Electronic Supplementary Material (ESI) for RSC Advances.

Iptycene-Functionalized Silica Gel for the Purification of Fullerenes Using Flash Chromatography

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General Experimental Procedures:

Solvents used in synthesis were HPLC grade and taken from a solvent purification system. Solvents used for column chromatography were reagent grade and used as purchased. All solvents used, anthracene and pentacene were purchased from Sigma-Aldrich Co. Bis(diethoxyphosphoryl)acetylene was purchased from STREM Chemicals, Inc. A mixture of 70% C_{60}, 28% C_{70} and 2% higher fullerenes was purchased from SES Research. SiliaSphere® 20 µm silica gel and SiliaFlash® P60, 40 – 63 µm silica gel were provided by SiliCycle Inc. Flash chromatography was performed on a CombiFlash® Rf+, purchased from Teledyne Isco Inc.

^{1}H-NMR spectra were recorded on a Brüker AVANCE300 (300 MHz) δ or Brüker AC300 (300 MHz) δ NMR spectrometers using the proton signal of deuterated chloroform as the internal standard. ^{13}C-NMR spectra were broad band decoupled and recorded on a Brüker AVANCE300 (75.5 MHz) δ or Brüker AC300 (75.5 MHz) δ NMR spectrometers using the carbon signal of deuterated chloroform as the internal standard. ^{31}P-NMR spectra were broadband decoupled and recorded on a Brüker AC300 (121.4 MHz) δ NMR spectrometers with phosphoric acid in water as the external reference. ^{29}Si-NMR spectra were recorded on a Brüker AVANCE500 (99.3 MHz) δ NMR spectrometers with tetramethylsilane as the internal standard. The following abbreviations are used for NMR peak multiplicities: s, singlet; t, triplet; dd, doublet of doublets; m, multiplet; br, broad. Chemical shifts are reported in parts per million (ppm) relative to chloroform (δ 7.26) for ^{1}H-NMR, chloroform (δ 77.0) for ^{13}C-NMR, phosphoric acid in water (δ 0.00) for ^{31}P-NMR and tetramethyl silane (δ 0.00) for ^{29}Si-NMR. High resolution mass spectra (HRMS) were obtained via electrospray ionization (ESI) which were measured on a Thermo Scientific Q ExactiveTM Plus Hybrid Quadrupole-OrbitrapTM at the University of Waterloo Mass Spectrometry Facility.

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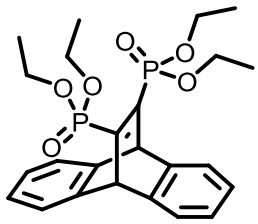
1. Experimental

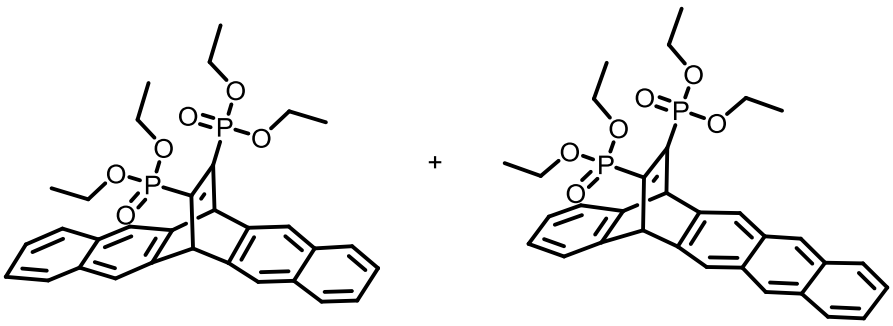
1.1 Synthesis of tetraethyl ((9s,10s)-9,10-dihydro-9,10-ethenoanthracene-11,12-diyl)bis(phosphonate) (1)



The synthesis of **1** was based on a modified procedure by Acheson et al.[1] To a 25 mL thick-walled, glass pressure tube was added anthracene (0.8965 g, 5.03 mmol), bis(diethoxyphosphoryl)acetylene (0.500 g, 1.68 mmol) and 20 mL of dry toluene. The tube was then sealed with a Teflon screw cap. The resulting mixture was heated with stirring at 160 °C for 5 days. The solution was allowed to cool, was then filtered and the filtrate was concentrated by rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using ethyl acetate as the mobile phase to give yellow oil **1** in 50% yield. Rf = 0.15. R_f = 0.15. ^{1}H NMR in $CDCl_3$: 7.36 ppm (m, 4H), 7.00 ppm (m, 4H), 5.79 ppm (t, 2H, 6.4 Hz), 4.01 ppm (m,

8H), 1.24 ppm (t, 12H, 7.4 Hz). ^{31}P NMR in $CDCl_3$ with phosphoric acid in water as the external reference: 14.34 ppm. Spectral data matched literature values reported by Acheson.

1.2 Synthesis of tetraethyl ((6s,13s)-6,13-dihydro-6,13-ethenopentacene-15,16-diyl)bis(phosphonate) (2a) and tetraethyl ((5R,14S)-5,14-dihydro-5,14-ethenopentacene-15,16-diyl)bis(phosphonate) (2b)



2a + **2b**

(5.5 : 1)

To a 25 mL thick-walled, glass pressure tube was added pentacene (1.05356 g, 3.79 mmol), bis(diethoxyphosphoryl)acetylene (1.12870 g, 3.79 mmol) and 20 mL of dry toluene. The tube was then sealed with a Teflon screw cap. The resulting mixture was heated and stirred at 180 °C for 5 days. The solution was allowed to cool, was then filtered and the filtrate was concentrated by rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using ethyl acetate as the mobile phase to give an oily, yellow, inseparable mixture of isomers (**2a** and **2b** in a 5.5:1 ratio respectively) in an overall 64% yield. R_f = 0.15. Spectral data for isomer **2a**: ^{1}H NMR in $CDCl_3$: 7.83 ppm (s, 4H), 7.74 ppm (m, 4H), 7.42 ppm (m, 4H), 6.00 ppm (t, 2H, 6.6 Hz), 4.04 ppm (br m, 8H), 1.25 ppm (t, 12H, 7.1 Hz). ^{13}C NMR in $CDCl_3$: 151.5 ppm (dd, 8.6 Hz, 189.7 Hz), 139.2 ppm, 131.9 ppm, 127.6 ppm, 126.0 ppm, 122.3 ppm, 62.6 ppm (t, 2.9 Hz), 54.3 ppm (t, 11.5 Hz), 16.2 ppm (t, 2.9 Hz). ^{31}P NMR in $CDCl_3$ with phosphoric acid in water as the external reference: 14.34 ppm. m/z (calc.) = 829.28424, m/z (found) = 829.28363. Spectral data for isomer **2b**: ^{1}H NMR in $CDCl_3$: 8.28 ppm (s, 2H), 7.94 ppm (m, 2H), 7.90 ppm (s, 2H), 7.42 ppm (m, 4H)*, 7.10 ppm (m, 2H), 5.90 ppm (t, 2H, 6.9 Hz), 4.03 (br m, 8H)*, 1.25 (t, 12H)*. ^{13}C NMR in $CDCl_3$: 151.5 ppm (dd, 8.6 Hz, 189.7 Hz)*, 142.2 ppm, 138.6 ppm, 131.9 ppm*, 130.2 ppm, 128.0 ppm, 125.9 ppm*, 125.2 ppm, 123.9 ppm, 121.8 ppm, 62.5 ppm (t, 2.9 Hz)*, 54.3 ppm (t, 11.5 Hz)*, 16.2 ppm (t, 2.9 Hz)*. ^{31}P NMR in $CDCl_3$ with

phosphoric acid in water as the external reference: 14.30 ppm*. Peaks labelled with an asterisk (*) are either partially or completely overlapped with those of **2a**.

