

SUPPORTING INFORMATION

Fabrication of hybrid photodiode systems: BODIPY Decorated Cyclotriphosphazene covalently grafted Graphene Oxides

Emrah Özcan^{1,2}, Burcu Topaloğlu Aksoy¹, Esra Tanrıverdi Eçik³, Ayşegül Dere⁴,
Abdulkerim Karabulut⁵, Fahrettin Yakuphanoglu^{4,6}, Bünyemin Çoşut^{1*}

¹ Department of Chemistry, Gebze Technical University, Gebze, Kocaeli, Turkey

² Institute of Physics, Faculty of Science, University of South Bohemia, Branišovská 1760,
370 05, České Budějovice, Czech Republic

³ Department of Chemistry, Ataturk University, Erzurum, Turkey

⁴ Nanoscience and Nanotechnology Laboratory, Firat University, Elazig, Turkey

⁵ Department of Basic Sciences, Faculty of Sciences, Erzurum Technical University,
Erzurum, Turkey

⁶ Department of Physics, Faculty of Science, Firat University, Elazig, Turkey

* Author for correspondence:

Dr. Bünyemin Çoşut, Department of Chemistry, Gebze Technical University, Gebze 41400,
Kocaeli, Turkey

Tel: 00 90 262 6053015

Fax: 00 90 262 6053105

e-mail : bc@gtu.edu.tr

TABLE OF CONTENTS

Experimental Details	5
Materials	5
Characterization Equipment	5
Fabrication of the diodes	6
Synthesis	6
Synthesis of Compound 1	7
Synthesis of Compound 2	7
Synthesis of Compound 3	8
Synthesis of Compound 4	8
Synthesis of Compound 5	9
Synthesis of Compound 6	10
Synthesis of Compound 7	11
Synthesis of Compound 8	11
Synthesis of GO-Cl	12
Synthesis of Compound 9	13
Synthesis of Compound 10	13
Figure S1: Chemical structure and synthetic pathway of compounds 1-3	14
Figure S2: Chemical structure and synthetic pathway of compounds 4-6	15
Figure S3: Synthetic pathway of Bodipy Decorated Cyclophosphazenes (7 - 8)	16
Figure S4: Synthetic pathway of GO-Cl	17
Figure S5: Positive ion and linear mode MALDI TOF-MS spectrum of compound 1	17
Figure S6: The ³¹P NMR spectrum of compound 1 in CDCl₃	18
Figure S7: The ¹H NMR spectrum of compound 1 in CDCl₃	18
Figure S8: The ¹³C NMR spectrum of compound 1 in CDCl₃	19
Figure S9: Positive ion and linear mode MALDI TOF-MS spectrum of compound 2	19

Figure S10: The ^{31}P NMR spectrum of compound 2 in CDCl_3	20
Figure S11: The ^1H NMR spectrum of compound 2 in CDCl_3	20
Figure S12: The ^{13}C NMR spectrum of compound 2 in CDCl_3	21
Figure S13: Positive ion and linear mode MALDI TOF-MS spectrum of compound 3	21
Figure S14: The ^{31}P NMR spectrum of compound 3 in CDCl_3	22
Figure S15: The ^1H NMR spectrum of compound 3 in CDCl_3	22
Figure S16: The ^{13}C NMR spectrum of compound 3 in CDCl_3	23
Figure S17: Positive ion and linear mode MALDI TOF-MS spectrum of compound 4	23
Figure S18: The ^1H NMR spectrum of compound 4 in CDCl_3	24
Figure S19: The ^{13}C NMR spectrum of compound 4 in CDCl_3	24
Figure S20: Positive ion and linear mode MALDI TOF-MS spectrum of compound 5	25
Figure S21: The ^1H NMR spectrum of compound 5 in CDCl_3 (aromatic region)	25
Figure S22: The ^1H NMR spectrum of compound 5 in CDCl_3 (aliphatic region)	26
Figure S23: The ^{13}C NMR spectrum of compound 5 in CDCl_3	26
Figure S24: Positive ion and linear mode MALDI TOF-MS spectrum of compound 6	27
Figure S25: The ^1H NMR spectrum of compound 6 in CDCl_3 (aromatic region)	27
Figure S26: The ^1H NMR spectrum of compound 6 in CDCl_3 (aliphatic region)	28
Figure S27: The ^{13}C NMR spectrum of compound 6 in CDCl_3	28
Figure S28: Positive ion and linear mode MALDI TOF-MS spectrum of compound 7	29
Figure S29: The ^{31}P NMR spectrum of compound 7 in d_8 -THF	29
Figure S30: The ^1H NMR spectrum of compound 7 in d_8 -THF (aliphatic region)	30
Figure S31: The ^1H NMR spectrum of compound 7 in d_8 -THF (aromatic region)	30
Figure S32: The ^{13}C NMR spectrum of compound 7 in d_8 -THF (aliphatic region).....	31
Figure S33: The ^{13}C NMR spectrum of compound 7 in d_8 -THF (aromatic region)	31
Figure S34: The ^{31}P NMR spectrum of compound 8 in d_8 -THF	32
Figure S35: The ^1H NMR spectrum of compound 8 in d_8 -THF (aliphatic region)	32

Figure S36: The ¹ H NMR spectrum of compound 8 in d ₈ -THF (aromatic region)	33
Figure S37: The ¹³ C NMR spectrum of compound 8 in d ₈ -THF (aliphatic region)	33
Figure S38: The ¹³ C NMR spectrum of compound 8 in d ₈ -THF (aromatic region)	34
Figure S39: FT-IR spectra of GO and GO-COCl compounds.....	34
Figure S40: FT-IR Spectra of compound 9 and GO-COCl	35
Figure S41: Raman Spectra of compound 9 and GO.....	35
Figure S42: FT-IR Spectra of compounds 10 and GO-COCl.....	36
Figure S43: Raman Spectra of compound 10 and GO.....	36
Figure S44: TGA Thermogram Spectra of compounds 9 and GO	37
Figure S45: TGA Thermogram Spectra of compound 10 and GO.....	37
Figure S46: DSC Thermograms of Compounds 9 and 10	38
Figure S47: SEM image and EDX result of Compound 9	38
Figure S48: SEM image and EDX result of Compound 10	39
Figure S49: TEM images of compound 9 , and 10 , respectively.....	39
Figure S50: AFM images of Compound 9 , and 10 , respectively.....	39
Figure S51: Photoconductivity Measurement System used in the Study	40

1. Experimental Setup

1.1. Materials

All reagents were purchased from Aldrich and used without further purification and all solvents were obtained from Merck. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F₂₅₄. Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM). Suction column chromatography was performed on silica gel (Merck, Kieselgel 60 Å, 70-230 mesh).

1.2. Characterization Equipment

Mass analyses were recorded by a Bruker MS MALDI TOF spectrometer (Bremen, Germany) and 2,5-dihydroxybenzoic acid was used as a matrix. ¹H, ¹³C, and ³¹P NMR spectra were lined out for all compounds in CDCl₃ on a Varian INOVA 500 MHz spectrometer (West Sussex, UK) and TMS was used as an internal reference for ¹H and ¹³C measurements. PerkinElmer Spectrum 100 FT-IR spectrophotometer was used for obtaining FT-IR data. Electronic absorption spectra in the UV-Vis region were measured by a Shimadzu 2101 UV-Vis spectrophotometer (Tokyo, Japan). Fluorescence excitation and emission spectra were performed on a Varian Eclipse spectrofluorometer (Melbourne, Australia) using 1 cm path length cuvettes at room temperature. The fluorescence lifetimes were obtained using Horiba-Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument (N.J., USA) with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 510 nm for **9** and **10**. Signal acquisition was performed using a TCSPC module. Raman analysis were performed by a completely automated Renishaw InVia Reflex Raman Microscopy system (Renishaw Plc., New Mills, Wotton-under-Edge, UK) equipped with a 514 nm Ar lasers. SEM and EDX characterizations were taken by using a Philips XL30 SFEG Scanning electron microscopy (SEM). TEM measurements were recorded with Tecnai G² F20 S-TWIN 200 kV. AFM images were

recorded by using A Park Systems XE 100 Atomic Force Microscope (Park Systems Corp., Korea). For thermal measurements, Mettler Toledo TGA/SDTA 851 Thermogravimetric Analysis (TGA) Instrument and Differential Scanning Calorimeter DSC 821 equipped with METTLER TOLEDO STAR software at a heating rate of 10°C/min under nitrogen was performed. For analysis of the diode properties, FYTRONIX FY-5000 electronic device was used. The cyclic voltammetry (CV) measurements were carried out with an electrochemical analyzer of CHI440B. Electrochemical properties of cyclotriphosphazene-BODIPY derivatives (**CP-BD1 (7)**; **CP-BD2 (8)**) and prepared hybrid materials (**GO-CP-BD1 (9)**;**GO-CP-BD2 (10)**) were investigated by cyclic voltammetry. The electrochemical data were obtained from the oxidation and reduction cyclic voltammograms as shown in Fig. 7. The HOMO energy level of materials were calculated using the equation: $\text{HOMO} = -[\text{E}_{\text{ox}} - \text{E}_{1/2}(\text{ferrocene}) + 4.8]$ V, where E_{ox} is the onset oxidation potential of the substance under investigation and $\text{E}_{1/2}(\text{ferrocene})$ is the onset oxidation potential of ferrocene vs. Ag/Ag^+ . The band gap (E_g) was calculated from the onset absorption edge in the UV-vis spectrum of materials.

1.3. Fabrication of the diodes

The diodes were prepared from p-type silicon wafer and synthesized organic materials. Firstly, the solutions of two graphene oxide covalently functionalized with BODIPY decorated cyclotriphosphazene hybrid materials (**9** and **10**) were prepared. Secondly, an ohmic contact was prepared on a p-type silicon wafer cleaned using various chemical baths by thermal evaporation system at about 10^{-5} Torr and was thermally treated at 570 °C for 5 min under nitrogen atmosphere. The front surface of the silicon was cleaned again and the solutions were coated on p-Si wafer using a FYTRONIX FY-10 drop coater for 30 s. Then, the films were dried at 50 °C for 10 min. The diode structure was completed by evaporating of Al on organic

films. The photoconduction characteristics of Al/compound (**9**) or (**10**) /p-Si/Al diode were performed with FYTRONIX FY-5000 electronic devices characterization system (Turkey).

1.4. Synthesis

Among the present compounds in this study; **1**, **2** [20], and **4** [21] were synthesized and purified as described in the given the literature routes.

Synthesis of Compound 1

At the first stage, the trimer (1.2 g, 3.44 mmol) was dissolved in 50.0 mL of THF in a 100 mL necked flask under argon atmosphere and Cs₂CO₃ (5.62 g, 5.0 mmol) was added to the this mixture. After dissolution was achieved, 4-iodophenol (3.79 g, 17.2 mmol) was dissolved with 20 mL of THF and added dropwise to the reaction medium. The reaction mixture was controlled by thin layer chromatography and stirred at room temperature for 24 h. until all starting material was consumed. The reaction mixture was separated from salts by filtration through G4. The solvent of the filtrate (THF) was removed under reduced pressure. The crude product was purified by column chromatography using petroleum ether:dichloromethane (2:1) solvent system as the mobile phase, and compound 1 was purely collected (2.9 g, 67 %). MALDI-TOF (m/z) Calc. 1265.32 m/z, Found: 1265.40 [M⁺] (Fig S1). ³¹P NMR (500 MHz, CDCl₃) δP 22.3 (t, J=82.0 Hz, 1P, PClOR), 6.7 (d, J=82.0 Hz, 2P, P(OR)₂) ppm (Fig S2). ¹H NMR (500 MHz, CDCl₃) δH 7.6 (m, 5H, Ar-CH), 7.5 (m, 5H, Ar-CH), 6.8 (m, 5H, Ar-CH), 6.6 (m, 5H, Ar-CH) ppm (Fig S3). ¹³C NMR (126 MHz, CDCl₃) δC 149.7, 139.1, 138.3, 123.4 ppm (Fig S4).

Synthesis of Compound 2

Compound **1** (0.3 g, 0.24 mmol) was dissolved in 35.0 mL of dry THF under an argon atmosphere. Cs₂CO₃ (0.23 g, 0.72 mmol) and 4-acetamidophenol (0.54 g, 0.36 mmol) were added to the reaction mixture. The reaction mixture was controlled by thin layer chromatography and stirred at room temperature until all starting material (**1**) was finished. The reaction mixture was separated from salts by filtration through G4. The solvent of the filtrate (THF) was removed under reduced pressure. The residue was purified by silica gel column chromatography using tetrahydrofuran: hexane (3:1) solvent as eluent and compound **2** was collected (0.26 g, 80 %). MALDI-TOF (m/z) Calc. 1380.11 m/z, Found: 1380.78 [M⁺] (Fig S5). ³¹P NMR (500 MHz, CDCl₃) δP 8.7 (broad, 3P, AB₂) ppm (Fig S6). ¹H NMR (500 MHz, CDCl₃) δ_H 7.5 (m, 10H, Ar-CH), 7.3 (d, *J*=8.5 Hz, 2H, Ar-CH), 6.8 (d, *J*=8.5 Hz, 2H, Ar-CH), 6.6 (m, 10H, Ar-CH), 2.3 (s, 1H, NH), 2.2 (s, 3H, CH₃) ppm (Fig S7). ¹³C NMR (126 MHz, CDCl₃) δ_C 150.0, 139.0, 138.4, 138.1, 123.7, 123.2, 122.8, 122.4, 89.1, 30.4 ppm (Fig S8).

Synthesis of Compound 3 (CP)

Compound **2** (0.25 g, 0.18 mmol) was dissolved with 20.0 mL of methanol under an argon atmosphere. And then, NaOH (0.8 g, 20.0 mmol) dissolved in 1.5 mL of purified water was added to the reaction mixture. The reaction mixture was controlled by thin layer chromatography and stirred under reflux at the boiling point of the solvent for 24 h. until the starting material was finished. The reaction mixture was filtered through G4 by washing with DCM. The solvent of the filtrate was partially removed under reduced pressure and compound **3** was obtained (0.18 g, 74 %). MALDI-TOF (m/z) Calc. 1338.07 m/z, Found: 1338.06 [M⁺] (Fig S9). ³¹P NMR (500 MHz, CDCl₃) δP 8.9 (broad, 3P, AB₂) ppm (Fig S10). ¹H NMR (500 MHz, CDCl₃) δ_H 7.5 (m, 10H, Ar-CH), 6.7 (m, 10H, Ar-CH), 6.6 (d, *J*=8.8 Hz, 2H, Ar-CH), 6.5 (d, *J*=8.8 Hz, 2H, Ar-CH), 3.7 (s, 2H, NH) ppm (Fig S11). ¹³C NMR (126 MHz, CDCl₃) δ_C 150.1, 138.6, 138.5, 138.4, 123.3, 123.1, 121.6, 121.5 ppm (Fig S12).

Synthesis of Compound 4

300 mL of dichloromethane was put in a 1 L round bottom flask and argon gas was bubbled through it for 15 minutes. Propargyl benzaldehyde (1.0 g, 6.25 mmol) and 2,4-dimethyl-pyrrole (1.3 mL, 12.5 mmol) were added to the reaction mixture, respectively. And then, two drops of trifluoroacetic acid were added and the reaction mixture was stirred at room temperature during the night under argon atmosphere. Reaction was followed by thin layer chromatography. P-chloroaniline (1.5 g, 6.25 mmol) was added dropwise and after 30 minutes, triethylamine (5.0 mL) and $\text{BF}_3 \cdot \text{OEt}_2$ (5.0 mL) were added, respectively. The reaction mixture was controlled by using thin layer chromatography and stirred at room temperature for 3 h. The reaction mixture was extracted three times in dichloromethane: water system. The organic phase was dried over Na_2SO_4 and then the solvent was removed under reduced pressure. Compound 4 was purified (520 mg, 22 %) by silica gel column chromatography using dichloromethane:hexane (1:1) solvent system as the mobile phase solvent. MALDI-TOF (m/z) Calc. 379.17 m/z, Found: 379.13 $[\text{M}^+]$ (Fig S13). ^1H NMR (500 MHz, CDCl_3) δ 7.2 (d, $J=8.8$ Hz, 2H, Ar-CH), 7.1(d, $J=8.8$ Hz, 2H, Ar-CH), 6 (s, 2H, Ar-CH), 4.8 (s, 2H, OCH_2), 2.6 (broad, 6H+1H, CH_3 , CCH), 1.4 (s, 6H, CH_3), ppm (Fig S14). ^{13}C NMR (126 MHz, CDCl_3) δ 158.1, 155.3, 143.1, 141.5, 131.8, 129.2, 128.1, 121.2, 115.6, 78.0, 75.9, 56.0, 14.5 ppm (Fig S15).

Synthesis of Compound 5 (BD1)

Compound 4 (150.0 mg, 0.4 mmol) was dissolved with 30.0 mL of benzene in a 100.0 mL round bottom reaction flask and 4- (di-p-tolylamino) benzaldehyde (300 mg, 1.0 mmol) was added to the reaction flask. 300 μL of piperidine and 300 μL of acetic acid were added to the reaction medium, respectively. The reaction mixture was heated at reflux using Dean-Stark apparatus until all aldehyde was used up. The reaction mixture was controlled by using thin layer chromatography and stirred for 2 h. The reaction mixture was extracted in dichloromethane:water system. The organic phase was dried over Na_2SO_4 and then

dichloromethane was removed using rotary evaporator. Compound **5** was purified (230 mg, 61%) by silica gel column chromatography using dichloromethane:hexane (2:1) solvent system as the mobile phase. MALDI-TOF (m/z) Calc. 944.41 m/z , Found: 944.9 [M^+] (Fig S16). 1H NMR (500 MHz, $CDCl_3$) δ_H 7.6 (d, $J = 16.6$ Hz, 2H, *trans*-CH), 7.5 (d, $J = 8.5$ Hz, 4H, Ar-CH), 7.3 (d, $J = 8.6$ Hz, 2H, Ar-CH), 7.3 (d, $J = 16.5$ Hz, 2H, *trans*-CH), 7.2 (m, 12H, Ar-CH), 7.1 (m, 8H, Ar-CH), 7.0 (d, $J = 8.6$ Hz, 4H, Ar-CH), 6.6 (s, 2H, Ar-CH), 4.8 (s, 2H, OCH_2), 2.6 (s, 1H, CCH), 2.3 (s, 12H, $PhCH_3$) 1.5 (s, 6H, CH_3) ppm (Fig S17 and S18). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 158.0, 157.9, 152.5, 148.9, 144.7, 141.4, 135.6, 133.3, 130.0, 129.9, 129.6, 128.5, 125.2, 121.3, 117.5, 116.9, 115.5, 115.4, 110.0, 78.1, 75.9, 56.0, 20.8, 14.8 ppm (Fig S19).

Synthesis of Compound 6 (BD2)

Compound **4** (150.0 mg, 0.4 mmol) was dissolved with 30.0 mL of benzene in a 100 mL round bottom reaction flask and 4- (Diphenylamino) benzaldehyde (271.0 mg, 1.0 mmol) was added to the mixture. 300 μ l of piperidine and 300 μ l of acetic acid were added to the reaction medium, respectively. The reaction mixture was heated at reflux using Dean-Stark until all aldehyde was used up. The reaction mixture was controlled by using thin layer chromatography and stirred for 2 h. The reaction mixture was extracted three times in dichloromethane:water system. The organic phase was dried over Na_2SO_4 and then dichloromethane was removed using rotary evaporator. Compound **6** was isolated (230 mg, 65%) by silica gel column chromatography using dichloromethane:hexane (2:1) solvent system as the mobile. MALDI-TOF (m/z) Calc. 889.36 m/z , Found: 889.36 [M^+] (Fig S20). 1H NMR (500 MHz, $CDCl_3$) δ_H 7.6 (d, $J = 16.1$ Hz, 2H, *trans*-CH), 7.5 (d, $J = 8.6$ Hz, 4H, Ar-CH), 7.33 (m, 8H, Ar-CH), 7.26 (d, $J = 8.6$ Hz, 2H, Ar-CH), 7.2 (m, 8H, Ar-CH), 7.1 (m, 8H, Ar-CH), 7.0 (d, $J = 8.6$ Hz, 4H, Ar-CH), 6.6 (s, 2H, Ar-CH), 4.8 (s, 2H, OCH_2), 2.6 (s, 1H, CCH), 1.5 (s, 6H, CH_3) ppm (Fig S21 and S22). ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 158.0, 152.5, 148.5, 147.2, 141.6, 137.3, 135.5, 133.6, 130.4,

129.8, 129.3, 128.5, 125.0, 123.5, 122.5, 117.5, 117.4, 116.9, 115.5, 78.1, 75.9, 56.0, 14.8 ppm (Fig S23).

Synthesis of Compound 7 (CP-BD1)

10.0 mL of THF and 5.0 mL of isopropylamine were placed in the tap-and-shrink reaction tube. Compound **3** (22.0 mg, 0.017 mmol) and Compound **5** (160.5 mg, 0.17 mmol) were added to the reaction medium. Argon gas was bubbled through the reaction mixture for 30 minutes. Pd (PPh₃)₂Cl₂ (23.8 mg, 0.03 mmol) and CuI (8.0 mg, 0.04 mmol) were added to the reaction medium and stirred for 48 h. in an argon atmosphere. Solvent (THF) was removed by rotary evaporator and the remaining reaction mixture was extracted with dichloromethane: water system. The organic phase was dried over Na₂SO₄ and then dichloromethane was removed using rotary evaporator. Compound **7** was isolated (76.0 mg, 85 %) by silica gel column chromatography using dichloromethane as the mobile phase. MALDI-TOF (m/z) Calc. 5420.29 m/z, Found: , [M+H] 5420.53, [M+Na] 5443.12, [M+K] 5459.69 m/z (Fig S24). ³¹P NMR (500 MHz, d₈-THF) δP 9.18 ppm, 9.10 ppm (J= 63.3 Hz, 3P, AB₂) (Fig S25). ¹H NMR (500 MHz, d₈-THF) δH 7.6 (J = 16.2 Hz, 10H, trans-CH), 7.4 (d, J = 8.5 Hz, 20H, Ar-CH), 7.3 (d, J = 16.2 Hz, 10H, trans-CH), 7.2 (d, J = 8.3 Hz, 10H, Ar-CH), 7.1 (m, 40 H, Ar-CH), 7.0 (m, 40 H, Ar-CH), 6.9 (m, 40H+10H, Ar-CH), 6.7 (s, 10H, Ar-CH), 5.8 (s, 10H, OCH₂), 2.3 (s, 60H, PhCH₃), 1.6 (s, 30H, CH₃) ppm (Fig S26 and S27). ¹³C NMR (126 MHz, d₈-THF) δC 158.5, 152.3, 151.7, 148.9, 144.8, 141.0, 138.3, 137.2, 137.0, 134.9, 133.6, 133.0, 132.8, 130.0, 129.8, 129.7, 128.0, 127.8, 126.0, 125.0, 124.9, 127.7, 124.6, 124.4, 121.2, 117.2, 117.1, 115.7, 34.1, 29.7, 20.4, 19.9, 14.1ppm (Fig S28 and S29).

