Supporting Information

Discrete Multifunctional Sequence-Defined Oligomers with Controlled Chirality

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Table of Contents

1 GENERAL CONSIDERATIONS

Reagents and solvents were obtained from commercial sources and used without further purification. All reactions were carried out under argon atmosphere. Flash column chromatography was carried out using silica gel 230-400 mesh (Sigma-Aldrich) as the stationary phase. Milli-Q water (resistivity 18.2 MΩ.cm) was obtained from a Merck Millipore system. NMR spectra were recorded on Bruker-300 and Bruker-500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual solvent. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, quint= quintet, m= multiplet.

High-resolution mass spectra (HRMS) were measured on a Q-Exactive (Orbitrap) from ThermoFisher using an atmospheric pressure chemical ionization (APCI) source. Electrospray ionisation mass spectrometry (ESI-MS) and ESI-MS/MS were performed on an SYNAPT G2-Si high definition mass spectrometer (Waters) equipped with a NanoLockSpray dual electrospray ion source (Waters). Precut fused silica PicoTipR Emitters (outer diameters: 360 µm; inner diameter: 20 µm; 10 µm tip; 2.5" length (Waters)) were used to carry samples for nanoelectrospray injecting the test solution.

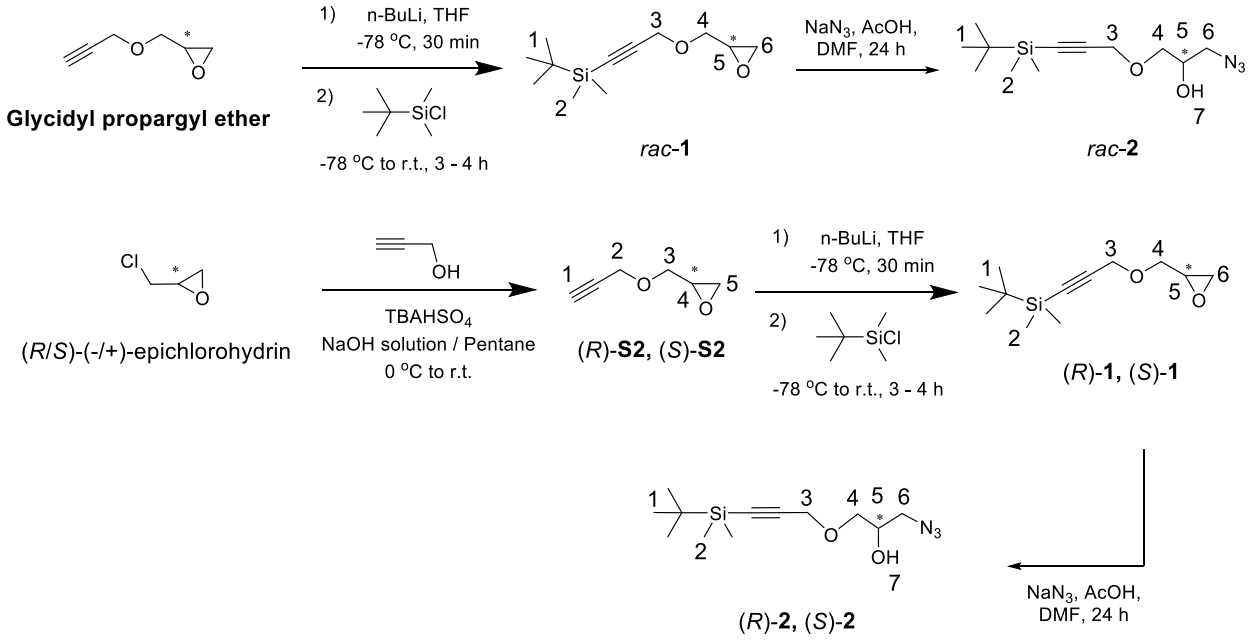
Chiral high-performance liquid chromatography (Chiral HPLC) and HPLC were performed on a Waters 600 Controller with a Waters 996 photodiode array detector and a Waters 717 plus autosampler. For Chiral HPLC, a CHIRALPAK IA column (4.6 × 250 mm) was used to separate samples under a mobile phase of iso-hexane/EtOH mixture (v/v = 9/1) at a flow rate of 1 mL/min. For HPLC, a Waters symmetry C18 column (4.6 × 100 mm, 5 µm particle size) was used to separate samples under a gradient mobile phase of H_2O/CH_3CN (from v/v = 9/1 to v/v = 1/9) with 0.1% HCOOH in 5 min at a flow rate of 1 mL/min. The detection wavelength was set to 245 nm.

UV-vis absorption and Circular Dichroism measurements were recorded using a Chirascan Plus CD Spectrophotometer from Applied Photophysics. The spectra were recorded between 200 and 400 nm, with a bandwidth of 1 nm, time per point 1 s and two repetitions. The solvent reference spectra were used as baselines and were automatically subtracted from the CD spectra of the samples. The measurements were carried out using suprasil quartz cells (Hellma Analytics) of 2 or 5 mm path length for experiments performed at high or low concentration, respectively.

2 EXPERIMENTAL PROCEDURES

2.1 Synthesis of precursors

2.1.1 Synthesis of *rac*-**2**, (*R*)-**2** and (*S*)-**2**



The compounds *rac*-**2**, (*R*)-**2** and (*S*)-**2** were prepared according to the literature.[1, 2] (*R*)-**S2**, **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 4.21 (t, *J* = 2.4 Hz, 2H, H_2), 3.82 (dd, *J* = 11.3, 3.0 Hz, 1H, H_5), 3.48 (dd, *J* = 11.3, 5.9 Hz, 1H, H_5), 3.17 (ddt, *J* = 5.8, 4.1, 2.9 Hz, 1H, H_4), 2.80 (dd, *J* = 5.0, 4.1 Hz, 1H, H_3), 2.63 (dd, *J* = 5.0, 2.7 Hz, 1H, H_3), 2.45 (t, *J* = 2.4 Hz, 1H, H_1); **^{13}C NMR (75 MHz, $CDCl_3$):** δ= 79.4, 75.0, 70.4, 58.6, 50.6, 44.4.

(*S*)-**S2**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.21 (t, *J* = 2.4 Hz, 2H, H_2), 3.82 (dd, *J* = 11.3, 3.0 Hz, 1H, H_5), 3.48 (dd, *J* = 11.3, 5.9 Hz, 1H, H_5), 3.17 (ddt, *J* = 5.8, 4.2, 2.8 Hz, 1H, H_4), 2.80 (dd, *J* = 5.0, 4.1 Hz, 1H, H_3), 2.63 (dd, *J* = 5.0, 2.7 Hz, 1H, H_3), 2.45 (t, *J* = 2.4 Hz, 1H, H_1). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 79.4, 75.0, 70.43, 58.6, 50.6, 44.4.

rac-**1**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.22 (d, *J* = 4.6 Hz, 2H, H_3), 3.80 (dd, *J* = 11.3, 3.3 Hz, 1H, H_6), 3.50 (dd, *J* = 11.3, 5.7 Hz, 1H, H_6), 3.17 (dddd, *J* = 5.8, 4.1, 3.3, 2.7 Hz, 1H, H_5), 2.81 (dd, *J* = 5.0, 4.1 Hz, 1H, H_4), 2.63 (dd, *J* = 5.0, 2.7 Hz, 1H, H_4), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.7, 90.3, 70.3, 59.38, 50.6, 44.6, 26.2, 16.6, -4.6.

(*R*)-**1**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.22 (d, *J* = 4.8 Hz, 2H, H_3), 3.80 (dd, *J* = 11.3, 3.3 Hz, 1H, H_6), 3.49 (dd, *J* = 11.3, 5.7 Hz, 1H, H_6), 3.17 (dddd, *J* = 5.8, 4.1, 3.2, 2.6 Hz, 1H, H_5), 2.81 (dd, *J* = 5.0, 4.1 Hz, 1H, H_4), 2.63 (dd, *J* = 5.0, 2.7 Hz, 1H, H_4), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.7, 90.3, 70.3, 59.4, 50.6, 44.6, 26.2, 16.6, -4.6.

(*S*)-**1**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.22 (d, *J* = 4.7 Hz, 2H, H_3), 3.80 (dd, J = 11.3, 3.2 Hz, 1H, H_6), 3.49 (dd, J = 11.3, 5.7 Hz, 1H, H_6), 3.17 (dddd, J = 5.8, 4.1, 3.2, 2.6 Hz, 1H, H_5), 2.81 (dd, J = 5.0, 4.1 Hz, 1H, H_4), 2.63 (dd, J = 5.0, 2.7 Hz, 1H,

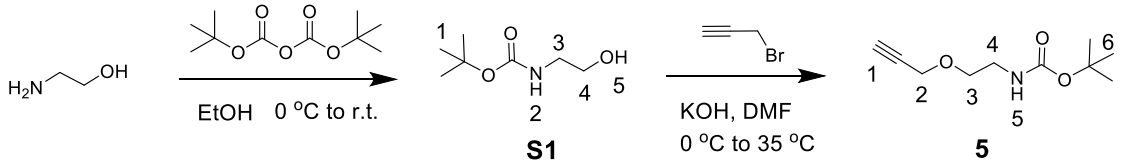
H_4), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.69, 90.29, 70.27, 59.37, 50.62, 44.61, 26.16, 16.59, -4.57.

rac-**2**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.21 (s, 2H, H_3), 3.97 (ddd, J = 10.5, 6.0, 4.8 Hz, 1H, H_5), 3.58 (m, 2H, H_6), 3.39 (dd, J = 5.5, 3.1 Hz, 2H, H_4), 2.43 (brs, 1H, H_7), 0.94 (s, 9H, H_1), 0.12 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.5, 90.7, 71.0, 69.7, 59.6, 53.6, 26.1, 16.6, -4.6. **HRMS** *m/z*= 270.1633 (calcd. for $C_{12}H_{24}N_3O_2Si$ 270.1632 $[M+H]^+$)

(*R*)-**2**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.21 (s, 2H, H_3), 3.97 (tdd, J = 6.1, 4.9, 4.2 Hz, 1H, H_5), 3.58 (m, 2H, H_6), 3.38 (dd, J = 5.5, 3.1 Hz, 2H, H_4), 2.42 (brs, 1H, H_7), 0.94 (s, 9H, H_1), 0.12 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.5, 90.7, 71.0, 69.7, 59.6, 53.6, 26.1, 16.6, -4.6.

(*S*)-**2**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 4.21 (s, 2H, H_3), 3.97 (p, J = 5.9 Hz, 1H, H_5), 3.58 (m, 2H, H_6), 3.39 (dd, J = 5.5, 3.1 Hz, 2H, H_4), 2.44 (brs, 1H, H_7), 0.94 (s, 9H, H_1), 0.12 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 101.5, 90.7, 71.0, 69.7, 59.6, 53.6, 26.2, 16.6, -4.6.

2.1.2 Synthesis of **5**

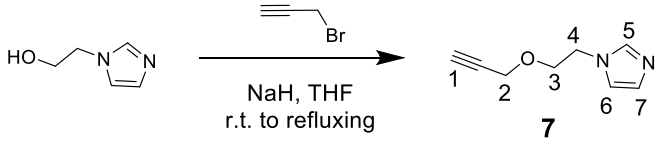


Compound **5** was prepared according to the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.97 (brs, 1H, H_2), 3.69 (dd, J = 4.3, 1.9 Hz, 2H, H_3), 3.29 (m, 2H, H_4), 2.55 (brs, 1H, H_5), 1.44 (s, 9H, H_1).

Compound **5**, (3.8 g, 65% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (brs, 1H, H_5), 4.15 (d, J = 2.4 Hz, 2H, H_2), 3.58 (dd, J = 5.5, 4.7 Hz, 2H, H_4), 3.34 (t, J = 5.4 Hz, 2H, H_3), 2.44 (t, J = 2.4 Hz, 1H, H_1), 1.44 (s, 9H, H_6).

2.1.3 Synthesis of **7**

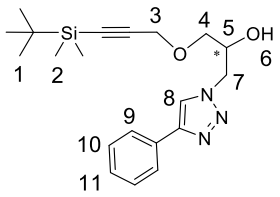


Compound **7** was prepared according to the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, J = 1.2 Hz, 1H, H_5), 7.05 (t, J = 1.1 Hz, 1H, H_6), 6.98 (t, J = 1.3 Hz, 1H, H_7), 4.19 – 4.10 (m, 4H, H_2 and H_4), 3.78 (dd, J = 5.6, 4.8 Hz, 2H, H_3), 2.43 (t, J = 2.4 Hz, 1H, H_1).

2.2 Synthesis of monomers

2.2.1 Synthesis of *rac*-**4a**, (*R*)-**4a** and (*S*)-**4a**



rac-**4a,** (*R*)-**4a,** (*S*)-**4a**

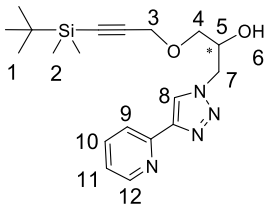
Compound *rac*-**2** (269 mg, 1 mmol) and phenylacetylene (165 μL, 1.5 equiv.) were added into a flask followed by EtOH (7 mL) with stirring. Water (1 mL), sodium ascorbate solution (40 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (16 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50℃ followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 1/9 to 3/7) to give the final product *rac*-**4a** as a white solid (371 mg, 1 mmol, quantitative yield). The products (*R*)-**4a** (371 mg, 1 mmol, quantitative yield) and (*S*)-**4a** (457 mg, 1.25 mmol, 82%) were prepared following the same protocol.

rac-**4a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ= 7.87 (s, 1H, H_8), 7.76 (dt, *J* = 8.2, 1.4 Hz, 2H, H_9), 7.40 (m, 2H, H_{10}), 7.31 (m, 1H, H_{11}), 4.60 (dd, *J* = 13.9, 3.4 Hz, 1H, H_7), 4.44 (dd, *J* = 13.9, 7.2 Hz, 1H, H_7), 4.32 (dddd, *J* = 7.2, 3.6, 2.3, 1.2 Hz, 1H, H_5), 4.22 (s, 2H, H_3), 3.65 (dd, *J* = 9.8, 4.6 Hz, 1H, H_4), 3.55 (dd, *J* = 9.7, 4.6 Hz, 1H, H_4), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 147.7, 130.5, 128.9, 128.3, 125.8, 121.3, 101.4, 90.9, 70.8, 69.3, 59.7, 53.2, 26.2, 16.6, -4.6. **HRMS** *m/z*= 372.2100 (calcd. for $C_{20}H_{30}N_3O_2Si$ 372.2102 $[M+H]^+$)

(*R*)-**4a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.85 (s, 1H, H_8), 7.76 – 7.67 (m, 2H, H_9), 7.42 – 7.27 (m, 3H, H_{10} and H_{11}), 4.60 (dd, *J* = 13.6, 2.9 Hz, 1H, H_7), 4.48 – 4.38 (m, 1H, H_7), 4.38 – 4.30 (m, 1H, H_5), 4.23 (s, 2H, H_3), 3.69 – 3.52 (m, 2H, H_4), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 147.2, 130.0, 128.5, 127.8, 125.3, 120.9, 101.0, 90.4, 70.4, 68.9, 59.3, 52.9, 25.7, 16.1, -5.0. **HRMS** *m/z*= 372.2101 (calcd. for $C_{20}H_{30}N_3O_2Si$ 372.2102 $[M+H]^+$).

(*S*)-**4a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 (s, 1H, H_8), 7.78 – 7.69 (m, 2H, H_9), 7.43 – 7.28 (m, 3H, H_{10} and H_{11}), 4.60 (dd, *J* = 13.8, 3.2 Hz, 1H, H_7), 4.43 (dd, *J* = 13.8, 7.3 Hz, 1H, H_7), 4.34 (dddd, J = 7.7, 5.7, 4.5, 3.1 Hz, 1H, H_5), 4.23 (s, 2H, H_3), 3.69 – 3.53 (m, 2H, H_4), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 147.6, 130.5, 128.9, 128.3, 125.7, 121.4, 101.4, 90.9, 70.8, 69.3, 59.7, 53.3, 26.2, 16.6, -4.6. **HRMS** *m/z*= 372.2100 (calcd. for $C_{20}H_{30}N_3O_2Si$ 372.2102 $[M+H]^+$).

2.2.2 Synthesis of *rac*-**4b**, (*R*)-**4b** and (*S*)-**4b**



rac-**4b,** (*R*)-**4b,** (*S*)-**4b**

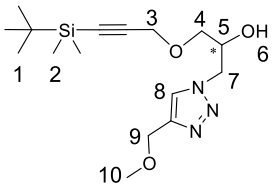
Compound *rac*-**2** (347 mg, 1.29 mmol) and 2-ethynylpyridine (206 µL, 1.5 equiv.) were added into a flask followed by EtOH (7 mL) with stirring. Water (1 mL), sodium ascorbate solution (52 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (21 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 1/2 to 3/1) to give the final product *rac*-**4b** as a brown oil (415 mg, 1.12 mmol, 87%). The products (*R*)-**4b** (366 mg, 0.98 mmol, 98%) and (*S*)-**4b** (657 mg, 1.76 mmol, quantitative yield) were prepared following the same protocol.

rac-**4b**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.53 (ddt, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{12}), 8.32 (s, 1H, H_8), 8.12 (dq, *J* = 8.0, 1.0 Hz, 1H, H_9), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H, H_{10}), 7.21 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H_{11}), 4.63 (dd, J = 14.0, 3.5 Hz, 1H, H_7), 4.54 – 4.42 (m, 1H, H_7), 4.33 (p, *J* = 4.8 Hz, 1H, H_5), 4.22 (s, 2H, H_3), 3.69 – 3.51 (m, 2H, H_4), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.2, 149.3, 148.0, 137.2, 123.9, 1223.0, 120.8, 101.4, 90.8, 70.9, 69.4, 59.7, 53.4, 26.2, 16.6, -4.6. **HRMS** *m/z*= 373.2054 (calcd. for $C_{19}H_{29}N_4O_2Si$ 373.2054 $[M+H]^+$).

(*R*)-**4b**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.50 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{12}), 8.32 (s, 1H, H_8), 8.10 (dt, *J* = 7.9, 1.1 Hz, 1H, H_9), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H, H_{10}), 7.20 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H_{11}), 4.64 (dd, *J* = 13.8, 3.2 Hz, 1H, H_7), 4.46 (dd, *J* = 13.9, 7.4 Hz, 1H, H_7), 4.39 – 4.31 (m, 1H, H_5), 4.23 (s, 2H, H_3), 3.73 – 3.52 (m, 2H, H_4), 0.91 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.1, 149.3, 147.9, 137.2, 123.9, 123.0, 120.4, 101.5, 90.8, 71.0, 69.4, 59.7, 53.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 373.2056 (calcd. for $C_{19}H_{29}N_4O_2Si$ 373.2054 $[M+H]^+$).

(*S*)-**4b**, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (ddd, *J* = 5.0, 1.8, 0.9 Hz, 1H, H_{12}), 8.32 (s, 1H, H_8), 8.09 (dt, *J* = 8.0, 1.1 Hz, 1H, H_9), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H, H_{10}), 7.20 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H_{11}), 4.64 (dd, *J* = 13.8, 3.1 Hz, 1H, H_7), 4.45 (dd, *J* = 13.8, 7.5 Hz, 1H, H_7), 4.35 (tt, *J* = 4.5, 1.8 Hz, 1H, H_5), 4.23 (s, 2H, H_3), 3.73 – 3.52 (m, 2H, H_4), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.2, 147.8, 137.2, 124.0, 122.9, 120.4, 101.5, 90.7, 71.0, 69.4, 59.7, 53.5, 26.1, 16.6, -4.6. **HRMS** *m/z*= 373.2055 (calcd. for $C_{19}H_{29}N_4O_2Si$ 373.2054 $[M+H]^+$).

2.2.3 Synthesis of *rac*-**4c**, (*R*)-**4c** and (*S*)-**4c**



rac-**4c,** (*R*)-**4c,** (*S*)-**4c**

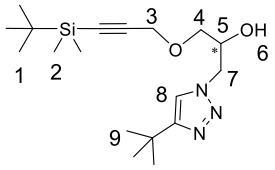
Compound *rac*-**2** (539 mg, 2 mmol) and methyl propargyl ether (210 mg, 1.5 equiv.) were added into a flask followed by EtOH (15 mL) with stirring. Water (1 mL), sodium ascorbate aqueous solution (40 mg/mL, 2 mL, 0.2 equiv.) and $CuSO_4$ aqueous solution (16 mg/mL, 2 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added to the mixture followed by air bubbling for 30 min. Thereafter, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 3/7 to 7/3) to give the final product *rac*-**4c** as a colorless oil (676 mg, 1.99 mmol, 99%). The products (*R*)-**4c** (311 mg, 0.92 mmol, 92%) and (*S*)-**4c** (415 mg, 1.22 mmol, 82%) were prepared following the same protocol.

rac-**4c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (s, 1H, H_8), 4.61 – 4.49 (m, 3H, H_7 and H_9), 4.48 – 4.33 (m, 1H, H_7), 4.20 (s, 3H, H_3 and H_5), 3.67 – 3.44 (m, 2H, H_4), 3.40 (s, 3H, H_{10}), 2.77 (brs, 1H, H_6), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 145.0, 124.1, 101.4, 90.8, 70.7, 69.3, 66.0, 59.6, 58.5, 53.1, 26.2, 16.6, -4.6. **HRMS** *m/z*= 340.2053 (calcd. for $C_{16}H_{30}N_3O_3Si$ 340.2051 $[M+H]^+$).

(*R*)-**4c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (s, 1H, H_8), 4.61 – 4.50 (m, 3H, H_7 and H_9), 4.38 (dd, *J* = 14.0, 7.2 Hz, 1H, H_7), 4.30 – 4.17 (m, 3H, H_3 and H_5), 3.66 – 3.45 (m, 2H, H_4), 3.40 (s, 3H, H_{10}), 2.91 (brs, 1H, H_6), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 145.0, 124.1, 101.4, 90.8, 70.7, 69.3, 66.0, 59.6, 58.5, 53.1, 26.1, 16.6, -4.6. **HRMS** *m/z*= 340.2049 (calcd. for $C_{16}H_{30}N_3O_3Si$ 340.2051 $[M+H]^+$).

(*S*)-**4c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (s, 1H, H_8), 4.62 – 4.50 (m, 3H, H_7 and H_9), 4.39 (dd, *J* = 14.0, 7.2 Hz, 1H, H_7), 4.20 (s, 3H, H_3 and H_5), 3.66 – 3.46 (m, 2H, H_4), 3.40 (s, 3H, H_{10}), 2.75 (brs, 1H, H_6), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 145.0, 124.1, 101.4, 90.8, 70.7, 69.3, 66.0, 59.6, 58.5, 53.1, 26.1, 16.6, -4.6. **HRMS** *m/z*= 340.2051 (calcd. for $C_{16}H_{30}N_3O_3Si$ 340.2051 $[M+H]^+$).

2.2.4 Synthesis of *rac*-**4d**, (*R*)-**4d** and (*S*)-**4d**



***rac*-4d, (*R*)-4d, (*S*)-4d**

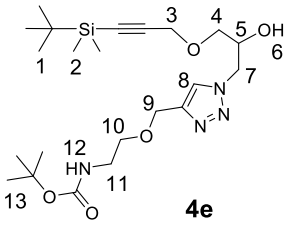
Compound *rac*-**2** (539 mg, 2 mmol) and 3,3'-dimethyl-1-butyne (370 µL, 1.5 equiv.) were added into a flask followed by EtOH (15 mL) with stirring. Water (1 mL), sodium ascorbate aqueous solution (40 mg/mL, 2 mL, 0.2 equiv.) and $CuSO_4$ aqueous solution (16 mg/mL, 2 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 1/9 to 3/7) to give the final product *rac*-**4d** as a colorless oil (640 mg, 1.82 mmol, 91%). The products (*R*)-**4d** (343 mg, 0.98 mmol, 98%) and (*S*)-**4d** (501 mg, 1.42 mmol, 95%) were prepared following the same protocol.

rac-**4d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (s, 1H, H_8), 4.50 (dd, *J* = 13.9, 3.4 Hz, 1H, H_7), 4.34 (dd, *J* = 13.9, 7.2 Hz, 1H, H_7), 4.24 (dddd, *J* = 5.9, 2.9, 1.7, 0.6 Hz, 1H, H_5), 4.20 (s, 2H, H_3), 3.65 – 3.46 (m, 2H, H_4), 3.19 (brs, 1H, H_6), 1.33 (s, 9H, H_9), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.2, 101.5, 90.7, 70.9, 69.4, 59.6, 52.9, 30.8, 30.5, 26.6, 16.6, -4.6. **HRMS** *m/z*= 352.2415 (calcd. for $C_{18}H_{34}N_3O_2Si$ 352.2415 $[M+H]^+$).

(*R*)-**4d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 (s, 1H, H_8), 4.50 (dd, *J* = 13.8, 3.2 Hz, 1H, H_7), 4.34 (dd, *J* = 13.8, 7.3 Hz, 1H, H_7), 4.29 – 4.23 (m, 1H, H_5), 4.20 (s, 2H, H_3), 3.64 – 3.46 (m, 2H, H_4), 3.21 (brs, 1H, H_6), 1.33 (s, 9H, H_9), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.3, 101.5, 90.7, 70.9, 69.4, 59.6, 52.9, 30.8, 30.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 352.2414 (calcd. for $C_{18}H_{34}N_3O_2Si$ 352.2415 $[M+H]^+$).

(*S*)-**4d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 (s, 1H, H_8), 4.50 (dd, *J* = 13.8, 3.3 Hz, 1H, H_7), 4.34 (dd, *J* = 13.8, 7.3 Hz, 1H, H_7), 4.29 – 4.22 (m, 1H, H_5), 4.20 (s, 2H, H_3), 3.65 – 3.46 (m, 2H, H_4), 3.18 (brs, 1H, H_6), 1.33 (s, 9H, H_9), 0.93 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.3, 101.5, 90.7, 70.9, 69.4, 59.6, 52.9, 30.8, 30.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 352.2413 (calcd. for $C_{18}H_{34}N_3O_2Si$ 352.2415 $[M+H]^+$).

2.2.5 Synthesis of **4e**

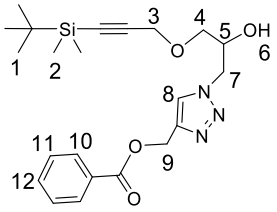


4e

Compound *rac*-**2** (158 mg, 0.59 mmol) and compound **5** (142 mg, 1.2 equiv.) were added into a flask followed by EtOH (7 mL) with stirring. Water (1 mL), sodium ascorbate aqueous solution (24 mg/mL, 1 mL, 0.2 equiv.) and $CuSO_4$ aqueous solution (9 mg/mL, 1 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 3/7 to 8/2) to give the final product **4e** as a colorless oil (237 mg, 0.51 mmol, 86%).

4e, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.69 (s, 1H, H_8), 4.96 (brs, 1H, H_{12}), 4.69 – 4.51 (m, 3H, H_9 and H_7), 4.38 (dd, J = 14.1, 7.4 Hz, 1H, H_7), 4.21 (m, 3H, H_3 and H_5), 3.58 (m, 4H, H_4 and H_{11}), 3.30 (brs, 2H, H_{10}), 2.78 (brs, 1H, H_6), 1.42 (s, 9H, H_{13}), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.1, 144.8, 124.2, 101.4, 90.8, 79.5, 70.8, 69.7, 69.3, 64.4, 59.6, 53.2, 40.5, 28.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 469.2841 (calcd. for $C_{22}H_{41}N_4O_5Si$ 469.2841 $[M+H]^+$).

2.2.6 Synthesis of **4f**

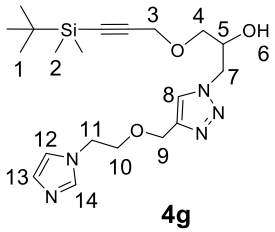


4f

Compound ***rac*-2** (269 mg, 1 mmol) and compound **6** (176 mg, 1.1 equiv.) were added into a flask followed by EtOH (7 mL) under argon with stirring. Water (1 mL), sodium ascorbate aqueous solution (40 mg/mL, 1 mL, 0.2 equiv.) and $CuSO_4$ aqueous solution (16 mg/mL, 1 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 15/85 to 50/50) to give the final product **4f** as a colorless oil (350 mg, 0.81 mmol, 82%).

4f, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.08 – 7.98 (m, 2H, H_{10}), 7.83 (s, 1H, H_8), 7.60 – 7.50 (m, 1H, H_{12}), 7.46 – 7.37 (m, 2H, H_{11}), 5.46 (s, 2H, H_9), 4.56 (dd, *J* = 14.0, 3.5 Hz, 1H, H_7), 4.40 (dd, *J* = 14.0, 7.2 Hz, 1H, H_7), 4.32 – 4.22 (m, 1H, H_5), 4.20 (s, 2H, H_3), 3.67 – 3.46 (m, 2H, H_4), 2.80 (brs, 1H, H_6), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.6, 143.0, 133.3, 129.9, 129.8, 128.5, 125.5, 101.3, 90.9, 70.7, 69.3, 59.6, 58.2, 53.1, 26.1, 16.6, -4.6. **HRMS** *m/z*= 430.2158 (calcd. for $C_{22}H_{32}N_3O_4Si$ 430.2157 $[M+H]^+$).

2.2.7 Synthesis of **4g**

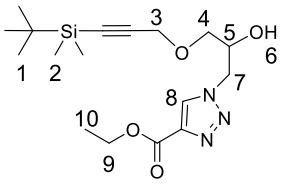


4g

Compound ***rac*-2** (269 mg, 1 mmol) and compound **7** (180 mg, 1.2 equiv.) were added into a flask followed by EtOH (7 mL) with stirring. Water (1 mL), sodium ascorbate aqueous solution (40 mg/mL, 1 mL, 0.2 equiv.) and $CuSO_4$ aqueous solution (16 mg/mL, 1 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 100/0 to 90/10) to give the final product **4g** as a brown oil (421 mg, quantitative yield).

4g, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 (s, 1H, H_8), 7.28 (s, 1H, H_{14}), 6.87 (brs, 2H, H_{12} and H_{13}), 4.66 – 4.49 (m, 3H, H_7 and H_9), 4.33 – 4.09 (m, 4H, H_3, H_5 and H_7), 4.06 – 3.98 (m, 2H, H_{11}), 3.88 – 3.74 (m, 2H, H_{10}), 3.62 (dd, *J* = 5.3, 4.0 Hz, 2H, H_4), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.1, 137.3, 128.4, 124.4, 119.8, 101.7, 90.5, 71.3, 68.9, 68.7, 64.1, 59.6, 54.0, 47.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 420.2426 (calcd. for $C_{20}H_{34}N_5O_3Si$ 420.2425 $[M+H]^+$).

2.2.8 Synthesis of **4h**



4h

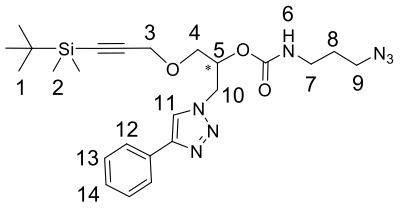
Compound ***rac*-2** (269 mg, 1 mmol) and compound **8** (120 mg, 1.2 equiv.) were added into a flask followed by EtOH (7 mL) with stirring. Water (1 mL), sodium ascorbate aqueous solution (40 mg/mL, 1 mL, 0.2 equiv.) and $CuSO_4$

aqueous solution (16 mg/mL, 1 mL, 0.1 equiv.) were successively added to the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (50 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 25/75 to 75/25) to give the final product **4h** as a colorless oil (367 mg, quantitative yield).

4h, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.23 (s, 1H, H_8), 4.62 (dd, J = 14.1, 3.4 Hz, 1H, H_7), 4.42 (m, 3H, H_7 and H_9), 4.26 (ddd, J = 5.8, 2.8, 1.4 Hz, 1H, H_5), 4.21 (s, 2H, H_3), 3.68 – 3.40 (m, 2H, H_4), 3.00 (brs, 1H, H_6), 1.40 (t, J = 7.1 Hz, 3H, H_{10}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.8, 140.2, 129.1, 101.2, 91.0, 70.6, 69.1, 61.4, 59.7, 53.3, 26.1, 16.5, 14.4, -4.6. **HRMS** *m/z*= 368.2000 (calcd. for $C_{17}H_{30}N_3O_4Si$ 368.2000 $[M+H]^+$).

2.3 Synthesis of dimers

2.3.1 Synthesis of *rac*-**5a**, (*R*)-**5a** and (*S*)-**5a**



rac-**5a,** (*R*)-**5a,** (*S*)-**5a**

Compound *rac*-**4a** (372 mg, 1 mmol) was added in a flask followed by CH_2Cl_2 (10 mL), 4-nitrophenyl chloroformate (242 mg, 1.2 equiv.) and pyridine (162 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were successfully added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were combined, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azidopropylamine[5, 6] (200 mg, 2 mmol) and Et_3N (279 μL, 2 mmol). The mixture was stirred for 2 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product *rac*-**5a** was obtained after passing the residue through a chromatography column (EtOAc/n-hexane = 1/9 to 3/7) as a yellow oil (455 mg, 0.92 mmol, 92%). (*R*)-**5a** (470 mg, quantitative yield) and (*S*)-**5a** (590 mg, quantitative yield) were obtained following the same protocol.

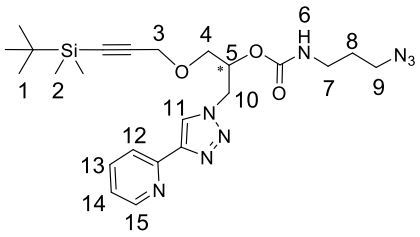
rac-**5a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 – 7.78 (m, 3H, H_{11} and H_{12}), 7.45 – 7.37 (m, 2H, H_{13}), 7.36 – 7.29 (m, 1H, H_{14}), 5.27 (dd, J = 6.0, 4.6 Hz, 1H, H_5), 5.05 (d, J = 6.3 Hz, 1H, H_6), 4.68 (dd, J = 5.5, 3.2 Hz, 2H, H_{10}), 4.22 (d, J = 0.7 Hz, 2H, H_3), 3.65 (d, J = 4.9 Hz, 2H, H_4), 3.30 (t, J = 6.5 Hz, 2H, H_9), 3.21 (td, J = 6.5, 2.2 Hz, 2H, H_7), 1.72 (p, J = 6.6 Hz, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 148.0, 130.6, 129.0, 128.3, 125.8, 120.7, 101.1,

71.1, 68.1, 59.6, 50.5, 49.1, 38.7, 29.0, 26.1, 16.5, -4.6. **HRMS** *m/z*= 498.2641 (calcd. for $C_{24}H_{36}N_7O_3Si$ 498.2643 $[M+H]^+$).

(*R*)-**5a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.88 – 7.76 (m, 3H, H_{11} and H_{12}), 7.47 – 7.38 (m, 2H, H_{13}), 7.37 – 7.29 (m, 1H, H_{14}), 5.28 (dd, *J* = 6.0, 4.5 Hz, 1H, H_5), 5.00 (t, *J* = 6.1 Hz, 1H, H_6), 4.69 (dd, *J* = 5.5, 3.1 Hz, 2H, H_{10}), 4.23 (d, *J* = 0.7 Hz, 2H, H_3), 3.65 (d, *J* = 4.8 Hz, 2H, H_4), 3.31 (t, *J* = 6.5 Hz, 2H, H_9), 3.23 (qd, *J* = 6.6, 2.3 Hz, 2H, H_7), 1.80 – 1.65 (m, 2H, H_8), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 148.0, 130.6, 129.0, 128.4, 125.9, 120.7, 101.1, 91.0, 71.1, 68.1, 59.7, 50.5, 49.1, 38.7, 29.0, 26.1, 16.6, -4.6.

(*S*)-**5a**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87 – 7.75 (m, 3H, H_{11} and H_{12}), 7.47 – 7.37 (m, 2H, H_{13}), 7.37 – 7.29 (m, 1H, H_{14}), 5.28 (dd, *J* = 6.0, 4.6 Hz, 1H, H_5), 5.01 (t, *J* = 6.1 Hz, 1H, H_6), 4.69 (dd, *J* = 5.5, 3.1 Hz, 2H, H_{10}), 4.23 (d, *J* = 0.8 Hz, 2H, H_3), 3.65 (d, *J* = 4.8 Hz, 2H, H_4), 3.31 (t, *J* = 6.5 Hz, 2H, H_9), 3.23 (qd, *J* = 6.6, 2.3 Hz, 2H, H_7), 1.72 (t, *J* = 6.6 Hz, 2H, H_8), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 148.0, 130.6, 129.0, 128.4, 125.9, 120.7, 101.1, 91.0, 71.1, 68.1, 59.7, 50.5, 49.1, 38.7, 29.0, 26.1, 16.6, -4.6.

2.3.2 Synthesis of *rac*-**5b**, (*R*)-**5b** and (*S*)-**5b**



rac-**5b**, (*R*)-**5b**, (*S*)-**5b**

Compound *rac*-**4b** (430 mg, 1.15 mmol) was added to a flask followed by CH_2Cl_2 (15 mL), 4-nitrophenyl chloroformate (348 mg, 1.5 equiv.) and pyridine (187 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azidopropylamine (230 mg, 2 equiv.) and Et_3N (281 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product *rac*-**5b** was obtained after the residue was passed through a chromatography column (EtOAc/n-hexane = 2/8 to 5/5) as a brown oil (501 mg, 1 mmol, 87%). (*R*)-**5b** (221 mg, 0.44 mmol, 48%) and (*S*)-**5b** (561 mg, 1.13 mmol, 94%) were obtained following the same protocol.

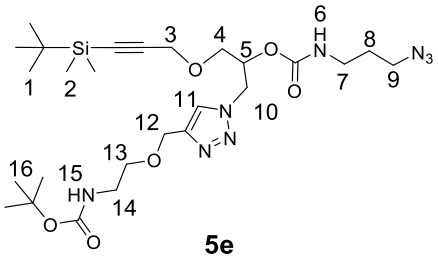
rac-**5b**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{15}), 8.24 – 8.09 (m, 2H, H_{11} and H_{12}), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H, H_{13}), 7.26 – 7.19 (m, 1H, H_{14}), 5.27 (dd, *J* = 5.9, 4.5 Hz, 1H, H_5), 5.17 – 5.03 (m, 1H, H_6), 4.71 (dd, *J* = 5.3, 2.5 Hz, 2H, H_{10}), 4.22 (d, *J* = 2.3 Hz, 2H, H_3), 3.65 (d, *J* = 4.9 Hz, 2H, H_4), 3.31 (t, *J* = 6.6 Hz, 2H, H_9), 3.22 (qd, *J* =

6.6, 1.8 Hz, 2H, H_7), 1.73 (p, *J* = 6.6 Hz, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 150.2, 149.4, 148.4, 137.2, 123.3, 123.1, 120.5, 101.2, 71.1, 68.0, 59.6, 50.7, 49.0, 38.6, 29.0, 26.1, 16.5, -4.6. **HRMS** *m/z*= 499.2594 (calcd. for $C_{23}H_{35}N_8O_3Si$ 499.2596 $[M+H]^+$).

(*R*)-**5b**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{15}), 8.32 – 8.08 (m, 2H, H_{11} and H_{12}), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H, H_{13}), 7.26 – 7.18 (m, 1H, H_{14}), 5.37 – 5.21 (m, 1H, H_5), 5.13 (t, *J* = 6.1 Hz, 1H, H_6), 4.81 – 4.57 (m, 2H, H_{10}), 4.22 (d, *J* = 2.5 Hz, 2H, H_3), 3.65 (d, *J* = 4.9 Hz, 2H, H_4), 3.31 (t, *J* = 6.6 Hz, 2H, H_9), 3.22 (qd, *J* = 6.7, 1.9 Hz, 2H, H_7), 1.73 (p, *J* = 6.6 Hz, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 150.2, 149.4, 148.4, 137.2, 123.3, 123.1, 120.5, 71.1, 68.0, 59.6, 50.7, 49.0, 38.6, 29.0, 26.1, 16.5, -4.6.

(*S*)-**5b**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{15}), 8.26 – 8.10 (m, 2H, H_{11} and H_{12}), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H, H_{13}), 7.23 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H_{14}), 5.36 – 5.22 (m, 1H, H_5), 5.09 (t, *J* = 6.2 Hz, 1H, H_6), 4.71 (dd, *J* = 5.3, 2.3 Hz, 2H, H_{10}), 4.22 (d, *J* = 2.3 Hz, 2H, H_3), 3.65 (d, *J* = 4.8 Hz, 2H, H_4), 3.31 (t, *J* = 6.6 Hz, 2H, H_9), 3.27 – 3.14 (m, 2H, H_7), 1.73 (p, *J* = 6.6 Hz, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.2, 150.3, 149.4, 148.5, 137.1, 123.3, 123.1, 120.4, 101.2, 71.1, 68.0, 59.6, 50.7, 49.0, 38.6, 29.0, 26.1, 16.5, -4.6.

2.3.3 Synthesis of **5e**



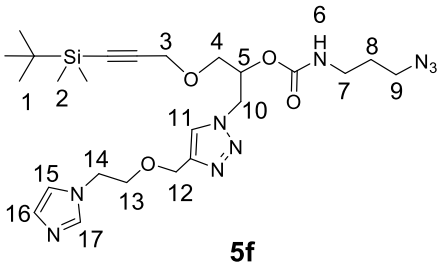
5e

Compound **4e** (200 mg, 0.43 mmol) was added into a flask followed by CH_2Cl_2 (10 mL), 4-nitrophenyl chloroformate (172 mg, 2 equiv.) and pyridine (74 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added into a flask followed by 3-azidopropylamine (107 mg, 2.5 equiv.) and Et_3N (159 μL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **5e** was obtained after the residue was passed through a chromatography column (EtOAc/n-hexane = 3/7 to 9/1) as a colorless oil (226 mg, 0.38 mmol, 89%).

5e, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.58 (s, 1H, H_{11}), 5.19 (m, 2H, H_5 and H_{15}), 4.93 (brs, 1H, H_6), 4.64 (m, 4H, H_{10} and H_{12}), 4.21 (d, *J* = 1.4 Hz, 2H, H_3), 3.71 – 3.49 (m, 4H, H_4 and H_{14}), 3.28 (m, 6H, H_7, H_9 and H_{13}), 1.84 – 1.67 (m, 2H, H_8), 1.43 (s, 9H, H_{16}), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 156.1, 155.2, 145.1, 123.6, 101.2, 71.1, 69.5,

68.1, 64.5, 59.6, 50.5, 49.1, 40.5, 38.7, 29.0, 28.5, 26.2, 16.6, -4.6. **HRMS** *m/z*= 595.3381 (calcd. for $C_{26}H_{47}N_8O_6Si$ 595.3382 $[M+H]^+$).

2.3.4 Synthesis of **5f**

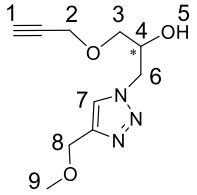


5f

Compound **4f** (390 mg, 0.93 mmol) was added into a flask followed by CH_2Cl_2 (10 mL), 4-nitrophenyl chloroformate (231 mg, 1.2 equiv.) and pyridine (163 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added into a flask followed by 3-azidopropylamine (191 mg, 2 equiv.) and Et_3N (279 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **5f** was obtained after the residue was passed through a chromatography column (CH_2Cl_2/MeOH = 100/0 to 95/5) as a yellow oil (438 mg, 0.80 mmol, 86%).

5f, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.50 (s, 1H, H_{11}), 7.15 (s, 1H, H_{17}), 7.13 – 7.05 (m, 1H, H_6), 7.02 (s, 1H, H_{15}), 6.91 (s, 1H, H_{16}), 5.18 (dt, *J* = 10.0, 5.6 Hz, 1H, H_5), 4.73 – 4.47 (m, 4H, H_{10} and H_{12}), 4.26 – 4.03 (m, 4H, H_3 and H_{14}), 3.81 – 3.65 (m, 2H, H_{13}), 3.62 – 3.42 (m, 2H, H_4), 3.38 (t, *J* = 6.7 Hz, 2H, H_9), 3.28 (q, *J* = 6.4 Hz, 2H, H_7), 1.82 (p, *J* = 6.6 Hz, 2H, H_8), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.6, 145.1, 138.0, 128.8, 123.5, 119.5, 101.4, 90.6, 70.5, 69.0, 67.8, 64.9, 59.6, 50.8, 49.2, 47.4, 38.5, 29.1, 26.2, 16.6, -4.6. **HRMS** *m/z*= 546.2969 (calcd. for $C_{24}H_{40}N_9O_4Si$ 546.2967 $[M+H]^+$).

2.3.5 Synthesis of *rac*-**6b**, (*R*)-**6b** and (*S*)-**6b**



rac-**6c**, (*R*)-**6c**, (*S*)-**6c**

Compound *rac*-**4c** (340 mg, 1 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by a tetrabutylammonium fluoride solution (1M in THF, 5 mL, 5 equiv.) with stirring at room temperature. The mixture

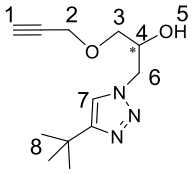
was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated under vacuum and the residue was purified by column chromatography (EtOAC/n-hexane = 5/5 to 10/0). The final product *rac*-**6c** was obtained as a colorless oil (160 mg, 0.71 mmol, 71%). (*R*)-**6c** (133 mg, 0.59 mmol, 70%) and (*S*)-**6c** (215 mg, 0.95 mmol, 82%) were obtained with the same protocol.

rac-**6c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.68 (s, 1H, H_7), 4.62 – 4.50 (m, 3H, H_6 and H_8), 4.39 (dd, J = 14.0, 7.0 Hz, 1H, H_6), 4.28 – 4.15 (m, 3H, H_2 and H_4), 3.65 – 3.45 (m, 2H, H_3), 3.38 (s, 3H, H_9), 2.78 (brs, 1H, H_5), 2.46 (t, J = 2.4 Hz, 1H, H_1). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.9, 124.2, 79.1, 75.4, 70.8, 69.1, 65.9, 58.8, 58.4, 53.0. **HRMS** *m/z*= 226.1188 (calcd. for $C_{10}H_{16}N_3O_3$ 226.1186 $[M+H]^+$).

(*R*)-**6c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (s, 1H, H_7), 4.59 – 4.50 (m, 3H, H_6 and H_8), 4.39 (dd, J = 14.0, 7.1 Hz, 1H, H_6), 4.28 – 4.16 (m, 3H, H_2 and H_4), 3.63 – 3.45 (m, 2H, H_3), 3.39 (s, 3H, H_9), 3.00 (brs, 1H, H_5), 2.46 (t, J = 2.4 Hz, 1H, H_1). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.9, 124.2, 79.1, 75.4, 70.8, 69.2, 66.0, 58.8, 58.4, 53.0.

(*S*)-**6c**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (s, 1H, H_7), 4.60 – 4.49 (m, 3H, H_6 and H_8), 4.39 (dd, J = 14.0, 7.1 Hz, 1H, H_6), 4.27 – 4.15 (m, 3H, H_2 and H_4), 3.62 – 3.45 (m, 2H, H_3), 3.39 (s, 3H, H_9), 2.81 (brs, 1H, H_5), 2.46 (t, J = 2.4 Hz, 1H, H_1). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.9, 124.2, 79.1, 75.4, 70.8, 69.1, 66.0, 58.8, 58.5, 53.0.

2.3.6 Synthesis of *rac*-**6d**, (*R*)-**6d** and (*S*)-**6d**



rac-**6d**, (*R*)-**6d**, (*S*)-**6d**

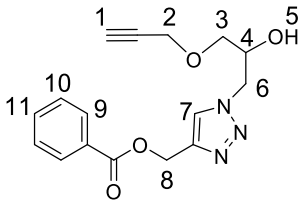
Compound *rac*-**4d** (352 mg, 1 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by a tetrabutylammonium fluoride solution (1M in THF, 5 mL, 5 equiv.) under stirring at room temperature. The mixture was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated under vacuum and the residue was purified by column chromatography (EtOAC/n-hexane = 1/9 to 3/7). The final product *rac*-**6d** was obtained as a colorless oil (213 mg, 0.90 mmol, 90%). (*R*)-**6d** (181 mg, 0.76 mmol, 84%) and (*S*)-**6d** (264 mg, 1.11 mmol, 93%) were obtained with the same protocol.

rac-**6d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (s, 1H, H_7), 4.50 (dd, J = 14.0, 3.8 Hz, 1H, H_6), 4.36 (dd, J = 13.9, 6.9 Hz, 1H, H_6), 4.29 – 4.21 (m, 1H, H_4), 4.19 (d, J = 2.4 Hz, 2H, H_2), 3.67 – 2.97 (m, 3H, H_3 and H_5), 2.45 (t, J = 2.4 Hz, 1H, H_1), 1.32 (s, 9H, H_8). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.4, 79.2, 75.3, 70.8, 69.2, 58.8, 52.7, 30.8, 30.5. **HRMS** *m/z*= 238.1551 (calcd. for $C_{12}H_{20}N_3O_2$ 238.1550 $[M+H]^+$).

(*R*)-**6d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (s, 1H, H_7), 4.50 (dd, *J* = 13.9, 3.7 Hz, 1H, H_6), 4.36 (dd, *J* = 13.9, 7.0 Hz, 1H, H_6), 4.30 – 4.23 (m, 1H, H_4), 4.19 (d, *J* = 2.4 Hz, 2H, H_2), 3.65 – 2.98 (m, 3H, H_3 and H_5), 2.45 (t, *J* = 2.4 Hz, 1H, H_1), 1.32 (s, 9H, H_8). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.4, 79.2, 75.3, 70.8, 69.2, 58.8, 52.8, 30.8, 30.5.

(*S*)-**6d**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (s, 1H, H_7), 4.50 (dd, *J* = 13.9, 3.7 Hz, 1H, H_6), 4.36 (dd, *J* = 13.9, 7.0 Hz, 1H, H_6), 4.31 – 4.20 (m, 1H, H_4), 4.19 (d, *J* = 2.4 Hz, 2H, H_2), 3.65 – 2.98 (m, 3H, H_3 and H_5), 2.45 (t, *J* = 2.4 Hz, 1H, H_1), 1.32 (s, 9H, H_8). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.6, 120.4, 79.2, 75.3, 70.8, 69.2, 58.8, 52.7, 30.8, 30.5.

2.3.7 Synthesis of **6g**

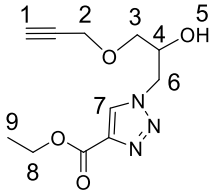


6g

Compound **4g** (320 mg, 0.74 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by a tetrabutylammonium fluoride solution (1M in THF, 3 mL, 4 equiv.) under stirring at room temperature. The mixture was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated under vacuum and the residue was followed by EtOAc (50 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) and brine (50 mL), dried with Na_2SO_4 and the solvent was evaporated. The residue **6g** was used for the next step without further purification.

6g, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.06 – 8.00 (m, 2H, H_9), 7.84 (s, 1H, H_7), 7.59 – 7.50 (m, 1H, H_{11}), 7.47 – 7.38 (m, 2H, H_{10}), 5.46 (s, 2H, H_8), 4.56 (dd, *J* = 14.1, 3.8 Hz, 1H, H_6), 4.42 (dd, *J* = 14.1, 6.9 Hz, 1H, H_6), 4.30 – 4.22 (m, 1H, H_4), 4.18 (d, *J* = 2.4 Hz, 2H, H_2), 3.65 – 3.45 (m, 2H, H_3), 2.44 (t, J = 2.4 Hz, 1H, H_1). **HRMS** *m/z*= 316.1292 (calcd. for $C_{16}H_{18}N_3O_4$ 316.1292 $[M+H]^+$).

2.3.8 Synthesis of **6h**



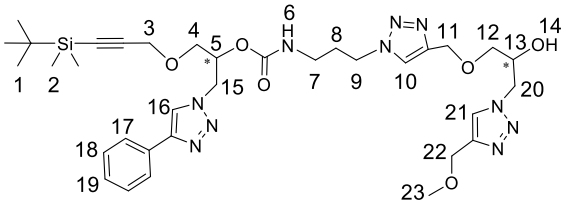
6h

Compound **4h** (320 mg, 0.87 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by a tetrabutylammonium fluoride solution (1M in THF, 3.5 mL, 4 equiv.) under stirring at room temperature. The mixture was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated

under vacuum and the residue was followed by EtOAc (50 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) and brine (50 mL), dried with Na_2SO_4 and evaporated to remove the solvent. The residue **6h** was used for the next step without further purification.

6h, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.24 (s, 1H, H_7), 4.63 (dd, J = 14.1, 3.6 Hz, 1H, H_6), 4.50 – 4.34 (m, 3H, H_6 and H_8), 4.32 – 4.22 (m, 1H, H_4), 4.20 (d, J = 2.4 Hz, 2H, H_2), 3.66 – 3.47 (m, 2H, H_3), 2.47 (t, J = 2.4 Hz, 1H, H_1), 1.40 (t, J = 7.1 Hz, 3H, H_9). **HRMS** *m/z*= 254.1134 (calcd. for $C_{11}H_{16}N_3O_4$ 254.1135 $[M+H]^+$).

2.3.9 Synthesis of *rac*-**FE**, (*R*,*R*)-**FE** and (*S*,*S*)-**FE**



rac-**FE,** (*R*,*R*)-**FE,** (*S*,*S*)-**FE**

Compound *rac*-**5a** (190 mg, 0.38 mmol) and compound *rac*-**6c** (85 mg, 0.38 mmol, 1 equiv.) were added into a flask followed by EtOH (3 mL). Then, a sodium ascorbate solution (15 mg in 0.5 mL water, 0.1 equiv.) and a $CuSO_4$ solution (6 mg in 0.5 mL water, 0.2 equiv.) were added into the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 2/8 to 7/3) to give the final product *rac*-**FE** as a colorless oil (257 mg, 0.36 mmol, 93%). The dimers (*R*,*R*)-**FE** (362 mg, 0.5 mmol, quantitative yield) and (*S*,*S*)-**FE** (639 mg, 0.88 mmol, quantitative yield) were obtained following the same protocol.

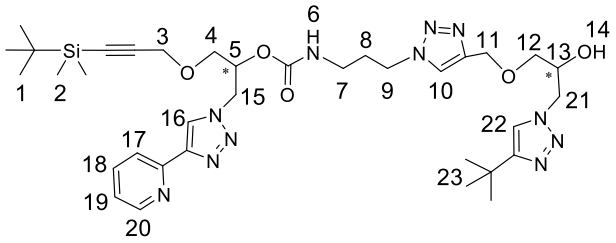
rac-**FE**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, J = 1.6 Hz, 1H, H_{16}), 7.78 (d, J = 7.3 Hz, 2H, H_{17}), 7.69 (d, J = 3.5 Hz, 1H, H_{21}), 7.61 (d, J = 10.8 Hz, 1H, H_{10}), 7.39 (t, J = 7.5 Hz, 2H, H_{18}), 7.32 (t, J = 7.3 Hz, 1H, H_{19}), 5.41 (brs, 1H, H_6), 5.30 (t, J = 5.5 Hz, 1H, H_5), 4.74 – 4.64 (m, 2H, H_{15}), 4.64 – 4.56 (m, 2H, H_{11}), 4.55 – 4.48 (m, 3H, H_{20} and H_{22}), 4.43 – 4.35 (m, 1H, H_{20}), 4.35 – 4.27 (m, 2H, H_9), 4.23 (d, J = 2.7 Hz, 2H, H_3), 4.16 (q, J = 5.9, 5.4 Hz, H_{13}), 3.74 – 3.62 (m, 2H, H_4), 3.57 – 3.42 (m, 2H, H_{12}), 3.39 (d, J = 0.8 Hz, 3H, H_{23}), 3.15 – 2.96 (m, 2H, H_7), 2.64 (brs, 1H, H_{14}), 2.13 – 1.93 (m, 2H, H_8), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.5, 129.0, 128.4, 125.8, 124.3, 123.6, 121.0, 71.3, 71.0, 69.3, 68.2, 65.9, 64.7, 59.7, 58.4, 53.6, 52.9, 50.8, 47.3, 37.7, 30.3, 26.1, 16.6, -4.6. **HRMS** *m/z*= 723.3749 (calcd. for $C_{34}H_{51}N_{10}O_6Si$ 723.3757 $[M+H]^+$).

(*R*,*R*)-**FE**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (s, 1H, H_{16}), 7.81 – 7.74 (m, 2H, H_{17}), 7.70 (s, 1H, H_{21}), 7.58 (s, 1H, H_{10}), 7.38 (t, J = 7.6 Hz, 2H, H_{18}), 7.34 – 7.28 (m, 1H, H_{19}), 5.51 (t, J = 6.2 Hz, 1H, H_6), 5.29 (m, 1H, H_5), 4.68 (t, J = 5.6 Hz, 2H, H_{15}), 4.63 – 4.55 (m, 2H, H_{11}), 4.53 – 4.49 (m, 3H, H_{20} and H_{22}), 4.39 (dd, J = 14.1, 6.9 Hz, 1H, H_{20}), 4.35 – 4.25 (m, 2H, H_9),

4.23 (d, *J* = 2.7 Hz, 2H, H_3), 4.15 (h, *J* = 4.7 Hz, 1H, H_{13}), 3.67 (qd, *J* = 10.4, 5.0 Hz, 2H, H_4), 3.53 – 3.41 (m, 2H, H_{12}), 3.38 (s, 3H, H_{23}), 3.18 – 2.95 (m, 2H, H_7), 2.49 (brs, 1H, H_{14}), 2.12 – 1.91 (m, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.6, 144.8, 130.4, 129.0, 128.4, 125.8, 124.3, 123.6, 121.0, 101.1, 71.4, 71.0, 69.3, 68.2, 65.9, 64.7, 59.7, 58.4, 52.9, 50.8, 47.2, 37.7, 30.3, 26.1, 16.6, -4.6.

(*S*,*S*)-**FE**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (s, 1H, H_{16}), 7.83 – 7.74 (m, 2H, H_{17}), 7.70 (s, 1H, H_{21}), 7.58 (s, 1H, H_{10}), 7.38 (t, *J* = 7.5 Hz, 2H, H_{18}), 7.34 – 7.28 (m, 1H, H_{19}), 5.49 (t, *J* = 6.3 Hz, 1H, H_6), 5.36 – 5.24 (m, 1H, H_5), 4.74 – 4.63 (m, 2H, H_{15}), 4.62 – 4.55 (m, 2H, H_{11}), 4.54 – 4.46 (m, 3H, H_{20} and H_{22}), 4.39 (dd, *J* = 14.0, 6.9 Hz, 1H, H_{20}), 4.35 – 4.25 (m, 2H, H_9), 4.23 (d, *J* = 2.8 Hz, 2H, H_3), 4.19 – 4.11 (m, 1H, H_{13}), 3.67 (qd, *J* = 10.4, 4.9 Hz, 2H, H_4), 3.56 – 3.41 (m, 2H, H_{12}), 3.38 (s, 3H, H_{23}), 3.22 – 2.80 (m, 3H, H_7 and H_{14}), 2.01 (ddq, *J* = 38.0, 13.9, 6.9 Hz, 2H, H_8), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.5, 144.9, 130.4, 129.0, 128.4, 125.8, 124.3, 123.6, 121.0, 101.1, 71.3, 71.0, 69.3, 68.3, 65.9, 64.7, 59.7, 58.4, 52.9, 50.8, 47.2, 37.7, 30.3, 26.1, 16.6, -4.6.

2.3.10 Synthesis of *rac*-**PB**, (*R*,*R*)-**PB** and (*S*,*S*)-**PB**



***rac*-PB, (*R*,*R*)-PB, (*S*,*S*)-PB**

Compound *rac*-**5b** (250 mg, 0.5 mmol) and compound ***rac*-6d** (120 mg, 0.5 mmol, 1 equiv.) were added into a flask followed by EtOH (6 mL). Then, a sodium ascorbate solution (20 mg in 1 mL water) and a $CuSO_4$ solution (8 mg in 1 mL water) were added into the mixture. The reaction was stirred for 2 h at 50℃ followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/n-hexane = 3/7 to 8/2) to give the final product *rac*-**PB** as a colorless oil (274 mg, 0.37 mmol, 80%). The dimers (*R*,*R*)-**PB** (344 mg, 0.47 mmol, 93%) and (*S*,*S*)-**PB** (623 mg, 0.85 mmol, 84%) were obtained following the same protocol.

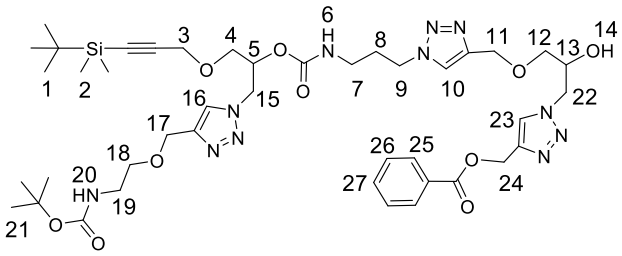
rac-**PB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.50 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, H_{16}), 8.30 (d, *J* = 25.7 Hz, 1H, H_{20}), 8.10 (t, *J* = 8.5 Hz, 1H, H_{17}), 7.76 (q, *J* = 7.2 Hz, 1H, H_{18}), 7.63 (d, *J* = 17.0 Hz, 1H, H_{10}), 7.40 (d, *J* = 3.5 Hz, 1H, H_{22}), 7.25 – 7.16 (m, 1H, H_{19}), 5.54 (brs, 1H, H_6), 5.32 (t, *J* = 4.5 Hz, 1H, H_5), 4.81 – 4.66 (m, 2H, H_{15}), 4.61 (dd, *J* = 11.6, 4.9 Hz, 2H, H_{11}), 4.54 – 4.45 (m, 1H, H_{21}), 4.44 – 4.27 (m, 3H, H_9 and H_{21}), 4.27 – 4.16 (m, 3H, H_3 and H_{13}), 3.75 – 3.63 (m, 2H, H_4), 3.61 – 3.43 (m, 2H, H_{12}), 3.23 – 2.94 (m, 2H, H_7), 2.19 – 1.97 (m, 3H, H_{12} and H_8), 1.31 (s, 9H, H_{23}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6, 155.6, 149.3, 144.6, 137.4, 123.6, 123.2, 120.4, 120.3, 90.9, 71.1, 69.5,

69.4, 68.2, 64.8, 59.7, 52.8, 51.0, 47.2, 37.6, 30.8, 30.5, 30.4, 26.2, 16.6, -4.6. **HRMS** *m/z*= 736.4075 (calcd. for $C_{35}H_{54}N_{11}O_5Si$ 736.4073 $[M+H]^+$).

(*R*,*R*)-**PB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.50 (dt, *J* = 4.8, 1.4 Hz, 1H, H_{16}), 8.30 (d, *J* = 11.9 Hz, 1H, H_{20}), 8.16 – 8.04 (m, 1H, H_{17}), 7.80 – 7.70 (m, 1H, H_{18}), 7.61 (s, 1H, H_{10}), 7.39 (d, *J* = 13.6 Hz, 1H, H_{22}), 7.22 (dt, *J* = 10.3, 4.1 Hz, 1H, H_{19}), 5.49 (brs, 1H, H_6), 5.33 (t, *J* = 5.8 Hz, 1H, H_5), 4.72 (qd, *J* = 14.4, 5.5 Hz, 2H, H_{15}), 4.65 – 4.55 (m, 2H, H_{11}), 4.53 – 4.45 (m, 1H, H_{21}), 4.44 – 4.31 (m, 2H, H_9), 4.31 – 4.24 (m, 1H, H_{21}), 4.24 – 4.18 (m, 3H, H_3 and H_{13}), 3.75 – 3.60 (m, 2H, H_4), 3.60 – 3.44 (m, 2H, H_{12}), 3.23 – 2.94 (m, 2H, H_7), 2.30 – 1.83 (m, 3H, H_8 and H_{14}), 1.31 (s, 9H, H_{23}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.3, 144.3, 123.3, 122.9, 120.2, 120.0, 100.9, 71.4, 70.9, 69.3, 67.9, 64.7, 59.4, 52.6, 50.7, 46.8, 37.4, 30.6, 30.2, 30.1, 25.9, 16.3, -4.9.

(*S*,*S*)-**PB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.56 – 8.44 (m, 1H, H_{16}), 8.32 (s, 1H, H_{20}), 8.17 – 8.03 (m, 1H, H_{17}), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H, H_{18}), 7.61 (s, 1H, H_{10}), 7.41 (s, 1H, H_{22}), 7.21 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H, H_{19}), 5.61 (brs, 1H, H_6), 5.36 – 5.25 (m, 1H, H_5), 4.80 – 4.67 (m, 2H, H_{15}), 4.66 – 4.55 (m, 2H, H_{11}), 4.48 (dd, *J* = 14.0, 3.9 Hz, 1H, H_{21}), 4.37 (ddd, *J* = 27.5, 13.3, 6.5 Hz, 2H, H_9), 4.31 – 4.25 (m, 1H, H_{21}), 4.24 – 4.17 (m, 3H, H_3 and H_{13}), 3.76 – 3.62 (m, 2H, H_4), 3.61 – 3.43 (m, 2H, H_{12}), 3.23 – 2.97 (m, 2H, H_7), 2.22 (brs, 1H, H_{14}), 2.15 – 1.90 (m, 2H, H_8), 1.31 (s, 9H, H_{23}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6, 155.6, 149.2, 144.6, 137.4, 123.6, 123.5, 123.2, 120.4, 120.2, 71.6, 71.1, 69.5, 68.2, 64.9, 59.6, 52.8, 50.9, 47.1, 37.6, 30.8, 30.5, 30.3, 26.1, 16.5, -4.6.

2.3.11 Synthesis of **A(Boc)O(Bz)**



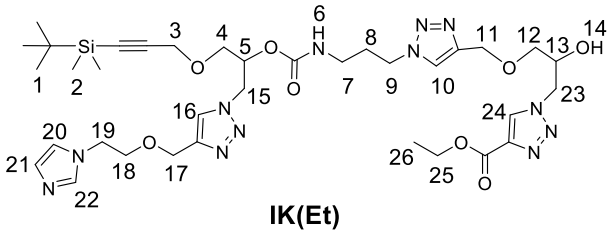
A(Boc)O(Bz)

Compound **5e** (200 mg, 0.34 mmol) and compound **6g** (108 mg, 0.34 mmol, 1 equiv.) were added into a flask followed by EtOH (4 mL). Then, a sodium ascorbate solution (16 mg in 0.75 mL water) and a $CuSO_4$ solution (6 mg in 0.75 mL water) were added into the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 95/5) to give the final product **A(Boc)O(Bz)** as a colorless oil (249 mg, 0.27 mmol, 81%).

