Electronic Supplementary Information

Synthesis of Discrete Catalytic Oligomers and their Potential in Silica-Supported Cooperative Catalysis

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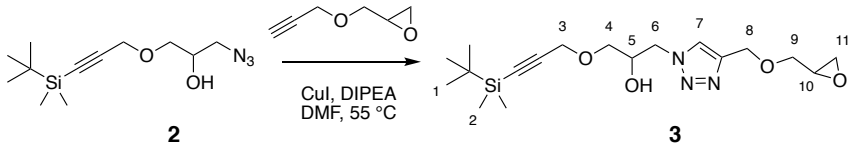
1 General considerations

Reagents were obtained from commercial sources and used without further purification. **1**, **2** **11**, **12** and 2-azidoethylamine were synthesized according to previous literature reports.[1-3] All reactions were carried out under argon. Flash column chromatography was carried out using silica gel 230-400 mesh (Sigma-Aldrich) as the stationary phase. Spherical silica gel (40-75 μm, 100 Å) was purchased from Sorbtech Technologies. Milli-Q water (resistivity 18.2 MΩ.cm) was obtained from a Milli-Q Reference system (Merck). FT-IR was measured on a Thermo Scientific FTIR Nexus 870 spectrometer. TGA was measured on a Mettler Toledo TGA/SDTA 851^e instrument. ICP-AES was performed on a Thermo Scientific ICAP 6500 spectrometer. Prior to analysis, the samples were treated with HNO_3-HF at 120 °C overnight. The residue was taken up in 1 mL HNO_3 and diluted to 25 mL with ultrapure water. NMR spectra were recorded on a Bruker-300 or a Bruker-500 spectrometer. 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: b= broad, s= singlet, d= doublet, t= triplet, q= quartet, quint= quintet, m= multiplet. Compounds with TEMPO radical were mixed with 1,2-diphenylhydrazine (2.0 equiv.) prior to NMR analysis. Specific surface area and pore size were obtained through nitrogen adsorption-desorption experiments using a Micromeritics Tristar 3000. Before analysis, the samples were degassed overnight under vacuum at 60 °C. BET and BJH approaches were applied to process the raw data. X-ray photoelectron spectroscopy (XPS) measurements were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments equipped with a monochromatized microfocused Al X-ray source (1486.6 eV operated at 20 mA and 10 kV). All binding energies were referenced to the C-(C, H) component of the C 1s peak fixed at 284.8 eV. The base pressure in the spectrometer was in the low 10^{-8} Torr range. Peak decomposition was achieved with Casa XPS (Casa Software Ltd., UK). GC was performed on a Shimadzu GC-2010 equipped with a FID detector. Aerobic oxidation experiments were performed under O_2 bubbling (5.5 mL/min) using a SLA5850 thermal mass flow controller from Brooks.

2 Synthesis

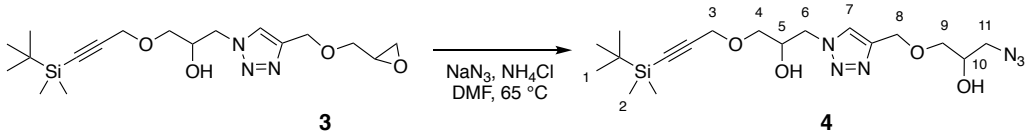
2.1 Chain elongation



2 **3**

To a solution of **2** (4.85 g, 17.96 mmol) in degassed DMF (90 mL) was added glycidyl propargyl ether (2.6 mL, 1.2 equiv.), DIPEA (16.0 mL, 5.0 equiv.) and CuI (341 mg, 0.1 equiv.). The solution was heated at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography over silica gel (ethyl acetate/hexane) to give **3** (5.38 g, 79 %) as a faint yellow oil.

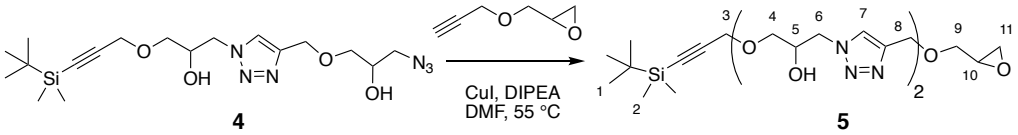
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.70 (s, 1H, H_7), 4.67 and 4.62 (d, AB system, 2H, *J*= 12.0 Hz, H_8), 4.53 (dd, 1H, *J*= 14.0 Hz, *J*= 3.5 Hz, H_6), 4.36 (dd, 1H, *J*= 14.0 Hz, *J*= 7.4 Hz, H_6), 4.19 (bs, 3H, H_{3+5}), 3.82 (dd, 1H, *J*= 11.5 Hz, *J*= 2.8 Hz, H_9), 3.58 (dd, 1H, *J*= 9.7 Hz, *J*= 4.8 Hz, H_4), 3.50 (dd, 1H, *J*= 9.7 Hz, *J*= 5.6 Hz, H_4), 3.41 (dd, 1H, *J*= 11.5 Hz, *J*= 6.1 Hz, H_9), 3.14 (ddd, 1H, *J*= 6.8 Hz, *J*= 5.1 Hz, *J*= 2.7 Hz, H_{10}), 2.77 (dd, 1H, *J*= 4.9 Hz, *J*= 4.2 Hz, H_{11}), 2.59 (dd, 1H, *J*= 5.0 Hz, *J*= 2.7 Hz, H_{11}), 0.90 (s, 9H, H_1), 0.09 (s, 6H, H_2); **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 144.6, 124.4, 101.4, 90.7, 77.4, 71.2, 70.7, 69.1, 64.6, 59.6, 53.1, 50.8, 44.3, 26.1, 16.5, -4.6; **HRMS** *m/z*= 382.2155 (calcd. for 382.2157 $C_{18}H_{32}O_4N_3{}^{28}Si$ $[M+H]^+$).



3 **4**

To a solution of **3** (6.44 g, 16.86 mmol) in DMF (45 mL) was added NaN_3 (6.60 g, 6.0 equiv.) and NH_4Cl (1.40 g, 1.5 equiv.). The reaction was heated to 65 °C and allowed to stir for 6 h. The solvent was evaporated and the residue was dissolved in water (80 mL) and extracted with ethyl acetate (4 × 100 mL), dried over Na_2SO_4 and concentrated under vacuum and purified by flash column chromatography (ethyl acetate/hexane) to give **4** (5.34 g, 74 %) as a faint yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.69 (s, 1H, H_7), 4.62 (bs, 2H, H_8), 4.54 (dd, *J*= 14.0 Hz, *J*= 3.1 Hz, H_6), 4.35 (dd, 1H, *J*= 14.0 Hz, *J*= 7.5 Hz, H_6), 4.18 (bs, 3H, H_{3+5}), 3.92 (dd, 1H, *J*= 10.3 Hz, *J*= 5.1 Hz, H_{10}), 3.79 (bs, 1H, H_{OH}), 3.61-3.48 (m, 5H, H_{4+9+OH}), 3.32-3.30 (m, 2H, H_{11}), 0.89 (s, 9H, H_1), 0.08 (s, 6H, H_2); **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 144.3, 124.3, 101.5, 90.5, 77.4, 71.9, 70.8, 69.6, 69.1, 64.6, 59.5, 53.5, 53.2, 26.1, 16.5, -4.7; **HRMS** *m/z*= 425.2327 (calcd. for 425.2327 $C_{18}H_{33}O_4N_6{}^{28}Si$ $[M+H]^+$).



4 **5**

To a solution of **4** (5.34 g, 12.59 mmol) in degassed DMF (125 mL) was added glycidyl propargyl ether (1.8 mL, 1.2 equiv.), DIPEA (11.2 mL, 5.0 equiv.) and CuI (239 mg, 0.1 equiv.). The solution was heated at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (methanol/DCM) to give **5** (3.75 g, 56 %) as a faint yellow oil.

^{1}H NMR (300 Hz, $CDCl_3$): δ= 7.72 (s, 1H, H_7), 7.69 (s, 1H, H_7), 4.58 and 4.55 (bs, 4H, H_8), 4.53-4.28 (m, 6H, H_{6+OH}), 4.18 (bs, 3H, H_{3+5}), 4.15-4.06 (m, 1H, H_5), 3.78 (ddd, 1H, *J*= 11.5 Hz, *J*= 2.7 Hz, *J*= 0.9 Hz, H_9), 3.55 (dd, 2H, *J*= 5.1 Hz, *J*= 0.9 Hz, H_4), 3.49-3.32 (m, 3H, H_{4+9}), 3.14-3.08 (m, 1H, H_{10}), 2.74 (dd, 1H, *J*= 4.8 Hz, *J*= 4.5 Hz, H_{11}), 2.56 (dd, 1H, *J*= 5.0 Hz, *J*= 2.7 Hz, H_{11}), 0.89 (s, 9H, H_1), 0.07 (s, 6H, H_2); **^{13}C NMR** (75 Hz, $CDCl_3$): δ= 144.3, 144.0, 124.5, 101.6, 90.4, 77.4, 71.1, 71.0 (×2), 68.9 (×2), 64.5, 64.4, 59.5, 53.5, 52.9, 50.8, 44.3, 26.1, 16.5, -4.7; **HRMS** *m/z*= 537.2842 (calcd. for 537.2851 $C_{24}H_{41}O_6N_6{}^{28}Si$ $[M+H]^+$).

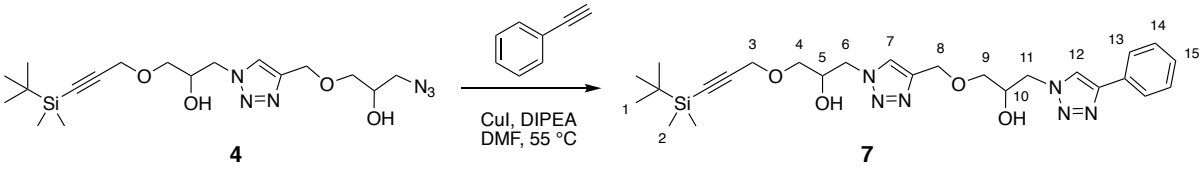
5 **6**

To a solution of **5** (3.40 g, 6.33 mmol) in DMF (15 mL) was added NaN_3 (2.50 g, 6.0 equiv.) and NH_4Cl (0.51 g, 1.5 equiv.). The reaction mixture was heated at 65 °C and allowed to stir for 6 h. The solvent was evaporated and the residue was dissolved in water (70 mL) and extracted with ethyl acetate (4 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated

under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **6** (3.20 g, 87 %) as a faint yellow oil.

^{1}H NMR (300 Hz, $CDCl_3$): δ= 7.72 (s, 1H, H_7), 7.69 (s, 1H, H_7), 4.70-4.64 (m, 1H, H_{OH}), 4.58-4.46 (m, 6H, H_{6+8}), 4.43-4.29 (m, 3H, H_{6+OH}), 4.24-4.21 (bs, 3H, H_{3+OH}), 4.15-4.09 (m, 2H, H_5), 3.92 (dq, 1H, J= 10.3 Hz, J= 5.3 Hz, H_{10}), 3.60-3.55 (m, 2H, H_4), 3.53-3.46 (m, 2H, H_4), 3.41 (bt, 2H, J= 5.7 Hz, H_9), 3.31 (d, 2H, J= 5.4 Hz, H_{11}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2); **^{13}C NMR** (75 Hz, $CDCl_3$): δ= 144.2, 143.9, 124.7, 124.6, 124.5, 124.3, 101.6, 90.5, 77.4, 72.1, 71.1, 70.9, 69.6, 69.0, 68.9, 64.5, 64.2, 59.6, 53.7, 53.5, 52.9, 26.1, 16.5, -4.6; **HRMS** *m/z*= 580.3024 (calcd. for 580.3022 $C_{24}H_{42}O_6N_9{}^{28}Si$ $[M+H]^+$).

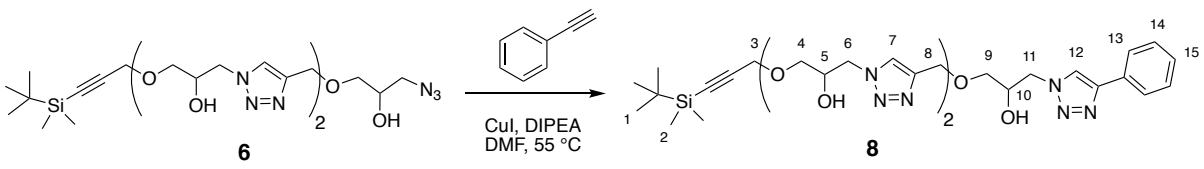
2.2 Chain termination



4 **7**

To a solution of **4** (8.70 g, 20.52 mmol) in degassed DMF (100 mL) was added phenyl acetylene (2.70 mL, 1.2 equiv.), DIPEA (18.2 mL, 5.0 equiv.) and CuI (389 mg, 0.1 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (200 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 150 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **7** (8.30 g, 77 %) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.90 (s, 1H, H_{12}), 7.72-7.69 (m, 3H, H_{7+13}), 7.37-7.24 (m, 3H, H_{14+15}), 4.67-4.24 (m, 10H, $H_{6+8+11+OH}$), 4.17 (bs, 4H, H_{3+5+10}), 3.55-3.41 (m, 4H, H_{4+9}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2); **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 147.3, 143.9, 130.4, 128.9, 128.2, 125.7, 124.5, 121.7, 101.6, 90.4, 77.4, 71.2, 71.1, 70.9, 69.0, 68.9, 64.4, 64.3, 59.5, 53.6, 53.0, 26.1, 16.5, -4.6; **HRMS** *m/z*= 527.2795 (calcd. for 527.2797 $C_{26}H_{39}O_4N_6{}^{28}Si$ $[M+H]^+$).

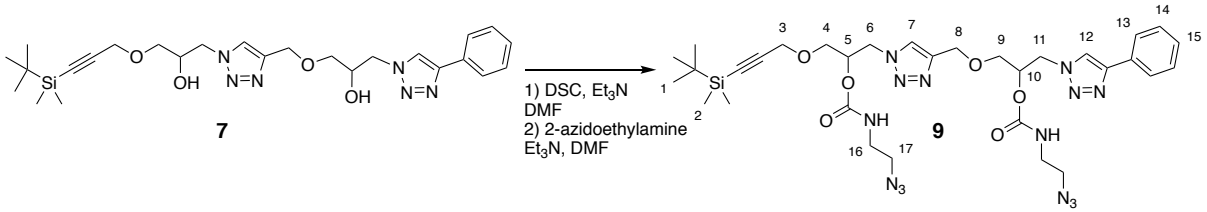


6 **8**

To a solution of **6** (3.00 g, 5.18 mmol) in degassed DMF (52 mL) was added phenyl acetylene (680 µL, 1.2 equiv.), DIPEA (4.6 mL, 5.0 equiv.) and CuI (98 mg, 0.1 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (100 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **8** (3.52 g, quant.) as a white solid.

^{1}H NMR (300 MHz, DMF-d_7): δ= 8.54 (s, 1H, H_{12}), 8.13 (s, 2H, H_7), 7.96-7.92 (m, 2H, H_{13}), 7.50-7.45 (m, 2H, H_{14}), 7.37-7.33 (m, 1H, H_{15}), 5.61 (dd, 3H, J= 11.7 Hz, J= 5.8 Hz, H_{OH}), 4.67 (d, 4H, J= 5.1 Hz, H_8), 4.64-4.37 (m, 6H, H_{6+11}), 4.32 (bs, 2H, H_3), 4.26-4.12 (m, 3H, H_{5+10}), 3.61-3.53 (m, 6H, H_{4+9}) 0.94 (s, 9H, H_1), 0.12 (s, 6H, H_2); **^{13}C NMR** (75 Hz, DMF-d_7): δ= 146.8, 131.6, 129.1, 128.0, 125.5, 122.4, 103.4, 89.1, 79.4, 72.2, 71.8, 69.2, 64.6, 59.1, 53.5, 25.8, 16.4, -5.0; **HRMS** *m/z*= 682.3489 (calcd. for 682.3491 $C_{32}H_{48}O_6N_9{}^{28}Si$ $[M+H]^+$).

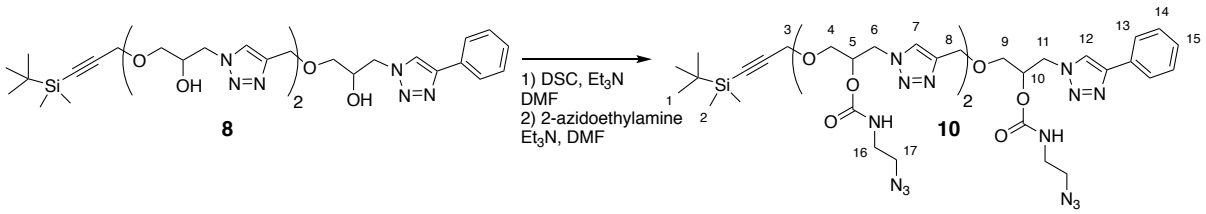
2.3 Lateral chain functionalization



To a solution of **7** (8.30 g, 15.78 mmol) in DMF (80 mL) was added DSC (9.70 mg, 2.4 equiv.) and triethylamine (6.6 mL, 3.0 equiv.) and the reaction mixture was stirred at room temperature overnight. On the second day, a solution of 2-azidoethylamine (4.00 g, 3.0 equiv.) and triethylamine (6.6 mL, 3.0 equiv.) in DMF (20 mL) was added and the solution was stirred overnight at room temperature. To the resulting reaction mixture DCM (100 mL) was added and the organic layer washed with water (3 × 50 mL). The aqueous layer was back-extracted with DCM (2 × 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **9** (9.30 g, 79 %) as a a yellowish orange viscous liquid.

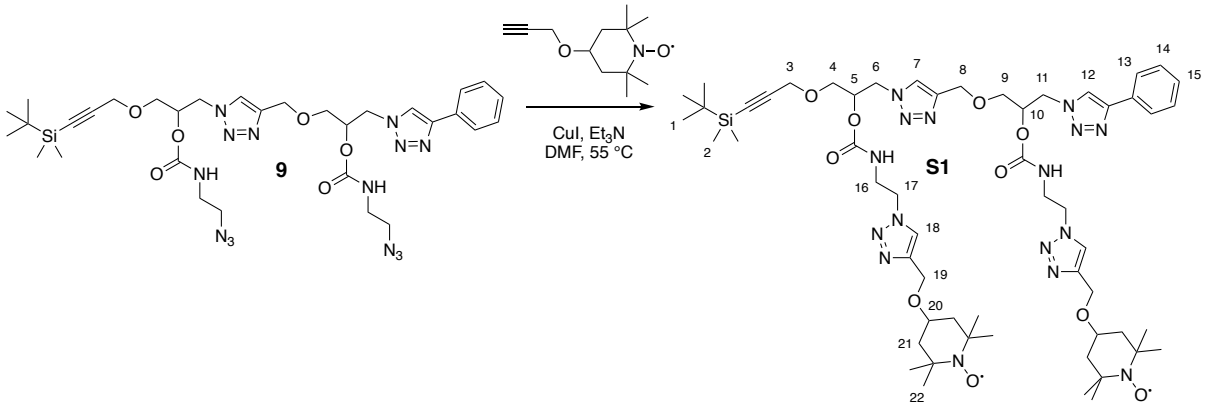
^{1}H NMR (300 MHz, CD_3OD): δ= 8.29 (s, 1H, H_{12}), 8.00 (s, 1H, H_7), 7.86-7.83 (m, 2H, H_{13}), 7.48-7.37 (m, 3H, H_{14+15}), 5.27 (bs, 2H, H_{5+10}), 4.76-4.61 (m, 6H, H_{6+8+11}), 4.26 (bs, 2H, H_3),

3.68-3.67 (m, 4H, H_{4+9}), 3.44-3.26 (m, 8H, H_{16+17}), 0.97 (s, 9H, H_1), 0.14 (s, 6H, H_2); **^{13}C NMR** (75 MHz, CD_3OD): δ= 157.3, 148.8, 131.6, 130.0, 129.3, 126.7, 126.1, 123.3, 103.1, 90.8, 72.5,70.0, 69.8, 69.4, 65.2, 60.1, 54.4, 51.7, 51.4, 41.4, 26.5, 17.2, -4.5; **HRMS** *m/z*= 751.3505 (calcd. for 751.3567 $C_{32}H_{47}O_6N_{14}{}^{28}Si$ $[M+H]^+$).



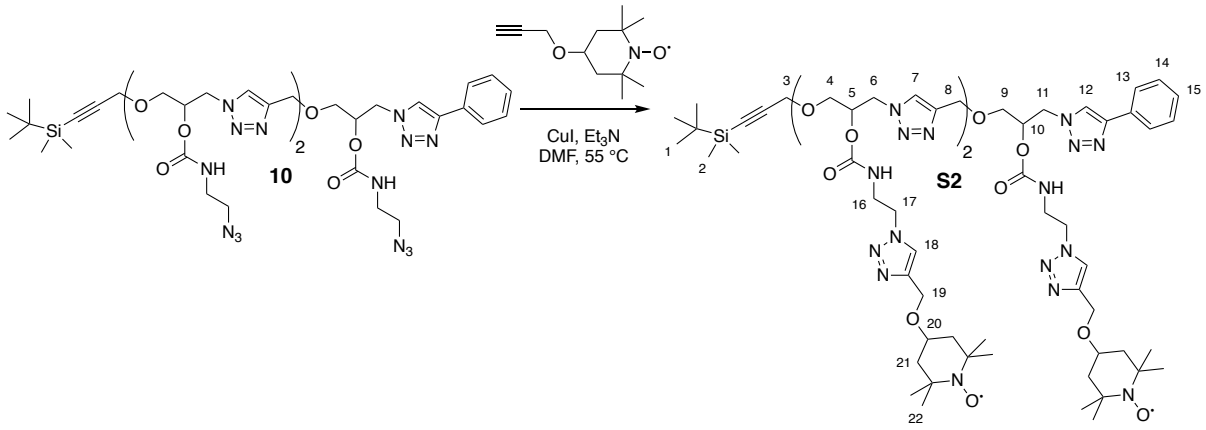
To a solution of **8** (500 mg, 0.734 mmol) in DMF (15 mL) was added DSC (846 mg, 4.5 equiv.) and triethylamine (613 µ L, 6 equiv.) and the reaction mixture was stirred at room temperature overnight. On the second day, a solution of 2-azidoethylamine (284 µL, 4.5 equiv.) and triethylamine (613 µL, 6 equiv.) in DMF (4 mL) was added and the solution was stirred overnight at room temperature. To the resulting reaction mixture DCM (100 mL) was added and the organic layer washed with water (3 × 50 mL). The aqueous layer was back-extracted with (2 × 100 mL) DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **10** (550 mg, 74 %) as a yellowish orange viscous liquid.

^{1}H NMR (300 MHz, CD_3OD): δ= 8.27 (s, 1H, H_{12}), 7.97 (s, 1H, H_7), 7.95 (s, 1H, H_7), 7.81 (d, 2H, *J*= 7.1 Hz, H_{13}), 7.46-7.32 (m, 3H, H_{14+15}), 5.30-5.20 (m, 3H, H_{5+10}), 4.74-4.63 (m, 10H, H_{6+8+11}), 4.25 (bs, 2H, H_3), 3.68-3.59 (m, 6H, H_{4+9}), 3.37-3.23 (m, 12 H, H_{16+17}), 0.95 (s, 9H, H_1), -0.11 (s, 6H, H_2); **^{13}C NMR** (75 Hz, CD_3OD) δ= 157.4, 148.8, 145.5, 131.6, 130.0, 129.3, 126.7, 126.2, 123.2, 103.1, 90.8, 72.5, 69.8, 69.4, 65.1, 60.0, 51.7, 41.4, 26.5, 17.2, -4.5; **HRMS** *m/z*= 1018.4651 (calcd. for 1018.4647 $C_{41}H_{60}O_9N_{21}{}^{28}Si$ $[M+H]^+$).



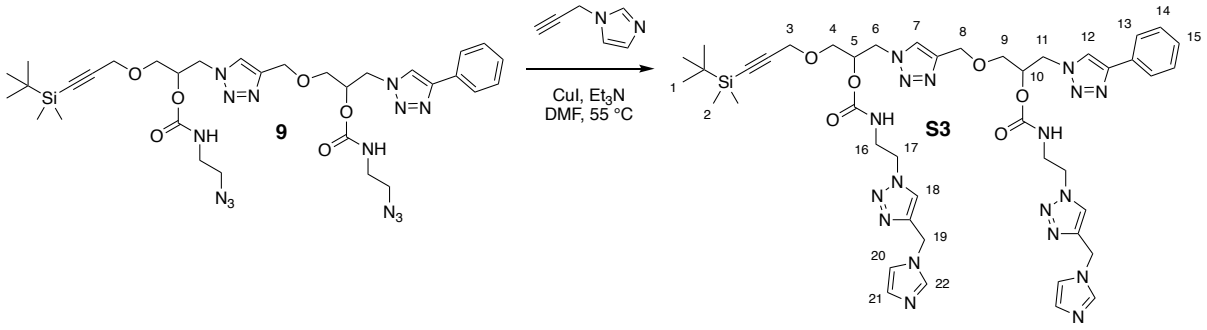
To a solution of **9** (1.5 g, 2.00 mmol) in degassed DMF (20 mL) was added **11** (1.02 g, 2.4 equiv.), Et_3N (2.8 mL, 10.0 equiv.) and CuI (77 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (100 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **S1** (1.8 g, 77 %) as a orange viscous liquid.

