Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Frustrated Behavior of Lewis/Brønsted Pairs inside Molecular Cages

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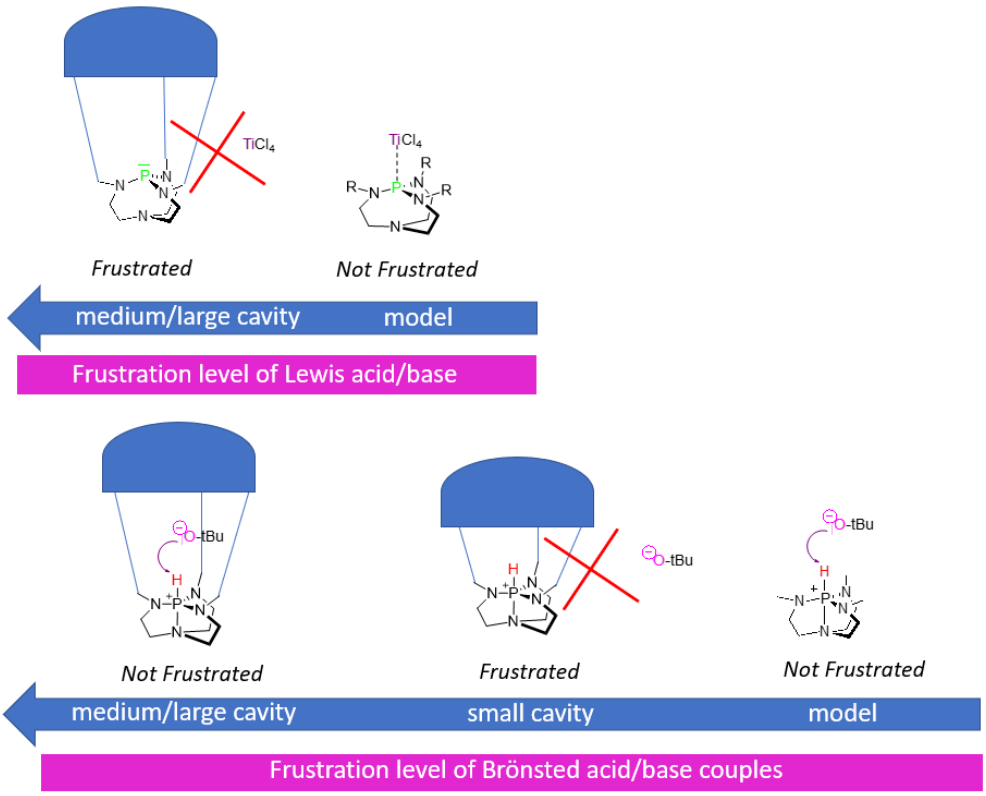
Table

I/ General method

Commercial reagents were used directly as received without further purification. All reactions were performed in oven-dried glassware under a positive pressure of argon, unless otherwise noted. Fritted glass was subsequently neutralized with saturated $NaHCO_3$ solution, twice rinsed with distilled water and acetone, then oven-dried. Dichloromethane, tetrahydrofuran and toluene were dried prior to use through standard procedures or obtained from a solvent drying System BRAUN MB-SPS800. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AC 400 (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR in $CDCl_3$ or CD_2Cl_2). Chemical shifts were reported in ppm on the δ scale relative to residual $CDCl_3$ (δ = 7.26 for 1H NMR and δ = 77.16 for ^{13}C NMR), CD_2Cl_2 (δ = 5.32 for ^{1}H NMR and 53.84 for ^{13}C NMR) as the internal references. Coupling constant (J) are reported in Hertz unit (Hz). Multiplicities are described with standard following abbreviations: s = singlet, br = broad, d = doublet, t = triplet, q = quadruplet, m = multiplet. Column chromatographies were performed with gel 60 (Macherey-Nagel® Si 60, 0.040-0.063 mm). Analytical thin layer chromatography (TLCs) were carried out on Merck®Kieselgel 60 F254 plates and achieved under a 254 nm UV light. High-resolution mass spectra (HRMS) were performed on a SYNAPT G2 HDMS (Waters) spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted.

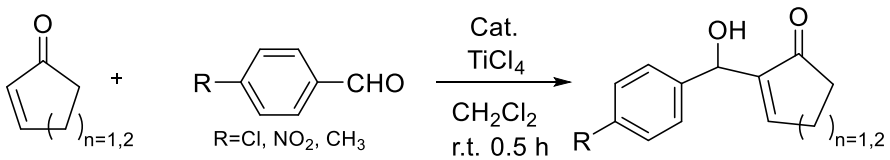
II/ Experimental section

Simplified examples of frustrated pairs.



Scheme S1 : Top: simplified examples of frustrated Lewis behavior involving pro-azaphosphatrane (green: Lewis basic site, purple: Lewis acid site) ; bottom: simplified examples of frustrated Brønsted behavior involving azaphosphatrane (red: Brønsted acid site, pink Brønsted basic site)

MBH reactions between cyclopentenone (n = 1) or cyclohexenone (n = 2) and benzaldehyde derivatives.

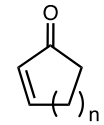
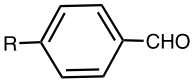


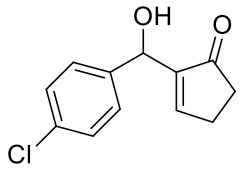
General procedure.

Para-substituted benzaldehyde (0.3 mmol) was placed in a 5 mL oven-dried Schlenk tube and dissolved in anhydrous dichloromethane (1 mL). 2-Cyclopenten-1-one or 2-cyclohexen-1-one (0.9 mmol) was added and a solution of P@**4** (30 mg, 0.03 mmol) in anhydrous dichloromethane (1 mL) was added drop-wise. The mixture was stirred under argon atmosphere at room temperature, and a solution of

titanium chloride in anhydrous dichloromethane (1 M) (0.3 mL, 0.3 mmol) was then added. The mixture was stirred for 0.5 hour and then quenched with a saturated aqueous solution of $NaHCO_3$ (3.0 mL). The mixture was stirred for an additional 0.5 hour. The inorganic precipitate was filtered and the organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give the crude product, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give the pure compound (Table S1).

Table S1. Experimental details

	n = 1			n = 2		
 R =	Cl	CH_3	NO_2	Cl	CH_3	NO_2
Eluent: petroleum ether: ethyl acetate	2.5:1	3:1	1:1	2:1	5:1	2:1
Yield % (mg)	74% (47)	51% (30)	55% (37)	71% (50)	66% (42)	86% (63)



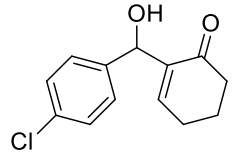
2-((4-chlorophenyl)(hydroxy)methyl)cyclopent-2-en-1-one:

4-chlorobenzaldehyde (42 mg, 0.3 mmol)
2-Cyclopenten-1-one (76 µL, 0.9 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.22 (m, 4H), 7.20 (td, *J* = 1.3 Hz, 2.6 Hz, 1H), 5.43 (s, 1H), 3.63 (br s, 1H), 2.54-2.48 (m, 2H), 2.36 (dd, *J* = 2.0 Hz, 6.75 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.6, 159.6, 147.6, 140.0, 133.6, 128.7, 127.8, 69.2, 35.3, 26.8.

These data are consistent with literature.[1]



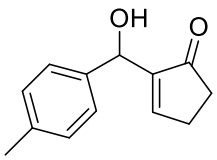
2-((4-chlorophenyl)(hydroxy)methyl)cyclohex-2-en-1-one:

4-chlorobenzaldehyde (42 mg, 0.3 mmol)
2-Cyclohexen-1-one (91 µL, 0.9 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.20 (m, 4H), 6.72 (t, *J* = 4.3 Hz, 1H), 5.48 (s, 1H), 3.48 (br s, 1H), 2.40 (dd, *J* = 5.8 Hz, 7.1 Hz, 2H), 2.36 (dd, *J* = 4.3 Hz, 10.3 Hz, 2H), 1.96 (quintuplet, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.3, 147.5, 140.9, 140.5, 133.3, 128.5, 127.9, 72.0, 38.6, 25.9, 22.6.

These data are consistent with literature.[1]



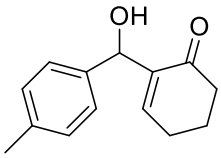
2-(hydroxy(p-tolyl)methyl)cyclopent-2-en-1-one:

4-methylbenzaldehyde (36 μL, 0.3 mmol)
2-cyclopenten-1-one (75 μL, 0.9 mmol)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35 – 7.22 (m, 3H), 7.22 – 7.08 (m, 2H), 5.53 (s, 1H), 3.43 (br s, 1H), 2.62-2.55 (m, 2H), 2.48 – 2.43 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.7, 159.3, 147.9, 138.6, 137.7, 129.3, 126.4, 69.9, 35.4, 26.7, 21.2.

These data are consistent with literature.[1]



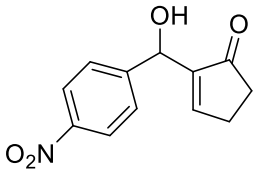
2-(hydroxy(p-tolyl)methyl)cyclohex-2-en-1-one:

4-methylbenzaldehyde (36 μL, 0.3 mmol)
2-cyclohexen-1-one (91 μL, 0.9 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.75 (td, *J* = 1.1 Hz, 4.2 Hz, 1H), 5.53 (d, *J* = 3.6 Hz, 1H), 3.36 (d, *J* = 5.3 Hz, 1H), 2.45 (dd, *J*= 6.3 Hz, 8.1 Hz, 2H), 2.42-2.36 (m, 2H), 2.34 (s, 3H), 1.99 (quintuplet, *J* = 5.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.6, 147.3, 141.3, 138.9, 137.3, 129.2, 126.5, 72.6, 38.8, 25.9, 22.7, 21.3.

These data are consistent with literature.[1]



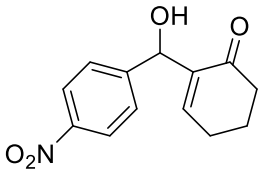
2-(hydroxy(4-nitrophenyl)methyl)cyclopent-2-en-1-one:

4-nitrobenzaldehyde (45 mg, 0.3 mmol)
2-cyclopenten-1-one (76 μL, 0.9 mmol)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.21 (dt, *J* = 3.1 Hz, 8.8 Hz, 2H), 7.58 (dt, *J* = 2.3 Hz, 9.6 Hz, 2H), 7.29 (td, *J* = 1.2 Hz, 2.7 Hz, 1H), 5.67 (s, 1H), 3.61 (br s, 1H), 2.67-2.59 (m, 2H), 2.52 – 2.45 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.4, 159.9, 148.6, 146.8, 127.2, 123.9, 69.2, 35.3, 26.9.

These data are consistent with literature.[1]



2-(hydroxy(4-nitrophenyl)methyl)cyclohex-2-en-1-one:

4-nitrobenzaldehyde (45 mg, 0.3 mmol)
2-cyclohexen-1-one (87 μL, 0.9 mmol)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.17 (dt, *J* = 2.4 Hz, 8.8 Hz, 2H), 7.54 (dtd, *J* = 0.6 Hz, 2.2 Hz, 9.2 Hz, 2H), 6.82 (td, *J* = 1.0 Hz, 4.2 Hz, 1H), 5.60 (d, *J* = 5.2 Hz, 1H), 3.58 (d, *J* = 5.9 Hz, 1H), 2.49 – 2.38 (m, 4H), 2.00 (quintuplet, *J* = 6.1 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.2, 149.5, 148.2, 147.4, 140.4, 127.3, 123.6, 72.1, 38.5, 25.9, 22.5.

These data are consistent with literature.[1]

[1] J. Yang, B. Chatelet, V. Dufaud, D. Herault, S. Michaud-Chevallier, V. Robert, J.-P. Dutasta, A. Martinez, *Angew. Chem. Inter. Ed.*, 2018, **57**, 4212-14215

