

Supporting Information

Rigid PN Cages as 3-Dimensional Building Blocks for Crystalline or Amorphous Networked Materials

Mohsen Shayan,^{a,‡} Maryam F. Abdollahi,^{a,‡} Mason Chester Lawrence,^b Etienne C. Guinand,^b Maxime Goulet,^c Tanner George,^d Jason D. Masuda,^d Michael J. Katz,^{*b} Audrey Laventure,^{*c} Ulrike Werner-Zwanziger,^a Saurabh S. Chitnis^{*a}

^a Chemistry Department, Dalhousie University 6274 Coburg Road, Halifax, Nova Scotia, B3H 4R2, Canada

^b Department of Chemistry, Memorial University of Newfoundland 45 Arctic Avenue, St. John's, Newfoundland, A1C 5S7, Canada.

^c Département de Chimie, Université de Montréal CP 6128, Succursale Centre-Ville, Montréal, QC H3C 3J7, Canada.

^d Department of Chemistry, Saint Mary's University 923 Robie Street, Halifax, Nova Scotia, B3H 3C3 Canada.

‡ Equal contribution

E-mail: saurabh.chitnis@dal.ca, mkatz@mun.ca, audrey.laventure@umontreal.ca

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Experimental

The manipulations of air sensitive materials were carried out using Schlenk and glovebox techniques under an atmosphere of dry nitrogen. Solvent was dried over Na-benzophenone or activated using 3 Å prior to use. Reaction glassware was placed in an oven at 200 °C prior to use and Krytox was used for all assembling of the glass joints. Evaporation and concentration of the solvents were performed using a rotary evaporator or under high vacuum and the solid compounds were dried in a vacuum oven for thermal analysis. Flash column chromatography was carried out through 240–400 mesh silica gel, and thin-layer chromatography (TLC) was carried out via silica gel F254-covered plastic sheets, which were visualized under UV irradiation. Melting points (m.p.) were measured using a MEL-TEMP II melting point apparatus.

Solution nuclear magnetic resonance (NMR) spectra are referenced to tetramethylsilane (^1H , ^{13}C), H_3PO_4 (^{31}P), and trichlorofluoromethane (^{19}F) on a Bruker AV-300, Bruker AV-400, Bruker AV-500 spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to the signals of the internal reference or residual solvent (CDCl_3 $\delta_{\text{H}} = 7.24$ ppm, $\delta_{\text{C}} = 77.0$ ppm; $\text{DMSO}-d_6$ $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.5$ ppm). Coupling constants (J) are given in Hz. With respect to the solid-state NMR, the ^1H , ^{19}F , and ^{31}P Magic Angle Spinning (MAS) NMR experiments were carried out on a Bruker Avance spectrometer with a 16.4 T magnet (700.25 MHz ^1H , and 283.46 MHz ^{31}P Larmor frequencies). These experiments were conducted using a probe head for rotors of 2.5 mm diameter. The single pulse ^{31}P ssNMR with ^1H decoupling experiments were referenced against $\text{NH}_4\text{H}_2\text{PO}_4$ at 0.81 ppm. ^{19}F Hahn-echo ssNMR experiments were spinning speed synchronized to one rotor period and referenced against PTFE (Teflon) at -123.1 ppm. The ^1H MAS NMR experiments included background suppression.^[1] The chemical shift reference was calculated from the ^{31}P reference^[2] based on the IUPAC conversion factor.

The ^{31}P SASSY NMR experiments follow the pulse sequence introduced by A. J. Simpson^[3] here applied to ^{31}P nuclei. These experiments were conducted on a Bruker Avance DSX/Tecmag NMR spectrometer with a 9.4 T magnet. The sample was filled into liquid tight inserts spun in 4mm rotors. The $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization (CP) section with CP contact time of 2.6 ms, and 30 ms high power Spinal-64 decoupling was followed by low power Waltz decoupling (pulses 81 μs) for a total of 655 ms decoupling. The mobile, not cross-polarizing component of the sequence used a 5.3 μs ^{13}C single excitation pulse. The data were acquired in two interleaved, differently phase cycled sets, that were added or subtracted to obtain the solid and mobile components, respectively.

The ^{13}C Magic Angle Spinning (MAS) NMR experiments were carried out on a Bruker Avance DSX/Tecmag NMR spectrometer with a 9.4 T magnet (400.24 MHz ^1H , 100.64 MHz ^{13}C , Larmor frequencies) using a probe head for rotors of 4 mm diameter. The ^{13}C chemical shift scale was referenced against the carbonyl resonance of glycine at 176.06 ppm. Infrared spectra were recorded on a Thermo Scientific Nicolet NXR 9650 FT-

Infrared Spectrometer instrument equipped with a 1064 nm Nd:YVO₄ laser and InGaAs detector, on KBr plates or pellets.

Single crystal diffraction experiments were performed on two instruments. Samples **7** and **9** were analyzed using a Bruker D8 Venture diffractometer. Reflections were integrated using the APEX 3 or 4 software suite (SAINT, SADABS)^[4] and solved using SHELXT^[5] and refined using SHELXL^[6] with or without the Olex2 software GUI.^[7] samples **5** and **6** were analyzed at 100(2) K on an XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Crystal was mounted on nylon CryoLoops with Paraton-N. The data collection and reduction were processed within CrysAlisPro (Rigaku OD, 2019). A multiscan absorption correction was applied to the collected reflections. Using OLEX2,^[7] structures were solved with the SHELXT structure solution program^[5] using intrinsic phasing and refined with the SHELXL refinement package^[6] using Least Squares minimization. All non-hydrogen atoms were refined anisotropically, and the organic hydrogen atoms were generated geometrically.

C, H, and N elemental analyses was performed on an Elementar UniCube instrument using acetanilide as calibration standards. Samples were sealed within tin capsules and weighed immediately prior to combustion.

Electro-Spray Ionization (ESI) mass spectra were obtained using a Bruker microTOF instrument.

Powder X-ray diffraction (PXRD) was carried out via a Rigaku Ultima IV X-ray diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were placed on to a zero-background silicon wafer and the spectra were collected at 3 counts/s for an hour.

Thermogravimetric analyses (TGA) were performed with a Discovery TGA 5500 (TA Instruments) using alumina sample pans. All TGA experiments were carried out with a heating rate of 10 °C/min between 25 and 1000 °C in a nitrogen atmosphere (25 mL/min). Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q2000 (TA Instruments) calibrated with indium using a heating rate of 10 °C/min in a nitrogen atmosphere (50 mL/min) between -10 °C up to a temperature equivalent to a total mass loss of 3 % from the TGA analysis. All DSC analyses were preceded by an initial isotherm at 15 °C for 3 h to purge the sample from the remaining solvent.

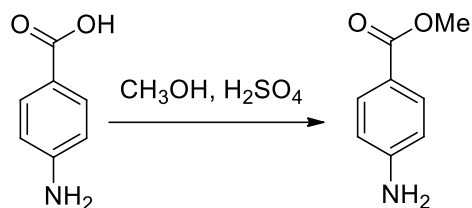
Gas adsorption isotherm data were collected on a Micromeritics Smart VacPrep instrument and the samples were thermally prepared for N₂ adsorption. Samples were initially heated to 45 °C (5 °C/min) for 90 min. Afterwards, the sample was heated at 60 °C for 600 min. From 70-100 °C the sample was heated for 300 minutes in 10 °C increments. For samples dried under supercritical CO₂, the samples were prepared as previously described. Briefly, the pores of the sample were exchanged for ethanol by soaking the material in ethanol followed by daily replacement of ethanol to remove any

desorbed solvents. After the pores were fully exchanged (4 days), the sample was placed in a Samdri-PVT-3D instrument (tousimis). The chamber was cooled to ~ 0 °C and the sample chamber was filled with liquid CO₂. Three times over the course of a day, the chamber was exchanged with fresh liquid CO₂. Afterwards, the sample was heated until the pressure and temperature were above the supercritical pressure and temperature. The CO₂ was subsequently evaporated slowly overnight. After the samples were prepared, the nitrogen gas adsorption isotherm was measured at 77 K and 278 K respectively. A VWR water circulator was used to maintain 278 K. Samples were measured on a Micromeritics 3Flex instrument with subsequent data analysis performed using the associated software.

Methyl 4-aminobenzoate,^[8] methyl 4-azidobenzoate,^[9] 4-azido benzoic acid,^[10] and 4,4'-diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl^[11] were prepared according to literature procedures with minor modifications.

Synthetic Procedures

Synthesis of methyl 4-aminobenzoate



4-Aminobenzoic acid (137.1 g/mol, 39.5 mmol, 5.42 g) was dissolved in methanol (30 mL). To this solution was added conc. H₂SO₄ (5 mL, 93.3 mmol) dropwise followed by heating to reflux for 6 h. The reaction was monitored using TLC (hexanes/ethyl acetate, 50:50 v/v). Upon completion, the solvent was removed *in vacuo* and the crude product was dissolved in EtOAc. Saturated NaHCO₃ was added until no foam observed. Water was added to this solution and the product was extracted using EtOAc (3×50 mL) followed by drying over anhydrous Na₂SO₄ and filtering off the solids. The solvent was evaporated under vacuum and afforded methyl 4-aminobenzoate as a light yellow solid (5.22 g, 34.5 mmol, 87%). Data are consistent with literature values.^[8]

¹H NMR (300 MHz, CDCl₃): δ 7.86 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.65 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.08 (s, 2H, NH₂), 3.87 (s, 3H, CH₃) ppm.

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 167.3 (s, -CO₂), 151.0 (s, C_{Ar}-NH₂), 131.8 (s, C_{Ar}), 119.9 (s, C_{Ar}), 113.9 (s, C_{Ar}-CO₂), 51.7 (s, -OCH₃) ppm.

Synthesis of methyl 4-azidobenzoate



Methyl 4-aminobenzoate (151.2 g/mol, 6.50 mmol, 0.982 g) was dissolved in acetonitrile (15 mL) and placed in an ice bath under N₂ atmosphere. t-Butylnitrite (103.1 g/mol, 1.43 mL, 1.24 g, 12.0 mmol) was added dropwise using a syringe. It was followed by dropwise addition of a dilute solution of trimethylsilyl azide (115.2 g/mol, 1.07 mL, 0.937 g, 8.13 mmol) in acetonitrile (10 mL) and warming to room temperature. The reaction was continued at rt and under N₂ for 2 h. Completion of the reaction was monitored using TLC (hexanes/ethyl acetate, 70:30 v/v). The solvent was evaporated *in vacuo* and column chromatography was performed to isolate methyl 4-azidobenzoate as a light orange solid (0.633 g, 3.57 mmol, 55%). Data are consistent with literature values.^[9]

¹H NMR (300 MHz, CDCl₃): δ 8.04 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.08 (d, *J* = 8.8 Hz, 2H, Ar-H), 3.93 (s, 3H, CH₃) ppm.

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 165.8 (s, -CO₂), 144.9 (s, C_{Ar}-N₃), 131.7 (s, C_{Ar}), 126.0 (s, C_{Ar}), 119.0 (s, C_{Ar}-CO₂), 47.3 (s, -OCH₃) ppm.

Synthesis of 4-Azido benzoic acid

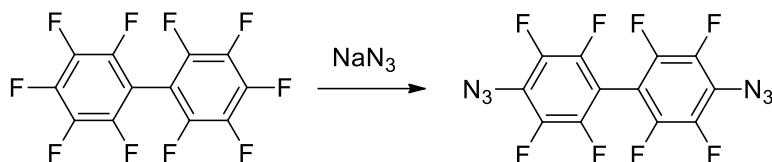


4-Amino benzoic acid (137.1 g/mol, 1.82 mmol, 0.250 g) was dissolved in acetonitrile (4 mL) and was placed in an ice bath. t-Butylnitrite (103.1 g/mol, 0.4 mL, 0.352 g, 3.42 mmol) was added dropwise using a syringe, followed by dropwise addition of a solution of trimethylsilyl azide (115.2 g/mol, 0.3 mL, 0.263 g, 2.28 mmol) in acetonitrile (2 mL) and warming to room temperature. The reaction was monitored using TLC (hexanes/ethyl acetate, 40:60 v/v). After almost 1.5 h stirring and upon completion of the reaction, the solvent was evaporated *in vacuo* and the product was purified and isolated using column chromatography to obtain a light yellow solid (0.282 mg, 1.73 mmol, 95%). Data are consistent with literature values.^[10]

¹H NMR (500 MHz, DMSO-*d*₆): δ 12.79 (s, 1H, -CO₂H), 7.97 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.23 (d, *J* = 8.7 Hz, 2H, Ar-H) ppm.

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ 167.0 (s, -CO₂H), 144.4 (s, C_{Ar}-N₃), 131.7 (s, C_{Ar}), 127.7 (s, C_{Ar}), 119.6 (s, C_{Ar}-CO₂H) ppm.

Synthesis of 4,4'-diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl

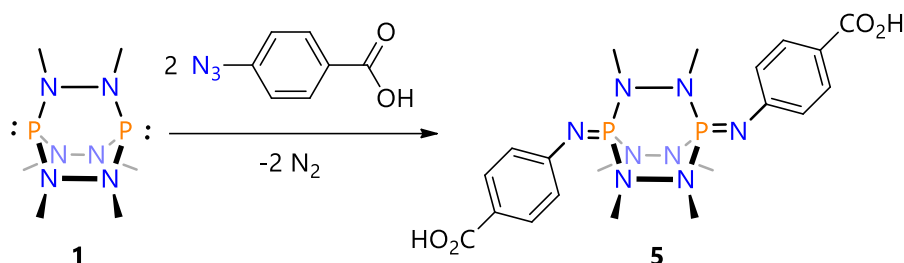


Perfluoro-1,1'-biphenyl (334.1 g/mol, 29.9 mmol, 10.0 g) was dissolved in DMF (50 mL) in a round bottom flask at rt. NaN₃ (65.02 g/mol, 59.9 mmol, 3.90 g) was dissolved in DMF (5 mL) and added portion-wise to the reaction flask under stirring which formed a milky suspension. The progress of the reaction was monitored with TLC using hexanes as the eluent. After 18 h and upon completion of the reaction water was added to the reaction mixture and cooled down in an ice bath which led to precipitate formation. It was then filtered using suction filtration to obtain a white solid as the product (10.1 g, 26.6 mmol, 93%). Data are consistent with literature values.^[11]

¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -140.40 to -140.46 (m, 4F), -152.00 to -152.08 (m, 4F) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 144.43 (dd, ¹J_{CF} = 256.2 Hz, ²J_{CF} = 13.2 Hz, C_{Ar}-F), 140.71 (dd, ¹J_{CF} = 253.6 Hz, ²J_{CF} = 15.46 Hz, C_{Ar}-F), 122.05 (t, ²J_{CF} = 12.26 Hz, C_{Ar}), 101.90 (t, ²J_{CF} = 15.95 Hz, C_{Ar}-N₃) ppm.

Synthesis of Compound 5



Inside a glovebox **1** (236.1 g/mol, 5.71 mmol, 1.35 g) and 4-azidobenzoic acid (163.1 g/mol, 12.6 mmol, 2.05 g) were added to a 100 mL Schlenk flask. THF (53 mL) was added to this mixture and the reaction solution was stirred at 65 °C for 24 h which led to the formation of light yellow precipitate. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo* to give a yellow solid. The solid was triturated with ethanol until the supernatant was colorless. The white solid was dried in vacuum oven at 50 °C overnight to afford compound **5** as a white solid (0.926 g, 1.83 mmol, 32%).

mp: 263-265 °C.

IR (KBr pellet, cm⁻¹): 3050, 2965, 2937, 2899, 2663, 2555, 2126, 1919, 1681, 1595, 1554, 1515, 1461, 1376, 1310, 1290, 1203, 1169, 1130, 1095, 1055, 969, 851, 817, 773, 698, 672, 638 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆): δ 12.27 (s, 2H, -CO₂H), 7.72 (d, *J* = 8.5 Hz, 4H, Ar-H), 6.82 (d, *J* = 8.5 Hz, 4H, Ar-H), 2.91 (m, 18H, N-Me) ppm.

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ 167.8 (s, -CO₂H), 151.6 (apparent t, *J* = 3.90, C_{Ar}), 131.2 (s, C_{Ar}), 122.9 (apparent t, *J* = 7.53, C_{Ar}), 121.4 (s, C_{Ar}), 36.8 (apparent t, *J* = 1.92, N-Me) ppm.

³¹P NMR (202 MHz, DMSO-*d*₆): -4.12 (s, 4P, cage) ppm.

Elemental analysis: calc./expt. for C₂₀H₂₈N₈O₄P₂: C – 47.43/47.60, H – 5.57/5.60, N – 22.13/22.04.

HRMS (ESI, negative mode): *m/z* calcd for C₂₀H₂₈N₈O₄P₂ [M-H]⁻ 505.1636, found: 505.1626, error: 2 ppm.

X-Ray (CCDC): 2297661.

Synthesis of Compound 6

Compound **5** (506.4 g/mol, 0.249 mmol, 0.126 g) was added to a 20 mL vial followed by the addition of 13.08 mL DMF. 3.520 mL of a 30.0 mg/mL stock solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMF (prepared by dissolving 0.896 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 29.8 mL DMF) was added to the vial followed by 1.00 mL deionized water. The vial was capped, and the mixture was swirled then sonicated for 5 min to afford a clear colorless solution. This solution was divided into two 20 mL vials, sealed with Teflon tape and capped. The vials were placed in a fitting aluminum block inside a preheated oven at 80 °C and heated for 4 days. The light-yellow solution was decanted, and the colorless crystals were scraped off the vial by spatula and further washed with 3×7 mL DMF. The crystals were soaked in 7 mL DMF overnight then washed with 3×10 mL chloroform. Crystals floating on chloroform were harvested by pipetting chloroform from the bottom of the vial and left drying under ambient air overnight to afford large colorless crystals (0.115 g, 0.161 mmol, 65%).

Decomposition onset points (TGA): 5% decomposition at 239.5 °C.

IR (KBr pellet, cm^{-1}): 3408, 3060, 2958, 2933, 2896, 2797, 1664, 1621, 1597, 1515, 1375, 1202, 1174, 1142, 1094, 972, 855, 675.

^1H ssNMR: δ 7.8 (Ar-H), 6.6 (Ar-H), 4.4 (N-Me), 2.6- 1.7 (N-Me) ppm.

^{31}P ssNMR: δ 1.8 (sharp, cage), -1.0 (sharp, cage) ppm.

^{13}C ssNMR: δ 171.1, 165.9, 161.9, 150.7, 130.5, 123.9, 119.5, 107.8, 40.7, 38.2, 36.1, 31.2 ppm.

Elemental analysis: calc./expt. for $\text{C}_{52}\text{H}_{80}\text{Zn}_2\text{N}_{20}\text{O}_{12}\text{P}_4$: C – 43.62/43.5, H – 5.63/5.41, N – 19.56/19.48.

X-ray (CCDC): 2297659.

Synthesis of Compound 7

Compound **5** (506.4 g/mol, 0.249 mmol, 0.126 g) was added to a 20 mL vial followed by the addition of 13.57 mL DMF. 3.21 mL of a stock solution of 15.08 mg/mL CoCl₂ in DMF (prepared by dissolving 0.448 g CoCl₂ in 29.7 mL DMF) was added to the vial followed by 1.00 mL deionized water. The vial was capped, and the mixture was swirled then sonicated for 5 min to afford a clear colorless solution. This solution was divided into two 20 mL vials, sealed with Teflon tape and capped. The vials were placed in a fitting aluminum block inside a preheated oven at 80 °C and heated for 4 days. The clear blue solution was decanted, and the dark blue crystals were scraped off the vial by spatula and further washed with 3×7 mL DMF. The crystals were soaked in 7 mL DMF overnight then washed with 3×10 mL chloroform. Crystals floating on chloroform were harvested by pipetting chloroform from the bottom of the vial and left drying under ambient air overnight to afford large dark blue crystals (0.0976 g, 0.136 mmol, 55%).

It is noteworthy that compound 7 is paramagnetic. This leads to very broad lines as can be seen in ¹H and ³¹P NMR spectra, figures S20-S21.

Decomposition onset points (TGA): 5% decomposition at 251.1 °C.

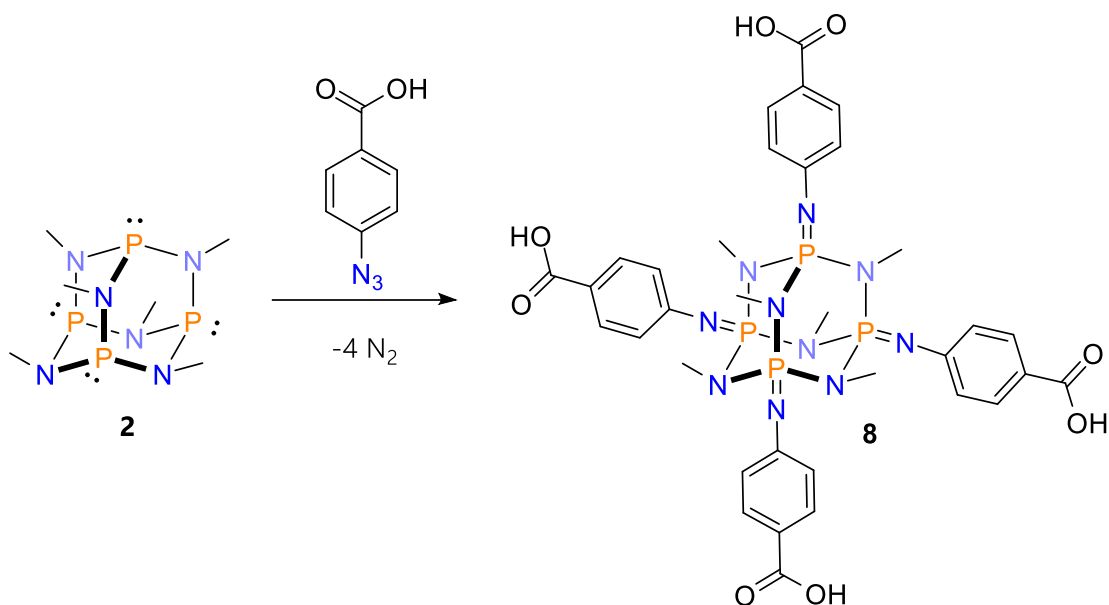
IR (KBr pellet, cm⁻¹): 3424, 3059, 2959, 2933, 2896, 2796, 2554, 1918, 1598, 1516, 1373, 1202, 1171, 1094, 973, 855, 721, 675.

¹H ssNMR: δ 38.3, 1.3 ppm.

Elemental analysis: calc./expt. for C₅₂H₈₀Co₂N₂₀O₁₂P₄: C – 44.01/43.63, H – 5.68/5.37, N – 19.74/19.57.

X-ray (CCDC): 2294196 and 2294197.

Synthesis of Compound 8



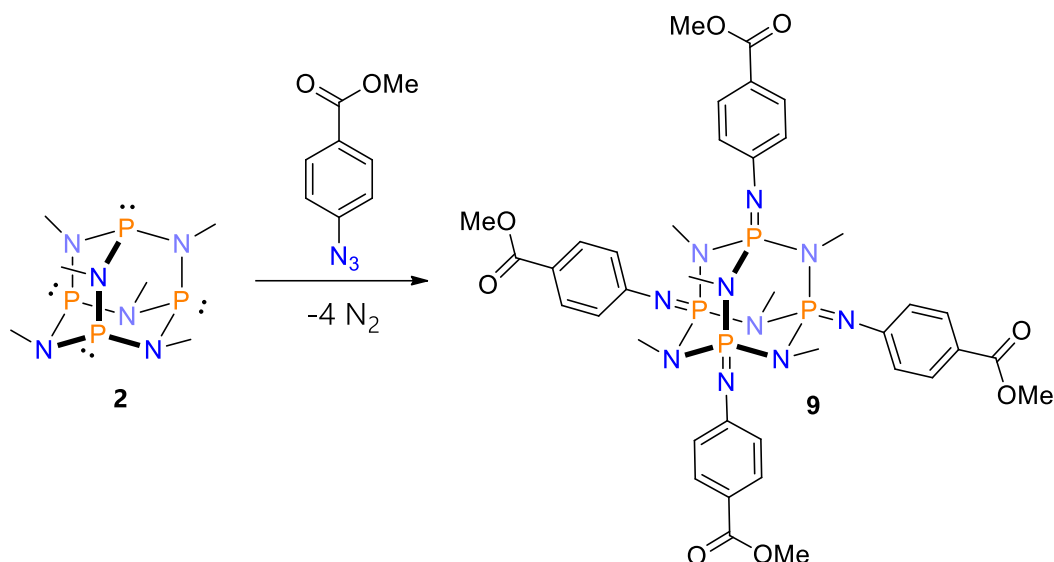
Inside a glovebox, **2** (298.1 g/mol, 0.033 mmol, 0.010 g) and 4-azidobenzoic acid (163.1 g/mol, 0.151 mmol, 0.024 g) were dissolved in THF (0.7 mL) to form a clear yellow solution and transferred to an NMR tube. The NMR tube was then placed in an oil bath at 100 °C and stirred for 2 days. The emergence of N₂ bubbles as well as formation of some orange precipitate was observed during the first few hours. Finally, acetonitrile was added to crash out crude product as an orange solid (**8**) (0.002 g, 0.002 mmol, 7.0%).

Despite several trials to improve the yield of the reaction and scale up the synthesis, satisfactory results were not obtained. Compound **8** was therefore only characterized in-situ by NMR spectroscopy.

¹H NMR (300 MHz, DMSO-*d*₆): δ 12.43 (s, 4H, -CO₂H), 7.81 (d, *J* = 8.4 Hz, Ar-H), (d, *J* = 8.4 Hz, 8H, Ar-H), 3.07-3.14 (m, 18H, N-Me) ppm.

³¹P NMR (122 MHz, DMSO-*d*₆): -10.33 (s, 4P, cage) ppm.

