Supporting Information

Interchromophore Orientation Scaffolding by *m*-Terphenyl Oxacyclophanes

Anshuman Mangalum, Brad P. Morgan, Jessica M. Hanley, Kristine M. Jecen, Charles J. McGill, Grant A. Robertson and Rhett C. Smith*

Department of Chemistry and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, SC 29634

Email: rhett@clemson.edu

Supporting Information Figures I.: Data for 6, 7, OC1 and OC2

Supporting Information Figures II.: Data for compounds 2-5.

Supporting Information Figures II.: Data for 10, 11 and 13.

Experimental

Materials.

All the reactions were performed under inert nitrogen atmosphere unless otherwise specified. Toluene was dried by passage through alumina columns under N_2. All other solvents and reagents were obtained from commercial sources and used without purification. Sonogashira reaction was carried out in MBraun dry box and coupling of cyclophane using standard Schlenk techniques under an atmosphere of N_2. Compounds **1**,[S1] 1,2-dihydroxy-3,6-diiodobenzene,[S2] 1,4-dihydroxy-2,5-diiodobenzene,[S3] 1,4-dibromo-2,5-diiodobenzene,[S4] 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,5-dimethoxybenzene (**13**) and 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,3-dimethoxybenzene (**11**)[S5] were synthesized by adaptation of the reported methods. NMR spectra were acquired on a Bruker ARX spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C, or on a Bruker Avance spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shift are reported in ppm and referenced to tetramethylsilane or residual solvent signal. Glass backed sorbtech silica gel preparative TLC plates were used for preparative TLC purification, were pore diameter of the gel was 60Å. Gel was mixed with fluorescent indicator (UV254) of 500 μm thickness

General Procedures for Spectroscopy. Absorption spectra were collected using a Varian Cary-50 Bio spectrophotometer and photoluminescence (PL) data were recorded using a Varian Eclipse spectrofluorimeter in Teflon-stopper-sealed Spectrosil cuvettes with a path length of 1 cm in dry, N_2-degassed THF. Quantum yields (Φ) were calculated relative to quinine bisulfate solution in 1 M H_2SO_4 (aq) ($\Phi = 0.546$).[S6]

*Preparation of **2**:*

To a solution of **1** (6.35 g, 13.7 mmol) in 100 mL $CHCl_3$, *N*-bromosuccinimide (6.10 g, 34.2 mmol) and benzoyl peroxide (0.033 g, 0.01 mol) were added. The solution was heated to reflux under nitrogen for 5 d. The succinimide was removed by filtration and the filtrate was washed three times with 100 mL of water. The filtrate was placed in a flask and product formed after approximately 1 h. 50 mL of acetonitrile was added to the flask and the product was filtered. To a solution of the product and 100 mL of benzene, another portion of *N*-bromosuccinimide (6.10 g, 34.2 mmol) and benzoyl peroxide (0.0330 g, 0.0100 mol) were added. After another 5 d of reflux under nitrogen, and additional amount of *N*-bromosuccinimide (12.2 g, 5.00 mol) and benzoyl peroxide (0.0330 g, 0.0100 mol) were added. The solution was heated to reflux under nitrogen for 2 d. The product was filtered and 10 mL of acetonitrile were added. The solid product that was filtered still exhibited a brown color indicative of bromine. The produced was dissolved in 50 mL of dichloromethane and washed with aqueous Na_2SO_3 (50 mL of H_2O and 2 g Na_2SO_3) three times. The dichloromethane was evaporated, and the product was recrystallized in hexane to yield 2.78 g (26.0%) of **2** as a solid. For preparation of **3** or **5**, we found that it was not necessary for compound **2** to be further purified, as mixed monobrominated (CH_2Br) and dibrominated ($CHBr_2$) sites are all smoothly converted to **3** or **5** in the subsequent steps. The NMR spectra for the material used in the next steps are shown in Figures S30-31, and indicate that the materials is >95% pure. (Chemical shifts of two isomers are reported without further assigning to syn- or anti-) ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.35 (s, 1.2H), 6.42 (s, 0.8H), 7.08 - 7.11 (d, 0.8H, J = 6 Hz), 7.14 - 7.17 (d, 1.2H, J = 6 Hz) 7.43 - 7.48 (m, 2H), 7.53 (s, 2H), 7.56 - 7.62 (m, 2H), 8.10 - 8.13 (d, 2H, J = 9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 38.2, 38.3, 103.3, 104.2, 122.5, 129.2, 129.4, 129.6, 129.7, 129.9, 130.0, 131.8, 132.0, 139.0, 139.2, 146.8, 146.7, 146.8.

*Preparation of **3**:*

To a solution of **2** (2.00 g, 2.60 mmol) in a solution of THF (10 mL) and EtOH (absolute, 50 mmol), NaOAc (1.40 g, 6.60 mmol) and $AgNO_3$ (1.70 g, 15.0 mmol) was stirred at room temperature. The mixture rapidly forms a white precipitant. The solution was heated to reflux for 16 h and brought to room temperature. The solvent was evaporated after the removal of the solid by filtration. The resulting solid was dissolved in chloroform (30 mL) and 10 % hydrochloric acid (1 mL) was added. The reaction mixture stirred at room temperature for 18 h and was then washed with water (3 × 100 mL). The solvent was removed and enough diethyl ether was placed in flask to dissolve the product. The diethyl ether solution was pipetted into pentane, and the precipitate formed was filtered and dried. The product was recrystallized in hexane to yield 0.870 g (68.1%) of **3** as a solid. (Chemical shifts of two isomers are reported without further assigning to syn- or anti-) ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.31 - 7.36 (m, 3H), 7.51 - 7.73 (m, 5H), 8.04 - 8.06 (m, 2H), 9.90 (s, 1H), 9.93 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 104.1, 104.3, 122.3, 122.4, 128.3, 128.9, 129.1, 129.2, 130.4, 130.7, 132.0, 132.2, 133.2, 133.4, 133.8, 134.0, 146.0, 146.1, 146.2, 146.4, 190.7, 190.8. HRMS calcd for $C_{20}H_{13}BrIO_2$ $(M+H)^+$: 490.9144, found: 489.9141.

*Preparation of **4**:*

In the dry box, a solution of **3** (0.306 g, 0.623 mmol), methanol (2 mL), and THF (1.5 mL) was added drop by drop to $NaBH_4$ (0.470 g, 1.25 mmol) in THF (5 mL). The reaction mixture stirred 5 d in the dry box until a dark yellow solid had formed and the mixture was no longer able to stir. THF (3 mL) was added to solution and 15% hydrochloric acid (1 mL) was slowly added. The reaction mixture stirred for 1 h and the solvent was removed. Diethyl ether (20 mL) was added and washed with water (3 × 10 mL). The solvent was removed and the product was recrystallized in pentane to yield 0.298 g (96.5 %) of **4** as a white solid. A small amount (ca. 5%) of aldehyde **3** remained in the sample, as determined from aldehydic peak at ca. 9.9 ppm. This sample was used without further purification in the next step; however, note that this synthetic avenue was abandoned in favor of the more efficient route shown in Scheme 1 of the manuscript. The material can be obtained in pure crystalline form by diffusion of pentane into a CH_2Cl_2 solution of **4** (see the results of single crystal X-ray diffraction, Figure S43 and Table S4). For NMR data, chemical shifts of two isomers are reported without further assigning to syn- or anti-) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.71 (s, 2H), 4.26 - 4.66 (q, 4H, J_1 = 12.5 Hz, J_2 = 47.0 Hz), 7.16 – 7.19 (m, 2H), 7.38 – 7.43 (m, 4H), 7.47 – 7.51 (m, 2H), 7.58 – 7.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 63.1, 63.2, 104.4, 104.9, 122.1, 127.6, 127.7, 127.8, 127.9, 128.8, 128.9, 129.2, 129.48 131.2, 131.4, 137.9, 137.9, 142.6 142.7, 148.1, 148.2.

*Preparation of **5** from **4**:*

To a solution of **4** (0.298 g, 0.601 mmol), benzene (2 mL), and one drop of pyridine, slowly add solution of PBr_3 (0.0729 g, 0.270 mmol) and benzene (3 mL). Solution was stirred for 16 h and then reaction mixture was extracted three times with water (30 mL). All the volatile were removed under reduced pressure. Recrystallization from ethanol gave 0.164 g (43.0%) of **5** as an off-white solid.

*Preparation of **5** from **2**:*

Solution of compound **2** (10.1 g, 15.6 mmol) in 50 mL of anhydrous THF was cooled to 0 °C in ice bath and stirred under nitrogen atmosphere. Diethyl phosphite (51.7 g, 374 mmol) was then added dropwise, followed by the addition of ethyldiisopropylamine (48.4 g, 374 mmol). After the reaction mixture was stirred at room temperature for 20 h, it was poured into 150 mL of water and extracted with diethyl ether (4 × 50 mL). The organic layer was washed with 100 mL of 1 M HCl followed by 100 mL of saturated aqueous sodium chloride solution. The organic layers were then collected, dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Residue was washed with ethanol, yielding 5.41 g of **5** as an off white solid (55.0 %). (Chemical shifts of two isomers are reported without further assigning to syn- or anti-) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.19 – 4.47 (m, 4H), 7.19 – 7.21 (m, 2H), 7.39 – 7.66 (m, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 31.2, 31.3, 104.3, 104.7, 121.9, 122.0, 128.5, 128.6, 129.1, 129.2, 130.1, 130.2, 130.5, 130.6, 131.8, 131.9, 134.9, 135.0, 143.6, 143.7, 147.3, 147.3. HRMS calcd for $C_{20}H_{15}Br_3I$ $(M+H)^+$: 617.7690, found: 617.7687.

Preparation of *1,4-bis(4-t-butylphenylethynyl)-2,6-bis(o-tolyl) benzene (**10**):* Detailed studies on this material will be reported in a full paper. Briefly, compound **1** was degassed and taken into dry box along with pressure flask. In pressure flask, compound **1** (0.95 g, 2.0 mmol) was dissolved in 5 mL of toluene. Tetrakis(triphenylphosphine) palladium(0) (0.047 mg, 0.041 mmol) and copper iodide (0.0160 mg, 0.0818 mmol) was added into the solution. In another vial, *t*-butylphenylacetylene (1.3 g, 8.1 mmol) was dissolved in diisopropyl amine (5 mL). This solution was added into the pressure flask drop wise. Pressure flask was capped and taken out from the dry box. Reaction mixture was stirred for 48 h at 90 °C. Reaction mixture was passed through silica, followed by washing with 30 mL of ether. Organic layer was extracted with sat. sodium bicarbonate solution (4 × 100 mL). Organic layer was collected and dried over sodium sulfate, volatiles were removed under reduced pressure. Pure light yellow solid compound was obtained by using glass backed sorbtech silica gel preparative TLC plates, where pore diameter of the gel was 60 Å. The gel was mixed with a fluorescent indicator (UV254) of 500μm thickness. (R_f: 0.3, 10% ethylacetate:pentane). (0.30 g, 25 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 9H, 3 × CH_3), 1.35 (s, 9H, 3 × CH_3), 2.30 (s, 6H, 2 × CH_3), 6.70 (d, 2H; J = 6.0 Hz, Aromatic), 7.18 (d, 2H; *J* = 9.0 Hz, Aromatic), 7.35 (m, 12H, Aromatic), 7.50 (m, 4H, Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 31.0, 31.1, 34.6, 34.8, 87.3, 88.6, 91.3, 97.0, 120.0, 120.2, 122.5, 125.0, 125.3, 125.4, 127.6, 129.6, 130.9, 131.0, 131.3, 136.4, 140.4, 144.4, 151.2, 151.7. HRMS (MALDI) calcd for $C_{44}H_{42}$ (M^+): 570.3287, found: 570.3134.

*Preparation of **7**:*

In a 2 neck flask, under N_2, K_2CO_3 (2.20 g, 15.9 mmol) and DMF (60 mL) was stirred at 90 °C for 15 min. In a separate vial, **5** (346 mg, 0.560 mmol) and 1,2-dihydroxy-3,6-diiodobenzene (0.20 g, 0.56 mmol) was dissolved in DMF (10 mL). This solution was added into preheated flask dropwise via syringe pump for 4 days and reaction mixture was stirred for next 3 days. DMF was removed under reduced pressure and residue was dissolved in minimum amount of CH_2Cl_2 and solution was filtered through silica. Silica was washed with CH_2Cl_2 (20 mL). CH_2Cl_2 was collected and removed under reduced pressure. Compound was further purified by prep TLC (95:5 hexane: ethylacetate), yielding white solid. (50 mg, 10 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.27 (d, 2H; *J* = 10 Hz, O-CH_2), 5.33 (d, 2H; *J* = 10 Hz, O-CH_2), 7.32 (s, 2H, Aromatic), 7.39 (s, 2H, Aromatic), 7.45 (dd, 2H; J_1 = 9 Hz, J_2 = 2 Hz, Aromatic), 7.55 – 7.49 (m, 4H, Aromatic), 7.72 (dd, 2H; J_1 = 9 Hz, J_2 = 2 Hz, Aromatic). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 75.9, 94.4, 102.4, 121.4, 128.5, 128.8, 129.0, 130.8, 130.9, 134.5, 136.6, 144.3, 148.3, 153.0. HRMS calcd for $C_{26}H_{16}BrI_3NaO_2$ $(M+Na)^+$: 842.7384, found: 842.7366.

*Preparation of **OC2**:*

7 were degassed and taken into dry box along with pressure flask. In pressure flask, compound **7** (20.0 mg, 0.024 mmol) was dissolved in 20 mL of toluene. Tetrakis(triphenylphosphine) palladium(0) (0.005 g, 0.004 mmol) and ~2 mg of copper iodide was added into the solution. In another vial, 4-*t*-butylphenylacetylene (60 mg, 0.38 mmol) was dissolved in diisopropyl amine

(10 mL). This solution was added into the pressure flask drop wise. Pressure flask was capped and taken out from the dry box. Reaction mixture was stirred at room temperature for 3 h and then stirred for 48 h at 90 °C. 20 mL of CH_2Cl_2 was added to the reaction mixture and passed through silica. Silica was washed with CH_2Cl_2 (10 mL) and organic layer was extracted with sat. sodium bicarbonate solution (4 × 50 mL). Organic layer was collected and dried over sodium sulfate, volatiles were removed under reduced pressure. Prep TLC (Pentane) was done for purification, yielding white solid (10.0 mg, 41.6 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 - 1.34 (m, 36H, 12 × CH_3), 5.73 (d, 2H; *J* = 3 Hz, O-CH_2), 5.96 (d, 2H; *J* = 3 Hz, O-CH_2), 7.42 – 7.37 (m, 20H, Aromatic), 7.44 (s, 2H, Aromatic), 7.51 – 7.47 (m, 16H, Aromatic), 7.71 (m, 4H, Aromatic). HRMS calcd for $C_{74}H_{69}O_2$ $(M+H)^+$: 989.5298, found: 989.5294.

Preparation of ***6:***

In a 2 neck flask, under N_2, K_2CO_3 (2.20 g, 15.9 mmol) and DMF (60 mL) was stirred at 90 °C for 15 min. In a separate vial, **5** (346 mg, 0.560 mmol) and 1,4-dihydroxy-2,5-diiodobenzene (0.20 g, 0.55 mmol) was dissolved in DMF (10 mL). This solution was added into preheated flask dropwise via syringe pump for 4 days and reaction mixture was stirred for next 3 days. DMF was removed under reduced pressure and residue was dissolved in minimum amount of CH_2Cl_2 and solution was filtered through silica. Silica was washed with CH_2Cl_2 (20 mL). CH_2Cl_2 was collected and removed under reduced pressure. Compound was further purified by prep TLC (95:5 hexane: ethylacetate), yielding white solid. (60 mg, 13 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.90 (d, 1H; *J* = 12 Hz, O-CH_2), 5.09 (d, 1H; *J* = 12 Hz, O-CH_2), 5.50 (d, 1H; *J* = 12 Hz, O-CH_2), 5.92 (d, 1H; *J* = 12 Hz, O-CH_2), 6.89 (s, 1H, Aromatic), 7.10 (s, 1H, Aromatic), 7.28 (b, 2H, Aromatic), 7.50 - 7.33 (m, 6H, Aromatic), 7.64 (m, 2H, Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.3, 73.5, 87.3, 91.1, 108.6, 121.6, 128.1, 128.3, 128.8, 128.9, 129.0, 130.2, 130.7, 131.0, 132.9, 133.1, 133.2, 133.4, 133.5, 143.6, 147.6, 147.9, 152.4, 154.7. Elemental analysis calculated for $C_{26}H_{16}OBrI_3O_2$: C, 38.04; H, 1.96. Found: C, 38.15; H, 1.84.

Preparation of ***OC1:***

In a pressure flask, **6** (20.0 mg, 0.024 mmol) was dissolved in 20 mL of toluene. Tetrakis(triphenylphosphine)palladium(0) (0.005 g, 0.004 mmol) and ~2 mg of copper iodide was added into the solution. In another vial, 4-*t*-butylphenylacetylene (60 mg, 0.38 mmol) was dissolved in diisopropyl amine (10 mL). This solution was added into the pressure flask drop wise. Pressure flask was capped and taken out from the dry box. Reaction mixture was stirred at room temperature for 3 h and then stirred for 48 h at 90 °C. 20 mL of CH_2Cl_2 was added to the reaction mixture and passed through silica. Silica was washed with CH_2Cl_2 (10 mL) and organic layer was extracted with sat. sodium bicarbonate solution (4 × 50 mL). Organic layer was collected and dried over sodium sulfate, volatiles were removed under reduced pressure. Preparative TLC (pentane) was done for purification, yielding white solid (12 mg, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 - 1.34 (m, 36H, 12 × CH_3), 5.72 (d, 2H; J = 3 Hz, O-CH_2), 5.96 (d, 2H; J = 3 Hz, O-CH_2), 7.44 – 7.35 (m, 13H, Aromatic), 7.50 – 7.47 (m, 10H, Aromatic), 7.68 (m, 4H, Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.1, 34.6, 34.8, 34.9, 73.4, 81.5, 88.1, 90.7, 118.9, 119.5, 120.1, 120.2, 125.3, 125.3, 125.4, 125.8, 128.0, 128.3, 130.5, 131.3, 131.4, 131.6, 132.2, 134.6, 151.4, 151.5, 151.6, 152.5. HRMS calcd for $C_{74}H_{69}O_2$ $(M+H)^+$: 989.5298, found: 989.5292.

Supporting Information Figures I.: Data for 6, 7, OC1 and OC2.

^{1}H NMR (500 MHz) in $CDCl_3$

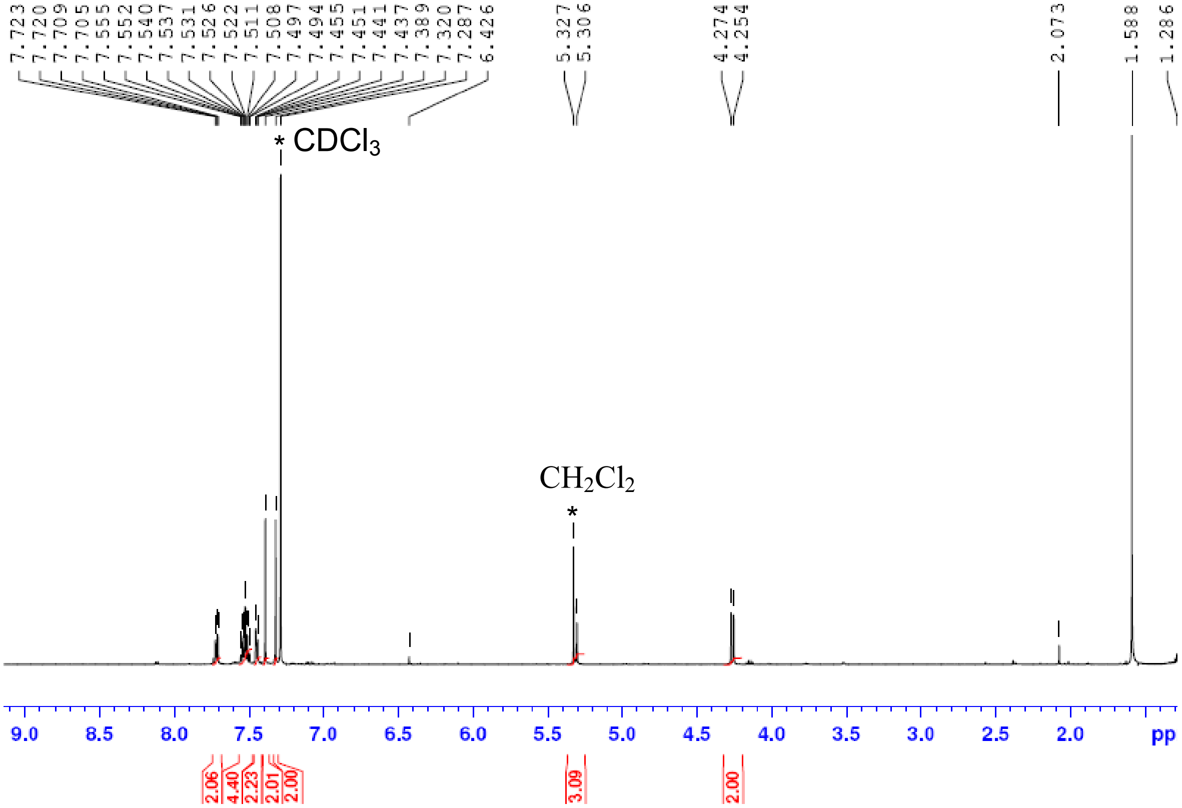

Figure S1. ^{1}H NMR spectrum of **7** ($CDCl_3$, 500 MHz)

^{1}H NMR (500 MHz) in $CDCl_3$

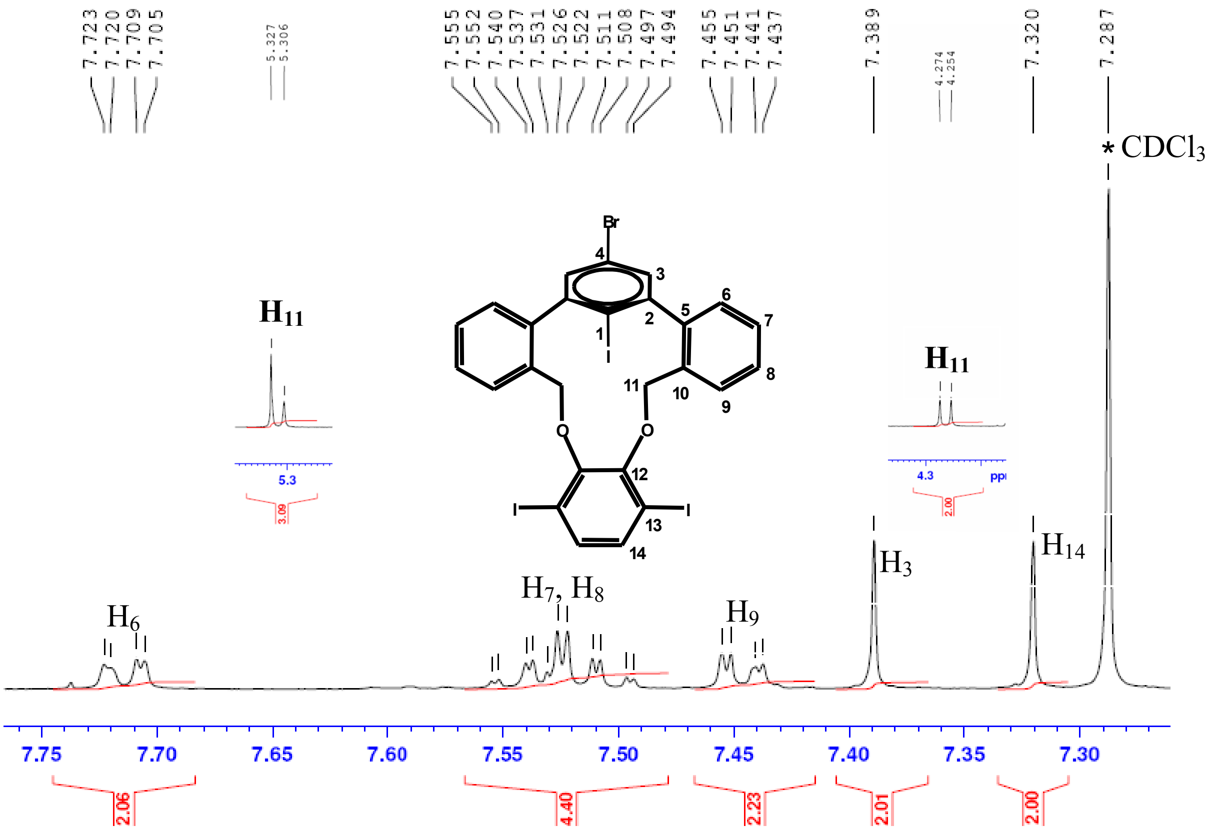

Figure S2. Aromatic and aliphatic region of the ^{1}H NMR spectrum of **7** ($CDCl_3$, 500 MHz).

