H,H) = 9.7 Hz, $^3$$J$(H,H) =
4.6 Hz, 1H), 5.12 – 4.89 (m, 2H), 4.82 – 4.71 (m, 1H), 3.88 (br s, 1H), 3.28 – 3.04 (m, 4H),
2.65 – 2.47 (m, 2H), 2.48 – 2.19 (m, 4H), 2.11 – 1.95 (m, 1H), 1.95 – 1.72 (m, 6H), 1.53
– 1.38 (m, 5H), 1.33 – 1.22 (m, 6H), 0.86 (t, $^3$$J$(H,H) = 6.5 Hz, 3H); $^{13}$C NMR (101
MHz, CD$_3$OD): 175.1 (C), 170.0 (C), 169.9 (C), 167.8 (C), 164.1 (C), 162.3 (C), 149.2
(C), 135.7 (CH), 135.6 (CH), 130.4 (CH), 130.3 (CH), 129.3 (CH), 128.9 (CH), 125.3
(C), 125.2 (C), 59.4 (CH), 56.5 (CH), 54.2 (CH), 49.1 (CH), 45.8 (CH$_2$), 39.6 (CH$_2$),
39.5 (CH$_2$), 32.4 (CH$_2$), 31.4 (CH$_2$), 30.6 (CH$_2$), 29.9 (CH$_2$), 28.9 (CH$_2$), 28.0 (CH$_2$),
27.8 (CH$_2$), 25.3 (CH$_2$), 24.5 (CH$_2$), 23.2 (CH$_2$), 22.3 (CH$_2$), 13.1 (CH$_3$); MS (ESI,
CH₂Cl₂/MeOH 1:1): 891 (100, [M+H]+); HRMS (ESI, +ve) calcd for C₄₈H₅₉O₈N₅S₂ ([M+H]+): 890.3252, found: 890.3251.

2.2. NDI Catalysts with Chiral Sulfoxide and Sulfone Core Substituents

Scheme S2. Reagents and conditions: (a) mCPBA, CH₂Cl₂, 0 °C, 7 h, 67%; (b) stereoisomers were separated by flash column chromatography and semi-preparative HPLC (CHIRALPAK ID, 250 mm x 10 mm, Daicel); (c) TFA, CH₂Cl₂, rt, 2 h, quantitative; (d) mCPBA, CH₂Cl₂, rt, overnight, 64%; (e) TFA, CH₂Cl₂, rt, 2 h, quantitative.

**Compound (Fn)-16.** To a solution of 15 (50 mg, 0.048 mmol) in CH₂Cl₂ (25 mL), mCPBA (23 mg, 0.11 mmol) was added at 0 °C. The mixture was then stirred for 7 h at 0 °C. The resulting mixture was subjected to liquid/liquid extraction with aqueous Na₂S₂O₃ (10%, 30 mL), brine (10 mL), dried over Na₂SO₄ and concentrated in vacuo. Stereoisomers were separated by silica gel column chromatography (CH₂Cl₂/EtOAc 3:1; Rf (CH₂Cl₂/EtOAc 3:1): 0.35 (F1), 0.25 (F3), 0.15 (F2 + F4)) and then
semi-preparative HPLC (CHIRALPAK ID, 250 mm x 10 mm, Daicel, 
CH₂Cl₂/isopropanol 90:10, 3 mL/min and detection at λₗₐₜ = 450 nm). The retention 
times of four isomers (F1)-16, (F2)-16, (F3)-16 and (F4)-16 were 5.1 min, 7.5 min, 20.2 
min and 22.5 min, respectively.

**Compound (F1)-16.** Mp: 169 – 170 °C; CD (CH₂Cl₂): 456 (+7.13); IR (neat): 
3330 (w), 3059 (w), 2928 (m), 1661 (s), 1438 (m), 1391 (m), 1366 
(m), 1302 (s), 1243 (s), 1204 (m), 1155 (m), 1075 (m), 1040 (m), 845 (w), 792 (m), 747 
(m), 687 (m), 638 (m), 573 (m); ¹H NMR (400 MHz, CDCl₃): 9.75 – 9.34 (m, 2H), 8.06 
– 7.69 (m, 4H), 7.45 – 7.25 (m, 6H), 6.21 – 6.02 (m, 1H), 5.62 – 5.46 (m, 1H), 4.98 – 
4.58 (m, 4H), 2.84 – 2.62 (m, 1H), 2.51 – 2.25 (m, 2H), 2.23 – 1.70 (m, 7H), 1.60 – 1.42 (m, 10H), 1.35 – 1.14 (m, 28H), 0.82 (t, 
³J (H,H) = 6.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): 171.8 (C), 167.6 (C), 162.9 (C), 
162.4 (C), 161.5 (C), 154.7 (C), 145.2 (C), 144.6 (C), 131.6 (CH), 131.0 (CH), 129.5 
(CH), 129.4 (CH), 129.3 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 126.9 (CH), 126.7 
(CH), 125.2 (CH), 81.4 (C), 81.3 (C), 58.7 (CH), 55.2 (CH), 55.1 (CH), 48.4 (CH), 47.2 
(CH₂), 40.2 (CH₂), 33.6 (CH₂), 32.1 (CH₂), 31.5 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 28.1 
(CH), 26.6 (CH₂), 24.6 (CH₂), 23.9 (CH₂), 22.6 (CH₂), 14.1 (CH₃); MS (ESI, 
CH₂Cl₂/MeOH 1:1): 978 (100, [M-Boc+H⁺]); HRMS (ESI, +ve) calcd for 
C₅₂H₅₉N₅O₁₀S₂ ([M-BOC+H⁺]): 978.3776, found: 978.3774.

