Supporting Information for

Truxene-Based Covalent Organic Polyhedrons Constructed through Alkyne Metathesis

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Materials and general method

Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. Tetrahydrofuran (THF), toluene, CH_2Cl_2 and dimethylformamide (DMF) are purified by the MBRAUN solvent purification systems. All reactions were conducted under dry nitrogen in oven-dried glassware, unless otherwise specified. Alkyne metathesis reactions were conducted in glovebox under argon environment unless otherwise specified. The solvents used in alkyne metathesis were dried over 4 Å molecular sieves. Solvents were evaporated using a rotary evaporator after workup. Unless otherwise specified, the purity of the compounds was ≥ 95 % based on ^{1}H NMR spectral integration. Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 32-63 µm from Dynamic Absorbents Inc. Fractions were analyzed by TLC using TLC silica gel F254 250 µm precoated-plates from Dynamic Absorbents Inc. The Mo precursor,[1] **4a**,[2] and **4b**[3] are synthesized according to the reported procedure without any modification.

Analytical gel permeation chromatography (GPC) was performed using a Tosoh EcoSEC with a 15 cm TSKgel SuperHM-N column in chloroform.

NMR spectra were taken on Bruker 300 and Inova 400 or 500 spectrometers at 293 K. C*H*Cl_3 residue in $CDCl_3$ (7.27 ppm) was used as internal references for ^{1}HNMR; $CDCl_3$ (77.23 ppm) were used as internal reference for ^{13}CNMR. ^{1}HNMR data were reported in order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (J, Hz), number of protons.

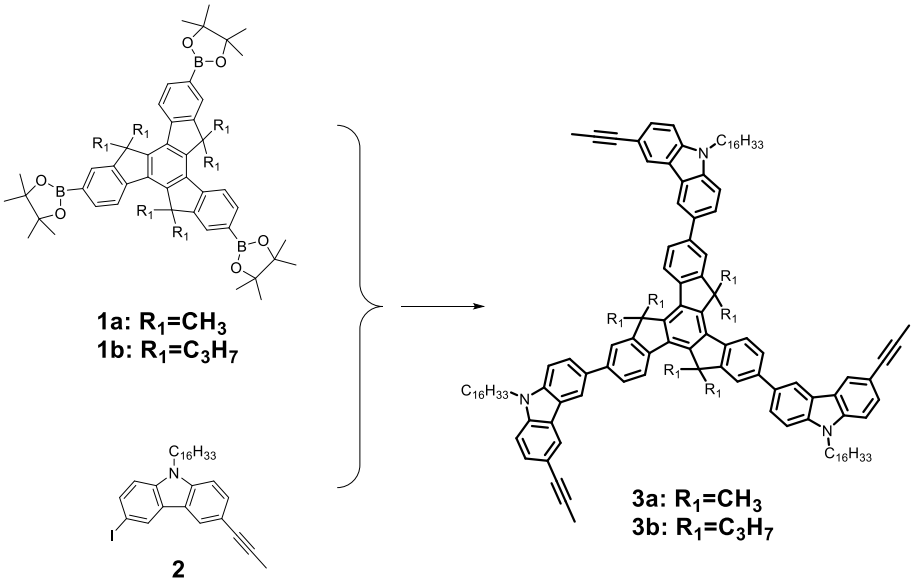
Absorption spectra were measured using an Agilent Cary 5000 UV-Vis-NIR Spectrophotometer. Emission spectra were measured using an SLM 8000C Spectrofluorometer with the appropriate wavelength-dependent correction applied to the raw data.

MALDI-TOF was conducted on a Shimadzu MALDI 8020 instrument.

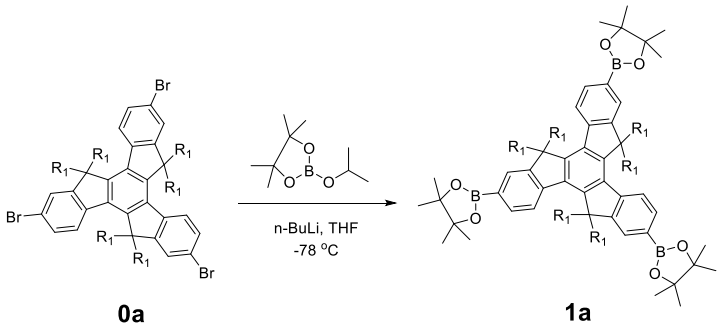
Quantum chemistry calculations were performed with ORCA 4.2 program package.[4] Semi empirical calculations were performed with xTB program.[5] Ground state geometry are optimized using PBE functional[6] with the def2-SVP basis set[7] in toluene solvent modeled by SMD solvation model.[8] Geometries are also optimized by GFN2-xTB method[5] in xTB package in order to

compute the frequencies and thermal corrections at an acceptable cost. The free energies are calculated by zero-point energies from DFT calculations and thermal corrections from xTB calculations.[9]

Experimental Procedures

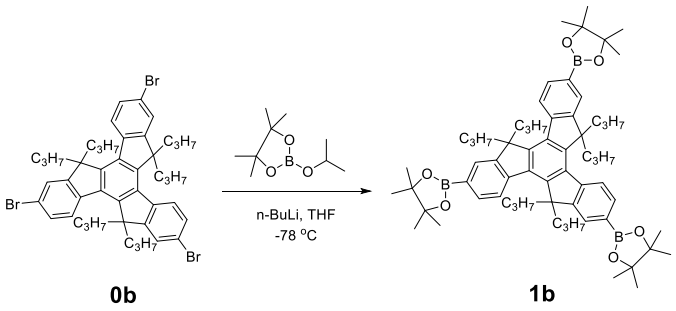


Scheme S1. The general synthetic scheme to monomer **3a** and **3b.**



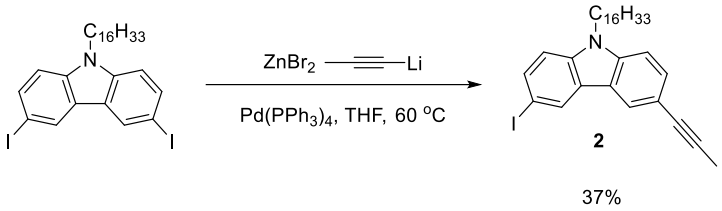
Compound 1a: To a solution of compound **0a**[10] (1.33 g, 2.00 mmol) in 80 mL distilled anhydrous THF at -78 ℃ was slowly added of *n*-butyllithium (2.5 M in hexane, 4 mL, 10 mmol) under nitrogen atmosphere. The mixture was continuously stirred at -78 ℃ for 2 h. Then 2-isopropoxy-

4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.80 g, 15.0 mmol) was added and the mixture was kept stirring at -78 ℃ for another 2 h. The mixture was gradually warmed to room temperature and stirred for 8 h. The reaction was then quenched with water (20 mL). The volatiles were removed and the resulting precipitate was then dissolved in dichloromethane (50 mL). The organic solution was washed with water (3 x 50 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography (hexanes: CH_2Cl_2: EtOAc = 1: 1: 0.1) to afford **1a** as a white solid (1.40 g, 85%): IR (ATR) ν = 3460, 2983, 1627, 1350, 1250, 1130, 1080, 975, 907, 832, 757, 683 cm^{-1}; ^1H NMR (300 MHz, Chloroform-d) δ 8.38 – 8.31 (m, 3H), 8.02 – 7.98 (m, 3H), 7.96 – 7.90 (m, 3H), 1.93 (s, 18H), 1.43 (s, 36H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.66, 149.88, 139.51, 135.61, 133.09, 128.56, 125.02, 83.81, 67.96, 46.95, 25.60, 24.93, 23.92; HR-MS (ESI): Calcd for $C_{51}H_{64}B_3O_6$ [M+H$^+$] 805.4982; Found, 805.4987.

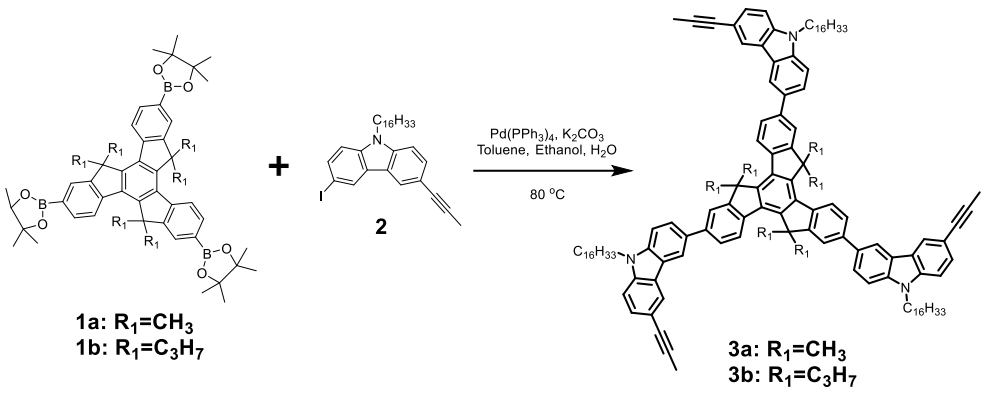


Compound 1b: To a solution of compound **0b**[11] (1.66 g, 2.00 mmol) in anhydrous THF (80 mL) at -78 ℃ was slowly added of n-butyllithium (2.5 M in hexane, 10.0 mmol, 4.0 mL) under nitrogen atmosphere. The mixture was continuously stirred at -78 ℃ for 2 h. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.80 g, 15.0 mmol) was added, and the mixture was kept stirring at -78 ℃ for another 2 h. The mixture was gradually warmed to room temperature and stirred for 8 h. The reaction was then quenched with water (20 mL) and the volatiles were removed through rotary evaporation. The resulting precipitate was dissolved in dichloromethane (50 mL). The organic solution was washed with water (3 x 50 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes: CH_2Cl_2: EtOAc = 1: 1: 0.1) to give the product (1.65 g, 85 %): IR (ATR) ν = 3460, 2990, 2868, 1620, 1350, 1250, 1145, 965, 837, 679 cm^{-1}; ^1H NMR (300 MHz, Chloroform-d) δ 8.41 (d, *J* = 8.0 Hz, 3H), 7.96 – 7.85 (m, 6H), 2.88 (dd, *J* = 15.1, 7.8 Hz, 6H), 2.28 – 2.12 (m, 6H), 1.44 (s, 36H), 0.66 – 0.45 (m, 30H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.84, 146.59, 143.14, 138.22, 132.97, 128.29, 123.98, 122.30, 83.77,

82.84, 55.85, 39.24, 39.18, 26.21, 24.99, 17.30, 14.49, 14.43, 13.89; HR-MS (ESI): Calcd for $C_{63}H_{88}B_3O_6$ [M+H$^+$] 973.6860; Found, 973.6865.