Synthesis of Compound 8 (CP-BD2)

10.0 mL of THF and 5.0 mL of isopropylamine were placed in the tap-and-shrink reaction tube. Compound **3** (22.0 mg, 0.02 mmol) and Compound **6** (151.0 mg, 0.17 mmol) were added to the reaction medium. Argon gas was bubbled through the reaction mixture for 30 minutes. Pd (PPh₃)₂Cl₂ (23.8 mg, 0.03 mmol) and CuI (8.0 mg, 0.04 mmol) were added to the reaction medium and stirred for 48 h. in an argon atmosphere. Solvent (THF) was removed by rotary evaporator and the remaining reaction mixture was extracted with dichloromethane: water system. The organic phase was dried over Na₂SO₄ and then dichloromethane was removed using rotary evaporator. Compound **8** was isolated (60.0 mg, 70 %) by silica gel column chromatography using dichloromethane as the mobile phase. ³¹P NMR (500 MHz, d₈-THF) δP 9.02 ppm, 8.92 ppm (J=73.8 Hz, 3P, AB₂) (Fig S30). ¹H NMR (500 MHz, d₈-THF) δH 7.6 (J = 16.3 Hz, 10H, trans-CH), 7.5 (d, J = 8.6 Hz, 20H, Ar-CH), 7.35 (broad, 4H, Ar-CH), 7.3 (m, 40H+10H, Ar-CH, trans-CH), 7.2 (d, J = 8.4 Hz, 10H, Ar-CH), 7.1 (m, 40 H, Ar-CH), 7.0 (m, 40H+10H, Ar-CH), 6.9 (broad, 20H Ar-CH), 6.7 (s, 10H, Ar-CH), 5.8 (s, 10H, OCH₂), 1.6 (s, 30H, CH₃) ppm (Fig S31 and S32). ¹³C NMR (126 MHz, d₈-THF) δC 158.4, 152.2, 151.6, 148.5, 147.2, 141.4, 138.5, 136.9, 134.9, 133.6, 130.6, 129.6, 129.1, 128.1, 127.9, 126.1, 125.7, 124.9, 124.8, 123.3, 122.3, 117.4, 117.1, 115.7, 110.0, 109.9, 109.8, 34.1, 29.8, 25.4, 20.5, 14.2 ppm (Fig S33 and S34).

Synthesis of GO-Cl

Graphene oxide (90.0 mg) was put in a 50.0 mL three necked reaction flask and partially dissolved in 1.5 mL of DMF under argon atmosphere. 6 mL of SOCl₂ was put into the reaction medium. The reaction was stirred under argon atmosphere with a reflux condenser at 70°C for 24 h. The reaction mixture was washed with DMF and the filtrate was completely removed in the rotary evaporator with the help of vacuum pump. A solid blackish GO-Cl compound was

isolated. IR ν (cm^{-1}): 2933 (C-H) instead of 3200 (-COOH) peak at the GO, 2111 and 2087 (C-H), 1696.7 (C=O), 1626.8- 1407.6 (C=C) (Fig S35).

Synthesis of Compound 9 (GO-CP-BD1)

In a 25 mL three-neck reaction flask, GO-Cl (30.0 mg) was dissolved in 10 mL of dry THF. Compound **7** (15.0 mg, 5.7 mmol) was added to the reaction medium and stirred for 72 h. under argon atmosphere and at room temperature. The reaction mixture was washed with diethylether (4 \times 200 mL) and the solid portion was found to be black-yellowish. The residue was filtered through G4 and completely dried under vacuum to isolate compound **9**. IR ν (cm^{-1}): 3390 (Secondary N-H), 1635 (N-H), (Fig S36). Raman ν (cm^{-1}): 1425 (D band), 1603 (G band), 1517 (C=C) (Fig S37).

Synthesis of Compound 10 (GO-CP-BD2)

In a 25 mL three-neck reaction flask, GO-Cl (30.0 mg) was dissolved in 10 mL of dry THF. Compound **8** (15.0 mg, 2.76 mmol) was added to the reaction medium and stirred for 72 h. under argon atmosphere and at room temperature. The reaction mixture was washed with diethylether (4 \times 200 mL) and the solid portion was found to be black-yellowish. The residue was filtered through G4 and completely dried under vacuum to isolate compound **10**. IR ν (cm^{-1}): 3390 (Secondary N-H), 1637 (N-H), (Fig S38). Raman ν (cm^{-1}): 1423 (D band), 1605 (G band), 1505 (C=C) (Fig S39).

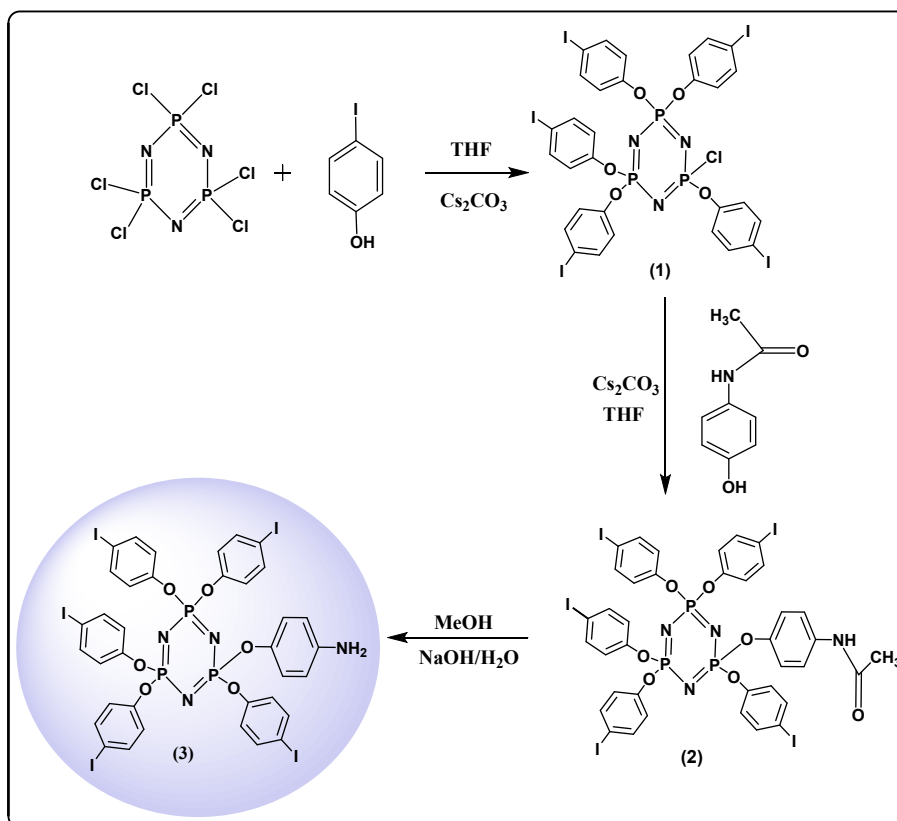


Figure S1. Chemical structure and synthetic pathway of compounds 1-3

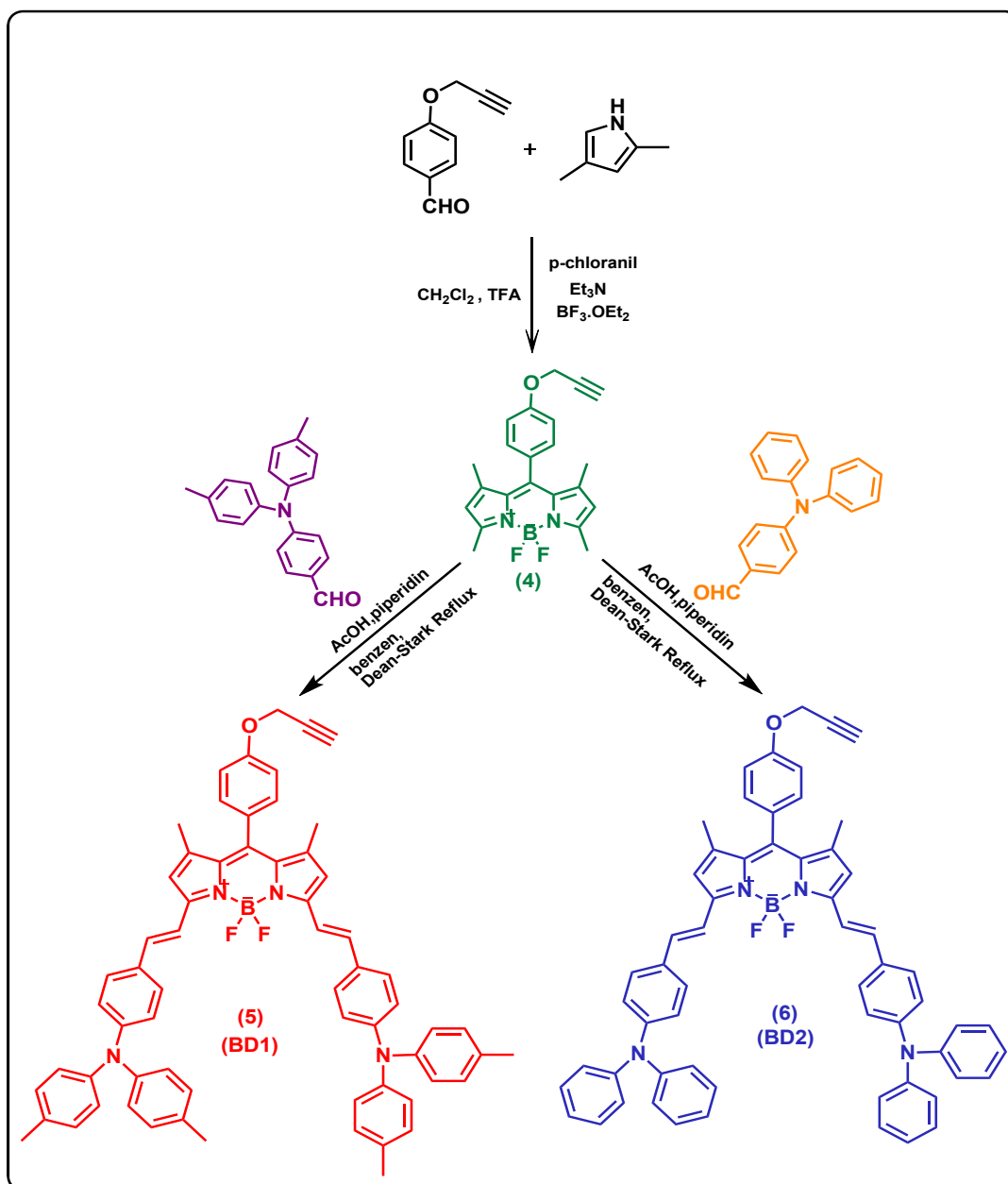


Figure S2. Chemical structure and synthetic pathway of compounds 4-6

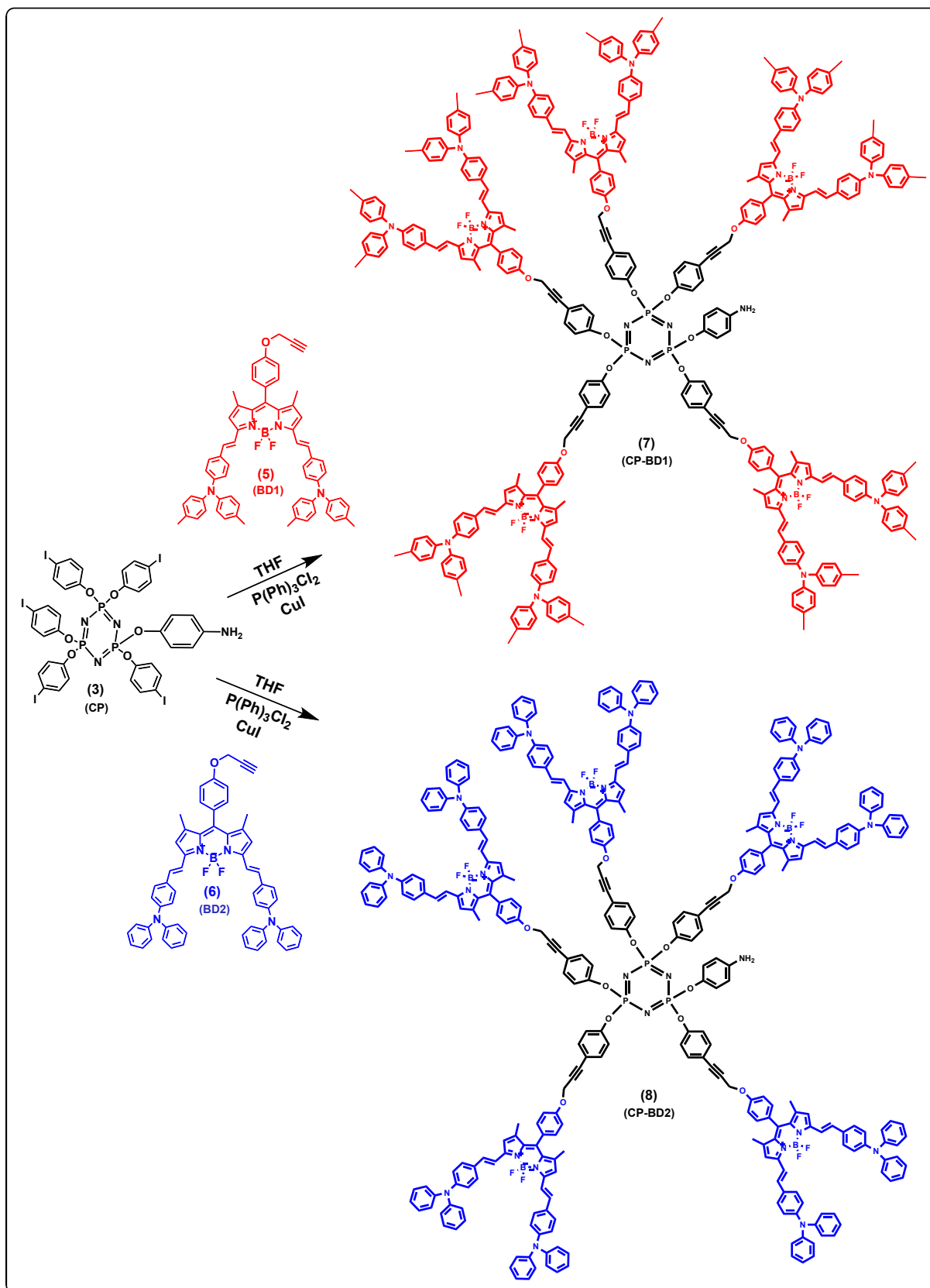


Figure S3. Synthetic pathway of Bodipy Decorated Cyclophosphazene Compounds (7 - 8)