III / NMR spectra

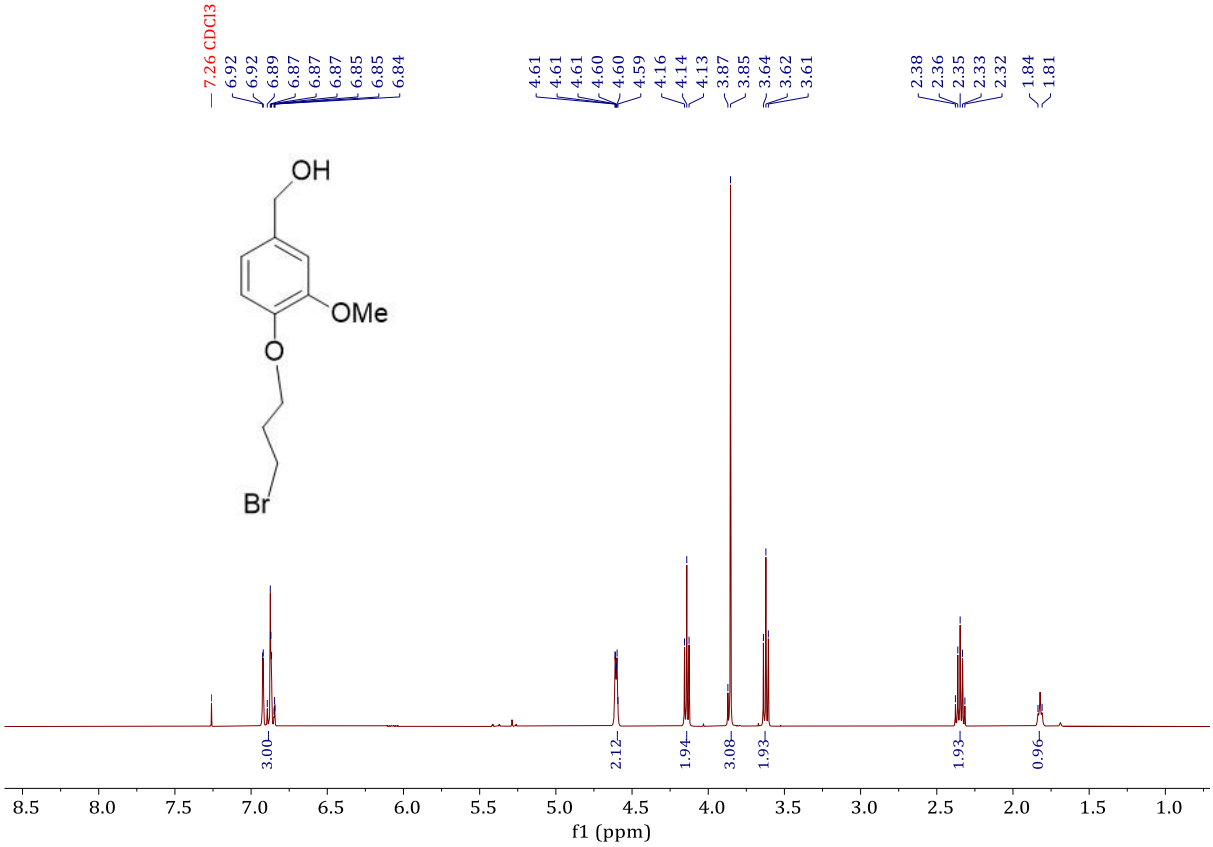


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

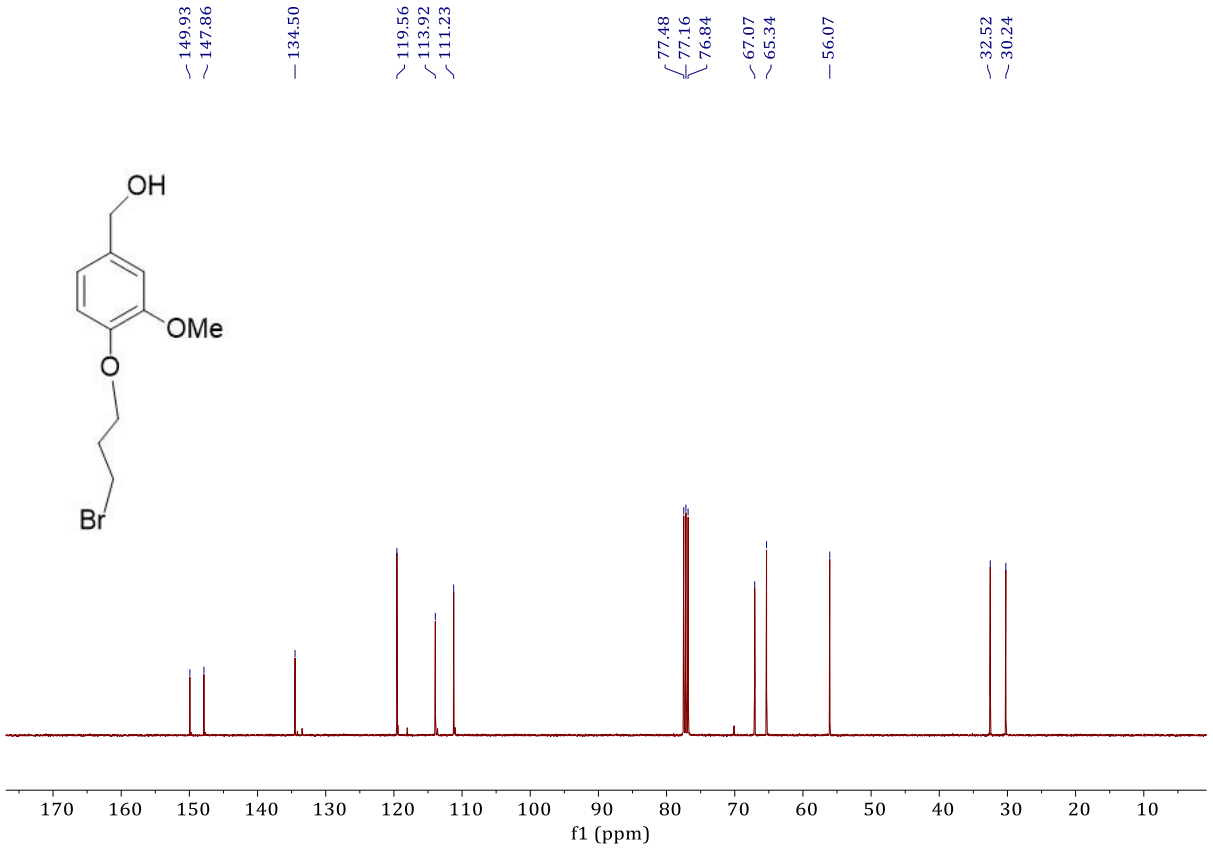


Figure S2 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8**

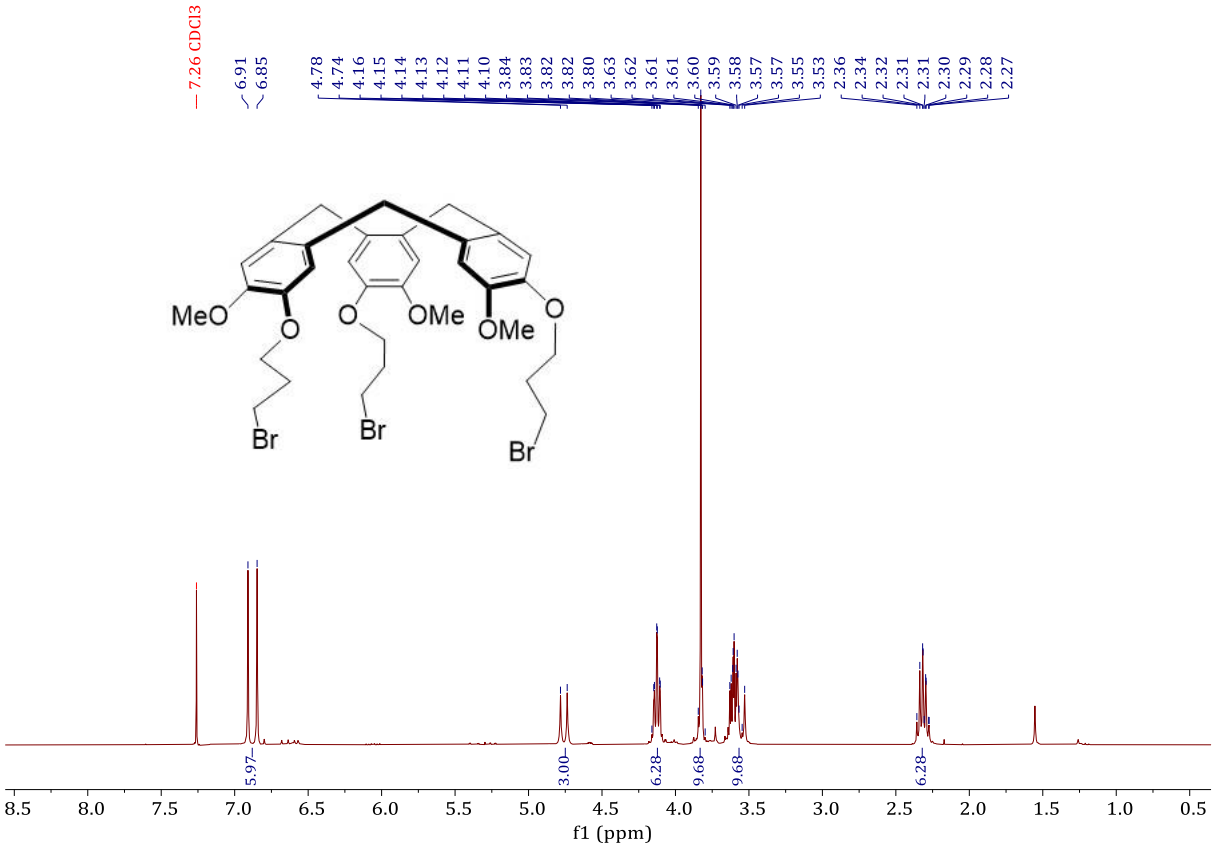


Figure S3 ^{13}H NMR (300 MHz, $CDCl_3$) spectrum of **9**

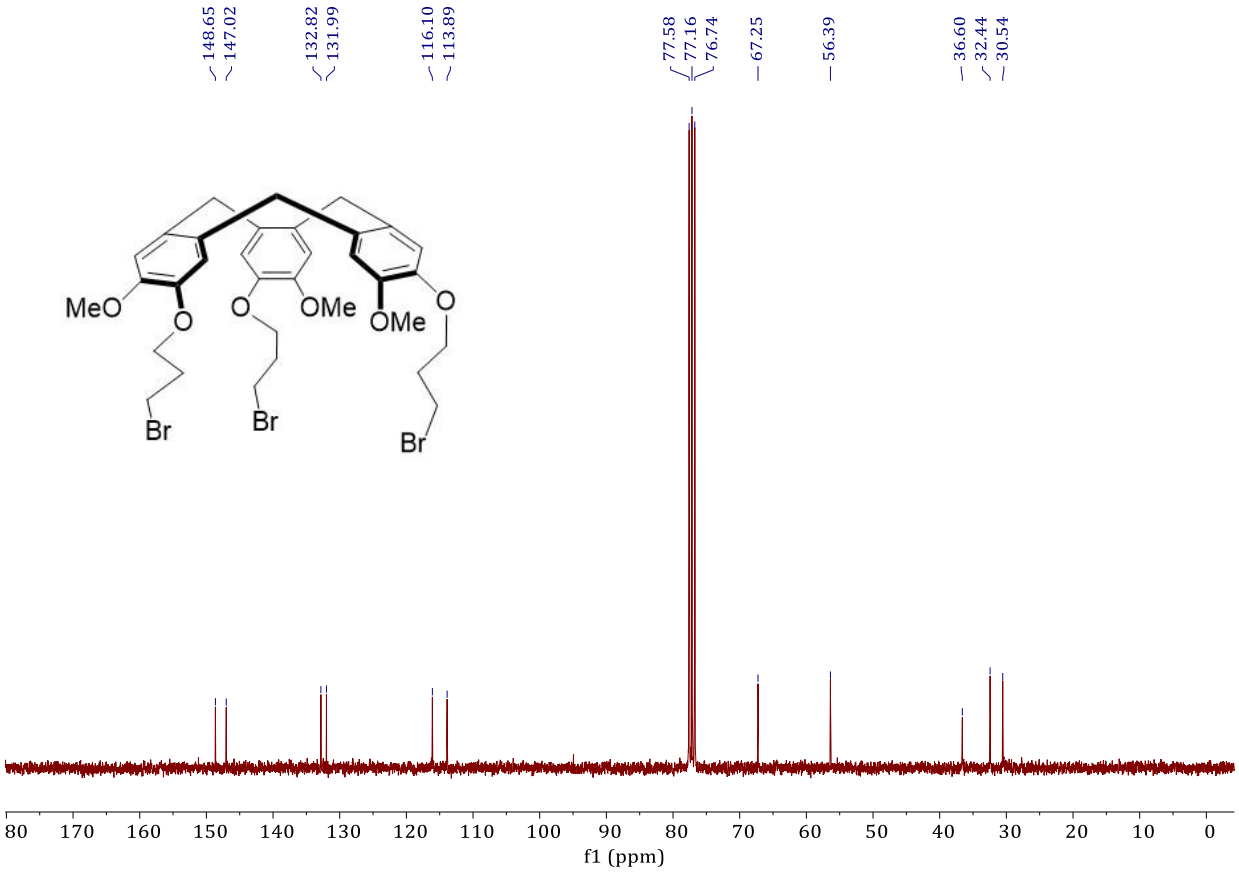


Figure S4 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **9**

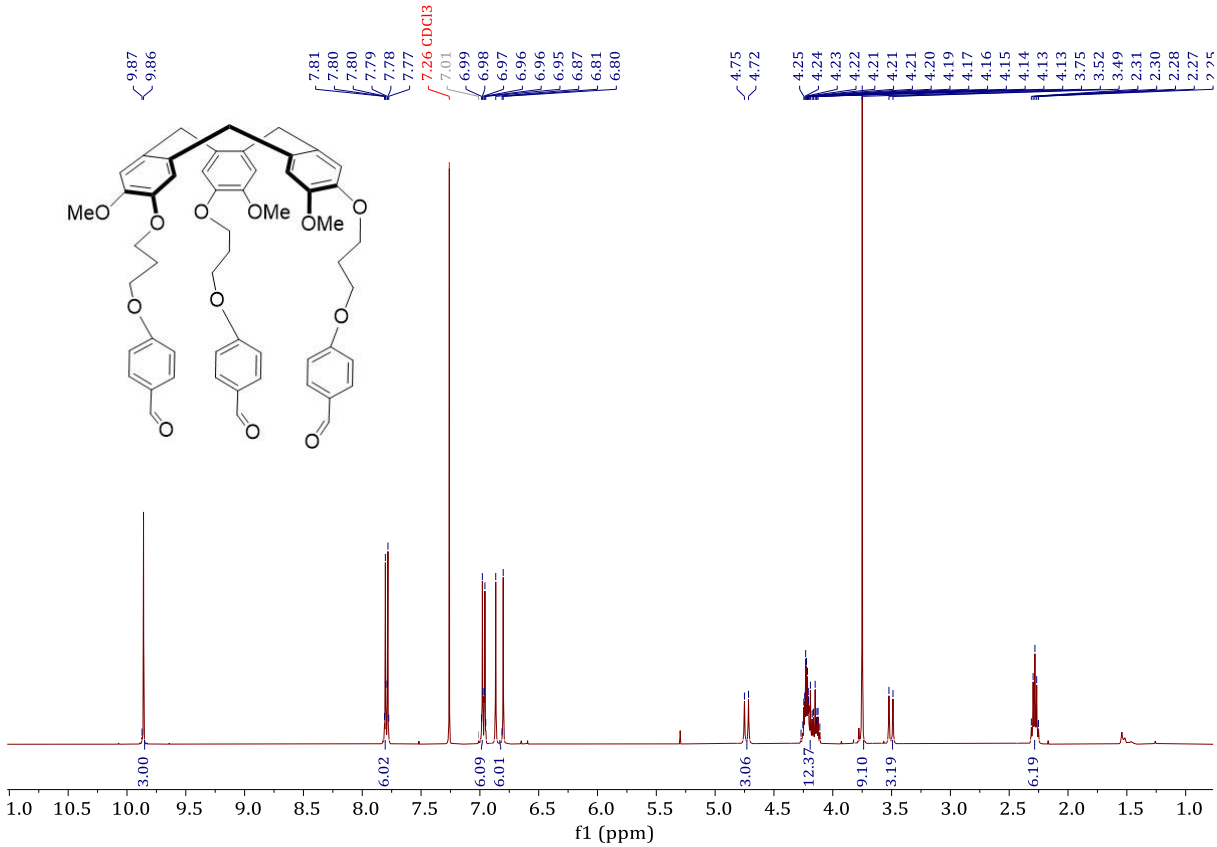


Figure S5 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7**

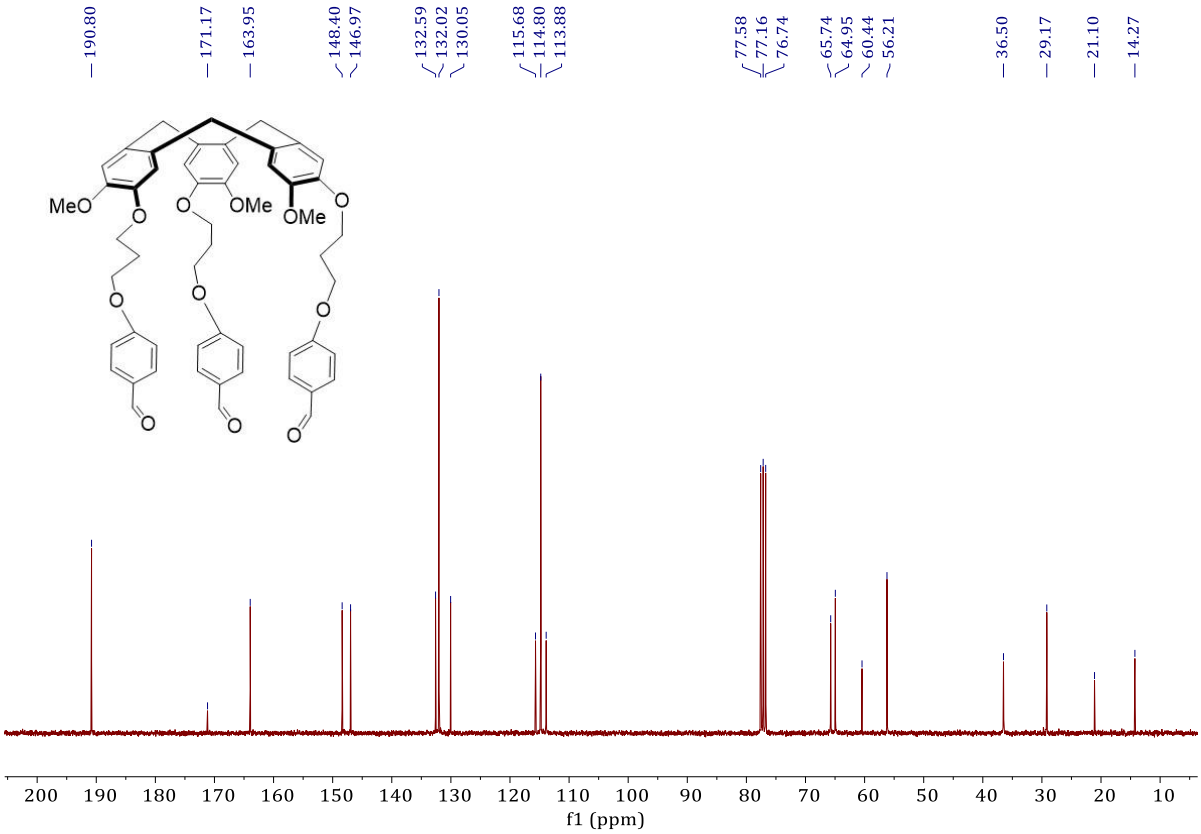


Figure S6 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **7**

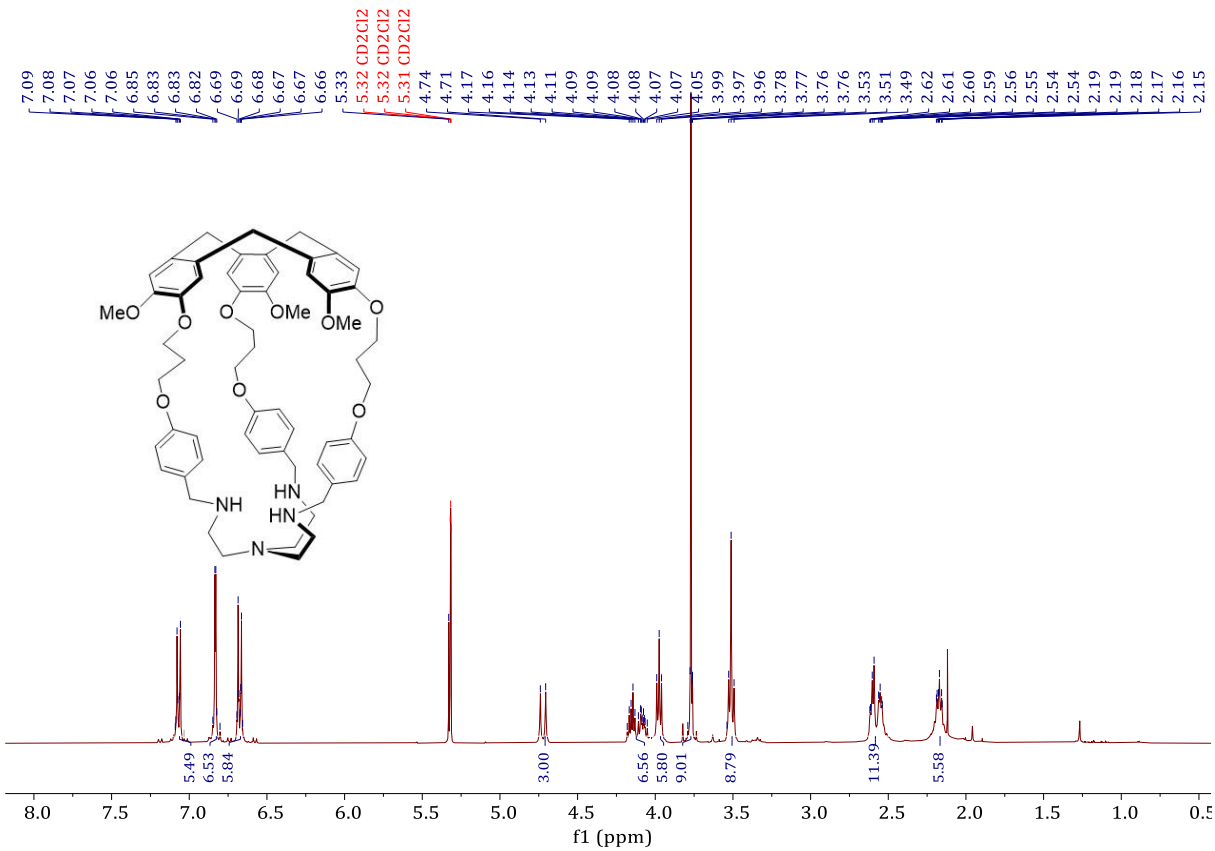


Figure S7 ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of hemicryptophane **4**

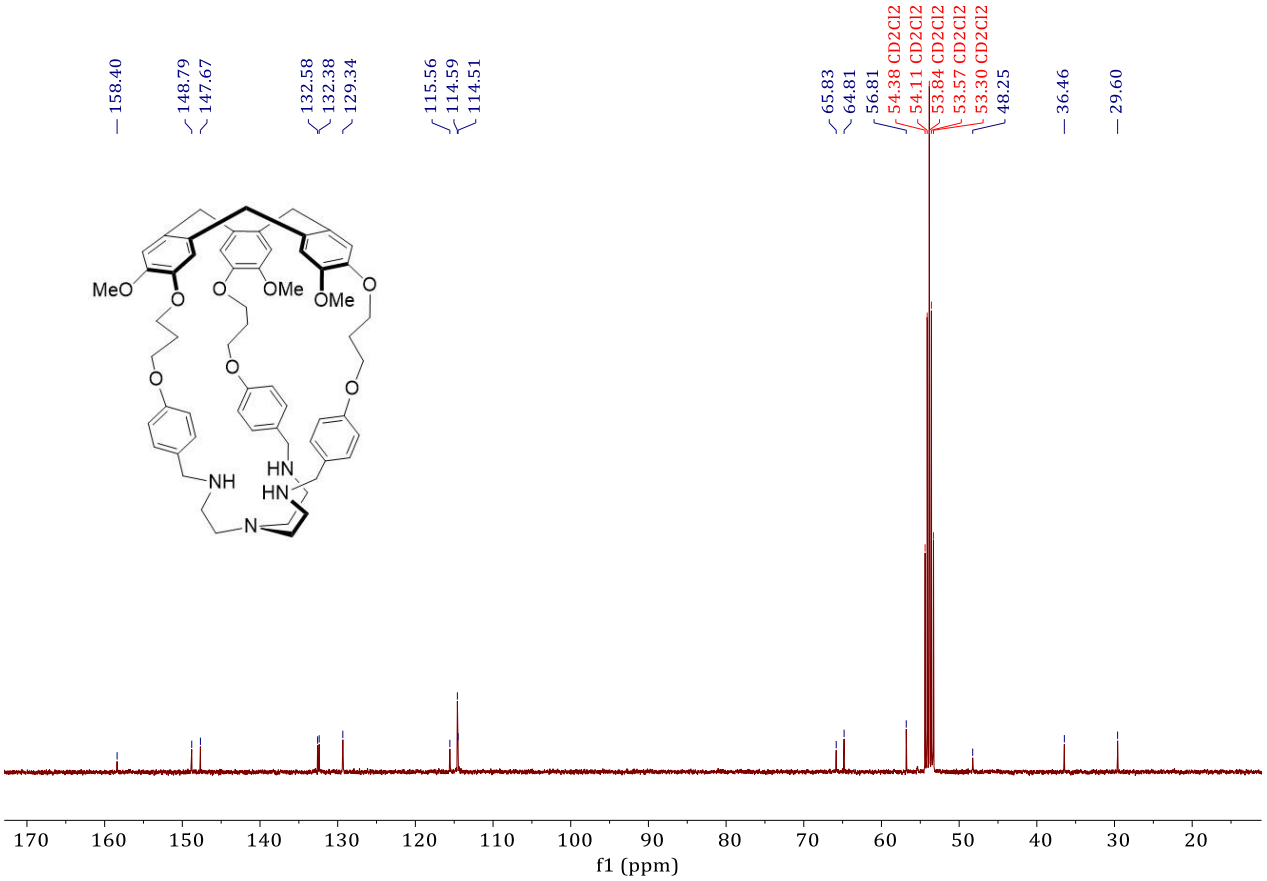


Figure S8 ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of hemicryptophane **4**