Compound 2: A 50 mL centrifuge tube was charged with anhydrous $ZnBr_2$ (9.00 g, 40.0 mmol, 1.0 eq), which was subsequently dissolved in anhydrous THF (40 mL). The resulting solution was added to freshly-made propynyl lithium (1.84 g, 40.0 mmol, 1.0 eq) dropwise under argon. The resulting zinc reagent was transferred to a 250 mL flame-dried Schenk tube charged with 9-hexadecyl-3,6-diiodocarbazole[12] (25.7 g, 40.0 mmol, 1.0 eq) and $Pd(PPh_3)_4$ (2.31 g, 2.00 mmol, 0.05 eq). The resulting solution was further diluted with anhydrous THF (120 mL). The mixture was heated at 60 °C for 16 h under argon. All volatiles were removed, and the crude product was purified by column chromatography (gradient, CH_2Cl_2/hexane = 1/50 to 1/30 v/v). The product was obtained as a white solid (8.30 g, 37 %): m.p. 52~53 °C; IR (ATR) ν = 3500, 3073, 2931, 2854, 2200, 2051, 1859, 1621, 1474, 1269, 1200, 1017, 806, 719, 564 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.7 Hz, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 7.69 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 4.22 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.83 (h, *J* = 6.8 Hz, 2H), 1.40 – 1.19 (m, 26H), 1.01 – 0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.02, 139.72, 134.25, 129.95, 129.42, 125.08, 123.97, 121.59, 114.85, 111.01, 108.91, 83.92, 81.64, 80.48, 43.38, 32.08, 29.85, 29.84, 29.82, 29.78, 29.73, 29.68, 29.60, 29.52, 29.48, 29.01, 27.36, 22.85, 14.28, 4.56; HR-MS (ESI): Calcd for $C_{31}H_{43}NI$ [M+H$^+$] 556.2440; Found, 556.2448.

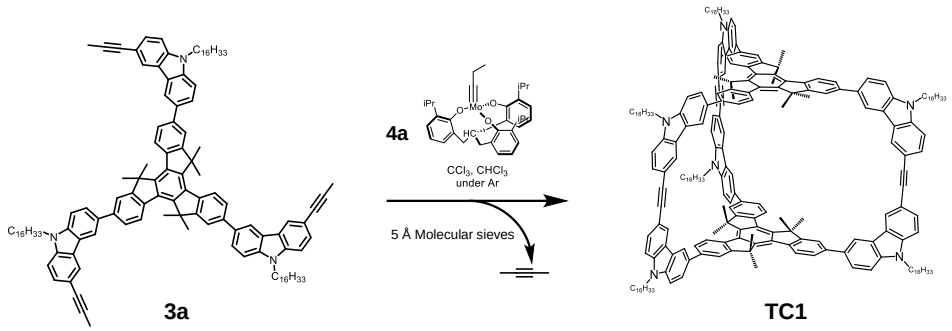


Compound 3a and 3b: The general Suzuki's procedure was followed for the synthesis of truxene monomers **3a** and **3b**.

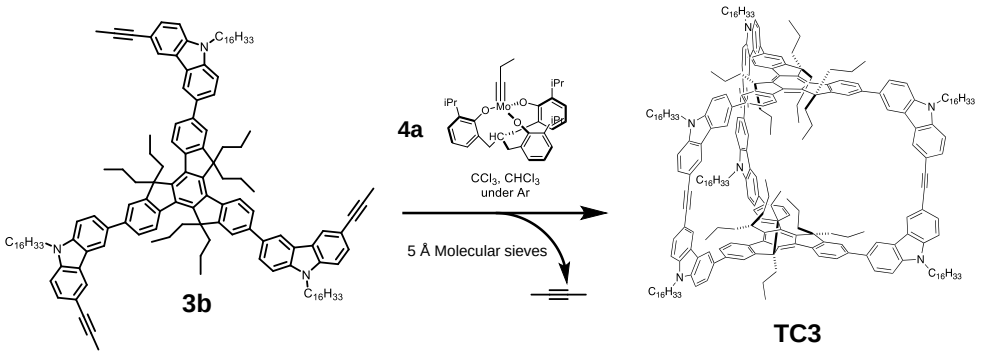
For compound **3a**: Compound **1a** (402 mg, 0.50 mmol, 1.0 eq) and compound **2** (1.05 g, 1.90 mmol, 3.6 eq) were coupled using $Pd(PPh_3)_4$ (cat. 150 mg), K_2CO_3 (10 mL of a 1.5 M aqueous solution), toluene (30 mL), and EtOH (7.5 mL) at 80 °C. After the reaction was cooled to room temperature, the mixture was washed with sat. NH_4Cl (50 mL). The organic phase was collected, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (CH_2Cl_2: Hexane, 1 : 1 v/v) to provide the product **3a** as a light yellow solid (640 mg, 75%): m.p. 70.1~71.0 °C. IR (ATR) ν = 2921, 2851, 2169, 1479, 1453, 1386, 1293, 1271, 1222, 1151, 879, 801 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.49 – 8.39 (m, 6H), 8.29 (d, *J* = 1.5 Hz, 3H), 7.93 – 7.85 (m, 6H), 7.81 (dd, *J* = 8.2, 1.9 Hz, 3H), 7.57 – 7.48 (m, 6H), 7.35 (d, *J* = 8.5 Hz, 3H), 4.33 (t, *J* = 7.3 Hz, 6H), 2.13 (s, 9H), 2.06 (s, 18H), 1.47 – 1.18 (m, 84H), 0.88 (t, *J* = 6.9 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.33, 148.25, 140.52, 140.32, 140.18, 135.53, 135.39, 132.75, 129.33, 125.98, 125.60, 125.50, 123.91, 123.11, 122.95, 121.20, 118.98, 114.26, 109.17, 108.78, 83.52, 80.65, 47.07, 43.36, 31.93, 29.71, 29.67, 29.42, 29.37, 29.05, 27.33, 24.32, 22.70, 14.13, 4.44; MALDI-TOF : Calcd for $C_{126}H_{153}N_3$ [M^+] 1709.2098, observed: 1708.7613.

For compound **3b**: Similar synthetic approach was used to synthesize compound **3b** as light yellow solid (660 mg, 70% yield): m.p. 67.2~68.5 °C; IR (ATR) ν = 2955, 2921, 2851, 2195, 1476, 1453, 1375, 1356, 1289, 1267, 1151, 879, 801 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.3 Hz, 3H), 8.44 (d, *J* = 1.7 Hz, 3H), 8.29 (d, *J* = 1.5 Hz, 3H), 7.90 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.85 – 7.77 (m, 6H), 7.59 – 7.49 (m, 6H), 7.35 (d, *J* = 8.5 Hz, 3H), 4.34 (t, *J* = 7.3 Hz, 6H), 3.08 – 2.99 (m, 6H), 2.30 – 2.20 (m, 6H), 2.13 (s, 9H), 1.96 – 1.88 (m, 6H), 1.45 – 1.39 (m, 6H), 1.29 – 1.23

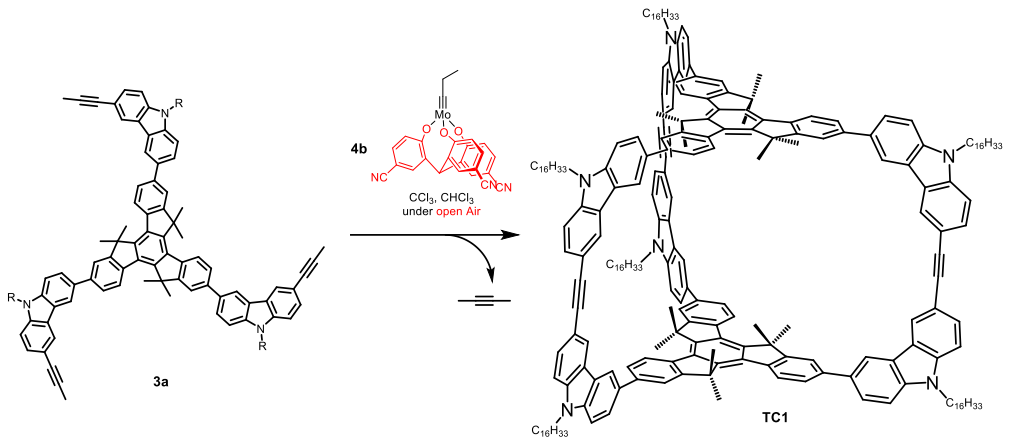
(m, 75H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.74 (q, *J* = 7.6 Hz, 9H), 0.62 (t, *J* = 7.2 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.55, 145.03, 140.29, 140.19, 139.90, 138.97, 138.08, 132.82, 129.32, 125.61, 125.26, 125.00, 123.90, 123.10, 122.99, 120.85, 118.88, 114.23, 109.14, 108.78, 83.51, 80.68, 55.89, 43.37, 39.65, 31.94, 29.71, 29.67, 29.38, 29.33, 27.35, 22.71, 17.49, 14.67, 14.14, 4.46; MALDI-TOF: Calcd for $C_{138}H_{177}N_3$ [M^+] 1877.3976; Found, 1877.4267.