**Compound (F2)-16.** Mp: 168 – 170 °C; CD (CH₂Cl₂): 424 (+14.3), 386 
(-3.96), 379 (+1.74), 370 (-0.34), 359 (+8.76), 289 (-35.00); IR (neat): 3352 (w), 2931 
(m), 1533 (m), 1439 (m), 1393 (m), 1366 (m), 1302 (s), 1243 (s), 1204 (m), 
1041 (m), 921 (w), 844 (w), 792 (m), 747 (m), 687 (m), 637 (m), 573 (m); ¹H NMR 
(400 MHz, CDCl₃): 9.71 (s, 1H), 9.63 (s, 1H), 7.92 – 7.68 (m, 4H), 7.37 – 7.21 (m, 6H), 
6.19 – 6.08 (m, 1H), 5.64 – 5.52 (m, 1H), 4.81 – 4.63 (m, 2H), 3.93 – 3.77 (m, 1H), 3.28 
– 3.17 (m, 2H), 2.92 – 2.53 (m, 2H), 2.52 – 2.39 (m, 2H), 2.26 – 2.14 (m, 2H), 2.09 – 
1.98 (m, 1H), 1.89 – 1.77 (m, 2H), 1.55 – 1.48 (m, 10H), 1.34 – 1.18 (m, 28H), 0.83 (t, 
³J (H,H) = 6.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): 170.8 (C), 166.7 (C), 161.7 (C), 
161.3 (C), 160.6 (C), 155.0 (C), 144.7 (C), 144.2 (C), 130.5 (CH), 130.3 (CH), 128.2 
(CH), 128.0 (CH), 126.8 (CH), 126.6 (C), 125.9 (CH), 125.4 (CH), 80.2 (C), 79.5 (C), 
57.7 (CH), 54.0 (CH), 46.9 (CH), 46.1 (CH₂), 39.1 (CH₂), 32.1 (CH₂), 31.2 (CH₂), 30.9
(CH₂), 30.4 (CH₂), 28.7 (CH₂), 28.4 (CH₂), 27.3 (CH₂), 27.0 (CH), 25.5 (CH₂), 24.5 (CH₂), 23.6 (CH₂), 22.8 (CH₂), 21.6 (CH₂), 13.0 (CH₃); MS (ESI, CH₂Cl₂/MeOH 1:1): 978 (100, [M-Boc+H]+); HRMS (ESI, +ve) calcd for C_{57}H_{67}N_{10}O_{12}S₂ ([M+H]⁺): 1078.4300, found: 1078.4298.

**Compound (F3)-16.** Mp: 176 – 178 °C; CD (CH₂Cl₂): 426 (-18.90), 386 (+5.13), 378 (-1.97), 371 (+3.19), 360 (-6.97), 287 (+46.31); IR (neat): 3318 (w), 3061 (w), 2930 (m), 2859 (m), 1660 (s), 1532 (m), 1438 (m), 1391 (m), 1366 (m), 1233 (s), 1205 (m), 1175 (m), 1042 (m), 999 (w), 917 (w), 845 (w), 792 (m), 746 (m), 729 (m), 688 (m), 638 (m), 850 (m); ¹H NMR (400 MHz, CDCl₃): 9.76 – 9.36 (m, 2H), 7.97 – 7.67 (m, 4H), 7.37 – 7.21 (m, 6H), 6.21 – 6.00 (s, 1H), 5.65 – 5.45 (m, 1H), 4.96 – 4.65 (m, 2H), 3.95 – 3.54 (m, 1H), 3.50 – 2.97 (m, 4H), 2.96 – 2.57 (m, 2H), 2.54 – 2.35 (m, 2H), 2.31 – 2.11 (m, 2H), 2.12 – 2.00 (m, 1H), 1.98 – 1.55 (m, 6H), 1.53 – 1.40 (m, 4H), 1.34 – 0.96 (m, 28H), 0.81 (t, 3J (H,H) = 6.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): 171.8 (C), 167.5 (C), 162.9 (C), 162.6 (C), 161.7 (C), 161.5 (C), 156.3 (C), 145.3 (C), 144.8 (C), 131.2 (CH), 130.9 (CH), 129.4 (CH), 129.1 (CH), 128.5 (CH), 127.6 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.0 (CH), 125.1 (CH), 81.3 (C), 81.1 (C), 58.8 (CH), 55.3 (CH), 48.2 (CH), 47.2 (CH₂), 46.9 (CH₃), 40.2 (CH₃), 33.4 (CH₂), 33.2 (CH₂), 32.3 (CH₂), 31.4 (CH₂), 29.7 (CH₂), 29.4 (CH₂), 28.3 (CH), 28.0 (CH₂), 26.5 (CH₂), 25.5 (CH₂), 24.5 (CH₂), 23.8 (CH₂), 22.5 (CH₂), 14.0 (CH₃); MS (ESI, CH₂Cl₂/MeOH 1:1): 978 (100, [M-Boc+H]+); HRMS (ESI, +ve) calcd for C_{55}H_{57}N_{10}O_{12}S₂ ([M-BOC+H⁺]): 978.3776, found: 978.3777.