Synthesis of Compound 9



Inside a glovebox, **2** (298.1 g/mol, 0.335 mmol, 0.100 g) and methyl 4-azidobenzoate (177.2 g/mol, 1.34 mmol, 0.238 g) were added to 38 mL pressure tube equipped with a threaded PTFE cap. THF (15 mL) was added to form a clear colorless solution and formed N₂ bubbles during the first few hours. The pressure tube was placed in an oil bath at 100 °C and stirred for 19 h to form a yellow clear solution. The progress of the reaction was monitored using TLC (hexanes/ethyl acetate, 70:30 v/v). Upon completion, the reaction solution was concentrated *in vacuo* and the residue was subjected to silica flash column chromatography to afford compound **9** as a white solid (0.250 g, 0.279 mmol, 83%).

mp: 175.9-177.6 °C.

IR (NaCl plates, cm⁻¹): 3034, 2990, 2948, 1714, 1599, 1560, 1513, 1434, 1380, 1306, 1273, 1170, 1094, 1033, 966, 900, 854, 822, 771, 700, 675.

¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.4 Hz, 8H, Ar-H), 6.94 (d, *J* = 8.5 Hz, 8H, Ar-H), 3.90 (s, 12H, O-Me), 3.17-3.23 (m, 18H, N-Me) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.0 (s, -CO₂), 149.7 (s, C_{Ar}), 131.3 (s, C_{Ar}), 123.0-122.8 (m, C_{Ar}), 122.4 (s, C_{Ar}), 51.8 (s, O-Me), 33.1 (s, N-Me) ppm.

³¹P NMR (162 MHz, CDCl₃): -11.35 (s, 4P, cage) ppm.

Elemental analysis: calc./expt. for C₃₈H₄₆N₁₀O₈P₄: C – 51.01/50.66, H – 5.18/5.17, N – 15.65/15.45.

HRMS (ESI, positive mode): *m/z* calcd for C₃₈H₄₆N₁₀O₈P₄ [M+Na]⁺: 917.2343, found: 917.2320, error: 2.5 ppm.

X-Ray (CCDC) : 2290656.

Attempted basic hydrolysis of compound 9:

To a solution of compound **9** (894.7 g/mol, 0.032 mmol, 0.029 g) in THF/H₂O (4 mL, 3:1 v/v) equipped with stir bar was added KOH (0.171 mmol, 0.010 g). The reaction mixture stirred at 70 °C for 2 h followed by heating to 87 °C for 48 h. Gradually, the formation of an orange solution was observed. The solution was acidified using acetic acid, washed with water, and extracted with EtOAc. The organic layer was concentrated *in vacuo*. The progress of the reaction and the final crude product were monitored via TLC and ³¹P NMR spectroscopy (Figure S50) which showed a mixture of byproducts and the unconsumed compound **9** as the major material. Addition of more KOH did not result in formation of compound **8**, suggesting the observed peaks correspond to side-products rather than intermediates.

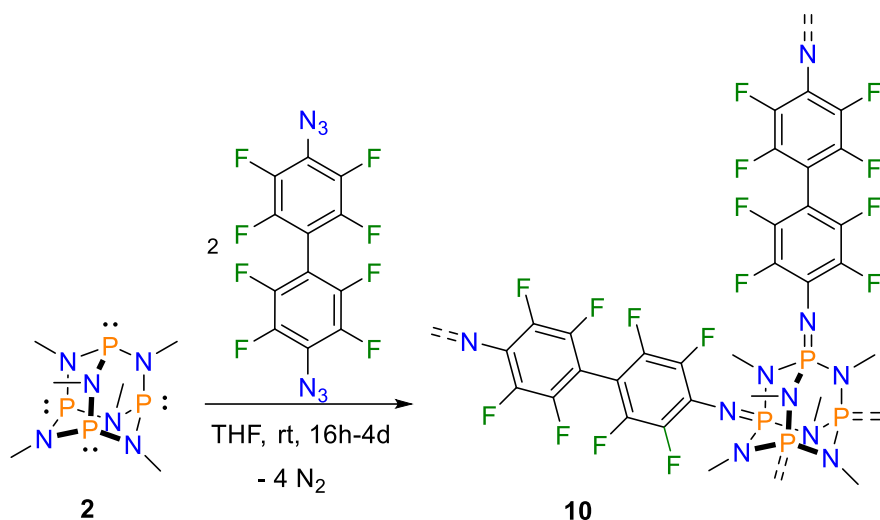
Attempted acidic hydrolysis of compound 9:

To a solution of compound **9** (894.7 g/mol, 0.011 mmol, 0.010 g) in THF (1.5 mL) was added 1.0 M HCl (0.5 mL). The mixture was transferred to an NMR tube and heated to reflux for 2 h. The reaction was monitored using ³¹P NMR spectroscopy (Figure S51) which indicated the decomposition of the starting material under acidic condition.

Attempted ZnBr₂ catalyzed hydrolysis of compound 9:

To a solution of compound **9** (894.7 g/mol, 0.029 mmol, 0.026 g) in DCM (5mL) equipped with stir bar was added ZnBr₂ (0.58 mmol, 0.130 g). The mixture stirred at room temperature for 24 h. The cloudy solution was then treated with H₂O (20 mL) and stirred for 2h. Following this step, the reaction mixture was heated to 50 °C and stirred at this temperature for 48 h. The progress of the reaction was monitored via TLC and crude ³¹P NMR which indicated only the unconsumed starting material exists.

Synthesis of compound **10**



Procedure for solution and film synthesis:



Figure S1. Film made by drop casting the viscous solution of **10** on a Teflon mold.

Inside a glovebox, **2** (298.1 g/mol, 0.248 mmol, 0.0740 g) and 4,4'-Diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (380.2 g/mol, 0.499 mmol, 0.190 g) were added to 25 mL pressure tube equipped with a threaded PTFE cap. THF (9.60 mL) was added to obtain a clear yellow solution. The reaction vessel was capped and stirred at room temperature overnight, followed by heating to 60 °C in an oil bath for four days with stirring. A pale yellow slightly cloudy solution was obtained (**10**). Volatiles were removed under vacuum while stirring the solution to obtain a 2 mL clear light yellow highly viscous solution. This viscous solution was used for drop-casting on a Teflon mold (**Figure S1**).

Procedure for gel synthesis:

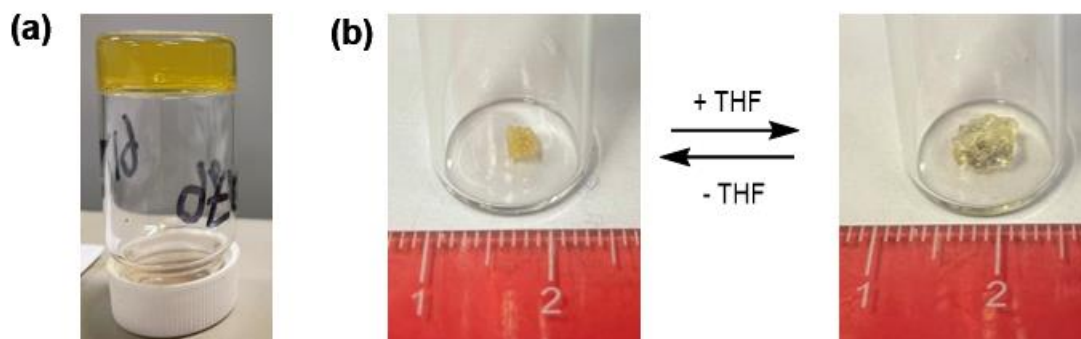


Figure S2. a) Gel formed in the vial. **b)** Swelling of the gel in THF (THF removed from the vial after swelling).

Inside a glovebox, **2** (298.2 g/mol, 0.294 mmol, 0.0878 g) and 4,4'-Diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (380.2 g/mol, 0.589 mmol, 0.224 g) were added to a 4 Dr vial. THF (3.75 mL) was added to obtain a clear yellow solution (nitrogen bubbles emerge immediately). The vial was capped and left for two days at room temperature in the glove box without stirring upon which a yellow clear gel was obtained (**10**) (**Figure S2. a**). Volatiles were removed under vacuum to obtain a yellow hard solid. The solid material was soaked in THF overnight to obtain a soft gel again (**Figure S2. b**). Similarly, this gel swells in dichloromethane and ethanol. The gel was washed by repeating the swelling two more times and replacing the THF with fresh THF in each round. Finally, the gel was dried under vacuum for two days at ambient temperature to obtain a hard solid. The solid was crushed with a mortar and pestle for analysis by $^{31}\text{P}\{^1\text{H}\}$, ^{19}F , and ^1H solid-state NMR spectroscopy.

Decomposition onset points (TGA): 5% decomposition at 267.4 °C.

IR (NaCl plate, cm^{-1}): 3668, 3439, 2953, 2893, 2827, 2537, 2393, 2123, 1777, 1648, 1480, 1322, 1219, 1034, 966, 870, 721, 676.

^1H ssNMR: δ 3.1 (N-Me) ppm. The peak at 1.3 ppm corresponds to residual THF.

^{31}P ssNMR: δ 2.2 to-12.2 (broad, cage) ppm.

^{19}F ssNMR: δ -144.2 (sharp, Ar-F), -155.1 (sharp, Ar-F) ppm.

Synthesis of compound 12

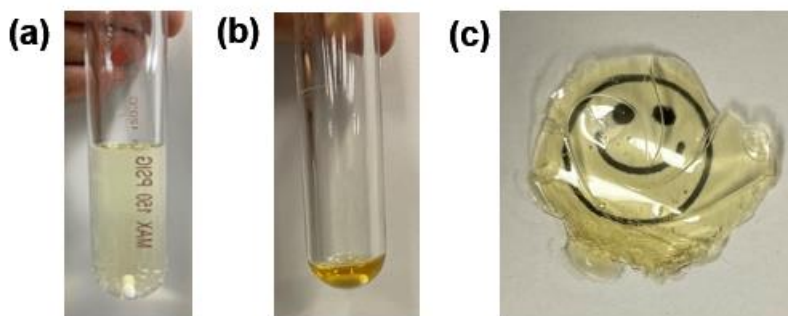
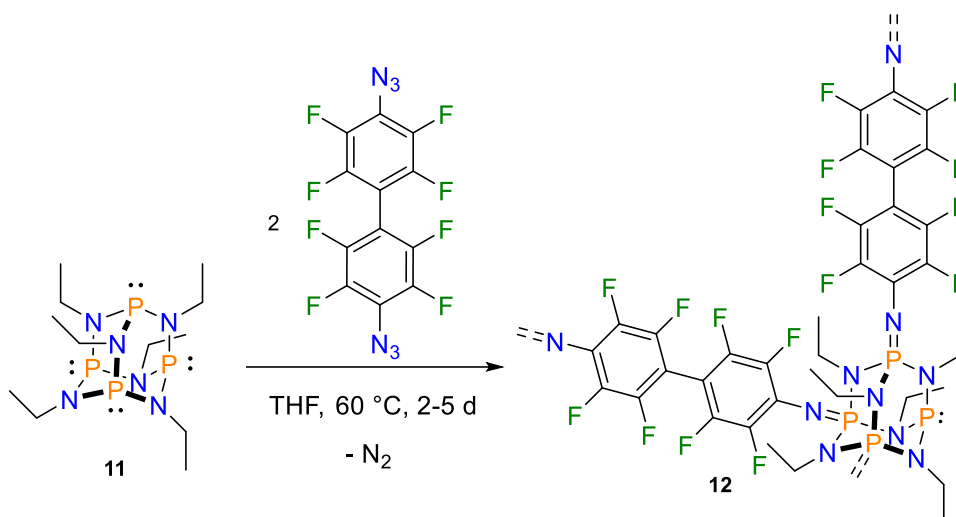


Figure S3. **a)** Reaction solution, **b)** concentrated viscous solution, **c)** film made by drop casting the viscous solution on a Teflon mold.

Procedure for solution and film synthesis:

Inside a glovebox, **11** (382.3 g/mol, 0.253 mmol, 0.0967 g) and 4,4'-Diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (380.2 g/mol, 0.507 mmol, 0.193 g) were added to a 25 mL pressure tube equipped with a threaded PTFE cap. THF (9.70 mL) was added to obtain a clear yellow solution then the reaction vessel was capped and heated to 60 °C in an oil bath for five days with stirring. A pale-yellow clear solution was obtained (**12**) (**Figure S3. a**). Volatiles were removed under vacuum when stirring the solution to obtain a 1 mL clear yellow viscous solution (**Figure S3. b**). This viscous solution was used for

making films by drop-casting on a Teflon mold (**Figure S3. c**). $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F NMR spectra of the polymer solution are shown.

Procedure for gel synthesis:

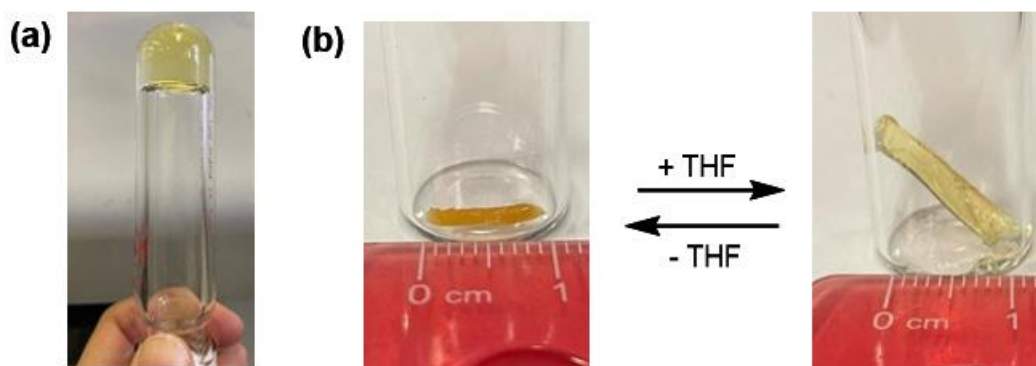


Figure S4. a) Gel formed in the reaction vessel, **b)** swelling of the gel in THF (THF removed from the vial after swelling)

Inside a glovebox, **11** (382.3 g/mol, 0.267 mmol, 0.102 g) and 4,4'-Diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (380.2 g/mol, 0.535 mmol, 0.203 g, 2.00 equ.) were added to 25 mL pressure tube equipped with a threaded PTFE cap. THF (3.40 mL) was added to obtain a clear yellow solution then the reaction vessel was capped and heated to 60 °C in an oven for two days, without stirring. A light-yellow clear gel was obtained (**12**) (**Figure S4. a**). Volatiles were removed under vacuum to obtain yellow hard solid. The solid material was soaked in THF overnight to obtain a soft gel again. This gel can absorb 500-600% (w/w) THF by swelling (**Figure S4. b**). Similarly, this gel swells in dichloromethane, acetone, ethyl acetate, DMF, diethyl ether, dioxane, toluene, and xylene. The gel was washed by repeating the swelling two more times and replacing the THF with fresh THF in each round. Finally, the gel was dried under vacuum for two days at ambient temperature to obtain a hard solid. The solid was crushed with a mortar and pestle for analysis by ^{19}F , ^{31}P , and ^1H solid-state NMR spectroscopy.

Decomposition onset points (TGA): 5% decomposition at 357.9 °C.

IR (NaCl plate, cm^{-1}): 3406, 2979, 2936, 2875, 2536, 2470, 2394, 2122, 1647, 1530, 1479, 1382, 1315, 1217, 1165, 1054, 965, 930, 884, 772, 720, 672, 634.

^1H ssNMR: δ 3.2 (N-Me), 1.3 (N-Me) ppm.

³¹P ssNMR: δ 66.2 (sharp, cage), 2.6 to -9.7 (broad, cage) ppm.

¹⁹F ssNMR: δ -144.1 (sharp, Ar-F), -154.9 (sharp, Ar-F) ppm.

NMR Spectra

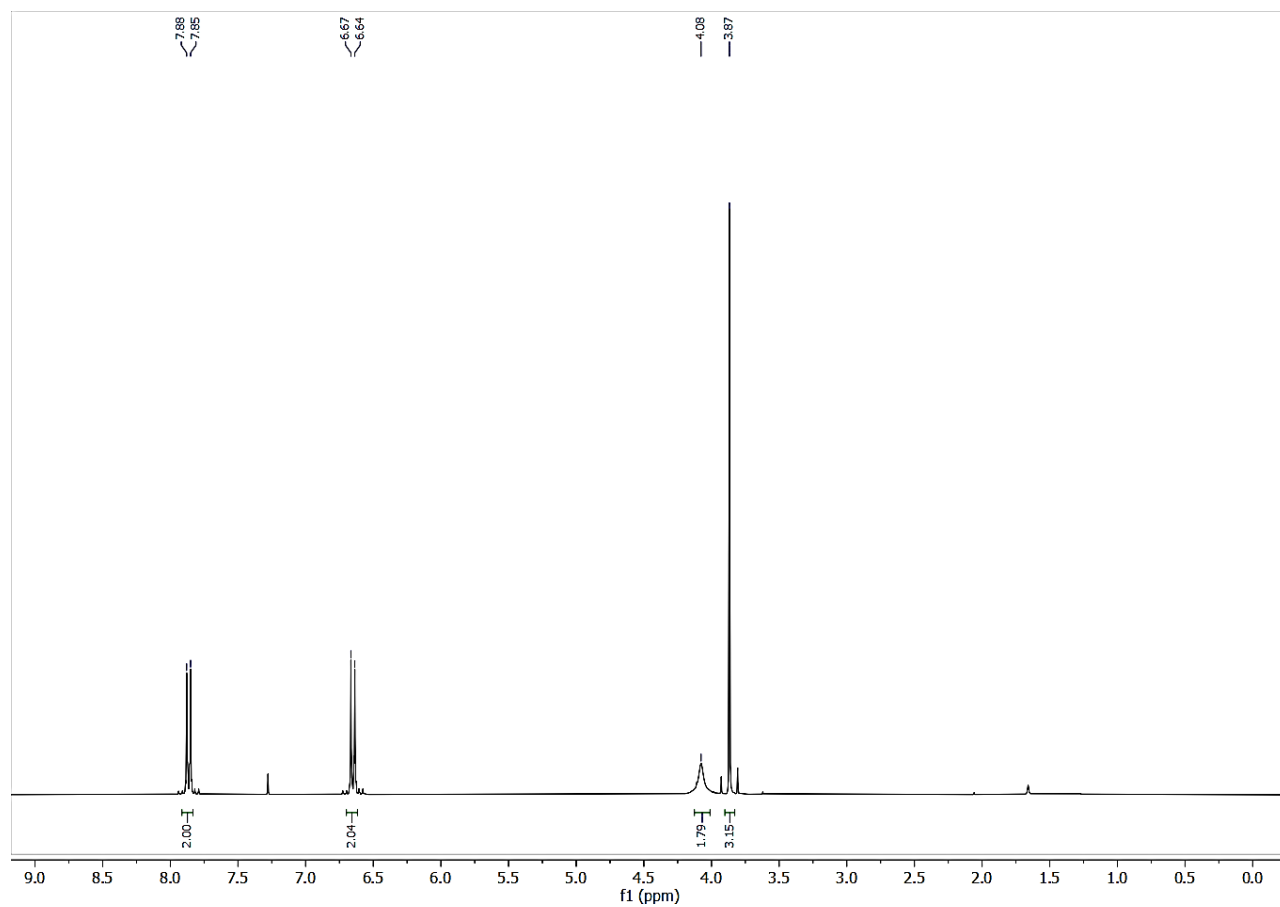


Figure S5. ^1H NMR spectrum (300 MHz, CDCl_3) of methyl 4-aminobenzoate.

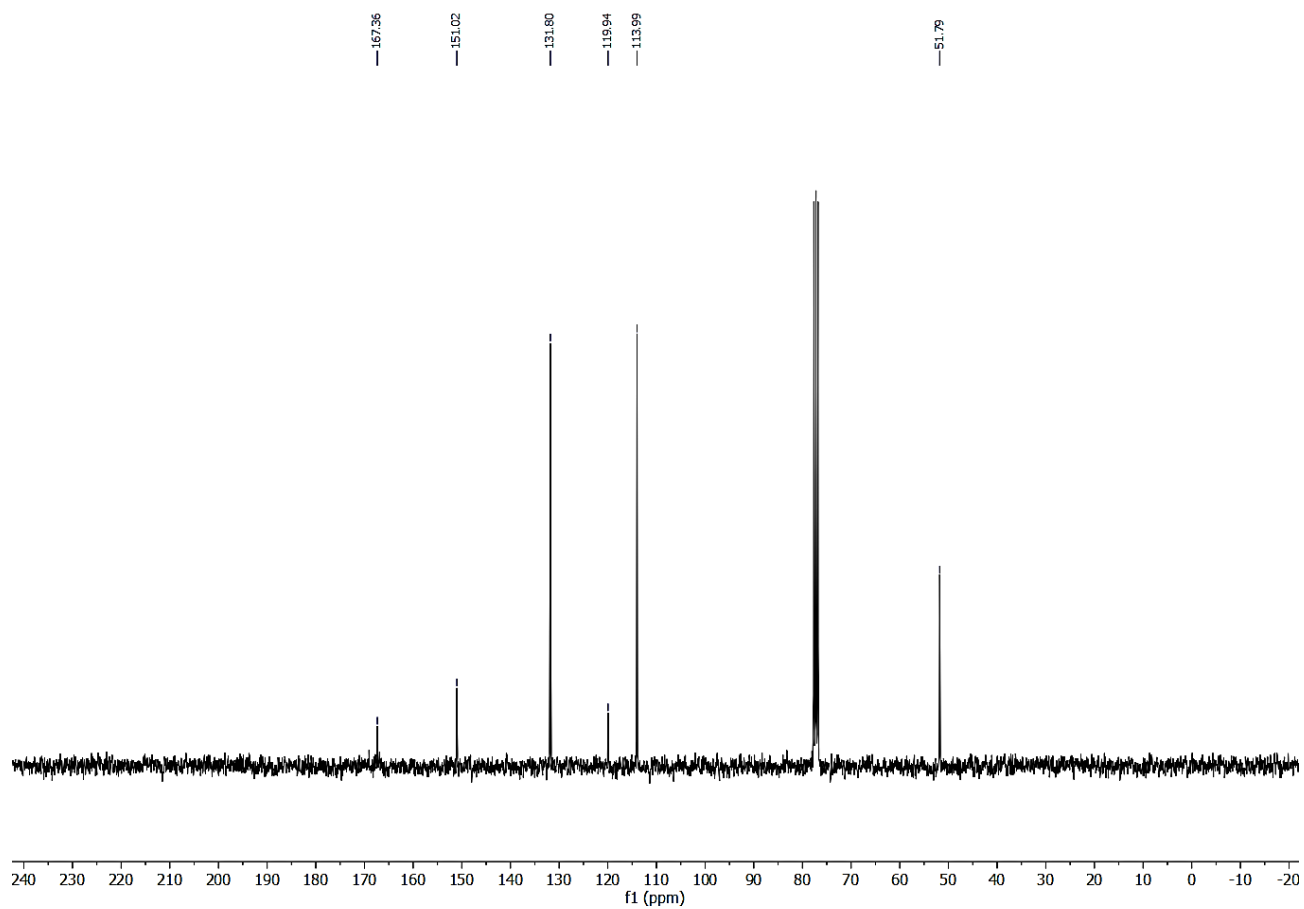


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3) of methyl 4-aminobenzoate.

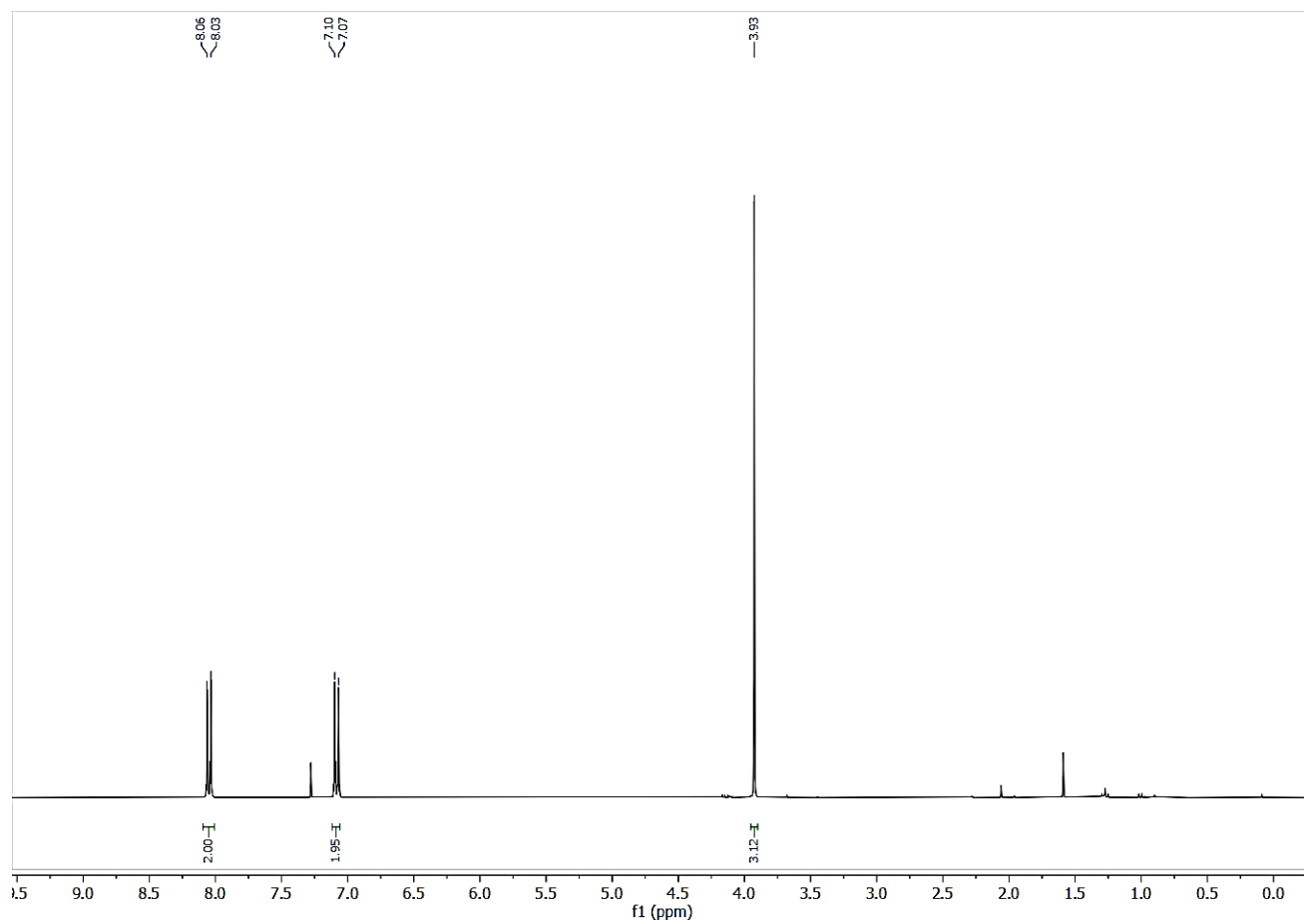


Figure S7. ^1H NMR spectrum (300 MHz, CDCl_3) of methyl 4-azidobenzoate.

