Remote Control of Anion–π Catalysis on Fullerene-Centered Catalytic Triads

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1. Materials and Methods

As in references S1 and S2, reagents for synthesis were purchased from Sigma-Aldrich, Fluka, Acros, Apollo Scientific, TCI and Bachem. Fullerene C$_{60}$ was purchased from Solaris Chem Inc. Column chromatography was carried out on silica gel (SiliaFlash® P60, SILICYCLE, 230–400 mesh). Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck). Melting points (Mp) were measured on a Melting Point M-565 (BUCHI). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a temperature controller. $[\alpha]^{25}_{D}$ 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) and are reported as wavenumbers $\nu$ in cm$^{-1}$ with band intensities indicated as s (strong), m (medium), w (weak). Electrochemical measurements were done on an Electrochemical Analyzer with Picomp booster and Faraday cage (CH Instruments 660C). $^1$H and $^{13}$C spectra were recorded (as indicated) either on a Bruker 400 MHz or 500 MHz spectrometer and are reported as chemical shifts ($\delta$) 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). MALDI MS analysis for the characterization of new compounds was performed using Bruker MALDI Autoflex Speed TOF/TOF and is reported as mass-per-charge ratio $m/z$. ESI-MS were performed on a ESI API 150EX and are reported as $m/z$ (%). Accurate mass determinations using ESI (HRMS) were performed on a Sciex QSTAR Pulsar mass spectrometer.

**Abbreviations:** DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; HBTU: $N,N,N',N'$-Tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate; MAHT: Malonic acid half thioesters; $m$CPBA: 3-Chloroperbenzoic acid; MEP: Molecular Electrostatic Potential; NDI: Naphthalenediimide; oDCB: 1,2-Dichlorobenzene; rt: Room temperature; TCE: 1,1,2,2-Tetrachloroethane; TEA: Triethylamine; TFA: Trifluoroacetic acid.
2. Synthesis

Scheme S1. (a) HBTU, TEA, CH₂Cl₂, 20 min, rt, 87%; (b) 7, I₂, DBU, toluene, 2 h, rt, 57%; (c) TFA, CH₂Cl₂, rt, overnight, *quant.*; (d) 10, HBTU, TEA, CH₂Cl₂, 4 h, rt, 90%.

**Compound 23** was synthesized as described in ref [S3].

**Compound 24** was synthesized as described in ref [S4].

**Compound 8.** To a solution of 24 (136 mg, 0.956 mmol), 23 (184 mg, 1.155 mmol) and TEA (266 µL, 1.91 mmol) in dry CH₂Cl₂ (5 mL), HBTU (436 mg, 1.15 mmol) was added and the mixture was stirred at rt for 20 min. The reaction mixture was diluted with CH₂Cl₂ (20 mL), washed with NaHCO₃ (sat. 3 x 20 mL) and aq. NaCl (sat. 1 x 20 mL), dried over Na₂SO₄ and concentrated *in vacuo* to give pure product 8 as a colorless oil (238 mg, 87%). IR (neat): 3302 (w), 2932 (m), 2860 (w), 1731 (s), 1649 (s), 1549 (m), 1453 (m), 1368 (m), 1255 (m), 1144 (s), 1038 (m), 955 (m), 844 (m); ¹H NMR (400 MHz, CDCl₃): 7.01 (s, 1H), 3.58 – 3.46 (m, 1H), 3.16 (s, 2H), 2.46 – 2.37 (m, 1H), 2.35 – 2.25 (m, 1H), 2.20 (s, 6H), 1.86 – 1.73 (m, 2H), 1.66 – 1.59 (m, 1H), 1.44 (s, 9H), 1.32 – 0.99 (m, 5H); ¹³C NMR (101 MHz, CDCl₃): 168.1 (C), 165.6 (C), 82.0 (C), 66.4 (CH), 51.3 (CH), 44.2 (CH₂), 40.1 (CH₃), 32.6 (CH₂), 28.0 (CH₃), 25.3 (CH₂), 24.7 (CH₂), 21.6 (CH₂); HRMS (ESI, +ve) calcd for C₁₅H₂₈N₂O₃ ([M+H]⁺): 285.2173, found: 285.2176.

**Compound 25.** To a solution of 8 (134 mg, 0.471 mmol), C₆₀ fullerene 7 (605 mg, 0.840 mmol) and I₂ (213 mg, 0.840 mmol) in toluene (300 mL), DBU (141 µL, 0.940 mmol) was added dropwise. The resulting mixture was allowed to react for 2 h and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted C₆₀ was recovered using toluene and 25 was eluted using CH₂Cl₂/MeOH 20:1). After this, solvent was evaporated and the residue was triturated with MeOH (2 x 20 mL), affording 25 as a brown powder (270 mg, 57%). Rf (CH₂Cl₂/MeOH 10:1): 0.56; Mp: >300 °C (decomp.); IR (neat): 3360 (w), 2930 (m), 2860 (m), 2180 (w), 1719 (m), 1677 (s), 1504 (m), 1449 (m), 1368 (m), 1248 (m), 1249
Compound 9. To a solution of 25 (80 mg, 80 µmol) in CH₂Cl₂ (5 mL), TFA (2 mL) was added and the mixture was stirred at rt overnight. After this time, solvent was evaporated and the residue was triturated with CH₂Cl₂ (2 x 10 mL), affording 25 as a brown powder (85 mg, quant). Mpf: >300 °C (decomp.); IR (neat): 2935 (w), 1670 (m), 1530 (w), 1428 (w), 1319 (w), 1177 (s), 1133 (s), 989 (w), 751 (s), 699 (m), 667 (w); ¹H NMR (400 MHz, TCE-d₂/CD₃OD 9:1): 4.40 – 4.25 (m, 1H), 3.53 – 3.39 (m, 1H), 2.98 (s, 6H), 2.19 – 2.07 (m, 2H), 2.06 – 1.97 (m, 1H), 1.88 – 1.80 (m, 1H), 1.58 – 1.38 (m, 4H); ¹³C NMR (101 MHz, TCE-d₂/CD₃OD 9:1): 167.7 (C), 164.8 (C), 148.2 (C), 146.3 (C), 146.0 (C), 145.5 (C), 145.4 (C), 145.4 (C), 145.1 (C), 145.0 (C), 145.0 (C), 144.9 (C), 144.9 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.5 (C), 144.5 (C), 144.5 (C), 144.4 (C), 144.4 (C), 144.3 (C), 144.3 (C), 144.3 (C), 144.2 (C), 144.1 (C), 144.1 (C), 143.7 (C), 143.7 (C), 143.6 (C), 143.5 (C), 142.9 (C), 142.8 (C), 142.8 (C), 142.8 (C), 142.7 (C), 142.7 (C), 142.7 (C), 142.5 (C), 142.4 (C), 141.9 (C), 141.9 (C), 141.7 (C), 141.4 (C), 141.4 (C), 140.6 (C), 140.5 (C), 140.5 (C), 140.4 (C), 137.0 (C), 136.8 (C), 77.6 (C), 72.2 (C), 68.2 (CH), 56.0 (C), 42.7 (CH), 36.9 (CH₃), 32.2 (CH₂), 24.2 (CH₂), 24.0 (CH₂), 22.7 (CH₂); HRMS (ESI, +ve) calcd for C₇₁H₁₈N₂O₃ ([M+H]+): 947.1390, found: 947.1397.

Compound 6. To a solution of 9 (170 mg, 0.160 mmol), 10 (130 mg, 0.607 mmol) and TEA (340 µL, 2.44 mmol) in CHCl₃ (20 mL), HBTU (240 mg, 0.633 mmol) was added and the mixture was stirred at rt for 4 h. After this time, the solvent was evaporated and the residue was purified by silica gel chromatography (CH₂Cl₂/MeOH 20:1), affording 6 as a brown powder (165 mg, 90%). Rᵣ (CH₂Cl₂/MeOH 20:1): 0.25; Mpf: >300 °C (decomp.); IR (neat): 3326 (m), 2928 (s), 2857 (m), 1678 (s), 1517 (s), 1449 (m), 1365 (w), 1320 (w), 1262 (m), 1167 (s), 1015 (w), 735 (s); ¹H NMR (400 MHz, CDCl₃): 7.89 (br s, 1H), 7.54 (br s, 1H), 4.92 (d, ³J(H,H) = 7.9 Hz, 1H), 4.04 – 3.82 (m, 2H), 3.63 – 3.46 (m, 1H), 2.66 – 2.46 (m, 2H), 2.31 (s, 6H), 2.23 – 2.17 (m, 2H), 1.99 – 1.86 (m, 2H), 1.84 – 1.75 (m, 3H), 1.50 – 1.29 (m, 17H); ¹³C NMR (101 MHz, CDCl₃): 163.5 (C), 163.0 (C), 156.5 (C),
146.8 (C), 146.4 (C), 145.7 (C), 145.3 (C), 145.3 (C), 145.2 (C), 145.2 (C), 145.3 (C), 145.3 (C), 145.3 (C), 145.2 (C), 145.2 (C), 145.2 (C), 145.0 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.6 (C), 144.5 (C), 144.5 (C), 143.9 (C), 143.9 (C), 143.2 (C), 143.1 (C), 143.1 (C), 143.0 (C), 142.9 (C), 142.4 (C), 142.4 (C), 142.3 (C), 142.1 (C), 141.0 (C), 141.0 (C), 140.8 (C), 137.9 (C), 79.7 (C), 74.4 (C), 73.4 (C), 66.5 (CH), 58.3 (C), 54.5 (CH), 52.2 (C), 40.5 (CH3), 33.1 (CH2), 32.5 (CH2), 32.3 (CH2), 28.8 (CH3), 25.3 (CH2), 24.9 (CH2), 24.8 (CH2), 21.4 (CH2); HRMS (ESI, +ve) calcd for C82H38N4O4 ([M+H]+): 1143.2966, found: 1143.2963.

Scheme S2. (a) 1) TEA, DMF, microwave, 5 min, 75 ºC; 2) microwave, 15 min, 140 ºC, 47% (13), 60% (14); (b) mCPBA, CHCl3, 15 min, 0 ºC, 93%; (c) mCPBA, CHCl3, 5 h, rt, 96%.

**Compound 10** was synthesized as described in ref [S5].

**Compound 28** was synthesized as described in ref [S6].

**Compound 13.** A dispersion of 27 (300 mg, 1.12 mmol) and 10 (240 mg, 1.12 mmol) in dry DMF (10 mL) was sonicated for 5 min. The reaction mixture was heated under microwave irradiation in a pressure tight vessel for 5 min at 75 ºC and then 15 min at 140 ºC. After this, 26 (150 µL, 1.12 mmol) and TEA (160 µL, 1.12 mmol) were added and the reaction mixture was again heated under microwave irradiation for 5 min at 75 ºC and 15 min at 140 ºC. After this time, the solvent was evaporated and the residue was purified by silica gel chromatography (CH2Cl2/acetone 80:1), affording 13 as a pale pink powder (285 mg, 47%). Rf (CH2Cl2/acetone 40:1): 0.40; Mp: 115 – 116 ºC; IR (neat): 3367 (w), 2930 (m), 2859 (m), 1707 (s), 1659 (s), 1580 (m), 1453 (m), 1329 (s), 1245 (s),
1168 (m), 1087 (w), 768 (s); $^1$H NMR (400 MHz, CDCl$_3$): 8.75 – 8.57 (m, 4H), 4.90 – 4.73 (m, 1H), 4.59 – 4.41 (m, 2H), 4.11 (t, $^3$J(H,H) = 7.7 Hz, 2H), 2.88 – 2.58 (m, 1H), 2.19 – 2.02 (m, 1H), 1.91 – 1.74 (m, 3H), 1.73 – 1.61 (m, 2H), 1.53 – 1.42 (m, 1H), 1.41 – 1.23 (m, 8H), 0.92 – 0.66 (m, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$): 164.2 (C), 163.1 (C), 162.8 (C), 155.3 (C), 131.2 (C), 130.8 (C), 130.6 (C), 127.7 (C), 126.6 (C), 126.3 (C), 125.9 (C), 78.7 (C), 58.8 (CH), 49.1 (CH), 40.9 (CH$_2$), 33.5 (CH$_2$), 31.4 (CH$_2$), 28.8 (CH$_2$), 28.0 (CH$_2$), 27.7 (CH$_3$), 26.7 (CH$_2$), 25.8 (CH$_2$), 24.9 (CH$_2$), 22.5 (CH$_2$), 14.0 (CH$_3$); HRMS (ESI, +ve) calcd for C$_{31}$H$_{37}$N$_3$O$_6$ ([M+H]$^+$): 548.2755, found: 548.2757.

**Compound 14.** A dispersion of 28 (389 mg, 1.00 mmol) and 10 (214 mg, 1.00 mmol) in dry DMF (8 mL) was sonicated for 5 min. The reaction mixture was heated under microwave irradiation for 5 min at 75 ºC and then 15 min at 140 ºC. After this, 26 (132 µL, 1.00 mmol) and TEA (140 µL, 1.00 mmol) were added and the reaction mixture was again heated under microwave irradiation for 5 min at 75 ºC and 15 min at 140 ºC. After this time, the solvent was evaporated and the residue was purified by silica gel chromatography (CH$_2$Cl$_2$/MeOH 60:1), affording 14 as a bright red powder (404 mg, 60%). $R_f$ (CH$_2$Cl$_2$/MeOH 60:1): 0.35; Mp: 226 – 227 ºC; IR (neat): 3353 (w), 2927 (m), 2857 (m), 1694 (s), 1644 (s), 1548 (m), 1518 (m), 1443 (s), 1366 (m), 1239 (s), 1211 (s), 1191 (s), 890 (m), 786 (m); $^1$H NMR (400 MHz, CDCl$_3$): 8.72 – 8.47 (m, 2H), 4.98 – 4.83 (m, 1H), 4.61 – 4.32 (m, 2H), 4.16 (t, $^3$J(H,H) = 7.8 Hz, 2H), 3.34 – 3.12 (m, 4H), 2.93 – 2.72 (m, 1H), 2.20 – 2.11 (m, 1H), 1.98 – 1.88 (m, 2H), 1.88 – 1.79 (m, 1H), 1.79 – 1.67 (m, 2H), 1.59 – 1.48 (m, 6H), 1.48 – 1.99 (m, 9H), 0.95 – 0.80 (m, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$): 164.7 (C), 163.2 (C), 162.7 (C), 162.3 (C), 155.3 (C), 148.8 (C), 147.9 (C), 128.0 (CH), 127.7 (CH), 125.0 (C), 124.9 (C), 124.5 (C), 123.5 (C), 119.2 (C), 118.8 (C), 118.4 (C), 78.7 (C), 58.5 (CH), 49.0 (CH), 41.1 (CH$_2$), 33.6 (CH$_2$), 31.5 (CH$_2$), 28.5 (CH$_2$), 28.3 (CH$_2$), 27.9 (CH$_2$), 27.7 (CH$_3$), 26.8 (CH$_2$), 26.3 (CH$_2$), 25.8 (CH$_2$), 24.9 (CH$_2$), 22.5 (CH$_2$), 14.0 (CH$_3$), 12.8 (CH$_3$); HRMS (ESI, +ve) calcd for C$_{35}$H$_{45}$N$_3$O$_6$S$_2$ ([M+H]$^+$): 668.2822, found: 668.2822.

