Eur. J. Org. Chem. **2016** · ISSN 1099–0682

SUPPORTING INFORMATION

DOI: 10.1002/ejoc.201501426
Title: Introverted Phosphorus-Au Cavitands for Catalytic Use
Author(s): Michael P. Schramm, Mao Kanaura, Kouhei Ito, Masataka Ide, Tetsuo Iwasawa*

Contents

a) Standard Reaction Conditions for Hydration of Terminal Alkynes.

5.0 mg of Au-Cl cavitand (0.0028 mmoles, 5 mol %, typically cavitand **3**) and 0.7 mg of AgOTf (0.0028 mmoles, 5 mol %) were mixed in a small 1.0 mL vial with 0.55 mL of deuterated solvent (typically, [D_8]toluene) and heated to 85 °C (or 60 °C for $CDCl_3$) for 30 minutes. Terminal alkyne (0.056 mmoles) was added to the vial and the solution was transferred to an NMR tube and heated for an additional 1 hour, and then NMR was acquired at multiple intervals.

b) Standard Reaction Conditions for Conia-Ene Reaction of 8

5.0 mg of Au-Cl cavitand (0.0028 mmoles, 5 mol %, typically cavitand **3**) and ~ 0.7 mg of AgOTf (0.0028 mmoles, 5 mol %) were mixed in a small 1.0 mL vial with 0.55 mL of deuterated solvent (typically, [D_8]toluene) and heated to 85 °C (or 60 °C for $CDCl_3$) for 30 minutes. Ketoester alkyne **8** (11.0 mg, 0.056 mmoles) was added to the vial and the solution was transferred to an NMR tube and heated for an additional 1 hour, and then NMR was acquired at multiple intervals.

c) Consecutive NMR spectra for reactions of ethynylbenzene with AgOTf, H_2O, and 3.

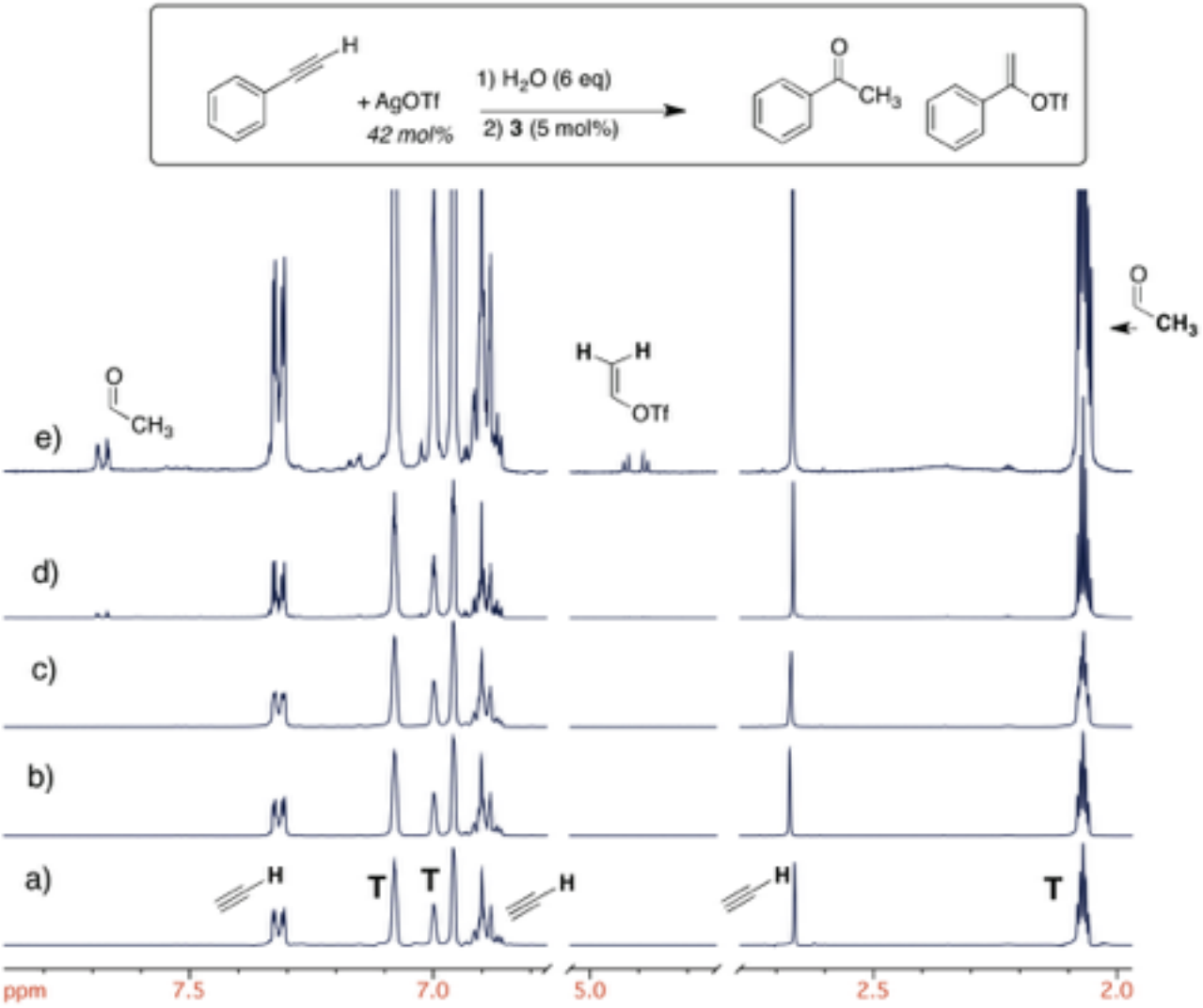
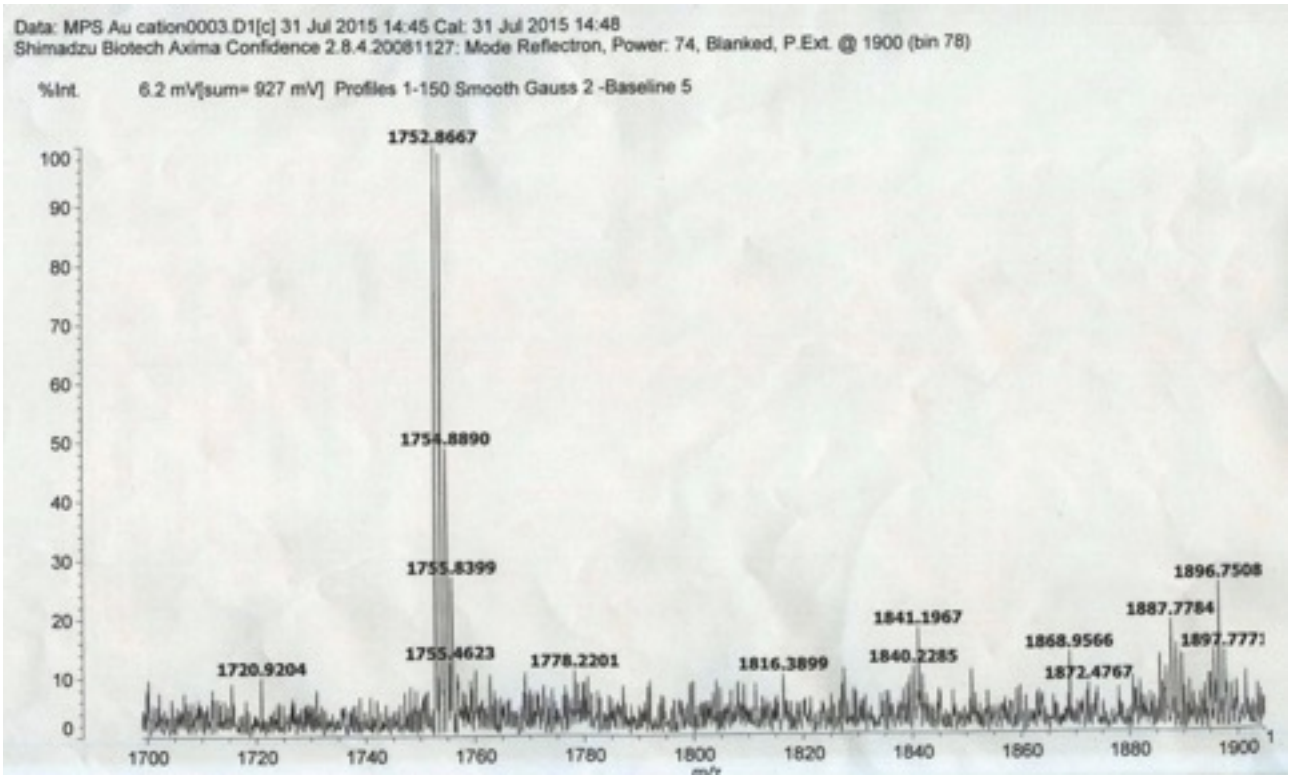


Figure S1. ^{1}H NMR (400 MHz, [D_8]toluene) a) ethynylbenzene (0.019 mmol), b) 42 mol% AgOTf added, c) 6 eq of water added and heated to 85 °C for 1 hour, d) **3** (5 mol%) added and heated for 1 hour and e) heated for 12 more hours.

d) Data of HRMS of 3 mixed with AgOTf.



