Supporting Information

Dynamic Self-Assembly of Supramolecular Catalysts from Precision Macromolecules

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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. 2D NMR DOSY experiments were recorded on a Bruker Avance 500 MHz Spectrometer equipped with a 5 mm BBO probehead. All NMR samples were equilibrated at the measurement temperature of 303 K for 5 min before data collection. Spinning was deactivated to avoid convection. ^{1}H NMR spectra were acquired with the zg pulse program from the Bruker library using 32 scans and calibrated to the CD_3CN residual signal (δ = 1.94 ppm) as an internal reference.

2D ^{1}H DOSY experiments were performed using the standard Bruker ledbpgp2s pulse program with 16 t1 increments on 32 K data points. The acquisition time was 2.04 s and the relaxation delay was 10.0 s (D1). Diffusion time was set between 0.2 – 0.1 s (D20) and rectangular gradient pulse duration was between 1.0 – 0.8 ms (P30). Gradient recovery delays of 0.15 ms followed the application of each gradient pulse. Data was accumulated by linearly varying the

diffusion encoding gradients over a range from 2 to 95 % for 16 gradient increment values with 32 scans each. Individual rows of the quasi-2D diffusion databases were phased and baseline corrected. NMR data processing was performed using Topspin software, and the actual diffusion coefficients used for diffusion analysis were measured by T1/T2 relaxation module.

The diffusion coefficient at 30°C measured over different displacement ranges corresponding to protons of the oligomers were averaged to obtain the average diffusion coefficient $\overline{D}$. The hydrodynamic radii of the single oligomers were obtained from DOSY measurements performed at 30°C and 1 mM to avoid aggregation; the radii were computed from the Stokes-Einstein equation using $\mu_0 = 0.355$ mPa.s for the dynamic viscosity.[1] The average diffusion coefficient of equimolar mixtures of two oligomers were measured for a molar concentration in each oligomer of 1, 2.5 and 5 mM, corresponding to 0.5, 1.25 and 2.5 mol% relative to the (virtual) concentration of 0.2 M in alcohol used in the catalytic experiments.

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.

LC-QTOF-MS/MS analysis were performed on an SYNAPT G2-Si high definition mass spectrometer (Waters) equipped with a NanoLockSpray dual electrospray ion source (Waters). Samples were diluted 2 to 10 times in 50% (v/v) acetonitrile, 0.1% formic acid or in 50% (v/v) methanol, 0.1% formic depending on the quality and the intensity of the signal. Coated fused silica PicoTip™ Econo12 Emitters for nanoelectrospray, outer diameters: 1 µm Tip (New Objective, USA) were filled with 5 µL of samples and placed on the Universal NanoFlow™ Sprayer (Waters). The eluent was sprayed at a spray voltage of 2.8 k. The source temperature was set to 100 °C. The cone gas flow was 20 L/h with a nano flow gas pressure of 0.3 bar. MS spectra were acquired and processed with MassLynx software (Waters). Full scan MS and MS2 spectra (*m/z* 50 to 2000) were in resolution mode (20,000 resolution FWHM at *m/z* 400) with a scan time of 0.1 sec. Tandem mass spectra of the precursor were generated in the trapping region of the ion mobility cell by using a collision energy ramp from 10 V to 70 V. Charged ions are selected to be submitted to the MSMS fragmentation over the *m/z* range from 50 to 2000 with a scan time of 0.25 sec. For the post-acquisition lock mass correction of the data in the MS method, the doubly charged monoisotopic ion of [Glu^1]-fibrinopeptide B was used at 100 fmol/µL using the reference sprayer of the nanoESI source with a frequency of 30 s at 0.5 µL/min into the mass spectrometer.

SEC analysis was performed on an Agilent 1260 Infinity multi-detector system (MDS) equipped with light scattering (LS), differential refractive index (DRI), and viscometer detectors. The separations of the injected samples were done using a set of two Agilent PLgel Mixed E columns (3 µm particle diameter, 7.5 mm ID x 300 mm length) offering a good resolution in the domain of 100 to 20000 g/mol (polystyrene equivalent). The solvent was dimethyl formamide

(DMF) containing 0.1% LiBr, and the flow rate was 1 mL/min. The injection volume was 100 µL. The columns and detectors were kept at a constant temperature of 60°C. The samples were prepared at a concentration of 3 mg/mL and filtered on 0.2 µm filters before injection. The classical SEC interpretation involves a calibration with polystyrene (PS) standards and the measured molar masses are relative to PS. Absolute molar masses can be measured with SEC using LS and DRI detectors, which were calibrated by injecting a PS standard with narrow molar mass distribution (Mw = 11600 g/mol, dn/dc for PS in DMF = 0.16 mL/g, concentration of 1 mg/mL).

Aerobic oxidation experiments were performed from 30 °C to 60 °C under O_2 bubbling (4.93 mL/min) using a SLA5850 thermal mass flow controller from Brooks, in a 0.2M solution of alcohol in the mixture solvent of acetonitrile (95%) and dimethyl sulfoxide (5%) (2 mmol of alcohol in 1 mL mixture solvent). Different loadings of catalytic oligomers were used, expressed in mol% relative to the amount of alcohol, keeping a 1:1 pyridyltriazole (P):Cu molar ratio (except for single oligomers missing P units, in which case Cu was introduced in equimolar amounts as the oligomer). Before the experiments, different catalytic oligomers were dissolved in acetonitrile or acetonitrile and dimethyl sulfoxide mixture solvent, and the CuI was separately dissolved in acetonitrile at a suitable concentration (stock solutions). For catalytic experiments, alcohol and *p*-xylene (used as internal standard) was introduced into 2 mL vials, followed by catalytic oligomers and an appropriate amount of acetonitrile and dimethyl sulfoxide. The mixture was stirred to form a uniform solution, then a controlled amount of CuI solution was added into the mixture under stirring. The reaction time was counted when the mixture was at the set temperature and O_2 was introduced. Although the solution was turbid just after copper salt addition, it turned transparent and greenish during reaction (Figure S0).

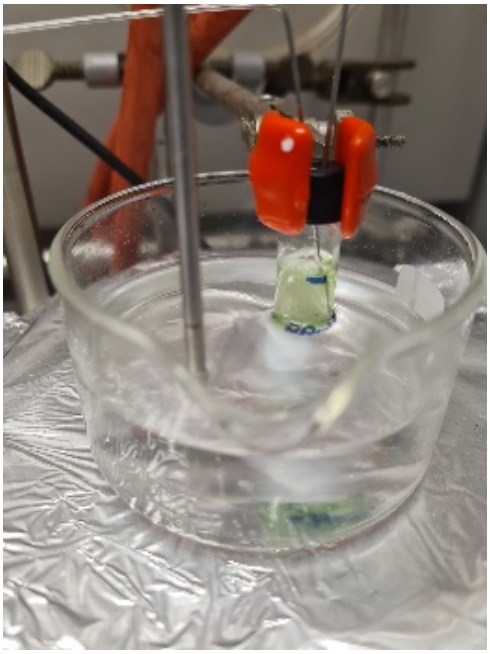


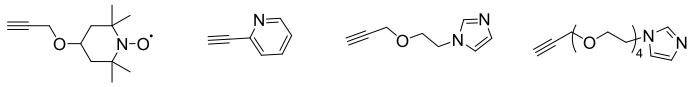
Figure S0. Picture of the catalytic medium during reaction at 30°C for the O_a/O_{b1} system, with 2.5 mol% M units.

10 μL aliquots were then taken at selected time points and diluted by 990 μL acetonitrile to prepare a gas chromatograph (GC) sample. GC was performed on a Shimadzu GC-2010 equipped with an FID detector, with *p*-xylene (internal standard) only used for the detection of possible experimental problems. Benzaldehyde, benzyl alcohol, cinnamaldehyde, cinnamyl alcohol, *trans* 2-hexen-1-al, *trans* 2-hexen-1-ol, octanal, octanol, cyclohexanecarboxaldehyde and cyclohexanemethanol were detected at 9.1, 11.3, 5.74, 5.34, 7.47, 8.0, 3.1, 3.5, 3.2- and 2.9-min elution time, respectively. The yields were computed as the ratios between the area below the aldehyde peak and the sum of the areas below the aldehyde and alcohol peaks. No other oxidation product than the aldehyde was detected in the chromatograms. The slope of the yield versus time was defined as the catalytic rate; the turnover frequency was obtained by dividing the rate by the molar content in M units in the catalyst, except for single oligomers with no M units, in which case the rate was divided by the molar content in oligomer.

2 EXPERIMENTAL SYNTHETIC PROCEDURES

2.1 Synthesis of precursors

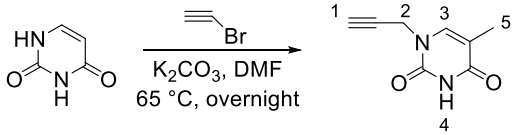
2.1.1 Synthesis of catalytic units



4 **5** **6** **7**

The compounds **4**, **5**, **6** and **7** were reported in our previous work.[2–6]

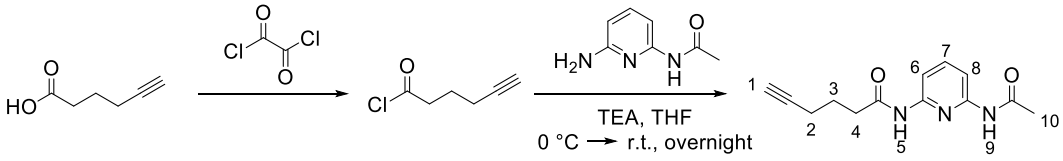
2.1.2 Synthesis of base T



Base T

Thymine (5 g, 39.7 mmol, 1 equiv.) and K_2O_3 (2.743 g, 19.8 mmol, 0.5 equiv.) were added into a flask followed by DMF (200 mL) and propargyl bromide (W% = 80% in toluene) (4.42 mL, 39.7 mmol, 1 equiv.), and the mixture was stirred at 60 °C overnight.[7,8] After that, the solvent was removed under reduced pressure. Milli-Q water (250 mL) was added into the residue and extracted with EtOAc (150 × 3 mL). The organic phase was collected, and dried with Na_2SO_4 before being concentrated with reduced pressure. The crude product was purified by flash chromatography on silica gel column (EtOAc /*n*-hexane = 3/7 to 6/4) to give the final product base T as a white solid (3.055 g, 47%). **Base T**, **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 11.36 (s, 1H, H_4), 7.56 (d, J = 1.3 Hz, 1H, H_3), 4.47 (d, J = 2.5 Hz, 2H, H_2), 3.39 (t, J = 2.5 Hz, 1H, H_1), 1.77 (d, J = 1.2 Hz, 3H, H_5). **^{13}C NMR (75 MHz, DMSO-*d*$_6$)** δ 164.12, 150.35, 140.10, 109.37, 78.65, 75.63, 36.29, 11.90. **HRMS** *m/z* = 165.0659 (calcd. for $C_8H_8N_2O_2$ 165.0659 $[M+H]^+$).

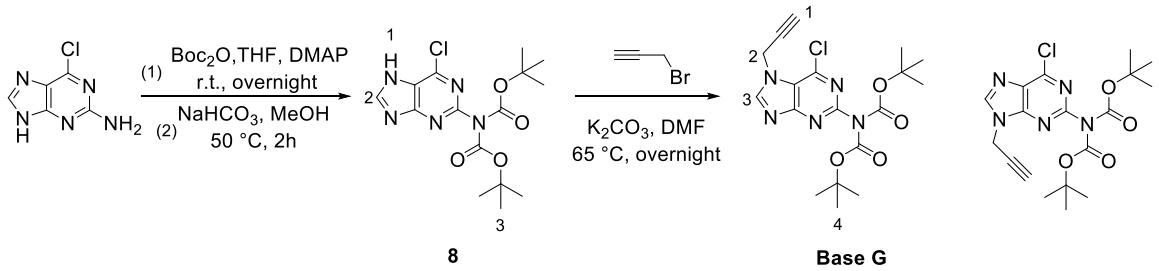
2.1.3 Synthesis of base D



Base D

5-Hexynoic acid (3.24 g, 28.9 mmol, 1.1 equiv.) was added into anhydrous THF (30 mL) followed by oxalyl chloride (5 g, 39.4 mmol, 1.4 equiv.) added dropwise at 0 ℃. Then, a few drops of DMF were added into the mixture, and the mixture was stirred at room temperature for 2 h. After that, the mixture was concentrated via distillation in vacuo to give the product 5-hexynoic chloride without further purification.[9] 2,6-Diaminopyridine (3.976 g, 26.3 mmol, 1 equiv.) and triethylamine (3.992 g, 39.4 mmol, 1.5 equiv.) were dissolved in dry THF (80 mL), then the mixture was cooled to 0 °C in an ice bath. 5-Hexynoyl chloride in anhydrous THF (20 mL) was added dropwise within 1 h. Then the mixture was stirred at 0 °C for 1 h followed by overnight stirring at room temperature.[10] The solvent was removed under reduced pressure, and then the residue was dissolved in DCM (100 mL) and washed with 0.5 mol/L HCl (50 × 3 mL). NaOH aq (1mol/L) was used to neutralize excess acid before washing with saturated NaCl. The organic layer was collected, dried with Na_2SO_4 and concentrated under reduced pressure. The final product was a light-yellow solid (5.03 g, 78%) after recrystallization in EtOAc. **Base D**, **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.96 – 7.52 (m, 5H, H_5, H_6, H_7, H_8 and H_9), 2.53 (t, J = 7.3 Hz, 2H, H_2), 2.32 (td, J = 6.7, 2.6 Hz, 2H, H_4), 2.19 (s, 3H, H_{10}), 2.02 – 1.89 (m, 3H, H_1 and H_3). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 170.88, 168.66, 149.53, 149.43, 141.06, 109.59(2C), 83.36, 69.64, 36.09, 24.88, 23.79, 17.89. **HRMS** *m/z* = 246.1235 (calcd. for $C_{13}H_{15}N_3O_2$ 246.1237 $[M+H]^+$).

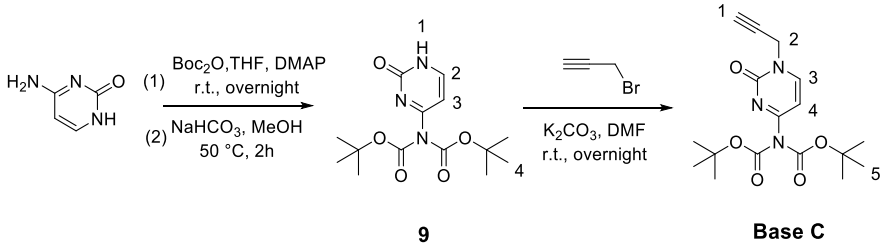
2.1.4 Synthesis of base G



Compound **8** was synthesized according to the reported literature.[11] **8**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.39 (s, 1H, H_1), 6.46 (s, 1H, H_2), 1.49 (s, 18H, H_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.09, 151.45, 150.82, 150.70, 145.97, 129.33, 84.51, 28.01. **HRMS** *m/z* = 370.1275 (calcd. for $C_{15}H_{20}ClN_5O_4$ 370.1277 $[M+H]^+$).

Compound **8** (4.24 g, 11.5 mmol, 1 equiv.) and K_2O_3 (0.794 g, 5.75 mmol, 0.5 equiv.) were added into a flask followed by DMF (60 mL) and propargyl bromide (W% = 80% in toluene) (1.28 mL, 11.5 mmol, 1 equiv.) and the resulting reaction mixture was stirred at 60 °C overnight. The solvent was removed under reduced pressure. Milli-Q water (100 mL) was added into the residue and extracted with EtOAc (100 × 3 mL). The organic phase was collected, and dried with Na_2SO_4 before concentrated with reduced pressure. The crude product was purified by flash chromatography on silica gel column (EtOAc /*n*-hexane = 1/9 to 5/5) to give a homolog white solid, namely the substitution by propargyl occurred are at both N and NH, with the product substituted by propargyl at the N atom being dominant (2:1). We selected *tert*-butyl (*tert*-butoxycarbonyl) (6-chloro-7-(prop-2-yn-1-yl)-7H-purin-2-yl) carbamate as base G (1.88 g, 40%). **Base G**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.35 (s, 1H, H_3), 5.03 (d, J = 2.6 Hz, 2H, H_2), 2.58 (t, J = 2.6 Hz, 1H, H_1), 1.45 (s, 18H, H_4). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 152.31, 152.26, 151.61, 150.75, 145.18, 130.16, 83.96, 76.17, 75.06, 33.91, 28.04. **HRMS** *m/z* = 408.14340 (calcd. for $C_{18}H_{22}ClN_5O_4$ 408.14331 $[M+H]^+$).

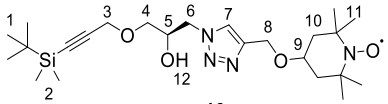
2.1.5 Synthesis of base C



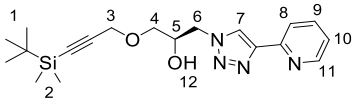
Compound **9** was synthesized according to the reported literature.[11] **^{1}H NMR (300 MHz, $CDCl_3$)** δ 13.13 (s, 1H, H_1), 7.74 (d, J = 7.2 Hz, 1H, H_2), 7.12 (d, J = 7.1 Hz, 1H, H_3), 1.56 (s, 18H, H_4). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 163.80, 158.67, 149.59, 145.92, 96.90, 85.13, 27.84. **HRMS** *m/z*= 312.1553 (calcd. for $C_{14}H_{21}N_3O_5$ 312.1554 $[M+H]^+$).

The synthetic route of Base **C** was the same as base **G.** Compound **9** (4.98 g, 16 mmol, 1 equiv.) was used, after the reaction, **base C** was obtained as a light-yellow solid (3.86 g, 69%) purified by flash chromatography on silica gel column (EtOAc /*n*-hexane = 1/9 to 5/5). **Base C**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.92 (d, J = 7.5 Hz, 1H, H_3), 7.10 (d, J = 7.5 Hz, 1H, H_4), 4.67 (d, J = 2.6 Hz, 2H, H_2), 2.56 (t, J = 2.6 Hz, 1H, H_1), 1.55 (s, 18H, H_5). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.66, 154.54, 149.63, 145.89, 96.74, 85.15, 77,16, 75.99, 38.98, 27.83. **HRMS** *m/z* = 350.1712 (calcd. for $C_{17}H_{23}N_3O_5$ 350.1711 $[M+H]^+$).

2.2 Synthesis of monomers

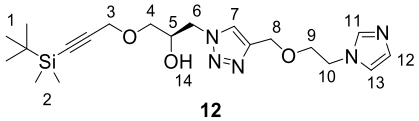


Compound **(*R*)-3** (540 mg, 2 mmol, 1.3 equiv.) and compound **4** (329 mg, 1.6 mmol, 1 equiv.) were added into a flask followed by adding EtOH (14 mL) under stirring. Water (4 mL), sodium ascorbate solution (80 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (32 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (100 mL) and Na_2EDTA (0.05 M, 100 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 5/5) to give the final product **10** as a brown oil (665 mg, 77%). **HRMS** *m/z* = 479.3050 (calcd. for $C_{24}H_{43}N_4O_4Si$• 479.3048 $[M+H]^+$).



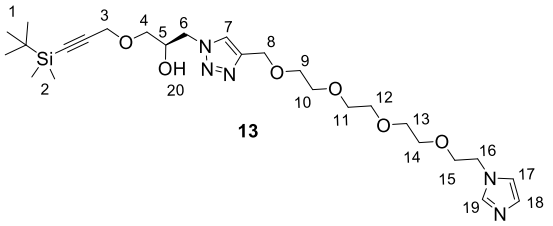
11

The compound **P** was reported in our previous work.[2]



12

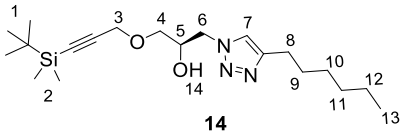
Compound **(*R*)-3** (1.08 g, 4 mmol, 1 equiv.) and compound **6** (0.6 g, 1 equiv.) were added into a flask followed by EtOH (42 mL) with stirring. Water (12 mL), sodium ascorbate solution (160 mg in 6 mL water, 0.2 equiv.) and $CuSO_4$ solution (64 mg in 4 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50°C followed by cooling to room temperature. Then, EtOAc (150 mL) and Na_2EDTA (0.05 M, 150 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 (150 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 5/95) to give the final product **12** as a yellow oil (1.68 g, 100 %). **12, ^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.47 (s, 1H, H_7), 7.24 (s, 1H, H_{11}), 6.87 (d, *J* = 21.4 Hz, 2H, H_{12} and H_{13}), 4.58 (m, 3H, H_6 and H_8), 4.25 (m, 4H, H_3, H_5 and H_6), 4.03 (m, 2H, H_{10}), 3.83 (m, 2H, H_9), 3.63 (dd, *J* = 5.2, 3.7 Hz, 2H, H_4), 0.94 (s, 9H, H_1), 0.12 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 144.14, 137.30, 128.42, 124.42, 119.74, 101.69, 90.49, 71.29, 68.92, 68.72, 64.09, 59.61, 54.01, 47.50, 26.16, 16.57, -4.57. **HRMS** *m/z* = 420.2427 (calcd. for $C_{20}H_{33}N_5O_3Si$ 420.2425 $[M+H]^+$).



13

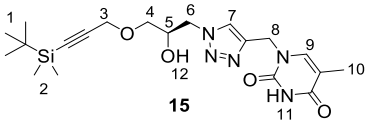
Compound **(*R*)-3** (0.369 g, 1.37 mmol, 1 equiv.) and compound **7** (0.387 g, 1.37 mmol, 1 equiv.) were added into a flask followed by EtOH (9.6 mL) with stirring. Water (4.1 mL), sodium ascorbate solution (55 mg in 2 mL water, 0.2 equiv.) and $CuSO_4$ solution (22 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH / DCM = 2/100 to 8/100) to give the final product **13** as a yellow oil (0.7 g, 93%).**13**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.77 (s, 1H, H_7), 7.47 (s, 1H, H_{19}), 6.96 (d, *J* = 19.6 Hz, 2H, H_{17} and H_{18}), 4.67 (d, *J* = 0.6 Hz, 2H, H_8), 4.61 (dd, *J* = 13.9, 3.0 Hz, 1H, H_6), 4.34 (dd, *J* = 13.9, 8.0 Hz, 1H, H_6), 4.25 – 4.14 (m, 3H, H_3 and H_5), 4.09 (dd, *J* = 5.6, 4.4 Hz, 2H, H_{16}), 3.76 – 3.70 (m, 2H, H_{15}), 3.68 – 3.55 (m, 14H, H_4, H_9, H_{10}, H_{11}, H_{12}, H_{13} and H_{14}), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C**

NMR (75 MHz, $CDCl_3$) δ 144.74, 137.26, 128.07, 124.29, 119.63, 101.56, 90.35, 71.11, 70.72, 70.70, 70.55(3C), 70.28, 69.73, 68.88, 64.67, 59.46, 53.46, 47.30, 26.03, 16.43, -4.70. **HRMS** *m/z* = 552.3214 (calcd. for $C_{26}H_{45}N_5O_6Si$ 552.3212 $[M+H]^+$).



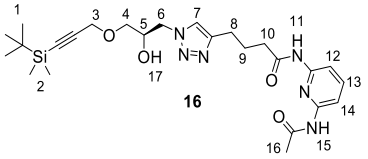
14

Compound **(*R*)-3** (4.31 g, 16 mmol, 1 equiv.) and 1-octyne (1.763 g, 16 mmol, 1 equiv.) were added into a flask followed by EtOH (112 mL) with stirring. Water (48 mL), sodium ascorbate solution (640 mg in 24 mL water, 0.2 equiv.) and $CuSO_4$ solution (256 mg in 20 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 (300 mL) and Na_2EDTA (0.05 M, 200 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 (300 × 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 = 0/10 to 4/6) to give the final product **14** as a colorless oil (5.564 g, 92%). **14**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.39 (s, 1H, H_7), 4.50 (dd, J = 13.9, 3.5 Hz, 1H, H_6), 4.37 (d, J = 7.1 Hz, 1H, H_6), 4.20 (s, 3H, H_3 and H_5), 3.64 – 3.44 (m, 2H, H_4), 3.35 – 2.84 (m, 1H, H_{14}), 2.76 – 2.61 (m, 2H, H_8), 1.63 (quint, J = 7.7 Hz, 2H, H_9), 1.42 – 1.22 (m, 6H, H_{10}, H_{11} and H_{12}), 0.92 (s, 12H, H_1 and H_{13}), 0.10 (s, 6H, H_2).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 148.35, 122.28, 101.48, 90.72, 70.83, 69.30, 59.63, 52.95, 31.69, 29.49, 29.07, 26.15, 25.74, 22.69, 16.55, 14.19, -4.59. **HRMS** *m/z* = 380.2728 (calcd. for $C_{20}H_{37}N_3O_2Si$ 380.2728 $[M+H]^+$).



15

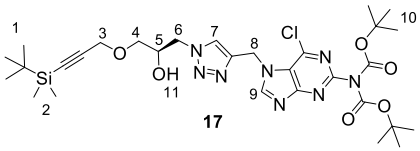
Compound **(*R*)-3** (1.347 g, 5 mmol, 1 equiv.) and **base T** (0.821 g, 5 mmol, 1 equiv.) were added into a flask followed by EtOH (35 mL) with stirring. Water (15 mL), sodium ascorbate solution (200 mg in 6 mL water, 0.2 equiv.) and $CuSO_4$ solution (80 mg in 4 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (200 mL) and Na_2EDTA (0.05 M, 200 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 DCM (200 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was washed with *n*-hexane (50 × 3 mL) and dried to give the final product **15** as a white solid (2.168 g, 100%). **15**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.05 (s, 1H, H_{11}), 7.90 (s, 1H, H_7), 7.35 (d, J = 1.4 Hz, 1H, H_9), 5.01 – 4.88 (m, 2H, H_8), 4.56 (dd, J = 14.1, 3.2 Hz, 1H, H_6), 4.38 (dd, J = 14.0, 7.7 Hz, 1H, H_6), 4.22 (s, 3H, H_3 and H_5), 3.67 – 3.47 (m, 2H, H_4), 1.89 (d, J = 1.1 Hz, 3H, H_{10}), 0.92 (s, 9H, H_1), 0.11 (s, 6H , H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.19, 151.13, 141.94, 140.43, 125.30, 111.46, 101.31, 90.94, 70.84, 69.27, 59.64, 53.35, 43.15, 26.15, 16.56, 12.43, -4.58. **HRMS** *m/z* = 434.2218 (calcd. for $C_{20}H_{31}N_5O_4Si$ 434.2218 $[M+H]^+$).



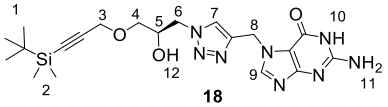
16

Compound **(*R*)-3** (0.674 g, 2.5 mmol, 1 equiv.) and **base D** (0.613 g, 2.5 mmol, 1 equiv.) were added into a flask followed by EtOH (17.5 mL) with stirring. Water (7.5 mL), sodium ascorbate solution (100 mg in 3 mL water, 0.2 equiv.) and $CuSO_4$ solution (40 mg in 2.5 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 (100 mL) and Na_2EDTA (0.05 M, 100 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 (100 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was crystallized from cold EtOAc, the final product **16** was

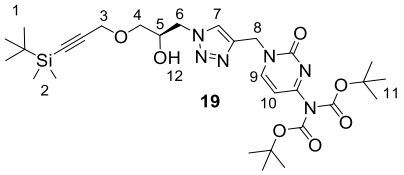
obtained as a yellow solid (1.262 g, 98%) after removing the solvent. **16**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.39 (s, 1H, H_{11}), 8.17 (s, 1H, H_{15}), 7.85 (t, J = 7.3 Hz, 2H, H_{12} and H_{14}), 7.66 (t, J = 8.0 Hz, 1H, H_{13}), 7.48 (s, 1H, H_7), 4.53 (dd, J = 14.0, 3.4 Hz, 1H, H_6), 4.39 (dd, J = 14.0, 7.5 Hz, 1H, H_6), 4.21 (s, 3H, H_3 and H_5), 3.68 – 3.50 (m, 2H, H_4), 2.79 (t, J = 6.9 Hz, 2H, H_8), 2.41 (t, J = 7.1 Hz, 2H, H_{10}), 2.20 (s, 3H, H_{16}), 2.14 – 2.01 (m, 2H, H_9), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.97, 169.28, 149.76, 149.57, 146.88, 140.86, 123.08, 109.55(2C), 101.31, 90.90, 70.96, 69.25, 59.65, 53.24, 36.37, 26.12, 25.18, 24.78, 24.25, 16.54, -4.60. **HRMS** *m/z* = 515.2800 (calcd. for $C_{25}H_{38}N_6O_4Si$ 515.2797 $[M+H]^+$).



Compound **(*R*)-3** (0.808 g, 3 mmol, 1 equiv.) and **base G** (1.224 g, 3 mmol, 1 equiv.) were added into a flask followed by EtOH (21 mL) with stirring. Water (9 mL), sodium ascorbate solution (120 mg in 4 mL water, 0.2 equiv.) and $CuSO_4$ solution (48 mg in 3 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 (150 mL) and Na_2EDTA (0.05 M, 200 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 DCM (150 × 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 = 5/5 to 0/10) to give the final product **17** as foamy white solid (1.727 g, 85%). **17**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.32 (s, 1H, H_9), 7.92 (s, 1H, H_7), 5.53 (s, 2H, H_8), 4.53 (dd, J = 14.0, 3.3 Hz, 1H, H_6), 4.34 (dd, J = 14.1, 7.7 Hz, 1H, H_6), 4.19 (s, 3H, H_3 and H_5), 3.60 (dd, J = 9.7, 4.5 Hz, 1H, H_4), 3.49 (dd, J = 9.7, 5.6 Hz, 1H, H_4), 1.48 (s, 18H, H_{10}), 0.92 (s, 9H, H_2), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.21, 152.48, 151.98, 151.48, 151.00, 145.96, 130.14, 125.12, 101.26, 90.93, 84.04, 70.69, 69.17, 59.63, 53.36, 39.52, 28.05, 26.14, 16.55, -4.59. **HRMS** *m/z* = 677.2993 (calcd. for $C_{30}H_{45}ClN_8O_6Si$ 677.2993 $[M+H]^+$).

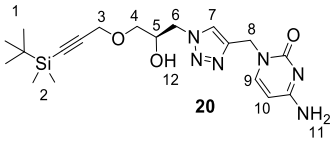


Compound **G** (0.211 g, 0.3 mmol, 1 equiv.) was added in a flask followed by TFA (3 mL) and Milli-Q water (1 mL). The mixture was stirred for 48 h at room temperature. Then, the mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **18** was obtained after passing the residue through a chromatography column (MeOH/DCM = 0/100 to 15/85) as a white solid (0.126 g, 88%). **18**, **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 10.57 (s, 1H, H_{10}), 8.01 (s, 1H, H_9), 7.77 (t, J = 6.2 Hz, 1H, H_{12}), 7.64 (s, 1H, H_7), 7.39 – 7.09 (m, 5H, H_{14}, H_{15} and H_{16}), 6.45 (s, 2H, H_{11}), 5.20 (s, 3H, H_8 and H_{12}), 4.57 (t, J = 6.3 Hz, 2H, H_6), 4.30 – 3.97 (m, 4H, H_3 and H_{13}), 3.56 (td, J = 10.5, 9.9, 4.6 Hz, 2H, H_4), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (75 MHz, DMSO-*d*$_6$)** δ 156.76, 153.73, 151.02, 142.34, 137.09, 124.34, 116.37, 103.17, 88.84, 71.27, 68.04, 58.58, 52.94, 37.82, 25.86, 16.12, -4.76. **HRMS** *m/z* = 459.2280 (calcd. for $C_{20}H_{30}N_8O_3Si$ 459.2283 $[M+H]^+$).



Compound **(*R*)-3** (1.617 g, 6 mmol, 1 equiv.) and **base C** (2.096 g, 6 mmol, 1 equiv.) were added into a flask followed by EtOH (42 mL) with stirring. Water (18 mL), sodium ascorbate solution (240 mg in 10 mL water, 0.2 equiv.) and $CuSO_4$ solution (96 mg in 6 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 (200 mL) and Na_2EDTA (0.05 M, 200 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and

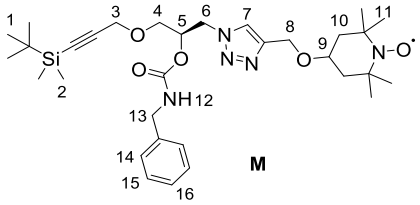
the water phase was extracted with EtOAc (200 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc /*n*-hexane = 5/5 to 0/10) to give the final product **19** as foamy light-yellow solid (2.785 g, 75%). **19**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.94 (s, 1H, H_7), 7.86 (d, J = 7.4 Hz, 1H, H_9), 7.04 (d, J = 7.3 Hz, 1H, H_{10}), 5.08 (s, 2H, H_8), 4.52 (dd, J = 14.0, 3.5 Hz, 1H, H_6), 4.36 (dd, J = 14.0, 7.4 Hz, 1H, H_6), 4.20 (s, 3H, H_3 and H_5), 3.63 – 3.45 (m, 2H, H_4), 1.54 (s, 18H, H_{11}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.71, 155.08, 149.62, 148.01, 101.43, 96.84, 90.76, 85.12, 70.69, 69.20, 59.61, 53.31, 45.53, 27.82, 26.16, 16.56, -4.58. **HRMS** *m/z* = 619.3270 (calcd. for $C_{29}H_{46}N_6O_7Si$ 619.3270 $[M+H]^+$).



20

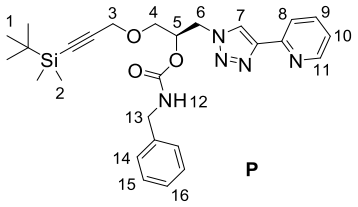
Compound **19** (0.31 g, 0.5 mmol, 1 equiv.) was added in a flask followed by DCM (3 mL) and TFA (1.5 mL). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **20** was obtained after passing the residue through a chromatography column (MeOH/DCM = 2/98 to 7/93) as a yellow solid (0.21 mg, 100 %). **20**, **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 7.92 (s, 1H, H_7), 7.66 (d, J = 7.2 Hz, 1H, H_9), 7.04 (d, J = 27.7 Hz, 2H, H_{11}), 5.66 (d, J = 7.2 Hz, 1H, H_{10}) , 5.36 (d, J = 5.7 Hz, 1H, H_{12}), 4.88 (s, 2H, H_8), 4.41 (dd, J = 13.9, 3.6 Hz, 1H, H_6), 4.23 (d, J = 11.9 Hz, 3H, H_3 and H_6), 4.00 - 3.94 (m, 1H, H_5), 3.41 (td, J = 9.7, 5.6 Hz, 2H, H_4), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, DMSO-*d*$_6$)** δ 166.00, 155.53, 145.77, 142.81, 124.51, 103.19, 93.57, 88.84, 71.28, 68.06, 58.58, 52.85, 43.43, 25.88, 16.14, -4.75. **HRMS** *m/z* = 419.2219 (calcd. for $C_{19}H_{30}N_6O_3Si$ 419.2221 $[M+H]^+$).

2.3 Termination of monomers



M

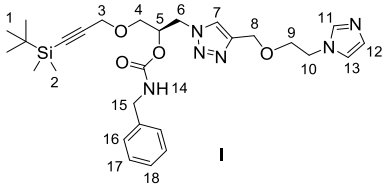
Compound **10** (240 mg, 0.4 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (151 mg, 1.5 equiv.) and pyridine (64.6 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (100 mg, 2 equiv.) and Et_3N (215 µL, 3 equiv.). The mixture was stirred for 1 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 **M** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 1/9 to 5/5) as a brown oil (239 mg, 97 %). **HRMS** *m/z* = 612.3579 (calcd. for $C_{32}H_{51}N_5O_5Si$• 612.3576 $[M+H]^+$).



P

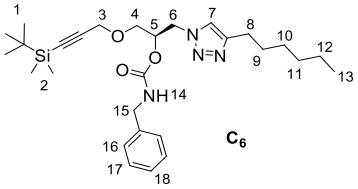
Compound **11** (224 mg, 0.6 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (181 mg, 1.5 equiv.) and pyridine (73 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed

by benzylamine (129 mg, 2 equiv.) and Et_3N (251 µL, 3 equiv.). The mixture was stirred for 1 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 **P** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 1/9 to 5/5) as a white solid (288 mg, 91%). **P**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.58 - 8.55 (m, 1H, H_{11}), 8.20 - 8.16 (m, 2H, H_7 and H_8), 7.78 (td, J = 7.7, 1.8 Hz, 1H, H_9), 7.31 - 7.21 (m, 6H, H_{10}, H_{14}, H_{15} and H_{16}), 5.34 - 5.22 (m, 2H, H_5 and H_{12}), 4.73 (dd, J = 5.3, 2.3 Hz, 2H, H_6), 4.28 (dd, J = 31.8, 4.1 Hz, 4H, H_3 and H_{13}), 3.66 (d, J = 4.9 Hz, 2H, H_4), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.17, 150.38, 149.50, 148.57, 138.01, 137.06, 128.83, 127.72, 127.63, 123.26, 123.01, 120.46, 101.23, 90.92, 71.26, 67.97, 59.66, 50.64, 45.29, 26.16, 16.56, -4.60. **HRMS** *m/z* = 506.2584 (calcd. for $C_{27}H_{35}N_5O_3Si$ 506.2582 $[M+H]^+$).



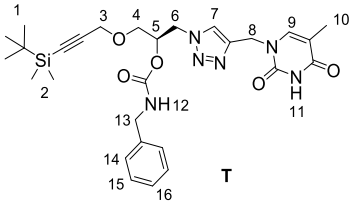
I

Compound **12** (210 mg, 0.5 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (151 mg, 1.5 equiv.) and pyridine (61 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (107 mg, 2 equiv.) and Et_3N (210 µL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (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 **I** was obtained after passing the residue through a chromatography column (MeOH/DCM = 0/100 to 5/95) as a yellow oil (277 mg, 100%). **I**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.27 - 7.17 (m, 8H, H_7, H_{16}, H_{17} and H_{18}), 7.06 (s, 1H, H_{11}), 6.99 (t, J = 6.0 Hz, 1H, H_{14}), 6.79 (d, J = 18.0 Hz, 2H, H_{12} and H_{13}), 5.13 - 5.10 (m, 1H, H_5), 4.58 - 4.44 (m, 4H, H_6 and H_8), 4.27 (t, J = 5.8 Hz, 2H, H_{15}), 4.10 - 4.03 (m, 2H, H_3), 3.96 (t, J = 4.9 Hz, 2H, H_{10}), 3.62 - 3.58 (m, 2H, H_9), 3.49 - 3.37 (m, 2H, H_4), 0.83 (s, 9H, H_1), 0.01 (s, 6H, H_2).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.59, 145.04, 138.76, 137.93, 128.97, 128.74, 127.75, 127.50, 123.48, 119.39, 101.41, 90.68, 70.74, 68.99, 67.90, 64.83, 59.60, 50.75, 47.28, 45.15, 26.17, 16.57, -4.57. **HRMS** *m/z* = 553.2953 (calcd. for $C_{28}H_{40}N_6O_4Si$ 553.2953 $[M+H]^+$).



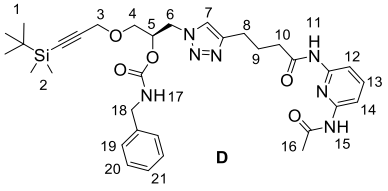
C_6

Compound **14** (227 mg, 0.6 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (181 mg, 1.5 equiv.) and pyridine (72 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (129 mg, 2 equiv.) and Et_3N (25 µL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (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 **C_6** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane =10/90 to 70/30) as a colorless oil (303 mg, 99%). **C_6**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.43 – 7.13 (m, 6H, H_7, H_{16}, H_{17} and H_{18}), 5.24 (dd, J = 6.0, 4.6 Hz, 1H, H_5), 5.10 (d, J = 6.2 Hz, 1H, H_{14}), 4.61 (t, J = 5.9 Hz, 2H, H_6), 4.34 (d, J = 6.0 Hz, 2H, H_{15}), 4.21 (s, 2H, H_3), 3.63 (dd, J = 4.9, 2.9 Hz, 2H, H_4), 2.69 (t, J = 7.7 Hz, 2H, H_8), 1.63 (d, J = 21.7 Hz, 2H, H_9), 1.39 – 1.24 (m, 6H, H_{10}, H_{11} and H_{12}), 0.93 (d, J = 1.2 Hz, 9H, H_1), 0.90 – 0.84 (m, 3H, H_{12}), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 13C 155.27, 148.74, 138.07, 128.89, 127.80, 127.62, 121.55, 101.30, 90.84, 71.44, 68.20, 59.64, 50.21, 45.30, 31.72, 29.57, 29.08, 26.17, 25.82, 22.71, 16.57, 14.21, -4.56. **HRMS** *m/z* = 513.3260 (calcd. for $C_{28}H_{44}N_4O_3Si$ 513.3255 $[M+H]^+$).



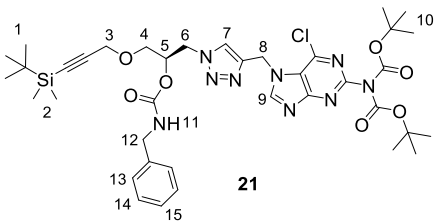
T

Compound **15** (434 mg, 1 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (300 mg, 1.5 mmol, 1.5 equiv.) and pyridine (121 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (200 mg, 2 mmol, 2 equiv.) and Et_3N (418 µL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (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 **T** was obtained after passing the residue through a chromatography column (MeOH/DCM =0/100 to 3/100) as a white solid (567 mg, 100%). **T**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.11 (s, 1H, H_{11}), 7.76 (s, 1H, H_7), 7.38 – 7.19 (m, 6H, H_9, H_{14}, H_{15} and H_{16}), 5.45 (t, J = 6.0 Hz, 1H, H_{12}), 5.22 (dd, J = 6.5, 4.2 Hz, 1H, H_5), 4.90 (d, J = 3.1 Hz, 2H, H_8), 4.63 (dd, J = 7.7, 5.4 Hz, 2H, H_6), 4.30 (dd, J = 6.1, 2.6 Hz, 2H, H_{13}), 4.20 (d, J = 2.5 Hz, 2H, H_3), 3.64 (dd, J = 4.9, 3.3 Hz, 2H, H_4), 1.86 (d, J = 1.2 Hz, 3H, H_{10}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.15, 155.18, 142.14, 140.31, 128.85, 127.74, 127.59, 124.97, 111.43, 101.22, 90.93, 71.27, 68.10, 59.63, 50.81, 45.23, 43.16, 26.17, 16.56, 12.39, -4.57. **HRMS** *m/z* = 589.25680 (calcd. for $C_{28}H_{38}N_6O_5Si$ 589.25652 $[M+H]^+$).



D

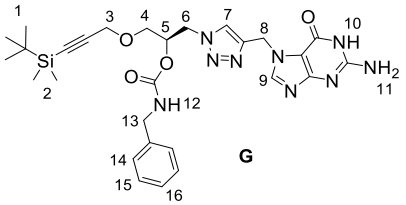
Compound **16** (257 mg, 1 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (151 mg, 1.5 mmol, 1.5 equiv.) and pyridine (61 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (107 mg, 2 mmol, 2 equiv.) and Et_3N (210 µL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (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 **D** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane =25/75 to 100/0) as a white solid (567 mg, 100%). **D**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.47 (s, 1H, H_{11}), 8.01 – 7.74 (m, 3H, H_{12}, H_{13} and H_{15}), 7.66 (t, J = 8.1 Hz, 1H, H_{14}), 7.41 – 7.14 (m, 6H, H_7, H_{19}, H_{20} and H_{21}), 5.44 – 5.23 (m, 2H, H_5 and H_{17}), 4.61 (d, J = 5.5 Hz, 2H, H_6), 4.31 (d, J = 6.0 Hz, 2H, H_{18}), 4.23 (s, 2H, H_3), 3.68 (d, J = 5.0 Hz, 2H, H_4), 2.77 (d, J = 7.8 Hz, 2H, H_8), 2.32 (t, J = 7.1 Hz, 2H, H_{10}), 2.21 – 1.90 (m, 5H, H_9 and H_{16}), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.79, 168.83, 155.39(2C), 149.77, 147.21, 140.75, 137.94, 128.90, 127.81, 127.49, 122.42, 109.45(2C), 101.14, 91.10, 71.56, 68.43, 59.74, 50.76, 45.22, 36.03, 26.16, 25.22, 24.80, 24.05, 16.57, -4.57. **HRMS** *m/z* = 648.3327 (calcd. for $C_{33}H_{45}N_7O_5Si$ 648.3324 $[M+H]^+$).



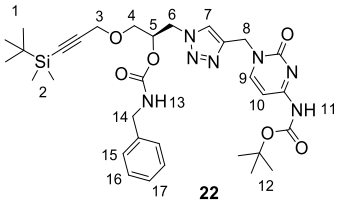
21

Compound **17** (260 mg, 0.38 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (160 mg, 1.5 equiv.) and pyridine (64 µL, 1.5 equiv.). The mixture was stirred for 2 h at room

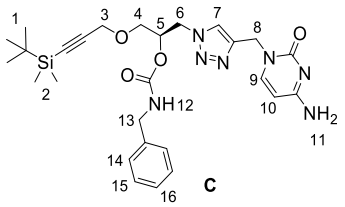
temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (114 mg, 2 equiv.) and Et_3N (221 µL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then EtOAc (50 mL) and water (50 mL) were added to the mixture. The organic 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 **21** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 2/8 to 6/4) as foamy white solid (306 mg, 95%). **21**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.27 (s, 1H, H_9), 7.80 (s, 1H, H_7), 7.32 - 7.24 (m, 5H, H_{13}, H_{14} and H_{15}), 7.18 – 7.11 (m, 2H, H_{13}), 5.47 (dd, J = 15.5, 4.3 Hz, 3H, H_8 and H_{11}), 5.16 (quint, J = 4.1 Hz, 1H, H_5), 4.71 – 4.46 (m, 2H, H_6), 4.28 – 4.01 (m, 4H, H_3 and H_{12}), 3.72 – 3.54 (m, 2H, H_4), 1.48 (s, 18H, H_{10}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.12, 152.55, 151.53, 151.21, 145.97, 141.35, 138.12, 128.80, 127.67, 127.52, 124.90, 101.23, 90.89, 84.19, 71.25, 68.18, 59.65, 51.06, 45.03, 39.67, 28.06, 26.16, 16.56, -4.57. **HRMS** *m/z* = 832.3337 (calcd. for $C_{38}H_{52}ClN_9O_7Si$ 832.3340 $[M+Na]^+$).



Compound **C13** (270 mg, 0.34 mmol, 1 equiv.) was added in a flask followed by TFA (3 mL) and Milli-Q water (1mL). The mixture was stirred for 48 h at room temperature. Then, the mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **G** was obtained after passing the residue through a chromatography column (MeOH/DCM = 3/97 to 8/92) as a white solid (0.16 g, 81%). **G**, **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 10.57 (s, 1H, H_{10}), 8.01 (s, 1H, H_9), 7.77 (t, J = 6.2 Hz, 1H, H_{12}), 7.64 (s, 1H, H_7), 7.39 – 7.09 (m, 5H, H_{14}, H_{15} and H_{16}), 6.45 (s, 2H, H_{11}), 5.20 (s, 3H, H_5 and H_8), 4.57 (t, J = 6.3 Hz, 2H, H_6), 4.30 – 3.97 (m, 4H, H_3 and H_{13}), 3.56 (td, J = 10.5, 9.9, 4.6 Hz, 2H, H_4), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (75 MHz, DMSO-*d*$_6$)** δ 156.75, 155.34, 153.63, 151.00, 142.51, 139.41, 136.93, 128.19, 126.83, 126.72, 124.23, 116.38, 102.74, 89.22, 70.49, 68.24, 58.59, 50.14, 43.66, 37.75, 25.81, 16.06, -4.81. **HRMS** *m/z* = 592.2811 (calcd. for $C_{28}H_{37}N_9O_4Si$ 592.2811 $[M+H]^+$).



One Boc-protected compound **19** (450 mg, 0.88 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (266 mg, 1.5 equiv.) and pyridine (106 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in ACN (5 mL) and added to a flask followed by benzylamine (189 mg, 2 equiv.) and Et_3N (368 µL, 3 equiv.). The mixture was stirred for 1 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 **22** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 5/5 to 10/0) as foamy white solid (545 mg, 95%). **22**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.83 (d, J = 7.1 Hz, 2H, H_7 and H_{11}), 7.36 – 7.21 (m, 6H, H_9, H_{14}, H_{15} and H_{16}), 7.16 (d, J = 7.3 Hz, 1H, H_{10}), 5.34 (t, J = 6.0 Hz, 1H, H_{13}), 5.19 (quint, J = 5.1 Hz, 1H, H_5), 5.07 (s, 2H, H_8), 4.62 (d, J = 5.1 Hz, 2H, H_6), 4.31 (t, J = 5.3 Hz, 2H, H_{14}), 4.20 (d, J = 3.2 Hz, 2H, H_3), 3.61 (dd, J = 4.9, 3.6 Hz, 2H, H_4), 1.49 (s, 9H, H_{12}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.88, 155.87, 155.16, 151.17, 148.33, 141.88, 138.21, 128.83, 127.67, 127.64, 125.66, 101.28, 95.44, 90.87, 83.02, 71.17, 68.00, 59.62, 50.67, 45.42, 45.23, 28.16, 26.17, 16.56, -4.57. **HRMS** *m/z* = 652.3272 (calcd. for $C_{32}H_{45}N_7O_6Si$ 652.3273 $[M+H]^+$).

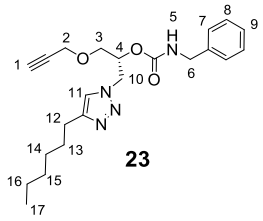


C

Compound **22** (530 mg, 0.81 mmol, 1 equiv.) was added in a flask followed by DCM (3 mL) and TFA (1.5 mL). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **C** was obtained after passing the residue through a chromatography column (MeOH/DCM = 2/98 to 7/93) as a yellow solid (438 mg, 98%). **C**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.82 (s, 1H, H_7), 7.50 (d, J = 7.2 Hz, 1H, H_9), 7.36 – 7.17 (m, 5H, H_{14}, H_{15} and H_{16}), 6.06 (s, 1H, H_{11}), 5.66 (dd, J = 11.7, 6.7 Hz, 2H, H_{10} and H_{12}), 5.20 (quint, J = 5.6 Hz, 1H, H_5), 4.94 (s, 2H, H_8), 4.60 (d, J = 4.3 Hz, 2H, H_6), 4.37 – 4.05 (m, 4H, H_3 and H_{13}), 3.60 (dd, J = 4.9, 2.7 Hz, 2H, H_4), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.00, 156.45, 155.29, 145.91, 142.77, 138.36, 128.78, 127.60(3C), 125.41, 101.32, 94.62, 90.84, 71.17, 68.11, 59.60, 50.70, 45.14, 44.80, 26.17, 16.56, -4.57. **HRMS** *m/z* = 552.2752 (calcd. for $C_{27}H_{37}N_7O_4Si$ 552.2749 $[M+H]^+$).

2.4 Synthesis of C_6GMPTC_6

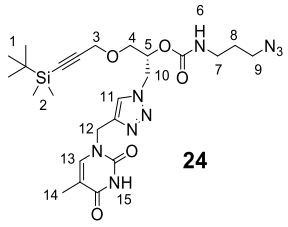
2.4.1 C_6 end-capping



23

Compound **14** (2.92 g, 7.7 mmol, 1 equiv.) was added in a flask followed by EtOAc (15 mL) and TBAF (15.4 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in EtOAc (150 mL) and washed with brine (3 × 100 mL), dried with Na_2SO_4 and concentrated under vacuum. The residue was redissolved in DCM (20 mL), 4-nitrophenyl chloroformate (2.33 g, 11.5 mmol, 1.5 equiv.) and pyridine (934 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (20 mL) and added to a flask followed by 3-azido-1-propylamine (1.65 g, 16.5 mmol, 2 equiv.) and Et_3N (3.22 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then EtOAc (150 mL) and water (100 mL) were added to the mixture. The organic phase was washed with water (2 × 100 mL) and brine (2 × 100 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **23** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 1/9 to 4/6) as a brown oil (3.06 g, 100%). **23**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.14 (m, 6H, H_7, H_8, H_9 and H_{10}), 5.30 – 5.06 (m, 2H, H_4 and H_5), 4.61 (dd, J = 6.8, 5.5 Hz, 2H, H_{10}), 4.42 – 4.30 (m, 2H, H_6), 4.20 (d, J = 2.4 Hz, 2H, H_2), 3.62 (t, J = 4.7 Hz, 2H, H_3), 2.69 (t, J = 7.7 Hz, 2H, H_{12}), 2.44 (t, J = 2.4 Hz, 1H, H_1), 1.73 – 1.49 (m, 2H, H_{13}), 1.44 – 1.20 (m, 6H, H_{14}, H_{15} and H_{16}), 1.04 – 0.79 (m, 3H, H_{17}). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 148.72, 128.89, 128.79, 127.81, 127.62, 121.70, 79.00,75.41, 71.34, 68.18, 58.85, 50.07, 45.29, 31.71, 29.53, 29.06, 25.78, 22.70, 14.20. **HRMS** *m/z* = 399.2389 (calcd. for $C_{32}H_{51}N_5O_5Si$• 399.2391 $[M+H]^+$).

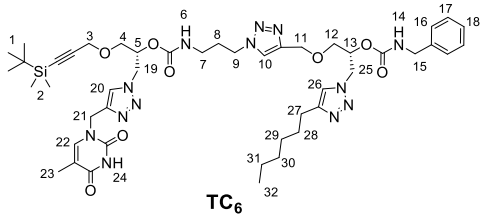
2.4.2 Synthesis of 24



24

Compound **15** (1.734 g, 4 mmol, 1 equiv.) was added in a flask followed by DCM (15 mL), 4-nitrophenyl chloroformate (1.21 g, 6 mmol, 1.5 equiv.) and pyridine (485 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (15 mL) and added to a flask followed by 3-azido-1-propylamine (0.801 g, 8 mmol, 2 equiv.) and Et_3N (1.67 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then DCM (150 mL) and water (150 mL) were added to the mixture. The organic phase was washed with water (2 × 150 mL) and brine (2 × 150 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **24** was obtained after passing the residue through a chromatography column (MeOH/DCM = 0/100 to 3/100) as a white solid (2.234 g, 100%). **24**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.50 (s, 1H, H_{15}), 7.78 (s, 1H, H_{11}), 7.34 (q, J = 1.2 Hz, 1H, H_{13}), 5.35 (t, J = 6.0 Hz, 1H, H_6), 5.17 (quint, J = 4.5 Hz, 1H, H_5), 4.94 (d, J = 3.9 Hz, 2H, H_{12}), 4.71 – 4.53 (m, 2H, H_{10}), 4.20 (d, J = 2.5 Hz, 2H, H_3), 3.63 (dd, J = 4.8, 2.8 Hz, 2H, H_4), 3.43 – 3.13 (m, 6H, H_7 and H_9), 1.89 (d, J = 1.2 Hz, 3H, H_{14}), 1.77 (dt, J = 9.9, 6.6 Hz, 2H, H_8), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.32, 155.19, 151.32, 142.17, 140.41, 124.98, 111.45, 90.91, 71.16, 68.11, 59.61, 50.83, 49.07, 43.25, 38.66, 38.11, 29.02, 26.14, 16.55, 12.43, -4.60. **HRMS** *m/z* = 560.2760 (calcd. for $C_{24}H_{37}N_9O_5Si$ 560.2760 $[M+H]^+$).

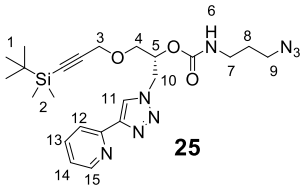
2.4.3 Synthesis of TC_6



TC_6

Compound **24** (1.12 g, 2 mmol, 1 equiv.) and Compound **23** (0.797 g, 2 mmol, 1 equiv.) were added into a flask followed by EtOH (14 mL) with stirring. Water (6 mL), sodium ascorbate solution (80 mg in 3 mL water, 0.2 equiv.) and $CuSO_4$ solution (32 mg in 2 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, DCM (60 mL) and Na_2EDTA (0.05 M, 60 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 DCM (60 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 1/99 to 5/95) to give the final product **TC_6** as foamy white solid (1.757 g, 92%). **TC_6**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.51 (s, 1H, H_{24}), 7.77 (d, J = 20.6 Hz, 2H, H_{10} and H_{20}), 7.37 – 7.15 (m, 7H, H_{16}, H_{17}, H_{18}, H_{22} and H_{26}), 5.81 (t, J = 6.1 Hz, 1H, H_6), 5.64 (t, J = 6.0 Hz, 1H, H_{14}), 5.18 (dd, J = 11.4, 6.1 Hz, 2H, H_5 and H_{13}), 4.88 (q, J = 15.0 Hz, 2H, H_{21}), 4.72 – 4.51 (m, 6H, H_{11}, H_{19} and H_{25}), 4.43 – 4.28 (m, 4H, H_9 and H_{15}), 4.25 – 4.13 (m, 2H, H_3), 3.70 – 3.50 (m, 4H, H_4 and H_{12}), 3.09 (t, J = 7.0 Hz, 2H, H_7), 2.65 (t, J = 7.7 Hz, 2H, H_{27}), 2.05 (quint, J = 8.3 Hz, 2H, H_8), 1.84 (d, J = 1.2 Hz, 3H, H_{23}), 1.60 (quint, J = 7.5 Hz, 2H, H_{28}), 1.30 - 1.26 (m, 6H, H_{29}, H_{30} and H_{31}), 0.92 (s, 9H, H_1), 0.89 – 0.83 (m, 3H, H_{32}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.44, 155.61, 155.47, 151.21, 150.13, 149.45, 148.69, 148.35, 144.54, 144.24, 142.26, 140.38, 138.25, 137.18, 128.80, 127.66, 127.55, 125.27, 123.61, 123.58, 123.12, 121.80, 120.32, 111.27, 101.20, 90.95, 71.40, 71.15, 70.89, 68.56, 68.38, 68.27, 64.93, 64.80, 59.62, 50.94, 50.41, 50.05, 47.45, 47.26, 45.14, 37.80, 37.72, 31.66, 30.28, 30.16, 29.48, 29.02, 26.13, 25.70, 22.67, 16.53, 14.19, 12.39, -4.62. **HRMS** *m/z* = 958.5074 (calcd. for $C_{46}H_{67}N_{13}O_8Si$ 958.5078 $[M+H]^+$).

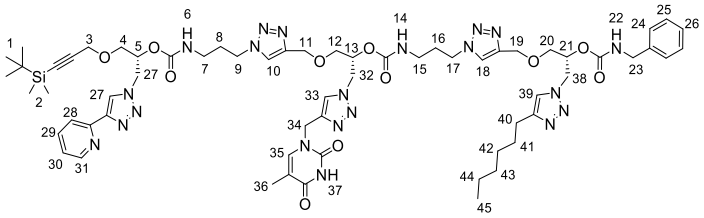
2.4.4 Synthesis of 25



25

Synthesis of **25** was prepared according to our previous work.[2]

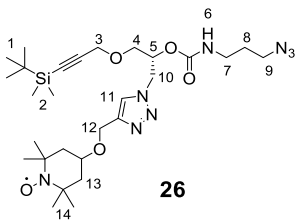
2.4.5 Synthesis of PTC_6



PTC_6

Compound **TC_6** (1.246 g, 1.3 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (3.9 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **25** (0.648 g, 1.3 mmol, 1 equiv.) was added into the residue followed by EtOH (9.1 mL) with stirring. Water (3.9 mL), sodium ascorbate solution (52 mg in 2 mL water, 0.2 equiv.) and $CuSO_4$ solution (20.8 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product **PTC_6** as foamy white solid (1.651 g, 95%). **PTC_6**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.79 (s, 1H, H_{37}), 8.58 – 8.47 (m, 1H, H_{31}), 8.33 (s, 1H, H_{27}), 8.08 (dt, J = 7.9, 1.1 Hz, 1H, H_{28}), 7.85 – 7.59 (m, 4H, H_{10}, H_{18}, H_{29} and H_{33}), 7.35 – 7.15 (m, 8H, H_{24}, H_{25}, H_{26}, H_{30}, H_{35} and H_{39}), 6.01 (t, J = 6.1 Hz, 1H, H_6), 5.89 (t, J = 6.2 Hz, 1H, H_{14}), 5.69 (t, J = 6.1 Hz, 1H, H_{22}), 5.38 – 5.25 (m, 1H, H_5), 5.22 – 5.06 (m, 2H, H_{13} and H_{21}), 4.88 (s, 2H, H_{34}), 4.77 – 4.50 (m, 10H, H_{11}, H_{19}, H_{27}, H_{32} and H_{38}), 4.44 – 4.15 (m, 8H, H_3, H_9, H_{17} and H_{23}), 3.68 (dd, J = 6.8, 4.8 Hz, 2H, H_{20}), 3.54 (dd, J = 25.0, 6.3 Hz, 4H, H_4 and H_{12}), 3.08 (ddd, J = 34.0, 26.4, 6.5 Hz, 4H, H_7 and H_{15}), 2.63 (t, J = 7.7 Hz, 2H, H_{40}), 2.08 - 2.00 (m, 4H, H_8 and H_{16}), 1.89 – 1.78 (m, 3H, H_{36}), 1.58 (quint, J = 7.5 Hz, 2H, H_{41}), 1.34 – 1.20 (m, 6H, H_{42}, H_{43} and H_{44}), 0.90 (s, 9H, H_1), 0.85 (t, J = 7.5 Hz, 3H, H_{45}), 0.08 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.45, 155.61, 155.48, 151.21, 150.13, 149.46, 148.69, 148.35, 144.54, 144.24, 142.27, 140.38, 138.25, 137.18, 128.80, 127.67, 127.56, 125.28, 123.61(2C), 123.58, 123.12, 121.80, 120.32, 111.27, 101.20, 90.95, 71.40, 71.15, 70.89, 68.56, 68.38, 68.27, 64.93, 64.80, 59.62, 50.94, 50.41, 50.05, 47.45, 47.26, 45.14, 43.26, 37.81, 37.72, 31.66, 30.28, 30.16, 29.48, 29.03, 26.13, 25.70, 22.67, 16.53, 14.19, 12.39, -4.61. **HRMS** m/z = 1342.6734 (calcd. for $C_{63}H_{87}N_{21}O_{11}Si$ 1342.6736 $[M+H]^+$).

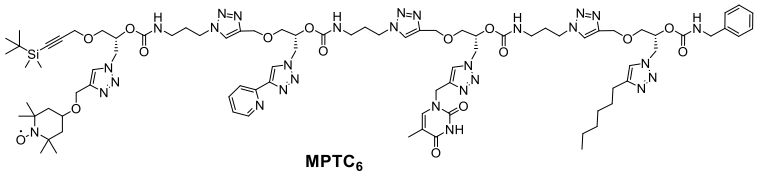
2.4.6 Synthesis of 26



26

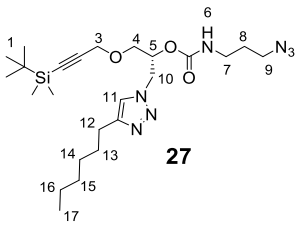
Compound **10** (0.72 g, 1.5 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.455 g, 2.3 mmol, 1.5 equiv.) and pyridine (260 μL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (15 mL) and added to a flask followed by 3-azido-1-propylamine (300 g, 3 mmol, 2 equiv.) and Et_3N (645 μL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then DCM (60 mL) and water (60 mL) were added to the mixture. The organic phase was washed with water (2 × 60 mL) and brine (2 × 60 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **26** was obtained after passing the residue through a chromatography column (EtOAc/*n*-hexane = 2/8 to 7/3) as a pink oil (0.89 g, 98%). **26**, **HRMS** *m/z* = 605.3591 (calcd. for $C_{28}H_{49}N_8O_5Si^{\bullet}$ 605.3590 $[M+H]^+$).

2.4.7 Synthesis of $MPTC_6$



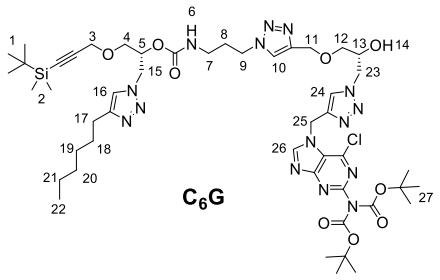
Compound **PTC_6** (1.53 g, 1.14 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (3.42 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **26** (0.69 g, 1.14 mmol, 1 equiv.) was added into the residue followed by EtOH (8 mL) with stirring. Water (3.4 mL), sodium ascorbate solution (34.2 mg in 1.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (18.2 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product **$MPTC_6$** as foamy white solid (1.651 g, 57%). **$MPTC_6$**, **HRMS** *m/z* = 1833.9468 (calcd. for $C_{85}H_{122}N_{29}O_{16}Si^{\bullet}$ 1833.9466 $[M+H]^+$).

2.4.8 Synthesis of 27



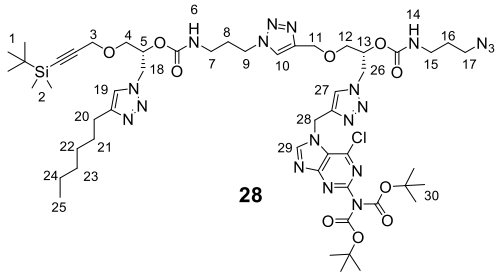
Compound **14** (2.66 g, 7 mmol, 1 equiv.) was added in a flask followed by DCM (30 mL), 4-nitrophenyl chloroformate (2.12 g, 10.5 mmol, 1.5 equiv.) and pyridine (849 μL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (30 mL) and added to a flask followed by 3-azido-1-propylamine (1.4 g, 14 mmol, 2 equiv.) and Et_3N (2.93 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then EtOAc (200 mL) and water (200 mL) were added to the mixture. The organic phase was washed with water (2 × 200 mL) and brine (2 × 200 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **27** was obtained after passing the residue through a chromatography column (EtOAc /*n*-hexane = 0/10 to 5/5) as a colorless oil (3.54 g, 100%). **27**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.31 (s, 1H, H_{11}), 5.20 (quint, J = 5.5 Hz, 1H, H_5), 4.94 (d, J = 6.4 Hz, 1H, H_6), 4.69 – 4.48 (m, 2H, H_{10}), 4.20 (s, 2H, H_3), 3.61 (dd, J = 5.0, 1.9 Hz, 2H, H_3), 3.35 (t, J = 6.5 Hz, 2H, H_4), 3.24 (d, J = 6.5 Hz, 2H, H_9), 2.74 – 2.59 (m, 2H, H_7), 1.78 - 1.62 (m, 4H, H_8 and H_{13}), 1.41 – 1.22 (m, 6H, H_{14}, H_{15} and H_{16}), 0.93 (s, 12H, H_1 and H_{17}), 0.11 (d, J = 1.0 Hz, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.27, 148.74, 121.54, 101.25, 90.87, 71.25, 68.18, 59.63, 50.23, 49.13, 38.71, 31.71, 29.58, 29.07, 26.42, 26.16, 25.81, 22.71, 16.57, 14.20, -4.57. **HRMS** *m/z* = 506.3269 (calcd. for $C_{24}H_{43}N_7O_3Si$ 506.3269 $[M+H]^+$).

2.4.9 Synthesis of C_6G



Compound **17** (1.016 g, 1.5 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (3 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **27** (0.759 g, 1.5 mmol, 1 equiv.) was added into the residue followed by EtOH (10.5 mL) with stirring. Water (4.5 mL), sodium ascorbate solution (60 mg in 2.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (24 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 4/96) to give the final product **C_6G** as foamy white solid (1.38 g, 86%). **C_6G**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.35 (s, 1H, H_{26}), 7.93 (s, 1H, H_{24}), 7.70 (s, 1H, H_{10}), 7.36 (s, 1H, H_{16}), 5.53 (s, 2H, H_{25}), 5.34 (s, 1H, H_6), 5.26 – 5.19 (m, 1H, H_5), 4.67 – 4.48 (m, 5H, H_{11}, H_{15} and H_{23}), 4.42 – 4.32 (m, 3H, H_9 and H_{23}), 4.21 (d, J = 1.5 Hz, 2H, H_3), 4.17 – 4.11 (m, 1H, H_{13}), 3.69 – 3.53 (m, 3H, H_4 and H_{12}), 3.47 (dd, J = 10.0, 5.5 Hz, 1H, H_{12}), 3.23 – 2.98 (m, 2H, H_7), 2.65 (t, J = 7.8 Hz, 2H, H_{17}), 2.10 - 2.00 (m, 2H, H_8), 1.61 (quint, J = 7.3 Hz, 2H, H_{18}), 1.46 (s, 18H, H_{27}), 1.35 – 1.22 (m, 6H, H_{19}, H_{20} and H_{21}), 0.92 (s, 9H, H_1), 0.86 (t, J = 7.3 Hz, 3H, H_{22}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.51, 152.54, 151.99, 151.34, 150.95, 148.55, 146.18, 144.51, 141.04, 130.10, 125.16, 123.47, 121.93, 101.17, 90.99, 83.99, 71.48, 71.06, 69.20, 68.20, 64.78, 59.65, 53.21, 50.51, 47.42, 39.46, 37.80, 31.67, 30.41, 29.52, 29.02, 28.04, 26.15, 25.66, 22.68, 16.56, 14.19, -4.57. **HRMS** *m/z* = 1068.5326 (calcd. for $C_{63}H_{87}N_{21}O_{11}Si$ 1068.5325 $[M+H]^+$).

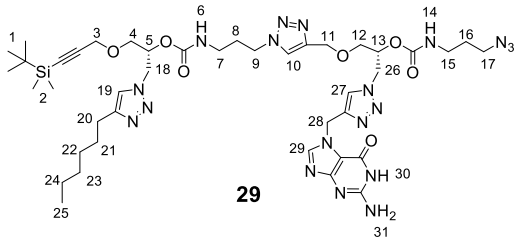
2.4.10 Synthesis of 28



Compound **C_6G** (1.23 g, 1.15 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.588 g, 2.5 equiv.) and pyridine (232 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.3 g, 3 mmol, 2.6 equiv.) and Et_3N (0.8 mL, 5 equiv.). The mixture was stirred for 2 h at room temperature, then DCM (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 **28** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 5/95) as a foamy-yellow solid (1.374 g, 100%). **28**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.35 (s, 1H, H_{29}), 7.83 (s, 1H, H_{27}), 7.70 (s, 1H, H_{10}), 7.35 (s, 1H, H_{19}), 5.58 – 5.49 (m, 2H, H_{28}), 5.42 (t, J = 6.1 Hz, 2H, H_6 and H_{14}), 5.22 (dd, J = 6.6, 4.5 Hz, 1H, H_5), 5.04 (d, J = 7.6 Hz, 1H, H_{13}), 4.68 – 4.46 (m, 6H, H_{11}, H_{18} and H_{26}), 4.38 (t, J = 6.6 Hz, 2H, H_9), 4.20 (d, J =

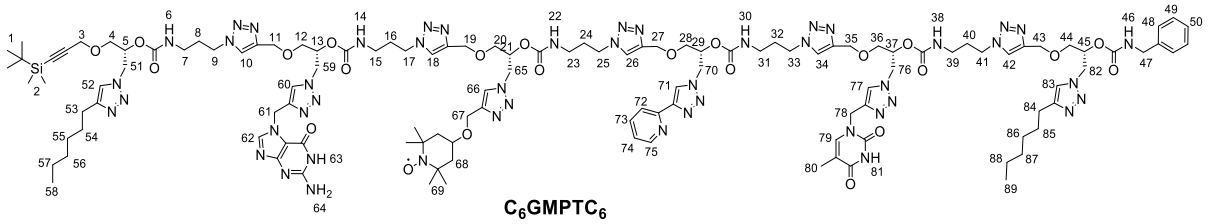
1.7 Hz, 2H, H_3), 3.60 (dd, J = 15.3, 4.8 Hz, 3H, H_4 and H_{12}), 3.48 (dd, J = 10.3, 6.0 Hz, 1H, H_4), 3.29 – 2.97 (m, 6H, H_7, H_{15} and H_{17}), 2.66 (t, J = 7.8 Hz, 2H, H_{20}), 2.00 - 2.10 (tm, 4H, H_8 and H_{16}), 1.62 (tt, J = 9.7, 6.9 Hz, 2H, H_{21}), 1.48 (s, 18H, H_{30}), 1.36 – 1.22 (m, 6H, H_{22}, H_{23} and H_{24}), 0.92 (s, 9H, H_1), 0.88 – 0.83 (m, 3H, H_{25}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.51, 155.16, 152.57, 151.91, 151.42, 151.23, 148.64, 146.24, 144.35, 141.40, 130.23, 125.06, 123.48, 121.80, 101.19, 90.93, 84.25, 71.10, 70.98, 68.38, 68.19, 64.84, 59.63, 50.81, 50.39, 49.03, 47.40, 39.65, 38.51, 37.83, 31.67, 29.59, 29.54, 29.02, 28.96, 28.03, 26.14, 25.72, 22.67, 16.55, 14.18, -4.59. **HRMS** m/z = 1216.5685 (calcd. for $C_{52}H_{80}ClN_{19}O_{10}Si$ 1216.5686 $[M+Na]^+$).

2.4.11 Synthesis of 29



Compound **28** (1.2 g, 1 mmol, 1 equiv.) was added in a flask followed by TFA (6 mL) and Milli-Q water (2 mL). The mixture was stirred for 48 h at room temperature. The mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed with brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **29** was obtained after passing the residue through a chromatography column (MeOH/DCM = 0/100 to 12/88) as a yellow solid (0.685 g, 70%). **29**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.67 – 7.50 (m, 3H, H_{10}, H_{27}, H_{29} and H_{30}), 7.39 (s, 1H, H_{19}), 7.00 - 5.80 (bm, 2H, H_{31}), 5.15 (d, J = 40.1 Hz, 4H, H_5, H_6, H_{13} and H_{14}), 4.90 – 4.10 (m, 10H, H_3, H_9, H_{11}, H_{18} and H_{26}), 3.78 – 2.89 (m, 10H, H_4, H_7, H_{12}, H_{15} and H_{17}), 2.64 (s, 2H, H_{20}), 2.04 (s, 2H, H_8), 1.76 – 1.50 (m, 4H, H_{16} and H_{21}), 1.38 – 1.14 (m, 6H, H_{22}, H_{23} and H_{24}), 0.97 – 0.75 (m, 12H, H_1 and H_{25}), 0.09 (d, J = 2.5 Hz, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ from 155.80 to 144.23(9C), 123.78, 121.98, 121.92, from 101.34 to 90.83(9C), 71.05, 70.99, 68.22, 64.65, 59.61(2C), 50.41, 49.01(2C), 47.63, 38.48, 37.97, 31.68, 30.37, 30.34, 29.54, 29.03, 26.15, 25.74, 22.68, 16.55, 14.20, -4.57. **HRMS** m/z = 976.5155 (calcd. for $C_{42}H_{65}N_{19}O_7$ Si 976.5156 $[M+H]^+$).

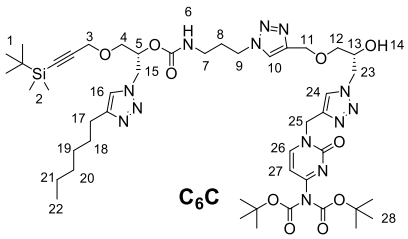
2.4.12 Synthesis of C_6GMPTC$_6$



Compound **MPTC$_6$** (0.734cg, 0.4 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (1.2 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **29** (0.39 g, 0.4 mmol, 1 equiv.) was added into the residue followed by EtOH (2.8 mL) with stirring. Water (1.2 mL), sodium ascorbate solution (12 mg in 0.5 mL water, 0.15 equiv.) and $CuSO_4$ solution (6.4 mg in 0.5 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 5/95) to give the final product **C$_6$GMPTC$_6$** as foamy white solid (0.524 g, 49%). **C$_6$GMPTC$_6$**, **TOF MS ES +** m/z = 2695,3744 (calcd. for $C_{121}H_{173}N_{48}O_{23}Si$• 2695,3685 $[M+H]^+$).

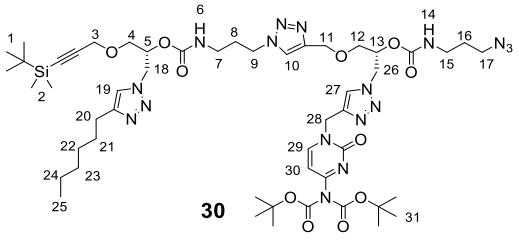
2.5 Synthesis of Hexamer C_6CIIDC_6

2.5.1 Synthesis of C_6C



Compound **19** (1.55 g, 2.5 mmol, 1 equiv.) was added in a flask followed by EtOAc (10 mL) and TBAF (3.75 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (100 mL) and washed with brine (3 × 100 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **25** (1.264 g, 2.5 mmol, 1 equiv.) was added into the residue followed by EtOH (17.5 mL) with stirring. Water (7.5 mL), sodium ascorbate solution (100 mg in 4 mL water, 0.2 equiv.) and $CuSO_4$ solution (40 mg in 3 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, DCM (100 mL) and Na_2EDTA (0.05 M, 100 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 DCM (100 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 5/94) to give the final product **C_6C** as foamy white solid (1.92 g, 76%). **C_6C**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (s, 1H, H24), 7.87 (d, J = 7.4 Hz, 1H, H_{26}), 7.74 (s, 1H, H_{10}), 7.35 (s, 1H, H_{16}), 7.03 (d, J = 7.4 Hz, 1H, H_{27}), 5.53 (t, J = 6.2 Hz, 1H, H_6), 5.21 (dd, J = 6.9, 4.5 Hz, 1H, H_5), 5.08 (s, 2H, H_{25}), 4.67 – 4.46 (m, 5H, H_{11}, H_{15} and H_{23}), 4.45 – 4.31 (m, 3H, H_9 and H_{23}), 4.20 (d, J = 1.5 Hz, 2H, H_3), 4.15 (quint, J = 6.1, 5.7 Hz, 1H, H_{13}), 3.85 (d, J = 5.8 Hz, 1H, H_{14}), 3.72 – 3.43 (m, 4H, H_4 and H_{12}), 3.10 (dt, J = 36.1, 7.2 Hz, 2H, H_7), 2.64 (t, J = 7.8 Hz, 2H, H_{17}), 2.07 (dt, J = 13.5, 6.8 Hz, 2H, H_8), 1.61 (dd, J = 9.2, 5.8 Hz, 2H, H_{18}), 1.52 (s, 18H, H_{28}), 1.41 – 1.22 (m, 6H, H_{19}, H_{20} and H_{21}), 0.92 (s, 9H, H_1), 0.86 (t, J = 7.2 Hz, 3H, H_{22}), 0.10 (s, 6H, H_2).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.69, 155.57, 155.06, 149.63, 148.64, 148.17, 144.69, 141.66, 125.79, 123.54, 121.79, 101.28, 96.80, 90.83, 85.10, 71.35, 71.16, 69.19, 68.27, 64.88, 59.62, 53.05, 50.38, 47.34, 45.53, 37.75, 31.68, 30.31, 29.55, 29.04, 27.81, 26.15, 25.75, 22.68, 16.56, 14.19, -4.57. **HRMS** *m/z* = 1010.5606 (calcd. for $C_{47}H_{75}N_{13}O_{10}Si$ 1010.5602 $[M+H]^+$).

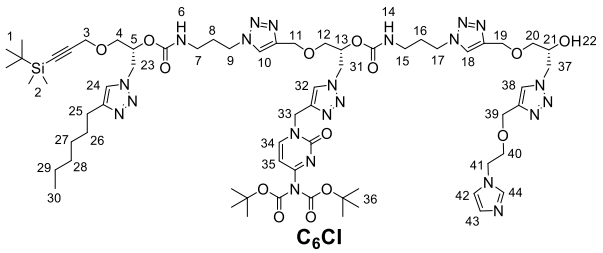
2.5.2 Synthesis of 30



Compound **C_6C** (1.9 g, 1.88 mmol, 1 equiv.) was added in a flask followed by DCM (10 mL), 4-nitrophenyl chloroformate (0.947 g, 4.7 mmol, 2.5 equiv.) and pyridine (380 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (10 mL) and added to a flask followed by 3-azido-1-propylamine (0.565 g, 5.6 mmol, 3 equiv.) and Et_3N (1.05 mL, 5 equiv.). The mixture was stirred for 2 h at room temperature, then DCM (100 mL) and water (100 mL) were added to the mixture. The organic phase was washed with water (2 × 100 mL) and brine (2 × 100 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **30** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 5/95) as a foamy-yellow solid (2.136 g, 100%). **30**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.76 (m, 3H, H_{10}, H_{27} and H_{29}), 7.35 (s, 1H, H_{19}), 7.04 (d, J = 7.3 Hz, 1HHz, 1H, H_{30}), 5.71 (t, J = 6.2 Hz, 1H, H_6), 5.38 (t, J = 6.0 Hz, 1H, H_{14}), 5.22 (t, J = 5.7 Hz, 1H, H_5), 5.15 – 5.00 (m, 3H, H_{13} and H_{28}), 4.75 - 4.50 (m, 6H, H_{11},

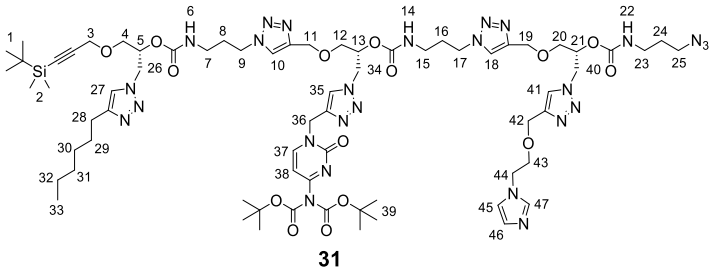
H_{18} and H_{26}), 4.41 (t, J = 6.5 Hz, 2H, H_9), 4.19 (d, J = 1.8 Hz, 2H, H_3), 3.70 – 3.01 (m, 10H, H_4, H_7, H_{12}, H_{15} and H_{17}), 2.66 (quint, J = 7.8 Hz, 2H, H_8), 2.10 (dd, J = 10.5, 3.7 Hz, 2H, H_{16}), 1.82 – 1.69 (m, 2H, H_{21}), 1.66 - 2.55 (m, 2H, H_{20}), 1.52 (s, 18H, H_{31}), 1.36 – 1.23 (m, 6H, H_{22}, H_{23} and H_{24}), 0.92 (s, 9H, H_1), 0.86 (t, J = 7.0 Hz, 3H, H_{25}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 162.74, 155.54, 155.16, 149.60, 148.68, 148.21, 144.55, 141.66, 126.15, 123.56, 121.72, 101.24, 96.84, 90.86, 85.11, 71.16, 70.60, 68.27, 68.07, 65.01, 59.61, 50.32, 50.22, 47.35, 45.79, 38.63, 37.99, 37.79, 31.68, 30.23,29.57, 29.10, 29.05, 27.80, 26.15, 25.78, 22.68, 16.55, 14.19, -4.58. **HRMS** *m/z* = 1136.6147 (calcd. for $C_{51}H_{81}N_{17}O_{11}Si$ 1136.6144 $[M+H]^+$).

2.5.3 Synthesis of C_6CI



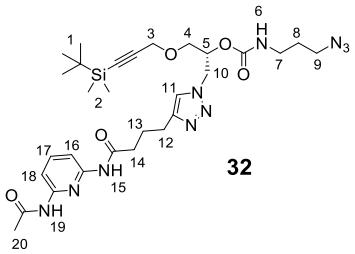
Compound **12** (0.189 g, 0.45 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.9 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **30** (0.511 g, 0.45 mmol, 1 equiv.) was added into the residue followed by EtOH (3.15 mL) with stirring. Water (1.35 mL), sodium ascorbate solution (18 mg in 0.6 mL water, 0.2 equiv.) and $CuSO_4$ solution (7.2 mg in 0.5 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 10/90) to give the final product **C_6CI** as a foamy white solid (0.53 g, 82%). **C_6CI**, **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.91 – 7.84 (m, 2H, H_{32} and H_{38}), 7.80 (s, 1H, H_{10}), 7.79 (s, 1H, H_{34}), 7.52 (s, 1H, H_{18}), 7.36 (s, 2H, H_{24} and H_{44}), 7.04 (d, J = 7.4 Hz, 1H, H_{35}), 6.89 (d, J = 21.4 Hz, 2H, H_{42} and H_{43}), 6.00 - 5.90 (m, 2H, H_6 and H_{14}), 5.22 (quint, J = 5.6 Hz, 1H, H_5), 5.13 – 4.98 (m, 3H, H_{13} and H_{33}), 4.73 – 4.49 (m, 11H, H_{11}, H_{19}, H_{23}, H_{31}, H_{37} and H_{39}), 4.45 – 4.28 (m, 5H, H_9, H_{17} and H_{37}), 4.24 – 4.10 (m, 3H, H_3 and H_{21}), 4.05 (dd, J = 6.1, 3.9 Hz, 2H, H_{41}), 3.84 – 3.73 (m, 2H, H_{12}), 3.67 – 3.44 (m, 6H, H_4, H_{20} and H_{40}), 3.20 - 3.00 (m, 4H, H_7 and H_{15}), 2.65 (t, J = 7.8 Hz, 2H, H_{25}), 2.13 – 2.01 (m, 4H, H_8 and H_{16}), 1.61 (quint, J = 7.8, 7.1 Hz, 2H, H_{26}), 1.51 (s, 18H, H_{36}), 1.35 – 1.22 (m, 6H, H_{27}, H_{28} and H_{29}), 0.92 (s, 9H, H_1), 0.88 – 0.82 (m, 3H, H_{30}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 162.72, 155.59, 155.48, 155.18, 149.59, 148.66, 148.37, 144.77, 144.47, 144.16, 124.50, 123.69, 123.63, 121.79, 101.25, 96.90, 90.86, 85.20, 71.84, 71.03, 70.73, 69.08, 68.90, 68.26, 64.92, 64.20, 59.61, 53.63, 50.37, 47.53, 47.42, 45.77, 37.80, 31.68, 30.34, 30.27, 29.56, 29.04, 27.79, 26.15, 25.76, 22.69, 16.56, 14.21, -4.58. **HRMS** *m/z* = 1441.7629 (calcd. for $C_{65}H_{100}N_{22}O_{14}Si$ 1441.7631 $[M+H]^+$).