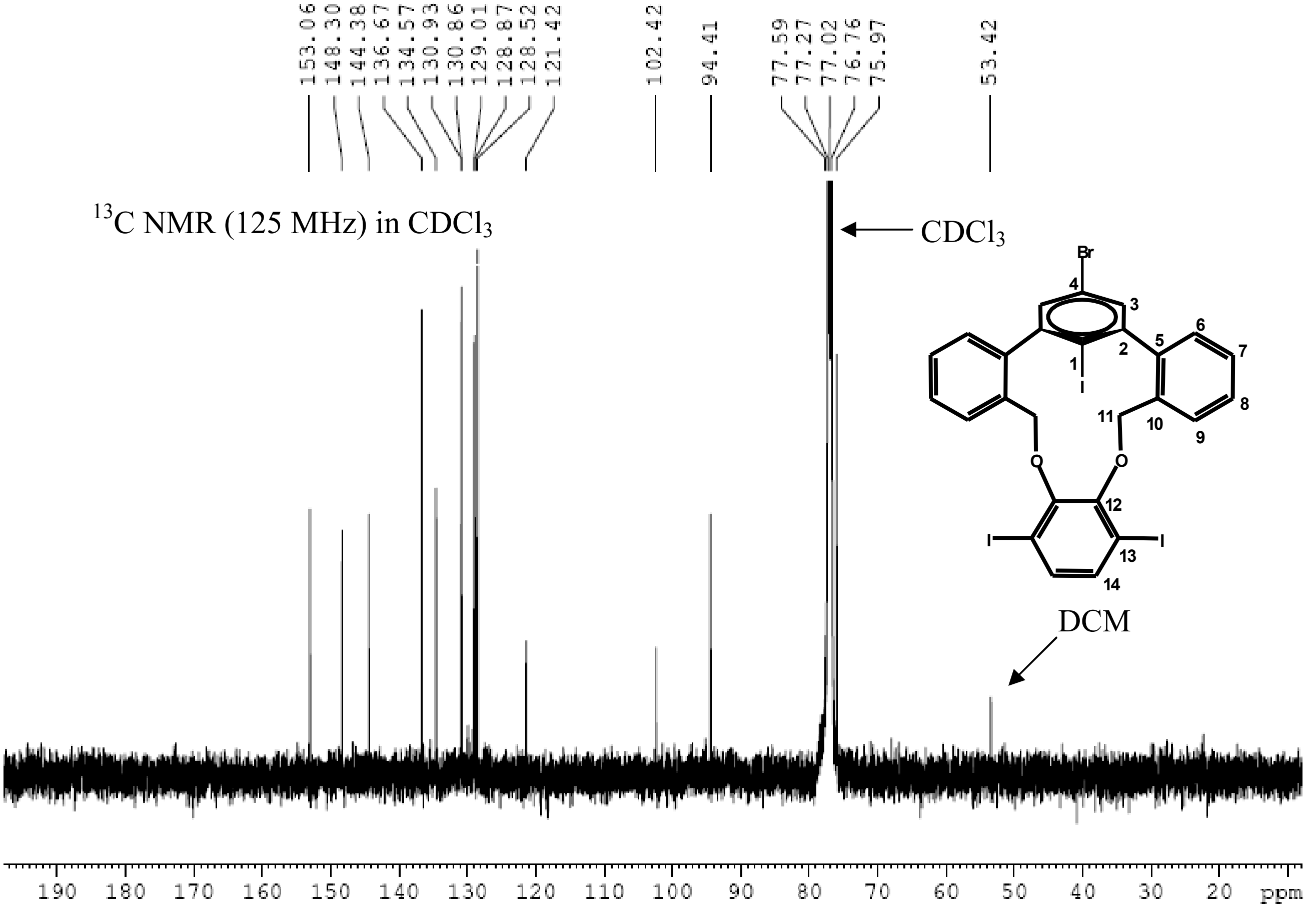

Figure S3. Carbon-13 NMR spectrum of **7** (CDCl$_3$, 125 MHz)

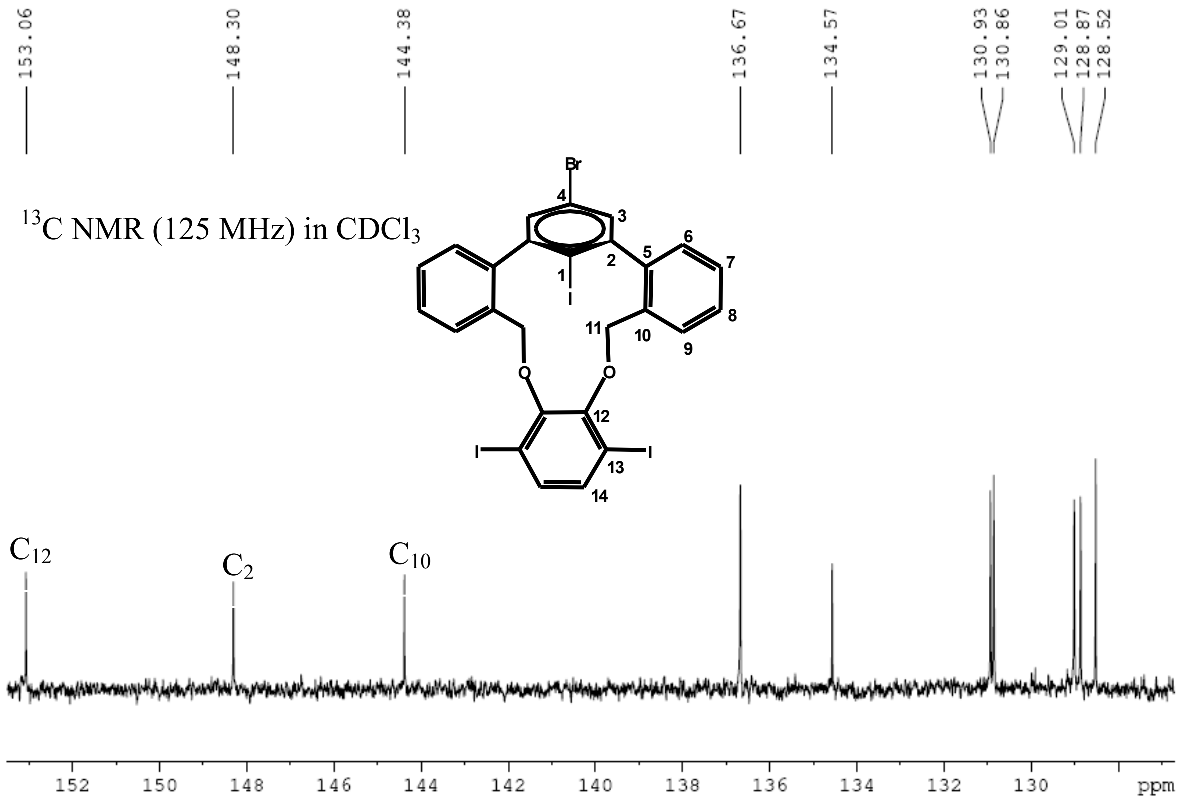

Figure S4. Aromatic region of the Carbon-13 NMR spectrum of **7** (CDCl$_3$, 125 MHz)

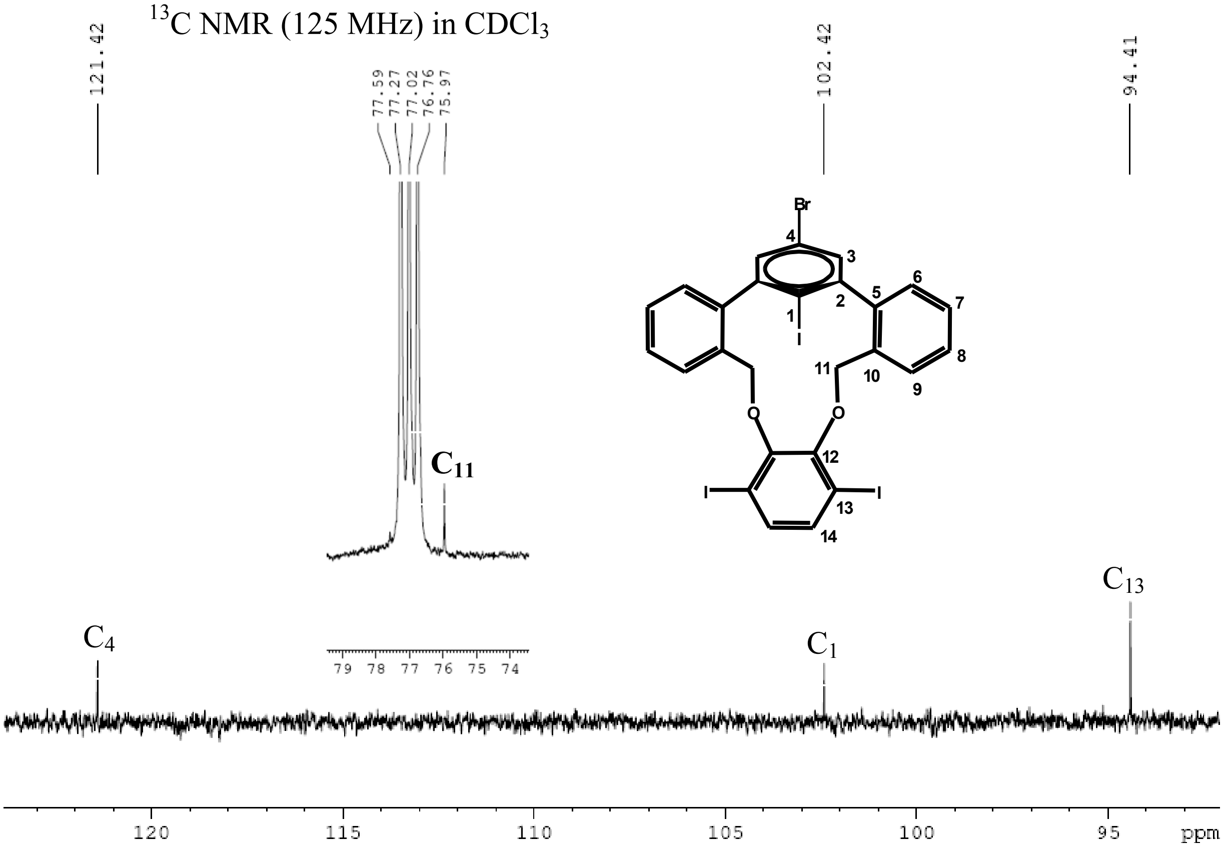

Figure S5. Aromatic and aliphatic region of the Carbon-13 NMR spectrum of **7** (CDCl$_3$, 125 MHz)

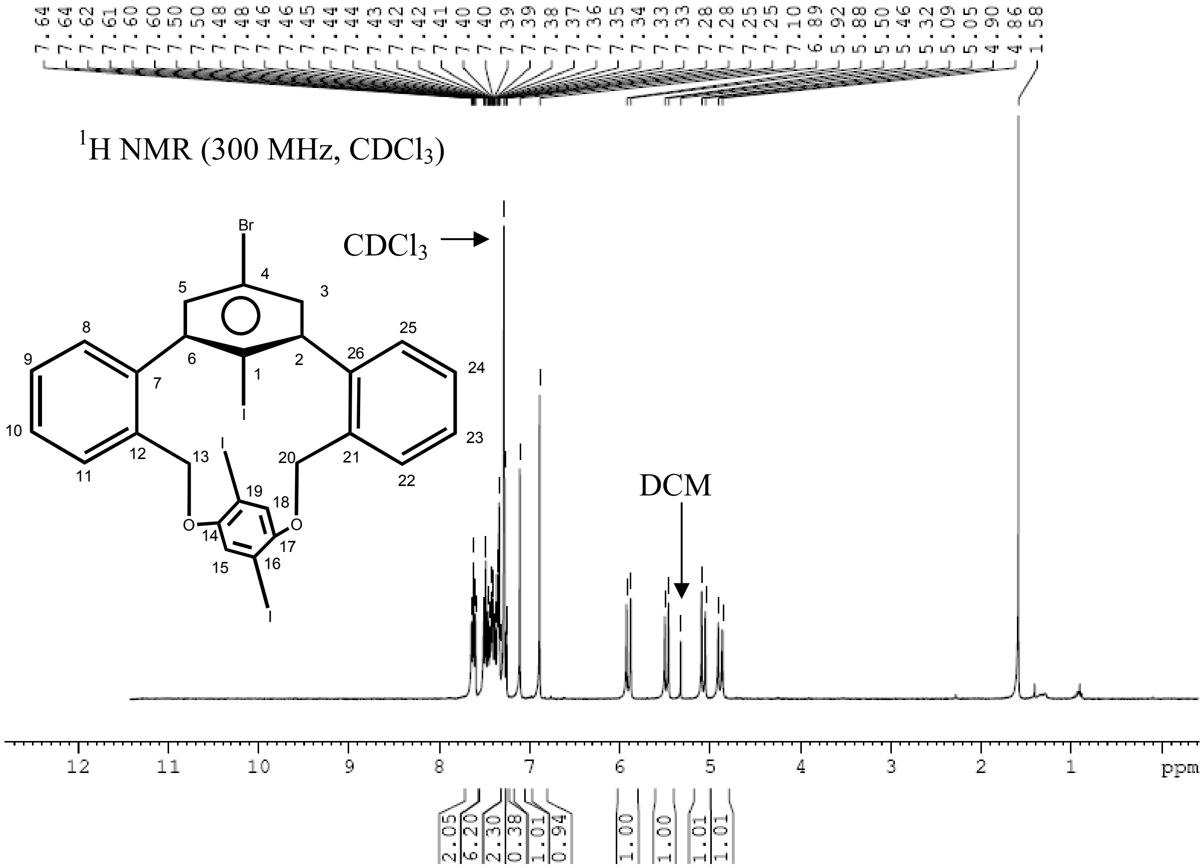

Figure S6. ^{1}H NMR spectrum of **6** (CDCl$_3$, 300 MHz)

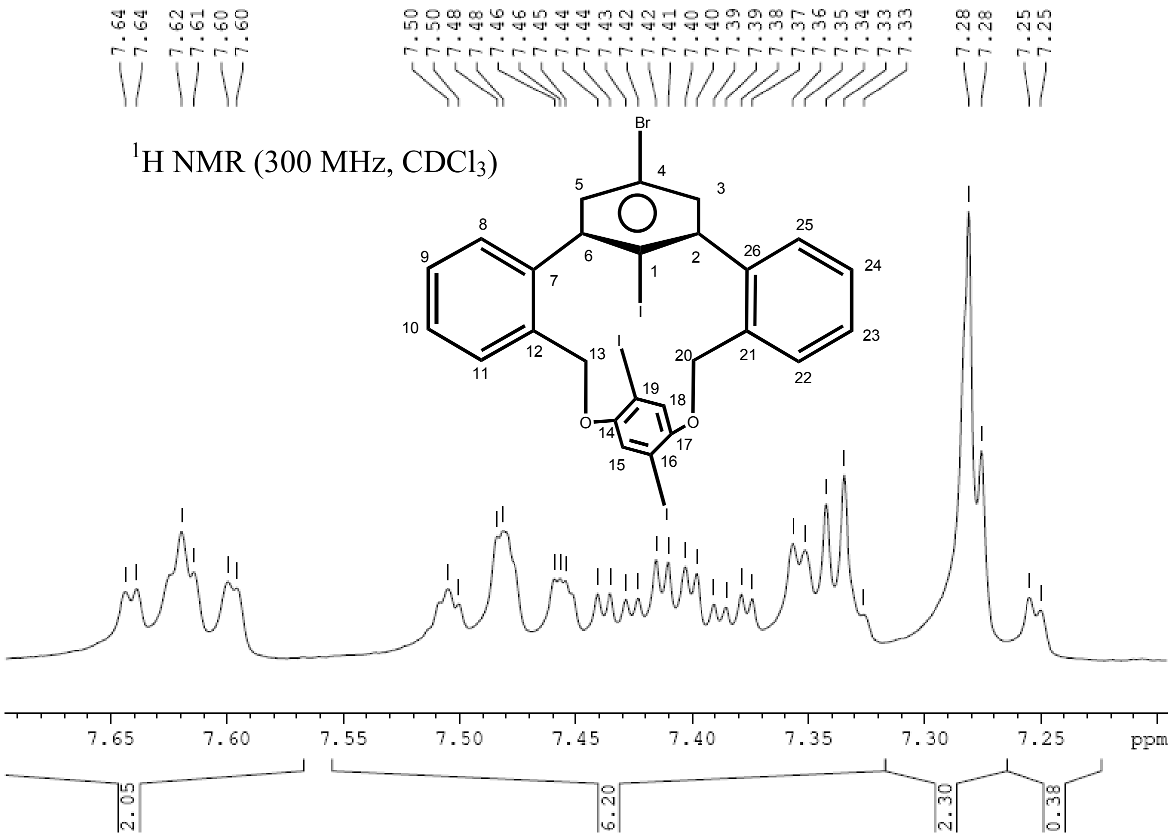

Figure S7. Aromatic region of the ^{1}H NMR of **6** (CDCl$_3$, 300 MHz)

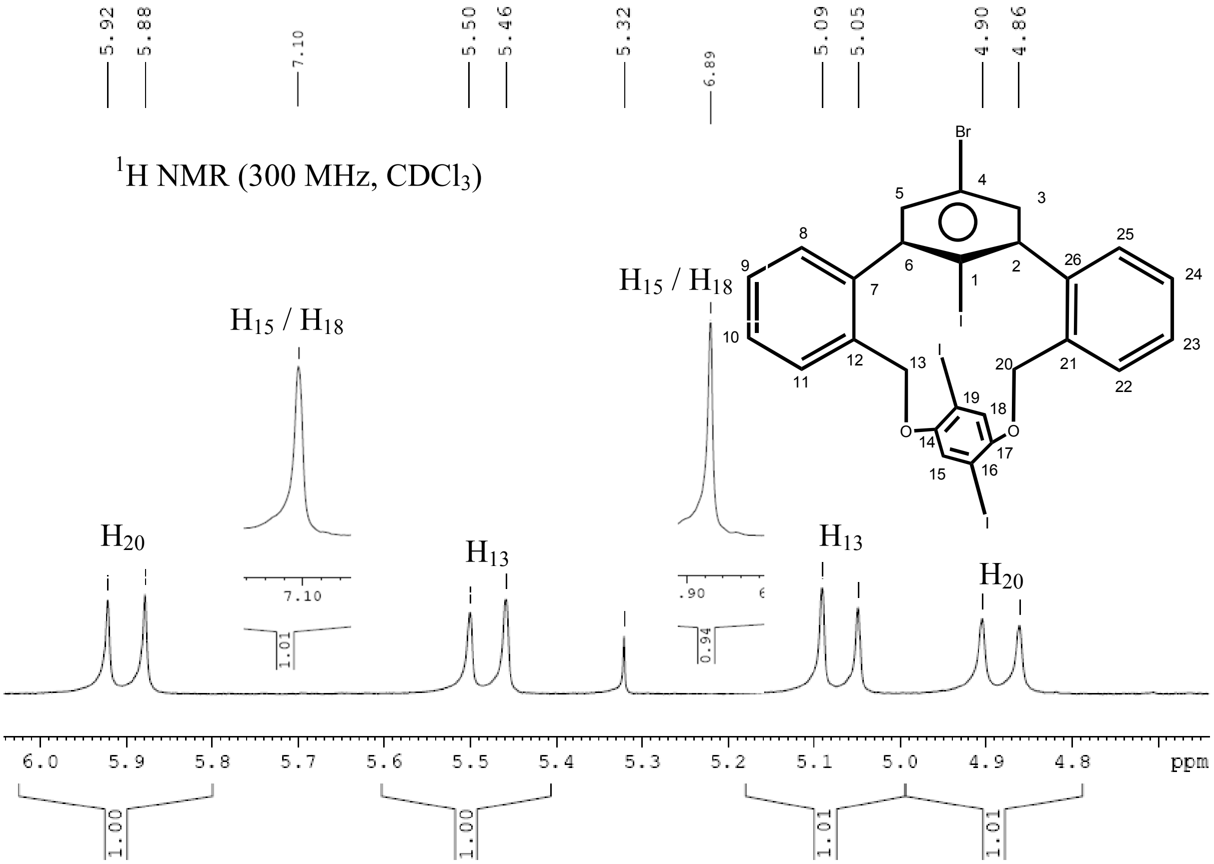

Figure S8. Aromatic and aliphatic region of the ^{1}H NMR of **6** (CDCl$_3$, 300 MHz)

^{1}H-^{1}H COSY (300 MHz, CDCl$_3$)

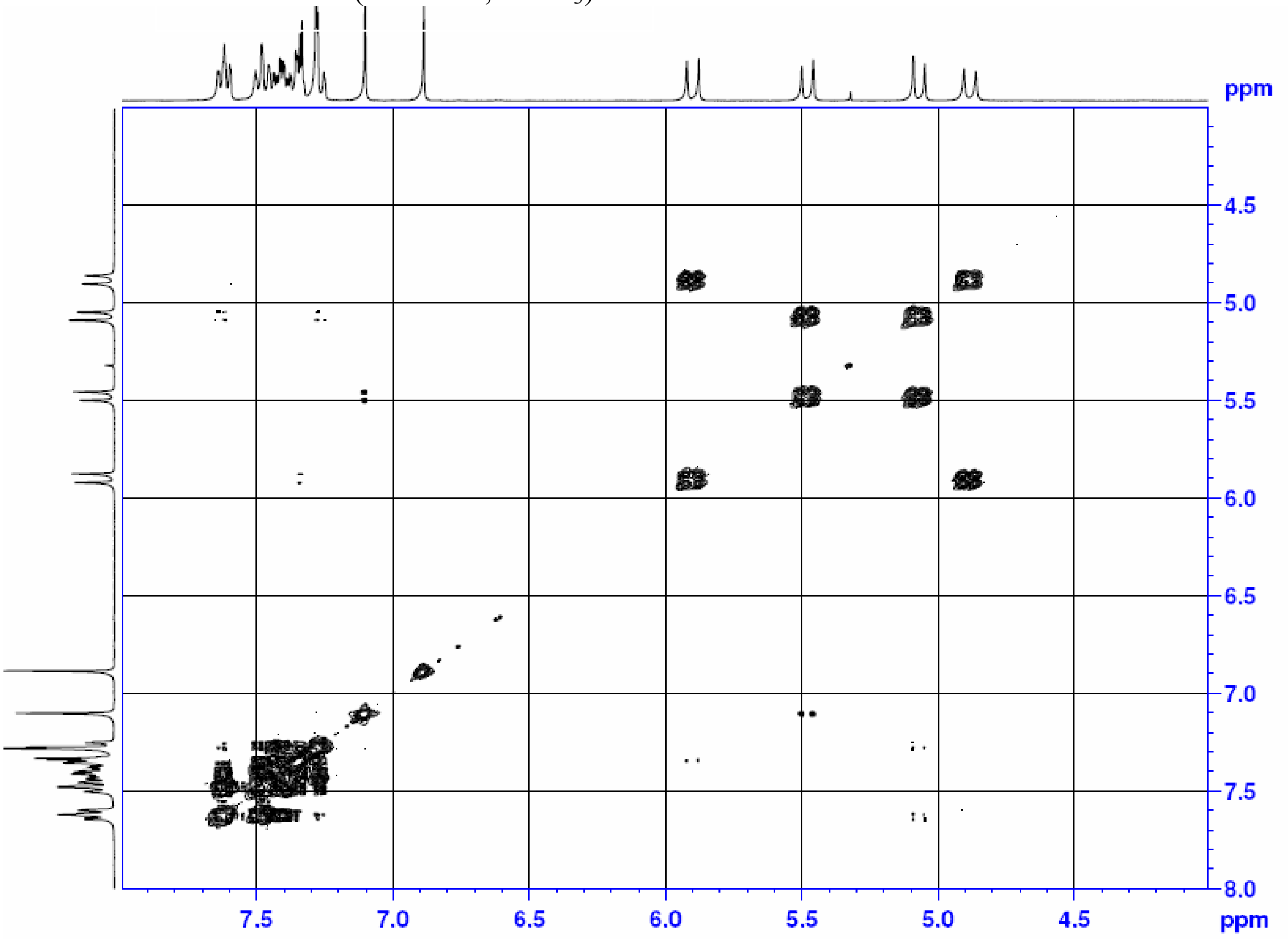

Figure S9. Aromatic and aliphatic region of the ^{1}H NMR of **6** (CDCl$_3$, 300 MHz)

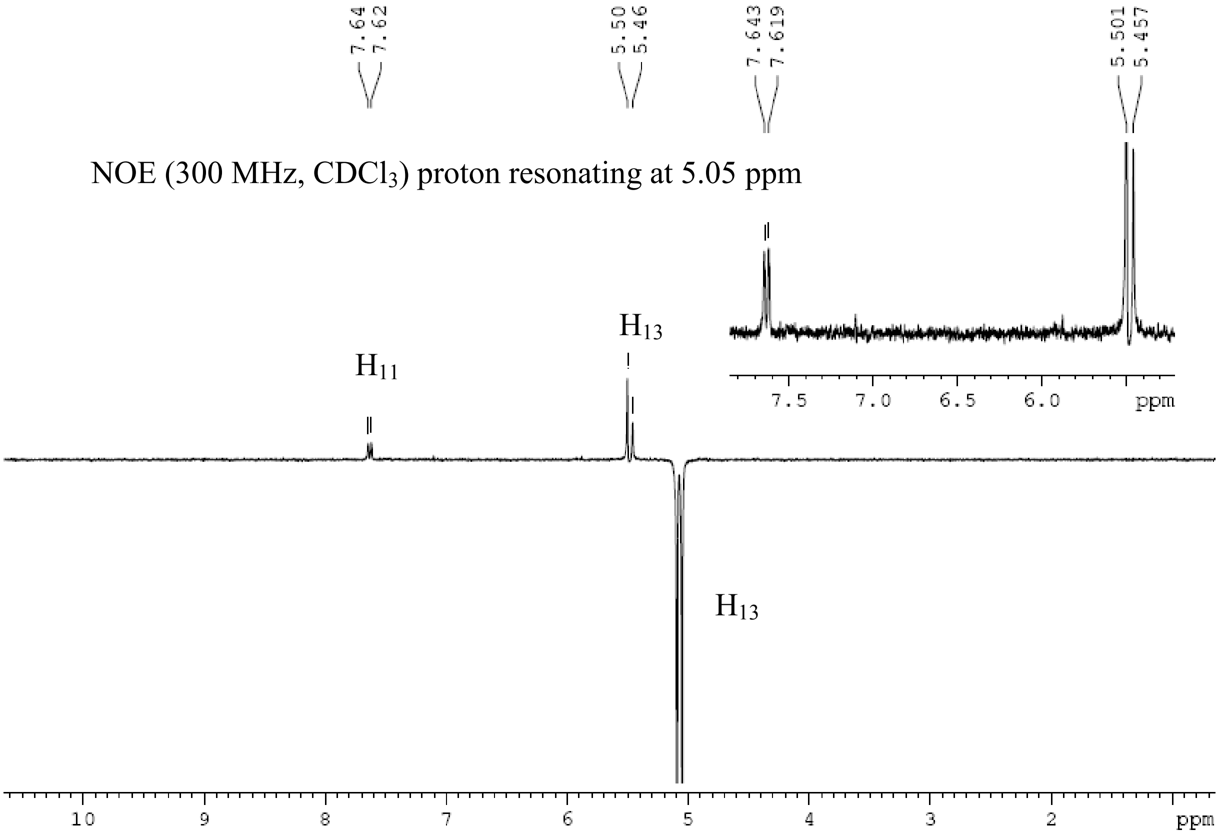

Figure S10. Nuclear Overhauser Effect spectrum of **6** ($CDCl_3$, 300 MHz) for proton resonating at 5.05 ppm