1.3 Functionalization of Silica Gel

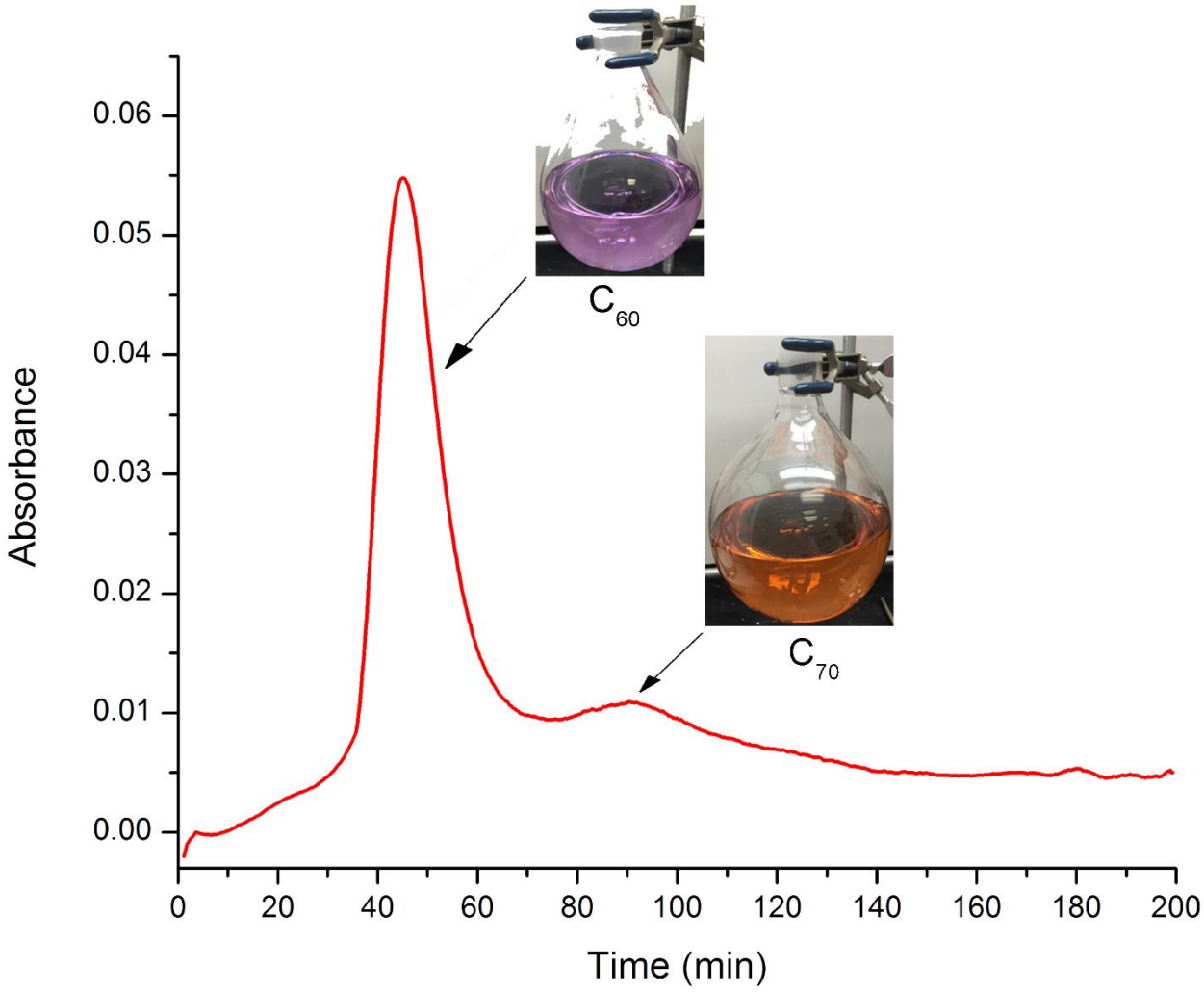
To a 250 mL round bottom flask was added SiliaSphere® 20 µm silica gel (12 g), 2 (mixture of 2a and 2b) (6.99 g, 12.13 mmol) and 75 mL of acetonitrile. The resulting slurry was heated at reflux with stirring for 4 hours. The resulting slurry was allowed to cool, concentrated by rotary evaporator, transferred to a 150 mL beaker and placed in a vacuum oven at 140 °C for 4 hours. The resulting silica gel was orange in colour and was washed with dichloromethane to remove any unreacted 2. The functionalization of the resulting silica gel was verified by 29Si SSNMR with TMS as the internal standard.

1.4 Method for Purification of Fullerenes

25 mg of a fullerene mixture was added to a 1L round bottom flask, dissolved in toluene and sonicated. Approximately 1 g of SiliaFlash® P60, 40 – 63 µm silica gel was then added to the solution and the resulting mixture was concentrated by rotary evaporator until dry. The silica gel was then loaded into an empty cartridge and placed on the CombiFlash® Rf+ system. A column was loaded with 12 g of **1** or **2**-functionalized silica gel and was also placed on the CombiFlash® Rf+ system. The separation was then run using varying degrees of toluene and hexanes as the mobile phase. UV-Vis detection was set to 260 nm, 290 nm and 380 nm with the signal gain set to 3x.