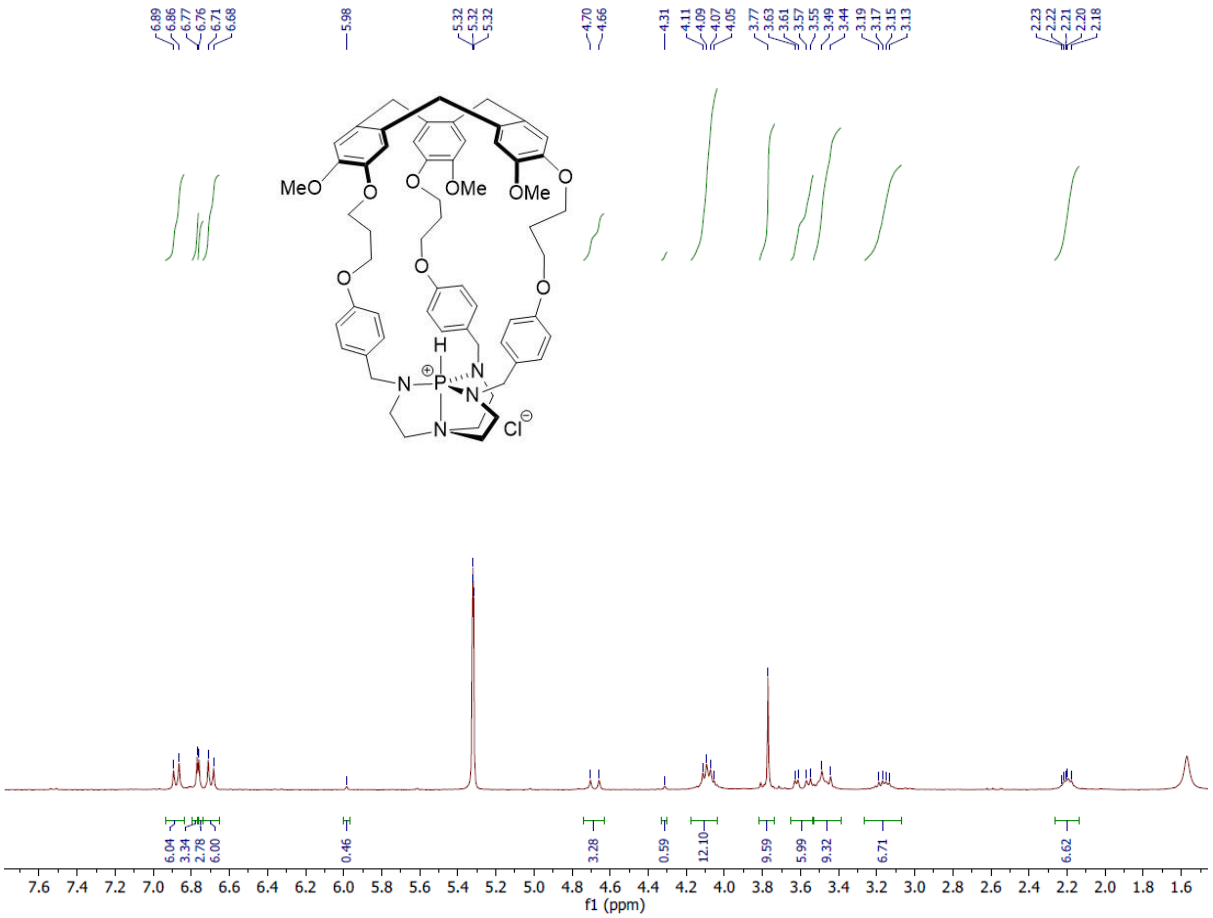


Figure S9 ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of P-H^{+}@**4**

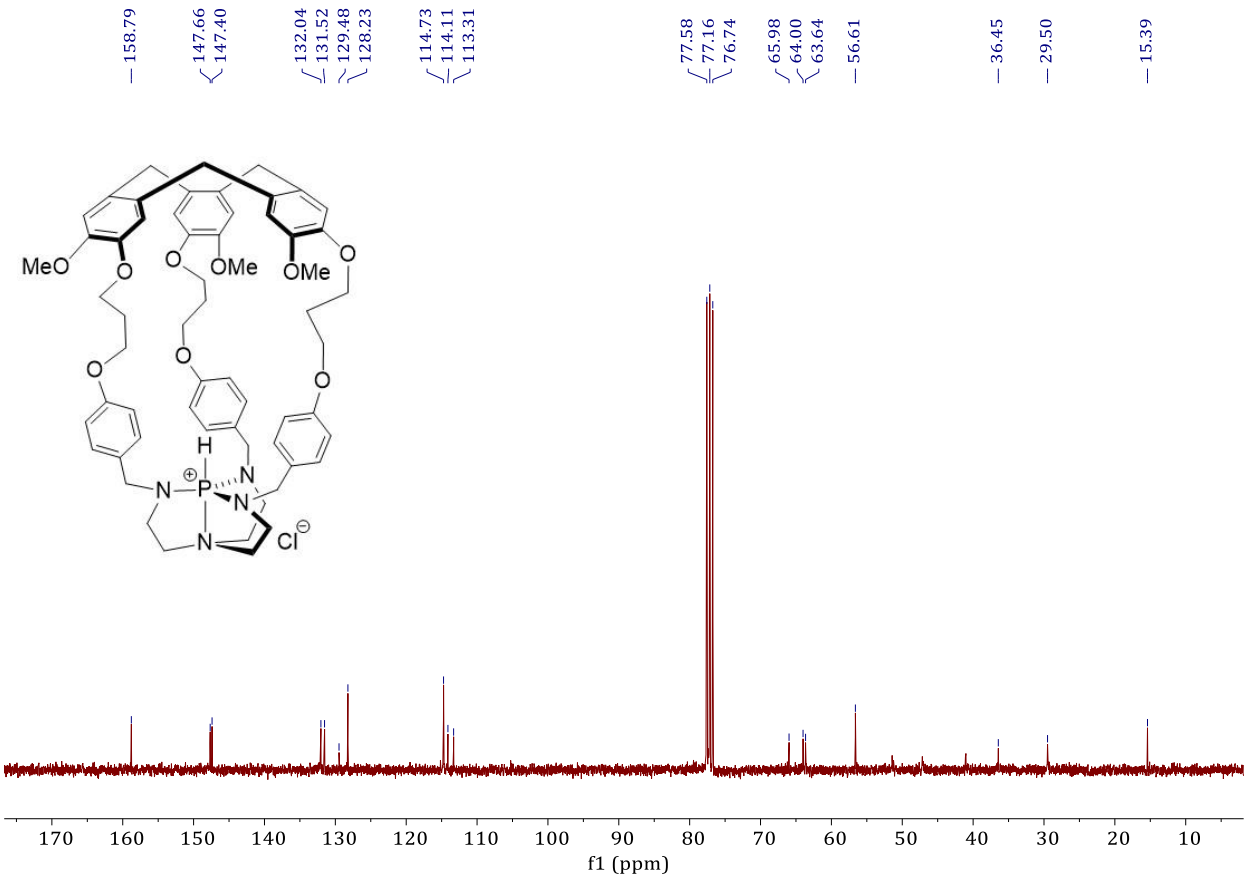


Figure S10 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of P-H^+@**4**

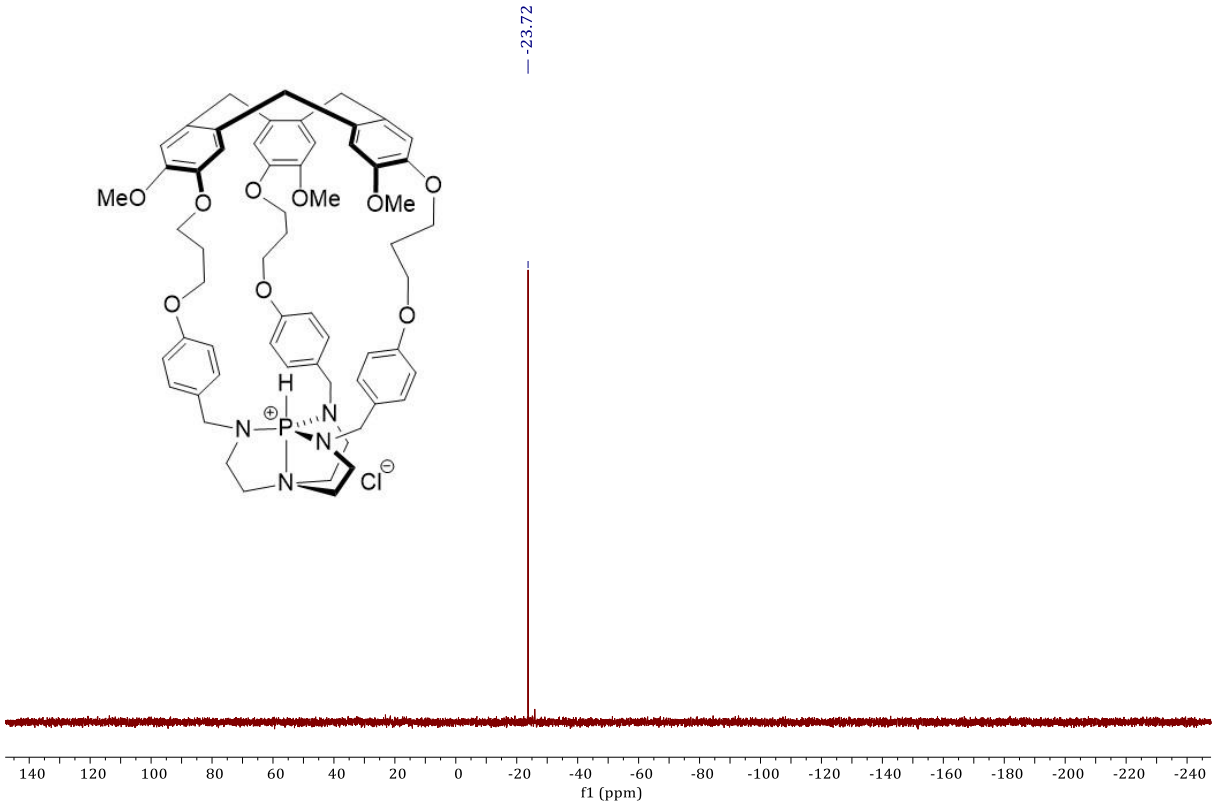


Figure S11 ^{31}P CPD NMR (162 MHz, $CDCl_3$) spectrum of PH^+@**4**

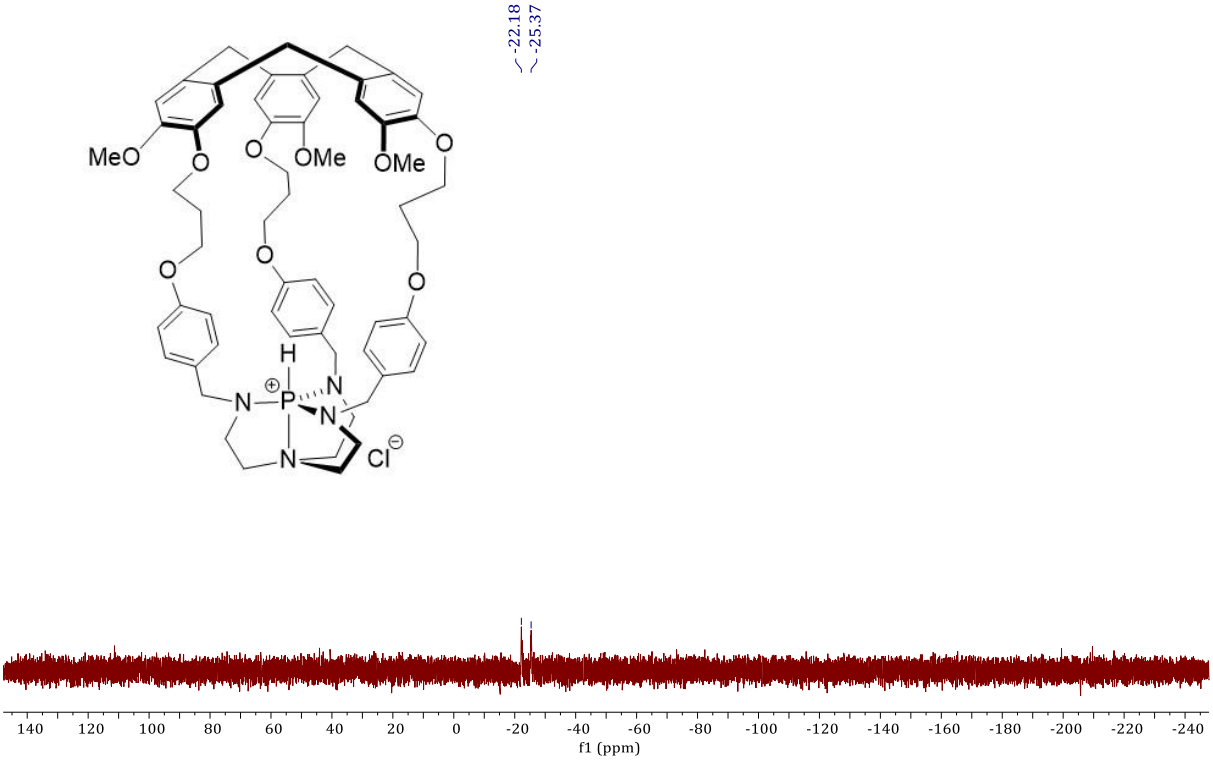


Figure S12 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of PH^+@**4**

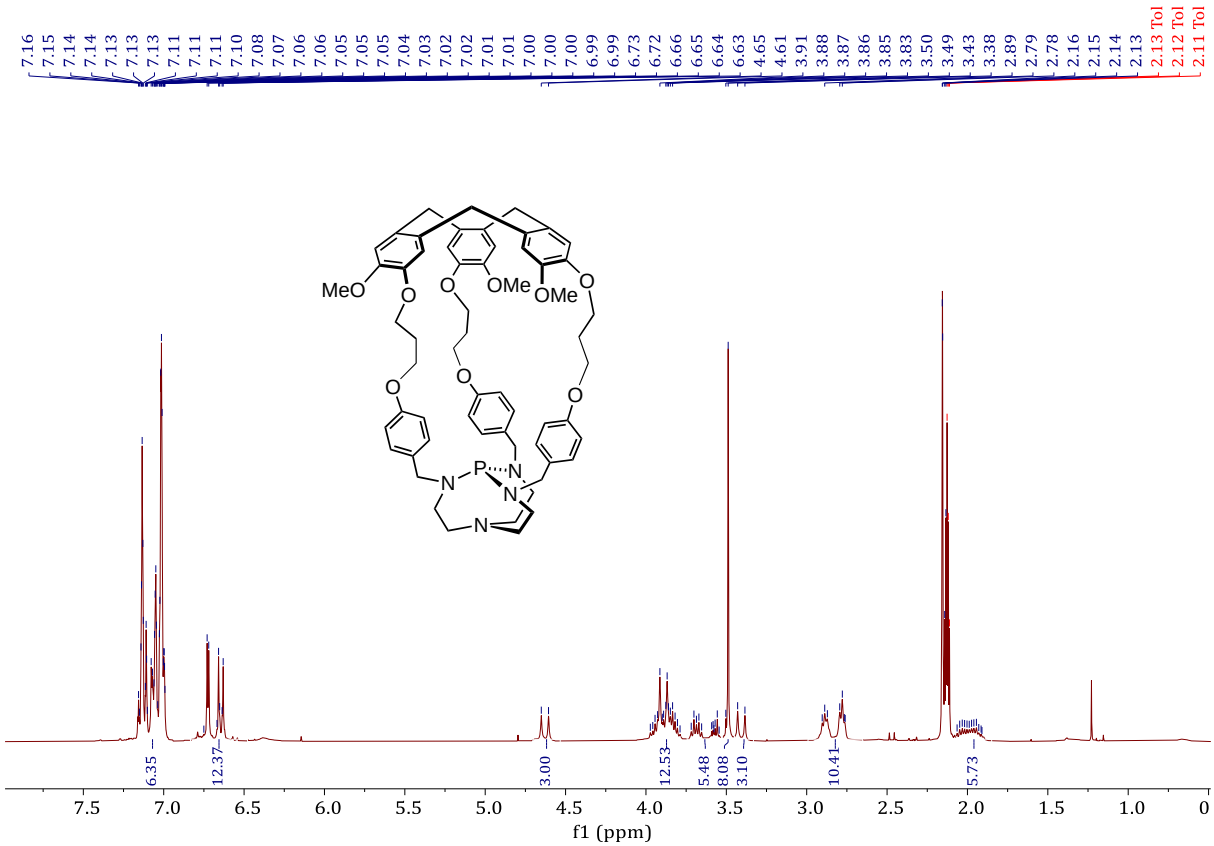


Figure S13 ^{1}H NMR (162 MHz, Toluene-d_8) spectrum of hemicryptophane P@**4**

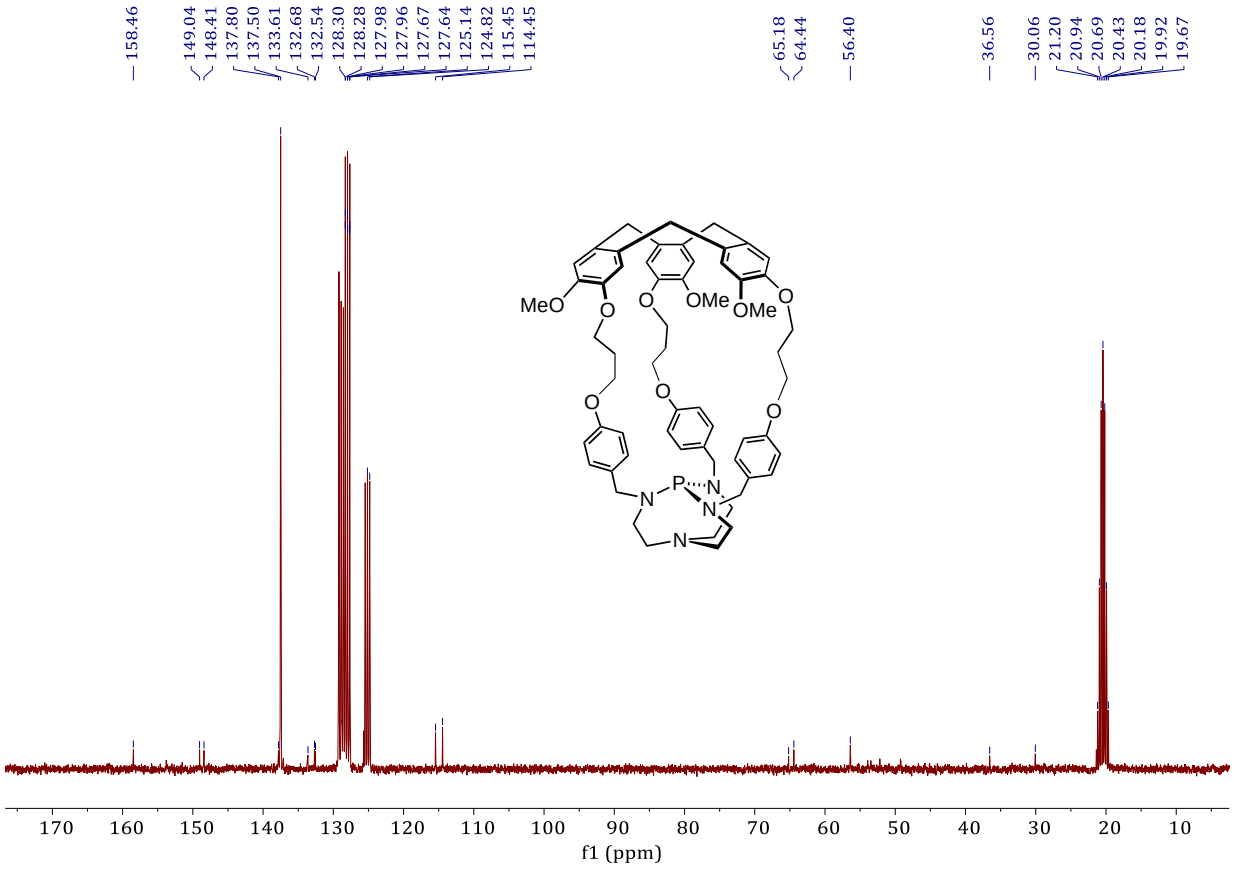


Figure S14 ^{13}C NMR (101 MHz, toluene-d_8) spectrum of hemicryptophane P@**4**

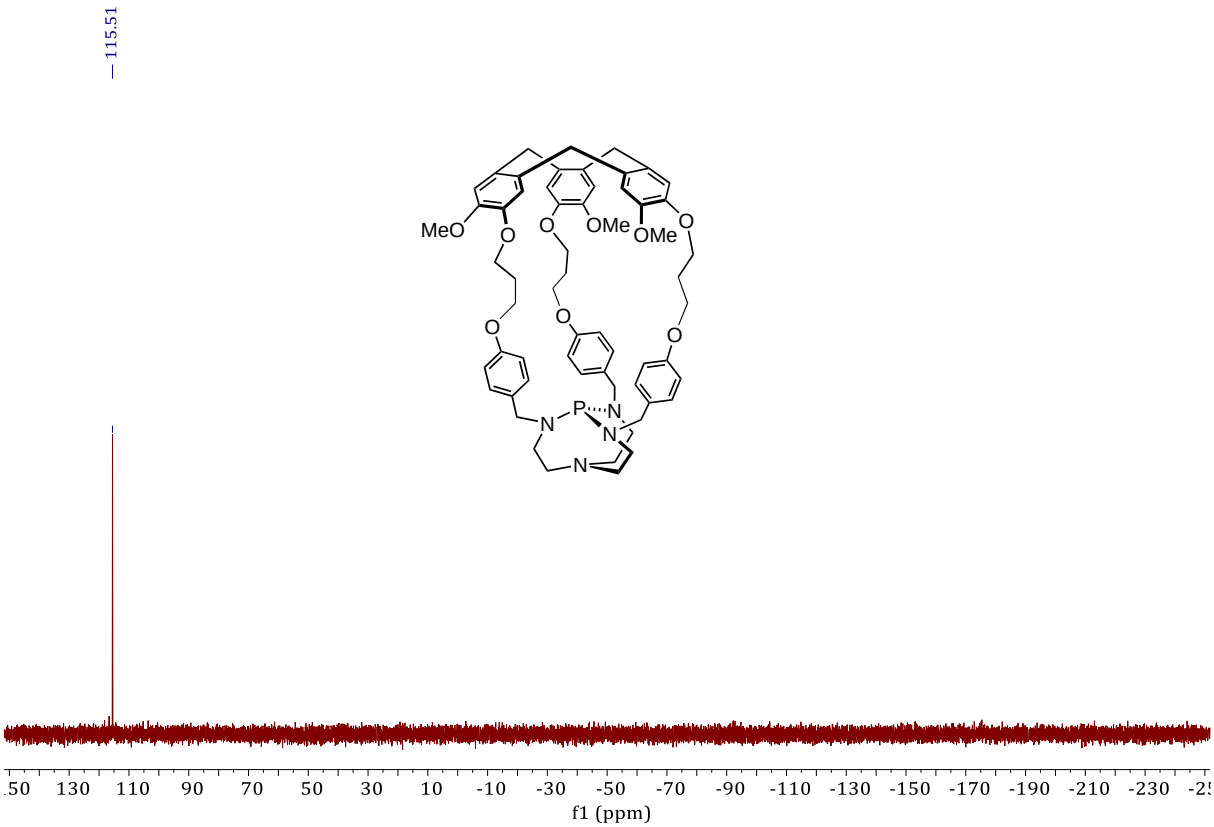


Figure S15 ^{31}P CPD NMR (121 MHz, toluene-d_8) spectrum of P@**4**