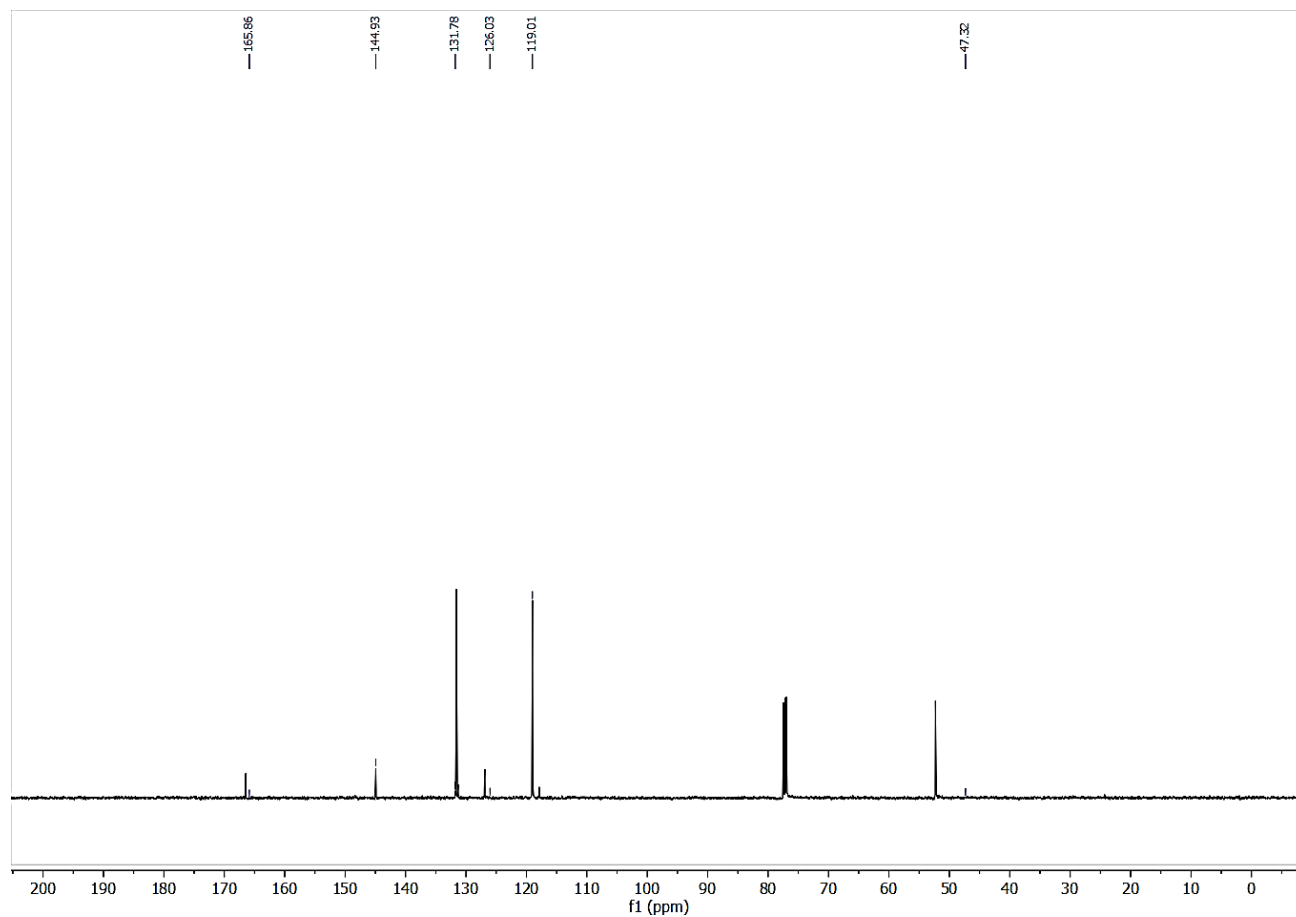


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3) of methyl 4-azidobenzoate.

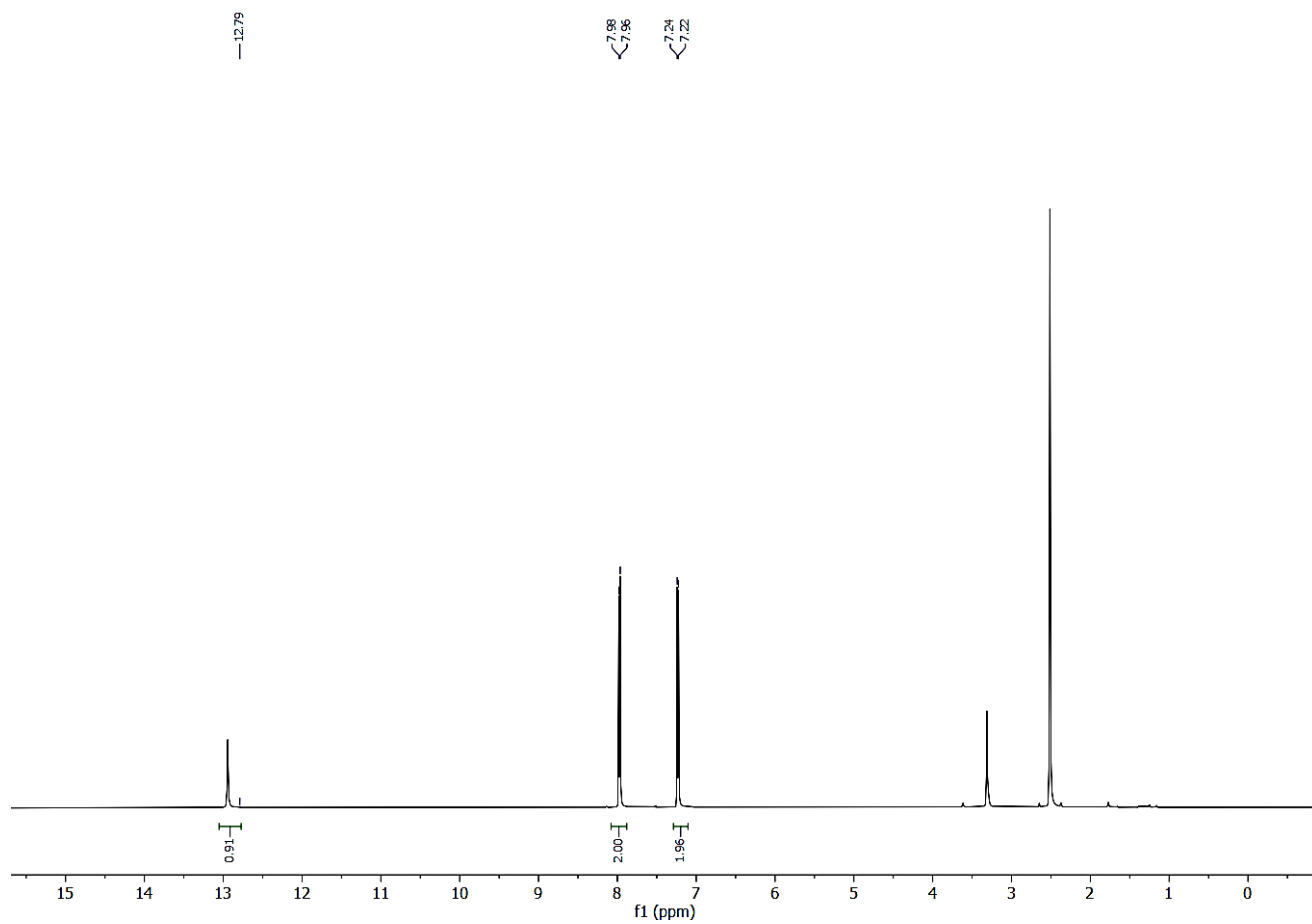


Figure S9. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of 4-Azido benzoic acid.

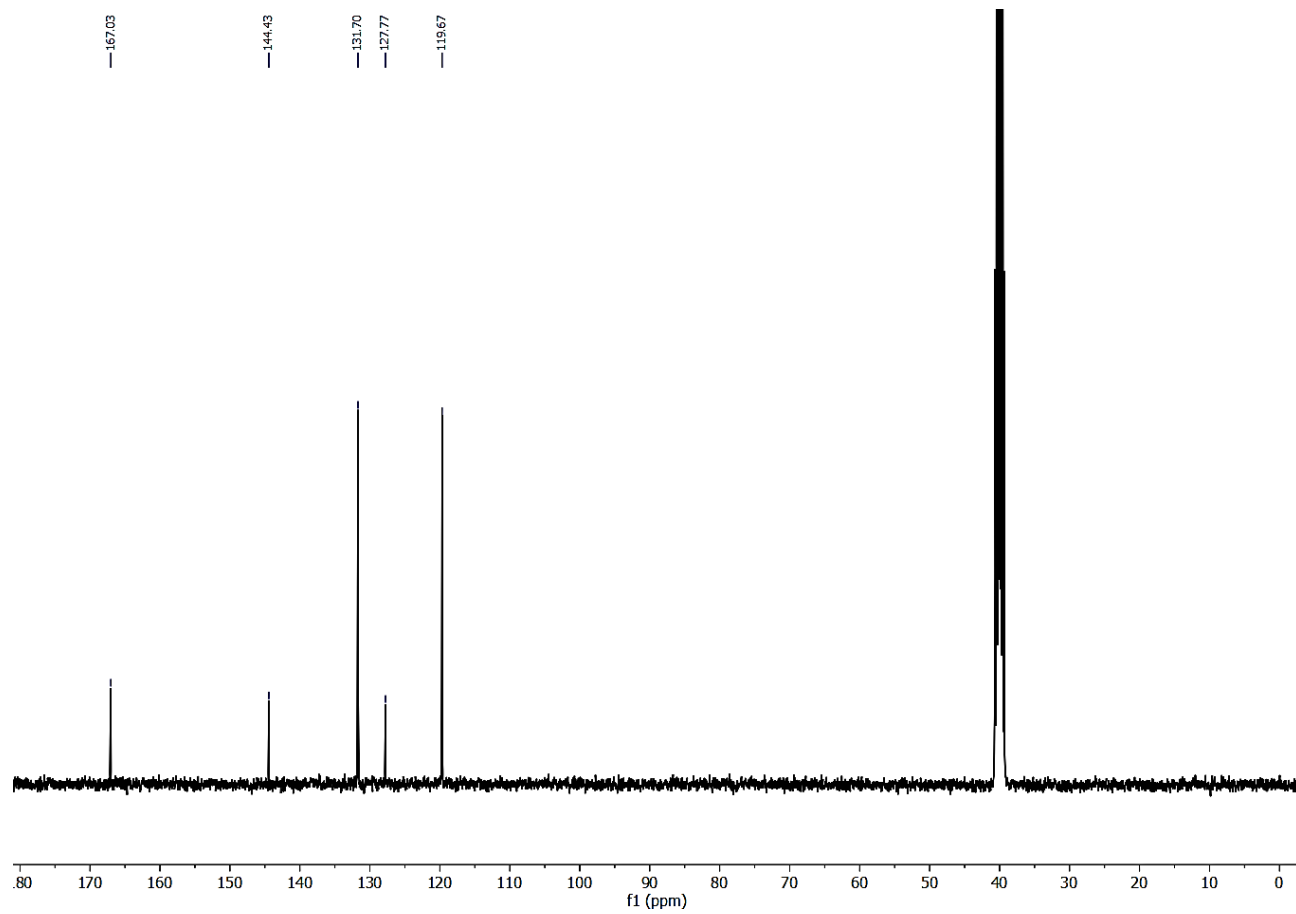


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, DMSO- d_6) of 4-Azido benzoic acid.

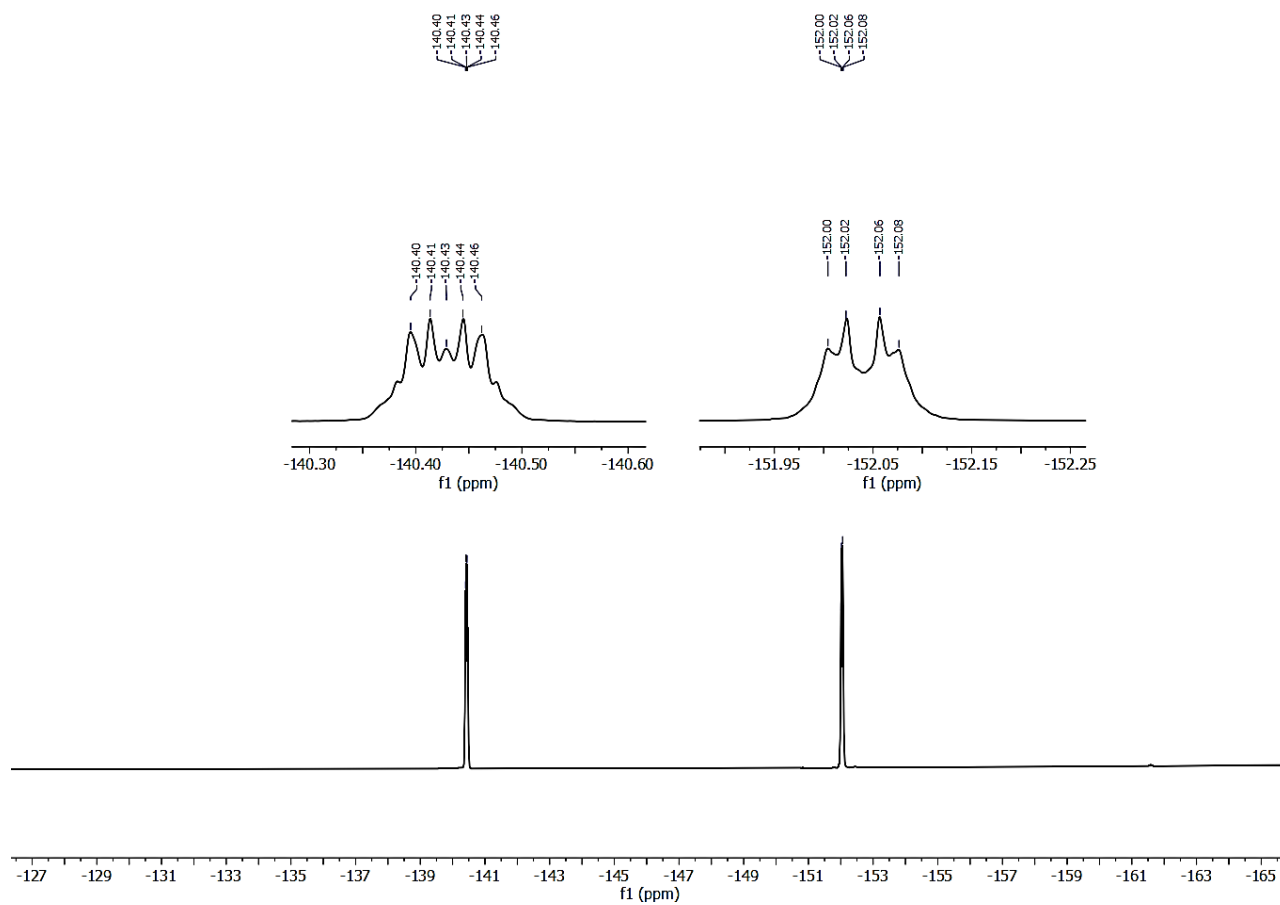


Figure S11. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (377 MHz, CDCl_3) spectrum of monomer 4,4'-diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl in CDCl_3 .

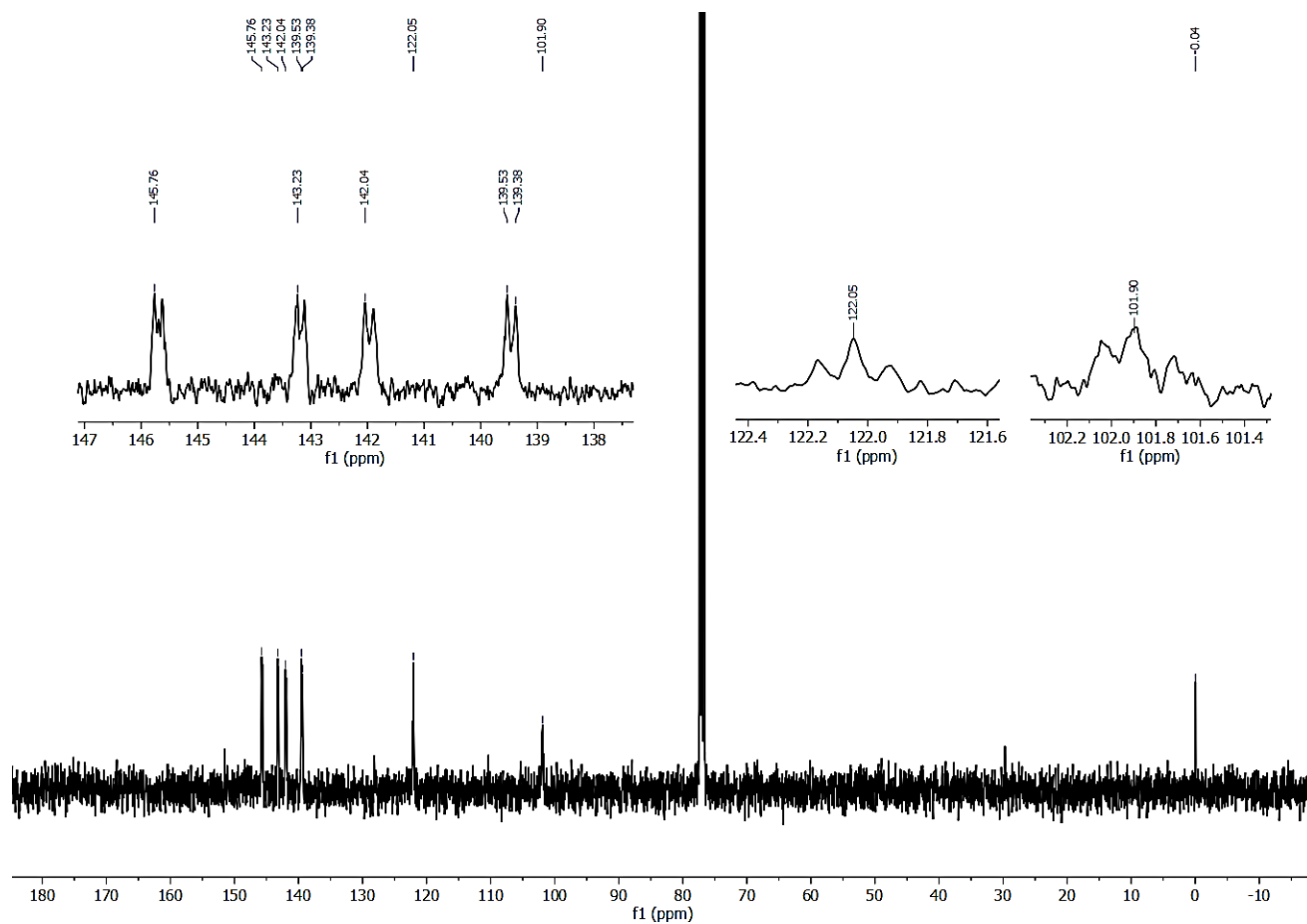


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of monomer 4,4'-diazido-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl in CDCl_3 .

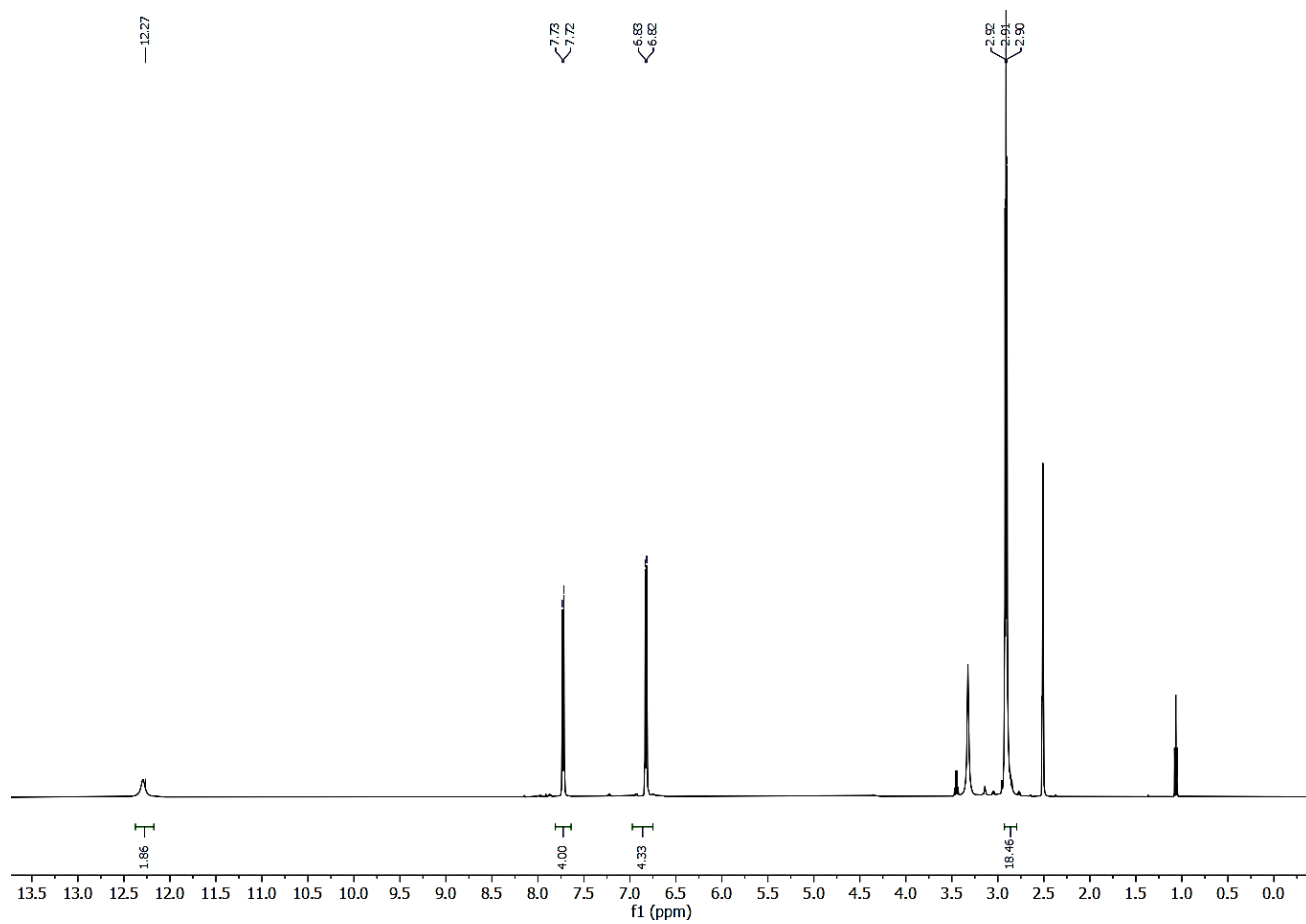


Figure S13. ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$) of **5**.

