Supporting Information

Introverted Brønsted Acid Cavitands

for Selective Conjugate Addition Reactions

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Dedicated to Professor François Diederich who sadly passed away on the 23rd of September 2020.

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Contents

1. Portions of NMR spectra of **1**•C_5H_5N (Figure 1S).

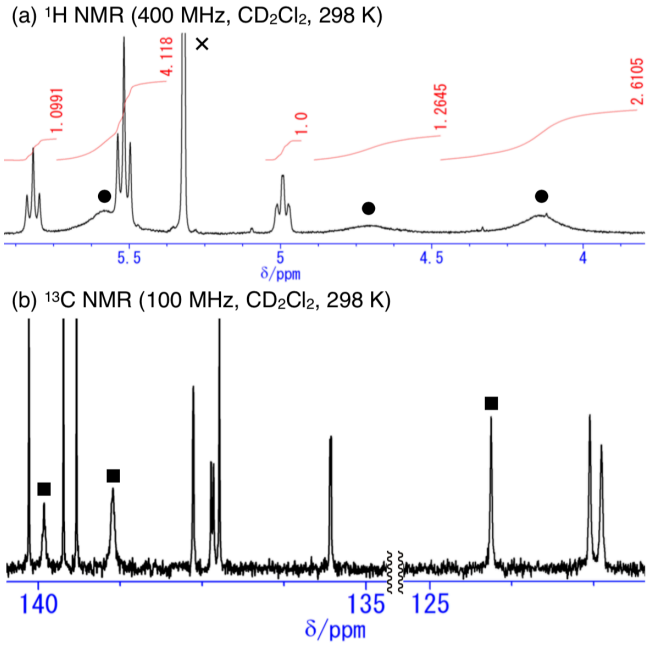


Figure 1S. Portions of the spectra of **1**•C_5H_5N for (a) ^1H NMR (400 MHz, CD_2Cl_2, 298 K) from 3.8 to 5.9 ppm, and (b) ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K) from 122.1 to 125.2 ppm and from 134.8 to 140.4 ppm. ●: The broad peaks of 5.58, 4.70, and 4.14 ppm correspond to 2-, 4-, and 3-positioned protons of an interior pyridine with properly integral values of 2 : 1 : 2, respectively; ■: Three kinds of carbon peaks in an encapsulated pyridine located at 139.9, 138.9, 124.1 ppm for 2-, 4-, 3-positioned carbons, respectively.

2. ^{1}H NMR spectra of **1**•(2-vinyl)pyridine, **2**•(2-vinyl)pyridine, **3**•(2-vinyl)pyridine, **4**•(2-vinyl)pyridine. (Figure 2S (a)-(d)).

Compound **1**•(2-vinyl)pyridine (^{1}H NMR spectrum in $CDCl_3$)

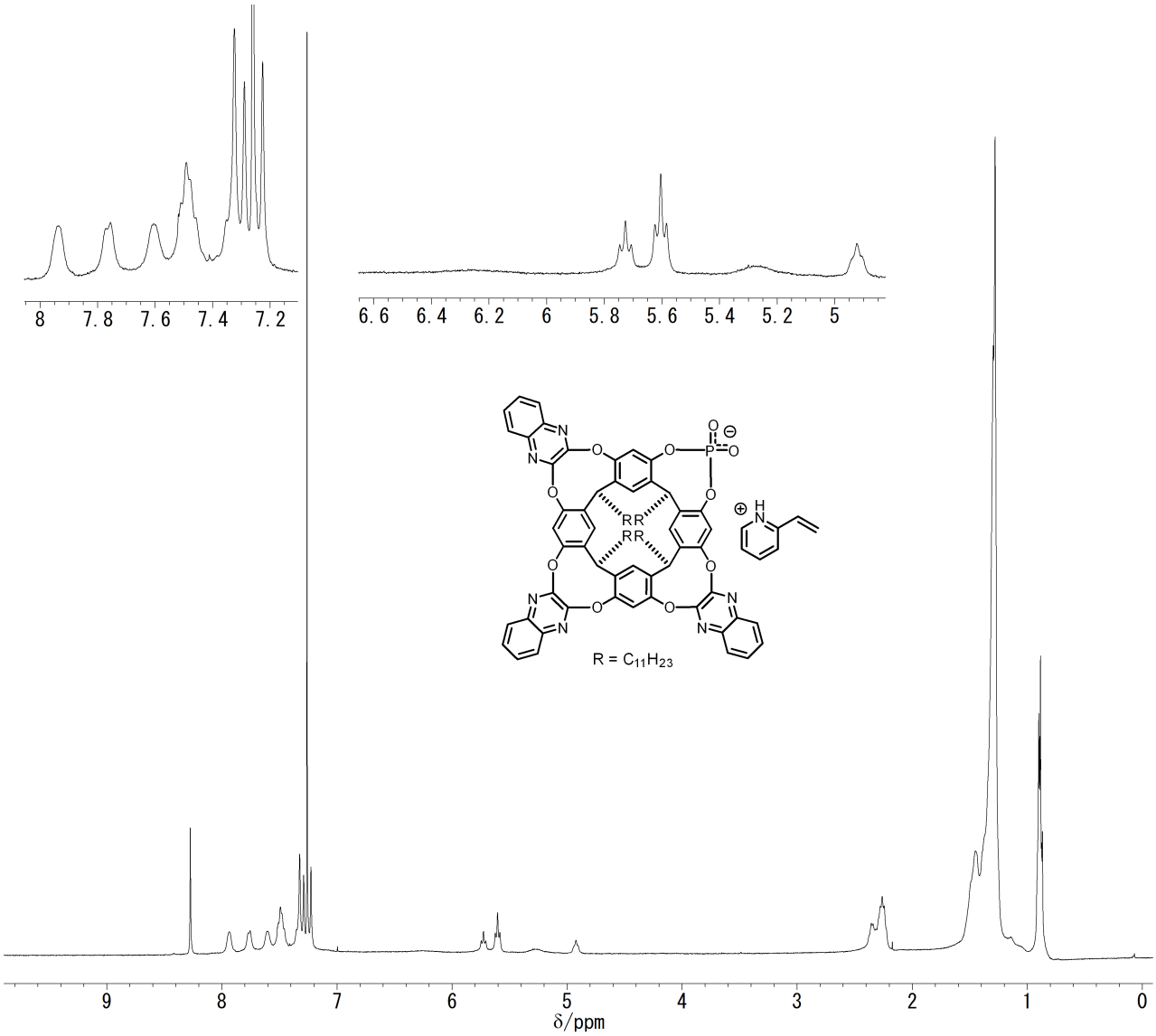


Figure 2S (a). ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**•(2-vinyl)pyridine: 8.27 (s, 2H), 7.94 (m, 2H), 7.75 (m, 2H), 7.61 (m, 2H), 7.49 (m, 4H), 7.32 (m, 4H), 7.29 (s, 2H), 7.23 (s, 2H), 6.23 (brs, 1H, C*H*$_2$=CH-), 5.73 (t, *J* = 8.0 Hz, 1H), 5.60 (t, *J* = 8.0 Hz, 2H), 5.22 (brs, 1H, C*H*$_2$=CH-), 4.92 (brs, 1H) 2.36-2.26 (m, 8H), 1.45-1.28 (m, 72H), 0.90-0.87 (m, 12H) ppm.

Compound **2**•(2-vinyl)pyridine (^{1}H NMR spectrum in $CDCl_3$)

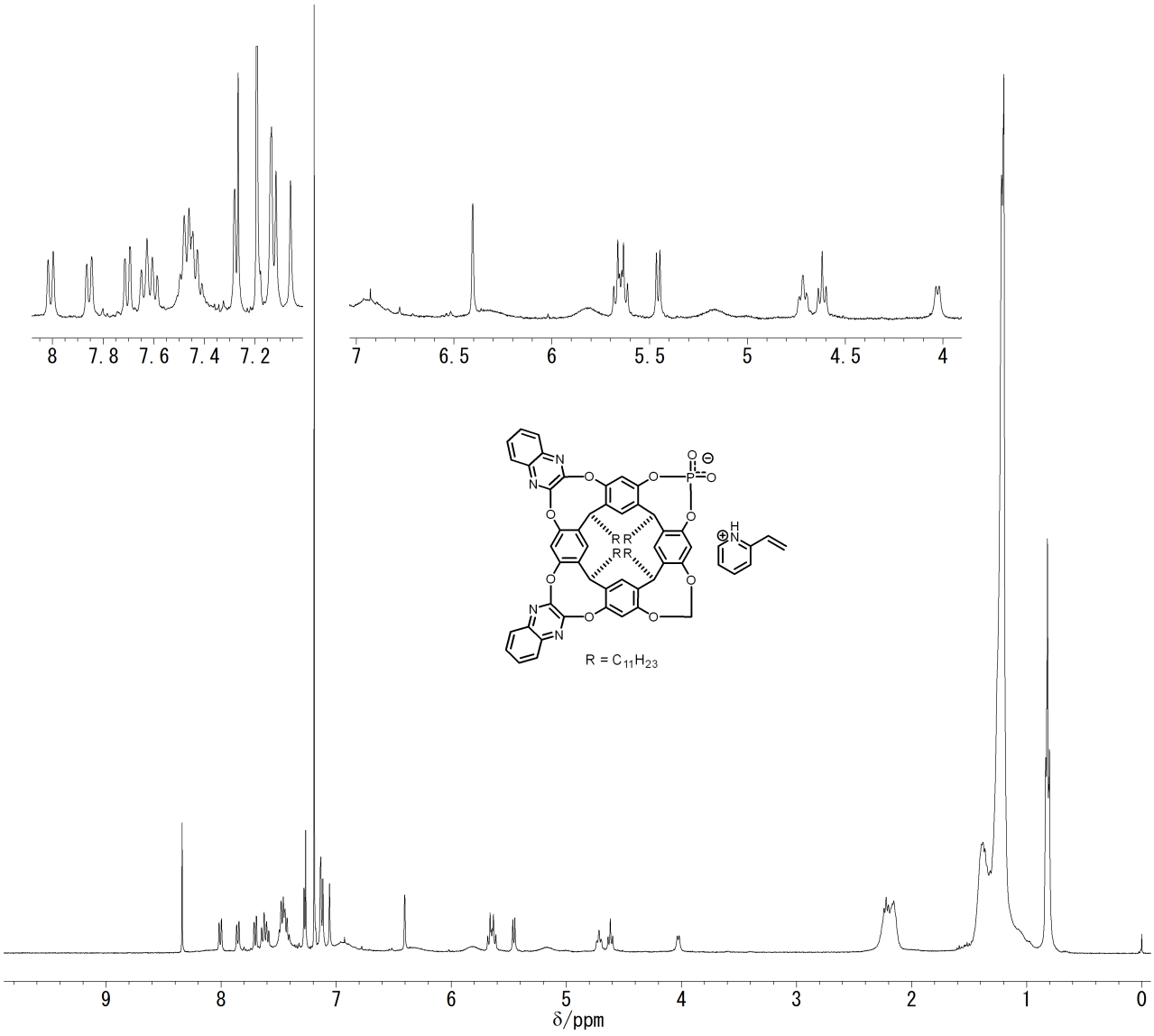


Figure 2S (b). ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**•(2-vinyl)pyridine: 8.41 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.55-7.48 (m, 4H, including one proton of the pyridine ring), 7.35 (s, 1H), 7.33 (s, 1H), 7.20 (m, 2H), 7.18 (s, 1H), 7.13 (s, 1H), 7.00 (brs, 1H, CH_2=C*H*-), 6.47 (s, 1H), 5.90 (brs, 1H, C*H*$_2$=CH-), 5.73 (t, *J* = 8.0 Hz, 1H), 5.70 (t, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 7.2 Hz, 1H, -O-C*H*$_2$-O-), 5.21 (brs, 1H, C*H*$_2$=CH-), 4.79 (t, *J* = 8.0 Hz, 1H), 4.69 (t, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 7.2 Hz, 1H, -O-C*H*$_2$-O-), 2.29-2.22 (m, 8H), 1.45-1.27 (m, 72H), 0.90-0.87 (m, 12H) ppm.

Compound **3**•(2-vinyl)pyridine (^{1}H NMR spectrum in $CDCl_3$)

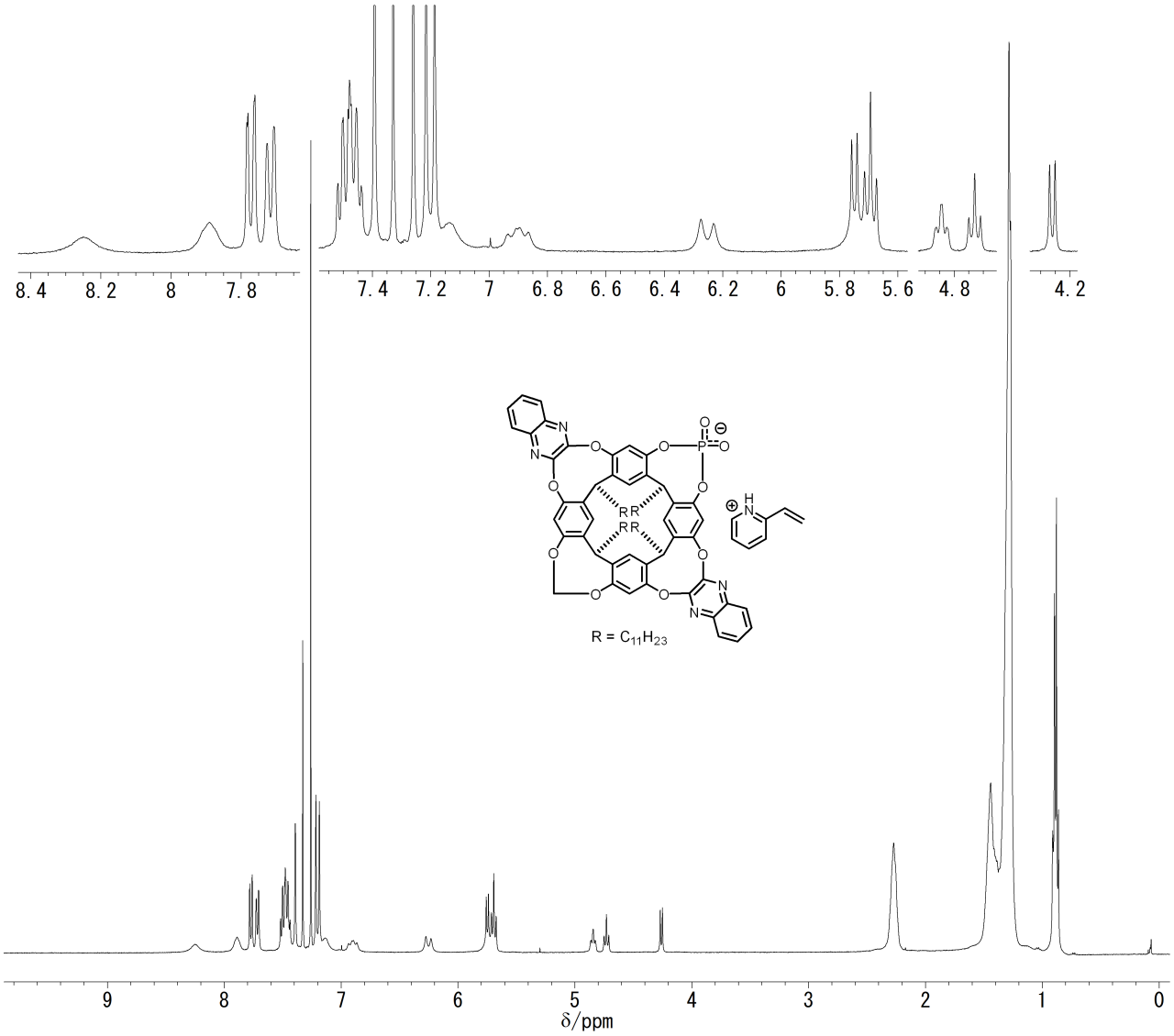


Figure 2S (c). ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**•(2-vinyl)pyridine: 8.25 (brs, 1H, 6-positioned proton of pyridine ring), 7.89 (brs, 1H, 3-positioned proton of the pyridine ring), 7.77 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 7.52-7.44 (m, 5H, including 4-positioned proton of the pyridine ring), 7.39 (s, 2H), 7.33 (s, 2H), 7.22 (s, 2H), 7.19 (s, 2H), 7.13 (brs, 1H, 5-positioned proton of the pyridine ring), 6.90 (dd, J = 17.2, 12.4 Hz, 1H, CH_2=C*H*-), 6.25 (d, J = 17.2 Hz, 1H, C*H*$_2$=CH-), 5.80-5.65 (br, 1H, C*H*$_2$=CH-), 5.75 (d, J = 7.4 Hz, 1H, -O-C*H*$_2$-O-), 5.69 (t, J = 8.2 Hz, 2H), 4.84 (t, J = 8.2 Hz, 1H), 4.73 (t, J = 8.2 Hz, 1H), 4.26 (d, J = 7.4 Hz, 1H, -O-C*H*$_2$-O-), 2.27 (m, 8H), 1.44-1.27 (m, 72H),

0.91-0.86 (m, 12H) ppm.

