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Effect of *tert*-butyl substituents in triphenylsulfonium cation on spectral properties and photochemical activity of photoacid generators

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Materials and Instrumentation

Triphenylsulfonium triflate (CAS 526940, 95.8%), tris[2-(2-methoxyethoxy)ethyl]amine (CAS 301248, 95%), surfactant FC-4430 (3M) (surfactant), potassium perfluorobutanesulfonate (CAS 29420-49-3, 98%), 4-bromo-*tert*-butylbenzene (CAS 3972-65-4, 97%), magnesium (CAS 7439-95-4) were purchased from Merck. Benzene (CAS 54682-86-9, 99%), trimethylchlorosilane (CAS 75-77-4, 99.6%), anhydrous aluminum chloride (CAS 7446-70-0, 99.9%), thionyl chloride (CAS 7719-09-7, 97%) were purchased from Angene Chemical. 1-Methoxy-2-propanol (BASF, Solvenon PM, 99.98%) and 1-methoxy-2-propanol acetate (JIANGSU SANMU, 99.9%) were used as solvents for the preparation of photoresist.

Analysis of compounds by high-performance liquid chromatography was performed on a Shimadzu HPLC instrument. The column – Phenomenex Luna C18 150×4.6 mm, 5 μm, 100Å, acetonitrile flow rate – 1 mL/min, column temperature – 40°C.

Analysis of compounds by nuclear magnetic resonance spectroscopy (NMR) on ^{1}H, ^{13}C, ^{19}F nuclei was performed on a Bruker AVANCE III instrument, 500 MHz. The field frequency for ^{1}H spectra was 500 MHz, ^{13}C spectra – 126 MHz, ^{19}F spectra – 470 MHz, solvent – $CDCl_3$, sample temperature – 22.5°C.

Chemical analysis was performed using Vario Microcube instrument. Laser analysis of elemental composition was carried out on LEA-S500 machine (SOL instruments, Belarus) with laser energy of 25 J.

The film thickness on the quartz substrate was determined from the interference reflectance spectra measured on a SILAB TUV9DCS spectrophotometer using a mirror reflection attachment.

The electronic absorption spectrum (EAS) was recorded on a Hewlett Packard 8453 device.

Synthesis of compounds

Synthesis of terpolymer I. A terpolymer based on 3-hydroxyadamantan-1-yl methacrylate (GAMA), 2-methyl-2-adamantyl methacrylate (MAMA) and (5-oxooxolan-3-yl)-2-methylprop-2-enoate (GBLMA) was used as a film-forming agent. The mole fractions of the monomers GAMA: MAMA: GBLMA = 0.1: 0.6: 0.3. The samples were obtained by radical polymerization in a tetrahydrofuran solution. Azobisisobutyronitrile was used as an initiator of radical polymerization. The resulting polymer was purified by reprecipitation from a solution in tetrahydrofuran into hexane (the ratio of polymer solution: precipitant = 1: 10 (by volume)). The molecular weight characteristics of the resulting copolymer were determined M_n = 6060, M_w = 13040, M_w/M_n = 2.15.

*Synthesis of triphenylsulfonium iodide (***1***).* Benzene (65.5 g; 0.84 mol) and anhydrous aluminum chloride (22.4 g; 0.168 mol) are placed in a 250 mL three-necked flask equipped with a reflux condenser, dropping funnel and stirring bar. The flask with the reagents is cooled to 0°C in an ice bath, and thionyl chloride (5 g; 0.042 mol) is added in small portions with vigorous stirring. The mixture is stirred on a magnetic stirrer for an hour at room temperature, then heated to 60-70°C and stirred for an additional 10 hours. Then the flask is cooled to room temperature and 100 mL of bidistilled water is added. The mixture is poured into a separatory funnel and the benzene layer is separated. The aqueous fraction is washed three times with benzene (50 mL) until a clear solution is obtained. Aqueous KI (30%, 100 mL) is added to the washed aqueous layer. The resulting white precipitate of triphenylsulfonium iodide is extracted three times with dichloromethane (50 mL). The organic layer is separated, kept over anhydrous sodium sulfate and filtered. The solution is evaporated on a rotary evaporator at a bath temperature of 40°C. The resulting white crystals of triphenylsulfonium iodide are collected from the flask with a teflon spatula. The yield of **1** was 72% (11.8 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.85 (m, 6H); 7.79 (m, 3H); 7.73 (m, 6H). Elemental analysis (%), calculated for $C_{18}H_{15}IS$: C, 55.40; H, 3.87; I, 32.52; S, 8.21. Found: C, 55.21; H, 3.81; S, 8.23. mp = 245°C (mp = 248-250° [S1]).

*Synthesis of tris(4-tert-butylphenyl)sulfonium iodide (***2***).*The synthesis and isolation of compound **2** were carried out under conditions similar to those described above for compound **1**. *tert*-Butylbenzene (20 g; 0.149 mol), anhydrous aluminum chloride (4 g; 0.03 mol), and thionyl chloride (0.9 g; 0.0075 mol) were used. The yield of **2** was 48% (2.0 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.58 (d, 6H, *J*=8.64 Hz); 7.49 (d, 6H, *J*= 8.74 Hz); 1.33 (s, 27H). Elemental analysis (%), calculated for $C_{30}H_{39}IS$: C, 64.51; H, 7.04; I, 22.72; S, 5.74. Found: C, 64.22; H, 6.98; S, 5.80. mp = 152°C.

*Synthesis of triphenylsulfonium nonaflate (***PAG1***).* Sodium perfluorobutanesulfonate (3.59 g; 0.011 mol) and compound **1** (3.63 g; 0.009 mol) are placed in a 100 mL single-neck round-bottomed flask with a stir bar. Bidistilled water and dichloromethane (50 mL each) are added. The mixture is stirred for 8 hours, then transferred to a separatory funnel. The organic layer is separated, and the product is extracted from the aqueous phase with dichloromethane (3 × 50 mL). The

combined organic phase is kept over anhydrous sodium sulfate and filtered. The solution is evaporated on a rotary evaporator; the resulting crystals are removed from the flask and washed on a filter with diethyl ether (50 mL). The yield was 54% (2.73 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.76-7.72 (m, 9H), 7.69-7.66 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 134.69; 131.66; 131.18; 124.37. ^{19}F NMR (470 MHz, $CDCl_3$, δ ppm): -80.40; -114.84; -121.38; -125.67. mp = 83°C. Spectral characteristics and mp agree well with previously reported data.[S2]

Synthesis of (4-tert-butylphenyl)magnesium bromide. This was obtained according to the procedure reported by C. D. McCune et al.[S3] The yield of the product was determined by titration with sulfuric acid (0.1 N) with phenolphthalein. The yield was of 70% (19.9 g).

Synthesis of diphenyl sulfoxide. This was obtained according to the procedure reported by G. A. Olah et al.[S4] The yield was 72% (37.7 g). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.66 (m, 4H); 7.45 (m, 6H). $T_{m.}$ =68°C. Spectral characteristics and mp agree well with previously reported data.[S5]

*Synthesis of tris(4-tert-butylphenyl)sulfonium nonaflate (***PAG2***).* Synthesis and isolation of **PAG2** were carried out under conditions similar to those described above for **PAG1**. Sodium perfluorobutanesulfonate (6.9 g; 0.021 mol) and compound **2** (10.0 g; 0.018 mol) were used. Yield 38% (5.0 g).^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.65 (d, 6H); 7.63 (d, 6H); 1.33 (s, 27H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 158.70; 130.84; 128.67; 121.35; 35.46; 30.89. ^{19}F NMR (470 MHz, $CDCl_3$, δ, ppm): -80.87; -114.52; -121.49; -125.89. Spectral characteristics agree well with previously reported data.[S2] mp = 198°C.