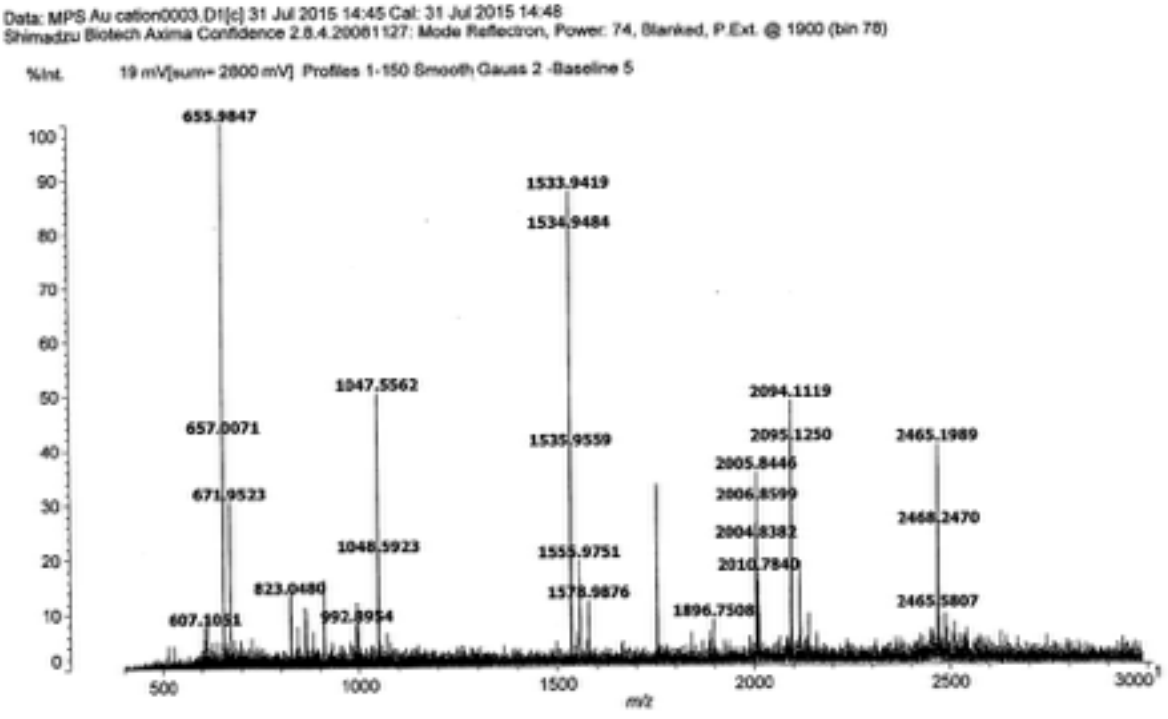
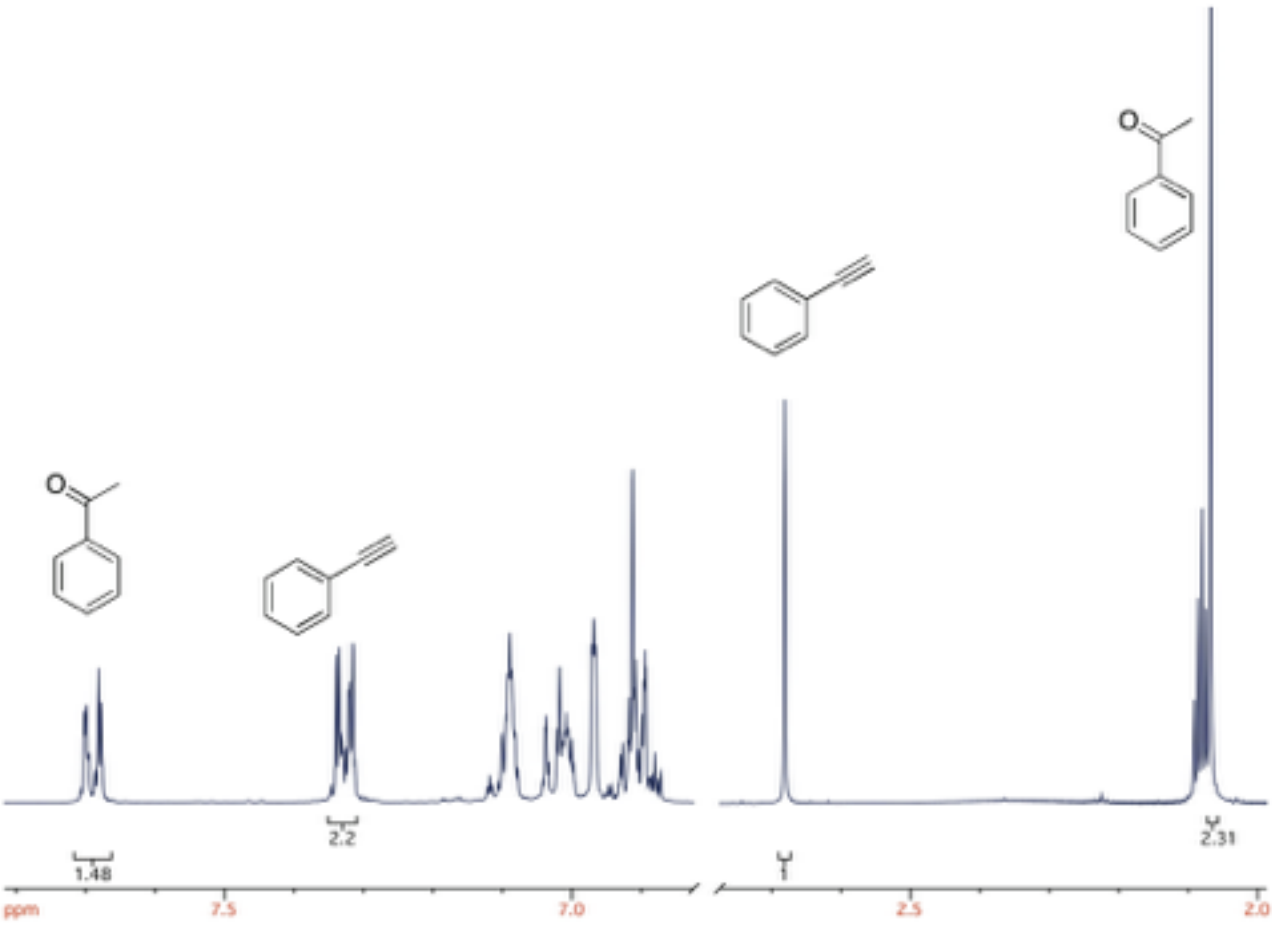


Figure 2S. HRMS (MALDI-TOF) of **3** mixed with AgOTf in CH_2Cl_2 after sitting for 15 minutes. Top for only species in region of interest is [**3** - Cl]$^+$ (calculated: 1752.8758, observed: 1752.8667), and bottom for the spectrum in full region.

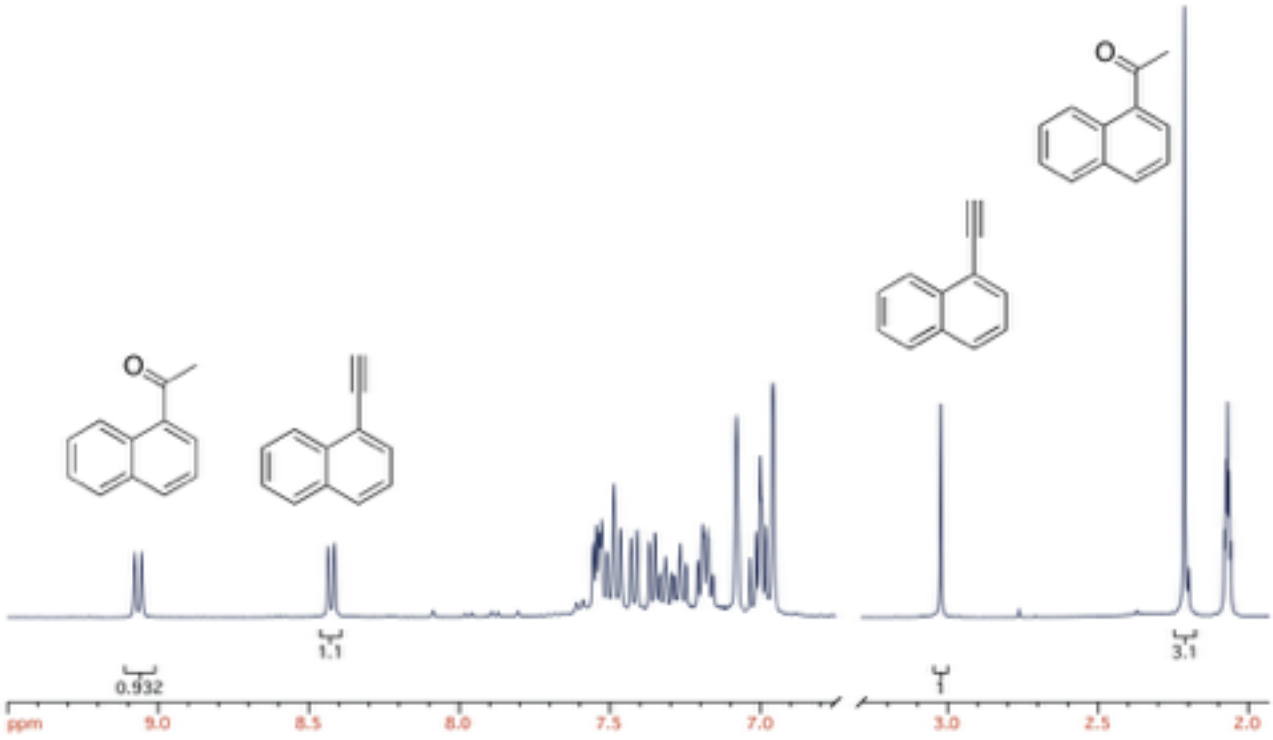
e) Representative ^{1}H NMR spectrum (400 MHz) for the hydration of ethynylbenzene to benzophenone.

Reactions were carried out with 0.056 mmoles of substrate, 0.056 mmoles water, 5% **3**, 5% AgOTf, 0.55 mL of [D_8]toluene, under 85 °C for 19 hours. The spectrum shown below is the representative portion of up- and down-field for ease of view.



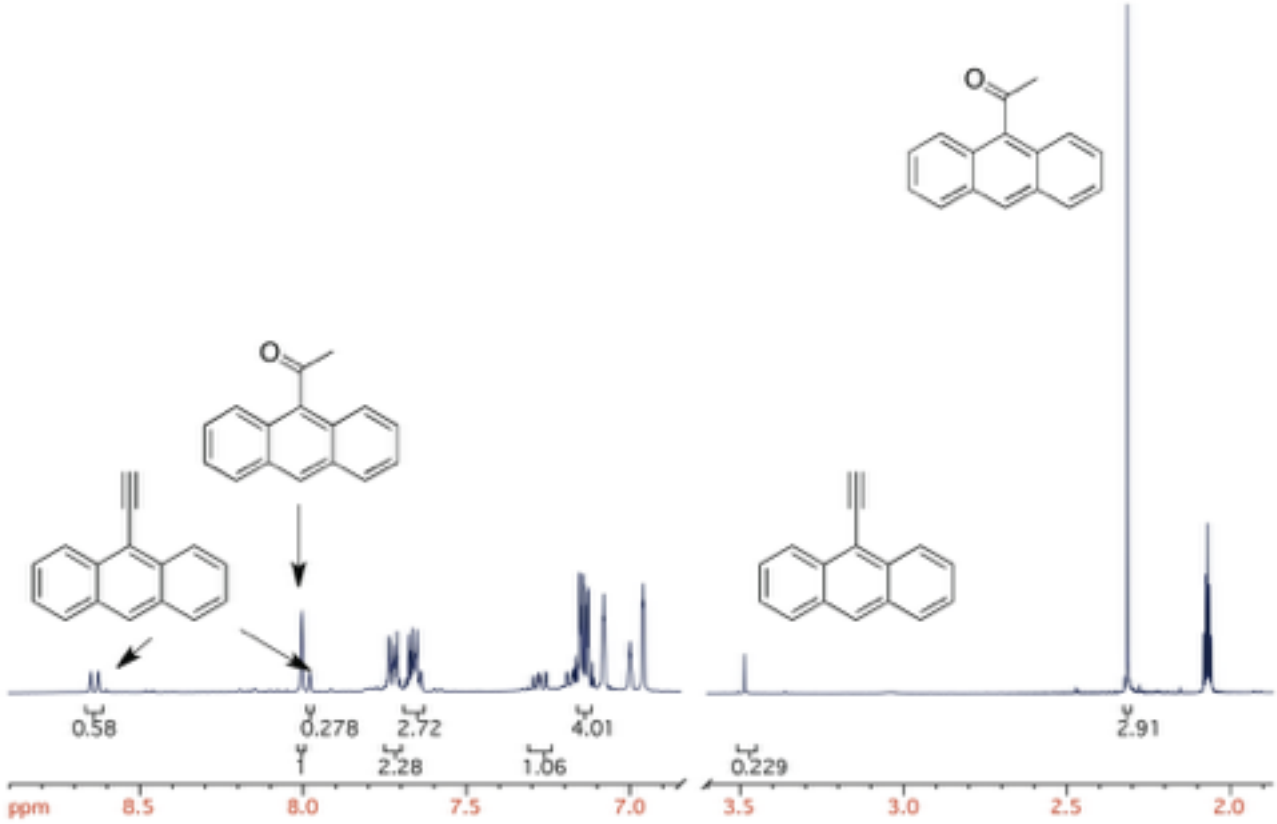
f) Representative ^{1}H NMR spectrum (400 MHz) for the hydration of 1-ethynylbenzene to 1-(naphthalen-1-yl)ethan-1-one.

Reactions were carried out with 0.056 mmoles of substrate, 0.056 mmoles water, 5% **3**, 5% AgOTf, 0.55 mL [D_8]toluene, under 85 °C for 19 hours. The spectrum shown below is the representative portion of up- and down-field for ease of view.



g) Representative ^{1}H NMR spectrum (400 MHz) for the hydration of 9-ethynylanthracene to 1-(anthracen-9-yl)ethan-1-one.