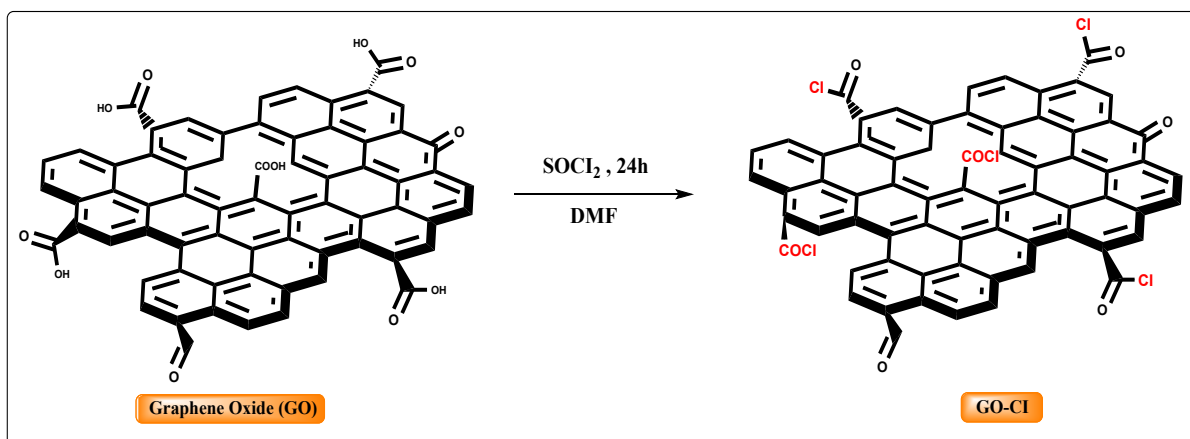


Figure S4. Synthetic pathway of GO-Cl

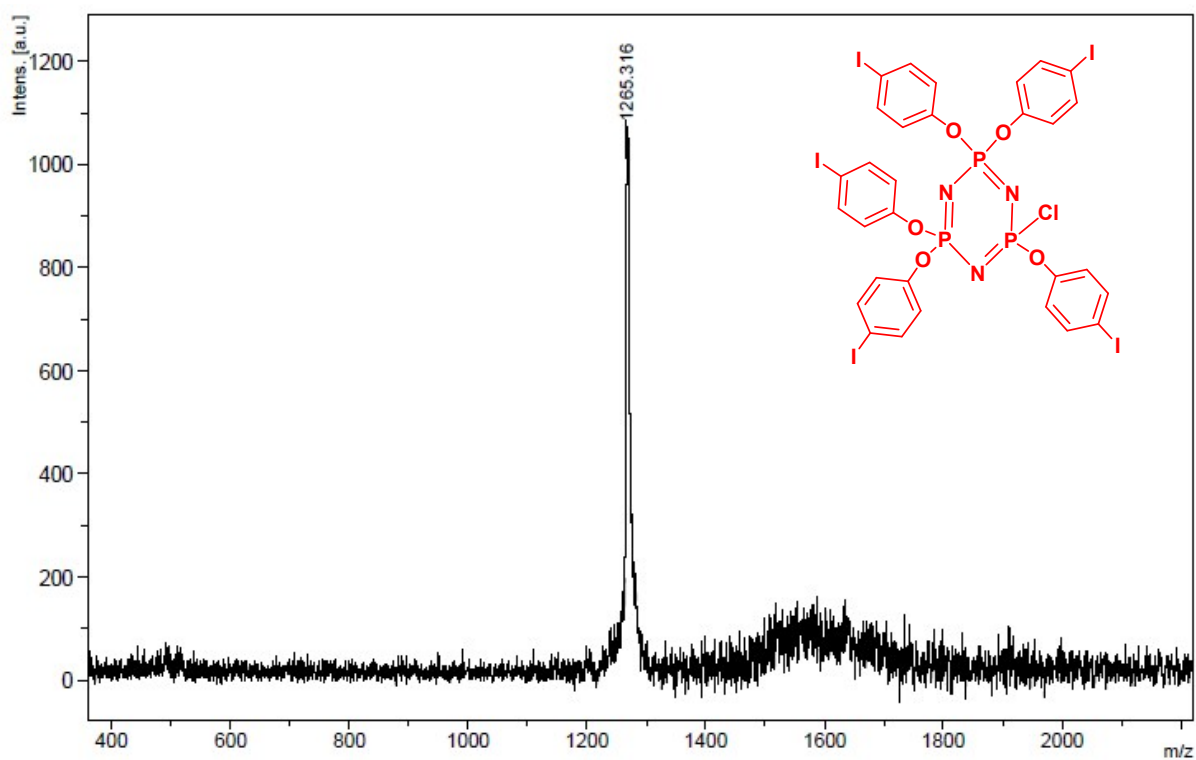


Figure S5. Positive ion and linear mode MALDI TOF-MS spectrum of compound **1**

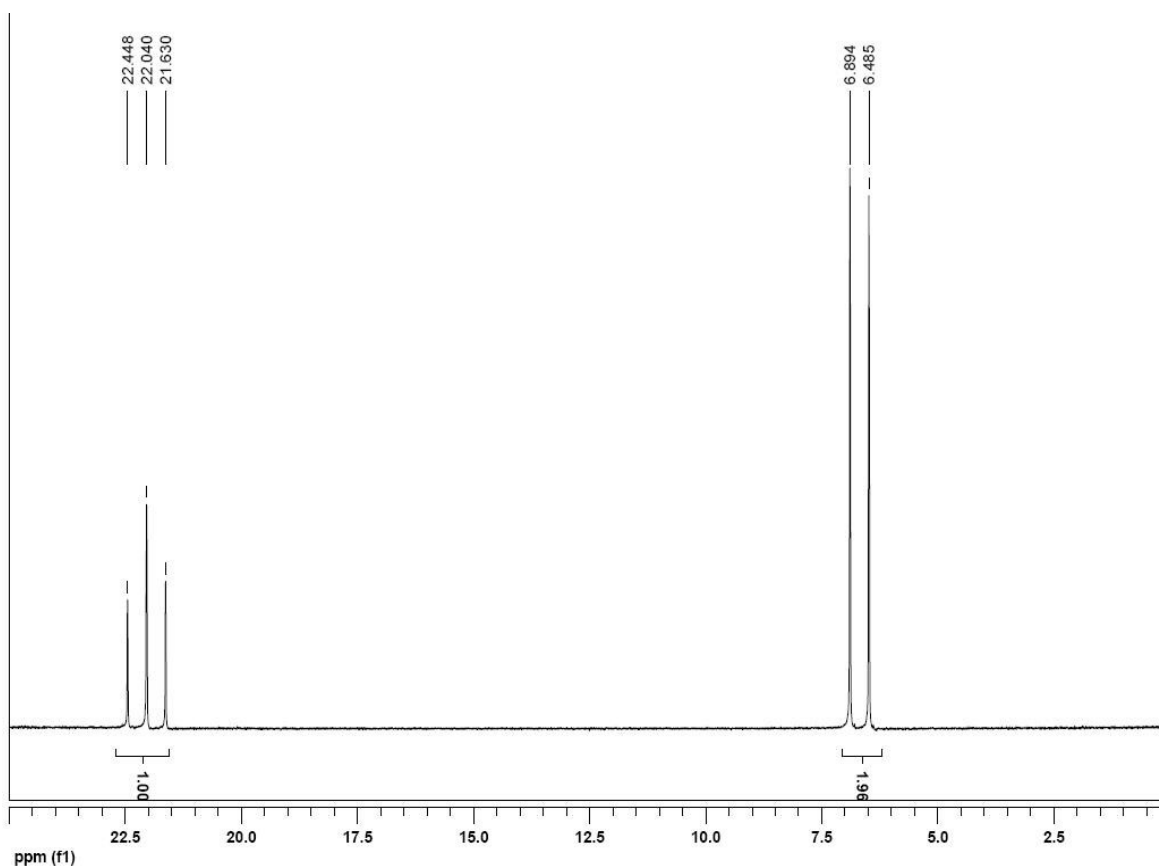


Figure S6. The ^{31}P NMR spectrum of compound **1** in CDCl_3

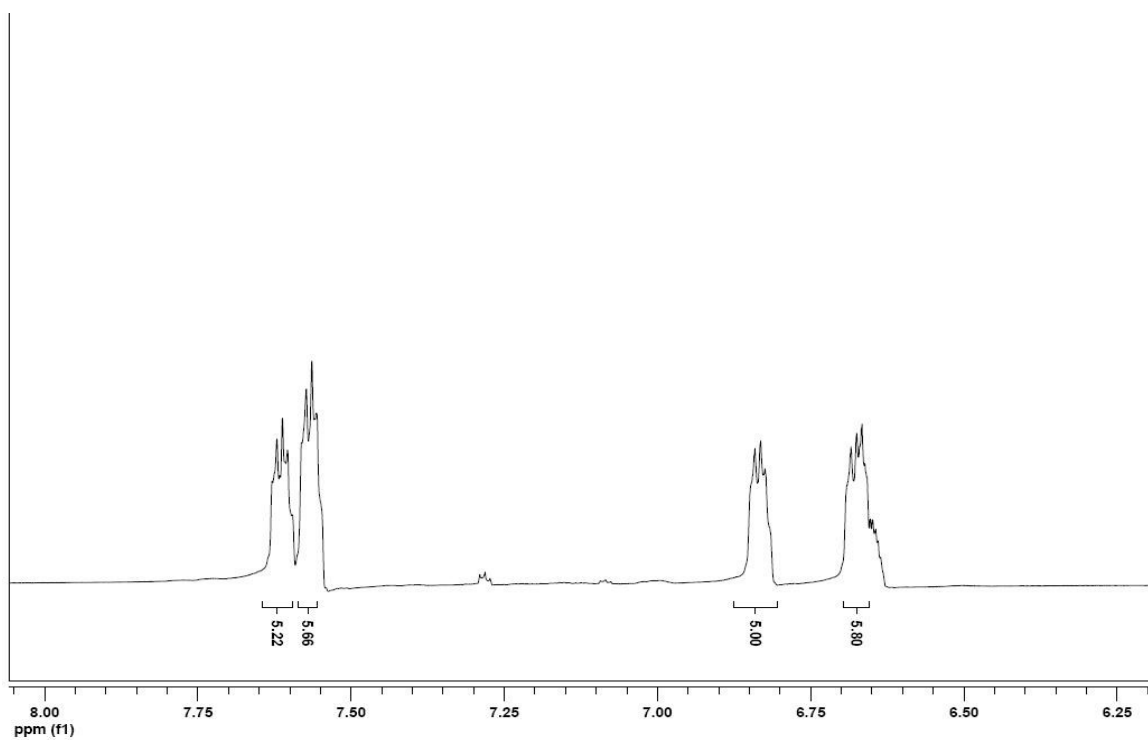


Figure S7. The ^1H NMR spectrum of compound **1** in CDCl_3

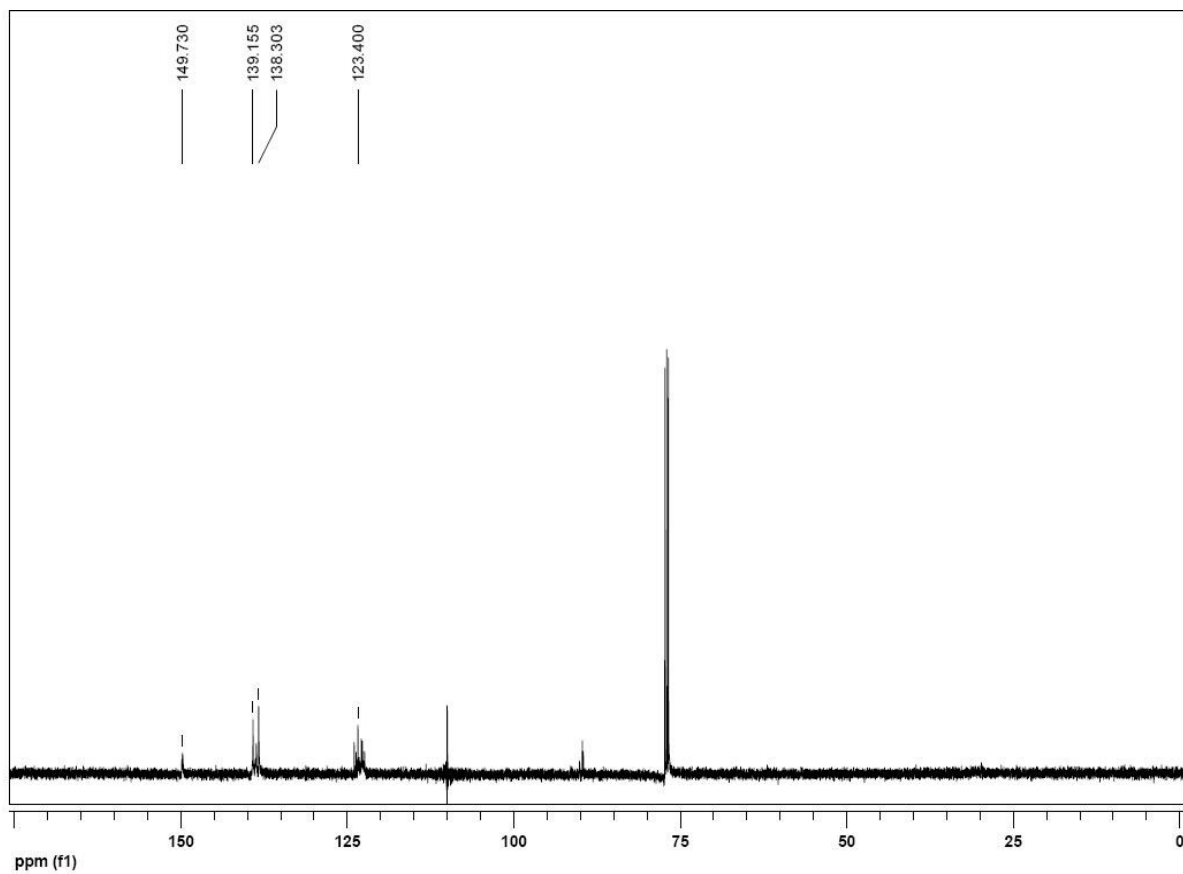


Figure S8. The ^{13}C NMR spectrum of compound **1** in CDCl_3

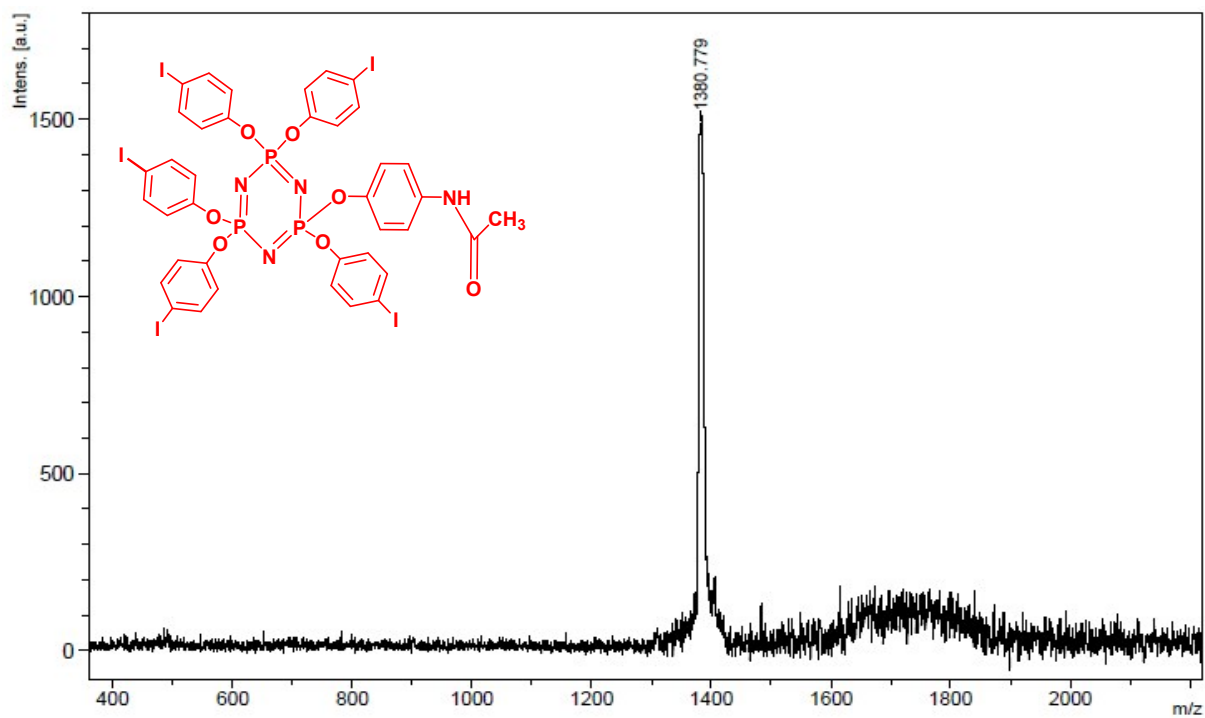


Figure S9. Positive ion and linear mode MALDI TOF-MS spectrum of compound **2**

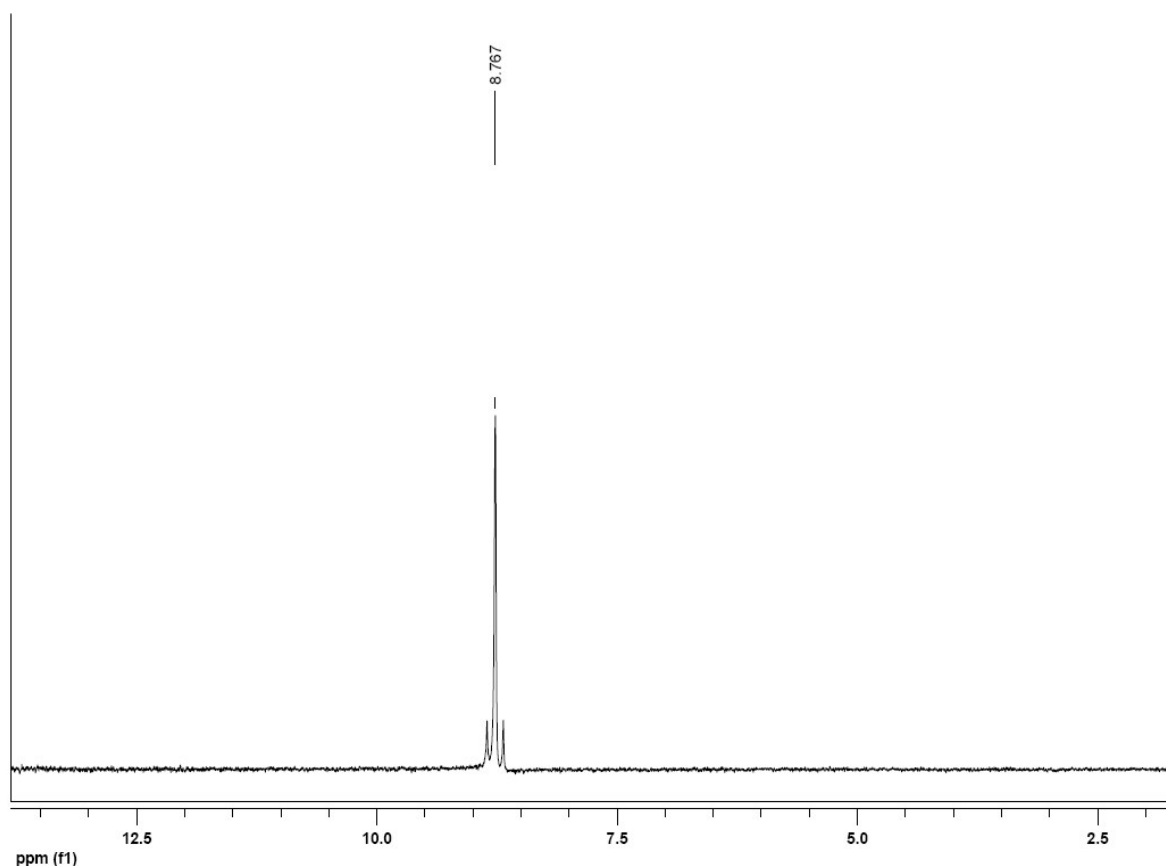


Figure S10. The ^{31}P NMR spectrum of compound **2** in CDCl_3

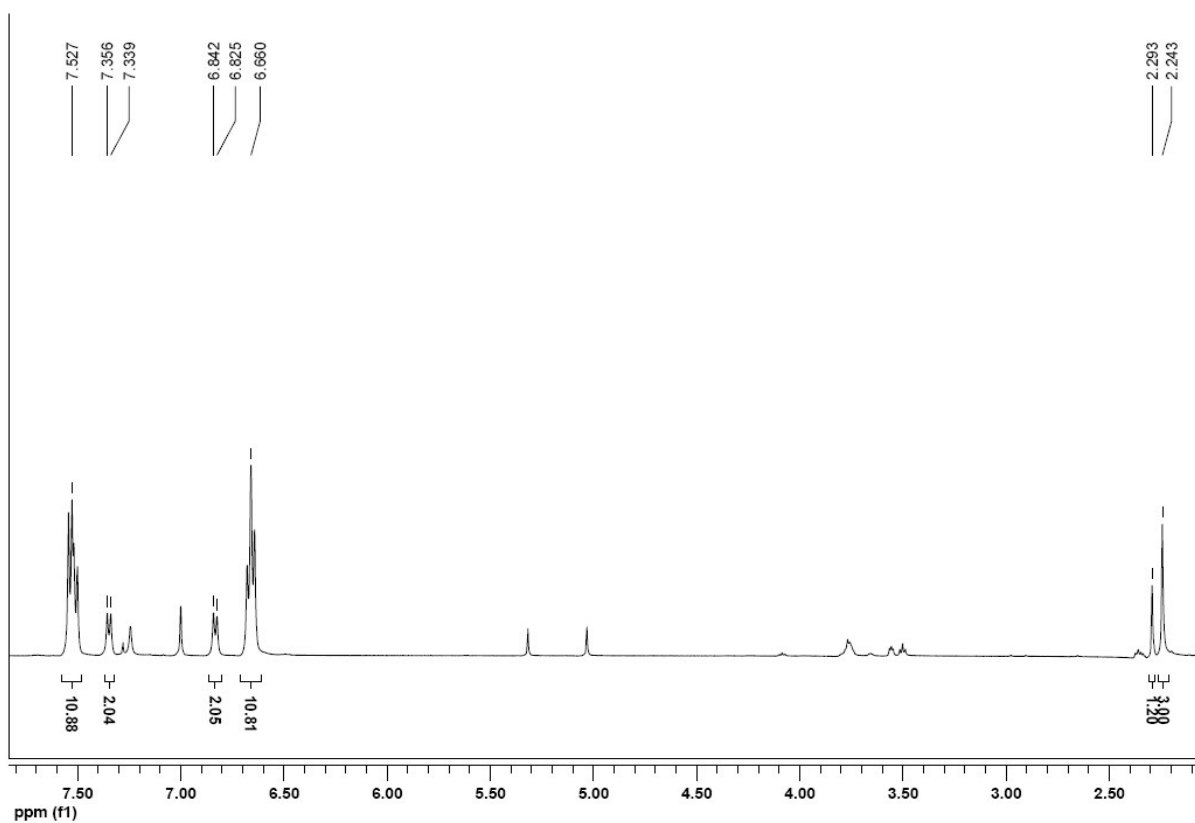


Figure S11. The ^1H NMR spectrum of compound **2** in CDCl_3