^{1}H NMR (500 MHz, CDO_3D, 1,2-diphenylhydrazine): δ= 8.31 (s, 1H, H_{12}), 8.01-7.87 (m, 4H, $H_{7+13+18}$), 7.48-7.39 (m, 3H, H_{14+15}), 5.45-5.26 (m, 2H, H_{5+10}), 4.72-4.49 (m, 14H, $H_{6+8+11+17+19}$), 4.28 (s, 2H, H_3), 3.84 (bs, 2H, H_{20}), 3.73-3.53 (m, 8H, H_{4+9+16}), 2.00 (bs, 4H, H_{21}), 1.49 (bs, 4H, H_{21}), 1.25-1.19 (m, 24H, H_{22}), 1.00 (s, 9H, H_1), 0.17 (s, 6H, H_2); **^{13}C NMR** (125 MHz, CDO_3D,1,2-diphenylhydrazine): δ= 157.1 (×2), 153.7, 151.1, 148.6, 148.4, 146.3, 145.4, 132.2, 131.6, 131.5, 130.2, 129.9, 129.3, 129.2, 126.6 (×2), 126.2, 125.3, 125.1, 123.7, 123.3, 119.6, 113.2, 103.4, 103.1, 90.8, 79.4, 72.6, 72.4, 72.2, 71.8, 71.3, 70.0, 69.9, 69.6, 69.3, 65.1, 62.0, 60.0, 59.9, 54.3, 52.6, 51.7, 51.6, 50.7, 45.5, 41.8, 39.4, 32.6, 28.8, 26.5, 21.2, 17.2, -4.4; **HRMS** *m/z*= 1171.6537 (calcd. for 1171.6555 $C_{56}H_{87}O_{10}N_{16}{}^{28}Si$ $[M+H]^+$).



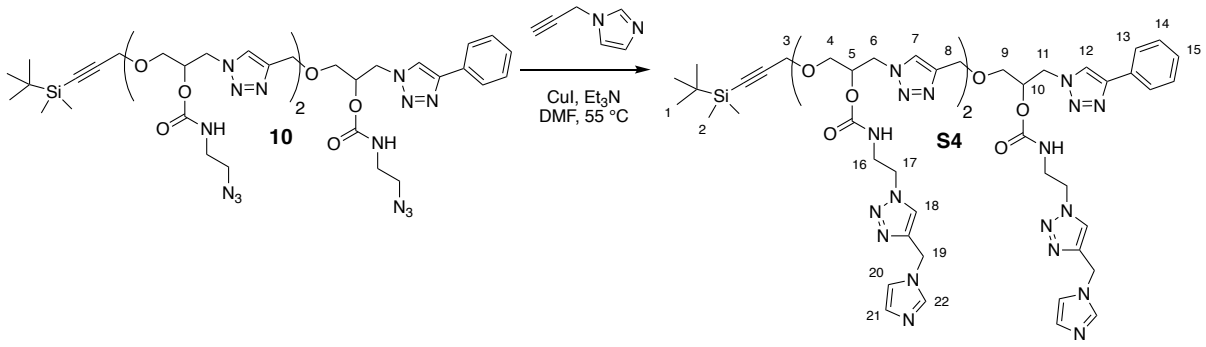
To a solution of **10** (660 mg, 0.65 mmol) in degassed DMF (7 mL) was added **11** (491 mg, 3.6 equiv.), Et_3N (1.4 mL, 15 equiv.) and CuI (37 mg, 0.3 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **S2** (620 mg, 58 %) as a orange-white solid.

^{1}H NMR (500 MHz, DMF-d_7, 1,2-diphenylhydrazine): δ= 8.53 (s, 1H, H_{12}), 8.16-8.11 (m, 4H, $H_{7+13+18}$), 7.51-7.46 (m, 3H, H_{14+15}), 5.24 (bs, 3H, H_{5+10}), 4.78-4.69 (m, 10H, H_{6+8+11}), 4.61 (m, 6H, H_{19}), 4.52 (m, 6H, H_{17}), 4.32 (bs, 2H, H_3), 3.84-3.62 (m, 12H, $H_{4+9+16+20}$), 1.96 (d, 6H, J= 12.3 Hz, H_{21}), 1.33 (t, 6H, J= 11.6 Hz, H_{21}), 1.13-1.12 (m, 36H, H_{22}), 0.94 (s, 9H, H_1), -0.13 (s, 6H, H_2); **^{13}C NMR** (125 MHz, DMF-d_7, 1,2-diphenylhydrazine): δ= 155.9, 1532.5, 150.7, 147.2, 145.4, 144.4, 131.8, 129.7, 129.1, 128.1, 125.6, 125.2, 124.2, 123.0, 122.6, 120.4, 118.2, 112.2, 103.1, 89.5, 71.5, 70.4, 68.8, 64.5, 61.4, 59.2, 58.5, 50.5, 49.4, 45.1, 41.3, 32.5, 25.9, 20.6, 16.4, -5.0; **HRMS** *m/z*= 1647.9037 (calcd. for 1647.9051 $C_{77}H_{119}O_{15}N_{24}{}^{28}Si$ $[M+H]^+$).



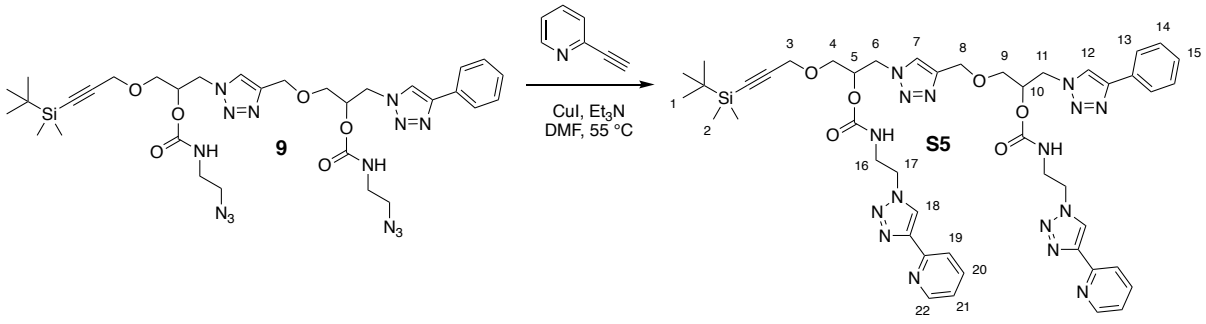
To a solution of **9** (1.20 g, 1.6 mmol) in degassed DMF (16 mL) was added **12** (407 mg, 2.4 equiv.), Et_3N (2.2 mL, 10.0 equiv.) and CuI (61 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **S3** (1.00 g, 65 %) as a pale brown solid.

^{1}H NMR (500 MHz, CD_3OD): δ= 8.26 (s, 1H, H_{12}), 7.98-7.96 (m, 3H, H_{7+18}), 7.81-7.72 (m, 4H, H_{13+22}), 7.42-7.33 (m, 3H, H_{14+15}), 7.16-7.14 (m, 2H, H_{20}), 6.94 (s, 2H, H_{21}), 5.30-5.27 (m, 4H, H_{19}), 5.14 (bs, 2H, H_{5+10}), 4.77-4.53 (m, 8H, H_{6+8+11}), 4.51-4.34 (m, 4H, H_{17}), 4.23-4.21 (m, 2H, H_3), 3.75-3.38 (m, 8H, H_{4+9+16}), 0.93 (s, 9H, H_1), 0.10 (s, 6H, H_2); **^{13}C NMR** (500 MHz, CD_3OD): δ= 157.4 (×2), 148.8, 145.5, 144.3, 144.2, 138.4, 131.7, 130.0, 129.4, 129.3, 129.2, 126.7 (×2), 126.4, 125.6, 123.4, 120.8, 103.2, 90.8, 72.7, 72.5, 72.3, 70.1, 69.8, 69.4, 65.2, 60.1, 58.5, 54.5, 52.8, 51.8, 51.0, 47.8, 42.6 (×2), 41.9, 37.4, 26.8, 26.5, 24.8, 17.2, 13.9, -4.5; **HRMS** *m/z*= 963.4626 (calcd. for 963.4629 $C_{44}H_{59}O_6N_{18}{}^{28}Si$ $[M+H]^+$).



To a solution of **10** (700 mg, 0.69 mmol) in degassed DMF (7 mL) was added **12** (263 mg, 3.6 equiv.), Et_3N (15 equiv., 1.45 mL) and CuI (40 mg, 0.3 equiv.). The reaction mixture was stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried using anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **S4** (400 mg, 44 %) as a orange-white solid.

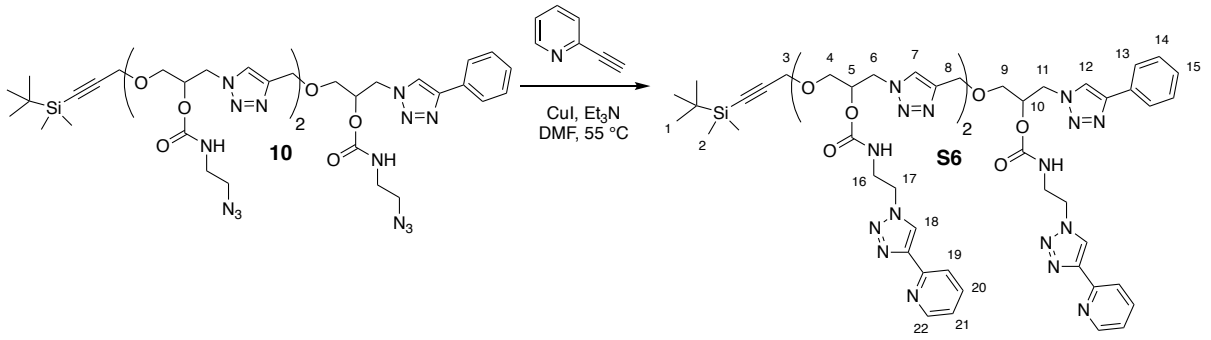
^{1}H NMR (500 MHz, CD_3OD): δ= 8.27 (s, 1H, H_{12}), 7.97-7.95 (m, 5H, H_{7+18}), 7.81-7.75 (m, 5H, H_{13+22}), 7.43-7.29 (m, 3H, H_{14+15}), 7.16 (s, 3H, H_{20}), 6.94 (s, 3H, H_{21}), 5.31-5.26 (m, 6H, H_{19}), 5.18-5.09 (m, 3H, H_{5+10}), 4.71-4.57 (m, 10H, H_{6+8+11}), 4.42 (bs, 6H, H_{17}), 4.21 (s, 2H, H_3), 3.61-3.41 (m, 12H, H_{4+9+16}), 0.92 (s, 9H, H_1), 0.09 (s, 6H, H_2); **^{13}C NMR** (125 MHz, CD_3OD): δ= 157.3, 148.8, 145.5, 144.3 (×2), 138.4, 131.7, 130.1, 129.4, 129.3, 126.7, 126.4, 125.6, 123.5, 120.8, 103.2, 90.7, 72.5, 69.8, 69.5, 65.1, 60.1, 51.7, 51.0, 47.8, 42.6, 41.9, 26.5, 17.2, 9.3, -4.5; **HRMS** *m/z*= 1336.6236 (calcd. for 1336.6226 $C_{57}H_{76}O_8N_{30}{}^{28}Si$ $[M+H]^+$).



To a solution of **9** (1.56 g, 2.08 mmol) in degassed DMF (13 mL) was added 2-ethynylpyridine (505 µL, 2.4 equiv.), Et_3N (2.8 mL, 10.0 equiv.) and CuI (77 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na_2EDTA (100 mL) was added and the reaction mixture was stirred at room

temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give **S5** (1.38 g, 69 %) as a orange solid.

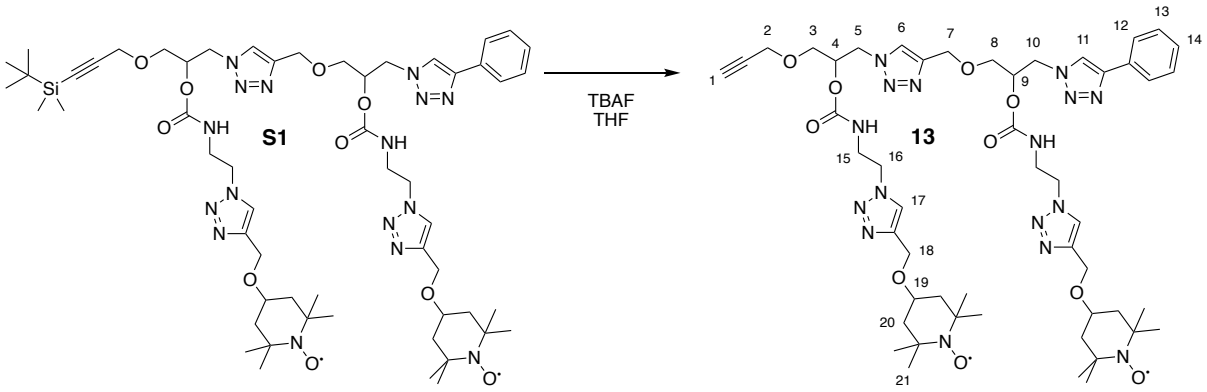
^{1}H NMR (300 MHz, DMF-d_7): δ= 8.64-8.51 (m, 4H, H_{18+22}), 8.15-7.93 (m, 6H, $H_{7+12+13+19+20}$), 7.67-7.34 (m, 5H, $H_{14+15+21}$), 5.63-5.24 (m, 2H, H_{5+10}), 4.84-4.58 (m, 10H, $H_{6+8+11+17}$), 4.31 (bs, 2H, H_3), 3.75-3.53 (m, 8H, H_{4+9+16}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2); **^{13}C NMR** (75 MHz, DMF-d_7): δ= 155.9, 155.8, 147.1, 137.2, 131.6, 131.4, 129.0, 128.0, 125.6, 125.4, 125.1, 123.8, 122.4, 122.3, 103.3, 102.9, 89.4, 89.1, 79.3, 71.8, 71.3 (×2), 69.2, 69.0, 68.7, 64.6, 64.4, 59.1, 59.0, 53.6, 53.4, 51.5, 50.5 (×2), 49.8, 46.3, 41.2, 41.1, 28.2, 26.1, 25.8, 16.3, -5.1; **HRMS** *m/z* = 957.4409 (calcd. for 957.4411 $C_{46}H_{57}O_6N_{16}{}^{28}Si$ $[M+H]^+$).



To a solution of **10** (700 mg, 0.69 mmol) in degassed DMF (7 mL) was added 2-ethynylpyridine (250 µL, 3.6 equiv.), Et_3N (1.5 mL, 15 equiv.) and CuI (40 mg, 0.3 equiv.). The reaction mixture was stirred at 55 °C overnight. After cooling to room temperature 0.05 M Na_2EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried using anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM/Et_3N) to give **S6** (620 mg, 68 %) as a brownish-black solid.

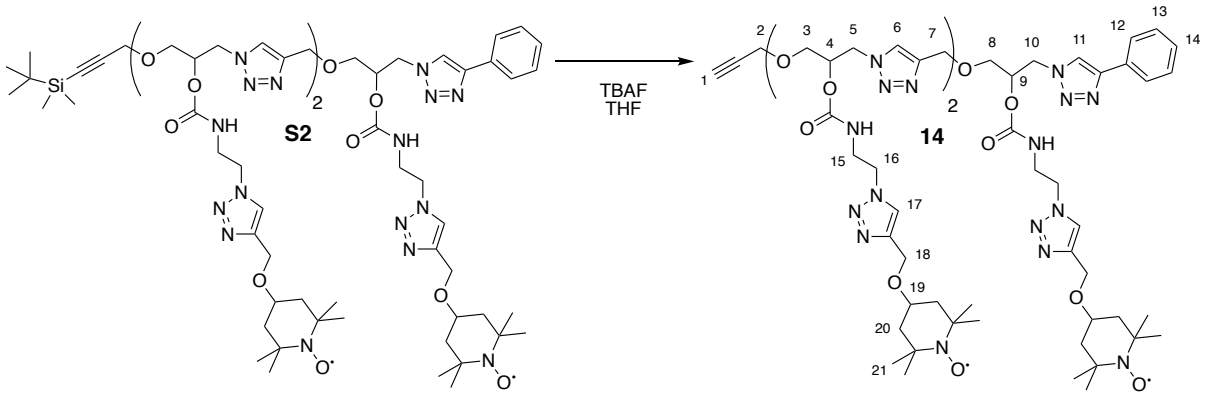
^{1}H NMR (500 MHz, CD_3OD): δ= 8.51 (bs, 3H, H_{22}), 8.44-8.40 (m, 3H, H_{18}), 8.23 (d, 1H, J= 3.5 Hz, H_{12}), 8.02-7.74 (m, 10H, $H_{7+13+19+20}$), 7.36-7.27 (m, 6H, $H_{14+15+21}$), 5.27-5.10 (m, 3H, H_{5+10}), 4.72-4.53 (m, 16H, $H_{6+8+11+17}$), 4.18 (bs, 2H, H_3), 3.66-3.50 (m, 12H, H_{4+9+16}), 0.90 (s, 9H, H_1), 0.07 (s, 6H, H_2); **^{13}C NMR** (125 MHz, CD_3OD) δ= 157.4, 157.3, 151.1, 1504, 148.8, 145.6, 138.8, 131.6, 130.0, 129.3, 126.7, 126.3, 124.8, 124.5, 123.4, 121.5, 103.2,

90.7, 79.5, 72.6, 69.7, 69.4, 65.1, 60.1, 51.8, 51.7, 51.6, 51.1, 42.0, 35.8, 32.2, 26.5, 17.2, -4.5; **HRMS** *m/z*= 1327.5914 (calcd. for 1327.5913 $C_{62}H_{75}O_9N_{24}{}^{28}Si$ $[M+H]^+$).



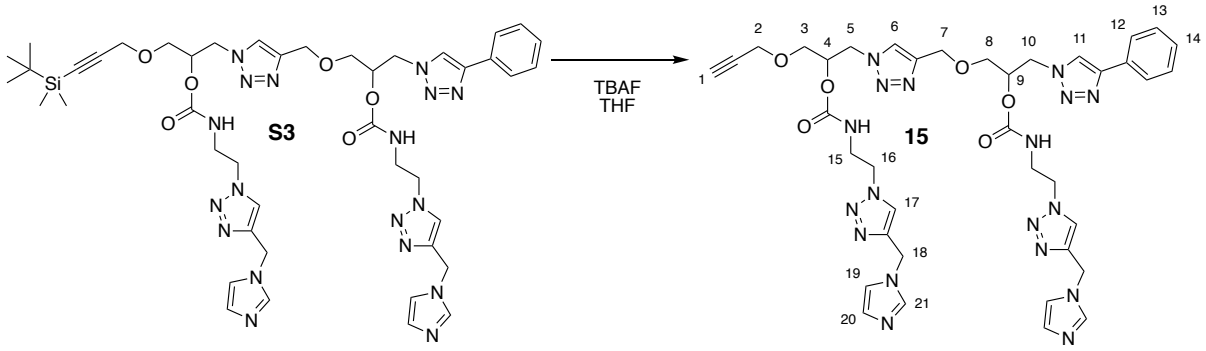
To a solution of **S1** (1.80 g, 1.54 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.6 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with NH_4Cl (3 × 50 mL) and water (2 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentred under vacuum to yield **13** (1.20 g, 74 %).

^{1}H NMR (300 MHz, CD_3OD, 1,2-diphenylhydrazine): δ= 8.25 (s, 1H, H_{11}), 7.97-7.92 (m, 3H, H6+17), 7.81 (t, 2H, *J*= 8.2 Hz, H_{12}), 7.42 (t, 2H, *J*= 7.4 Hz, H_{13}), 7.33 (t, 1H, *J*= 7.0 Hz, H_{14}), 5.19-5.15 (m, 2H, H_{4+9}), 4.71-4.35 (m, 14H, $H_{5+7+10+16+18}$), 4.22-4.13 (m, 2H, H_2), 3.78-3.75 (m, 2H, H_{19}), 3.67-3.45 (m, 8H, H_{3+8+15}), 3.31 (m, 1H, H_1) 1.94-1.91 (m, 4H, H_{20}), 1.44-1.36 (m, 4H, H_{20}), 1.17-1.12 (m, 24H, H_{21}); **^{13}C NMR** (75 MHz, CD_3OD, 1,2-diphenylhydrazine): δ= 157.2 (×2), 153.8, 148.7, 148.4, 146.4, 132.2, 131.7, 131.6, 130.2, 130.0, 129.8, 129.3, 129.2, 126.7, 126.6, 126.3, 126.2, 125.4, 123.7, 123.3, 121.4, 79.5, 72.6, 72.4, 72.1, 71.9, 70.1, 69.9, 69.6, 69.3, 65.1, 62.0, 60.0, 59.4, 59.3, 54.4, 54.3, 52.6, 51.6, 50.8, 45.5, 41.9, 32.6, 21.2; **HRMS** *m/z*= 1057.5690 (calcd. for $C_{50}H_{73}O_{10}N_{16}$ 1057.5690 $[M+H]^+$).



To a solution of **S2** (1.50 g, 0.91 mmol) in THF (30 mL) was added TBAF (1.0 M in THF, 1.0 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with NH_4Cl (2 × 50 mL) and water (2 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentred under vacuum to yield **14** (1.25 g, 89 %).

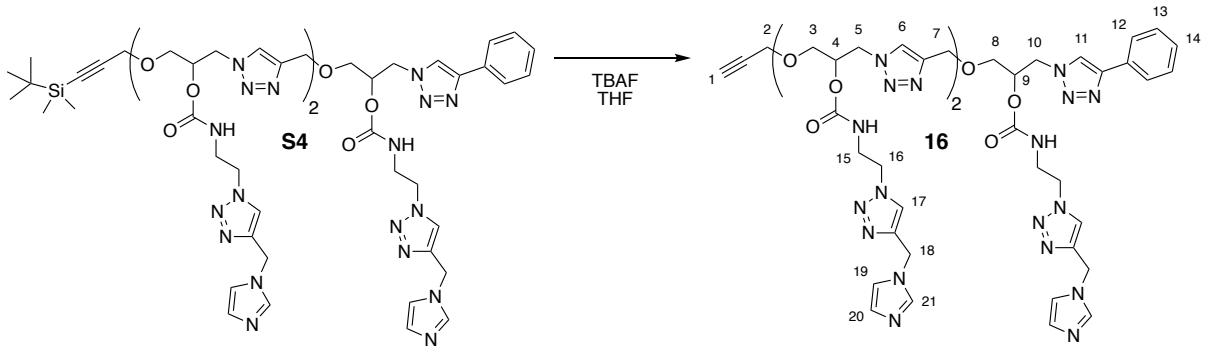
^{1}H NMR (500 MHz, DMF-d_7, 1,2-diphenylhydrazine): δ= 8.53 (s, 1H, H_{11}), 8.17-8.12 (m, 5H, H_{6+17}), 7.95-7.94 (m, 2H, H_{12}), 7.53-7.46 (m, 3H, H_{13+14}), 5.22 (bs, 3H, H_{4+9}), 4.82-4.68 (m, 10H, H_{5+7+10}), 4.64-4.61 (m, 6H, H_{18}), 4.55-4.48 (m, 6H, H_{16}), 4.27 (d, 2H, J= 1.6 Hz, H_2), 3.83-3.77 (m, 3H, H_{19}), 3.71-3.50 (m, 12H, H_{3+8+15}), 1.97-1.95 (m, 6H, H_{20}), 1.35-1.31 (m, 6H, H_{20}), 1.13-1.11 (m, 36H, H_{21}); **^{13}C NMR** (125 MHz, DMF-d_7, 1,2-diphenylhydrazine): δ= 155.8, 152.7, 150.6, 147.1, 145.4, 144.4, 144.0, 131.8, 131.5, 129.7, 129.1, 128.1, 128.0, 127.4, 125.6, 125.5, 125.3, 124.2, 122.9, 122.5, 122.4, 120.3, 118.2, 112.1, 80.3, 80.0, 79.4, 76.9, 76.6, 72.2, 71.8, 71.5, 71.4, 70.3, 69.2, 69.1, 68.9, 68.8, 68.7, 64.6, 64.5, 61.4, 58.5 (×2), 58.4, 53.7, 53.4, 50.6, 50.5, 49.4, 45.0, 44.9, 41.3, 32.5, 20.4; **HRMS** *m/z*= 1534.8268 (calcd. for 1534.8264 $C_{71}H_{106}O_{15}N_{24}$ $[M+H]^+$).



To a solution of **S3** (1.00 g, 1.04 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.1 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was concentrated under reduced pressure followed by purification by flash column chromatography (methanol/DCM) to yield **15** (0.620 g, 70 %).