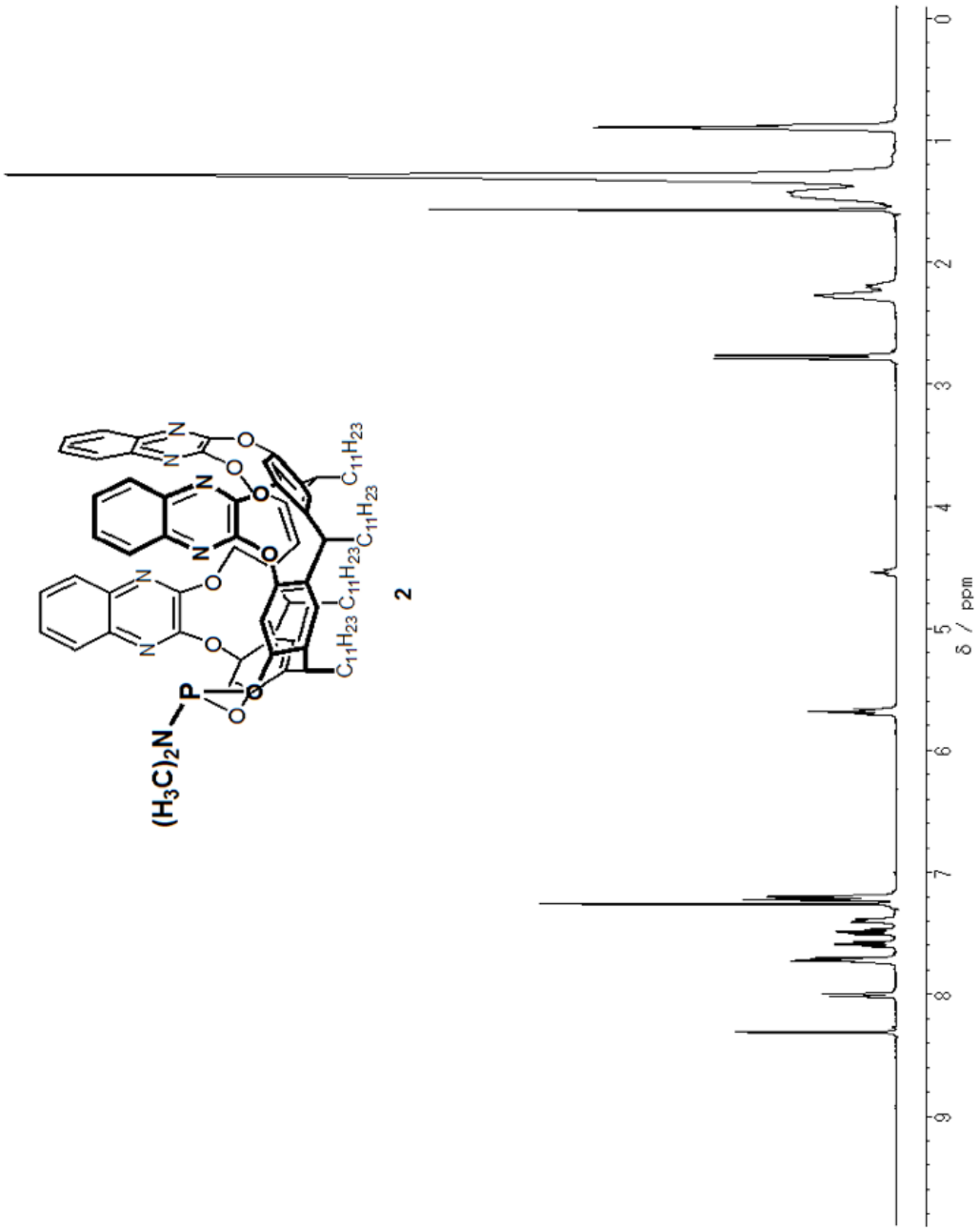
Reactions were carried out with 0.056 mmoles of substrate, 0.056 mmoles water, 5% **3**, 5% AgOTf, 0.55 mL [D_8]toluene, under 85 °C and 1 hour. The spectrum shown below is the representative portion of up- and down-field for ease of view.



h) The ^{1}H and ^{13}C NMR spectra of all new compounds for 2-7.