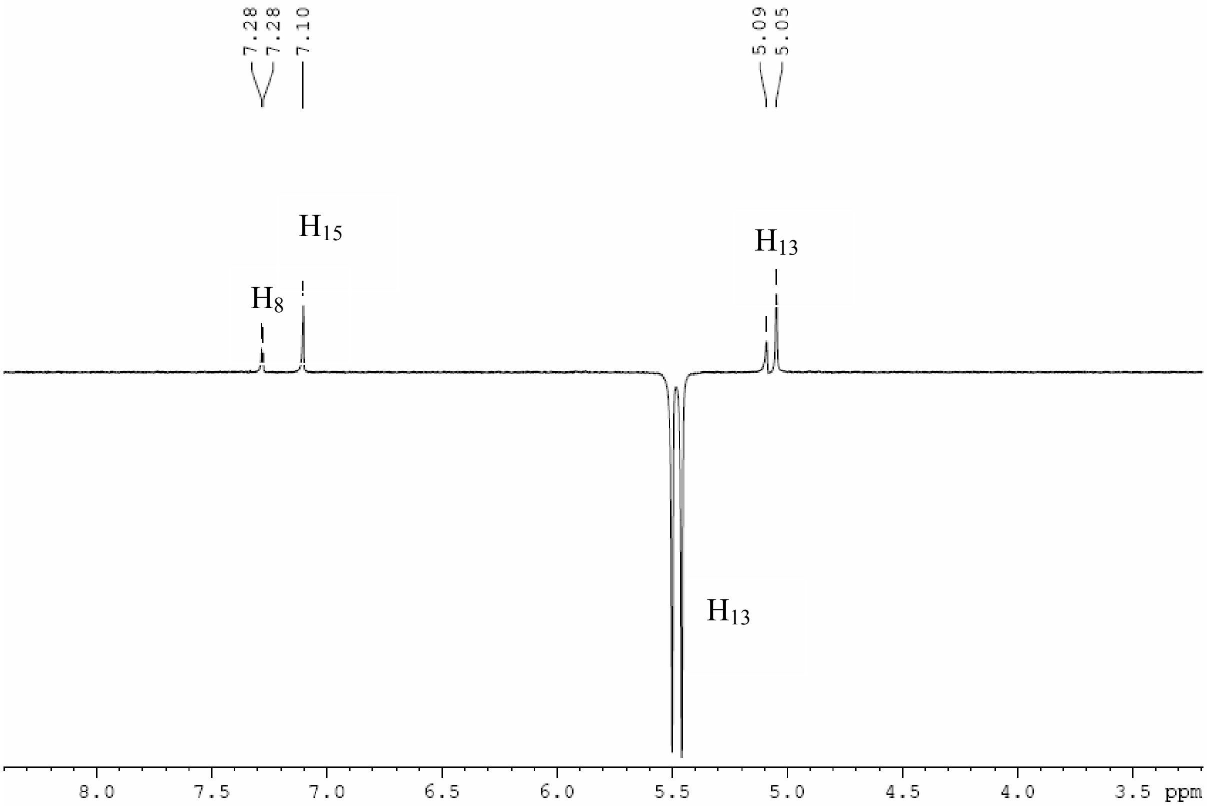

Figure S11. Nuclear Overhauser Effect spectrum of **6** ($CDCl_3$, 300 MHz) for proton resonating at 5.50 ppm

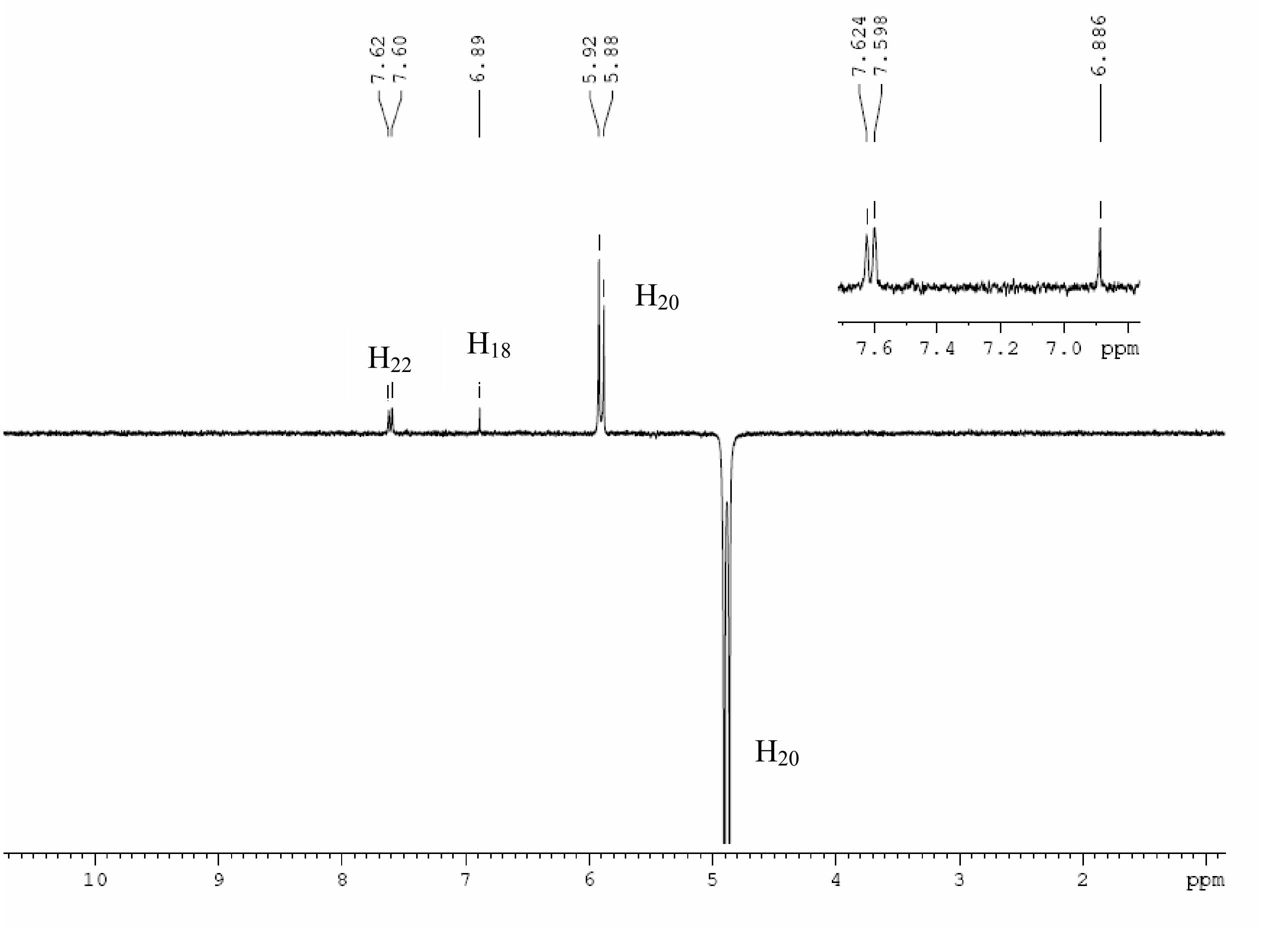

Figure S12. Nuclear Overhauser Effect spectrum of **6** ($CDCl_3$, 300 MHz) for proton resonating at 4.86 ppm

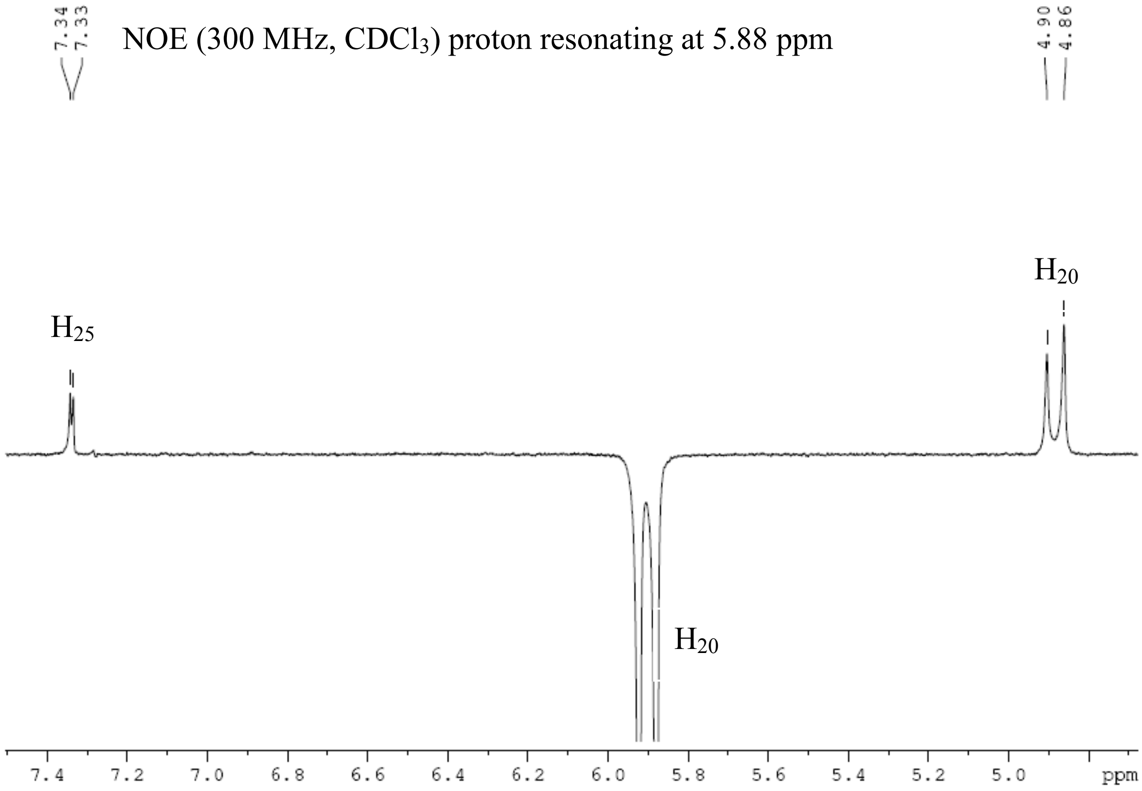

Figure S13. Nuclear Overhauser Effect spectrum of **6** ($CDCl_3$, 300 MHz) for proton resonating at 5.88 ppm

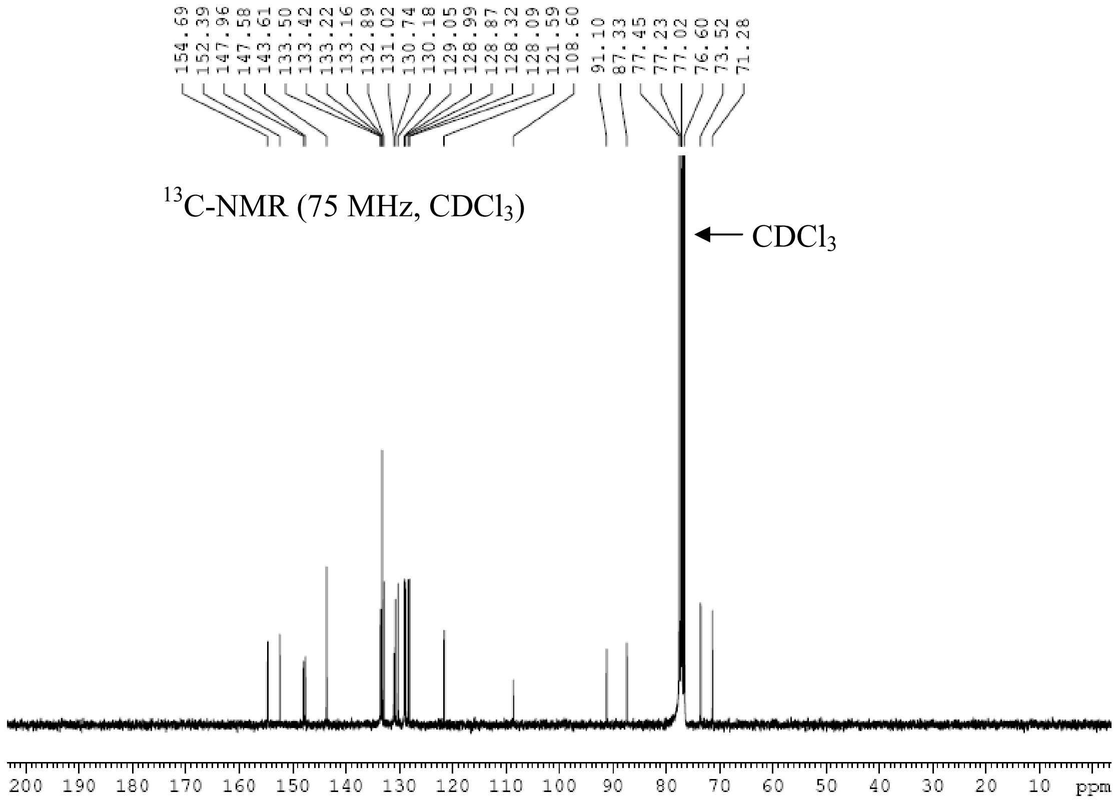

Figure S14. Carbon-13 NMR spectrum of **6** ($CDCl_3$, 75 MHz)

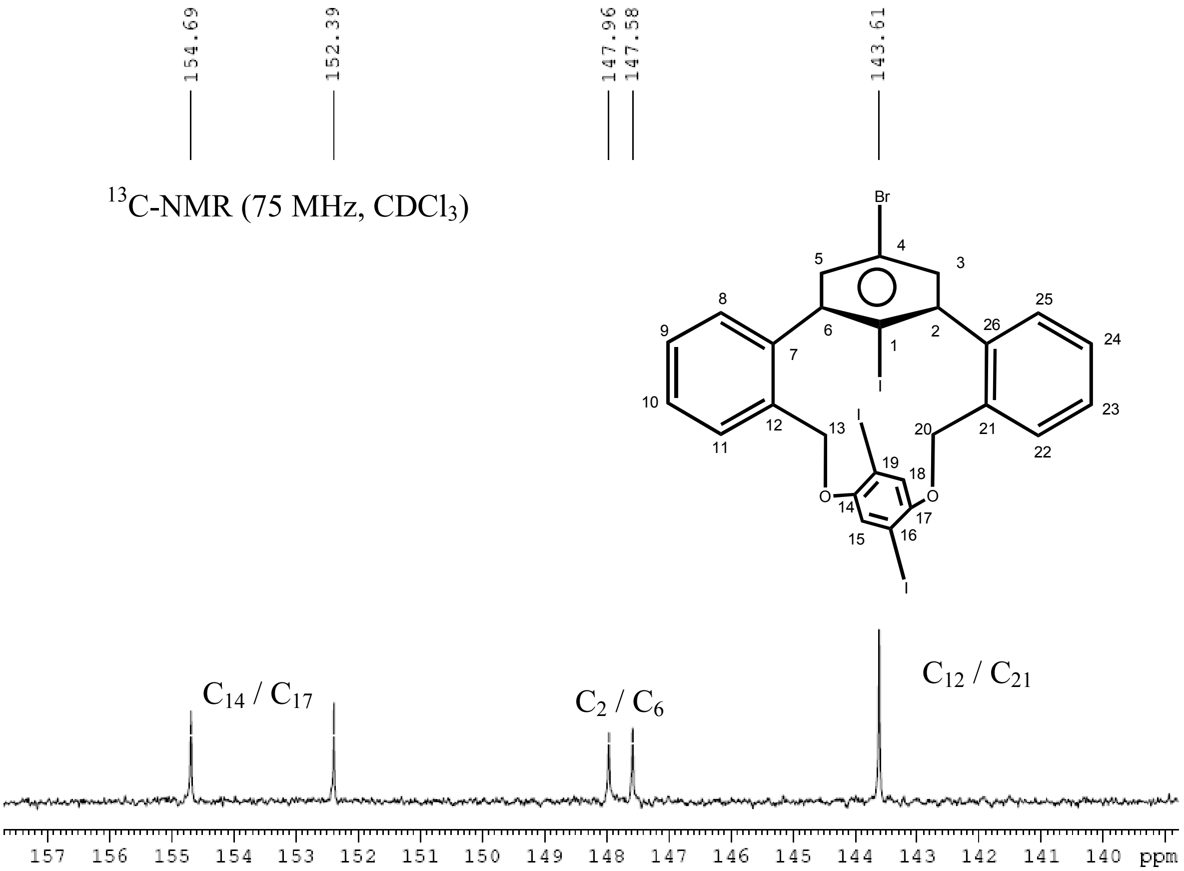

Figure S15. Aromatic region of the Carbon-13 NMR spectrum of **6** ($CDCl_3$, 75 MHz)

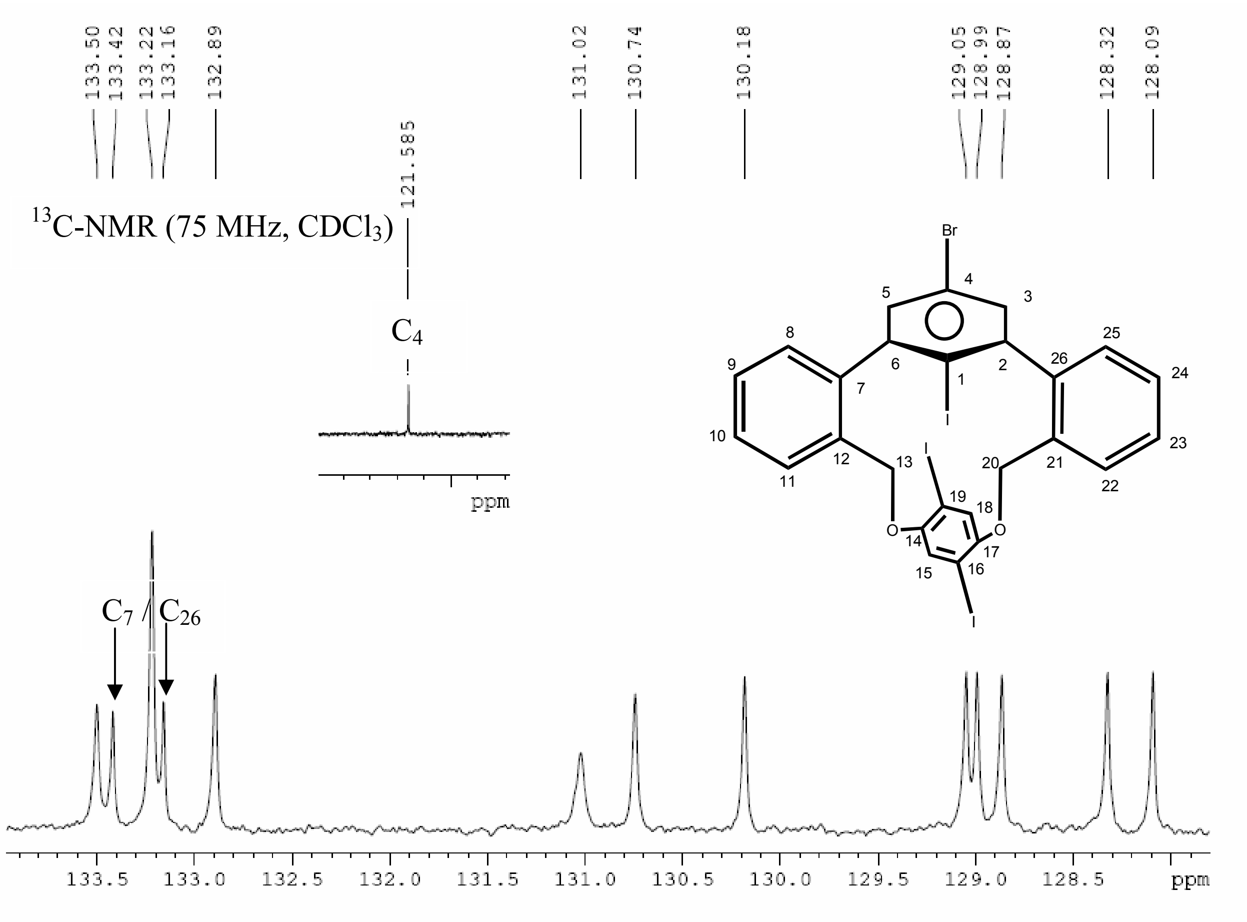

Figure S16. Aromatic region of the Carbon-13 NMR spectrum of **6** (CDCl$_3$, 75 MHz)

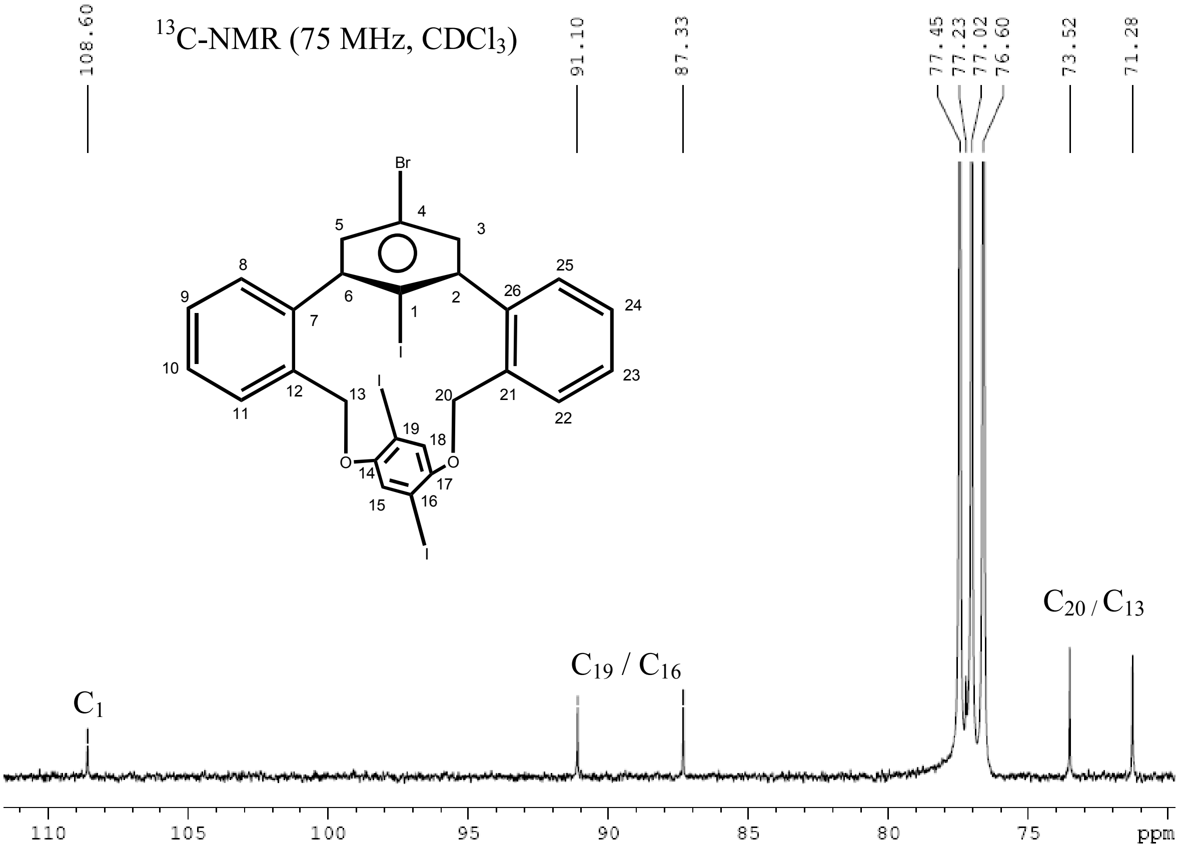

Figure S17. Aromatic and aliphatic region of the Carbon-13 NMR spectrum of **6** ($CDCl_3$, 75 MHz)