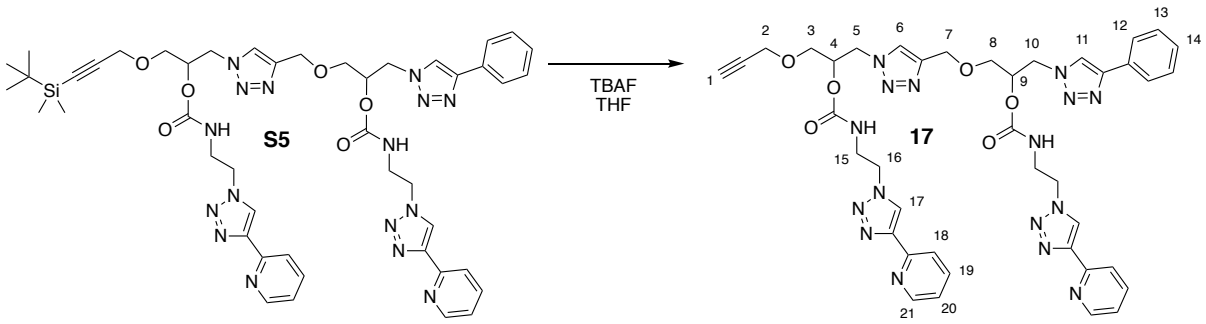
^{1}H NMR (500 MHz, CD_3OD): δ= 8.29 (s, 1H, H_{11}), 7.99-7.97 (m, 4H, H_{6+17}), 7.82-7.76 (m, 4H, H_{12+21}), 7.42-7.31 (m, 3H, H_{13+14}), 7.16 (s, 2H, H_{19}), 6.95 (s, 2H, H_{20}), 5.31-5.27 (m, 4H, H_{18}), 5.16-5.11 (m, 2H, H_{4+9}), 4.67-4.53 (m, 8H, H_{5+7+10}), 4.43-4.42 (m, 4H, H_{16}), 4.16 (s, 2H, H_2), 3.64-3.44 (m, 10H, $H_{3+8+15+NH}$), 2.91 (s, 1H, H_1); **^{13}C NMR** (125 MHz, CD_3OD): δ= 157.3 (×2), 148.7, 145.5, 144.2 (×2), 131.6, 130.0, 129.4, 129.2, 126.7, 126.5, 125.6, 123.5,

120.9, 80.2, 79.6, 76.7, 72.5 (×2), 70.0, 69.8, 69.4, 65.1, 59.4, 51.7 (×2), 51.0, 42.6 (×2), 41.9, 32.1, 26.8; **HRMS** *m/z* = 849.3761 (calcd. for 849.3764 $C_{38}H_{45}O_6N_{18}$ $[M+H]^+$).



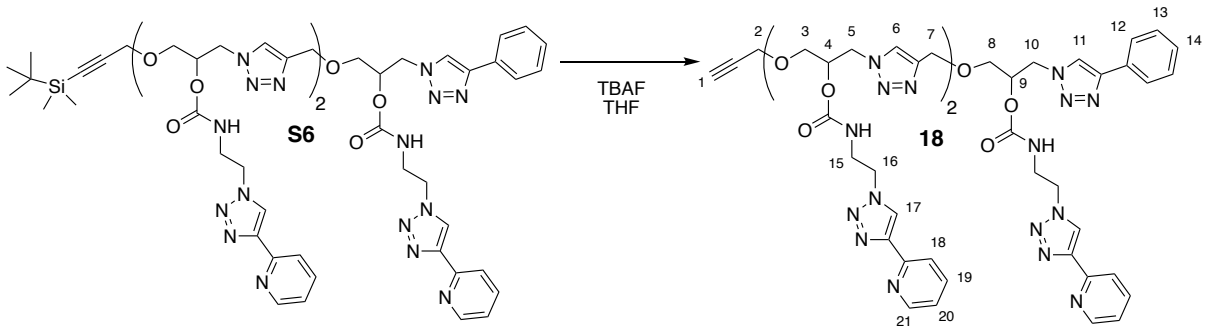
To a solution of **S4** (1.00 g, 0.75 mmol) in THF (30 mL) was added TBAF (1.0 M in THF, 0.8 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was concentrated under vacuum followed by purification by flash column chromatography (methanol/DCM/Et_3N) to yield **16** (0.81 g, 89 %).

^{1}H NMR (500 MHz, CD_3OD): δ= 8.27 (s, 1H, H_{11}), 7.98-7.90 (m, 5H, H_{6+17}), 7.81-7.77 (m, 4H, H_{12+21}), 7.41-7.31 (m, 3H, H_{13+14}), 7.18 (bs, 3H, H_{19}), 6.97 (s, 3H, H_{20}), 5.31-5.27 (m, 6H, H_{18}), 5.17-5.09 (m, 3H, H_{4+9}), 4.73-4.57 (m, 10H, H_{5+7+10}), 4.42 (bs, 6H, H_{16}), 4.17 (bs, 2H, H_2), 3.70-3.43 (m, 12H, H_{3+8+15}), 2.90 (bs, 1H, H_1); **^{13}C NMR** (125 MHz, CD_3OD): δ= 157.3, 148.8, 145.5, 144.3, 144.2, 131.7, 130.0, 129.4, 126.7, (×2), 126.4, 125.6, 123.5, 80.2, 76.6, 76.4, 72.5, 70.1, 69.8, 69.4, 65.1, 62.6, 59.4, 54.4, 51.7, 51.0, 47.8, 42.7, 41.9, 29.6, 24.8, 20.7, 13.9, 9.2; **HRMS** *m/z* = 1222.5374 (calcd. for 1222.5375 $C_{53}H_{64}O_9N_{27}$ $[M+H]^+$).



To a solution of **S5** (1.38 g, 1.44 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.5 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with NH_4Cl (4 × 50 mL) and $NaHCO_3$ (2× 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentred under vacuum to yield **17** (1.04 g, 85 %).

^{1}H NMR (500 MHz, CD_3OD): δ= 8.58-8.41 (m, 2H, H_{21}), 8.42-8.41 (m, 2H, H_{17}), 8.27-8.26 (m, 1H, H_{11}), 8.01-7.96 (m, 3H, H_{6+18}), 7.87-7.78 (m, 4H, H_{12+19}), 7.44-7.31 (m, 5H, $H_{13+14+20}$), 5.20-5.16 (m, 2H, H_{4+9}), 4.68-4.39 (m, 10H, $H_{5+7+10+16}$), 4.20-4.16 (m, 2H, H_2), 3.64-3.53 (m, 8H, H_{3+8+15}), 2.89 (s, 1H, H_1); **^{13}C NMR** (125 Hz, CD_3OD): δ= 157.3, 157.2, 150.9, 150.3, 148.6, 148.4, 145.6, 145.4, 145.3, 145.1, 138.7 (×2), 131.6, 131.4, 129.9, 129.2 (×2), 126.6 (×2), 126.3, 126.2, 124.6, 124.3, 123.3, 121.4, 80.3, 80.1, 79.4, 76.6, 76.3, 72.6, 72.4, 72.1, 70.0, 69.9, 69.5, 69.2, 65.1 (×2), 59.3, 54.3, 54.2, 51.6, 50.9, 47.8, 41.9, 26.8, 24.7, 20.6, 13.9, 9.2; **HRMS** *m/z*= 843.3544 (calcd. for 843.3546 $C_{40}H_{43}O_6N_{16}{}^{28}Si$ $[M+H]^+$).



To a solution of **S6** (0.8 g, 0.60 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 0.6 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with saturated $NaHCO_3$ (2 × 50 mL) and saturated NH_4Cl (2 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentred under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to yield **18** (0.65 g, 89 %).

^{1}H NMR (500 MHz, CD_3OD): δ= 8.52-8.50 (m, 3H, H_{21}), 8.39-8.38 (m, 3H, H_{17}), 8.21 (m, 1H, H_{11}), 8.04-7.74 (m, 10H, $H_{6+12+18+19}$), 7.36-7.27 (m, 6H, $H_{13+14+20}$), 5.26-5.09 (m, 3H, H_{4+9}), 4.70-4.52 (m, 16H, $H_{5+7+10+16}$), 4.14 (s, 2H, H_2), 3.72-3.45 (m, 12H, H_{3+8+15}), 2.86 (s, 1H, H_1); **^{13}C NMR** (125 MHz, CD_3OD): δ= 157.3, 151.1, 150.5, 148.7, 145.5, 138.8, 131.6, 130.0, 129.3, 126.7, 126.3, 124.7, 124.4, 123.4, 121.5, 80.2, 79.5, 76.6, 72.5, 69.7, 69.4, 65.1, 59.4, 51.7, 51.0, 42.0, 32.1, 13.9; **HRMS** *m/z* = 1213.5049 (calcd. for 1213.5048 $C_{56}H_{61}O_9N_{24}$ $[M+H]^+$).

3 ^{1}H and ^{13}C NMR spectra

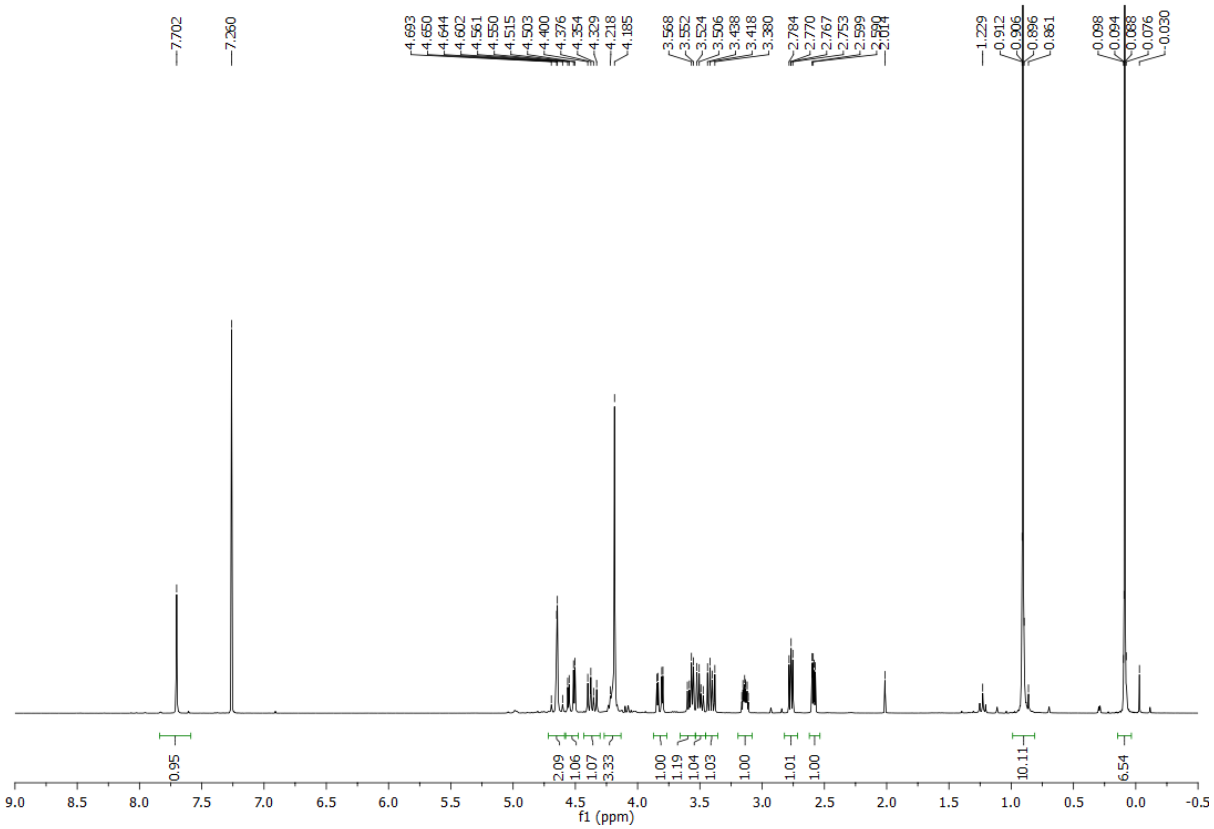


Figure S1. ^{1}H NMR of **3**.

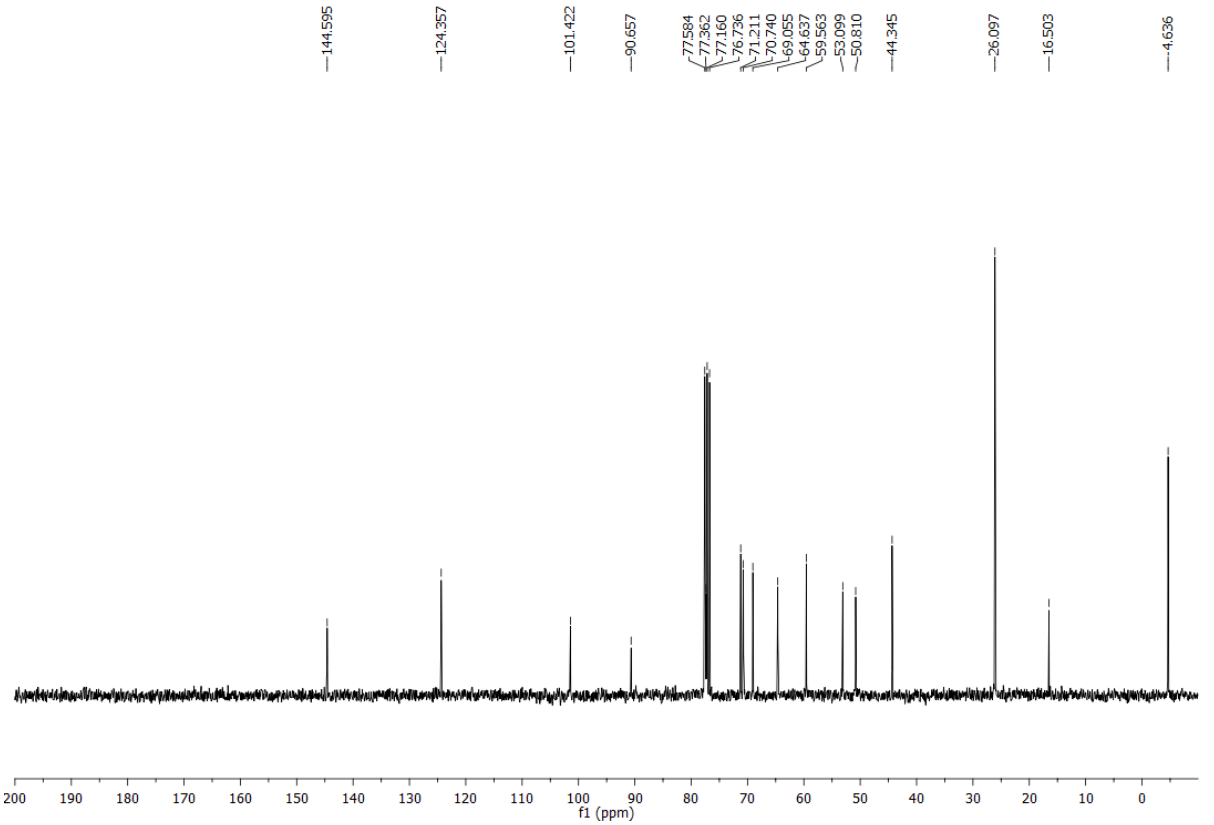


Figure S2. ^{13}C NMR of **3**.

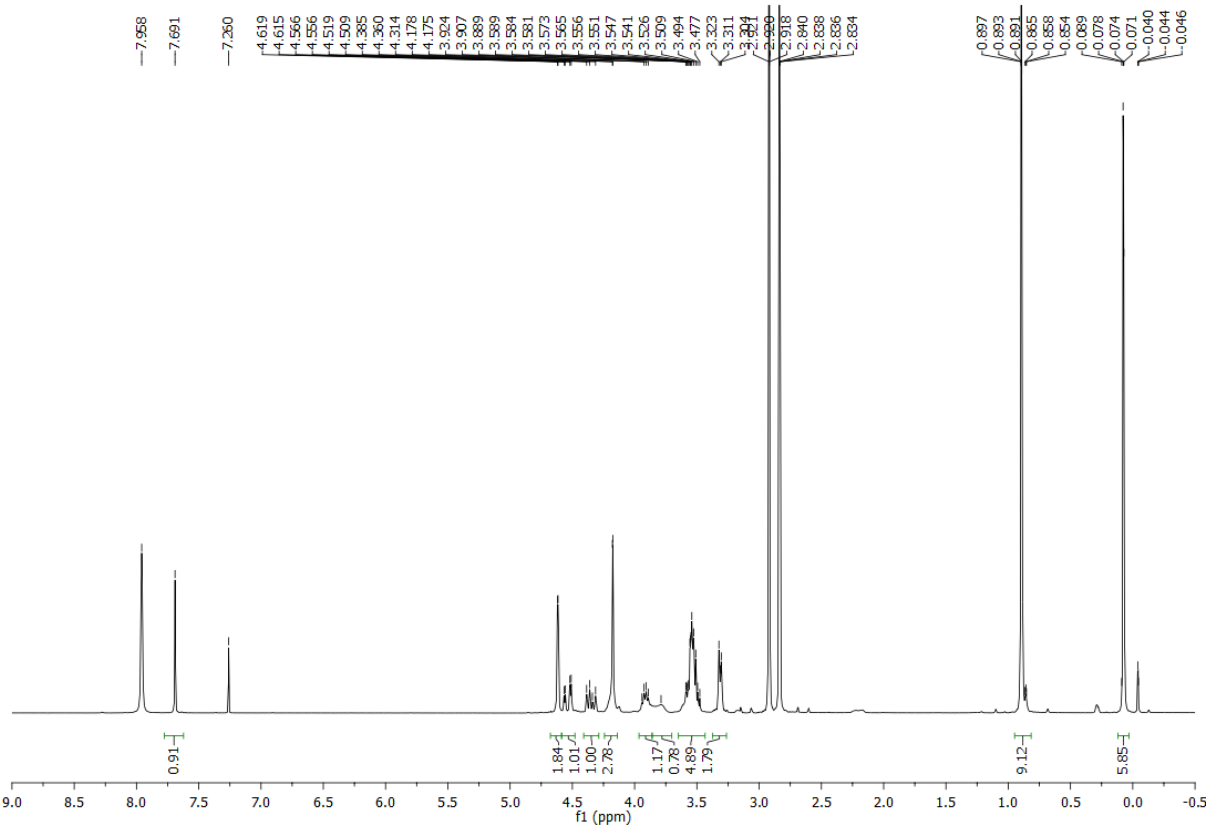


Figure S3. ^{1}H NMR of **4**.

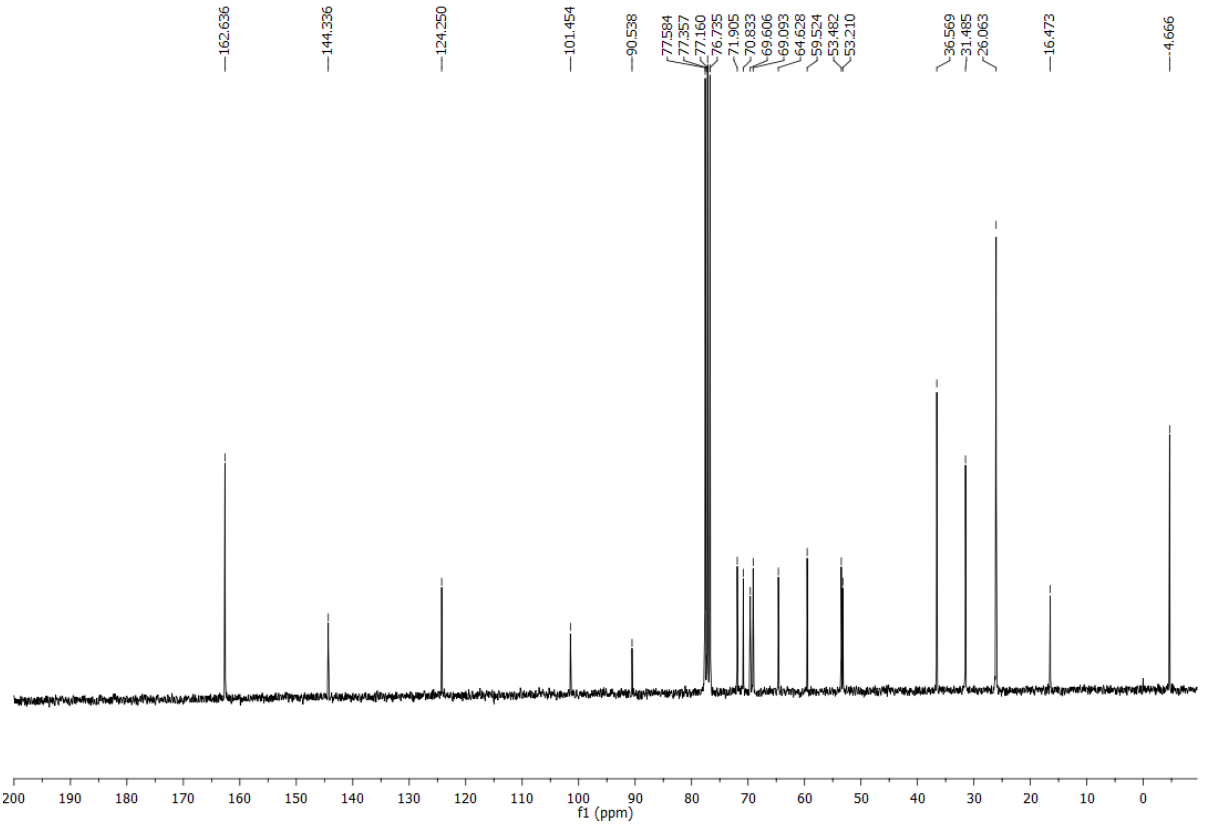


Figure S4. ^{13}C NMR of **4**.

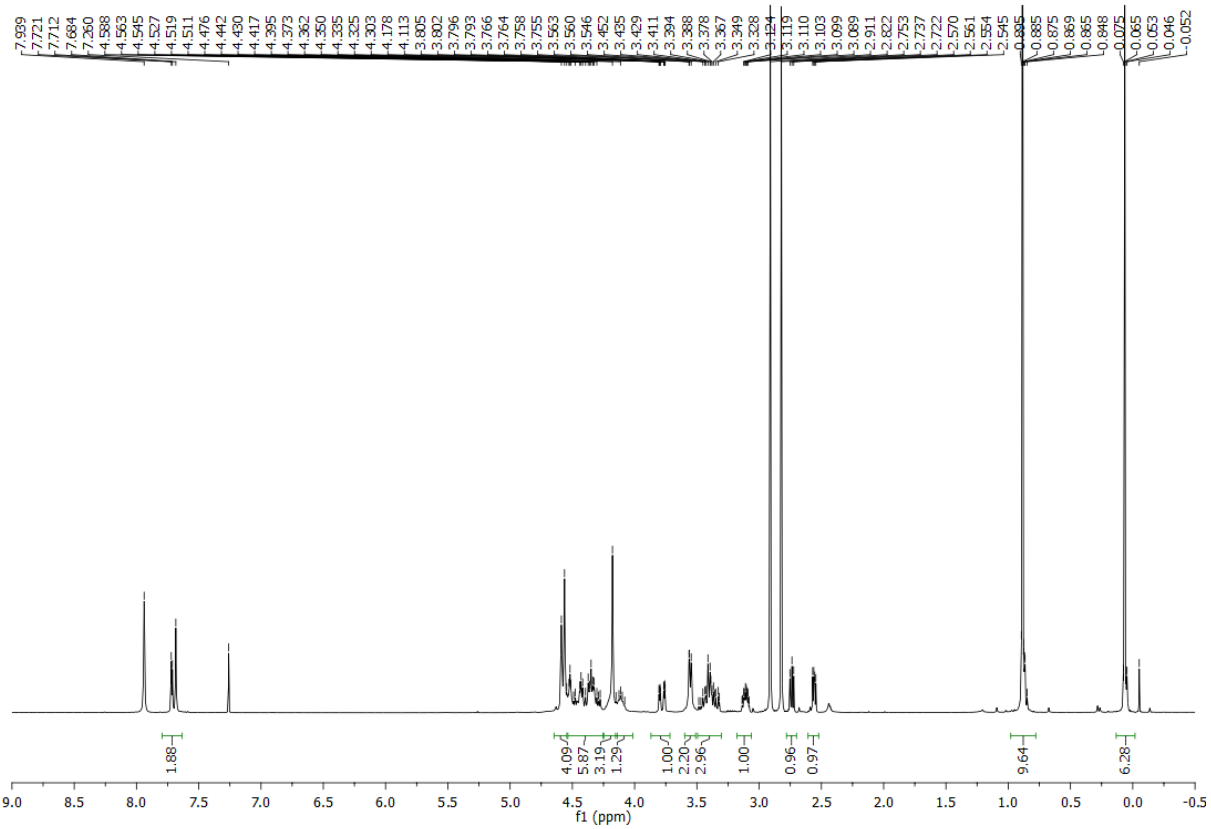


Figure S5. ^{1}H NMR of **5**.