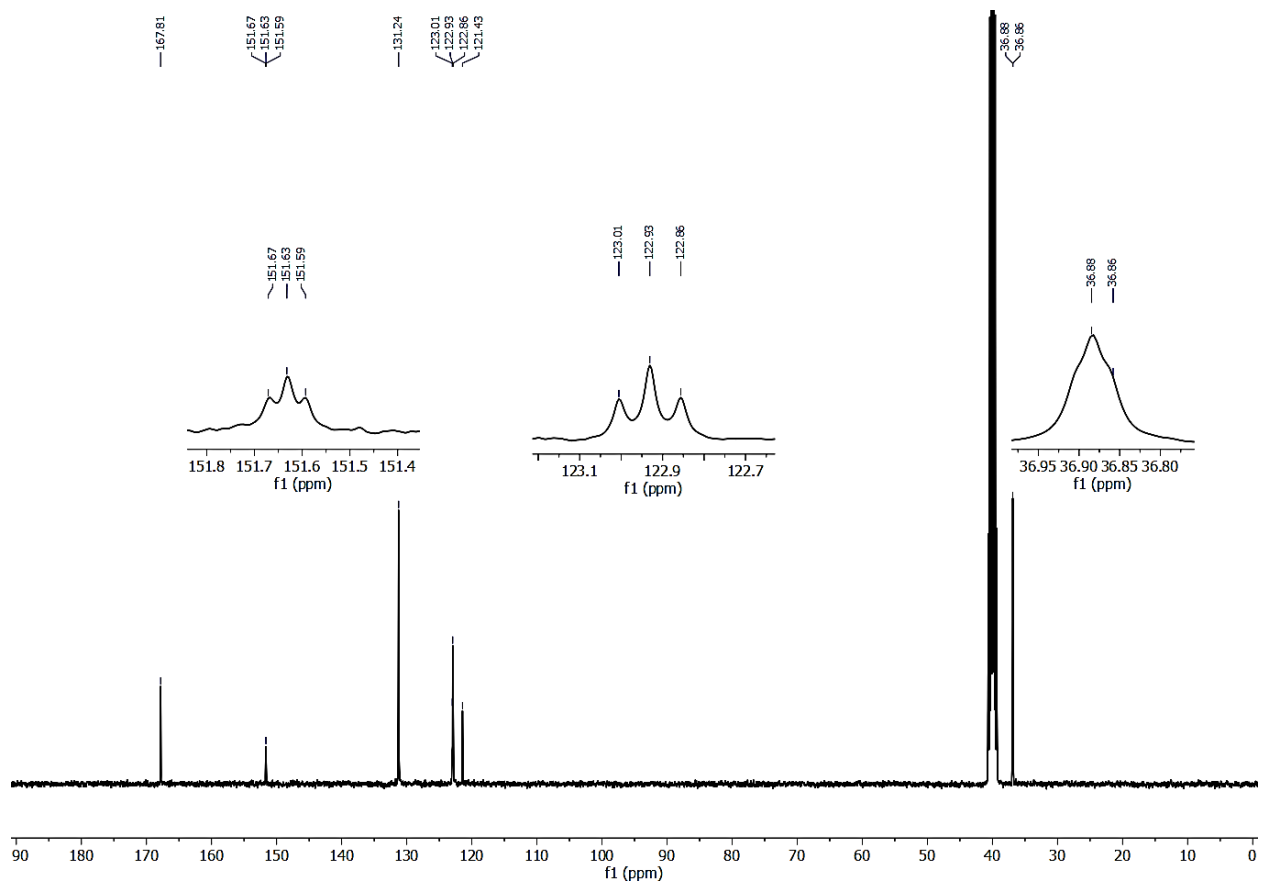


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{DMSO-}d_6$) of **5**.

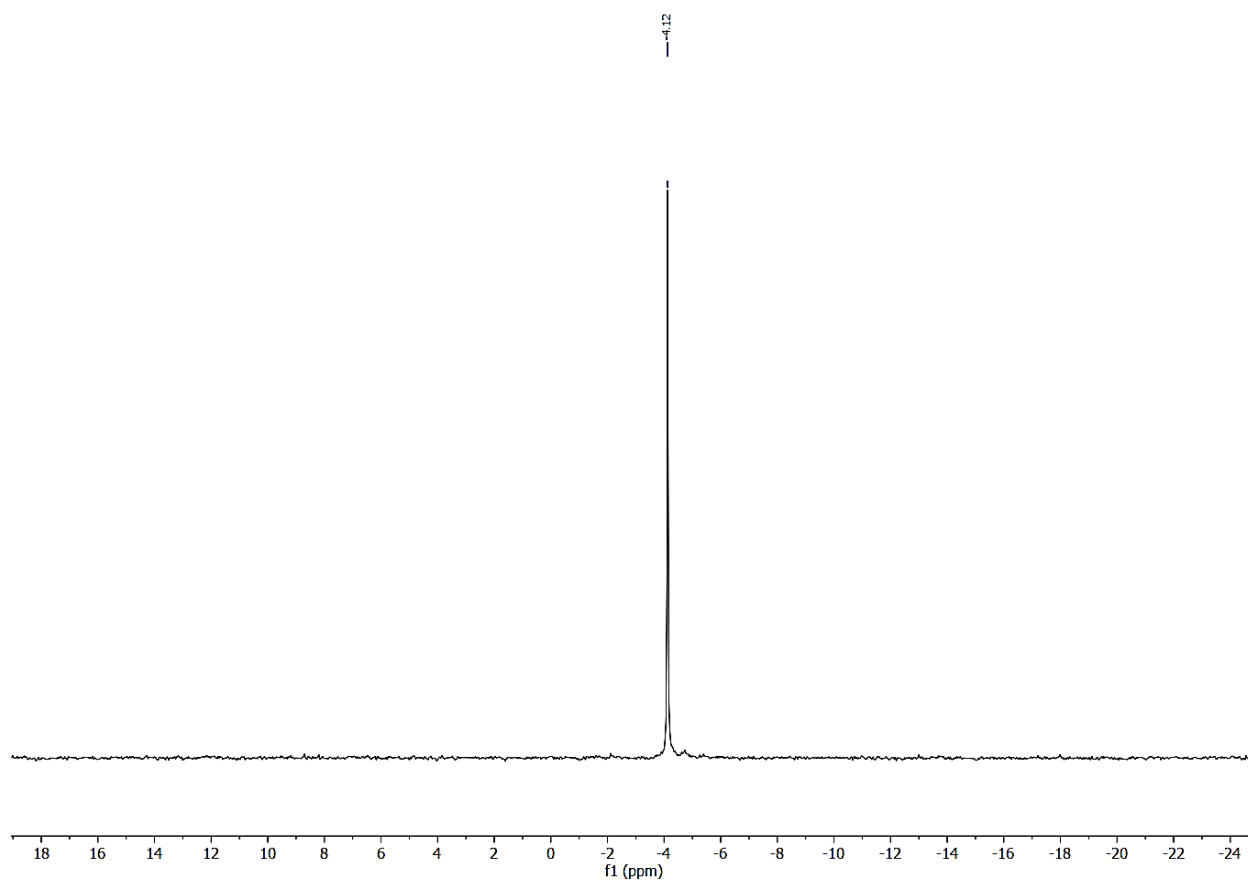


Figure S15. ^{31}P NMR spectrum (202 MHz, $\text{DMSO-}d_6$) of **5**.

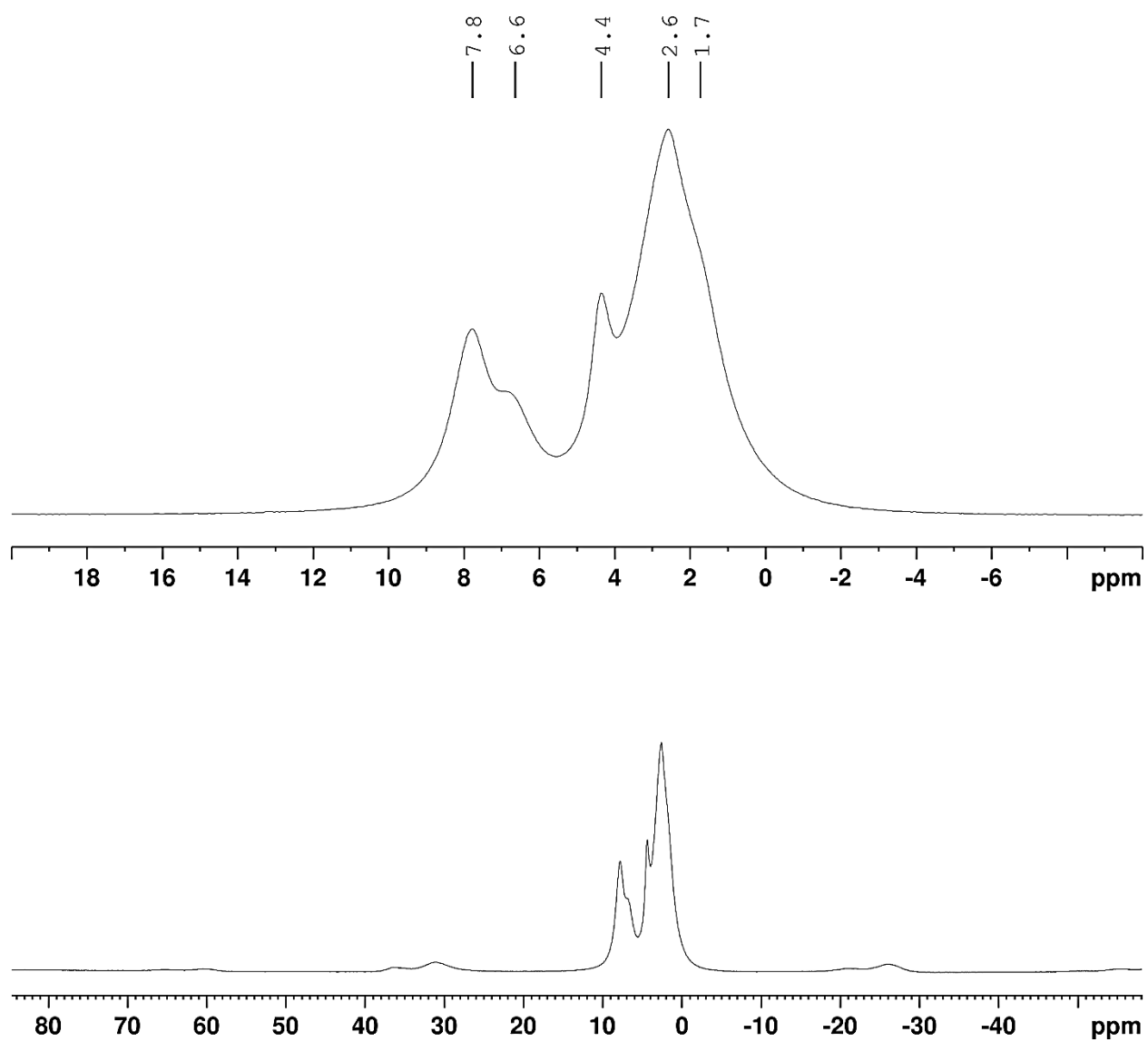


Figure S16. Solid state ^1H MAS NMR spectrum of **6** at 20 kHz MAS. Unlabelled peaks are spinning sidebands.

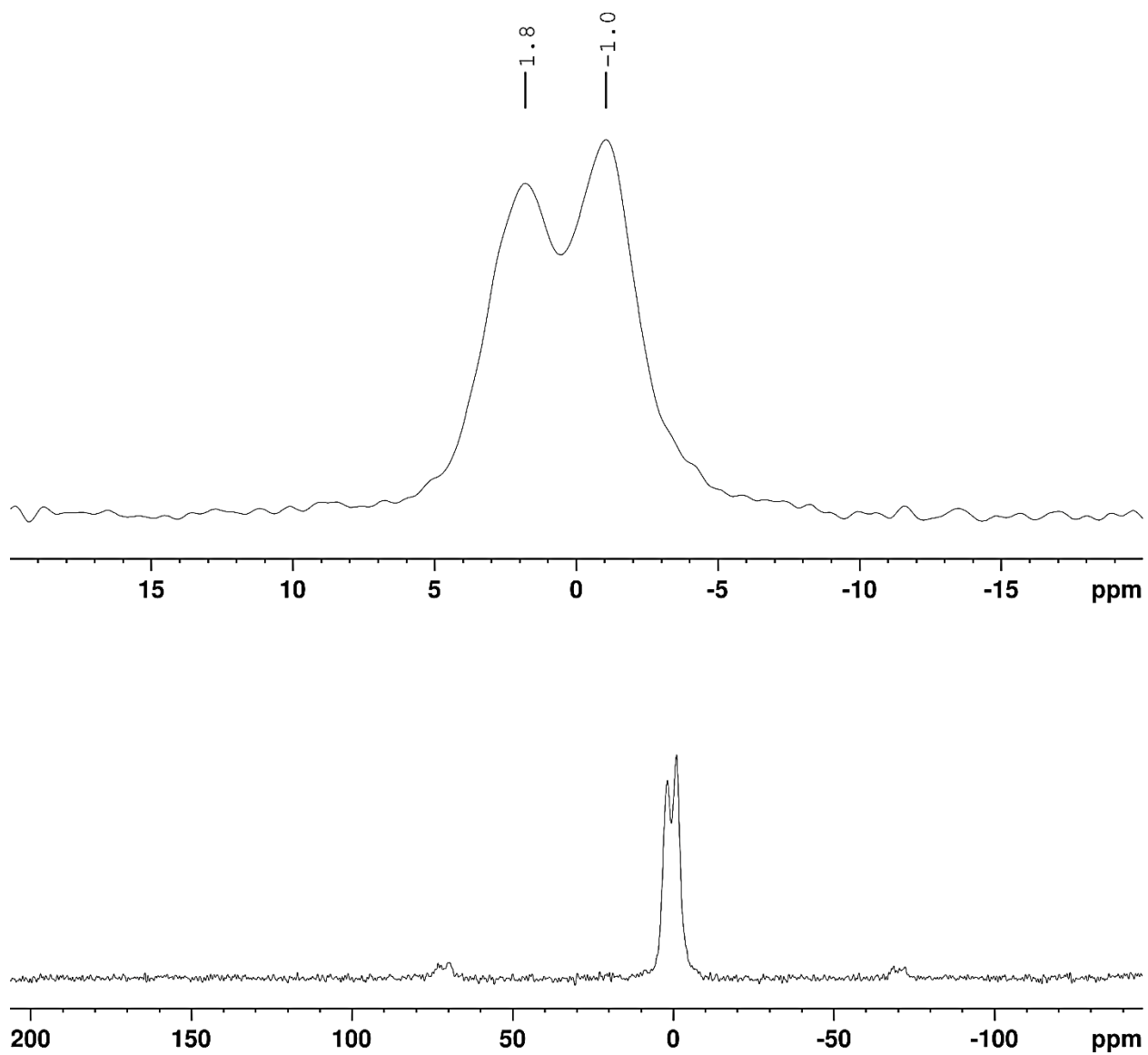


Figure S17. Solid state ^{31}P MAS NMR spectrum of **6** at 20 kHz MAS. Unlabelled peaks are spinning sidebands.

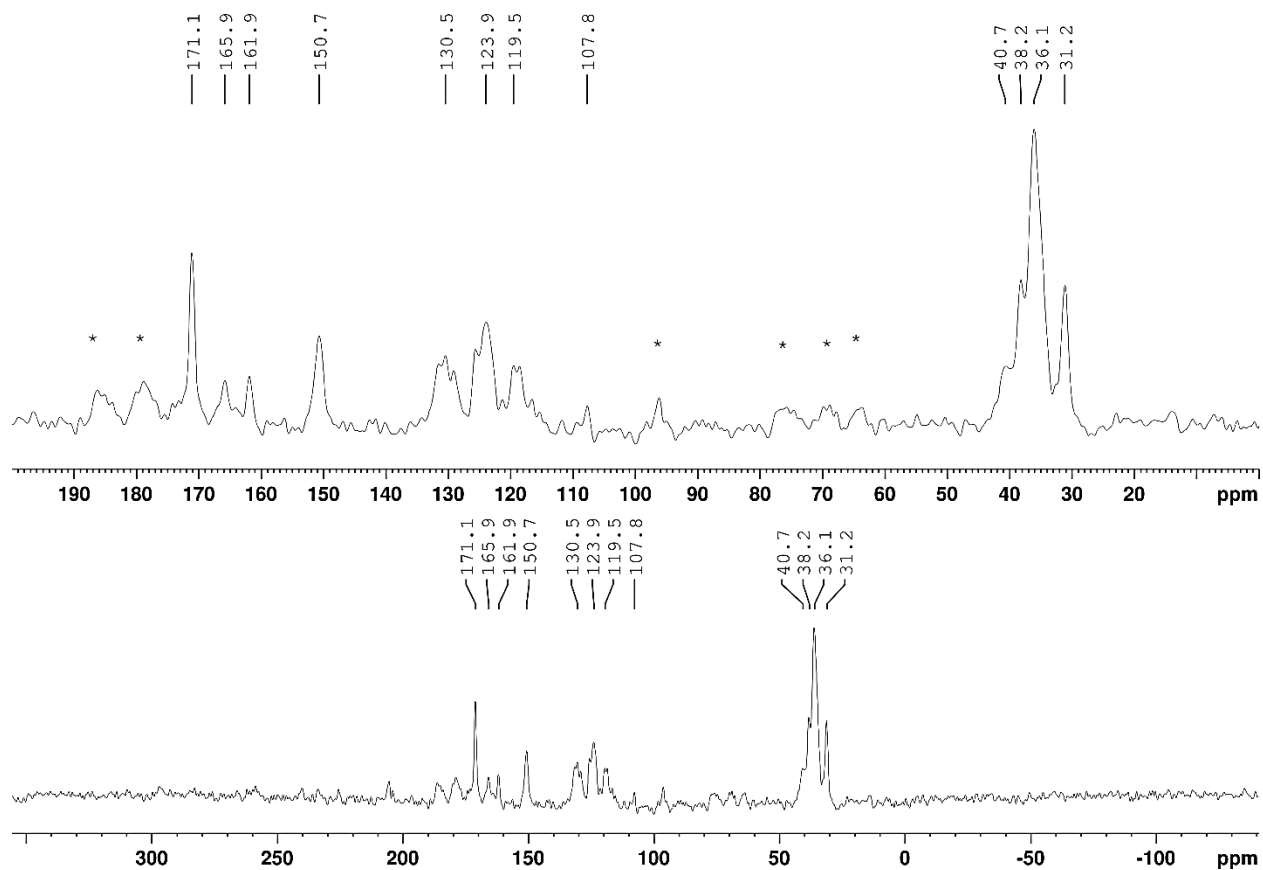


Figure S18. ^{13}C CP/MAS NMR spectra of **6** at 5.5 kHz MAS. Asterisks denote spinning side bands.

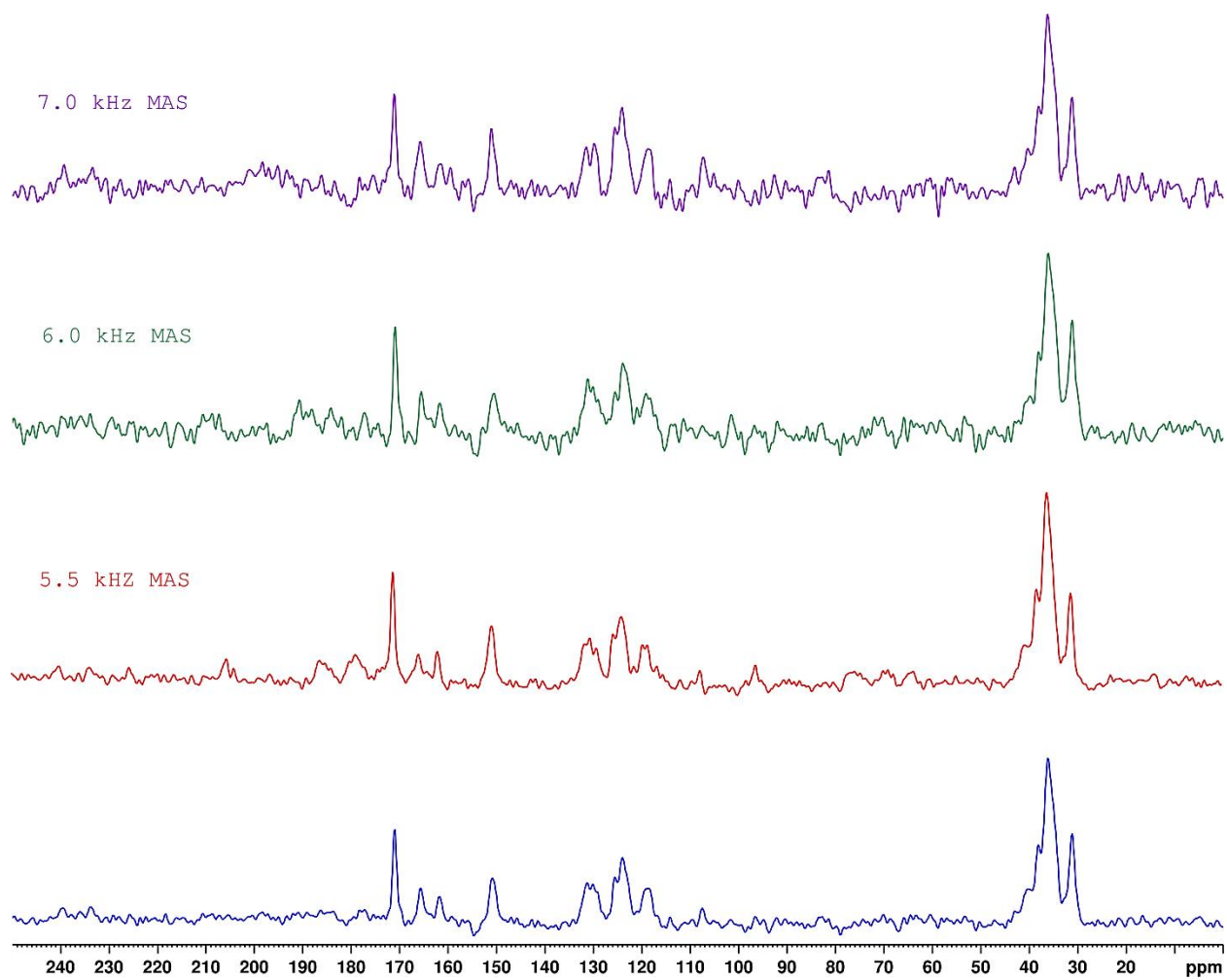


Figure S19. ^{13}C CP/MAS NMR spectra showing spinning speed comparison of **6**. The bottom trace shows the addition of the three top spectra.

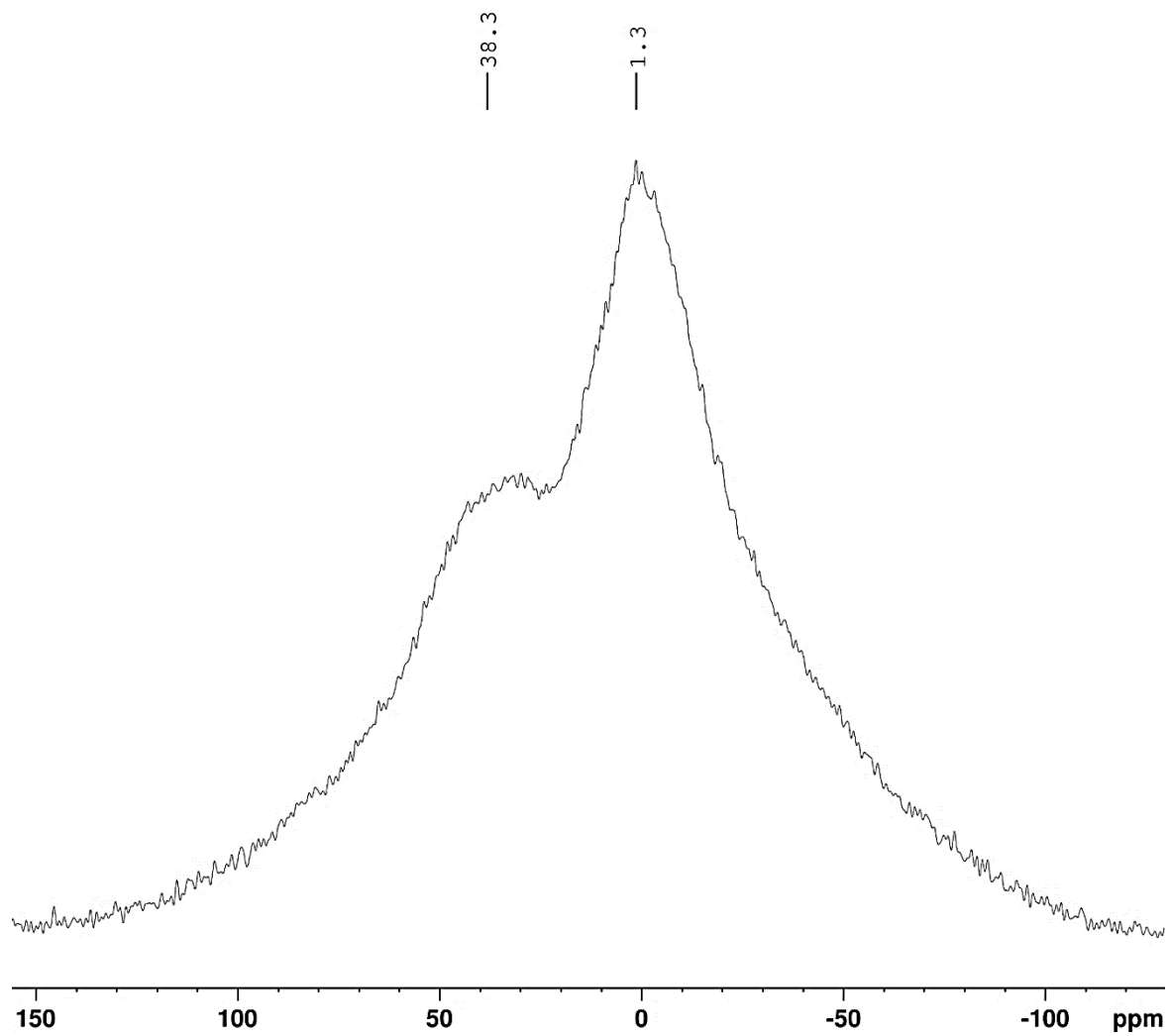


Figure S20. Solid state ^1H MAS NMR spectrum of **7** at 10 kHz MAS. Paramagnetic sample.