**Compound 15.** To a solution of 14 (200 mg, 0.300 mmol) in CHCl$_3$ (10 mL) at 0 ºC, mCPBA (168 mg, 0.749 mmol) is added portionwise. After 15 min, the reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL) and quenched with Na$_2$S$_2$O$_3$ (10%, 20 mL). The organic phase was washed with NaHCO$_3$ (sat. 2 x 20 mL) and aq. NaCl (sat. 1 x 20 mL), dried over Na$_2$SO$_4$ and solvent was removed. Then, the residue was purified by silica gel chromatography (CH$_2$Cl$_2$/MeOH 40:1), affording 15 as a mixture of isomers as a bright orange powder (195 mg, 93%). $R_f$ (CH$_2$Cl$_2$/MeOH 20:1): 0.25; Mp: >140 ºC (decomp.); IR (neat): 3302 (w), 2932 (m), 1702 (m), 1654 (w), 1504 (m), 1444 (m), 1367 (m), 1304 (s), 1242 (s), 1165 (m), 1050 (s), 791 (w); $^1$H NMR (400 MHz, CDCl$_3$): 9.54 – 9.23 (m, 2H), 4.89 – 4.71 (m, 1H), 4.71 – 4.48 (m, 1H), 4.48 – 4.34 (m, 1H), 4.18 – 4.05 (m, 2H), 3.46 – 2.80
(m, 4H), 2.79 – 2.58 (m, 1H), 2.16 – 1.99 (m, 1H), 1.93 – 1.74 (m, 3H), 1.68 (p, $^3J\ (H,H) = 7.6$ Hz, 2H), 1.54 – 1.43 (m, 1H), 1.42 – 1.22 (m, 12H), 1.21 – 1.08 (m, 2H), 0.89 – 0.80 (m, 3H), 0.80 – 0.59 (m, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$): 163.2 (C), 163.1 (C), 162.7 (C), 162.6 (C), 162.6 (C), 162.5 (C), 161.4 (C), 155.6 (C), 155.5 (C), 154.5 (C), 154.3 (C), 154.2 (C), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 127.6 (C), 127.6 (C), 127.2 (C), 127.2 (C), 126.4 (C), 125.4 (C), 125.3 (C), 124.1 (C), 124.1 (C), 122.5 (C), 122.4 (C), 78.8 (C), 78.4 (C), 59.6 (CH), 59.4 (CH), 49.3 (CH$_2$), 49.1 (CH$_2$), 48.7 (CH), 47.7 (CH$_2$), 47.4 (CH$_2$), 41.3 (CH$_2$), 33.2 (CH$_2$), 33.2 (CH$_2$), 31.4 (CH$_2$), 28.4 (CH$_2$), 28.3 (CH$_2$), 28.1 (CH$_2$), 27.9 (CH$_2$), 27.5 (CH$_3$), 26.7 (CH$_2$), 25.6 (CH$_2$), 24.8 (CH$_2$), 24.8 (CH$_2$), 22.5 (CH$_2$), 14.0 (CH$_3$), 7.2 (CH$_3$), 7.1 (CH$_3$), 6.6 (CH$_3$), 6.6 (CH$_3$); HRMS (ESI, +ve) calcd for C$_{35}$H$_{45}$N$_3$O$_8$S$_2$ ([M+H]$^+$): 700.2721, found: 700.2720.

**Compound 16.** To a solution of 14 (150 mg, 0.225 mmol) in CHCl$_3$ (8 mL) at rt, $m$CPBA (250 mg, 1.12 mmol) is added portionwise. After 4 h, 1 eq. more of $m$CPBA is added and the mixture is allowed to react 1 h more. Then, the reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL) and quenched with Na$_2$S$_2$O$_3$ (10%, 20 mL). The organic phase was washed with NaHCO$_3$ (sat. 2 x 20 mL) and aq. NaCl (sat. 1 x 20 mL), dried over Na$_2$SO$_4$ and solvent was removed, affording 16 as a pale yellow powder (158 mg, 96%). $R_f$ (CH$_2$Cl$_2$/MeOH 20:1): 0.54; Mp: >180 °C (decomp.); IR (neat): 3394 (w), 2932 (m), 2859 (w), 1712 (m), 1669 (s), 1514 (m), 1435 (m), 1305 (s), 1238 (m), 1133 (s), 1046 (m), 717 (m); $^1$H NMR (400 MHz, CDCl$_3$): 9.50 (s, 1H), 9.44 (s, 1H), 4.82 (s, 1H), 4.56 – 4.39 (m, 2H), 4.19 (t, $^3J\ (H,H) = 6.6$ Hz, 3H), 4.09 – 3.70 (m, 4H), 2.82 – 2.67 (m, 1H), 2.17 – 2.04 (m, 1H), 1.94 – 1.69 (m, 4H), 1.58 – 1.21 (m, 15H), 0.88 (t, $^3J\ (H,H) = 7.0$ Hz, 3H), 0.81 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$): 162.0 (C), 160.7 (C), 155.7 (C), 145.3 (C), 133.7 (CH), 133.7 (CH), 129.4 (C), 129.1 (C), 126.9 (C), 126.4 (C), 78.9 (C), 60.2 (CH), 50.5, 49.2 (CH), 42.0 (CH$_2$), 33.4 (CH$_2$), 31.5 (CH$_2$), 27.9 (CH$_2$), 27.7 (CH$_3$), 26.8 (CH$_2$), 25.6 (CH$_2$), 24.8 (CH$_2$), 22.6 (CH$_2$), 14.1 (CH$_3$), 8.0 (CH$_3$), 7.6 (CH$_3$): HRMS (ESI, +ve) calcd for C$_{35}$H$_{45}$N$_3$O$_{10}$S$_2$ ([M+H]$^+$): 732.2619, found: 732.2619.
Compound 29. To a solution of 13 (100 mg, 0.183 mmol) in CH$_2$Cl$_2$ (5 mL), TFA (2 mL) was added and the mixture was stirred at rt for 2 h. After this time, solvent was evaporated, affording 29 as a pale pink powder (100 mg, quant.). Mp: >130 °C (decomp.); IR (neat): 2925 (m), 2855 (w), 1699 (m), 1655 (s), 1581 (m), 1454 (m), 1330 (m), 1250 (m), 1180 (s), 1120 (s), 1087 (m), 766 (m), 719 (m); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 4:1): 8.68 – 8.53 (m, 4H), 4.97 (td, $^3$J(H,H) = 11.8, 4.1 Hz, 1H), 4.33 – 4.17 (m, 1H), 4.09 (t, $^3$J(H,H) = 7.5 Hz, 2H), 2.56 – 2.38 (m, 1H), 2.25 – 2.09 (m, 1H), 1.91 – 1.72 (m, 3H), 1.72 – 1.60 (m, 2H), 1.53 – 1.18 (m, 10H), 0.86 – 0.75 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$/CD$_3$OD 4:1): 163.0 (C), 131.1 (CH), 130.8 (CH), 130.5 (CH), 127.4 (C), 127.2 (C), 126.9 (C), 126.6 (C), 55.5 (CH), 50.0 (CH), 41.0 (CH$_2$), 31.4 (CH$_2$), 31.2 (CH$_2$), 28.1 (CH$_2$), 27.9 (CH$_2$), 26.7 (CH$_2$), 25.1 (CH$_2$), 23.9 (CH$_2$), 22.5 (CH$_2$), 13.9 (CH$_3$); HRMS (ESI, +ve) calcd for C$_{26}$H$_{29}$N$_3$O$_4$ ([M+H]$^+$): 448.2231, found: 448.2229.
**Compound 2.** To a solution of 9 (30 mg, 28 µmol), 29 (64 mg, 110 µmol) and TEA (60 µL, 0.43 mmol) in CH₂Cl₂ (5 mL), HBTU (43 mg, 110 µmol) was added and the mixture was stirred at rt for 4 h. After this time, the mixture was poured directly on a pad of silica gel and the product was eluted (CH₂Cl₂/MeOH 30:1), dried and purified by PTLC (CH₂Cl₂/MeOH 50:1), affording 2 as a brown powder (28 mg, 73%). \( R_f \) (CH₂Cl₂/MeOH 20:1): 0.30; Mp: >300 °C (decomp.); IR (neat): 2927 (w), 2859 (w), 1662 (s), 1522 (m), 1450 (m), 1323 (m), 1182 (s), 1129 (s), 989 (w), 747 (s); \(^1\)H NMR (400 MHz, CDCl₃): 8.77 – 8.56 (m, 4H), 7.34 (br s, 1H), 7.32 (br s, 1H), 5.36 – 5.22 (m, 1H), 5.19 – 5.08 (m, 1H), 4.13 (t, \(^3\)J(H,H) = 7.5 Hz, 2H), 3.72 – 3.55 (m, 1H), 2.86 – 2.61 (m, 2H), 2.49 – 2.27 (m, 2H), 2.11 (s, 6H), 2.00 – 1.74 (m, 7H), 1.73 – 1.48 (m, 6H), 1.46 – 1.10 (m, 8H), 0.93 (t, \(^3\)J(H,H) = 7.0 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl₃): 164.3 (C), 163.0 (C), 162.7 (C), 162.6 (C), 162.1 (C), 147.0 (C), 145.8 (C), 145.4 (C), 145.3 (C), 145.2 (C), 145.1 (C), 145.0 (C), 145.0 (C), 145.0 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.6 (C), 144.5 (C), 144.5 (C), 144.4 (C), 144.4 (C), 144.3 (C), 144.2 (C), 143.9 (C), 143.8 (C), 143.7 (C), 143.6 (C), 143.5 (C), 143.0 (C), 142.9 (C), 142.9 (C), 142.8 (C), 142.7 (C), 142.7 (C), 142.6 (C), 142.4 (C), 142.3 (C), 142.1 (C), 142.0 (C), 142.0 (C), 141.8 (C), 141.6 (C), 141.3 (C), 140.7 (C), 140.7 (C), 140.6 (C), 139.9 (C), 139.2 (C), 137.9 (C), 137.7 (C), 137.3 (C), 131.5 (CH), 131.1 (CH), 131.0 (CH), 127.4 (C), 127.0 (C), 126.9 (C), 126.5 (C), 126.3 (C), 74.3 (C), 73.2 (C), 66.2 (CH), 59.0 (C), 56.9 (CH), 52.3 (CH), 49.6 (CH), 40.9 (CH₂), 40.0 (CH₃), 33.5 (CH₂), 31.8 (CH₂), 31.6 (CH₂), 28.6 (CH₂), 28.3 (CH₂), 26.9 (CH₂), 25.7 (CH₂), 25.2 (CH₂), 24.8 (CH₂), 24.7 (CH₂), 22.6 (CH₂), 21.2 (CH₂), 14.2 (CH₃); HRMS (ESI, +ve) calcd for C₉₇H₄₅N₅O₆ ([M+H]^+): 1376.3443, found: 1376.3420.

**Note:** NMR spectra of compounds containing sulfur substituted NDIs are complex due to the presence of stereo-isomers.[⁸⁷] Here all observed \(^{13}\)C NMR signals are listed.

**Compound 30.** To a solution of 14 (200 mg, 0.300 mmol) in CH₂Cl₂ (6 mL), TFA (2 mL) was added and the mixture was stirred at rt for 2 h. After this time, solvent was evaporated, affording 30 as a bright red powder (204 mg, quant.). Mp: 218 – 219 °C (decomp.); IR (neat): 3205 (w), 2932 (m), 1692 (m), 1644 (m), 1444 (m), 1371 (w), 1317 (m), 1241 (m), 1194 (s), 1133 (s), 893 (w), 787 (m); \(^1\)H NMR (400 MHz, CDCl₃/CD₃OD 4:1): 8.53 – 8.46 (m, 2H), 5.05 – 4.93 (m, 1H), 4.37 – 4.21 (m, 1H), 4.06 (t, \(^3\)J(H,H) = 7.6 Hz, 2H), 3.20 – 3.01 (m, 4H), 2.60 – 2.38 (m, 1H), 2.24 – 2.12 (m, 1H), 1.89 – 1.76 (m, 3H), 1.63 (p, \(^3\)J(H,H) = 7.6 Hz, 2H), 1.53 – 1.17 (m, 18H), 0.78 (t, \(^3\)J(H,H) = 7.0 Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl₃/CD₃OD 4:1): 163.3 (C), 162.4 (C), 148.5 (C), 148.4 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 125.2 (C), 124.8 (C), 124.8 (C), 124.5 (C), 123.6 (C), 119.7 (C), 119.0 (C), 118.9 (C), 55.9 (CH), 55.5 (CH), 50.1 (CH), 49.9 (CH), 41.1 (CH₂), 31.4 (CH₂), 31.1 (CH₂), 28.0 (CH₂), 27.8 (CH₂), 26.7 (CH₂), 26.3 (CH₂), 26.1 (CH₂), 25.1 (CH₂), 23.9
(CH₂), 23.8 (CH₂), 22.5 (CH₂), 13.8 (CH₃), 12.7 (CH₃), 12.6 (CH₃); HRMS (ESI, +ve) calcd for C₃₀H₃₇N₃O₄S₂ ([M+H]+): 568.2298, found: 568.2301.