2.5.4 Synthesis of 31



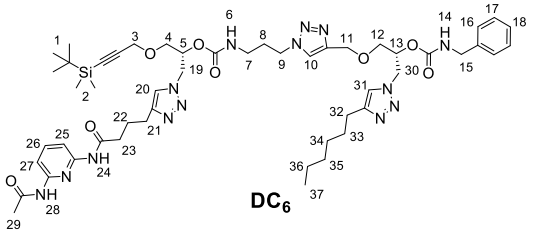
Compound **C_6CI** (0.5 g, 0.35 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.175 g, 0.9 mmol, 2.5 equiv.) and pyridine (70 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (10 mL) and added to a flask followed by 3-azido-1-propylamine (0.104 g, 3 equiv.) and Et_3N (0.24 mL, 5 equiv.). The mixture was stirred for 2 h at room temperature, then DCM (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 **31** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 10/90) as a foamy-white solid (0.45 g, 83%). **31**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.73 (m, 4H, H_{10}, H_{18}, H_{35} and H_{41}), 7.54 – 7.39 (m, 2H, H_{22} and H_{37}), 7.35 (s, 1H, H_{27}), 7.19 (s, 1H, H_{47}), 7.07 – 6.86 (m, 3H, H_{38}, H_{45} and H_{46}), 5.90 (dt, J = 71.8, 6.3 Hz, 2H, H_6 and H_{14}), 5.33 – 4.89 (m, 5H, H_5, H_{13}, H_{21}, H_{22}, and H_{36}), 4.79 – 4.32 (m, 16H, H_9, H_{11}, H_{17}, H_{19}, H_{26}, H_{34}, H_{40} and H_{42}), 4.30 – 4.02 (m, 4H, H_3 and H_{44}), 3.78 – 2.97 (m, 14H, H_4, H_7, H_{12}, H_{15}, H_{20}, H_{23} and H_{43}), 2.65 (t, J = 7.8 Hz, 2H, H_{28}), 2.20 – 1.93 (m, 7H, H_8, H_{16} and H_{24}), 1.66 – 1.57 (m, 2H, H_{29}), 1.51 (s, 18H, H_{39}), 1.36 – 1.19 (m, 8H, H_{30}, H_{31} and H_{32}), 0.92 (s, 9H, H_1), 0.88 – 0.82 (m, 3H, H_{33}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.72, 155.67, 155.57, 155.46, 155.09, 149.60, 148.68, 148.29, 145.08, 144.50, 141.65, 126.14, 123.71, 123.61, 121.74, 101.25, 96.82, 90.85, 85.14, 71.10, 70.69, 70.28, 69.01, 68.27, 67.91, 64.95, 64.84, 59.60, 50.66, 50.34, 49.14, 47.47, 47.39, 38.46, 37.83, 37.81, 31.68, 30.27, 29.57, 29.10, 29.05, 27.79, 26.15, 25.77, 22.69, 16.56, 14.21, -4.58. **HRMS** *m/z* = 1567.8190 (calcd. for $C_{69}H_{106}N_{26}O_{15}Si$ 1567.8173 $[M+H]^+$).

2.5.5 Synthesis of 32



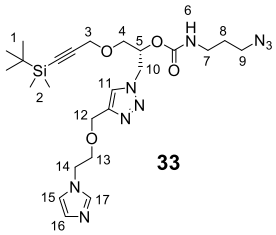
Compound **16** (1.8 g, 3.5 mmol, 1 equiv.) was added in a flask followed by DCM (15 mL), 4-nitrophenyl chloroformate (1.06 g, 5.2 mmol, 1.5 equiv.) and pyridine (425 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (10 mL) and added to a flask followed by 3-azido-1-propylamine (0.7 g, 2 equiv.) and Et_3N (1.46 mL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (150 mL) and water (150 mL) were added to the mixture. The organic phase was washed with water (2 × 150 mL) and brine (2 × 150 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **32** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 3/97) as a foamy-white solid (2.243 g, 100%). **32**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.44 (br s, 1H, H_{15}), 8.10 – 7.75 (m, 3H, H_{16}, H_{18} and H_{19}), 7.67 (t, J = 8.1 Hz, 1H, H_{17}), 7.38 (s, 1H, H_{11}), 5.28 (quint, J = 5.2 Hz, 1H, H_5), 5.13 (t, J = 6.1 Hz, 1H, H_6), 4.59 (d, J = 5.6 Hz, 2H, H_{10}), 4.23 (s, 2H, H_3), 3.66 (d, J = 4.9 Hz, 2H, H_4), 3.43 – 3.13 (m, 5H, H_7 and H_9), 2.81 (t, J = 6.9 Hz, 2H, H_{12}), 2.51 – 2.27 (m, 2H, H_{14}), 2.19 (s, 3H, H_{20}), 2.08 (td, J = 6.9, 2.5 Hz, 2H, H_{13}), 1.81 – 1.66 (m, 2H, H_8), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.77, 168.85, 158.29, 155.32, 149.74, 147.21, 140.78, 122.41, 109.60, 109.48, 101.07, 91.09, 71.41, 68.37, 59.73, 50.76, 49.10, 38.73, 36.07, 28.99, 26.15, 25.22, 24.82, 24.09, 16.57, -4.58. **HRMS** *m/z* = 641.3337 (calcd. for $C_{29}H_{44}N_{10}O_5Si$ 641.3338 $[M+H]^+$).

2.5.6 Synthesis of DC_6



Compound **32** (2 g, 3.1 mmol, 1 equiv.) and compound **23** (1.244 g, 3.1 mmol, 1 equiv.) were added in a flask followed by EtOH (21.8 mL) with stirring. Water (9.4 mL), sodium ascorbate solution (125 mg in 5 mL water, 0.2 equiv.) and $CuSO_4$ solution (50 mg in 4 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, DCM (100 mL) and Na_2EDTA (0.05 M, 100 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 DCM (100 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 5/95) to give the final product **DC_6** as foamy-white solid (2.68 g, 83%). **DC_6**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.64 (br s, 1H, H_{24}), 8.37 (br s, 1H, H_{28}), 7.84 (br s, 2H, H_{25} and H_{27}), 7.73 (s, 1H, H_{10}), 7.64 (s, 1H, H_{26}), 7.40 (s, 1H, H_{20}), 7.34 – 7.19 (m, 6H, H_{16}, H_{17}, H_{18} and H_{31}), 5.63 (t, J = 6.2 Hz, 2H, H_6 and H_{14}), 5.35 - 5.20 (m, 2H, H_5 and H_{13}), 4.68 – 4.50 (m, 6H, H_{11}, H_{19} and H_{30}), 4.42 – 4.17 (m, 6H, H_3, H_9 and H_{15}), 3.78 – 3.47 (m, 4H, H_4 and H_{12}), 3.26 – 2.90 (m, 2H, H_7), 2.87 – 2.54 (m, 4H, H_{21} and H_{32}), 2.34 (s, 2H, H_{23}), 2.16 (s, 3H, H_{29}), 2.00 (quint, J = 7.4 Hz, 2H, H_{22}), 1.59 (quint, J = 7.7 Hz, 2H, H_{33}), 1.37 – 1.21 (m, 6H, H_{34}, H_{35} and H_{36}), 0.92 (s, 9H, H_1), 0.89 – 0.81 (m, 3H, H_{37}), 0.11 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.93, 169.21, 155.52, 149.95, 149.80, 148.72, 147.26, 144.46, 140.64, 138.17, 128.82, 127.72, 127.56, 123.67, 122.54, 121.84, 109.57, 101.13, 91.05, 71.46, 71.30, 68.48, 64.90, 59.71, 50.89, 50.05, 47.39, 45.18, 37.83, 36.06, 31.67, 30.18, 29.49, 29.04, 26.14, 25.71, 25.21, 24.71, 24.23, 22.68, 16.55, 14.19, -4.58. **HRMS** *m/z* = 1039.5657 (calcd. for $C_{51}H_{74}N_{14}O_8Si$ 1039.5657 $[M+H]^+$).

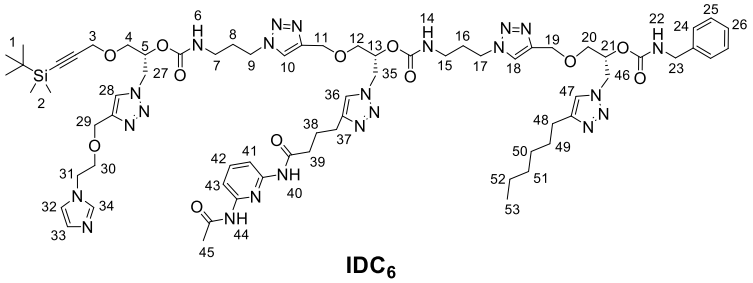
2.5.7 Synthesis of 33



33

Compound **12** (0.59 g, 1.4 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.423 g, 2.1 mmol, 1.5 equiv.) and pyridine (170 µL, 1.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.28 g, 2.8 mmol, 2 equiv.) and Et_3N (0.585 mL, 3 equiv.). The mixture was stirred for 1 h at room temperature, then DCM (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 **33** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 7/93) as a foamy-white solid (0.661 g, 86%). **33**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.56 (br s, 1H, H_{11}), 7.22 (s, 1H, H_{17}), 7.04 (s, 1H, H_{15}), 6.92 (dd, J = 6.7, 2.6 Hz, 1H, H_{16}), 6.77 (t, J = 5.9 Hz, 1H, H_6), 5.32 – 5.05 (m, 1H, H_5), 4.71 – 4.50 (m, 4H, H_{10} and H_{12}), 4.26 – 4.04 (m, 4H, H_3 and H_{14}), 3.77 - 3.73 (m, 2H, H_{13}), 3.62 – 3.48 (m, 2H, H_4), 3.41 – 3.21 (m, 4H, H_7 and H_9), 1.81 (quint, J = 6.7 Hz, 2H, H_8), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.55, 144.97, 128.43, 126.34, 123.51, 115.93, 101.35, 90.70, 70.61, 68.94, 67.87, 64.81, 59.59, 50.91, 50.80, 49.14, 47.48, 38.53, 29.10, 26.15, 16.56, -4.59. **HRMS** *m/z* = 546,2971 (calcd. for $C_{24}H_{39}N_9O_4Si$ 546,2967 $[M+H]^+$).

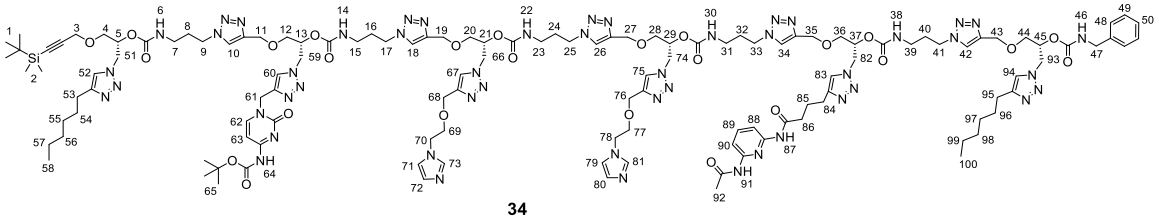
2.5.8 Synthesis of IDC_6



IDC_6

Compound **DC$_6$** (0.485 g, 0.47 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.93 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **33** (0.254 g, 0.47 mmol, 1 equiv.) was added into the residue followed by EtOH (3.26 mL) with stirring. Water (1.4 mL), sodium ascorbate solution (18.7 mg in 0.6 mL water, 0.2 equiv.) and $CuSO_4$ solution (7.5 mg in 0.5 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 10/90) to give the final product **IDC$_6$** as foamy white solid (0.432 g, 63%). **IDC$_6$**, **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.90 (br s, 1H, H_{40}), 8.80 (br s, 1H, H_{44}), 8.08 (s, 1H, H_{28}), 7.80 - 7.75 (m, 4H, H_{10}, H_{18}, H_{41} and H_{43}), 7.62 (t, J = 8.1 Hz, 1H, H_{42}), 7.49 (s, 1H, H_{36}), 7.47 (s, 1H, H_{47}), 7.35 – 7.19 (m, 6H, H_{24}, H_{25}, H_{26} and H_{34}), 7.15 (br s, 1H, H_{32}), 7.05 (br s, 1H, H_{33}), 6.93 (t, J = 6.5 Hz, 1H, H_6), 6.30 (s, 1H, H_{14}), 5.80 (t, J = 6.0 Hz, 1H, H_{22}), 5.20 - 5.10 (m, 3H, H_5, H_{13} and H_{21}), 4.70 – 4.49 (m, 12H, H_{11}, H_{19}, H_{27}, H_{29}, H_{35} and H_{46}), 4.44 – 4.11 (m, 10H, H_3, H_9, H_{17}, H_{23} and H_{31}), 3.82 – 3.44 (m, 8H, H_4, H_{12}, H_{20} and H_{30}), 3.27 – 2.95 (m, 4H, H_{27} and H_{15}), 2.85 – 2.53 (m, 4H, H_{37} and H_{48}), 2.48 – 2.26 (m, 2H, H_{39}), 2.16 (s, 3H, H_{45}), 2.10 - 1.95 (m, 6H, H_8, H_{16} and H_{38}), 1.74 – 1.48 (m, 2H, H_{49}), 1.37 – 1.18 (m, 6H, H_{50}, H_{51} and H_{52}), 0.91 (s, 9H, H_1), 0.88 – 0.81 (m, 3H, H_{53}), 0.09 (s, 6H, H_{53}). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.19, 169.62, 155.77, 155.75, 155.56(2C), 150.13, 149.95, 148.71, 147.17, 144.51, 144.36, 144.20, 140.55, 138.29, 128.80(2C), 127.67, 127.54, 124.14, 123.94, 123.78, 121.93, 120.69, 109.58, 109.51, 101.28, 90.82, 71.44, 71.14, 70.83, 68.63, 68.39, 68.17, 64.84, 64.71, 64.46, 59.60, 50.95, 50.53, 50.12, 47.65, 47.58, 45.10, 37.83, 36.06, 31.67, 30.34, 30.18, 29.50, 29.04, 26.15, 25.71, 25.06, 24.65, 22.68, 16.55, 14.21, -4.58. **HRMS** *m/z* = 1470.7658 (calcd. for $C_{69}H_{99}N_{23}O_{12}Si$ 1470.7686 $[M+H]^+$).

2.5.9 Synthesis of 34

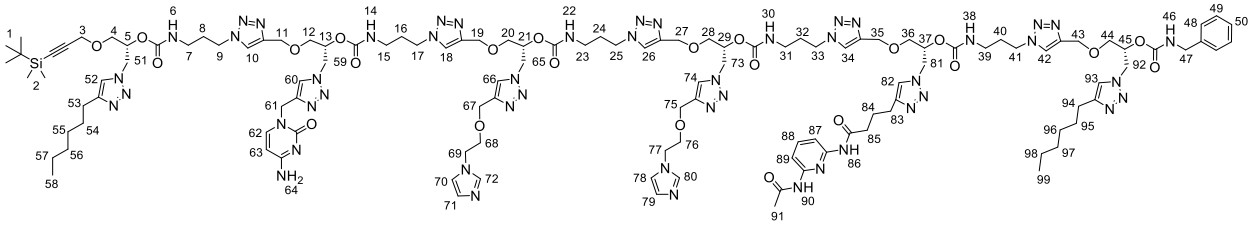


34

Compound I**DC$_6$** (0.32 g, 0.22 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.66 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **31** (0.32 g, 0.22 mmol, 1 equiv.) was added into the residue followed by EtOH (1.54 mL) with stirring. Water (0.66 mL), sodium ascorbate solution (8.8 mg in 0.3 mL water, 0.2 equiv.) and $CuSO_4$ solution (3.5 mg in 0.2 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 5/95) to give the final product **34** as foamy white solid (0.437 g, 70%). **34**, **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.12 (br s, 1H, H_{87}), 9.10 (br s, 1H, H_{91}), 7.92 – 7.69 (m, 9H, H_{10}, H_{18}, H_{34}, H_{42}, H_{60}, H_{62}, H_{64}, H_{67} and H_{75}), 7.61 (t, J = 7.3 Hz, 3H, H_{42}, H_{88} and H_{90}), 7.46 - 7.40 (m, 3H, H_{73}, H_{81} and H_{89}), 7.40 - 7.30 (m, 3H, H_{52}, H_{83} and H_{94}), 7.30 – 7.13 (m, 6H, H_{48}, H_{49}, H_{50} and H_{63}), 6.98 - 6.93 (m, 4H, H_{71}, H_{72}, H_{79} and H_{80}), 6.40 (br s, 1H, H_{22}), 6.35 (br s, 1H, H_{30}), 6.11 – 5.87 (m, 2H, H_6 and H_{14}), 5.26 – 4.97 (m, 8H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{38}, H_{45} and H_{46}), 4.74 – 4.15 (m, 42H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{33}, H_{35}, H_{41}, H_{43}, H_{47}, H_{51}, H_{59}, H_{61}, H_{66}, H_{68}, H_{74}, H_{76} and H_{82}), 4.14 – 4.03 (m, 4H, H_{70} and H_{78}), 3.77 – 3.34 (m, 16H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44}, H_{69} and H_{77}), 3.21 – 2.87 (m, 12H, H_7, H_{15}, H_{23}, H_{31}, H_{39} and H_{84}), 2.70 - 2.60 (m, 4H, H_{53} and

H_{95}), 2.34 (s, 2H, H_{86}), 2.14 (s, 3H, H_{92}), 2.12 – 1.88 (m, 12H, H_8, H_{16}, H_{24}, H_{32}, H_{40} and H_{85}), 1.60 - 1.50 (m, 4H, H_{54} and H_{96}), 1.46 (s, 9H, H_{65}), 1.35 – 1.18 (m, 12H, H_{55}, H_{56}, H_{57}, H_{97}, H_{98} and H_{99}), 0.90 (s, 9H, H_1), 0.87 – 0.81 (m, 6H, H_{58} and H_{100}), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.57, 163.33, 155.88, 155.88, 155.86, 155.71, 155.62, 155.56, 155.56, 148.65, 148.64, 147.17, 144.84, 144.23, 141.84, 140.55, 138.34, 137.79, 128.75, 128.10, 127.60, 127.51, 123.99, 123.86, 123.71, 122.82, 121.87, 121.74, 119.83, 109.62, 109.56, 101.22, 95.75, 90.85, 82.87, 71.43, 70.98, 70.62, 69.00, 68.36, 68.25, 64.79, 64.71, 64.60, 59.57, 50.65, 50.35, 50.10, 47.66, 47.53, 47.37, 45.89, 45.40, 45.07, 37.83, 36.03, 31.65, 30.31, 30.20, 29.54, 29.48, 29.02, 28.13, 26.13, 25.74, 25.09, 24.60, 22.66, 16.54, 14.19, -4.59. **TOF MS ES +** *m/z* = 2822.6011 (calcd. for $C_{128}H_{184}N_{48}O_{25}Si$ 2822.4444 $[M+H]^+$).

2.5.10 Synthesis of C_6CIIDC_6

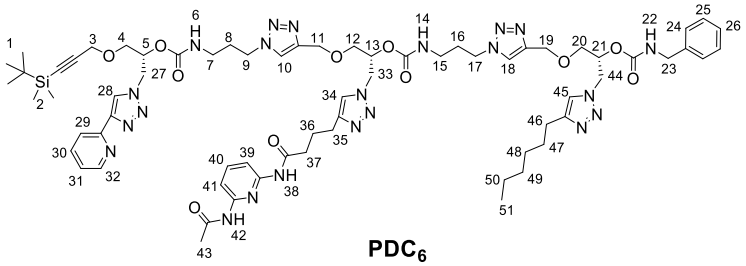


C_6CIIDC_6

Compound **34** (0.39 g, 0.138 mmol, 1 equiv.) was added in a flask followed by TFA (1.5 mL) and DCM (3 mL). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product was precipitated from the residue with the addition of Et_2O followed by drying under vacuum to give the **C_6CIIDC_6** as a white solid (0.313 g, 83%). **C_6CIIDC_6, ^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.09 (br s, 2H, H_{86} and H_{90}), 7.90 – 7.68 (m, 8H, H_{10}, H_{18}, H_{34}, H_{42}, H_{60}, H_{62} , H_{66} and H_{74}), 7.70 - 7.60 (m, 3H, H_{26}, H_{87} and H_{89}), 7.52 (d, J = 6.9 Hz, 1H, H_{52}), 7.48 – 7.31 (m, 5H, H_{72}, H_{80}, H_{82}, H_{88} and H_{92}), 7.31 – 7.16 (m, 5H, H_{48}, H_{49} and H_{50}), 6.98 - 6.95 (m, 6H, H_{64}, H_{70}, H_{71}, H_{78} and H_{79}) 6.56 (br s, 1H, H_{22}), 6.52 (br s, 1H, H_{30}), 6.20 (s, 1H, H_{63}), 6.05 (s, 1H, H_6), 5.79 (t, J = 6.8 Hz, 1H, H_{14}), 5.33 – 4.79 (m, 8H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{38}, H_{45} and H_{46}), 4.76 – 4.16 (m, 40H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{33}, H_{35}, H_{41}, H_{43}, H_{47}, H_{51}, H_{59}, H_{61}, H_{65}, H_{67}, H_{73}, H_{75} and H_{81}), 4.14 – 4.03 (m, 4H, H_{69} and H_{77}), 3.75 – 3.39 (m, 16H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44}, H_{68} and H_{76}), 3.15 - 2.90 (m, 10H, H_7, H_{15}, H_{23}, H_{31}, H_{39} and H_{83}), 2.70 - 2.630 (m, 4H, H_{39} and H_{94}), 2.33 (br s, 2H, H_{85}), 2.13 (s, 3H, H_{92}), 2.11 – 1.87 (m, 12H, H_{55}, H_{56}, H_{57}, H_{96}, H_{97} and H_{98}), 1.60 - 1.50 (m, 4H, H_{54} and H_{95}), 1.35 – 1.18 (m, 12H, H_{54}, H_{55}, H_{56}, H_{96}, H_{97} and H_{98}), 0.91 (s, 9H, H_1), 0.86 – 0.81 (m, 6H, H_{58} and H_{99}), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.24, 171.33, 165.68, 156.16, 155.90, 155.78, 155.66, 155.61, 150.22, 150.02, 148.65, 147.53, 147.18, 144.79, 144.20, 144.16, 140.97, 140.47, 138.40, 137.74, 128.76, 127.92, 127.60, 127.50, 124.15, 123.94, 122.90, 121.93, 121.85, 119.93, 109.73, 109.61, 101.26, 95.08, 90.88, 71.45, 71.00, 70.72, 69.03, 68.64, 68.25, 64.67, 64.52, 59.60, 50.63, 50.46, 50.32, 50.14, 47.68, 47.59, 47.39, 45.05, 38.61, 37.86, 31.66, 30.30, 29.82, 29.54, 29.49, 29.04, 29.02, 26.14, 25.74, 22.68, 16.55, 14.21, -4.57. **TOF MS ES +** *m/z* = 2723.4556 (calcd. for $C_{122}H_{175}N_{49}O_{23}Si$ 2723,3873 $[M+H]^+$).

2.6 Synthesis of C_6CIPDC_6

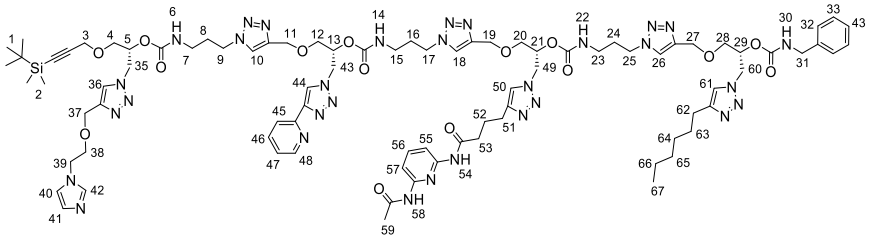
2.6.1 Synthesis of PDC_6



PDC_6

Compound **DC$_6$** (2.08 g, 2 mmol, 1 equiv.) was added in a flask followed by EtOAc (10 mL) and TBAF (4 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (100 mL) and washed with brine (3 × 100 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **25** (1 g, 2 mmol, 1 equiv.) was added into the residue followed by EtOH (14 mL) with stirring. Water (6 mL), sodium ascorbate solution (80 mg in 3 mL water, 0.2 equiv.) and $CuSO_4$ solution (16 mg in 2 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, DCM (60 mL) and Na_2EDTA (0.05 M, 60 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 DCM (60 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product **PDC$_6$** as foamy-white solid (2.85 g, 100%). **PDC$_6$**, **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.83 (s, 1H, H_{38}), 8.67 (s, 1H, H_{42}), 8.49 (d, J = 4.9 Hz, 1H, H_{32}), 8.27 (s, 1H, H_{28}), 8.07 (d, J = 7.9 Hz, 1H, H_{29}), 7.88 – 7.69 (m, 5H, H_{10}, H_{18}, H_{30}, H_{39} and H_{41}), 7.61 (s, 1H, H_{40}), 7.49 (s, 1H, H_{34}), 7.33 (s, 1H, H_{45}), 7.31 – 7.16 (m, 6H, H_{24}, H_{25}, H_{26} and H_{31}), 6.29 (t, J = 6.4 Hz, 1H, H_6), 6.05 – 5.73 (m, 2H, H_{14} and H_{22}), 5.32 (quint, J = 7.6 Hz, 1H, H_5), 5.25 -5.10 (m, 2H, H_{13} and H_{21}), 4.79 – 4.47 (m, 10H, H_{11}, H_{19}, H_{27}, H_{33} and H_{44}), 4.43 – 4.13 (m, 8H, H_3, H_9, H_{17} and H_{23}), 3.73 – 3.39 (m, 6H, H_4, H_{12} and H_{20}), 3.20 – 2.94 (m, 4H, H_7 and H_{15}), 2.79 – 2.53 (m, 4H, H_{35} and H_{46}), 2.35 (s, 2H, H_{37}), 2.15 (s, 3H, H_{43}), 2.05 - 1.95 (m, 6H, H_8, H_{16} and H_{36}), 1.70 – 1.48 (m, 2H, H_{47}), 1.34 – 1.18 (m, 6H, H_{48}, H_{49} and H_{50}), 0.89 (s, 9H, H_1), 0.87 – 0.82 (m, 3H, H_{51}), 0.08 (s, 6H, H_2). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.05, 169.45, 155.71, 155.67, 155.54, 150.08, 149.90, 149.43, 148.66, 148.41, 147.13, 144.37, 144.22, 140.47, 138.28, 137.12, 128.78, 127.65, 127.53, 123.89, 123.76, 123.51, 123.12, 121.89, 120.33, 109.49(2C), 101.16, 90.96, 71.48, 71.18, 71.09, 68.58, 68.45, 68.23, 59.62, 59.08, 50.94, 50.46, 50.07, 47.54, 47.27, 45.11, 37.86, 37.71, 36.11, 31.66, 30.21, 29.49, 29.03, 26.13, 25.71, 24.66, 24.38, 24.11, 22.67, 19.85, 14.19, -4.62. **HRMS** *m/z* = 1423.7313 (calcd. for $C_{68}H_{94}N_{22}O_{11}Si$ 1423.7314 $[M+H]^+$).

2.6.2 Synthesis of IPDC$_6$

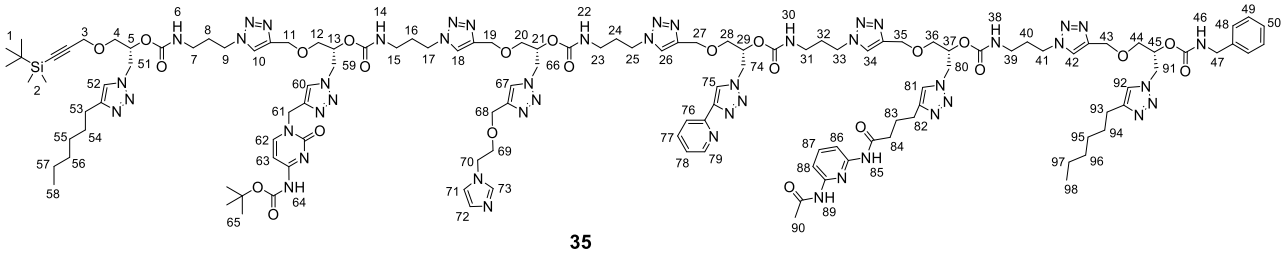


IPDC$_6$

Compound I**DC$_6$** (1.3 g, 0.92 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (1.84 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **25** (0.5 g, 1 equiv.) was added into the residue followed by EtOH (6.4 mL) with stirring. Water (2.7 mL), sodium ascorbate solution (36.6 mg in 1.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (14.7 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 3/97 to 10/90) to give the final product IPDC$_6$ as foamy-white solid (1.43 g, 84%). I**PDC$_6$**, **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.80 (s, 1H, H_{54}), 8.70 (s, 1H, H_{58}), 8.50 (br d, J = 4.9 Hz, 1H, H_{48}), 8.24 (s, 1H, H_{44}), 8.04 (d, J = 7.9 Hz, 1H, H_{45}), 7.92 – 7.66 (m, 6H, H_{36}, H_{42}, H_{46}, H_{55}, H_{56} and H_{57}), 7.62 (t, J = 8.0 Hz, 1H, H_{10}), 7.55 – 7.36 (m, 2H, H_{18} and H_{26}), 7.34 – 7.12 (m, 8H, H_{32}, H_{33}, H_{34}, H_{47}, H_{50} and H_{61}), 7.00 (br s, 1H, H_{40}), 6.9 (br s, 1H, H_{41}), 6.26 - 6.20 (m, 2H, H_6 and H_{14}), 5.80 (t, J = 6.0 Hz, 1H, H_{22}), 5.32 – 5.06 (m, 4H, H_5, H_{13}, H_{21} and H_{29}), 4.75 – 4.47 (m, 15H, H_{19}, H_{27}, H_{30}, H_{35}, H_{37}, H_{43} and H_{49}), 4.41 – 4.02 (m, 12H, H_9, H_{17}, H_{25}, H_{31}, H_{39} and H_{60}), 3.76 – 3.44 (m, 10H, H_3, H_{12}, H_{20}, H_{28} and H_{38}), 3.27 – 2.92 (m, 6H, H_4, H_7 and H_{15}), 2.79 – 2.54 (m, 4H, H_{23} and H_{51}), 2.33 (s, 3H, H_{53} and H_{62}), 2.15 (s, 3H, H_{62}), 2.13 – 1.90 (m, 8H, H_8, H_{16}, H_{23} and H_{52}), 1.58 (quint,

J = 7.5 Hz, 2H, H_{63}), 1.34 – 1.18 (m, 6H, H_{64}, H_{65} and H_{66}), 0.91 (s, 9H, H_1), 0.87 – 0.81 (m, 4H, H_{59}), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.15, 169.56, 155.79, 155.75, 155.61, 155.57, 150.14, 149.99, 149.35, 148.71, 147.17, 144.93, 144.39, 144.22, 144.17, 140.55(2C), 138.28, 137.36, 128.79(2C), 127.66, 127.53, 123.93, 123.78, 123.71, 123.24, 122.92, 121.92(2C), 120.43, 109.58, 109.49, 101.32, 90.78, 71.41, 71.12, 70.99, 70.70, 69.05, 68.61, 68.40, 68.06, 64.83, 64.75, 64.65, 59.60, 50.85, 50.78, 50.43, 50.10, 47.64, 47.56, 47.38, 45.11, 37.84, 36.09, 31.67, 30.37, 30.18, 29.49, 29.04, 26.15, 25.70, 25.07, 24.63, 22.69, 16.56, 14.21, -4.57. **TOF MS ES +** m/z = 1855,0697 (calcd. for $C_{86}H_{119}N_{31}O_{15}Si$ 1854,9344 $[M+H]^+$).

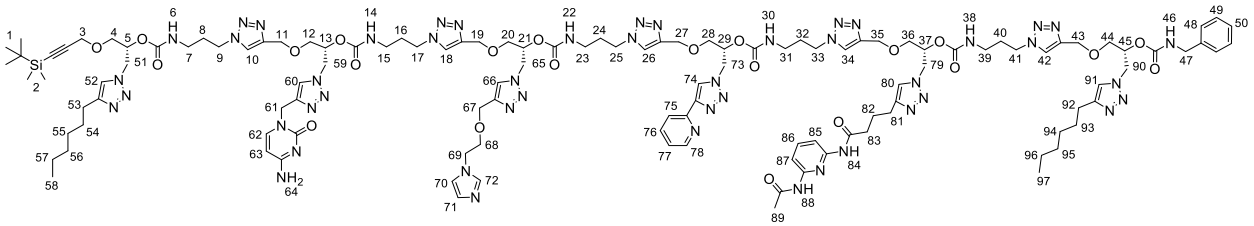
2.6.3 Synthesis of 35



35

Compound **IPDC$_6$** (0.427 g, 0.23 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.69 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **30** (0.261 g, 0.23 mmol, 1 equiv.) was added into the residue followed by EtOH (1.61 mL) with stirring. Water (0.69 mL), sodium ascorbate solution (9.2 mg in 0.3 mL water, 0.2 equiv.) and $CuSO_4$ solution (3.7 mg in 0.2 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 7/93) to give the final product **35** as foamy-white solid (0.57 g, 84%). **35**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.05 (br s, 1H, H_{85}), 9.00 (br s, 1H, H_{89}), 8.47 (s, 1H, H_{64}), 8.30 (s, 1H, H_{79}), 8.13 – 7.42 (m, 15H, H_{10}, H_{18}, H_{26}, H_{34}, H_{42}, H_{60}, H_{62}, H_{67}, H_{73}, H_{76}, H_{77}, H_{86}, H_{87}, H_{88}), 7.38 – 7.13 (m, 10H, H_{48}, H_{49}, H_{50}, H_{52}, H_{63}, H_{78}, H_{81} and H_{92}), 7.11 – 6.98 (m, 2H, H_{71} and H_{72}), 6.67 – 6.16 (m, 3H, H_6, H_{14} and H_{22}), 6.12 – 5.83 (m, 2H, , H_{30} and H_{38}), 5.37 – 4.92 (m, 8H, H_5, H_{13}, H_{21}, H_{29}, H_{30}, H_{37}, H_{45} and H_{46}), 4.80 – 4.12 (m, 42H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{33}, H_{35}, H_{41}, H_{43}, H_{47}, H_{51}, H_{59}, H_{61}, H_{66}, H_{68}, H_{70} H_{74}, H_{80} and H_{91}), 3.78 – 3.37 (m, 14H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44} and H_{69}), 3.24 – 2.95 (m, 10H, H_7, H_{15}, H_{23}, H_{31} and H_{39}), 2.80 – 2.48 (m, 6H, H_{53} , H_{82} and H_{93}), 2.34 (s, 2H, H_{84}), 2.08 (d, J = 51.0 Hz, 15H, H_8, H_{16}, H_{24}, H_{32}, H_{40}, H_{83} and H_{90}), 1.60 - 1.50 (m, 4H, H_{54} and H_{94}), 1.49 (s, 9H, H_{65}), 1.35 – 1.18 (m, 12H, H_{55}, H_{56}, H_{57}, H_{95}, H_{96} and H_{97}), 0.90 (s, 9H, H_1), 0.85 - 0.83 (m, 6H, H_{58} and H_{98}), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.34, 169.35, 155.90, 155.86, 155.68, 155.65, 155.57, 154.93, 150.24, 150.02, 149.62, 149.38, 148.65, 147.18, 146.76, 144.30, 144.23, 144.18, 144.09, 144.03, 140.54, 140.50, 138.41, 137.43, 137.41, 128.76, 127.60, 127.56, 127.50, 124.09, 123.87, 123.34, 123.25, 123.15, 123.05, 122.98, 121.88, 120.45, 118.61, 109.54, 109.45, 101.26, 100.96, 90.90, 85.31, 85.26, from 71.46 to 70.96(6C), from 68.75 to 68.23(7C), 64.71, 59.61, 59.56, 55.90, 50.54, 50.50, 50.38, 50.35, 50.17, 50.11, 47.62, 47.48, 45.97, 45.05, 37.84, 36.10, 31.67, 30.25, 29.55, 29.04, 28.14, 27.79, 26.16, 25.72, 25.05, 24.58, 22.69, 16.56, 14.22, -4.56. **TOF MS ES +** m/z = 2776,6165 (calcd. for $C_{126}H_{178}N_{48}O_{24}Si$ 2776,4026 $[M+H]^+$).

2.6.4 Synthesis of C_6CIPDC_6

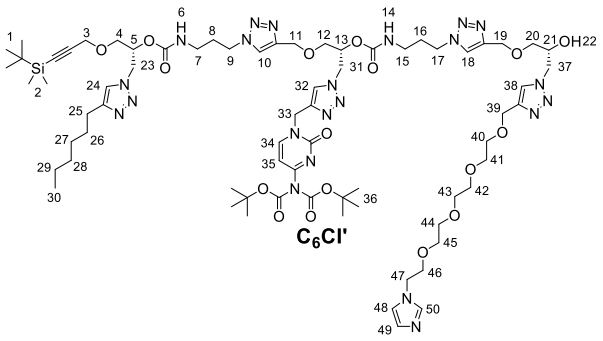


C_6CIPDC_6

Compound **35** (0.5 g, 0.138 mmol, 1 equiv.) was added in a flask followed by TFA (1.5 mL) and DCM (3 mL). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product was precipitated from the residue with the addition of Et_2O followed by drying under vacuum to give the **C_6CIPDC_6** as a white solid (0.21 g, 44%). **C_6CIIDC_6, ^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.00 (br s, 1H, H_{84}), 9.00 (br s, 1H, H_{88}), 8.48 (d, J = 4.9 Hz, 1H, H_{78}), 8.29 (s, 1H, H_{75}), 8.02 (d, J = 8.0 Hz, 1H, H_{74}), 7.89 – 7.57 (m, 11H, H_{10}, H_{18}, H_{34}, H_{42}, H_{60}, H_{62}, H_{66}, H_{76}, H_{85} and H_{87}), 7.55– 7.32 (m, 6H, H_{52}, H_{72}, H_{77}, H_{80}, H_{76}, H_{86} and H_{91}), 7.31 – 7.12 (m, 6H, H_{48}, H_{49}, H_{50} and H_{77}), 7.04 – 6.35 (m, 6H, H_{22}, H_{63}, H_{64}, H_{70} and H_{71}), 6.16 (s, 1H, H_{63}), 5.98 (s, 1H, H_6), 5.77 (br s, 1H, H_{14}), 5.29 – 4.84 (m, 8H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{38}, H_{45} and H_{46}), 4.77 – 4.02 (m, 42H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{33}, H_{35}, H_{41}, H_{43}, H_{47}, H_{51}, H_{59}, H_{61}, H_{65}, H_{67}, H_{69} H_{73}, H_{79} and H_{90}), 3.73 – 3.38 (m, 14H, H_4, H_{12}, H_{20}, H_{28}, H_{36}, H_{44} and H_{68}), 3.20 – 2.90 (m, 10H, H_7, H_{15}, H_{23}, H_{31} and H_{39}), 2.73 – 2.58 (m, 6H, H_{53}, H_{81} and H_{92}), 2.33 (s, 2H, H_{83}), 2.18 – 1.87 (m, 12H, H_{55}, H_{56}, H_{57}, H_{94}, H_{95} and H_{96}), 1.60 - 1.50 (m, 4H, H_{54} and H_{93}), 1.35 – 1.18 (m, 15H, H_{55}, H_{56}, H_{57}, H_{94}, H_{95} and H_{96}), 0.91 (s, 9H, H_1), 0.87 – 0.81 (m, 6H, H_{58} and H_{97}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.25, 169.76, 165.91, 155.89, 155.85, 155.81, 155.77, 155.66, 155.62, 155.24, 150.22, 150.18, 150.02, 149.98, 149.42, 148.64, 148.14, 147.17, 146.13, 144.31, 144.19, 144.15, 144.08, 144.00, 142.66, 140.48(2C), 138.40, 137.27(2C), 128.75, 127.72, 127.59, 127.49, 124.21, 124.08, 123.86, 123.79, 123.21, 122.96, 121.95, 121.88, 120.37, 119.96, 109.58, 109.50, 102.21, 101.26, 90.88, 71.45, 71.15, 71.12, 71.06, 70.98, 70.78, 69.02, 68.84, 68.58, 68.46, 68.39, 68.23, 64.79, 64.70, 59.60, 53.57, 50.83, 50.67, 50.55, 50.48, 50.32, 50.15, 47.60, 47.41, 45.04, 37.87, 36.08, 31.66, 30.25, 29.53, 29.48, 29.03, 26.14, 25.73, 25.09, 24.58, 22.67, 16.55, 14.21, -4.57. **TOF MS ES +** m/z = 2676,3304 (calcd. for $C_{121}H_{170}N_{48}O_{22}Si$ 2676,3501 $[M+H]^+$).

2.7 Synthesis of Heptamer $C_6CI'IPDC_6$

2.7.1 Synthesis of C_6CI'

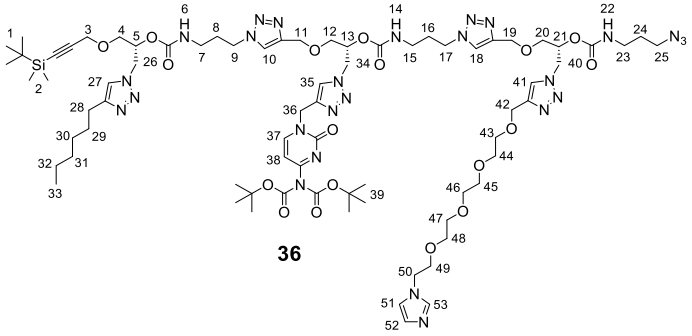


C_6CI'

Compound **13** (0.257 g, 0.47 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.94 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **30** (0.53 g, 0.47 mmol, 1 equiv.) was added into the residue followed by EtOH (3.3 mL) with stirring. Water (1.4 mL), sodium ascorbate solution (18.8 mg in 0.6 mL water, 0.2 equiv.) and $CuSO_4$ solution (7.5 mg in 0.4 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 0/100 to 9/91) to give the final product **C_6CI'** as foamy-white solid (0.624 g, 85%). **C_6CI'**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.74 (m, 5H, H_{10}, H_{18}, H_{32}, H_{34} and H_{38}), 7.51 (s, 1H, H_{50}), 7.36 (s, 1H, H_{24}), 7.06 – 6.88 (m, 3H, H_{35}, H_{48} and H_{49}), 6.00 (t, J = 6.2 Hz, 1H, H_6), 5.90 (t, J = 6.2 Hz, H_{14}), 5.21 (quint, J = 5.4 Hz, 1H, H_5), 5.13 – 4.97 (m, 3H, H_{13} and H_{33}), 4.71 – 4.51 (m, 11H, H_{11}, H_{19}, H_{23}, H_{31}, H_{37} and H_{39}), 4.45 - 4.35 (m, 5H, H_9, H_{17}, H_{21} and H_{37}), 4.22 – 4.06 (m, 4H, H_3 and H_{47}), 3.75 – 3.46 (m, 21H, H_4, H_{12}, H_{20}, H_{22}, H_{40}, H_{41}, H_{42}, H_{43}, H_{44}, H_{45} and H_{46}), 3.20 - 3.00 (m, 4H, H_7 and H_{15}), 2.65 (t, J = 7.8 Hz, 2H, H_{25}), 2.13 – 2.00 (m, 4H, H_8 and H_{16}), 1.66 – 1.56 (m, 2H, H_{26}), 1.51 (s, 18H, H_{36}), 1.35 – 1.21 (m, 6H, H_{27}, H_{28} and H_{29}), 0.92 (s, 9H, H_1), 0.88 – 0.83 (m, 3H, H_{30}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.72, 155.59, 155.49, 155.20, 149.60, 148.66, 148.40, 144.79, 144.76, 144.49, 141.60, 128.67, 126.22, 124.55, 123.69, 123.63, 121.79, 119.77, 101.26, 96.91, 90.85, 85.20, 71.79, from 71.04 to 70.49(8C), 69.82, 69.10, 68.25, 64.92, 64.71, 59.60, 53.38, 50.37(2C), 47.51, 47.42, 47.28, 45.77, 37.79, 31.68, 30.32, 29.56, 29.04, 27.79, 26.15, 25.75, 22.69, 16.56, 14.21, -4.58. **HRMS** *m/z* = 1573.8422 (calcd. for $C_{71}H_{112}N_{22}O_{17}Si$ 1573.8418 $[M+H]^+$).

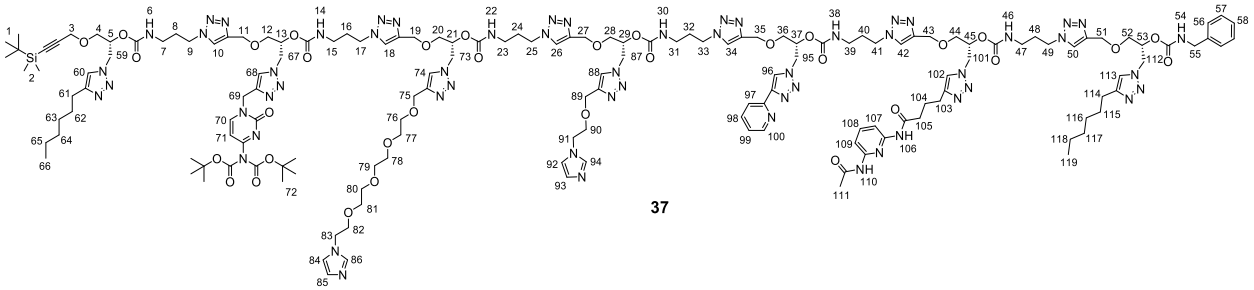
2.7.2 Synthesis of 36



36

Compound **C_6CI'** (0.6 g, 0.4 mmol, 1 equiv.) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.20 g, 1 mmol, 2.5 equiv.) and pyridine (81 μL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.12 g, 1.2 mmol, 3 equiv.) and Et_3N (0.28 mL, 5 equiv.). The mixture was stirred for 2 h at room temperature, then DCM (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 **36** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 10/90) as a foamy-white solid (0.52 g, 80%). **36**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 – 7.74 (m, 4H, H_{10}, H_{18}, H_{35} and H_{42}), 7.66 (s, 1H, H_{37}), 7.56 (s, 1H, H_{53}), 7.36 (s, 1H, H_{27}), 7.07 – 6.96 (m, 3H, H_{38}, H_{51} and H_{52}), 6.04 (quint J = 6.0 Hz, 1H, H_5), 6.00 (quint, J = 6.0 Hz, 1H, H_{22}), 5.86 (quint, J = 6.1 Hz, 1H, H_{13}), 5.26 – 4.94 (m, 5H, H_6, H_{14}, H_{21} and H_{36}), 4.72 – 4.51 (m, 12H, H_{11}, H_{19}, H_{26}, H_{34}, H_{40} and H_{39}), 4.46 – 4.33 (m, 4H, H_9 and H_{17}), 4.20 (br s, 2H, H_{50}), 4.10 (t, J = 5.1 Hz, 2H, H_3), 3.77 – 3.42 (m, 20H, H_4, H_{12}, H_{20}, H_{22}, H_{43}, H_{44}, H_{45}, H_{46}, H_{47}, H_{48} and H_{49}), 3.32 (t, J = 6.6 Hz, 2H, H_{17}), 3.23 – 2.99 (m, 6H, H_{15}, H_{23} and H_{25}), 2.65 (t, J = 7.8 Hz, 2H, H_{28}), 2.17 – 2.00 (m, 4H, H_8 and H_{16}), 1.70 (quint, J = 7.1 Hz, 2H, H_{24}), 1.60 (quint, J = 7.0 Hz, H_{29}), 1.51 (s, 18H, H_{39}), 1.35 – 1.23 (m, 6H, H_{30}, H_{31} and H_{32}), 0.92 (s, 9H, H_1), 0.88 – 0.83 (m, 3H, H_{33}), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.72, 155.58, 155.50, 155.14, 149.59, 148.67, 148.36, 145.17, 144.50, 144.38, 141.63, 137.67, 128.97, 126.20, 124.10, 123.78, 123.61, 121.76, 119.75, 101.25, 96.87, 90.85, 85.17, 71.08, 70.98, from 70.75 to 70.58(7C), 69.83, 68.48, 68.26, 64.94, 64.65, 59.60, 50.38, 50.35, 49.05, 47.46, 47.40, 47.20, 45.77, 38.50, 37.79, 31.68, 30.34, 30.27, 29.57, 29.04, 27.79, 26.15, 25.77, 22.68, 16.56, 14.20, -4.58. **HRMS** *m/z* = 1699.8971 (calcd. for $C_{75}H_{118}N_{26}O_{18}Si$ 1699.8959 $[M+H]^+$).

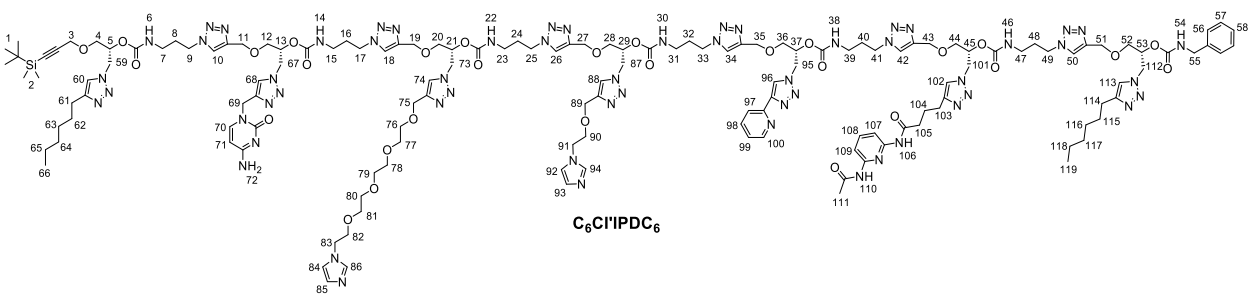
2.7.3 Synthesis of 37



37

Compound **IPDC$_6$** (0.54 g, 0.29 mmol, 1 equiv.) was added in a flask followed by EtOAc (5 mL) and TBAF (0.87 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature, then 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **36** (0.494 g, 0.29 mmol, 1 equiv.) was added into the residue followed by EtOH (2 mL) with stirring. Water (0.87 mL), sodium ascorbate solution (11.6 mg in 0.4 mL water, 0.2 equiv.) and $CuSO_4$ solution (4.6 mg in 0.3 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, DCM (30 mL) and Na_2EDTA (0.05 M, 30 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 DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 3/97 to 15/85) to give the final product **37** as foamy-white solid (0.57 g, 84%). **37**, **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.98 (br s,, 1H, H_{106}), 8.90 (br s, 1H, H_{110}), 8.48 (d, J = 5.0 Hz, 1H, H_{100}), 8.27 (s, 1H, H_{96}), 8.03 (d, J = 7.9 Hz, 1H, H_{97}), 7.95 – 7.50 (m, 15H, H_{10}, H_{18}, H_{26}, H_{34}, H_{42}, H_{50}, H_{68}, H_{70}, H_{74}, H_{88}, H_{98}, H_{107}, H_{108} and H_{109}), 7.48 – 7.10 (m, 11H, H_{56}, H_{57}, H_{58}, H_{60}, H_{88}, H_{94}, H_{99}, H_{102} and H_{113}), 7.08 – 6.85 (m, 5H, H_{71}, H_{84}, H_{85}, H_{92} and H_{93}), 6.71 – 5.75 (m, 5H, H_6, H_{14}, H_{22}, H_{30} and H_{38}), 5.31 – 4.94 (m, 9H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, H_{45}, H_{46}, H_{53} and H_{54}), 4.79 – 4.46 (m, 31H, H_{11}, H_{19}, H_{27}, H_{35}, H_{43}, H_{51}, H_{59}, H_{67}, H_{73}, H_{75}, H_{87}, H_{89}, H_{95}, H_{101} and H_{112}), 4.43 – 4.15 (m, 16H, H_3, H_9, H_{17}, H_{25}, H_{33}, H_{42}, H_{47} and H_{55}), 4.43 – 4.01 (m, 20H, H_3, H_9, H_{17}, H_{25}, H_{33}, H_{41}, H_{47}, H_{55}, H_{83} and H_{91}), 3.89 – 3.31 (m, 30H, H_4, H_{12}, H_{20}, H_{22}, H_{28}, H_{36}, H_{44}, H_{52}, H_{77}, H_{78}, H_{79}, H_{80}, H_{81}, H_{82} and H_{90}), 3.29 – 2.95 (m, 12H, H_7, H_{15}, H_{23}, H_{31}, H_{39} and H_{47}), 2.82 – 2.25 (m, 13H, H_{61}, H_{103}, H_{105} and H_{114}), 2.10 - 1.90 (m, 16H, H_8, H_{16}, H_{24}, H_{32}, H_{40}, H_{48}, H_{104} and H_{111}), 1.50 - 1.60 (m, 4H, H_{62} and H_{115}), 1.50 (s, 16H, H_{72}), 1.35 – 1.19 (m, 12H, H_{63}, H_{64}, H_{65}, H_{116}, H_{117} and H_{118}), 0.91 (s, 9H, H_1), 0.87 – 0.79 (m, 6H, H_{66} and H_{119}), 0.09 (s, 6H, H_2). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 169.59, 162.68, from 155.88 to155.60(7C), 150.05, 149.61, 149.43, 148.67, 148.64, 148.24, 147.16, 145.02, 144.89, 144.37, 144.27, 144.20, 144.16, 141.68, 140.53, 140.49, 138.34, 137.89, 137.61, 137.23, 128.77(2C), 127.62, 127.52(2C), 124.36, 123.99, 123.92, 123.86, 123.72, 123.18, 122.89, 121.90, 121.80, 120.32, 119.91, 119.78, 109.58, 109.49, 101.26, 96.86, 90.84, 85.20, 71.43, 71.04, 70.66, 70.62, 70.60, 70.54, 70.43, 69.79, 69.08, 68.66, 68.24, 64.75, 64.60, 64.50, 59.59, 50.81, 50.67, 50.46, 50.42, 50.32, 50.10, 47.66, 47.55, 47.45, 47.27, 45.07, 37.83, 36.07, 31.66, 30.26, 29.55, 29.49, 29.02, 27.77, 26.13, 25.74, 25.71, 25.08, 24.61, 22.67, 16.54, 14.20, -4.59. **TOF MS ES +** m/z = 3439,0331 (calcd. for $C_{155}H_{223}N_{57}O_{33}Si$ 3439,7366 $[M+H]^+$).

2.7.4 Synthesis of C_6CI'IPDC$_6$



C$_6$CI'IPDC$_6$

Compound **37** (0.556 g, 0.16 mmol, 1 equiv.) was added in a flask followed by TFA (1.5 mL) and DCM (3 mL). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The mixture was neutralized with saturated $NaHCO_3$ and extracted with DCM (3 × 50 mL). The organic phase was washed brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product was precipitated from the residue with the addition of Et_2O followed by drying under vacuum to give the **C_6CI'IPDC$_6$** as a foamy-white solid (0.47 g, 90%). **C_6CI'IPDC$_6$, ^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.15 (br s, H, H_{106}), 9.10 (br s, 1H, H_{110}), 8.47 (d, J = 4.9 Hz, 1H, H_{100}), 8.30 (s, 1H, H_{96}), 8.02 (d, J = 8.0 Hz, 1H, H_{97}), 7.92 – 7.64 (m, 11H, H_{10}, H_{18}, H_{26}, H_{34}, H_{42}, H_{50}, H_{68}, H_{70}, H_{74}, H_{88} and H_{98}), 7.62 – 7.12 (m, 14H, H_{56}, H_{57}, H_{58}, H_{60}, H_{88}, H_{94}, H_{99}, H_{102}, H_{107}, H_{108}, H_{109} and H_{113}), 7.03 – 6.79 (m, 5H, H_{30}, H_{84}, H_{85}, H_{92} and H_{93}), 6.70 - 6.60 (m, 4H, H_{22}, H_{71} and H_{72}), 6.13 (br s, 1H, H_6), 6.07 (br s, 1H, H_{14}), 5.71 (t, J = 7.1 Hz, 1H, H_{38}), 5.29 – 4.78 (m, 7H, H_5, H_{13}, H_{21}, H_{29}, H_{37}, $H_{45}$and H_{53}), 5.00 - 4.80 (m, 2H, H_{46} and H_{54}), , 4.76 – 4.43 (m, 32H, H_{11}, H_{19}, H_{27}, H_{35}, H_{43}, H_{51}, H_{59}, H_{67}, H_{73}, H_{75}, H_{87}, H_{89}, H_{95}, H_{101} and H_{112}), 4.42 – 4.16 (m, 16H, H_3, H_9, H_{17}, H_{25}, H_{33}, H_{42}, H_{47} and H_{55}), 4.10 - 4.05 (m, 4H, H_{83} and H_{91}), 3.73 – 3.38 (m, 30H, H_4, H_{12}, H_{20}, H_{22}, H_{28}, H_{36}, H_{44}, H_{52}, H_{77}, H_{78}, H_{79}, H_{80}, H_{81}, H_{82} and H_{90}), 3.10 - 2.95 (m, 12H, H_7, H_{15}, H_{23}, H_{31}, H_{39} and H_{47}), 2.75 - 2.60 (m, 8H, H_{61}, H_{103}, H_{105} and H_{114}), 2.10 - 1.90 (m, 16H, H_8, H_{16}, H_{24}, H_{32}, H_{40}, H_{48}, H_{104} and H_{111}), 1.60 - 1.50 (m, 4H, H_{62} and H_{115}), 1.35 – 1.19 (m, 12H, H_{63}, H_{64}, H_{65}, H_{116}, H_{117} and H_{118}), 0.91 (s, 9H, H_1), 0.85 - 0.83 (m, 7H, H_{66} and H_{119}), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.72, 161.41, 156.77, from 155.90 to155.62(7C), 150.22, 150.01, 149.42, 148.65, 148.16, 147.17, 144.98, 144.86, 144.33, 144.18, 144.10, 142.88, 140.50, 138.39, 137.29, 137.26, 128.76(2C), 127.60, 127.50(2C), 124.41, from 124.05 to 123.75(4C), 123.21, 122.91, 121.93, 121.85, 120.34, 119.72, 119.67, 109.61, 109.51, 101.26, 94.92, 90.88, 71.42, 71.15, 71.07, 70.98, 70.65, 70.59, 70.55, 70.50, 69.80, 69.15, 68.76, 68.71, 68.23, 64.69, 64.55, 64.48, 59.59, 50.82, 50.48, 50.32, 50.13, 47.67, 47.59, 47.12, 45.05, 37.87, 36.07, 31.65, 30.25, 29.53, 29.48, 29.03, 29.01, 26.14, 25.73, 25.70, 25.08, 24.58, 22.67, 16.55, 14.20, -4.58. **TOF MS ES +** *m/z* = 3239.6485 (calcd. for $C_{145}H_{207}N_{57}O_{29}Si$ 3239.6317 $[M+H]^+$).

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

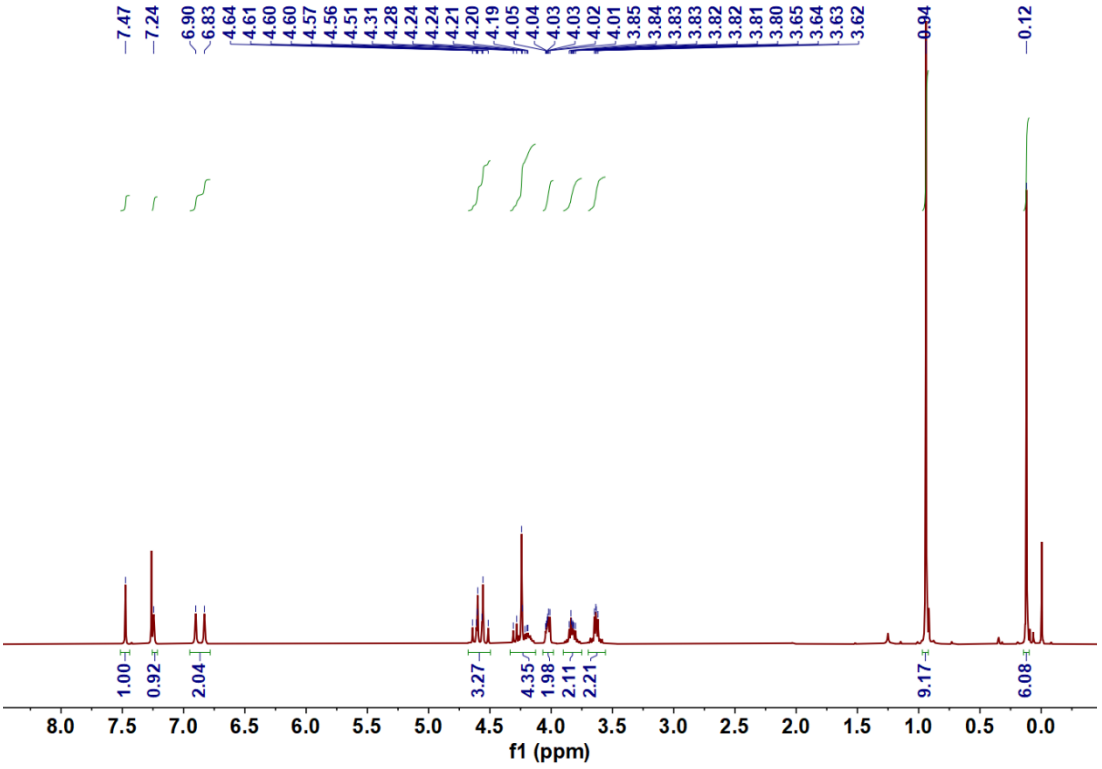


Figure S1. ^{1}H NMR of **12**.

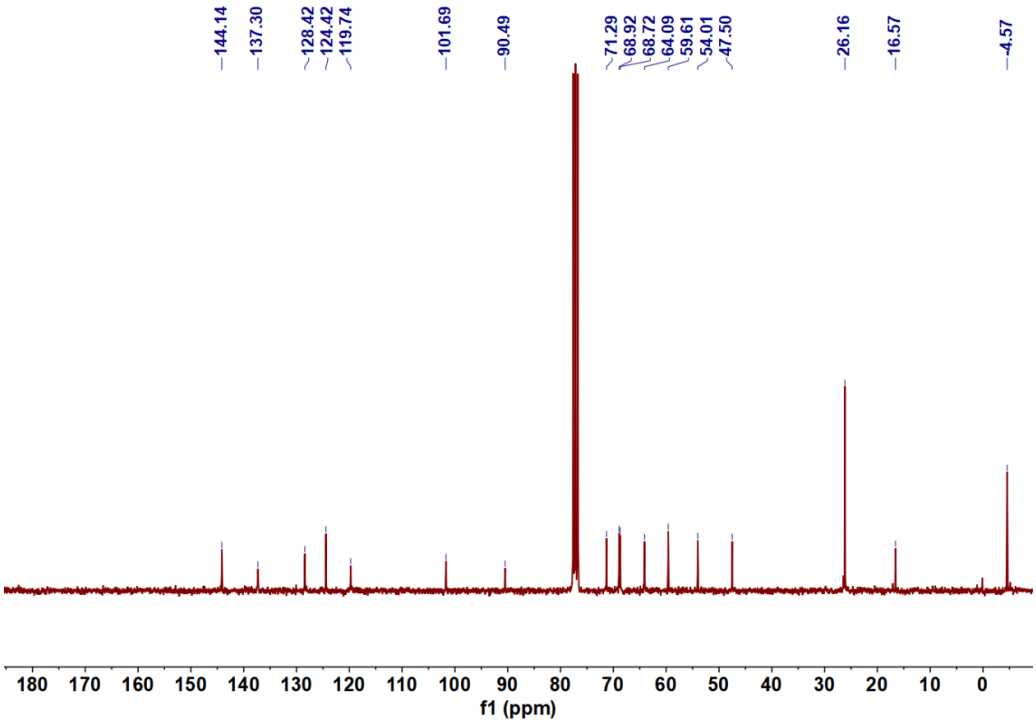


Figure S2. ^{13}C NMR of **12**.

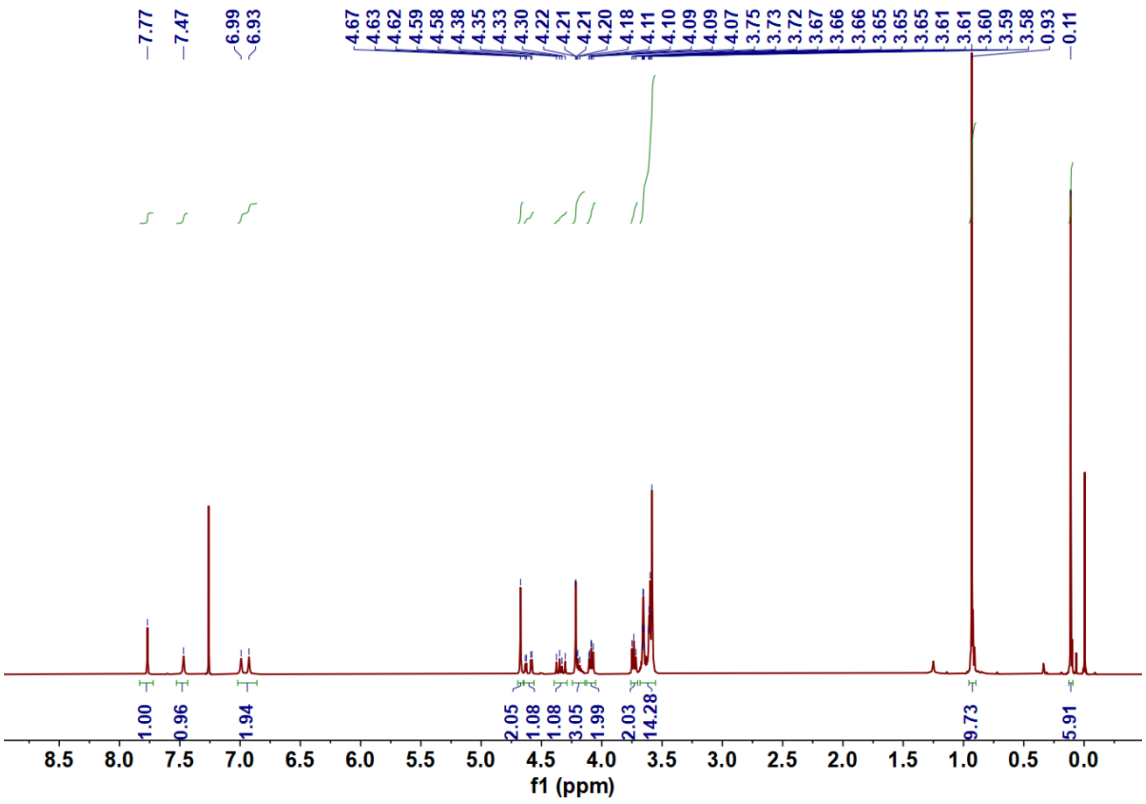


Figure S3. ^{1}H NMR of **13**.

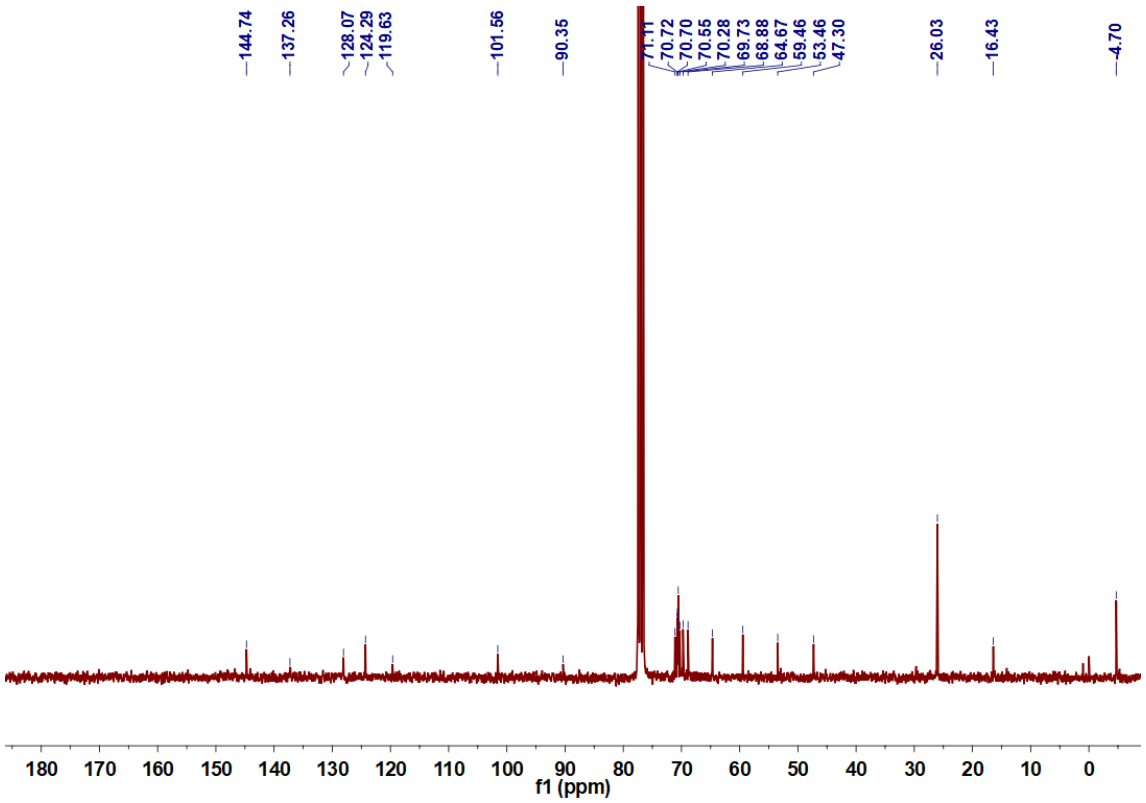


Figure S4. ^{13}C NMR of **13**.

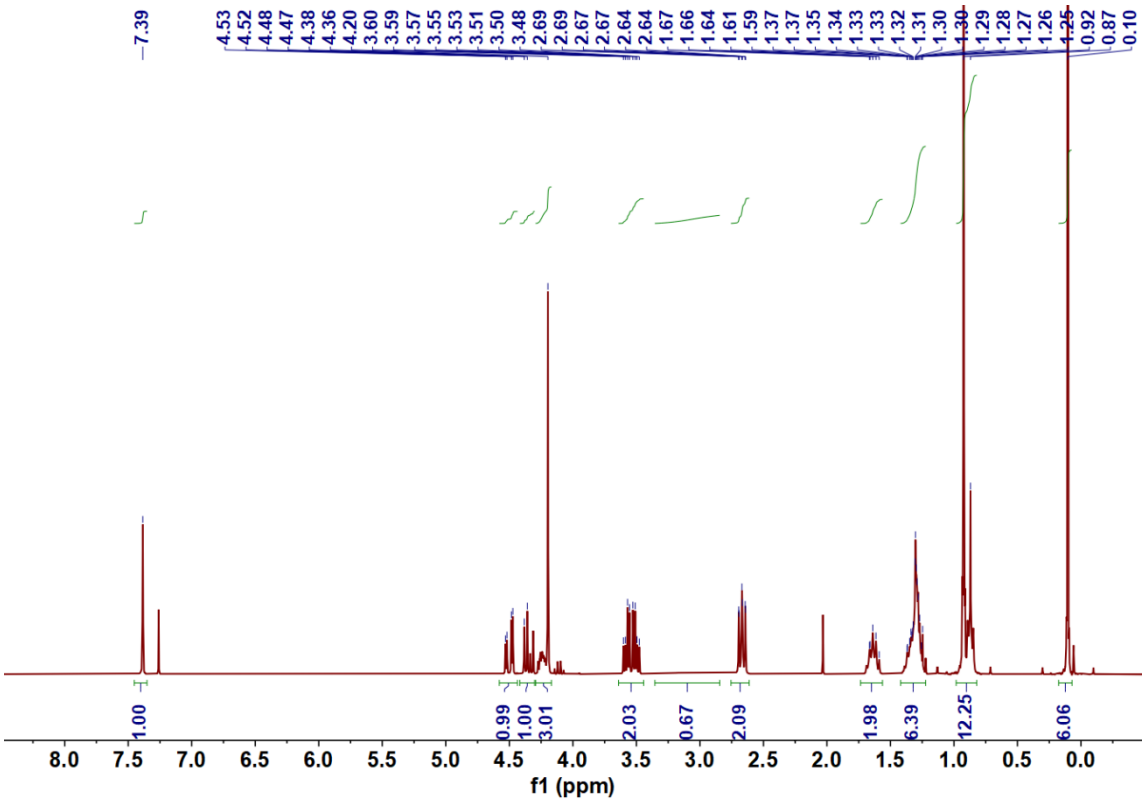


Figure S5. ^{1}H NMR of **14**.

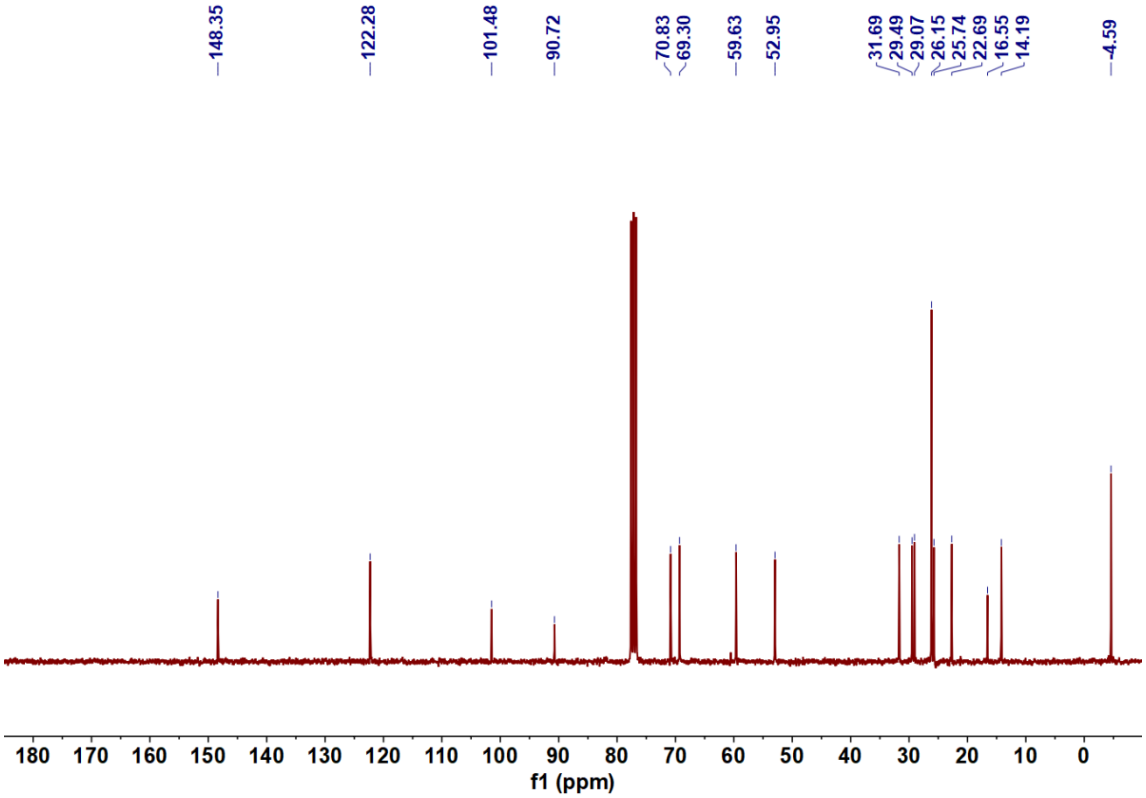


Figure S6. ^{13}C NMR of **14**.

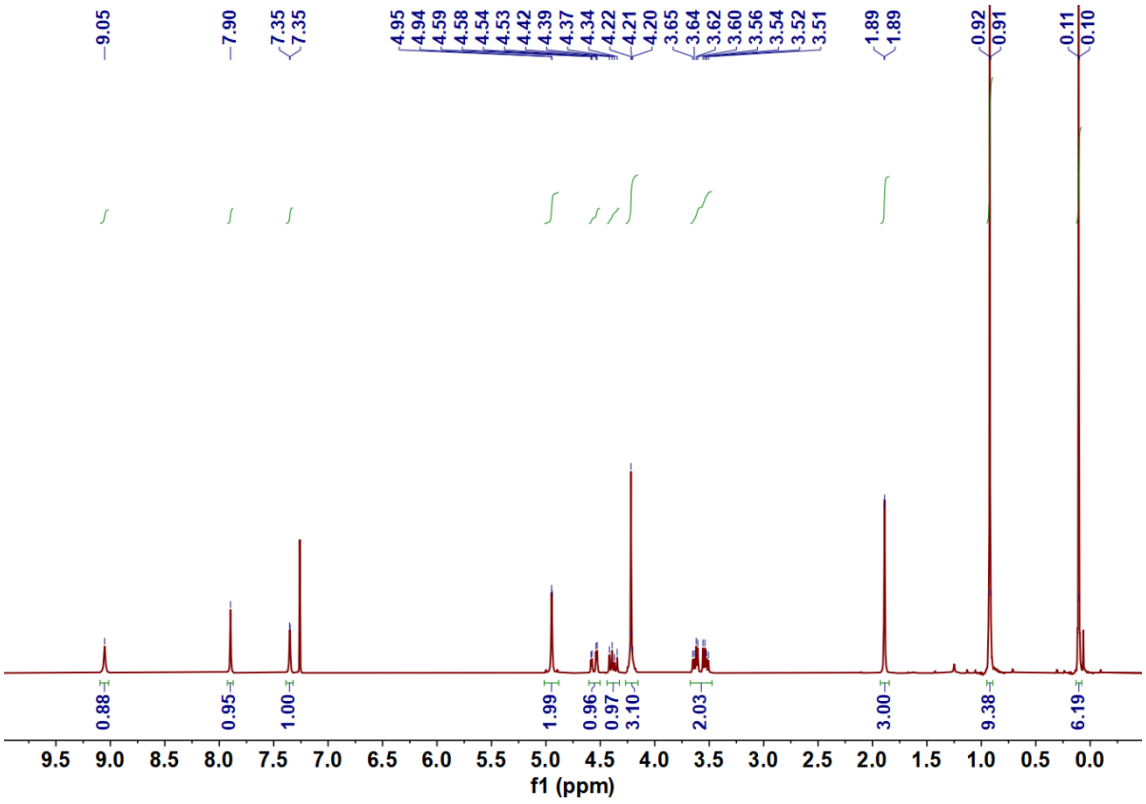


Figure S7. ^{1}H NMR of **15.**

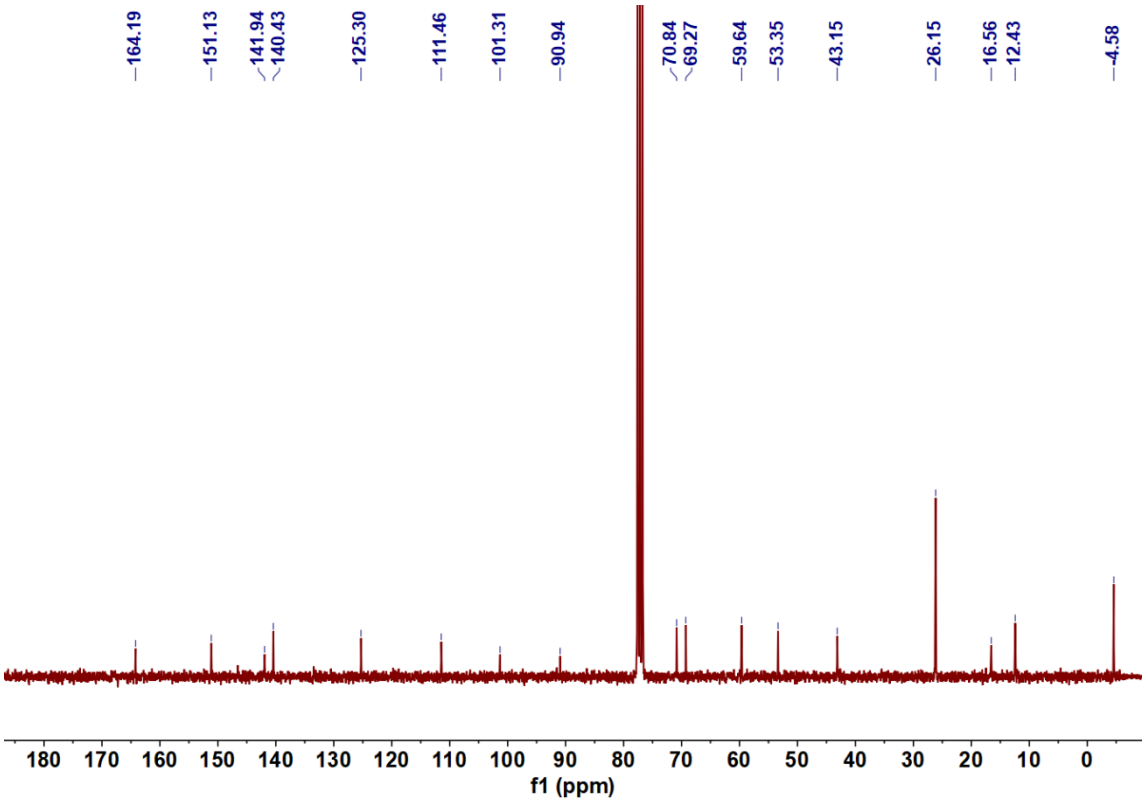


Figure S8. ^{13}C NMR of **15**.

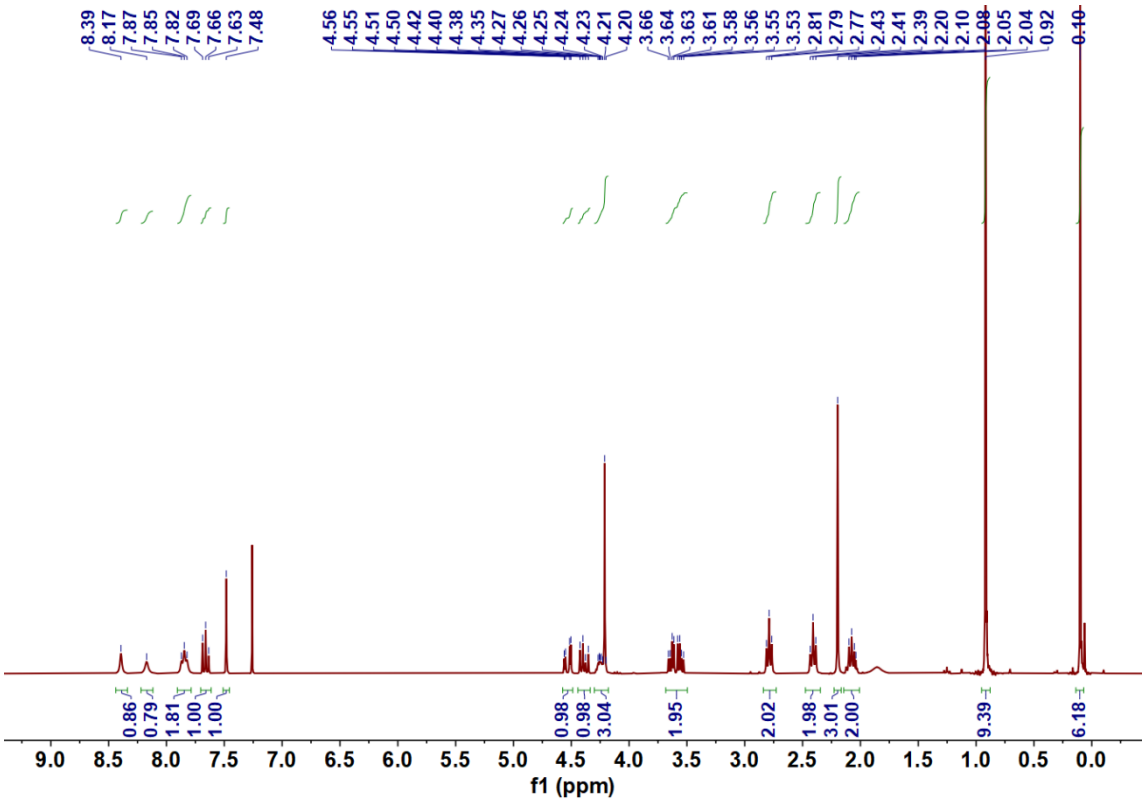


Figure S9. ^{1}H NMR of **16.**

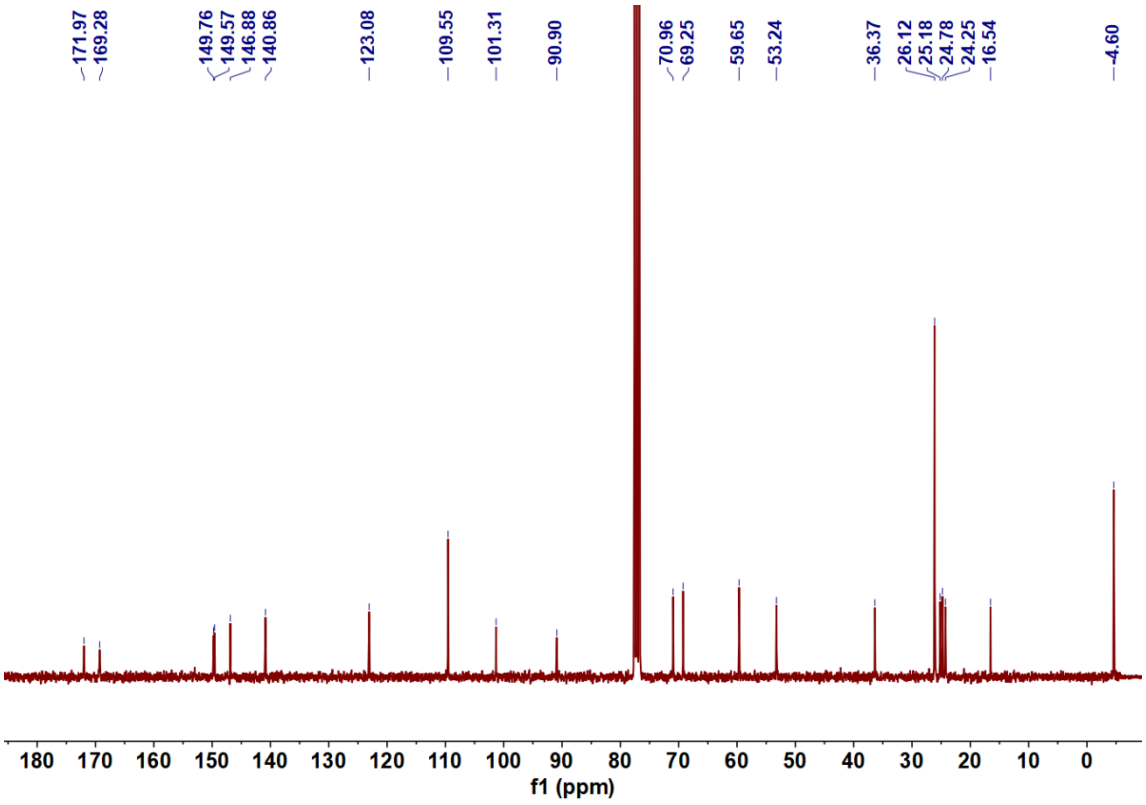


Figure S10. ^{13}C NMR of **16**.