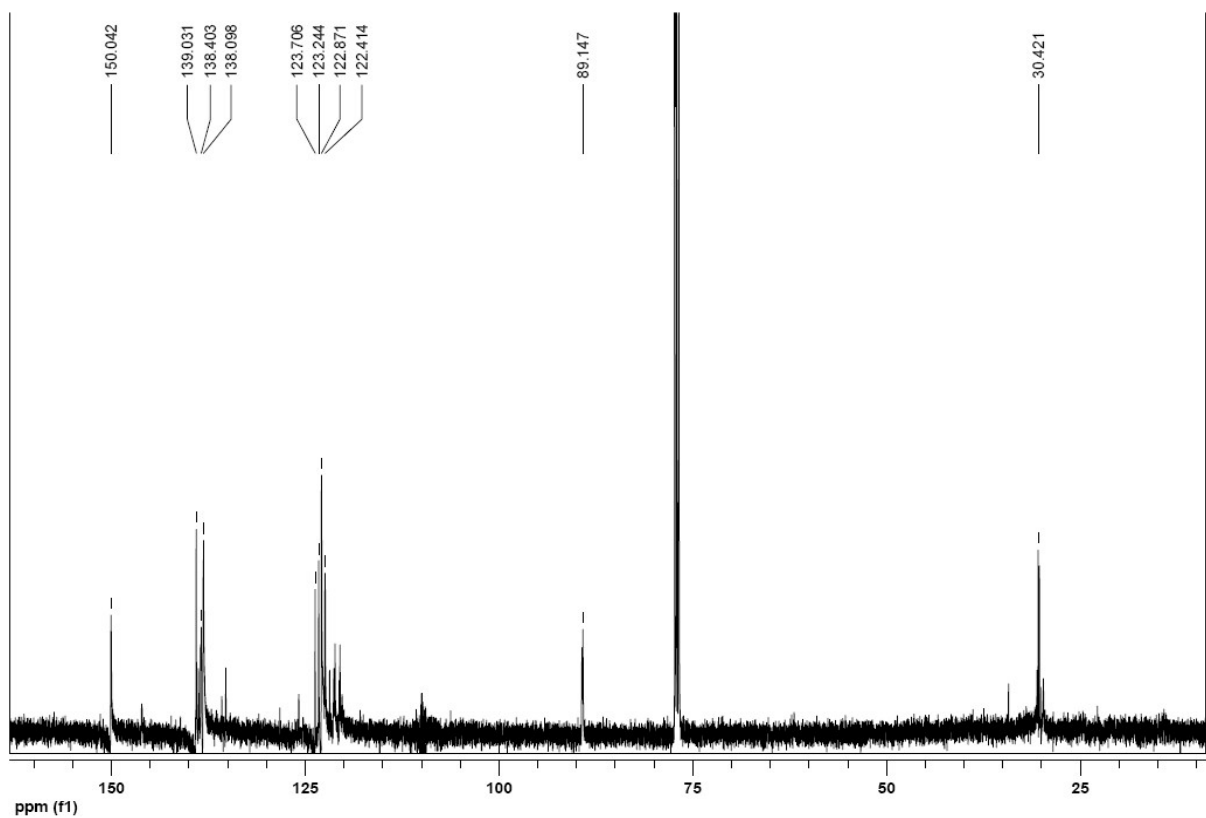


Figure S12. The ^{13}C NMR spectrum of compound **2** in CDCl_3

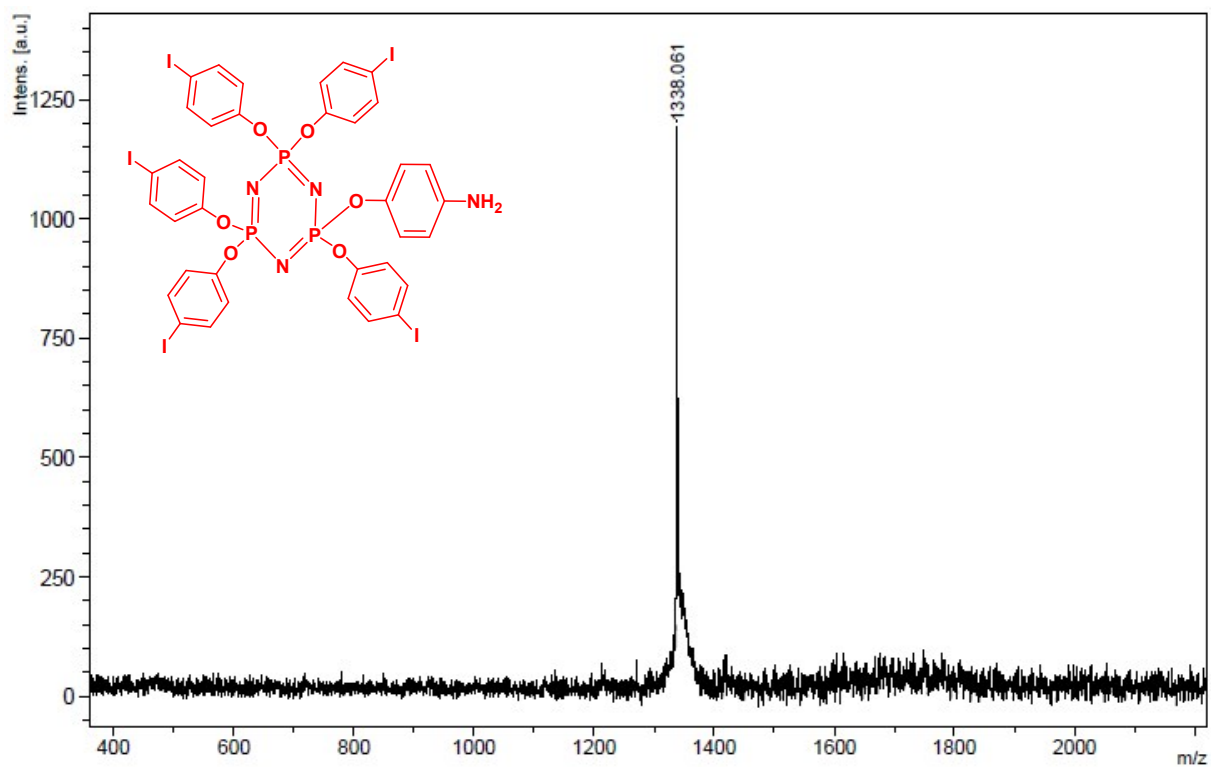


Figure S13. Positive ion and linear mode MALDI TOF-MS spectrum of compound **3**

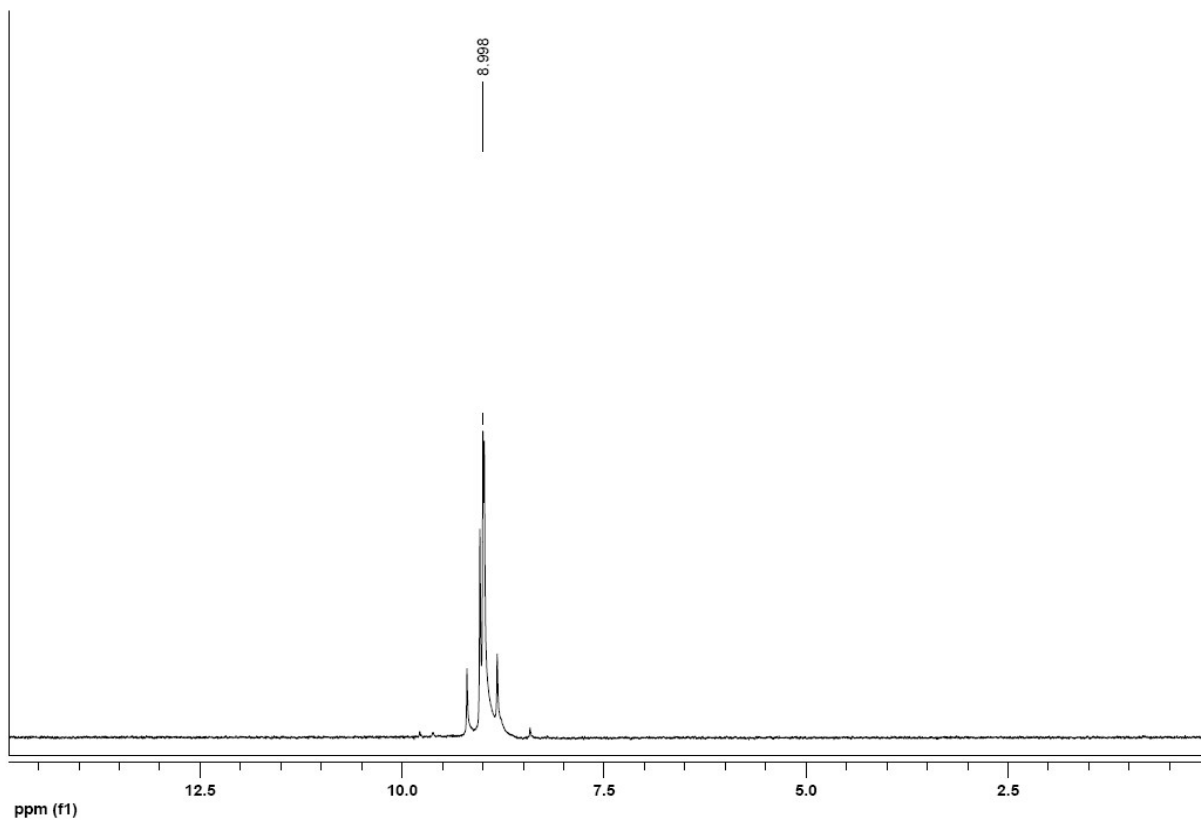


Figure S14. The ^{31}P NMR spectrum of compound **3** in CDCl_3

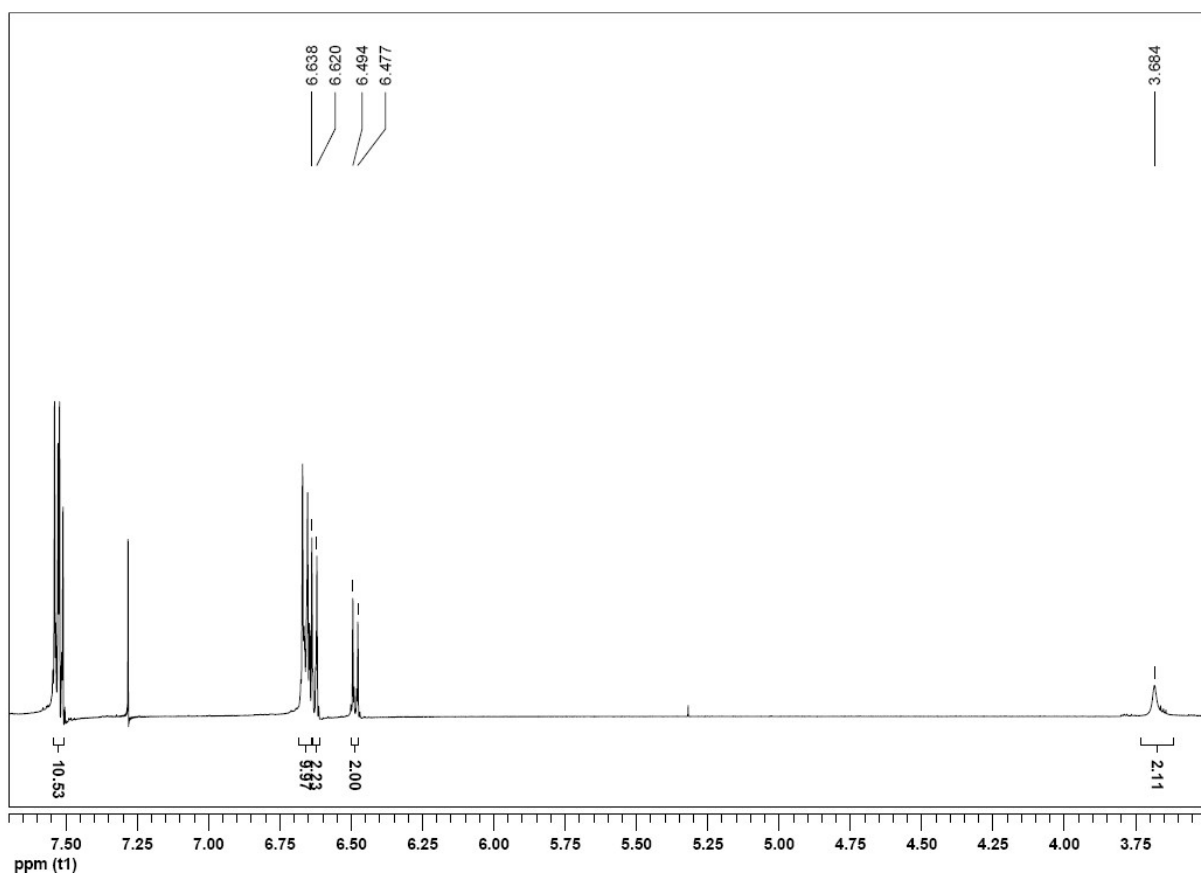


Figure S15. The ^1H NMR spectrum of compound **3** in CDCl_3

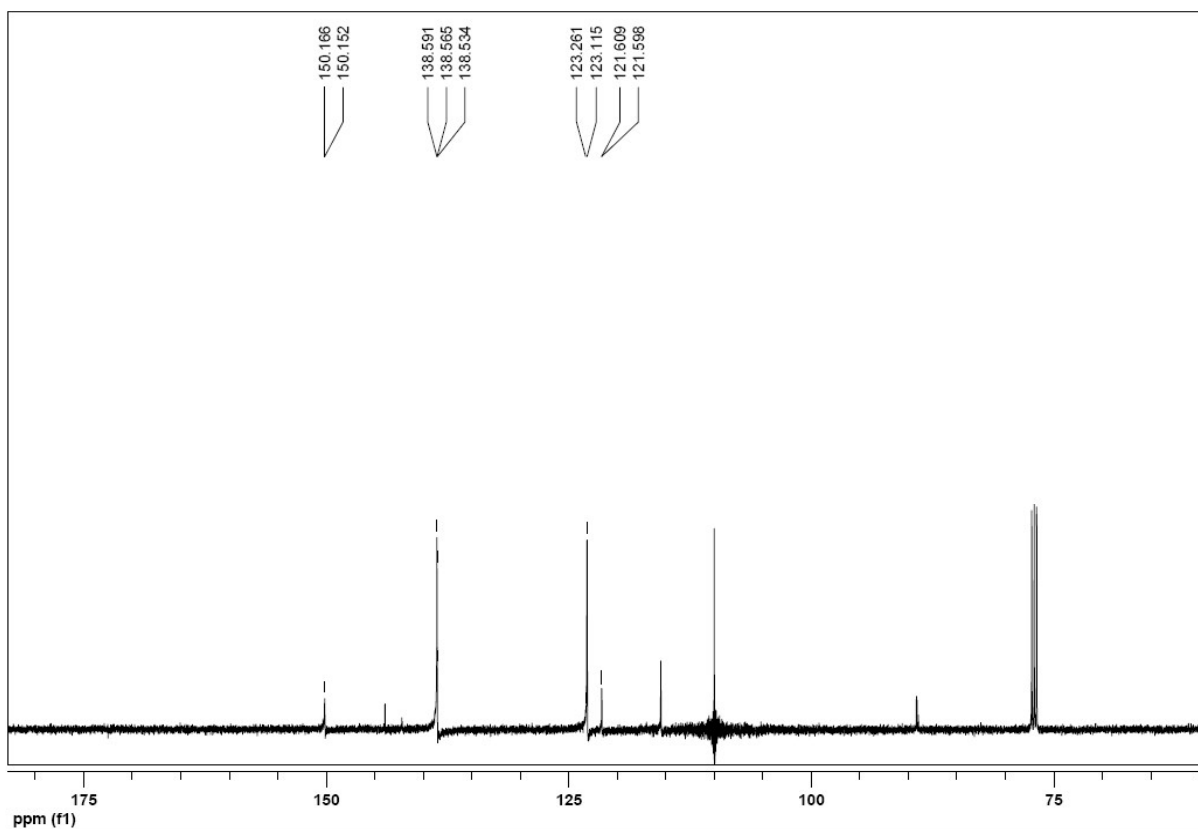


Figure S16. The ^{13}C NMR spectrum of compound **3** in CDCl_3

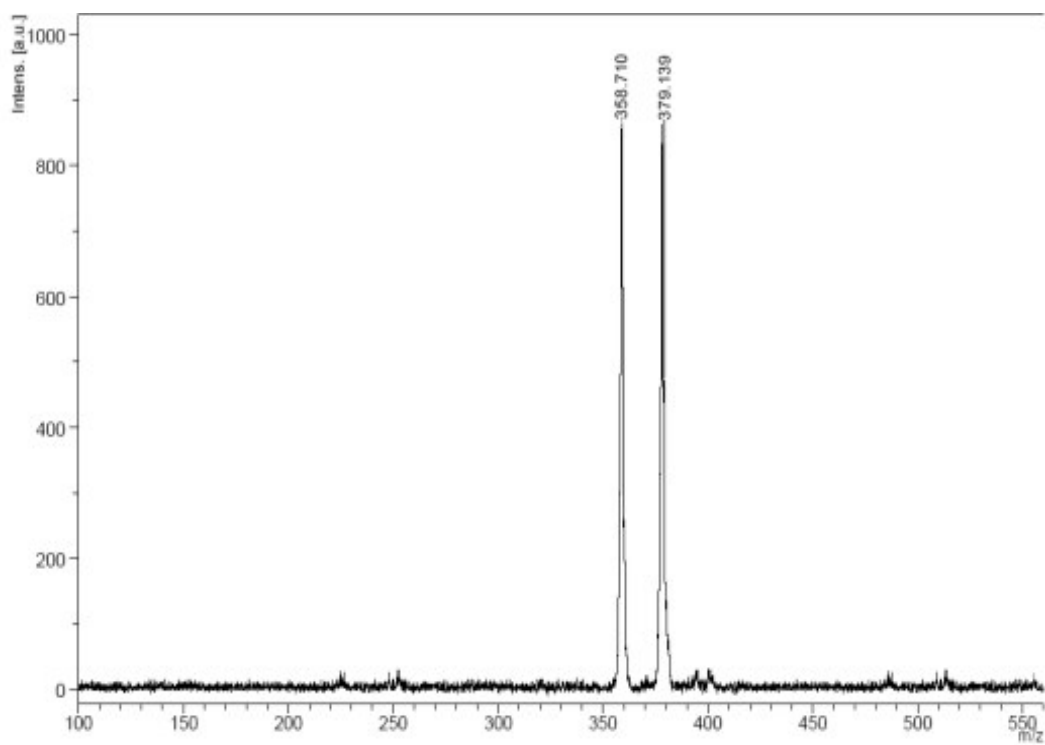


Figure S17. Positive ion and linear mode MALDI TOF-MS spectrum of compound **4**

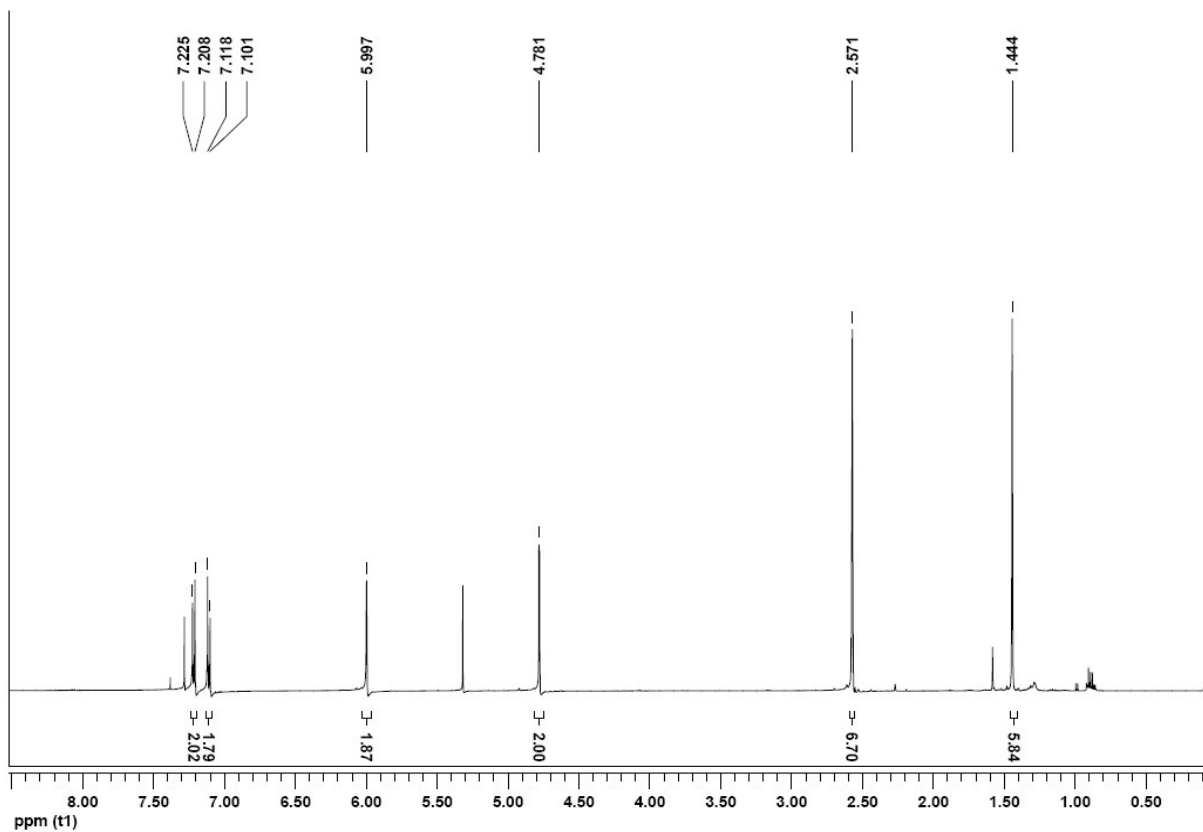


Figure S18. The ^1H NMR spectrum of compound **4** in CDCl_3

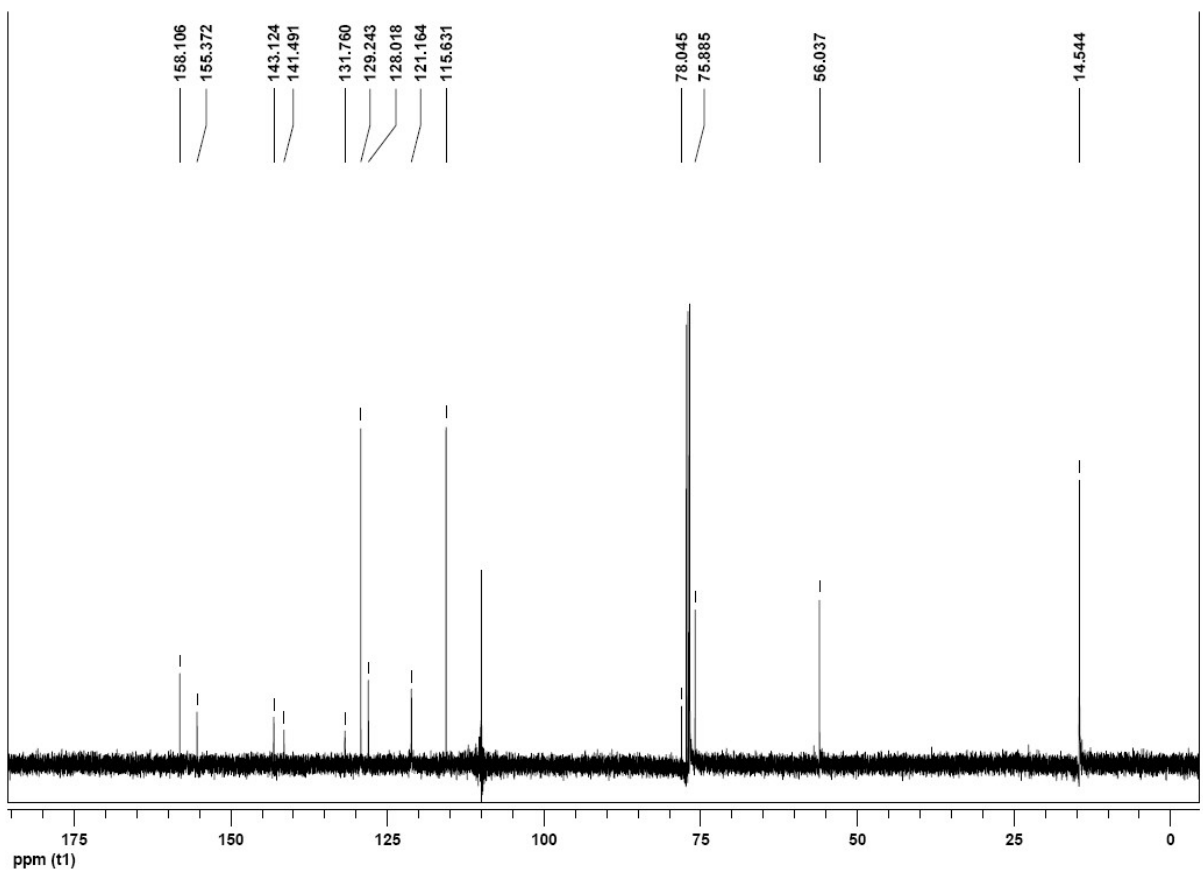


Figure S19. The ^{13}C NMR spectrum of compound **4** in CDCl_3