**Compound 3.** To a solution of 9 (78 mg, 73 µmol), 30 (150 mg, 0.220 mmol) and TEA (150 µL, 1.08 mmol) in dry CH₂Cl₂ (10 mL), HBTU (111 mg, 0.293 mmol) was added and the mixture was stirred at rt for 4 h. After this time, the solvent was evaporated and the residue was purified by silica gel chromatography (CH₂Cl₂/MeOH 40:1), affording 3 as a dark red powder (62 mg, 57%). Rf (CH₂Cl₂/MeOH 20:1): 0.30; Mp: >200 °C (decomp.); IR (neat): 2929 (w), 2856 (w), 1662 (s), 1526 (m), 1438 (m), 1320 (m), 1184 (s), 1127 (s), 748 (s); ¹H NMR (400 MHz, CDCl₃, δ₁/δ₂, isomeric peaks): 8.61/8.48 (s, 1H), 8.37 (s, 1H), 7.55 – 7.34 (m, 1H), 7.17 – 7.04 (m, 1H), 5.37 – 5.03 (m, 2H), 4.19 – 4.01 (m, 2H), 3.96 – 3.53 (m, 2H), 3.24 – 2.96 (m, 4H), 2.91 – 2.77 (m, 1H), 2.72 – 2.57 (m, 1H), 2.48 – 2.32 (m, 2H), 2.28/2.07 (s, 6H), 2.02 – 1.82 (m, 6H), 1.74 – 1.54 (m, 4H), 1.47/1.42 (t, ³J(H,H) = 7.6 Hz, 6H), 0.94 – 0.86 (m, 3H); ¹³C NMR (101 MHz, CDCl₃): 165.2 (C), 163.7 (C), 163.4 (C), 163.2 (C), 162.9 (C), 162.7 (C), 162.4 (C), 162.0 (C), 149.2 (C), 148.9 (C), 148.7 (C), 148.7 (C), 147.1 (C), 146.8 (C), 146.7 (C), 146.1 (C), 145.7 (C), 145.4 (C), 145.2 (C), 145.1 (C), 145.0 (C), 144.9 (C), 144.8 (C), 144.7 (C), 144.7 (C), 144.6 (C), 144.6 (C), 144.5 (C), 144.4 (C), 143.5 (C), 143.4 (C), 143.2 (C), 143.0 (C), 143.0 (C), 142.9 (C), 142.8 (C), 142.7 (C), 142.6 (C), 142.4 (C), 142.4 (C), 142.1 (C), 142.0 (C), 141.9 (C), 141.9 (C), 141.8 (C), 141.6 (C), 141.2 (C), 141.1 (C), 140.7 (C), 140.6 (C), 140.6 (C), 140.3 (C), 140.0 (C), 139.8 (C), 139.2 (C), 139.0 (C), 138.9 (C), 137.9 (C), 137.4 (C), 137.3 (C), 128.5 (CH), 128.4 (CH), 128.0 (CH), 125.3 (C), 125.2 (C), 125.1 (C), 124.6 (C), 124.3 (C), 123.4 (C), 120.0 (C), 119.2 (C), 118.9 (C), 74.3 (C), 74.0 (C), 73.3 (C), 73.1 (C), 66.5 (CH), 66.2 (CH), 59.3 (C), 58.2 (C), 57.4 (CH), 57.1 (CH), 52.4 (CH), 51.8 (CH), 49.8 (CH), 49.3 (CH), 41.1 (CH₂), 41.0 (CH₂), 40.4 (CH₃), 40.0 (CH₃), 33.6 (CH₂), 33.0 (CH₂), 32.6 (CH₂), 31.7 (CH₂), 31.7 (CH₂), 28.7 (CH₂), 28.4 (CH₂), 28.3 (CH₂), 27.0 (CH₂), 27.0 (CH₂), 26.6 (CH₂), 26.6 (CH₂), 25.9 (CH₂), 25.8 (CH₂), 25.3 (CH₂), 24.9 (CH₂), 24.7 (CH₂), 22.7 (CH₂), 22.7 (CH₂), 21.2 (CH₂), 21.2 (CH₂), 14.3 (CH₃), 13.1 (CH₃), 13.1 (CH₃); HRMS (ESI, +ve) calcd for C₁₄₁H₁₃₇N₃O₆S₂ ([M+H]+): 1496.3510, found: 1496.3535.

**Compound 31.** To a solution of 15 (120 mg, 0.171 mmol) in CH₂Cl₂ (3 mL), TFA (1 mL) was added and the mixture was stirred at rt for 2 h. After this time, solvent was evaporated, affording 31 as a bright red powder (122 mg, quant.). Mp: >140 °C (decomp.); IR (neat): 2950 (m), 2866 (w), 1705 (m), 1656 (s), 1445 (m), 1304 (s), 1245 (m), 1194 (m), 1132 (s), 1041 (m), 1016 (s), 792 (m); ¹H NMR (400 MHz, CDCl₃): 9.64 – 8.76 (m, 2H), 8.04 (br s, 2H), 5.20 – 5.01 (m, 1H), 4.49 – 4.04
(m, 3H), 3.47 – 2.79 (m, 4H), 2.64 – 2.41 (m, 1H), 2.41 – 2.22 (m, 1H), 2.03 – 1.79 (m, 3H), 1.79 – 1.62 (m, 3H), 1.50 – 1.16 (m, 15H), 0.96 – 0.82 (m, 3H); 13C NMR (101 MHz, CDCl3): 163.8 (C), 163.7 (C), 163.1 (C), 162.8 (C), 162.7 (C), 161.3 (C), 161.2 (C), 160.5 (C), 160.1 (C), 153.4 (C), 153.2 (C), 152.4 (C), 152.0 (C), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.0 (C), 126.8 (C), 126.6 (C), 126.3 (C), 124.2 (C), 123.0 (C), 122.9 (C), 56.1 (CH), 50.8 (CH), 49.8 (CH2), 49.5 (CH2), 49.0 (CH2), 48.9 (CH2), 48.8 (CH2), 41.5 (CH2), 31.5 (CH2), 31.5 (CH2), 27.9 (CH2), 26.8 (CH2), 26.8 (CH2), 25.0 (CH2), 23.8 (CH2), 22.7 (CH2), 22.6 (CH2), 14.1 (CH3), 7.5 (CH3), 7.3 (CH3), 7.3 (CH3), 7.1 (CH3), 7.0 (CH3); HRMS (ESI, +ve) calcd for C30H37N3O6S2 ([M+H]+): 600.2197, found: 600.2204.

**Compound 4.** To a solution of 9 (40 mg, 38 µmol), 31 (54 mg, 75 µmol) and TEA (53 µL, 0.38 mmol) in dry CH2Cl2 (6 mL), HBTU (57 mg, 0.15 mmol) was added and the mixture was stirred at rt for 4 h. After this time, the mixture was poured directly on a pad of silica gel and the product was eluted (CH2Cl2/MeOH 30:1), dried and completely purified by PTLC (CH2Cl2/MeOH 40:1), affording 4 as a dark orange powder (32 mg, 56%). Rf (CH2Cl2/MeOH 20:1): 0.25; Mp: >300 °C (decomp.); IR (neat): 3357 (w), 2928 (m), 2857 (m), 1680 (m), 1655 (s), 1521 (m), 1442 (m), 1371 (m), 1302 (s), 1242 (s), 1189 (m), 1060 (s), 905 (m), 790 (m), 725 (s), 644 (m); 1H NMR (500 MHz, CDCl3): 9.58 – 9.28 (m, 2H), 7.63 – 7.37 (m, 1H), 7.20 – 7.00 (m, 1H), 5.44 – 5.23 (m, 1H), 5.21 – 5.02 (m, 1H), 4.21 – 4.05 (m, 2H), 3.88 – 3.54 (m, 2H), 3.43 – 3.07 (m, 2H), 3.00 – 2.86 (m, 1H), 2.79 – 2.64 (m, 1H), 2.61 – 2.41 (m, 2H), 2.27 – 2.12 (m, 7H), 2.02 – 1.84 (m, 6H), 1.82 – 1.59 (m, 5H), 1.55 – 1.19 (m, 16H), 0.95 – 0.90 (m, 3H); 13C NMR (126 MHz, CDCl3): 163.1 (C), 163.1 (C), 163.0 (C), 163.0 (C), 162.9 (C), 162.9 (C), 162.8 (C), 162.5 (C), 162.4 (C), 161.1 (C), 161.1 (C), 156.4 (C), 156.0 (C), 155.6 (C), 155.5 (C), 155.1 (C), 147.0 (C), 146.9 (C), 146.3 (C), 146.3 (C), 145.7 (C), 145.6 (C), 145.5 (C), 145.5 (C), 145.4 (C), 145.4 (C), 145.3 (C), 145.3 (C), 145.2 (C), 145.2 (C), 145.2 (C), 145.1 (C), 145.1 (C), 145.1 (C), 145.0 (C), 145.0 (C), 144.9 (C), 144.9 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.8 (C), 144.7 (C), 144.7 (C), 144.6 (C), 144.6 (C), 144.5 (C), 144.5 (C), 144.4 (C), 144.4 (C), 144.3 (C), 144.3 (C), 144.3 (C), 144.3 (C), 144.3 (C), 144.2 (C), 144.1 (C), 144.1 (C), 144.0 (C), 143.9 (C), 143.9 (C), 143.8 (C), 143.8 (C), 143.7 (C), 143.7 (C), 143.5 (C), 143.5 (C), 143.5 (C), 143.3 (C), 143.2 (C), 143.1 (C), 143.1 (C), 143.0 (C), 143.0 (C), 142.9 (C), 142.8 (C), 142.7 (C), 142.7 (C), 142.7 (C), 142.5 (C), 142.5 (C), 142.4 (C), 142.4 (C), 142.3 (C), 142.3 (C), 142.2 (C), 142.1 (C), 142.1 (C), 142.0 (C), 142.0 (C), 142.0 (C), 141.9 (C), 141.8 (C), 141.4 (C), 141.3 (C), 141.1 (C), 140.9 (C), 140.9 (C), 140.8 (C), 140.8 (C), 140.7 (C), 140.7 (C), 140.6 (C), 140.5 (C), 139.9 (C), 139.9 (C), 139.6 (C), 139.5 (C), 139.3 (C), 139.0 (C), 138.6 (C), 138.2 (C), 138.1 (C), 138.0 (C), 138.0 (C), 137.8 (C), 137.8 (C), 137.7 (C), 137.7 (C), 137.6 (C), 137.5 (C), 137.4 (C), S11
Compound 32. To a solution of 16 (150 mg, 0.205 mmol) in CH₂Cl₂ (5 mL), TFA (1.5 mL) was added and the mixture was stirred at rt for 2 h. After this time, solvent was evaporated, affording 32 as a pale yellow powder (152 mg, quant.). Mp: >150 °C (decomp.); IR (neat): 3193 (w), 2929 (w), 1719 (m), 1669 (s), 1433 (m), 1374 (w), 1306 (s), 1202 (m), 1129 (s), 1047 (w), 717 (m); ¹H NMR (400 MHz, DMSO-d₆): 9.27 (s, 1H), 9.25 (s, 1H), 8.10 (br s, 3H), 5.05 – 4.83 (m, 1H), 4.23 – 3.94 (m, 7H), 2.42 – 2.27 (m, 1H), 2.20 – 2.11 (m, 1H), 1.99 – 1.90 (m, 1H), 1.90 – 1.79 (m, 2H), 1.70 (q, 3J(H,H) = 8.0 Hz, 2H), 1.63 – 1.50 (m, 1H), 1.46 – 1.21 (m, 14H), 0.88 (t, 3J(H,H) = 7.0 Hz, 3H); ¹³C NMR (101 MHz, DMSO-d₆): 161.1 (C), 160.5 (C), 158.3 (C), 158.0 (C), 143.3 (C), 131.1 (CH), 129.1 (C), 127.7 (C), 126.7 (C), 55.7 (CH), 55.6 (CH), 49.4 (CH), 49.3 (CH₂), 40.9 (CH₂), 30.9 (CH₂), 30.4 (CH₂), 27.2 (CH₂), 26.2 (CH₂), 24.7 (CH₂), 23.5 (CH₂), 22.0 (CH₂), 13.9 (CH₃), 7.3 (CH₃), 7.1 (CH₃); HRMS (ESI, +ve) calcd for C₁₀₁H₅₅N₅O₈S₂ ([M+H]⁺): 1528.3408, found: 1528.3391.