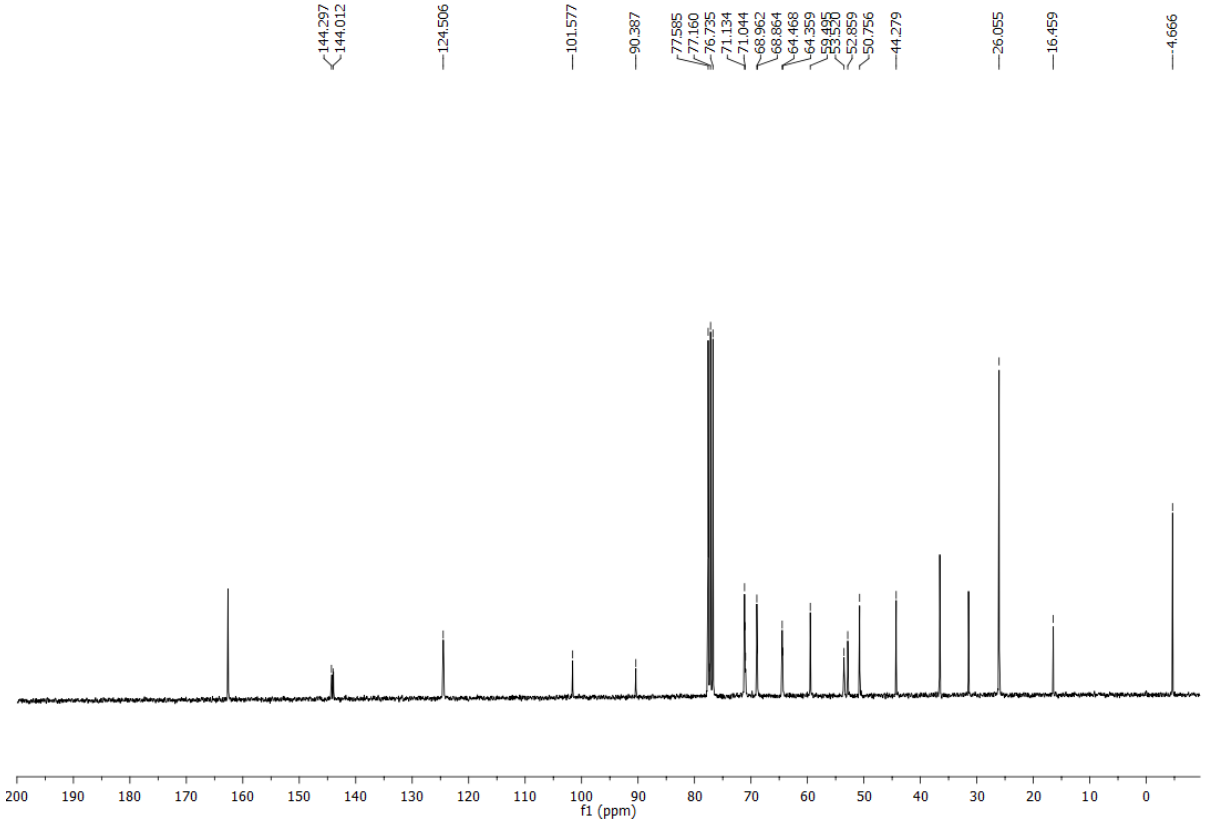


Figure S6. ^{13}C NMR of **5**.

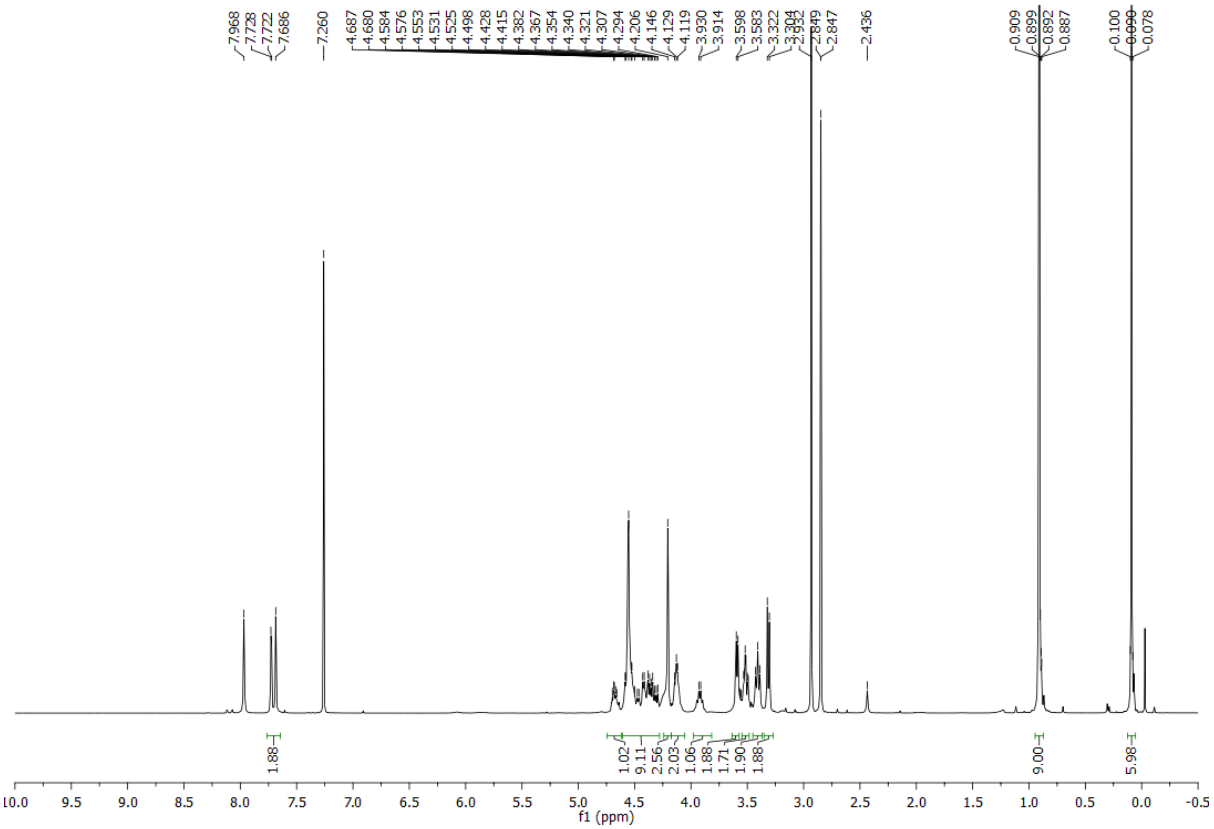


Figure S7. ^{1}H NMR of **6**.

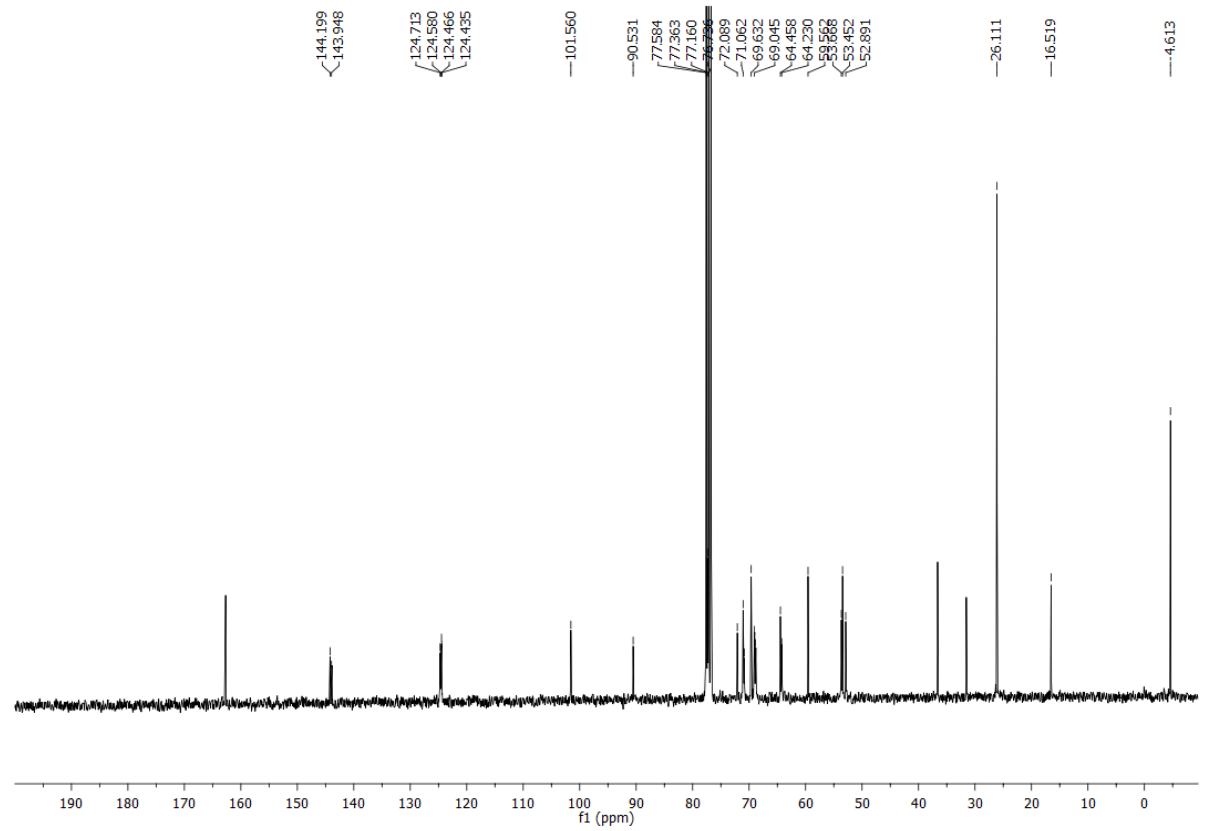


Figure S8. ^{13}C NMR of **6**.

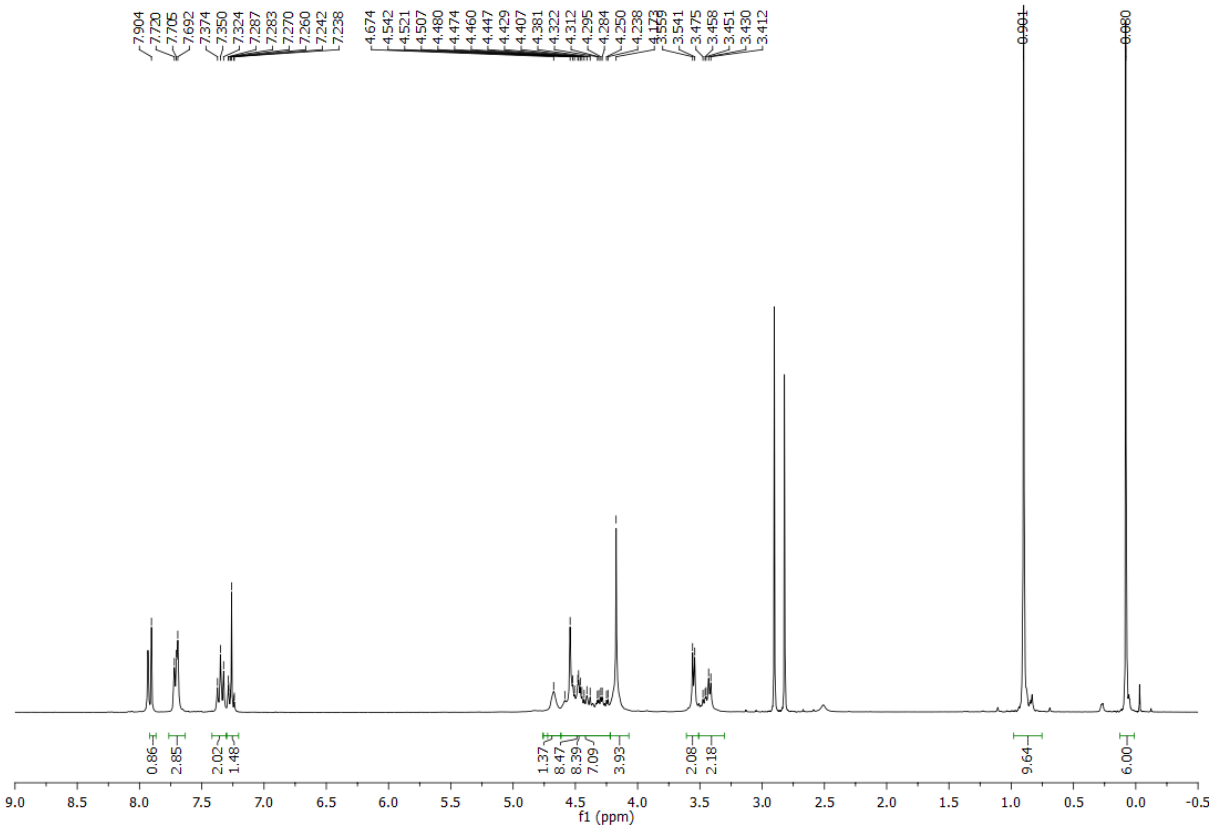


Figure S9. ^{1}H NMR of **7**.

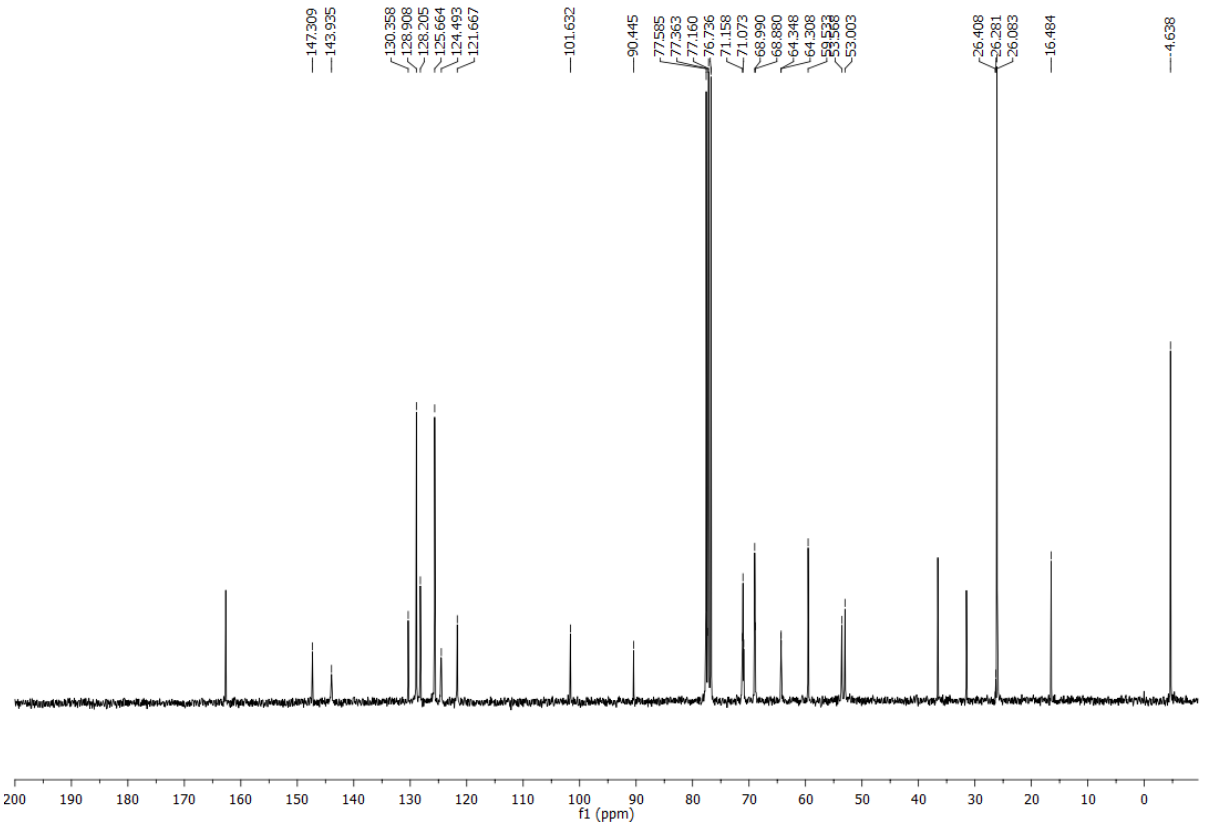


Figure S10. ^{13}C NMR of **7**.

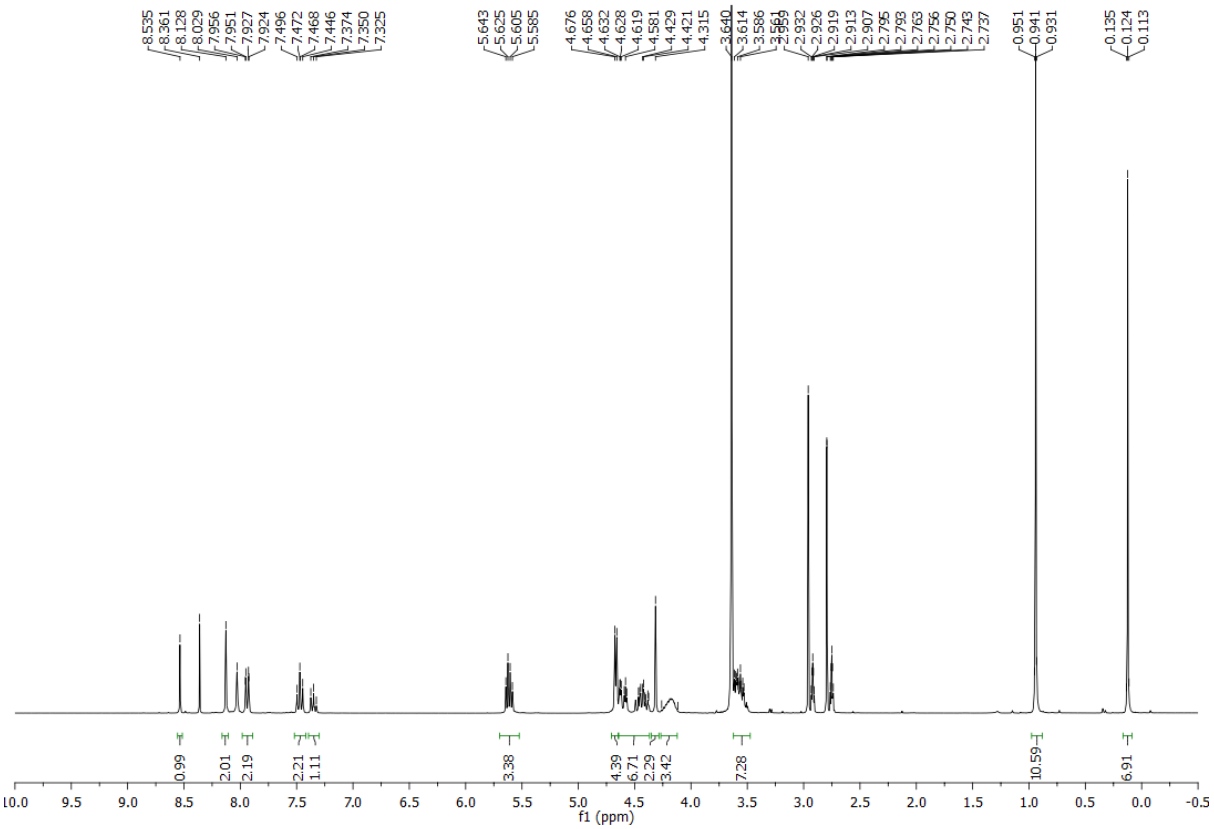


Figure S11. ^{1}H NMR of **8**.

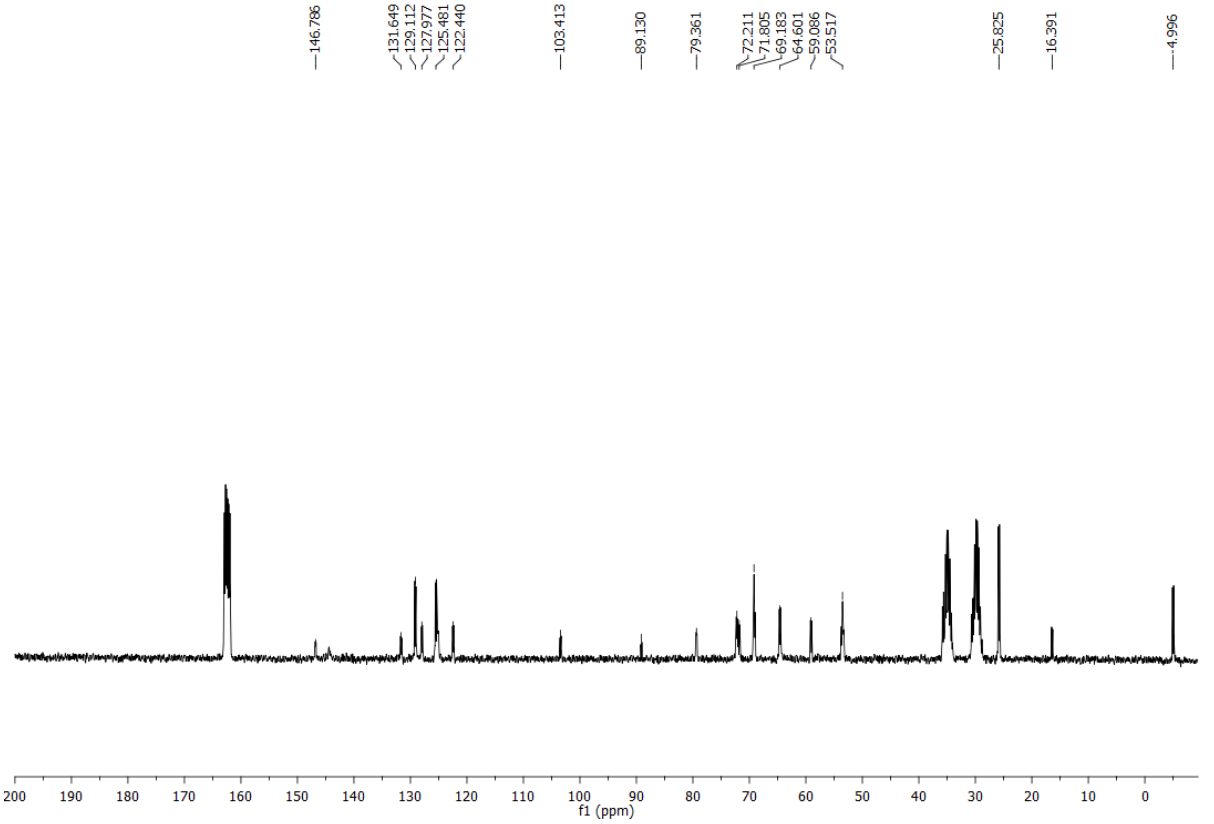


Figure S12. ^{13}C NMR of **8**.

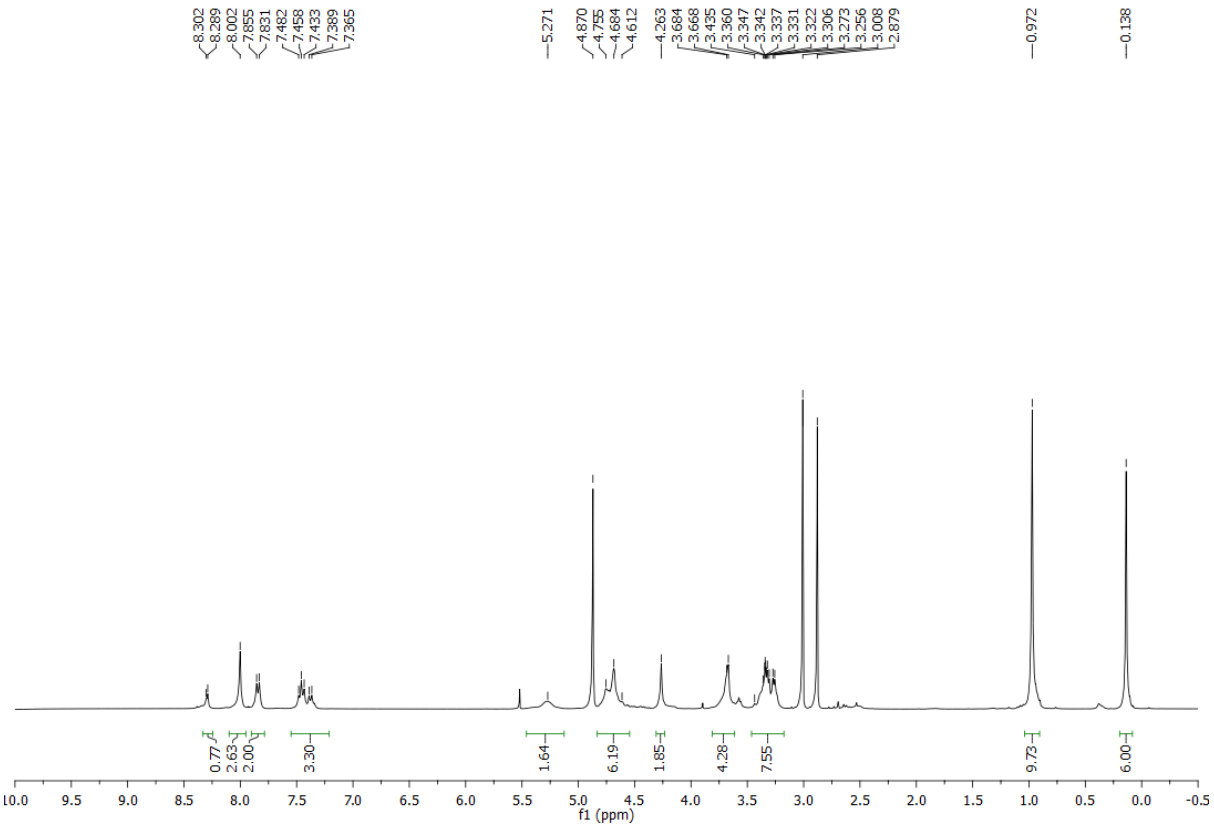


Figure S13. ^{1}H NMR of **9**.