Compound **4**•(2-vinyl)pyridine (^{1}H NMR spectrum in $CDCl_3$)

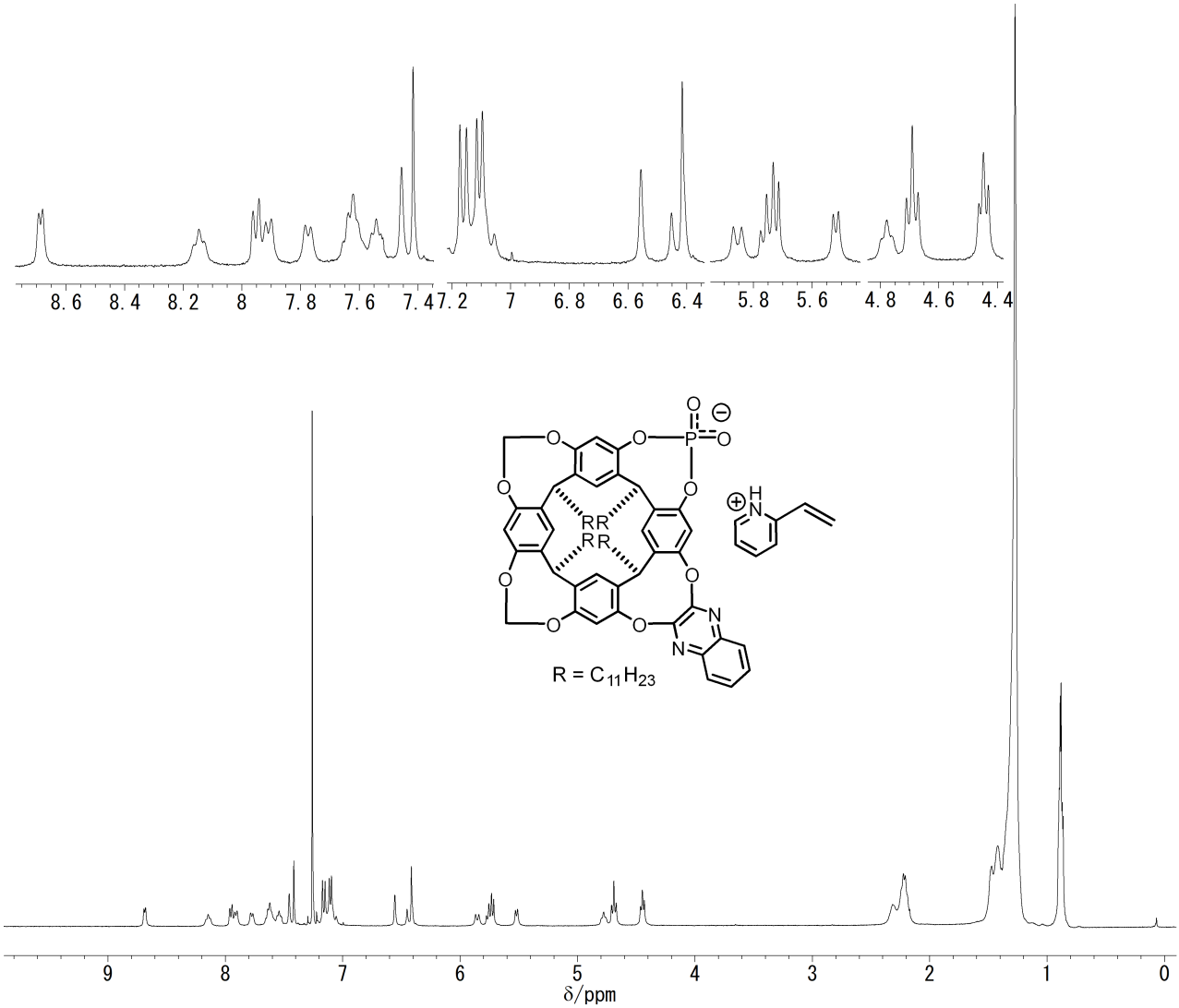
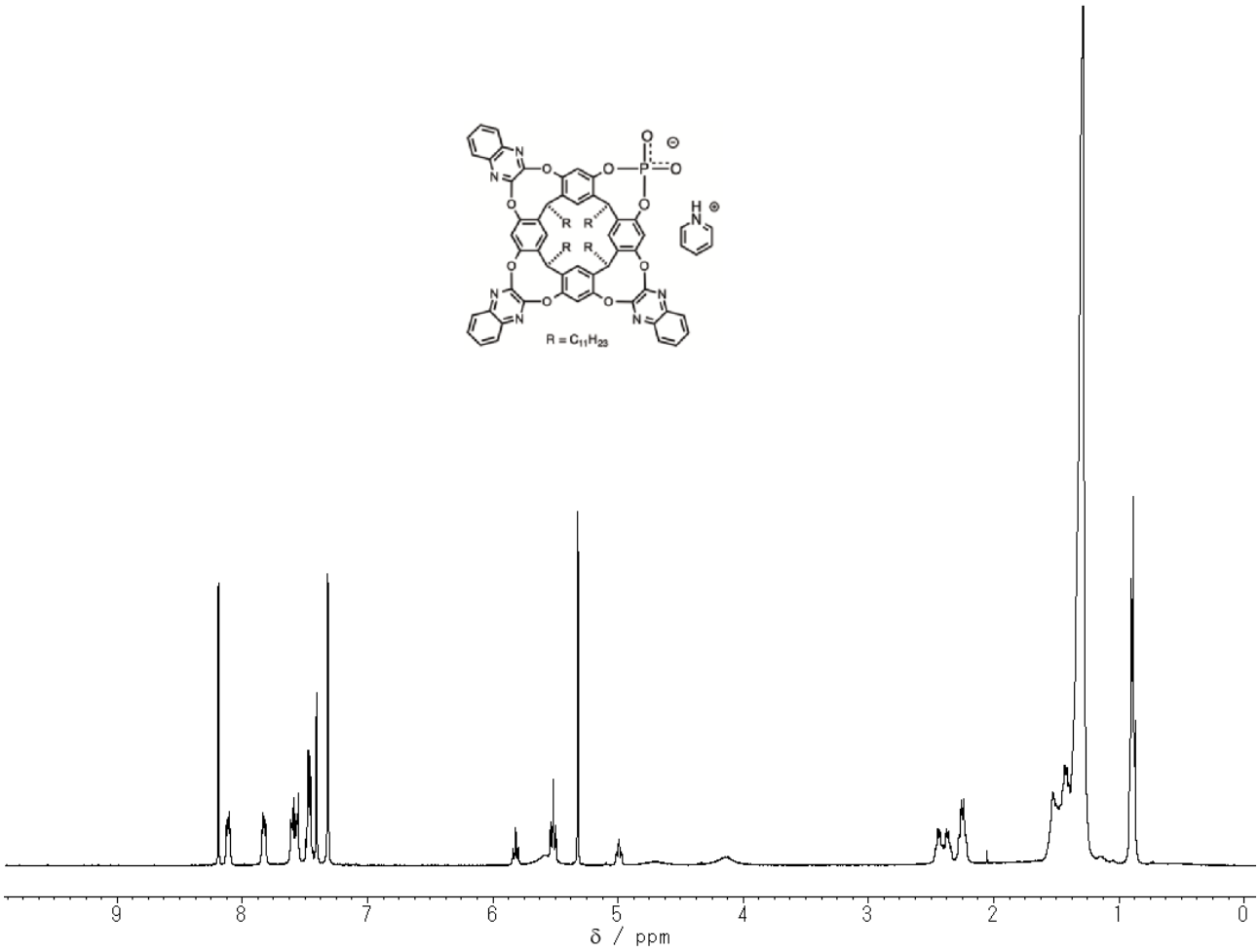


Figure 2S (d). ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**•(2-vinyl)pyridine: 8.69 (d, *J* = 5.7 Hz, 1H, 6-positioned proton of the pyridine ring), 8.16 (dd, *J* = 7.8, 7.8 Hz, 1H, 4-positioned proton of the pyridine ring), 7.95 (d, *J* = 7.8 Hz, 1H, 3-positioned proton of the pyridine ring), 7.91 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.64-7.54 (m, 3H, including 5-positioned proton of the pyridine ring), 7.46 (s, 1H), 7.42 (s, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 7.09 (dd, *J* = 14.6, 11.2 Hz, 1H, CH_2=C*H*-), 6.56 (s, 1H), 6.43 (d, *J* = 14.6 Hz, 1H, C*H*$_2$=CH-), 6.42 (s, 1H), 5.85 (d, *J* = 11.2 Hz, 1H, C*H*$_2$=CH-), 5.76 (t, *J* = 7.8 Hz, 1H), 5.72 (d, *J* = 7.2 Hz, 1H, -O-C*H*$_2$-O-), 5.52 (d, *J* = 7.2 Hz, 1H, -O-C*H*$_2$-O-), 4.78 (t, *J* = 7.8 Hz, 1H), 4.69 (t, *J* = 7.8 Hz, 2H), 4.45 (d, *J* = 7.2

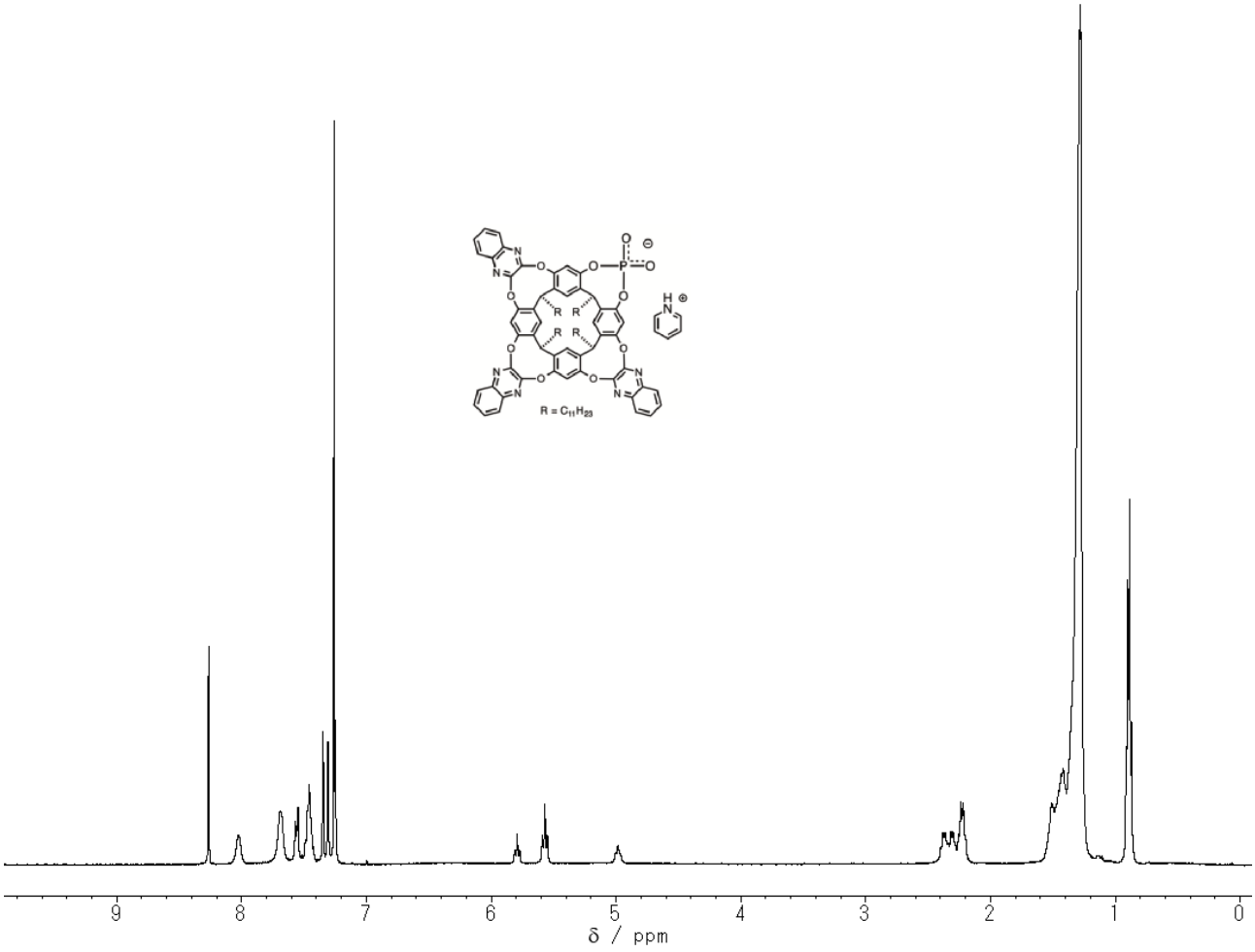
Hz, 1H, -O-C$\underline{H_2}$-O-), 4.44 (d, J = 7.2 Hz, 1H, -O-C$\underline{H_2}$-O-), 2.32-2.21 (m, 8H), 1.47-1.27 (m, 72H), 0.89-0.86 (m, 12H) ppm.

3. ^{1}H NMR and ^{13}C NMR and ^{31}P NMR spectra for all new compounds of **1**•C_5H_5N, **1**, **2**•C_5H_5N, **2**, **3**•C_5H_5N, **3**, **4**•C_5H_5N, **4**, **5**, **6**, and **7**.

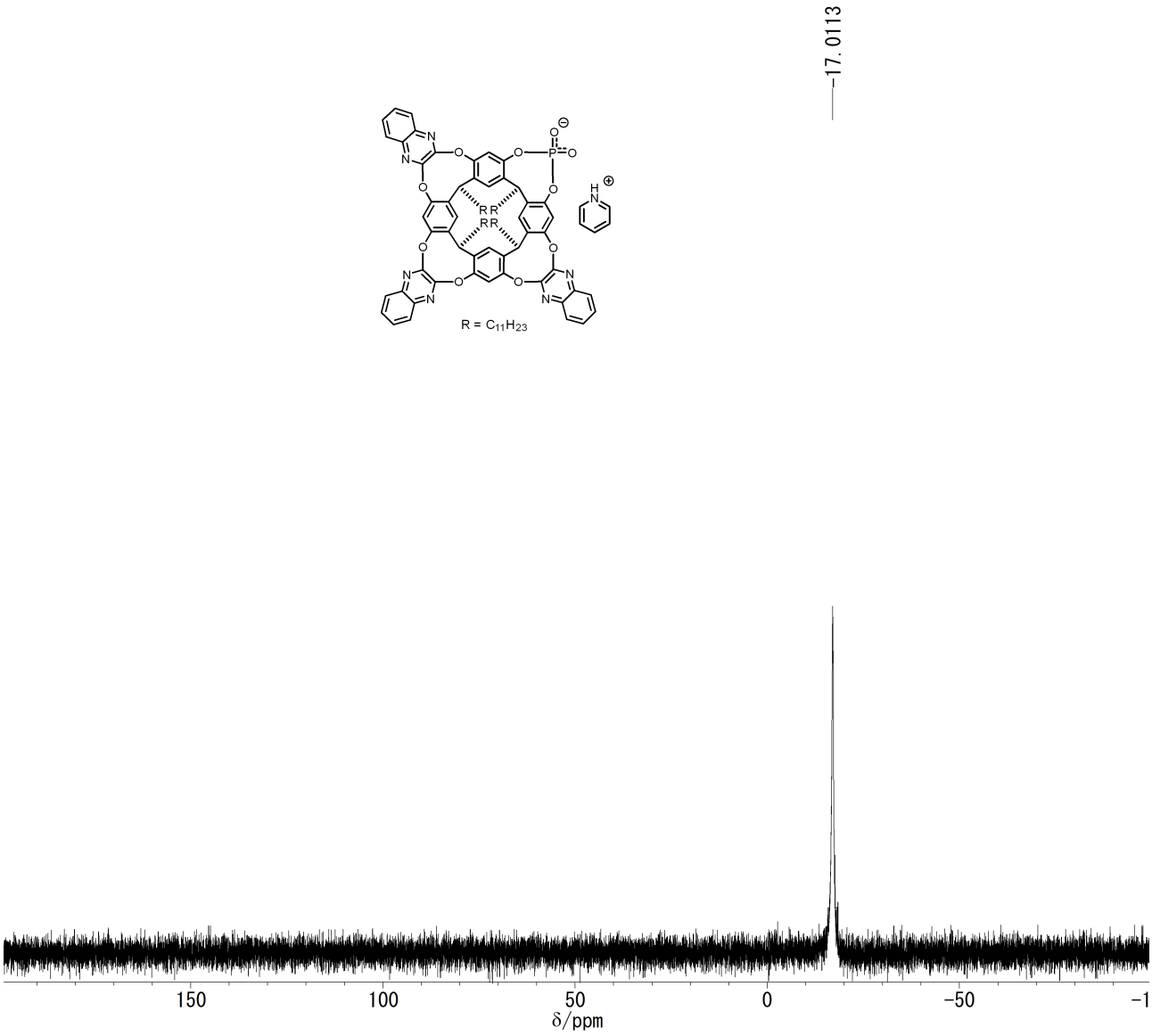
Compound **1**•C_5H_5N (^{1}H NMR spectrum in CD_2Cl_2)