TC1: The cage compound **TC1** was obtained through adsorption-driven alkyne metathesis. A 4 mL vial was charged with the Mo precursor (1.0 mg, 0.0015 mmol, 0.15 eq) and the ligand (0.7 mg, 0.0015 mmol, 0.15 eq) in an argon filled glovebox. 1.5 mL dry CCl_4 was added to the vial, the resulting solution was stirred at room temperature for 30 min, at which time the color of the solution was changed from brown to purple. The compound **3a** (17.3 mg, 0.01 mmol, 1.0 eq) and 5Å molecular sieves (30 mg) were added to the catalyst solution, followed by the addition of 1.5 mL dry $CHCl_3$ (stabilized by amylene). The resulting suspension was heated in a metal heating block at 55 °C in the glovebox for 16 h. The molecular sieves were removed by filtration, and the volatiles were removed under reduced pressure. The crude product was purified by gradient column chromatography (CH_2Cl_2/hexanes=1/4 to 1/3). The product was obtained as a white solid (10.0 mg, 61 %): m.p. 137.4~138.6 °C; IR (ATR) ν = 2921, 2851, 2206, 1606, 1472, 1386, 1349, 1293, 1233, 1147, 1132, 879, 801 cm^{-1}; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 1.6 Hz, 6H), 8.35 (d, *J* = 1.8 Hz, 12H), 7.77 (dd, *J* = 8.5, 1.7 Hz, 12H), 7.70 (dd, *J* = 8.5, 1.6 Hz, 6H), 7.61 (dd, *J* = 8.3, 1.7 Hz, 6H), 7.52 (d, *J* = 8.5 Hz, 6H), 7.44 (d, *J* = 8.6 Hz, 6H), 4.39 (d, *J* = 8.6 Hz, 12H), 1.96 (d, *J* = 8.2 Hz, 36H), 1.28 (s, 156H), 0.94 – 0.86 (m, 30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.25, 148.19, 141.33, 140.33, 140.25, 135.32, 134.02, 123.25, 123.02, 114.10, 108.70, 89.26, 46.95, 31.94, 29.70, 29.67, 29.37, 27.36, 24.75, 23.67, 22.70, 14.14; MALDI-TOF: Calcd for $C_{240}H_{288}N_6$ [M^+] 3256.2788; Found, 3256.1156.



TC3: The cage compound **TC3** was obtained through adsorption-driven alkyne metathesis. A 4 mL vial was charged with the Mo precursor (1.0 mg, 0.0015 mmol, 0.15 eq) and the ligand (0.7 mg, 0.0015 mmol, 0.15 eq) in an argon filled glovebox. 1.5 mL dry CCl_4 was added to the vial, the resulting solution was stirred at room temperature for 30 min, at which time the color of the solution was changed from brown to purple. The compound **3b** (18.8 mg, 0.01 mmol, 1.0 eq) and 5Å molecular sieves (30 mg) was added to the catalyst solution, followed by the addition of 1.5 mL dry $CHCl_3$ (stabilized by amylene). The resulting suspension was heated in a metal heating block at 55 ^oC in the glovebox for 16 h. The molecular sieves were removed by filtration, and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/hexanes=1/4). The product was obtained as a pale yellow solid (10.6 mg, 59 %): m.p. 110.3~111.1 °C; IR (ATR) ν = 2955, 2921, 2851, 2195, 1472, 1457, 1375, 1353, 1293, 1151, 1129, 883, 801 cm^{-1}; ^1H NMR (300 MHz, Chloroform-*d*) δ 8.56 – 8.47 (m, 6H), 8.41 (d, *J* = 8.1 Hz, 6H), 8.30 (dd, *J* = 5.0, 1.7 Hz, 6H), 7.85 – 7.74 (m, 6H), 7.75 – 7.65 (m, 12H), 7.60 (d, *J* = 6.6 Hz, 6H), 7.53 (dd, *J* = 8.6, 2.3 Hz, 6H), 7.44 (dd, *J* = 8.6, 3.4 Hz, 6H), 4.38 (s, 12H), 2.92 (d, *J* = 17.0 Hz, 12H), 2.20 (s, 12H), 1.96 (d, *J* = 8.1 Hz, 12H), 1.44 (d, *J* = 12.1 Hz, 24H), 1.28 (s, 156H), 0.94 – 0.82 (m, 36H), 0.64 (t, *J* = 7.1 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.55, 145.14, 140.92, 140.35, 140.20, 138.91, 138.23, 134.32, 134.10, 123.17, 113.99, 108.77, 89.05, 55.92, 55.78, 43.47, 31.93, 29.71, 29.37, 27.36, 22.70, 17.62, 14.58, 14.13; MALDI-TOF : Calcd for $C_{264}H_{336}N_6$ [M^+] 3592.6544; Found, 3592.6938.



Synthesis of TC1 in open air condition: A 4 mL vial was charged with the Mo precursor (0.2 mg, 0.0003 mmol, 0.15 eq) and the ligand (0.12 mg, 0.0003 mmol, 0.15 eq.) in an argon filled glovebox. 0.3 mL dry CCl_4 was added to the vial, the resulting suspension was stirred at room temperature for 30 min. The compound **3a** (3.5 mg, 0.002 mmol, 1.0 eq.) was added to the catalyst solution/suspension, followed by the addition of 0.3 mL CCl_4 and $CHCl_3$ (1:1 v:v mixture). The resulting solution in the vial was brought out of the glovebox and heated without a cap in a metal heating block at 55 ^oC for 2 h. Freshly degassed 1/1 mixture of CCl_4/$CHCl_3$ was added at intervals to keep the reaction from dryness. After cooling to the room temperature, all the volatiles were removed in *vacuo*. The residues were directly subjected to ^1H NMR and GPC analysis.

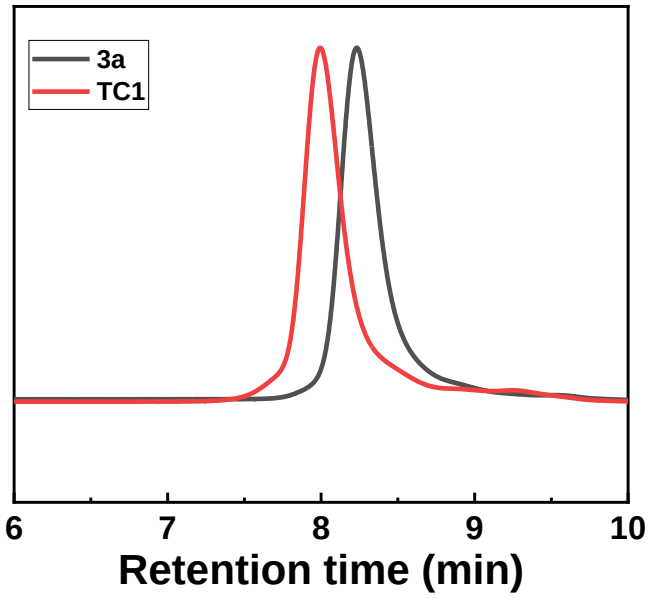


Fig. S1 The GPC traces (normalized) of **Monomer 3a** (black) and **TC1** (red).