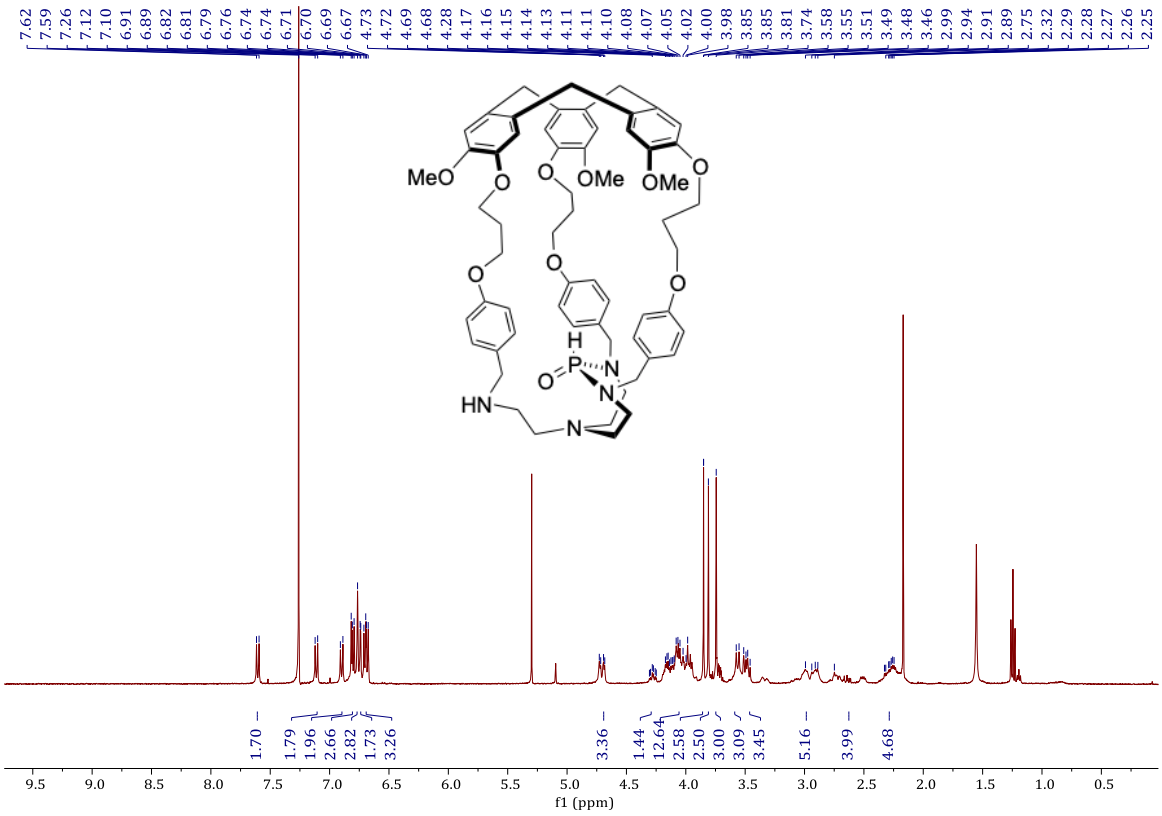


Figure S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**

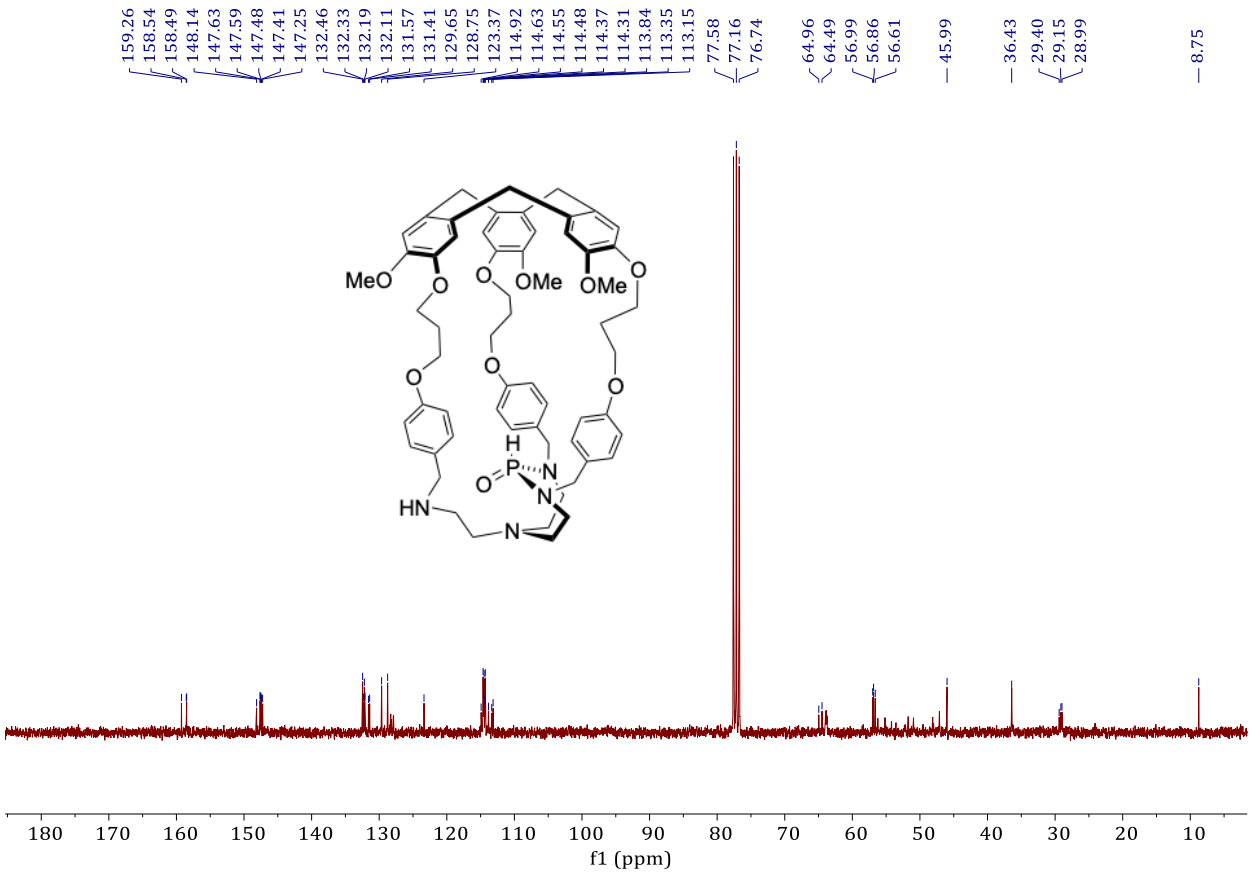


Figure S17 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13**

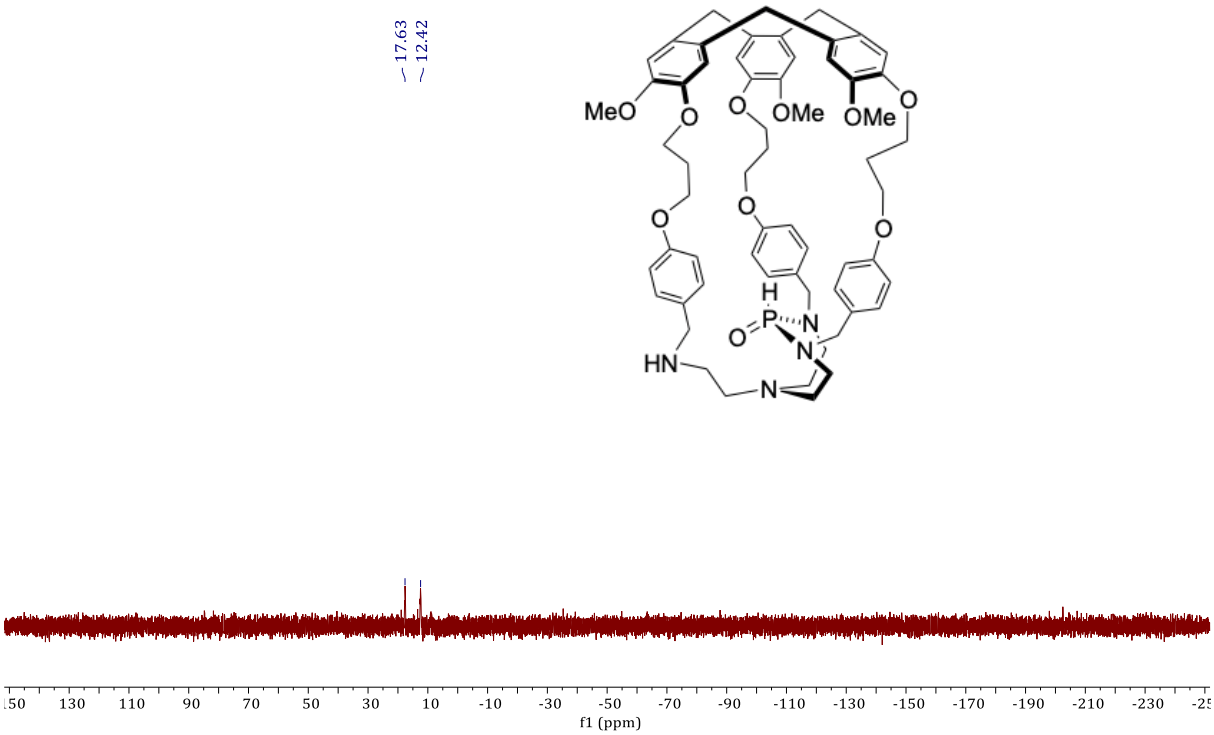


Figure S18 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of **13**

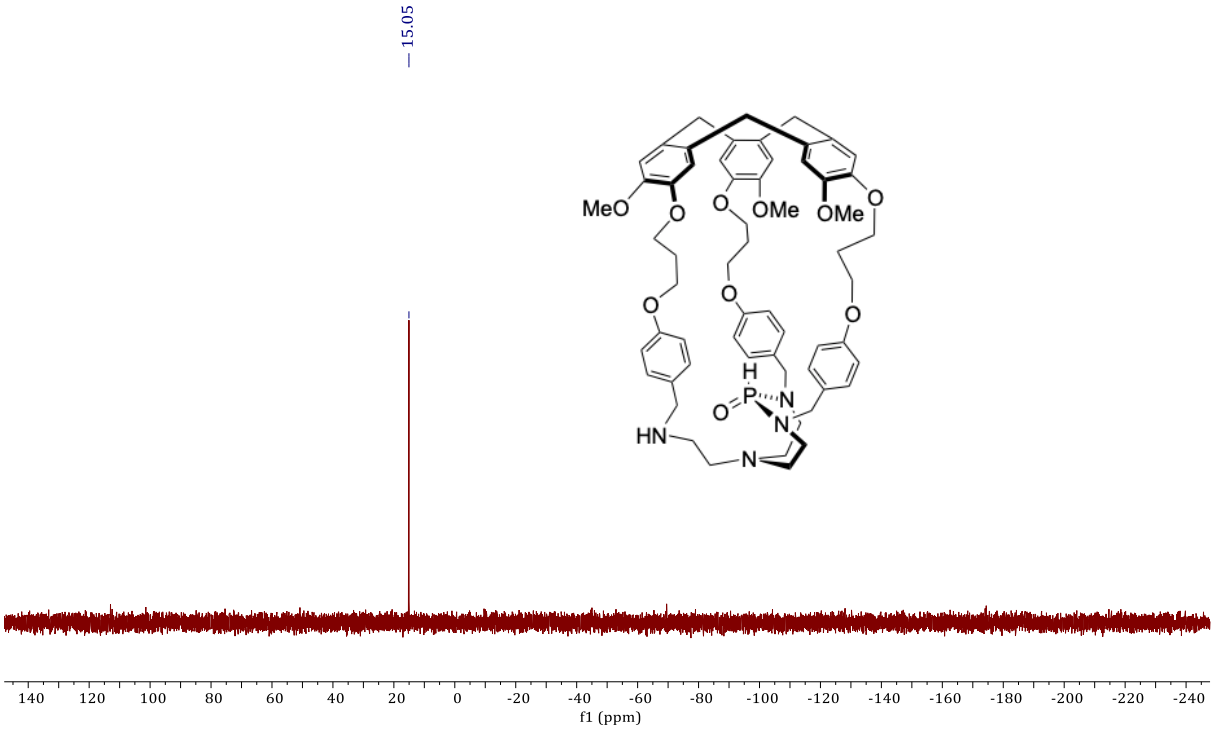


Figure S19 ^{31}P CPD NMR (162 MHz, $CDCl_3$) spectrum of **13**

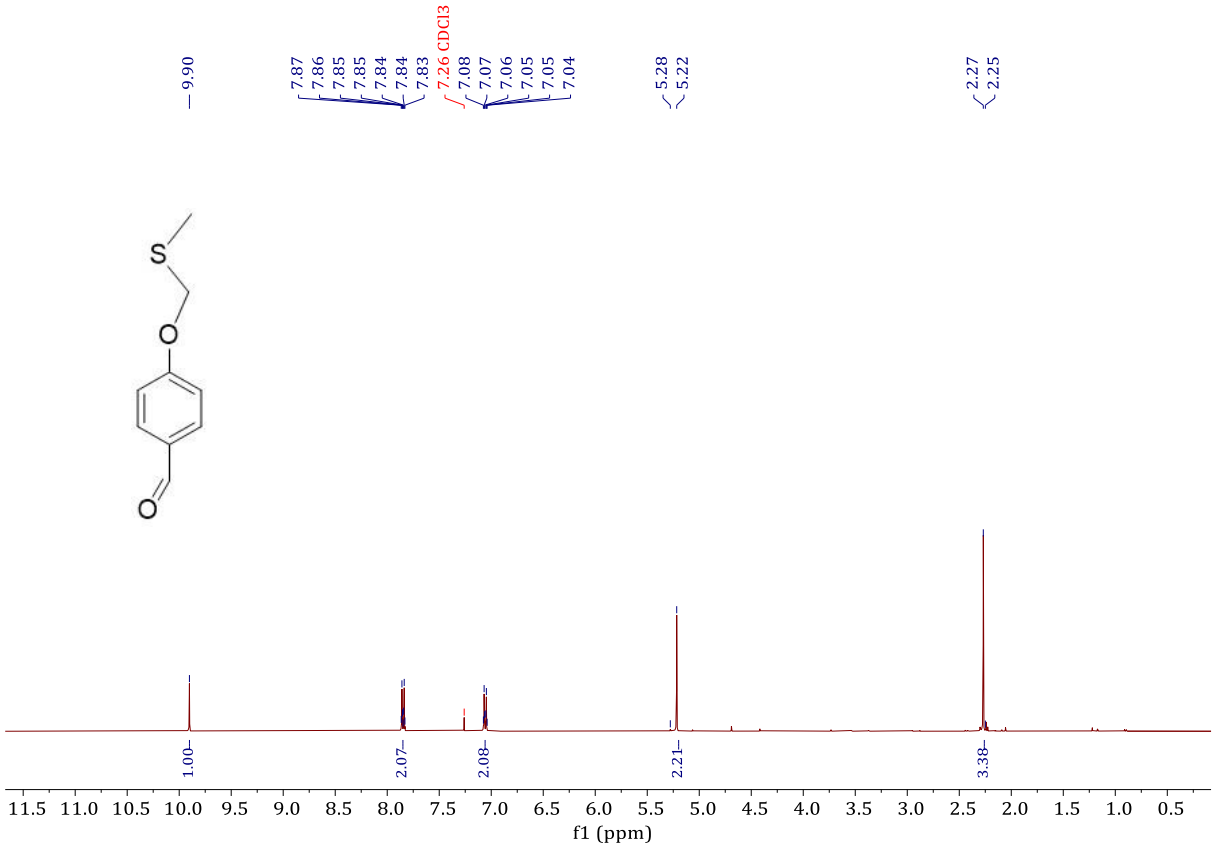


Figure S20 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

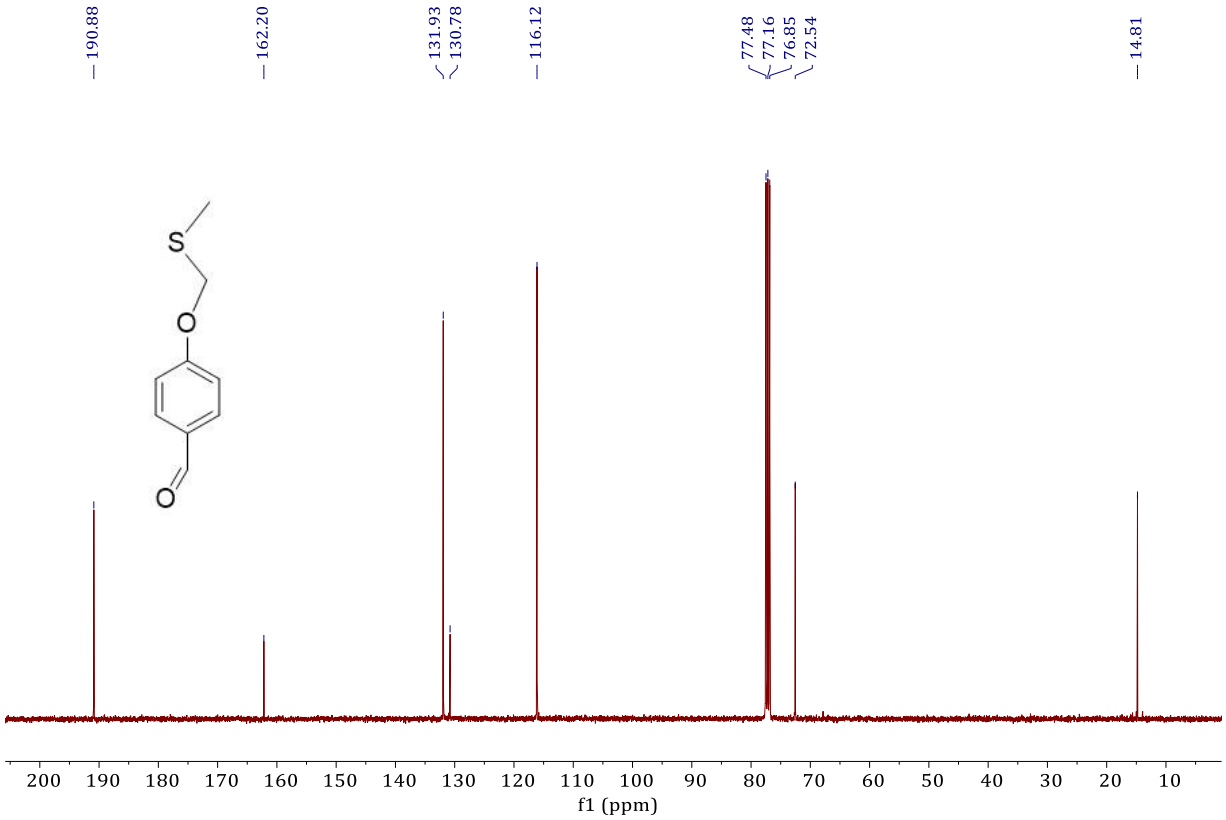


Figure S21 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **10**

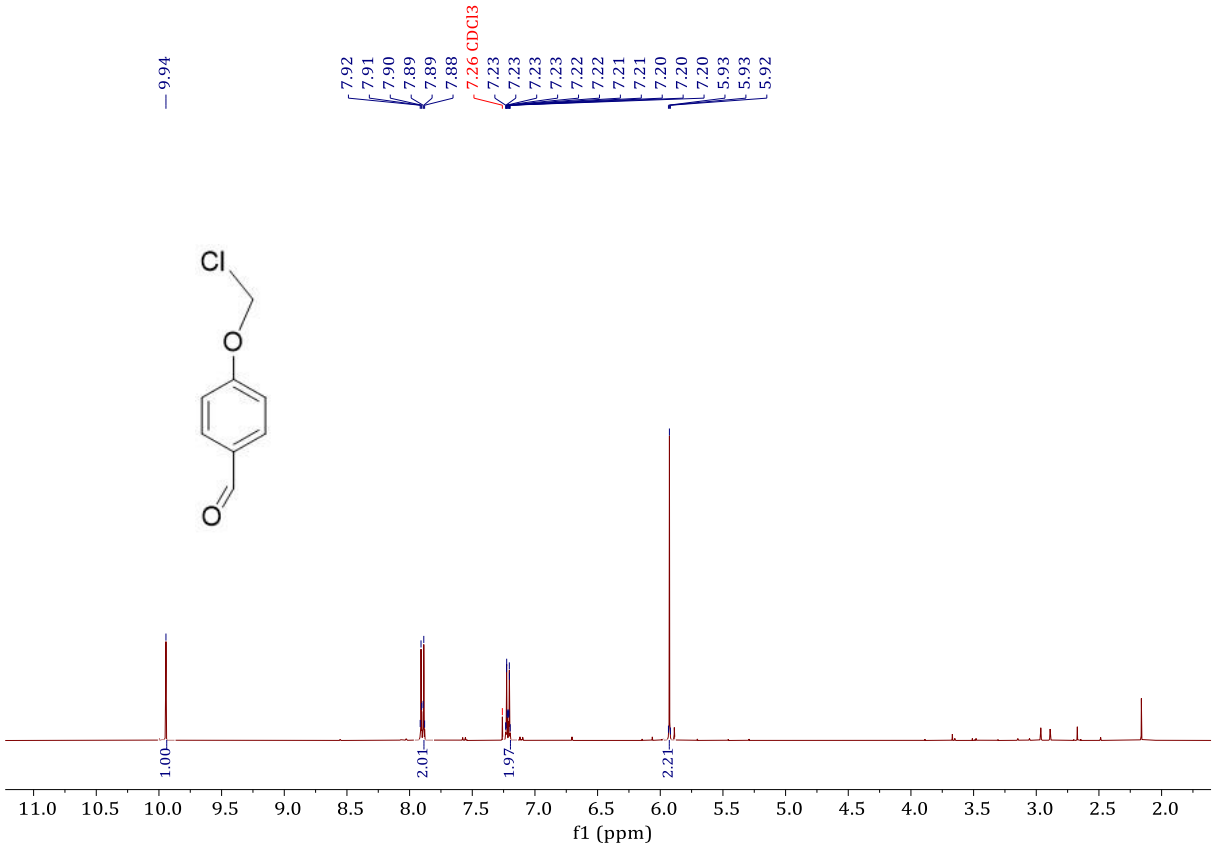


Figure S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