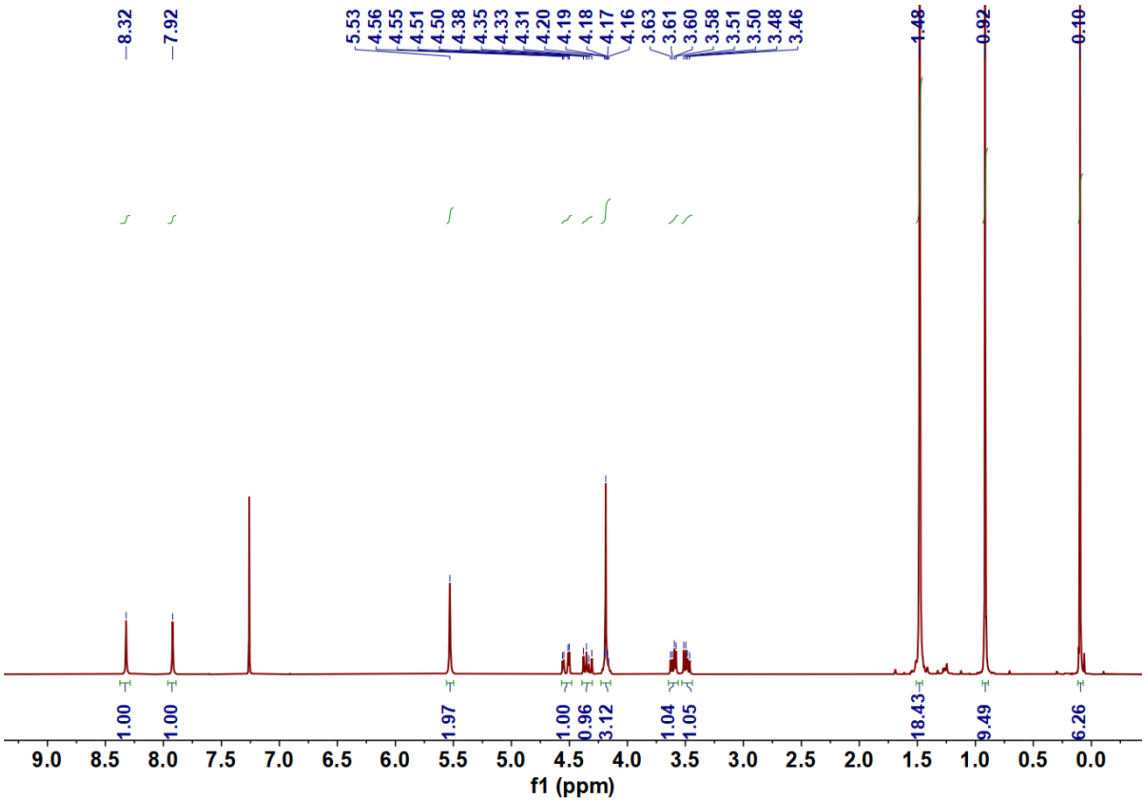


Figure S11. ^{1}H NMR of **17.**

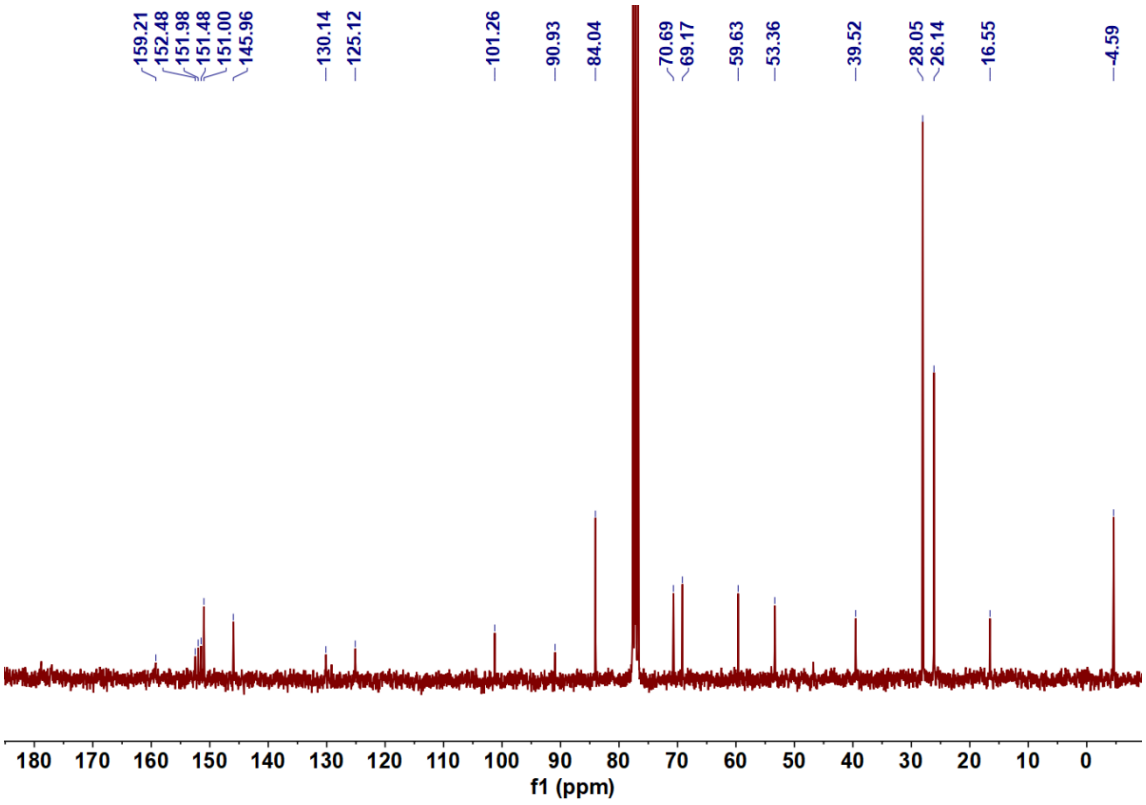


Figure S12. ^{13}C NMR of **17**.

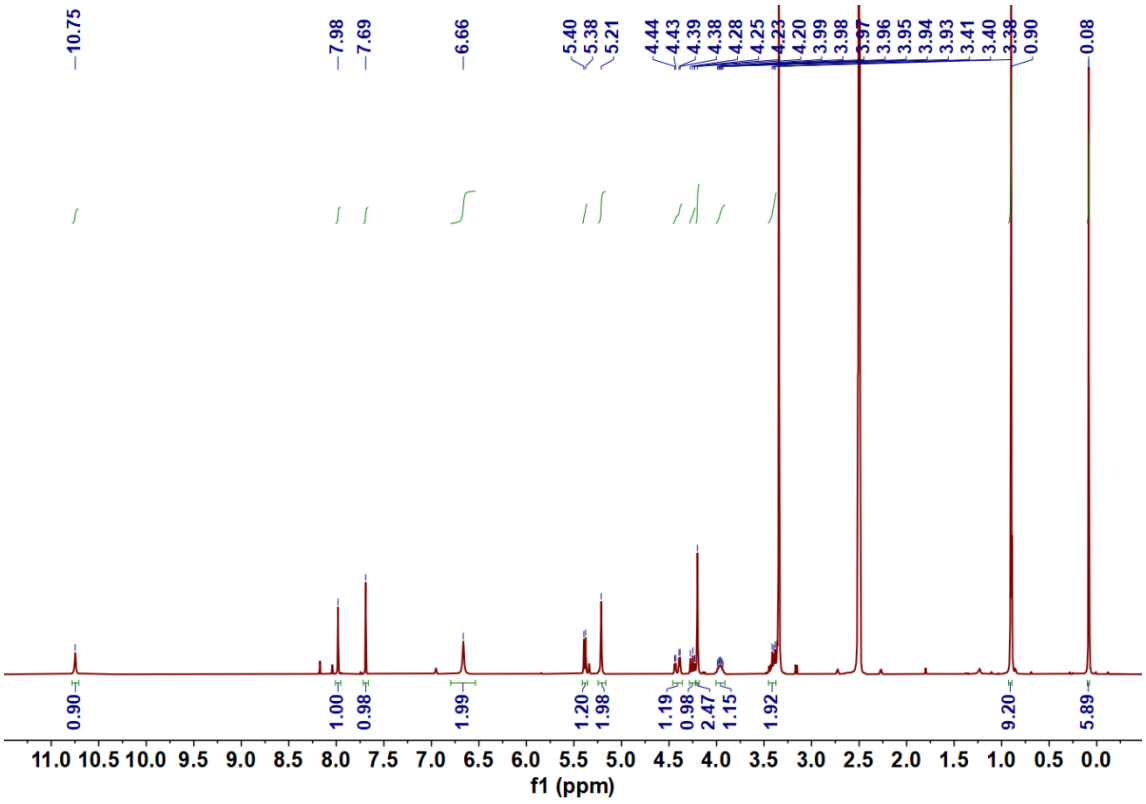


Figure S13. ^{1}H NMR of **18.**

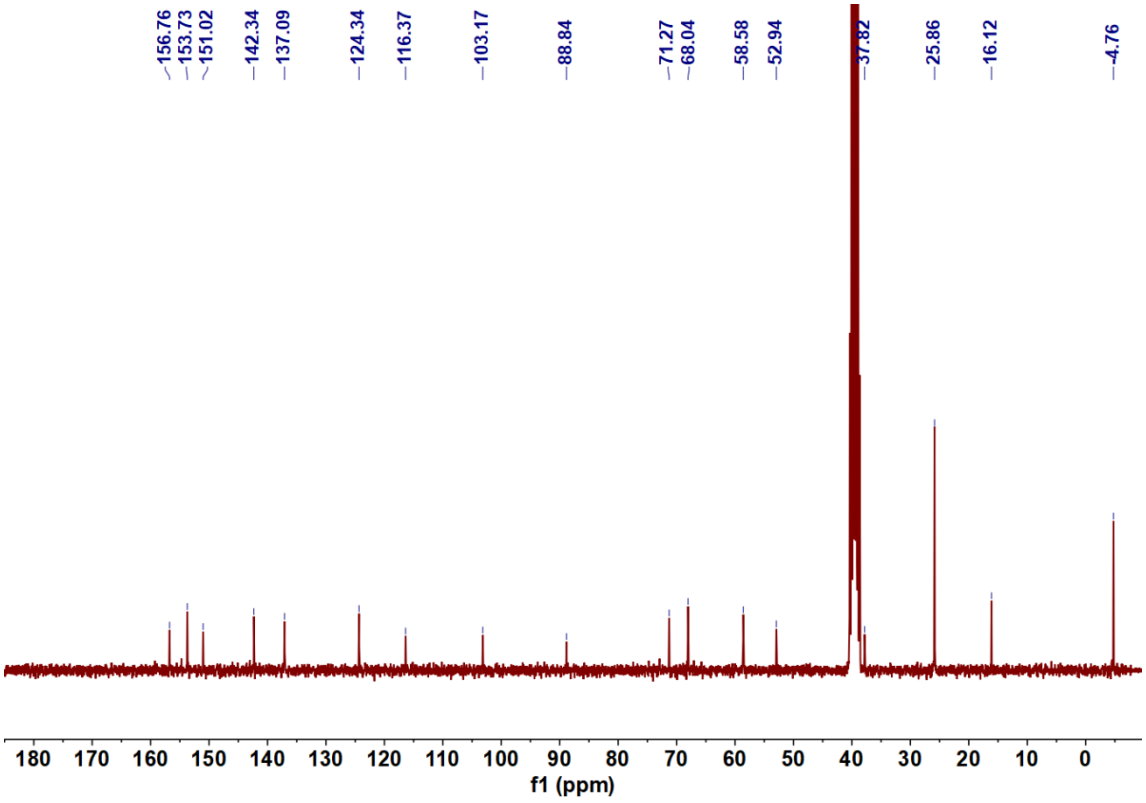


Figure S14. ^{13}C NMR of **18**.

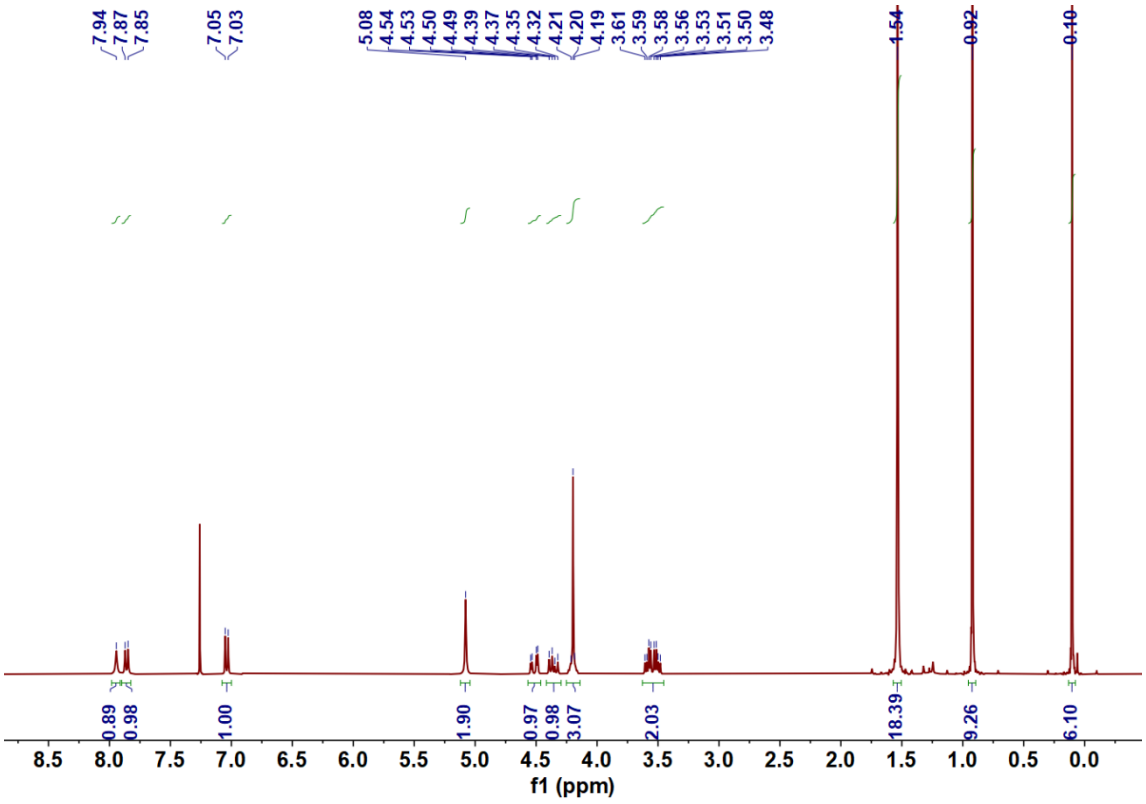


Figure S15. ^{1}H NMR of **19.**

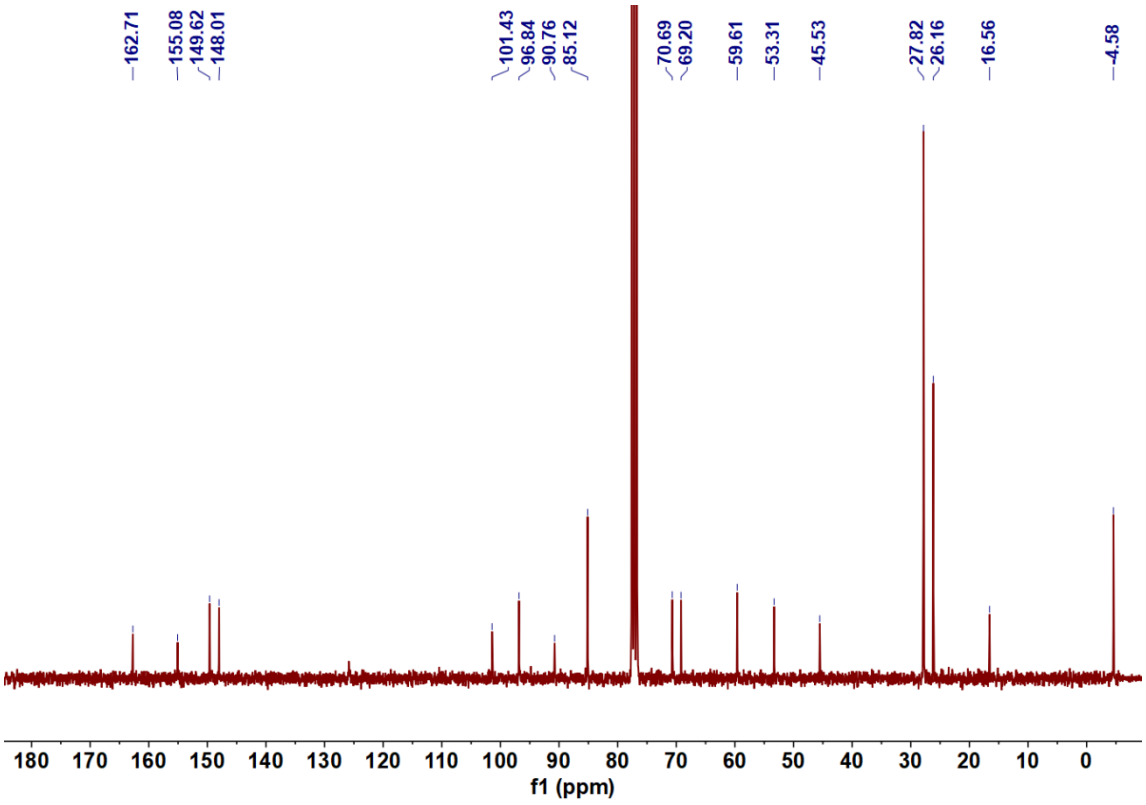


Figure S16. ^{13}C NMR of **19**.

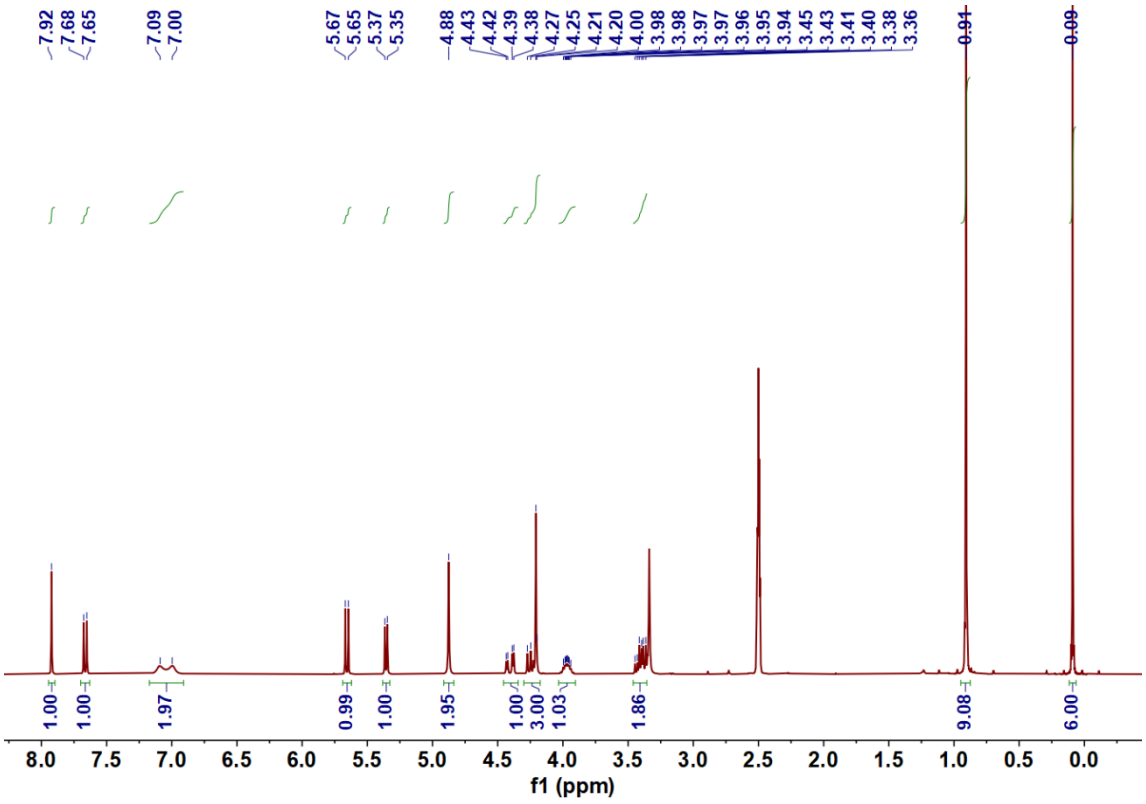


Figure S17. ^{1}H NMR of **20.**

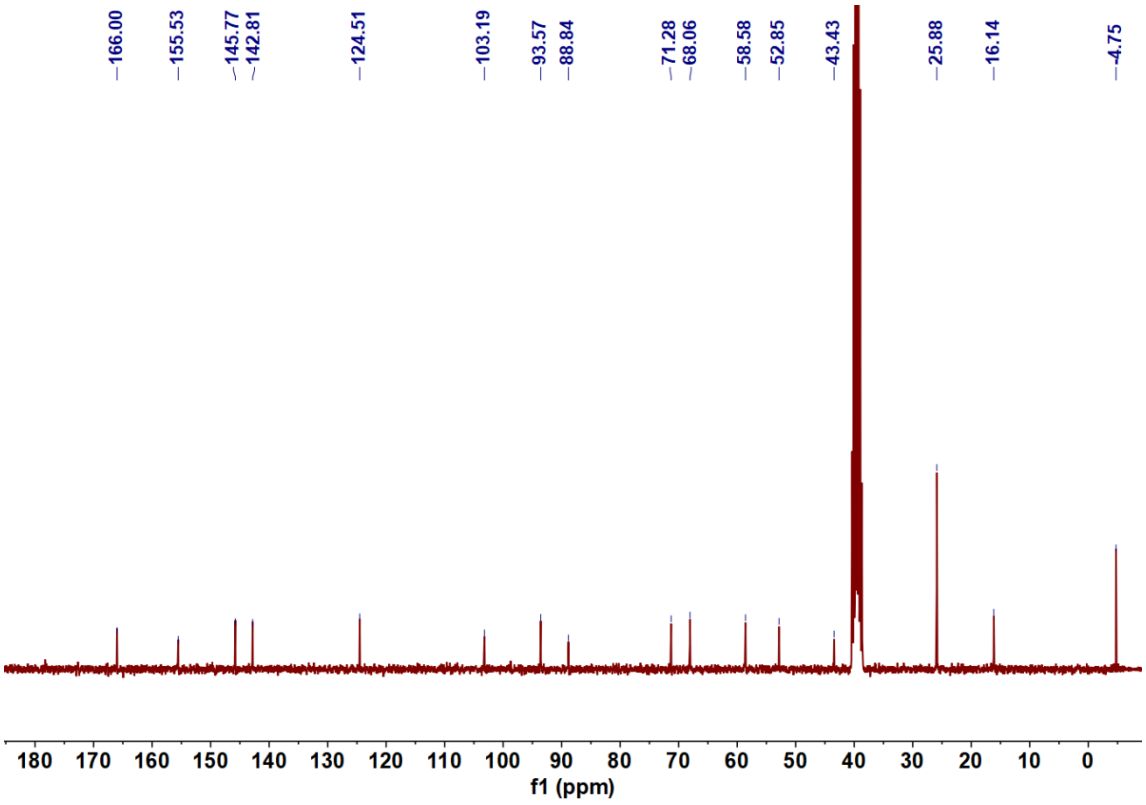


Figure S18. ^{13}C NMR of **20**.

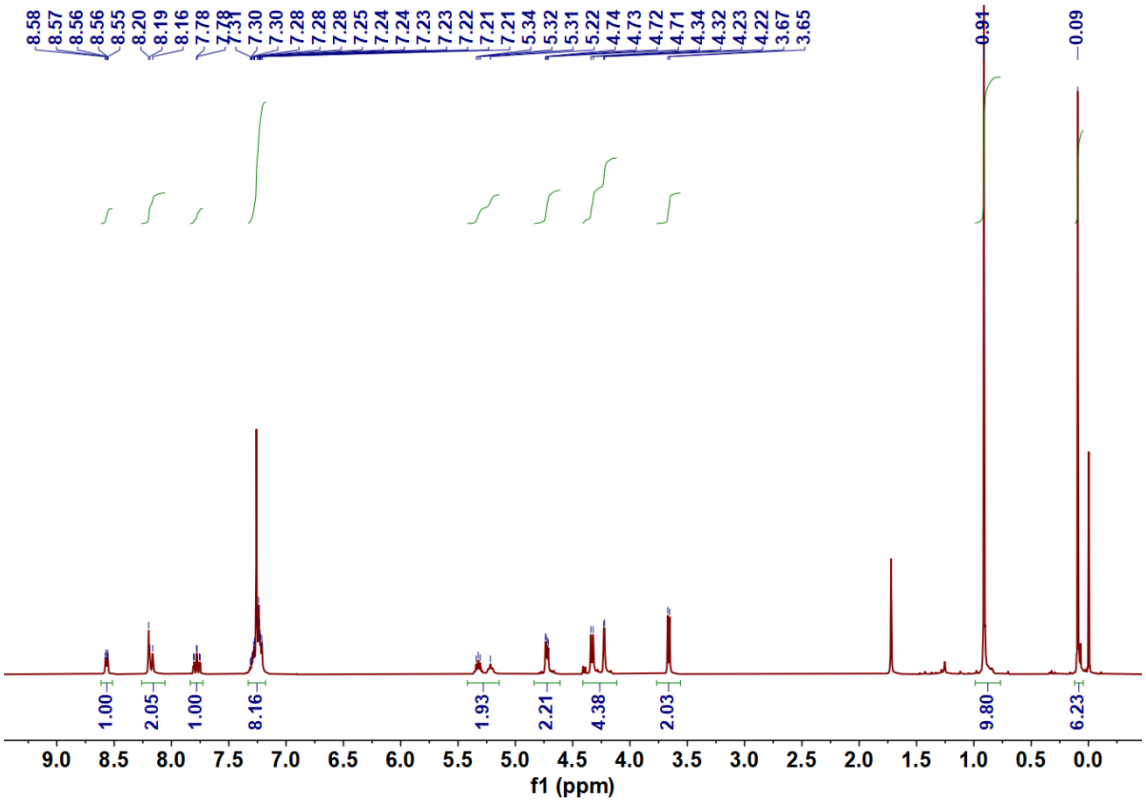


Figure S19. ^{1}H NMR of **P.**

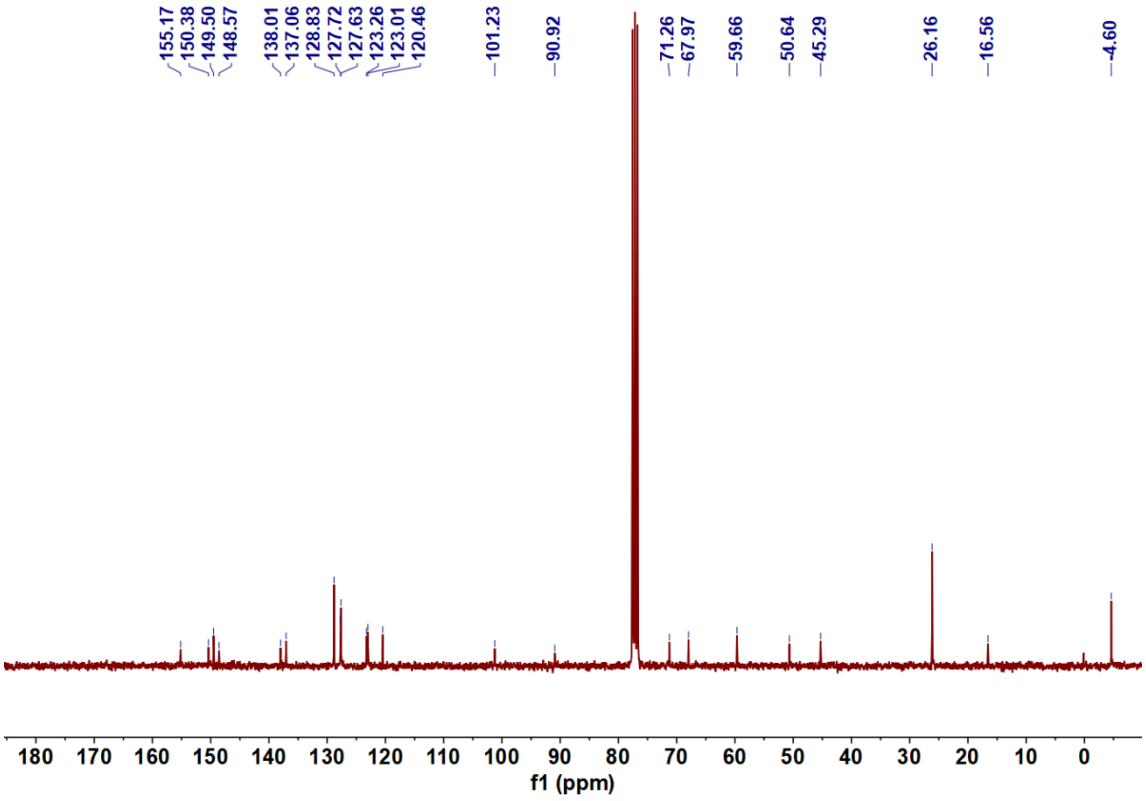


Figure S20. ^{13}C NMR of **P.**

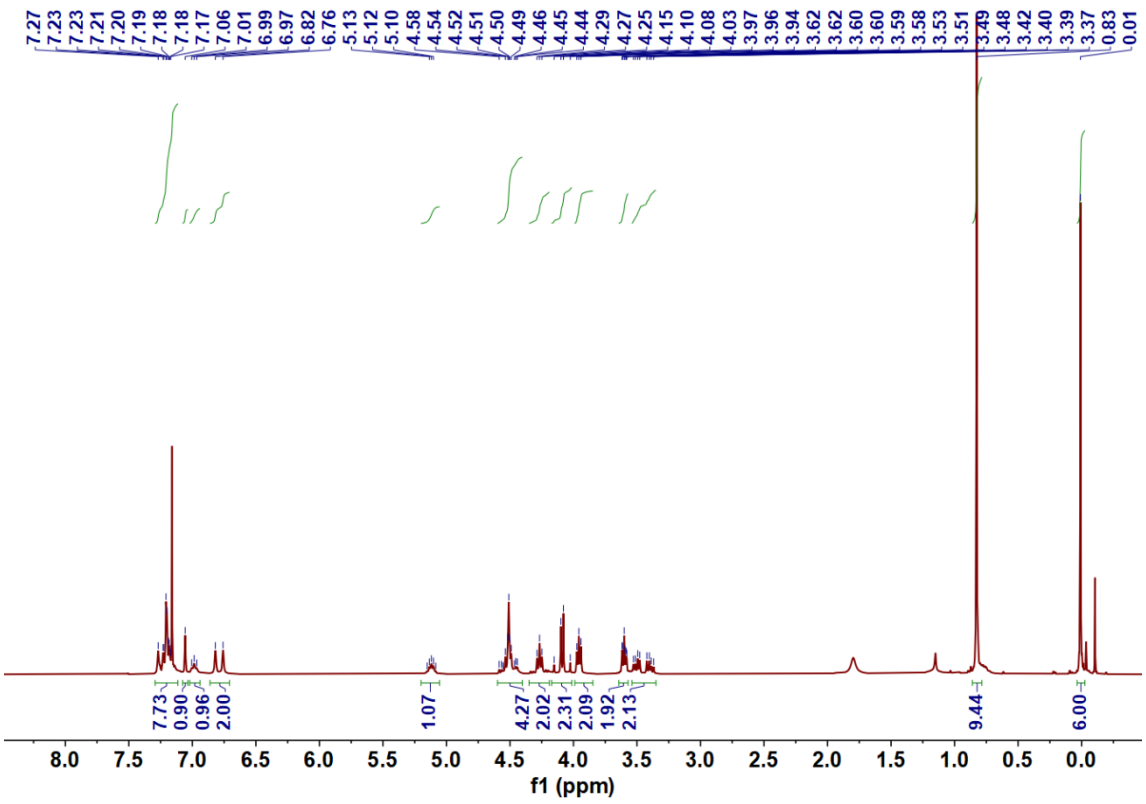


Figure S21. ^{1}H NMR of **I.**

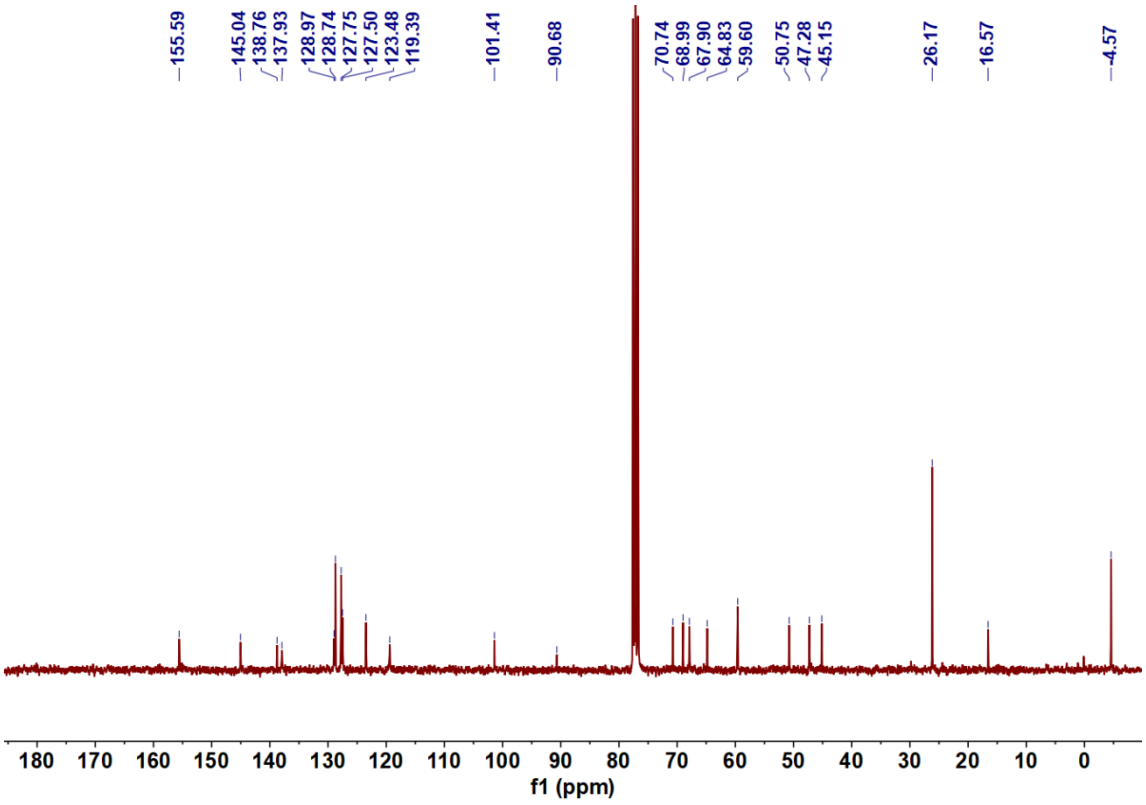


Figure S22. ^{13}C NMR of **I.**

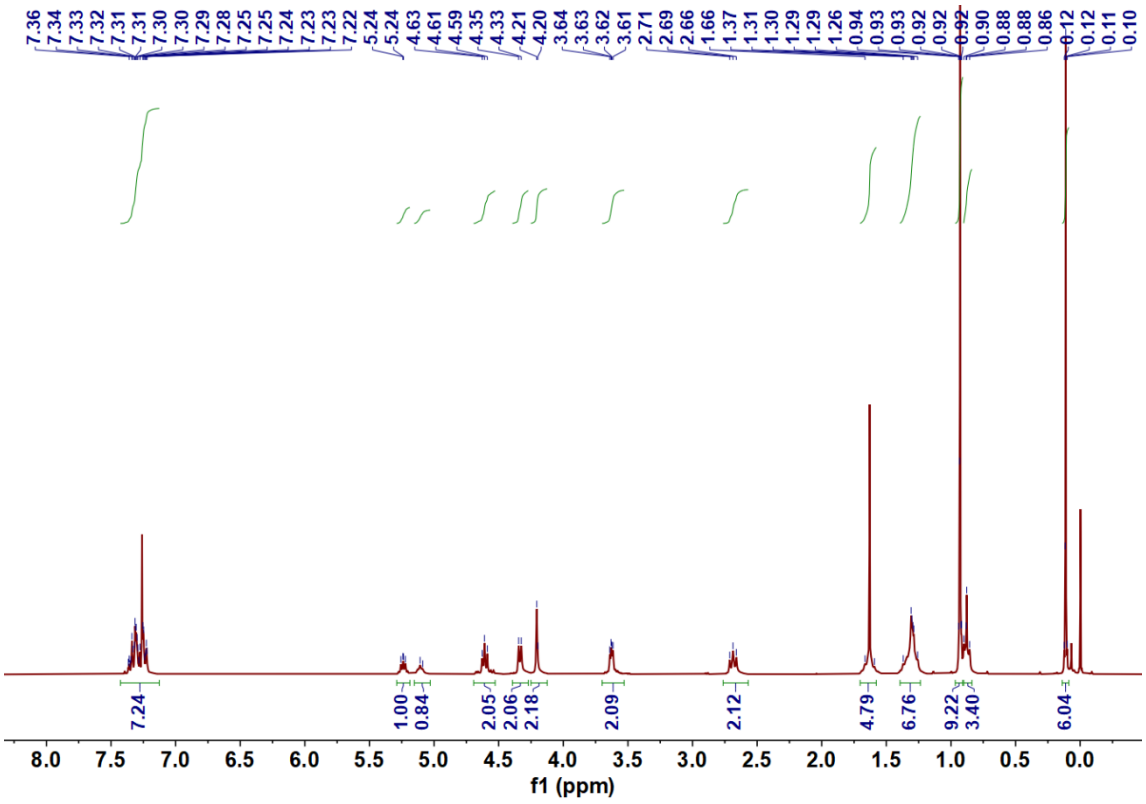


Figure S23. ^{1}H NMR of **C$_6$.**

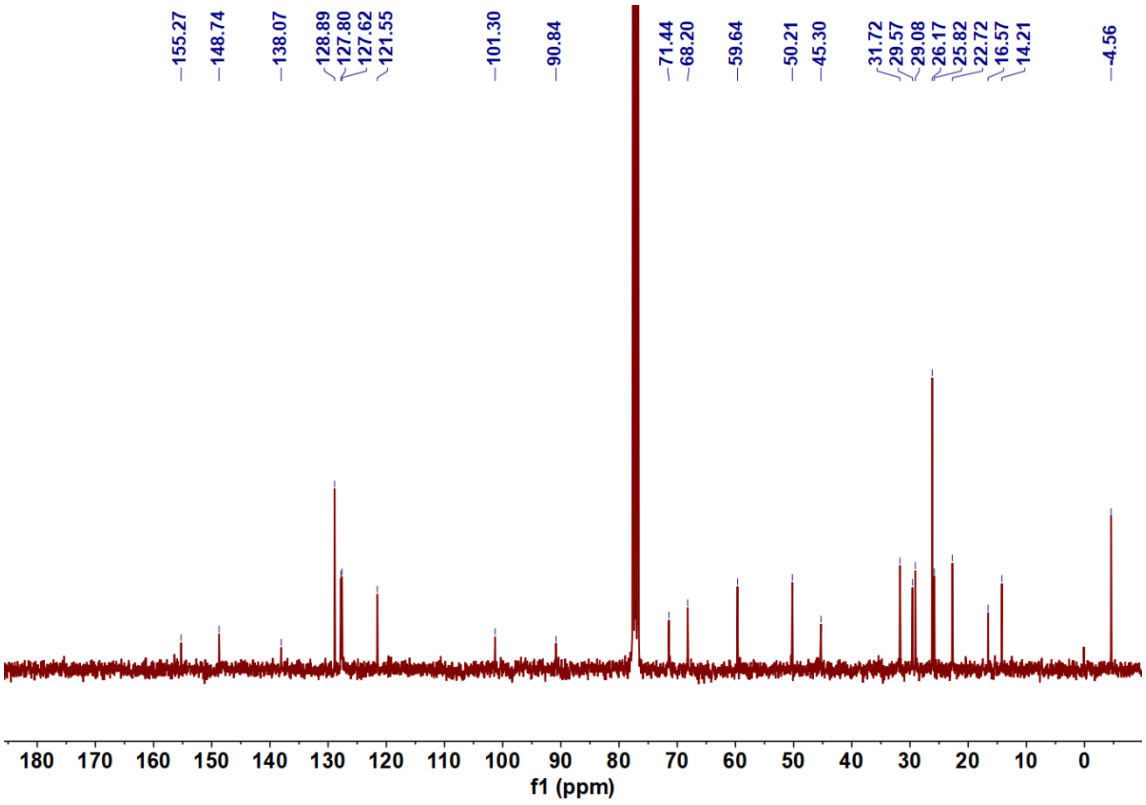


Figure S24. ^{13}C NMR of **C$_6$.**

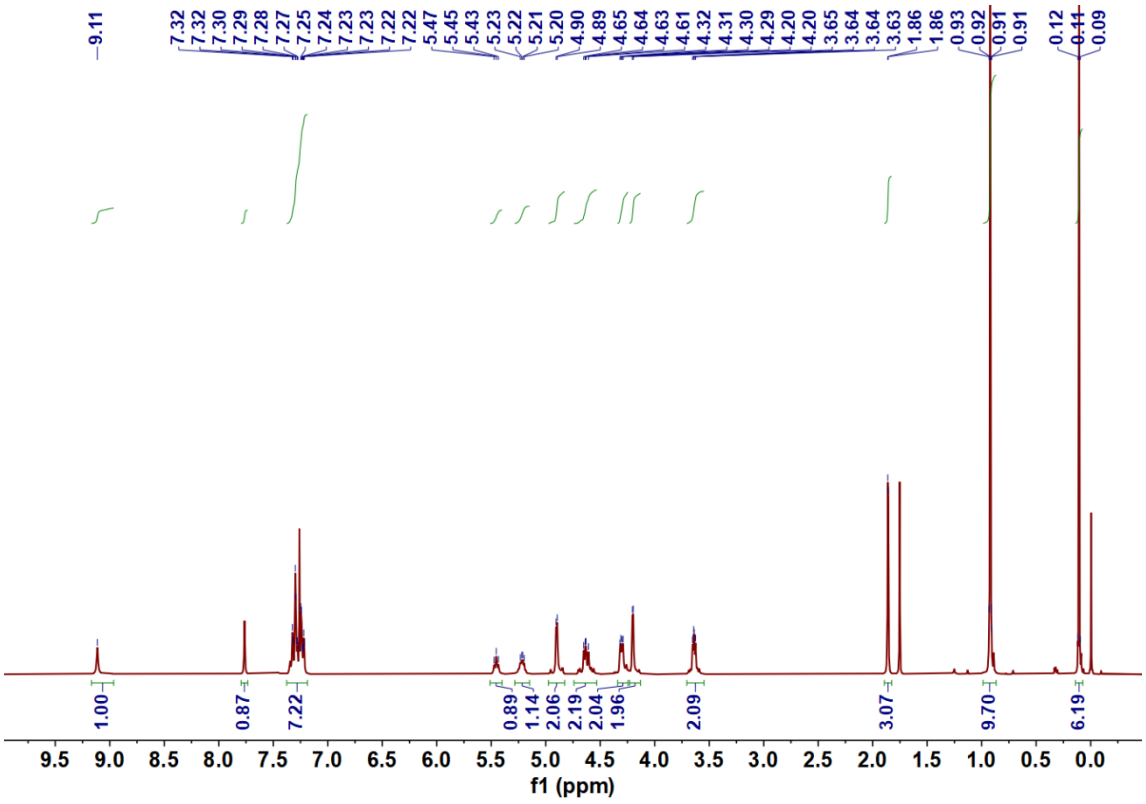


Figure S25. ^{1}H NMR of **T.**

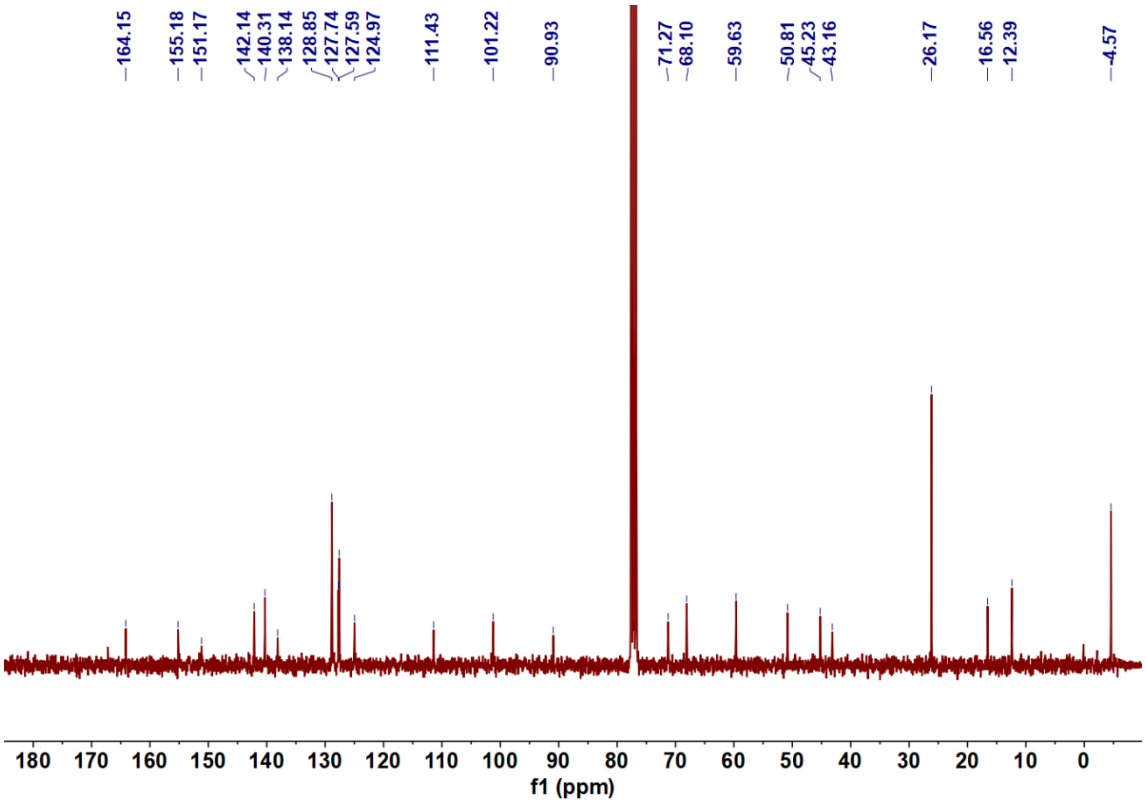


Figure S26. ^{13}C NMR of **T.**

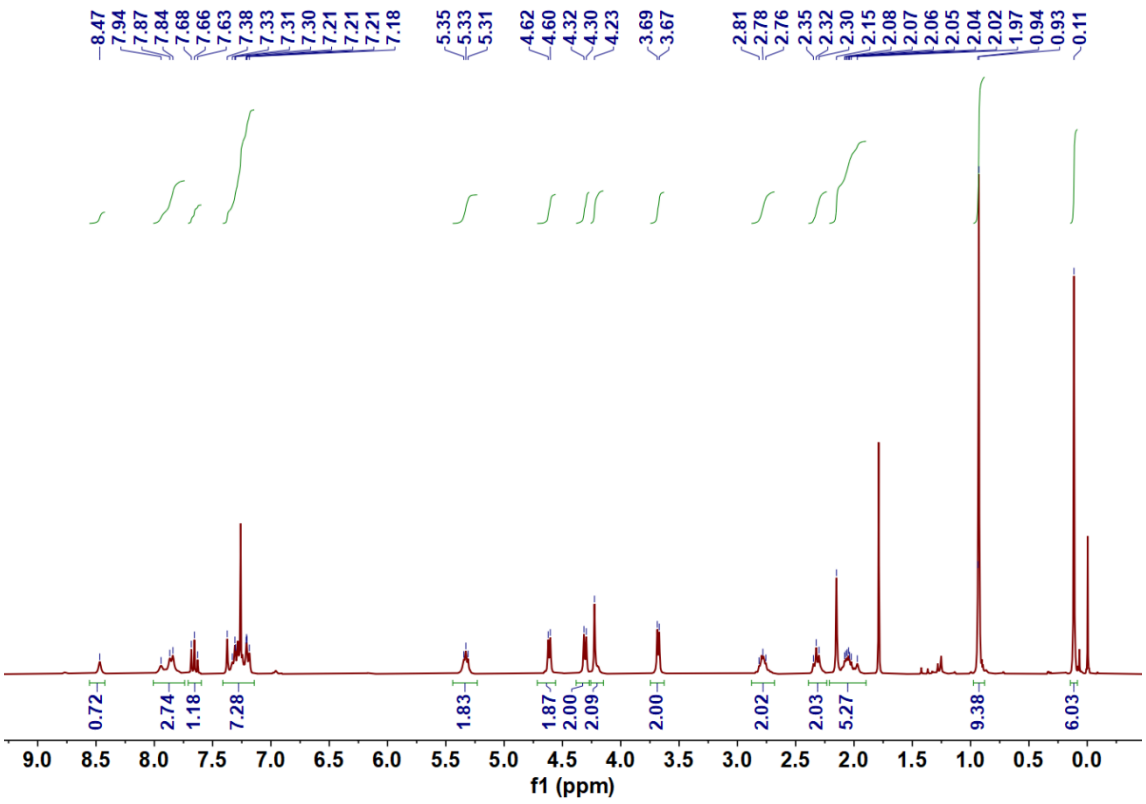


Figure S27. ^{1}H NMR of **D.**

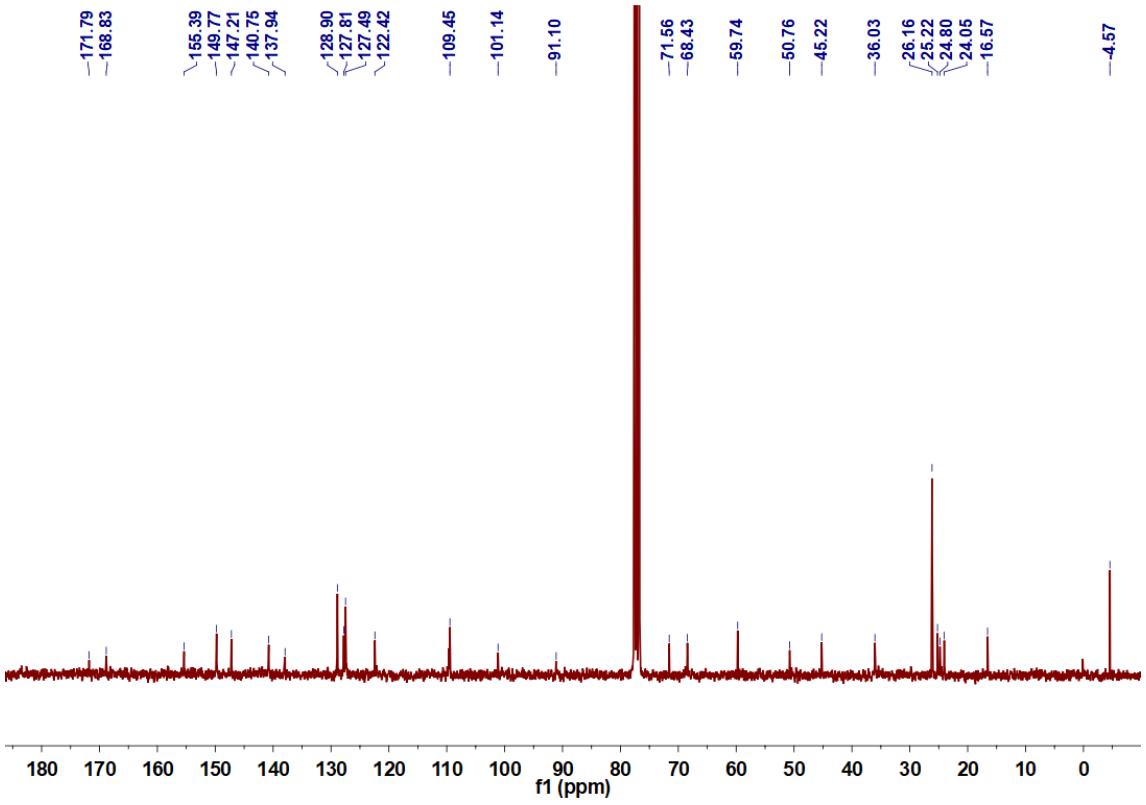


Figure S28. ^{13}C NMR of **D**.

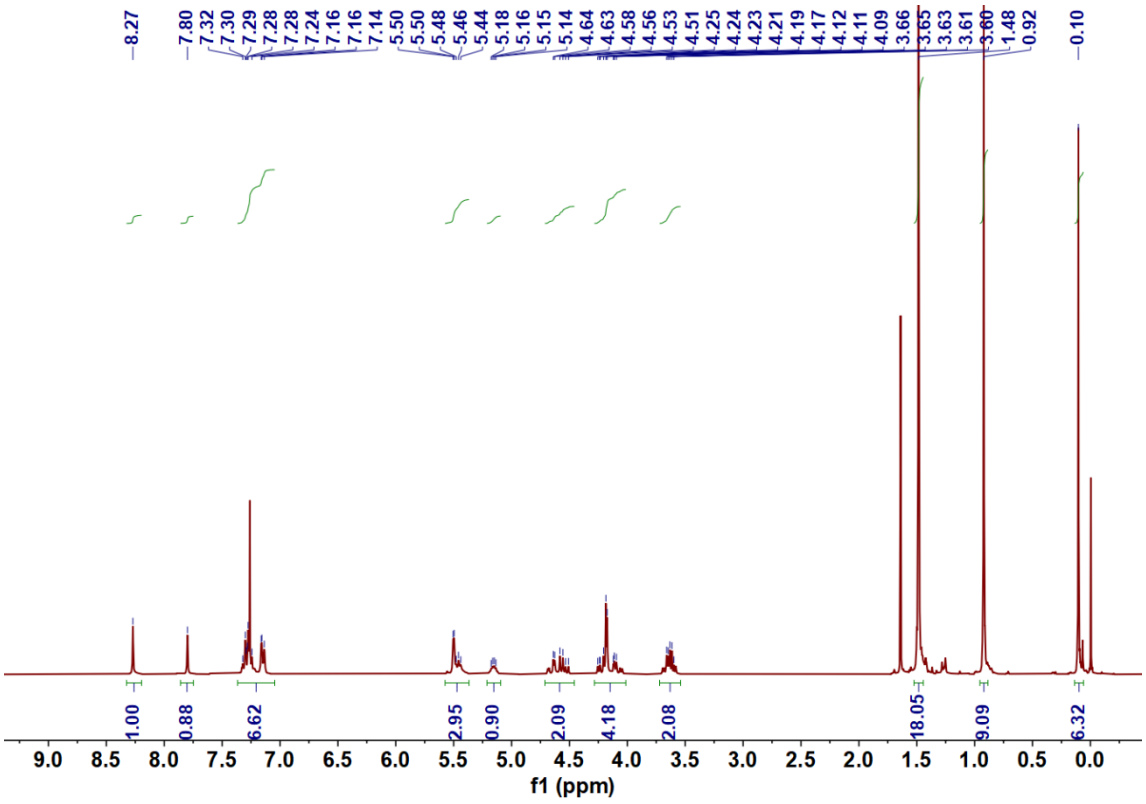


Figure S29. ^{1}H NMR of **21**.

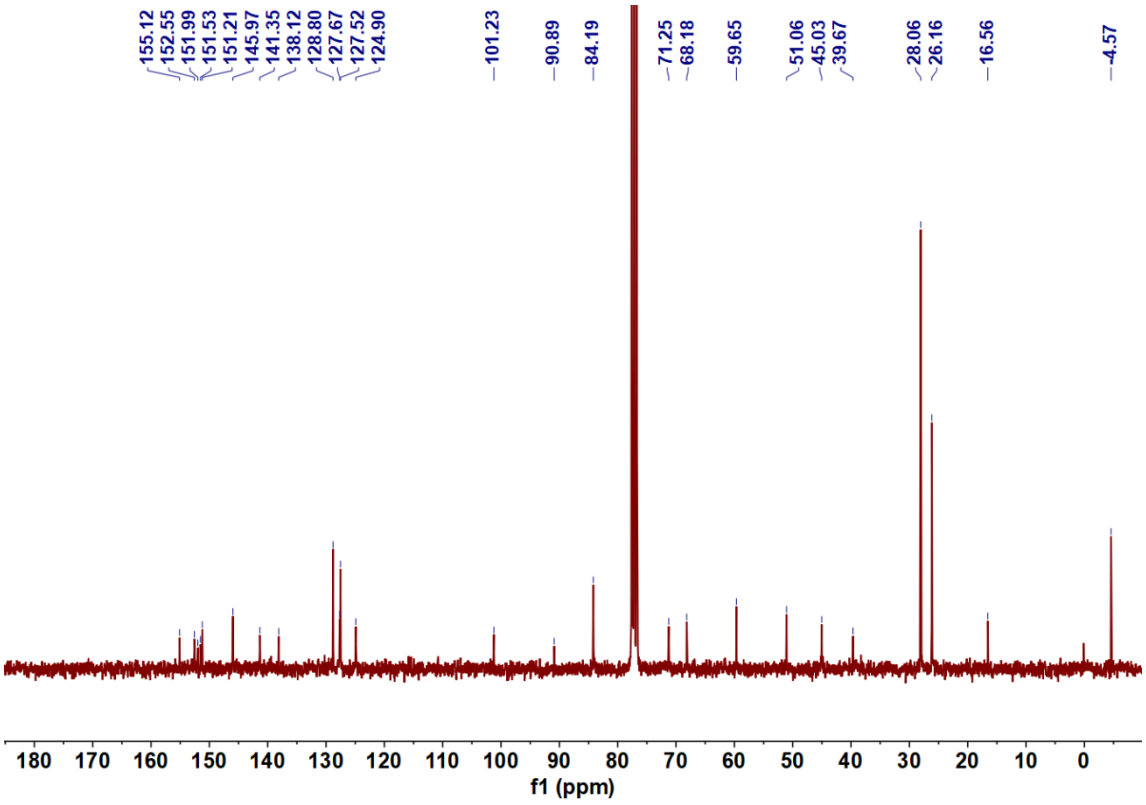


Figure S30. ^{13}C NMR of **21.**

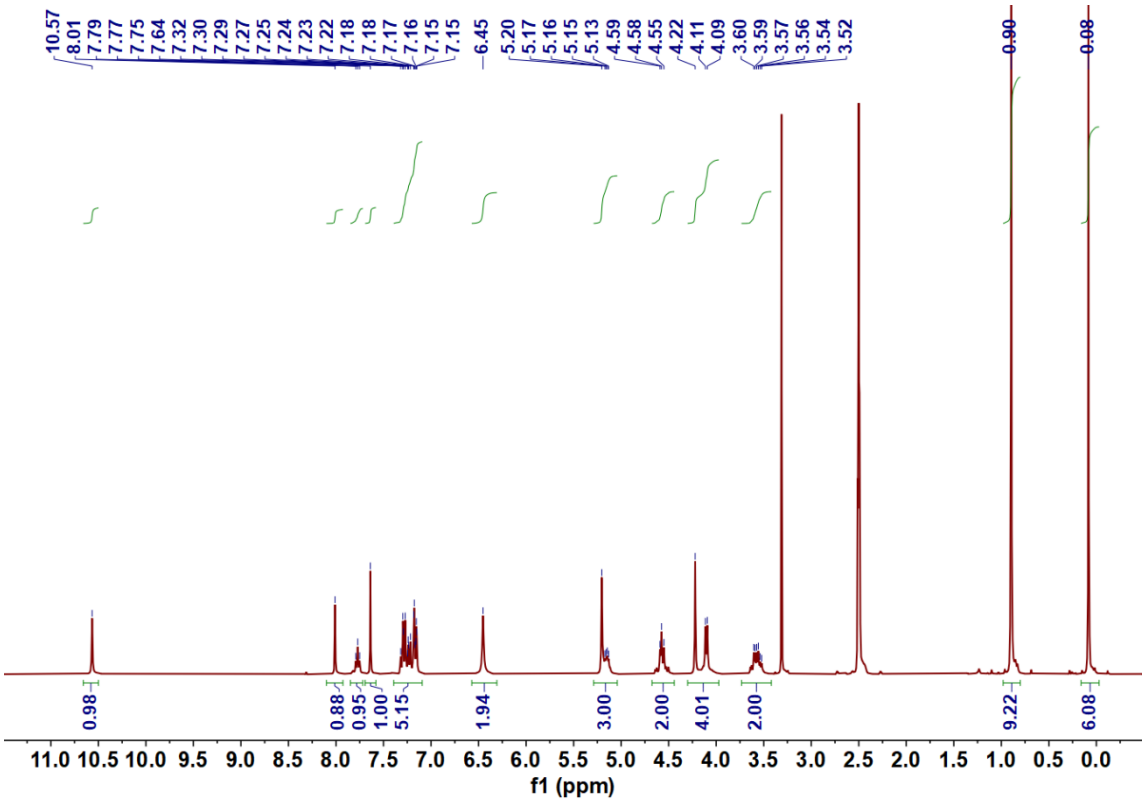


Figure S31. ^{1}H NMR of **G**.

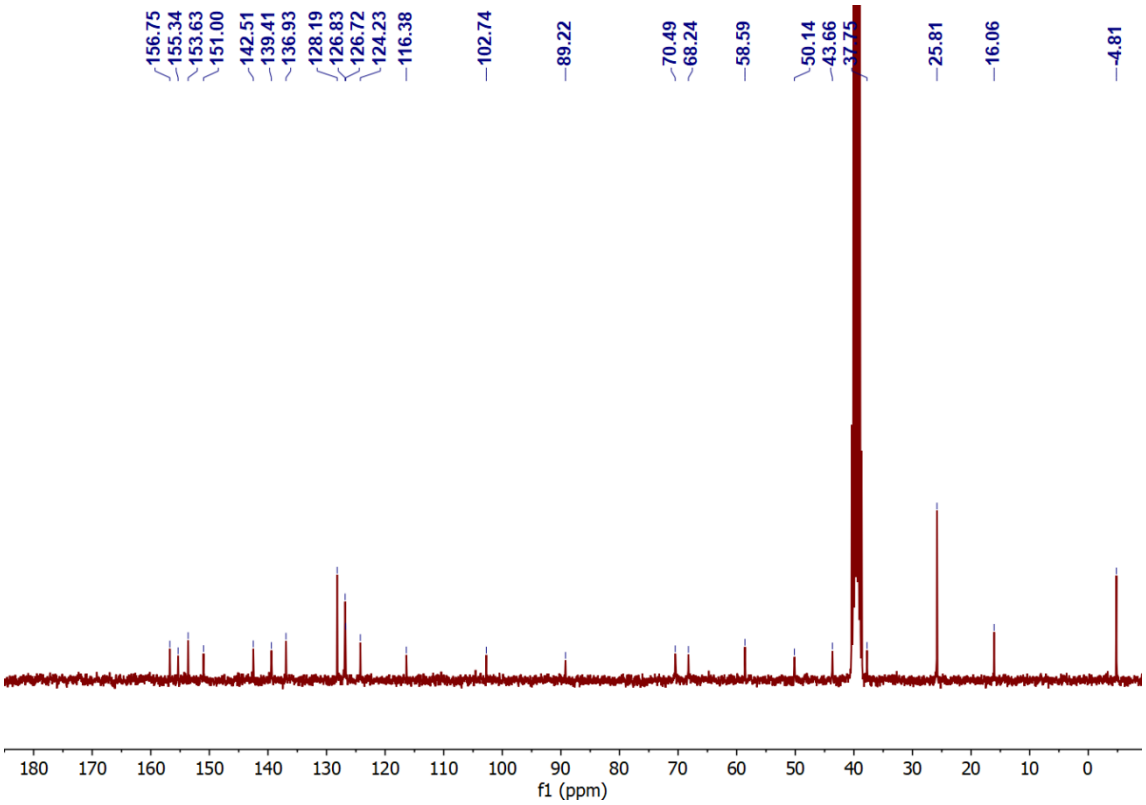


Figure S32. ^{13}C NMR of **G**.

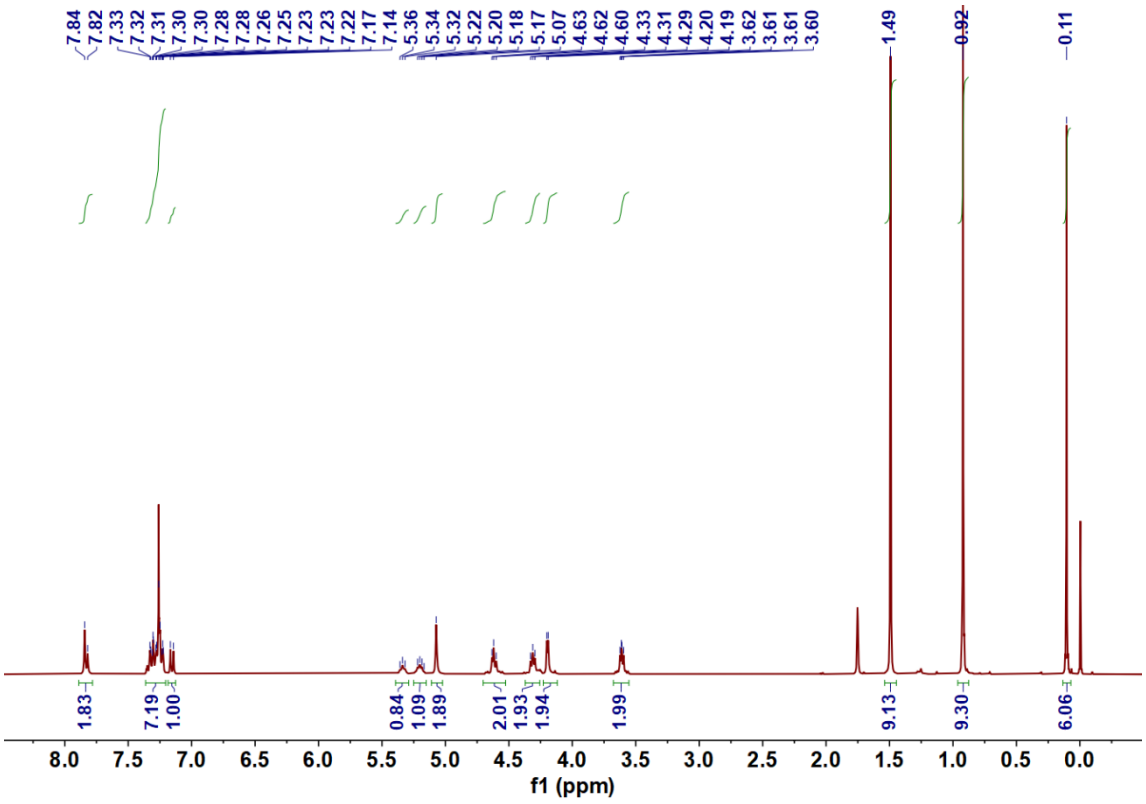


Figure S33. ^{1}H NMR of **22.**

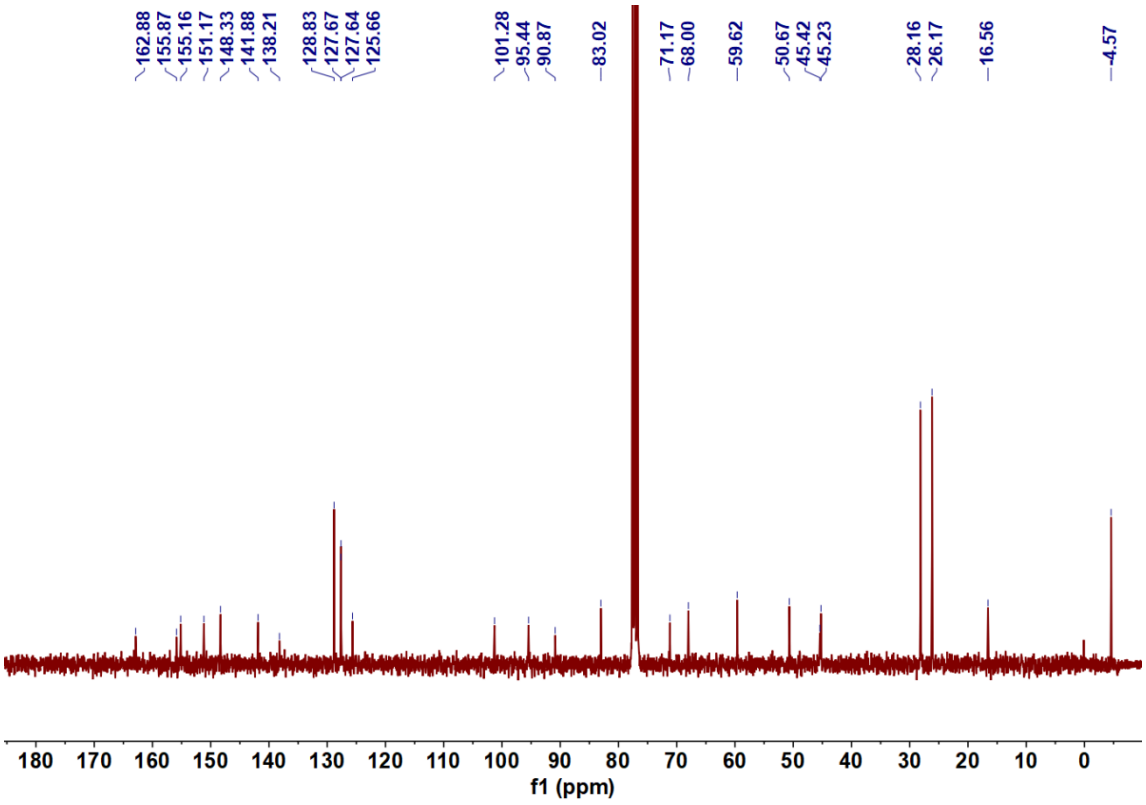


Figure S34. ^{13}C NMR of **22**.

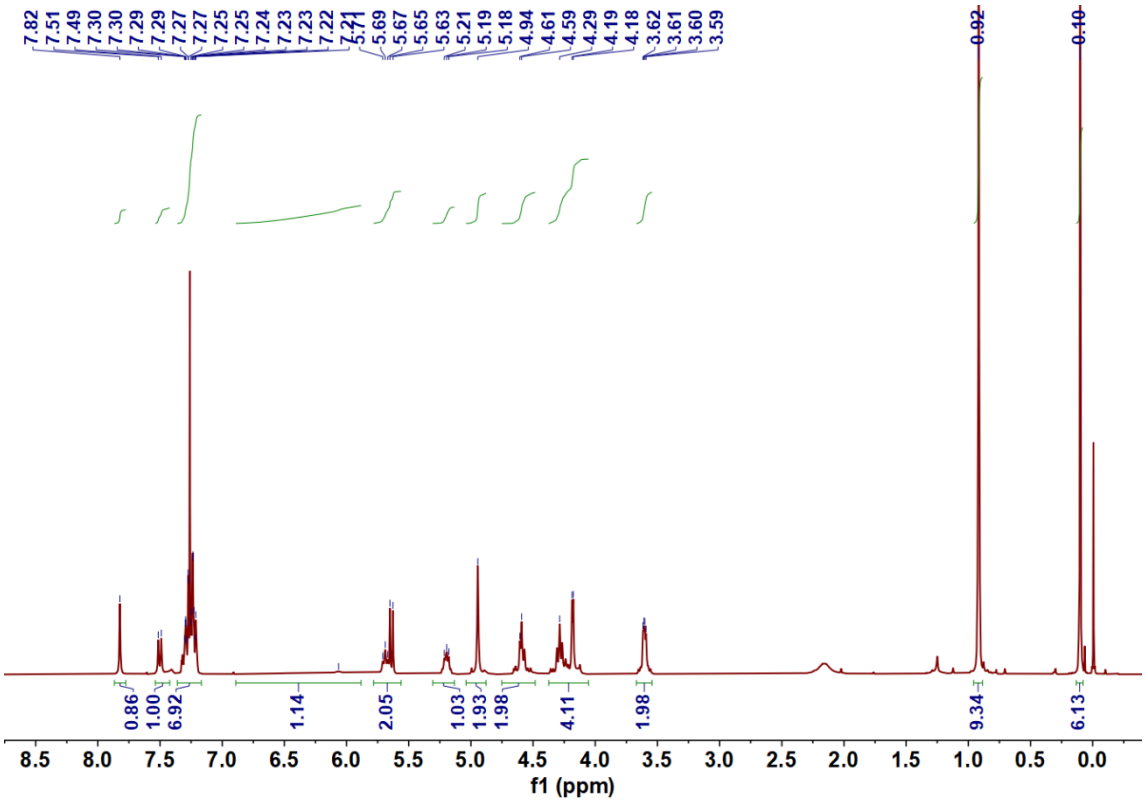


Figure S35. ^{1}H NMR of **C.**

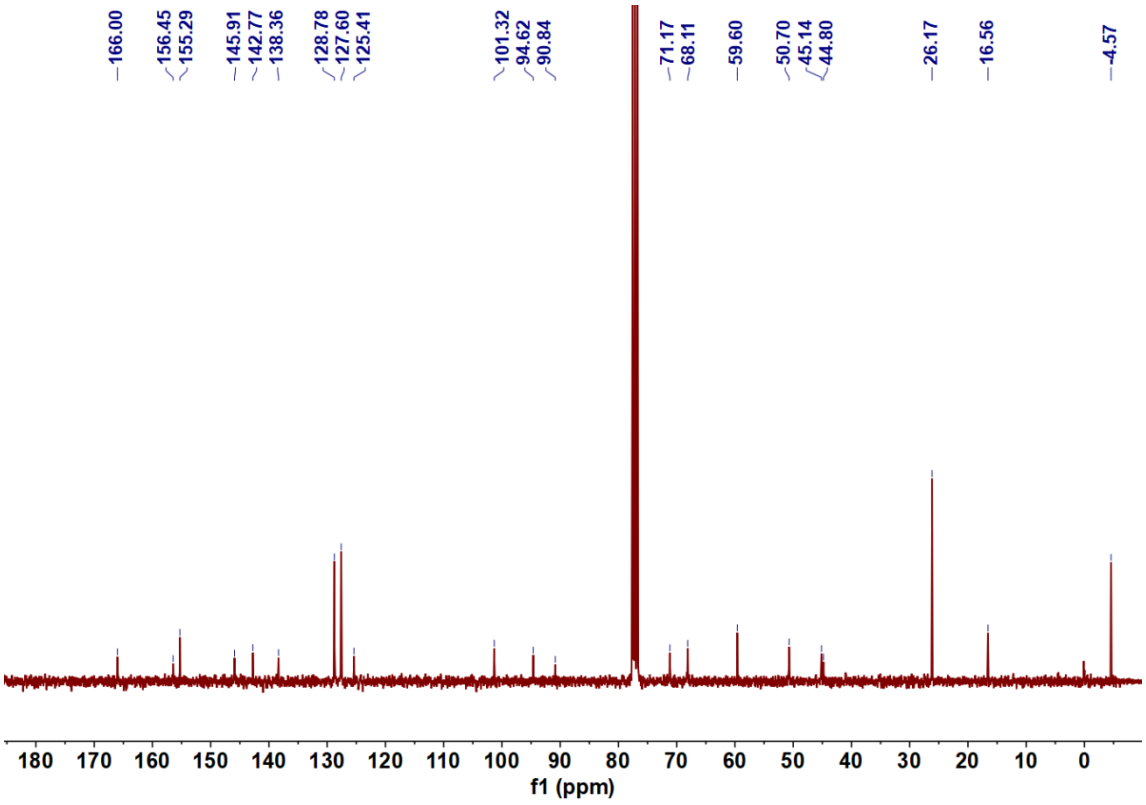


Figure S36. ^{13}C NMR of **C**.

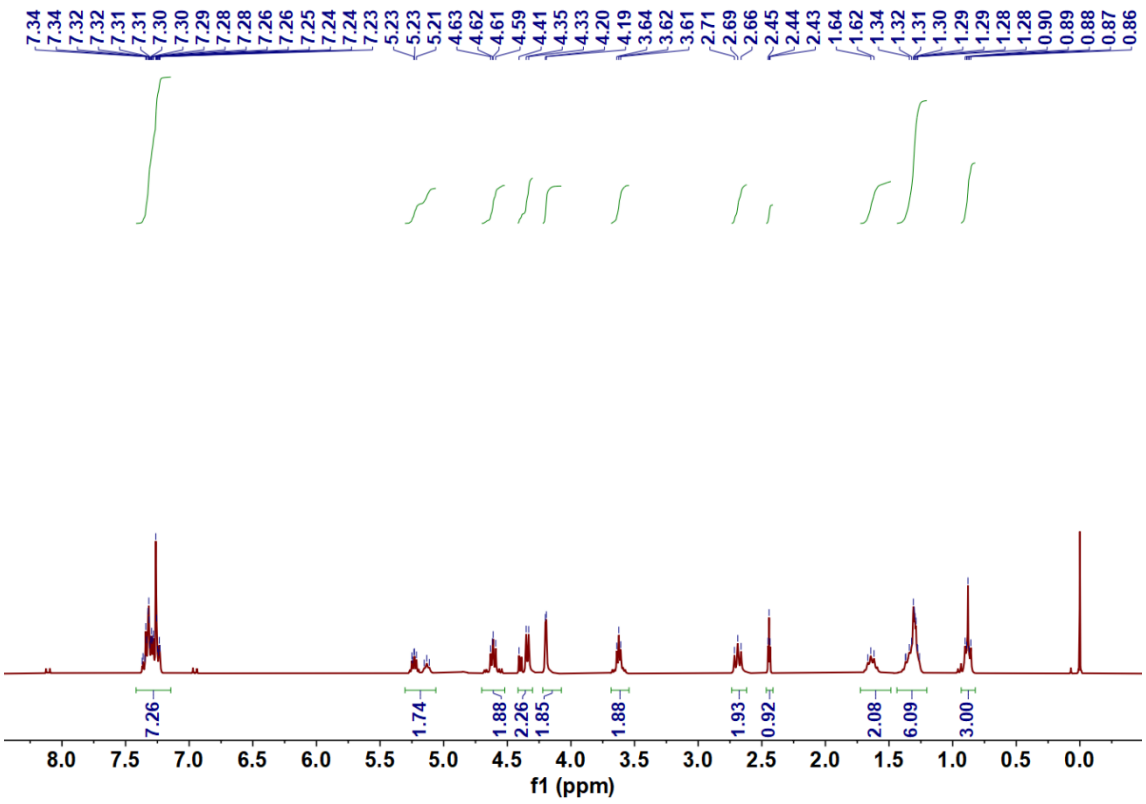


Figure S37. ^{1}H NMR of **23.**

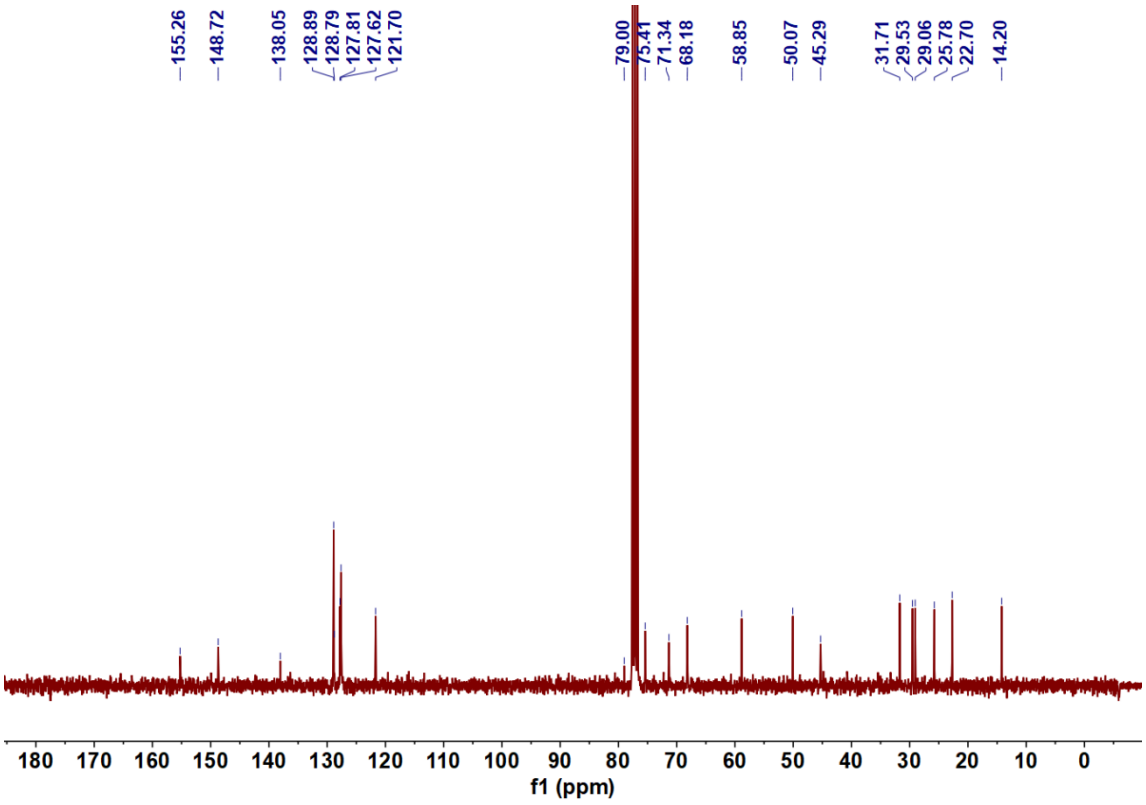


Figure S38. ^{13}C NMR of **23**.