Compound 5. To a solution of 9 (40 mg, 38 µmol), 32 (56 mg, 75 µmol) and TEA (53 µL, 0.380 mmol) in dry CH₂Cl₂ (6 mL), HBTU (57 mg, 0.150 mmol) was added and the mixture was stirred at rt for 4 h. After this time, the mixture was poured directly on a pad of silica gel and the product was eluted (CH₂Cl₂/MeOH 40:1), dried and completely purified by PTLC (CH₂Cl₂/MeOH 40:1), affording 5 as a dark purple powder (29 mg, 49%). Rₜ (CH₂Cl₂/MeOH 20:1): 0.30; Mp: >300 °C (decomp.); IR (neat): 2936 (w), 2858 (w), 1671 (s), 1529 (w), 1427 (m), 1301 (s), 1133 (s), 1045 (w), 791 (w), 710 (m); ¹H NMR (500 MHz, CDCl₃, 1% TFA, δ/δ: isomeric peaks): 9.52/9.34 (s, 1H), 9.47 (s, 1H), 9.40/8.67 (d, 3J(H,H) = 7.9 Hz, 1H), 9.21/8.17 (br s, 1H), 8.32/7.98 (d, 3J(H,H) = 7.4 Hz, 1H), 5.49 – 5.38/5.14 – 5.05 (m, 1H), 5.28 – 5.18 (m, 1H), 4.44 – 4.29 (m, 1H), 4.25 – 4.06 (m, 4H), 4.06 – 3.82 (m, 2H), 3.82 – 3.52 (m, 1H), 3.21 – 2.83 (m, 6H), 2.68 – 2.38 (m, 2H), 2.34 – 1.87 (m, 8H), 1.85 – 1.51 (m, 8H), 1.50 – 1.38 (m, 8H), 1.38 – 1.30 (m, 4H), 0.96 – 0.89 (m, 3H); ¹³C NMR (126 MHz, CDCl₃): 165.7 (C), 165.2 (C), 164.5 (C), 163.2 (C), 161.8 (C), 161.1 (C), 160.8 (C), 160.6 (C), 160.5 (C), 160.4 (C), 146.1 (C), 145.7 (C), 145.6 (C), 145.6 (C), 145.4 (C), 145.4 (C), 145.3 (C), 145.2 (C), 145.1 (C), 145.0 (C), 145.0 (C), 144.9 (C), 144.8 (C), 144.8 (C),
144.7 (C), 144.6 (C), 144.5 (C), 144.4 (C), 144.0 (C), 143.9 (C), 143.8 (C), 143.7 (C), 143.6 (C), 143.4 (C), 143.3 (C), 143.1 (C), 143.0 (C), 142.9 (C), 142.7 (C), 142.3 (C), 142.2 (C), 141.9 (C), 141.8 (C), 141.7 (C), 141.6 (C), 141.4 (C), 141.1 (C), 140.5 (C), 140.4 (C), 139.7 (C), 139.1 (C), 137.4 (C), 137.1 (C), 136.8 (C), 136.7 (C), 136.6 (C), 136.3 (C), 136.2 (C), 134.2 (CH), 134.1 (CH), 134.0 (CH), 129.9 (C), 129.7 (C), 129.6 (C), 129.2 (C), 128.1 (C), 127.8 (C), 127.7 (C), 127.5 (C), 127.3 (C), 127.1 (C), 73.3 (C), 72.4 (C), 72.2 (C), 72.0 (C), 68.5 (CH), 68.2 (CH), 57.3 (C), 57.0 (CH), 56.2 (C), 53.6 (CH₂), 53.0 (CH), 51.5 (CH), 51.3 (CH₂), 51.2 (CH), 50.8 (CH), 42.3 (CH₃), 42.2 (CH₂), 39.1 (CH₃), 38.8 (CH₃), 32.5 (CH₂), 32.2 (CH₂), 31.6 (CH₂), 31.5 (CH₂), 28.8 (CH₂), 28.4 (CH₂), 28.2 (CH₂), 28.1 (CH₂), 26.9 (CH₂), 25.4 (CH₂), 25.2 (CH₂), 24.8 (CH₂), 24.4 (CH₂), 24.1 (CH₂), 24.1 (CH₂), 24.0 (CH₂), 23.9 (CH₂), 23.8 (CH₂), 22.7 (CH₂), 14.2 (CH₃), 14.2 (CH₃), 7.5 (CH₃), 7.4 (CH₃), 7.4 (CH₃); HRMS (ESI, +ve) calcd for C₁₀₁H₅₃N₅O₁₀S₂ ([M+H]+): 1560.3306, found: 1560.3256.

Scheme S4. (a) HBTU, TEA, CH₂Cl₂, 1 h, rt, 95%; (b) 7, I₂, DBU, toluene, 2 h, rt, 41%; (c) TFA, CH₂Cl₂, rt, overnight, 97%; (d) 10, HBTU, TEA, CH₂Cl₂, 3 h, rt, 88%.

Compound 11. To a solution of 33 (475 µL, 2.68 mmol), 23 (515 mg, 3.22 mmol) and TEA (750 µL, 5.36 mmol) in dry CH₂Cl₂ (10 mL), HBTU (1.22 g, 3.22 mmol) was added and the mixture was stirred at rt for 1 h. The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with NaHCO₃ (sat. 3 x 20 mL) and aq. NaCl (sat. 1 x 20 mL), dried over Na₂SO₄ and concentrated in vacuo to give pure product 11 as a colorless solid (785 mg, 95%). Mp: 109 – 110 °C; IR (neat): 3290 (m), 2904 (s), 2849 (m), 1735 (s), 1644 (s), 1560 (m), 1450 (w), 1365 (w), 1328 (m), 1283 (m), 1239 (m), 1138 (m), 965 (m), 840 (m); ¹H NMR (400 MHz, CDCl₃): 7.19 (br s, 1H), 3.21 (s, 2H), 2.96 (d, 3J = 6.2 Hz, 2H), 1.98 – 1.93 (m, 3H), 1.72 – 1.66 (m, 3H), 1.63 – 1.58 (m, 3H), 1.52 – 1.42 (m, 15H); ¹³C NMR
(101 MHz, CDCl₃): 169.2 (C), 165.6 (C), 82.5 (C), 51.1 (CH₂), 42.5 (CH₂), 40.2 (CH₂), 37.0 (CH₂), 33.7 (C), 28.3 (CH), 28.1 (CH₃); HRMS (ESI, +ve) calcd for C₁₈H₂₉NO₃ ([M+H]⁺): 308.2220, found: 308.2219.

**Compound 34.** To a solution of 11 (0.24 g, 0.78 mmol), C₆₀ fullerene 7 (1.00 g, 1.39 mmol) and I₂ (0.35 g, 1.39 mmol) in toluene (500 mL), DBU (0.35 mL, 2.34 mmol) was added dropwise. The resulting mixture was allowed to react for 2 h and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted C₆₀ was recovered using CS₂ and 34 was eluted using CH₂Cl₂/CS₂ 2:1). After this, solvent was evaporated and the residue was triturated with MeOH (2 x 20 mL), affording 34 as a brown powder (330 mg, 41%). Rₚ (CS₂/CH₂Cl₂ 2:1): 0.40; Mp: >300 °C (decomp.); IR (neat): 3429 (w), 3345 (w), 2899 (s), 2845 (m), 1687 (m), 512 (m), 1520 (m), 1428 (m), 1367 (m), 1245 (s), 1185 (m), 1159 (s), 1116 (m), 844 (m), 732 (m); ¹H NMR (400 MHz, CDCl₃): 6.90 (t, 3J(H,H) = 6.5 Hz, 1H), 3.26 (d, 3J(H,H) = 6.5 Hz, 2H), 2.07 – 2.00 (m, 3H), 1.78 – 1.71 (m, 3H), 1.70 – 1.62 (m, 18H); ¹³C NMR (101 MHz, CDCl₃): 164.1 (C), 161.6 (C), 146.3 (C), 146.2 (C), 145.5 (C), 145.4 (C), 145.3 (C), 145.3 (C), 144.9 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.8 (C), 144.6 (C), 144.0 (C), 143.9 (C), 143.2 (C), 143.2 (C), 143.1 (C), 143.1 (C), 140.3 (C), 142.3 (C), 142.3 (C), 142.3 (C), 142.2 (C), 142.2 (C), 141.1 (C), 141.1 (C), 138.7 (C), 137.9 (C), 85.9 (C), 73.5 (C), 57.5 (C), 52.3 (CH₂), 40.4 (CH₂), 37.1 (CH₂), 34.6 (C), 28.4 (CH), 28.3 (CH₃); HRMS (ESI, +ve) calcd for C₇₈H₂₇NO₃ ([M+H]⁺): 1026.2064, found: 1026.2063.

**Compound 35.** To a solution of 34 (320 mg, 0.310 mmol) in CH₂Cl₂ (12 mL), TFA (4 mL) was added and the mixture was stirred at rt overnight. After this time, solvent was evaporated, affording 35 as a brown powder (290 mg, 97%). Mp: >300 °C (decomp.); IR (neat): 3367 (w), 2901 (m), 1778 (w), 1646 (m), 1535 (m), 1428 (m), 1206 (s), 1187 (s), 1159 (s), 902 (m), 799 (m), 728 (s), 698 (m); ¹H NMR (400 MHz, oDCB-d₄): 8.37 (s, 1H), 7.61 (s, 1H), 3.39 (s, 2H), 1.96 (s, 3H), 1.65 (s, 12H); ¹³C NMR (126 MHz, oDCB-d₄): 164.1 (C), 159.2 (C), 144.8 (C), 144.7 (C), 144.7 (C), 144.6 (C), 144.4 (C), 144.3 (C), 144.2 (C), 144.1 (C), 143.9 (C), 143.3 (C), 143.2 (C), 142.7 (C), 142.6 (C), 142.5 (C), 142.4 (C), 141.7 (C), 141.6 (C), 141.3 (C), 140.6 (C), 139.3 (C), 137.9 (C), 72.4 (C), 55.8 (C), 52.9 (CH₂), 40.0 (CH₂), 36.6 (CH₂), 34.1 (C), 28.2 (CH₃); HRMS (ESI, +ve) calcd for C₇₄H₁₉NO₃ ([M+H]⁺): 970.1438, found: 970.1456.

**Compound 36.** To a solution of 35 (32 mg, 33 µmol), 10 (21 mg, 100 µmol) and TEA (37 µL, 0.27 mmol) in dry CH₂Cl₂ (10 mL), HBTU (50 mg, 0.13 mmol) was added and the mixture was stirred at rt for 3 h. Then, 1 eq more of HBTU is added and the reaction mixture was stirred 1 h more.
After this time, the mixture was poured directly on a pad of silica gel and the product was eluted (CH$_2$Cl$_2$/MeOH 30:1), dried and triturated with MeOH (2 x 20 mL), affording 36 as a brown powder (34 mg, 88%). $R_t$ (CH$_2$Cl$_2$/MeOH 30:1): 0.43; Mp: >300 °C (decomp.); IR (neat): 3297 (w), 2899 (s), 2846 (m), 1715 (m), 1660 (s), 1536 (s), 1449 (m), 1428 (m), 1186 (m), 1157 (s), 727 (m), 696 (m); $^1$H NMR (500 MHz, CDCl$_3$): 7.89 (d, $^3$J (H,H) = 5.7 Hz, 1H), 7.58 (br s, 1H), 4.73 (d, $^3$J (H,H) = 5.7 Hz, 1H), 3.82 – 3.69 (m, 1H), 3.58 – 3.47 (m, 1H), 3.34 – 3.00 (m, 2H), 2.33 – 2.21 (m, 1H), 2.20 – 2.10 (m, 1H), 2.05 – 1.95 (m, 3H), 1.80 – 1.68 (m, 6H), 1.67 – 1.55 (m, 8H), 1.46 (s, 9H), 1.40 – 1.19 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$): 163.8 (C), 162.6 (C), 156.8 (C), 147.0 (C), 146.5 (C), 146.2 (C), 146.0 (C), 145.6 (C), 145.5 (C), 145.4 (C), 145.3 (C), 145.2 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.6 (C), 144.6 (C), 144.5 (C), 144.0 (C), 143.9 (C), 143.9 (C), 143.8 (C), 143.3 (C), 143.2 (C), 143.1 (C), 143.0 (C), 142.5 (C), 142.4 (C), 142.3 (C), 142.3 (C), 142.2 (C), 141.2 (C), 141.1 (C), 141.0 (C), 138.6 (C), 138.3 (C), 138.2 (C), 137.9 (C), 80.4 (C), 74.5 (C), 73.8 (C), 59.3 (C), 56.3 (CH), 53.9 (CH), 52.3 (CH$_2$), 40.5 (CH$_2$), 37.1 (CH$_2$), 34.7 (C), 33.0 (CH$_2$), 32.4 (CH$_2$), 28.7 (CH$_3$), 28.4 (CH), 24.8 (CH$_2$), 24.7 (CH$_2$); HRMS (ESI, +ve) calcd for C$_{85}$H$_{39}$N$_3$O$_4$ ([M+H$^+$]+): 1166.3013, found: 1166.3001.

Scheme S5. (a) TFA, CH$_2$Cl$_2$, rt, 2h, quant.; (b) 9, HBTU, TEA, CH$_2$Cl$_2$, rt, overnight, 55%.