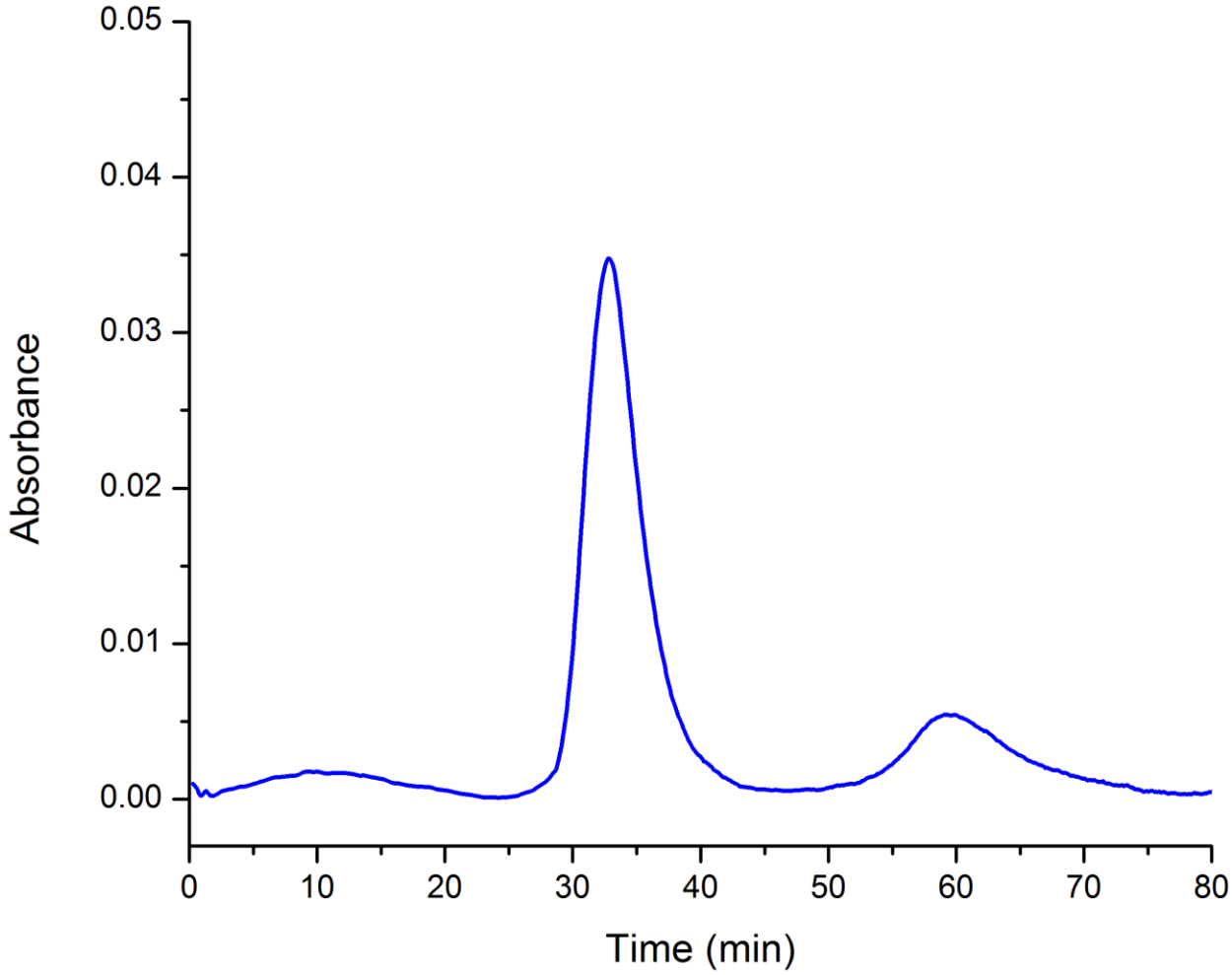
2. UV-Vis Data

2.1 UV-Vis Chromatogram of 2-Functionalized Silica Gel in Hexanes



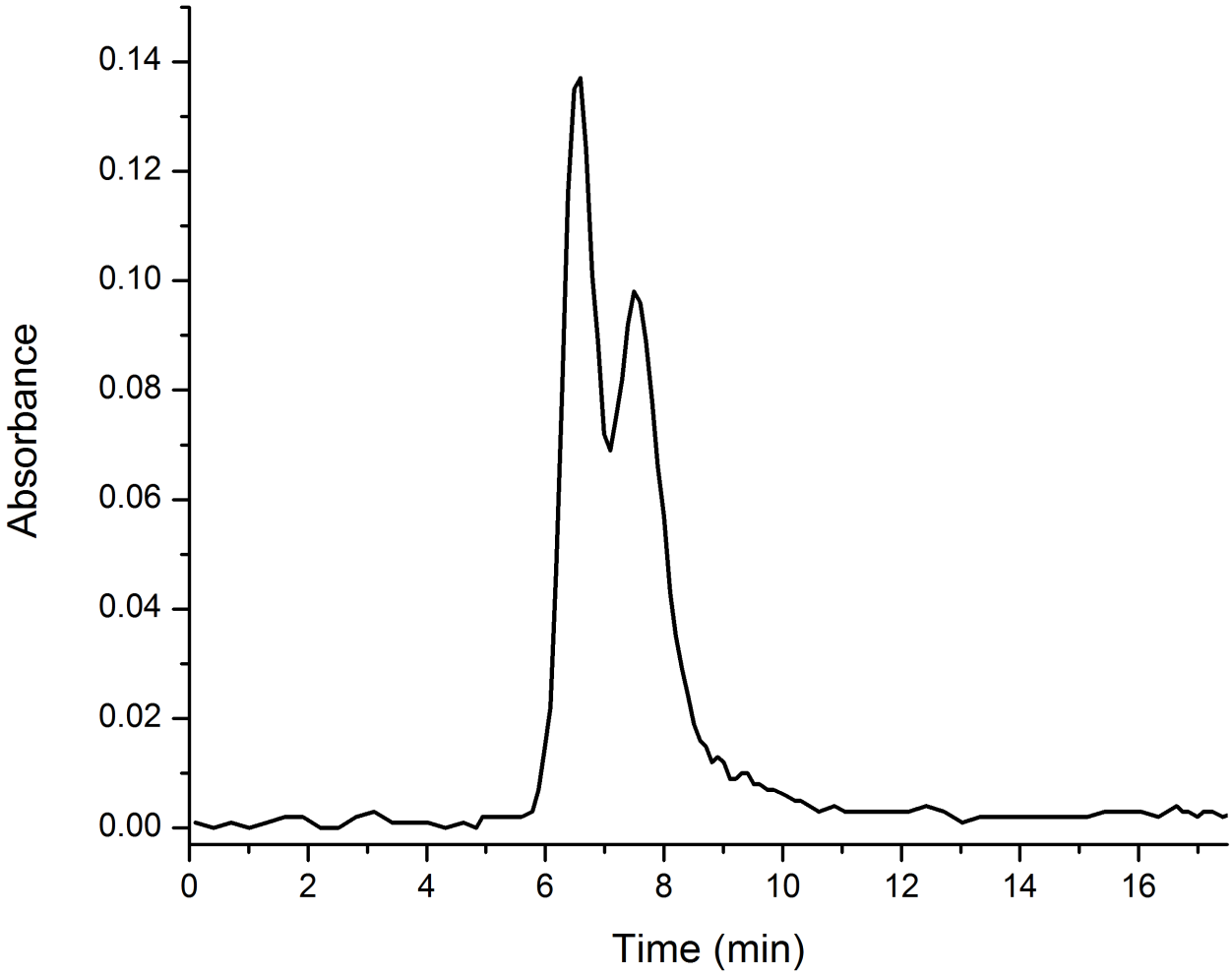
The UV-Vis chromatogram generated by the CombiFlash® Rf+ of a separation of fullerenes using **2**-functionalized silica gel and a hexanes mobile phase. Collected at 260 nm. The curve has been smoothed using 30 points of adjacent-averaging. The inset images represent the visual colour of each fraction: pink corresponding to C_{60} and orange corresponding to C_{70}.

2.2 UV-Vis Chromatogram of 2-Functionalized Silica Gel in 25% Toluene



The UV-Vis chromatogram generated by the CombiFlash® Rf+ of a separation of fullerenes using **2**-functionalized silica gel and a 25% toluene in hexanes mobile phase. Collected at 290 nm. The curve has been smoothed using 30 points of adjacent-averaging.

2.3 UV-Vis Chromatogram of 2-Functionalized Silica Gel in Toluene

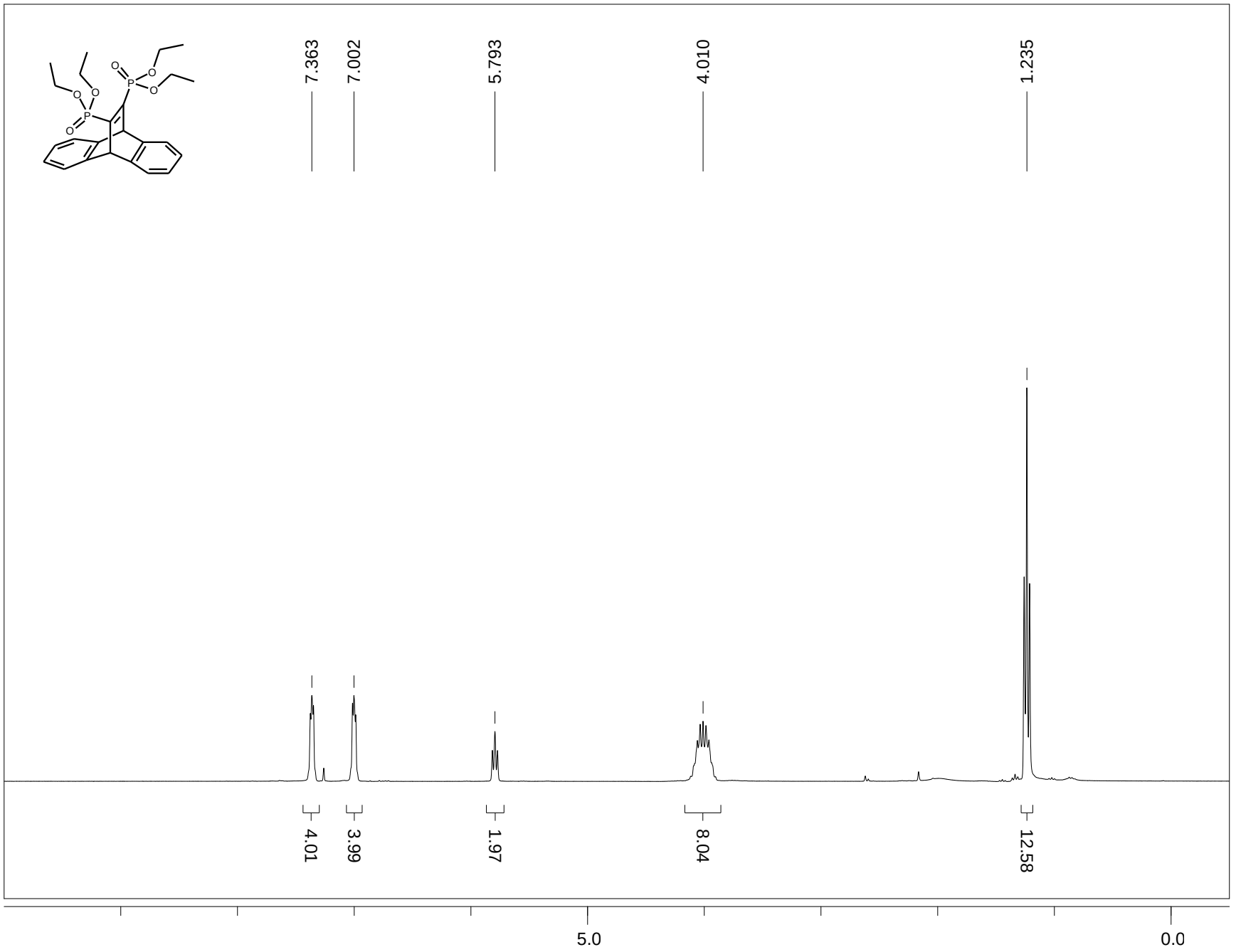


The UV-Vis chromatogram generated by the CombiFlash® Rf+ of a separation of fullerenes using **2**-functionalized silica gel and a 25% toluene in hexanes mobile phase. Collected at 380 nm.