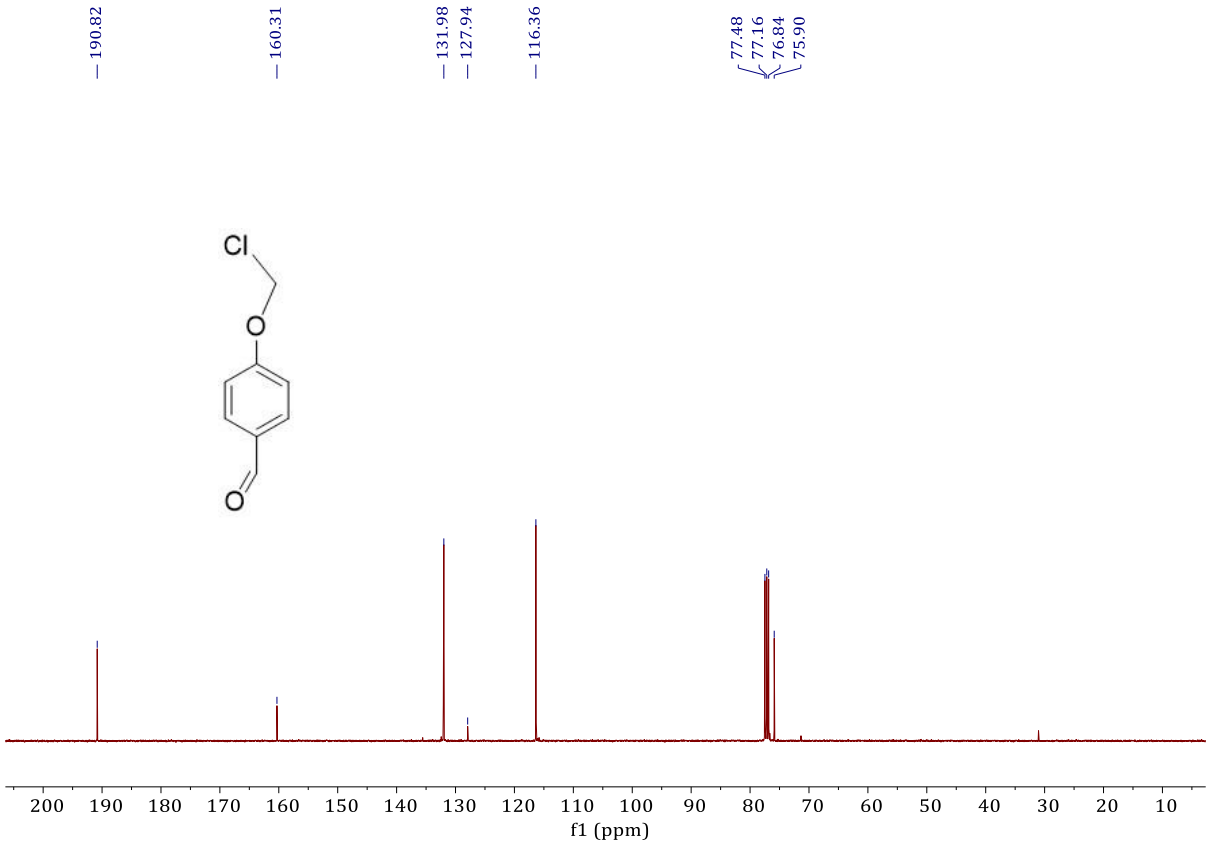


Figure S23 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**

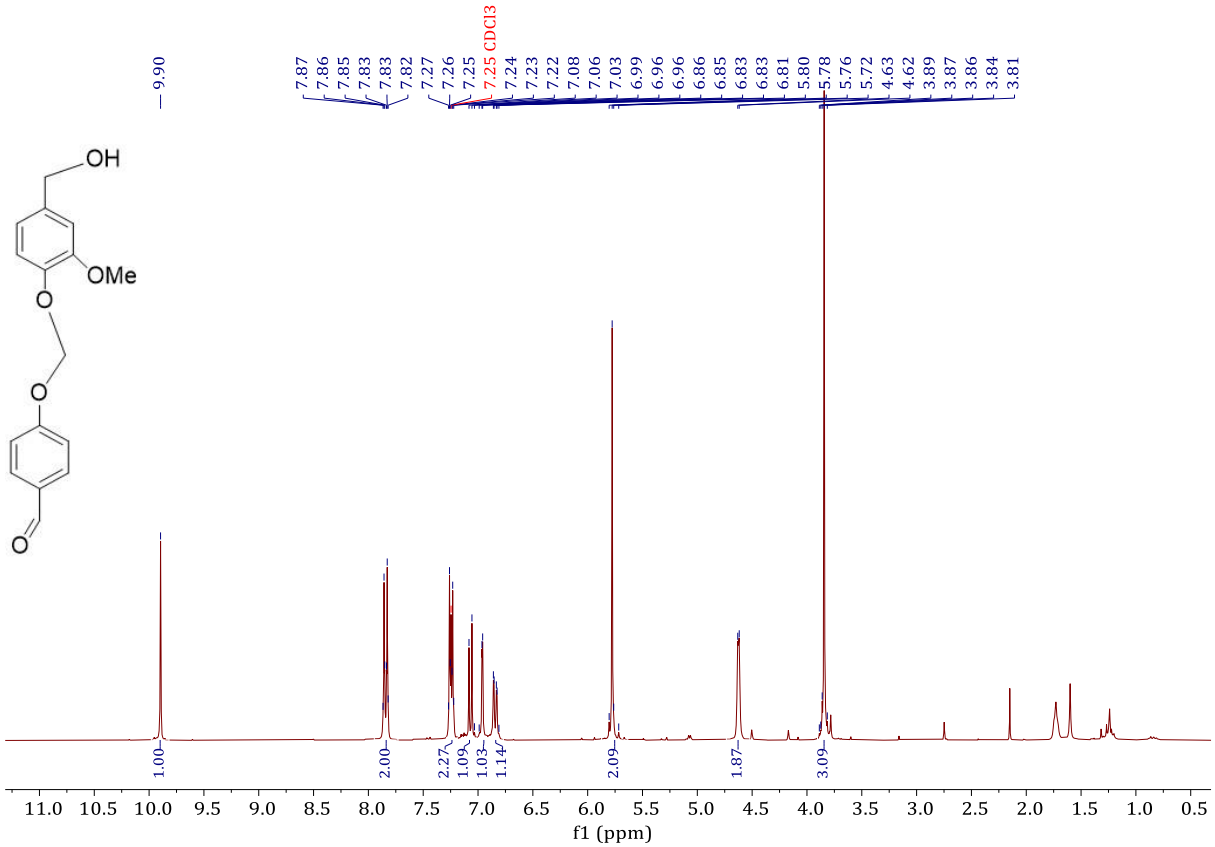


Figure S24 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **12**

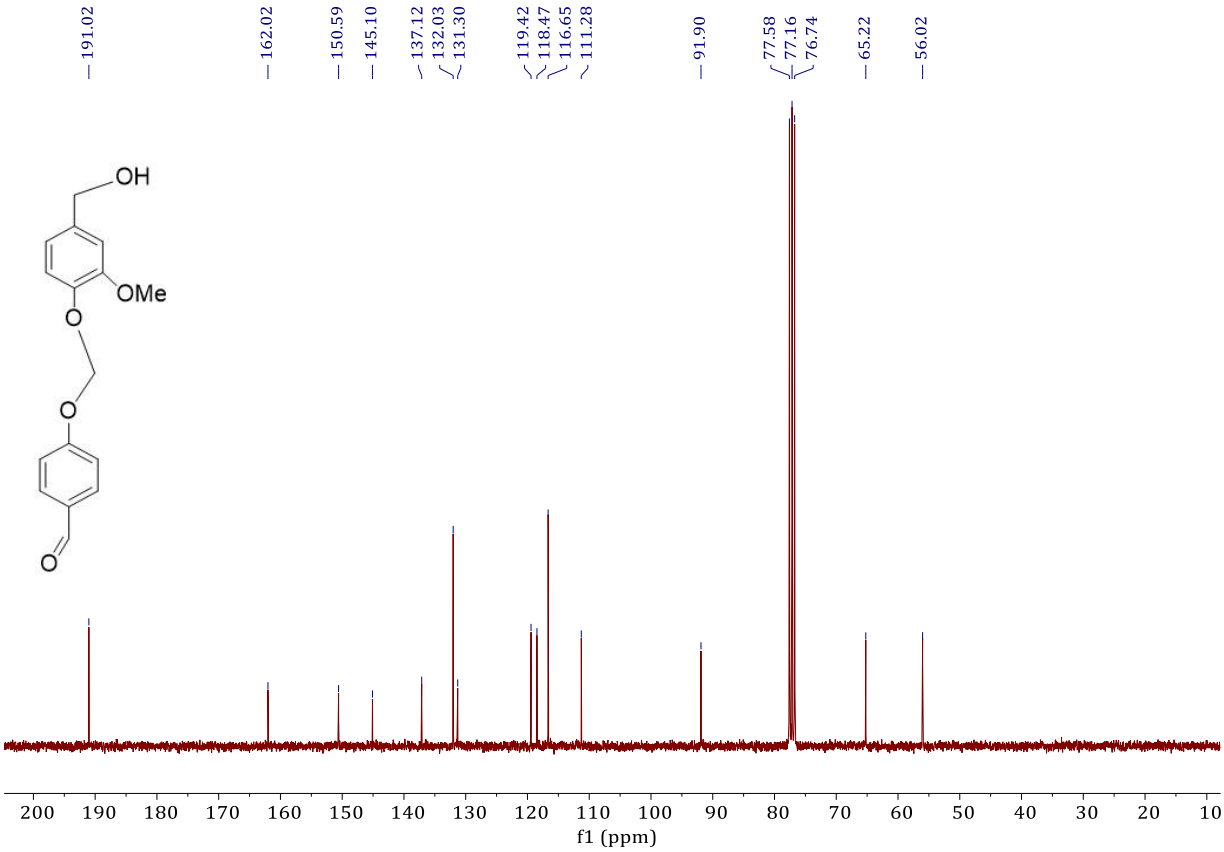


Figure S25 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **12**

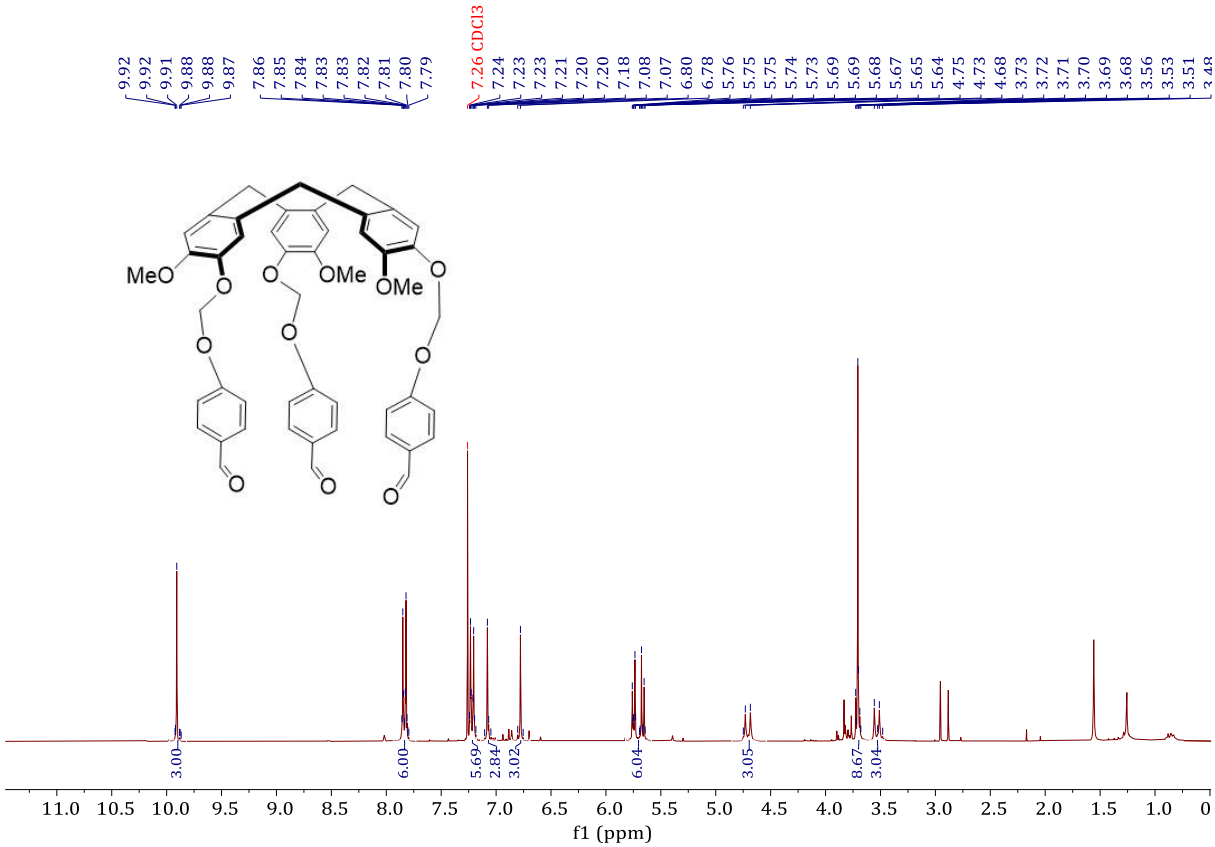


Figure S26 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5**

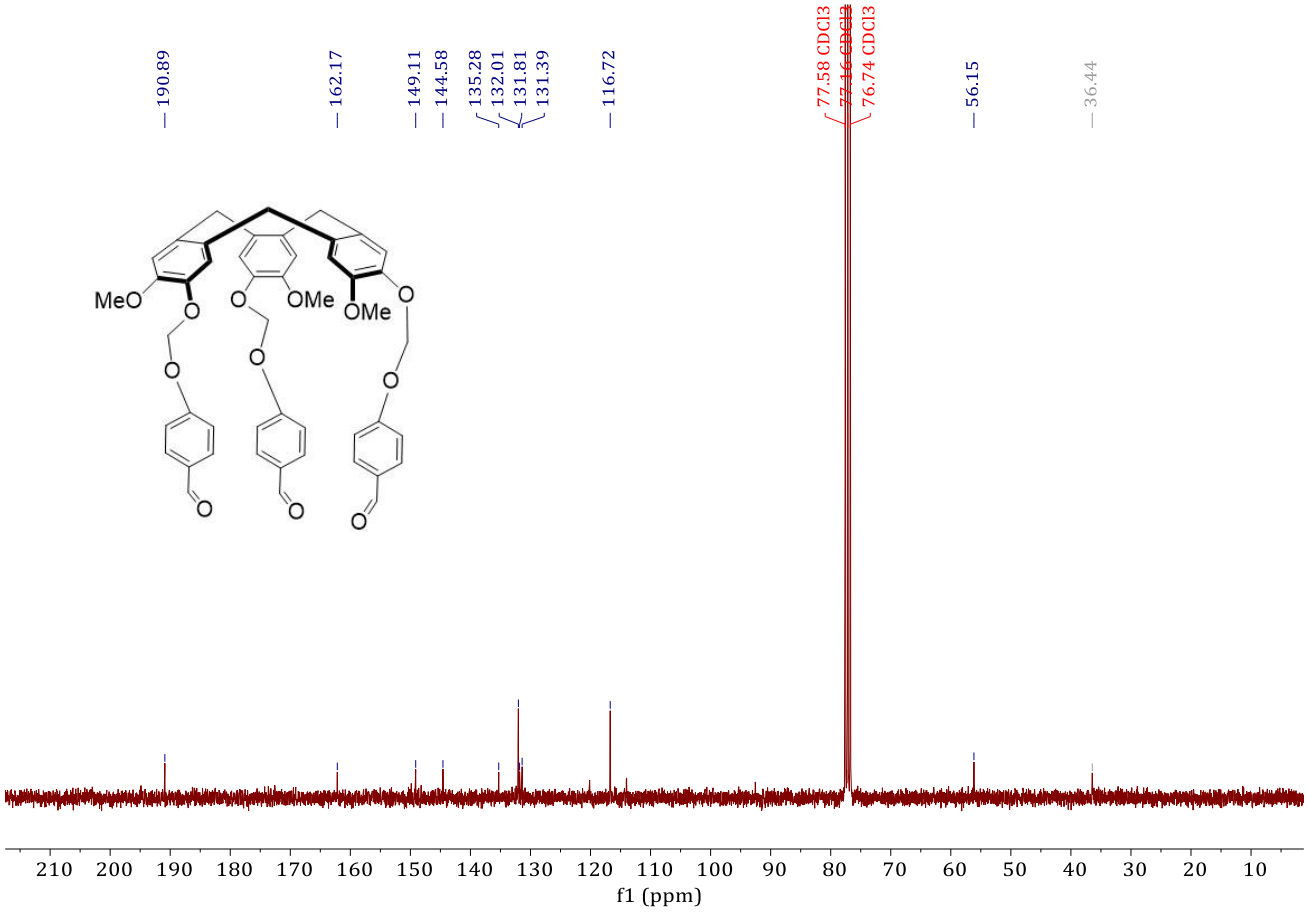


Figure S27 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **5**

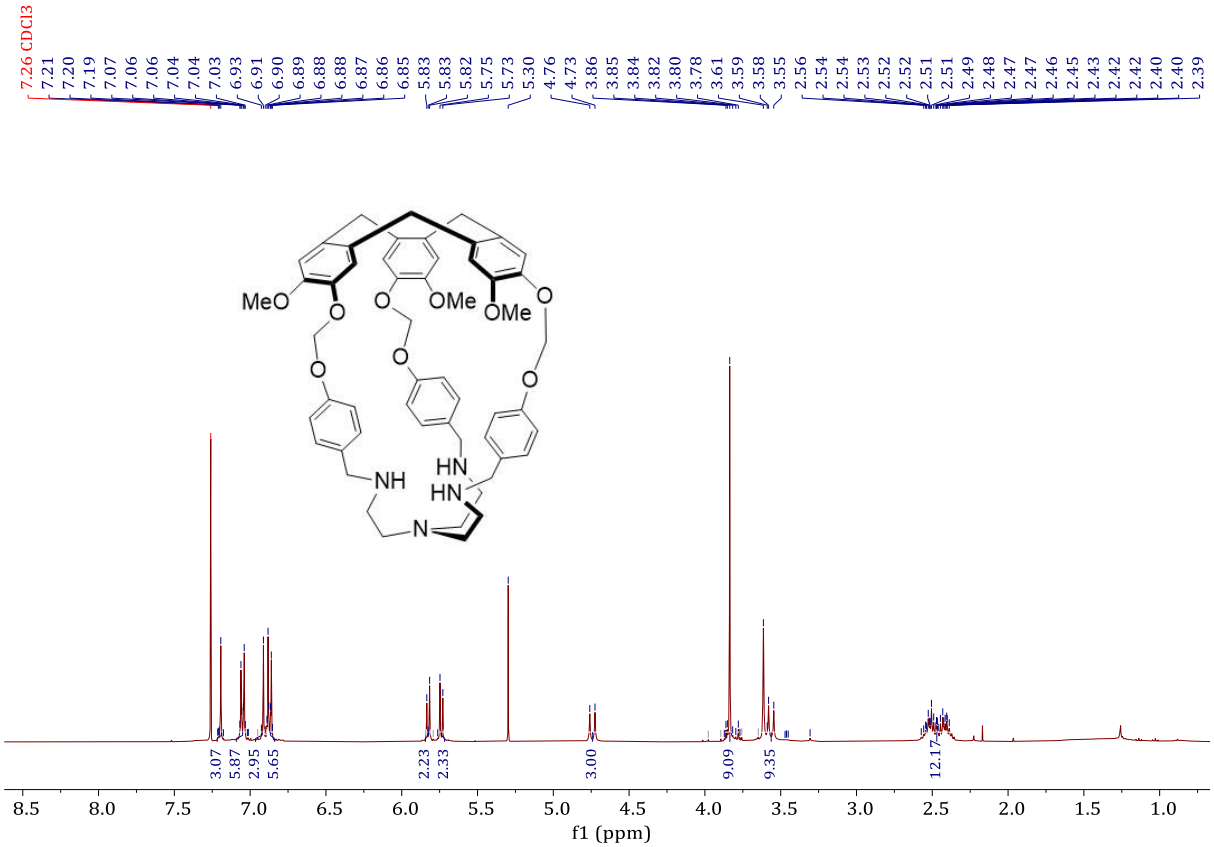


Figure S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of hemicryptophane **2**

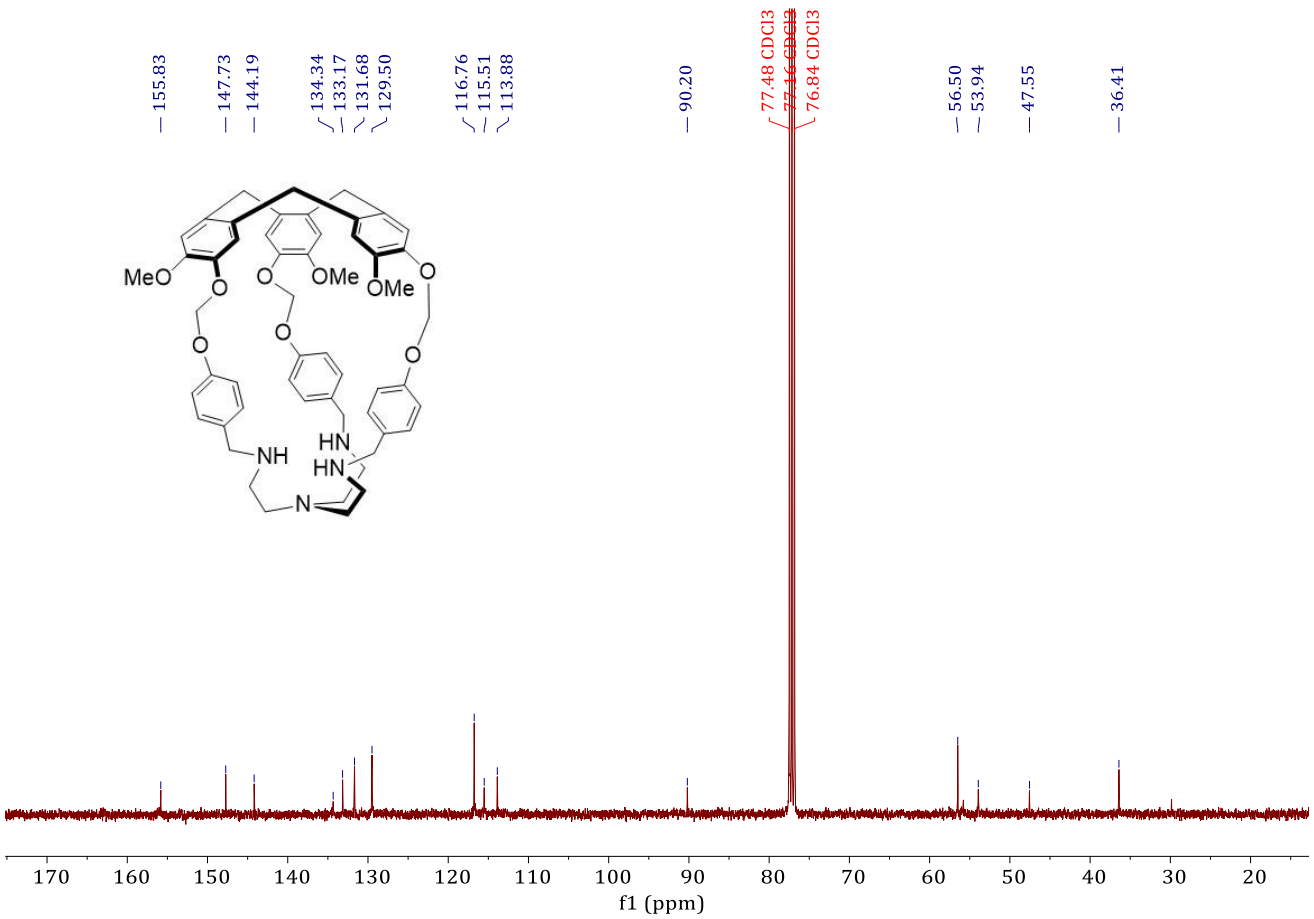


Figure S29 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of hemicryptophane **2**