**Compound 12.** To a solution of 36 (32 mg, 27 µmol) in CH$_2$Cl$_2$ (6 mL), TFA (2 mL) was added and the mixture was stirred at rt for 2 h. After this time, solvent was evaporated, affording 12 as a brown powder (32 mg, quant.). Mp: >300 °C (decomp.); IR (neat): 3282 (w), 2901 (m), 2847 (m), 1715 (m), 1660 (s), 1536 (s), 1449 (m), 1428 (m), 1186 (m), 1157 (s), 727 (m), 696 (m); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 19:1): 4.18 – 4.01 (m, 1H), 3.38 – 3.28 (m, 1H), 3.27 – 3.10 (m, 2H), 2.28 – 2.15 (m, 3H), 2.09 – 2.02 (m, 1H), 1.88 – 1.79 (m, 2H), 1.71 – 1.55 (m, 13H), 1.53 – 1.32 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$/CD$_3$OD 19:1): 164.3 (C), 163.7 (C), 146.9 (C), 146.3 (C), 145.7 (C), 145.6 (C), 145.5 (C), 145.4 (C), 145.3 (C), 144.8 (C), 144.8 (C), 144.8 (C), 144.7 (C), 144.7 (C), 144.6 (C), 144.6 (C), 144.5 (C), 144.5 (C), 144.4 (C), 143.8 (C), 143.3 (C), 143.2 (C), 143.1 (C), 143.0 (C), 142.5 (C), 142.4 (C), 142.3 (C), 142.2 (C), 141.2 (C), 141.1 (C), 141.0 (C), 138.6 (C), 138.3 (C), 138.2 (C), 137.9 (C), 80.4 (C), 74.5 (C), 73.8 (C), 59.3 (C), 56.3 (CH), 53.9 (CH), 52.3 (CH$_2$), 40.5 (CH$_2$), 37.1 (CH$_2$), 34.7 (C), 33.0 (CH$_2$), 32.4 (CH$_2$), 28.7 (CH$_3$), 28.4 (CH), 24.8 (CH$_2$), 24.7 (CH$_2$); HRMS (ESI, +ve) calcd for C$_{80}$H$_{31}$N$_3$O$_2$ ([M+H$^+$]+): 1066.2489, found: 1066.2498.
**Compound 1.** To a solution of 9 (30 mg, 28 µmol), 12 (67 mg, 57 µmol) and TEA (39 µL, 0.280 mmol) in dry CH$_2$Cl$_2$ (10 mL), HBTU (43 mg, 0.113 mmol) was added and the mixture was stirred at rt for 4 h, adding 1 eq more of HBTU every hour. Then, the reaction mixture was stirred at rt overnight. After this time, the mixture was poured directly on a pad of silica gel and the product was eluted (CH$_2$Cl$_2$/MeOH 20:1), dried and triturated with MeOH (2 x 20 mL), affording 1 as a brown powder (11 mg, 55%). $R_f$ (CH$_2$Cl$_2$/MeOH 9:1): 0.41; Mp: >300 °C (decomp.); IR (neat): 2901 (s), 2846 (m), 1659 (s), 1532 (s), 1429 (m), 1311 (w), 1157 (s), 902 (w), 797 (m), 726 (m), 699 (m); $^1$H NMR (400 MHz, CDCl$_3$): 8.61 (d, $^3$$J$ (H,H) = 9.4 Hz, 1H), 8.20 (d, $^3$$J$ (H,H) = 9.0 Hz, 1H), 7.95 (d, $^3$$J$ (H,H) = 6.5 Hz, 1H), 7.26 – 7.70 (m, 1H), 4.52 – 4.27 (m, 2H), 4.16 – 4.03 (m, 1H), 2.87 – 2.75 (m, 1H), 2.91 – 2.81 (m, 1H), 2.55 (s, 6H), 2.48 – 2.38 (m, 2H), 2.37 – 2.03 (m, 3H), 1.99 – 1.86 (m, 6H), 1.84 – 1.76 (m, 1H), 1.71 – 1.52 (m, 12H), 1.48 – 1.27 (m, 8H); $^{13}$C NMR (126 MHz, CDCl$_3$): 167.7 (C), 164.4 (C), 163.6 (C), 163.4 (C), 149.0 (C), 147.4 (C), 146.9 (C), 146.4 (C), 146.1 (C), 146.0 (C), 145.9 (C), 145.8 (C), 145.6 (C), 145.6 (C), 145.5 (C), 145.4 (C), 145.4 (C), 145.4 (C), 145.3 (C), 145.3 (C), 145.2 (C), 145.2 (C), 145.2 (C), 145.1 (C), 145.0 (C), 145.0 (C), 144.9 (C), 144.9 (C), 144.8 (C), 144.8 (C), 144.7 (C), 144.6 (C), 144.5 (C), 144.4 (C), 144.3 (C), 144.2 (C), 144.1 (C), 144.1 (C), 144.1 (C), 143.9 (C), 143.8 (C), 143.7 (C), 143.5 (C), 143.4 (C), 143.3 (C), 143.3 (C), 143.3 (C), 143.2 (C), 143.2 (C), 143.1 (C), 143.0 (C), 142.9 (C), 142.8 (C), 142.5 (C), 142.4 (C), 142.4 (C), 142.4 (C), 142.3 (C), 142.2 (C), 142.1 (C), 142.0 (C), 142.0 (C), 141.9 (C), 141.9 (C), 141.8 (C), 141.7 (C), 141.7 (C), 141.6 (C), 141.6 (C), 141.3 (C), 141.2 (C), 140.9 (C), 140.9 (C), 140.4 (C), 140.3 (C), 139.5 (C), 138.7 (C), 137.9 (C), 137.5 (C), 137.4 (C), 137.1 (C), 137.1 (C), 137.1 (C), 75.1 (C), 74.3 (C), 73.7 (C), 72.9 (C), 68.5 (CH), 58.9 (C), 57.4 (CH), 56.9 (C), 53.5 (CH$_2$), 52.9 (CH), 50.4 (CH), 41.6 (CH$_3$), 40.5 (CH$_2$), 36.9 (CH$_2$), 34.2 (C), 33.7 (CH$_2$), 32.4 (CH$_2$), 31.8 (CH$_2$), 28.3 (CH), 25.4 (CH$_2$), 25.4 (CH$_2$), 25.3 (CH$_2$), 24.7 (CH$_2$), 21.0 (CH$_2$); HRMS (ESI, +ve) caled for C$_{151}$H$_{47}$N$_5$O$_4$ ([M+H]$^+$): 1994.3701, found: 1994.3709.
3. Computational Studies

3.1. Theoretical Methods

The energies of all complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory. The calculations have been performed by using the program TURBOMOLE version 7.0.[8] For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3).[9] The minimum nature of the compounds has been confirmed by performing frequency calculations. The MEP surfaces have been carried out by means of the SPARTAN software.[10] In order to reproduce solvent effects, we have used the conductor-like screening model COSMO,[11] which is a variant of the dielectric continuum solvation models.[12] We have used THF as solvent.

3.2. Preliminary Geometry and MEP Surface Analysis of NDI-Based Catalysts

In Figures S1 and S2 we show the optimized geometries of catalysts 2–6. The distance between the π-system and the fullerene is quite short, thus indicating a strong interaction between both moieties. In Figure S3 we show the MEP surfaces and molecular polarizability values (α) of catalysts 2–6.

3.3. Details on Back-Donation

As mentioned in the main text, in catalysts 4 and 5, the electron deficient NDIs are expected to remove electron density from the fullerene and, consequently, increase the ability of the fullerene sphere to stabilize the enolate form of the substrate with the concomitant enhance of the addition product rate. However, the experimental trend does not follow the expected behavior considering the electron withdrawing ability of the substituents, that is (-SEt < -SOEt < -SO₂Et). It has been argued in the main text the existence of back-donation from the electron rich O atoms of the substituent to the fullerene in catalysts 4 and 5. To confirm this issue, we represent in Figure S4 the optimized geometries of catalysts 4, 4’ (same as 4 with an alternative conformation of the –SOEt groups) and 5. From the inspection of the geometries, it can be clearly observed that the O atoms are close to the π-system of the fullerene, thus counterbalancing the effect of the π–π interactions and supporting the back-donation.
**Figure S1.** RI-PB86-D3/def2-TZVP optimized geometries of catalysts 2-5. Distances in Å measured from the closest C atoms apart from catalyst 4 that it is measured from the middle of the NDI CC bond to the closest C atom of the NDI. H-atoms omitted for clarity.

**Figure S2.** RI-PB86-D3/def2-TZVP optimized geometries of catalyst 6.
**Figure S3.** MEP surfaces of catalyst 2-6 at the B3LYP/6-31+G* level of theory. Selected MEP values are indicated in kJ/mol. The molecular polarizabilities (α) are also indicated.

**Figure S4.** RI-PB86-D3/def2-TZVP optimized geometries of catalysts 4, 4’ and 5. Lone pair–π distances are measured from the ring centroid to the O atom in 4 and from a C atom of the fullerene to the O atoms in 5. H-atoms apart omitted for clarity. Distances in Å.
4. Spectroscopic Characterization

4.1. UV-Vis Spectra

*Figure S5.* UV-vis absorption spectra of catalysts and NDI references ($c = 25 \mu M$, CHCl$_3$). a) 2 (blue line), 13 (dotted blue line). b) 3 (red line), 14 (dotted red line). c) 4 (red line), 15 (dotted red line). d) 5 (red line), 16 (dotted red line). e) 1 (purple line). Catalyst 6 (black line in all spectra).
4.2. Circular Dichroism Spectra

**Figure S6.** CD spectra of catalyst and NDI references \((c = 50 \mu M, \text{CHCl}_3\)). a) 2 (blue line), 13 (dotted blue line). b) 3 (red line), 14 (dotted red line). c) 4 (red line), 15 (dotted red line). d) 5 (red line), 16 (dotted red line). e) 1 (purple line). Catalyst 6 (black line in all spectra). f) CD titration of catalyst 6 with additive 21.
5. Electrochemistry

Reduction potentials of 1-6 and 13-16 were determined using differential pulse voltammetry (DPV, scan rate 20 mV/s) vs Fc⁺/Fc in CH₂Cl₂ (supporting electrolyte: 100 mM TBAPF₆, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: SCE) (Figure S7). Each reduction potential of 1-5 was assigned to either fullerene centered, or NDI centered by comparing the reversibility in cyclic voltammetry (CV, scan rate 50 mV/s) with those of 6 (irreversible reduction wave) and of 13-16 (reversible reduction waves) (Figure S8).

5.1. Differential Pulse Voltammograms

Figure S7. Normalized differential pulse voltammograms relative to the internal Fc⁺/Fc standard (adjusted at 0 V). a) 2 (blue line), 13 (dotted blue line). b) 3 (red line), 14 (dotted red line). c) 4 (red line), 15 (dotted red line). d) 5 (red line), 16 (dotted red line). e) 1 (purple line). Catalyst 6 (black line in all voltammograms).
5.2. Cyclic Voltammograms

Figure S8. Cyclic voltammograms relative to the internal Fe⁺/Fe standard. a) 2 (blue line), 13 (dotted blue line). b) 3 (red line), 14 (dotted red line). c) 4 (red line), 15 (dotted red line). d) 5 (red line), 16 (dotted red line). e) 1 (purple line). Catalyst 6 (black line in all voltammograms). Dotted black line between voltammograms of catalyst 6 and 1-5 represents the shift in the irreversible first reduction wave of the fullerene (assigned in comparison with the reversible reduction waves of the NDIs).
6. **Catalyst Evaluation in MAHT Addition**

Scheme S6. Base catalyzed reaction between MAHT 17 and nitroolefin 18 to afford addition product 19 or decarboxylation product 20.

The catalysts were evaluated following a previously published protocol. Solutions of substrates 17 (200 mM) and 18 (2.0 M) and catalysts 1 to 6 (40 mM) were prepared in THF-d8 (conditions 1 in the manuscript) or CDCl3/THF-d8 1:1 (conditions 2 in the manuscript) and stirred at 20 °C until the reaction was completed (around 20-30 h) (Scheme S6). After this time, crude mixture was filtered through a pad of silica to remove the catalyst, using CDCl3 as eluent (0.7 mL). 1H NMR spectra of the mixture diluted in CDCl3 were recorded and integrals associated with the protons alpha to the carbonyl group of the addition product 19 (δ 3.07 ppm; d, 2H) and decarboxylation product 20 (δ 2.38 ppm; s, 3H) were observed. Addition/decarboxylation ratio A/D for MAHT addition was determined from the ratio of addition to decarboxylation products measured at the end of the reaction, according to the equation S1. Each catalyst was tested up to four times.

$$A/D = \frac{\int \text{Addition}}{\int \text{Decarboxylation}} \times \frac{H_D}{H_A}$$  \hspace{1cm} (S1)

here $H_A = 2.0$ and $H_D = 3.0$ for integrals measured at δ 3.07 and 2.38 ppm, respectively.

The spectroscopic data obtained for product 19 were identical to the ones reported in the literature.\[^{[S1,S2,S13]}\]
7. References

[S1] J. López-Andarias, A. Frontera, S. Matile, J. Am. Chem. Soc. 2017, 139, 13296–13299.

[S2] Y. Cotelle, S. Benz, A.-J. Avestro, T.R. Ward, N. Sakai, S. Matile, Angew. Chem. Int. Ed. 2016, 55, 4275–4279, Angew. Chem. 2016, 128, 4347–4351.

[S3] T. Kanemitsu, S. Furukoshi, M. Miyazaki, K. Nagata, T. Itoh, Tetrahedron: Asymmetry 2015, 26, 214–218.

[S4] N. R. Amarasinghe, P. Turner, M. H. Todd, Adv. Synth. Catal. 2012, 354, 2954–2958.

[S5] D. W. Lee, H. J. Ha, Synth. Commun. 2007, 37, 737–742.

[S6] F. N. Miros, Y. Zhao, G. Sargsyan, M. Pupier, C. Besnard, C. Beuchat, J. Mareda, N. Sakai, S. Matile, Chem. Eur. J. 2016, 22, 2648–2657.

[S7] M. Akamatsu, S. Matile, Synlett 2016, 27, 1041–1046.

[S8] R. Ahlrichs, M. Bär, M. Hacer, H. Horn, C. Kömel, Chem. Phys. Lett. 1989, 162, 165.

[S9] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.

[S10] Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O’Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerkson, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R.Z. Khalliuin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill, M. Head-Gordon, Phys. Chem. Chem. Phys., 2006, 8, 3172.

[S11] A. Klamt, G. Schüürmann, J. Chem. Soc., Perkin Trans. 2, 1993, 799.

[S12] A. Klampt, WIREs Comput. Mol. Sci., 2011, 1, 699.

[S13] Y. Zhao, S. Benz, N. Sakai, S. Matile, Chem. Sci. 2015, 6, 6219–6223.
8. **NMR Spectra**

**Figure S9.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8.

**Figure S10.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 8.
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 25.

Figure S12. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 25.
**Figure S13.** $^1$H NMR (400 MHz, TCE-d$_2$/CD$_3$OD 9:1) spectrum of 9.

**Figure S14.** $^{13}$C NMR (101 MHz, TCE-d$_2$/CD$_3$OD 9:1) spectrum of 9.
Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6.

Figure S16. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 6.
Figure S17. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13.

Figure S18. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 13.
Figure S19. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14.

Figure S20. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 14.
Figure S21. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 15.

Figure S22. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 15.
Figure S23. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 16.

Figure S24. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 16.
Figure S25. $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 4:1) spectrum of 29.

Figure S26. $^{13}$C NMR (101 MHz, CDCl$_3$/CD$_3$OD 4:1) spectrum of 29.

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**Figure S27.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2.

**Figure S28.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 2.
Figure S29. $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 4:1) spectrum of 30.

Figure S30. $^{13}$C NMR (101 MHz, CDCl$_3$/CD$_3$OD 4:1) spectrum of 30.
**Figure S31.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3.

**Figure S32.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 3.
**Figure S33.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 31.

**Figure S34.** $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 31.
Figure S35. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 4.

Figure S36. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 4.
Figure S37. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 32.

Figure S38. $^{13}$C NMR (101 MHz, DMSO-$d_6$) spectrum of 32.
Figure S39. $^1$H NMR (500 MHz, CDCl$_3$, 1% TFA) spectrum of 5.

Figure S40. $^{13}$C NMR (126 MHz, CDCl$_3$, 1% TFA) spectrum of 5.
Figure S41. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11

Figure S42. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 11.
Figure S43. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 34.