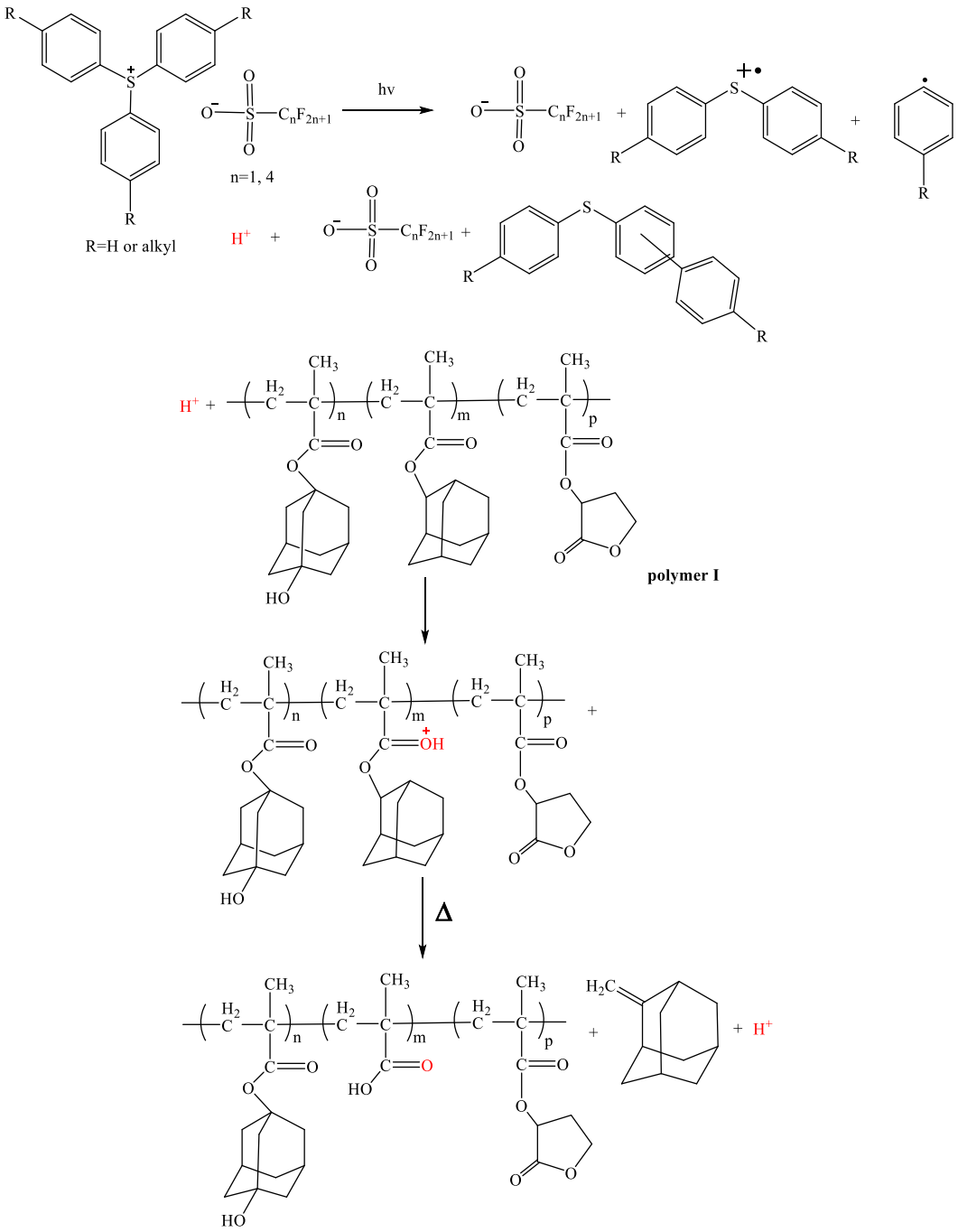
*Synthesis of 4-tert-butylphenyl(diphenyl)sulfonium nonaflate (***PAG3***).* This was obtained according to the previously reported procedure.[S6] Diphenyl sulfoxide (2.37 g; 0.012 mol), 4-$Bu^tC_6H_4MgBr$ (5 g; 0.024 mol), trimethylchlorosilane (2.55 g; 0.024 mol) and sodium perfluorobutanesulfonate (3.6 g; 0.011 mol) were used. Yield of the product was 49% (2.84 g).^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.78-7.67 (m, 14H); 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 159.09; 134.50; 131.57; 131.19; 131.02; 128.84; 124.80; 120.55; 35.49; 30.85. ^{19}F NMR (470 MHz, $CDCl_3$, δ, ppm): -80.87; -114.58; -121.54; -125.91. Spectral characteristics agree well with previously reported data.[S2] mp = 35°C.

Investigation of spectral characteristics of compounds and resist films

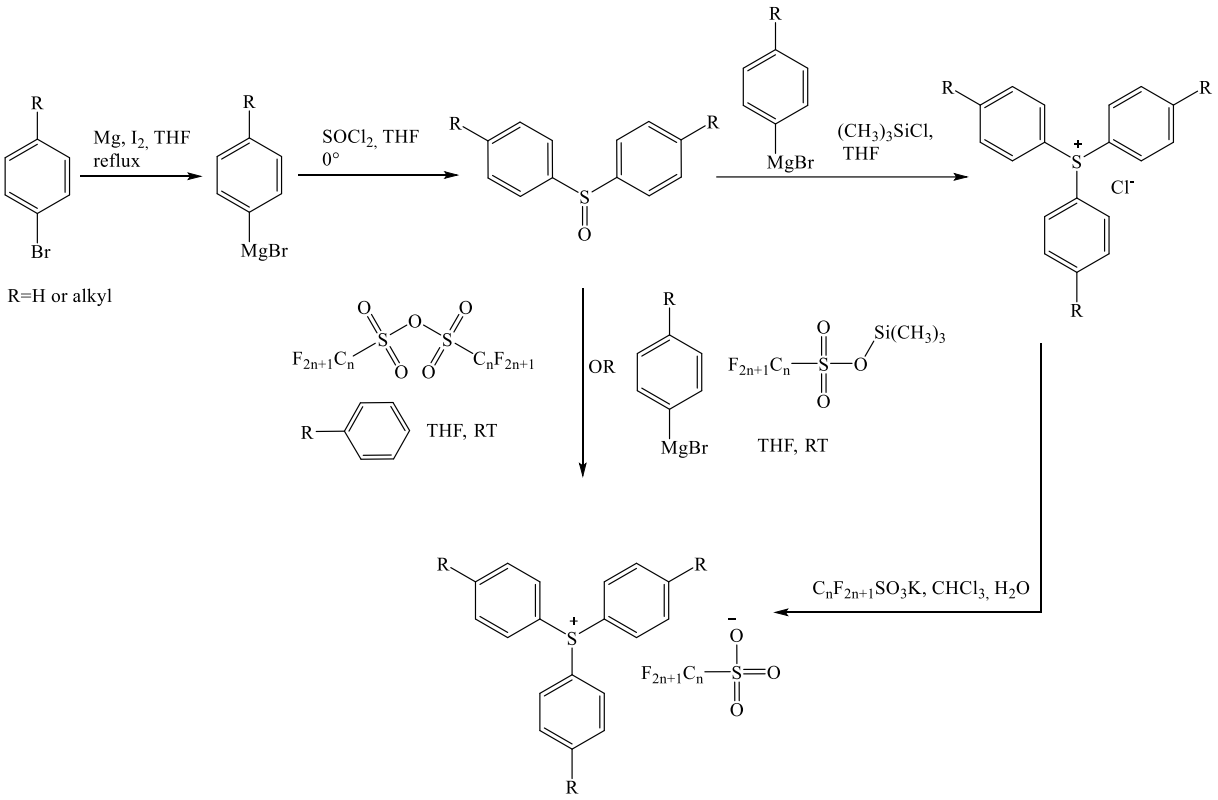
To perform spectral studies of photoacid generators in the film of the polymer matrix, equimolar (3.78×10^{-3} mol·kg^{-1}) solutions of PAGs were prepared in a 10% polymer solution (I) in mixture of 1-methoxy-2-propanol/1-methoxy-2-propanol acetate = 50/50 wt%. To obtain a smooth polymer film, 0.01% surfactant FC-4430 was added. The resist solution was filtered through a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.2 μm. The solution of resist obtained was applied to a quartz substrate by spin-coating at a spin rate of 3000 rpm, and then dried on a hot plate at 110°C for 90 s. The thickness of resist layer was measured of ~300 nm. The concentration of PAG in the resist layer was calculated with a correction of 5% for the residual solvent content, which according to A. Robinson et al.[S7], is ranged from 5 to 10% after film drying.