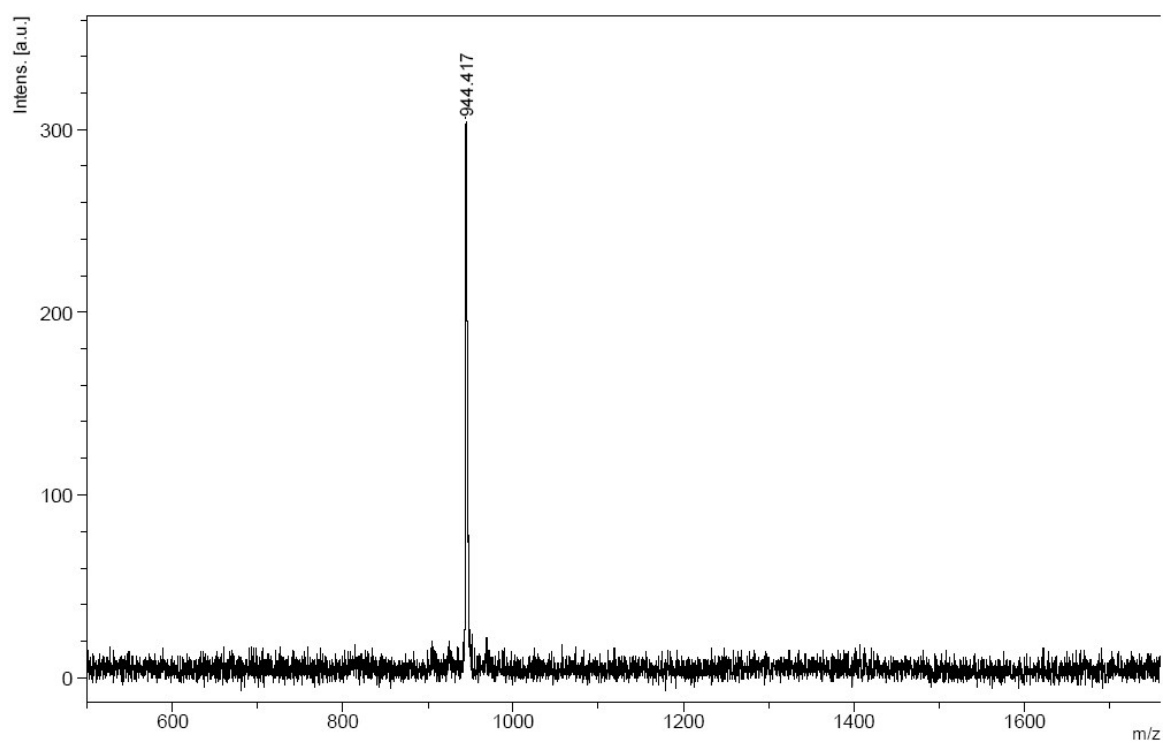


Figure S20. Positive ion and linear mode MALDI TOF-MS spectrum of compound **5**

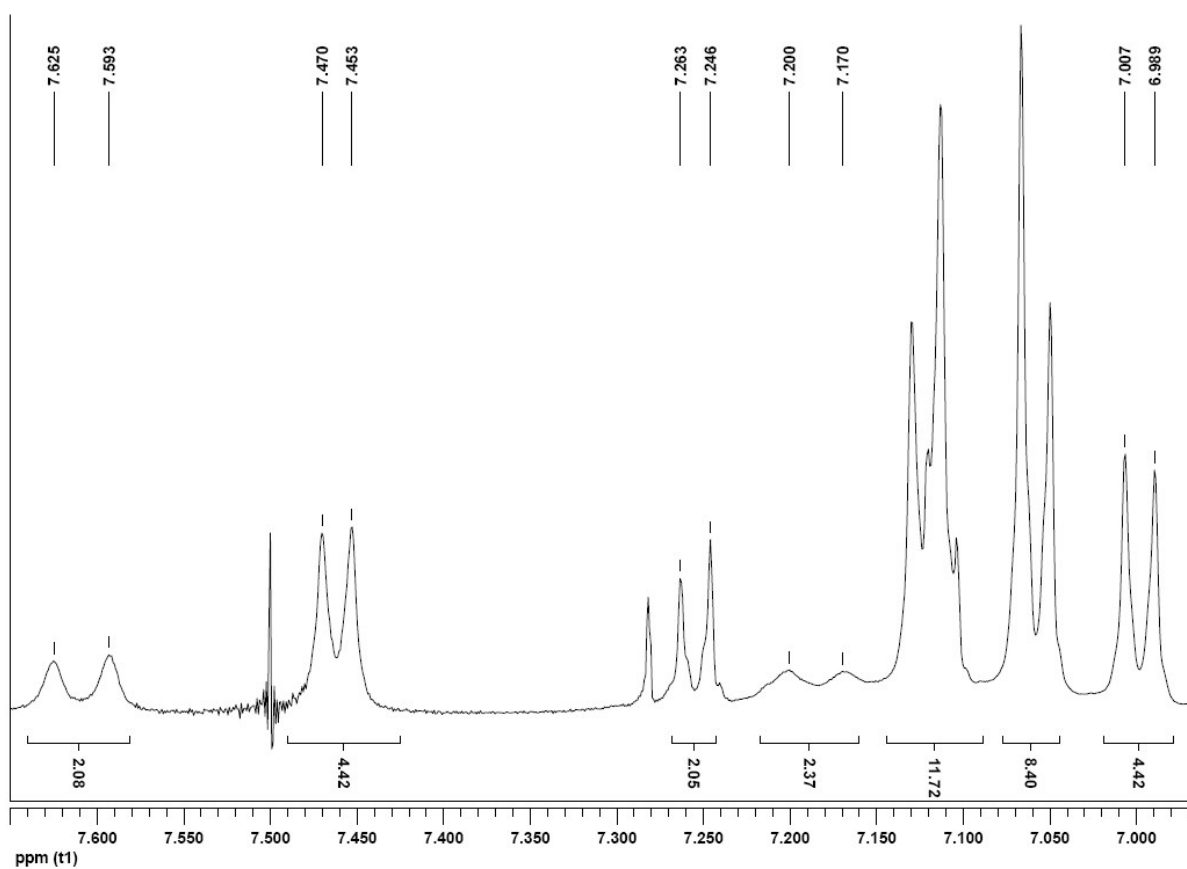


Figure S21. The ^1H NMR spectrum of compound **5** in CDCl_3 (aromatic region)

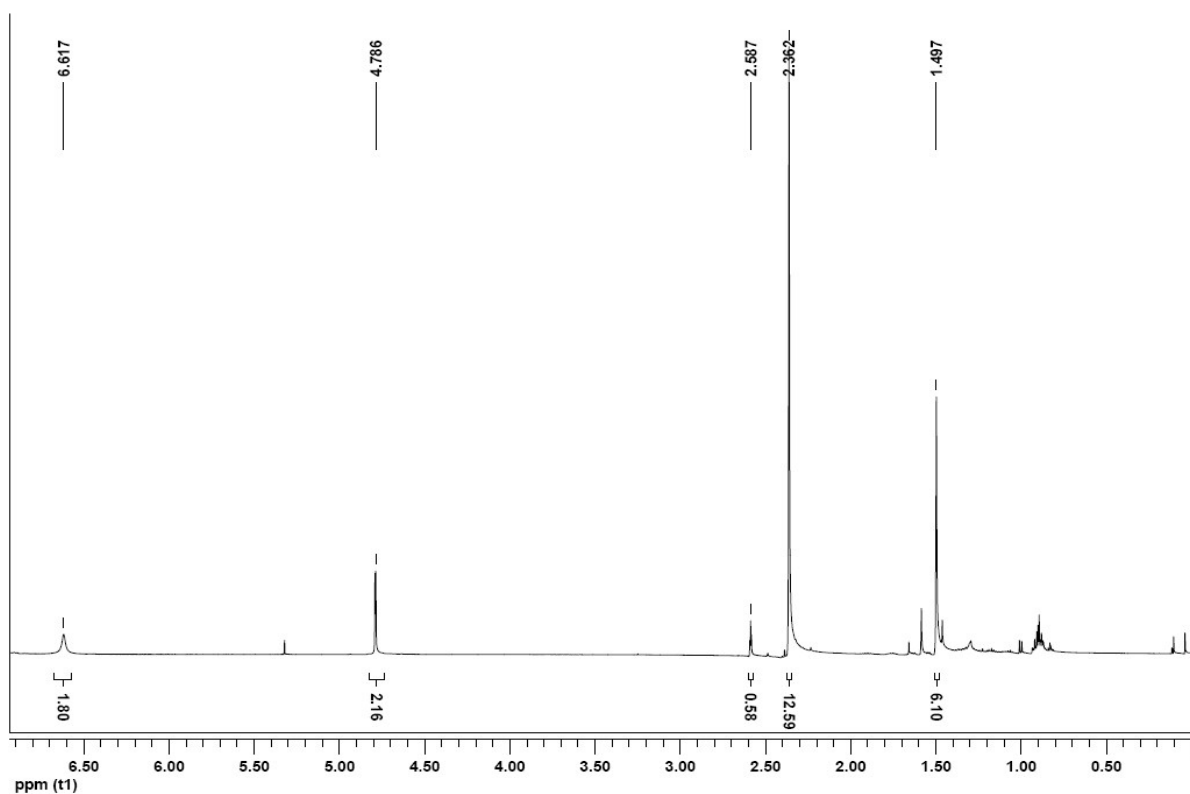


Figure S22. The ^1H NMR spectrum of compound **5** in CDCl_3 (aliphatic region)

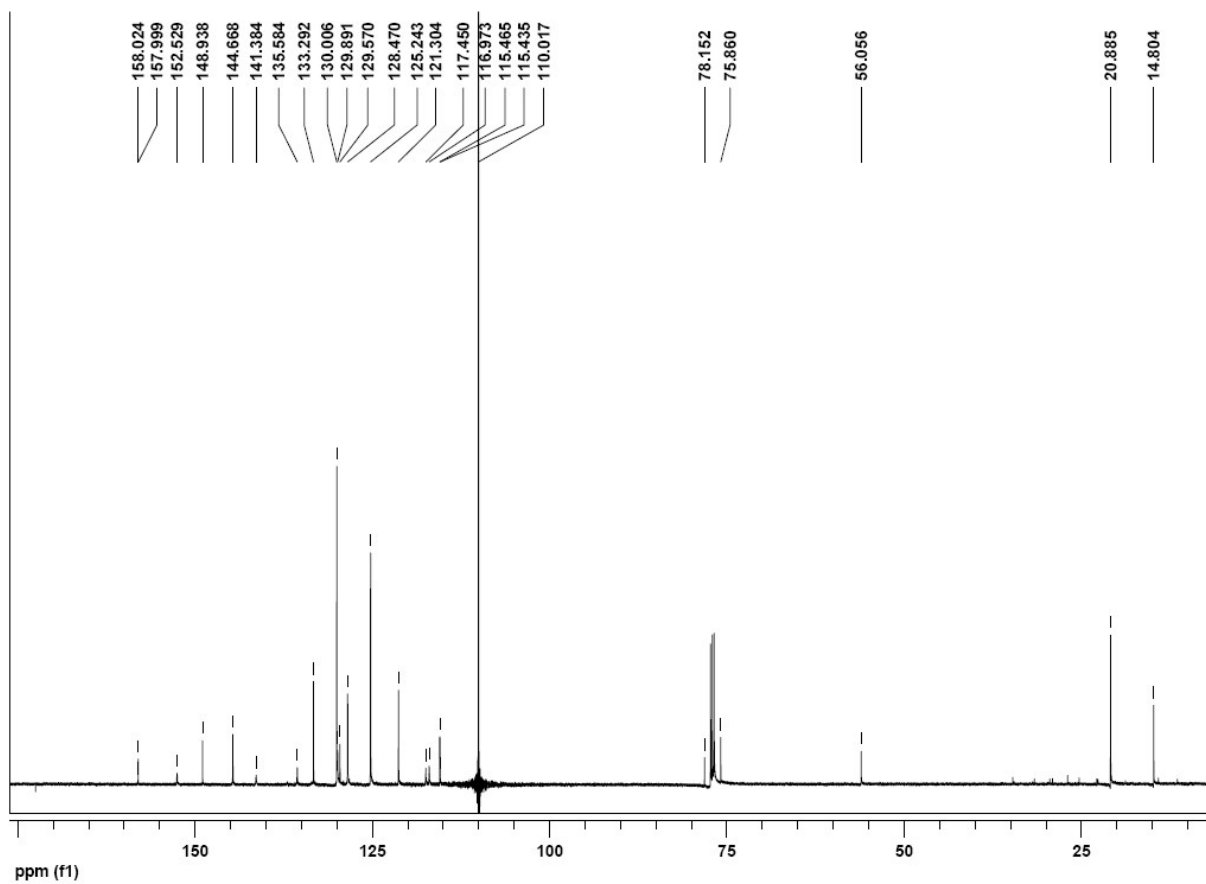


Figure S23. The ^{13}C NMR spectrum of compound **5** in CDCl_3

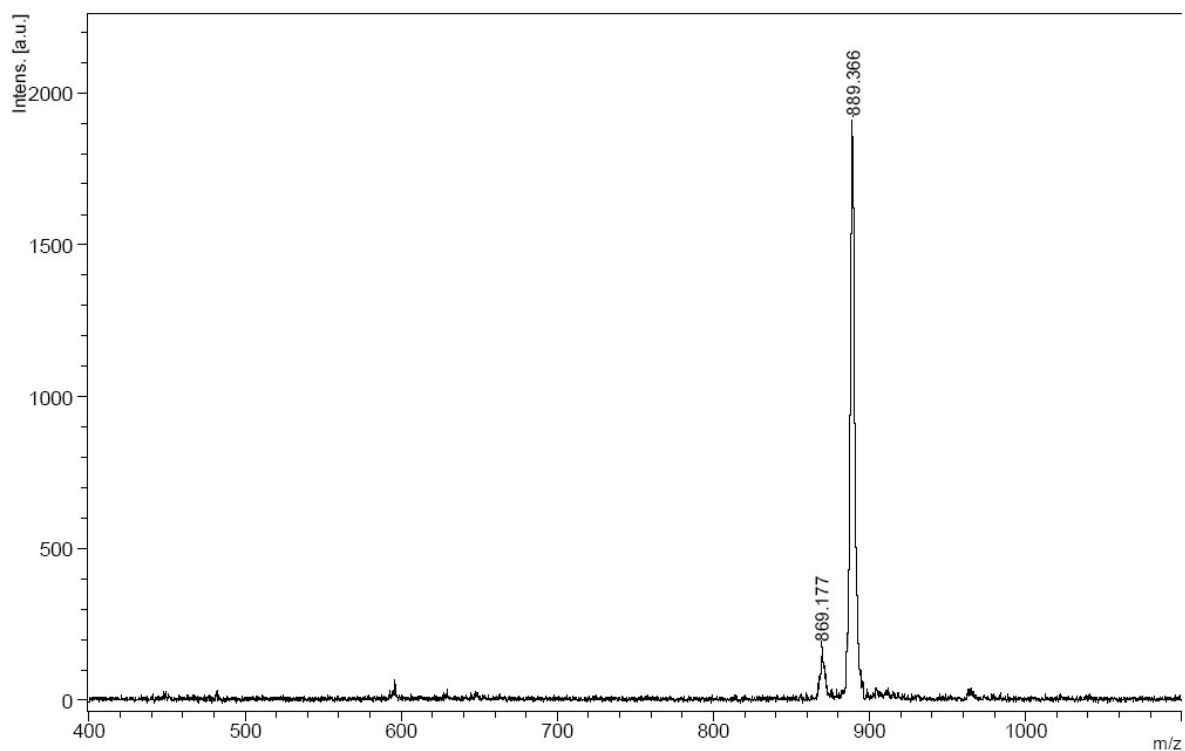


Figure S24. Positive ion and linear mode MALDI TOF-MS spectrum of compound **6**

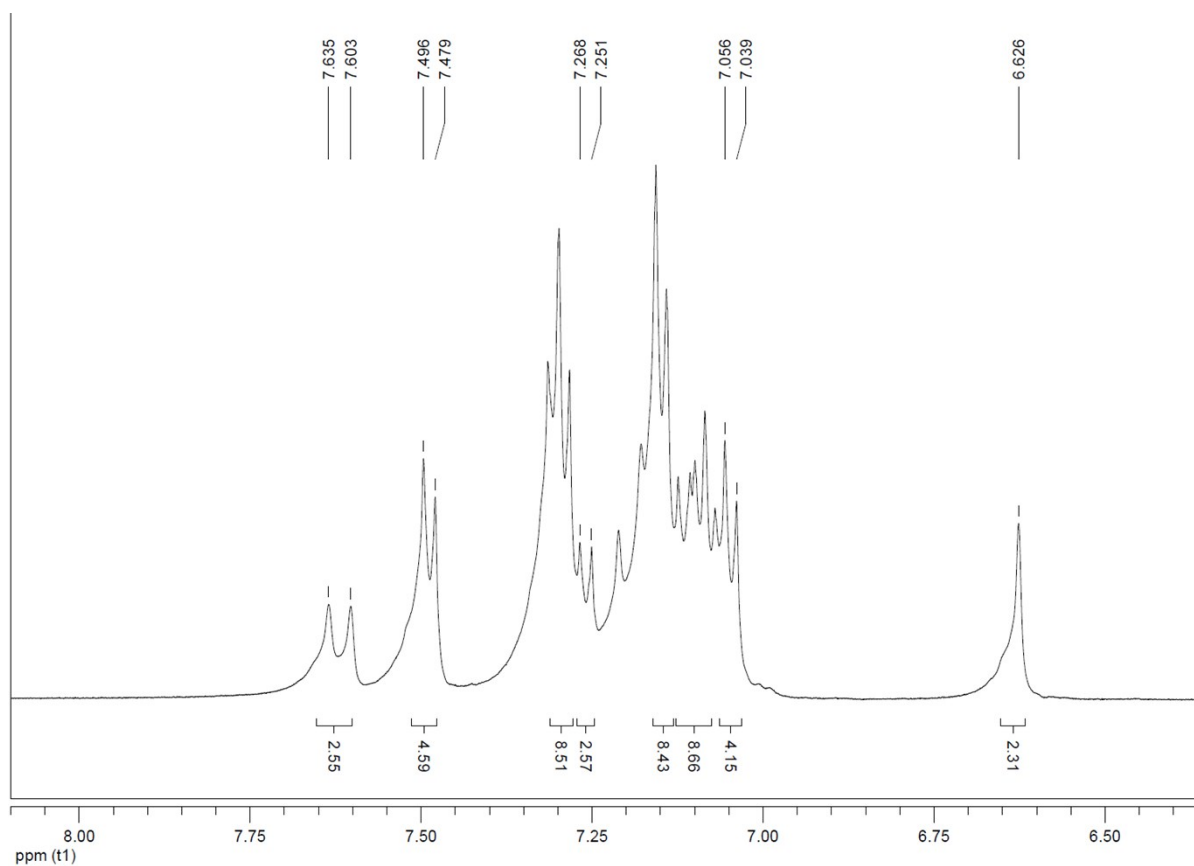


Figure S25. The ^1H NMR spectrum of compound **6** in CDCl_3 (aromatic region)

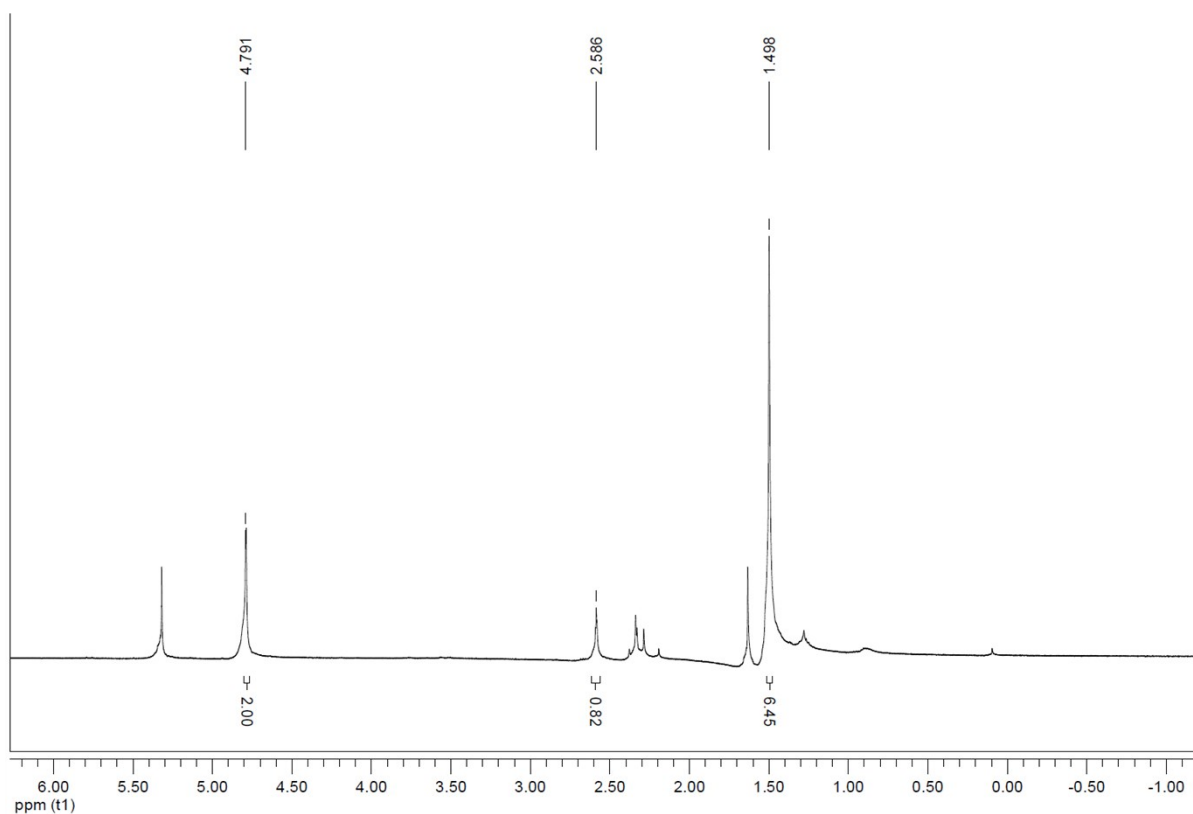


Figure S26. The ¹H NMR spectrum of compound 6 in CDCl₃ (aliphatic region)