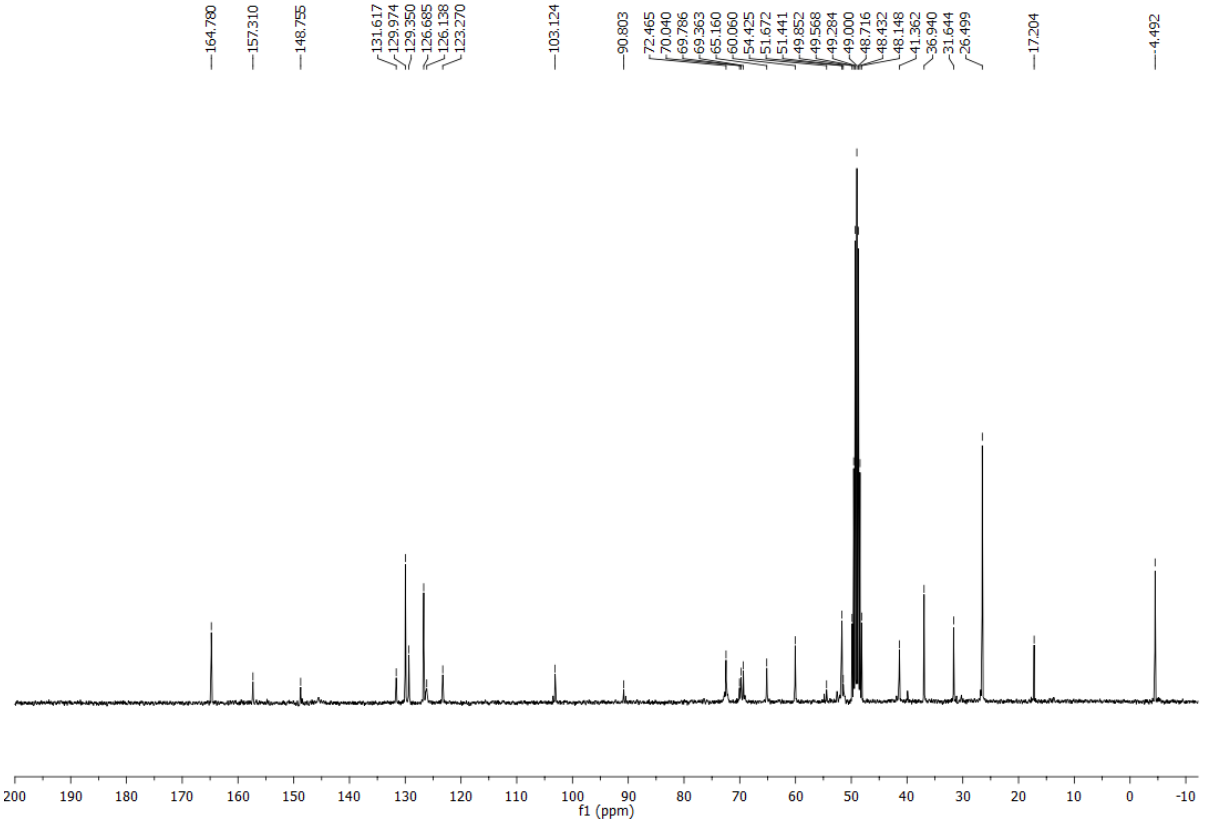


Figure S14. ^{13}C NMR of **9**.

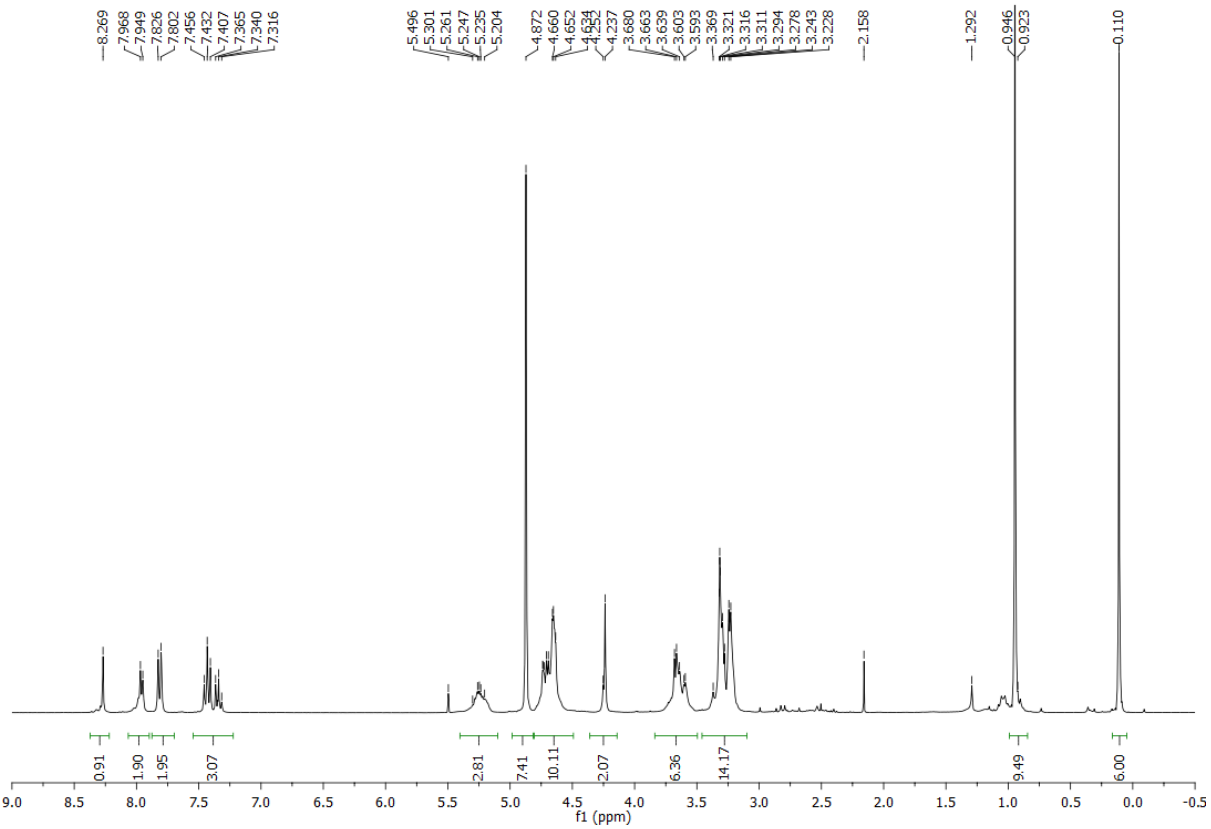


Figure S15. ^{1}H NMR of **10**.

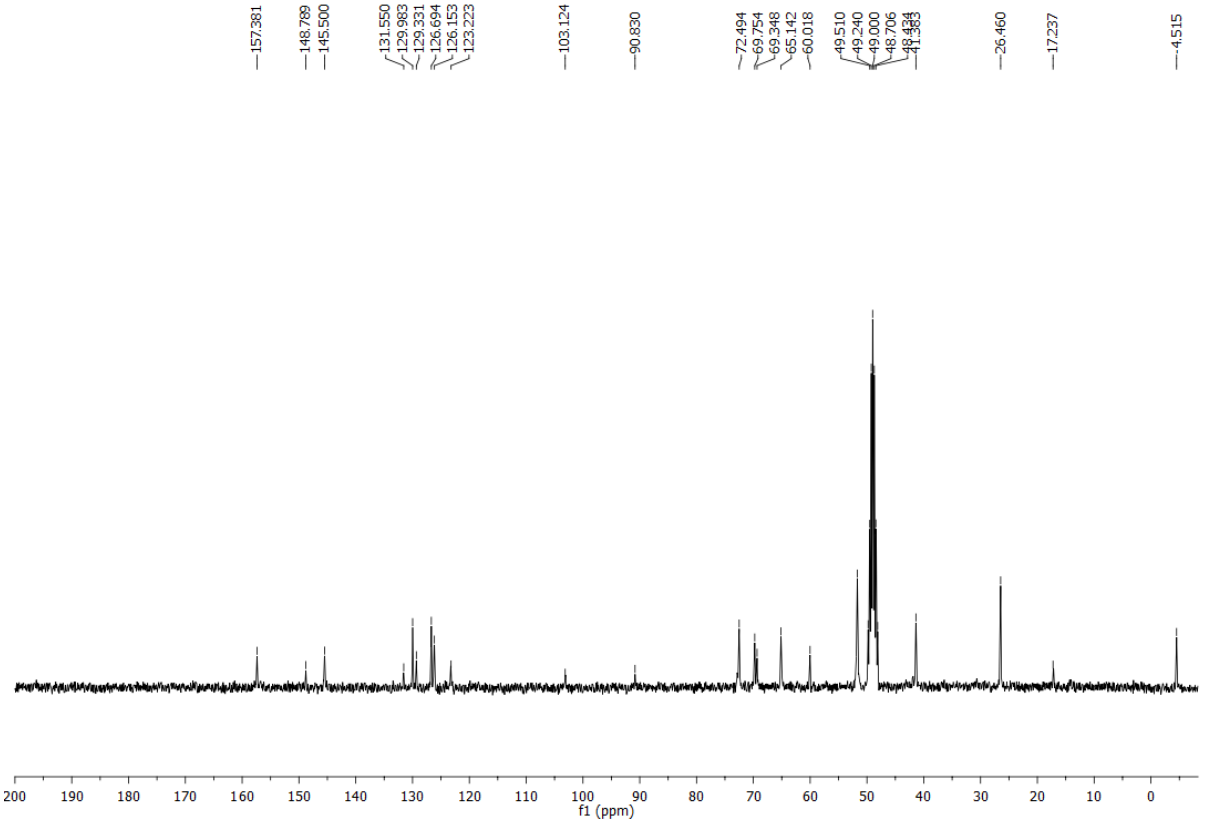


Figure S16. ^{13}C NMR of **10**.

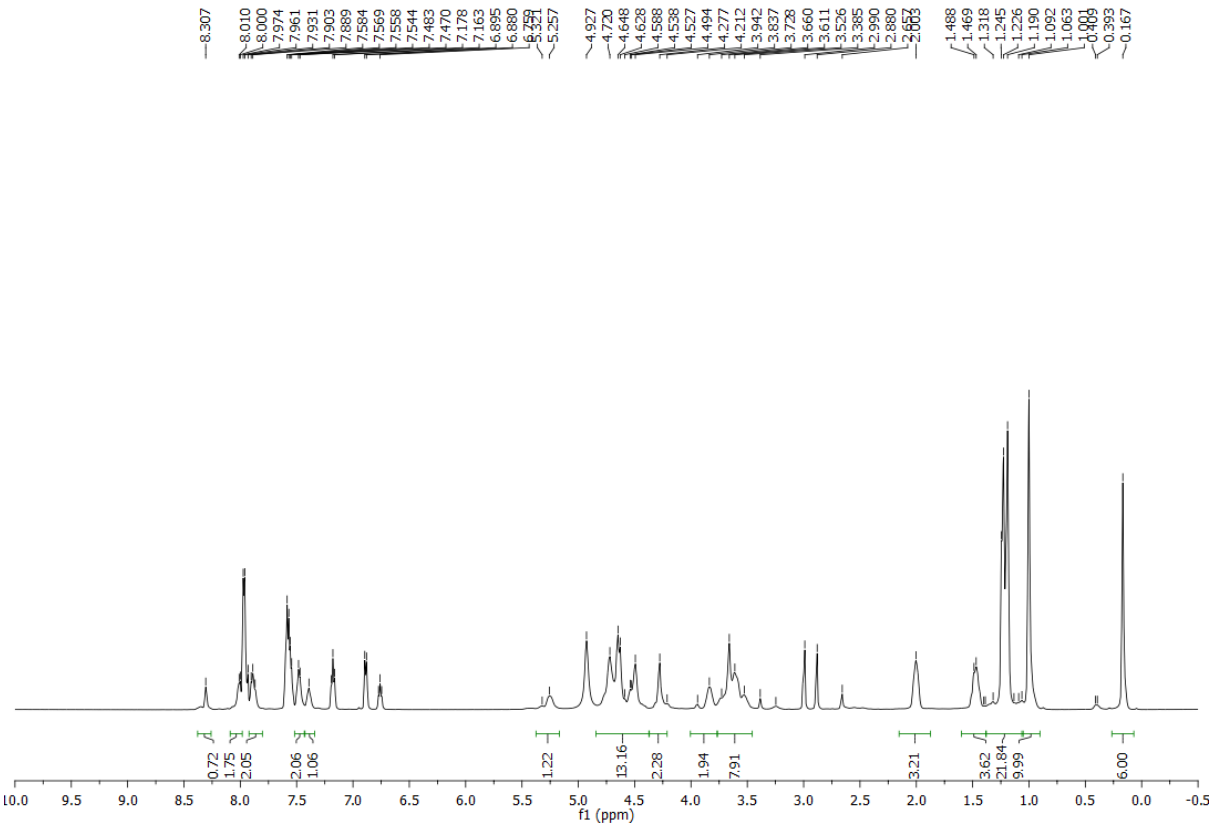


Figure S17. ^{1}H NMR of **S1**.

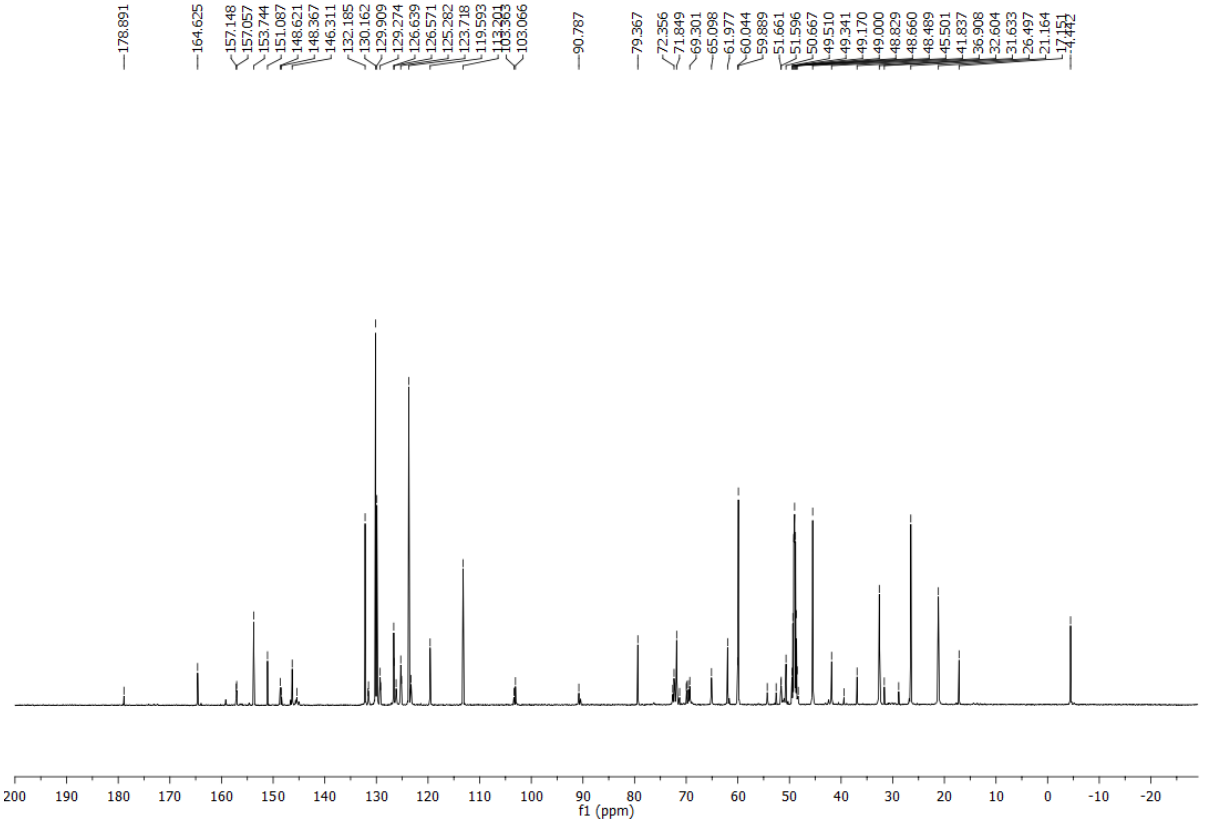


Figure S18. ^{13}C NMR of **S1**.

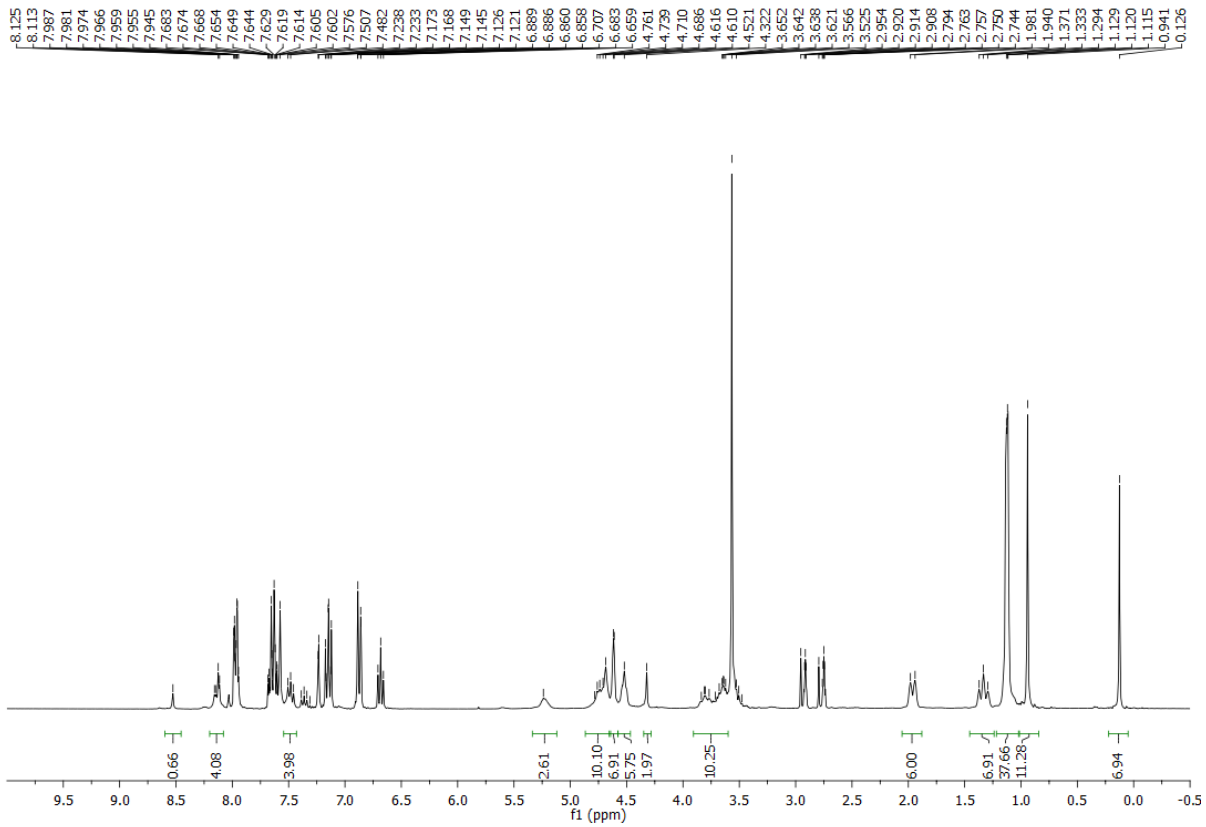


Figure S19. ^{1}H NMR of **S2**.

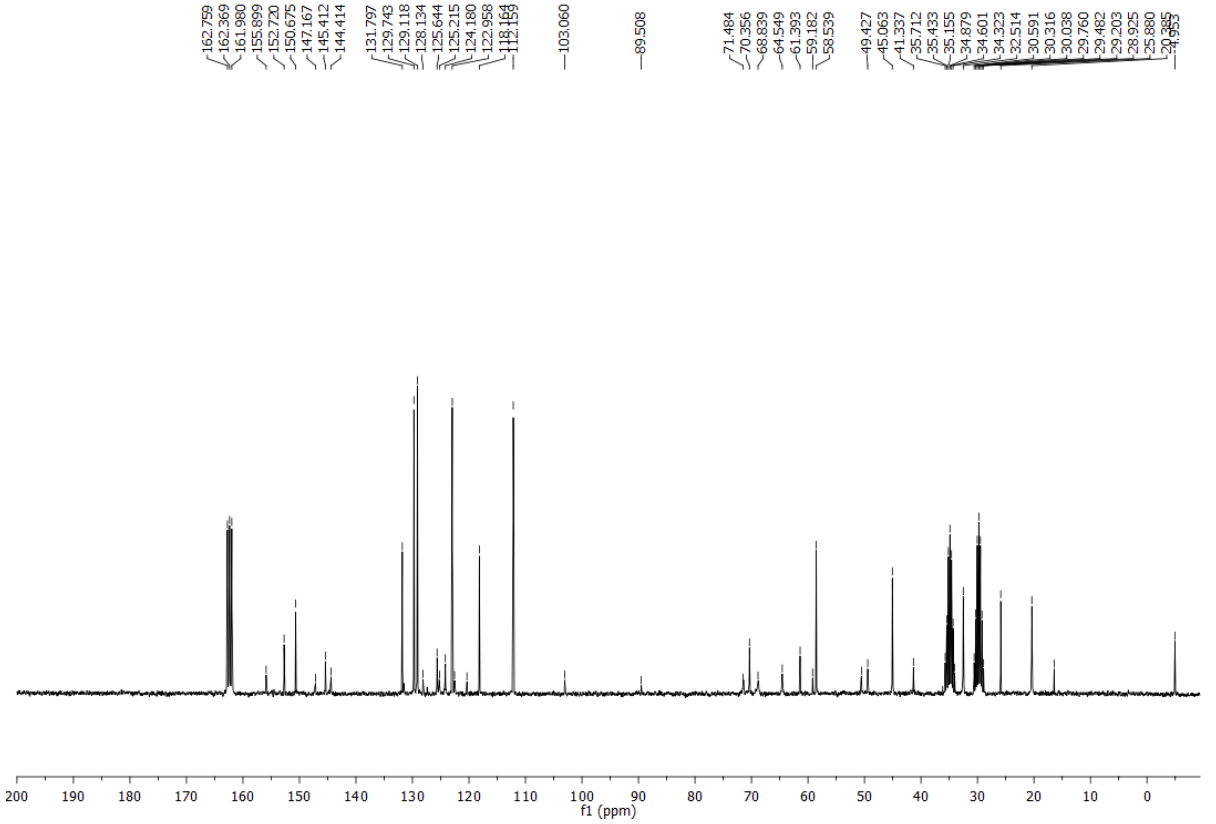


Figure S20. ^{13}C NMR of **S2**.

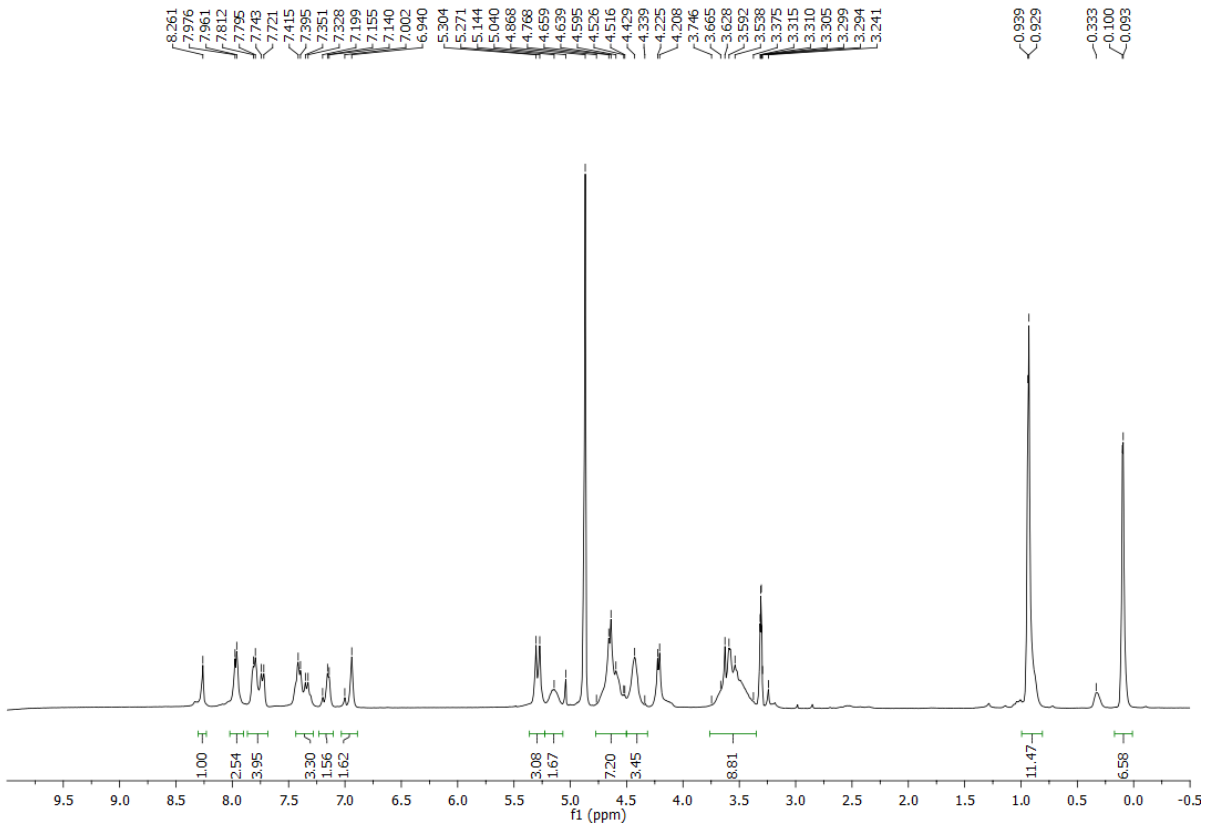


Figure S21. ^{1}H NMR of **S3**.