Thus, we estimate the error in determining of ε at 5%. The density of the resist layer (ρ, g·cm^{-3}) was estimated from the weight (by the difference in the weights of the substrate with and without coating) and the volume of the film (from the thickness and area of coating). The density of the resist layer was calculated to be 1.33 g·cm^{-3}, which is in good agreement with the literature data (1.39 g·cm^{-3} [S8]). The absorption spectrum was recorded with subtraction of the Fresnel reflection for films with thickness of ~ 1 μm. The results were normalized proportionally to the working film thickness of 300 nm. Using the relationship $D = \log(1/T)$, the optical density D obtained for a film with a thickness of 300 nm was used to determine its transmittance T and absorption (1-T).

To determine the Dill parameter C and the quantum yield Φ_{H^+} of chemically amplified photoresist, twelve samples containing the synthesized PAG were fabricated (four series by three samples). The samples in the series had different amount of the base tris[2-(2-methoxyethoxy)ethyl]amine: 0, 5, 10, 12.5 mol% relatively PAG concentration. The photoresist samples were applied to a 40 × 40 mm quartz plate by centrifugation, dried at 110 °C (90 s). The samples were exposed to light with the wavelength of 257 nm (half-width of 5 nm) provided by 2 W ultraviolet LED (3838, TiaoChongYi, China) with the size of 0.5 × 0.5 mm. The radiant power of the LED was 80 mW. A uniform luminous flux with a diameter of about 100 mm on substrates with resist film was formed using a diffuser (10 μm thick Teflon film) and a quartz condenser. The energy characteristics of the luminous flux were measured using a PM100D illuminance meter (THORLABS) with an S120VC photodetector head based on calibrated photodiode (200-1100 nm). The measured luminous flux power on the surface of the material was 30±0.1 μW cm^{-2}. The photoresist layer on the quartz plate was divided into six zones, which were exposed for different times and hence radiation doses. The step of exposure time for each zone was 15 s that corresponds to radiation dose of 0.45 mJ·cm^{-2}. After exposure, the samples were subjected to heating (110°C, 90 s) for removing protecting groups in polymer. The samples were developed for 60 s in a bath with a metal-free developer (PP-051MS, NIOPIK, JSC), washed with distilled water and dried in a centrifuge at room temperature. The minimum exposure dose corresponding to a fully developed zone was taken as the threshold dose E_0. The Dill parameter C was determined from the dependence of the ratio moles of base to moles of PAG relative to E_0.



Scheme S1 Acid-catalyzed deprotection reaction in a chemically amplified resist with polymer I.



Scheme S2. Synthesis of sulfonium PAGs by common methods. [S9,S10]

Table S1 Spectral characteristics of photoacid generators in a polymer matrix I.

Compound	λ, nm	ε, $cm^{-1} \cdot M^{-1}$
PAG1	**193** **235 (max)** **248**	**62 000** **19 000** **14 000**
PAG2	193 242 (max) 248	65 000 27 000 25 000
PAG3	193 238 (max) 248	64 000 21 000 17 000
PAG4	**193** **235 (max)** **248**	**62 000** **19 000** **14 000**

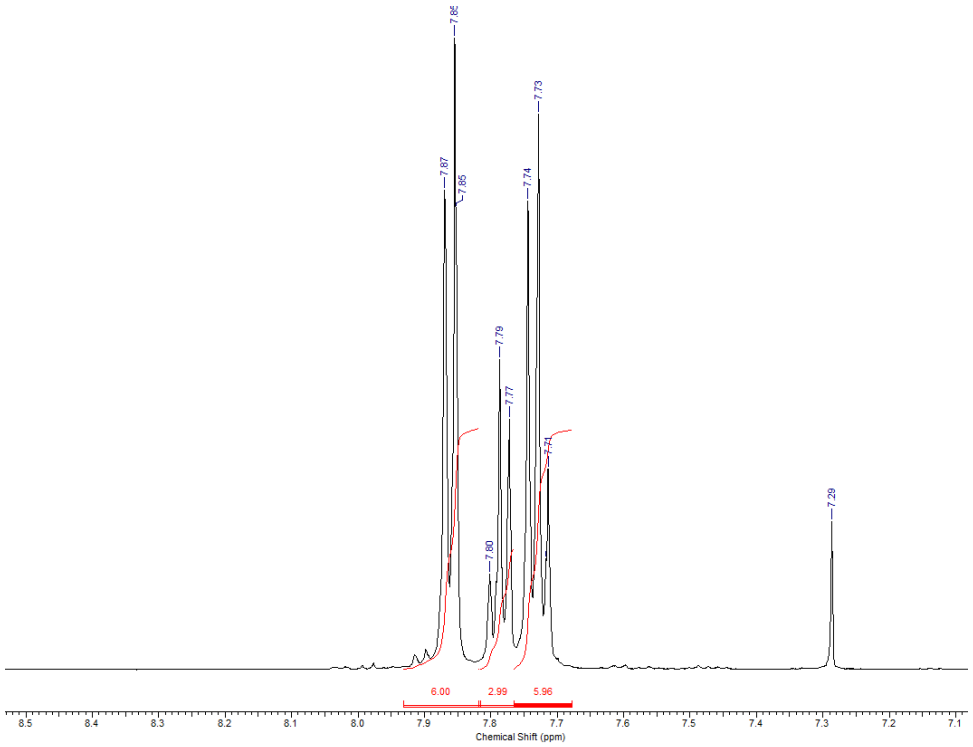


Figure S1. ^{1}H NMR spectrum of compound **1**.