Fluorescence titration of fullerene molecules with TC3

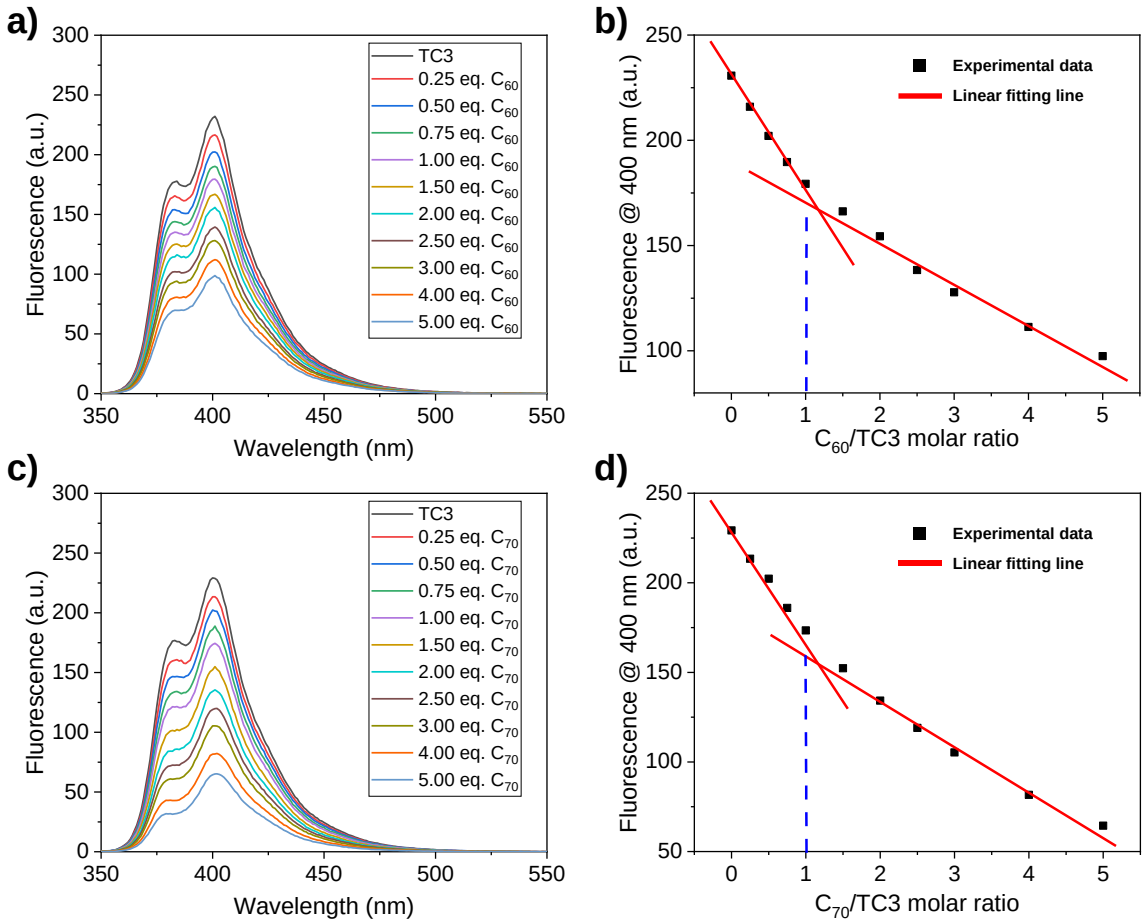


Fig. S2 Fluorescence titration of fullerene molecules with **TC3** in toluene. The COP concentration (1 μM) was held constant during the titration with 25 μM solution of fullerenes. Fluorescence titration spectra of cage **TC3** with the addition of C_{60} (a) and C_{70} (c). b) and d) are the plots of fluorescence intensity at 400 nm vs. the equivalent of fullerene molecules (C_{60} and C_{70}) added. The red lines are the fitting lines.

Binding Studies

The binding constants were calculated based on fluorescence-quenching titration experiments as shown below:

$$Tc_n + C_x \rightleftharpoons C_x@Tc_n$$

The initial concentration of Tc_n is c. Assuming when the C_x is added as total concentration x (ignore the total volume change), the concentration of $C_x@Tc_n$ is m. The binding constant K can be represented as below:

$$K = \frac{m}{(c-m)(x-m)}$$

Then the m can be solved as:

$$m = \frac{Kc + Kx + 1 - \sqrt{(Kc + Kx + 1)^2 - 4K^2cx}}{2Kc}$$

Meanwhile, based on Beer-Lambert Law, we have:
$\Delta F = \varepsilon bm, F_0 = \varepsilon bc$, ε and b are constants. Here ΔF is the absolute value of fluorescence intensity change during the titration; F_0 is the initial fluorescence intensity value.
We then set $X = \frac{x}{c}$ (the equivalence of fullerene to the cage), and $A = \frac{1}{Kc}$. The equation above can be converted to be:

$$\frac{\Delta F}{F_0} = \frac{1 + X + A - \sqrt{1 + X^2 + A^2 + 2A + AX - 2X}}{2}$$

A can be solved by nonlinear fitting. K can be derived from A and the initial concentration of the cages c. We used the relative emission counts at 400 nm for the calculation.

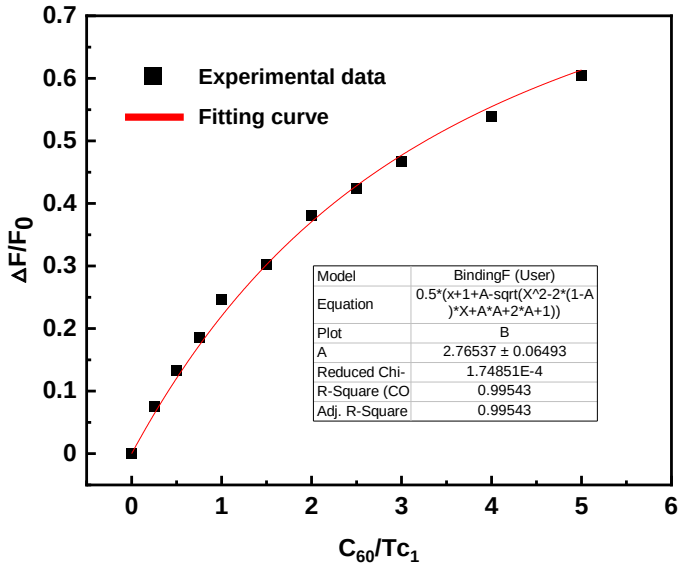


Fig. S3 Fitting curve of **TC1** (c =1.00×10^{-6} M) titrated with C_{60}.

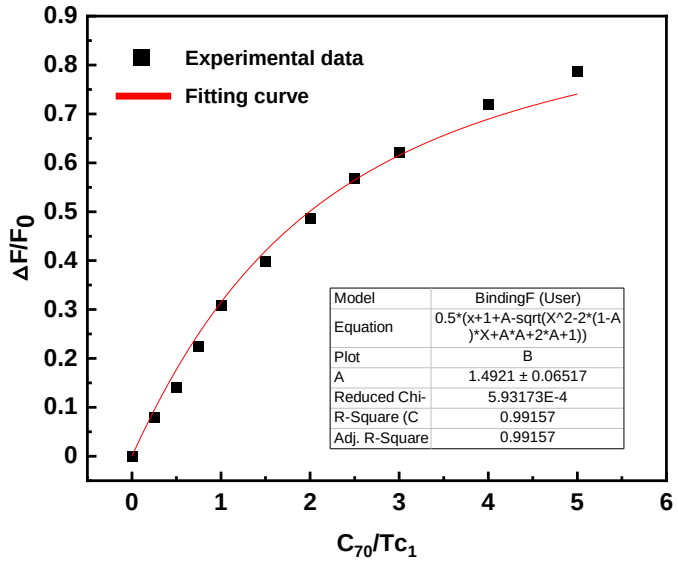


Fig. S4 Fitting curve of **TC1** (c = 1.00×10^{-6} M) titrated with C_{70}.

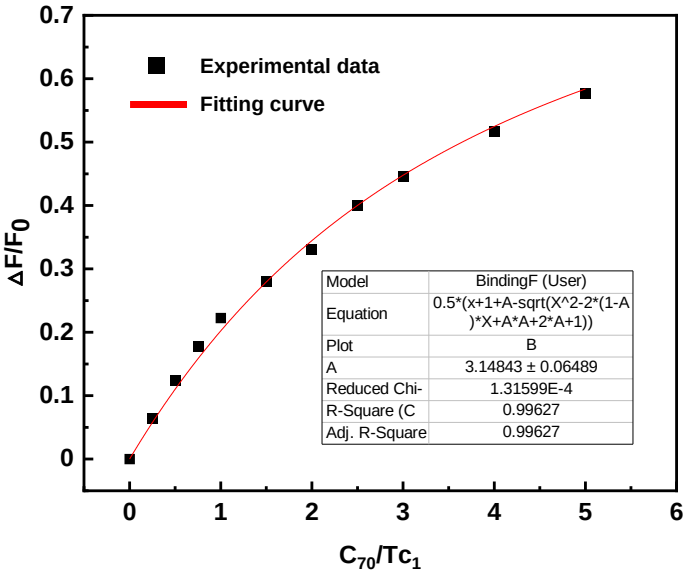


Fig. S5 Fitting curve of **TC3** (c = 1.00×10^{-6} M) titrated with C_{60}.

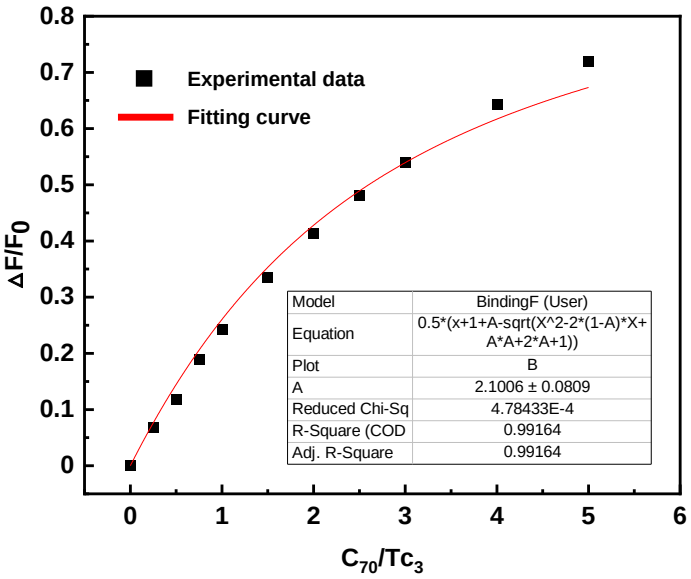


Fig. S6 Fitting curve of **TC3** (c = 1.00×10^{-6} M) titrated with C_{70}.