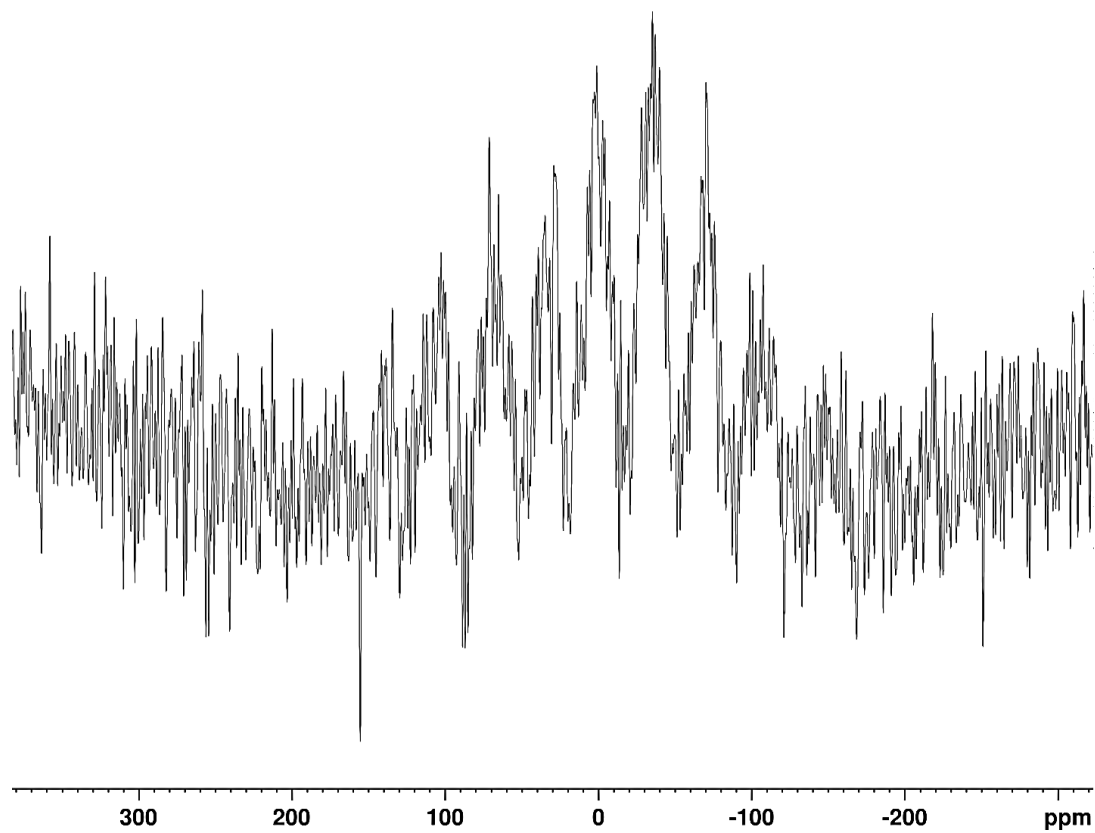


Figure S21. Solid state ^{31}P MAS NMR spectrum of **7**. Paramagnetic sample.

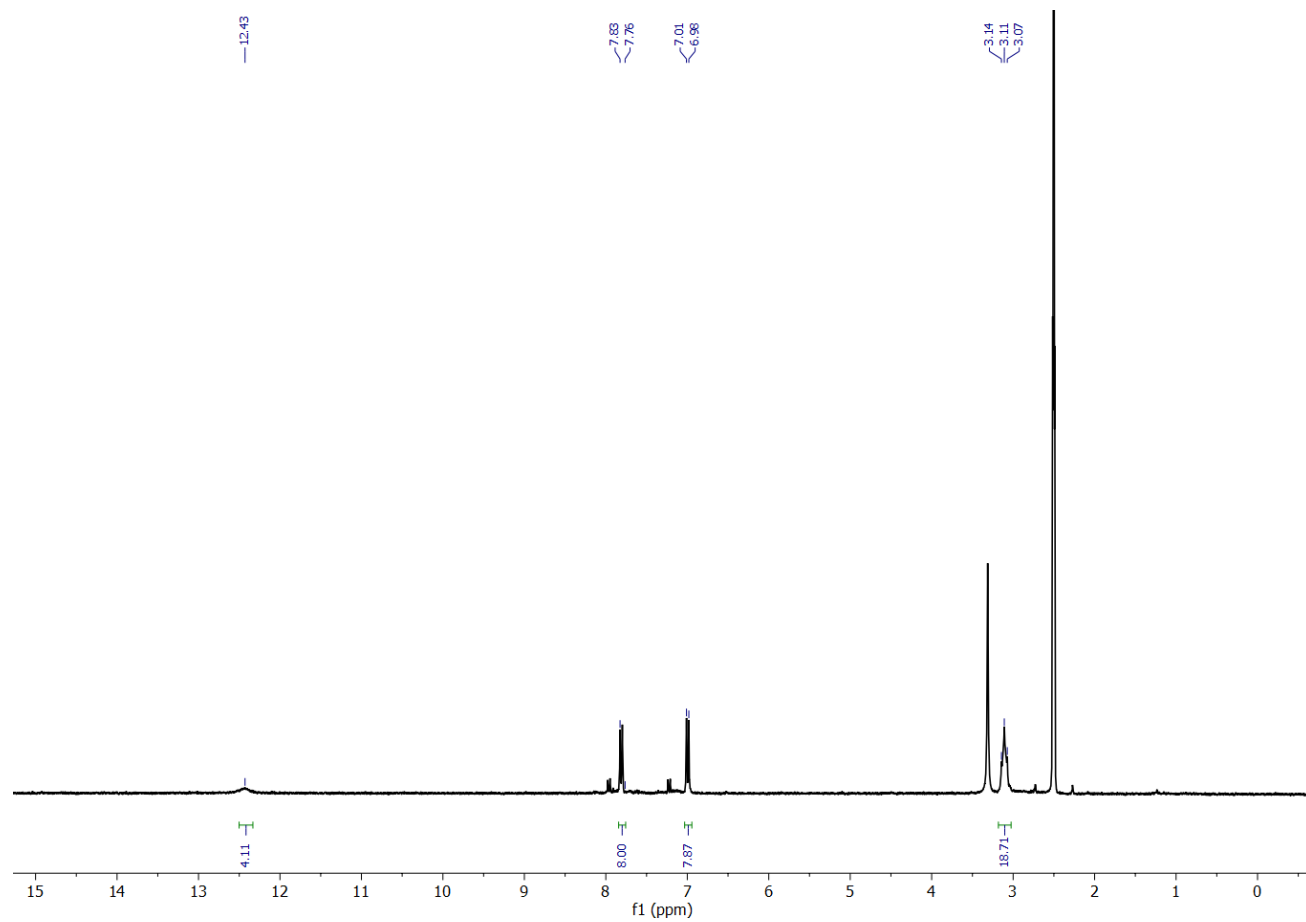


Figure S22. ^1H NMR spectrum (300 MHz, DMSO- d_6) of **8**.

1

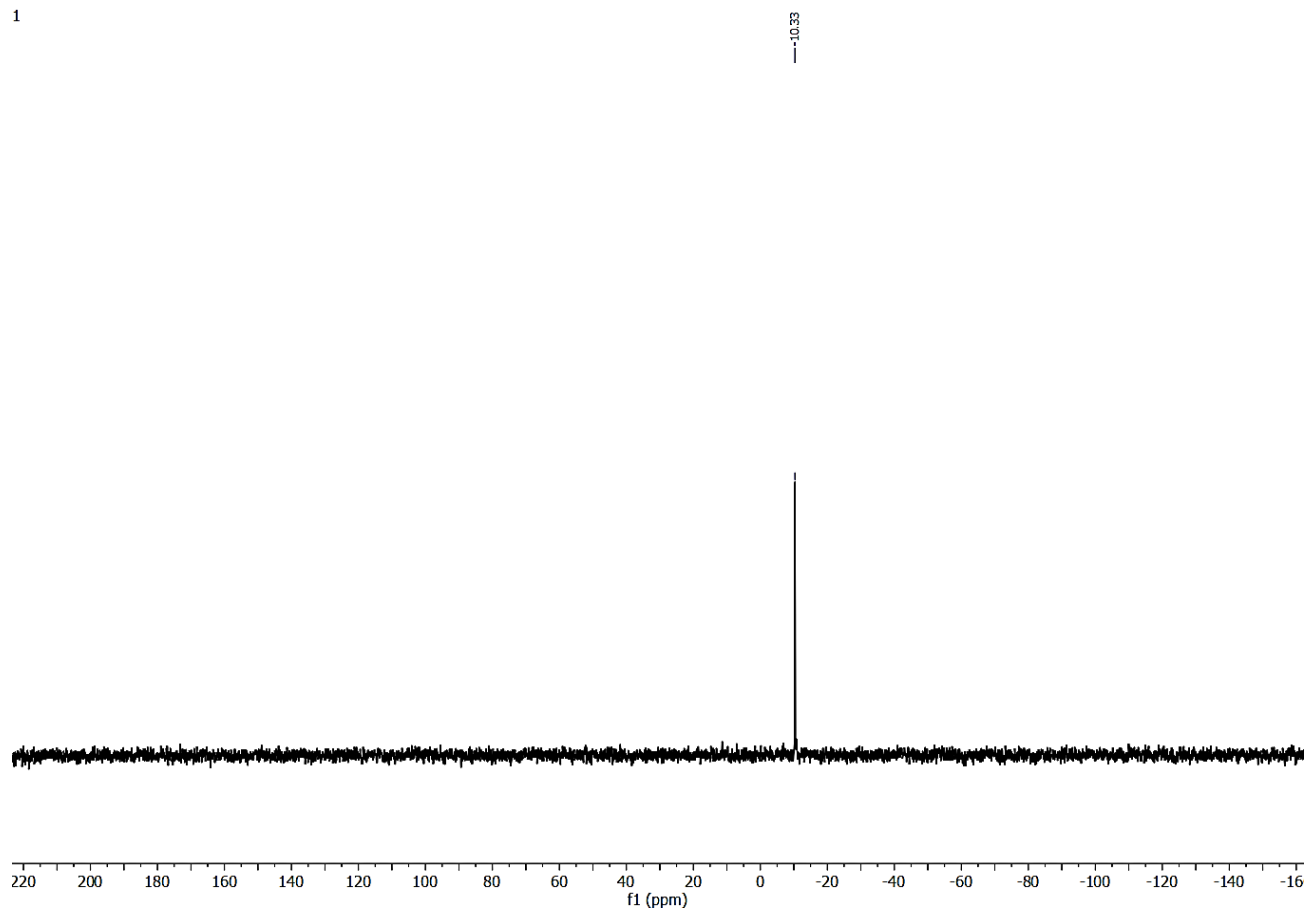


Figure S23. ^{31}P NMR spectrum (122 MHz, $\text{DMSO-}d_6$) of **8**.

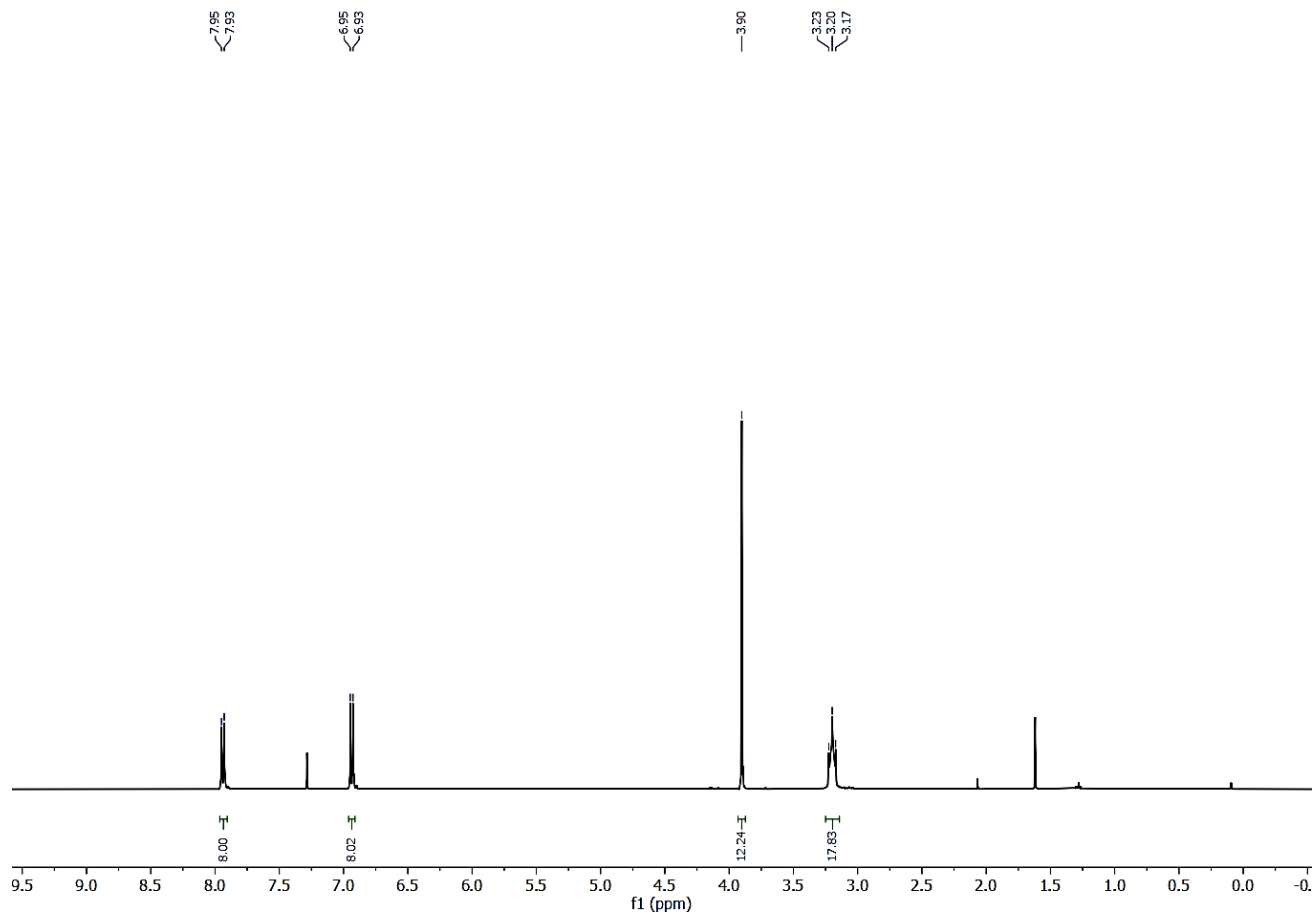


Figure S24. ¹H NMR spectrum (400 MHz, CDCl₃) of **9**.

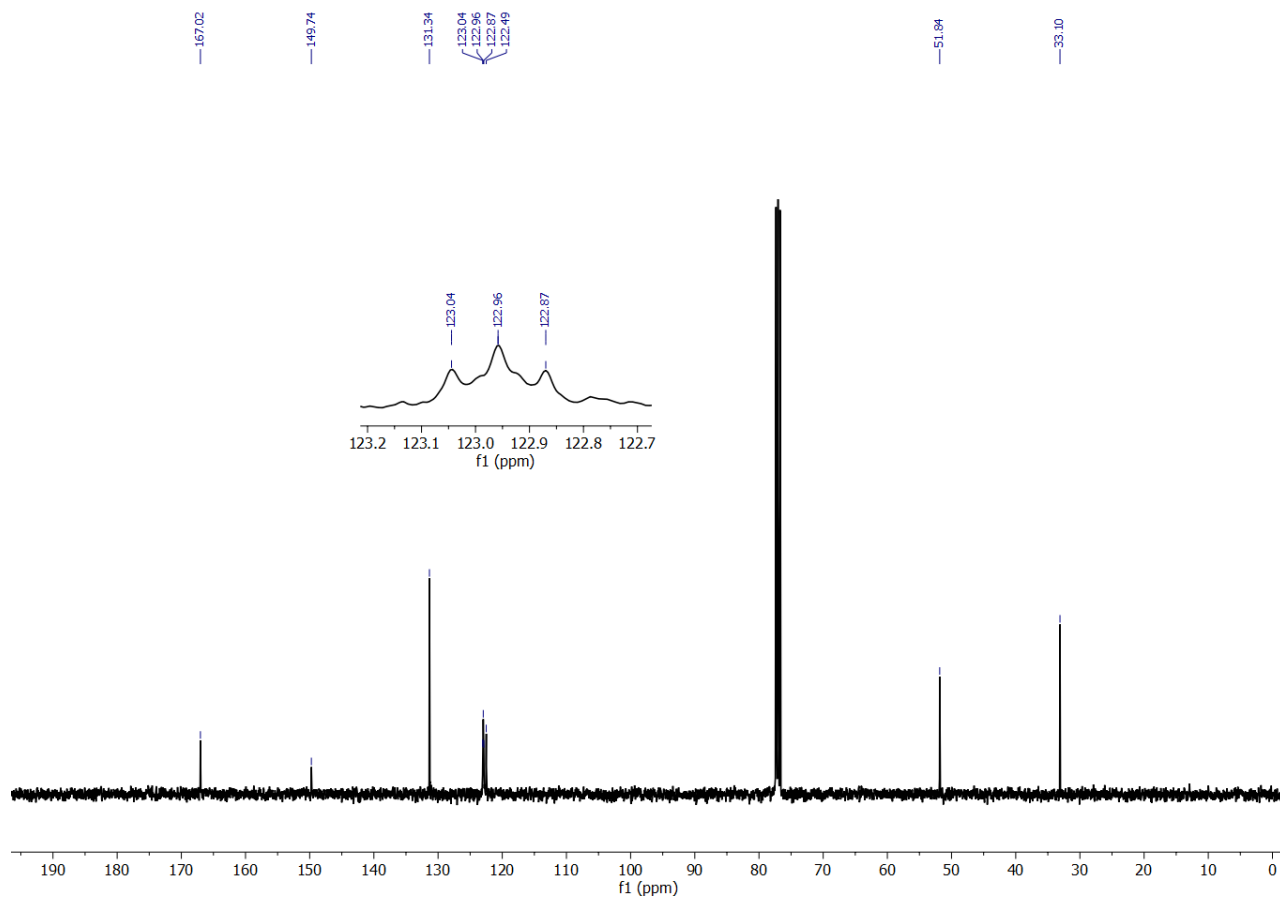


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **9**.

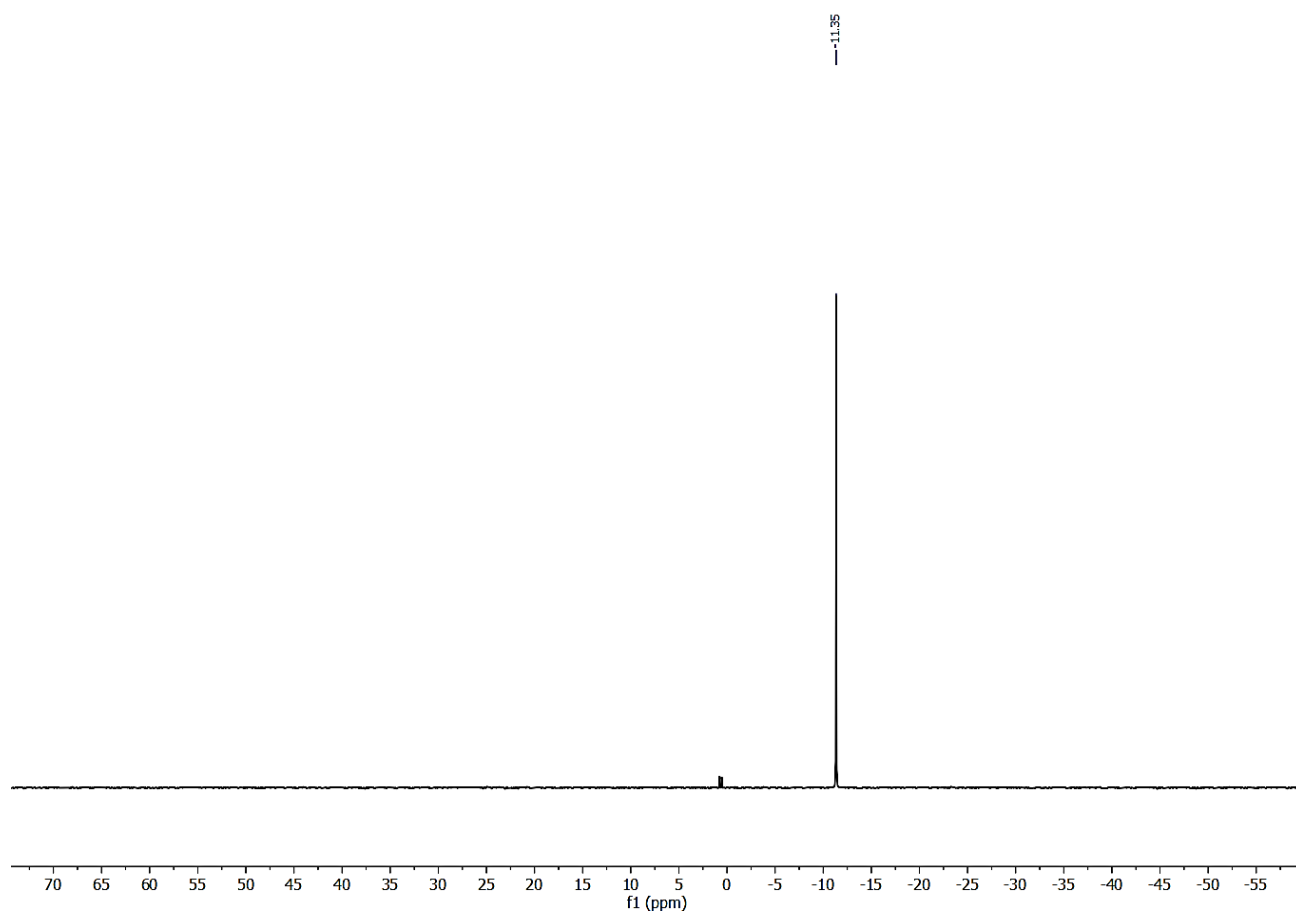


Figure S26. ^{31}P NMR spectrum (CDCl_3 , 162 MHz) of **9**.

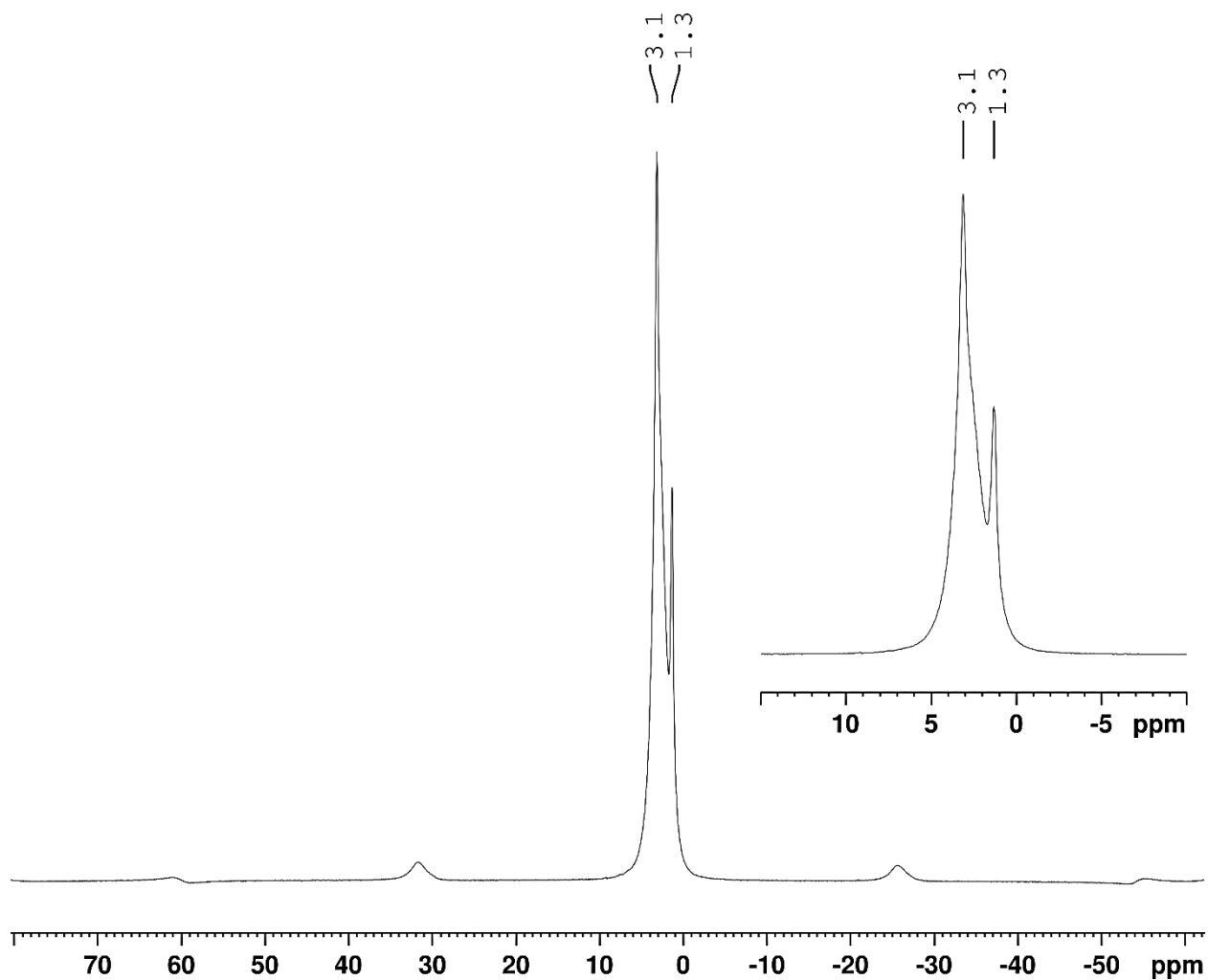


Figure S27. Solid state ^1H MAS NMR spectrum of **10** at 20 kHz MAS. Unlabelled peaks are spinning sidebands.