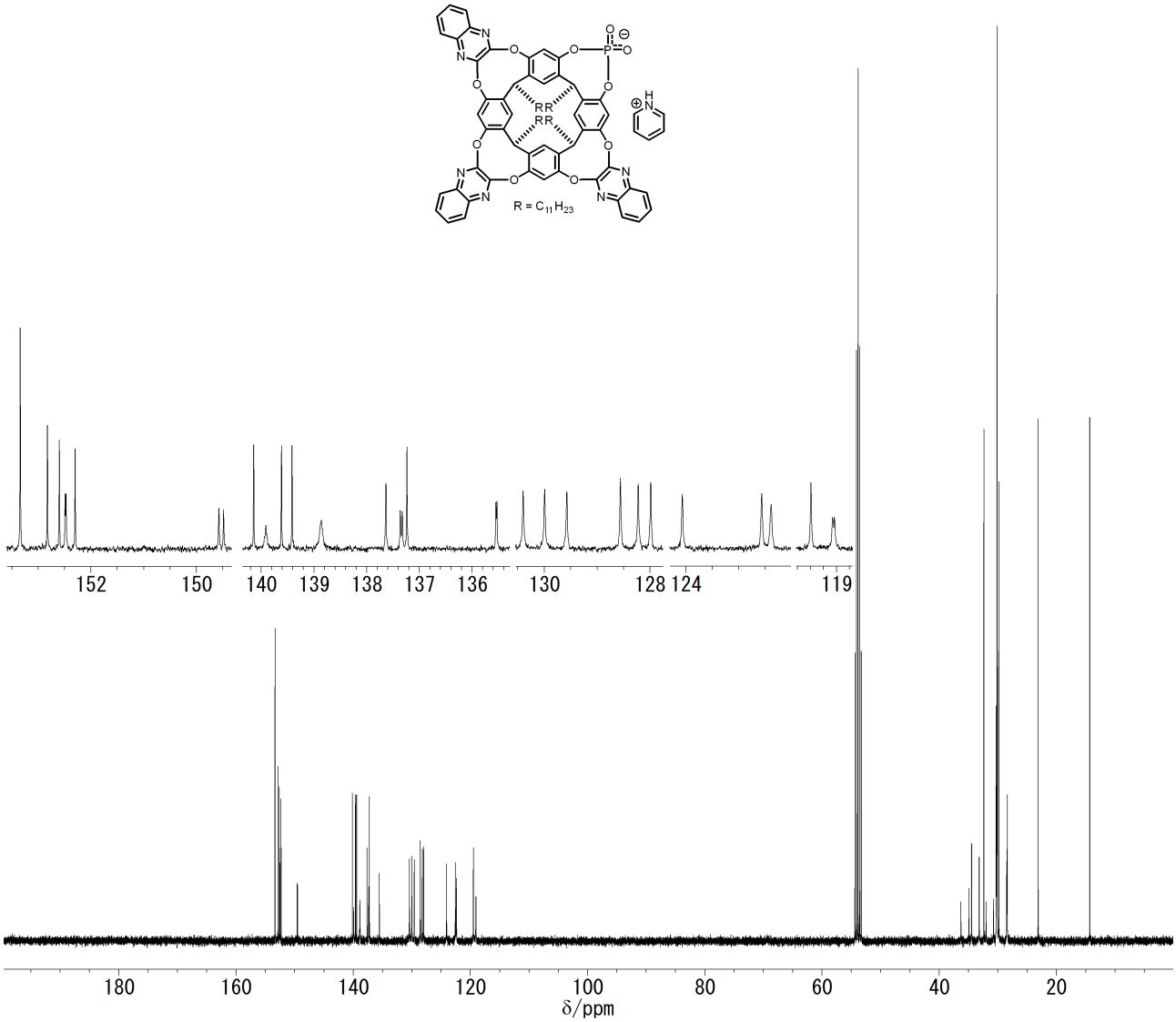
Compound **1**•C_5H_5N (^1H NMR spectrum in $CDCl_3$)



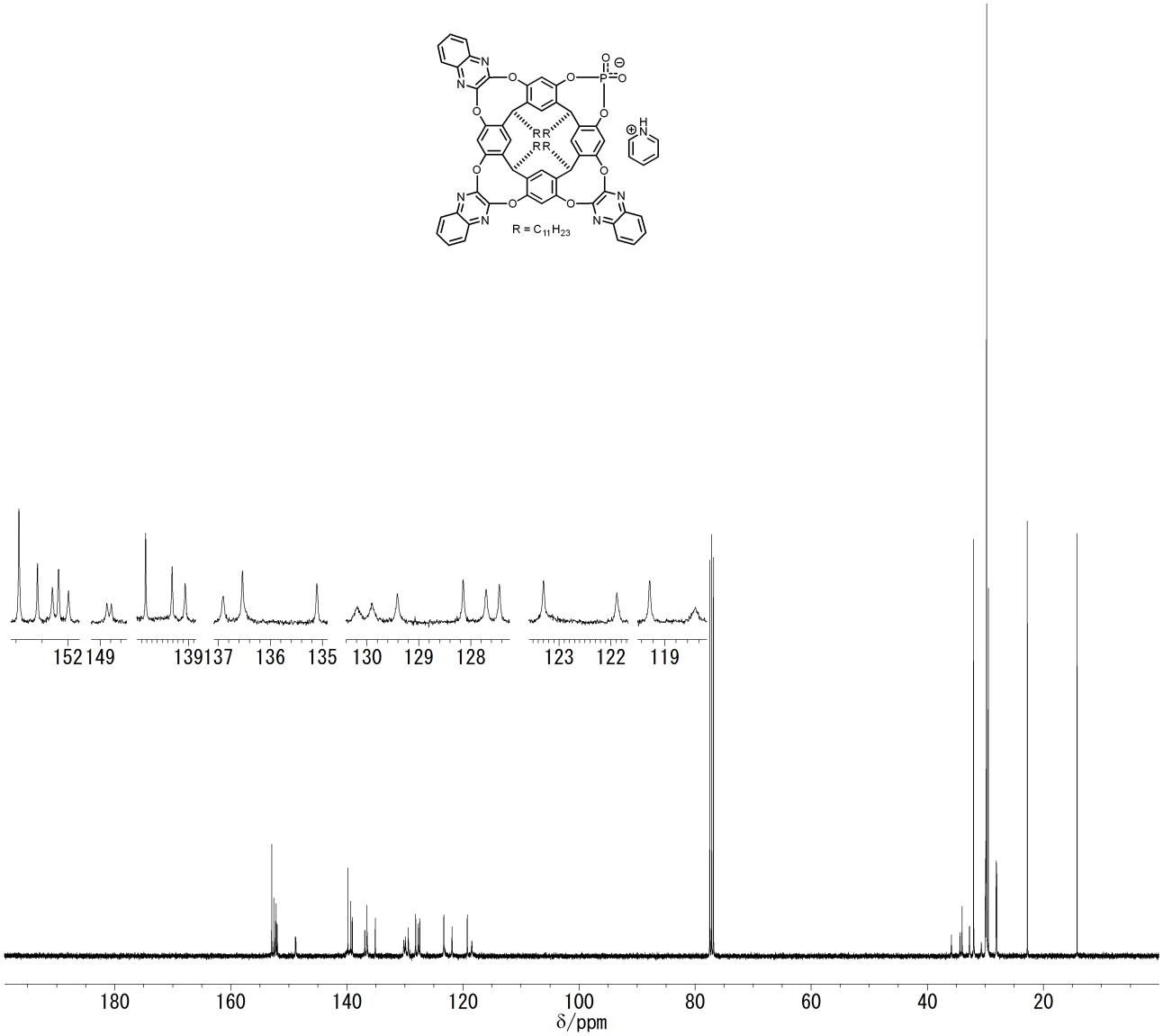
Compound **1**•C_5H_5N (^{31}P NMR spectrum in $CDCl_3$)



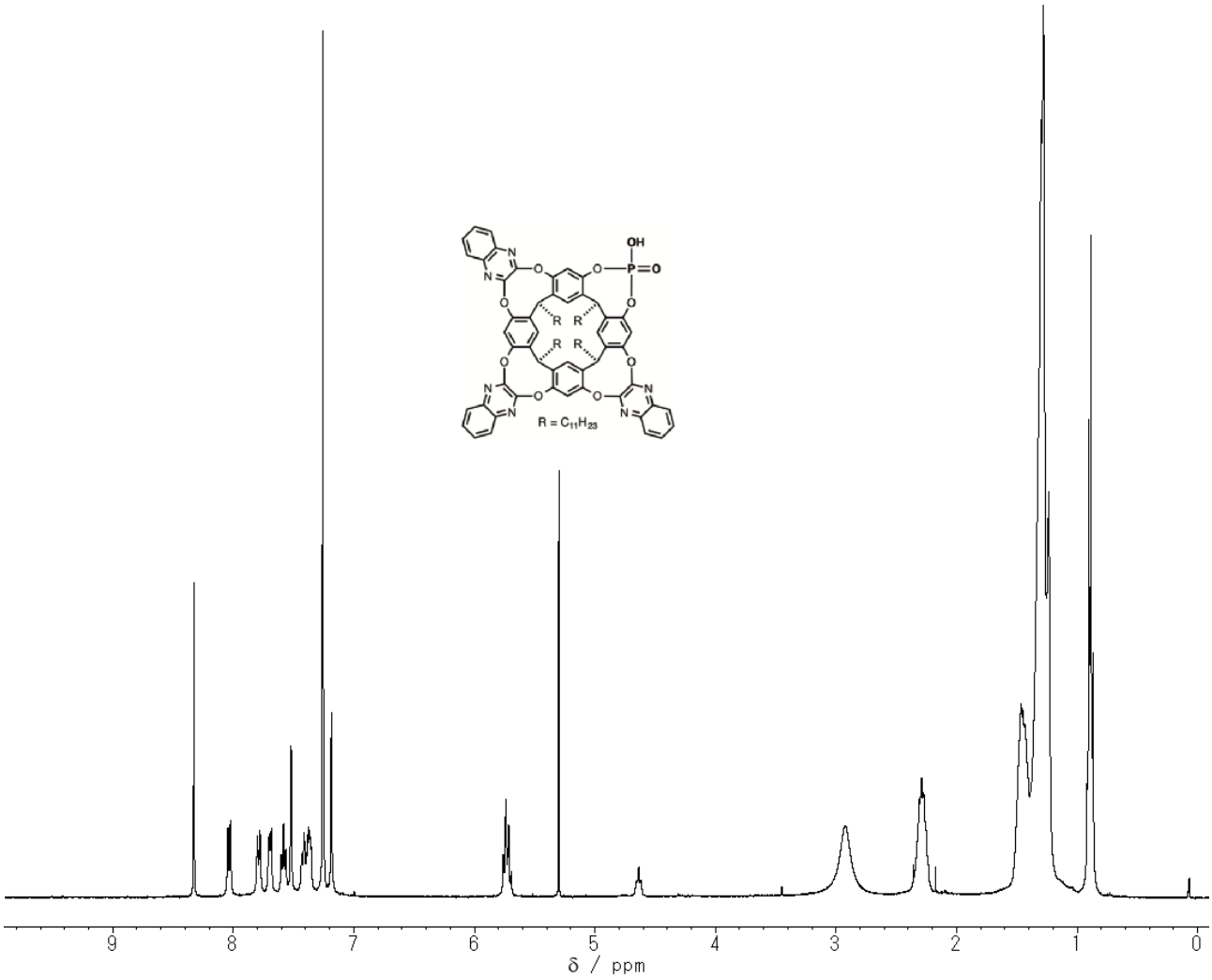
Compound **1**•C_5H_5N (^{13}C NMR spectrum in CD_2Cl_2)



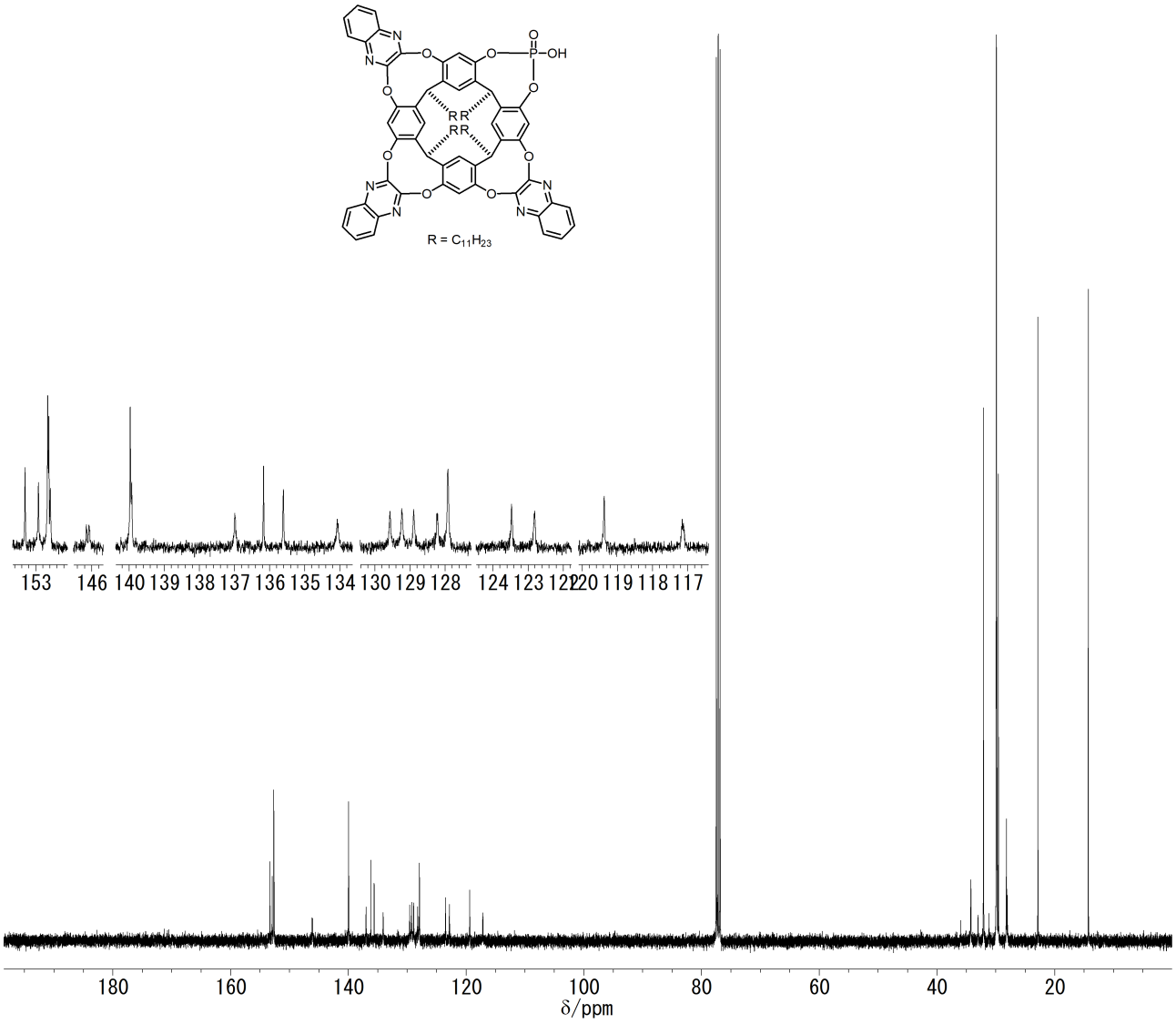
Compound **1**•C_5H_5N (^{13}C NMR spectrum in $CDCl_3$)



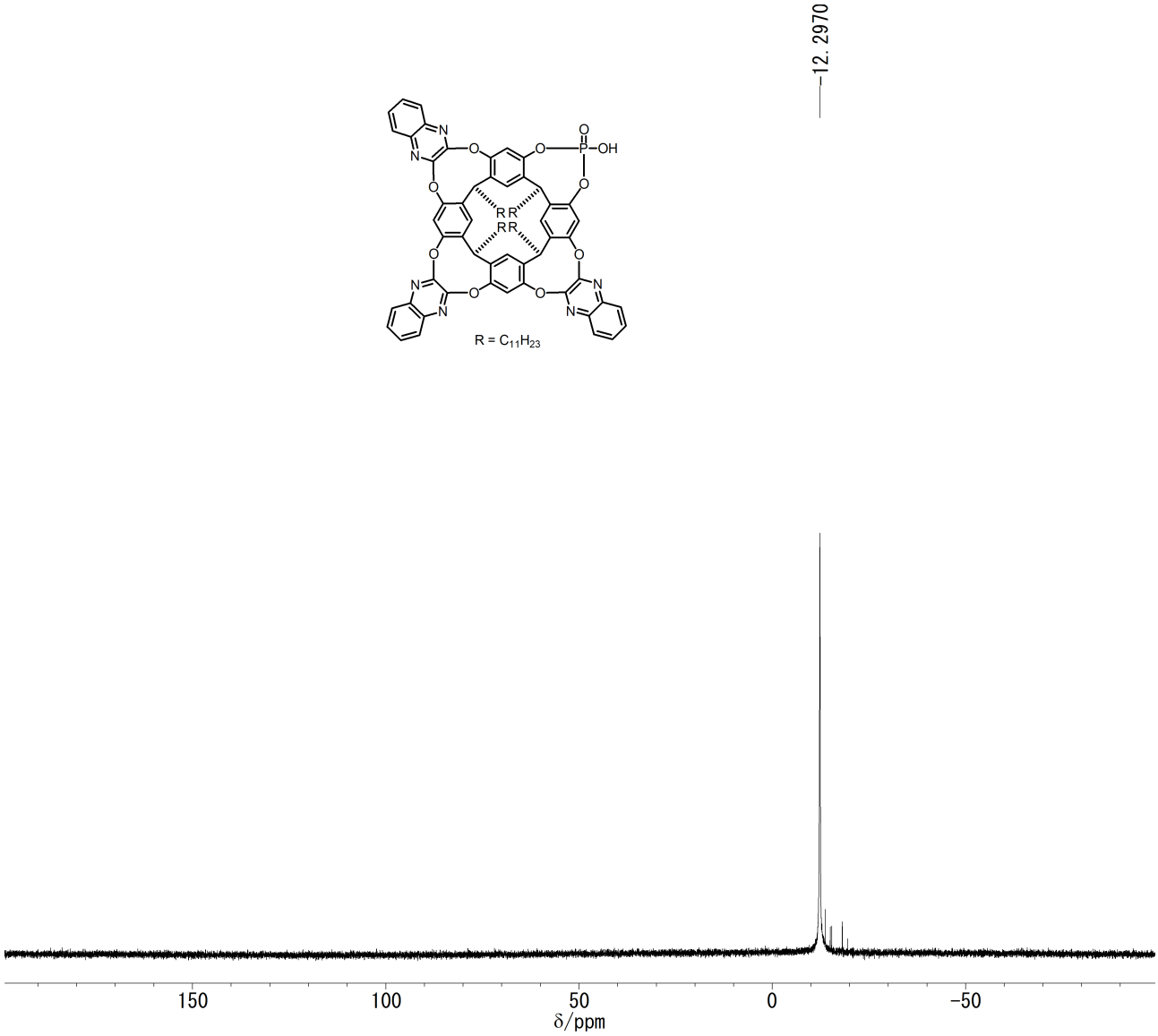
Compound free acid **1** (^{1}H NMR spectrum in $CDCl_3$)