Figure S44. $^{13}$C NMR (101 MHz, CDCl$_3$) spectrum of 34.
Figure S45. $^1$H NMR (400 MHz, oDCB-d$_4$) spectrum of 35.

Figure S46. $^{13}$C NMR (126 MHz, oDCB-d$_4$) spectrum of 35.
Figure S47. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 36.

Figure S48. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 36.
Figure S49. $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 19:1) spectrum of 12.

Figure S50. $^{13}$C NMR (101 MHz, CDCl$_3$/CD$_3$OD 19:1) spectrum of 12.
Figure S51. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1.

Figure S52. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of 1.
9. **HRMS Spectra**

**Figure S53.** HRMS of 8 for [M+H]^+.

**Figure S54.** HRMS of 25 for [M+H]^+.
Figure S55. HRMS of 9 for [M+H]⁺.

Figure S56. HRMS of 6 for [M+H]⁺.
Figure S57. HRMS of 13 for [M+H]⁺.

Figure S58. HRMS of 14 for [M+H]⁺.
Figure S59. HRMS of 15 for [M+H]+.

Figure S60. HRMS of 16 for [M+H]+.
**Figure S61.** HRMS of 29 for [M+H]$^+$.

**Figure S62.** HRMS of 2 for [M+H]$^+$. 
**Figure S63.** HRMS of 30 for [M+H]^+.

**Figure S64.** HRMS of 3 for [M+H]^+.
Figure S65. HRMS of 31 for [M+H]$^+$. 

Figure S66. HRMS of 4 for [M+H]$^+$. 
Figure S67. HRMS of 32 for [M+H]^+.

Figure S68. HRMS of 5 for [M+H]^+. 
**Figure S69.** HRMS of 11 for [M+H]$^+$. 

**Figure S70.** HRMS of 34 for [M+H]$^+$. 

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**Figure S71.** HRMS of 35 for [M+H]⁺.

**Figure S72.** HRMS of 36 for [M+H]⁺.
Figure S73. HRMS of 12 for [M+H]⁺.

Figure S74. HRMS of 1 for [M+H]⁺.
10. Cartesian Coordinates

Structures from *Figure 1*

(d)

| X | Y | Z |
|---|---|---|
| 1.4998376 | -0.9292481 | -3.0397186 |
| 0.1422974 | -0.6569086 | -3.4847084 |
| -0.3475903 | 0.6544146 | -3.4829326 |
| 0.4995873 | 1.7479383 | -3.0341705 |
| 1.8015380 | 1.4850635 | -2.5943831 |
| 2.3141470 | 0.1242264 | -2.5970577 |
| 1.4914553 | -2.1847981 | -2.3154732 |
| 0.1283986 | -2.6925078 | -2.3105478 |
| -0.7059709 | -1.7488836 | -3.0365638 |
| -2.0132419 | -1.4898651 | -2.6035232 |
| -1.7029913 | 0.9234849 | -3.0335040 |
| -0.3336239 | 2.6928885 | -2.3071845 |
| 0.1702250 | 3.3448300 | -1.1749813 |
| 1.5277179 | 3.0809844 | -0.7245497 |
| 2.3286409 | 2.1623278 | -1.4203497 |
| 3.1616808 | 1.2211412 | -0.6982353 |
| 3.1531911 | -0.0392510 | 1.4257386 |
| 3.1446923 | -1.2488681 | -0.7276181 |
| 2.2977858 | -2.3365179 | -1.1767694 |
| -0.3754468 | -3.3416012 | -1.1766977 |
| 0.4631657 | -3.5078889 | 0.0000000 |
| 1.7709945 | -3.0094892 | 0.0000000 |
| 2.2977858 | -2.3365179 | 1.1767694 |
| 3.1446923 | -1.2488681 | 0.7276181 |
| 3.1531911 | -0.0392510 | 1.4257386 |
| 3.1616808 | 1.2211412 | 0.6982353 |
| 2.3286409 | 2.1623278 | 1.4203497 |
| 1.5277179 | 3.0809844 | 0.7245497 |
| -1.6945595 | 2.1828370 | -2.3069611 |
| -1.6945595 | 2.1828370 | 2.3069611 |
| -2.5053711 | 2.3488070 | 1.1754238 |
| -3.3515408 | 1.2509208 | 0.7272477 |
| -3.3598842 | 0.0385561 | 1.4269638 |
| -2.5217140 | -0.1289078 | 2.6030879 |
| -0.3475903 | 0.6544146 | 3.4829326 |
| 0.4995873 | 1.7479383 | 3.0341705 |
| -0.3336239 | 2.6928885 | 2.3071845 |
| 0.1702250 | 3.3448300 | 1.1749813 |
| -0.6695852 | 3.5111793 | 0.0000000 |
| -1.9825714 | 3.0203958 | 0.0000000 |
| -3.3515408 | 1.2509208 | -0.7272477 |
| -3.3598842 | 0.0385561 | -1.4269638 |
| -3.3684236 | -1.2211572 | -0.6997483 |
| -3.3684236 | -1.2211572 | 0.6997483 |
| -2.5361079 | -2.1646625 | 1.4277808 |
| -2.0132419 | -1.4898651 | 2.6035232 |
| -0.7059709 | -1.7488836 | 3.0365638 |
| 0.1422974 | -0.6569086 | 3.4847084 |
| 1.8015380 | 1.4850635 | 2.5943831 |
| 2.3141470 | 0.1242264 | 2.5970577 |
| 1.4998376 | -0.9292481 | 3.0397186 |
| 1.4914553 | -2.1847981 | 2.3154732 |
| 0.1283986 | -2.6925078 | 2.3105478 |
c -2.8290350  1.2761641  -2.6044619
  c -4.6241166  -0.7609890  -3.4854026
  c -3.2887464  -1.1142178  -3.0350292
  c -2.4074842  -0.1150324  -2.6035791
  c -1.5863170  -0.3341654  -1.4251952
  c -1.4983659   0.9220600   0.6994606
  c -1.4983659   0.9220600   0.6994606
  c -2.6493688  1.9182455  1.4272419
  c -2.8290350  1.2761641  2.6044619
  c -4.1171175  1.6146250  3.0352166
  c -7.9948749  1.3601405  0.7264527
  c -5.5387718  -1.8002548  3.0374810
  c -6.8209262  -1.4580361  2.5970954
  c -7.3915798  -2.0976189  1.4234132
  c -6.5121100  -3.0611896  0.7262226
  c -5.3125138  -3.4078531  1.1744104
  c -3.3770720  -2.3078967  2.3073490
  c -3.2887464  -1.1142178  3.0350292
  c -4.6241166  -0.7609890  3.4854026
  c -5.0304206  0.5777073  3.4852018
  c -6.3683061   0.9322419  3.0369379
  c -7.2435216  -0.0658232  2.5967773
  c -8.1673857  -1.1071484  0.7030039
  c -8.1673857  -1.1071484  -0.7030039
  c -7.3915798  -2.0976189  -1.4234132
  c -6.6512110  -3.0611896  -0.7262226
  c -5.3125138  -3.4078531  -1.1744104
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  c -3.1436999  -3.2229190  0.0000000
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  c -1.5863170  -0.3341654  1.4251952
  c -1.6669971  -1.5435791  0.7271552
  c -1.6669971  -1.5435791  -0.7271552
  c -2.5781848  -2.5837642  -1.1761246
  c -3.3770720  -2.3078967  -2.3073490
  c -4.7662756  -2.7940775  -2.3091180
  c -5.5387718  -1.8002548  -3.0374810
  c -6.8209262  -1.4580361  -2.5970954
  c -8.0732431  0.1483901  1.4232279
  c -8.0732431  0.1483901  -1.4232279
  c -4.7662756  -2.7940775  2.3091180
  c  7.0029788  1.9453769  -2.3067157
  c  5.7713050  2.7163016  -2.3074002
  c  5.4060525  3.4542783  -1.1757833
  c  6.2608380  3.4496695  0.0000000
  c  7.4479788  2.7085545  0.0000000
  c  7.8263557  1.9411650  -1.1755726
  c  6.7604210  0.7095080  -3.0351276
  c  5.3804732  0.7165916  -3.4859953
  c  4.7678588  1.9547790  -3.0340915
  c  3.4376754  1.9610308  -2.6001459
  c  4.0241058  3.4628358  -0.7262918
  c  5.4060525  3.4542783  1.1757833
  c  5.7713050  2.7163016  2.3074002
  c  7.0029788  1.9453769  2.3067157
  c  7.8263557  1.9411650  1.1755726
  c  8.4406359  0.7025349  0.7258127
  c  8.4406359  0.7025349  -0.7258127
  c  8.2064785  -0.4877823  -1.4276449
  c  7.3523309  -0.4834574  -2.6012715
  c  4.6364784  -0.4722382  -3.4851943
| C     | 5.2497290 | -1.7102606 | -3.0327624 |
| C     | 6.5806289 | -1.7173385 | -2.6004726 |
| C     | 6.9597652 | -2.4848872 | -1.4266807 |
| C     | 7.9623472 | -1.7230702 | -0.6995195 |
| C     | 8.2064785 | -0.4877823 | 1.4276449 |
| C     | 7.3523309 | -0.4834574 | 2.6012715 |
| C     | 5.2497290 | -1.7102606 | 3.0327624 |
| C     | 4.0241058 | 3.4628358  | 0.7264255 |
| C     | 3.2561813 | -0.4660645 | 3.0362275 |
| C     | 2.6659376 | 0.7270595  | 2.6005842 |
| C     | 1.8137965 | 0.7318709  | 1.4263094 |
| C     | 2.1932331 | -1.6974826 | 1.1756093 |
| C     | 4.2462326 | -2.4725238 | 2.3071801 |
| C     | 5.2497290 | -1.7102606 | 3.0327624 |
| C     | 6.5806289 | -1.7173385 | 2.6004726 |
| C     | 6.9597652 | -2.4848872 | 1.4266807 |
| C     | 5.9927139 | -3.2174338 | 0.7264255 |
| C     | 4.6110405 | -3.2115571 | 1.1759659 |
| C     | 4.2462326 | -2.4725238 | 2.3071801 |
| C     | 3.0139788 | -1.7024183 | 2.3077140 |
| C     | 1.1597452 | -1.6973159 | 2.3976166 |
| C     | 1.9039466 | -1.7447568 | 1.163720 |
| C     | 1.3181337 | -2.2978298 | 0.0305395 |
| C     | 3.3754690 | -3.5909311 | 0.5377523 |
| C     | 4.6629185 | -5.2821660 | 0.4661585 |
| C     | 4.643863 | -6.5501732 | 1.0600065 |
| C     | 4.7377666 | -6.6599816 | 2.4974227 |
| C     | 4.848585 | -5.4976872 | 3.2752799 |
| C     | 4.0939747 | -5.3827491 | 4.5108840 |
| C     | 3.6639049 | -4.0021327 | 4.6506478 |
| C     | 2.4070827 | -3.7230790 | 5.2051811 |
| C     | 1.5829929 | -2.6932520 | 4.6150460 |
| C     | 0.1736619 | -2.1146703 | 2.4548099 |

**Compound 1**

| C     | -3.3708043 | -2.2401754 | 2.9607218 |
| C     | -3.3421189 | -1.9238095 | 1.5036368 |
| C     | -4.1702569 | -2.9595694 | 0.5567326 |
| C     | -4.8314024 | -4.0923602 | 1.2627371 |
| C     | -4.925053 | -4.1915335 | 2.6474505 |
| C     | -4.1532034 | -3.2507164 | 3.5082608 |
| C     | -2.0557501 | -1.9922904 | 3.4981756 |
| C     | -1.1597452 | -1.6973159 | 2.3976166 |
| C     | -1.9039466 | -1.7447568 | 1.163720 |
| C     | -1.3181337 | -2.2978298 | 0.0305395 |
| C     | -3.3754690 | -3.5909311 | 0.5377523 |
| C     | -4.6629185 | -5.2821660 | 0.4661585 |
| C     | -4.643863 | -6.5501732 | 1.0600065 |
| C     | -4.7377666 | -6.6599816 | 2.4974227 |
| C     | -4.848585 | -5.4976872 | 3.2752799 |
| C     | -4.0939747 | -5.3827491 | 4.5108840 |
| C     | -3.6639049 | -4.0021327 | 4.6506478 |
| C     | -2.4070827 | -3.7230790 | 5.2051811 |
| C     | -1.5829929 | -2.6932520 | 4.6150460 |
| C     | 0.1736619 | -2.1146703 | 2.4548099 |