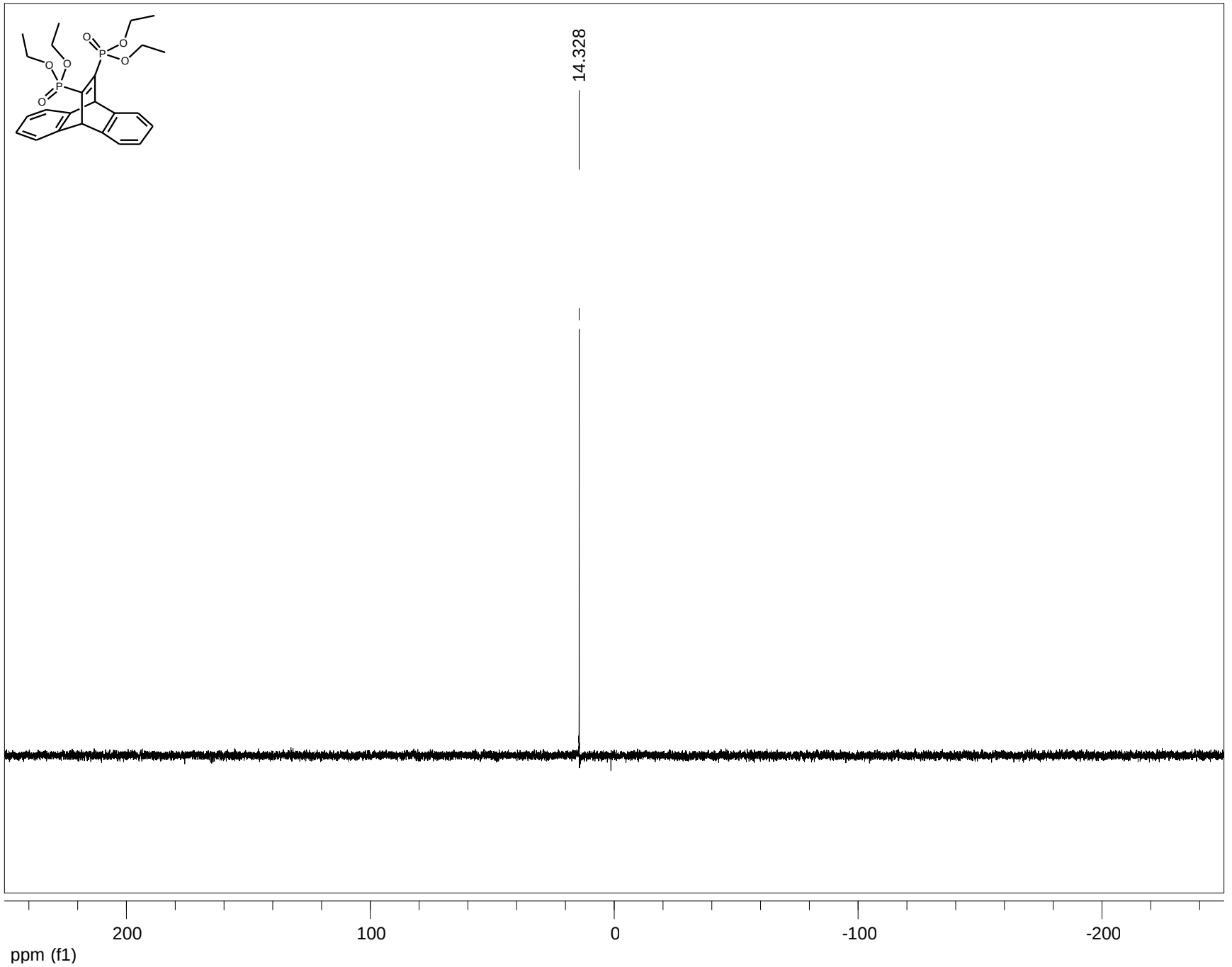
[1] R. M. Acheson and P. J. Ansell, *J. Chem. Soc. Trans. 1*, 1987, 1275–1281.