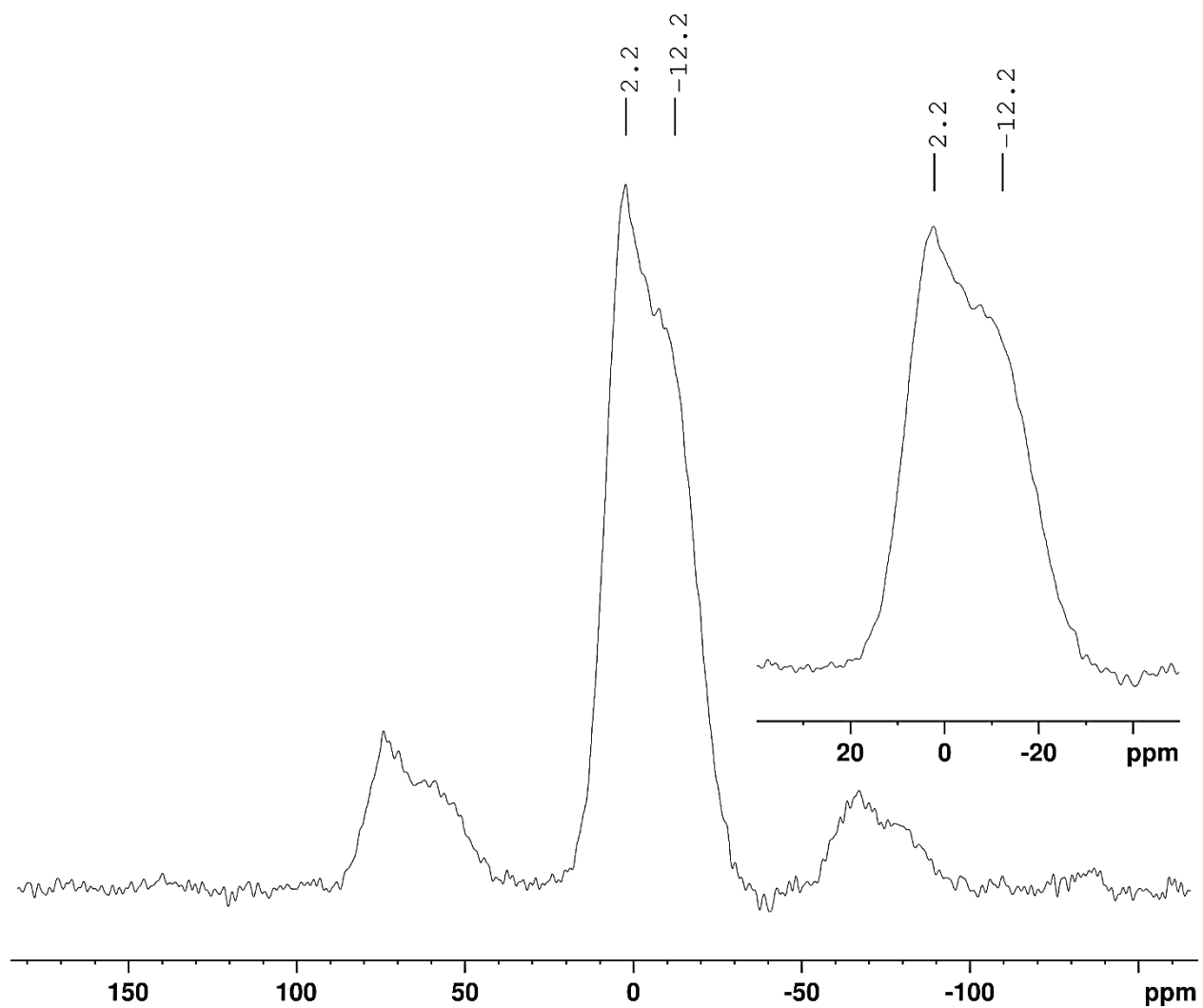


Figure S28. Solid state ^{31}P MAS NMR spectrum of **10**. Unlabelled peaks are spinning sidebands.

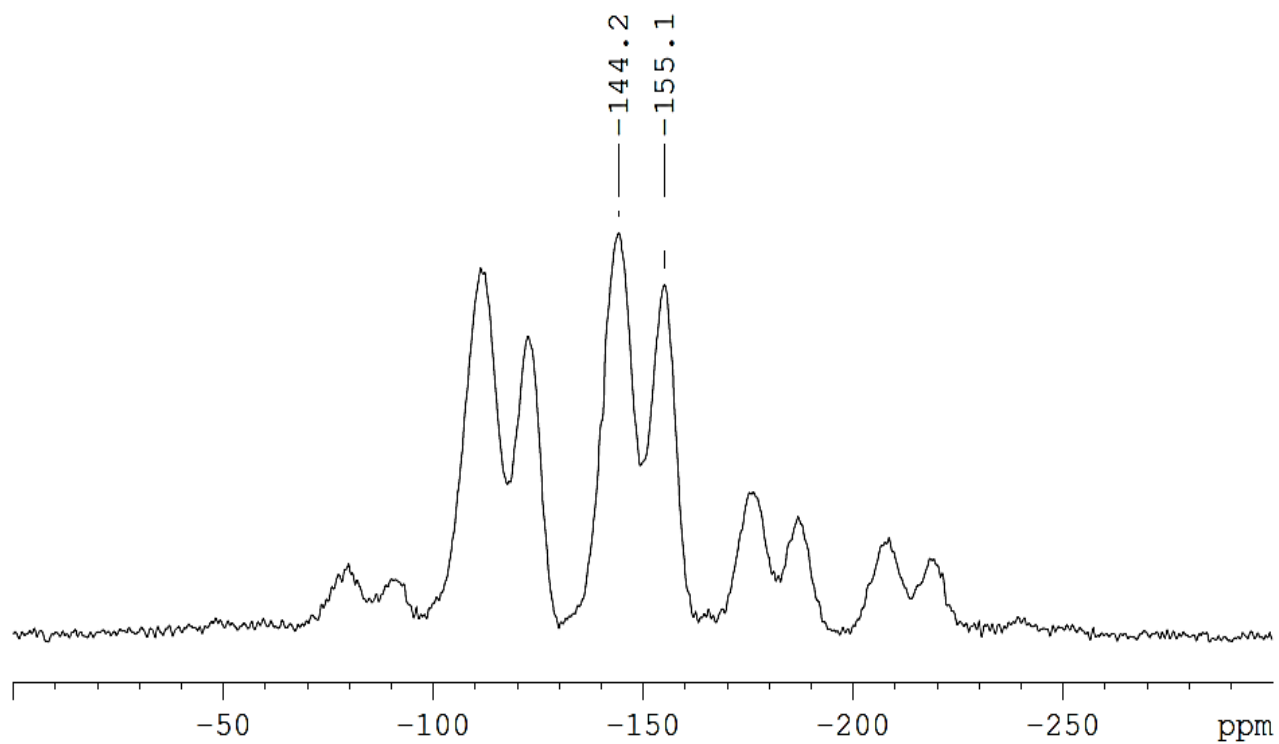


Figure S29. Solid state ^{19}F MAS NMR spectrum of **10**. Unlabelled peaks are spinning sidebands

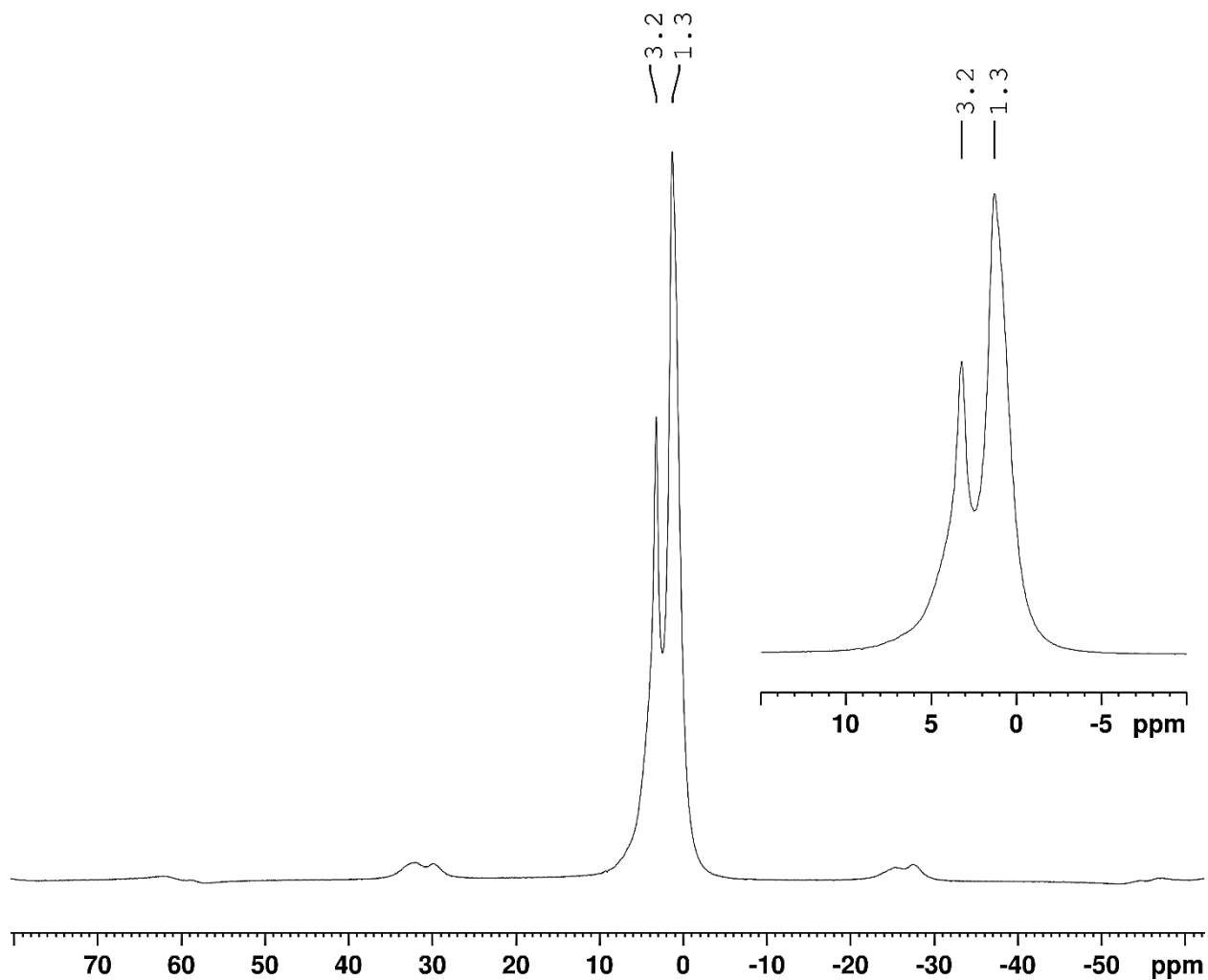


Figure S30. Solid state ^1H MAS NMR spectrum of **12**. Unlabelled peaks are spinning sidebands.

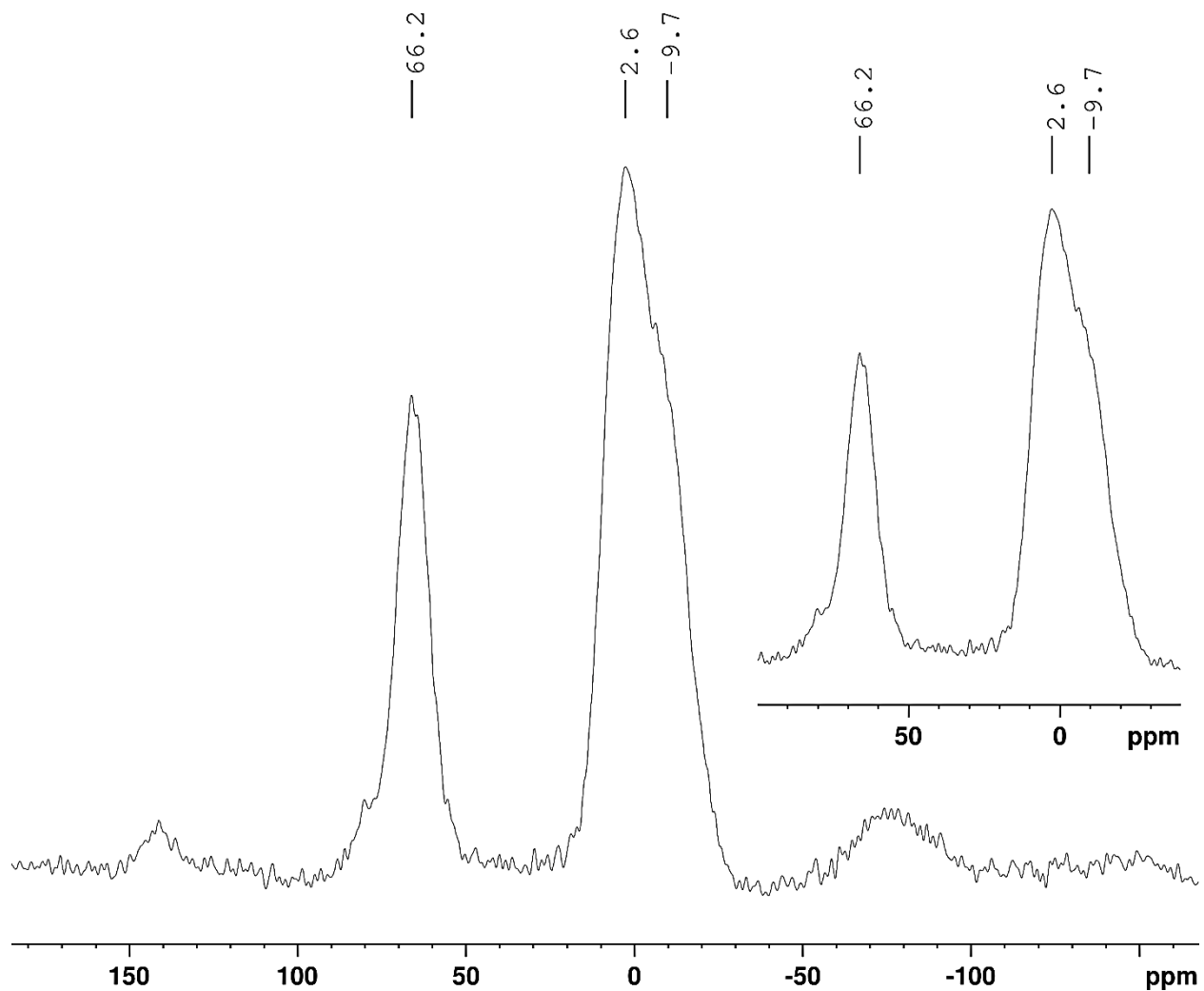


Figure S31. Solid state ^{31}P MAS NMR spectrum of **12**. Unlabelled peaks are spinning sidebands.

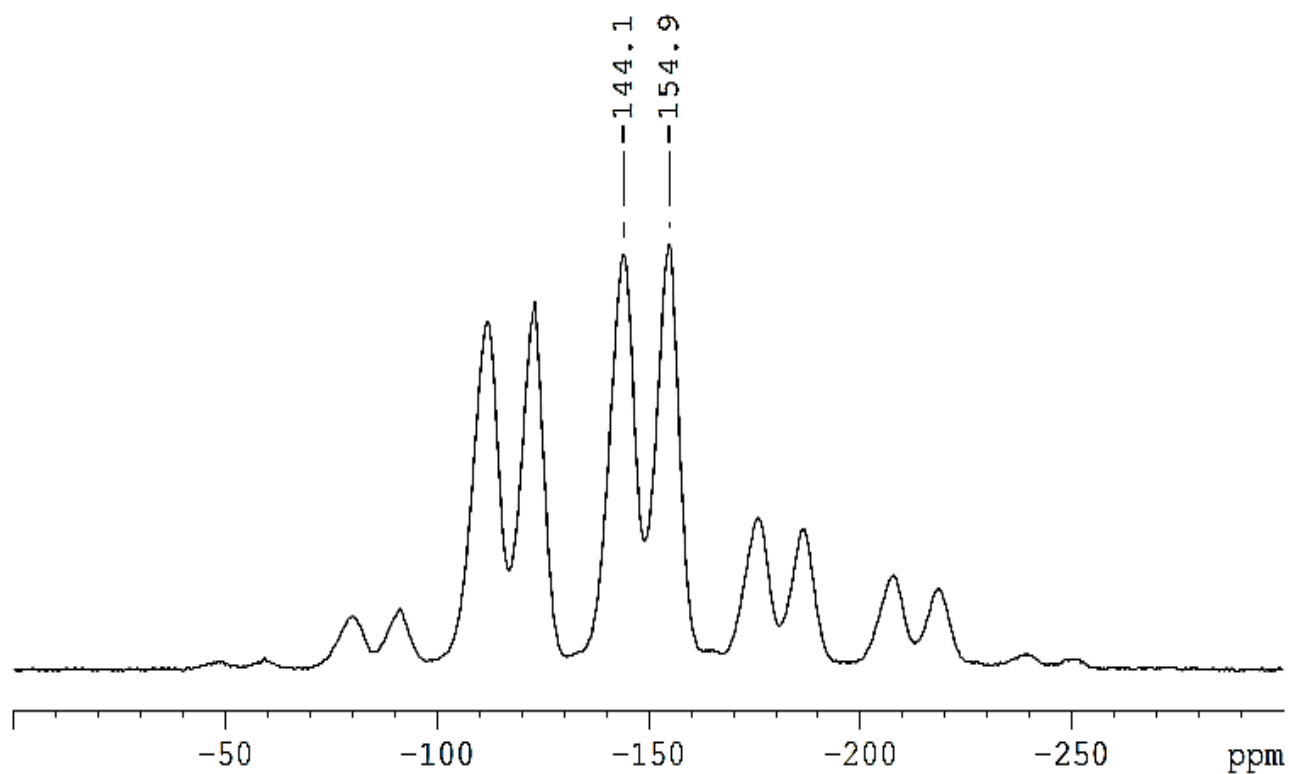


Figure S32. Solid state ^{19}F MAS NMR spectrum of **12**. Unlabelled peaks are spinning sidebands.

^{31}P SASSY

**Solid
component**

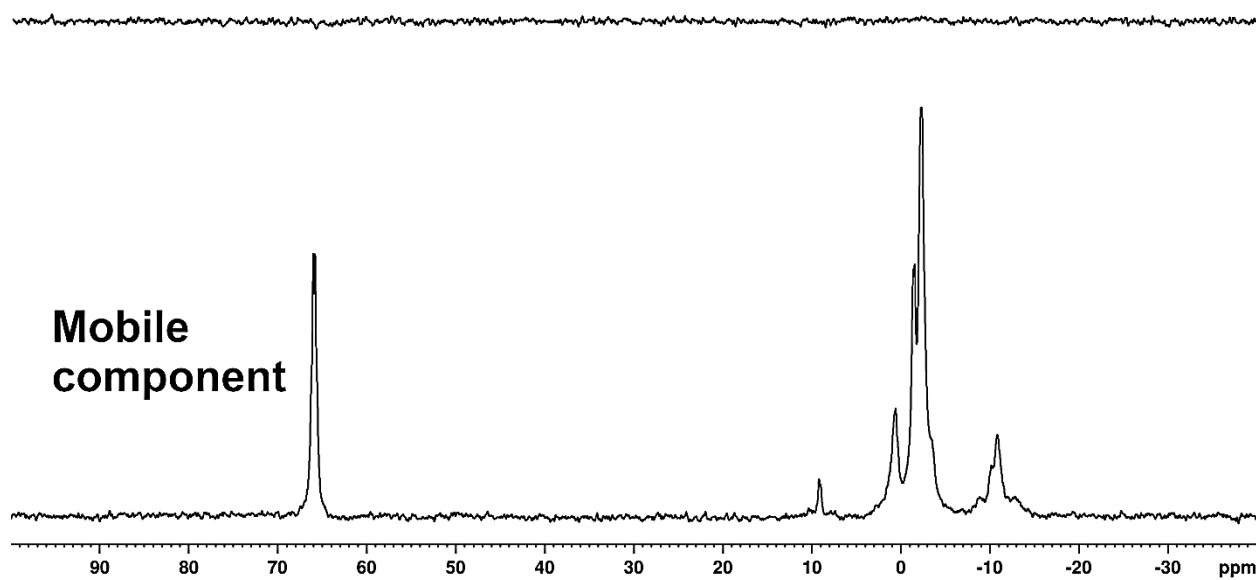


Figure S33. Solid (top) and Mobile (bottom) components of the ^{31}P SASSY NMR experiment of 12.

Mass Spectra

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	2023-09-01 1:52:21 PM	
Analysis Name	D:\Data\Xiao\Sept 01 2023\000002.d	Operator	x	
Method	Xiao all 1.m	Instrument	compact	8255754.20059
Sample Name	P2-linker neg			
Comment				

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

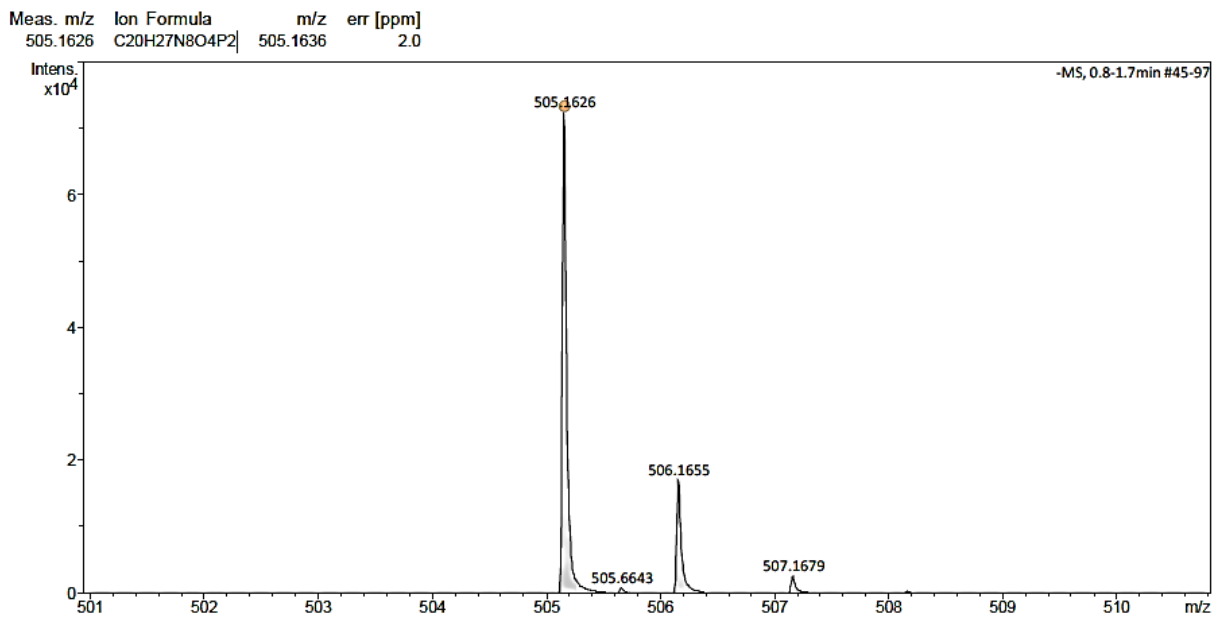


Figure S34. High resolution ESI-MS spectrum of ion [5-H]⁻.

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	2023-06-23 3:09:42 PM	
Analysis Name	D:\Data\Xiao\June 23 2023\000005.d	Operator	x	
Method	Xiao all 1.m	Instrument	compact	8255754.20059
Sample Name	MF4-1-10			
Comment				

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

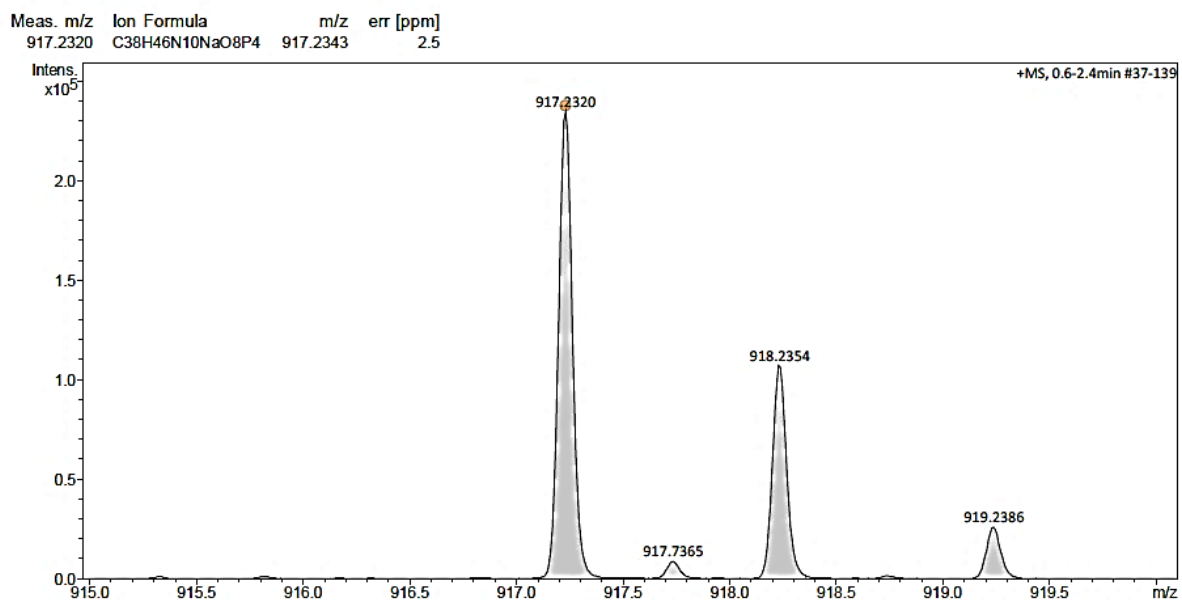


Figure S35. High resolution ESI-MS spectrum of ion [9+Na]⁺.