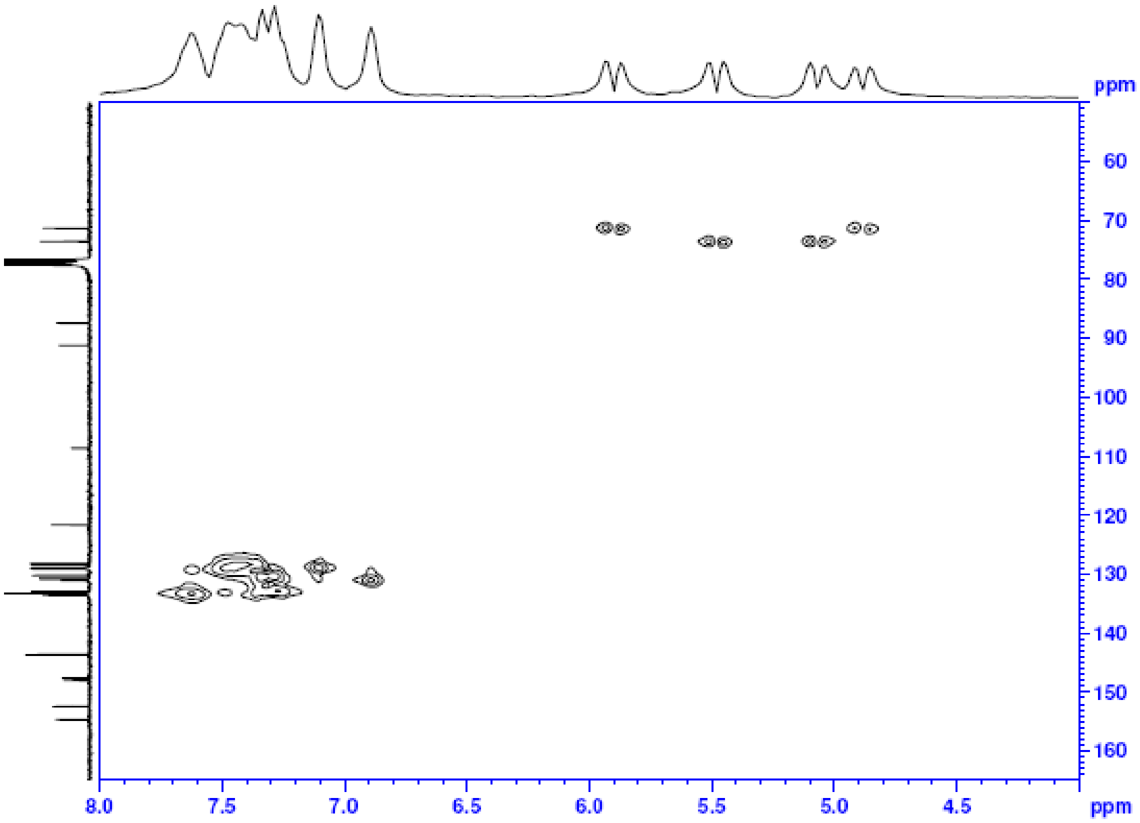

Figure S18. Heteronuclear Multiple Quantum Coherence (HMQC) spectrum of **6** (300 MHz for ^{1}H, 75 MHz for Carbon-13, in $CDCl_3$)

DEPT-135 (75 MHz, $CDCl_3$)

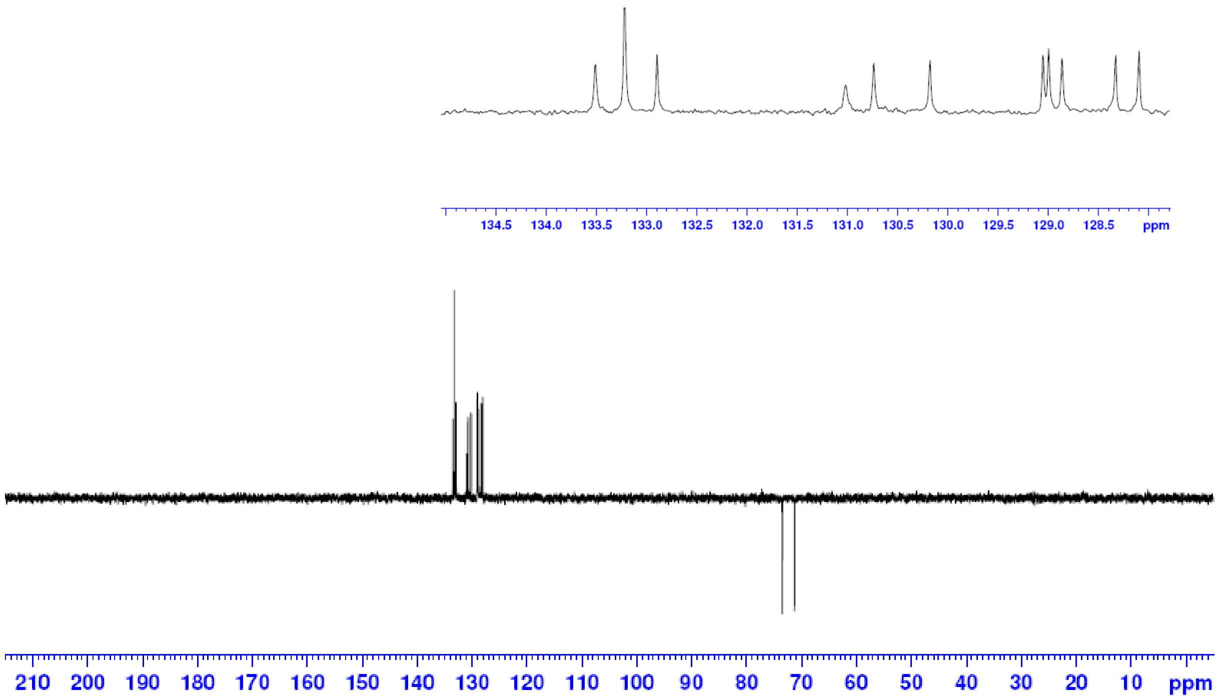

Figure S19. Distortionless Enhancement by Polarization Transfer (DEPT-135) spectrum of **6** ($CDCl_3$, 75 MHz)

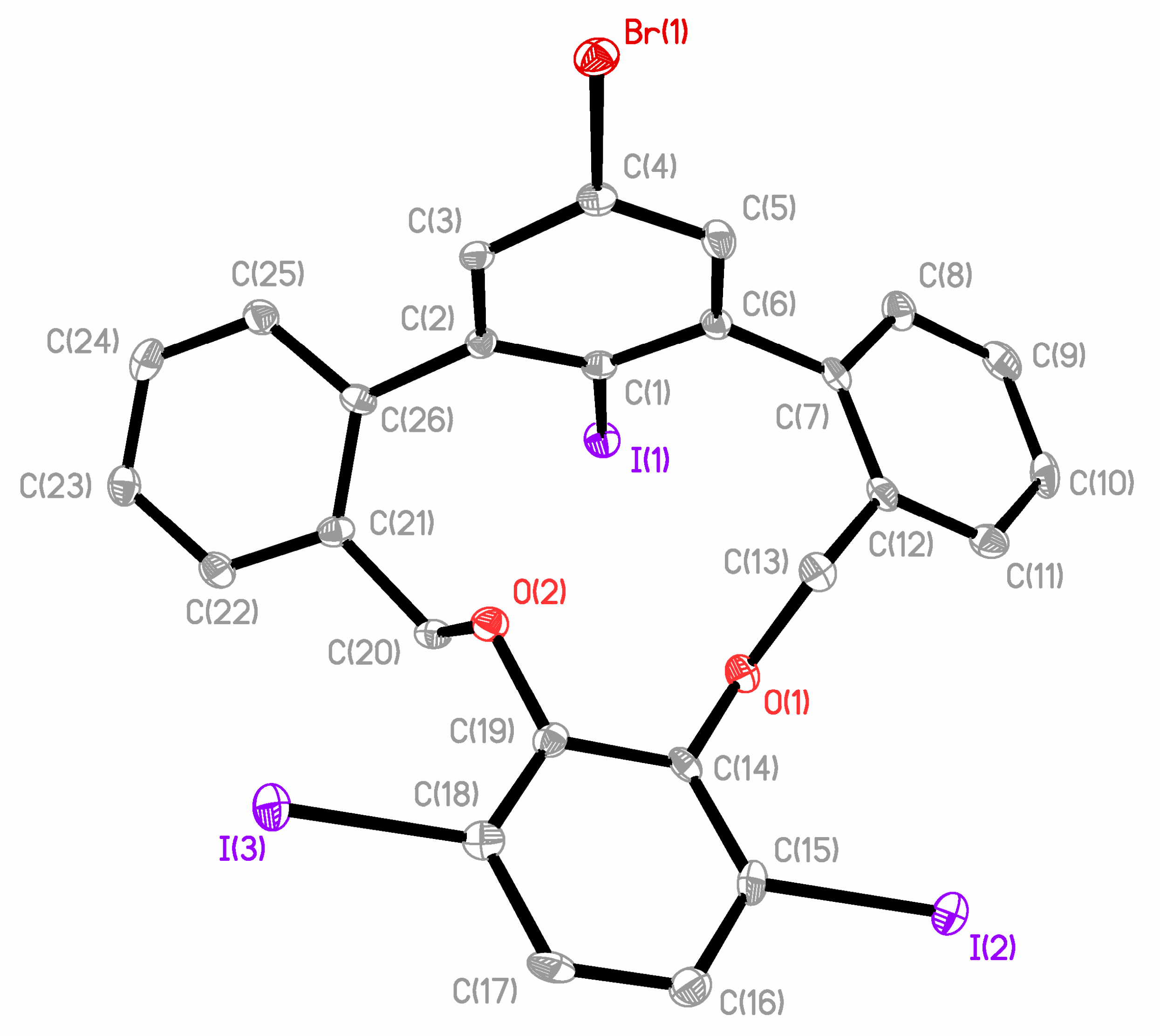

Figure S20. X-ray Crystal structure of **7** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table S1. Refinement details for **7**.

Empirical formula	$C_{26}H_{16}BrI_3O_2$
Formula weight (g/mol)	821.00
Temperature (K)	153 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{1/n}$
Unit cell dimensions	
a (Å)	7.6033(15)
b (Å)	19.178(4)
c (Å)	18.272(4)
α (deg)	90.00
β (deg)	100.12(3)
γ (deg)	90.00
Volume ($Å^3$)	2622.9(9)
Z	4
Calculated density (Mg/m^3)	2.079
Absorption coefficient (mm^{-1})	5.119
F(000)	1528
Crystal size (mm)	0.46 × 0.22 × 0.12
Crystal color and shape	colourless rod
Θ range for data collection (deg)	2.26 – 25.10
Limiting indices	$-9 < h < 8$ $0 < k < 22$ $0 < l < 21$
Reflections collected	4651
Independent reflections	4651
Completeness to *Θ*	25.10 (99.9 %)
Max. transmission	0.5787
Min. transmission	0.2017
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4651/0/289
Goodness of fit on F^2	1.120
Final R indices ($I > 2\sigma(I)$)	
R1	0.0372
wR2	0.0907
R indices (all data)	
R1	0.0413
wR2	0.0937

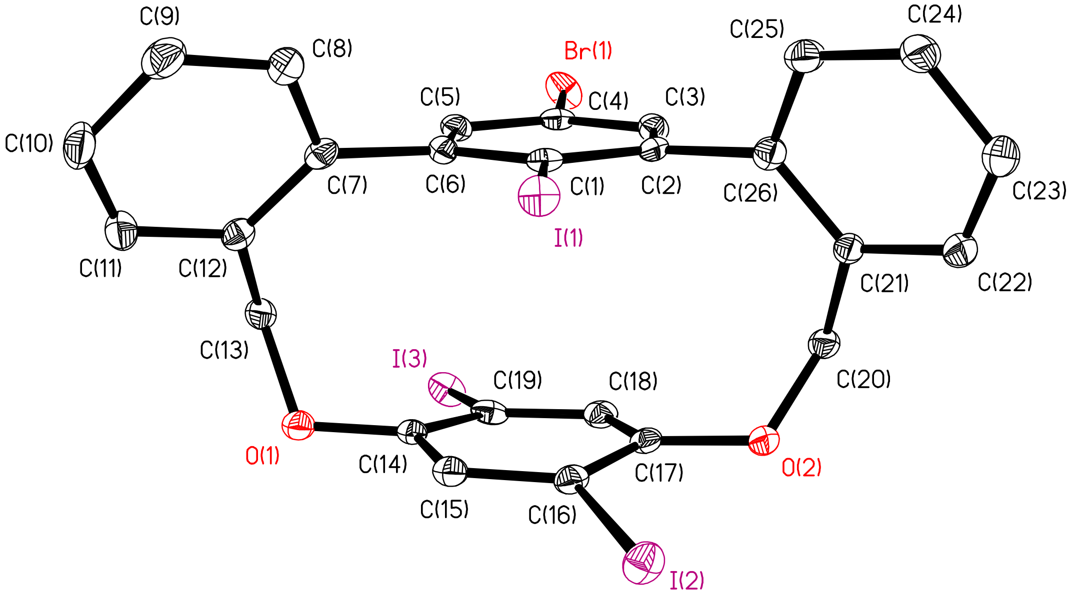

Figure S21. X-ray Crystal structure of **6** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table S2. Refinement details for **6**.

Empirical formula	$C_{26}H_{16}BrI_3O_2$
Formula weight (g/mol)	821.00
Temperature (K)	163 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{1/c}$
Unit cell dimensions	
a (Å)	10.633(2)
b (Å)	14.065(3)
c (Å)	32.946(7)
α (deg)	90.00
β (deg)	94.61(3)
γ (deg)	90.00
Volume (Å^3)	4911.3(17)
Z	8
Calculated density (Mg/m^3)	2.221
Absorption coefficient (mm^{-1})	5.467
F(000)	3056
Crystal size (mm)	0.41 × 0.12 × 0.07
Crystal color and shape	colourless plate
Θ range for data collection (deg)	2.36 – 26.36
Limiting indices	$-13 < h < 13$ $-11 < k < 17$ $-41 < l < 36$
Reflections collected	34118
Independent reflections	9932
Completeness to *Θ*	26.36 (99.1 %)
Max. transmission	0.6798
Min. transmission	0.2063
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9932/0/577
Goodness of fit on F^2	1.113
Final R indices ($I > 2\sigma(I)$)	
R1	0.0344
wR2	0.0729
R indices (all data)	
R1	0.0422
wR2	0.0771

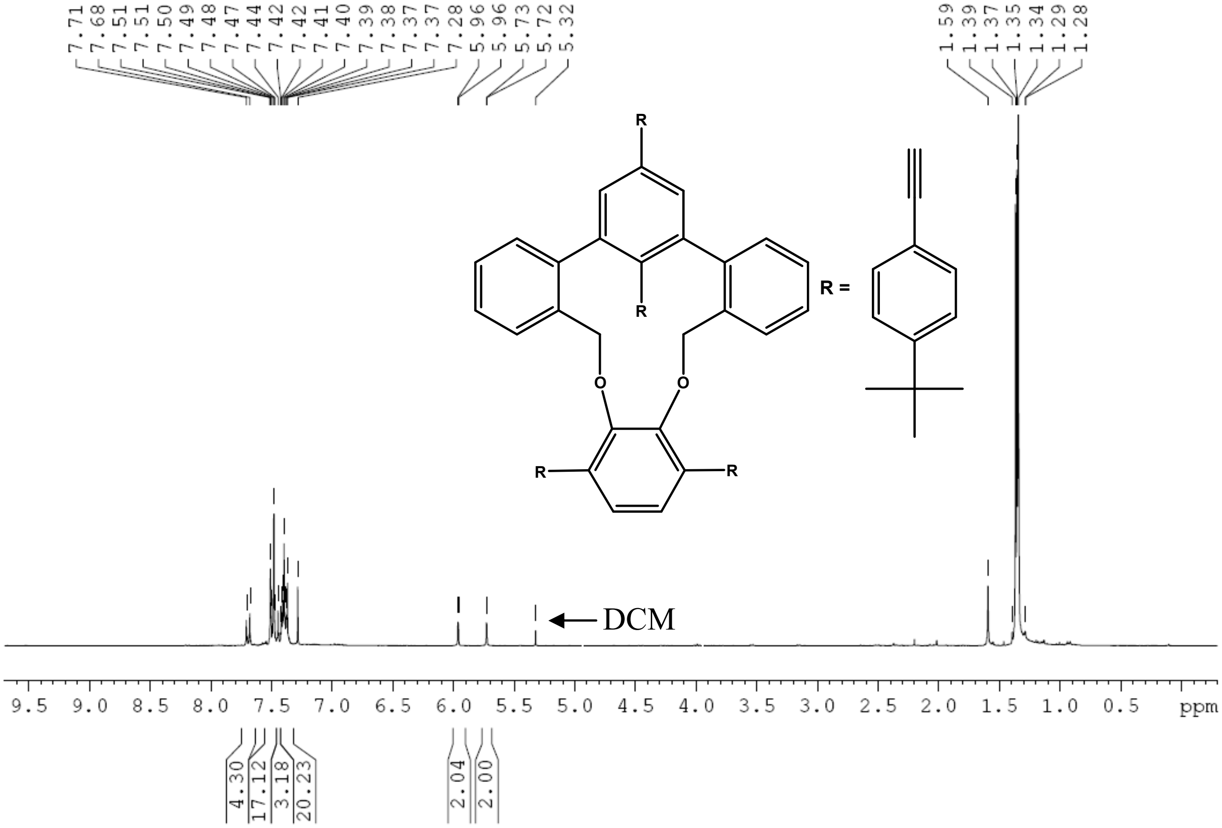

Figure S22. ^{1}H NMR spectrum of **OC2** ($CDCl_3$, 300 MHz)

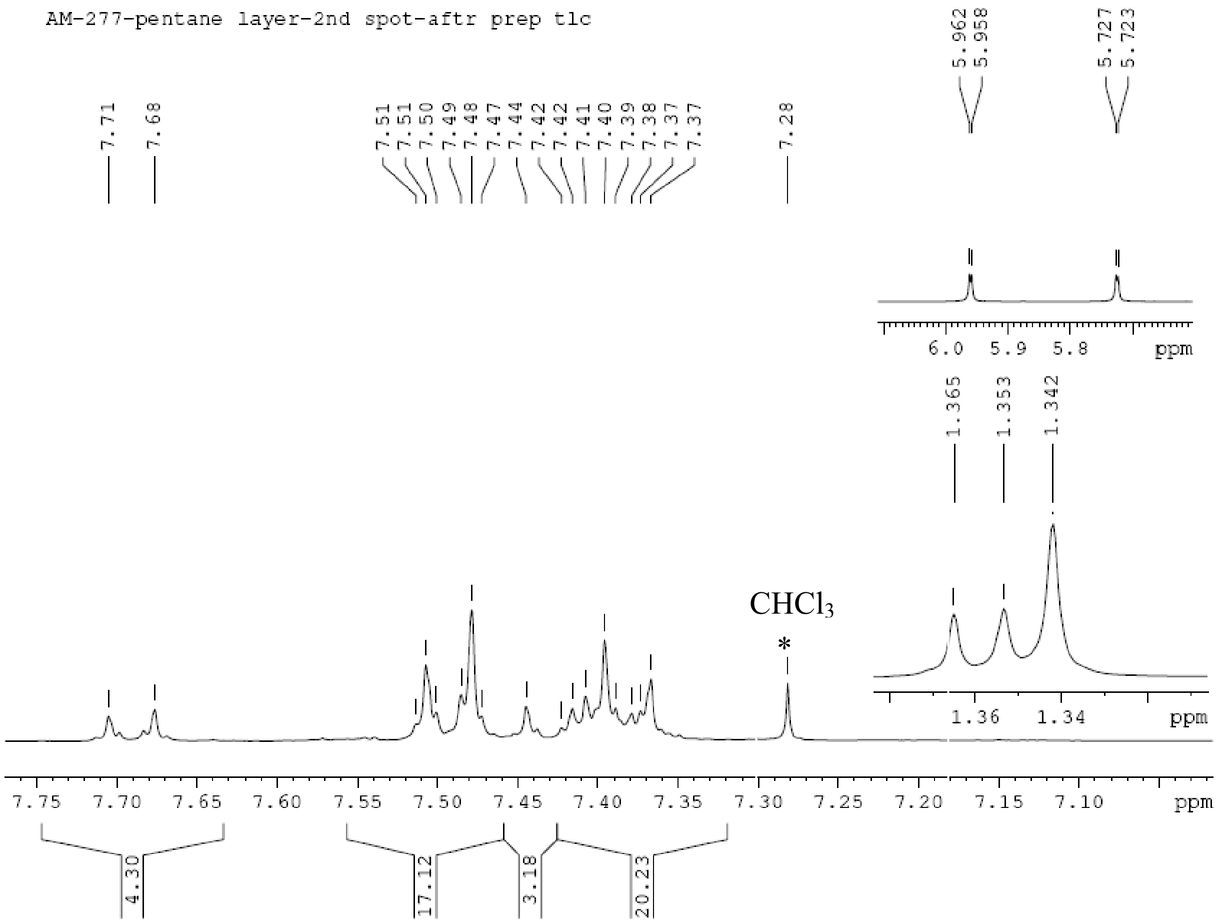

Figure S23. Aromatic and aliphatic region of the ^{1}H NMR spectrum of **OC2** ($CDCl_3$, 300 MHz)

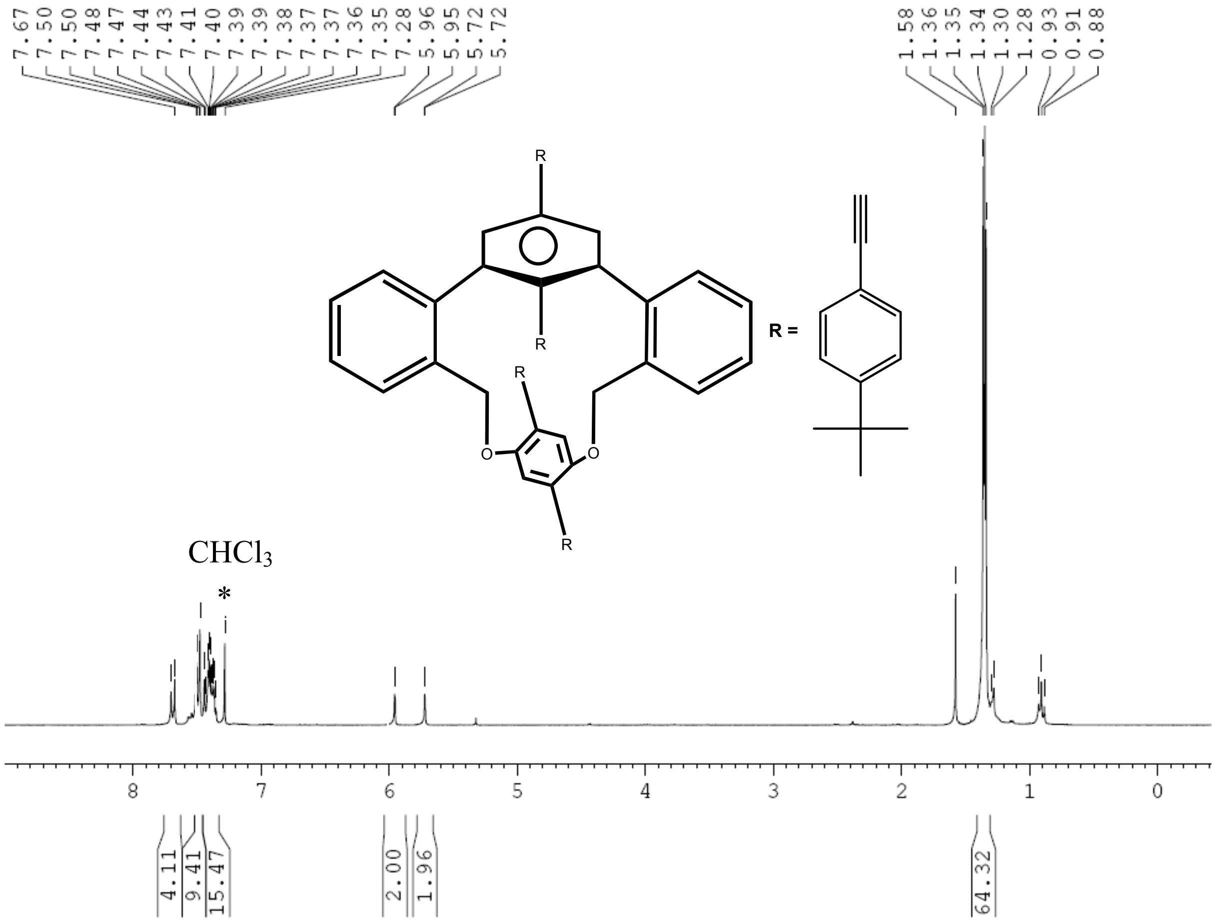

Figure S24. ^{1}H NMR spectrum of **OC1** (CDCl$_3$, 300 MHz)

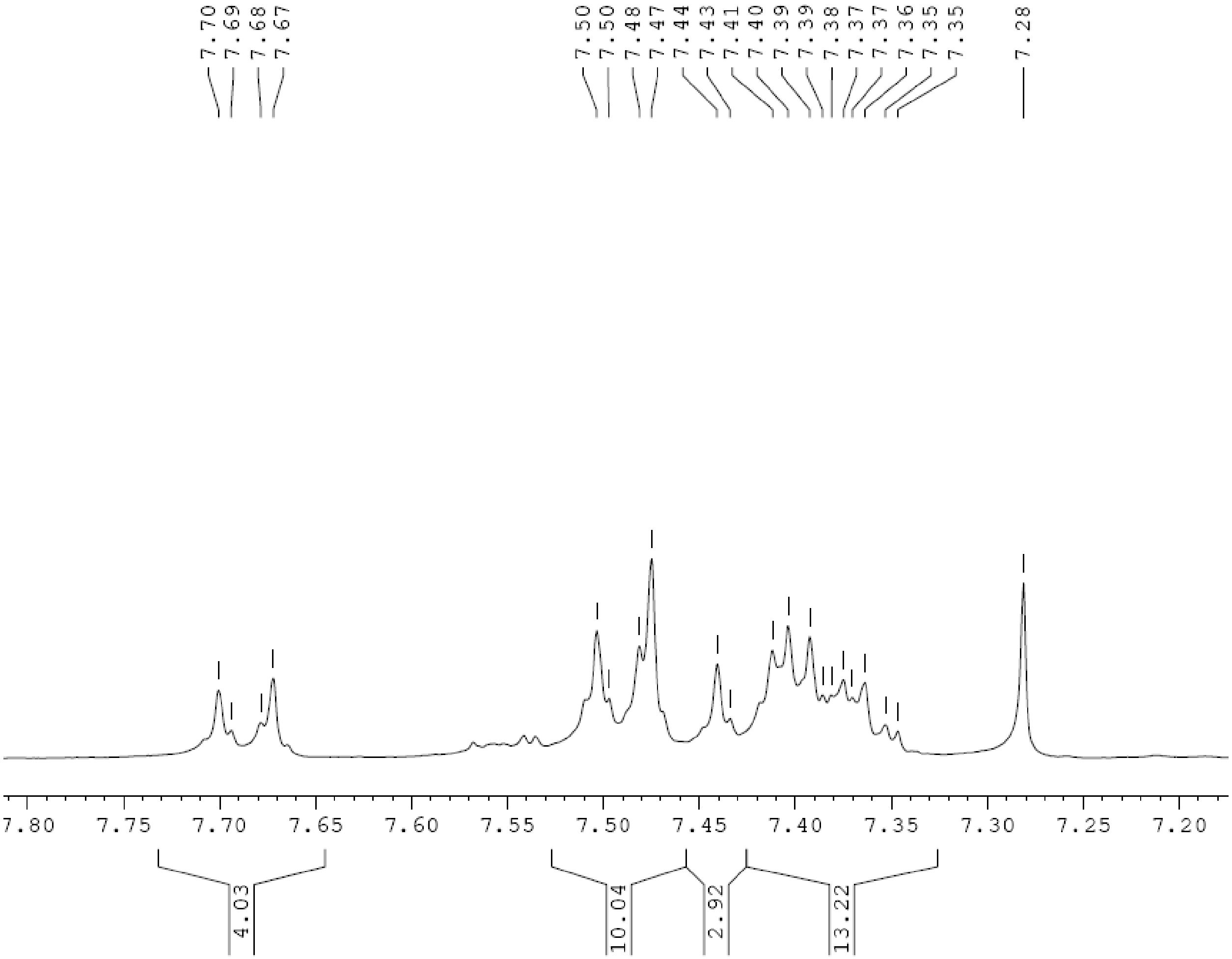

Figure S25. Aromatic region of ^{1}H NMR spectrum of **OC1** ($CDCl_3$, 300 MHz)