3. NMR Spectra

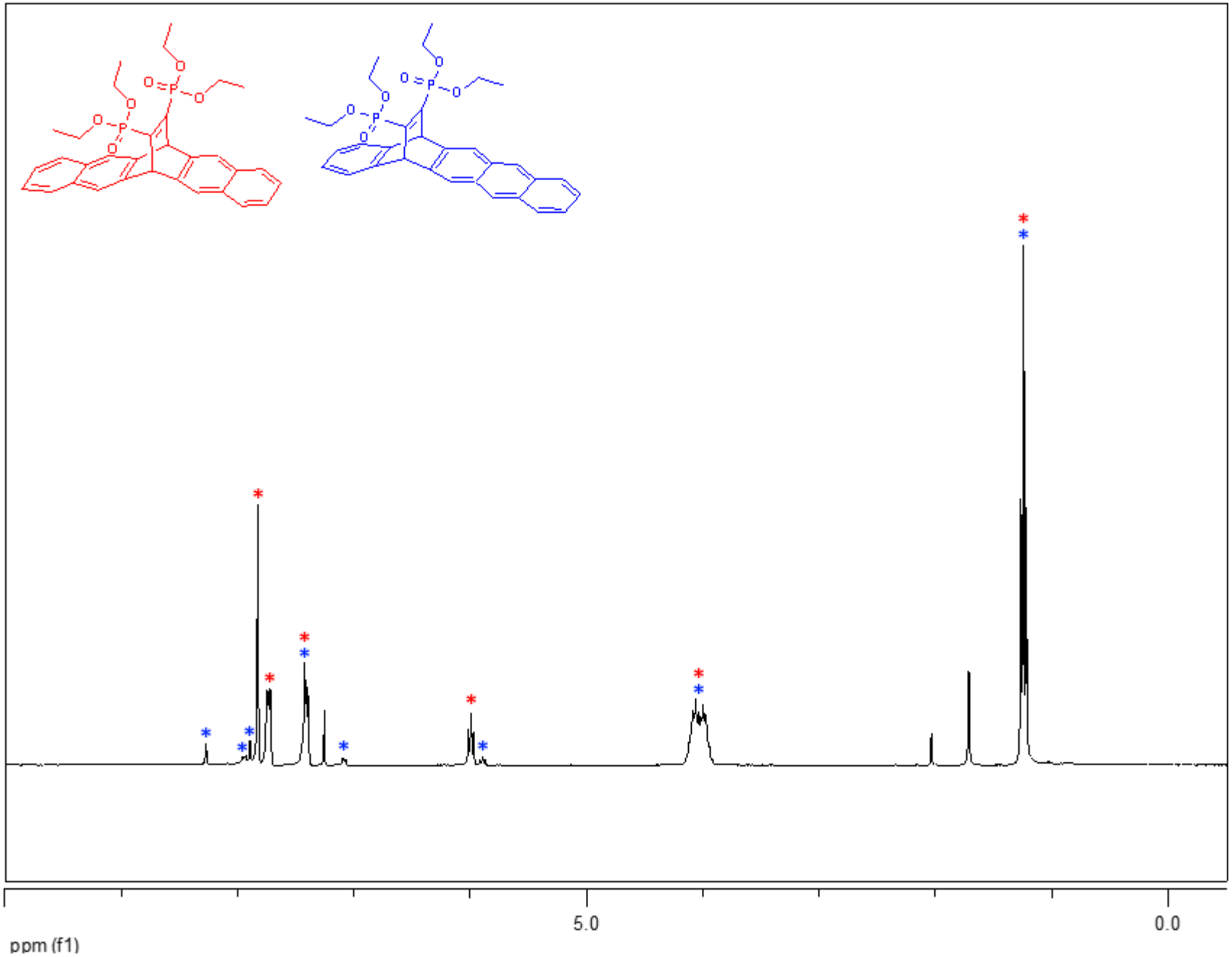
^{1}H NMR of **1**



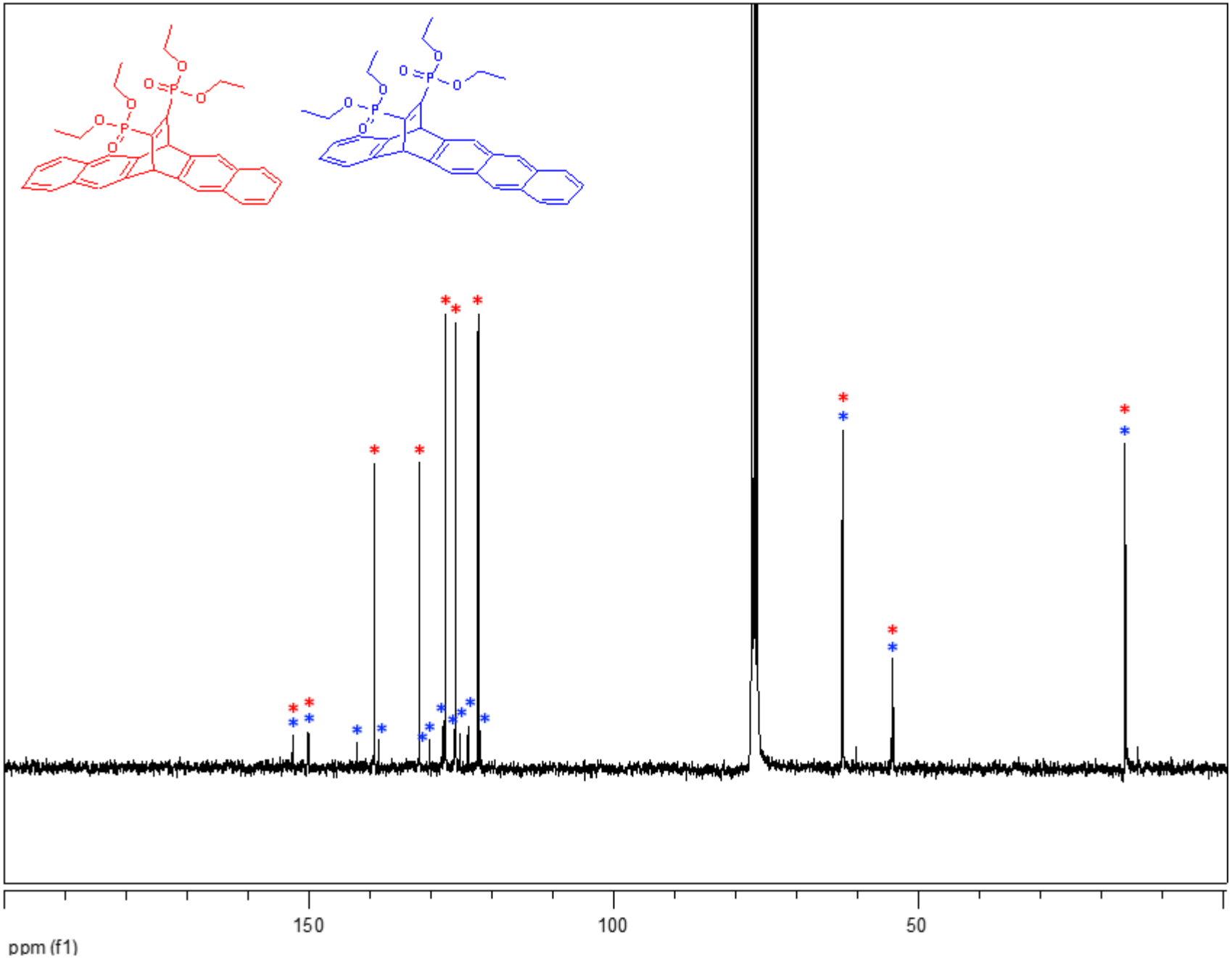
^{31}P NMR of **1**



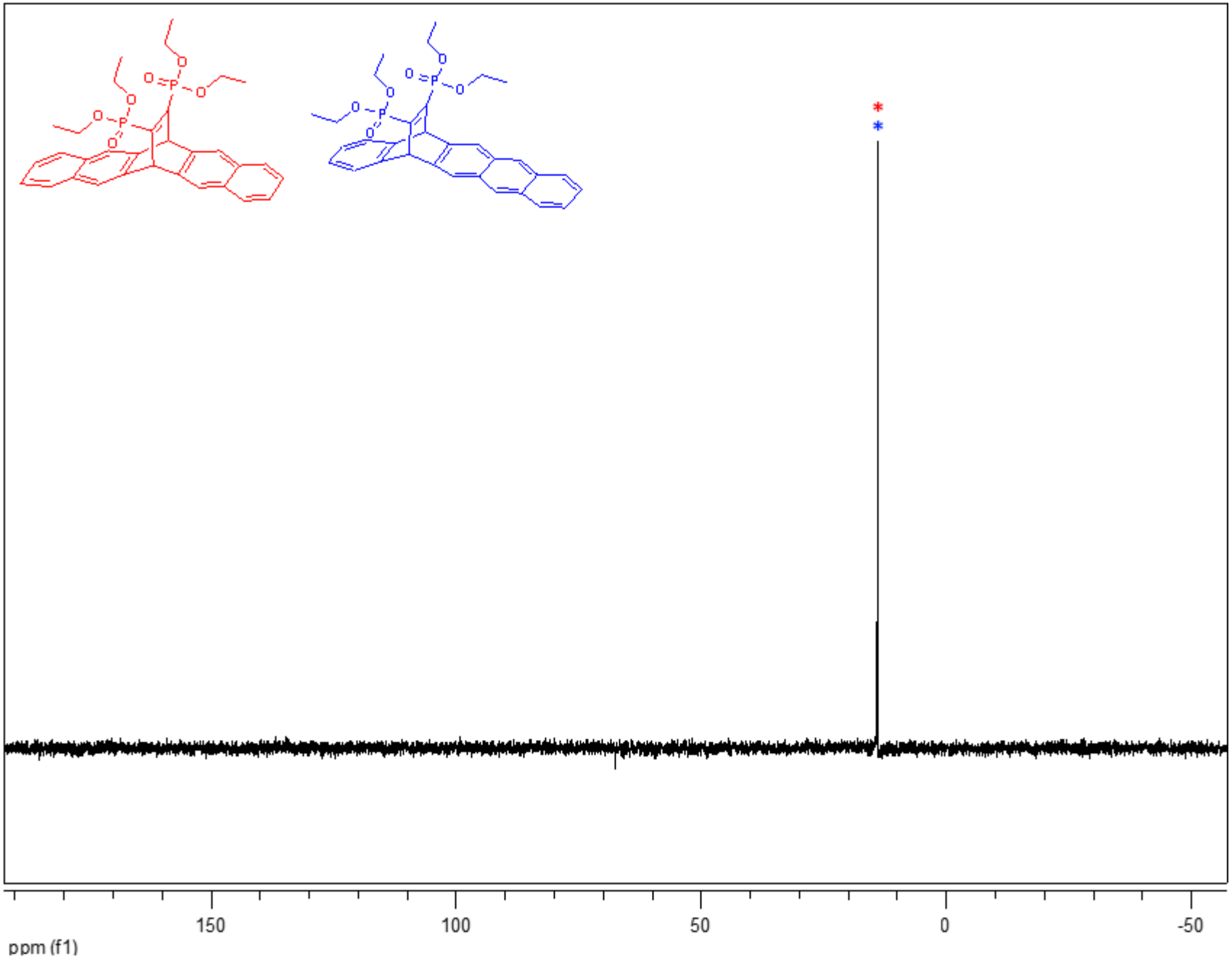
^{1}H NMR of **2a** and **2b** Mixture



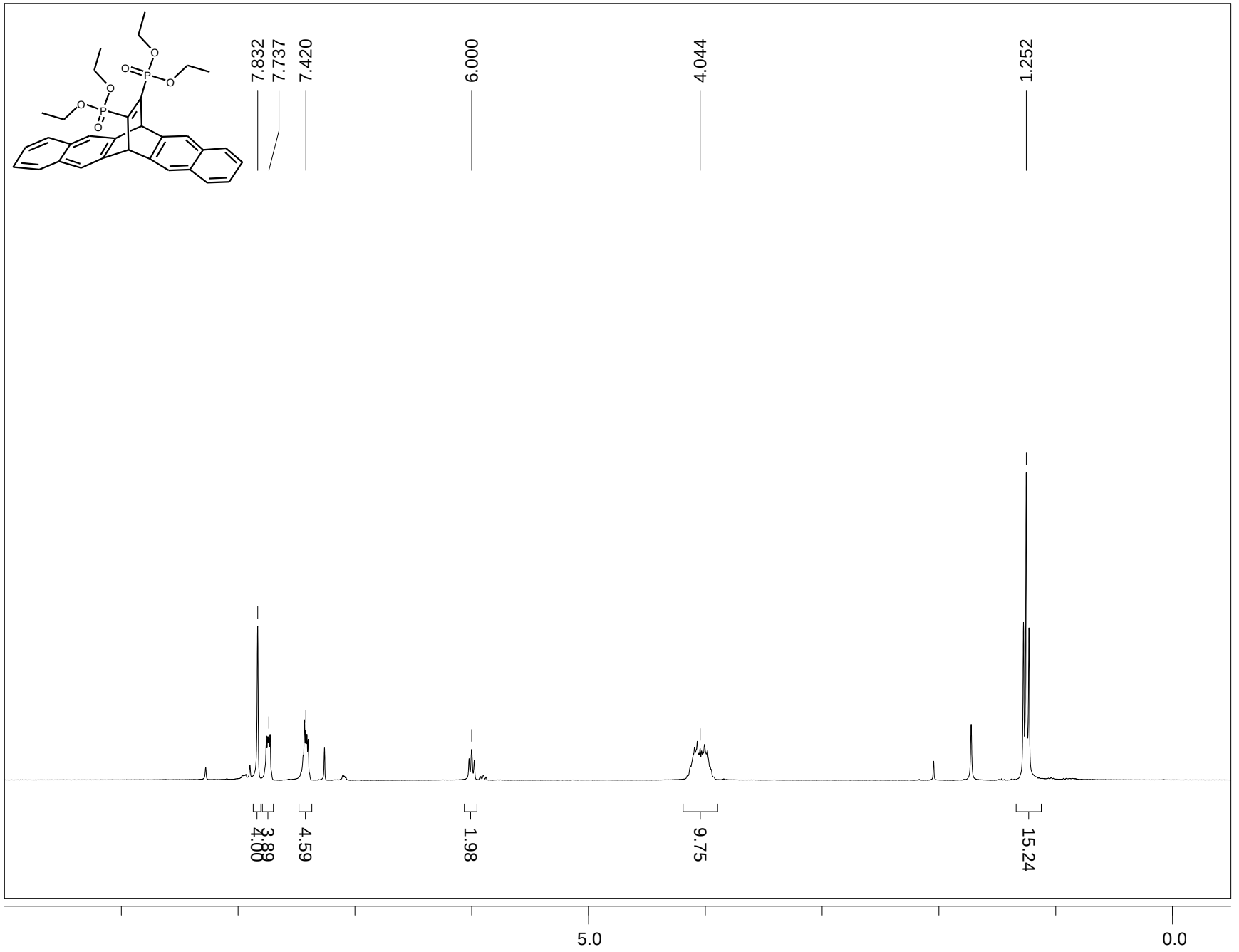
^{13}C NMR of **2a** and **2b** Mixture



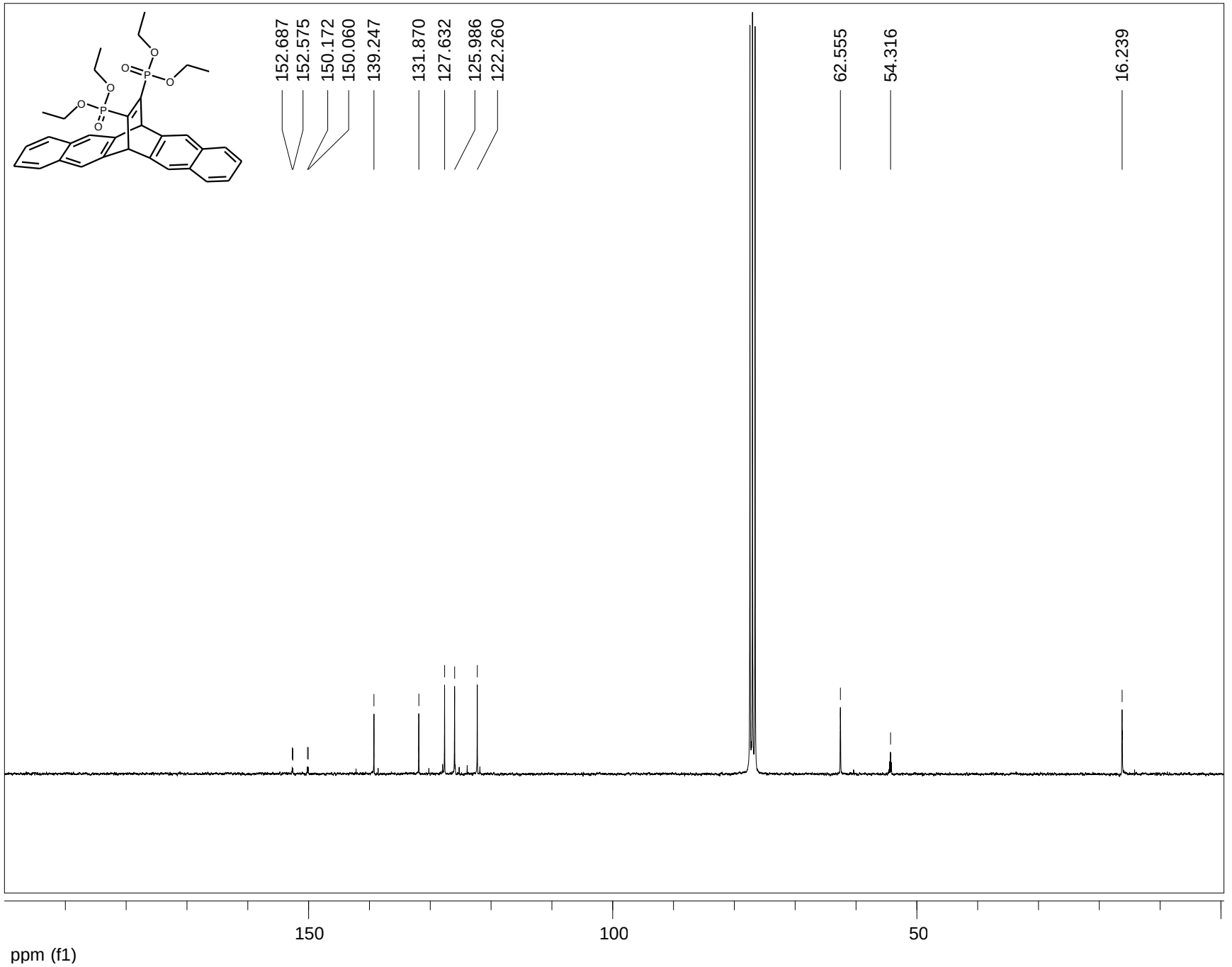
^{31}P NMR of **2a** and **2b** Mixture