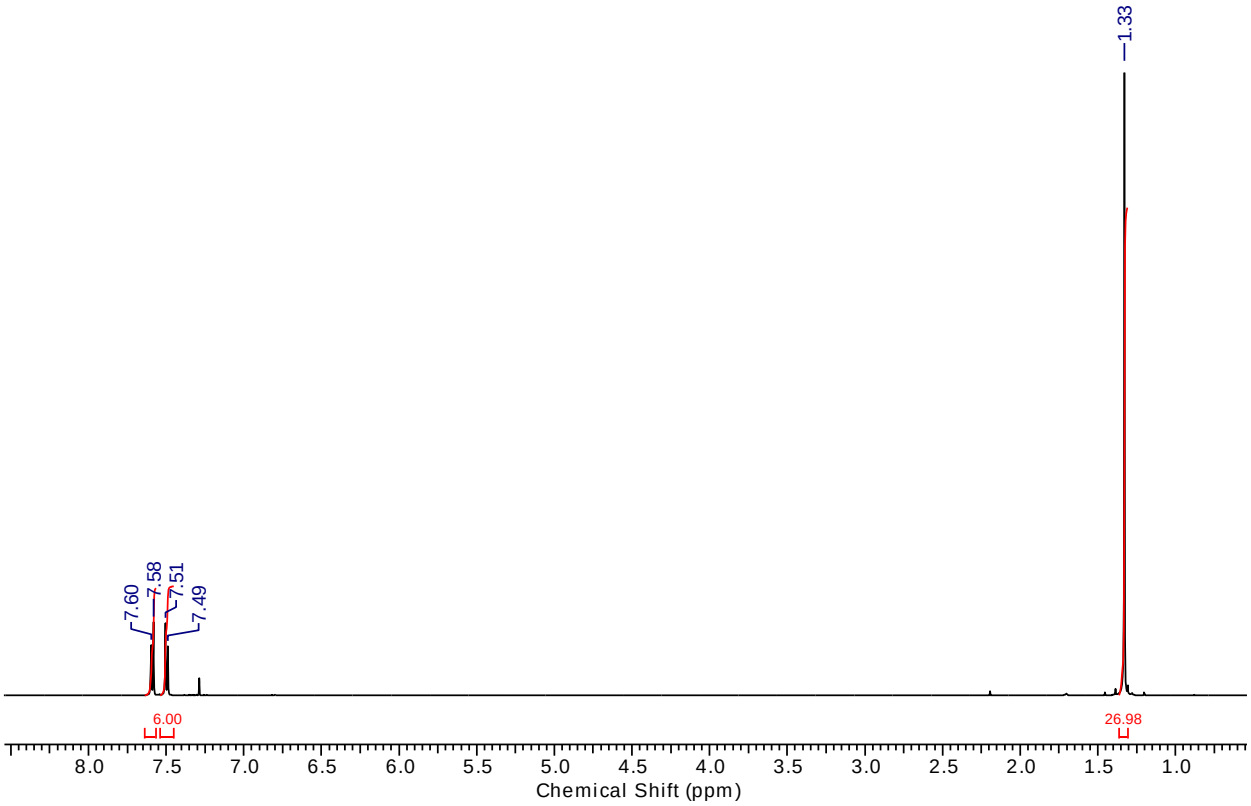


Figure S2. ^{1}H NMR spectrum of compound **2**.

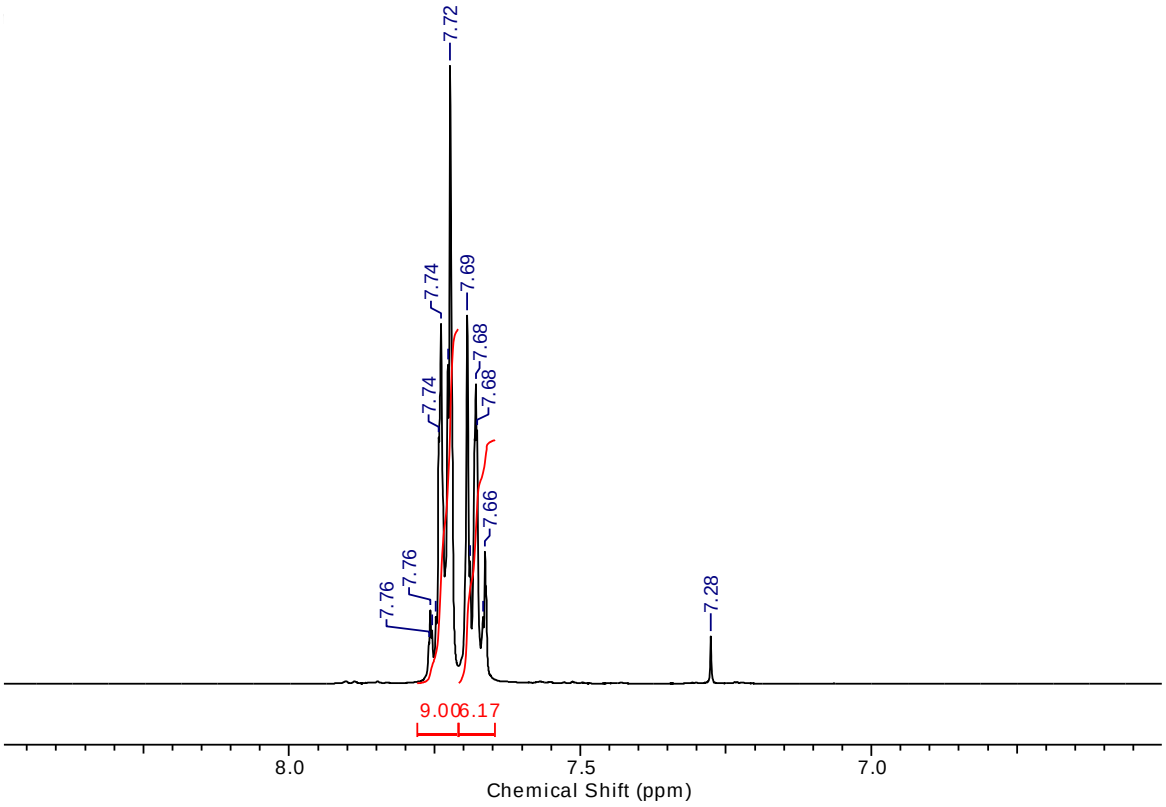


Figure S3. ^{1}H NMR spectrum of **PAG1**.