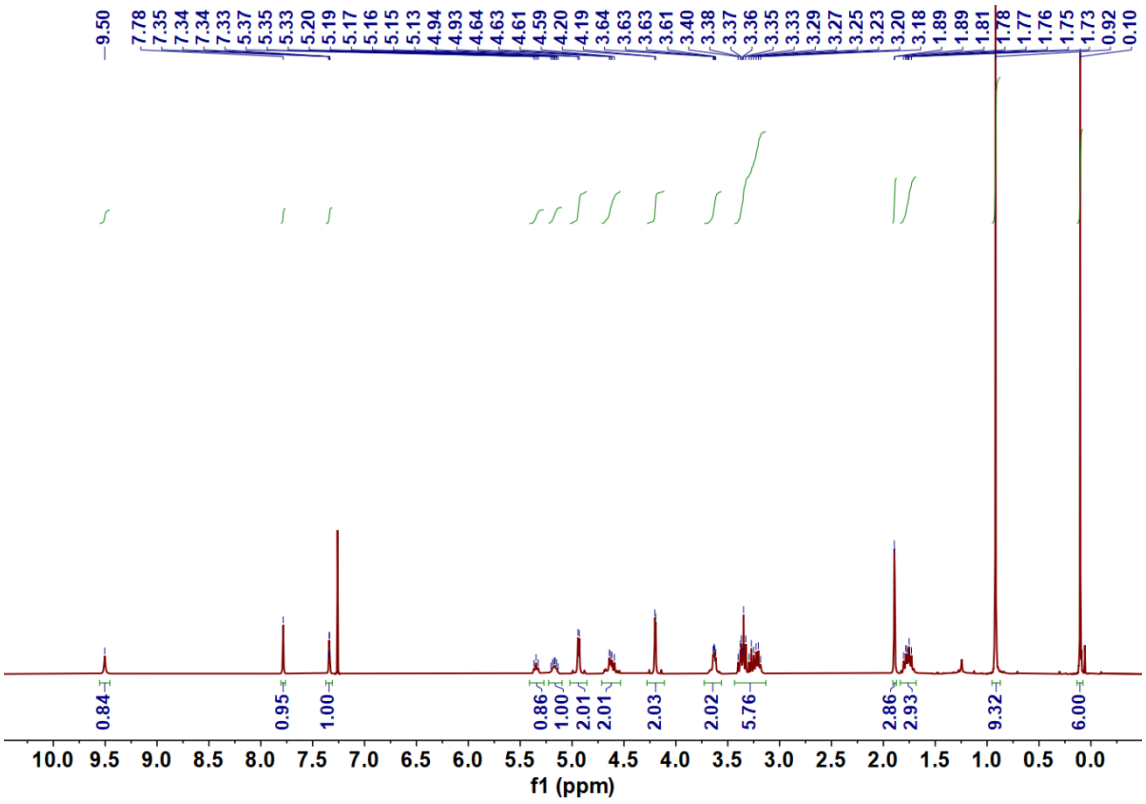


Figure S39. ^{1}H NMR of **24.**

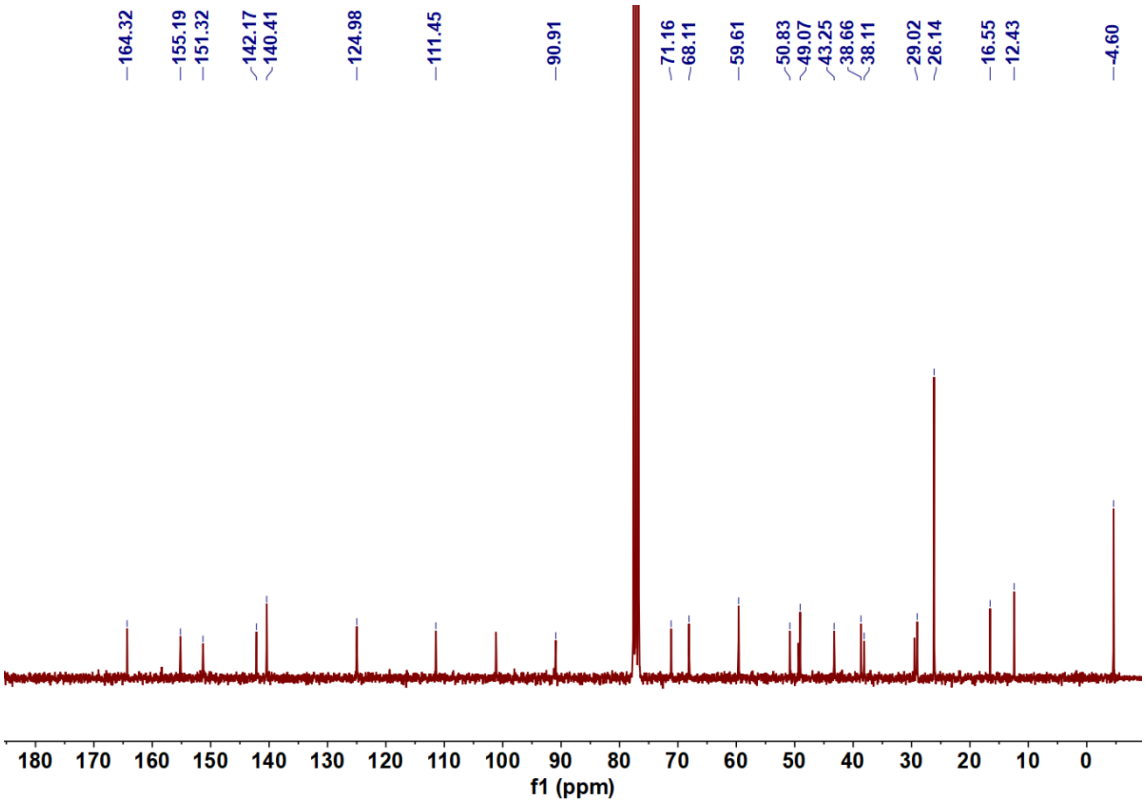


Figure S40. ^{13}C NMR of **24**.

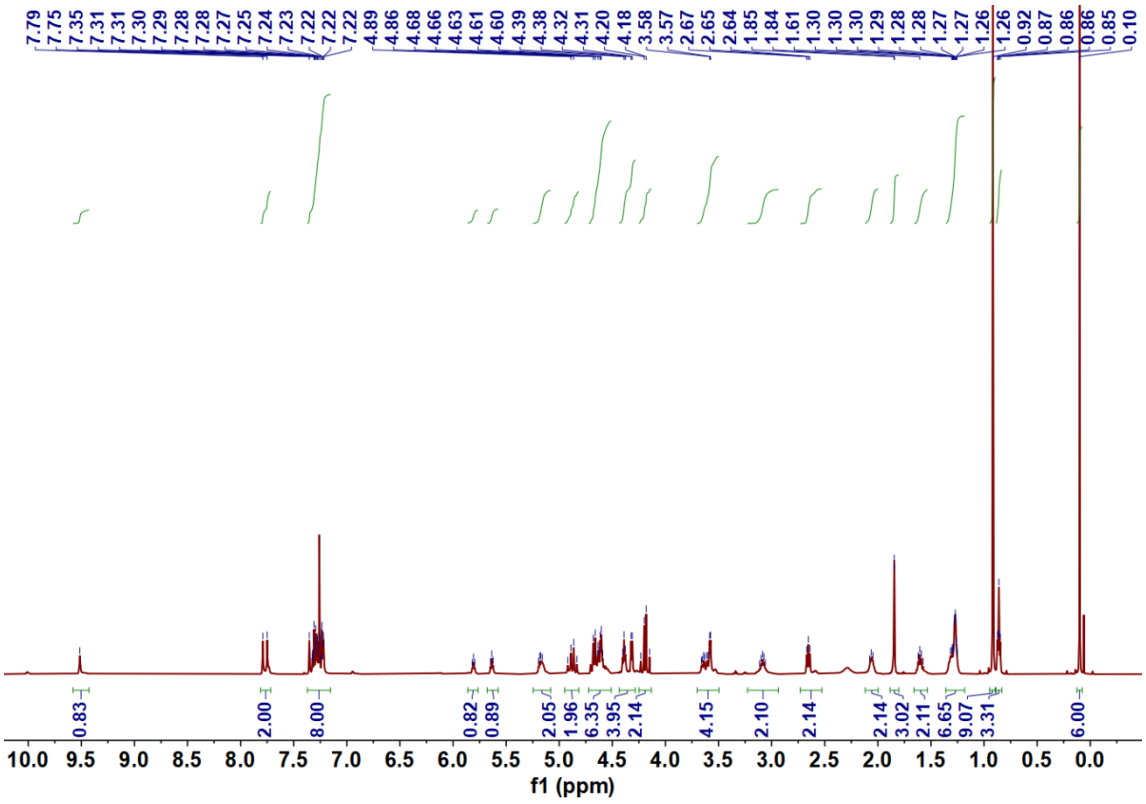


Figure S41. ^{1}H NMR of **TC$_6$.**

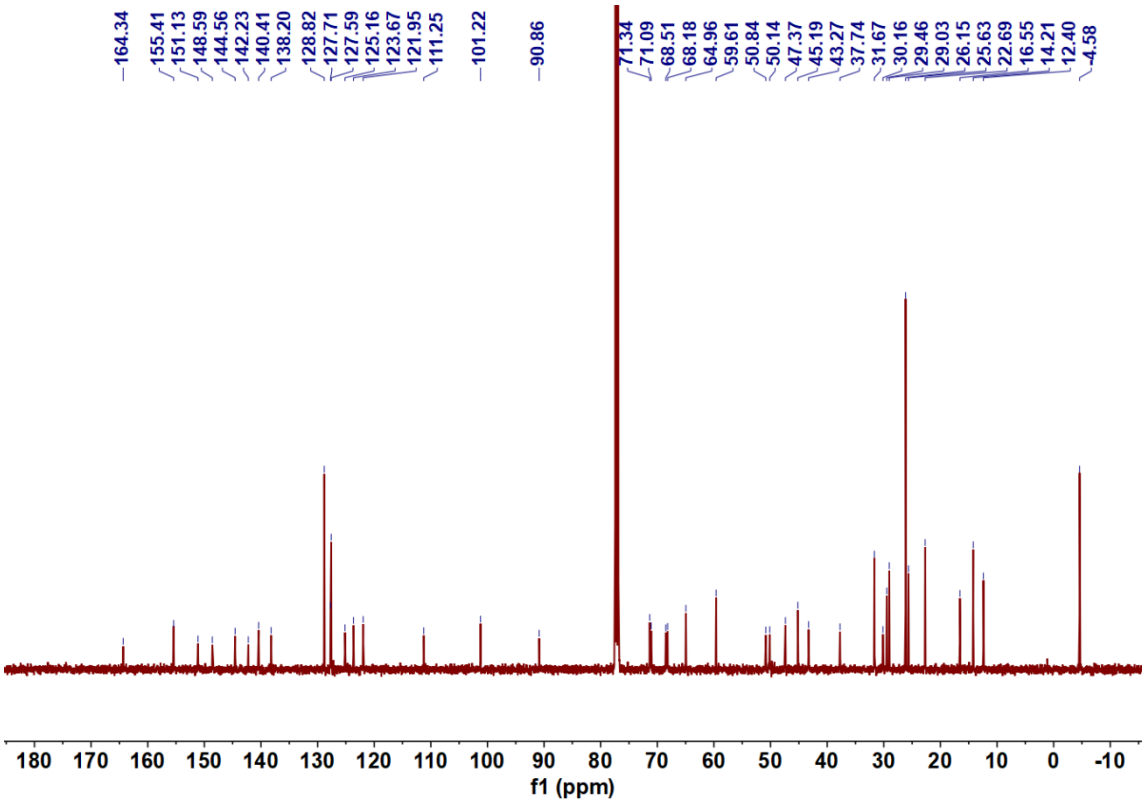


Figure S42. ^{13}C NMR of **TC$_6$**.

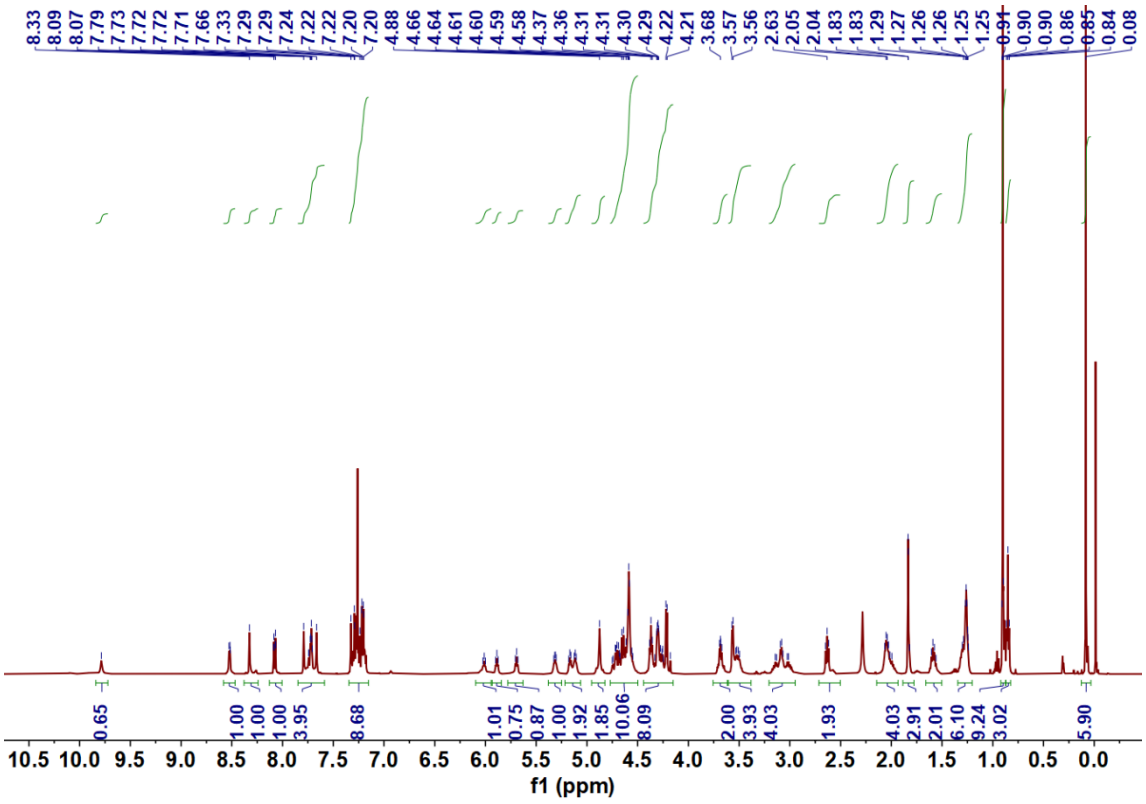


Figure S43. ^{1}H NMR of **PTC$_6$.**

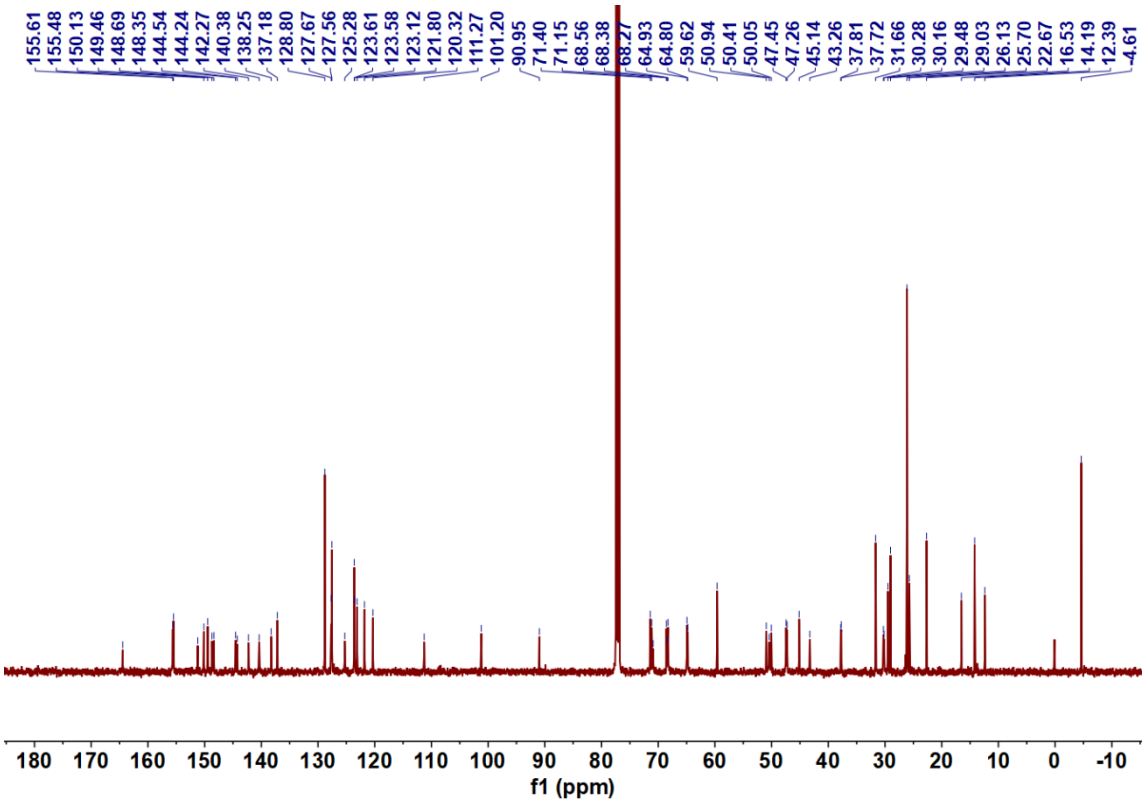


Figure S44. ^{13}C NMR of **PTC$_6$**.

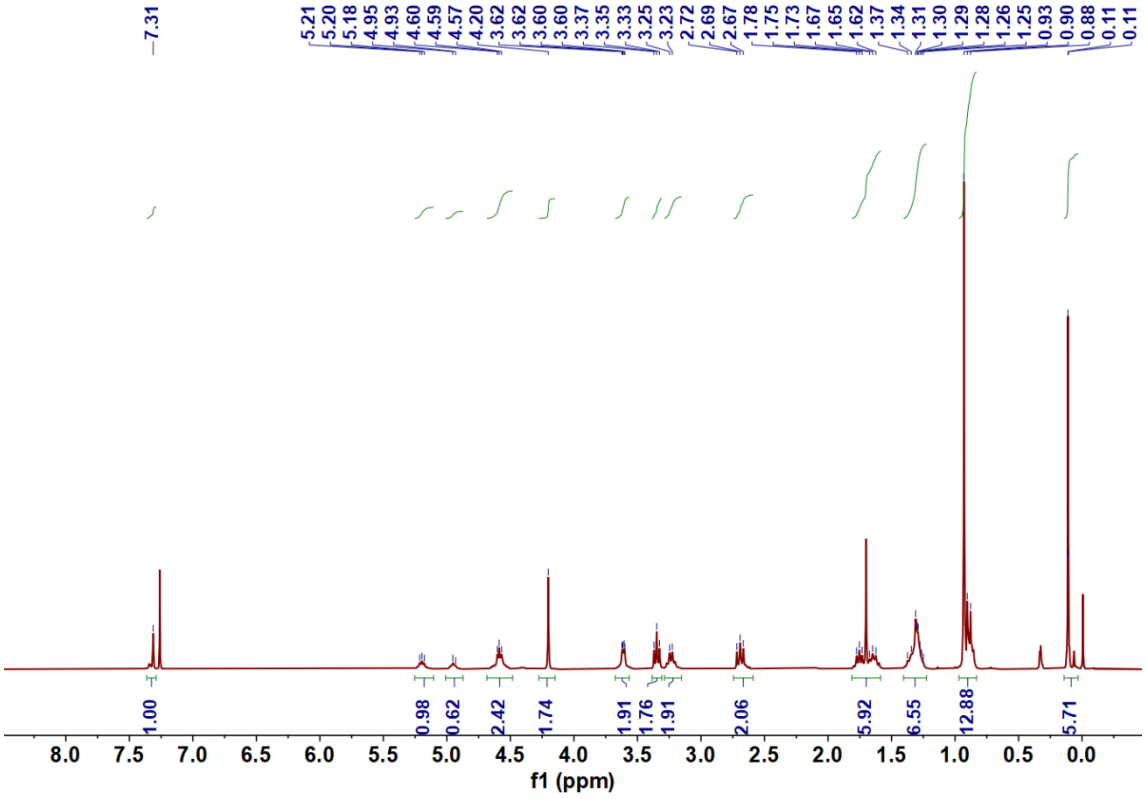


Figure S45. ^{1}H NMR of **27.**

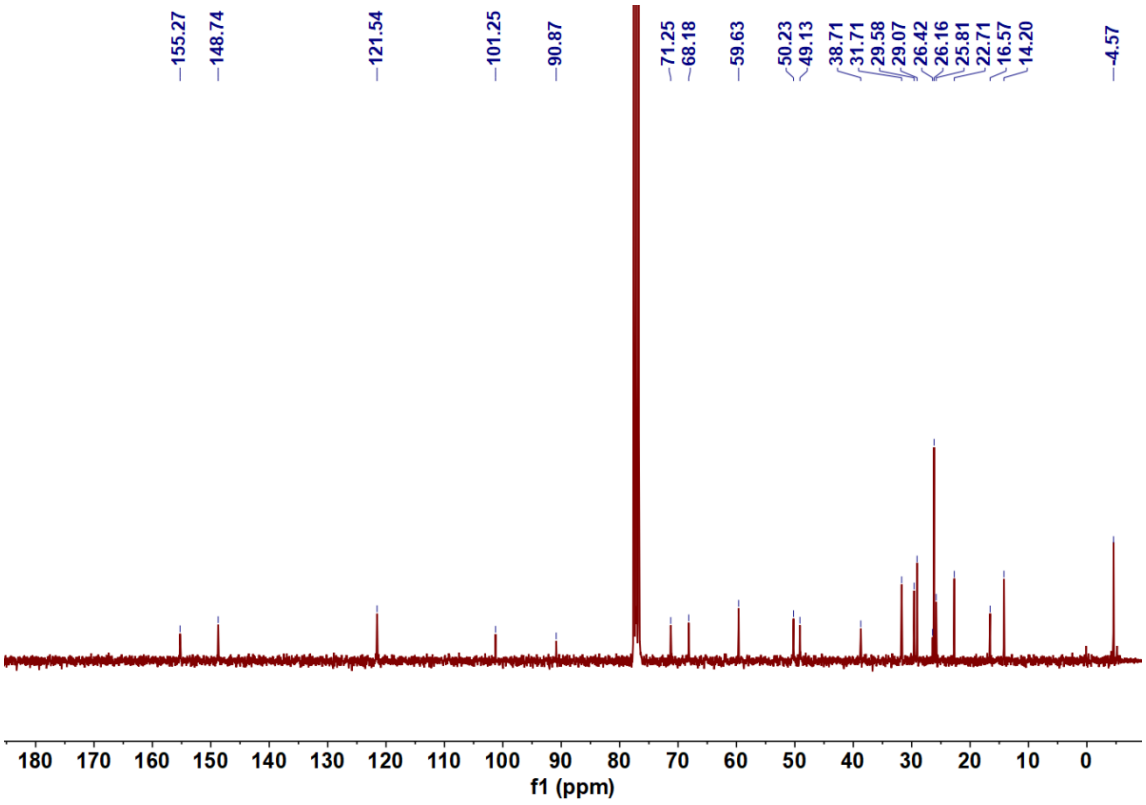


Figure S46. ^{13}C NMR of **27**.

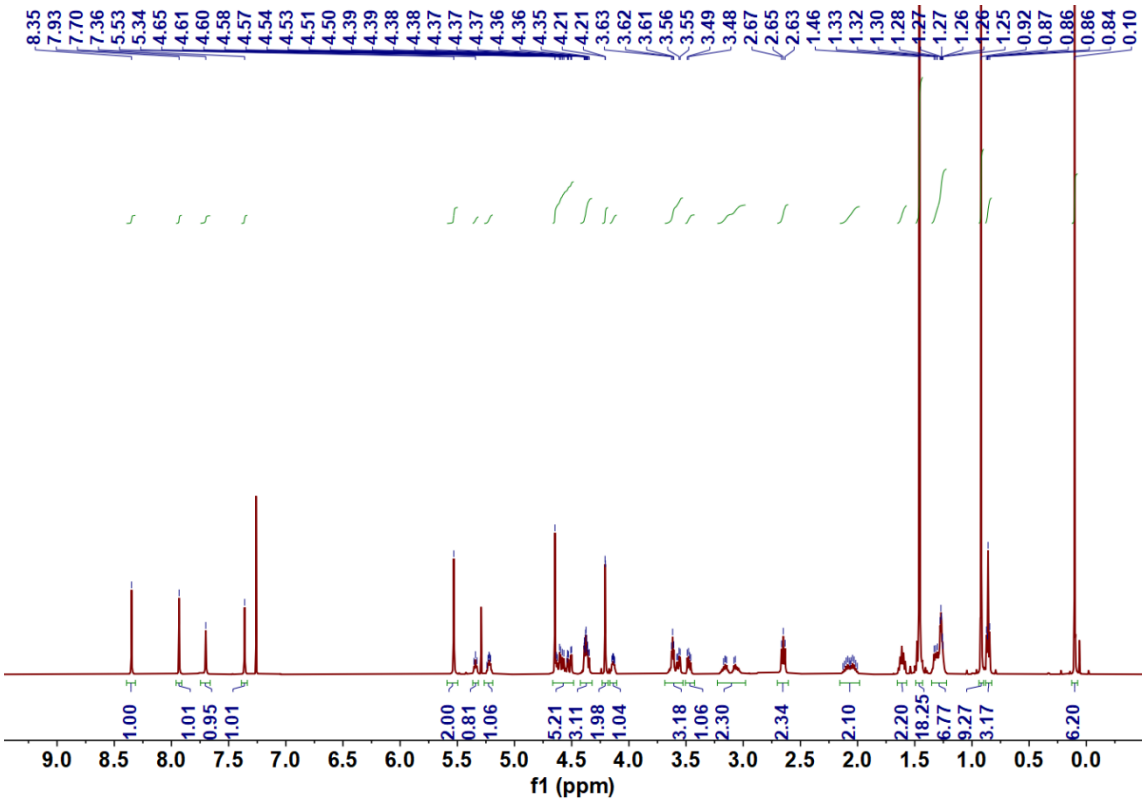


Figure S47. ^{1}H NMR of **C_6G.**

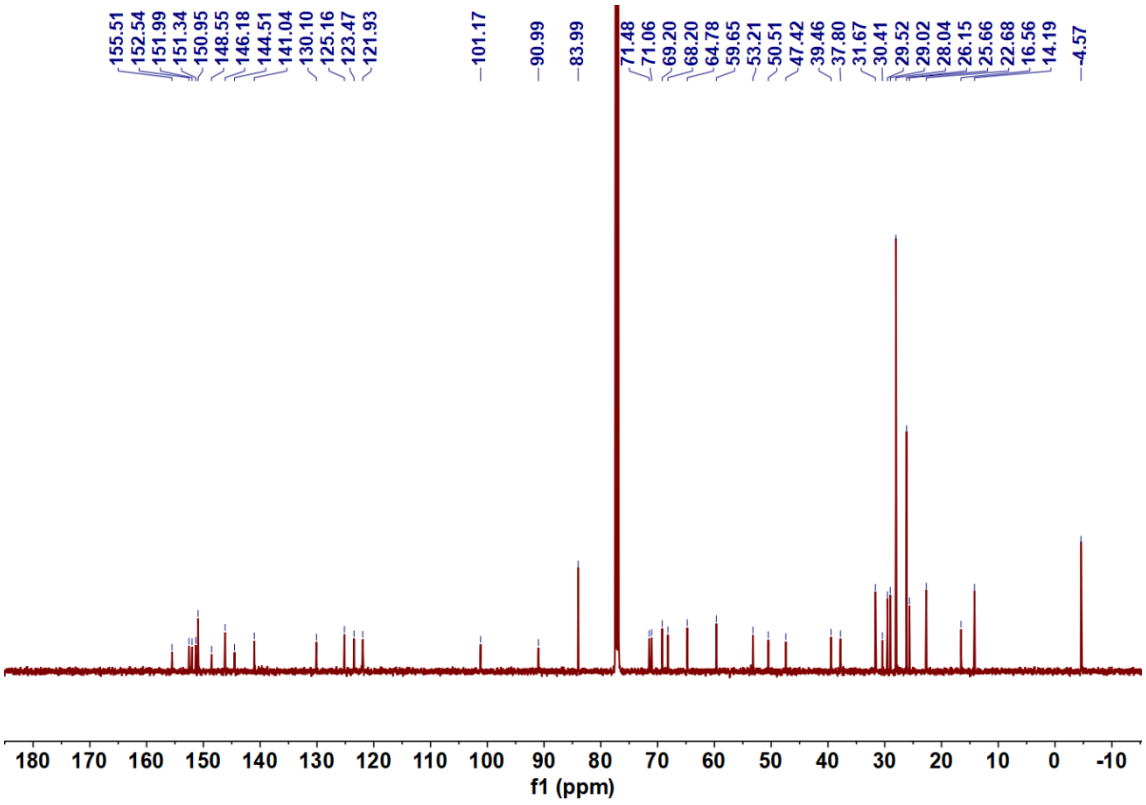


Figure S48. ^{13}C NMR of **C_6G**.

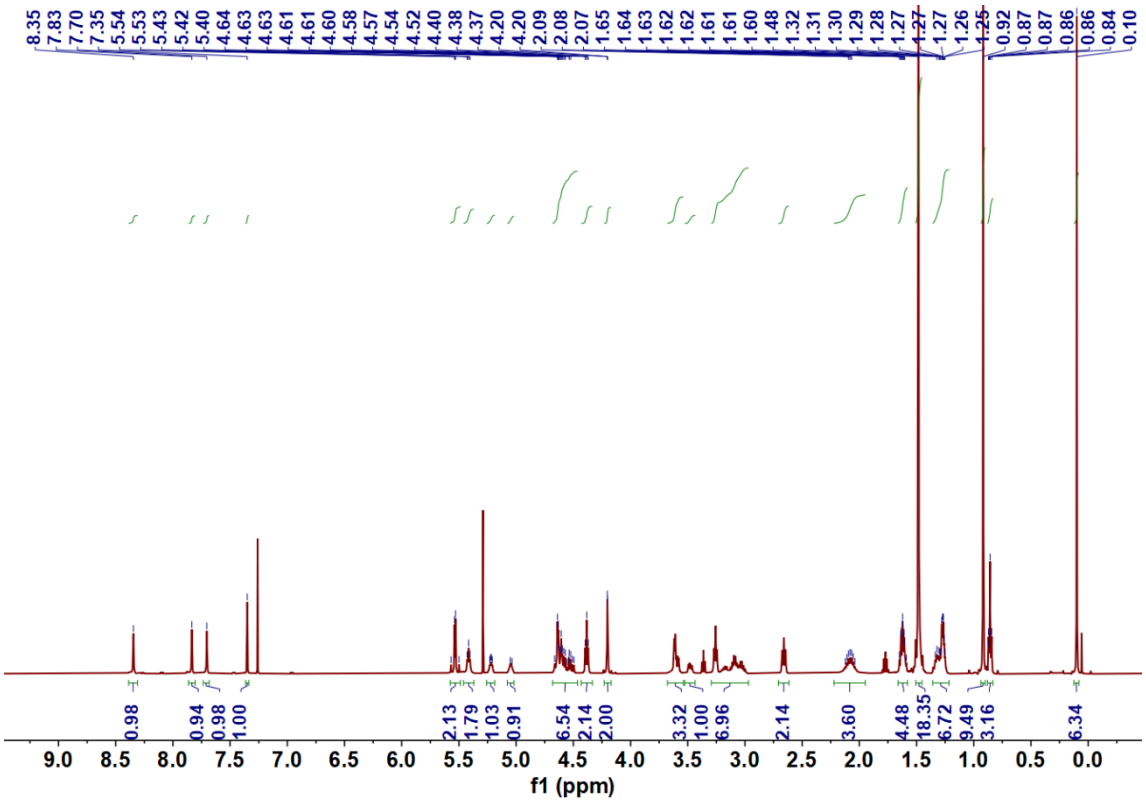


Figure S49. ^{1}H NMR of **28.**

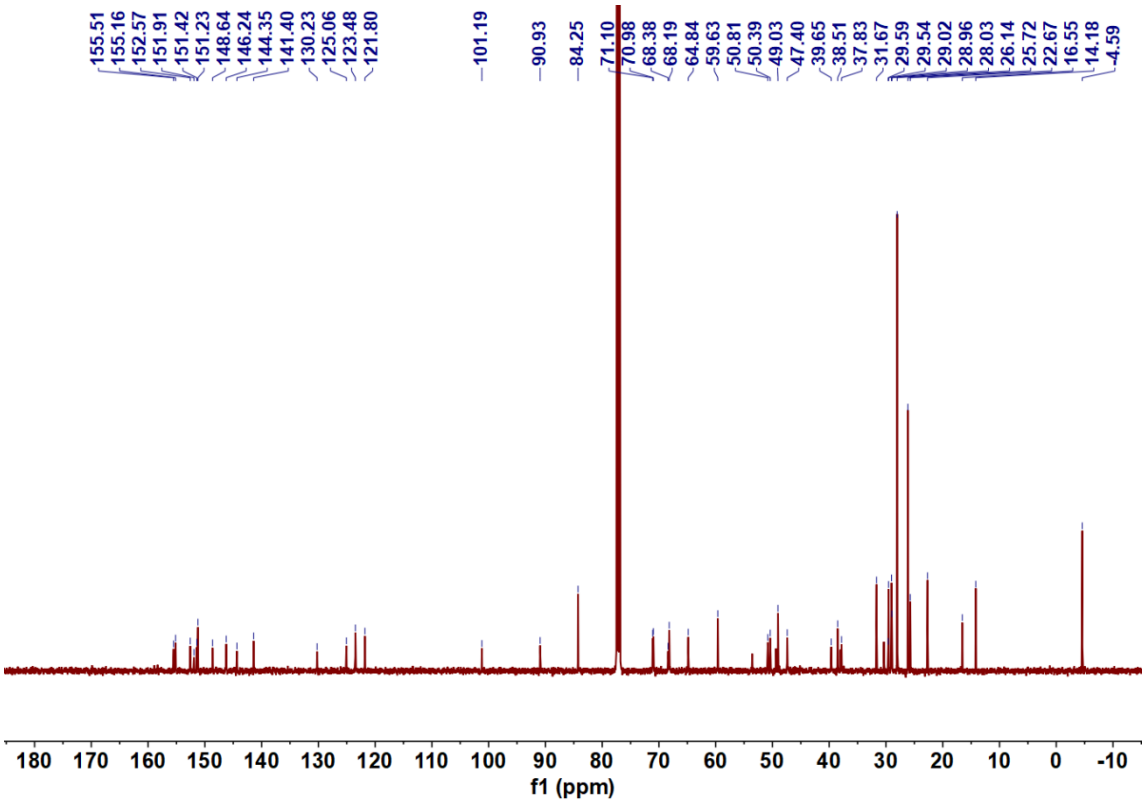


Figure S50. ^{13}C NMR of **28**.

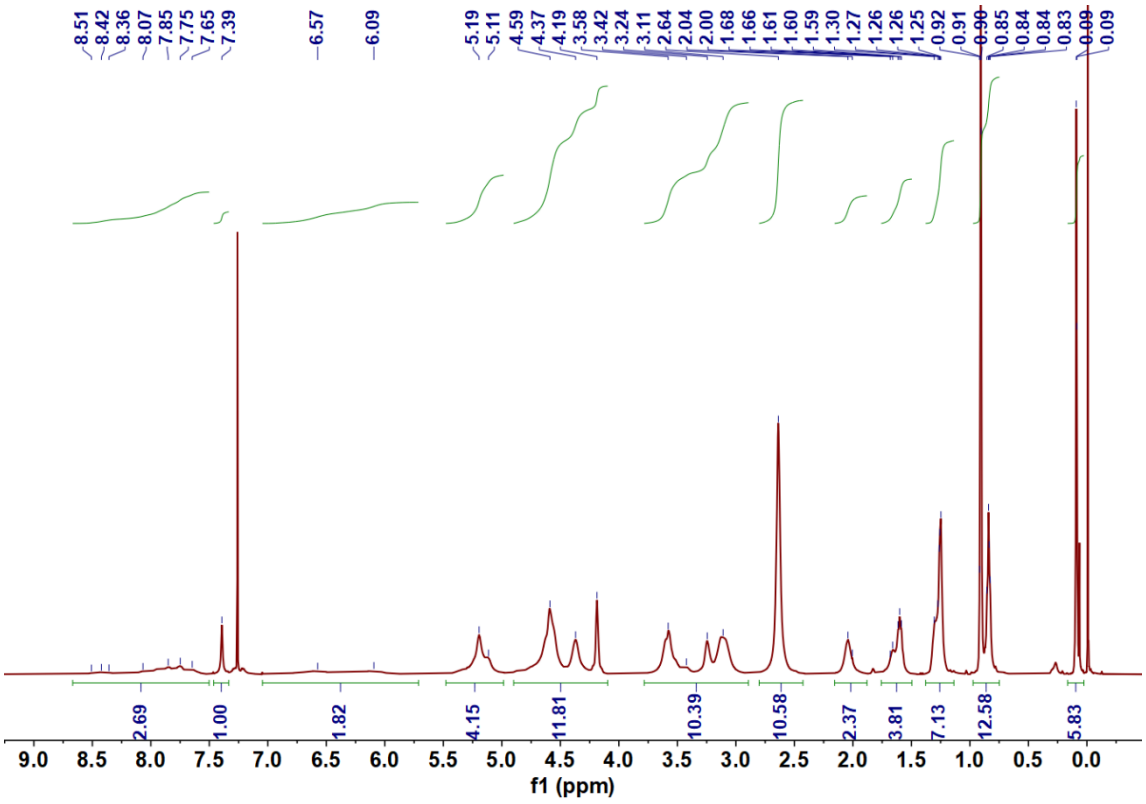


Figure S51. ^{1}H NMR of **29.**

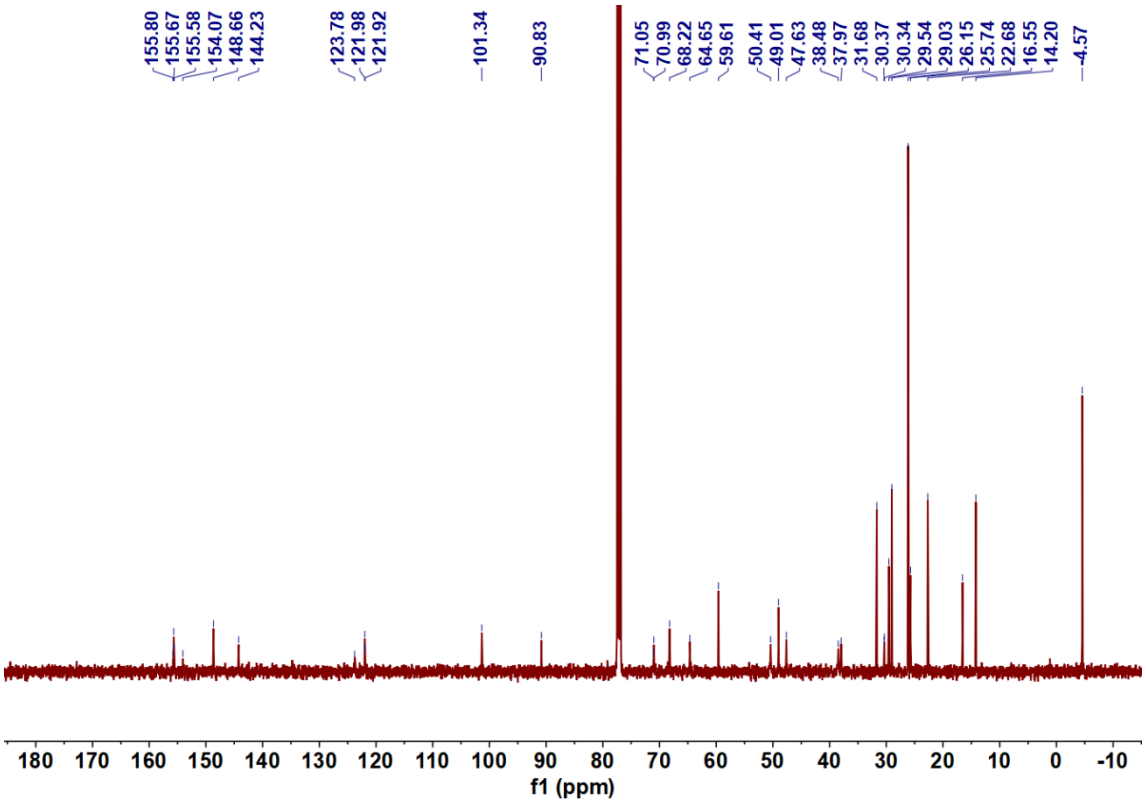


Figure S52. ^{13}C NMR of **29**.

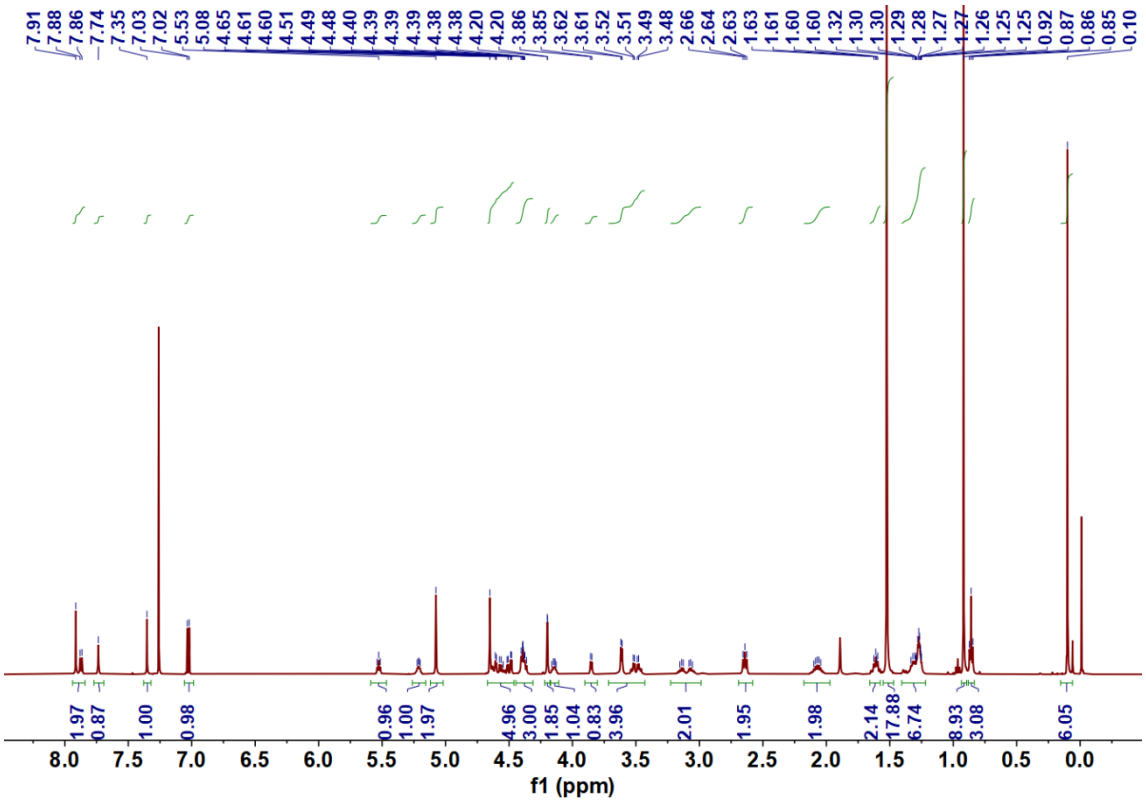


Figure S53. ^{1}H NMR of **C_6C.**

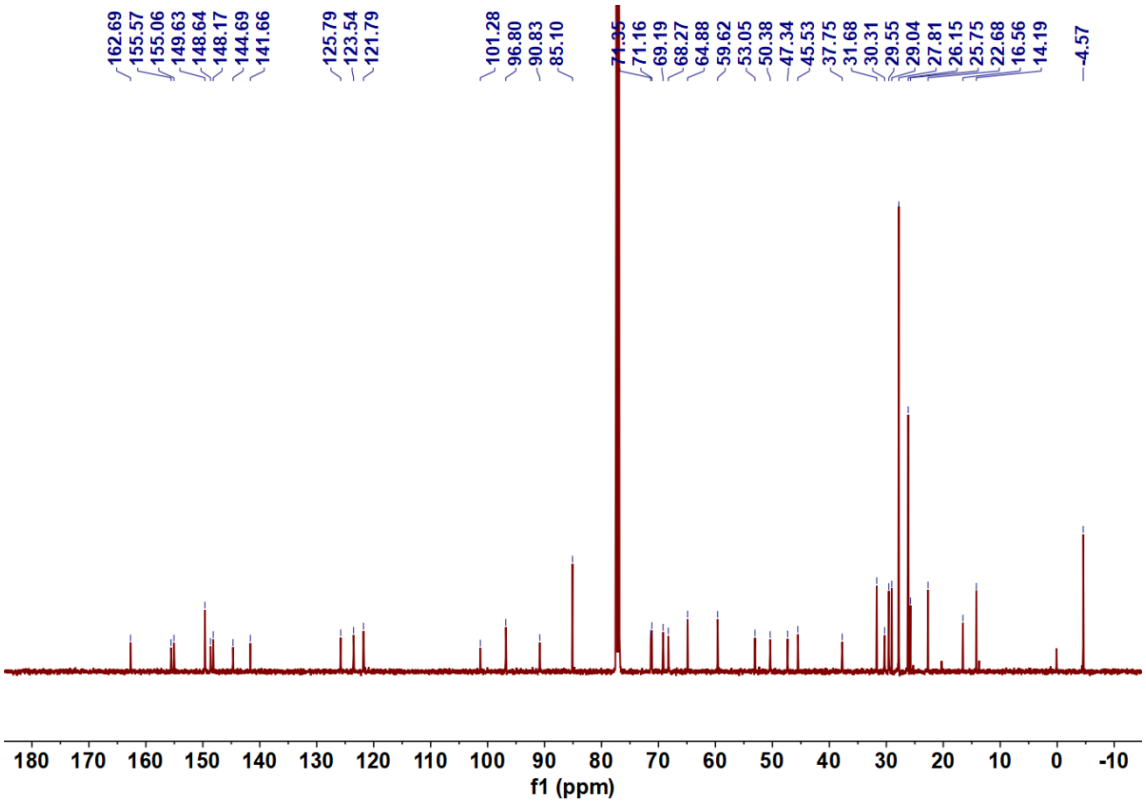


Figure S54. ^{13}C NMR of **C_6C**.

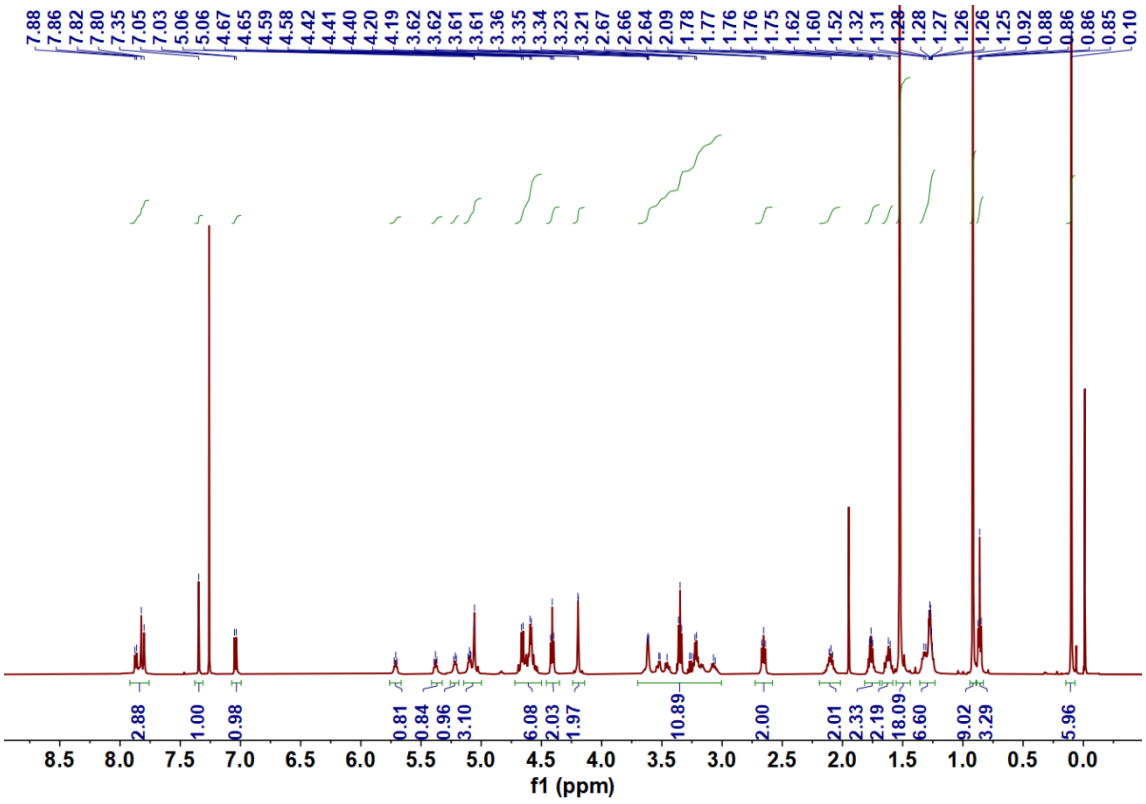


Figure S55. ^{1}H NMR of **30.**

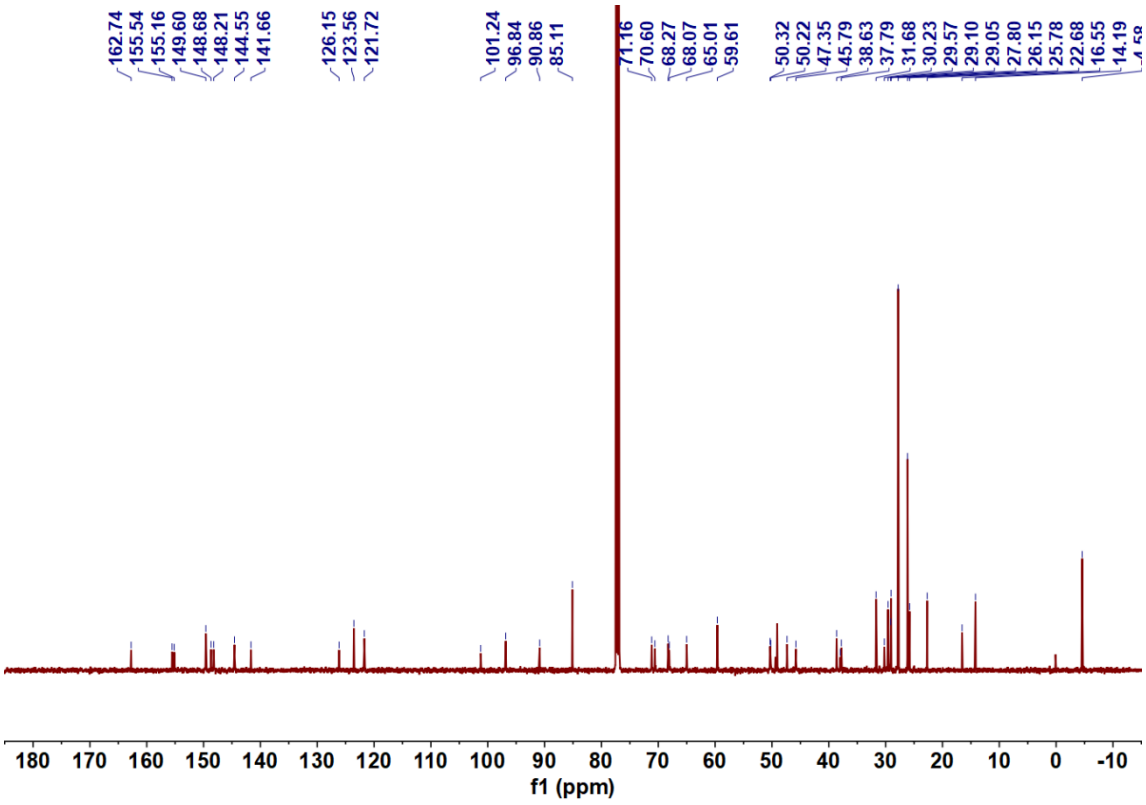


Figure S56. ^{13}C NMR of **30**.

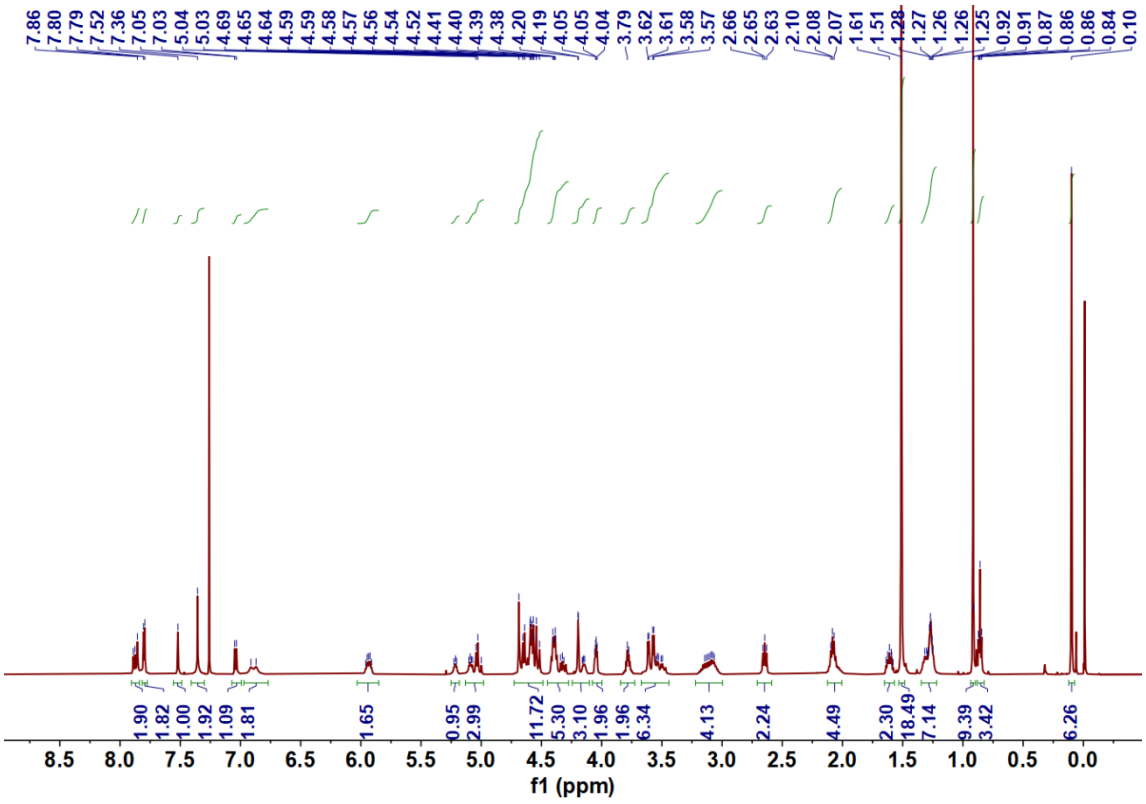


Figure S57. ^{1}H NMR of **C_6CI.**

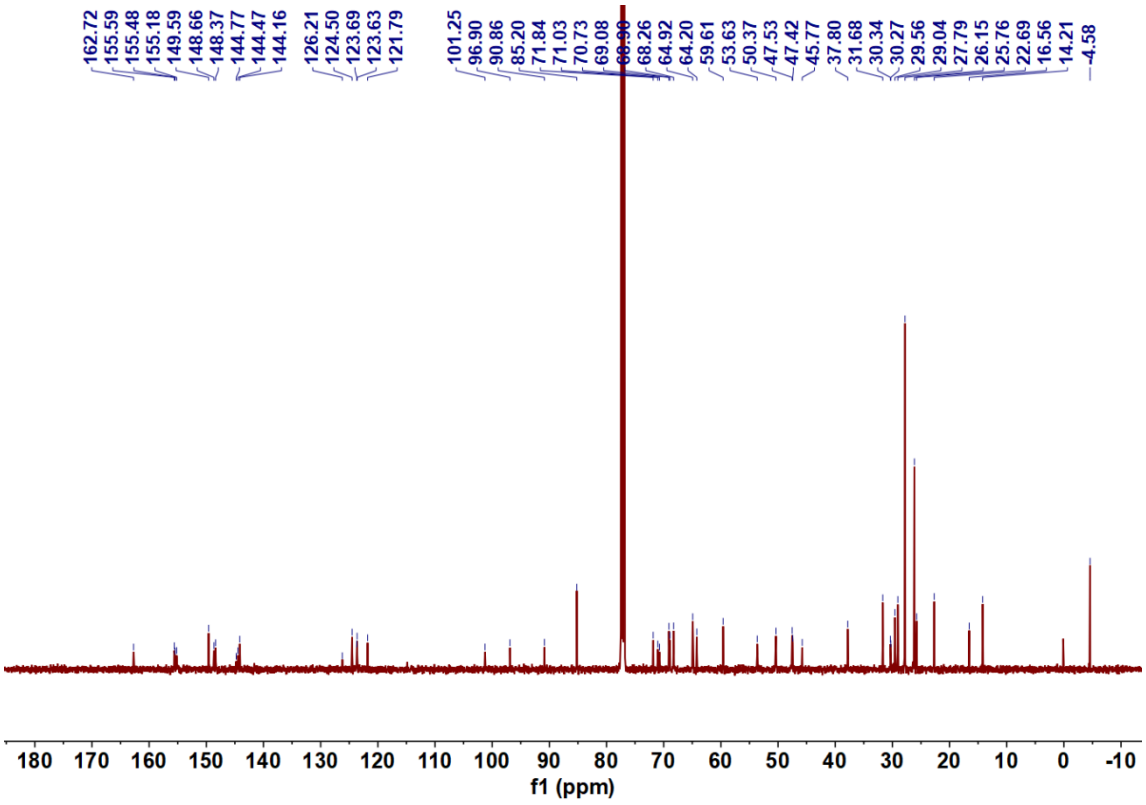


Figure S58. ^{13}C NMR of **C_6CI**.

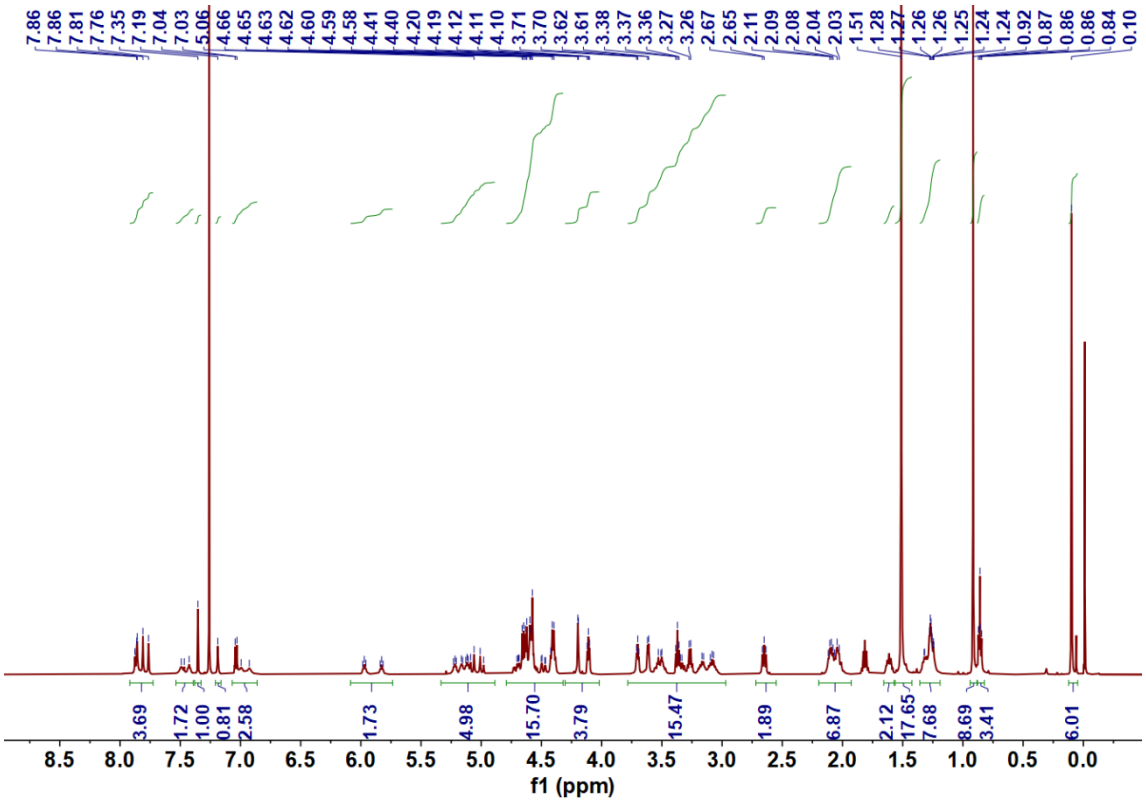


Figure S59. ^{1}H NMR of **31.**

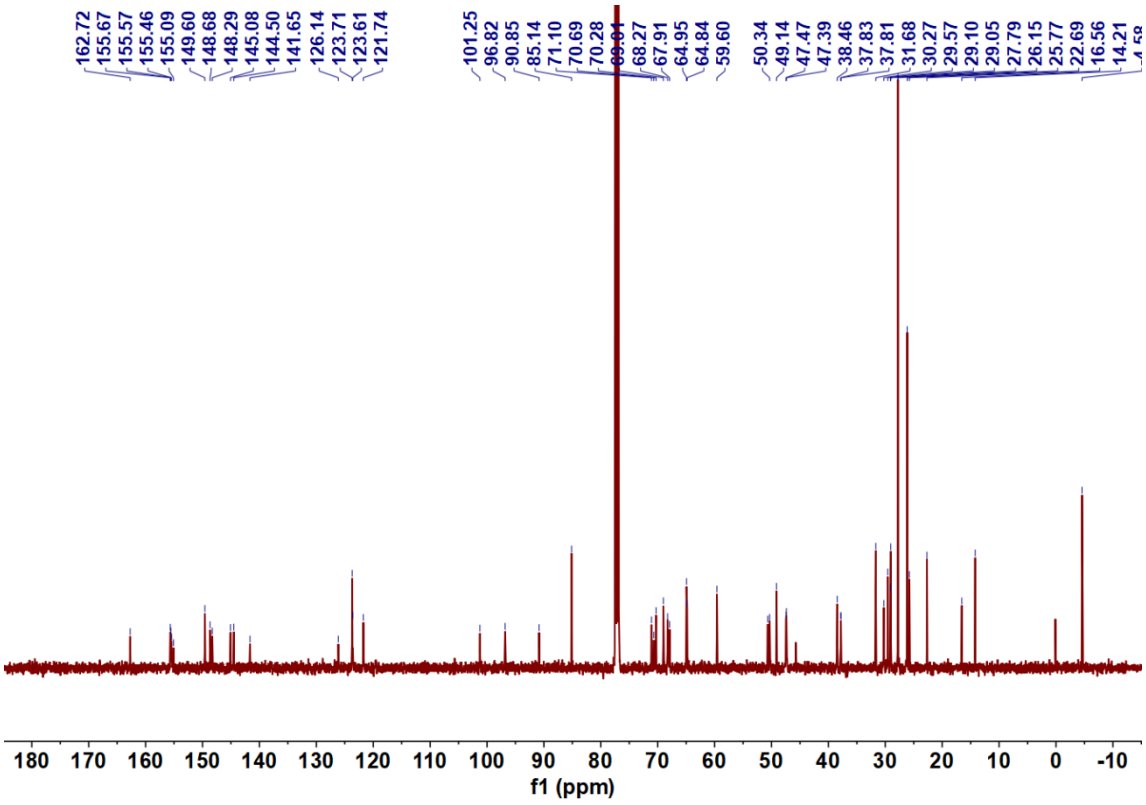


Figure S60. ^{13}C NMR of **31**.

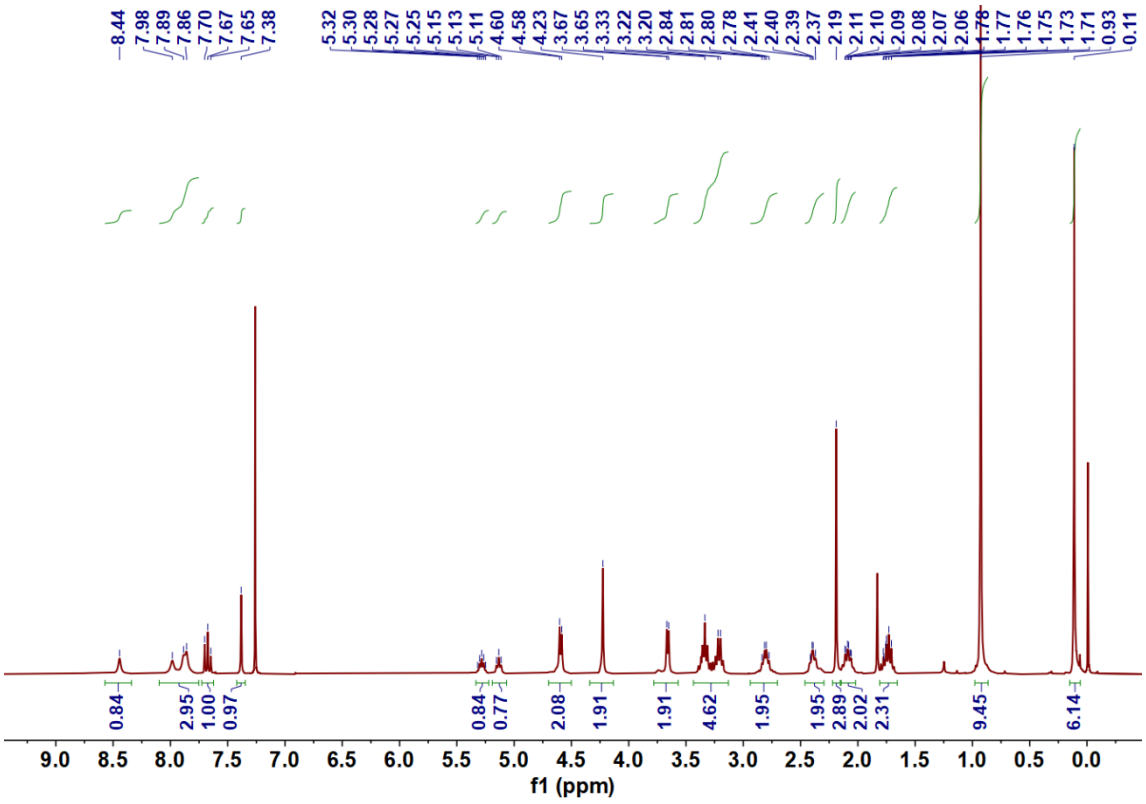


Figure S61. ^{1}H NMR of **32.**

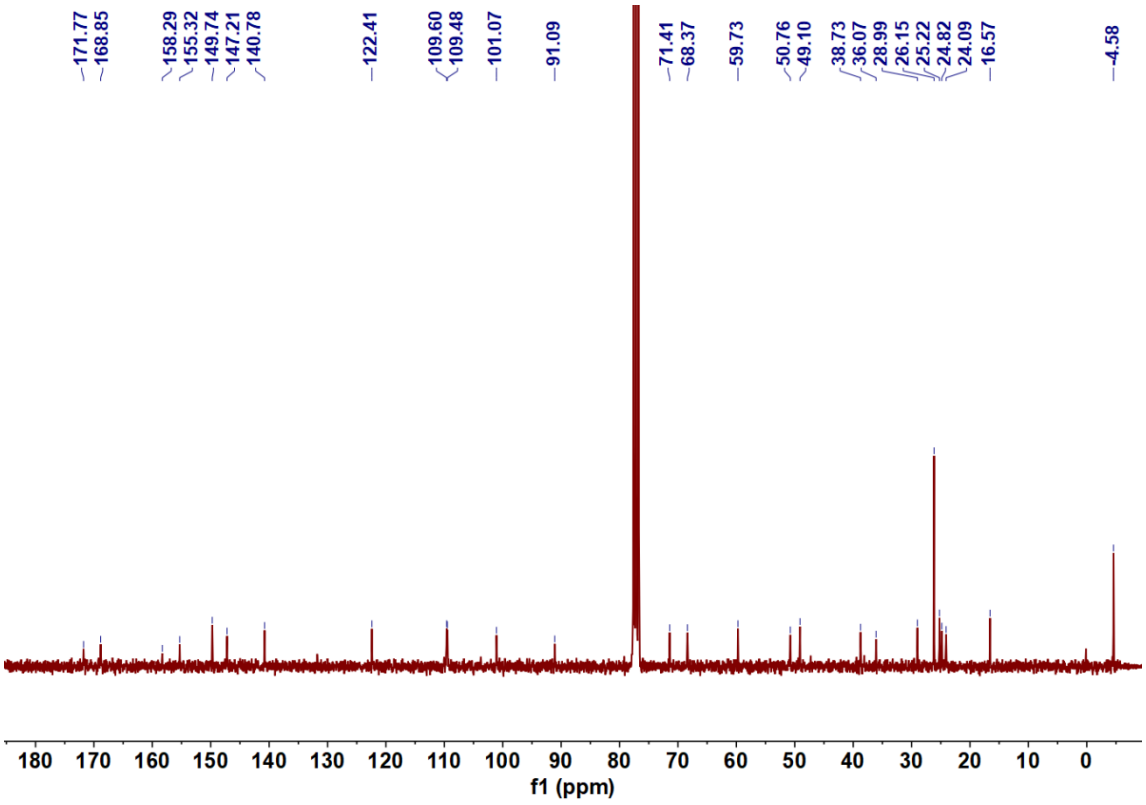


Figure S62. ^{13}C NMR of **32**.

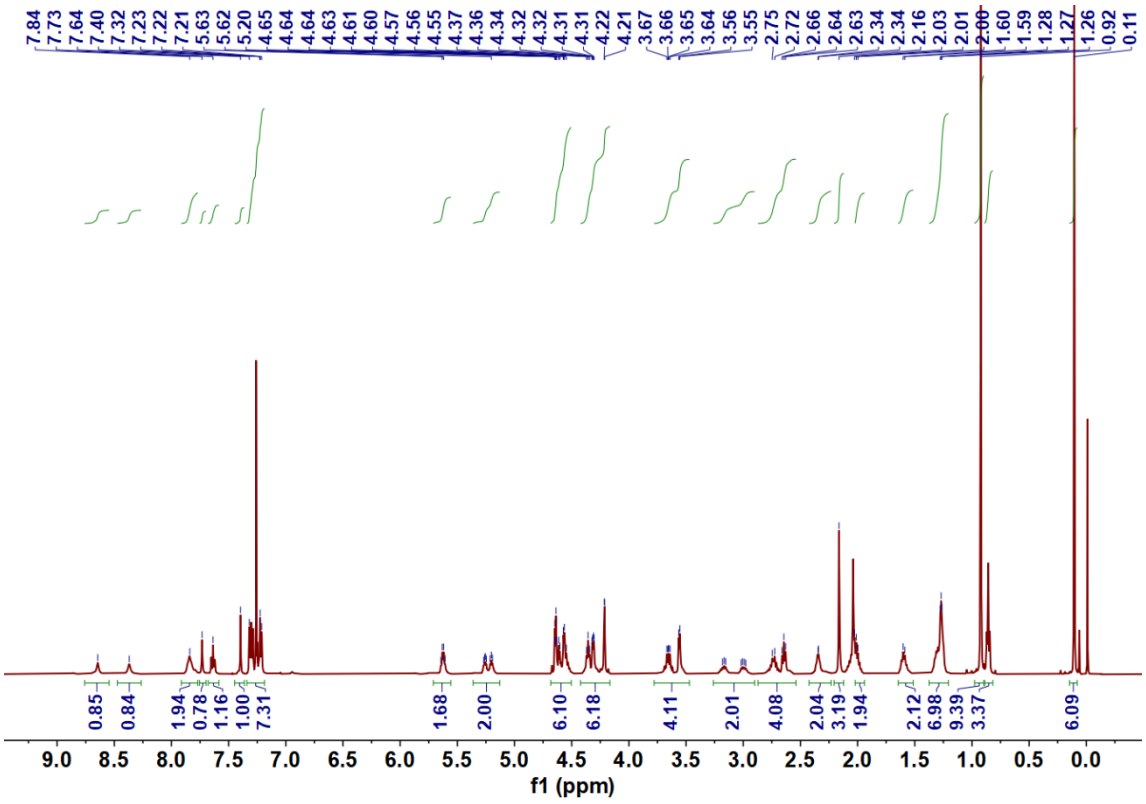


Figure S63. ^{1}H NMR of **DC$_6$.**

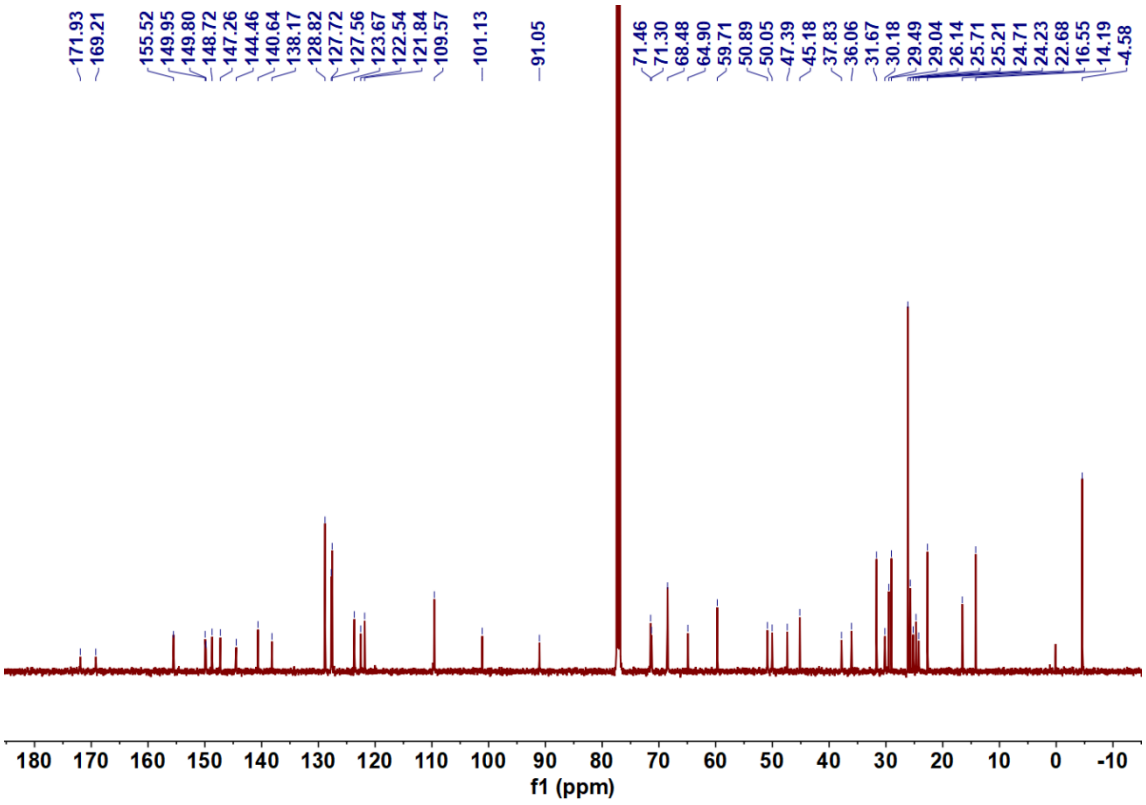


Figure S64. ^{13}C NMR of **DC$_6$**.

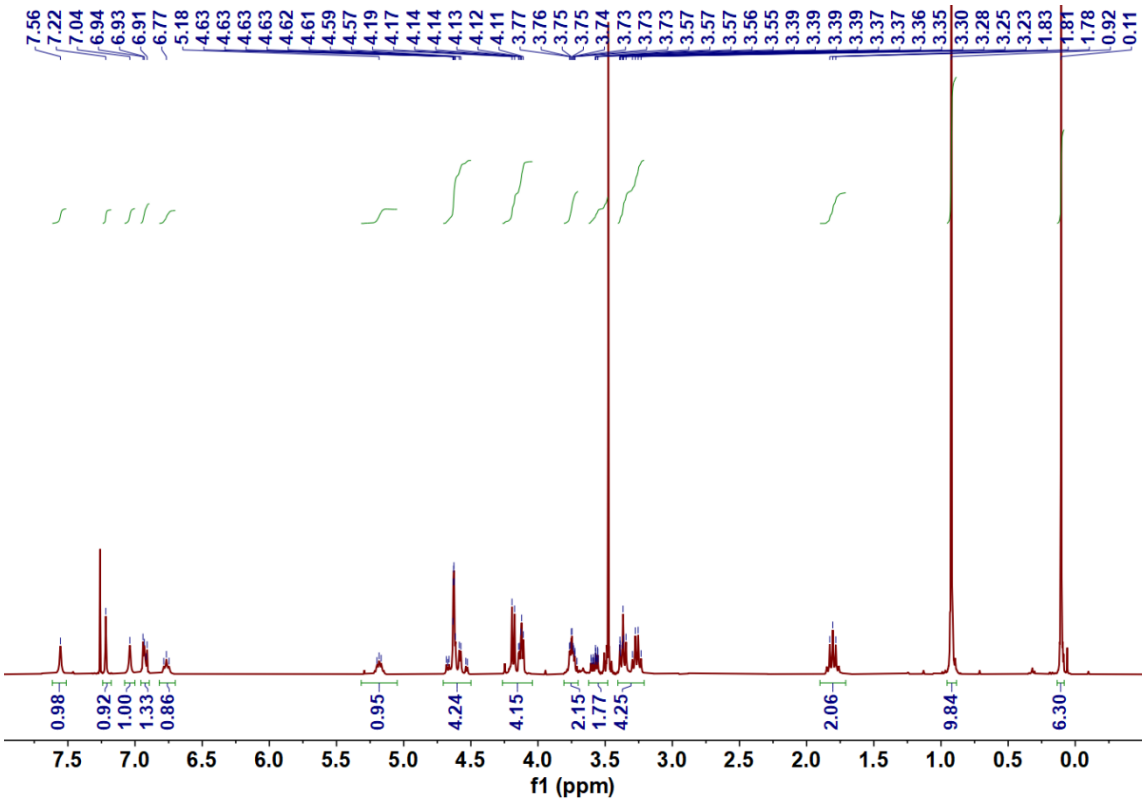


Figure S65. ^{1}H NMR of **33.**

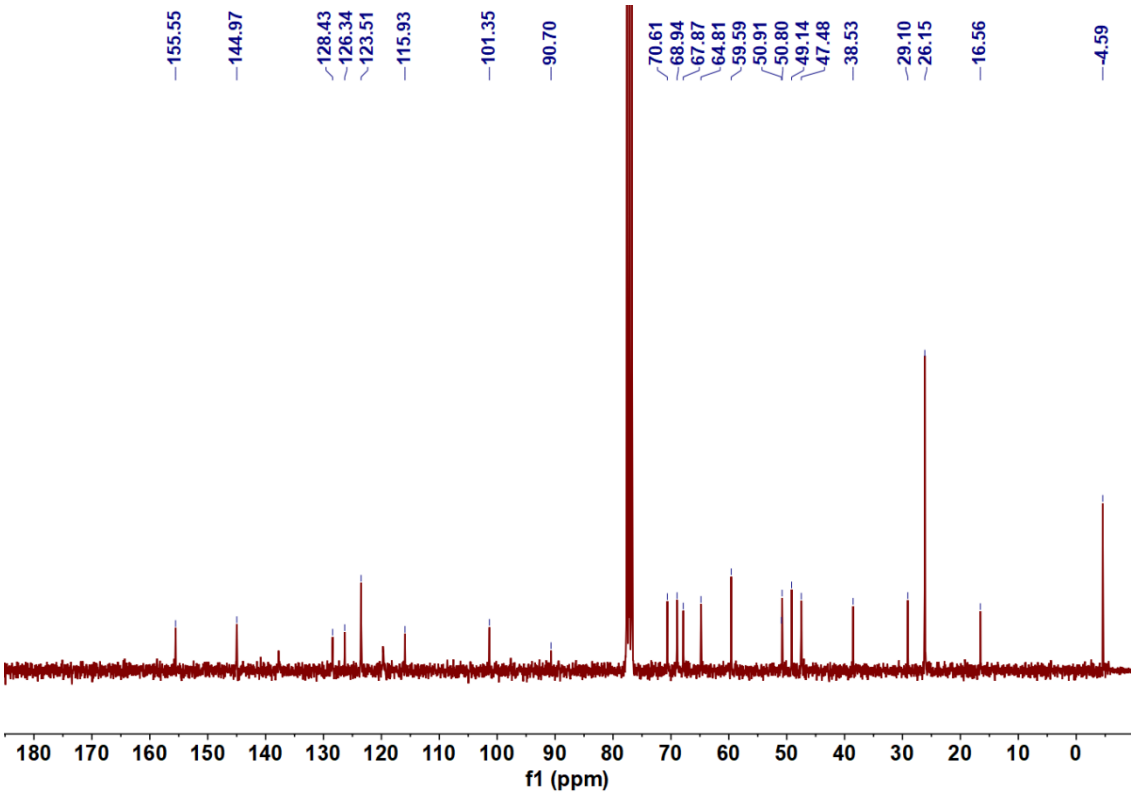


Figure S66. ^{13}C NMR of **33**.

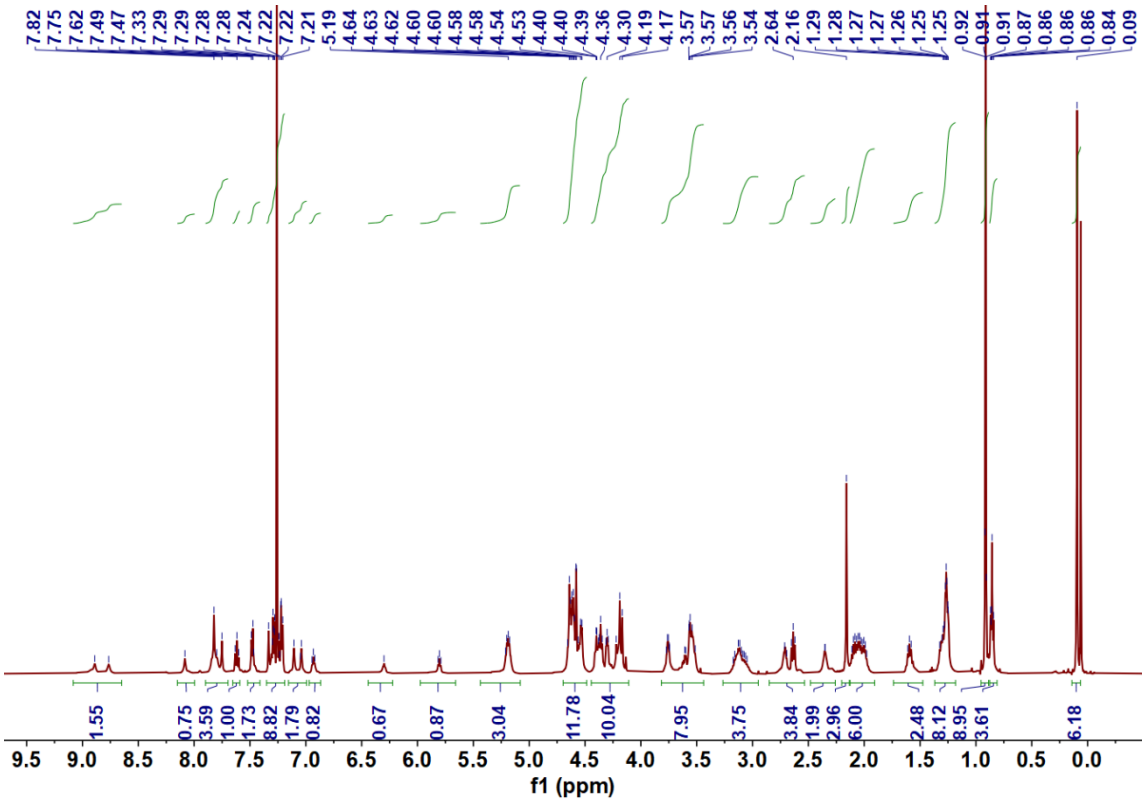


Figure S67. ^{1}H NMR of **IDC$_6$.**

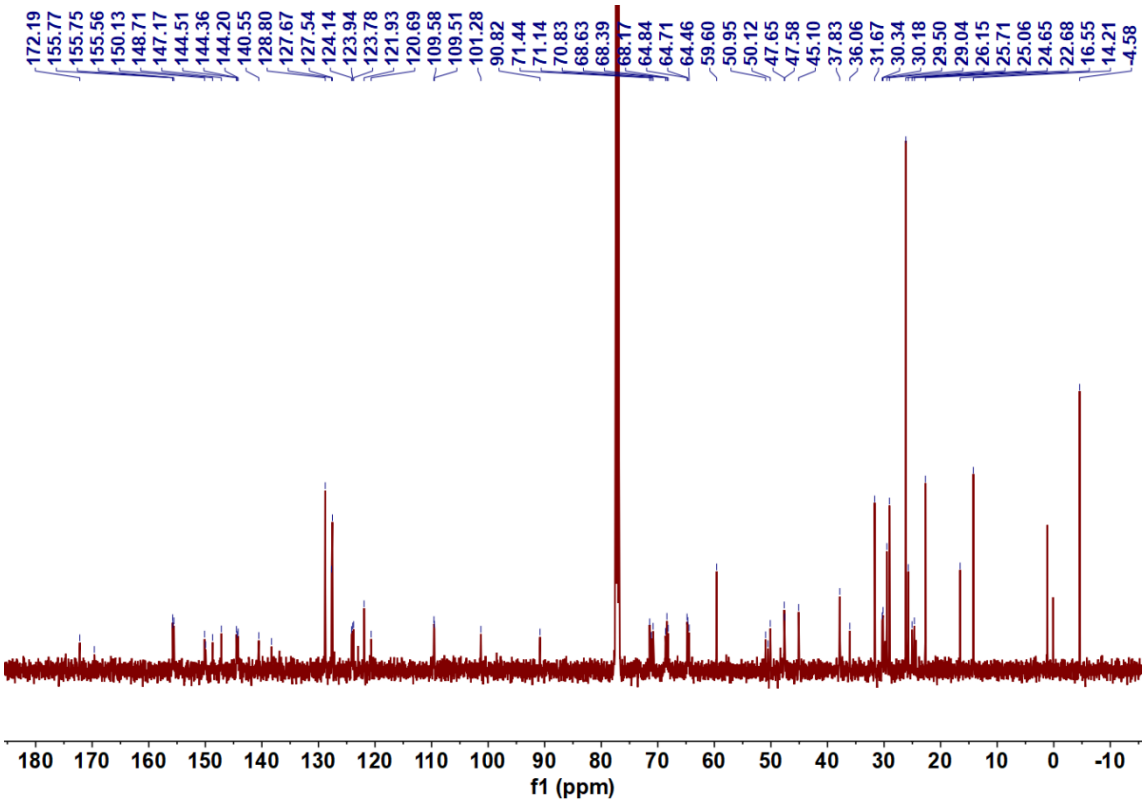


Figure S68. ^{13}C NMR of **IDC$_6$**.