^{1}H NMR of **2a**


7.832
7.737
7.420
6.000
4.044
1.252
4.00
3.89
4.59
1.98
9.75
15.24
5.0
0.0
ppm (f1)

^{13}C NMR of **2a**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152.575
150.172
150.060
139.247
131.870
127.632
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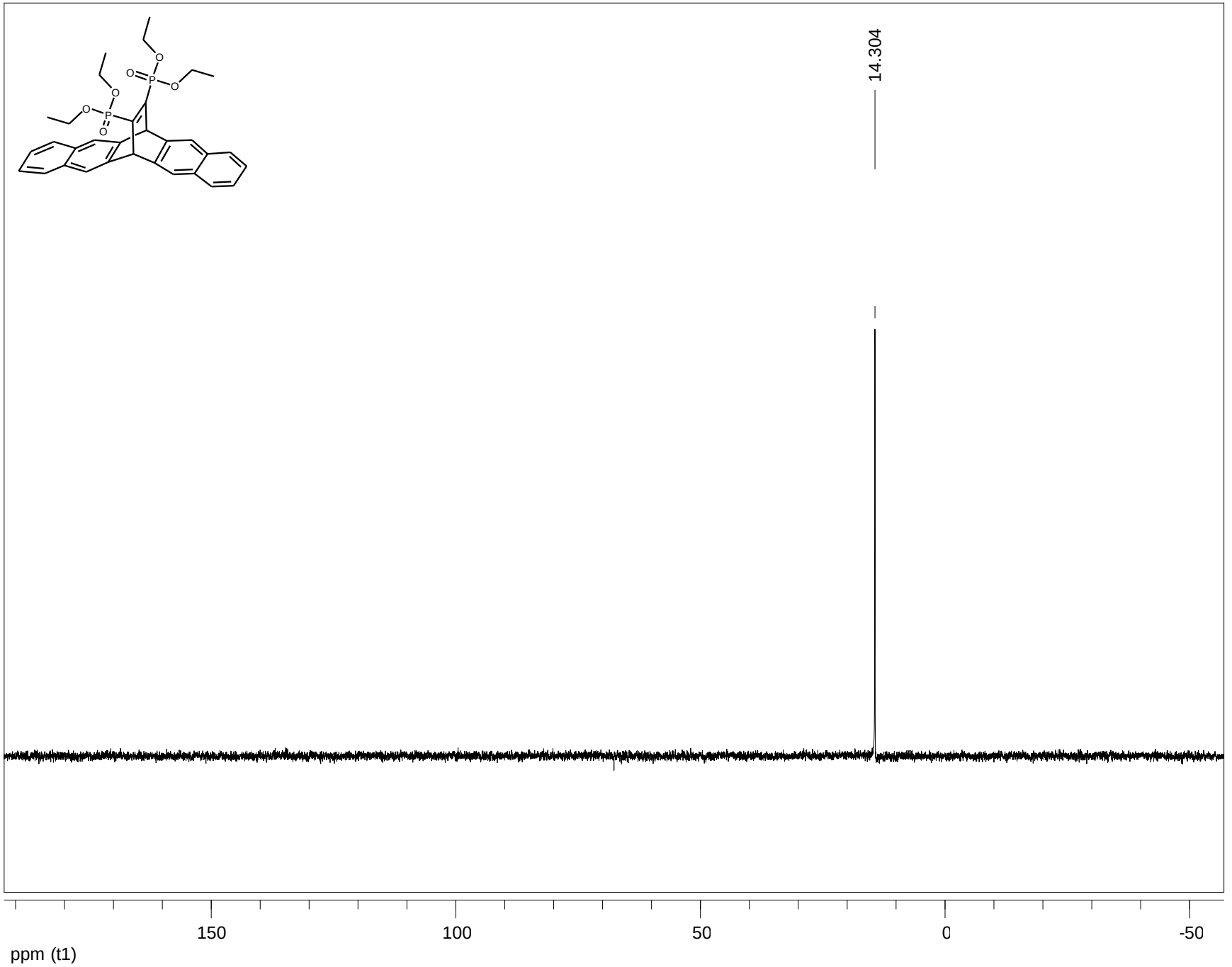
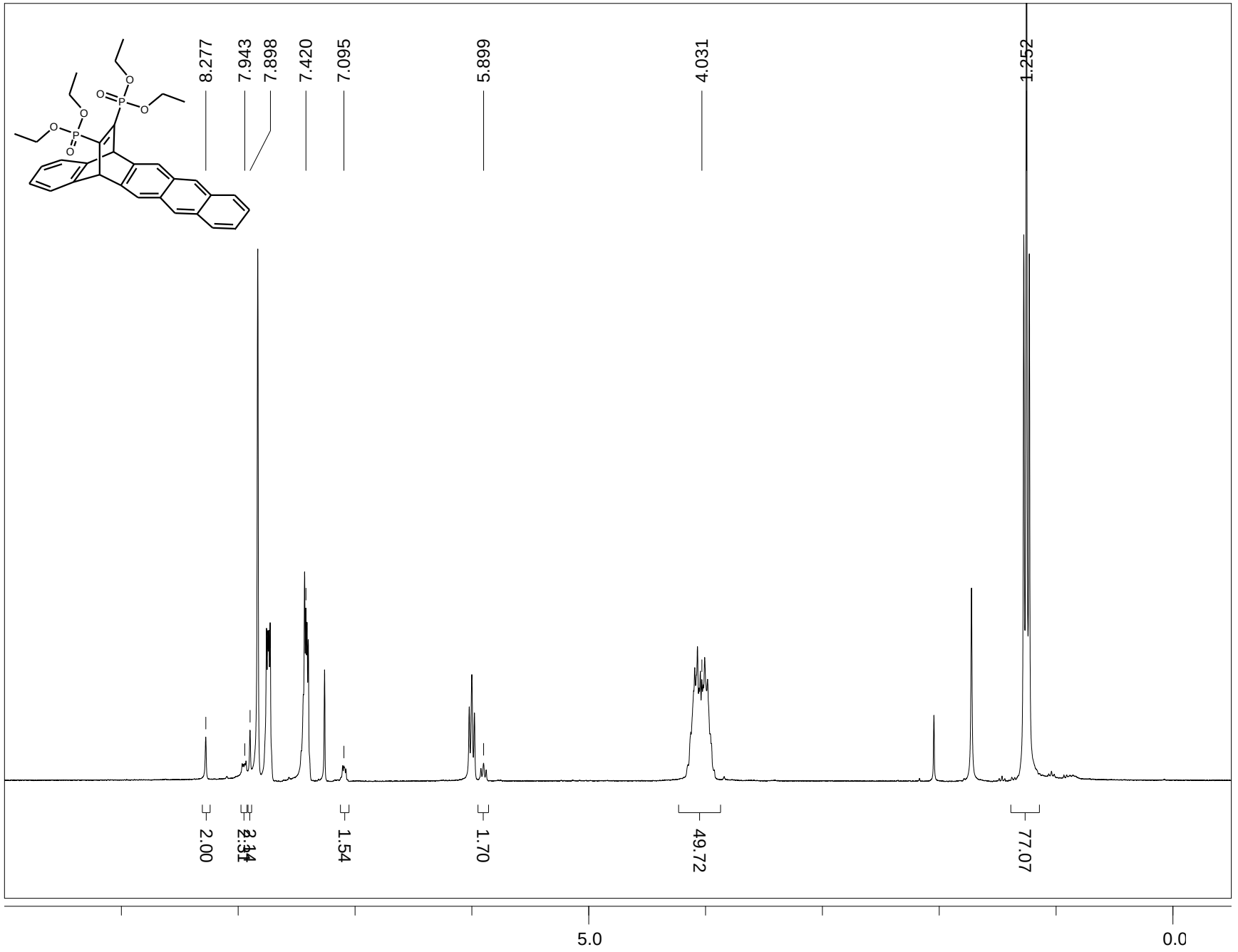
150
100
50
ppm (f1)