A(Boc)O(Bz), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07 – 7.98 (m, 2H, H_{25}), 7.86 (d, *J* = 3.1 Hz, 1H, H_{23}), 7.72 (d, *J* = 3.6 Hz, 1H, H_{10}), 7.60 (d, *J* = 1.2 Hz, 1H, H_{16}), 7.58 – 7.50 (m, 1H, H_{27}), 7.42 (ddt, *J* = 8.2, 6.7, 1.1 Hz, 2H, H_{26}), 5.45 (brs, 3H, H_6 and

H_{24}), 5.22 (t, *J* = 5.5 Hz, 1H, H_5), 5.04 (brs, 1H, H_{20}), 4.76 – 4.49 (m, 7H, H_{11}, H_{15}, H_{17} and H_{22}), 4.47 – 4.34 (m, 3H, H_9 and H_{22}), 4.26 – 4.14 (m, 3H, H_3 and H_{13}), 3.78 – 3.42 (m, 6H, H_4, H_{12} and H_{19}), 3.37 – 2.95 (m, 4H, H_7 and H_{18}), 2.45 (brs, 1H, H_{14}), 2.14 – 2.01 (m, 2H, H_8), 1.42 (s, 9H, H_{21}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 166.6, 156.2, 155.5, 144.6, 142.9, 133.4, 129.9, 128.5, 125.6, 123.8, 123.5, 101.2, 71.51, 71.0, 69.6, 69.4, 69.3, 68.2, 64.8, 64.4, 59.7, 58.2, 53.0, 50.7, 47.4, 40.5, 37.8, 30.4, 28.6, 26.2, 16.6, -4.6. **HRMS** *m/z*= 910.4605 (calcd. for $C_{42}H_{64}N_{11}O_{10}Si$ 910.4601 $[M+H]^+$).

2.3.12 Synthesis of **IK(Et)**



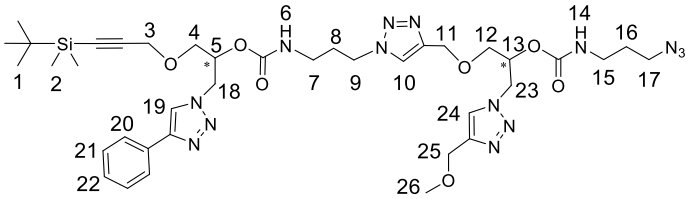
IK(Et)

Compound **5f** (380 mg, 0.7 mmol) and compound **6h** (177 mg, 0.7 mmol, 1 equiv.) were added into a flask followed by EtOH (7 mL). Then, a sodium ascorbate solution (32 mg in 1.5 mL water) and a $CuSO_4$ solution (12 mg in 1.5 mL water) were added into the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 90/10) to give the final product **IK(Et)** as a colorless oil (375 mg, 0.47 mmol, 68%).

IK(Et), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 3.8 Hz, 1H, H_{24}), 7.72 (d, *J* = 4.0 Hz, 1H, H_{16}), 7.65 – 7.39 (m, 1H, H_{22}), 7.32 (d, *J* = 6.1 Hz, 1H, H_{10}), 7.14 – 6.70 (m, 3H, H_6, H_{20} and H_{21}), 5.19 (d, *J* = 7.2 Hz, 1H, H_5), 4.71 – 4.54 (m, 7H, H_{11}, H_{15}, H_{17} and H_{23}), 4.50 – 4.32 (m, 5H, H_9, H_{23} and H_{25}), 4.28 – 4.04 (m, 5H, H_3, H_{13} and H_{19}), 3.78 – 3.67 (m, 2H, H_4), 3.63 – 3.47 (m, 4H, H_{12} and H_{18}), 3.14 (d, *J* = 6.0 Hz, 2H, H_7), 2.65 (brs, 1H, H_{14}), 2.18 – 1.98 (m, 2H, H_8), 1.38 (t, *J* = 7.1 Hz, 3H, H_{26}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 161.0, 155.8, 145.0, 144.5, 129.3, 123.7, 123.5, 101.3, 90.7, 71.6, 71.4, 70.8, 69.0, 68.9, 68.1, 64.8, 64.8, 64.7, 61.4, 59.6, 53.4, 53.4, 50.8, 47.6, 37.8, 30.4, 26.2, 16.6, 14.5, -4.6. **HRMS** *m/z*= 799.4028 (calcd. for $C_{35}H_{55}N_{12}O_8Si$ 799.4030 $[M+H]^+$).

2.4 Synthesis of tetramers

2.4.1 Synthesis of *rac*-**S3**, (*R*,*R*)-**S3** and (*S*,*S*)-**S3**



rac-**S3**, (*R*,*R*)-**S3**, (*S*,*S*)-**S3**

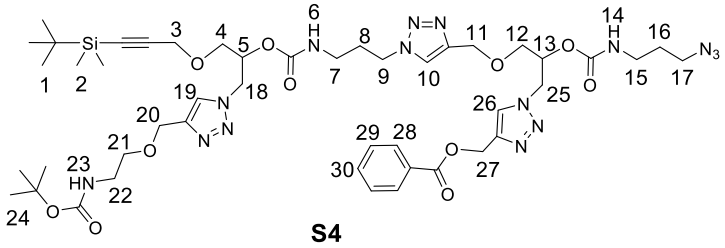
Compound *rac*-**FE** (379 mg, 0.5 mmol) was added into a flask followed by CH_2Cl_2 (10 mL), 4-nitrophenyl chloroformate (202 mg, 2 equiv.) and pyridine (85 μL, 2 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (10 mL) and added into a flask followed by 3-azidopropylamine (125 mg, 2.5 equiv.) and Et_3N (175 μL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product *rac*-**S3** was obtained after the residue was passed through a chromatography column (EtOAc/n-hexane = 2/8 to 7/3) as a colorless oil (307 mg, 0.36 mmol, 71%). (*R*,*R*)-**S3** (313 mg, 0.37 mmol, 78%) and (*S*,*S*)-**S3** (784 mg, quantitative yield) were obtained with the same protocol.

rac-**S3**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, J = 5.6 Hz, 1H, H_{19}), 7.83 – 7.71 (m, 2H, H_{20}), 7.64 (d, J = 1.6 Hz, 1H, H_{24}), 7.58 (d, J = 1.9 Hz, 1H, H_{10}), 7.38 (t, J = 7.6 Hz, 2H, H_{21}), 7.31 (t, J = 7.5 Hz, 1H, H_{22}), 5.54 (brs, 1H, H_6), 5.37 – 5.19 (m, 2H, H_5 and H_{13}), 5.13 (brs, 1H, H_{14}), 4.76 – 4.48 (m, 8H, H_{11}, H_{18}, H_{23} and H_{25}), 4.39 – 4.18 (m, 4H, H_3 and H_9), 3.75 – 3.60 (m, 2H, H_4), 3.60 – 3.47 (m, 2H, H_{12}), 3.41 – 3.29 (m, 5H, H_{17} and H_{26}), 3.39 – 3.30 (m, 3H, H_7 and H_{15}), 3.10 – 2.97 (m, 1H, H_{15}), 2.12 – 1.95 (m, 2H, H_8), 1.75 (p, J = 6.6 Hz, 2H, H_{16}), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.52, 155.28, 147.92, 130.51, 129.00, 128.40, 125.77, 123.68, 123.63, 120.92, 71.15, 71.11, 71.01, 68.25, 65.92, 64.86, 59.67, 58.42, 50.74, 50.21, 49.10, 47.25, 38.67, 37.77, 30.22, 29.02, 26.14, 16.56, -4.60. **HRMS** *m/z*= 849.4302 (calcd. for $C_{38}H_{57}N_{14}O_7Si$ 849.4298 $[M+H]^+$).

(*R*,*R*)-**S3**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (s, 1H, H_{19}), 7.82 – 7.74 (m, 2H, H_{20}), 7.64 (s, 1H, H_{24}), 7.58 (s, 1H, H_{10}), 7.38 (t, J = 7.6 Hz, 2H, H_{21}), 7.32 (d, J = 7.4 Hz, 1H, H_{22}), 5.53 (t, J = 6.2 Hz, 1H, H_6), 5.35 – 5.26 (m, 2H, H_5 and H_{13}), 5.13 (t, J = 5.1 Hz, 1H, H_{14}), 4.75 – 4.57 (m, 6H, H_{11}, H_{18} and H_{23}), 4.53 (s, 2H, H_{25}), 4.30 (q, J = 6.4 Hz, 2H, H_9), 4.23 (d, J = 3.3 Hz, 2H, H_3), 3.68 (dt, J = 10.1, 5.0 Hz, 2H, H_4), 3.52 (h, J = 5.6 Hz, 2H, H_{12}), 3.41 – 3.29 (m, 5H, H_{17} and H_{26}), 3.29 – 3.14 (m, 3H, H_7 and H_{15}), 3.03 (dd, J = 14.0, 6.5 Hz, 1H, H_{15}), 2.14 – 1.97 (m, 2H, H_8), 1.75 (dq, J = 13.3, 6.6 Hz, 2H, H_{16}), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.5, 155.3, 147.9, 145.2, 144.3, 130.5, 129.0, 128.4, 125.8, 123.7, 123.6, 120.9, 101.1, 91.0, 71.1, 71.0, 68.2, 65.9, 64.9, 59.7, 58.4, 50.8, 50.2, 49.1, 47.3, 38.7, 37.8, 30.2, 29.0, 26.1, 16.5, -4.6.

(*S*,*S*)-**S3**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (s, 1H, H_{19}), 7.82 – 7.75 (m, 2H, H_{20}), 7.64 (s, 1H, H_{24}), 7.58 (s, 1H, H_{10}), 7.38 (t, J = 7.5 Hz, 2H, H_{21}), 7.32 (d, J = 7.3 Hz, 1H, H_{22}), 5.54 (t, J = 6.3 Hz, 1H, H_6), 5.35 – 5.26 (m, 2H, H_5 and H_{13}), 5.18 – 5.03 (m, 1H, H_{14}), 4.78 – 4.56 (m, 6H, H_{11}, H_{18} and H_{23}), 4.53 (s, 2H, H_{25}), 4.29 (dt, J = 13.0, 6.5 Hz, 2H, H_9), 4.23 (d, J = 3.4 Hz, 2H, H_3), 3.68 (dt, J = 9.9, 5.0 Hz, 2H, H_4), 3.53 (h, J = 4.4 Hz, 2H, H_{12}), 3.41 – 3.29 (m, 5H, H_{17} and H_{26}), 3.28 – 3.12 (m, 3H, H_7 and H_{15}), 3.10 – 2.92 (m, 1H, H_{15}), 2.14 – 1.97 (m, 2H, H_8), 1.75 (p, J = 6.6 Hz, 2H, H_{16}), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.5, 155.3, 130.5, 129.0, 128.4, 125.8, 123.7, 123.6, 120.9, 71.1, 71.0, 68.2, 65.9, 64.9, 59.7, 58.4, 50.8, 50.2, 49.1, 47.3, 38.7, 37.8, 30.2, 29.0, 26.1, 16.6, -4.6.

2.4.2 Synthesis of **S4**

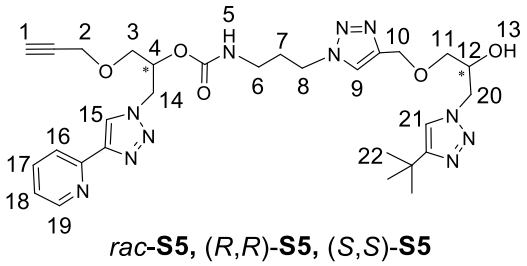


S4

Compound **A(Boc)O(Bz)** (240 mg, 0.26 mmol) was added into a flask followed by CH_2Cl_2 (10 mL), 4-nitrophenyl chloroformate (133 mg, 2.5 equiv.) and pyridine (70 μL, 3 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) were added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added into a flask followed by 3-azidopropylamine (80 mg, 3 equiv.) and Et_3N (120 μL, 3 equiv.). The reaction was stirred for 2 h at room temperature followed by the addition of EtOAc (50 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **S4** was obtained after the residue was passed through a chromatography column (CH_2Cl_2/MeOH = 10/0 to 9/1) as a colorless oil (274 mg, quantitative yield).

S4, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07 – 7.97 (m, 2H, H_{28}), 7.78 – 7.73 (m, 2H, H_{10} and H_{26}), 7.62 (s, 1H, H_{19}), 7.58 – 7.51 (m, 1H, H_{30}), 7.46 – 7.38 (m, 2H, H_{29}), 5.58 (brs, 1H, H_6), 5.44 (s, 2H, H_{27}), 5.36 – 5.19 (m, 2H, H_5 and H_{14}), 5.15 (t, J = 5.3 Hz, 1H, H_{13}), 4.99 (brs, 1H, H_{23}), 4.77 – 4.52 (m, 8H, H_{11}, H_{18}, H_{20} and H_{25}), 4.40 (d, J = 1.9 Hz, 2H, H_9), 4.20 (d, J = 4.4 Hz, 2H, H_3), 3.77 – 3.47 (m, 6H, H_4, H_{12} and H_{22}), 3.39 – 3.00 (m, 8H, H_7, H_{15}, H_{17} and H_{21}), 2.22 – 1.99 (m, 2H, H_8), 1.77 – 1.64 (m, 2H, H_{16}), 1.42 (s, 9H, H_{24}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.2, 155.5, 155.2, 145.1, 143.1, 133.4, 129.8, 128.6, 125.4, 123.8, 123.6, 71.0, 69.5, 68.3, 68.2, 64.9, 64.4, 59.6, 58.1, 50.6, 50.3, 49.1, 47.4, 40.5, 38.6, 37.8, 30.3, 29.0, 28.5, 26.1, 16.6, -4.6. **HRMS** *m/z*= 1036.5143 (calcd. for $C_{46}H_{70}N_{15}O_{11}Si$ 1036.5143 $[M+H]^+$).

2.4.3 Synthesis of *rac*-**S5**, (*R,R*)-**S5** and (*S,S*)-**S5**



rac-**S5,** (*R*,*R*)-**S5,** (*S*,*S*)-**S5**

Compound *rac*-**PB** (254 mg, 0.35 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by tetrabutylammonium fluoride solution (1M in THF, 3.5 mL, 10 equiv.) under stirring at room temperature. The mixture was stirred for 30 min and then 10 mL methanol was added. After stirring for 10 min, the mixture was concentrated by evaporation and the residue was purified by column chromatography (EtOAC/n-hexane = 4/6 to 10/0). The final product *rac*-**S5** was obtained as a yellow oil (218 mg, quantitative yield). (*R*,*R*)-**S5** (196 mg, 0.32 mmol, 78%) and (*S*,*S*)-**S5** (484 mg, 0.78 mmol, 96%) were obtained following the same protocol.

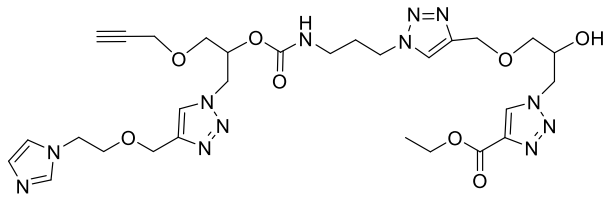
rac-**S5**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.50 (ddt, *J* = 4.2, 2.1, 1.1 Hz, 1H, H_{19}), 8.30 (d, *J* = 25.6 Hz, 1H, H_{15}), 8.10 (t, *J* = 8.4 Hz, 1H, H_{16}), 7.75 (tdd, *J* = 7.8, 5.8, 1.7 Hz, 1H, H_{17}), 7.63 (d, *J* = 16.2 Hz, 1H, H_9), 7.40 (d, *J* = 2.8 Hz, 1H, H_{21}), 7.22 (tt, *J* = 5.6, 2.0 Hz, 1H, H_{18}), 5.65 (brs, 1H, H_5), 5.34 – 5.27 (m, 1H, H_4), 4.79 – 4.66 (m, 2H, H_{14}), 4.62 (dd, *J* = 11.0, 4.4 Hz, 2H, H_{10}), 4.53 – 4.45 (m, 1H, H_{20}), 4.44 – 4.27 (m, 3H, H_8 and H_{20}), 4.23 – 4.17 (m, 3H, H_2 and H_{12}), 3.72 – 3.62 (m, 2H, H_3), 3.60 – 3.44 (m, 2H, H_{11}), 3.10 (ddd, *J* = 48.6, 14.1, 7.5 Hz, 2H, H_6), 2.48 (d, *J* = 1.4 Hz, 1H, H_1), 2.24 – 1.98 (m, 3H, H_7 and H_{13}), 1.31 (s, 9H, H_{22}). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.5, 144.6, 123.6, 123.3, 120.6, 120.3, 120.2, 75.7, 71.6, 71.5, 71.0, 69.6, 69.5, 68.1, 64.9, 58.9, 52.8, 52.8, 50.8, 50.8, 47.2, 47.1, 37.7, 37.6, 30.8, 30.5, 30.3. **HRMS** *m/z*= 622.3206 (calcd. for $C_{29}H_{40}N_{11}O_5$ 622.3208 $[M+H]^+$).

(*R*,*R*)-**S5**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H, H_{19}), 8.34 (s, 1H, H_{15}), 8.09 (dt, *J* = 8.0, 1.1 Hz, 1H, H_{16}), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H, H_{17}), 7.62 (s, 1H, H_9), 7.41 (s, 1H, H_{21}), 7.21 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H_{18}), 5.71 (brs, 1H, H_5), 5.37 – 5.24 (m, 1H, H_4), 4.72 (dd, *J* = 14.2, 5.4 Hz, 2H, H_{14}), 4.60 (d, *J* = 3.7 Hz, 2H, H_{10}), 4.48 (dd, *J* = 14.1, 3.9 Hz, 1H, H_{20}), 4.42 – 4.25 (m, 3H, H_8 and H_{20}), 4.20 (dd, *J* = 4.5, 2.4 Hz, 4H, H_2 and H_{12}), 3.75 – 3.62 (m, 2H, H_3), 3.53 (ddd, *J* = 38.8, 9.9, 4.8 Hz, 2H, H_{11}), 3.23 – 3.02 (m, 2H, H_6), 2.48 (t, *J* = 2.3 Hz, 1H, H_1), 2.28 (brs, 1H, H_{13}), 2.04 (dt, *J* = 18.5, 7.0 Hz, 2H, H_7), 1.30 (s, 9H, H_{22}). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6, 155.6, 149.2, 144.6, 137.4, 123.8, 123.6, 123.2, 120.4, 120.3, 79.0, 75.6, 71.6, 71.0, 69.5, 68.2, 64.9, 58.9, 52.8, 50.8, 47.2, 37.6, 30.8, 30.5, 30.3.

(*S*,*S*)-**S5**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 (dd, *J* = 4.8, 2.2 Hz, 1H, H_{19}), 8.32 (s, 1H, H_{15}), 8.09 (d, *J* = 7.9 Hz, 1H, H_{16}), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H, H_{17}), 7.62 (s, 1H, H_9), 7.41 (d, *J* = 2.3 Hz, 1H, H_{21}), 7.24 – 7.14 (m, 1H, H_{18}), 5.70 (brs, 1H, H_5), 5.35 – 5.25 (m, 1H, H_4), 4.72 (qd, *J* = 14.4, 5.4 Hz, 2H, H_{14}), 4.65 – 4.56 (m, 2H, H_{10}), 4.48 (dd, *J* = 14.1, 4.0 Hz, 1H, H_{20}), 4.42 – 4.25 (m, 3H, H_8 and H_{20}), 4.22 – 4.15 (m, 3H, H_2 and H_{12}), 3.75 – 3.61 (m, 2H, H_3), 3.53 (ddd, *J* = 37.4, 9.9, 4.8 Hz, 2H, H_{11}), 3.10 (ddt, *J* = 42.3, 14.5, 6.6 Hz, 2H, H_6), 2.48 (d, *J* = 2.3 Hz, 1H, H_1), 2.35 (brs, 1H, H_{13}), 2.04 (dtt, *J* =

27.3, 14.1, 6.7 Hz, 2H, H_7), 1.30 (s, 9H, H_{22}). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6, 155.6, 150.0, 149.3, 144.6, 137.3, 123.7, 123.6, 123.2, 120.4, 120.3, 79.0, 75.6, 71.6, 71.0, 69.5, 68.2, 64.9, 58.9, 52.8, 50.8, 47.2, 37.6, 30.8, 30.5, 30.3.

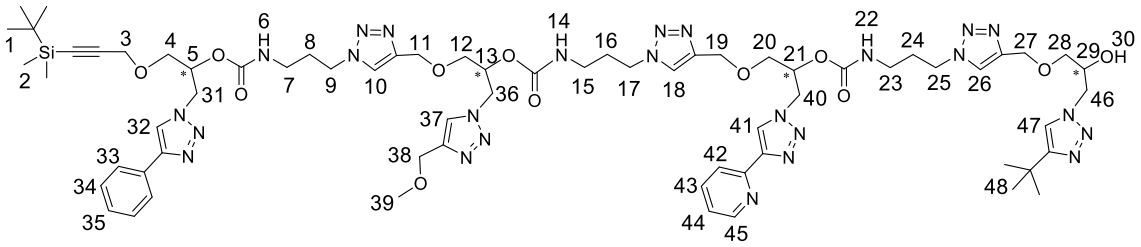
2.4.4 Synthesis of **S6**



S6

Compound **IK(Et)** (350 mg, 0.44 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by tetrabutylammonium fluoride solution (1M in THF, 1.76 mL, 4 equiv.) under stirring at room temperature. The mixture was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated under vacuum and the residue was followed by EtOAc (50 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and the solvent was evaporated. The residue **S6** was used for the next step without further purification. **HRMS** *m/z*= 685.3166 (calcd. for $C_{29}H_{41}N_{12}O_8$ 685.3165 $[M+H]^+$).

2.4.5 Synthesis of *rac*-**FEPB**, (*R*,*R*,*R*,*R*)-**FEPB** and (*S,S,S,S*)-**FEPB**



rac-**FEPB,** (*R*,*R*,*R*,*R*)-**FEPB,** (*S*,*S*,*S*,*S*)-**FEPB**

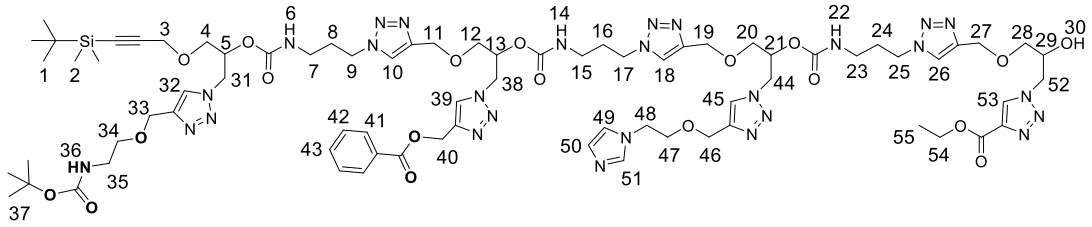
Compound *rac*-**S3** (273 mg, 0.32 mmol) and compound *rac*-**S5** (200 mg, 1 equiv.) were added into a flask followed by EtOH (4 mL). Then, a sodium ascorbate solution (13 mg in 0.75 mL water, 0.2 equiv.) and a $CuSO_4$ solution (5 mg in 0.75 mL water, 0.1 equiv.) were added into the mixture. The reaction was stirred for 2 h at 50℃ followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 9/1) to give the final product rac-**FEPB** as a white solid (340 mg, 0.23 mmol, 72%). The tetramers (*R*,*R*,*R*,*R*)-**FEPB** (286 mg, 0.19 mmol, 67%) and (*S,S,S,S*)-**FEPB** (699 mg, 0.48 mmol, 95%) were obtained following the same protocol.

rac-**FEPB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.11 (brs, 1H, H_{41}), 8.60 (s, 1H, H_{45}), 8.38 (brs, 1H, H_{42}), 8.12 (brs, 1H, H_{43}), 7.89 (brs, 2H, H_{18} and H_{32}), 7.81 – 7.71 (m, 3H, H_{10} and H_{33}), 7.64 (brs, 2H, H_{26} and H_{37}), 7.55 (brs, 1H, H_{44}), 7.43 (s, 1H, H_{47}), 7.37 (t, *J* = 7.5 Hz, 2H, H_{34}), 7.30 (d, *J* = 7.3 Hz, 1H, H_{35}), 6.71 (brs, 1H, H_{22}), 6.01 – 5.73 (m, 2H, H_6 and H_{14}), 5.30 (d, *J* = 4.7 Hz, 1H, H_{21}), 5.16 (brs, 2H, H_5 and H_{13}), 4.88 – 4.53 (m, 12H, H_{11}, H_{19}, H_{27}, H_{31}, H_{36} and H_{40}), 4.53 – 4.44 (m, 3H, H_{38} and H_{29}), 4.43 – 4.26 (m, 7H, H_9, H_{17}, H_{25} and H_{46}), 4.22 (d, *J* = 3.2 Hz, 3H, H_3 and H_{46}), 3.79 – 3.38 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.37 – 3.28 (m, 3H, H_{39}), 3.22 – 2.96 (m, 6H, H_7, H_{15} and H_{23}), 2.16 – 1.87 (m, 6H, H_8, H_{16} and H_{24}), 1.29 (s, 9H, H_{48}), 0.91 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.6, 155.4, 144.6, 129.0, 128.4, 125.8, 123.9, 121.0, 120.4, 91.0, 71.7, 71.1, 70.9, 69.5, 68.4, 68.3, 65.8, 65.0, 64.9, 64.7, 59.7, 58.4, 52.9, 50.4, 47.5, 47.3, 37.9, 37.5, 30.8, 30.5, 30.3, 30.2, 26.1, 16.6, -4.6. **HRMS** *m/z*= 1470.7442 (calcd. for $C_{67}H_{96}N_{25}O_{12}Si$ 1470.7434 $[M+H]^+$).

(*R*,*R*,*R*,*R*)-**FEPB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 4.9 Hz, 1H, H_{45}), 8.30 (s, 1H, H_{41}), 8.06 (d, *J* = 8.0 Hz, 1H, H_{42}), 7.91 (s, 1H, H_{32}), 7.80 – 7.71 (m, 4H, H_{18}, H_{33} and H_{43}), 7.63 (s, 3H, H_{10}, H_{26} and H_{37}), 7.42 (s, 1H, H_{47}), 7.36 (dd, *J* = 8.3, 6.8 Hz, 2H, H_{34}), 7.32 – 7.26 (m, 1H, H_{45}), 7.21 (t, *J* = 6.2 Hz, 1H, H_{44}), 6.18 – 5.78 (m, 3H, H_6, H_{14} and H_{22}), 5.36 – 5.08 (m, 3H, H_5, H_{13} and H_{21}), 4.76 – 4.54 (m, 12H, H_{11}, H_{19}, H_{27}, H_{31}, H_{36} and H_{40}), 4.52 – 4.42 (m, 3H, H_{38} and H_{29}), 4.40 – 4.13 (m, 10H, H_3, H_9, H_{17}, H_{25}, and H_{46}), 3.73 – 3.47 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.32 (s, 3H, H_{39}), 3.21 – 2.94 (m, 6H, H_7, H_{15} and H_{23}), 2.14 – 1.89 (m, 6H, H_8, H_{16} and H_{24}), 1.62 (brs, 1H, H_{30}), 1.29 (s, 9H, H_{48}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.6, 149.2, 144.4, 137.5, 130.4, 129.0, 128.4, 125.8, 124.0, 123.8, 123.7, 123.6, 123.2, 121.0, 120.5, 120.4, 71.7, 71.1, 70.9, 69.4, 68.6, 68.5, 68.3, 65.8, 64.9, 64.8, 64.7, 59.7, 58.4, 52.9, 50.8, 50.4, 47.5, 47.4, 47.3, 37.8, 37.7, 30.8, 30.5, 30.3, 26.1, 16.6, -4.6. **HRMS** *m/z*= 1470.7536 (calcd. for $C_{67}H_{96}N_{25}O_{12}Si$ 1470.7434 $[M+H]^+$).

(*S*,*S*,*S*,*S*)-**FEPB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.54 – 8.44 (m, 1H, H_{45}), 8.30 (s, 1H, H_{41}), 8.05 (d, *J* = 8.0 Hz, 1H, H_{42}), 7.91 (s, 1H, H_{32}), 7.82 – 7.70 (m, 4H, H_{18}, H_{33} and H_{43}), 7.63 (d, *J* = 3.2 Hz, 3H, H_{10}, H_{26} and H_{37}), 7.42 (s, 1H, H_{47}), 7.36 (dd, *J* = 8.3, 6.8 Hz, 2H, H_{34}), 7.32 – 7.27 (m, 1H, H_{45}), 7.23 – 7.17 (m, 1H, H_{44}), 6.15 – 5.76 (m, 3H, H_6, H_{14} and H_{22}), 5.37 – 5.08 (m, 3H, H_5, H_{13} and H_{21}), 4.74 – 4.54 (m, 12H, H_{11}, H_{19}, H_{27}, H_{31}, H_{36} and H_{40}), 4.52 – 4.42 (m, 3H, H_{38} and H_{29}), 4.40 – 4.15 (m, 10H, H_3, H_9, H_{17}, H_{25} and H_{46}), 3.75 – 3.43 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.32 (s, 3H, H_{39}), 3.20 – 2.98 (m, 6H, H_7, H_{15} and H_{23}), 2.37 (brs, 1H, H_{30}), 2.12 – 1.88 (m, 6H, H_8, H_{16} and H_{24}), 1.28 (s, 9H, H_{48}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.7, 155.6, 149.2, 137.4, 130.5, 129.0, 128.4, 125.7, 124.0, 123.7, 123.6, 123.2, 121.0, 120.4, 120.4, 71.7, 71.1, 70.9, 69.4, 68.6, 68.5, 68.3, 65.8, 64.9, 64.8, 64.7, 59.7, 58.3, 52.9, 50.8, 50.4, 47.5, 47.4, 47.3, 37.8, 37.7, 30.8, 30.5, 30.2, 26.1, 16.5, -4.6. **HRMS** *m/z*= 1470.7368 (calcd. for $C_{67}H_{96}N_{25}O_{12}Si$ 1470.7434 $[M+H]^+$).

2.4.6 Synthesis of **A(Boc)O(Bz)IK(Et)**

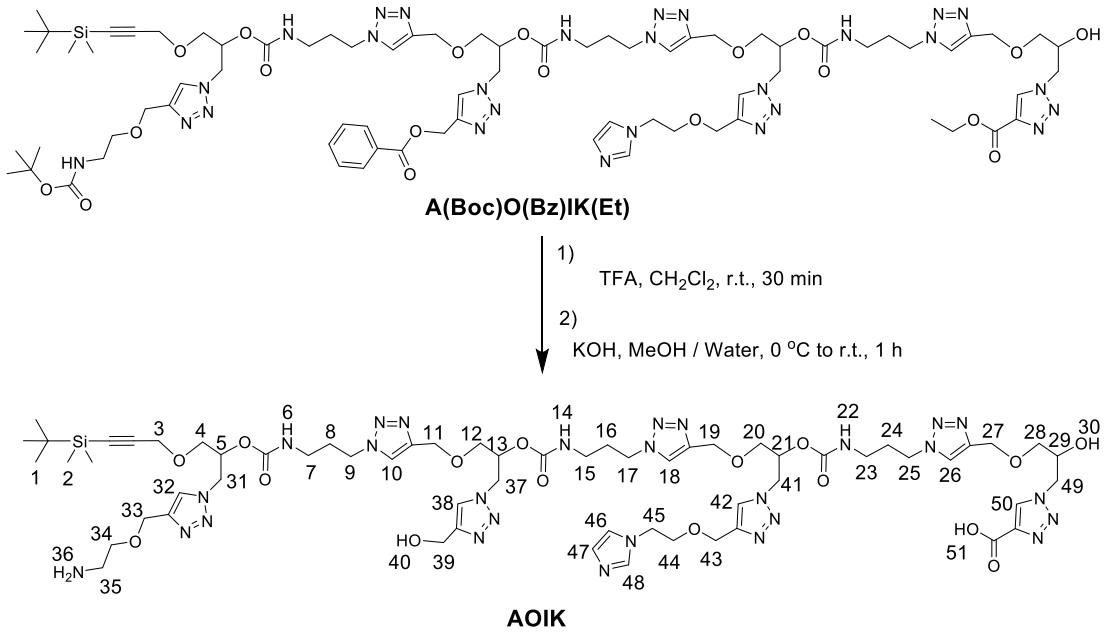


A(Boc)O(Bz)IK(Et)

Compound **S4** (240 mg, 0.23 mmol) and compound **S6** (159 mg, 1 equiv.) were added into a flask followed by EtOH (4 mL). Then, a sodium ascorbate solution (11 mg in 0.75 mL water, 0.2 equiv.) and a $CuSO_4$ solution (4 mg in 0.75 mL water, 0.1 equiv.) were added into the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. EtOAc (50 mL) and Na_2EDTA (0.05 M, 50 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 30 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 9/1) to give the final product **A(Boc)O(Bz)IK(Et)** as a white solid (244 mg, 0.14 mmol, 61%).

A(Boc)O(Bz)IK(Et), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.88 (brs, 1H, H_{51}), 8.34 (d, J = 2.3 Hz, 1H, H_{53}), 7.97 (d, J = 7.5 Hz, 2H, H_{41}), 7.95 – 7.84 (m, 4H, H_{10}, H_{18}, H_{45} and H_{49}), 7.82 (s, 1H, H_{39}), 7.68 (s, 1H, H_{32}), 7.58 – 7.48 (m, 1H, H_{43}), 7.39 (t, J = 7.8 Hz, 2H, H_{42}), 7.31 (s, 2H, H_{26} and H_{50}), 6.93 (brs, 1H, H_{22}), 6.39 (brs, 1H, H_{14}), 5.94 (brs, 1H, H_6), 5.46 – 5.34 (m, 2H, H_{40}), 5.29 – 5.07 (m, 4H, H_5, H_{13}, H_{21} and H_{36}), 4.72 – 4.46 (m, 18H, H_{11}, H_{19}, H_{27}, H_{31}, H_{33}, H_{38}, H_{44}, H_{46} and H_{48}), 4.44 – 4.31 (m, 10H, H_9, H_{17}, H_{25}, H_{52} and H_{54}), 4.19 (d, J = 5.3 Hz, 3H, H_3 and H_{29}), 3.82 (brs, 2H, H_{47}), 3.71 – 3.37 (m, 10H, H_{12}, H_{20}, H_{28}, H_{34} and H_{35}), 3.26 (brs, 2H, H_4), 3.19 – 2.98 (m, 6H, H_7, H_{15}, H_{23}), 2.13 – 1.98 (m, 6H, H_8, H_{16} and H_{24}), 1.40 (s, 9H, H_{37}), 1.35 (t, J = 7.1 Hz, 3H, H_{55}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 166.5, 161.0, 156.2, 155.8, 155.6, 145.0, 144.2, 144.0, 139.8, 133.5, 129.8, 129.7, 129.5, 128.6, 125.67, 124.1, 123.9, 121.9, 101.3, 90.9, 79.5, 71.5, 71.0, 69.5, 68.9, 68.6, 68.4, 68.2, 67.6, 64.7, 64.3, 64.2, 61.4, 59.6, 58.1, 53.5, 50.7, 49.5, 47.7, 47.6, 40.5, 37.8, 30.3, 30.2, 28.5, 26.2, 16.6, 14.5, 1.1, -4.6. **HRMS** *m/z*= 1720.8249 (calcd. for $C_{75}H_{110}N_{27}O_{19}Si$ 1720.8235 $[M+H]^+$).

2.4.7 Synthesis of **AOIK**

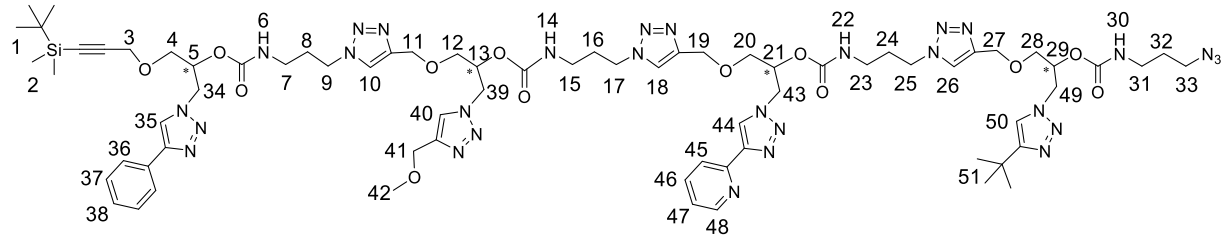


Compound **A(Boc)O(Bz)IK(Et)** (150 mg, 0.087 mmol) was added into a flask followed by DCM (5 mL) and TFA (0.5 mL). The mixture was stirred for 30 min at room temperature followed by evaporation. After that, the residue was added MeOH (3 mL) and water (2 mL) under stirring in an ice bath. KOH (112 mg, 2 mmol) was carefully added into the mixture at 0°C. After the mixture was stirred for 1 h at room temperature, HCl (1 M) was added to bring the solution pH to 5. Then, the solvent was removed by evaporation and the residue was suspended in MeOH (5 mL) followed by filtration to remove insoluble salts. After solvent evaporation, the residue was washed with diethyl ether to give the final product **AOIK** as a white solid (131 mg, quantitative yield).

AOIK, **^{1}H NMR (500 MHz, CD_3OD)** δ 8.98 (brs, 1H, H_{48}), 8.49 (s, 1H, H_{50}), 8.47 – 8.33 (m, 4H, H_{10}, H_{18}, H_{38} and H_{42}), 8.24 (d, J = 14.0 Hz, 2H, H_{26} and H_{32}), 7.66 (brs, 1H, H_{46}), 7.56 (brs, 1H, H_{47}), 5.34 – 5.20 (m, 3H, H_5, H_{13} and H_{21}), 4.84 – 4.62 (m, 18H, H_{11}, H_{19}, H_{27}, H_{31}, H_{33}, H_{37}, H_{41}, H_{43} and H_{45}), 4.60 – 4.43 (m, 10H, H_9, H_{17}, H_{25}, H_{39} and H_{49}), 4.29 – 4.17 (m, 3H, H_3 and H_{29}), 3.90 (t, J = 4.8 Hz, 2H, H_{44}), 3.83 – 3.65 (m, 8H, H_4, H_{12}, H_{20} and H_{34}), 3.64 – 3.52 (m, 2H, H_{28}), 3.23 – 3.02 (m, 8H, H_7, H_{15}, H_{23} and H_{35}), 2.18 – 2.07 (m, 6H, H_8, H_{16} and H_{24}), 0.94 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (125 MHz, CD_3OD)** δ 162.6, 157.5, 145.4, 140.2, 137.4, 130.8, 130.2 – 128.6 (m), 126.3, 126.2, 125.7, 125.6, 125.6, 124.2, 103.2, 90.8, 72.6, 72.5, 70.1, 69.9, 69.6, 69.3, 67.0, 65.2, 64.8, 64.7, 60.1, 56.4, 52.6, 52.0, 51.9, 51.7, 40.6, 38.7, 38.6, 31.4, 31.4, 26.5, 17.2, -4.5. **HRMS** m/z= 744.8611 (calcd. for $C_{61}H_{95}N_{27}O_{16}Si$ 744.8604 $[M+2H]^{2+}/2$).

2.5 Synthesis of octamer

2.5.1 Synthesis of *rac*-**S7** and (*R*,*R*,*R*,*R*)-**S7**



rac-**S7,** (*R*,*R*,*R*,*R*)-**S7**

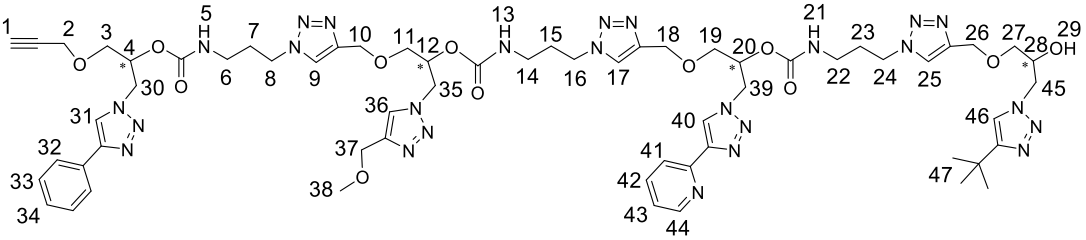
Compound *rac*-**FEPB** (104 mg, 0.07 mmol) was added into a flask followed by CH_2Cl_2 (5 mL), 4-nitrophenyl chloroformate (42 mg, 3 equiv.) and pyridine (20 μL, 3 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. Water (50 mL) and EtOAc (50 mL) was added to the residue followed by extraction with EtOAc (3 × 50 mL). The organic phases were collected, dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in CH_3CN (5 mL) and added into a flask followed by 3-azidopropylamine (30 mg, 4 equiv.) and TEA (42 μL, 4 equiv.). The mixture was stirred for 2 h at room temperature followed by addition of EtOAc (50 mL) and water (50 mL). The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product *rac*-**S7** was obtained after the residue was passed through a chromatography column (DCM/MeOH = 10/0 to 95/5) as a white solid (87 mg, 0.05 mol, 77%). (*R*,*R*,*R*,*R*)-**S7** (182 mg, 0.11 mmol, quantitative yield) was obtained following the same protocol.

rac-**S7**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 (brs, 1H, H_{48}), 8.27 (s, 1H, H_{44}), 8.06 (d, J = 7.7 Hz, 1H, H_{45}), 7.91 (s, 1H, H_{35}), 7.81 – 7.61 (m, 7H, H_{10}, H_{18}, H_{26}, H_{36}, H_{40} and H_{46}), 7.43 – 7.28 (m, 4H, H_{37}, H_{38} and H_{50}), 7.22 (s, 1H, H_{47}), 6.14 (brs, 1H, H_{22}), 6.03 – 5.71 (m, 2H, H_6 and H_{14}), 5.65 – 5.48 (m, 1H, H_{30}), 5.38 – 5.03 (m, 4H, H_5, H_{13}, H_{21} and H_{29}), 4.79 – 4.43 (m, 16H, H_{11}, H_{19}, H_{27}, H_{34}, H_{39}, H_{41}, H_{43} and H_{49}), 4.42 – 4.20 (m, 8H, H_3, H_9, H_{17} and H_{25}), 3.62 – 3.44 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.33 (d, J = 2.5 Hz, 5H, H_{33} and H_{42}), 3.26 – 2.94 (m, 8H, H_7, H_{15}, H_{23} and H_{31}), 2.14 – 1.92 (m, 6H, H_8, H_{16} and H_{24}), 1.73 (p, J = 6.6 Hz, 2H, H_{32}), 1.29 (s, 9H, H_{51}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.9, 155.6, 144.5, 130.5, 129.0, 125.8, 123.8, 121.5 – 120.6 (m), 101.2, 71.4, 68.6, 68.3, 65.8, 64.9, 59.7, 58.4, 50.8, 49.1, 47.5, 38.6, 37.8, 30.8, 30.8, 30.5, 30.3, 30.3, 26.1, 16.6, -4.6. **HRMS** *m/z*= 1618.7799 (calcd. for $C_{71}H_{102}N_{29}O_{13}Si$ 1618.7795 $[M+H]^+$).

(*R*,*R*,*R*,*R*)-**S7**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.51 (d, J = 4.8 Hz, 1H, H_{48}), 8.28 (s, 1H, H_{44}), 8.05 (d, J = 7.9 Hz, 1H, H_{45}), 7.93 (s, 1H, H_{35}), 7.84 – 7.59 (m, 7H, H_{10}, H_{18}, H_{26}, H_{36}, H_{40} and H_{46}), 7.36 (dd, J = 14.6, 6.8 Hz, 3H, H_{37} and H_{50}), 7.32 – 7.27 (m, 1H, H_{38}), 7.24 – 7.17 (m, 1H, H_{47}), 6.22 (d, J = 6.4 Hz, 1H, H_{22}), 6.10 – 5.96 (m, 1H, H_{14}), 5.86 (t, J = 6.3 Hz, 1H, H_6), 5.65 (d, J = 6.4 Hz, 1H, H_{30}), 5.36 – 5.05 (m, 4H, H_5, H_{13}, H_{21} and H_{29}), 4.76 – 4.45 (m, 16H, H_{11}, H_{19}, H_{27}, H_{34}, H_{39}, H_{41}, H_{43} and H_{49}), 4.41 – 4.16 (m, 8H, H_3, H_9, H_{17} and H_{25}), 3.71 – 3.53 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.32 (d, J = 3.4 Hz, 5H, H_{33} and H_{42}), 3.24 – 3.01 (m, 8H, H_7, H_{15}, H_{23} and H_{31}), 2.11 – 1.97 (m, 6H, H_8, H_{16} and H_{24}), 1.73 (p, J = 6.6 Hz, 2H,

H_{32}), 1.29 (s, 9H, H_{51}), 0.91 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.6, 149.4, 147.9, 144.3, 137.3, 130.5, 129.0, 128.4, 125.8, 124.0, 123.7, 123.2, 121.1, 120.4, 119.9, 101.2, 71.3, 71.1, 70.9, 68.6, 68.3, 65.8, 64.9, 64.8, 59.7, 58.4, 57.8, 50.8, 50.7, 50.4, 50.0, 49.9, 49.1, 49.0, 47.5, 47.4, 39.2, 38.6, 38.0, 37.8, 31.5, 30.8, 30.5, 30.3, 29.1, 26.2, 26.1, 23.7, 16.5, -4.6.

2.5.2 Synthesis of rac-**S8** and (S,S,S,S)-**S8**



rac-**S8,** (*S*,*S*,*S*,*S*)-**S8**

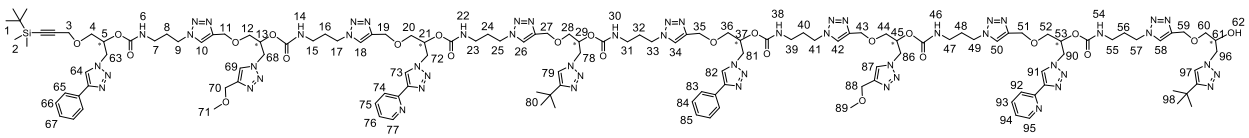
Compound *rac*-**FEPB** (150 mg, 0.1 mmol) was dissolved in EtOAc (5 mL) and added into a flask followed by a tetrabutylammonium fluoride solution (1M in THF, 0.4 mL, 4 equiv.) at room temperature. The mixture was stirred for 30 min and then methanol (10 mL) was added. After stirring for 10 min, the mixture was concentrated under vacuum and the residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 95/5). The final product *rac*-**S8** was obtained as a white solid (128 mg, 0.09 mmol, 94%). (*S*,*S*,*S*,*S*)-**S8** (266 mg, 0.20 mmol, 96%) was obtained following the same protocol.

rac-**S8**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.44 (d, *J* = 4.9 Hz, 1H, H_{44}), 8.25 (dd, *J* = 12.5, 3.6 Hz, 1H, H_{40}), 8.06 – 7.93 (m, 2H, H_{31} and H_{41}), 7.80 – 7.72 (m, 3H, H_{17} and H_{32}), 7.72 – 7.58 (m, 4H, H_9, H_{25}, H_{36} and H_{42}), 7.43 (d, *J* = 2.3 Hz, 1H, H_{46}), 7.32 (t, *J* = 7.6 Hz, 2H, H_{33}), 7.23 (d, *J* = 7.4 Hz, 1H, H_{34}), 7.18 – 7.11 (m, 1H, H_{43}), 6.39 – 6.17 (m, 3H, H_5, H_{13} and H_{21}), 5.33 – 5.06 (m, 3H, H_4, H_{12} and H_{20}), 4.72 – 4.50 (m, 12H, H_{10}, H_{18}, H_{26}, H_{30}, H_{35} and H_{39}), 4.49 – 4.40 (m, 3H, H_{28} and H_{37}), 4.39 – 4.11 (m, 10H, H_2, H_8, H_{16}, H_{24} and H_{45}), 3.69 – 3.41 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 3.27 (s, 3H, H_{38}), 3.11 – 2.94 (m, 6H, H_6, H_{14} and H_{22}), 2.47 (td, *J* = 2.4, 0.8 Hz, 1H, H_1), 1.98 (s, 6H, H_7, H_{15} and H_{23}), 1.61 (brs, 1H, H_{29}), 1.24 (s, 9H, H_{47}). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.4, 155.6, 149.9, 149.4, 148.1, 147.7, 144.9, 144.4, 144.2, 137.1, 130.4, 128.9, 128.3, 125.6, 124.1, 123.8, 123.7, 123.1, 121.4, 120.4, 120.2, 79.0, 75.6, 71.7, 71.1, 70.8, 69.2, 69.2, 68.6, 68.5, 68.2, 65.6, 64.7, 64.6, 58.9, 58.7, 58.2, 52.9, 50.7, 50.5, 50.4, 47.5, 47.3, 47.3, 37.8, 37.7, 37.6, 30.7, 30.4, 30.2, 29.7, 23.9, 19.7, 13.7. **HRMS** *m/z*= 1356.6579 (calcd. for $C_{61}H_{82}N_{25}O_{12}$ 1356.6569 $[M+H]^+$).

(*S*,*S*,*S*,*S*)-**S8**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.53 – 8.46 (m, 1H, H_{44}), 8.33 (s, 1H, H_{40}), 8.06 (d, *J* = 8.1 Hz, 1H, H_{41}), 7.95 (s, 1H, H_{31}), 7.83 – 7.71 (m, 4H, H_9, H_{17} and H_{32}), 7.65 (d, *J* = 5.7 Hz, 3H, H_{25}, H_{36} and H_{42}), 7.43 (d, *J* = 1.6 Hz, 1H, H_{46}), 7.37 (dd, *J* = 8.3, 6.8 Hz, 2H, H_{33}), 7.32 – 7.27 (m, 1H, H_{34}), 7.21 (dt, *J* = 6.9, 2.7 Hz, 1H, H_{43}), 6.24 – 5.92 (m, 3H, H_5, H_{13} and H_{21}), 5.37 – 5.06 (m, 3H, H_4, H_{12} and H_{20}), 4.76 – 4.54 (m, 12H, H_{10}, H_{18}, H_{26}, H_{30}, H_{35} and H_{39}), 4.53 – 4.42 (m, 3H, H_{28} and H_{37}), 4.41 – 4.14 (m, 10H, H_2, H_8, H_{16}, H_{24} and H_{45}), 3.71 – 3.47 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 3.32 (s, 3H, H_{38}), 3.18 – 2.99 (m, 6H, H_6, H_{14} and H_{22}), 2.48 (t, *J* = 2.4 Hz, 1H, H_1), 2.29 (brs, 1H, H_{29}), 2.14 – 1.91 (m, 6H, H_7, H_{15}

and H_{23}), 1.28 (s, 9H, H_{47}). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.6, 149.9, 149.2, 147.8, 145.1, 144.6, 144.4, 144.3, 129.0, 128.4, 125.7, 124.0, 123.8, 123.7, 123.2, 121.3, 120.9, 120.4, 75.7, 71.7, 71.1, 70.8, 69.4, 68.6, 68.5, 68.2, 65.8, 64.9, 64.8, 64.7, 58.9, 58.4, 52.9, 50.9, 50.8, 50.6, 50.5, 47.5, 47.4, 47.3, 37.8, 37.7, 30.8, 30.5, 30.3.

2.5.3 Synthesis of *rac*-**FEPBFEPB** and (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB**



***rac*-FEPBFEPB, (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-FEPBFEPB**

Compound *rac*-**S7** (40 mg, 0.025 mmol) and compound *rac*-**S8** (34 mg, 1 equiv.) were added into a flask followed by EtOH (2 mL). Then, a sodium ascorbate solution (2 mg in 0.35 mL water, 0.2 equiv.) and a $CuSO_4$ solution (0.4 mg in 0.35 mL water, 0.1 equiv.) were added into the mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. EtOAc (10 mL) and Na_2EDTA (0.05 M, 10 mL) were added into the mixture followed by air bubbling for 30 min. After that, the mixture was extracted with EtOAc (3 × 10 mL) and the organic phases were collected, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/0 to 9/1) to give the final product *rac*-**FEPBFEPB** as a white solid (42 mg, 0.014 mmol, 57%). The octamer (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB** (64 mg, 0.022 mmol, 50%) was obtained following the same protocol.

rac-**FEPBFEPB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.93 – 8.69 (m, 2H, H_{77} and H_{95}), 8.53 (d, J = 5.8 Hz, H_{73} and H_{91}), 8.24 (brs, 2H, H_{74} and H_{92}), 8.13 – 7.87 (m, 4H, H_{10}, H_{42}, H_{75} and H_{93}), 7.84 – 7.57 (m, 13H, H_{18}, H_{26}, H_{34}, H_{50}, H_{58}, H_{64}, H_{65}, H_{69}, H_{82}, H_{83} and H_{87}), 7.49 – 7.30 (m, 8H, H_{66}, H_{67}, H_{79}, H_{84}, H_{85} and H_{97}), 7.29 – 7.26 (m, 2H, H_{76} and H_{94}), 6.75 – 5.79 (m, 7H, H_6, H_{14}, H_{22}, H_{30}, H_{38}, H_{46} and H_{54}), 5.36 – 5.08 (m, 7H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{45} and H_{53}), 4.77 – 4.44 (m, 33H, H_{11}, H_{19}, H_{27}, H_{35}, H_{43}, H_{51}, H_{59}, H_{61}, H_{63}, H_{68}, H_{70}, H_{72}, H_{78}, H_{81}, H_{86}, H_{88} and H_{90}), 4.38 – 4.17 (m, 18H, H_3, H_9, H_{17}, H_{25}, H_{33}, H_{41}, H_{49}, H_{57} and H_{96}), 3.72 – 3.43 (m, 16H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44}, H_{52} and H_{60}), 3.38 – 3.24 (m, 6H, H_{71} and H_{89}), 3.24 – 2.98 (brs, 14H, H_7, H_{15}, H_{23}, H_{31}, H_{39}, H_{47} and H_{55}), 2.10 – 1.94 (m, 14H, H_8, H_{16}, H_{24}, H_{32}, H_{40}, H_{48} and H_{56}), 1.29 – 1.23 (m, 18H, H_{80} and H_{98}), 0.89 (s, 9H, H_1), 0.07 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.8, 155.6, 145.0, 144.3, 144.2, 130.5, 129.0, 128.4, 125.7, 125.7, 124.0, 123.9, 123.8, 121.5, 121.1, 120.4, 120.1, 71.8, 71.3, 71.1, 70.7, 69.4, 68.3, 65.8, 64.8, 64.7, 59.6, 58.3, 52.9, 50.9, 50.8, 50.4, 47.5, 47.4, 45.9, 37.8, 37.6, 30.8, 30.5, 30.4, 30.2, 29.8, 26.1, 8.7, -4.6. **HRMS** *m/z*= 1476.8142 (calcd. for $C_{132}H_{184}N_{54}O_{25}Si$ 1476.7278 $[M+2H]^{2+}/2$).

(*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.48 (d, J = 4.9 Hz, 2H, H_{77} and H_{95}), 8.30 (d, J = 12.0 Hz, 2H, H_{73} and H_{91}), 8.03 (d, J = 8.0 Hz, 2H, H_{74} and H_{92}), 7.98 (s, 1H, H_{10}), 7.92 (s, 1H, H_{42}), 7.81 – 7.59 (m, 15H, H_{18}, H_{26}, H_{34}, H_{50}, H_{58}, H_{64}, H_{65}, H_{69}, H_{75} H_{82}, H_{83}, H_{87} and H_{93}), 7.43 (d, J = 1.5 Hz, 1H, H_{97}), 7.39 – 7.31 (m, 5H, H_{66}, H_{79}, and H_{84}), 7.31 – 7.26 (m, 2H, H_{67} and H_{85}), 7.22 – 7.15 (m, 2H, H_{76} and H_{94}), 6.45 – 5.86 (m, 7H, H_6, H_{14}, H_{22}, H_{30}, H_{38}, H_{46} and H_{54}), 5.38 – 5.06 (m, 7H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{45} and H_{53}), 4.73 – 4.43 (m, 33H, H_{11}, H_{19}, H_{27}, H_{35}, H_{43}, H_{51}, H_{59}, H_{61}, H_{63}, H_{68}, H_{70}, H_{72}, H_{78}, H_{81}, H_{86}, H_{88} and H_{90}), 4.40 – 4.16 (m, 18H, H_3, H_9, H_{17}, H_{25}, H_{33}, H_{41}, H_{49}, H_{57} and H_{96}), 3.71 – 3.43 (m, 16H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44}, H_{52} and H_{60}), 3.30 (d, J = 5.4 Hz, 6H, H_{71} and H_{89}), 3.06 (brs, 14H, H_7, H_{15}, H_{23}, H_{31}, H_{39},

H_{47} and H_{55}), 2.01 (brs, 14H, H_8, H_{16}, H_{24}, H_{32}, H_{40}, H_{48} and H_{56}), 1.26 (s, 18H, H_{80} and H_{98}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 155.7, 149.9, 149.3, 145.0, 144.2, 137.4, 129.0, 128.4, 125.8, 125.7, 124.0, 123.8, 123.2, 121.4, 121.1, 120.4, 101.2, 91.0, 71.3, 71.1, 70.9, 68.3, 65.8, 64.7, 59.7, 58.3, 52.9, 50.8, 50.5, 47.5, 37.8, 30.8, 30.5, 30.5, 30.3, 29.8, 26.1, 16.5, -4.6. **HRMS** *m/z*= 1476.7087 (calcd. for $C_{132}H_{184}N_{54}O_{25}Si$ 1476.7278 $[M+2H]^{2+}/2$).

3 ^{1}H AND ^{13}C NMR SPECTRA

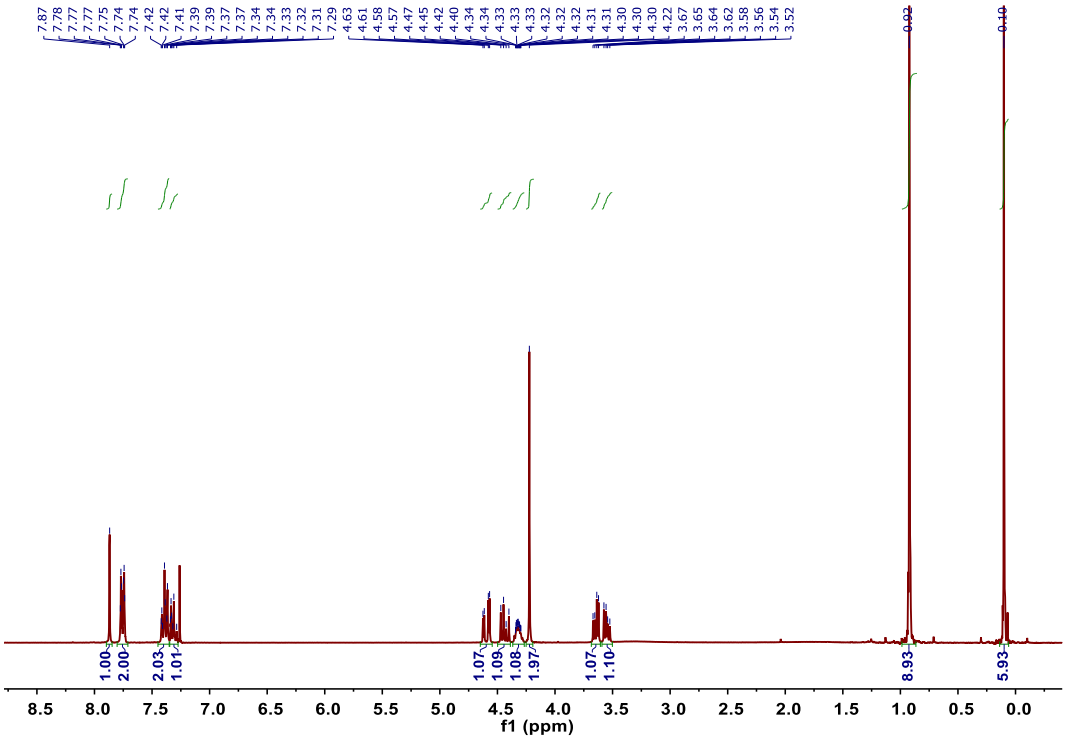


Figure S1. ^{1}H NMR of *rac*-**4a**.

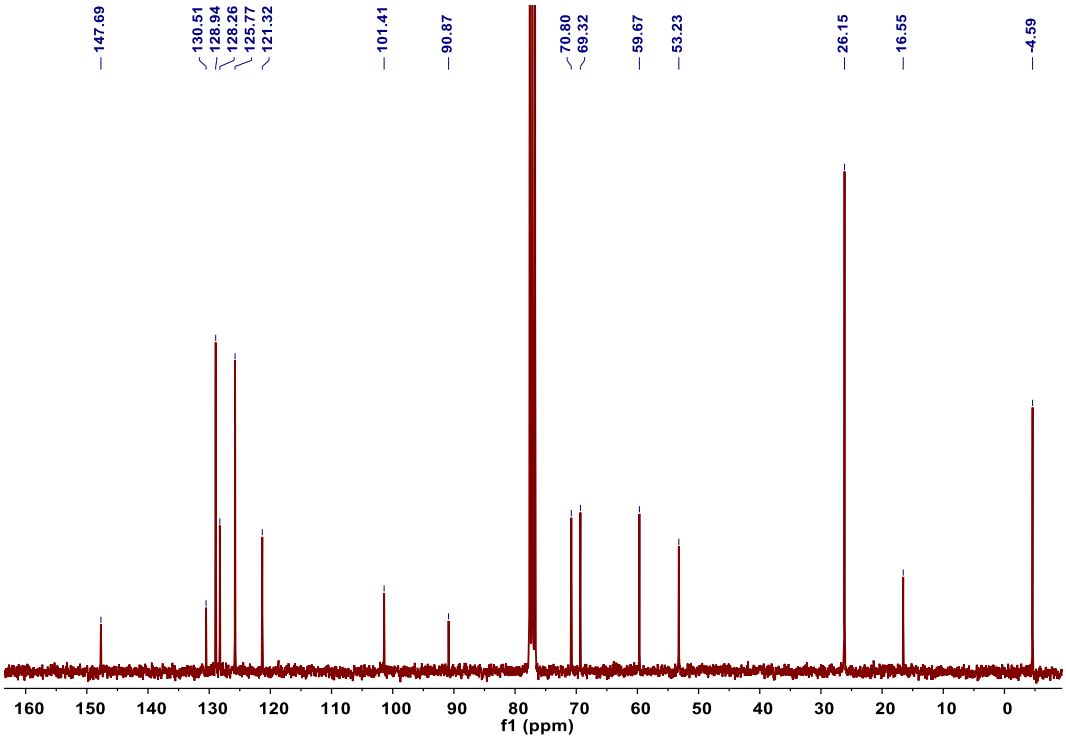


Figure S2. ^{13}C NMR of *rac*-**4a**.

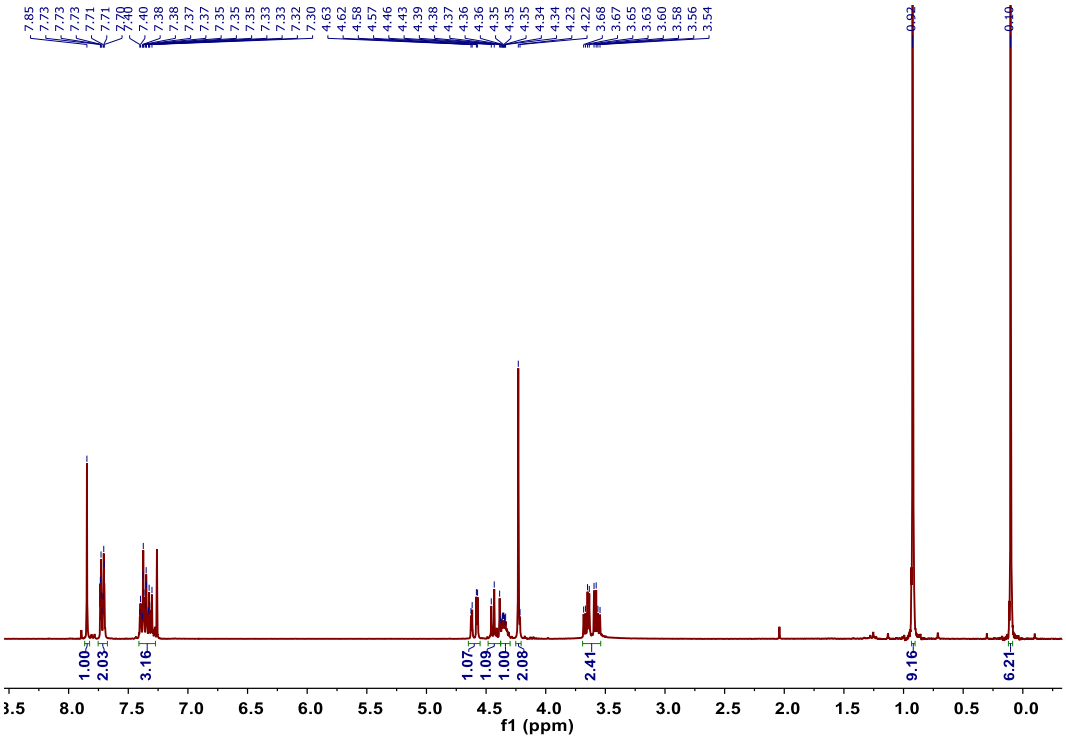


Figure S3. ^{1}H NMR of (*R*)-**4a**.

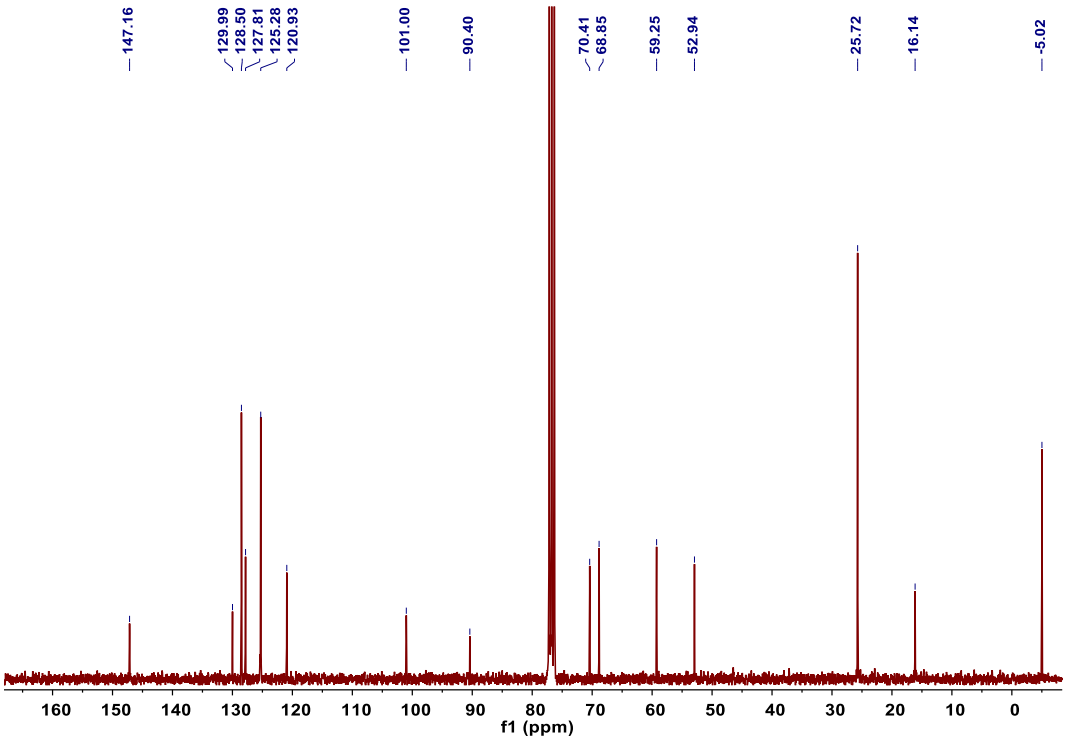


Figure S4. ^{13}C NMR of (*R*)-**4a**.