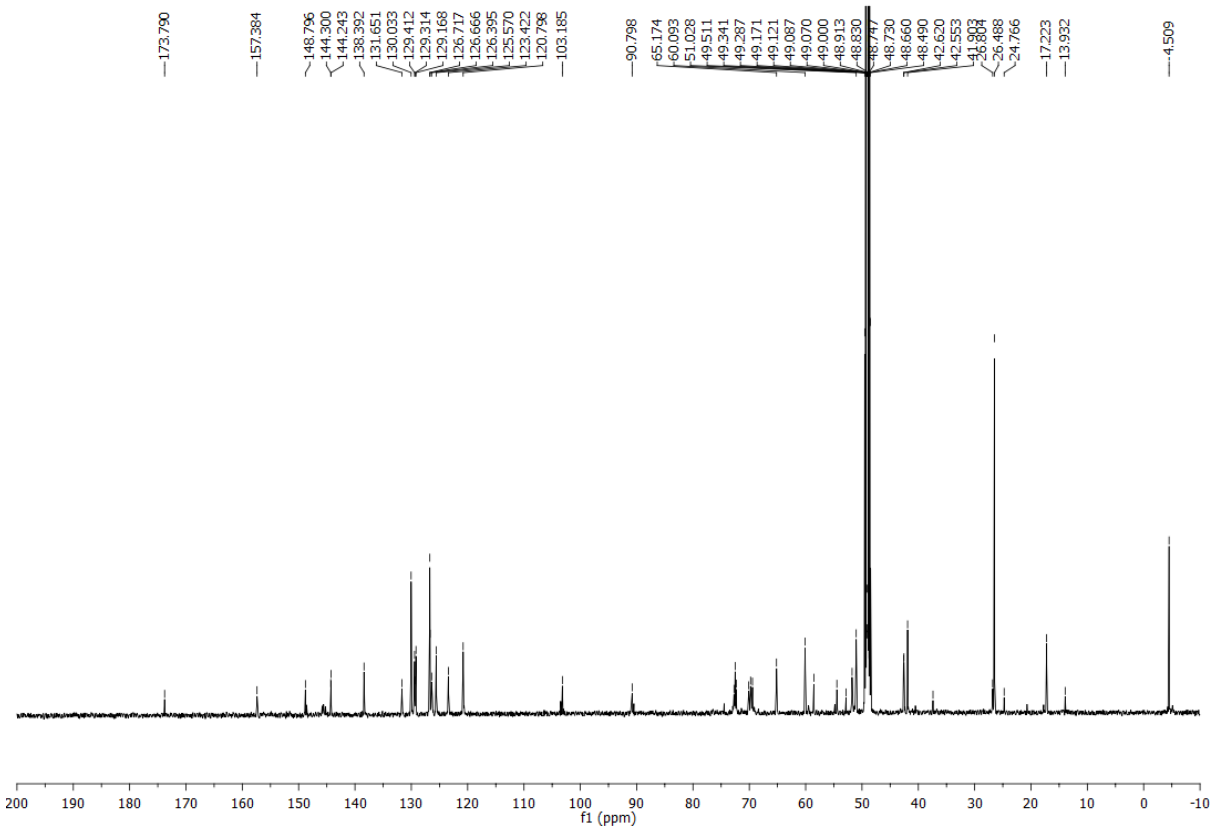


Figure S22. ^{13}C NMR of **S3**.

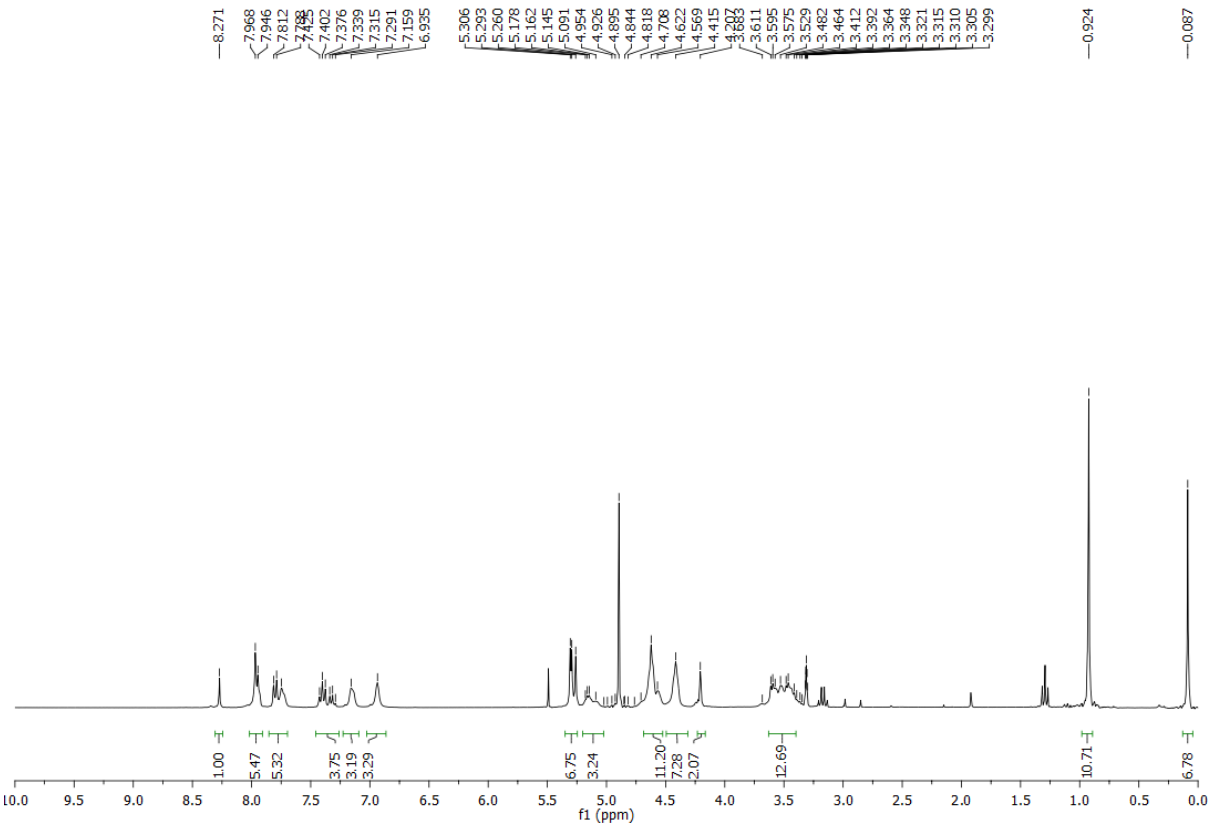


Figure S23. ^{1}H NMR of **S4**.

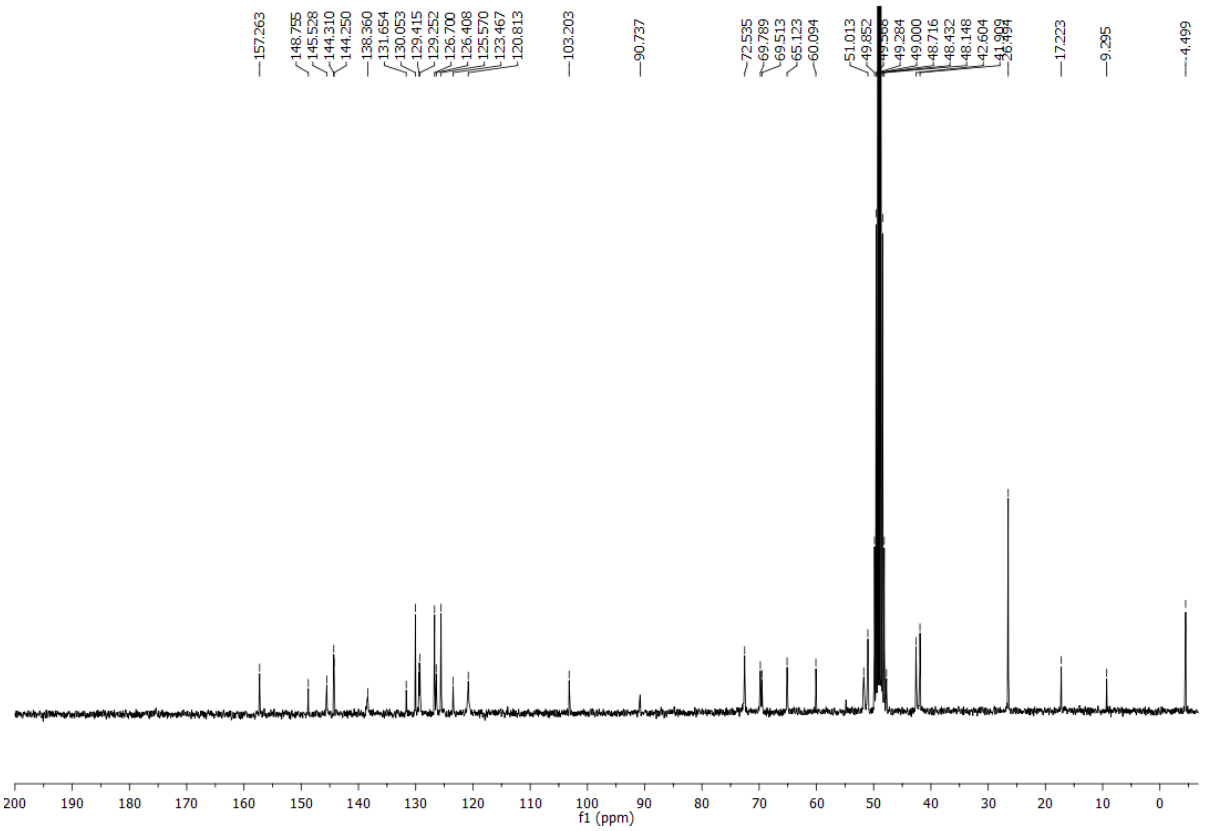


Figure S24. ^{13}C NMR of **S4**.

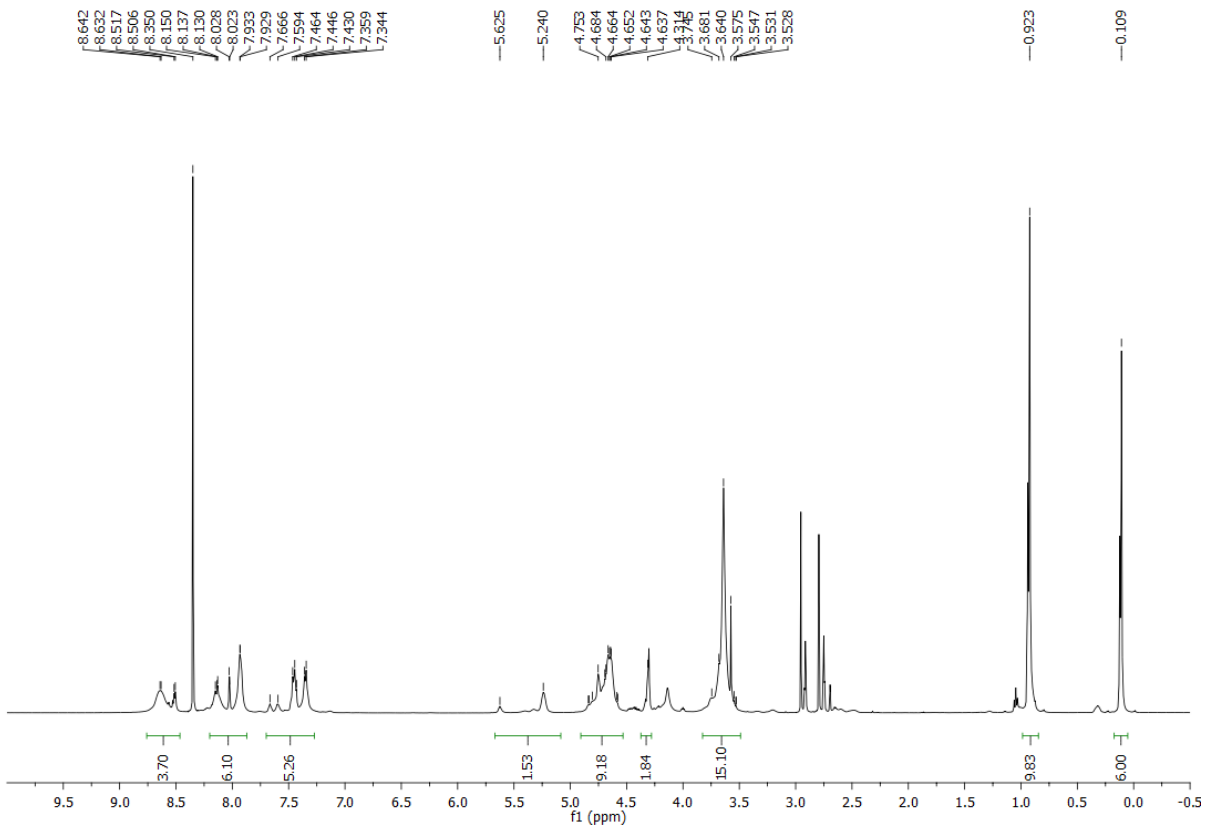


Figure S25. ^{1}H NMR of **S5**.

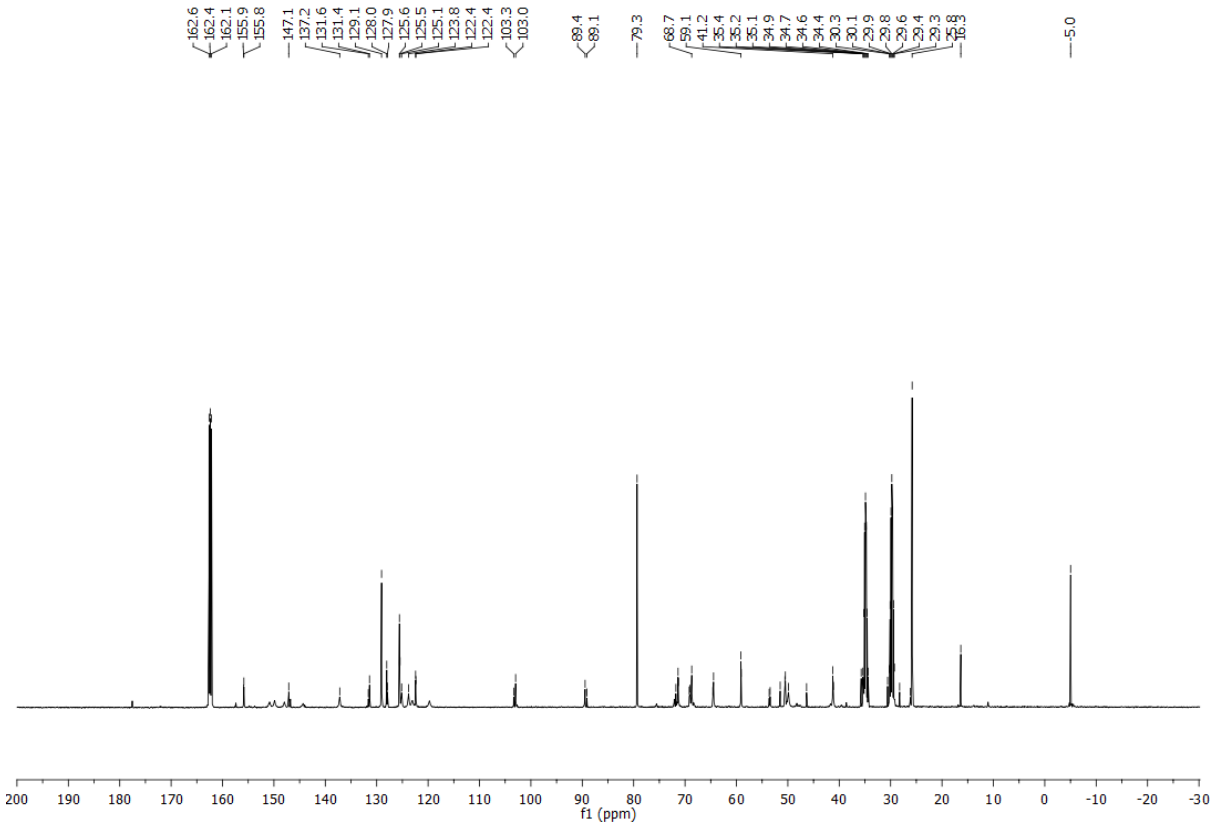


Figure S26. ^{13}C NMR of **S5**.

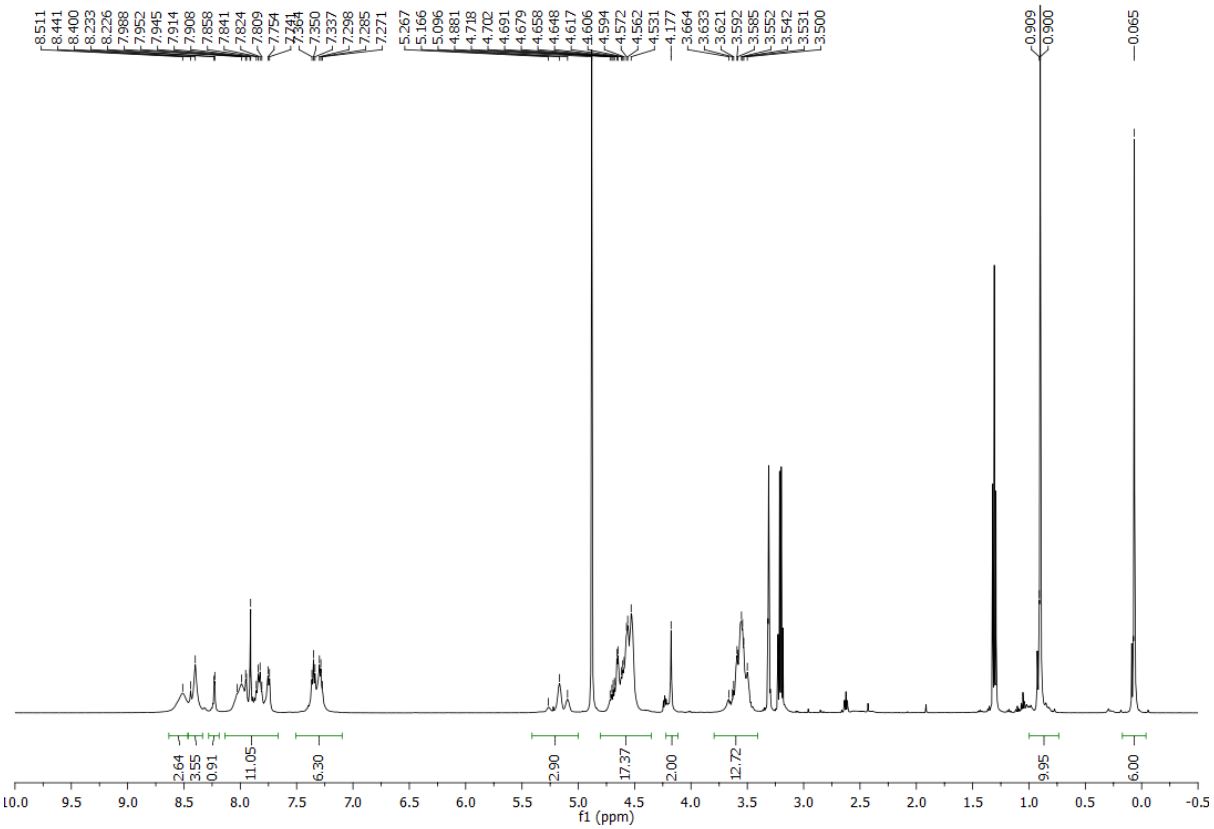


Figure S27. ^{1}H NMR of **S6**.

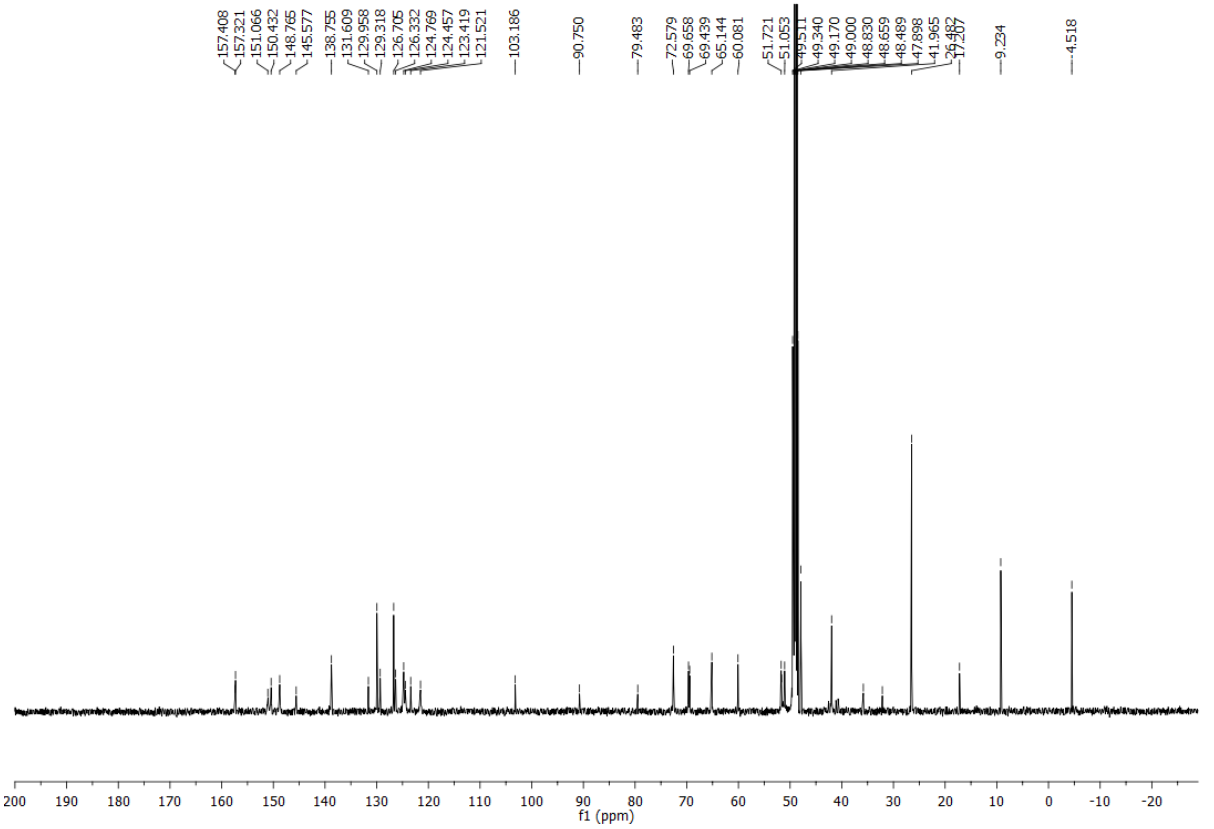


Figure S28. ^{13}C NMR of **S6**.

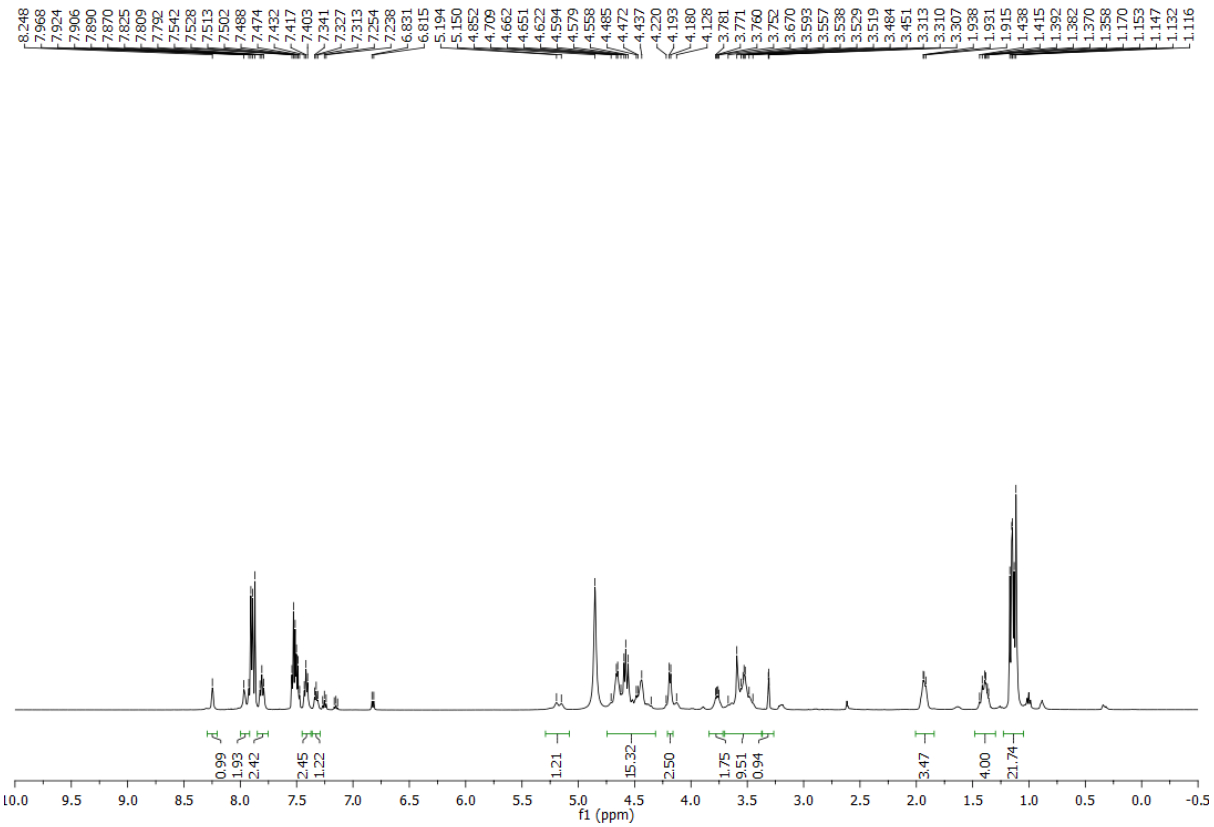


Figure S29. ^{1}H NMR of **13**.