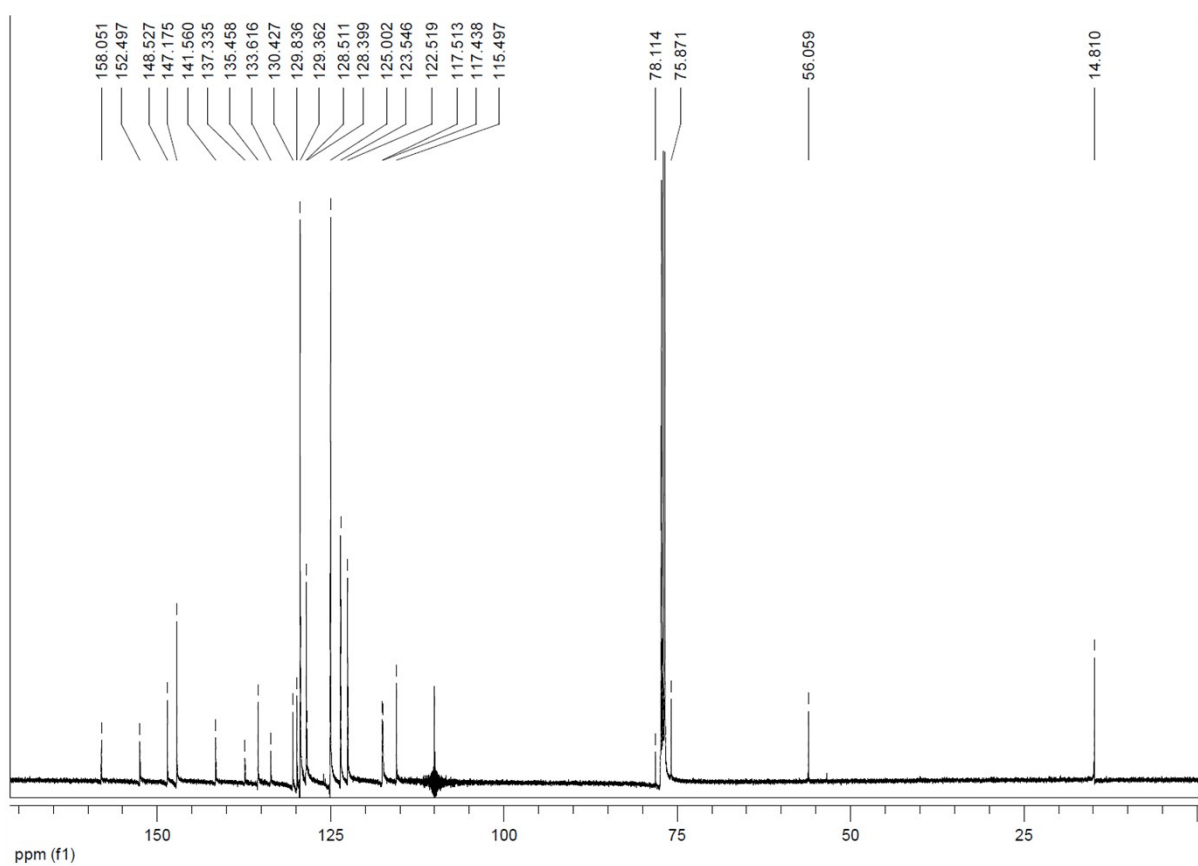


Figure S27. The ¹³C NMR spectrum of compound 7 in CDCl₃

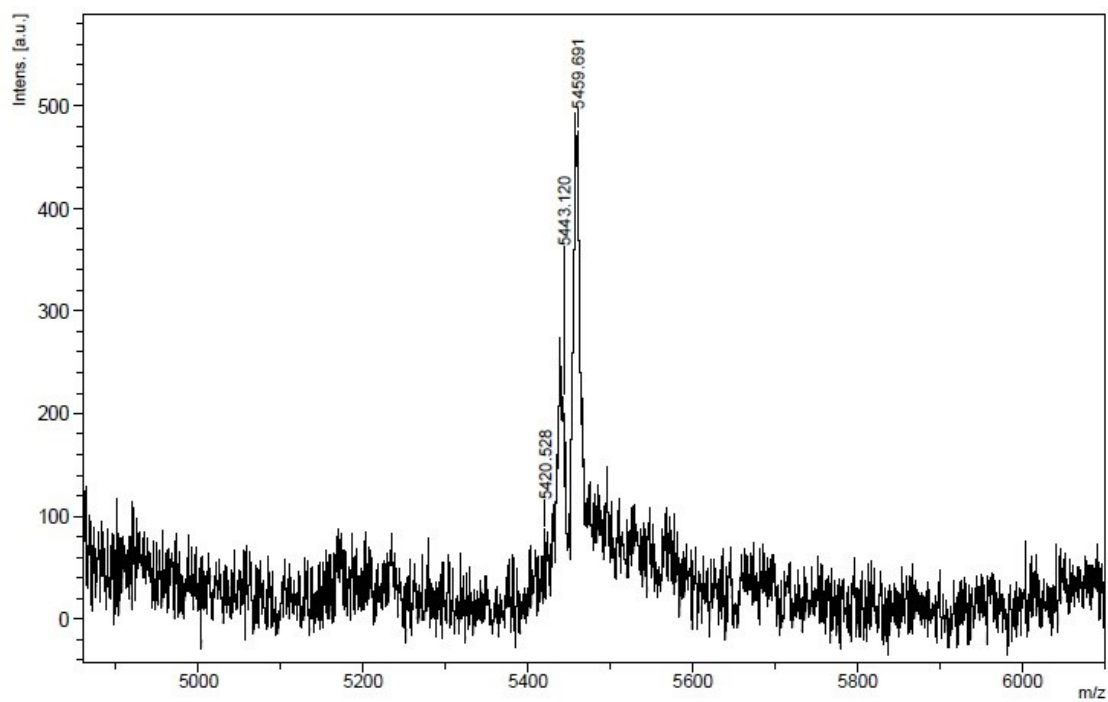


Figure S28. Positive ion and linear mode MALDI TOF-MS spectrum of compound 7

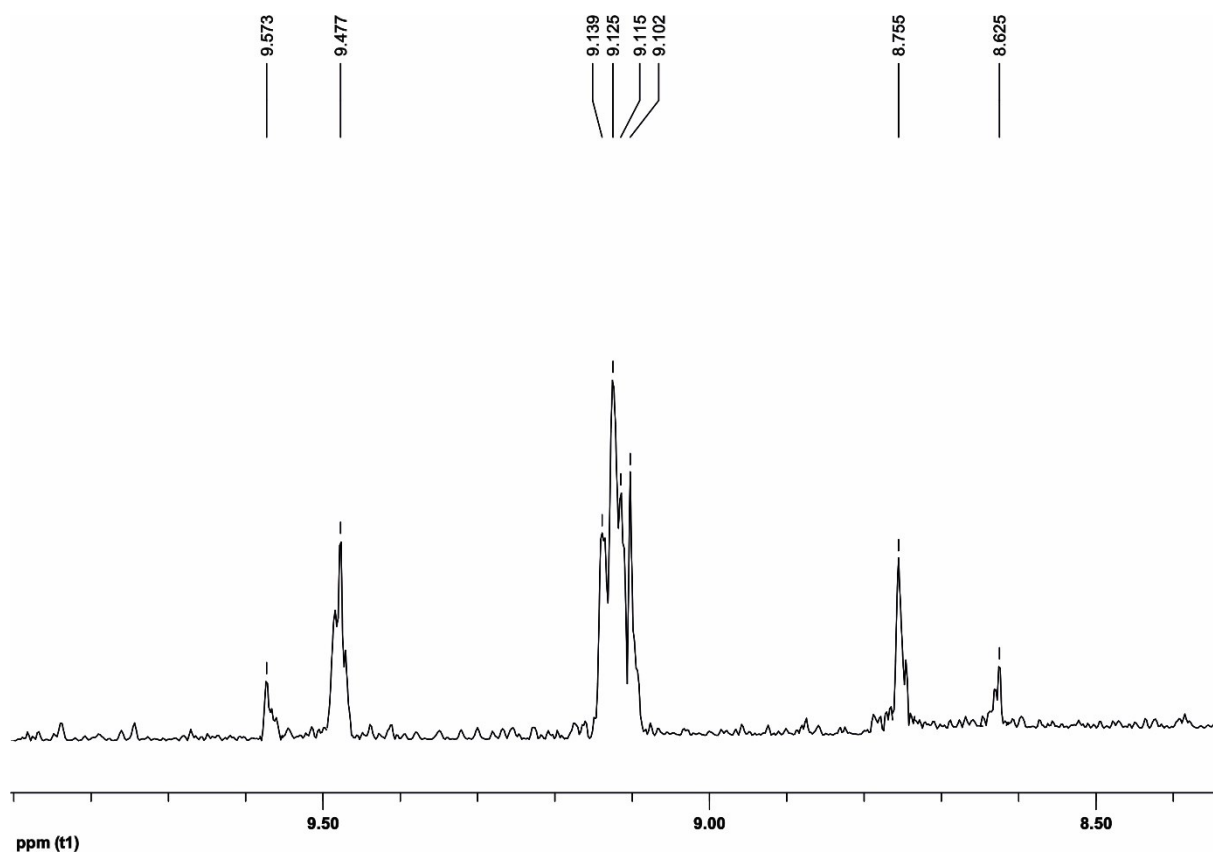


Figure S29. The ^{31}P NMR spectrum of compound 7 in $\text{d}_8\text{-THF}$

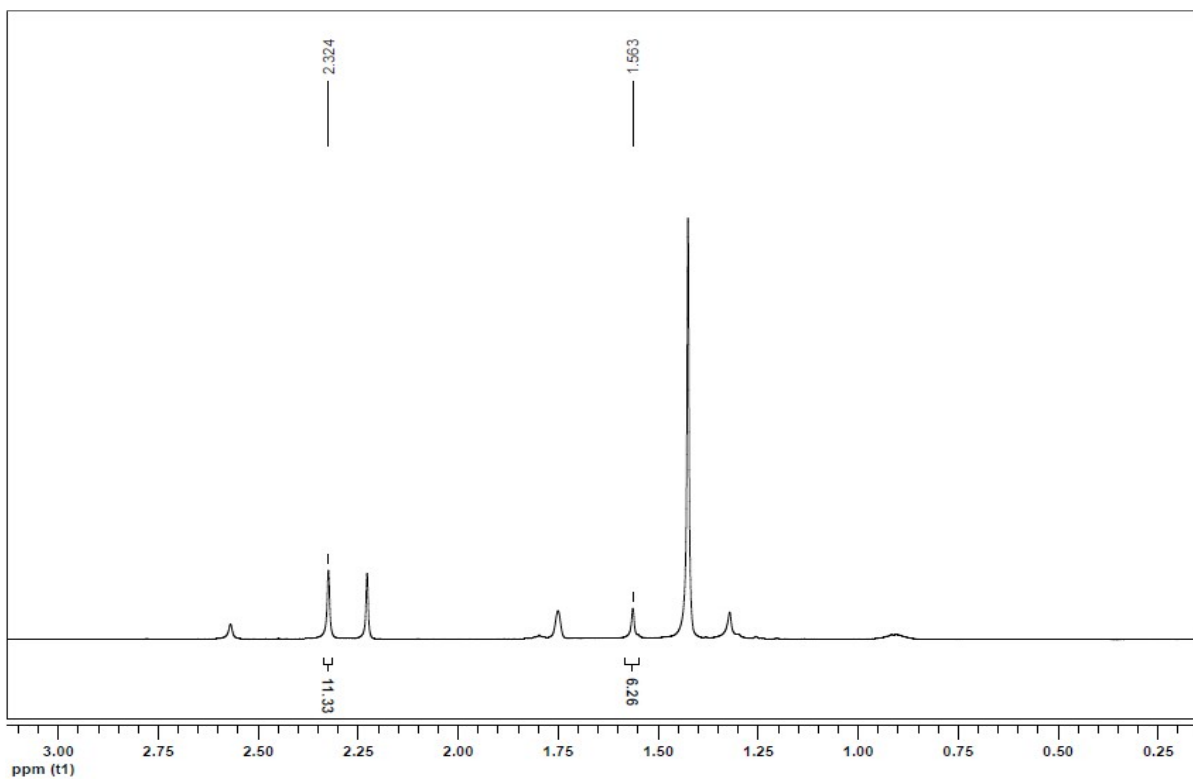


Figure S30. The ^1H NMR spectrum of compound 7 in d_8 -THF (aliphatic region)

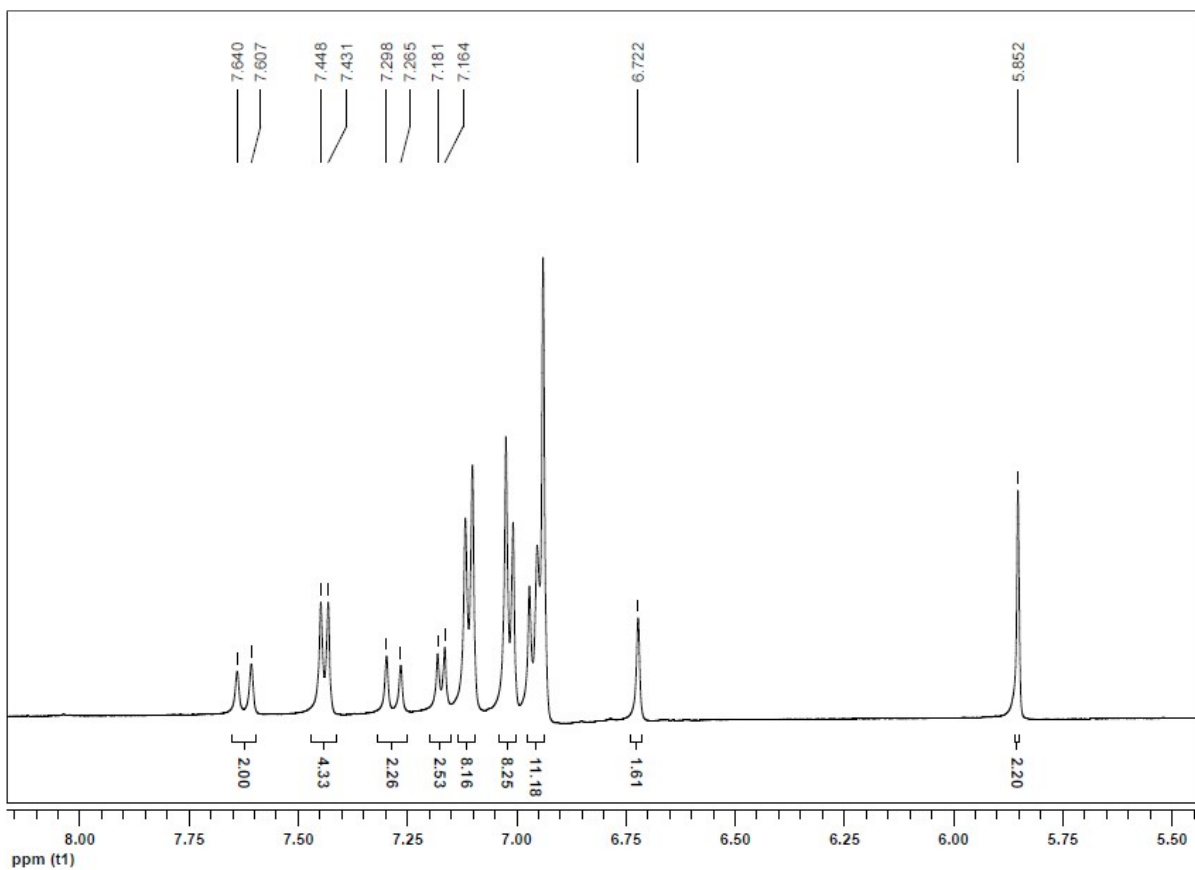


Figure S31. The ^1H NMR spectrum of compound 7 in d_8 -THF (aromatic region)

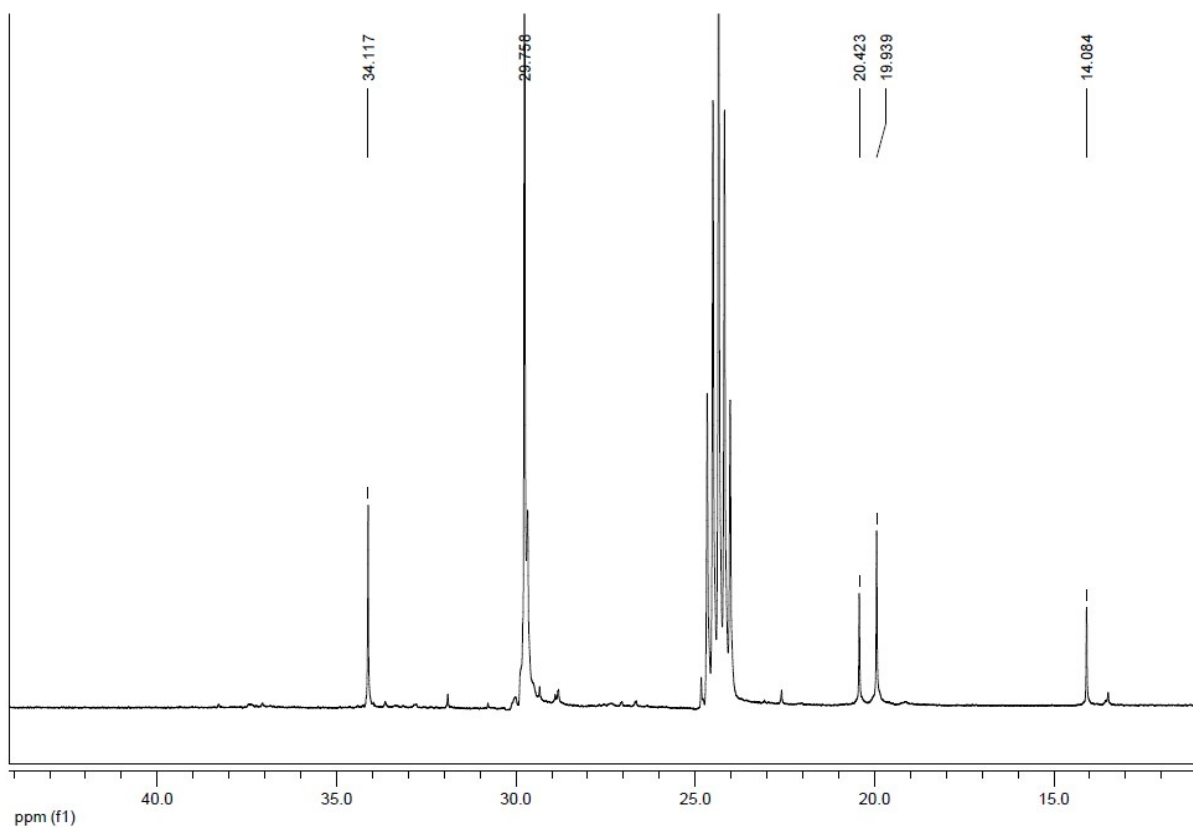


Figure S32. The ^{13}C NMR spectrum of compound **7** in d_8 -THF (aliphatic region)

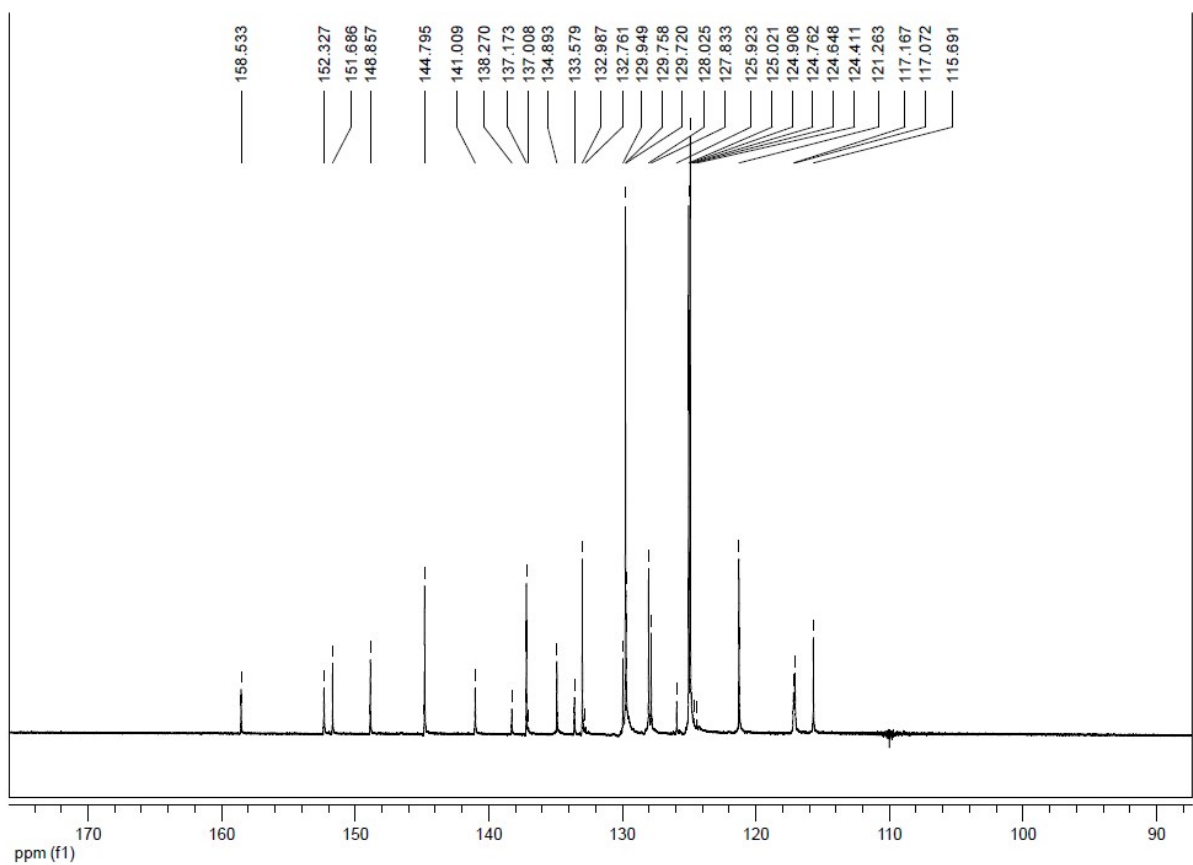


Figure S33. The ^{13}C NMR spectrum of compound **7** in d_8 -THF (aromatic region)