**Compound (F4)-16.** Mp: 200 – 202 °C; CD (CH₂Cl₂): 363 (-0.74); IR (neat): 3326 (w), 3060 (w), 2933 (m), 2863 (m), 1660 (s), 1529 (m), 1474 (m), 1439 (m), 1390 (m), 1366 (m), 1303 (s), 1243 (s), 1205 (m), 1155 (s), 1076 (m), 1045 (m), 999 (m), 920 (m), 845 (m), 791 (m), 748 (m), 687 (m), 638 (m), 581 (m); ¹H NMR (400 MHz, CDCl₃): 9.73, (s, 1H), 9.35 (s, 1H) 7.91 – 7.67 (m, 4H), 7.42 – 7.22 (m, 6H), 7.23 – 6.05 (m, 1H), 5.55 (dd, 3J (H,H) = 8.7 Hz, 3J (H,H) = 5.2 Hz, 1H), 4.90 – 4.59 (m, 2H), 4.06 – 3.48 (m, 1H), 3.38 – 3.04 (m, 3H), 2.67 – 2.38 (m, 3H), 2.30 – 2.14 (m, 2H), 2.09 – 1.97 (m, 1H), 1.91 – 1.74 (m, 2H), 1.72 – 1.55 (m, 4H), 1.53 – 1.38 (m, 4H), 1.28 – 1.13 (m, 10H), 0.82 (t, 3J (H,H) = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): 171.9 (C), 167.6 (C), 162.7 (C), 162.6 (C), 161.6 (C), 155.9 (C), 145.7 (C), 145.5 (C), 131.4 (CH), S8
131.3 (CH), 129.1 (CH), 129.1 (CH), 128.0 (CH), 127.6 (C), 127.5 (C), 127.2 (C), 127.0 (CH), 126.8 (CH), 126.5 (C), 126.0 (CH), 81.2 (C), 80.7 (C), 58.8 (CH), 55.3 (CH), 48.0 (CH), 46.9 (CH), 40.2 (CH), 33.0 (CH), 32.5 (CH), 31.5 (C), 29.4 (CH), 28.3 (CH), 28.0 (CH), 27.9 (CH), 26.5 (CH), 25.5 (CH), 24.5 (CH), 24.0 (CH), 22.6 (CH), 14.0 (CH).

MS (ESI, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 1:1): 978 (100, [M-Boc+H]+); HRMS (ESI, +ve) calcd for C\textsubscript{52}H\textsubscript{59}N\textsubscript{5}O\textsubscript{10}S\textsubscript{2} ([M-BOC+H]+): 978.3776, found: 978.3776.

**Compound (Fn)-8.** A solution of pure isomer of (Fn)-\textbf{16} (18 mg, 0.02 mmol) in TFA (1 mL) and CH\textsubscript{2}Cl\textsubscript{2} (1 mL) was stirred for 2 h at rt. The mixture was concentrated and dried in vacuo to afford pure (Fn)-\textbf{8} (TFA salt, quantitative) as a yellow solid.