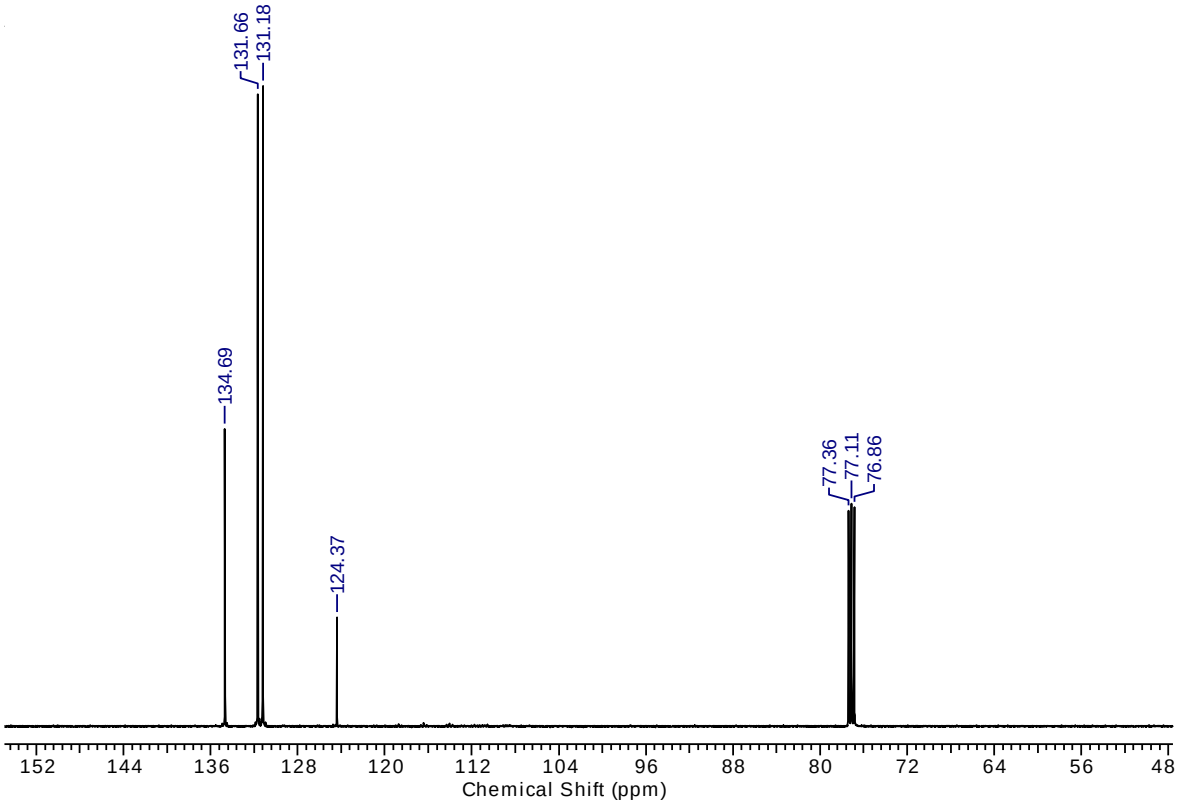


Figure S4. ^{13}C NMR spectrum of **PAG1**.

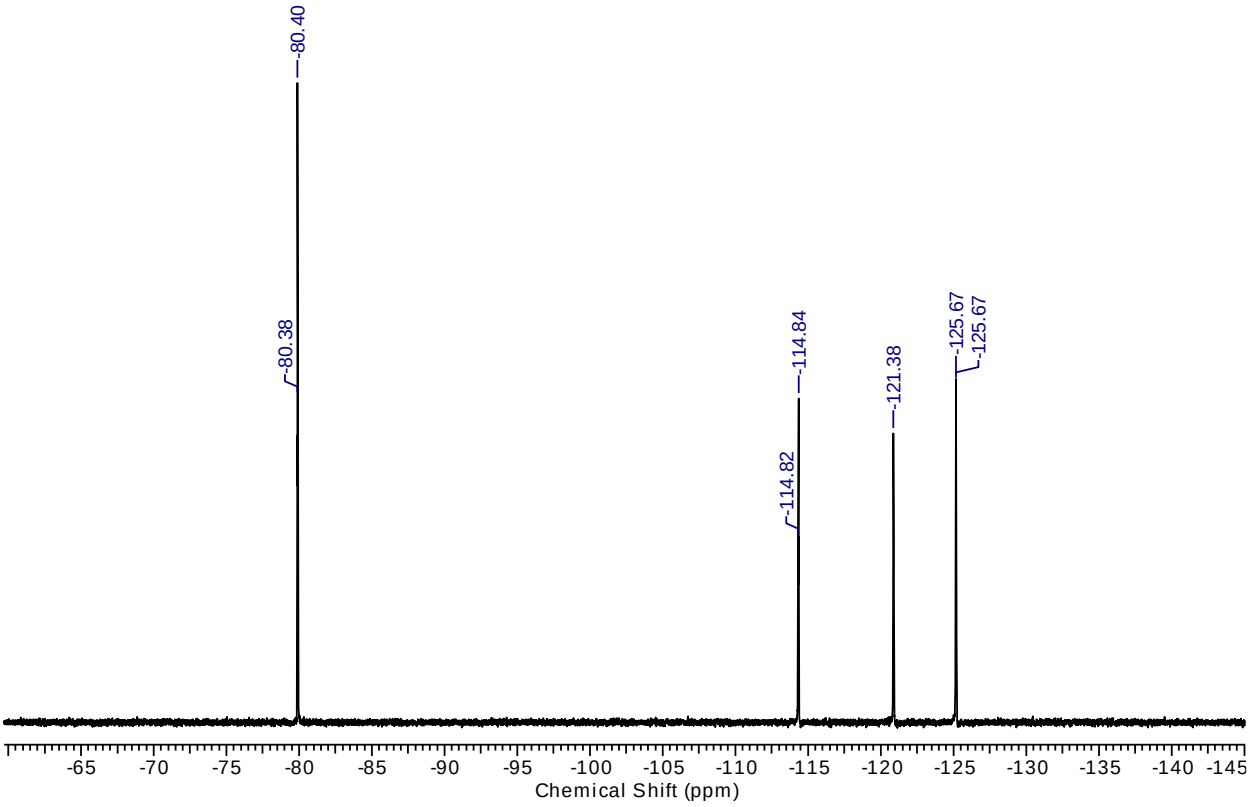


Figure S5. ^{19}F NMR spectrum of **PAG1**.

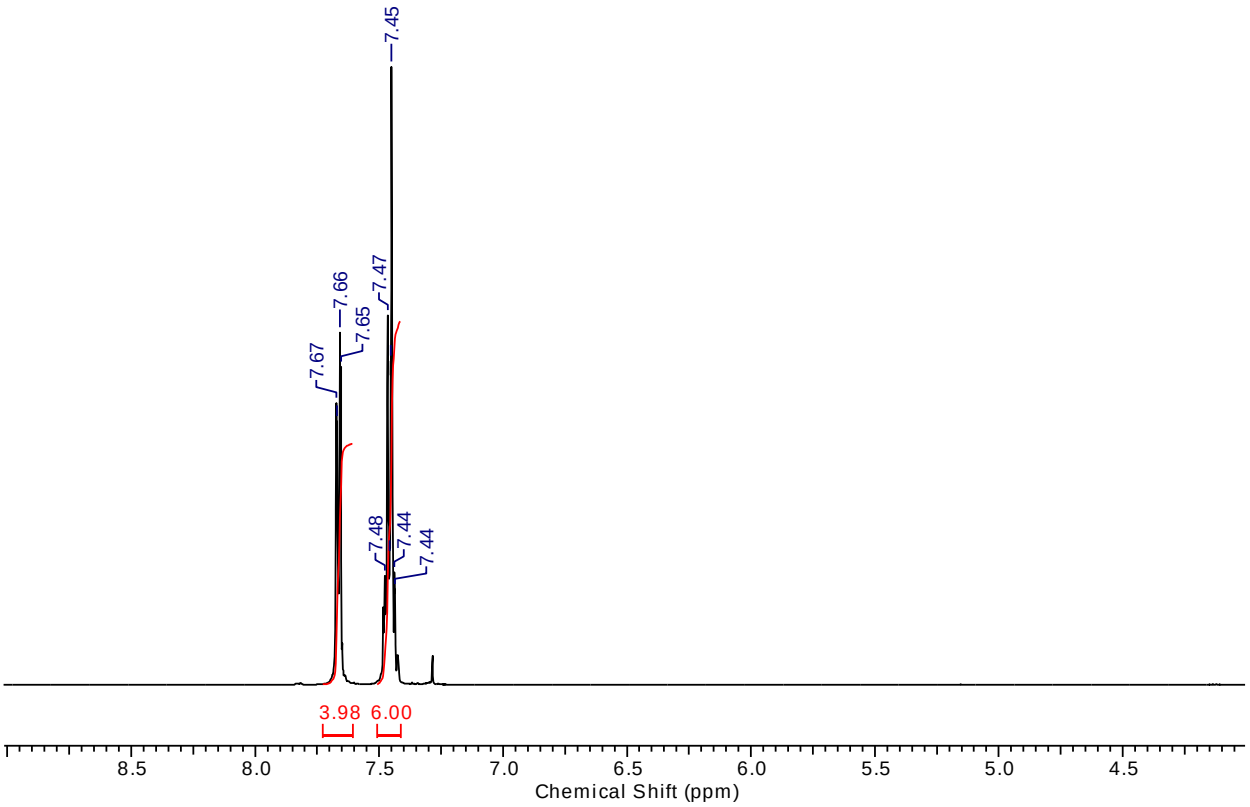


Figure S6. ^{1}H NMR spectrum of diphenyl sulfoxide.