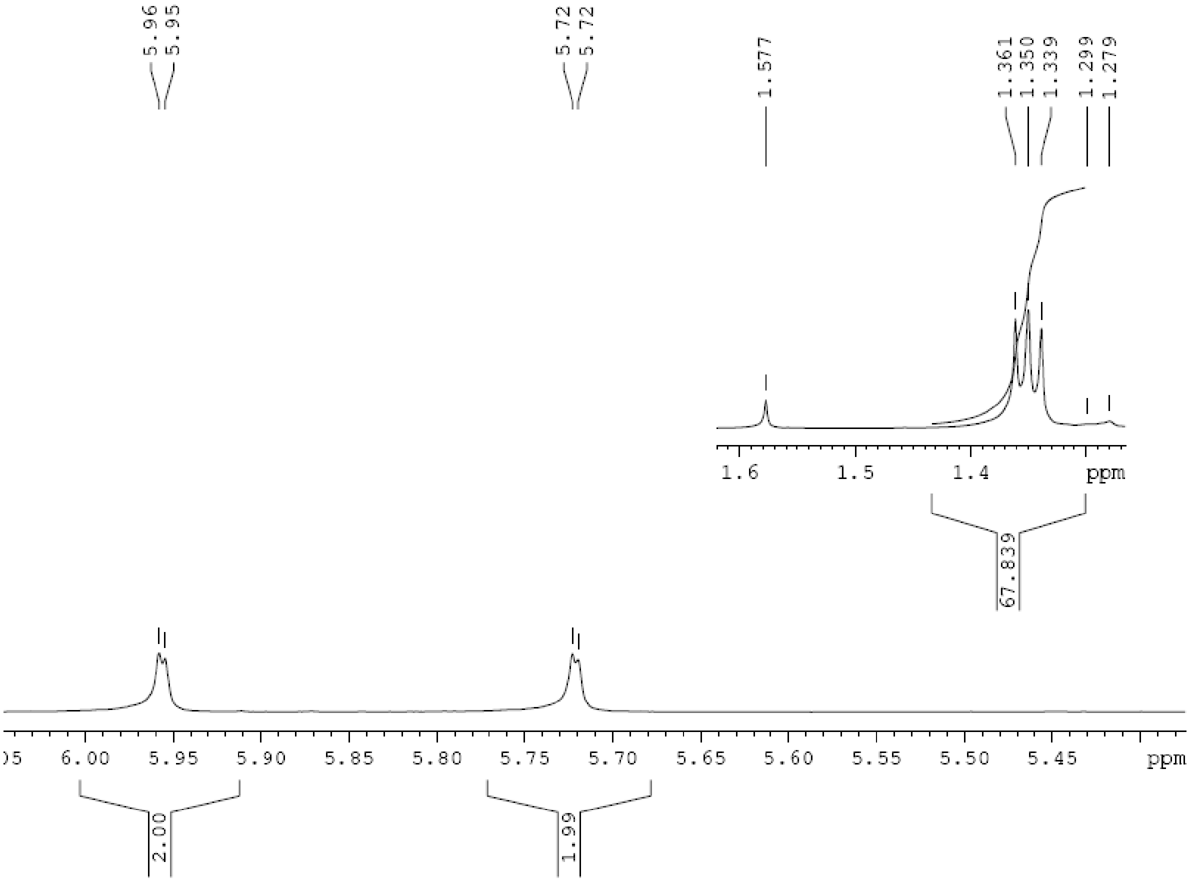

Figure S26. Aliphatic region of ^{1}H NMR spectrum of **OC1** ($CDCl_3$, 300 MHz)

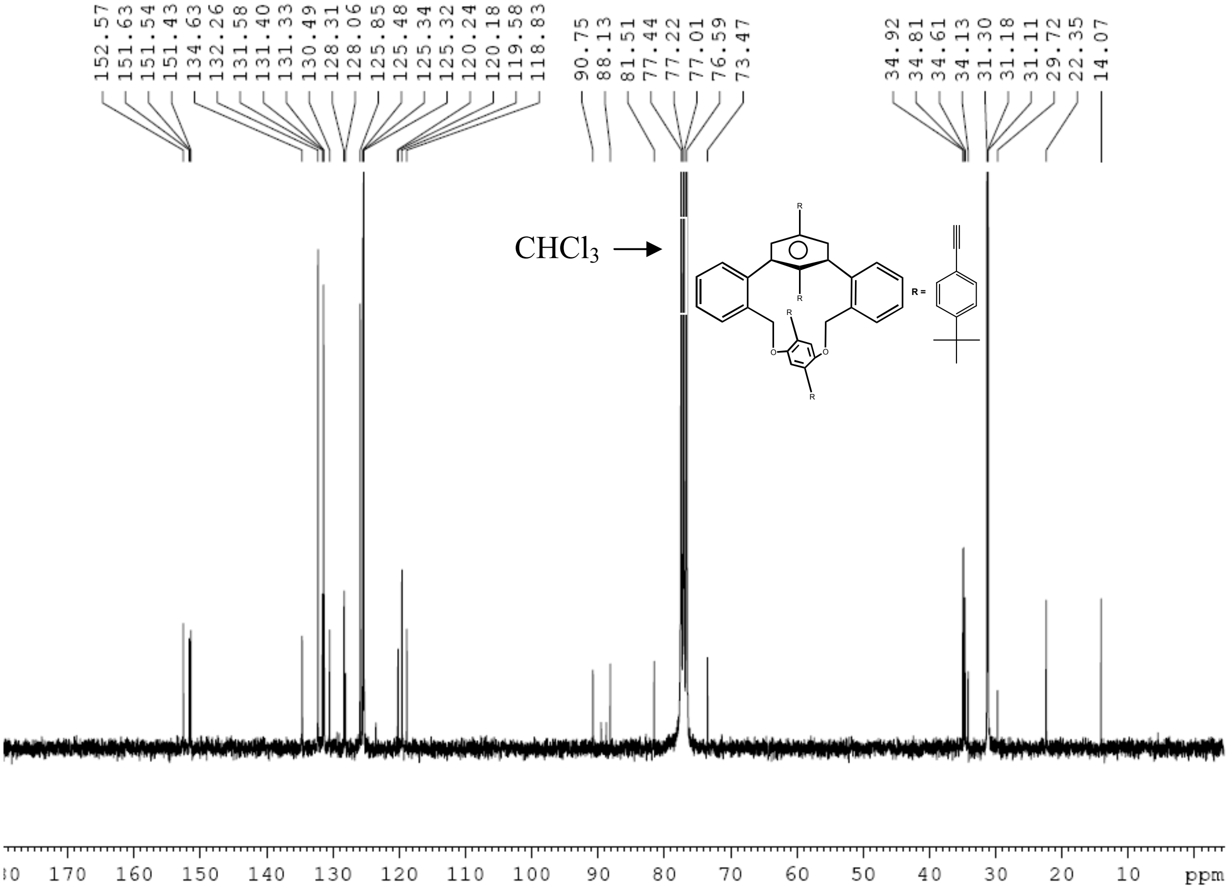

Figure S27. Carbon-13 NMR spectrum of **OC1** (CDCl$_3$, 75 MHz)

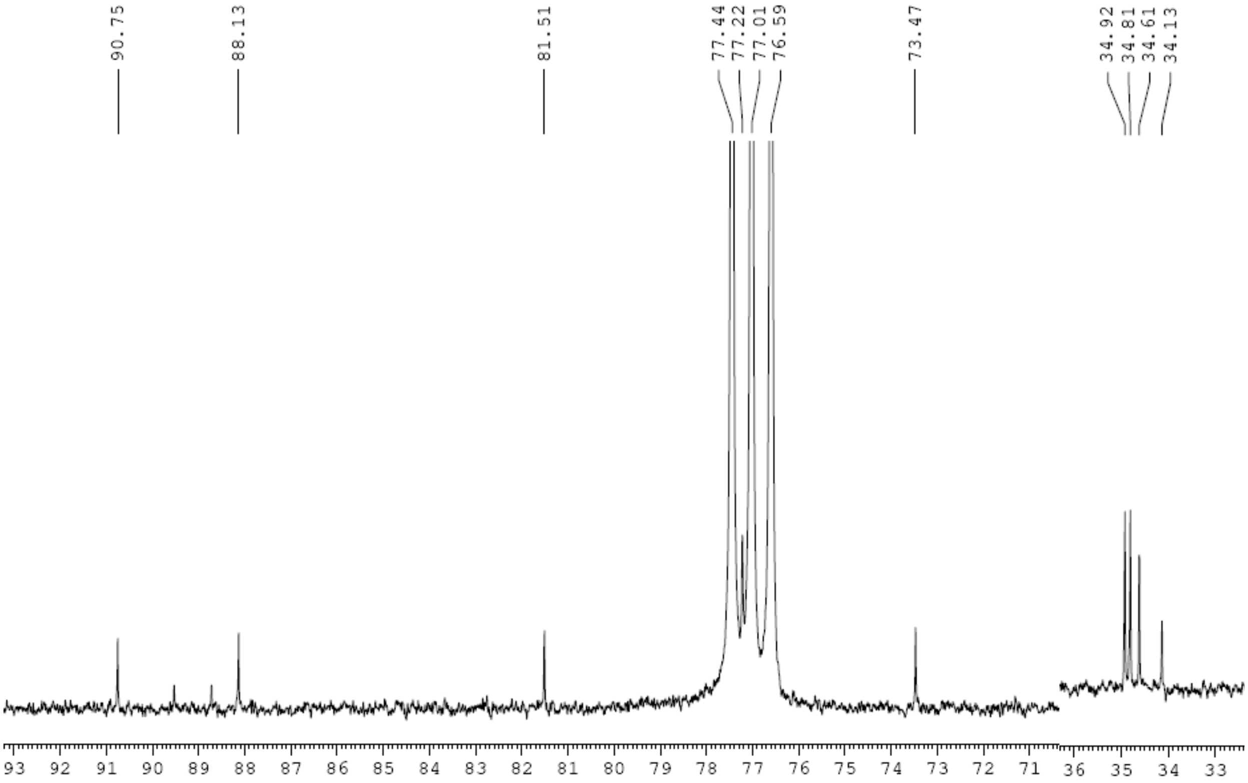

Figure S28. Aliphatic and Aromatic region of Carbon-13 NMR spectrum of **OC1** ($CDCl_3$, 75 MHz)

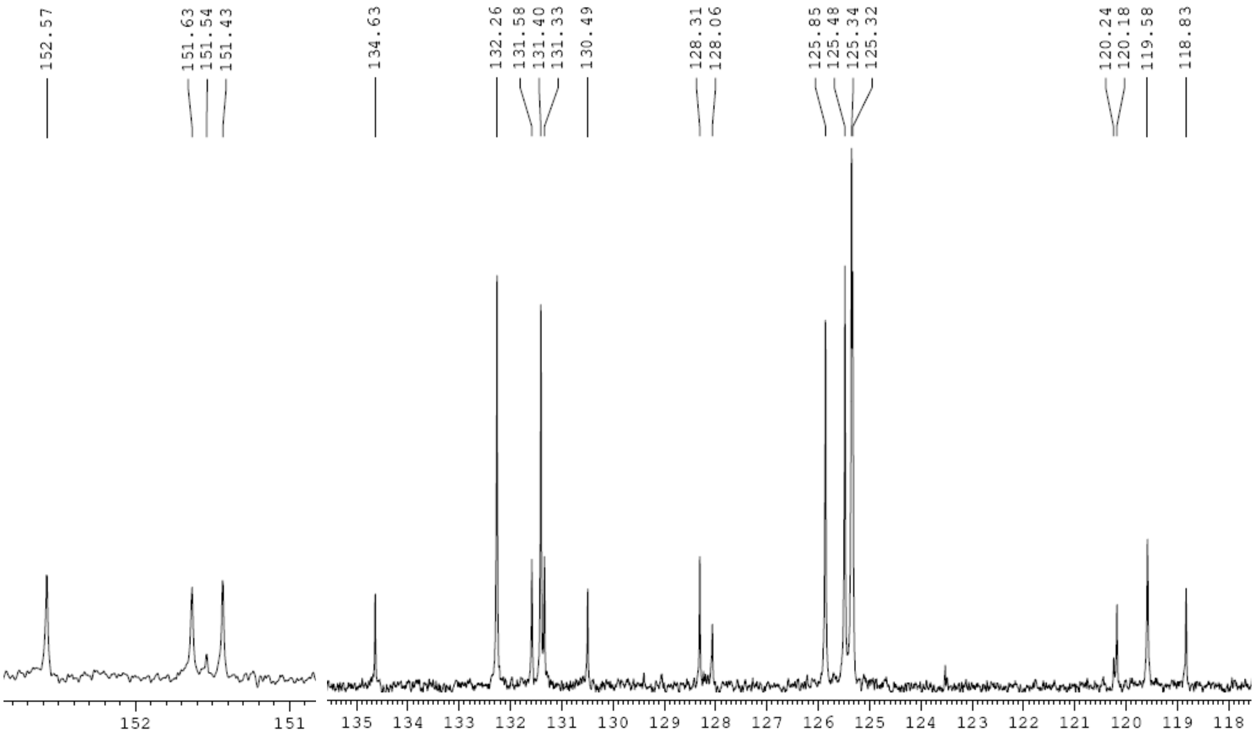

Figure S29. Aromatic region of Carbon-13 NMR spectrum of **OC1** ($CDCl_3$, 75 MHz)

Supporting Information Figures II.: Data for compounds 2-5.

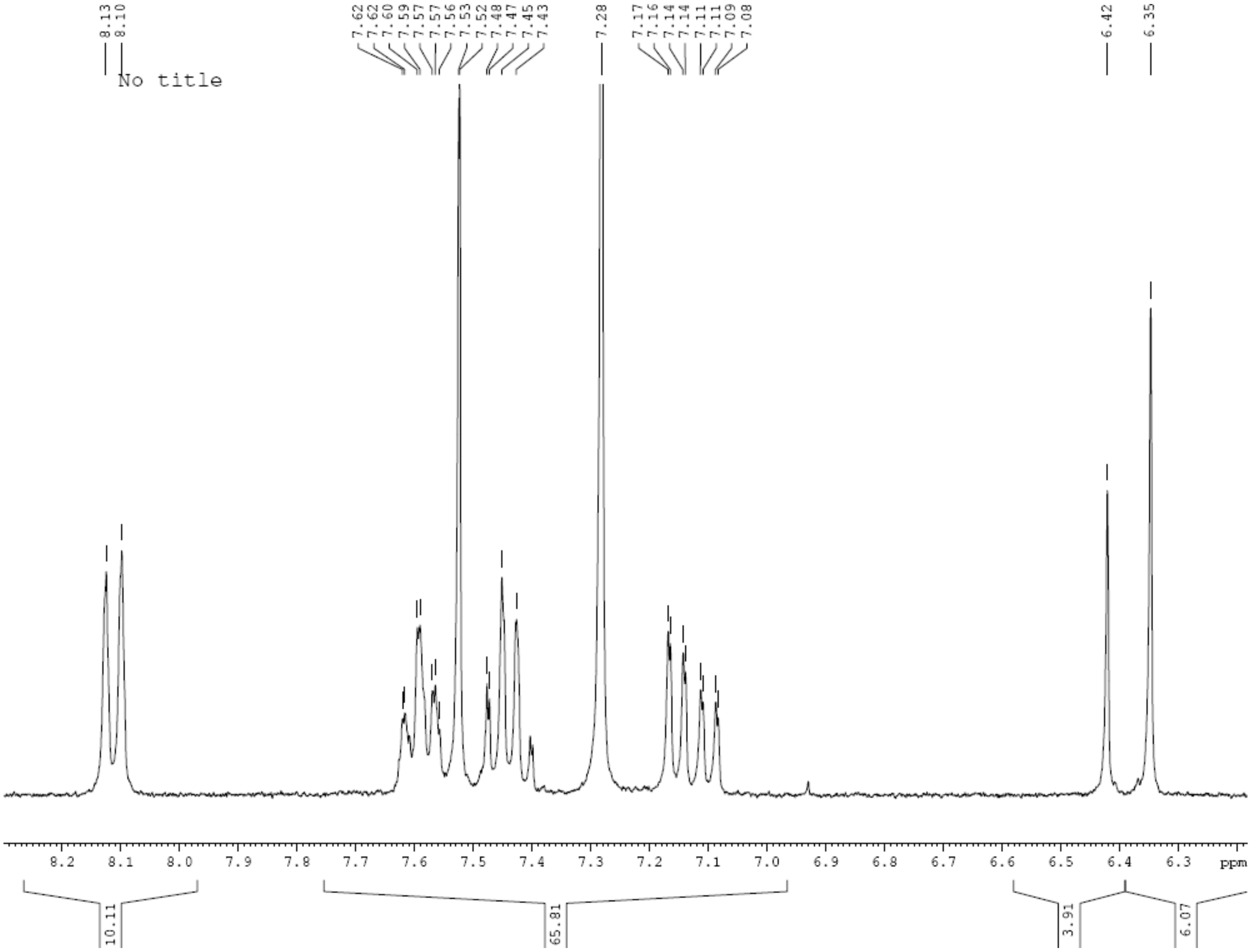

Figure S30. Proton NMR spectrum of **2** ($CDCl_3$, 300 MHz; no peaks other than a water peak from the NMR solvent appear outside this range).

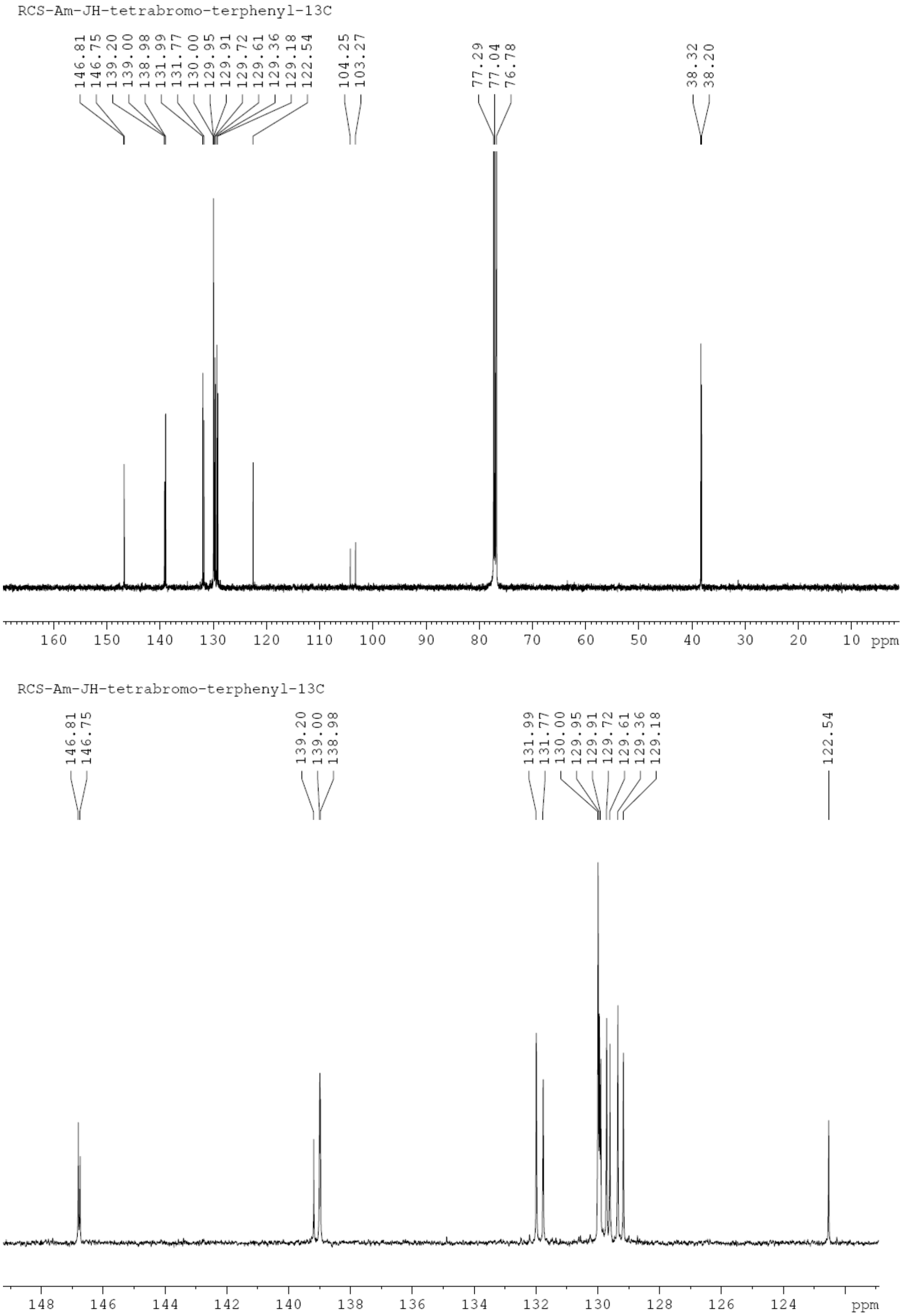

Figure S31. Carbon-13 NMR spectrum of **2** ($CDCl_3$, 125 MHz) from 0-170 ppm (upper) and an inset from 121-149 ppm (lower)

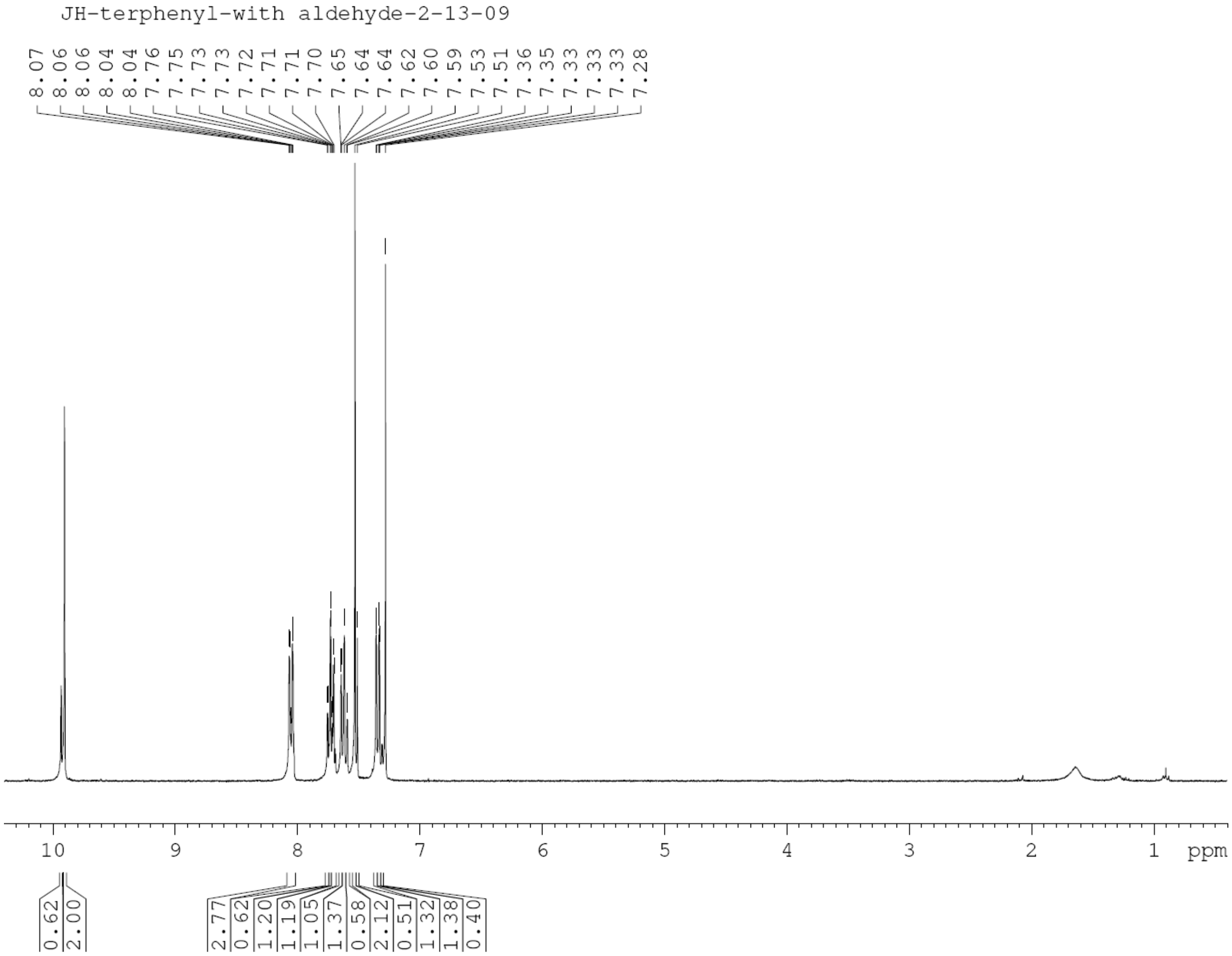

Figure S32. Proton NMR spectrum of **3** ($CDCl_3$, 300 MHz)