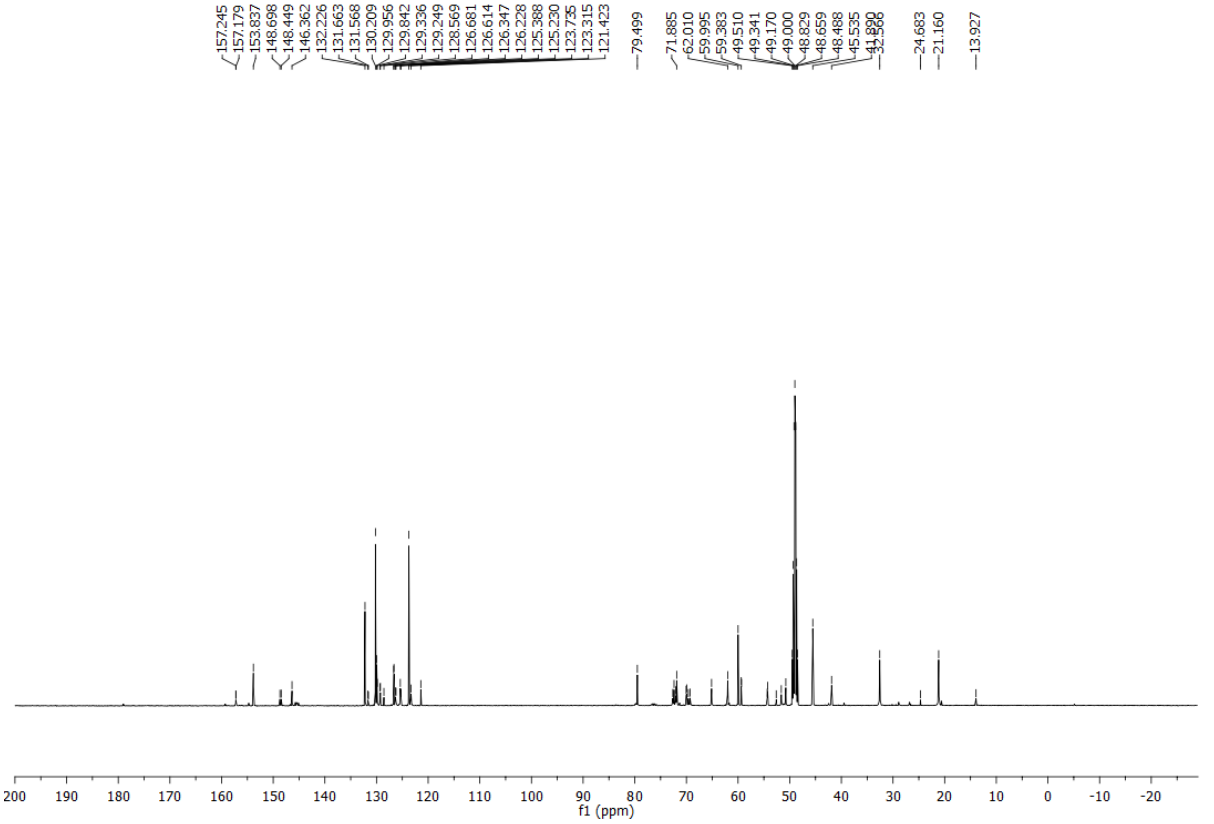


Figure S30. ^{13}C NMR of **13**.

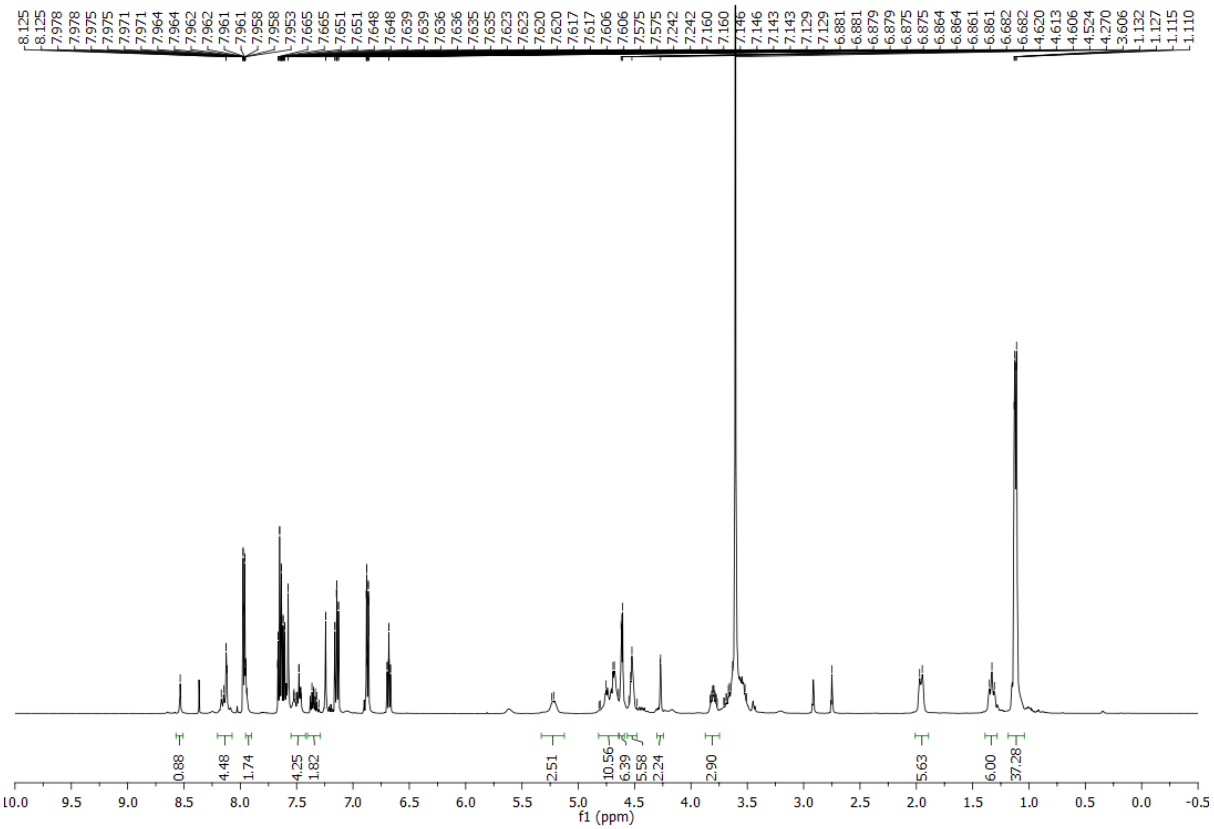


Figure S31. ^{1}H NMR of **14**.

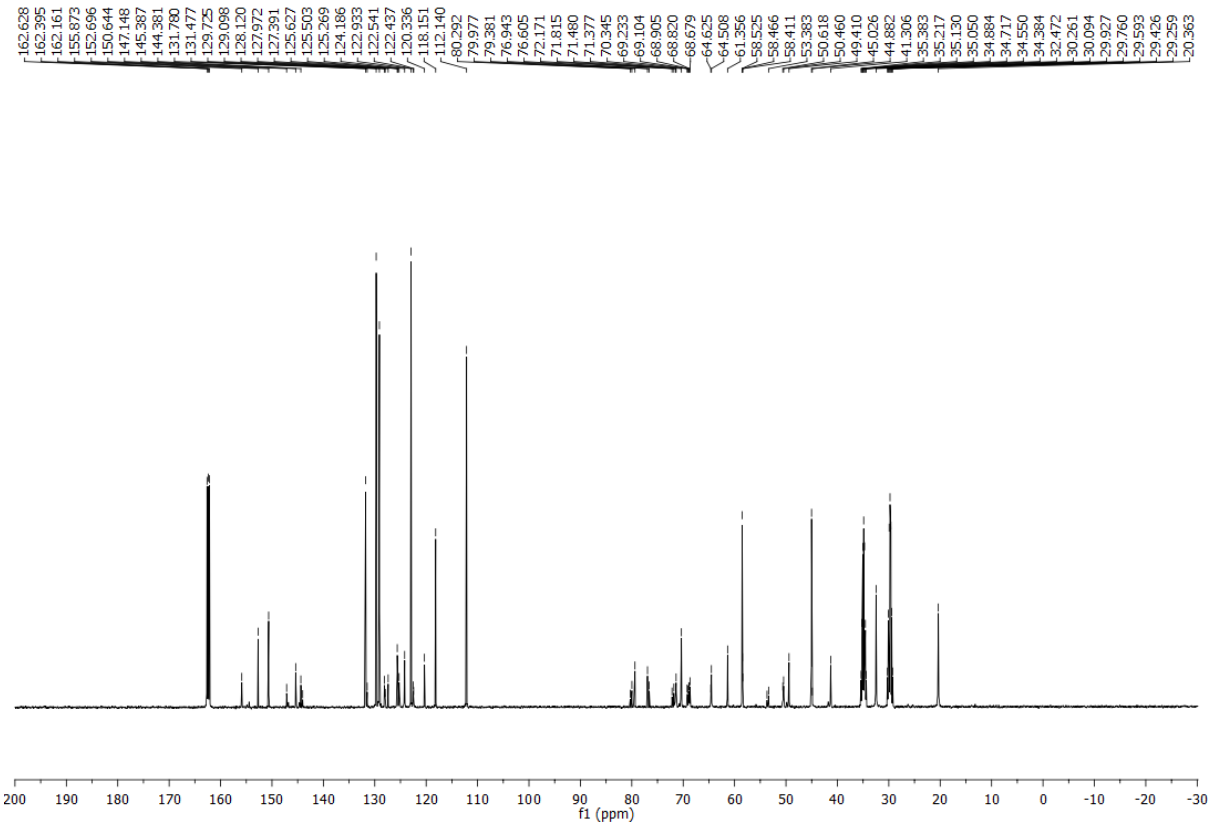


Figure S32. ^{13}C NMR of **14**.

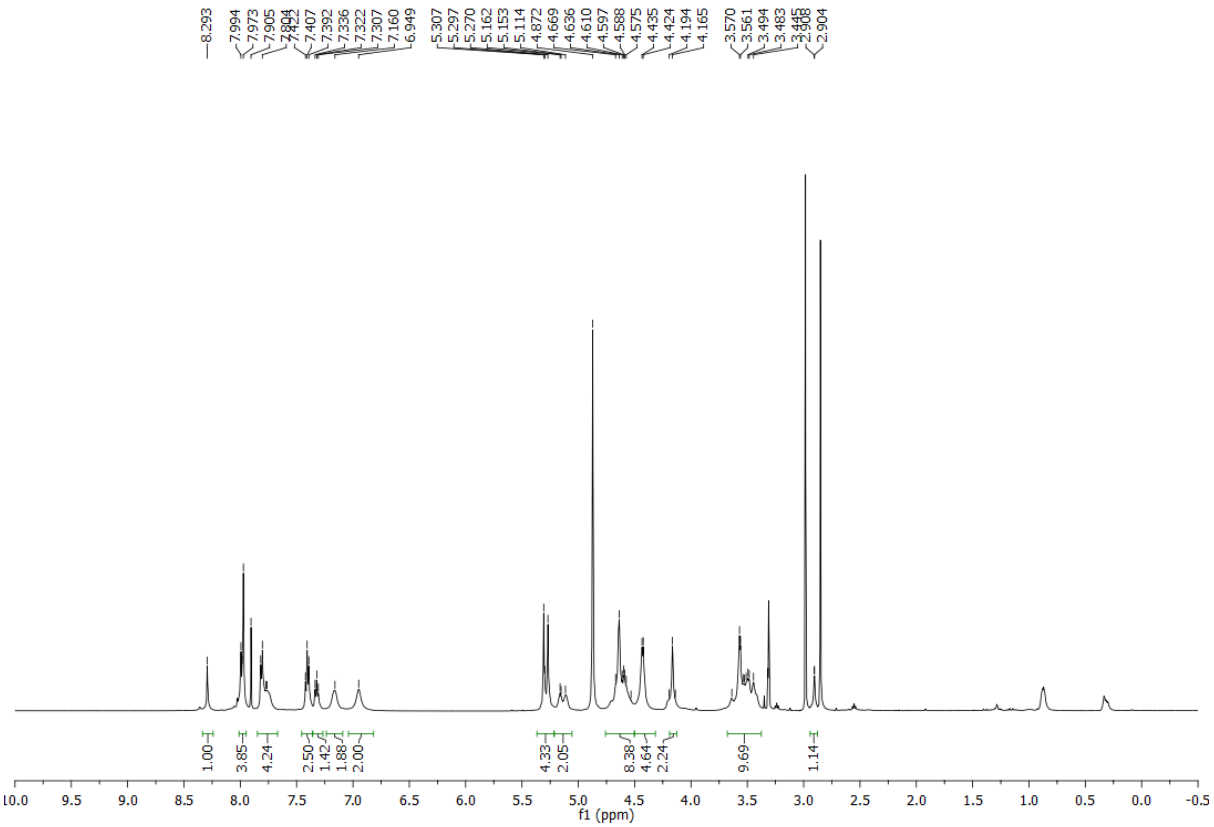


Figure S33. ^{1}H NMR of **15**.

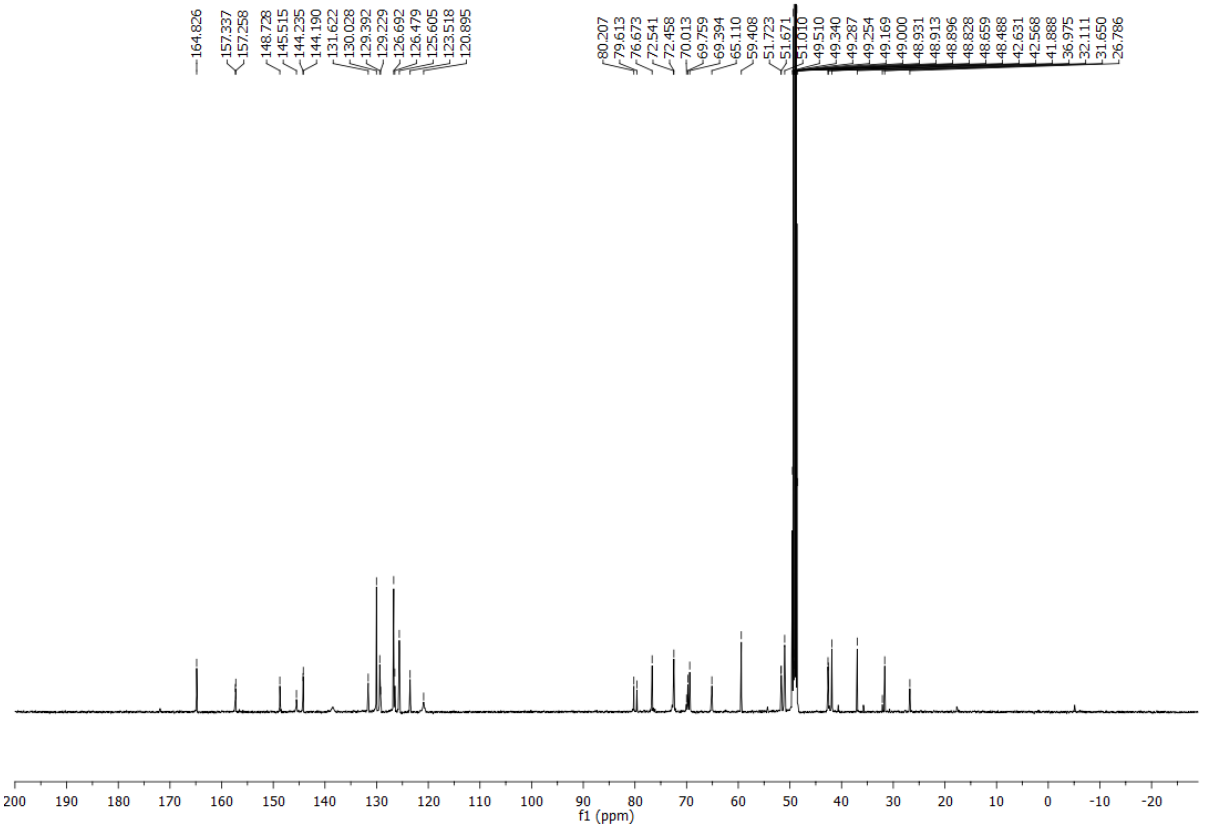


Figure S34. ^{13}C NMR of **15**.

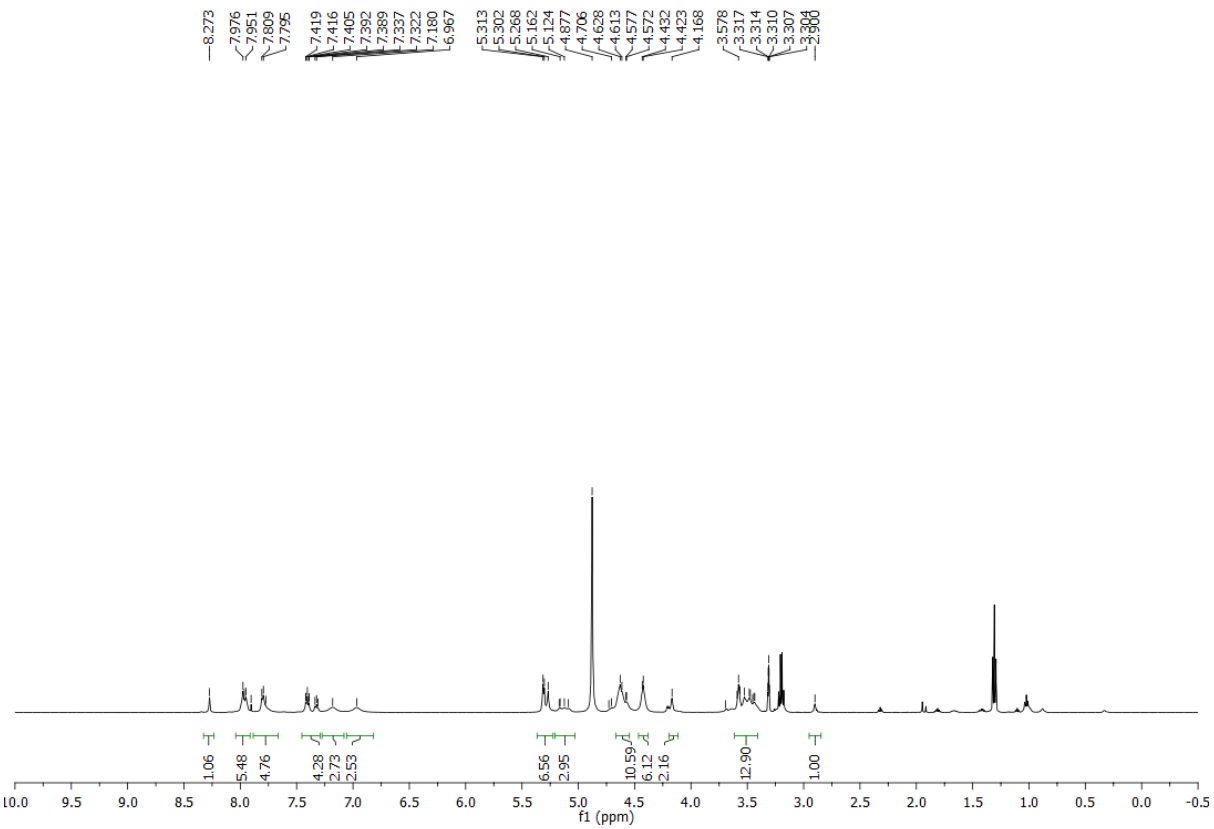


Figure S35. ^{1}H NMR of **16**.

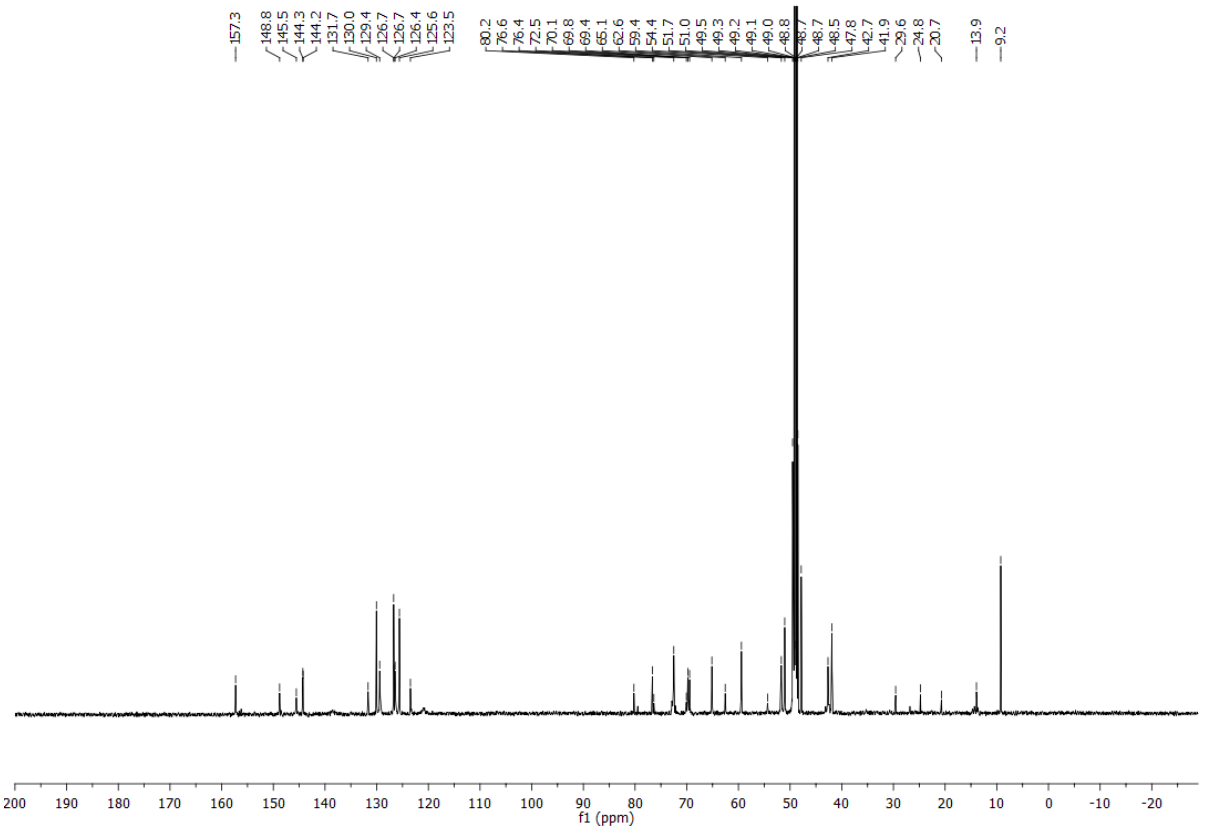


Figure S36. ^{13}C NMR of **16**.