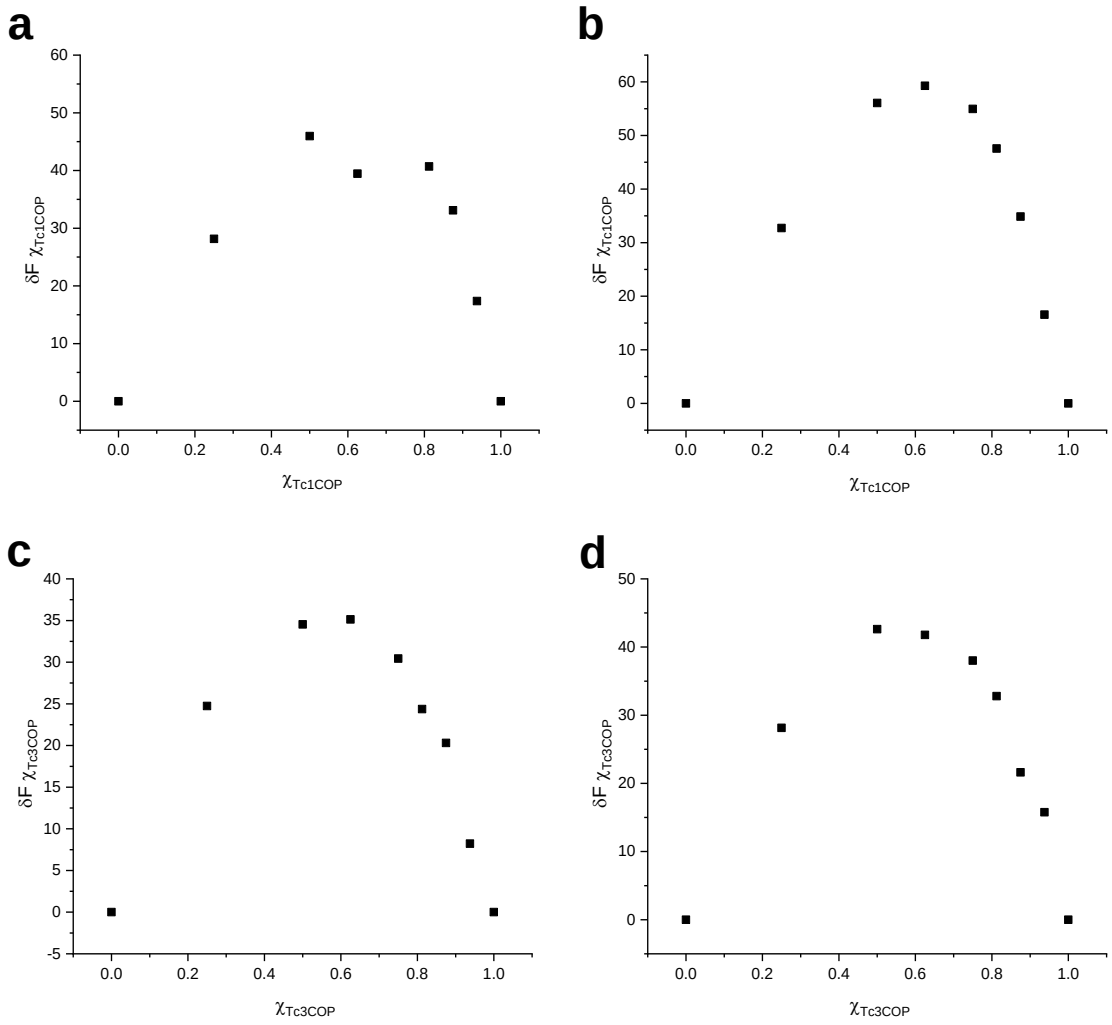


Fig. S7 Job's plots for the complex formation: a) C_{60}@**TC1**, b) C_{70}@**TC1**, c) C_{60}@**TC3**, d) C_{70}@**TC3**.

Table S1. Volume occupancy of the complexes.

Complex	Host Volume (Å^3)	Guest Volume (Å^3)	Volume Occupancy
C_{60}@TC1	778.5	407.7	52.3 %
C_{70}@TC1	797.0	443.2	55.6 %
C_{60}@TC3	736.6	407.7	55.3 %
C_{70}@TC3	765.8	443.2	57.9 %

NMR characterization of new compounds

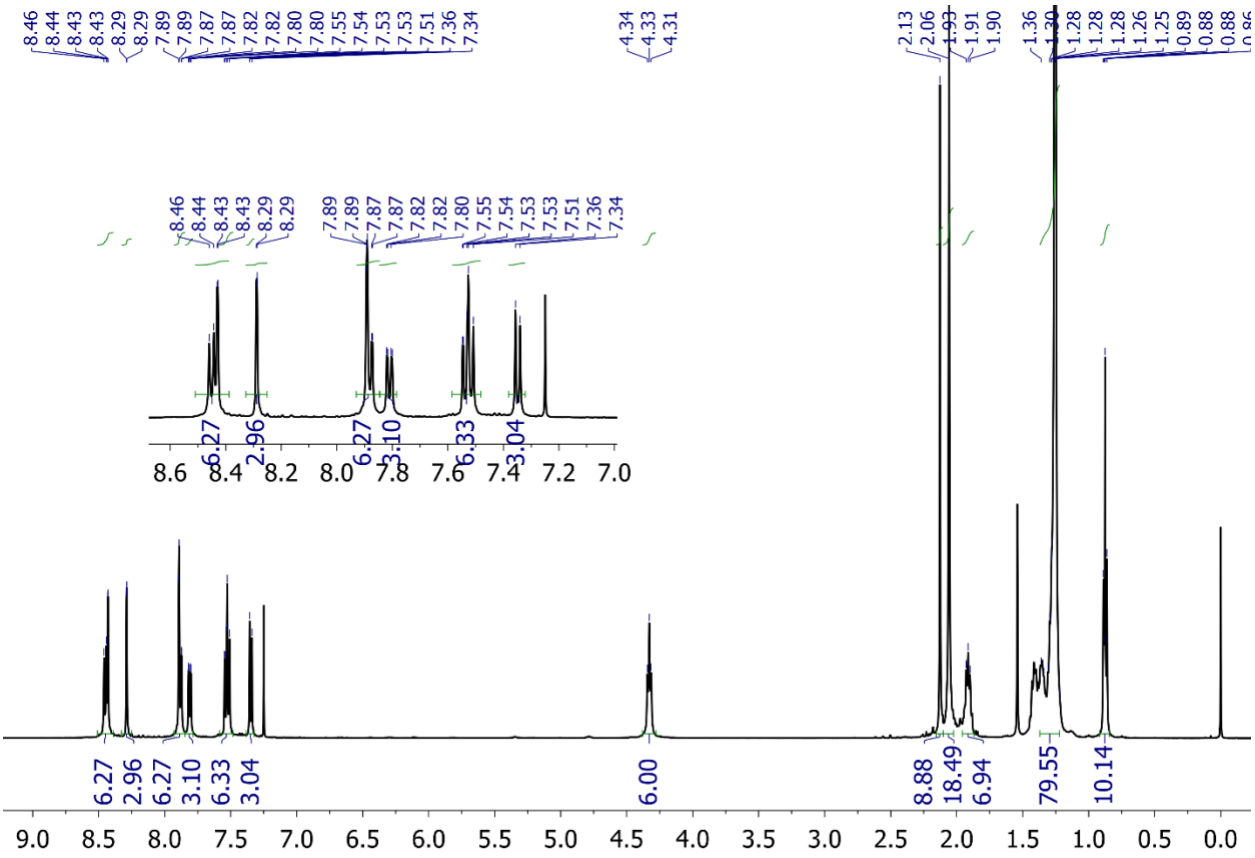


Fig. S8 ^{1}H NMR spectrum of **compound 3a** in $CDCl_3$.

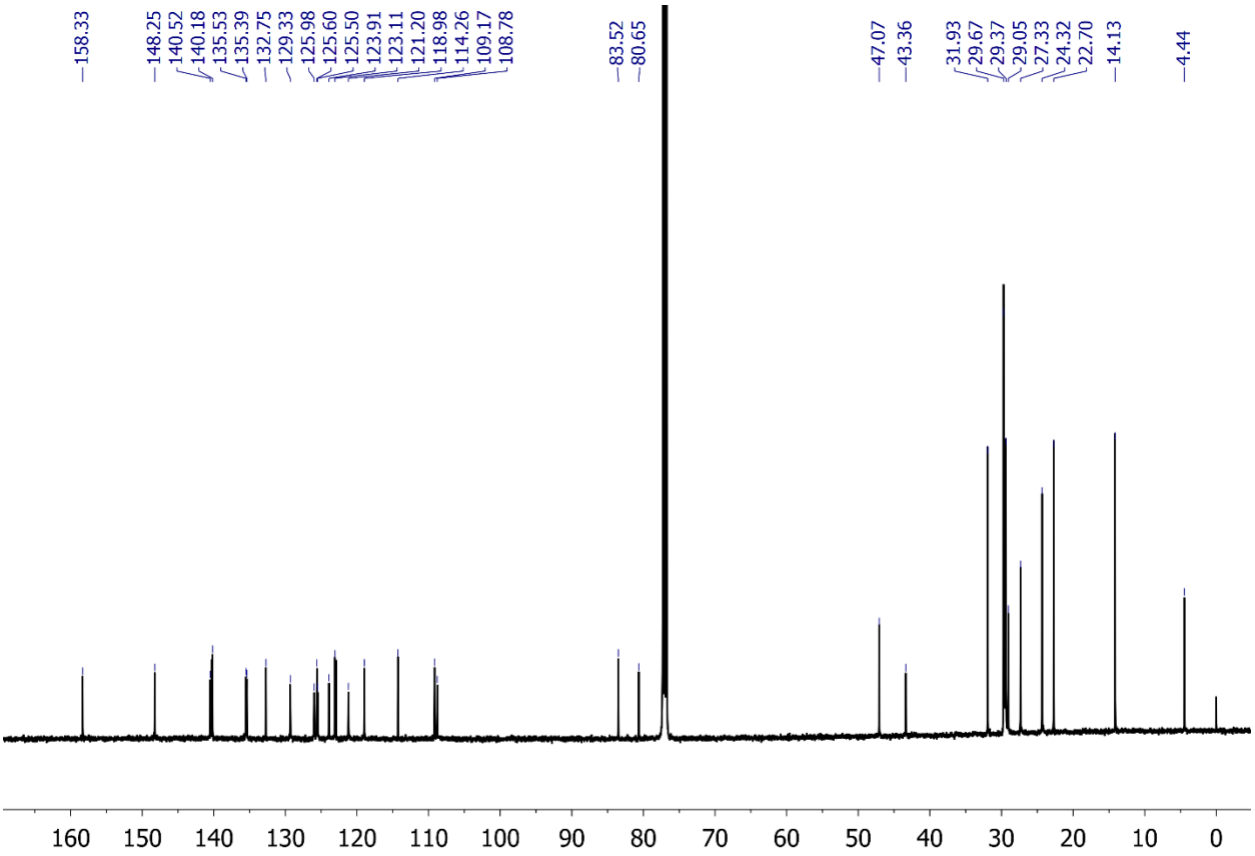


Fig. S9 ^{13}C NMR spectrum of **compound 3a** in $CDCl_3$.