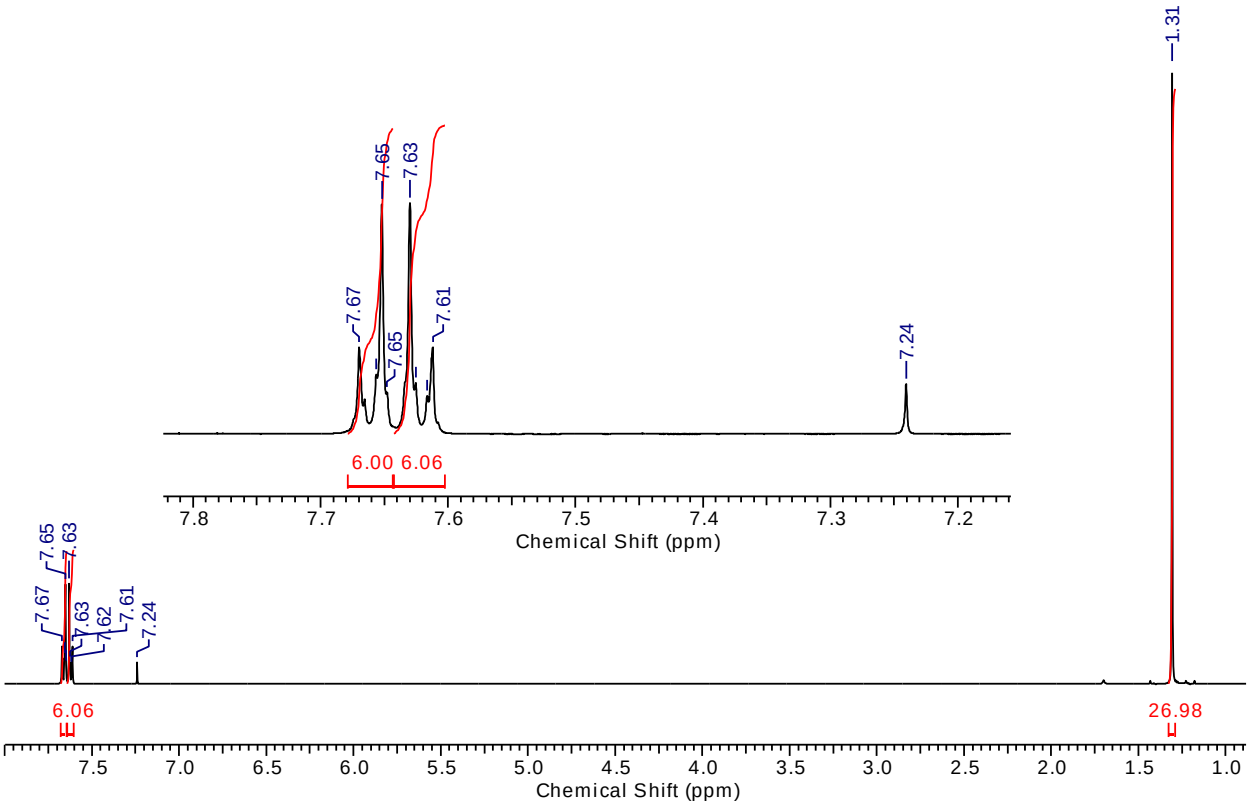


Figure S7. ^{1}H NMR spectrum of **PAG2**.

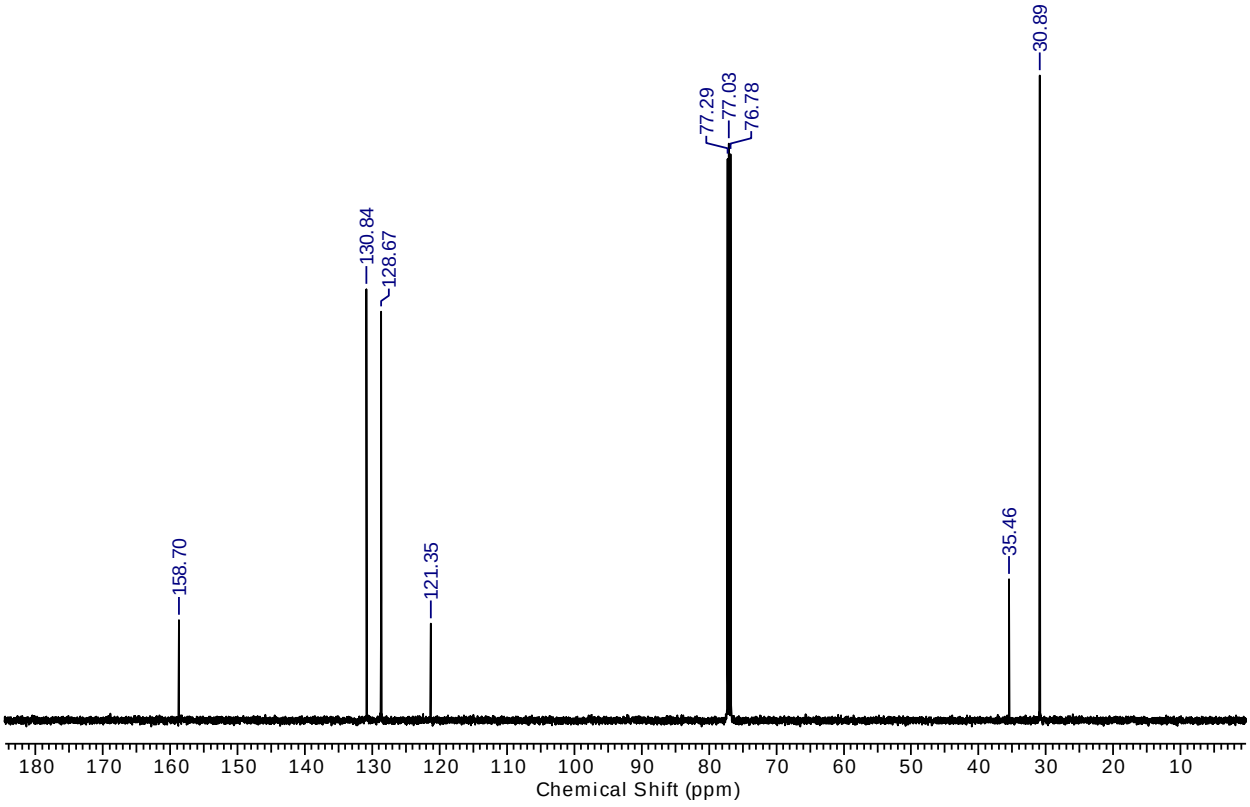


Figure S8. ^{13}C NMR spectrum of **PAG2**.