**Compound (F1)-8.** Mp: decomp. >185 °C; CD (CH\textsubscript{2}Cl\textsubscript{2}): 448 (+3.01), 299 (+4.93), 271 (-5.61); IR (neat): 3063 (w), 2925 (m), 2854 (m), 1660 (w), 1559 (m), 1440 (m), 1376 (m), 1304 (m), 1245 (m), 1199 (m), 1172 (m), 1135 (m), 1075 (m), 1034 (m), 829 (w), 793 (m), 749 (m), 720 (m), 686 (m), 638 (m), 599 (m), 588 (w); \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}OD): 9.69 – 9.14 (m, 2H), 8.00 – 7.68 (m, 4H), 7.53 – 7.21 (m, 6H), 5.63 – 5.45 (m, 1H), 5.05 – 4.78 (m, 2H), 3.96 – 3.68 (m, 1H), 3.17 – 2.89 (m, 4H), 2.77 – 2.41 (m, 2H), 2.39 – 2.07 (m, 4H), 2.05 – 1.97 (m, 1H), 1.93 – 1.66 (m, 6H), 1.48 – 1.36 (m, 4H), 1.32 – 1.17 (m, 8H), 0.82 (t, \textsuperscript{3}J (H,H) = 6.0 Hz, 3H); \textsuperscript{13}C NMR (126 MHz, CD\textsubscript{3}OD): 176.1 (C), 170.7 (C), 169.4 (C), 164.2 (C), 163.9 (C), 163.0 (CH), 129.2 (CH), 129.2 (CH), 128.2 (C), 127.5 (CH), 127.2 (CH), 60.9 (CH), 59.5 (CH), 56.2 (CH), 50.6 (CH), 47.3 (CH), 41.0 (CH), 33.7 (CH), 32.8 (CH), 31.7 (CH), 31.3 (CH), 30.8 (CH), 30.3 (CH), 29.0 (CH), 27.7 (CH), 26.6 (CH), 25.8 (CH), 24.9 (CH), 24.6 (CH), 23.7 (CH), 14.5 (CH); MS (ESI, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 1:1 with 0.1% HCOOH): 922 (100, [M+H]+); HRMS (ESI, +ve) calcd for C\textsubscript{48}H\textsubscript{51}N\textsubscript{5}O\textsubscript{10}S\textsubscript{2} ([M+BOC+H]+): 922.3150, found: 922.3156.

**Compound (F2)-8.** Mp: decomp. >184 °C; CD (CH\textsubscript{2}Cl\textsubscript{2}): 448 (+3.01), 352 (+7.90), 283 (-66.4), 250 (+108.25); IR (neat): 3063 (w), 2926 (m), 2855 (m), 1706 (m), 1659 (s), 1559 (m), 1440 (m), 1378 (m), 1304 (m), 1245 (m), 1199 (m), 1173 (m), 1134
(m), 1073 (m), 1034 (m), 830 (w), 793 (m), 748 (m), 720 (m), 687 (m), 581 (w); $^1$H NMR (500 MHz, CD$_3$OD): 9.52 – 9.47 (s, 2H), 7.81 – 7.71 (m, 4H), 7.39 – 7.32 (m, 6H), 5.64 – 5.51 (m, 1H), 4.92 – 4.81 (m, 2H), 3.90 – 3.70 (m, 1H), 3.20 – 2.95 (m, 4H), 2.61 – 2.37 (m, 2H), 2.38 – 2.09 (m, 4H), 2.07 – 1.97 (m, 1H), 1.87 – 1.69 (m, 6H), 1.49 – 1.41 (m, 4H), 1.27 – 1.18 (m, 8H), 0.83 (t, $^3$J(H,H) = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, CD$_3$OD): 176.1 (C), 170.7 (C), 169.4 (C), 164.3 (C), 163.9 (C), 163.5 (C), 161.3 (C), 161.0 (C), 154.8 (C), 146.0 (C), 133.1 (CH), 132.9 (CH), 130.5 (CH), 129.4 (C), 129.2 (C), 128.8 (C), 128.5 (C), 128.2 (CH), 128.2 (CH), 127.7 (CH), 127.4 (CH), 60.8 (CH), 59.4 (CH), 56.3 (CH), 50.2 (CH), 47.2 (CH$_2$), 41.0 (CH$_2$), 33.6 (CH$_2$), 32.8 (CH$_2$), 31.7 (CH$_2$), 31.2 (CH$_2$), 30.8 (CH$_2$), 30.3 (CH$_2$), 29.2 (CH$_2$), 27.7 (CH$_2$), 26.6 (CH$_2$), 25.9 (CH$_2$), 24.9 (CH$_2$), 24.7 (CH$_2$), 23.8 (CH$_2$), 14.5 (CH$_2$); MS (ESI, CH$_2$Cl$_2$MeOH 1:1 with 0.1% HCOOH): 922 (100, [M+H]$^+$); HRMS (ESI, +ve) calcd for C$_{48}$H$_{51}$N$_2$O$_{10}$S$_2$ ([M+H]$^+$): 922.3150, found: 922.3150.