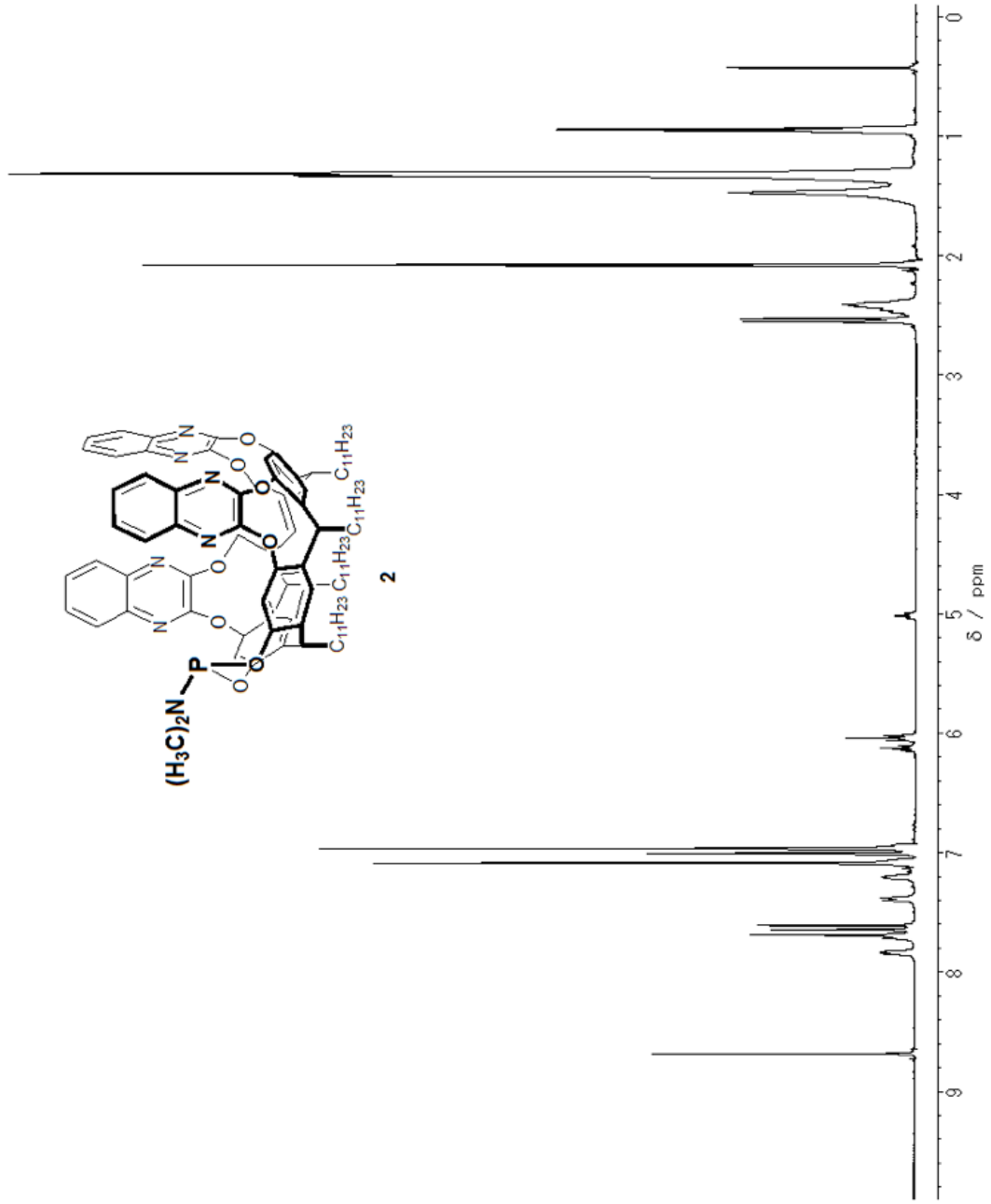
Compound 2

^{1}H NMR spectrum in $CDCl_3$



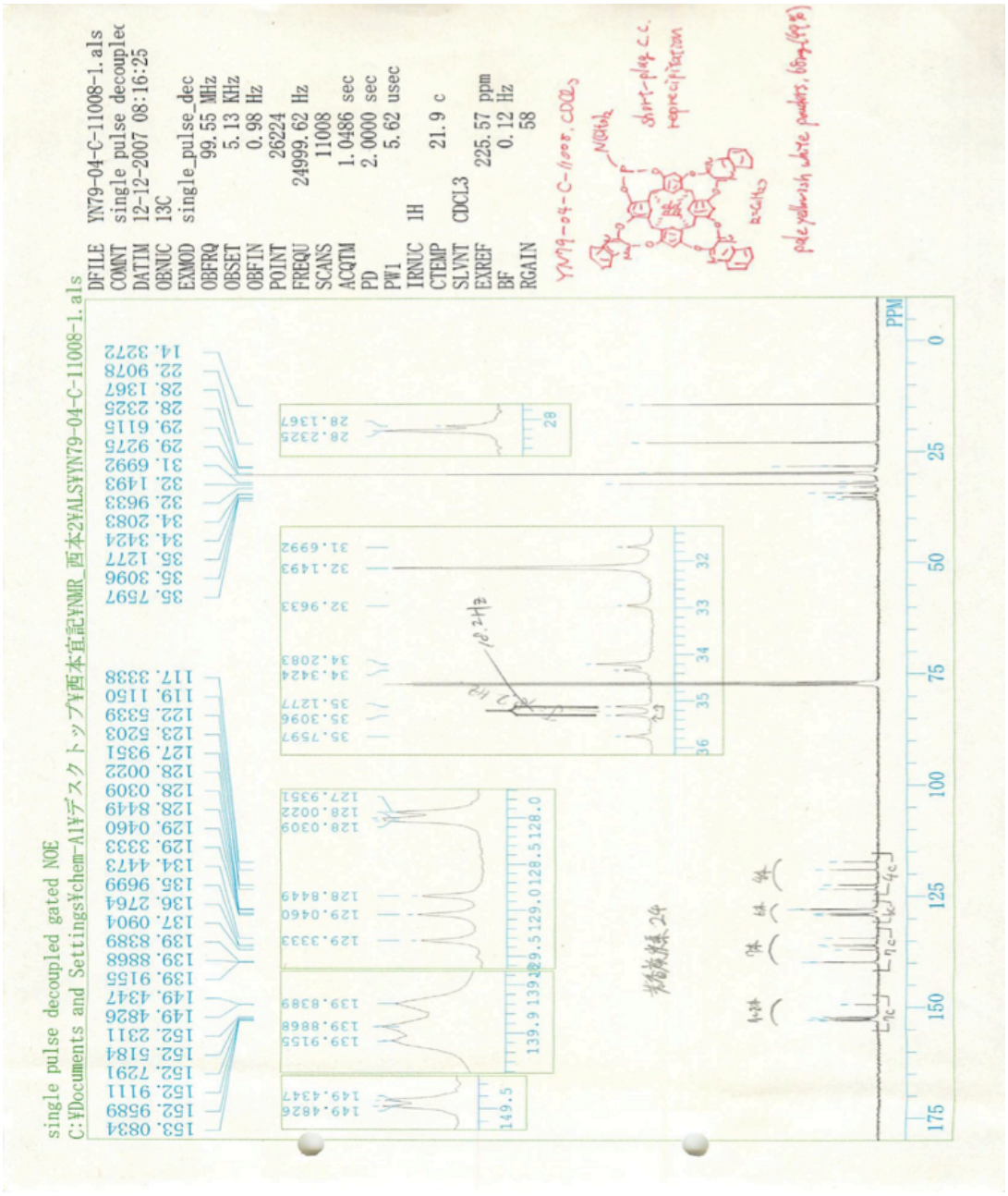
Compound 2

^{1}H NMR spectrum in toluene-d_8



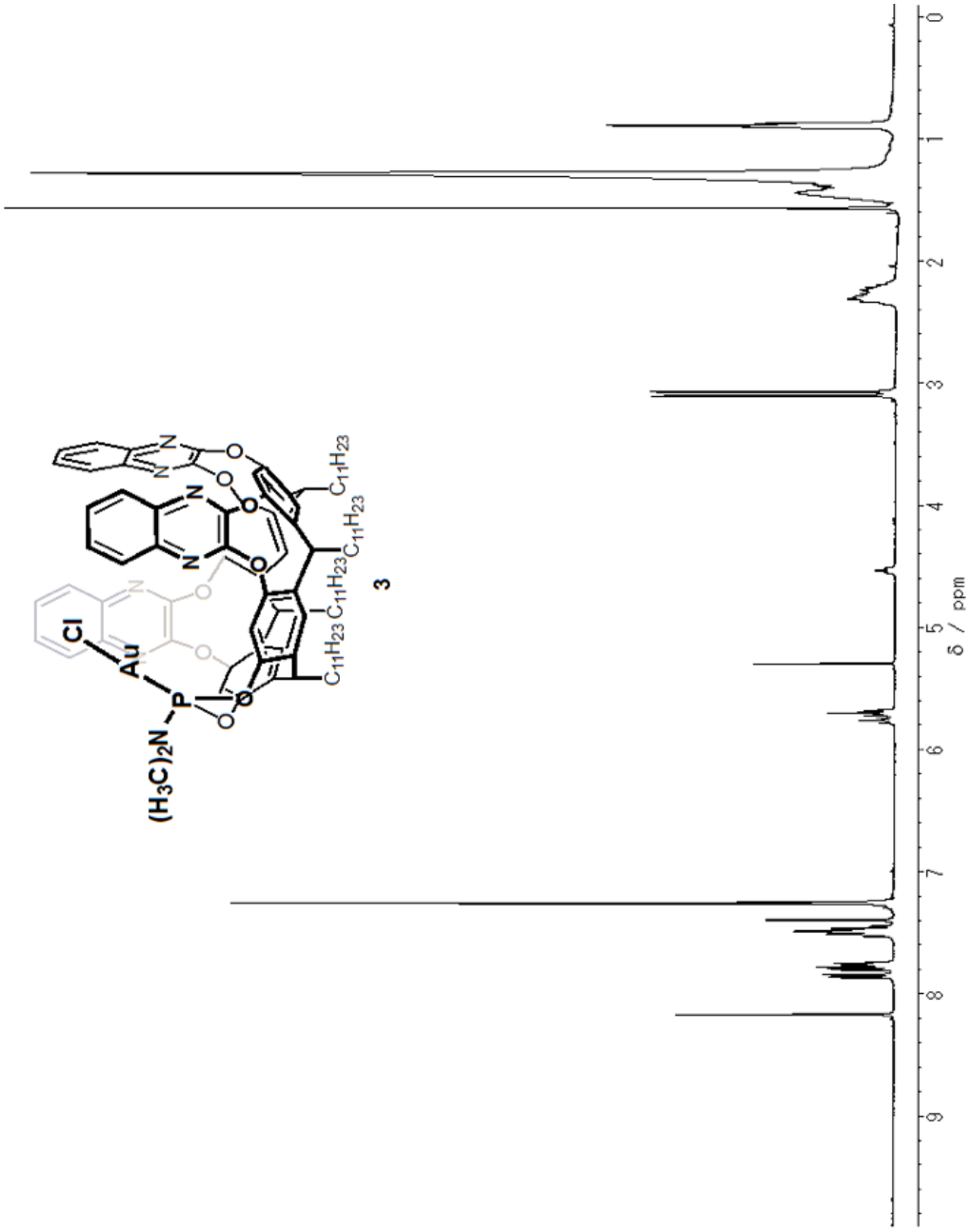
Compound 2

^{13}C NMR spectrum in $CDCl_3$



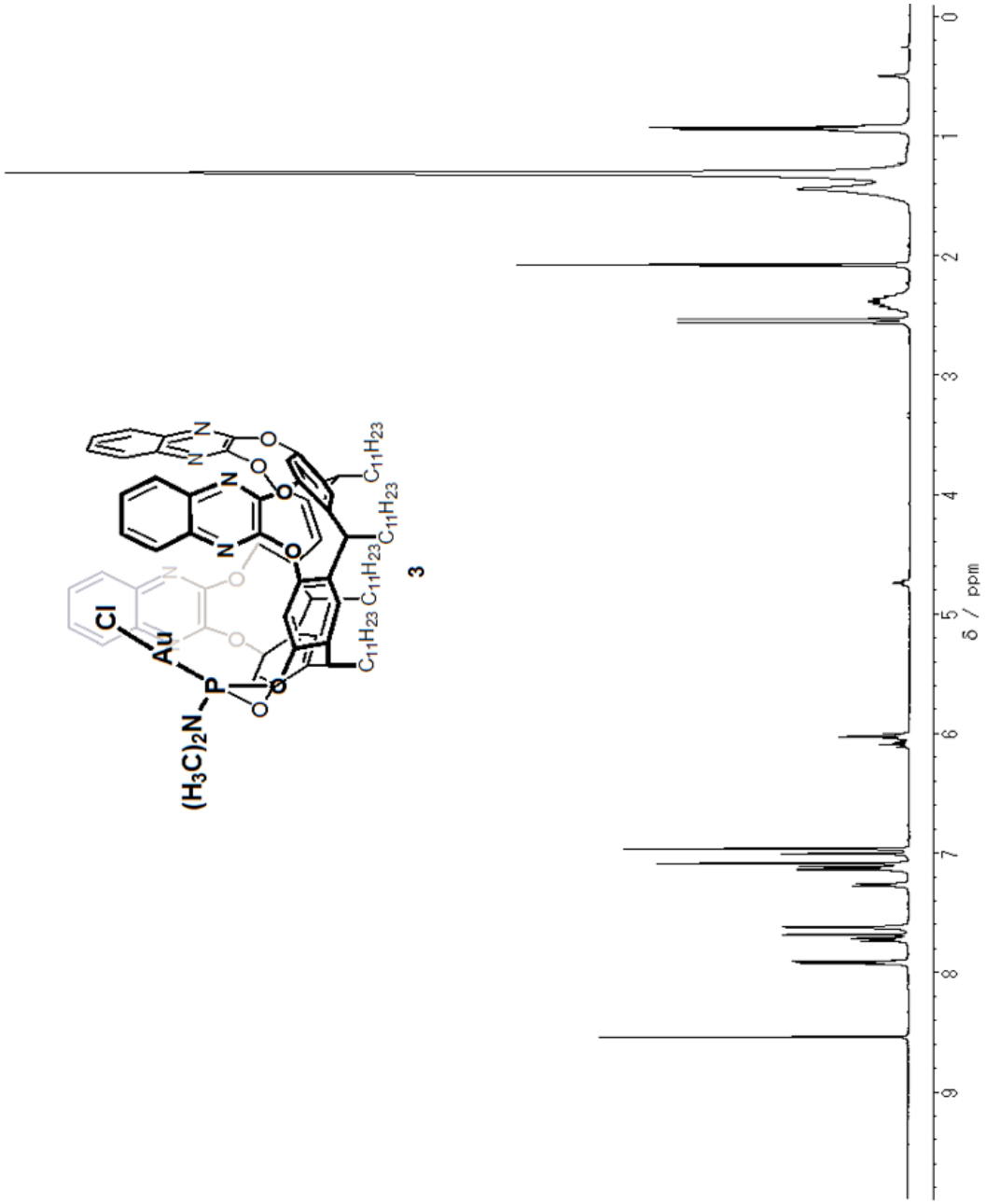
Compound 3

^{1}H NMR spectrum in $CDCl_3$