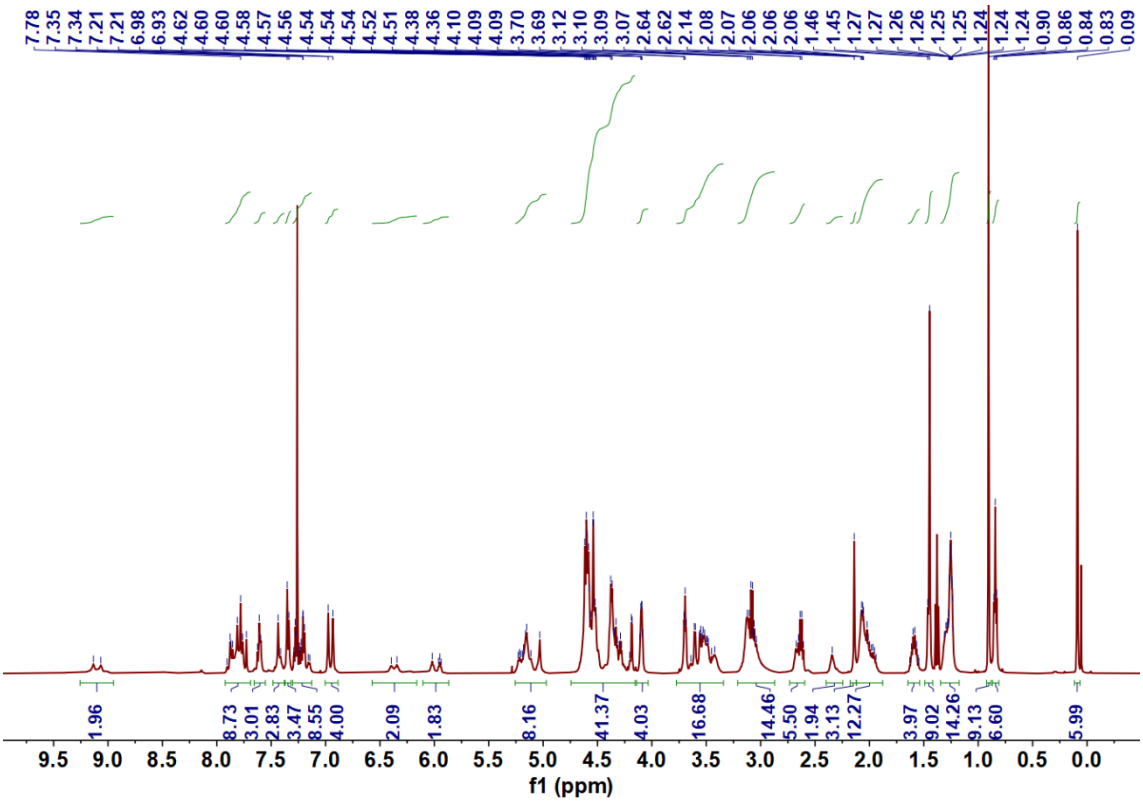


Figure S69. ^{1}H NMR of **34.**

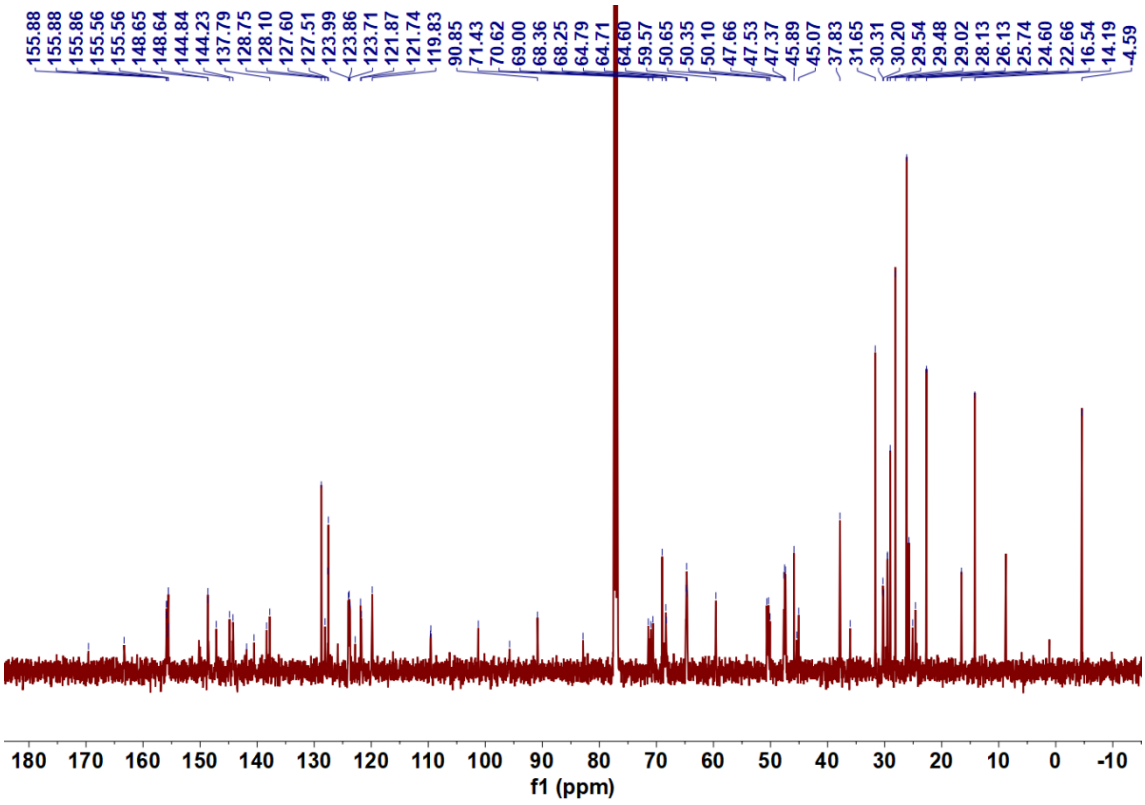


Figure S70. ^{13}C NMR of **34**.

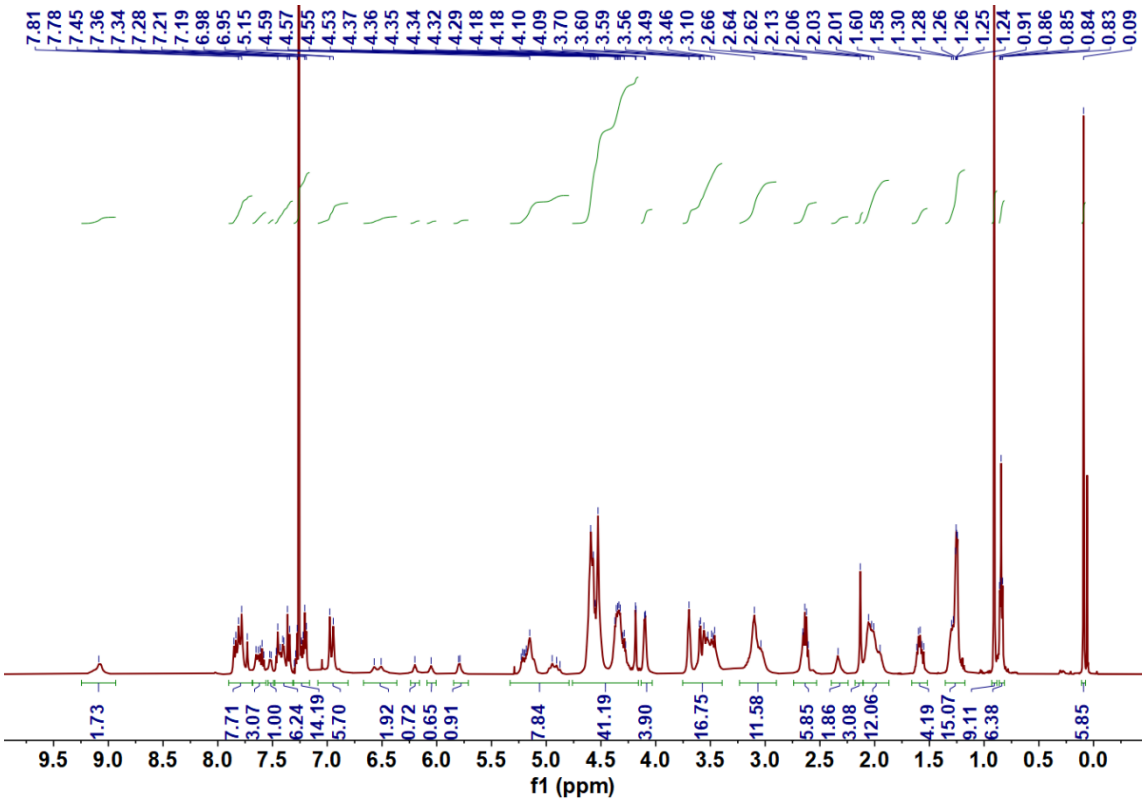


Figure S71. ^{1}H NMR of **C_6CIIDC_6.**

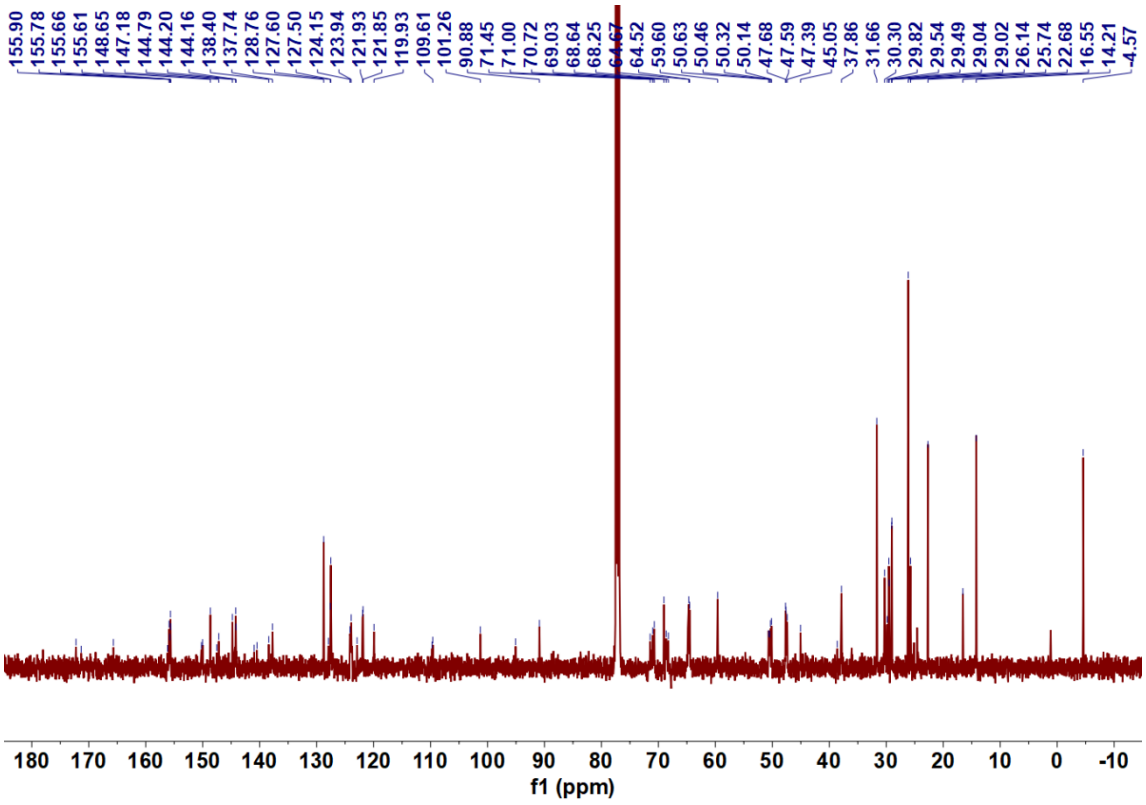


Figure S72. ^{13}C NMR of **C_6CIIDC_6**.

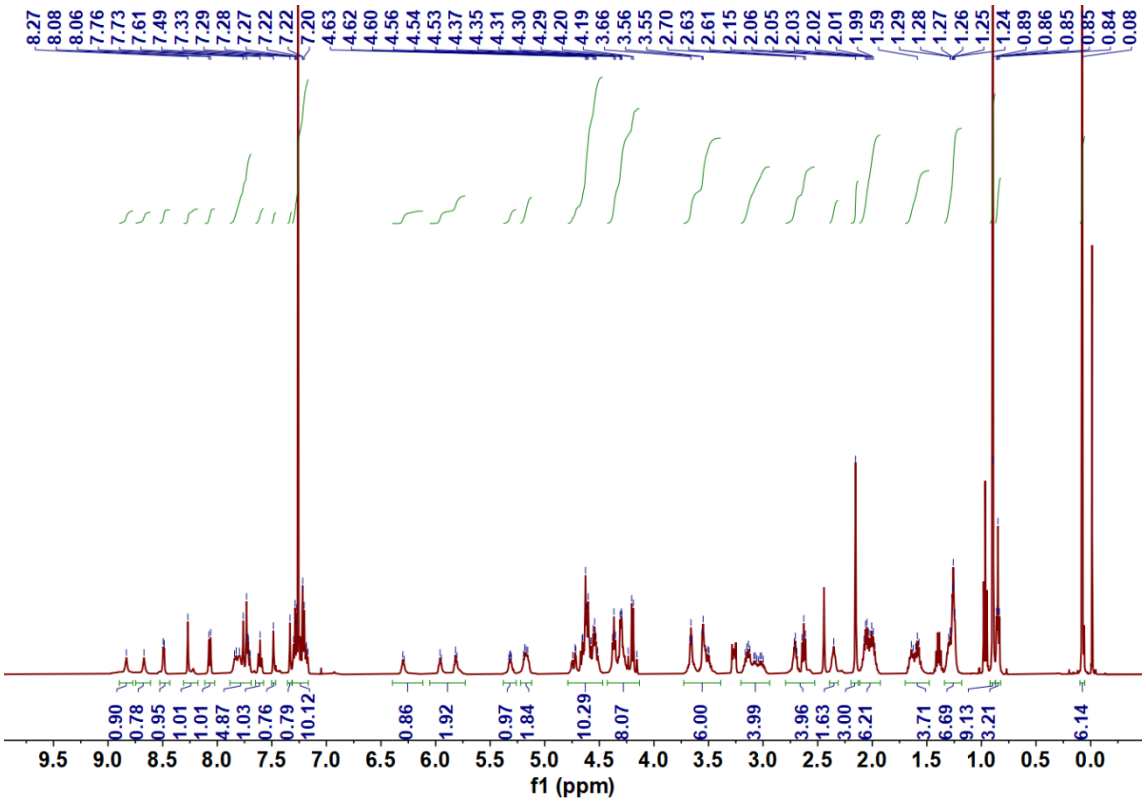


Figure S73. ^{1}H NMR of **PDC$_6$.**

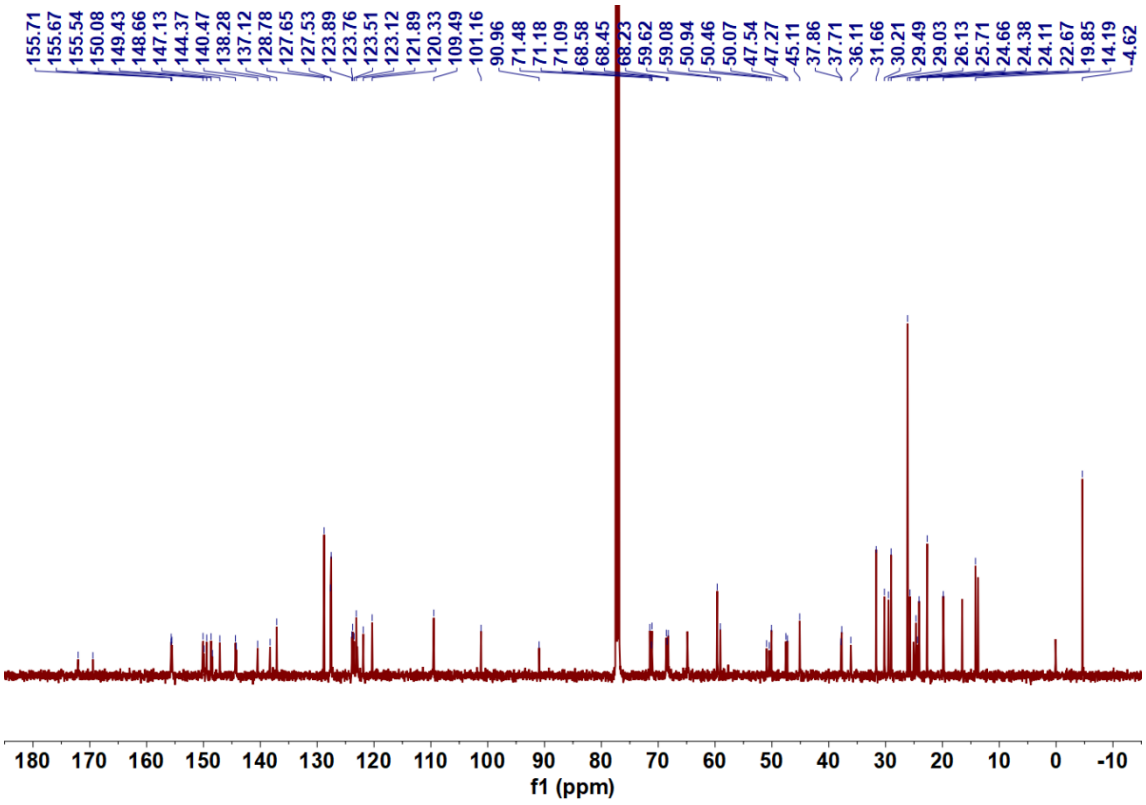


Figure S74. ^{13}C NMR of **PDC$_6$**.

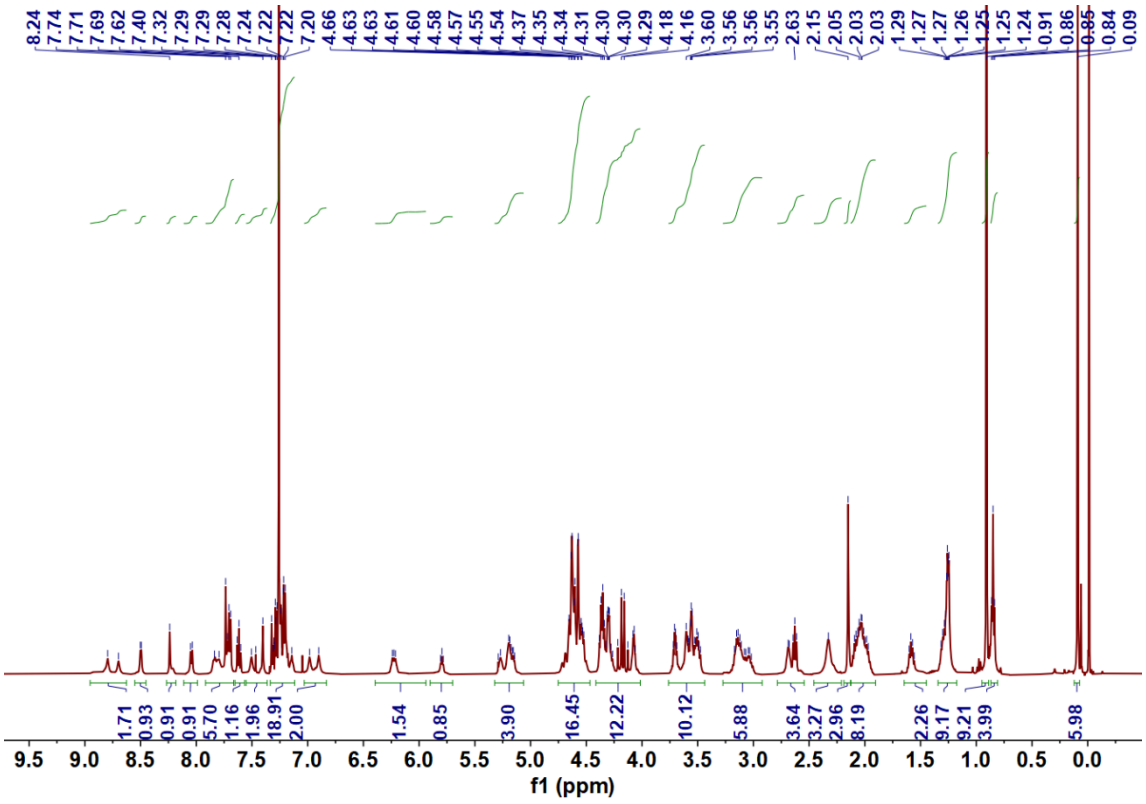


Figure S75. ^{1}H NMR of **IPDC$_6$.**

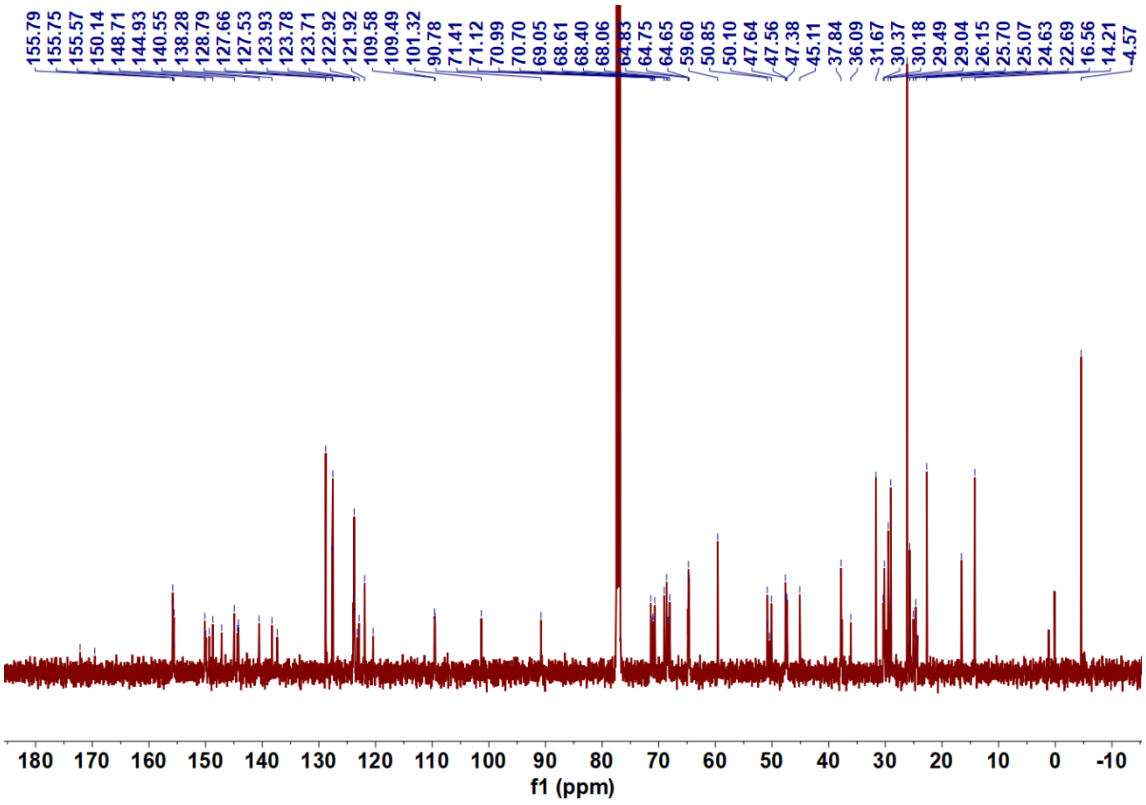


Figure S76. ^{13}C NMR of **IPDC$_6$**.

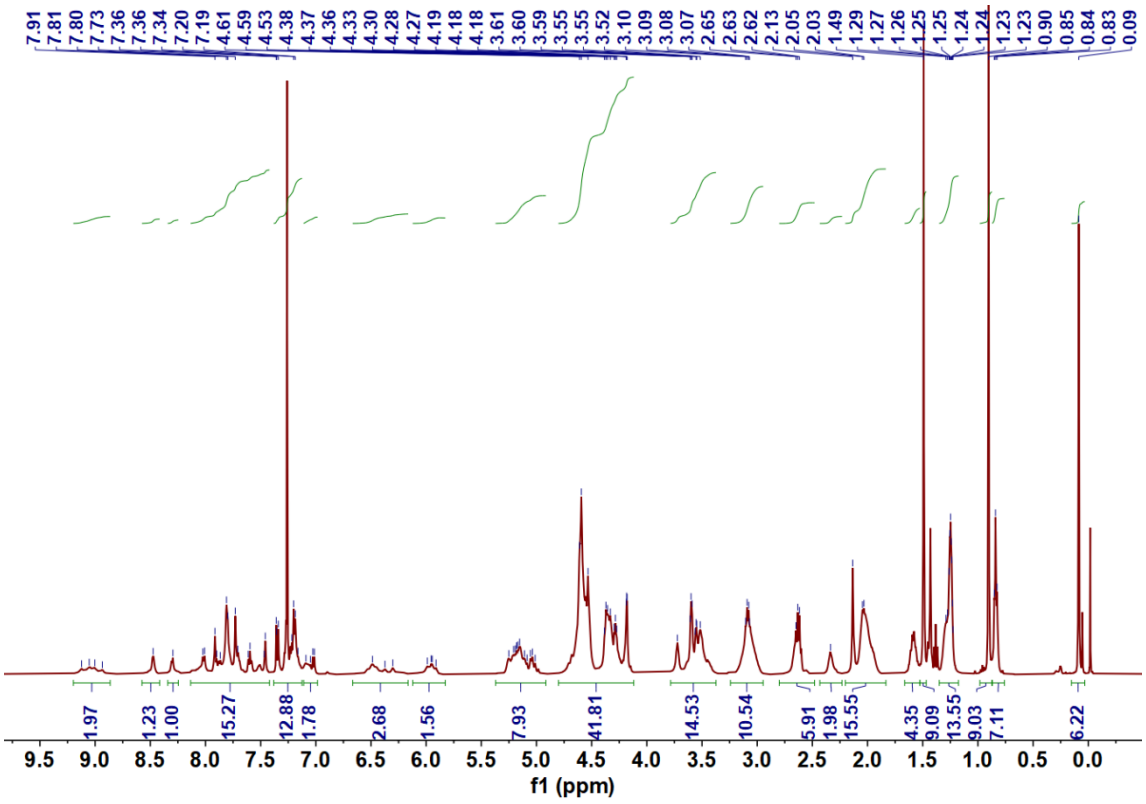


Figure S77. ^{1}H NMR of **35.**

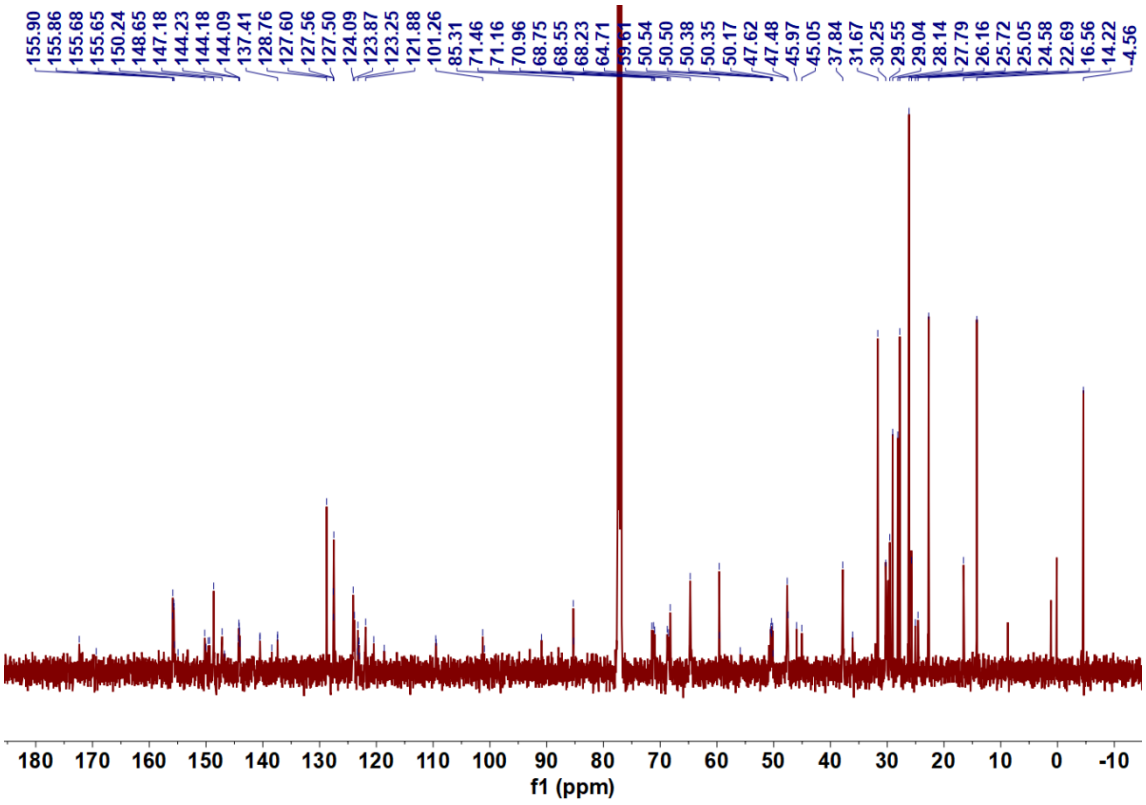


Figure S78. ^{13}C NMR of **35**.

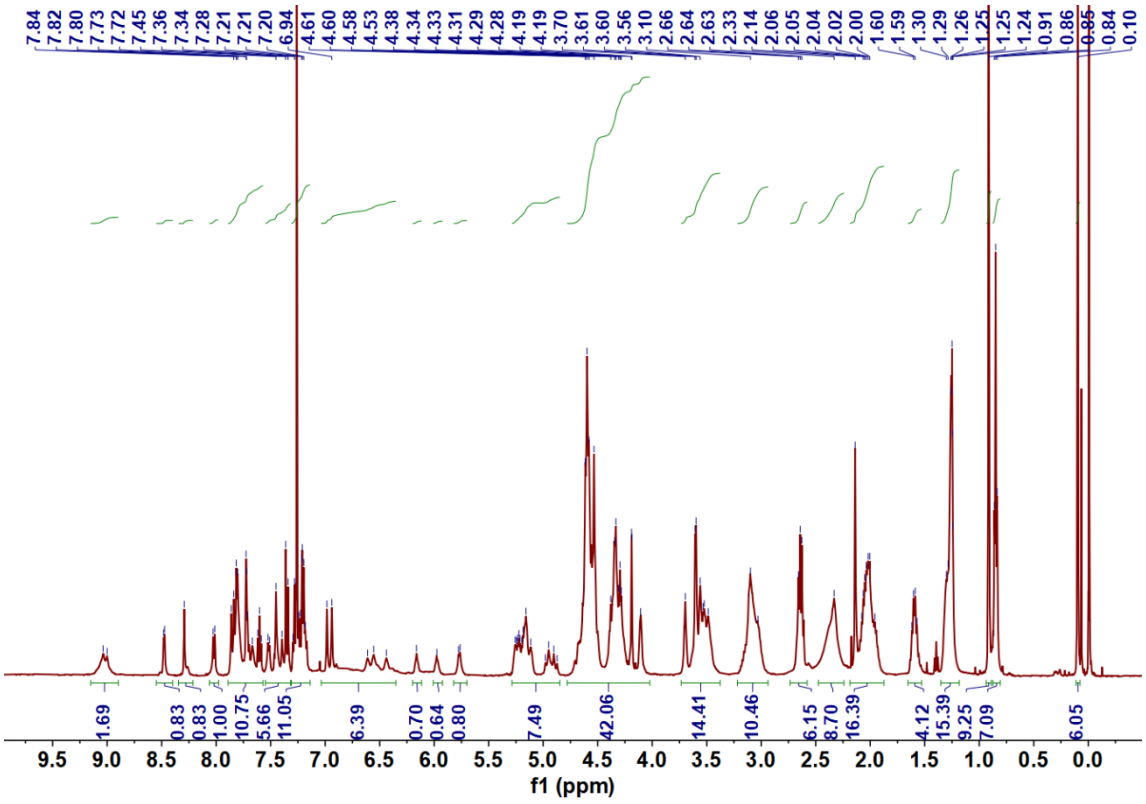


Figure S79. ^{1}H NMR of **C_6CIPDC$_6$.**

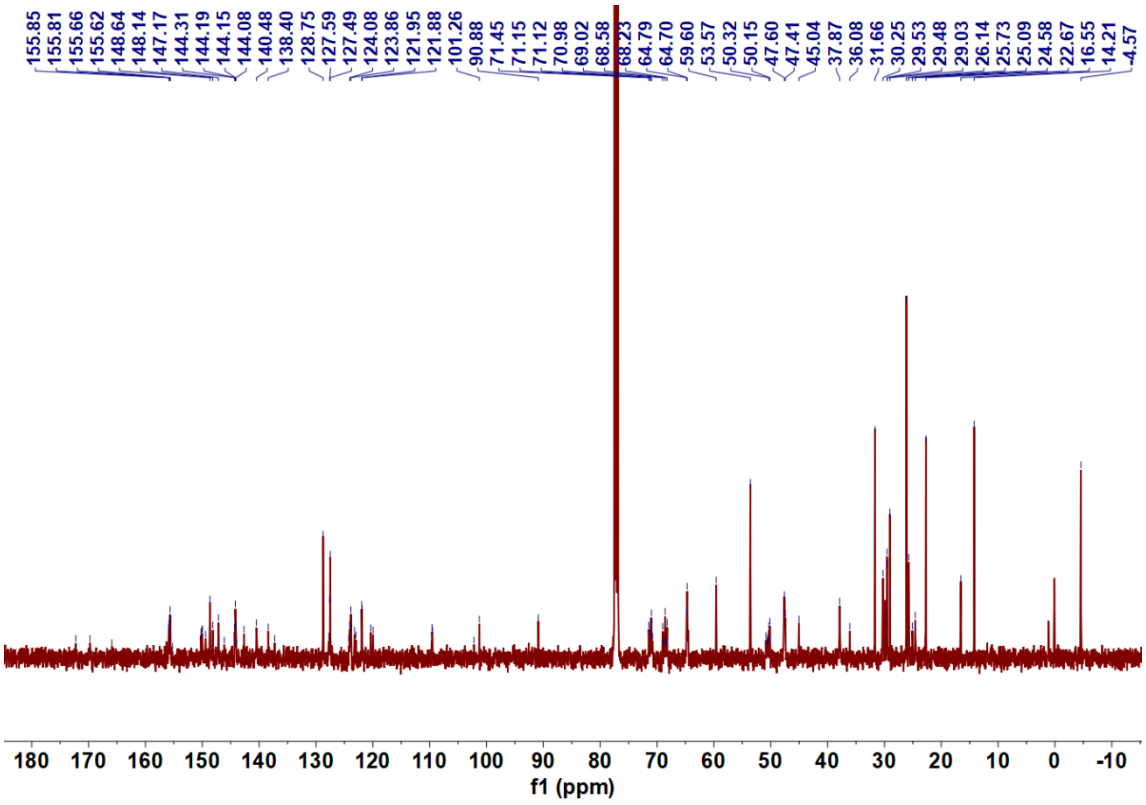


Figure S80. ^{13}C NMR of **C_6CIPDC$_6$**.

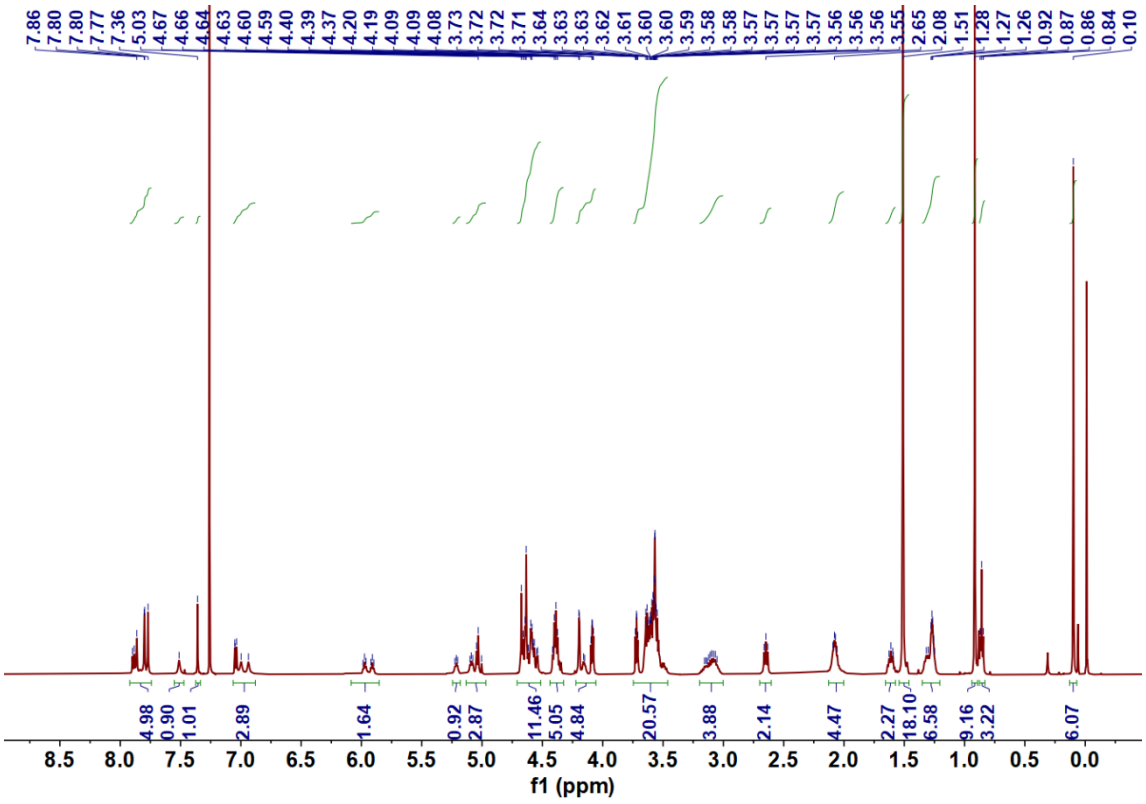


Figure S81. ^{1}H NMR of **C_6CI'.**

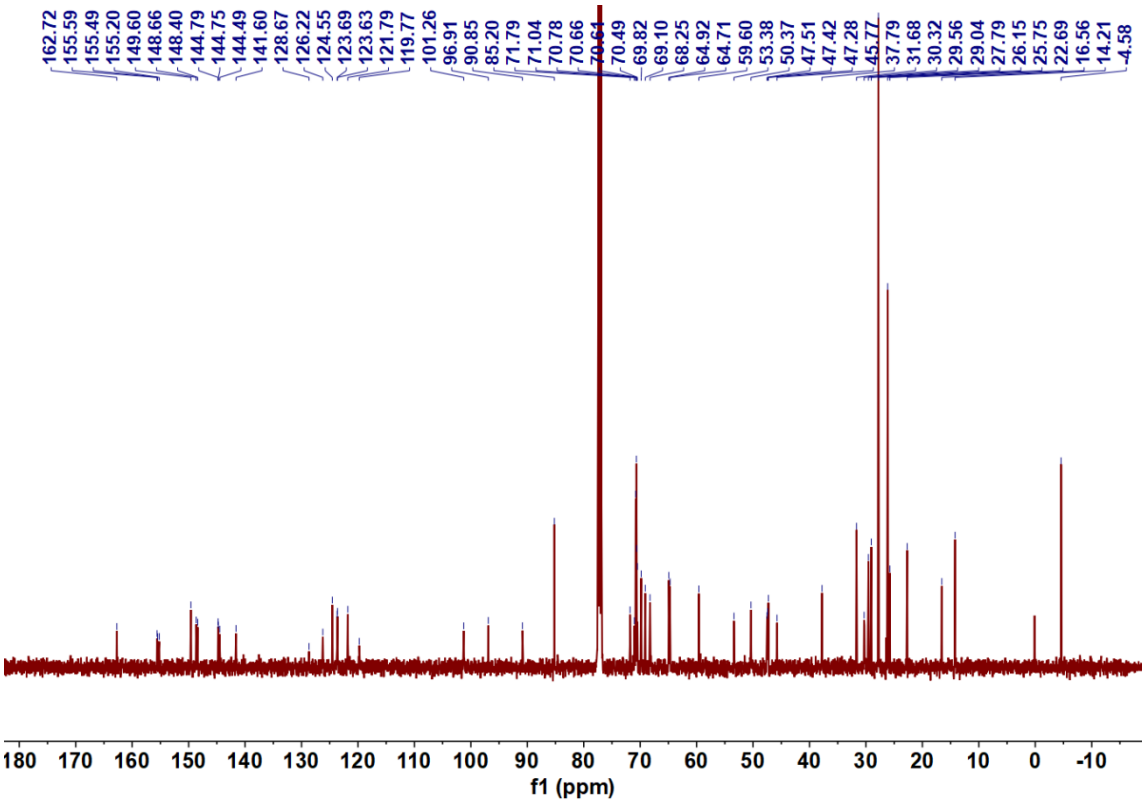


Figure S82. ^{13}C NMR of **C_6CI'.**

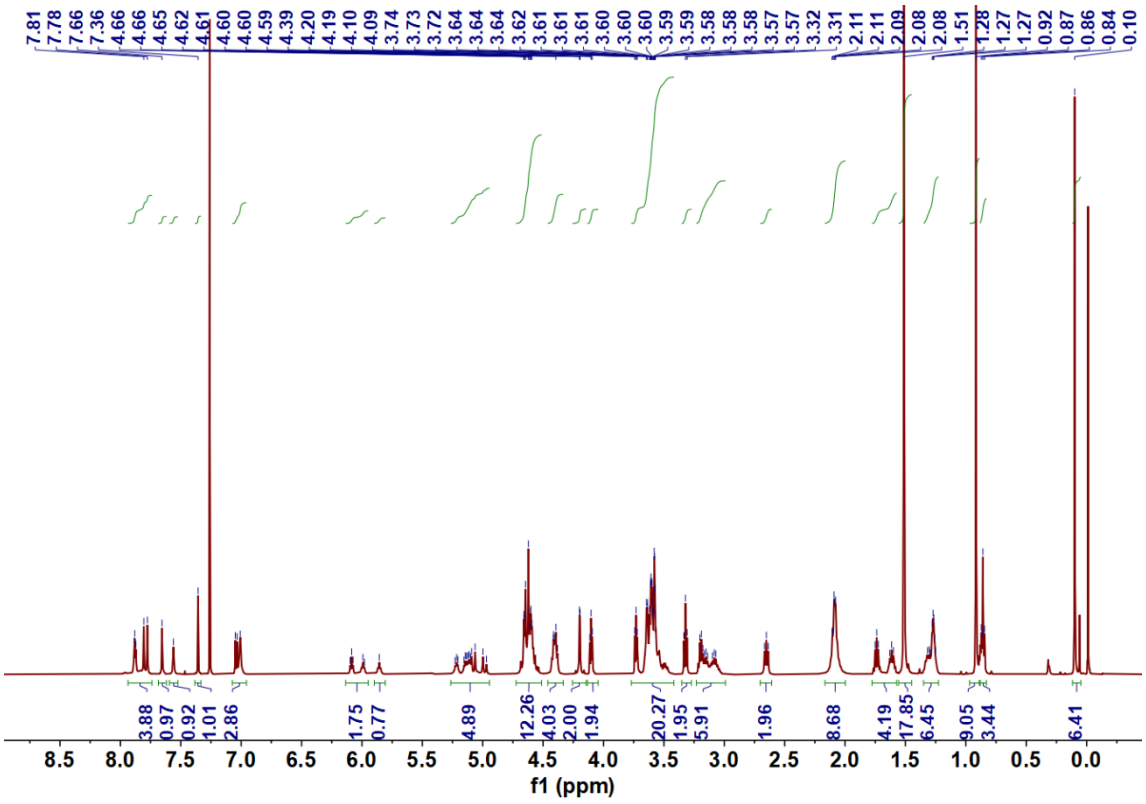


Figure S83. ^{1}H NMR of **36.**

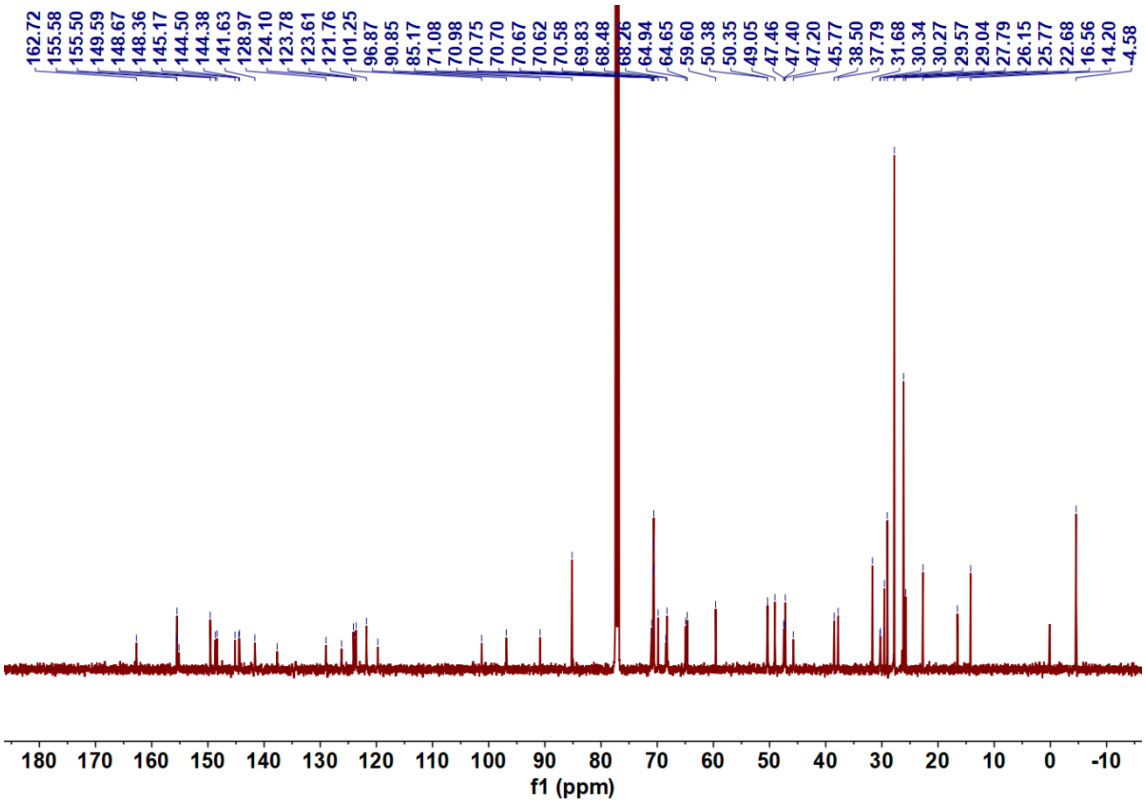


Figure S84. ^{13}C NMR of **36.**

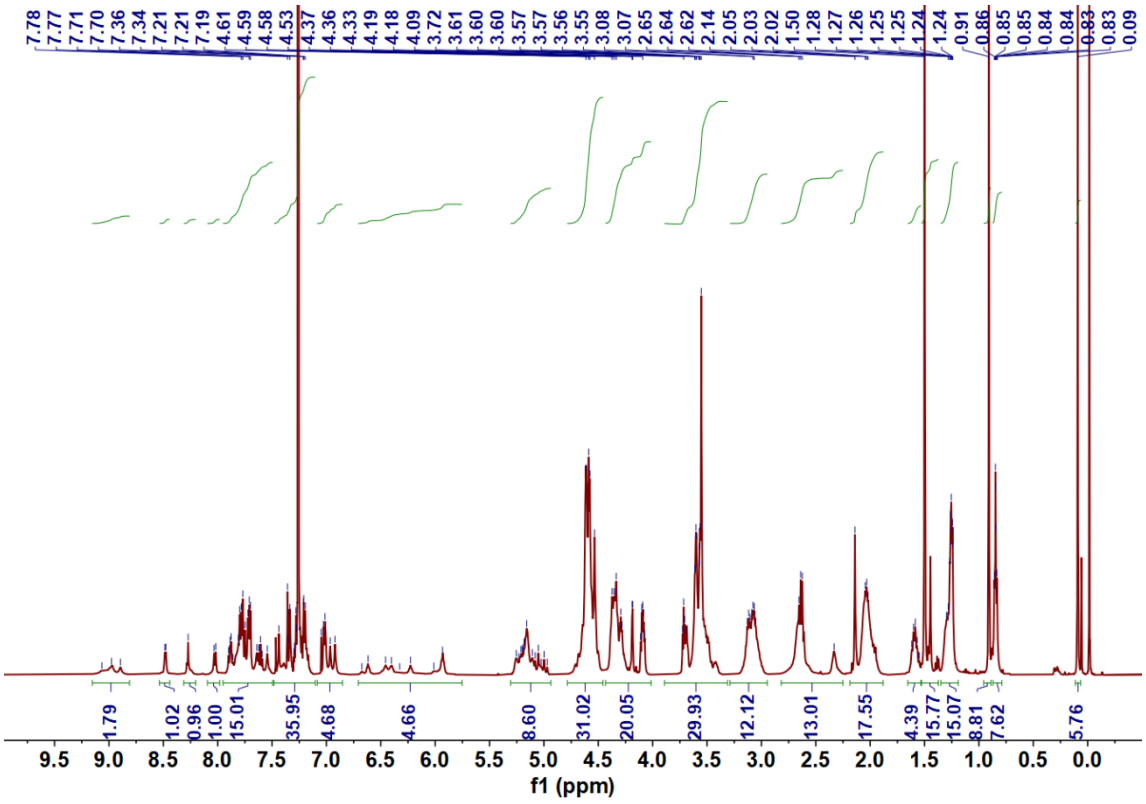


Figure S85. ^{1}H NMR of **37.**

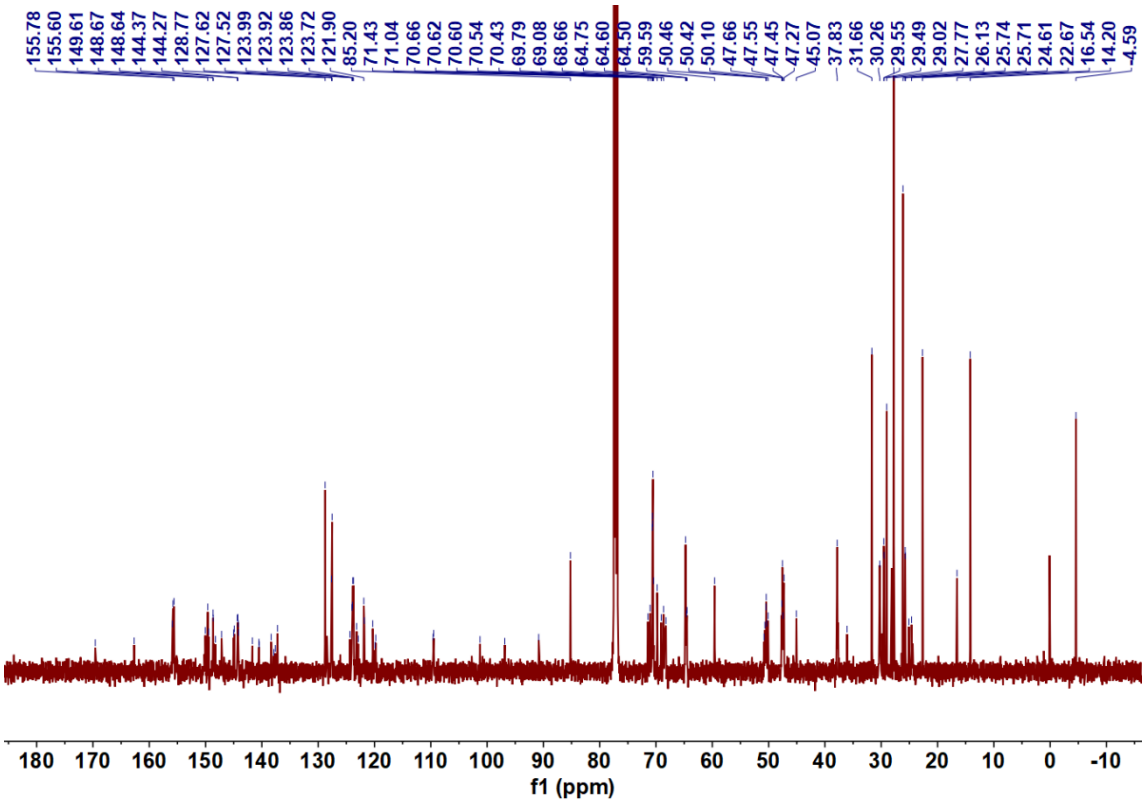


Figure S86. ^{13}C NMR of **37.**

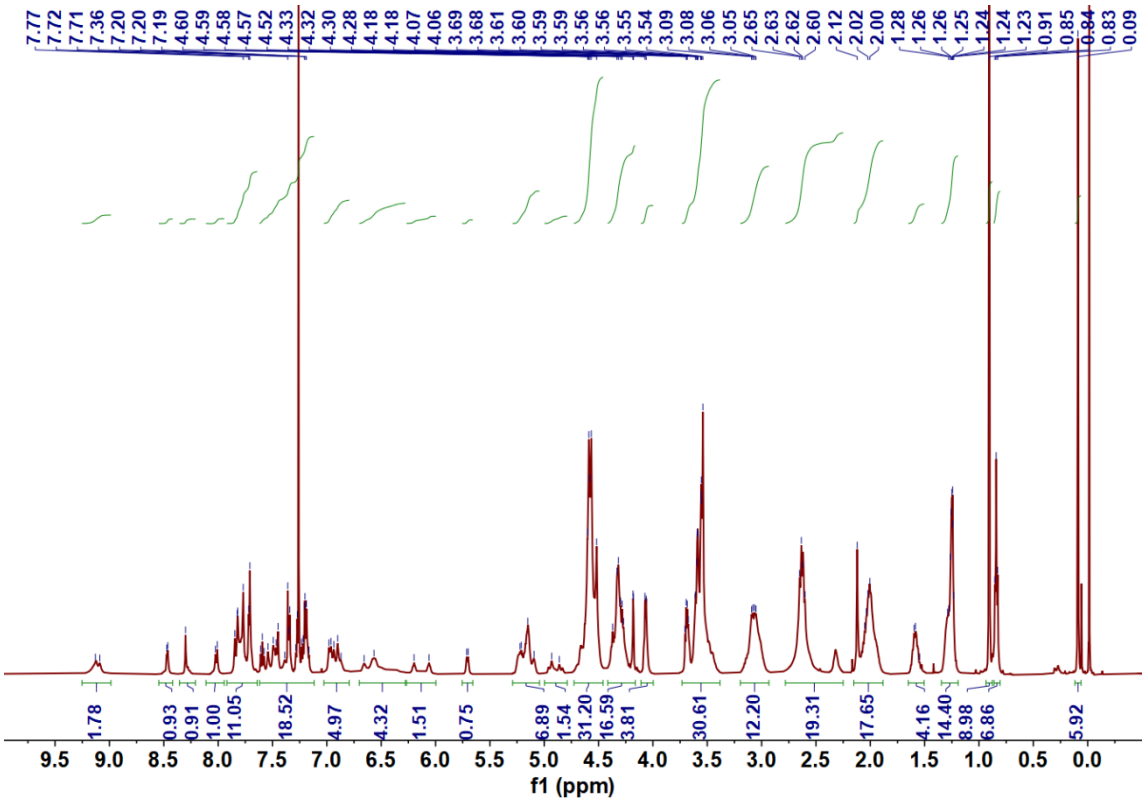


Figure S87. ^{1}H NMR of **C_6CI'IPDC_6.**

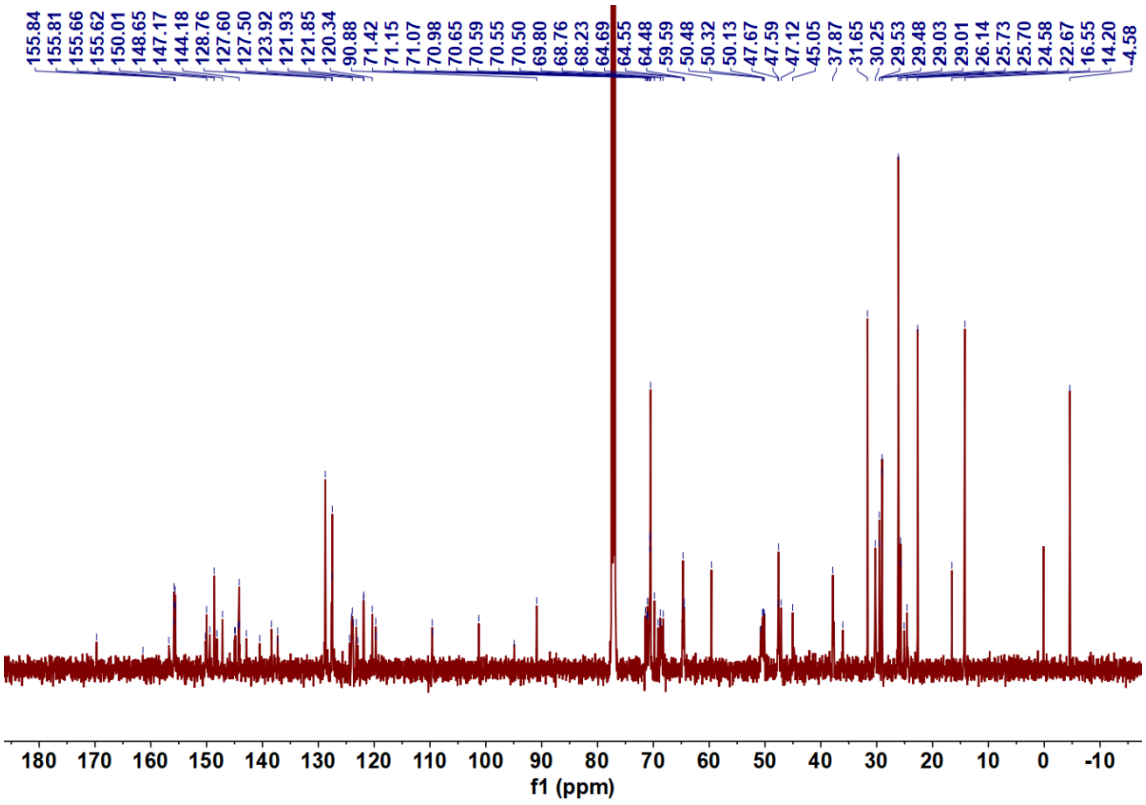


Figure S88. ^{13}C NMR of **C_6CI'IPDC_6.**

4 MS SPECTRA

4.1 HRMS

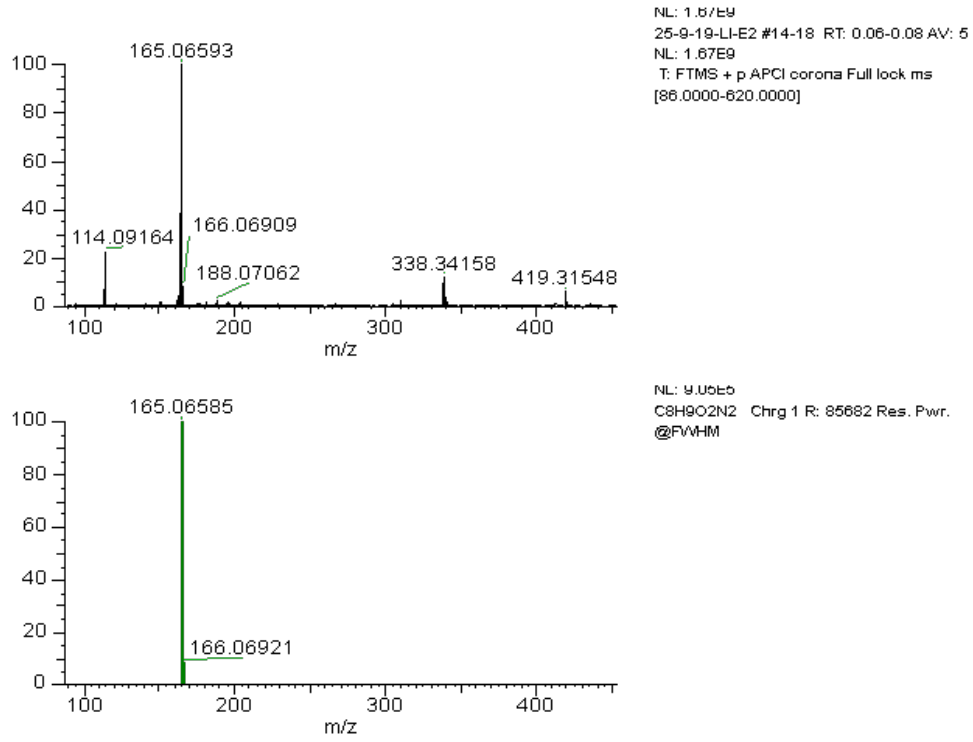


Figure S89. ESI-MS of **Base T**.

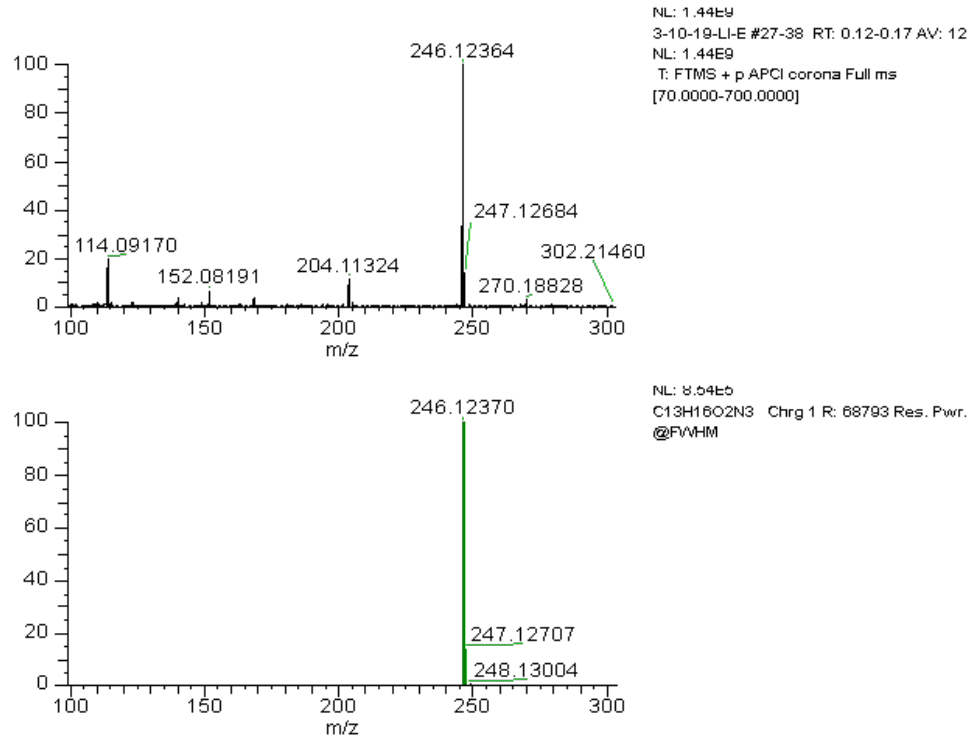


Figure S90. ESI-MS of **Base D**.

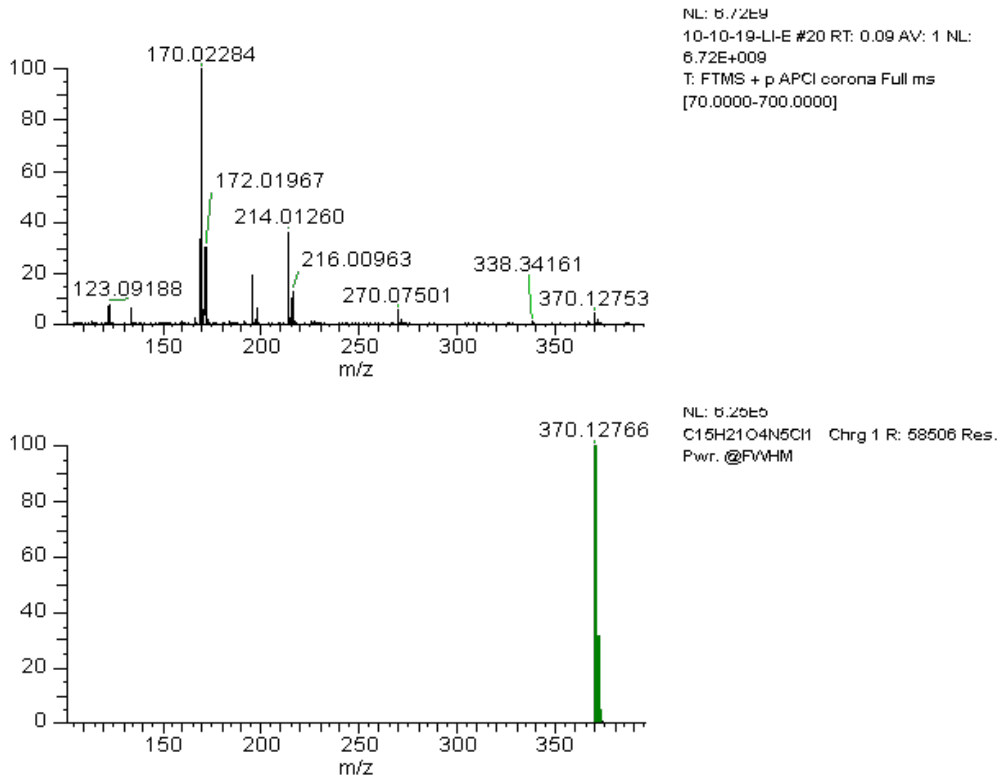


Figure S91. ESI-MS of **8**.

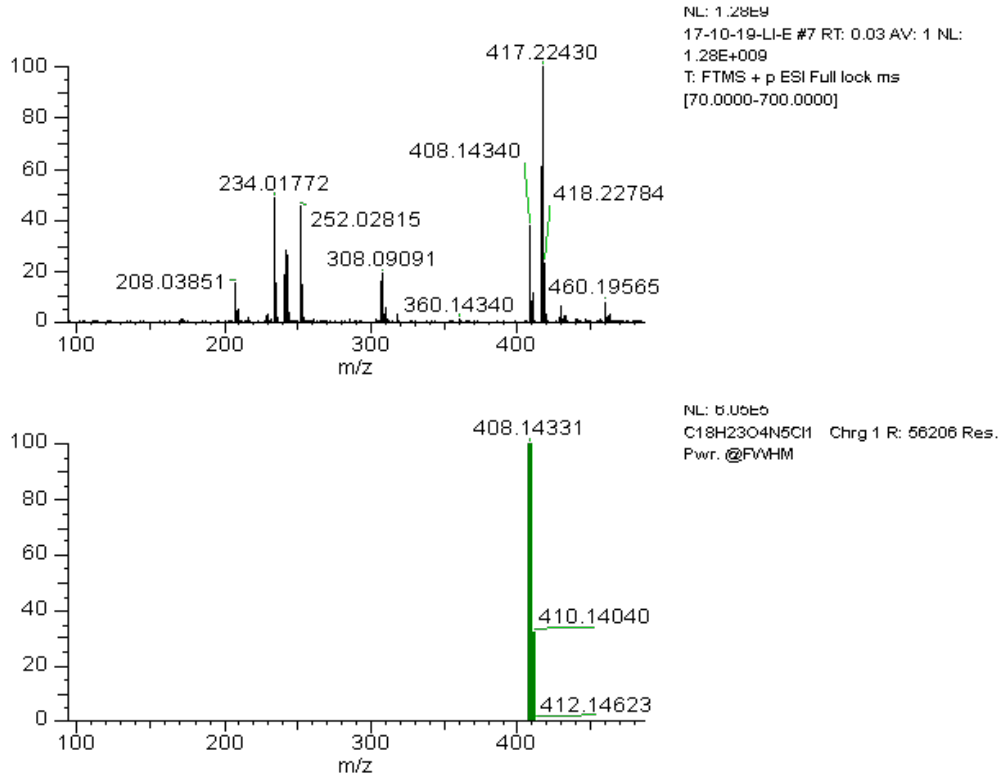


Figure S92. ESI-MS of **Base G**.

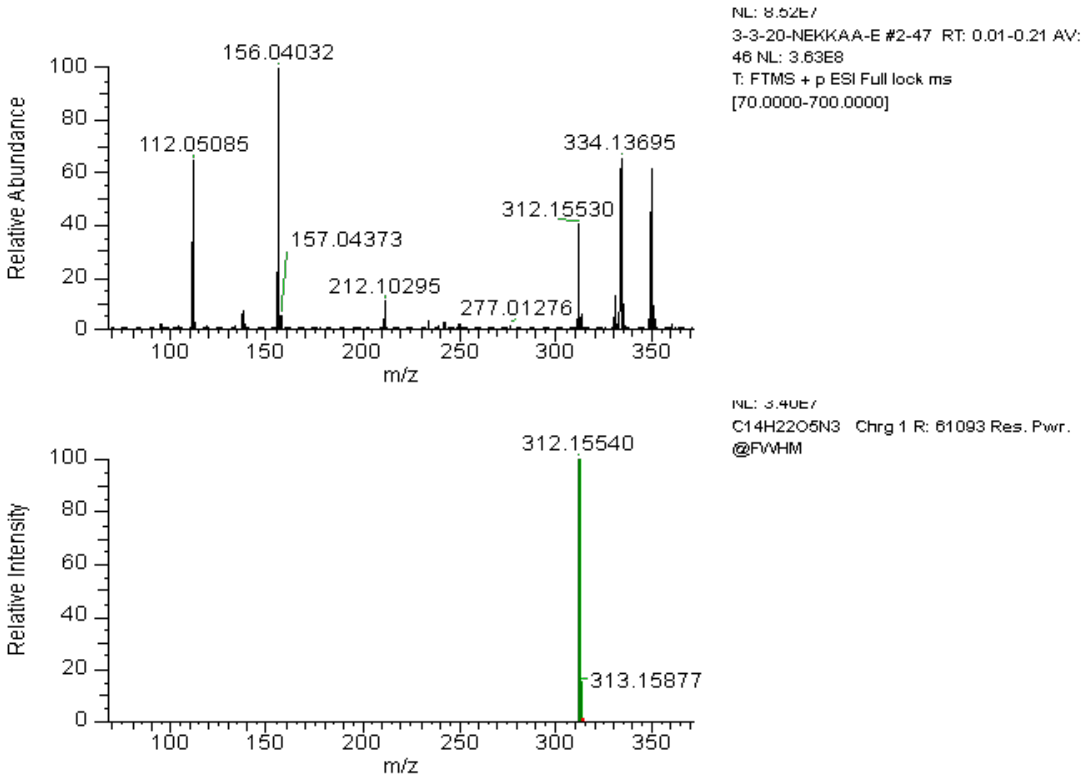


Figure S93. ESI-MS of **9**.

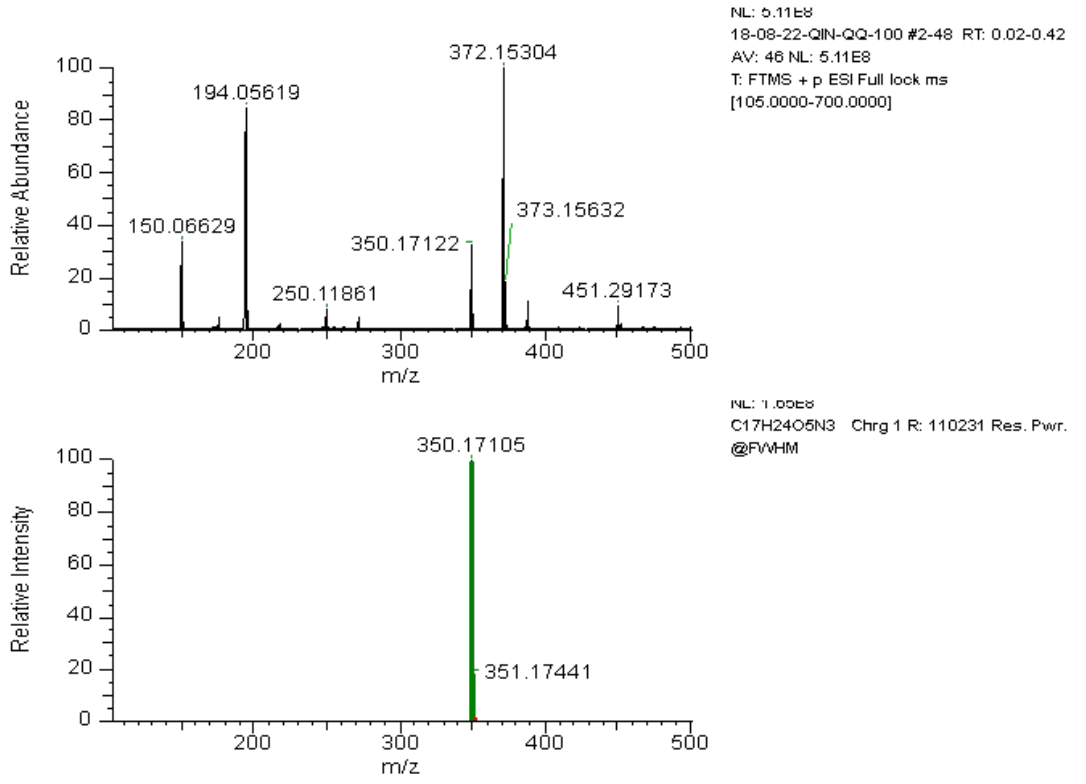


Figure S94. ESI-MS of **Base C**.

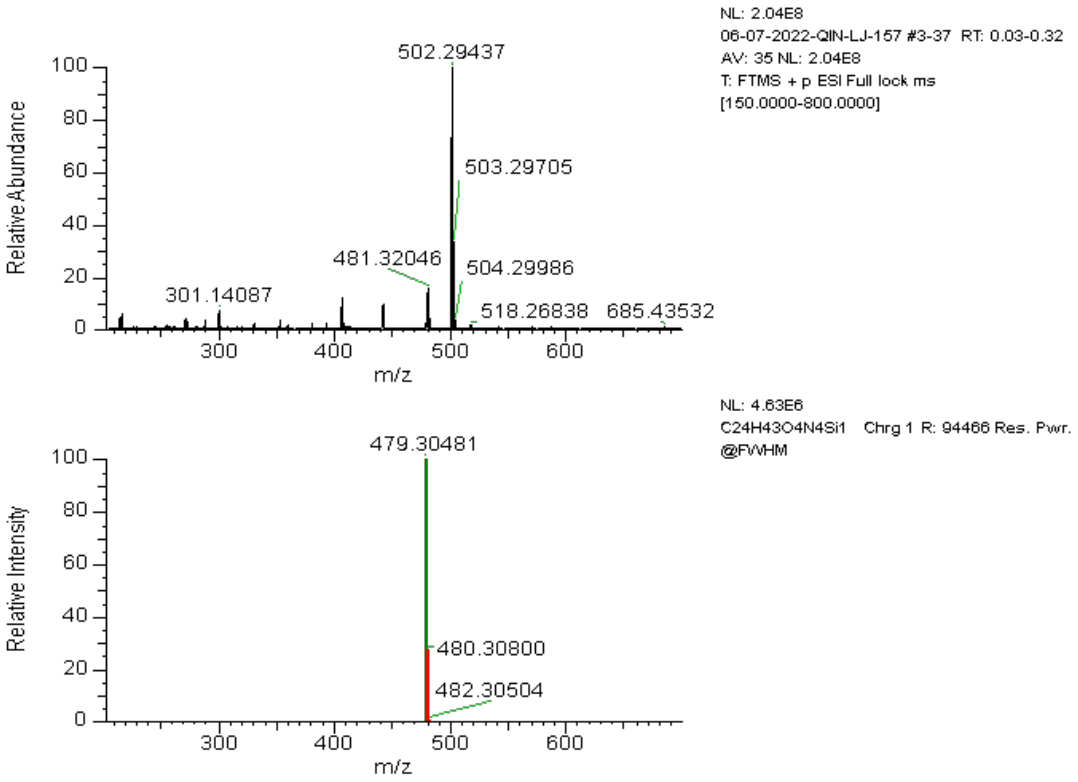


Figure S95. ESI-MS of **10**.

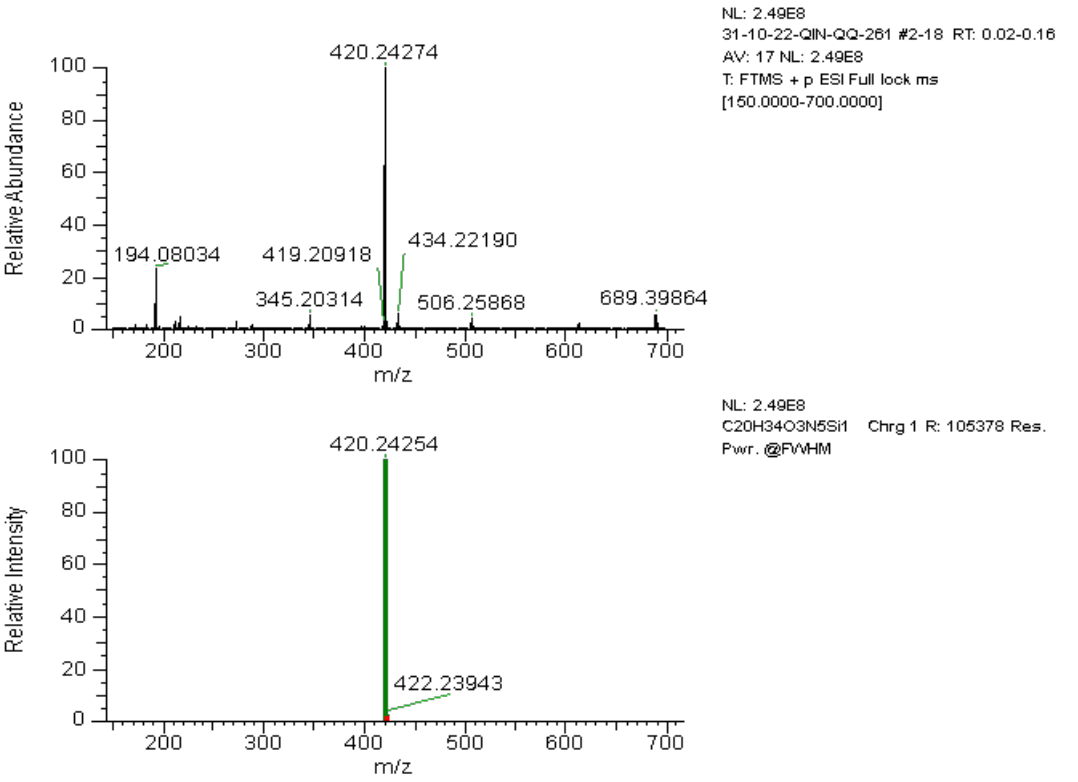


Figure S96. ESI-MS of **12**.

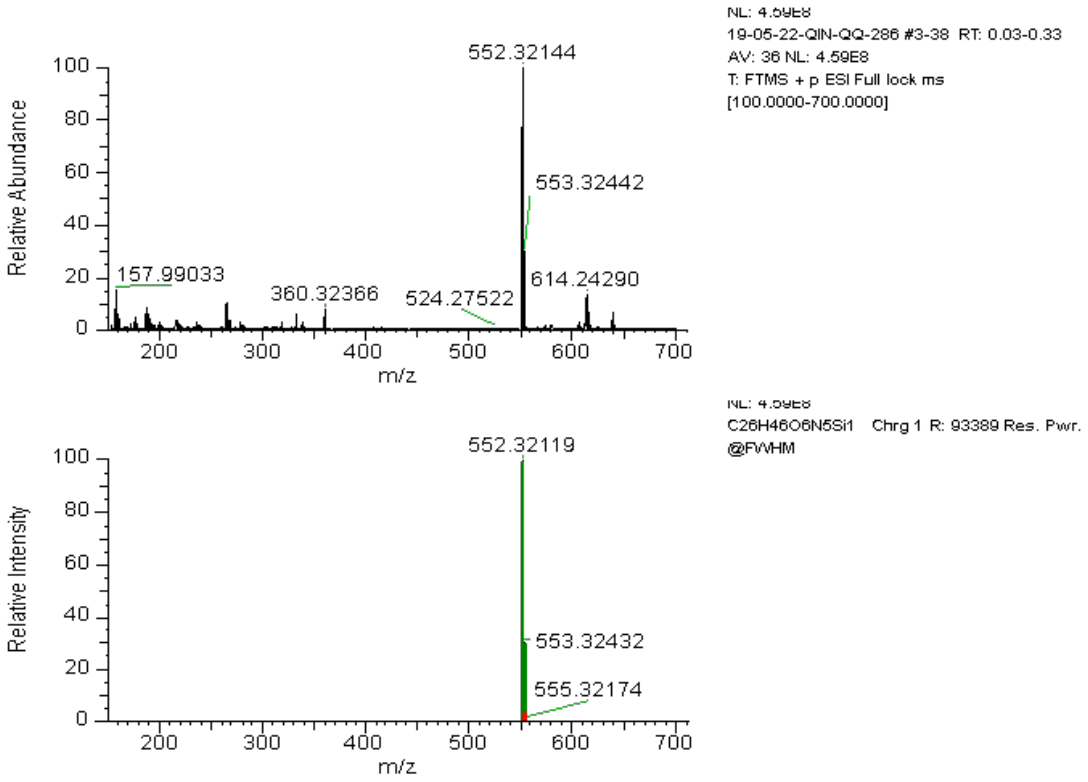


Figure S97. ESI-MS of **13**.

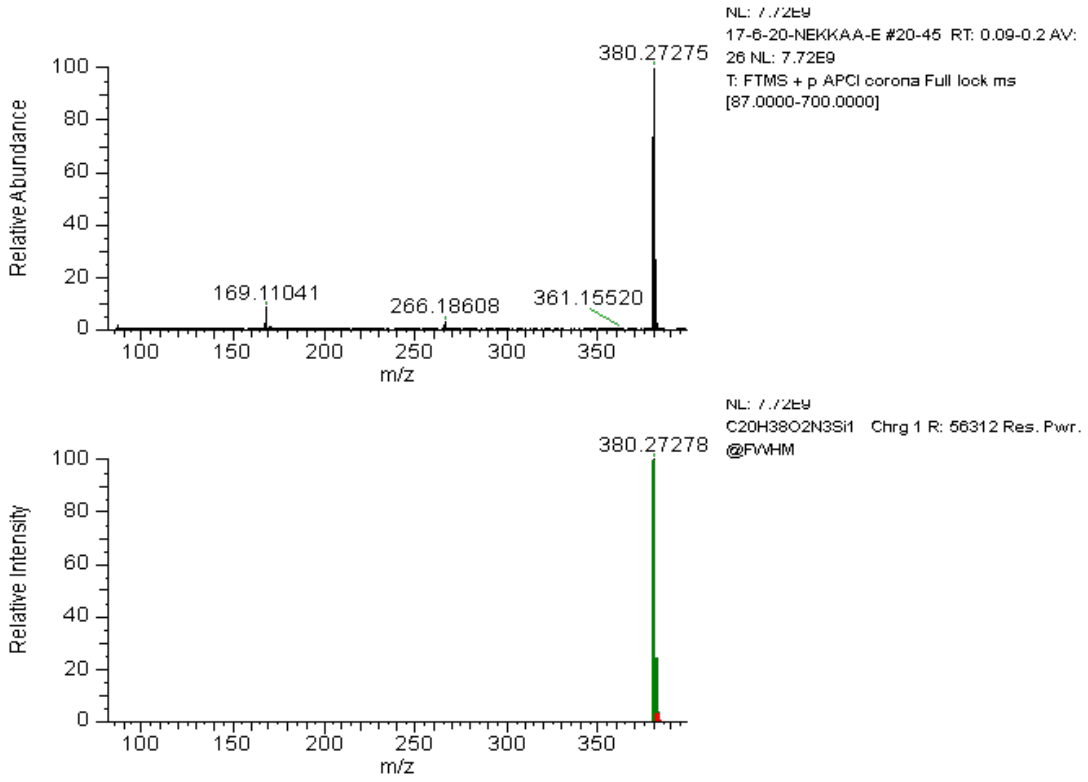


Figure S98. ESI-MS of **14**.