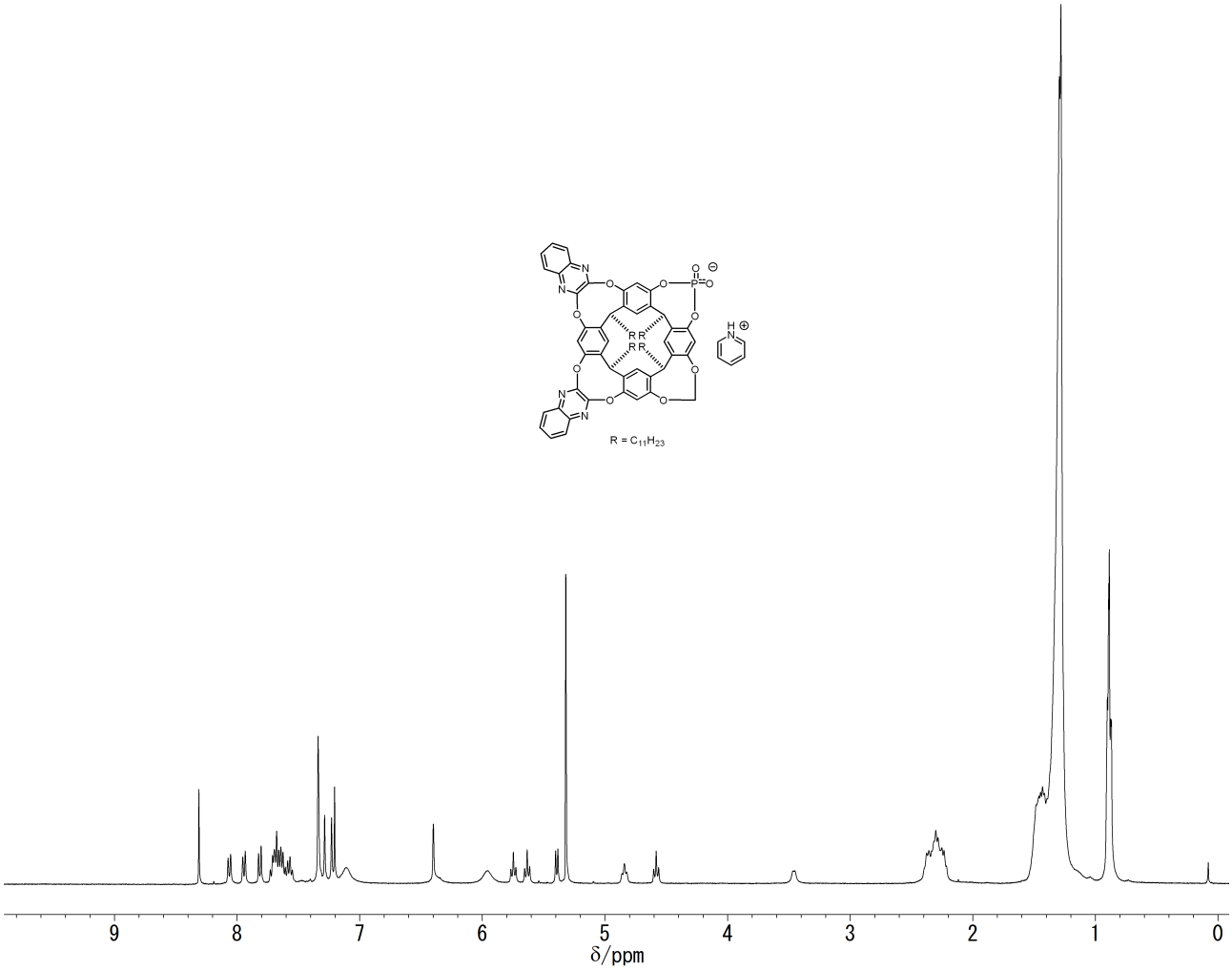
Compound free acid **1** (^{13}C NMR spectrum in $CDCl_3$)



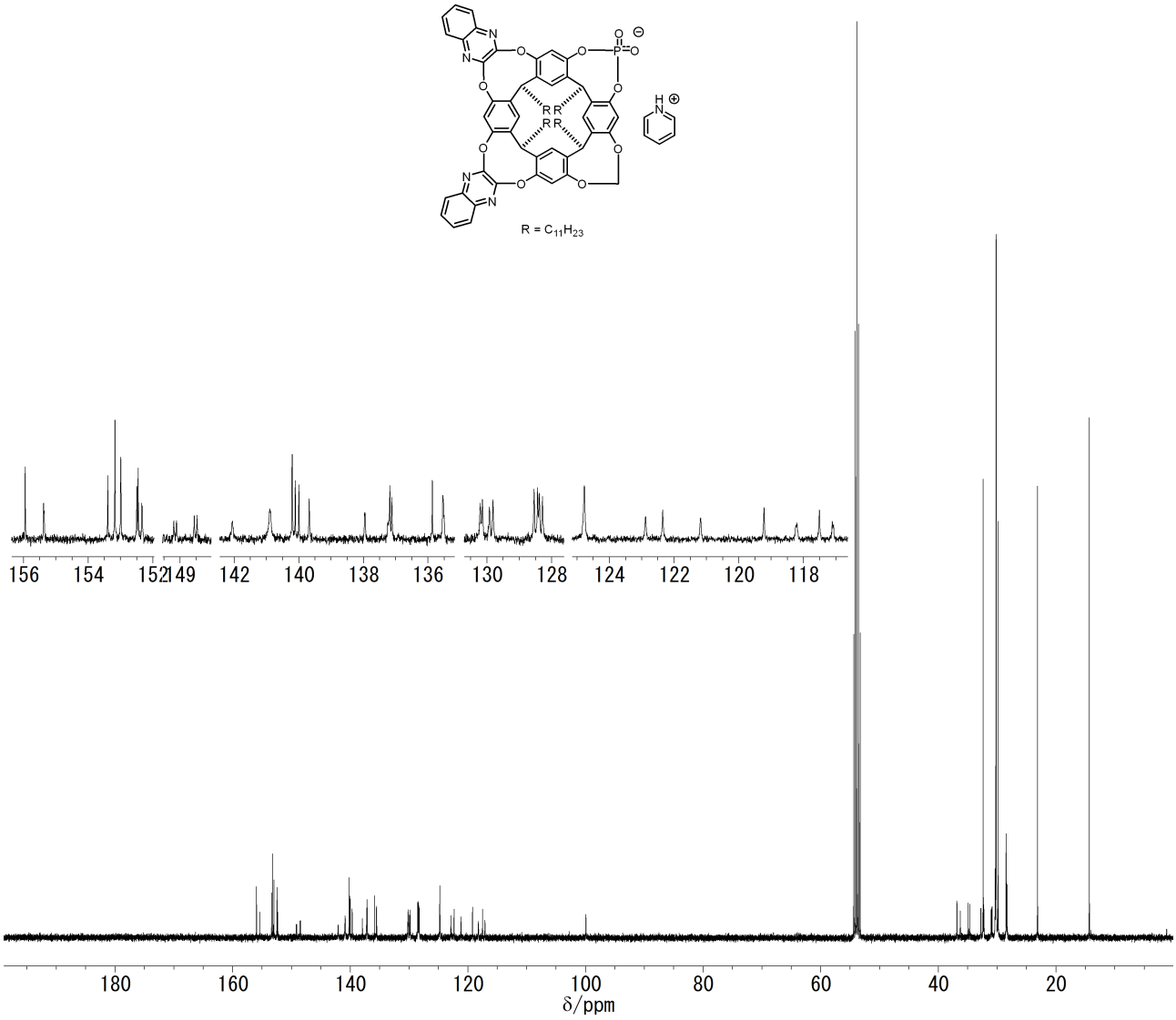
Compound free acid **1** (^{31}P NMR spectrum in $CDCl_3$)



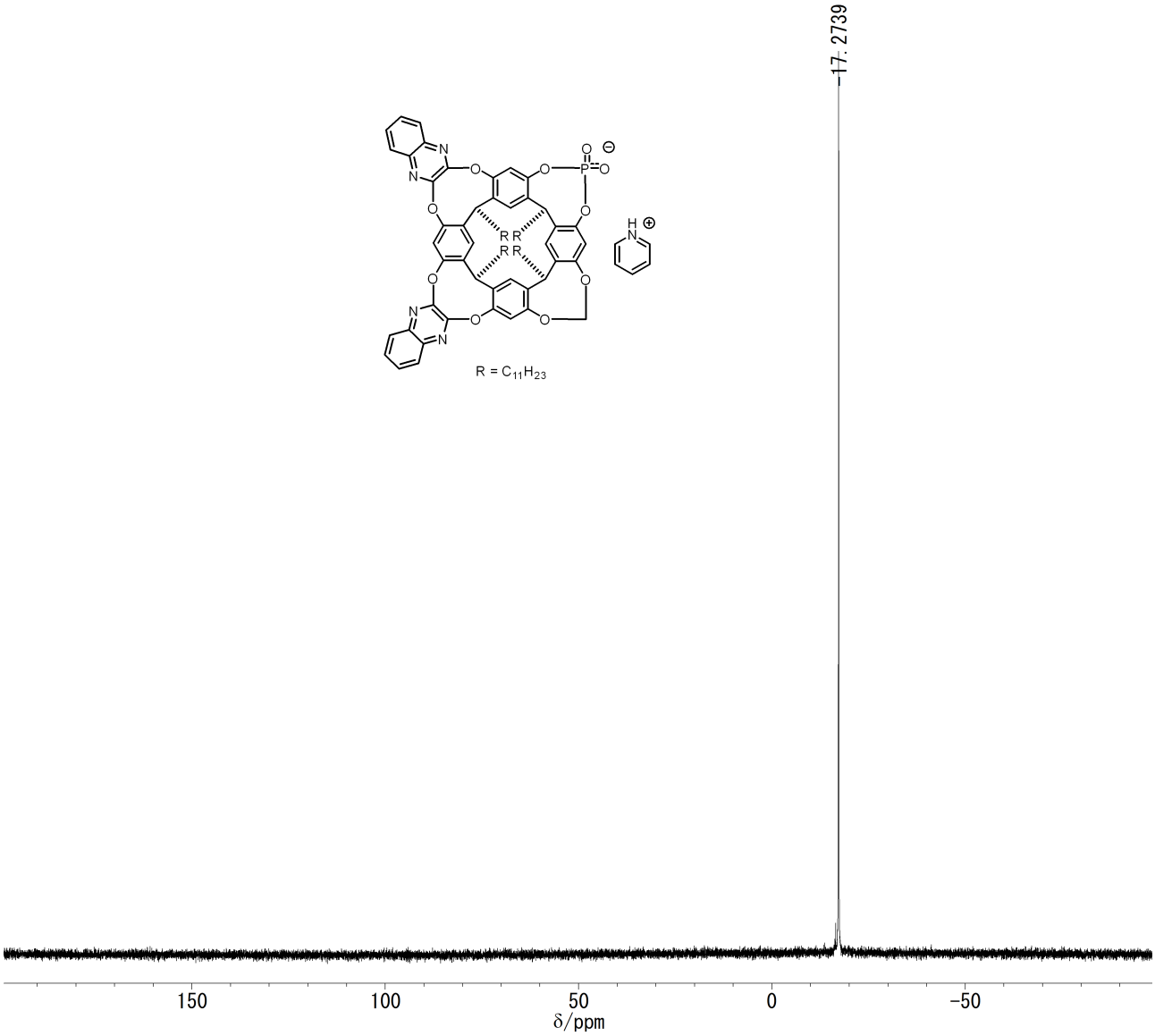
Compound **2**•C_5H_5N (^1H NMR spectrum in CD_2Cl_2)



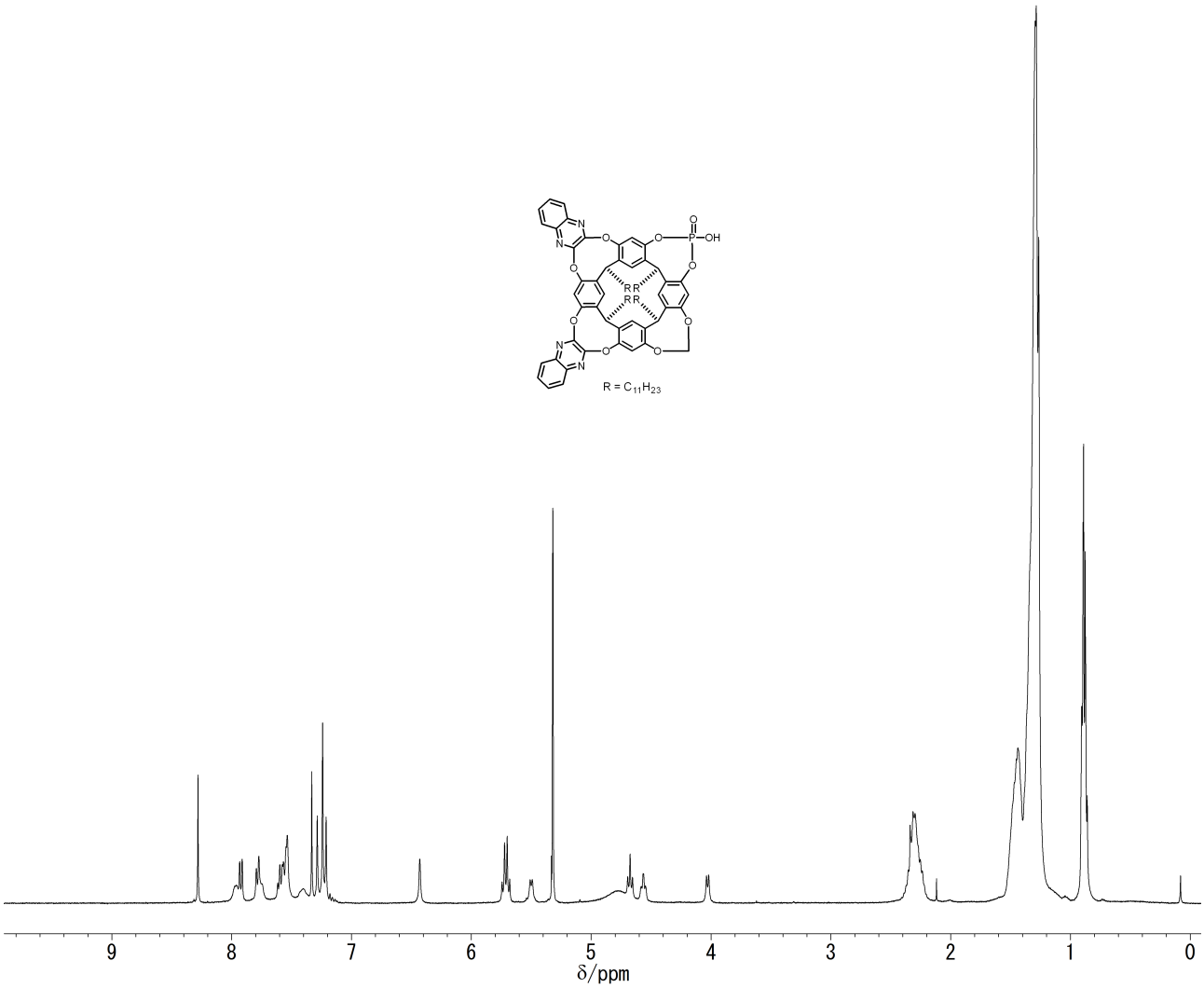
Compound **2**•C_5H_5N (^{13}C NMR spectrum in CD_2Cl_2)



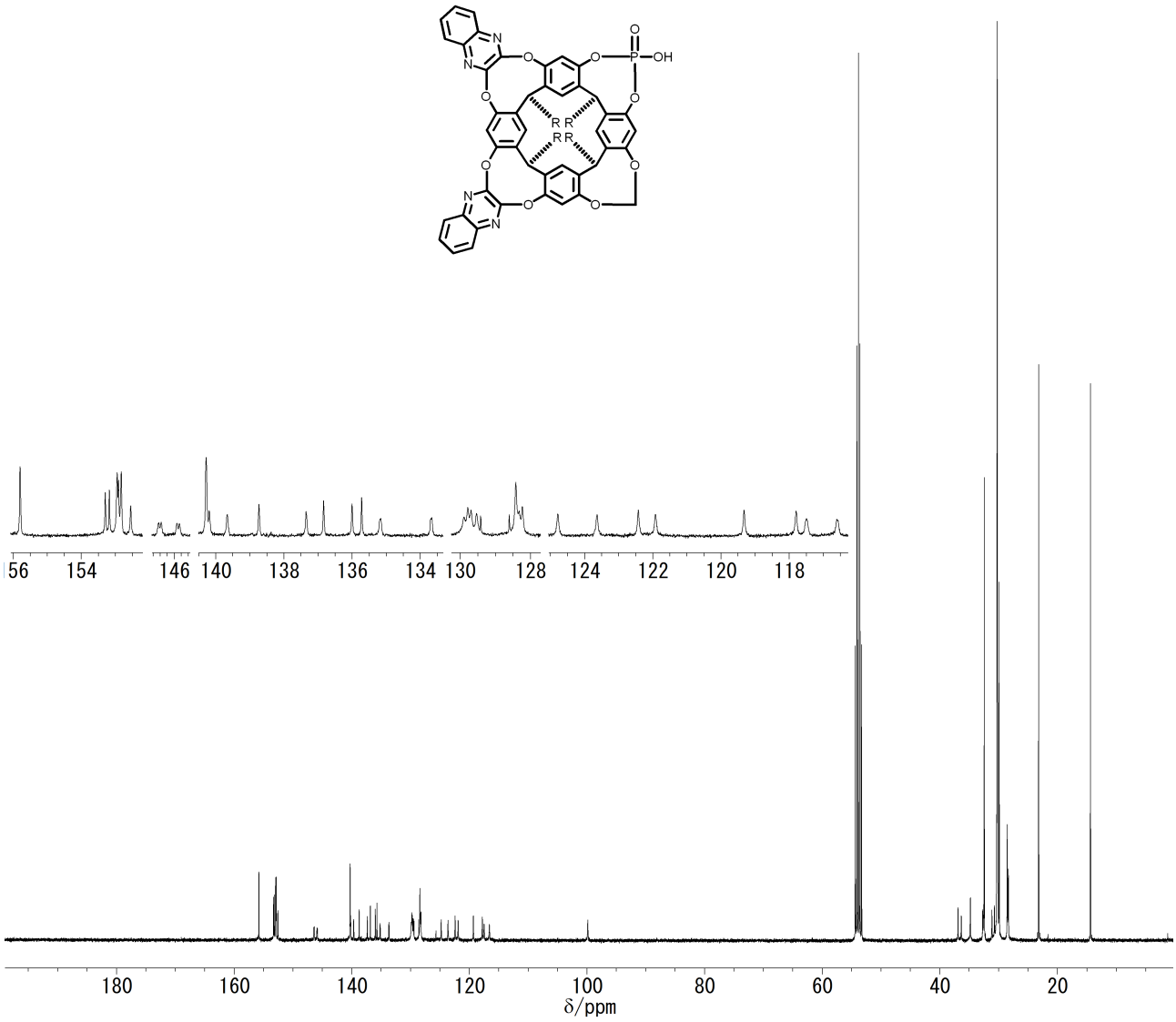
Compound **2**•C_5H_5N (^{31}P NMR spectrum in CD_2Cl_2)