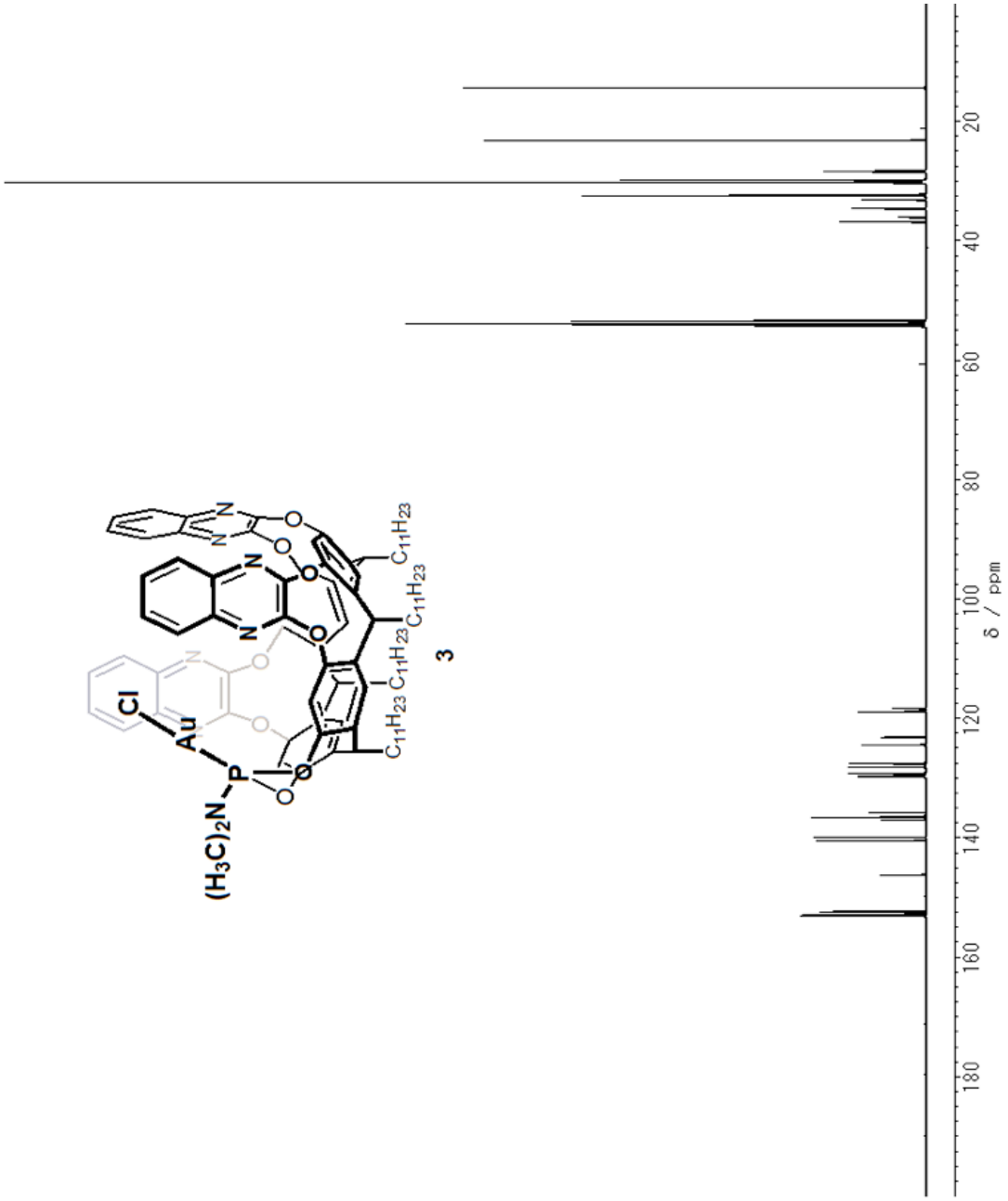
Compound 3

^{1}H NMR spectrum in toluene-d_8



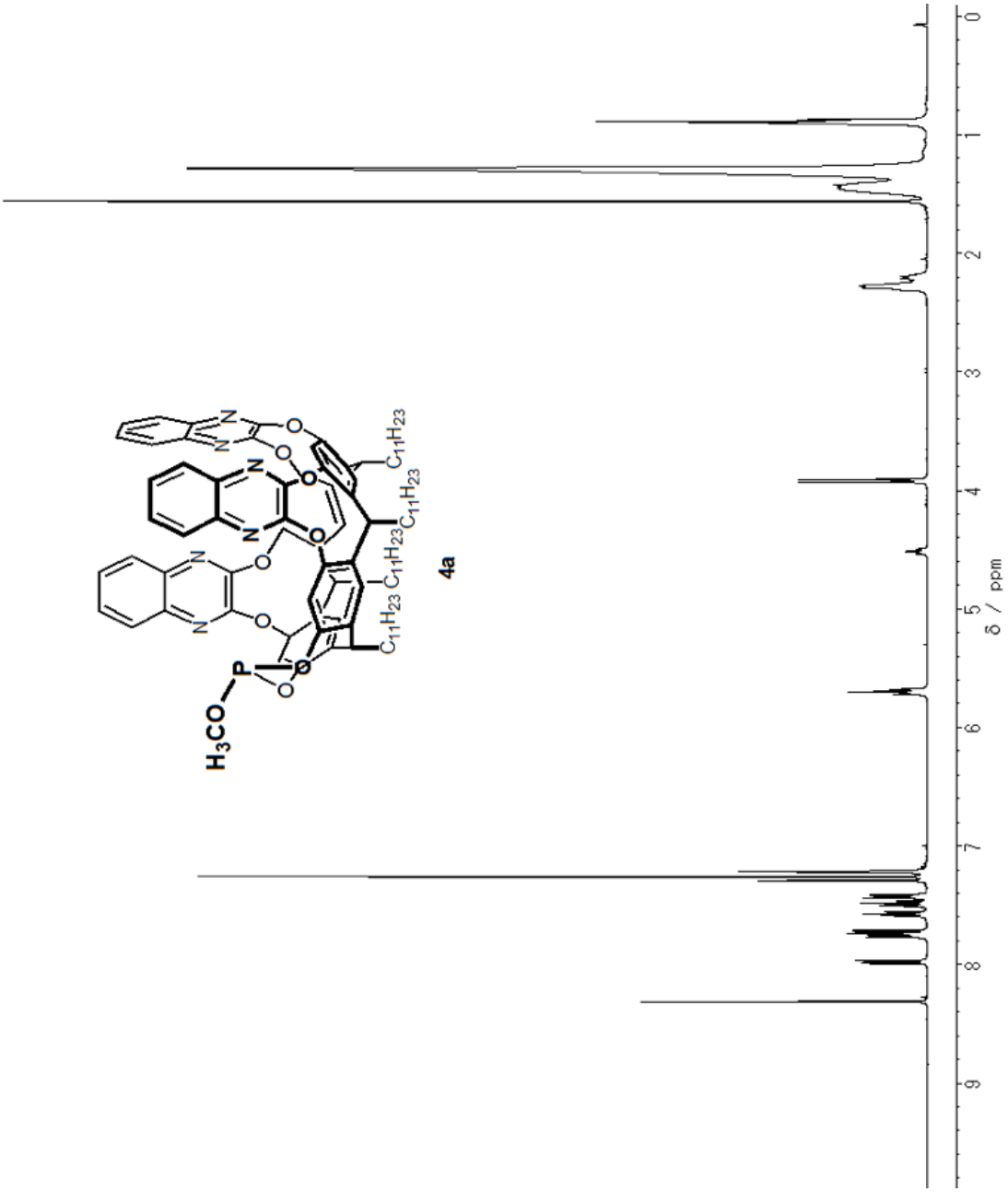
Compound 3

^{13}C NMR spectrum in CD_2Cl_2



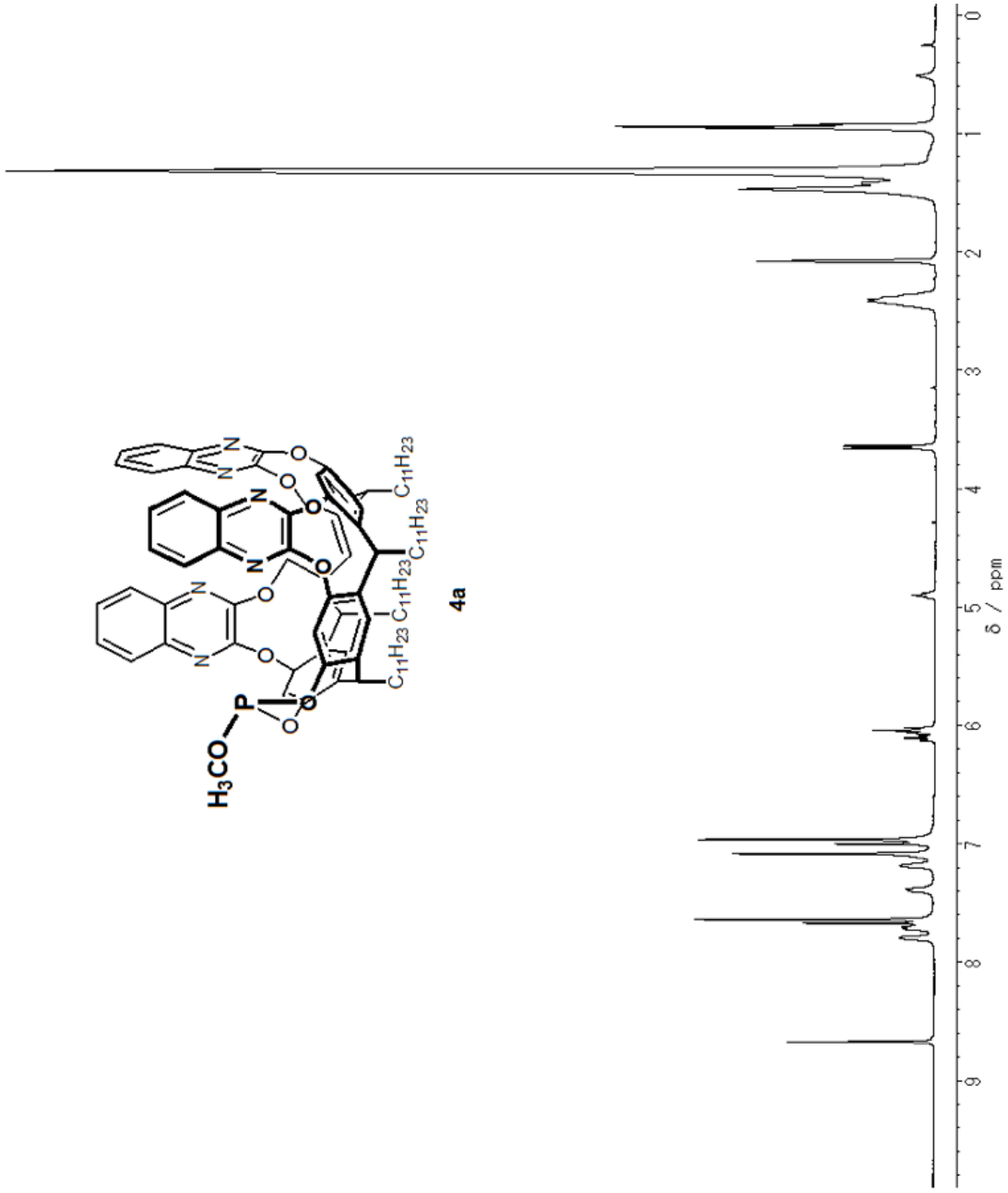
Compound 4a

^{1}H NMR spectrum in $CDCl_3$



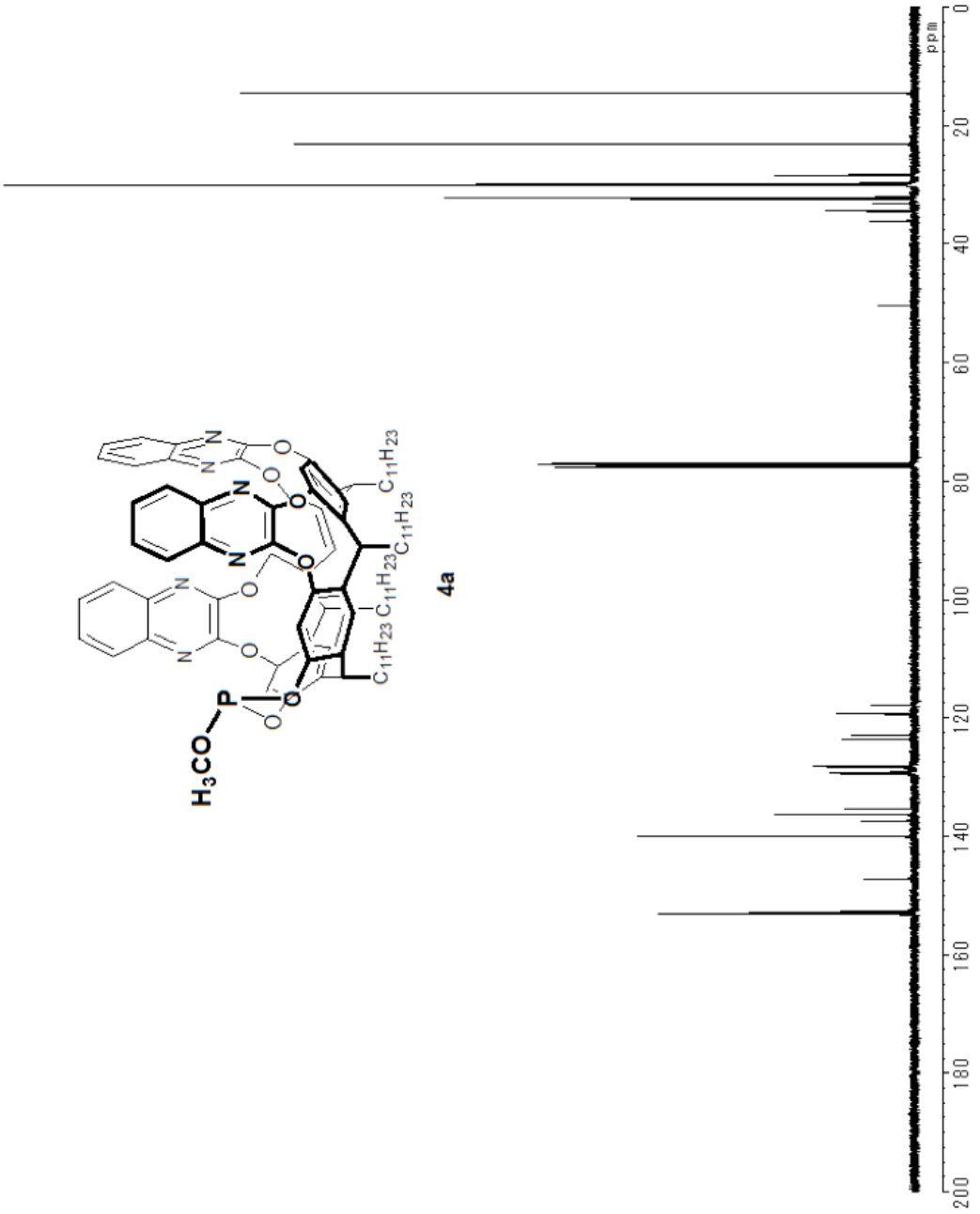
Compound 4a