IR Spectra

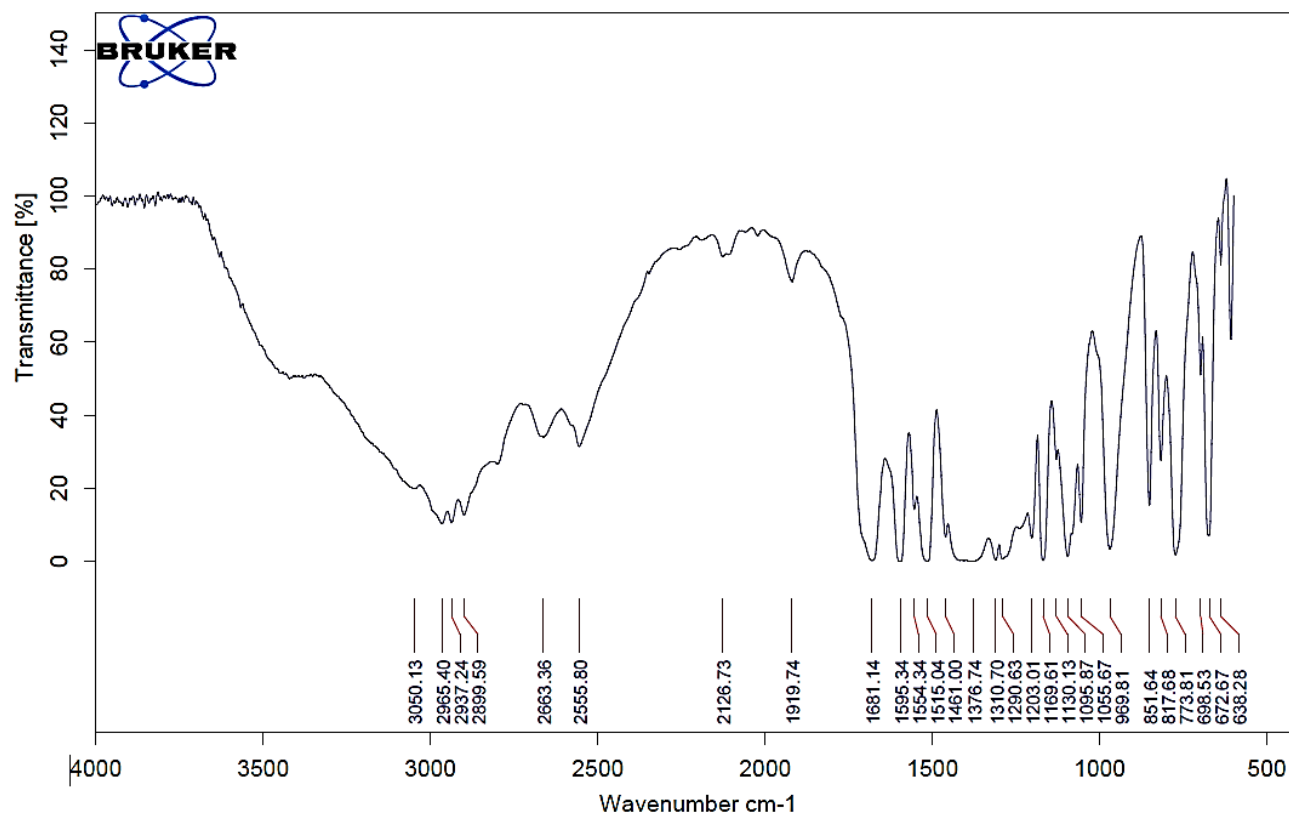


Figure S36. Infrared spectrum (KBr pellet) of 5.

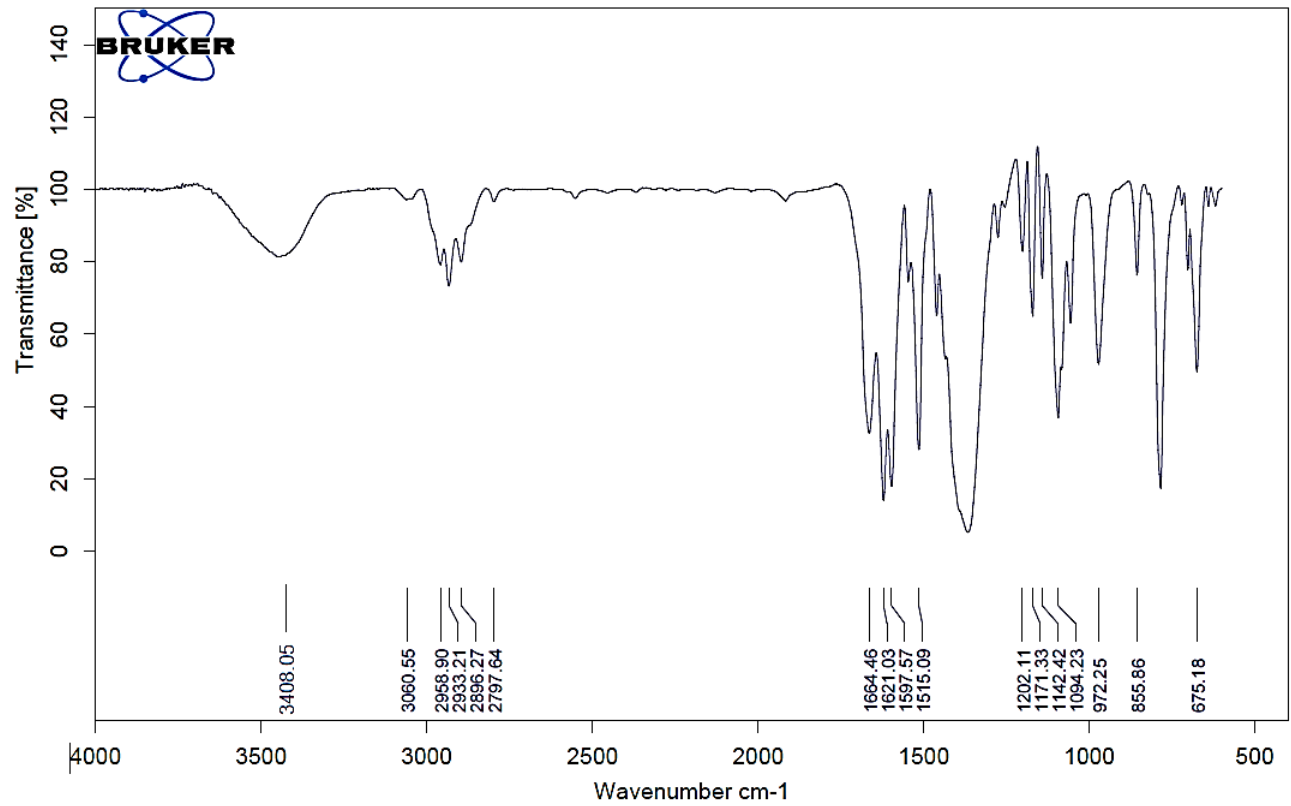


Figure S37. Infrared spectrum (KBr pellet) of **6**.

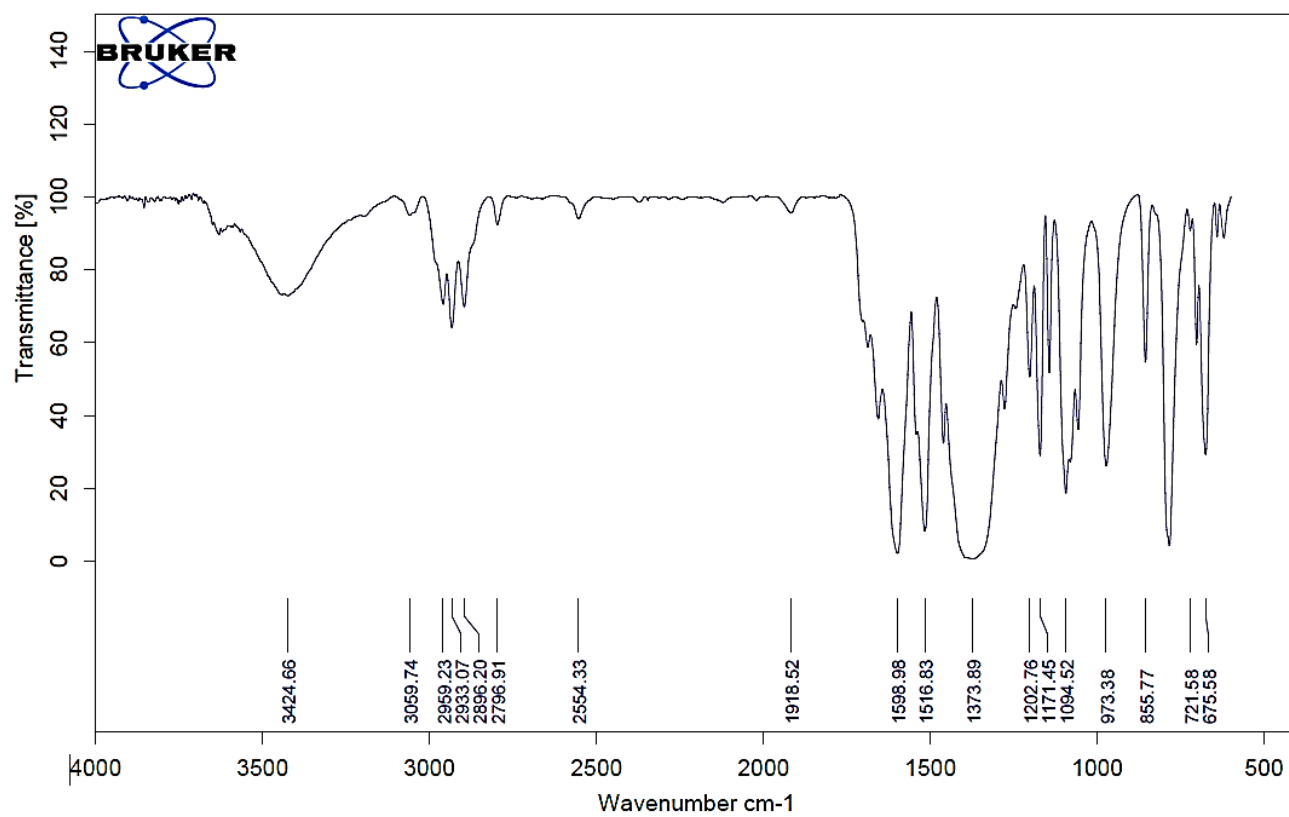


Figure S38. Infrared spectrum (KBr pellet) of **7**.

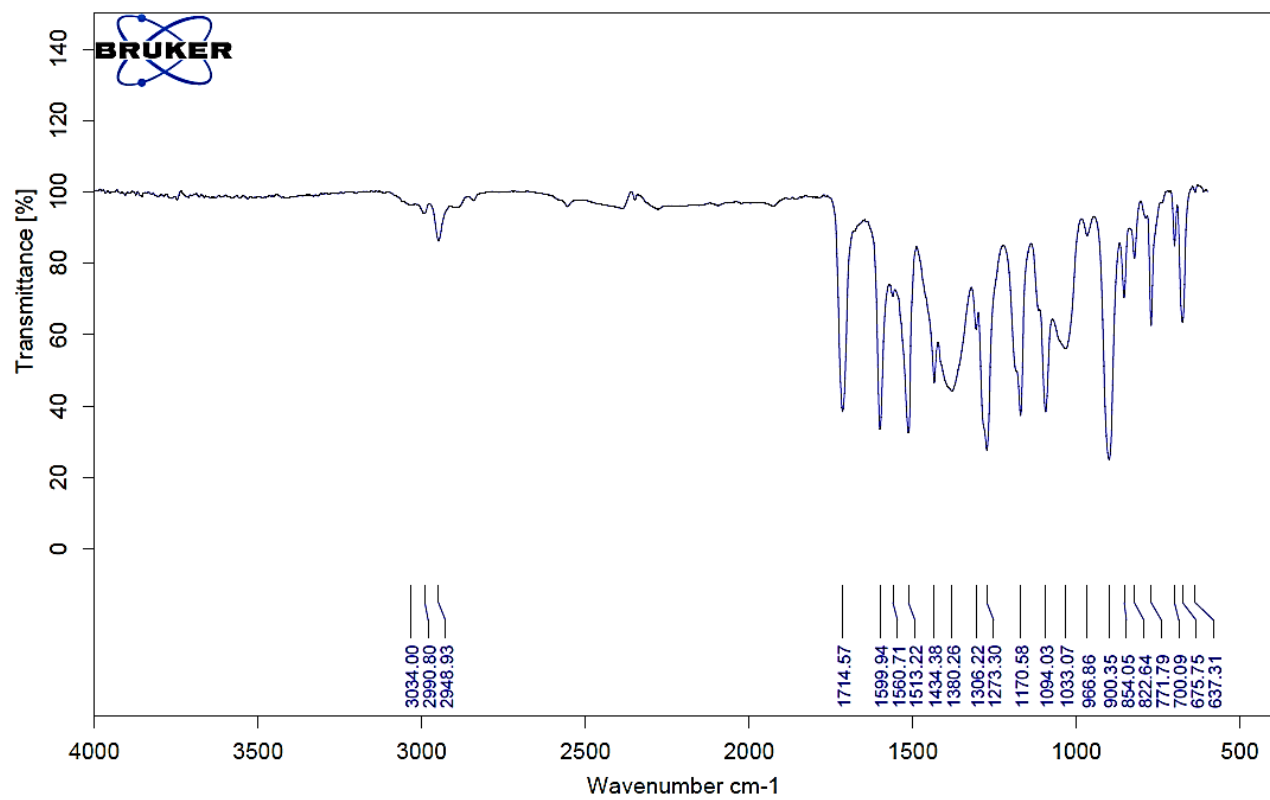


Figure S39. Infrared spectrum (KBr plate) of **9**.

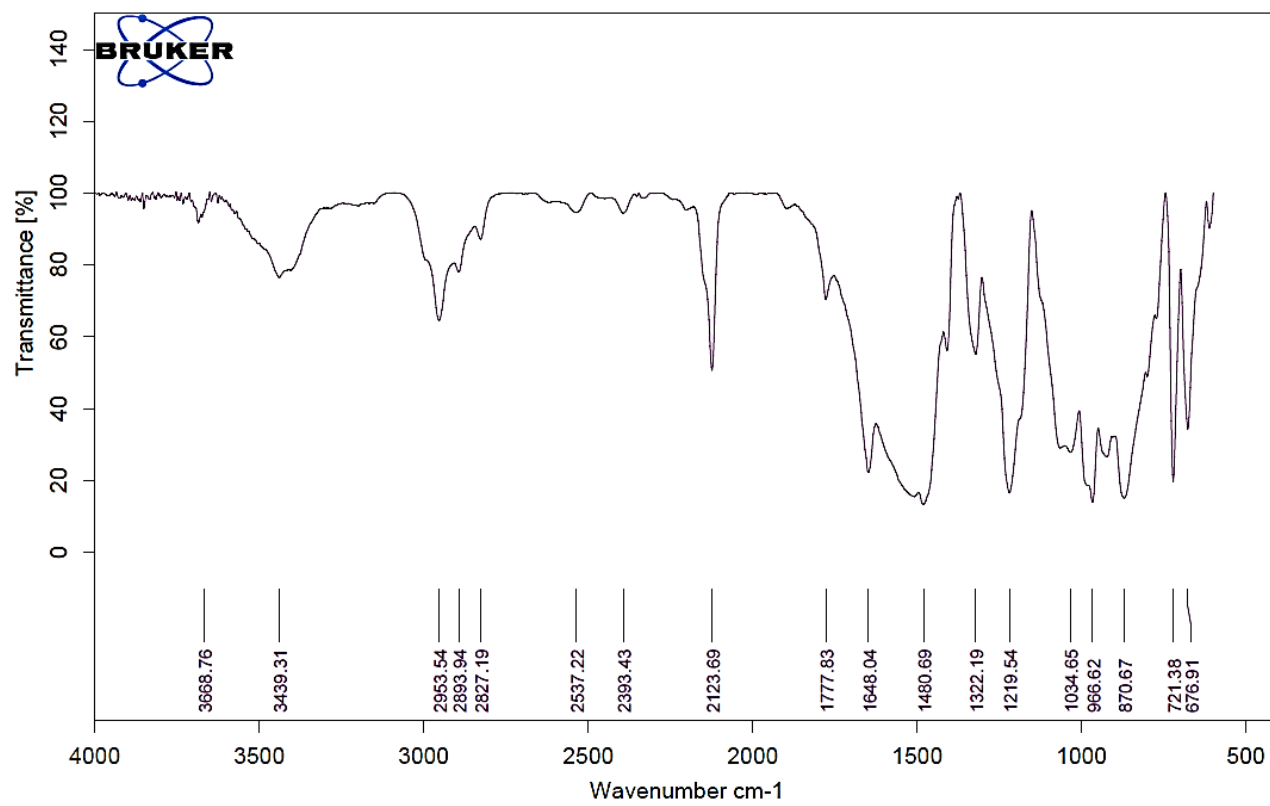


Figure S40. Infrared spectrum (KBr pellet) of **10**.

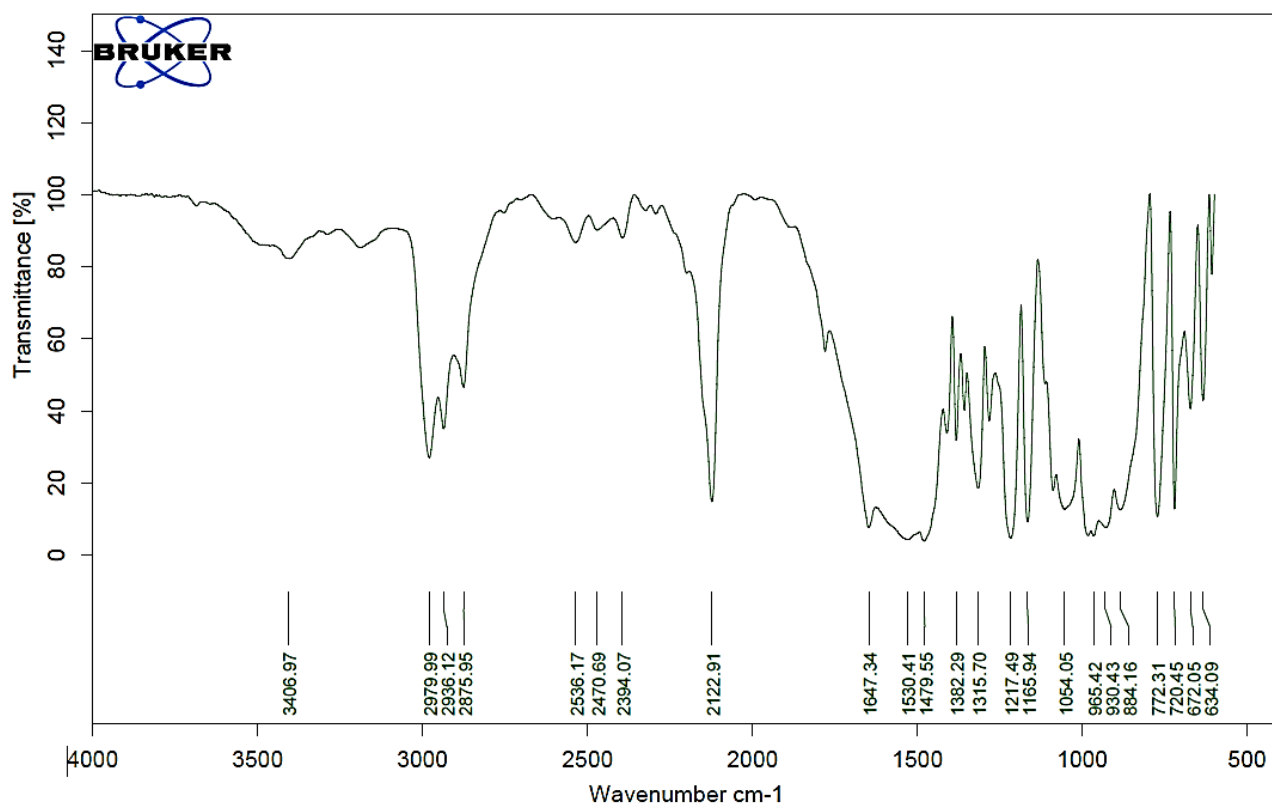


Figure S41. Infrared spectrum (KBr pellet) of **12**.

X-ray Single Crystallographic Analysis

Table S1. Crystallographic data and structure refinement of compound **5**.

Empirical formula	C ₁₅ H _{18.8} N ₅ O ₂ P
Formula weight	332.12
Temperature/K	99.9(3)
Crystal system	triclinic
Space group	P-1
a/Å	9.04350(15)
b/Å	10.15596(16)
c/Å	10.73364(12)
α/°	108.6532(12)
β/°	99.9637(12)
γ/°	113.6479(16)
Volume/Å ³	802.40(3)
Z	0.5
ρ _{calc} /cm ³	1.375
μ/mm ⁻¹	1.673
F(000)	349.6
Crystal size/mm ³	0.2 × 0.2 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.2728 to 158.4802
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	26957
Independent reflections	3431 [R _{int} = 0.0605, R _{sigma} = 0.084]
Data/restraints/parameters	3431/42/330
Goodness-of-fit on F ²	1.000
Final R indexes [>=2σ (I)]	R ₁ = 0.0447, wR ₂ = 0.1097
Final R indexes [all data]	R ₁ = 0.0486, wR ₂ = 0.1126
Largest diff. peak/hole / e Å ⁻³	0.30/-0.52

Table S2. Crystallographic data and structure refinement of compound **6**.

Empirical formula	C ₅₂ H ₈₀ N ₂₀ O ₁₂ P ₄ Zn ₂
Formula weight	1431.98
Temperature/K	200.00
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	17.7137(4)
b/Å	10.1405(2)
c/Å	18.5083(4)
α/°	90
β/°	92.4670(10)
γ/°	90
Volume/Å ³	3321.49(12)
Z	2
ρ _{calc} /cm ³	1.432
μ/mm ⁻¹	2.405
F(000)	1496.0
Crystal size/mm ³	0.09 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.764 to 140.138
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -22 ≤ l ≤ 21
Reflections collected	48110
Independent reflections	6237 [R _{int} = 0.0709, R _{sigma} = 0.0386]
Data/restraints/parameters	6237/294/530
Goodness-of-fit on F ²	1.664
Final R indexes [I >= 2σ (I)]	R ₁ = 0.1352, wR ₂ = 0.3327
Final R indexes [all data]	R ₁ = 0.1846, wR ₂ = 0.4196
Largest diff. peak/hole / e Å ⁻³	5.79/-0.83

Table S3. Crystallographic data and structure refinement of compound **7**.

Empirical formula	C ₂₃ H ₃₃ CoN ₉ O ₅ P ₂
Formula weight	636.45
Temperature/K	150.00
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	12.2983(7)
b/Å	10.2366(5)
c/Å	22.8341(12)
α/°	90
β/°	94.766(2)
γ/°	90
Volume/Å ³	2864.7(3)
Z	4
ρ _{calc} /cm ³	1.476
μ/mm ⁻¹	0.762
F(000)	1324.0
Crystal size/mm ³	0.14 × 0.11 × 0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.904 to 52.038
Index ranges	-15 ≤ h ≤ 15, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	79685
Independent reflections	5643 [R _{int} = 0.1306, R _{sigma} = 0.0543]
Data/restraints/parameters	5643/107/513
Goodness-of-fit on F ²	1.137
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0671, wR ₂ = 0.1400
Final R indexes [all data]	R ₁ = 0.1134, wR ₂ = 0.1611
Largest diff. peak/hole / e Å ⁻³	0.68/-0.81

Table S4. Crystallographic data and structure refinement of compound **9**.

Empirical formula	C ₃₈ H ₄₆ N ₁₀ O ₈ P ₄
Formula weight	894.73
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	9.9127(3)
b/Å	12.0311(4)
c/Å	17.7893(7)
α/°	96.0190(10)
β/°	99.7040(10)
γ/°	95.5610(10)
Volume/Å ³	2065.42(12)
Z	2
ρ _{calc} /cm ³	1.439
μ/mm ⁻¹	0.248
F(000)	936.0
Crystal size/mm ³	0.4 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.904 to 63.016
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26
Reflections collected	142913
Independent reflections	13734 [R _{int} = 0.0517, R _{sigma} = 0.0315]
Data/restraints/parameters	13734/0/551
Goodness-of-fit on F ²	1.183
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0564, wR ₂ = 0.1368
Final R indexes [all data]	R ₁ = 0.0798, wR ₂ = 0.1692
Largest diff. peak/hole / e Å ⁻³	1.08/-0.56

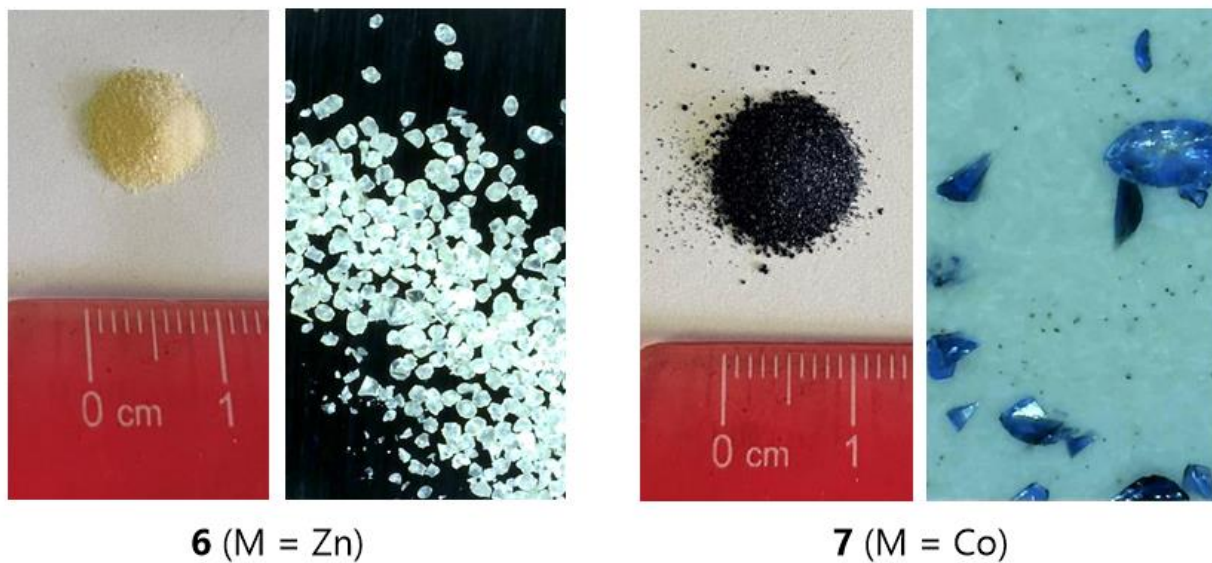


Figure S42. Photographs of isolated crystals of **6** and **7**.