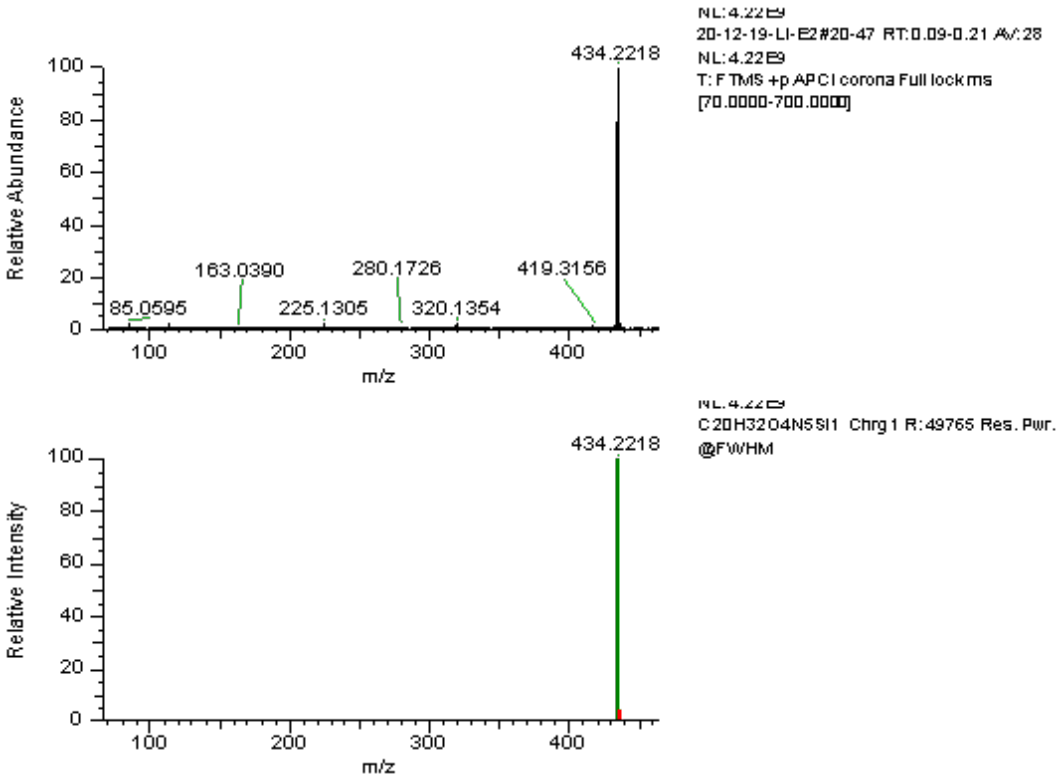


Figure S99. ESI-MS of **15**.

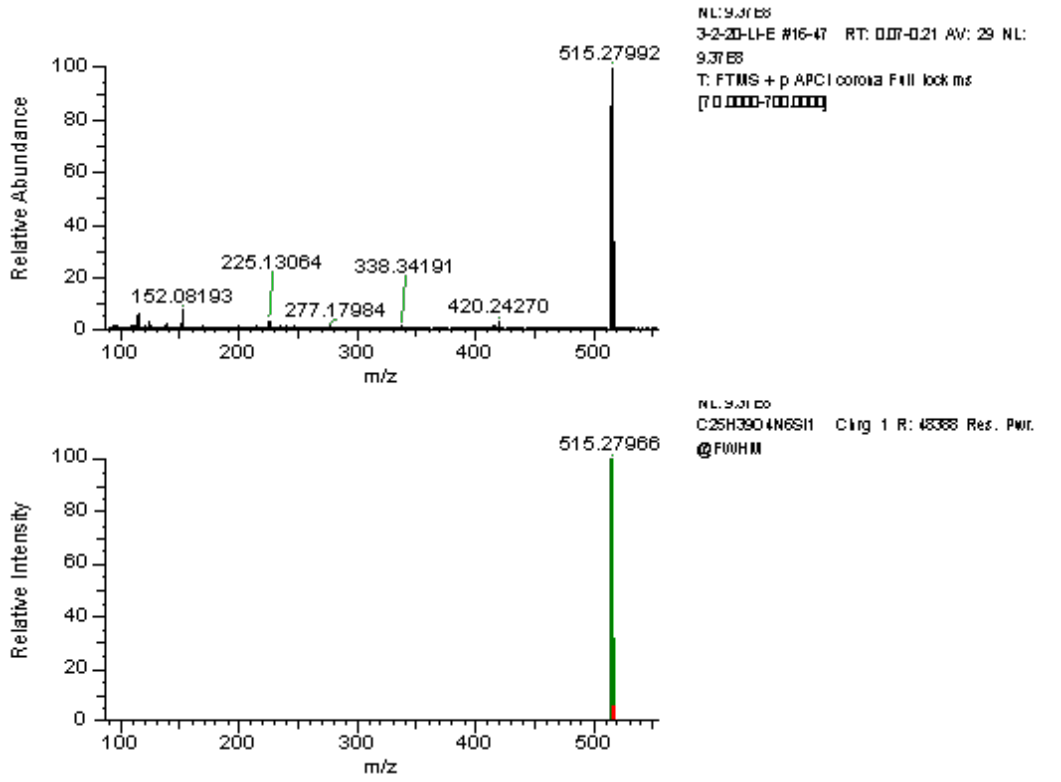


Figure S100. ESI-MS of **16**.

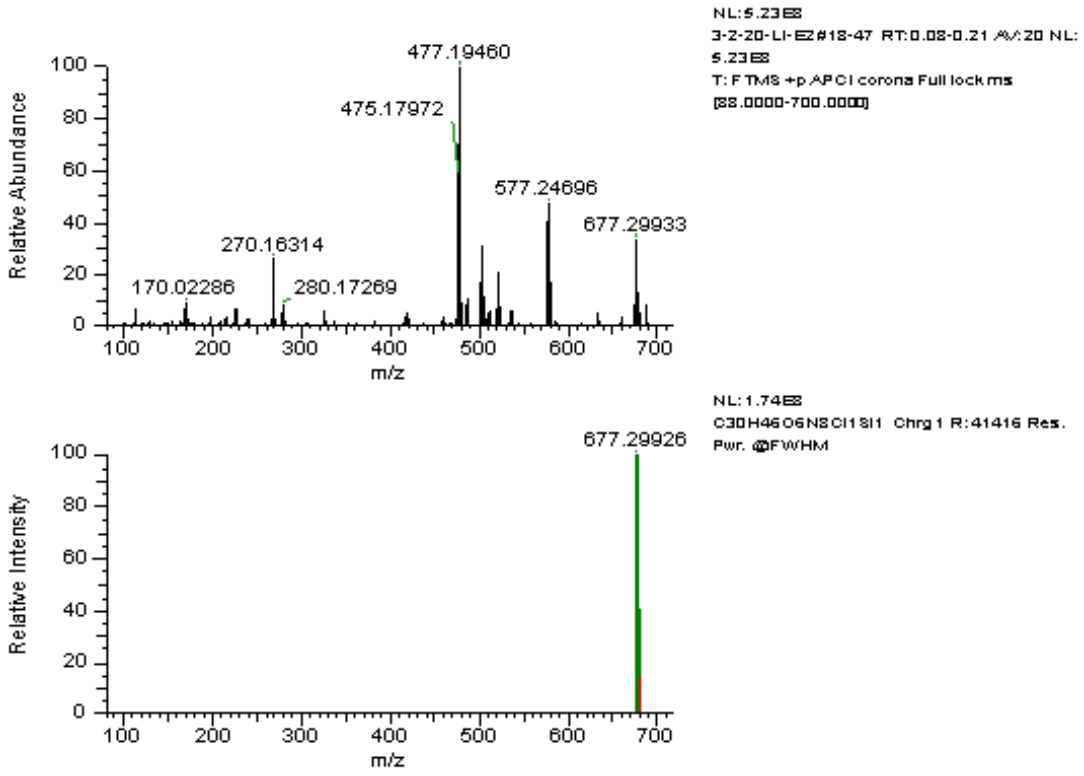


Figure S101. ESI-MS of **17**.

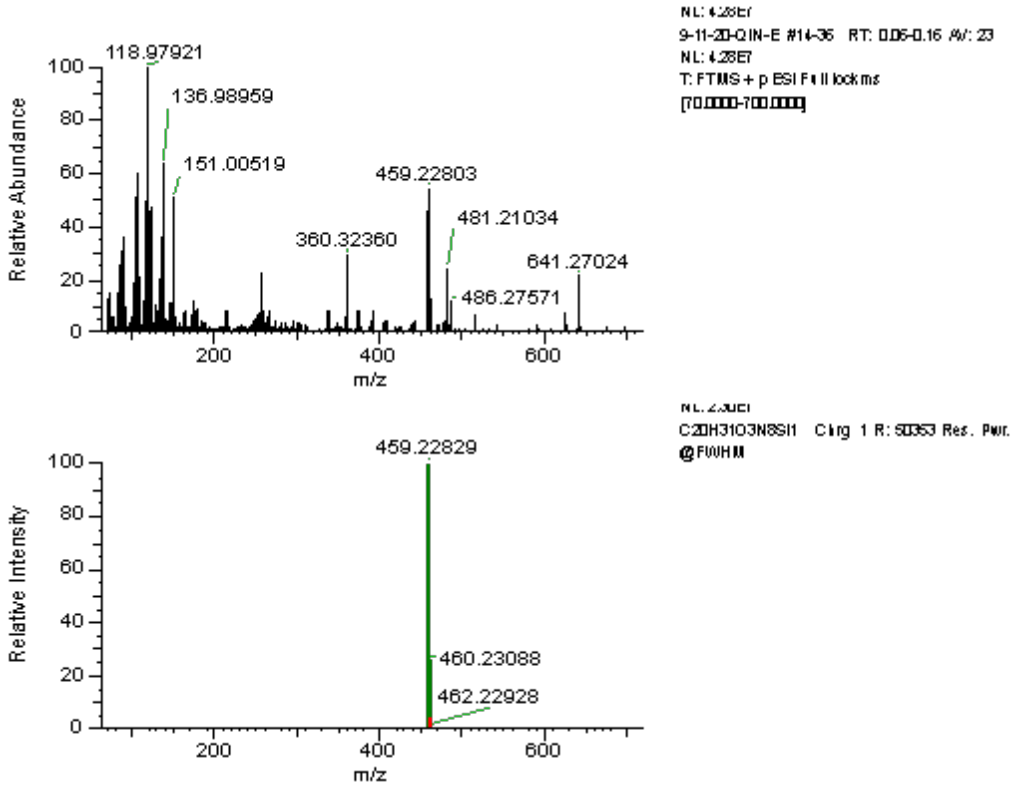


Figure S102. ESI-MS of **18**.

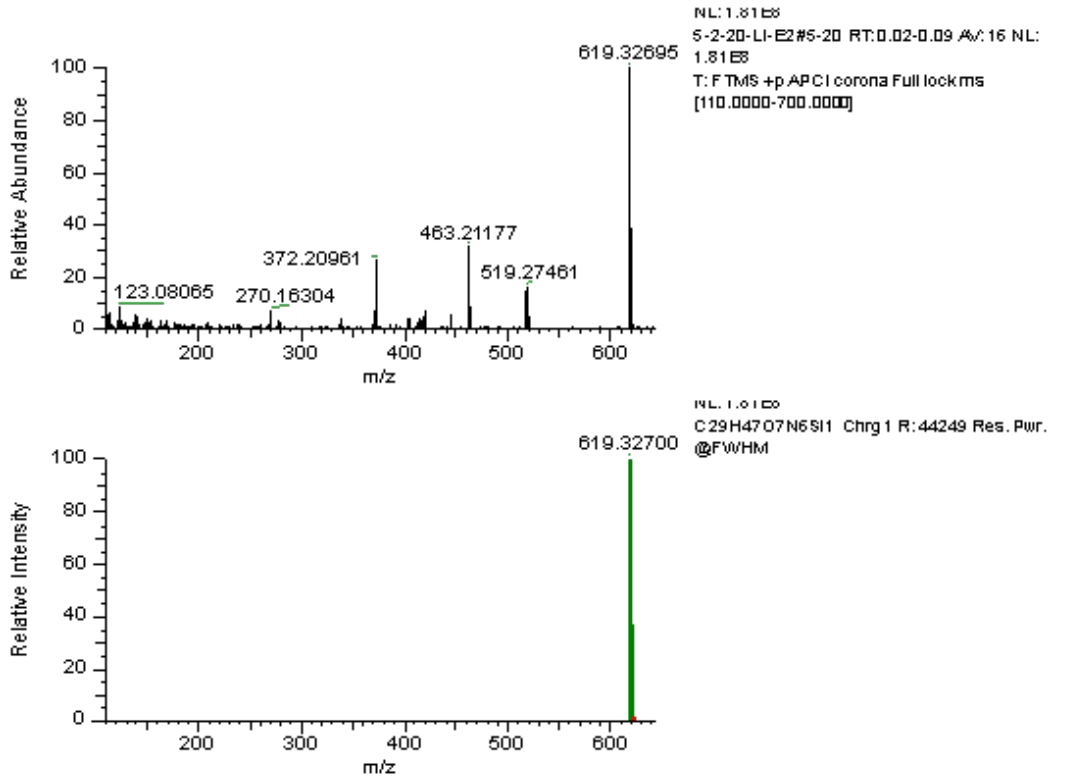


Figure S103. ESI-MS of **19**.

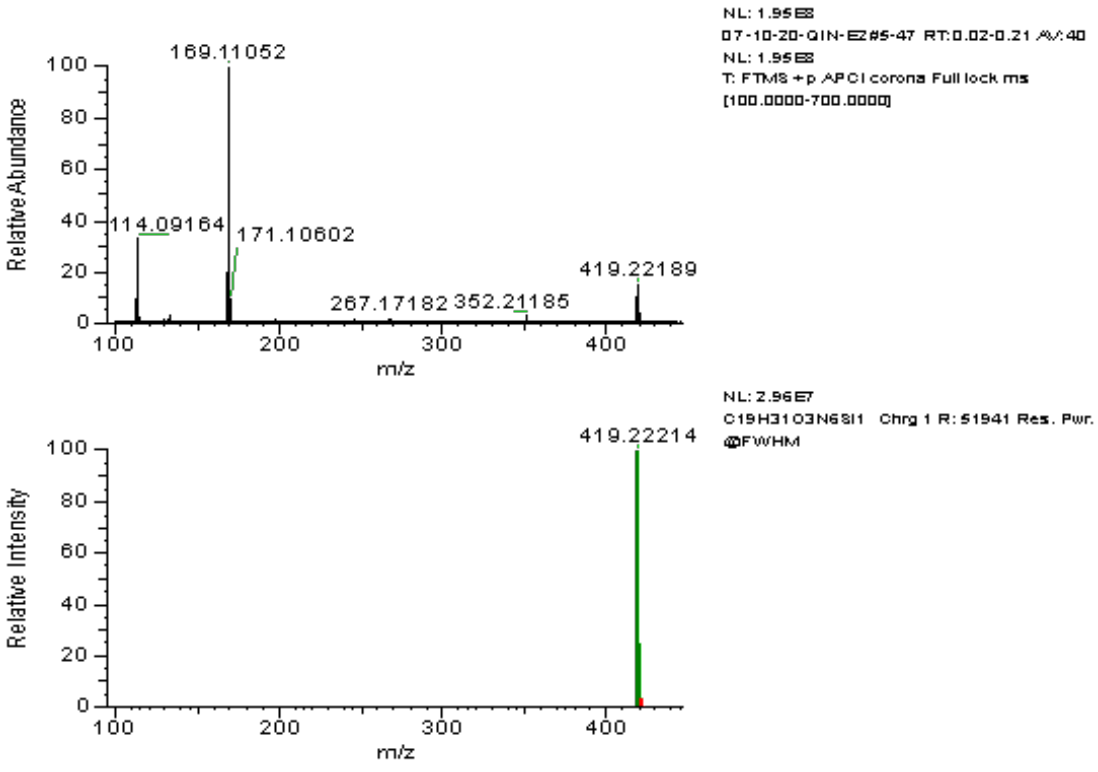


Figure S104. ESI-MS of **20**.

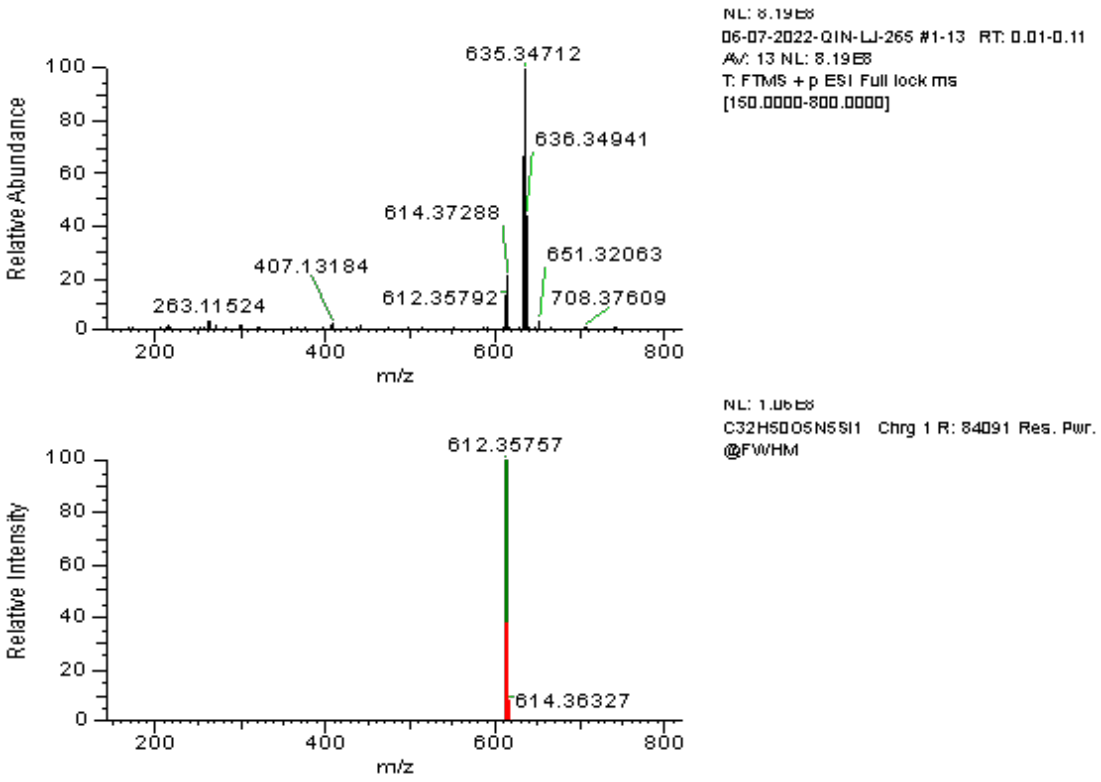


Figure S105. ESI-MS of **M**.

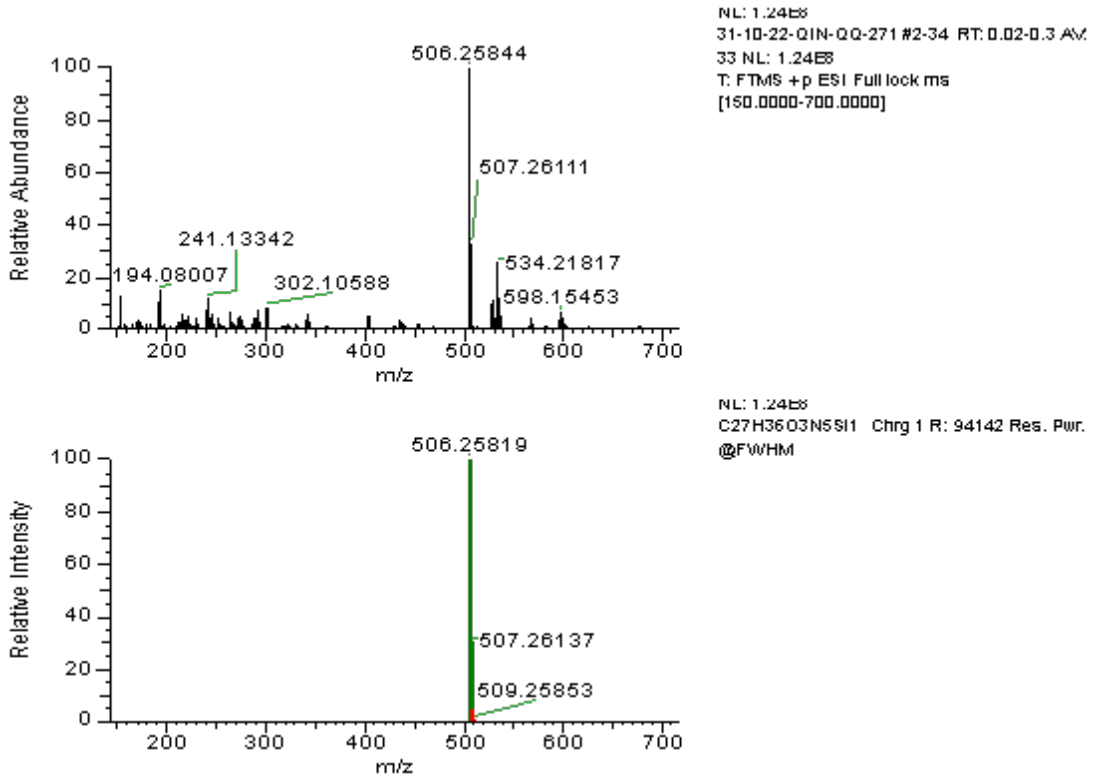


Figure S106. ESI-MS of **P**.

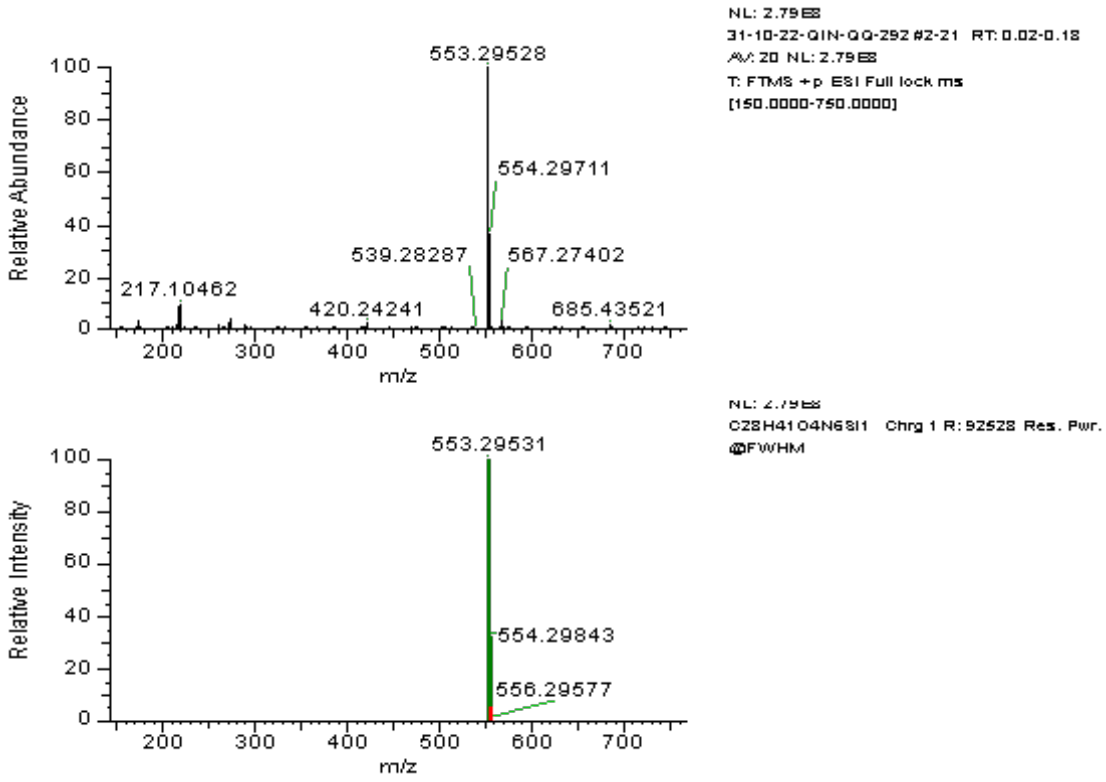


Figure S107. ESI-MS of **I**.

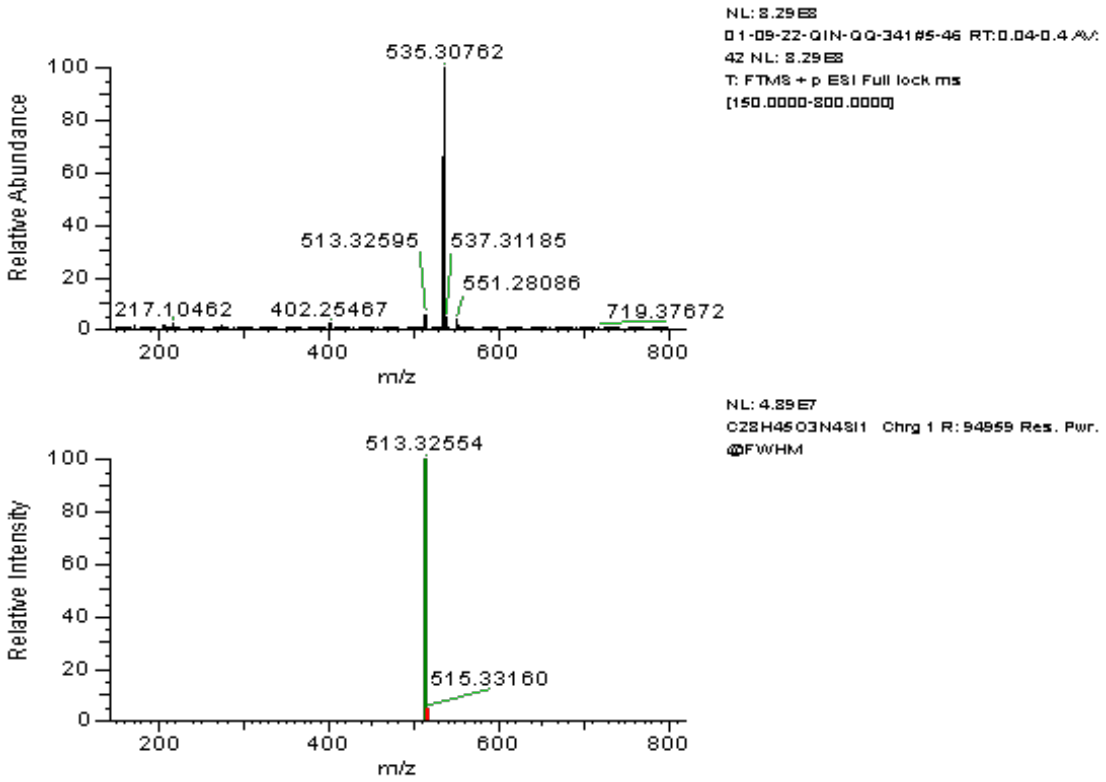


Figure S108. ESI-MS of **C$_6$**.

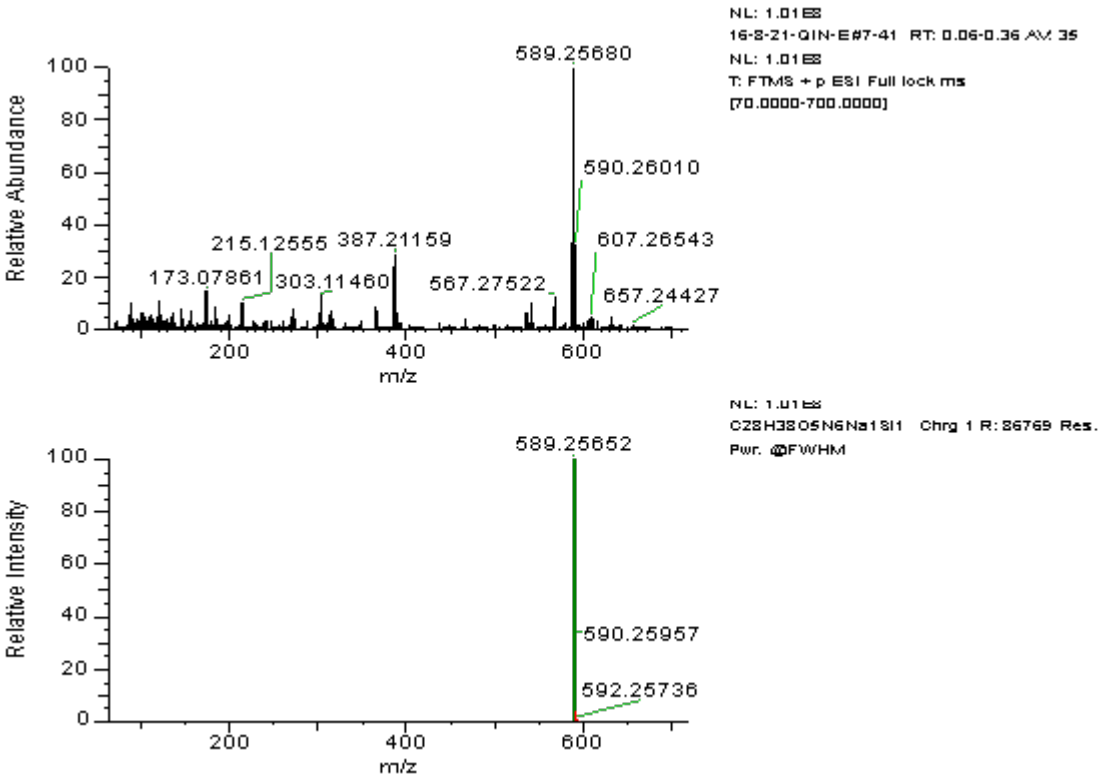


Figure S109. ESI-MS of **T**.

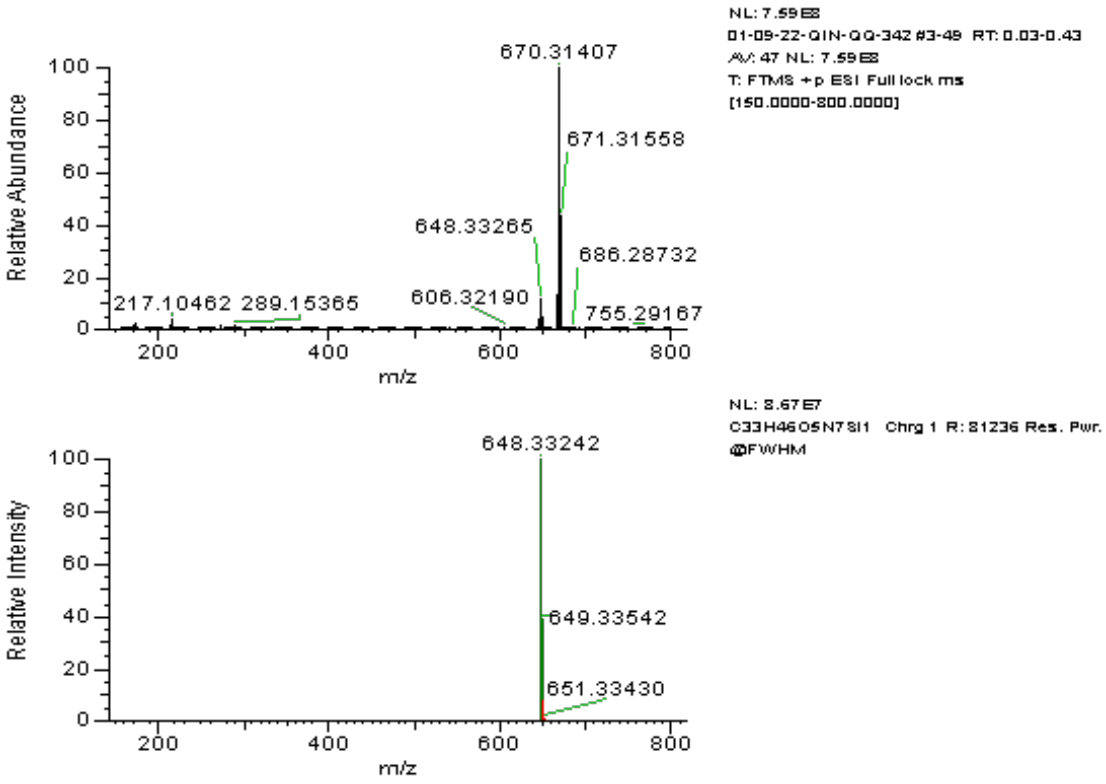


Figure S110. ESI-MS of **D**.

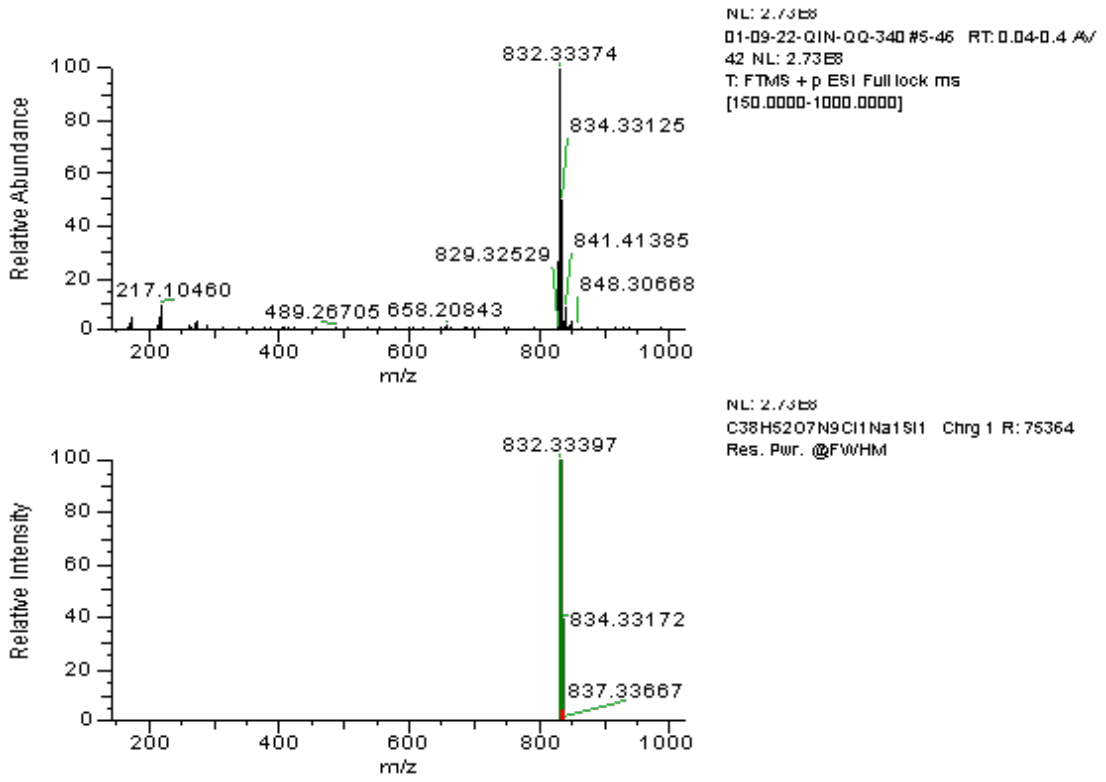


Figure S111. ESI-MS of **21**.

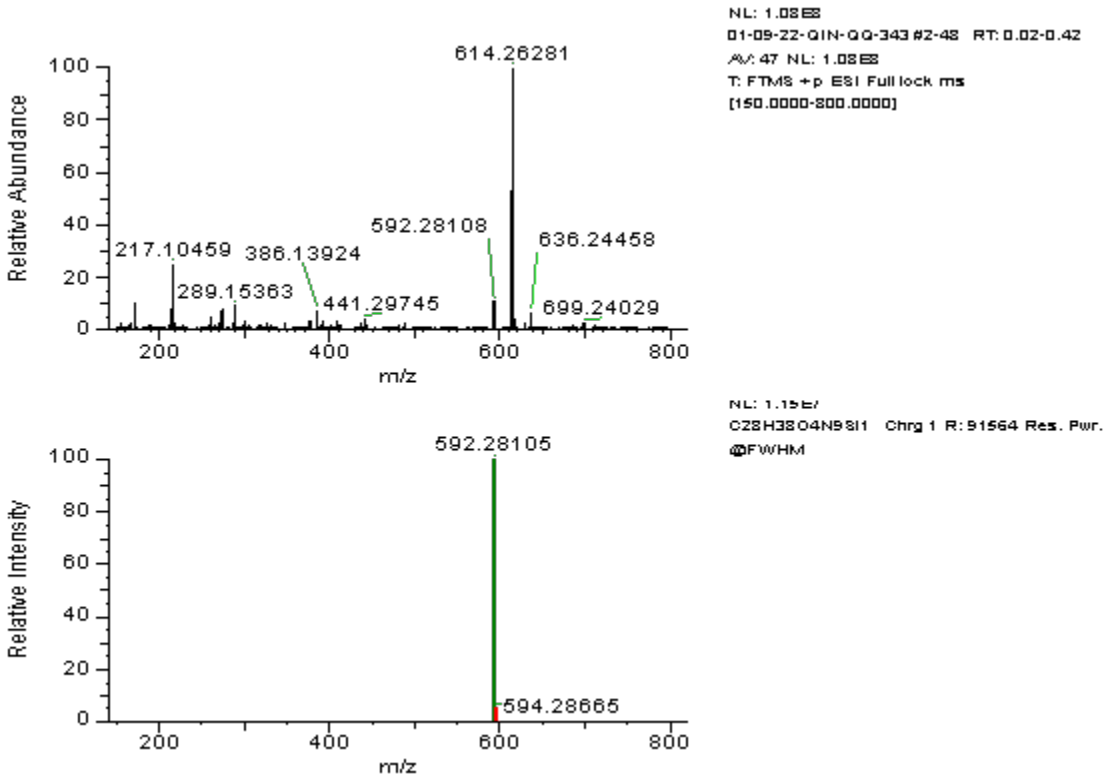


Figure S112. ESI-MS of **G**.

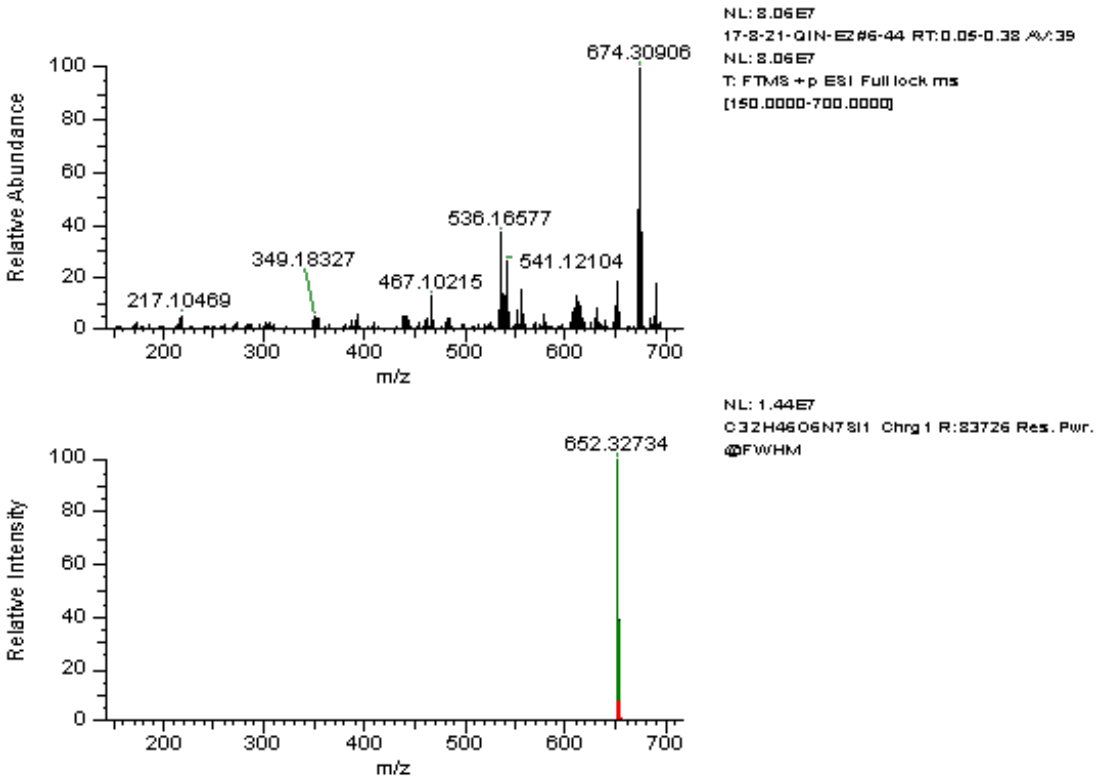


Figure S101. ESI-MS of **22**.

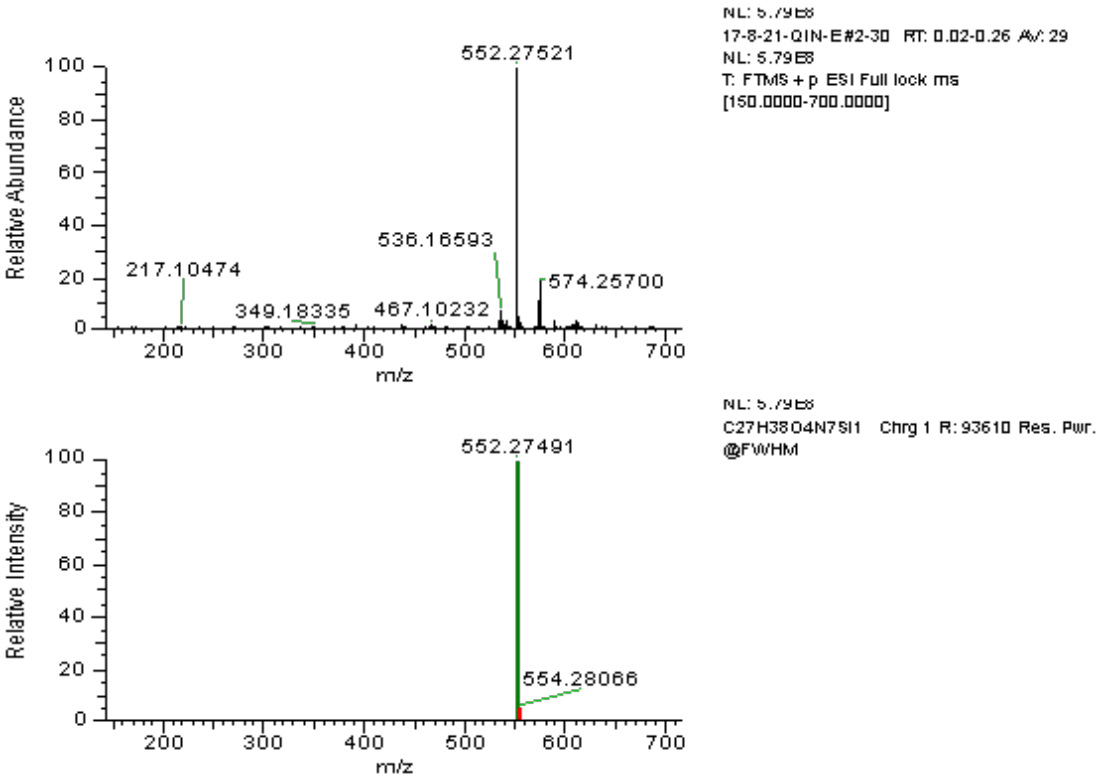


Figure S113. ESI-MS of **C**.

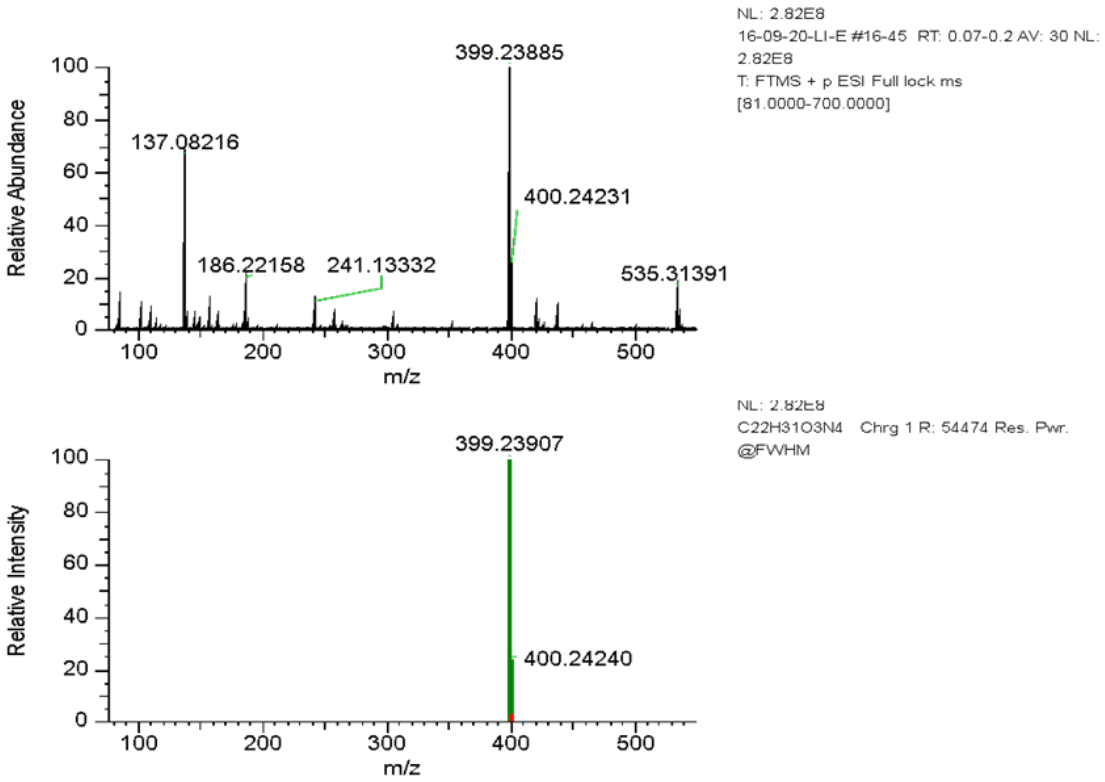


Figure S114. ESI-MS of **23**.

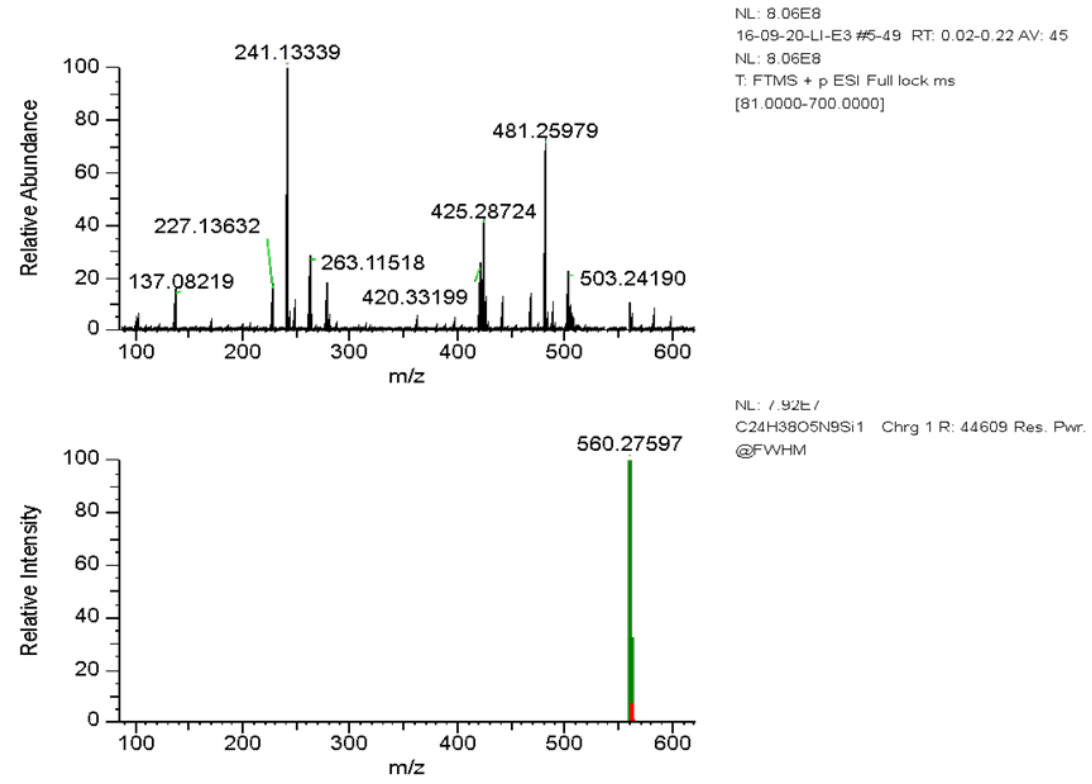


Figure S115. ESI-MS of **24**.

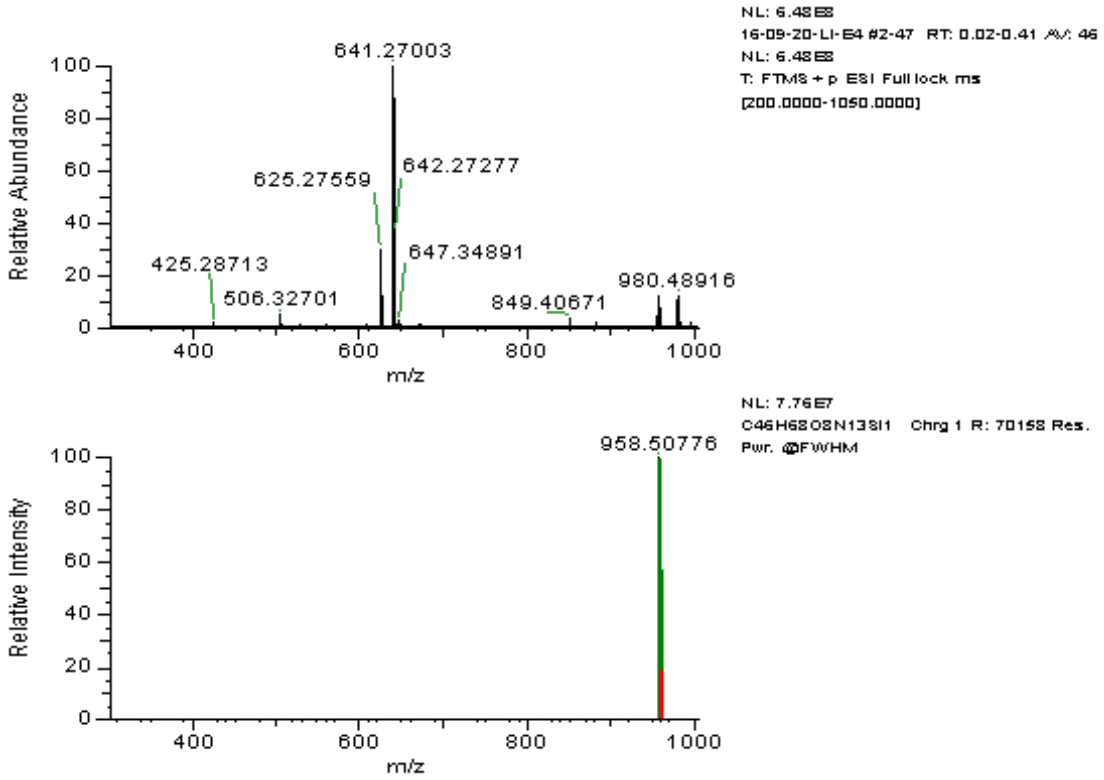


Figure S116. ESI-MS of **TC$_6$**.

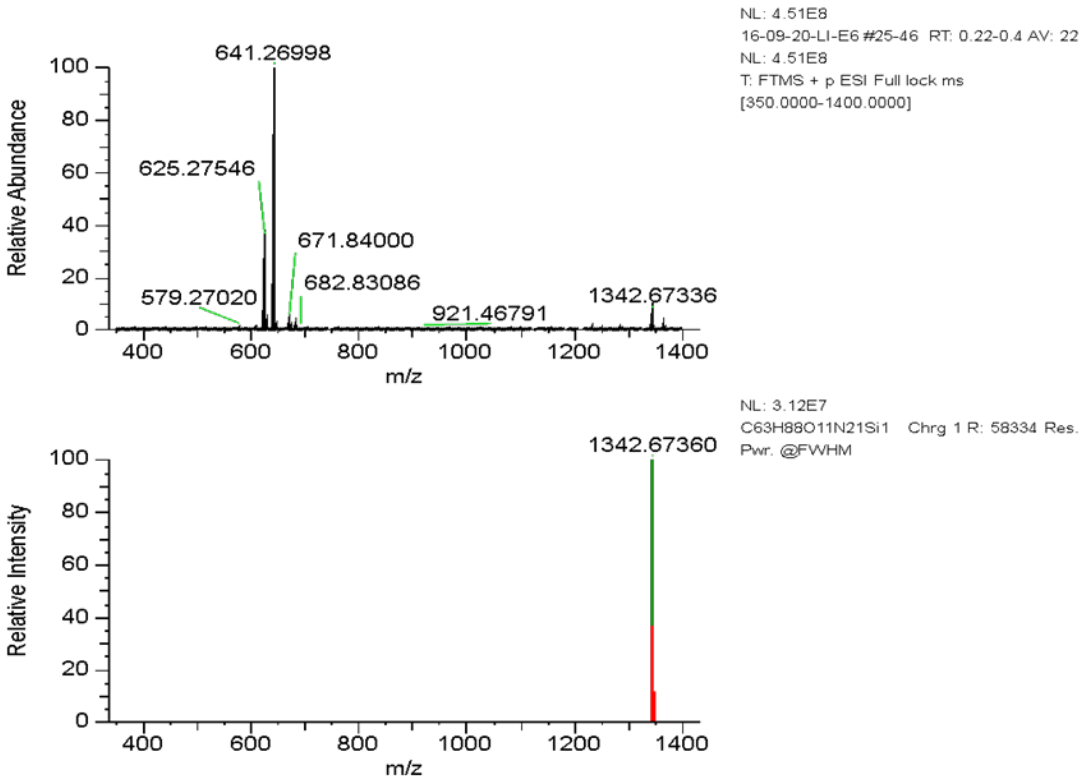


Figure S117. ESI-MS of **PTC$_6$**.

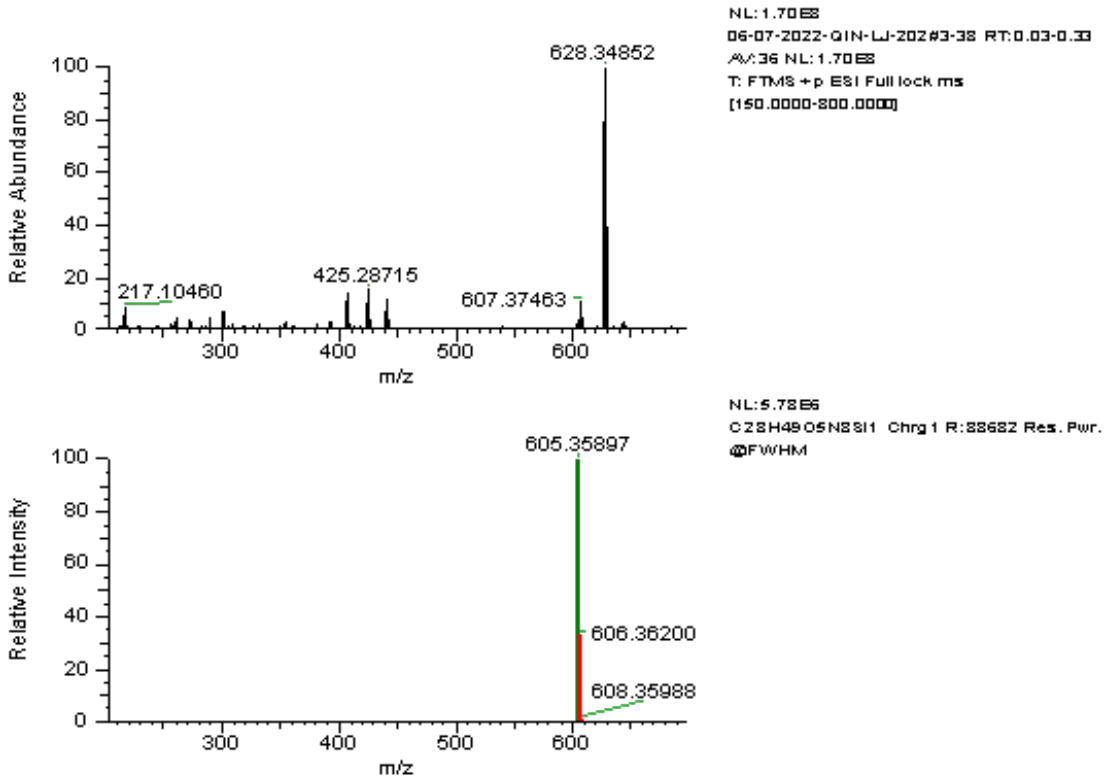


Figure S118. ESI-MS of **26**.

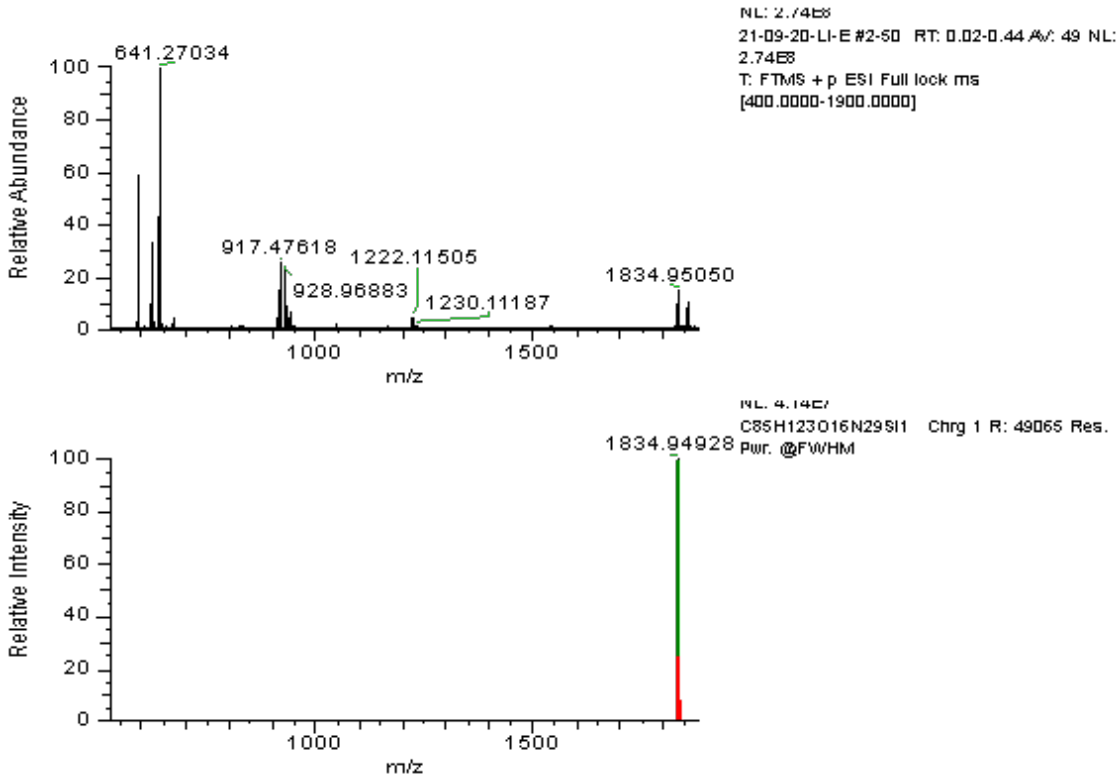


Figure S119. ESI-MS of **MPTC$_6$**.

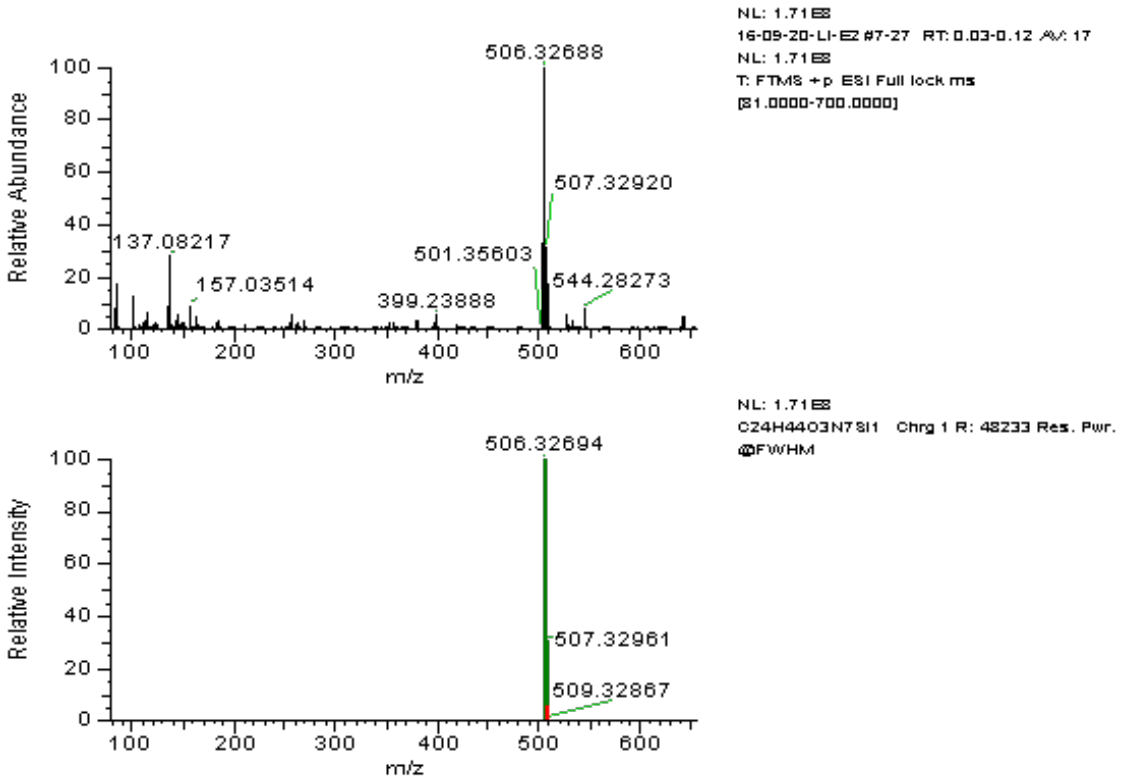


Figure S120. ESI-MS of **27**.

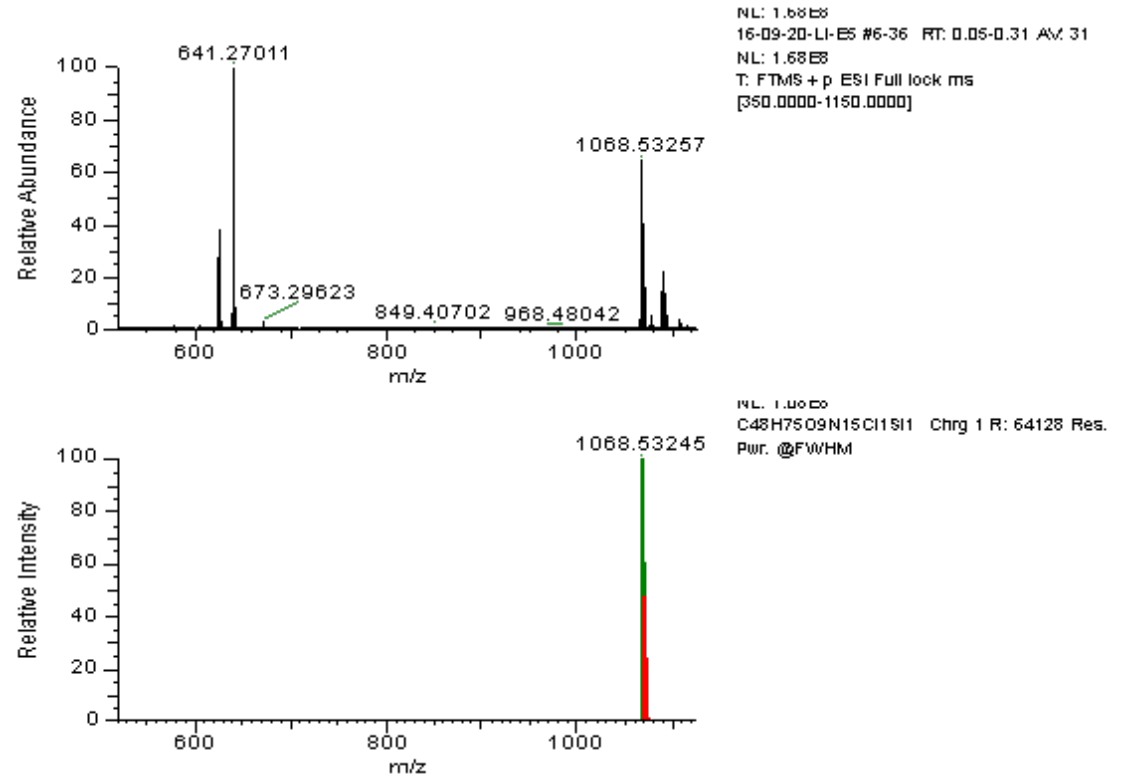


Figure S121. ESI-MS of **C$_6$G**.

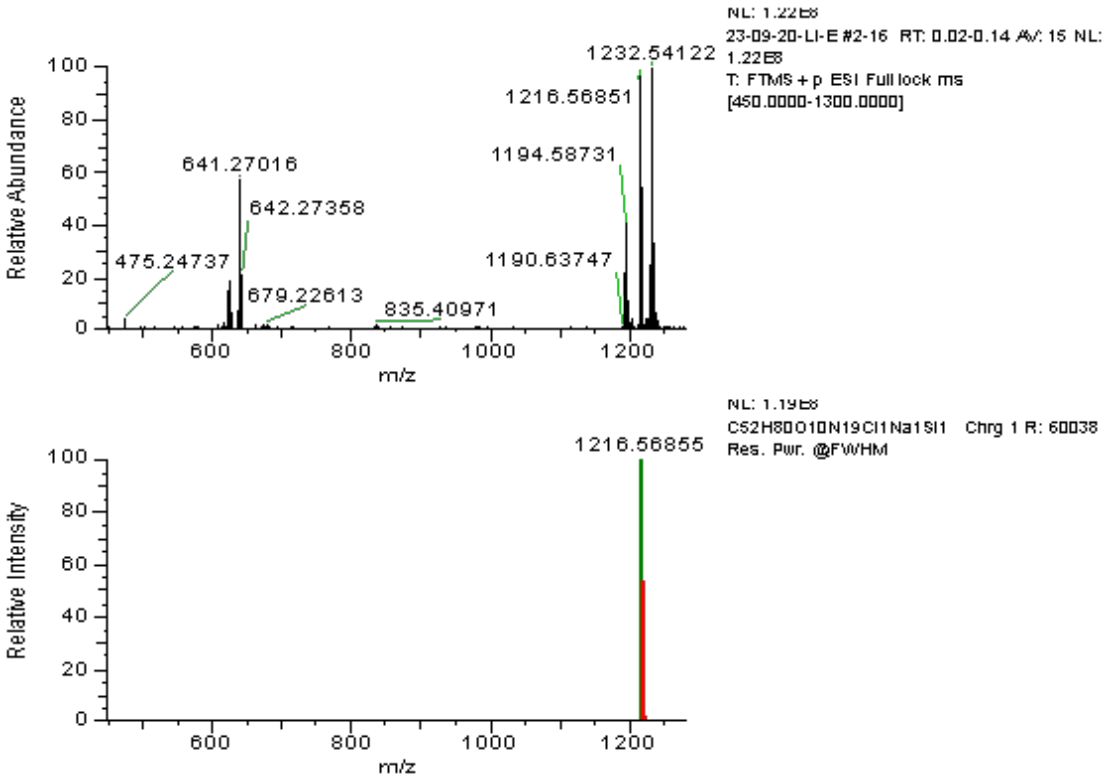


Figure S122. ESI-MS of **28**.

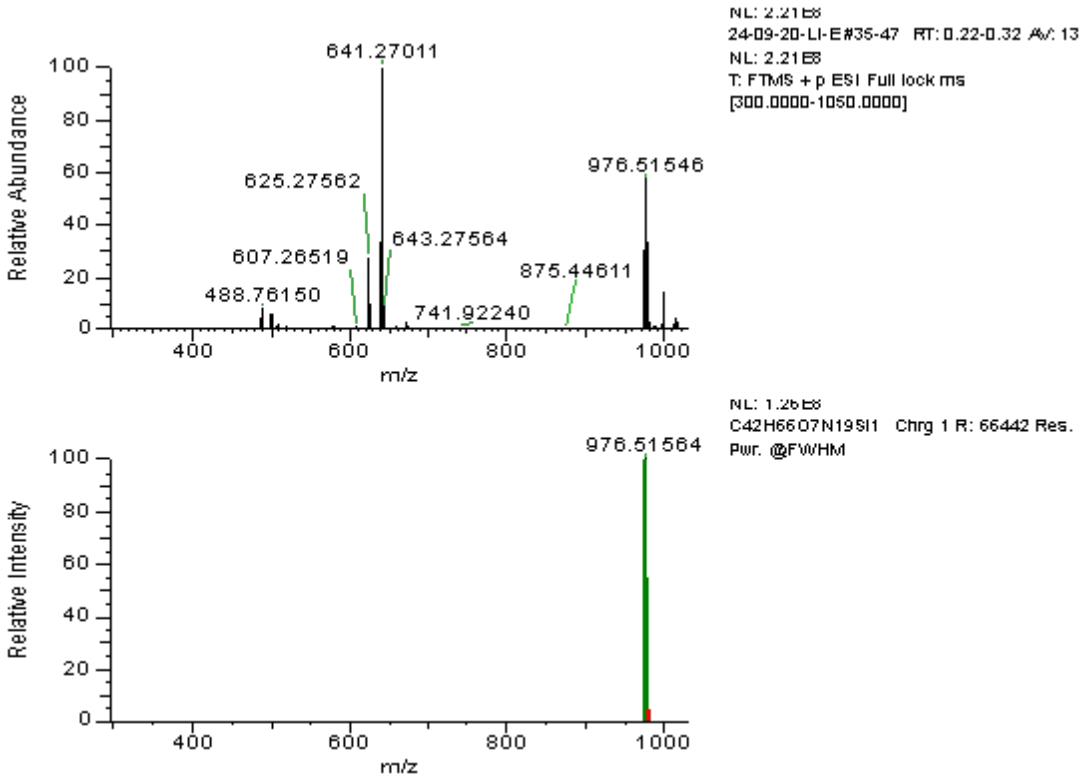


Figure S123. ESI-MS of **29**.

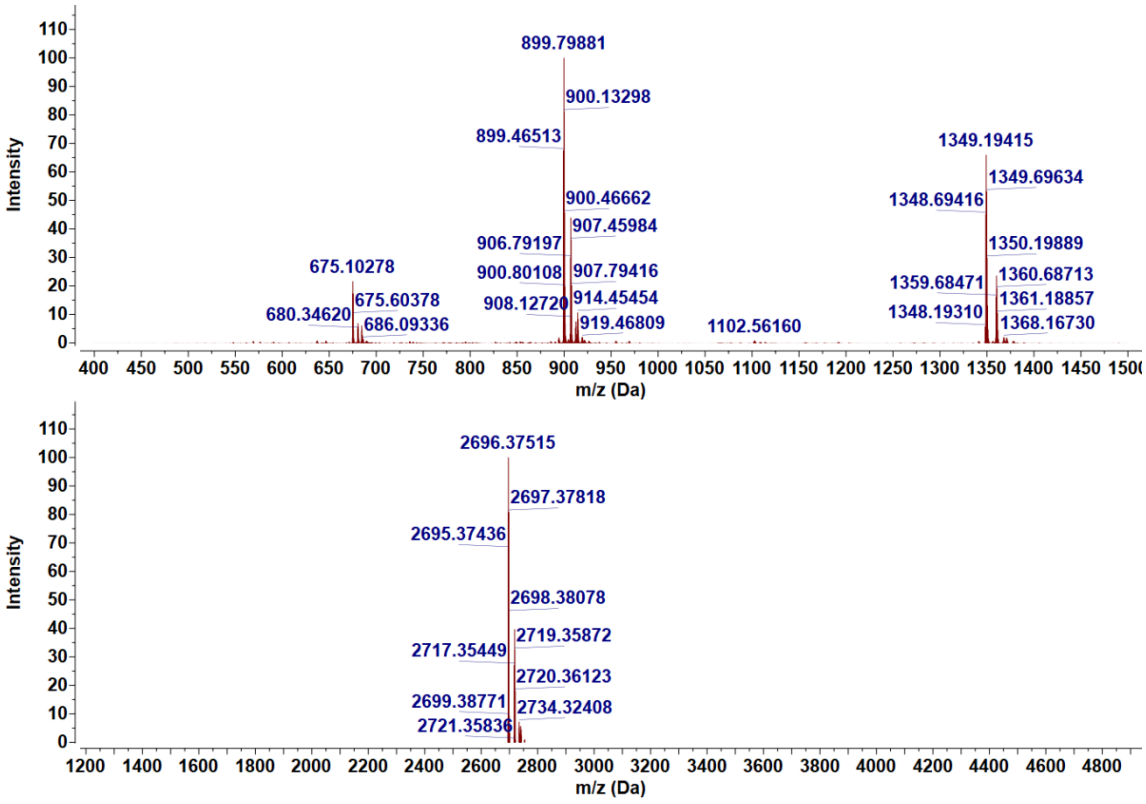


Figure S124. TOF MS ES + of **C_6GMPTC_6**.

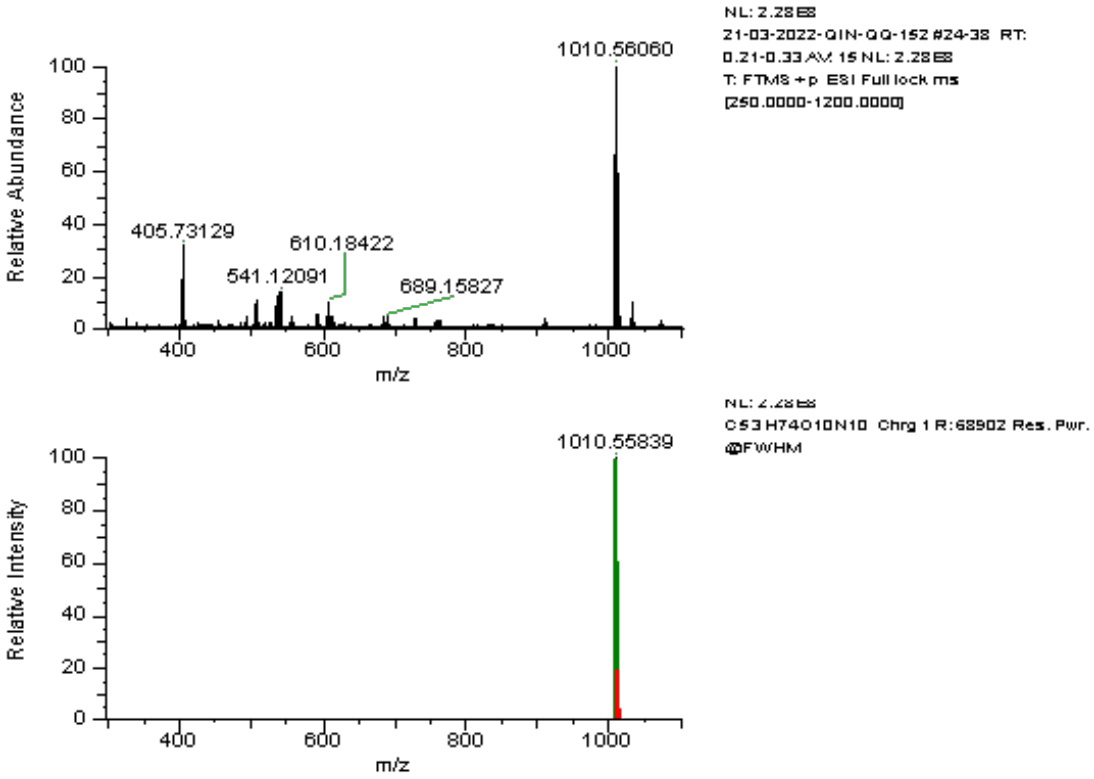


Figure S125. ESI-MS of **C_6C**.

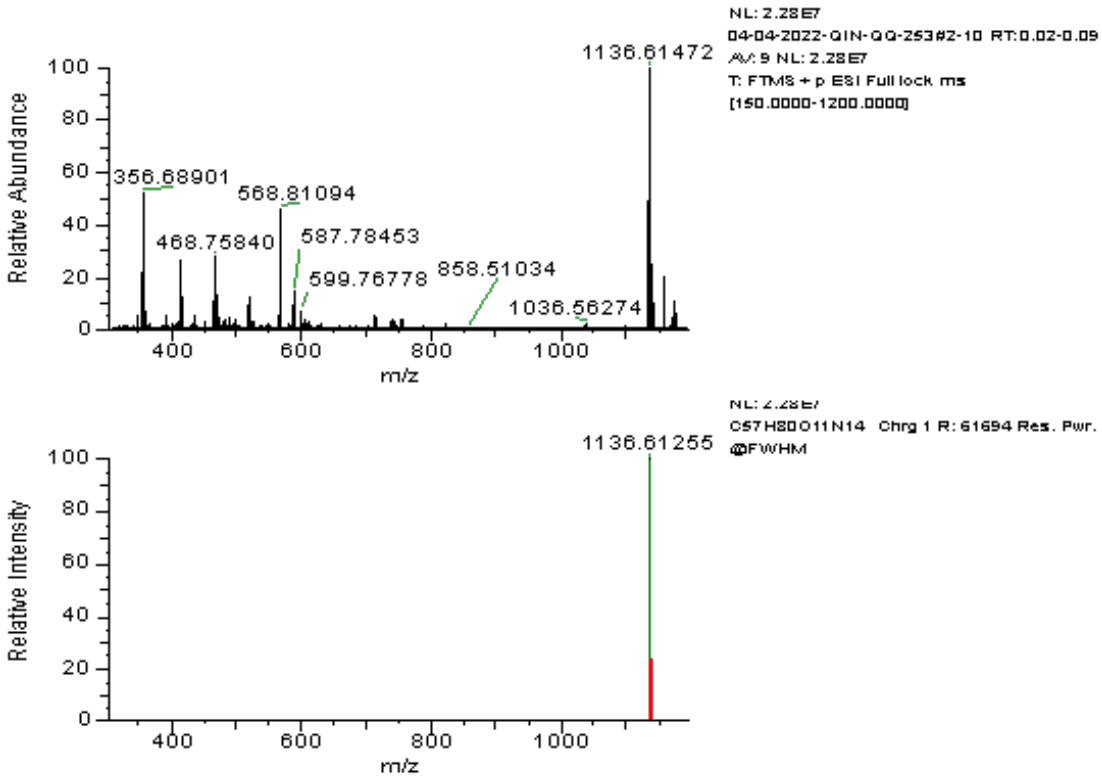


Figure S126. ESI-MS of **30**.

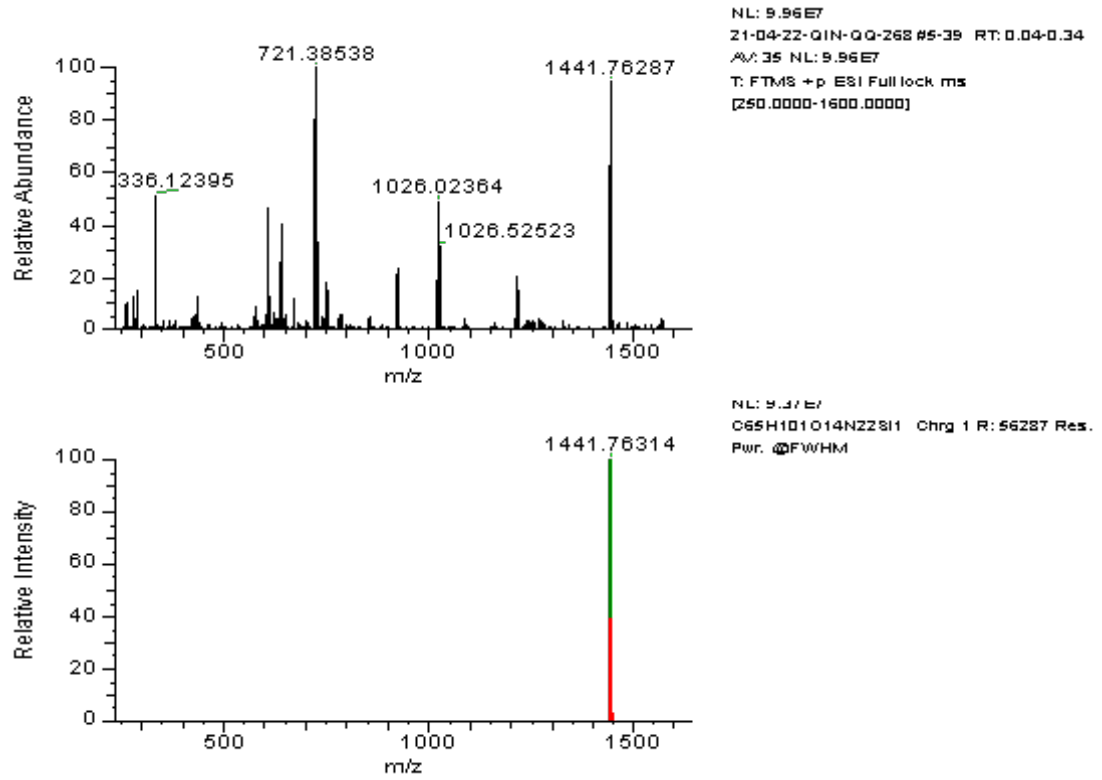


Figure S127. ESI-MS of **C_6CI**.

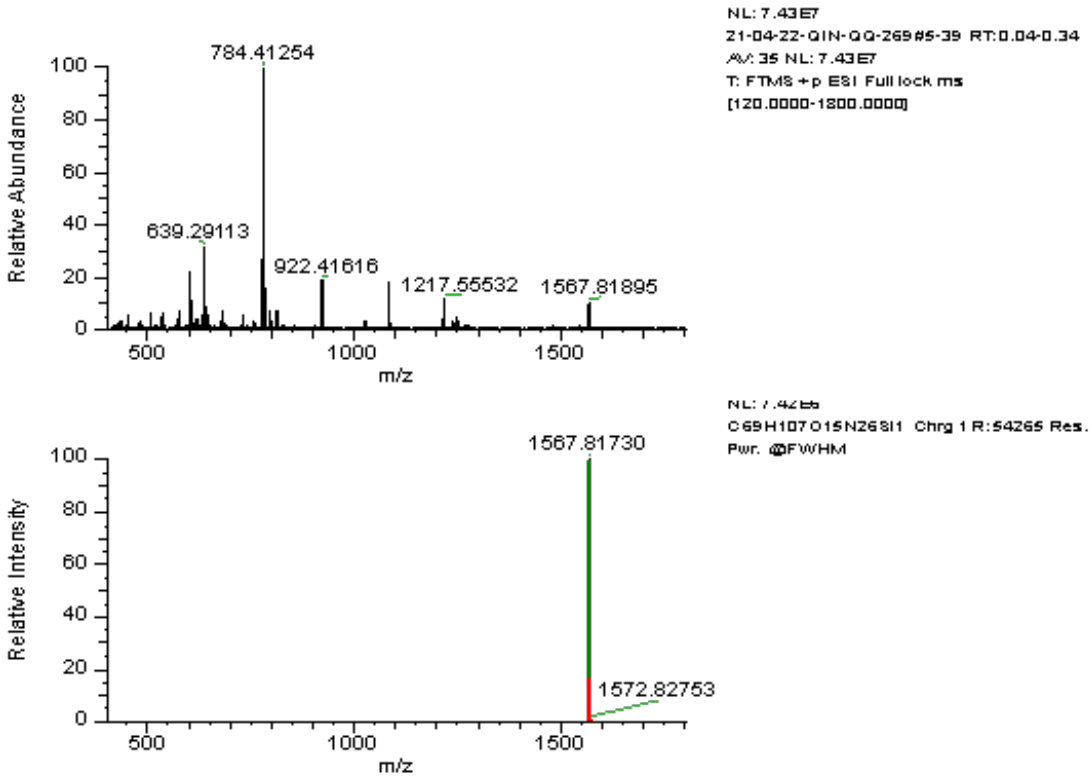


Figure S128. ESI-MS of **31**.