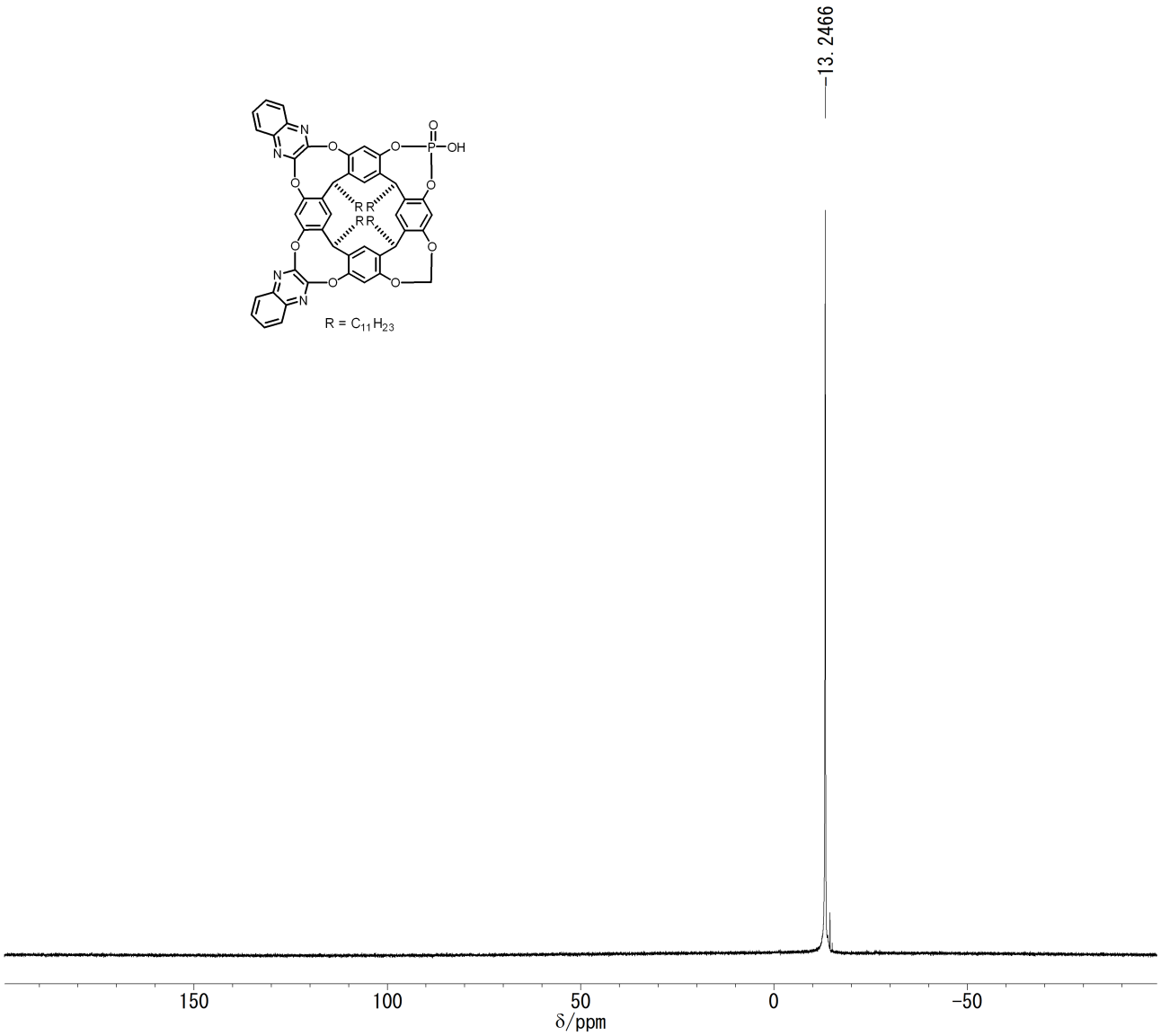
Compound free acid **2** (^{1}H NMR spectrum in CD_2Cl_2)



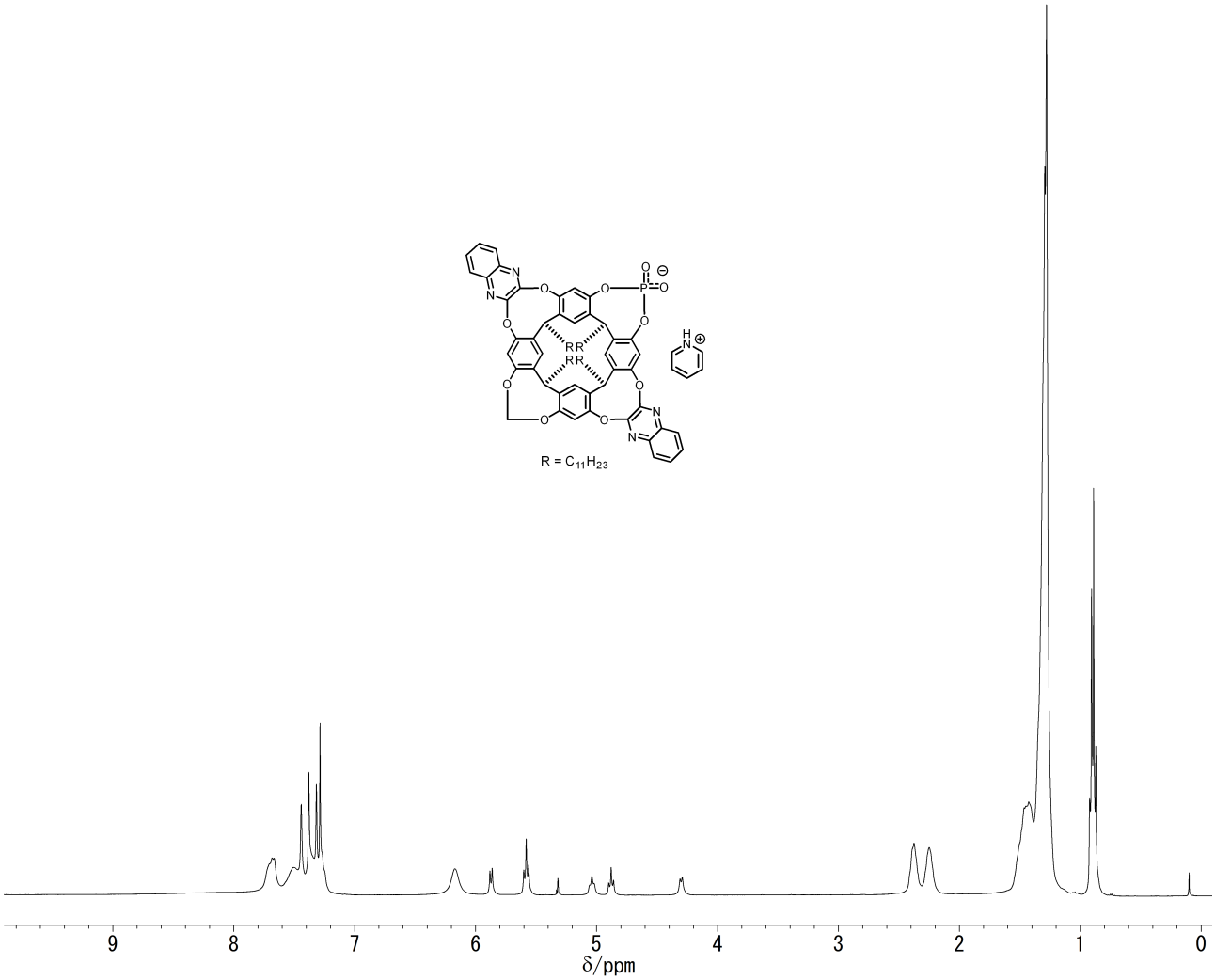
Compound free acid **2** (^{13}C NMR spectrum in CD_2Cl_2)



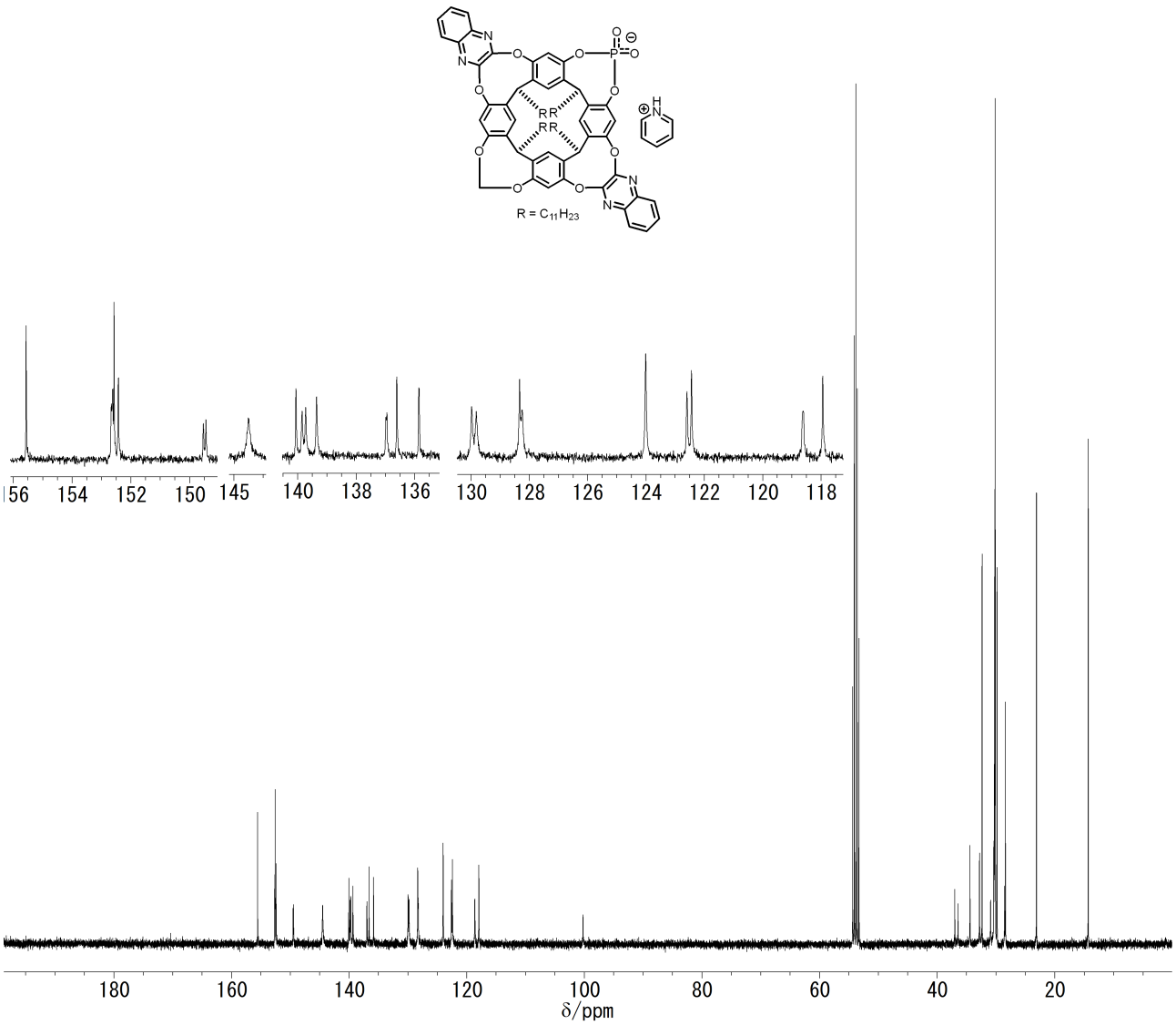
Compound free acid **2** (^{31}P NMR spectrum in CD_2Cl_2)



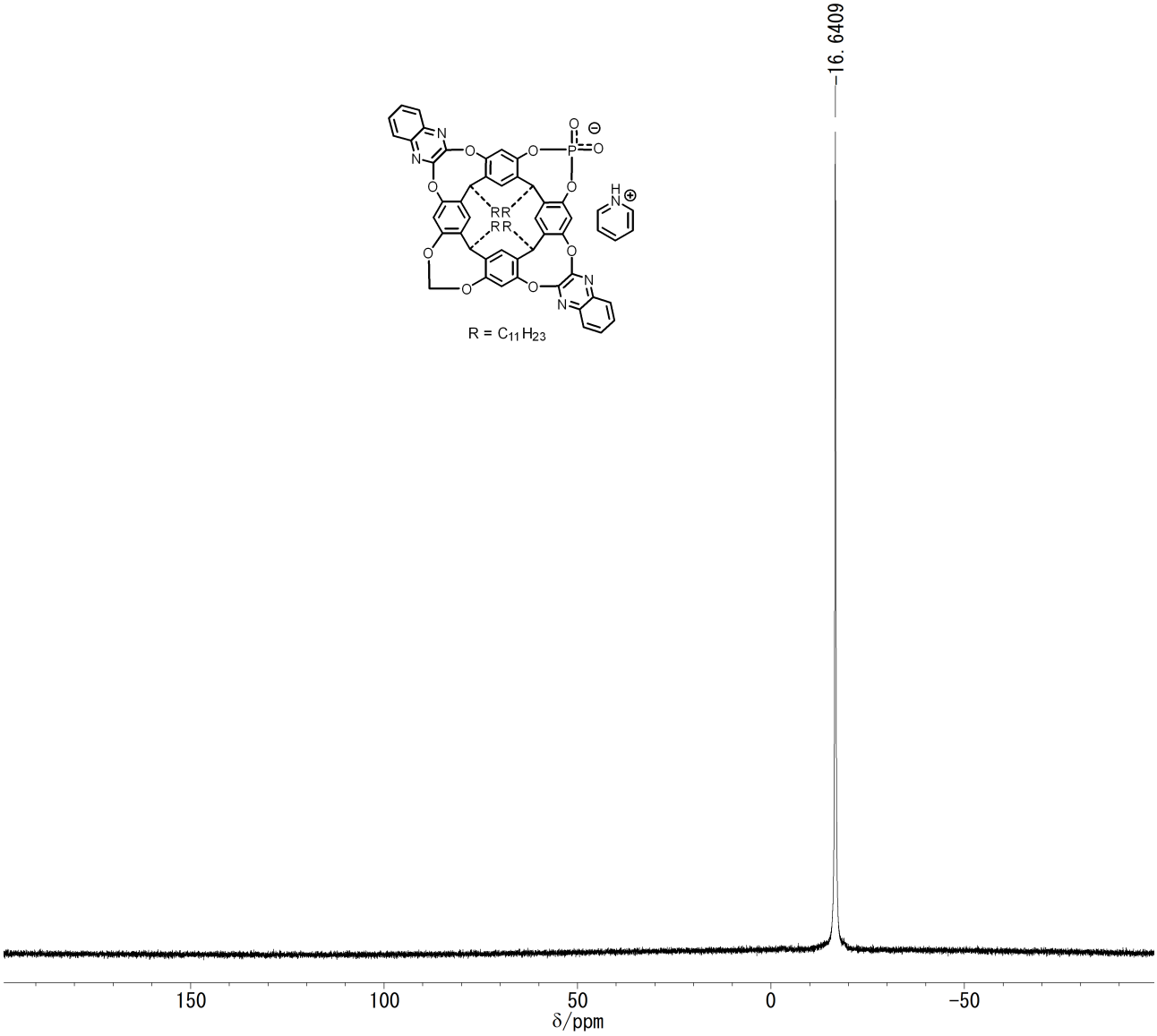
Compound **3**•C_5H_5N (^{1}H NMR spectrum in CD_2Cl_2)