**Compound (F3)-8.** Mp: decomp. >195 °C; CD (CH$_2$Cl$_2$): 414 (-15.83), 376 (+4.06), 280 (+31.3); IR (neat): 3378 (w), 3062 (m), 2926 (m), 2857 (m), 1658 (s), 1555 (m), 1439 (m), 1377 (m), 1304 (m), 1244 (m), 1196 (m), 1175 (m), 1134 (m), 1073 (m), 1032 (m), 830 (w), 793 (m), 747 (m), 720 (m), 686 (m), 637 (m), 582 (w), 565 (w); $^1$H NMR (400 MHz, CD$_3$OD): 9.59 – 9.40 (s, 2H), 7.89 – 7.68 (m, 4H), 7.41 – 7.33 (m, 6H), 5.61 – 5.45 (m, 1H), 4.89 – 4.80 (m, 2H), 3.95 – 3.74 (m, 1H), 3.17 – 2.92 (m, 3H), 2.94 – 2.81 (m, 1H), 2.37 – 2.21 (m, 3H), 2.09 – 1.95 (m, 1H), 1.88 – 1.64 (m, 6H), 1.49 – 1.41 (m, 2H), 1.36 – 1.29 (m, 2H), 1.23 – 1.14 (m, 8H), 0.81 (t, $^3$J(H,H) = 6.0 Hz, 3H); $^{13}$C NMR (101 MHz, CD$_3$OD): 174.9 (C), 169.4 (C), 162.7 (C), 161.9 (C), 153.8 (C), 144.7 (C), 131.5 (CH), 129.2 (CH), 129.1 (CH), 127.9 (C), 126.8 (CH), 126.6 (CH), 126.0 (CH), 59.4 (CH), 57.6 (CH), 54.7 (CH), 45.9 (CH$_2$), 39.7 (CH$_2$), 32.5 (CH$_2$), 31.3 (CH$_2$), 30.2 (CH$_2$), 29.8 (CH$_2$), 28.8 (CH$_2$), 27.8 (CH$_2$), 26.3 (CH$_2$), 25.2 (CH$_2$), 24.4 (CH$_2$), 23.5 (CH$_2$), 22.9 (CH$_2$), 22.2 (CH$_2$), 13.0 (CH$_2$); MS (ESI, CH$_2$Cl$_2$MeOH 1:1 with 0.1% HCOOH): 922 (100, [M+H]$^+$); HRMS (ESI, +ve) calcd for C$_{48}$H$_{51}$N$_2$O$_{10}$S$_2$ ([M+H]$^+$): 922.3150, found: 922.3150.

**Compound (F4)-8.** Mp: decomp. >220 °C; CD (CH$_2$Cl$_2$): 337 (-1.84), 274 (+5.85); IR (neat): 3375 (w), 3055 (w), 2934 (m), 2520 (w), 1653 (s), 1558 (m), 1439 (m), 1303 (m), 1243 (m), 1189 (m), 1134 (m), 1075 (m), 1048 (m), 946 (w), 832 (m),
792 (m), 748 (m), 721 (m), 684 (m), 635 (m), 578 (w); \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}OD): 9.51 – 9.37 (m, 2H), 7.86 – 7.74 (m, 4H), 7.43 – 7.30 (m, 6H), 5.67 – 5.51 (m, 1H), 4.95 – 4.82 (m, 2H), 3.93 – 3.67 (m, 1H), 3.19 – 2.93 (m, 4H), 2.71 – 2.43 (m, 2H), 2.41 – 2.17 (m, 4H), 2.07 – 1.97 (m, 1H), 1.86 – 1.68 (m, 6H), 1.51 – 1.43 (m, 2H), 1.40 – 1.35 (m, 2H), 1.30 – 1.16 (m, 8H), 0.81 (t, \textit{J} (H,H) = 8.0 Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CD\textsubscript{3}OD): 174.9 (C), 169.4 (C), 162.8 (C), 161.8 (C), 154.0 (C), 144.8 (C), 131.6 (CH\textsubscript{2}), 129.2 (CH\textsubscript{2}), 127.9 (C), 126.6 (CH\textsubscript{2}), 126.1 (CH\textsubscript{2}), 59.4 (CH), 57.6 (CH), 54.8 (CH), 39.7 (CH\textsubscript{2}), 32.5 (CH\textsubscript{2}), 31.3 (CH\textsubscript{2}), 30.2 (CH\textsubscript{2}), 28.8 (CH\textsubscript{2}), 27.9 (CH\textsubscript{2}), 26.3 (CH\textsubscript{2}), 25.2 (CH\textsubscript{2}), 24.5 (CH\textsubscript{2}), 23.4 (CH\textsubscript{2}), 23.0 (CH\textsubscript{2}), 22.3 (CH\textsubscript{2}), 13.0 (CH\textsubscript{3}); MS (ESI, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 1:1 with 0.1% HCOOH): 922 (100, [M+H]+); HRMS (ESI, +ve) calcd for C\textsubscript{48}H\textsubscript{51}N\textsubscript{5}O\textsubscript{10}S\textsubscript{2} ([M+H]+): 922.3150, found: 922.3149.