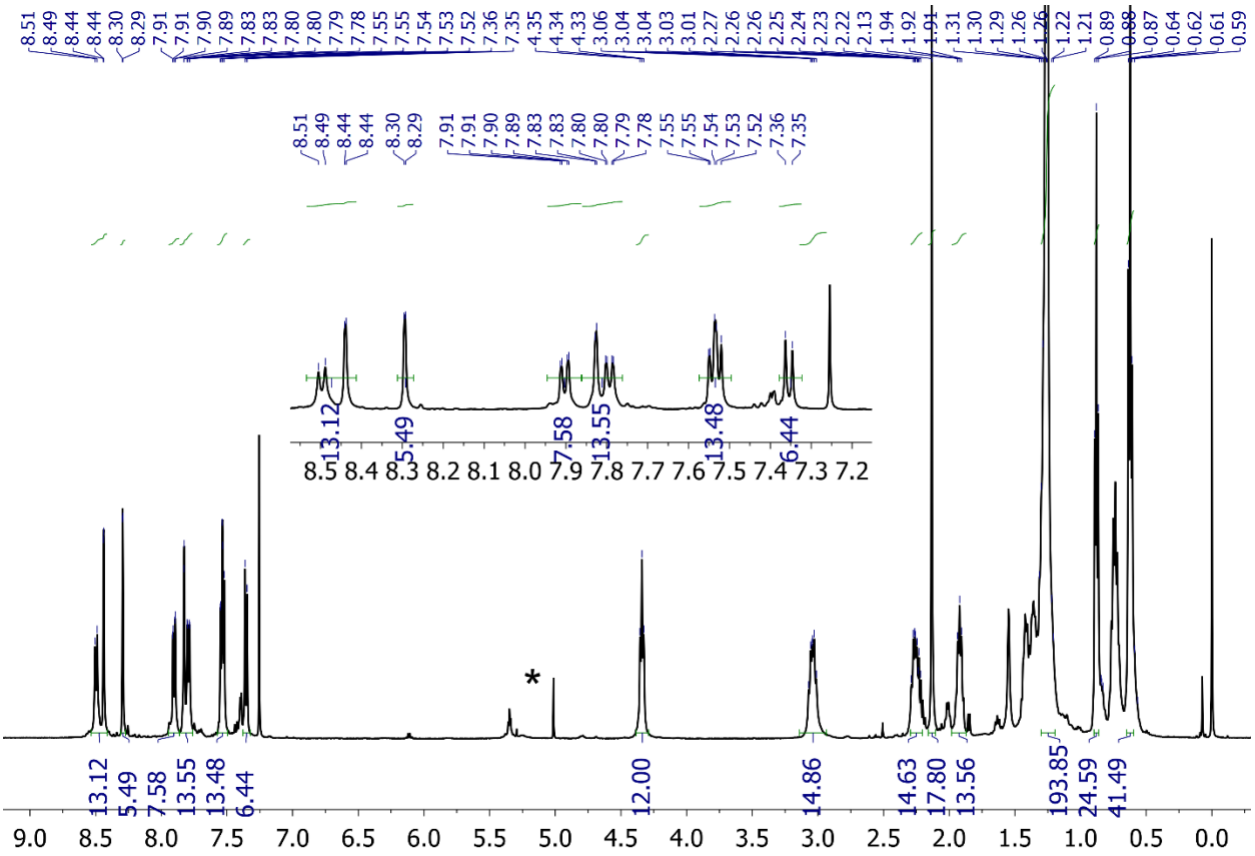


Fig. S10 ^{1}H NMR spectrum of **compound 3b** in $CDCl_3$.

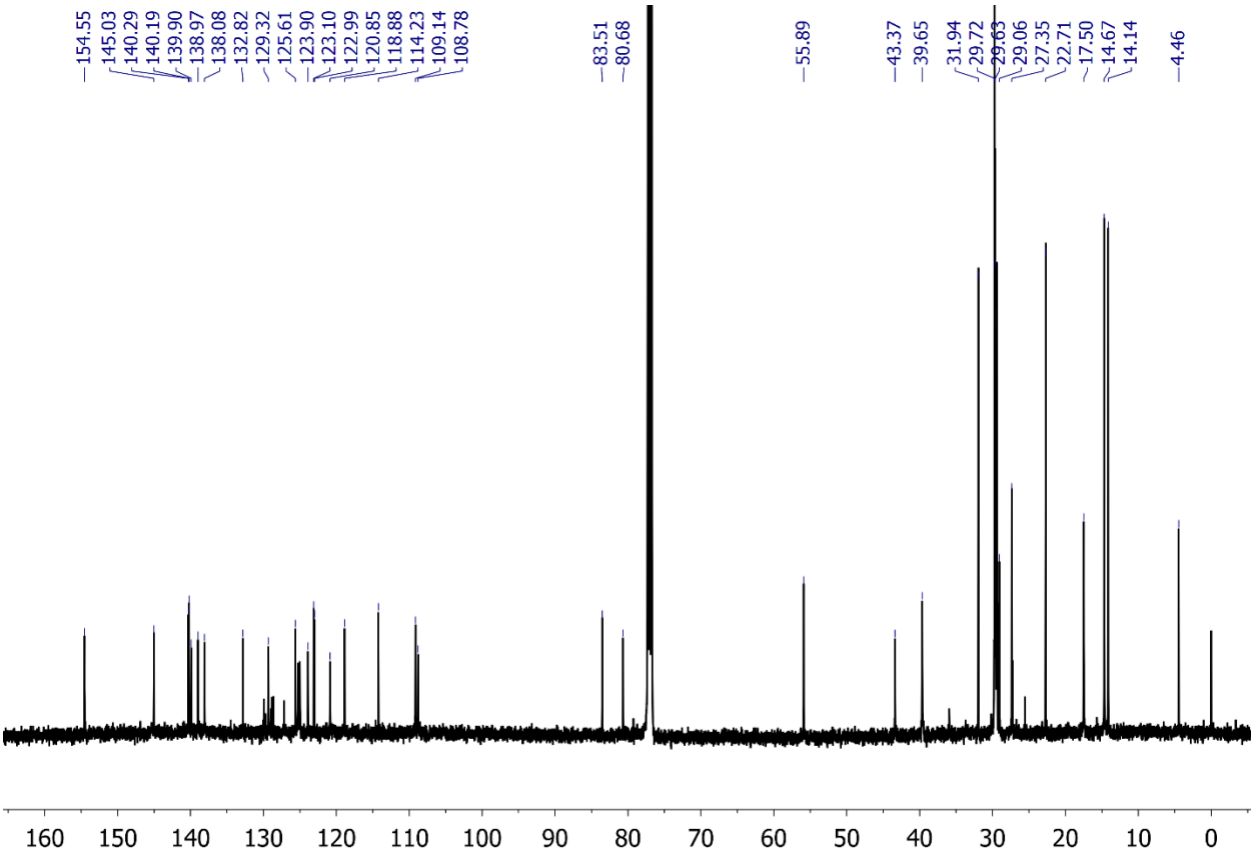


Fig. S11 ^{13}C NMR spectrum of **compound 3b** in $CDCl_3$.