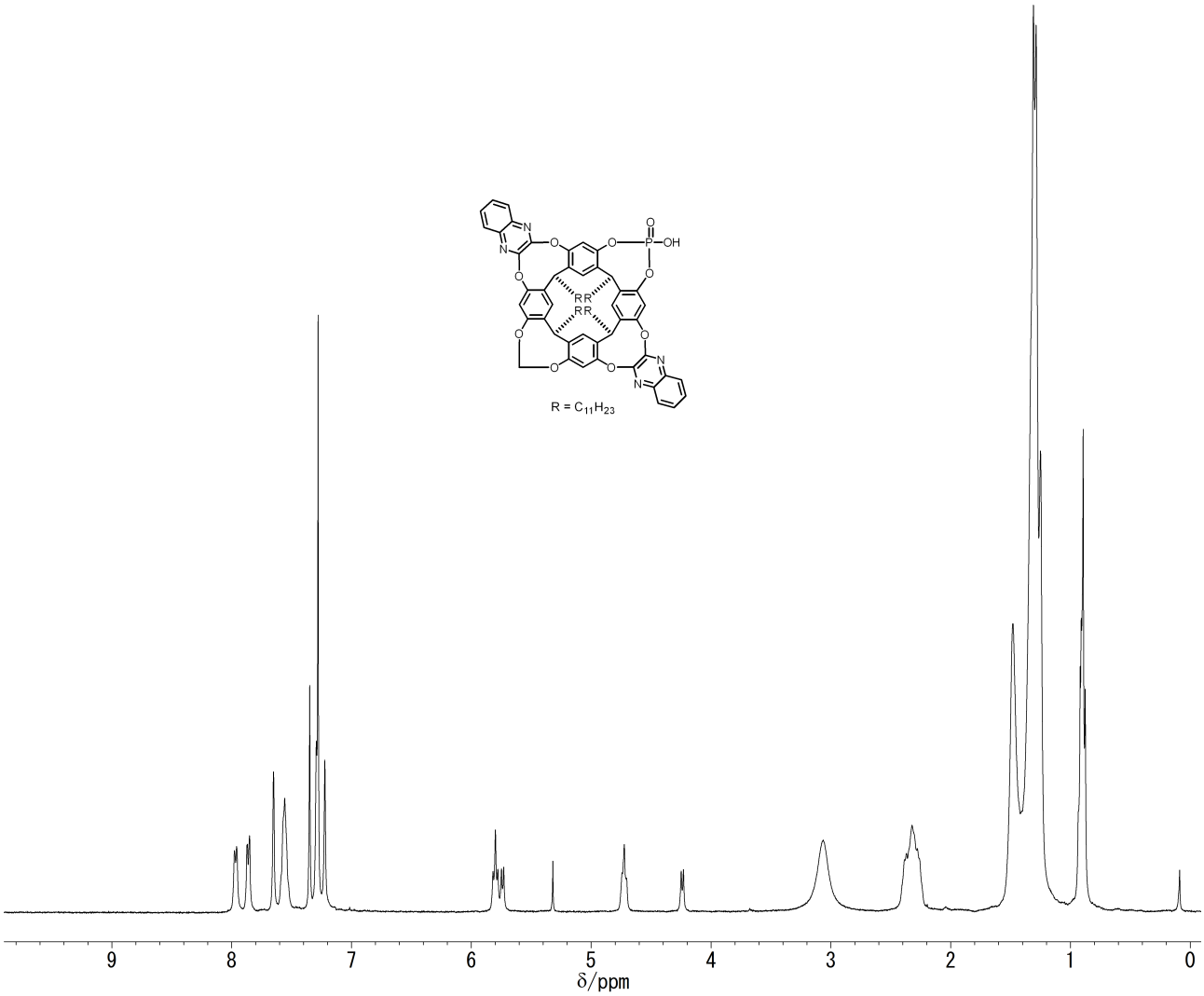
Compound **3**•C_5H_5N (^{13}C NMR spectrum in CD_2Cl_2)



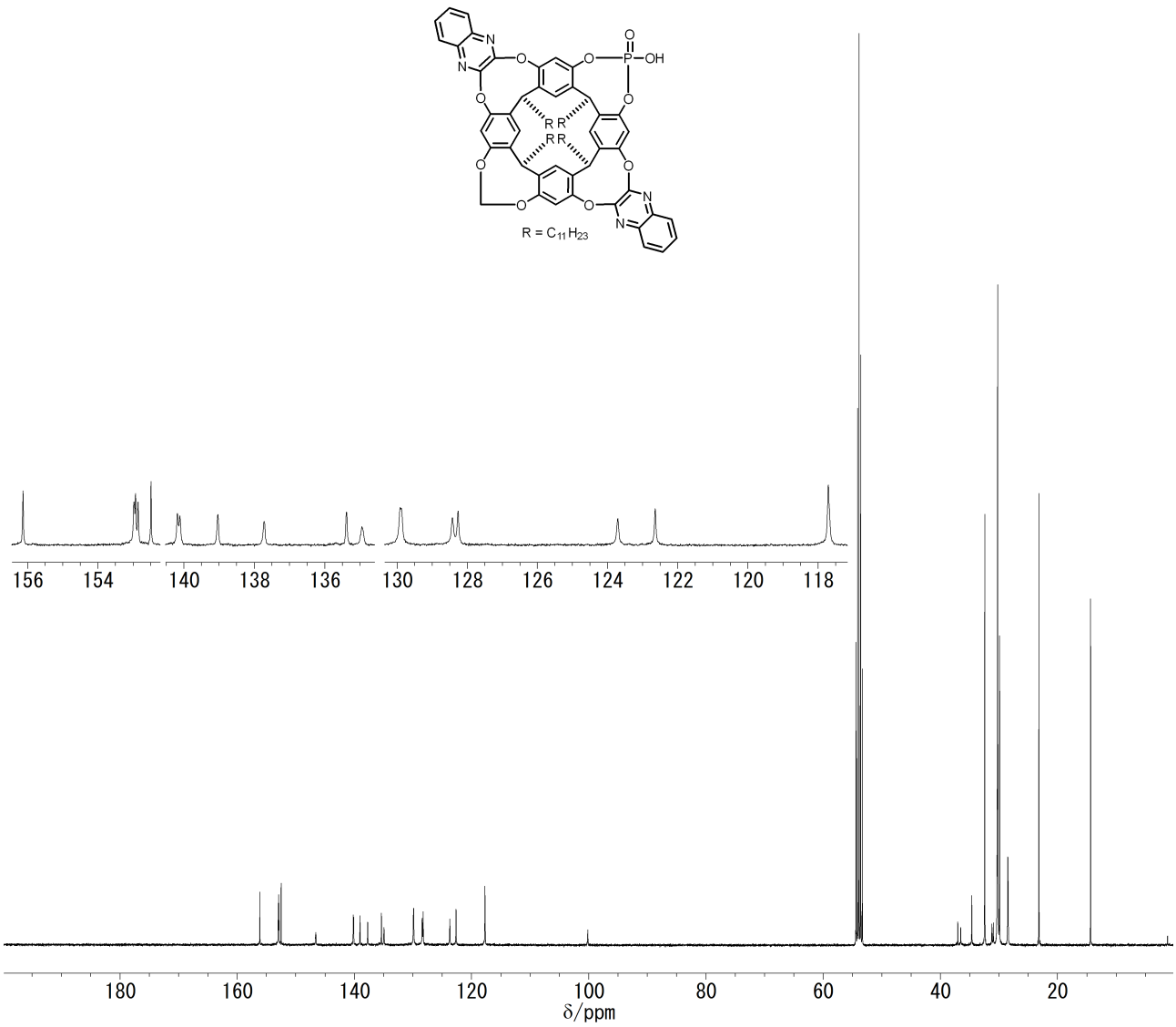
Compound **3**•C_5H_5N (^{31}P NMR spectrum in CD_2Cl_2)



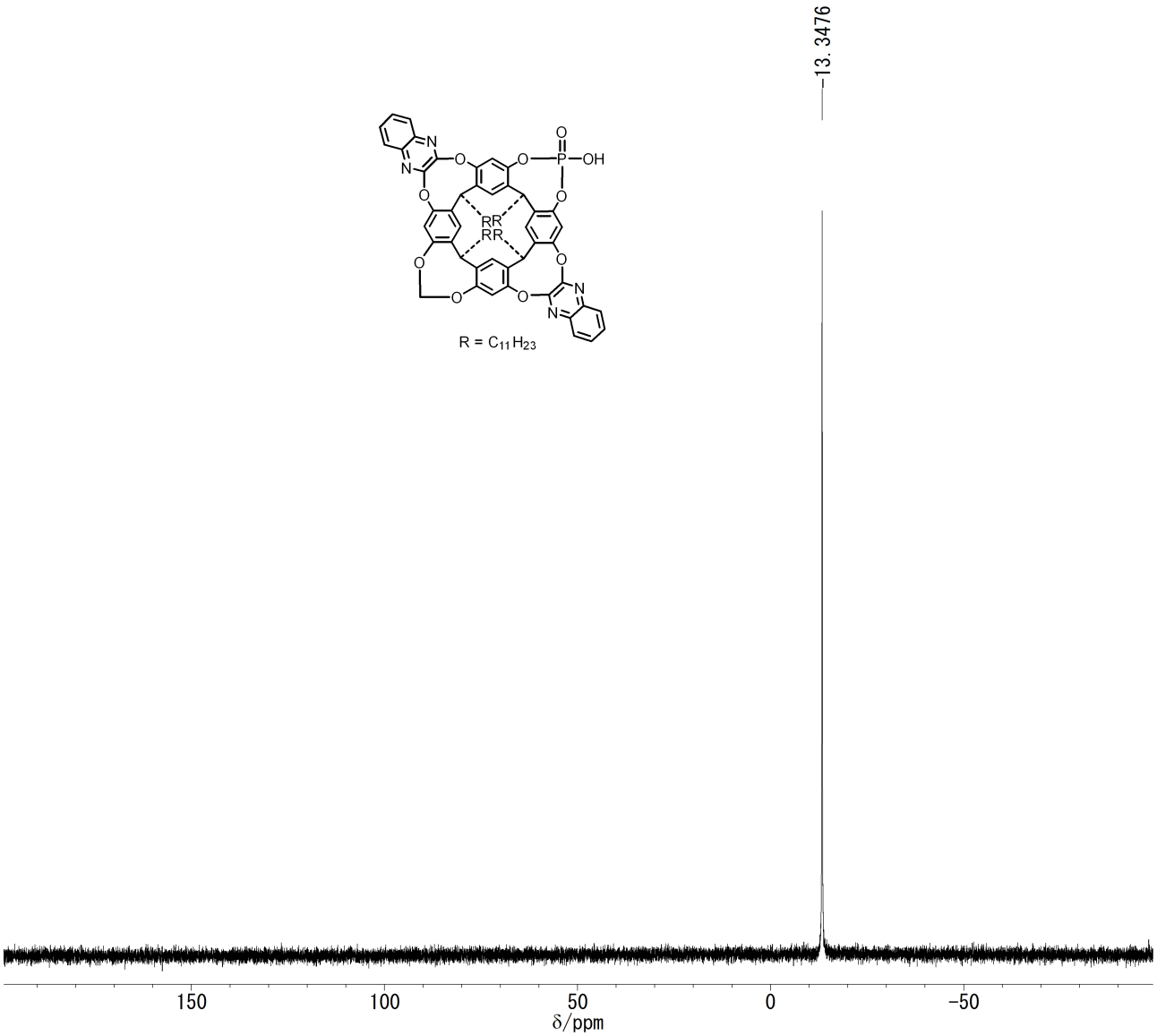
Compound free acid **3** (^{1}H NMR spectrum in CD_2Cl_2)



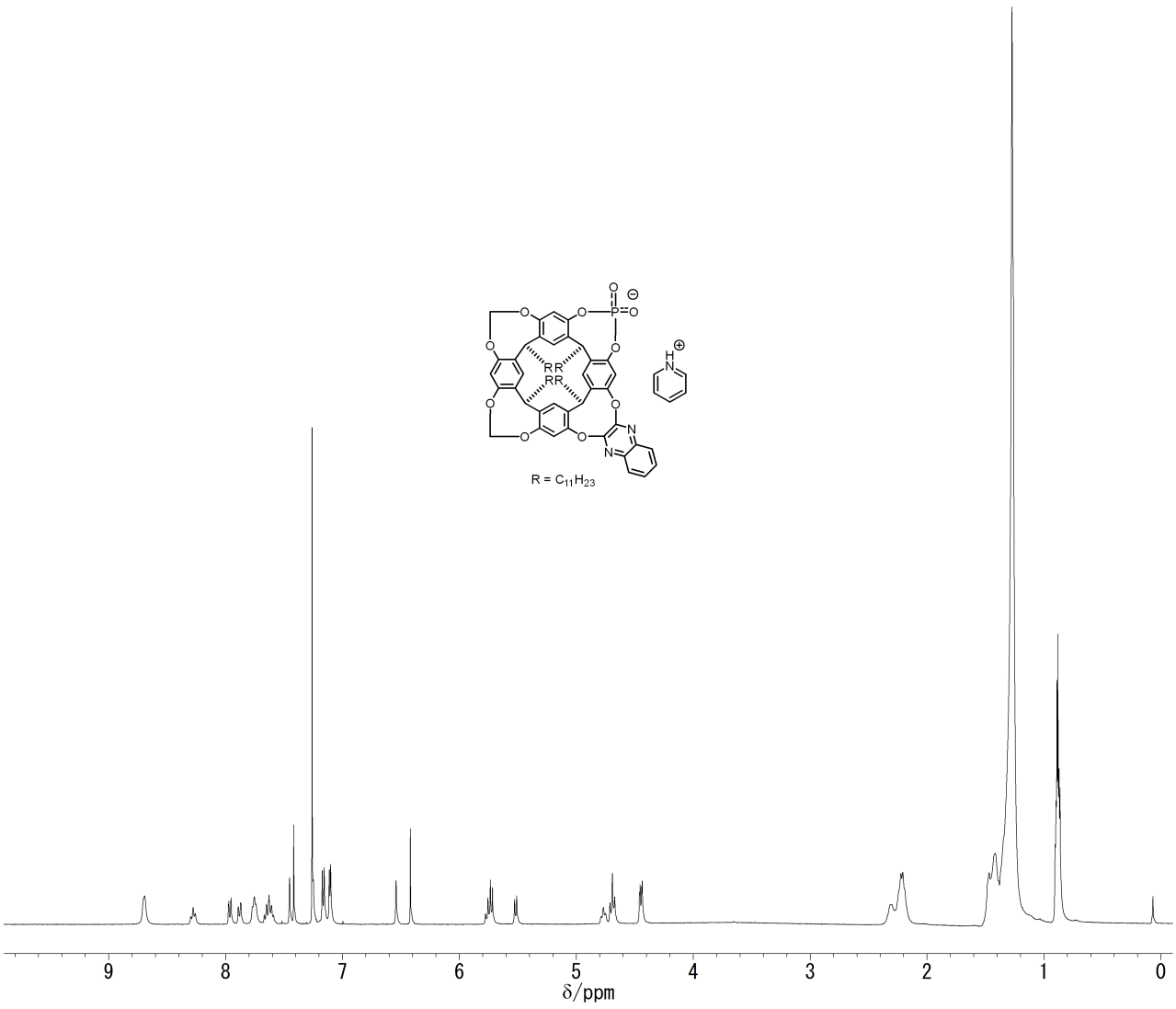
Compound free acid **3** (^{13}C NMR spectrum in CD_2Cl_2)



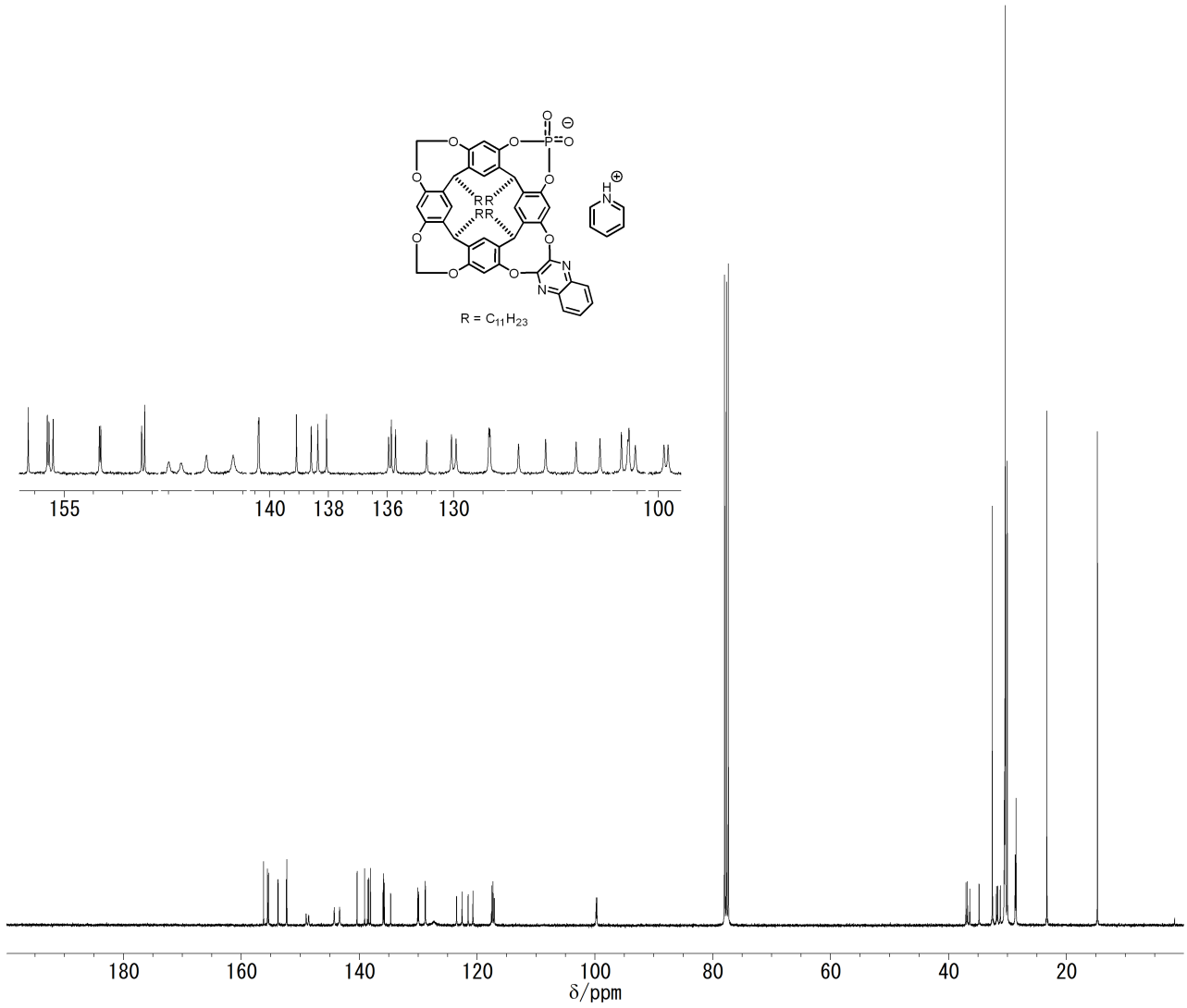
Compound free acid **3** (^{31}P NMR spectrum in CD_2Cl_2)