**Compound 17.** To a solution of 15 (52 mg, 0.050 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL), mCPBA (86 mg, 0.50 mmol) was added at rt. The mixture was then stirred for 20 h. The resulting mixture was subjected to liquid/liquid extraction with aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (10%, 30 mL), brine (10 mL) and concentrated in vacuo. Silica gel column chromatography of the residue (CH\textsubscript{2}Cl\textsubscript{2}/EtOAc 2:1; \textit{R} \textsubscript{f} (CH\textsubscript{2}Cl\textsubscript{2}/EtOAc 2:1): 0.60) gave pure 17 (36 mg, 64%) as a pale yellow solid. Mp: 172 – 174 °C; IR (neat): 3400 (m), 2927 (m), 2856 (m), 1720 (m), 1672 (s), 1525 (m), 1433 (m), 1392 (m), 1367 (m), 1307 (s), 1262 (m), 1243 (m), 1218 (m), 1194 (s), 1085 (m), 1001 (w), 943 (w), 892 (w), 850 (w), 791 (m), 754 (m), 724 (m), 683 (m), 644 (m), 588 (m), 556 (m); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 9.66 (s, 2H), 7.94 (s, 4H), 7.63 – 7.30 (m, 6H), 6.18 – 5.88 (br, 1H), 5.40 (t, \textit{J} (H,H) = 8.0 Hz, 1H), 4.88 – 4.47 (br, 2H), 3.33 – 3.05 (m, 3H), 2.50 – 2.29 (m, 2H), 2.24 – 2.08 (m, 2H), 2.04 – 1.95 (m, 1H), 1.92 – 1.69 (m, 3H), 1.58 – 1.39 (m, 6H), 1.39 – 1.29 (m, 12H), 1.32 – 1.14 (m, 18H), 0.90– 0.76 (m, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): 172.0 (C), 167.3 (C), 160.9 (C), 159.4 (C), 139.9 (C), 133.6 (CH), 133.3 (CH), 129.3 (C), 128.7 (CH), 81.2 (C), 65.7 (CH\textsubscript{2}), 59.3 (CH), 55.6 (CH), 47.0 (CH\textsubscript{2}), 40.1 (CH\textsubscript{2}), 32.3 (CH\textsubscript{2}), 31.9 (CH\textsubscript{2}), 31.5 (CH\textsubscript{2}), 30.1 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 28.0 (CH), 26.9 (CH\textsubscript{2}), 26.6 (CH\textsubscript{2}), 25.5 (CH\textsubscript{2}), 24.5 (CH\textsubscript{2}), 23.9 (CH\textsubscript{2}), 22.7 (CH\textsubscript{2}), 22.6 (CH\textsubscript{2}), 14.0 (CH\textsubscript{3}); MS (ESI, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 1:1): 1010 (100, [M-Boc+H]+); HRMS (ESI, +ve) calcd for C\textsubscript{48}H\textsubscript{51}N\textsubscript{5}O\textsubscript{10}S\textsubscript{2} ([M-Boc+H]+): 1010.3674, found: 1010.3674.

**Compound 9.** A solution of 17 in TFA (1 mL) and CH\textsubscript{2}Cl\textsubscript{2} (1 mL) was stirred for 2 h at
rt. The mixture was concentrated and dried in vacuo to afford pure 9 (TFA salt, quantitative) as a colorless solid. Mp: decomp. >178 °C; IR (neat): 3392 (w), 2932 (w), 1659 (s), 1449 (m), 1432 (m), 1308 (m), 1196 (s), 1139 (s), 1082 (m), 844 (m), 798 (m), 756 (m), 723 (s), 683 (m), 643 (m), 588 (m), 553 (m); \(^1\)H NMR (400 MHz, CD\(_3\)OD): 9.61 (s, 1H), 9.54 (s, 1H), 8.02 – 7.86 (m, 4H), 7.65 – 7.42 (m, 6H), 5.50 – 5.41 (m, 1H), 4.73 – 4.65 (m, 2H), 3.17 – 2.93 (m, 4H), 2.78 – 2.54 (m, 1H), 2.50 – 2.39 (m, 1H), 2.11 – 1.96 (m, 3H), 1.88 – 1.63 (m, 6H), 1.44 – 1.32 (m, 4H), 1.27 – 1.14 (m, 8H), 0.82 (t, \(J_{(H,H)} = 6.0 \text{ Hz}, 3H)\); \(^1^3\)C NMR (126 MHz, CD\(_3\)OD): 176.2 (C), 170.6 (C), 169.3 (C), 168.3 (C), 163.1 (C), 162.8 (C), 162.6 (C), 162.3 (C), 141.6 (C), 135.5 (C), 134.8 (CH), 134.0 (C), 133.9 (CH), 132.4 (CH), 131.2 (CH), 129.9 (CH), 129.8 (CH), 129.5 (CH), 129.0 (CH), 119.3 (CH), 117.0 (CH), 69.1 (CH\(_2\)), 60.9 (CH), 56.3 (CH), 41.0 (CH), 40.2 (CH\(_2\)), 36.5 (CH\(_2\)), 35.0 (CH\(_2\)), 33.1 (CH\(_2\)), 32.7, (CH\(_2\)) 31.6 (CH\(_2\)), 31.4 (CH\(_2\)), 30.8 (CH\(_2\)), 30.5 (CH\(_2\)), 30.2 (CH\(_2\)), 27.7 (CH\(_2\)), 26.9 (CH\(_2\)), 26.5 (CH\(_2\)), 26.1 (CH\(_2\)), 25.7 (CH\(_2\)), 25.0 (CH\(_2\)), 24.4 (CH\(_2\)), 24.1 (CH\(_2\)), 23.8 (CH\(_2\)), 14.4 (CH\(_3\)); MS (ESI, MeOH with 0.1% HCOOH): 954 (100, \([\text{M}+\text{H}]^+\)); HRMS (ESI, +ve) caled for C\(_{48}\)H\(_{51}\)N\(_3\)O\(_{12}\)S\(_2\) ([\(\text{M}+\text{H}]^+\]): 954.3048, found: 954.3047.
3. Catalyst Evaluation