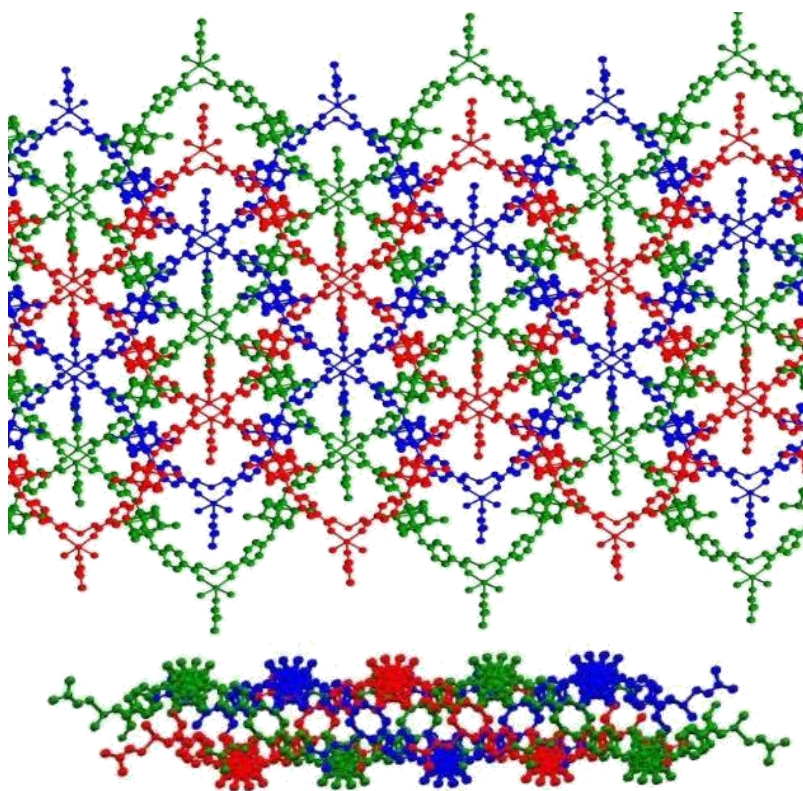


Figure S43. Two views of the triply interpenetrated structures of **6** and **7**.

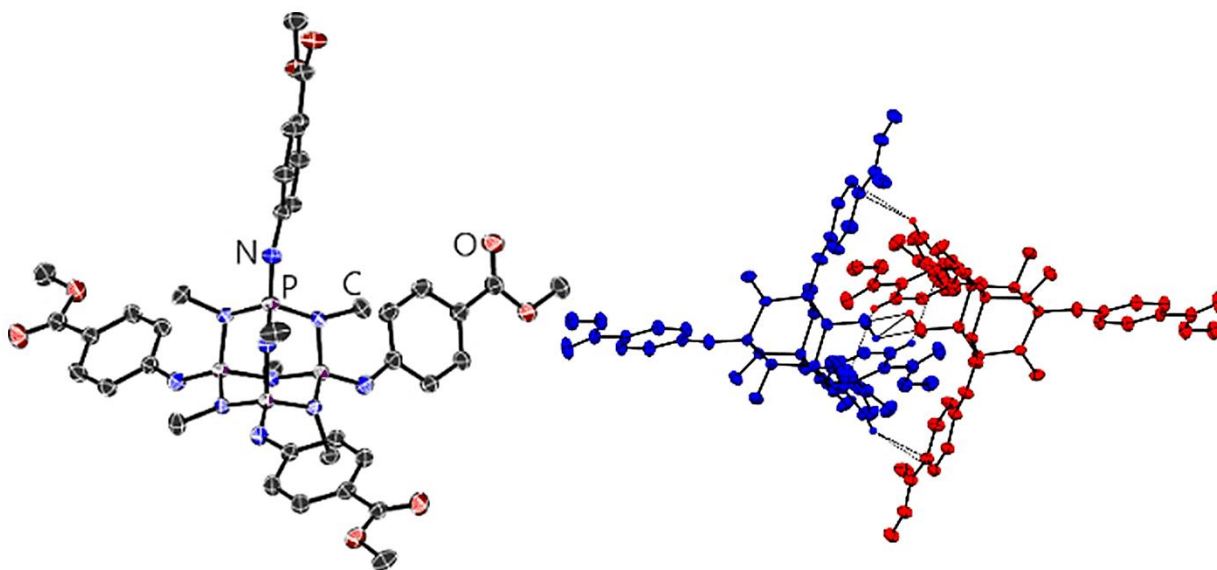


Figure S44. Two views of the molecular structure of **9** in the solid state. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level.

PXRD Analysis

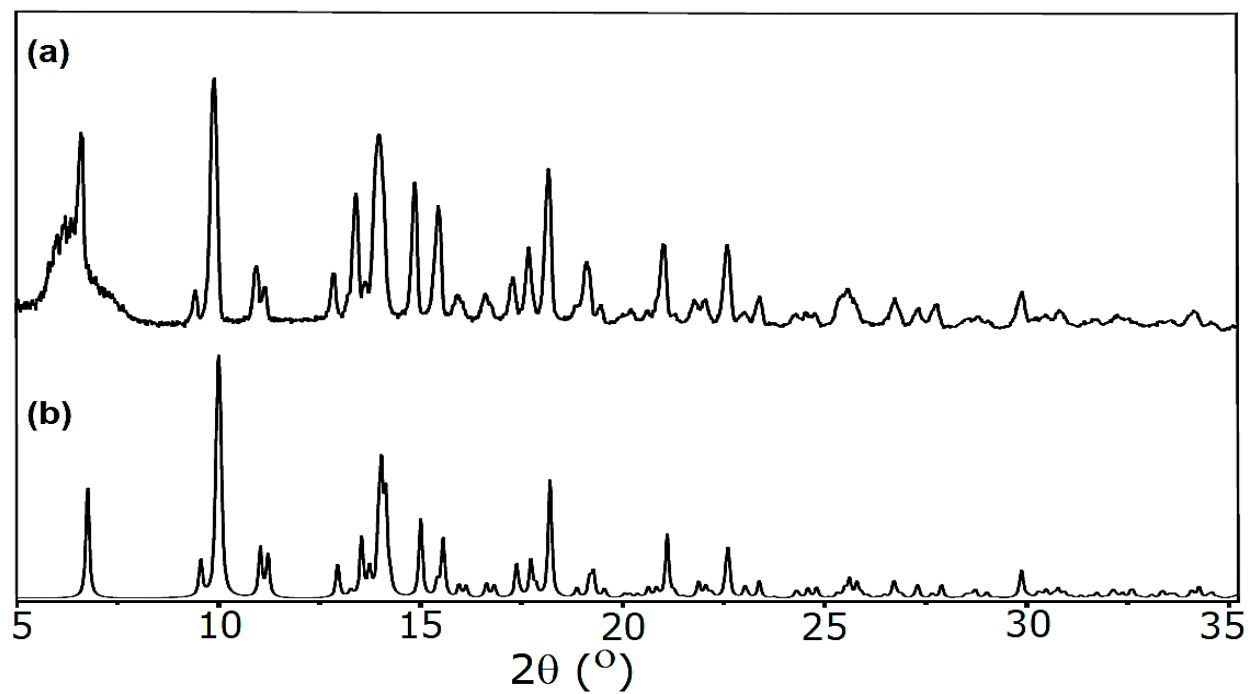


Figure S45. (a) Experimental, (b) simulated PXRD patterns of compound (6).

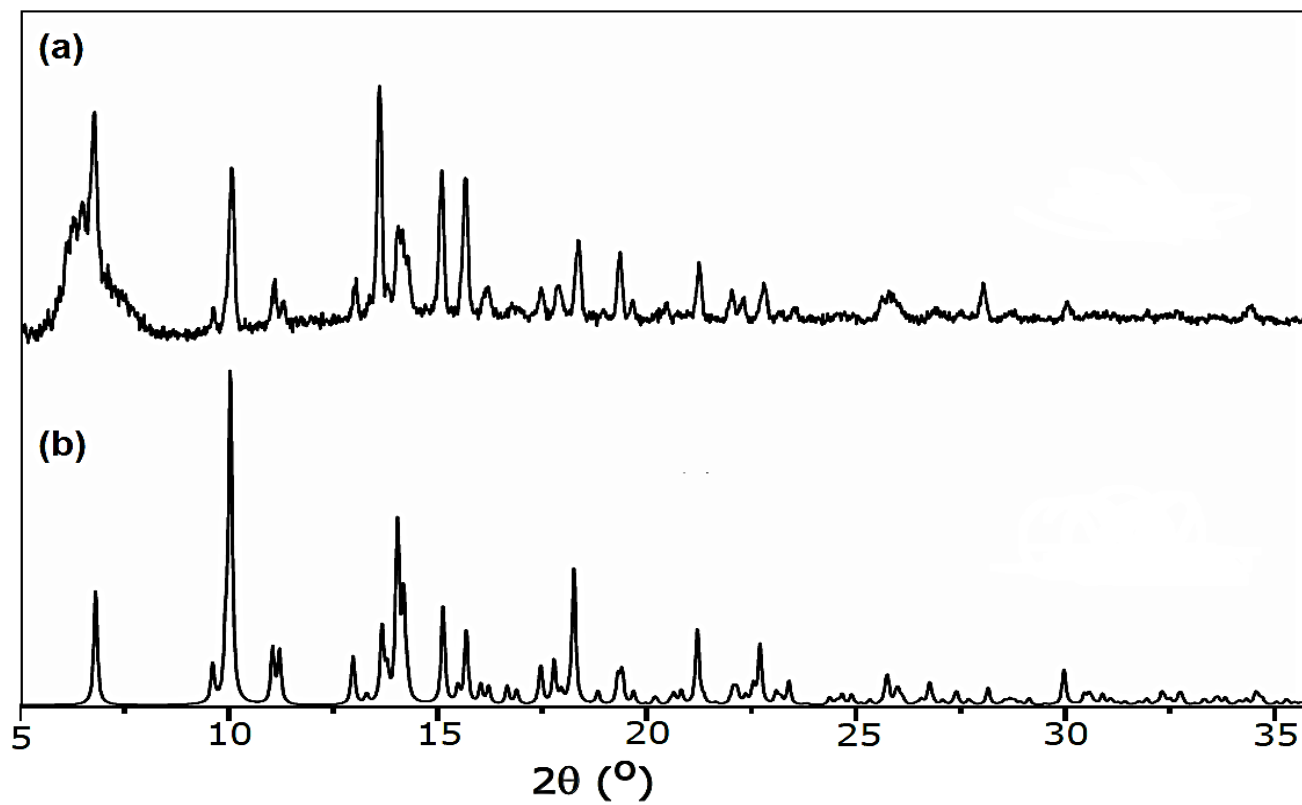


Figure S46. (a) Experimental, (b) simulated PXRD patterns of compound (7).

Thermal Analysis (DSC/TGA)

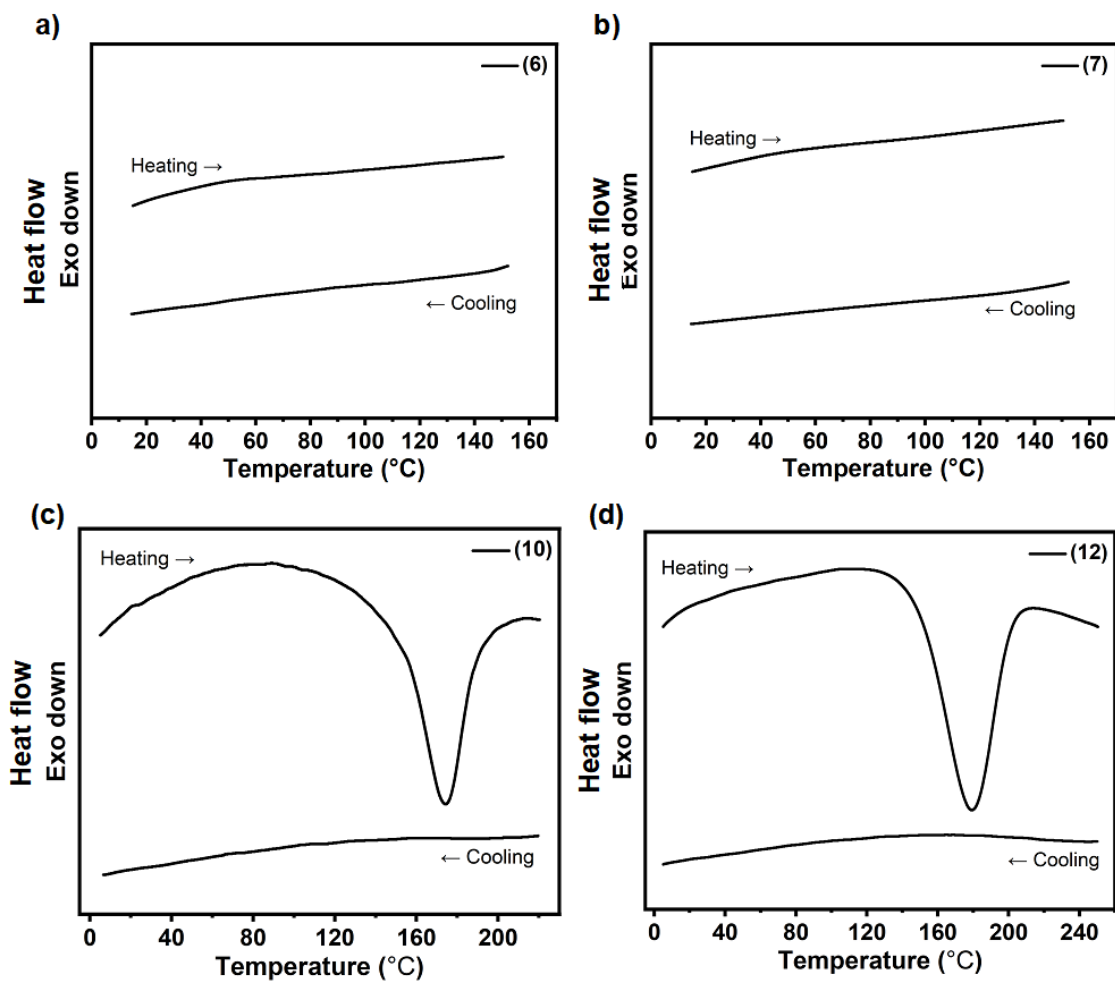


Figure S47. DSC thermograms (first heating and cooling cycle) for compounds **6**, **7**, **10**, and **12**.

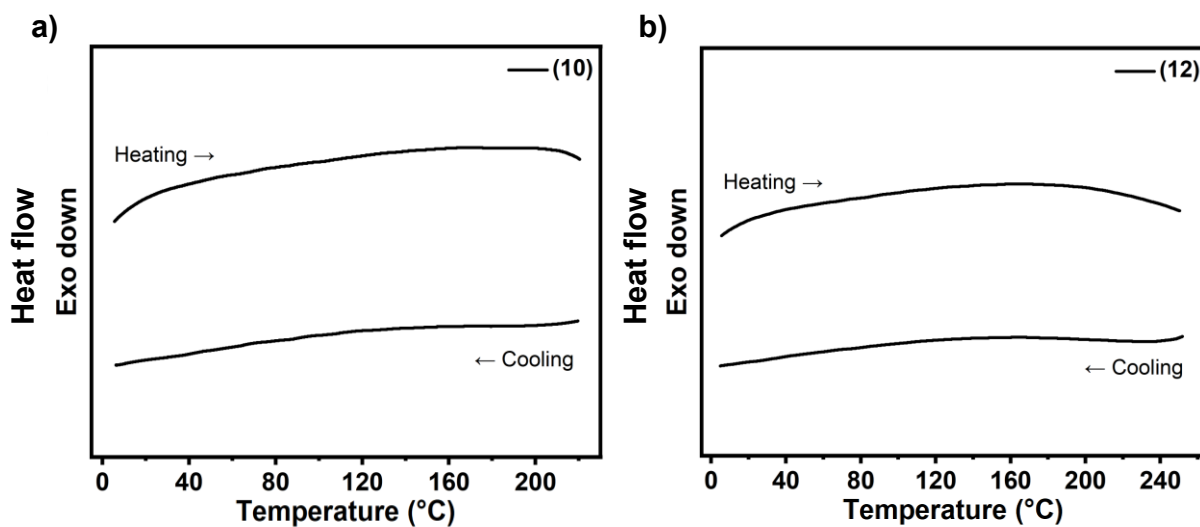


Figure S48. DSC thermograms (second heating and cooling cycle) for compounds **10** and **12**.

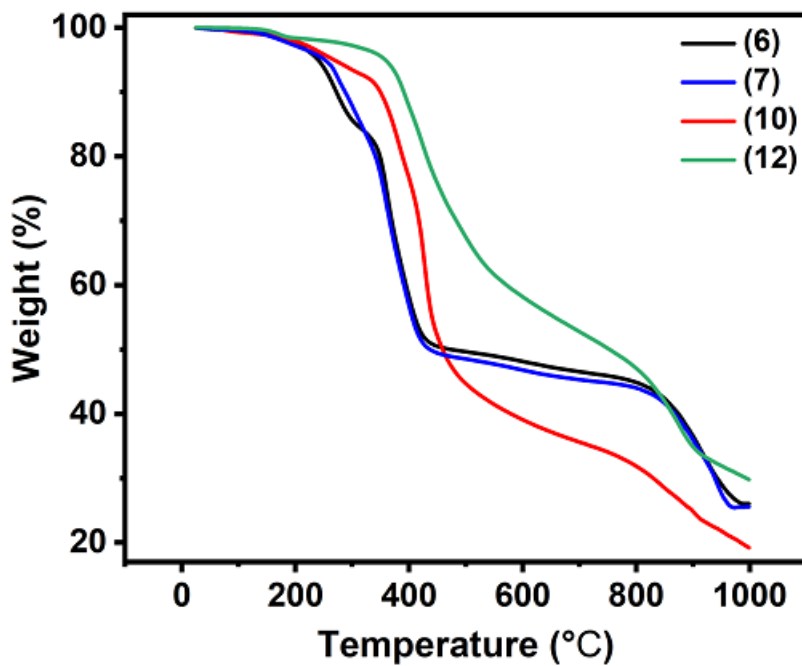


Figure S49. Thermogravimetric analysis of **6**, **7**, **10**, and **12**.

Additional figures added during revision

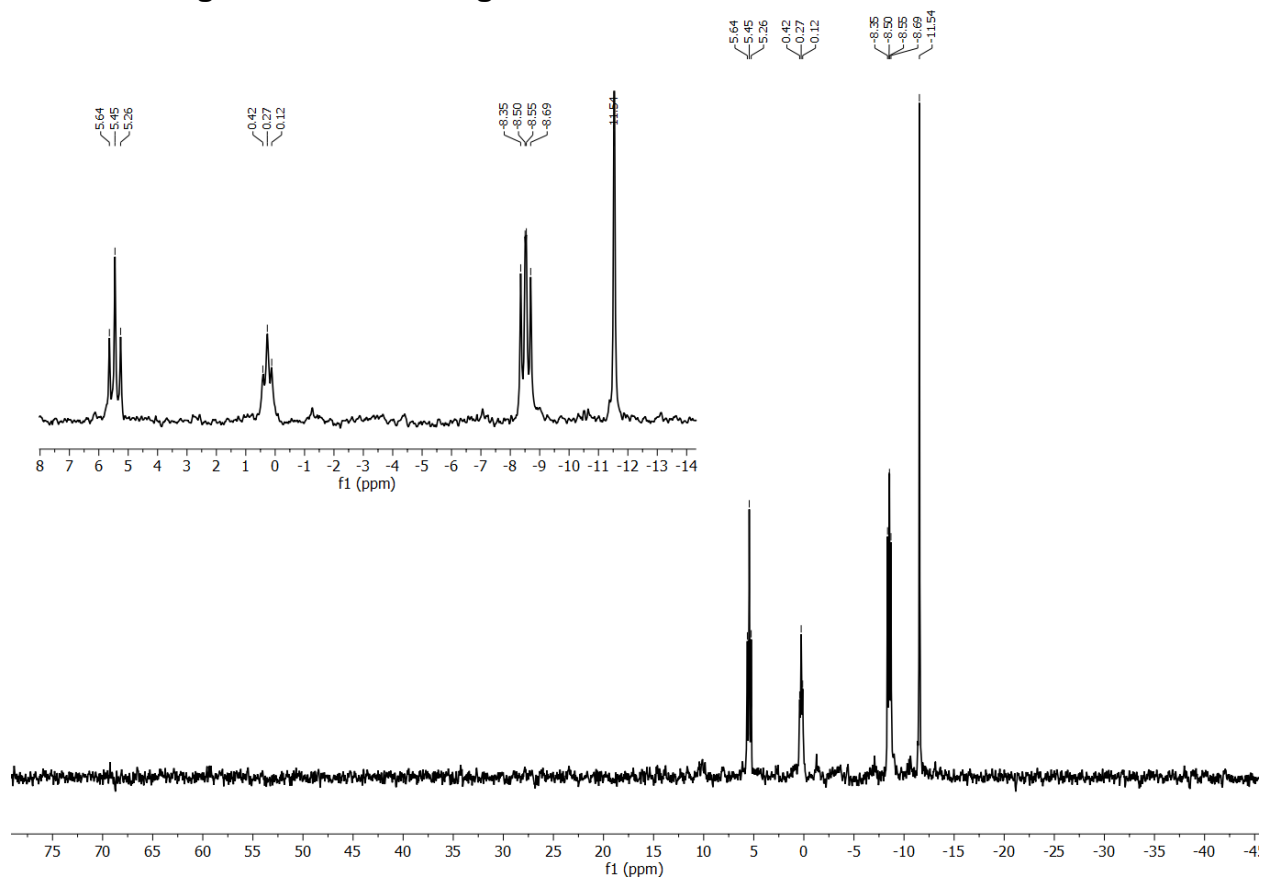


Figure S50. ^{31}P NMR spectrum for the attempted basic hydrolysis of compound **9** with KOH. No evidence of compound **8** was detected and addition of more KOH and prolonged reaction time did not lead to formation of **8**.

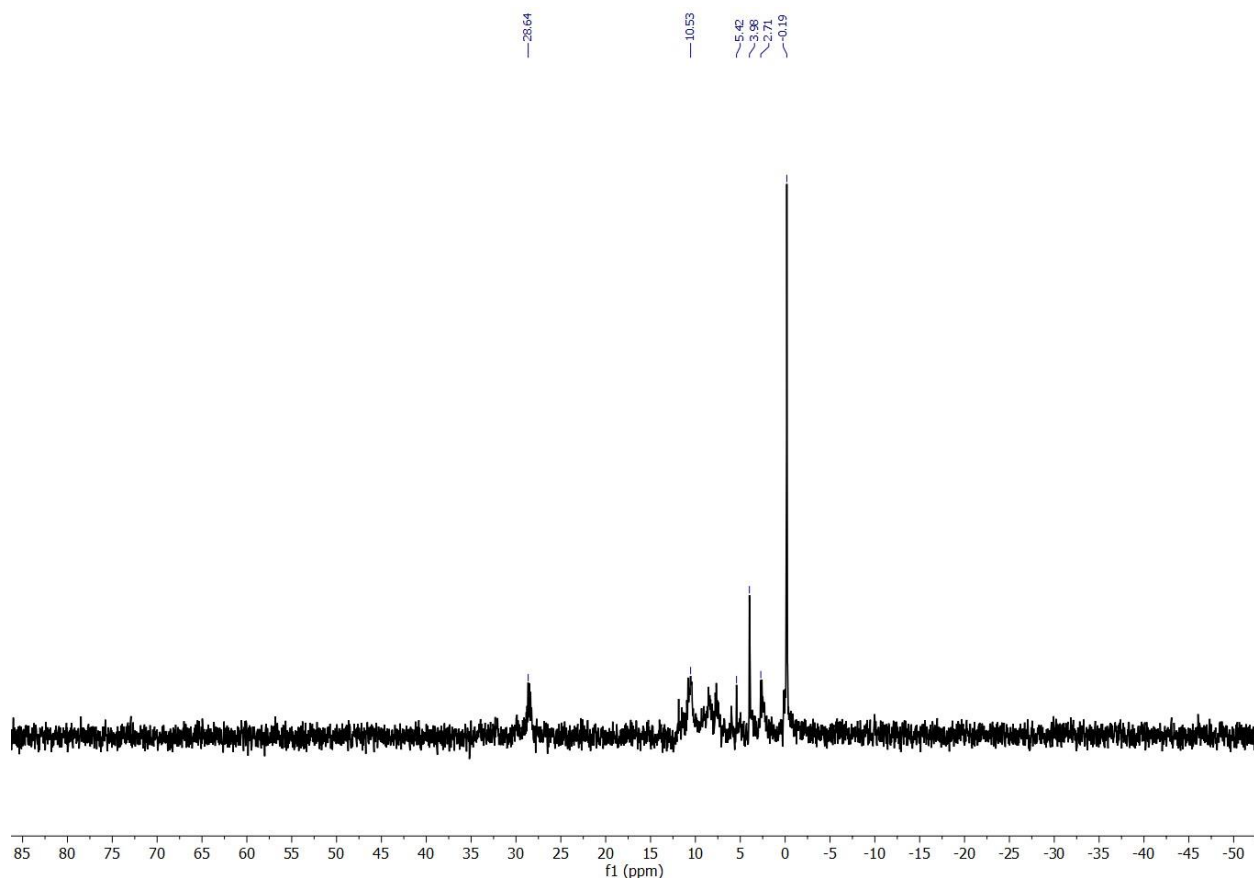


Figure S51. ^{31}P NMR spectrum for the attempted acidic hydrolysis of compound **9** with HCl and water. No evidence of compound **8** was detected.

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