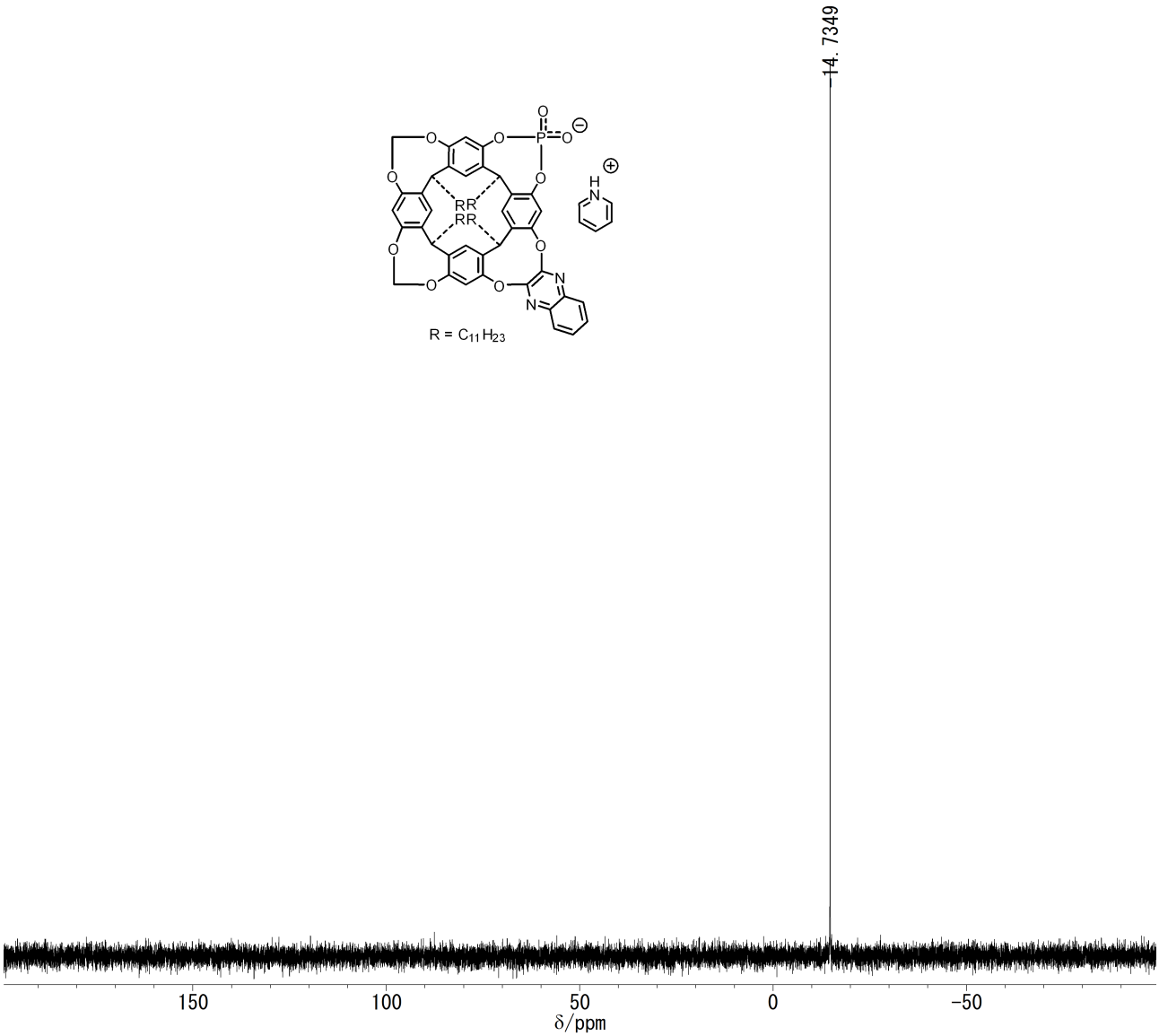
Compound **4**•C_5H_5N (^{1}H NMR spectrum in $CDCl_3$)



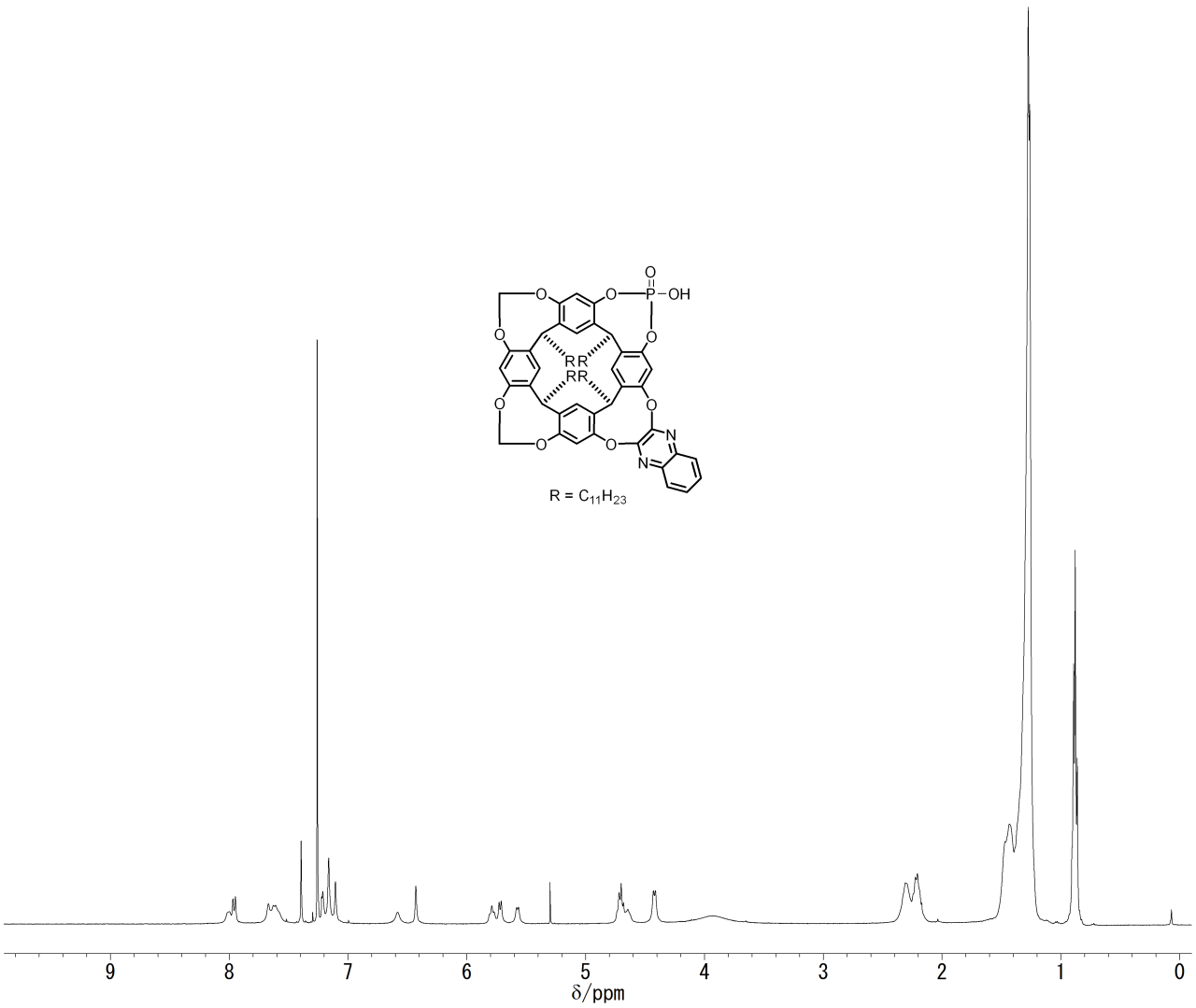
Compound **4** •C_5H_5N(^{13}C NMR spectrum in $CDCl_3$)



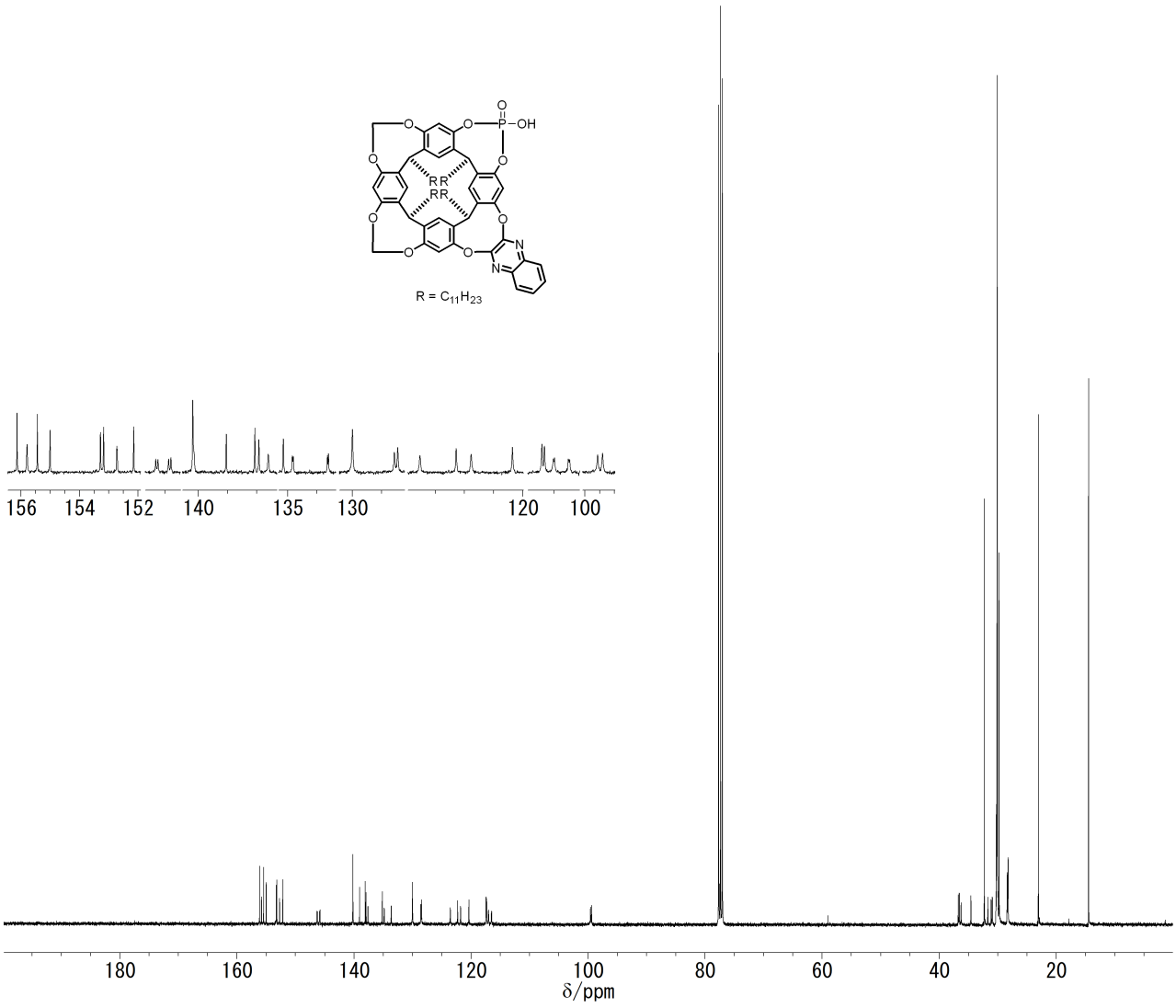
Compound **4**•C_5H_5N (^{31}P NMR spectrum in $CDCl_3$)



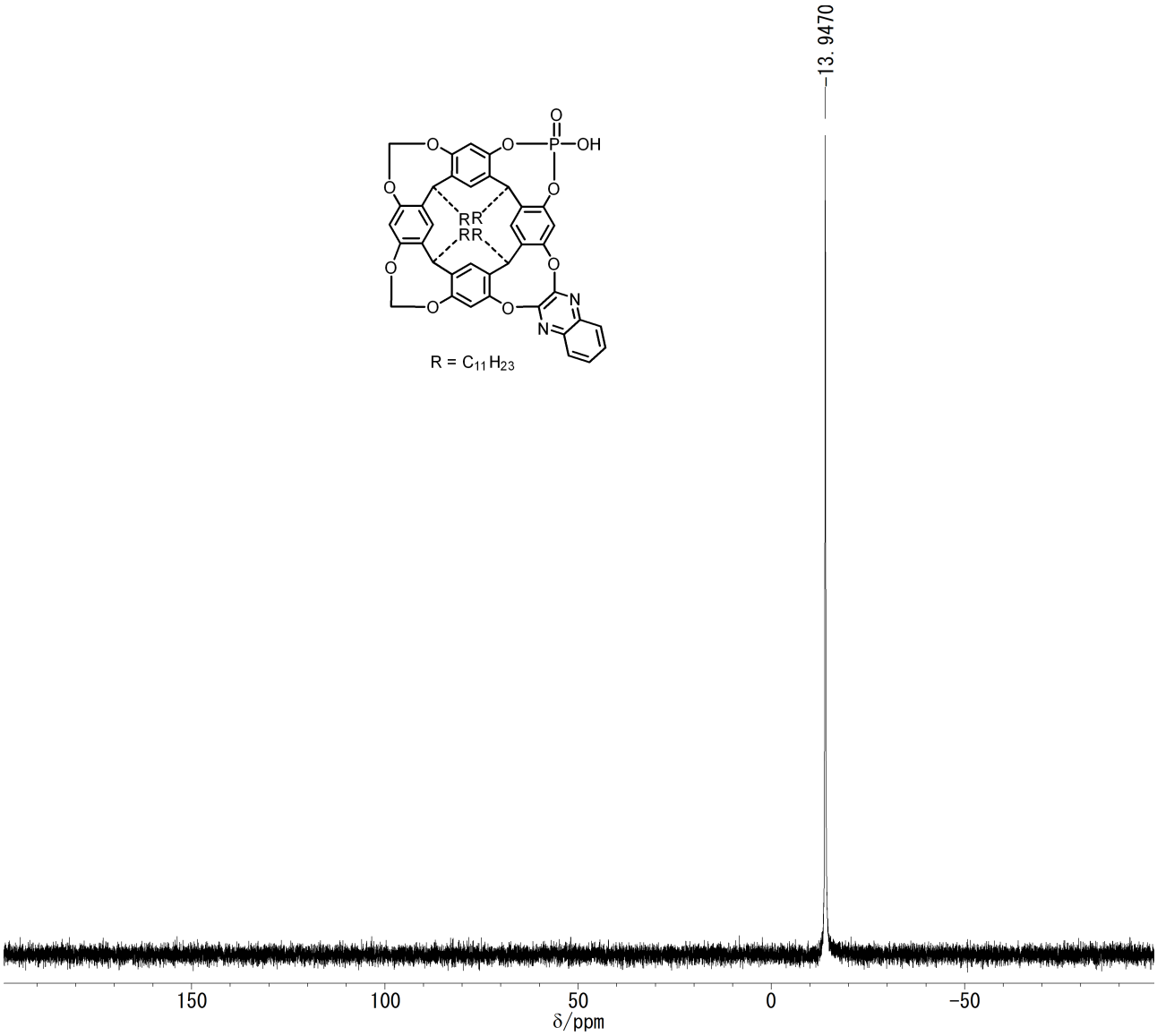
Compound free acid **4** (^{1}H NMR spectrum in $CDCl_3$)



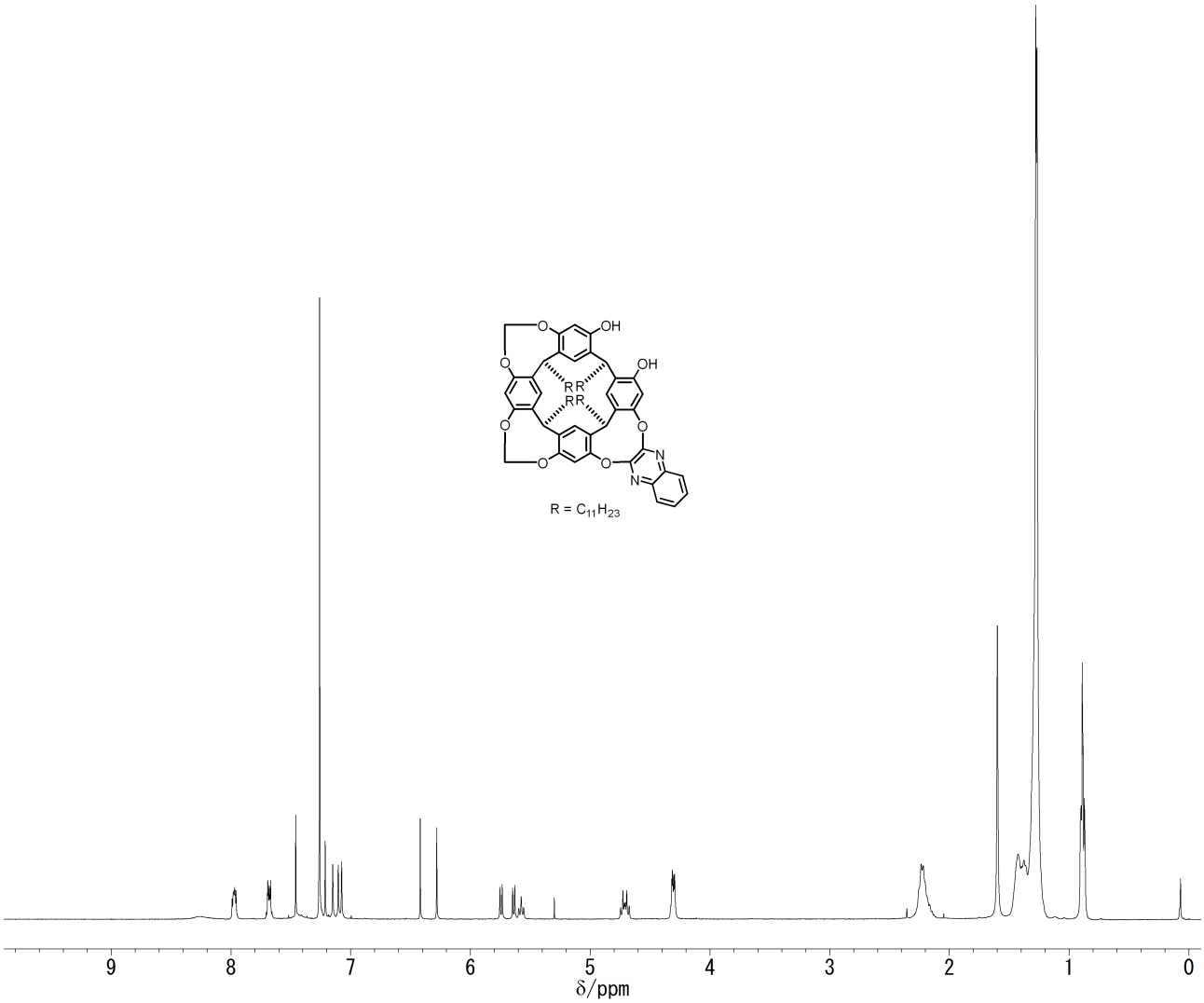
Compound free acid **4** (^{13}C NMR spectrum in $CDCl_3$)