Solutions of substrates 1 (1 M) and 2 (0.5 M) and catalysts 5, 7–9 (50 mM) were prepared in CDCl$_3$/CD$_3$OD 1:1, benzene-$d_6$, toluene-$d_8$, nitrobenzene or 1,3-dimethoxybenzene, and stirred at 20 °C. $^1$H NMR of the mixture diluted in CDCl$_3$ was recorded. 1,1,2,2-tetrachloroethane (0.5 M) was used as an internal standard (Figures S4 and S5 as representative examples). The concentration of the product 3 was determined from the integration of pertinent resonances. Concentrations of products were plotted against time, and the initial velocities were determined from the linear fitting (Figure S6). From equation (S1), the apparent second-order rate constants were obtained.

$$k_{app} = \frac{v_{ini}}{([1]_0 [2]_0)} \quad (S1)$$

Then the rate enhancements $k_{rel}$ were calculated from equation (S2).

$$k_{rel} = \frac{k_{app}(1)}{k_{app}(2)} \quad (S2)$$

Transition-state stabilizations $\Delta E_a$ were determined by equation (S3).

$$\Delta E_a = -RT \ln k_{rel} \quad (S3)$$

The spectroscopic data obtained for products 3 were identical to the ones reported in the literature.$^S$ Product mixtures were analyzed by chiral HPLC, using previously reported conditions (i.e., column: Chiralcel AD-H column; mobile phase: $n$-hexane/$i$-PrOH 99.25/0.75, 0.8 mL/min, 1 mL/min, rt; detection: 254 nm, Figures S7–S11).$^S$ The retention times found for the four stereoisomers of 3 were identical with the ones reported in the literature (Figures S7–S11).
4. Supplementary Figures

Figure S1. $^1$H NMR spectra of 11 (A) and a proline derivative 18 (B) in CDCl$_3$ at rt (bottom). These proline derivatives were heated in DMF in the presence of 5 eq. TEA for 15 min at 145 °C, and purified with liquid/liquid extraction (top). The dotted lines show the signal positions of $\alpha$-protons of proline moieties. Unchanged NMR signals of $\alpha$-protons and constant $[\alpha]^{20}_D$ (= 0.74 or 0.73 (11, before or after the reaction), = 0.73 or 0.72 (18, before or after the reaction); c = 10 mg/mL) confirmed that stereochemistry is not affected during the synthesis of the NDI catalysts with the microwave reactor.
Figure S2. HPLC traces of 15 (A), the mixture of (Fn)-16 (B), (F1)-16 (C), (F2)-16 (D), (F3)-16 (E) and (F4)-16 (F) with CH₂Cl₂/EtOH 96:4 as eluent, 1.0 mL/min, analytical HPLC (CHIRALPAK ID, 250 mm x 4.6 mm, Daicel).
Figure S3. CD spectra of the isolated sulfoxide stereoisomers (F1, black), (F2, blue), (F3, red), (F4, green) for (F1-4)-16 in CH₂Cl₂.
Figure S4. $^1$H NMR spectra of a mixture of butyraldehyde (1 M), trans-$\beta$-nitrostyrene (500 mM) and catalyst 7 (50 mM) in CDCl$_3$/CD$_3$OD 1:1 at 20 °C diluted in CDCl$_3$. The red arrow shows the formation of product, the blue ones show the consumption of butyraldehyde and trans-$\beta$-nitrostyrene. 1,1,2,2-tetrachloroethane is used as an internal standard (black).
Figure S5. $^1$H NMR spectra of a mixture of butyraldehyde (1 M), trans-β-nitrostyrene (500 mM) and catalyst 9 (50 mM) in CDCl$_3$/CD$_3$OD 1:1 at 20 °C diluted in CDCl$_3$. The red arrow shows the formation of product, the blue ones show the consumption of butyraldehyde and trans-β-nitrostyrene. 1,1,2,2-tetrachloroethane is used as an internal standard (black).
Figure S6. Plot of product concentration as a function of reaction time in the presence of 10 mol% 7 (●), 8 (■, F1: black, F2: blue, F3: red and F4: green), 9 (▲), CDCl₃/CD₃OD 1:1, room temperature. The initial velocity was determined by the linear fitting.
Figure S7. Chiral HPLC traces obtained using Chiralcel AD-H column ($n$-hexane/i-PrOH 99.25:0.75, rt, 0.8 mL/min, 254 nm) for the catalytic reaction with 7 (A), (F1)-8 (B), (F2)-8 (C), (F3)-8 (D), (F4)-8 (E) and 9 (F) in CDCl$_3$/CD$_3$OD 1:1. D: $R_t = 42$ min: Minor side product.
Figure S8. Chiral HPLC traces obtained using Chiralcel AD-H column (n-hexane/i-PrOH 99.25:0.75, rt, 0.8 mL/min, 254 nm) for the catalytic reaction with 7 (A), (F1)-8 (B), (F2)-8 (C), (F4)-8 (D) and 9 (E) in toluene-d₈.
Figure S9. Chiral HPLC traces obtained using Chiralcel AD-H column (n-hexane/i-PrOH 99.25:0.75, rt, 0.8 mL/min, 254 nm) for the catalytic reaction with 7 (A), (F1 – 4)-8 (B – E) and 9 (F) in benzene-\textsubscript{d}_{6}.
**Figure S10.** Chiral HPLC traces obtained using Chiralcel AD-H column (n-hexane/i-PrOH 99.25:0.75, rt, 0.8 mL/min, 254 nm) for the catalytic reaction with (F4)-8 in nitrobenzene (A), and (F3)-8 or (F4)-8 in 1,3-dimethoxybenzene (B and C).