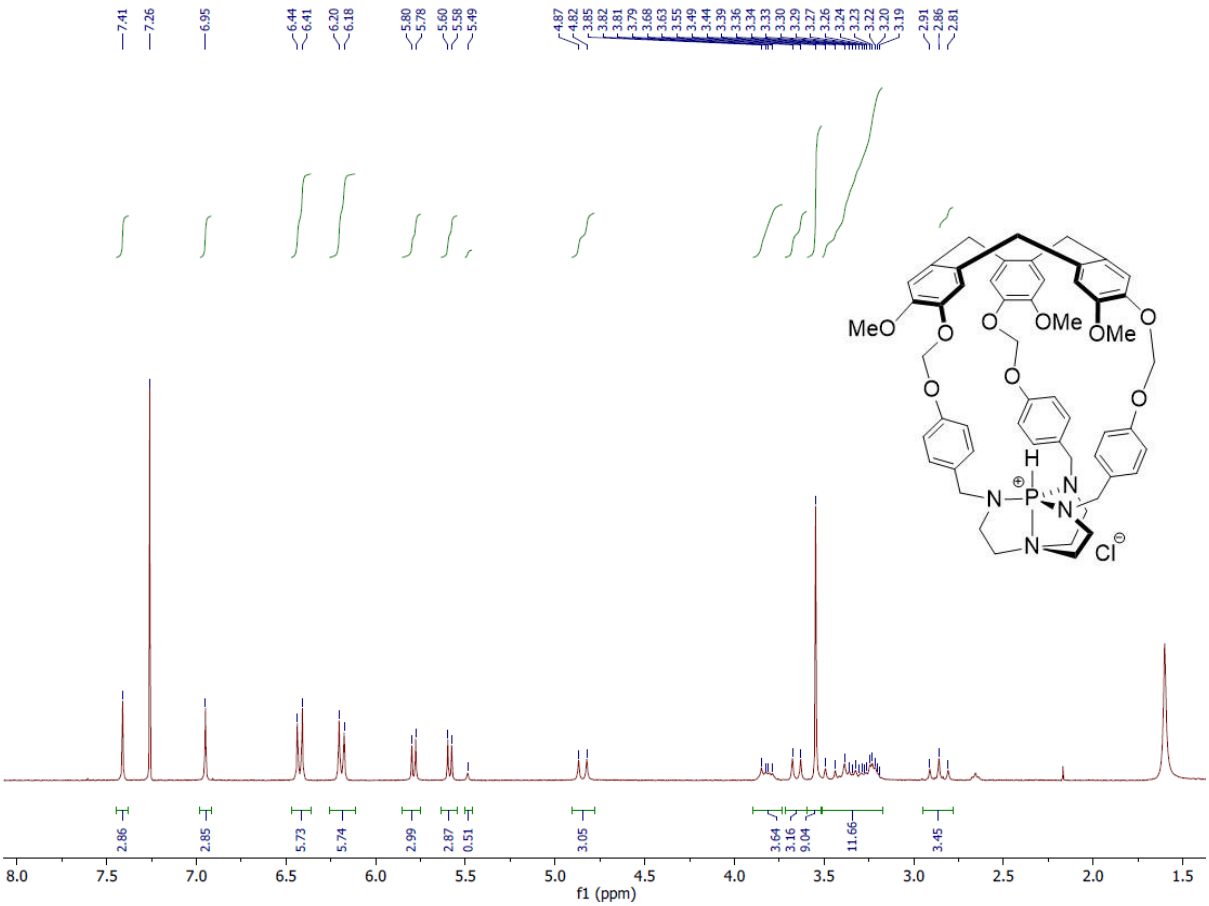


Figure S30 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of PH^{+}@**2**

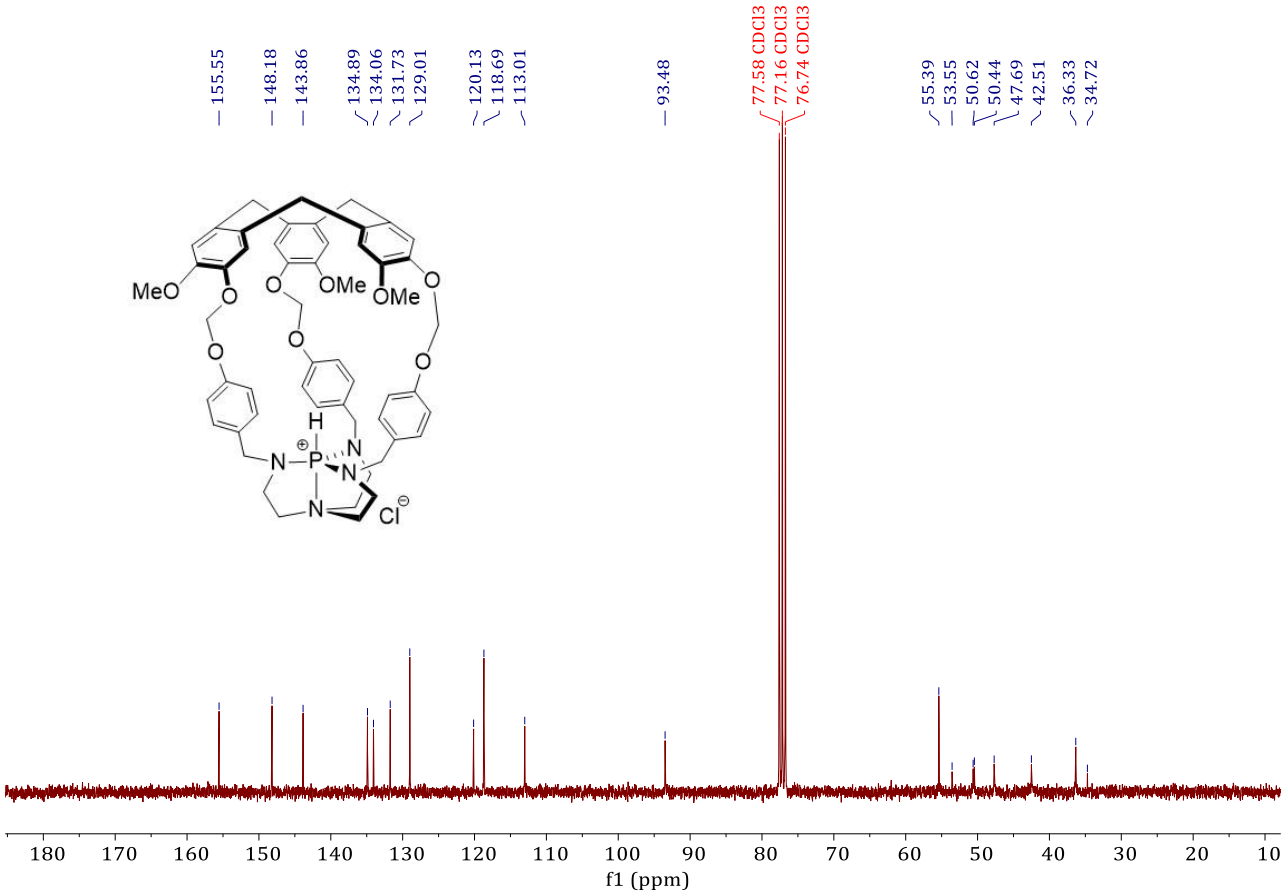


Figure S31 ^{1}C NMR (75 MHz, $CDCl_3$) spectrum of PH^{+}@**2**

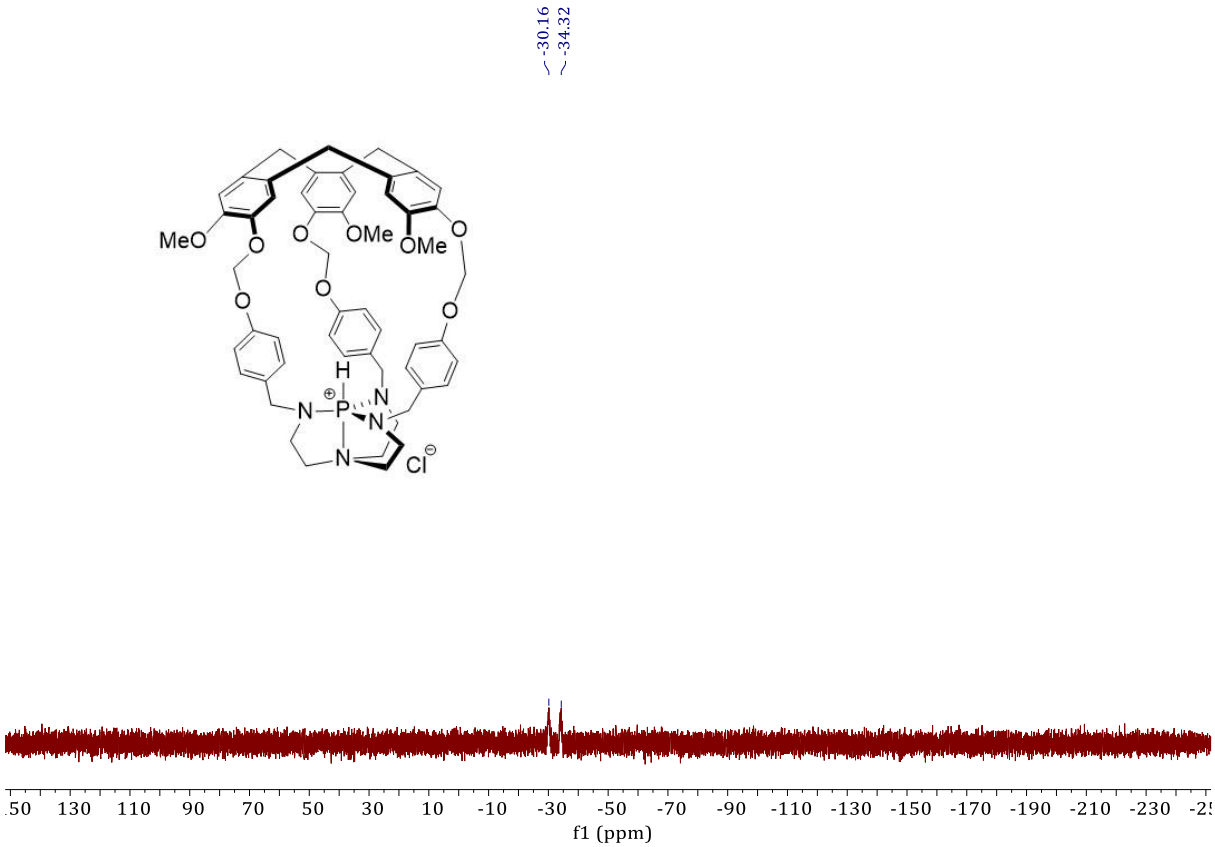


Figure S32 ^{31}P NMR (121 MHz, $CDCl_3$) spectrum of PH^+@**2**

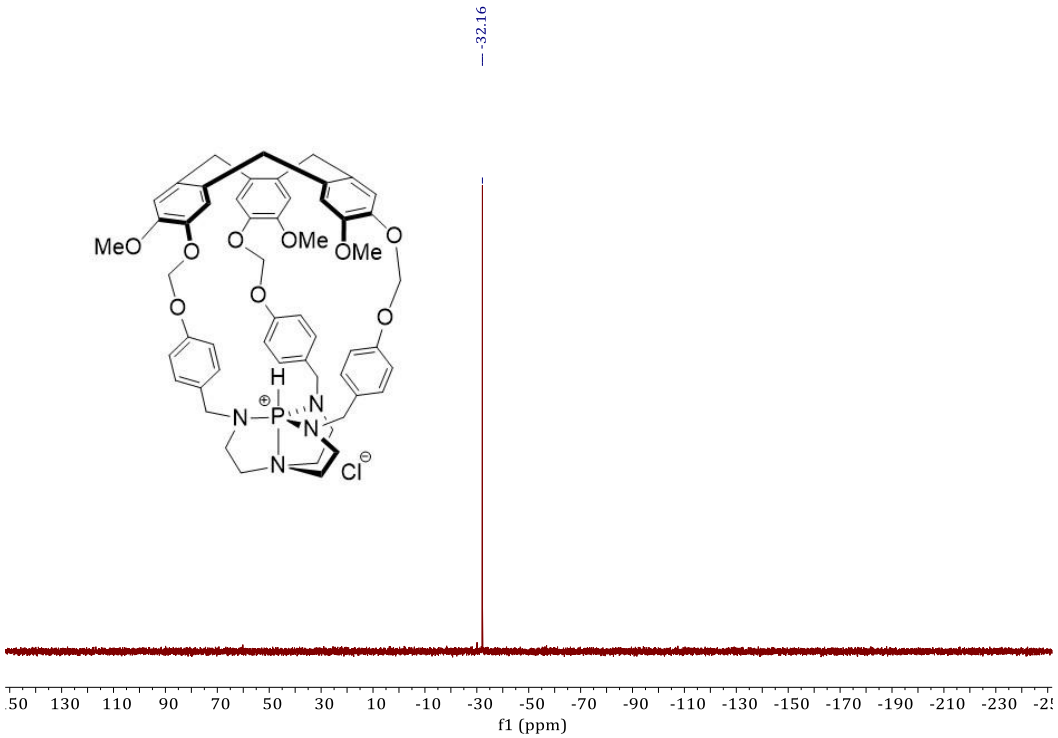


Figure S33 ^{31}P CPD NMR (121 MHz, $CDCl_3$) spectrum of PH^+@**2**

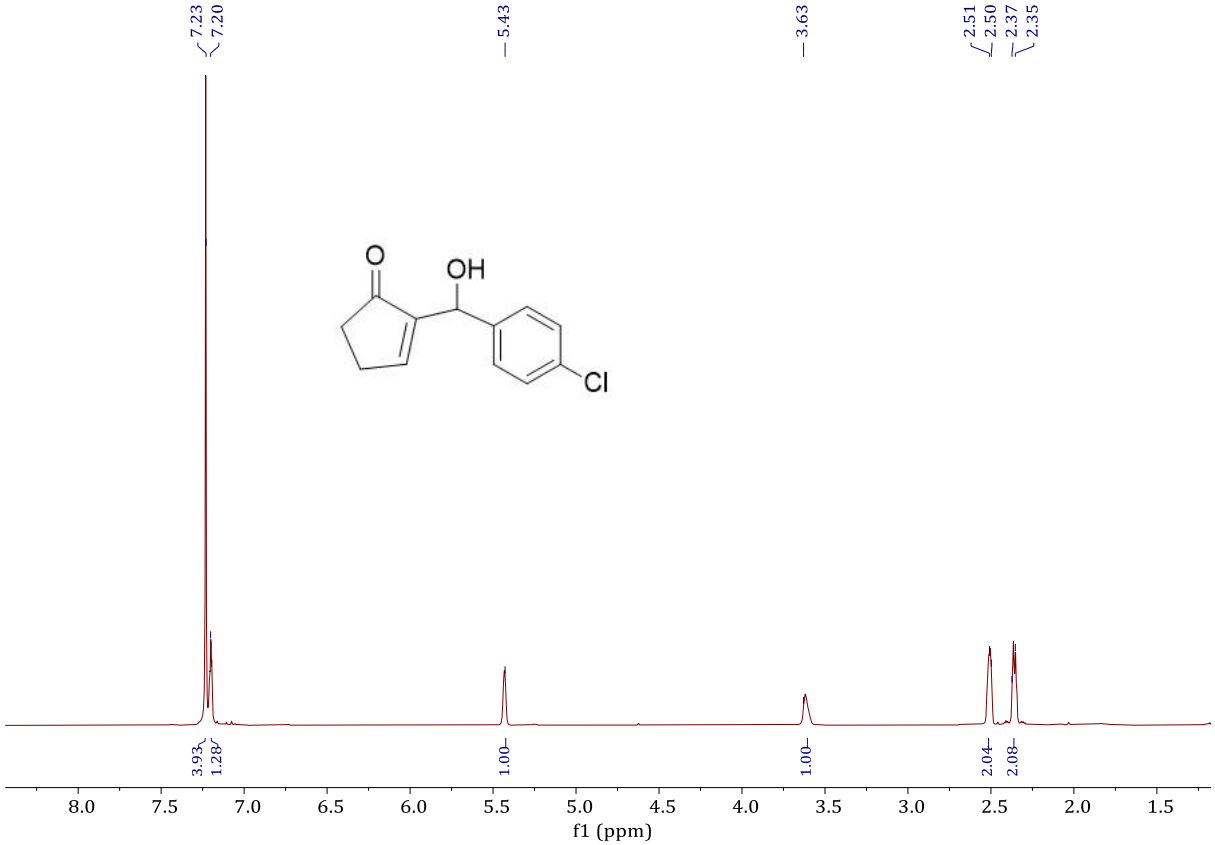


Figure S34 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2-((4-chlorophenyl)(hydroxy)methyl)cyclopent-2-en-1-one**

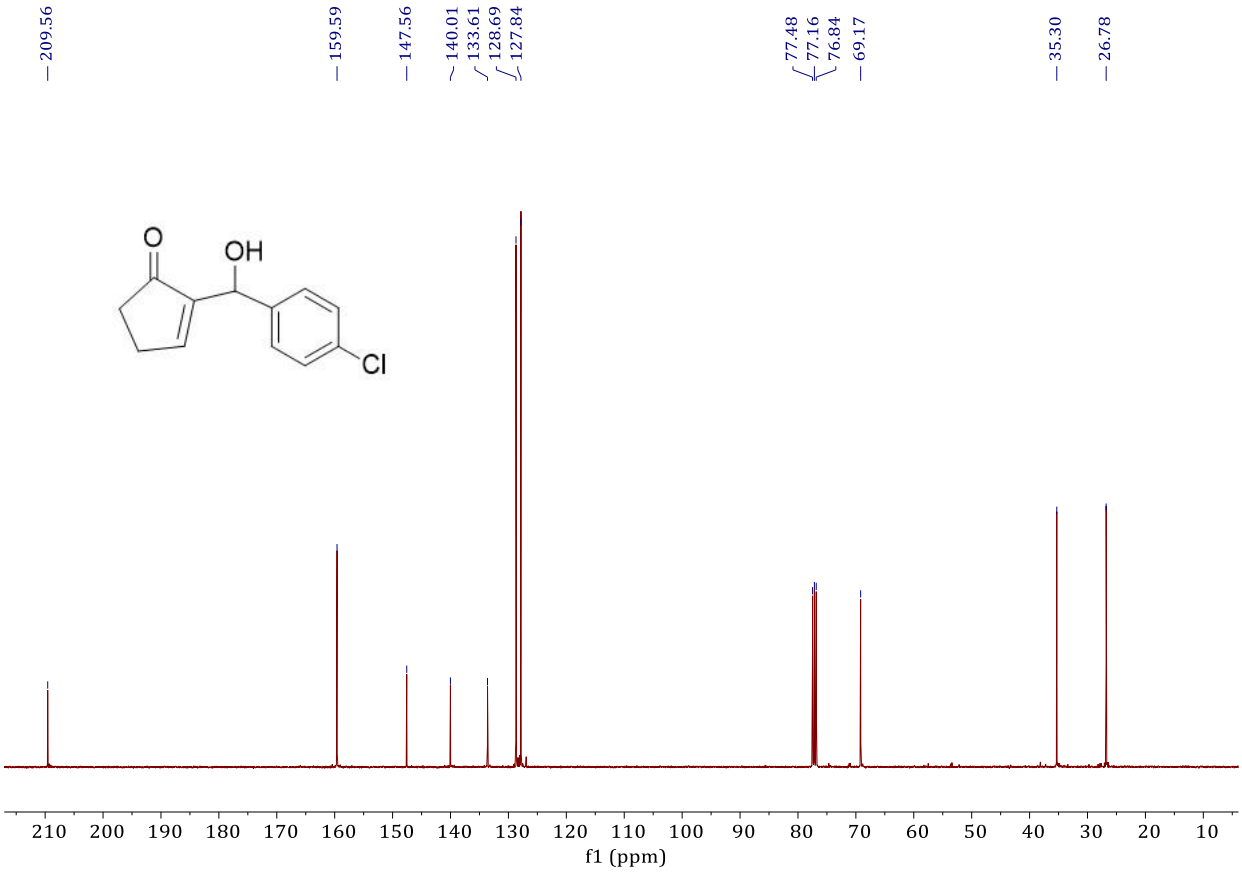


Figure S35 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2-((4-chlorophenyl)(hydroxy)methyl)cyclopent-2-en-1-one**

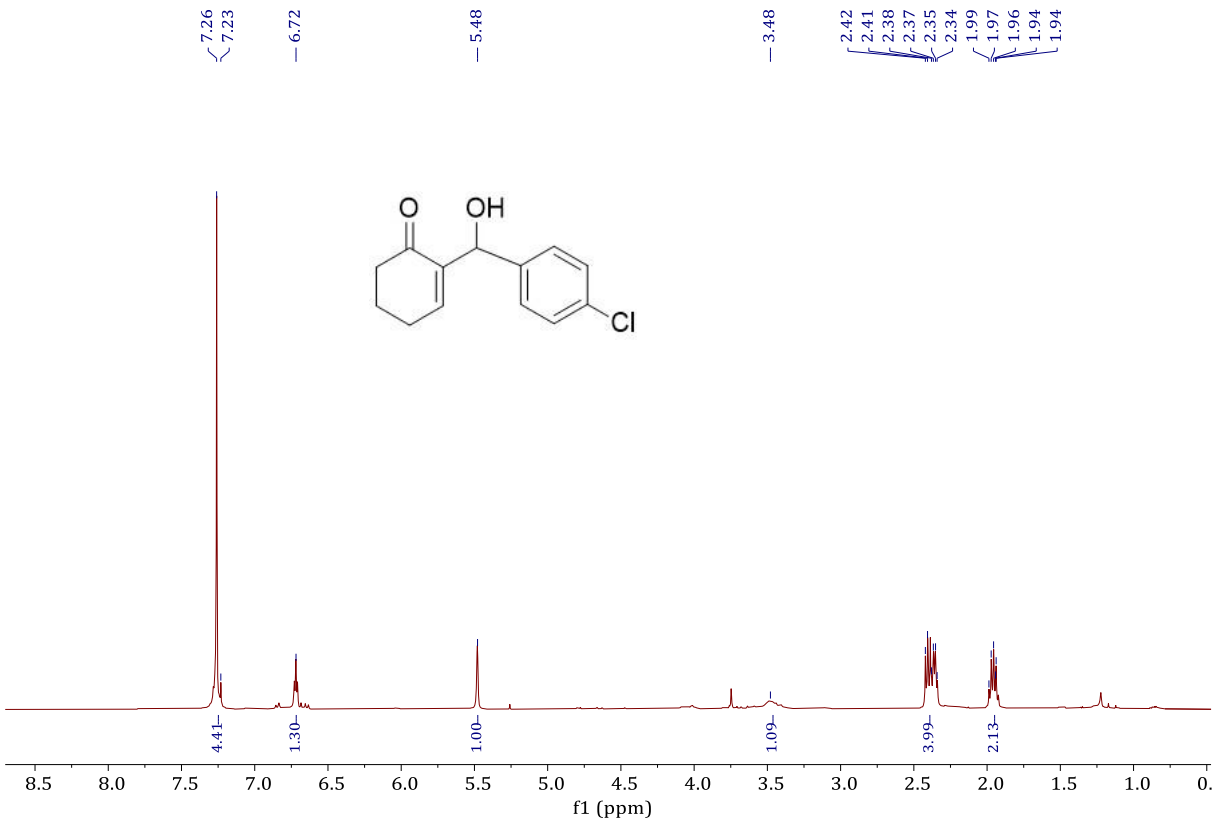


Figure S36 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2-((4-chlorophenyl)(hydroxy)methyl)cyclohex-2-en-1-one**

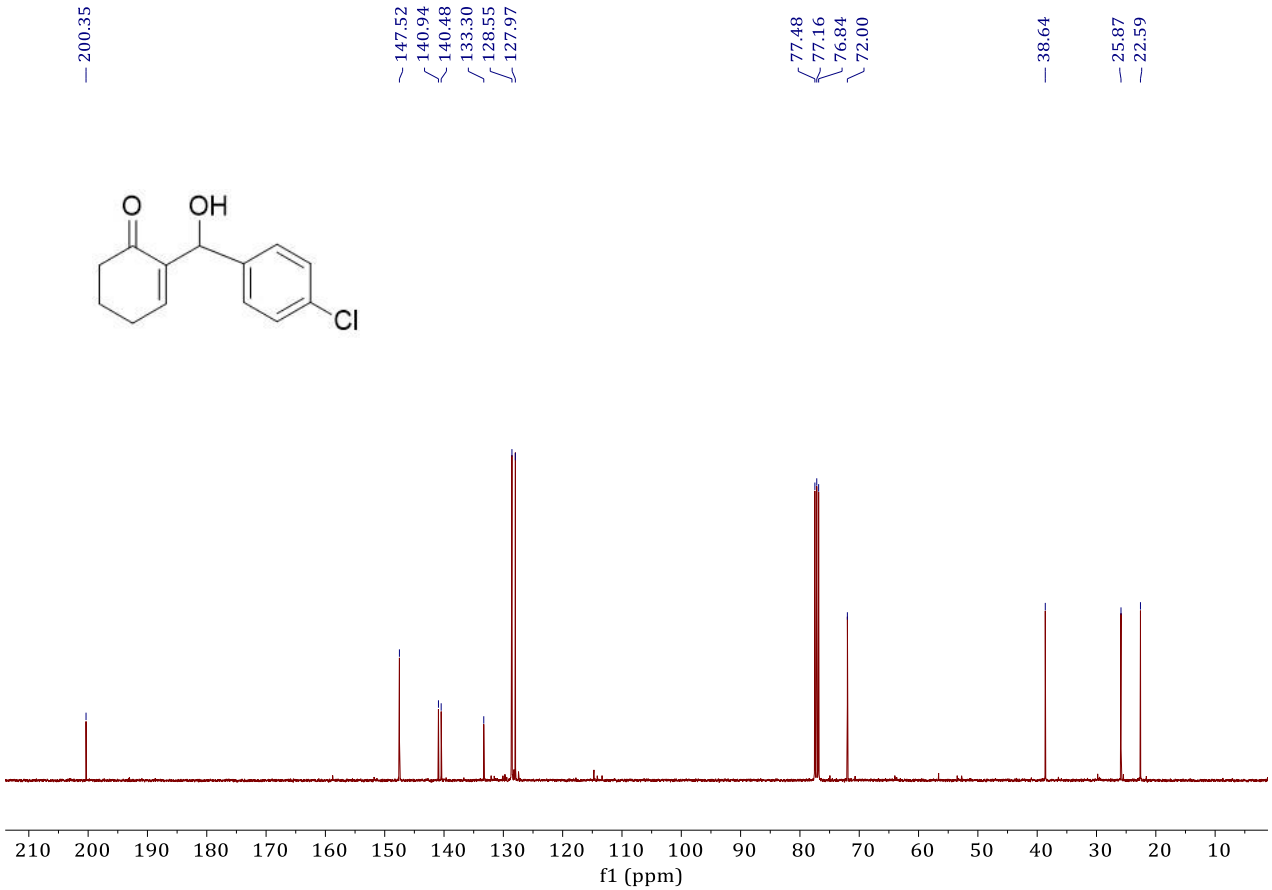


Figure S37 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2-((4-chlorophenyl)(hydroxy)methyl)cyclohex-2-en-1-one**