^{1}H NMR spectrum in toluene-d_8



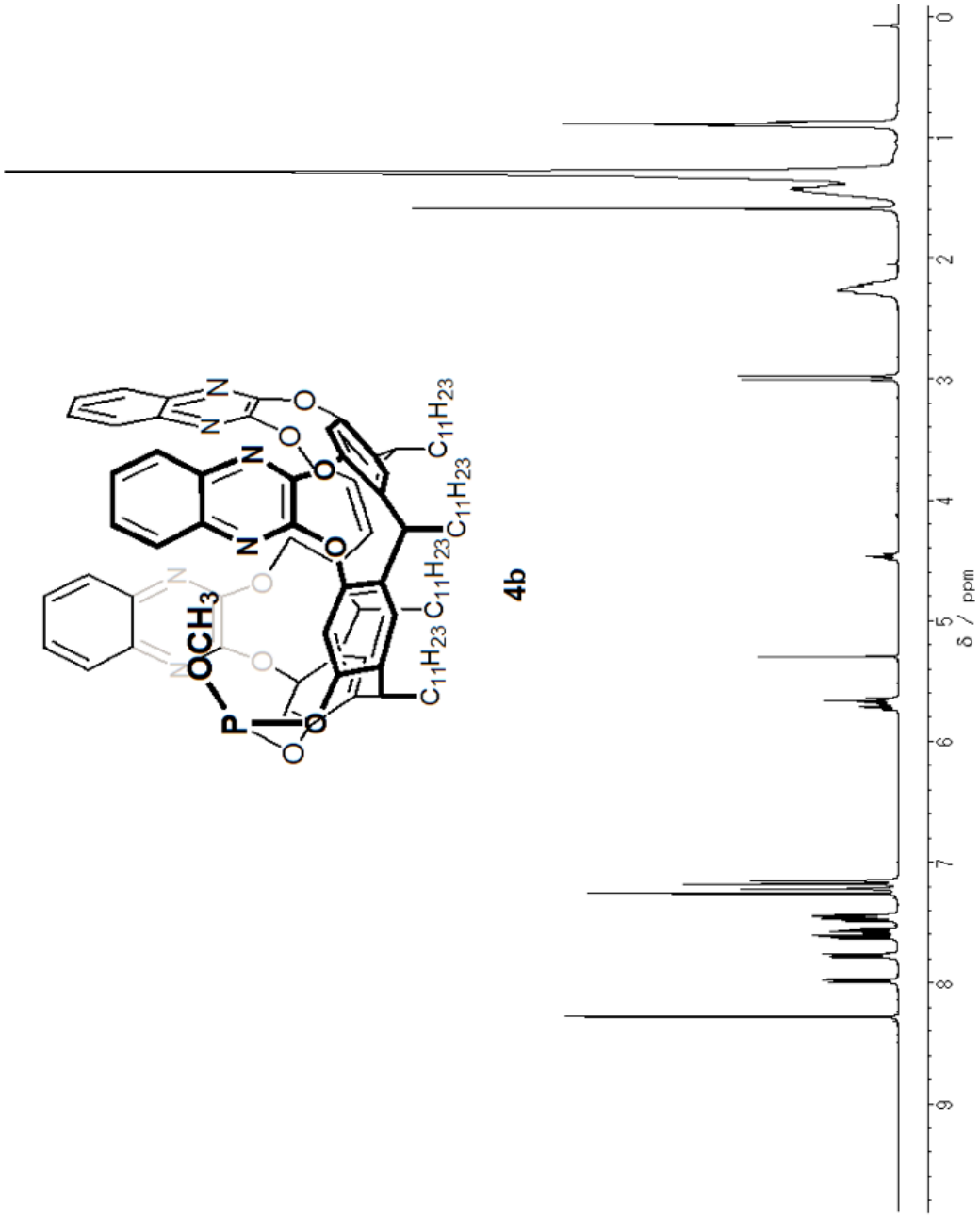
Compound 4a

^{13}C NMR spectrum in $CDCl_3$



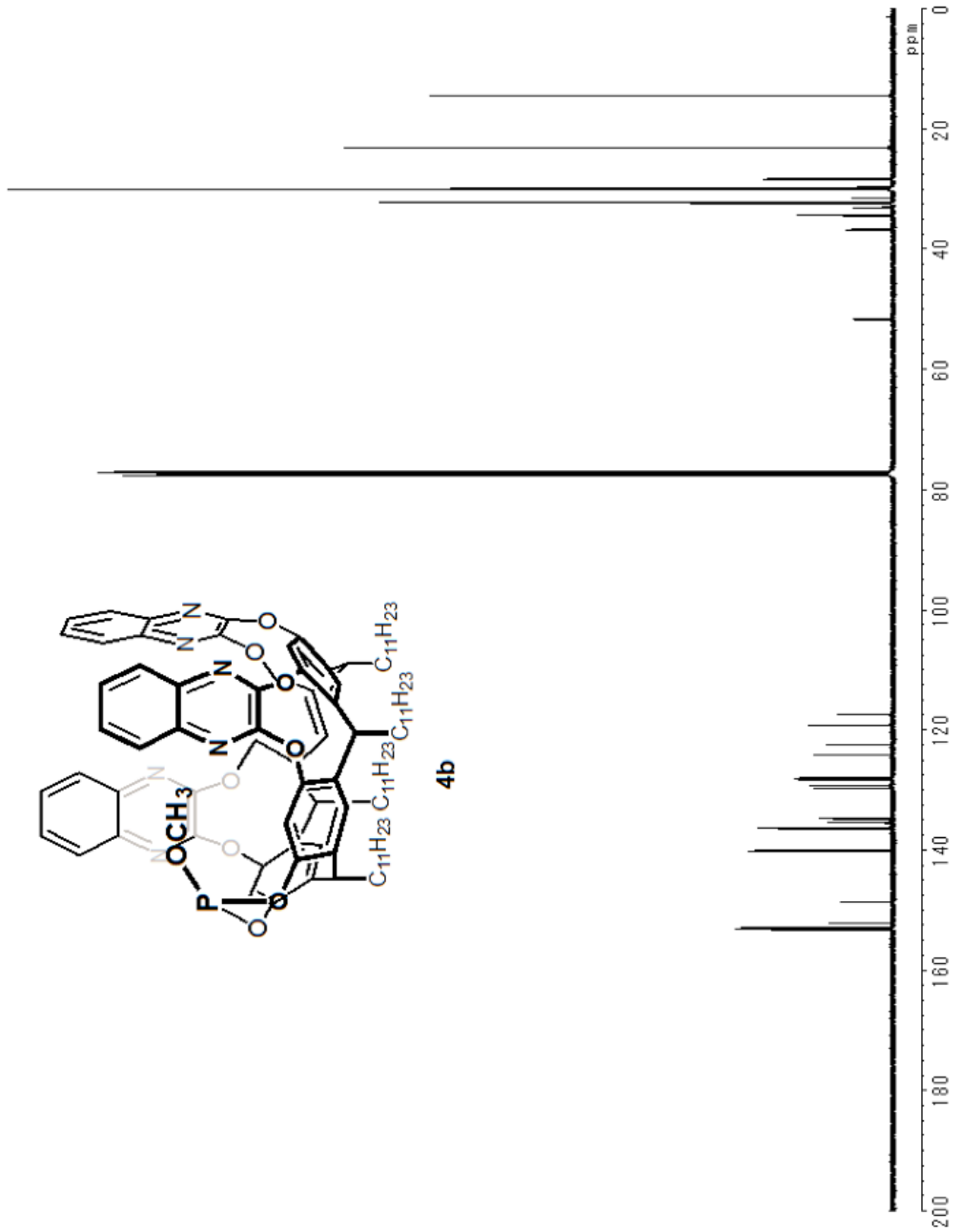
Compound 4b

^{1}H NMR spectrum in $CDCl_3$



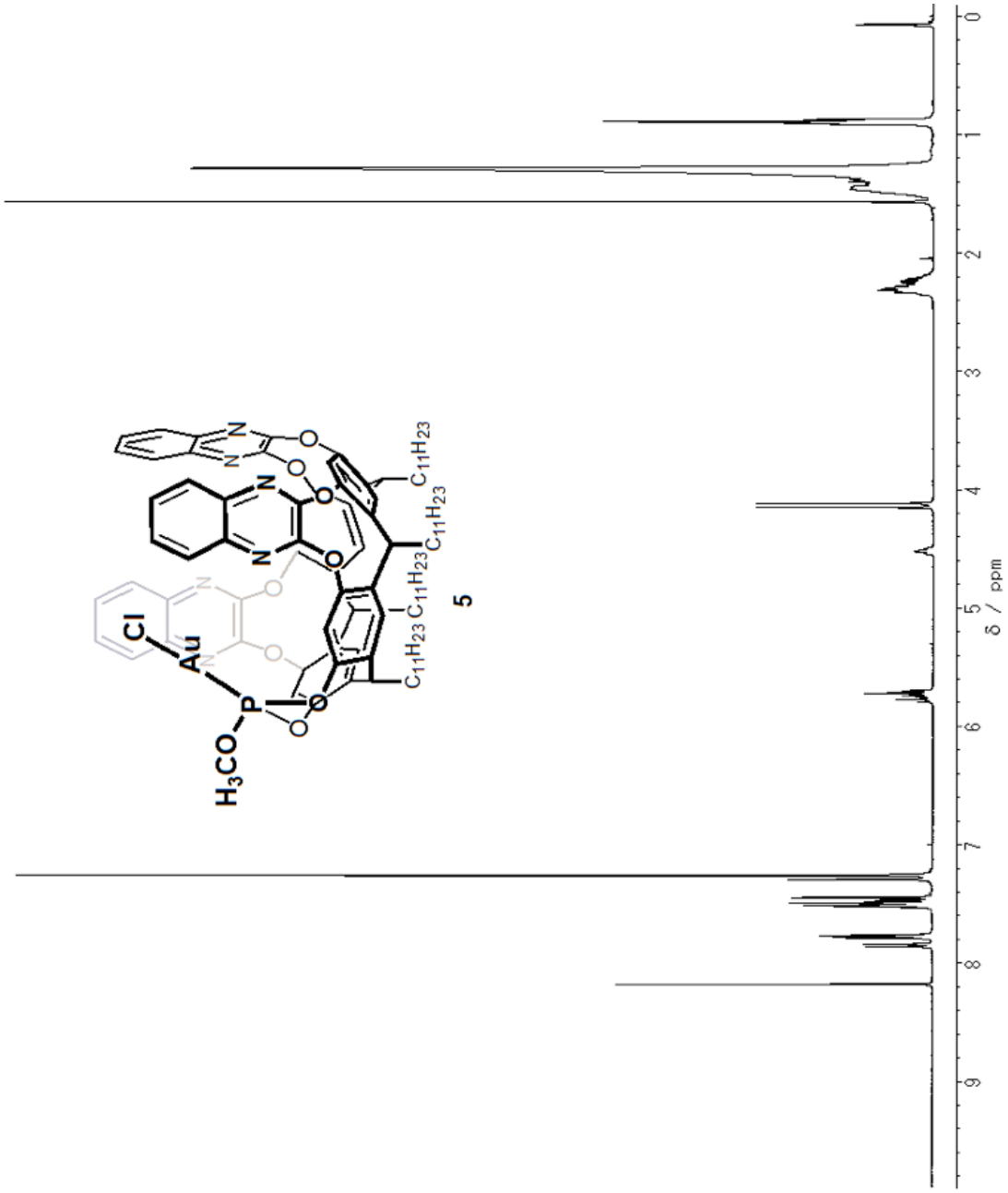
Compound 4b

^{13}C NMR spectrum in $CDCl_3$



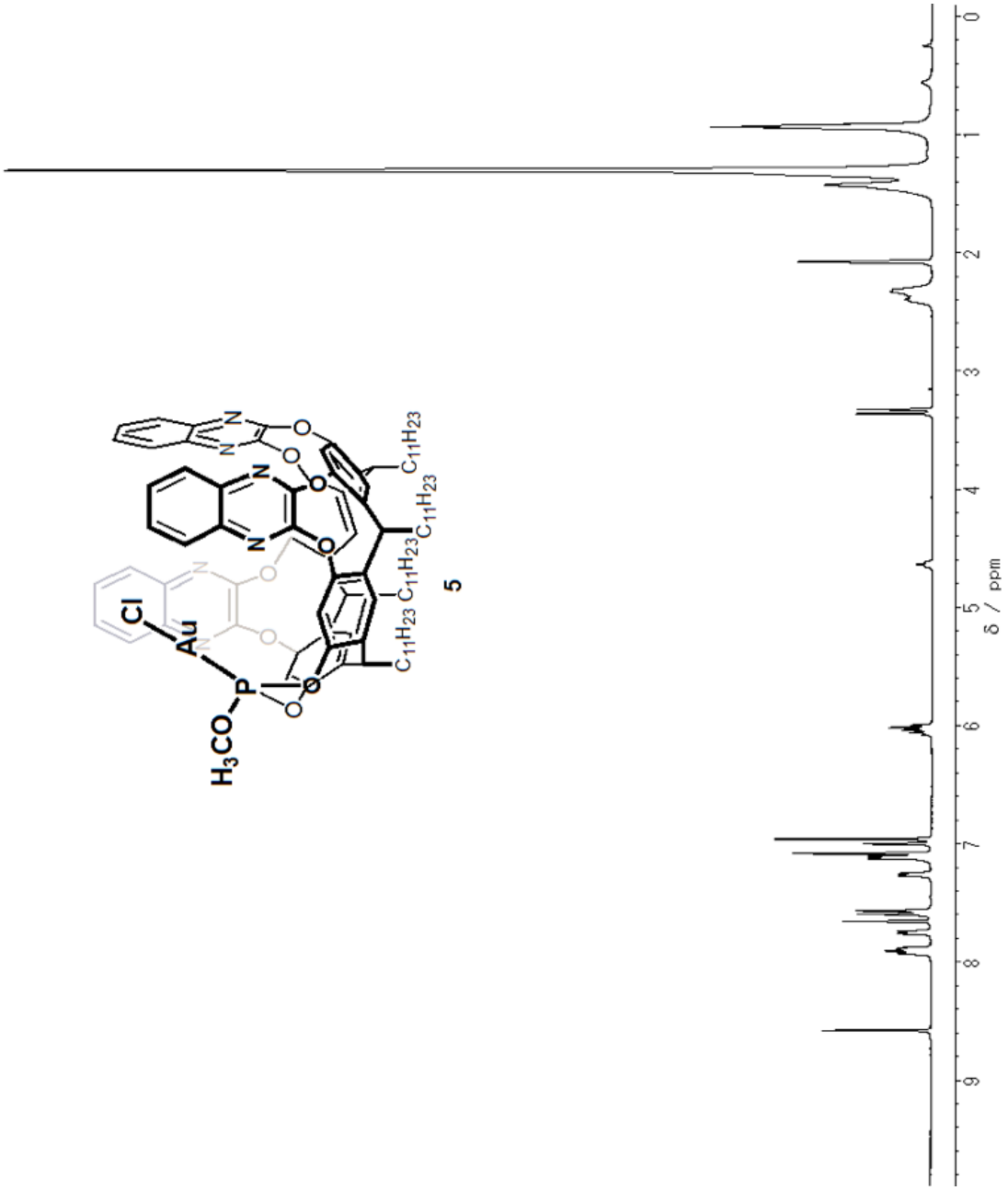