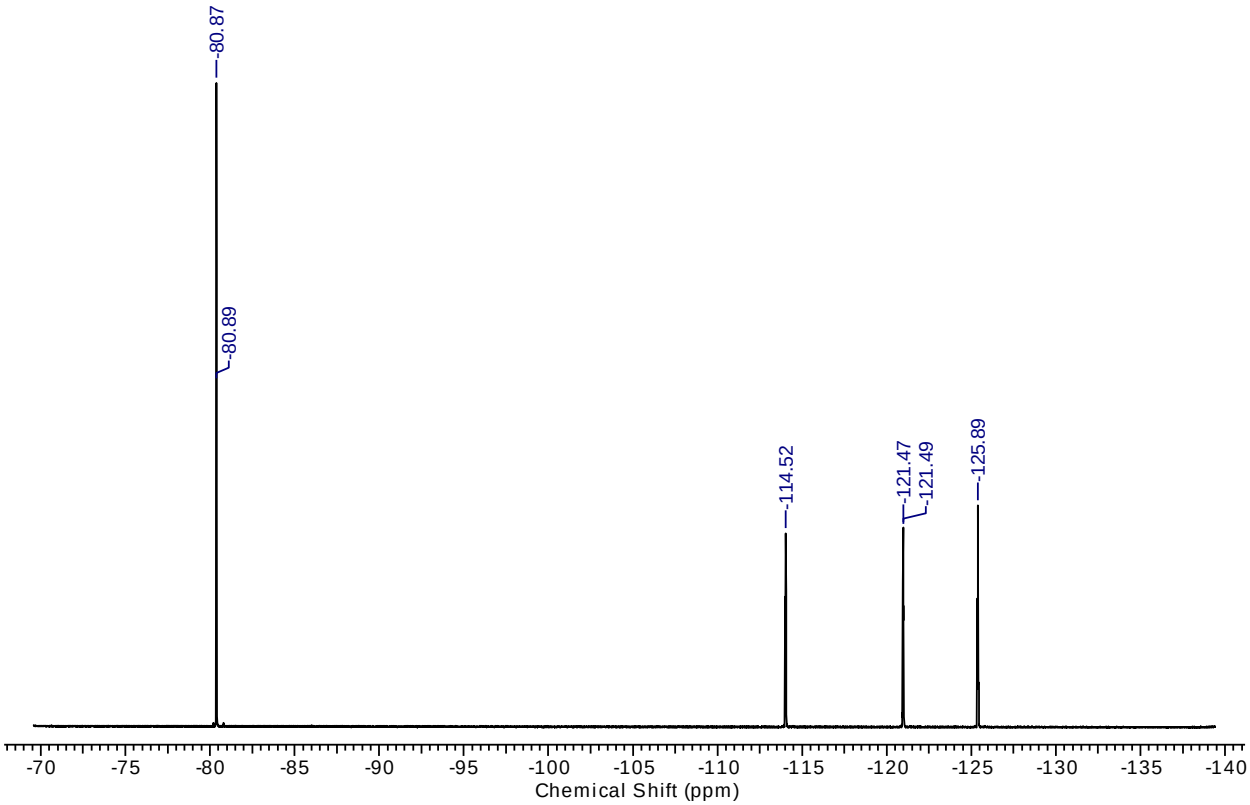


Figure S9. ^{19}F NMR spectrum of **PAG2**.

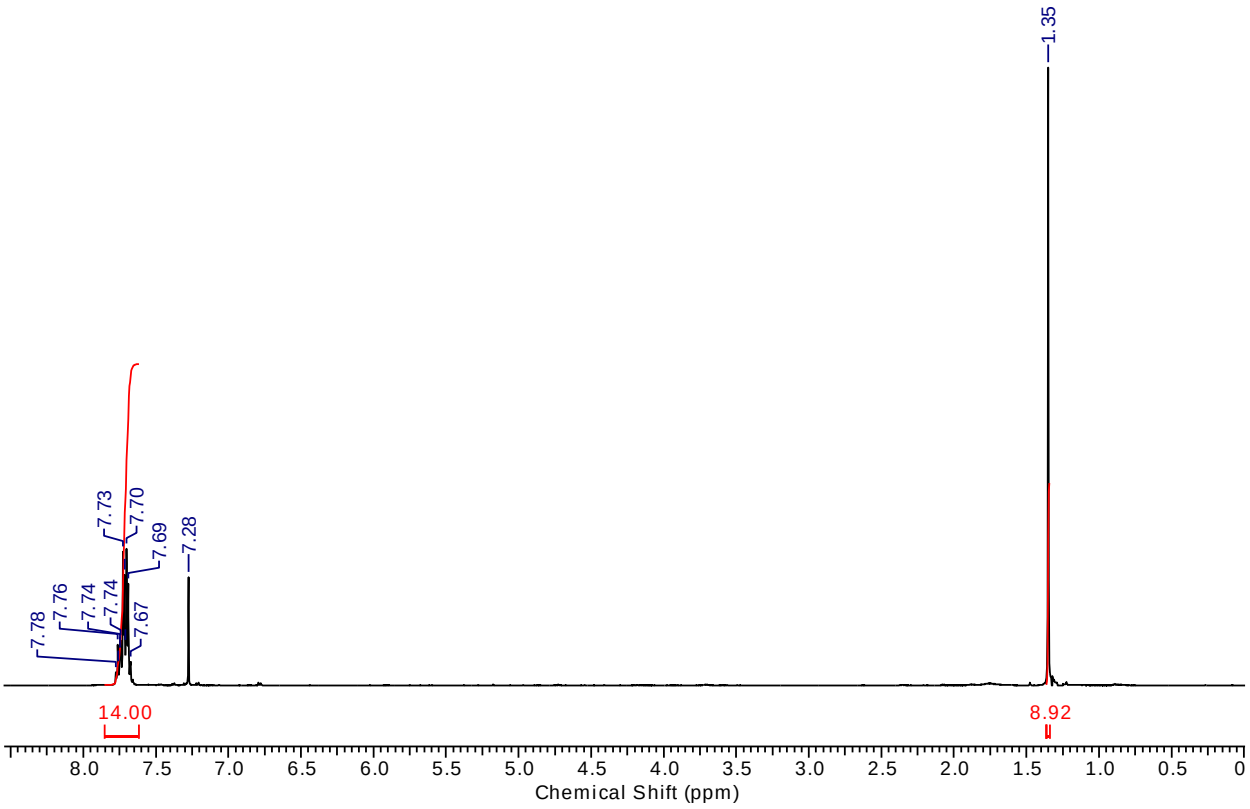


Figure S10. ^{1}H NMR spectrum of **PAG3**.