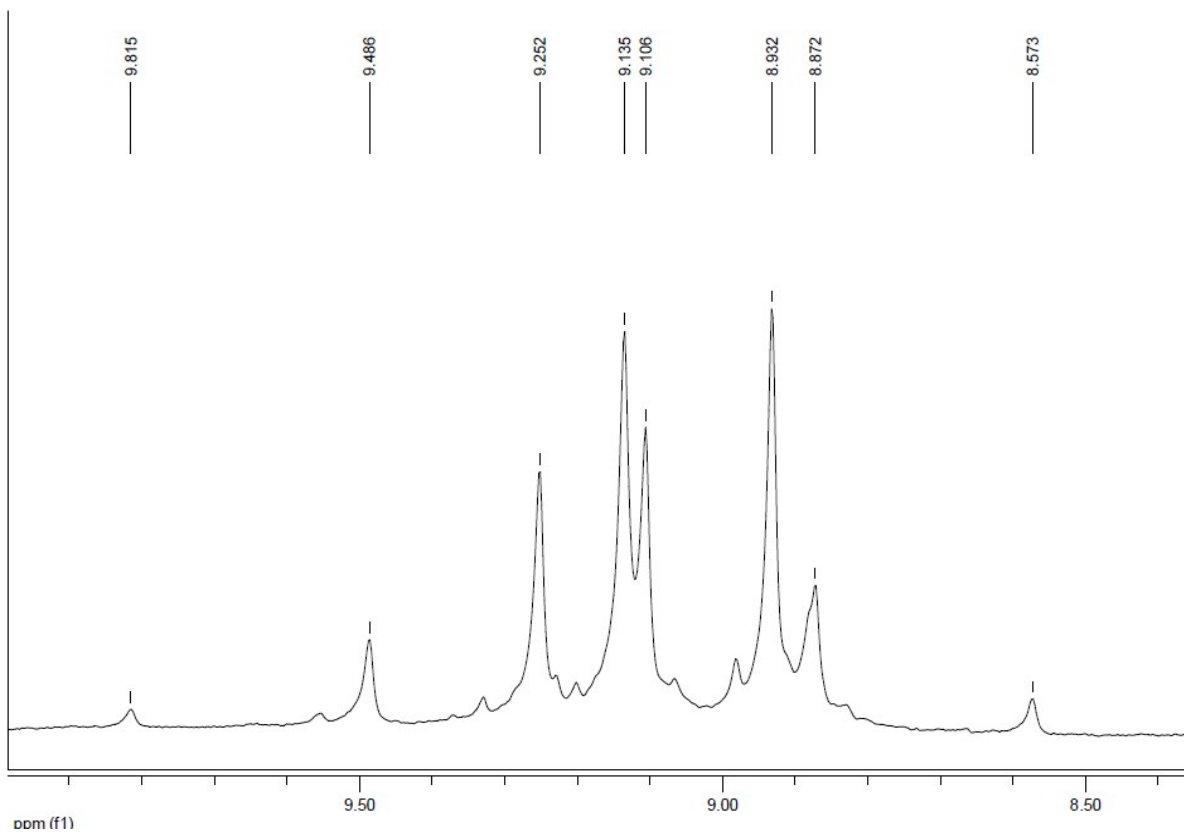


Figure S34. The ^{31}P NMR spectrum of compound **8** in d_8 -THF

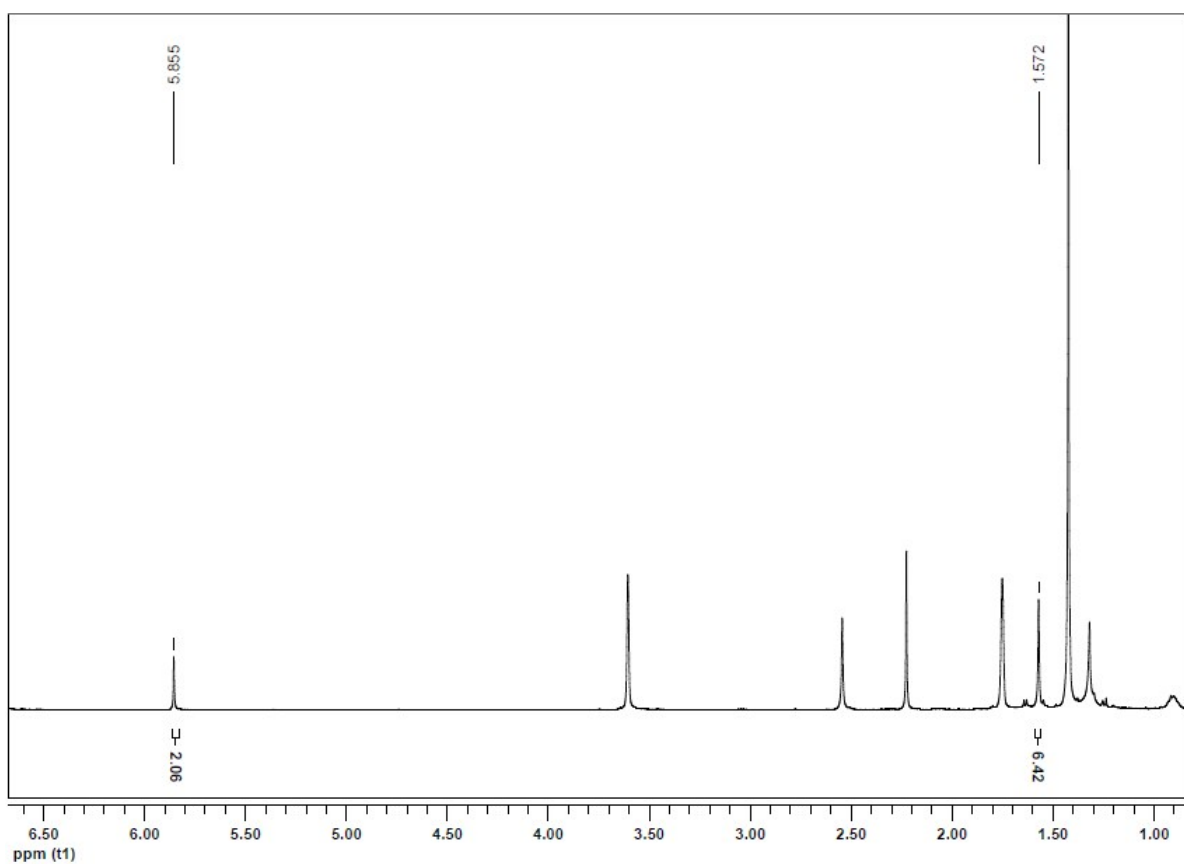


Figure S35. The ^1H NMR spectrum of compound **8** in d_8 -THF (aliphatic region)

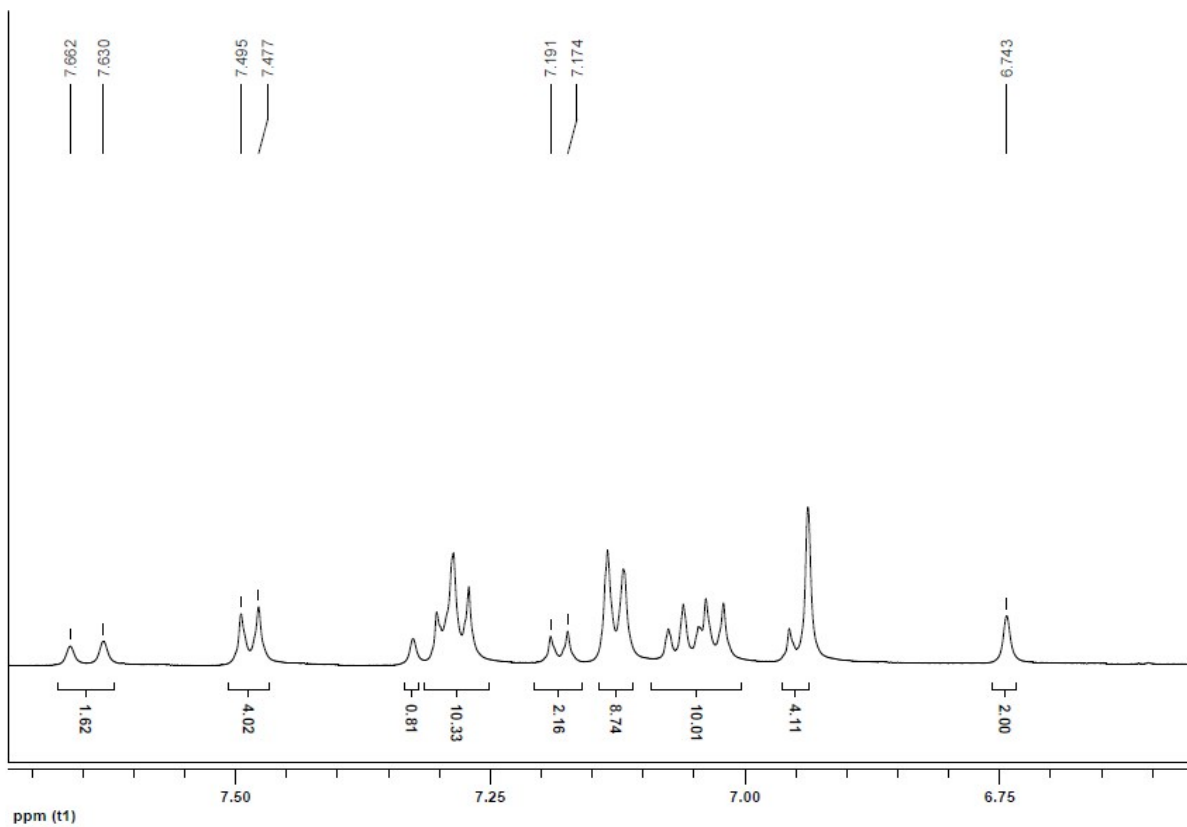


Figure S36. The ^1H NMR spectrum of compound **8** in d_8 -THF (aromatic region)

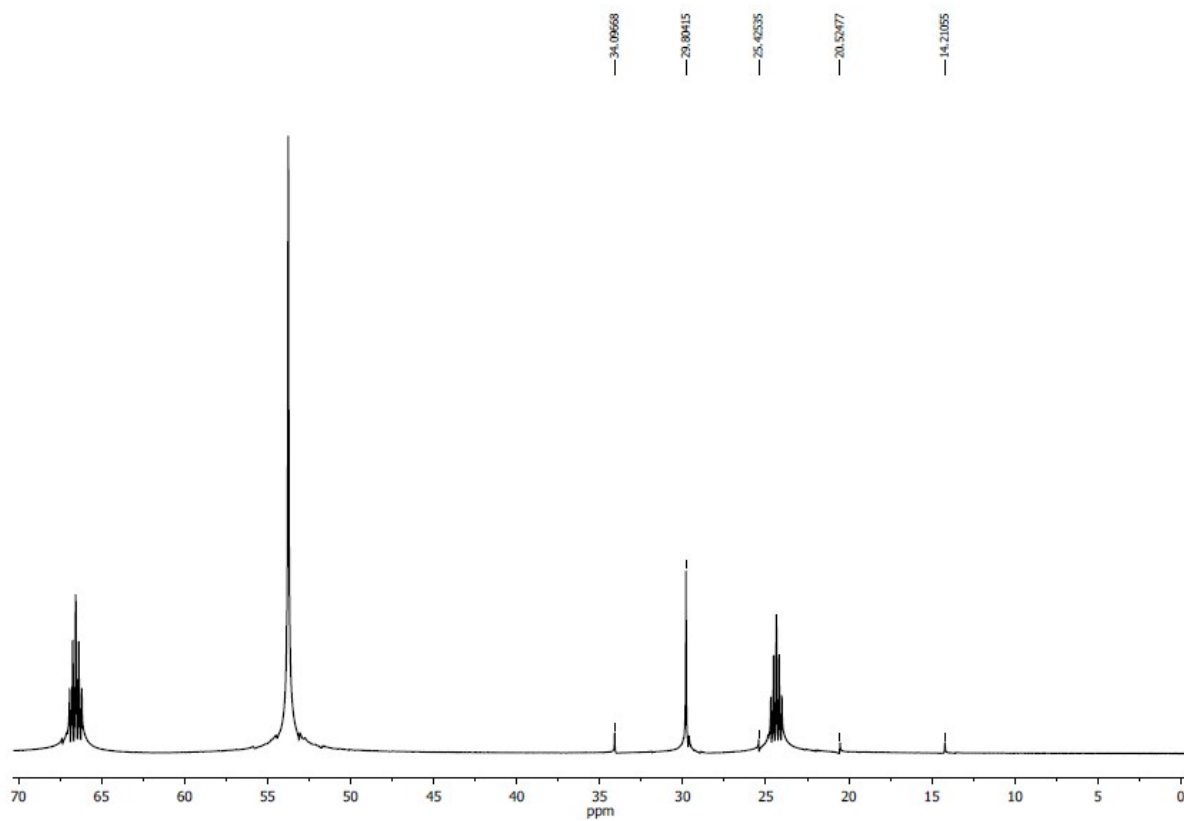


Figure S37. The ^{13}C NMR spectrum of compound **8** in d_8 -THF (aliphatic region)

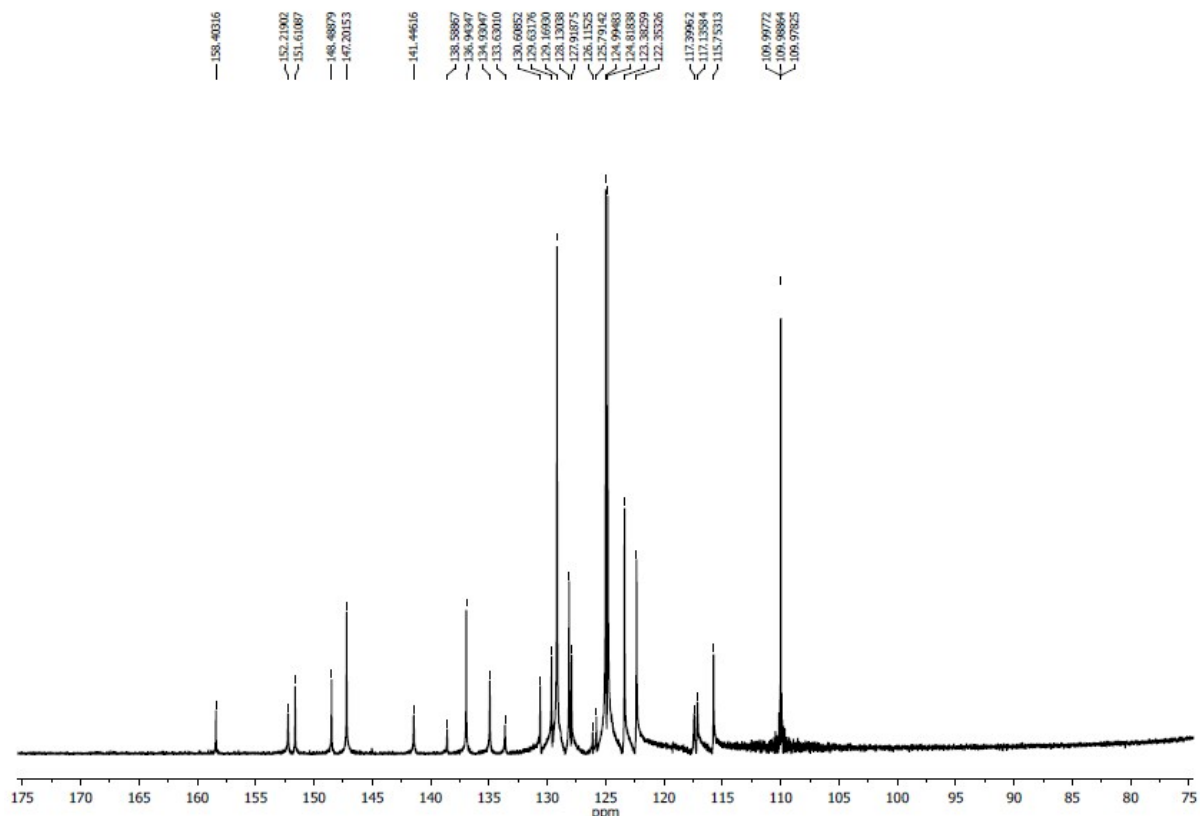


Figure S38. The ^{13}C NMR spectrum of compound **8** in d_8 -THF (aromatic region)