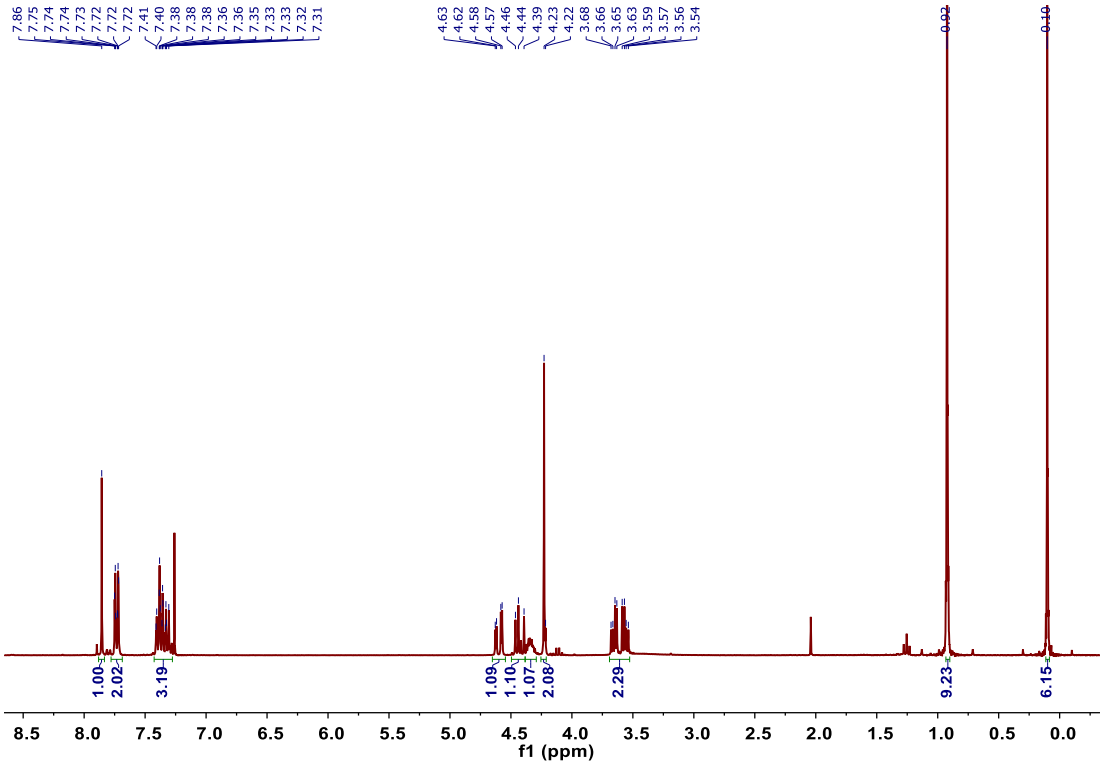


Figure S5. ^{1}H NMR of (*S*)-**4a**.

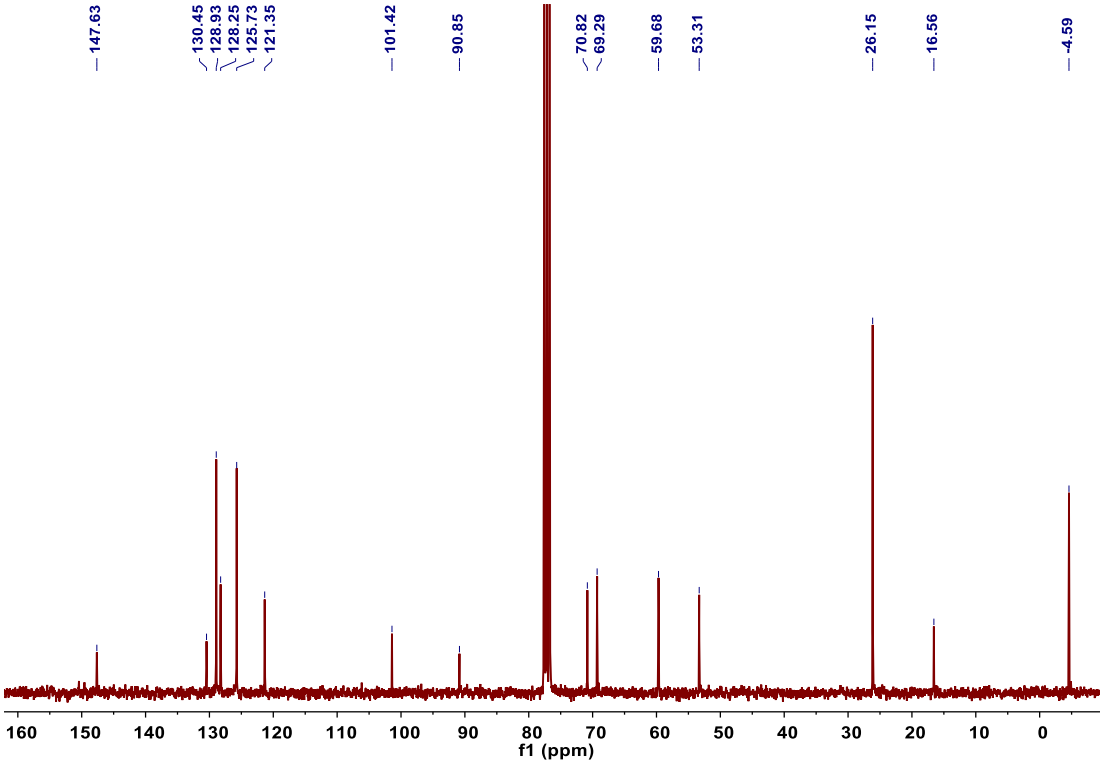


Figure S6. ^{13}C NMR of (*S*)-**4a**.

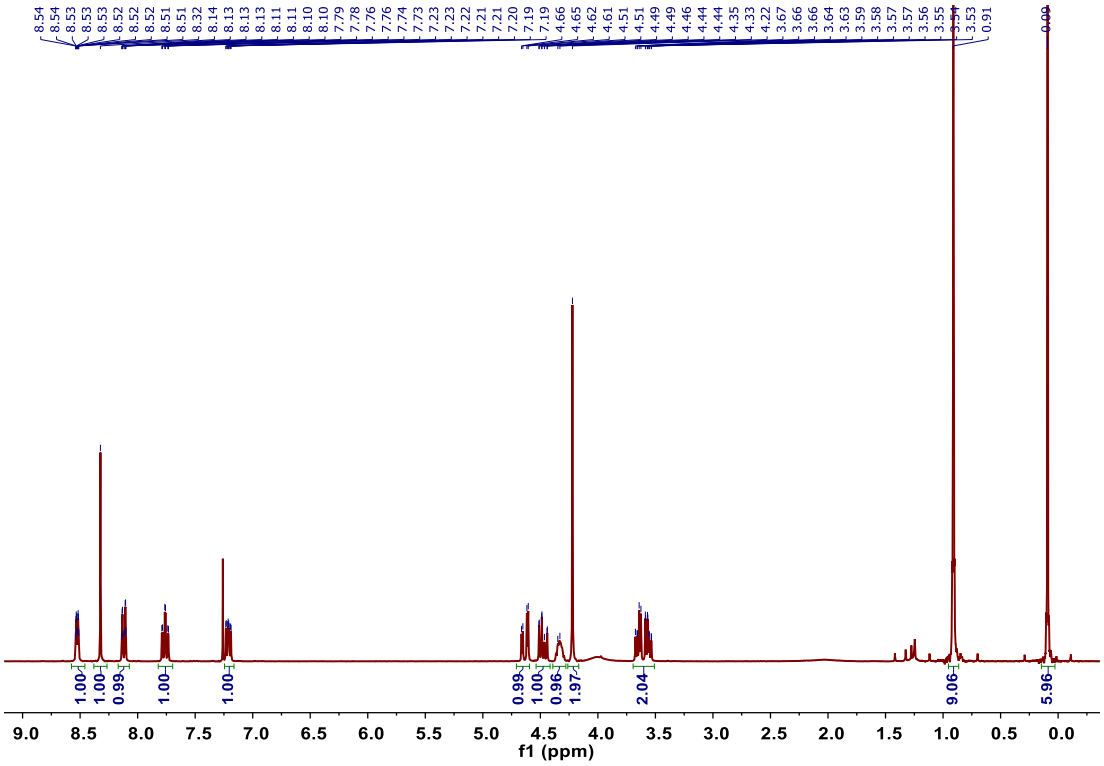


Figure S7. ^{1}H NMR of *rac*-**4b**.

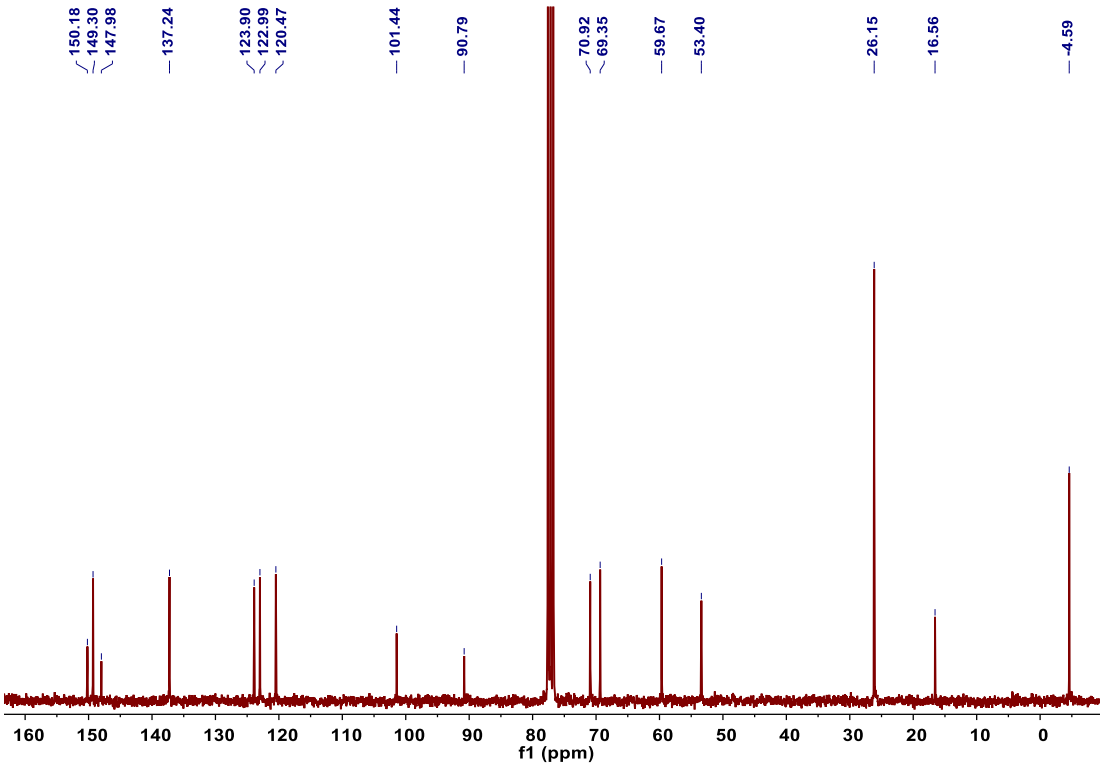


Figure S8. ^{13}C NMR of *rac*-**4b**.

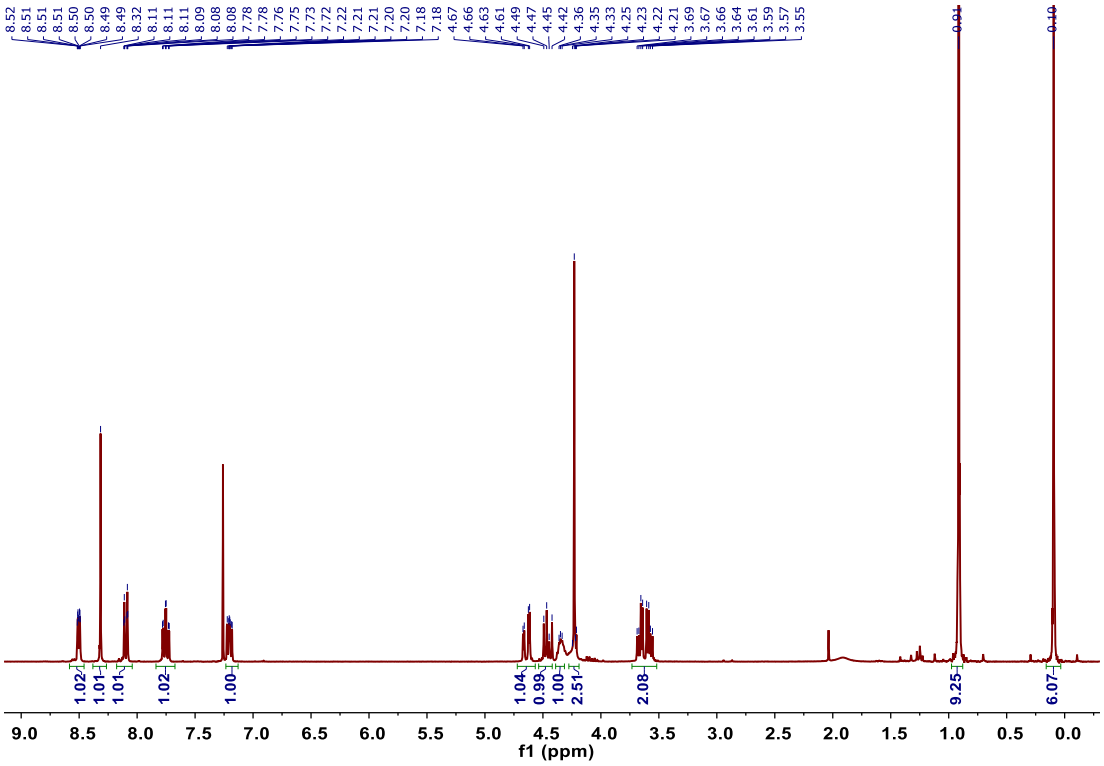


Figure S9. ^{1}H NMR of (*R*)-**4b**.

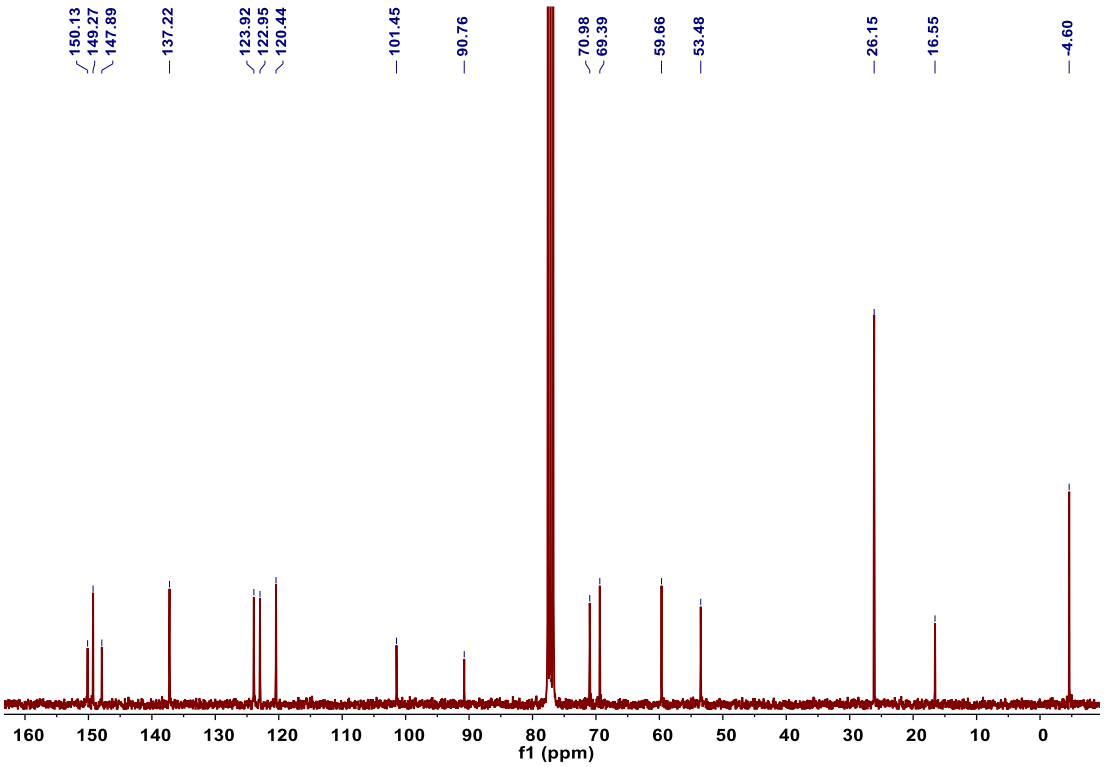


Figure S10. ^{13}C NMR of (*R*)-**4b**.

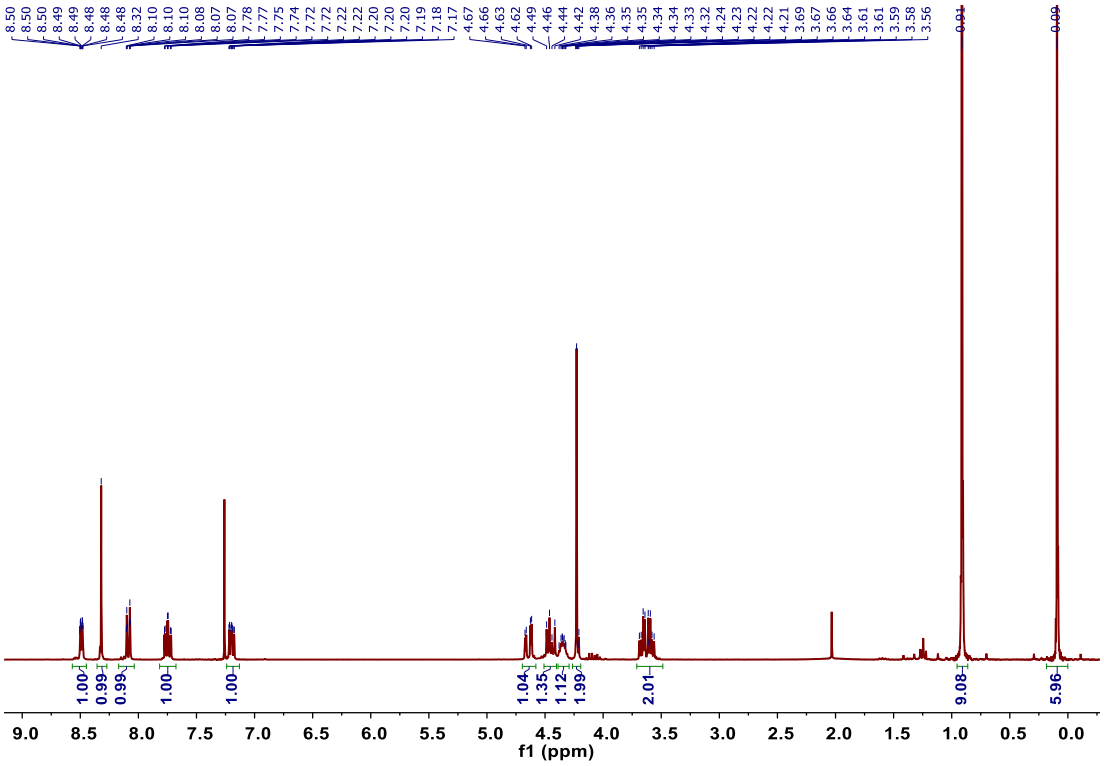


Figure S11. ^{1}H NMR of (*S*)-**4b**.

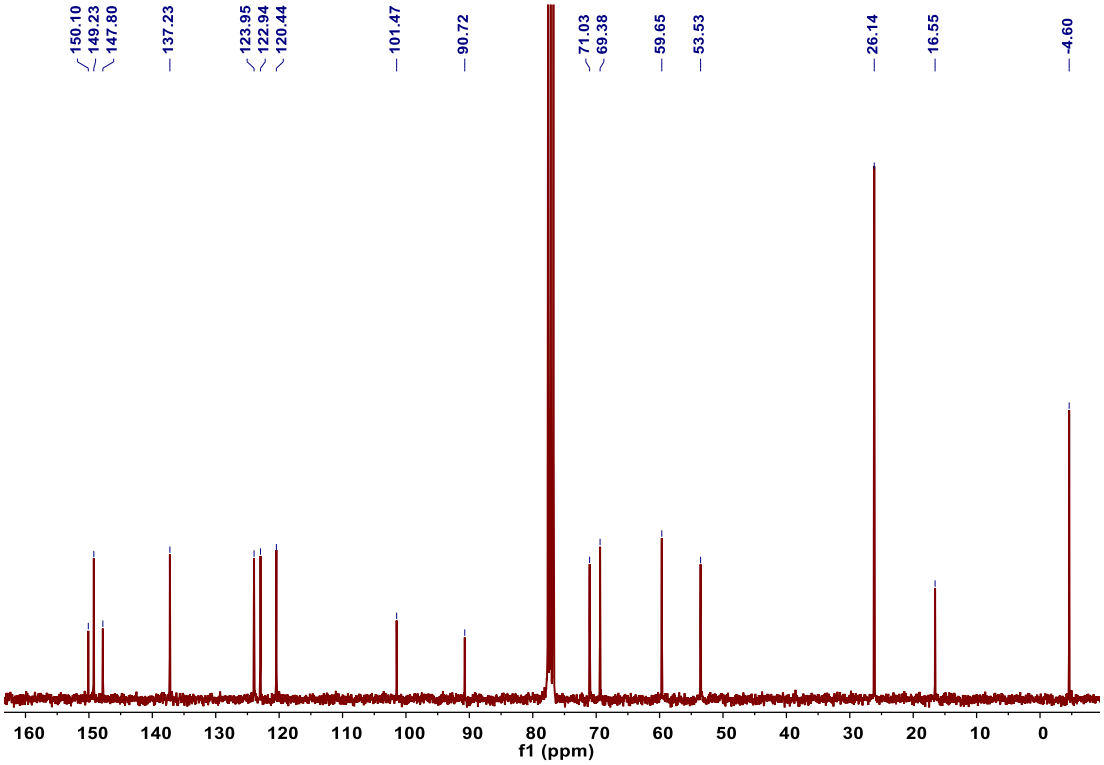


Figure S12. ^{13}C NMR of (*S*)-**4b**.

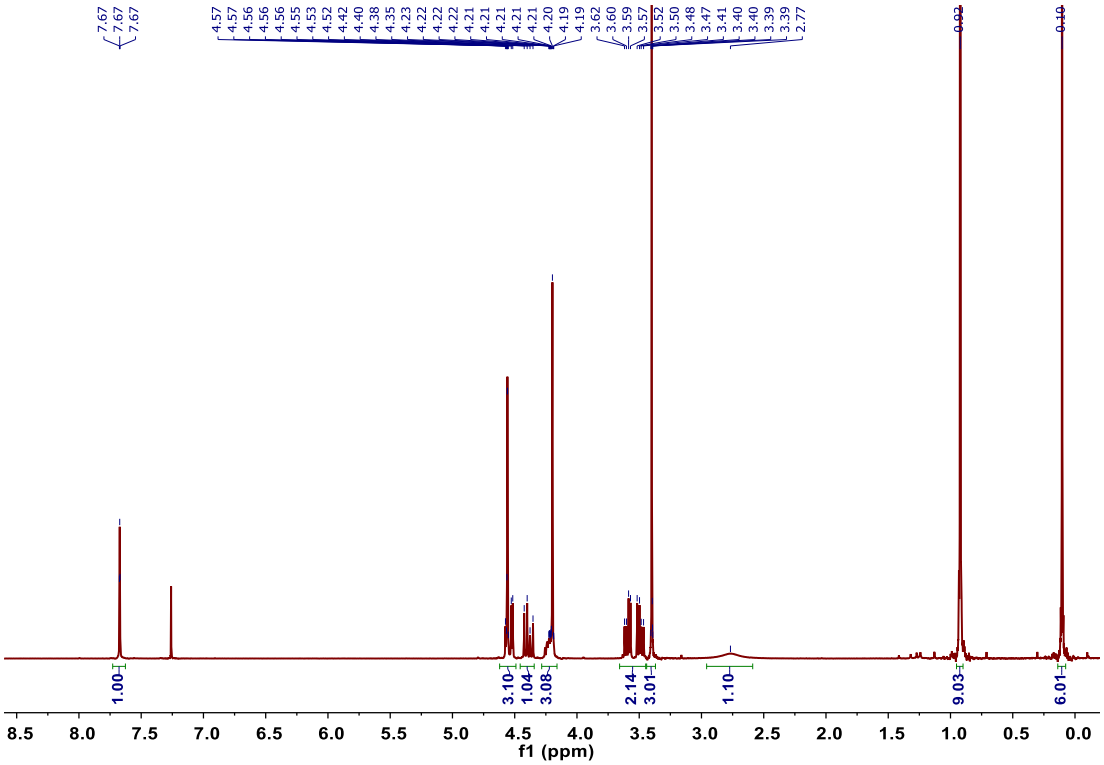


Figure S13. ^{1}H NMR of *rac*-**4c**.

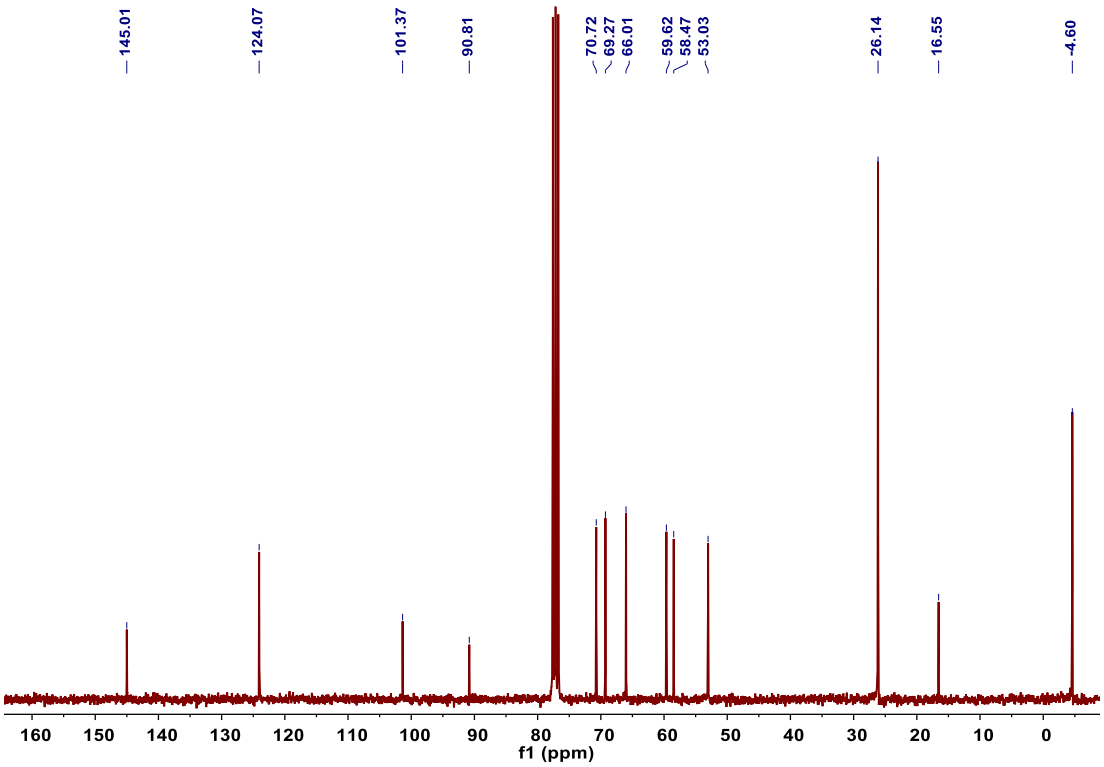


Figure S14. ^{13}C NMR of *rac*-**4c**.

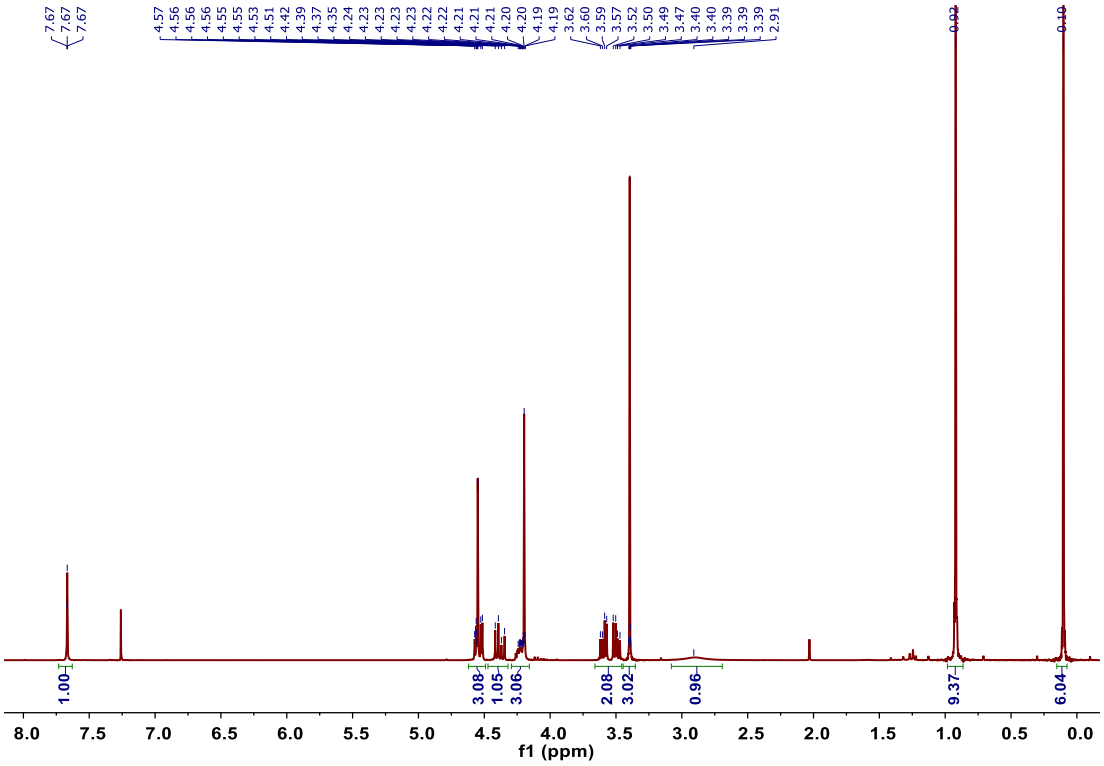


Figure S15. ^{1}H NMR of (*R*)-**4c**.

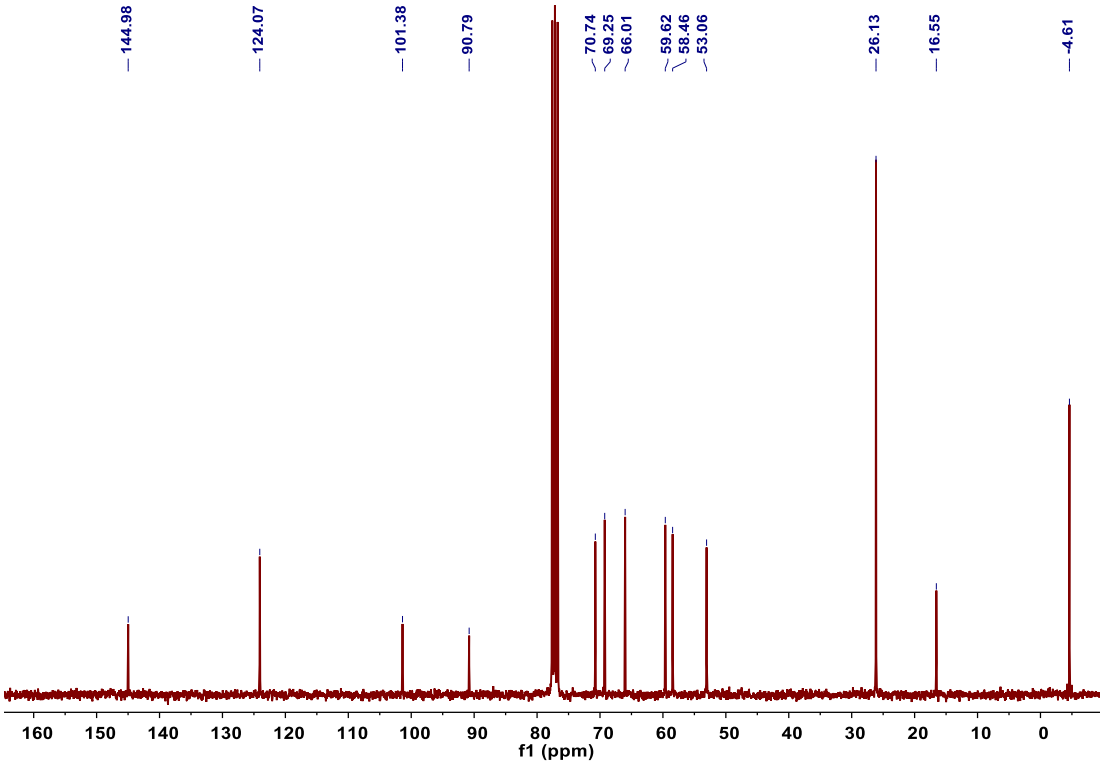


Figure S16. ^{13}C NMR of (*R*)-**4c**.

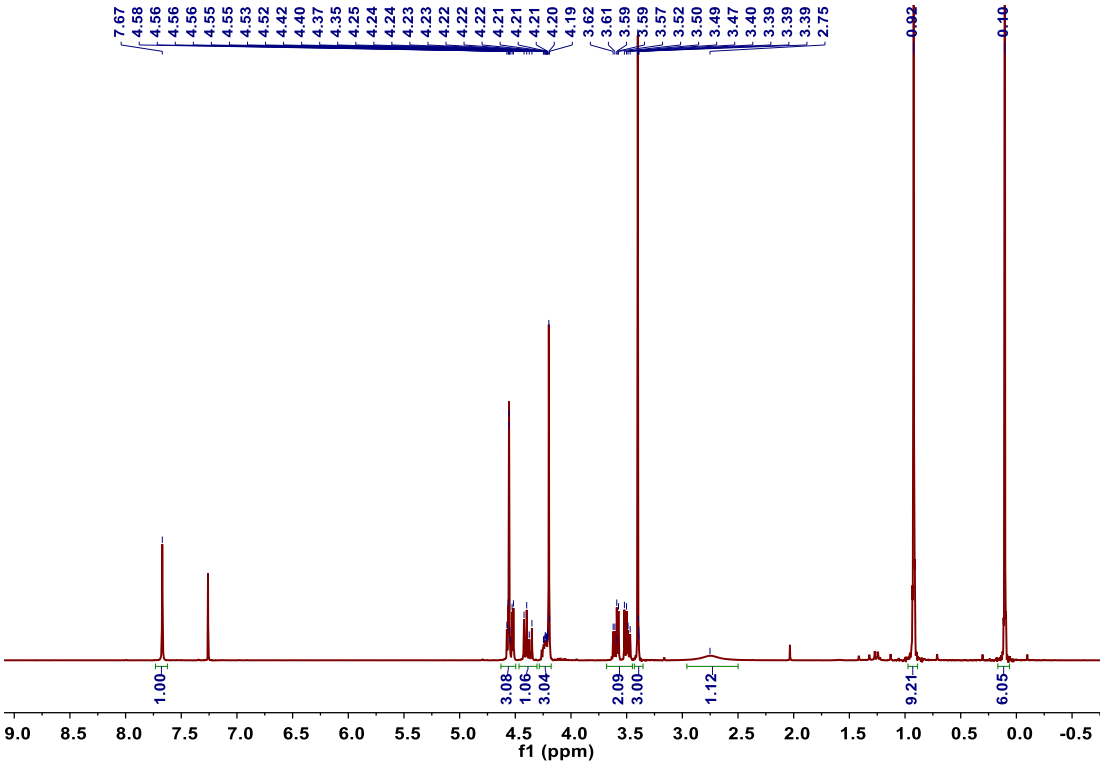


Figure S17. ^{1}H NMR of (*S*)-**4c**.

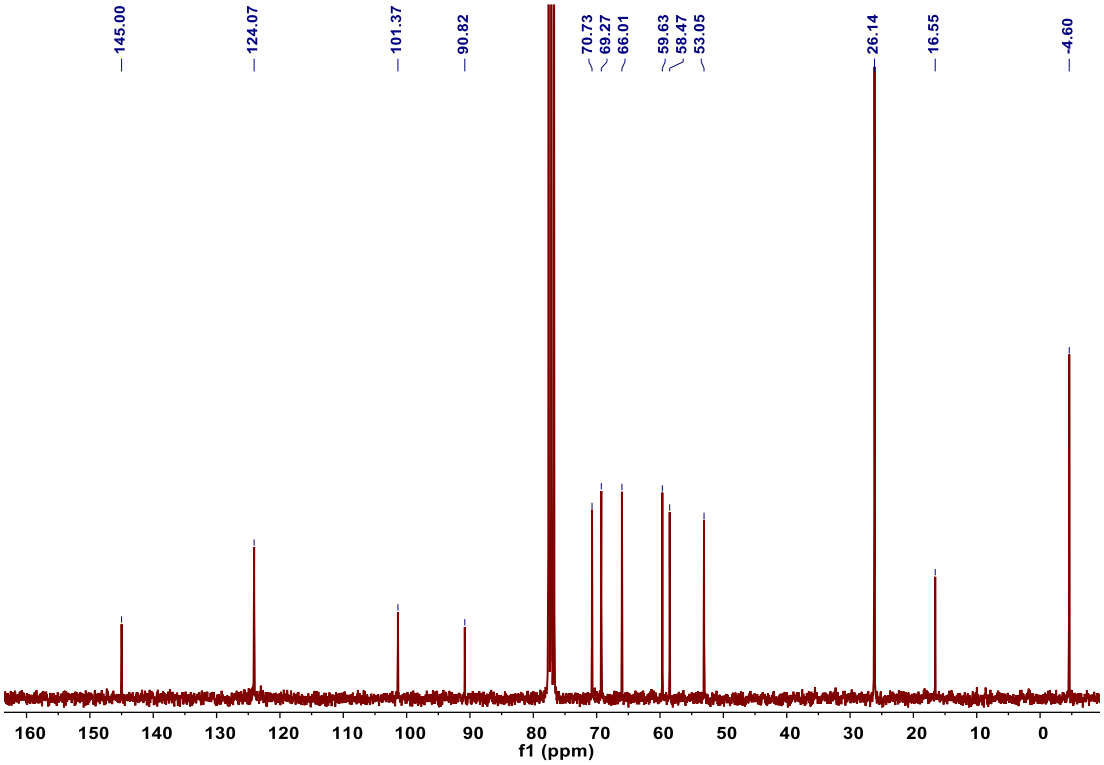


Figure S18. ^{13}C NMR of (*S*)-**4c**.

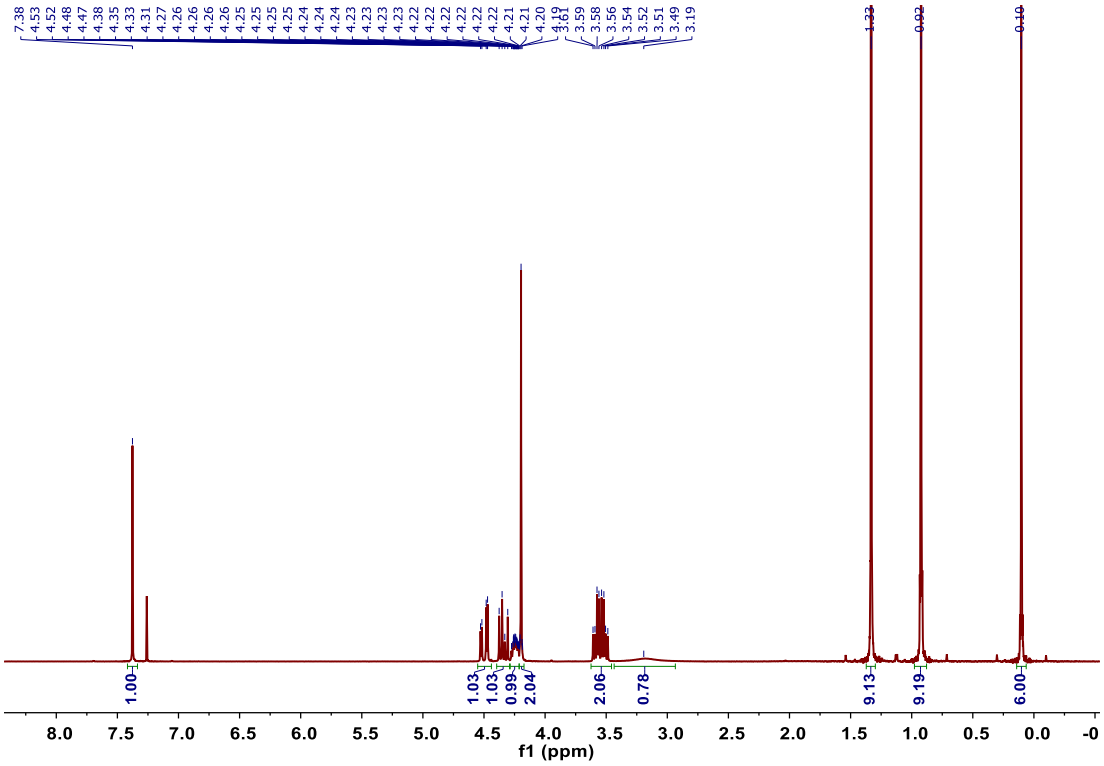


Figure S19. ^{1}H NMR of *rac*-**4d**.

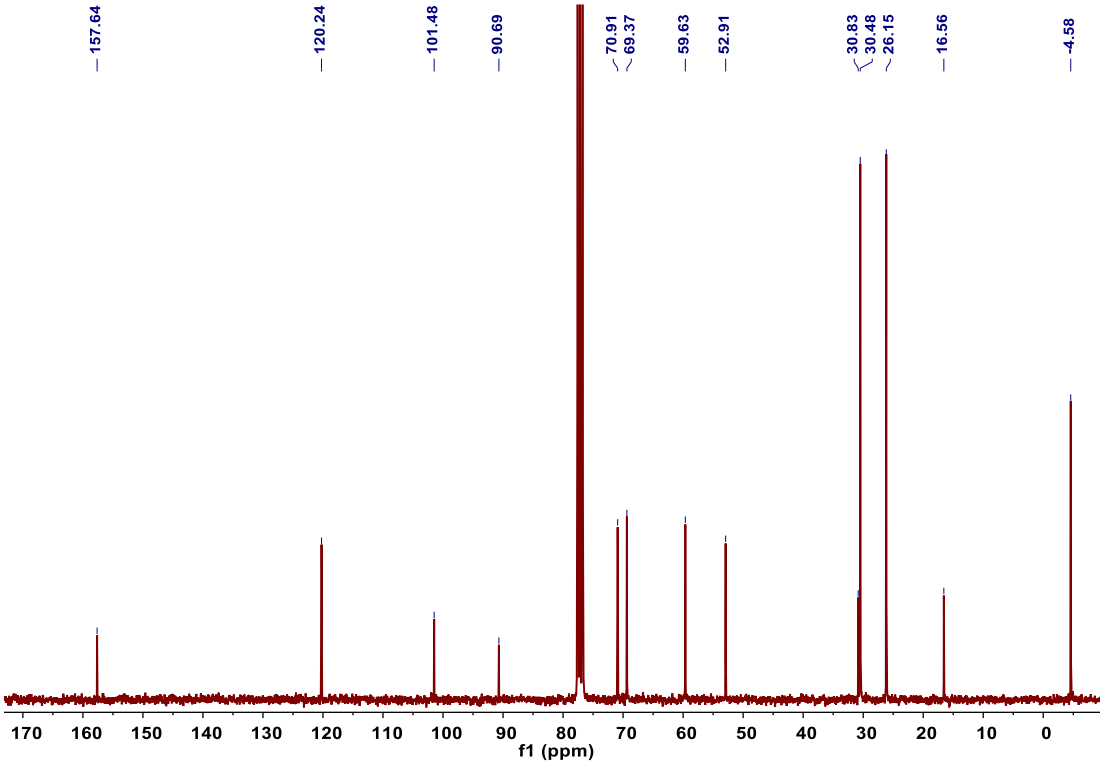


Figure S20. ^{13}C NMR of *rac*-**4d**.

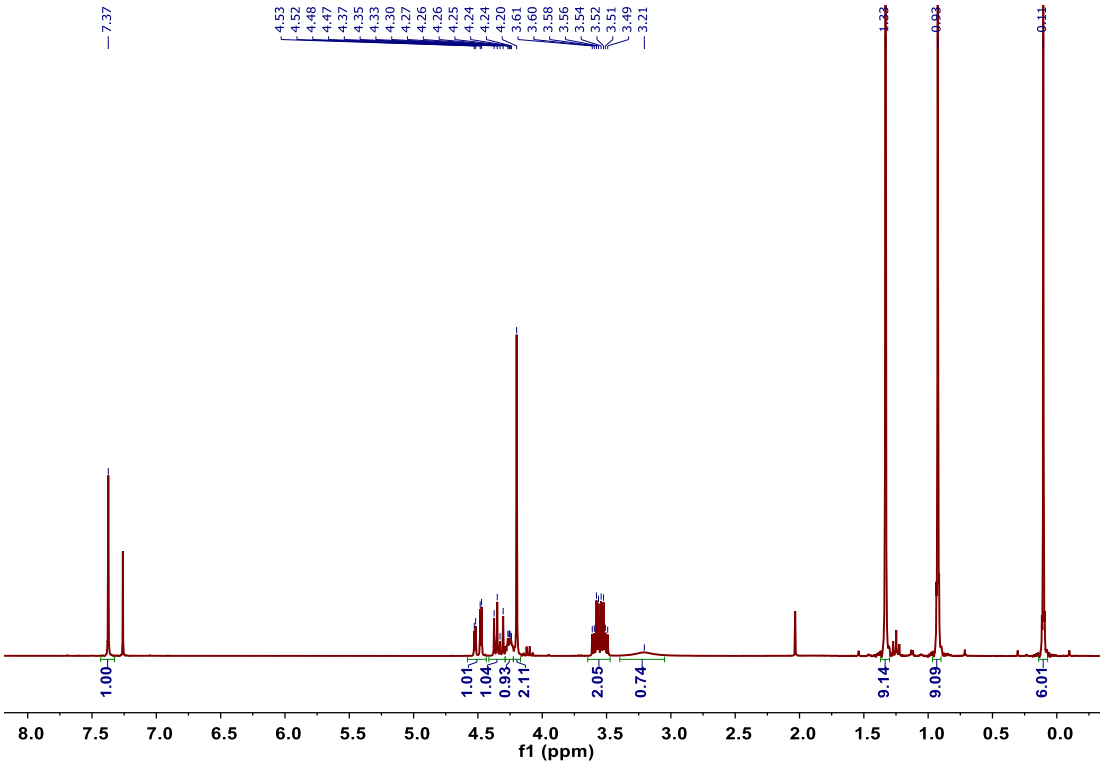


Figure S21. ^{1}H NMR of (*R*)-**4d**.

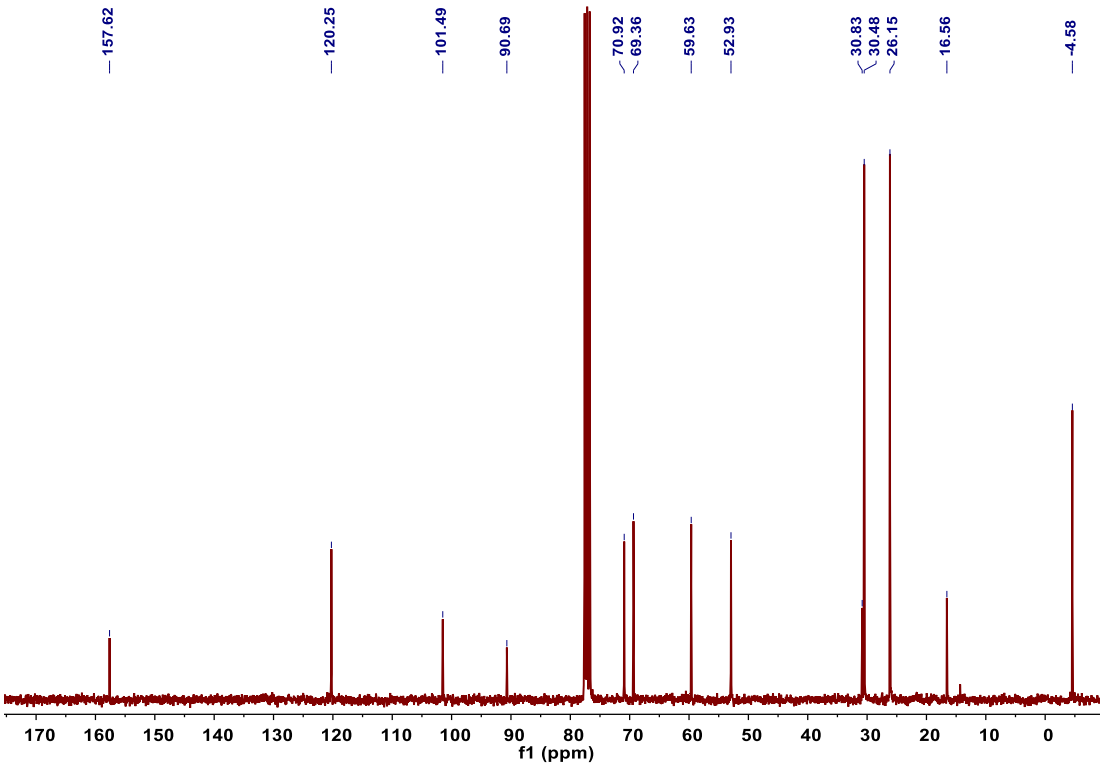


Figure S22. ^{13}C NMR of (*R*)-**4d**.

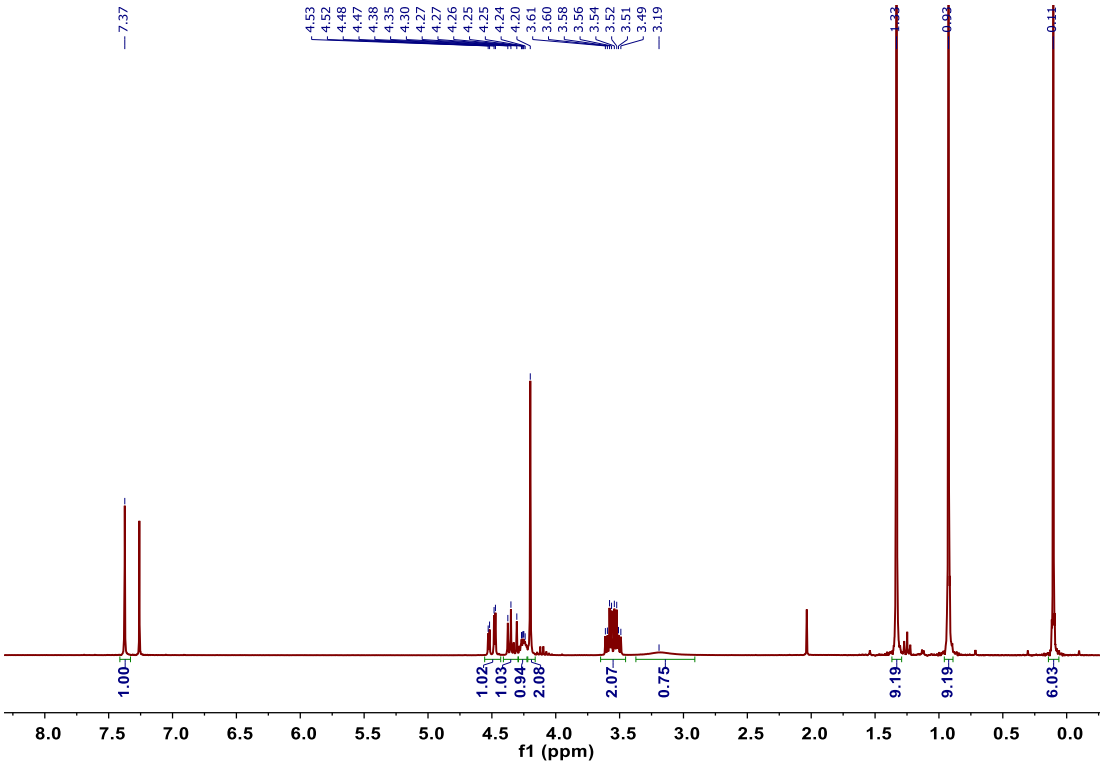


Figure S23. ^{1}H NMR of (*S*)-**4d**.

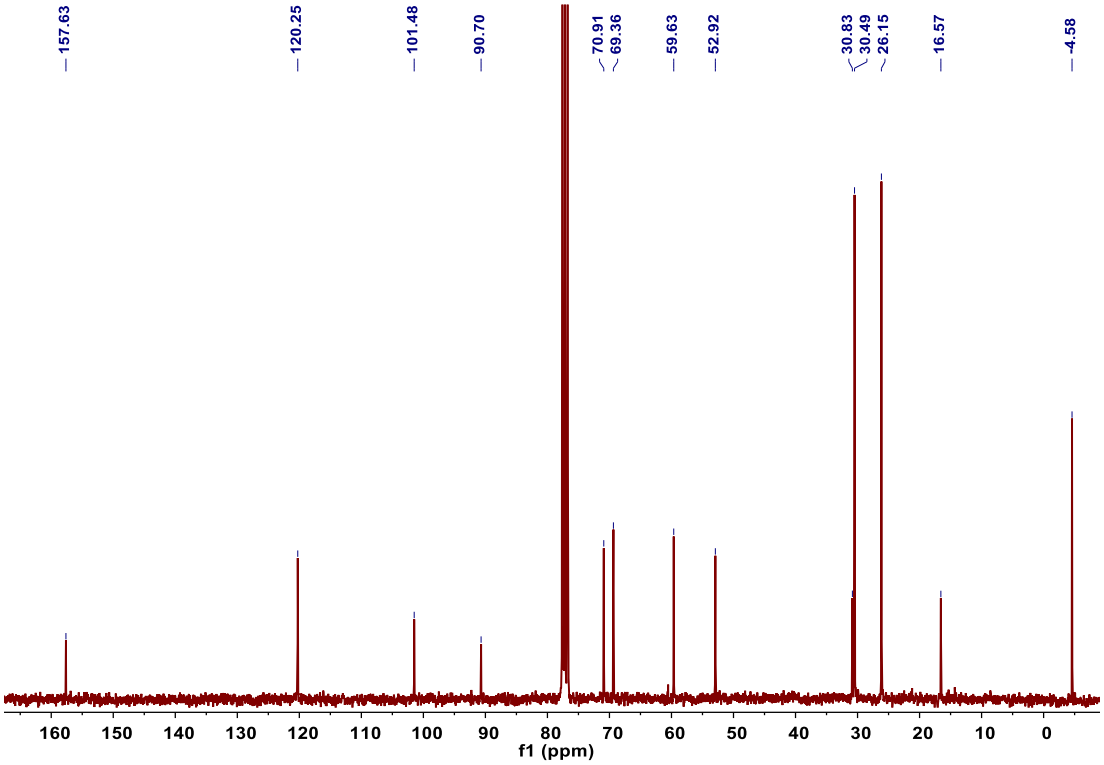


Figure S24. ^{13}C NMR of (*S*)-**4d**.

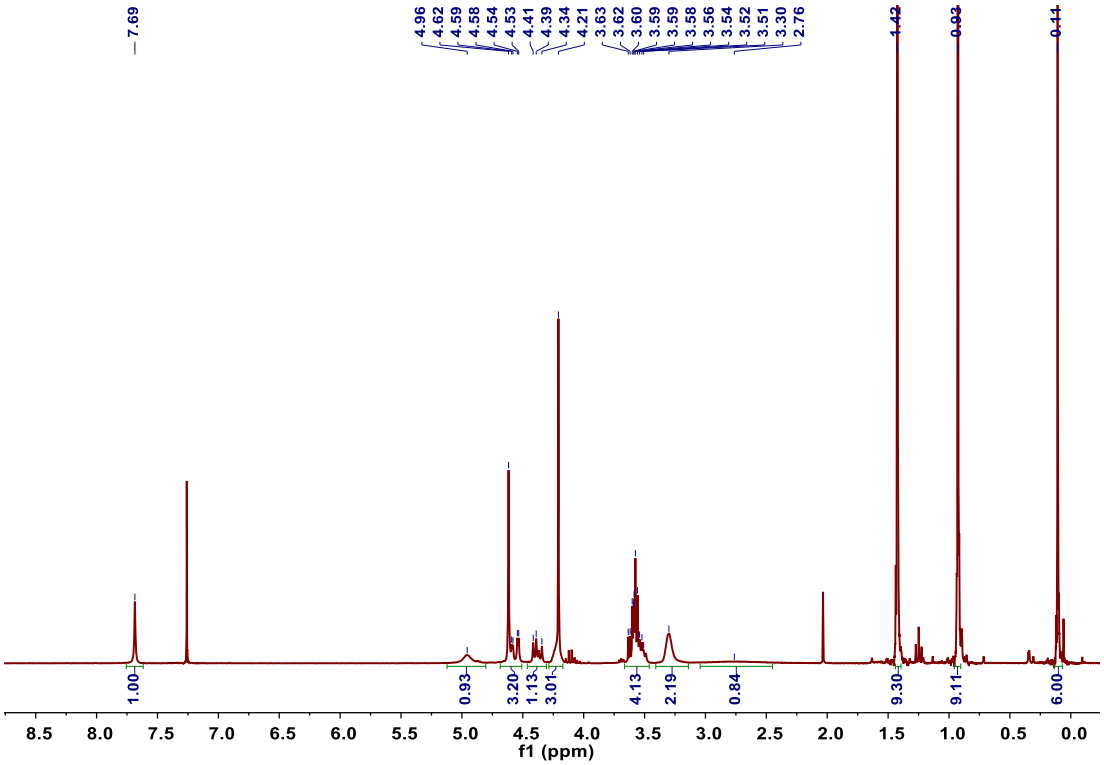


Figure S25. ^{1}H NMR of **4e**.

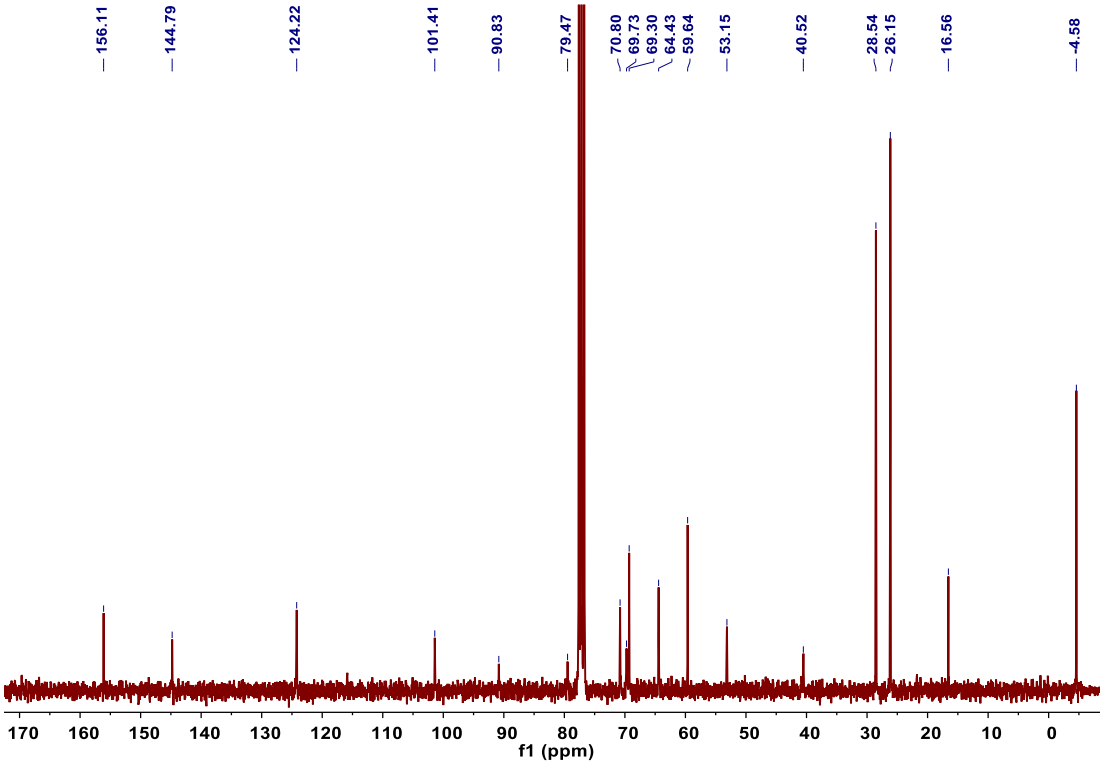


Figure S26. ^{13}C NMR of **4e**.

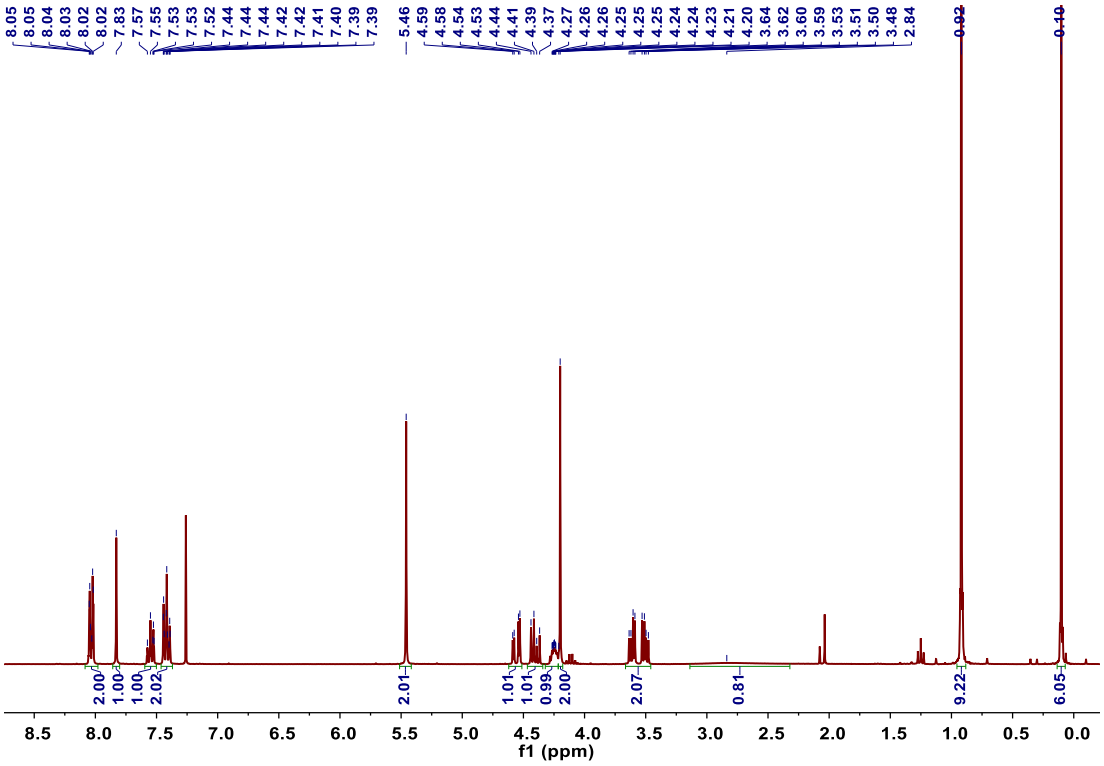


Figure S27. ^{1}H NMR of **4f**.

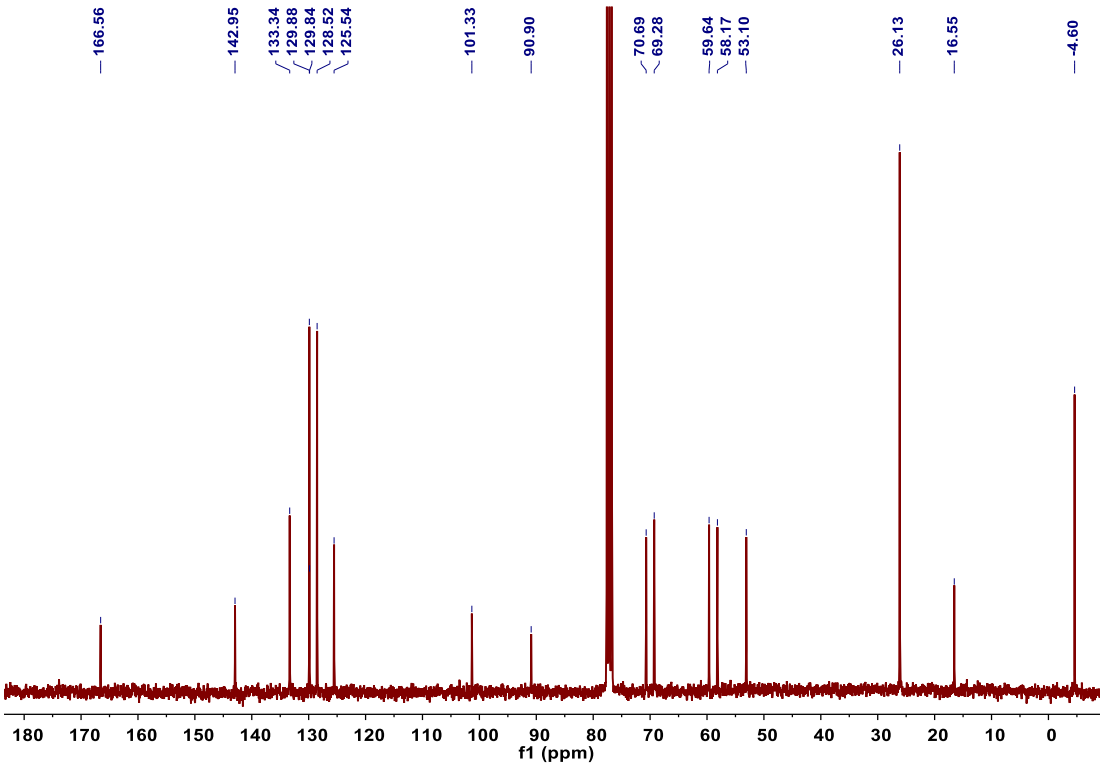


Figure S28. ^{13}C NMR of **4f**.