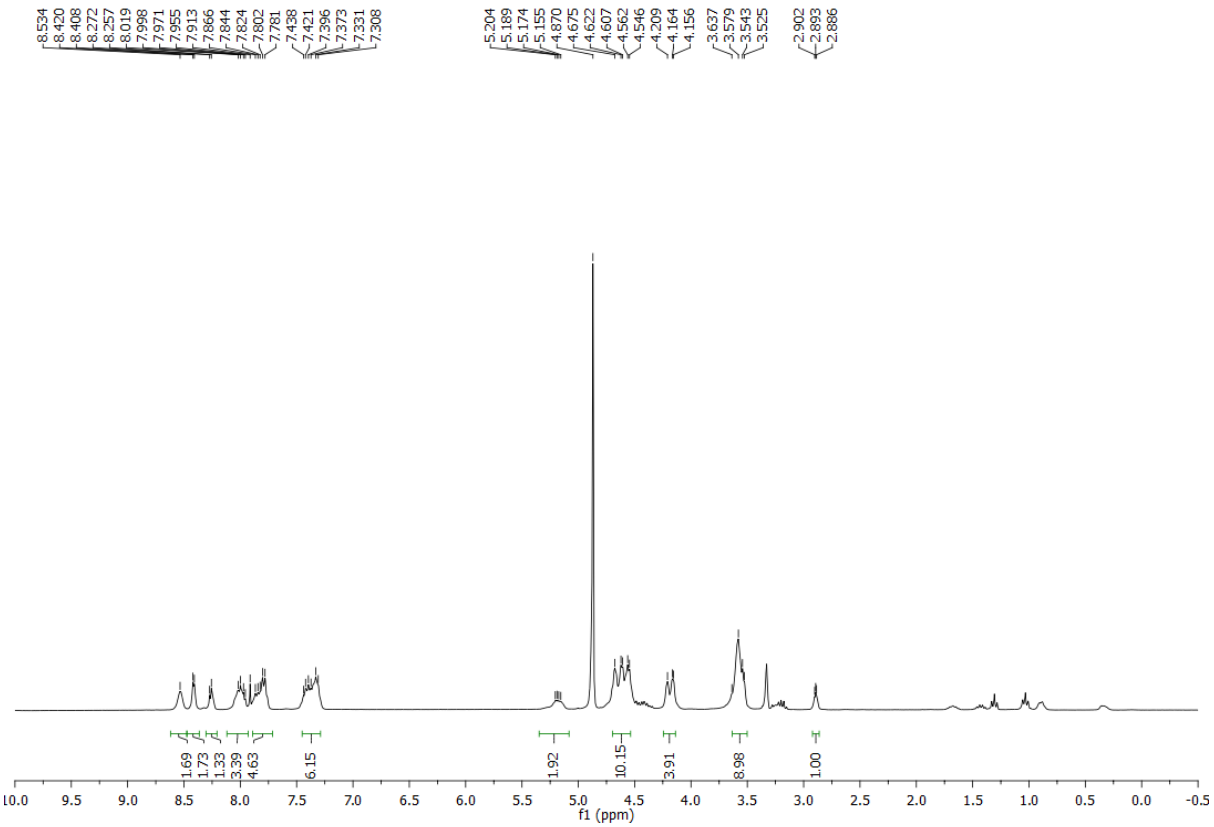


Figure S37. ^{1}H NMR of **17**.

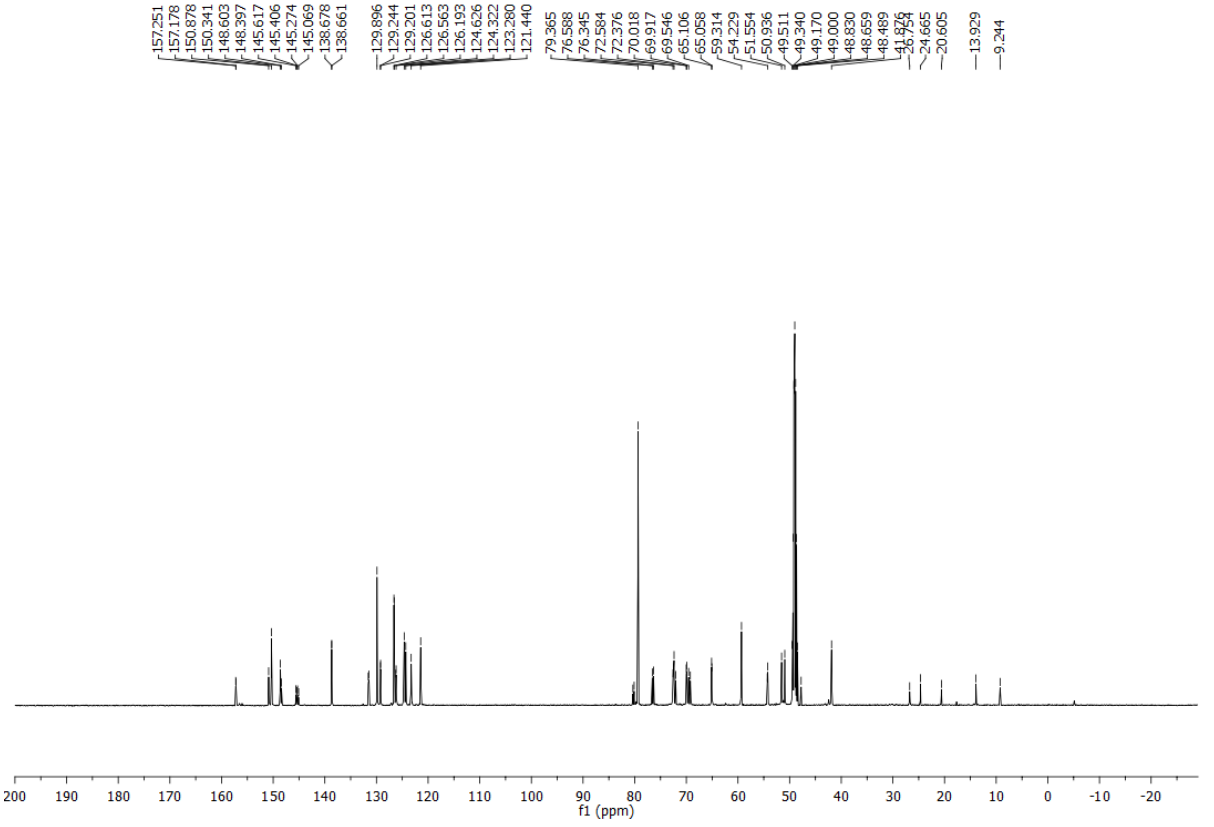


Figure S38. ^{13}C NMR of **17**.

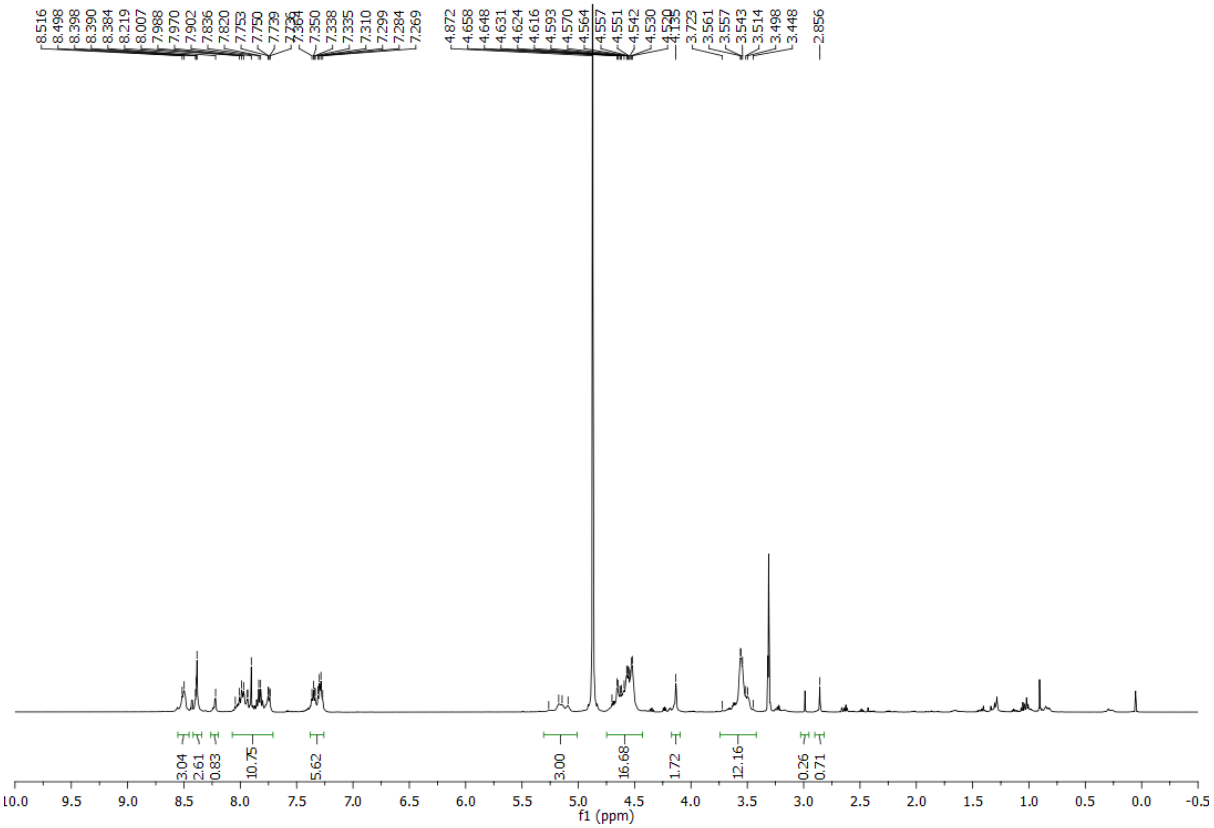


Figure S39. ^{1}H NMR of **18**.

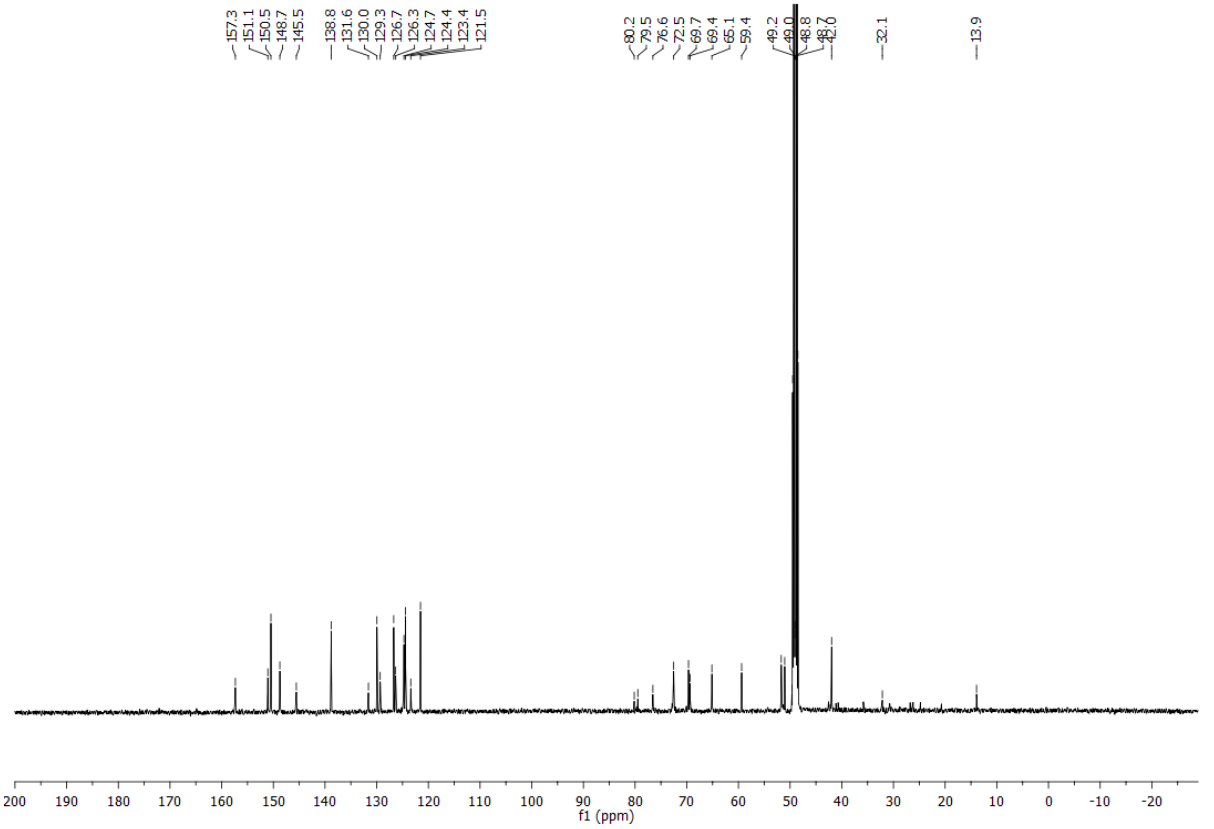


Figure S40. ^{13}C NMR of **18**.

4 Preparation of supported catalysts

4.1 Preparation of azide functionalized silica

Azide functionalized silica (SiO_2-N_3/TMS) was prepared from activated silica (SiO_2) according to our previous literature report.[2] Commercially available spherical silica gel (Sorbtech Technologies, 40-75 μm, 100 Å) was activated by boiling in HCl 6 M for 1 day. The silica was filtered and washed with deionized water until neutral pH and dried in oven for 2 days at 120 °C. The resulting silica was then placed in a round-bottom flask and heated at 120 °C under vacuum for 2 hours. The flask was then allowed to cool to room temperature and toluene (20 mL/g) was added together with AzPTMS (2 mmol/g) and the resulting mixture refluxed overnight. The silica was then filtered, washed with toluene and CH_2Cl_2. The obtained azide functionalized silica was dried in vacuum oven at 50 °C overnight. The flask was then cooled with liquid nitrogen and HMDS (1.5 mL/g) was added under vacuum. The resulting mixture was finally heated at 80 °C for 8 hours. The silica was filtered, washed with CH_2Cl_2 and dried under vaccum oven to give SiO_2-N_3/TMS.

4.2 Preparation of catalyst 19

SiO_2-N_3/TMS was suspended in degassed DMF (15 mL/g). **11**, **12** and 2-ethynyl pyridine were added (1:1:1 molar ratio, 1.2 equiv. *vs* N_3 loading) subsequently followed by Et_3N (5.0 equiv. *vs* N_3 loading) and CuI (0.4 equiv. *vs* N_3 loading). The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH_3CN (150 mL) and CH_2Cl_2 (150 mL) and keep in glovebox.

4.3 Preparation of catalyst 20

SiO_2-N_3/TMS was suspended in degassed DMF (15 mL/g). Dimers **13**, **15** and **17** were added (1:1:1 molar ratio, 1.2 equiv. *vs* N_3 loading) subsequently followed by Et_3N (5.0 equiv. *vs* N_3 loading) and CuI (0.8 equiv. *vs* N_3 loading). The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH_3CN (150 mL) and CH_2Cl_2 (150 mL) and keep in glovebox.

4.4 Preparation of catalyst 21

SiO_2-N_3/TMS was suspended in degassed DMF (15 mL/g). Trimers **14**, **16** and **18** were added (1:1:1 molar ratio, 1.2 equiv. *vs* N_3 loading) subsequently followed by Et_3N (5.0 equiv. *vs* N_3 loading) and CuI (1.2 equiv. *vs* N_3 loading).The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH_3CN (150 mL) and CH_2Cl_2 (150 mL) and keep in glovebox.

5 TGA

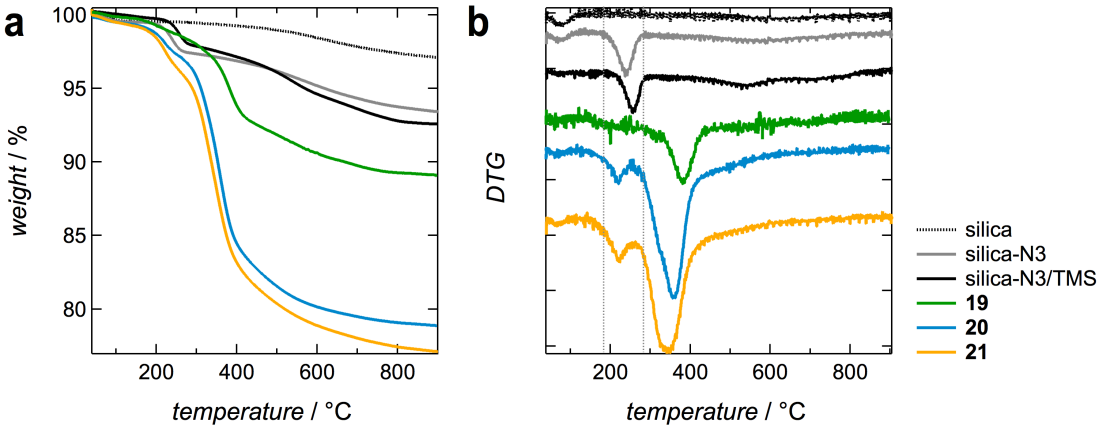


Figure S41. (a) TGA and (b) DTG curves of silica, silica-N_3, silica-N_3/TMS, **19**, **20** and **21**.

6 FT-IR

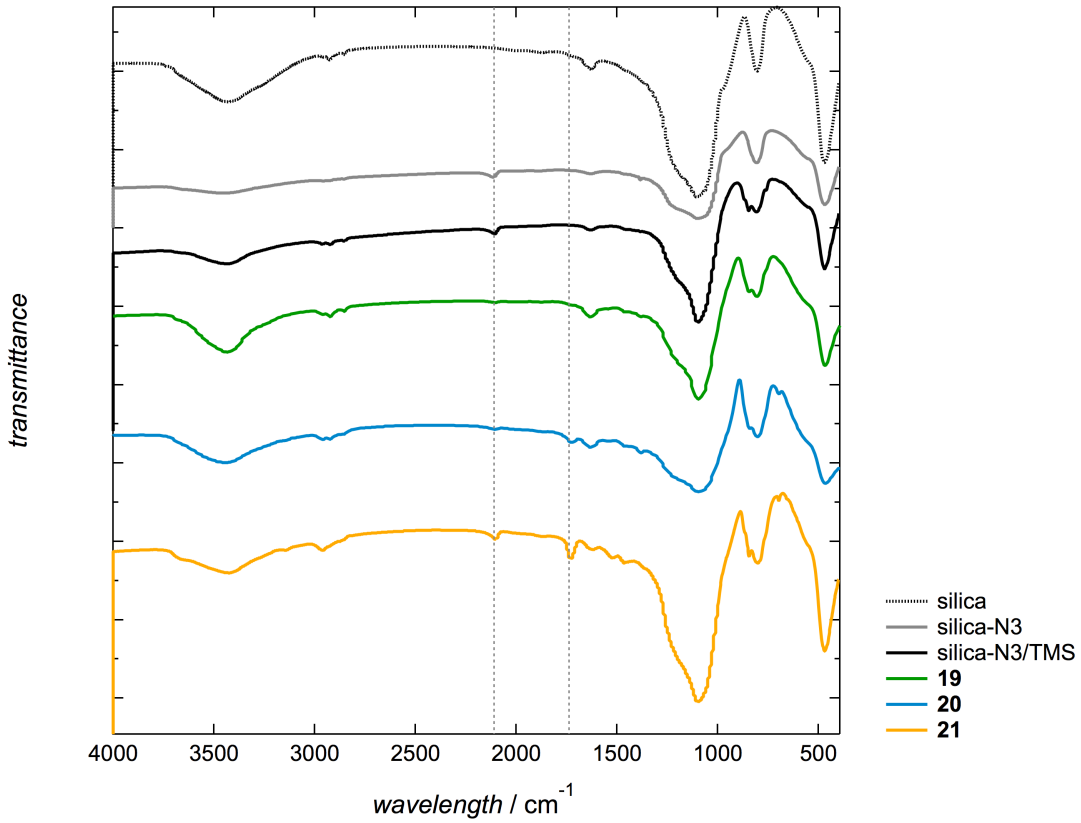


Figure S42. FT-IR spectra of silica, silica-N_3, silica-N_3/TMS, **19**, **20** and **21**.

7 XPS

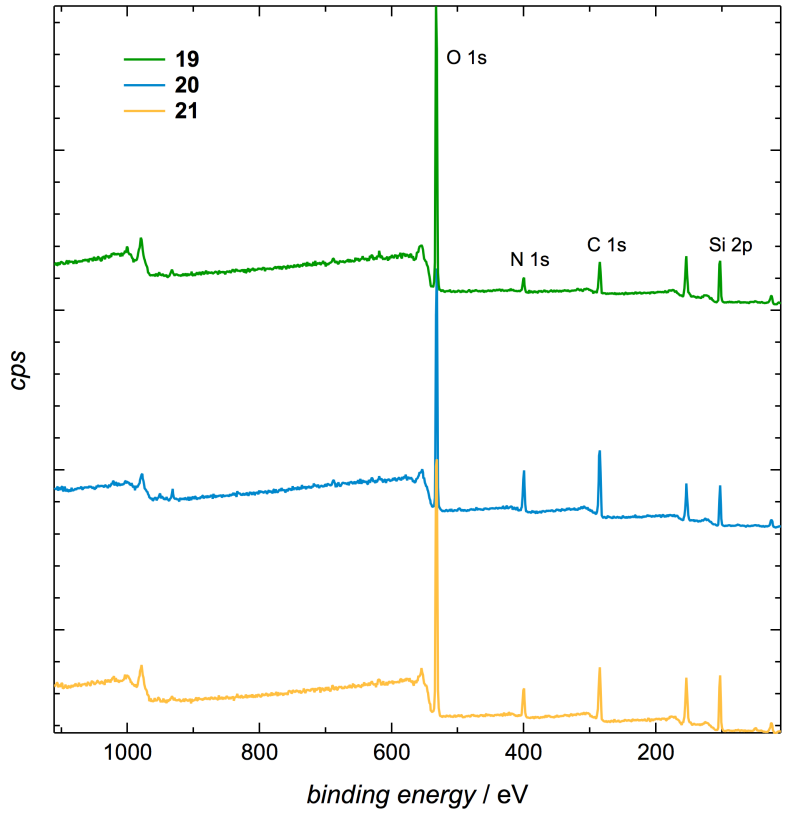


Figure S43. XPS survey scan of **19**, **20** and **21**.

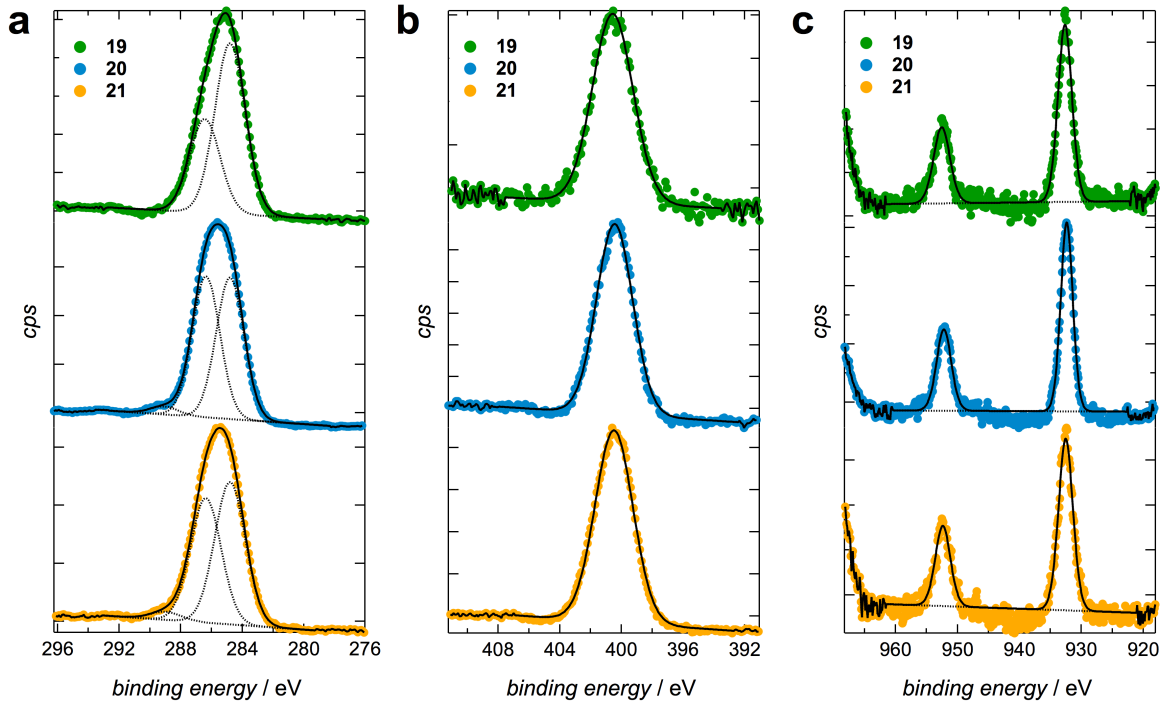


Figure S44. (a) C 1*s*, (b) N 1*s* and (c) Cu 2*p* HR XPS spectra of **19**, **20** and **21**.

8 ICP-AES

catalyst	Cu (mmol/g)	Cu (mmol/g) after run 1	4
19	0.08	0.09	-
20	0.09	0.08	-
21	0.10	0.10	0.09

9 Physisorption

catalyst	surface area (mmol/g)	pore volume BJH desorption (cm^3/g)	pore size BJH desorption (nm)
SiO_2	288	0.86	8.7
SiO_2-N_3-TMS	214	0.60	7.0
19	208	0.48	6.0
20	167	0.41	6.5
21	160	0.41	7.1

10 References

1. S. Angelos, Y. W. Yang, K. Patel, J. F. Stoddart and J. I. Zink, *Angew. Chem. Int. Ed.*, 2008, **47**, 2222-2226.
2. A. E. Fernandes, O. Riant, K. F. Jensen and A. M. Jonas, *Angew. Chem. Int. Ed.*, 2016, **55**, 11044-11048.
3. P. Chandra, A. M. Jonas and A. E. Fernandes, *J. Am. Chem. Soc.*, 2018, **140**, 5179-5184.