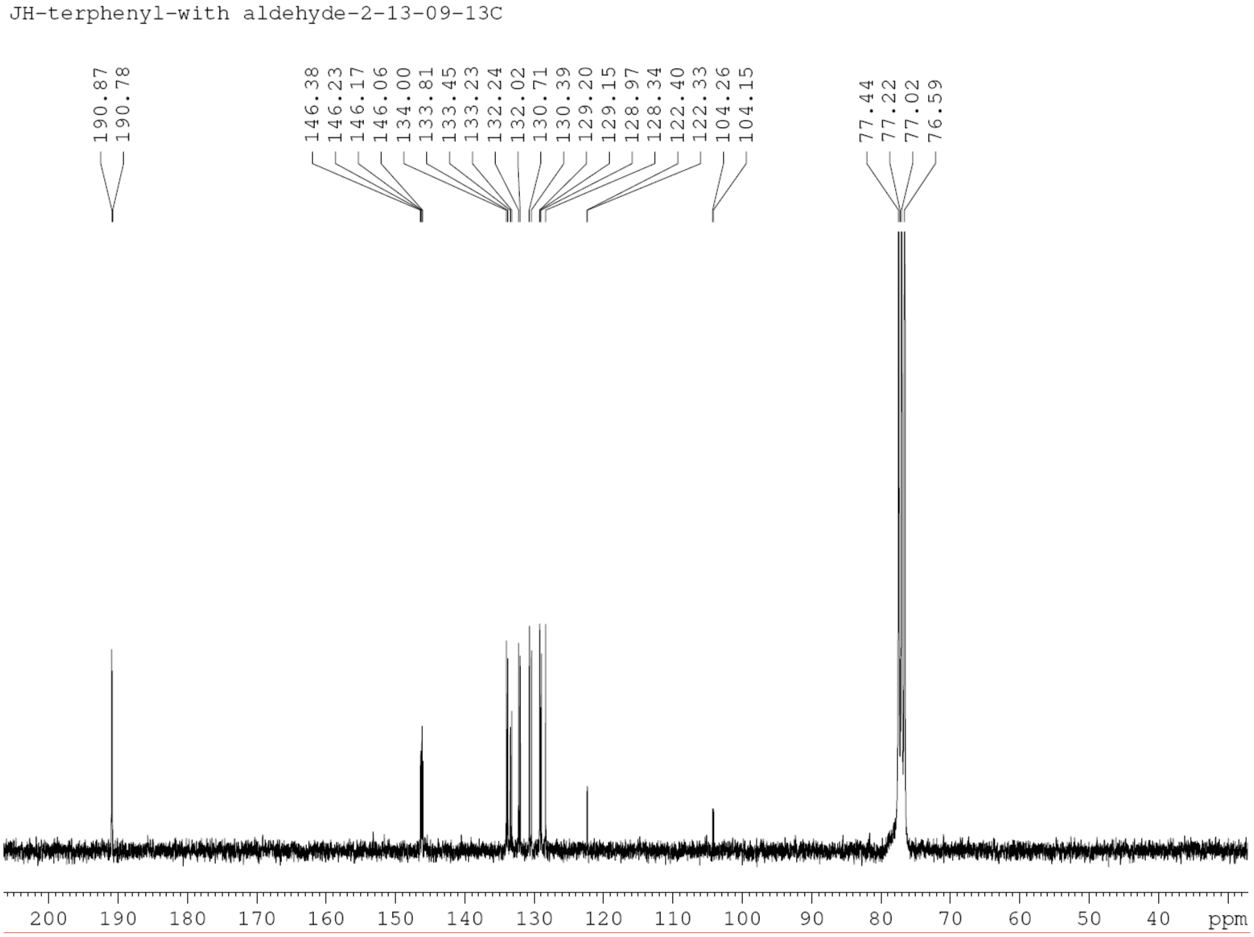

Figure S33. Carbon-13 NMR spectrum of **3** ($CDCl_3$, 125 MHz)

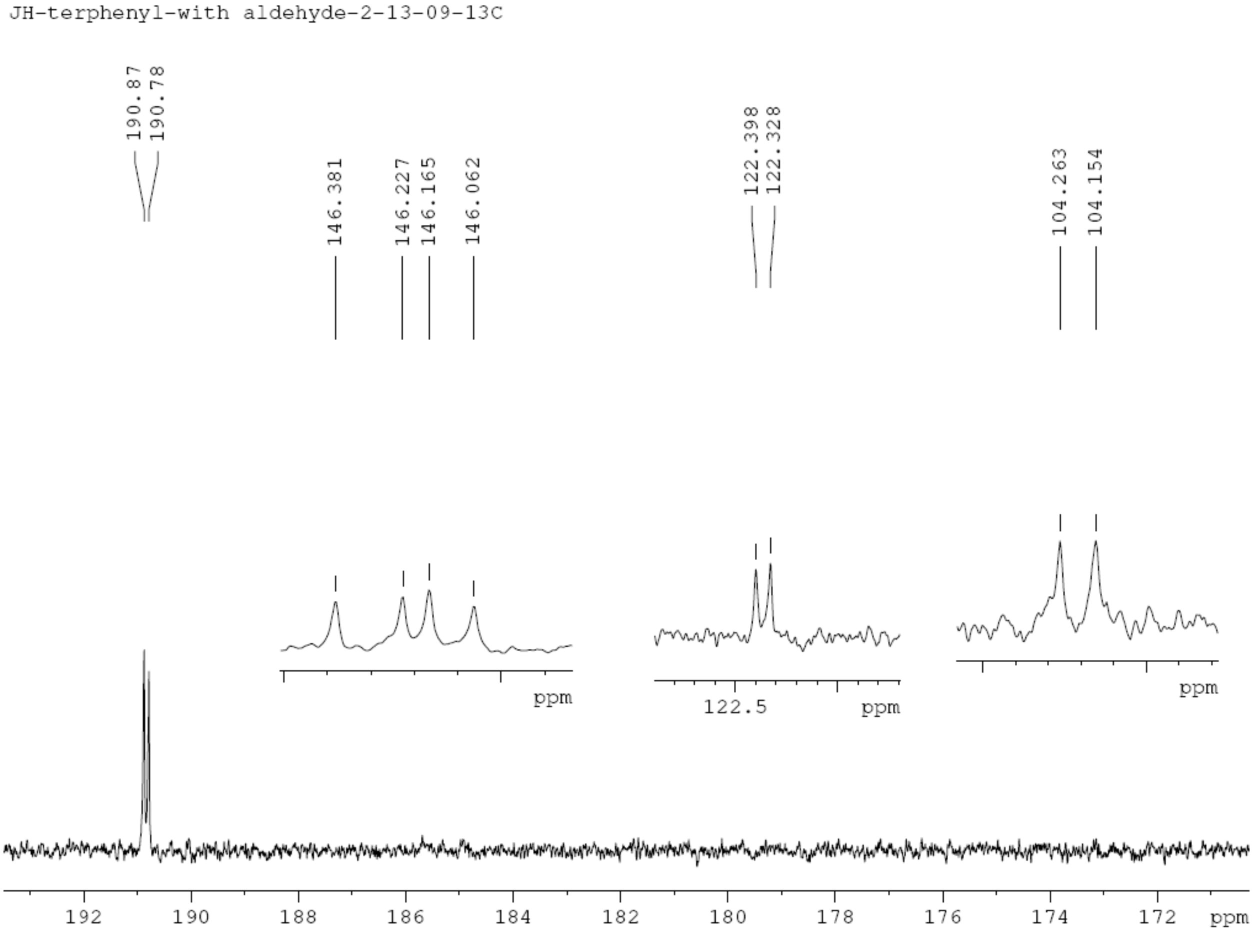

Figure S34. Expansion (128-135 ppm) of Carbon-13 NMR spectrum of **3** ($CDCl_3$, 125 MHz)

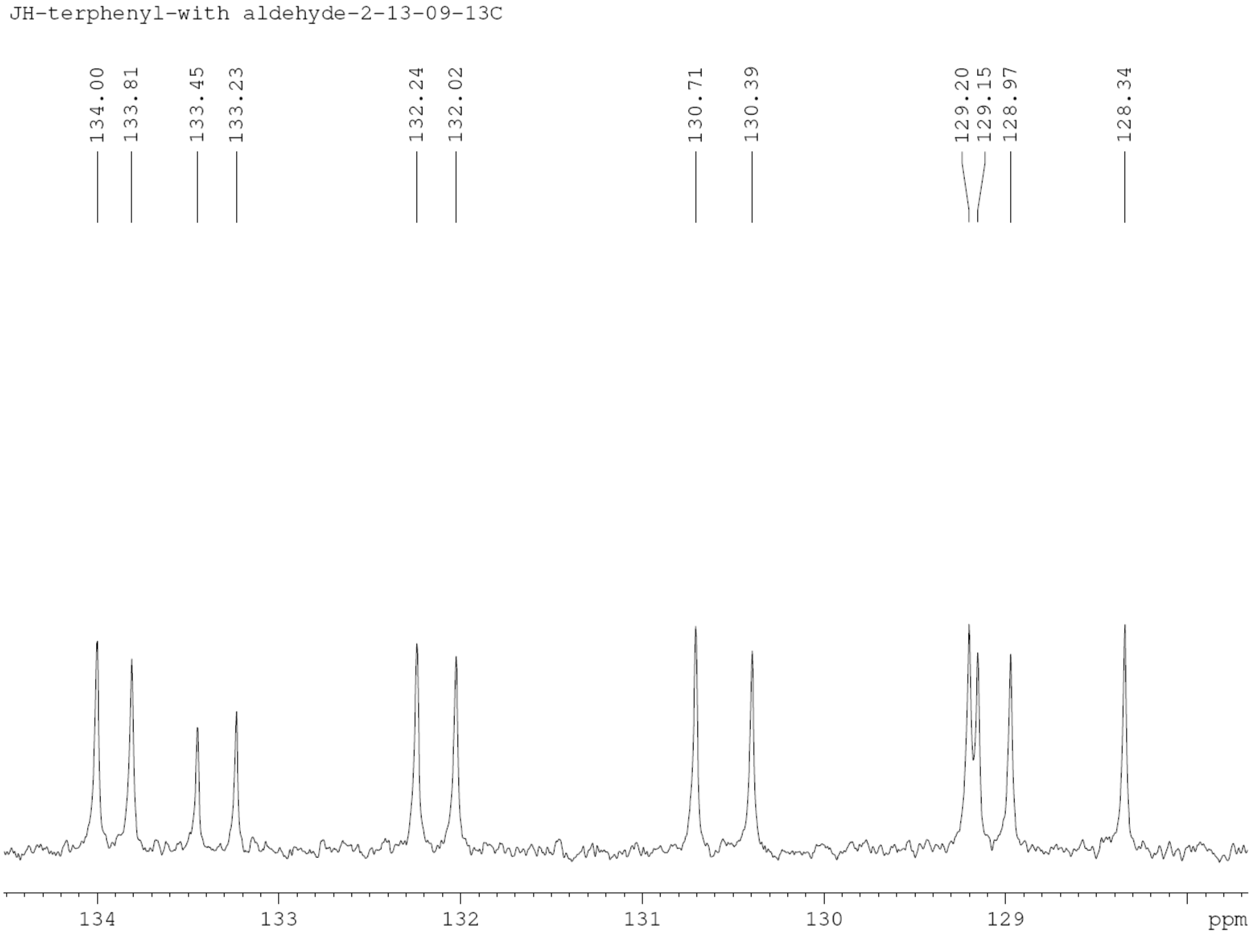

Figure S35. Expansion (170-194 ppm) of Carbon-13 NMR spectrum of **3** ($CDCl_3$, 125 MHz)

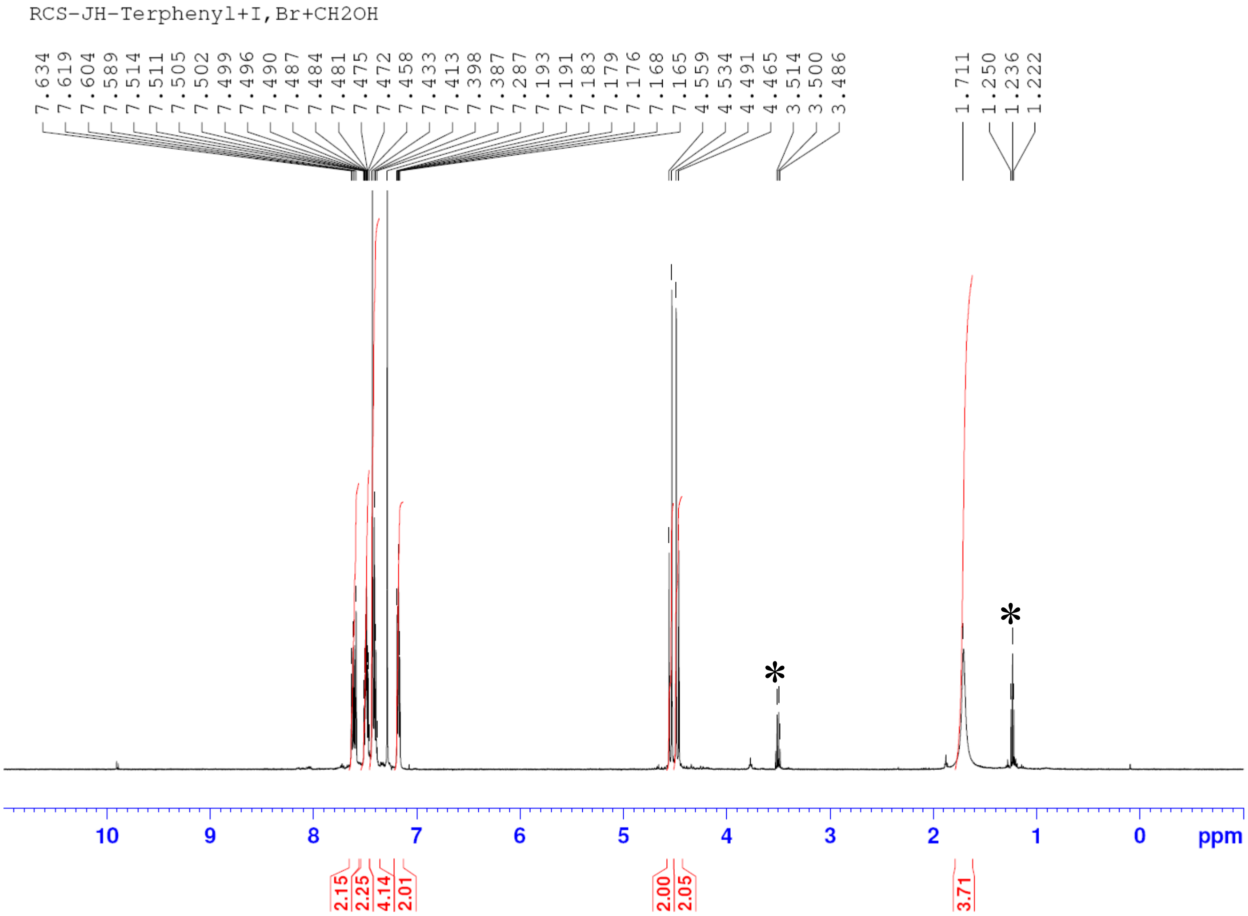

Figure S36. Proton NMR spectrum of **4** ($CDCl_3$, 300 MHz). Note the small amount (ca. 5%) of aldehyde **3** remaining in the sample, evident from the aldehydic peaks at ca. 9.9 ppm. This sample was used without further purification in the next step (this synthetic avenue was abandoned in favor of the more efficient route shown in Scheme 1 of the manuscript). Peaks marked with an asterisk are attributable to diethyl ether.

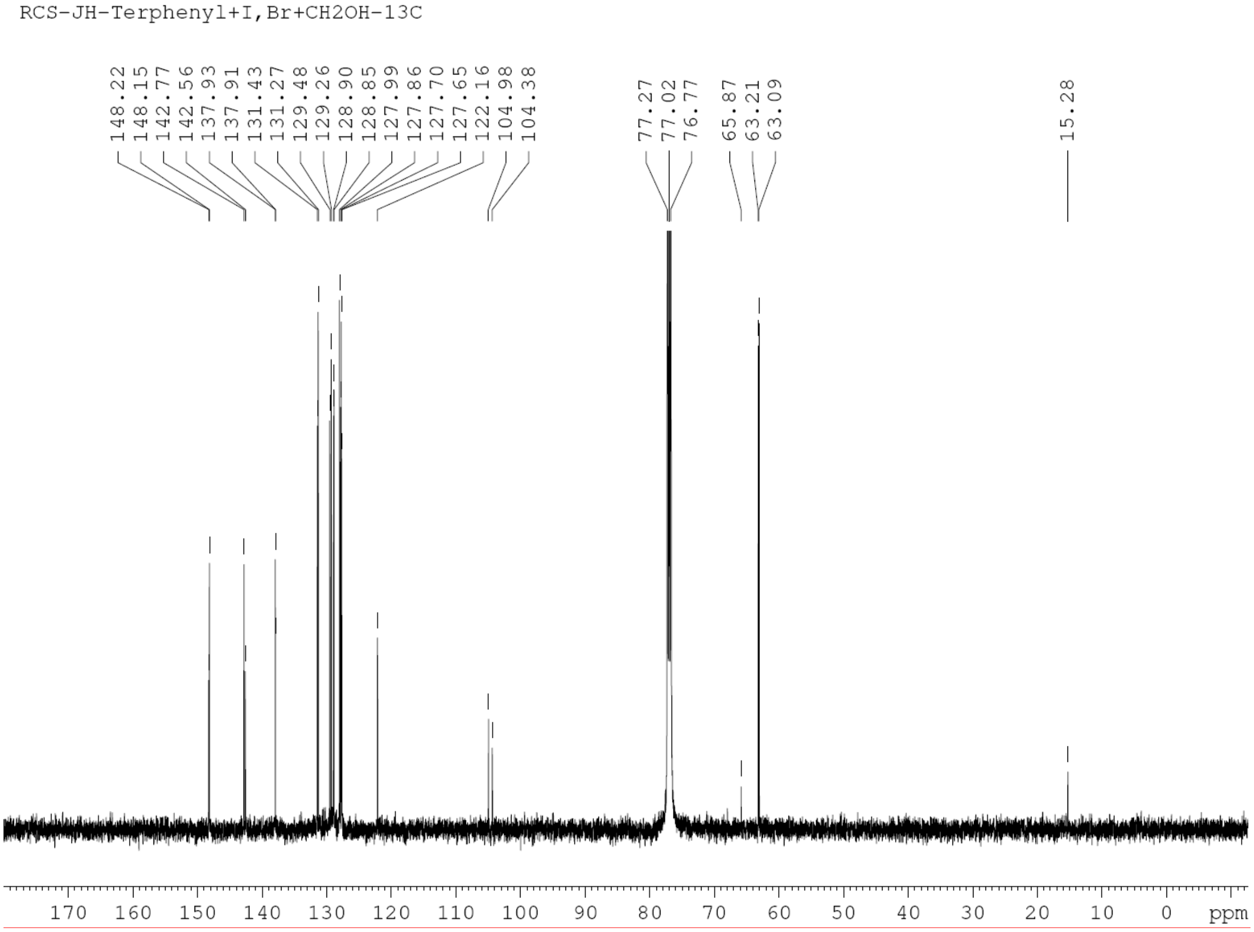

Figure S37. Carbon-13 NMR spectrum of **4** ($CDCl_3$, 125 MHz)

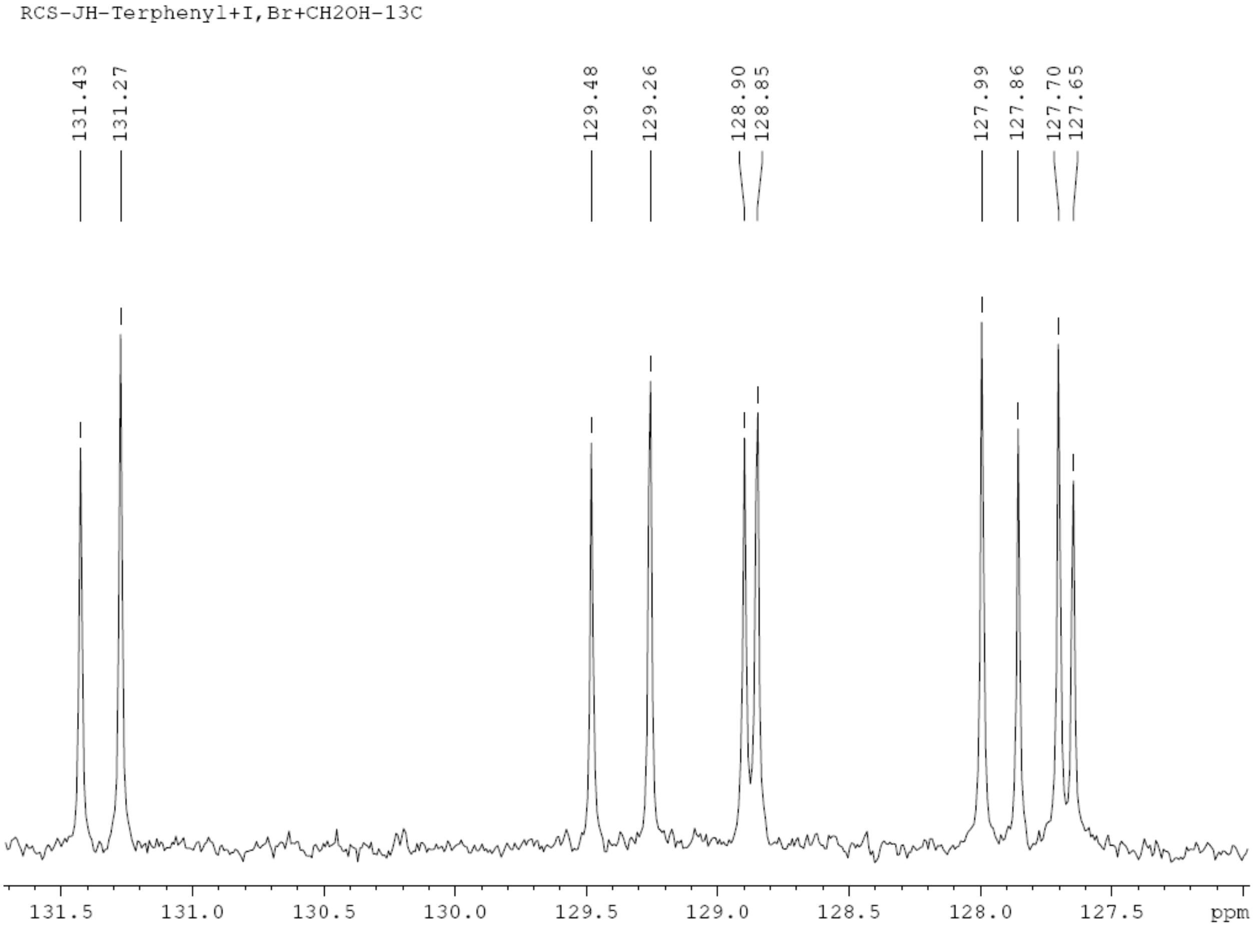

Figure S38. Expansion (127-132 ppm) of Carbon-13 NMR spectrum of **4** ($CDCl_3$, 125 MHz)

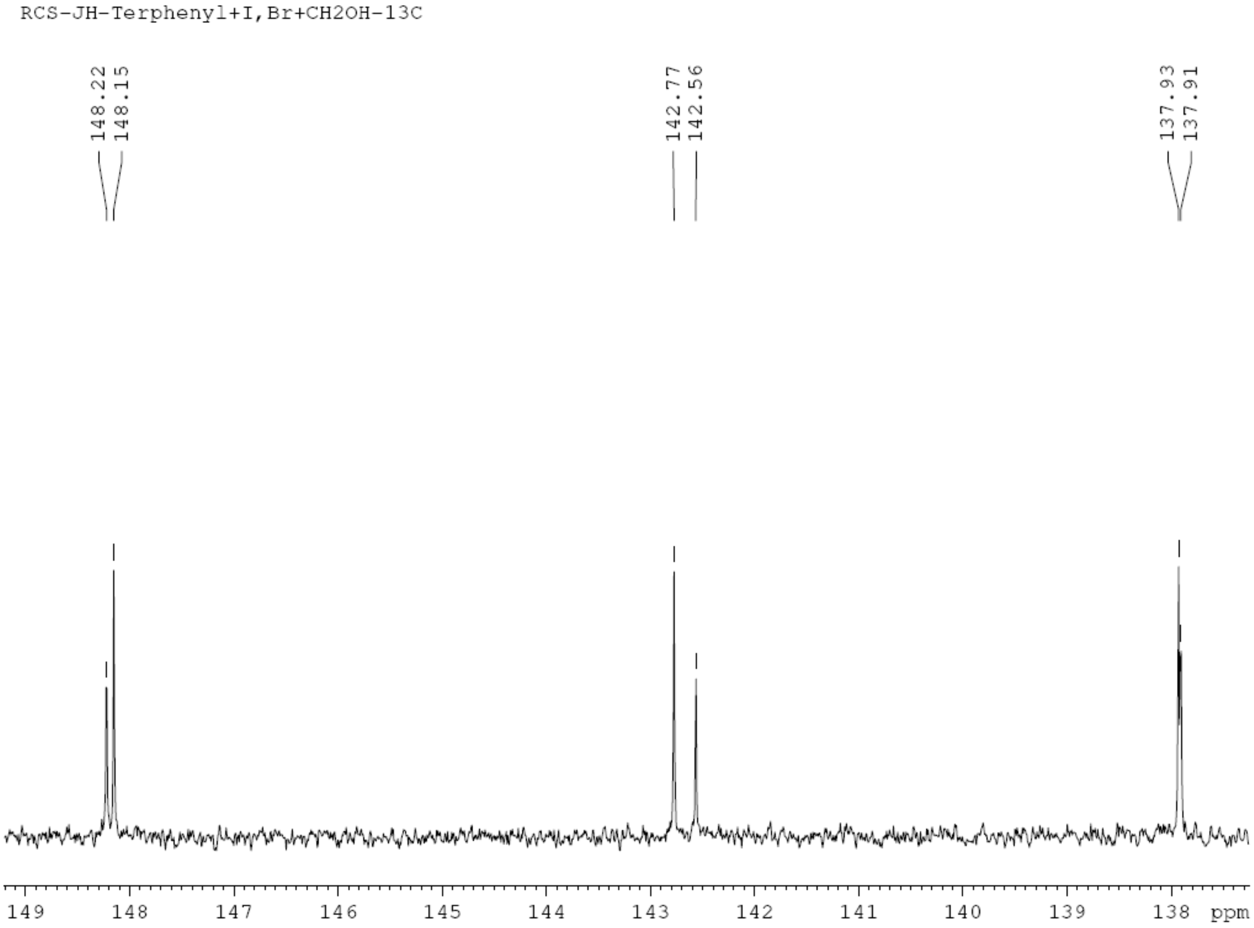

Figure S39. Expansion (137-149 ppm) of Carbon-13 NMR spectrum of **4** ($CDCl_3$, 125 MHz)