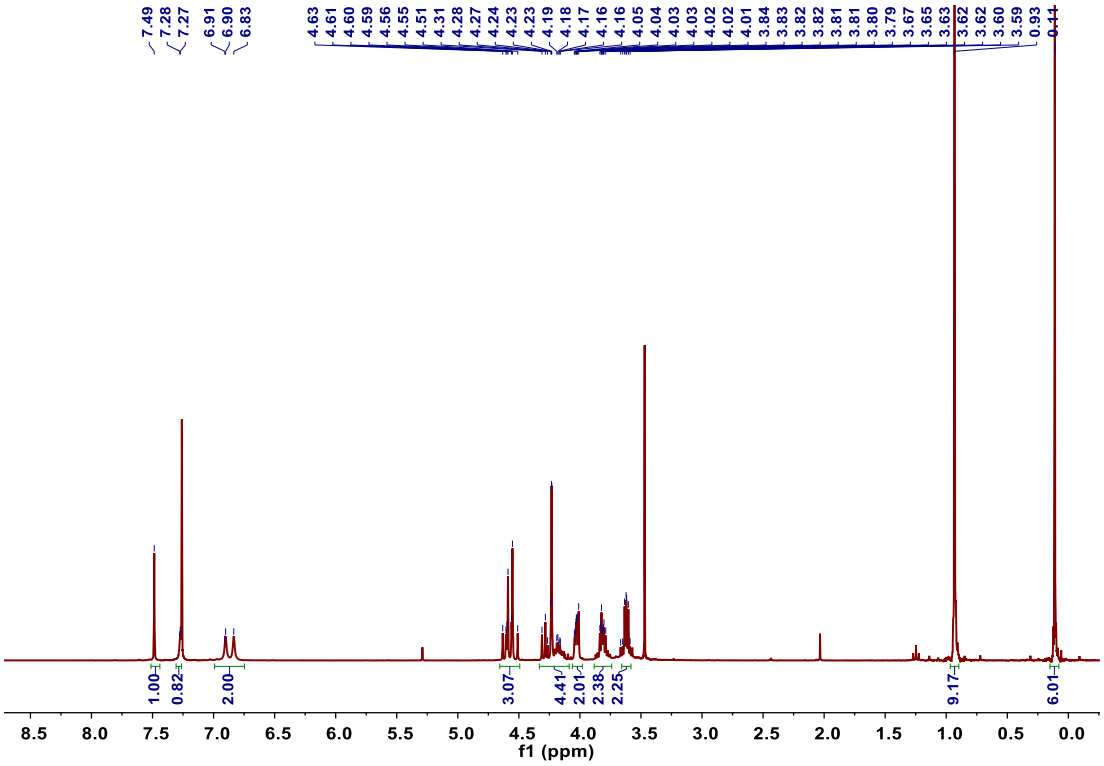


Figure S29. ^{1}H NMR of **4g**.

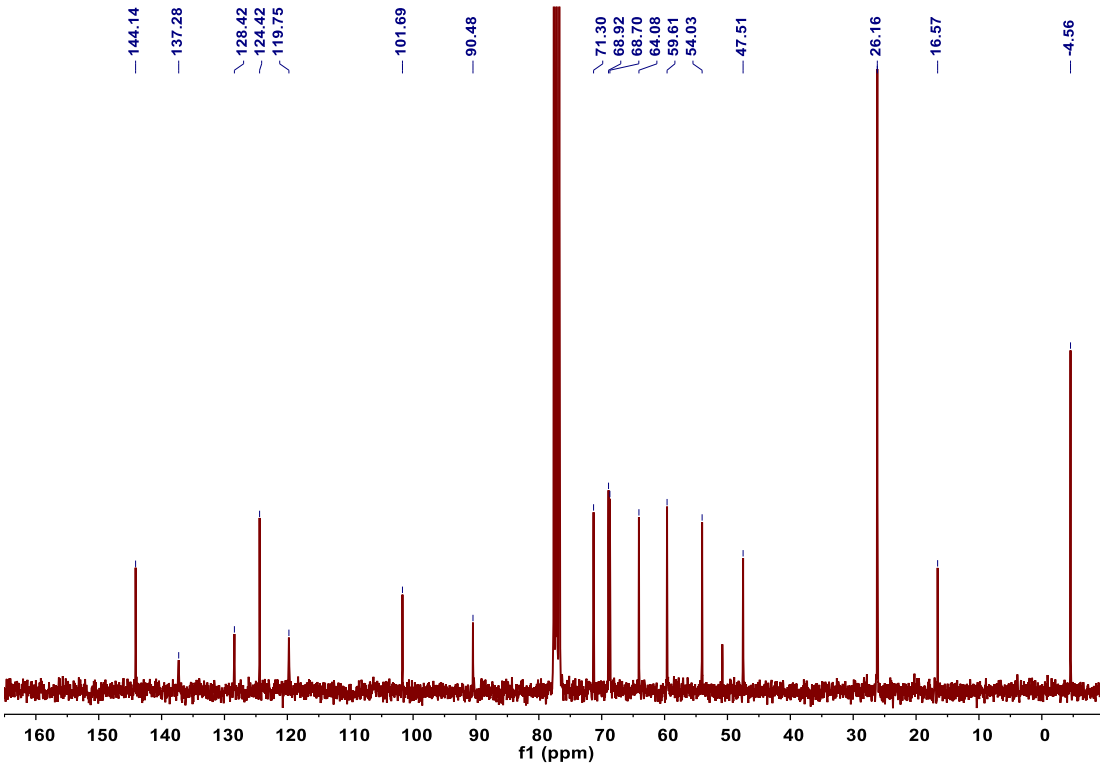


Figure S30. ^{13}C NMR of **4g**.

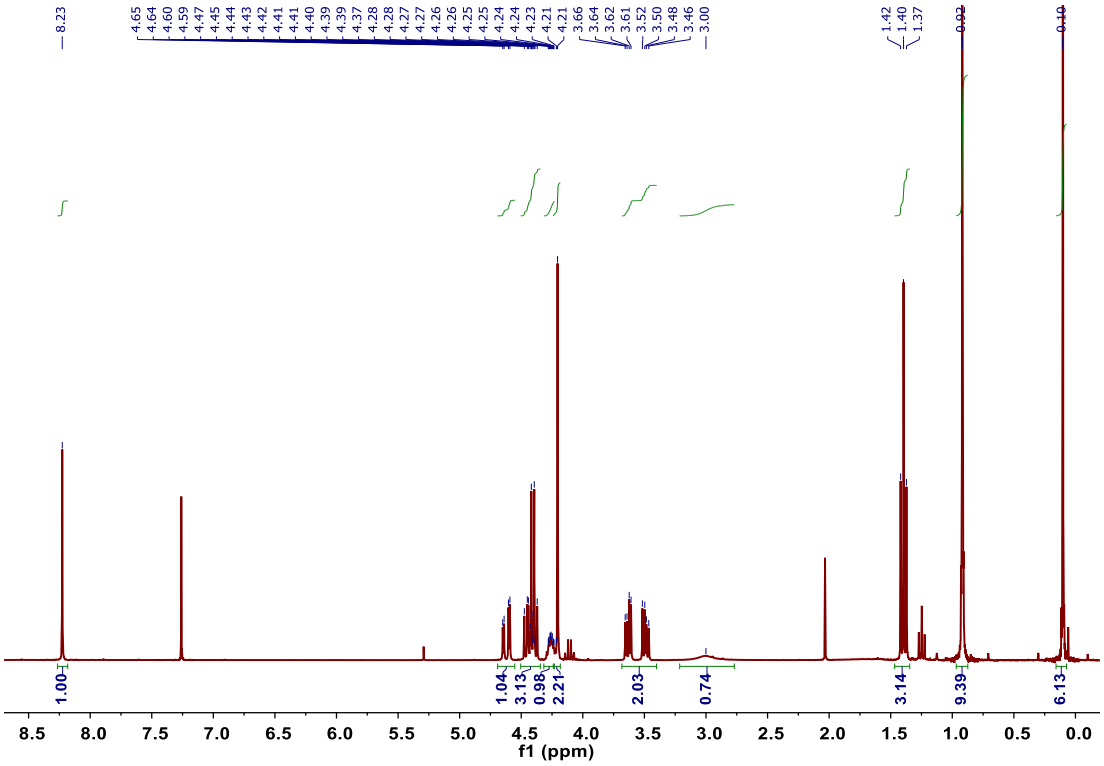


Figure S31. ^{1}H NMR of **4h**.

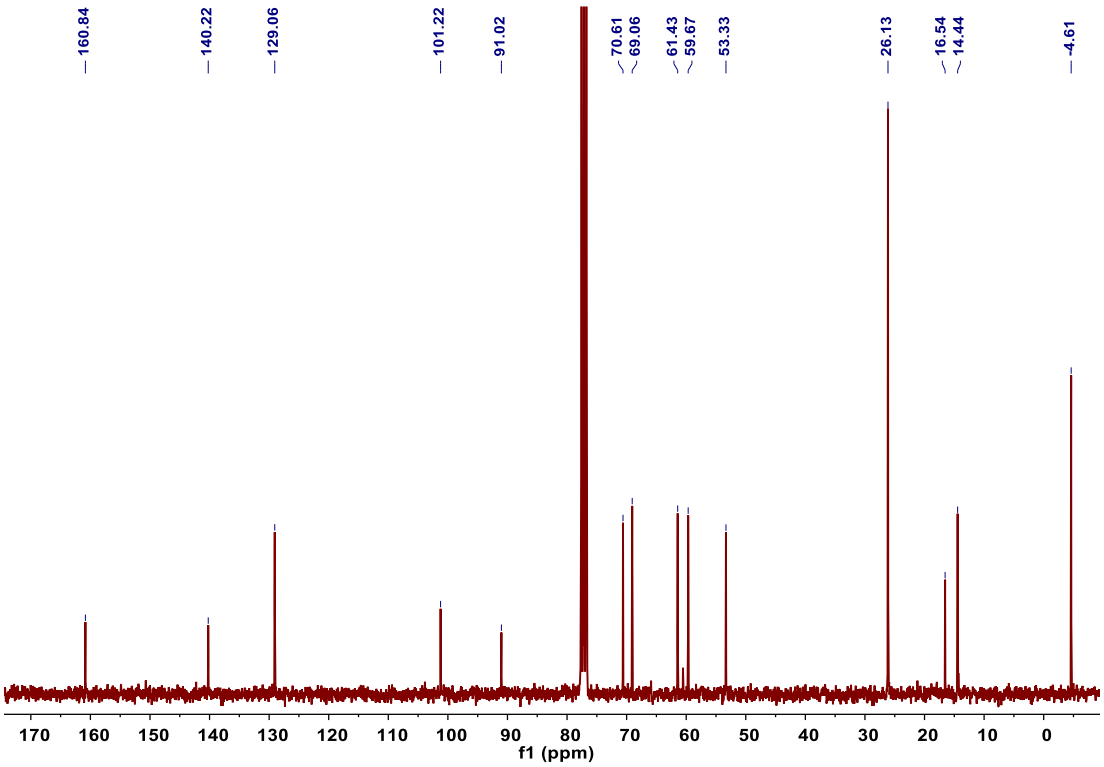


Figure S32. ^{13}C NMR of **4h**.

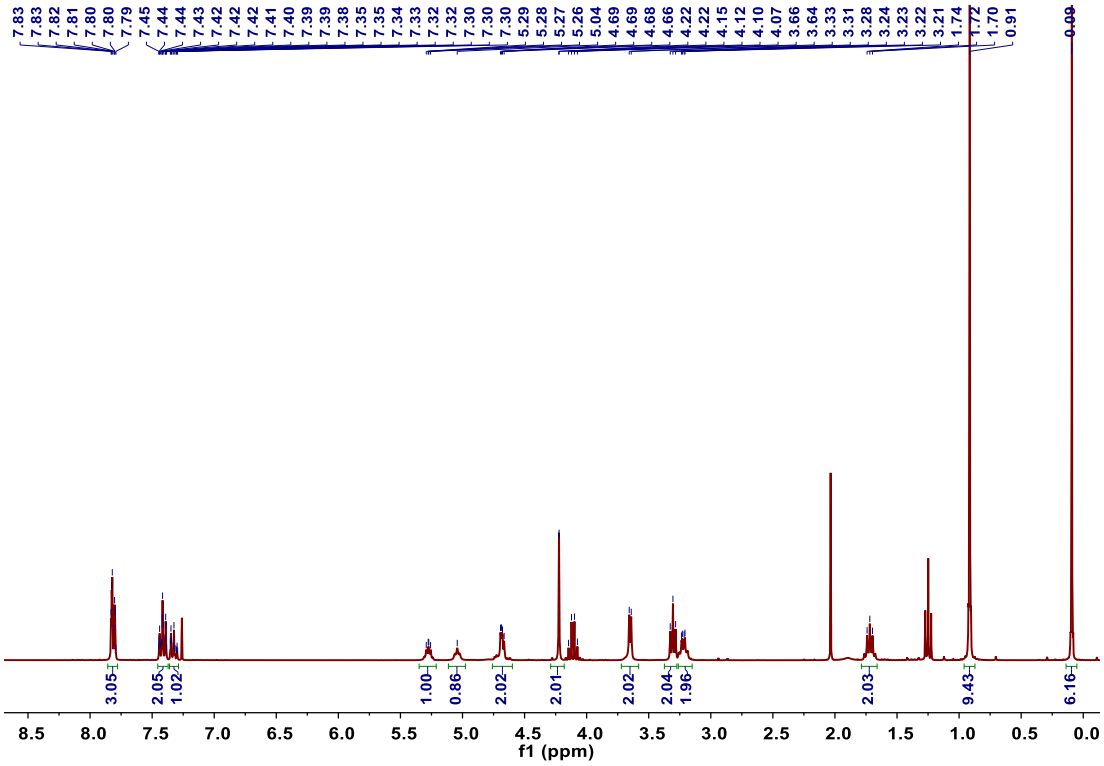


Figure S33. ^{1}H NMR of *rac*-**5a**.

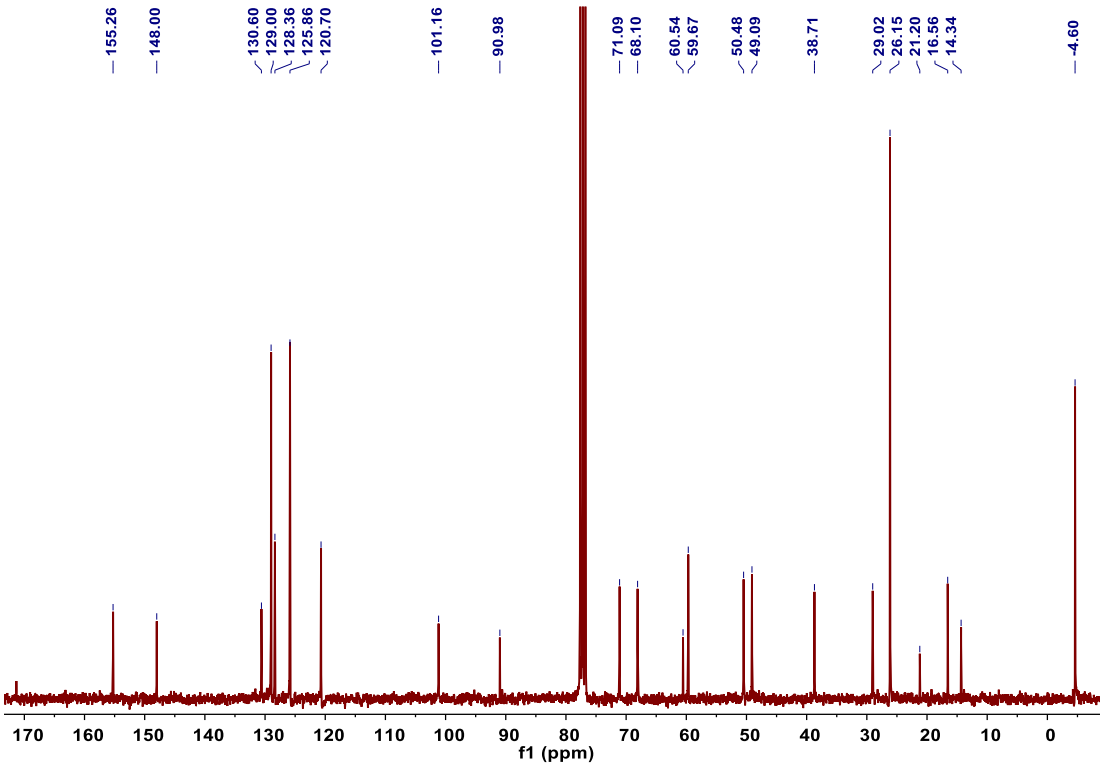


Figure S34. ^{13}C NMR of *rac*-**5a**.

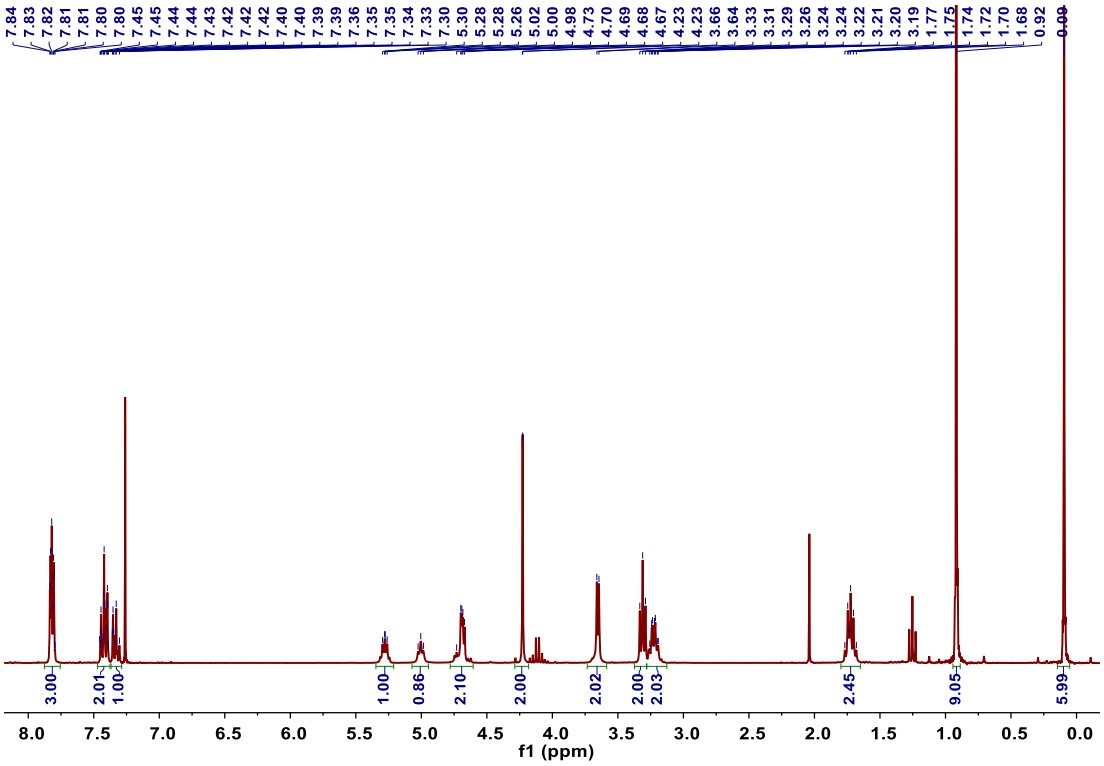


Figure S35. ^{1}H NMR of (*R*)-**5a**.

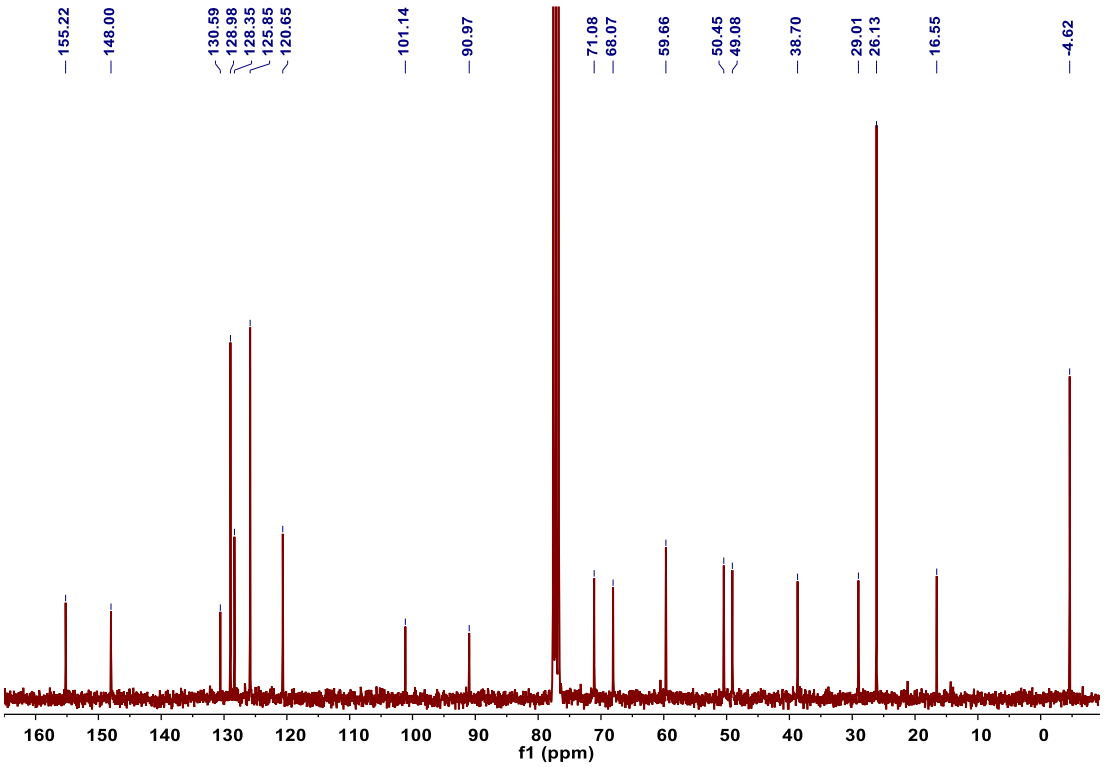


Figure S36. ^{13}C NMR of (*R*)-**5a**.

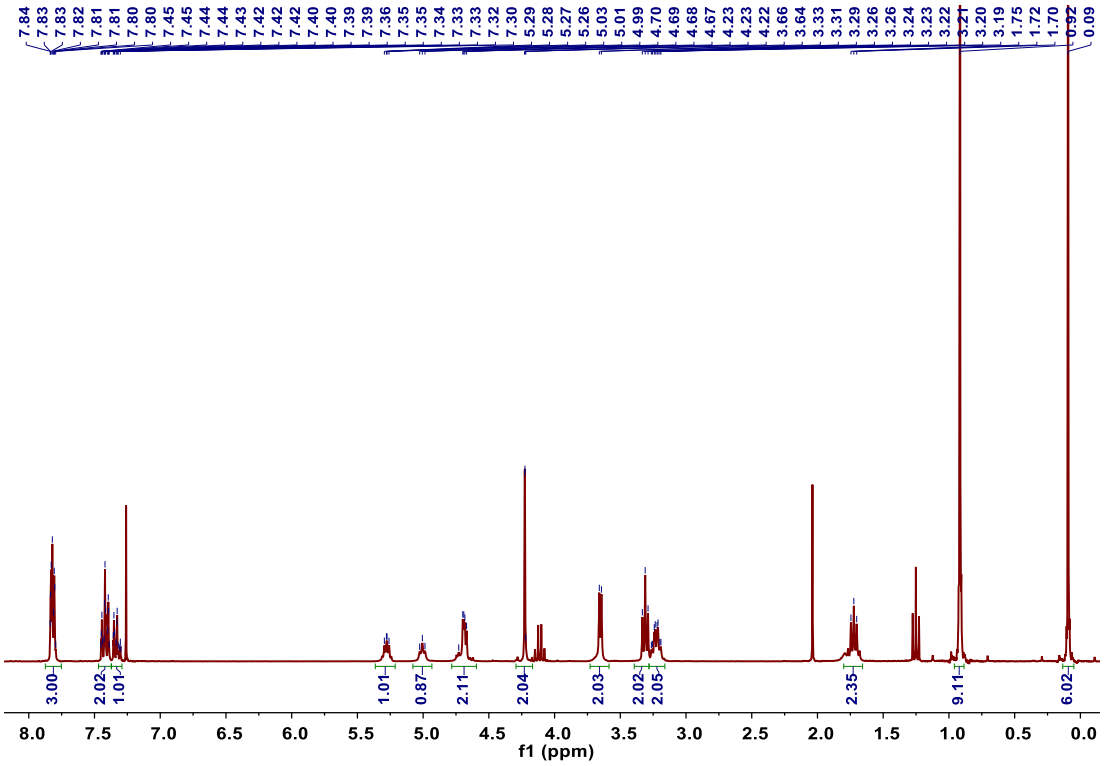


Figure S37. ^{1}H NMR of (*S*)-**5a**.

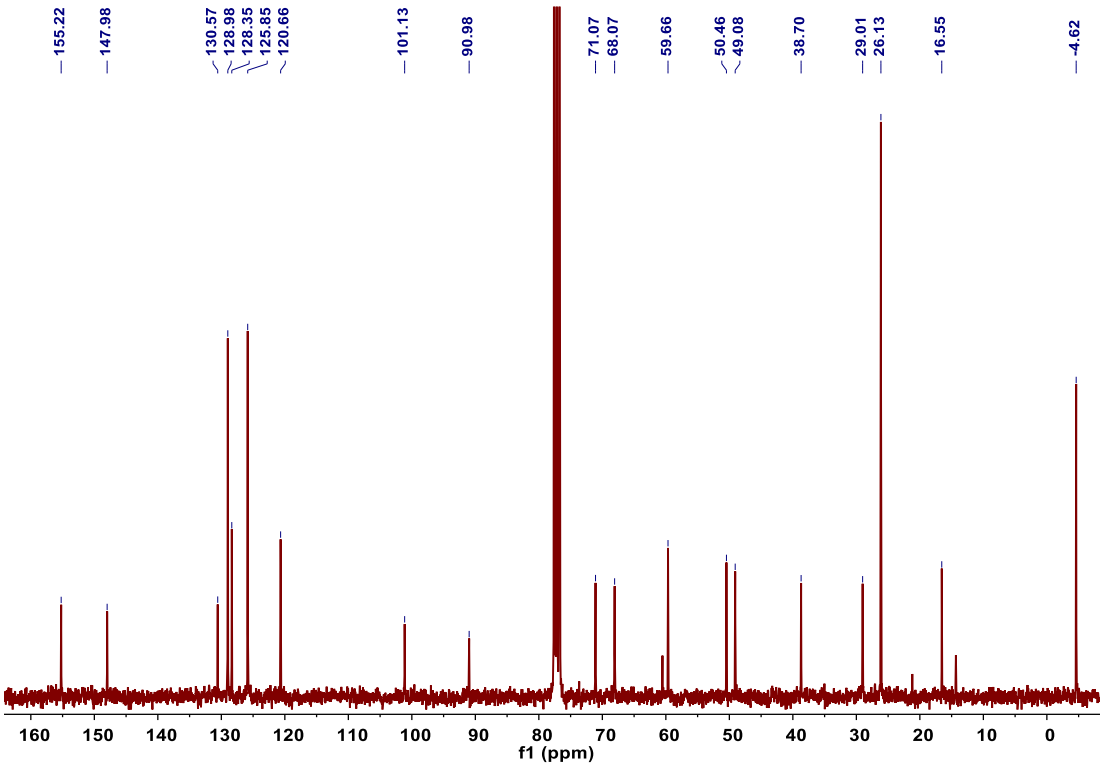


Figure S38. ^{13}C NMR of (*S*)-**5a**.

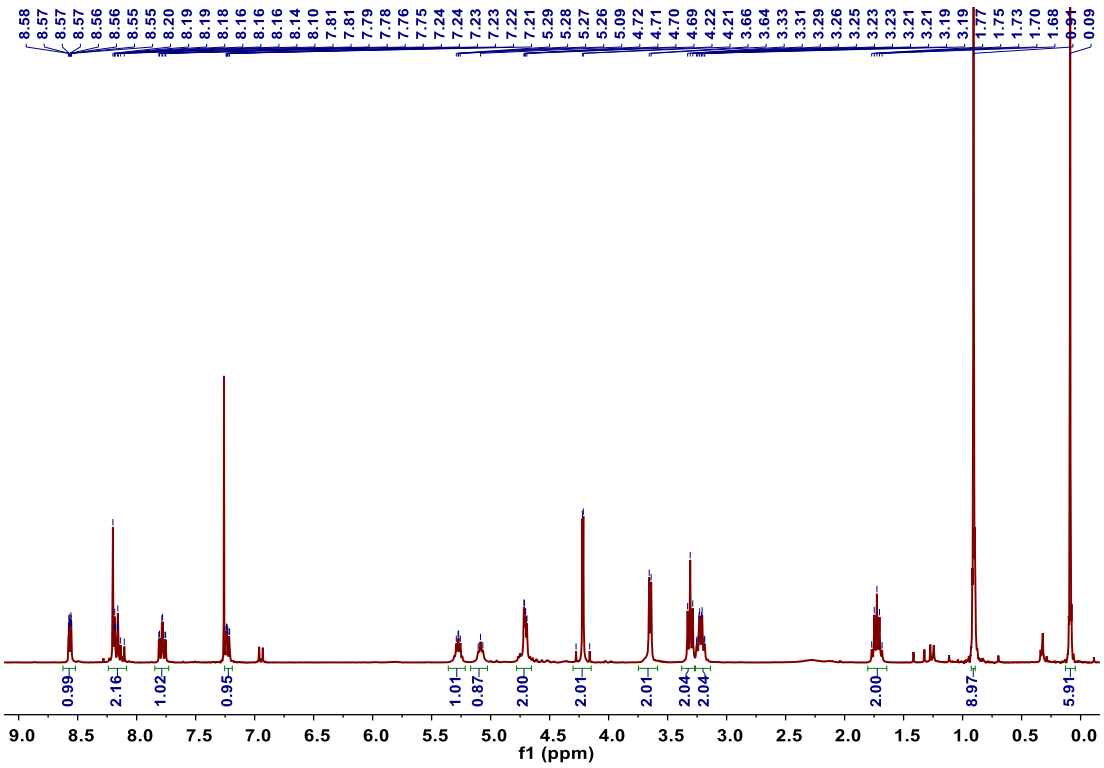


Figure S39. ^{1}H NMR of *rac*-**5b**.

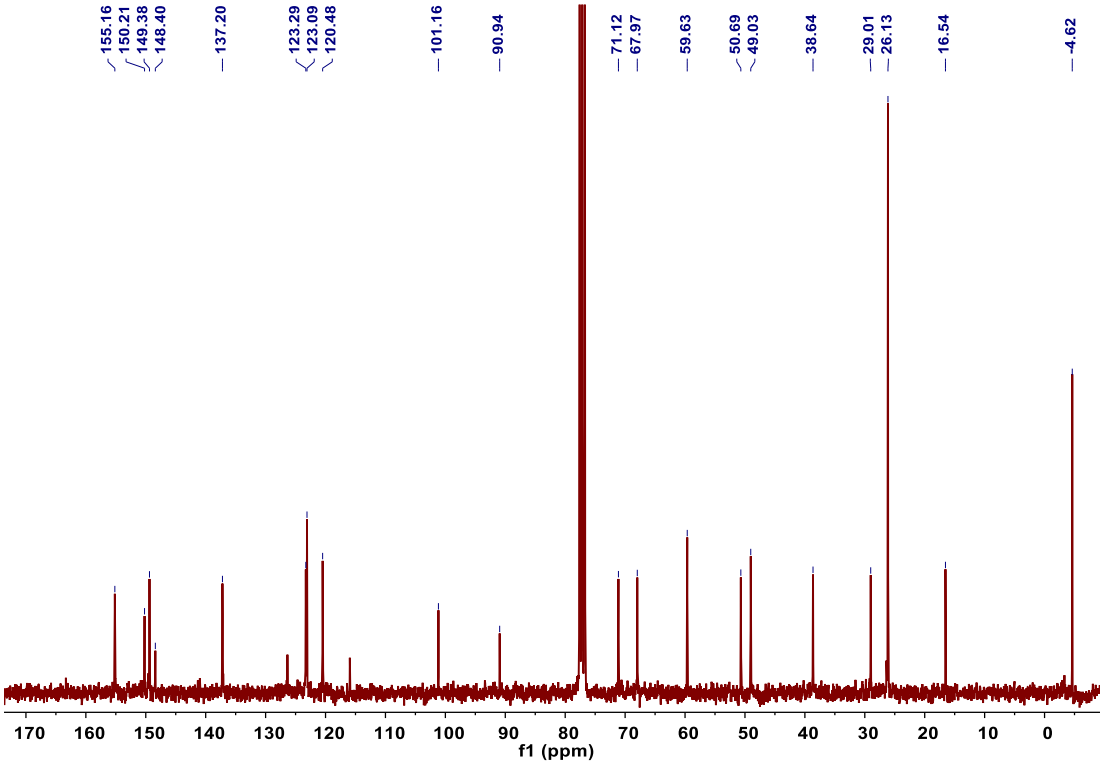


Figure S40. ^{13}C NMR of *rac*-**5b**.

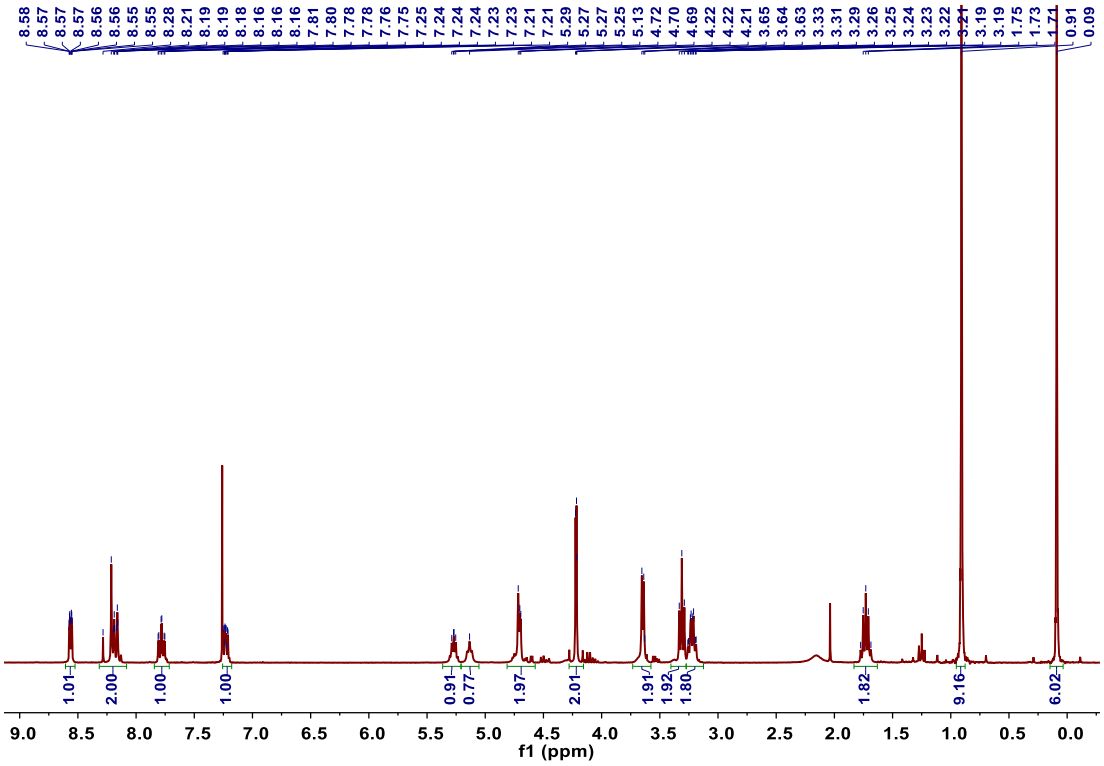


Figure S41. ^{1}H NMR of (*R*)-**5b**.

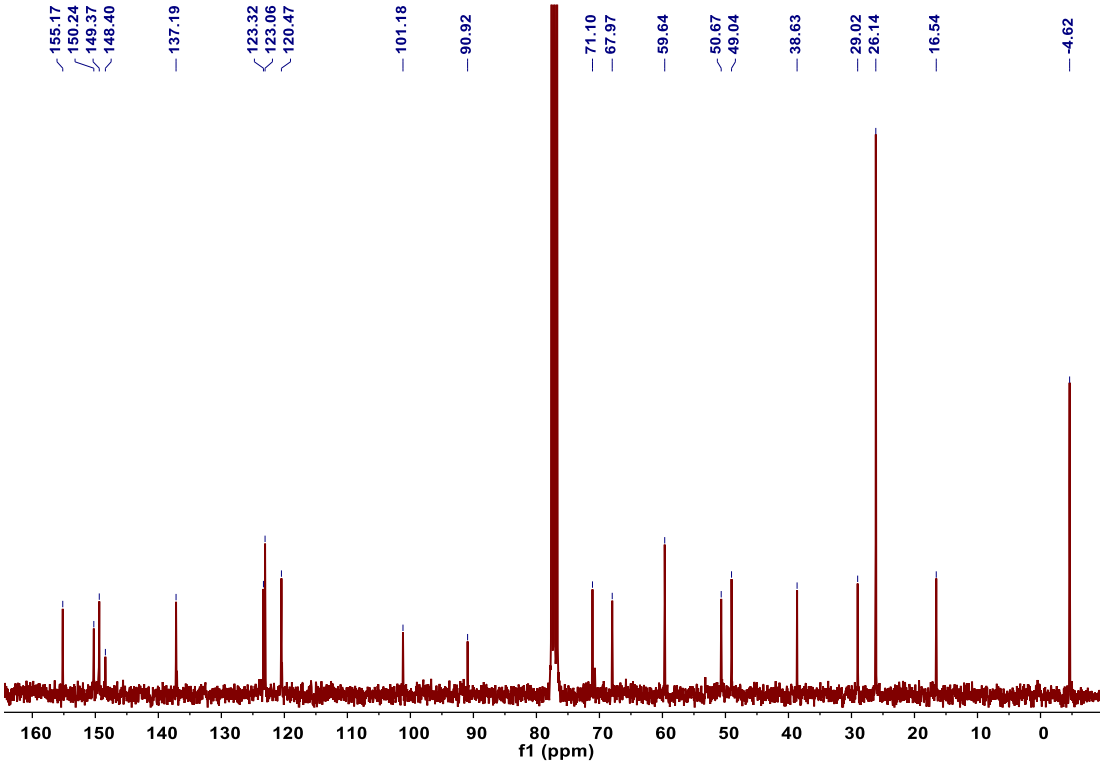


Figure S42. ^{13}C NMR of (*R*)-**5b**.

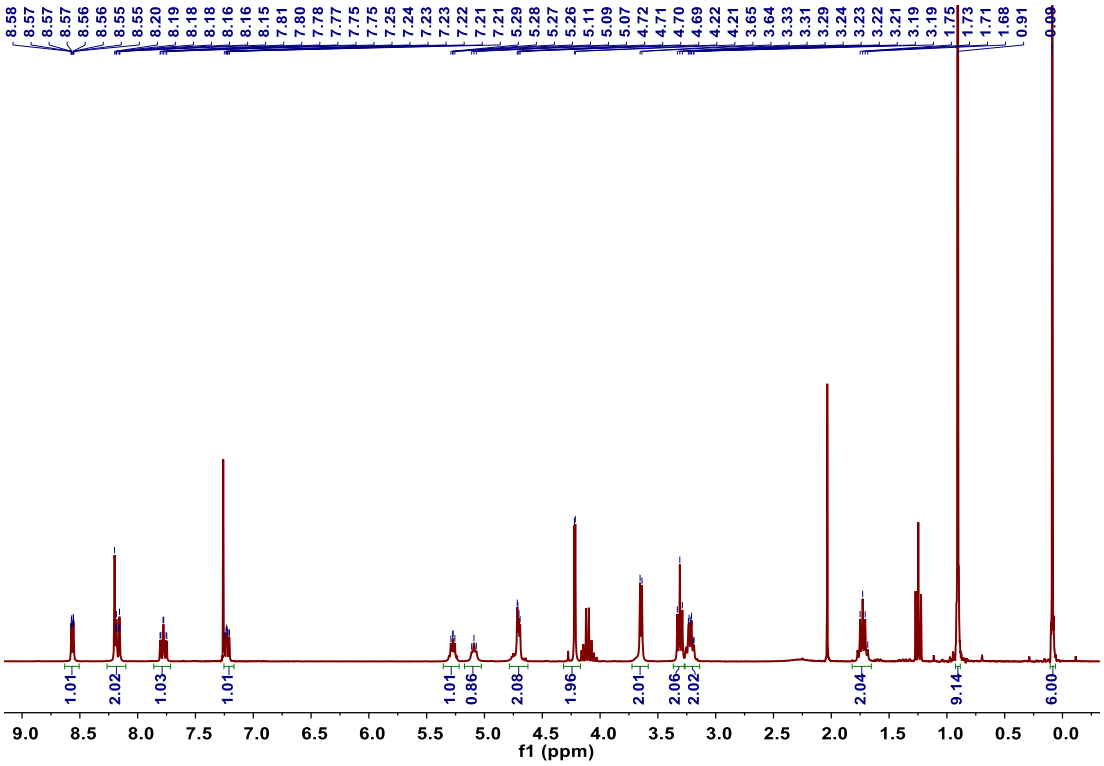


Figure S43. ^{1}H NMR of (*S*)-**5b**.

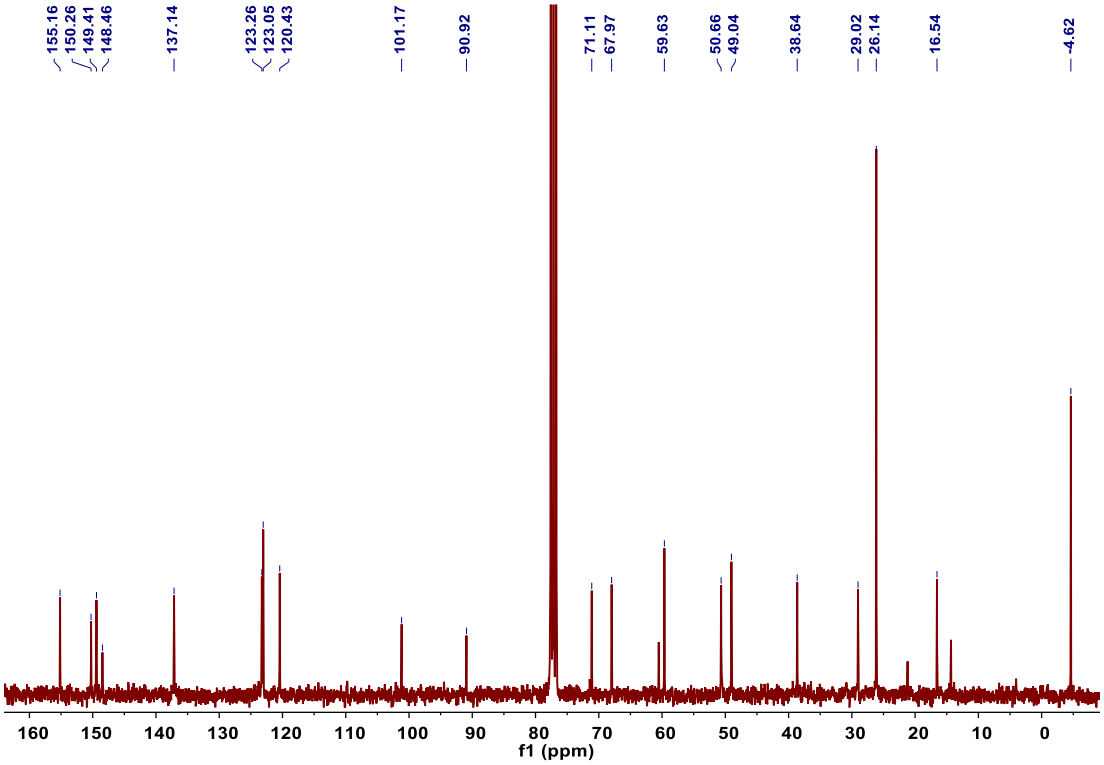


Figure S44. ^{13}C NMR of (*S*)-**5b**.

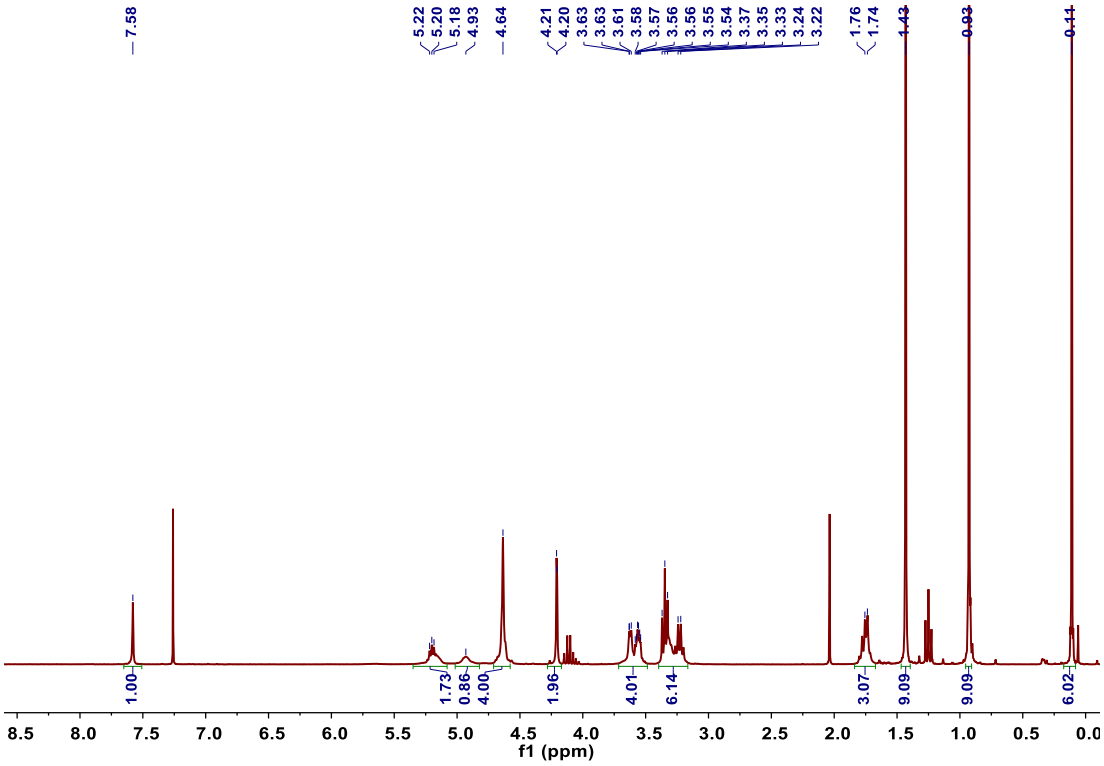


Figure S45. ^{1}H NMR of **5e**.

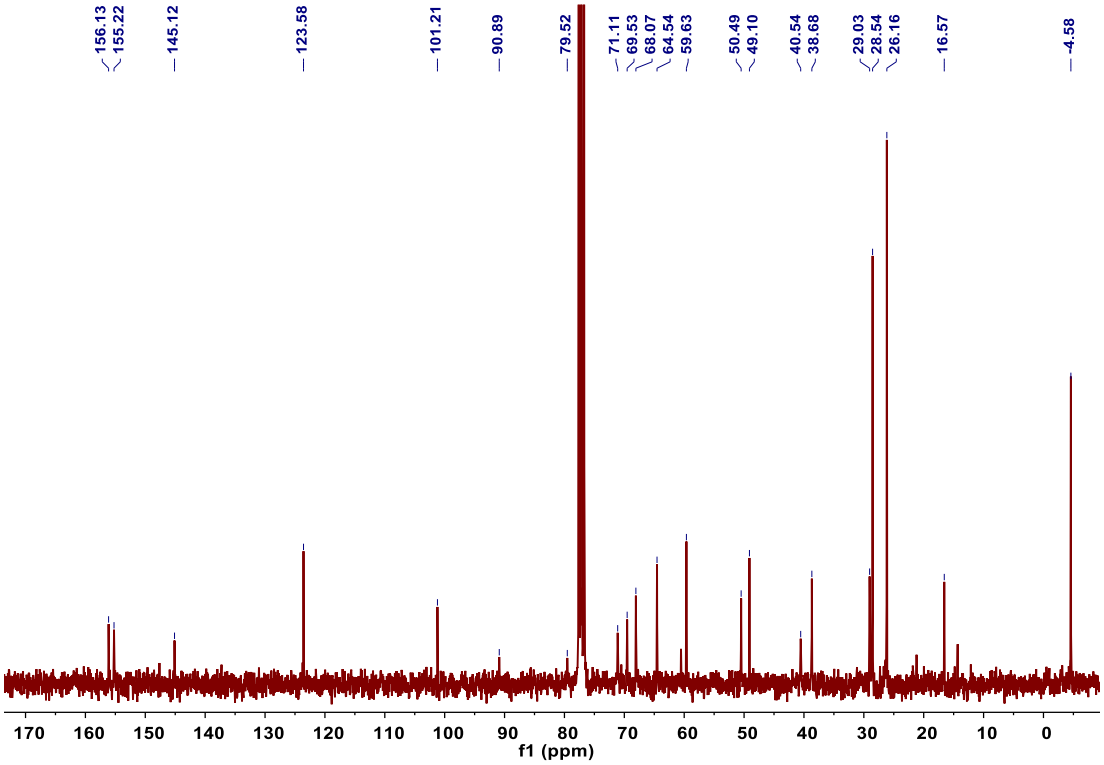


Figure S46. ^{13}C NMR of **5e**.

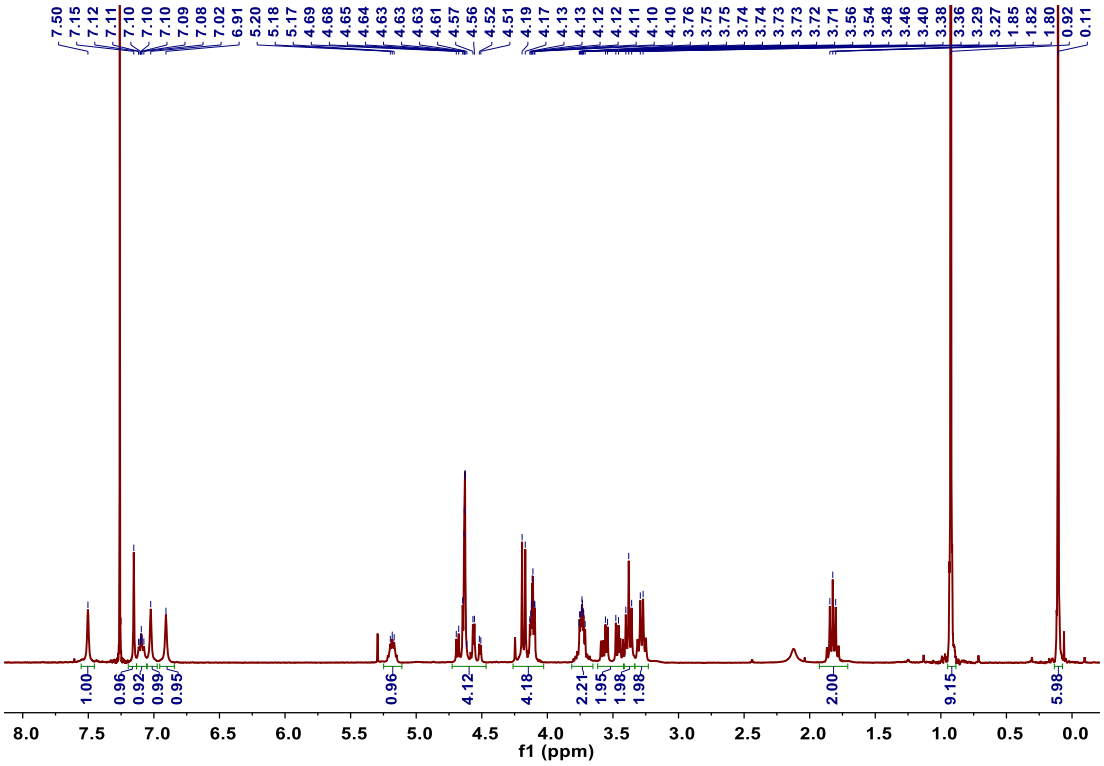


Figure S47. ^{1}H NMR of **5f**.

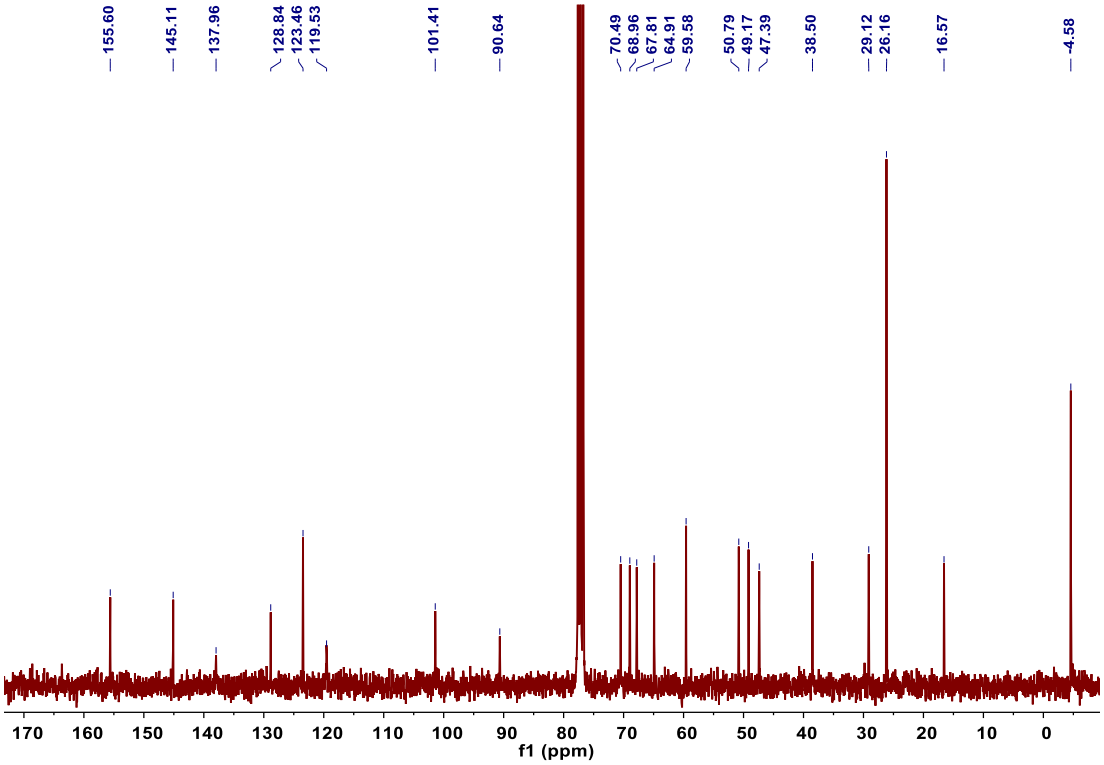


Figure S48. ^{13}C NMR of **5f**.

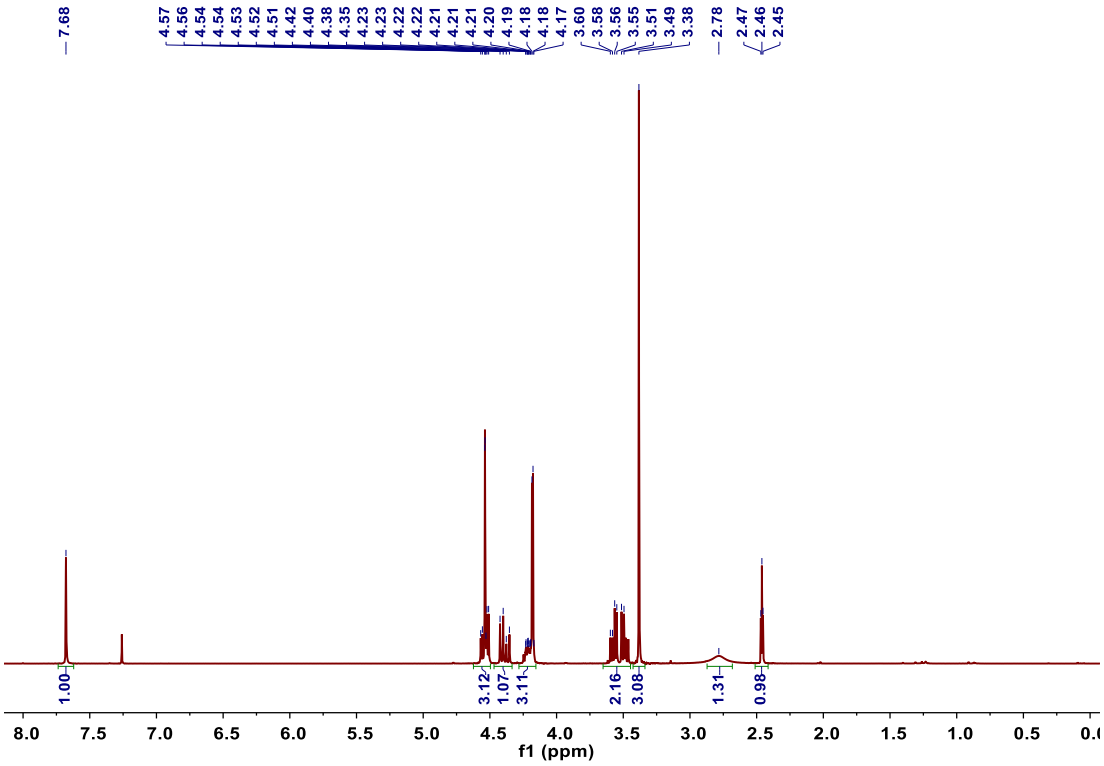


Figure S49. ^{1}H NMR of *rac*-**6c**.

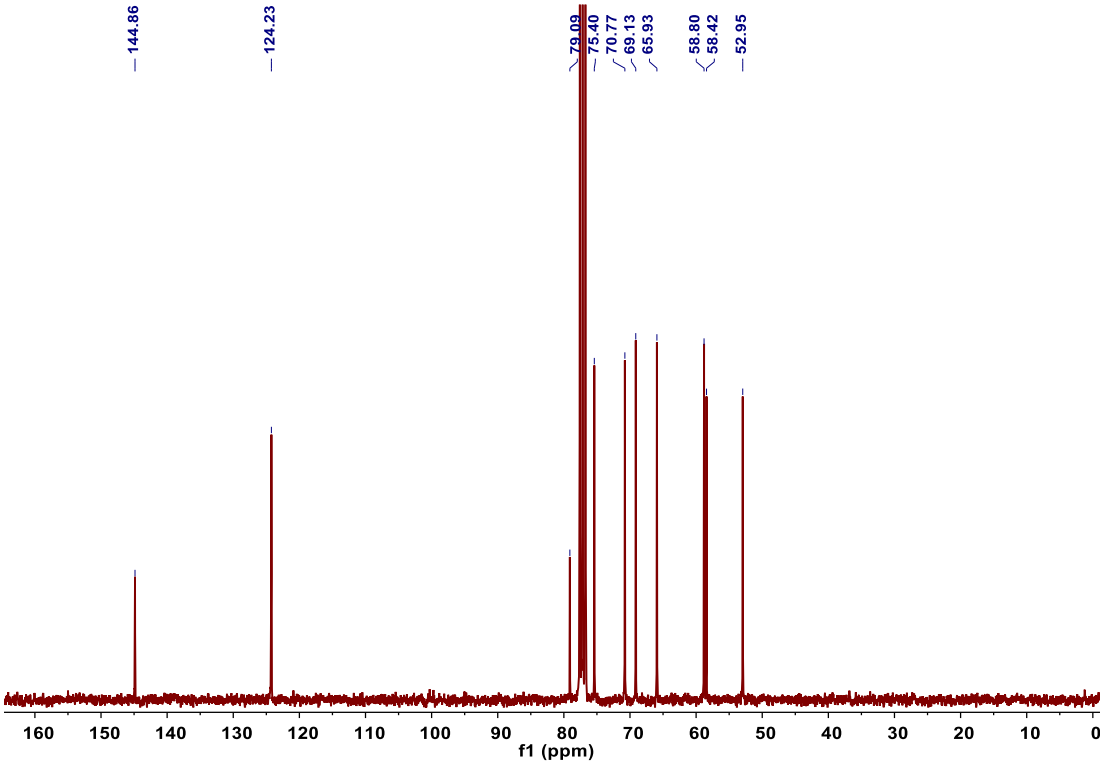


Figure S50. ^{13}C NMR of *rac*-**6c**.

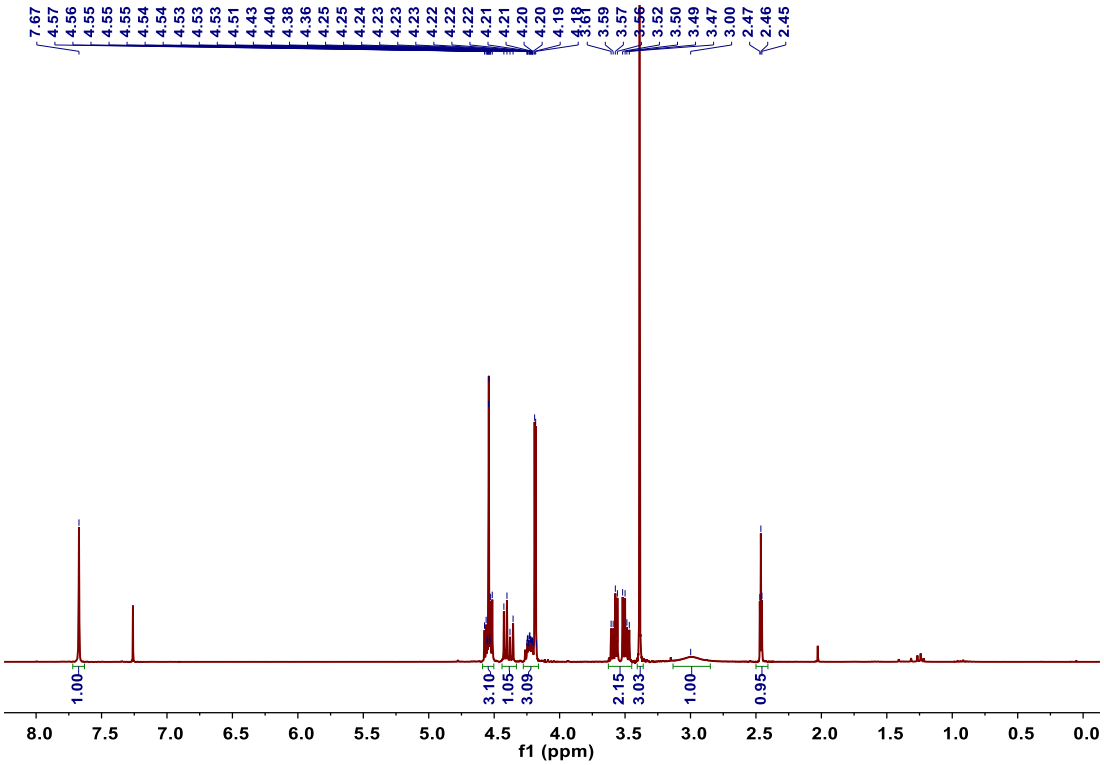


Figure S51. ^{1}H NMR of (*R*)-**6c**.

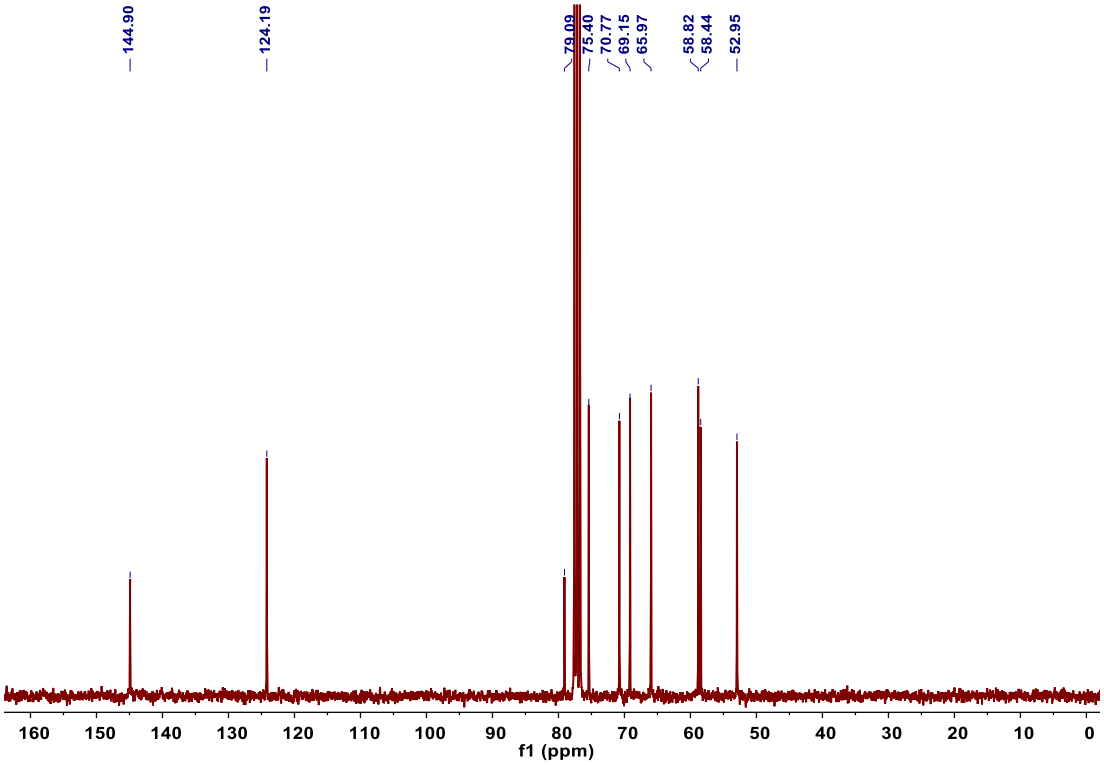


Figure S52. ^{13}C NMR of (*R*)-**6c**.