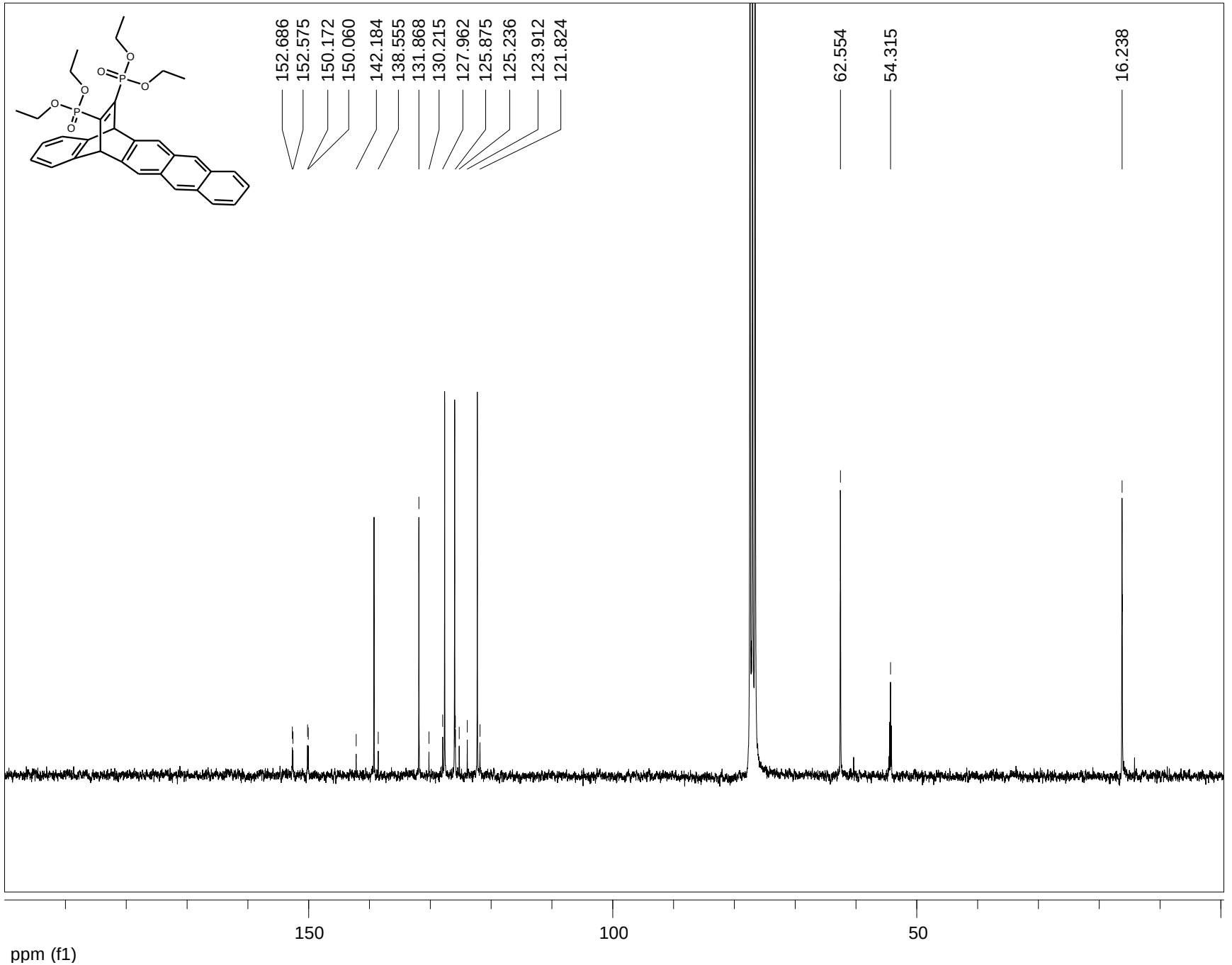
^{31}P NMR of **2a**



^{1}H NMR of **2b**


8.277
7.943
7.898
7.420
7.095
5.899
4.031
1.252
2.00
2.14
2.31
1.54
1.70
49.72
77.07
5.0
0.0
ppm (t1)