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|   | C    | C    | C    | C    | C    |
|---|------|------|------|------|------|
| 0.6664698 | -2.8415438 | 3.6096747 |
| -0.1966232 | -3.1280241 | 4.6709554 |
| 0.1674765 | -4.4389087 | 5.2967633 |
| -1.5359193 | -4.8063249 | 5.6278701 |
| -1.9536453 | -6.1343802 | 5.4884400 |
| -3.2605818 | -6.4275387 | 4.9241066 |
| -3.1397699 | -7.6281245 | 4.1105555 |
| -3.8662635 | -7.7429224 | 2.9025721 |
| -3.7690725 | -9.7584466 | -0.634327 |
| -1.0004605 | -8.4160625 | 0.6817843 |
| -1.4684195 | -7.7047217 | -0.4288590 |
| -0.6495705 | -6.6593623 | -1.0233273 |
| 0.6075244 | -6.3684253 | 0.4838253 |
| 1.0946206 | -7.1088060 | 0.6656627 |
| 0.2156535 | -8.2279131 | 2.6853345 |
| -1.1485690 | -8.6010200 | 3.0220334 |
| -1.8993555 | -8.7189937 | 1.7845051 |
| -3.234370 | -8.3006397 | 1.7346859 |
| -3.7180121 | -7.5622734 | 0.5804876 |
| -2.8532318 | -7.2683947 | -0.4775087 |
| -1.5290909 | -5.505123 | -1.4389790 |
| -1.1283326 | -4.2449180 | -1.2887069 |
| 0.1792893 | -3.9476969 | -0.7314456 |
| 1.0331706 | -4.9854694 | -0.3417604 |
| 1.7957905 | -4.8763011 | 0.8933717 |
| 1.8294273 | -6.1857850 | 1.5178516 |
| 1.7456036 | -6.3012628 | 2.9104819 |
| 0.9208238 | -7.3401707 | 3.5044539 |
| -1.7581518 | -8.0677923 | 4.1639012 |
| -1.0242627 | -7.1440702 | 5.0165225 |
| 0.2906097 | -6.7893071 | 4.6932563 |
| 0.7275308 | -5.4114248 | 4.8359627 |
| 1.6283654 | -5.1097293 | 3.7330897 |
| 1.6009600 | -3.8469183 | 3.1321477 |
| 1.6832176 | -3.7280485 | 1.6837795 |
| 0.7986487 | -2.6524445 | 1.2710350 |
| 0.0587998 | -2.7532352 | 0.0848989 |
| -2.8823292 | -5.9546695 | -1.1090983 |
| -2.0638438 | -3.2352343 | -0.8297398 |
| 0.3058317 | -8.1123444 | 1.2391485 |
| -4.5233702 | -1.5075603 | 0.6709526 |
| -5.7435093 | -1.0171932 | 1.4559463 |
| -5.6688288 | 0.0278231 | 2.1048634 |
| -6.8656340 | -1.7600589 | 1.3100219 |
| -6.7919701 | -2.6285515 | 0.7889270 |
| -4.3528106 | -0.6544171 | -0.5996048 |
| -4.5242819 | -1.1556387 | -1.7101741 |
| 0.7467338 | 4.4775472 | -0.6498870 |
| 1.0828189 | 3.2660227 | -1.4543891 |
| 0.7714649 | 1.8402914 | -0.7472734 |
| 0.1647107 | 1.9267940 | 0.6130351 |
| -0.2235783 | 3.1261167 | 1.2019815 |
| 0.0771719 | 4.4184762 | 0.5646868 |
| 1.8079970 | 5.4402298 | -0.8218543 |
| 2.8825028 | 4.8180444 | -1.5735133 |
| 2.5044941 | 3.4591272 | -1.8706306 |
| 3.4608869 | 2.4522893 | -1.8141315 |
| 1.9240220 | 0.9109245 | -0.6120653 |
| 0.7730305 | 0.9063303 | 1.4308487 |
| 0.8910312 | 1.0564729 | 2.8174753 |
| 0.4509080 | 2.2834828 | 3.4369510 |
| -0.0829938 | 3.3033324 | 2.6367057 |
H -3.5881801 3.6099081 -3.2964973
H -3.3806698 2.4274138 -4.5983367
C 0.5614888 1.4916814 -3.3057956
O 0.3827855 0.2720572 -3.3927527
N 1.0288904 2.2863321 -4.2898385
H 1.3702104 3.2246704 -4.0511234
C 1.5932769 1.8171160 -5.5493491
C 0.5921289 1.0650604 -6.4359636
C 2.1205709 3.0700743 -6.2856832
H 2.4349499 1.032394 -7.5923019
C 1.2521880 0.6625160 -7.7612064
H -0.2716591 1.7250646 -6.6251119
H 0.2203160 0.1857924 -5.8943192
C 2.8151005 2.6523968 -7.5923019
C 1.8448468 1.8744984 -8.4936416
H 0.5201270 0.1478576 -8.4012394
H 2.0545932 -0.0674116 -7.5574307
H 3.1974947 3.5458722 -8.1133573
H 3.6866640 2.0187779 -7.3590197
H 2.3560681 1.5548224 -9.4143947
H 1.0257829 2.5459944 -8.8061358
N -4.0827075 0.6519345 -0.3524227
N 2.8854801 3.9270954 -5.3625746
C 4.2066195 3.4197831 -5.0038040
H 4.6138908 4.0280505 -4.1850798
H 4.1333812 2.3871770 -4.6390655
H 4.9297739 3.4462972 -5.8439186
C 2.9371671 5.3272169 -5.7677052
H 1.9200405 5.6988872 -5.9548552
H 3.3738322 5.9124787 -4.9522562
H 3.5463681 5.5028382 -6.6790566
H 1.2271833 3.6638835 -6.550963
H -6.2125627 0.8520213 -1.9778535
H -6.3798023 2.0010513 -0.6382002
H -4.1193552 0.9196629 0.6314473
C -8.1166633 -1.4489597 1.9817276
H -8.9361486 -1.3741932 1.2534436
H -8.3646745 -2.2212089 2.7246191
H -7.9962317 -0.4860561 2.4902115

**Compound 2**

C -0.1497938 1.3030884 0.0099033
C 0.1540944 0.5504990 -1.2355171
C 0.0805522 -1.0892259 -1.1155302
C -0.2722149 -1.6030014 0.2356852
C -0.6587734 -0.7771759 1.2839811
C -0.6046916 0.6929253 1.1709977
C 0.7717448 2.4110766 0.1021171
C 1.7534605 2.2811288 -0.9585912
C 1.4541005 1.0909138 -1.7168009
C 2.4908760 0.2872472 -2.1752760
C 1.3251878 -1.8110662 -1.4985698
C 0.5513407 -2.7584219 0.5066044
C 0.8904106 -3.1184240 1.9169605
C 0.4595276 -2.2808617 2.9122418
C -0.2784229 -1.1238812 2.6388118
C -0.0023117 0.0984233 3.3650944
C -0.1942972 1.2158499 2.4625383
C 0.6521498 2.3288930 2.5544717
C 1.1501431 2.9396962 1.3420970
C 3.0758683 2.6899561 -0.7461466
C 3.4701693 3.2298945 0.5453226
C -0.0899609  0.8872273 -5.5721527
C -1.1299226  0.3521712 -6.5658476
C  0.1504428  2.3944666 -5.8057824
H  0.8525505  0.3307428 -5.7330957
C -0.6663717  0.5949600 -8.0075914
H -2.0880338  0.8671937 -6.3801074
H -1.2895219  0.7171998 -6.3736935
C  0.6503660  2.6221127 -7.2424883
C -0.3619728  2.0775233 -8.2614897
H -1.4300776  0.2335882 -8.7125527
H  0.2427623 -0.0080888 -8.2001038
C  0.8271923  3.6958247 -7.4097705
C  1.6185853  2.1124890 -9.2850043
H  0.0159647  2.2233954 -9.2850043
C -0.2975510  2.6584083 -8.1865462
C -3.0989489  3.2638123  3.2602149
C -2.4111867  3.3070924  4.4849167
C -2.1738218 -2.1419879  5.2037783
C -2.6477304 -0.9011320  4.7177564
C -3.3250916 -0.8558781  3.4653793
C -3.5369565 -2.0518363  2.7405212
C -2.3841122  0.3051938  5.4093655
C -2.8173375  1.5159848  4.8830995
C -3.4904198  1.5590745  3.6507933
C -3.7298612  0.3908147  2.9369539
C -4.3860368  0.4613104  1.6070881
C -4.8201763 -0.7495606  0.8729121
C -4.1939088 -2.0157355  1.4062642
C -1.3447314 -2.1881139  6.4329871
C -1.0769013 -0.9604800  7.0634875
C -1.5614996  0.2951907  6.6470096
C -0.8738249 -3.2290810  6.8838559
C -1.2891482  1.3210611  7.2608224
C -4.8290827  1.5100820  1.1582332
C -4.4651941 -3.0472315  0.7960898
C -3.2722858 -4.1715091  2.6828026
C -2.0232533 -4.2469334  4.8772620
C -2.5887815  2.4311924  5.4286025
C -3.8091892  2.5072056  3.2185115
C -0.1879518  0.0189004  8.2288024
C -0.952249  0.0084378  8.6333969
C  0.7926608  0.4026949  7.9192070
C -0.6043829  1.7029541  8.9774760
N  0.9629912  0.5960943 -4.7165322
C  2.3724683  2.5882345 -4.7360879
H  2.8413133  2.9031234 -3.7934072
H  2.4765951  1.4978407 -4.8058008
H  2.9397289  3.0498086  5.5698862
C  0.7943389  4.4056423 -4.5546952
C -0.2739419  4.6478001 -4.4695271
H  1.2919600  4.7247919 -3.6274953
H  1.2226729  4.9997182  5.3897302
H -0.8380526  2.8805330 -5.7125824
H -6.7434709 -2.0076446 -0.1816655
H -7.0657394  0.3468532  0.3653038

**Compound 3**
C  0.0121510  1.2239620 -0.3237117
C  0.3232574  0.4922479 -1.5735023
C  0.2841462 -1.1503606 -1.4734816
C -0.0675207  1.6872457 -0.1302499
C -0.4825360 -0.8826502  0.9235531

S68
| C | -0.4623382 | 0.5895270 | 0.8260674 |
| C | 0.8823630 | 2.3527305 | -0.2101977 |
| C | 1.8772681 | 2.2574710 | -1.2621429 |
| C | 1.6141080 | 1.0684053 | -2.0353945 |
| C | 2.6735668 | 0.2949681 | -2.4931716 |
| C | 1.5507739 | 1.8772681 | -1.2621429 |
| C | 1.9426595 | -1.1521820 | -4.2627269 |
| C | 1.7060955 | -2.3384019 | 3.5513989 |
| C | 1.2364394 | 2.8767589 | 1.0388224 |
| C | 3.1875708 | 2.6952391 | -1.0323992 |
| C | 5.1322699 | -2.7839505 | 2.2336215 |
| C | 4.7790170 | -3.2982055 | 0.9811380 |
| C | 5.2637883 | -2.6582403 | -0.232465 |
| C | 6.0875381 | -1.5314662 | -0.1446777 |
| C | 6.4584367 | -1.0011652 | 1.1543777 |
| C | 5.5250913 | -0.8001520 | 3.4336563 |
| C | 5.2637883 | -3.2982055 | 0.9811380 |
| C | 6.0875381 | -1.5314662 | -0.1446777 |
| C | 6.4584367 | -1.0011652 | 1.1543777 |
| C | 5.5250913 | -0.8001520 | 3.4336563 |
| C | 4.3808387 | -1.4671067 | 4.0328292 |
| C | 4.1380092 | -2.6937498 | 3.2926027 |
| C | 2.8262492 | -3.129015 | 3.058442 |
| C | 4.6612400 | -3.6543050 | 1.7551707 |
| C | 3.4163801 | -3.7398297 | 0.7381617 |
| C | 4.2009429 | -2.7061742 | -1.2216840 |
| C | 3.9881538 | -1.6195756 | -2.0819435 |
| C | 4.8469699 | -0.4523281 | -1.9882175 |
| C | 5.1341747 | 0.8157899 | -0.3032671 |
| C | 4.8757657 | 0.4506862 | 1.0561348 |
| C | 6.0457121 | 1.2329952 | 2.1291627 |
| C | 5.5533965 | 0.5952952 | 3.3391699 |
| C | 3.3034298 | -0.7118914 | 4.5114353 |
| C | 3.3327784 | 0.7413671 | 4.4125870 |
| C | 4.4375938 | 1.3813676 | 3.8392322 |
| C | 4.2414816 | 2.5057174 | 2.9399457 |
| C | 5.2361293 | 2.037553 | 1.8825474 |
| C | 4.9050259 | 2.7699093 | 0.5715265 |
| C | 5.3566933 | 1.9536764 | -0.5438252 |
| C | 4.2939025 | 1.9096753 | -1.5330195 |
| C | 4.0346111 | 0.7254792 | -2.2388551 |
| C | 3.0655838 | -3.3693510 | -0.6234235 |
| C | 2.6430589 | -1.1753822 | -2.3984065 |
| C | 5.9884775 | -1.6138438 | 2.3215292 |
| C | -0.6006519 | -0.3600455 | -2.3855822 |
| C | -2.1031184 | -0.1996664 | -2.1317462 |
| O | -2.6316215 | 0.9046966 | -2.2290953 |
| N | -2.7530401 | -1.3630366 | -1.8832235 |
| H | -2.1945827 | -2.207690 | -1.8451699 |
| C | -4.9005843 | -0.6215406 | -0.8085851 |
| H | -4.7675816 | 0.4193808 | -1.1271167 |
Compound 4

C  -0.0455101  1.0763259  -0.3707238
C   0.3267413   0.4155896  -1.6491354
C   0.3604204  -1.2276898  -1.6212198
C   0.0331763  -1.8395555  -0.3030834
C  -0.4192669  -1.1010473   0.7841225
C  -0.4671142   0.3726959   0.7488458
C   0.7933182   2.2399016  -0.2066492
C   1.7933235   2.2375310  -1.2576718
C   1.5886582   1.0719161  -2.0819500
C   2.6824652   0.3985633  -2.5709554
C   1.6590525  -1.8371816  -2.0239506
C   0.9367243  -2.9456987  -0.0824634
C   1.2892819   3.3508873   1.2109463
C   0.7887287  -2.6087537   2.3452345
C  -0.0310486  -1.4962509   2.1252326
C   0.1618380  -0.2975863   2.9166831
C  -0.1007508   0.8499425   2.0703008
C   0.6623414   2.0102568   2.2326678
C   1.1225081   2.7243402   1.0639456
C   3.0815399   2.7263181  -1.0062592
C   3.420281   3.2218353   0.3168965
C   2.4624921   3.2203070   1.3325846
C   2.8268898   2.8098550   2.6790607
C   1.7097160   2.0618996   3.2369290
C   1.9513809   0.9540486   4.0585368
C   1.1522727  -0.2493457   3.9021447
C   2.0146516  -1.4007335   4.1156157
C   1.8338442  -2.5604502   3.3528796
C   1.9313966  -2.9443212  -1.1379722
C   5.2781977  -2.7922737   2.0261409
C   4.9501587  -3.2678275   0.7517071
C   5.4059226  -2.5544906  -0.4320231
C   6.1757970  -1.3952137  -0.2932702
C   6.5200991  -0.9047249   1.0285614
C   5.5768733  -0.8462777   3.3114671
C   4.4642594  -1.5908381   3.8777605
C   4.2798770  -2.7943269   3.0848646