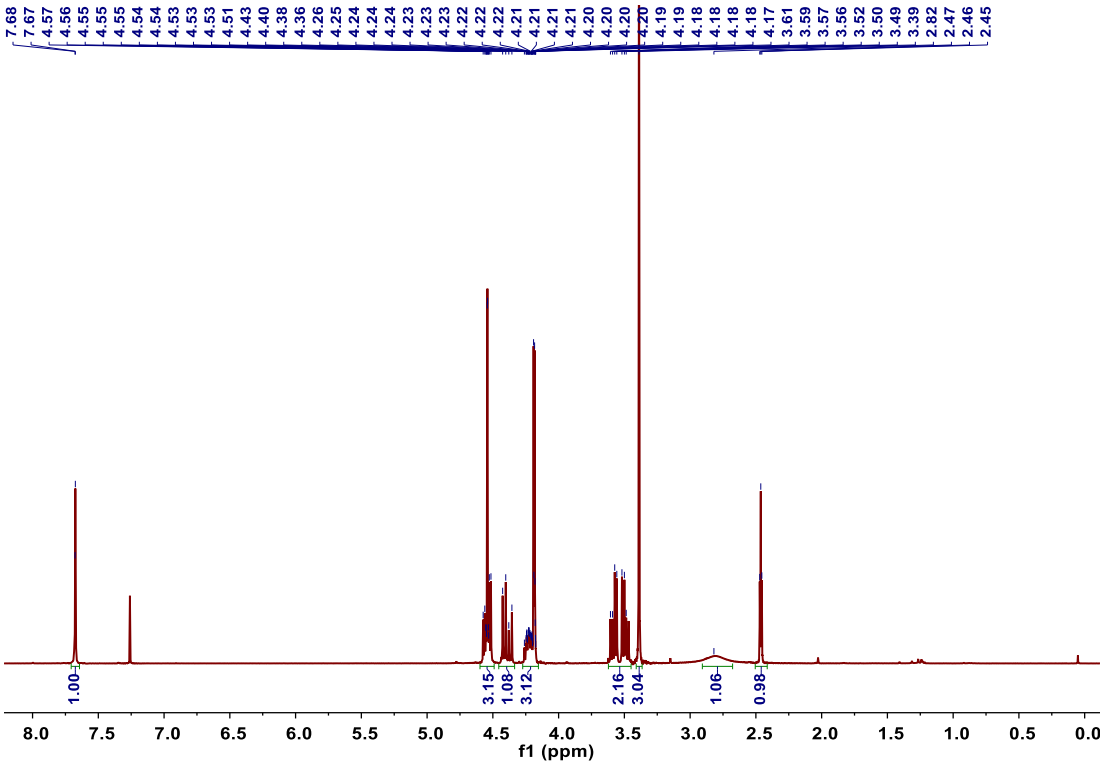


Figure S53. ^{1}H NMR of (*S*)-**6c**.

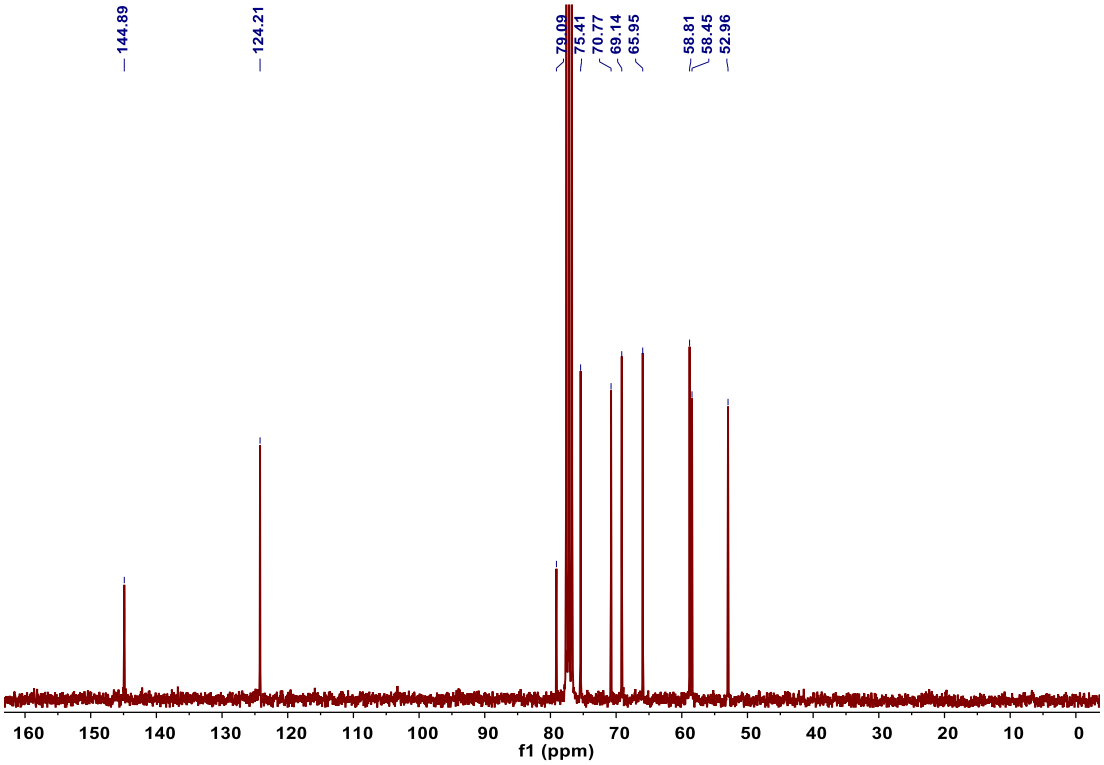


Figure S54. ^{13}C NMR of (*S*)-**6c**.

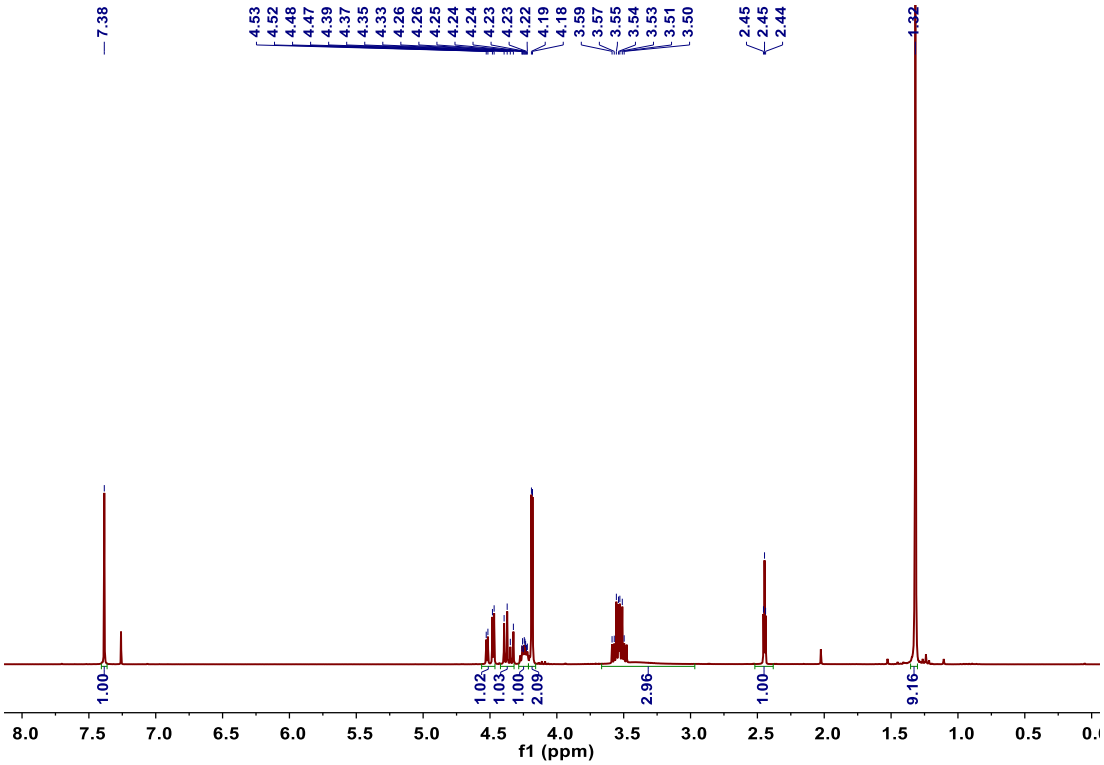


Figure S55. ^{1}H NMR of *rac*-**6d**.

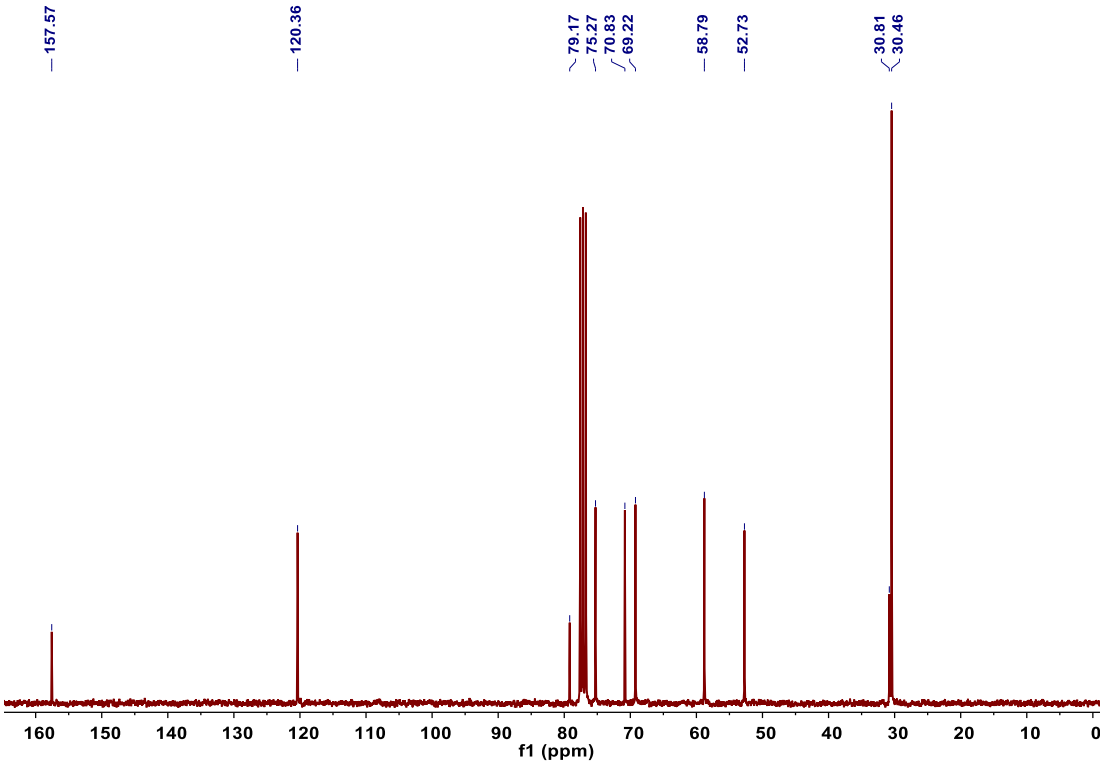


Figure S56. ^{13}C NMR of *rac*-**6d**.

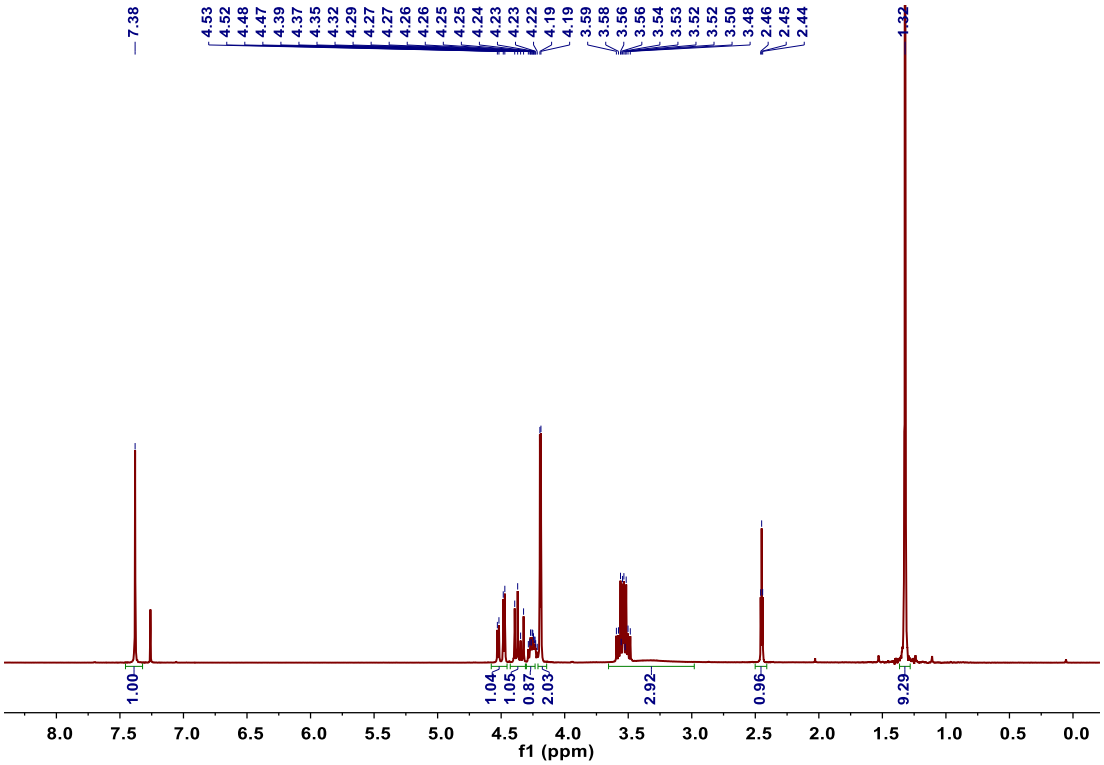


Figure S57. ^{1}H NMR of (*R*)-**6d**.

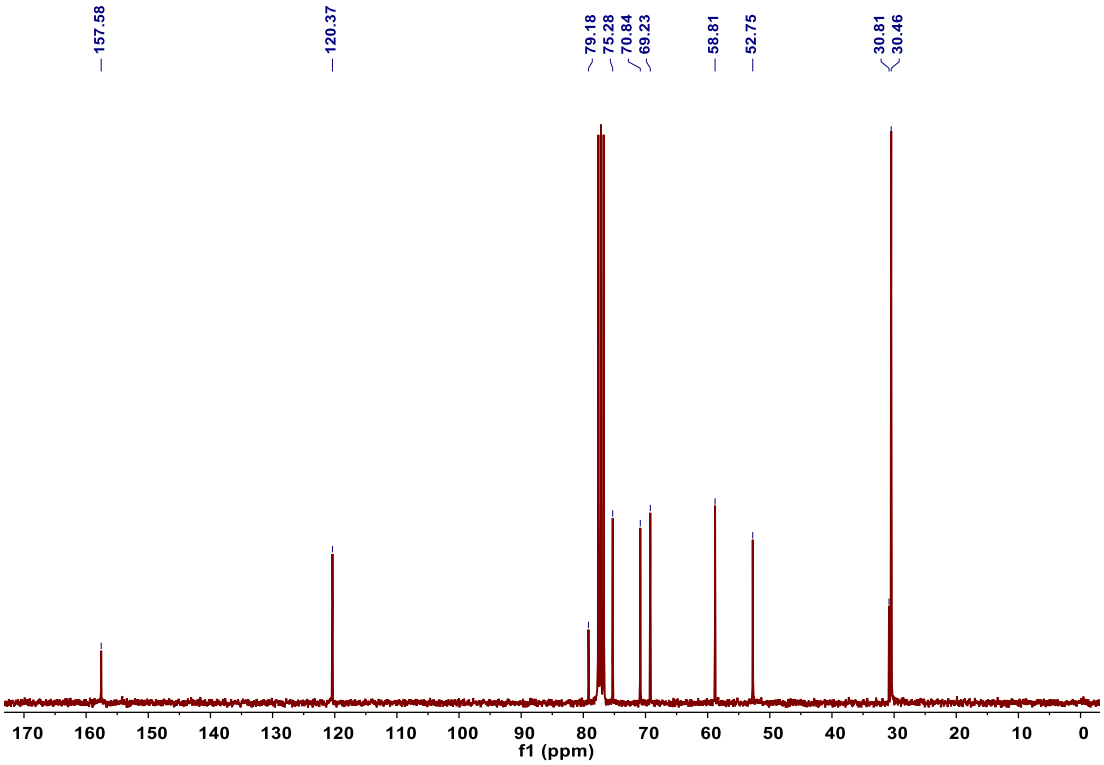


Figure S58. ^{13}C NMR of (*R*)-**6d**.

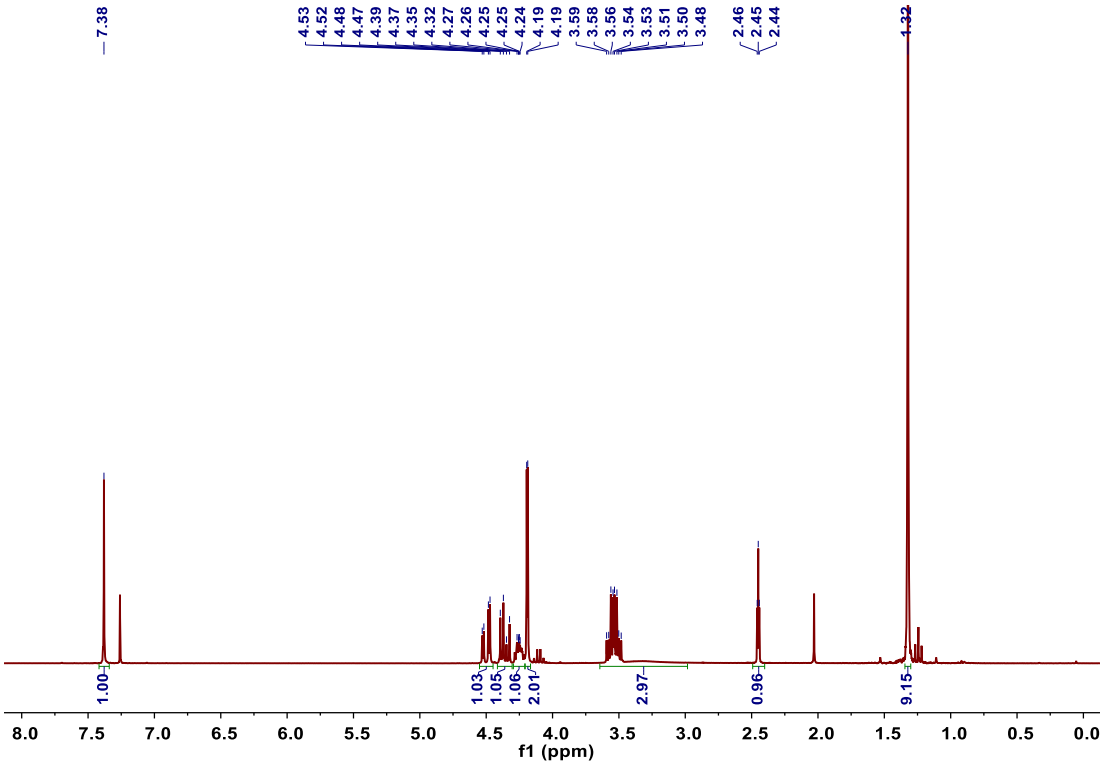


Figure S59. ^{1}H NMR of (*S*)-**6d**.

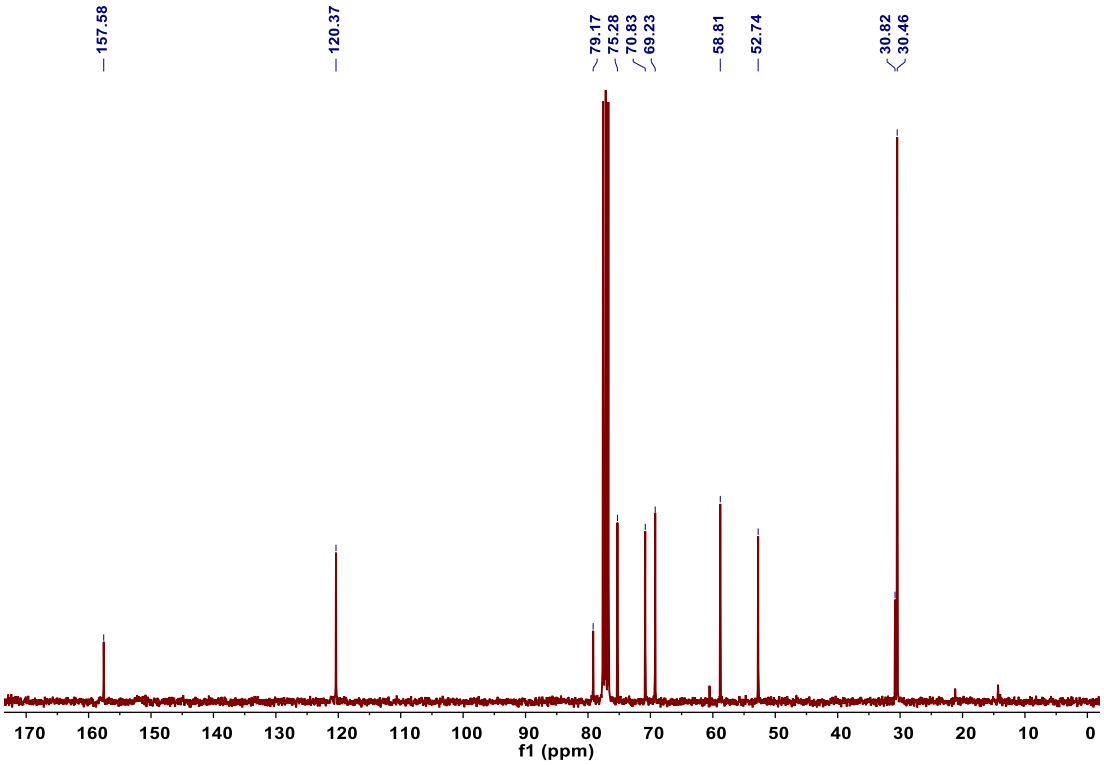


Figure S60. ^{13}C NMR of (*S*)-**6d**.

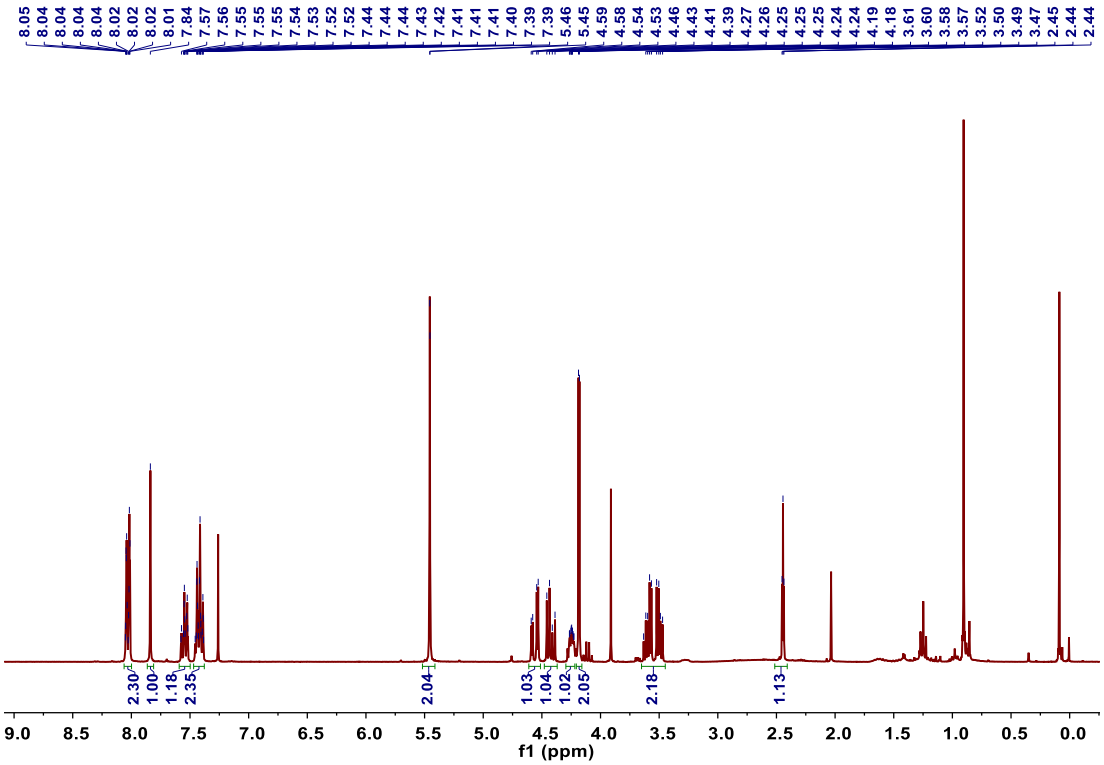


Figure S61. ^{1}H NMR of **6g**.

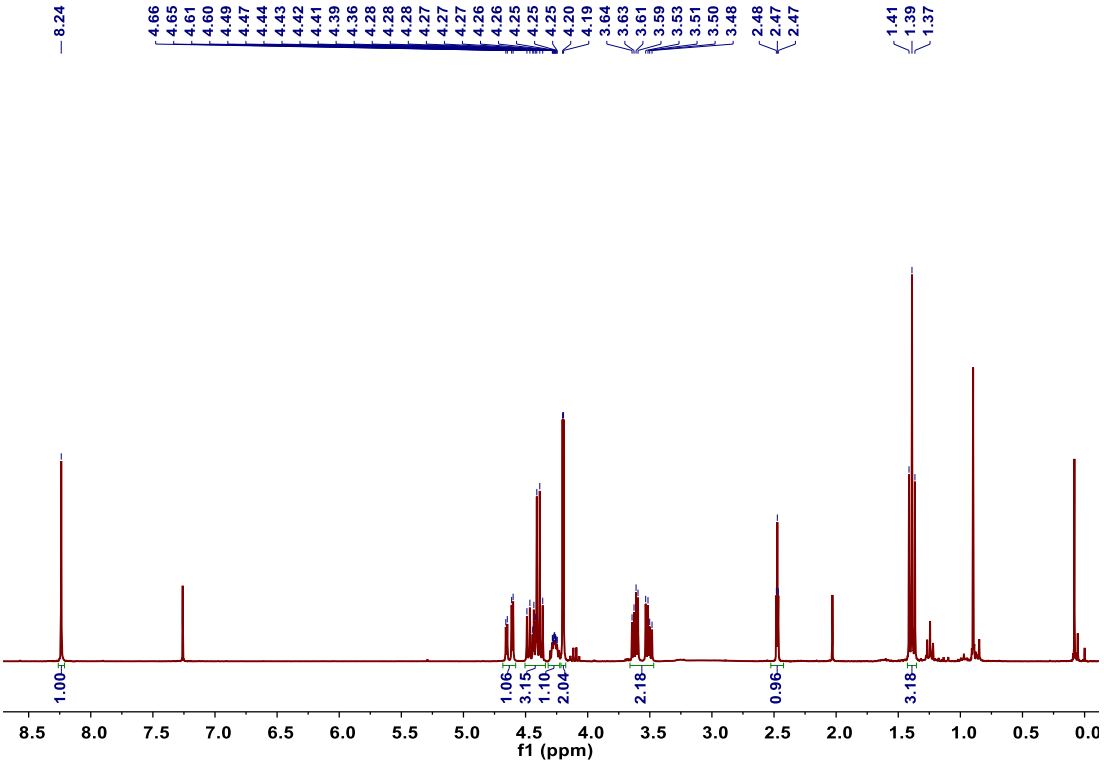


Figure S62. ^{1}H NMR of **6h**.

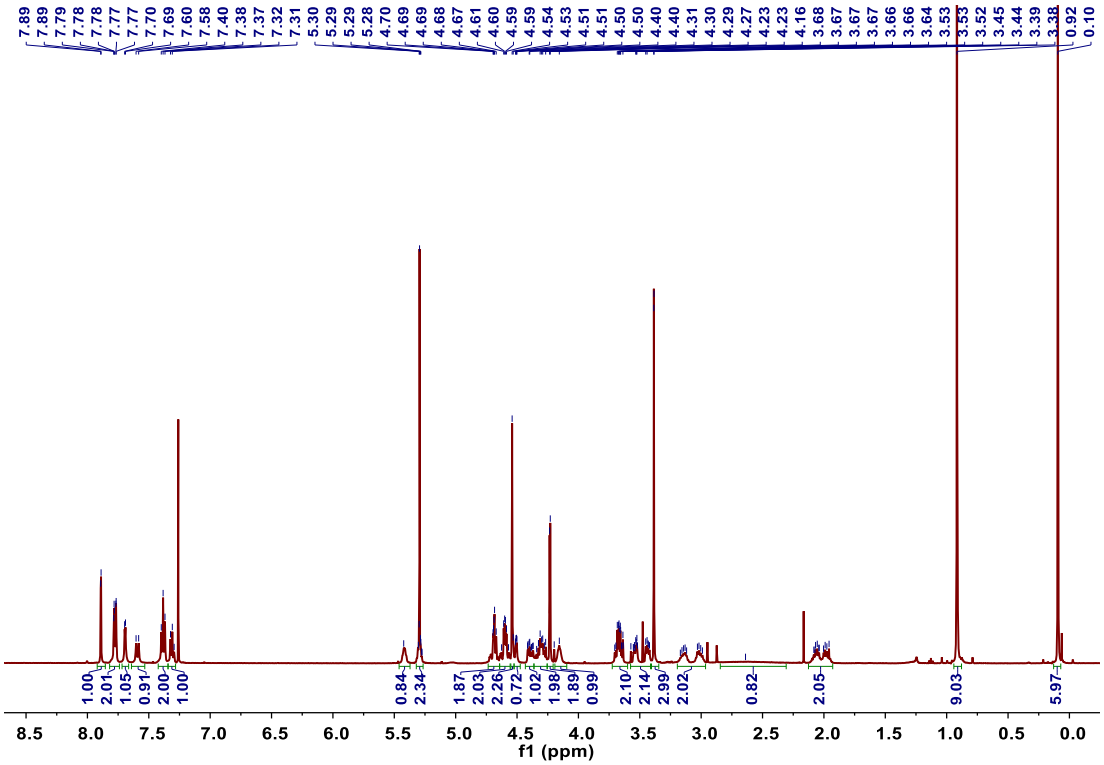


Figure S63. ^{1}H NMR of *rac*-**FE**.

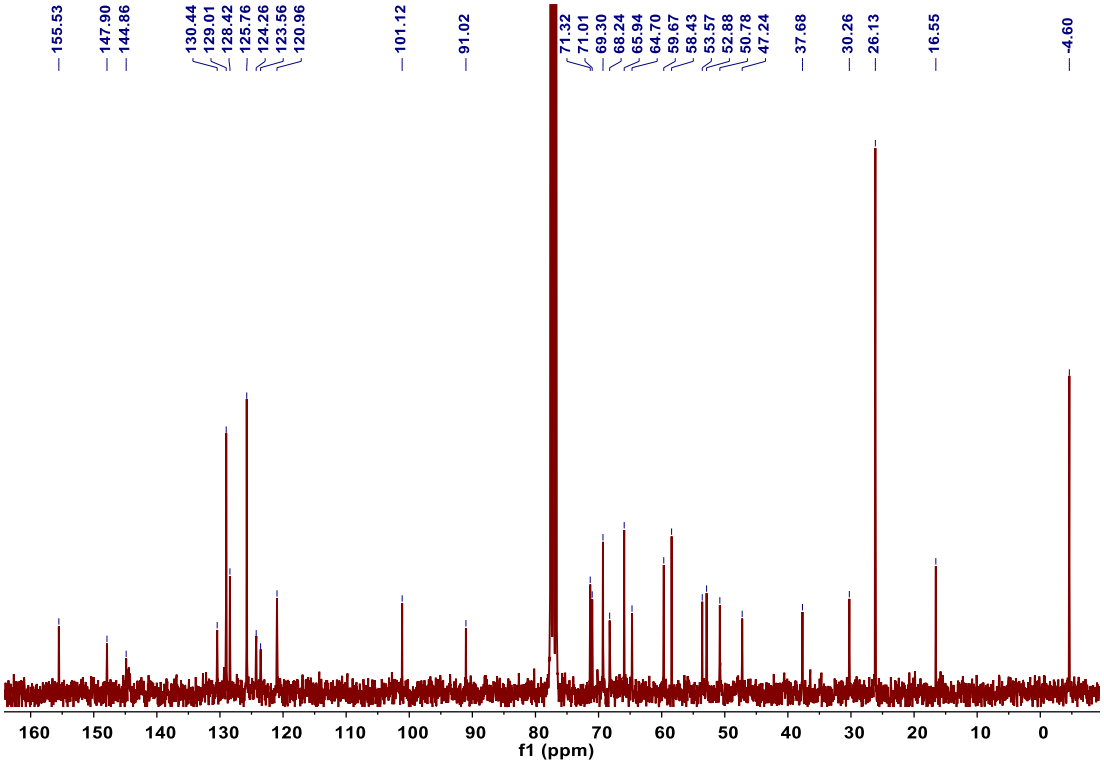


Figure S64. ^{13}C NMR of *rac*-**FE**.

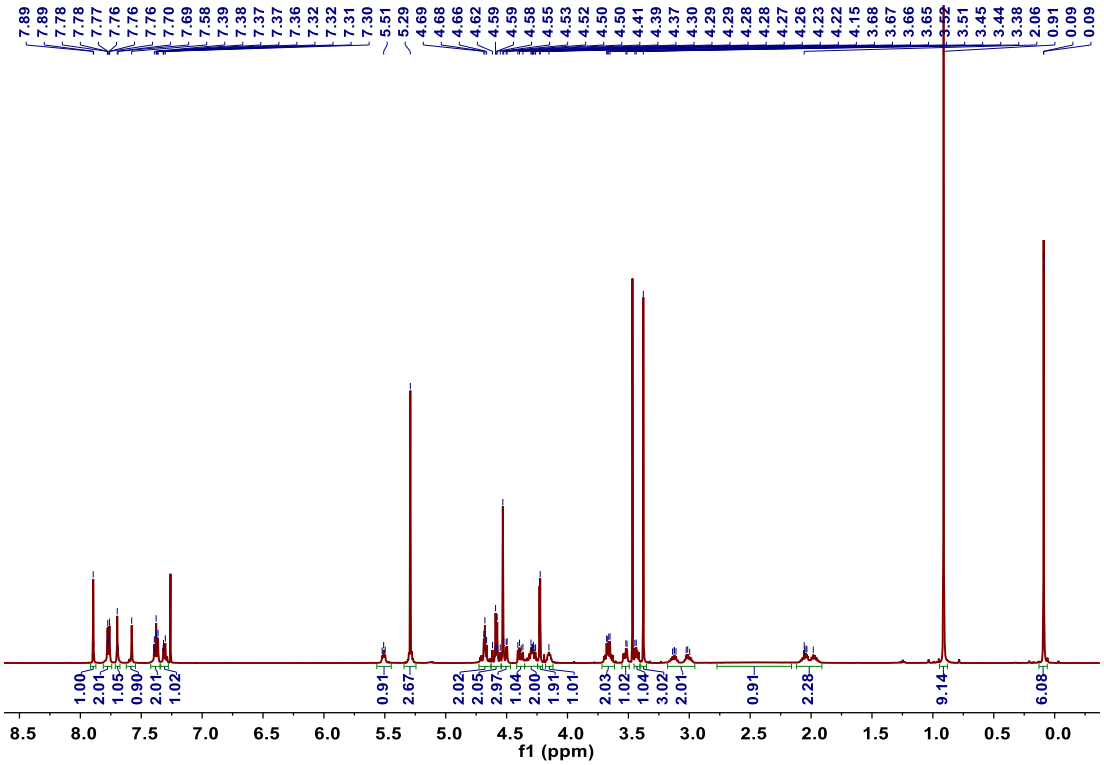


Figure S65. ^{1}H NMR of (*R*,*R*)-**FE**.

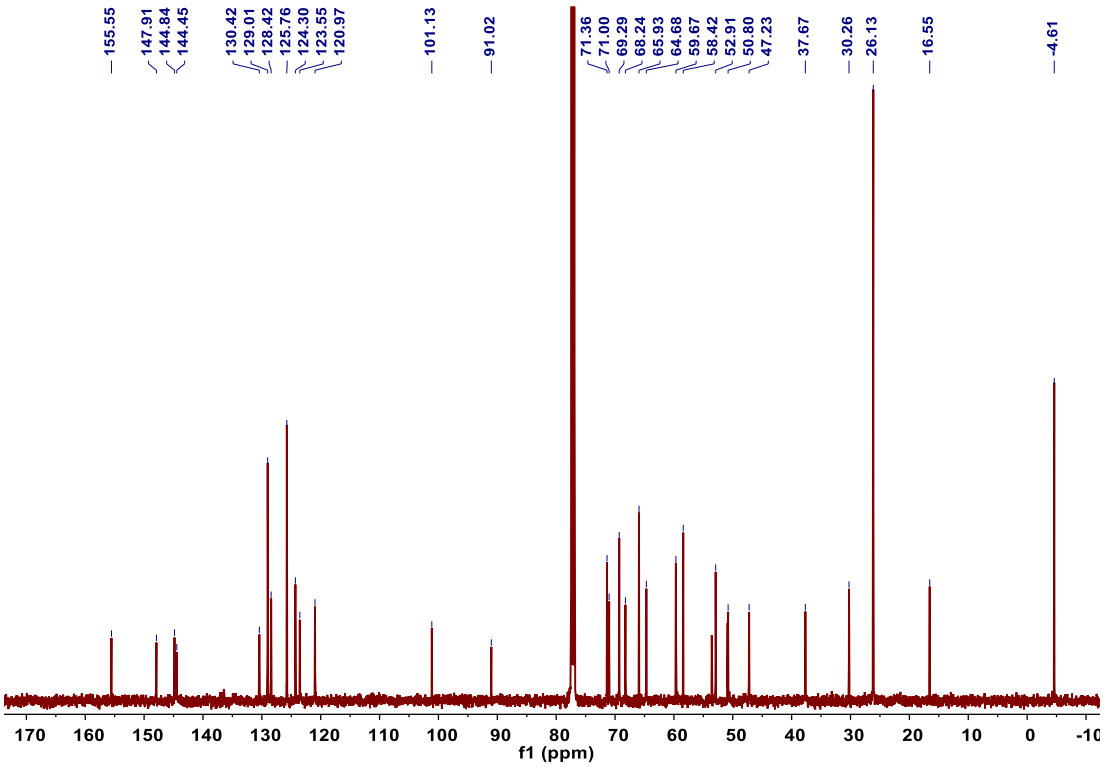


Figure S66. ^{13}C NMR of (*R*,*R*)-**FE**.

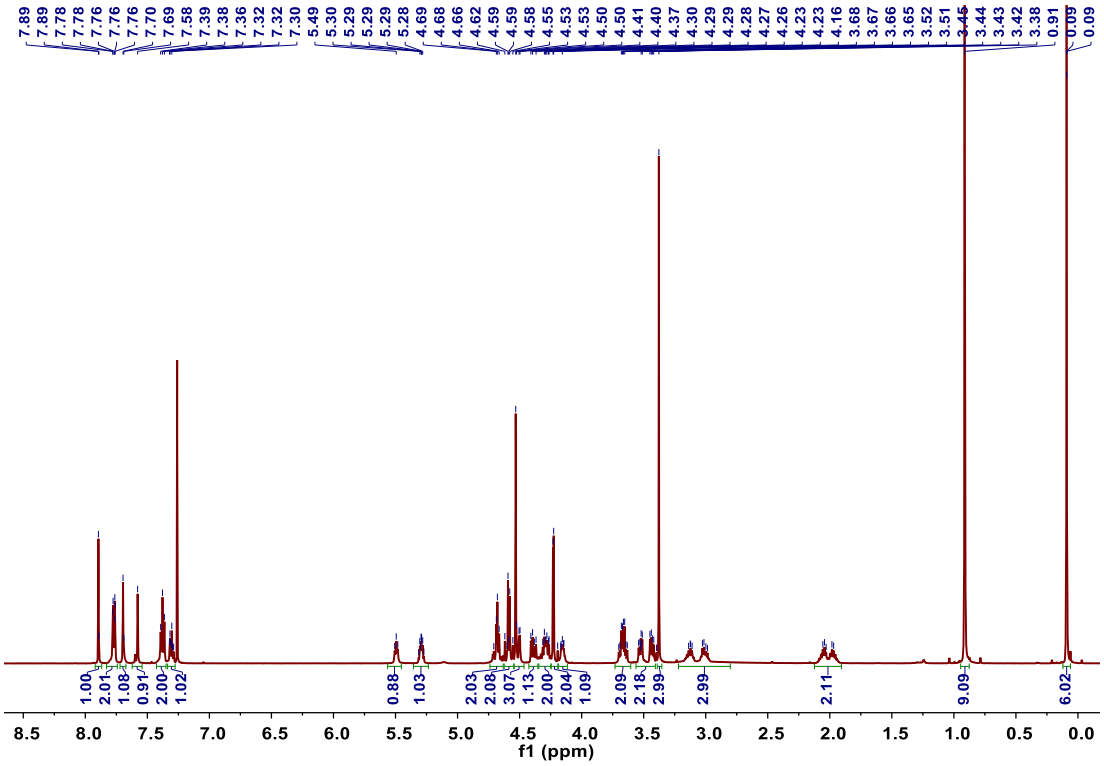


Figure S67. ^{1}H NMR of (*S*,*S*)-**FE**.

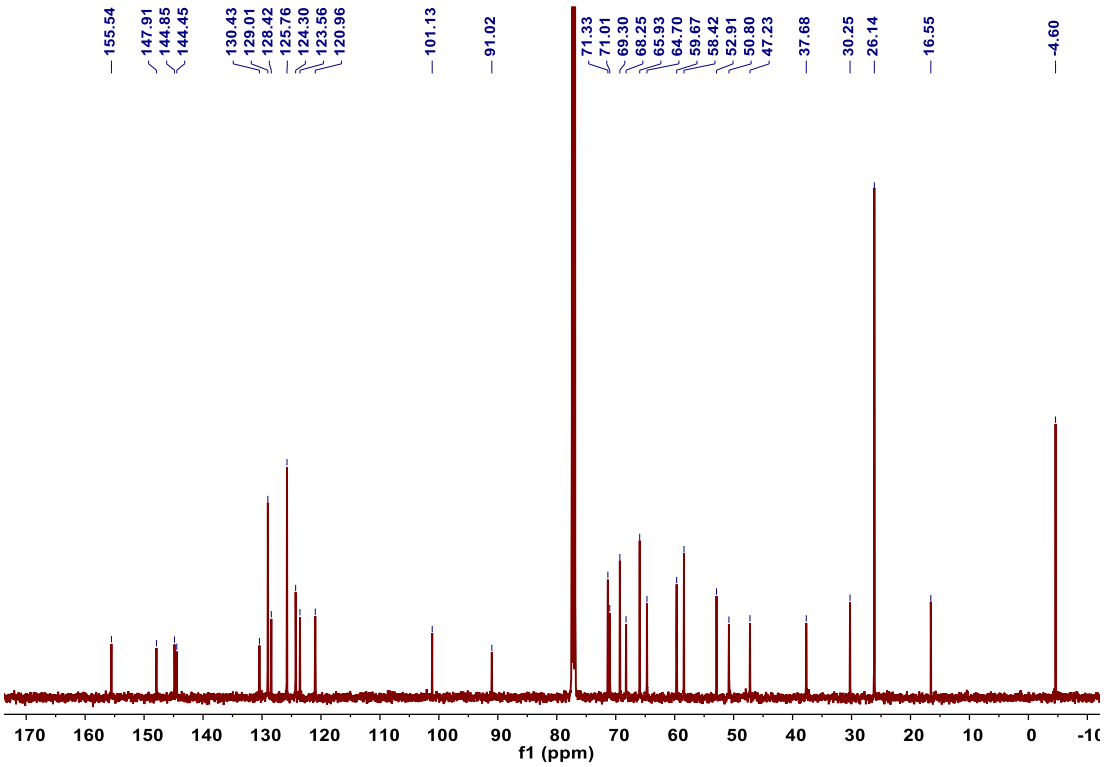


Figure S68. ^{13}C NMR of (*S*,*S*)-**FE**.

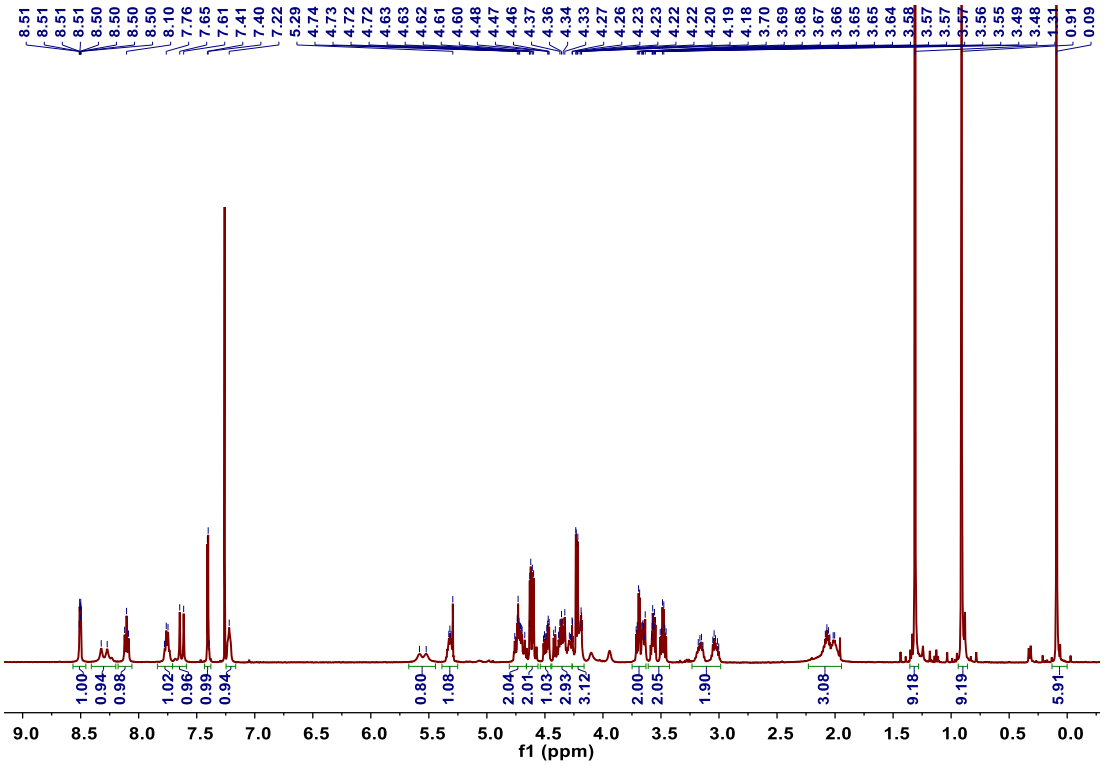


Figure S69. ^{1}H NMR of *rac*-**PB**.

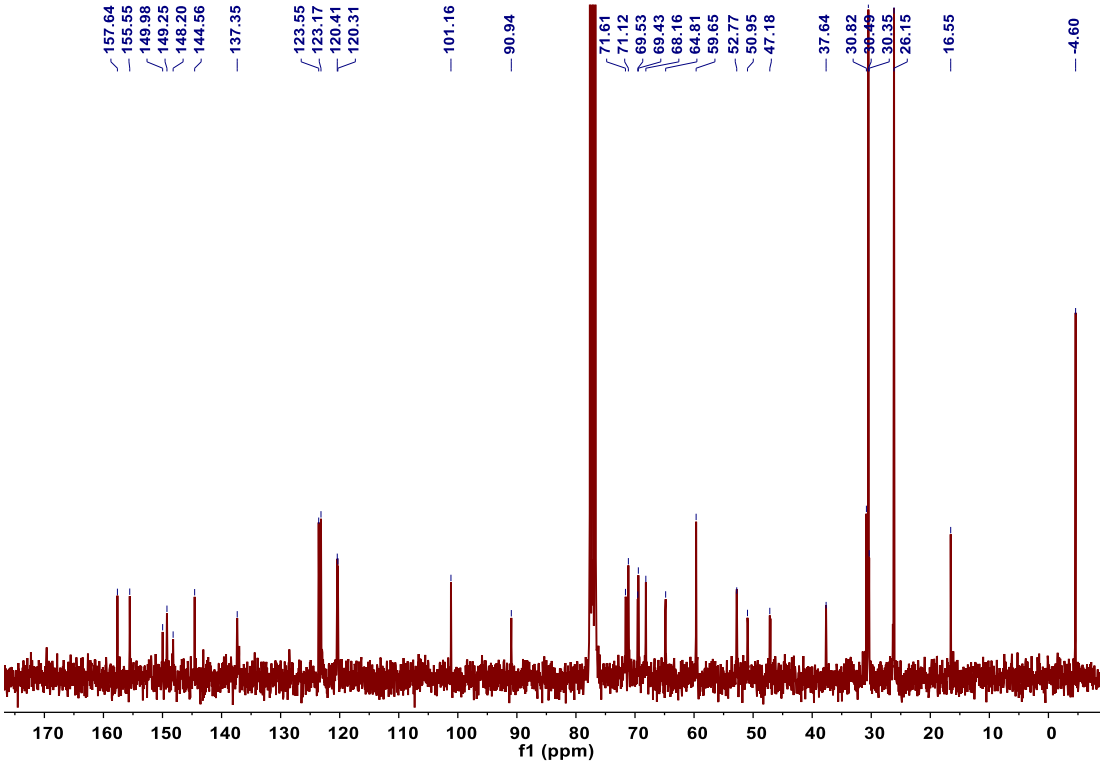


Figure S70. ^{13}C NMR of *rac*-**PB**.

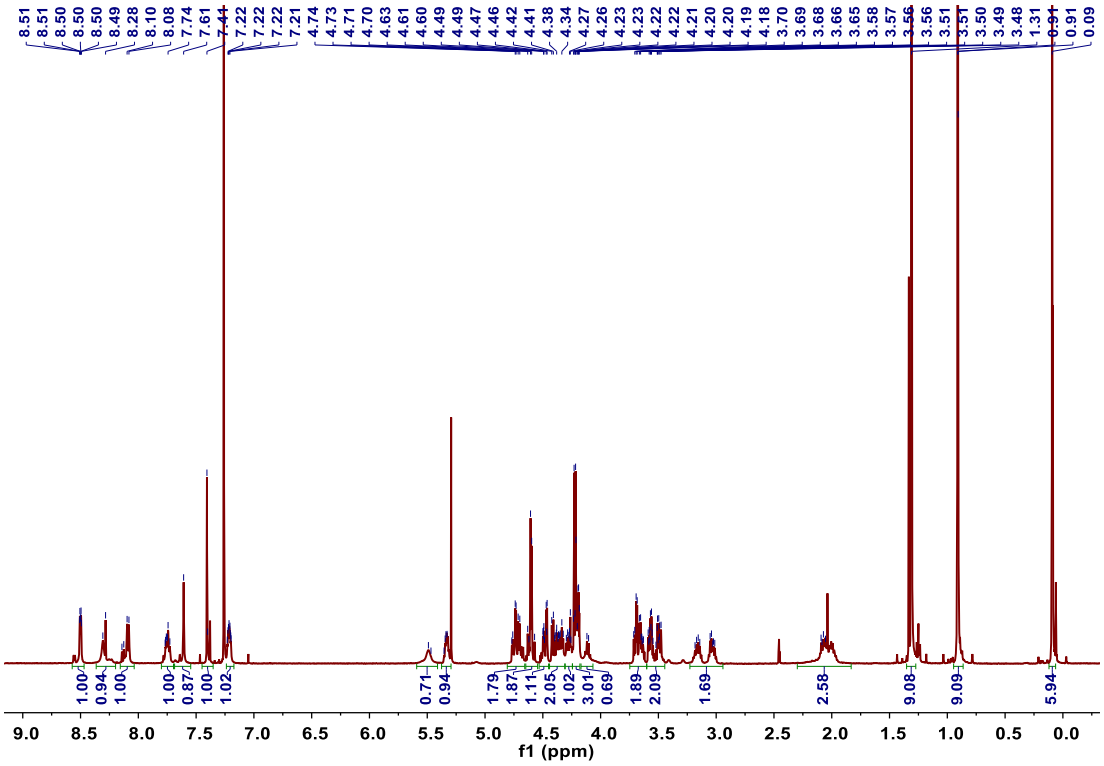


Figure S71. ^{1}H NMR of (*R*,*R*)-**PB**.

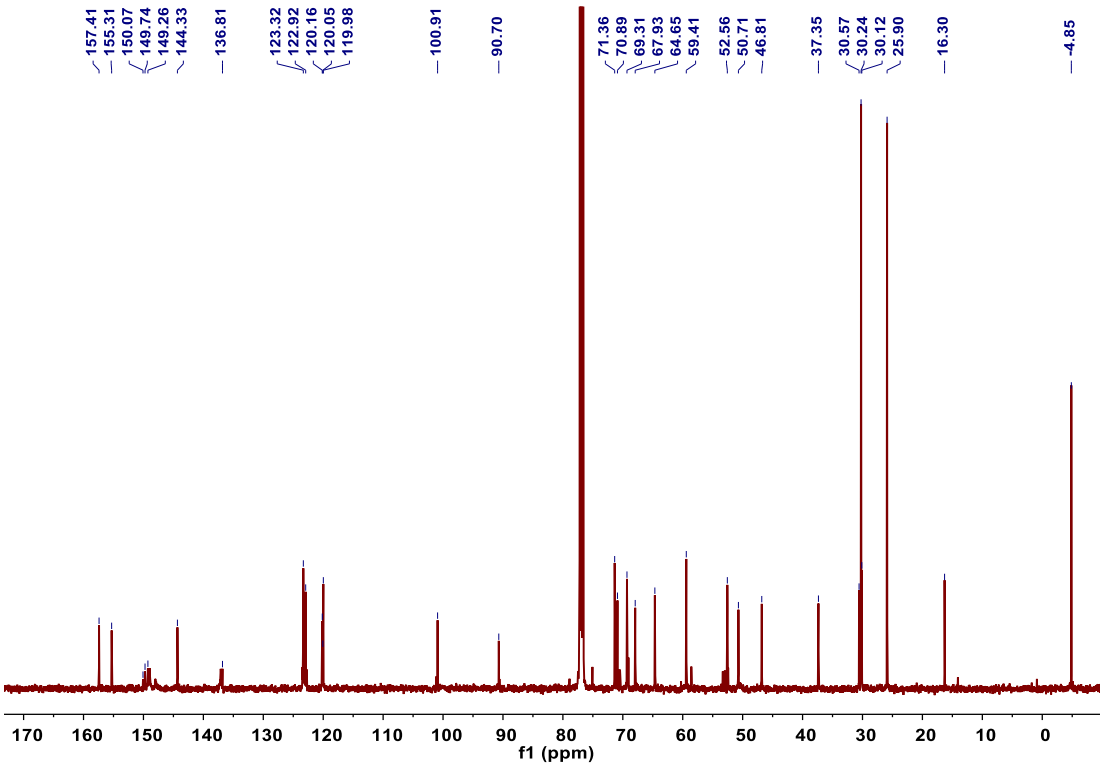


Figure S72. ^{13}C NMR of (*R*,*R*)-**PB**.

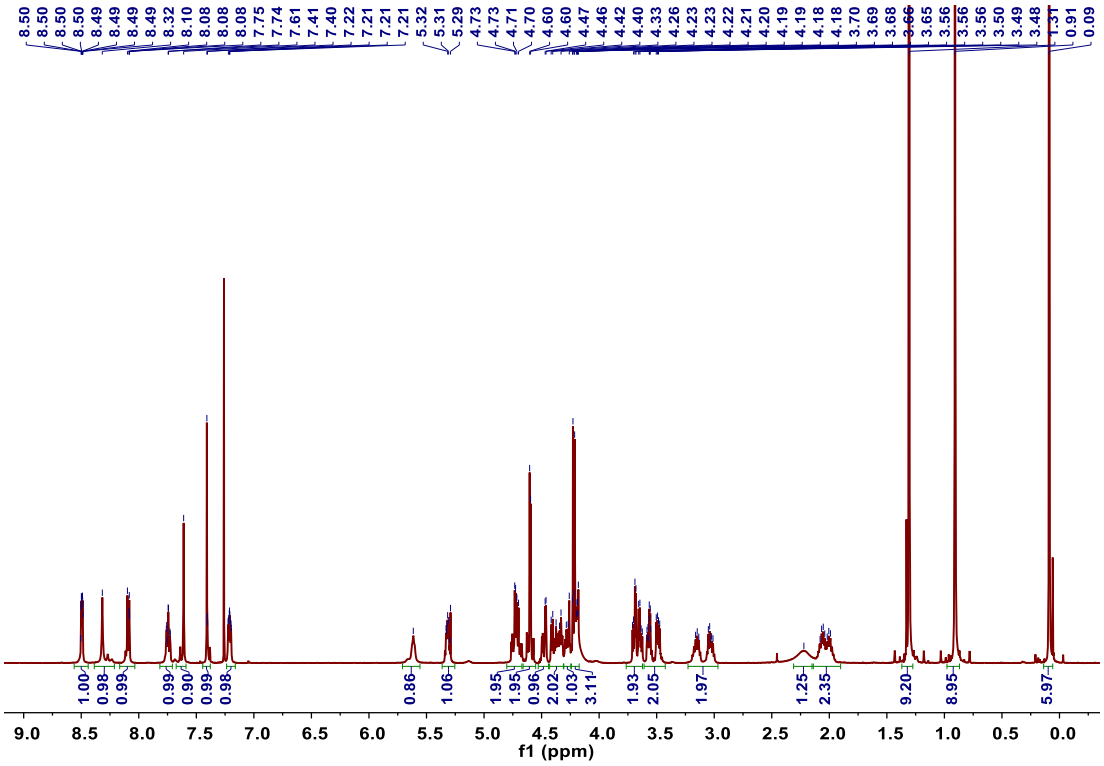


Figure S73. ^{1}H NMR of (*S*,*S*)-**PB**.

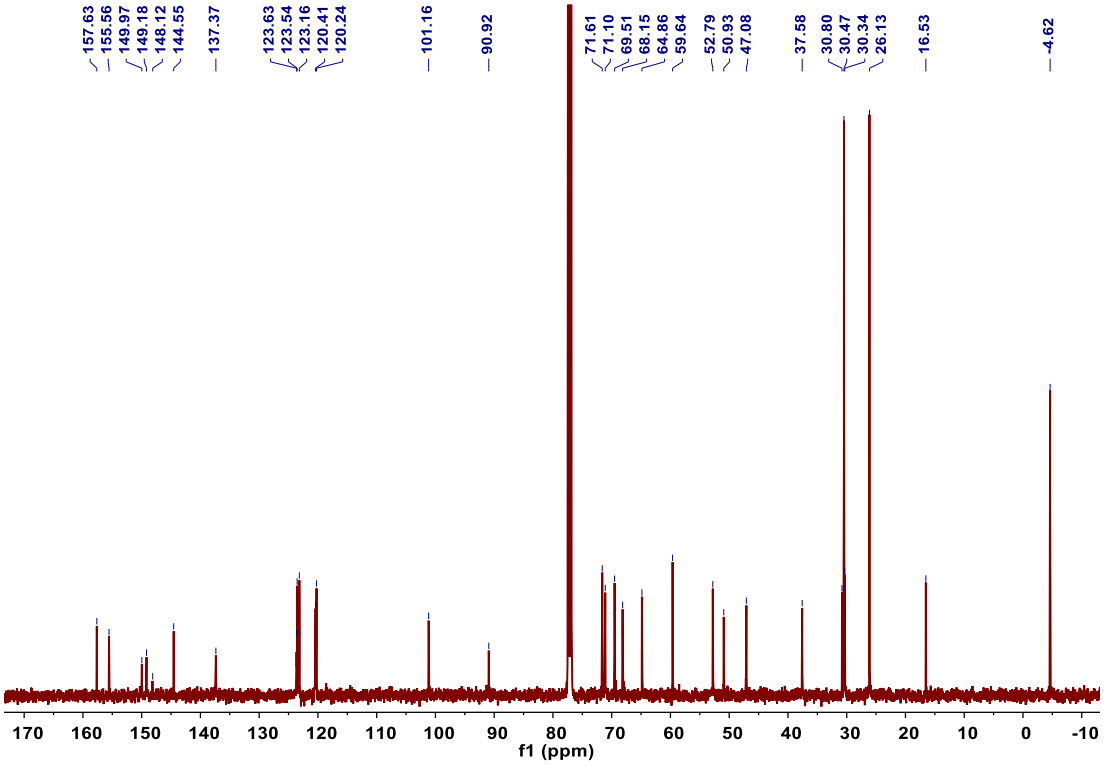


Figure S74. ^{13}C NMR of (*S*,*S*)-**PB**.

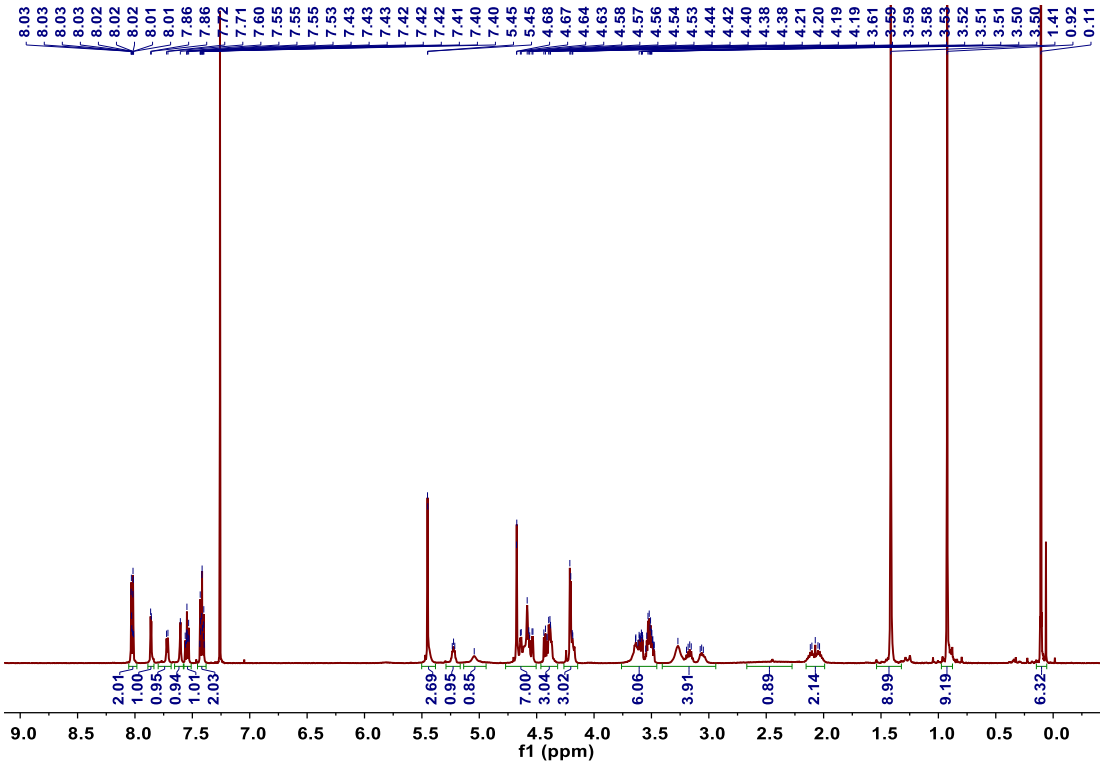


Figure S75. ^{1}H NMR of **A(Boc)O(Bz)**.

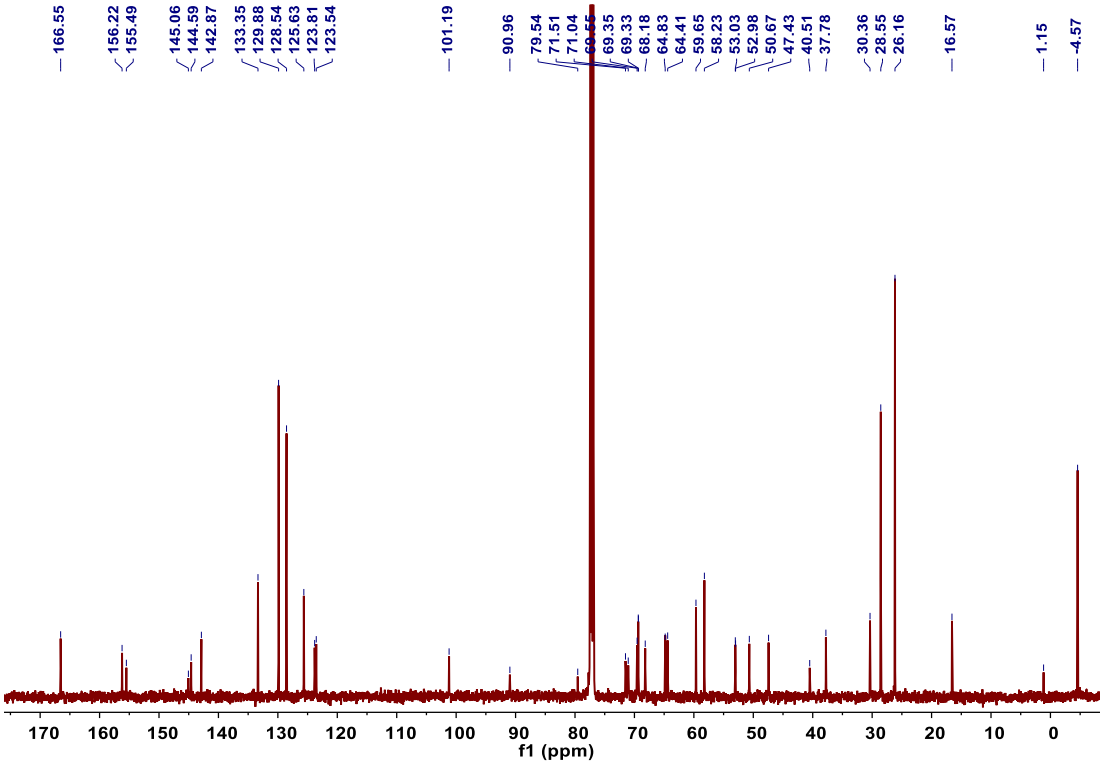


Figure S76. ^{13}C NMR of **A(Boc)O(Bz)**.