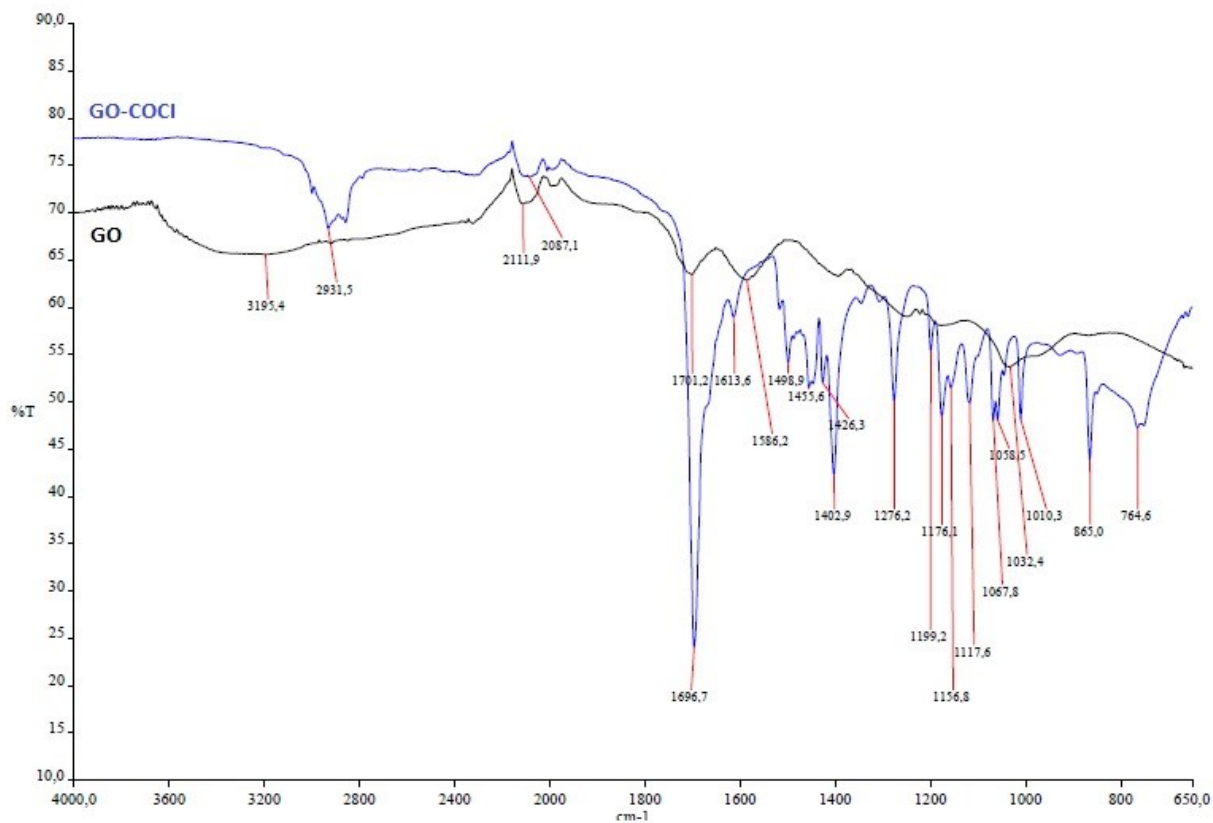


Figure S39. FT-IR spectra of GO and GO-COCl compounds

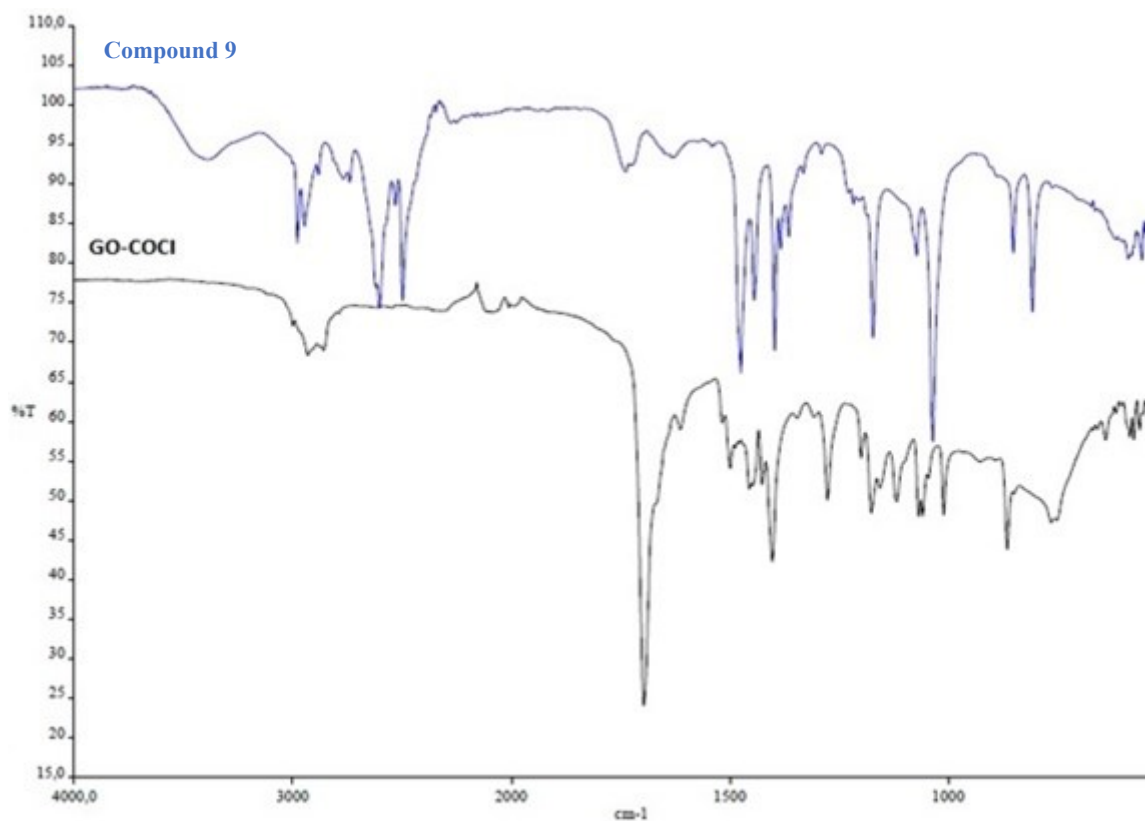


Figure S40. FT-IR Spectra of compound **9** and GO-COCl

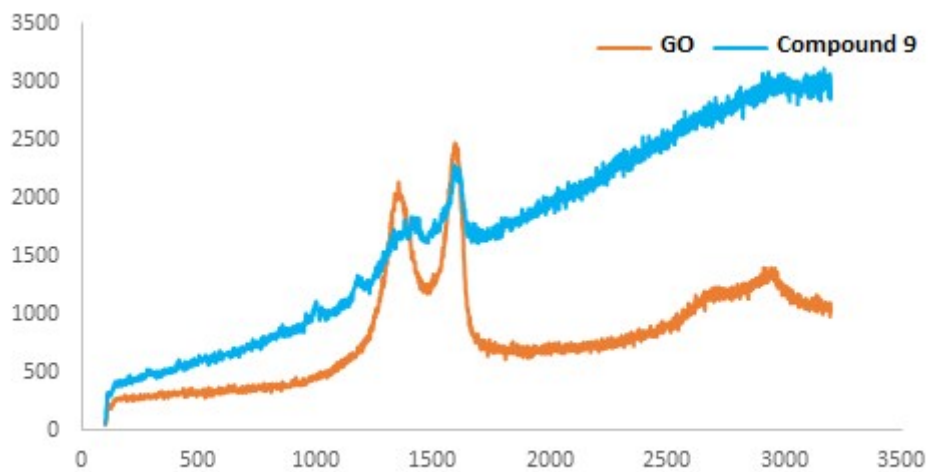


Figure S41. Raman Spectra of compound **9** and GO

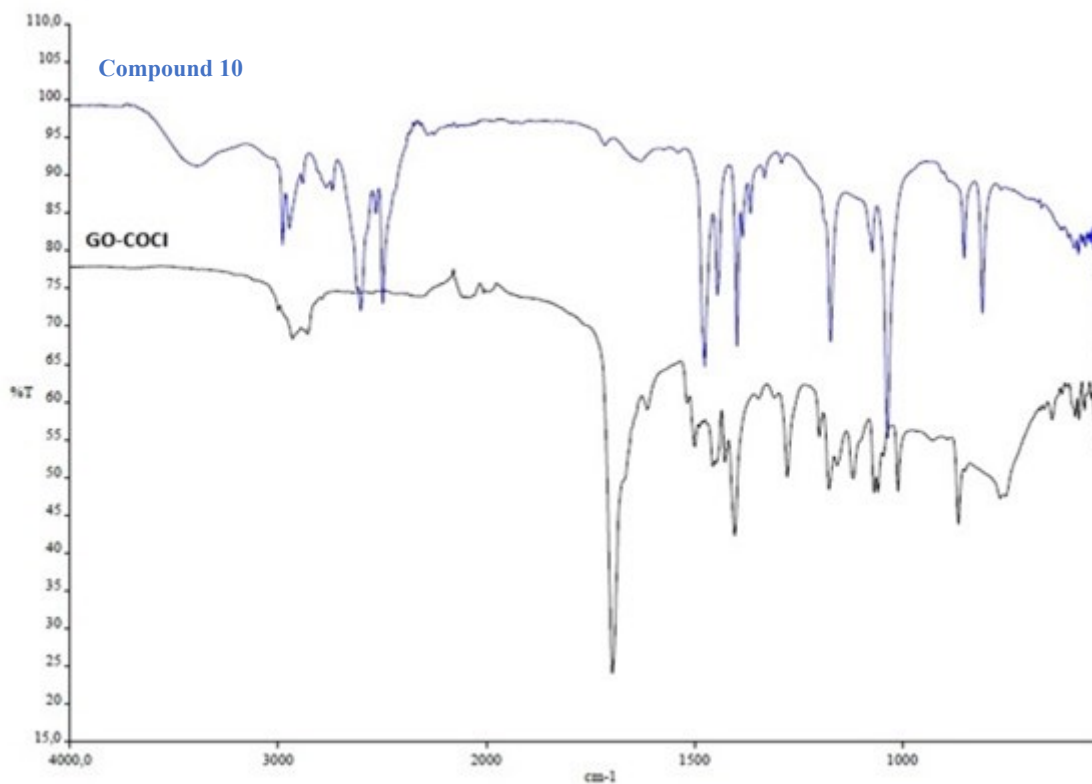


Figure S42. FT-IR Spectra of compounds **10** and GO-COCl

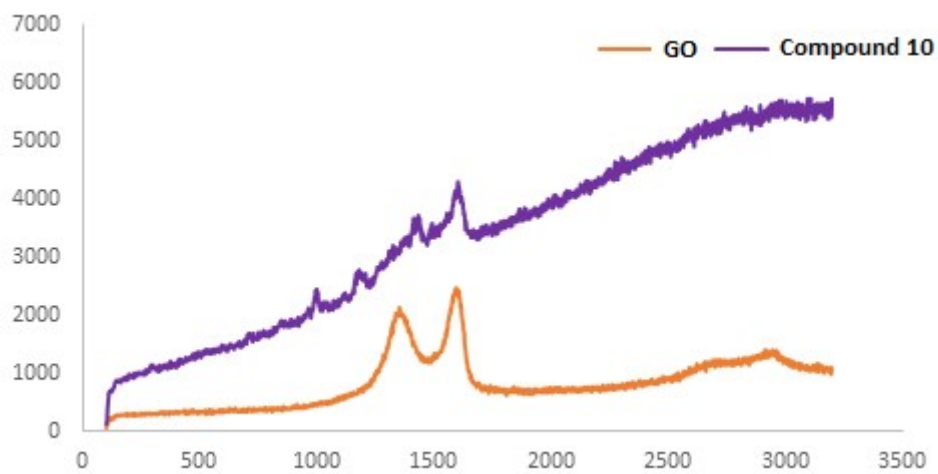


Figure S43. Raman Spectra of compound **10** and GO

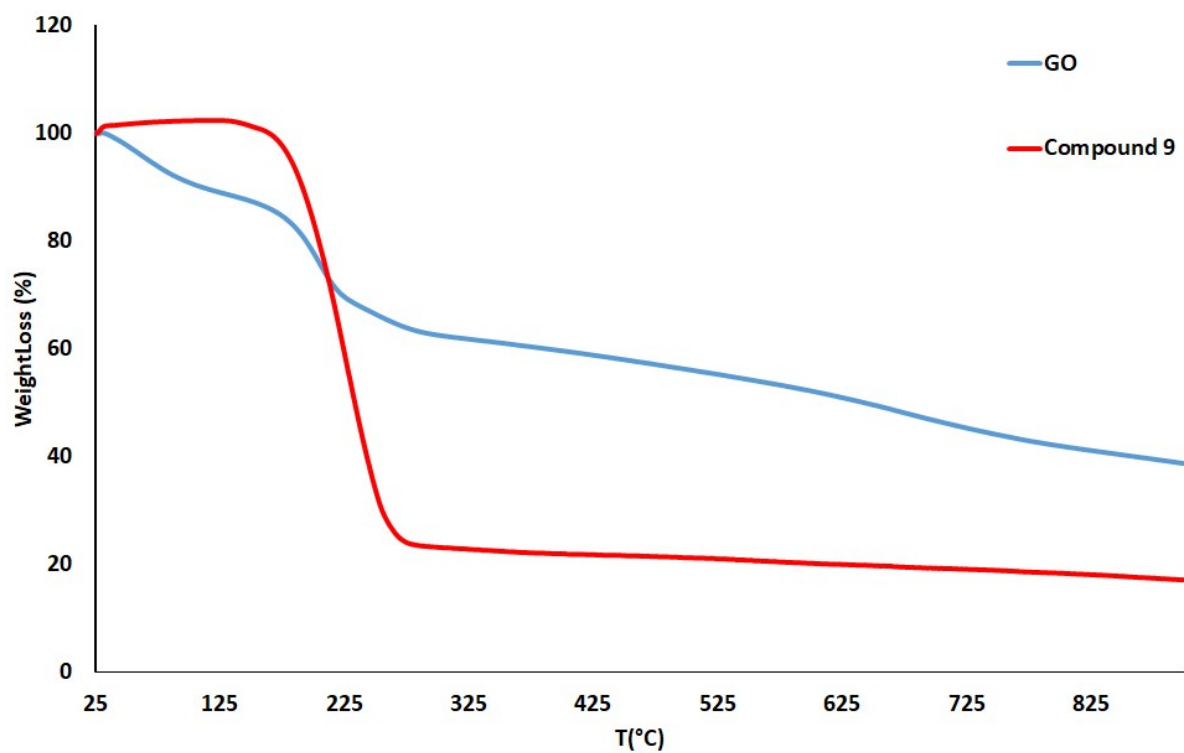


Figure S44. TGA Thermogram Spectrum of compounds **9** and **GO**

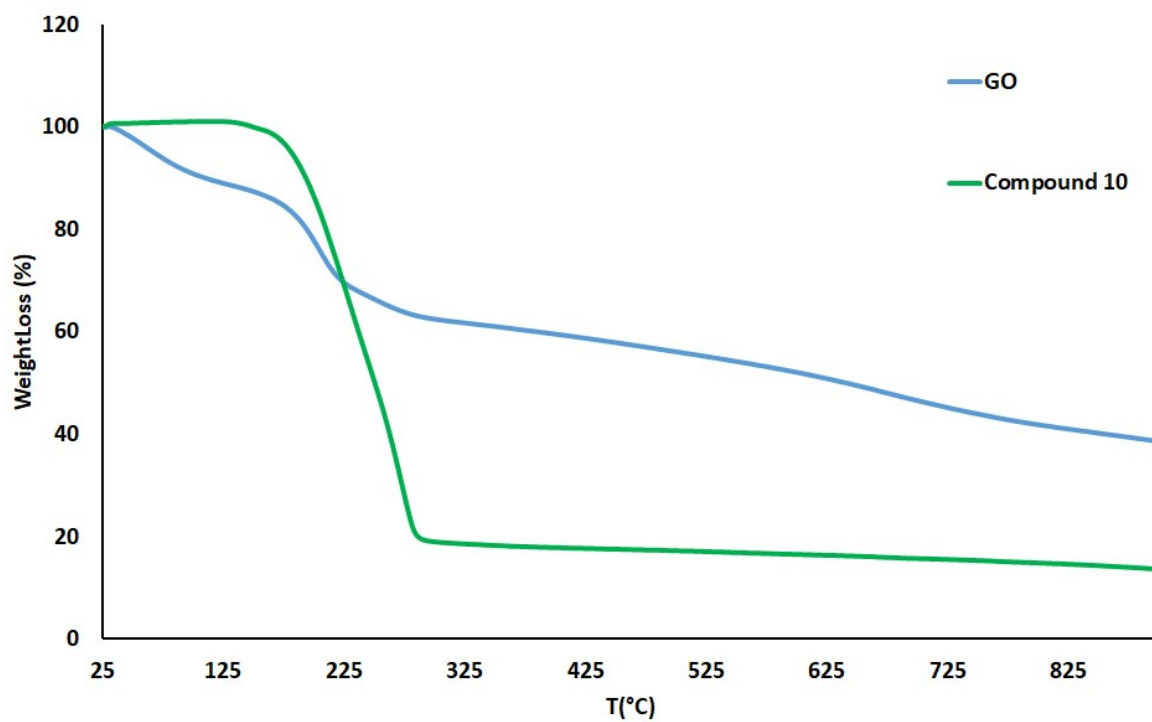


Figure S45. TGA Thermogram Spectrum of compound **10** and **GO**

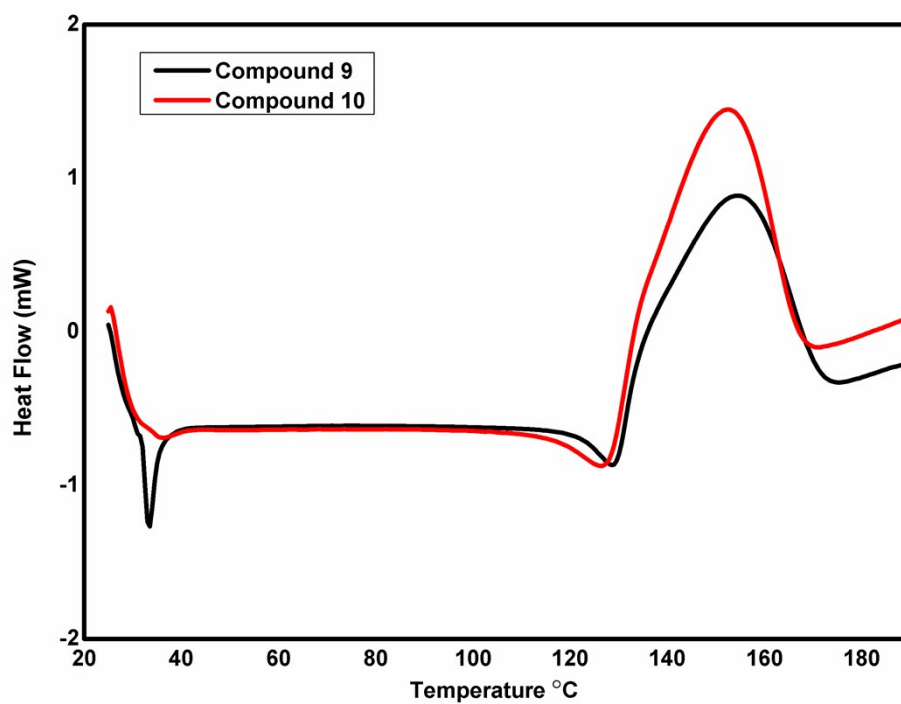


Figure S46. DSC Thermograms of Compounds 9 and 10

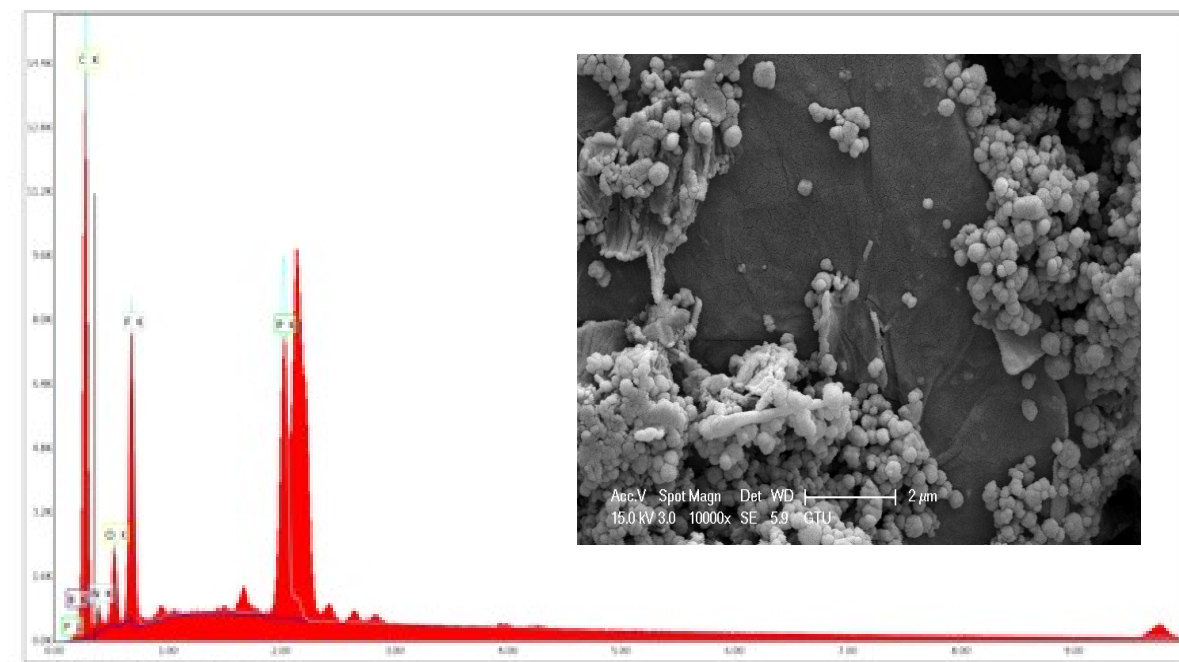


Figure S47. SEM image and EDX result of Compound 9

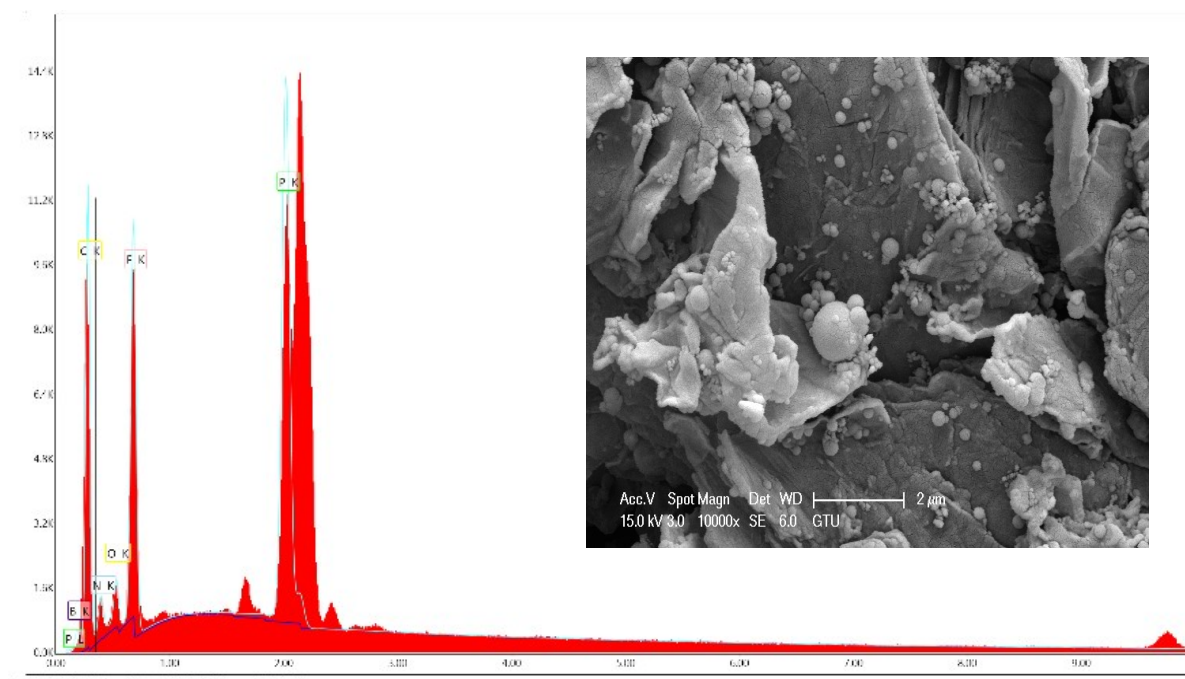


Figure S48. SEM image and EDX result of Compound **10**

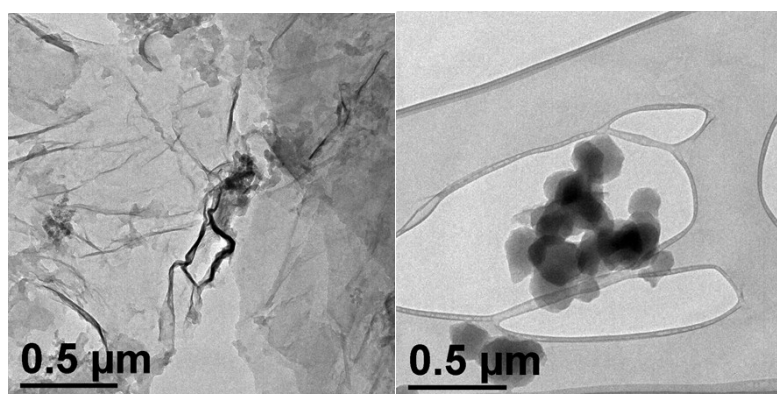


Figure S49. TEM images of compound **9**, and **10**, respectively

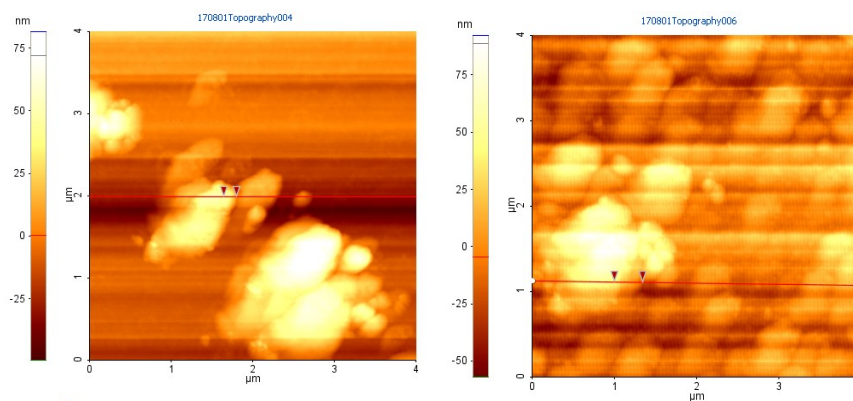


Figure S50. AFM images of Compound **9**, and **10**, respectively



Figure S51. Photoconductivity measurement system used in the Study