S71
C -2.2274202 -2.9055429 4.3593059
C -1.9883585 -1.6694910 4.9765778
C -2.4329415 -0.4754200 4.3484829
C -3.0683985 -0.5161009 3.0728764
C -3.3052149 -1.7778412 2.4825201
C -2.1883769 0.7894312 4.9303790
C -2.5316243 1.9486596 4.2537572
C -3.0711854 1.9189217 2.9564531
C -3.3771590 0.6783890 2.3731348
C -4.0377244 0.5802432 1.0433507
N -4.1764207 -0.7038713 0.4590780
C -3.9193026 -1.8976311 1.1352866
C -1.1994087 -1.5605531 6.2318381
N -0.9878957 -0.2782241 6.7676061
C -1.4630850 0.9188626 6.2187548
O -0.7133435 -2.5326256 6.7990448
O -1.2628378 2.0046597 6.7544950
O -4.4889347 1.5670545 0.4770830
O -4.1801605 -2.9944539 0.6437109
H -3.1364274 -3.8739232 2.6286212
H -2.3053830 2.8855509 4.7563377
C -0.1804811 -0.2235532 7.9925478
H -0.1304113 0.8190915 8.3143686
H 0.8237099 -0.6141161 7.7854634
H -0.6411124 -0.8504283 8.7649177
N 0.9116112 3.1606340 -4.9231166
C 2.3558645 2.9556723 -4.8954793
H 2.7432385 3.2627157 -3.9140065
H 2.5940455 1.8923874 -5.0251291
H 2.8978225 3.5343811 -5.6713820
C 0.5610591 4.5565649 -4.6885198
H -0.5314700 4.6629269 -4.6391901
H 0.9778796 4.8751401 -3.7222981
H 0.9460229 5.2490504 -5.4675489
H -0.8199988 2.9296774 -6.0152751
H -6.4469964 -2.0686381 -0.4004243
H -6.7679408 -0.3553341 -0.0495030
S 0.32350747 3.4558795 1.9300207
S -1.6581439 -4.4633235 5.1963660
C -1.9996210 -5.6945703 3.8626159
H -1.8837858 -6.6248742 4.4391691
H -3.0548130 -5.6365742 3.5598021
C -1.0045414 -5.6295354 2.7082131
H -1.1502684 -4.7422670 2.079148
H 0.0300416 -5.6021814 3.0787747
H -1.1100468 -6.5155291 2.0669357
C -2.5628658 4.7325679 3.1023954
H -3.1051106 4.6373920 4.0550918
H -2.9280813 5.6529774 2.6217216
C -1.0465523 4.7572444 3.2296903
H -0.5904765 4.7298599 2.2313516
H -0.7277537 5.6783820 3.7371542
H -0.6585577 3.9032348 3.7966362
O -2.1986541 3.3340907 0.8479628
O -2.6649627 -4.7495212 6.2710556

**Compound 5**

C 0.0907051 1.7548964 -0.6232084
C 0.3595428 0.8134409 -1.7436328
C 0.1901588 -0.7820434 -1.3897332
C -0.2181460 -1.0746518 0.0088110
C -0.5664579 -0.0839388 0.9182955

S73
|   | C   |     |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|-----|-----|
|   | -0.4167394 | 1.3477965 | 0.6028217 |
| C | 1.0833260 | 2.8016703 | -0.6675432 |
| C | 2.0697383 | 2.4599749 | -1.6755628 |
| C | 1.7023691 | 1.1953973 | 2.0697383 |
| C | 2.6924462 | 0.2705982 | 2.4599749 |
| C | 1.3847324 | -0.2296898 | 1.1609669 |
| C | 0.5238466 | -0.2580239 | 1.0365259 |
| C | 0.8245171 | 0.4592805 | 2.2287336 |
| C | 0.2296898 | -0.2580239 | 1.0365259 |
| C | 1.0979111 | 1.0365259 | 2.8769144 |
| C | 0.0060588 | 2.0211548 | 1.8153032 |
| C | 0.9252093 | 3.0770668 | 1.7674134 |
| C | 1.4787351 | 3.4767475 | 0.4941693 |
| C | 3.4132496 | 2.8097972 | -1.4913665 |
| C | 3.8244349 | 3.5038198 | -0.2812270 |
| C | 2.8754698 | 3.8289546 | 0.6927777 |
| C | 3.1835536 | 3.6438079 | 2.1007932 |
| C | 1.9757229 | 3.1782256 | 2.7660357 |
| C | 2.0663296 | 2.2291925 | 3.7910975 |
| C | 1.1074945 | 1.1380254 | 3.8526052 |
| C | 1.8082339 | -0.0558901 | 4.3040762 |
| C | 1.4738494 | -1.3076907 | 3.7737799 |
| C | 1.5039124 | -2.5726875 | -0.5529974 |
| C | 4.8486596 | -2.2556625 | 2.6013690 |
| C | 4.4562840 | -2.9227065 | 1.4353283 |
| C | 5.0007502 | -2.5201791 | 0.1474588 |
| C | 5.9215807 | -1.4695081 | 0.0778431 |
| C | 6.3328862 | -0.7817243 | 1.2875554 |
| C | 5.4113532 | -0.1531955 | 3.4923681 |
| C | 4.2089242 | -0.6170509 | 4.1648000 |
| C | 3.8610528 | -1.9173219 | 3.6162245 |
| C | 2.5189338 | -2.2602047 | 3.4277794 |
| C | 2.1136540 | -2.9485522 | 2.2132735 |
| C | 3.0599660 | -3.2758284 | 1.2389666 |
| C | 3.9418365 | -2.6248874 | -0.8420613 |
| C | 3.8314942 | -1.6690006 | -1.8622539 |
| C | 4.7898642 | -0.5797808 | -1.9309493 |
| C | 5.8171343 | -0.4832337 | -0.9855033 |
| C | 6.1781719 | 0.8132297 | -0.4340911 |
| C | 6.4920208 | 0.6300828 | 0.9711509 |
| C | 6.1175278 | 1.6031618 | 1.9049072 |
| C | 5.5648382 | 1.2032707 | 3.1885871 |
| C | 3.2024430 | 0.2950054 | 4.5066340 |
| C | 3.3618890 | 1.7073307 | 4.1883823 |
| C | 4.5224542 | 2.1517276 | 3.5439963 |
| C | 4.4314004 | 3.1377877 | 2.4809471 |
| C | 5.4186183 | 2.7991111 | 1.4675009 |
| C | 5.1204866 | 2.9785892 | 0.1121079 |
| C | 5.5061223 | 1.9649106 | -0.8579843 |
| C | 4.4467137 | 1.8633414 | -1.8464238 |
| C | 4.0870641 | 0.6126254 | -2.3680565 |
| C | 2.7489644 | -3.0873151 | -0.1696518 |
| C | 2.5324931 | -1.1609669 | -2.2663797 |
| C | 5.8045438 | -1.1605066 | 2.5255170 |
| C | -0.6385169 | -0.0723608 | -2.4165585 |
| C | -2.1251825 | 0.1625732 | -2.1095086 |
| O | -2.5928375 | 1.2881980 | -1.9690051 |
| N | -2.8218562 | -0.9995934 | -2.0424114 |
| H | -2.3135803 | -1.8453642 | -2.2919501 |
| C | -4.8894219 | -0.3571076 | -0.7672972 |
| H | -4.7479790 | 0.7180823 | -0.9312426 |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 1.4759343 | 3.9334313 | -5.6035259 |
| H    | 0.4347737  | 4.2807854  | -5.5382757  |
| H    | 2.0116773  | 4.3320846  | -4.7299432  |
| H    | 1.9443668  | 4.3629640  | -6.5138694  |
| H    | -0.2937596 | 2.4253955  | -6.5482325  |
| H    | -6.5442544 | -1.7310501 | -0.5291253 |
| H    | -6.8044149 | -0.1276653 | 0.1982153   |
| S    | -3.6100902 | 3.2072079  | 3.1095070   |
| C    | -1.1236368 | -5.0726271 | 4.0189535   |
| C    | -1.3910427 | -5.9945283 | 2.4683316   |
| H    | -1.0741508 | -6.9882899 | 2.8211109   |
| H    | -2.4732912 | -6.0540859 | 2.2902543   |
| C    | -0.5724761 | -5.5430513 | 1.2679648   |
| H    | -0.2937596 | -2.4253955 | 1.5463411   |
| H    | -6.2966281 | 0.4713257  | 0.1982153   |
| C    | -2.7791135 | 4.2205292  | 4.3755389   |
| H    | -3.1909758 | 3.9493746  | 5.3568413   |
| H    | -3.2117053 | 5.1980145  | 4.1104841   |
| C    | -1.2591918 | 4.2457174  | 4.3068056   |
| H    | -0.9292880 | 4.5099177  | 3.2955296   |
| C    | -0.8711035 | 4.9951266  | 5.0100661   |
| C    | -0.8094478 | 3.2787112  | 4.5676680   |
| O    | -0.9147028 | 3.4824759  | 1.8604313   |
| O    | -0.3109976 | -4.8263400 | 4.0937863   |
| O    | -1.8530327 | -5.8161390 | 5.0335343   |
| O    | -5.0335041 | 3.4446745  | 3.2916378   |

**Compound 6**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -0.1997607 | 1.3962243 | 1.2398527 |
| C    | 0.0162490  | 0.6778409 | -0.0515495 |
| C    | -0.0422576 | -0.9414160 | 0.0334335 |
| C    | -0.3300680 | -1.5082461 | 1.3800654 |
| C    | -0.6455692 | -0.7171170 | 2.4800573 |
| C    | -0.5813144 | 0.7529480  | 2.4102253 |
| C    | 0.7356325  | 2.4915378  | 1.3089940 |
| H    | 1.6487607  | 2.3929979  | 0.1854890 |
| C    | 1.2934804  | 1.2331002  | -0.5955912 |
| C    | 2.29662630 | 0.43522340 | -1.13195110 |
| C    | 1.15554880 | -1.67297990 | -0.45967180 |
| O    | 0.49087770 | -2.6815407 | 1.55652780 |
| C    | 0.90597980 | -3.08505980 | 2.83216360 |
| C    | 0.54719480 | -2.28594950 | 3.98194040 |
| C    | -0.21026370 | -1.11844090 | 3.80569230 |
| C    | 0.12846220 | 0.08044520 | 4.55277720 |
| C    | -0.0966160 | 1.22811240 | 3.69120500 |
| C    | 0.76813150 | 2.32894580 | 3.76153740 |
| C    | 1.19617930 | 2.97283260 | 2.54158330 |
| C    | 2.98621350 | 2.78148700 | 0.33278080 |
| C    | 3.46443440 | 3.27548530 | 1.61400620 |
| C    | 2.58635080 | 3.36969830 | 2.69711620 |
| C    | 3.01817880 | 2.96210690 | 4.02263650 |
| C    | 1.89249910 | 2.31699830 | 4.68081050 |
| C    | 2.10873620 | 1.20897710 | 5.50629340 |
| C    | 1.20660050 | 0.07037540 | 5.44274960 |
| C    | 1.99544140 | -1.13929850 | 5.61776920 |
| C    | 1.67020530 | -2.29714540 | 4.90346680 |
| C    | 1.40106880 | -2.78164170 | 0.43005100 |
| C    | 4.97737930 | -2.82487610 | 3.33494960 |
| C    | 4.51991660 | -3.29976600 | 2.10119830 |
| C    | 4.93947090 | -2.64877360 | 0.86998650 |
| C    | 5.80289730 | -1.55026890 | 0.92273140 |
H  1.27625860  1.55110950  -6.60668640
H  -0.55923910  1.99371620  -8.23015730
H  -1.54362770  2.72329160  -6.95862690
N  -5.12449840  -1.82890040  1.58896600
N  1.25930560  2.54658950  -3.90329250
C  2.54364170  1.89572040  -4.15400590
H  3.23089800  2.13305460  -3.33188040
H  2.42271540  0.80407450  -4.17719990
H  3.02010520  2.21633800  -5.10093900
H  1.80269100  4.49210290  -4.66155400
H  -0.65327910  2.84585280  -4.60663260
H  -7.20324060  -2.01014250  -0.32769770
H  -7.56148790  -0.71173080  0.82478070
C  -3.82282270  -1.40742370  2.23419510
H  -3.71290730  -1.94888630  3.17989470
H  -3.00011870  -1.65838170  1.56648980
C  -3.83759690  -0.32732210  2.40548990
C  -5.01898000  -3.27844860  1.20644060
H  -4.14343910  -3.41557840  0.56555180
H  -4.89725920  -3.86904750  2.12111040
H  -5.93157160  -3.58728510  0.68674210
C  -6.19668290  -1.68266040  2.85736530
H  -6.33703940  -0.61897040  2.85793630
H  -7.13131780  -2.12905220  2.29078200
H  -5.85785760  -2.20226090  3.54032030

Compound 4'

C  -0.0590087  1.0588646  -0.3560701
C  0.3092443  0.4001658  -1.6369731
C  0.3465950  -1.2420486  -1.6091292
C  0.0275117  -1.8568032  -0.2896973
C  -0.4214987  -1.1207565  0.8012863
C  -0.4720172  0.3529839  0.7659053
C  0.7761913  2.2255496  -0.1965107
C  1.7704490  2.2276795  -1.2529839
C  1.5659197  1.0617273  -2.0763985
C  2.6591804  0.3636417  -2.5716142
C  1.6457136  -1.8484449  -2.0193903
C  0.9374833  -2.9586359  -0.0746198
C  1.3000147  -3.3601701  1.2169236
C  0.8039584  -2.6210542  2.3542681
C  -0.0256771  -1.5154337  2.1412208
C  0.1676965  -0.3151982  2.9323644
C  -0.0999936  0.8311232  2.0858815
C  0.6595794  1.9947194  2.2436504
C  1.1109062  2.7101982  1.0724070
C  3.0582418  2.7212252  -1.0087118
C  3.4062515  3.2174591  0.3127259
C  2.4502814  3.2116910  1.3338425
C  2.8234273  2.8026981  2.6783221
C  1.7118130  2.0505040  3.2420583
C  1.9618408  0.9424579  4.0609314
C  1.1656312  -0.2638024  3.9100703
C  2.0343026  -1.4119952  4.1178512
C  1.8541827  -2.5686755  3.3541680
C  1.9266848  -2.9534513  -1.1358057
C  5.2910055  -2.7903334  2.0102263
C  4.9577176  -3.2668826  0.7373873
C  5.4040296  -2.5514280  -0.4484184

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