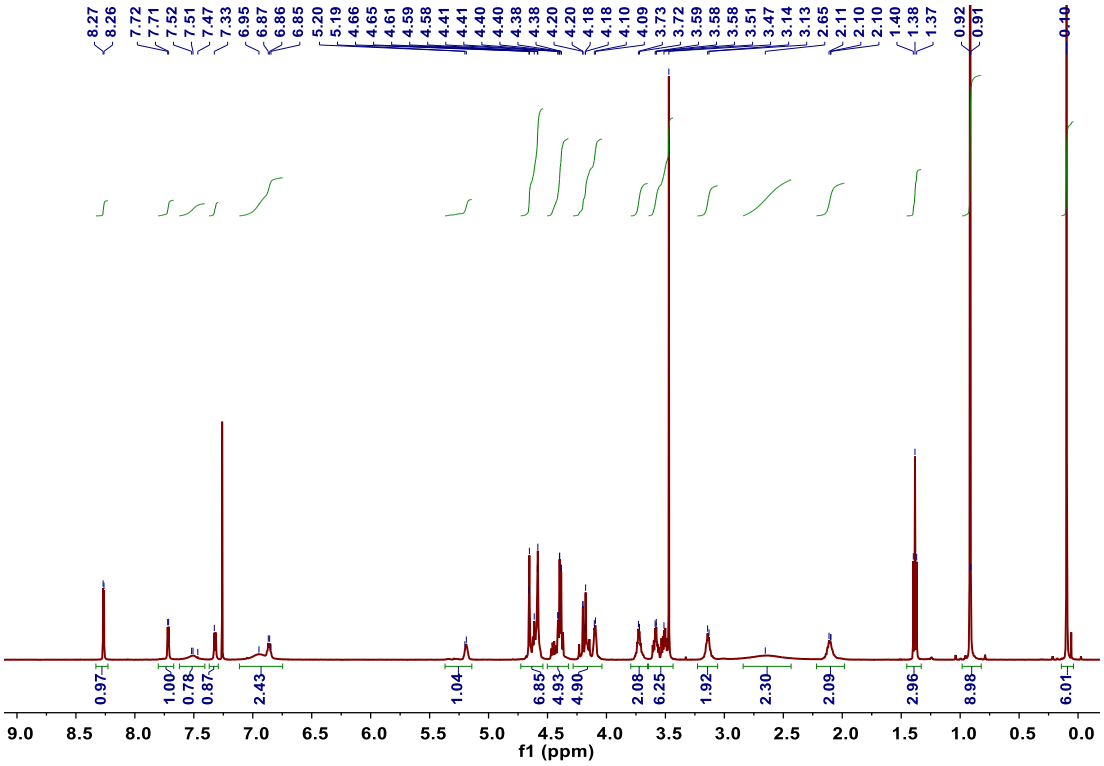


Figure S77. ^{1}H NMR of **IK(Et)**.

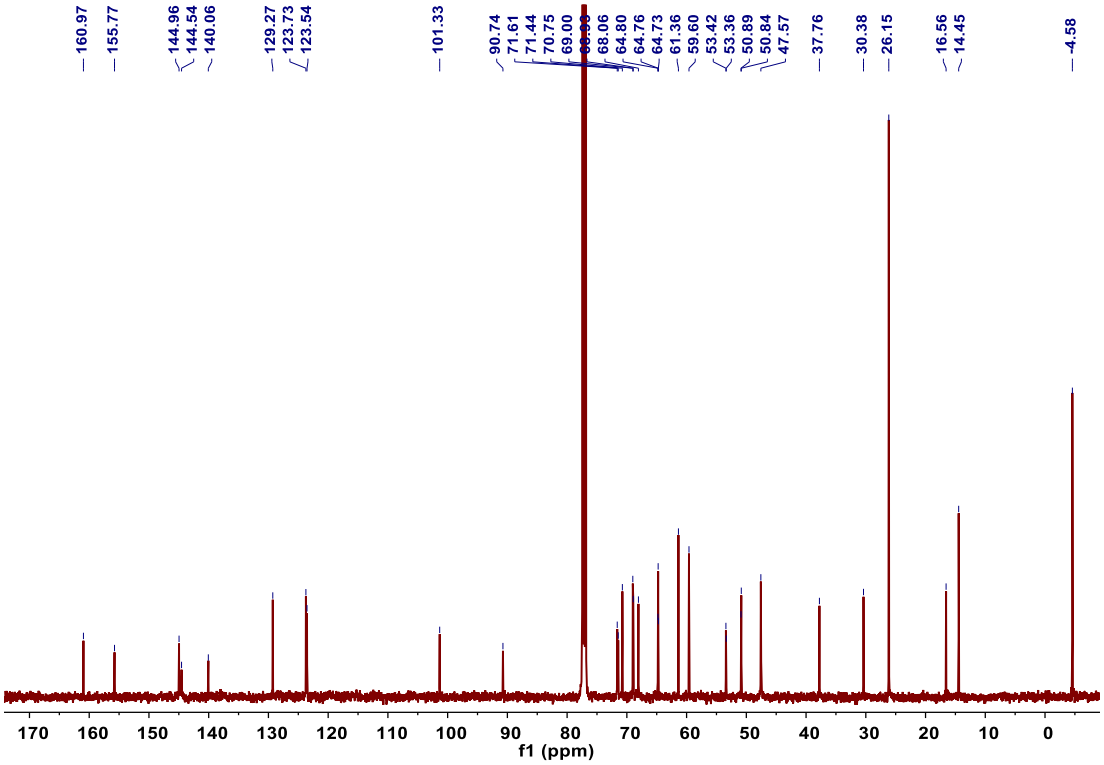


Figure S78. ^{13}C NMR of **IK(Et)**.

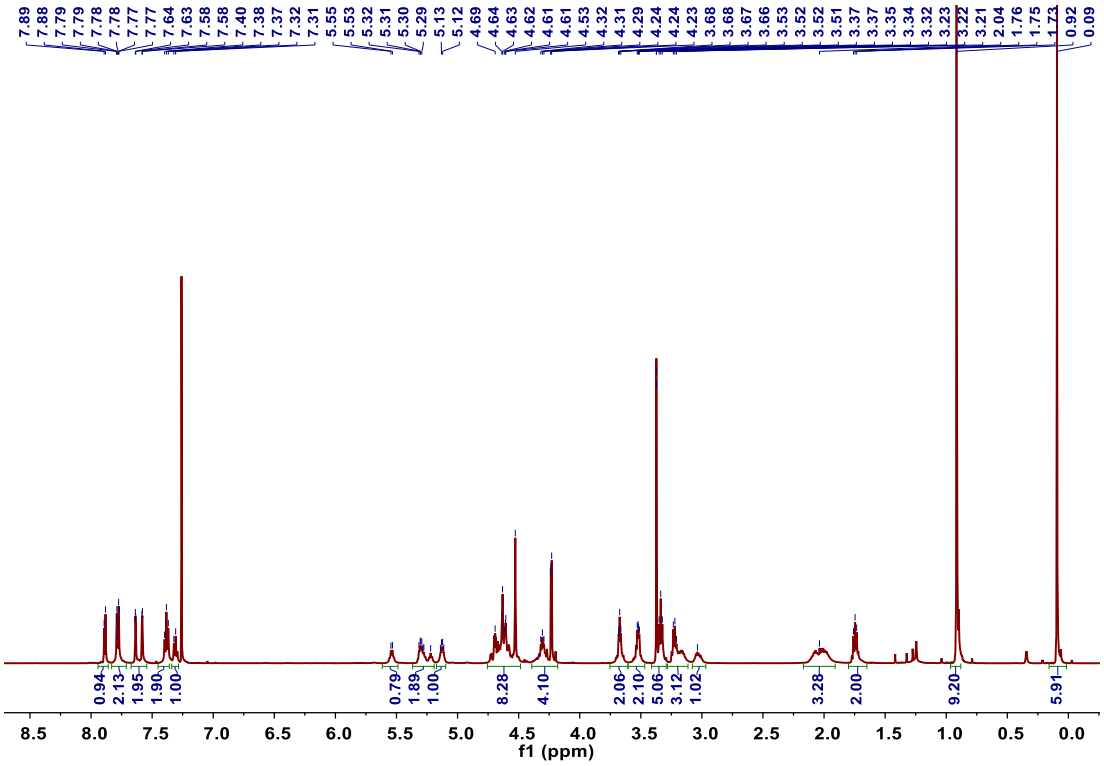


Figure S79. ^{1}H NMR of *rac*-**S3**.

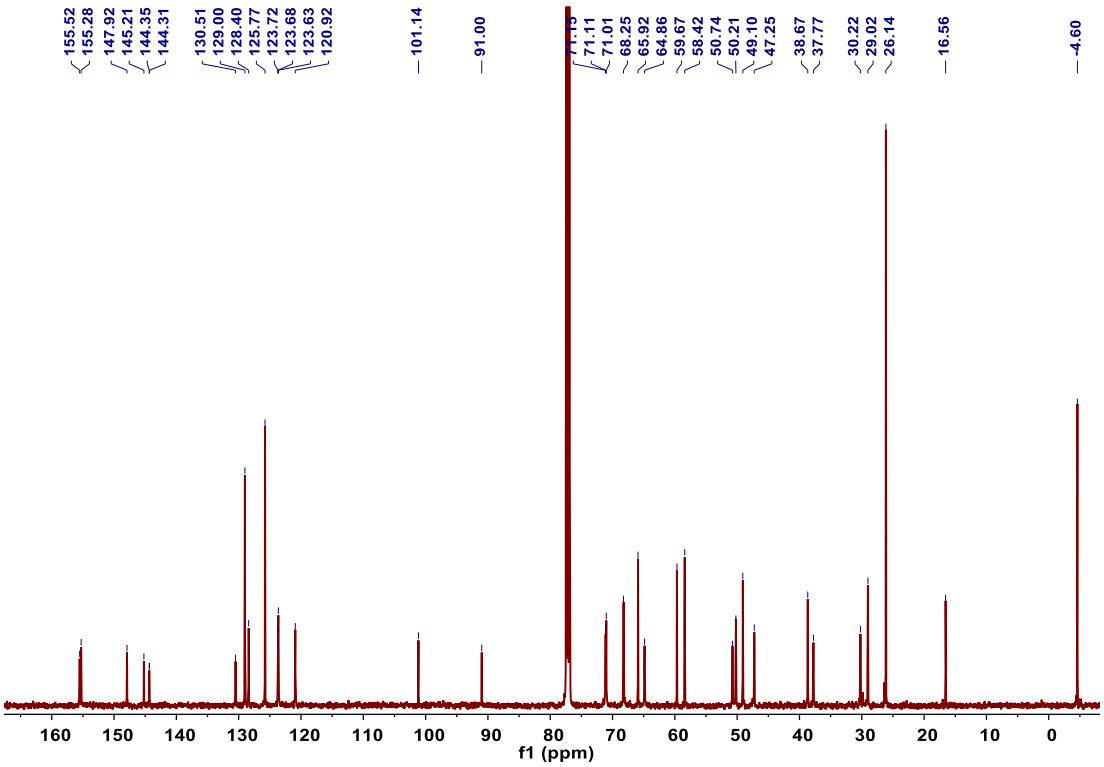


Figure S80. ^{13}C NMR of *rac*-**S3**.

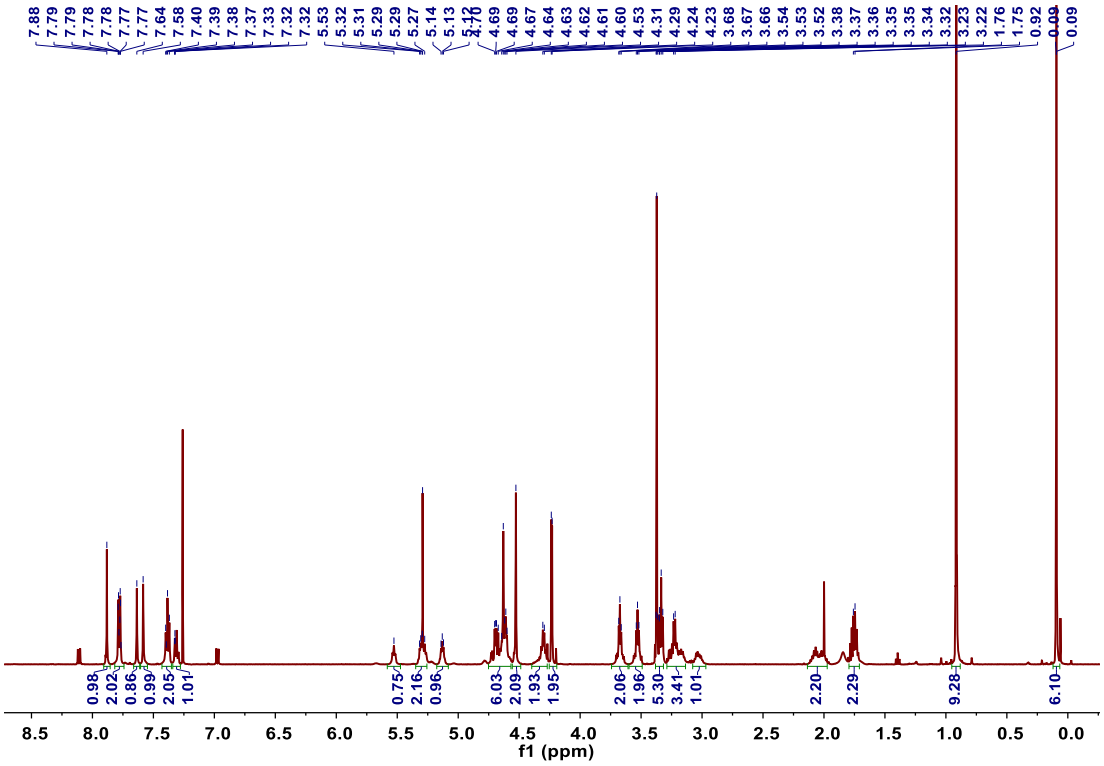


Figure S81. ^{1}H NMR of (*R*,*R*)-**S3**.

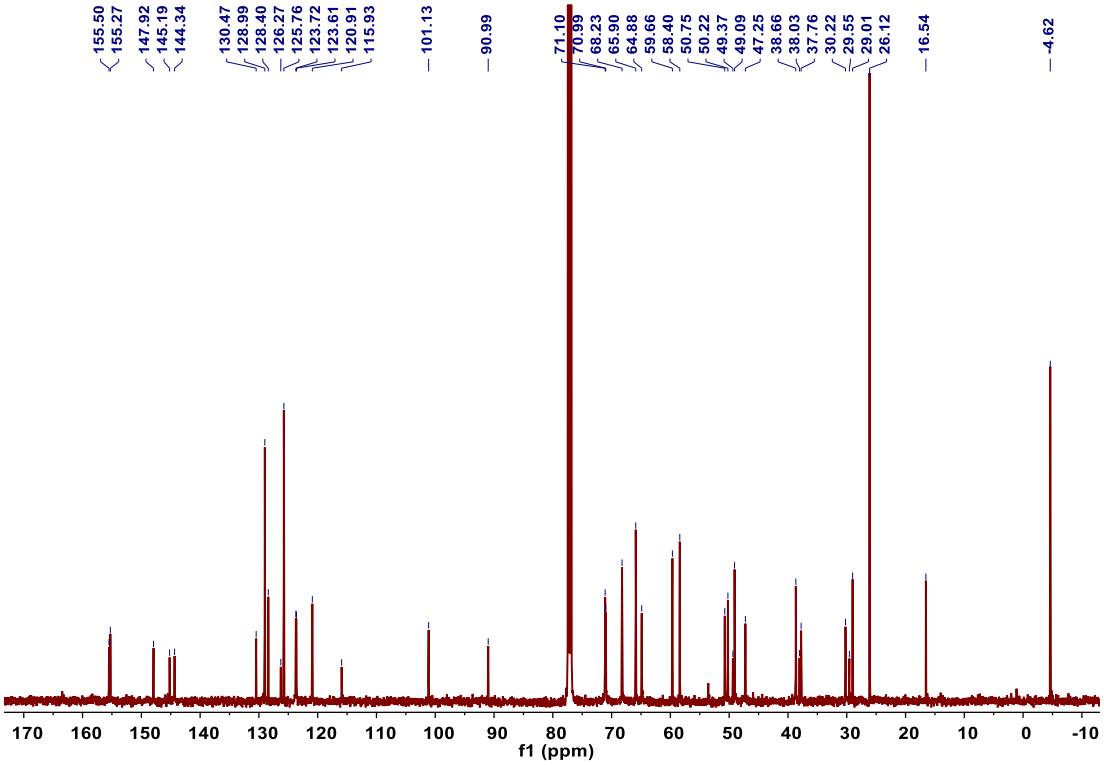


Figure S82. ^{13}C NMR of (*R*,*R*)-**S3**.

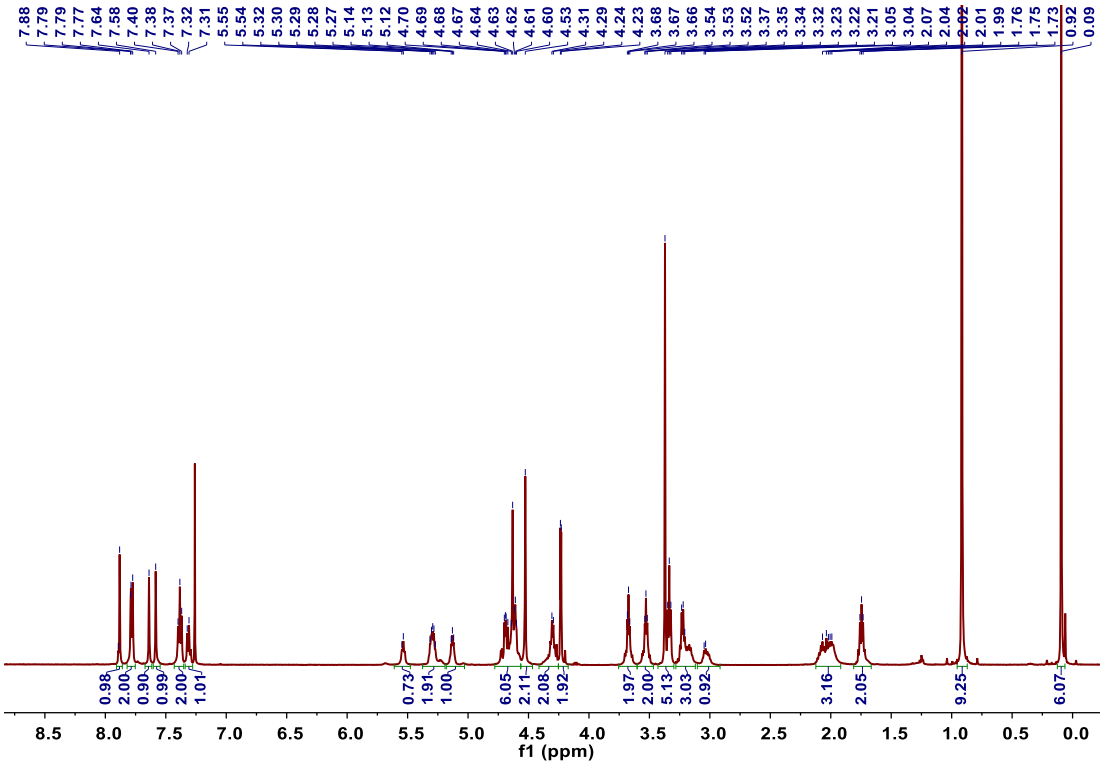


Figure S83. ^{1}H NMR of (*S*,*S*)-**S3**.

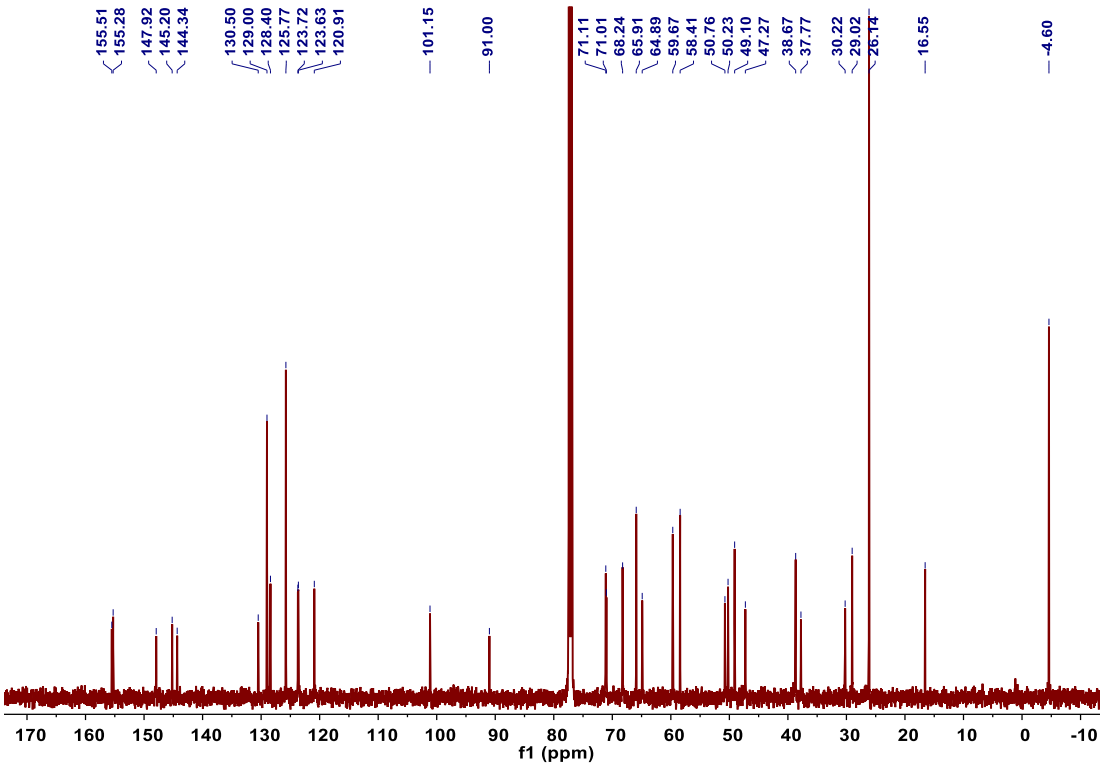


Figure S84. ^{13}C NMR of (*S*,*S*)-**S3**.

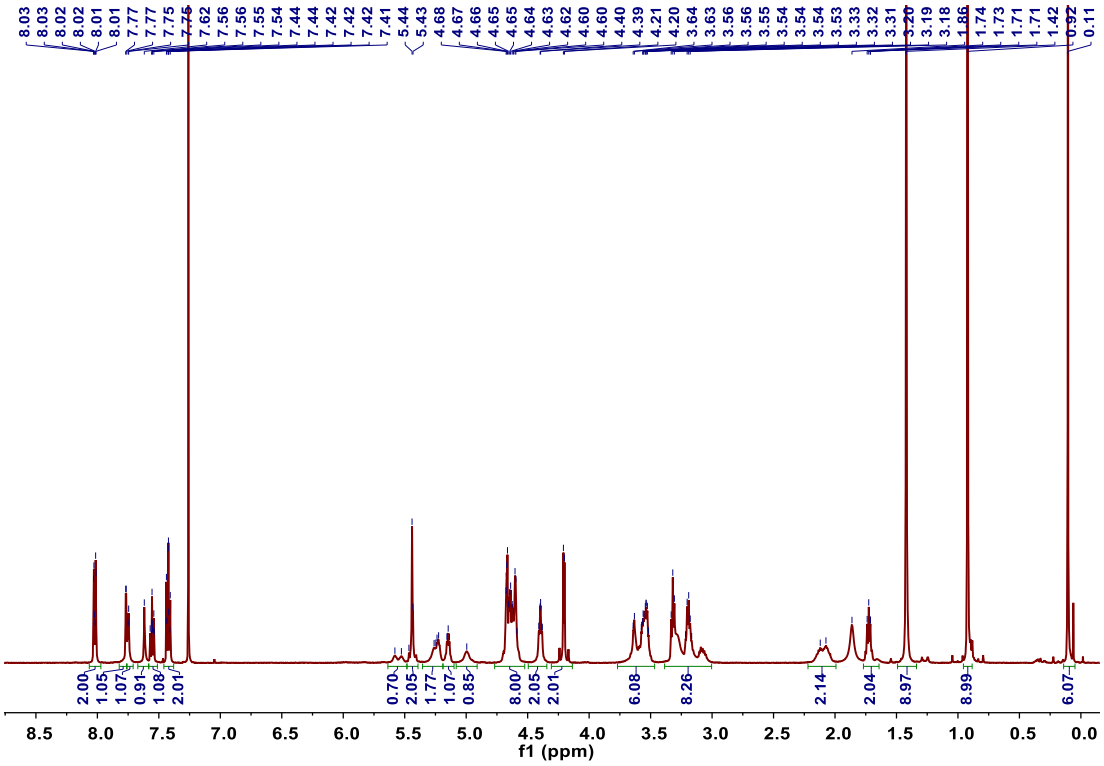


Figure S85. ^{1}H NMR of **S4**.

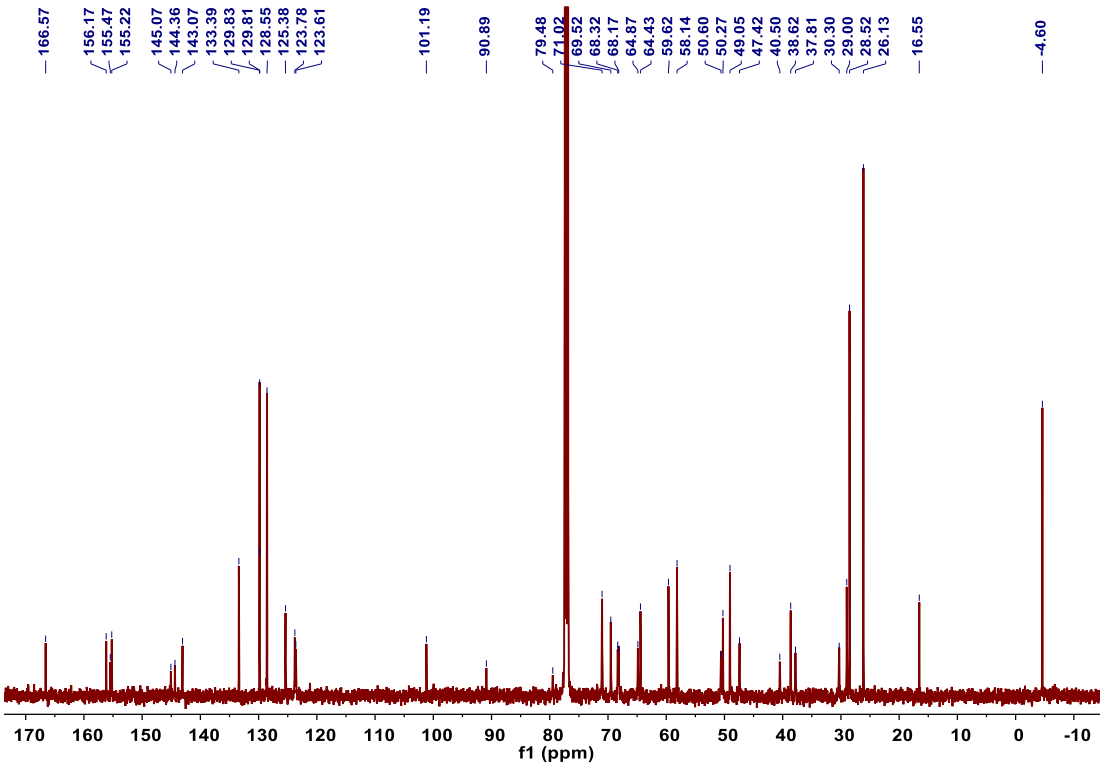


Figure S86. ^{13}C NMR of **S4**.

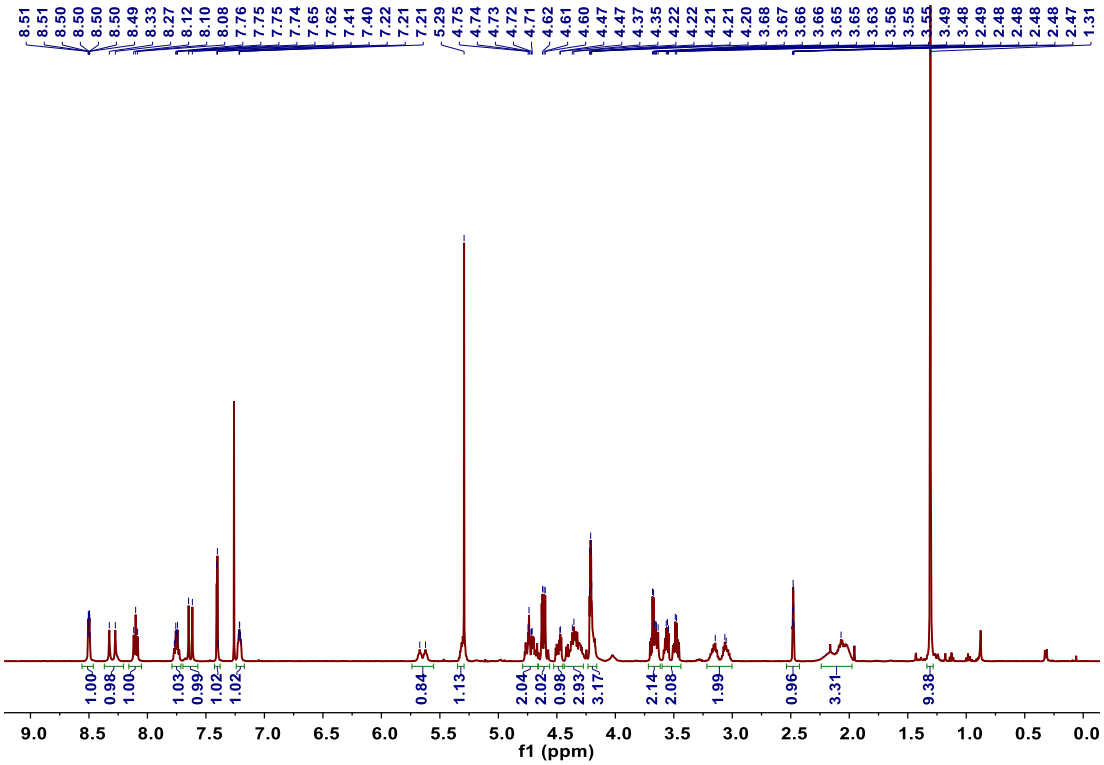


Figure S87. ^{1}H NMR of *rac*-**S5**.

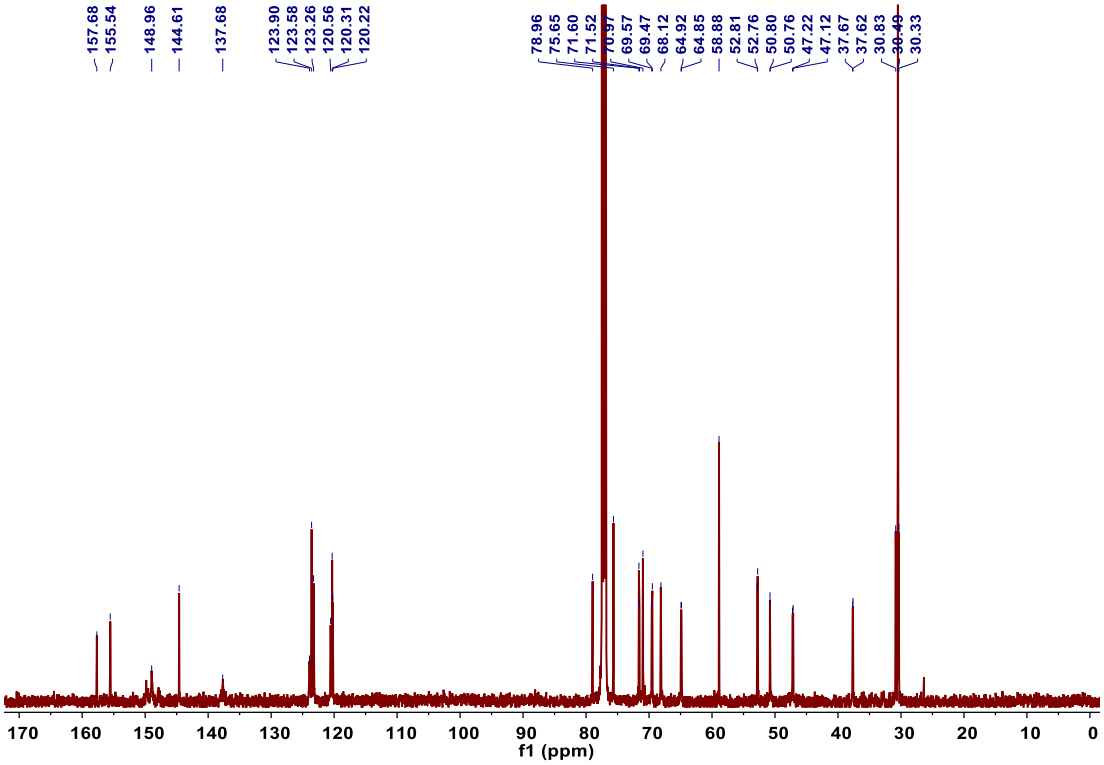


Figure S88. ^{13}C NMR of *rac*-**S5**.

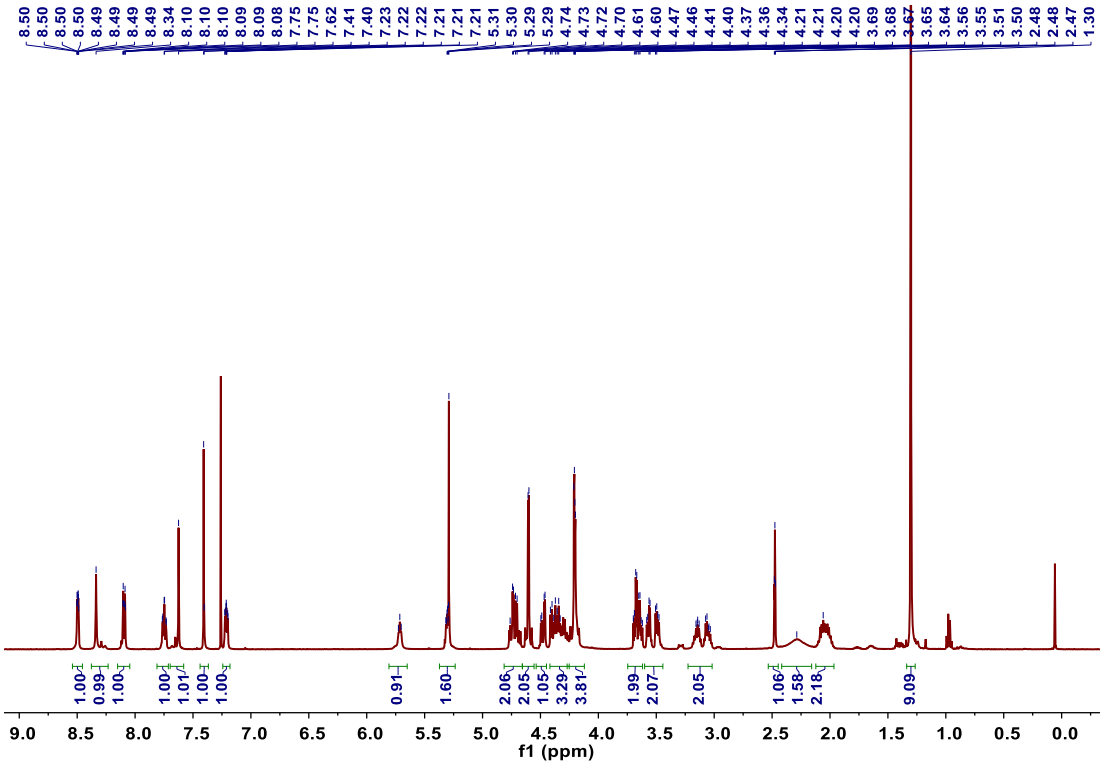


Figure S89. ^{1}H NMR of (*R*,*R*)-**S5**.

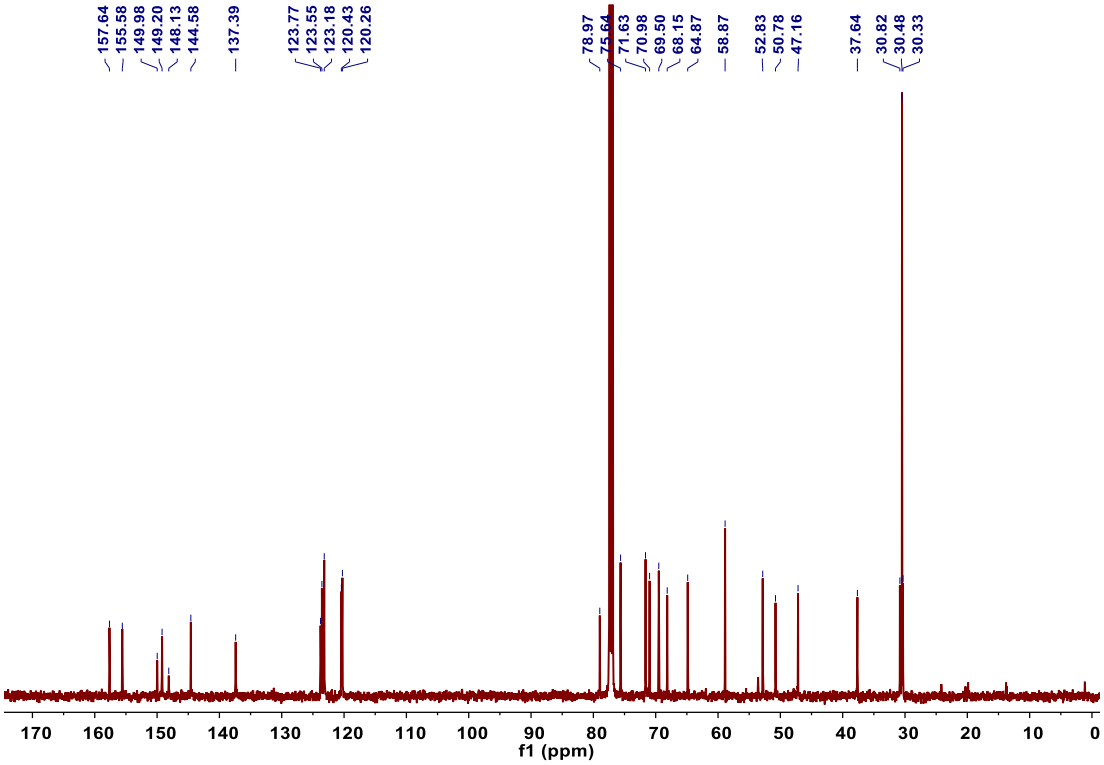


Figure S90. ^{13}C NMR of (*R*,*R*)-**S5**.

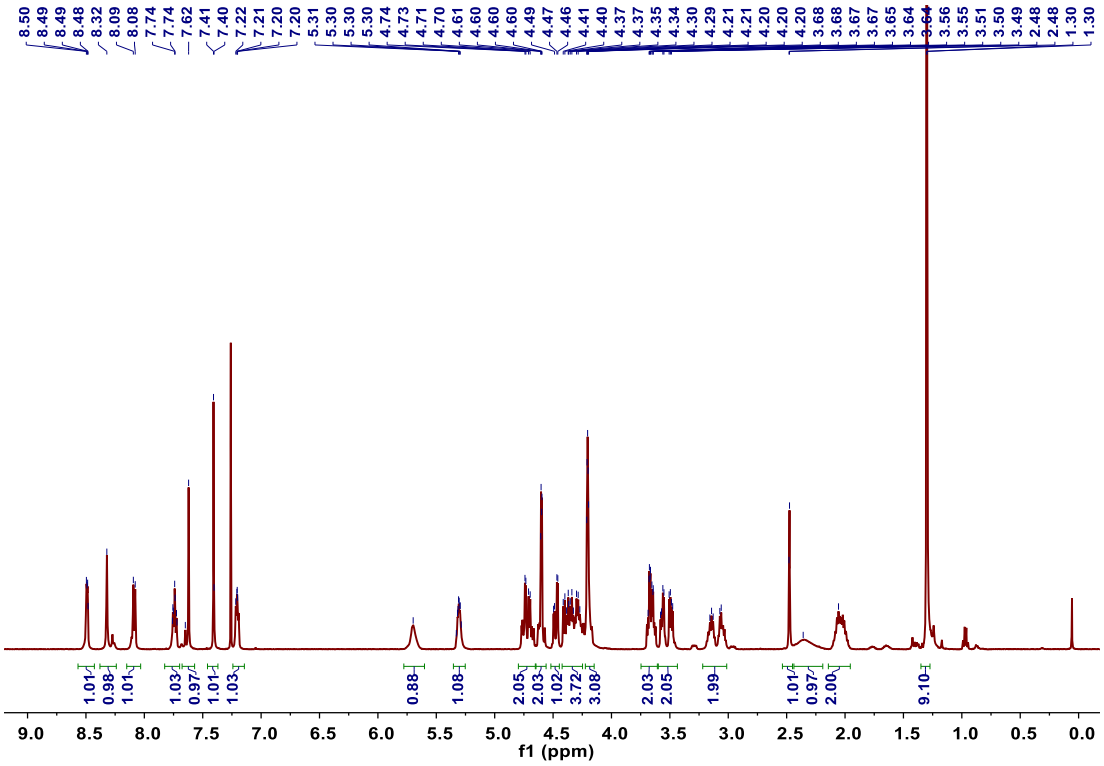


Figure S91. ^{1}H NMR of (*S*,*S*)-**S5**.

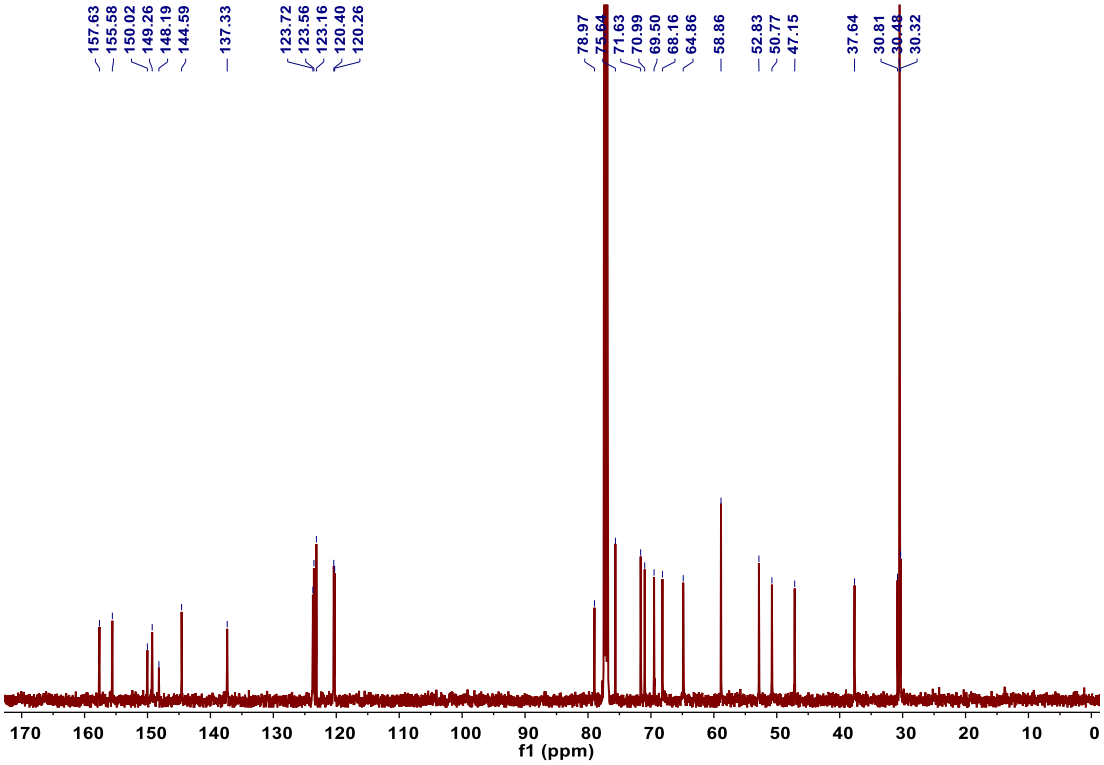


Figure S92. ^{13}C NMR of (*S*,*S*)-**S5**.

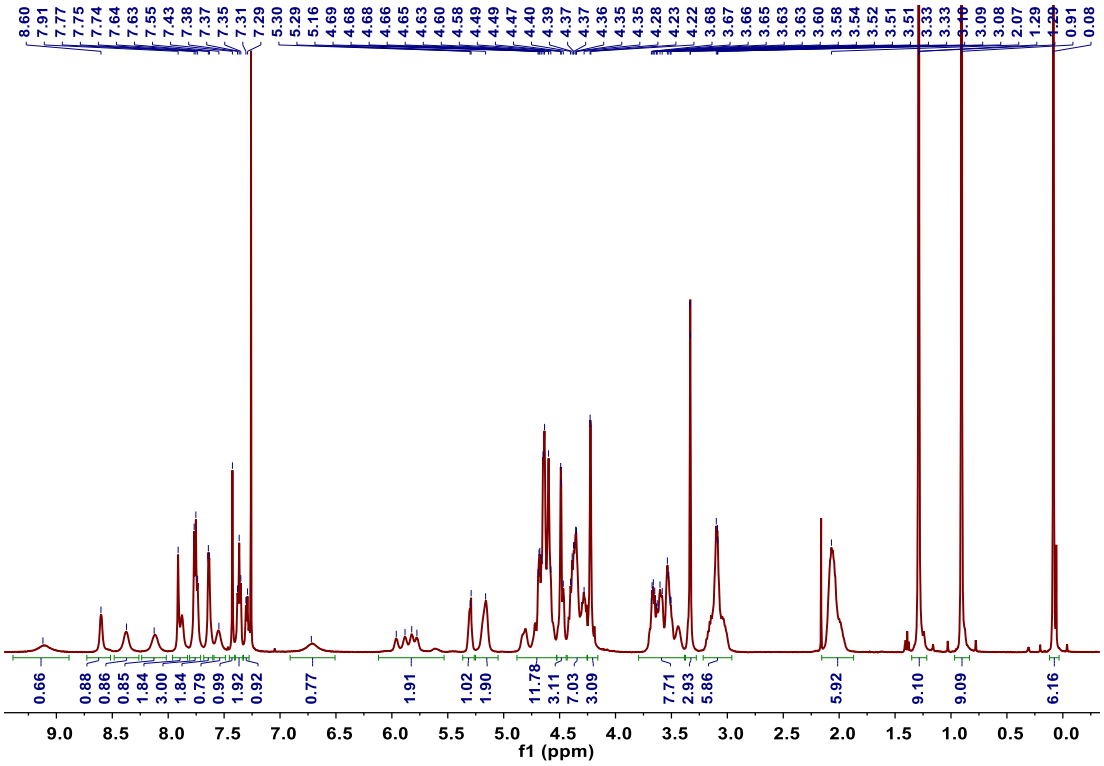


Figure S93. ^{1}H NMR of *rac*-**FEPB**.

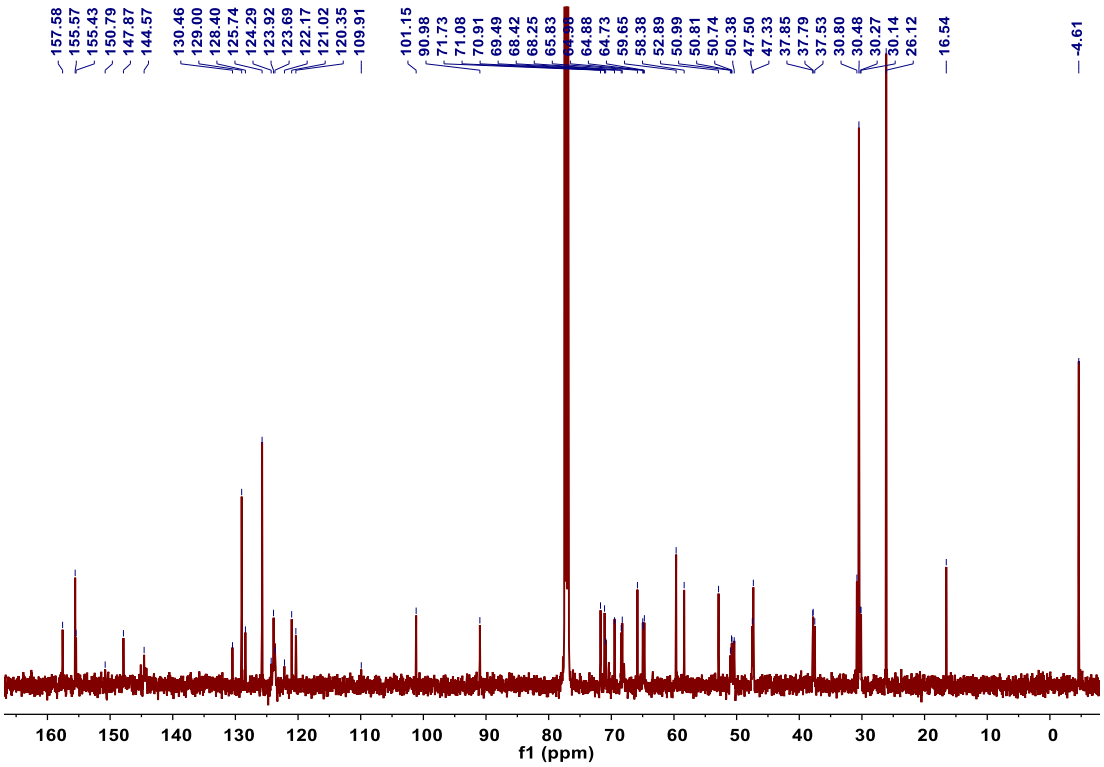


Figure S94. ^{13}T NMR of *rac*-**FEPB**.

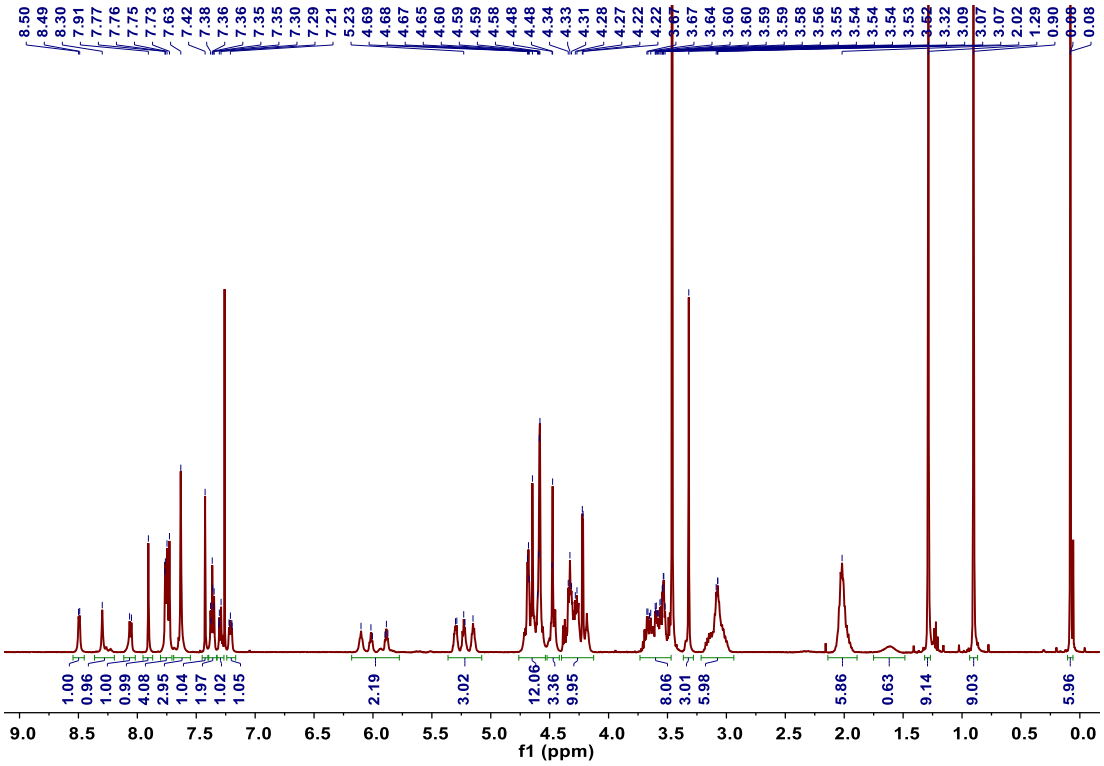


Figure S95. ^{1}H NMR of (*R*,*R*,*R*,*R*)-**FEPB**.

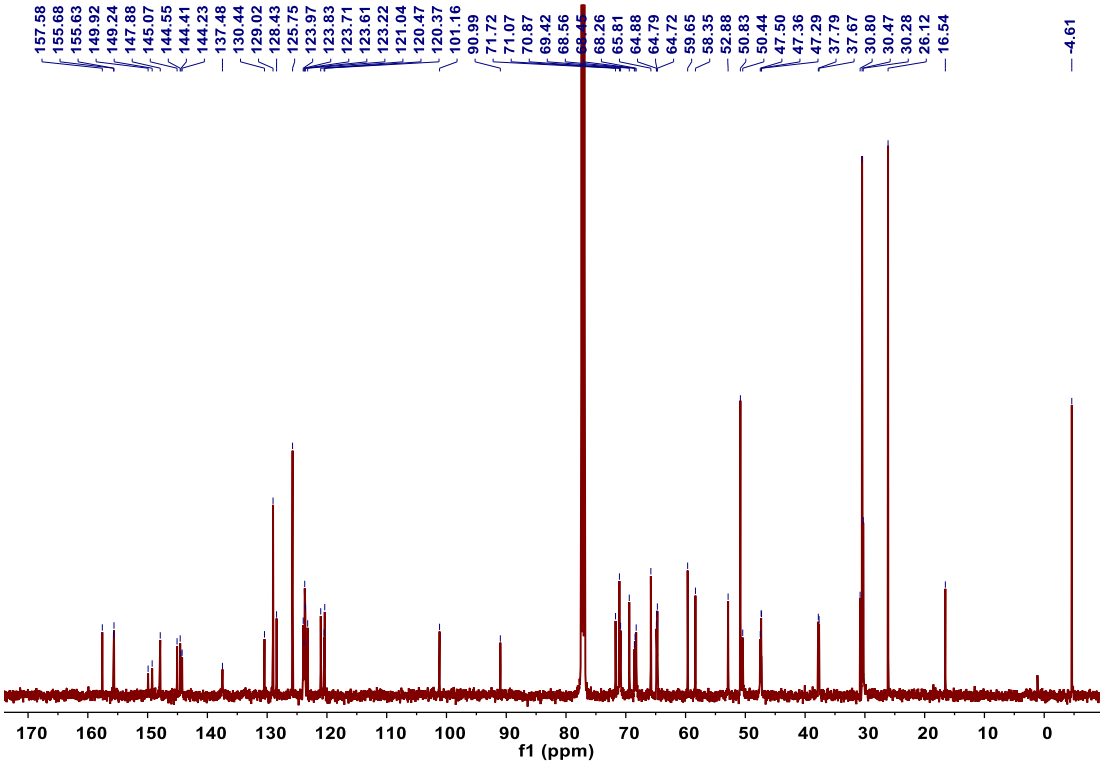


Figure S96. ^{13}C NMR of (*R*,*R*,*R*,*R*)-**FEPB**.

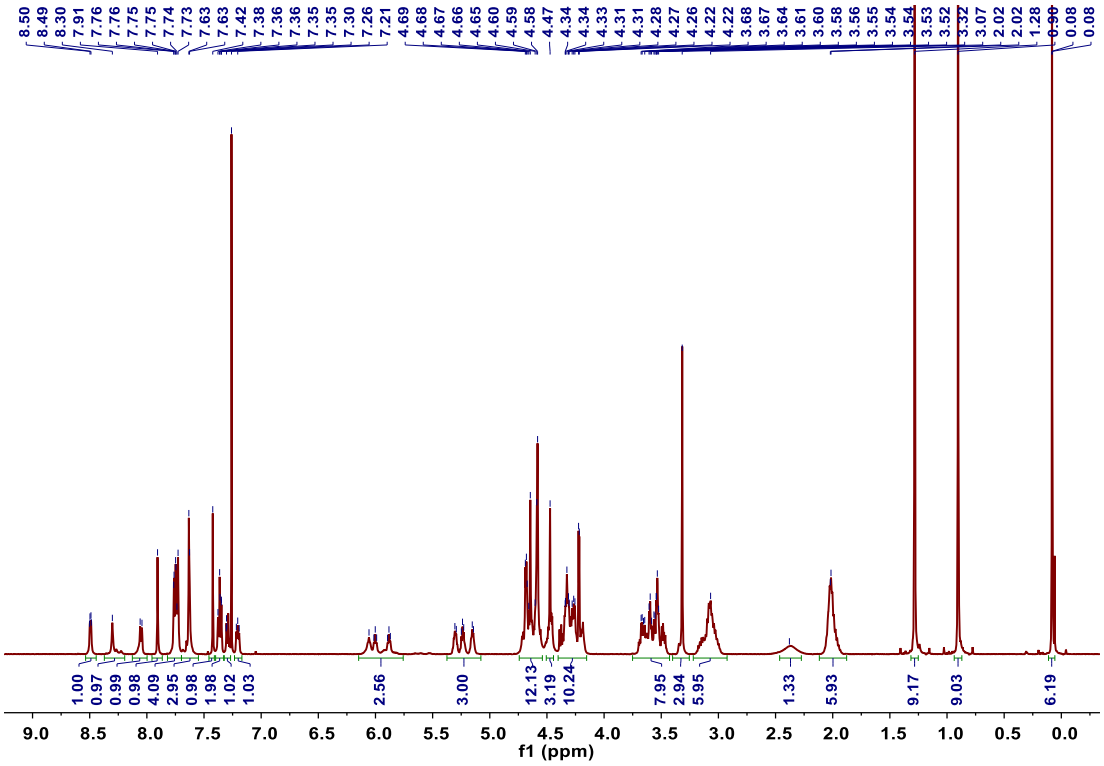


Figure S97. ^{1}H NMR of (*S*,*S*,*S*,*S*)-**FEPB**.

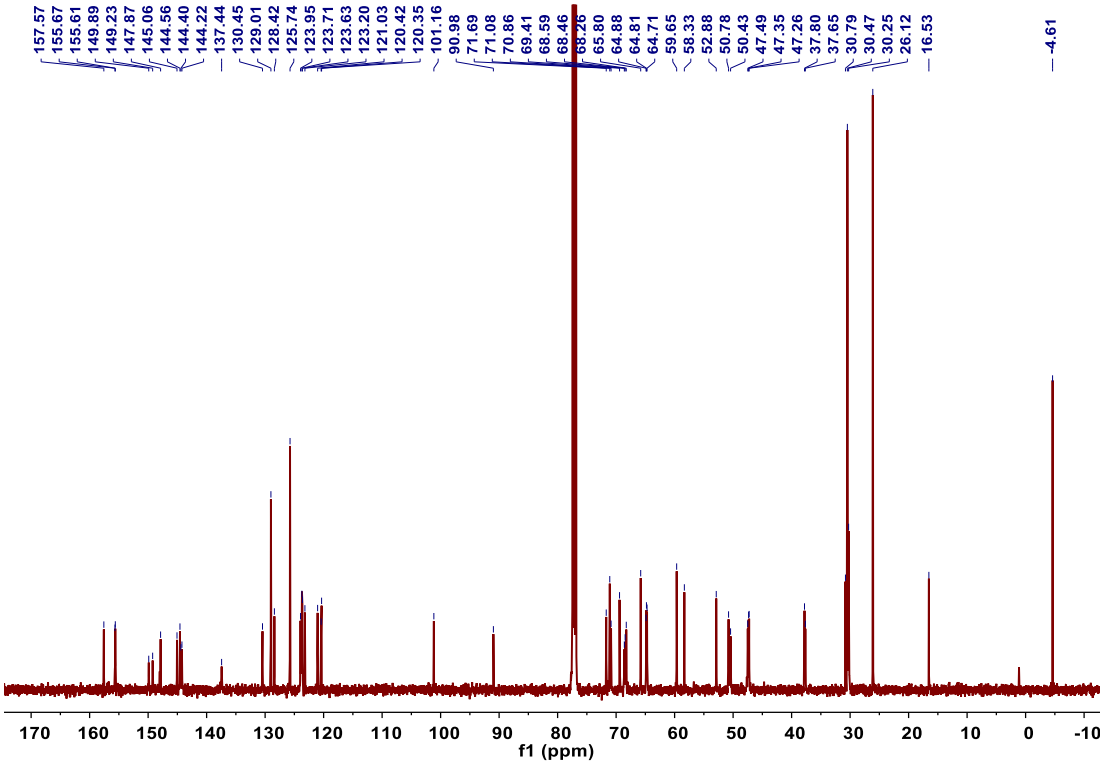


Figure S98. ^{13}C NMR of (*S*,*S*,*S*,*S*)-**FEPB**.

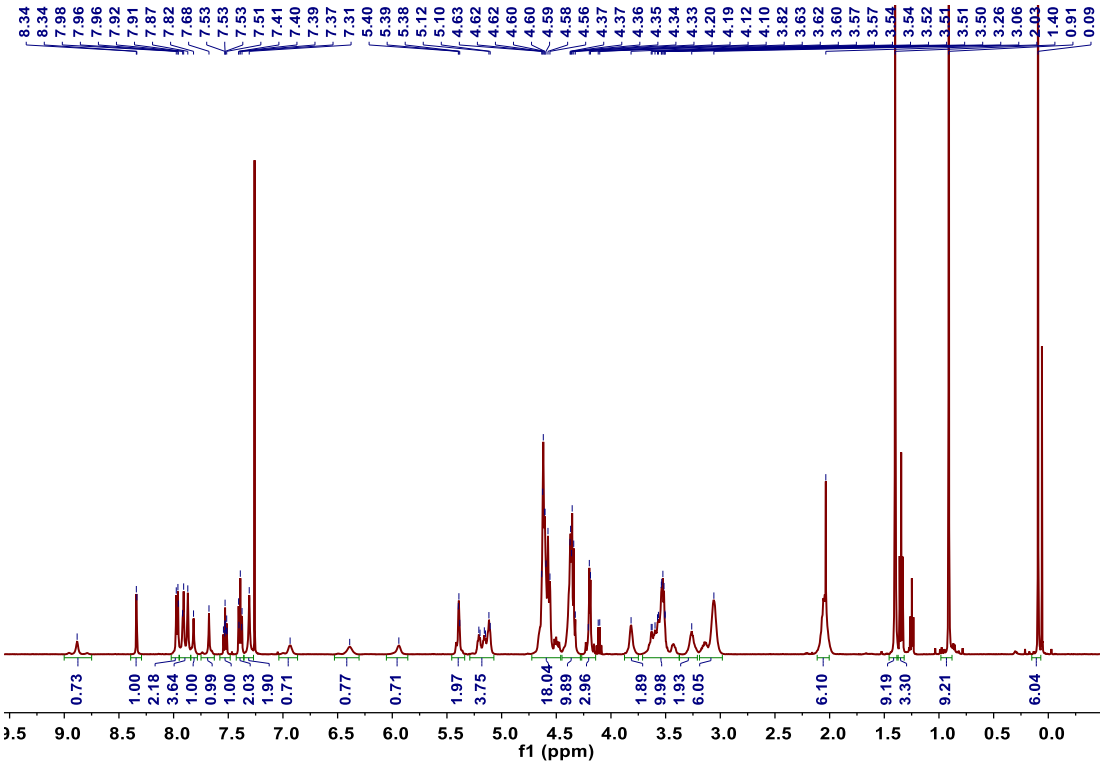


Figure S99. ^{1}H NMR of **A(Boc)O(Bz)IK(Et)**.

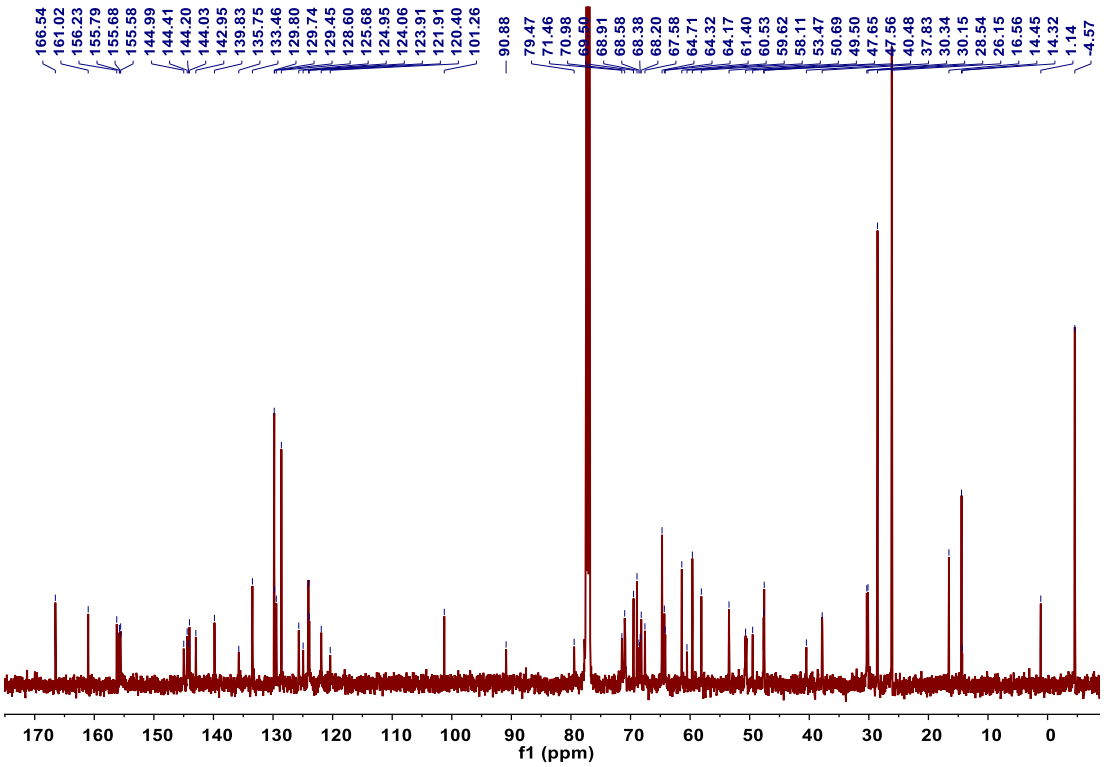


Figure S100. ^{13}C NMR of **A(Boc)O(Bz)IK(Et)**.