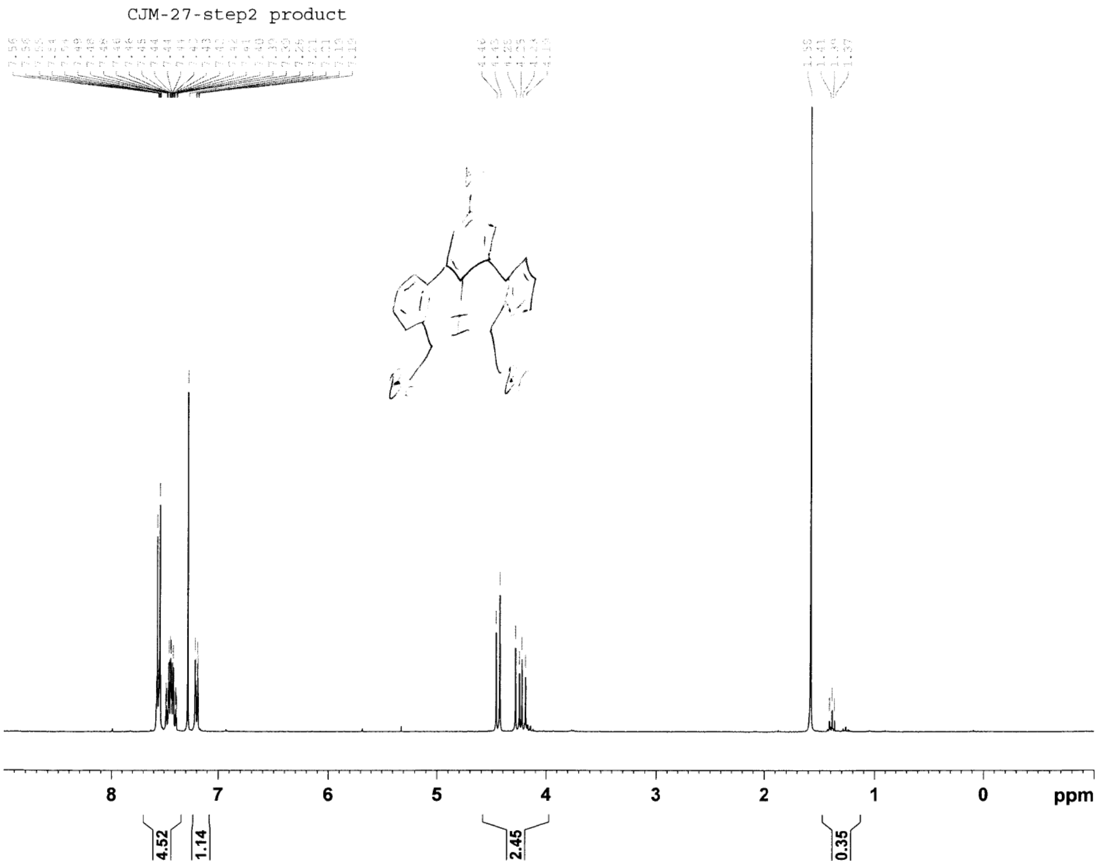

Figure S40. Proton NMR spectrum of **5** ($CDCl_3$, 300 MHz)

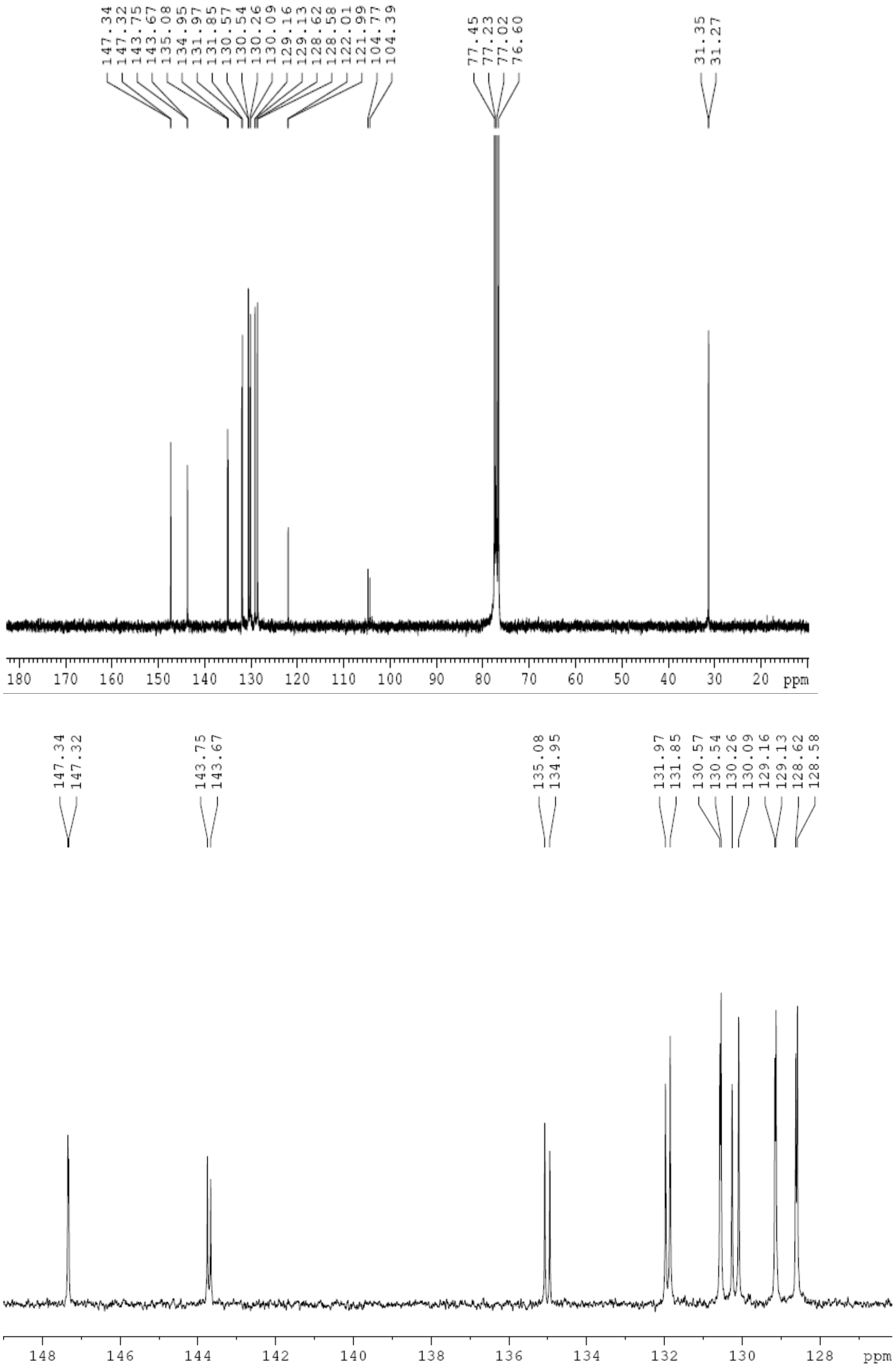

Figure S41. Carbon-13 NMR spectrum of **5** ($CDCl_3$, 125 MHz) from 10-185 ppm (upper) and an inset from 126-149 ppm (lower)

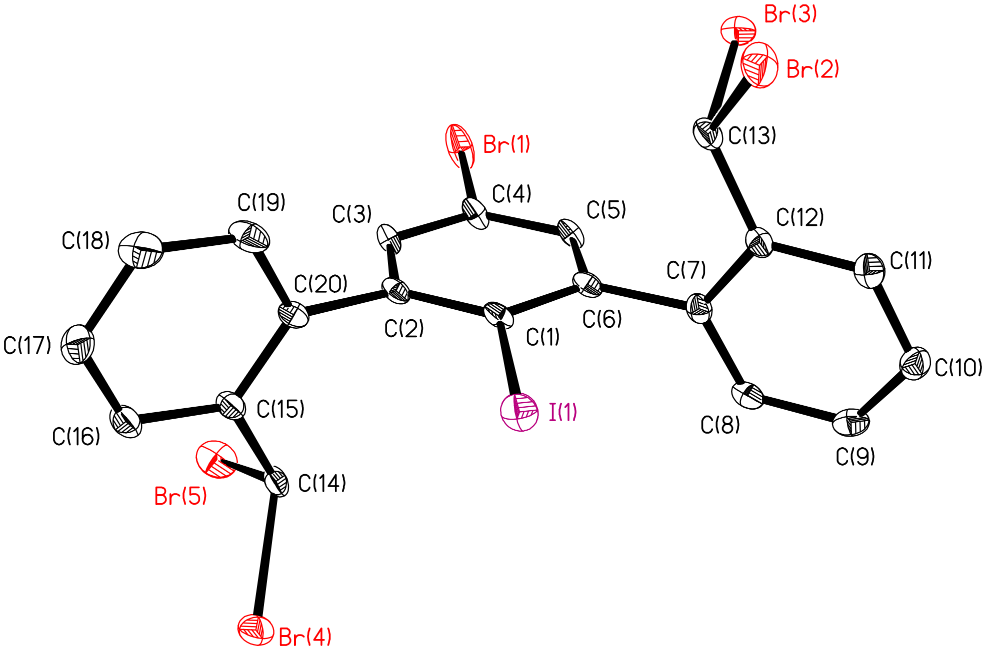

Figure S42 X-ray crystal structure of **2**

Table S3. Refinement details for **2**

Empirical formula	$C_{20}H_{12}Br_5I$
Formula weight (g/mol)	778.75
Temperature (K)	153 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	10.327(2)
b (Å)	10.367(2)
c (Å)	11.470(2)
α (deg)	68.30(3)
β (deg)	75.05(3)
γ (deg)	76.79(3)
Volume ($Å^3$)	1090.2(4)
Z	2
Calculated density (Mg/m^3)	2.372
Absorption coefficient (mm^{-1})	10.634
F(000)	720
Crystal size (mm)	0.36 × 0.26 × 0.14
Crystal color and shape	colourless chip
Θ range for data collection (deg)	2.65 - 25.10
Limiting indices	$-12 < h < 12$ $-11 < k < 12$ $-11 < l < 13$
Reflections collected	8438
Independent reflections	3862
Completeness to *Θ*	25.10 (99.0 %)
Max. transmission	0.9197
Min. transmission	0.8108
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3862/0/235
Goodness of fit on F^2	1.080
Final R indices ($I > 2\sigma(I)$)	
R1	0.0316
wR2	0.0759
R indices (all data)	
R1	0.0353
wR2	0.0790

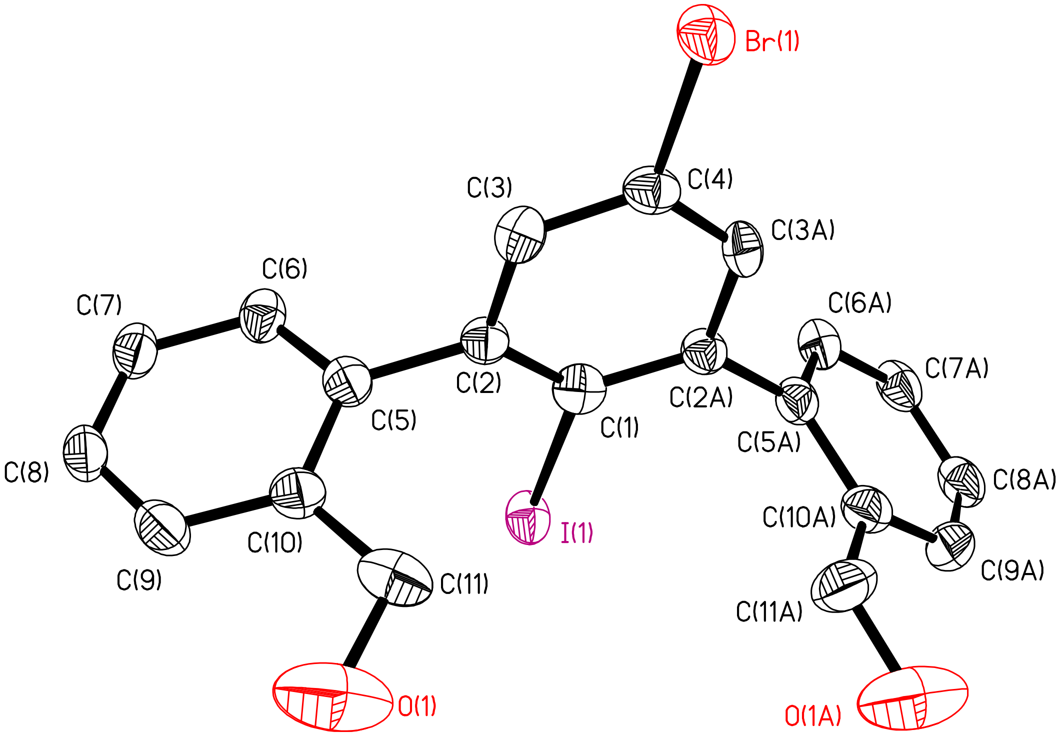

Figure S43 X-ray crystal structure of **4**

Table S4. Refinement details for **4**

Empirical formula	$C_{20}H_{16}BrIO_2$
Formula weight (g/mol)	495.14
Temperature (K)	153 (2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	I4/m
Unit cell dimensions	
a (Å)	21.861(3)
b (Å)	21.861(3)
c (Å)	16.153(3)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
Volume (Å^3)	7720(2)
Z	16
Calculated density (Mg/m^3)	1.707
Absorption coefficient (mm^{-1})	3.738
F(000)	3840
Crystal size (mm)	0.48 × 0.11 × 0.05
Crystal color and shape	colorless chip
Θ range for data collection (deg)	3.59 - 25.10
Limiting indices	$-22 < h < 25$
	$-26 < k < 23$
	$-19 < l < 12$
Reflections collected	13542
Independent reflections	3562
Completeness to Θ	25.10 (99.4 %)
Max. transmission	0.8351
Min. transmission	0.2670
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3562/0/245
Goodness of fit on F^2	1.053
Final R indices ($I > 2\sigma(I)$)	
R1	0.0674
wR2	0.1660
R indices (all data)	
R1	0.0820
wR2	0.1795

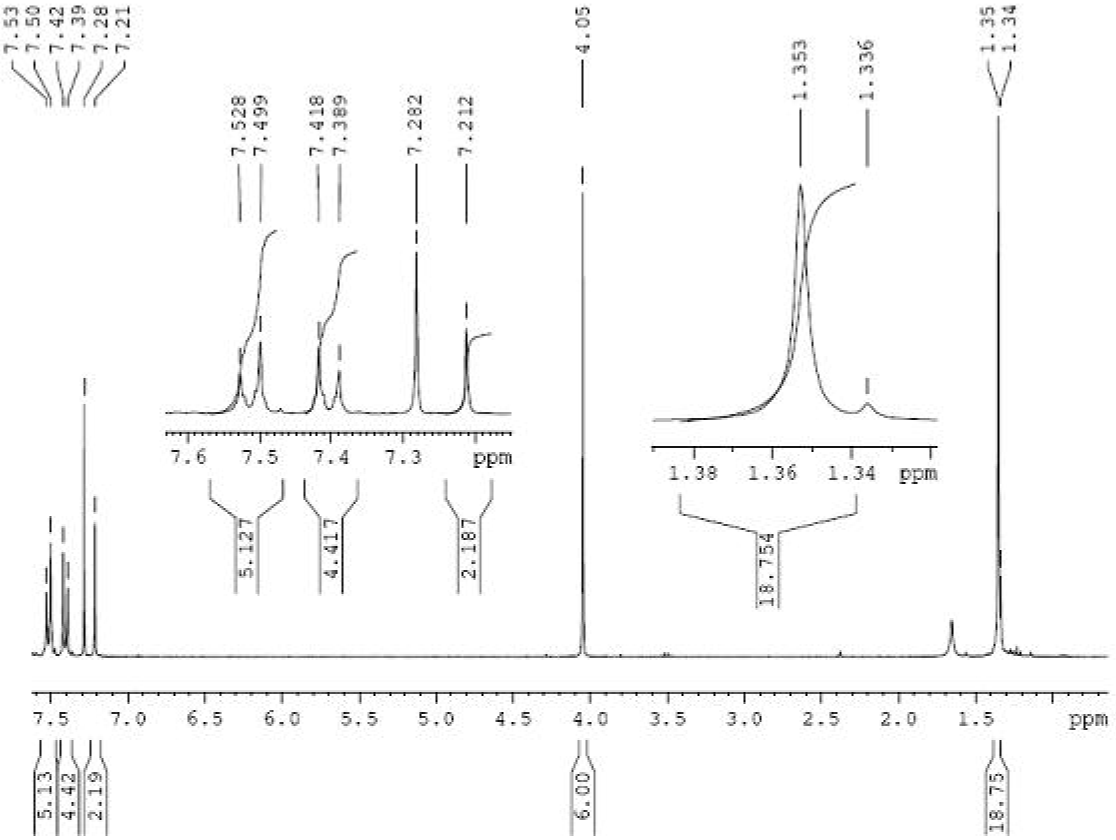

Figure S44 Proton NMR spectrum of 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,3-dimethoxy benzene (**11**) ($CDCl_3$, 300 MHz)

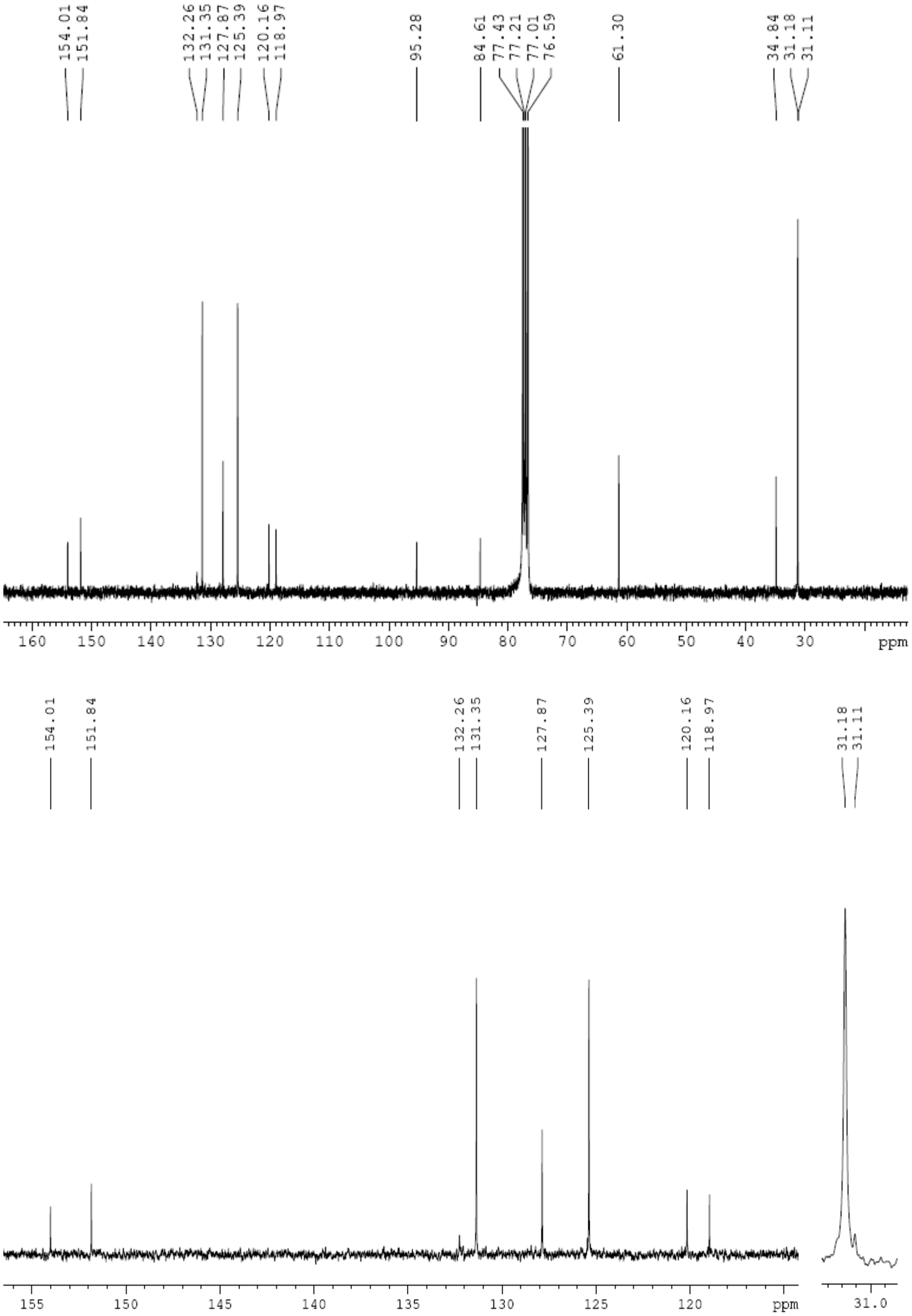

Figure S45 Carbon-13 NMR spectrum of 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,3-dimethoxy benzene (**11**) ($CDCl_3$, 75 MHz) from 20-160 ppm (upper) and an inset of aromatic and aliphatic region expansion (lower)

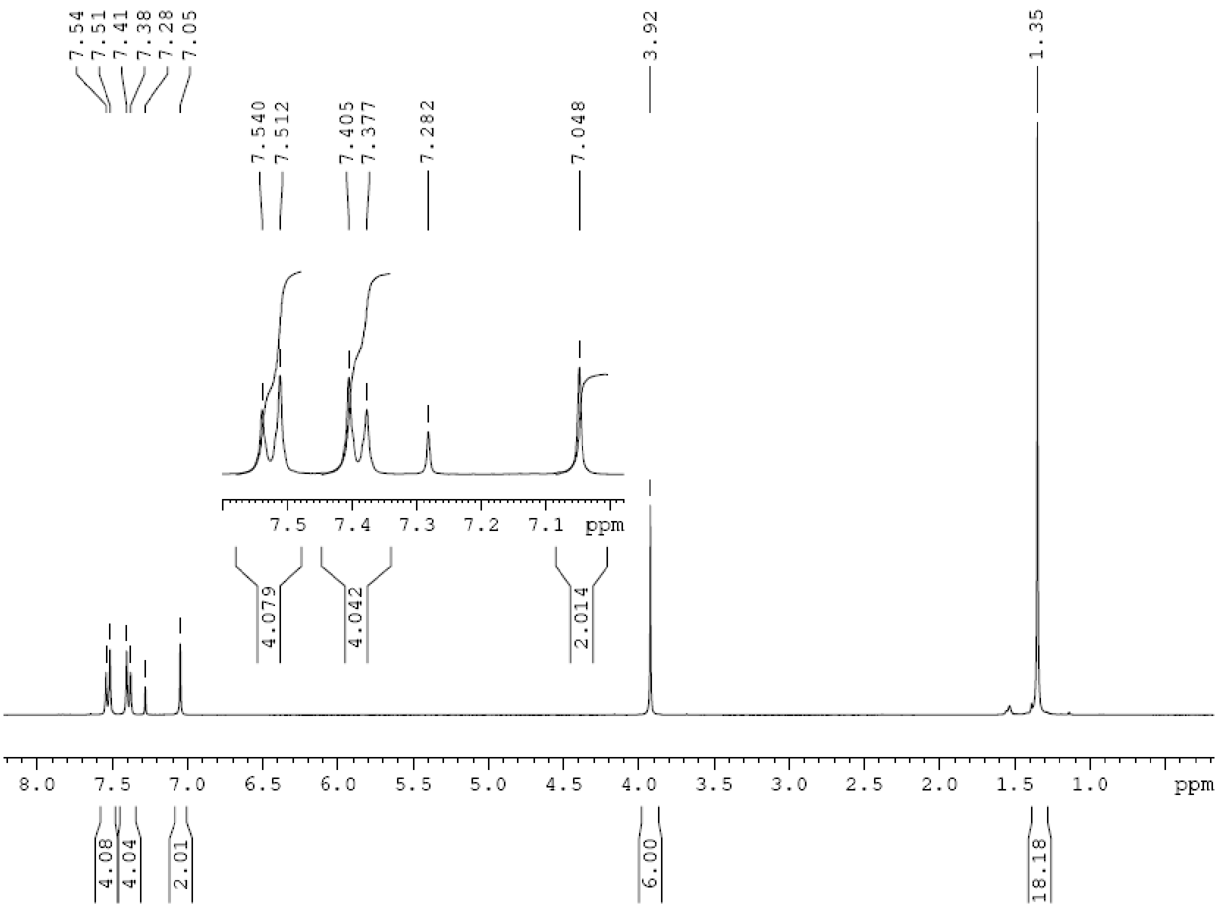

Figure S46 Proton NMR spectrum of 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,5-dimethoxy benzene (**13**) (CDCl$_3$, 300 MHz)