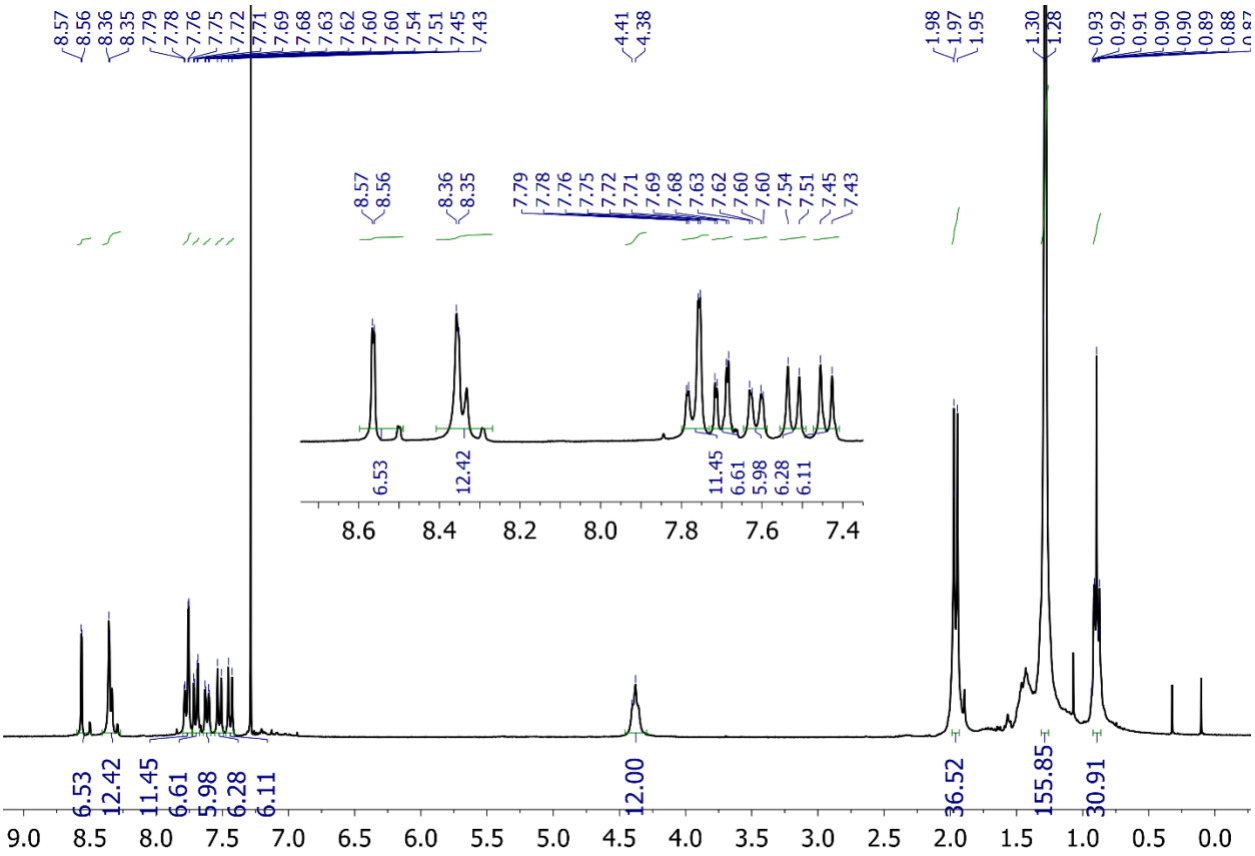


Fig. S7 ^{1}H NMR spectrum of **TC1** in $CDCl_3$.

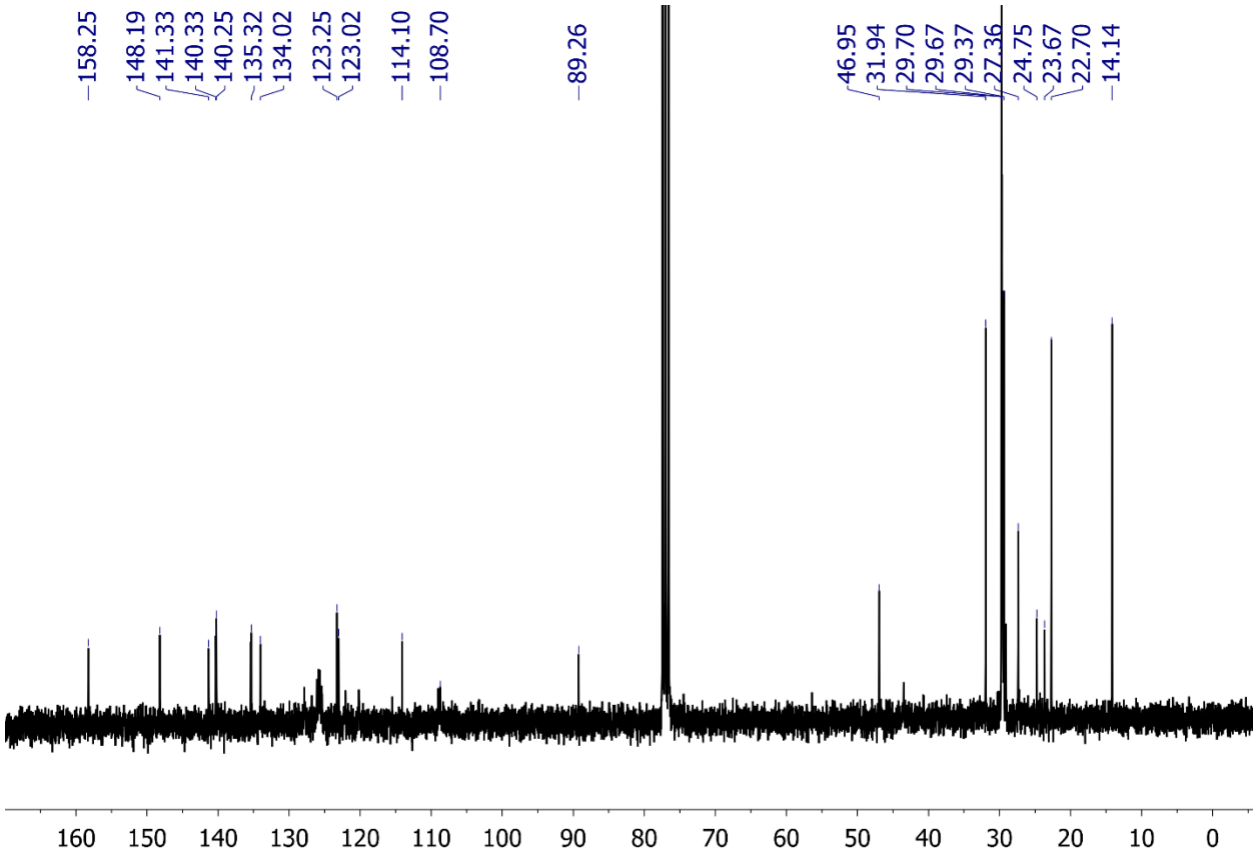


Fig. S8 ^{13}C NMR spectrum of **TC1** in $CDCl_3$.

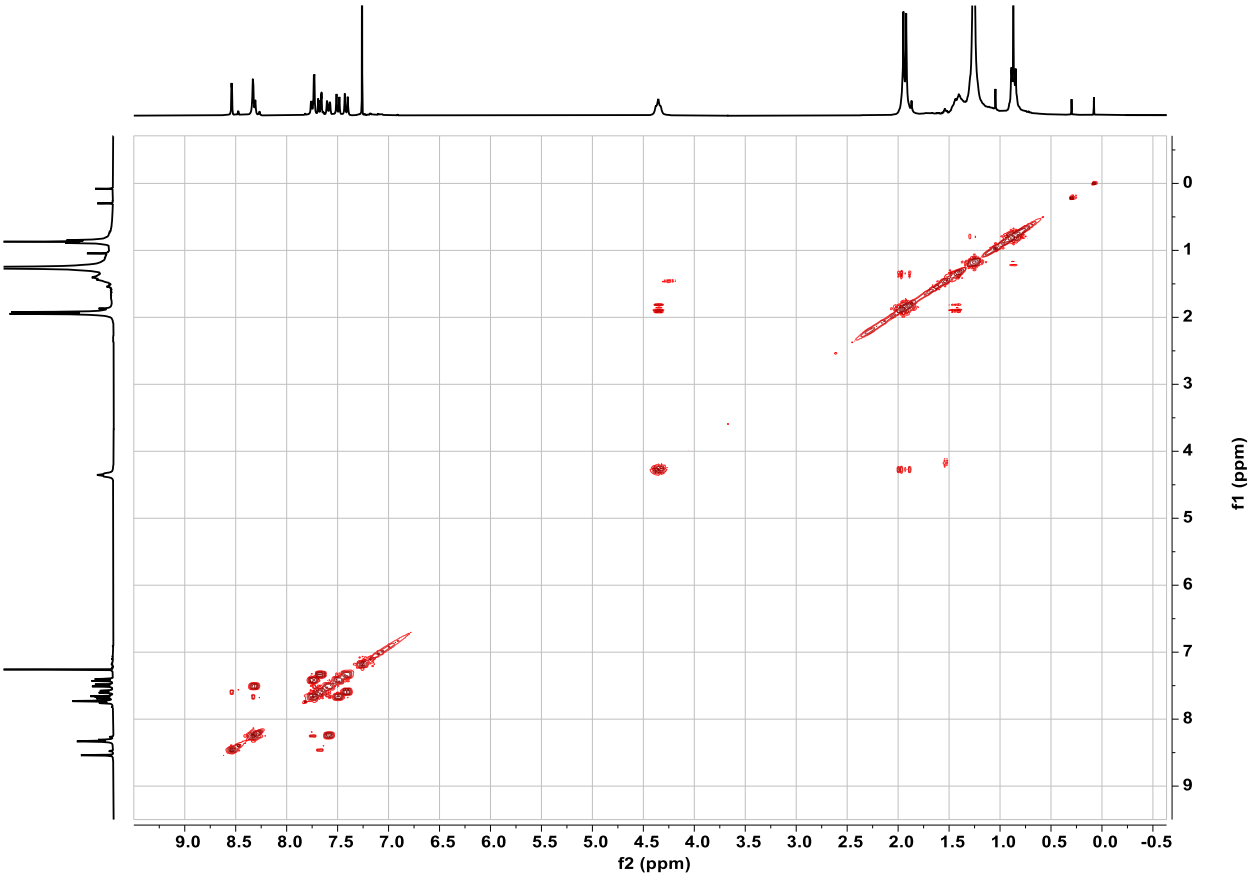


Fig. S9 2D COSY spectrum of **TC1** in $CDCl_3$.