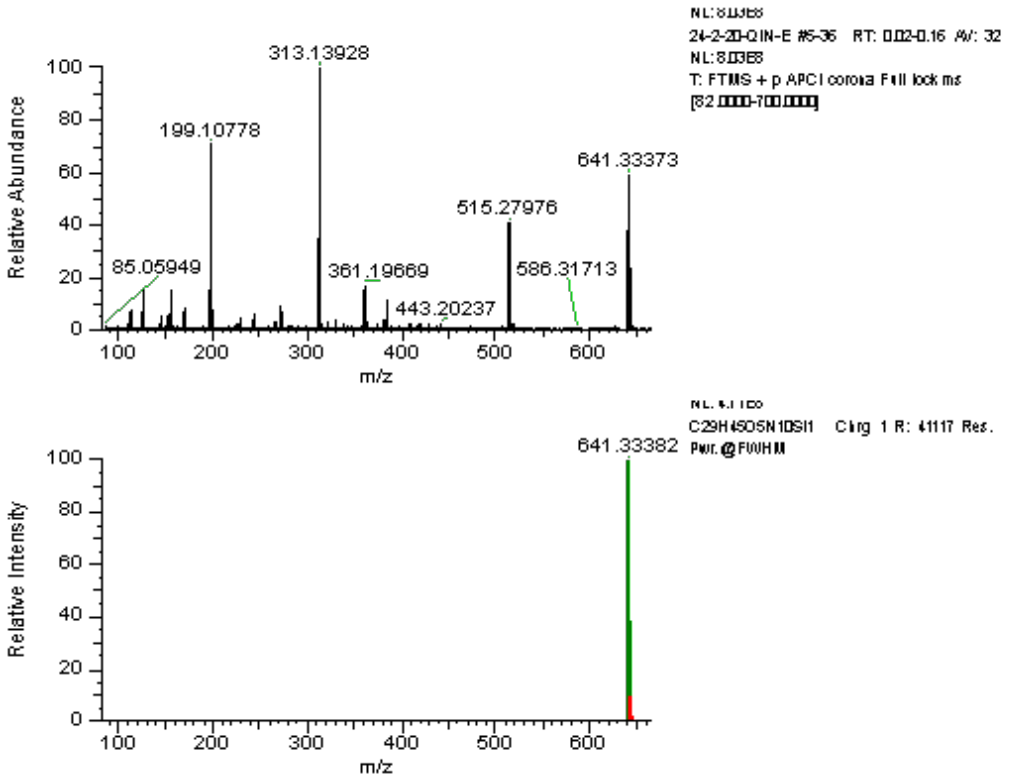


Figure S129. ESI-MS of **32**.

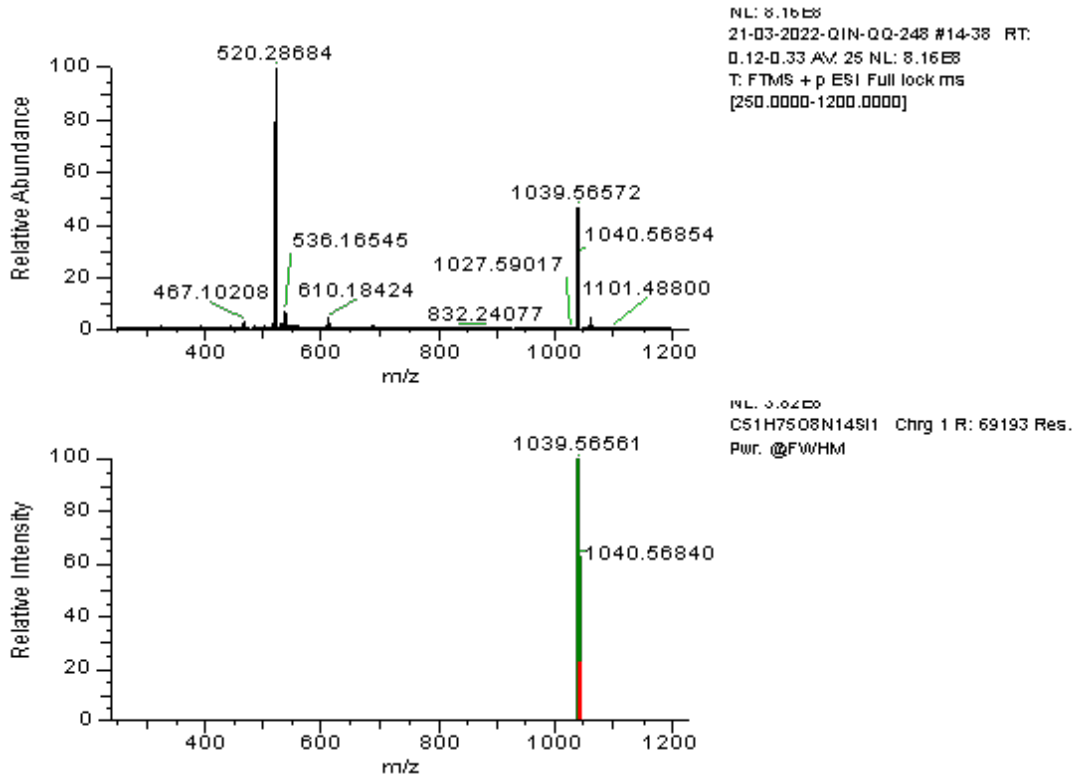


Figure S130. ESI-MS of **DC$_6$**.

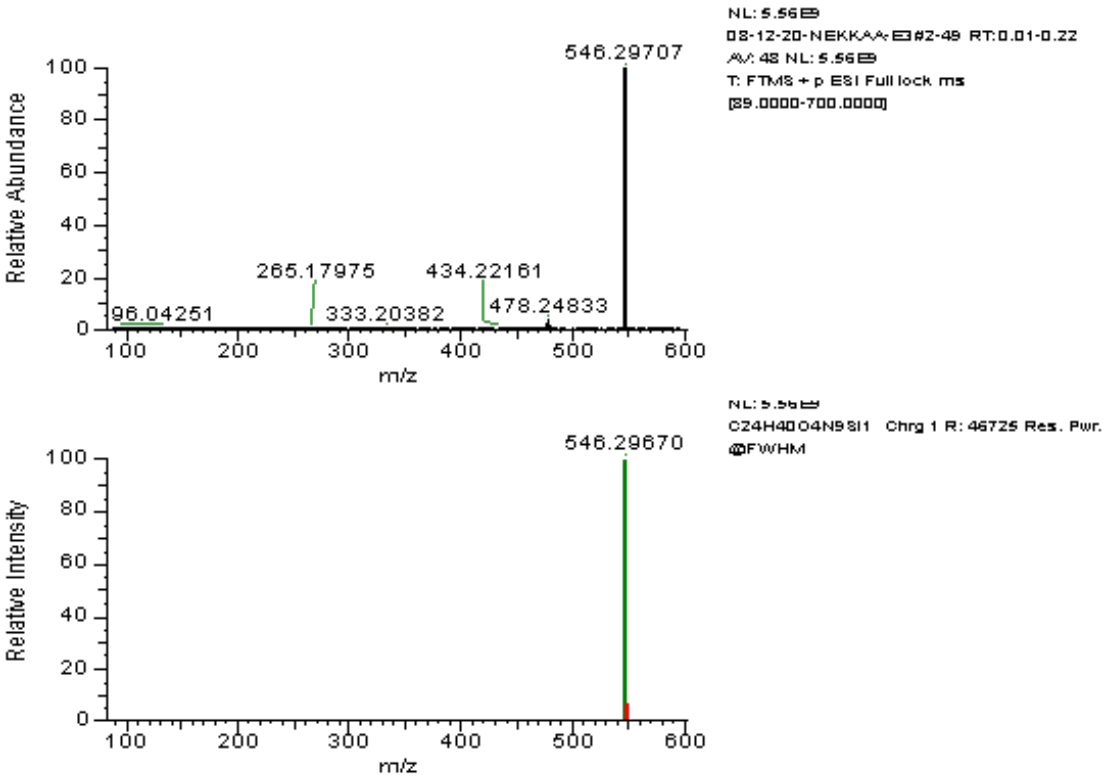


Figure S131. ESI-MS of **33**.

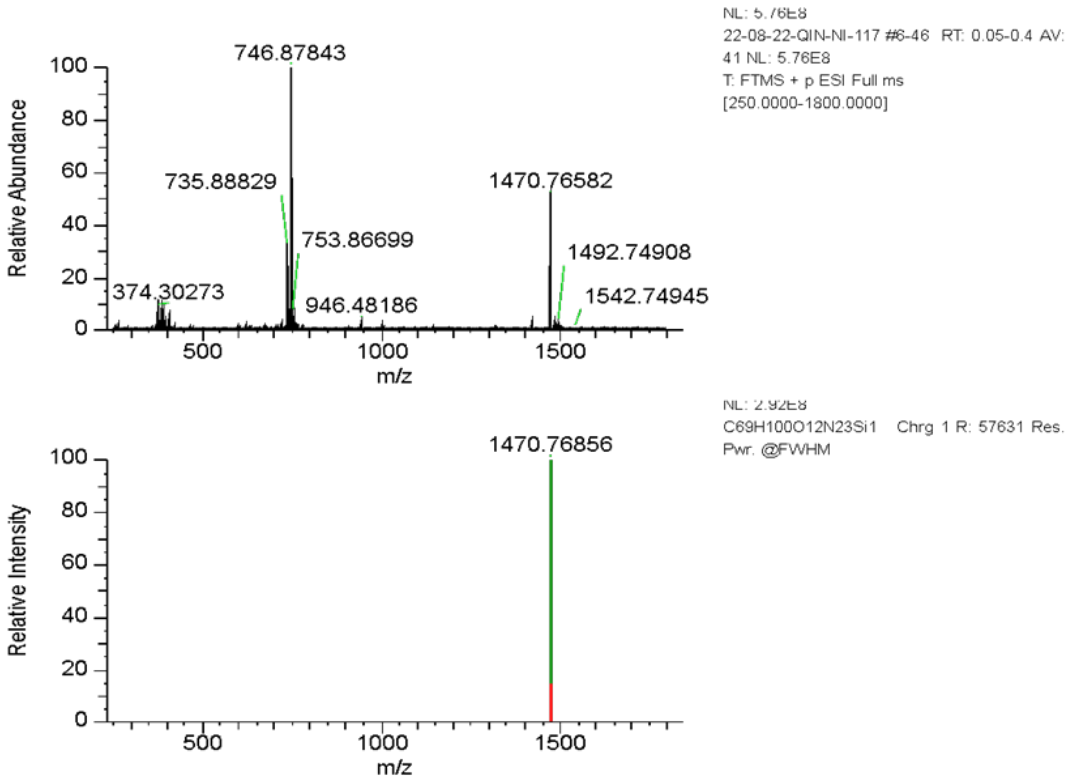


Figure S132. ESI-MS of **IDC$_6$**.

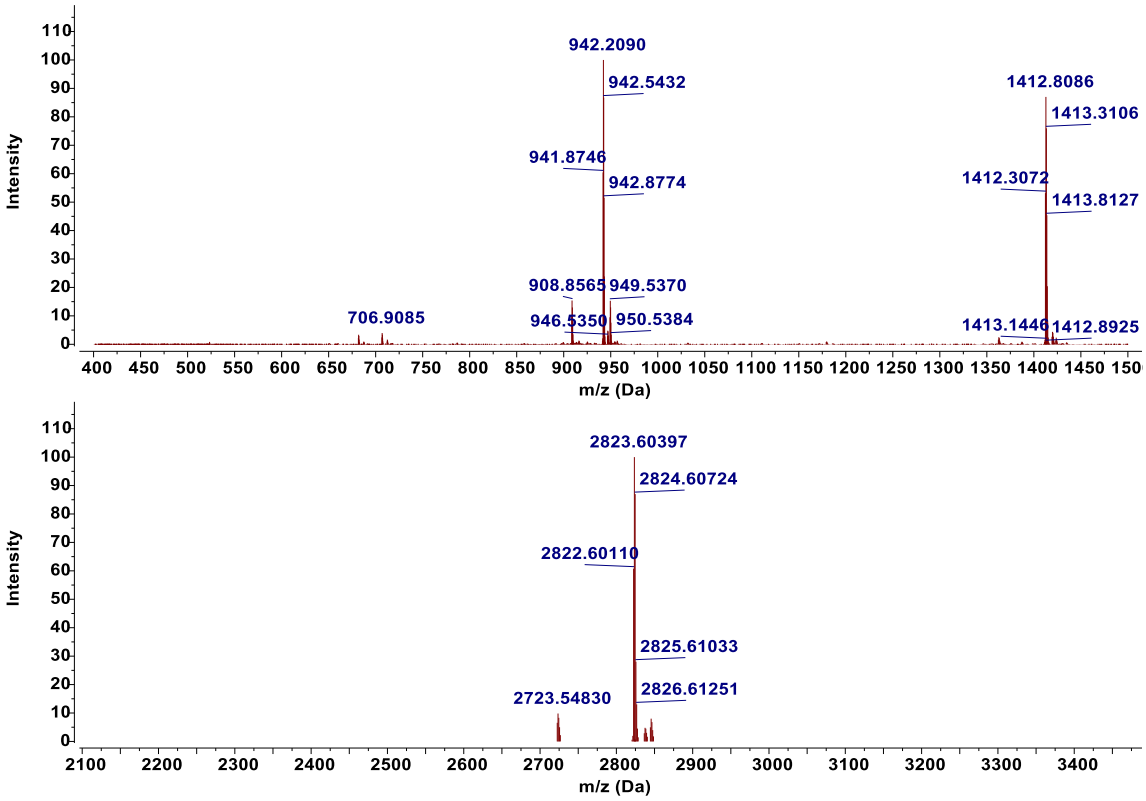


Figure S133. TOF MS ES + of **34**.

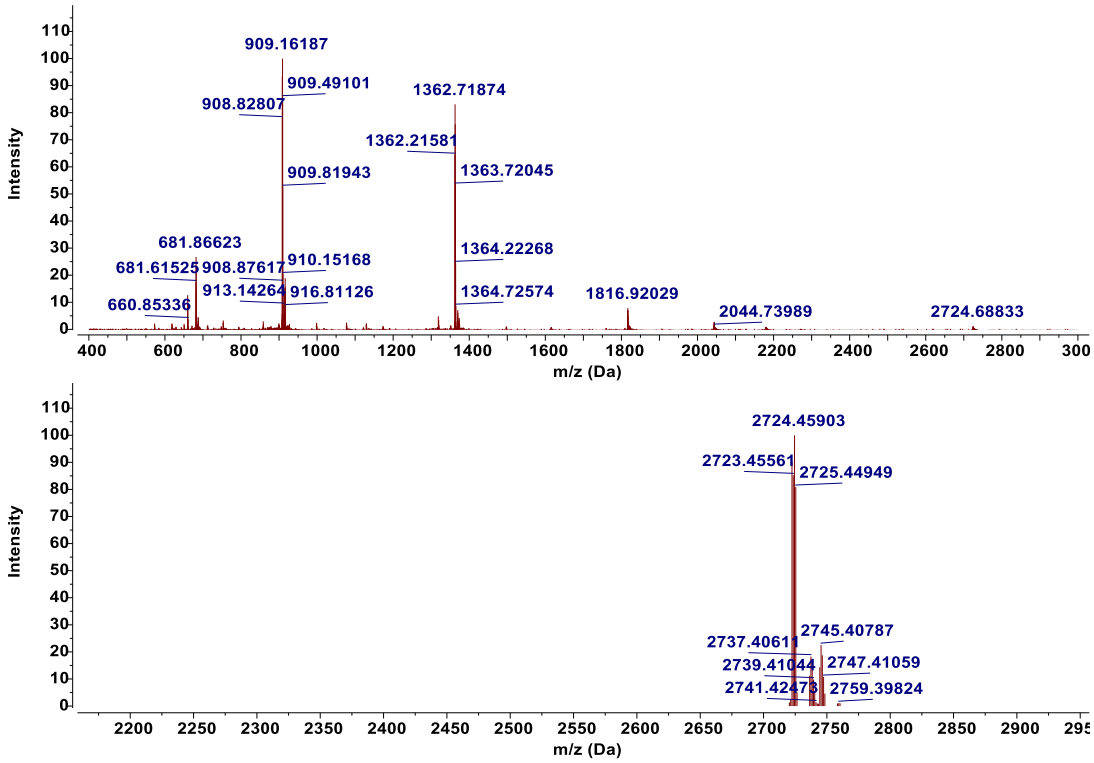


Figure S134. TOF MS ES + of **C_6CIIDC$_6$**.

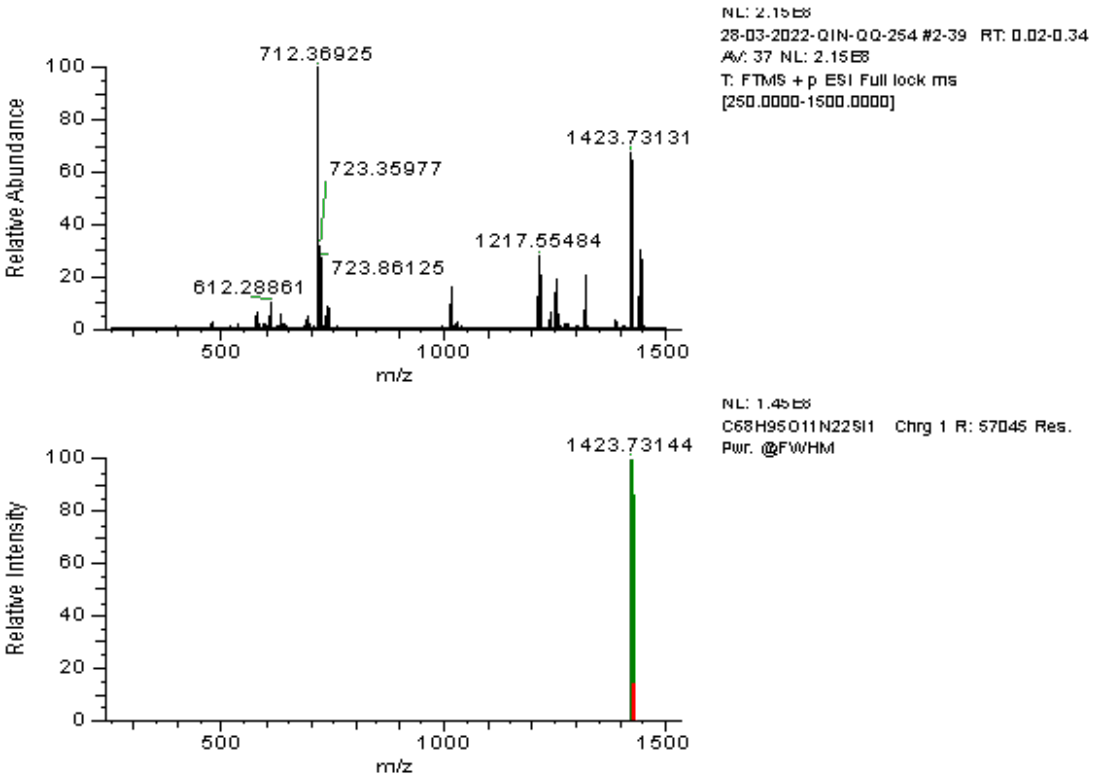


Figure S135. ESI-MS of **PDC$_6$**.

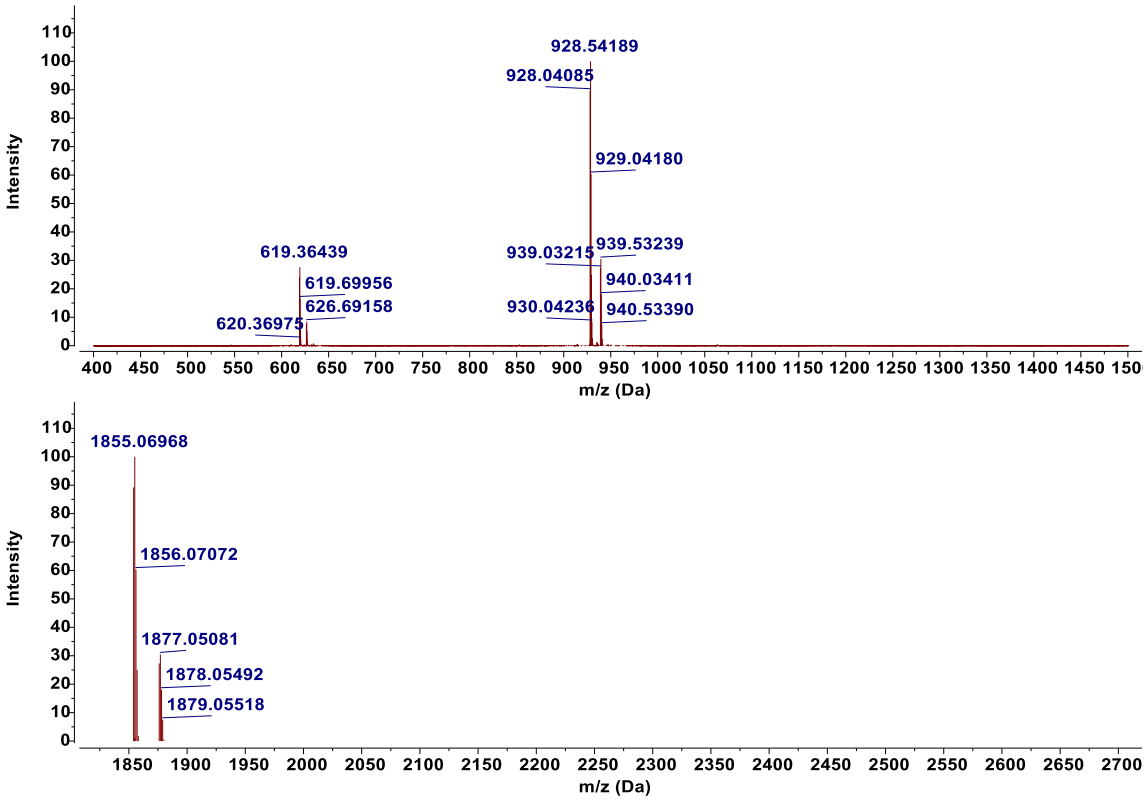


Figure S136. TOF MS ES + of **IPDC$_6$**.

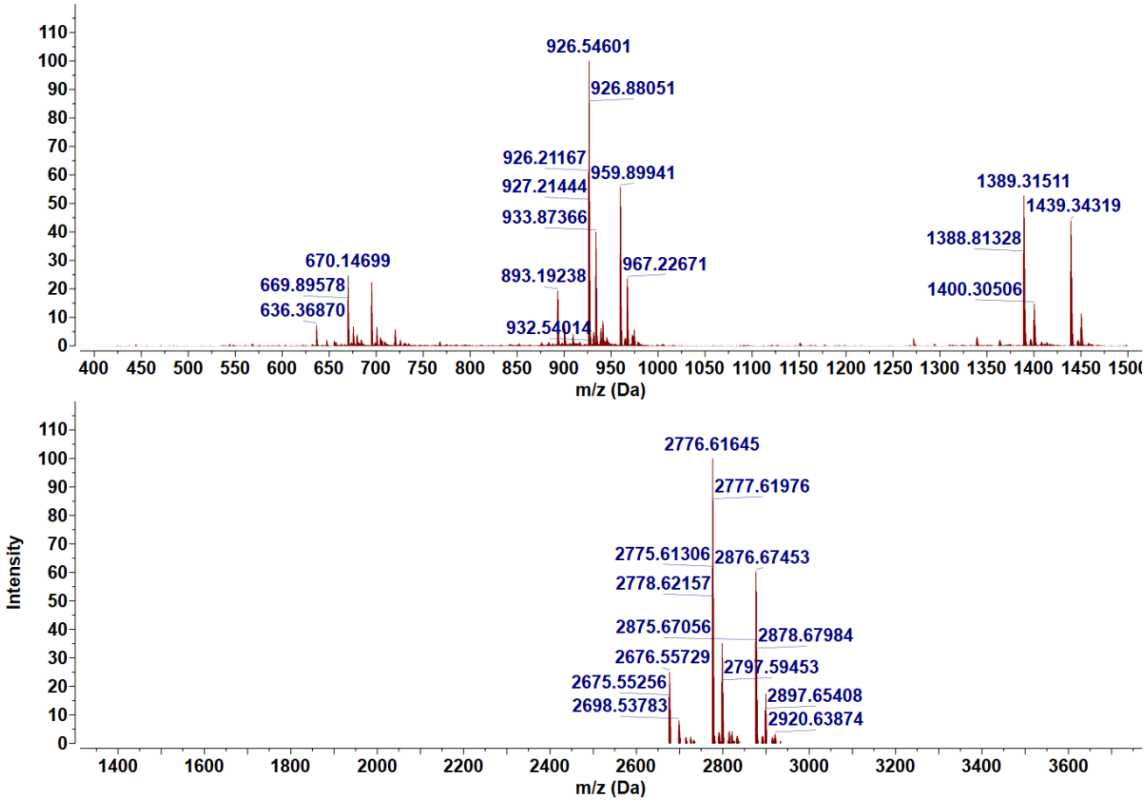


Figure S137. TOF MS ES + of **35**.

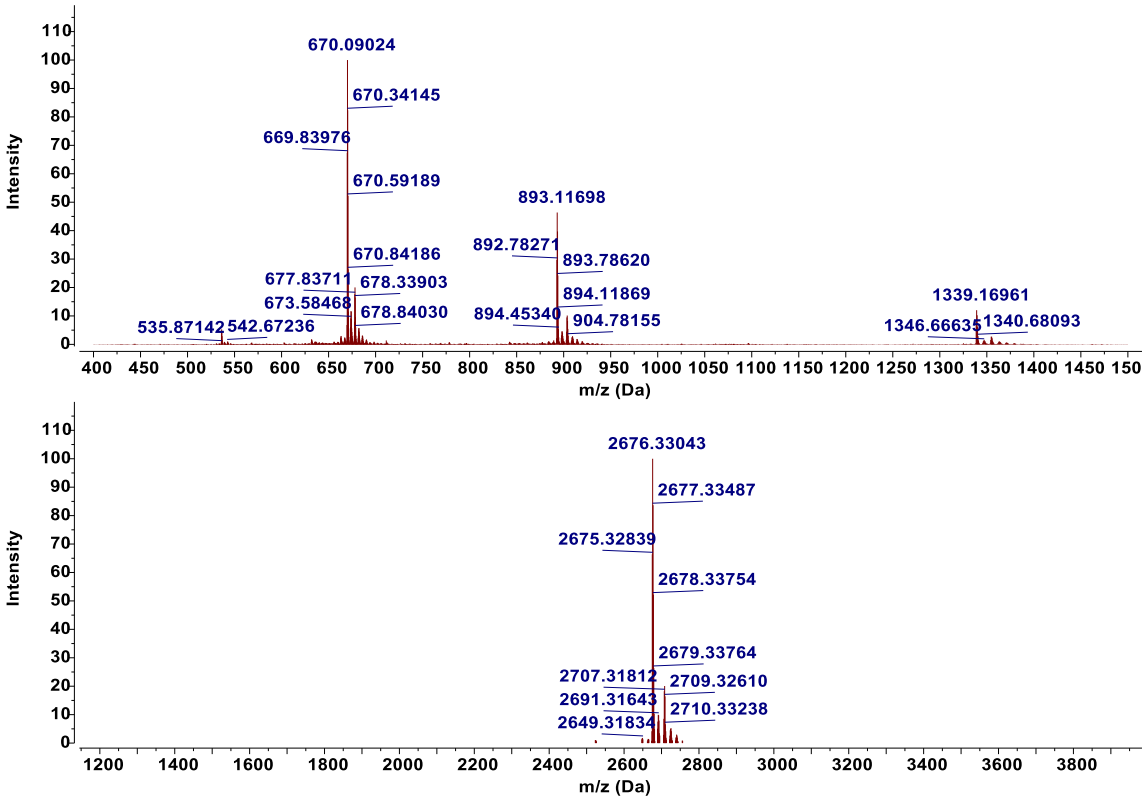


Figure S138. TOF MS ES + of **C_6CIPDC$_6$**.

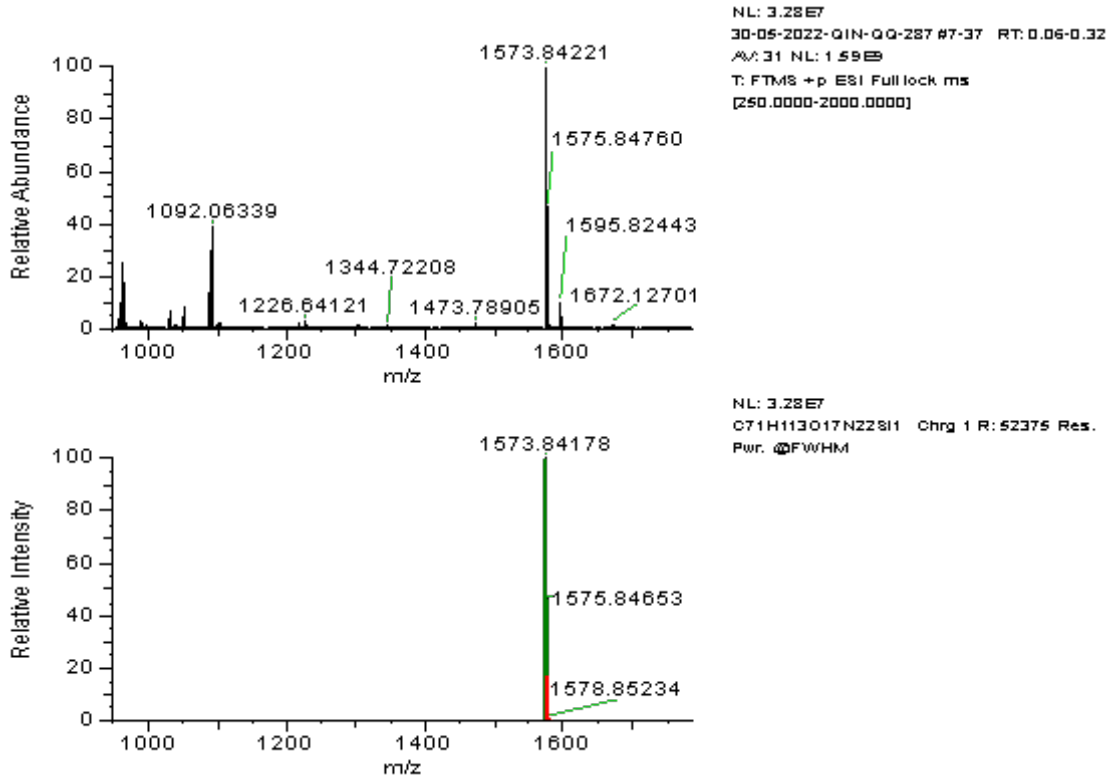


Figure S139. ESI-MS of **C_6CI'**.

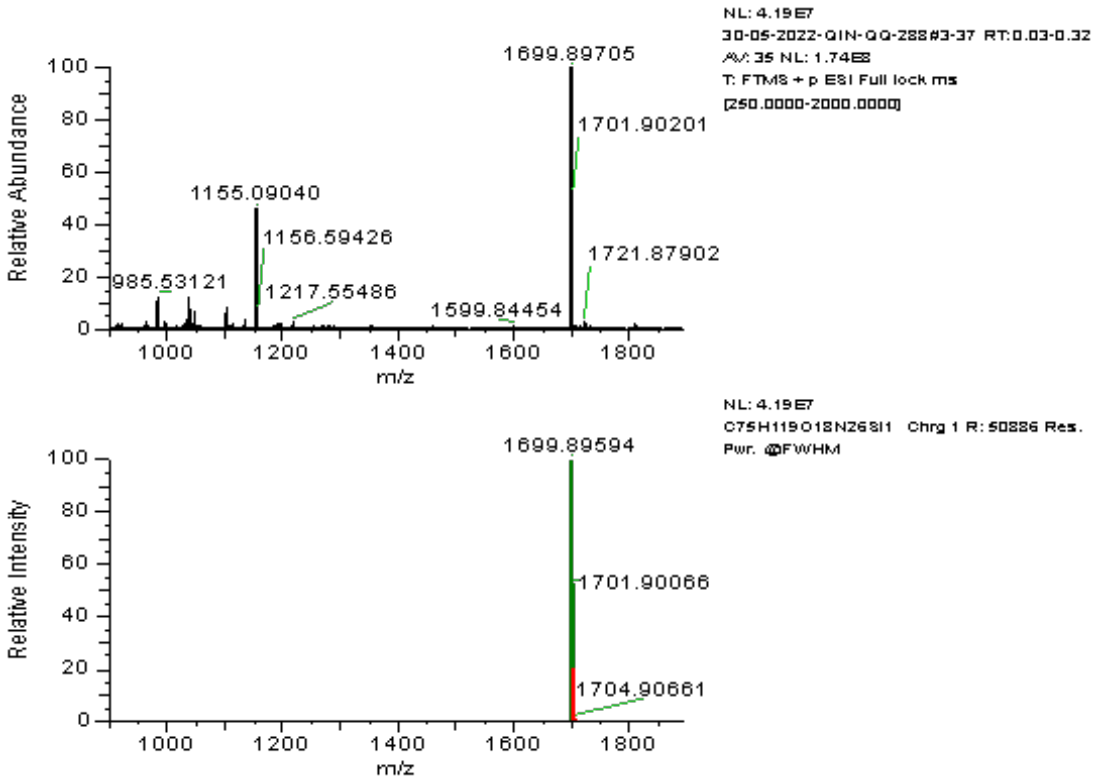


Figure S140. ESI-MS of **36**.

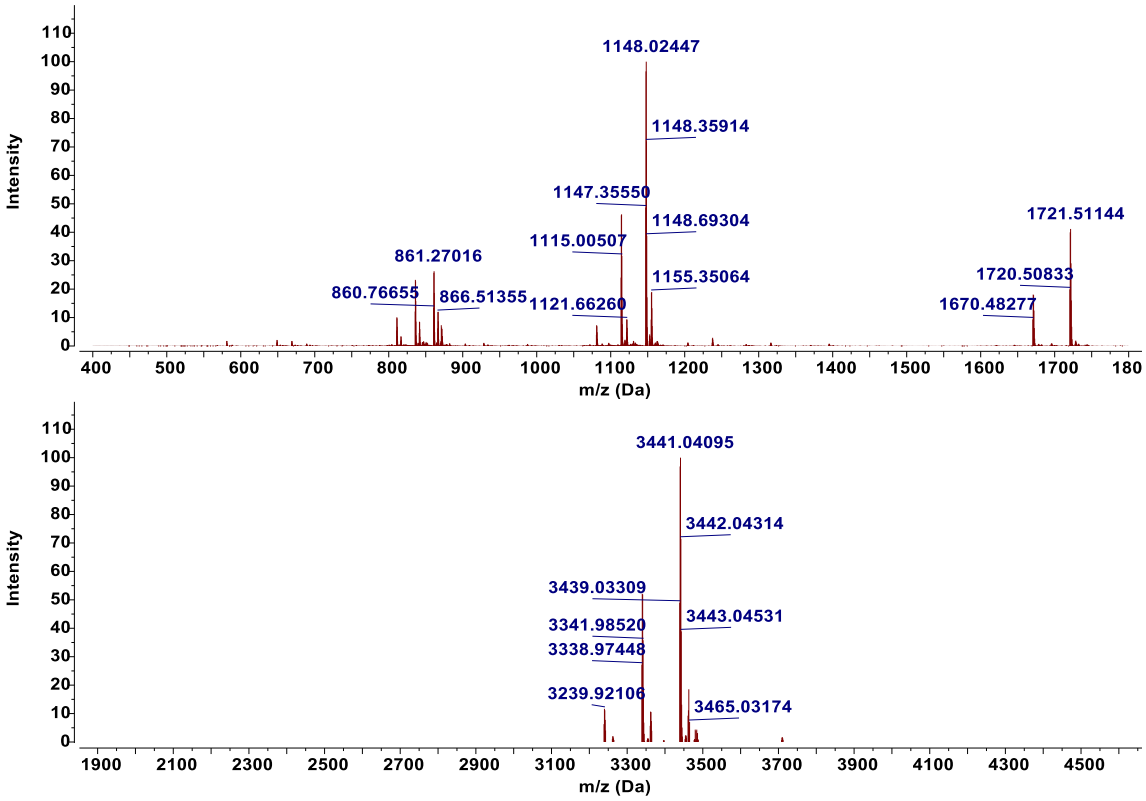


Figure S141. TOF MS ES + of **37**.

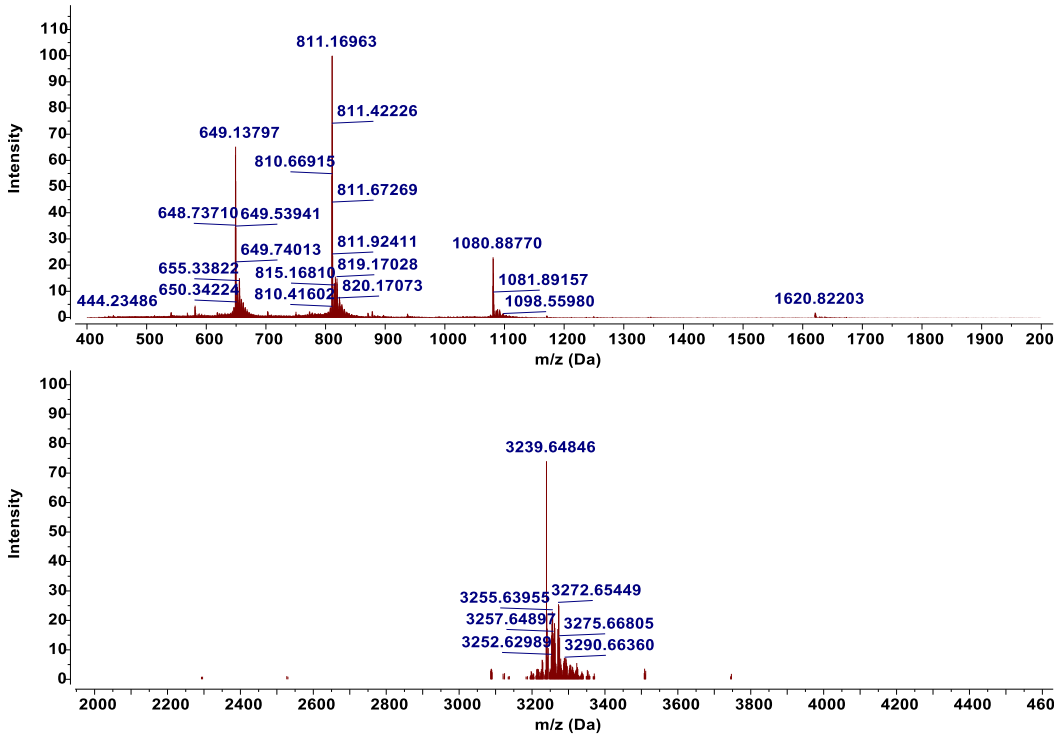


Figure S142. TOF MS ES + of **C_6CI'IPDC$_6$**.

4.2 TOF-MS/MS

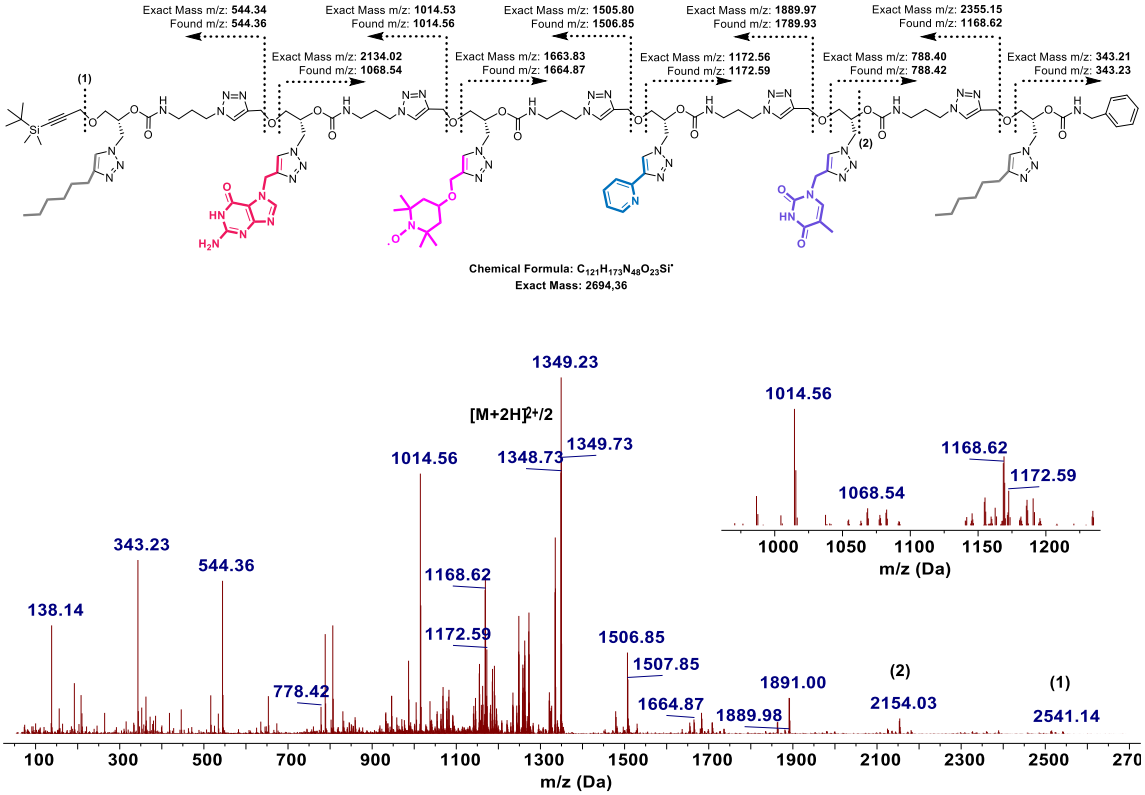


Figure S143. TOF-MS/MS of **C_6GMPTC$_6$**.

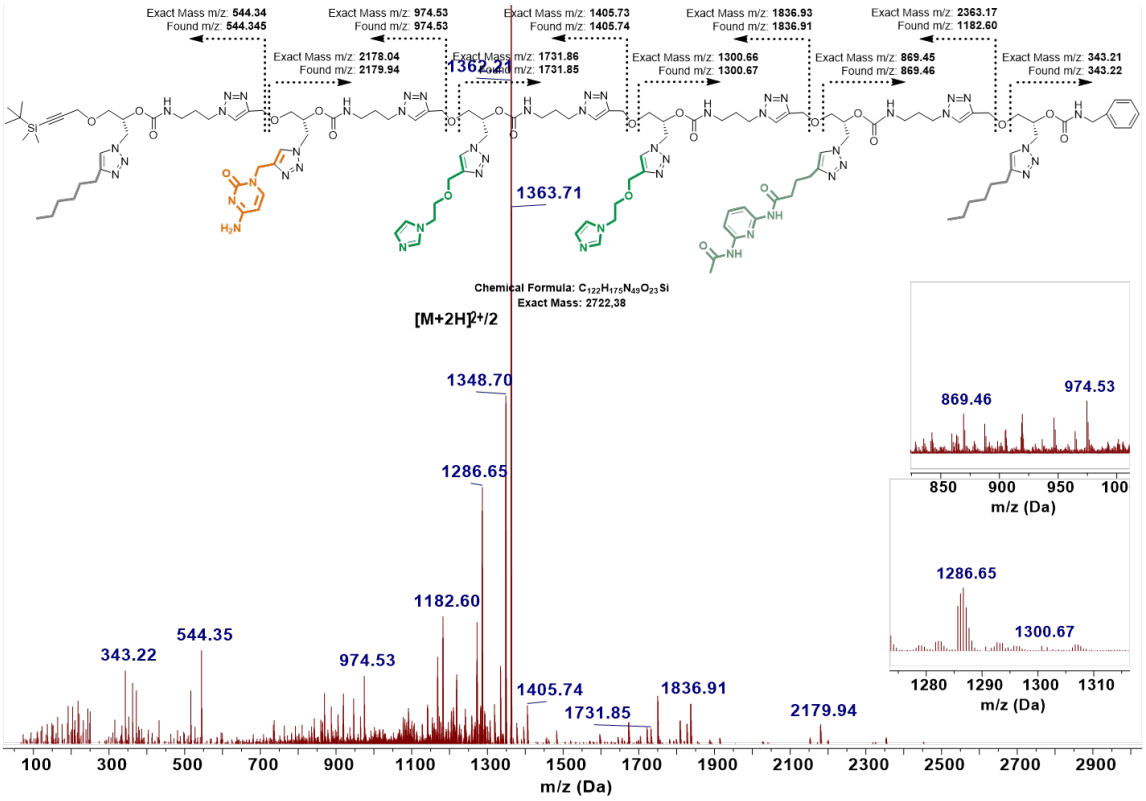


Figure S144. TOF-MS/MS of **C$_6$CIIDC$_6$**.

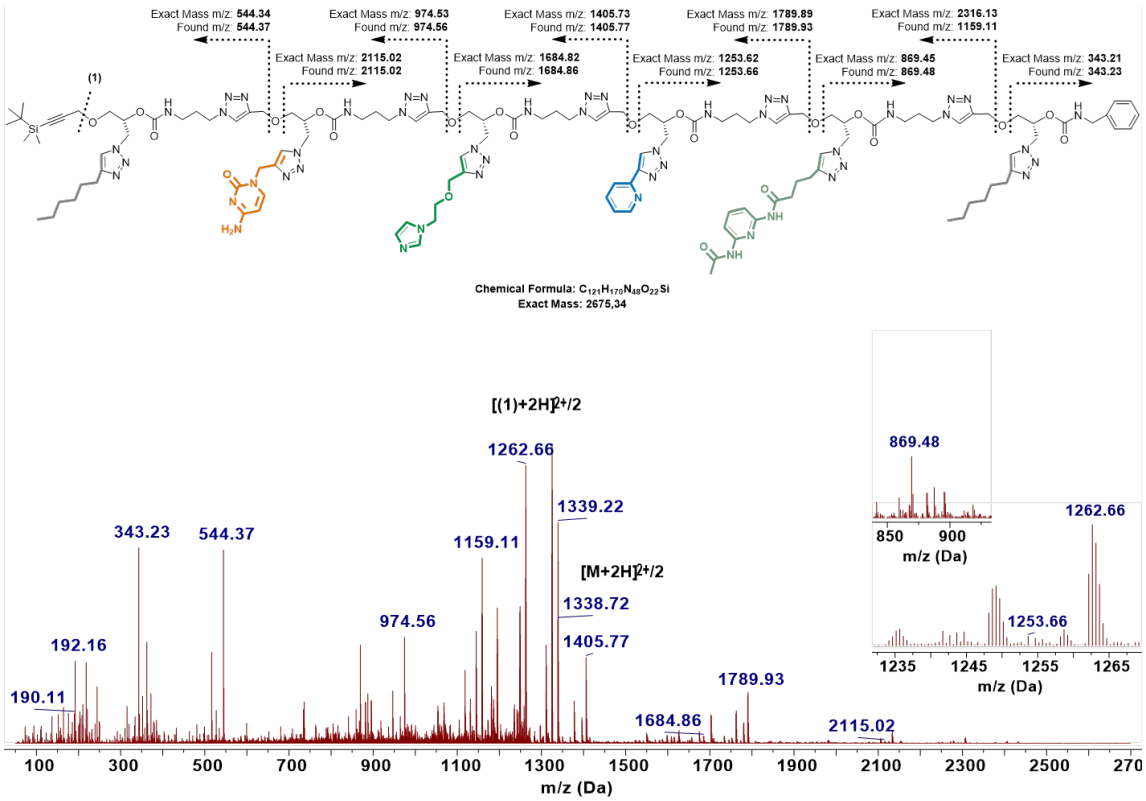


Figure S145. TOF-MS/MS of **C$_6$CIPDC$_6$**.

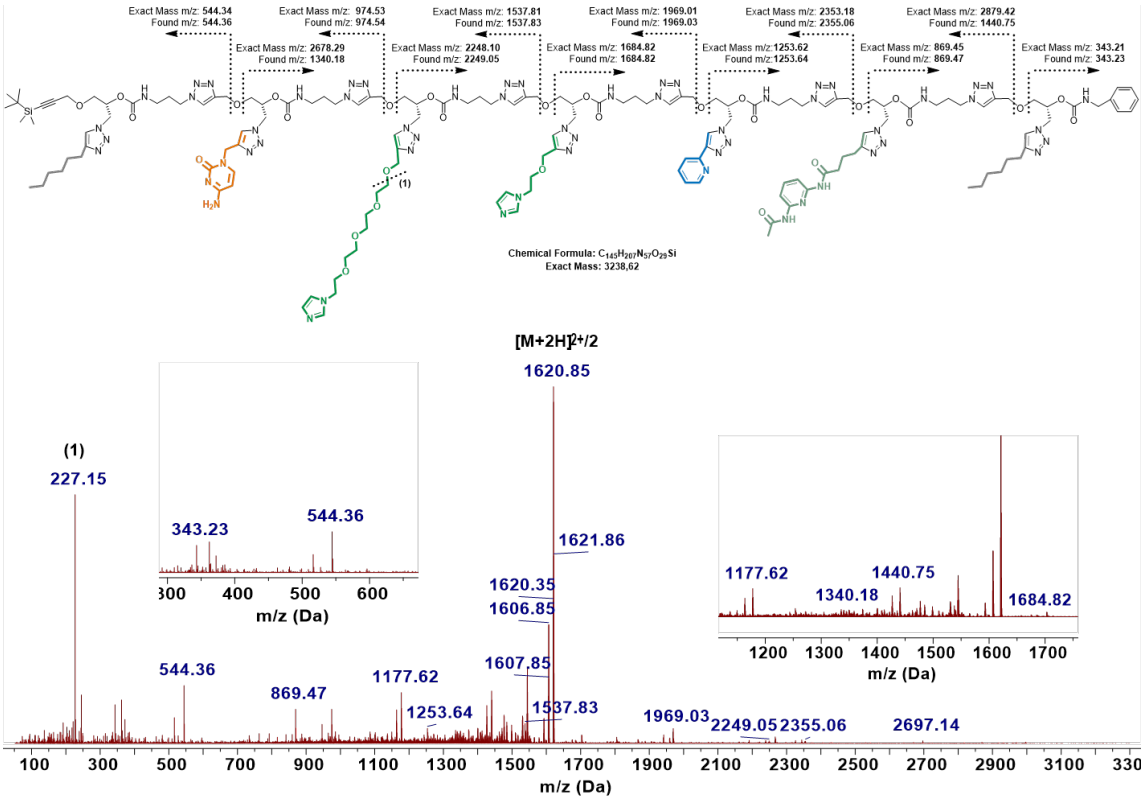


Figure S146. TOF-MS/MS of **C_6CI'IPDC$_6$**.

5 SEC-GPC

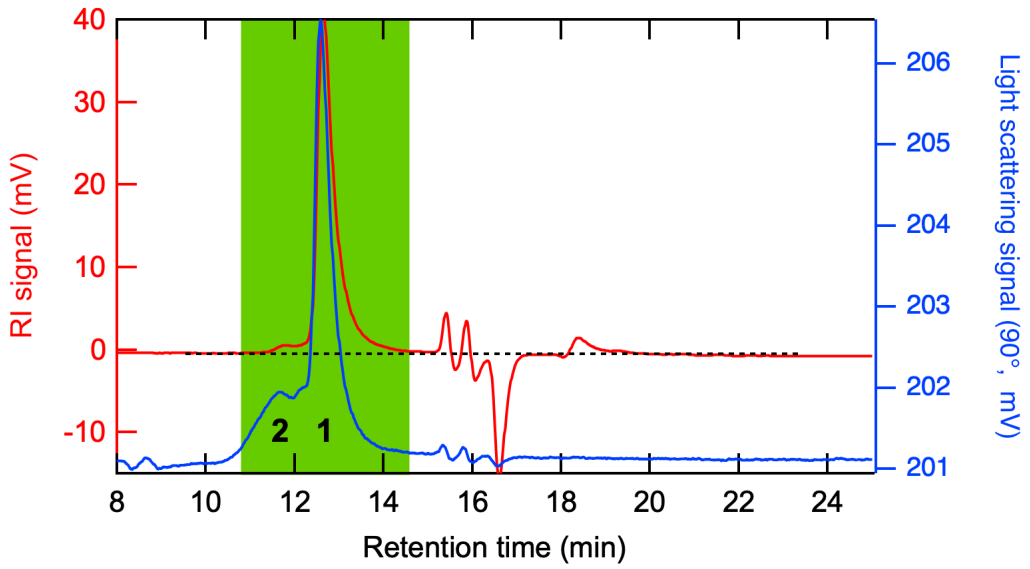


Figure S147. SEC-GPC trace of **C_6GMPTC$_6$** (O_a) in DMF (differential refractive index detector, red, left vertical axis; light scattering detector (90° scattering angle), blue, right vertical axis). The region highlighted in green is where the sample elutes. The main peak (1) corresponds to the oligomer (Mn=7488 g/mol, Mw=7559 g/mol in PS equivalents). The small peak (2) (Mn=14187 g/mol, Mw=14360 g/mol in PS equivalents) is due to a dimer aggregate, at double the mass. Usually, the light scattering detector is used to evaluate the absolute molar mass if the compound concentration is known accurately. However, in this case, the molar mass of the main compound was known accurately, so the light-scattering data was used to measure the purity of the compound (better than 98%) and the mass lost by filtration (*ca.* 25%, due to aggregation).

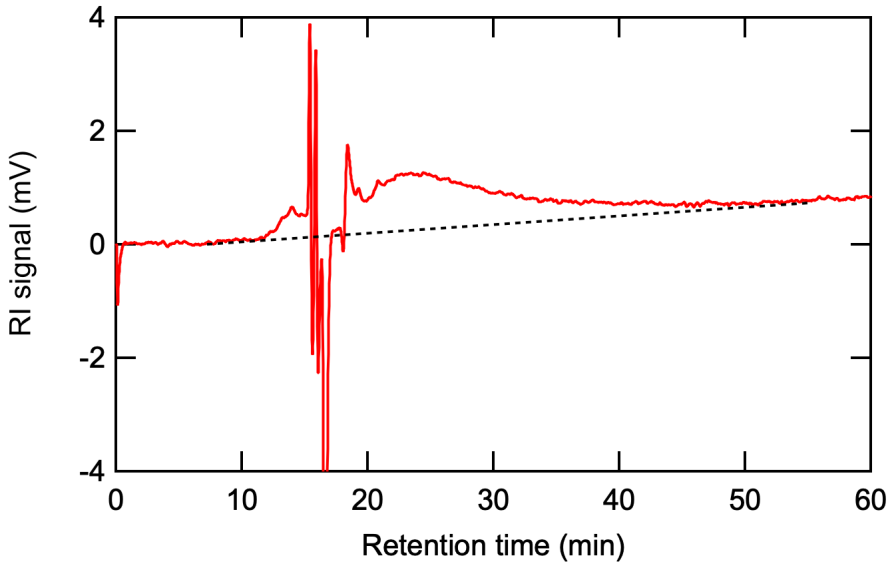


Figure S148. SEC-GPC trace of **C_6CI'IPDC$_6$** (O_{b1}) in DMF (differential refractive index detector). Strong adsorption on the column and oligomer aggregation prevent an accurate determination of the molar mass of the sample.

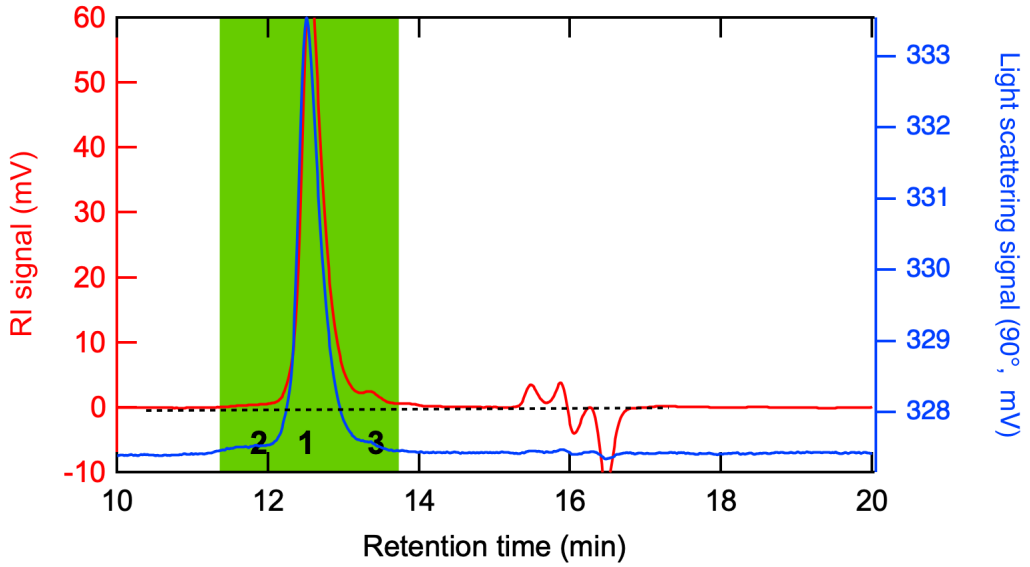


Figure S149. SEC-GPC trace of **C_6CIIDC$_6$** (O_{b2}) in DMF (differential refractive index detector, red, left vertical axis; light scattering detector (90° scattering angle), blue, right vertical axis). The region highlighted in green is where the sample elutes. The main peak (1) corresponds to the oligomer with a molar mass of 2722 g/mol. The small peak (2) is due to aggregates, at double the mass. The small peak (3) is an impurity of low molar mass. The light-scattering data was used to evaluate the purity of the compound (better than 95%) and the mass lost by filtration (*ca.* 6%, due to aggregation).

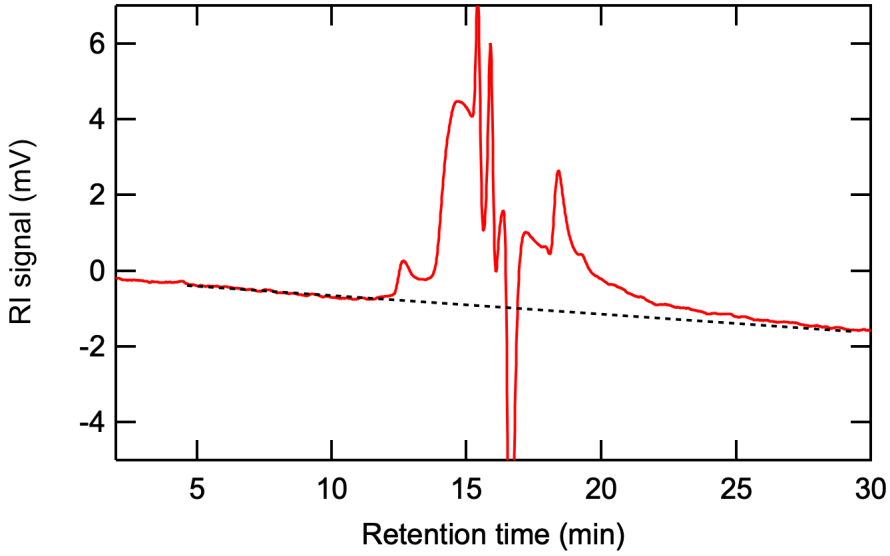


Figure S150. SEC-GPC trace of **C_6CIPDC$_6$** (O_{b3}) in DMF (differential refractive index detector). Strong adsorption on the column and oligomer aggregation prevent an accurate determination of the molar mass of the sample.

6 DOSY RESULTS

Preparation of the O_a (C_6GMPTC_6) NMR sample was carried out by filling a 5 mm NMR tube with 0.50 mL of a solution of O_a in a 95:5 (*v*/*v*) CD_3CN/DMSO-d_6 mixture (*conc*: 1mmol/L (=0.5 mol%)). The O_{b1} ($C_6CI'IPDC_6$) NMR samples were instead prepared using two equimolar amounts of phenylhydrazine. The two compounds were mixed and then dissolved in 0.50 mL of a 95:5 (*v*/*v*) CD_3CN/DMSO-d_6 mixture (*conc*: 1mmol/L (=0.5 mol%)). A series of NMR samples containing an equimolar amount of O_a and O_{b1} was obtained by filling 5 mm NMR tubes with 0.25 mL of a solution of O_a and 0.25 mL of a solution of O_{b1}, both prepared at the same concentration with a 95:5 (*v*/*v*) CD_3CN/DMSO-d_6 solvent mixture. The final NMR tube concentrations are as follows: 1 mmol/L each (=0.5 mol%), 2.5 mmol/L each (=1.25 mol%) and 5 mmol/L each (=5 mol%). The average diffusion coefficient of the pure monomers and their hydrodynamic radii obtained from the Stokes-Einstein equation are in Table S1. Tables of DOSY diffusion coefficients depending on NMR displacement for samples O_a, O_{b1} and O_a/O_{b1} at different concentrations are available at https://doi.org/10.14428/DVN/1XCNOK.

Table S1. Average diffusion coefficient $\overline{D}$ and hydrodynamic radius *r* of oligomers O_a and O_{b1}, measured by DOSY NMR in deuterated acetonitrile:DMSO 95:5 vol:vol (1 mM).

	O_a[a]	O_{b1}[a,b]
$\overline{D}$ ± standard error (m^2/s)[c]	$1.26x10^{-9} \pm 3.4x10^{-11}$ ($1.9x10^{-10}$)	Meas. 1: $1.15x10^{-9} \pm 3.8x10^{-11}$ ($2.3x10^{-10}$) Meas. 2: $1.02x10^{-9} \pm 3.6x10^{-11}$ ($2.3x10^{-10}$)
Average $\overline{D}$ (m^2/s)	$1.26x10^{-9} \pm 3.4x10^{-11}$	$1.09x10^{-9} \pm 2.6x10^{-11}$
r ± standard error (nm)[d]	0.5 ± 0.01	Meas.1: 0.54 ± 0.02 Meas. 2: 0.61 ± 0.02
Average *r* (nm)	0.5 ± 0.01	0.57 ± 0.014

[a] Standard deviations are indicated between parentheses. [b] Two independent measurements were performed for O_{b1}. [c] DOSY-average diffusion coefficient; the averages and standard errors were computed from the set of diffusion coefficients obtained for all protons. [d] DOSY-average hydrodynamic radius computed from the average diffusion coefficients using the Stokes-Einstein relationship.

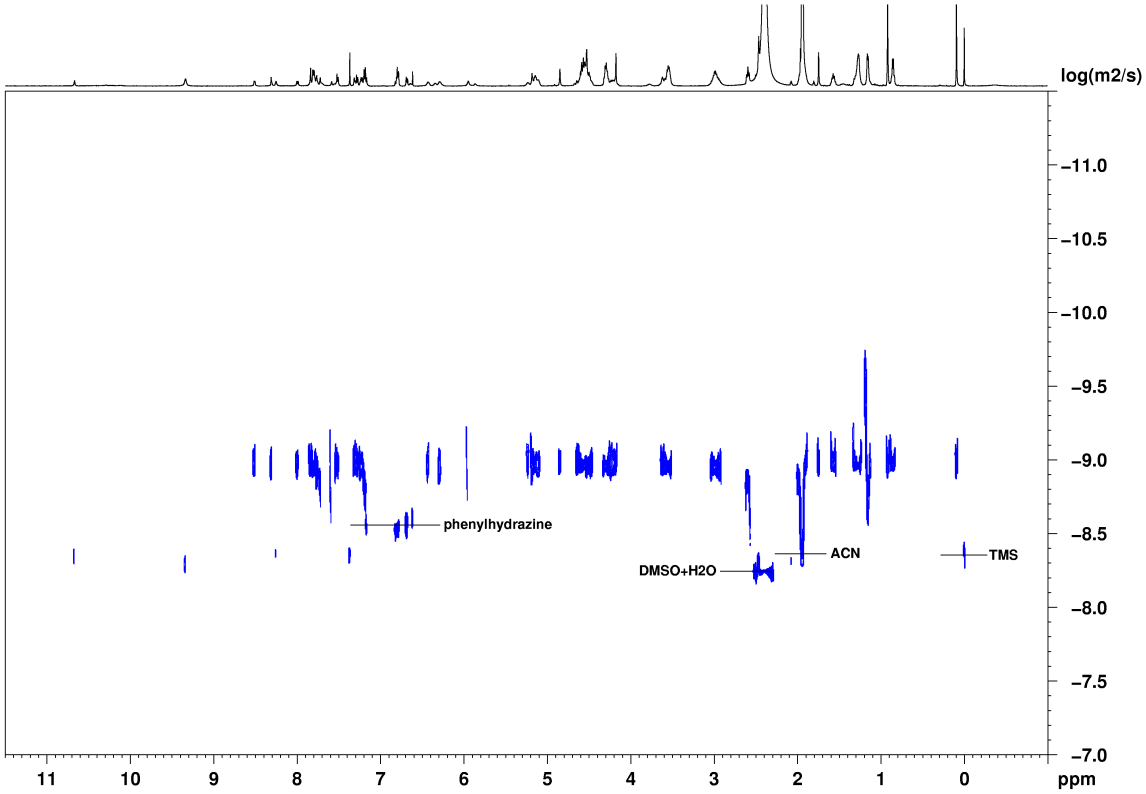


Figure S151. ^{1}H DOSY NMR spectrum of **Oa** in 95:5 CD_3CN/DMSO-d_6 at 0.5 mol%.

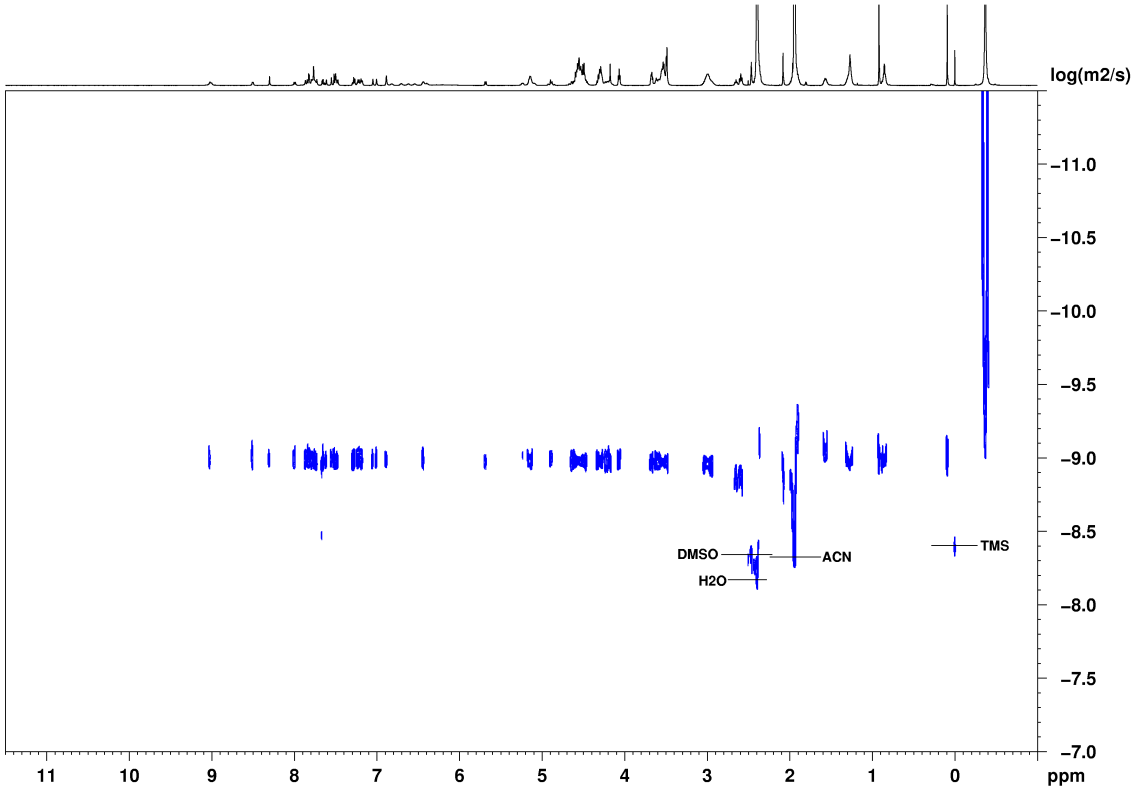


Figure S152. ^{1}H DOSY NMR spectrum of **Ob1** in 95:5 CD_3CN/DMSO-d_6 at 0.5 mol%.

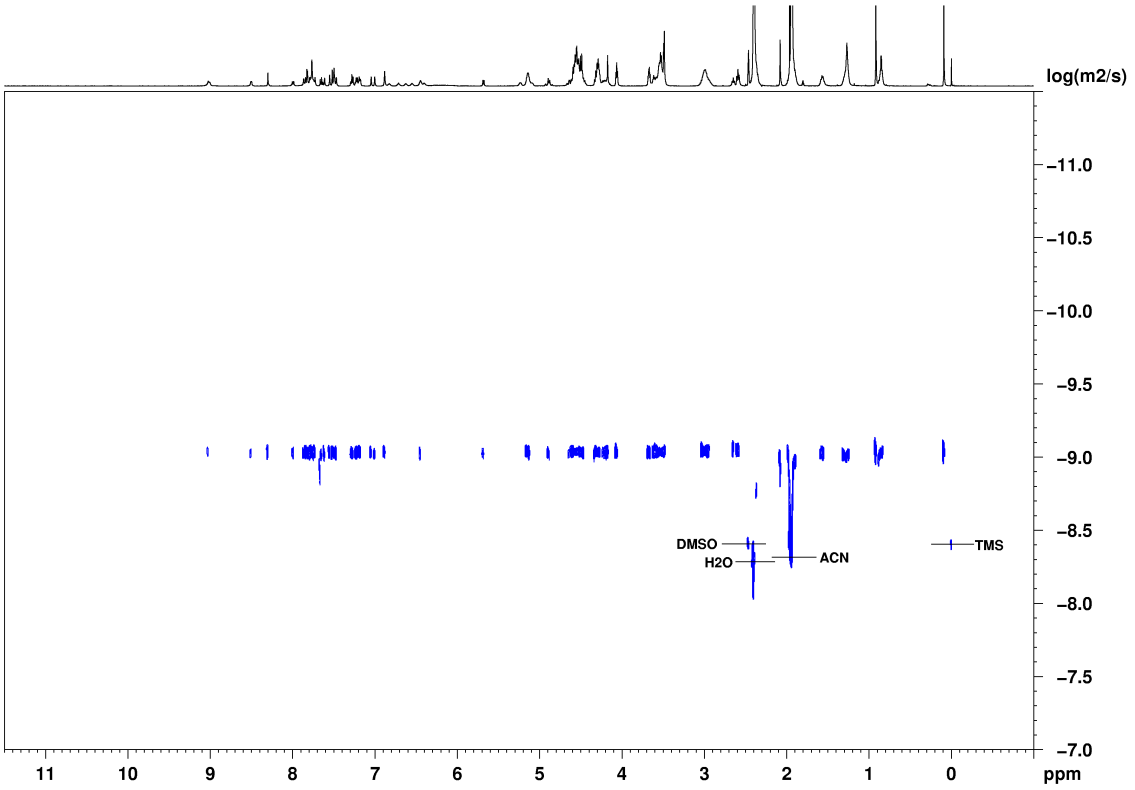


Figure S153. ^{1}H DOSY NMR spectrum of **Ob1** in 95:5 CD_3CN/DMSO-d_6 at 0.5 mol%.

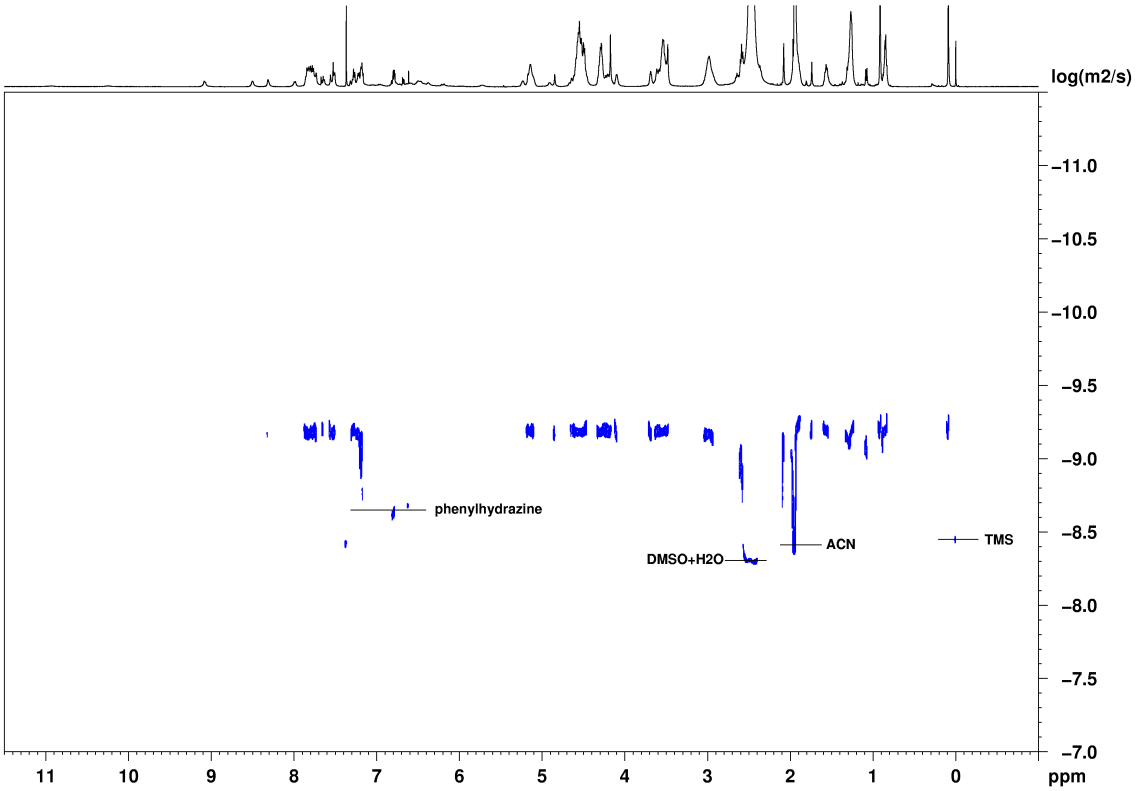


Figure S154. ^{1}H DOSY NMR spectrum of **Oa**+**Ob1** in 95:5 CD_3CN/DMSO-d_6 at 0.5 mol%.

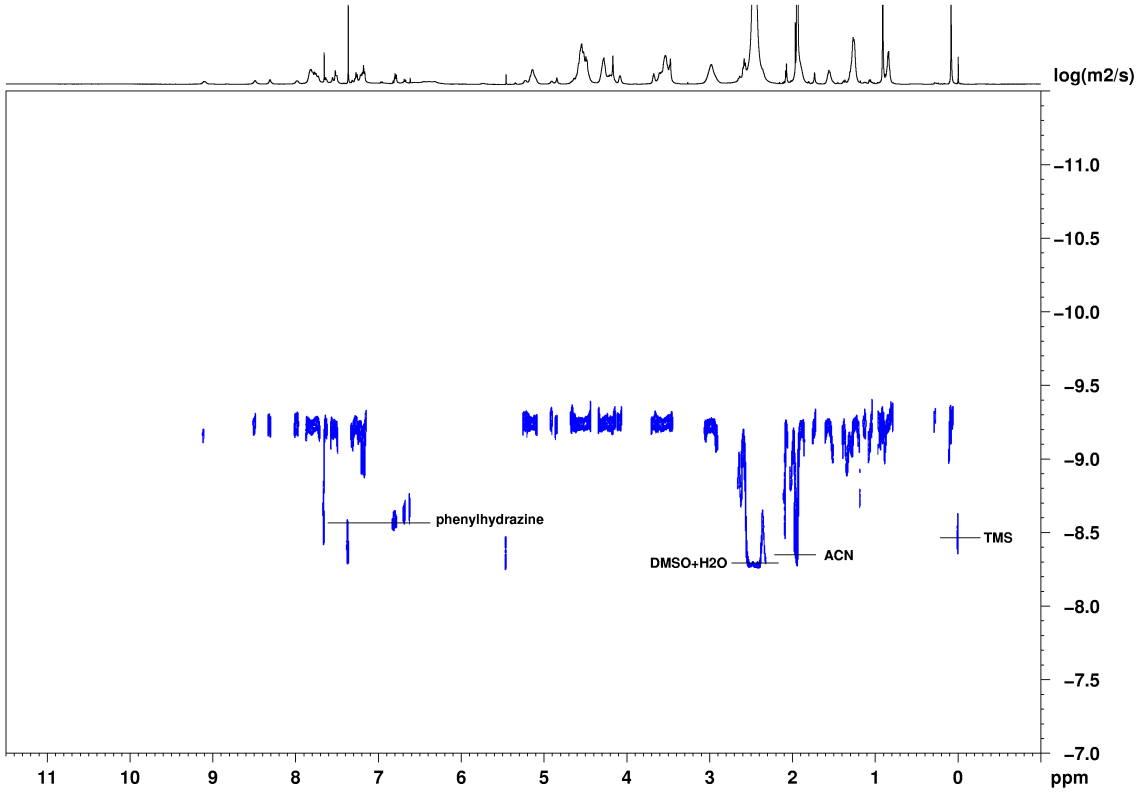


Figure S155. ^{1}H DOSY NMR spectrum of **Oa**+**Ob1** in 95:5 CD_3CN/DMSO-d_6 at 1.25 mol%.

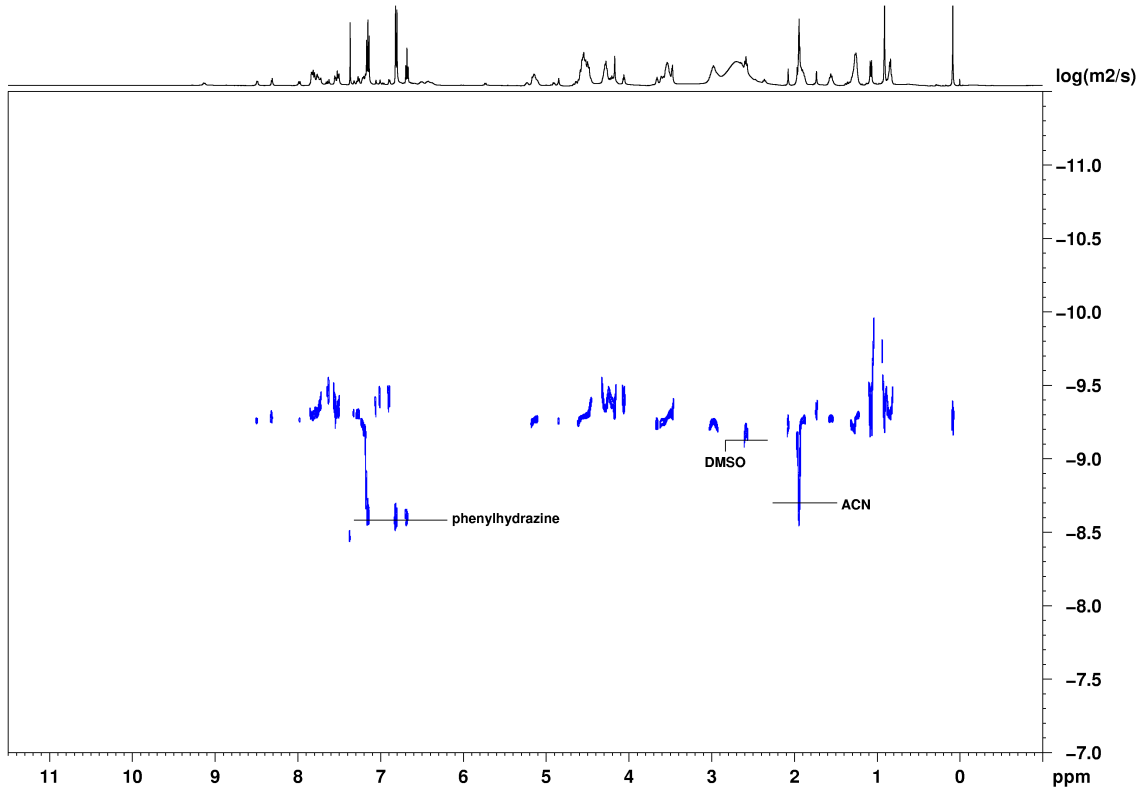


Figure S156. ^{1}H DOSY NMR spectrum of **Oa**+**Ob1** in 95:5 CD_3CN/DMSO-d_6 at 5 mol%.

7 NMR STUDY OF COPPER/BASE INTERACTIONS

Although the pyridyltriazole group is a strong ligand for Cu, the base analogues may compete with it. Proton NMR experiments were thus performed with monomer P combined with either monomers G, T, D, or C (in 1:1 molar ratio) in the presence of increasing amounts of CuI. Limited competing complexation of $Cu^{(I)}$ happens with monomers G and to a lesser extent C, and negligible complexation of $Cu^{(I)}$ happens with D or T (Figure S156). This limited competition probably contributes to a decreased activity of catalytic sites, which is taken into consideration in the factors p_C, p_L and p_f in the expressions of the turnover frequency of each species.

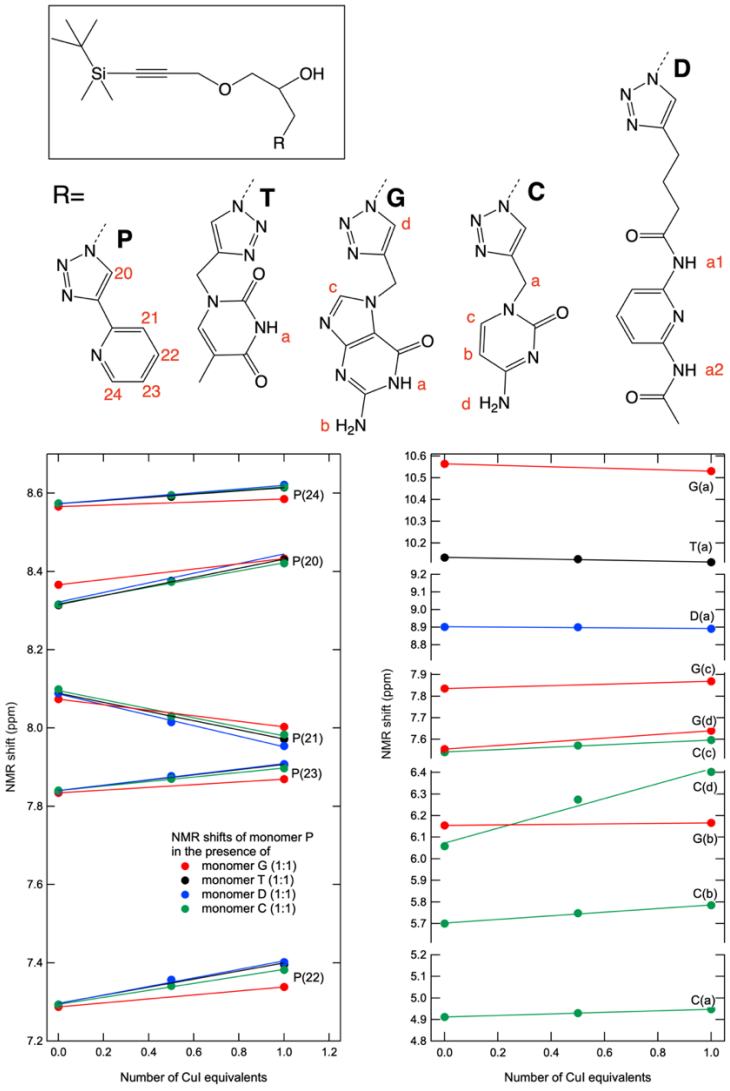


Figure S157. Variation of the proton NMR displacements in P:X 1:1 monomer mixtures, with X=G, D, T or C, in the presence of increasing amounts of CuI. The left graph provides the NMR displacements of the protons of the pyridyltriazole ligand; the right graph is for the protons of the base analogues. The data indicate a small competition for copper by base G, as testified by the slightly reduced variation of the chemical displacements of the pyridyltriazole protons in the presence of Cu and G. The proton displacements of C in the presence of Cu and P are also modified, indicating also partial interaction with copper; however, this does not modify the effect of Cu on the displacements of the pyridyltriazole.