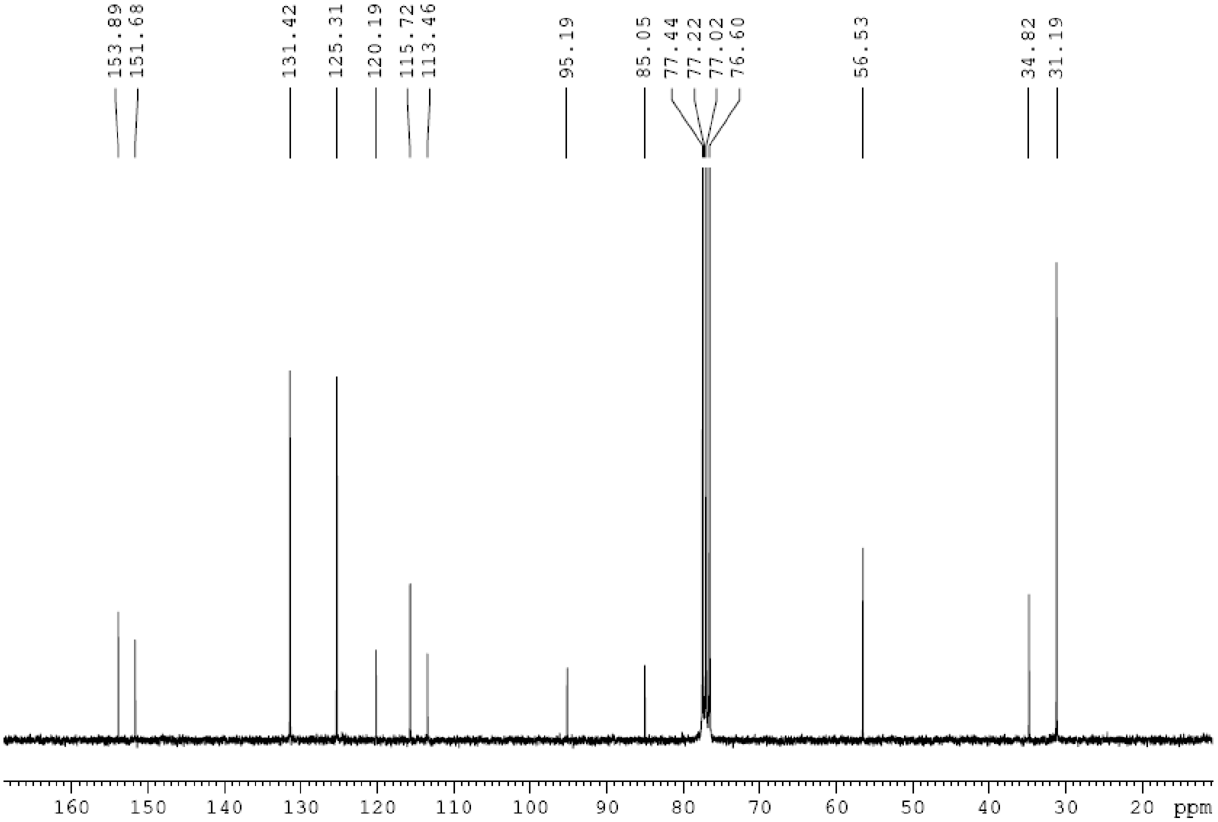

Figure S47 Carbon-13 NMR spectrum of 1,4-bis(2-(4-*t*-butylphenyl)ethynyl)-2,5-dimethoxy benzene (**13**) ($CDCl_3$, 75 MHz) from 20-160 ppm

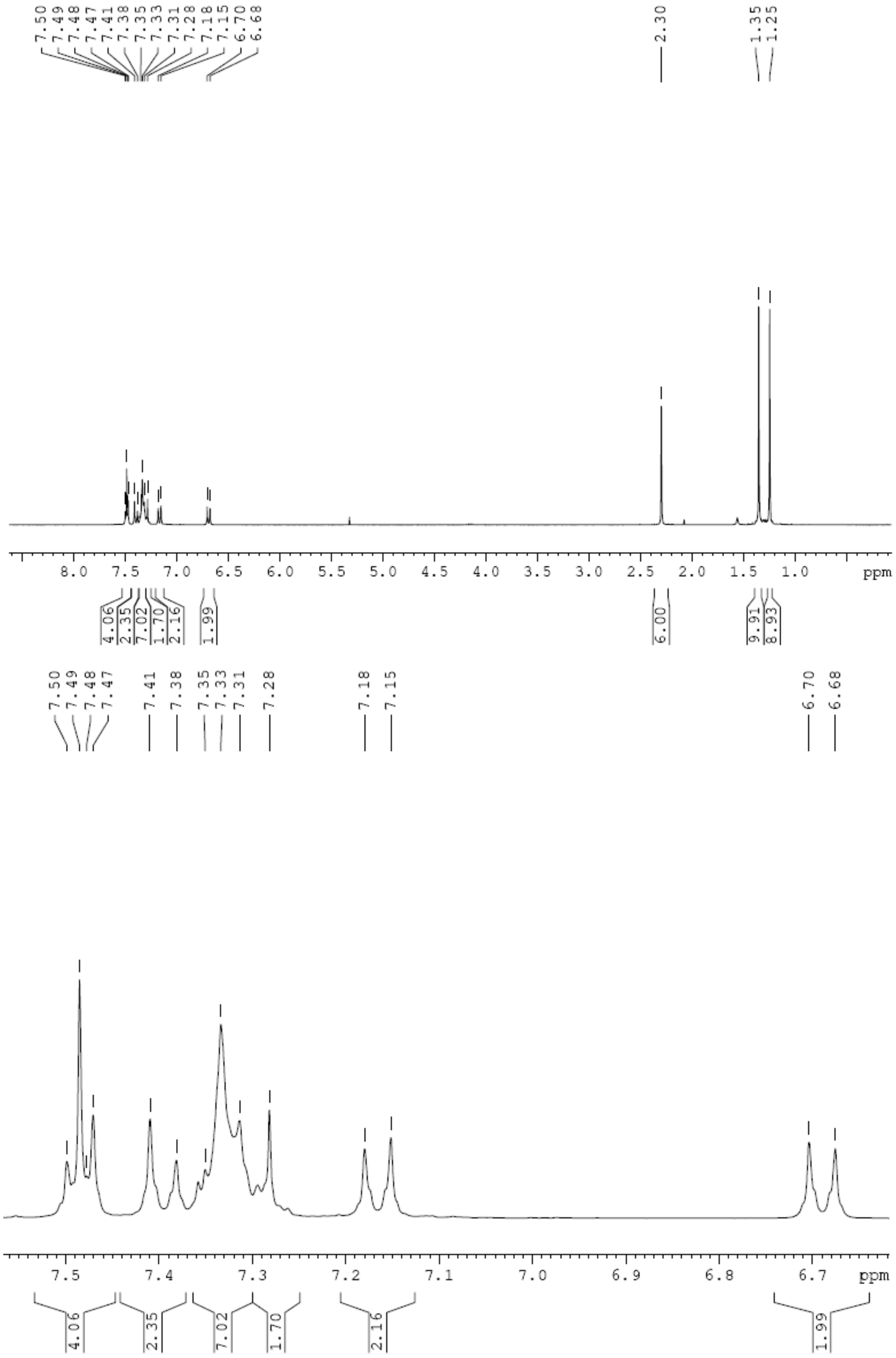

Figure S48 Proton NMR spectrum of 1,4-bis(4-*t*-butylphenylethynyl)-2,6-bis(*o*-tolyl) benzene (**10**) ($CDCl_3$, 300 MHz) (upper) and an inset of aromatic region expansion (lower)

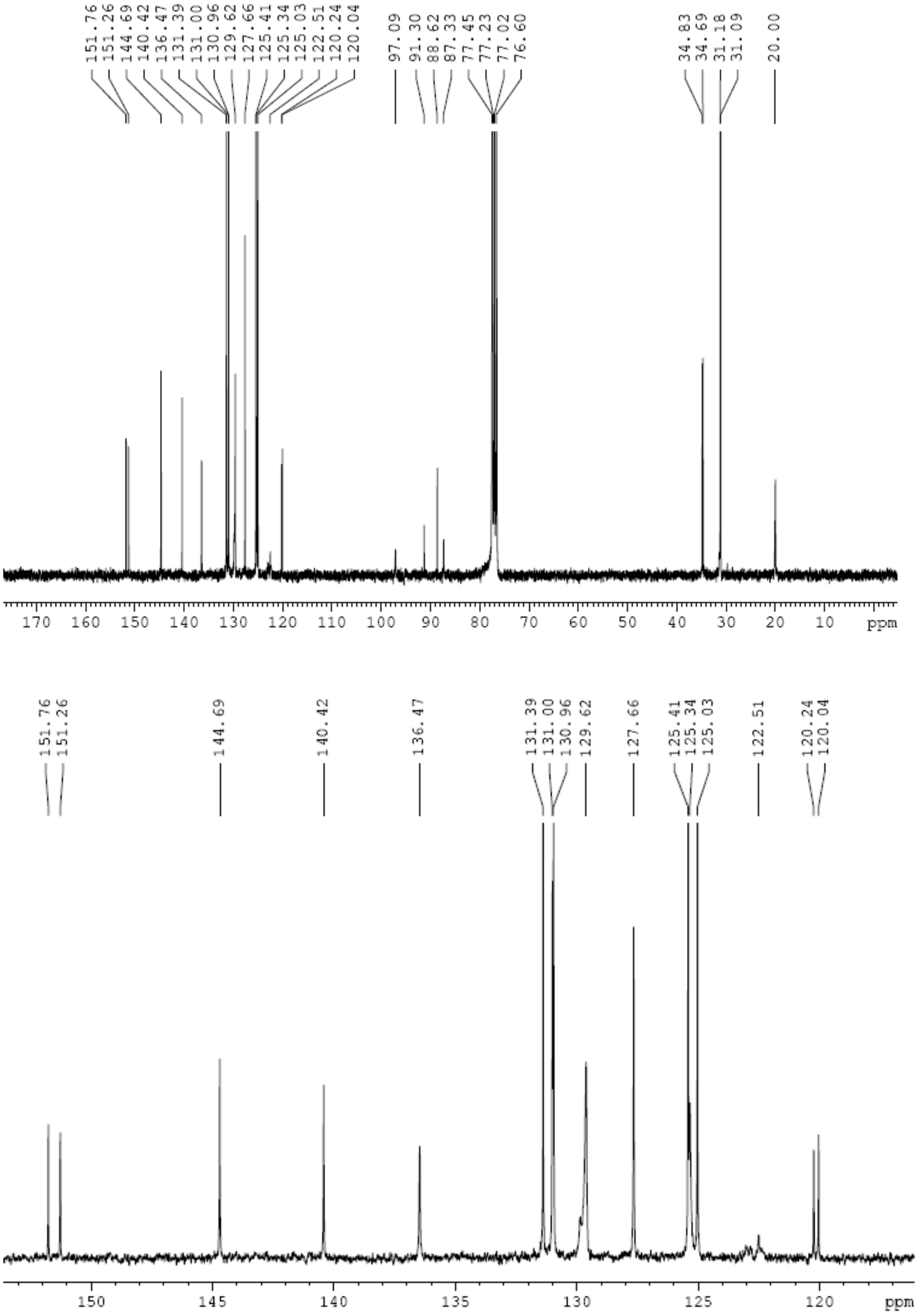

Figure S49 Carbon-13 NMR spectrum of 1,4-bis(4-*t*-butylphenylethynyl)-2,6-bis(*o*-tolyl) benzene (**10**) ($CDCl_3$, 75 MHz) from 10-170 ppm (upper) and an inset from 117-153 ppm (lower)

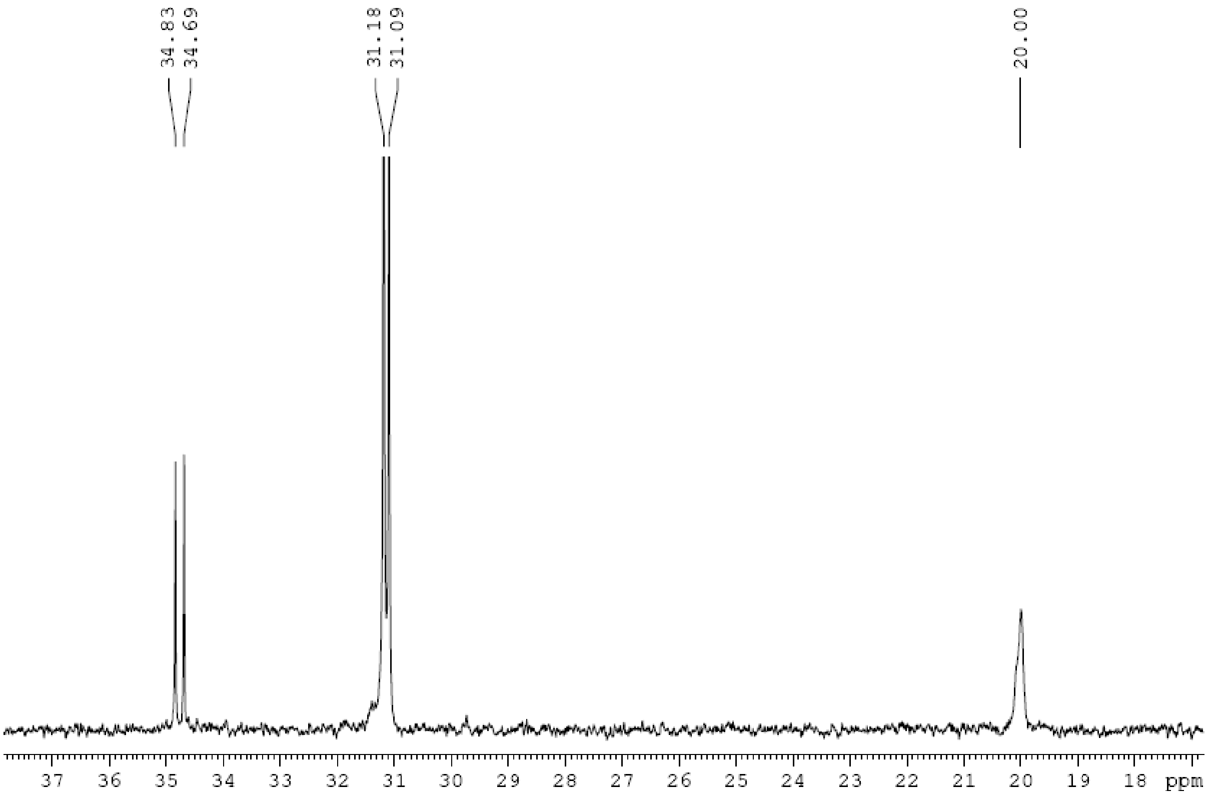

Figure S50 Expansion (17-37 ppm) of Carbon-13 NMR spectrum of 1,4-bis(4-*t*-butylphenylethynyl)-2,6-bis(*o*-tolyl) benzene (**10**) ($CDCl_3$, 75 MHz)

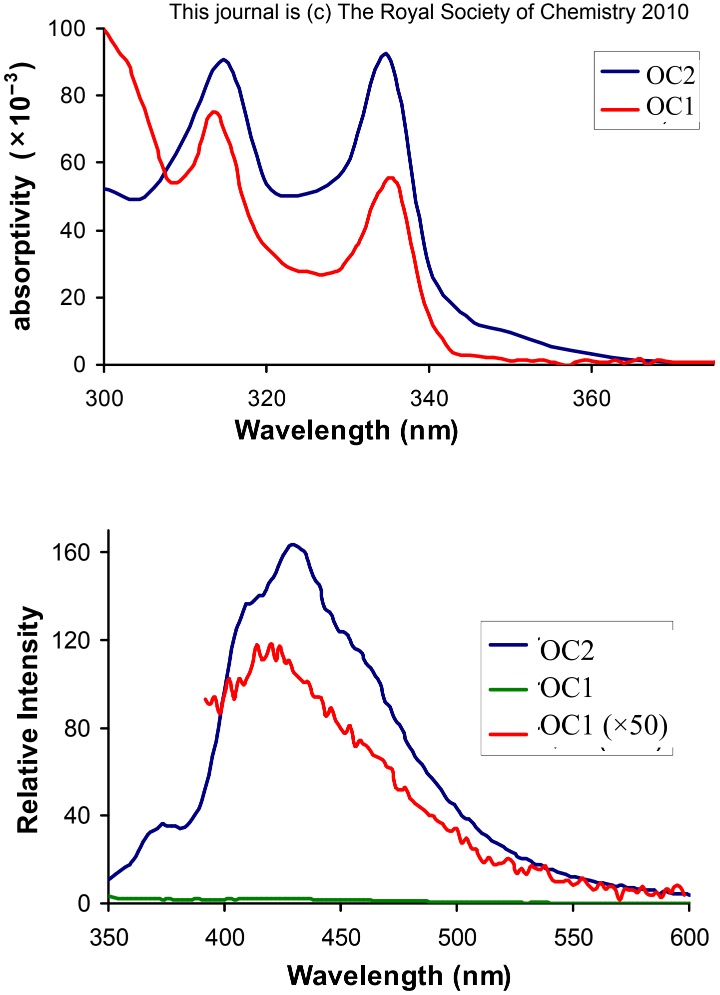

Figure S51. Absorption (top, 5.9 μM for **OC1** and 5.2 μM for **OC2**) and emission spectra (bottom, 0.59 μM for **OC1** and 0.52 μM for **OC2**) of **OC1** and **OC2**. All spectra were collected in THF.

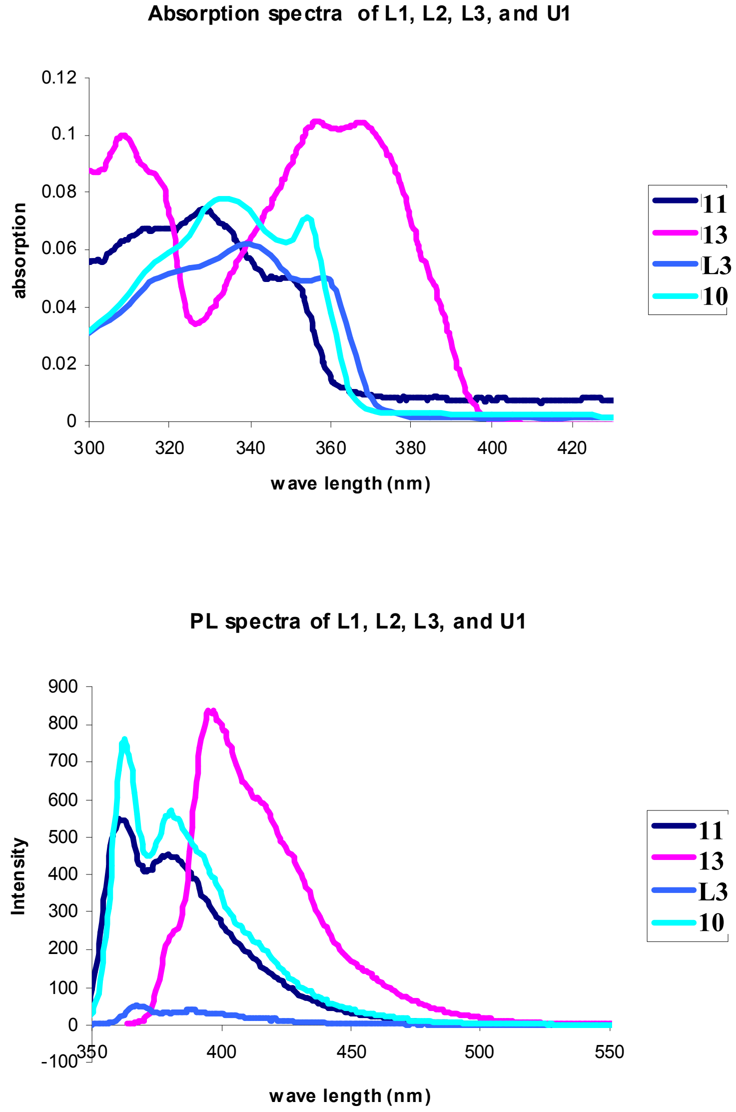

Figure S52. Absorption (top, 66 μM for **11,** 46 μM for **13,** 62 μM for **L3** and 95 μM for **10**) and emission spectra (bottom, 66 μM for **11,** 46 μM for **13,** 62 μM for **L3** and 95 μM for **10**) of **11, 13, L3,** and **10**. All spectra were collected in THF. **L3** = 1,4-bis(2-(4-t-butylphenyl)ethynyl)-2,5-dibromobenzene.

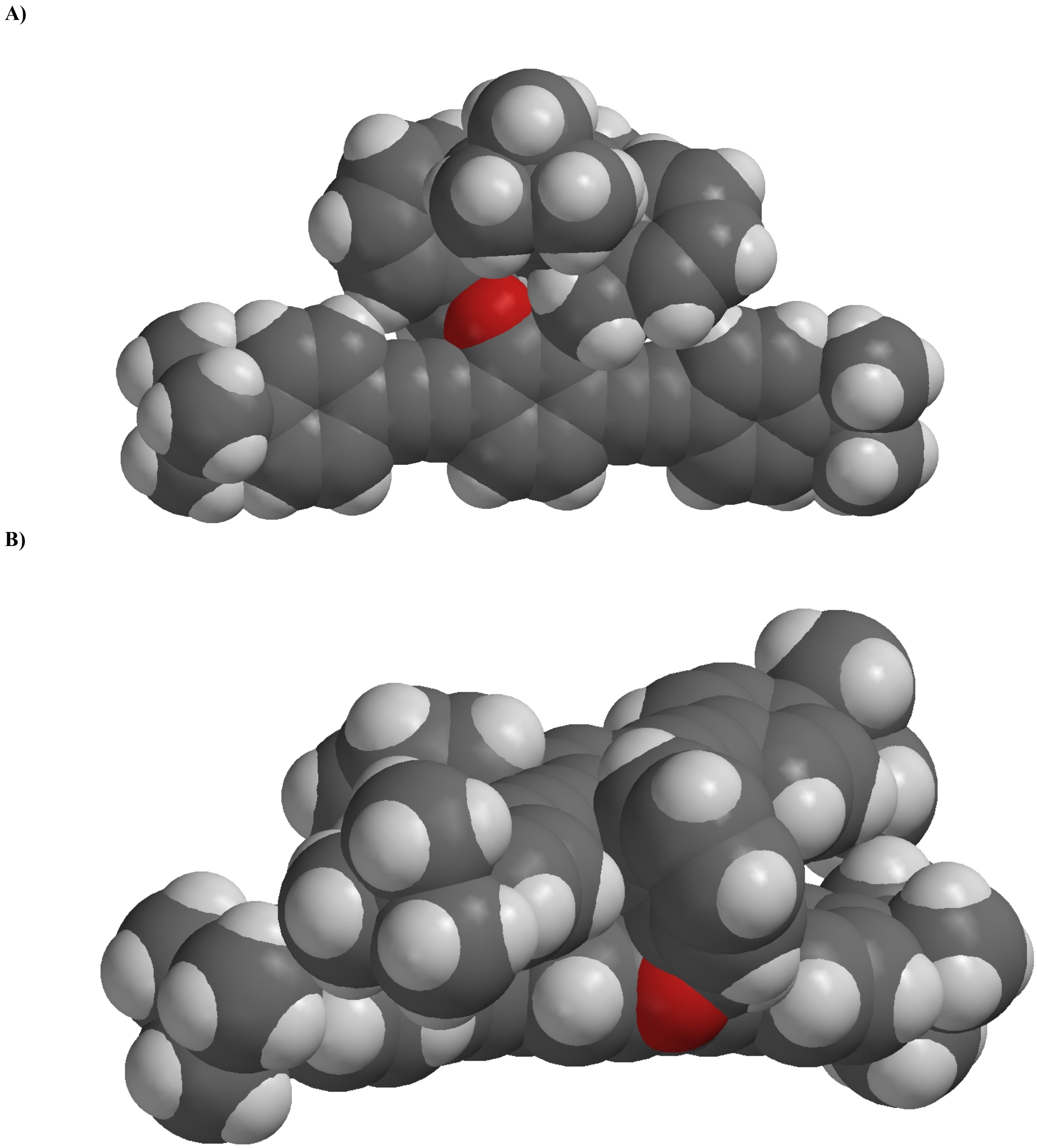

Figure S53. Space filling models of **OC2** (A) and **OC1** (B) shown in approximately the same orientation as in Figure 1 in the manuscript. Geometries were calculated by semiempirical methods at the PM3 level of theory.

References

[S1] C. J. F. Du, H. Hart, K. K. D. Ng, *J. Org. Chem.* **1986**, *51*, 3162-3165.

[S2] Zhu, Z.; Swager, T. M. *Org. Lett.* **2001**, *3*, 3471-3474.

[S3] Ramey, M. B.; Hiller, J. A.; Rubner, M. F.; Tan, C.; Schanze, K. S.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 234-243.

[S4] Wang, C.; Hu, R.; Liang, S.; Chen, J.; Yang, Z.; Pei, J. *Tet. Lett.* **2005**, *46*, 8153-8157.

[S5] Solomin, V. A.; Hritz, W. *Macromol. Chem. Phys.* **1994**, *195*, 303-314.

[S6] *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, 2006.