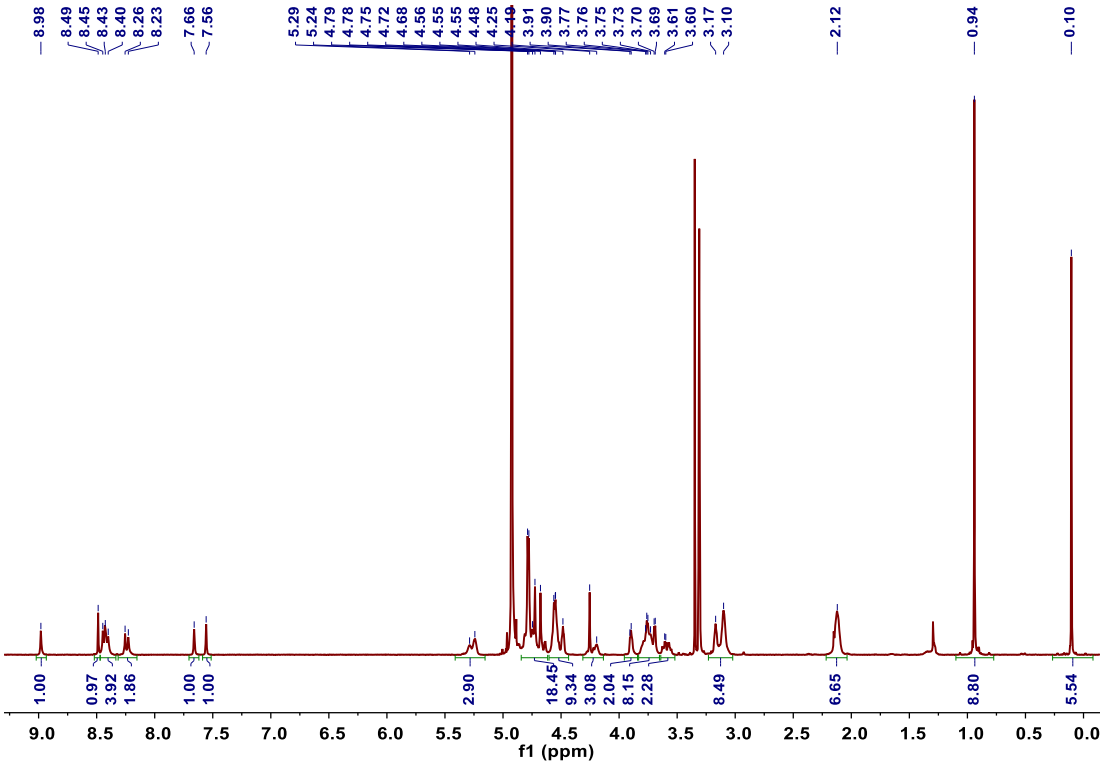


Figure S101. ^{1}H NMR of **AOIK**.

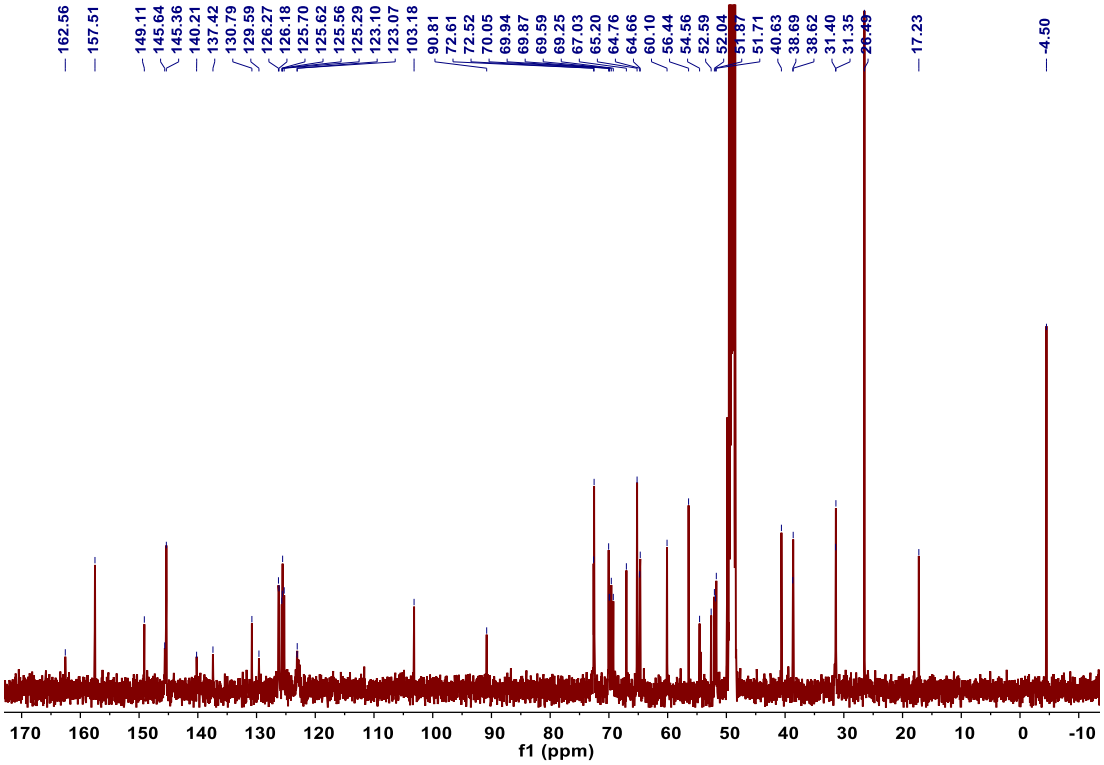


Figure S102. ^{13}C NMR of **AOIK**.

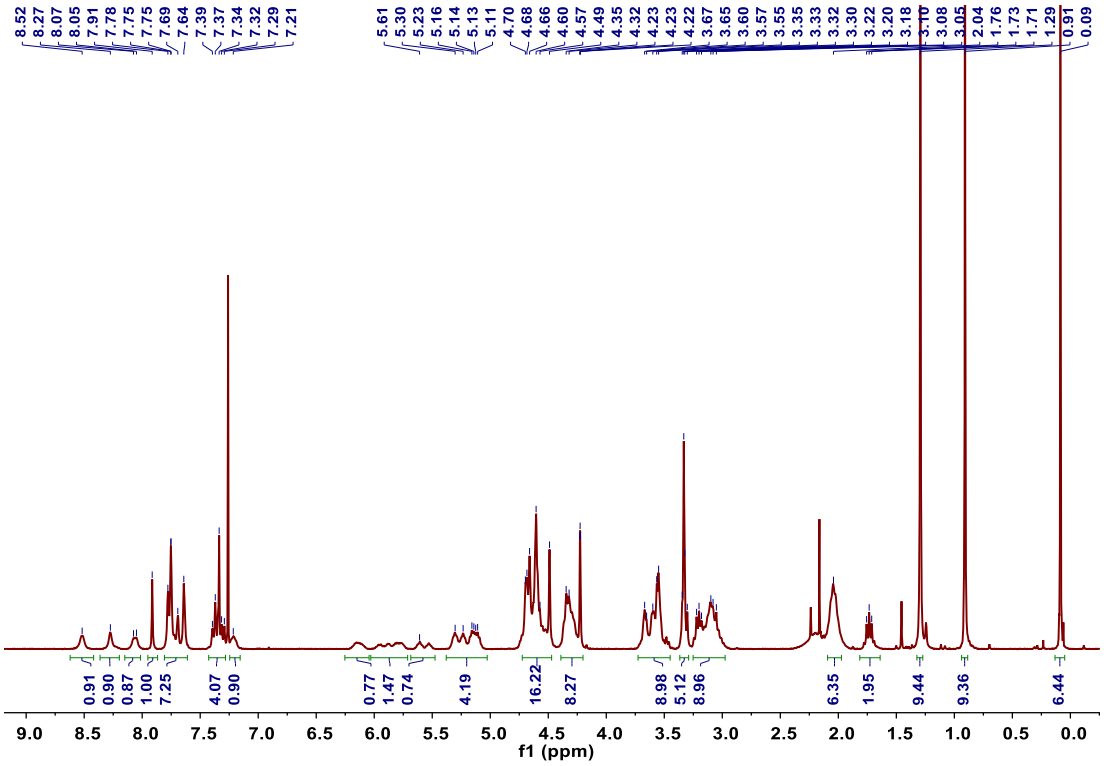


Figure S103. ^{1}H NMR of *rac*-**S6**.

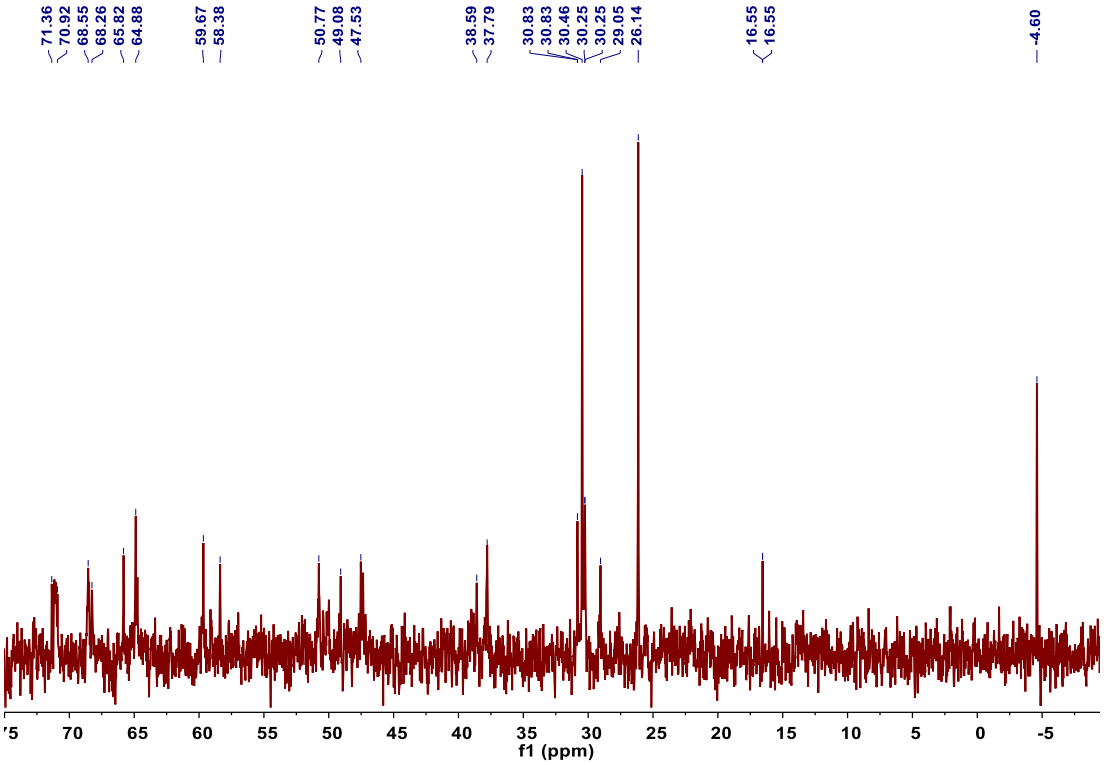


Figure S104. ^{13}C NMR of *rac*-**S6**.

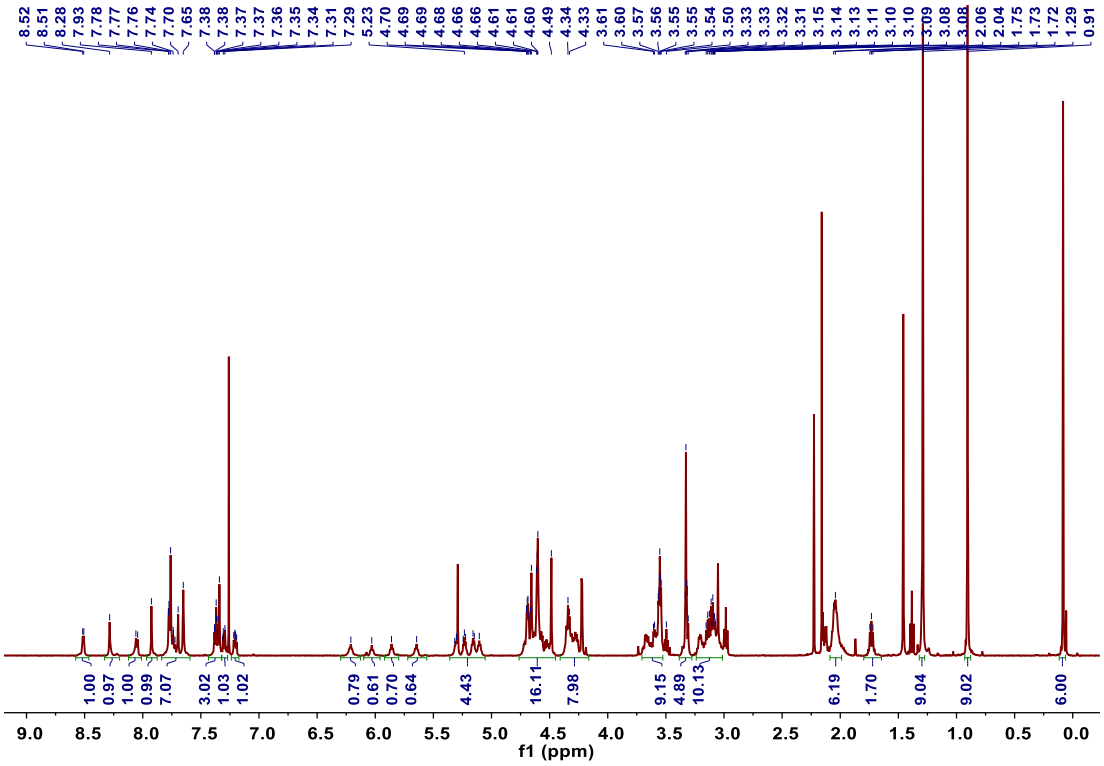


Figure S105. ^{1}H NMR of (*R*,*R*,*R*,*R*)-**S6**.

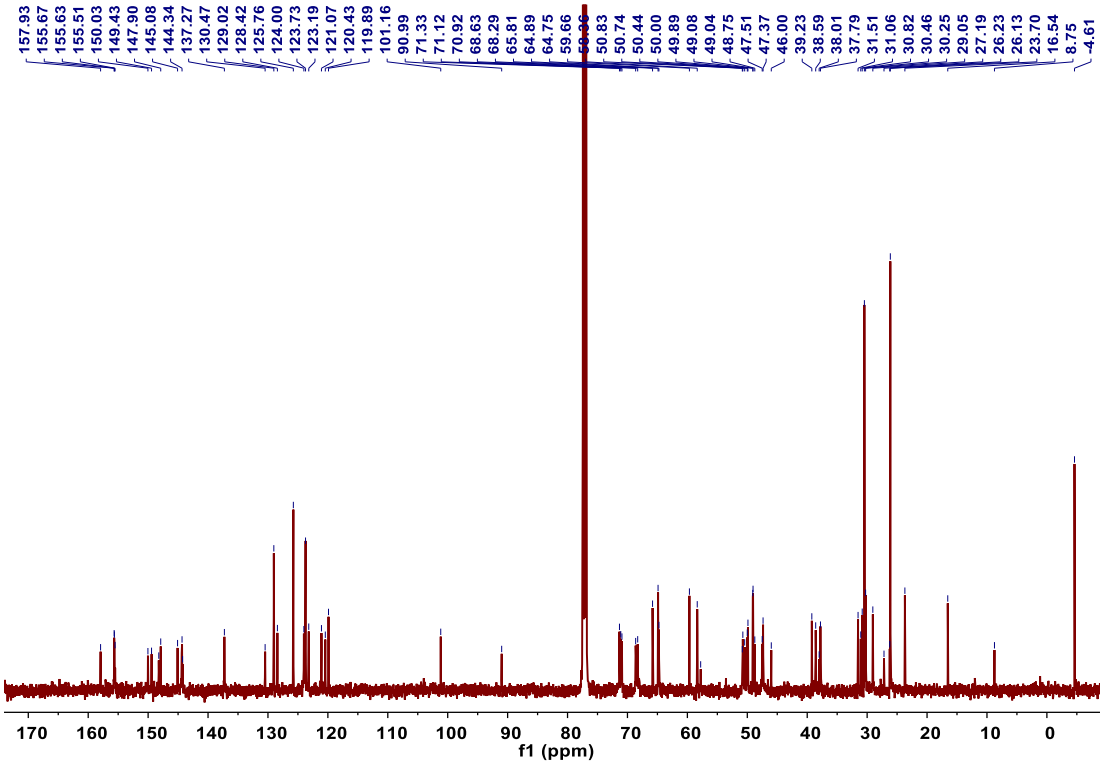


Figure S106. ^{13}C NMR of (*R*,*R*,*R*,*R*)-**S6**.

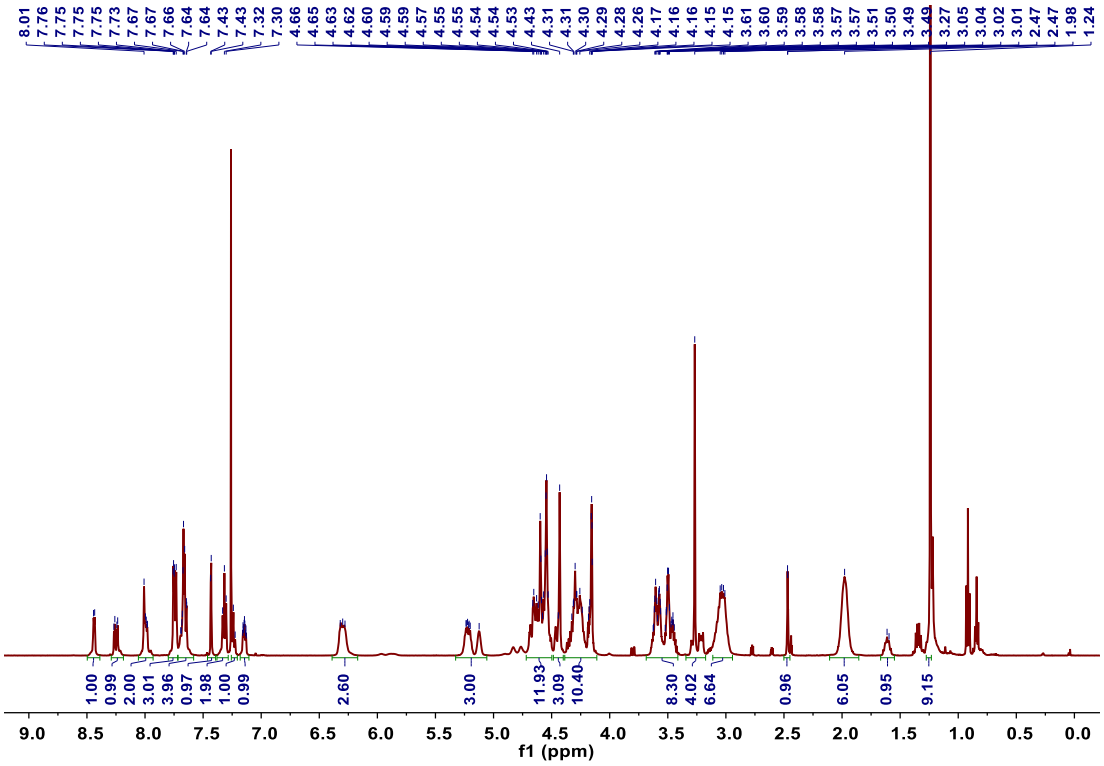


Figure S107. ^{1}H NMR of *rac*-**S7**.

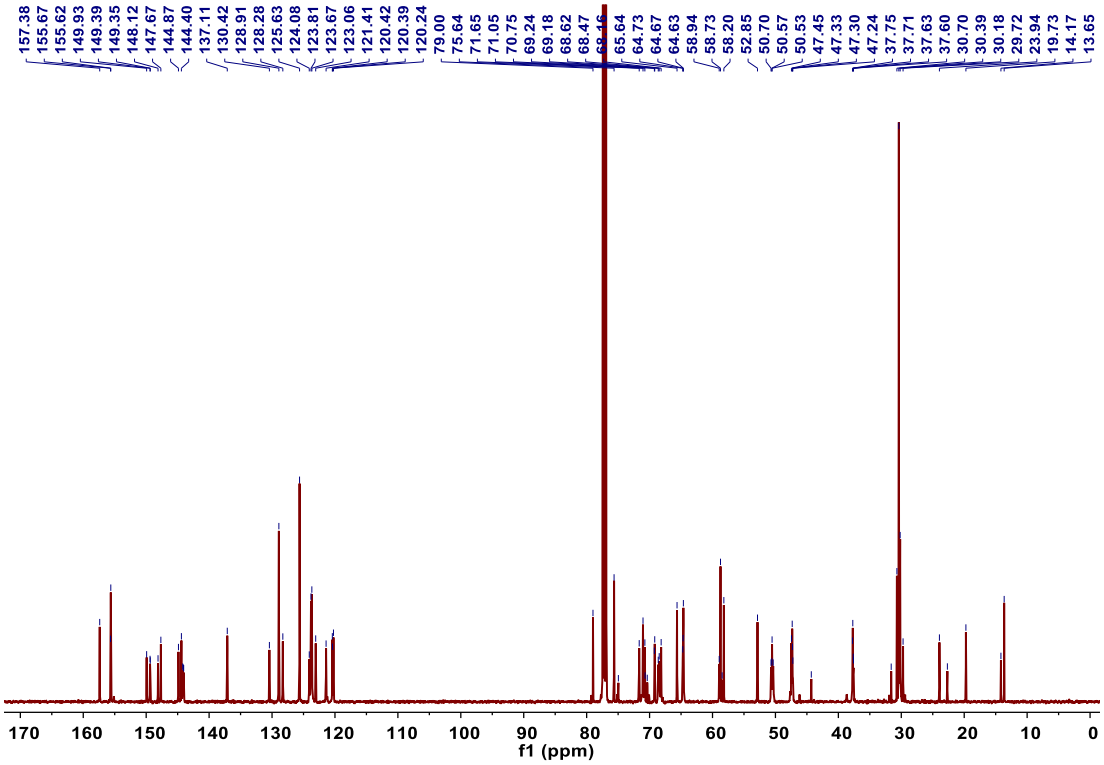


Figure S108. ^{13}C NMR of *rac*-**S7**.

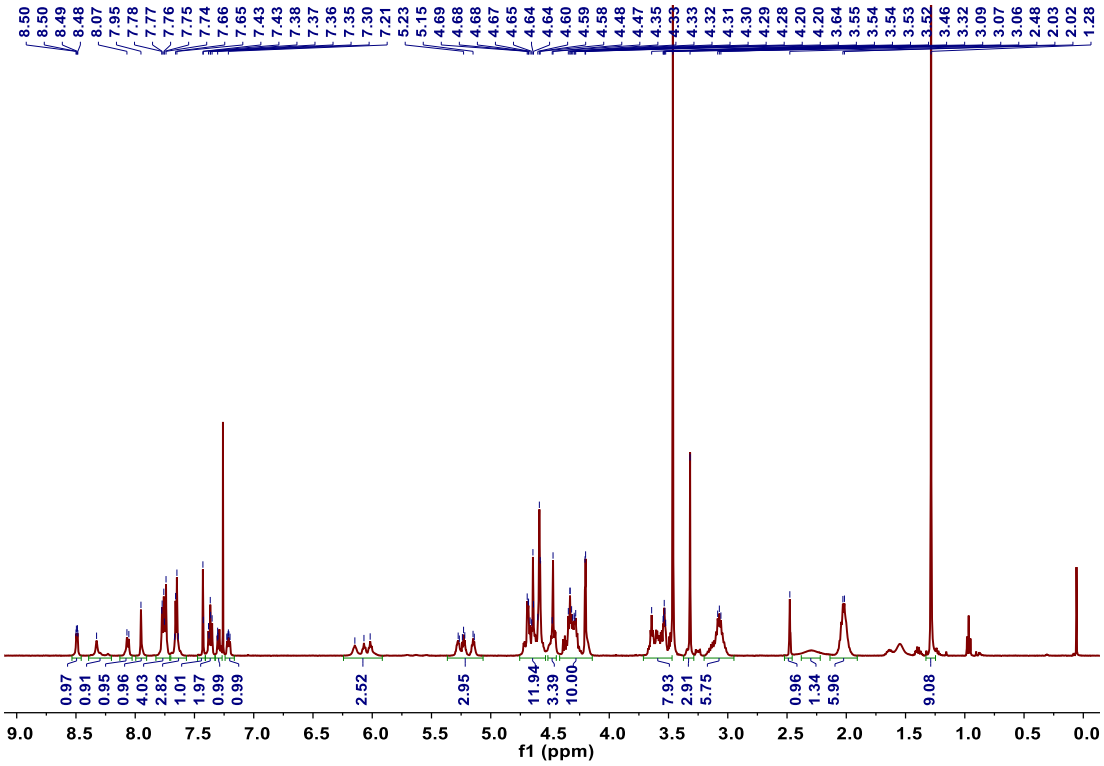


Figure S109. ^{1}H NMR of (*S*,*S*,*S*,*S*)-**S7**.

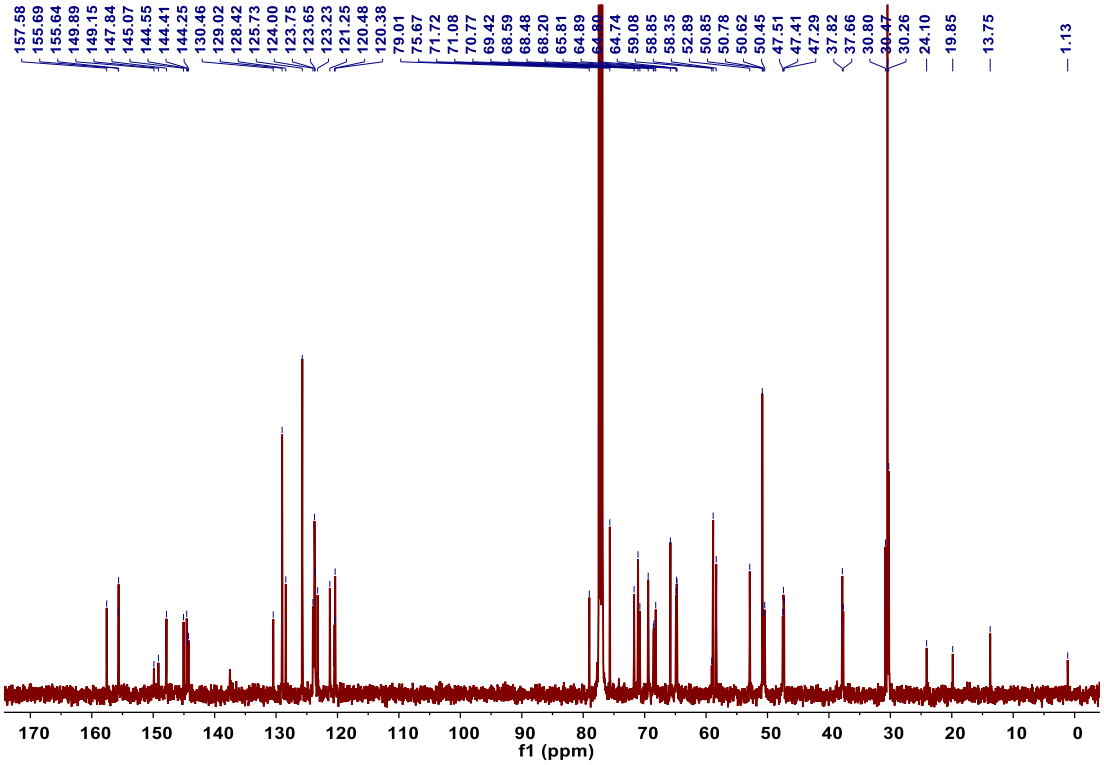


Figure S110. ^{13}C NMR of (*S*,*S*,*S*,*S*)-**S7**.

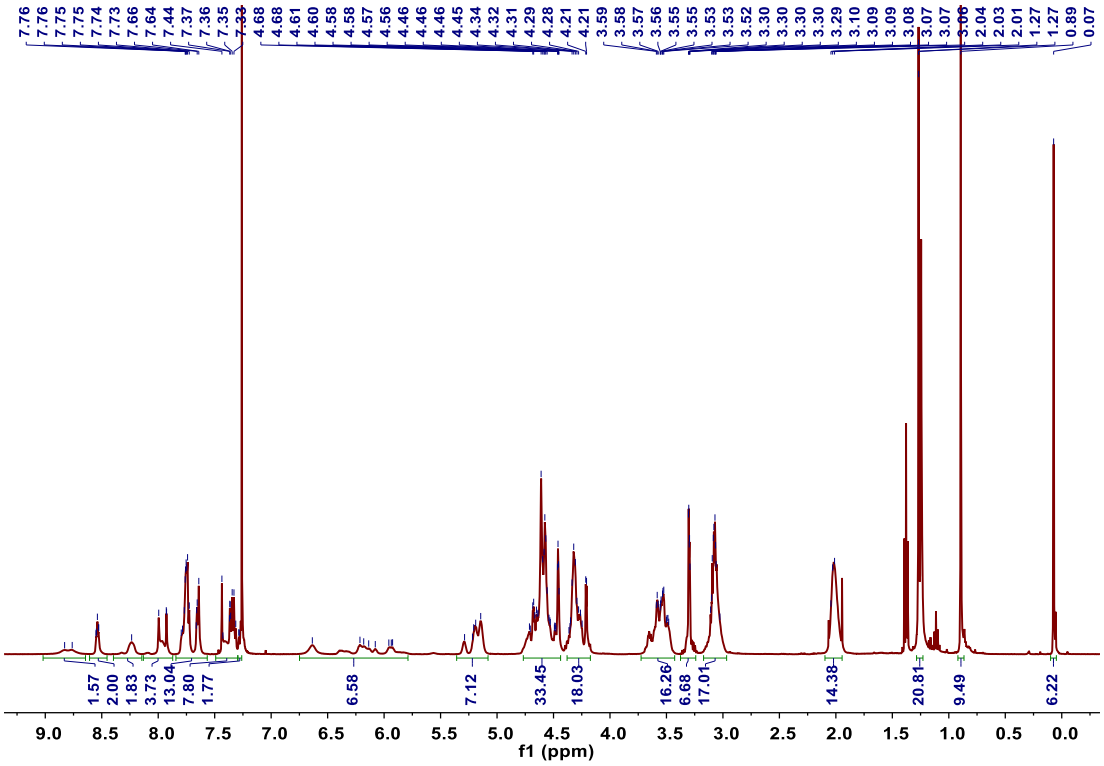


Figure S111. ^{1}H NMR of *rac*-**FEPBFEPB**.

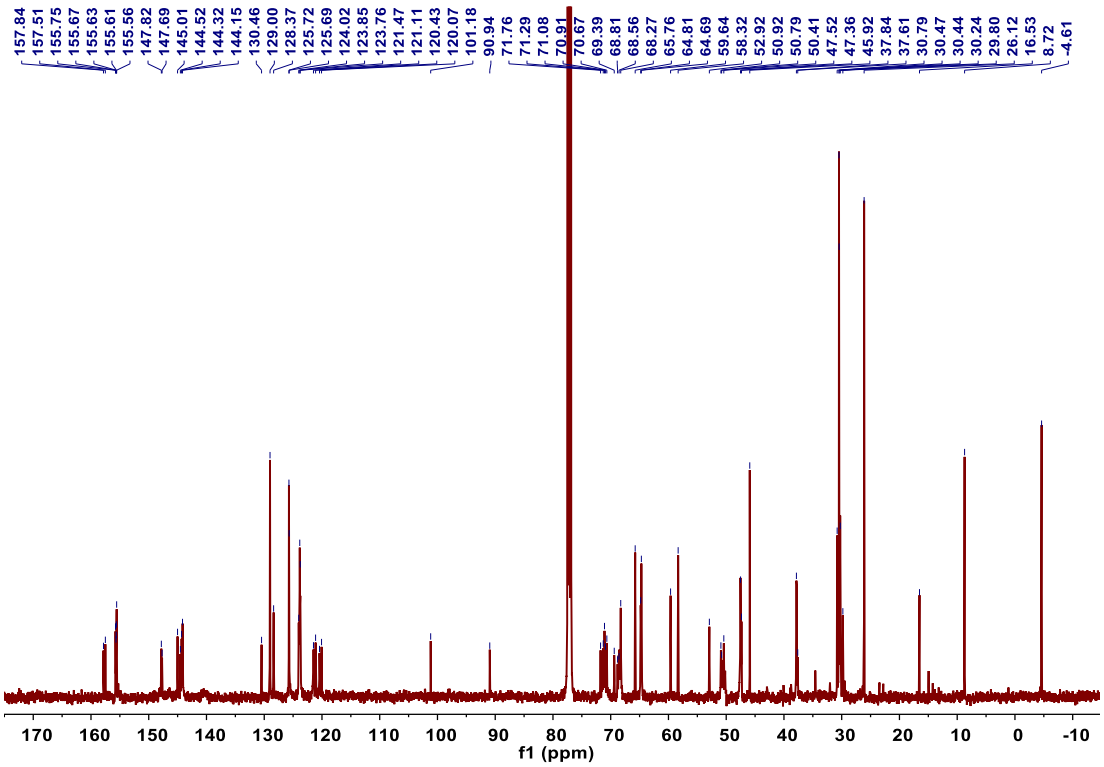


Figure S112. ^{13}C NMR of *rac*-**FEPBFEPB**.

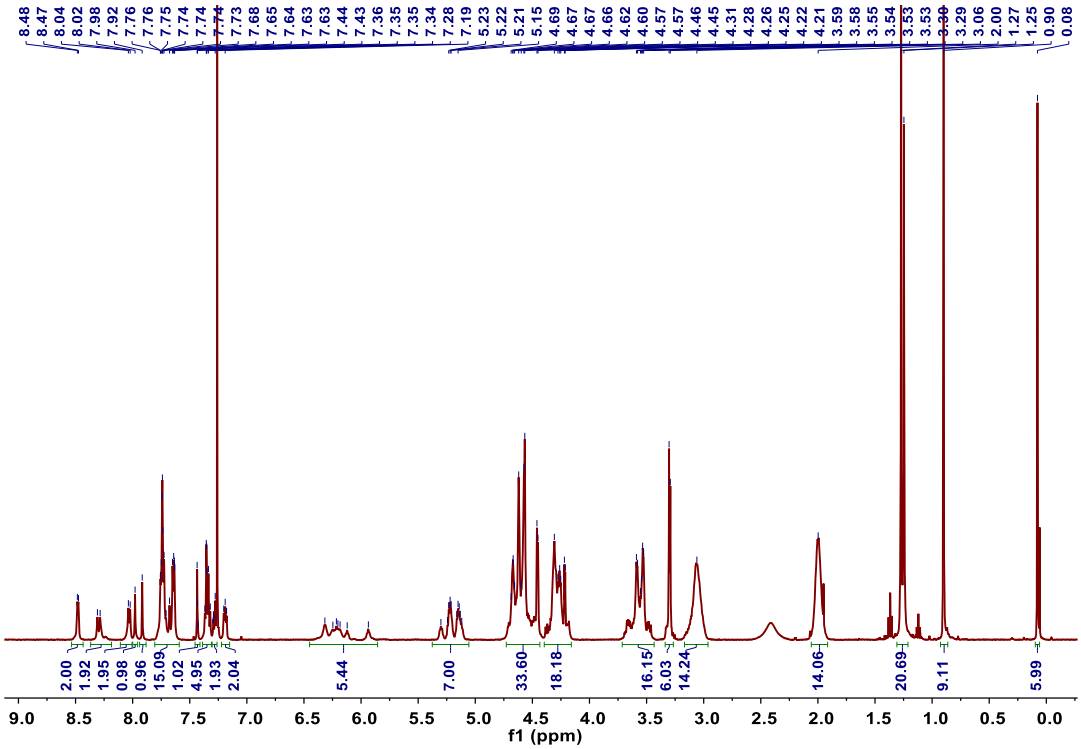


Figure S113. ^{1}H NMR of (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB**.

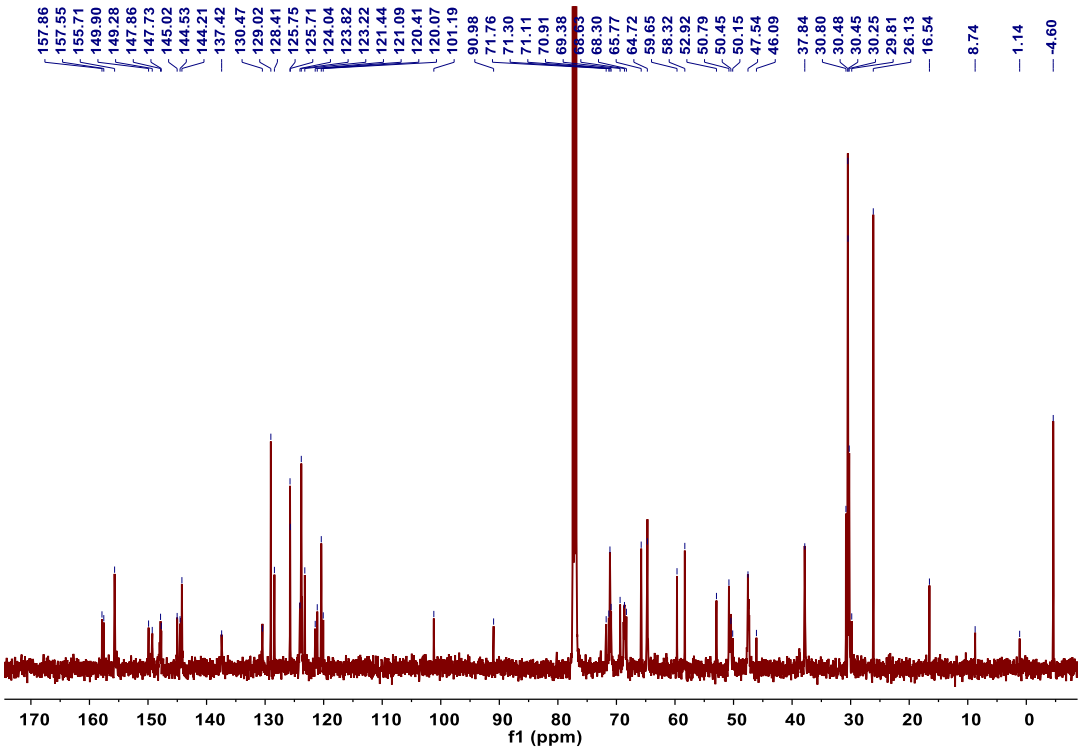


Figure S114. ^{13}C NMR of (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB**.

4 MS SPECTRA

4.1 HRMS

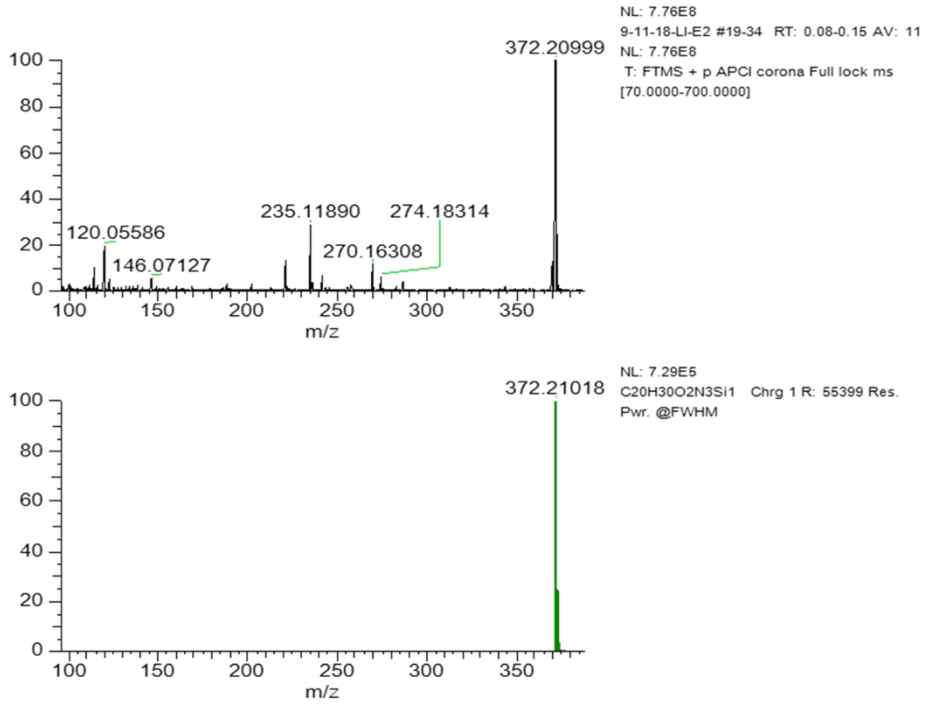


Figure S115. APCI-MS of *rac*-**4a**.

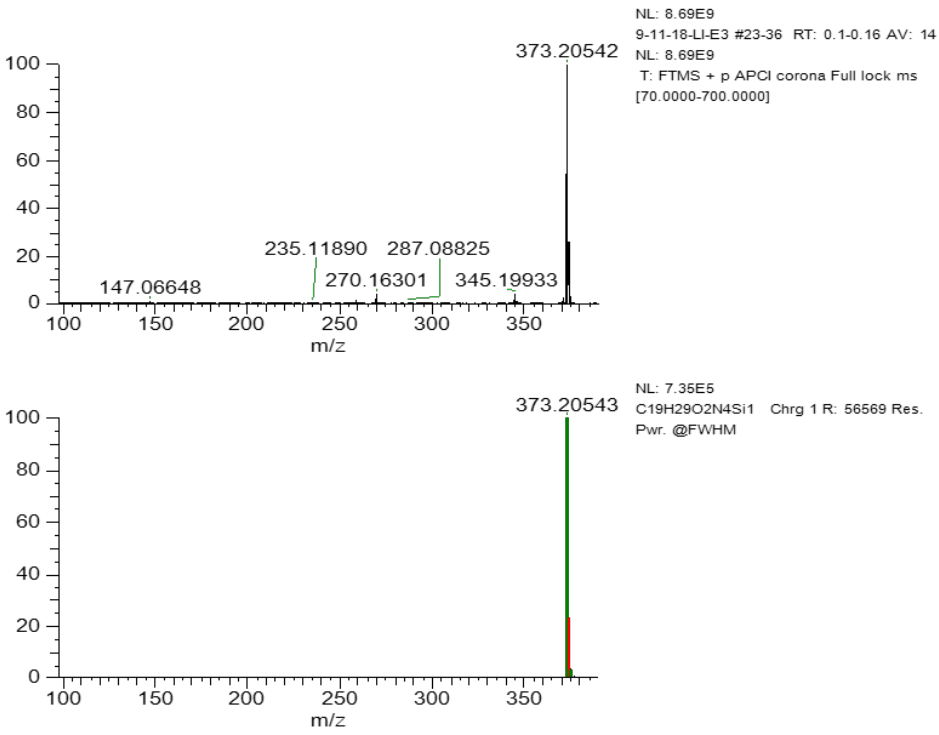


Figure S116. APCI-MS of *rac*-**4b**.

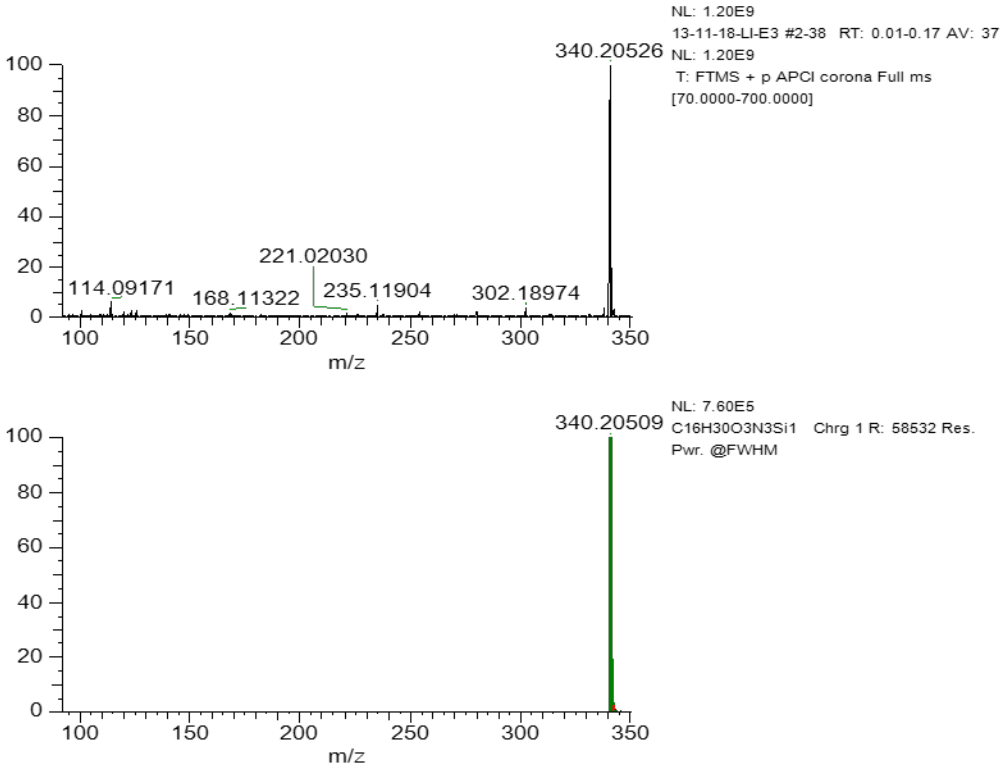


Figure S117. APCI-MS of *rac*-**4c**.

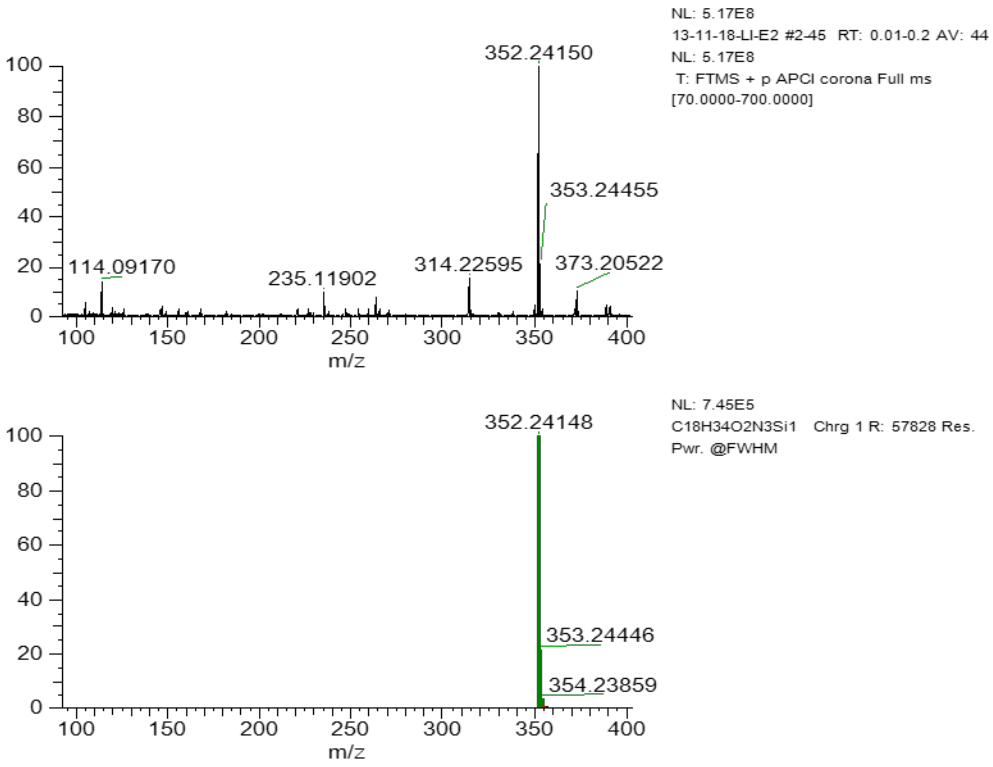


Figure S118. APCI-MS of *rac*-**4d**.

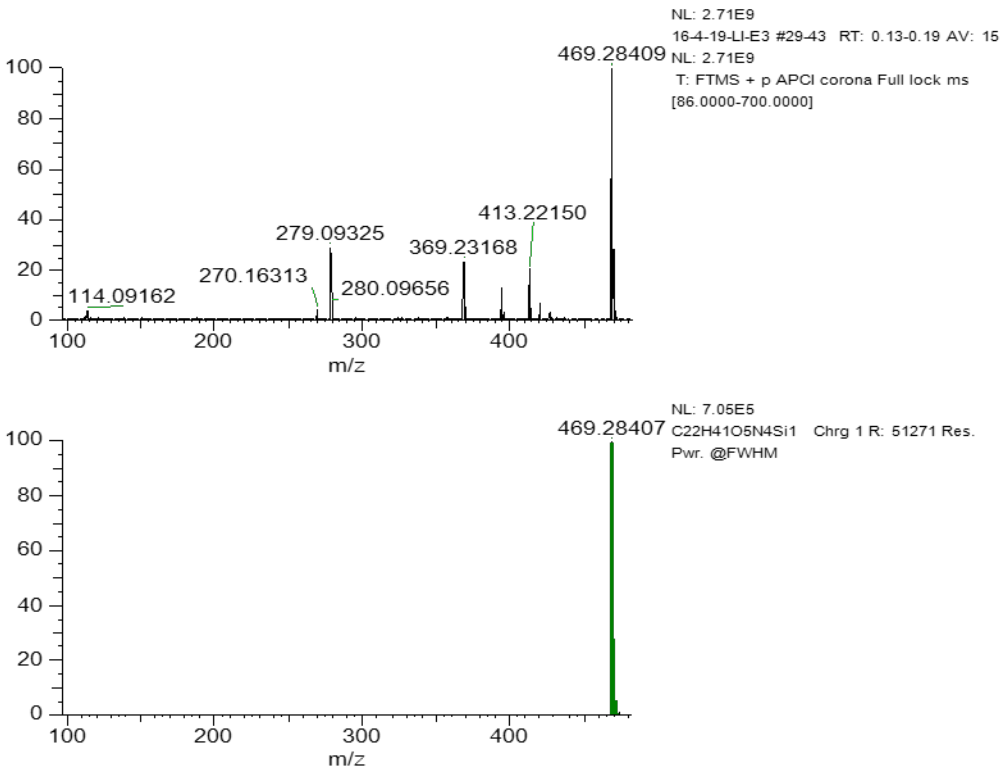


Figure S119. APCI-MS of **4e**.

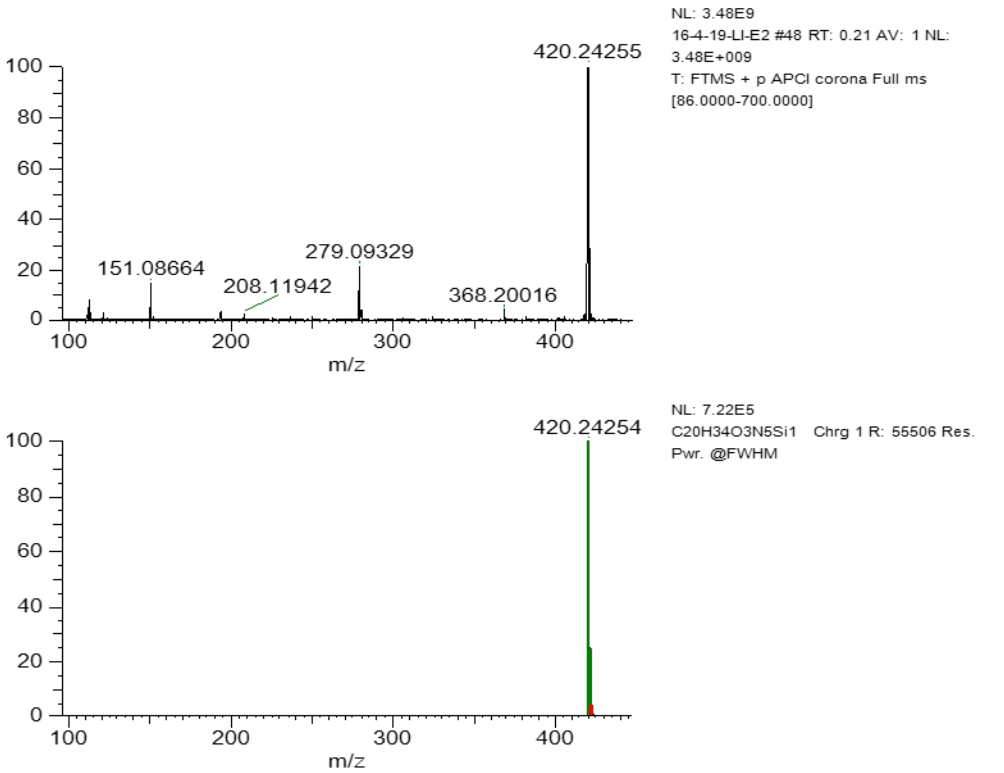


Figure S120. APCI-MS of **4f**.

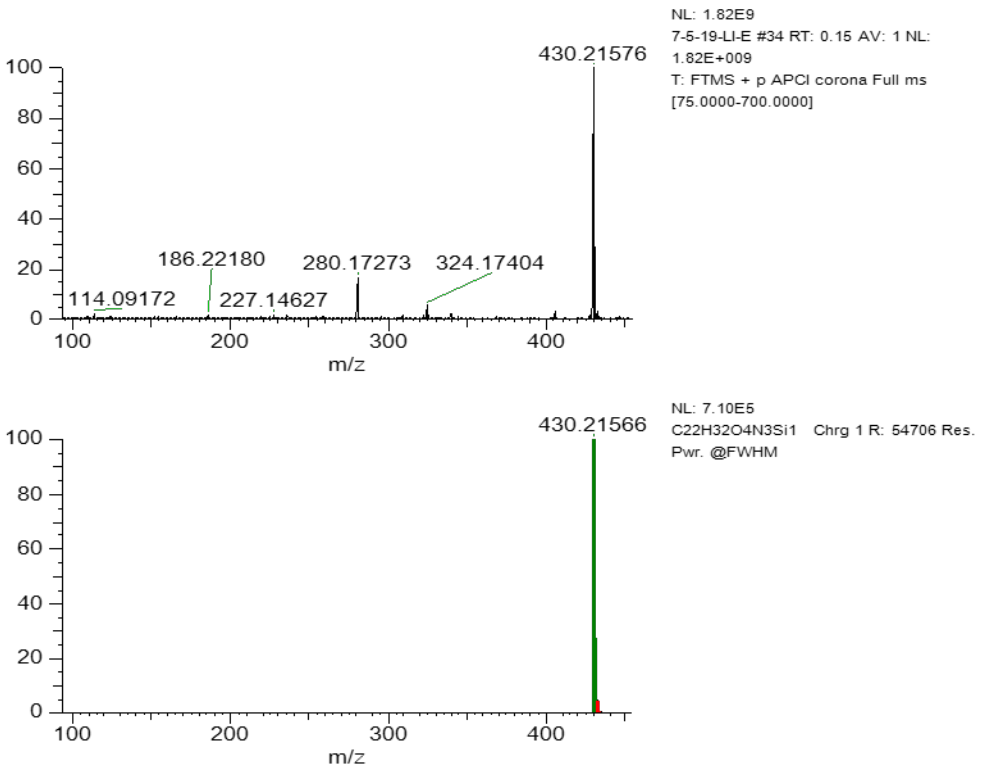


Figure S121. APCI-MS of **4g**.

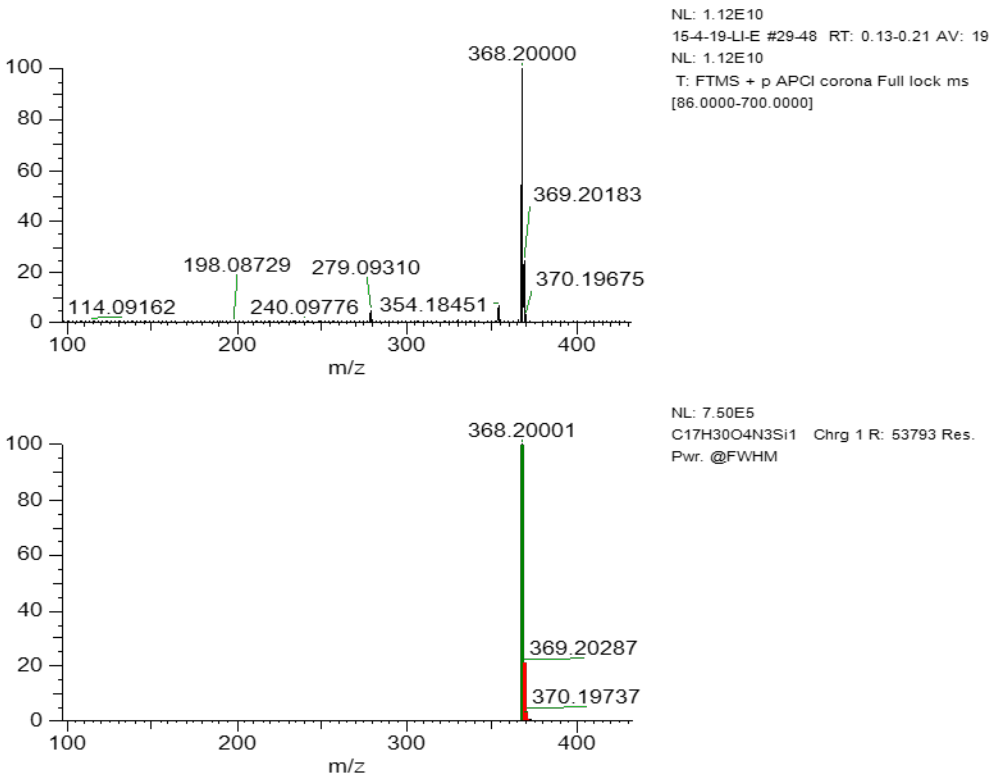


Figure S122. APCI-MS of **4h**.

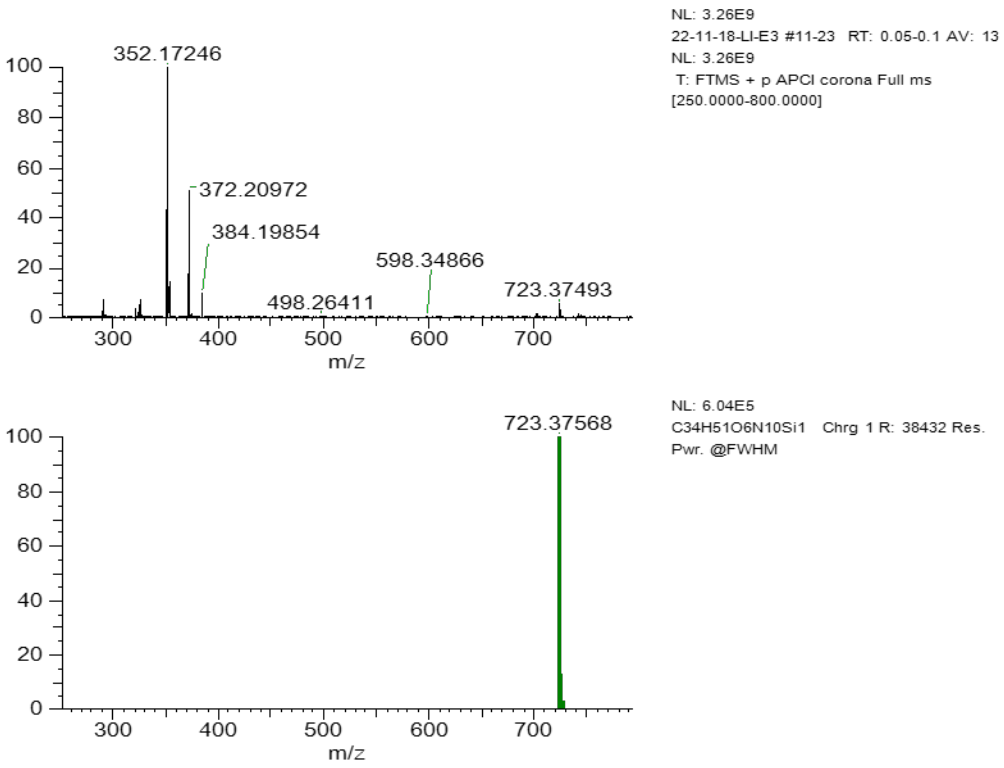


Figure S123. APCI-MS of *rac*-**FE**.

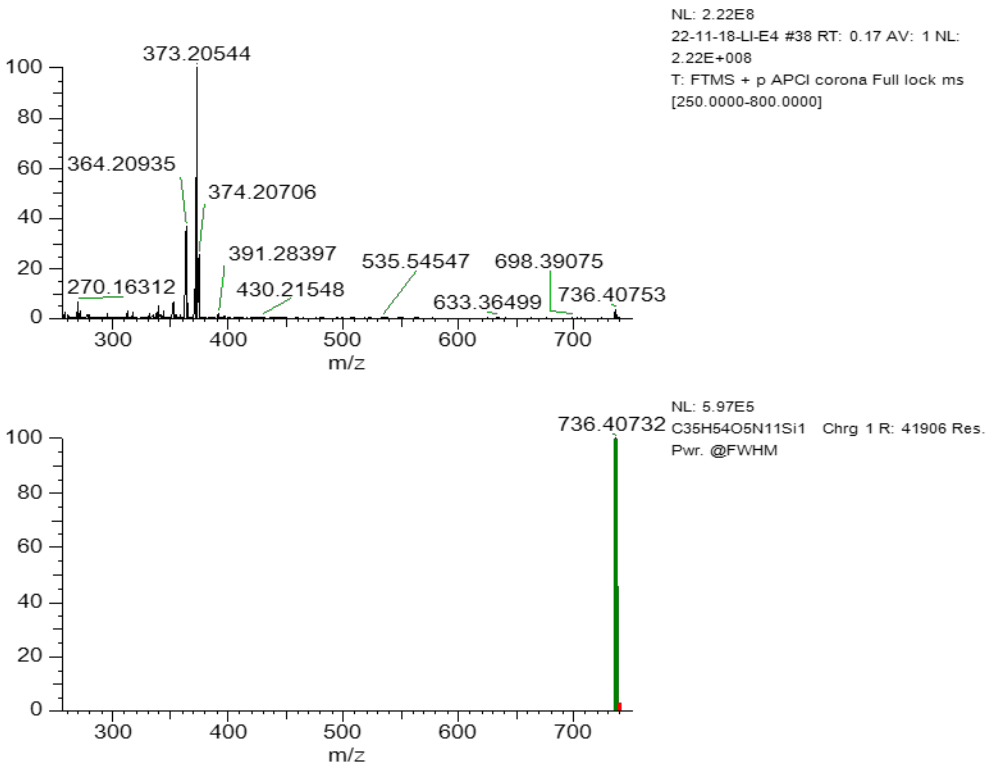


Figure S124. APCI-MS of *rac*-**PB**.

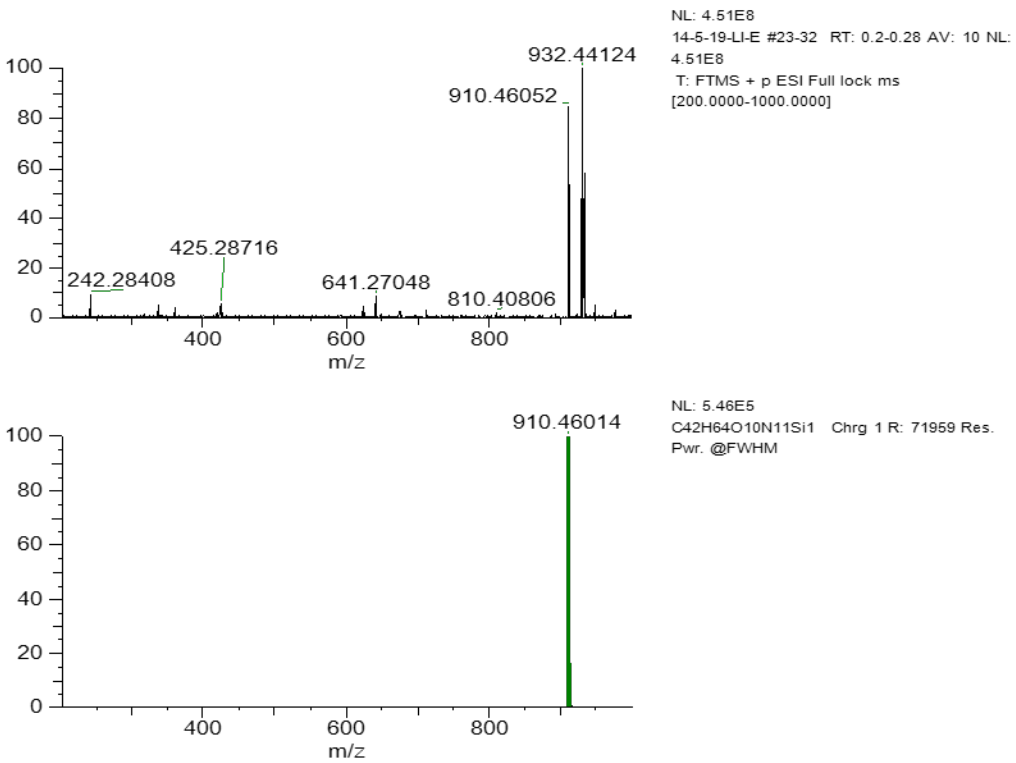


Figure S125. APCI-MS of **A(Boc)O(Bz)**.