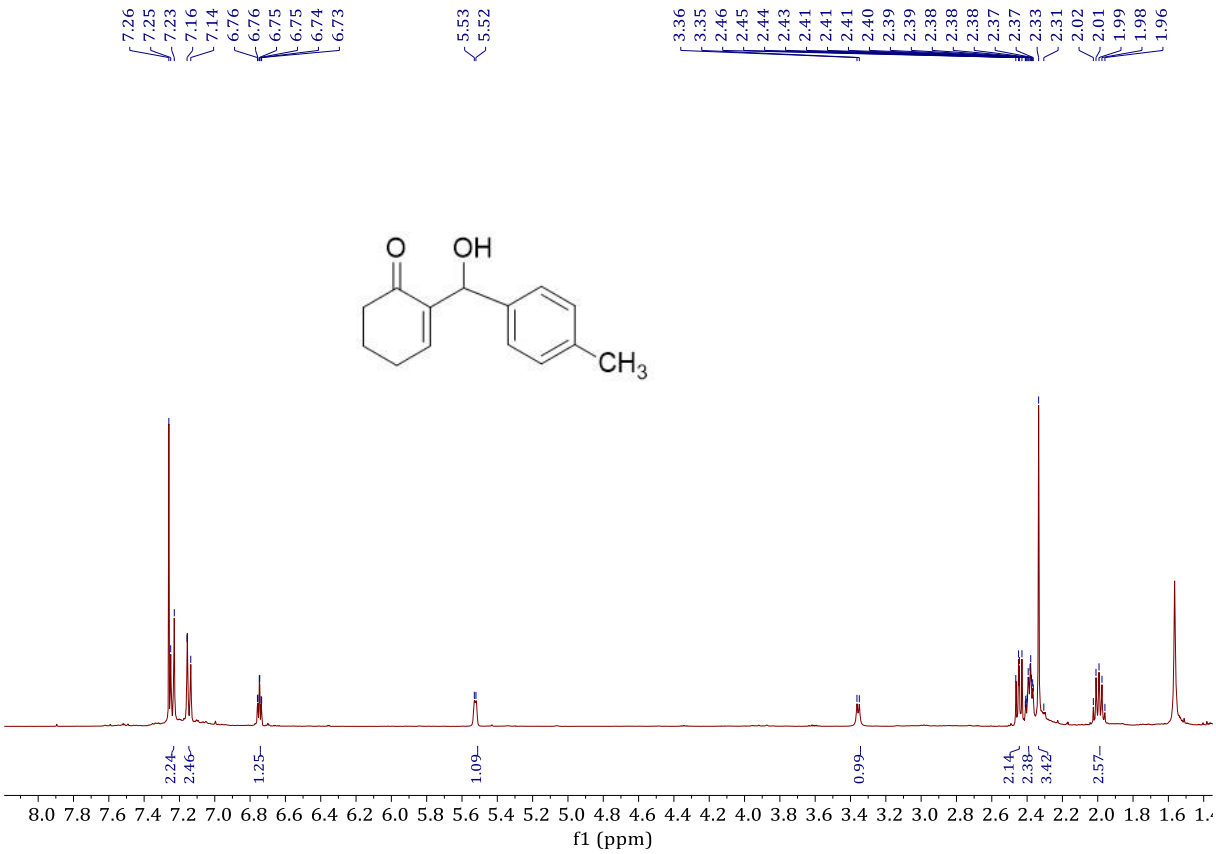


Figure S38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2-(hydroxy(p-tolyl)methyl)cyclohex-2-en-1-one**

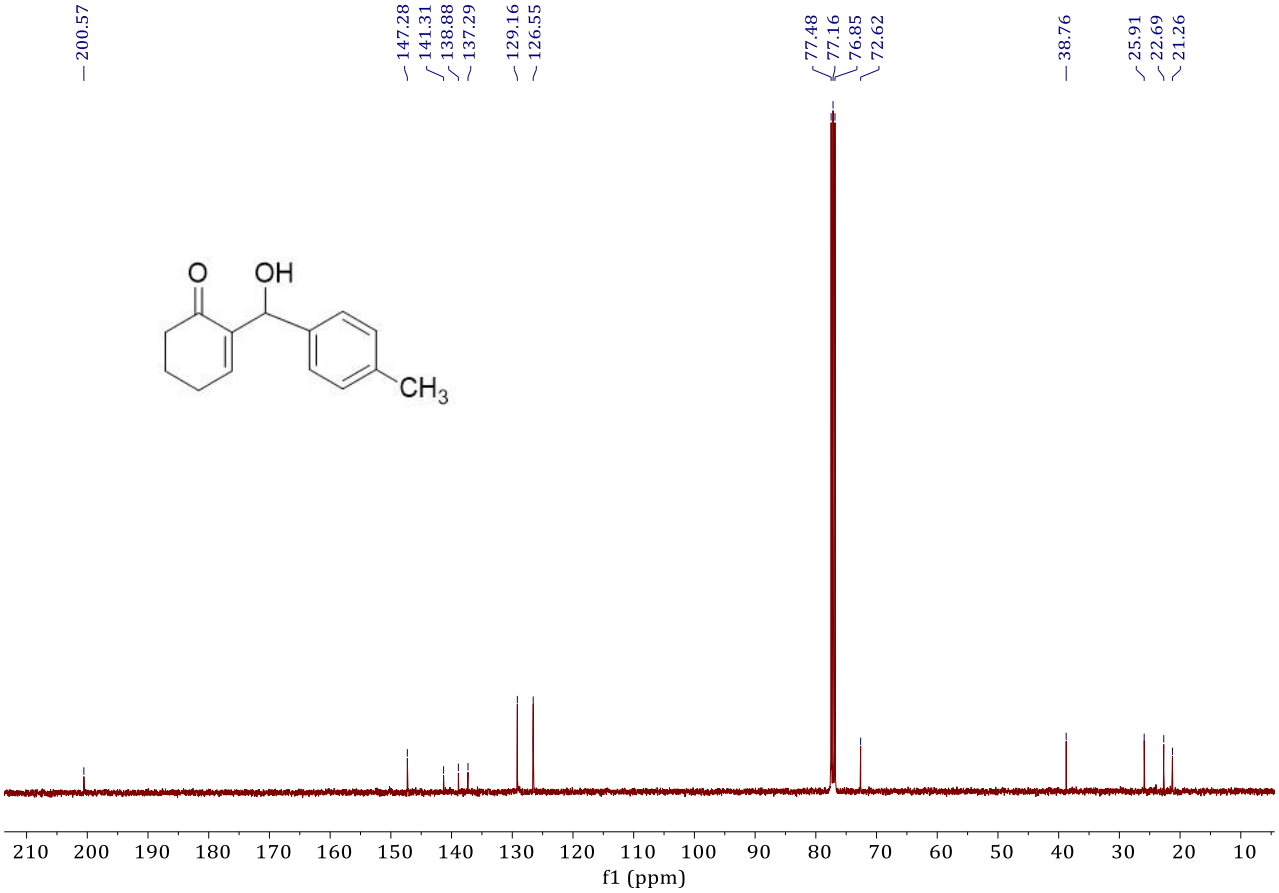


Figure S39 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2-(hydroxy(p-tolyl)methyl)cyclohex-2-en-1-one**

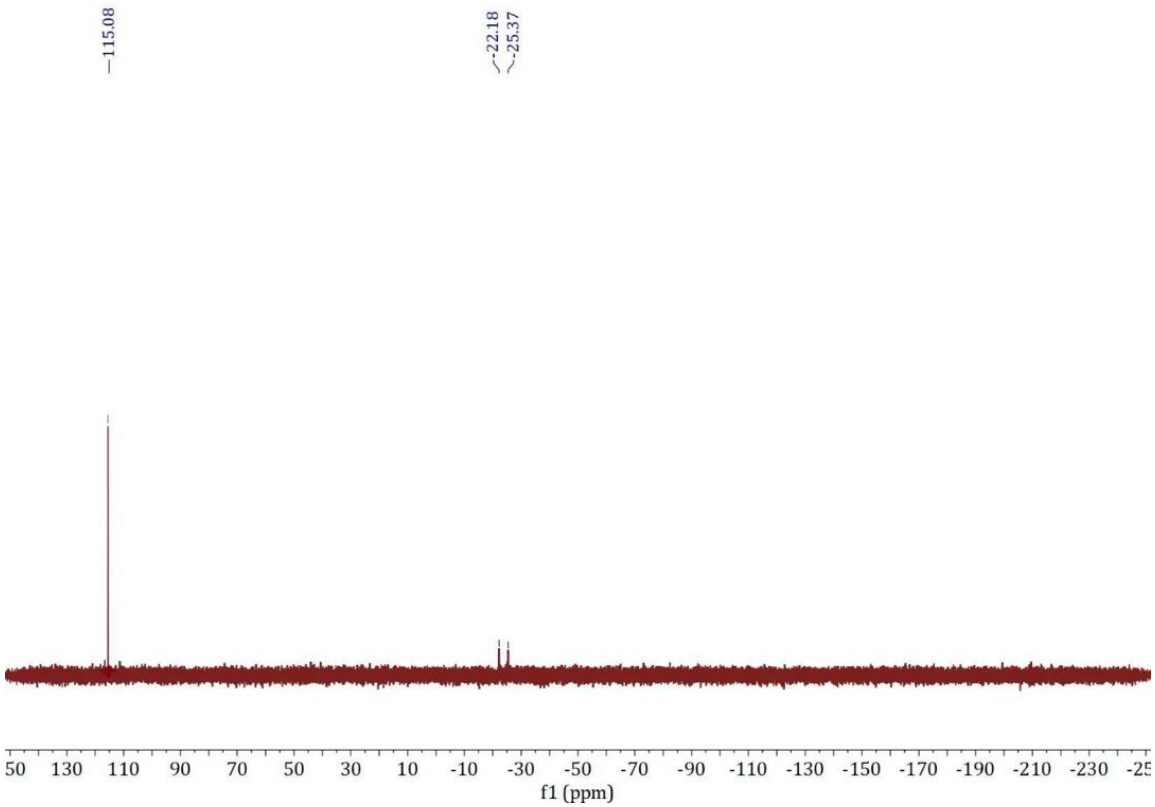


Figure S40 ^{31}P NMR (121 MHz, $CDCl_3$) spectrum of P@**4** with $TiCl_4$

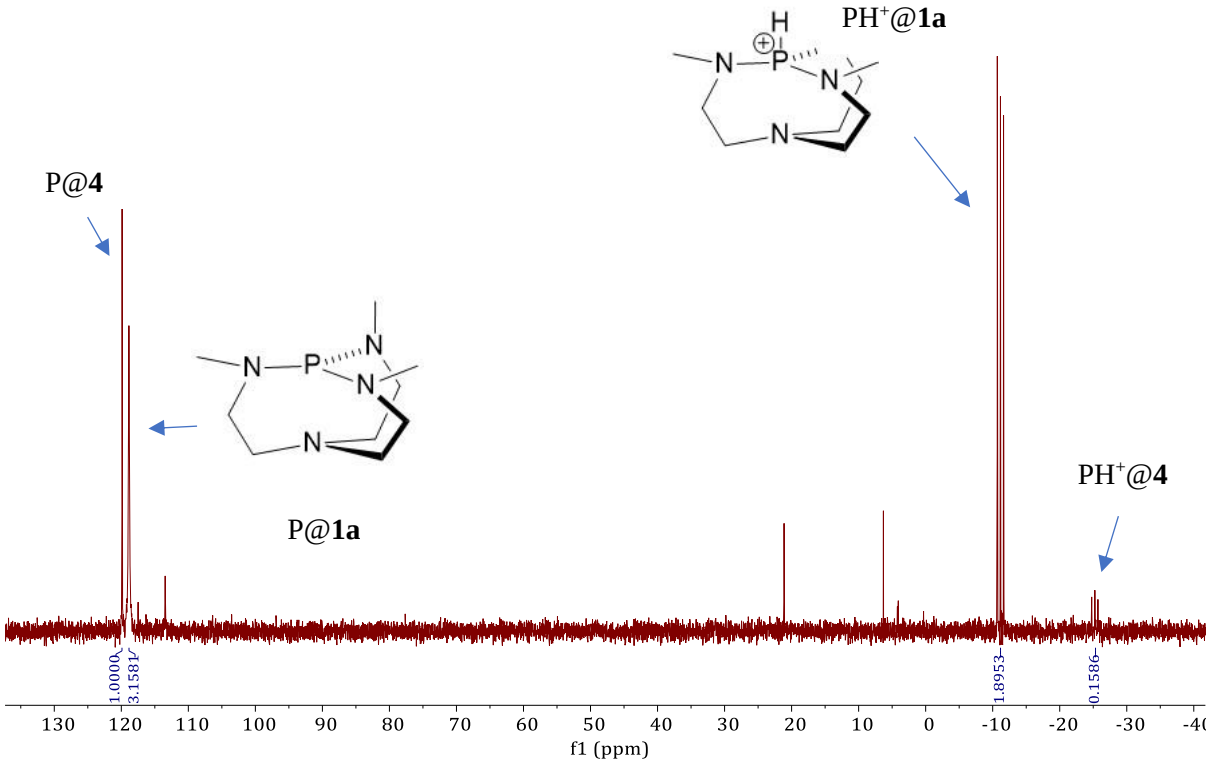


Figure S41 ^{31}P NMR (162 MHz, CD_3CN) spectrum of competition experiment

$$\frac{K_a^{PH^+@\mathbf{3}}}{K_a^{PH^+@\mathbf{1a}}}=\frac{[P@\mathbf{4}][PD^+@\mathbf{1a}]}{[PD^+@\mathbf{4}][P@\mathbf{1a}]}=\frac{1\times1.8953}{0.1586\times3.1581}=3.78$$

with $K_a^{PH^+@\mathbf{1a}}=1.26\times10^{-33}$

$K_a^{PH^+@\mathbf{4}}=4.77\times10^{-33}$

V / Kinetics experiment

Rate constants of proton exchange of P@4

$$PH^+@\mathbf{4} \quad + \quad CNCD_2^- \overset{k_1/k_{-1}}{\Longleftrightarrow} \quad P@\mathbf{4} \quad + \quad CNCHD_2 \qquad (1)$$

$$P@\mathbf{4} \quad + \quad CNCD_3 \overset{k_2/k_{-2}}{\Longleftrightarrow} \quad PD^+@\mathbf{4} \quad + \quad CNCD_2^- \qquad (2)$$

$$-\frac{d([PH^+@\mathbf{4}])}{dt} = k_1[PH^+@\mathbf{4}][CD_2CN^-] = +\frac{d([P@\mathbf{4}])}{dt}$$

$$\frac{d\left(\frac{[P@\mathbf{4}]}{[PH^+@\mathbf{4}]}\right)}{dt} = \frac{\frac{d[P@\mathbf{4}]}{dt}[PH^+@\mathbf{4}] - \frac{d[PH^+@\mathbf{4}]}{dt}[P@\mathbf{4}]}{([PH^+@\mathbf{4}])^2}$$

$$= k_1[CD_2CN^-] + \frac{k_1[CD_2CN^-][P@\mathbf{4}]}{[PH^+@\mathbf{4}]}$$

$$= k_1[CD_2CN^-]\left(1 + \frac{[P@\mathbf{4}]}{[PH^+@\mathbf{4}]}\right)$$

$$with \quad [CD_2CN^-] = \frac{K_e}{K_a^{PH^+@\mathbf{1a}}}\frac{[P@\mathbf{1a}]}{[PH^+@\mathbf{1a}]}$$

$$\rightarrow \frac{d\left(\frac{[P@\mathbf{4}]}{[PH^+@\mathbf{4}]}\right)}{dt} = \frac{k_1 K_e}{K_a^{PH^+@\mathbf{1a}}} \times \frac{[P@\mathbf{1a}](1+[P@\mathbf{4}]/[PH^+@\mathbf{4}])}{[PH^+@\mathbf{1a}]}$$

$$and \qquad k_{-1} = \frac{K_e k_1}{K_a^{PH^+@\mathbf{4}}}$$

	t(min)	[P@**4**]	[PH$^+$@**4**]	[PH$^+$@**1a**]	[P@**1a**]	[P@**4**]/[PH$^+$@**4**]	d([P@**4**]/[PH$^+$@**4**])/dt	(1+[P@**4**]/[PH$^+$@**4**])	[PH$^+$**1a**]/[P@**1a**]	$k_1K_e/K_a^{PH^+@1a}$
1	0	0.8791	5.1547	3.3261	18.0362	0.170543388	-	1.170543388	0.184412459	-
2	30	1.0141	7.6105	5.4794	27.5649	0.133250115	0.000781901	1.133250115	0.198781784	0.000137152
3	60	0.0715	0.3288	0.263	1.2295	0.217457421	0.001361967	1.217457421	0.213908093	0.000239299
4	90	0.0675	0.314	0.2787	1.2281	0.214968153	0.000773014	1.214968153	0.226935917	0.000144386
5	120	0.0796	0.3017	0.2875	1.2192	0.26383825	0.001394787	1.26383825	0.235810367	0.000260243
6	150	0.0844	0.2826	0.2977	1.1809	0.298655343	0.001481176	1.298655343	0.252095859	0.000287527
7	180	1.8574	5.2661	5.7805	23.0259	0.352708836	0.001344158	1.352708836	0.25104339	0.000249456
8	210	1.8955	4.9973	5.8713	22.0822	0.379304825	0.001005577	1.379304825	0.265883834	0.000193842
9	240	0.1045	0.253	0.3176	1.1688	0.413043478	0.001711783	1.413043478	0.271731691	0.00032918
10	270	2.2723	4.7142	6.1381	21.9193	0.482011794	0.002335643	1.482011794	0.280031753	0.000441329
11	300	2.2478	4.0634	5.8139	20.0513	0.553182064	0.001052017	1.553182064	0.289951275	0.000196393
12	330	2.1566	3.9561	5.9179	19.8868	0.545132833	0.001394391	1.545132833	0.297579299	0.000268548
13	360	2.547	3.9994	6.2663	20.2325	0.636845527	0.00162535	1.636845527	0.309714568	0.00030754
14	390	2.1678	3.3732	5.6442	17.9871	0.64265386	0.00125138	1.64265386	0.313791551	0.000239048
15	420	0.151	0.2121	0.3646	1.1543	0.711928336	0.00142173	1.711928336	0.315862427	0.000262319
16	450	2.3093	3.1723	5.7199	17.8746	0.727957633	0.001933399	1.727957633	0.320001566	0.000358047
17	480	2.6647	3.2185	6.267	18.9661	0.827932267	0.002488504	1.827932267	0.330431665	0.000449842
18	510	0.1644	0.1874	0.3737	1.1224	0.877267876	0.00232931	1.877267876	0.332947256	0.00041312
19	540	2.8723	2.9682	6.1574	18.2002	0.967690856	0.002008543	1.967690856	0.338314964	0.000345339
20	570	2.8771	2.8835	6.2613	18.1298	0.997780475	0.001347088	1.997780475	0.345359574	0.000232873
21	600	2.9219	2.7867	6.3152	18.0553	1.048516166	0.002732266	2.048516166	0.349769874	0.000466515
22	630	3.043	2.6194	6.2539	17.2318	1.161716424	0.001425204	2.161716424	0.362927843	0.000239276
23	660	2.991	2.6375	6.5362	18.0737	1.134028436	0.002910767	2.134028436	0.361641501	0.000493271
24	690	3.0441	2.2779	5.9077	16.0721	1.336362439	0.003806461	2.336362439	0.367574866	0.000598862
26	750	2.8877	2.2432	6.2449	16.8988	1.287312767	0.001059781	2.287312767	0.36954695	0.000171222
27	780	3.0853	2.1636	6.0147	16.1186	1.426002958	0.003658205	2.426002958	0.373152755	0.000562682
28	810	3.0778	2.0426	6.2022	15.9919	1.506805052	0.001054464	2.506805052	0.387833841	0.000163139
29	840	2.9635	1.9899	6.3054	16.0508	1.489270818	0.002360166	2.489270818	0.392840232	0.000372466

Table S2 Proton transfer kinetic data between PH$^+$@**4** and P@**4 (**P@**1a** as monitor**)**

$$\text{Defining} \qquad X_i=\frac{k_1K_e}{K_a^{PH^+@\mathbf{1a}}} \quad (i=1,2,3,\ldots,29.)$$

$$so \qquad \sum_{i=1}^{29} X_i = 0.008422915 \qquad X = 0.00031196$$

According to

$$\frac{d\left(\frac{[P@\mathbf{4}]}{[PH^+@\mathbf{4}]}\right)}{dt}=\frac{k_1K_e}{K_a^{PH^+@\mathbf{1a}}}\times\frac{[P@\mathbf{1a}](1+[P@\mathbf{4}]/[PH^+@\mathbf{4}])}{[PH^+@\mathbf{1a}]}$$

$$\frac{k_1K_e}{K_a^{PH^+@\mathbf{1a}}}=\frac{X}{60}=5.2\times10^{-6}\ \text{L.mol}^{-1}.\text{s}^{-1}$$

with $K_e=10^{-32.2}$ $K_a^{PH^+}@\mathbf{4}=4.77\times10^{-33}$

$k_1=1.04\times10^{-6}$ L.mol^{-1}.s^{-1}

$k_{-1}=1.37\times10^{-6}$ L.mol^{-1}.s^{-1}

VI/ Mass spectra

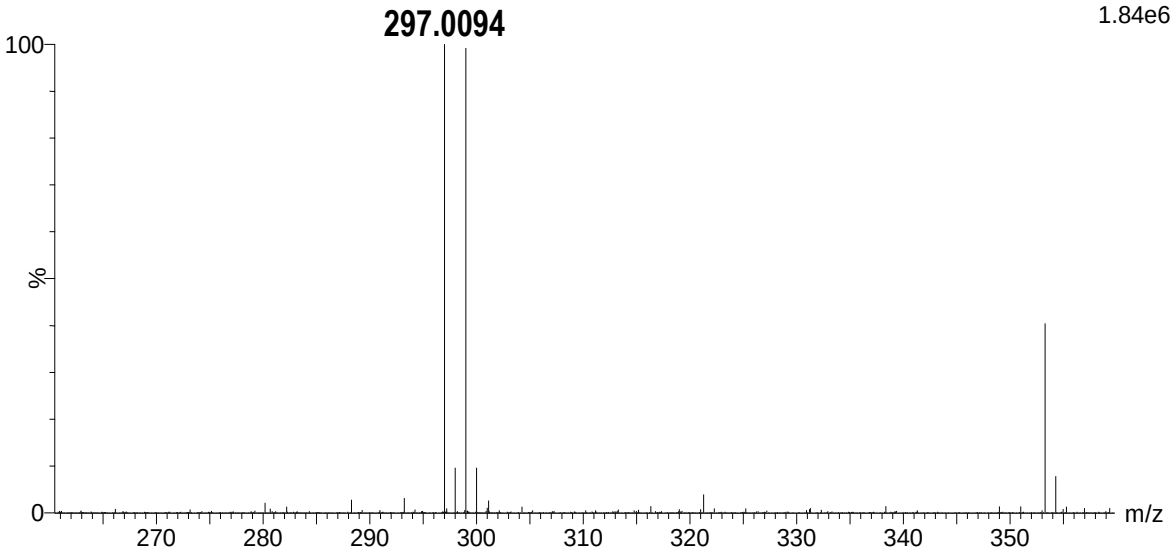


Figure S42 Positive ESI-HRMS spectra of **8**: *m/z* $[M+Na]^+$ calcd for $C_{11}H_{15}BrO_3$, 297.0097; found at 297.0094

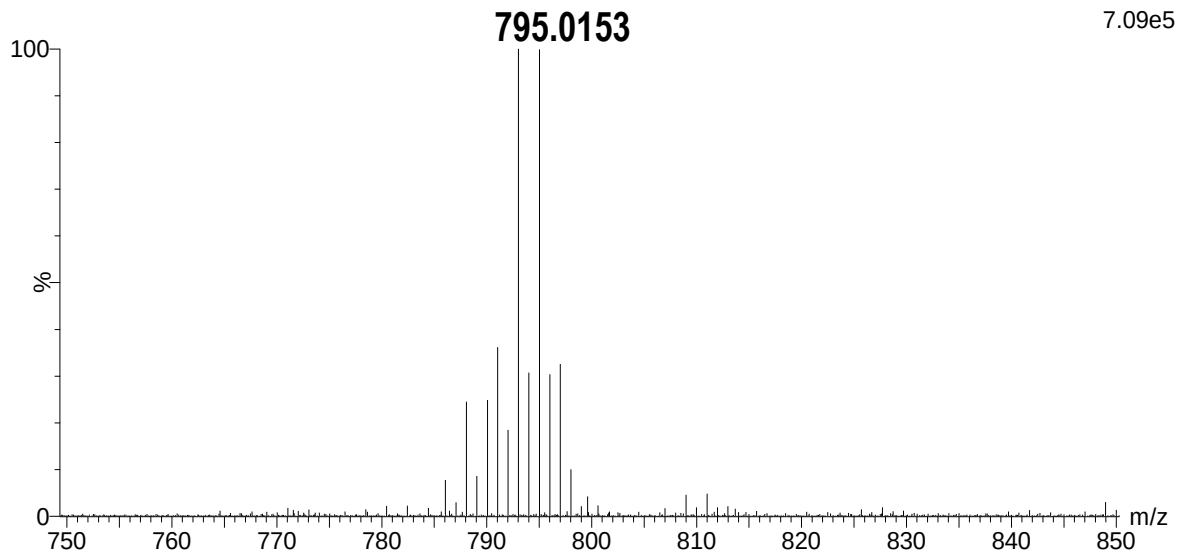


Figure S43 Positive ESI-HRMS spectra of **9**: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{39}Br_3O_6$, 795.0154; found at 795.0153