**Figure S11.** Chiral HPLC traces obtained using Chiralcel AD-H column (n-hexane/i-PrOH 99.25:0.75, rt, 0.8 mL/min, 254 nm) for the catalytic reaction with (F3)-5 in toluene-d₈ (A) or benzene-d₆ (B).
5. References


(S4) Zhao, Y.; Cotelle, Y.; Avestro, A.; Sakai, N.; Matile, S. J. Am. Chem. Soc. 2015, 8–11.


6. NMR Spectra

6.1. NDI Catalyst with Sulfide Core Substituents

Figure S12. $^1$H-NMR spectrum of 13 in CDCl$_3$.

Figure S13. $^{13}$C-NMR spectrum of 13 in CDCl$_3$. 
Figure S14. $^1$H-NMR spectrum of 15 in CDCl$_3$.

Figure S15. $^{13}$C-NMR spectrum of 15 in CDCl$_3$. 
Figure S16. $^1$H-NMR spectrum of 7 in CD$_3$OD.

Figure S17. $^{13}$C-NMR spectrum of 7 in CD$_3$OD.
6.2. NDI Catalysts with Chiral Sulfoxide and Sulfone Core Substituents

**Figure S18.** $^1$H-NMR spectrum of (F1)-16 in CDCl$_3$.

**Figure S19.** $^{13}$C-NMR spectrum of (F1)-16 in CDCl$_3$. 
Figure S20. $^1$H-NMR spectrum of (F2)-16 in CDCl$_3$.

Figure S21. $^{13}$C-NMR spectrum of (F2)-16 in CDCl$_3$. 
Figure S22. $^1$H-NMR spectrum of (F3)-16 in CDCl$_3$. Atropisomerism is expected to account for unusual peak patterns (see Fig. 2 in main text). Deprotected (F3)-8 shows, e.g., one single peak for NDI protons (see Fig. S30).

Figure S23. $^{13}$C-NMR spectrum of (F3)-16 in CDCl$_3$. 

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Figure S24. $^1$H-NMR spectrum of (F4)-16 in CDCl$_3$.

Figure S25. $^{13}$C-NMR spectrum of (F4)-16 in CDCl$_3$. 
Figure S26. $^1$H-NMR spectrum of (F1)-8 in CD$_3$OD.

Figure S27. $^{13}$C-NMR spectrum of (F1)-8 in CD$_3$OD.
Figure S28. $^1$H-NMR spectrum of (F2)-8 in CD$_3$OD.

Figure S29. $^{13}$C-NMR spectrum of (F2)-8 in CD$_3$OD.
Figure S30. $^1$H-NMR spectrum of (F3)-8 in CD$_3$OD.

Figure S31. $^{13}$C-NMR spectrum of (F3)-8 in CD$_3$OD.
Figure S32. $^1$H-NMR spectrum of (F4)-8 in CD$_3$OD.

Figure S33. $^{13}$C-NMR spectrum of (F4)-8 in CD$_3$OD.
Figure S34. $^1$H-NMR spectrum of 17 in CDCl$_3$.

Figure S35. $^{13}$C-NMR spectrum of 17 in CDCl$_3$. 
Figure S36. $^1$H-NMR spectrum of 9 in CD$_3$OD.

Figure S37. $^{13}$C-NMR spectrum of 9 in CD$_3$OD.