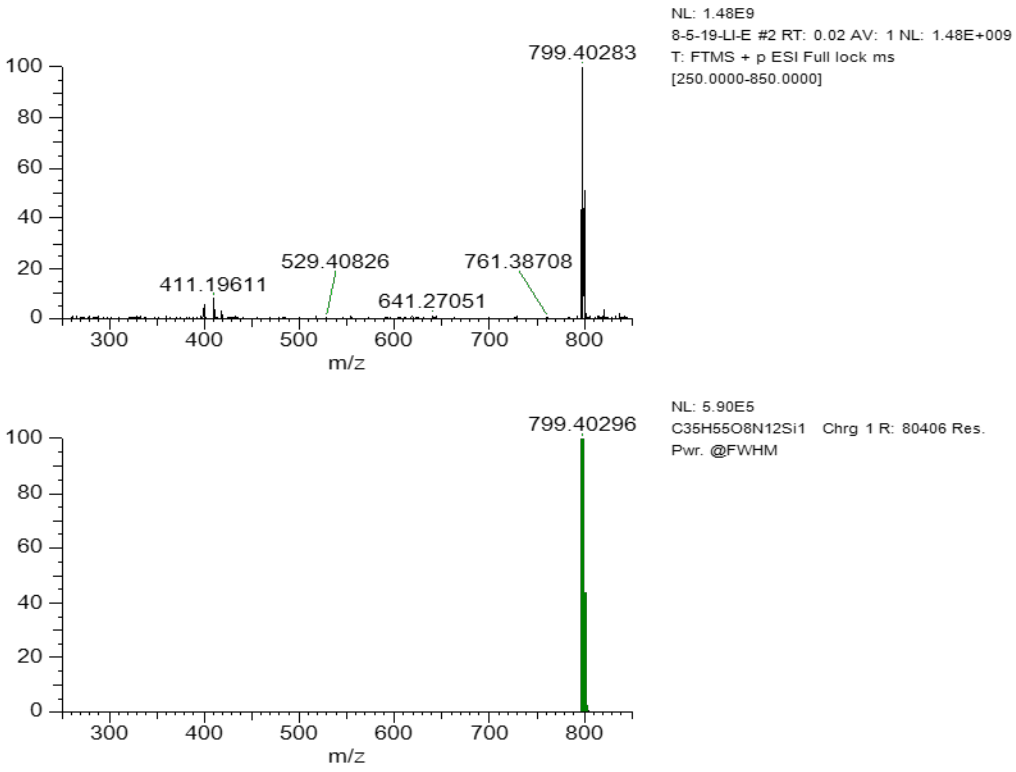


Figure S126. APCI-MS of **IK(Et)**.

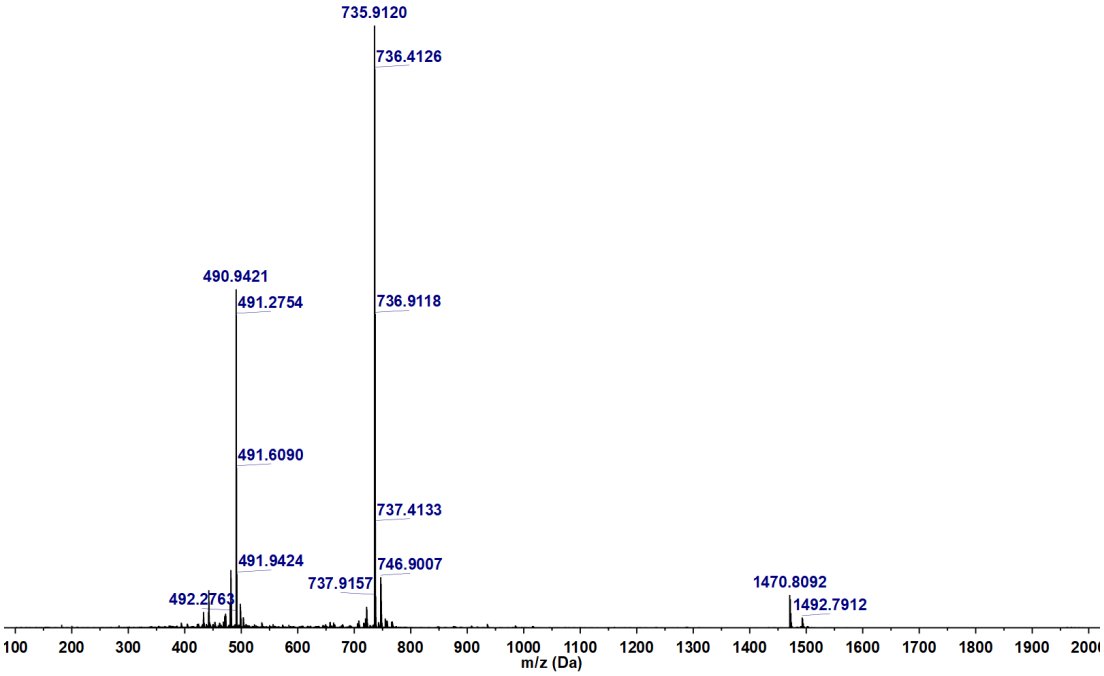


Figure S127. ESI-MS of *rac*-**FEPB**.

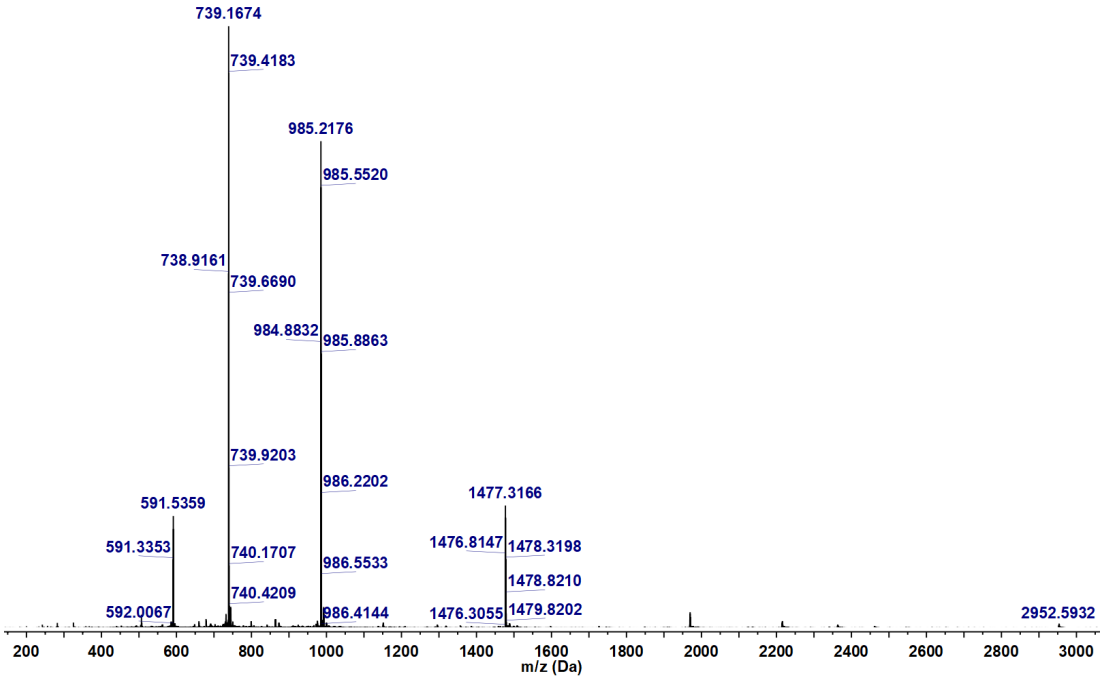


Figure S128. ESI-MS of *rac*-**FEPBFEPB**.

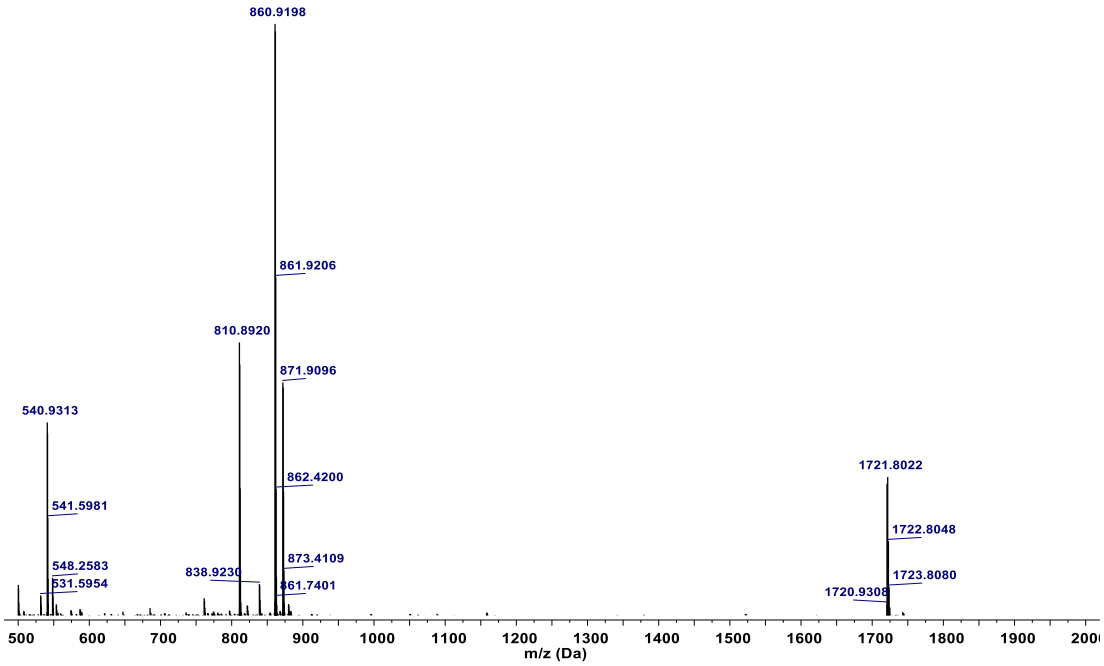


Figure S129. ESI-MS of **A(Boc)O(Bz) IK(Et)**.

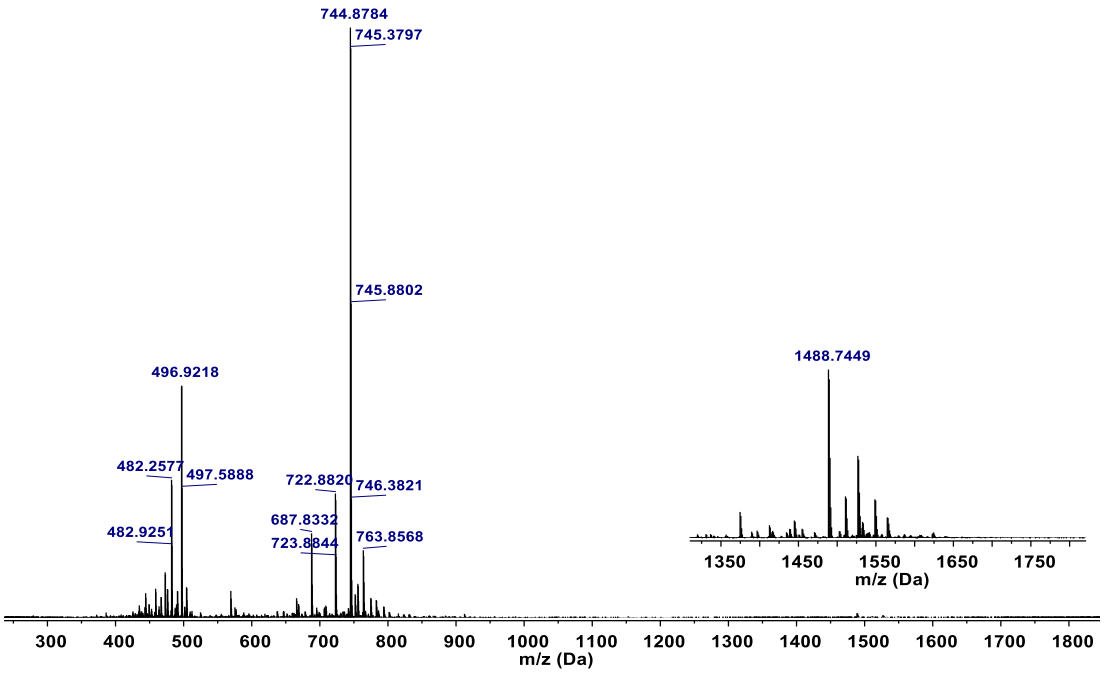


Figure S130. ESI-MS of **AOIK**.

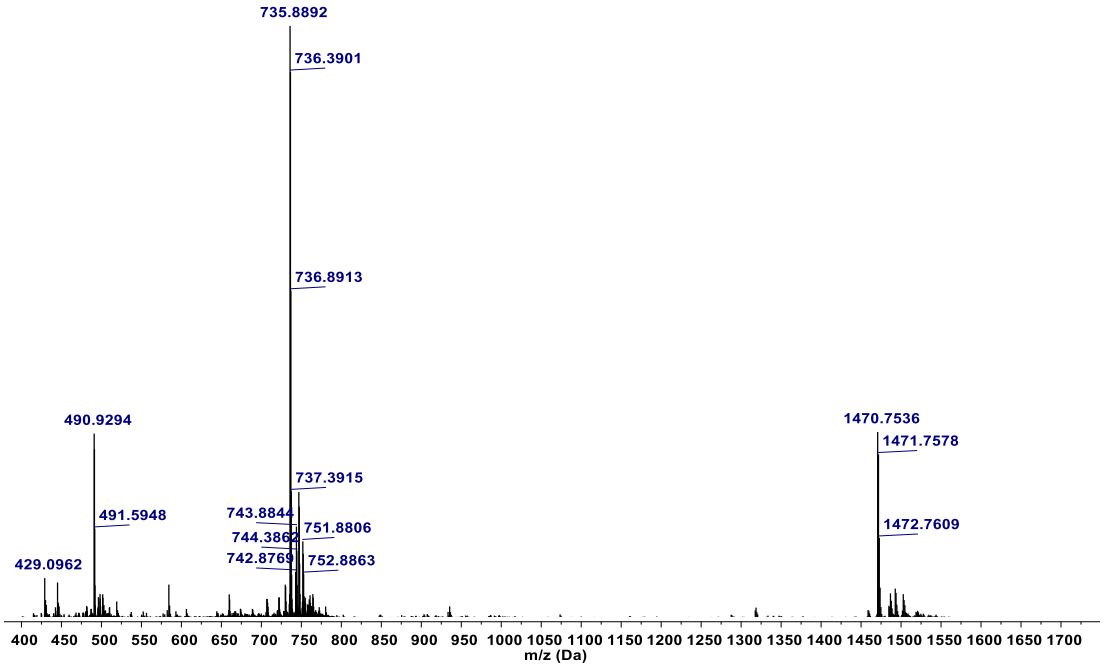


Figure S131. ESI-MS of (*R,R,R,R*)-**FEPB**.

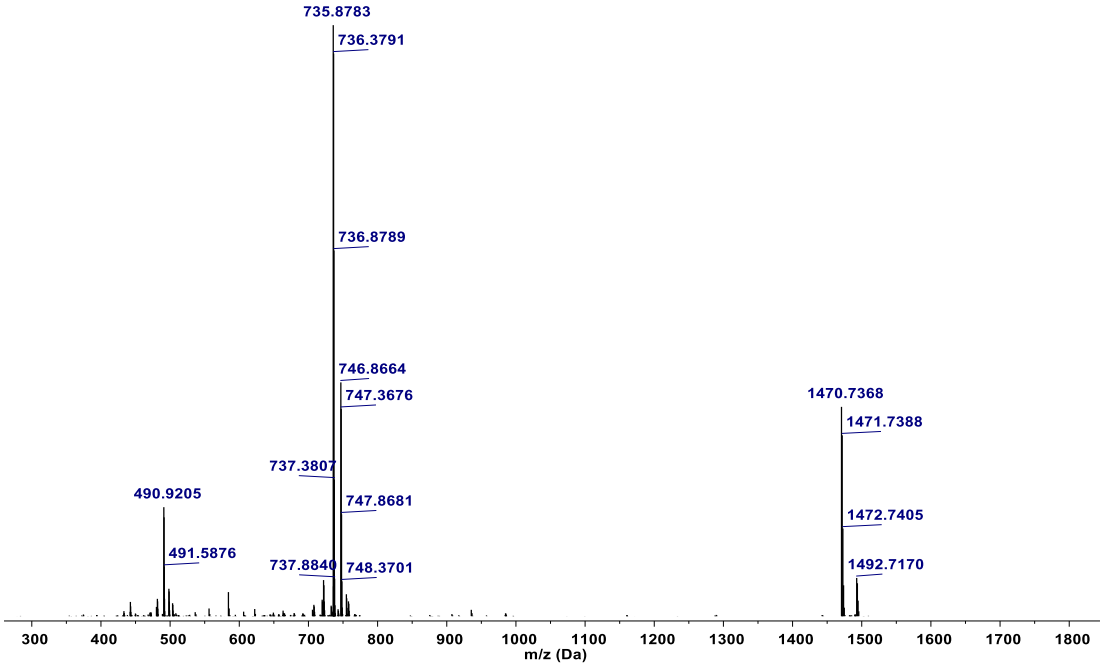


Figure S132. ESI-MS of (*S,S,S,S*)-**FEPB**.

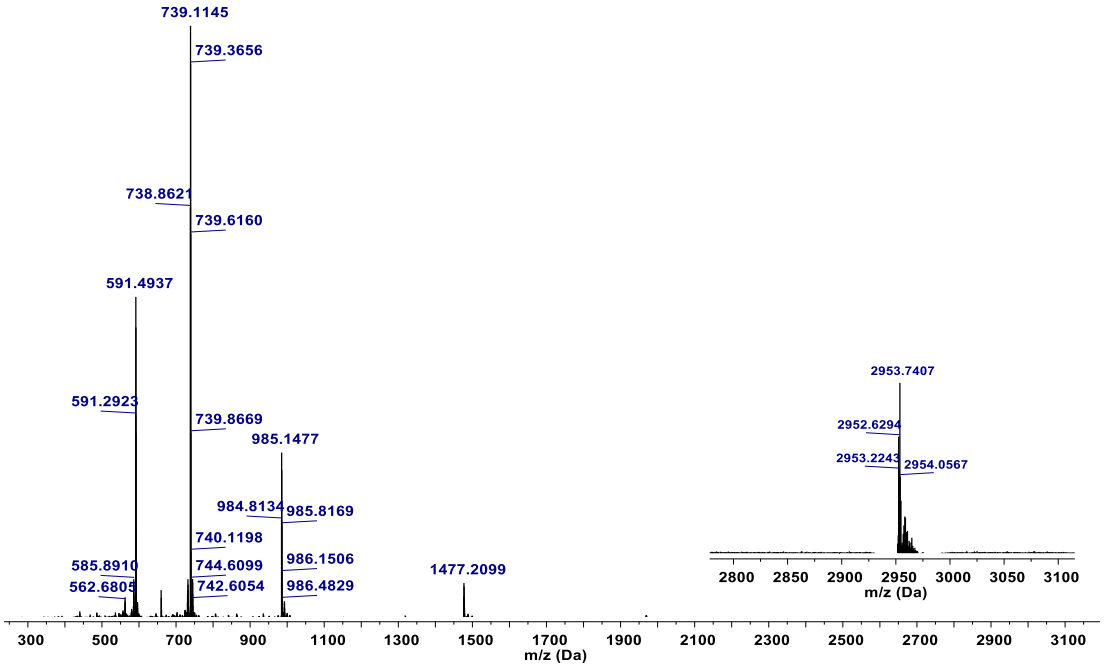


Figure S133. ESI-MS of (*R,R,R,R,S,S,S,S*)-**FEPBFEPB**.

4.2 ESI-MS/MS

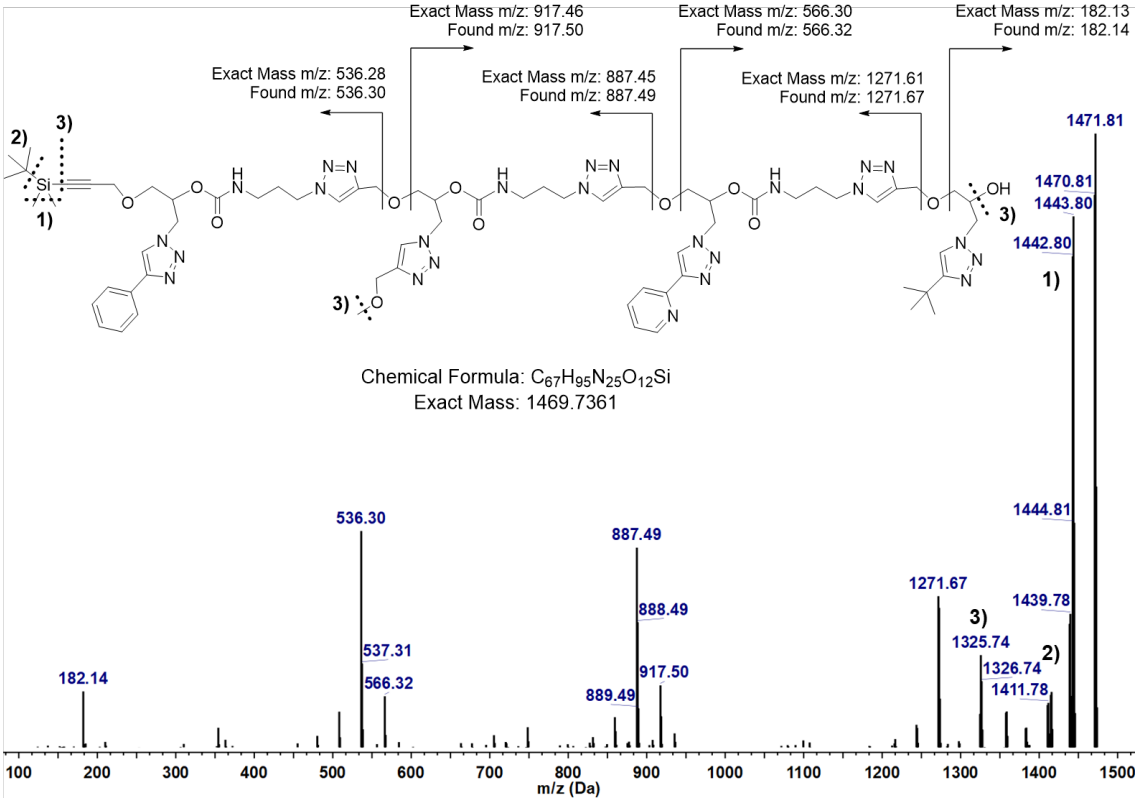


Figure S134. ESI-MS/MS of *rac*-**FEPB**.

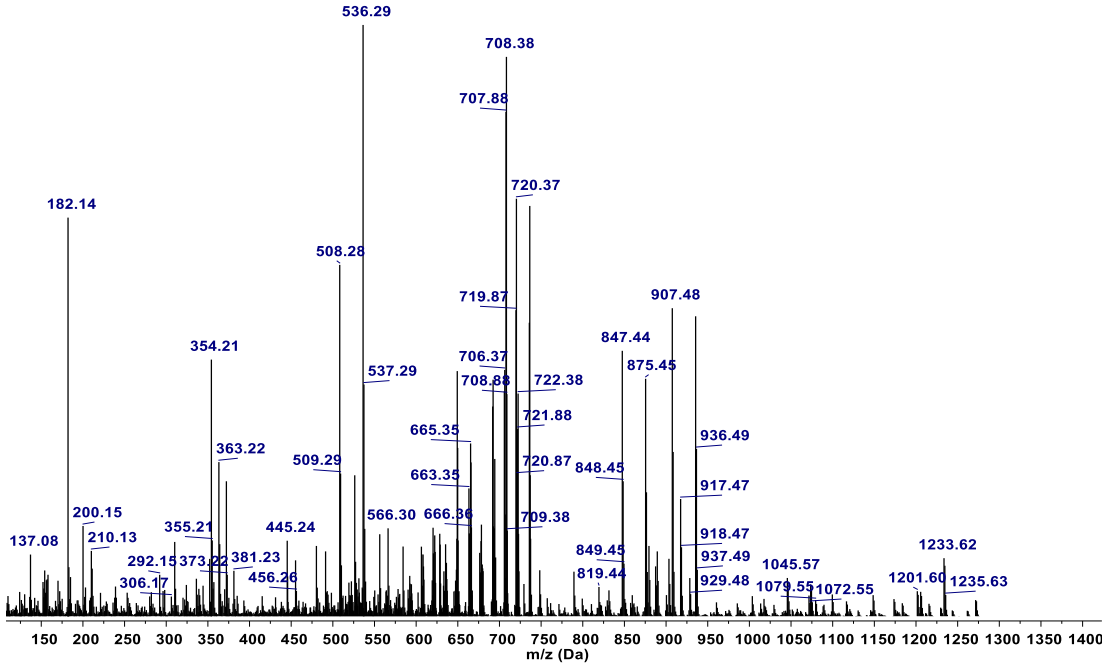


Figure S135. ESI-MS/MS of (*R,R,R,R*)-**FEPB**.

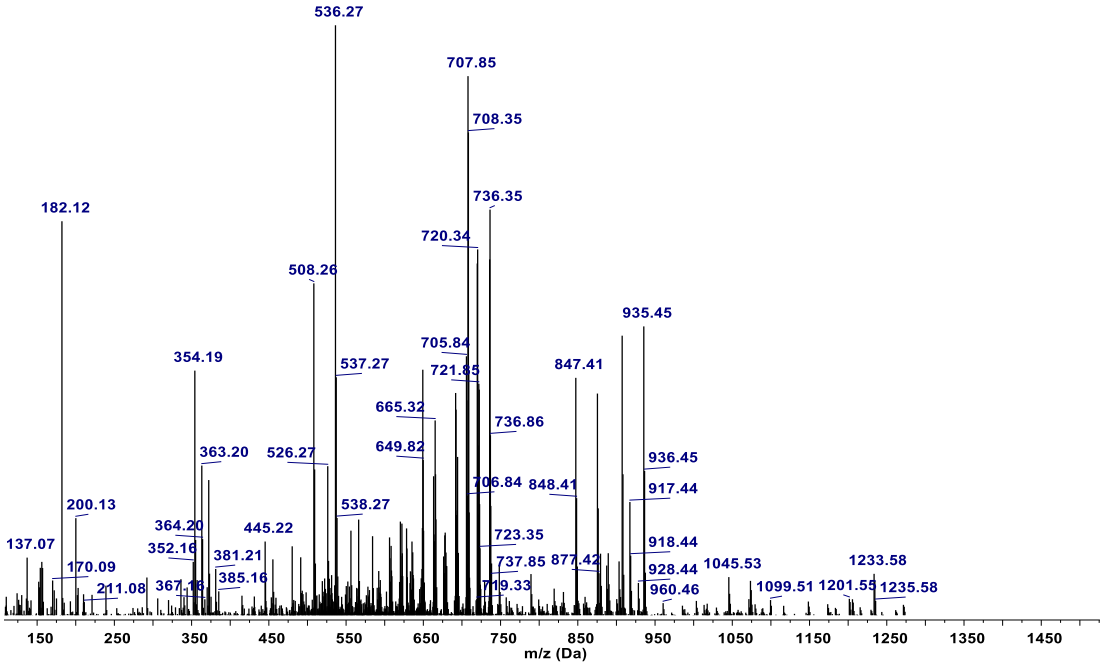


Figure S136. ESI-MS/MS of (*S,S,S,S*)-**FEPB**.

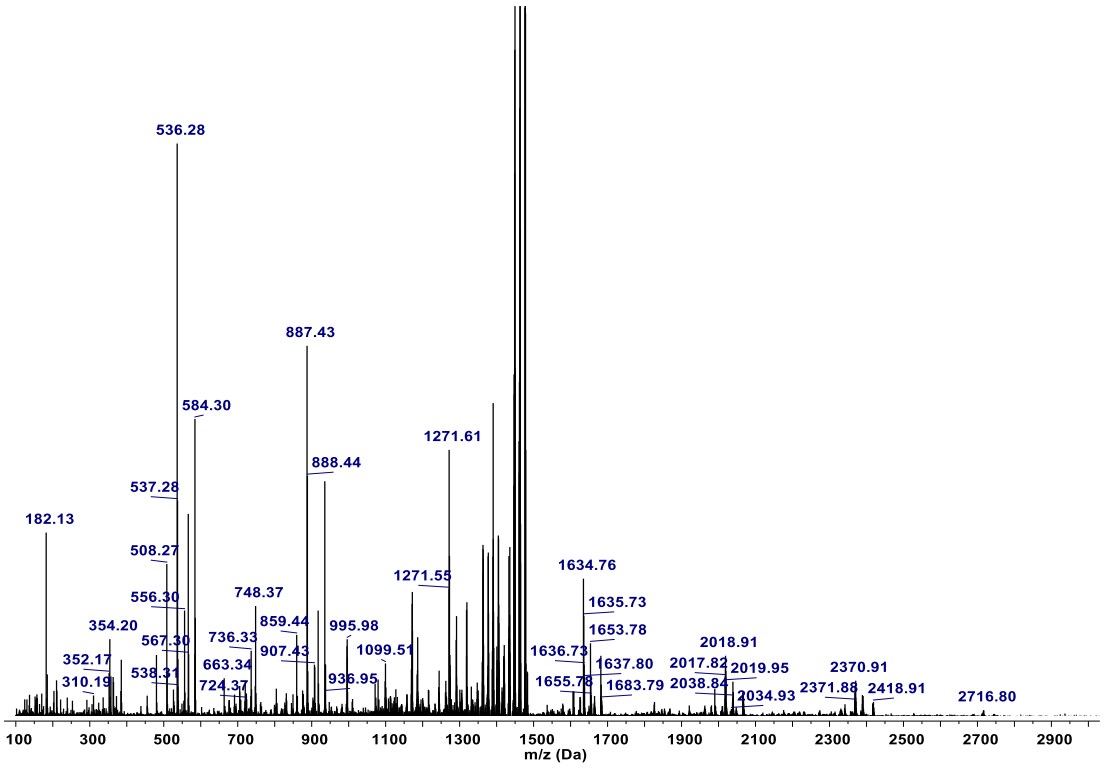


Figure S137. ESI-MS/MS of (*R,R,R,R,S,S,S,S*)-**FEPBFEPB**.

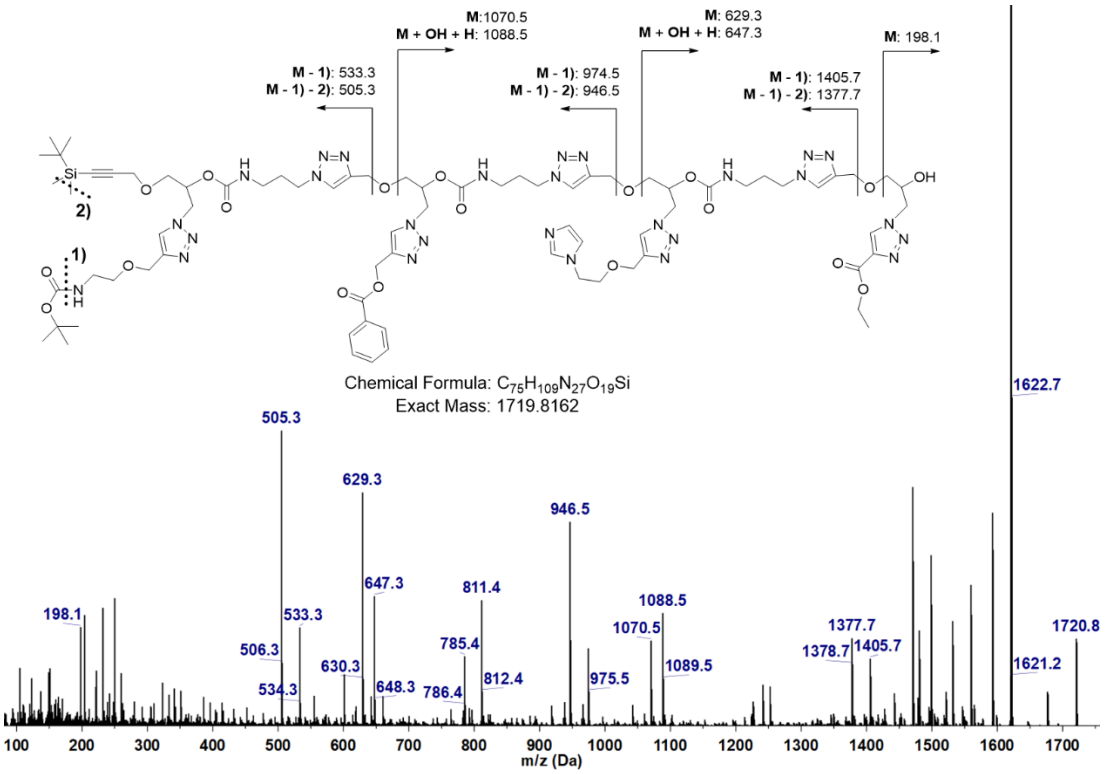


Figure S138. ESI-MS/MS of **A(Boc)O(Bz) IK(Et)**.

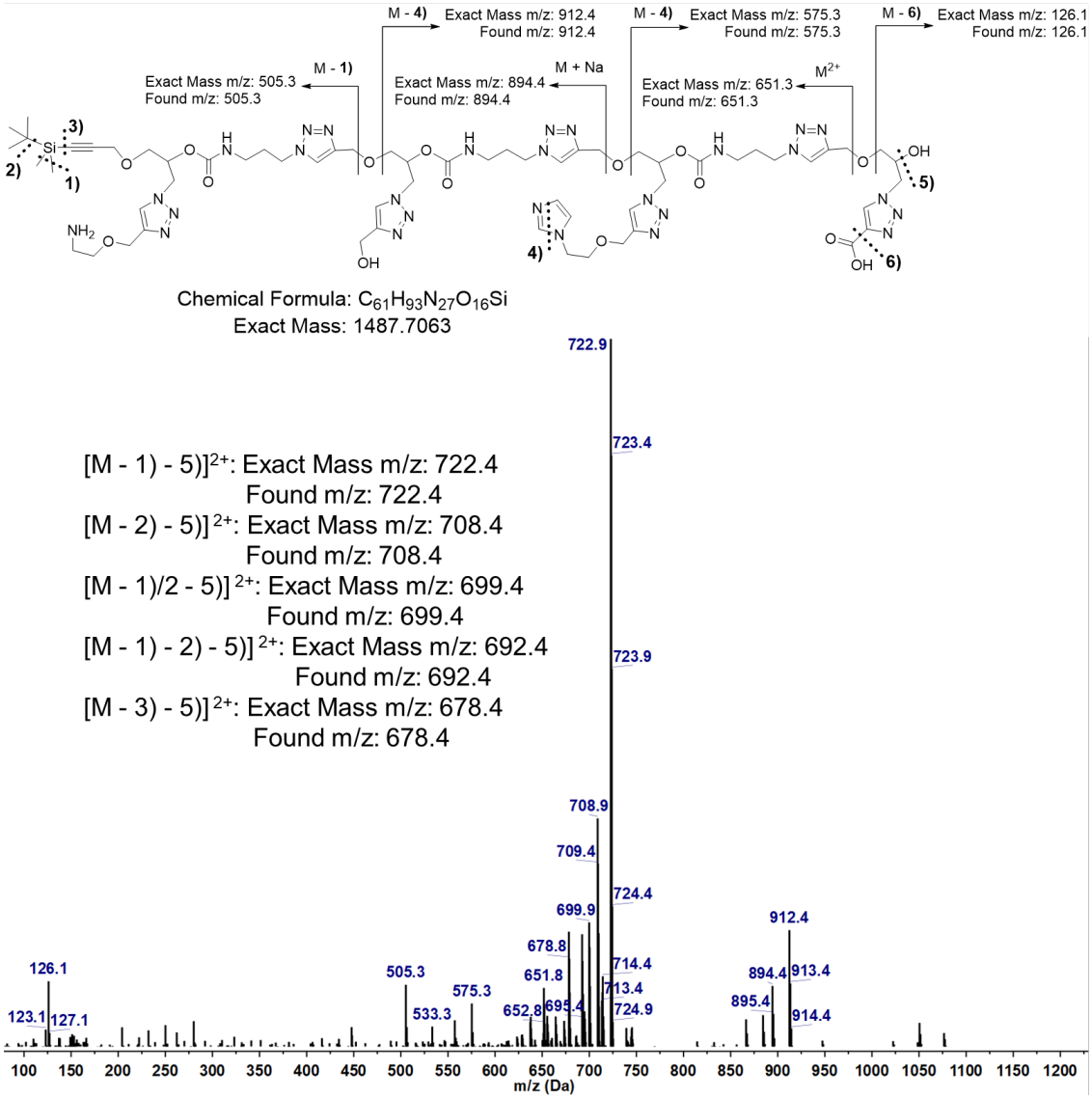


Figure S139. ESI-MS/MS of **AOIK** in positive mode.

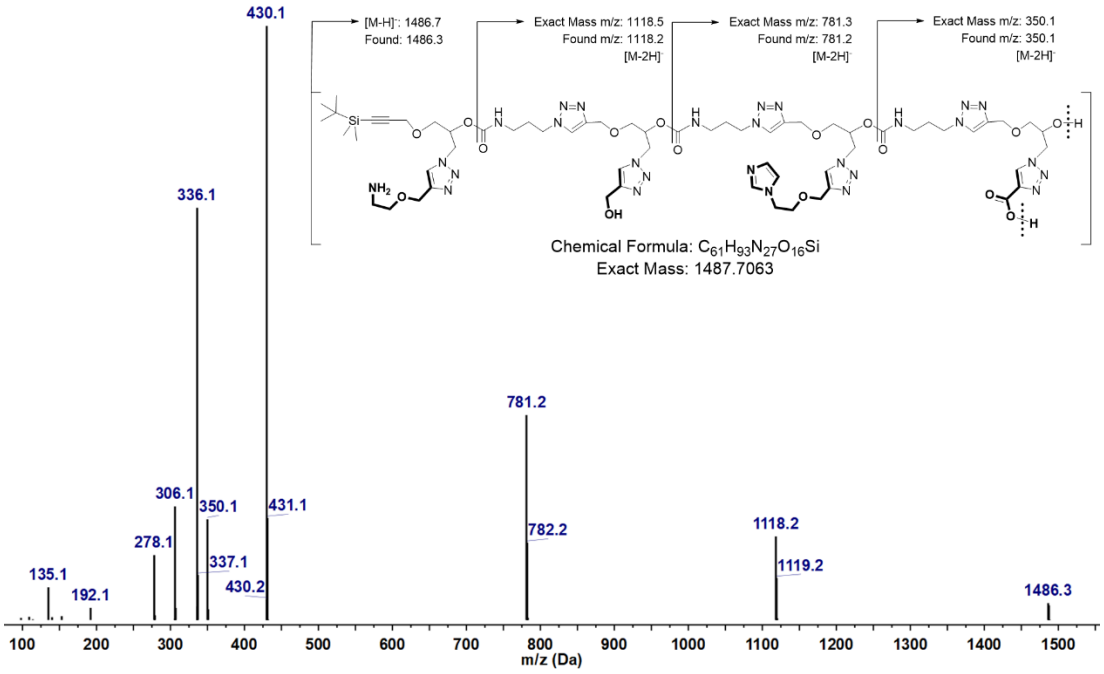


Figure S140. ESI-MS/MS of **AOIK** in negative mode.

5 CHIRAL HPLC

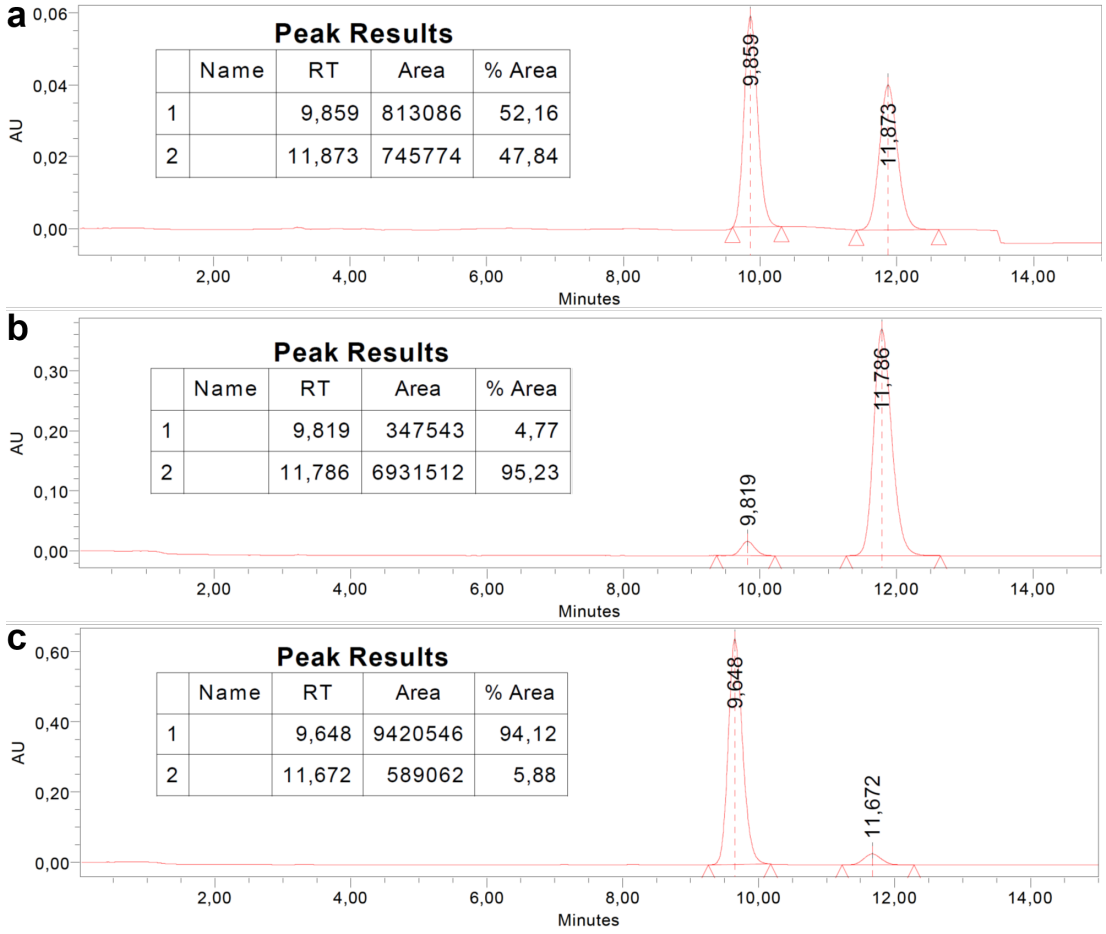


Figure S141. Chiral HPLC traces of monomer *rac*-**4a** (a), (*R*)-**4a** (b) and (*S*)-**4a** (c) in isohexane/EtOH (v/v = 90/10).

6 UV-VIS ABSORPTION AND CIRCULAR DICHROISM

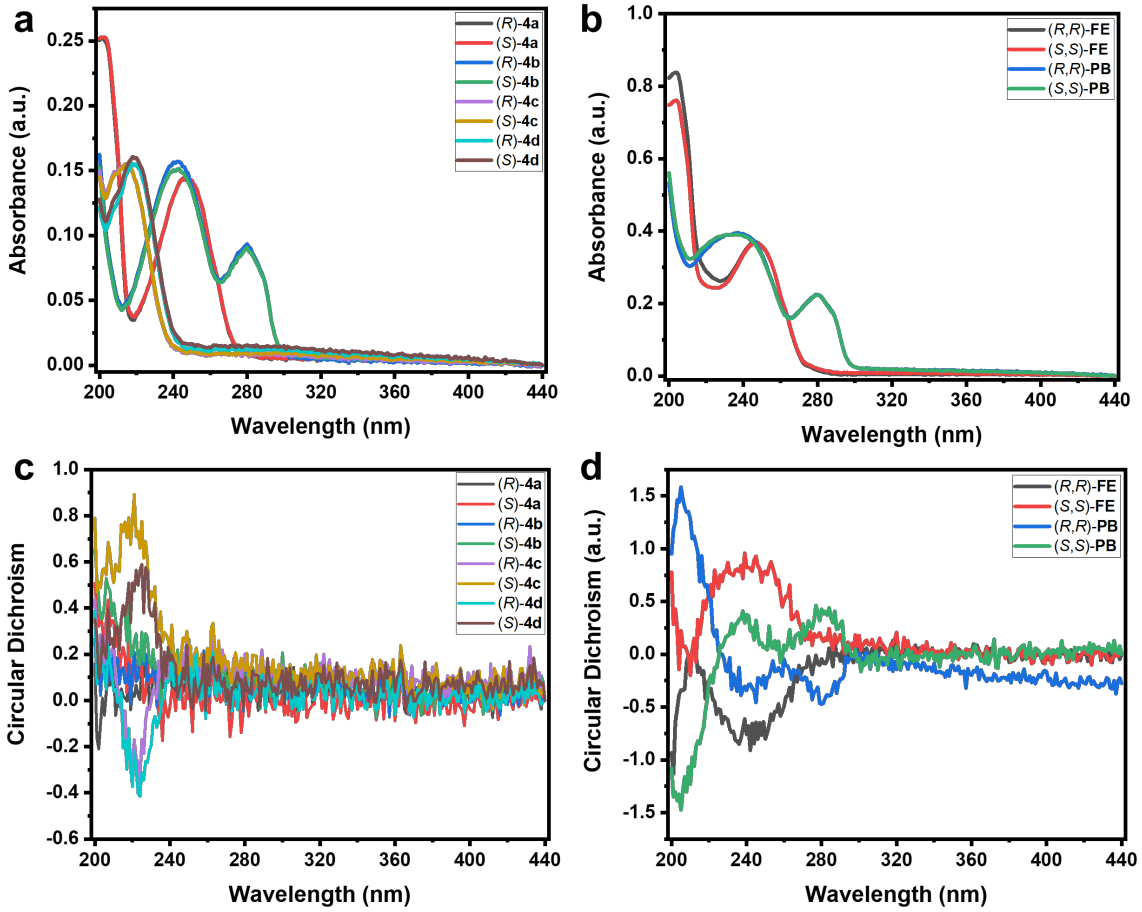


Figure S142. (a,b) UV-vis absorption and (c,d) Circular Dichroism spectra of stereocontrolled monomers (a,c) and stereocontrolled dimers (b,d) in CH_3CN (concentration: 30 μM).

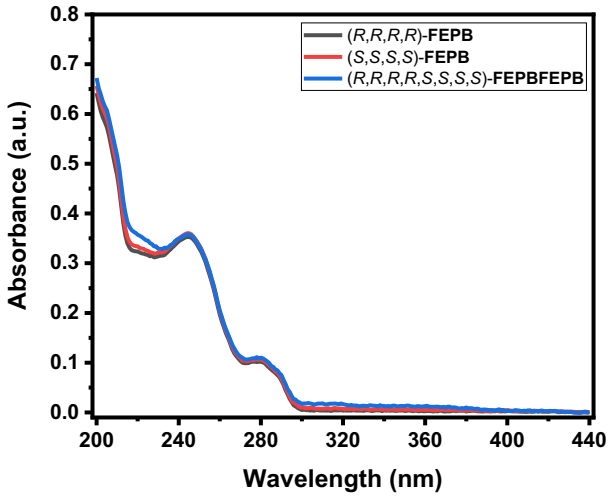


Figure S143. UV-vis absorption spectra of stereocontrolled tetramers (*R*,*R*,*R*,*R*)-**FEPB** (30 μM), (*S*,*S*,*S*,*S*)-**FEPB** (30 μM) and octamer (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB** (15 μM) in CH_3CN.

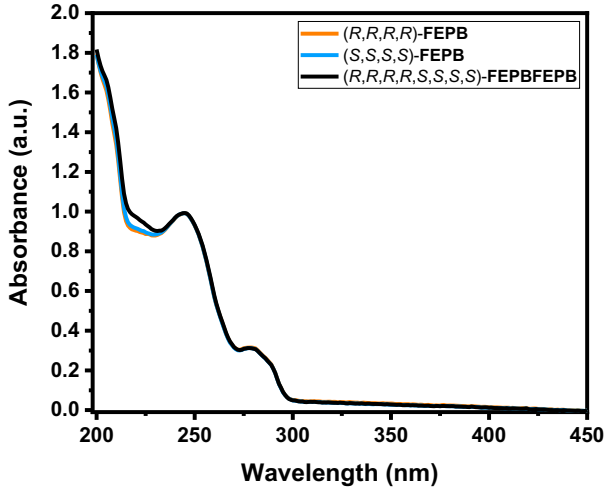


Figure S144. UV-vis absorption spectra of stereospecific tetramers (*R*,*R*,*R*,*R*)-**FEPB** (150 μM), (*S*,*S*,*S*,*S*)-**FEPB** (150 μM) and octamer (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB** (75 μM) in CH_3CN.

7 ALL-ATOM MOLECULAR DYNAMICS (MD) SIMULATIONS

The starting conformation of the (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB** octamer was built within BIOVIA Discovery Studio Visualizer.[7] All calculations were then achieved with the GPU version of AMBER16 package.[8] The AM1-BCC method, as implemented in the antechamber module of AMBER16, was used to calculate atomic charges of the octamer [9] whereas the GAFF 2.1 Force Field (FF) was employed for other force field parameters.[10] Molecular mechanics calculations were performed to optimize the geometry of the octamer molecule. For this, a two-step minimization procedure was considered, i.e., 2000 steps of steepest descent optimization followed by 8000 steps conjugate gradient optimization. In order to conduct a relevant conformational sampling on the microsecond regime with reasonable computational resources, the MD simulations were achieved in an implicit solvent using the Generalized Born solvation model.[11] A dielectric constant of 36.64 was considered, i.e., the dielectric constant of acetonitrile at room temperature. The MD production stage was performed for a simulation time of 2.5 µs. A 2 fs time step was used as the SHAKE algorithm constrained the length of covalent bonds that involved hydrogen atoms. Temperature was maintained at 293.15 K by using a Langevin thermostat with a damping coefficient of 1.0 ps^{-1}. MD snapshots were recorded each 0.5 ns, resulting in a 5000 frames trajectory at the end of the production MD. For MD simulations of the assemblies of 2 chains and 5 chains, the starting distances between the octamer structures was superior to 25 Å to prevent any bias in the assembly mode due to initial intermolecular interactions before the MD simulations. Trajectory analyses and extraction of MD snapshots were done with the CPPTRAJ AmberTool16 module. Radius of gyration (Rg) was calculated in reference to the heavy atoms, with omissions of hydrogen atoms. Per-monomer Root-Mean-Square-Fluctuations (RMSF) were calculated in reference to the central chiral carbon atoms. Hydrogen bonds were detected by using the default parameters of the *hbond* command implemented in CPPTRAJ, i.e., a distance cutoff between acceptor to donor heavy atoms of 3.0 Å and an angle cutoff of 135°. For rendering of MD snapshots, we used PyMOL 2.2.0.[12] In-house R scripts were used for statistical analyses of the raw data issued from MD trajectories.[13]

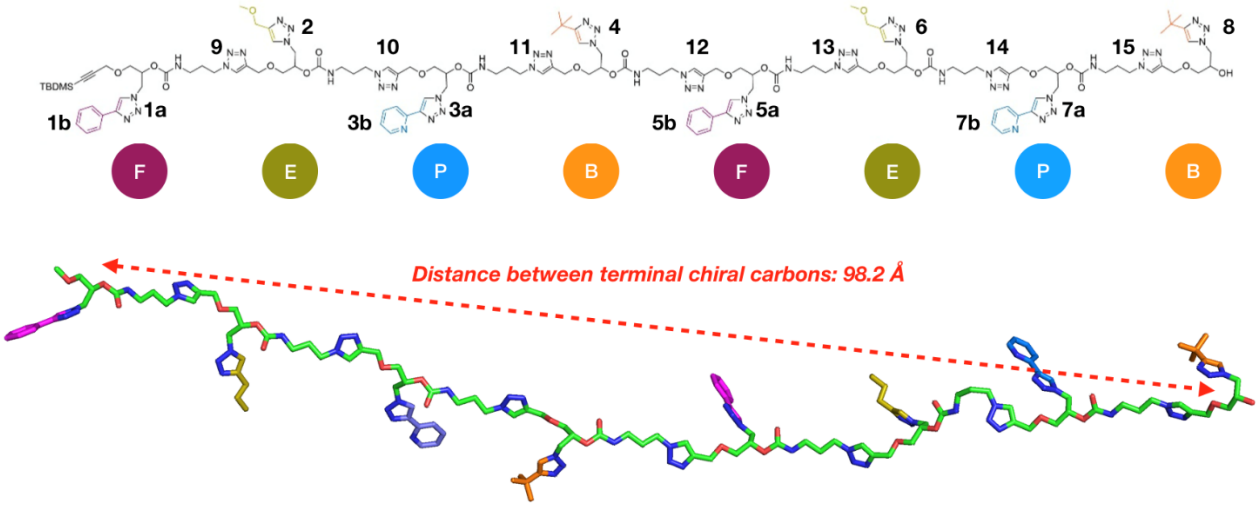
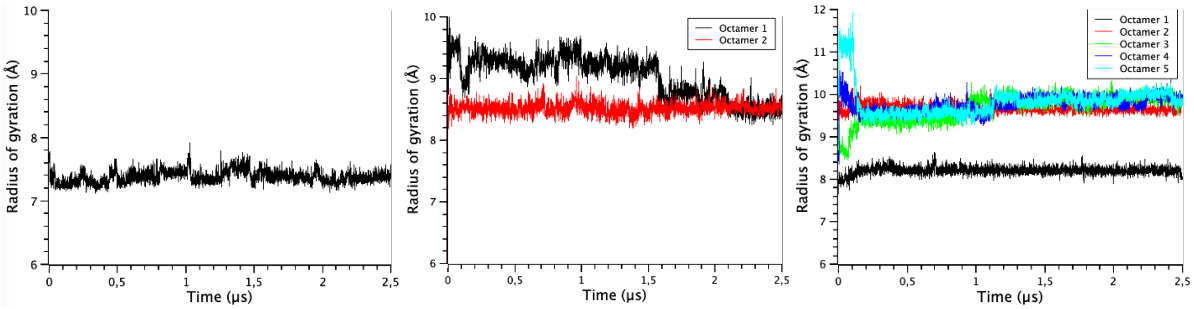


Figure S145. Top: chemical structure of the modeled (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-FEPBFEPB octamer. The labelling corresponds to the aromatic groups discussed in the text (**1-8** for side-chain aromatic groups, **9-15** for backbone aromatic groups). Bottom: starting elongated conformation for MD simulations.



System	Octamer index	0-2.5 μs		0-0.5 μs		2.0-2.5 μs	
		Avg. (Å)	St.Dev. (Å)	Avg. (Å)	St.Dev. (Å)	Avg. (Å)	St.Dev. (Å)
1-chain	1	7.4	0.1	7.4	0.1	7.3	0.1
2-chains	1	9.0	0.3	9.3	0.2	8.5	0.1
	2	8.5	0.1	8.5	0.1	8.5	0.1
5-chains	1	8.2	0.1	8.2	0.1	8.2	0.1
	2	9.7	0.1	9.7	0.1	9.6	0.1
	3	9.7	0.3	9.2	0.3	9.9	0.1
	4	9.8	0.2	9.7	0.2	9.9	0.1
	5	9.8	0.4	9.9	0.7	10.0	0.1

Figure S146. Top: Radii of gyration throughout MD time for 1 chain (left), and in assemblies of 2 chains (middle) and 5 chains (right). Bottom: Average and standard deviations of radii of gyration for each individual chain in a single chain or assemblies. Statistics were calculated on the first 500 ns and last 500 ns of the MD simulations.

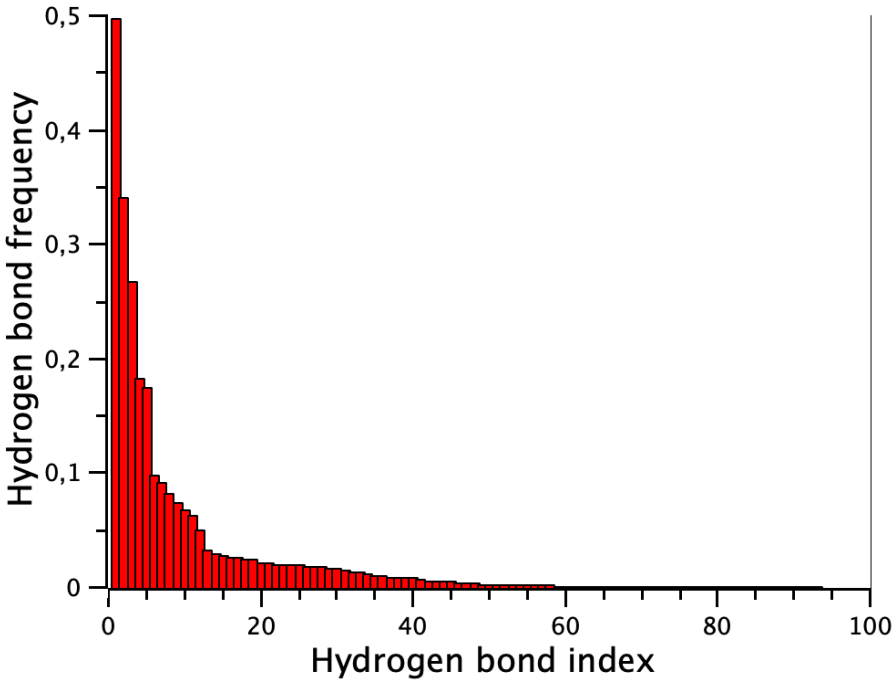
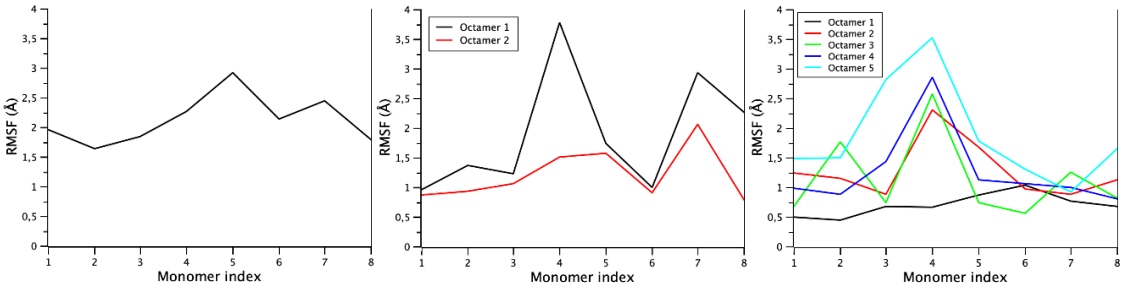


Figure S147. Frequency of the 93 H-bonds detected for all the conformations of a 2.5 µs MD simulation of the (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB** octamer.



System	Octamer index	Avg. (Å)	Min (Å)	Max (Å)
1-chain	1	2.1	1.6 (2)	2.9 (5)
2-chains	1	1.9	1.0 (1)	3.8 (4)
	2	1.2	0.8 (8)	2.1 (7)
5-chains	1	0.7	0.5 (2)	1.0 (6)
	2	1.3	0.9 (7)	2.3 (4)
	3	1.1	0.6 (6)	2.6 (4)
	4	1.3	0.8 (8)	2.9 (4)
	5	1.9	0.9 (7)	3.5 (4)

Figure S148. Top: Root Mean Square Fluctuations (RMSF) profiles per monomer issued from MD simulations of 1 chain (left), and assemblies of 2 chains (middle) and 5 chains (right). Bottom: Statistics with average, minimum and maximum RMSF values.

8 HPLC OF (*R*,*R*,*R*,*R*)-FEPB, (*S*,*S*,*S*,*S*)-FEPB AND (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-FEPBFEPB OLIGOMERS

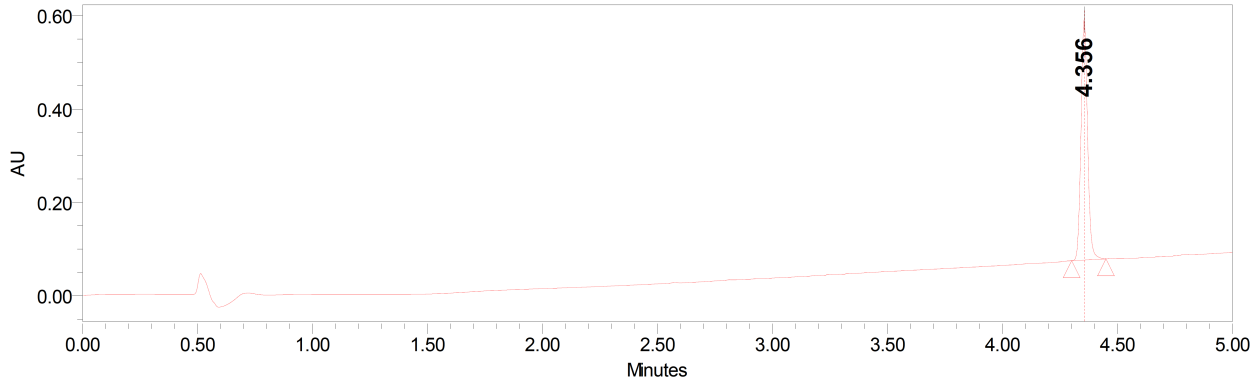


Figure S149. HPLC trace of (*R*,*R*,*R*,*R*)-**FEPB**.

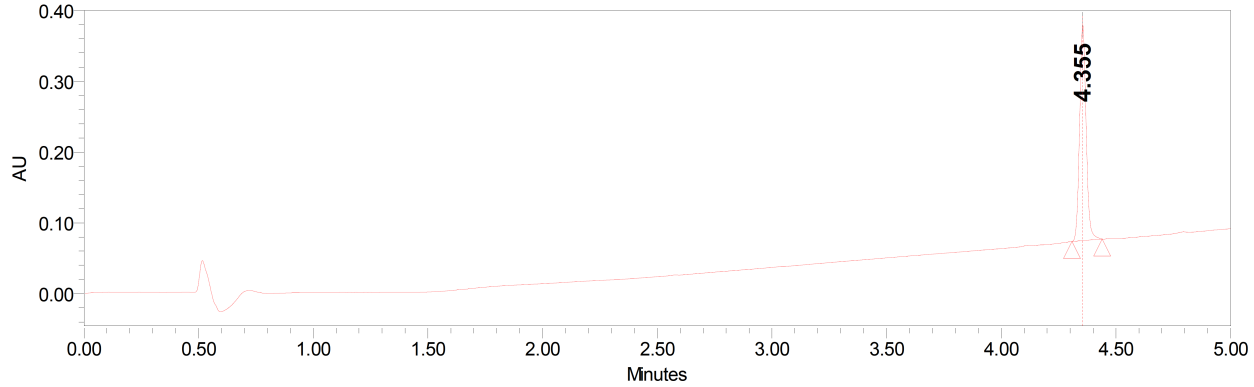


Figure S150. HPLC trace of (*S*,*S*,*S*,*S*)-**FEPB**.

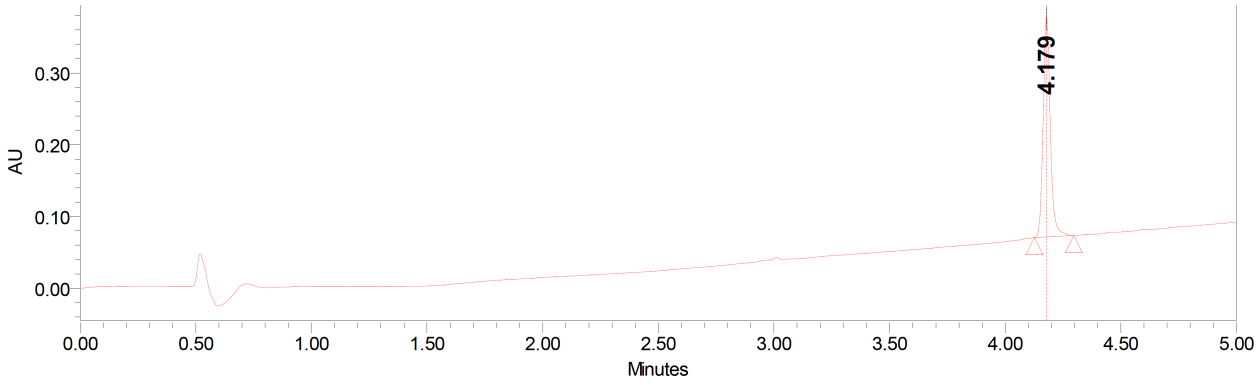


Figure S151. HPLC trace of (*R*,*R*,*R*,*R*,*S*,*S*,*S*,*S*)-**FEPBFEPB**.

9 REFERENCES

(1) Barnes, J. C.; Ehrlich, D. J.; Gao, A. X.; Leibfarth, F. A.; Jiang, Y.; Zhou, E.; Jamison, T. F.; Johnson, J. A. *Nat. Chem.* **2015,** *7*, 810-815.

(2) Golder, M. R.; Jiang, Y.; Teichen, P. E.; Nguyen, H. V.; Wang, W.; Milos, N.; Freedman, S. A.; Willard, A. P.; Johnson, J. A. *J. Am. Chem. Soc.* **2018,** *140*, 1596-1599.

(3) Chang, T. C.; Lai, C. H.; Chien, C. W.; Liang, C. F.; Adak, A. K.; Chuang, Y. J.; Chen, Y. J.; Lin, C. C. *Bioconjugate Chem.* **2013,** *24*, 1895-1906.

(4) Goren, K.; Portnoy, M. *Chem. Commun.* **2010,** *46*, 1965-1967.

(5) Shi, Y.; Pierce, J. G. *Org. Lett.* **2015,** *17*, 968-971.

(6) Hatzakis, N. S.; Engelkamp, H.; Velonia, K.; Hofkens, J.; Christianen, P. C.; Svendsen, A.; Patkar, S. A.; Vind, J.; Maan, J. C.; Rowan, A. E.; Nolte, R. J. *Chem. Commun.* **2006**, 2012-2014.

(7) Dassault Systèmes BIOVIA, Discovery Studio, San Diego: Dassault Systèmes.

(8) Case, D. A.; III Cheatham, T. E.; Darden, T.; Gohlke, H.; Luo, R.; Jr Merz, K.; Onufriev, A.; Simmerling, C.; Wang, B.; Woods, R. J. *J. Comput. Chem.* **2005**, *26*, 1668-1688.

(9) Jakalian, A.; Jack, D. B.; Bayly, C. I. *J. Comput. Chem.*, **2002**, *23*, 1623-1641.

(10) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2004**, *25*, 1157−1174.

(11) Hawkins, G.; Cramer, C.; Truhlar, D. *Chem. Phys. Lett*. **1995**, *246*, 122−129.

(12) The Pymol Molecular Graphics System, version 2.0; Schrödinger LLC; www.pymol.org.

(13) R Core Team. R; R Foundation for Statistical Computing: Vienna, Austria, 2013; www.R-project.org