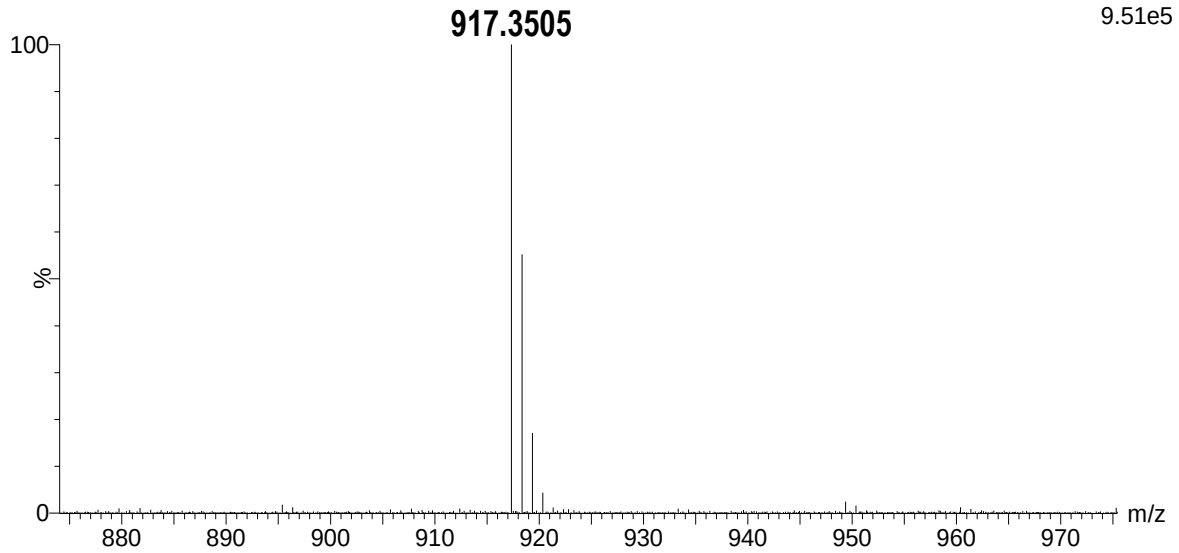


Figure S44 Positive ESI-HRMS spectra of **7**: *m/z* $[M+Na]^+$ calcd for $C_{54}H_{54}O_{12}$, 917.3507; found at 917.3505

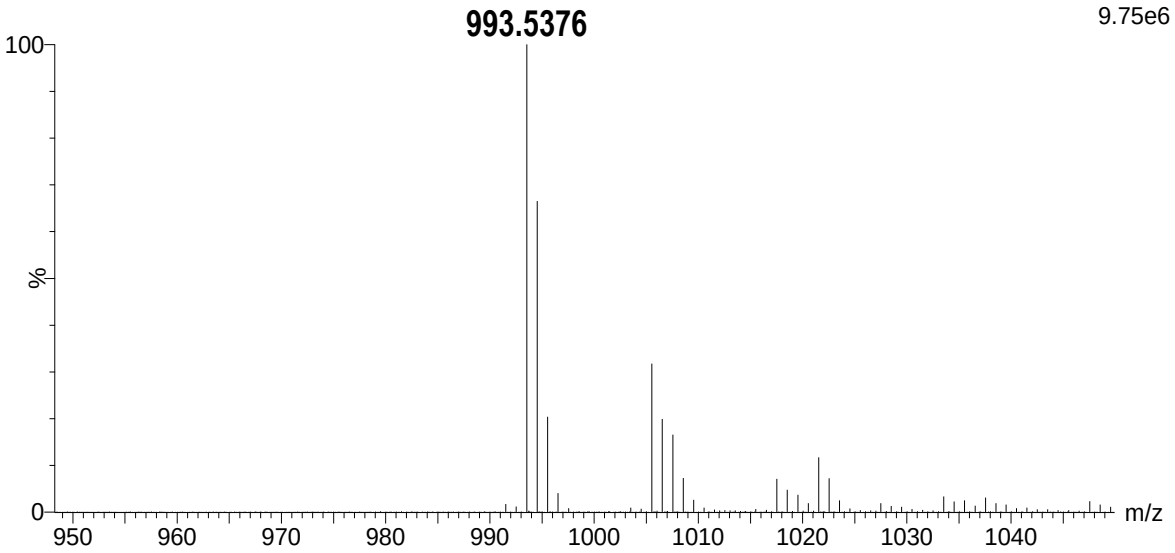


Figure S45 Positive ESI-HRMS spectra of hemicryptophane **4**: *m/z* $[M+H]^+$ calcd for $C_{60}H_{72}N_4O_{9,}$ 993.5372; found at 993.5376

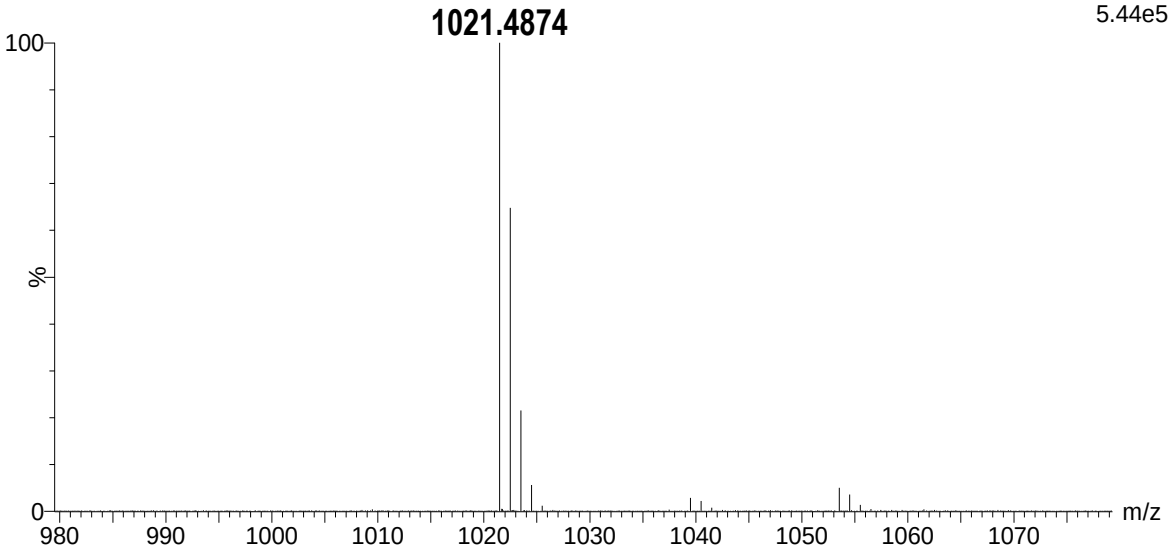


Figure S46 Positive ESI-HRMS spectra of $\mathbf{P}H^+$@**4**: *m/z* $[M]^+$ calcd for $C_{60}H_{70}N_4O_9P^+$, 1021.4875; found at 1021.4874

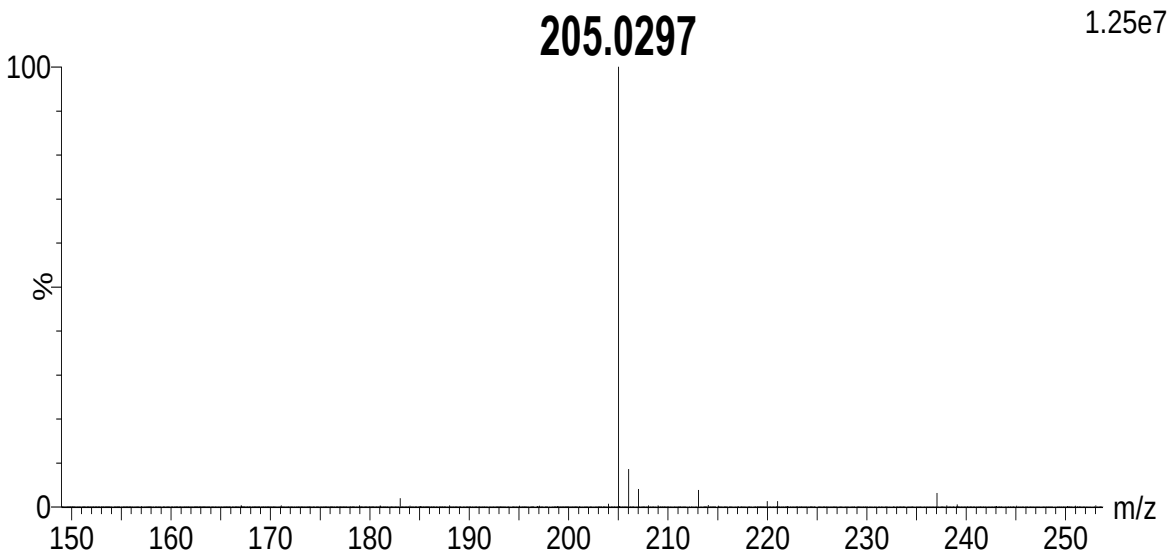


Figure S47 Positive ESI-HRMS spectra of **10**: *m/z* $[M+Na]^+$ calcd for $C_9H_{10}O_2S$, 205.0294; found at 205.0297

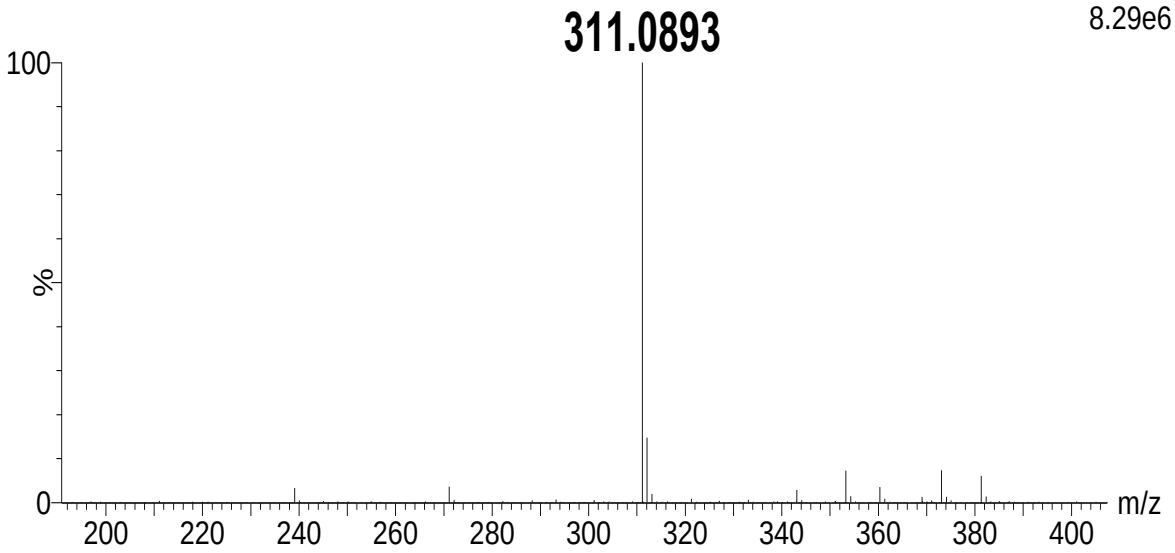


Figure S48 Positive ESI-HRMS spectra of **12**: *m/z* $[M+Na]^+$ calcd for $C_{16}H_{16}O_5$, 311.0890; found at 311.0893

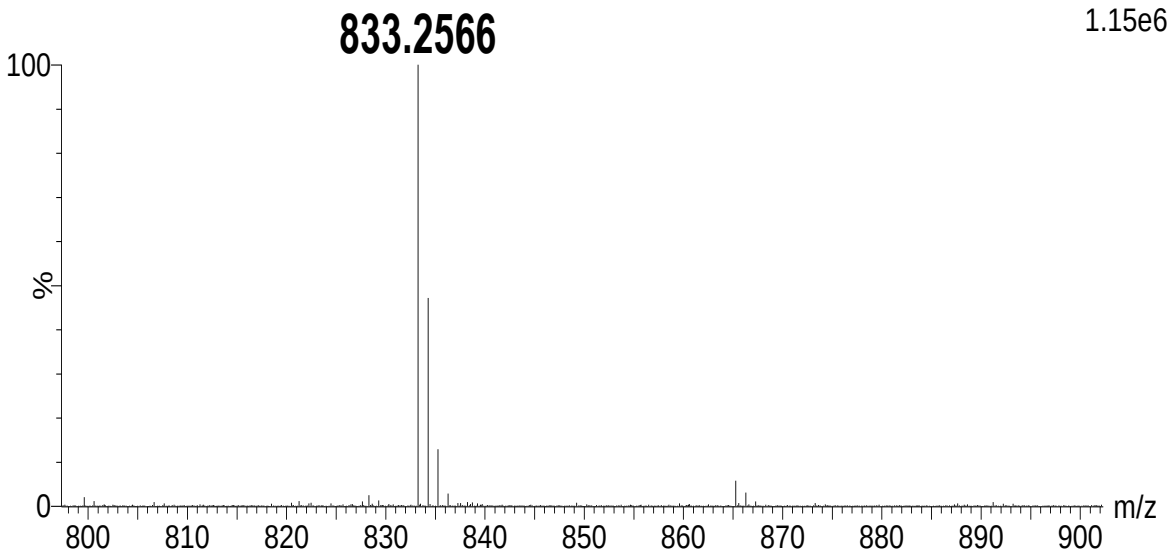


Figure S49 Positive ESI-HRMS spectra of **5**: *m/z* $[M+Na]^+$ calcd for $C_{48}H_{42}O_{12,}$ 833.2568; found at 833.2566

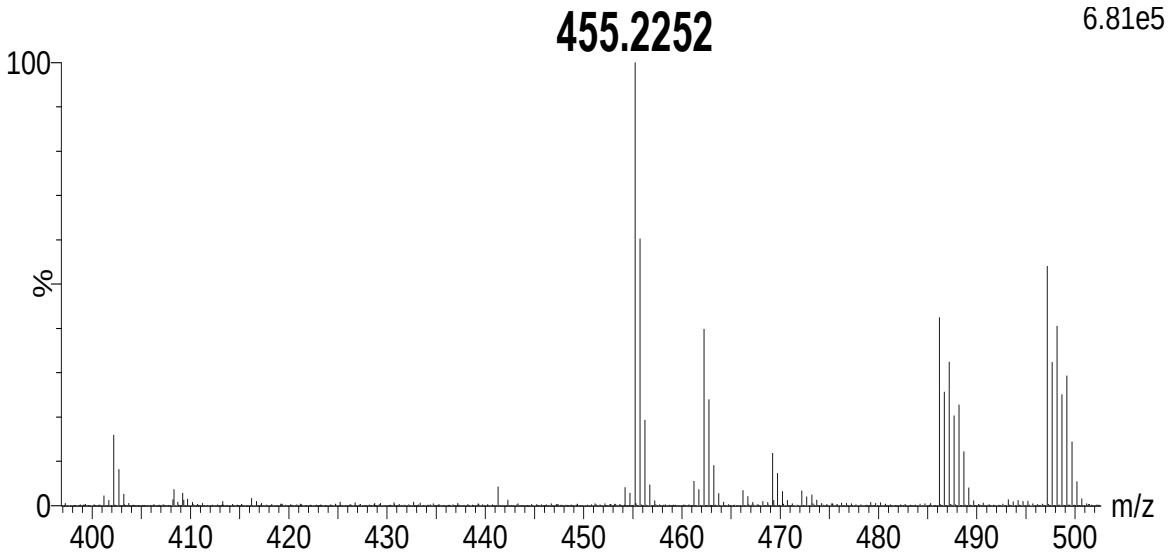


Figure S50 Positive ESI-HRMS spectra of hemicryptophane **2**: *m/z* $[M+2H]^+$ calcd for $C_{54}H_{60}N_4O_{9,}$ 455.2253; found at 455.2252

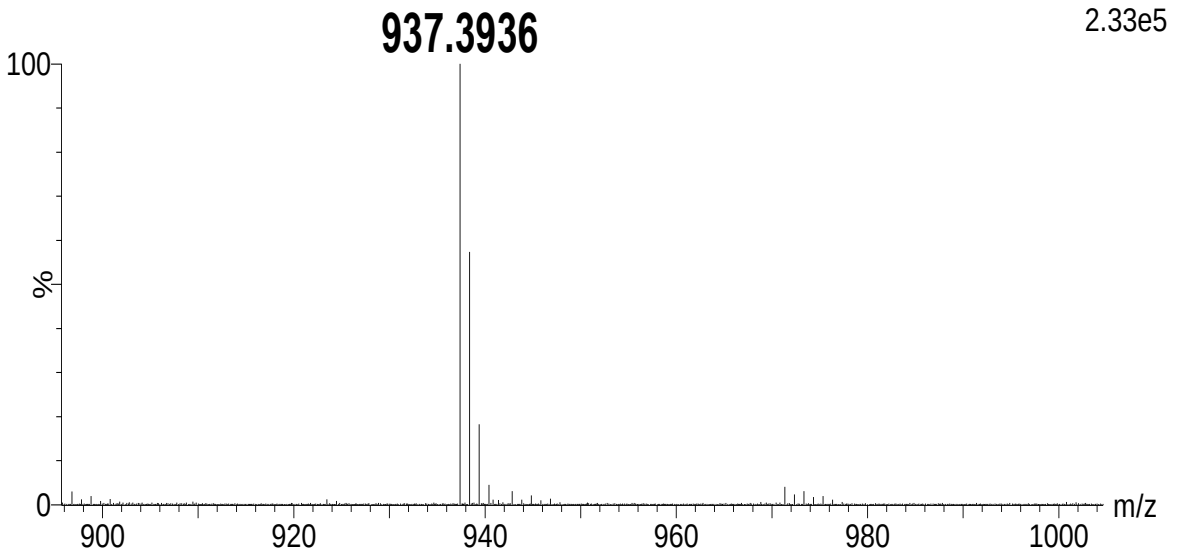


Figure S51 Positive ESI-HRMS spectra of **P**H^+@**2**: *m/z* $[M+Na]^+$ calcd for $C_{54}H_{58}N_4O_9P^+$, 937.3936; found at 937.3936

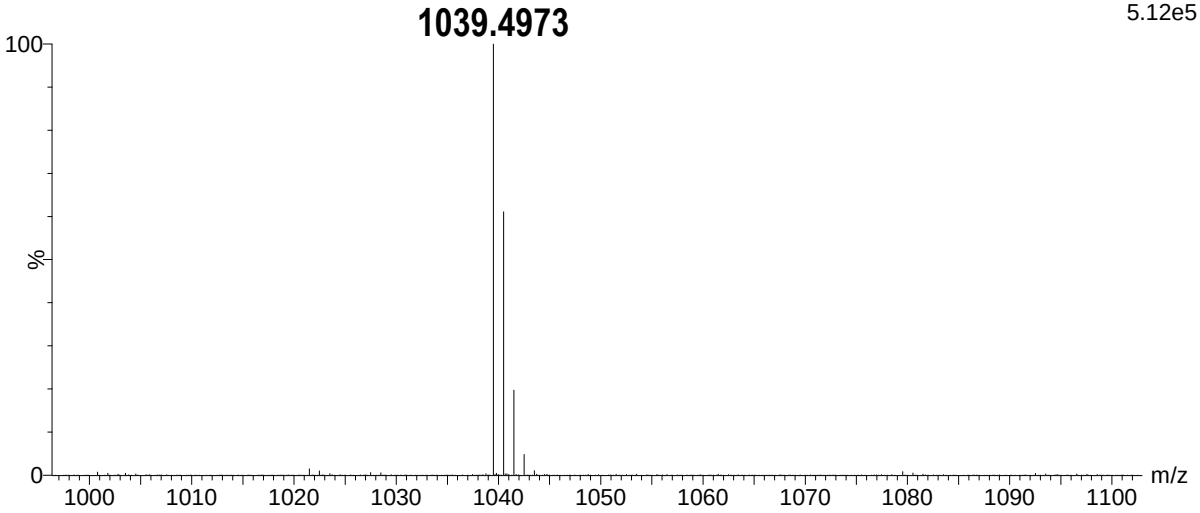


Figure S52 Positive ESI-HRMS spectra of **13**: *m/z* $[M+H]^+$ calcd for $C_{60}H_{71}N_4O_{10}P$, 1039.4981; found at 1039.4973

VII/ Crystallographic data

Table S3 Crystallographic data for P-H$^+$@**2** and **13**

Reference	P-H$^+$@**2** (CCDC: 2093016)	**13** (CCDC: 2099451)
Empirical formula	$C_{58}H_{68}ClN_4O_{10}P$	$C_{61}H_{66.6}Br_{0.6}Cl_3N_4O_{10}P$
Formula weight	1047.58	1201.04
Temperature/K	180.01(10)	153.01(10)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	10.2610(2)	12.4213(8)
b/Å	10.87103(19)	29.5258(19)
c/Å	26.4434(4)	17.9736(8)
α/°	82.7150(14)	90
β/°	86.3036(16)	102.414(6)
γ/°	77.2137(17)	90
Volume/Å^3	2851.32(10)	6437.7(7)
Z	2	4
ρ_{calc}g/cm^3	1.220	1.239
μ/mm^{-1}	1.340	2.419
F(000)	1112.0	2510.0
Crystal size/mm^3	0.24 × 0.22 × 0.06	0.16 × 0.08 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.744 to 141.766	5.858 to 141.642
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-32 \le l \le 32$	$-13 \le h \le 15$, $-33 \le k \le 35$, $-21 \le l \le 20$
Reflections collected	49135	29490
Independent reflections	10867 [R_{int} = 0.0415, R_{sigma} = 0.0260]	11984 [R_{int} = 0.0899, R_{sigma} = 0.1362]
Data/restraints/parameters	10867/16/690	11984/56/757
Goodness-of-fit on F^2	1.048	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1779	R_1 = 0.1294, wR_2 = 0.2712
Final R indexes [all data]	R_1 = 0.0717, wR_2 = 0.1845	R_1 = 0.2146, wR_2 = 0.3175
Largest diff. peak/hole / e Å^{-3}	1.26/-0.59	0.53/-0.41