Compound 5

^{1}H NMR spectrum in $CDCl_3$



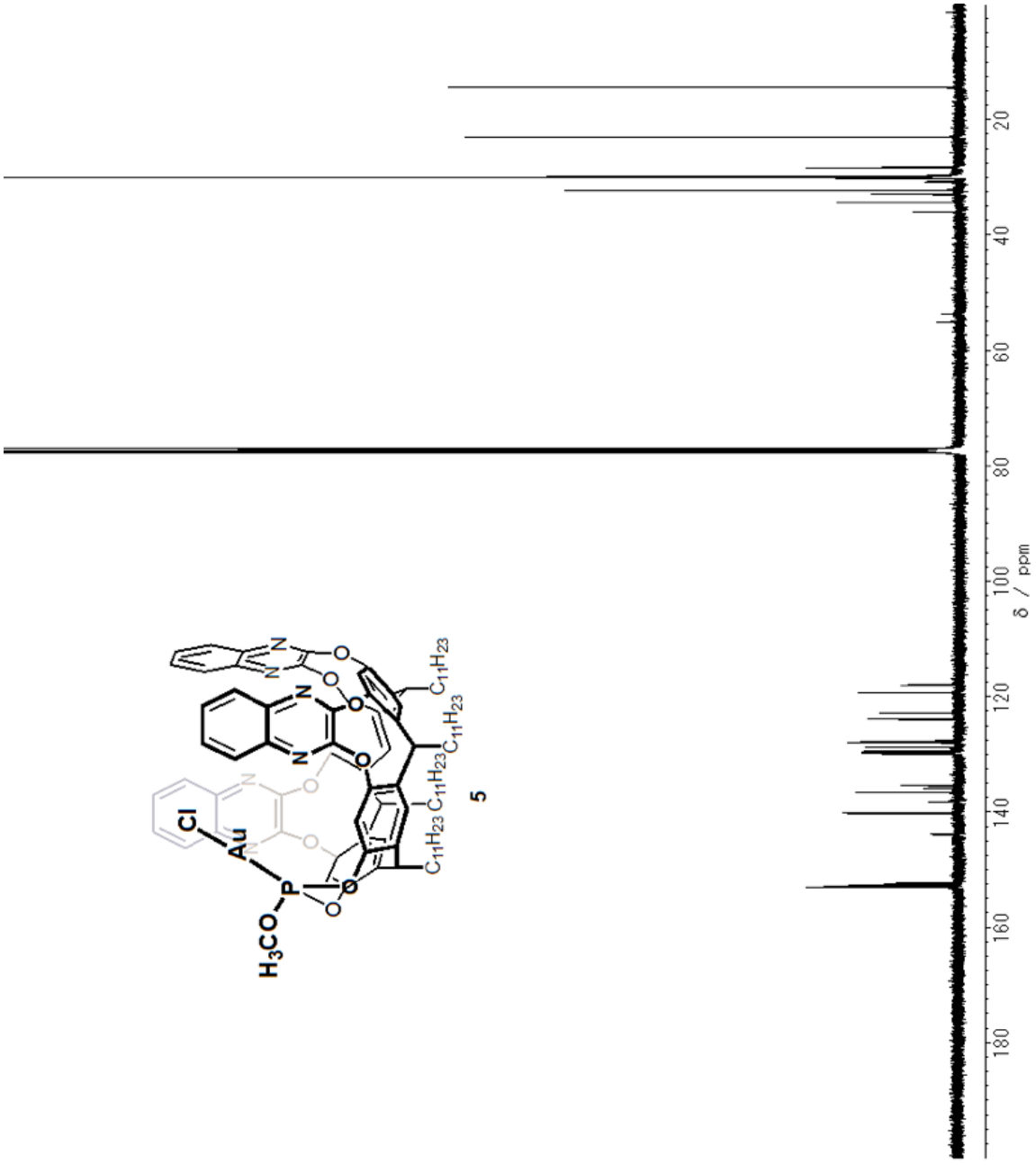
Compound 5

^{1}H NMR spectrum in toluene-d_8



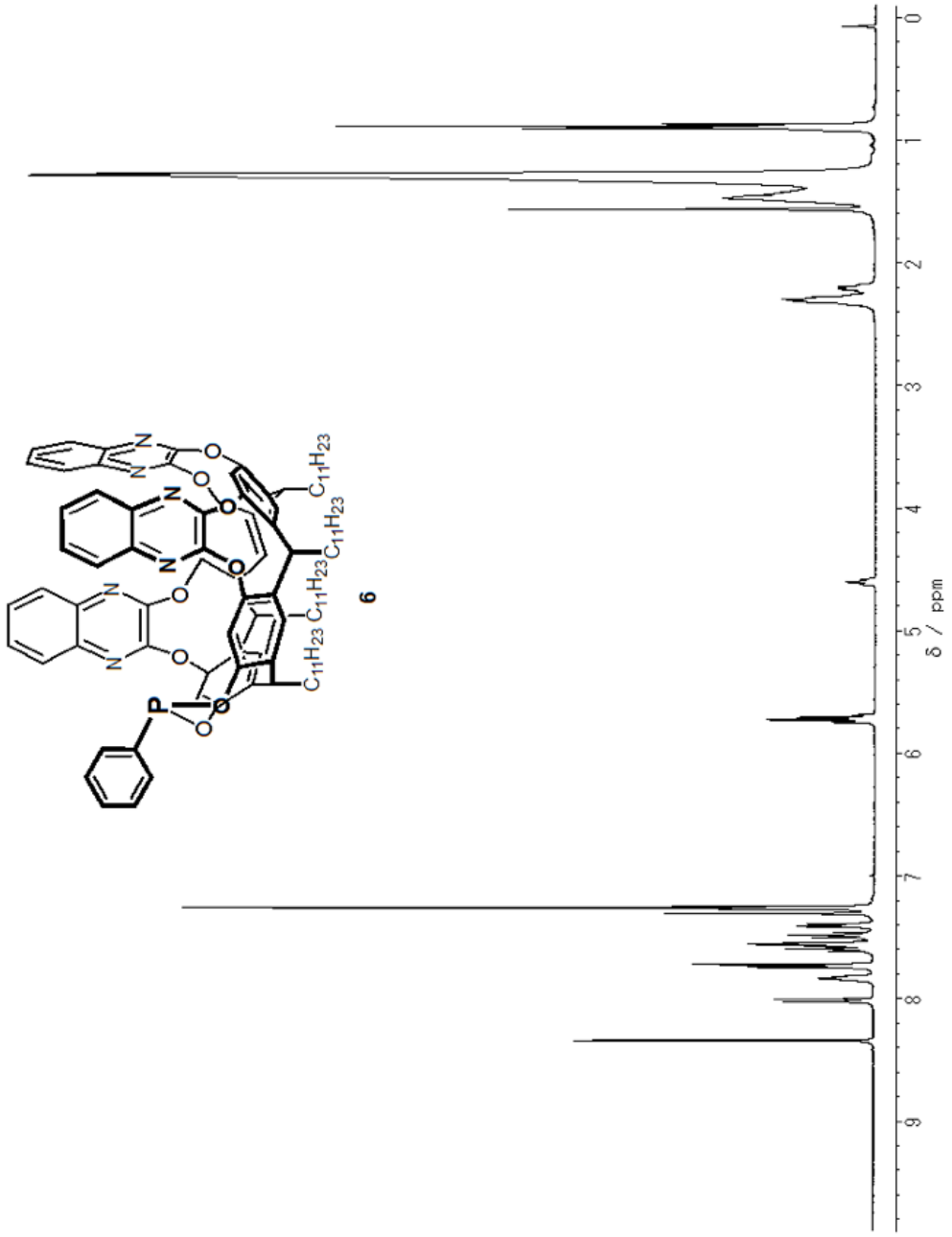
Compound 5

^{13}C NMR spectrum in $CDCl_3$



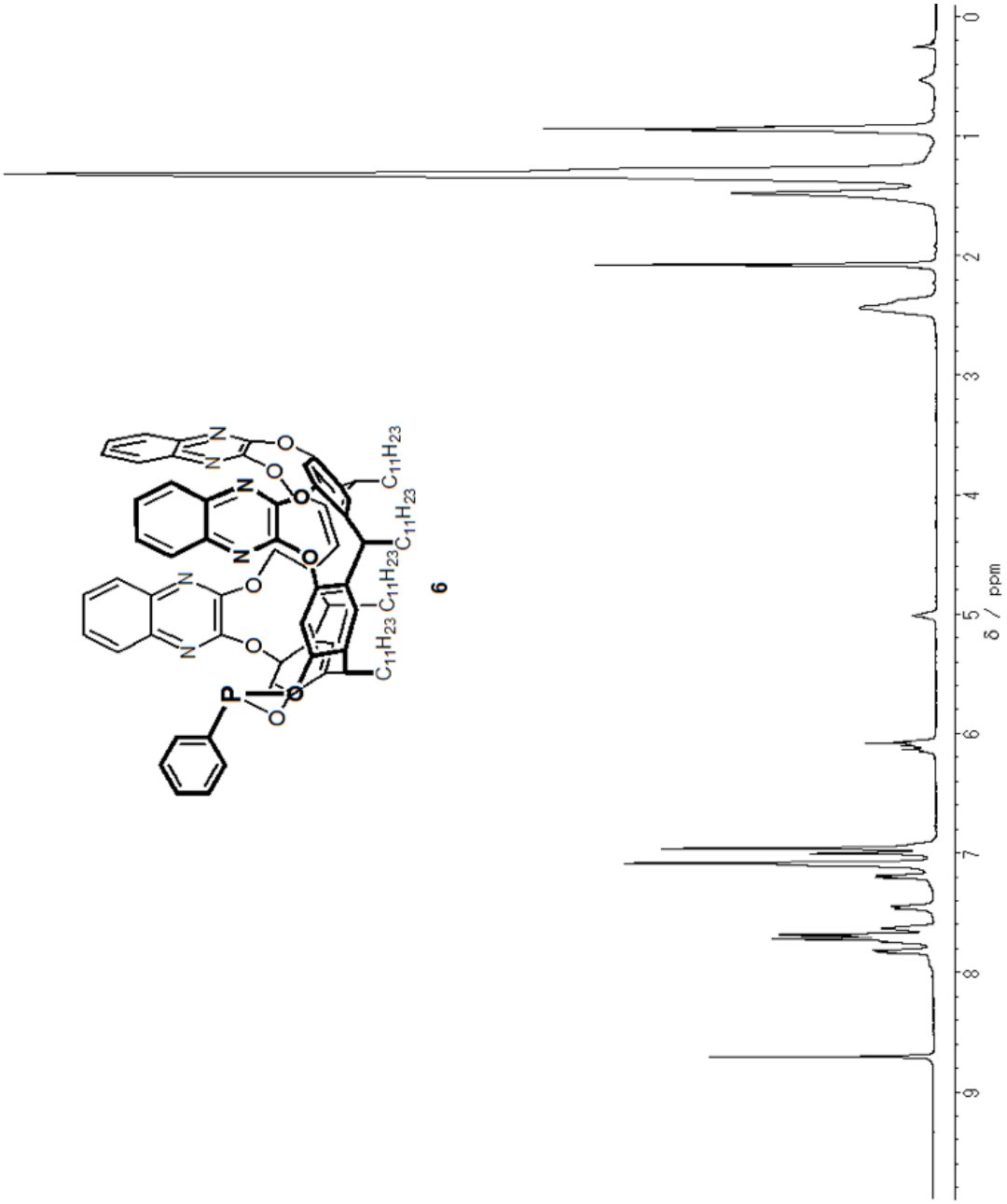
Compound 6

^{1}H NMR spectrum in $CDCl_3$