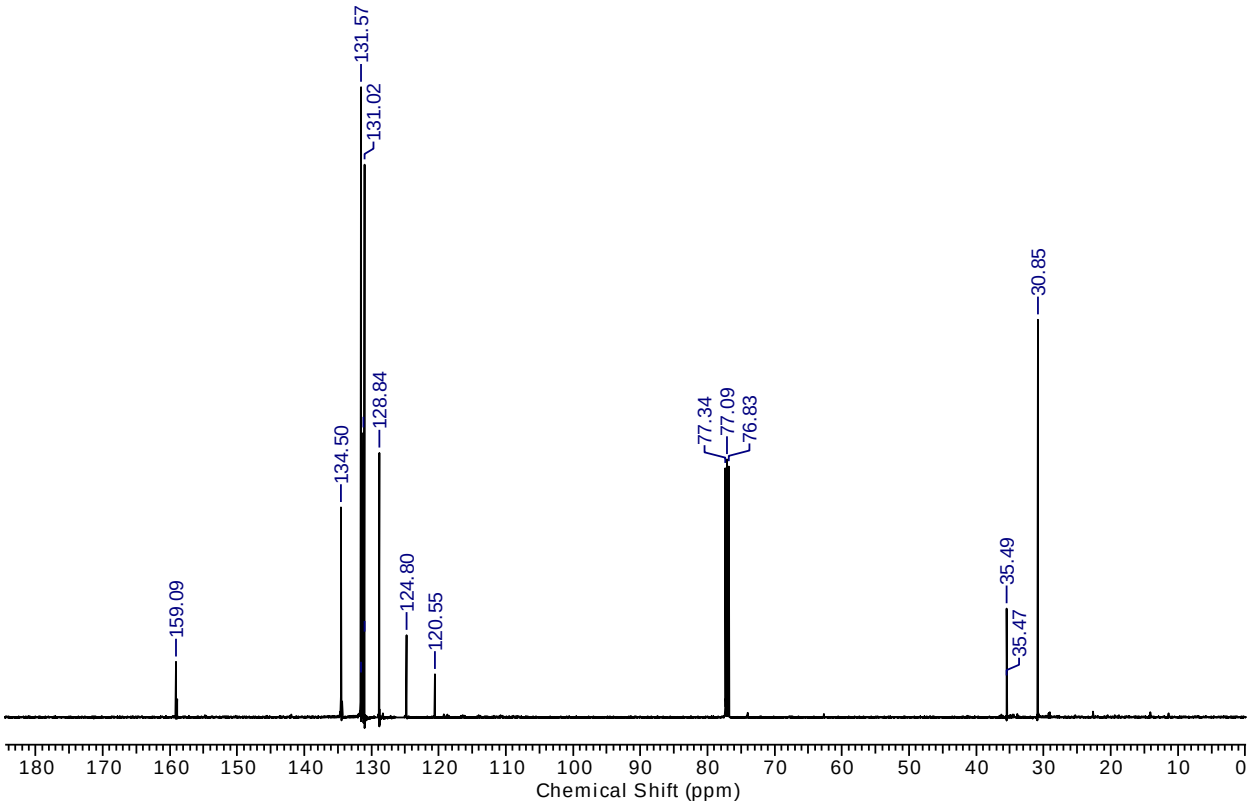


Figure S11. ^{13}C NMR spectrum of **PAG3**.

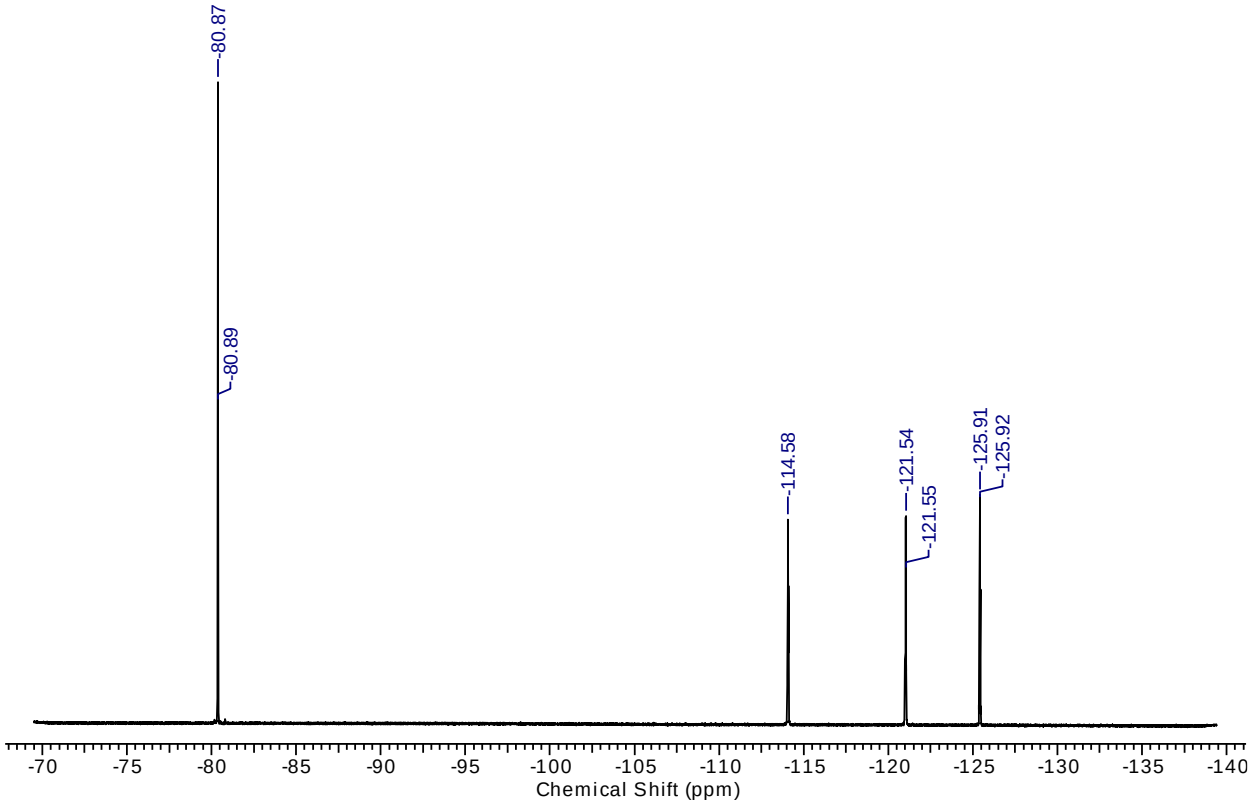


Figure S12. ^{19}F NMR spectrum of **PAG3**.

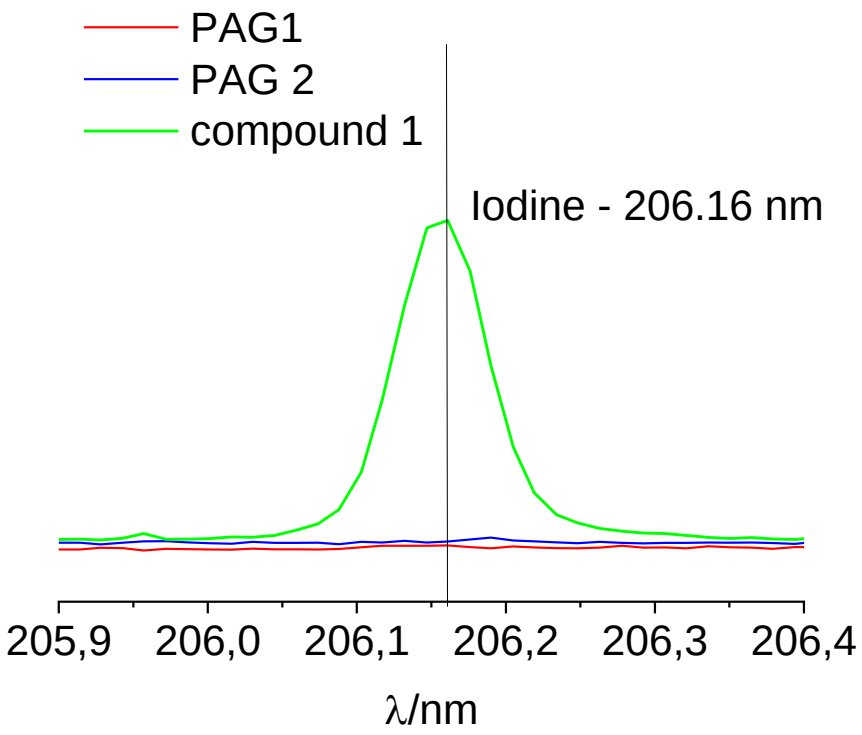


Figure S13. AES spectra of reference sample – compounds **1 PAG1** and **PAG2**.

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