^{13}C NMR of **2b**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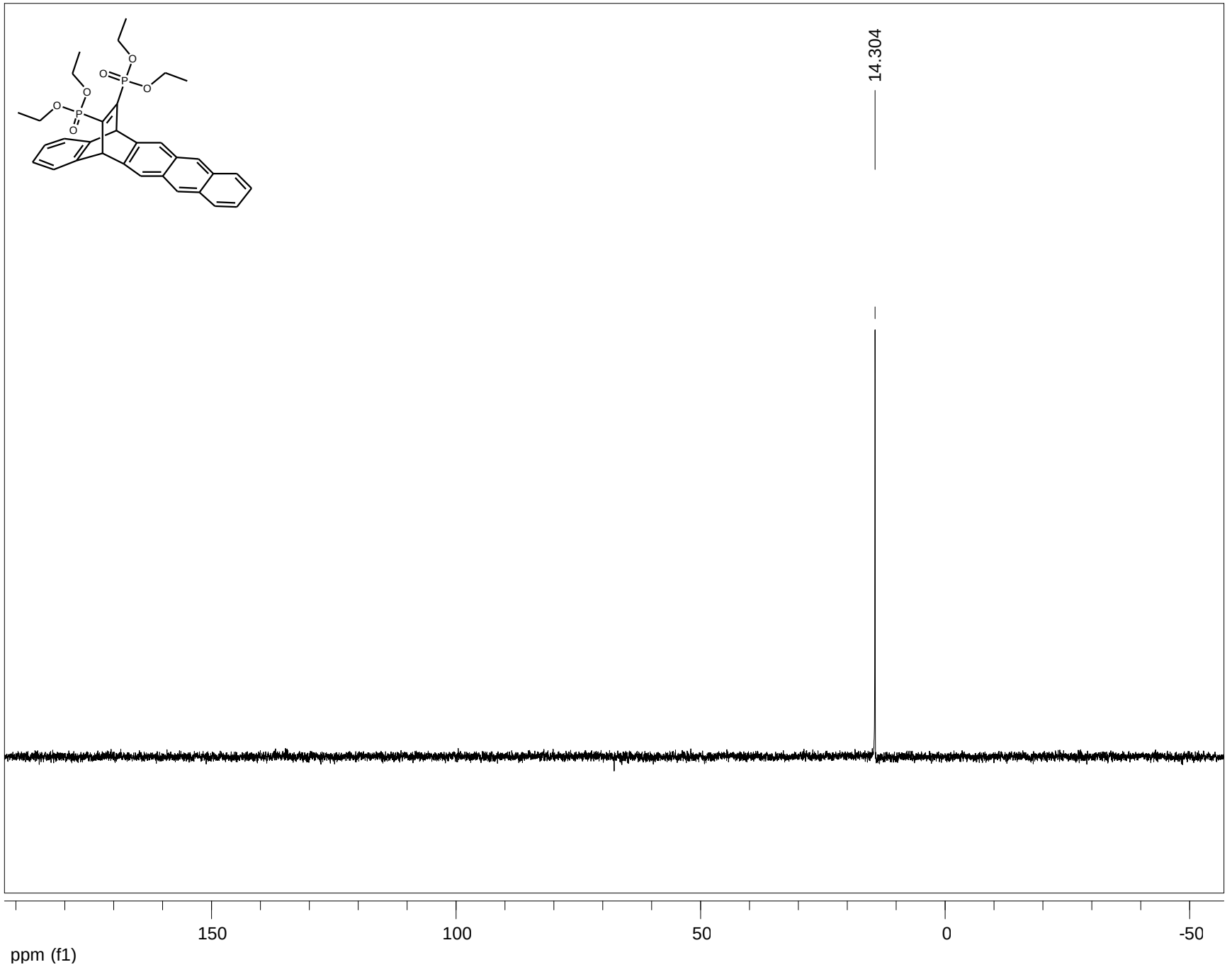
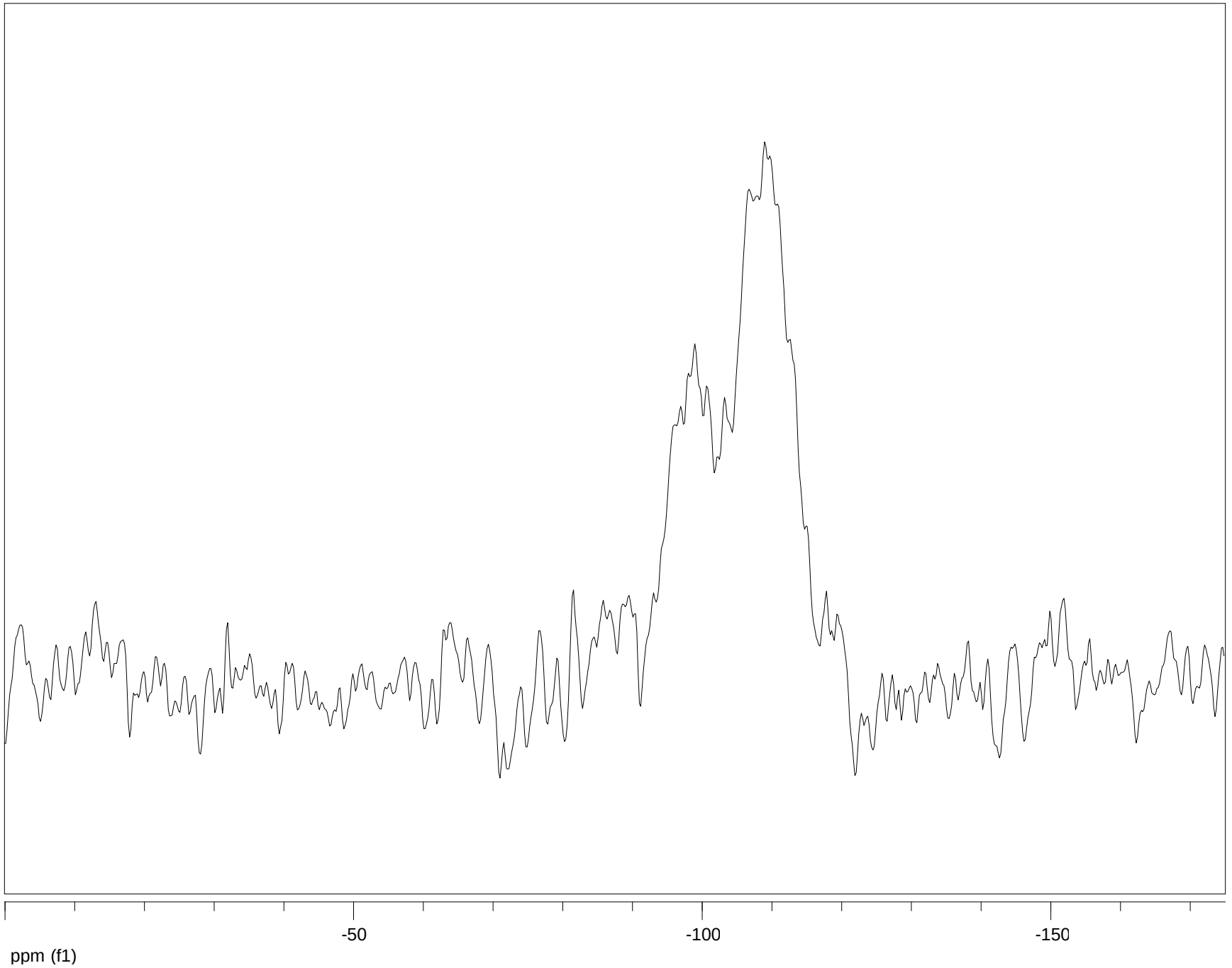
150.172
150.060
142.184
138.555
131.868
130.215
127.962
125.875
125.236
123.912
121.824
62.554
54.315
16.238
150
100
50
ppm (f1)

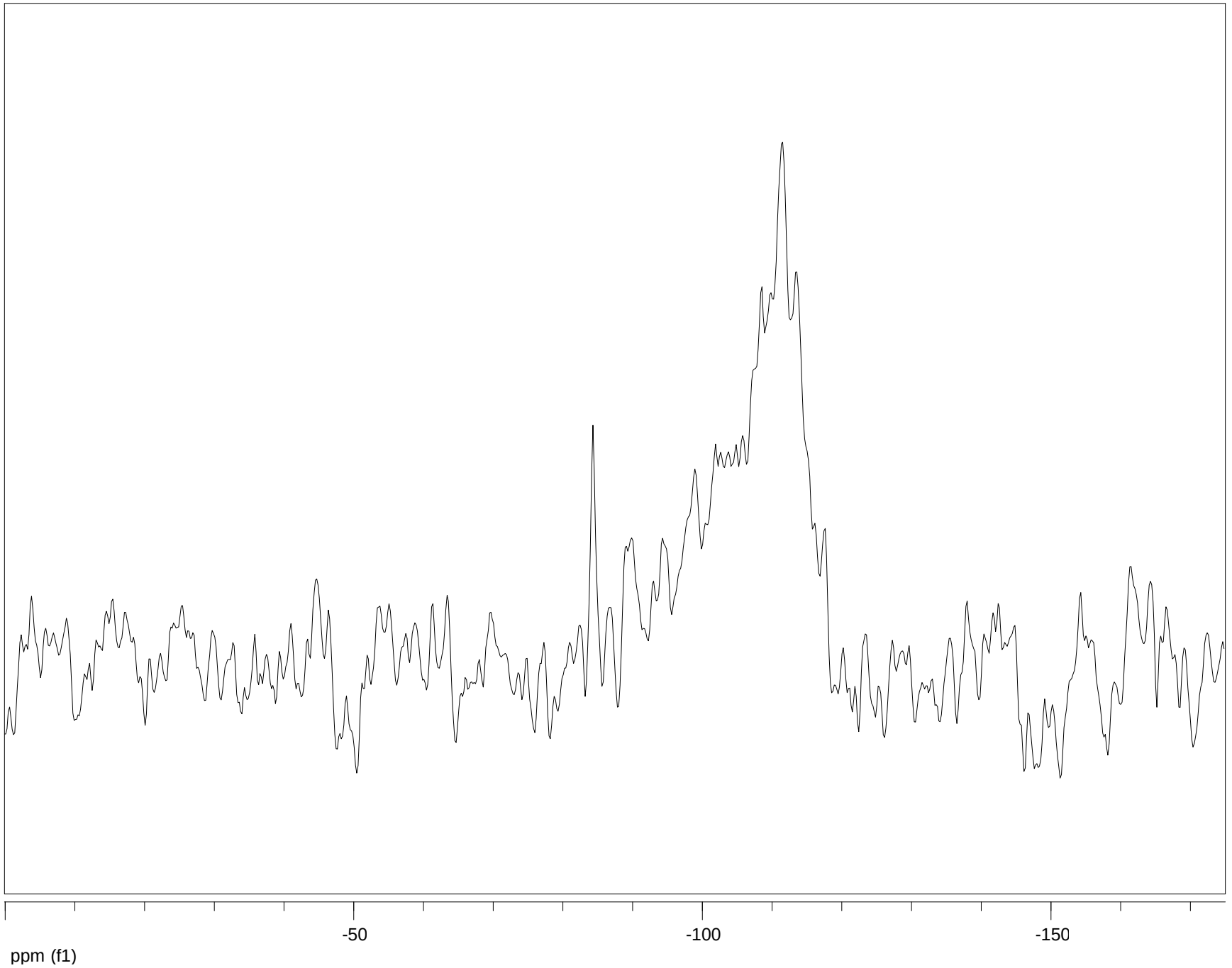
^{31}P NMR of **2b**



^{29}Si SSNMR of 7 w/w% of **1** on Silica Gel



^{29}Si SSNMR of 14 w/w% of **1** on Silica Gel



^{29}Si SSNMR of 28 w/w% of **1** on Silica Gel