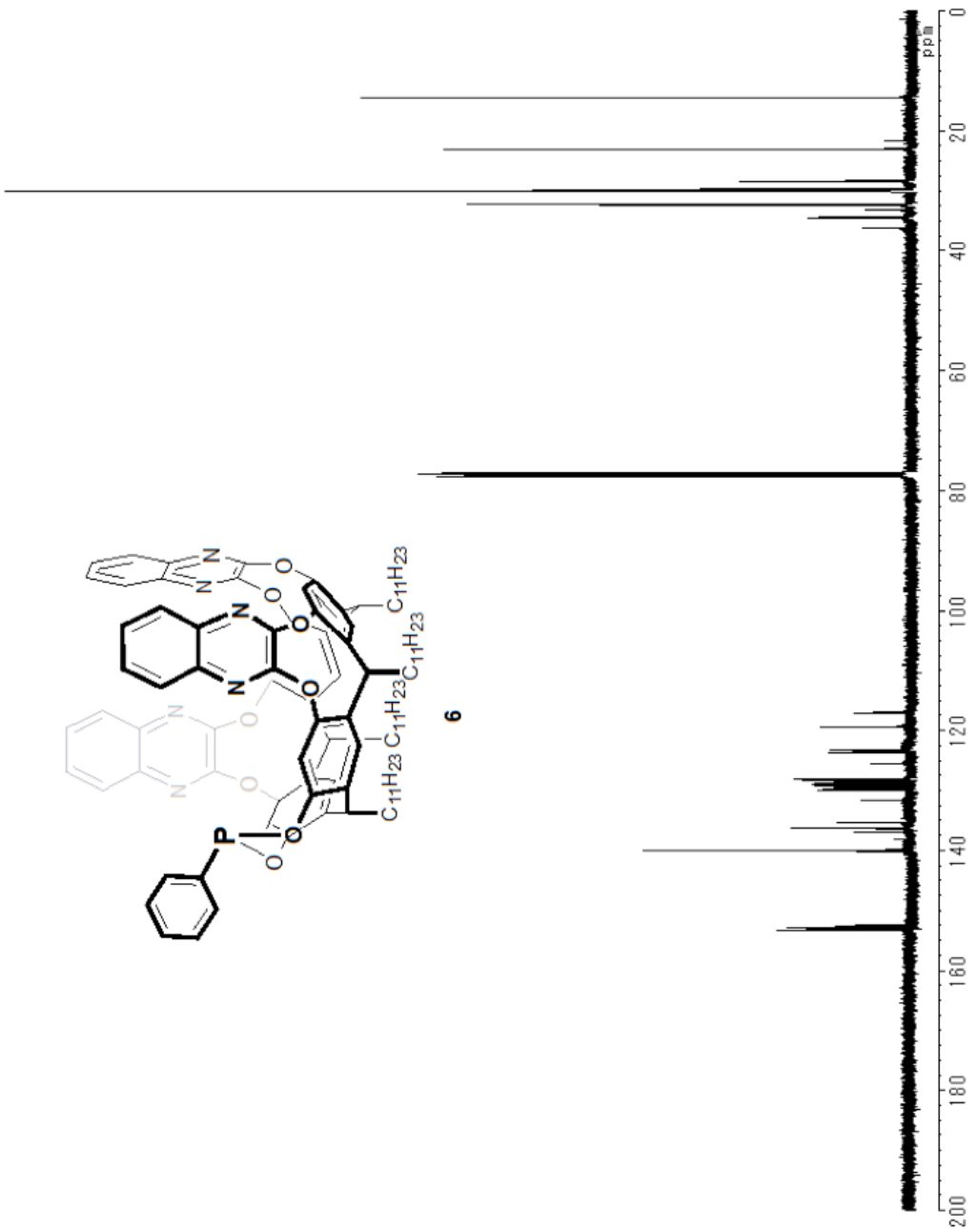
Compound 6

^{1}H NMR spectrum in toluene-d_8



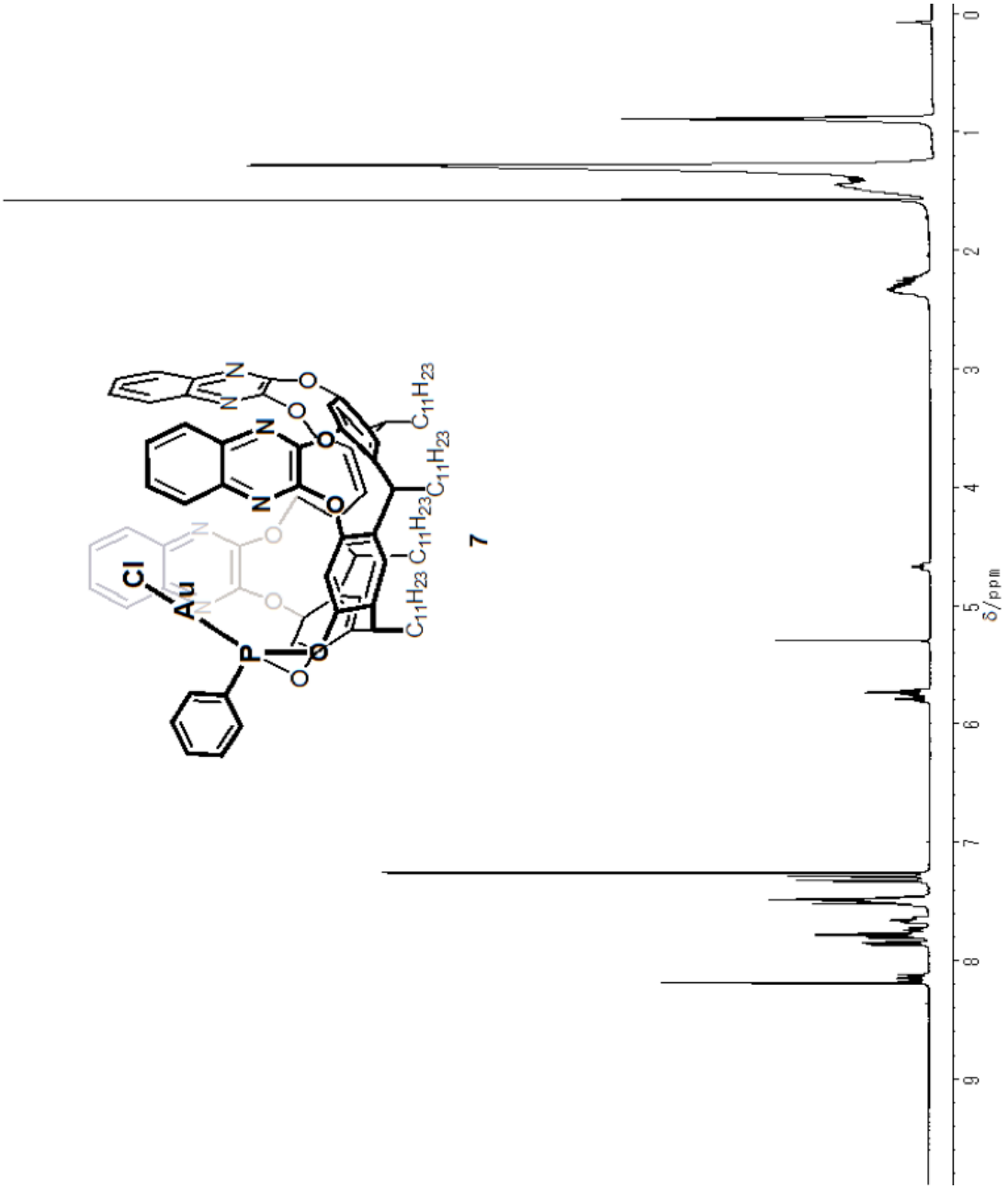
Compound 6

^{13}C NMR spectrum in $CDCl_3$



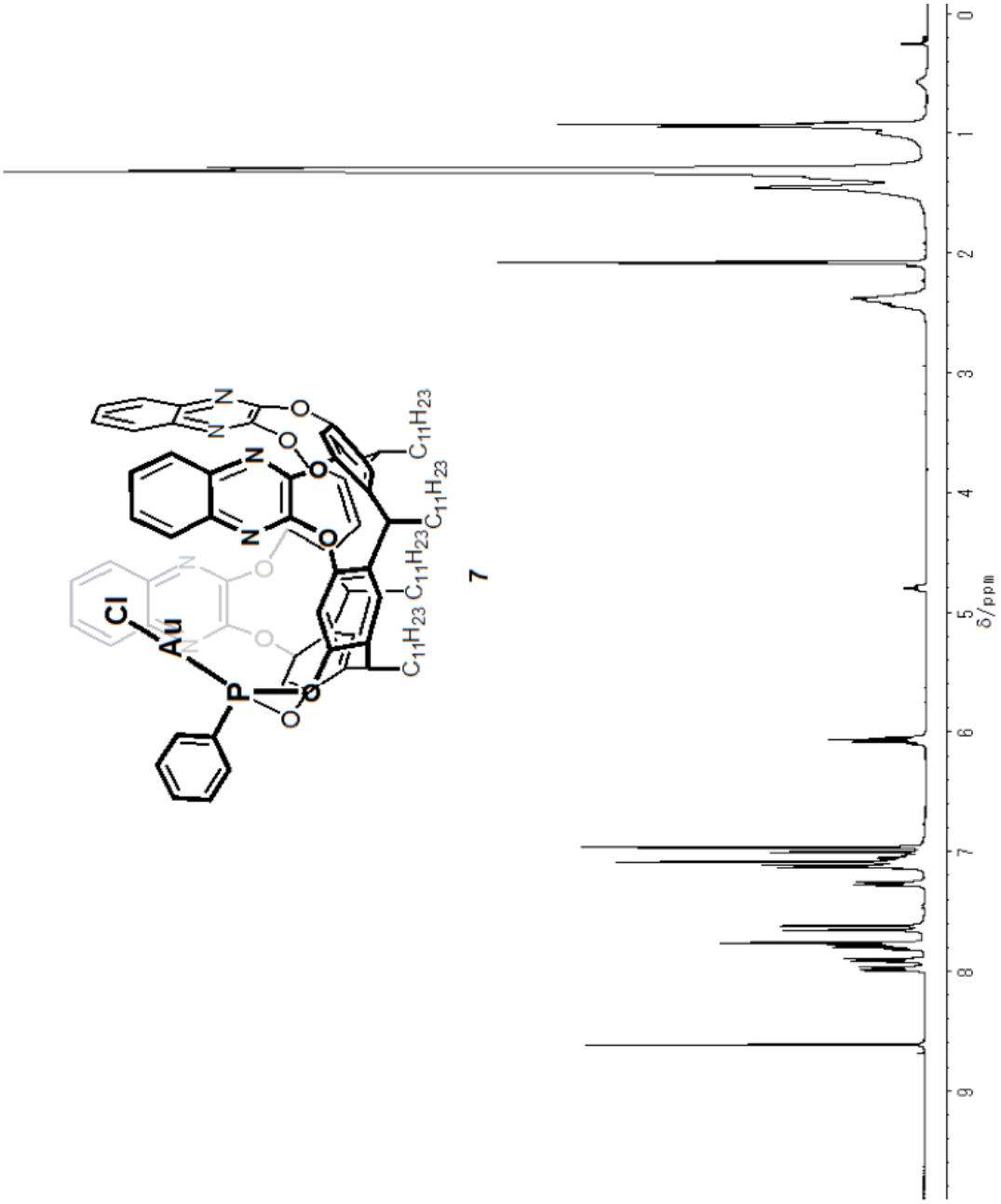
Compound 7

^{1}H NMR spectrum in $CDCl_3$



Compound 7

^{1}H NMR spectrum in toluene-d_8



Compound 7

^{13}C NMR spectrum in $CDCl_3$