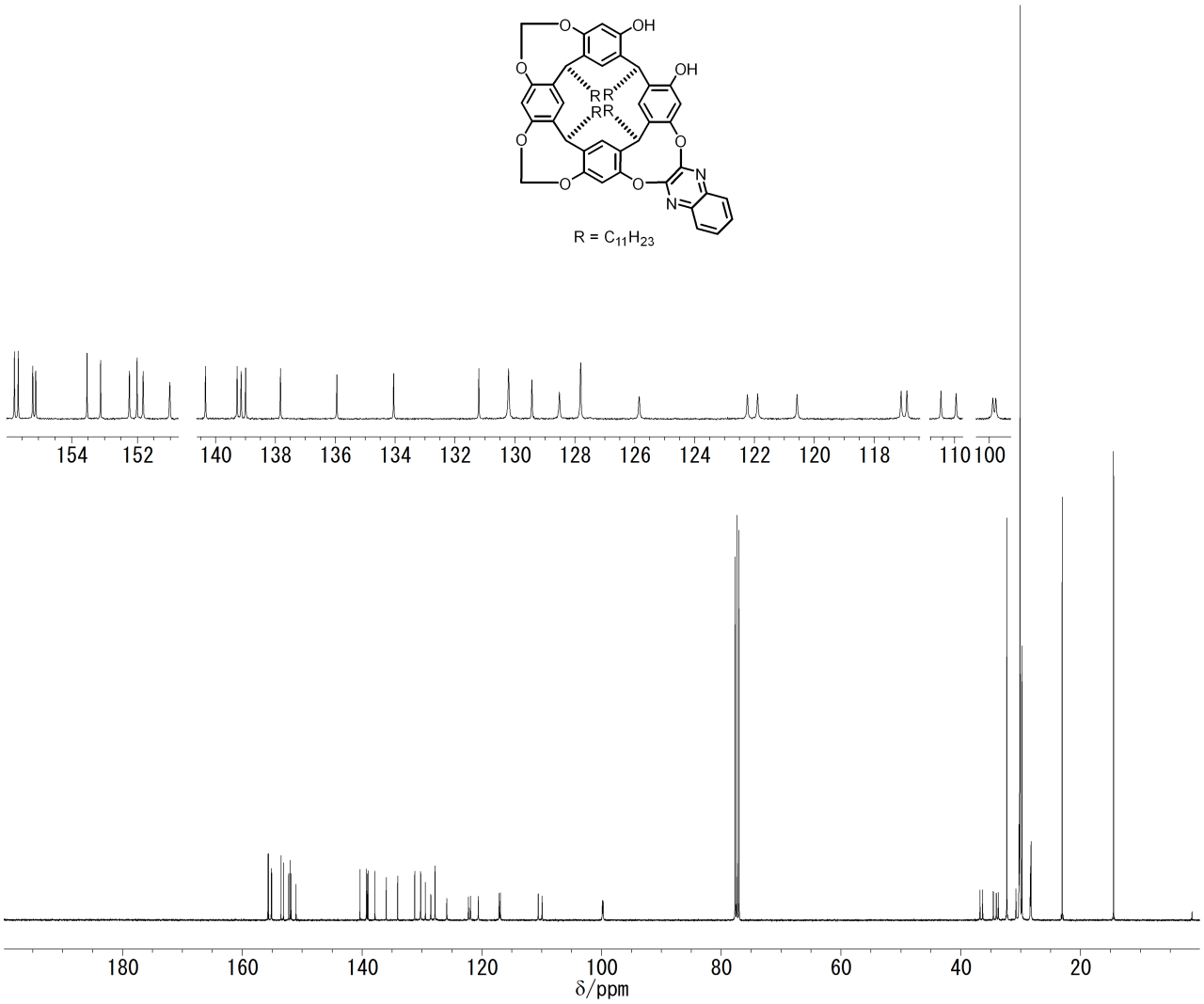
Compound free acid **4** (^{31}P NMR spectrum in $CDCl_3$)



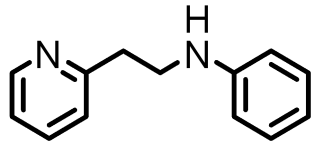
Compound **5** (^{1}H NMR spectrum in $CDCl_3$)

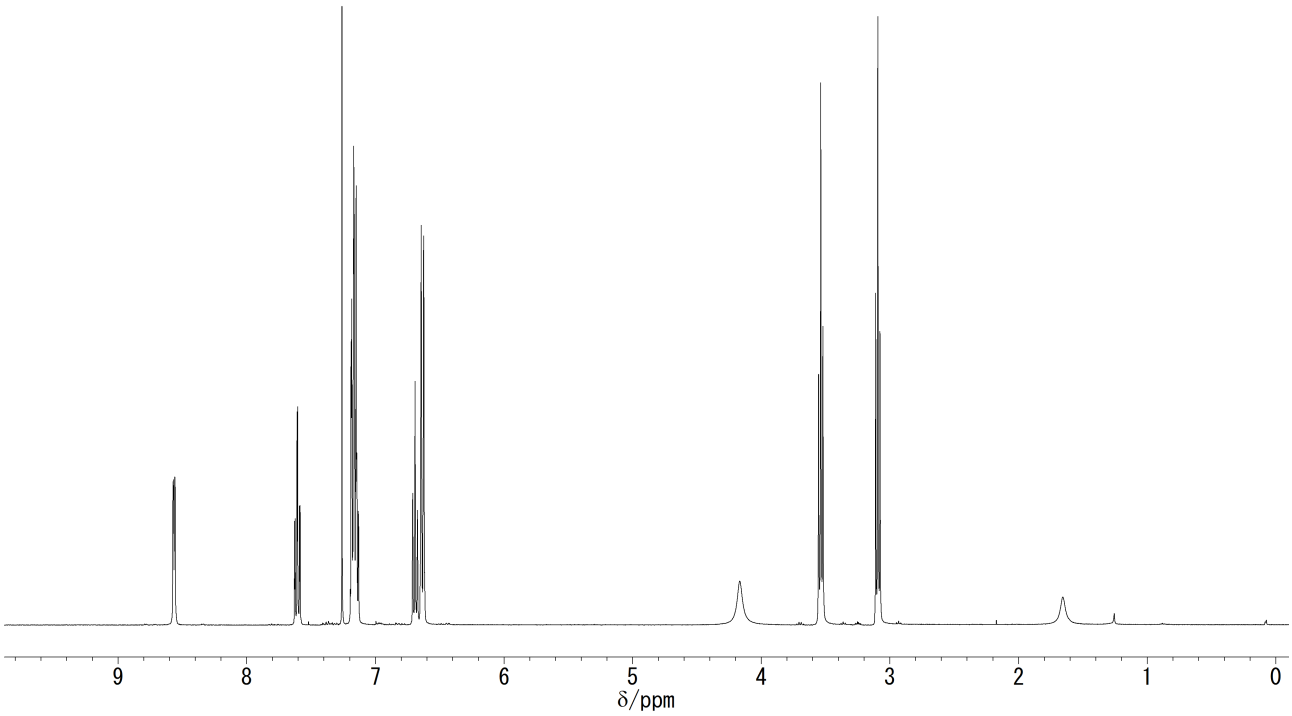


Compound **5** (^{13}C NMR spectrum in $CDCl_3$)

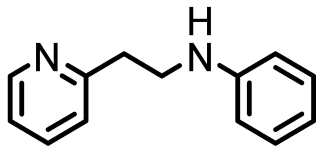


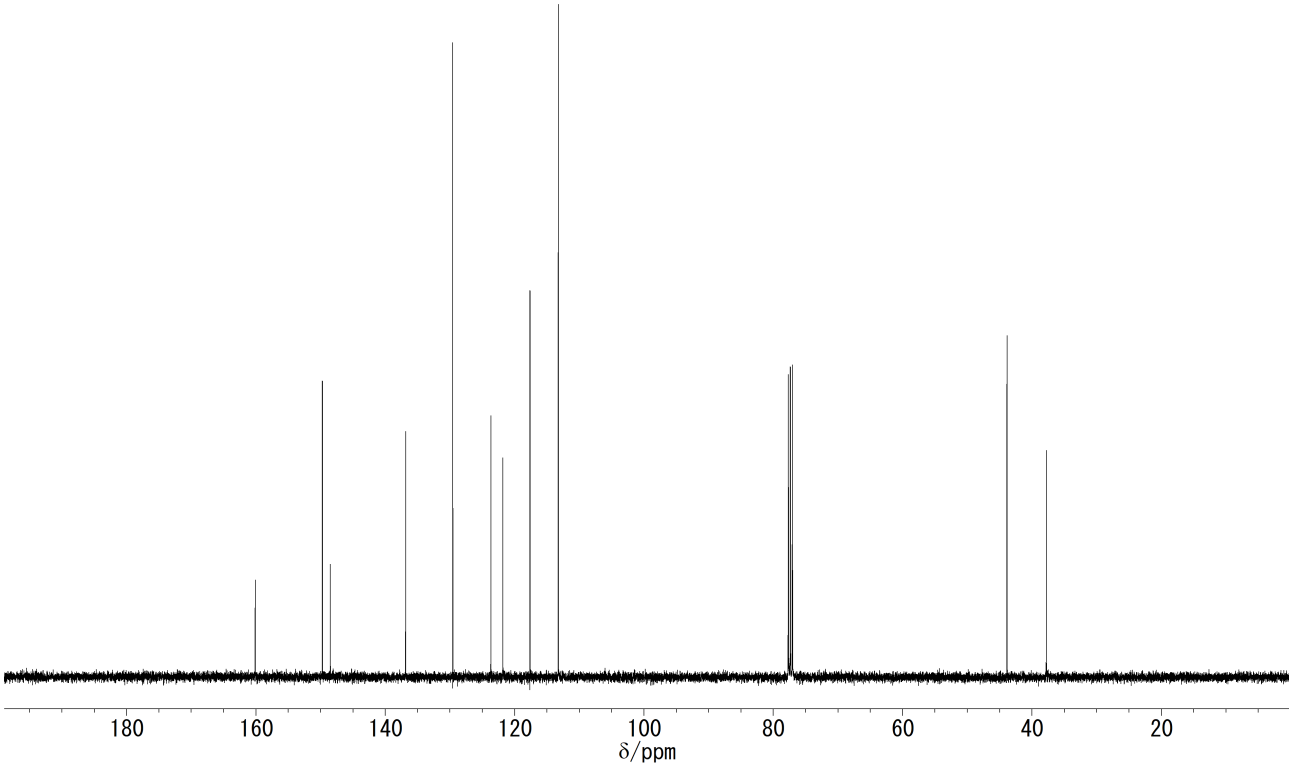
Compound **6** (^{1}H NMR spectrum in $CDCl_3$)



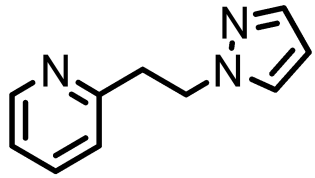


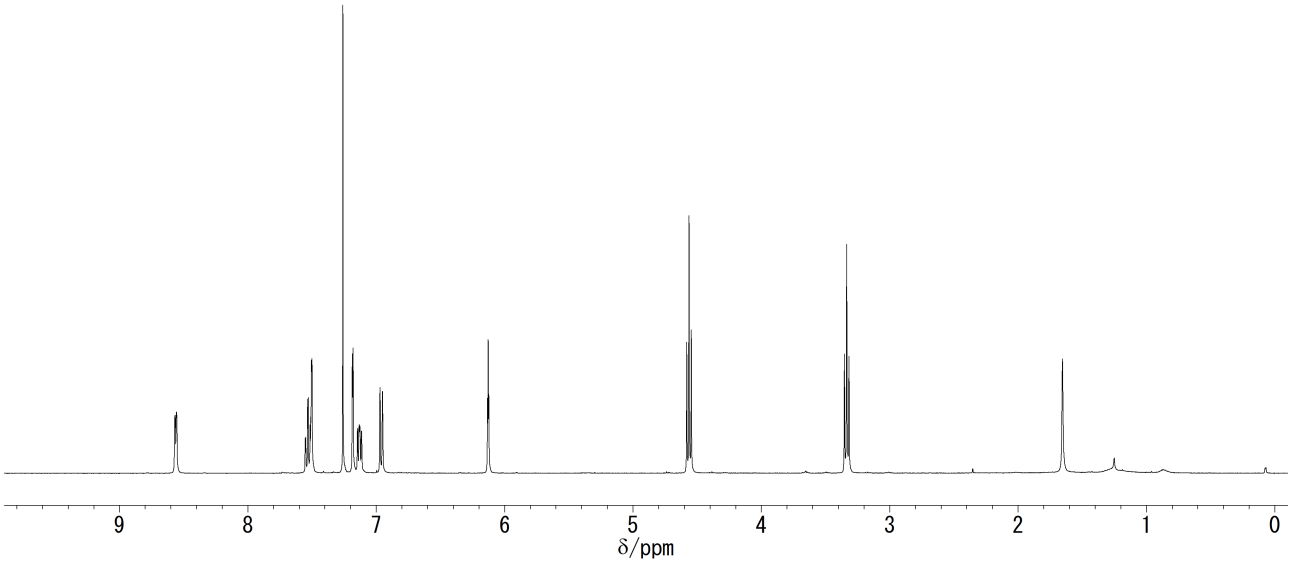
Compound **6** (^{13}C NMR spectrum in $CDCl_3$)



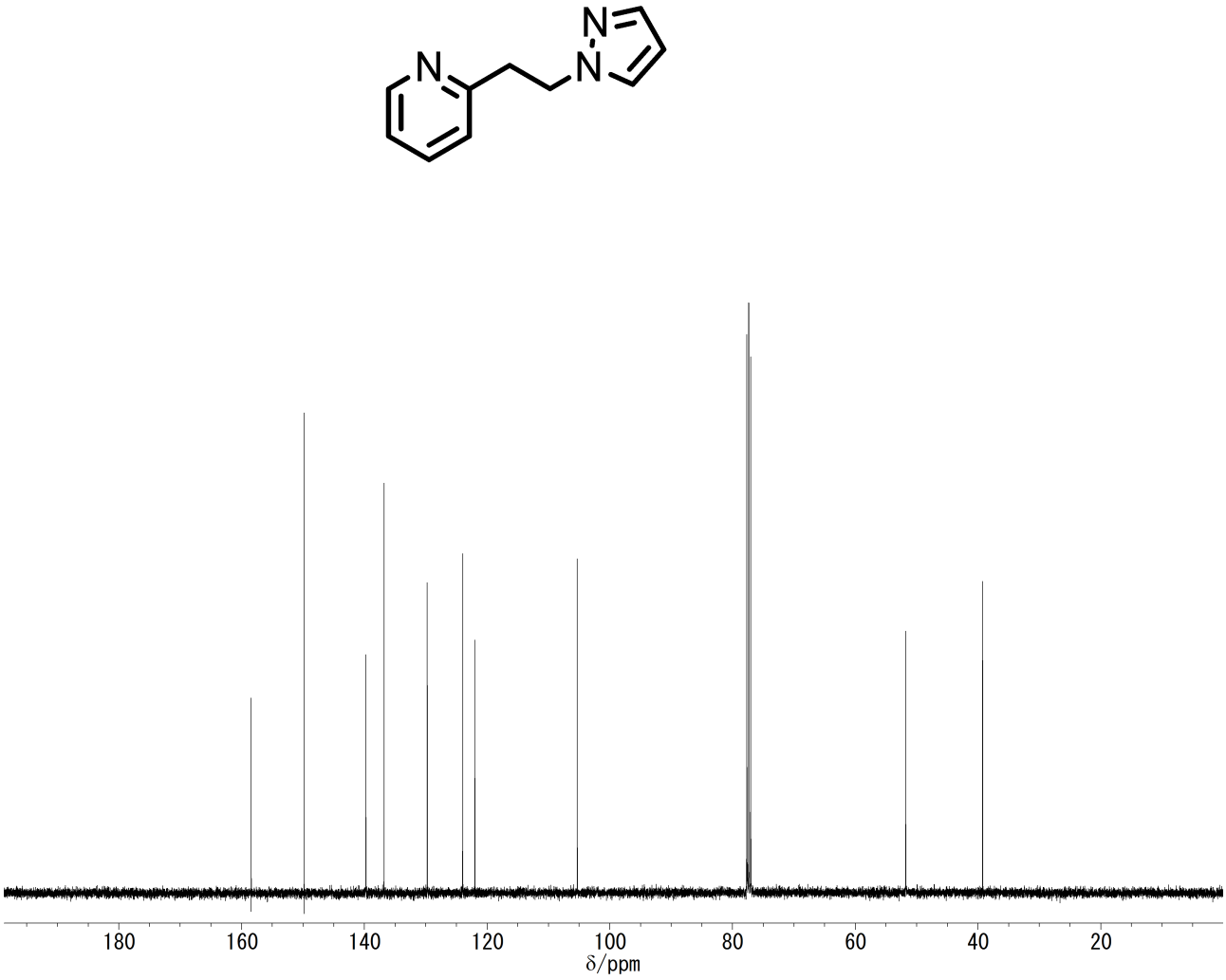


Compound **7** (^{1}H NMR spectrum in $CDCl_3$)





Compound **7** (^{13}C NMR spectrum in $CDCl_3$)



4. HRMS (ESI) data of **1**•C_5H_5N.