8 GRAPHS OF YIELDS VERSUS TIME FOR THE AEROBIC OXIDATION OF ALCOHOLS

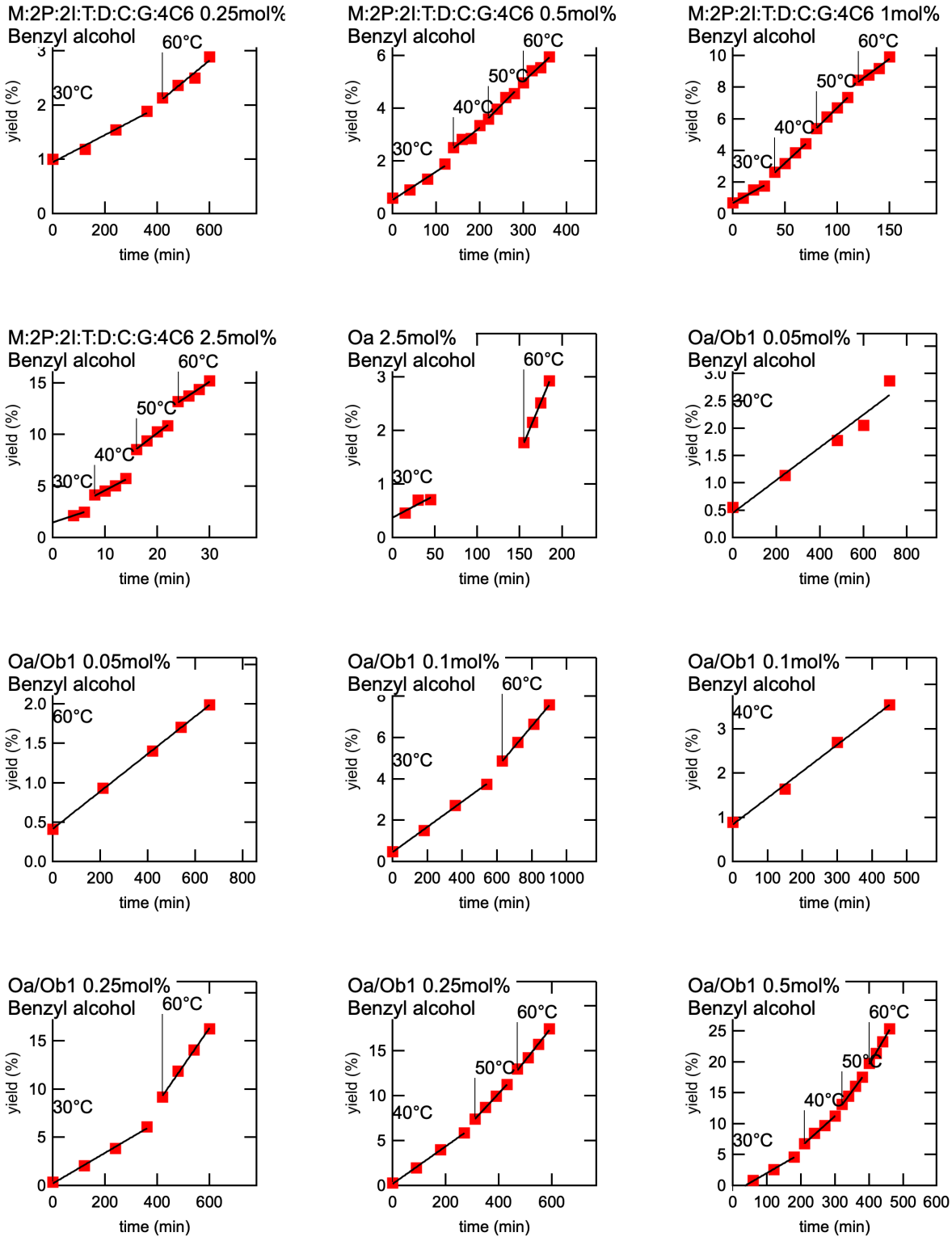


Figure S158 - part 1

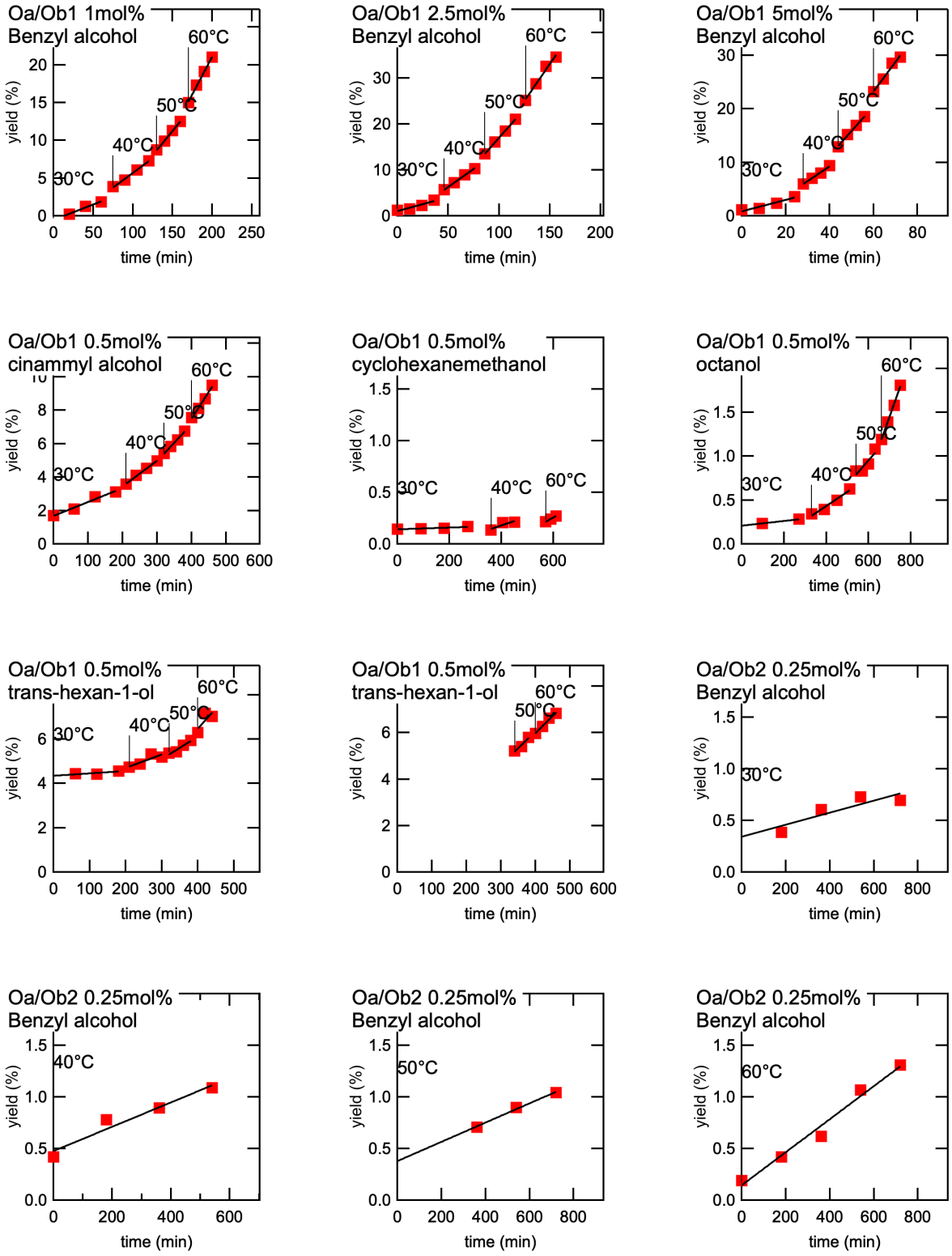


Figure S158 - part 2

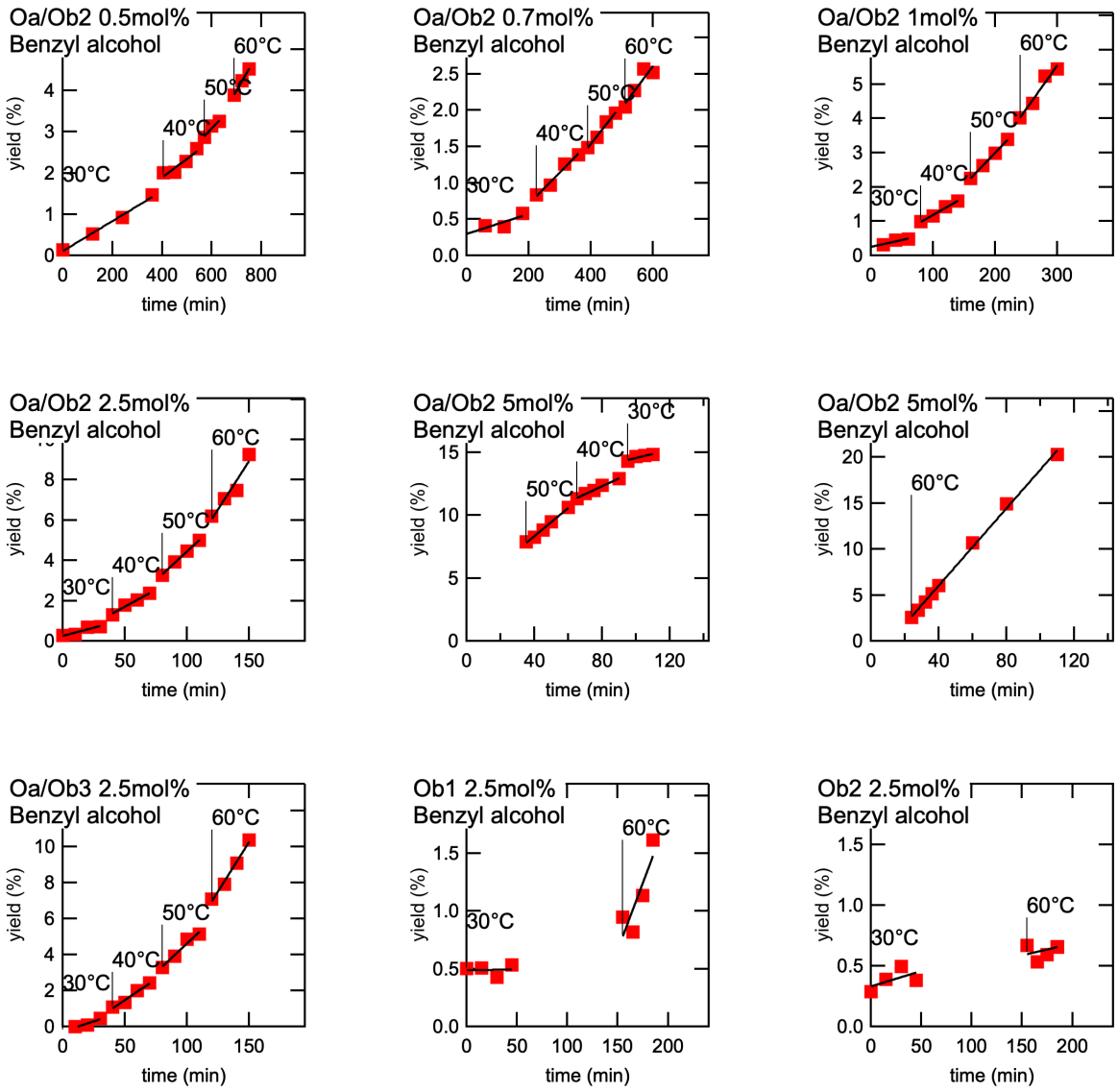


Figure S158 - part3. Yields of aldehyde *vs* reaction time for the aerobic oxidation of alcohols. The different catalytic systems are indicated in each panel ("M:2P:2I:T:D:C:G:4C6" refers to the system made of all separated monomer units at the same concentration as the complete O_a/O_{b1} system), together with the concentration relative to the alcohol concentration (0.2M), the experiment temperature, and the alcohol.

9 MATHEMATICAL MODELS OF THE COMPOSITION AND PROPERTIES OF THE CONSTITUTIONAL LIBRARIES

Composition of the libraries

The different species co-existing in a solution of O_a and O_b oligomers, each introduced at the initial molar concentration n, are listed in Figure S159.

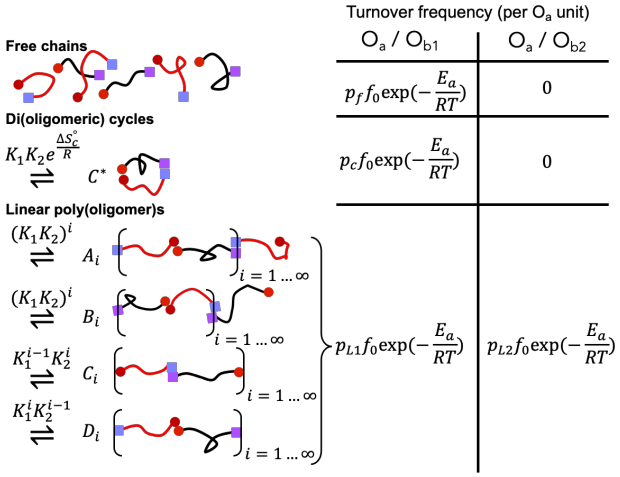


Figure S159. Libraries of co-existing species in solutions of the complementary oligomers, and parameters used to model the catalytic activity of the system.

The binding constants for two complementary chain end segments are $K_m = \exp(-(\Delta H_m^\circ - T\Delta S_m^\circ)/RT)$, $m = 1{,}2$ with ΔH_m° and ΔS_m° the standard enthalpy and entropy of binding (m=1 for G- and C-containing end segments, and m=2 for D- and T-containing end segments). Therefore, the equilibrium constant for cycle formation is $K^* \triangleq K_1K_2 \exp(\Delta S_c^\circ)$ in which ΔS_c° is the standard entropy cost for cycle formation; likewise, the equilibrium constants for the different linear poly(oligomers) are $(K_1K_2)^i$ for A_i and B_i, $K_1^{i-1}K_2^i$ for C_i and $K_1^iK_2^{i-1}$ for D_i (Figure S159). Defining the molar concentration at equilibrium as a for free O_a, b for free O_b, n^* for di(oligomeric cycles), a_i, b_i, c_i and d_i for A_i, B_i, C_i and D_i, respectively, and neglecting supramolecular rings combining more than two strands as they are entropically much less likely to form and are not expected to result in catalytic activities significantly different from linear chains, the equilibrium equations are:

$$K^* = \frac{n^*}{ab}$$

$$(K_1K_2)^i = \frac{a_i}{a^ib^{i+1}}$$

$$(K_1K_2)^i = \frac{b_i}{a^{i+1}b^i}$$

$$K_1^{i-1}K_2^i = \frac{c_i}{a^ib^i}$$

$$K_1^iK_2^{i-1} = \frac{d_i}{a^ib^i}\ , i = 1 \cdots \infty\ .$$

The mass balance equation for O_a is:

$$n = n^* + a + \sum_{i=1}^{\infty}(i+1)b_i + \sum_{i=1}^{\infty} i\,(a_i + c_i + d_i) = K^* ab + \frac{a(1 + K_1K_2b^2 + (K_1 + K_2)b)}{(1 - K_1K_2ab)^2}$$

for which we have used $\sum_{i=0}^{\infty} i\,x^{i-1} = (1-x)^{-2}$ if $|x| < 1$.

A similar equation can be obtained from the mass balance on O_b; however, this second equation is redundant since the two oligomers are introduced at the same concentration, and a=b at equilibrium. Therefore, the equilibrium concentration in free O_a oligomer, a, can be obtained by solving:

$$n = K^* a^2 + \frac{a(1 + (K_1 + K_2)a + K_1K_2a^2)}{(1 - K_1K_2a^2)^2}$$

which is equivalent to numerically finding the physically-compatible root of:

$$K_1^2K_2^2K^*a^6 - (K_1^2K_2^2n + 2K_1K_2K^*)a^4 + K_1K_2a^3 + (K^* + K_1 + K_2 + 2K_1K_2n)a^2 + a - n = 0\,.$$

The fraction of O_a oligomers in free chains, di(oligomeric) cycles and linear chains is then a/n, K^*a^2/n and $1 - (a + K^*a^2)/n$, respectively. The average degree of poly(oligomerization) by number of the set of linear chains, excluding free oligomers and cycles, is:

$$< N >= \frac{\sum_{i=1}^{\infty} 2i(c_i + d_i) + (2i+1)(a_i + b_i)}{\sum_{i=1}^{\infty} c_i + d_i + a_i + b_i} = \frac{2}{1 - K_1K_2ab} + \frac{K_1K_2(a+b)}{K_1 + K_2 + K_1K_2(a+b)}$$

in which b=a at equilibrium.

Catalytic activity of the constitutional libraries

The different co-existing species each contribute to the measured catalytic activity, here defined as the turnover frequency (*f*) measured by dividing the initial rate of oxidation (moles of alcohol converted per unit time) by the number of moles of introduced catalyst (defined here as the number of introduced M units).

Each member of the constitutional libraries has a specific probability that its required catalytic groups meet in space, which depends on conformational sampling and on the probability that two atoms of copper be properly complexed in the site. Additionally, access of the substrate to the catalytic site, and diffusion of the products from it, may differ between species. Therefore, each species *j* existing into the solution is assigned a specific turnover frequency, *per O_a it contains*, $f_j = p_j f_0 \exp(-E_a/RT)$, in which f_0 and E_a are the intrinsic frequency and activation energy associated to a complete catalytic site, and p_j takes into account the probability of formation of a complete catalytic site for species *j*, as well as other factors such as the ease of diffusion of substrate and products to and from the site, etc.

For di(oligomeric) cycles, the contribution to the total turnover frequency is thus $f_c = p_c f_0 \exp(-E_a/RT)\,K^*a^2/n$, with $p_c = 0$ if the cycle does not contain the five groups required for the catalysis.

Linear chains collectively comprise all needed groups for catalysis. Folding of the chains may bring these groups in close proximity; additionally, the chains dynamically redistribute their component oligomers intra- and inter-molecularly, thereby adding supplementary degrees of freedom for the creation of a catalytically-active site. Therefore, they are assigned a collective turnover frequency $f_L = p_L f_0 \exp(-E_a/RT)\,(1 - (a + K^*a^2)/n)$, with p_L different for each considered system.

Free oligomer chains only contribute to catalysis when they encounter by chance. For incomplete systems, this requires the random meeting of three chains, which is improbable and neglected. For the complete system, chance encounter of one O_a and one O_b is needed for catalysis. Therefore, in this case, $f_f = p_f f_0 \exp(-E_a/RT)\,a^2/n$. It should be noted that the units of p_f are different from the ones of p_c and p_L.

Combining these expressions leads to the expression of the turnover frequency of the catalytic solutions, $f = f_c + f_L + f_f$.

For the complete O_a/O_{b1} system:

$$f = p_c f_0 \exp(-E_a/RT)\, K^* a^2/n + p_{L1} f_0 \exp(-E_a/RT)\,(1 - (a + K^* a^2)/n) + p_f f_0 \exp(-E_a/RT)\, a^2/n$$

For the incomplete O_a/O_{b2} system:

$$f = p_{L2} f_0 \exp(-E_a/RT)\,(1 - (a + K^* a^2)/n)$$

with n the number of moles of introduced O_a, and a the number of free O_a chains at equilibrium, computed using the equations of the previous section.

Fits of the model to the experimental catalytic data

The theoretical expressions for the turnover frequencies were fitted simultaneously to all the experimental data acquired on both the O_a/O_{b1} and the O_a/O_{b2} systems, for the whole set of concentrations and temperatures. The fit parameters and their optimal values obtained by the Marquardt-Levenberg fitting procedure are given in Table S2.

Table S2. Parameters obtained from the fit of the catalytic data.[a]

	O_a/O_{b1}	O_a/O_{b2}
ΔH_1° (kJ/mol, G---C pairing)	-45.0 ± 0.2	Same as for O_a/O_{b1}
ΔS_1° (J/mol.K, G---C pairing)	-82 ± 10	Same as for O_a/O_{b1}
ΔH_2° (kJ/mol, D---T pairing)	-41.2 ± 0.2	Same as for O_a/O_{b1}
ΔS_2° (J/mol.K, D---T pairing)	-72 ± 11	Same as for O_a/O_{b1}
ΔS_c° (J/mol.K)	-49 ± 0.7	Same as for O_a/O_{b1}
E_a (kJ/mol)	52.9 ± 1	Same as for O_a/O_{b1}
$p_c f_0$ (1/min)	$1.7\text{x}10^8 \pm 7.1\text{x}10^7$	0
$p_{Li} f_0$ (1/min), i=1,2	$1.0\text{x}10^7 \pm 0.4\text{x}10^7$	$1.2\text{x}10^7 \pm 0.4\text{x}10^7$
$p_f f_0$ (1/min.mol)	$1.7\text{x}10^9 \pm 1\text{x}10^9$	0

[a] The standard errors are the square roots of the corresponding diagonal elements of the covariance matrix.

Model of the diffusion coefficients measured by DOSY NMR

Diffusion coefficients D are obtained from DOSY proton NMR experiments, in which the signal intensity at a given chemical shift, I, is fitted as a function of gradient strength g according to the Stejskal–Tanner equation:[12]

$$I(g) = I(0) \exp\left(-D(\gamma g \delta)^2 \left(\Delta - \frac{\delta}{3}\right)\right)$$

in which γ is the proton magnetogyric ratio, δ is the duration of a pulse and Δ the time between two pulses. For a system composed of different species in dynamic equilibrium at the timescale of the experiment (*ca.* 0.1 ms), the diffusion coefficient $\overline{D}$ is an average performed over the N different coexisting species:

$$I(g) = I(0)\exp\left(-\overline{D}(\gamma g\delta)^2\left(\Delta - \frac{\delta}{3}\right)\right) = \sum_{j=1}^{N} I_j(0)\exp\left(-D_j(\gamma g\delta)^2\left(\Delta - \frac{\delta}{3}\right)\right)$$

in which $I_j(0)$ is the contribution of species j having diffusion coefficient D_j. Developing to first order leads to:

$$\overline{D} = \frac{\sum_{j=1}^{N} I_j(0)D_j}{I(0)} = \frac{\sum_{j=1}^{N} q_j n_j D_j}{\sum_{j=1}^{N} q_j n_j}$$

with n_j the molar concentration in species j, and q_j the number of equivalent protons of species j at the considered NMR displacement.

Suppose that there are q_0 equivalent protons belonging to oligomer O_a, and that we measure the diffusion coefficient at the NMR displacement of these protons. The number of equivalent protons of any species, q_j, at this specific NMR displacement is then equal to the product of q_0 and the number of O_a oligomers which this species contains, $N_{Oa,j}$:

$$q_j = q_0 N_{Oa,j}$$

Therefore, the average diffusion coefficient measured at this specific NMR displacement only depends on the number of oligomers O_a in each species, and on the concentration of each species:

$$\overline{D} = \frac{\sum_{j=1}^{N} N_{Oa,j} n_j D_j}{\sum_{j=1}^{N} N_{Oa,j} n_j} = \frac{\sum_{j=1}^{N} N_{Oa,j} n_j D_j}{n}$$

with n the total initial concentration of O_a, as before. At equilibrium, the catalyst solution comprises free O_a and O_b oligomers each at the molar concentration a, cyclic di(oligomers) at the molar concentration $n^* = K^* a^2$, and linear poly(oligomeric) chains of different types, A_i, B_i, C_i and D_i, $i = 1 \ldots \infty$, at the molar concentrations $a_i = b_i = (K_1K_2)^i a^{2i+1}$, $c_i = K_1^{i-1}K_2^i a^{2i}$, and $d_i = c_i K_1/K_2$, respectively (see companion article). Therefore,

$$\overline{D} = \frac{1}{n}\left(aD_{Oa} + n^*D^* + \sum_{i=1}^{\infty}(ia_iD_{Ai} + (i+1)b_iD_{Bi} + ic_iD_{Ci} + id_iD_{Di})\right)$$

$$\overline{D} = \frac{1}{n}\Bigg(aD_{Oa} + K^*a^2D^* + \sum_{i=1}^{\infty}\Big(i(K_1K_2)^i a^{2i+1}D_{Ai} + (i+1)(K_1K_2)^i a^{2i+1}D_{Bi} + iK_1^{i-1}K_2^i a^{2i}(D_{Ci} + D_{Di}K_1/K_2)\Big)\Bigg)$$

in which D_{Oa}, D^*, D_{Ai}, D_{Bi}, D_{Ci}, D_{Di} are the diffusion coefficients of the oligomer O_a, di(oligomeric) cycles, and linear chains A_i, B_i, C_i and D_i, respectively.

Since species A_i and B_i contain the same total number of oligomers, $D_{Ai} \approx D_{Bi}$; the same holds true for C_i and D_i, leading to $D_{Ci} \approx D_{Di}$. Defining

$$D_{ABi} = (D_{Ai} + D_{Bi})/2 \text{ and}$$

$$D_{CDi} = (D_{Ci} + D_{Di})/2$$

leads to:

$$\overline{D} \approx \frac{1}{n}\left(aD_{Oa} + K^* a^2 D^* + \sum_{i=1}^{\infty} \left((2i+1)(K_1K_2)^i a^{2i+1} D_{ABi} + 2i(K_1K_2)^{i-1} a^{2i} K_{12} D_{CDi} \right) \right)$$

in which $K_{12} = (K_1 + K_2)/2$.

To progress further, expressions are needed for the diffusion coefficients. In the non-draining approximation which applies to our oligomers which form coiled globules (as indicated by molecular dynamics simulations), the diffusion coefficient of a chain may be estimated by the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\mu_0 r}$$

in which k is the Boltzmann constant, T is temperature, μ_0 is the viscosity of the medium (*i.e.*, the solvent in our very dilute conditions), and r is the hydrodynamic radius of the chain. The hydrodynamic radii of the free oligomers, r_a and r_b for O_a and O_b, respectively, can be obtained by measuring their diffusion coefficients D_{Oa} and D_{Ob} by DOSY NMR at low concentrations.

The diffusion coefficients of the other species can then be obtained from the hydrodynamic radii of the oligomers. In the non-draining limit, the hydrodynamic radius of a poly(oligomeric) chain containing m O_a and n O_b oligomers is:

$$r_{mn} = \left(m r_a^{1/\nu} + n r_b^{1/\nu} \right)^{\nu}$$

in which $\nu = 0.5$ in a theta solvent and ~0.57 in a good solvent with excluded volume interactions, according to numerical simulations.[13] If r_a is close to r_b, which is the case in our system, then:

$$r_{mn} \approx \left(\frac{r_a^{1/\nu} + r_b^{1/\nu}}{2} \right)^{\nu} (m+n)^{\nu} = \overline{r}(m+n)^{\nu}$$

in which $\overline{r}$ is the average hydrodynamic radius of the two oligomers. Then, the diffusion coefficients of the poly(oligomeric) components of the catalytic medium are:

$$D_{Ai} = D_{Bi} = D_{ABi} \approx \frac{kT}{6\pi\mu_0\overline{r}} \frac{1}{(2i+1)^{\nu}}$$

$$D_{Ci} = D_{Di} = D_{CDi} \approx \frac{kT}{6\pi\mu_0\overline{r}} \frac{1}{(2i)^{\nu}}$$

Likewise, the diffusion coefficient of the di(oligomeric) cycles is:

$$D^* \approx \frac{kT}{6\pi\mu_0 \left(r_a^{1/\nu} + r_b^{1/\nu} \right)^{\nu} h^*} \approx \frac{kT}{6\pi\mu_0\overline{r}} \frac{1}{2^{\nu}} \frac{1}{h^*}$$

in which h^* is the ratio between the hydrodynamic radius of a cyclic di(oligomer) and a linear di(oligomer). According to numerical simulations performed on flexible chains,[13] $h^* \approx 0.82$ in a theta solvent and $h^* \approx 0.89$ in a good solvent with positive excluded volume.

Introducing these diffusion coefficients in the expression of the diffusion constant of the mixture, measured by DOSY on a proton belonging to oligomer O_a, gives the diffusion coefficient of the equilibrated mixture:

$$\overline{D} \approx \frac{kT}{6\pi\mu_0\overline{r}}\frac{1}{n}\left(a + \frac{K^* a^2}{2^\nu h^*} + \sum_{i=1}^{\infty}\left((2i+1)^{(1-\nu)}(K_1K_2)^i a^{2i+1} + (2i)^{(1-\nu)}(K_1K_2)^{i-1}a^{2i}K_{12}\right)\right).$$

In this expression, the terms of the infinite series successively correspond to dimers ($2i$=2), trimers ($2i$+1=3), tetramers ($2i$=4), etc. The terms of this series will become negligible from some value $i = i_\infty$, leading to:

$$\overline{D} \approx \frac{kT}{6\pi\mu_0\overline{r}}\frac{1}{n}\left(a + \frac{K^* a^2}{2^\nu h^*} + \sum_{i=1}^{i_\infty}\left((2i+1)^{(1-\nu)}(K_1K_2)^i a^{2i+1} + (2i)^{(1-\nu)}(K_1K_2)^{i-1}a^{2i}K_{12}\right)\right).$$

The same equation is obtained if one considers a proton belonging to the O_b oligomer; therefore, this is the final expression for the average diffusion coefficient of the mixture.

10 ALL-ATOM MOLECULAR DYNAMICS (MD) SIMULATIONS

Simulation protocol

The oligomeric chains were built as a series of fragments, or residues, with the Avogadro software **(Figure S160)**.[14]

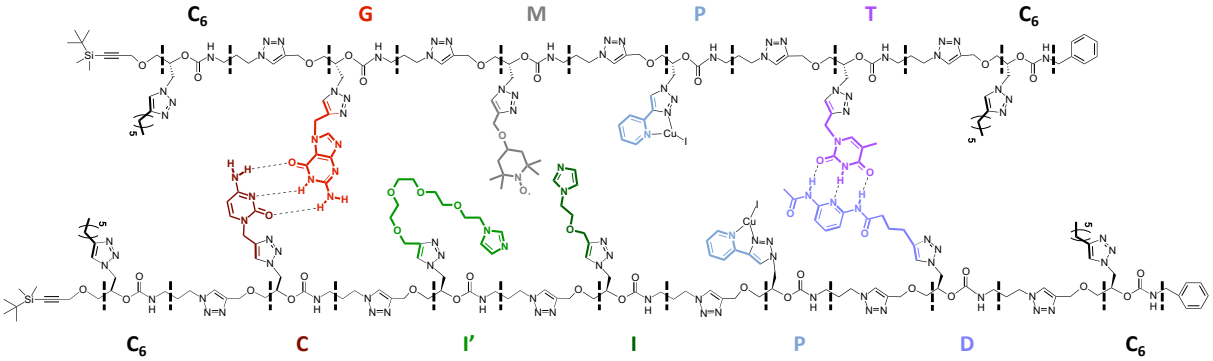


Figure S160. Chemical structure of the complete O_a/O_{b1} catalytic system. The two strands, O_a and O_{b1}, are decomposed into a series of 28 residues, separated by black dots. The residues containing the functional side-chains are identified by letters.

These fragments were subsequently connected to one another to form the complete strands. The calculations were then performed with the AMBER16 simulation package, while free energy calculations were performed with the 2020 version of *ambertools*.[15] The atomic partial charges were assigned to the fragments using the *antechamber* module[16] of AMBER16 with the semi-empirical AM1-BCC method.[17] Structural parameters and partial charges of the 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) radical were used as reported by Stendardo *et al.* after an ab-initio re-parameterization.[18] Structural parameters and partial charges of the pyridyltriazole copper ligands were obtained by calculations at the quantum-chemical level using density functional theory (DFT) with the B3LYP/6-31G** model and extra basis sets LanL2DZ and MIDI! for the copper and iodine atoms, respectively. All other force-field parameters were given by the *General Amber Force-Field* (GAFF) 2.1.[19] The individual molecular fragments were then connected in the desired sequence with the *LEaP* module of AMBER16 to constitute the complete oligomeric chains. When building the complete O_a/O_b catalytic system, the second strand was translated by 40 Å in the *x*, *y* and *z* directions in order to avoid contacts between the two oligomers in the starting structure. A geometry optimization was then performed by molecular mechanics, with a total of 10,000 steps distributed in 1,000 steps of steepest descent and 9,000 steps of conjugated gradient, in order to get a stable starting point for the subsequent MD simulations. These were carried out with an implicit solvent model, the Generalized-Born (GB) model, to ensure a sufficient conformational sampling in a reasonable computational time.[20] The dielectric constant was set as the one of acetonitrile at 20 °C ($\varepsilon = 37.5$). For the catalytic system, constituted of the two strands O_a and O_b, two replicas of 10 µs were realized. Each oligomer was also simulated alone in two replicas of 5 µs. The timestep was fixed to 1 fs and the temperature was maintained at 300 K with a Langevin thermostat, with a collision frequency of 1 ps^{-1}. A bond restraint was applied in the simulations of the two strands to avoid that they translate in opposite directions and never meet each other, as we are not in periodic conditions: when the distance between the chains exceeds about 75 Å, a

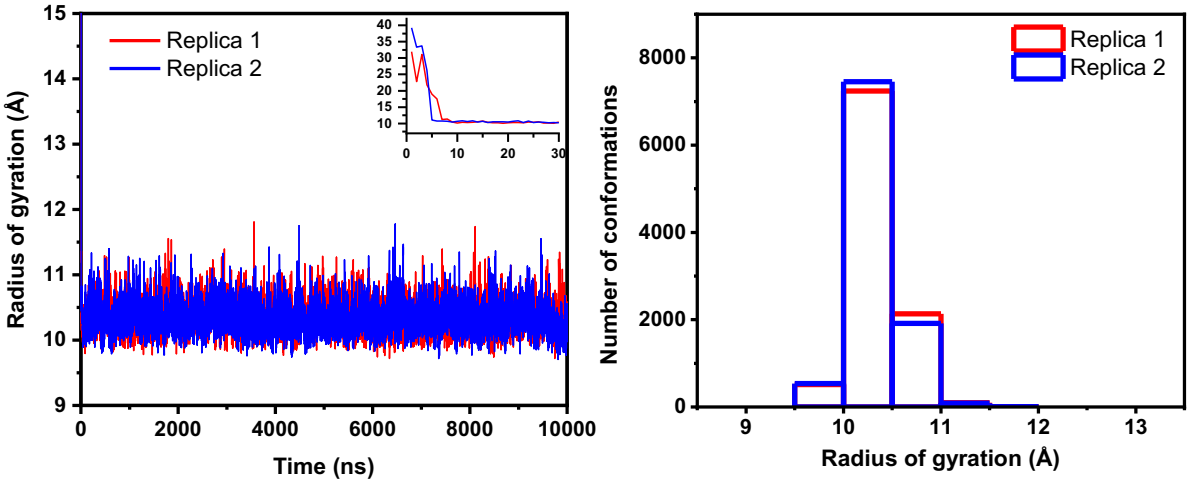
force constant of 10 kcal.mol^{-1}.Å^{-2} is activated to prevent the chains from moving further away. An infinite cut-off was selected for the non-bonded interactions. A snapshot was saved each ns during the MD simulations and extracted for further analyses, giving a total of 20,000 conformations for the complete catalytic assembly and 10,000 for each oligomeric chain alone. The GPU version of AMBER16 was used for all minimizations and MD simulations.[21] PyMOL 2.5.4 was used to visualize the snapshots and to extract images.[22]

Analyses of the trajectories

The analyses were performed using the *cpptraj* program of AMBER16. Mass-weighted radii of gyration (R_g) were computed with respect to heavy atoms (all atoms except hydrogens). End-to-end distances were calculated as the distance between the carbon directly linked to the silicon in the tert-butyl moiety at one end, and the carbon in para position of the phenyl ring at the other end. Hydrogen-bonds were detected with the default *cpptraj* parameters, i.e., a distance cutoff of 3.0 Å between the acceptor and the donor heavy atom and an angle cutoff of 135° between the donor, the hydrogen atom and the acceptor. Aromatic interactions (parallel stacking) were found with geometric criterion: two aromatic units are considered in interaction if the distance between their centres of mass is less than or equal to 5.0 Å and if the angle between the normal vectors of their planes is comprised between 45 and 135°. The heatmaps of H-bonds and stacking interactions were built with in-house scripts. The residue decomposition follows the sequence order and corresponds to the fragments used to build the chains, as is represented in Figure S160. Solvent-accessible surface-area (SASA) values were calculated with the LCPO model, as implemented within *cpptraj*.[23] The per-residue ΔSASA was simply computed as the difference between the SASA calculated for a residue in the complex of two chains and the SASA calculated for the same residue in the oligomer alone (the conformations of the individual oligomers were, in this case, obtained by removing the other chain in the trajectory of the complex). The ΔSASA can only be inferior or equal to 0: a residue that would be located far from the interface of the two strands, without contact with the second chain, would have a ΔSASA of 0, meaning that it is as accessible with or without the second chain. In contrast, a residue that would be buried at the interface would have a highly negative ΔSASA, showing that it is much less accessible in the presence of the second strand.

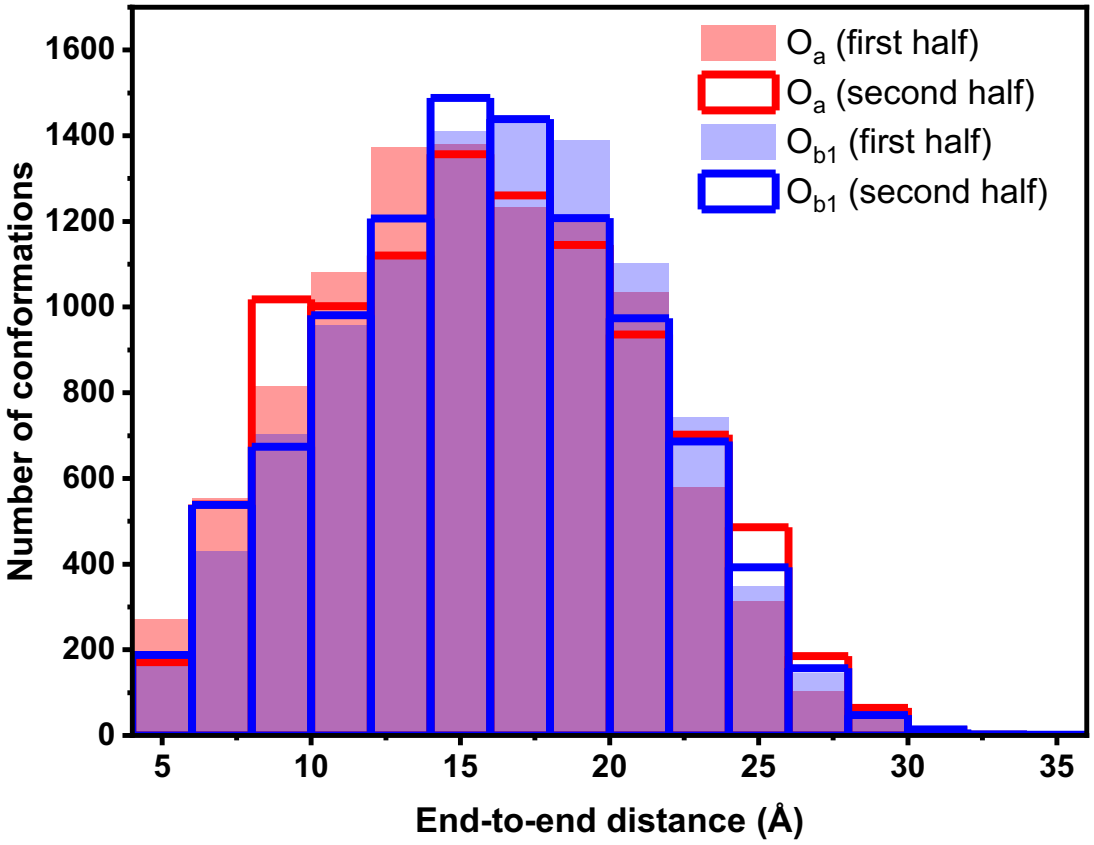
Binding enthalpy calculations were performed with the Molecular Mechanics Poisson-Boltzmann Surface Area (MM-PBSA) method, using the parallelized version of the Python program *MMPBSA.py* 14.0, implemented in Amber.[24] The binding enthalpy is given as the difference between the energy calculated for the complex (here, the complete catalytic system) and the sum of energies for the receptor (O_a) and ligand (O_b) alone. The "multiple-trajectory" approach was followed, which means that the conformations for the complex, receptor and ligand were obtained by independent simulations. *MMPBSA.py* post-processes the trajectories and calculates the energy of each frame with an implicit representation of the solvent. The energy is divided in two parts: an internal contribution and a solvation contribution. The internal contribution was given by the force-field and can be seen as the energy of the system in vacuum (bonds, angles, dihedrals, van der Waals and electrostatics). The solvation contribution is further divided into a polar and a non-polar part. The polar part represents the electrostatic interactions between the solute and the solvent and was obtained by solving the PB equation with a finite difference method. The non-polar part was calculated as the sum of a favourable "dispersion term" and an unfavourable "cavity term", representing the stabilizing solute-

solvent dispersion interactions and the cost of creating a cavity in the solvent, respectively. These two terms are proportional to the SASA. Several calculations were carried out by varying the internal dielectric constant, i.e., the dielectric constant of the solute, ranging from 1 to 4. The default value is set to 1, but in some cases, a better agreement with experimental results was obtained with higher values of the internal dielectric constant.[25,26] In our case, a better agreement was reached with an internal dielectric value of 4. The first 100 ns of each replica were skipped for the calculations to let the systems reach equilibrium, giving a total of 19,800 conformations for the O_a/O_{b1} complex and 9,800 conformations for the oligomeric strands alone. The external dielectric constant was fixed at 37.5, the one of acetonitrile at room temperature, as was done during the MD simulations. *MMPBSA.py* offers the possibility to decompose the energy by residue and by pairs of residues (using the same residue division as the one shown in Figure S160). The residue pairwise decomposition scheme was used to highlight pairs of residues playing an important part in the binding of the two oligomeric chains.



	Avg. (Å)	Std. Dev. (Å)	Initial (before assembly) (Å)	Final (Å)
Replica 1	**10.3**	**0.4**	**32.0**	**10.3**
Replica 2	**10.3**	**0.5**	**39.2**	**10.1**

Figure S161. Top: radii of gyration of the di(oligomeric) complex for the two replicas as a function of the simulation time with a zoom on the first 30 ns on the inset, showing the decrease of the R_g and its stabilization around 10 Å, related to the formation of the complex, in about 10 ns for each replica (left) and distributions of the radii for the 10,000 conformations sampled in each replica, with a bin size of 0.5 Å (right). Bottom: average, standard deviation, initial and final values of the radii of gyration for the two replicas.



	Avg (Å)	Std dev (Å)	Max (Å)	Min (Å)
O_a (first half)	**15.5**	**5.2**	**34.9**	**4.3**
O_a (second half)	**15.8**	**5.4**	**32.4**	**4.4**
O_{b1} (first half)	**16.2**	**5.1**	**32.8**	**4.4**
O_{b1} (second half)	**15.9**	**5.2**	**34.9**	**4.2**

Figure S162. Top: distributions of the end-to-end distances for the 20,000 conformations obtained during the simulation of the di(oligomeric) cycle, for each oligomeric chain, highlighting the wide variety of conformations accessible to the chains inside the complex. The distributions are similar for the first and second halves of the simulation, showing that the strands remain strongly flexible during the 10 μs. The bin size is 2 Å. Bottom: average, standard deviation, maximum and minimum values of the end-to-end distance for each chain.

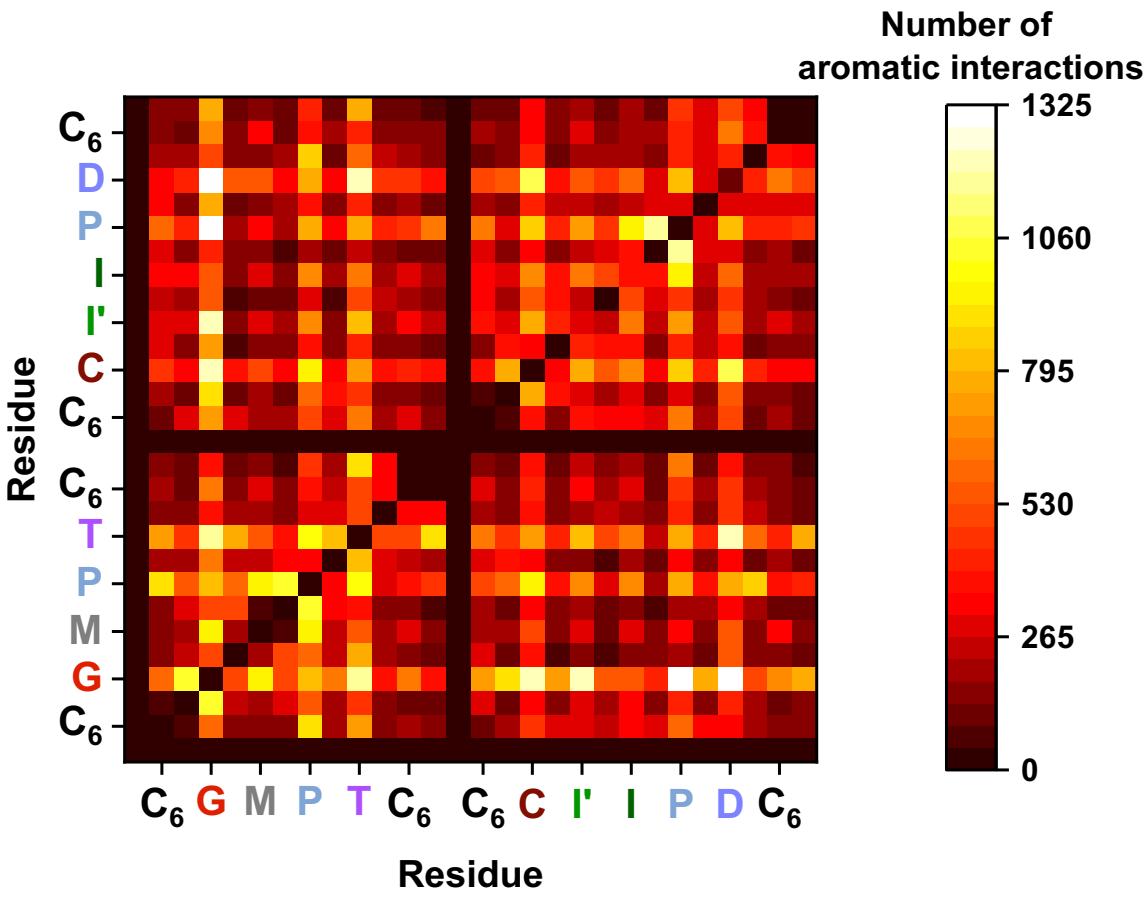


Figure S163. Heatmap showing the decomposition of the aromatic interactions (parallel stacking) by pairs of residues. Each square, localized at the crossing of a pair of residues, indicate, by its colour, the number of interactions detected between two residues. The map is symmetric with respect to the diagonal. The map is rather homogeneous, showing that most aromatic units can be close to each other and stabilize the system, even though the most persistent interactions usually involve at least one nucleobase analogue.

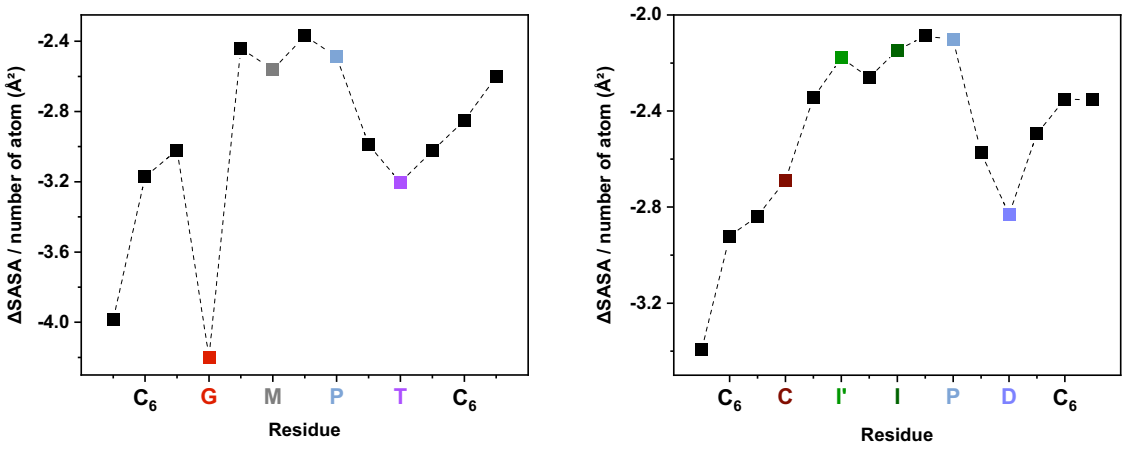
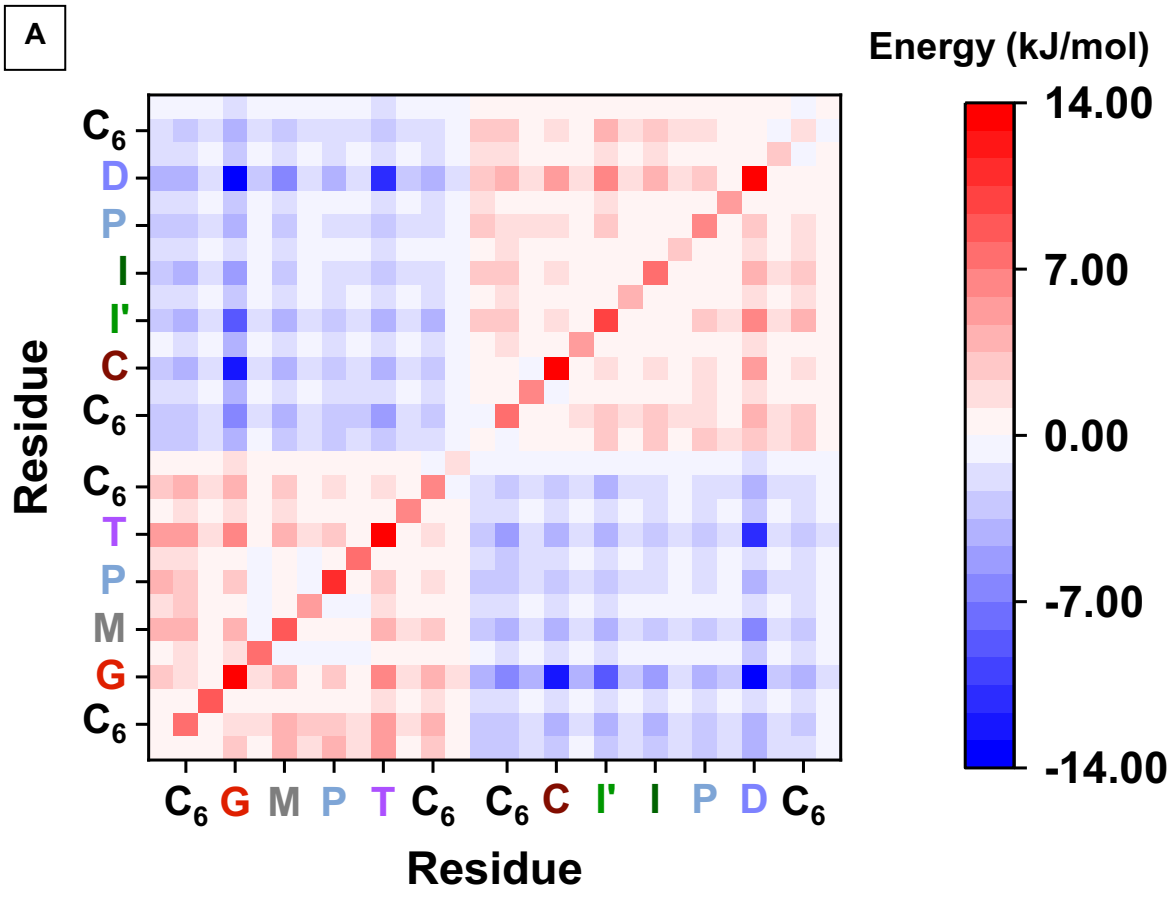
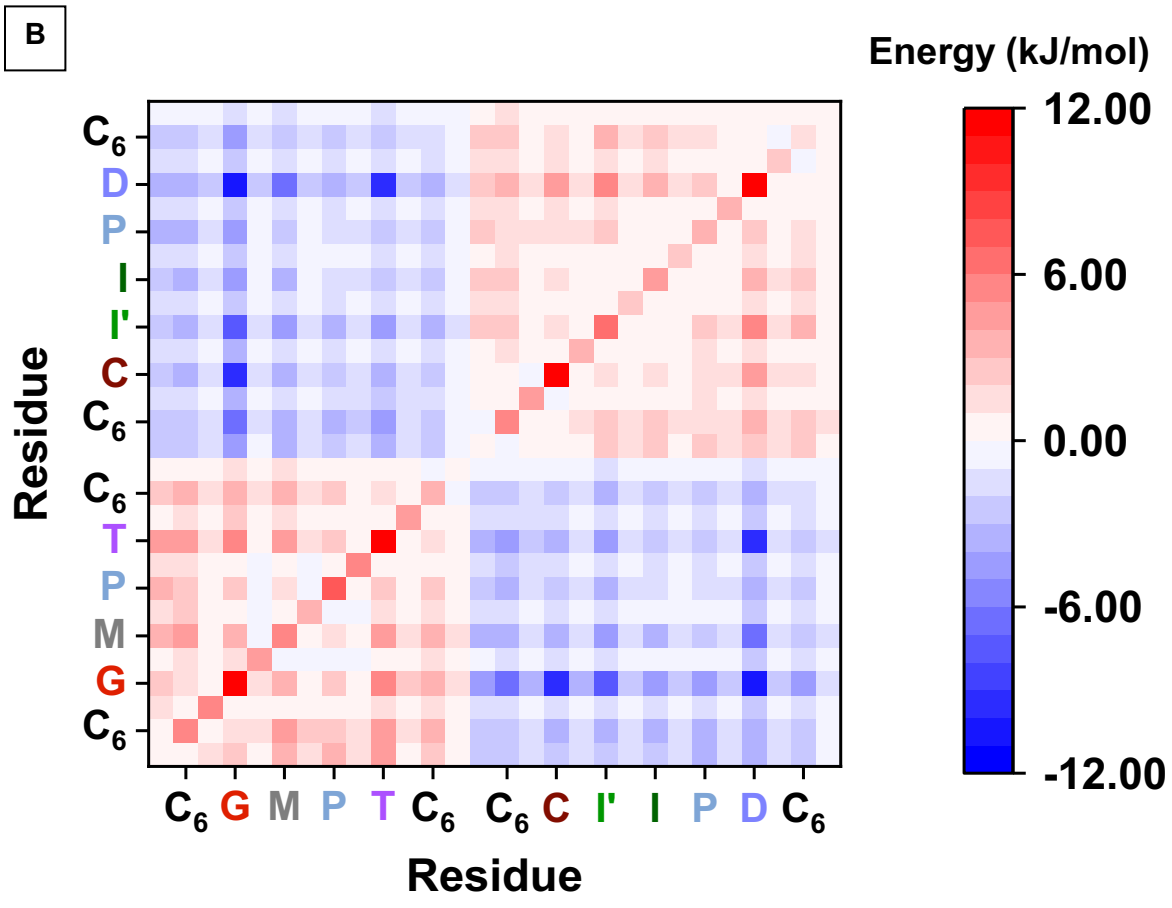
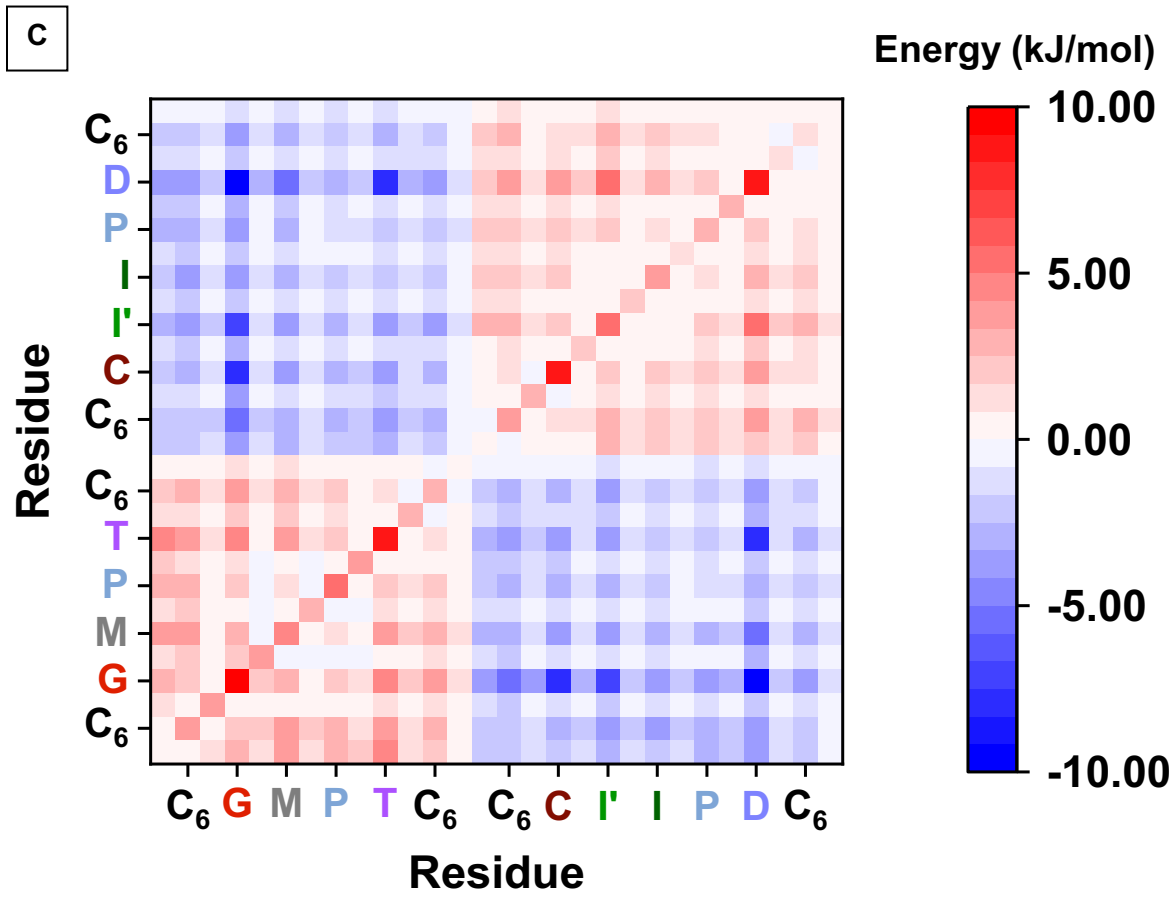
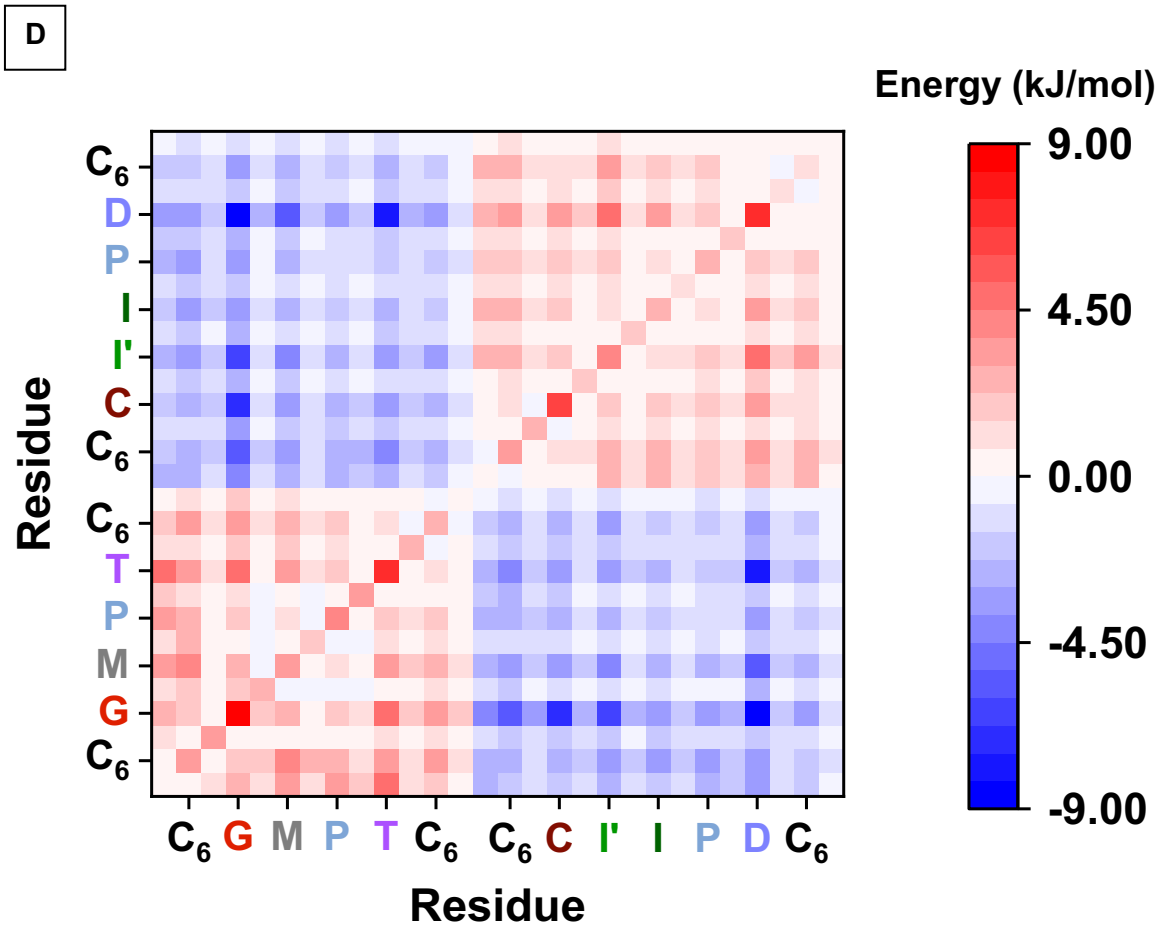


Figure S164. Per-residue ΔSASA values normalized by the number of atoms in each residue and averaged over the whole simulation, for the oligomeric strands O_a (left) and O_{b1} (right). The more negative the ΔSASA, the more the residue is hindered by the other strand in the di(oligomeric) complex, i.e., the more it is at the interface of the two strands. This graph shows that, for each chain, the catalytic units (M, P, I', I) tend to be among the less buried residues. This makes them more accessible to the surrounding environment, which could be catalytic substrates, for example.


A
Energy (kJ/mol)
14.00
7.00
0.00
-7.00
-14.00
Residue
C6 D P I I' C C6 C6 T P M G C6
C6 G M P T C6 C6 C I' I P D C6
Residue


B
Energy (kJ/mol)
12.00
6.00
0.00
-6.00
-12.00
Residue
C6 D P I I' C C6 C6 T P M G C6
C6 G M P T C6 C6 C I' I P D C6
Residue


C
Energy (kJ/mol)
10.00
5.00
0.00
-5.00
-10.00
Residue
C6 D P I I' C C6 C6 T P M G C6
C6 G M P T C6 C6 C I' I P D C6
Residue


D
Energy (kJ/mol)
9.00
4.50
0.00
-4.50
-9.00
Residue
C6 D P I I' C C6 C6 T P M G C6
C6 G M P T C6 C6 C I' I P D C6
Residue

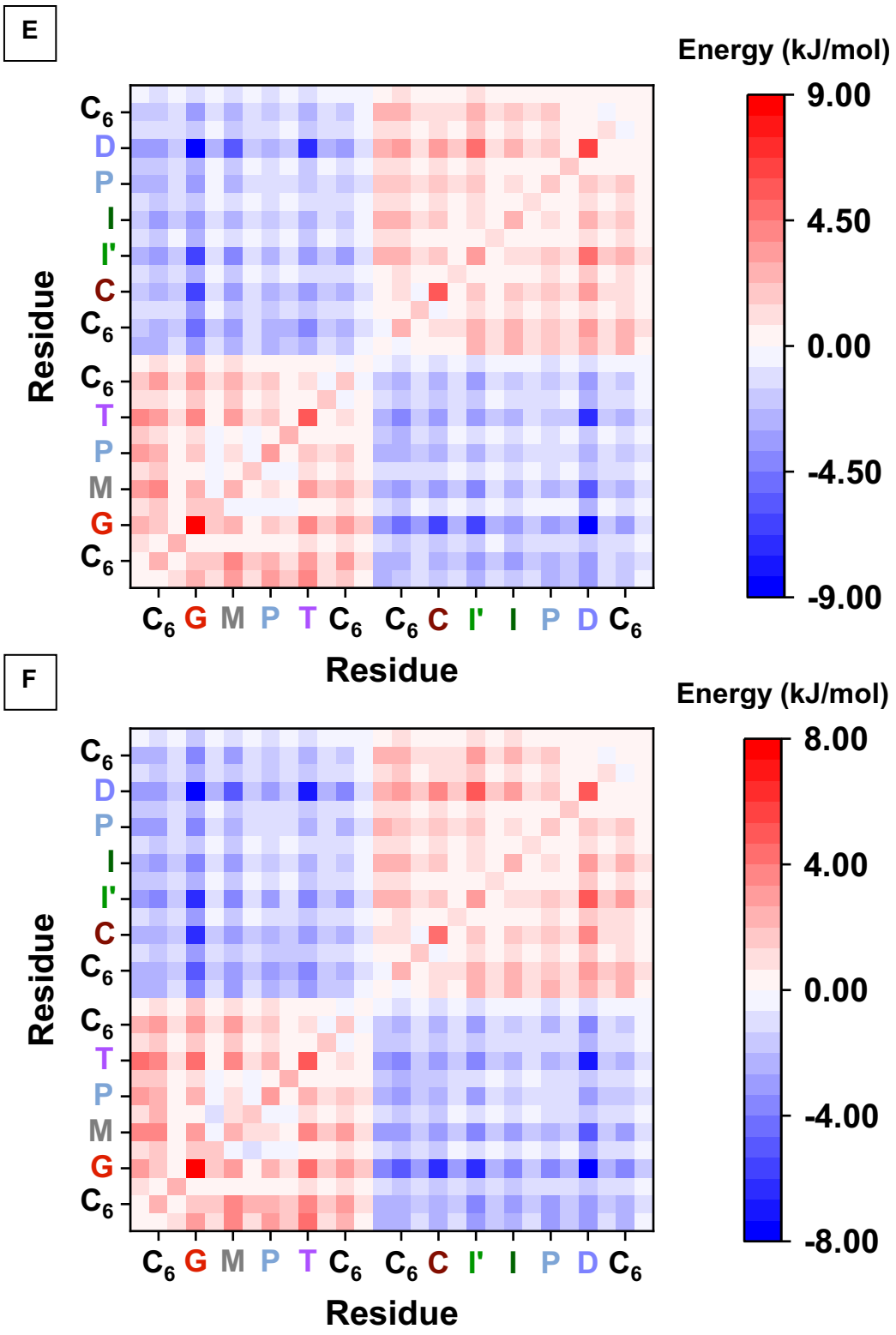


Figure S165. Heatmaps showing the decomposition of the binding energy by pairs of residues. The most stabilizing residue-residue interactions are localized for the pairs G---D, T---D and G---C. This highlights again the role of the nucleobase analogues in the stabilization of the complex. **A.** Internal dielectric constant = 1. **B.** Internal dielectric constant = 1.5. **C.** Internal dielectric constant = 2. **D.** Internal dielectric constant = 2.5. **E.** Internal dielectric constant = 3. **F.** Internal dielectric constant = 3.5.

11 MOLECULAR NETWORK ANALYSIS

The 3D conformations were converted into 2D networks. In this representation, all heavy atoms constitute *nodes*, and two nodes are connected by an *edge* if their distance is inferior or equal to 5 Å. This cutoff value allows to take into account hydrogen bonding interactions as well as aromatic stacking. In practice, one network file was created for each conformation of the catalytic system O_a/O_b from MD simulation, as soon as the duplex was formed (interchain distance < 14 Å) using in-house scripts, resulting in a total of 19,988 networks for O_a/O_{b1} and 19,953 for O_a/O_{b2}. These files, representing one conformation each, have been used to build one global network for each system, following this procedure: two nodes are considered connected by an edge only if they have been in contact during at least 10 % of the MD time, i.e., if their contact was detected in at least 10 % of the 19,998 conformations for O_a/O_{b1} and of the 19,953 conformations for O_a/O_{b2}. The resulting network is thus focusing on persistent contacts and neglecting more transient interactions. All edges are undirected and unweighted. To analyze and visualize the network, the *Cytoscape* 3.9.1 software[27] was used with its included analyzer *NetworkAnalyzer* 4.4.8.[28] Two descriptors were chosen to characterize the nodes inside the network. The betweenness centrality C_b for one node relies to the number of shortest paths connecting two other nodes passing through this node, i.e., the importance of the node to put the other ones into communication. The closeness centrality C_c for one node reflects the reciprocal of the average shortest paths length connecting this node to all the other nodes in the network: the higher the closeness, the more "central" is the node in the network, the more easily it communicates with the other nodes.

The network file was then submitted to the *Infomap* algorithm, in order to detect communities or modules, which are defined as highly connected groups of nodes.[29] The modular representation obtained can thus be thought as a coarse-grained view of the previous network. Various methods exist to decipher the modular topology of a network: the one that we used is called the *map equation*.[30,31] It is a flow-based method, which means that it focuses on "how is flowing, propagating the information from one node to another?". The propagation of information is materialized by a random walker that can move on the links between nodes while an information cost, in bits, can be associated with the movements of the walker. The main idea behind the *map equation* is that finding modules in the network can be seen as an encoding problem: to compress, reduce at best the information cost, it is necessary to efficiently partition, modularize the network. The *map equation*, based on Shannon's source coding theorem, gives the theoretical lower limit of the information cost associated with one step of the random walker, on average, on the network.[32] *Infomap* is the algorithm used to minimize the map equation. The principle is as follows: each node begins in its own module. Then, the nodes were moved into their neighbouring module that reduces the most the *map equation*. This operation is repeated, the newly formed modules are merged with their neighbours, until no more minimization can be attained. The main goal of *Infomap* is thus to find the best partition of the network, i.e., the optimal organization of nodes inside the optimal number of modules, to reduce the most efficiently the information cost associated with the movements of a random walker. A two-level partition of the network was chosen, such as there is only one layer of modules containing the nodes (no possibility to have "module of modules").

Visualization and analysis of the network was done with the 2.6.0 version of the web server utility of *Infomap*.

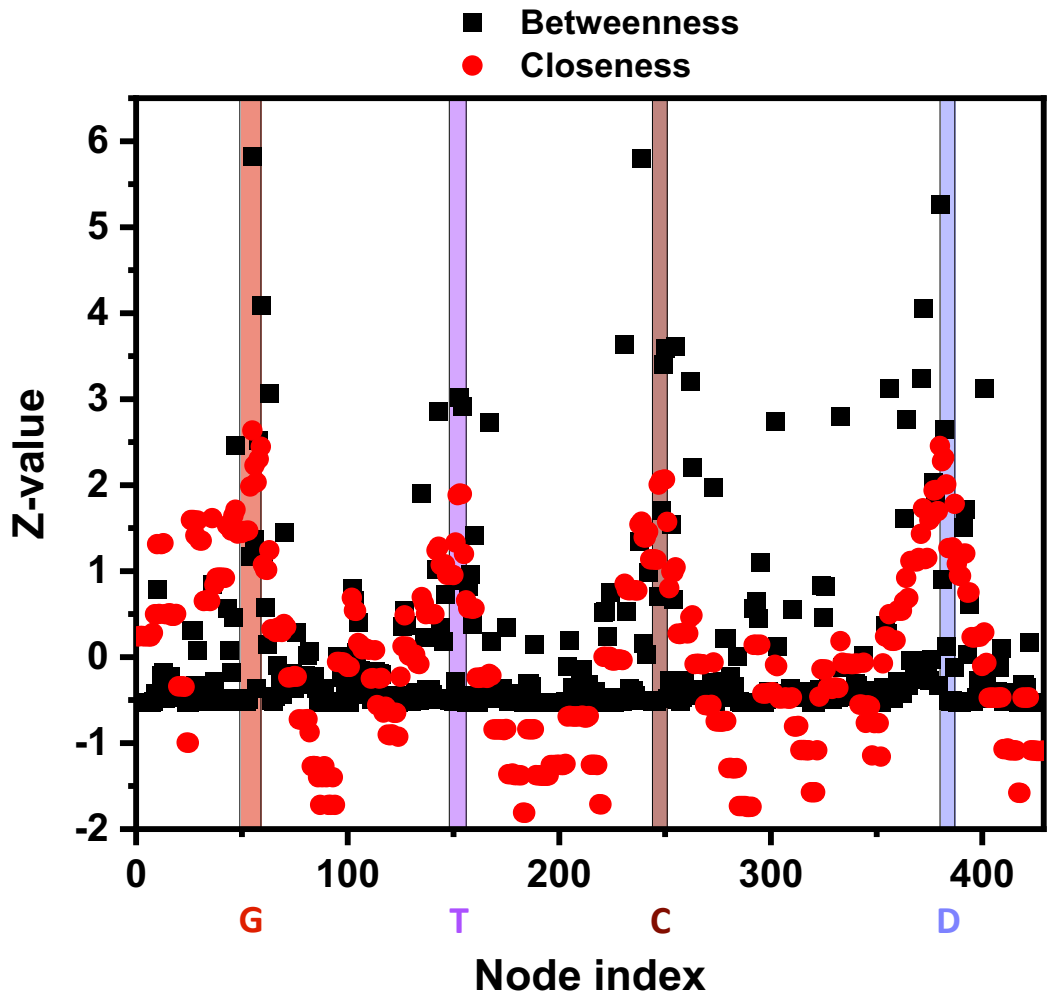


Figure S166. Betweenness and closeness centralities for each node in the O_a/O_{b1} network, presented with their z-values. The nodes belonging to the four nucleobase analogs are highlighted. This graph shows that maxima of C_c (closeness centrality) and high values of C_b (betweenness centrality) tend to be located at or near the nodes of the bases, which demonstrates their role in the assembly of the two chains.

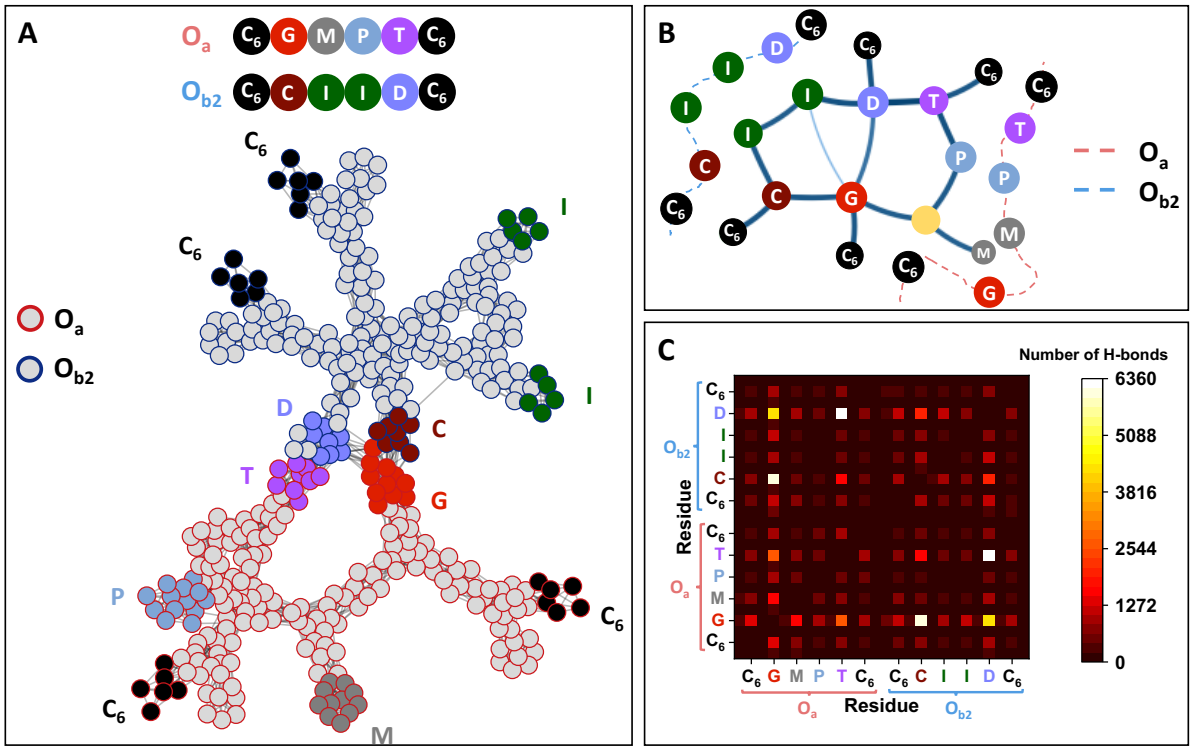


Figure S167. Molecular simulations of the assembly of O_a and O_{b2} oligomers into catalytically-incomplete supramolecular cycles. A. Network representation of the system, highlighting the persistent contacts observed during the MD simulation (see details in Supplementary Information). Heavy atoms constitute the nodes of the network. The nodes belonging to the strand O_a are circled in red while the nodes belonging to the strand O_{b2} are circled in blue. The nodes belonging to functional groups are identified by the corresponding code and colour. **B.** Modular representation of the network. Modules are named and coloured according to the functional unit included (but may contain other nodes). The module in yellow contains backbone nodes. For clarity, the primary structures of the two strands are sketched in dashed lines next to the modular network. **C.** Heatmap showing the decomposition of the hydrogen-bonds by pair of residues. Each square, localized at the crossing of a pair of residues, indicates by the scale bar the number of interactions detected between the two residues along the simulation. The residues from functional units are annotated while the backbone and chain-ends residues are hidden, for the sake of clarity. The map is symmetric with respect to the diagonal. White squares indicating the highest number of interactions are localized for the pairs G---C and T---D. Interactions are also found for the pair G---D. The map is very similar to the one of the O_a/O_{b1} system (Figure 2 in the companion article), showing that the composition of the catalytic centre does not strongly modify the interactions leading to the assembly of the chains.

12 EXPERIMENTS SUPPORTING THE NEED OF A BINUCLEAR COPPER COMPLEX FOR AN EFFICIENT CATALYSIS

The di(oligomeric) cycles formed in the O_a/O_{b1} system comprise two P bidentate ligands, two I auxiliary ligands, and one TEMPO radical. In contrast, the supramolecular cycles of the O_a/O_{b2} system lack one P-Cu, whereas the supramolecular cycles of the O_a/O_{b3} system lack one I. Experiments were thus performed in which one equivalent of monomer P and copper was added to the O_a/O_{b2} system, and one equivalent of *N*-methyl imidazole (analogue to I) was added to the O_a/O_{b3} system for a concentration in M units of 2.5 mol%. Experiment in which one equivalent of *N*-methyl imidazole is added to the O_a/O_{b2} system were also performed.

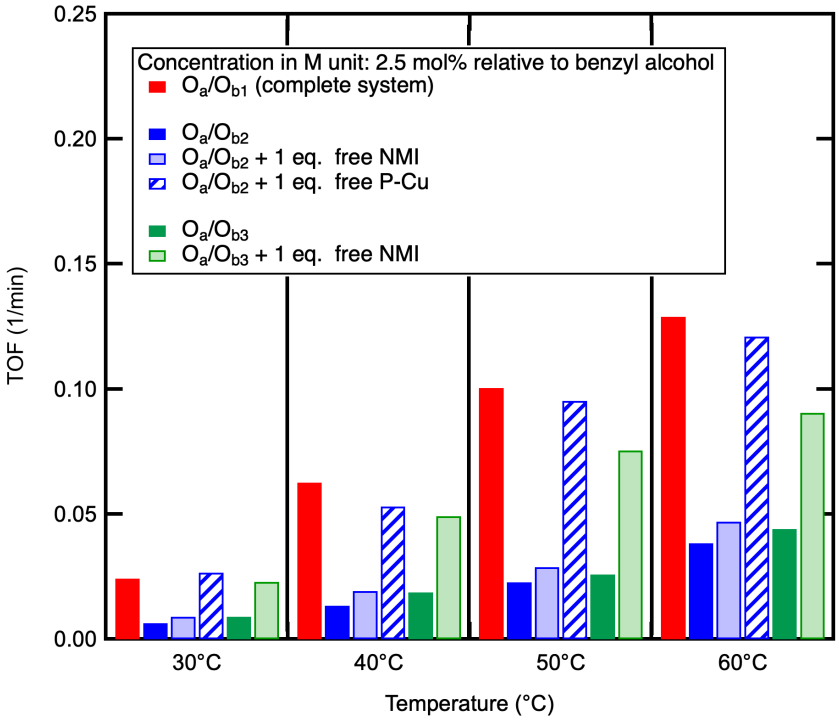


Figure S168. TOF of the three systems measured at different temperatures and 2.5 mol% concentration in M units. For the O_a/O_{b2} and O_a/O_{b3} systems which form di(oligomeric) supramolecular cycles that lack either one P-Cu or one I unit, one equivalent of free P-Cu and/or free NMI (analogue to I) was added as indicated.

As Figure S168 shows, the incomplete O_a/O_{b2} (dark blue) and O_a/O_{b3} (dark green) systems have a much lower catalytic efficiency than the complete O_a/O_{b1} system (red). Adding one P-Cu equivalent to the O_a/O_{b2} system (striped blue) brings the TOF close to the one of the complete system, whereas adding one NMI equivalent (light blue) does not change significantly the TOF; likewise, adding one NMI equivalent to the O_a/O_{b3} system (light green) brings the TOF close to the one of the complete system. In each case, the addition of the missing unit results in an efficiency similar to the one of the complete system, which strongly supports the need to form a binuclear copper complex involving two bidentate P ligands and two auxiliary I (or NMI) ligands.

13 REFERENCES

[1] M. del C. Grande, M. García, C. M. Marschoff, *J. Chem. Eng. Data* 2009, *54*, 652–658.

[2] J. Li, M. Leclercq, M. Fossepré, M. Surin, K. Glinel, A. M. Jonas, A. E. Fernandes, *Polym. Chem.* 2020, *11*, 4040–4046.

[3] J. Li, Q. Qin, S. Kardas, M. Fossépré, M. Surin, A. E. Fernandes, K. Glinel, A. M. Jonas, *ACS Catal.* 2022, *12*, 2126–2131.

[4] A. E. Fernandes, O. Riant, A. M. Jonas, K. F. Jensen, *RSC Adv.* 2016, *6*, 36602–36605.

[5] P. Chandra, A. M. Jonas, A. E. Fernandes, *J. Am. Chem. Soc.* 2018, *140*, 5179–5184.

[6] A. E. Fernandes, O. Riant, K. F. Jensen, A. M. Jonas, *Angew. Chem. Int. Ed.* 2016, *128*, 11210–11214.

[7] D. D. Vo, C. Staedel, L. Zehnacker, R. Benhida, F. Darfeuille, M. Duca, *ACS Chem. Biol.* 2014, *9*, 711–721.

[8] R. A. Kramer, K. H. Bleicher, H. Wennemers, *Helv. Chim. Acta* 2012, *95*, 2621–2634.

[9] R. Kolb, N. C. Bach, S. A. Sieber, *Chem. Commun.* 2013, *50*, 427–429.

[10] C.-C. Cheng, Y.-S. Wang, F.-C. Chang, D.-J. Lee, L.-C. Yang, J.-K. Chen, *Chem. Commun.* 2014, *51*, 672–675.

[11] A. Porcheddu, G. Giacomelli, I. Piredda, M. Carta, G. Nieddu, *Eur. J. Org. Chem.* 2008, *2008*, 5786–5797.

[12] P. W. Kuchel, G. Pagès, K. Nagashima, S. Velan, V. Vijayaragavan, V. Nagarajan, K. H. Chuang, *Concepts Magn. Reso. A* 2012, *40A*, 205–214.

[13] E. Uehara, T. Deguchi, *J. Chem. Phys.* 2016, *145*, 164905.

[14] M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. R. Hutchison, *J. Cheminf.* 2012, *4*, 17.

[15] D. A. Case, T. E. Cheatham, T. Darden, H. Gohlke, R. Luo, K. M. Merz, A. Onufriev, C. Simmerling, B. Wang, R. J. Woods, *J. Comput. Chem.* 2005, *26*, 1668–1688.

[16] J. Wang, W. Wang, P. A. Kollman, D. A. Case, *J. Mol. Graph. Model.* 2006, *25*, 247–260.

[17] A. Jakalian, B. L. Bush, D. B. Jack, C. I. Bayly, *J. Comput. Chem.* 2000, *21*, 132–146.

[18] E. Stendardo, A. Pedone, P. Cimino, M. C. Menziani, O. Crescenzi, V. Barone, *Phys. Chem. Chem. Phys.* 2010, *12*, 11697–11709.

[19] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, *J. Comput. Chem.* 2004, *25*, 1157–1174.

[20] G. D. Hawkins, C. J. Cramer, D. G. Truhlar, *Chem. Phys. Lett.* 1995, *246*, 122–129.

[21] A. W. Götz, M. J. Williamson, D. Xu, D. Poole, S. L. Grand, R. C. Walker, *J. Chem. Theory Comput.* 2012, *8*, 1542–1555.

[22] *Schrödinger LLC, The PyMOL Molecular Graphics System, Version 2.5.4*, n.d.

[23] J. Weiser, P. S. Shenkin, W. C. Still, *J. Comput. Chem.* 1999, *20*, 217–230.

[24] B. R. Miller, T. D. McGee, J. M. Swails, N. Homeyer, H. Gohlke, A. E. Roitberg, *J. Chem. Theory Comput.* 2012, *8*, 3314–3321.

[25] H. Sun, Y. Li, S. Tian, L. Xu, T. Hou, *Phys. Chem. Chem. Phys.* 2014, *16*, 16719–16729.

[26] S. Genheden, U. Ryde, *Expert Opin. Drug Dis.* 2015, *10*, 449–461.

[27] P. Shannon, A. Markiel, O. Ozier, N. S. Baliga, J. T. Wang, D. Ramage, N. Amin, B. Schwikowski, T. Ideker, *Genome Res.* 2003, *13*, 2498–2504.

[28] Y. Assenov, F. Ramírez, S.-E. Schelhorn, T. Lengauer, M. Albrecht, *Bioinformatics* 2007, *24*, 282–284.

[29] L. Bohlin, D. Edler, A. Lancichinetti, M. Rosvall, in *Measuring Scholarly Impact: Methods and Practice* (Eds.: Y. Ding, R. Rousseau, D. Wolfram), Springer Cham, 2014, pp. 3–34.

[30] M. Rosvall, C. T. Bergstrom, *Proc. Natl. Acad. Sci.* 2008, *105*, 1118–1123.

[31] M. Rosvall, D. Axelsson, C. T. Bergstrom, *Eur. Phys. J. Spec. Top.* 2009, *178*, 13–23.

[32] C. E. Shannon, *Bell Syst. Techn. J.* 1948, *27*, 379-423,623-656.