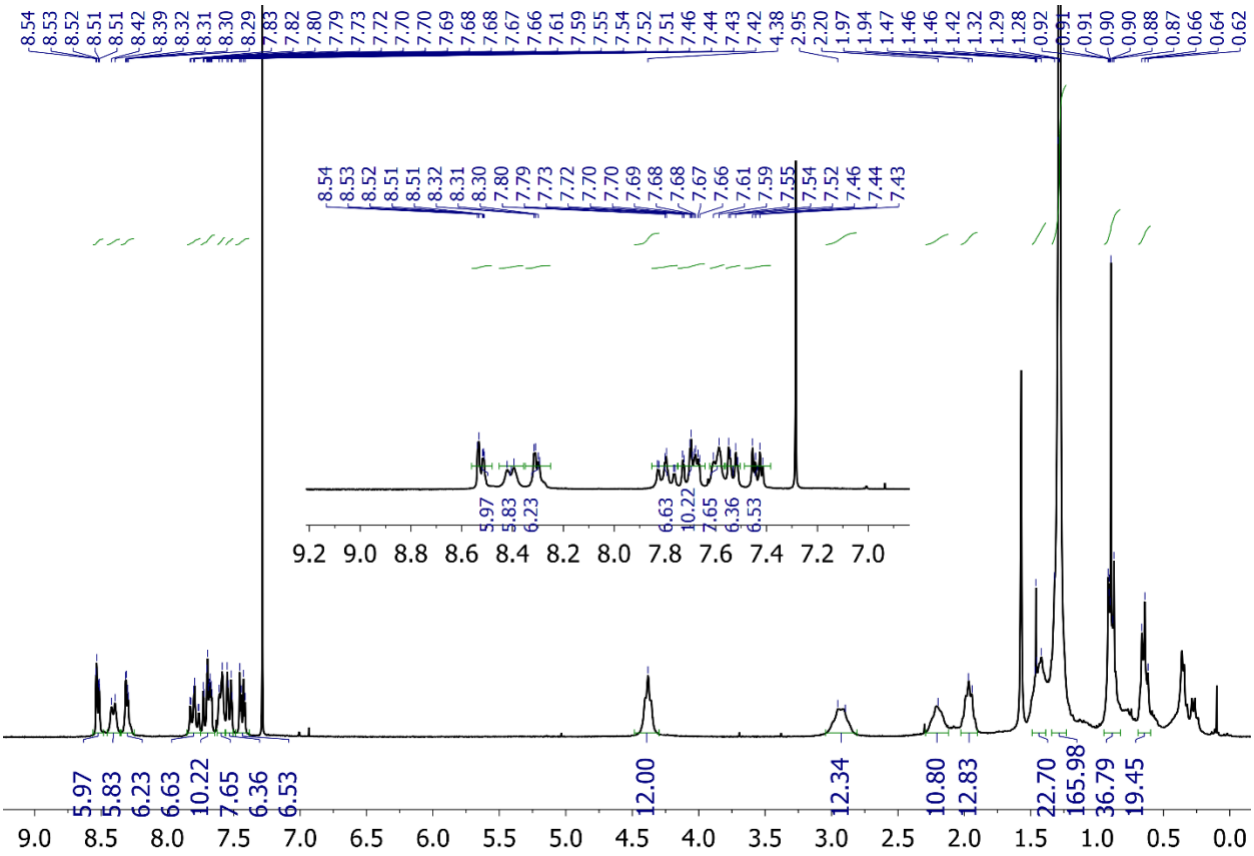


Fig. S10 ^{1}H NMR spectrum of **TC3** in $CDCl_3$.

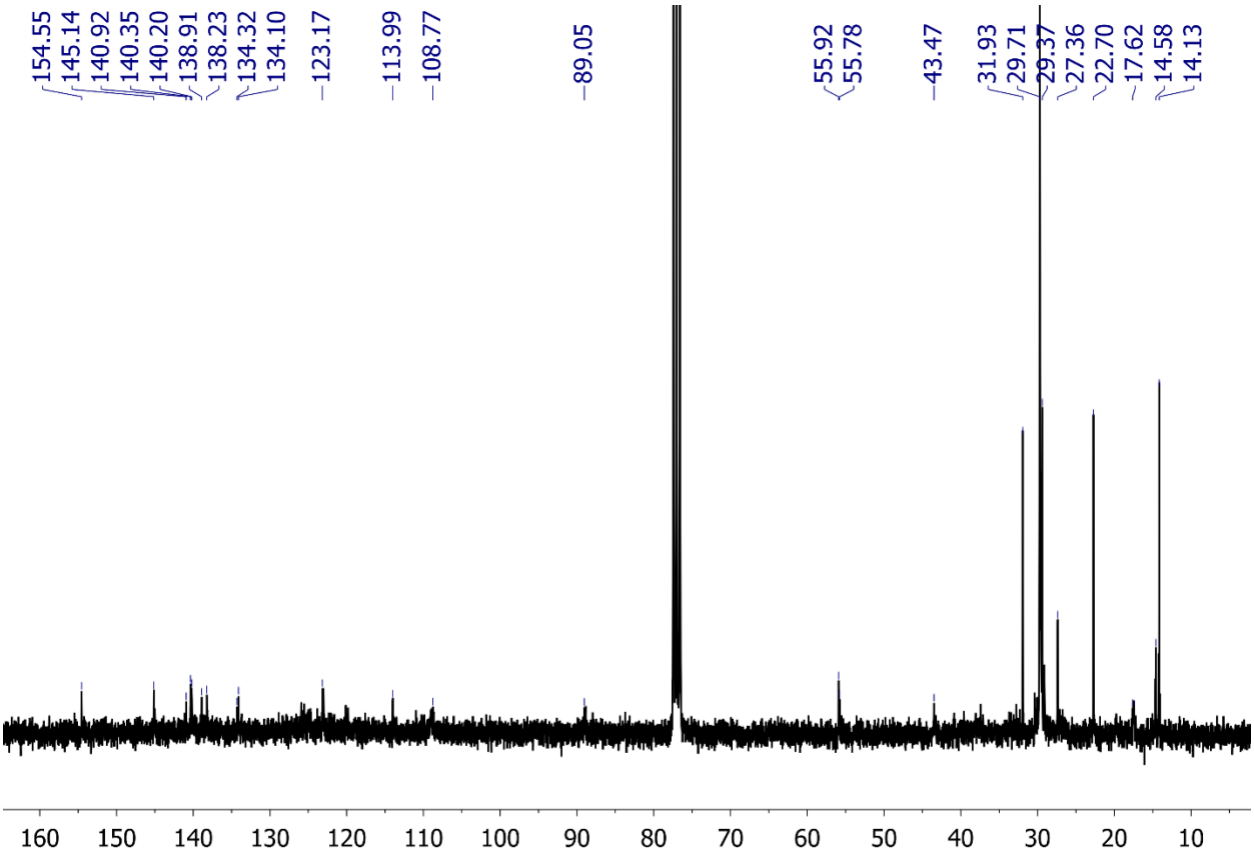


Fig. S11 ^{13}C NMR spectrum of **TC3** in $CDCl_3$.

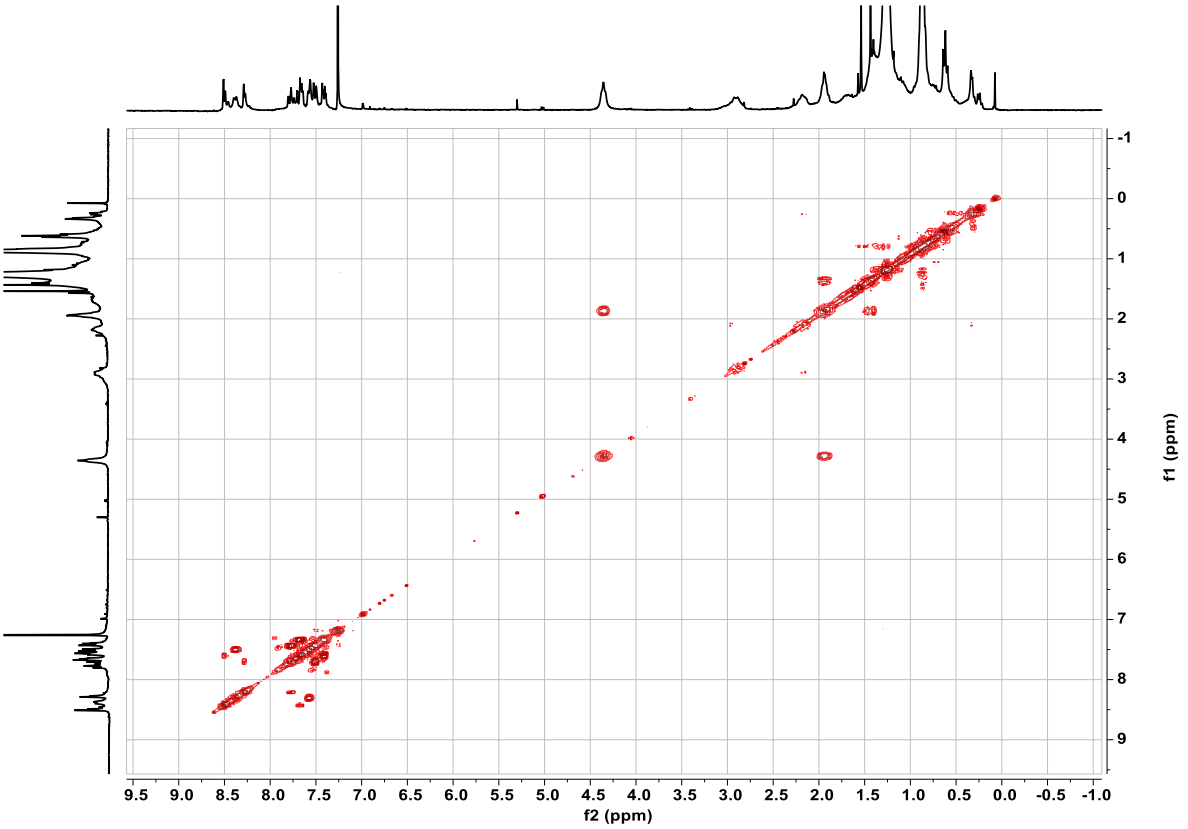


Fig. S12 2D COSY spectrum of **TC3** in $CDCl_3$.

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